Stereoselective Radical Transformations by Co(II)-Based Metalloradical Catalysis

by

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Chapter 1. Co(II)-Based Metalloradical Catalysis for Stereoselective Radical Cyclopropanation of Alkenes

This Account summarizes our group's recent efforts in developing metalloradical catalysis as a one-electron approach for catalytic radical cyclopropanation of alkenes with diazo compounds.

Chapter 2. Asymmetric Radical Process for General Synthesis of Chiral Heteroaryl Cyclopropanes

We have developed a Co(II)-based metalloradical system that is highly effective for asymmetric radical cyclopropanation of alkenes with in situ-generated α-heteroaryldiazomethanes. Through fine-tuning the cavity-like environments of newly-developed D_2-symmetric chiral amidoporphyrins as the supporting ligand, the optimized Co(II)-based metalloradical system is broadly applicable to pyridyl and other heteroaryldiazomethanes for asymmetric cyclopropanation of a wide range of alkenes, providing general access to valuable chiral heteroaryl cyclopropanes in high yields with excellent diastereoselectivities and enantioselectivities.

Chapter 3. Enantioselective Metalloradical 1,6-C–H Alkylation of In Situ-Generated Alkyldiazomethanes for Synthesis of Chiral Piperidines

We have disclosed an effective Co(II)-based metalloradical system as a fundamentally different approach to harness the potential of 1,6-HAA radical process, enabling asymmetric 1,6-C–H alkylation of in situ-generated α-alkyldiazomethanes to construct

chiral piperidines. Supported by an optimal D_2-symmetric chiral amidoporphyrin ligand, the Co(II)-catalyzed alkylation system is capable of activating a wide array of α-alkyldiazomethanes containing C(sp^3)–H bonds with varied steric and electronic properties, providing access to chiral α-substituted piperidines in good to high yields with high enantioselectivities from readily accessible 4-aminobutanal derivatives. In addition to practical attributes, such as operational simplicity and mild conditions, the metalloradical system is highlighted by its tolerance to different functional groups as well as compatibility with heteroaryl units.

Chapter 4. Design and Synthesis of A Novel D_2-Symmetric Chiral Porphyrin for Co(II)-Based Metalloradical Catalysis

A novel D_2-symmetric chiral amidoporphyrin derived from chiral cyclopropanecarboxamide containing diphenyl units has been effectively constructed based on Co(II)-catalyzed asymmetric cyclopropanation of alkenes.

DEDICATION

This thesis is dedicated to the loving memory of my grandfather

Zhirui Yang

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TABLE OF CONTENTS

CHAPTER 1

COBALT(II)-BASED METALLORADICAL CATALYSIS FOR STEREOSELECTIVE RADICAL CYCLOPROPANATION OF ALKENES

1.1. INTRODUCTION

Over the past decades, there has been a rapid growth in the development of radical reactions as powerful tools for modern organic synthesis owing to their rich reactivities and unique attributes.[1] Despite significant advancements, general strategies for addressing the longstanding issues of controlling reactivity and selectivity in radical reactions, especially enantioselectivity, remain to be developed and pose a formidable task in the field.[2] Among considerable endeavors,[3] metalloradical catalysis (MRC) represents a

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fundamentally different approach for achieving stereoselective radical reactions by exploiting metalloradical complexes as open-shell catalysts for catalytic generation and regulation of metal-stabilized organic radicals (Figure 1.1A).[4,5,6] To this end, Co(II) complexes of porphyrins [Co(Por)], as stable 15e-metalloradicals with a well-defined low spin d^7 electronic configuration, have emerged as a new class of privileged catalysts for homolytic activation of diazo compounds to generate unprecedented α-Co(III)-alkyl radicals upon release of N_2 as the sole byproduct (Figure 1.1B).[7] Through the employment

[4] For selected reviews and highlights on Co(II)-based MRC, see: (a) Lu, H. J.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899–1909. (b) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775–2823. (c) Demarteau, J.; Debuigne, A.; Detrembleur, C. *Chem. Rev.* **2019**, *119*, 6906–6955. (d) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626–4638. (e) Singh, R.; Mukherjee, A. *ACS Catal.* **2019**, *9*, 3604–3617. (e) Singh, R.; Mukherjee, A. *ACS Catal.* **2019**, *9*, 3604–3617. (f) Roy, S.; Das, S. K.; Khatua, H.; Das, S.; Chattopadhyay, B. *Acc. Chem. Res.* **2021**, *54*, 4395–4409.

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of modularly-designed D_2-symmetric chiral amidoporphyrins with tunable environments as the supporting ligands, the initially-generated C-centered radicals, which remain covalently bonded with the cobalt complex, retain the reactive nature of radicals and can be precisely governed to engage in common radical reactions, such as radical addition and H-atom abstraction as well as radical substitution, leading to the development of new catalytic processes of stereoselective radical transformations.[7g-i, 8]

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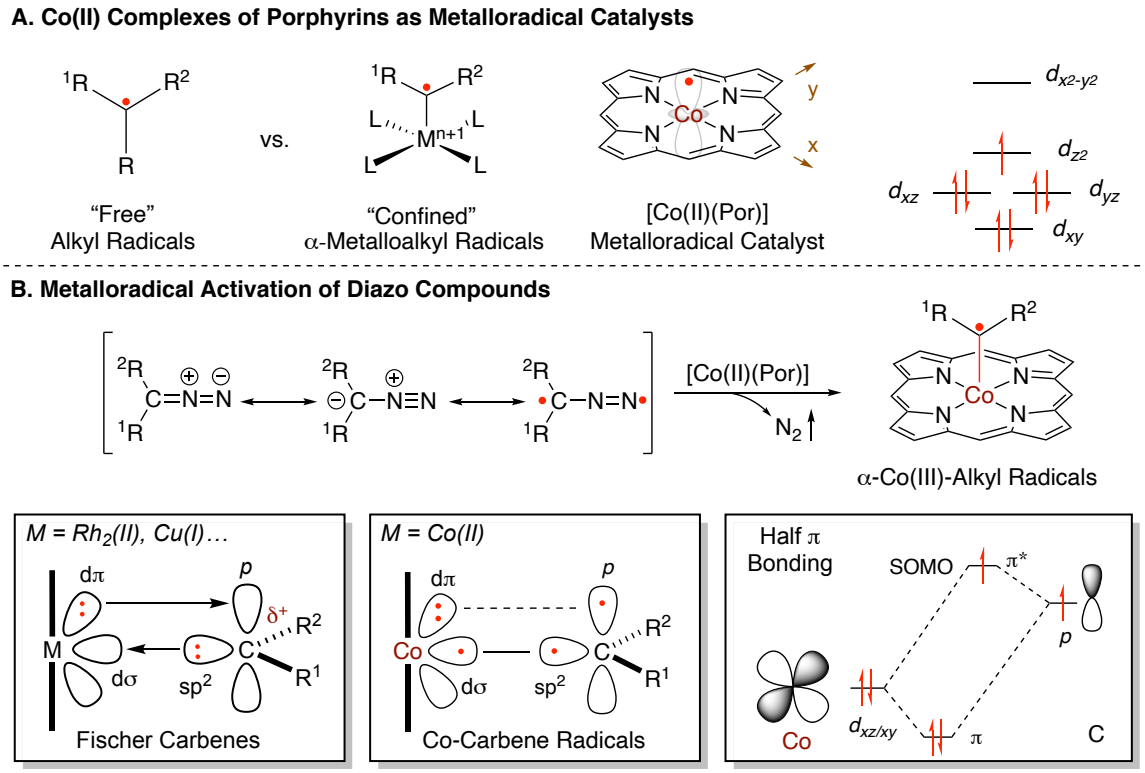
Figure 1.1. Co(II)-Based Metalloradical Catalysis as A Conceptually Different Approach Toward Controlling Radical Reactions

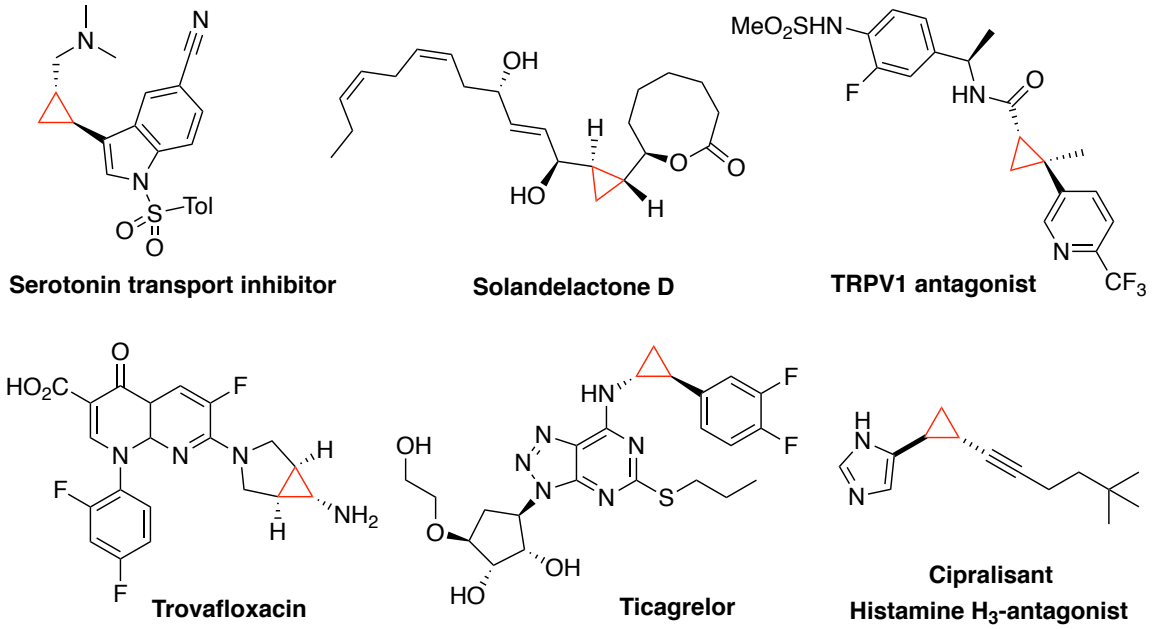


Chiral cyclopropanes are the smallest class of carbocyclic compounds with its three-membered ring structure. In addition to their fundamental significance, chiral cyclopropanes are of practical importance as they exist as recurring units in numerous natural products and bioactive compounds, in addition to serving as versatile chiral synthons for stereoselective organic synthesis (Figure 1.2).[9] Among synthetic methods, metal-catalyzed asymmetric cyclopropanation of alkenes with diazo compounds represents the most general approach for stereoselective synthesis of chiral cyclopropanes.[10] While a

[9] Talele, T. T. *J. Med. Chem.* **2016**, *59*, 8712–8756. (b) Ebner, C.; Carreira, E. M. *Chem. Rev.* **2017**, *117*, 11651–11679.

[10] (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911–935. (c) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050. (d) Intrieri, D.; Carminati, D. M.; Gallo, E. *Dalton Trans.* **2016**, *45*, 15746–16048.

Figure 1.2. Selected Examples of Natural Products and Bioactive Compounds Containing Cyclopropane Motifs



number of transition metal-based catalytic systems have been successfully developed for asymmetric cyclopropanation with acceptor-substituted diazo compounds, such as diazoacetates, [11] other important classes of diazo compounds, including acceptor/acceptor [12] - and donor-substituted diazo compounds, [13] have proven to be challenging as carbene sources for the catalytic transformation presumably due to the

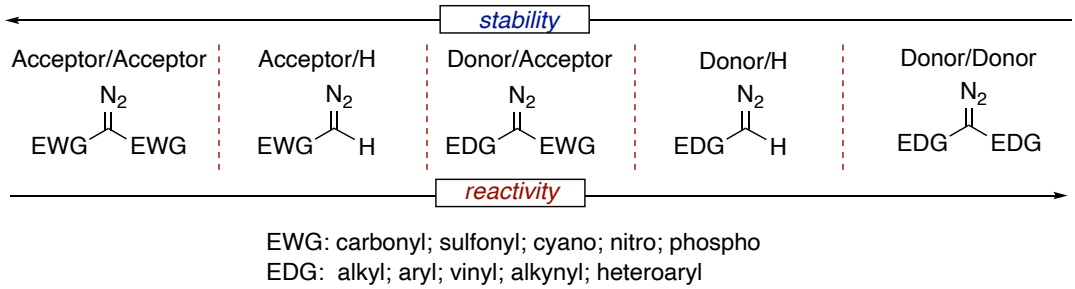
[11] (a) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726–728. (b) Doyle, M. P.; Winchester, W. R.; Hoorn, J. A. A.; Lynch, V.; Simonsen, S. H.; Ghosh, R. *J. Am. Chem. Soc.* **1993**, *115*, 9968–9978. (c) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224. (d) Lo, M. M. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270–10271. (e) Che, C.-M.; Huang, J.-S.; Lee, F.-W.; Li, Y.; Lai, T.-S.; Kwong, H.-L.; Teng, P.-F.; Lee, W.-S.; Lo, W.-C.; Peng, S.-M.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 4119–4129. (f) Davies, H. M. L.; Antoulinakis, E. G. *Org. React.* **2001**, *57*, 1. (g) Pellissier, H. *Tetrahedron* **2008**, *64*, 7041–7095. (h) Caballero, A.; Prieto, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Eur. J. Org. Chem.* **2009**, 1137–1144. (i) Coelho, P. S.; Brustad, E. M.; Kannan, A.; Arnold, F. H. *Science* **2013**, *339*, 307–310. (j) Wei, Y.; Tinoco, A.; Steck, V.; Fasan, R.; Zhang, Y. *J. Am. Chem. Soc.* **2018**, *140*, 1649–1662. (k) Shaw, S.; White, J. D. *Chem. Rev.* **2019**, *119*, 9381–9426.

[12] Doyle, M. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 850–852.

[13] Allouche, E. M. D.; Charette, A. B. *Synthesis* **2019**, *51*, 3947–3963.

electrophilic nature of the metallocarbene intermediates involved in the existing catalytic systems. For the same reason, asymmetric cyclopropanation of electron-deficient olefins, such as α,β-unsaturated carbonyl compounds and nitriles, remains a major challenge in the field. In addition to the limited substrate scope, existing catalytic systems typically require the use of excess olefins and slow addition of diazo compounds as dimerization of diazo compounds is a common side reaction. To address these and other issues, it calls for the development of new catalytic approach that is fundamentally different from existing catalytic systems. This Account aims to summarize Zhang group's recent efforts in developing Co(II)-based MRC as a one-electron approach for asymmetric radical cyclopropanation of various alkenes with different classes of diazo compounds (Figure 1.3).

Figure 1.3. Classes of diazo compounds (EWG = electron withdrawing group; EDG = electron donating group)



1.2. COBALT(II) COMPLEXES OF D_2-SYMMETRIC AMIDOPORPHYRINS AS METALLORADICAL CATALYSTS

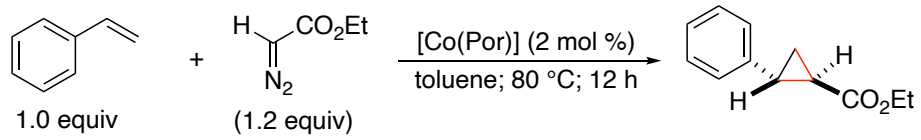
Inspired by the extraordinary catalytic capability of heme-containing enzymes in nature, metalloporphyrins have been recognized for their potential utility as effective catalysts in organic synthesis. Owing to the unique ligand environment and metal coordination mode, metalloporphyrin-based systems have been shown to exhibit exceptional selectivities and

high catalytic turn overs.[14] Since the first demonstration of rhodium porphyrins for catalytic cyclopropanation in 1980,[15] a number of metalloporphyrins, including iron, ruthenium, and osmium complexes of porphyrins, have been utilized to catalyze selective cyclopropanation and related carbene transfer reactions.[11e,16] Only until 2003, Zhang[17] and Cenini and coworkers[18] independently disclosed for the first time the catalytic capability of Co(II) complexes of porphyrins [Co(Por)] for olefin cyclopropanation with diazo compounds. In addition to the disclosure of the new catalytic activity, Zhang and coworkers further showed that [Co(Por)] are even superior catalysts for olefin cyclopropanation in comparison with other common metalloporphyrins, including Fe(III), Ru(II) and Rh(III) complexes of porphyrins.[17] It was found that the common side products resulting from competitive carbene dimerization of diazo compounds was minimized in [Co(Por)]-based catalytic system for olefin cyclopropanation. Consequently, the Co(II)-based catalytic system can operate in a one-pot fashion with alkenes as the limiting reagents and without the need of slow addition of diazo compounds, a practically desirable protocol that is atypical for most catalytic systems. With the support of chiral porphyrins, asymmetric induction was demonstrated for Co(II)-catalyzed olefin cyclopropanation. More importantly, a significant ligand effect on reactivity as well as diastereoselectivity and

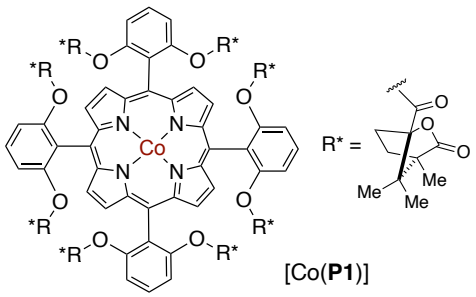
[14] Kadish, K. M.; Smith, K. M.; Guilard, R., The Porphyrin Handbook. Academic Press: San Diego, 2003.
[15] Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489–3492.
[16]) (a) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645–652. (b) Smith, D. A.; Reynolds, D. N.; Woo, L. K. *J. Am. Chem. Soc.* **1993**, *115*, 2511–2513. (c) Wolf, J. R.; Hamaker, C. G.; Djukic, J.-P.; Kodadek, T.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 9194–9199. (d) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2002**, *231*, 151–164. (e) Morandi, B.; Carreira, E. M. *Science* **2012**, *335*, 1471–1474. (f) Allouche, E. M. D.; Al-Saleh, A.; Charette, A. B. *Chem. Commun.* **2018**, *54*, 13256–13259. (g) Damiano, C.; Sonzini, P.; Gallo, E. *Chem. Soc. Rev.* **2020**, *49*, 4867–4905.
[17] Huang, L.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 8179–8184.
[18] Penoni, A.; Wanke, R.; Tollari, S.; Gallo, E.; Musella, D.; Ragaini, F.; Demartin, F.; Cenini, S. *Eur. J. Org. Chem.* **2003**, 1452–1460.

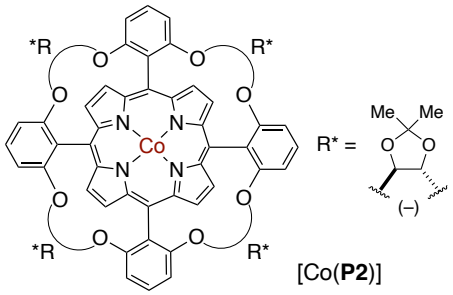
enantioselectivity was revealed in Co(II)-based catalytic system for asymmetric cyclopropanation (Scheme 1.1).

Scheme 1.1. Ligand Effect on Asymmetric Olefin Cyclopropanation by Co(II) Complexes of Chiral Porphyrins



entry	[Co(Por)]	yield (%)	*cis*:*trans*	*cis* (% ee)	*trans* (% ee)
1	[Co(**P1**)]	73	64:36	77	62
2	[Co(**P2**)]	84	48:52	31	10





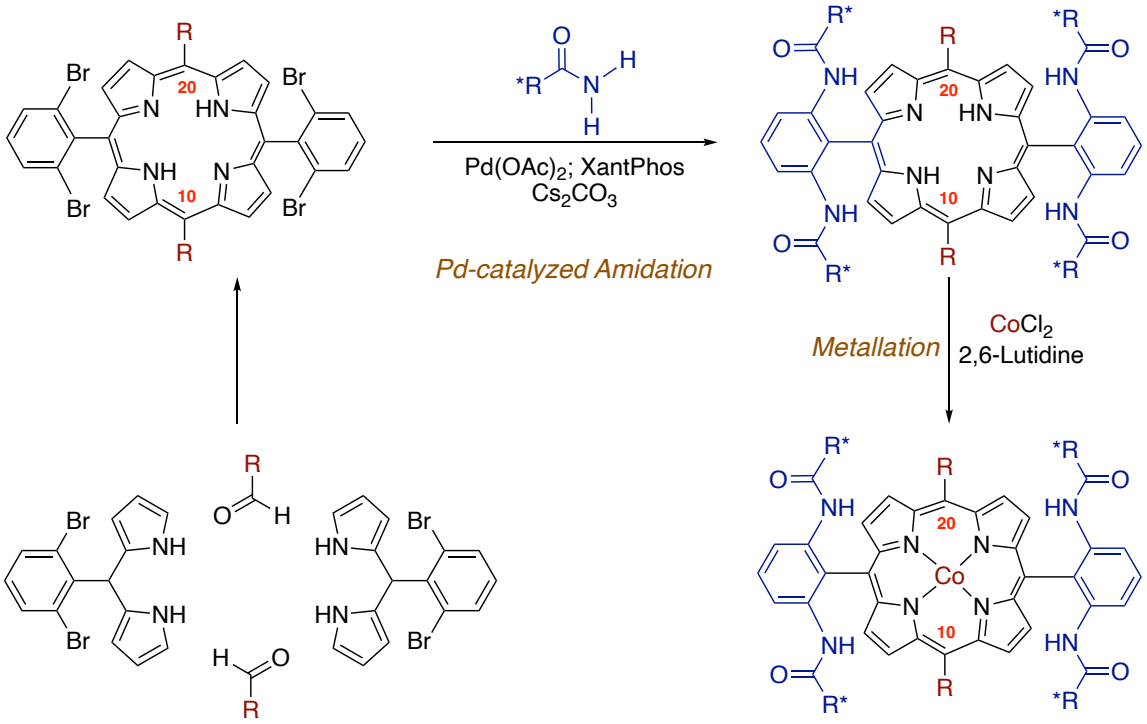
For example, with D_4-symmmetric chiral esterporphyrin **P1** as the supporting ligand, Co(II)-based catalytic system could catalyze asymmetric cyclopropanation of styrene with ethyl diazoacetate (EDA) under the practical protocol, affording the desired cyclopropane in good yield (73%) as *cis*-dominant product (*cis*:*trans* = 64:36) with moderate enantioselectivities (77% ee and 62% ee for *cis*- and *trans*-cyclopropane, respectively). When the supporting ligand was replaced by D_2-symmmetric chiral etherporphyrin **P2**, the Co(II)-catalyzed reaction produced the cyclopropane in higher yield (84%) as *trans*-dominant product (*cis*:*trans* = 48:52) with significantly lower enantioselectivities (31% ee and 10% ee for *cis*- and *trans*-cyclopropane, respectively).[17] Mechanistically, Zhang and coworkers proposed a catalytic cycle for the Co(II)-catalyzed cyclopropanation involving

"a Co(III)-carbene complex with Co–C single bond and carbon-based radical character".[17] Through both experimental and computational studies, the proposed Co(III)-carbene radicals, which is systematically termed as α-Co(III)-alkyl radicals, have since been well established as key intermediates in diverse catalytic radical processes via Co(II)-based metalloradical catalysis. On the basis of these initial results, it was envisioned that the design and synthesis of new chiral porphyrin ligands would improve both reactivity and stereoselectivities of radical cyclopropanation by [Co(Por)] and might lead to the discovery of new catalytic radical transformations.

As stable 15e-metalloradicals, Co(II) complex of porphyrins exhibit several unique features that render them versatile and efficient catalysts, such as excellent thermal and metal coordination stability as well as minimal complication resulting from potential *cis*-coordination. Moreover, the introduction of peripheral substituents within the porphyrin ligands essentially permits flexibility in design of [Co(Por)] with varied electronic, steric, and chiral environments. However, the preparation of porphyrin derivatives bearing different substituents often requires tedious purification and typically gives low yields.[19] Within this context, in 2004, Zhang and coworkers developed a general and efficient method for the modular construction of D_2-symmetric chiral amidoporphyrins (D_2-Por*) via Pd-catalyzed amidation reactions of 5,10-bis(2',6'-dibromophenyl)porphyrin synthons with chiral amides (Scheme 1.2).[20] A series of 5,10- dibromophenyl)porphyrins containing different *meso*-R groups at 10 and 20 position can be readily accessed by MacDonald porp-

[19] Kadish, K. M.; Smith, K. M.; Guilard, R., The Porphyrin Handbook. Academic Press: San Diego, 2003; pp. 75–132.
[20] Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719.

Scheme 1.2. Modular Construction of Co(II) Complexes of D_2-Symmetric Chiral Amidoporphyrins

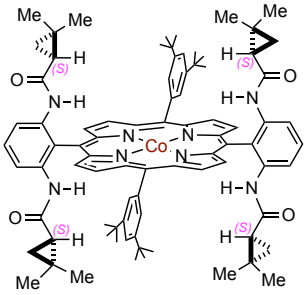


-hyrin synthesis using Lindsey's condition.[21] The resulting tetrabromoporphyrin synthons can be efficiently coupled with optically pure amides under the optimized Pd-catalyzed quadruple amidation conditions,[22] enabling the construction of a "toolbox" of D_2-symmetric chiral amidoporphyrins with varied *ortho*-chiral R* and *meso*-achiral R groups (Scheme 1.3). Followed by facile cobalt metalation, the corresponding Co(II) complexes of D_2-symmetric chiral amidoporphyrins can be furnished as stable purple solids in overall high yields.[20] The nearly perpendicular arrangement between the *meso*-phenyl rings and the porphyrin plane, in combination with the *trans*-amide conformation, could direct the *ortho* chiral amide units toward the center of the porphyrins, providing the requisite rigidity

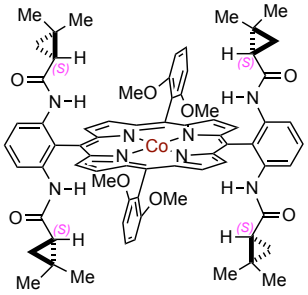
[21] Lindsey, J. S.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969–4970.
[22] Gao, G.-Y.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1837–1840.

for asymmetric induction. Though the combined use of chiral R^* and *meso*-R groups, it may be possible to control diastereoselectivity as well as enantioselectivity. Furthermore, it was hypothesized that the N–H moieties of the amide units are capable of engaging in potential H–bonding interactions with the substrates, which could play an important role in controlling reactivity and selectivity of Co(II)-based metalloradical systems that will be discussed later in details.

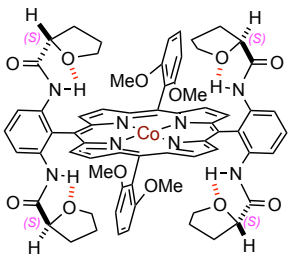
Scheme 1.3. Selected Examples of Co(II) Complexes of D_2-Symmetric Chiral Amidoporphyrins



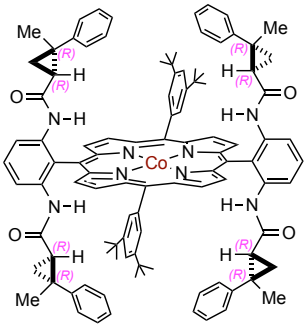
[Co(**P3**)]
(**P3** = 3,5-Di^{t}Bu-ChenPhyrin)



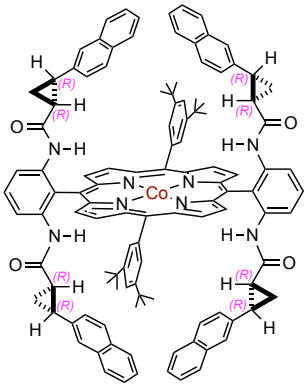
[Co(**P4**)]
(**P4** = 2,6-DiMeO-ChenPhyrin)



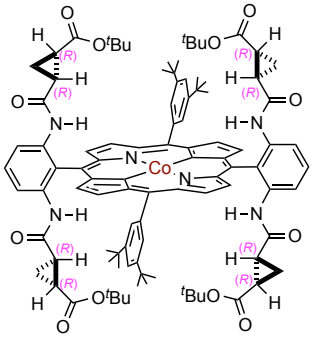
[Co(**P5**)]
(**P5** = 2,6-DiMeO-ZhuPhyrin)



[Co(**P6**)]
(**P6** = 3,5-Di^{t}Bu-QingPhyrin)



[Co(**P7**)]
(**P7** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin)



[Co(**P8**)]
(**P8**= 3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin)

1.3. COBALT(II)-CATALYZED INTERMOLECULAR RADICAL CYCLOPROPANATION

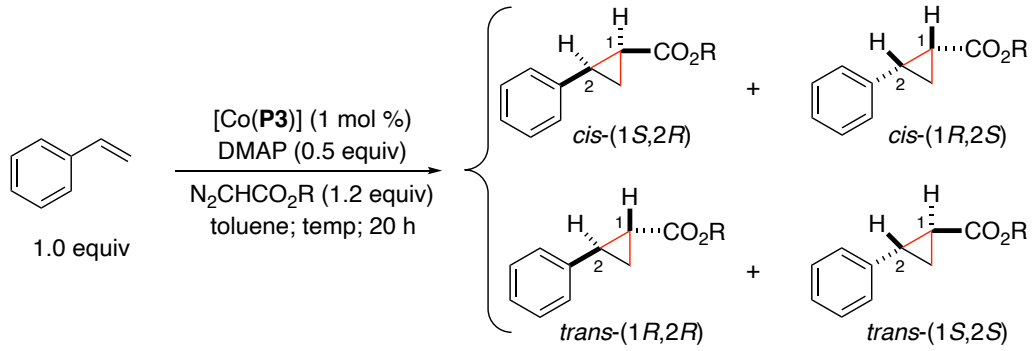
1.3.1. Intermolecular Radical Cyclopropanation with Acceptor-Substituted Diazo Compounds

To demonstrate the catalytic capability of the new class of metalloradical catalyst [Co(D_2-Por*)], asymmetric cyclopropanation of styrene with diazoacetate was evaluated as the model reaction (Scheme 1.4).[20] The first-generation metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin) proved to be effective in catalyzing the asymmetric radical cyclopropanation with *tert*-butyl diazoacetate (*t*-BDA). Moreover, during the course of the studies, a significant *trans*-effect of potential coordinating additives[23] was revealed in influencing the stereoselectivity of the radical cyclopropanation process. In the presence of substoichiometric amount of DMAP (4-(dimethylamino)pyridine) as additives, both the diastereoselectivity and enantioselectivity could be substantially enhanced, affording the desired cyclopropane product up to 85% yield with >99:1 dr and 98% ee. In addition to high yield and stereoselectivity, the [Co(**P3**)]-catalyzed asymmetric cyclopropanation can operate effectively in a one-pot fashion with styrene as the limiting reagent and without slow addition of the diazo compound.

After developing the highly asymmetric cyclopropanation of styrene with diazoacetate using [Co(**P3**)], Zhang and coworkers explored the catalytic reactivity of [Co(**P3**)] toward more challenging substrates, such as electron-deficient olefins (Scheme 1.5). As discussed earlier, asymmetric cyclopropanation of electron-deficient olefins has proven to be a formidable challenge in existing catalytic systems presumably attributed to the electrophil-

[23]Chen, Y.; Zhang, X. P. *Synthesis* **2006**, *10*, 1697–1700.

Scheme 1.4. Asymmetric Cyclopropanation of Styrene Catalyzed by D_2-Symmetric Chiral Co(II) Porphyrin [Co(P3)]

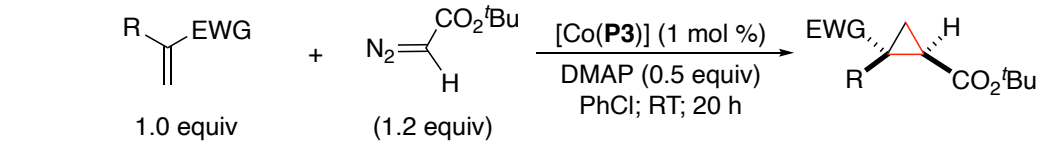


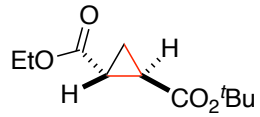
entry	R	temp	yield (%)	*trans*:*cis*	ee (%)	config
1	Et	RT	82	97:3	78	1*R*, 2*R*
2	^{t}Bu	RT	84	>99:1	95	1*R*, 2*R*
3	^{t}Bu	–20 °C	85	>99:1	98	1*R*, 2*R*

-lic nature of the metallocarbene intermediates.[10] Considering that neutral radicals typically react under mild conditions with a high degree of tolerance toward electronic properties of the substrates, a radical-mediated asymmetric cyclopropanation could potentially address the aforementioned issues with electron-deficient olefins. In 2007, Zhang and coworkers found that under a practical one-pot protocol using 1 mol % of [Co(**P3**)] in the presence of DMAP, a wide range of electron-deficient olefins, including unsaturated esters, amides, ketones, and nitriles could be effectively cyclopropanated with EDA and *t*-BDA, delivering the corresponding electrophilic cyclopropane derivatives in moderate to high yields with high stereoselectivities.[24] Evidently, the unique profile of reactivity and selectivity exhibited by the Co(II)-based metalloradical cyclopropanation toward electron-deficient olefins suggests the involvement of catalytic intermediates that are distinctly different from the previously reported systems.

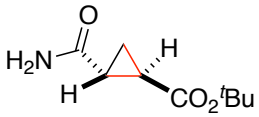
[24] Chen, Y.; Ruppel, J. V.; Zhang, X. P. *J. Am. Chem. Soc.* **2007**, *129*, 12074–12075.

Scheme 1.5. [Co(P3)]-Catalyzed Asymmetric Radical Cyclopropanation of Electron-Deficient Olefins

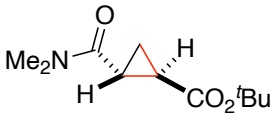




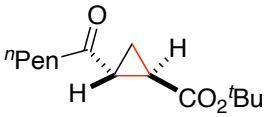
92% yield
99:1 dr; 91% ee



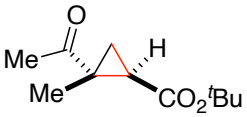
77% yield
99:1 dr; 97% ee



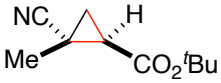
86% yield
99:1 dr; 96% ee



94% yield
99:1 dr; 96% ee



84% yield
97:3 dr; 87% ee



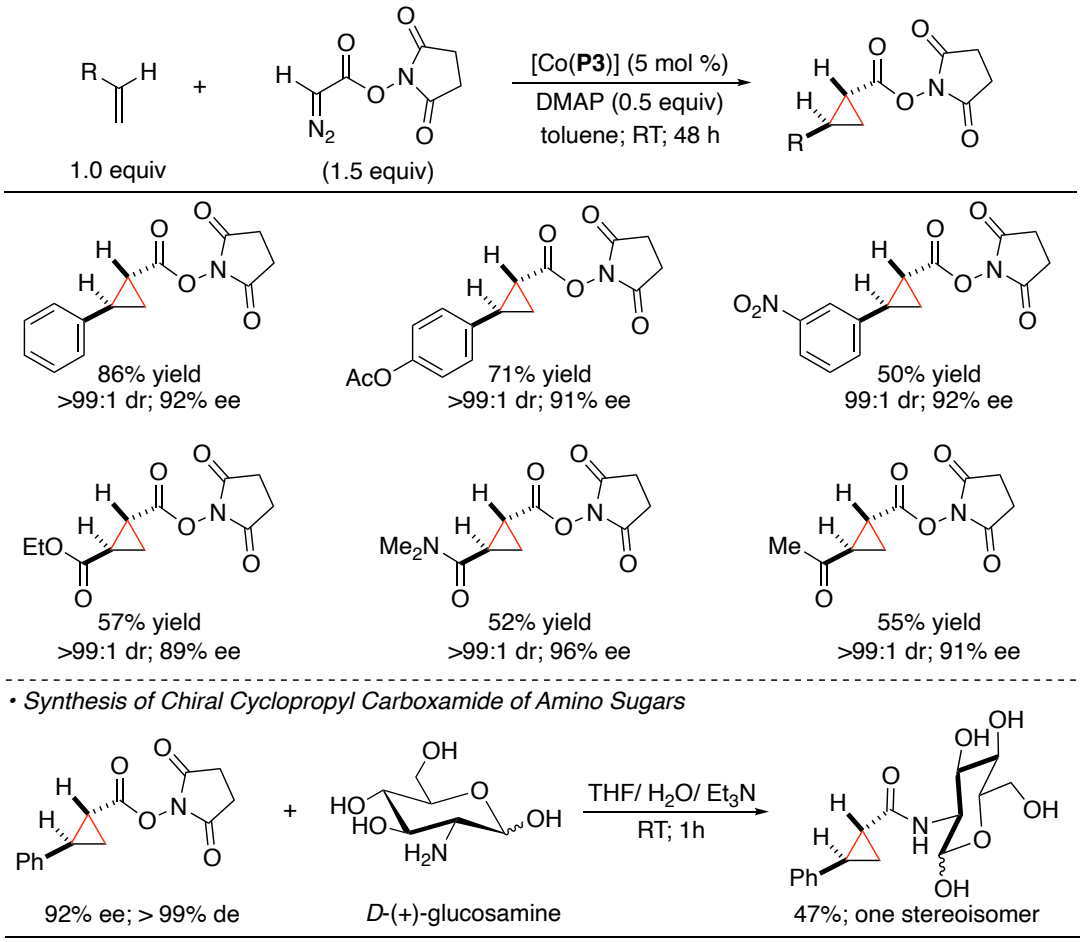
87% yield
62:38 dr; 95% ee

In addition to alkyl diazoacetates, the Co(II)-based MRC could be successfully applied for asymmetric cyclopropanation with succinimidyl diazoacetate, leading to the general synthesis of biologically important cyclopropyl carboxamides (Scheme 1.6).[25] After extensive ligand screening, it was found that the steric bulkiness of the succinimidyl diazoacetate essentially governed the reactivity difference of the metalloradical catalysts. Among different [Co(D_2-Por*)], [Co(**P3**)] was identified as the optimal catalyst for catalyzing the asymmetric cyclopropanation of styrene with succinimidyl diazoacetate in the presence of DMAP. Under the optimized conditions, it was revealed that the Co(II)-based catalytic system exhibits a high degree of functional group tolerance as demonstrated with the reactions of acetoxyl- and nitro-substituted styrenes to form the corresponding cyclopropanes in moderate to high yields with excellent stereoselectivities. Electron-

[25] Ruppel, J. V.; Gauthier, T. J.; Snyder, N. L.; Perman, J. A.; Zhang, X. P. *Org. Lett.* **2009**, *11*, 2273–2276.

deficient olefins, which are typically challenging substrates, could be effectively cyclopropanated by [Co(**P3**)] as well, furnishing the functionalized electrophilic cyclopropanes with excellent control of stereoselectivities albeit in lower yields. Subsequently, the authors have demonstrated the potential applications of the enantioenriched succinimidyl cyclopropyl carboxylate derivatives as versatile synthons for the general synthesis of chiral cyclopropyl carboxamides (Scheme 1.6).

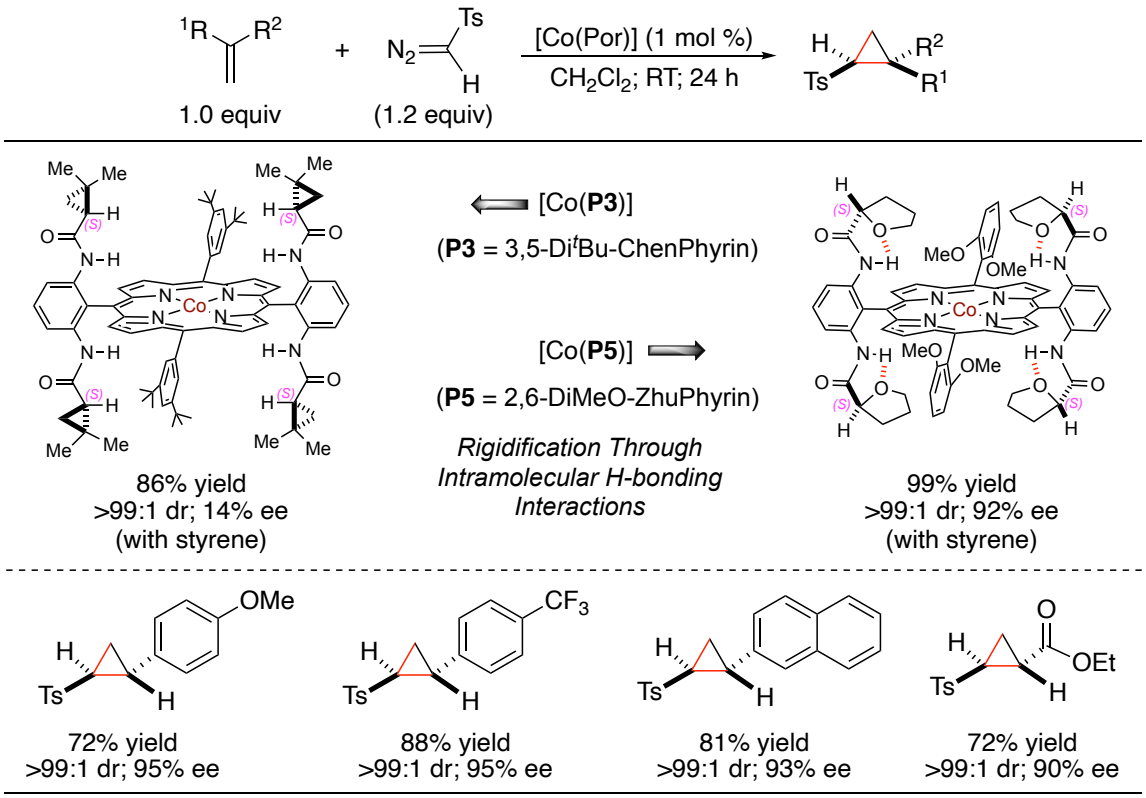
Scheme 1.6. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with Succinimidyl Diazoacetates



In 2008, Zhang and coworkers reported a Co(II)-based metalloradical system that is highly effective for asymmetric radical cyclopropanation employing diazosulfones as the

carbene precursor (Scheme 1.7).[26] Unexpectedly, [Co(**P3**)], which was previously shown to be the optimal catalyst for the cyclopropanation with diazoacetates, was found to be

Scheme 1.7. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with Diazosulfones



ineffective in terms of enantioselectivity in catalyzing the reaction with tosyldiazomethanes. To this end, Zhang and coworkers designed and synthesized a new chiral metalloradical catalyst [Co(**P5**)] (**P5** = 2,6-DiMeO-ZhuPhyrin)] featuring enhanced conformational rigidity as a result of unique intramolecular H-bonding interactions in (*S*)-2-tethydrafurancarboxamide units. The new metalloradical catalyst [Co(**P5**)] could effectively activate tosyldiazomethane for asymmetric cyclopropanation with styrene, delivering the desired product in 99% yield with >99:1 dr and 92% ee. In addition to styrene,

[26] Zhu, S.; Ruppel, J. V.; Lu, H.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043.

the [Co(**P5**)]-catalyzed cyclopropanation was shown to be generally applicable to a broad range of styrene derivatives as well as electron-deficient olefins, resulting in the high-yielding formation of the corresponding cyclopropyl sulfones with high diastereoselectivities and enantioselectivities.

In an effort to gain insights into the working details as well as the basis of unique reactivity and selectivity profiles of Co(II)-catalyzed asymmetric radical cyclopropanation, the Zhang group collaborated with Prof. de Bruin and coworkers and conducted a series of computational and experimental studies. Accordingly, density functional theory (DFT) calculations in combination with electronic paramagnetic resonance (EPR) and high-resolution mass spectrometry (HRMS) disclosed a stepwise radical mechanism involving α- and γ-metalloalkyl radicals as the key intermediates.[7a]

As illustrated in Scheme 1.8, the catalytic cycle begins with the metalloradical activation of the diazo compound by [Co(Por)] to generate α-Co(III)-alkyl radical intermediate with release of dinitrogen as the byproduct. The resulting Co-supported C-centered radical is capable of undergoing radical addition to the C=C double bond of the olefin substrate to form γ-Co(III)-alkyl radical intermediate (Figure 1.4). Finally, the last step of 3-*exo*-*tet* cyclization of γ-Co(III)-alkyl radical intermediate is a nearly barrierless process, leading to the formation of cyclopropane product while regenerating the metalloradical catalyst [Co(Por)].

Scheme 1.8. Proposed Catalytic Cycle of Co(II)-Catalyzed Asymmetric Radical Cyclopropanation

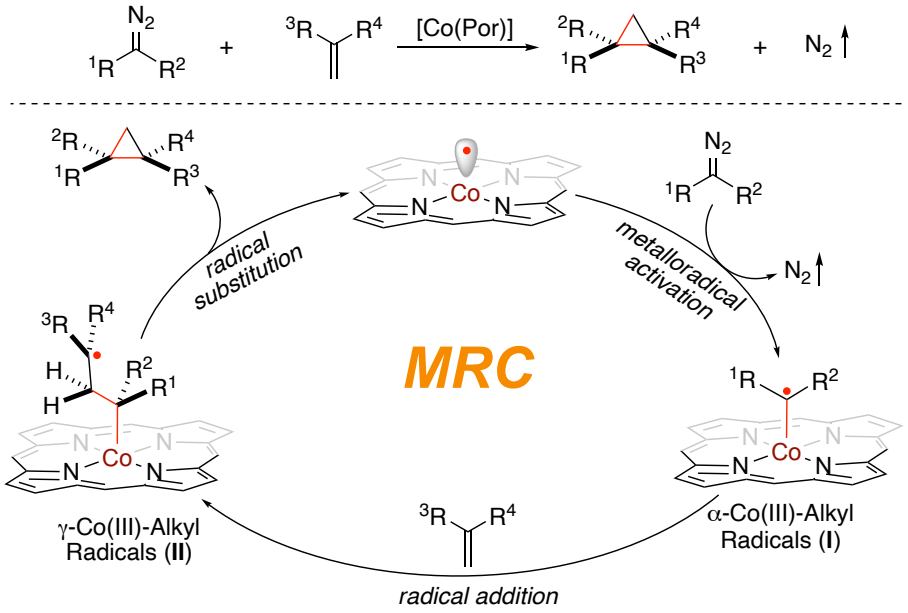
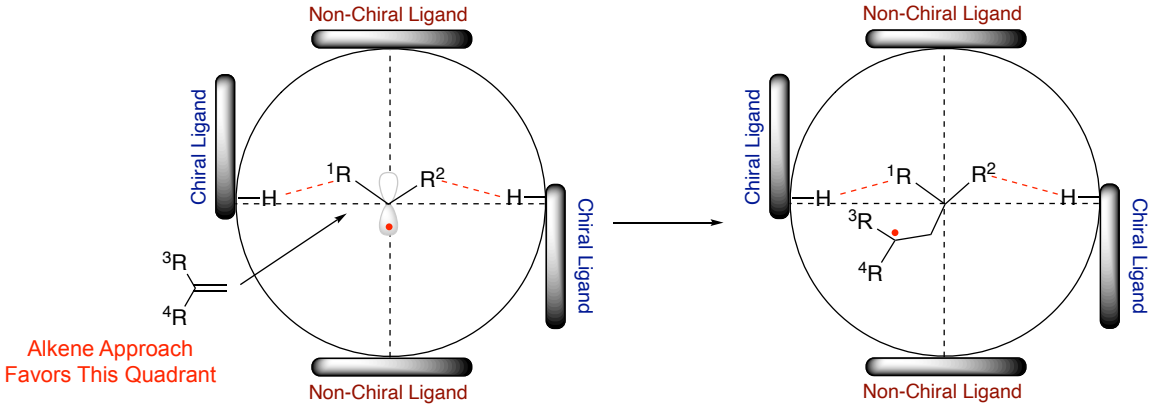


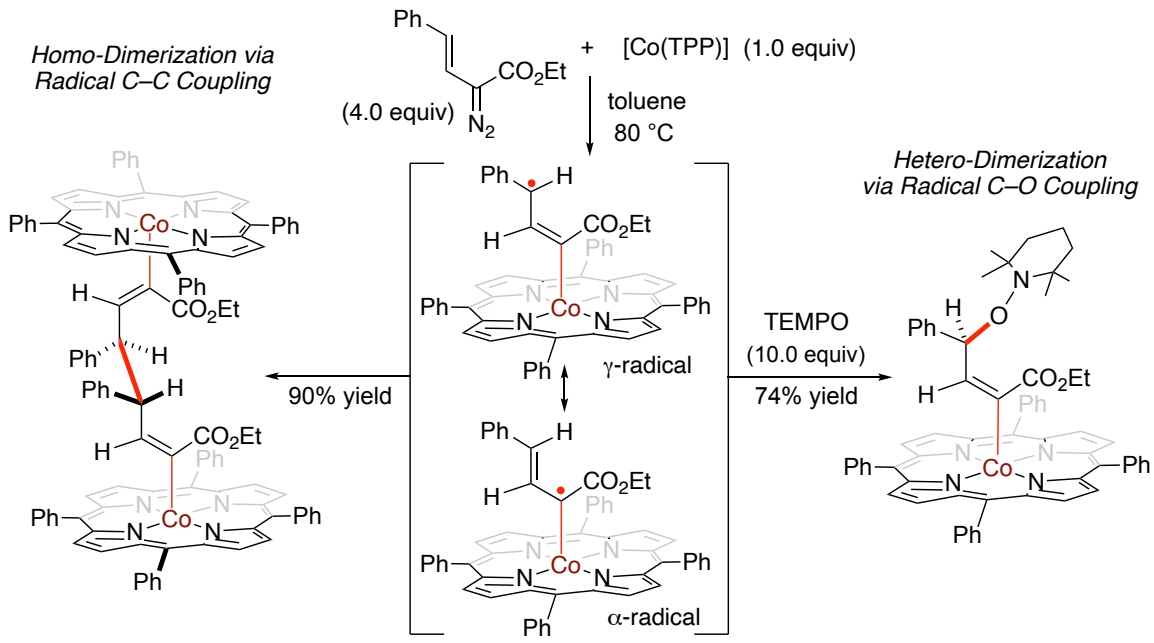
Figure 1.4. Proposed Stereochemical Model of Co(II)-Based Radical Cyclopropanation



To probe the existence of α-Co(III)-alkyl radical intermediate in the proposed mechanism, ethyl styryldiazoacetate was employed as the carbene source for a stoichiometric reaction with [Co(TPP)] (TPP = 5,10,15,20-tetraphenylprophyrin) in the absence of olefin substrates (Scheme 1.9).[7c] The initially formed α-Co(III)-allylic radical,

which could exist in its resonance form of γ-Co(III)-allylic radical, was found to undergo radical dimerization, forming a dinuclear Co(III) porphyrin complex in 90% yield whose structure was further confirmed by X-ray crystallography. Alternatively, the γ-Co(III)-allylic radical could be effectively captured by an excess amount of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to afford a mononuclear Co(III) complex via C–O bond formation in 74% yield. Taken together with the previous DFT calculations, these experimental results provided another corroborating evidence for the proposed stepwise radical mechanism of Co(II)-catalyzed asymmetric radical cyclopropanation.

Scheme 1.9. Probing of α-Co(III)-Alkyl Radicals by Dimerization and TEMPO Trapping

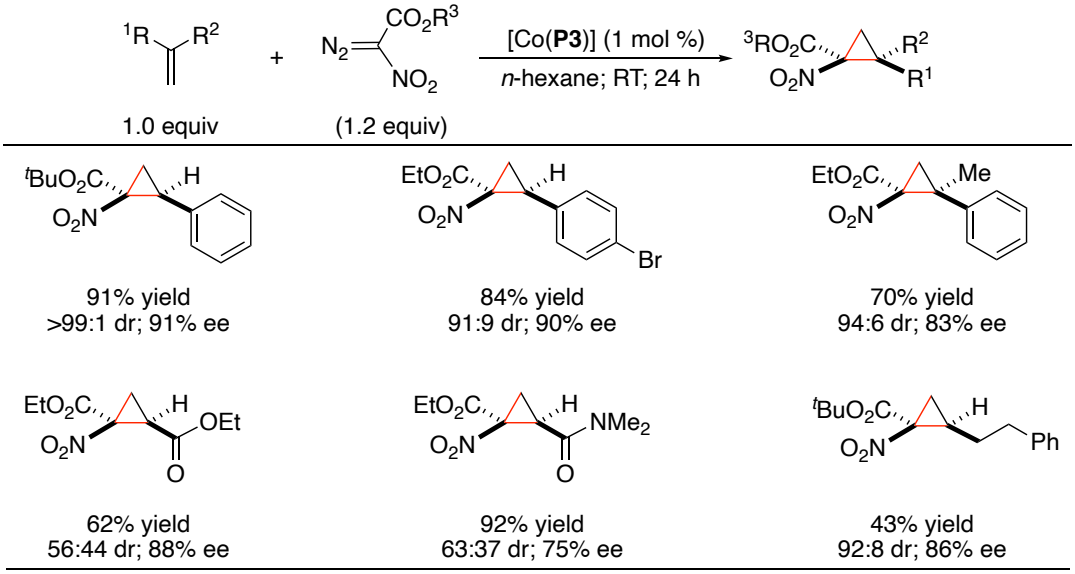


1.3.2. Intermolecular Radical Cyclopropanation with Acceptor/Acceptor-Substituted Diazo Compounds

In 2008, Zhang and coworkers initiated their effort to develop a new Co(II)-based catalytic system for asymmetric cyclopropanation with acceptor/acceptor-substituted diazo

compounds in the hope of addressing the longstanding challenges associated with existing catalytic systems involving electrophilic metallocarbene intermediates.[10]

Scheme 1.10. Co(II)-Catalyzed Asymmetric *Z*-Cyclopropanation with α-Nitrodiazoacetates



Their first target was α-nitrodiazoacetates considering that the resulting cyclopropanes may serve as valuable precursor for α-amino acids and aminocyclopropanes (Scheme 1.10).[27] Through systematic ligand evaluations, [Co(**P3**)] was identified to be the optimal catalyst for the asymmetric cyclopropanation with α-nitrodiazoacetates, even at room temperature.[28] It was rationalized that the effectiveness of [Co(**P3**)] toward α-nitrodiazoacetate is presumably attributed to the two potential H-bonding interactions between the chiral amido N–H moieties on the **P3** ligand and the respective N=O (-NO_2 group) and C=O (-CO_2R group) units of the diazo compound. Such noncovalent attractive

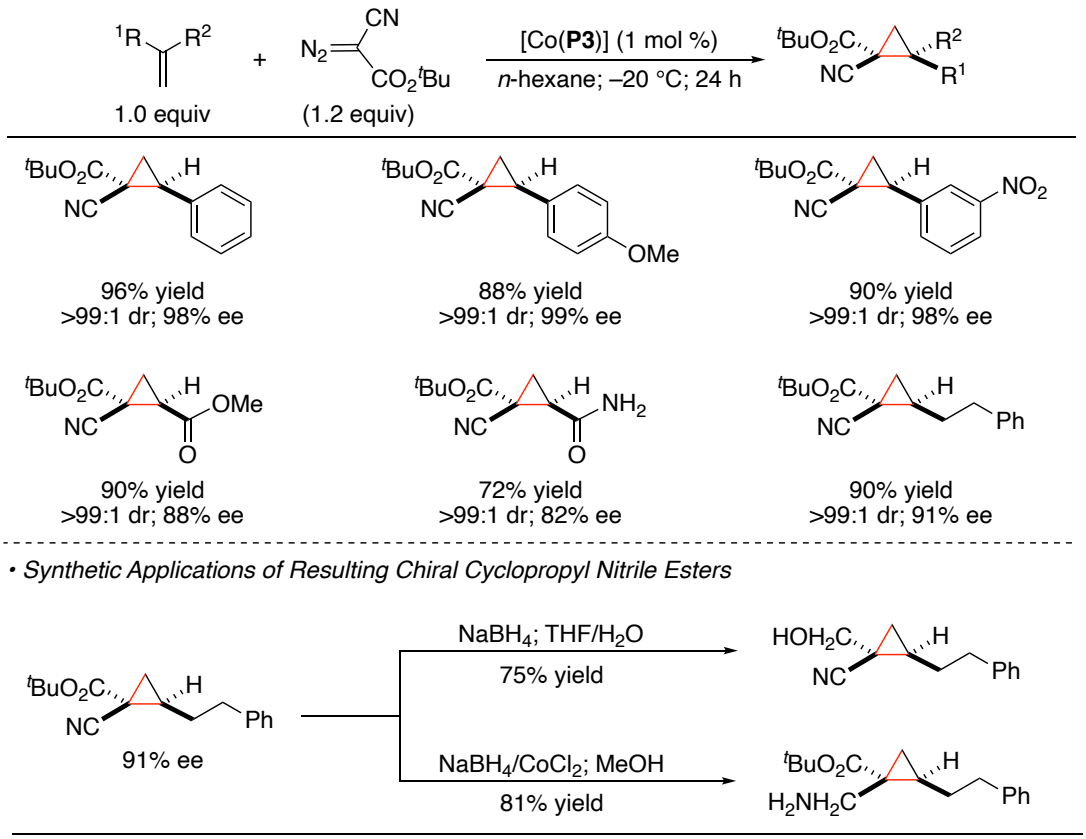
[27] (a) Wurz, R. P.; Charette, A. B. *J. Org. Chem.* **2004**, *69*, 1262–1269. (b) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2005**, *7*, 2313–2316.
[28] Zhu, S.; Perman, J. A.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8460–8463.

interactions are postulated to be essential in promoting the formation of the corresponding α-Co(III)-alkyl radical intermediate while enhancing its rigidity for subsequent addition reaction with the olefin substrate, which would lead to a more effective and selective catalytic process.[28] As one salient feature of the Co(II)-based metalloradical system, electron-deficient olefins, such as α,β-unsaturated esters and amides could be utilized for asymmetric cyclopropanation by [Co(**P3**)] albeit with diminished diastereoselectivities. Gratifyingly, [Co(**P3**)] proved to be similarly effective for catalyzing the asymmetric cyclopropanation of more challenging aliphatic olefins, forming the alkyl-substituted cyclopropane nitroesters in moderate yields with good stereoselectivities. Moreover, it is noted that the Co(II)-catalyzed radical cyclopropanation process exhibits an atypical (*Z*)-diastereoselectivity in contrast to the previously reported systems.

To further exploit the unique potential of Co(II)-based MRC for asymmetric cyclopropanation with acceptor/acceptor-substituted diazo compounds, Zhang and coworkers sought to explore the feasibility of employing α-cyanodiazoacetate as the carbene source, which represents a class of acceptor/acceptor-substituted diazo compounds that has not been successfully utilized for asymmetric olefin cyclopropanation. In 2010, Zhang and coworkers reported the first catalytic system for asymmetric cyclopropanation with α-cyanodiazoacetate (Scheme 1.11).[29] Given that a cyano group is generally considered as a stronger H-bonding acceptor than a nitro group, we envisioned the existence of similar double H-bonding interactions in the resulting α-Co(III)-alkyl radical intermediate.

[29] Zhu, S.; Xu, X.; Perman, J. A.; Zhang, X. P. *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799.

Scheme 1.11. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with α-Cyanodiazoacetates

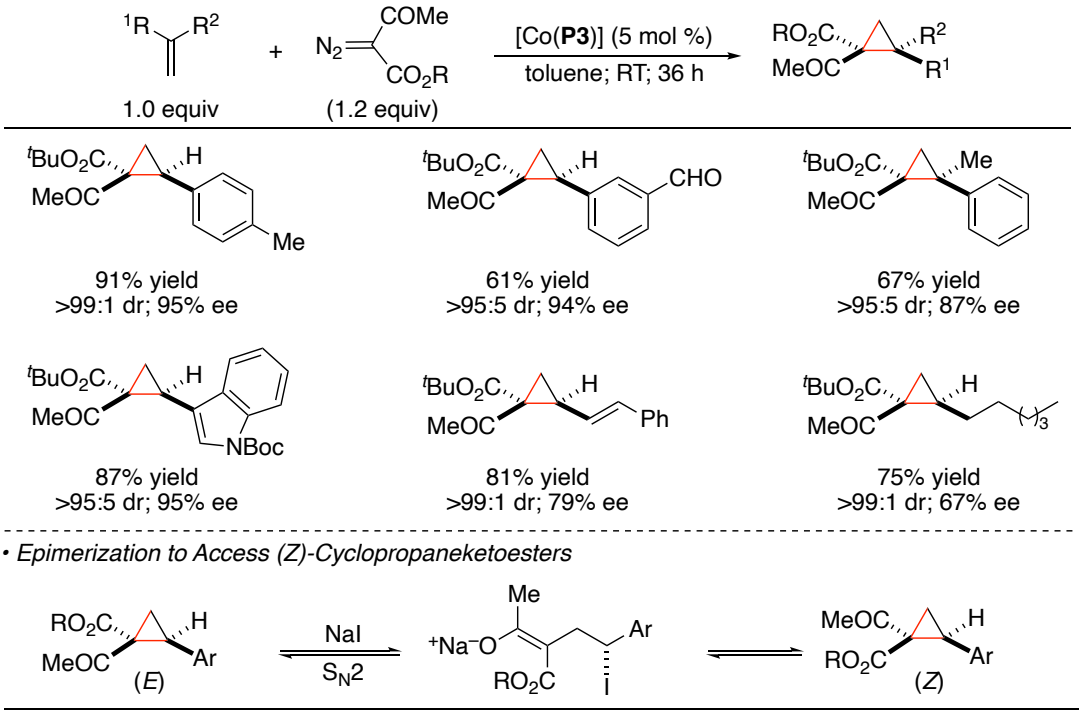


Using styrene as a model substrate, [Co(**P3**)] was found to be equally effective for the cyclopropanation reaction with α-cyanodiazoacetate. Further optimization of the reaction conditions revealed that the use of *tert*-butyl α-cyanodiazoacetate in *n*-hexane at –20 °C would afford the desired 1,1-cyclopropanenitrile ester in high yield with complete (*E*)-diastereoselectivity and 98% ee. In addition to styrene derivatives, the [Co(**P3**)]-based cyclopropanation is highlighted by a broad scope of olefins, including both electron-rich and electron-deficient substrates containing various functionalities. In this work, the resulting enantioenriched cyclopropanenitrile esters were also utilized in several stereospecific transformations.

While attempting to extend the application of Co(II)-based cyclopropanation to other acceptor/acceptor-substituted diazo compounds, Zhang and coworkers uncovered that dicarbonyl diazo compound, such as α-ketodiazoacetates bearing both ketone and ester functionalities could also be utilized as viable carbene sources (Scheme 1.12).[30] At the beginning of the investigations, it was unclear whether the metalloradical catalyst [Co(D_2-Por*)] could still render effective control of both enantioselectivity and diastereoselectivity for the cyclopropanation reaction with α-ketodiazoacetate. In view of the similar sizes of the two geminal carbonyl groups, could the incoming olefin substrate effectively discriminate the two prochiral faces of α-Co(III)-alkyl radical intermediate during the first C–C bond forming step? For the same consideration, additional uncertainty might arise from the subsequent 3-*exo*-*tet* cyclization of γ-Co(III)-alkyl radical intermediate. Through the identification of the optimal metalloradical catalyst [Co(**P3**)], it was demonstrated that *tert*-butyl acetodiazoacetate could be effectively activated, even at room temperature for the cyclopropanation of a wide range of olefins. In addition to high enantioselectivity, the Co(II)-based cyclopropanation system exhibits a distinct sense of diastereoselectivity from the previously reported systems involving electrophilic metallocarbenes, enabling for the first time the direct synthesis of chiral (*E*)-1,1-cyclopropane ketoesters. In this work, an iodide-promoted stereospecific epimerization process was also disclosed, which allows practical access to the corresponding (*Z*)-diastereomers with retention of the original optical purity.

[30] Xu, X.; Zhu, S.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 11857–11861.

Scheme 1.12. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with α-Ketodiazoacetates

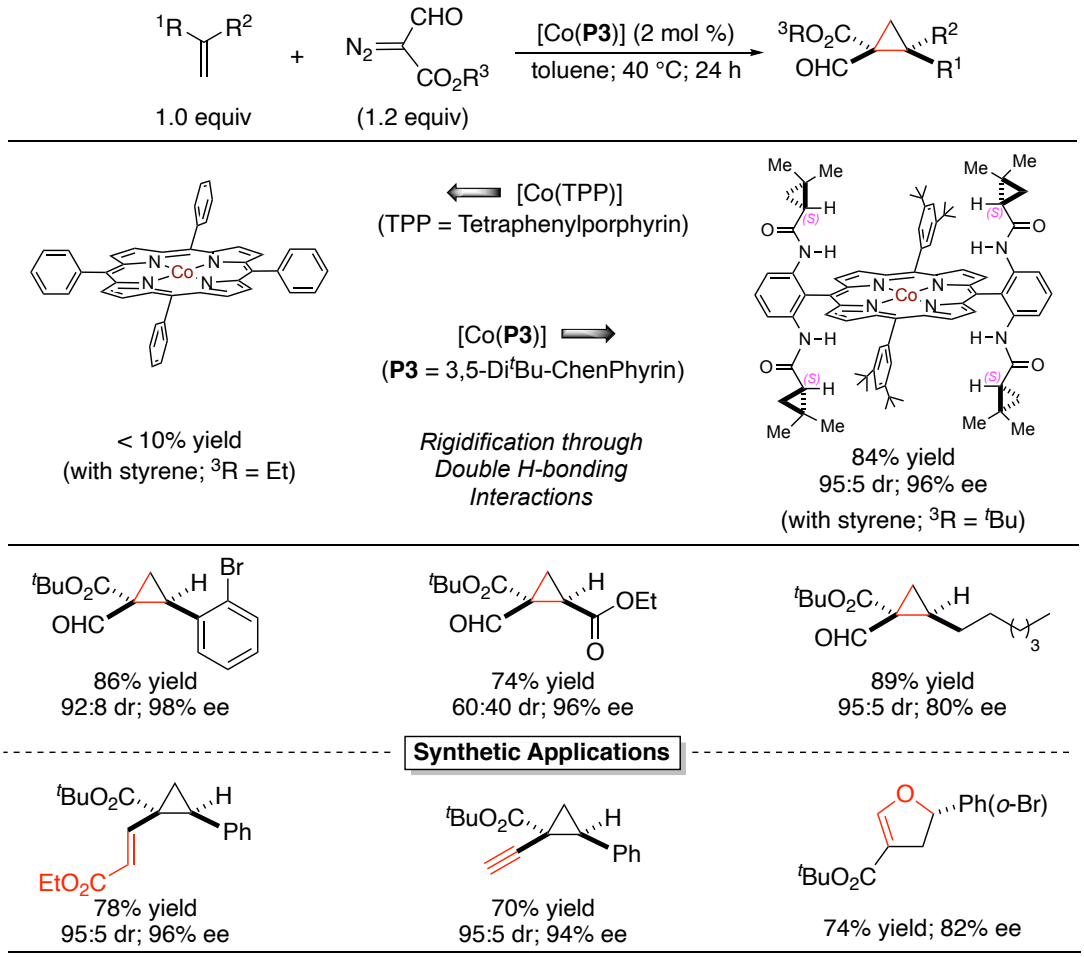


Recently, Zhang developed a new Co(II)-based catalytic system that is highly effective in activating α-formyldiazoacetates for asymmetric radical cyclopropanation, providing a general access to 1,1-cyclopropaneformylesters in high yields with excellent control of both diastereoselectivity and enantioselectivity (Scheme 1.13).[31] Given that many existing systems are incompatible with the aldehyde functionality,[32] this work represents the first application of α-formyl diazo compounds for metal-catalyzed asymmetric cyclopropanation. During the initial evaluation, a dramatic difference in catalytic performance was observed between the optimal metalloradical [Co(**P3**)] and [Co(TPP)],

[31] Xu, X.; Wang, Y.; Cui, X.; Wojtas, L.; Zhang, X. P. *Chem. Sci.* **2017**, *8*, 4347–4351.
[32] Wenkert, E.; Ananthanarayan, T. P.; Ferreira, V. F.; Hoffmann, M. G.; Kim, H. S. *J. Org. Chem.* **1990**, *55*, 4975–4976.

which is consistent with the hypothesized role of the double H-bonding interactions in activating the diazo compound while stabilizing the resulting C-centered radical intermediate for exquisite stereocontrol. Under the optimized conditions, it was further demonstrated that the Co(II)-catalyzed cyclopropanation features a broad scope of olefins as well as high functional group tolerance. As potential applications, the resulting enantioenriched 1,1-cyclocylopropaneformyl esters could be readily transformed into various chiral cyclopropane derivatives and 2,3-dihydrofurans while retaining high enantiopurity.

Scheme 1.13. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with α-Formyldiazoacetates



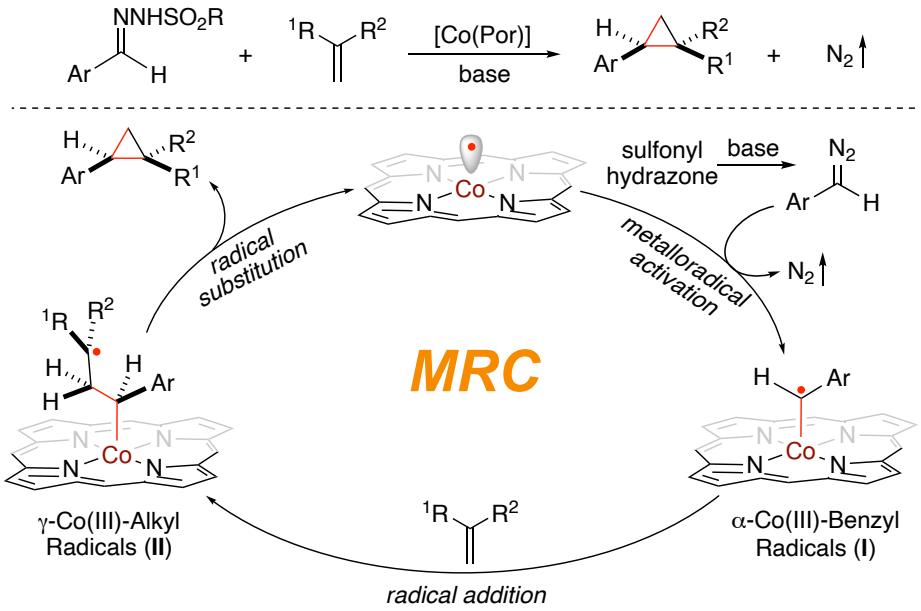
1.3.3. Intermolecular Radical Cyclopropanation with Donor-Substituted Diazo Compounds

Having recognized the remarkable catalytic capability of [Co(D_2-Por*)] in activating different acceptor- and acceptor/acceptor-substituted diazo compounds for asymmetric radical cyclopropanation, Zhang and coworkers aimed to explore whether the Co(II)-based catalytic system could be applied to other types of diazo compounds with substituents beyond carbonyl groups. Specifically, it would be highly appealing if the Co(II)-based metalloradical system could be applied for the asymmetric cyclopropanation with donor-substituted diazo compounds, which remains as an ongoing challenge in the field. This underdevelopment is largely attributed to the inherent instability of donor-substituted diazo compounds as well as their propensity towards unwanted dimerization.[33] To circumvent this issue, Zhang and coworkers envisioned the use of *N*-sulfonyl hydrazones as stable diazo precursors for the in situ-generation of less stabilized donor-substituted diazo compounds in the presence of base (Scheme 1.14).[34]

[33] (a) Doyle, M. P.; High, K. G.; Oon, S.-M.; Osborn, A. K. *Tetrahedron Lett.* **1989**, *30*, 3049–3052. (b) Regitz, M.; Maas, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: London, 1996. (c) Aggarwal, V. K.; de Vicente, J.; Bonnert, R. V. *Org. Lett.* **2001**, *3*, 2785–2788.

[34] (a) Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479–1492. (b) Xia, Y.; Wang, J. *Chem. Soc. Rev.* **2017**, *46*, 2306–2362.

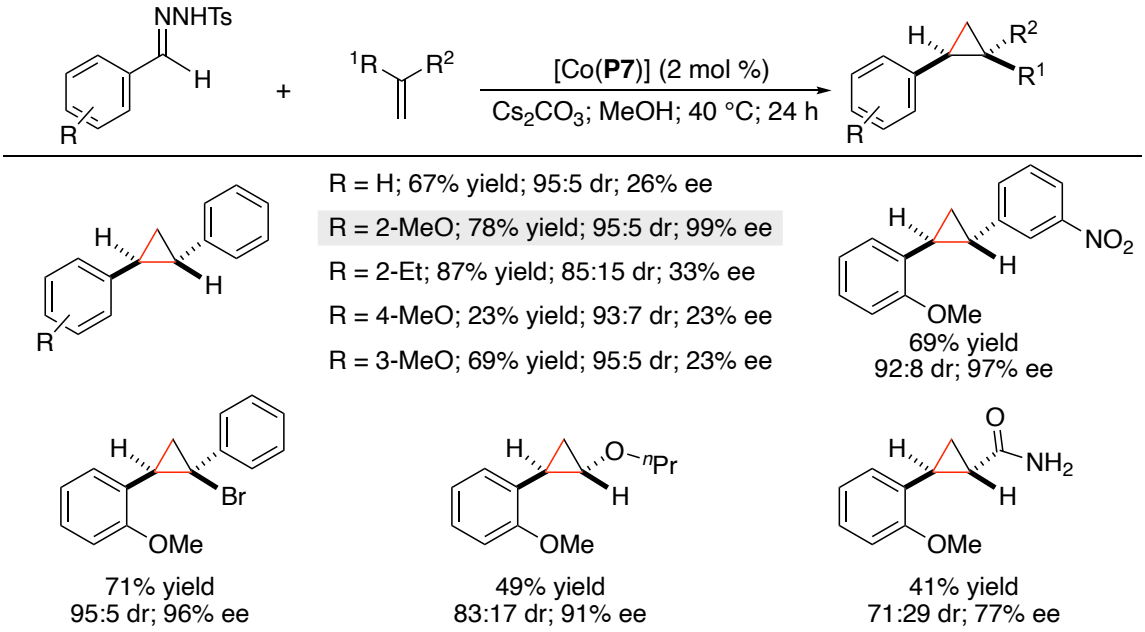
Scheme 1.14. Proposed Mechanism of Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with In Situ-Generated α-Aryldiazomethanes



However, it was unclear whether the Co(II)-based catalytic system would be compatible with the basic condition required for the in situ-generation protocol. Additionally, it would be crucially important to match the rate of generation of diazo compounds with the ensuing metalloradical activation in order to inhibit dimerization and azine formation.[33c] On the basis of our previous studies, the potential H-bonding interactions between the chiral amide units of the porphyrin ligands and the carbonyl groups of the diazo compounds have been postulated to facilitate effective asymmetric induction. In the absence of carbonyl functionalities, what element could be exploited for the stereoselective control of the radical cyclopropanation processes would be another elusive question.

To address these and related issues, in 2017, Zhang reported the first Co(II)-based metalloradical system that is highly effective for the asymmetric cyclopropanation of alkenes with α-aryldiazomethanes, generated in situ from the corresponding *N*-sulfonyl hydrazones in the presence of base (Scheme 1.15).[7d] Initial experiments were performed to

Scheme 1.15. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with In Situ-Generated α-Aryldiazomethanes

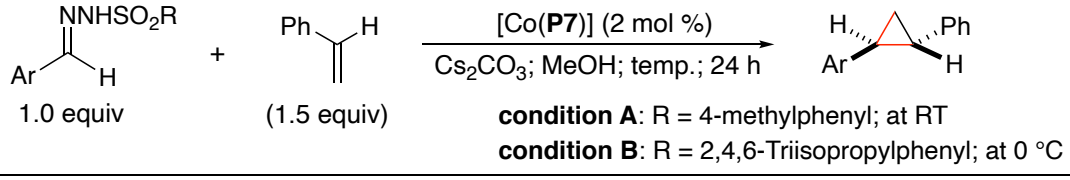


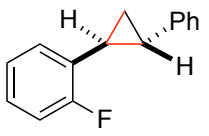
examine the feasibility of Co(II)-based MRC for asymmetric cyclopropanation of styrene with different substituted benzaldehyde tosylhydrazones under basic conditions. Using second-generation metalloradical catalyst [Co(**P7**)] (**P7** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin) containing naphthyl groups in the chiral amide units, *o*-methoxybenzaldehyde tosylhydrazone was found to be an effective radical precursor to provide the desired 1,2-bisaryl cyclopropane in good yield (78%) with high diastereoselectivity (95:5 dr) and excellent enantioselectivity (99% ee). Conversely, the asymmetric induction of the cyclopropanation process was significantly diminished when the *o*-OMe substituent was replaced by the sterically comparable *o*-Et group. Moreover, non-substituted phenyldiazomethane as well as *m*- and *p*-methoxyphenyldiazomethanes proved to be less effective radical precursors for the cyclopropanation reaction (Scheme 1.15). Based on these observations, we hypothesized that the installation of H-bonding acceptors such as

methoxy group at the *ortho*-position is necessary for engaging in potential H-bonding interactions with the amido group of the chiral ligand, which could rigidify the conformation of radical intermediates for effective control of asymmetric induction. In addition to styrene, we revealed that different classes of alkanes, including the more challenging electron-rich and electron-deficient nonaromatic olefins, could be effectively cyclopropanated by [Co(**P7**)] under the optimized conditions.

Guided by the hypothesis of H-bonding interactions, the scope of sulfonyl hydrazones was also evaluated as radical precursors for [Co(**P7**)]-catalyzed asymmetric cyclopropanation (Scheme 1.16). Notably, fluoroarene-based tosylhydrazones were shown to be more reactive radial precursors, allowing for the productive formation of fluorinated cyclopropanes even at room temperature.[7d] Interestingly, the use of the corresponding trishydrazone (2,4,6-triisopropylphenylsulfonyl hydrazone) enabled the cyclopropanation process to proceed at 0 °C, affording the cyclopropanes with improved stereoselectivities.[7d]

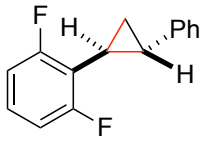
Scheme 1.16. Asymmetric Cyclopropanation of Styrene with Different Sulfonyl Hydrazones Catalyzed by [Co(P7)]





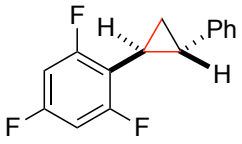
condition A: 58% yield
96:4 dr; 71% ee

condition B: 75% yield
>99:1 dr; 76% ee



condition A: 90% yield
94:6 dr; 86% ee

condition B: 83% yield
>99:1 dr; 93% ee



condition A: 85% yield
96:4 dr; 88% ee

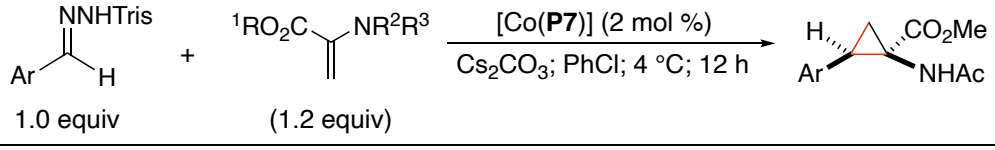
condition B: 85% yield
>99:1 dr; 93% ee

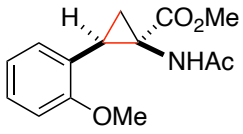
More recently, the reported procedure of Co(II)-catalyzed cyclopropanation of alkenes with in situ generated α-aryldiazomethanes can be extended to the use of dehydroaminocarboxylates for the direct synthesis of chiral cyclopropyl α-amino acid derivatives, which may serve as important non-proteinogenic α-amino acid building blocks for the design and preparation of peptides with restricted conformations.[35] In addition to the inherent steric hindrance of 1,1-disubstituted olefins, the synthetic challenge associated with the preparation of such cyclopropanes is largely due to the electronic incompatibility of dehydroaminocarboxylates as electron-deficient olefins with the existing catalytic systems involving electrophilic metallocarbene intermediates. Considering that the metalloradical system would be less sensitive to the electronic requirements of the substrates, Zhang and coworkers explored the suitability of dehydroaminocarboxylates for Co(II)-catalyzed asymmetric radical cyclopropanation (Scheme 1.17).[7e] In the preliminary studies, a similar positive effect of installing -OMe group at the *ortho*-position of the in situ-generated α-aryldiazomethane was observed, which could be effectively activated by [Co(**P7**)] (**P7** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin) for the cyclopropanation reaction of dehydroaminocarboxylate, affording the desired chiral cyclopropyl α-amino ester in excellent yield (98%) with high (*Z*)-diastereoselectivity (82:18 dr) and excellent enantioselectivity (93% ee). Having established the optimal reaction conditions, a broad combination of α-aryldiazomethanes and dehydroaminocarboxylates with varied steric and electronic properties was evaluated for the [Co(**P7**)]-based catalytic system, providing

[35] (a) Jiménez, A. I.; Marraud, M.; Cativiela, C. *Tetrahedron Lett.* **2003**, *44*, 3147–3150. (b) Brackmann, F.; de Meijere, A. *Chem. Rev.* **2007**, *107*, 4493–4537.

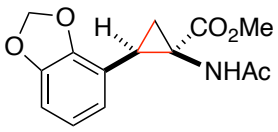
practical access to different α-amino-β-arylcyclopropanecarboxylates in high yields with excellent stereoselectivities.

Scheme 1.17. Asymmetric Radical Cyclopropanation of Dehydroaminocarboxylates with α-Aryldiazomethanes

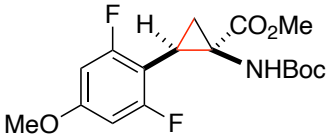




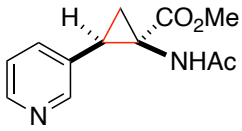
98% yield
82:18 dr; 93% ee



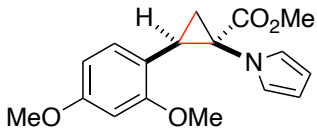
94% yield
80:20 dr; 82% ee



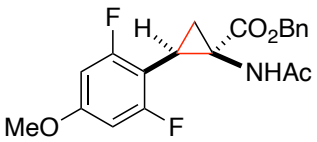
88% yield
65:35 dr; 98% ee



91% yield
73:27 dr; 61% ee



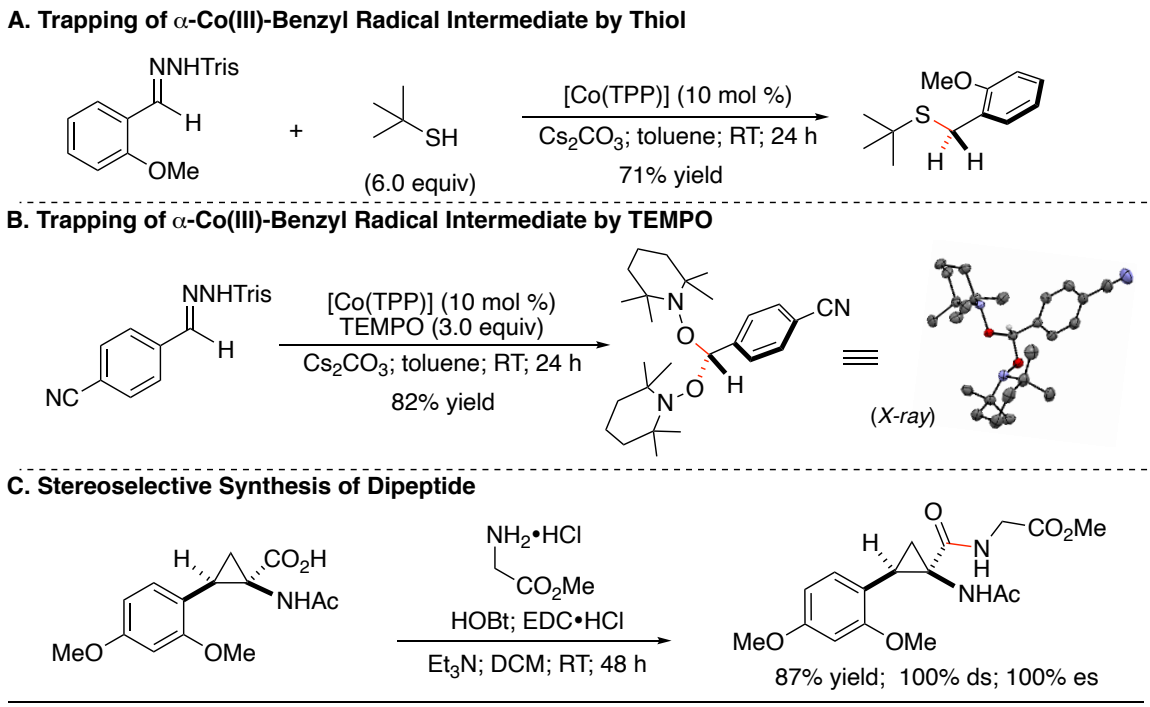
80% yield
80:20 dr; 90% ee



92% yield
81:19 dr; 75% ee

Furthermore, Zhang and coworkers performed detailed DFT calculations to gain insights into the basis of reactivity and stereoinduction, including the revelation of a network of multiple noncovalent attractive interactions, such as multiple H-bonding and π-stacking interactions in the optimized structures of intermediates and transition states.[7e] In addition to computational elucidation, the proposed stepwise radical mechanism is further supported by EPR spectroscopy as well as trapping experiments with thiol and TEMPO (Scheme 1.18). To demonstrate the synthetic applications of this new catalytic system, Zhang and coworkers also showcased the resulting enantioenriched α-amino-β-arylcyclopropanecarboxylates can serve as useful building blocks for the synthesis of dipeptides that may possess interesting biological properties (Scheme 1.18).

Scheme 1.18. Mechanistic Studies on Co(II)-Catalyzed Radical Cyclopropanation of Dehydroaminocarboxylates with α-Aryldiazomethanes



In 2021, Zhang and coworkers leveraged the analogous α-heteroaryldiazomethanes for the stereoselective preparation of valuable chiral heteroaryl cyclopropanes,[36] which was anticipated to be challenging in view of the potential competitive coordination of the heteroaryl moieties to the metal center.[33b,37] To date, there have been only a few reports on metal-based catalytic systems for direct synthesis of heteroaryl cyclopropanes from α-heteroaryldiazomethanes.[16f,38] Systematic reaction and catalyst development led to the

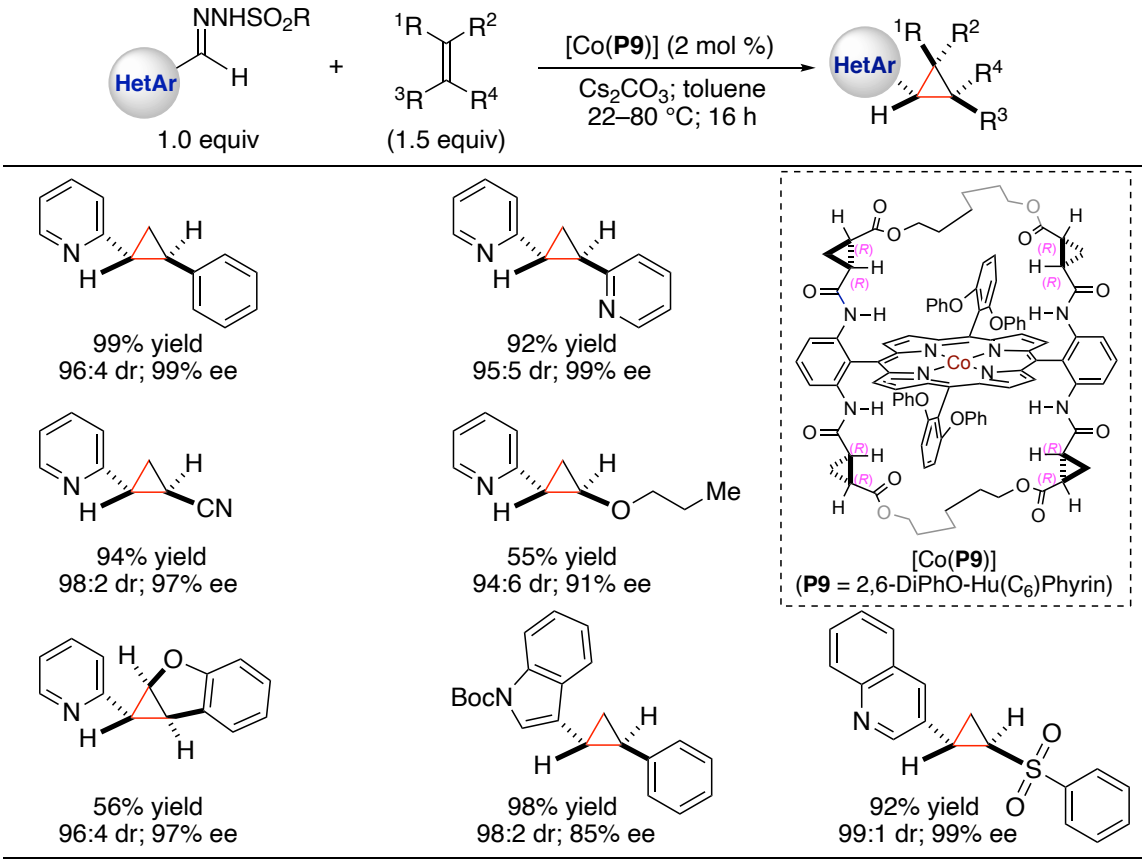
[36] (a) Liu, H.; Kerdesky, F. A.; Black, L. A.; Fitzgerald, M.; Henry, R.; Esbenshade, T. A.; Hancock, A. A.; Bennani, Y. L. *J. Org. Chem.* **2004**, *69*, 192–194. (b) Butcher, K. J.; Denton, S. M.; Field, S. E.; Gillmore, A. T.; Harbottle, G. W.; Howard, R. M.; Laity, D. A.; Ngono, C. J.; Pibworth, B. A. *Org. Process Res. Dev.* **2011**, *15*, 1192–1200.

[37] Bajaj, P.; Sreenilayam, G.; Tyagi, V.; Fasan, R. *Angew. Chem., Int. Ed.* **2016**, *55*, 16110–16114.

[38] (a) Liu, Z.; Zhang, X.; Zanoni, G.; Bi, X. *Org. Lett.* **2017**, *19*, 6646–6649. (b) Roy, S.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2018**, *57*, 2238–2243. (c) Sharland, J.; Wei, B.; Hardee, D.; Hodges, T.; Gong, W.; Voight, E.; Davies, H. *Chem. Sci.* **2021**, *12*, 11181–11190.

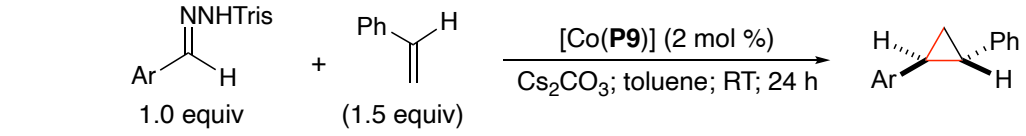
identification of a newly-synthesized C_6-bridged metalloradical catalyst [Co(**P9**)] (**P9** = 2,6-DiPhO-Hu(C_6)Phyrin) as the optimal catalyst for the cyclopropanation reaction, resulting in almost quantitative formation of 2-pyridylcyclopropane (99%) with high diastereoselectivity (92% de) as essentially one enantiomer of the major (*E*)-isomer (99% ee).[7f] Furthermore, the [Co(**P9**)]-based catalytic system was demonstrated to exhibit a broad substrate scope, including several classes of challenging olefin substrates, enabling a general method for the stereoselective synthesis of highly enantioenriched heteroaryl cyclopropanes (Scheme 1.19).

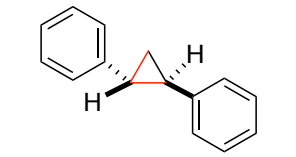
Scheme 1.19. Co(II)-Catalyzed Asymmetric Radical Cyclopropanation with α-Heteroaryldiazomethanes



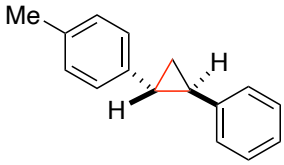
In addition, Zhang and coworkers revealed that the newly-developed bridged catalyst [Co(**P9**)] could be applied to α-aryldiazomethanes beyond those containing H-bonding acceptors at the *ortho*-position, which is perceived as a major limitation in the previous systems.[7d,7e] Accordingly, a wide array of α-aryldiazomethanes without H-bonding acceptors could also be employed as effective radical precursors for asymmetric cyclopropanation by [Co(**P9**)], forming the corresponding arylcyclopropanes in similarly high yields with the same high level of stereoselectivities (Scheme 1.20).[7f] Together with the wide scope of α-heteroaryldiazomethanes, [Co(**P9**)]-catalyzed asymmetric radical cyclopropanation constitutes a general protocol for the stereoselective preparation of both aryl- and heteroarylcyclopropanes.

Scheme 1.20. Asymmetric Radical Cyclopropanation of Styrene with Aryldiazomethanes Catalyzed by [Co(P9)]

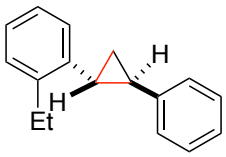




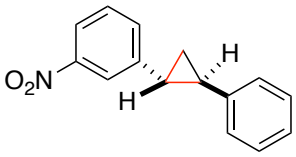
97% yield
94:6 dr; 97% ee



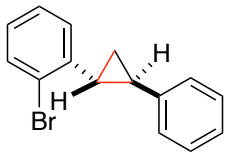
95% yield
93:7 dr; 98% ee



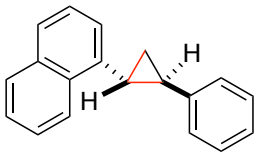
57% yield
96:4 dr; 89% ee



89% yield
98:2 dr; 96% ee



89% yield
96:4 dr; 93% ee



91% yield
95:5 dr; 97% ee

1.4. COBALT(II)-CATALYZED INTRAMOLECULAR RADICAL CYCLOPROPANATION

In parallel with the development of asymmetric intermolecular cyclopropanation, its intramolecular variant has also attracted growing research interest as a powerful strategy for the stereoselective construction of complex [*n*.1.0] bicyclic ring structures, which may serve as versatile structural motifs in many biologically active compounds and natural products.[39] Despite significant progress, the realization of asymmetric intramolecular cyclopropanation remains challenging, with success being reported mostly with acceptor- and acceptor/donor-substituted diazo compounds.[40] Inspired by the recent demonstration of Co(II)-based MRC for asymmetric intermolecular cyclopropanations, Zhang and coworkers further explored the metalloradical approach for asymmetric intramolecular cyclopropanation with acceptor/acceptor-substituted diazo compounds.[41] Considering the more demanding steric requirements associated with the double cyclization reactions, it was unclear whether the confined chiral cavity environment of [Co(D_2-Por*)] could accommodate the intramolecular catalytic process.

---

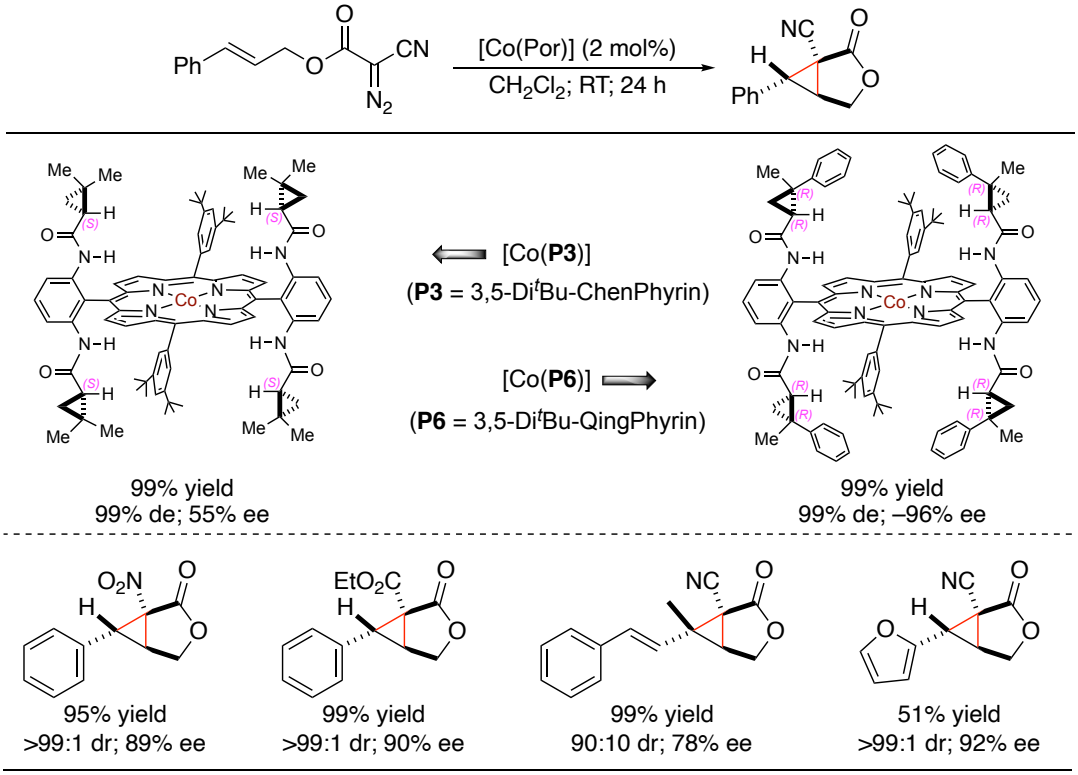
[39] (a) Monn, J. A.; Valli, M. J.; Massey, S. M.; Wright, R. A.; Salhoff, C. R.; Johnson, B. G.; Howe, T.; Alt, C. A.; Rhodes, G. A.; Robey, R. L.; Griffey, K. R.; Tizzano, J. P.; Kallman, M. J.; Helton, D. R.; Schoepp, D. D. *J. Med. Chem.* **1997**, *40*, 528–537. (b) Li, J.; Lowary, T. L. *Org. Lett.* **2008**, *10*, 881–884.

[40] (a) Doyle, M. P.; Pieters, R. J.; Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Mueller, P. *J. Am. Chem. Soc.* **1991**, *113*, 1423–1424. (b) Doyle, M. P.; Davies, S. B.; Hu, W. *Org. Lett.* **2000**, *2*, 1145–1147. (c) Uchida, T.; Saha, B.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 2521–2524. (d) Xu, Z.-J.; Fang, R.; Zhao, C.; Huang, J.-S.; Li, G.-Y.; Zhu, N.; Che, C.-M. *J. Am. Chem. Soc.* **2009**, *131*, 4405–4417. (e) Shen, J.-J.; Zhu, S.-F.; Cai, Y.; Xu, H.; Xie, X.-L.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2014**, *53*, 13188–13191. (f) Nakagawa, Y.; Chanthamath, S.; Shibatomi, K.; Iwasa, S. *Org. Lett.* **2015**, *17*, 2792–2795. (g) Marichev, K. O.; Ramey, J. T.; Arman, H.; Doyle, M. P. *Org. Lett.* **2017**, *19*, 1306–1309. (h) Ren, X.; Chandgude, A. L.; Fasan, R. *ACS Catal.* **2020**, *10*, 2308–2313.

[41] Xu, X.; Lu, H. J.; Ruppel, J. V.; Cui, X.; de Mesa, S. L.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 15292–15295.

The initial efforts were focused on the identification of a suitable D_2-symmetric chiral amidoporphyrin ligand for the asymmetric intramolecular cyclopropanation with cinnamyl α-cyanodiazoacetate as a model substrate (Scheme 1.21).

Scheme 1.21. Asymmetric Intramolecular Cyclopropanation of Acceptor-Substituted Diazoacetates by Co(II)-MRC

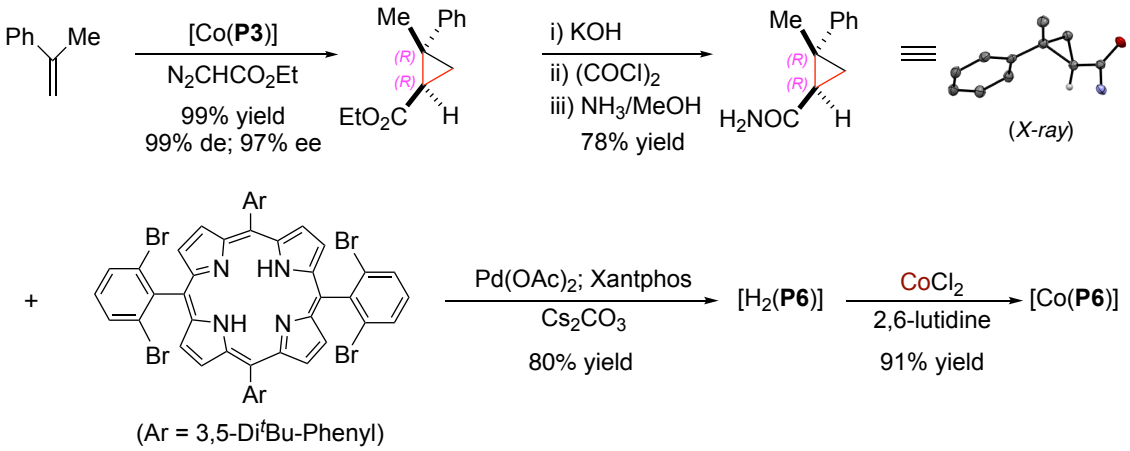


[Co(**P3**)], which was previously shown to be the optimal catalyst for asymmetric intermolecular cyclopropanation with α-cyanodiazoacetate[29] was found to be capable of activating cinnamyl α-cyanodiazoacetate for the intramolecular cyclopropanation process, affording the desired bicyclic product in nearly quantitative yield (99%) as a single diastereomer (99% de) while exhibiting significant enantioselectivity (55% ee). To further improve the enantioselectivity of this catalytic system, a new generation of metalloradical catalyst [Co(**P6**)] (**P6** = 3,5-Di^{t}Bu-QingPhyrin) containing cyclopropanecarboxyamides

with two contiguous stereogenic centers was developed based on [Co(**P3**)]-catalyzed asymmetric intermolecular cyclopropanation (Scheme 1.22).[41]

Switching [Co(**P3**)] to second-generation metalloradical catalyst [Co(**P6**)] led to significant enhancement in enantioselectivity (99%) without affecting the yield and diastereoselectivity. It is noted that the sense of asymmetric induction also switched in favor of the opposite enantiomer with the use of [Co(**P6**)]. Similarly, the new metalloradical catalyst [Co(**P6**)] could be successfully applied for the asymmetric intramolecular cyclopropanation with various α-substituted allyl diazoacetates, enabling a streamlined synthesis of highly enantioenriched 3-oxabicyclo[3.1.0]hexan-2-one derivatives that may serve as valuable intermediates for stereoselective organic synthesis.

Scheme 1.22. Synthetic Approach to Construct [Co(P6)] (P6 = 3,5-Di^{t}Bu-QingPhyrin)



1.5. NEXT-GENERATION D_2-SYMMETRIC CHIRAL PORPHYRINS: CATALYST ENGINEERING BY DISTAL BRIDGING

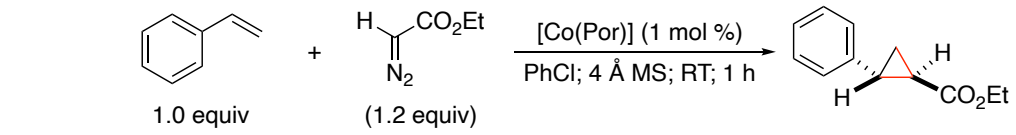
Since the first introduction in 2004,[20] Co(II)-complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have emerged as a privileged class of metalloradical catalysts capable of controlling reactivity and stereoselectivity in various radical catalytic systems based on Co(II)-MRC. The key to the success of these radical processes lies in the

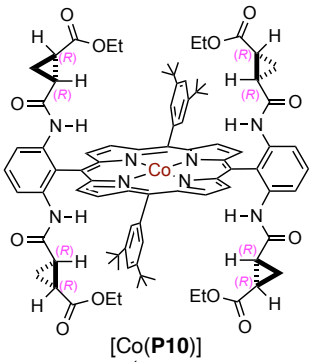
judicious modulation of D_2-symmetric chiral amidoporphyrin ligands to adopt proper steric, electronic, and chiral environments that maximize noncovalent attractive interactions with the reacting substrates and active radical intermediates. On the basis of the remarkable ligand effect observed with existing [Co(D_2-Por*)], Zhang and coworkers reported the synthesis of D_2-symmetric chiral amidoporphyrins containing alkyl bridges across two chiral amide units on both sides of the porphyrin plane.[42] The new-generation metalloradical catalyst [Co(HuPhyrin)] whose cavity can be fine-tuned by varying the length of alkyl bridges features a more rigid chiral environment as a result of the bridging effect.

Using asymmetric cyclopropanation of styrene with EDA as a model reaction, the catalytic performance of C_4-bridged metalloradical catalyst [Co(**P11**)] (**P11** = 3,5-Di^{t}Bu-Hu(C_4)Phyrin) and C_6-bridged metalloradical catalyst [Co(**P12**)] (**P12** = 3,5-Di^{t}Bu-Hu(C_6)Phyrin) was evaluated (Scheme 1.23). Both bridged catalysts proved to be superior in terms of reactivity and stereoselectivity as compared to the open-analogue [Co(**P10**)] (**P10** = 3,5-Di^{t}Bu-Tao(Et)Phyrin). Furthermore, the difference in performance between [Co(**P11**)] and [Co(**P12**)] demonstrates that even a subtle modification to the distal alkyl bridges can give rise to significant improvements in reactivity as well as stereoselectivity, manifesting the immense power of catalyst development in controlling radical processes.

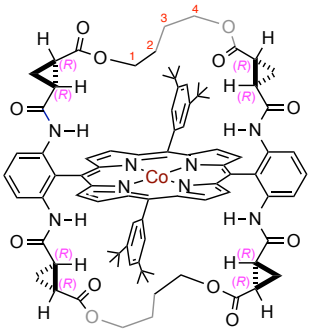
[42] Hu, Y.; Lang, K.; Tao, J.; Marshall, M. K.; Cheng, Q.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2019**, *58*, 2670–2674.

Scheme 1.23. Bridging Effect on Co(II)-Catalyzed Asymmetric Cyclopropanation of Styrene with EDA

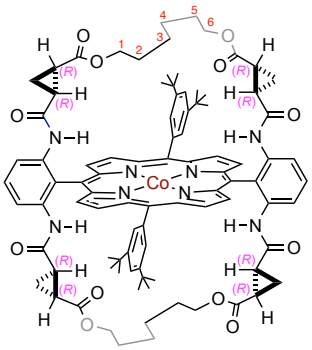




[Co(**P10**)]
(**P10** = 3,5-Di^{t}Bu-Tao(Et)Phyrin)
73% yield; 90% de; 14% ee



[Co(**P11**)]
(**P11** = 3,5-Di^{t}Bu-Hu(C_4)Phyrin)
93% yield; 90% de; 96% ee



[Co(**P12**)]
(**P12** = 3,5-Di^{t}Bu-Hu(C_6)Phyrin)
84% yield; 90% de; 88% ee

1.6. CONCLUSIONS AND OUTLOOK

This Account outlined Zhang and coworkers' recent endeavors toward developing metalloradical catalysis as a conceptually different approach for catalytic radical cyclopropanation with diazo compounds in the past decades. Attributed to the underlying stepwise radical mechanism, the Co(II)-catalyzed cyclopropanation exhibits a unique profile of reactivity and selectivity that is fundamentally distinct from the existing ionic systems involving metallocarbenes. Through the identification of suitable D_2-symmetric chiral amidoporphyrins as the supporting ligands, the Co(II)-based metalloradical system has been shown to effectively activate different classes of diazo compounds as carbene sources for asymmetric radical cyclopropanation of a wide range of alkenes, providing access to a plethora of chiral cyclopropane derivatives in high yields with excellent stereoselectivities. In particular, [Co(D_2-Por*)] exhibit capability in activating various acceptor/acceptor-substituted diazo compounds, which are attractive but typically

challenging candidates for asymmetric olefin cyclopropanation. More broadly, the Co(II)-based cyclopropanation process is highlighted by its exceptional catalytic reactivity toward electron-deficient olefins owing to the salient features of radical- mediated reaction pathway. In parallel, the application of Co(II)-based MRC has been extend to the intramolecular variant of asymmetric radical cyclopropanation, allowing for the stereoselective construction of densely functionalized 3-oxabicyclo[3.1.0]hexan-2-one derivatives, which may serve as valuable chiral building blocks in a myriad of potential synthetic and biological applications. Using *N*-sulfonyl hydrazones as stable diazo surrogates, the feasibility of employing in situ-generated α-aryldiazomethanes and α-heteroaryldiazomethanes has been demonstrated as effective radical precursors for Co(II)-catalyzed olefin cyclopropanation. Furthermore, detailed computational and experimental results have shed light on the underlying stepwise radical mechanism as well as the basis of asymmetric induction. Theses mechanistic insights may have far-reaching implications for future catalyst design and optimization of novel radical reactions. While significant advances have been achieved to date, the development of Co(II)-based asymmetric radical cyclopropanation still confronts foreseen challenges. For instance, the utilization of other types of diazo compounds, especially with substituents beyond C(sp^2)-based carbonyl and aryl groups has remained elusive. The formidable challenges associated with controlling reactivity and selectivity of radical reactions can be essentially translated into a solvable problem of rational catalyst design and development. It is our hope that this Account will provide a useful perspective and stimulate further exploration of untapped potential of radical reactions in stereoselective organic synthesis.

CHAPTER 2

ASYMMETRIC RADICAL PROCESS FOR GENERAL SYNHTESIS OF CHIRAL HETEROARYL CYCLOPROPANES

(Portions of this chapter have appeared in the following publication: Wang, X.; Ke, J.; Zhu, Y.; Deb, A.; Xu, Y.; Zhang, X. P. *J. Am. Chem. Soc.* 2021, *143*, 11121–11129)

2.1. INTRODUCTION

Radical chemistry has been increasingly explored for the development of new synthetic tools in modern organic synthesis.[1] Despite tremendous endeavors, long-standing challenges associated with control of reactivity and enantioselectivity remain largely unresolved for many radical reactions.[2] Among recent advances,[3] metalloradical catalysis (MRC), which involves the generation and utilization of metal-stabilized organic radicals as catalytic intermediates to harness the potential of radical chemistry, has emerged as a

[1] For selected books, see: *Radical Reactions in Organic Synthesis*; Oxford University Press, 2003. (b) Chatgilialoglu, C.; Studer, A., *Encyclopedia of Radicals in Chemistry, Biology, and Materials*; John Wiley & Sons, 2012. For selected reviews, see: (c) Zard, S. Z. *Chem. Soc. Rev.* **2008**, *37*, 1603–1618. (d) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, *40*, 102–113. (e) Quiclet-Sire, B.; Zard, S. Z. *Pure Appl. Chem.* **2011**, *83*, 519–551. (f) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322–5363. (g) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58–102.

[2] For selected reviews, see: (a) Bar, G.; Parsons, A. F. *Chem. Soc. Rev.* **2003**, *32*, 251–263. (b) Sibi, M. P.; Manyem, S.; Zimmerman, J. *Chem. Rev.* **2003**, *103*, 3263–3295. (c) Brimioulle, R.; Lenhart, D.; Maturi, M. M.; Bach, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 3872–3890.

[3] For selected examples on approaches to controlling radical reactivity and stereoselectivity, see: (a) Du, J. N.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. *Science* **2014**, *344*, 392–396. (b) Huo, H.; Shen, X.; Wang, C.; Zhang, L.; Röse, P.; Chen, L.-A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E. *Nature* **2014**, *515*, 100–103. (c) Kainz, Q. M.; Matier, C. D.; Bartoszewicz, A.; Zultanski, S. L.; Peters, J. C.; Fu, G. C. *Science* **2016**, *351*, 681–684. (d) Zhang, W.; Wang, F.; McCann, S. D.; Wang, D. H.; Chen, P. H.; Stahl, S. S.; Liu, G. S. *Science* **2016**, *353*, 1014–1018. (e) Kern, N.; Plesniak, M. P.; McDouall, J. J. W.; Procter, D. J. *Nat. Chem.* **2017**, *9*, 1198–1204. (f) Morrill, C.; Jensen, C.; Just-Baringo, X.; Grogan, G.; Turner, N. J.; Procter, D. J. *Angew. Chem., Int. Ed.* **2018**, *57*, 3692–3696. (g) Proctor, R. S. J.; Davis, H. J.; Phipps, R. J. *Science* **2018**, *360*, 419–422. (h) Biegasiewicz, K. F.; Cooper, S. J.; Gao, X.; Oblinsky, D. G.; Kim, J. H.; Garfinkle, S. E.; Joyce, L. A.; Sandoval, B. A.; Scholes, G. D.; Hyster, T. K. *Science* **2019**, *364*, 1166–1169. (i) Huang, H.-M.; McDouall, J. J. W.; Procter, D. J. *Nat. Catal.* **2019**, *2*, 211–218. (j) Nakafuku, K. M.; Zhang, Z.; Wappes, E. A.; Stateman, L. M.; Chen, A. D.; Nagib, D. A. *Nat. Chem.* **2020**, *12*, 697–704.

conceptually new approach to guide the discovery of catalytic solutions toward controlling the reactivity and stereoselectivity of radical processes.[4,5,6] As stable 15e-metalloradicals, cobalt(II) complexes of porphyrins ([Co(Por)]) exhibit unique capability of homolytically activating diazo compounds to generate α-Co(III)-alkyl radicals as key intermediates for various radical transformations.[7] Specifically, with D_2-symmetric chiral amidoporphyrins (D_2-Por*) as the supporting ligands, these Co-stabilized carbon-centered radicals can engage in asymmetric radical cyclopropanation of alkenes for the preparation of optically active three-membered carbocycles.[8] While donor-substituted diazo compounds such as in

[4] For selected reviews and highlights on Co(II)-based MRC, see: (a) Lu, H. J.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899–1909. (b) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775–2823. (c) Demarteau, J.; Debuigne, A.; Detrembleur, C. *Chem. Rev.* **2019**, *119*, 6906–6955. (d) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626–4638. (e) Singh, R.; Mukherjee, A. *ACS Catal.* **2019**, *9*, 3604–3617.

[5] For selected examples of Ti(III)-based radical processes, see: (a) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561–8562. (b) Rajanbabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986–997. (c) Gansäuer, A.; Hildebrandt, S.; Michelmann, A.; Dahmen, T.; von Laufenberg, D.; Kube, C.; Fianu, G. D.; Flowers II, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7003–7006. (d) Funken, N.; Mühlhaus, F.; Gansäuer, A. *Angew. Chem., Int. Ed.* **2016**, *55*, 12030–12034. (e) Hao, W.; Wu, X.; Sun, J. Z.; Siu, J. C.; MacMillan, S. N.; Lin, S. *J. Am. Chem. Soc.* **2017**, *139*, 12141–12144. (f) Yao, C. B.; Dahmen, T.; Gansäuer, A.; Norton, J. *Science* **2019**, *364*, 764–767. (g) Ye, K. Y.; McCallum, T.; Lin, S. *J. Am. Chem. Soc.* **2019**, *141*, 9548–9554.

[6] For selected examples of metalloradical-mediated radical processes, see: (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944. (b) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897–7898. (c) Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 2051–2061. (d) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920–6922. (e) Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662–14665. (f) Kuo, J. L.; Hartung, J.; Han, A.; Norton, J. R. *J. Am. Chem. Soc.* **2015**, *137*, 1036–1039. (g) Roy, S.; Khatua, H.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2019**, *58*, 11439–11443. (h) Das, S. K.; Roy, S.; Khatua, H.; Chattopadhyay, B. *J. Am. Chem. Soc.* **2020**, *142*, 16211–16217. (i) Zhang, Z.; Gevorgyan, V. *Org. Lett.* **2020**, *22*, 8500–8504.

[7] (a) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902. (b) Belof, J. L.; Cioce, C. R.; Xu, X.; Zhang, X. P.; Space, B.; Woodcock, H. L. *Organometallics* **2011**, *30*, 2739–2746. (c) Lu, H.; Dzik, W. I.; Xu, X.; Wojtas, L.; de Bruin, B.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521.

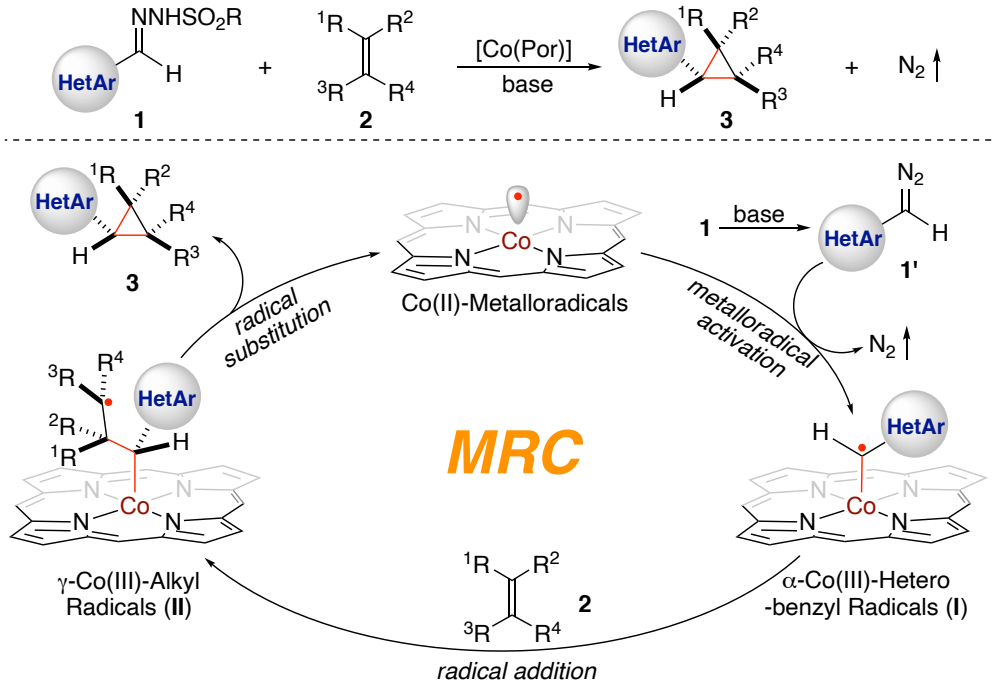
[8] (a) Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719. (b) Caselli, A.; Gallo, E.; Ragaini, F.; Ricatto, F.; Abbiati, G.; Cenini, S. *Inorg. Chim. Acta.* **2006**, *359*, 2924–2932. (c) Chen, Y.; Ruppel, J. V.; Zhang, X. P. *J. Am. Chem. Soc.* **2007**, *129*, 12074–12075. (d) Fantauzzi, S.; Gallo, E.; Rose, E.; Raoul, N.; Caselli, A.; Issa, S.; Ragaini, F.; Cenini, S. *Organometallics* **2008**, *27*, 6143–6151. (e) Zhu, S.; Ruppel, J. V.; Lu, H.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043. (f) Zhu, S.; Xu, X.; Perman, J. A.; Zhang, X. P. A *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799. (g) Xu, X.; Lu, H. J.; Ruppel, J.

situ-generated α-aryldiazomethanes have recently been demonstrated as suitable radical precursors for Co(II)-based asymmetric radical cyclopropanation,[8k,8n] the analogous α-heteroaryldiazomethanes have remained underexploited for stereoselective synthesis of valuable chiral heteroaryl cyclopropanes.[9] With this in mind, we sought to explore the feasibility of developing a catalytic process that would employ α-heteroaryldiazomethanes for asymmetric cyclopropanation of alkenes via Co(II)-MRC (Scheme 2.1).

V.; Cui, X.; de Mesa, S. L.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 15292–15295. (h) Paul, N. D.; Mandal, S.; Otte, M.; Cui, X.; Zhang, X. P.; de Bruin, B. *J. Am. Chem. Soc.* **2014**, *136*, 1090–1096. (i) Reddy, A. R.; Hao, F.; Wu, K.; Zhou, C. Y.; Che, C. M. *Angew. Chem., Int. Ed.* **2016**, *55*, 1810–1815. (j) Chirila, A.; Gopal Das, B.; Paul, N. D.; de Bruin, B. *ChemCatchem* **2017**, *9*, 1413–1421. (k) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2017**, *139*, 1049–1052. (l) Wang, Y.; Wen, X.; Cui, X.; Zhang, X. P. *J. Am. Chem. Soc.* **2018**, *140*, 4792–4796. (m) Wen, X.; Wang, Y.; Zhang, X. P. *Chem. Sci.* **2018**, *9*, 5082–5086. (n) Lee, W.-C. C.; Wang, D.-S.; Zhang, C.; Xie, J.; Li, B.; Zhang, X. P. *Chem* **2021**, *7*, 1588–1601.

[9] For selected examples of stereoselective synthesis of heteroaryl cyclopropanes, see: (a) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168–12175. (b) Davies, H. M. L.; Townsend, R. J. *J. Org. Chem.* **2001**, *66*, 6595–6603. (c) Marcin, L. R.; Denhart, D. J.; Mattson, R. J. *Org. Lett.* **2005**, *7*, 2651–2654. (d) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 18034–18035. (e) Grimster, N.; Zhang, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2010**, *132*, 2510–2511. (f) Jin, C.; Decker, A. M.; Huang, X.-P.; Gilmour, B. P.; Blough, B. E.; Roth, B. L.; Hu, Y.; Gill, J. B.; Zhang, X. P. *ACS Chem. Neurosci.* **2014**, *5*, 576–587. (g) Bajaj, P.; Sreenilayam, G.; Tyagi, V.; Fasan, R. *Angew. Chem., Int. Ed.* **2016**, *55*, 16110–16114. (h) Fu, L.; Mighion, J. D.; Voight, E. A.; Davies, H. M. L. *Chem. Eur. J.* **2017**, *23*, 3272–3275. (i) Moore, E. J.; Steck, V.; Bajaj, P.; Fasan, R. *J. Org. Chem.* **2018**, *83*, 7480–7490. (j) Vargas, D. A.; Khade, R. L.; Zhang, Y.; Fasan, R. *Angew. Chem., Int. Ed.* **2019**, *58*, 10148–10152. (k) Wei, B.; Sharland, J. C.; Lin, P.; Wilkerson-Hill, S. M.; Fullilove, F. A.; McKinnon, S.; Blackmond, D. G.; Davies, H. M. L. *ACS Catal.* **2020**, *10*, 1161–1170. (l) Nam, D.; Steck, V.; Potenzino, R. J.; Fasan, R. *J. Am. Chem. Soc.* **2021**, *143*, 2221–2231. (m) Sharland, J. C.; Wei, B.; Hardee, D. J.; Hodges, T. R.; Gong, W.; Voight, E. A.; Davies, H. M. L. *Chem. Sci.* **2021**, *12*, 11181–11190.

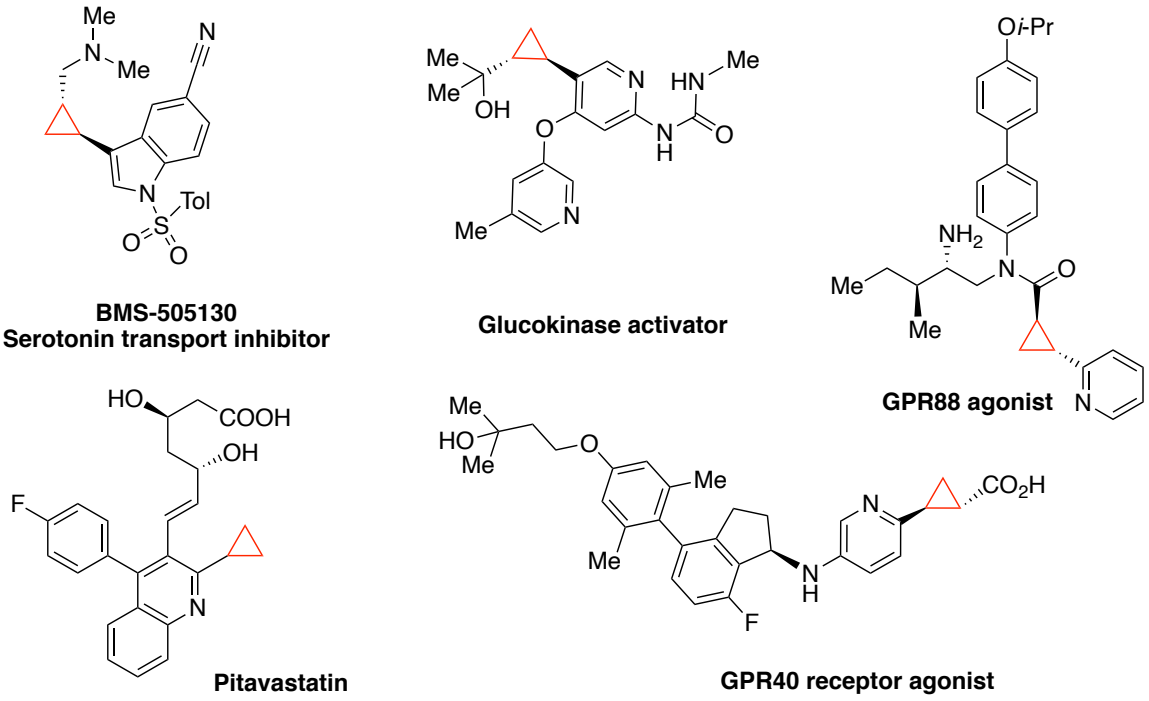
Scheme 2.1. Working Proposal for Synthesis of Heteroaryl Cyclopropanes from Alkenes via Co(II)-Based MRC



In view of the intrinsic properties of heteroaryl moieties, the proposed Co(II)-based catalytic process presented several fundamental challenges. Besides the concerns with efficiency of metalloradical activation of α-heteroaryldiazomethanes **1′** generated in situ from the corresponding hydrazones **1** in the presence of base, whether the subsequent radical addition of the initially-formed α-Co(III)-heterobenzyl radicals **I** to the alkene substrates **2** could be rendered enantioselective is an unanswered question, primarily owing to the potential competitive coordination of the heteroaryl moieties to the metal center. On this basis, additional uncertainty of controlling reactivity and diastereoselectivity might also arise from the following 3-*exo*-*tet* cyclization of the resulting γ-Co(III)-alkyl radicals **II** while forging the second C–C bond (Scheme 2.1). Furthermore, the presence of heteroatoms was anticipated to engage in potential H-bonding interactions with the amide

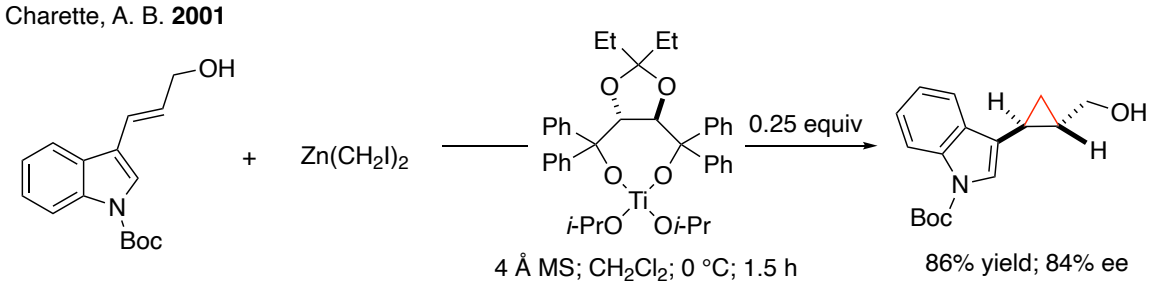
units of the amidoporphyrin ligands that could pose potential complication in controlling both reactivity and selectivity in these Co(II)-based radical processes. To address these and related issues, we envisioned the prospect of designing a suitable D_2-symmetric chiral amidoporphyrin ligand with proper steric, electronic and chiral environments that could direct the Co(II)-based catalysis for productive cyclopropanation with effective stereocontrol. If realized, it would enable the development of a new catalytic system for asymmetric olefin cyclopropanation with in situ generated α-heteroaryldiazomethanes to furnish valuable chiral heteroaryl cyclopropanes.

Figure 2.1. Selected Examples of Important Bioactive Compounds Containing Heteroaryl Cyclopropane Motifs



Heteroaryl cyclopropanes are ubiquitous structural motifs in many pharmaceuticals and biologically important molecules (Figure 2.1).[10] Nevertheless, the methods for their stereoselective synthesis remain rather limited.[9] Among advances in the realm, Charette and coworkers disclosed an enantioselective Simmons-Smith cyclopropanation of indolyl-substituted allylic alcohol using bis(iodomethyl)zinc and titanium-TADDOLate complex (Scheme 2.2).[9a] Mattson and coworkers later explored an alternative strategy involving asymmetric cyclopropanation of vinylindole with diazoacetate catalyzed by pybox-Ru(II) complex (Scheme 2.3).[9c]

Scheme 2.2. Enantioselective Simmons-Smith Cyclopropanation

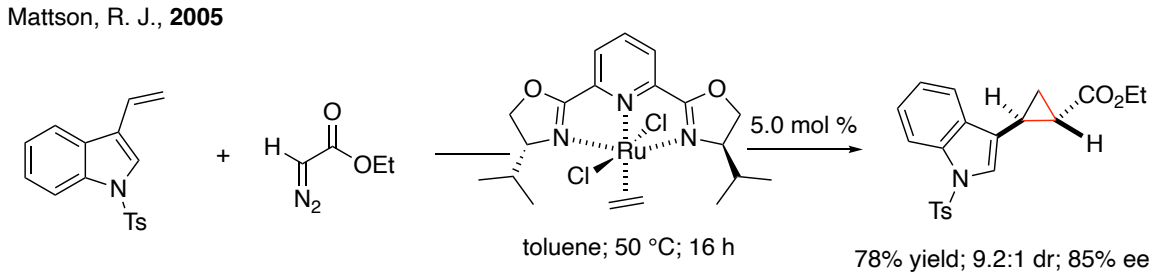


While most of these previous systems employed heteroaryl olefins for cyclopropanation with carbene precursors,[9,10b] transition-metal catalyzed asymmetric cyclopropanation of

[10] (a) Liu, H.; Kerdesky, F. A.; Black, L. A.; Fitzgerald, M.; Henry, R.; Esbenshade, T. A.; Hancock, A. A.; Bennani, Y. L. *J. Org. Chem.* **2004**, *69*, 192–194. (b) Butcher, K. J.; Denton, S. M.; Field, S. E.; Gillmore, A. T.; Harbottle, G. W.; Howard, R. M.; Laity, D. A.; Ngono, C. J.; Pibworth, B. A. *Org. Process Res. Dev.* **2011**, *15*, 1192–1200. (c) MacKinnon, C. H.; Lau, K.; Burch, J. D.; Chen, Y.; Dines, J.; Ding, X.; Eigenbrot, C.; Heifetz, A.; Jaochico, A.; Johnson, A.; Kraemer, J.; Kruger, S.; Krülle, T. M.; Liimatta, M.; Ly, J.; Maghames, R.; Montalbetti, C. A.; Ortwine, D. F.; Pérez-Fuertes, Y.; Shia, S.; Stein, D. B.; Trani, G.; Vaidya, D. G.; Wang, X.; Bromidge, S. M.; Wu, L. C.; Pei, Z. *Bioorg Med. Chem. Lett.* **2013**, *23*, 6331–6335. (d) Kohn, T. J.; Du, X.; Lai, S.; Xiong, Y.; Komorowski, R.; Veniant, M.; Fu, Z.; Jiao, X.; Pattaropong, V.; Chow, D.; Cardozo, M.; Jin, L.; Conn, M.; DeWolf, W. E.; Kraser, C. F.; Hinklin, R. J.; Boys, M. L.; Medina, J. C.; Houze, J.; Dransfield, P.; Coward, P. *ACS Med. Chem. Lett.* **2016**, *7*, 666–670. (e) Talele, T. T. *J. Med. Chem.* **2016**, *59*, 8712–8756.

alkenes with heteroaryldiazomethanes represents an appealing approach for the general synthesis of heteroaryl cyclopropanes with the potential to control both diastereoselectivity

Scheme 2.3. Asymmetric Cyclopropanation of Vinylindole with Diazoacetate



and enantioselectivity.[10] In contrast to the well-precedented asymmetric cyclopropanation with other types of diazo compounds,[11] only a few catalytic systems involving the use of heteroaryldiazomethanes have been reported.[12,13] This underdevelopment is largely attributed to the inherent instability of α-heteroaryldiazomethanes as well as their high propensity for unwanted formal dimerization.[12,14] Moreover, it is known that rhodium- and other existing metal-based catalytic systems of cyclopropanation could suffer from the

[11] For general reviews on metal-catalyzed olefin cyclopropanation with diazo compounds, see: (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911–935. (c) Intrieri, D.; Carminati, D. M.; Gallo, E. *Dalton Trans.* **2016**, *45*, 15746–16048.

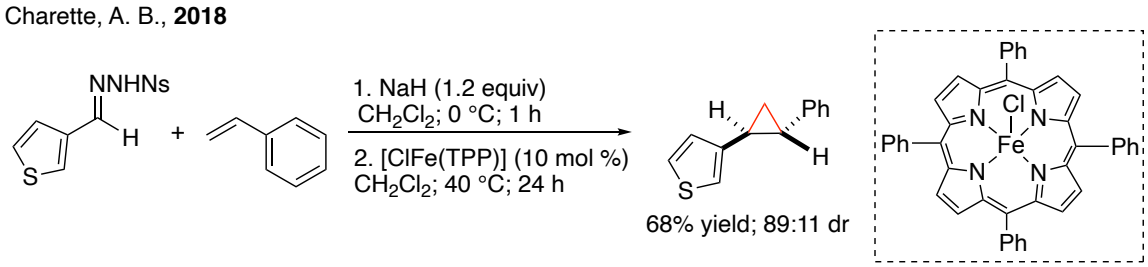
[12] Allouche, E. M. D.; Charette, A. B. *Synthesis* **2019**, *51*, 3947–3963.

[13] For selected examples of olefin cyclopropanation with in situ-generated α-heteroaryldiazomethanes, see: (a) Zimmerman, H. E.; Ignatchenko, A. *J. Org. Chem.* **1999**, *64*, 6635–6645. (b) Barluenga, J.; Quiñones, N.; Tomás-Gamasa, M.; Cabal, M.-P. *Eur. J. Org. Chem.* **2012**, 2312–2317. (c) Roda, N. M.; Tran, D. N.; Battilocchio, C.; Labes, R.; Ingham, R. J.; Hawkins, J. M.; Ley, S. V. *Org. Biomol. Chem.* **2015**, *13*, 2550–2554. (d) Liu, Z.; Zhang, X.; Zanoni, G.; Bi, X. *Org. Lett.* **2017**, *19*, 6646–6649. (e) Allouche, E. M. D.; Al-Saleh, A.; Charette, A. B. *Chem. Commun.* **2018**, *54*, 13256–13259. (f) Roy, S.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2018**, *57*, 2238–2243. (g) Zhang, Z.; Yadagiri, D.; Gevorgyan, V. *Chem. Sci.* **2019**, *10*, 8399–8404. (h) Shang, Z.-H.; Zhang, Z.-X.; Weng, W.-Z.; Wang, Y.-F.; Cheng, T.-W.; Zhang, Q.-Y.; Song, L.-Q.; Shao, T.-Q.; Liu, K.-X.; Zhu, Y.-P. *Adv. Synth. Catal.* **2021**, *363*, 490–496.

[14] (a) Doyle, M. P.; High, K. G.; Oon, S.-M.; Osborn, A. K. *Tetrahedron Lett.* **1989**, *30*, 3049–3052. (b) Regitz, M.; Maas, G. Academic Press: London, 1996. (c) Aggarwal, V. K.; de Vicente, J.; Bonnert, R. V. *Org. Lett.* **2001**, *3*, 2785–2788. (d) Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479–1492.

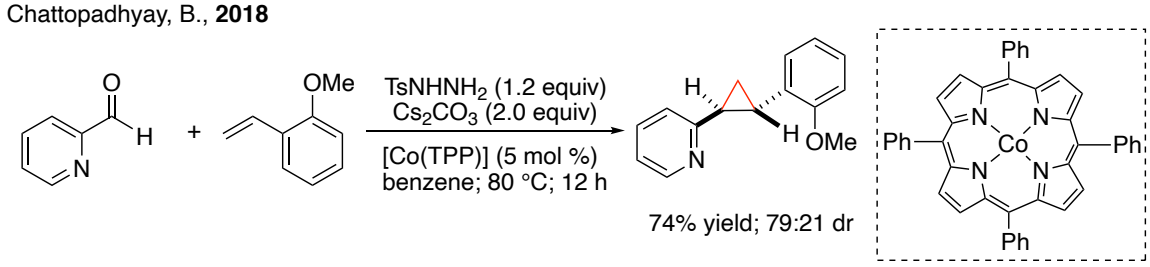
notorious catalyst poisoning effect in the presence of nitrogen- and sulfur-containing heterocycles.[9g,10b]

Scheme 2.4. [ClFe(TPP)]-Catalyzed Olefin Cyclopropanation with α-Heteroaryldiazomethanes



One notable example of cyclopropanation of alkenes with α-heteroaryldiazomethanes could be found in a recent report by Charette and coworkers on Fe-based catalytic system involving in situ-generation of diazo compounds from *N*-nosylhydrazones (Scheme 2.4).[13e] Chattopadhyay and coworkers also developed a [Co(TPP)]-catalyzed (TPP = 5,10,15,20-tetraphenylporphyrin) metalloradical cyclopropanation with 2-pyridyldiazomethanes, which could be generated in situ from readily accessible *N*-tosylhydrazone precursors in the presence of base (Scheme 2.5).[13f] While these in situ-generation protocols offer a novel alternative for catalytic synthesis of heteroaryl cyclopropanes in their racemic forms, the

Scheme 2.5 [Co(TPP)]-Catalyzed Olefin Cyclopropanation with α-Heteroaryldiazomethanes



enantioselective variant of this transformation is an attractive process that remains elusive. Moreover, it would be desirable to develop new catalytic systems that are generally applicable for stereoselective synthesis of diverse types of chiral heteroaryl cyclopropanes. We herein report the development of a new Co(II)-based catalytic system that is highly efficient for asymmetric cyclopropanation of alkenes with in situ-generated α-heteroaryldiazomethanes. Through the support of a new bridged D_2-symmetric chiral amidoporphyrin ligand, the Co(II)-catalyzed system allows for efficient activation of 2-pyridyldiazomethanes and other common α-heteroaryldiazomethanes for asymmetric cyclopropanation of a broad range of alkenes, affording the valuable chiral heteroaryl cyclopropanes in high yields with both excellent diastereoselectivities and enantioselectivities. Furthermore, we present detailed computational and experimental studies that shed light on the underlying stepwise radical mechanism.

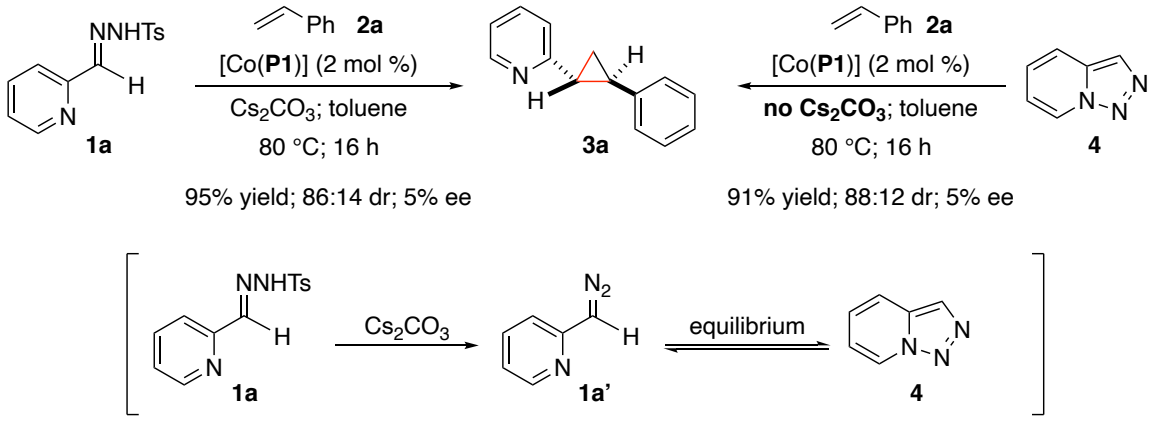
2.2. RESULTS AND DISCUSSION

2.2.1. Condition Optimization for Asymmetric Radical Cyclopropanation of Alkenes with α-Heteroaryldiazomethanes

At the outset of this project, 2-pyridyldiazomethane (**1a'**), which was in situ generated from the corresponding tosylhydrazone **1a** in the presence of Cs_2CO_3, was investigated as the representative α-heteroaryldiazomethane for asymmetric radical cyclopropanation of styrene (**2a**) by a series of Co(II) complexes of D_2-symmetric chiral amidoporphyrin ligands [Co(D_2-Por*)] (Figure 2.2). It was found that first-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)[8a] could promote the conversion to 2-pyridylcyclopropane **3a** in 20% yield with moderate diastereoselectivity (89:11 dr) and insignificant asymmetric induction (8% ee) (Figure 2.2; entry 1). Other than **3a**,

[1,2,3]triazolo[1,5-*a*]pyridine (**4**) was also formed in 53% yield (entry1), presumably through ring-chain tautomerism of in situ-generated 2-pyridyldiazomethane (**1a'**).[13f,13g] To facilitate formation of open-form **1a'**, elevated reaction temperature (80 °C) was employed to afford cyclopropane product **3a** in 95% yield with 86:14 dr and 5% ee (entry 2).

Scheme 2.6. Control Experiment



In addition, we performed a control experiment with pyridyltriazole **4** as diazo precursor in the absence of Cs_2CO_3 (Scheme 2.6). Interestingly, the desired cyclopropane **3a** could be obtained in a similarly high yield and stereoselectivities, suggesting that pyridyltriazole **4** could undergo ring-chain tautomerism at elevated temperature to deliver its diazo tautomer **1a'**, which upon metalloradical activation would generate the reactive α-Co(III)-pyridyl radical intermediate by [Co(Por)].

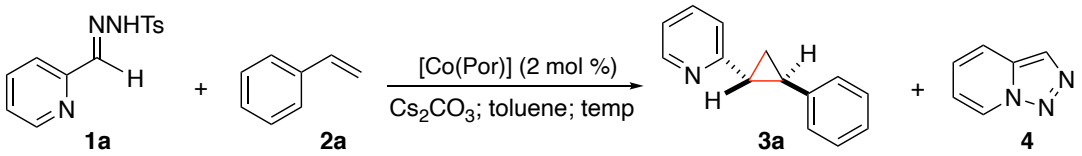
Switching to second-generation metalloradical catalyst [Co(**P8**)] (**P8** = 3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin)[15] bearing chiral amide units with ester moieties resulted in the formation of **3a** in 86% yield with further improved diastereoselectivity (94:6 dr) and a significant level of enantioselectivity (40% ee) (entry 3). To further enhance the asymmetric induction

[15] Hu, Y.; Lang, K.; Tao, J.; Marshall, M. K.; Cheng, Q.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem., Int. Ed.* **2019**, *58*, 2670–2674.

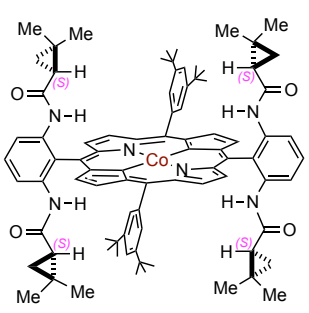
of this catalytic system, we then turned our attention to new-generation metalloradical catalysts [Co(HuPhyrin)], the Co(II) complexes of bridged D_2-symmetric chiral amidoporphyrins featuring more rigid cavity-like environments. When the C_4-bridged [Co(**P11**)] (**P11** = 3,5-Di^{t}Bu-Hu(C_4)Phyrin)[15] was employed as the catalyst under the same conditions, it indeed enhanced both reactivity and stereoselectivities of the cyclopropanation reaction substantially, generating **3a** in high yield (92%) with both excellent diastereoselectivity (99:1 dr) and enantioselectivity (90% ee) (entry 4). When the alkyl bridge was further extended to C_6-linker in [Co(**P12**)] (**P12** = 3,5-Di^{t}Bu-Hu(C_6)Phyrin),[15] cyclopropane **3a** was produced with a higher enantioselectivity (92% ee) while maintaining the excellent yield (94%) and diastereoselectivity (99:1 dr) (entry 5). Subsequent use of analogous catalyst [Co(**P13**)] (**P13** = 2,6-DiMeO-Hu(C_6)Phyrin),[16] which bears 2,6-dimethoxyphenyl instead of 3,5-di-*tert*-butylphenyl groups as the 5,15-diaryl substituents, led to the production of **3a** in a comparable yield (91% yield) with the same high level of stereoselectivities (99:1 dr and 92% ee) (entry 6). Aiming at further improving the catalytic system, we synthesized a new C_6-bridged catalyst [Co(**P9**)] (**P9** = 2,6-DiPhO-Hu(C_6)Phyrin) by replacing the methoxy groups in **P13** with phenoxy groups. Gratifyingly, [Co(**P9**)] could catalyze the cyclopropanation reaction to afford 2-pyridylcyclopropane **3a** in almost quantitative yield (99%) with high diastereoselectivity (96:4 dr) and outstanding enantioselectivity (99% ee) (entry 7).

[16] Lang, K.; Torker, S.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2019**, *141*, 12388–12396.

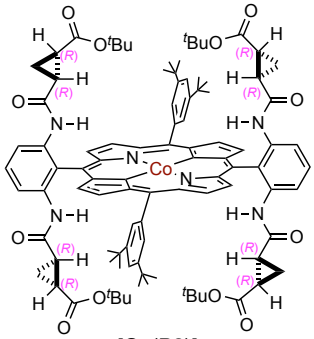
Figure 2.2. Evaluation of Reaction Conditions[a]



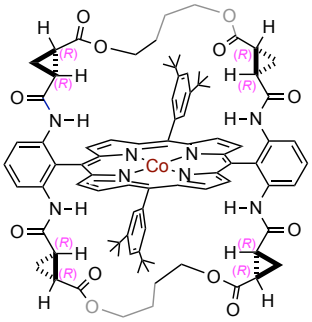
entry	[Co(Por)]	temp (°C)	**3a** yield (%)	**3a** (*E*):(*Z*)	**3a** ee (%)	**4** yield (%)
1	[Co(**P2**)]	40	20	89:11	8	53
2	[Co(**P2**)]	80	95	86:14	5	–
3	[Co(**P8**)]	80	86	94:6	40	–
4	[Co(**P11**)]	80	92	99:1	90	–
5	[Co(**P12**)]	80	94	99:1	92	–
6	[Co(**P13**)]	80	91	99:1	92	–
7	[Co(**P9**)]	80	99	96:4	99	–



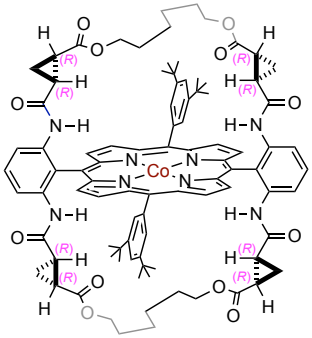
[Co(**P2**)]
(**P2** = 3,5-Di^{t}Bu-ChenPhyrin)



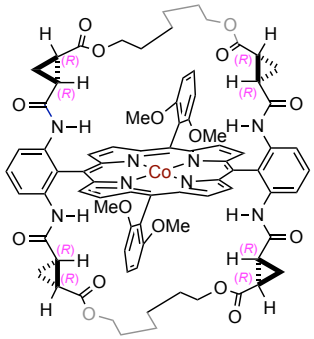
[Co(**P8**)]
(**P8** = 3,5-Di^{t}Bu-Tao(^{t}Bu)Phyrin)



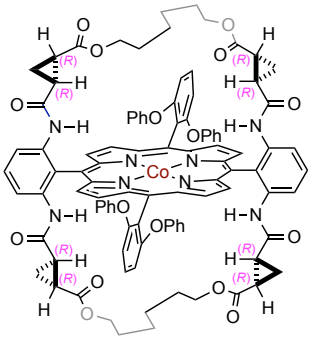
[Co(**P11**)]
(**P11** = 3,5-Di^{t}Bu-Hu(C_4)Phyrin)



[Co(**P12**)]
(**P12** = 3,5-Di^{t}Bu-Hu(C_6)Phyrin)



[Co(**P13**)]
(**P13** = 2,6-DiMeO-Hu(C_6)Phyrin)



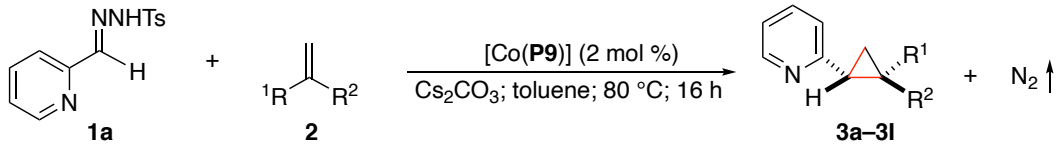
[Co(**P9**)]
(**P9** = 2,6-DiPhO-Hu(C_6)Phyrin)

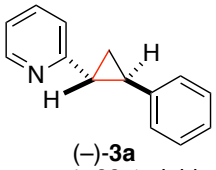
[a]Carried out with **1a** (0.10 mmol), **2a** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) using [Co(Por)] (2 mol %) in toluene (1.0 mL) for 16 h; Isolated yields; Diastereomeric excess (de) determined by ^{1}H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major (*E*)-isomer determined by chiral HPLC; Ts = 4-toluenesulfonyl.

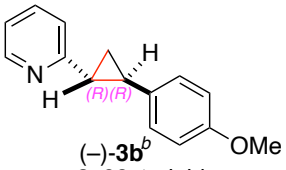
2.2.2. Asymmetric Radical Cyclopropanation of Different Alkenes with 2-Pyridyldiazomethanes

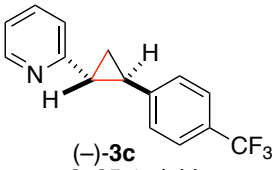
Under the optimized conditions, the scope and versatility of [Co(**P9**)]-catalyzed asymmetric cyclopropanation with in situ-generated 2-pyridyldiazomethane (**1a'**) were explored by employing different types of alkenes as the substrates (Table 2.1). Like formation of **3a** from styrene (Table 2.1; entry 1), its derivatives bearing electron-donating and electron-withdrawing aryl substituents could also be effectively cyclopropanated by [Co(**P6**)] with **1a'**, producing the desired cyclopropanes **3b** and **3c** in similarly high yields and stereoselectivities (entries 2 and 3). The absolute configuration of the major enantiomer of **3b** was established as (*R*,*R*). Additionally, this [Co(**P6**)]-based metalloradical system was shown to tolerate various functional groups as exemplified by the stereoselective formation of **3d**–**3f** containing aryl substituents of halogen, pinacolborane, and formyl functionalities at different positions (entries 4–6). Besides mono-substituted olefins, 1,1-disubstituted olefins like α-substituted styrenes could serve as suitable substrates as well, affording the trisubstituted cyclopropanes **3g** and **3h** with excellent control of the newly-generated quaternary stereogenic centers (entries 7 and 8). In addition to the extended aromatic olefins such as formation of **3i** from 2-vinylnaphthalene (entry 9), both conjugated dienes and enynes could be regio- and chemoselectively cyclopropanated to form cyclopropanes **3j**–**3l** in high yields with excellent stereoselectivities (entries 10–12).

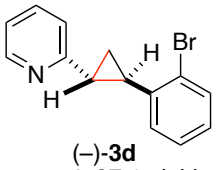
Table 2.1. Asymmetric Radical Cyclopropanation of Styrene Derivatives with In Situ-Generated 2-Pyridyldiazomethanes by [Co(P9)][a]

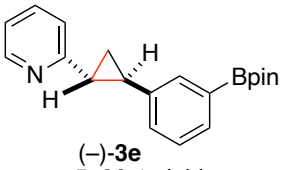


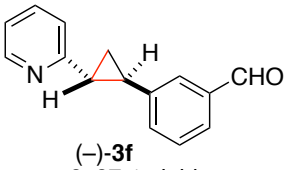

(–)-**3a**
entry 1: 99% yield
96:4 dr; 99% ee

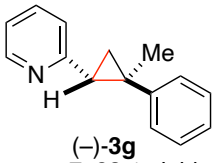

(–)-**3b**[b]
entry 2: 98% yield
95:5 dr; 99% ee

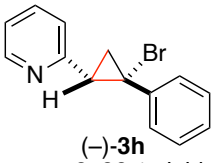

(–)-**3c**
entry 3: 95% yield
94:6 dr; 99% ee

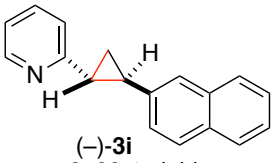

(–)-**3d**
entry 4: 97% yield
90:10 dr; 97% ee

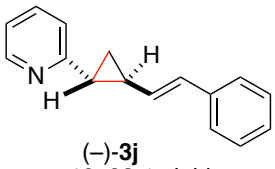

(–)-**3e**
entry 5: 90% yield
93:7 dr; 97% ee

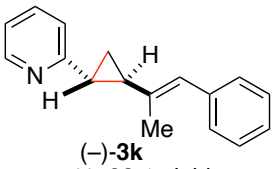

(–)-**3f**
entry 6: 87% yield
94:6 dr; 96% ee

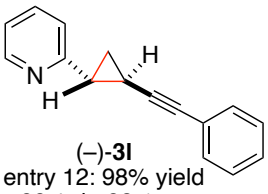

(–)-**3g**
entry 7: 82% yield
98:2 dr; 98% ee


(–)-**3h**
entry 8: 86% yield
99:1 dr; 97% ee


(–)-**3i**
entry 9: 90% yield
95:5 dr; 98% ee


(–)-**3j**
entry 10: 93% yield
96:4 dr; 98% ee


(–)-**3k**
entry 11: 98% yield
99:1 dr; 93% ee

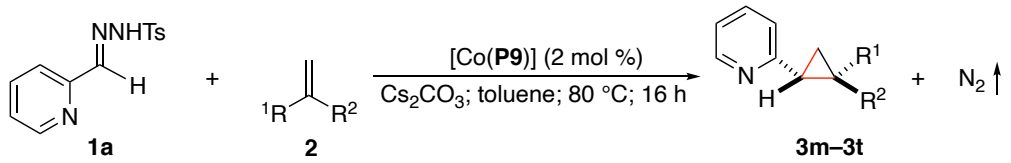

(–)-**3l**
entry 12: 98% yield
99:1 dr; 98% ee

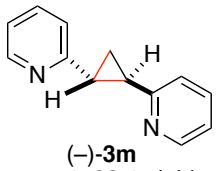
[a]Carried out with **1a** (0.10 mmol), **2** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) at 80 °C for 16 h using [Co(**P9**)] (2 mol %) in toluene (1.0 mL); Ts = 4-toluenesulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^1H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major isomer determined by chiral HPLC. [b]Absolute configuration determined by X-ray crystallography.

The Co(II)-based cyclopropanation was further highlighted by its unique reactivity towards various heteroaromatic olefins as shown with the highly stereoselective synthesis of 1,2-bisheteroaryl cyclopropanes **3m**–**3t** containing pyridine, thiophene, benzofuran, benzothiophene, indole, and quinoline (Table 2.2, entries 1–8). Given that both heteroarene and cyclopropane are prevalent structural motifs in bioactive compounds,[10] the access of

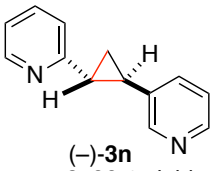
bisheteroaryl cyclopropanes in high enantiopurity may find potential applications in drug research and development.

Table 2.2. Asymmetric Radical Cyclopropanation of Heteroaromatic Olefins with In Situ-Generated 2-Pyridyldiazomethanes by [Co(P9)][a]

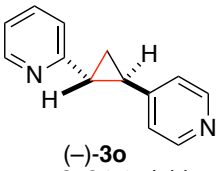




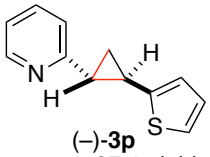
(–)-**3m**
entry 1: 92% yield
95:5 dr; 99% ee



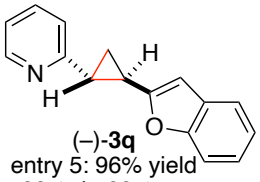
(–)-**3n**
entry 2: 86% yield
98:2 dr; 99% ee



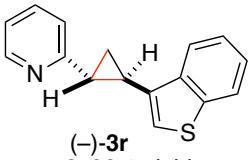
(–)-**3o**
entry 3: 94% yield
95:5 dr; 99% ee



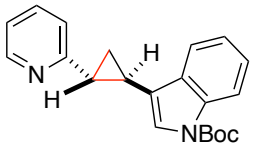
(–)-**3p**
entry 4: 97% yield
96:4 dr; 98% ee



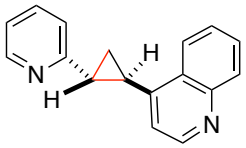
(–)-**3q**
entry 5: 96% yield
99:1 dr; 99% ee



(–)-**3r**
entry 6: 96% yield
75:25 dr; 98% ee



(–)-**3s**
entry 7: 93% yield
95:5 dr; 99% ee



(–)-**3t**
entry 8: 90% yield
85:15 dr; 98% ee

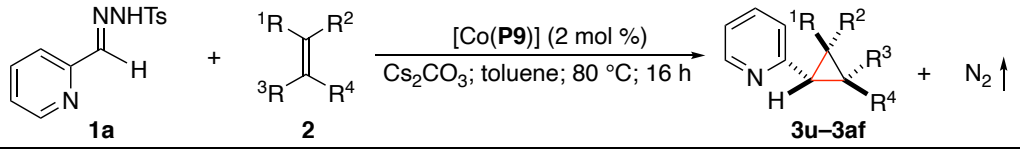
[a]Carried out with **1a** (0.10 mmol), **2** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) at 80 °C for 16 h using [Co(**P9**)] (2 mol %) in toluene (1.0 mL); Ts = 4-toluenesulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^1H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major isomer determined by chiral HPLC.

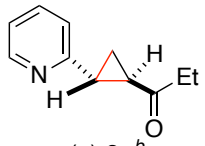
Moreover, electron-deficient olefins such as acrylketones, acrylates, acrylamides and acrylonitriles, which are known to be challenging substrates,[17] could all be utilized for asymmetric cyclopropanation by [Co(**P9**)], furnishing the functionalized electrophilic cyclopropanes **3u**–**3z** in high yields with excellent control of stereoselectivities (Table 2.3;

[17] Doyle, M. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 850–852.

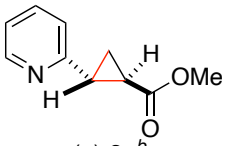
entries 1–6). Similar to electron-deficient olefins, the catalytic cyclopropanation could also be applied to electron-rich olefins such as vinyl benzoate and vinyl propyl ether for highly

Table 2.3. Asymmetric Radical Cyclopropanation of Electron-Rich and Electron-Deficient Olefins with In Situ-Generated 2-Pyridyldiazomethanes by [Co(P9)][a]

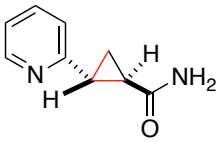




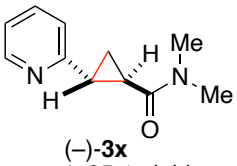
(–)-**3u**[b]
entry 1: 94% yield
99:1 dr; 98% ee



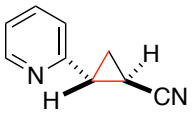
(–)-**3v**[b]
entry 2: 91% yield
99:1 dr; 95% ee



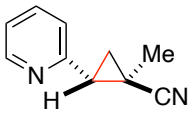
(–)-**3w**
entry 3: 70% yield
99:1 dr; 98% ee



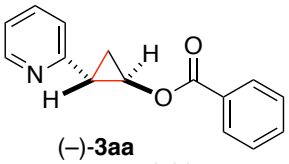
(–)-**3x**
entry 4: 95% yield
99:1 dr; 99% ee



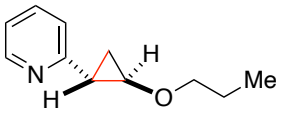
(–)-**3y**[b]
entry 5: 94% yield
98:2 dr; 97% ee



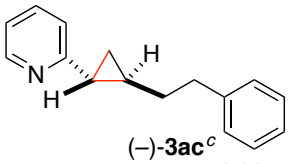
(–)-**3z**[b]
entry 6: 91% yield
87:13 dr; 98% ee



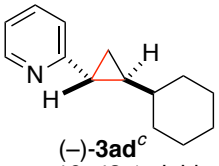
(–)-**3aa**
entry 7: 49% yield
92:8 dr; 98% ee



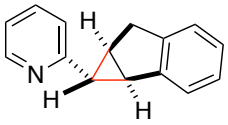
(–)-**3ab**[c]
entry 8: 55% yield
94:6 dr; 91% ee



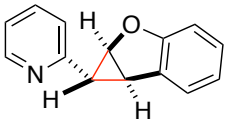
(–)-**3ac**[c]
entry 9: 55% yield
88:12 dr; 49% ee



(–)-**3ad**[c]
entry 10: 43% yield
94:6 dr; 94% ee



(–)-**3ae**[c]
entry 11: 43% yield
58:42 dr; 81%/93% ee



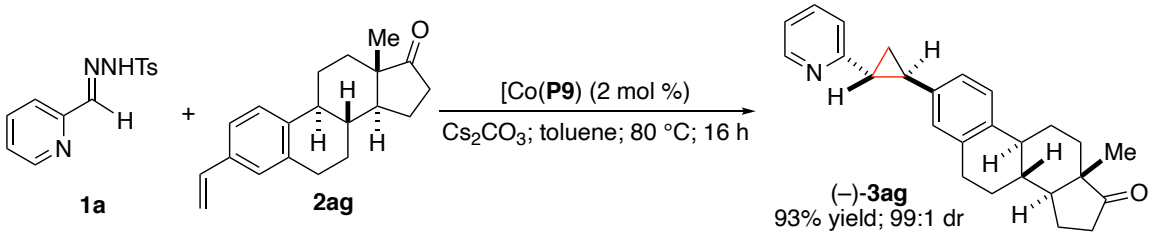
(–)-**3af**[c]
entry 12: 56% yield
96:4 dr; 97% ee

[a]Carried out with **1a** (0.10 mmol), **2** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) at 80 °C for 16 h using [Co(**P9**)] (2 mol %) in toluene (1.0 mL); Ts = 4-toluenesulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major isomer determined by chiral HPLC. [b]With **2** (0.30 mmol). [c]With **2** (1.0 mmol).

stereoselective formation of cyclopropyl ester **3aa** and cyclopropyl ether **3ab** albeit in relatively lower yields (entries 7 and 8). Notably, the [Co(**P9**)]-based system proved to be similarly effective for the asymmetric cyclopropanation of aliphatic olefins, affording the

alkyl-substituted pyridylcyclopropanes **3ac** and **3ad** in moderate yields with moderate to excellent stereoselectivities (entries 9 and 10). Gratifyingly, internal olefins such as indene and benzofuran, which are typically challenging substrates for asymmetric cyclopropanation due to steric factors,[10j] could also be cyclopropanated to form the fused cyclopropanes **3ae** and **3af** in moderate yields with high enantioselectivities despite varied diastereoselectivities (entries 11 and 12). It is worth mentioning that the Co(II)-based system was amenable to late-stage derivatization of biologically complex molecules as exemplified by the high-yielding formation of cyclopropane derivative of estrone **3ag** with excellent diastereoselectivity (Scheme 2.7).

Scheme 2.7. Late-Stage Derivatization



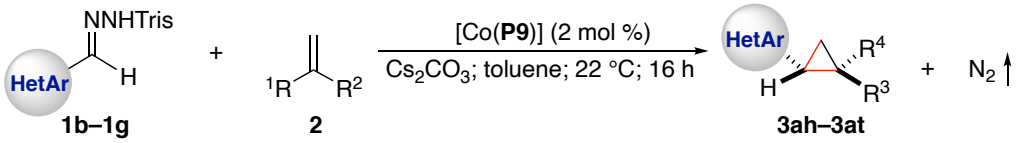
2.2.3. Asymmetric Radical Cyclopropanation of Alkenes with Different α-Heteroaryldiazomethanes

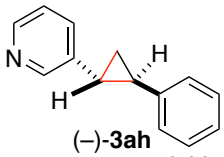
In addition to the representative 2-pyridyldiazomethane (**1a'**), it was demonstrated that metalloradical catalyst [Co(**P9**)] could effectively activate different types of α-heteroaryldiazomethanes for asymmetric cyclopropanation of alkenes (Table 2.4). For instance, 3-pyridyldiazomethane (**1b'**) generated from the corresponding trishydrazone (2,4,6-triisopropylbenzenesulfonyl hydrazone) was found to be a competent radical precursor even at room temperature for the Co(II)-based asymmetric cyclopropanation. As shown with styrene (monosubstituted olefin), α-bromostyrene (1,1-disubstituted olefin), 1-

phenyl-1,3-butadiene (conjugated diene), and methyl acrylate (electron-deficient olefin) as representative substrates, [Co(**P9**)] could effectively activate in situ-generated **1b'** at room temperature for highly asymmetric cyclopropanation reactions, leading to productive formation of the corresponding 3-pyridylcyclopropanes **3ah**, **3ai**, **3aj** and **3ak** with exceptional control of stereoselectivities (Table 2.4; entries 1–4). Likewise, other heteroaryldiazomethanes, including those generated in situ from the trishydrazones derived from 5-bromo-3-pyridyl, 4-pyridyl, 3-thienyl, 3-indolyl and 3-quinolinyl carboxaldehydes, were all shown to be effective radical precursors for [Co(**P6**)]-catalyzed asymmetric olefin cyclopropanation as exemplified with the room temperature reactions of styrene as the model substrate, affording the corresponding heteroaryl cyclopropanes **3al**–**3ap** in moderate to high yields with excellent stereoselectivities (entries 5–9). The absolute configurations of the newly-generated stereogenic centers in **3al** and **3ao** were both established as (*R*,*R*) by X-ray crystallography.

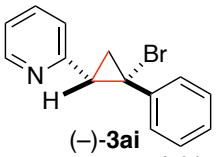
In addition, 3-quinolinyldiazomethane (**1g'**) was also investigated for Co(II)-based cyclopropanation reactions of selected alkenes ranging from α-chlorostyrene to electron-deficient olefins. Gratifyingly, almost all of these alkene substrates could be effectively cyclopropanated, allowing for the high-yielding formation of 3-quinolinylcyclopropanes **3aq**–**3at** with excellent stereoselectivities (entries 10–13). The only exception was observed for the reaction of methyl vinyl ketone, which afforded the corresponding cyclopropane **3ar** with excellent enantioselectivity but in lower yield with diminished diastereoselectivity (entry 11). The absolute configuration of the major enantiomer of **3aq** was determined to be (*S*,*S*) by X-ray crystallography.

Table 2.4. Asymmetric Olefin Cyclopropanation with Different In Situ-Generated α-Heteroaryldiazomethanes by [Co(P9)][a]

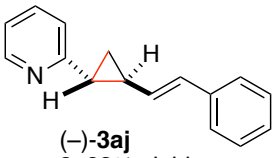




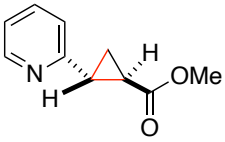
(–)-**3ah**
entry 1: 91% yield
95:5 dr; 99% ee



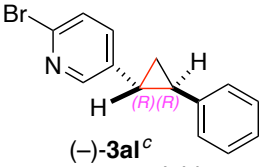
(–)-**3ai**
entry 2: 58% yield
99:1 dr; 99% ee



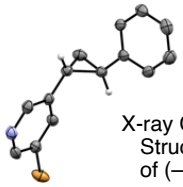
(–)-**3aj**
entry 3: 83% yield
91:9 dr; 98% ee



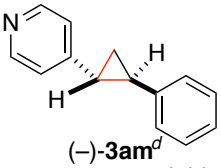
(–)-**3ak**[b]
entry 4: 91% yield
90:10 dr; 97% ee



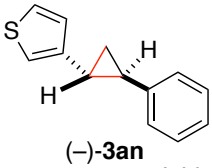
(–)-**3al**[c]
entry 5: 90% yield
97:3 dr; 99% ee



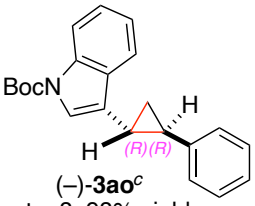
X-ray Crystal Structure of (–)-**3al**



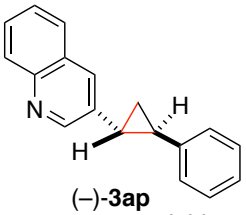
(–)-**3am**[d]
entry 6: 42% yield
95:5 dr; 89% ee



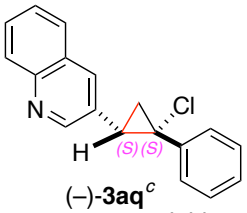
(–)-**3an**
entry 7: 71% yield
95:5 dr; 93% ee



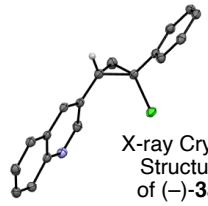
(–)-**3ao**[c]
entry 8: 98% yield
98:2 dr; 85% ee



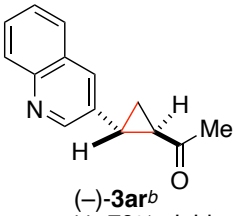
(–)-**3ap**
entry 9: 96% yield
93:7 dr; 99% ee



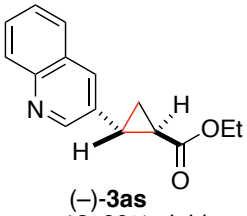
(–)-**3aq**[c]
entry 10: 95% yield
99:1 dr; 99% ee



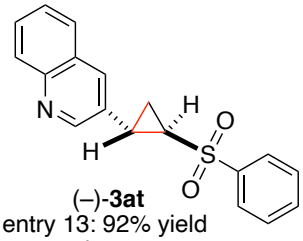
X-ray Crystal Structure of (–)-**3ac**



(–)-**3ar**[b]
entry 11: 70% yield
77:23 dr; 98% ee



(–)-**3as**
entry 12: 90% yield
96:4 dr; 99% ee



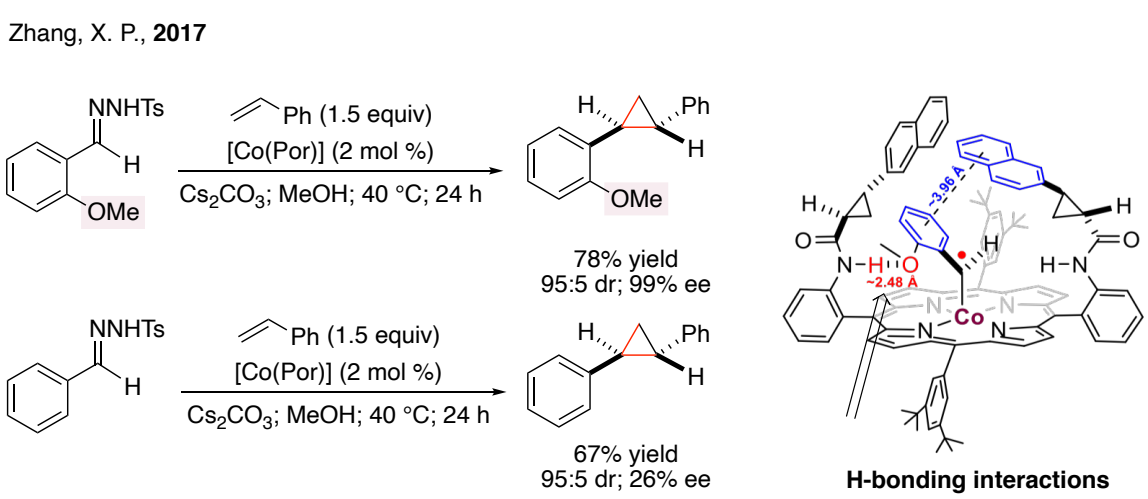
(–)-**3at**
entry 13: 92% yield
99:1 dr; 99% ee

[a]Carried out with **1b–1g** (0.10 mmol), **2** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) at 22 °C for 16 h using [Co(**P9**)] (2 mol %) in toluene (1.0 mL); Tris = 2,4,6-triisopropylbenzensulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major isomer determined by chiral HPLC. [b]With **2** (0.30 mmol). [c]Absolute configuration determined by X-ray crystallography. [d]With Ts = 4-toluenesulfonyl at 60 °C.

2.2.4. Asymmetric Radical Cyclopropanation of Alkenes with Different α-Aryldiazomethanes

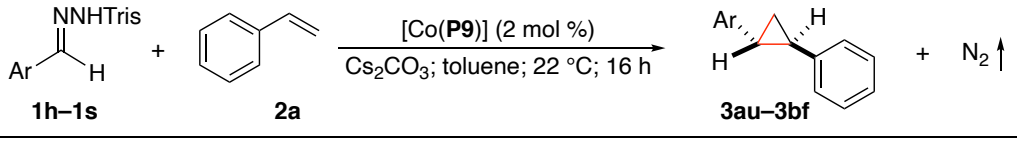
Considering that the [Co(**P9**)]-based catalytic system could productively utilize various α-heteroaryldiazomethanes containing heteroatom at different positions, we sought to explore the possibility of employing α-aryldiazomethanes for asymmetric cyclopropanation (Table 2.5), which has been largely limited to those with α-aryl groups containing H-bonding acceptors at the *ortho*-position (Scheme 2.8).[8k,8n]

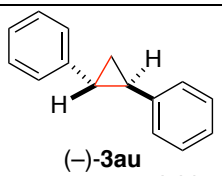
Scheme 2.8. Limitation to α-Aryldiazomethanes Containing *Ortho*-Methoxy Group

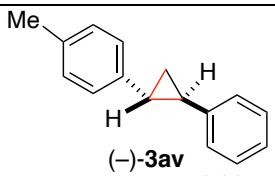


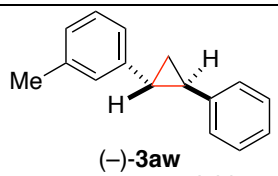
To our delight, it was found that [Co(**P9**)] could effectively activate α-phenyldiazomethane (**1h'**) derived from benzaldehyde trishydrazone (**1h**) as the radical precursor for asymmetric cyclopropanation of styrene (**2a**) under the standard conditions, affording the desired 1,2-diphenylcyclopropane (**3au**) in high yield with high diastereoselectivity and excellent enantioselectivity (Table 2.5; entry 1). Encouraged by this positive outcome, we then evaluated a wide array of α-aryldiazomethanes without H-bonding acceptors for asymmetric cyclopropanation by [Co(**P9**)].

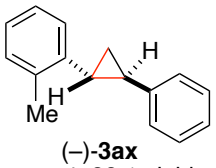
Table 2.5. Scope of Co(II)-Catalyzed Asymmetric Radical Cyclopropanation of Styrene with α-Aryldiazomethanes[a]

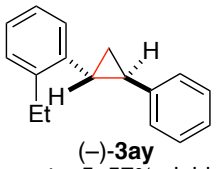


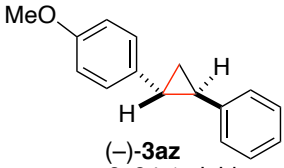

(–)-**3au**
entry 1: 97% yield
94:6 dr; 97% ee

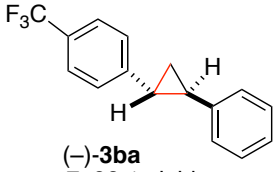

(–)-**3av**
entry 2: 95% yield
93:7 dr; 98% ee

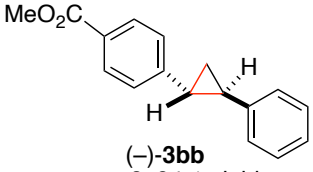

(–)-**3aw**
entry 3: 92% yield
95:5 dr; 97% ee

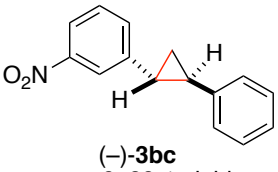

(–)-**3ax**
entry 4: 86% yield
95:5 dr; 97% ee

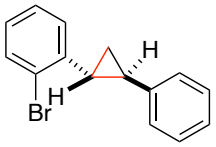

(–)-**3ay**
entry 5: 57% yield
96:4 dr; 89% ee

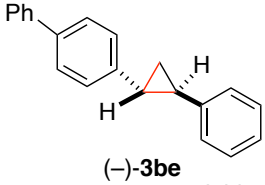

(–)-**3az**
entry 6: 94% yield
94:6 dr; 97% ee

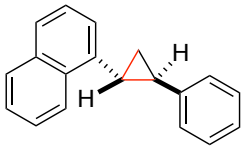

(–)-**3ba**
entry 7: 96% yield
93:7 dr; 99% ee


(–)-**3bb**
entry 8: 94% yield
94:6 dr; 97% ee


(–)-**3bc**
entry 9: 89% yield
98:2 dr; 96% ee


(–)-**3bd**
entry 10: 89% yield
96:4 dr; 93% ee


(–)-**3be**
entry 11: 90% yield
95:5 dr; 98% ee


(–)-**3bf**
entry 12: 91% yield
95:5 dr; 97% ee

[a]Carried out with **1h–1s** (0.10 mmol), **2a** (0.15 mmol) and Cs_2CO_3 (0.20 mmol) using [Co(**P9**)] (2 mol %) in toluene (1.0 mL) at 22 °C for 16 h; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR of crude reaction mixture; Enantiomeric excess (ee) of the major (*E*)-isomer determined by chiral HPLC; Tris = 2,4,6-triisopropylbenzene sulfonyl.

In addition to non-substituted α-phenyldiazomethane, α-aryldiazomethanes bearing methyl substituent at different aryl positions, including *p*-Me (**1i'**), *m*-Me (**1j'**), and *o*-Me (**1k'**), could all be efficiently activated by [Co(**P9**)] for cyclopropanation of **2a**, furnishing the corresponding arylcyclopropanes **3av**–**3ax** in similarly high yields with the same high level of stereoselectivities (Table 2.5; entries 2–4). Notably, the sterically-encumbered *o*-

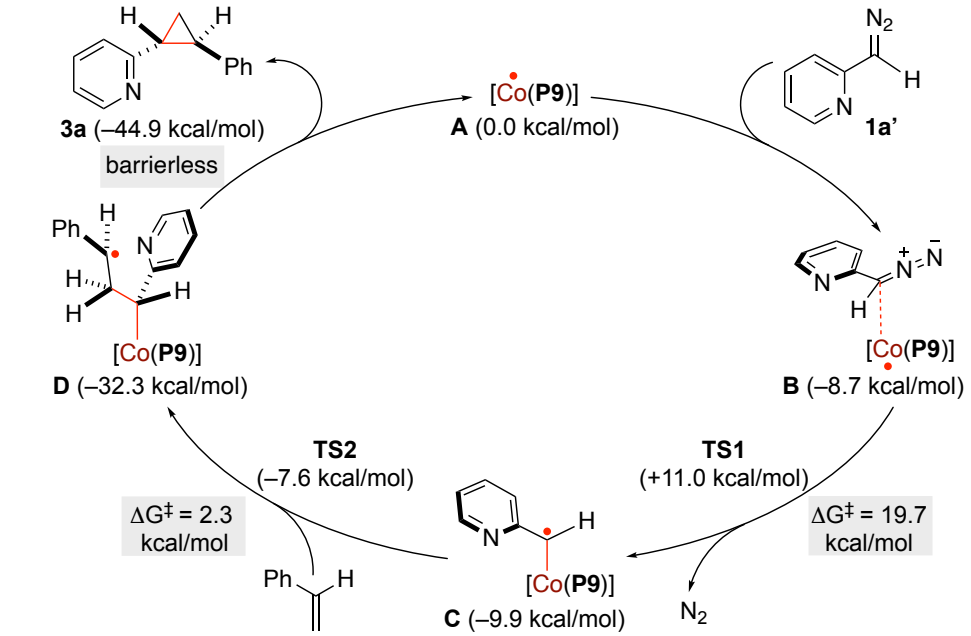
ethylphenyldiazomethane (**1l'**) was found to be also suitable for the catalytic reaction, forming cyclopropane **3ay** with high stereoselectivities albeit in lower yield (entry 5). It was further shown that the [Co(**P9**)]-based system could use α-aryldiazomethanes containing substituents with varied electronic properties at different aryl positions, such as *p*-OMe (**1m'**), *p*-CF_3 (**1n'**), *p*-CO_2Me (**1o**'), and *m*-NO_2 (**1p'**), for the reaction, enabling high-yielding formation of the desired cyclopropanes **3az**–**3bc** with excellent stereoselectivities (entries 6–9). Additionally, halogenated aryldiazomethanes were also suitable for the catalytic process as exemplified by the stereoselective synthesis of cyclopropane **3bd** with *o*-bromophenyldiazomethane (**1q'**) (entry 10). Furthermore, the Co(II)-based catalytic system could be applicable to α-aryldiazomethanes bearing extended aromatic systems, including *p*- biphenyldiazomethane (**1r'**) and 2-naphthyldiazo methane (**1s'**), delivering the corresponding cyclopropanes **3be** and **3bf** in high yields with excellent control of stereoselectivities (entries 11–12). Evidently, [Co(**P9**)] represents a powerful new catalyst that is generally applicable for asymmetric olefin cyclopropanation with both α-heteroaryldiazomethanes and α-aryldiazomethanes.

2.2.5. Mechanistic Studies on Co(II)-Catalyzed Radical Olefin Cyclopropanation with α-Heteroaryldiazomethanes

To gain insight into the proposed stepwise radical mechanism (Scheme 2.1), a combination of computational and experimental studies was conducted with collaboration of fellow labmates Jing Ke and Yiling Zhu. First, density functional theory (DFT) calculations were performed to elucidate the details of the catalytic pathway and associated energetics for the cyclopropanation reaction of styrene (**2a**) with 2-pyridyldiazomethane (**1a'**) by [Co(**P9**)] (Scheme 2.9; see Scheme S1 in Experimental Section for details). The geometry

optimizations were performed with the Gaussian 16[18] at the BP86[19,20]/lanl2dz[16,21] level of theory in the gas phase at room temperature. To further improve the accuracy of energies, single point energies were carried out at the B3LYP[22]/def2-tzvp[16,21] level of theory along with Grimme's dispersion correction[23] (D3BJ) and SMD[24] solvation model (in toluene).

Scheme 2.9. DFT Calculations on Energetics of [Co(P6)]-Catalyzed Cyclopropanation[a]



[a]Applied BP86/LANL2DZ for geometry optimization and B3LYP/def2-tzvp for calculations of single point energies (kcal/mol) along with Grimme's dispersion correction and SMD (toluene) solvation model.

The DFT calculations reveal the initial formation of intermediate **B** between the catalyst and 2-pyridyldiazomethane through multiple noncovalent attractive interactions, including

[18] Frisch, M. J. *et al.*, *Gaussian 16*, *Revision A.03*, Gaussian, Inc., Wallingford CT, **2016**.
[19] Schultz, N. E.; Zhao, Yan; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127–11143.
[20] Suarez, A. I. O.; Jiang, H.-L.; Zhang, X. P.; de Bruin, B. *Dalton Trans.* **2011**, *40*, 5697–5705.
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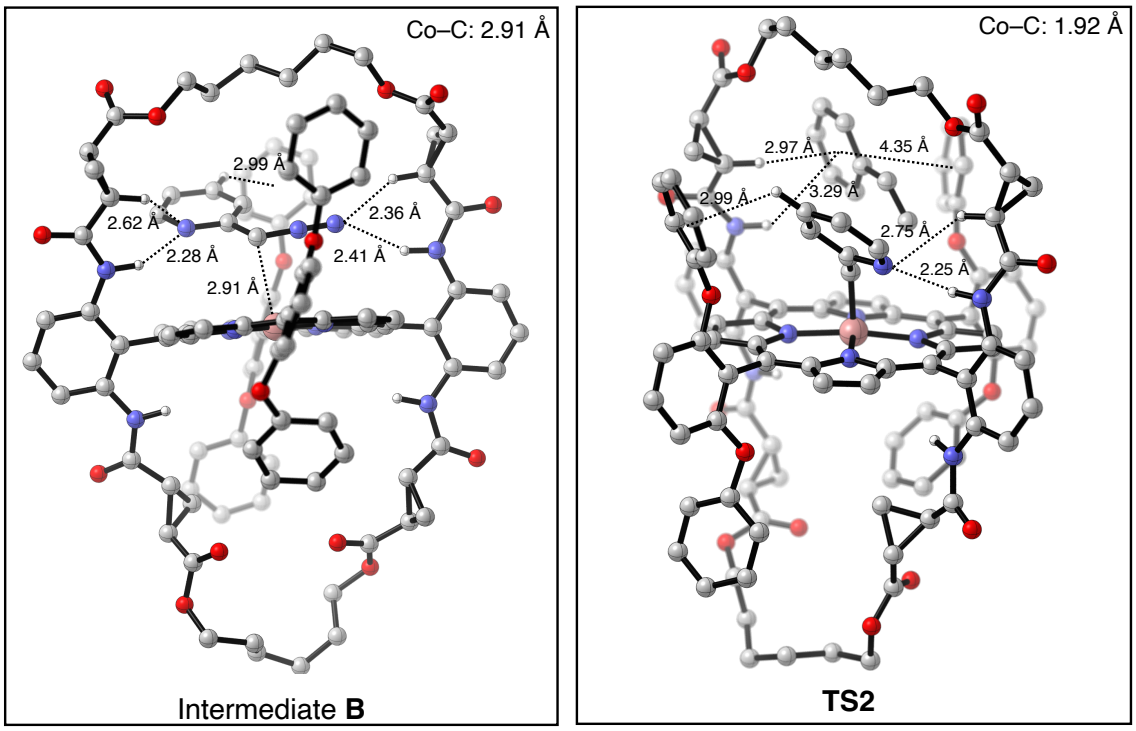
[24] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys.Chem. B* **2009**, *113*, 6378–6396.

H-bonding and π-stacking interactions (Figure 2.3; see Scheme S2 in Experimental Section). The noncovalent complexation, which is exergonic by 8.7 kcal/mol, positions the α-carbon atom of diazo **1a'** in close proximity to the Co(II)-metalloradical center of [Co(**P9**)] (C---Co: ~2.91 Å) for further interactions. The ensuing metalloradical activation, which is slightly exergonic by 1.2 kcal/mol, is found to be associated with a relatively high but accessible activation barrier (**TS1**: $\Delta G^{\ddagger}$ = 19.7 kcal/mol), affording α-Co(III)-pyridyl radical intermediate **C** with the release of dinitrogen as the byproduct. The subsequent radical addition of the resulting radical intermediate **C** to alkene **2a**, which is highly exergonic by 22.4 kcal/mol, proceeds through an exceedingly low activation barrier (**TS2**: $\Delta G^{\ddagger}$ = 2.3 kcal/mol), delivering γ-Co(III)-alkyl radical intermediate **D**.

Figure 2.3. DFT-Optimized Models Showing Noncovalent Attractive Interactions

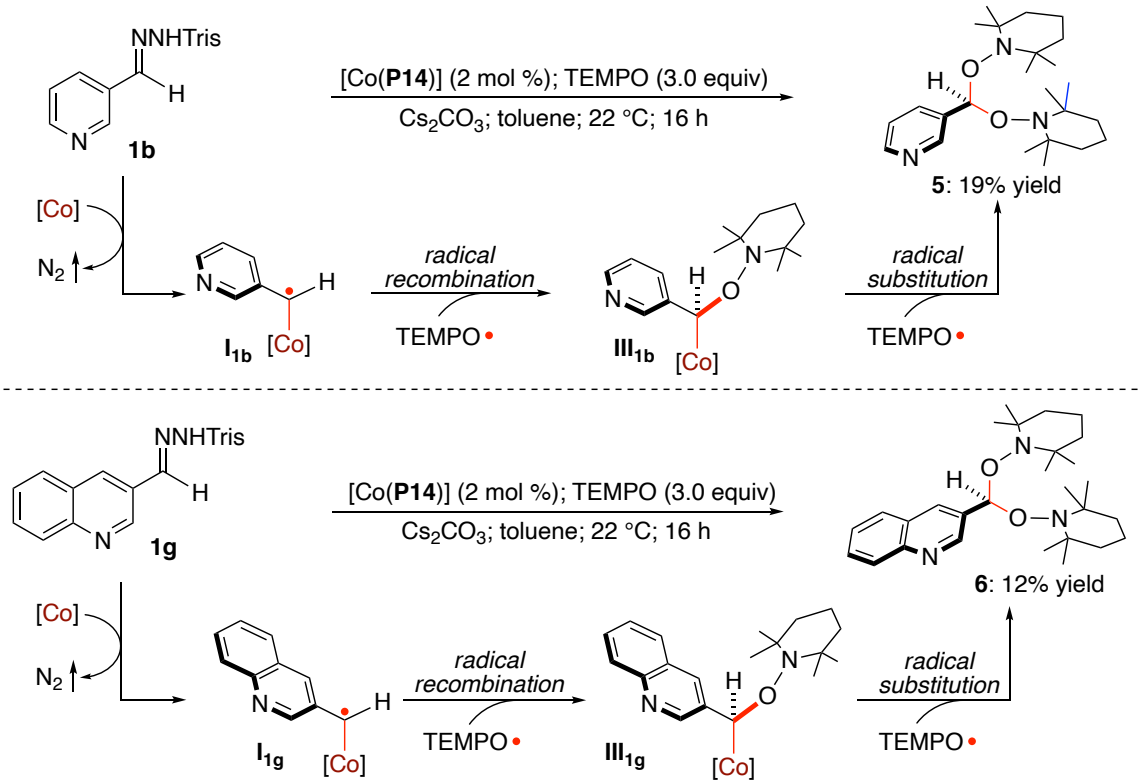


As illustrated in the DFT-optimized structure of **TS2** (Figure 2.3; see Scheme S2 in Experimental Section), there exists a network of noncovalent attractive interactions, such as multiple H-bonding and π-stacking interactions, between the substrates and the catalyst that synergistically lower the activation barrier of the transition state. According to the DFT calculations, the final step of 3-*exo-tet* cyclization of γ-Co(III)-alkyl radical intermediate **D**, which is exergonic by 12.6 kcal/mol, is a nearly barrierless process, leading to the formation of cyclopropane product **3a** while regenerating the metalloradical catalyst [Co(**P6**)].

In an effort to directly trap α-Co(III)-heterobenzyl radical intermediate **I**, the metalloradical activation of 3-pyridyldiazomethane (**1b'**) by [Co(**P14**)] (**P14** = 3,5-Di^{t}Bu-IbuPhyrin)] [25] was carried out in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) without alkene substrates, resulting in the isolation of bis-TEMPO-trapped product **5** in 19% yield (Scheme 2.10). The observation of compound **5** evidently implies the initial formation of α-Co(III)-pyridyl radical $\mathbf{I_{1b}}$, which was presumably captured by TEMPO through radical recombination to generate Co(III)-alkyl intermediate $\mathbf{III_{1b}}$. Subsequent radical substitution reaction of intermediate $\mathbf{III_{1b}}$ with a second molecule of TEMPO was likely responsible for the final formation of **5**. Similarly, bis-TEMPO-trapped product **6** was isolated in 12% yield from the metalloradical activation of 3-quinolinyldiazomethane (**1g'**) by [Co(**P14**)] in the presence of TEMPO, indicating the existence of α-Co(III)-heterobenzyl radical intermediate $\mathbf{I_{1g}}$ and the following Co(III)-alkyl intermediate $\mathbf{III_{1g}}$ (Scheme 2.10).

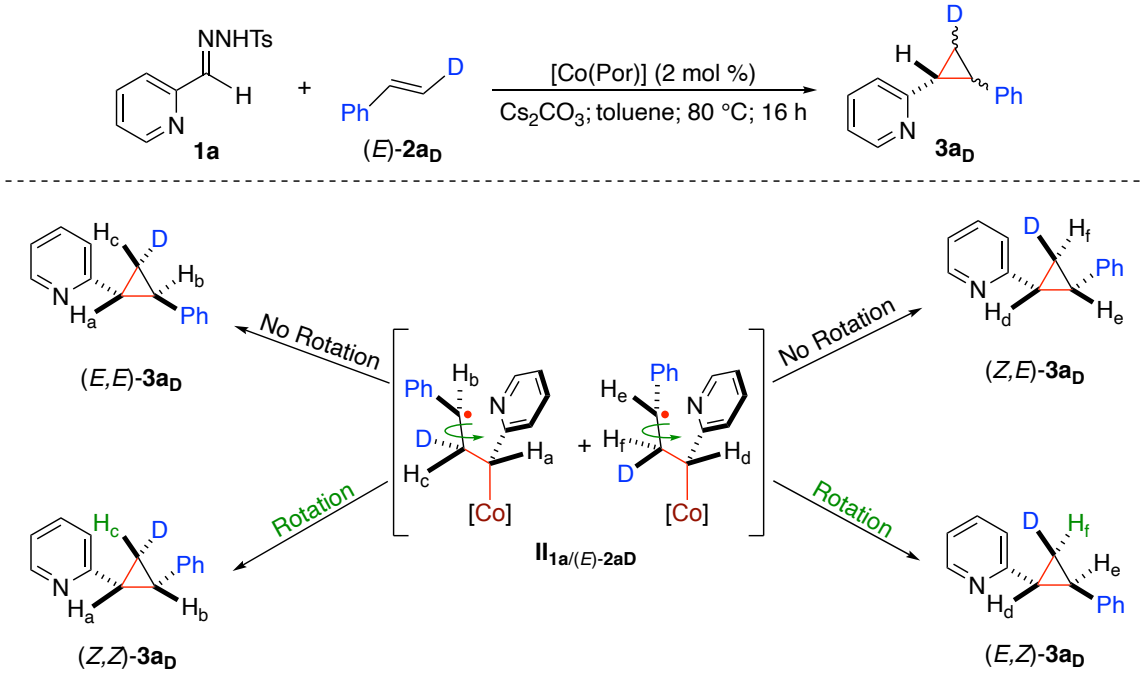
[25] Ruppel, J. V.; Jones, J. E.; Huff, C. A.; Kamble, R. M.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2008**, *10*, 1995–1998.

Scheme 2.10. Trapping of α-Co(III)-Heterobenzyl Radicals by TEMPO

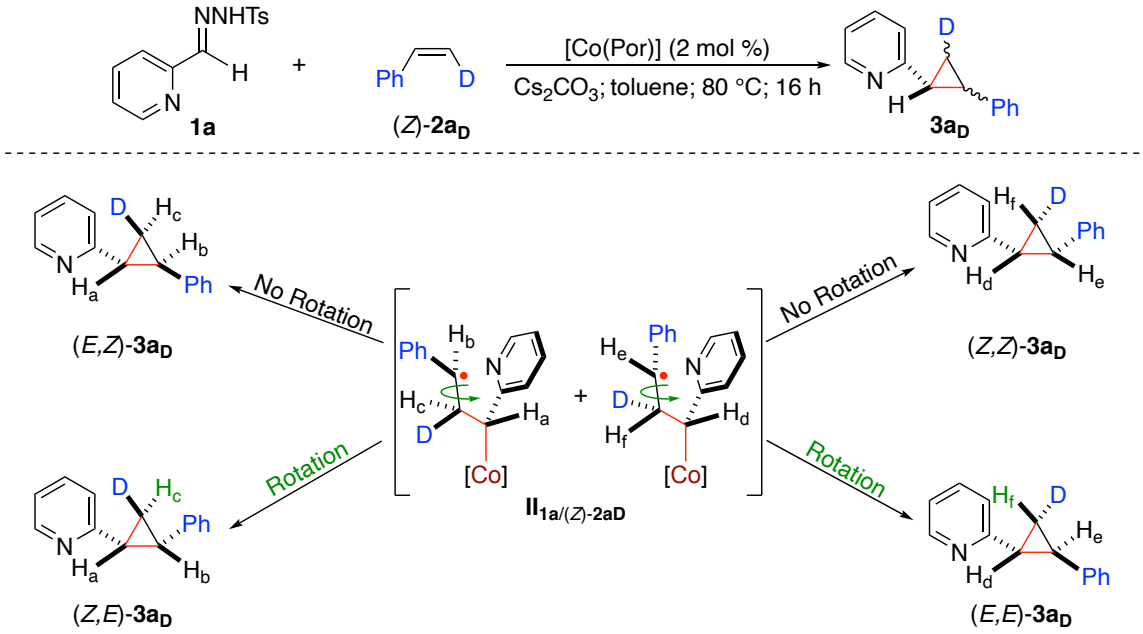


To probe the involvement of γ-Co(III)-alkyl radical intermediate **II** in the proposed mechanism (Scheme 2.1), both isotopomers of β-deuterostyrene (*E*)-**2a**$_{\mathbf{D}}$ and (*Z*)-**2a**$_{\mathbf{D}}$ were employed as substrates for Co(II)-catalyzed cyclopropanation with 2-pyridyl tosylhydrazone (**1a**) (Schemes 2.11 and 2.12). Unlike a concerted mechanism that results in stereospecific cyclopropane products, a stepwise radical mechanism may give rise to the formation of four possible diastereomers of cyclopropanes due to the potential rotation of the β-C–C bond in γ-Co(III)-alkyl radical intermediate **II** before cyclization. As expected, both reactions of (*E*)-**2a**$_{\mathbf{D}}$ and (*Z*)-**2a**$_{\mathbf{D}}$ with **1a** afforded the cyclopropane products as a mixture of four different diastereomers: (*E*,*E*)-**3a**$_{\mathbf{D}}$, (*Z*,*Z*)-**3a**$_{\mathbf{D}}$, (*Z*,*E*)-**3a**$_{\mathbf{D}}$, and (*E*,*Z*)-**3a** (Schemes 2.11 and 2.12). Among them, (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a**$_{\mathbf{D}}$ are formed due to β-C–C bond rotation in γ-Co(III)-alkyl radical intermediate **II** for cyclopropanation reaction of

Scheme 2.11 Probing of γ-Co(III)-Alkyl Radicals by Cyclopropanation of (*E*)-β-Deuterostyrene



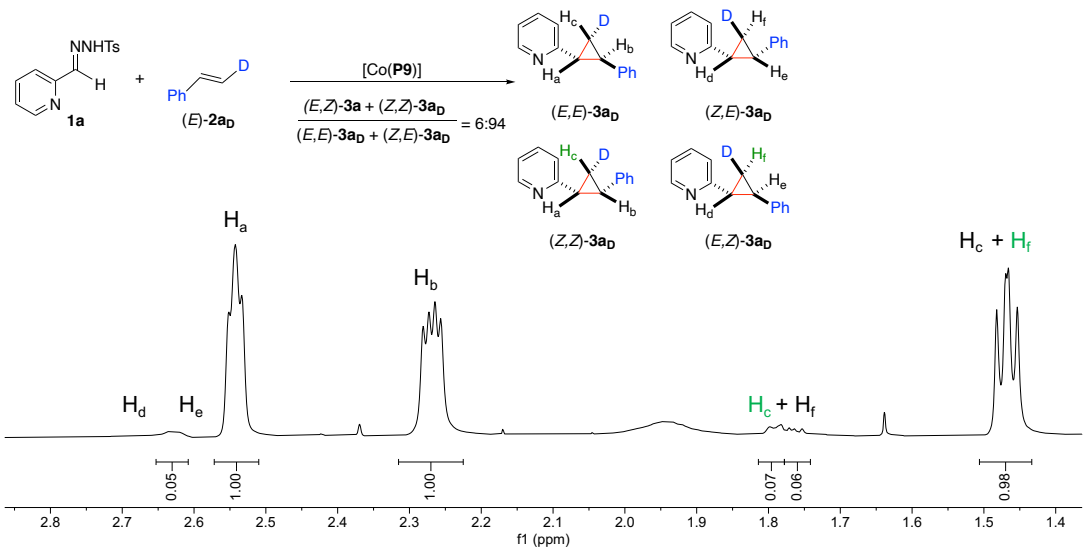
Scheme 2.12. Probing of γ-Co(III)-Alkyl Radicals by Cyclopropanation of (*Z*)-β-Deuterostyrene

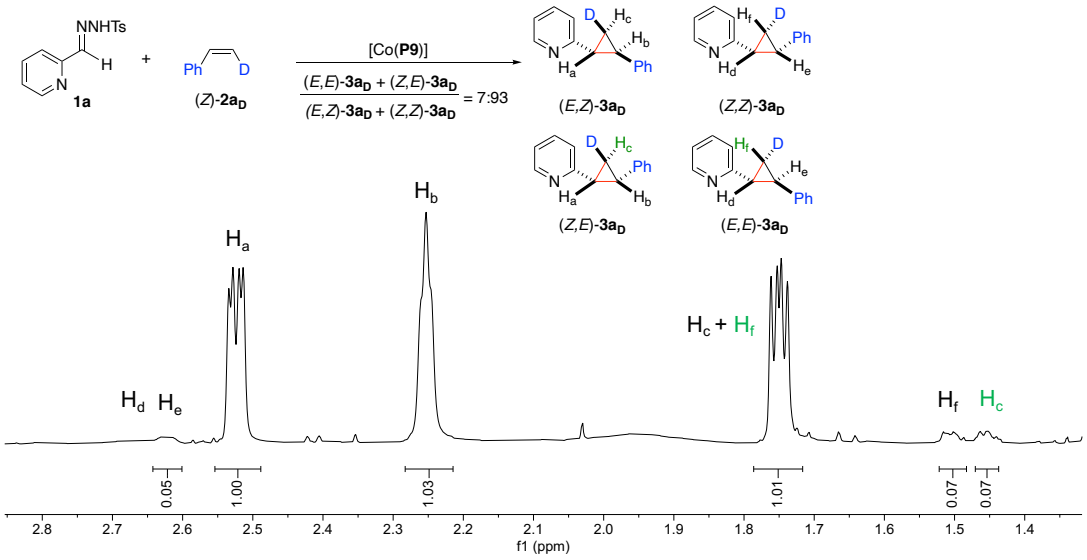


(*E*)-**2a$_D$**. The isotopic ratio between the diastereomers of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a$_D$** and that of (*E*,*E*)-**3a$_D$** and (*Z*,*E*)-**3a$_D$** could be determined by ^{1}H NMR analysis. Similarly, diastereomers of (*E*,*E*)-**3a$_D$** and (*Z*,*E*)-**3a$_D$** are formed for reaction of (*Z*)-**2a$_D$**, and the isotopic ratio between diastereomers of (*E*,*E*)-**3a$_D$** and (*Z*,*E*)-**3a$_D$** and that of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a$_D$** could also be analyzed.

When the bridged [Co(**P9**)] (**P9** = 2,6-DiPhO-Hu(C$_6$)Phyrin)] was used as the catalyst, the isotopic ratio between the diastereomers of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a$_D$** and that of (*E*,*E*)-**3a$_D$** and (*Z*,*E*)-**3a$_D$** was determined to be 6:94 for the cyclopropanation reaction of (*E*)-**2a$_D$**. Accordingly, the isotopic ratio between diastereomers of (*E*,*E*)-**3a$_D$** and (*Z*,*E*)-**3a$_D$** and that of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a$_D$** was determined to be 7:93 for the reaction of (*Z*)-**2a$_D$** (Scheme 2.13). The observation of both (*E*)- and (*Z*)- isotopomers of (*E*)-**3a** in both reactions evidently suggested the rotation of β-C–C bond in the corresponding γ-Co(III)-alkyl radical intermediates **II$_{1a/(E)\text{-}2aD}$** and **II$_{1a/(Z)\text{-}2aD}$**.

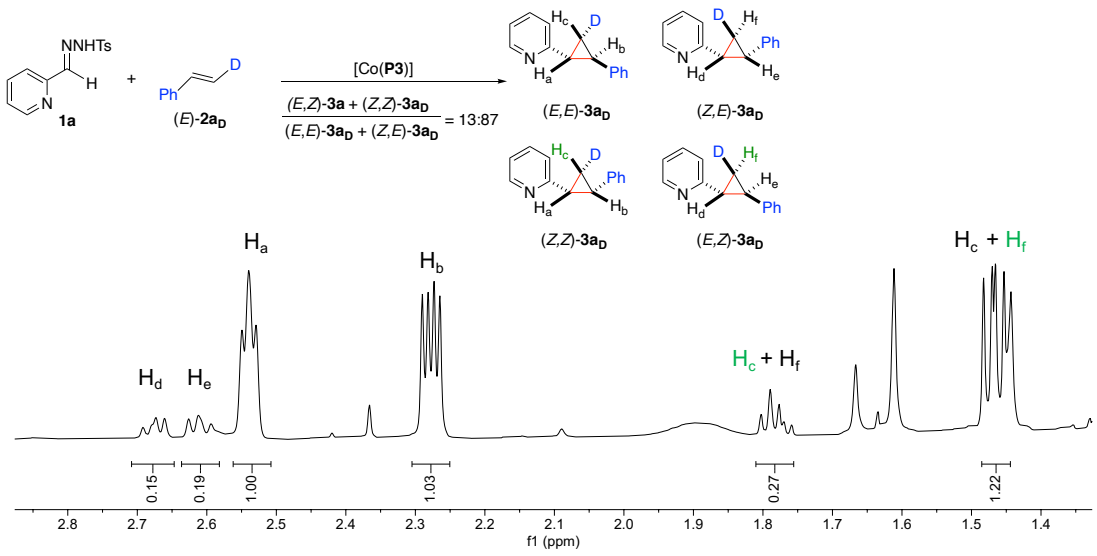
Scheme 2.13. ^{1}H Spectrum for Cyclopropane Isotopomers 3a$_D$ from [Co(P9)]-Catalyzed Cyclopropanation

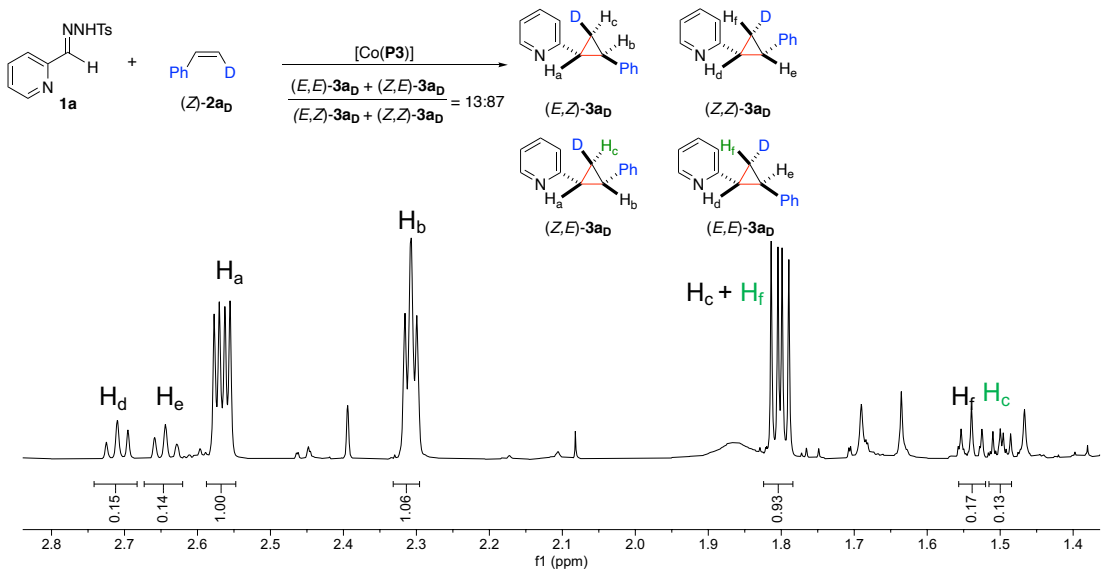




When the non-bridged [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)] was employed as the catalyst, the isotopic ratios changed for both reactions of (*E*)-**2a$_D$** (from 6:94 to 13:87) and (*Z*)-**2a$_D$** (from 7:93 to 13:87), indicating a higher degree of the β-C–C bond rotation in the less-hindered catalyst environment (Scheme 2.14).

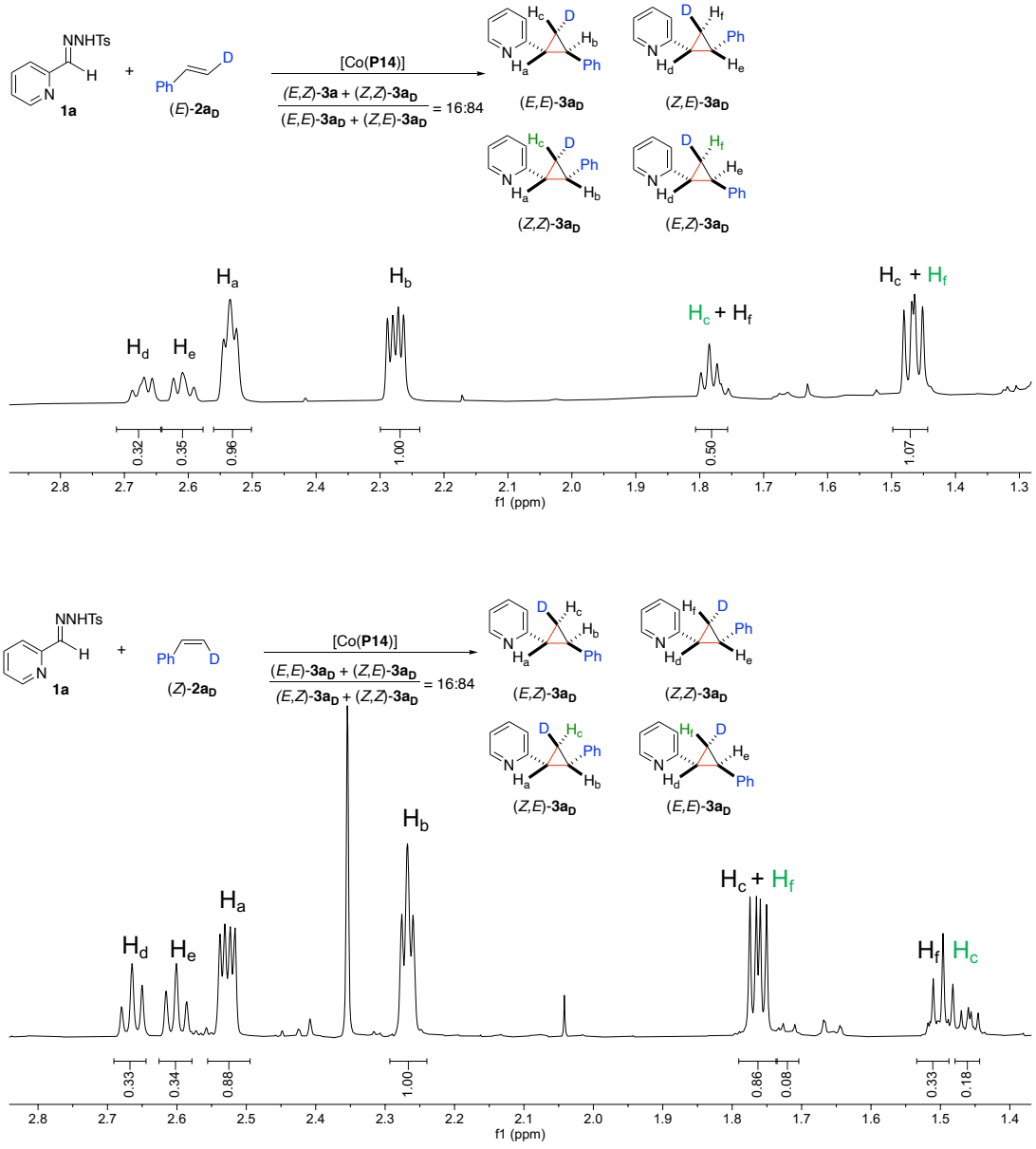
Scheme 2.14. ^{1}H NMR Spectrum for Cyclopropane Isotopomers 3a$_D$ from [Co(P3)]-Catalyzed Cyclopropanation





Accordingly, the use of even less-hindered catalyst [Co(**P14**)] (**P14** = 3,5-Di^{t}Bu-IbuPhyrin)] allowed a further increase in the degree of the β-C–C bond rotation, changing the isotopic ratios to 16:84 and 16:84, respectively, for the two reactions (Scheme 2.15). Collectively, these experimental results, together with the DFT calculations, provided corroborating evidence for the proposed stepwise radical mechanism of the Co(II)-catalyzed asymmetric cyclopropanation with heteroaryldiazomethanes.

Scheme 2.15. ^{1}H NMR Spectrum for Cyclopropane Isotopomers 3a$_D$ from [Co(P14)]-Catalyzed Cyclopropanation



2.3. CONCLUSIONS AND OUTLOOK

In summary, we have applied Co(II)-based metalloradical catalysis (MRC) for the successful development of asymmetric radical cyclopropanation of alkenes with heteroaryldiazomethanes. With the newly-synthesized bridged D_2-symmetric chiral

amidoporphyrin 2,6-DiPhO-Hu(C_6)Phyrin as the optimal supporting ligand, the Co(II)-based metalloradical system can effectively activate different types of heteroaryldiazomethanes even at room temperature for olefin cyclopropanation, offering a general approach for stereoselective synthesis of chiral heteroaryl cyclopropanes. In addition to styrene derivatives, the Co(II)-catalyzed cyclopropanation is highlighted by an extraordinarily broad scope of alkenes, including several types of challenging substrates, affording a diverse range of heteroaryl cyclopropanes in high yields with both excellent diastereoselectivities and enantioselectivities. Furthermore, both computational and experimental studies have provided several lines of evidence in elucidating the underlying stepwise radical mechanism of the Co(II)-based olefin cyclopropanation involving α- and γ-metalloalkyl radicals as the key intermediates. In view of the ubiquity of the resulting enantioenriched heteroaryl cyclopropanes in biologically important compounds, we hope this Co(II)-catalyzed asymmetric radical cyclopropanation process will find wide applications in organic synthesis related to drug discovery.

2.4. EXPERIMENTAL SECTION

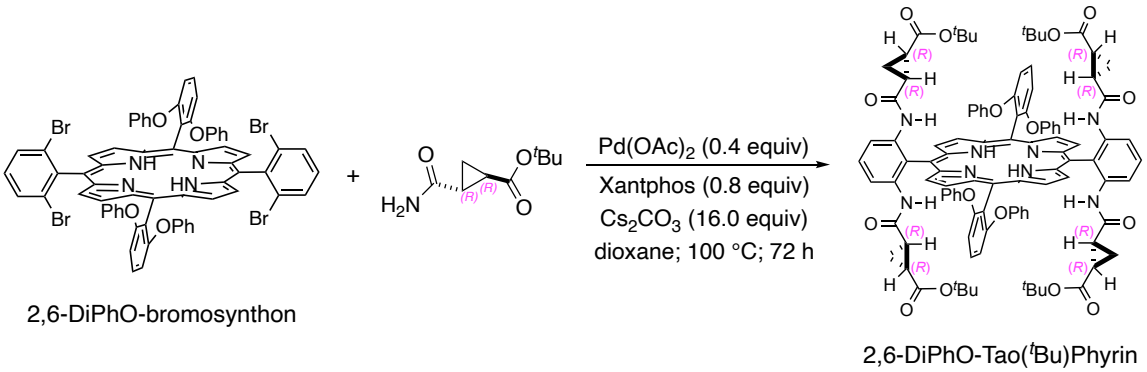
2.4.1. General Considerations

All cyclopropanation reactions were performed in anhydrous solvents under N_2 atmosphere in an oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR spectra were acquired using Varian INOVA 400 (400 MHz), Bruker 500 (500 MHz), or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to residual solvent peak ($CHCl_3$ δ = 7.26 ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, br = broad, m = multiplet), and coupling constants *J* (Hz). ^{13}C NMR spectra were acquired using Varian INOVA 400 (100 MHz), Bruker 500 (125 MHz), or INOVA 600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ δ = 77.16 ppm or (DMSO-d_6 δ = 39.52 ppm) as the internal standard. In ^{13}C NMR analysis, peaks for carbon atoms adjacent to a boron center were generally not observed owing to quadrupolar broadening. ^{11}B spectra were externally referenced to a standard of BF_3•Et_2O (δ = 0.0 ppm). ^{19}F NMR spectrum was acquired using Varian Bruker 500 (470 MHz) or INOVA 600 (564 MHz) spectrometer. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu

HPLC system with Chiralcel OD-H, OJ-H, AD-H, AS-H, IA, IB, IC, ID, IE and IF columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals or TCI and were used without further purification.

2.4.2. Synthesis and Characterization of Catalysts

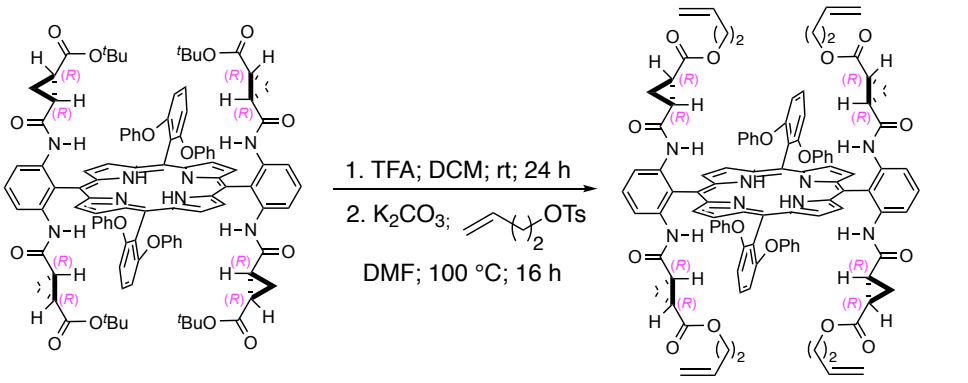
2.4.2.1. Experimental Procedure for Preparation of 2,6-DiPhO-Tao(ᵗBu)Phyrin



2,6-DiPhO-Tao(ᵗBu)Phyrin was synthesized according to our previous reported procedure.[8a] 2,6-DiPhO-bromosynthon[8m] (300 mg, 0.231 mmol, 1.0 equiv), the chiral amide (1*R*,2*R*)-*tert*-butyl-2-carbamoylcyclopropane-1-carboxylate[15] (685 mg, 3.70 mmol, 16.0 equiv), $Pd(OAc)_2$ (20.74 mg, 0.0924 mmol, 0.4 equiv), Xantphos (107 mg, 0.184 mmol, 0.8 equiv) and Cs_2CO_3 (1.20 g, 3.70 mmol, 16.0 equiv) were placed in an oven-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. Under nitrogen atmosphere, the screw cap was replaced with a rubber septum. Dioxane (0.02 M) was added via a gas tight syringe. The tube was then purged with nitrogen for 1 min and sealed with Teflon screw cap. After stirring at 100 °C for 72 h, the resulting mixture was cooled down to room temperature, diluted with EtOAc,

filtered through a short pad of celite and concentrated under vacuum. The crude mixture was further purified by flash column chromatography (eluent: 4:1 to 2:1 Hexanes/EtOAc) to afford the title compound (238 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, J = 4.8 Hz, 4H), 8.80 (d, J = 4.8 Hz, 4H), 8.47 (br, 4H), 7.86 (t, J = 8.4 Hz, 2H), 7.65 (t, J = 8.5 Hz, 2H), 7.07 – 6.98 (m, 12H), 6.82 (t, J = 7.4 Hz, 4H), 6.78 – 6.74 (m, 8H), 6.64 (br, 4H), 1.79 (ddd, J = 9.1, 5.8, 3.7 Hz, 4H), 0.95 (s, 36H), 0.85 – 0.79 (m, 4H), 0.47 (br, 4H), 0.24 (br, 4H), –2.53 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.35, 169.10, 159.20, 156.28, 139.15, 132.58, 130.73, 130.37, 129.53, 123.61, 123.38, 121.99, 119.45, 118.06, 112.73, 112.16, 107.12, 80.55, 77.36, 27.75, 23.97, 22.94, 14.83. UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 423 (5.54), 515 (4.31), 545 (3.64), 589 (3.81), 643 (3.26). HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{104}H_{99}N_8O_{16}^+$: 1715.71736, Found: 1715.71326.

2.4.2.2. Experimental Procedure for Preparation of 2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin



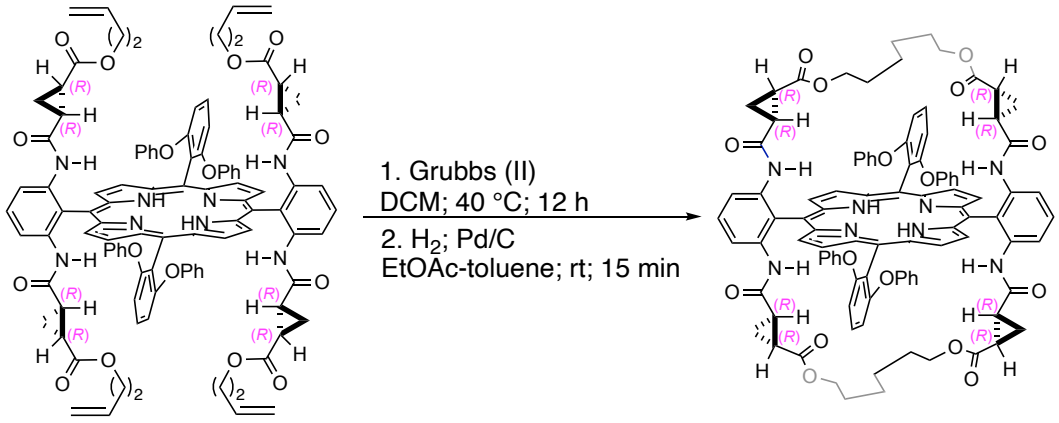
2,6-DiPhO-Tao(^{t}Bu)Phyrin

2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin

2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin was synthesized according to our previous reported procedure.[15] TFA (1.50 mL, 19.5 mmol, 100.0 equiv) was added to a solution of **2,6-DiPhO-Tao(^{t}Bu)Phyrin** (335 mg, 0.195 mmol, 1.0 equiv) in DCM (0.05 M), and the reaction was stirred at room temperature overnight prior to evaporation of all the volatiles.

The crude mixture was transferred to an oven-dried Schlenk tube followed by the addition of anhydrous K_2CO_3 (1.35 g, 9.76 mmol, 50.0 equiv). The tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen. Under nitrogen atmosphere, but-3-enyl 4-methylbenzenesulfonate (883 mg, 3.90 mmol, 20.0 equiv) was added, followed by the addition of DMF (0.05 M) via a gas tight syringe. The reaction mixture was heated at 100 °C for 12 h. After cooling down to room temperature, the reaction mixture was diluted with EtOAc and water. The organic layer was separated and concentrated under vacuum. Further purification by flash column chromatography (eluent: 3:1 to 2:1 Hexanes/EtOAc) to afford the title compound (206 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (d, *J* = 4.7 Hz, 4H), 8.82 (d, *J* = 4.8 Hz, 4H), 8.51 (br, 4H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 8.5 Hz, 2H), 7.08 – 7.01 (m, 12H), 6.84 (t, *J* = 7.3 Hz, 4H), 6.82 – 6.76 (m, 8H), 6.66 (br, 4H), 5.34 (dd, *J* = 17.2, 9.1 Hz, 4H), 4.72 – 4.67 (m, 8H), 3.60 – 3.44 (m, 8H), 1.94 – 1.82 (m, 12H), 0.95 – 0.89 (m, 4H), 0.50 (br, 4H), 0.34 (br, 4H), –2.52 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.14, 168.65, 159.22, 156.17, 139.05, 133.65, 130.82, 130.51, 129.58, 123.71, 122.99, 121.76, 119.56, 117.86, 116.99, 112.77, 112.02, 107.01, 63.43, 32.64, 24.35, 21.82, 14.83. UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 423 (5.67), 515 (4.44), 543 (3.81), 587 (3.96), 642 (3.45). HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{104}H_{91}N_8O_{16}^+$: 1707.65476, Found: 1707.65015.

2.4.2.3. Experimental Procedure for Preparation of [H_2(P9)]

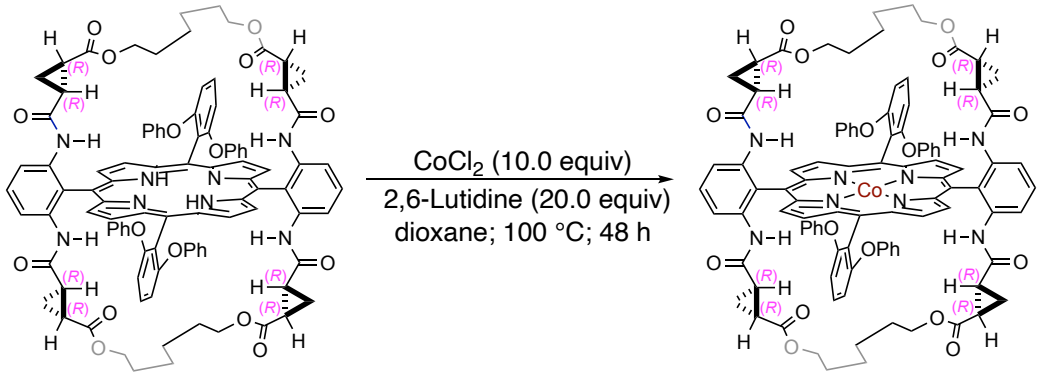


2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin [H_2(**P9**)]

2,6-DiPhO-Hu(C_6)Phyrin [H_2(**P9**)] was synthesized according to our previous reported procedure.[15] Grubbs 2nd generation catalyst (10.3 mg, 12.2 μmol, 0.1 equiv) was added to a solution of 2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin (206 mg, 0.122 mmol, 1.0 equiv) in DCM (0.001 M), and the reaction mixture was stirred at 40 ˚C for 12 h. After the reaction finished, the resulting mixture was concentrated under vacuum and purified by flash column chromatography (1:1:1 to 1:2:1 Hexanes/EtOAc/DCM) to afford the mixture of *trans* and *cis* isomers, which was in turn dissolved in EtOAc-toluene (V/V=2/1, 0.02 M) in the presence of 10% Pd/C (1 mg per mg of porphyrin). Hydrogen gas was bubbled through the reaction mixture until the reaction was completed based on the crude ^{1}H NMR (typically for 15 min). The reaction mixture was filtered through a short pad of celite and concentrated under vacuum. The resulting crude was purified by flash column chromatography (eluent: 1:2:1 Hexanes/EtOAc/DCM) to afford the title compound (145 mg, 71% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (d, J = 4.7 Hz, 4H), 8.90 (d, J = 4.7 Hz, 4H), 8.38 (d, J = 8.4 Hz, 4H), 7.90 (t, J = 8.5 Hz, 2H), 7.66 (t, J = 8.6 Hz, 2H), 7.14 – 7.07 (m, 8H), 7.01 (d, J = 8.6 Hz, 4H), 6.91 (t, J = 7.4 Hz, 4H), 6.87 – 6.81 (m, 8H), 6.62

(br, 4H), 3.56 – 3.52 (m, 4H), 3.34 – 3.30 (m, 4H), 1.92 (ddd, J = 9.3, 5.9, 3.8 Hz, 4H), 0.95 – 0.91 (m, 4H), 0.83 – 0.74 (m, 8H), 0.62 – 0.54 (m, 12H), 0.27 – 0.22 (m, 4H), –2.58 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.70, 168.53, 159.33, 156.10, 138.75, 130.88, 130.45, 129.64, 123.90, 122.85, 122.59, 119.73, 119.48, 112.98, 111.43, 107.59, 64.16, 27.28, 24.49, 23.75, 22.31, 14.68. UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 423 (5.51), 515 (4.26), 547 (3.64), 588 (3.78), 641 (3.26). HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{100}H_{87}N_8O_{16}^+$: 1655.6235, Found: 1655.61731.

2.4.2.3. Experimental Procedure for Preparation of [Co(P9)]



[H_2(**P9**)] [Co(**P9**)]

[Co(**P9**)] was synthesized according to our previous reported procedure.[8a] Free base porphyrin [H_2(**P9**)] (145 mg) and anhydrous $CoCl_2$ (10.0 equiv) were placed in an oven-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen. Under nitrogen atmosphere, 2,6-Lutidine (20.0 equiv) and anhydrous dioxane (0.02 M) were added. The tube was purged with nitrogen for 1 min and sealed with Teflon screw cap. The reaction mixture was stirred at 100 °C for 48 h prior to being cooled down to room temperature. The reaction mixture was diluted with EtOAc, washed with water 2 times and then concentrated under vacuum. The compound [Co(**P9**)] was isolated as a purple solid (118 mg, 79% yield) after purification by flash column

chromatography (eluent: 1:2:1 Hexanes/EtOAc/DCM). UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 415 (5.19), 528 (4.01). HRMS (ESI) ($[M]^+$) Calcd. For $C_{100}H_{84}CoN_8O_{16}^+$: 1711.53373, Found: 1711.52722.

2.4.3. Synthesis and Characterization of *N*-Sulfonyl Hydrazones

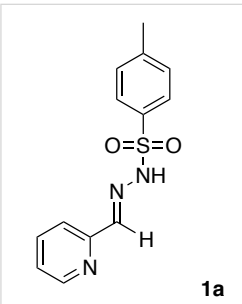
2.4.3.1. Experimental Procedure for Preparation of *N*-Tosylhydrazones

To a stirred solution of tosylhydrazide (1.0 mmol) in methanol (10.0 mL) at room temperature, aldehyde (1.0 equiv) was added dropwise (or portionwise if solid).[8k] After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by trituration.

2.4.3.2. Experimental Procedure for Preparation of *N*-2,4,6-Triisopropylbenzenesulfonyl Hydrazones

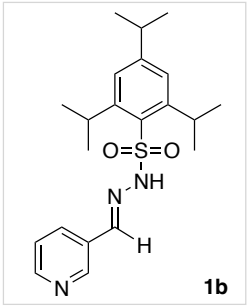
To a stirred solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (1.0 mmol) in THF (10.0 mL) at room temperature, aldehyde (1.0 equiv) was added dropwise (or portionwise if solid).[8k] After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by trituration.

2-Pyridinecarboxaldehyde tosylhydrazone (1a) Yield: 78%. R_f = 0.43 (1:3 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.5 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.84 (m, 3H), 7.71 (td, *J* = 7.7, 1.7 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.25 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.52, 149.37, 147.17, 144.54, 136.85, 135.47, 129.90, 128.07, 124.57, 120.83, 21.74. IR (neat, cm^{-1}): 3189.65, 1586.65, 1494.53, 1360.06, 1166.01, 1067.70, 941.03, 671.04. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{14}N_3O_2S^+$: 276.08012, Found: 276.08104.

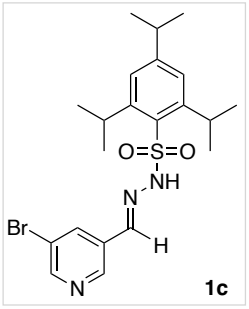


1a

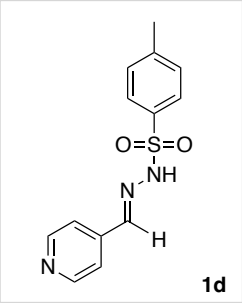
3-Pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1b) Yield: 82%. R_f = 0.50 (1:3 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.3 Hz, 1H), 8.57 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.10 (br, 1H), 7.93 – 7.90 (m, 1H), 7.77 (s, 1H), 7.30 – 7.26 (m, 1H), 7.19 (s, 2H), 4.25 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 7.0 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.85, 151.56, 150.91, 149.01, 142.63, 133.71, 131.25, 129.73, 124.10, 123.77, 34.33, 30.20, 25.01, 23.65. IR (neat, cm^{-1}): 3172.82, 2958.71, 1600.00, 1462.37, 1318.69, 1165.36, 944.50, 673.65. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{30}N_3O_2S^+$: 388.20532, Found: 388.20490.



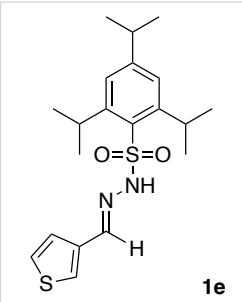
5-Bromo-3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1c) Yield: 68%. R_f = 0.32 (2:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.2 Hz, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 8.14 (s, 1H), 8.11 – 8.10 (m, 1H), 7.71 (s, 1H), 7.20 (s, 2H), 4.23 (hept, *J* = 6.8 Hz, 2H), 2.93 – 2.89 (m, 1H), 1.32 (d, *J* = 6.7 Hz, 12H), 1.26 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.13, 151.67, 151.46, 146.55, 140.41, 136.26, 131.36, 130.99, 124.21, 121.34, 34.36, 30.30, 25.02, 23.65. IR (neat, cm^{-1}): 3168.68, 2952.85, 1602.02, 1460.03, 1321.22, 1166.46, 1054.56, 964.21. 868.25. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{29}N_3O_2SBr^+$: 466.11584, Found: 466.11543.



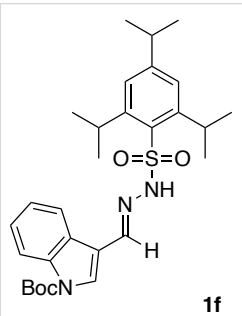
4-Pyridinecarboxaldehyde tosylhydrazone (1d) Yield: 72%. R_f = 0.23 (1:3 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 6.1 Hz, 2H), 8.08 (br, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.44 (d, *J* = 6.1 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 150.33, 144.43, 143.91, 140.92, 136.00, 129.92, 127.33, 120.80, 21.12. IR (neat, cm^{-1}): 3032.92, 1595.62, 1484.90, 1372.66, 1168.01, 1075.72, 941.71, 816.12. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{14}N_3O_2S^+$: 276.08012, Found: 276.07983.



3-Thiophenecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1e) Yield: 83%. R_f = 0.41 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.81 (m, 2H), 7.42 (s, 1H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.26 (d, *J* = 5.3 Hz, 1H), 7.18 (s, 2H), 4.26 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 7.9 Hz, 12H), 1.25 (d, *J* = 8.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.64, 151.52, 141.98, 136.67, 131.35, 127.35, 126.74, 125.30, 124.04, 34.33, 30.19, 25.02, 23.67. IR (neat, cm^{-1}): 3172.18, 2951.18, 1600.04, 1456.70, 1315.85, 1165.34, 1035.93, 788.04. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{29}N_2O_2S_2^+$: 393.16650, Found: 393.16684.

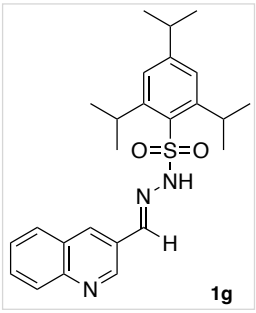


***N*-Boc-1*H*-indole-3-carboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1f)** Yield: 76%. R_f = 0.45 (2:1 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.95 (s, 1H), 7.72 (s, 1H), 7.33 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.22 – 7.17 (m, 3H), 4.32 (hept, *J* = 6.7 Hz, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.66 (s, 9H), 1.33 (d, *J* = 6.7 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR



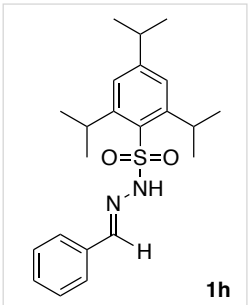
(125 MHz, $CDCl_3$) δ 153.64, 151.45, 149.25, 141.59, 135.99, 131.30, 128.78, 126.89, 125.61, 124.00, 123.62, 122.95, 116.12, 115.03, 84.70, 34.35, 30.20, 28.27, 25.10, 23.67. IR (neat, cm^{-1}): 3210.74, 2961.08, 1737.56, 1370.03, 1150.43, 1095.34, 909.03, 694.54. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{29}H_{40}N_3O_4S^+$: 526.27340, Found: 526.27256.

3-Quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1g) Yield:



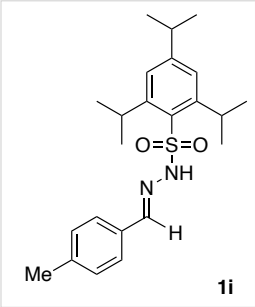
71%. R_f = 0.52 (1:1 Hexanes/EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.1 Hz, 1H), 8.21 (s, 1H), 8.15 (br, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.60 – 7.52 (m, 1H), 7.21 (s, 2H), 4.30 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 7.0 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.87, 151.62, 148.51, 148.31, 143.25, 135.05, 131.26, 130.70, 129.30, 128.34, 127.57, 127.55, 126.86, 124.13, 34.33, 30.26, 25.07, 23.64. IR (neat, cm^{-1}): 3189.20, 2959.43, 1620.26, 1462.31, 1314.83, 1165.48, 940.50, 882.11. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{32}N_3O_2S^+$: 438.22097, Found: 438.22048.

Benzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1h) Yield: 79%. R_f = 0.42



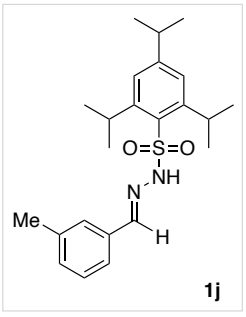
(3:1 Hexanes/EtOAc). ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.76 (s, 1H), 7.57 – 7.53 (m, 2H), 7.36 – 7.30 (m, 3H), 7.18 (s, 2H), 4.29 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 7.0 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.64, 151.54, 146.47, 133.49, 131.39, 130.39, 128.73, 127.43, 124.04, 34.33, 30.22, 25.02, 23.67. IR (neat, cm^{-1}): 3184.35, 2961.81, 1601.24, 1442.75, 1375.14, 1167.70, 1036.03, 953.32.

4-Methylbenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1i) Yield: 63%.



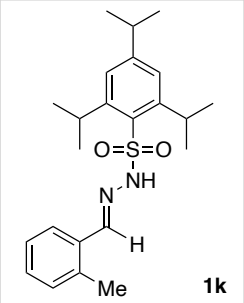
R_f = 0.40 (3:1 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.74 (s, 1H), 7.47 – 7.41 (m, 2H), 7.18 (s, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.29 (hept, *J* = 6.7 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 2.34 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.54, 151.51, 146.76, 140.70, 131.47, 130.80, 129.43, 127.39, 123.99, 34.30, 30.19, 25.00, 23.65, 21.56. IR (neat, cm^{-1}): 3180.13, 2958.55, 1601.72, 1451.06, 1376.12, 1322.84, 1166.29, 1036.59, 965.47. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{33}N_2O_2S^+$: 401.22573, Found: 401.22592.

3-Methylbenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1j) Yield: 76%.



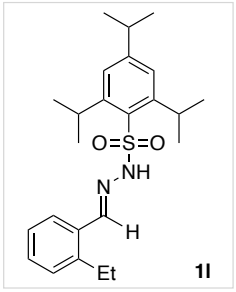
R_f = 0.50 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.71 (s, 1H), 7.43 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.18 – 7.15 (m, 3H), 4.28 (hept, *J* = 6.8 Hz, 2H), 2.89 (hept, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.62, 151.56, 146.68, 138.50, 133.38, 131.46, 131.28, 128.63, 127.74, 124.95, 124.04, 34.34, 30.24, 25.03, 23.67, 21.34. IR (neat, cm^{-1}): 3174.70, 2956.20, 1599.97, 1432.69, 1301.83, 1152.29, 1035.53, 900.84. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{33}N_2O_2S^+$: 401.22573, Found: 401.22521.

2-Methylbenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1k) Yield: 79%.

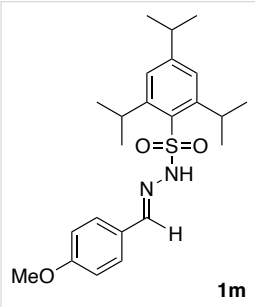


R_f = 0.45 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.10 (m, 4H), 4.27 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.63, 151.50, 145.40, 137.01, 131.53, 131.38, 130.96, 130.08, 127.28, 126.19, 124.00, 34.34, 30.21, 25.01, 23.68, 19.78. IR (neat, cm^{-1}): 3165.07, 2957.59, 1598.55, 1422.18, 1294.00, 1151.53, 1034.42, 927.28. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{33}N_2O_2S^+$: 401.22573, Found: 401.22674.

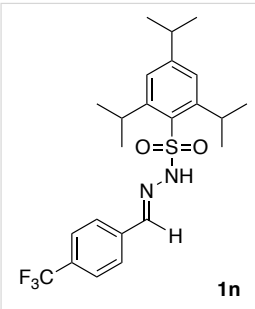
2-Ethylbenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1l) Yield: 71%. R_f = 0.58 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.98 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.18 – 7.09 (m, 4H), 4.25 (hept, *J* = 7.0 Hz, 2H), 2.88 (hept, *J* = 6.9 Hz, 1H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 12H), 1.23 (d, *J* = 8.5 Hz, 6H), 1.09 (t, *J* = 8.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.63, 151.47, 145.06, 143.20, 131.38, 130.76, 130.36, 129.35, 127.26, 126.24, 124.01, 34.34, 30.19, 26.08, 24.99, 23.67, 15.98. IR (neat, cm^{-1}): 3208.30, 2960.31, 1599.28, 1426.46, 1320.70, 1152.03, 1036.88, 943.17. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{35}N_2O_2S^+$: 415.24138, Found: 415.24276.



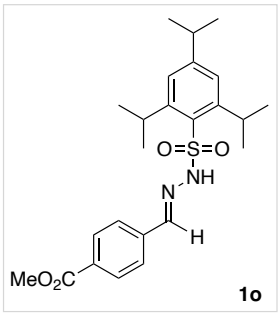
4-Methoxybenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1m) Yield: 83%. R_f = 0.35 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (br, 1H), 7.72 (s, 1H), 7.52 – 7.47 (m, 2H), 7.18 (s, 2H), 6.88 – 6.81 (m, 2H), 4.28 (hept, *J* = 6.8 Hz, 2H), 3.80 (s, 3H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.46, 153.52, 151.50, 146.76, 131.51, 129.01, 126.25, 124.00, 114.19, 55.49, 34.32, 30.20, 25.03, 23.67. IR (neat, cm^{-1}): 3198.45, 2959.56, 1605.94, 1514.36, 1300.45, 1253.45, 1165.49, 1035.04, 944.05. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{33}N_2O_3S^+$: 417.22064, Found: 417.22008.



4-(Trifluoromethyl)benzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1n) Yield: 89%. R_f = 0.31 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (br, 1H), 7.78 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 2H), 4.26 (hept, *J* = 6.9 Hz, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.95, 151.60, 144.23, 136.86, 131.89 (q, *J* = 34.0 Hz), 131.16, 127.50, 126.12 (q, *J* = 273.4 Hz), 125.73 (q, *J* = 3.8 Hz), 124.14, 34.35, 30.26, 25.01, 23.66. ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.91. IR (neat, cm^{-1}): 3450.22, 3176.27, 2960.65, 1457.91, 1324.32, 1275.41, 1163.74, 1128.97, 1066.13. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{30}N_2O_2F_3S^+$: 455.19746, Found: 455.19733.

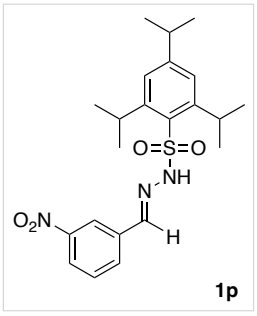


4-(Methoxycarbonyl)benzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1o)

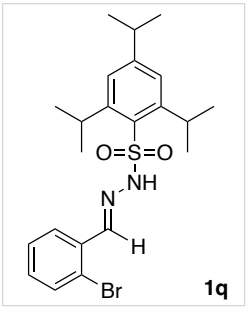


Yield: 73%. R_f = 0.52 (2:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.77 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 2H), 4.26 (hept, *J* = 6.8 Hz, 2H), 3.91 (s, 3H), 2.90 (hept, *J* = 6.6 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.62, 153.88, 151.59, 144.72, 137.60, 131.47, 131.23, 130.00, 127.20, 124.12, 52.42, 34.34, 30.26, 25.02, 23.66. IR (neat, cm^{-1}): 3178.94, 2959.44, 1723.13, 1602.35, 1277.52, 1168.72, 1055.95, 946.47. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{33}N_2O_4S^+$: 445.21555, Found: 445.21508.

3-Nitrobenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1p) Yield: 68%. R_f = 0.44 (2:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.21 – 8.16 (m, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.82 (s, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.21 (s, 2H), 4.27 (hept, *J* = 6.8 Hz, 2H), 2.91 (hept, *J* = 7.1 Hz, 1H), 1.33 (d, *J* = 6.5 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.85, 150.46, 148.13, 142.34, 135.69, 133.13, 132.34, 130.37, 123.94, 123.66, 120.05, 33.34, 29.23, 24.67, 23.33. IR (neat, cm^{-1}): 3170.57, 2960.81, 1600.68, 1533.84, 1345.34, 1294.55, 1150.78, 1036.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{30}N_3O_4S^+$: 432.19515, Found: 432.19583.

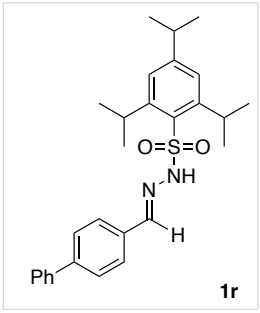


2-Bromobenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1q) Yield: 79%.



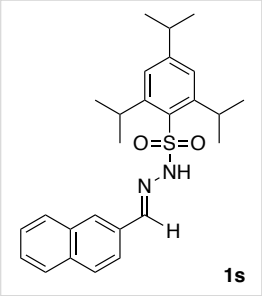
R_f = 0.56 (5:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.16 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.16 (m, 3H), 4.28 (hept, *J* = 6.7 Hz, 2H), 2.91 (hept, *J* = 7.0 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.73, 151.54, 144.96, 133.11, 132.49, 131.42, 131.34, 127.90, 127.56, 124.10, 124.06, 34.33, 30.24, 25.01, 23.66. IR (neat, cm^{-1}): 3188.79, 2958.28, 1598.44, 1426.49, 1323.03, 1165.31, 1037.35, 931.68. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{30}N_2O_2SBr^+$: 465.12059, Found: 465.11968.

4-Phenylbenzaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1r) Yield: 74%.



R_f = 0.48 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.79 (s, 1H), 7.64 – 7.61 (m, 2H), 7.59 – 7.56 (m, 4H), 7.45 – 7.41 (m, 2H), 7.38 – 7.33 (m, 1H), 7.19 (s, 2H), 4.30 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.67, 151.54, 146.12, 143.17, 140.32, 132.42, 131.41, 129.01, 127.94, 127.88, 127.42, 127.18, 124.06, 34.34, 30.24, 25.04, 23.68. IR (neat, cm^{-1}): 3185.70, 2960.10, 1602.06, 1376.42, 1321.51, 1168.65, 1052.42, 1036.60, 943.11. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{35}N_2O_2S^+$: 463.24138, Found: 463.23993.

2-Naphthaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1s) Yield: 73%. R_f = 0.42 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.91 (s, 1H), 7.85 (s, 1H), 7.84 – 7.75 (m, 4H), 7.51 – 7.46 (m, 2H), 7.20 (s, 2H), 4.33 (hept, *J* = 6.8 Hz, 2H), 2.90 (hept, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.68, 151.57, 146.61, 134.41, 133.11, 131.45, 131.21, 129.01, 128.61, 128.46, 127.99, 127.30, 126.78, 124.07, 123.12, 34.33, 30.28, 25.07, 23.67. IR (neat, cm^{-1}): 3177.75, 2956.13, 1601.90, 1378.37, 1317.63, 1167.14, 1037.27, 954.15. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{33}N_2O_2S^+$: 437.22573, Found: 437.22626.

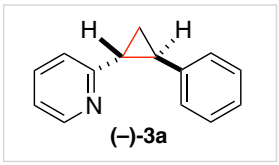


2.4.4. Synthesis and Characterization of Aryl- and Heteroaryl Cyclopropanes

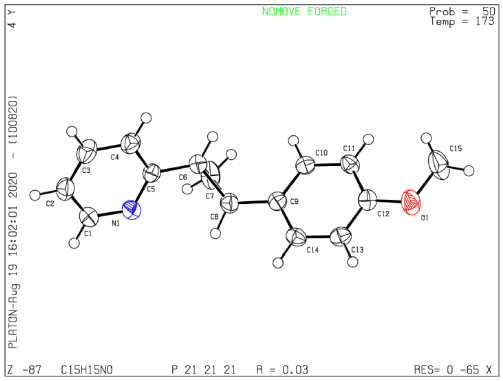
2.4.4.1. Experimental Procedure for [Co(Por)]-Catalyzed Asymmetric Cyclopropanation

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol, 1.0 equiv), [Co(Por)] (2 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, olefin (1.5–10.0 equiv) and anhydrous toluene (1.0 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22–80 °C for 16 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum and purified by flash column chromatography.

2-((1*R*,2*R*)-2-Phenylcyclopropyl)pyridine (3a) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 99%. dr: 96:4. R_f = 0.34 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-355.7° (*c* = 2.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.0 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 – 7.15 (m, 4H), 7.07 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 2.54 (ddd, *J* = 8.9, 6.1, 4.2 Hz, 1H), 2.29 (ddd, *J* = 8.6, 5.6, 4.2 Hz, 1H), 1.79 (ddd, *J* = 8.8, 5.6, 4.5 Hz, 1H), 1.48 (ddd, *J* = 8.5, 6.1, 4.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.24, 149.55, 142.43, 135.98, 128.50, 126.02, 125.94, 122.13, 120.75, 29.52, 28.25, 19.06. IR (neat, cm^{-1}): 1595.08, 1567.49, 1473.29, 1442.90, 1207.26, 745.52, 697.05. HPLC analysis (*E*)-isomer: ee = 99%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 8.15 min, t_{minor} = 6.94 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{14}N^+$: 196.11208, Found: 196.11143.

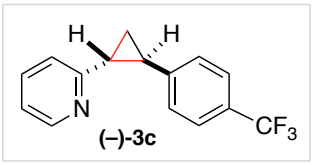


2-((1*R*,2*R*)-2-(4-Methoxyphenyl)cyclopropyl)pyridine (3b) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 98%. dr: 95:5. R_f = 0.30 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-392.7° (*c* = 2.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.1 Hz, 1H), 7.54 (td, *J* = 7.6, 1.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.93 – 6.75 (m, 2H), 3.79 (s, 3H), 2.49 (ddd, *J* = 9.0, 6.1, 4.2 Hz, 1H), 2.20 (ddd, *J* = 8.5, 5.4, 4.2 Hz, 1H), 1.72 (ddd, *J* = 8.9, 5.5, 4.5 Hz, 1H), 1.41 (ddd, *J* = 8.6, 6.1, 4.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.46,



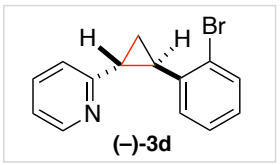
158.04, 149.52, 135.95, 134.42, 127.14, 122.04, 120.65, 113.99, 55.47, 29.12, 27.61, 18.70. IR (neat, cm^{-1}): 1594.80, 1514.56, 1473.47, 1246.04, 1035.94, 905.42, 823.41, 745.89. HPLC analysis (*E*)-isomer: ee = 99%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 13.88 min, t_{minor} = 11.39 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{16}NO^+$: 226.12264, Found: 226.12349. The absolute configuration of the major (*E*)-isomer was assigned as (1*R*,2*R*) by X-ray crystallography.

2-((1*R*,2*R*)-2-(4-(Trifluoromethyl)phenyl)cyclopropyl)pyridine (3c) was obtained



through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 95%. dr: 94:6. R_f = 0.43 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-322.8° (*c* = 2.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.6 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.08 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 2.60 (ddd, *J* = 9.6, 5.8, 4.2 Hz, 1H), 2.31 (ddd, *J* = 9.5, 4.9, 3.7 Hz, 1H), 1.86 – 1.83 (m, 1H), 1.53 – 1.46 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.49, 149.65, 146.75, 136.11, 128.16 (q, *J* = 32.4 Hz), 126.22, 125.43 (q, *J* = 3.9 Hz), 124.49 (q, *J* = 271.5 Hz), 122.25, 121.05, 30.00, 27.85, 19.42. ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.30 (s, 3F). IR (neat, cm^{-1}): 1618.51, 1592.84, 1474.04, 1323.46, 1162.73, 1067.82, 906.69, 825.82, 745.93. HPLC analysis (*E*)-isomer: ee = 99%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 6.32 min, t_{minor} = 5.64 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{13}NF_3^+$: 264.09946, Found: 264.09941.

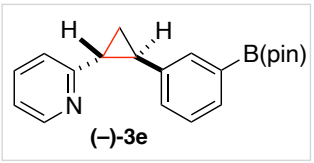
2-((1*R*,2*R*)-2-(2-Bromophenyl)cyclopropyl)pyridine (3d) was obtained through the



general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield:

97%. dr: 90:10. R_f = 0.52 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-122.7° (*c* = 1.9, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 3.5 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.30 – 7.23 (m, 2H), 7.14 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.10 – 7.06 (m, 2H), 2.76 (ddd, *J* = 8.8, 6.2, 4.6 Hz, 1H), 2.20 (ddd, *J* = 8.5, 5.4, 4.5 Hz, 1H), 1.81 (ddd, *J* = 8.8, 5.5, 4.6 Hz, 1H), 1.48 (ddd, *J* = 8.6, 6.3, 4.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.09, 149.50, 141.34, 135.97, 132.63, 127.68, 127.51, 127.43, 126.45, 122.18, 120.84, 28.88, 28.27, 17.36. IR (neat, cm^{-1}): 1587.49, 1473.06, 1270.11, 1148.66, 1023.52, 907.20, 794.01, 743.88. HPLC analysis (*E*)-isomer: ee = 97%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 7.57 min, t_{minor} = 6.96 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{13}NBr^+$: 274.02259, Found: 274.02201.

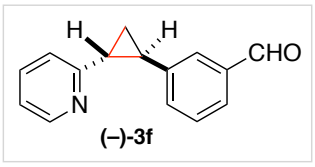
2-((1*R*,2*R*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropyl)pyridine (3e) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 90%. dr: 93:7. R_f = 0.41 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-250.0° (*c* = 1.7, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 6.9 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.61 (s, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.05 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 2.55 (ddd, *J* = 9.0, 6.1, 4.2 Hz, 1H), 2.29 (ddd, *J* = 8.6, 5.5, 4.2 Hz, 1H), 1.79 – 1.73 (m, 1H), 1.53 (ddd, *J* = 8.6, 6.1, 4.5 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.35, 149.52, 141.62, 135.94, 132.43, 132.28, 129.20, 127.91, 122.10, 120.69, 83.91, 29.52, 28.30, 25.01, 18.73. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.24. IR (neat, cm^{-1}): 2977.20, 1587.80, 1473.44, 1355.23, 1143.53, 964.23, 845.56, 707.17, 679.34. HPLC analysis (*E*)-isomer: ee = 97%. IC (95% hexanes: 5% isopropanol, 0.8



(–)-3e

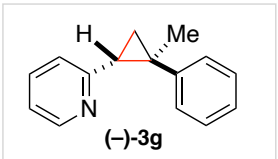
mL/min): t_{major} = 7.22 min, t_{minor} = 6.78 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{25}BNO_2^+$: 322.19729, Found: 322.19686.

3-((1*R*,2*R*)-2-(Pyridin-2-yl)cyclopropyl)benzaldehyde (3f) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 87%. dr: 94:6. R_f = 0.33 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-349.5° (*c* = 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.50 (d, *J* = 6.7 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.65 (s, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 (d, *J* = 5.9 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.09 (dd, *J* = 7.5, 4.8 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.34 (ddd, *J* = 9.2, 5.6, 4.3 Hz, 1H), 1.85 – 1.82 (m, 1H), 1.52 (ddd, *J* = 8.7, 6.0, 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.56, 160.57, 149.46, 143.69, 136.72, 136.27, 132.65, 129.14, 127.84, 126.50, 122.25, 121.05, 29.59, 27.72, 19.23. IR (neat, cm^{-1}): 3005.00, 1697.11, 1587.92, 1473.88, 1437.79, 1213.25, 1148.71, 785.45, 690.37. HPLC analysis (*E*)-isomer: ee = 96%. ID (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 15.18 min, t_{minor} = 12.97 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{14}NO^+$: 224.10699, Found: 224.10687.



(–)-3f

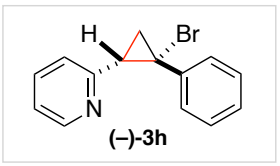
2-((1*R*,2*R*)-2-Methyl-2-phenylcyclopropyl)pyridine (3g) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 82%. dr: 98:2. R_f = 0.45 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-242.0° (*c* = 1.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.3 Hz, 1H), 7.60 (td, *J* = 7.7, 1.9 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 7.24 – 7.19 (m, 1H), 7.11 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 2.51 (dd, *J* = 8.6, 6.3 Hz, 1H), 1.74 (dd, *J* = 6.3, 4.9 Hz, 1H), 1.53



(–)-3g

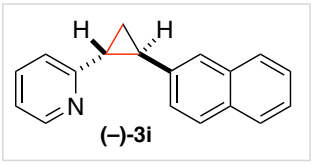
(dd, J = 8.7, 4.9 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.23, 149.06, 147.69, 135.82, 128.48, 127.03, 125.98, 124.40, 120.88, 33.28, 29.17, 19.73, 19.00. IR (neat, cm^{-1}): 3005.53, 1589.02, 1495.62, 1118.95, 1030.52, 876.82, 765.55, 698.79. HPLC analysis (*E*)-isomer: ee = 98%. IC (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 6.87 min, t_{minor} = 7.31 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{16}N^+$: 210.12773, Found: 210.12697.

2-((1*S*,2*S*)-2-Bromo-2-phenylcyclopropyl)pyridine (3h) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 86%. dr: 99:1. R_f = 0.36 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-115.5° (c = 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 7.3 Hz, 1H), 7.71 (td, J = 7.7, 1.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.43 – 7.33 (m, 3H), 7.33 – 7.27 (m, 1H), 7.22 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H), 2.73 (dd, J = 9.7, 7.6 Hz, 1H), 2.29 (dd, J = 7.5, 6.7 Hz, 1H), 1.95 (dd, J = 9.7, 6.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.24, 149.19, 144.22, 136.17, 128.80, 128.74, 128.26, 124.18, 122.08, 41.33, 32.63, 20.85. IR (neat, cm^{-1}): 3058.53, 1591.26, 1494.96, 1149.08, 1038.78, 954.47, 741.78, 696.26. HPLC analysis (*Z*)-isomer: ee = 97%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 16.21 min, t_{minor} = 8.98 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{13}NBr^+$: 274.02259, Found: 274.02183.



(–)-3h

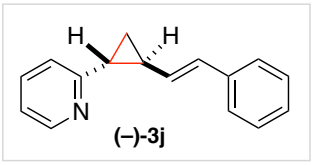
2-((1*R*,2*R*)-2-(Naphthalen-2-yl)cyclopropyl)pyridine (3i) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 90%. dr: 95:5. R_f = 0.31 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-466.0° (c = 1.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 4.2 Hz, 1H), 7.84 –



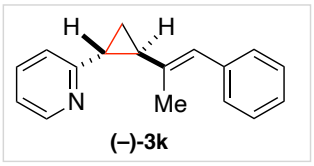
(–)-3i

7.72 (m, 3H), 7.62 (s, 1H), 7.56 (td, J = 7.6, 1.8 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.29 (dd, J = 8.3, 1.6 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.08 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 2.71 (ddd, J = 8.9, 6.1, 4.2 Hz, 1H), 2.39 (ddd, J = 8.6, 5.5, 4.2 Hz, 1H), 1.85 (ddd, J = 8.8, 5.6, 4.6 Hz, 1H), 1.60 (ddd, J = 8.5, 6.1, 4.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.22, 149.61, 139.90, 136.03, 133.66, 132.20, 128.13, 127.76, 127.48, 126.24, 125.25, 124.89, 124.27, 122.19, 120.81, 29.58, 28.52, 19.01. IR (neat, cm^{-1}): 3052.65, 1593.09, 1473.31, 1269.73, 1148.24, 990.13, 814.59, 769.19. HPLC analysis (*E*)-isomer: ee = 98%. IA (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 11.56 min, t_{minor} = 8.18 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}N^+$: 246.12773, Found: 246.12781.

2-((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)pyridine (3j) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 93%. dr: 96:4. R_f = 0.45 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-477.7° (*c* = 2.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, J = 5.8 Hz, 1H), 7.54 (td, J = 7.6, 2.3 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.21 – 7.16 (m, 2H), 7.07 – 7.03 (m, 1H), 6.53 (d, J = 15.7 Hz, 1H), 5.94 (dd, J = 15.7, 8.8 Hz, 1H), 2.23 – 2.14 (m, 2H), 1.65 (ddd, J = 8.5, 5.6, 4.4 Hz, 1H), 1.25 (ddd, J = 8.5, 5.8, 4.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.06, 149.51, 137.63, 135.96, 132.59, 128.88, 128.64, 126.94, 125.84, 122.02, 120.69, 27.69, 27.33, 17.77. IR (neat, cm^{-1}): 3023.41, 1591.42, 1473.47, 1242.33, 1148.60, 957.85, 765.10, 692.81. HPLC analysis (*E*)-isomer: ee = 98%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 9.82 min, t_{minor} = 8.54 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{16}N^+$: 222.12773, Found: 222.12748.

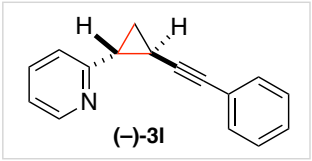


2-((1*R*,2*R*)-2-((*E*)-1-Phenylprop-1-en-2-yl)cyclopropyl)pyridine (3k) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 98%. dr: 99:1. R_f = 0.52 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-284.7° (*c* = 2.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.2 Hz, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 2H), 7.06 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.43 (s, 1H), 2.26 – 2.20 (m, 2H), 1.85 (s, 3H), 1.51 (ddd, *J* = 8.6, 5.6, 4.5 Hz, 1H), 1.39 (ddd, *J* = 8.3, 6.5, 4.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.76, 149.50, 138.41, 138.01, 135.97, 128.98, 128.18, 126.05, 124.63, 121.83, 120.64, 32.82, 25.32, 15.90, 15.74. IR (neat, cm^{-1}): 2918.57, 1588.00, 1473.50, 1211.59, 1148.50, 918.63, 743.14, 698.42. HPLC analysis (*E*)-isomer: ee = 93%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 8.06 min, t_{minor} = 6.17 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{18}N^+$: 236.14338, Found: 236.14311.



(–)-3k

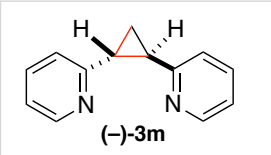
2-((1*R*,2*R*)-2-(Phenylethynyl)cyclopropyl)pyridine (3l) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 98%. dr: 99:1. R_f = 0.53 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-424.5° (*c* = 2.3, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.32 – 7.21 (m, 4H), 7.07 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 2.43 (ddd, *J* = 8.5, 5.7, 4.2 Hz, 1H), 2.11 (ddd, *J* = 8.8, 5.9, 4.2 Hz, 1H), 1.67 (ddd, *J* = 8.8, 5.8, 4.0 Hz, 1H), 1.43 (ddd, *J* = 8.5, 5.9, 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.51, 149.54, 136.03, 131.78, 128.33, 127.75, 123.83, 122.57, 121.17, 91.98, 77.12, 27.86, 18.87, 12.51. IR (neat, cm^{-1}): 2226.07, 1588.89, 1473.99, 1210.20, 1148.93,



(–)-3l

952.80, 854.76, 755.45, 690.95. HPLC analysis (*E*)-isomer: ee = 98%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 7.58 min, t_{minor} = 7.13 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{14}N^+$: 220.11208, Found: 220.11143.

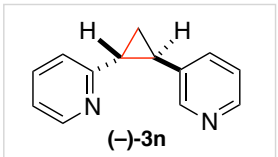
(1*R*,2*R*)-1,2-Di(pyridin-2-yl)cyclopropane (3m) was obtained through the general



(–)-3m

procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 92%. dr: 95:5. R_f = 0.32 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-452.0° (*c* = 0.7, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.8 Hz, 2H), 7.54 (td, *J* = 7.6, 1.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.06 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H), 2.68 – 2.61 (m, 2H), 1.80 – 1.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.12, 149.52, 135.98, 122.56, 120.83, 29.39, 19.67. IR (neat, cm^{-1}): 1590.15, 1448.89, 1434.78, 1334.78, 1200.03, 1149.00, 909.01, 799.87. HPLC analysis (*E*)-isomer: ee = 99%. AD-H (70% hexanes: 30% isopropanol, 0.8 mL/min): t_{major} = 7.03 min, t_{minor} = 5.64 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{13}N_2^+$: 197.10732, Found: 197.10720.

2-((1*R*,2*R*)-2-(Pyridin-3-yl)cyclopropyl)pyridine (3n) was obtained through the general

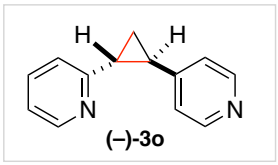


(–)-3n

procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 86%. dr: 98:2. R_f = 0.30 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-368.6° (*c* = 0.9, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 – 8.37 (m, 3H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.19 (m, 2H), 7.07 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.54 (ddd, *J* = 9.7, 6.1, 4.2 Hz, 1H), 2.34 – 2.23 (m, 1H), 1.82 – 1.79 (m, 1H), 1.46 (ddd, *J* = 8.6, 6.0, 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.48, 149.65, 148.53, 147.38, 137.87, 136.12, 132.97, 123.37, 122.20, 121.06, 29.17, 25.43, 18.72. IR (neat, cm^{-1}):

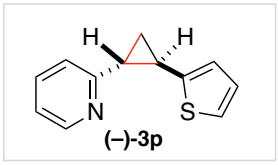
1588.00, 1473.87, 1431.53, 1212.60, 1046.43, 904.82, 804.72, 712.35. HPLC analysis (*E*)-isomer: ee = 99%. OD-H (70% hexanes: 30% isopropanol, 0.8 mL/min): t_{major} = 8.43 min, t_{minor} = 7.56 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{13}N_2^+$: 197.10732, Found: 197.10836.

2-((1*R*,2*R*)-2-(Pyridin-4-yl)cyclopropyl)pyridine (3o) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 94%. dr: 95:5. R_f = 0.34 (EtOAc only). $[\alpha]_D^{20}$ = (–)-377.6° (*c* = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 3.3 Hz, 1H), 8.46 (d, *J* = 6.2 Hz, 2H), 7.56 (td, *J* = 7.6, 1.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 7.5, 4.9 Hz, 1H), 7.04 (d, *J* = 6.2 Hz, 2H), 2.50 (ddd, *J* = 9.3, 5.9, 4.2 Hz, 1H), 2.34 (ddd, *J* = 9.4, 5.7, 4.1 Hz, 1H), 1.89 – 1.85 (m, 1H), 1.55 – 1.46 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.02, 151.89, 149.74, 149.67, 136.15, 122.32, 121.20, 121.13, 30.26, 27.19, 19.65. IR (neat, cm^{-1}): 1599.23, 1473.72, 1429.94, 1204.91, 1049.42, 908.49, 813.37, 758.28. HPLC analysis (*E*)-isomer: ee = 99%. AD-H (70% hexanes: 30% isopropanol, 0.8 mL/min): t_{major} = 11.33 min, t_{minor} = 7.91 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{13}N_2^+$: 197.10732, Found: 197.10702.



(–)-3o

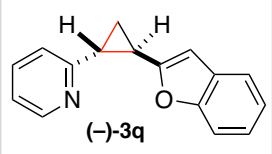
2-((1*R*,2*R*)-2-(Thiophen-2-yl)cyclopropyl)pyridine (3p) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 97%. dr: 96:4. R_f = 0.48 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-351.4° (*c* = 1.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.5 Hz, 1H), 7.55 (td, *J* = 7.6, 1.9 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H),



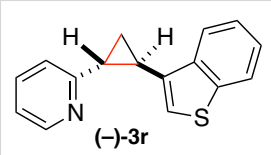
(–)-3p

6.85 (d, J = 3.5 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.31 (ddd, J = 8.6, 5.6, 4.2 Hz, 1H), 1.80 (ddd, J = 8.8, 5.6, 4.5 Hz, 1H), 1.47 (ddd, J = 8.6, 6.0, 4.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.56, 149.56, 146.91, 136.02, 126.99, 123.06, 122.39, 122.28, 120.90, 30.20, 23.50, 20.01. IR (neat, cm^{-1}): 3006.31, 1590.29, 1473.22, 1440.26, 1214.88, 1148.74, 848.51, 691.90. HPLC analysis (*E*)-isomer: ee = 98%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 6.75 min, t_{minor} = 6.15 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{12}H_{12}NS^+$: 202.06850, Found: 202.06905.

2-((1*R*,2*R*)-2-(Benzofuran-2-yl)cyclopropyl)pyridine (3q) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 96%. dr: 99:1. R_f = 0.50 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-493.2° (*c* = 2.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 4.4 Hz, 1H), 7.56 (td, J = 7.6, 1.8 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.27 – 7.16 (m, 3H), 7.08 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 6.46 (s, 1H), 2.70 (ddd, J = 9.0, 6.1, 4.2 Hz, 1H), 2.58 (ddd, J = 8.7, 5.7, 4.3 Hz, 1H), 1.81 (ddd, J = 9.0, 5.7, 4.2 Hz, 1H), 1.71 (ddd, J = 8.7, 6.0, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.07, 158.65, 154.39, 149.62, 136.07, 129.21, 123.24, 122.72, 122.52, 121.06, 120.16, 110.78, 101.34, 27.23, 21.62, 17.01. IR (neat, cm^{-1}): 1592.79, 1473.63, 1453.51, 1251.80, 1168.18, 948.66, 747.00, 670.27. HPLC analysis (*E*)-isomer: ee = 99%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 7.48 min, t_{minor} = 6.76 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{14}NO^+$: 236.10699, Found: 236.10707.



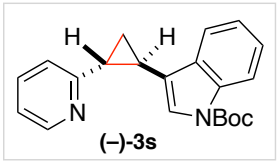
2-((1*R*,2*R*)-2-(Benzo[*b*]thiophen-3-yl)cyclopropyl)pyridine (3r) was obtained through



(–)-3r

the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 96%. dr: 75:25. R_f = 0.47 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-165.6° (*c* = 1.8, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.58 (td, *J* = 7.6, 1.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.11 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.08 (s, 1H), 2.78 – 2.73 (m, 1H), 2.29 – 2.23 (m, 1H), 1.79 (ddd, *J* = 9.0, 5.3, 4.3 Hz, 1H), 1.53 (ddd, *J* = 8.5, 6.2, 4.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.23, 149.64, 140.53, 139.79, 137.64, 136.12, 124.57, 124.13, 122.92, 122.28, 122.22, 120.89, 120.17, 26.96, 21.84, 16.94. IR (neat, cm^{-1}): 1591.23, 1472.90, 1426.70, 1351.16, 1048.29, 928.66, 761.24, 731.26. HPLC analysis (*E*)-isomer: ee = 98%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 8.40 min, t_{minor} = 6.67 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{14}NS^+$: 252.08415, Found 252.08426.

***tert*-Butyl 3-((1*R*,2*R*)-2-(pyridin-2-yl)cyclopropyl)-1*H*-indole-1-carboxylate (3s)** was

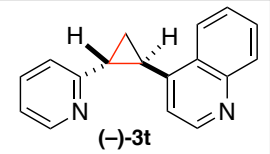


(–)-3s

obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 93%. dr: 95:5. R_f = 0.42 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-175.3° (*c* = 2.6, $CHCl_3$). ^{1}H NMR (600 MHz, CDC_3) δ 8.52 (d, *J* = 4.5 Hz, 1H), 8.12 (s, 1H), 7.61 – 7.55 (m, 2H), 7.39 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 7.09 (dd, *J* = 7.5, 4.8 Hz, 1H), 2.57 (ddd, *J* = 8.9, 6.7, 4.4 Hz, 1H), 2.30 – 2.25 (m, 1H), 1.74 (ddd, *J* = 9.1, 5.3, 4.2 Hz, 1H), 1.67 (s, 9H), 1.46 (ddd, *J* = 8.4, 6.1, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.37, 149.93, 149.57, 136.09, 131.09, 124.61, 122.60, 122.52, 122.13, 121.52, 120.81, 119.42, 115.38, 83.61, 28.38, 26.82, 18.92, 17.10. IR (neat, cm^{-1}): 1729.33, 1591.53,

1473.98, 1372.36, 1253.74, 1156.82, 1077.36, 744.41. HPLC analysis (*E*)-isomer: ee = 99%. OD-H (98% hexanes: 2% isopropanol, 0.5 mL/min): t_{major} = 13.56 min, t_{minor} = 12.77 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{23}N_2O_2^+$: 335.17540, Found: 335.17544.

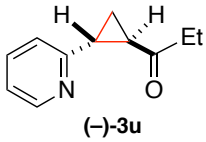
4-((1*R*,2*R*)-2-(Pyridin-2-yl)cyclopropyl)quinoline (3t) was obtained through the general



(–)-3t

procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 90%. dr: 85:15. R_f = 0.22 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-121.2° (*c* = 1.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.5 Hz, 1H), 8.57 (d, *J* = 4.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.70 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.51 (td, *J* = 7.0, 1.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.17 (d, *J* = 4.5 Hz, 1H), 7.14 (ddd, *J* = 7.5, 3.5, 2.4 Hz, 1H), 3.15 (ddd, *J* = 8.8, 6.2, 4.7 Hz, 1H), 2.36 – 2.29 (m, 1H), 1.92 (ddd, *J* = 10.0, 6.1, 3.9 Hz, 1H), 1.69 – 1.62 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.29, 150.24, 149.81, 148.59, 147.99, 136.28, 129.93, 129.45, 128.75, 126.66, 124.31, 122.52, 121.27, 117.39, 28.40, 24.19, 17.42. HPLC analysis (*E*)-isomer: ee = 98%. IC (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 20.97 min, t_{minor} = 17.35 min. IR (neat, cm^{-1}): 3005.23, 1587.98, 1567.02, 1473.25, 1428.53, 1211.04, 1149.37, 908.62, 760.17. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{15}N_2^+$: 247.12297, Found: 247.12285.

1-((1*R*,2*R*)-2-(Pyridin-2-yl)cyclopropyl)propan-1-one (3u) was obtained through the

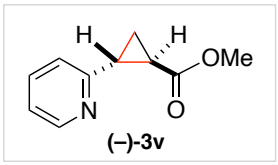


(–)-3u

general procedure using 3.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 94%. dr: 99:1. R_f = 0.32 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-378.6° (*c* = 0.8, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.7,

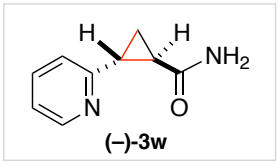
1.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.08 (ddd, J = 7.3, 4.8, 1.1 Hz, 1H), 2.71 – 2.53 (m, 4H), 1.64 – 1.59 (m, 2H), 1.09 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 209.95, 159.37, 149.49, 136.24, 122.74, 121.42, 37.31, 31.65, 29.39, 19.63, 8.01. IR (neat, cm^{-1}): 1698.77, 1593.43, 1392.77, 1120.21, 1031.18, 983.81, 889.73, 746.83. HPLC analysis (*E*)-isomer: ee = 98%. IF (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 10.67 min, t_{minor} = 9.89 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{11}H_{14}NO^+$: 176.10699, Found: 176.10595.

Methyl (1*R*,2*R*)-2-(pyridin-2-yl)cyclopropane-1-carboxylate (3v) was obtained through the general procedure using 3.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 91%. dr: 99:1. R_f = 0.30 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-312.4° (c = 1.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 6.6 Hz, 1H), 7.55 (td, J = 7.7, 1.8 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.08 (dd, J = 8.7, 4.8 Hz, 1H), 3.71 (s, 3H), 2.58 (ddd, J = 9.6, 6.1, 3.9 Hz, 1H), 2.26 (ddd, J = 9.0, 5.5, 3.9 Hz, 1H), 1.64 (ddd, J = 8.3, 6.1, 3.8 Hz, 1H), 1.59 (ddd, J = 9.2, 5.5, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.96, 158.89, 149.55, 136.15, 122.65, 121.45, 52.01, 27.40, 24.24, 17.43. IR (neat, cm^{-1}): 2951.64, 1724.32, 1594.50, 1475.14, 1435.87, 1334.28, 1200.40, 1169.81, 775.25. HPLC analysis (*E*)-isomer: ee = 95%. IE (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 13.58 min, t_{minor} = 15.45 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{10}H_{12}NO_2^+$: 178.08626, Found: 178.08713.



(–)-3v

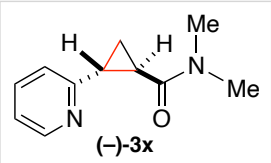
(1*R*,2*R*)-2-(Pyridin-2-yl)cyclopropane-1-carboxamide (3w) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield:



(–)-3w

70%. dr: 99:1. R_f = 0.28 (EtOAc only). $[\alpha]_D^{20}$ = (–)-246.0° (*c* = 1.0 , $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.8 Hz, 1H), 7.55 (ddd, *J* = 9.3, 6.9, 1.6 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.09 – 7.06 (m, 1H), 5.77 (d, *J* = 66.5 Hz, 2H), 2.57 (ddd, *J* = 9.5, 5.0, 3.4 Hz, 1H), 2.15 – 2.12 (m, 1H), 1.54 – 1.51 (m, 1H), 1.53 (ddd, *J* = 9.2, 5.7, 2.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.53, 159.49, 149.43, 136.24, 123.06, 121.38, 26.69, 25.50, 17.37. IR (neat, cm^{-1}): 338.142, 3198.69, 2921.27, 1644.94, 1431.26, 1365.07, 933.96, 772.19. HPLC analysis (*E*)-isomer: ee = 98%. ID (70% hexanes: 30% isopropanol, 0.8 mL/min): t_{major} = 10.63 min, t_{minor} = 8.49 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_9H_{11}N_2O^+$: 163.08659, Found: 163.08633.

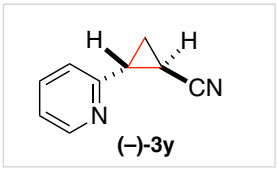
(1*R*,2*R*)-*N*,*N*-Dimethyl-2-(pyridin-2-yl)cyclopropane-1-carboxamide (3x) was



(–)-3x

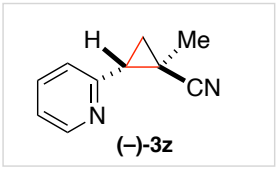
obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 95%. dr: 99:1. R_f = 0.27 (1:3 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-270.6° (*c* = 1.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.9 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.06 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.14 (s, 3H), 2.98 (s, 3H), 2.58 (ddd, *J* = 9.3, 5.8, 4.0 Hz, 1H), 2.45 (ddd, *J* = 8.2, 5.5, 4.0 Hz, 1H), 1.58 (ddd, *J* = 8.8, 5.5, 3.4 Hz, 1H), 1.52 (ddd, *J* = 8.8, 5.7, 3.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.12, 160.09, 149.48, 136.10, 122.99, 121.17, 37.49, 35.97, 26.58, 23.06, 17.59. IR (neat, cm^{-1}): 2926.78, 1636.03, 1592.86, 1495.69, 1373.06, 1263.96, 1139.35, 795.19. HPLC analysis (*E*)-isomer: ee = 99%. ID (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 33.05 min, t_{minor} = 15.83 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{11}H_{15}N_2O^+$: 191.11789, Found: 191.11757.

(1*R*,2*R*)-2-(Pyridin-2-yl)cyclopropane-1-carbonitrile (3y) was obtained through the general procedure using 3.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 94%. dr: 98:2. R_f = 0.33 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-277.1° (*c* = 0.9, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.0 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.11 (m, 1H), 2.63 (ddd, *J* = 8.9, 6.1, 4.3 Hz, 1H), 2.05 (ddd, *J* = 9.7, 5.8, 4.3 Hz, 1H), 1.71 (ddd, *J* = 9.0, 6.1, 4.6 Hz, 1H), 1.58 (ddd, *J* = 8.8, 5.9, 4.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.37, 149.76, 136.46, 123.09, 122.19, 121.27, 25.56, 16.52, 6.81. IR (neat, cm^{-1}): 2238.09, 1590.82, 1475.05, 1452.24, 1212.54, 1150.57, 941.64, 763.13. HPLC analysis (*E*)-isomer: ee = 97%. OD-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 13.27 min, t_{minor} = 11.21 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_9H_9N_2^+$: 145.07602, Found: 145.07647.



(–)-3y

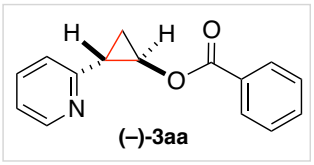
(1*R*,2*R*)-1-Methyl-2-(pyridin-2-yl)cyclopropane-1-carbonitrile (3z) was obtained through the general procedure using 3.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 91%. dr: 87:13. R_f = 0.26 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-283.3° (*c* = 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 3.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.16 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 2.83 (dd, *J* = 9.2, 7.0 Hz, 1H), 1.82 (dd, *J* = 7.1, 5.2 Hz, 1H), 1.67 (dd, *J* = 9.2, 5.3 Hz, 1H), 1.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.47, 149.13, 136.41, 125.35, 124.35, 122.22, 30.80, 18.40, 14.67, 12.33. IR (neat, cm^{-1}): 2232.26, 1590.85, 1474.90, 1446.52, 1150.77, 1086.40, 802.77, 756.34. HPLC analysis (*E*)-isomer: ee = 98%. OD-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 10.83 min, t_{minor} = 9.30 min. HRMS (DART) ($[M+H]^+$)



(–)-3z

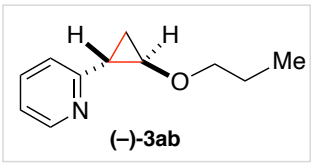
Calcd. for $C_{10}H_{11}N_2^+$: 159.09167, Found: 159.09178.

(1*R*,2*S*)-2-(Pyridin-2-yl)cyclopropyl benzoate (3aa) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 49%. dr: 92:8. R_f = 0.34 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-132.5° (*c* = 0.7, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.7 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.47 – 7.41 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.07 (m, 1H), 4.69 – 4.67 (m, 1H), 2.42 (ddd, *J* = 10.0, 6.9, 2.7 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.53 (ddd, *J* = 11.0, 6.5, 4.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.12, 159.16, 149.51, 136.12, 133.25, 129.97, 129.74, 128.52, 122.32, 121.17, 56.98, 24.81, 15.51. IR (neat, cm^{-1}): 1723.78, 1589.76, 1321.83, 1474.75, 1268.71, 1137.34, 1094.97, 709.61. HPLC analysis (*E*)-isomer: ee = 98%. IF (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 8.97 min, t_{minor} = 8.32 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{14}NO_2^+$: 240.10191, Found: 240.10166.



(–)-3aa

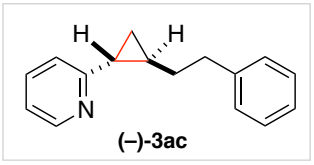
2-((1*S*,2*R*)-2-Propoxycyclopropyl)pyridine (3ab) was obtained through the general procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 55%. dr: 94:6. R_f = 0.42 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-77.1° (*c* = 0.8, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 6.0 Hz, 1H), 7.52 (td, *J* = 7.6, 1.8 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.02 (ddd, *J* = 7.3, 4.8, 1.1 Hz, 1H), 3.62 (ddd, *J* = 6.3, 3.8, 2.3 Hz, 1H), 3.51 (t, *J* = 6.7 Hz, 2H), 2.18 (ddd, *J* = 9.7, 6.0, 2.2 Hz, 1H), 1.63 – 1.57 (m, 2H), 1.39 – 1.33 (m, 1H), 1.31 (ddd, *J* = 9.5, 5.5, 3.8 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.79, 149.28, 135.92, 121.78, 120.55, 72.77, 62.13,



(–)-3ab

25.36, 22.93, 17.02, 10.72. IR (neat, cm^{-1}): 2962.34, 2924.53, 1589.74, 1474.29, 1450.77, 1376.03, 1169.24, 1084.12. HPLC analysis (*E*)-isomer: ee = 91%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 6.47 min, t_{minor} = 5.73 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{11}H_{16}NO^+$: 178.12264, Found: 178.12218.

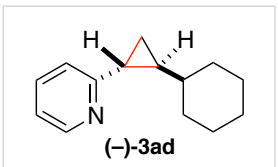
2-((1*R*,2*R*)-2-Phenethylcyclopropyl)pyridine (3ac) was obtained through the general



(–)-3ac

procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 55%. dr: 88:12. R_f = 0.45 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-45.4° (*c* = 0.9, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 6.9 Hz, 1H), 7.50 (td, *J* = 7.6, 1.8 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.19 – 7.14 (m, 3H), 7.04 – 6.97 (m, 2H), 2.81 – 2.71 (m, 2H), 1.80 – 1.66 (m, 3H), 1.45 – 1.37 (m, 1H), 1.23 – 1.20 (m, 1H), 0.82 (ddd, *J* = 8.4, 5.8, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.73, 149.26, 142.41, 135.82, 128.59, 128.38, 125.79, 121.31, 120.30, 36.19, 35.88, 25.15, 24.12, 16.92. IR (neat, cm^{-1}): 3024.45, 2921.01, 2853.10, 1588.98, 1474.17, 1148.26, 744.79, 698.73. HPLC analysis (*E*)-isomer: ee = 49%. OD-H (98% hexanes: 2% isopropanol, 0.8 mL/min): t_{major} = 9.94 min, t_{minor} = 8.50 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{18}N^+$: 224.14338, Found: 224.14298.

2-((1*R*,2*S*)-2-Cyclohexylcyclopropyl)pyridine (3ad) was obtained through the general

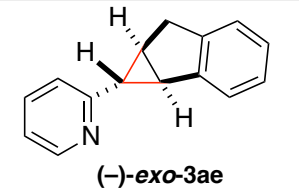


(–)-3ad

procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 43%. dr: 94:6. R_f = 0.53 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-87.7° (*c* = 0.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 6.7 Hz, 1H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.4, 4.9 Hz, 1H), 1.82 – 1.79 (m, 3H),

1.76 – 1.58 (m, 3H), 1.24 – 1.05 (m, 7H), 0.90 – 0.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.26, 149.16, 135.93, 121.08, 120.18, 42.77, 33.10, 32.64, 31.12, 26.64, 26.39, 26.37, 23.74, 15.78. IR (neat, cm^{-1}): 2921.66, 2850.07, 1590.12, 1473.99, 1207.77, 1148.01, 885.72, 743.97. HPLC analysis (*E*)-isomer: ee = 94%. IC (99% hexanes: 1% isopropanol, 0.5 mL/min): t_{major} = 12.84 min, t_{minor} = 13.40 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{20}N^+$: 202.15903, Found: 202.15983.

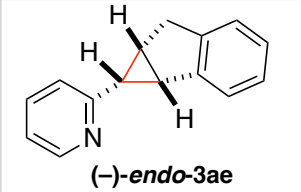
2-((1*R*,1a*R*,6a*S*)-1,1a,6,6a-Tetrahydrocyclopropa[*a*]inden-1-yl)pyridine (*exo*-3ae)



(–)-*exo*-3ae

was obtained through the general procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield (*exo* + *endo*): 43%. dr: 58:42. R_f = 0.48 (6:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-192.8° (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.3 Hz, 1H), 7.53 (td, *J* = 7.6, 1.9 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.08 (m, 3H), 7.07 – 7.03 (m, 1H), 3.37 (dd, *J* = 17.5, 6.5 Hz, 1H), 3.15 (d, *J* = 17.4 Hz, 1H), 2.98 (dd, *J* = 6.4, 2.0 Hz, 1H), 2.52 – 2.49 (m, 1H), 1.63 (t, *J* = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.16, 149.36, 145.81, 142.72, 135.99, 126.29, 125.94, 125.43, 123.83, 121.95, 120.56, 36.53, 36.28, 35.82, 28.13. IR (neat, cm^{-1}): 3041.44, 2912.87, 1715.18, 1590.13, 1566.88, 1472.65, 1440.22, 750.89. HPLC analysis (*exo*-isomer): ee = 81 %. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 7.84 min, t_{minor} = 7.30 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{14}N^+$: 208.11208, Found: 208.11160.

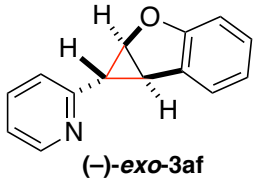
2-((1*R*,1a*S*,6a*R*)-1,1a,6,6a-Tetrahydrocyclopropa[*a*]inden-1-yl)pyridine (*endo*-3ae)



(–)-*endo*-3ae

was obtained through the general procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield (*exo* + *endo*): 43%. dr: 58:42. R_f = 0.43 (6:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-37.3° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 3.16 (dd, *J* = 17.5, 7.0 Hz, 1H), 3.00 (t, *J* = 7.8 Hz, 1H), 2.88 (d, *J* = 17.5 Hz, 1H), 2.61 (t, *J* = 8.3 Hz, 1H), 2.48 – 2.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.39, 148.85, 143.05, 142.86, 135.63, 126.16, 125.84, 125.65, 124.75, 124.57, 120.97, 32.18, 30.02, 28.89, 22.86. IR (neat, cm^{-1}): 3042.87, 2916.07, 1588.90, 1477.24, 1433.25, 1021.26, 794.71, 758.72. HPLC analysis (*endo*-isomer): ee = 93%. IA (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 8.55 min, t_{minor} = 8.17 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{14}N^+$: 208.11208, Found: 208.11183.

2-((1*R*,1a*S*,6b*R*)-1a,6b-Dihydro-1*H*-cyclopropa[*b*]benzofuran-1-yl)pyridine (*exo*-3af)

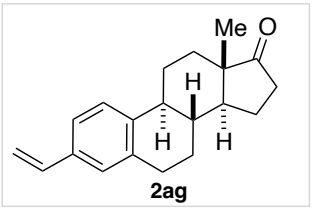


(–)-*exo*-3af

was obtained through the general procedure using 10.0 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 56%. dr: 96:4. R_f = 0.48 (6:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-224.4° (*c* = 1.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.0 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.08 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.96 – 6.88 (m, 2H), 5.13 (dd, *J* = 5.4, 1.3 Hz, 1H), 3.32 (dd, *J* = 5.4, 3.3 Hz, 1H), 1.68 (dd, *J* = 3.2, 1.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.31, 159.47, 149.56, 135.84, 130.72, 127.42, 124.29, 122.65, 120.96, 120.70,

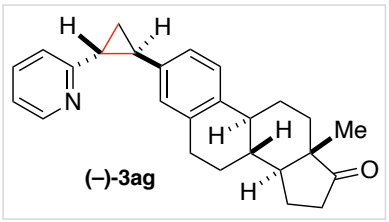
110.47, 69.14, 31.78, 27.57. IR (neat, cm^{-1}): 1589.29, 1566.75, 1473.70, 1462.31, 1245.27, 1065.90, 1001.41, 747.17. HPLC analysis (*exo*-isomer): ee = 97%. ID (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 7.01 min, t_{minor} = 7.46 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{12}NO^+$: 210.09134, Found: 210.09097.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-



cyclopenta[*a*]phenanthren-17-one (2ag) was prepared according to the literature.[26] **Known compound**. Yield: 59%. R_f = 0.33 (4:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.7 Hz, 1H), 2.91 (dd, *J* = 9.2, 4.2 Hz, 2H), 2.50 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.32 – 2.27 (m, 1H), 2.19 – 1.92 (m, 4H), 1.63 – 1.44 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 221.01, 139.66, 136.70, 135.35, 127.01, 125.67, 123.74, 113.32, 50.65, 48.13, 44.59, 38.30, 36.00, 31.73, 29.52, 26.64, 25.86, 21.73, 13.98.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((1*R*,2*R*)-2-(pyridin-2-yl)cyclopropyl)-

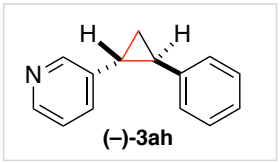


6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenijta[*a*]phenanthren-17-one (3ag) was obtained through the general procedure using 1.5 equiv of olefin with 2-pyridinecarboxaldehyde tosylhydrazone (**1a**) at 80 °C. Yield: 93%. dr: 99:1. R_f = 0.41 (3:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-149.8° (*c* = 2.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.9 Hz, 1H), 7.54 (td, *J* = 7.6, 1.8 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.06 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.96 (dd, *J* = 8.1, 2.0

[26] Crespin, L.; Biancalana, L.; Morack, T.; Blakemore, D. C.; Ley, S. V. *Org. Lett.* **2017**, *19*, 1084–1087.

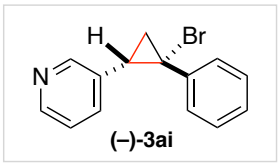
Hz, 1H), 6.92 (s, 1H), 2.90 (dd, J = 9.1, 4.2 Hz, 2H), 2.56 – 2.46 (m, 2H), 2.46 – 2.38 (m, 1H), 2.34 – 2.21 (m, 2H), 2.19 – 1.94 (m, 4H), 1.75 (ddd, J = 8.9, 5.5, 4.5 Hz, 1H), 1.66 – 1.42 (m, 7H), 0.91 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 221.01, 161.31, 149.46, 139.87, 137.51, 136.60, 136.02, 126.77, 125.56, 123.42, 122.11, 120.70, 50.60, 48.12, 44.42, 38.37, 35.99, 31.72, 29.54, 29.38, 27.92, 26.66, 25.90, 21.71, 18.79, 13.96. IR (neat, cm^{-1}): 2928.26, 1737.11, 1590.21, 1473.50, 1212.59, 1007.18, 748.32. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{30}NO^+$: 372.23219, Found: 372.23197.

3-((1*R*,2*R*)-2-Phenylcyclopropyl)pyridine (3ah) was obtained through the general procedure using 1.5 equiv of olefin with 3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1b**) at 22 °C. Yield: 91%. dr: 95:5. R_f = 0.40 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-252.5° (c = 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.44 (d, J = 4.6 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.34 – 7.28 (m, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.13 (m, 2H), 2.24 – 2.14 (m, 2H), 1.55 – 1.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.36, 147.26, 141.81, 132.84, 129.26, 128.64, 126.23, 125.95, 123.48, 27.96, 25.37, 17.98. IR (neat, cm^{-1}): 3027.05, 1603.41, 1572.98, 1481.13, 1425.29, 1193.12, 1025.40, 803.66. HPLC analysis (*E*)-isomer: ee = 99%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 24.42 min, t_{minor} = 28.73 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{14}N^+$: 196.11208, Found: 196.11254.



(–)-3ah

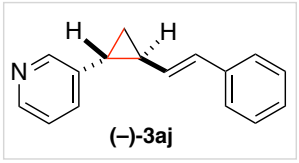
3-((1*S*,2*S*)-2-Bromo-2-phenylcyclopropyl)pyridine (3ai) was obtained through the general procedure using 1.5 equiv of olefin with 3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1b**) at 22 °C. Yield: 58%. dr: 99:1. R_f = 0.32 (2:1



(–)-3ai

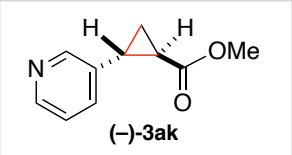
Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-90.5° (*c* = 1.3, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.56 (d, *J* = 4.8 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 2.49 (dd, *J* = 9.8, 7.7 Hz, 1H), 2.01 (dd, *J* = 10.5, 7.3 Hz, 1H), 1.89 (dd, *J* = 7.7, 5.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.96, 148.24, 143.77, 136.69, 133.88, 128.91, 128.62, 128.43, 123.09, 41.24, 28.61, 21.22. IR (neat, cm^{-1}): 3028.16, 1574.56, 1480.61, 1446.80, 1418.02, 1160.47, 1025.83, 752.06. HPLC analysis (*Z*)-isomer: ee = 99%. IE (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 27.74 min, t_{minor} = 21.56 min. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{14}H_{13}NBr^+$: 274.02259, Found: 274.02239.

3-((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)pyridine (**3aj)** was obtained through the general procedure using 1.5 equiv of olefin with 3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1b**) at 22 °C. Yield: 83%. dr: 91:9. R_f = 0.30 (2:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-328.4° (*c* = 2.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.4 Hz, 1H), 8.42 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.23 – 7.17 (m, 2H), 6.51 (d, *J* = 15.7 Hz, 1H), 5.91 (dd, *J* = 15.8, 8.6 Hz, 1H), 2.04 (ddd, *J* = 8.8, 5.8, 4.3 Hz, 1H), 1.89 – 1.83 (m, 1H), 1.36 – 1.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.26, 147.16, 137.80, 137.37, 132.77, 132.04, 129.09, 128.70, 127.14, 125.88, 123.40, 27.30, 23.23, 16.94. IR (neat, cm^{-1}): 3023.71, 1647.37, 1596.12, 1480.67, 1424.92, 1174.53, 959.18, 712.17. HPLC analysis (*E*)-isomer: ee = 98%. ID (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 13.84 min, t_{minor} = 11.95 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N^+$: 222.12773, Found: 222.12880.



(–)-3aj

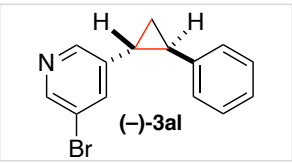
Methyl (1*R*,2*R*)-2-(pyridin-3-yl)cyclopropane-1-carboxylate (3ak) was obtained



(–)-3ak

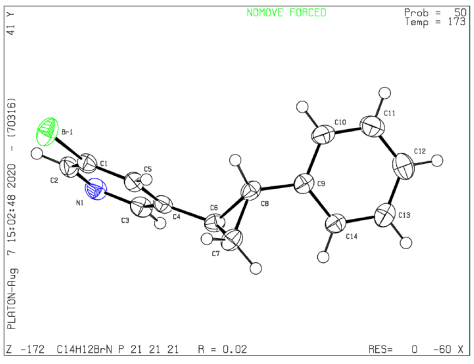
through the general procedure using 3.0 equiv of olefin with 3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1b**) at 22 °C. Yield: 91%. dr: 90:10. R_f = 0.33 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-233.6° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 – 8.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.20 (dd, *J* = 7.9, 4.8 Hz, 1H), 3.72 (s, 3H), 2.52 (ddd, *J* = 9.3, 6.5, 4.2 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.70 – 1.59 (m, 1H), 1.33 (ddd, *J* = 8.4, 6.2, 4.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.44, 148.55, 147.94, 135.74, 133.54, 123.47, 52.19, 23.70, 23.67, 16.70. IR (neat, cm^{-1}): 2952.54, 1726.14, 1437.88, 1274.44, 1174.66, 1199.69, 905.51, 712.81. HPLC analysis (*E*)-isomer: ee = 97%. AS-H (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 14.24 min, t_{minor} = 20.24 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{10}H_{12}NO_2^+$: 178.08626, Found: 178.08604.

3-Bromo-5-((1*R*,2*R*)-2-phenylcyclopropyl)pyridine (3al) was obtained through the



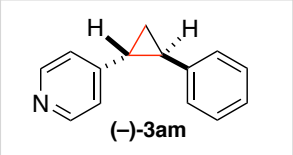
(–)-3al

general procedure using 1.5 equiv of olefin with 5-bromo-3-pyridinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1c**) at 22 °C. Yield: 90%. dr: 97:3. R_f = 0.49 (3:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-236.0° (*c* = 1.7, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.39 (s, 1H), 7.54 (s, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 7.14 (d, *J* = 6.9 Hz, 2H), 2.21 (ddd, *J* = 8.9, 6.0, 4.5 Hz, 1H), 2.14 (ddd, *J* = 8.8, 5.8, 4.5 Hz, 1H), 1.57– 1.54 (m, 1H), 1.49 – 1.45 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.17, 146.45, 141.21, 140.25, 135.49, 128.71, 126.46, 125.96, 120.96, 28.36, 24.88,



18.15. IR (neat, cm^{-1}): 3028.07, 1603.97, 1579.73, 1499.28, 1424.85, 1097.55, 1017.67, 913.04. HPLC analysis (*E*)-isomer: ee = 99%. OD-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 16.75 min, t_{minor} = 11.65 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{13}NBr^+$: 274.02259, Found: 274.02312. The absolute configuration of the major (*E*)-isomer was assigned as (1*R*,2*R*) by X-ray crystallography.

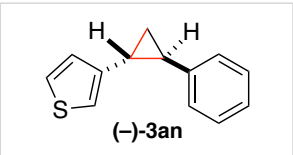
4-((1*R*,2*R*)-2-Phenylcyclopropyl)pyridine (3am) was obtained through the general



(–)-3am

procedure using 1.5 equiv of olefin with 4-pyridinecarboxaldehyde tosylhydrazone (**1d**) at 60 °C. Yield: 42%. dr: 95:5. R_f = 0.22 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-241.2° (*c* = 0.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.4 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 6.4 Hz, 2H), 2.26 (ddd, *J* = 9.1, 6.2, 4.5 Hz, 1H), 2.14 – 2.09 (m, 1H), 1.61 – 1.57 (m, 1H), 1.53 – 1.50 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.44, 149.47, 141.32, 128.68, 126.42, 125.98, 121.00, 29.35, 27.33, 19.05. IR (neat, cm^{-1}): 3025.25, 2924.14, 1599.51, 1498.48, 1417.07, 1206.97, 901.54, 813.39. HPLC analysis (*E*)-isomer: ee = 89%. OD-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 32.54 min, t_{minor} = 25.61 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{14}N^+$: 196.11208, Found: 196.11284.

3-((1*R*,2*R*)-2-Phenylcyclopropyl)thiophene (3an) was obtained through the general

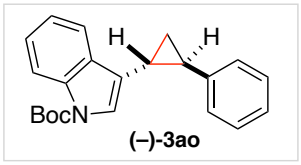


(–)-3an

procedure using 1.5 equiv of olefin with 3-thiophenecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1e**) at 22 °C. Yield: 71%. dr: 95:5. R_f = 0.45 (20:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-248.3° (*c* = 1.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.25 (m, 1H), 7.21 – 7.16 (m, 1H), 7.13 (dd, *J* = 8.2, 1.4 Hz, 2H),

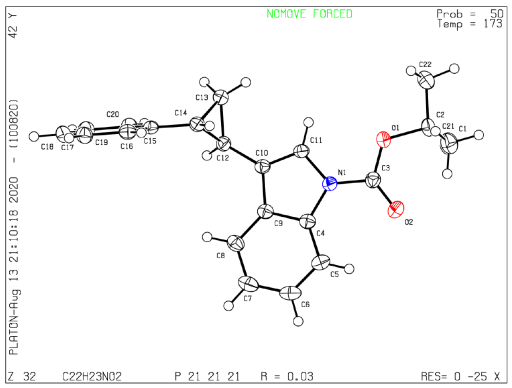
6.94 (dd, J = 3.1, 1.3 Hz, 1H), 6.91 (dd, J = 5.0, 1.3 Hz, 1H), 2.22 (ddd, J = 8.6, 6.0, 4.5 Hz, 1H), 2.14 (ddd, J = 8.6, 5.9, 4.5 Hz, 1H), 1.43 – 1.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.84, 142.53, 128.53, 126.30, 125.89, 125.86, 125.70, 118.50, 27.37, 23.83, 18.23. IR (neat, cm^{-1}): 3025.30, 1604.20, 1537.90, 1499.71, 1459.39, 1073.66, 776.57. HPLC analysis (*E*)-isomer: ee = 93%. OJ-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 17.71 min, t_{minor} = 20.83 min. HRMS (DART) ([M+H]$^+$) Calcd. For $C_{13}H_{13}S^+$: 201.07325, Found: 201.07289.

***tert*-Butyl 3-((1*R*,2*R*)-2-phenylcyclopropyl)-1*H*-indole-1-carboxylate (3ao)** was



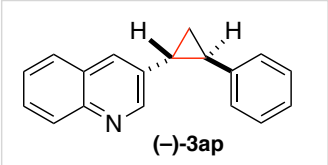
(–)-3ao

obtained through the general procedure using 1.5 equiv of olefin with *N*-Boc-1*H*-indole-3-carboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1f**) at 22 °C. Yield: 98%. dr: 98:2. R_f = 0.34 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-106.0° (c = 1.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.36 – 7.31 (m, 4H), 7.26 – 7.19 (m, 4H), 2.22 – 2.13 (m, 2H), 1.68 (s, 9H), 1.49 – 1.39 (m, 2H). ^{13}C NMR (125

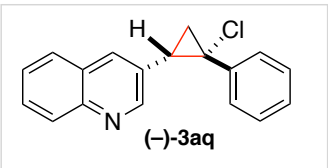


MHz, $CDCl_3$) δ 149.96, 142.68, 135.68, 131.12, 128.60, 126.03, 125.95, 124.64, 122.80, 122.62, 121.46, 119.40, 115.43, 83.64, 28.39, 25.57, 18.51, 16.11. IR (neat, cm^{-1}): 1730.69, 1452.06, 1374.29, 1255.18, 1157.34, 1088.11, 856.09, 746.20. HPLC analysis (*E*)-isomer: ee = 85%. OD-H (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 6.11 min, t_{minor} = 5.66 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{24}NO_2^+$: 334.18016, Found: 334.17963. The absolute configuration of the major (*E*)-isomer was assigned as (1*R*,2*R*) by X-ray crystallography.

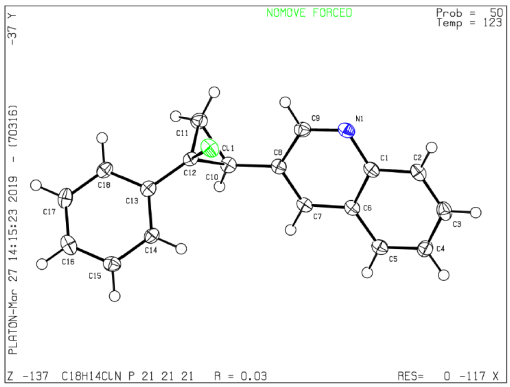
3-((1*R*,2*R*)-2-Phenylcyclopropyl)quinoline (3ap) was obtained through the general procedure using 1.5 equiv of olefin with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1g**) at 22 °C. Yield: 96%. dr: 93:7. R_f = 0.30 (3:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-414.2° (*c* = 1.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.25 – 7.17 (m, 3H), 2.36 (ddd, *J* = 8.3, 6.3, 4.5 Hz, 1H), 2.31 (ddd, *J* = 8.6, 6.5, 4.5 Hz, 1H), 1.65 – 1.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.55, 146.97, 141.82, 135.47, 131.11, 129.31, 128.71, 128.68, 128.20, 127.38, 126.93, 126.27, 125.97, 28.32, 25.71, 18.08. IR (neat, cm^{-1}): 3025.24, 1602.76, 1494.46, 1342.61, 1126.47, 1073.30, 912.98, 786.17. HPLC analysis (*E*)-isomer: ee = 99%. ID (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 29.44 min, t_{minor} = 26.78 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{16}N^+$: 246.12773, Found: 246.12896.



3-((1*S*,2*S*)-2-Chloro-2-phenylcyclopropyl)quinoline (3aq) was obtained through the general procedure using 1.5 equiv of olefin with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1g**) at 22 °C. Yield: 95%. dr: 99:1. R_f = 0.38 (3:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-248.3° (*c* = 2.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.3 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.45 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 2.80 (dd, *J* = 9.8, 7.8 Hz, 1H), 2.08 (dd, *J* = 9.9, 6.8 Hz, 1H), 2.00 (dd, *J* = 7.8, 6.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.34, 147.31, 142.21, 135.45, 129.96,

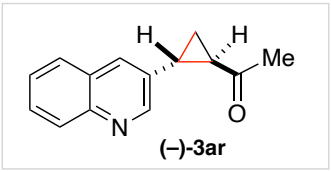


129.34, 129.33, 128.90, 128.27, 127.85, 127.77, 127.65, 126.96, 49.85, 30.04, 21.40. IR



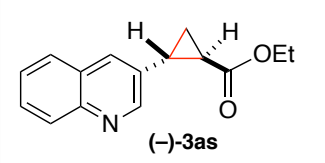
(neat, cm^{-1}): 1600.39, 1569.59, 1494.29, 1449.17, 1161.62, 1040.54, 757.12. HPLC analysis (*Z*)-isomer: ee = 99%. IF (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 30.71 min, t_{minor} = 27.88 min. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{18}H_{15}NCl^+$: 280.08875, Found: 280.08893. The absolute configuration of the major (*Z*)-isomer was assigned as (1*S*,2*S*) by X-ray crystallography.

1-((1*R*,2*R*)-2-(Quinolin-3-yl)cyclopropyl)ethan-1-one (3ar) was obtained through the



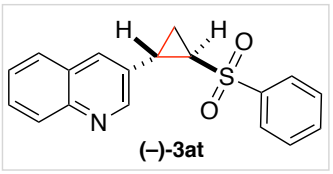
general procedure using 3.0 equiv of olefin with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1g**) at 22 °C. Yield: 70%. dr: 77:23. R_f = 0.23 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-327.6° (*c* = 0.9, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.56 – 7.51 (m, 1H), 2.72 (ddd, *J* = 10.3, 6.6, 4.1 Hz, 1H), 2.36 – 2.33 (m, 4H), 1.80 – 1.77 (m, 1H), 1.53 (ddd, *J* = 8.2, 6.6, 4.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.36, 150.19, 147.32, 133.27, 132.01, 129.42, 129.15, 127.92, 127.42, 127.14, 32.58, 31.10, 26.52, 18.91. IR (neat, cm^{-1}): 3004.58, 1697.41, 1494.12, 1354.81, 1178.26, 976.22, 753.39. HPLC analysis (*E*)-isomer: ee = 98%. IE (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 28.82 min, t_{minor} = 31.10 min. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{14}H_{14}NO^+$: 212.10699, Found: 212.10702.

Ethyl (1*R*,2*R*)-2-(quinolin-3-yl)cyclopropane-1-carboxylate (3as) was obtained through



the general procedure using 1.5 equiv of olefin with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1g**) at 22 °C. Yield: 90%. dr: 96:4. R_f = 0.28 (2:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-231.6° (*c* = 2.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 2.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 4.21 (q, *J* = 7.6 Hz, 2H), 2.74 – 2.67 (m, 1H), 2.04 (ddd, *J* = 8.5, 5.3, 4.2 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.45 (ddd, *J* = 8.6, 6.5, 4.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.01, 150.37, 147.32, 133.11, 132.09, 129.40, 129.10, 127.96, 127.44, 127.07, 61.10, 24.09, 23.90, 16.87, 14.39. IR (neat, cm^{-1}): 2981.08, 1719.87, 1409.27, 1337.94, 1181.43, 1047.72, 752.75. HPLC analysis (*E*)-isomer: ee = 99%. IE (90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 38.23 min, t_{minor} = 35.34 min. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{15}H_{16}NO_2^+$: 242.11756, Found: 242.11756.

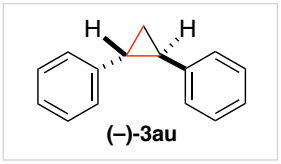
3-((1*S*,2*R*)-2-(Phenylsulfonyl)cyclopropyl)quinoline (3at) was obtained through the



general procedure using 1.5 equiv of olefin with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1g**) at 22 °C. Yield: 92%. dr: 99:1. R_f = 0.31 (1:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-65.0° (*c* = 2.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.3 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.75 (d, *J* = 2.3 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.59 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.52 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 3.04 (ddd, *J* = 10.4, 6.6, 4.6 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.05 – 2.01 (m, 1H), 1.66 – 1.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.07, 147.48, 140.35, 133.91, 132.98,

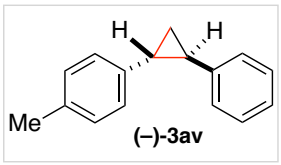
130.43, 129.61, 129.57, 129.39, 127.73, 127.66, 127.47, 127.31, 41.88, 21.77, 13.79. IR (neat, cm^{-1}): 1494.32, 1446.39, 1304.88, 1146.07, 1087.44, 968.80, 733.93. HPLC analysis (*E*)-isomer: ee = 99%. OD-H (80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 30.64 min, t_{minor} = 26.95 min. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{18}H_{16}NO_2S^+$: 310.08963, Found: 310.09007.

(1*R*,2*R*)-1,2-Diphenylcyclopropane (3au) was obtained through the general procedure



using 1.5 equiv of olefin with benzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1h**) at 22°C. Yield: 97%. dr: 94:6. R_f = 0.42 (Hexanes only). $[\alpha]_D^{20}$ = (–)-364.8° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.23 – 7.14 (m, 6H), 2.24 – 2.15 (m, 2H), 1.50 – 1.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.66, 128.53, 125.92, 125.88, 28.14, 18.32. IR (neat, cm^{-1}): 3028.19, 1603.28, 1498.87, 1450.32, 1030.32, 907.02, 735.59, 695.49. HPLC analysis (*E*)-isomer: ee = 97%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 6.75 min, t_{minor} = 6.01 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{15}^+$: 195.11683, Found: 195.11621.

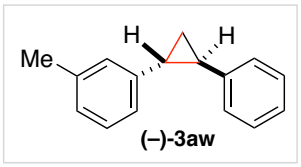
1-Methyl-4-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3av) was obtained through the



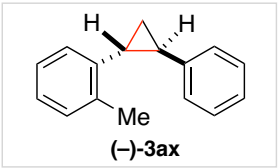
general procedure using 1.5 equiv of olefin with 4-methylbenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1i**) at 22°C. Yield: 95%. dr: 93:7. R_f = 0.38 (Hexanes only). $[\alpha]_D^{20}$ = (–)-369.4° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.23 – 7.11 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H), 2.18 – 2.12 (m, 2H), 1.45 – 1.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.83, 139.59, 135.42, 129.21, 128.51, 125.89, 125.86, 125.80, 27.96, 27.85, 21.11, 18.13. IR (neat, cm^{-1}): 3024.14, 2920.67,

1603.03, 1516.20, 1497.54, 1211.03, 1031.24, 809.20, 750.29, 695.67. HPLC analysis (*E*)-isomer: ee = 98%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 6.15 min, t_{minor} = 5.24 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{17}^+$: 209.13248, Found: 209.13275.

1-Methyl-3-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3aw) was obtained through the general procedure using 1.5 equiv of olefin with 3-methylbenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1j**) at 22°C. Yield: 92%. dr: 95:5. R_f = 0.44 (Hexanes only). $[\alpha]_D^{20}$ = (–)-356.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.24 – 7.15 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.95 (m, 2H), 2.37 (s, 3H), 2.21 – 2.13 (m, 2H), 1.50 – 1.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.75, 142.61, 138.11, 128.51, 128.45, 126.72, 126.67, 125.91, 125.84, 122.92, 28.11, 28.06, 21.57, 18.24. IR (neat, cm^{-1}): 3026.23, 2919.93, 1604.23, 1497.78, 1113.06, 1031.27, 923.33, 781.91, 695.03. HPLC analysis (*E*)-isomer: ee = 97%. IF (100% hexanes, 0.5 mL/min): t_{major} = 16.53 min, t_{minor} = 19.15 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{17}^+$: 209.13248, Found: 209.13282.

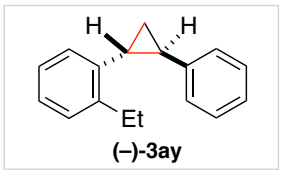


1-Methyl-2-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3ax) was obtained through the general procedure using 1.5 equiv of olefin with 2-methylbenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1k**) at 22°C. Yield: 86%. dr: 95:5. R_f = 0.41 (Hexanes only). $[\alpha]_D^{20}$ = (–)-192.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.24 – 7.11 (m, 7H), 2.37 (s, 3H), 2.24 – 2.21 (m, 1H), 2.09 – 2.06 (m, 1H), 1.49 (ddd, *J* = 8.7, 6.2, 5.0 Hz, 1H), 1.43 – 1.40 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.09,



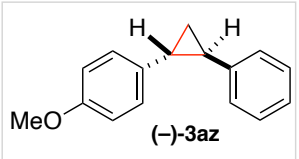
140.34, 138.08, 129.84, 128.54, 126.21, 126.00, 125.80, 125.69, 26.27, 26.07, 20.04, 16.49. IR (neat, cm^{-1}): 3062.67, 3024.39, 1603.22, 1491.19, 1458.43, 1113.67, 1030.88, 753.29, 696.20. HPLC analysis (*E*)-isomer: ee = 97%. IB (99.9% hexanes: 0.1% isopropanol, 0.8 mL/min): t_{major} = 8.56 min, t_{minor} = 7.45 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{17}^+$: 209.13248, Found: 209.13224.

1-Ethyl-2-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3ay) was obtained through the general procedure using 1.5 equiv of olefin with 2-ethylbenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1l**) at 22°C. Yield: 57%. dr: 96:4. R_f = 0.33 (Hexanes only). $[\alpha]_D^{20}$ = (–)-188.4° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.23 – 7.15 (m, 6H), 7.13 – 7.07 (m, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.28 – 2.24 (m, 1H), 2.10 – 2.06 (m, 1H), 1.51 – 1.47 (m, 1H), 1.42 – 1.38 (m, 1H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.75, 142.99, 139.63, 128.56, 128.14, 126.36, 126.01, 125.81, 125.53, 26.46, 26.14, 25.56, 16.75, 14.95. IR (neat, cm^{-1}): 3028.71, 2956.21, 2930.71, 2872.49, 1602.83, 1489.77, 1457.98, 1116.52, 752.13, 696.18. HPLC analysis (*E*)-isomer: ee = 89%. IF (100% hexanes, 0.5 mL/min): t_{major} = 13.21 min, t_{minor} = 14.41 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{19}^+$: 223.14813, Found: 223.14781.



(–)-3ay

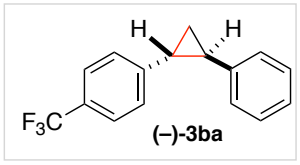
1-Methoxy-4-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3az) was obtained through the general procedure using 1.5 equiv of olefin with 4-methoxybenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1m**) at 22°C. Yield: 94%. dr: 94:6. R_f = 0.26 (20:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-323.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 – 7.14 (m, 2H), 7.12 – 7.07 (m, 2H), 6.88 – 6.84



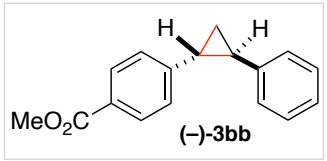
(–)-3az

(m, 2H), 3.81 (s, 3H), 2.18 – 2.08 (m, 2H), 1.42 – 1.39 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.02, 142.88, 134.67, 128.51, 127.07, 125.86, 125.78, 114.02, 55.48, 27.63, 27.45, 17.92. IR (neat, cm^{-1}): 3001.07, 2833.70, 1603.92, 1514.04, 1462.78, 1245.89, 1035.44, 823.28, 697.15. HPLC analysis (*E*)-isomer: ee = 97%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 8.37 min, t_{minor} = 7.16 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{17}O^+$: 225.12739, Found: 225.12767.

1-((1*R*,2*R*)-2-Phenylcyclopropyl)-4-(trifluoromethyl)benzene (3ba) was obtained through the general procedure using 1.5 equiv of olefin with 4-(trifluoromethyl)benzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1n**) at 22°C. Yield: 96%. dr: 93:7. R_f = 0.42 (Hexanes only). $[\alpha]_D^{20}$ = (–)-299.2° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.29 – 7.21 (m, 3H), 7.17 (d, *J* = 7.7 Hz, 2H), 2.25 – 2.22 (m, 2H), 1.59 – 1.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.93, 141.90, 128.65, 128.14 (q, *J* = 32.1 Hz), 126.23, 126.05, 125.96, 125.47 (q, *J* = 3.8 Hz), 124.51 (q, *J* = 272.2 Hz), 28.82, 27.89, 18.70. ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.25. IR (neat, cm^{-1}): 3028.88, 1618.95, 1497.31, 1324.51, 1163.44, 1117.66, 1067.93, 1015.72, 824.57. HPLC analysis (*E*)-isomer: ee = 99%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 6.70 min, t_{minor} = 5.76 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{14}F_3^+$: 263.10421, Found: 263.10378.

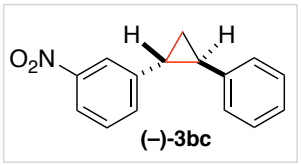


Methyl 4-((1*R*,2*R*)-2-phenylcyclopropyl)benzoate (3bb) was obtained through the general procedure using 1.5 equiv of olefin with 4-(methoxycarbonyl)benzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1o**) at 22°C. Yield: 94%. dr: 94:6. R_f =



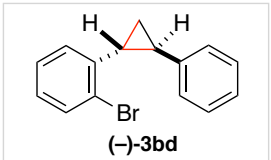
0.51 (8:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-362.0° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.22 – 7.14 (m, 5H), 3.91 (s, 3H), 2.26 – 2.19 (m, 2H), 1.57 – 1.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.17, 148.37, 141.96, 129.89, 128.60, 127.73, 126.16, 125.93, 125.64, 52.10, 29.04, 28.25, 18.98. IR (neat, cm^{-1}): 3025.65, 2950.24, 1716.33, 1608.87, 1434.59, 1277.00, 1181.01, 1111.59, 1017.91. HPLC analysis (*E*)-isomer: ee = 97%. IA (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 14.45 min, t_{minor} = 8.49 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2^+$: 253.12231, Found: 253.12345.

1-Nitro-3-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3bc) was obtained through the general procedure using 1.5 equiv of olefin with 3-nitrobenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1p**) at 22°C. Yield: 89%. dr: 98:2. R_f = 0.54 (8:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (–)-338.2° (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H), 7.52 – 7.41 (m, 2H), 7.33 – 7.31 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 2.29 – 2.24 (m, 2H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.64, 144.96, 141.48, 132.36, 129.34, 128.68, 126.36, 125.94, 120.92, 120.49, 28.79, 27.52, 18.68. IR (neat, cm^{-1}): 3028.40, 1603.50, 1526.14, 1348.86, 1075.34, 924.33, 867.15. HPLC analysis (*E*)-isomer: ee = 96%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 13.17 min, t_{minor} = 12.28 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{14}NO_2^+$: 240.10191, Found: 240.10197.



(–)-3bc

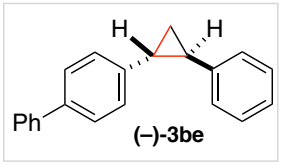
1-Bromo-2-((1*R*,2*R*)-2-phenylcyclopropyl)benzene (3bd) was obtained through the general procedure using 1.5 equiv of olefin with 2-bromobenzaldehyde 2,4,6-triisopropylbenzene sulfonyl



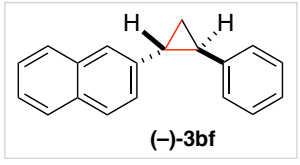
(–)-3bd

hydrazone (**1q**) at 22°C. Yield: 89%. dr: 96:4. R_f = 0.42 (Hexanes only). $[\alpha]_D^{20}$ = (–)-125.8° (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.29 – 7.18 (m, 4H), 7.11 – 7.04 (m, 2H), 2.51 – 2.45 (m, 1H), 2.17 – 2.10 (m, 1H), 1.47 – 1.42 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.30, 141.50, 132.66, 128.49, 127.56, 127.49, 127.04, 126.24, 126.21, 126.01, 28.05, 27.01, 17.24. IR (neat, cm^{-1}): 3058.29, 3026.34, 1603.91, 1476.11, 1214.07, 1023.15, 749.96, 695.59. HPLC analysis (*E*)-isomer: ee = 93%. ADH (100% hexanes, 0.5 mL/min): t_{major} = 14.57 min, t_{minor} = 17.12 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{14}Br^+$: 273.02734, Found: 273.02743.

4-((1*R*,2*R*)-2-phenylcyclopropyl)-1,1'-biphenyl (3be) was obtained through the general procedure using 1.5 equiv of olefin with 4-phenylbenzaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1r**) at 22°C. Yield: 90%. dr: 95:5. R_f = 0.21 (Hexanes only). $[\alpha]_D^{20}$ = (–)-399.6° (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.17 (m, 5H), 2.26 – 2.21 (m, 2H), 1.54 – 1.50 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.57, 141.87, 141.11, 138.89, 128.88, 128.56, 127.27, 127.19, 127.09, 126.30, 125.93, 125.92, 28.34, 27.95, 18.42. IR (neat, cm^{-1}): 3056.44, 3027.70, 1602.57, 1487.14, 1121.24, 823.97. HPLC analysis (*E*)-isomer: ee = 98%. IF (99.9% hexanes: 0.1% isopropanol, 0.8 mL/min): t_{major} = 22.98 min, t_{minor} = 19.92 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{19}^+$: 271.14813, Found: 271.14900.



2-((1*R*,2*R*)-2-phenylcyclopropyl)naphthalene (3bf) was obtained through the general procedure using 1.5 equiv of olefin with 2-naphthaldehyde 2,4,6-triisopropylbenzene sulfonyl hydrazone (**1s**) at 22°C. Yield: 91%. dr: 95:5. R_f = 0.33 (Hexanes only). $[\alpha]_D^{20}$ = (–)-336.0° (*c* =



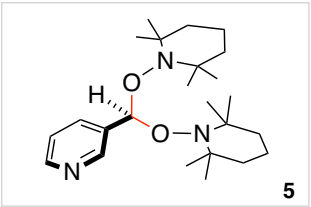
1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.62 (s, 1H), 7.50 – 7.47 (m, 1H), 7.45 – 7.43 (m, 1H), 7.36 – 7.33 (m, 2H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 2.37 (ddd, *J* = 8.7, 5.9, 4.5 Hz, 1H), 2.30 (ddd, *J* = 8.7, 5.9, 4.5 Hz, 1H), 1.63 – 1.60 (m, 1H), 1.58 – 1.54 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.61, 140.11, 133.67, 132.17, 128.57, 128.14, 127.76, 127.46, 126.25, 125.94, 125.23, 124.83, 124.02, 28.42, 28.26, 18.28. IR (neat, cm^{-1}): 3054.46, 3024.95, 1632.09, 1601.30, 1497.28, 1219.67, 813.58, 751.88, 698.47. HPLC analysis (*E*)-isomer: ee = 97%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 7.96 min, t_{minor} = 6.81 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{17}^+$: 245.13248, Found: 245.13248.

2.4.5. Mechanistic Studies of Stepwise Radical Mechanism

2.4.5.1. General Procedure for TEMPO Trapping Experiments

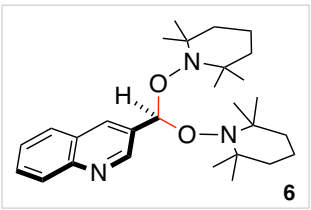
An oven-dried Schlenk tube was charged with sulfonyl hydrazone **1** (0.10 mmol, 1.0 equiv), [Co(**P1**)] (2 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, TEMPO (0.30 mmol, 3.0 equiv) and anhydrous toluene (1.0 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22 °C for 16 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum and purified by flash column chromatography.

1,1'-((Pyridin-3-ylmethylene)bis(oxy))bis(2,2,6,6-tetramethylpiperidine) (5) Yield: 19%. R_f = 0.33 (15:1 Hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.0 Hz, 1H), 8.51 (dd, *J* = 5.0, 1.7 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 6.09 (s,



1H), 1.49 (s, 12H), 1.36 – 1.20 (m, 12H), 0.98 (s, 6H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.69, 148.52, 136.41, 136.16, 122.79, 107.20, 60.74, 60.25, 40.69, 40.06, 34.52, 33.32, 21.34, 20.81, 17.28. IR (neat, cm^{-1}): 2974.24, 2930.02, 1467.64, 1376.57, 1362.48, 1132.32, 1084.29, 945.22, 713.19. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{24}H_{42}N_3O_2^+$: 404.32715, Found: 404.32774.

3-(Bis((2,2,6,6-tetramethylpiperidin-1-yl)oxyl)methyl)quinoline (6) Yield: 12%. R_f =



0.35 (15:1 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (d, J = 2.0 Hz, 1H), 8.15 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 6.26 (s, 1H), 1.55 (s, 12H), 1.28 (s, 12H), 0.99 (s, 6H), 0.45 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.73, 147.75, 135.18, 133.50, 129.35, 129.30, 128.28, 127.51, 126.43, 107.86, 60.82, 60.32, 40.77, 40.11, 34.60, 33.55, 21.41, 20.87, 17.32. IR (neat, cm^{-1}): 2973.66, 2929.43, 2870.84, 1572.03, 1466.04, 1362.41, 1132.18, 949.79, 903.44. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{28}H_{44}N_3O_2^+$: 454.34280, Found: 454.34263.

2.4.5.2. General Procedure for Cyclopropanation of (*E*)- and (*Z*)-β-Deuterostyrenes

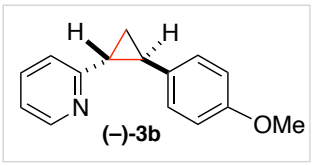
An oven-dried Schlenk tube was charged with 2-pyridinecarboxaldehyde tosylhydrazone **1a** (0.1 mmol, 1.0 equiv), [Co(Por)] (2 mol %) and Cs_2CO_3 (0.2 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, (*E*) or (*Z*)-β-deuterostyrene **2a$_D$** (0.15 mmol, 1.5 equiv) was added, followed by the addition of toluene (1.0 mL) as solvent via a gas tight syringe. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The mixture was stirred at 80 °C for 16 h. Following the completion of

the reaction, the reaction mixture was filtrated through a short pad of silica, concentrated under vacuum and purified by preparative TLC.

2.4.6. X-Ray Crystallography

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [27] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[28] Absorption correction was performed by multi-scan method implemented in SADABS.[29] Space groups were determined using XPREP implemented in APEX2.[20] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[30,31,32] program.

[27] Bruker (**2012**). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
[28] Bruker (**2012**). SAINT. Data Reduction Software.
[29] Sheldrick, G. M. (**1996**). *SADABS.* University of Gottingen, Germany.
[30] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837–838.
[31] Sheldrick, G. M. (**2012** Beta) SHELXL-97. Program for the Refinement of Crystal.
[32] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467–473.



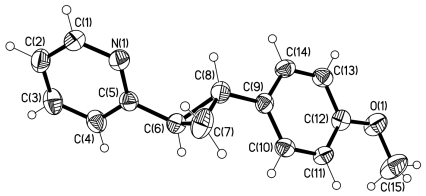
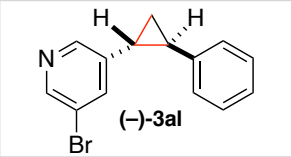


Table S1. Crystal data and structure refinement for (–)-3b

Identification code	C15H15NO	
Empirical formula	C15 H15 N O	
Formula weight	225.28	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.7035(5) ≈	α= 90∞.
	b = 7.6545(7) ≈	β= 90∞.
	c = 28.102(3) ≈	γ = 90∞.
Volume	1226.84(19) $≈^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.598 mm^{-1}	
F(000)	480	
Crystal size	0.360 x 0.180 x 0.120 mm^3	
Theta range for data collection	3.145 to 66.709∞.	
Index ranges	-6<=h<=6, -8<=k<=9, -33<=l<=33	
Reflections collected	25515	
Independent reflections	2148 [R(int) = 0.0263]	
Completeness to theta = 66.709∞	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6980	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2148 / 0 / 154	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0710	
R indices (all data)	R1 = 0.0284, wR2 = 0.0717	
Absolute structure parameter	0.05(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.121 and -0.137 $e.≈^{-3}$	



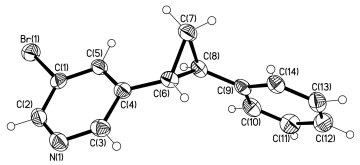
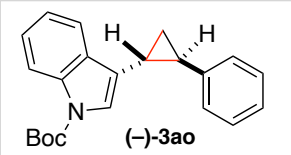


Table S2. Crystal data and structure refinement for (–)-3al

Identification code	C14H12BrN	
Empirical formula	C14 H12 Br N	
Formula weight	274.16	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.3856(5) ≈	α= 90∞.
	b = 7.7795(6) ≈	β= 90∞.
	c = 20.3419(15) ≈	γ = 90∞.
Volume	1168.77(15) $≈^3$	
Z	4	
Density (calculated)	1.558 Mg/m^3	
Absorption coefficient	4.531 mm^{-1}	
F(000)	552	
Crystal size	0.420 x 0.180 x 0.100 mm^3	
Theta range for data collection	4.347 to 66.624∞.	
Index ranges	-8<=h<=8, -9<=k<=9, -23<=l<=24	
Reflections collected	18297	
Independent reflections	2018 [R(int) = 0.0229]	
Completeness to theta = 66.624∞	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5921	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2018 / 0 / 145	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0167, wR2 = 0.0467	
R indices (all data)	R1 = 0.0168, wR2 = 0.0469	
Absolute structure parameter	-0.028(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.168 and -0.465 $e.≈^{-3}$	



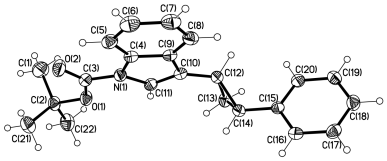
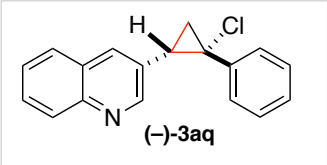


Table S3. Crystal data and structure refinement for (–)-3ao

Identification code	C22H23NO2	
Empirical formula	C22 H23 N O2	
Formula weight	333.41	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1640(7) ≈	α= 90∞.
	b = 11.4688(14) ≈	β= 90∞.
	c = 25.469(3) ≈	γ = 90∞.
Volume	1800.5(4) $≈^3$	
Z	4	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.616 mm^{-1}	
F(000)	712	
Crystal size	0.480 x 0.260 x 0.120 mm^3	
Theta range for data collection	3.471 to 66.600∞.	
Index ranges	-7<=h<=7, -13<=k<=13, -30<=l<=30	
Reflections collected	37857	
Independent reflections	3145 [R(int) = 0.0324]	
Completeness to theta = 66.600∞	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6790	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3145 / 0 / 226	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0284, wR2 = 0.0735	
R indices (all data)	R1 = 0.0288, wR2 = 0.0740	
Absolute structure parameter	0.08(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.160 and -0.179 $e.≈^{-3}$	



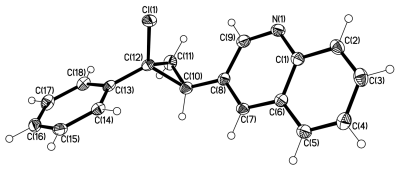


Table S4. Crystal data and structure refinement for (–)-3aq

Identification code	C18H14ClN	
Empirical formula	C18 H14 Cl N	
Formula weight	279.75	
Temperature	123(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8771(3) ≈	α= 90∞.
	b = 9.8218(5) ≈	β= 90∞.
	c = 23.3707(11) ≈	γ = 90∞.
Volume	1349.04(12) ≈^{3}	
Z	4	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	2.384 mm^{-1}	
F(000)	584	
Crystal size	0.520 x 0.300 x 0.140 mm^3	
Theta range for data collection	3.783 to 66.563∞.	
Index ranges	-6<=h<=6, -10<=k<=11, -27<=l<=27	
Reflections collected	7681	
Independent reflections	2353 [R(int) = 0.0259]	
Completeness to theta = 66.563∞	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5692	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2353 / 0 / 181	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0694	
R indices (all data)	R1 = 0.0260, wR2 = 0.0696	
Absolute structure parameter	0.010(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.237 and -0.197 e.≈$^{-3}$	

2.4.7. DFT Calculations

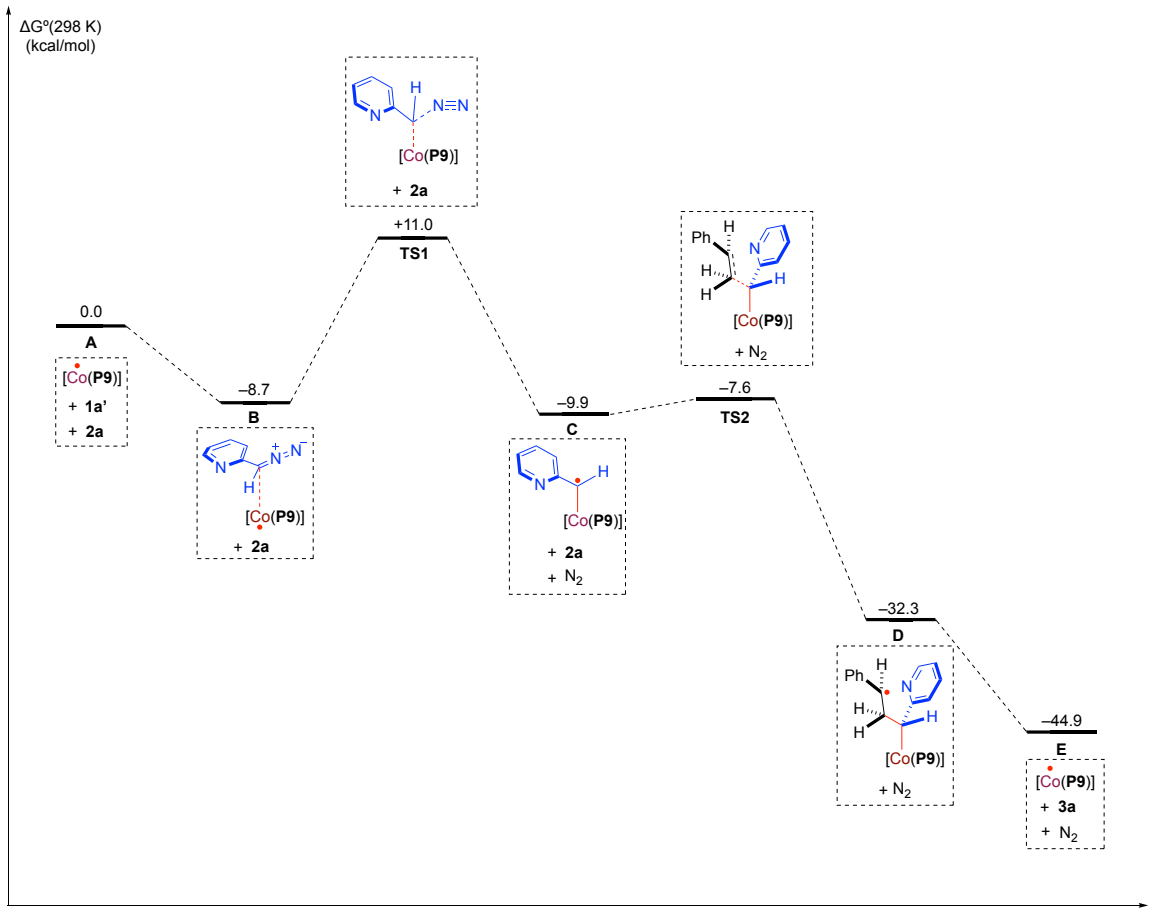
Considering the cost of time and computing resources for the large system with [Co(**P9**)], the geometry optimizations were performed with the Gaussian 16 at the BP86/lanl2dz level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy and thermal corrections (entropy and enthalpy, 298.15 K, 1 Atm) were obtained from these calculations. To further improve the accuracy of energies, single point energies were carried out at the B3LYP/def2-tzvp level of theory along with Grimme's dispersion correction (D3BJ) and SMD solvation model (in toluene).

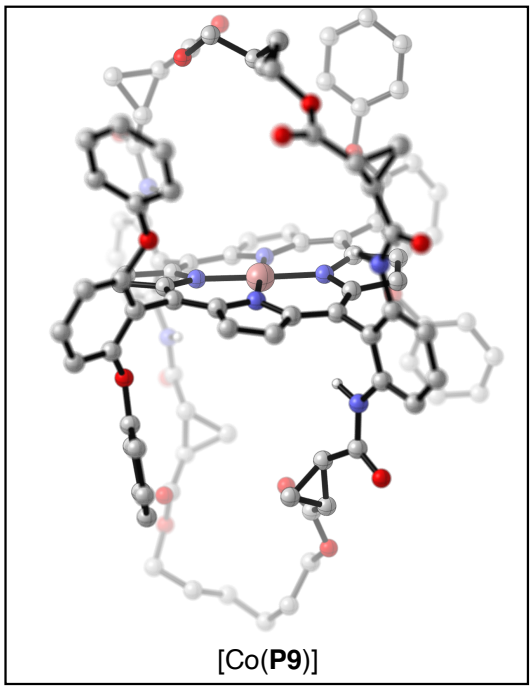
Independent Gradient Model (IGM)[33] analysis was performed with Multiwfn[34] software package using high quality grid option to generate files for further plotting. The visualization of IGM analysis results were presented with VMD[35] visualization software. As shown in Scheme S2, the 3D diagrams of optimized structures were generated with CYLview software.[36] The NCI (noncovalent interaction) visual representations of optimized structures were generated with VMD and rendered with Tachyon.[37]

[33] Lefebvre, C.; Rubez, G.; Khartabil, H.; Boisson, J.-C.; Contreras-García, J.; Hénon, E. *Phys. Chem. Chem. Phys.* **2017**, *19*, 17928–17936.
[34] Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580–592.
[35] Stone, J. E. Master's Thesis, University of Missouri, **1998**.

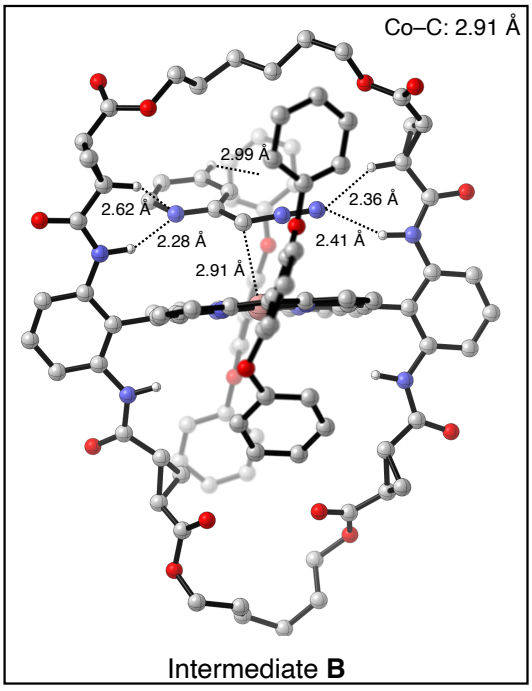
Scheme S1. Calculated Energy Diagram for [Co(P9)]-Catalyzed Radical Cyclopropanation of Styrene with 2-Pyridyldiazomethane



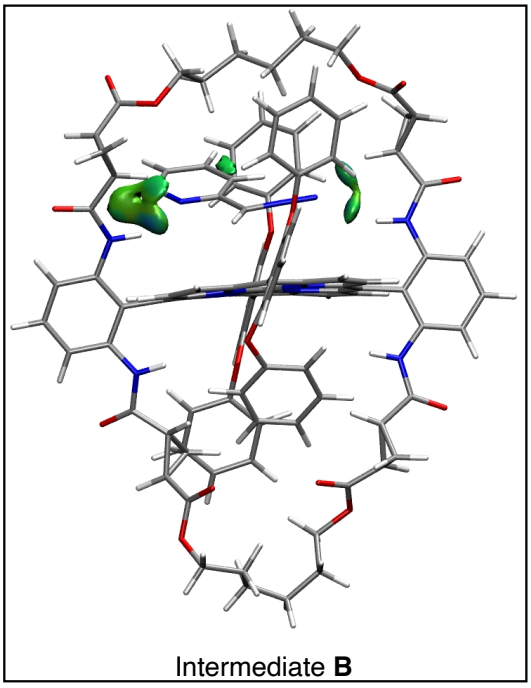
Scheme S2. Optimized Structure Models and NCI Visual Representation of Intermediates and Transition States



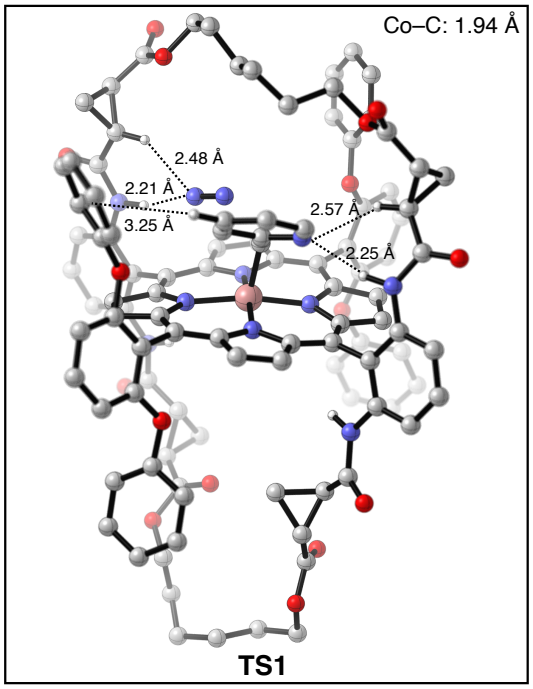
[Co(**P9**)]

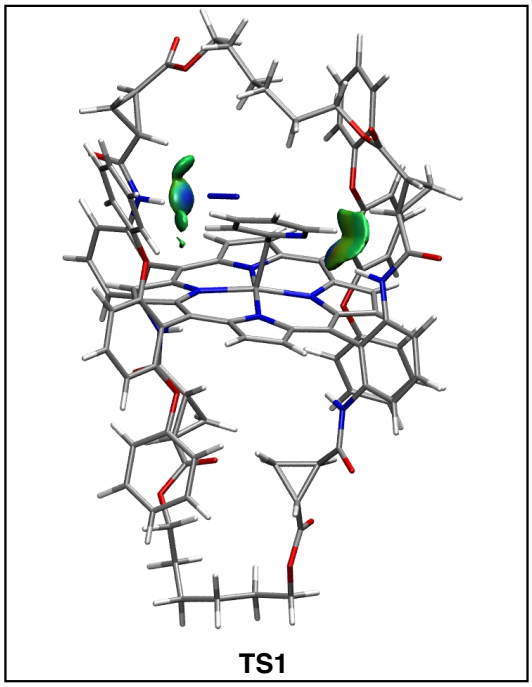


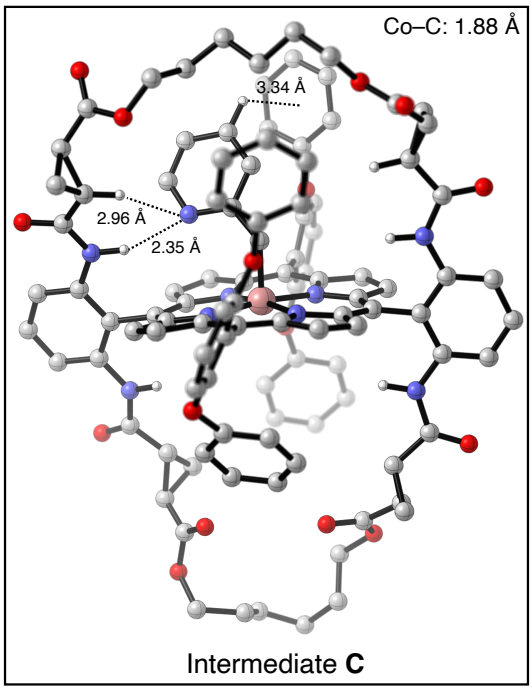
Intermediate **B**

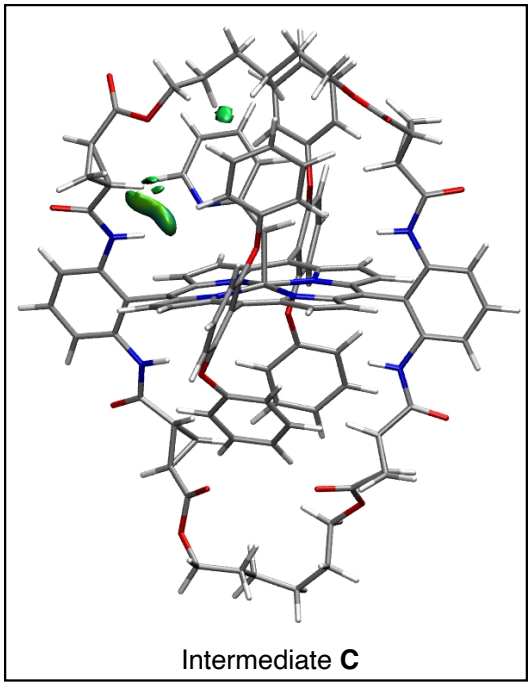


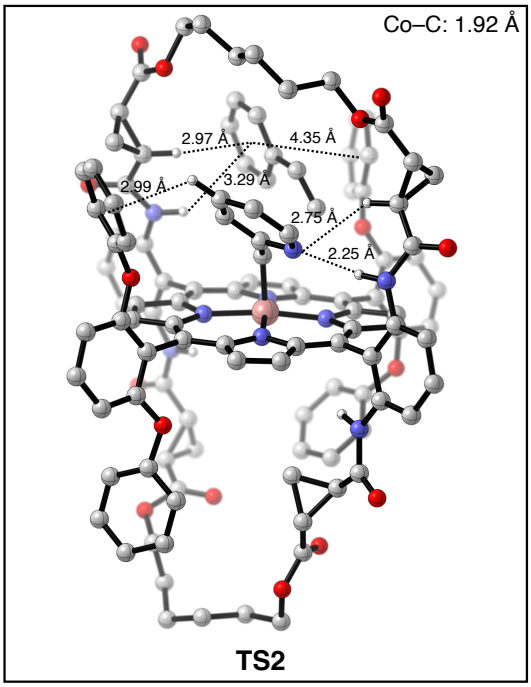
Intermediate **B**


Co–C: 1.94 Å
2.48 Å
2.21 Å
3.25 Å
2.57 Å
2.25 Å
TS1

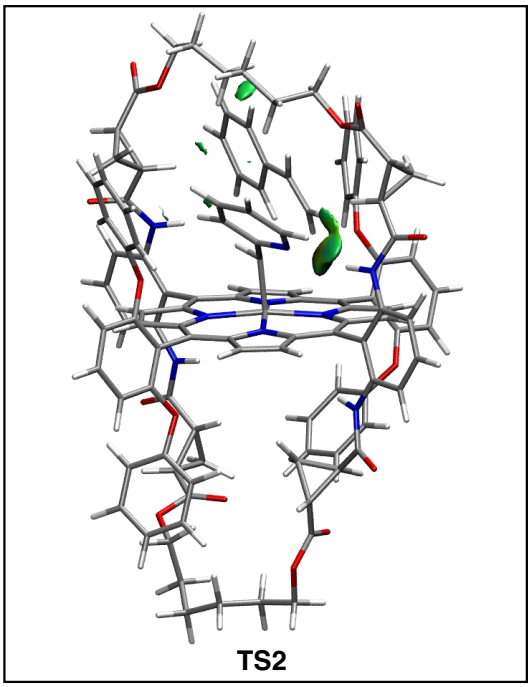

TS1


Co–C: 1.88 Å
3.34 Å
2.96 Å
2.35 Å
Intermediate C

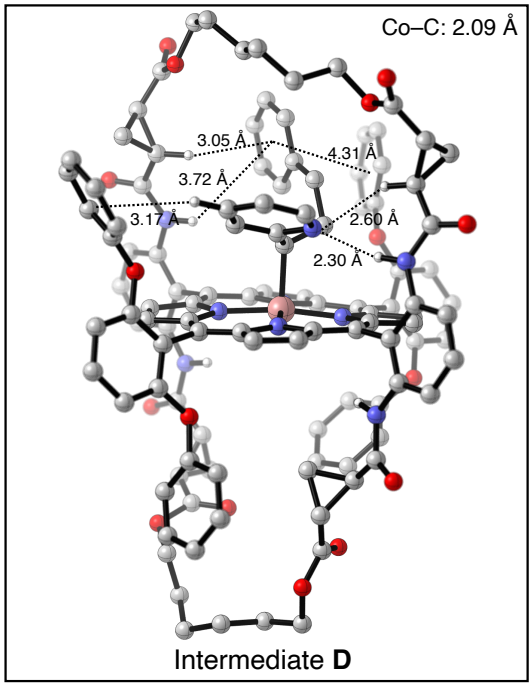

Intermediate C



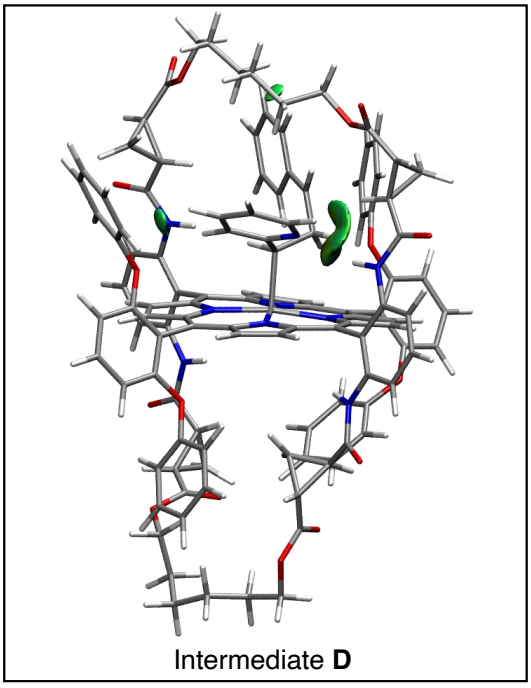
TS2



TS2



Intermediate **D**



Intermediate **D**

Intermediate A

$A_{[Co(II)(P9)]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.446803 Hartree
H_corr: 1.724596 Hartree
SCF: -6888.38 Hartree
S: 584.663 Cal/Mol-Kelvin
H: -6886.65 Hartree
G: -6886.93 Hartree

Cartesian Coordinates:

C	0.45453300	0.59833800	2.92526100
N	0.54431300	-0.38619100	1.91803000
H	0.70270100	0.58058900	5.17005600
C	0.84728900	-1.57778600	2.61219600
C	0.99378700	-1.31621100	4.03601300
H	1.24931300	-2.07281900	4.77625900
C	0.71910800	0.02050600	4.23591100
C	0.88265900	-2.86590800	2.05348500
N	0.30133100	-2.10742500	-0.26681500
C	-0.02387500	-2.83312800	-1.43287000
C	0.00157500	-4.26642200	-1.17057400
H	-0.22957100	-5.03257300	-1.90896200
C	0.38563800	-4.42702100	0.14283500
H	0.52367900	-5.35342700	0.69818300
C	0.55992400	-3.09630500	0.70589000
C	0.18577400	1.96713800	2.71984200
H	0.08238800	5.06271400	-0.75069900
C	0.10799800	4.13166800	-0.18663700
C	0.22260900	2.80945400	-0.78531500
H	-0.07461600	4.71056700	1.95738900
N	0.23772100	1.81268500	0.21287200
C	0.12943800	2.52459400	1.42702100
C	0.02620700	3.95622700	1.17810200
C	-0.25691700	-2.28431200	-2.71035100
H	0.06146800	1.80345000	-4.91702400
C	0.03537900	1.03586000	-4.14532400
C	-0.17387900	-0.31962800	-4.29306700
H	-0.34010700	-0.88846900	-5.20761800
C	-0.12328300	-0.90406400	-2.95903600
N	0.10530000	0.09324200	-1.98581800
C	0.17405500	1.29711300	-2.72021500

C	0.24676100	2.58883400	-2.17217700
Co	0.30272300	-0.14744900	-0.03162600
C	0.22270900	3.78038300	-3.08707900
C	1.39852400	4.53231900	-3.36757300
C	-0.99382400	4.22311000	-3.67217200
C	1.36768500	5.67720100	-4.20054000
C	-1.05063100	5.35070100	-4.52694600
C	0.13786400	6.07050300	-4.77744800
H	0.10914300	6.94955100	-5.43104900
C	1.15893900	-4.04829400	2.93957500
C	0.14256900	-4.60155400	3.76567800
C	2.42916100	-4.68958500	2.94798500
C	0.36957500	-5.74060000	4.57644300
C	2.68460800	-5.83132800	3.74667900
C	1.64611700	-6.34307700	4.55611000
H	1.82973000	-7.23552900	5.16481200
C	-0.06214400	2.85747700	3.91328700
C	1.00586500	3.51477700	4.59714300
C	-1.40451300	3.07287700	4.36097500
C	0.74362800	4.34691200	5.71963700
C	-1.67070600	3.89834400	5.48620100
C	-0.58969700	4.51777300	6.14697900
H	1.57500500	4.84533700	6.21976300
H	-2.70354800	4.04741800	5.80508100
H	-0.79164200	5.15692400	7.01415600
C	-0.63158200	-3.23199700	-3.82439000
C	-2.00575500	-3.54285900	-4.06420400
C	0.37078900	-3.90519600	-4.58989600
C	-2.36702700	-4.55273700	-4.99620600
C	0.01429800	-4.90950200	-5.52928500
C	-1.34994100	-5.22412400	-5.70567900
H	-3.41989600	-4.80423100	-5.13206500
H	0.80007200	-5.42644000	-6.08230600
H	-1.62696100	-6.00787000	-6.41999600
N	2.32728800	3.30688300	4.09648400
H	2.39226300	2.65149500	3.30969000
N	1.72425700	-3.51096600	-4.37410800
H	1.84466200	-2.72110900	-3.73075800
N	-2.98532800	-2.77981800	-3.36236100
H	-2.63235400	-1.93966000	-2.89204400
N	-2.44569400	2.44709300	3.61470500
H	-2.12384300	1.85208500	2.84385400
C	3.51015900	3.91771300	4.51010900

C 2.88496800 -4.03863100 -4.93941600
C -4.34793300 -3.05038600 -3.21146500
C -3.82250900 2.66222400 3.69515700
O -4.90658900 -4.12249900 -3.60287600
O -4.38726000 3.38638800 4.57426100
O 2.91736600 -5.05932500 -5.69781500
O 3.58458900 4.77810500 5.44481600
C -4.60116400 2.01629700 2.57442800
H -4.12655300 1.20693600 2.00836700
C -5.11273600 -1.94553900 -2.51983200
H -4.72674800 -0.92479000 -2.62211200
C -5.84374400 -2.24989400 -1.19592800
H -5.89916900 -1.44525900 -0.45662400
H -5.77401500 -3.26936400 -0.80504700
C -6.64482400 -2.08951100 -2.50974700
H -7.03567400 -3.01296200 -2.94505400
C -5.52947200 2.94927200 1.77500100
H -5.57795800 3.99352100 2.09469800
H -5.62558500 2.75802100 0.70288800
C -6.13151400 1.91165200 2.75158900
H -6.54231000 2.29877000 3.68668700
C -7.49491200 -0.87953500 -2.69158200
C -6.84635100 0.76231900 2.12986100
O -6.42026100 0.05957900 1.17663000
O -7.12061200 0.32092300 -2.65619700
O -8.10708000 0.60001800 2.71347100
O -8.82421000 -1.26702700 -2.89873400
C -9.07868800 -0.31649200 2.02755800
H -8.55420000 -0.82147900 1.19792800
H -9.38011000 -1.05805600 2.78785300
C -10.26768900 0.53683200 1.55157800
H -10.77102700 0.97088100 2.43668200
H -9.87576400 1.38881700 0.96430900
C -9.84635500 -0.17478200 -2.99195600
H -10.68669500 -0.66215300 -3.51467100
H -9.43222300 0.64399900 -3.60806300
C -10.24894200 0.32924700 -1.59422800
H -9.37472600 0.83178200 -1.14096900
H -11.03047200 1.10659700 -1.73356500
C -11.30276100 -0.25932100 0.70793700
H -11.68168800 -1.11629300 1.30292500
H -12.17535400 0.40261700 0.53060500
C -10.78670000 -0.78547600 -0.66126800

H -9.99548800 -1.54549500 -0.51260900
H -11.62122100 -1.31176900 -1.16943300
C 4.74507700 3.48661500 3.75580400
H 4.65432100 2.68717400 3.01304400
C 4.13696600 -3.27208100 -4.59453200
H 4.03581200 -2.34764500 -4.01717500
C 5.28645500 -3.33332100 -5.60286200
H 5.89930300 -2.43678300 -5.71730500
H 5.10722600 -3.93837400 -6.49596200
C 6.07771100 3.61240100 4.49947600
H 6.84844600 2.87359600 4.27089300
H 6.01636700 3.97462800 5.52941700
C 5.74982300 4.64294100 3.40885400
H 5.43593700 5.63641700 3.74001300
C 5.41860000 -4.11595100 -4.28338800
H 5.30236200 -5.20147100 -4.33590800
C 6.48105500 4.64539900 2.10922800
C 6.36100900 -3.64743100 -3.22702400
O 6.99962800 3.38364500 1.78888300
O 6.43303300 -2.24719500 -3.19104300
O 7.03130500 -4.39308500 -2.46877700
O 6.65058800 5.65689100 1.38049400
C 7.89458500 3.32081500 0.58403800
H 7.31822100 3.64907900 -0.30056300
H 8.72479400 4.03209300 0.74951500
C 8.37522400 1.87069200 0.46950900
H 9.26001800 1.85038700 -0.19991500
H 8.72434300 1.53467900 1.46618600
C 7.39776300 -1.63313100 -2.22496800
C 7.29642800 0.90354100 -0.07570100
H 6.34083800 1.07834100 0.45717900
H 7.10626900 1.14275500 -1.14300900
C 7.68973400 -0.58934300 0.07361100
H 7.59854700 -0.88255400 1.13722900
H 8.76197700 -0.72329800 -0.18862600
C 6.81992000 -1.53624800 -0.80246500
H 5.78314400 -1.14851900 -0.85224000
H 6.77384100 -2.54656100 -0.36092800
H 7.58504300 -0.63689100 -2.66056500
H 8.32645600 -2.23354100 -2.23113100
H 2.27919900 6.25130700 -4.38790700
H -1.99908300 5.64669200 -4.98452800
H 3.66299600 -6.31841700 3.72037800

H	-0.43868700	-6.15812700	5.18321700
O	2.56044900	4.07333600	-2.70659300
O	-2.11939700	3.40233100	-3.42673000
O	3.37743700	-4.13756900	2.05691100
O	-1.13015300	-3.99836000	3.63148000
C	3.83934400	4.65591000	-2.96651900
C	4.43915200	4.57439500	-4.24492100
C	4.52543700	5.20623100	-1.86240000
C	5.75078600	5.07823500	-4.41430500
H	3.89726300	4.11765100	-5.08018300
C	5.84091600	5.69871700	-2.04102100
H	4.03445600	5.23877200	-0.88488700
C	6.45182600	5.64162600	-3.31838900
H	6.22561800	5.02224100	-5.40080200
H	6.37251200	6.11780500	-1.17920000
H	7.46725600	6.02943200	-3.45852800
C	-3.39490200	3.93438700	-3.07816400
C	-3.59883800	5.24598200	-2.58678700
C	-4.46195400	3.01122500	-3.16820100
C	-4.90558800	5.62966600	-2.19863900
H	-2.76473400	5.94821300	-2.49193600
C	-5.75741700	3.40230100	-2.76291300
H	-4.26488500	1.99996400	-3.53618500
C	-5.98531300	4.71780200	-2.28461700
H	-5.07159600	6.64431800	-1.81737100
H	-6.56704500	2.66670100	-2.81049600
H	-6.99060100	5.02592600	-1.97527700
C	4.75907100	-4.49153200	2.13421500
C	5.50146600	-4.33867600	3.32938900
C	5.37757800	-4.88371500	0.92764300
C	6.88992000	-4.61019000	3.30763500
H	5.00772500	-4.00610400	4.24880900
C	6.76998200	-5.13908400	0.91505900
H	4.77451000	-4.97440200	0.01913300
C	7.52630400	-5.01160700	2.10617200
H	7.47417400	-4.49742400	4.22845500
H	7.24941900	-5.42201900	-0.02789700
H	8.60309300	-5.21477700	2.09679600
C	-2.09531200	-4.04946500	4.67733200
C	-3.43978000	-4.19450800	4.26864200
C	-1.75743900	-3.85273600	6.03777600
C	-4.46393300	-4.15253800	5.24275900
H	-3.66128600	-4.32899000	3.20523400

C	-2.79258400	-3.81820700	7.00096100
H	-0.71306900	-3.71726900	6.33744200
C	-4.14583300	-3.96944000	6.61095800
H	-5.50885500	-4.26257400	4.93124700
H	-2.53909800	-3.66129500	8.05578600
H	-4.94211600	-3.93689400	7.36269600

A_{1a}'
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.067656 Hartree
H_corr: 0.108155 Hartree
SCF: -396.0115859 Hartree
S: 85.238 Cal/Mol-Kelvin
H: -395.9034309 Hartree
G: -395.9439299 Hartree

Cartesian Coordinates:

C	2.57926300	0.43134200	0.00000700
C	1.56870200	1.42638700	0.00000300
N	-3.48625600	0.61552000	0.00004900
C	2.17819700	-0.92610900	-0.00013800
C	0.21418400	1.03738700	-0.00000700
N	-2.53428400	-0.09550900	-0.00005700
H	3.64119200	0.69633600	0.00001400
H	1.83528600	2.48929500	-0.00007500
C	-0.10042800	-0.35681900	0.00029700
N	0.87594700	-1.33194500	0.00005600
C	-1.46813200	-0.87918300	-0.00022700
H	2.92233500	-1.73186400	0.00003600
H	-0.58210000	1.79040200	-0.00018000
H	-1.63528000	-1.95865900	0.00025200

Intermediate B
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.541374 Hartree
H_corr: 1.834124 Hartree
SCF: -7284.429555 Hartree
S: 616.146 Cal/Mol-Kelvin
H: -7282.595431 Hartree
G: -7282.888181 Hartree

Cartesian Coordinates:

N	3.25355500	1.58381100	0.79717700
N	3.02586800	0.49842300	0.38144600
C	-0.17518400	2.29141200	1.97752700
N	-0.24465300	0.91635200	1.66122700
H	-0.44785800	3.49031500	3.87100000
C	-0.54340100	0.29023500	2.89197100
C	-0.66453700	1.27533100	3.95551900
H	-0.89284200	1.03743200	4.99309800
C	-0.43952700	2.51223200	3.39215300
C	-0.72068100	-1.08805800	3.09569000
N	-0.48025900	-1.69299100	0.67154900
C	-0.59905300	-2.92881800	0.00588200
C	-0.83262800	-4.00790700	0.95630200
H	-0.94831600	-5.05510000	0.68095300
C	-0.86399700	-3.43811500	2.20976100
H	-1.01102000	-3.92544600	3.17253700
C	-0.66761400	-2.00704000	2.03576200
C	0.11250600	3.33740100	1.07954900
H	1.17846700	4.03757100	-3.38710000
C	0.90802300	3.56472900	-2.44468000
C	0.67845000	2.13747800	-2.27354800
H	0.79158100	5.21479000	-0.95298400
N	0.35413600	1.84392600	-0.93143200
C	0.37744400	3.09980100	-0.28121700
C	0.71556300	4.16109700	-1.21889200
C	-0.50956100	-3.13899200	-1.38434600
H	0.62993500	-0.88406000	-5.28457900
C	0.39292800	-1.11196000	-4.24770200
C	-0.00293500	-2.31676600	-3.70936700
H	-0.14341100	-3.27280200	-4.21205100
C	-0.18930000	-2.10403500	-2.28078700
N	0.05701600	-0.75613300	-1.93880200
C	0.41586300	-0.14174300	-3.16191700
C	0.73662600	1.21580600	-3.33648100
Co	-0.05803000	0.06903600	-0.13125200
C	1.14551800	1.71516400	-4.69407600
C	2.48388900	2.16387900	-4.91840100
C	0.25935000	1.76833200	-5.81070200
C	2.91305900	2.66858400	-6.16854600
C	0.67377400	2.24981800	-7.07443900
C	1.99771100	2.70571500	-7.24417700
H	2.32131500	3.09486800	-8.21575000

C	-1.05900400	-1.57669000	4.47729000
C	-2.39613200	-1.94051400	4.81323100
C	-0.09217200	-1.65939700	5.51565800
C	-2.75529500	-2.38057900	6.11017700
C	-0.42520600	-2.07610400	6.82848200
C	-1.75903900	-2.43986900	7.10910700
H	-2.02826600	-2.76336400	8.12075600
C	0.10234800	4.75329200	1.60453500
C	1.28268300	5.36605500	2.13467500
C	-1.12317700	5.49547500	1.61536800
C	1.22397200	6.67687200	2.68712500
C	-1.18133300	6.79986700	2.17541000
C	-0.00477600	7.36537200	2.70440000
H	2.13260400	7.12187800	3.09285500
H	-2.13329000	7.33201400	2.19006200
H	-0.04444800	8.37102100	3.13843800
C	-0.80666200	-4.52237200	-1.90449300
C	-2.17223500	-4.93612500	-2.01532000
C	0.22743600	-5.44577600	-2.25130700
C	-2.50703200	-6.26157600	-2.39403800
C	-0.10744500	-6.76984700	-2.65372100
C	-1.46306400	-7.15833600	-2.70332800
H	-3.55611200	-6.56016700	-2.43670700
H	0.69260600	-7.45963900	-2.92498000
H	-1.71037100	-8.18386100	-3.00099000
N	2.50959700	4.63060900	2.08489300
H	2.46508800	3.70155500	1.64535600
N	1.58222500	-4.99674300	-2.17785500
H	1.75584500	-4.09730600	-1.69354900
N	-3.16547500	-3.93984500	-1.78776700
H	-2.80696800	-2.98023000	-1.73683700
N	-2.27152300	4.88540500	1.02333400
H	-2.09989700	3.98079500	0.57081600
C	3.75809400	5.04783000	2.55220300
C	2.69965600	-5.61732200	-2.74336400
C	-4.53743300	-4.08845800	-1.58347500
C	-3.56768900	5.39494300	0.93802000
O	-5.13341100	-5.20529500	-1.47034500
O	-3.95487500	6.47555000	1.48780400
O	2.68488500	-6.76102100	-3.30410800
O	3.97152900	6.16132000	3.13355300
C	-4.50869800	4.58338300	0.08199000
H	-4.15395000	3.63787500	-0.34294900

C -5.25271900 -2.76191500 -1.49677700
H -4.77486300 -1.91050600 -1.99533200
C -6.06318900 -2.40917900 -0.23475500
H -6.04415700 -1.36375200 0.08567700
H -6.11962800 -3.15342600 0.56375900
C -6.78881400 -2.76165400 -1.55344800
H -7.28094200 -3.73739600 -1.58107500
C -5.51150700 5.38937200 -0.75582900
H -5.45896200 6.47694400 -0.65926500
H -5.78785600 4.98560800 -1.73344100
C -6.01624800 4.62742700 0.48250200
H -6.26264300 5.21416300 1.36981900
C -7.44554100 -1.66425100 -2.32518700
C -6.83024200 3.40563100 0.23127800
O -6.66886500 2.60715000 -0.73048900
O -6.86266900 -0.67794700 -2.84452900
O -7.83263200 3.25748500 1.19259600
O -8.82459300 -1.86203100 -2.39223100
C -8.79442300 2.12338700 0.97241700
H -8.23366100 1.26791100 0.55742800
H -9.16022900 1.89051100 1.98643200
C -9.93094900 2.57179700 0.03778100
H -10.41413400 3.46671200 0.47569700
H -9.49521800 2.87906800 -0.93103000
C -9.61757000 -0.81228700 -3.12026700
H -10.56637200 -1.33182000 -3.33701600
H -9.08711600 -0.56912400 -4.05887200
C -9.83419500 0.45153200 -2.26927000
H -8.86430100 0.96358400 -2.13250600
H -10.47507900 1.13196900 -2.87083800
C -11.00666600 1.47257500 -0.18912800
H -11.45881100 1.19555400 0.78627600
H -11.82304900 1.92090100 -0.79204300
C -10.51421600 0.18150600 -0.90271400
H -9.81661300 -0.38103500 -0.25181400
H -11.38921700 -0.48416100 -1.05464200
C 4.90037300 4.08526300 2.33070500
H 4.70222800 3.14339200 1.81449200
C 3.96610500 -4.80314100 -2.67683400
H 3.92518900 -3.83228100 -2.17522700
C 4.94145100 -4.95930700 -3.84821300
H 5.51095800 -4.07471000 -4.14123800
H 4.63723200 -5.64763600 -4.64161600

C	6.02283200	4.11176500	3.37866500
H	6.54559000	3.17249400	3.57191100
H	5.87376000	4.78644500	4.22623300
C	6.27474100	4.78412100	2.02732400
H	6.21360800	5.87565900	1.99741900
C	5.29594800	-5.61119200	-2.50120800
H	5.18205600	-6.69636700	-2.43348700
C	7.21858500	4.21718300	1.02206100
C	6.38830300	-5.05488900	-1.65441500
O	7.56377300	2.88297500	1.28483600
O	6.50209300	-3.66221000	-1.81106500
O	7.14076100	-5.72399800	-0.90346000
O	7.69504000	4.85876500	0.04948700
C	8.62929200	2.30851300	0.39604300
H	8.26619100	2.33548600	-0.64811700
H	9.51692300	2.96273900	0.47736300
C	8.91042800	0.88125900	0.87462900
H	9.85610300	0.54835900	0.39745000
H	9.09394300	0.89402400	1.96742100
C	7.58696200	-2.98115400	-1.04233900
C	7.78652500	-0.12239100	0.52495900
H	6.83003000	0.22963600	0.95943800
H	7.64564200	-0.12362400	-0.57604600
C	8.07830400	-1.56285300	1.02154000
H	7.97991700	-1.59539400	2.12465800
H	9.13505700	-1.82780700	0.80030600
C	7.13566000	-2.62356200	0.38586700
H	6.10292100	-2.22467500	0.34873300
H	7.11156700	-3.54486300	0.99557700
H	7.79425300	-2.08020700	-1.64371600
H	8.47366600	-3.64129100	-1.02303200
H	3.93892000	3.02498600	-6.29672900
H	-0.05127300	2.25702600	-7.89318700
H	0.33671100	-2.10098400	7.61221900
H	-3.78914700	-2.65729100	6.33394600
O	3.33460900	2.09636700	-3.78674900
O	-1.03864400	1.20347700	-5.77110000
O	1.20936800	-1.20997700	5.17151600
O	-3.33145900	-1.82645200	3.75883700
C	4.74551900	2.28643800	-3.90891900
C	5.53561600	1.45262800	-4.73514600
C	5.32867300	3.26400400	-3.07343700
C	6.93969400	1.62752200	-4.73399600

H	5.06372700	0.68297400	-5.35530500
C	6.73565200	3.42261200	-3.07191000
H	4.68420700	3.87844100	-2.43688600
C	7.54146500	2.61032400	-3.90829500
H	7.56146400	0.99034000	-5.37370100
H	7.19248000	4.17403600	-2.41741200
H	8.62947600	2.74213900	-3.91649100
C	-2.04657800	1.65677300	-4.86719100
C	-2.06921400	2.96353300	-4.33186500
C	-3.08884400	0.73600800	-4.61532100
C	-3.15383700	3.33661900	-3.50076200
H	-1.26994900	3.67558300	-4.56284300
C	-4.16874000	1.12502800	-3.79152300
H	-3.03853600	-0.26017600	-5.06732400
C	-4.20096300	2.42462600	-3.22338600
H	-3.17669900	4.34948100	-3.07958900
H	-4.98947000	0.42793400	-3.58909800
H	-5.04023100	2.70266400	-2.57579100
C	2.34954500	-1.61006400	5.92128600
C	3.31570300	-0.60732600	6.16446500
C	2.57422400	-2.95445800	6.30750900
C	4.52404800	-0.95552500	6.81316000
H	3.10734100	0.42009000	5.84902800
C	3.78346200	-3.28572000	6.96297400
H	1.82498000	-3.72366900	6.09375500
C	4.76130500	-2.29215900	7.21864800
H	5.27440100	-0.18076600	7.00742700
H	3.96231900	-4.32345700	7.26736000
H	5.69522700	-2.55688400	7.72638700
C	-4.70613300	-2.13549900	4.00746200
C	-5.19216800	-3.40738300	3.63387400
C	-5.55965400	-1.13778300	4.52854500
C	-6.57094400	-3.68708600	3.79447100
H	-4.50228700	-4.14873100	3.21770400
C	-6.93556100	-1.43035300	4.68611900
H	-5.15075200	-0.15649600	4.79151400
C	-7.44261400	-2.70295800	4.32291100
H	-6.96064300	-4.66964500	3.50521900
H	-7.60821900	-0.66429000	5.08848900
H	-8.50881400	-2.92424400	4.44539700
C	2.99245400	-1.91574100	0.73082900
C	3.42946500	-1.85590600	2.08704800
C	3.69842300	-3.05411300	2.77479600

H	3.54292400	-0.89153300	2.59335700
C	3.05448100	-4.26527800	0.77262600
C	3.51463200	-4.28930500	2.10678400
H	4.03751200	-3.02563100	3.81519800
H	2.87964700	-5.19903800	0.22645600
H	3.71642300	-5.24410100	2.60118900
N	2.79679300	-3.11519300	0.07811500
C	2.73965800	-0.71174100	-0.07138400
H	2.44167400	-0.78844300	-1.12057300

Transition State TS1

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -251.8937 cm^{-1}
G_corr: 1.532815 Hartree
H_corr: 1.83204 Hartree
SCF: -7284.38968422 Hartree
S: 629.772 Cal/Mol-Kelvin
H: -7282.557644 Hartree
G: -7282.856869 Hartree

Cartesian Coordinates:

C	0.13185400	-2.30271800	1.99444800
N	0.00686100	-1.81576200	0.67215200
H	-0.13402700	-4.32252000	2.96338600
C	-0.34757400	-2.95377000	-0.08529500
C	-0.43441900	-4.13216400	0.76373800
H	-0.69590700	-5.12823900	0.41072200
C	-0.15476200	-3.72834300	2.05082600
C	-0.66019000	-2.96705400	-1.45627500
N	-0.57926800	-0.46905200	-1.69054600
C	-0.88086400	0.37442600	-2.78030300
C	-1.22773300	-0.40882500	-3.95781800
H	-1.49725900	0.01927000	-4.92209000
C	-1.13839400	-1.73520600	-3.59828400
H	-1.32574900	-2.61629700	-4.20978500
C	-0.75630500	-1.77709300	-2.19549700
C	0.49308700	-1.55251700	3.12680300
H	1.92826700	2.72201800	4.26560400
C	1.56248600	1.85915600	3.71110400
C	1.16243100	1.88958600	2.31302800
H	1.47917400	0.17627600	5.17012200
N	0.72657000	0.61682300	1.88714900

C	0.82725200	-0.18903900	3.04079000
C	1.32952100	0.58032400	4.16979900
C	-0.85678400	1.78119600	-2.77339400
H	0.52187200	5.32068300	-0.09803200
C	0.26558700	4.32538900	-0.45756300
C	-0.32996200	3.97030600	-1.64833700
H	-0.65896000	4.61154600	-2.46484500
C	-0.42837300	2.51766100	-1.65539900
N	0.04547800	1.97856900	-0.44252600
C	0.50431600	3.09886100	0.28595900
C	1.09106700	3.07105800	1.55982800
Co	0.21101400	0.06610700	0.04393400
C	1.56622100	4.35783300	2.17248100
C	2.91611200	4.78279700	2.04780500
C	0.68005400	5.19659000	2.90257700
C	3.37227000	5.99988200	2.61154300
C	1.11085500	6.41098200	3.49024300
C	2.45888200	6.80109100	3.33139900
H	2.80293100	7.74143100	3.77635400
C	-1.01792300	-4.27877200	-2.09971500
C	-2.37045100	-4.58593100	-2.43445600
C	-0.05218400	-5.29510300	-2.34756300
C	-2.74414500	-5.82605400	-3.00700300
C	-0.40145500	-6.55340200	-2.89585500
C	-1.74992600	-6.80247700	-3.22789500
H	-2.02962800	-7.77058700	-3.65795700
C	0.45919700	-2.21243900	4.48138900
C	1.60129500	-2.86405500	5.03963400
C	-0.76348800	-2.18406300	5.22639900
C	1.51228100	-3.48128700	6.31988100
C	-0.84983000	-2.79105200	6.50654700
C	0.29372200	-3.43154700	7.02795300
H	2.38954400	-3.98518800	6.72709200
H	-1.79188700	-2.74878000	7.05599700
H	0.23482700	-3.90568100	8.01446800
C	-1.25157300	2.50936000	-4.03020500
C	-2.63468200	2.66510000	-4.35765600
C	-0.25898600	3.03528500	-4.91744000
C	-3.02505300	3.25660000	-5.58858500
C	-0.65188300	3.64912300	-6.13923700
C	-2.02350200	3.73360800	-6.45971700
H	-4.08529200	3.33088200	-5.83615500
H	0.11586900	4.05111500	-6.80176000

H -2.31919700 4.19407600 -7.40947600
N 2.81140200 -2.85638400 4.28065800
H 2.79790800 -2.32213000 3.39991600
N 1.11146000 2.92804900 -4.53099100
H 1.33302200 2.30443400 -3.73334100
N -3.58773900 2.26867700 -3.37191800
H -3.20314400 2.04702300 -2.44683600
N -1.87474700 -1.53088100 4.61605300
H -1.69356700 -1.16517800 3.67536600
C 4.00997400 -3.49902700 4.59825200
C 2.19597600 3.62447200 -5.07114400
C -4.97861500 2.18807500 -3.48382700
C -3.15215800 -1.30434100 5.12628300
O -5.60853000 2.28044500 -4.58141700
O -3.54515000 -1.66757200 6.28015000
O 2.13989400 4.36833600 -6.10333400
O 4.18500800 -4.22434100 5.63052300
C -4.05568500 -0.55543700 4.17785200
H -3.68876800 -0.34731700 3.16633800
C -5.66682100 2.01792600 -2.14014700
H -5.56991200 2.87791100 -1.46431300
C -5.79460200 0.65428300 -1.44190000
H -5.76259000 0.63566000 -0.34774500
H -5.39895300 -0.23497300 -1.94207900
C -7.03036000 1.32111400 -2.11238800
H -7.38413900 0.88898700 -3.05130000
C -5.01541100 0.48123900 4.77511400
H -4.98354400 0.61267200 5.86010000
H -5.22738400 1.36659500 4.16965800
C -5.57623100 -0.86572700 4.27912000
H -5.87352500 -1.58756200 5.04279700
C -8.08931400 1.89137600 -1.23312100
C -6.36949300 -0.86611600 3.01685000
O -6.10094600 -0.20758300 1.97886800
O -7.91109400 2.67521000 -0.26665200
O -7.48730200 -1.69551900 3.15248700
O -9.35251700 1.42447000 -1.62537400
C -8.49006900 -1.71401800 2.03665200
H -8.09365800 -1.11289200 1.20036100
H -8.57209700 -2.77295000 1.73329800
C -9.82235700 -1.17693100 2.58502900
H -10.08544000 -1.75485300 3.49201200
H -9.68147800 -0.12765200 2.90697600

C	-10.51624800	1.88393100	-0.79896800
H	-11.37782800	1.73175800	-1.47128600
H	-10.38424500	2.95832500	-0.57666200
C	-10.64144600	1.06402400	0.49737900
H	-9.75496900	1.27048600	1.12441300
H	-11.52358000	1.44927600	1.05212000
C	-10.98770300	-1.27930500	1.56134000
H	-11.14214000	-2.34617400	1.29552400
H	-11.91769800	-0.94922900	2.06844100
C	-10.80602800	-0.45682900	0.25533300
H	-9.93406400	-0.82854500	-0.31736600
H	-11.69172300	-0.62631400	-0.39206800
C	5.13005800	-3.28748900	3.60964800
H	4.95934000	-2.61109400	2.76815100
C	3.48113100	3.44723000	-4.30176700
H	3.45122700	2.82678100	-3.40106600
C	4.47752500	4.60756100	-4.33481000
H	5.06827400	4.78550800	-3.43371300
H	4.17822300	5.48390200	-4.91670500
C	6.08513300	-4.46873800	3.38581600
H	6.51739400	-4.57335400	2.38803900
H	5.86037500	-5.38775800	3.93432100
C	6.56378200	-3.28339500	4.23660100
H	6.58315800	-3.43687300	5.31902600
C	4.79550500	3.34600400	-5.15210400
H	4.66472900	3.41588200	-6.23544500
C	7.62068300	-2.35290900	3.74851900
C	5.86193200	2.39431600	-4.72946200
O	7.64129200	-2.23886700	2.34746500
O	6.02886900	2.37930100	-3.33354800
O	6.54659200	1.68573400	-5.50954400
O	8.43834300	-1.75014900	4.48801700
C	8.76443500	-1.41255300	1.79120000
H	8.63837500	-0.37177600	2.14412200
H	9.70945300	-1.80856100	2.20633500
C	8.70804400	-1.52155400	0.26440000
H	9.67111800	-1.13865300	-0.13453000
H	8.65325100	-2.59251300	-0.01636800
C	7.05129400	1.42711300	-2.79198600
C	7.54282700	-0.73720300	-0.38571300
H	6.58271300	-1.05691500	0.06393300
H	7.65860000	0.33954900	-0.14297500
C	7.48172700	-0.93856900	-1.92268300

H	7.19909000	-1.98949100	-2.13293500
H	8.49568200	-0.80110900	-2.35795500
C	6.47935200	0.00634400	-2.64300100
H	5.53136800	0.05022700	-2.07271000
H	6.24665300	-0.38599200	-3.64978600
H	7.31691600	1.86830100	-1.81769300
H	7.92463800	1.42977800	-3.47055500
H	4.41160100	6.31428700	2.48309300
H	0.41255200	7.02634300	4.06427200
H	0.36067000	-7.32201100	-3.04836500
H	-3.78824300	-6.02230600	-3.26509400
O	3.74079500	3.94621100	1.25657500
O	-0.62551400	4.68000100	3.07209000
O	1.27200500	-4.98985400	-1.93869500
O	-3.30551600	-3.55535500	-2.18262600
C	5.16150800	4.00502900	1.38639500
C	5.90695600	4.08710400	0.19051700
C	5.79612300	3.88066900	2.64526700
C	7.32072800	4.06810600	0.26165600
H	5.38236300	4.15384200	-0.76745900
C	7.20896600	3.86172100	2.70074200
H	5.19863400	3.79092400	3.55860600
C	7.97565900	3.96157700	1.51292700
H	7.90670600	4.14986500	-0.66119100
H	7.70798500	3.76045900	3.67116800
H	9.07017900	3.95283500	1.56318100
C	-1.72766200	5.53901400	3.35920900
C	-2.63169100	5.08852400	4.34582400
C	-1.97191900	6.71972000	2.61858700
C	-3.80052500	5.84310400	4.60252600
H	-2.41324600	4.16257400	4.88712500
C	-3.14197200	7.46628800	2.89000900
H	-1.27197100	7.04080800	1.84001300
C	-4.05782500	7.03423500	3.88078000
H	-4.50793500	5.49962200	5.36577400
H	-3.34214900	8.37898700	2.31712600
H	-4.96516100	7.61449800	4.08123300
C	2.37715000	-5.77028300	-2.39109100
C	3.29900800	-6.18639200	-1.40556900
C	2.60800500	-6.01473900	-3.76697700
C	4.47285100	-6.86809700	-1.80591000
H	3.08985600	-5.97112200	-0.35290800
C	3.78218800	-6.70401700	-4.15119500

H	1.88721900	-5.67390900	-4.51793200
C	4.71653600	-7.13252000	-3.17581000
H	5.19234200	-7.19440600	-1.04657000
H	3.96831700	-6.89834300	-5.21367000
H	5.62493700	-7.66343000	-3.48085900
C	-4.70672600	-3.83410300	-2.24294500
C	-5.46896300	-3.13766700	-3.20524800
C	-5.31154100	-4.69719000	-1.30040200
C	-6.87310100	-3.31874000	-3.22912300
H	-4.96426300	-2.47086100	-3.91180700
C	-6.71425600	-4.87442000	-1.33983000
H	-4.69722800	-5.20711000	-0.55064800
C	-7.49705200	-4.18933000	-2.30272600
H	-7.47456200	-2.78058700	-3.97023300
H	-7.19363200	-5.54177200	-0.61441100
H	-8.58355000	-4.32903200	-2.32770700
C	2.34272700	-0.42549200	-1.99812200
C	2.57506500	-1.81377200	-2.20551600
C	2.98567100	-2.26976000	-3.47544100
H	2.44525000	-2.51487300	-1.37713000
C	2.82216100	0.01909600	-4.26498600
C	3.11816600	-1.33685600	-4.52916100
H	3.19567300	-3.33193800	-3.63580900
H	2.88587700	0.76588500	-5.06430500
H	3.43730200	-1.64168100	-5.53086000
N	2.45525000	0.48604000	-3.03273500
N	3.38535500	-0.71716000	0.48442200
N	3.27481700	-1.31461600	1.48661700
C	2.01738800	0.12022700	-0.64678600
H	2.40649300	1.14524100	-0.50248100

Intermediate C

$C_{[Co(III)(P9)]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.532528 Hartree
H_corr: 1.822339 Hartree
SCF: -7174.84839066 Hartree
S: 609.959 Cal/Mol-Kelvin
H: -7173.026052 Hartree
G: -7173.315863 Hartree

Cartesian Coordinates:

C	-0.26297000	2.46044900	1.74387600
N	-0.30021000	1.05400300	1.61977200
H	-0.55461500	3.90038400	3.45766500
C	-0.53352500	0.59539300	2.93369700
C	-0.66271000	1.71095800	3.85591400
H	-0.85444100	1.60806200	4.92286900
C	-0.51246900	2.86620200	3.11920700
C	-0.68689900	-0.74446000	3.32087500
N	-0.55225400	-1.63935900	0.98128100
C	-0.75015200	-2.93551900	0.47304100
C	-1.05888300	-3.87183600	1.54481400
H	-1.26231700	-4.93107600	1.39641800
C	-1.01468500	-3.16130400	2.72276500
H	-1.18916600	-3.51861000	3.73623500
C	-0.71629600	-1.78058400	2.37841800
C	0.01947700	3.37687000	0.71231800
H	1.32572800	3.45639100	-3.74315400
C	1.01379400	3.11682400	-2.75729600
C	0.82274400	1.72258100	-2.38728700
H	0.73249500	4.96317500	-1.54228900
N	0.41058400	1.61501900	-1.04353700
C	0.35620100	2.95304700	-0.58576900
C	0.71693100	3.87909000	-1.64975900
C	-0.61913200	-3.32966800	-0.87057800
H	0.95328600	-1.69517400	-4.92151200
C	0.63187500	-1.76763000	-3.88509700
C	0.11847200	-2.86224100	-3.22842700
H	-0.05612600	-3.86610600	-3.61270600
C	-0.15438500	-2.44773600	-1.85883900
N	0.15626600	-1.08438900	-1.67778500
C	0.62938500	-0.65868900	-2.94083600
C	0.96211700	0.65785900	-3.29660600
Co	0.06872600	-0.05209000	-0.00277200
C	1.38428900	0.96872000	-4.70569200
C	2.70170000	1.44304800	-4.98851100
C	0.50525000	0.82674700	-5.82140300
C	3.12062200	1.77184800	-6.30006500
C	0.90971600	1.13154200	-7.14127600
C	2.21679700	1.60888700	-7.37312200
H	2.53483400	1.86075800	-8.39071800
C	-0.89923300	-1.05836900	4.77534700
C	-2.19693100	-1.31500200	5.29968700
C	0.18784400	-1.09243800	5.69159700

C	-2.41032700	-1.61115700	6.66817800
C	0.00403800	-1.37484200	7.06751300
C	-1.30014400	-1.63679300	7.54027400
H	-1.45381000	-1.86060900	8.60182600
C	-0.02375600	4.85087200	1.04041200
C	1.14019700	5.53506500	1.51462100
C	-1.25246400	5.57806900	0.93726500
C	1.06677400	6.89510400	1.92188300
C	-1.32833600	6.93666800	1.34930200
C	-0.16870800	7.56813600	1.84064600
H	1.96365600	7.38746000	2.29894100
H	-2.28317000	7.45969400	1.28356400
H	-0.22733000	8.61401400	2.16284900
C	-0.89457200	-4.77036800	-1.20944100
C	-2.24310200	-5.23769700	-1.29123900
C	0.17583700	-5.69842200	-1.39919400
C	-2.52847500	-6.61175000	-1.50137600
C	-0.10737600	-7.07482800	-1.62306600
C	-1.45022600	-7.50782300	-1.65898100
H	-3.56710900	-6.94596800	-1.53232300
H	0.72011900	-7.76945100	-1.77155000
H	-1.66004600	-8.57132800	-1.82134500
N	2.37127300	4.80845500	1.54424100
H	2.32892600	3.86520800	1.14365700
N	1.51004500	-5.18705700	-1.36397200
H	1.62111300	-4.21488000	-1.02281000
N	-3.26801400	-4.25154200	-1.20233000
H	-2.93094400	-3.28285900	-1.21800100
N	-2.38008000	4.89908900	0.38391500
H	-2.19411700	3.95166100	0.03704400
C	3.60747900	5.24235500	2.02254400
C	2.65045300	-5.81903700	-1.86659800
C	-4.64482300	-4.41790400	-1.06014600
C	-3.67170400	5.39560700	0.19484000
O	-5.22803200	-5.53837800	-0.91420800
O	-4.07502600	6.52624500	0.61673200
O	2.68676400	-7.03445800	-2.24618300
O	3.80239000	6.36988900	2.58026100
C	-4.57791800	4.50314800	-0.61516300
H	-4.20915400	3.52011500	-0.92820900
C	-5.39498100	-3.11061800	-1.08710300
H	-4.86290500	-2.23579700	-1.47831300
C	-6.43423900	-2.81324400	0.01009000

H -6.50509500 -1.77978500 0.36030900
H -6.61041600 -3.59172100 0.75757100
C -6.89636600 -3.14733200 -1.42481300
H -7.35050600 -4.13348300 -1.55415900
C -5.53829300 5.22397300 -1.57324100
H -5.48231000 6.31556000 -1.58361600
H -5.77199800 4.72417800 -2.51704800
C -6.10220400 4.58916000 -0.29097000
H -6.38444200 5.25819300 0.52449300
C -7.42430300 -2.05504300 -2.29956300
C -6.90786600 3.34714100 -0.45828400
O -6.71754900 2.47113700 -1.34419400
O -6.75796800 -1.09003700 -2.75424300
O -7.93389100 3.27684800 0.48550200
O -8.78167800 -2.23809600 -2.55423800
C -8.87601100 2.11329300 0.34878200
H -8.29194800 1.23065800 0.03482600
H -9.26843300 1.97418800 1.36987800
C -9.98763200 2.45204900 -0.65911300
H -10.50030200 3.37401200 -0.32258300
H -9.52321200 2.67684100 -1.63718700
C -9.44904500 -1.21374700 -3.43112100
H -10.38754900 -1.71929300 -3.71500000
H -8.81181200 -1.05713800 -4.32072200
C -9.71003700 0.11743800 -2.70376900
H -8.74747200 0.63346200 -2.53603500
H -10.29580600 0.74811200 -3.40724500
C -11.03709600 1.31664400 -0.82126400
H -11.53341400 1.13220800 0.15439900
H -11.82791800 1.68732600 -1.50544900
C -10.49344000 -0.03168500 -1.37440100
H -9.84700200 -0.52582000 -0.62269700
H -11.35406000 -0.71515400 -1.52801000
C 4.75569100 4.27865200 1.83467300
H 4.57231400 3.33204900 1.31506200
C 3.86345600 -4.93352900 -2.00233300
H 3.81289100 -3.91380200 -1.61004700
C 4.70380400 -5.15908700 -3.26919800
H 5.18155800 -4.28037500 -3.70751800
H 4.34957600 -5.93419300 -3.95423400
C 5.85404800 4.30398700 2.91129800
H 6.37456400 3.36514600 3.11226200
H 5.67837500 4.97030700 3.76041700

C	6.13510300	4.98246800	1.57110800
H	6.05955100	6.07351300	1.54388200
C	5.24731700	-5.65429900	-1.91919300
H	5.19727700	-6.73066000	-1.73390600
C	7.11406200	4.43856300	0.58349700
C	6.41664000	-4.97893600	-1.28841100
O	7.52189100	3.13061800	0.87588200
O	6.45840700	-3.61146300	-1.60750700
O	7.28912900	-5.54567800	-0.58426500
O	7.56581800	5.08750200	-0.39546100
C	8.62126500	2.59360800	0.00099900
H	8.24463300	2.54534000	-1.03713700
H	9.45709500	3.31617600	0.04129700
C	9.01381200	1.21499500	0.53744900
H	9.96434300	0.92524900	0.04171200
H	9.23305000	1.29345400	1.62103900
C	7.62035600	-2.83163300	-1.07953300
C	7.95167900	0.12127600	0.27809800
H	6.99495100	0.41428800	0.75366800
H	7.75346500	0.07114200	-0.81260800
C	8.37784000	-1.27318900	0.80461800
H	8.43923200	-1.23826300	1.91098700
H	9.40397800	-1.51056600	0.44859600
C	7.40109300	-2.40583300	0.38292800
H	6.35831500	-2.05429900	0.50067100
H	7.52601500	-3.29117800	1.03235500
H	7.66708900	-1.96423800	-1.75873500
H	8.53235700	-3.44879600	-1.18153600
H	4.13173300	2.14907700	-6.47651400
H	0.19124800	0.99002700	-7.95361500
H	0.85847600	-1.37950400	7.74994000
H	-3.41810700	-1.82007700	7.03768900
O	3.54171400	1.59633100	-3.85847000
O	-0.77491900	0.23314700	-5.69183200
O	1.44703500	-0.74091900	5.14786000
O	-3.24257700	-1.32113900	4.34556600
C	4.93771700	1.85279200	-4.01825500
C	5.78537800	0.92607100	-4.66951100
C	5.44988200	3.01526600	-3.40231500
C	7.17400300	1.19234200	-4.72068500
H	5.36737700	0.01807000	-5.11711400
C	6.84254000	3.26597400	-3.44973100
H	4.76375900	3.70000100	-2.89405900

C	7.70468200	2.36005400	-4.11653600
H	7.83952400	0.48421100	-5.22802700
H	7.24472400	4.16152700	-2.96257700
H	8.78087900	2.56184900	-4.16463000
C	-1.82494200	0.84561300	-4.94290000
C	-1.87280500	2.23116100	-4.67239300
C	-2.87647300	-0.01897600	-4.56164200
C	-2.99739900	2.74890400	-3.98373200
H	-1.06331000	2.89219100	-4.99962700
C	-3.99462000	0.51297000	-3.88138700
H	-2.80335300	-1.08391200	-4.80624500
C	-4.05711500	1.89901200	-3.58426900
H	-3.04178700	3.82444200	-3.77130800
H	-4.82246800	-0.13940300	-3.58241400
H	-4.93076500	2.29107900	-3.05112200
C	2.65404600	-1.12381700	5.80058700
C	3.63182500	-0.11795600	5.96382300
C	2.90945800	-2.46647300	6.16651100
C	4.88971700	-0.46361200	6.51281300
H	3.39710000	0.90815900	5.66322700
C	4.16831500	-2.79655400	6.71981200
H	2.14640600	-3.23561900	6.00785200
C	5.16108300	-1.80026000	6.89602400
H	5.65195700	0.31245800	6.64757400
H	4.37520100	-3.83464100	7.00438400
H	6.13395800	-2.06345600	7.32595700
C	-4.59994200	-1.16610700	4.75804000
C	-5.52518200	-2.11922000	4.27978900
C	-5.01718800	-0.04725500	5.51696000
C	-6.89856000	-1.95331300	4.57974600
H	-5.16270100	-2.96473200	3.68656100
C	-6.39192200	0.10395500	5.81207300
H	-4.28429100	0.69197300	5.85715800
C	-7.33524400	-0.84673400	5.34842200
H	-7.62358300	-2.69094100	4.21708800
H	-6.72512500	0.96978400	6.39561900
H	-8.39888800	-0.72352400	5.58095200
C	2.60089100	-1.40053400	1.00166000
C	3.67933500	-1.11888800	1.93038600
C	4.37728600	-2.16284800	2.55447100
H	3.90175800	-0.07573800	2.18098800
C	3.01613300	-3.71573600	1.27665000
C	4.03272600	-3.50384300	2.23870500

H	5.15955900	-1.94289200	3.28942600
H	2.74484500	-4.74060100	0.99200300
H	4.53795900	-4.35491500	2.70499400
N	2.31444300	-2.72697400	0.65225400
C	1.86001100	-0.27153900	0.51946300
H	2.28357500	0.72368500	0.73563700

$C_{[N2]}$
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: -0.013594 Hartree
H_corr: 0.008229 Hartree
SCF: -109.560708554Hartree
S: 45.93 Cal/Mol-Kelvin
H: -109.5524796 Hartree
G: -109.5743026 Hartree

Cartesian Coordinates:

N	0.00000000	0.00000000	0.57307000
N	0.00000000	0.00000000	-0.57307000

$C_{[2a]}$
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.099513 Hartree
H_corr: 0.138461 Hartree
SCF: -309.796492304 Hartree
S: 81.974 Cal/Mol-Kelvin
H: -309.6580313 Hartree
G: -309.6969793 Hartree

Cartesian Coordinates:

C	-1.80367300	-1.06029300	0.00000000
C	-0.41103500	-1.30025800	0.00000000
C	0.52368900	-0.22415100	0.00000000
C	-2.29347400	0.26752500	0.00000000
C	0.01393200	1.10796100	0.00000000
C	-1.37608400	1.34941800	0.00000000
H	-2.50370300	-1.90413500	0.00000000
H	-3.37285400	0.45913400	0.00000000
H	-0.03630000	-2.33249700	0.00000000
H	0.70708900	1.95750300	0.00000000

H	-1.74926300	2.38061400	0.00000000
C	1.97164800	-0.53998900	0.00000000
C	3.01280800	0.33989400	0.00000000
H	2.20893300	-1.61528500	0.00000000
H	2.86955800	1.42734700	-0.00000100
H	4.04967000	-0.01332600	0.00000000

Transition State TS2

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -172.433 cm^{-1}
G_corr: 1.656566 Hartree
H_corr: 1.961559 Hartree
SCF: -7484.66562 Hartree
S: 641.911 Cal/Mol-Kelvin
H: -7482.704061 Hartree
G: -7483.009054 Hartree

Cartesian Coordinates:

H	-3.75529200	5.08463900	-0.12924900
C	-4.42600800	4.21723200	-0.12975800
H	-3.02800200	2.97638200	0.96942400
C	-4.00984600	3.01881100	0.48697200
H	-6.02496000	5.24605300	-1.21324800
C	-5.70587600	4.31392000	-0.73398800
C	-4.86750300	1.87375000	0.51741800
C	-6.56750700	3.19005900	-0.71494400
C	-6.15042400	1.98796100	-0.10200900
C	-4.48855000	0.60693400	1.16345400
H	-7.55708400	3.25693900	-1.18215500
H	-5.20854300	-0.21748500	1.04728100
H	-6.82217000	1.12035200	-0.09172500
C	0.10033100	1.50597500	-2.27684600
N	0.34222400	0.30318600	-1.57519800
H	0.15224000	2.10134800	-4.45449700
C	0.66466800	-0.62820600	-2.58789300
C	0.63215900	0.00016000	-3.89849900
H	0.85396800	-0.51264300	-4.83279700
C	0.27644900	1.31685300	-3.70955100
C	0.99987800	-1.97615100	-2.39006100
N	0.76362300	-1.87494200	0.10954600
C	0.91318500	-2.87029100	1.09293700
C	1.28202900	-4.14468200	0.49315500

H	1.45636600	-5.06103300	1.05497800
C	1.35207100	-3.94118700	-0.86661400
H	1.60002900	-4.65870900	-1.64713200
C	1.02841200	-2.54394600	-1.10819800
C	-0.19657800	2.75642000	-1.70508400
H	-0.49540200	4.81731700	2.44832500
C	-0.40999800	4.06811200	1.66335600
C	-0.23864400	2.64389300	1.90062000
H	-0.55955800	5.18389300	-0.25876200
N	-0.13218700	1.94345600	0.67719000
C	-0.26975900	2.94496100	-0.31175100
C	-0.44657000	4.25498700	0.29882800
C	0.73928600	-2.70350900	2.47716400
H	-0.19497200	0.57821100	5.62181700
C	-0.02887500	0.05602200	4.68202600
C	0.23689000	-1.27885400	4.48527300
H	0.33409600	-2.07032800	5.22681100
C	0.39098500	-1.47150600	3.04942500
N	0.20491000	-0.26076600	2.35419200
C	-0.03097100	0.69209100	3.37120400
C	-0.19978300	2.07424300	3.18705900
Co	0.13492800	-0.02225800	0.38827500
C	-0.31393100	2.96049000	4.39741200
C	-1.53068800	3.63235100	4.72467200
C	0.76864100	3.13158700	5.31135900
C	-1.66380300	4.42690700	5.88926400
C	0.66197500	3.93093400	6.47097300
C	-0.55993000	4.57665800	6.75584200
H	-0.66090800	5.18549000	7.66084900
C	1.36630400	-2.82398500	-3.57799100
C	2.72239900	-3.16303500	-3.85219700
C	0.38772900	-3.31795000	-4.48573500
C	3.09048000	-3.97204400	-4.95512400
C	0.72829600	-4.11238000	-5.60777400
C	2.08338700	-4.43833800	-5.82650200
H	2.35807900	-5.05845000	-6.68696700
C	-0.33600000	3.94483400	-2.62493000
C	-1.54268200	4.18242200	-3.34815400
C	0.78050300	4.81843100	-2.84879100
C	-1.64658400	5.27534300	-4.24791200
C	0.67603400	5.91059000	-3.75131700
C	-0.53883300	6.12492200	-4.43503100
H	-2.57452600	5.43054700	-4.79994300

H	1.54454400	6.55117700	-3.91144700
H	-0.61863400	6.96760400	-5.13087200
C	0.98136600	-3.88536800	3.37396600
C	2.32322800	-4.26085700	3.69465200
C	-0.10635000	-4.63327400	3.91402800
C	2.58609300	-5.40313800	4.49394600
C	0.15350000	-5.77009400	4.73022800
C	1.49043300	-6.13996700	4.99445000
H	3.61955000	-5.68296900	4.70887400
H	-0.68431300	-6.32697700	5.15119700
H	1.68213500	-7.02197000	5.61638500
N	-2.65860100	3.30058200	-3.16014900
H	-2.78118200	2.88780200	-2.22903000
N	-1.43013500	-4.18962300	3.60284700
H	-1.51728400	-3.48157200	2.84687900
N	3.35263100	-3.40304600	3.21121100
H	3.02225800	-2.54518100	2.75530700
N	1.99849500	4.52756500	-2.16214400
H	1.95509000	3.73580100	-1.51161500
C	-3.54839000	2.91552900	-4.16589400
C	-2.59580900	-4.52755100	4.29427100
C	4.73936800	-3.52487300	3.29514200
C	3.23860700	5.15497000	-2.29851500
O	5.35214300	-4.53366900	3.75701600
O	3.46605900	6.13663700	-3.07557300
O	-2.64866100	-5.38299500	5.23639300
O	-3.45669900	3.31123400	-5.37167400
C	4.33290400	4.57607800	-1.43591500
H	4.07884300	3.77765000	-0.72965800
C	5.43372200	-2.25573300	2.81834600
H	5.59601200	-1.51988500	3.61696100
C	5.19526600	-1.67538500	1.42409700
H	5.16300000	-0.58697300	1.32200000
H	4.57777700	-2.23435900	0.71354200
C	6.57125400	-2.31233400	1.78644700
H	6.82518700	-3.27640200	1.34065200
C	5.47550600	5.51677000	-1.04336200
H	5.39569800	6.54643300	-1.40205600
H	5.94049400	5.36045900	-0.06644400
C	5.74108600	4.45142000	-2.11658100
H	5.80025300	4.77907600	-3.15654500
C	7.70671300	-1.36794000	1.99301600
C	6.57146400	3.27269800	-1.73807500

O 6.66563100 2.78698500 -0.57919300
O 7.64640300 -0.29761500 2.65458400
O 7.24728000 2.75686100 -2.84342000
O 8.86337000 -1.80709100 1.34711300
C 8.12454700 1.56329300 -2.58759200
H 7.61733800 0.91167200 -1.85526100
H 8.17273500 1.06557000 -3.57026000
C 9.51506400 2.00563200 -2.10129100
H 9.90445800 2.76839400 -2.80365800
H 9.41641400 2.49125000 -1.11295000
C 10.07772200 -0.93213400 1.49927300
H 10.91377700 -1.63928300 1.36282200
H 10.07834100 -0.52445800 2.52591600
C 10.10845500 0.19948300 0.45777300
H 9.22958400 0.85286200 0.61039800
H 11.00556200 0.81542000 0.68448700
C 10.52628100 0.82706200 -2.02848800
H 10.62616400 0.37708400 -3.03882600
H 11.52220900 1.24691400 -1.77729300
C 10.18993700 -0.29655000 -1.00800100
H 9.24189300 -0.79966900 -1.28078400
H 10.98143800 -1.07231200 -1.07928300
C -4.63609800 1.95365900 -3.75106300
H -4.75357700 1.71726900 -2.68857500
C -3.82784100 -3.76423300 3.87439400
H -3.76212600 -3.11905500 2.99396000
C -4.76943200 -3.31427000 5.00071900
H -5.29453100 -2.36719000 4.85731900
H -4.46969700 -3.56985900 6.02074300
C -5.00540500 0.86964900 -4.78074200
H -5.34198200 -0.09307800 -4.38955600
H -4.41312700 0.85828400 -5.70034700
C -5.94592800 2.06131900 -4.60575900
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C -5.18661100 -4.49736100 4.11006400
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C -7.29566200 1.93551700 -3.98170700
C -6.30852000 -4.36555400 3.13973800
O -7.50046000 0.69267400 -3.35816400
O -6.37387000 -3.07729000 2.57757700
O -7.13022800 -5.27350500 2.85929900
O -8.18687100 2.82052700 -4.02628100
C -8.87374500 0.47412900 -2.79506100

H -9.00548300 1.14946300 -1.92788900
H -9.60922700 0.75849700 -3.56927200
C -8.98037100 -1.00257200 -2.40153300
H -10.03770700 -1.20101100 -2.12734700
H -8.75871100 -1.62688400 -3.28997100
C -7.49124700 -2.83153600 1.61126400
C -8.05511000 -1.40695800 -1.22920500
H -7.00770400 -1.16077100 -1.49386700
H -8.31572200 -0.79104700 -0.34250700
C -8.15193700 -2.91343000 -0.87726300
H -7.96187900 -3.50449800 -1.79639500
H -9.18778300 -3.16071100 -0.56092900
C -7.14276200 -3.36896300 0.21181000
H -6.12642700 -3.02418500 -0.06164900
H -7.11618300 -4.47304600 0.26111800
H -7.59816300 -1.73447800 1.62618100
H -8.40757800 -3.31077400 2.00300600
H -2.62197700 4.89854300 6.12380000
H 1.52971800 4.01374400 7.13152200
H -0.04823000 -4.45897900 -6.29509000
H 4.13927700 -4.22991300 -5.12491300
O -2.62195700 3.36770400 3.86266100
O 1.96379400 2.38102400 5.17971900
O -0.94180800 -2.89519800 -4.23929300
O 3.67245800 -2.68822100 -2.91422000
C -3.78744800 4.19510900 3.88569000
C -5.02982600 3.52826300 3.92458500
C -3.70704300 5.60212100 3.76136900
C -6.21932400 4.29006600 3.85126300
H -5.04845600 2.43622100 3.99306900
C -4.90472700 6.35119900 3.69483100
H -2.73317300 6.10094800 3.71167800
C -6.16221400 5.70061500 3.74249500
H -7.18826900 3.77902600 3.87390000
H -4.85282700 7.44176800 3.59705400
H -7.08636100 6.28638300 3.68536600
C 2.93684400 2.69145300 4.18644000
C 2.88057900 3.84394000 3.37190500
C 4.01283000 1.77794800 4.10159300
C 3.91892700 4.06027200 2.43327200
H 2.05675400 4.55855500 3.46861700
C 5.04354200 2.01142600 3.16488800
H 4.02500200 0.91066400 4.77006600

C	4.99542200	3.14878300	2.31761900
H	3.88060200	4.95233600	1.79582800
H	5.88805700	1.31499900	3.09665600
H	5.78122000	3.30085300	1.57078100
C	-2.04115800	-3.60598600	-4.80019400
C	-3.02987100	-2.83417500	-5.44941600
C	-2.19721200	-5.00075600	-4.61749800
C	-4.19723400	-3.47440400	-5.93069100
H	-2.87304500	-1.75739300	-5.56845700
C	-3.36520600	-5.62854900	-5.10935000
H	-1.42801200	-5.57687700	-4.09269400
C	-4.36761400	-4.87113800	-5.76612900
H	-4.96664100	-2.88289600	-6.43983200
H	-3.49430800	-6.70827300	-4.97185400
H	-5.26980600	-5.36419100	-6.14471400
C	5.05587900	-2.64305900	-3.26729200
C	5.96439400	-3.27346700	-2.39027400
C	5.50223400	-1.91344900	-4.39441100
C	7.35179900	-3.18216700	-2.65500300
H	5.58041900	-3.82350600	-1.52540300
C	6.89029000	-1.83917800	-4.65382300
H	4.77954200	-1.41337000	-5.04779700
C	7.81753600	-2.47397000	-3.78969400
H	8.06362100	-3.66717200	-1.97810700
H	7.24452900	-1.28255200	-5.52924200
H	8.89180300	-2.41716900	-3.99819800
C	-2.27549900	-1.78335100	-0.13297300
C	-3.01611100	-1.98980800	-1.34519700
C	-3.58446900	-3.24522200	-1.63449900
H	-3.10488300	-1.16333800	-2.05796200
C	-2.68721100	-4.02914700	0.47836600
C	-3.40763000	-4.30014900	-0.70831400
H	-4.13421800	-3.40313200	-2.56843500
H	-2.54016700	-4.82378600	1.22079300
H	-3.81617700	-5.29933800	-0.88813600
N	-2.14029200	-2.81730500	0.78986700
C	-1.72280000	-0.44590200	0.11841900
H	-2.10557000	0.32972800	-0.56943200
C	-3.32011800	0.35305800	1.85464300
H	-2.60762700	1.14433400	2.10267100
H	-3.17087100	-0.60570800	2.36013000

Intermediate D

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.661495 Hartree
H_corr: 1.964892 Hartree
SCF: -7484.71001440 Hartree
S: 638.553 Cal/Mol-Kelvin
H: -7482.745122 Hartree
G: -7483.048519 Hartree

Cartesian Coordinates:

H	4.28197000	4.61393800	0.23084300
C	4.81400500	3.67271700	0.04979700
H	3.06491700	2.69452800	-0.77254600
C	4.12212300	2.58351200	-0.51075500
H	6.72735400	4.41765200	0.81336000
C	6.19451200	3.57048300	0.36858300
C	4.79518300	1.33415100	-0.77452600
C	6.88067400	2.35266500	0.11078700
C	6.19811300	1.25705800	-0.44501200
C	4.13134700	0.19783000	-1.34774900
H	7.94690200	2.27420900	0.35359800
H	4.71530700	-0.72628400	-1.47020900
H	6.73141200	0.31839500	-0.64123200
C	0.07449500	1.51639300	2.32836100
N	-0.20159500	0.33907600	1.59430400
H	-0.00668700	2.07374300	4.51542700
C	-0.59618100	-0.59456200	2.58213000
C	-0.57418200	0.00943100	3.90536800
H	-0.85570900	-0.50461700	4.82232300
C	-0.14265300	1.30779400	3.75328300
C	-0.96942600	-1.92885200	2.35157500
N	-0.71488000	-1.77807100	-0.14395600
C	-0.87451500	-2.75058100	-1.15028400
C	-1.21147100	-4.04620100	-0.57683600
H	-1.37092200	-4.95322100	-1.15806400
C	-1.27737900	-3.87220500	0.78731800
H	-1.49538300	-4.61260500	1.55571800
C	-0.97672100	-2.47416200	1.05765500
C	0.41132700	2.77296100	1.79039000
H	0.57725700	4.97696200	-2.29584200
C	0.51217900	4.20018700	-1.53606100
C	0.26744800	2.79453200	-1.81535500
H	0.81940200	5.23383400	0.41282000

N	0.21206100	2.04847100	-0.61432200
C	0.44226700	3.00709500	0.40125500
C	0.63765300	4.33215400	-0.17051100
C	-0.76740000	-2.53212100	-2.53438500
H	-0.10361000	0.88547300	-5.60397300
C	-0.20058500	0.32684300	-4.67569200
C	-0.44082400	-1.01780900	-4.51308700
H	-0.58105700	-1.78161800	-5.27654200
C	-0.48980800	-1.26765700	-3.07859900
N	-0.27354600	-0.08090400	-2.34964000
C	-0.10605600	0.91062100	-3.34429300
C	0.12455800	2.27799200	-3.11754900
Co	-0.09159900	0.08692900	-0.38822800
C	0.24703700	3.20422400	-4.29656900
C	1.49363600	3.81923600	-4.62587800
C	-0.84190500	3.47340400	-5.17889800
C	1.64692600	4.66147900	-5.75356900
C	-0.71335500	4.31891900	-6.30343100
C	0.53502700	4.91267800	-6.58565200
H	0.64970800	5.55855200	-7.46291200
C	-1.43307100	-2.77672700	3.50487600
C	-2.80829800	-3.14017000	3.62403100
C	-0.56438300	-3.23715600	4.53428000
C	-3.29379000	-3.93536600	4.68983600
C	-1.02605500	-4.01561200	5.62432500
C	-2.39100900	-4.36428600	5.68591700
H	-2.75735900	-4.96669600	6.52456400
C	0.57670100	3.93880200	2.73756900
C	1.80684600	4.18071900	3.42574700
C	-0.53919500	4.80015900	3.00613000
C	1.93239200	5.28221000	4.31653400
C	-0.41357000	5.89589600	3.90166000
C	0.82438000	6.12376100	4.53468400
H	2.87505300	5.44099600	4.83974200
H	-1.28212300	6.52677100	4.09475300
H	0.92447200	6.97073800	5.22285000
C	-1.07576700	-3.67503600	-3.46280100
C	-2.44269400	-4.01020600	-3.72137300
C	-0.03870100	-4.42350100	-4.09482400
C	-2.77552000	-5.11514900	-4.54692300
C	-0.37059100	-5.51924900	-4.94110800
C	-1.72780000	-5.85204300	-5.14047000
H	-3.82551000	-5.36653800	-4.71038300

H 0.42961500 -6.07455800 -5.43178900
H -1.97465900 -6.70355900 -5.78507900
N 2.90342000 3.28670800 3.20314500
H 2.82914900 2.67377500 2.38400000
N 1.31201300 -4.03294600 -3.83806100
H 1.46320700 -3.34379700 -3.07803700
N -3.42854200 -3.15176600 -3.15418000
H -3.06133700 -2.31041100 -2.69581000
N -1.78104600 4.50241700 2.36524800
H -1.75433700 3.72500300 1.69683300
C 3.99906300 3.09264100 4.04832700
C 2.44449700 -4.42924300 -4.55204400
C -4.82052600 -3.25131000 -3.16808900
C -3.02221400 5.10834500 2.56965600
O -5.47025900 -4.24788700 -3.60609400
O -3.23097000 6.06693300 3.38038900
O 2.43444000 -5.25908100 -5.51814100
O 4.18845000 3.75132400 5.12118600
C -4.14696000 4.54297800 1.73689400
H -3.92192100 3.75358800 1.01111700
C -5.47100300 -1.97502300 -2.65237900
H -5.60899300 -1.21334600 -3.43141300
C -5.21224900 -1.43277200 -1.24601700
H -5.14407600 -0.34808200 -1.12310900
H -4.61672800 -2.02719300 -0.54610500
C -6.60720600 -2.01984400 -1.61902100
H -6.88407800 -2.98225700 -1.18407600
C -5.29170000 5.50103300 1.39452600
H -5.19031300 6.52423200 1.76594100
H -5.79140000 5.36408000 0.43206800
C -5.53158100 4.42204500 2.46208300
H -5.55440600 4.73820400 3.50700300
C -7.71663700 -1.04180700 -1.80302200
C -6.39626800 3.26629300 2.09267300
O -6.51943900 2.78364500 0.93541600
O -7.62926300 0.04476800 -2.43501800
O -7.07995400 2.77152700 3.20523200
O -8.88716800 -1.46897100 -1.17308200
C -8.02235100 1.63022500 2.94660400
H -7.55641300 0.95557200 2.20701300
H -8.09839000 1.13478300 3.92964000
C -9.38775600 2.15227200 2.46747600
H -9.74951800 2.90394100 3.19583800

H -9.25680500 2.67077500 1.49997000
C -10.07225300 -0.55144200 -1.28709300
H -10.93167600 -1.23696000 -1.19097600
H -10.05457300 -0.08958300 -2.29034400
C -10.06992800 0.52293600 -0.18593300
H -9.16925400 1.15374300 -0.30288000
H -10.94642000 1.17938500 -0.37637400
C -10.44928400 1.02428400 2.33550500
H -10.56792900 0.52299800 3.31957600
H -11.42626800 1.50102500 2.11356200
C -10.16657900 -0.05225200 1.24977200
H -9.23978300 -0.61265700 1.48161700
H -10.99050000 -0.79605400 1.28226600
C 4.95387200 1.98756400 3.65654400
H 4.89502700 1.56794700 2.64710200
C 3.72947600 -3.78170100 -4.09918200
H 3.69183000 -3.11890000 -3.22920000
C 4.76851500 -3.46206700 -5.17941600
H 5.38906700 -2.57683100 -5.02221200
H 4.49348100 -3.70252100 -6.21012500
C 5.38345500 1.05154600 4.80742500
H 5.59755000 0.01274800 4.54624800
H 4.92050800 1.23466200 5.78128900
C 6.36688300 2.11200400 4.31488700
H 6.46130700 3.01520800 4.92616900
C 5.00898900 -4.66907500 -4.25681500
H 4.83253200 -5.65429600 -4.69710900
C 7.62820300 1.76274900 3.59650500
C 6.07842400 -4.65592200 -3.22199800
O 7.69897300 0.40831000 3.23298100
O 6.26187400 -3.37730800 -2.66273600
O 6.76539100 -5.65164000 -2.88271000
O 8.56950400 2.56699800 3.37923800
C 9.01407400 -0.03361300 2.66338000
H 9.22406200 0.56248300 1.75528600
H 9.79636900 0.19027500 3.41189900
C 8.90334700 -1.53118300 2.36201400
H 9.92092000 -1.90246400 2.11890100
H 8.57976700 -2.06212500 3.27923400
C 7.33199700 -3.26049900 -1.62235500
C 7.94106200 -1.84983000 1.19411900
H 6.93978200 -1.43743100 1.42733100
H 8.30320800 -1.31695900 0.28950300

C	7.81576800	-3.36585800	0.90113200
H	7.47876800	-3.88117800	1.82334300
H	8.81499100	-3.78680700	0.65873100
C	6.81468400	-3.69675100	-0.23967400
H	5.84802100	-3.19394700	-0.03878300
H	6.62228500	-4.78503000	-0.26731700
H	7.59726800	-2.19107000	-1.65387700
H	8.19521600	-3.87736100	-1.93363200
H	2.62516900	5.09041300	-5.98774700
H	-1.58834900	4.47764400	-6.94006900
H	-0.33416900	-4.33217100	6.40928400
H	-4.35361800	-4.19798800	4.74459400
O	2.59310100	3.44384500	-3.81497600
O	-2.07338000	2.78236000	-5.06731300
O	0.78632500	-2.81074600	4.43827600
O	-3.65884500	-2.63113400	2.61378800
C	3.78499000	4.23118900	-3.79792800
C	5.00411000	3.53017000	-3.91241500
C	3.75532800	5.62723200	-3.56964000
C	6.21998300	4.24508300	-3.80742200
H	4.98583800	2.44707000	-4.06756000
C	4.97869700	6.33007800	-3.47243900
H	2.80007600	6.15279600	-3.46573900
C	6.21264200	5.64471900	-3.59317000
H	7.17034000	3.70594000	-3.88839700
H	4.96514800	7.41165900	-3.29458600
H	7.15696200	6.19444400	-3.51255300
C	-2.98114600	3.02361700	-3.99664300
C	-2.86512000	4.11502900	-3.10791500
C	-4.06450900	2.11867500	-3.92028700
C	-3.84999700	4.27607200	-2.10314600
H	-2.03705100	4.82562200	-3.19858000
C	-5.04201500	2.29654700	-2.91700700
H	-4.12417700	1.30115500	-4.64636200
C	-4.93253900	3.37053300	-1.99632800
H	-3.76553800	5.12037300	-1.40786900
H	-5.89180200	1.60640400	-2.85285900
H	-5.67832800	3.47669400	-1.20187400
C	1.80664500	-3.45849300	5.19497300
C	2.68184600	-2.62320300	5.92380500
C	2.01092300	-4.85836700	5.12634400
C	3.77840000	-3.20327100	6.60548800
H	2.49603000	-1.54468400	5.94588100

C	3.10701900	-5.42472500	5.81826700
H	1.32954700	-5.48693800	4.54311900
C	3.99224700	-4.60257800	6.55922300
H	4.46009100	-2.56179700	7.17530000
H	3.27159900	-6.50731500	5.77123600
H	4.83987000	-5.04769900	7.09179800
C	-5.02793000	-3.04847100	2.58706600
C	-5.38473700	-4.15982500	1.79209000
C	-5.99563600	-2.29001700	3.28074000
C	-6.75011300	-4.51915100	1.69162400
H	-4.60681200	-4.71631800	1.25896900
C	-7.35737500	-2.66262300	3.17543700
H	-5.68077100	-1.42813300	3.87860600
C	-7.73662200	-3.77450000	2.38373300
H	-7.04050100	-5.37435100	1.07110300
H	-8.11986000	-2.08614900	3.71186900
H	-8.79266800	-4.05253600	2.29788700
C	2.22050800	-1.78677000	-0.03274200
C	2.41639700	-2.15326500	1.33115400
C	2.77020300	-3.47461800	1.66608100
H	2.29948600	-1.39589500	2.11268600
C	2.66251600	-4.01017000	-0.69458500
C	2.90035700	-4.43076100	0.63200100
H	2.94230900	-3.75140400	2.71053900
H	2.73701100	-4.72834400	-1.52009000
H	3.17543500	-5.46984200	0.83884000
N	2.33793100	-2.72782000	-1.04150100
C	1.95114600	-0.35448300	-0.39019600
H	2.18006300	0.30375100	0.46664600
C	2.66172200	0.13093700	-1.68329600
H	2.27863500	1.11090800	-2.00068300
H	2.48265400	-0.59478300	-2.49301100

Intermediate E

$E_{[Co(II)(P6)]}$=$A_{[Co(II)(P9)]}$

$E_{[3a]}$

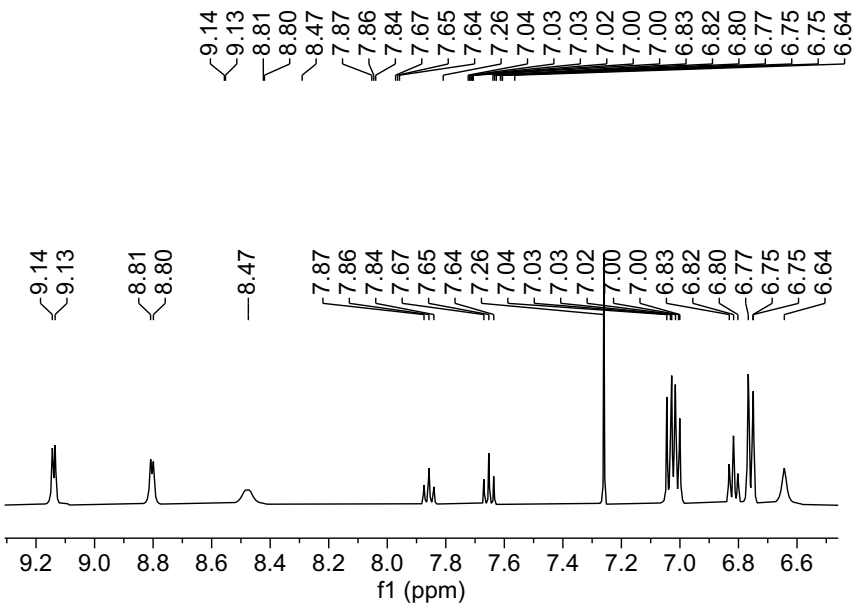
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.186841 Hartree
H_corr: 0.239936 Hartree
SCF: -595.949895 Hartree
S: 111.747 Cal/Mol-Kelvin

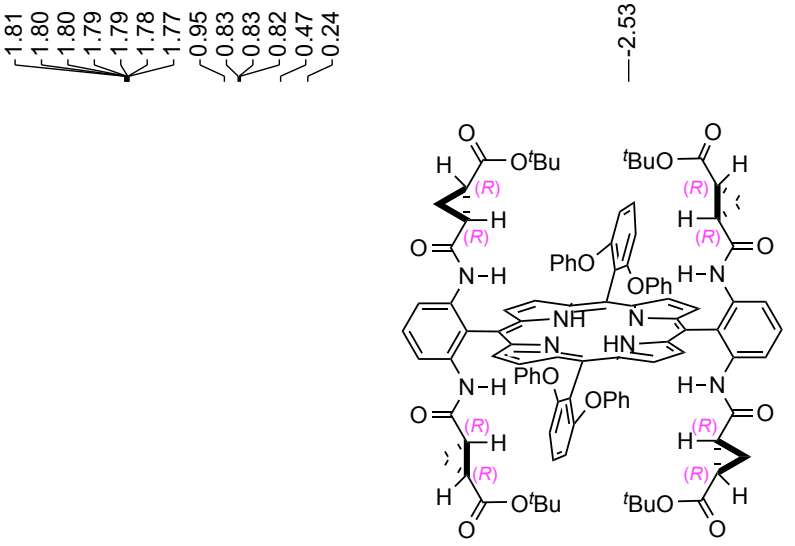
H: -596.0850148 Hartree
G: -596.1381098 Hartree

Cartesian Coordinates:

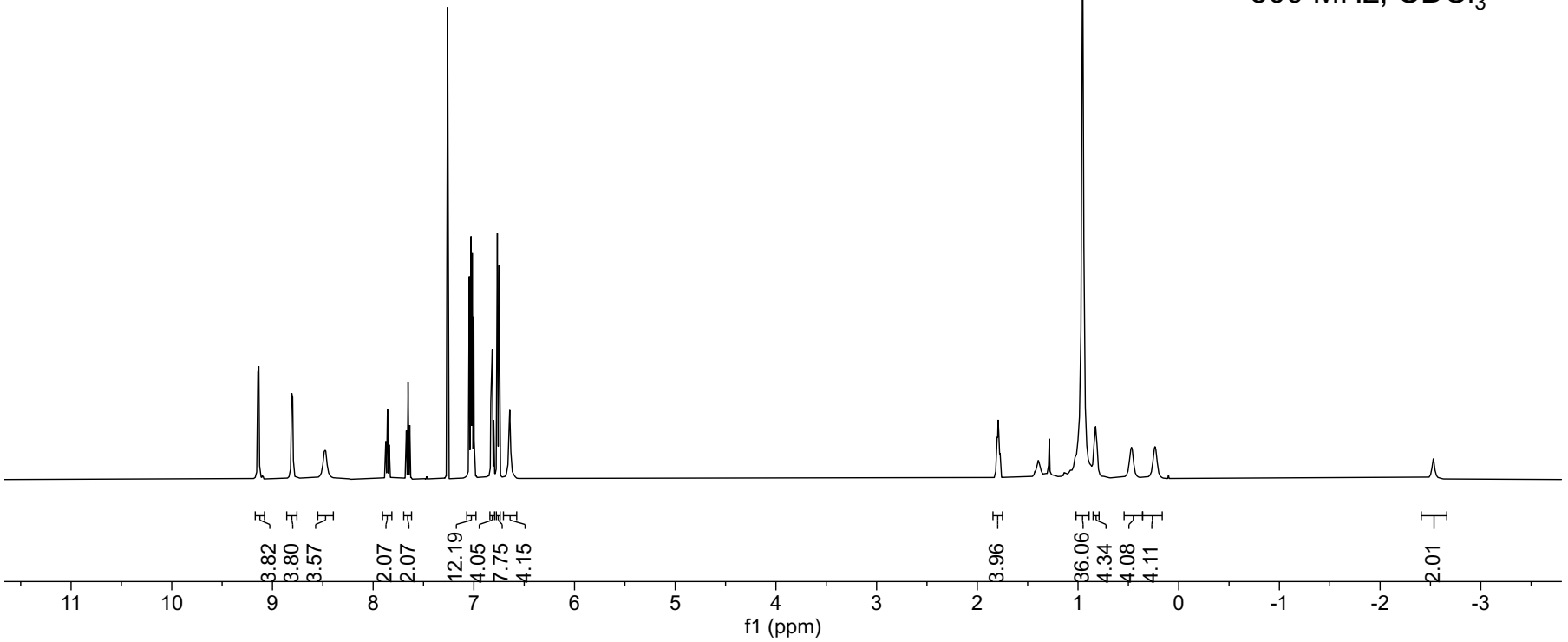
H	0.07866500	1.25055600	0.88539800
H	4.51601900	-1.99091800	-0.36545400
C	3.96410000	-1.04455800	-0.31259600
H	2.19284600	-1.96983700	0.53535000
C	2.64545800	-1.02892600	0.19580300
H	5.60062500	0.14260400	-1.14269700
C	4.57708700	0.15515600	-0.75024300
C	1.90776500	0.18605600	0.27764900
C	3.85519900	1.37051100	-0.67375100
C	2.53538800	1.38335000	-0.16691100
C	0.50575300	0.24444800	0.80017200
H	4.31945300	2.30619700	-1.00802400
H	1.98218100	2.32982600	-0.11176000
C	-1.93741700	-0.37065600	0.01844000
C	-2.66362100	-0.94840300	-1.06047400
C	-3.96799200	-0.48599300	-1.34297400
H	-2.20743500	-1.74393300	-1.66058900
C	-3.73188600	1.06968600	0.50707200
C	-4.52064900	0.54539400	-0.54495600
H	-4.54302400	-0.92028800	-2.16882800
H	-4.11623800	1.87101400	1.15055700
H	-5.52793500	0.93307000	-0.72919100
N	-2.47177400	0.63314100	0.79380200
C	-0.55703900	-0.82298800	0.35250500
C	-0.05458000	-0.76353300	1.80651000
H	0.59779400	-1.57002500	2.15679700
H	-0.76754600	-0.37462700	2.53933400
H	-0.16837400	-1.63289200	-0.27499000

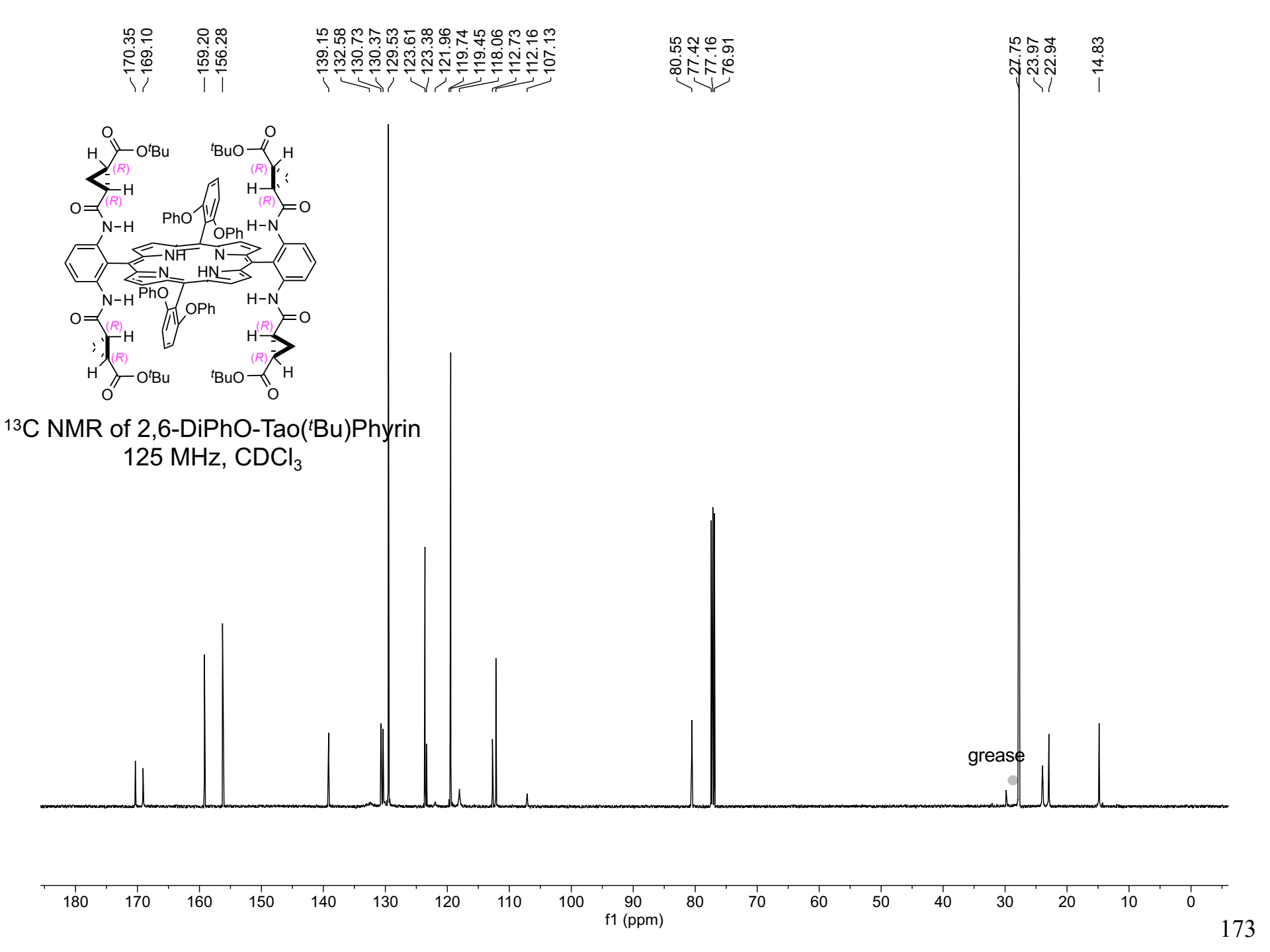
2.5. NMR/HPLC SPECTRAL DATA



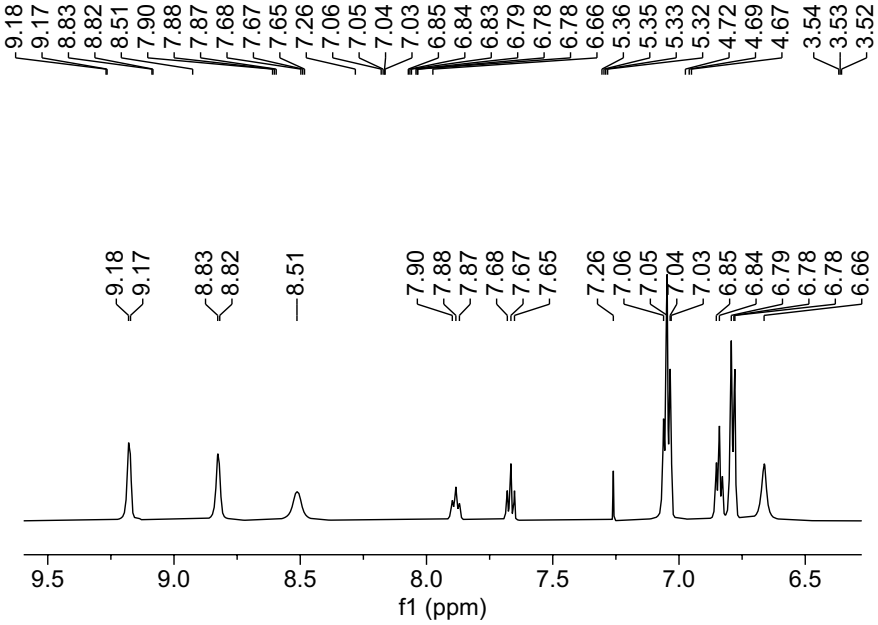


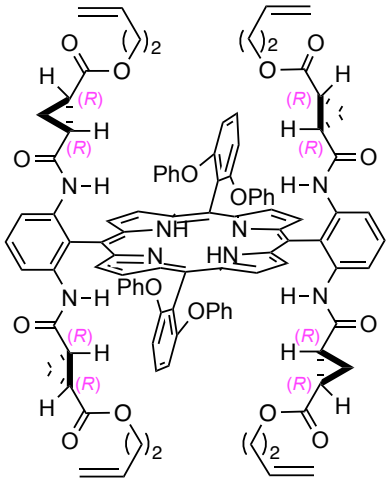
^{1}H NMR of 2,6-DiPhO-Tao(^{t}Bu)Phyrin
500 MHz, $CDCl_3$



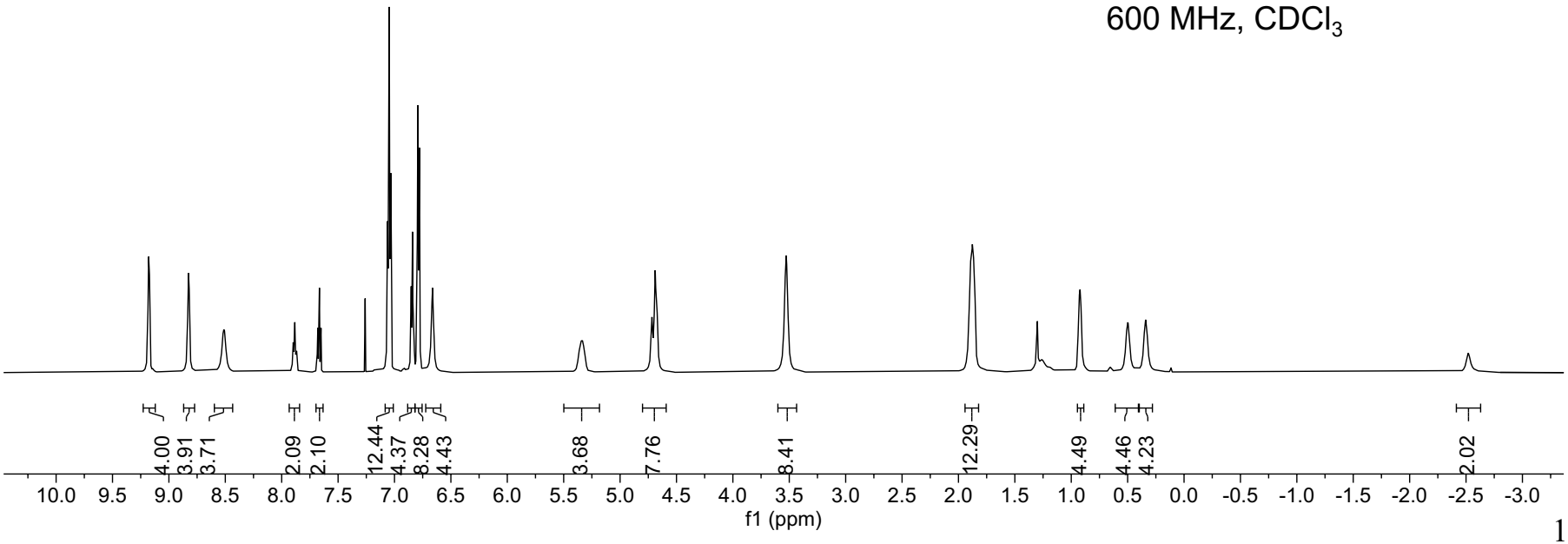


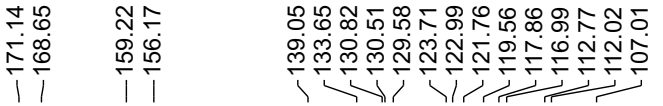
^{13}C NMR of 2,6-DiPhO-Tao(^{t}Bu)Phyrin
125 MHz, $CDCl_3$

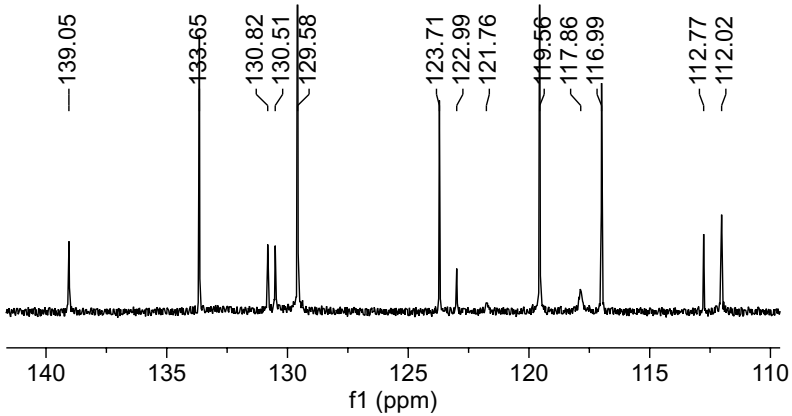


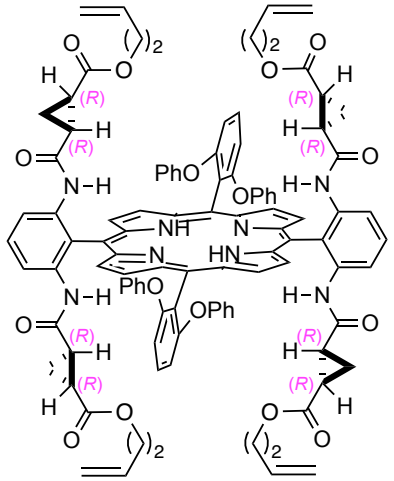


^{1}H NMR of 2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin
600 MHz, $CDCl_3$

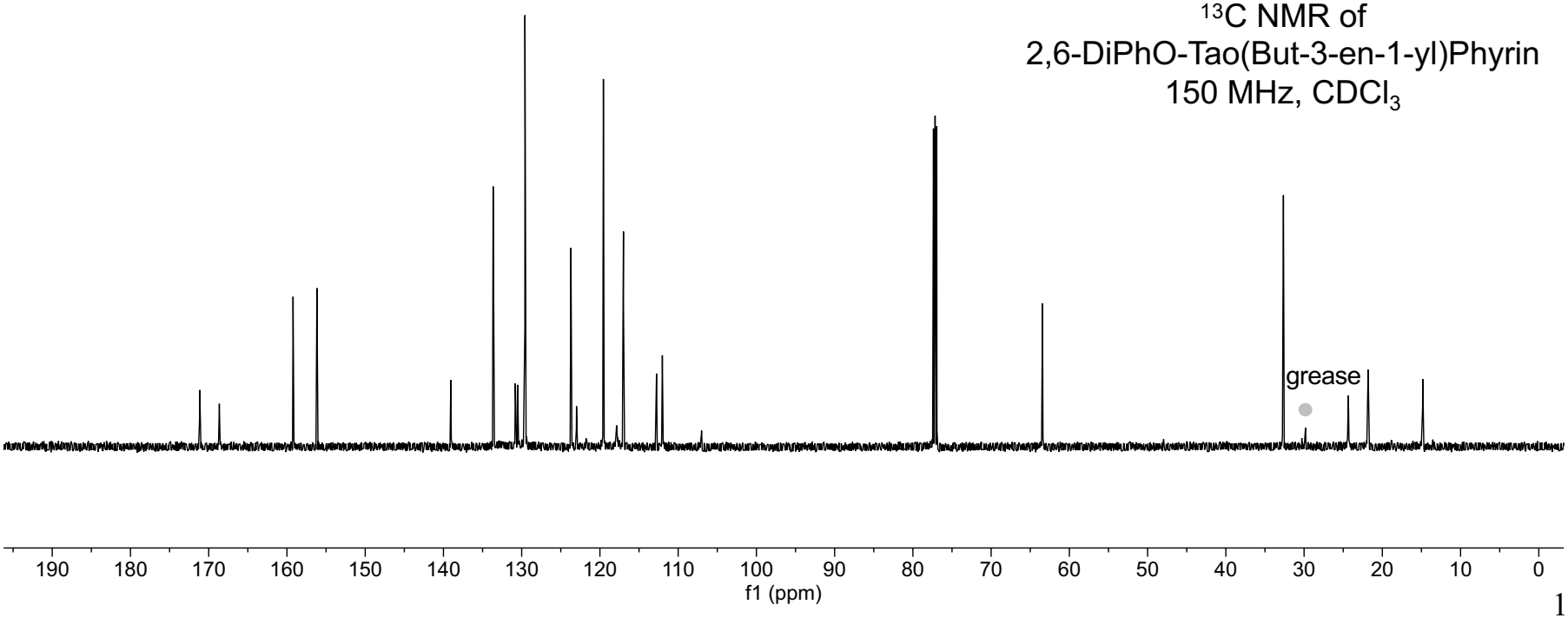




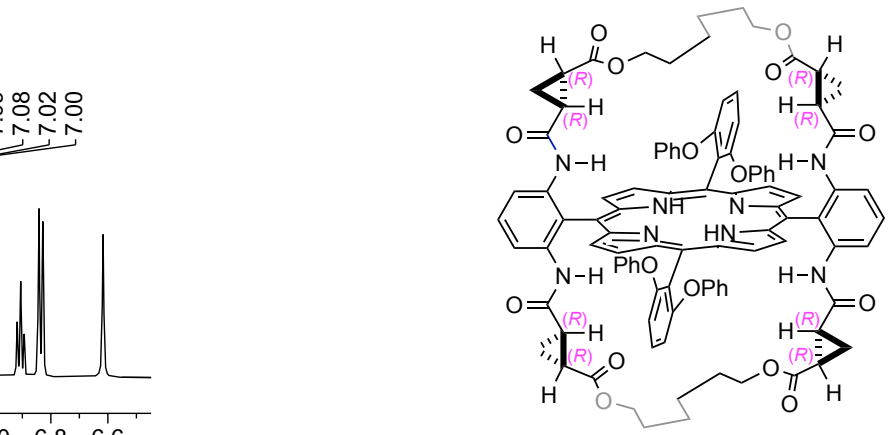


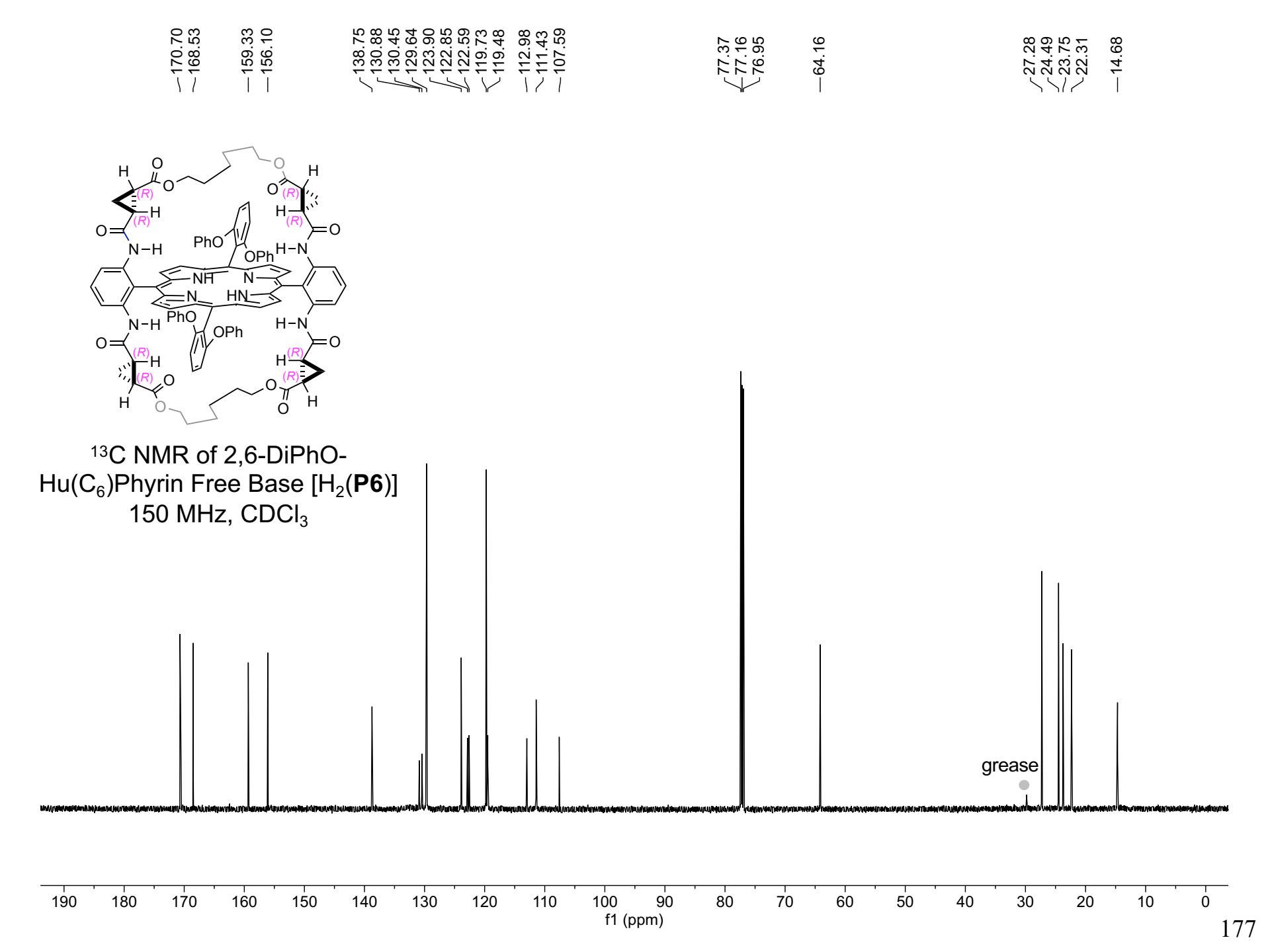


^{13}C NMR of
2,6-DiPhO-Tao(But-3-en-1-yl)Phyrin
150 MHz, $CDCl_3$



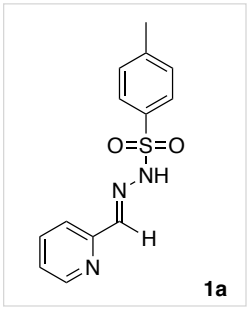
^{1}H NMR of 2,6-DiPhO-Hu(C_6)Phyrin
Free Base [H_2(**P6**)]
600 MHz, $CDCl_3$

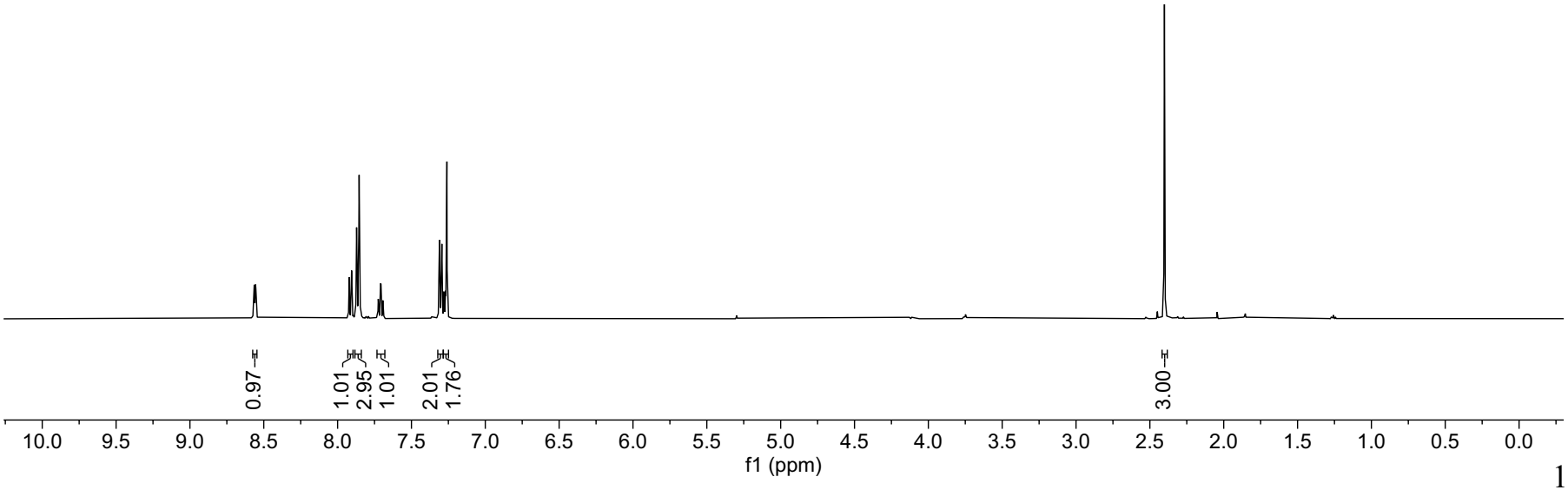




^{13}C NMR of 2,6-DiPhO-Hu(C_6)Phyrin Free Base [H_2(**P6**)]
150 MHz, $CDCl_3$

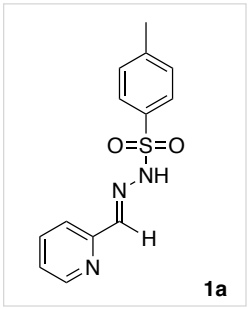
^{1}H NMR of **1a**, 500 MHz, $CDCl_3$

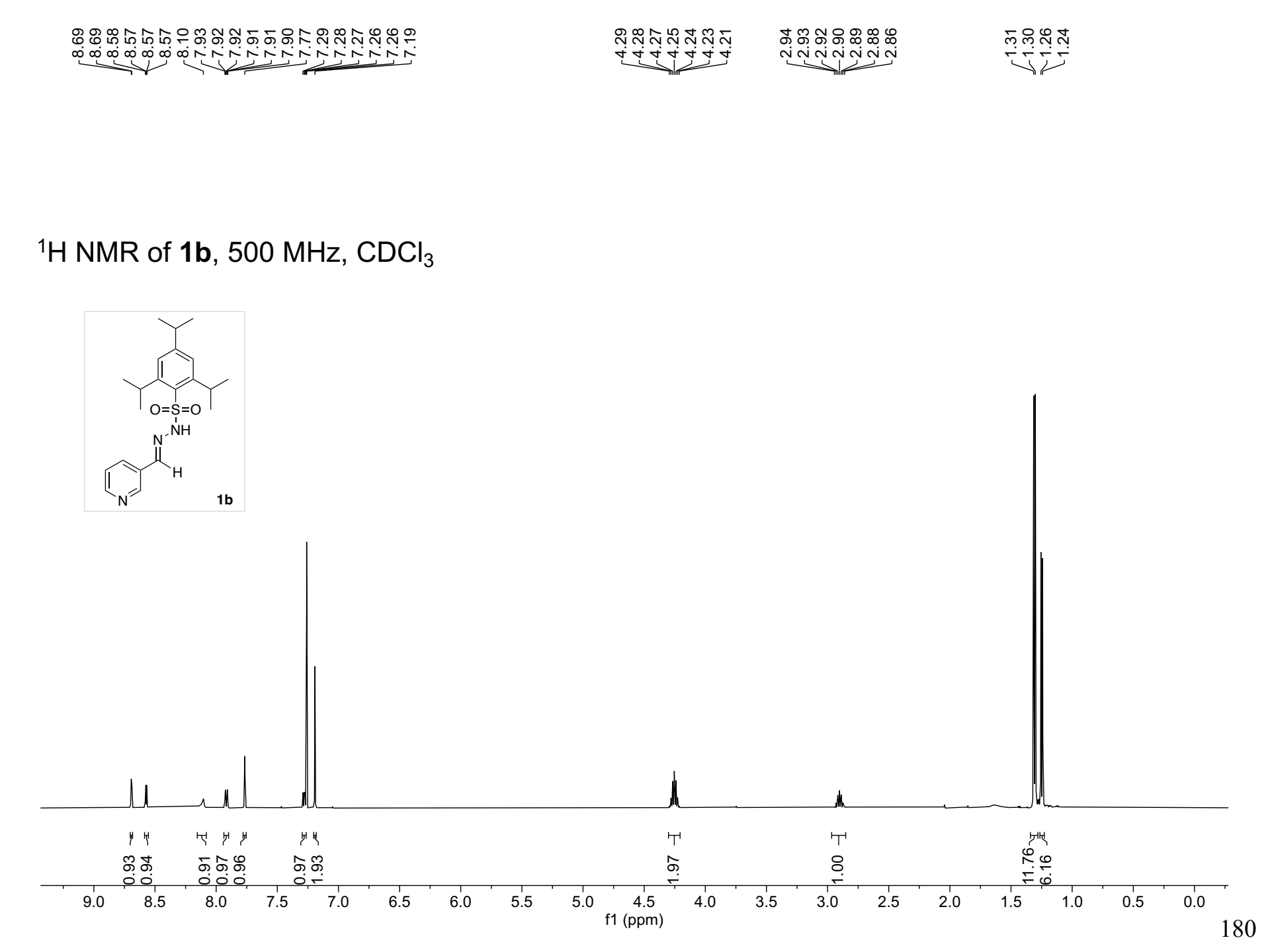




152.52
149.37
147.17
144.54
136.85
135.47
129.90
128.07
124.57
120.83
77.41
77.16
76.91
21.74

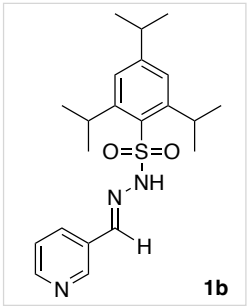
^{13}C NMR of **1a**, 125 MHz, $CDCl_3$





^{1}H NMR of **1b**, 500 MHz, $CDCl_3$

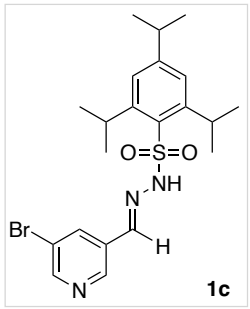
^{13}C NMR of **1b**, 125 MHz, $CDCl_3$

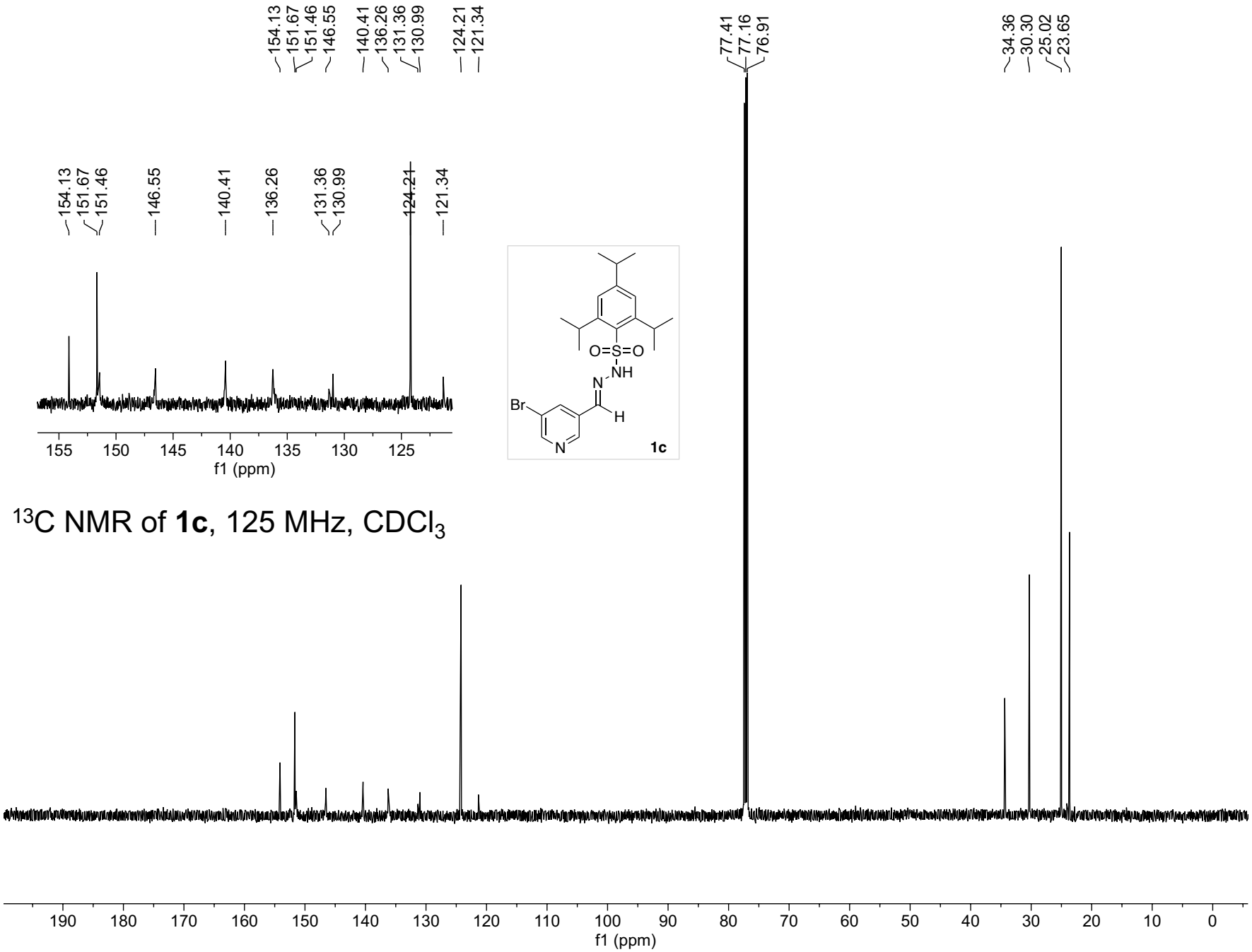


153.85
151.56
150.91
149.01
142.63
133.71
131.25
129.73
124.10
123.77
77.41
77.16
76.90
34.33
30.20
25.01
23.65

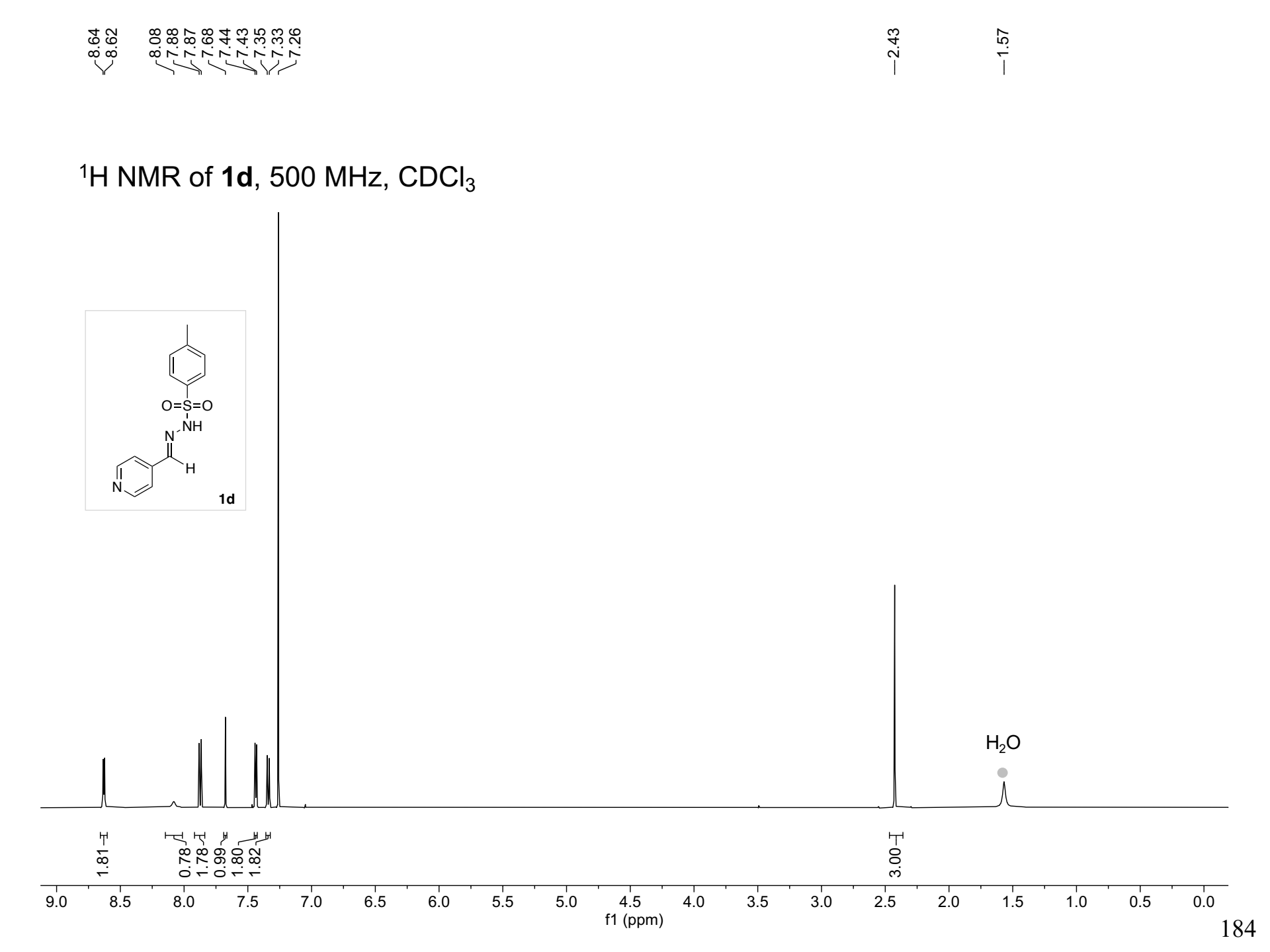
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of **1c**, 600 MHz, $CDCl_3$





^{13}C NMR of **1c**, 125 MHz, $CDCl_3$

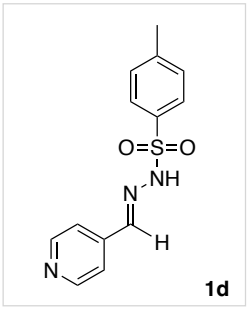

8.64
8.62
8.08
7.88
7.87
7.68
7.44
7.43
7.35
7.33
7.26
2.43
1.57
1H NMR of 1d, 500 MHz, CDCl3
O=S=O
NH
N
H
N
1d
H2O
1.81
0.78
1.78
0.99
1.80
1.82
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

150.33
144.43
143.91
140.92
136.00
129.92
127.33
120.80

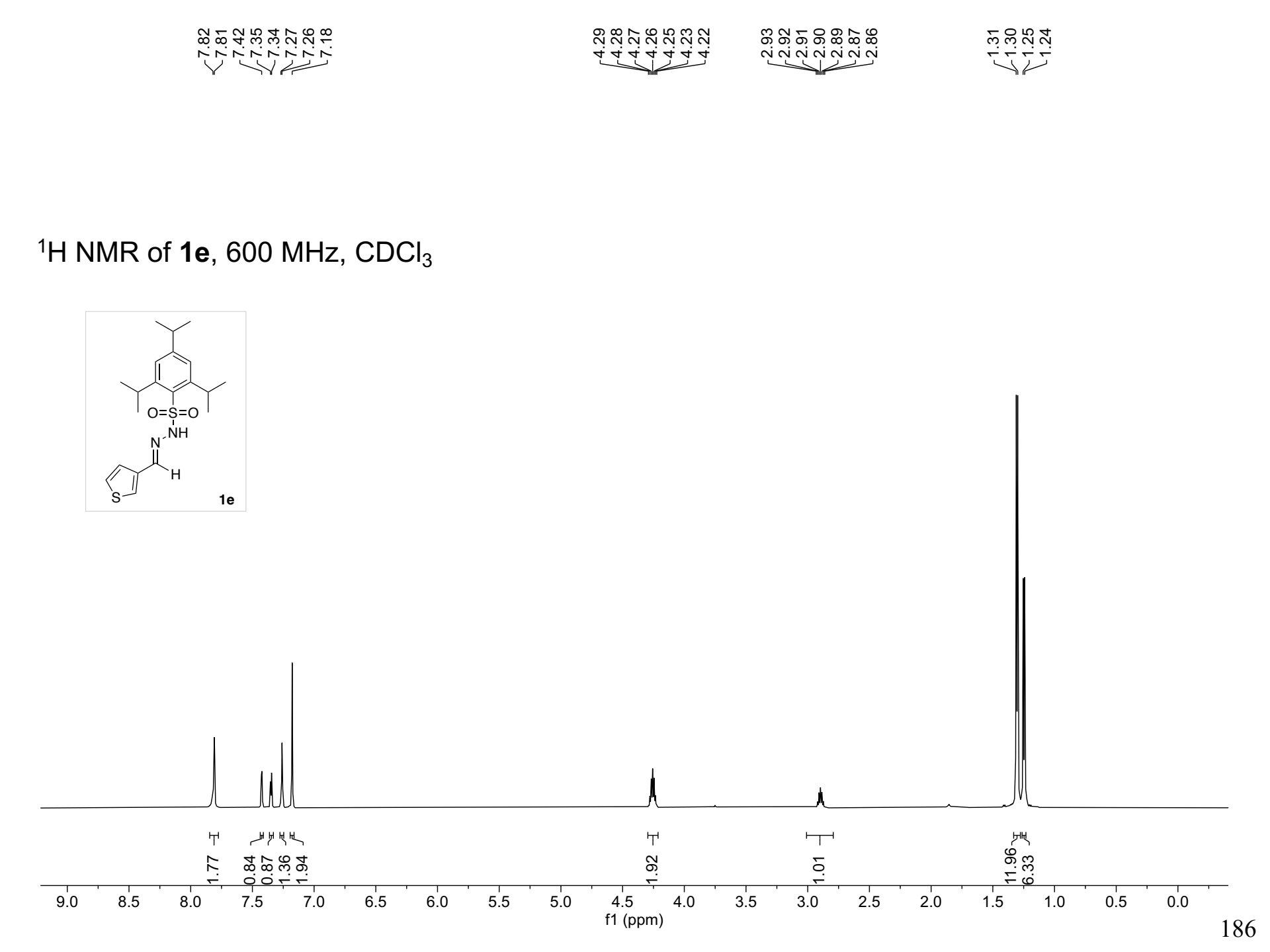
39.94
39.80
39.66
39.52
39.38
39.24
39.10

21.12

^{13}C NMR of **1d**, 150 MHz, DMSO-d_6

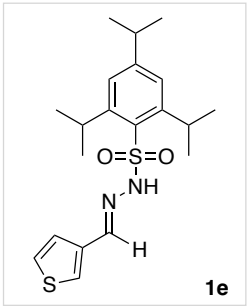


1d

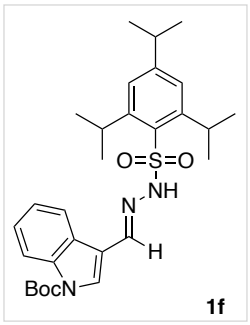


^{1}H NMR of **1e**, 600 MHz, $CDCl_3$

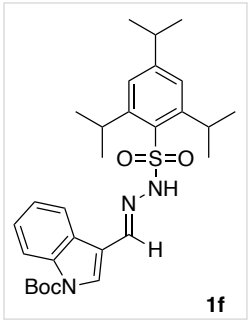
^{13}C NMR of **1e**, 150 MHz, $CDCl_3$



^{1}H NMR of **1f**, 500 MHz, $CDCl_3$



^{13}C NMR of **1f**, 125 MHz, $CDCl_3$

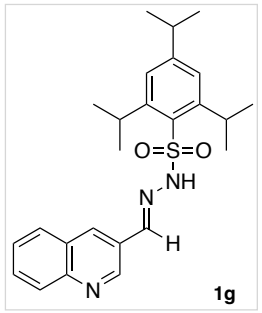


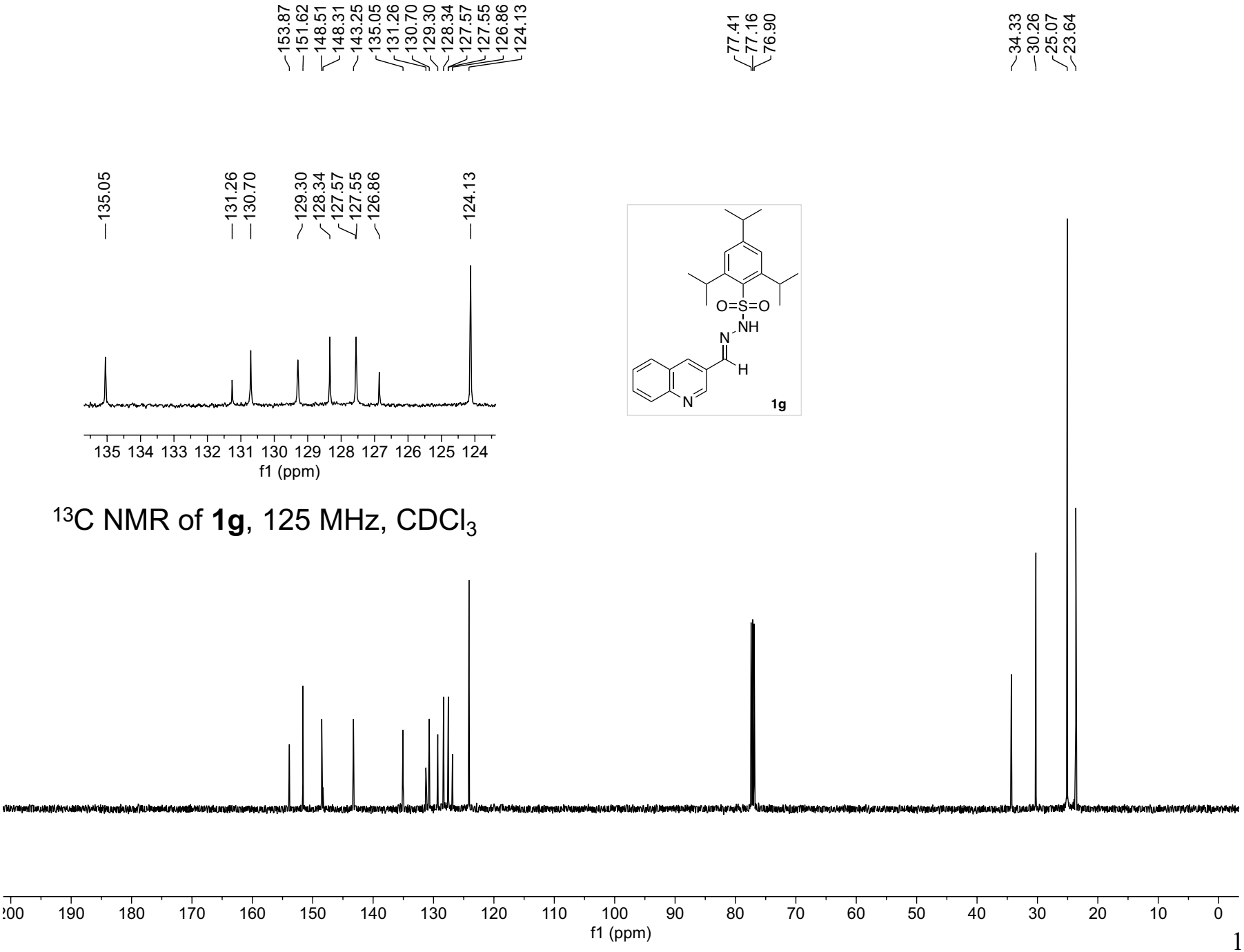
1f

153.64
151.45
149.25
141.59
135.99
131.30
128.78
126.89
125.61
124.00
123.62
122.95
116.12
115.03
84.70
77.41
77.16
76.91
34.35
30.20
28.27
25.10
23.67

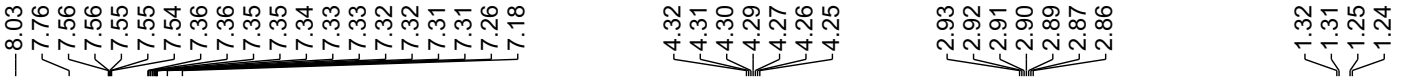
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR of **1g**, 500 MHz, $CDCl_3$

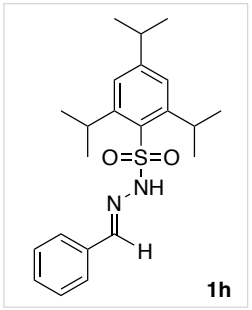




^{13}C NMR of **1g**, 125 MHz, $CDCl_3$

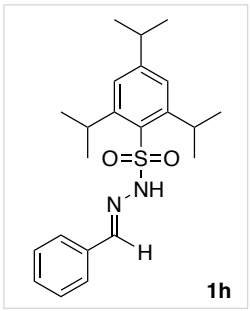


^{1}H NMR of **1h**, 600 MHz, $CDCl_3$

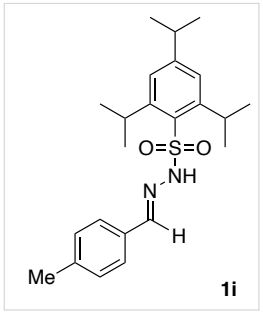


153.64
151.54
146.47
133.49
131.39
130.39
128.73
127.43
124.04
77.37
77.16
76.95
34.33
30.22
25.02
23.67

^{13}C NMR of **1h**, 150 MHz, $CDCl_3$

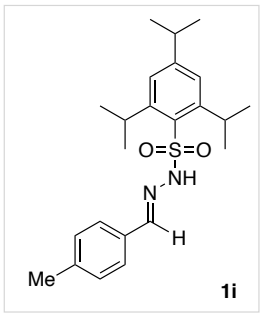


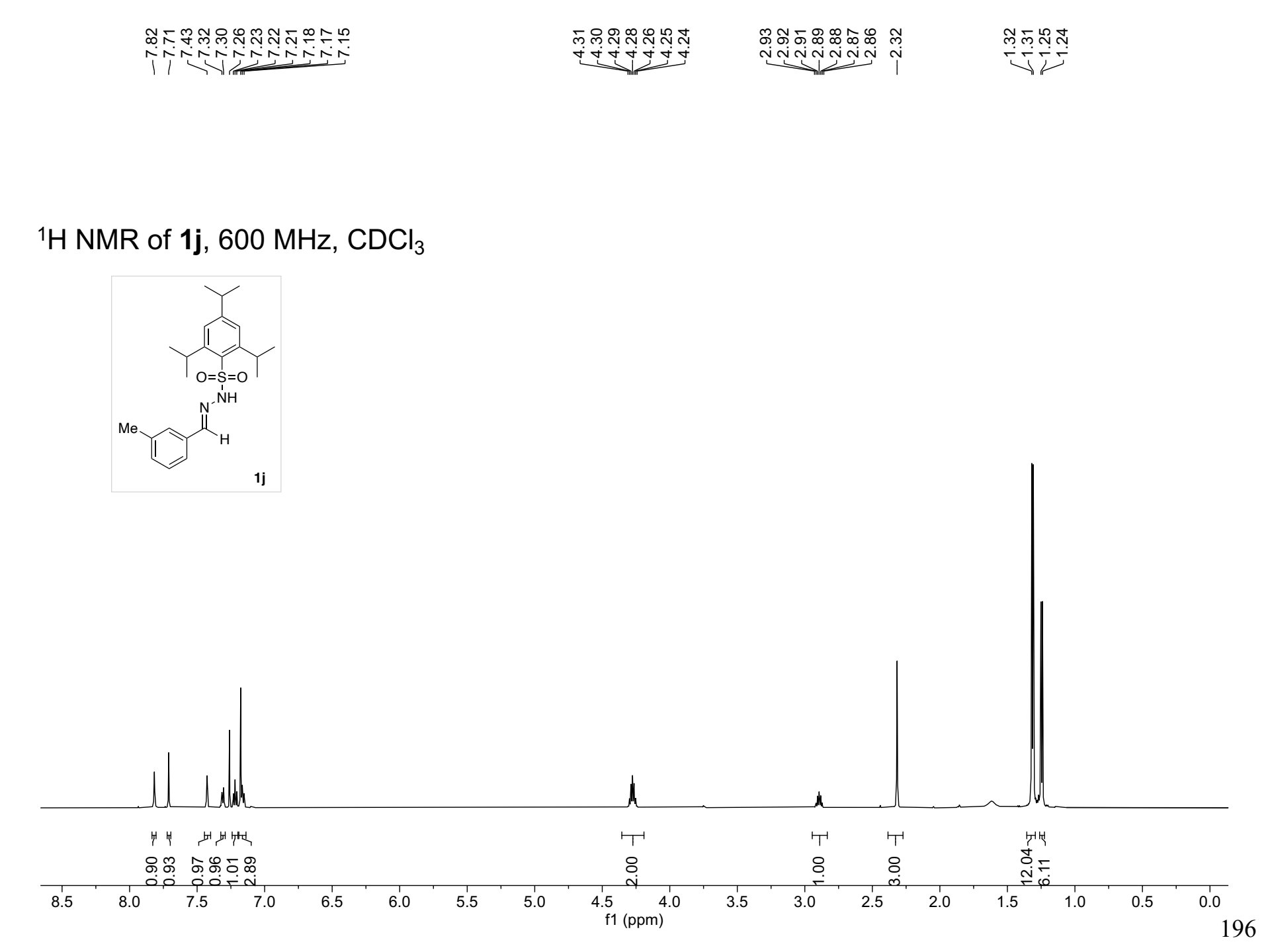
^{1}H NMR of **1i**, 500 MHz, $CDCl_3$



153.54
151.51
146.76
140.70
131.47
130.80
129.43
127.39
123.99
77.39
77.14
76.89
34.30
30.19
25.00
23.65
21.56

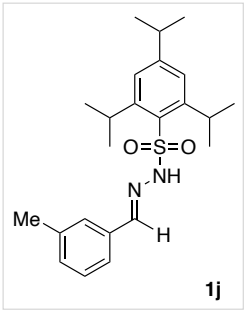
^{13}C NMR of **1i**, 125 MHz, $CDCl_3$





^{1}H NMR of **1j**, 600 MHz, $CDCl_3$

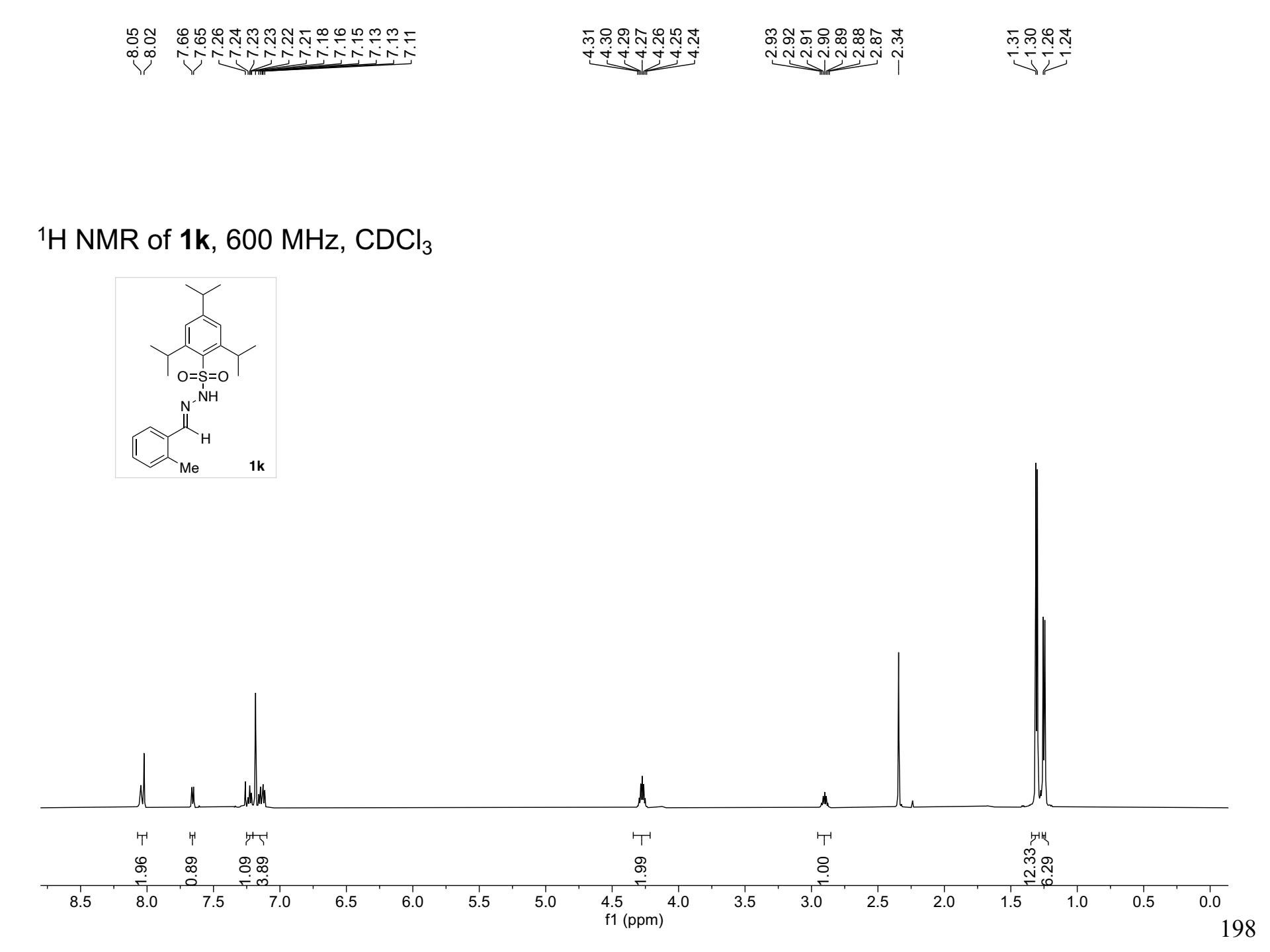
^{13}C NMR of **1j**,125 MHz, $CDCl_3$



153.62
151.56
146.68
138.50
133.38
131.46
131.28
128.63
127.74
124.95
124.04
77.41
77.16
76.91
34.34
30.24
25.03
23.67
21.34

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

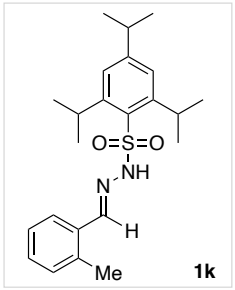
f1 (ppm)



^{1}H NMR of **1k**, 600 MHz, $CDCl_3$

153.63
151.50
145.40
137.01
131.53
131.38
130.96
130.08
127.28
126.19
124.00
77.37
77.16
76.95
34.34
30.21
25.01
23.68
19.78

^{13}C NMR of **1k**, 150 MHz, $CDCl_3$



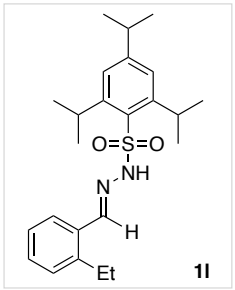
8.02
7.98
7.69
7.68
7.26
7.25
7.24
7.24
7.23
7.16
7.14
7.13
7.12

4.29
4.28
4.26
4.25
4.24
4.23
4.22

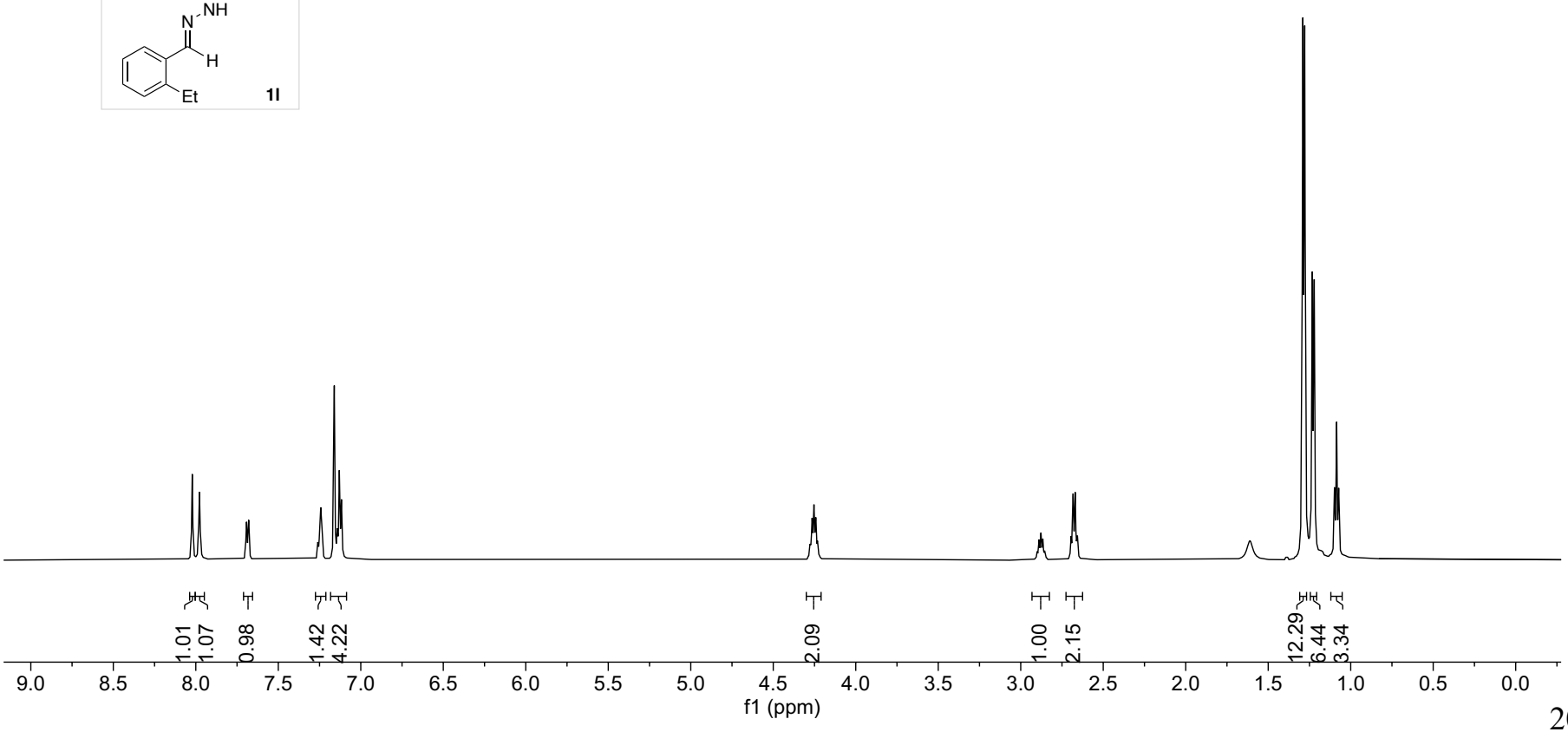
2.91
2.90
2.89
2.88
2.87
2.85
2.84
2.70
2.68
2.67
2.66

1.29
1.28
1.23
1.22
1.10
1.09
1.07

^{1}H NMR of **1l**, 600 MHz, $CDCl_3$

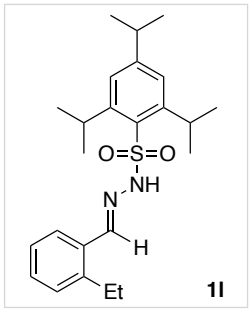


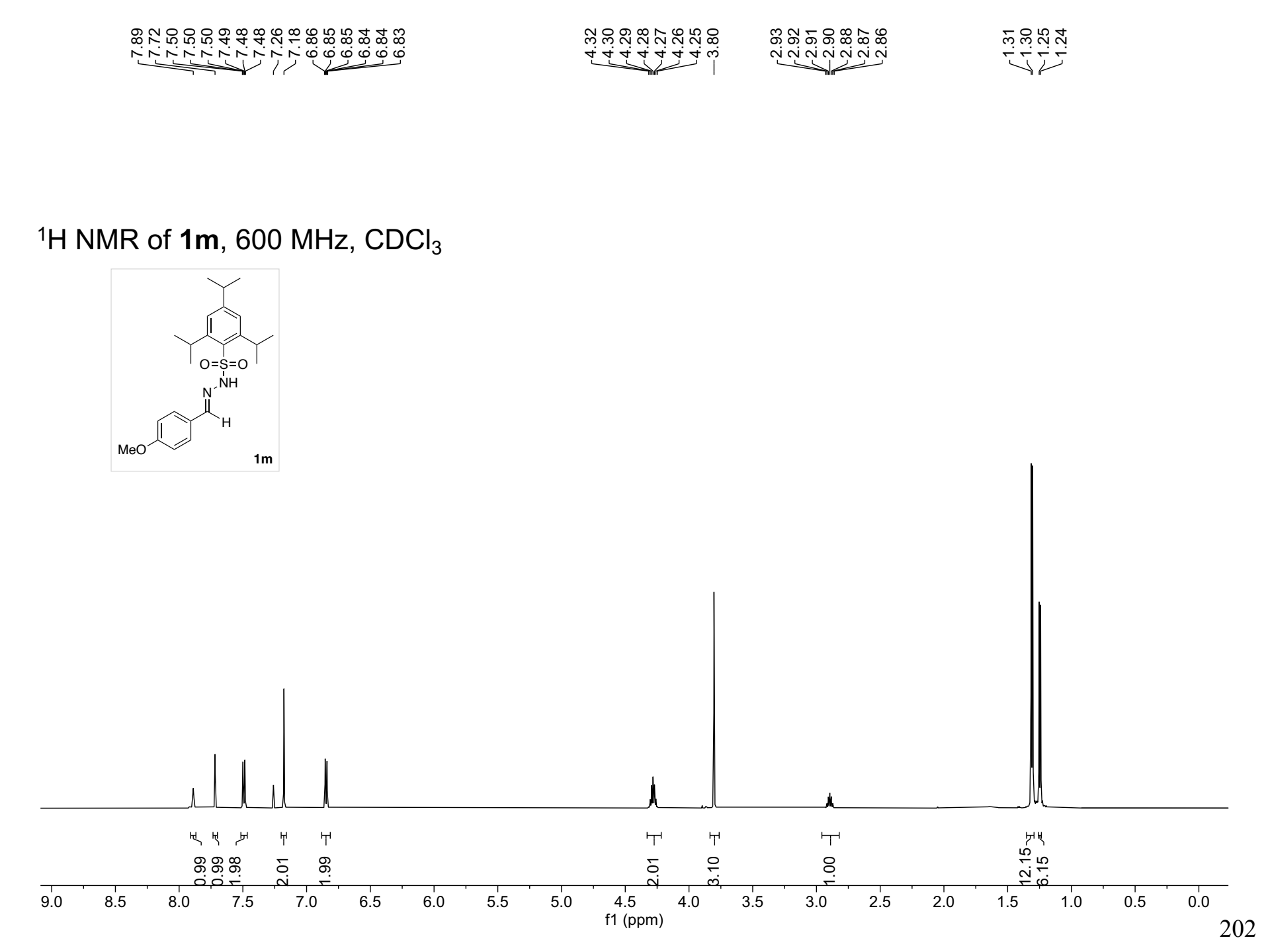
1l



153.63
151.47
145.06
143.20
131.38
130.76
130.36
129.35
127.26
126.24
124.01
77.37
77.16
76.95
34.34
30.19
26.08
24.99
23.67
15.98

^{13}C NMR of **1l**, 150 MHz, $CDCl_3$

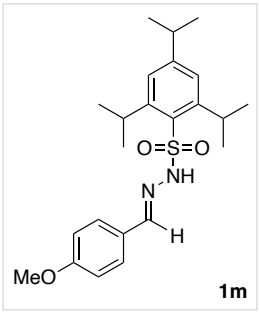




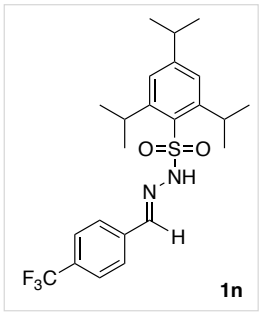
^{1}H NMR of **1m**, 600 MHz, $CDCl_3$

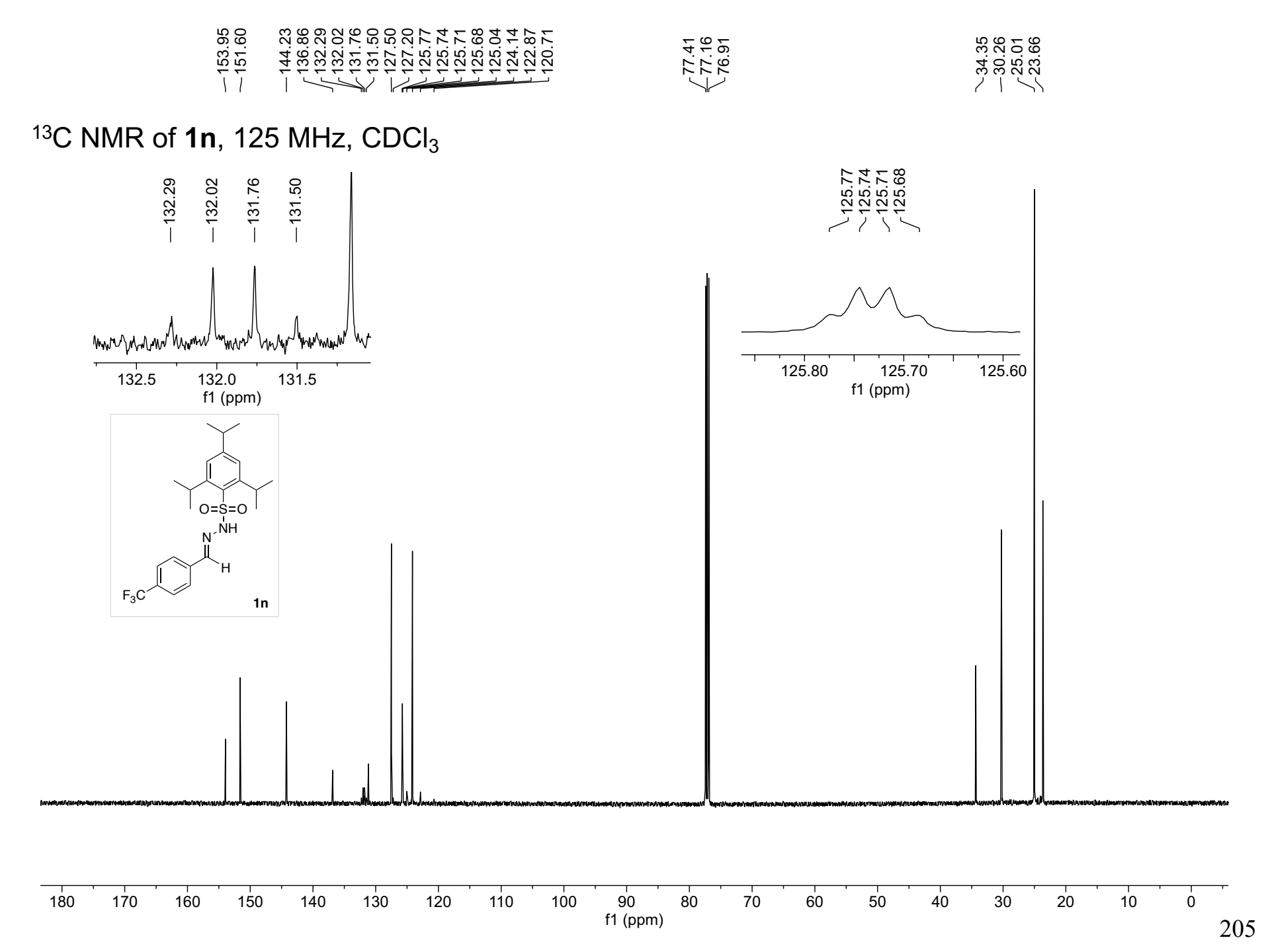
161.46
153.52
151.50
146.76
131.51
129.01
126.25
124.00
114.19
77.37
77.16
76.95
55.49
34.32
30.20
25.03
23.67

^{13}C NMR of **1m**, 150 MHz, $CDCl_3$



^{1}H NMR of **1n**, 600 MHz, $CDCl_3$

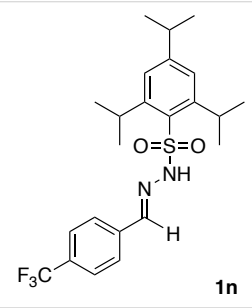


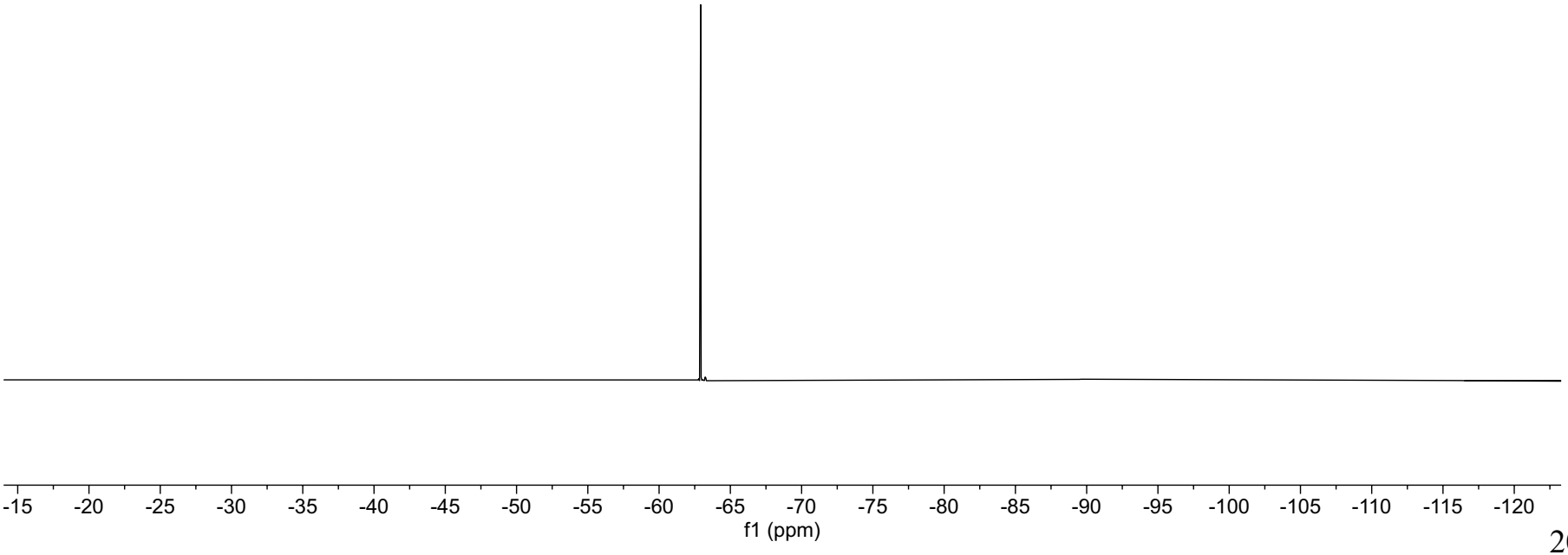


^{13}C NMR of **1n**, 125 MHz, $CDCl_3$

-62.91

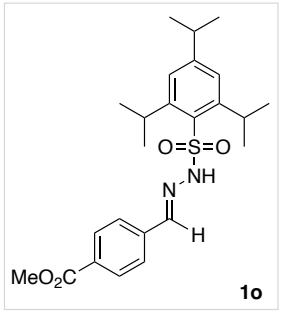
^{19}F NMR of **1n**, 564 MHz, $CDCl_3$

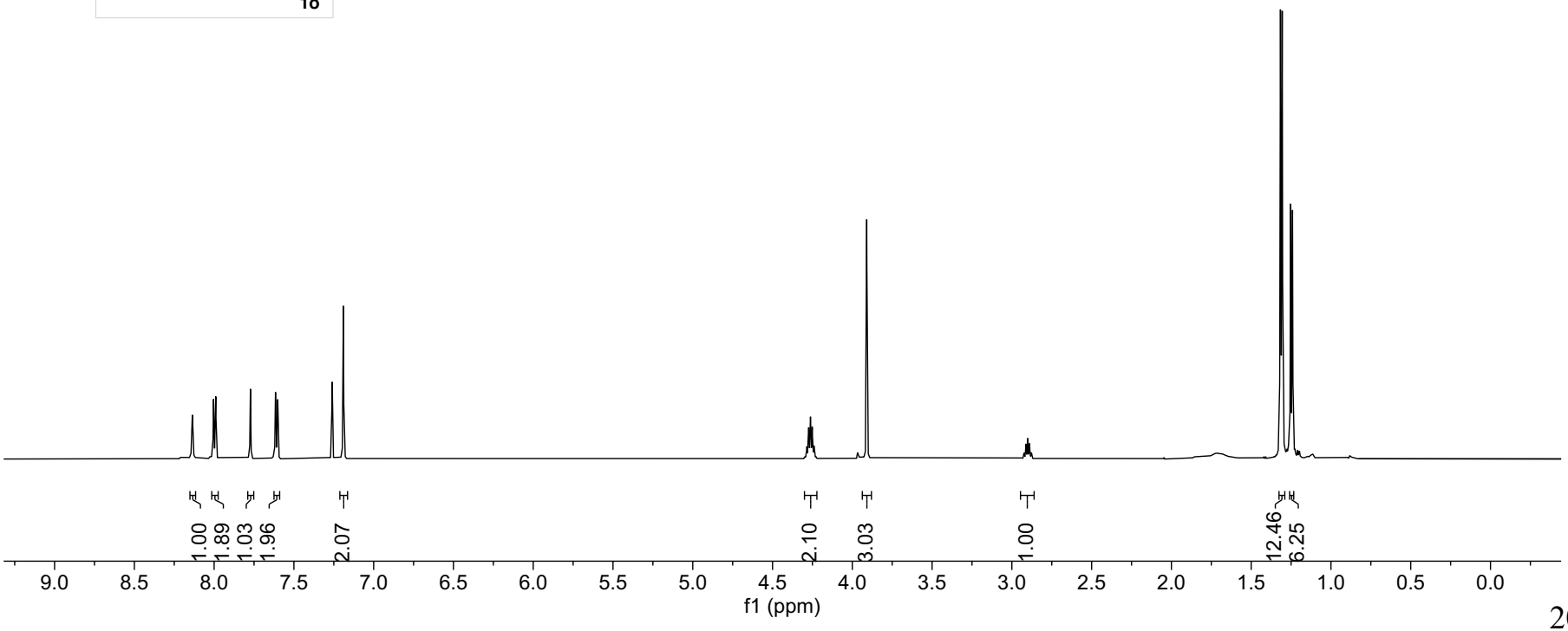




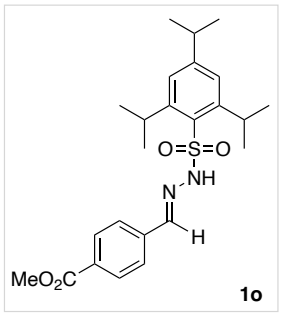
8.14
8.00
7.99
7.77
7.62
7.60
7.26
7.19
4.30
4.28
4.27
4.26
4.25
4.24
4.23
3.91
2.93
2.92
2.91
2.90
2.89
2.88
2.87
1.32
1.31
1.25
1.24

^{1}H NMR of **1o**, 600 MHz, $CDCl_3$





^{13}C NMR of **1o**, 150 MHz, $CDCl_3$



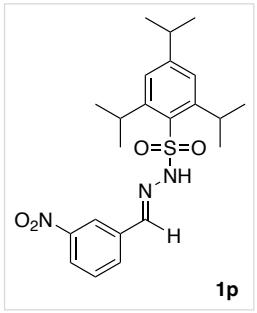
8.40 8.19 8.19 8.18 8.18 7.85 7.84 7.82 7.54 7.52 7.51 7.26 7.21

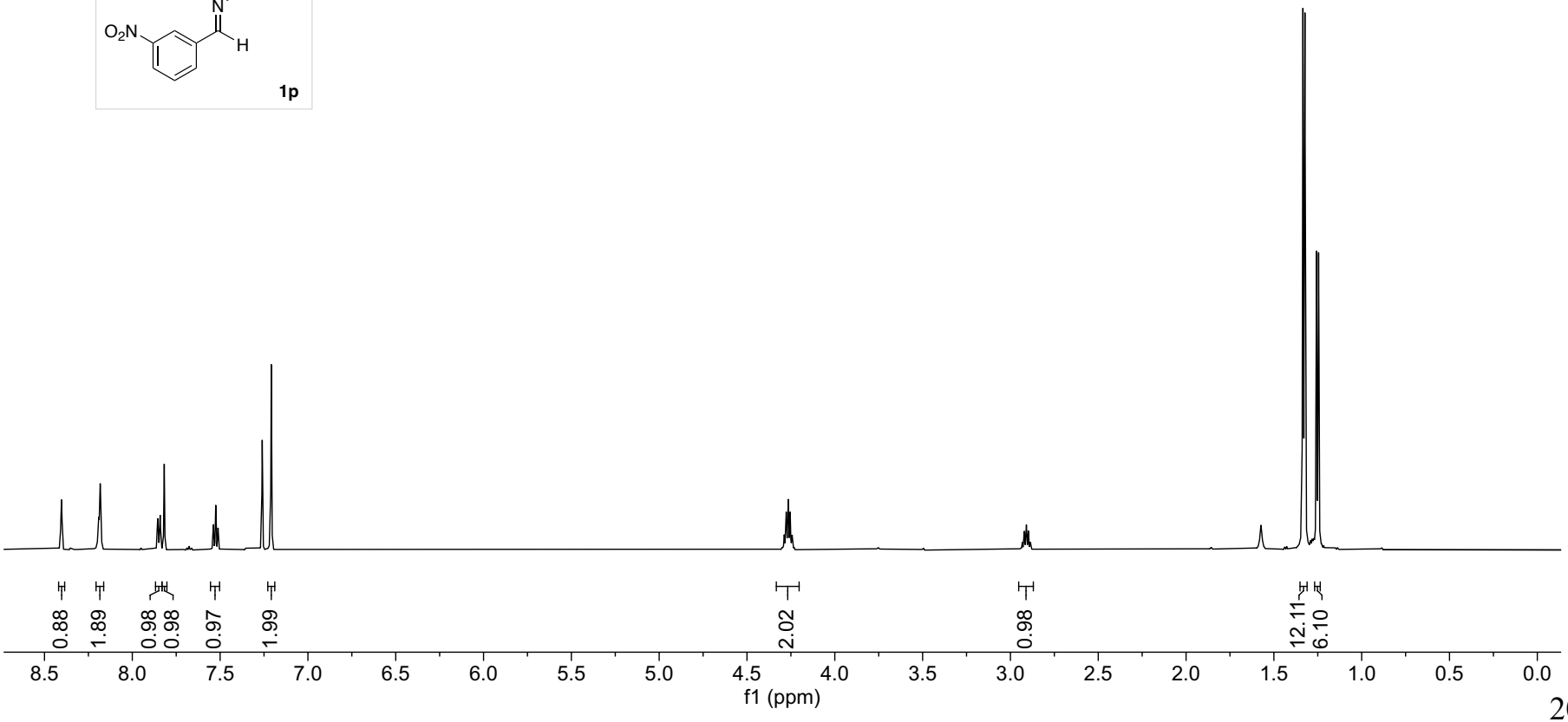
4.30 4.29 4.28 4.27 4.25 4.24 4.23

2.94 2.93 2.92 2.91 2.90 2.89 2.87

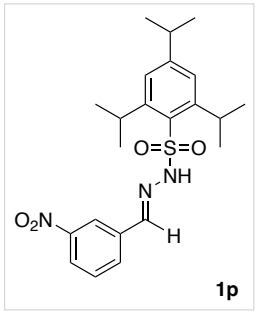
1.33 1.32 1.26 1.25

^{1}H NMR of **1p**, 600 MHz, $CDCl_3$

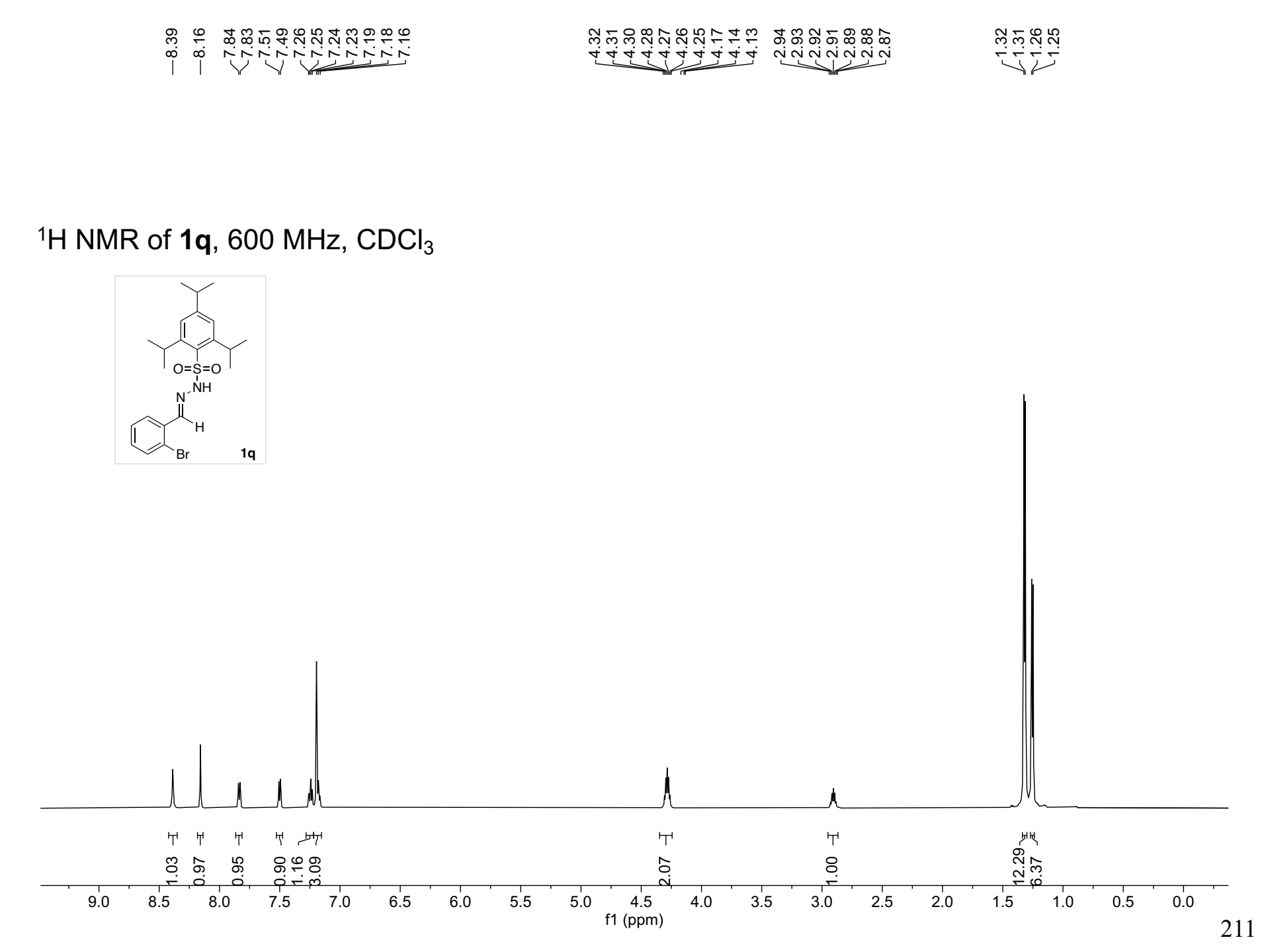




^{13}C NMR of **1p**, 150 MHz, DMSO-d_6



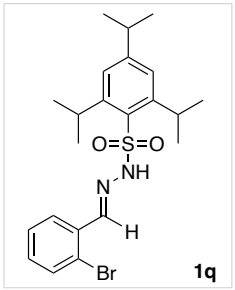
1p

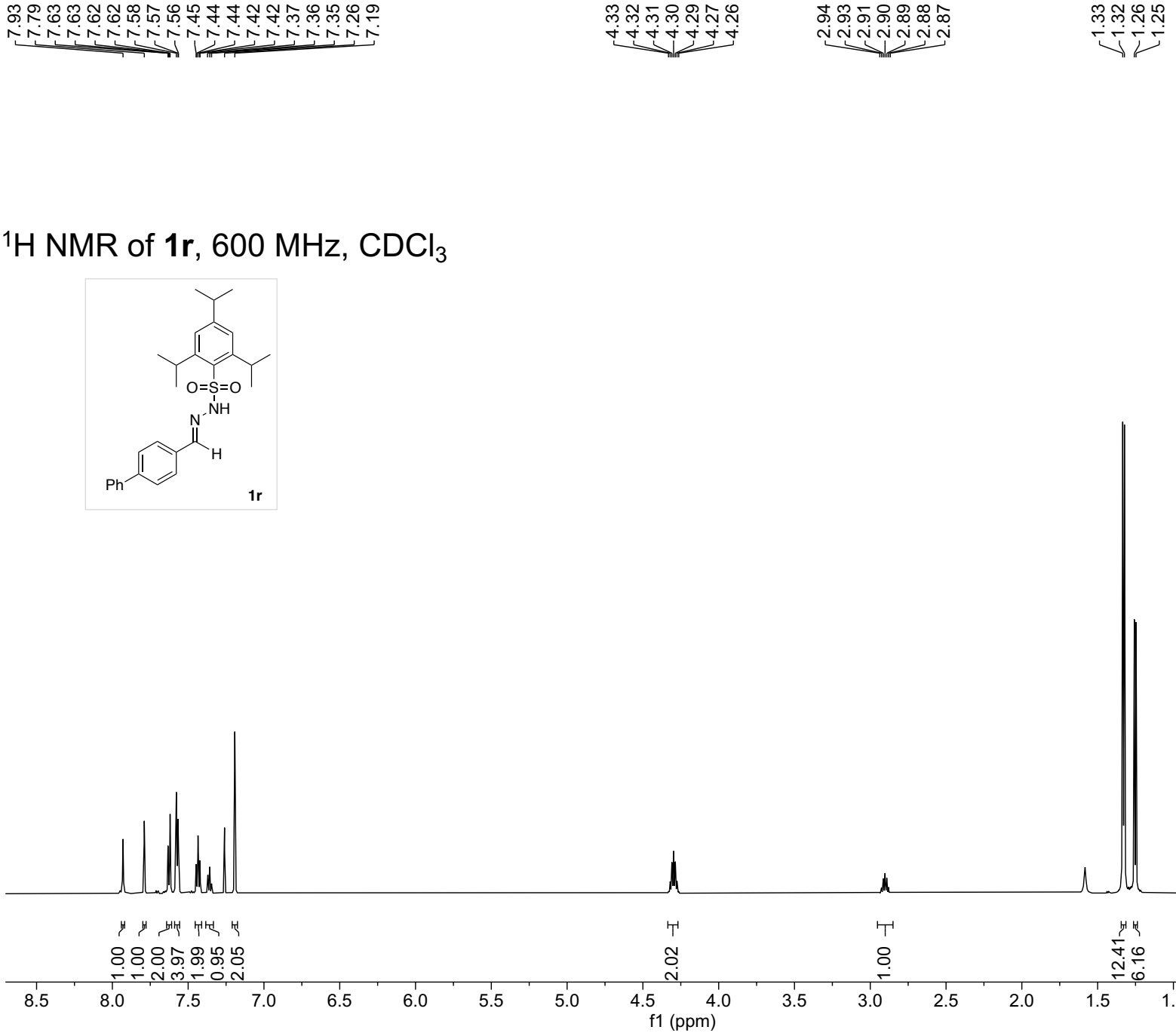


^{1}H NMR of **1q**, 600 MHz, $CDCl_3$

153.73
151.54
144.96
133.11
132.49
131.42
131.34
127.90
127.56
124.10
124.06
77.37
77.16
76.95
34.33
30.24
25.01
23.66

^{13}C NMR of **1q**, 150 MHz, $CDCl_3$

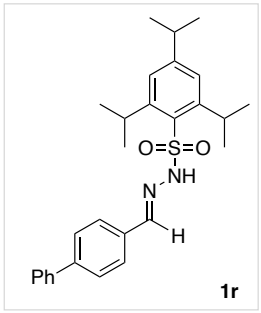


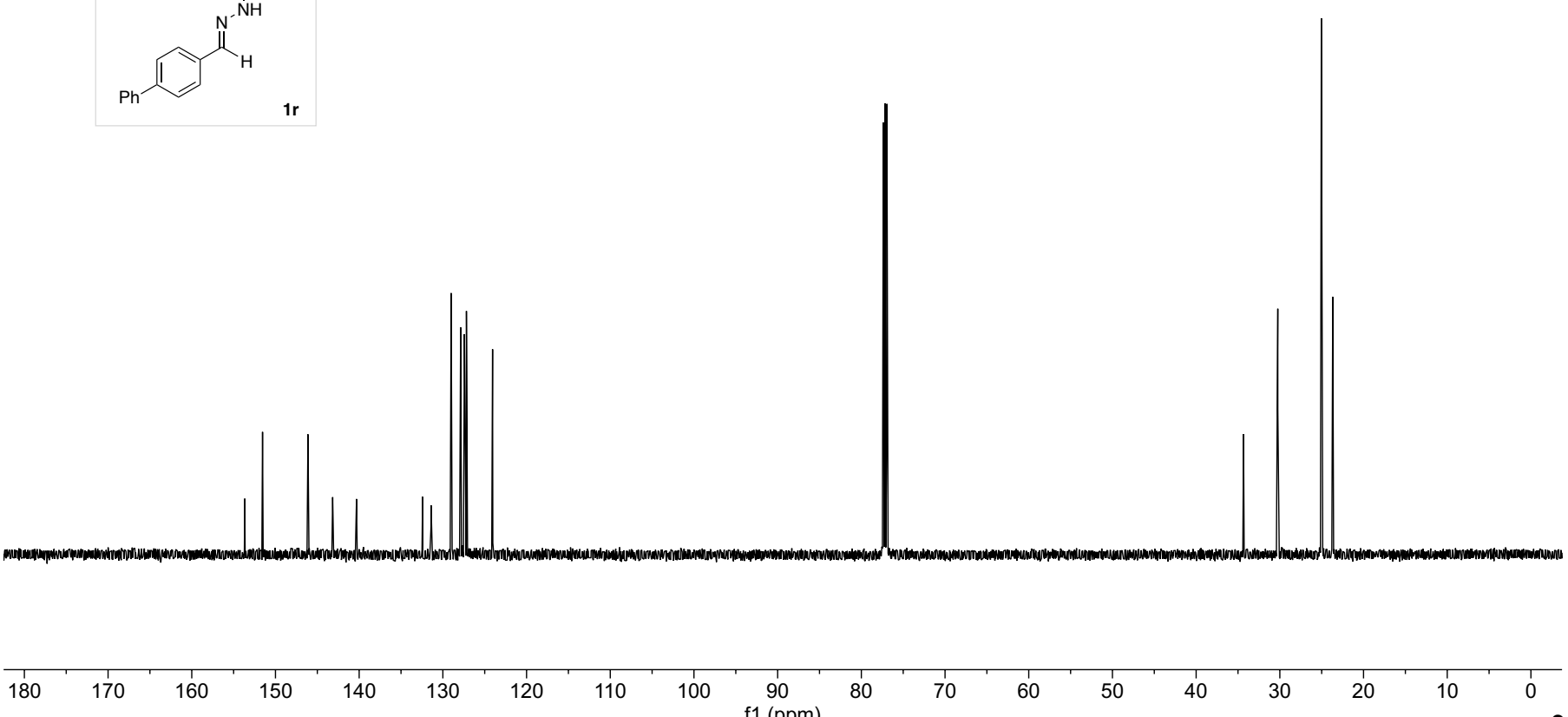


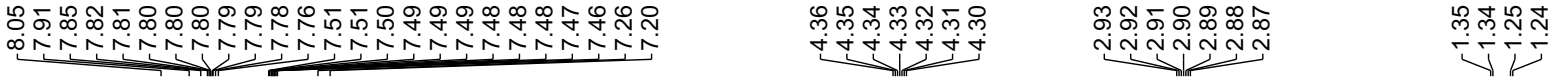
^{1}H NMR of **1r**, 600 MHz, $CDCl_3$

153.67
151.54
146.12
143.17
140.32
132.42
131.41
129.01
127.94
127.88
127.42
127.18
124.06
77.37
77.16
76.95
34.34
30.24
25.04
23.68

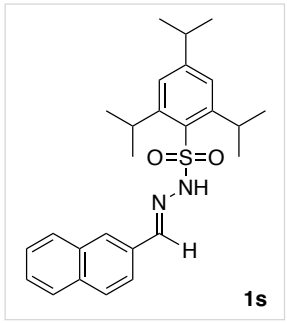
^{13}C NMR of **1r**, 150 MHz, $CDCl_3$

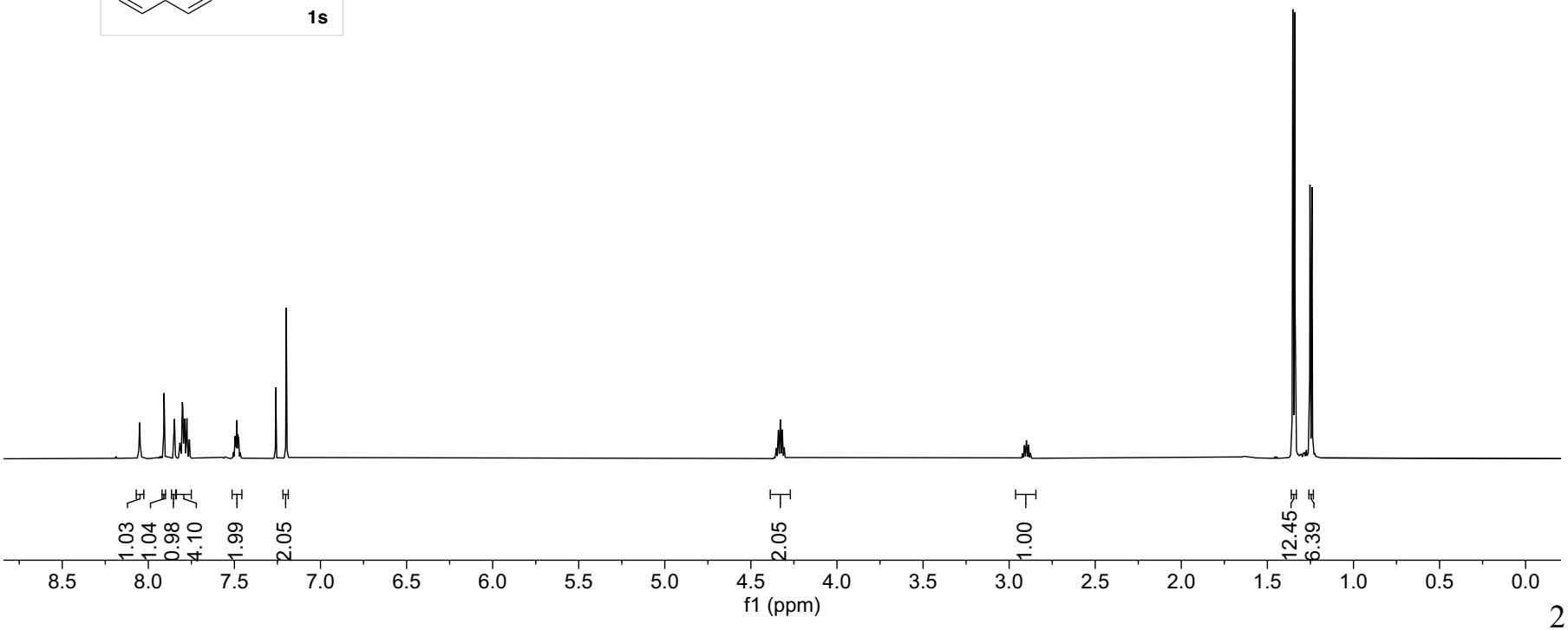






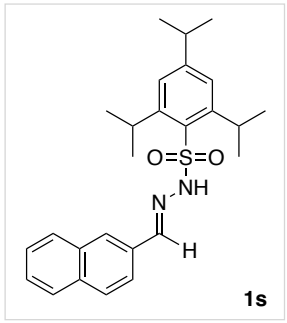
^{1}H NMR of **1s**, 600 MHz, $CDCl_3$

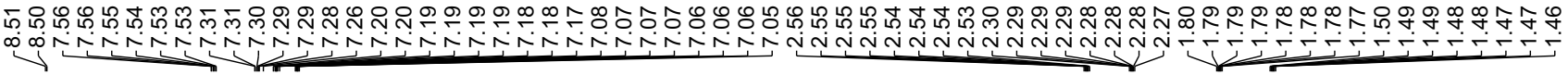




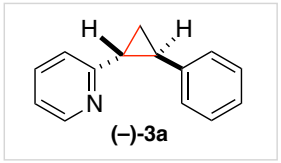
153.68
151.57
146.61
134.41
133.11
131.45
131.21
129.01
128.61
128.46
127.99
127.30
126.78
124.07
123.12
77.37
77.16
76.95
34.33
30.28
25.07
23.67

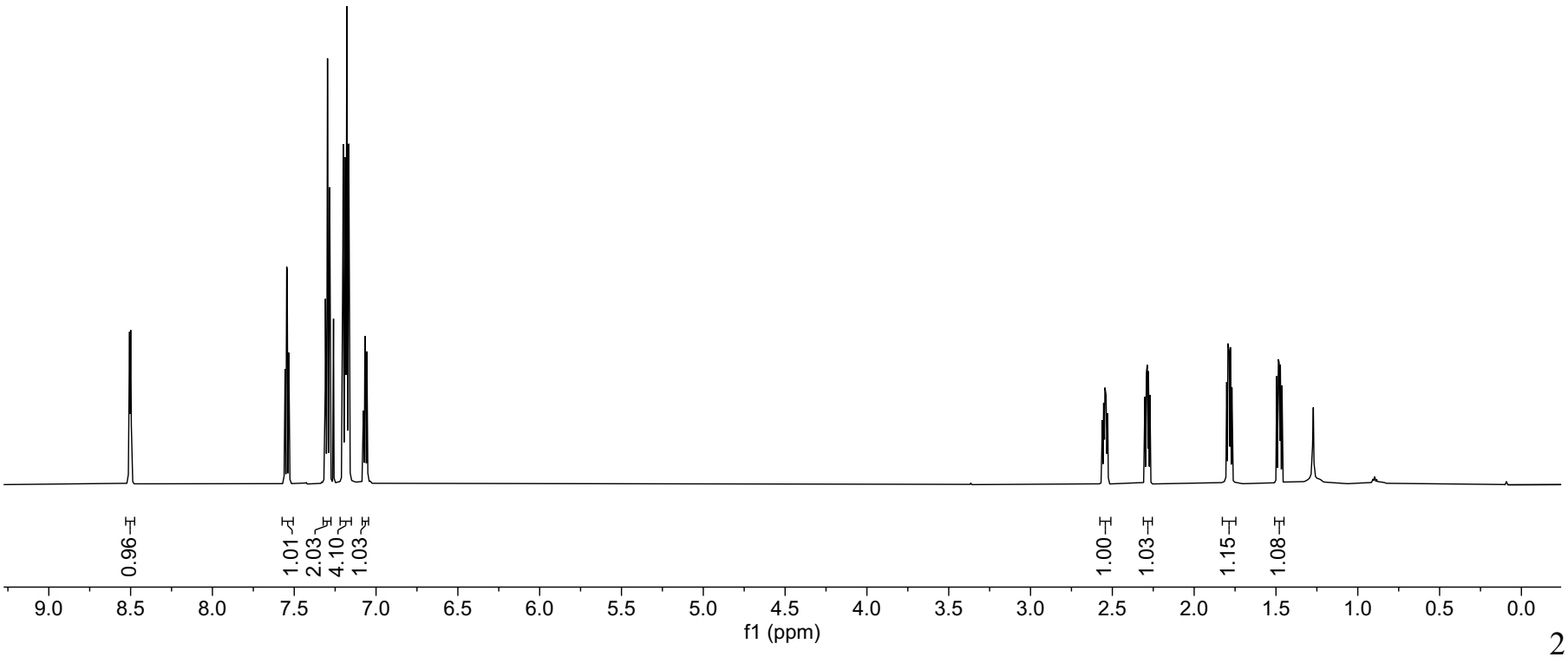
^{13}C NMR of **1s**, 150 MHz, $CDCl_3$

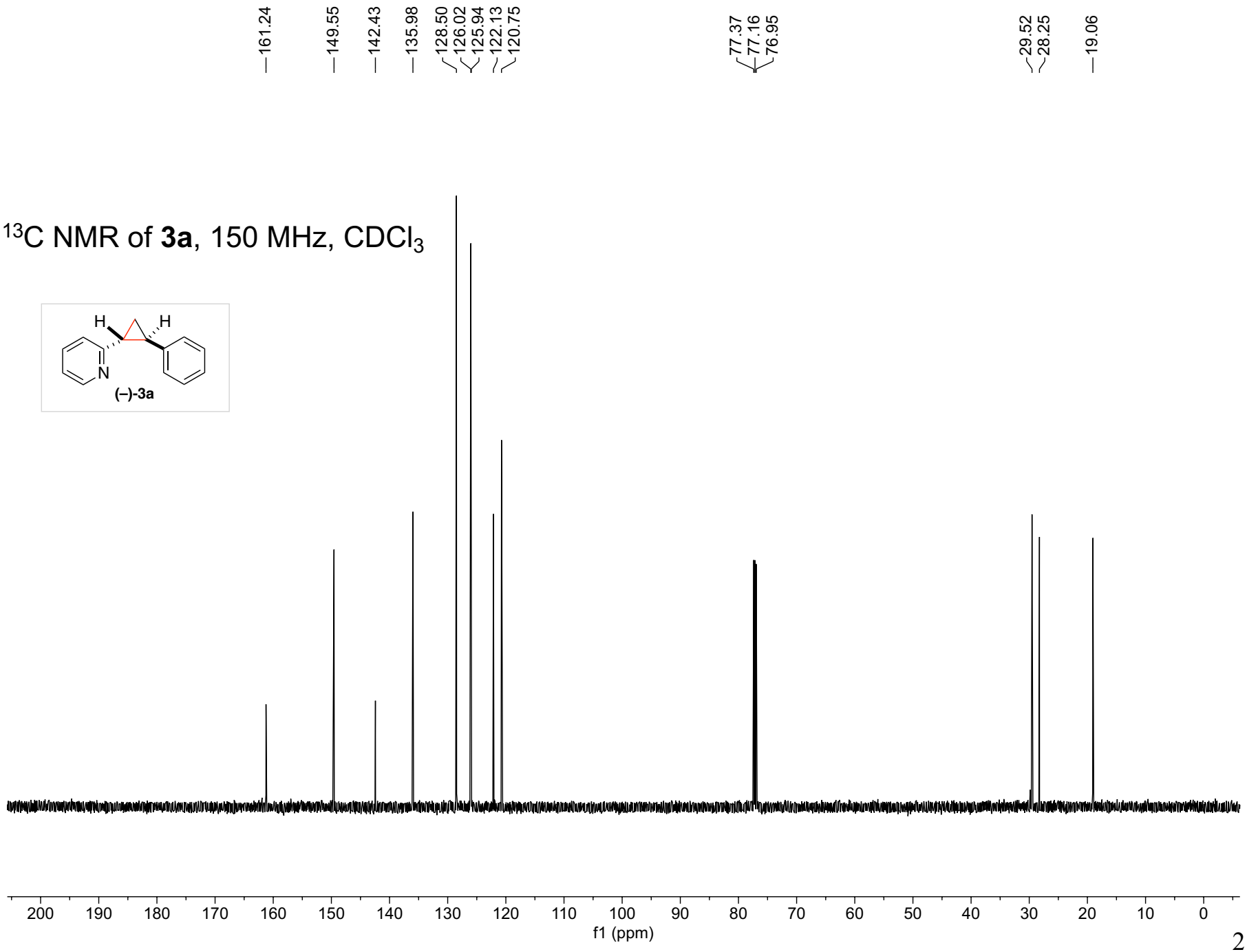


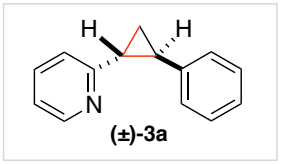


^{1}H NMR of **3a**, 600 MHz, $CDCl_3$






161.24
149.55
142.43
135.98
128.50
126.02
125.94
122.13
120.75
77.37
77.16
76.95
29.52
28.25
19.06
13C NMR of 3a, 150 MHz, CDCl3
H
H
N
(–)-3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

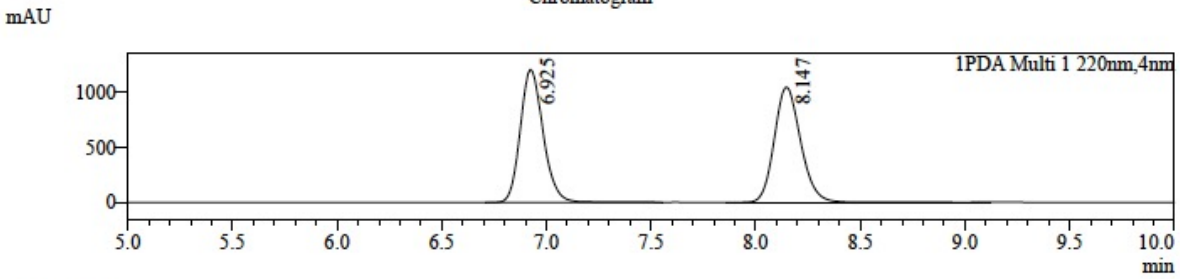


(±)-3a

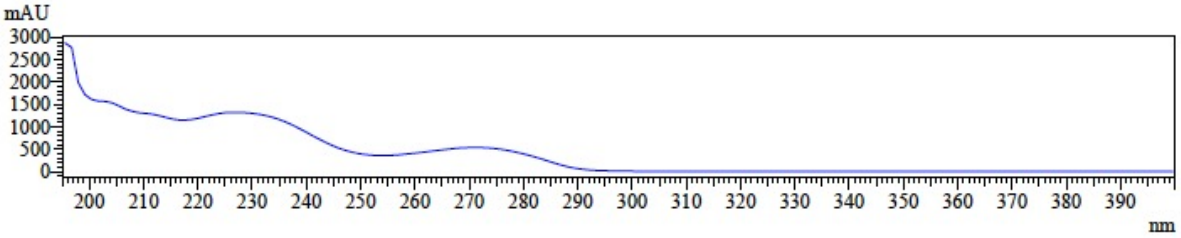
Sample Information

Sample Name	: XXW-0868--ID-5%-0.8mL
Sample ID	: XXW-0868--ID-5%-0.8mL
Data File	: XXW-0868--ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

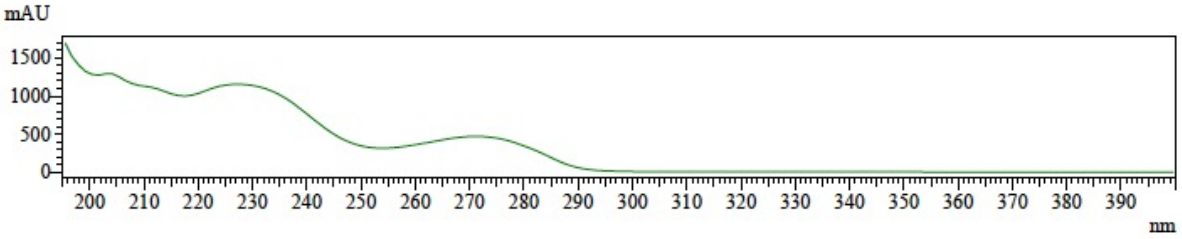
Chromatogram



UV Spectrum
Retention time = 6.925



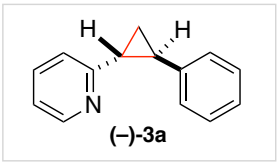
UV Spectrum
Retention time = 8.147



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.925	9205035	49.936
2	8.147	9228706	50.064
Total		18433741	100.000

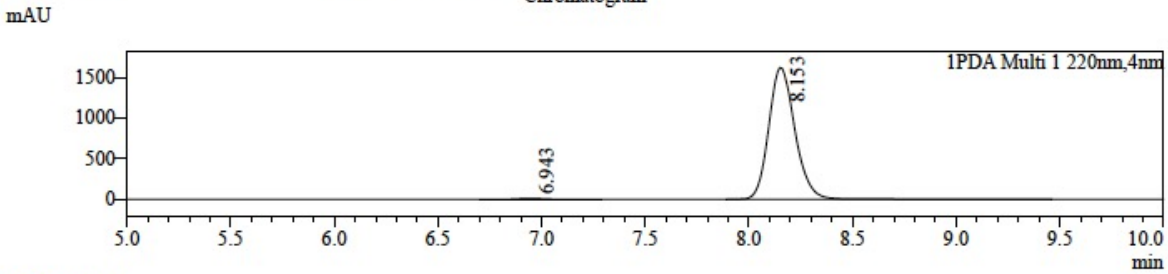


(–)-3a

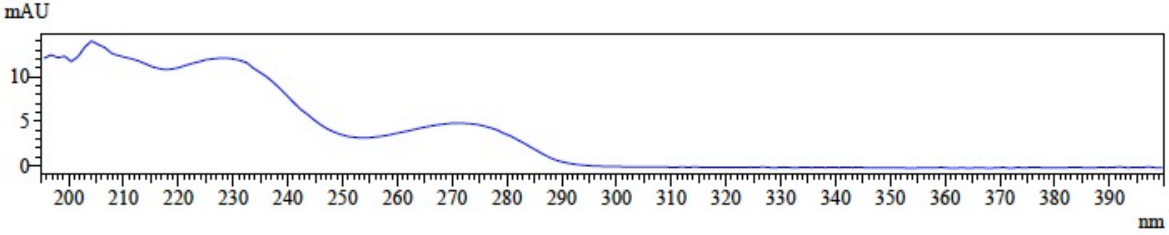
Sample Information

Sample Name	: XXW-0863-ID-5%-0.8mL
Sample ID	: XXW-0863-ID-5%-0.8mL
Data File	: XXW-0863-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

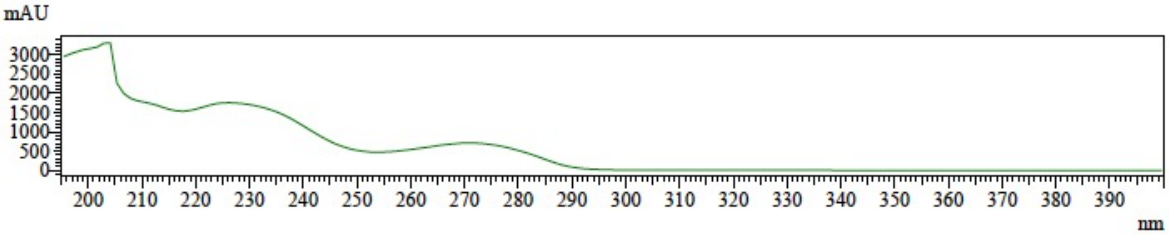
Chromatogram



UV Spectrum
Retention time = 6.943



UV Spectrum
Retention time = 8.153

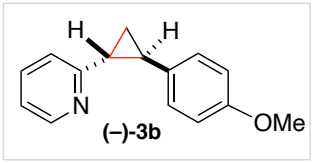


Peak Table

PDA Ch1 220nm

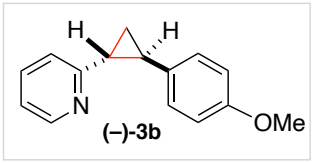
Peak#	Ret. Time	Area	Area%
1	6.943	86133	0.601
2	8.153	14247173	99.399
Total		14333305	100.000

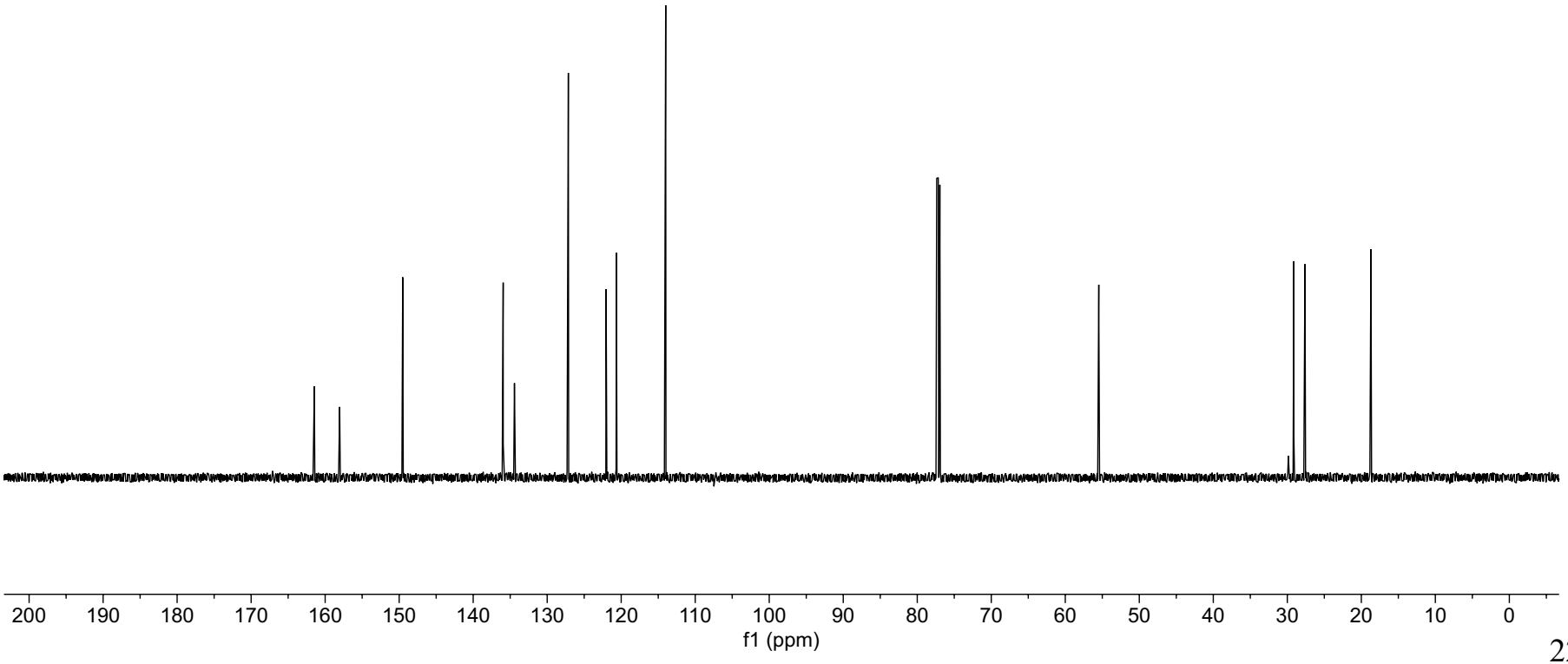
^{1}H NMR of **3b**, 500 MHz, $CDCl_3$



161.46
158.04
149.52
135.95
134.42
127.14
122.04
120.65
113.99
77.37
77.16
76.95
55.47
29.12
27.61
18.70

^{13}C NMR of **3b**, 150 MHz, $CDCl_3$

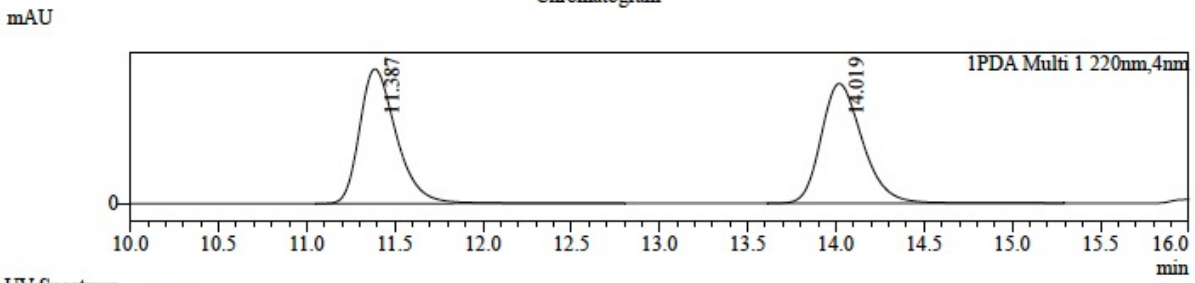




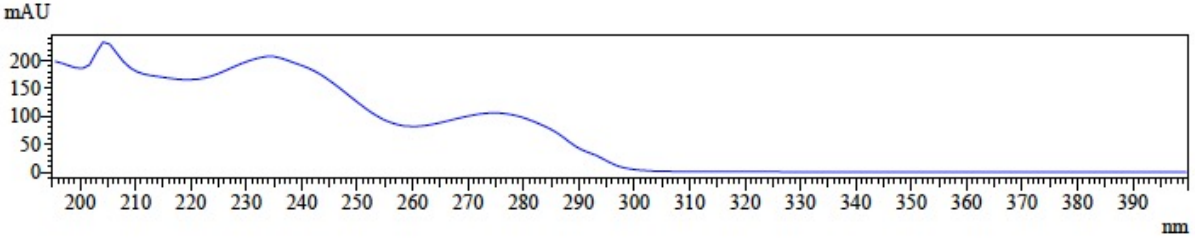
Sample Information

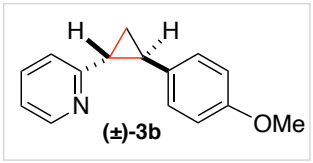
Sample Name	: XXW-0907-ID-5%-0.8mL
Sample ID	: XXW-0907-ID-5%-0.8mL
Data File	: XXW-0907-ID-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram



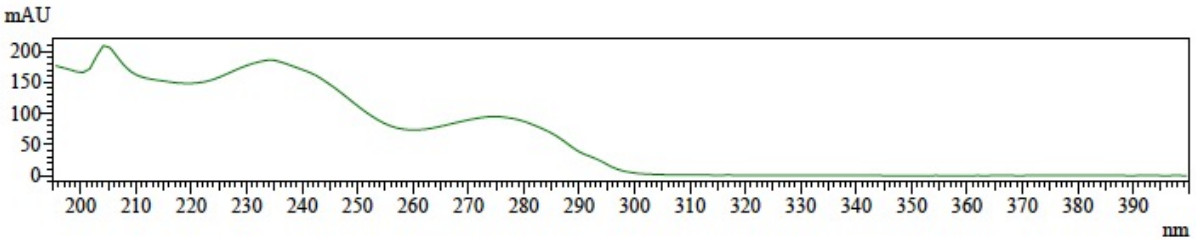
UV Spectrum
Retention time = 11.387





(±)-3b

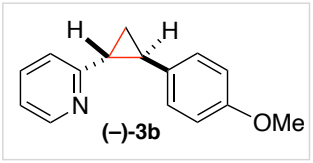
UV Spectrum
Retention time = 14.019



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	11.387	2449783	50.029
2	14.019	2446986	49.971
Total		4896769	100.000

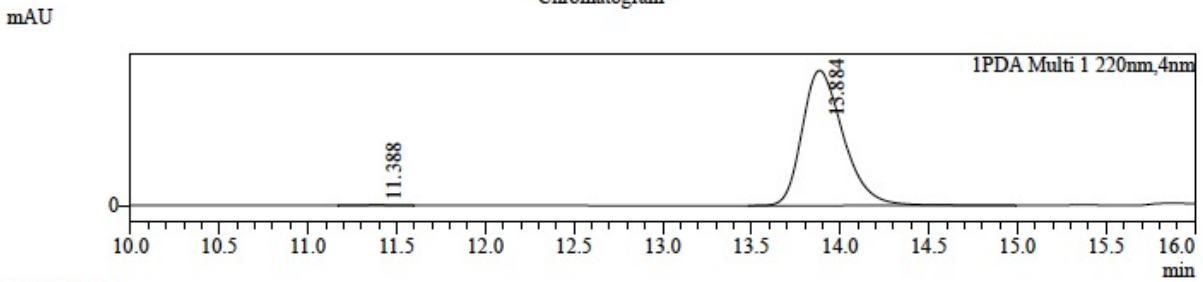


(–)-3b

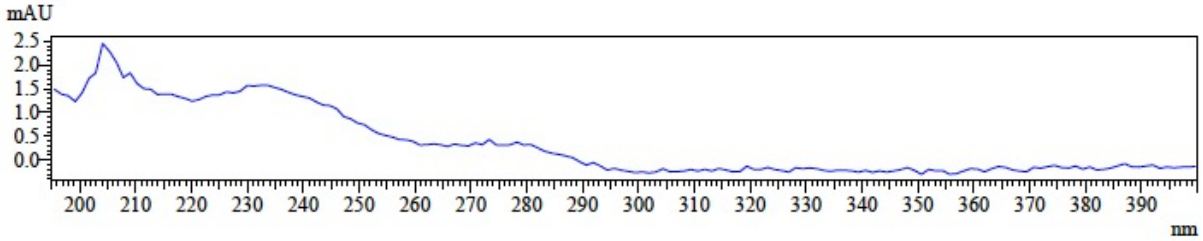
Sample Information

Sample Name	: XXW-1040-ID-5%-0.8mL
Sample ID	: XXW-1040-ID-5%-0.8mL
Data File	: XXW-1040-ID-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

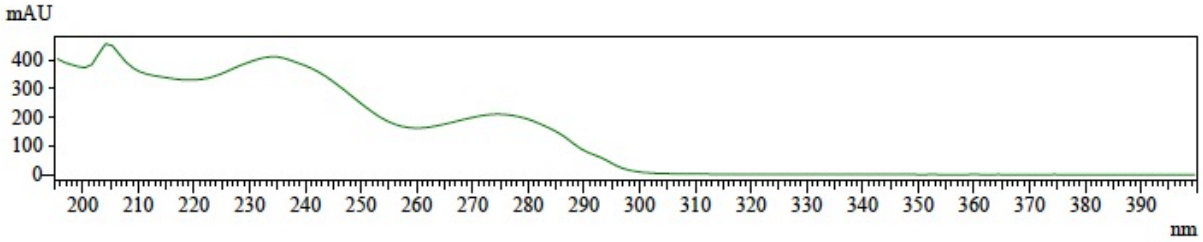
Chromatogram



UV Spectrum
Retention time = 11.388



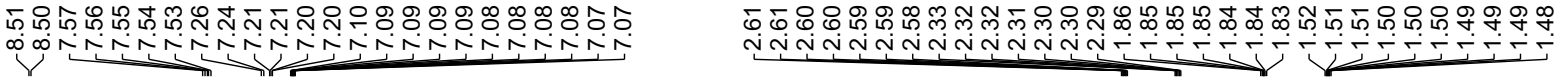
UV Spectrum
Retention time = 13.884



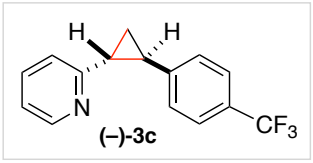
Peak Table

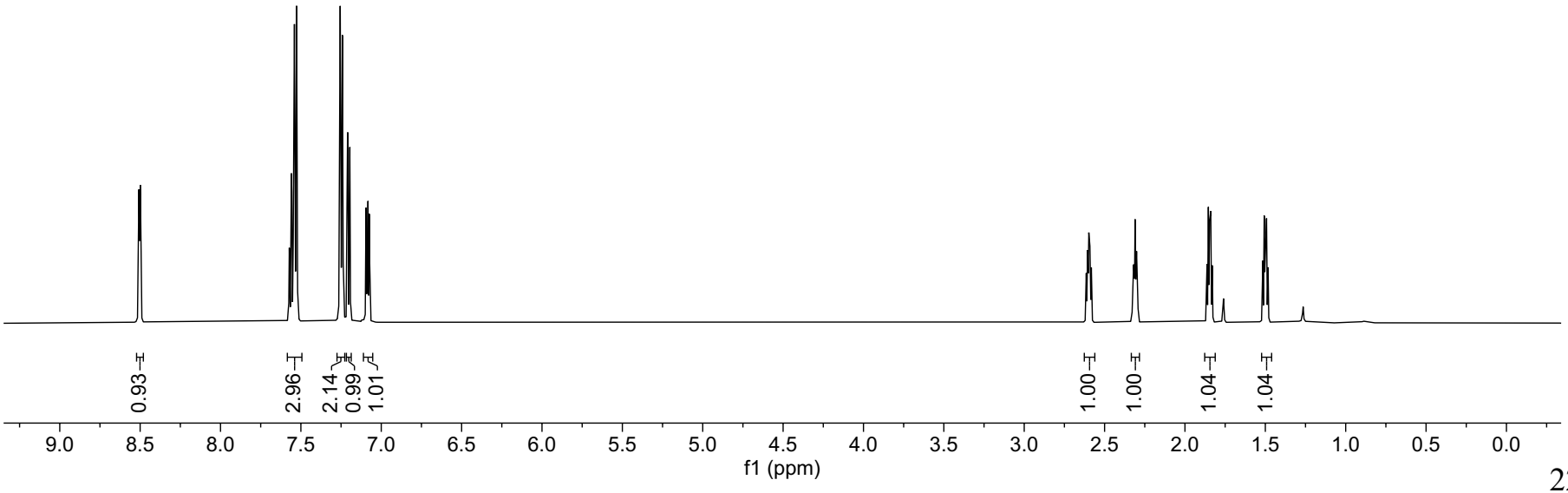
PDA Ch1 220nm

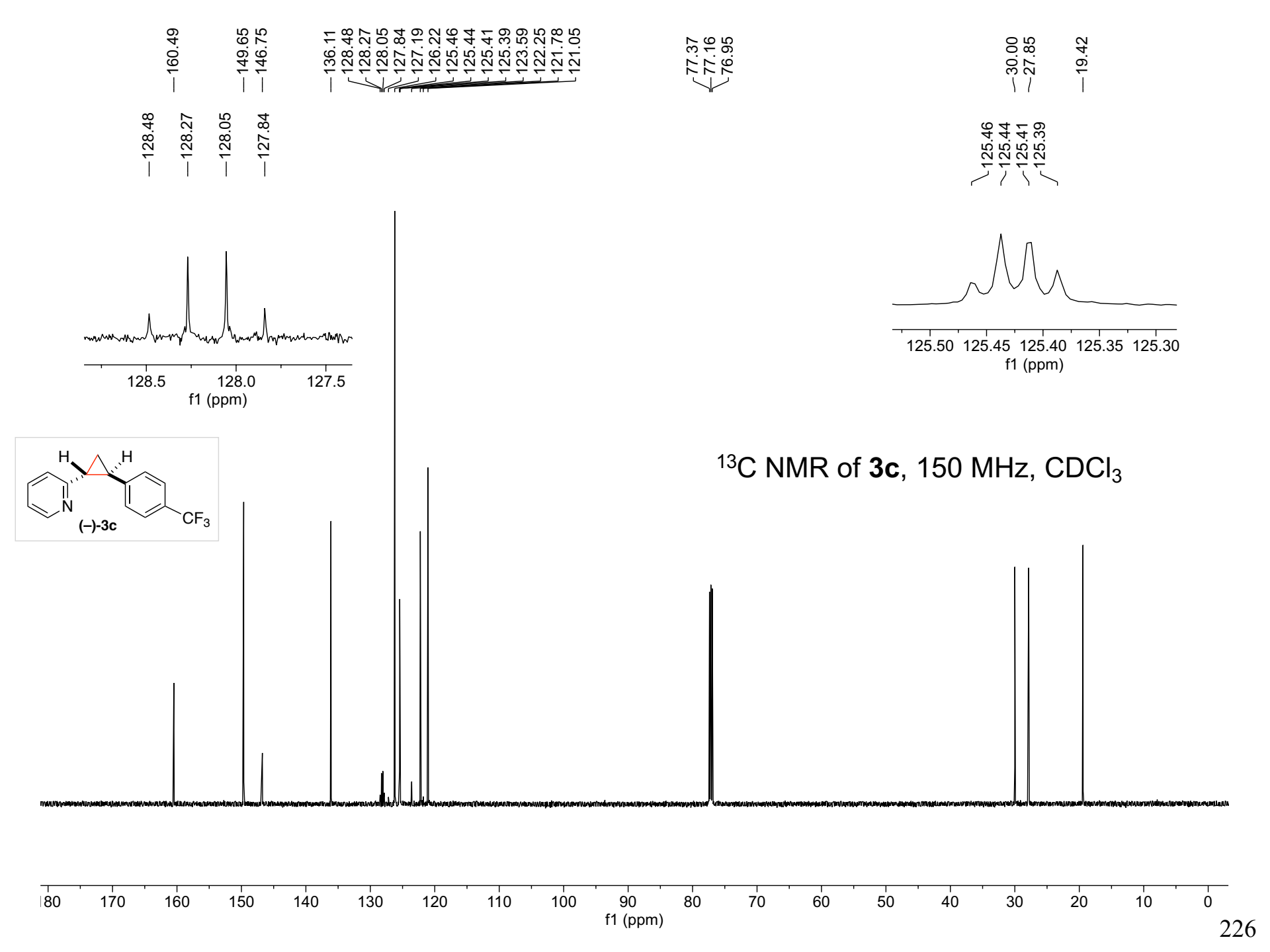
Peak#	Ret. Time	Area	Area%
1	11.388	10880	0.201
2	13.884	5401596	99.799
Total		5412476	100.000



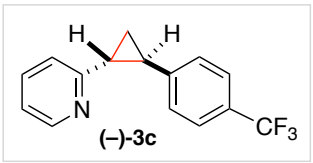
^{1}H NMR of **3c**, 600 MHz, $CDCl_3$






160.49
149.65
146.75
136.11
128.48
128.27
128.05
127.84
127.19
126.22
125.46
125.44
125.41
125.39
123.59
122.25
121.78
121.05
77.37
77.16
76.95
30.00
27.85
19.42
128.48
128.27
128.05
127.84
125.46
125.44
125.41
125.39
128.5
128.0
127.5
f1 (ppm)
125.50
125.45
125.40
125.35
125.30
f1 (ppm)
H
H
N
CF3
(–)-3c
13C NMR of 3c, 150 MHz, CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

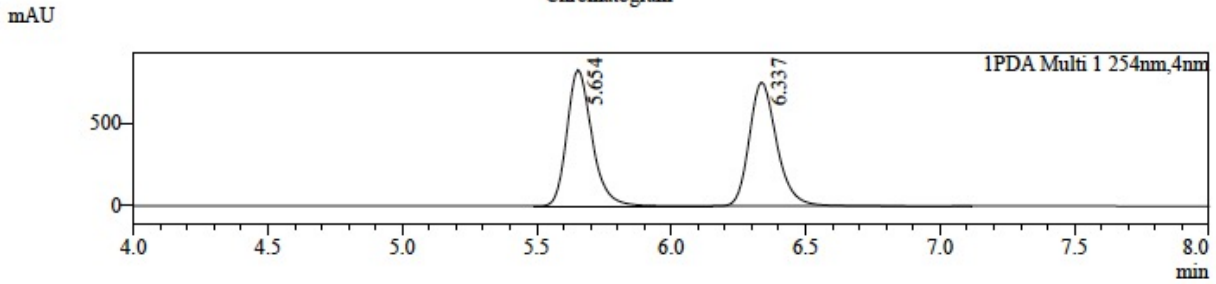
^{19}F NMR of **3c**, 564 MHz, $CDCl_3$



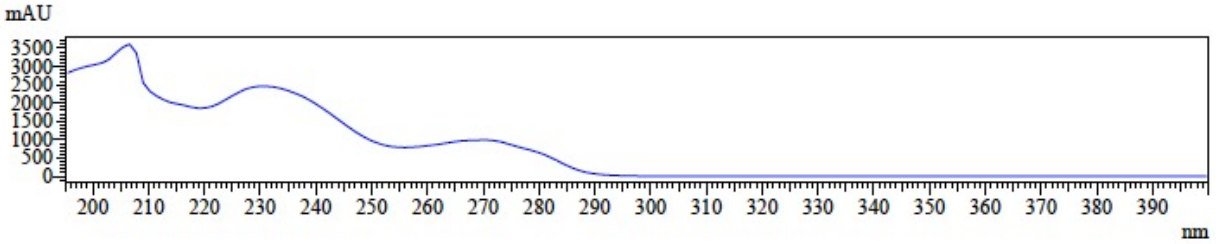
Sample Information

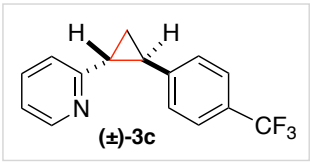
Sample Name	: XXW-0908-ID-5%-0.8mL
Sample ID	: XXW-0908-ID-5%-0.8mL
Data File	: XXW-0908-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram

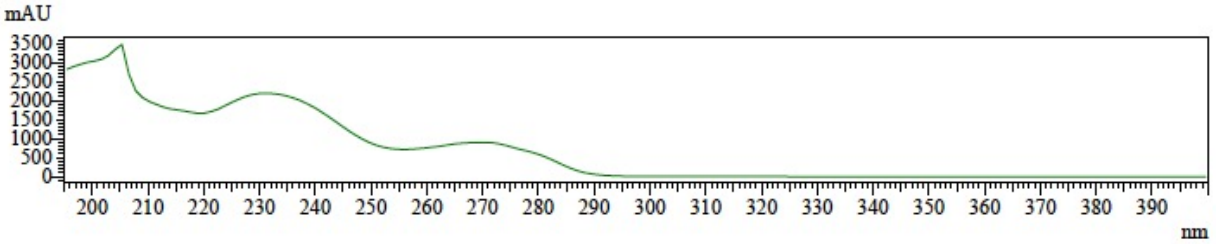


UV Spectrum
Retention time = 5.654





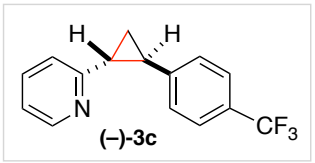
UV Spectrum
Retention time = 6.337



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.654	5386382	50.028
2	6.337	5380364	49.972
Total		10766746	100.000

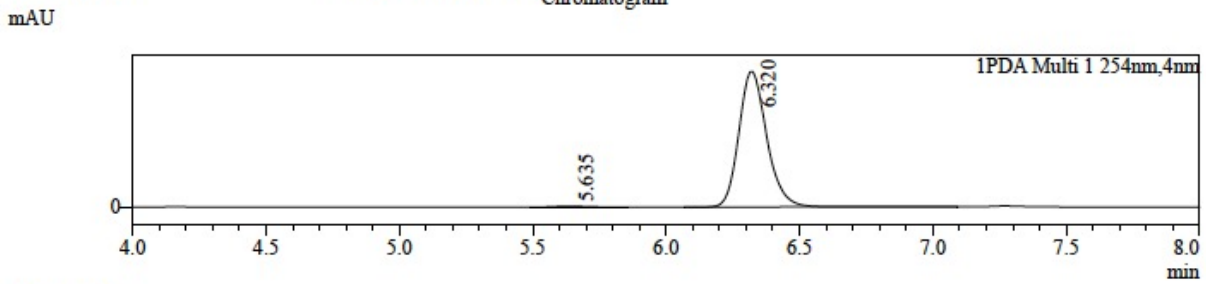


(–)-3c

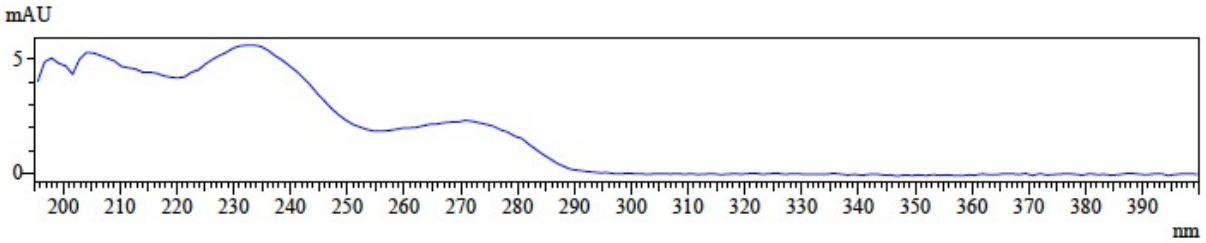
Sample Information

Sample Name	: XXW-1114--ID-5-%--0.8mL
Sample ID	: XXW-1114--ID-5-%--0.8mL
Data File	: XXW-1114--ID-5-%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

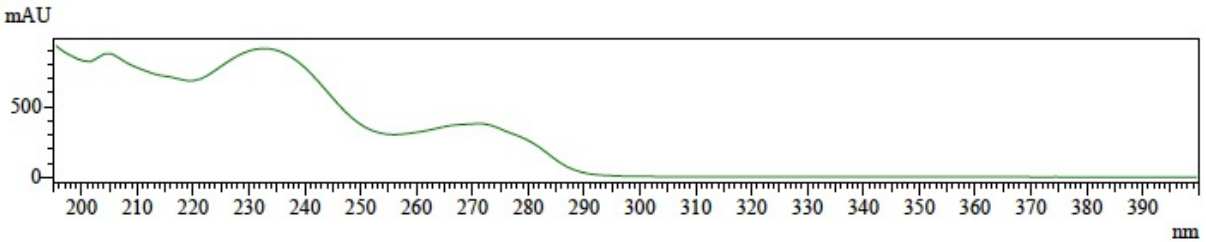
Chromatogram



UV Spectrum
Retention time = 5.635



UV Spectrum
Retention time = 6.320

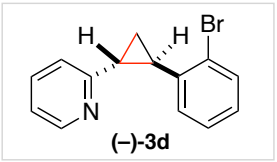


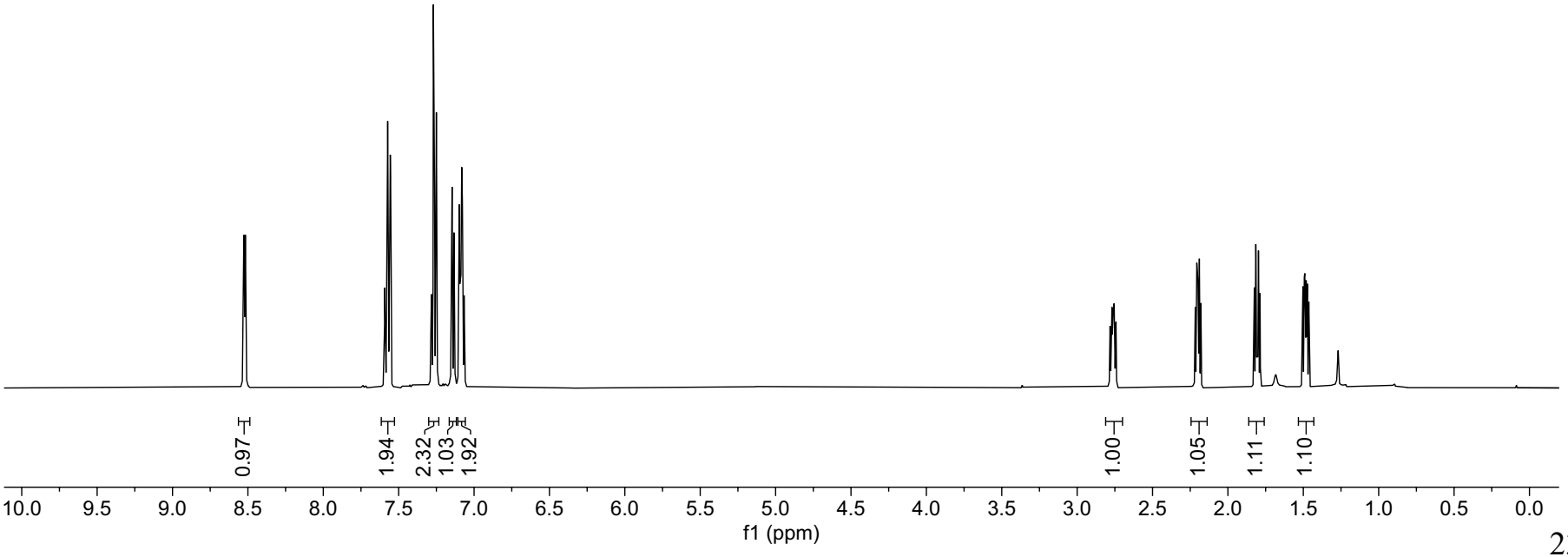
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.635	13046	0.561
2	6.320	2312257	99.439
Total		2325304	100.000

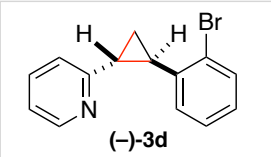
^{1}H NMR of **3d**, 500 MHz, $CDCl_3$



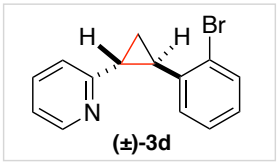


161.09
149.50
141.34
135.97
132.63
127.68
127.51
127.43
126.45
122.18
120.84
77.37
77.16
76.95
28.88
28.27
17.36

^{13}C NMR of **3d**, 150 MHz, $CDCl_3$



(–)-3d

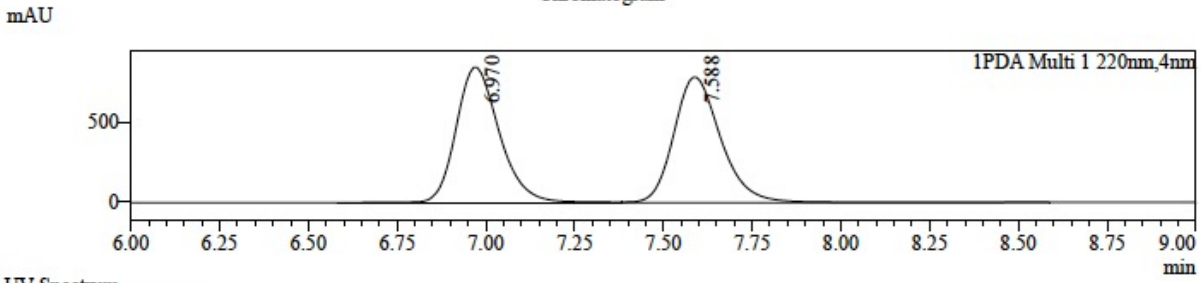


(±)-3d

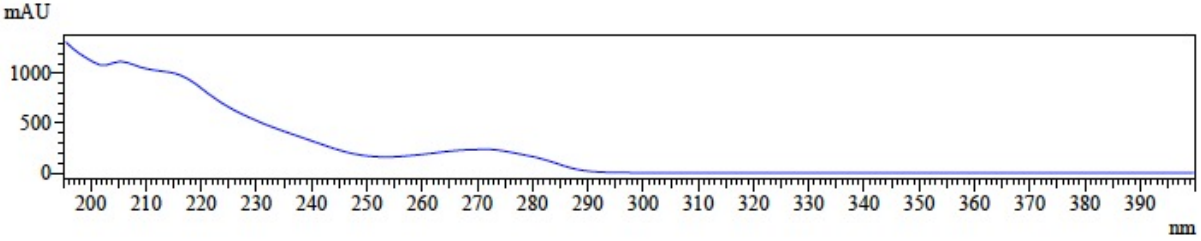
Sample Information

Sample Name	: XXW-0965-ID-5%-0.8mL
Sample ID	: XXW-0965-ID-5%-0.8mL
Data File	: XXW-0965-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

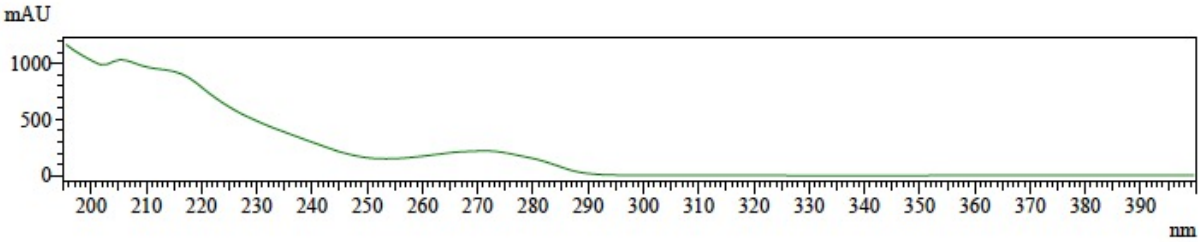
Chromatogram



UV Spectrum
Retention time = 6.970



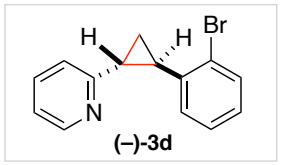
UV Spectrum
Retention time = 7.588



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.970	7238830	49.898
2	7.588	7268338	50.102
Total		14507169	100.000

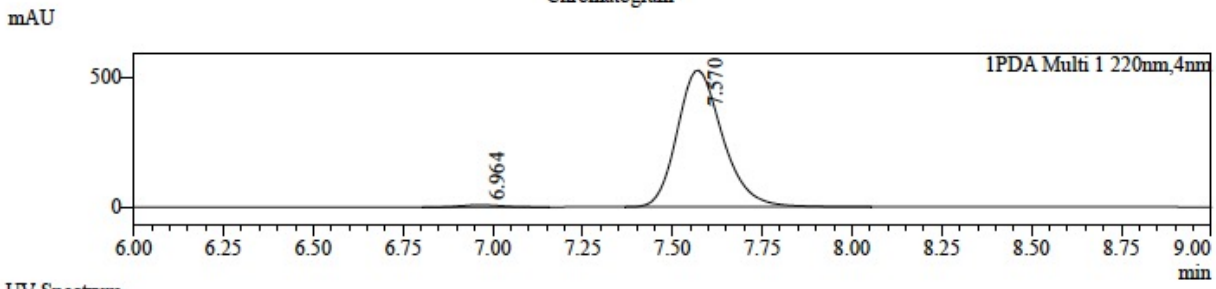


(–)-3d

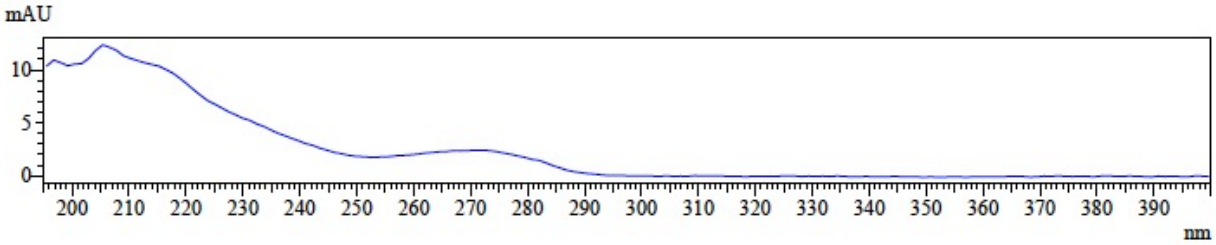
Sample Information

Sample Name	: XXW-1046-ID-5%-0.8mL
Sample ID	: XXW-1046-ID-5%-0.8mL
Data File	: XXW-1046-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

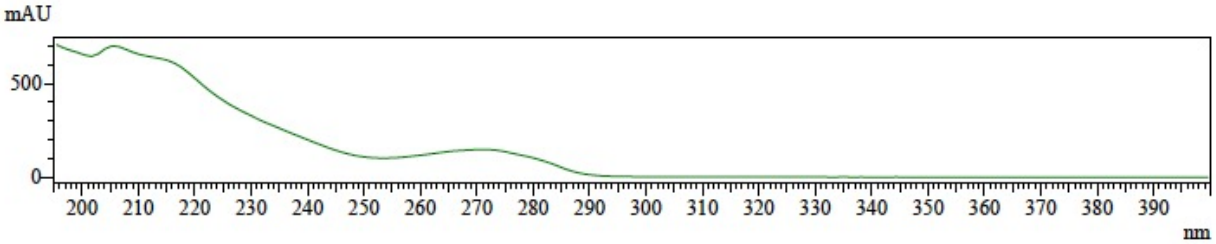
Chromatogram



UV Spectrum
Retention time = 6.964



UV Spectrum
Retention time = 7.570

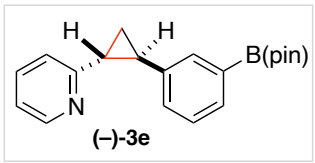


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.964	66186	1.415
2	7.570	4610794	98.585
Total		4676980	100.000

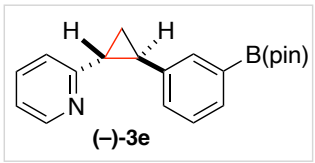
^{1}H NMR of **3e**, 500 MHz, $CDCl_3$



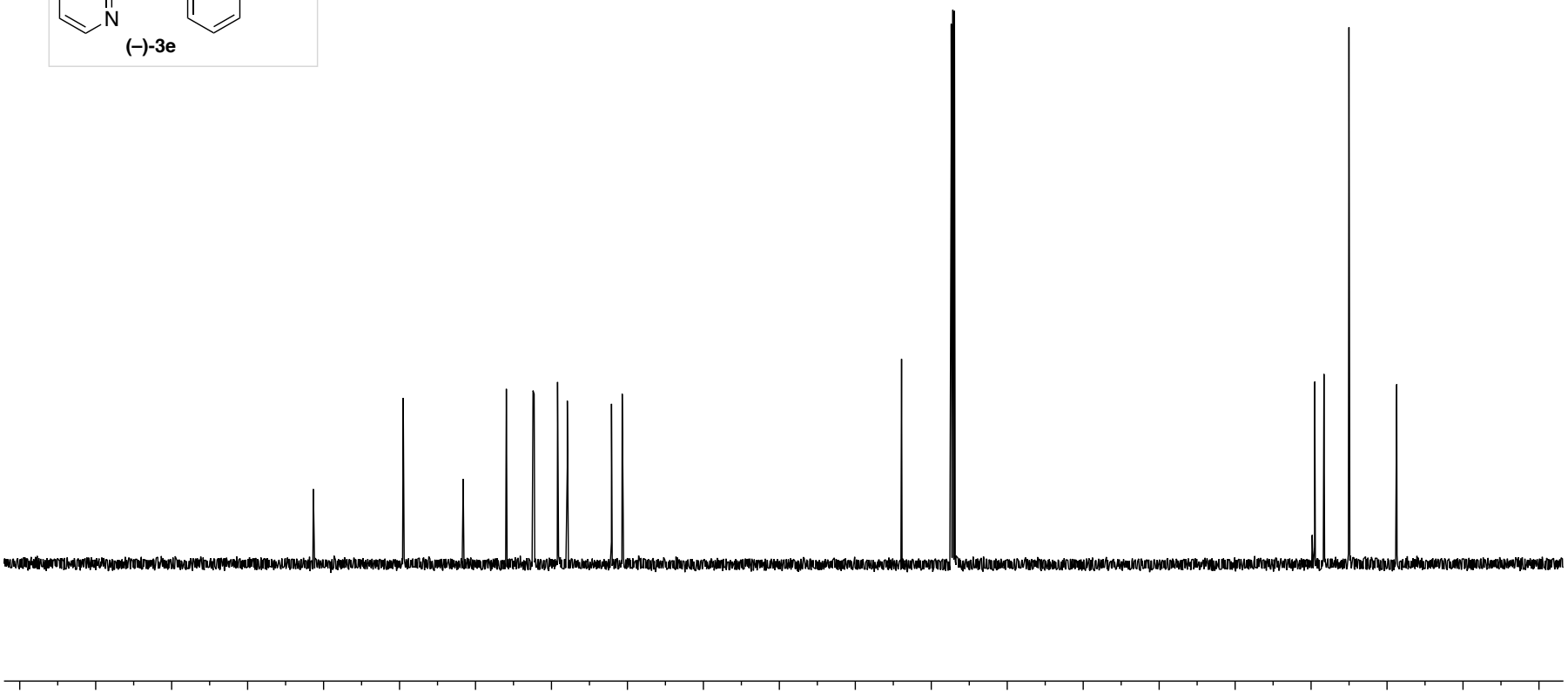
(–)-3e

161.35
149.52
141.62
135.94
132.43
132.28
129.20
127.91
122.10
120.69
83.91
77.37
77.16
76.95
29.52
28.30
25.01
18.73

^{13}C NMR of **3e**, 150 MHz, $CDCl_3$

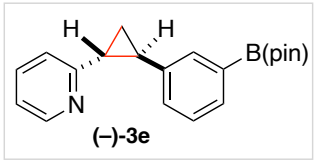


(–)-3e

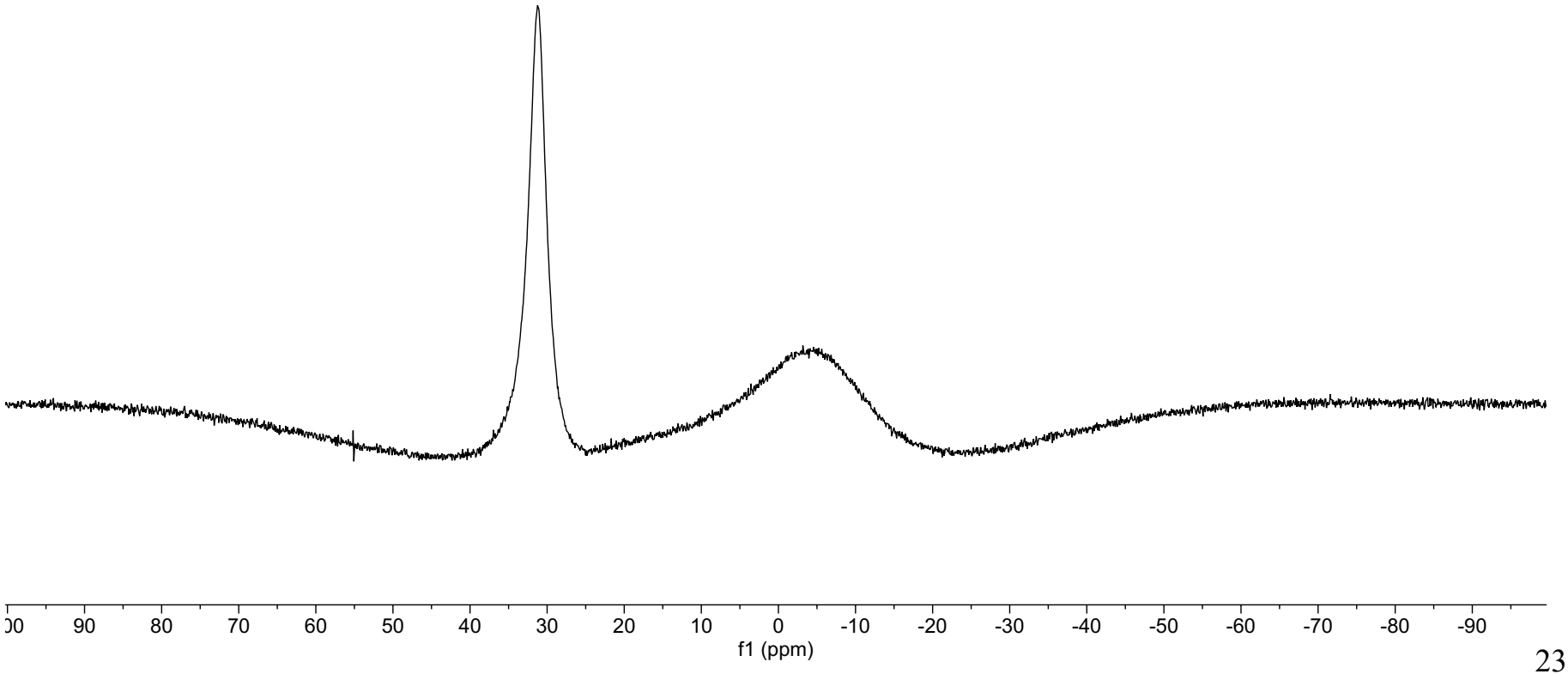


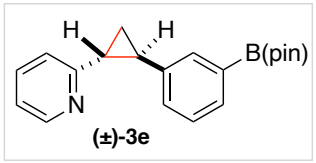
31.24

^{11}B NMR of **3e**, 160 MHz, $CDCl_3$



(–)-3e



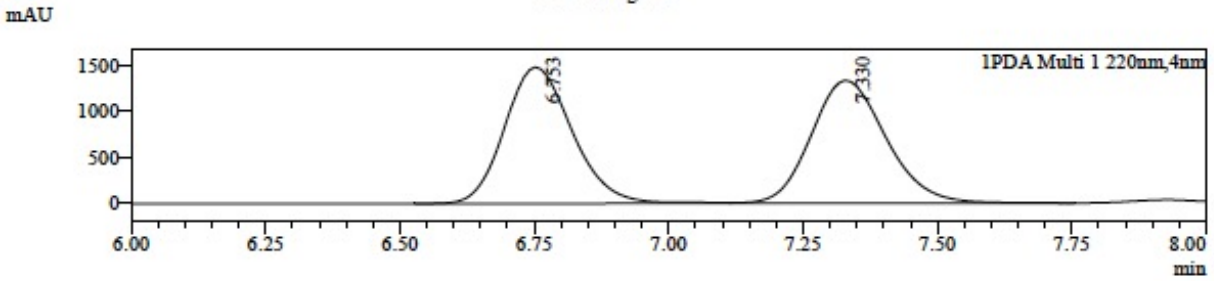


(±)-3e

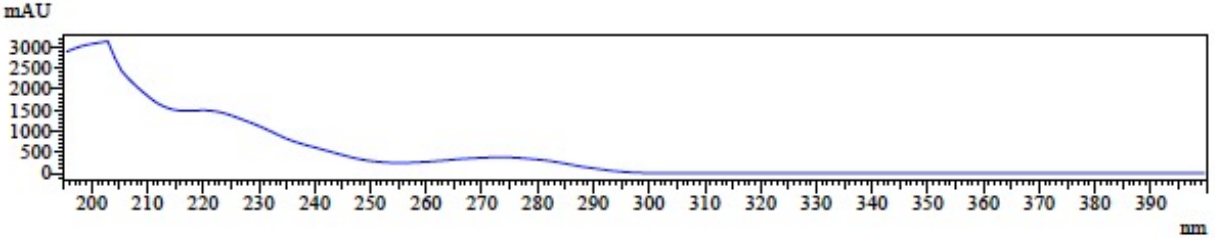
Sample Information

Sample Name	: XXW-0958-n1-IC-5%-0.8mL
Sample ID	: XXW-0958-n1-IC-5%-0.8mL
Data File	: XXW-0958-n1-IC-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

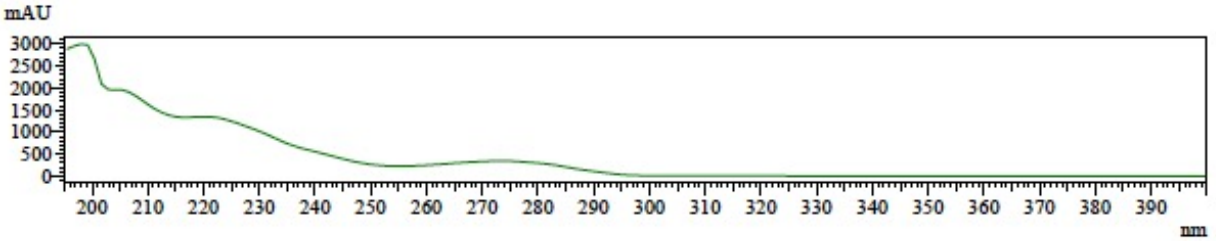
Chromatogram



UV Spectrum
Retention time = 6.753



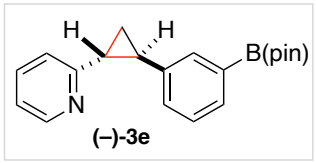
UV Spectrum
Retention time = 7.330



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.753	12959531	50.097
2	7.330	12909283	49.903
Total		25868814	100.000

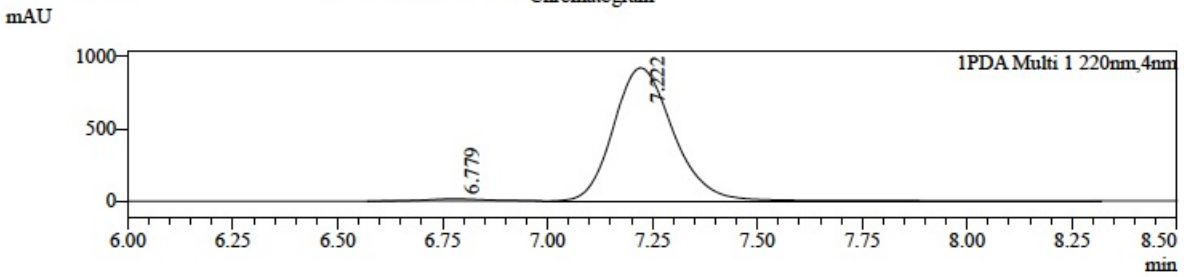


(–)-3e

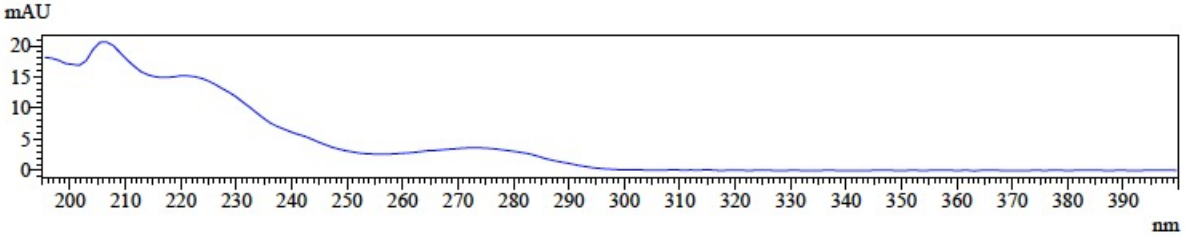
Sample Information

Sample Name	: XXW-1047-IC-5%-0.8mL
Sample ID	: XXW-1047-IC-5%-0.8mL
Data File	: XXW-1047-IC-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

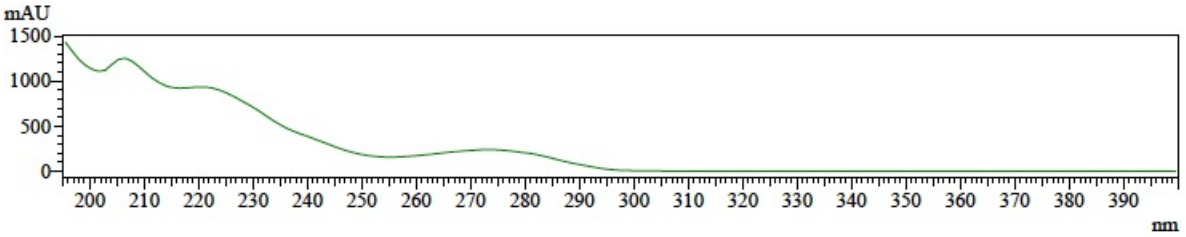
Chromatogram



UV Spectrum
Retention time = 6.779



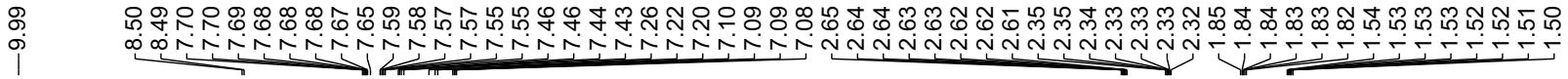
UV Spectrum
Retention time = 7.222



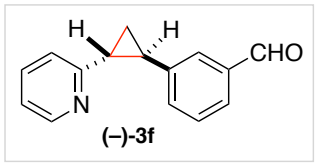
Peak Table

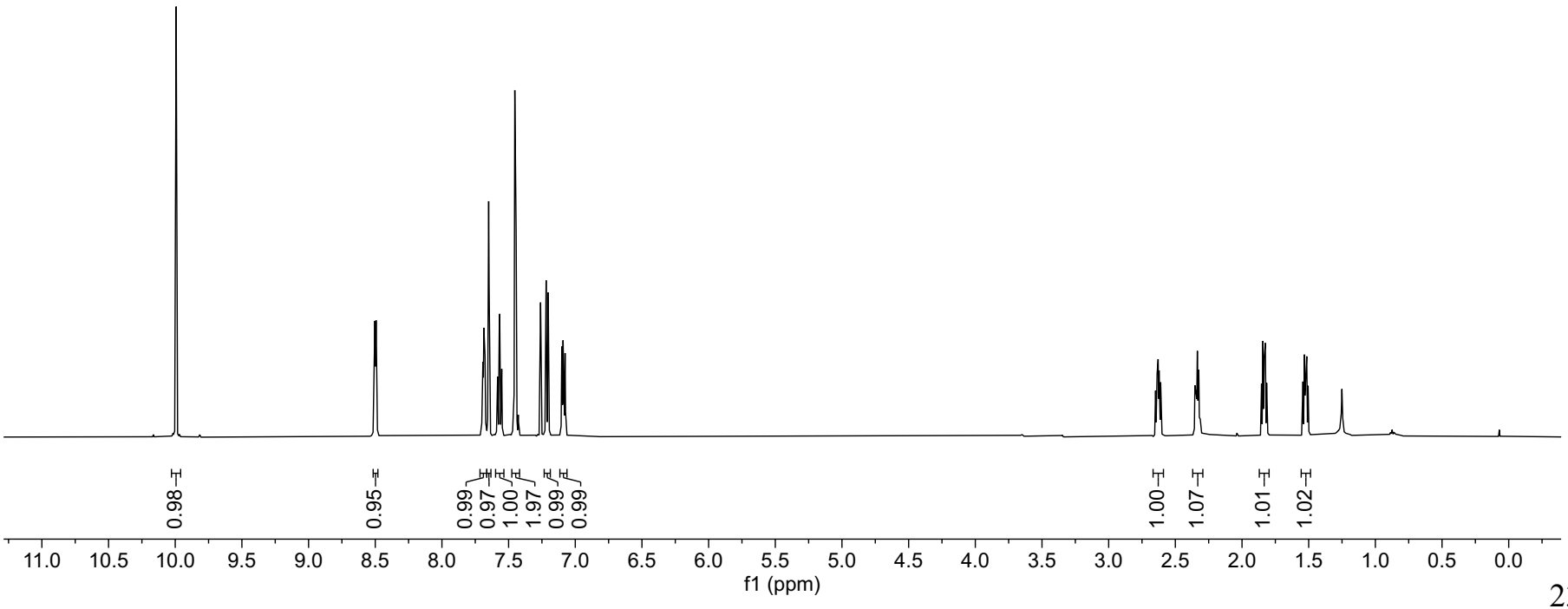
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.779	135561	1.456
2	7.222	9177073	98.544
Total		9312635	100.000



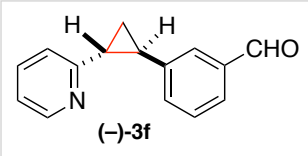
^{1}H NMR of **3f**, 500 MHz, $CDCl_3$



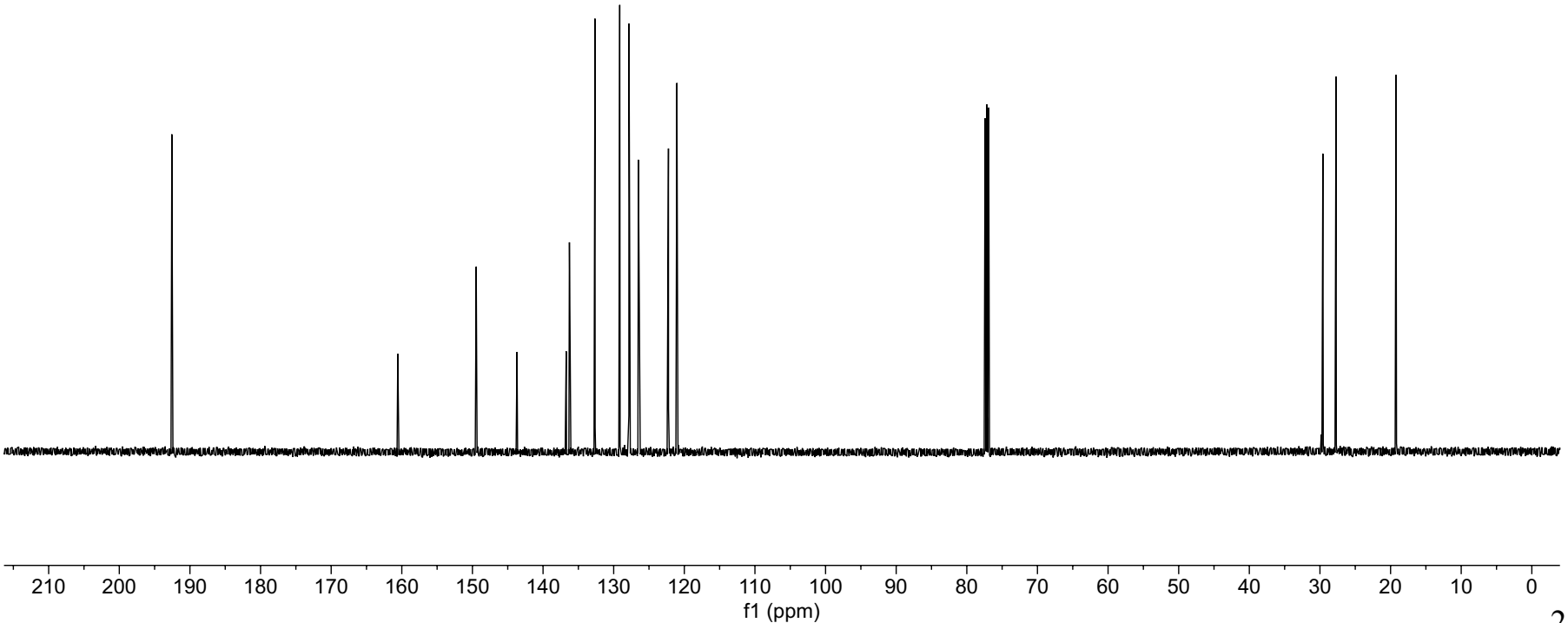


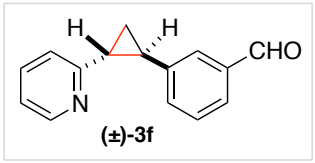
192.56
160.57
149.46
143.69
136.72
136.27
132.64
129.14
127.83
126.50
122.25
121.05
77.41
77.16
76.91
29.59
27.72
19.23

^{13}C NMR of **3f**, 125 MHz, $CDCl_3$



(–)-3f



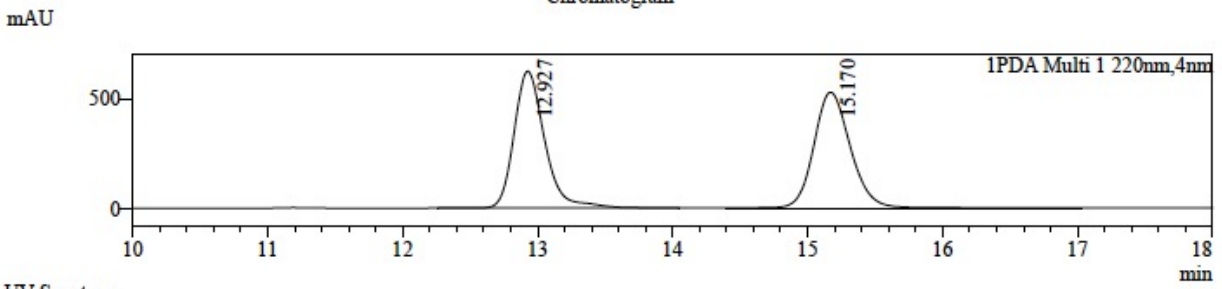


(±)-3f

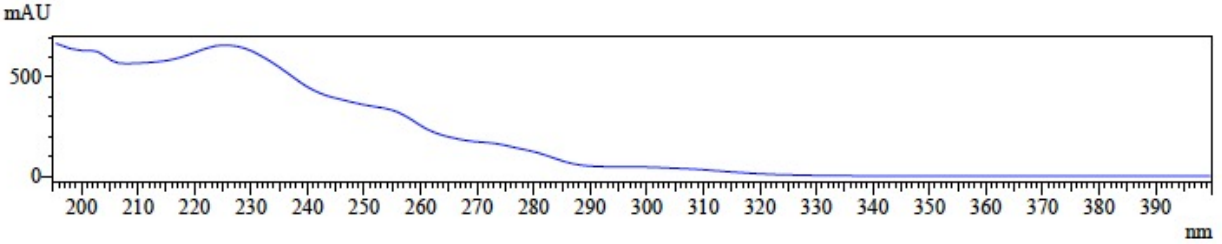
Sample Information

Sample Name	: XXW-0910-n1-ID-20%-0.8mL
Sample ID	: XXW-0910-n1-ID-20%-0.8mL
Data File	: XXW-0910-n1-ID-20%-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

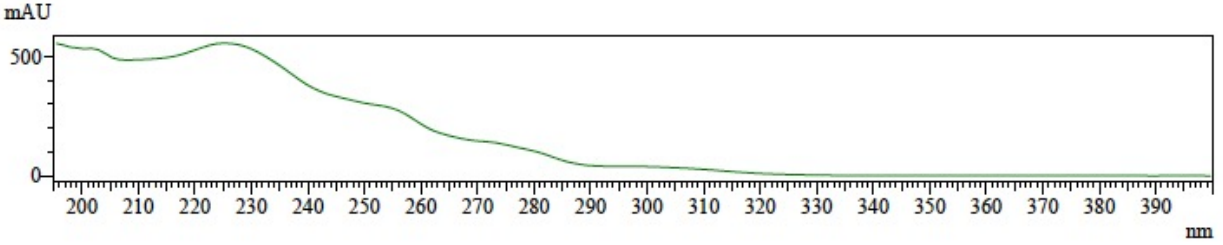
Chromatogram



UV Spectrum
Retention time = 12.927



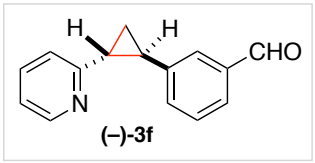
UV Spectrum
Retention time = 15.170



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.927	9811405	49.900
2	15.170	9850900	50.100
Total		19662305	100.000

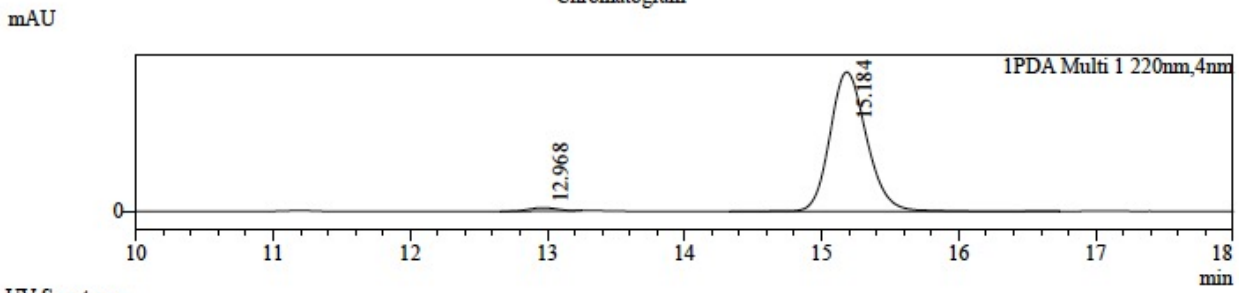


(–)-3f

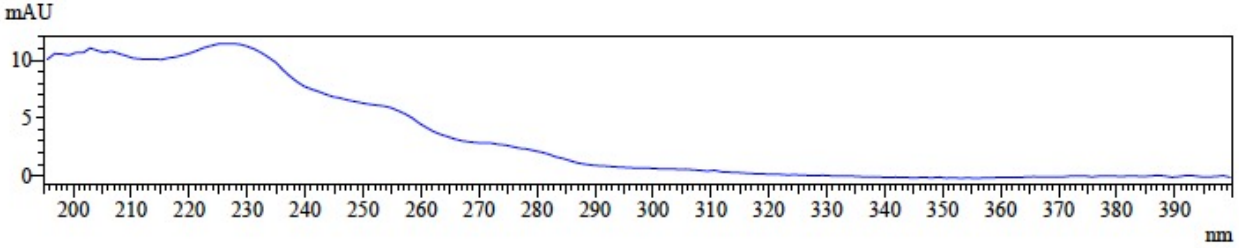
Sample Information

Sample Name	: XXW-1053-ID-20%-0.8mL
Sample ID	: XXW-1053-ID-20%-0.8mL
Data File	: XXW-1053-ID-20%-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

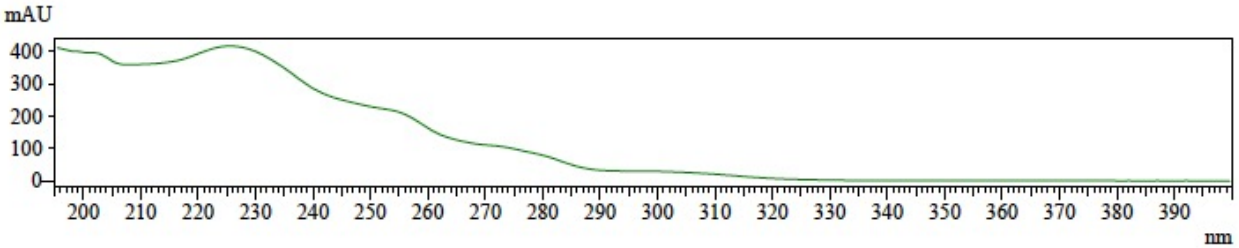
Chromatogram



UV Spectrum
Retention time = 12.968



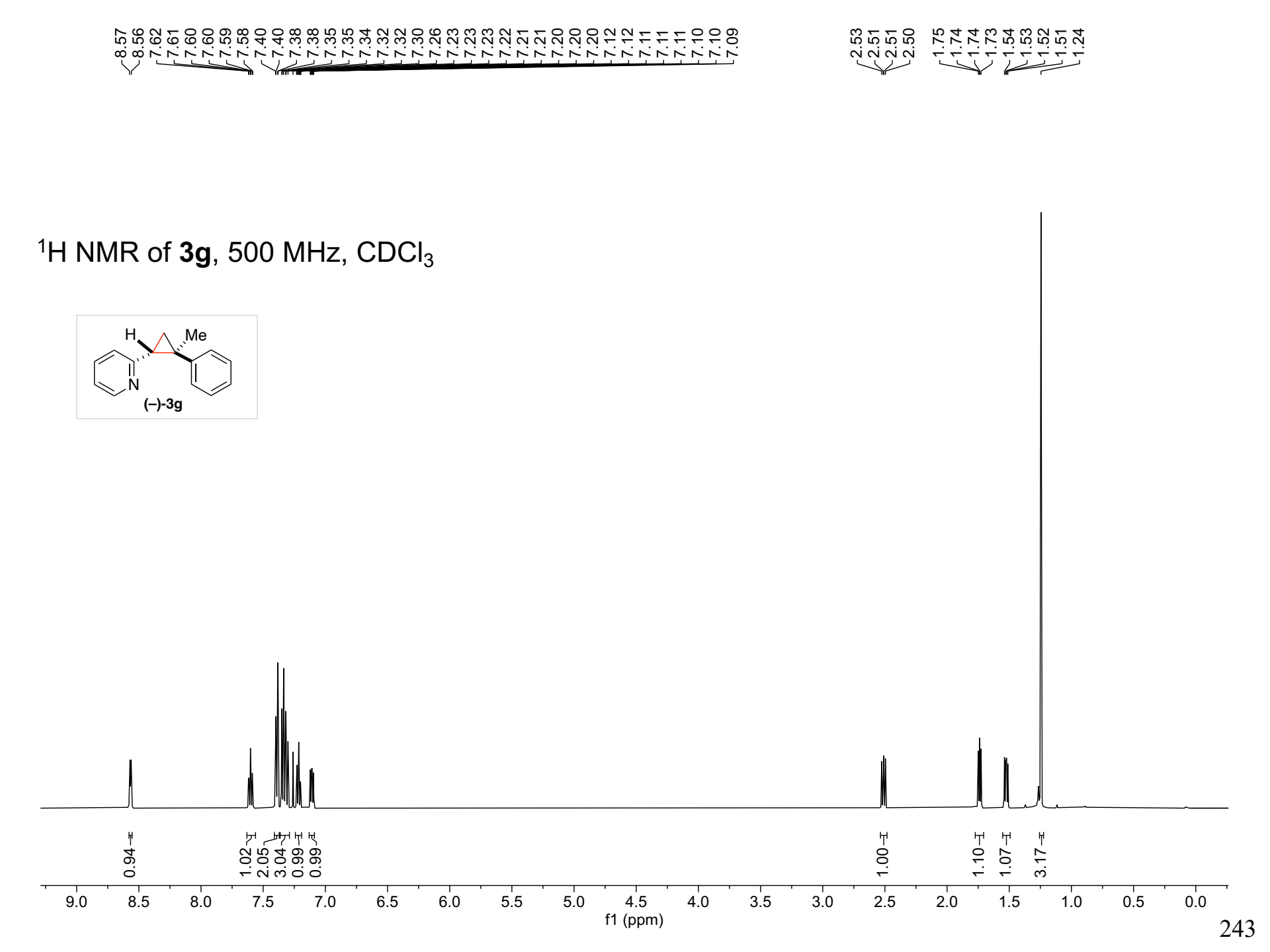
UV Spectrum
Retention time = 15.184



Peak Table

PDA Ch1 220nm

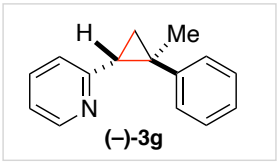
Peak#	Ret. Time	Area	Area%
1	12.968	136510	1.831
2	15.184	7319877	98.169
Total		7456386	100.000



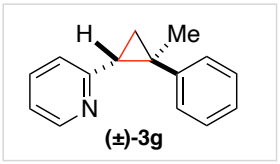
^{1}H NMR of **3g**, 500 MHz, $CDCl_3$

159.23
149.06
147.69
135.82
128.48
127.03
125.98
124.40
120.88
77.37
77.16
76.95
33.28
29.17
19.73
19.00

^{13}C NMR of **3g**, 150 MHz, $CDCl_3$



(–)-3g

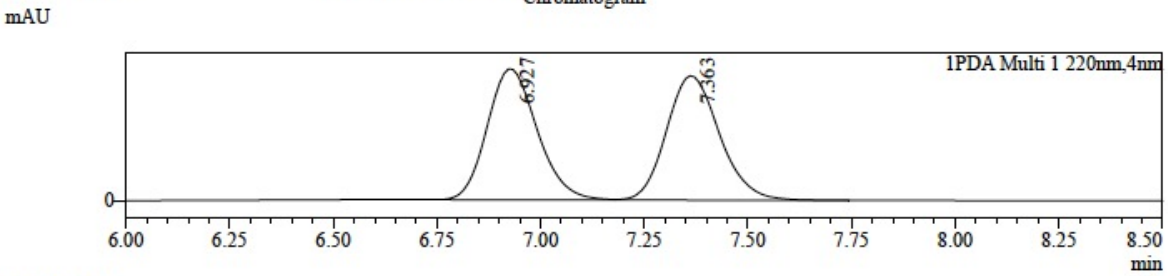


(±)-3g

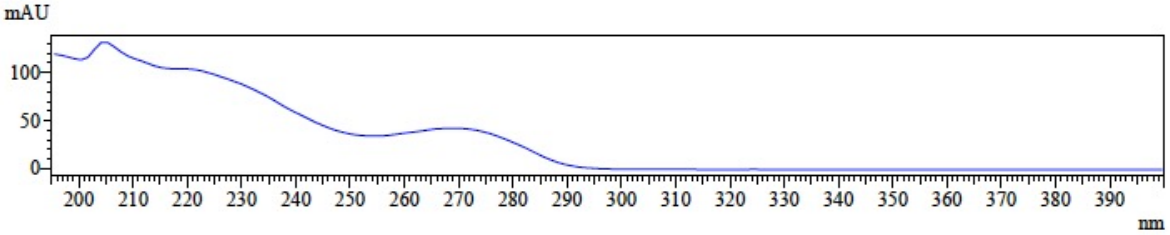
Sample Information

Sample Name	: XXW-0956-IC-5-%--0.8mL
Sample ID	: XXW-0956-IC-5-%--0.8mL
Data File	: XXW-0956-IC-5-%--0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

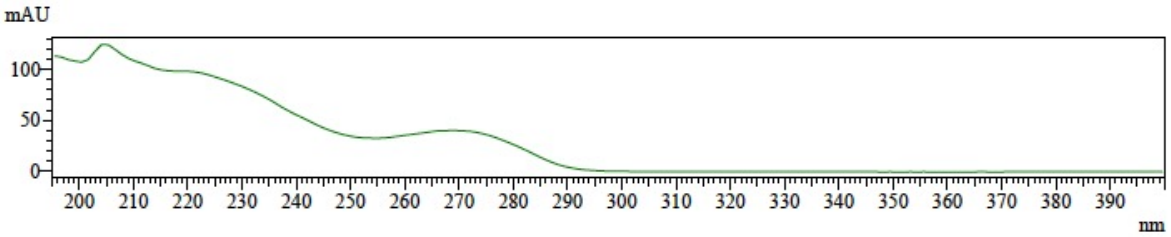
Chromatogram



UV Spectrum
Retention time = 6.927



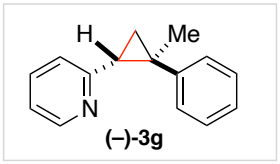
UV Spectrum
Retention time = 7.363



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.927	861886	49.856
2	7.363	866881	50.144
Total		1728767	100.000

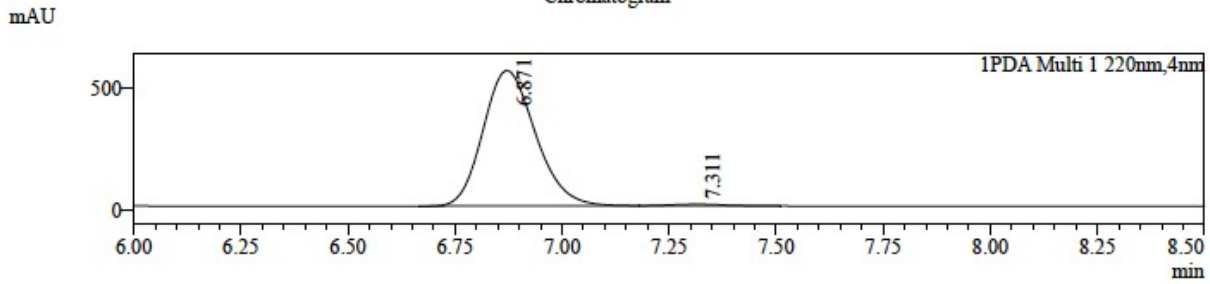


(–)-3g

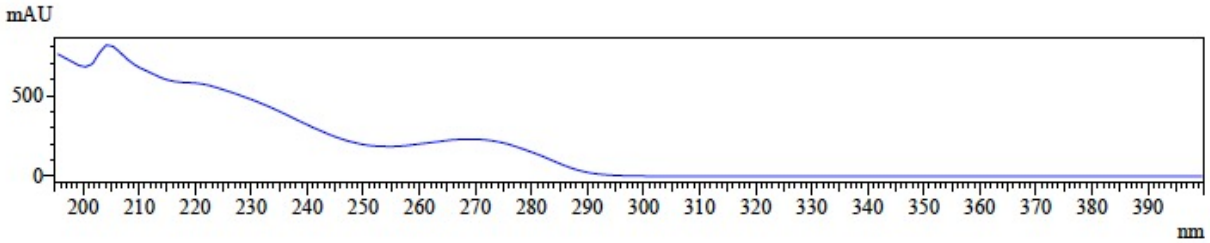
Sample Information

Sample Name	: XXW-1098-IC-5-%--0.8mL
Sample ID	: XXW-1098-IC-5-%--0.8mL
Data File	: XXW-1098-IC-5-%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

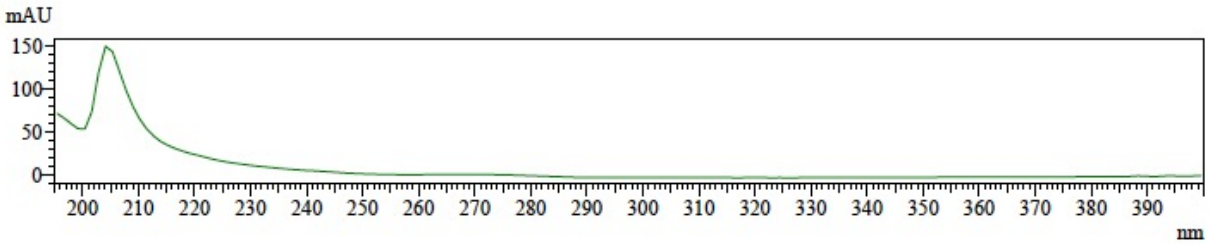
Chromatogram



UV Spectrum
Retention time = 6.871



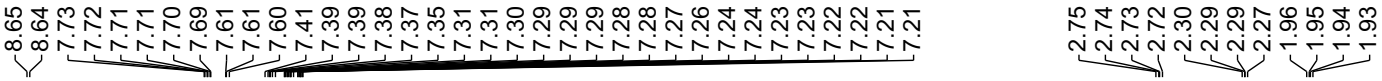
UV Spectrum
Retention time = 7.311



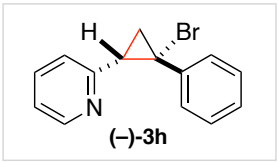
Peak Table

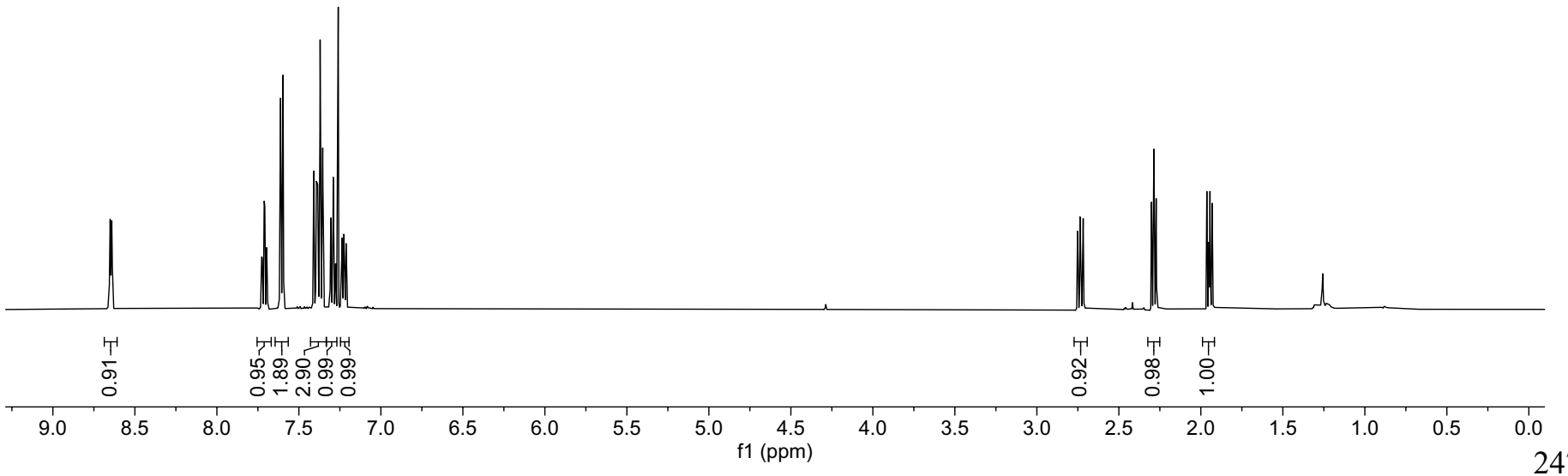
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.871	4722920	98.926
2	7.311	51283	1.074
Total		4774203	100.000



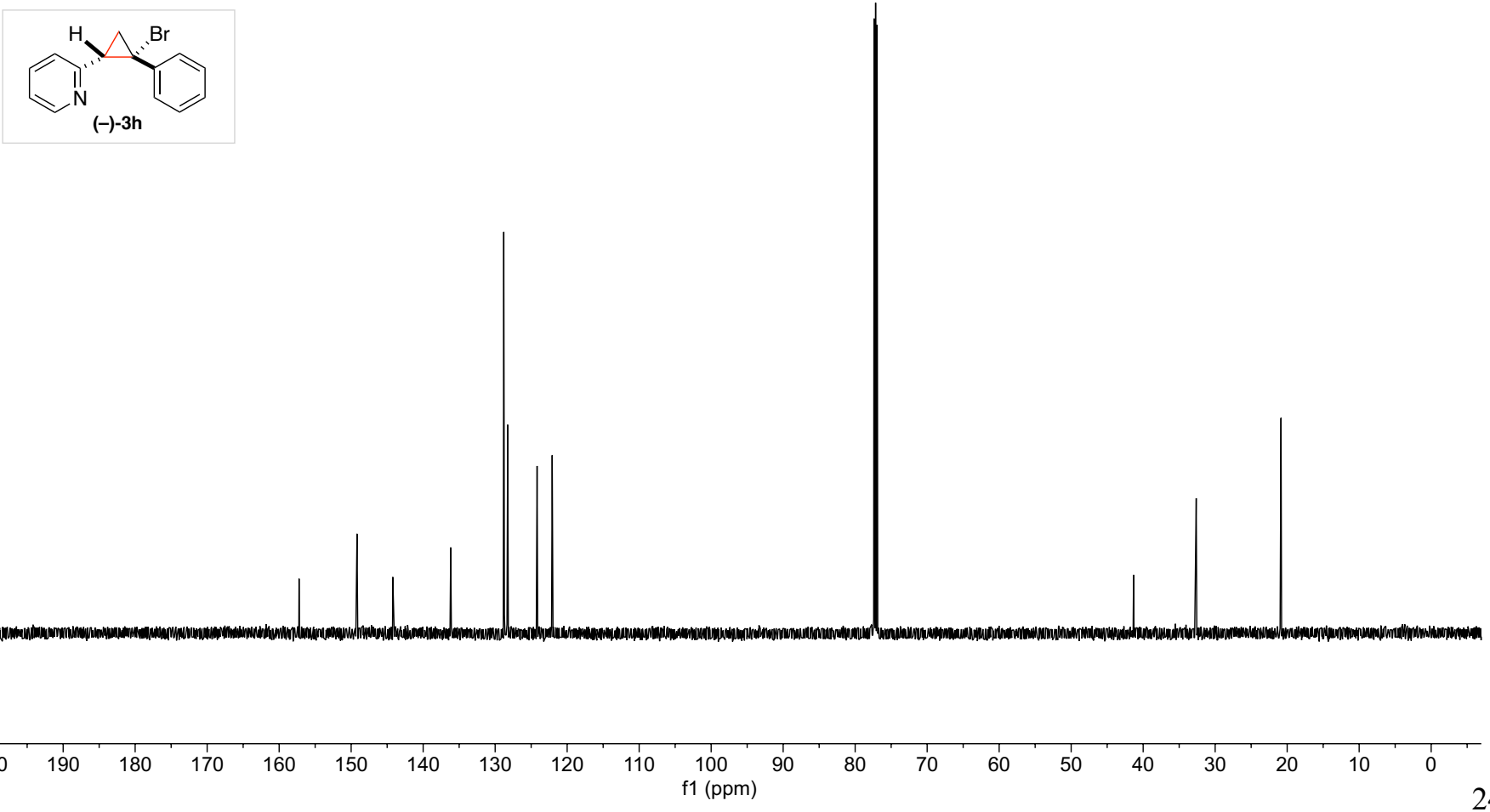
^{1}H NMR of **3h**, 500 MHz, $CDCl_3$

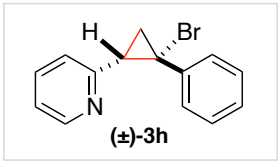




157.24
149.19
144.22
136.17
128.80
128.74
128.26
124.18
122.08
77.37
77.16
76.95
41.33
32.63
20.85

^{13}C NMR of **3h**, 150 MHz, $CDCl_3$



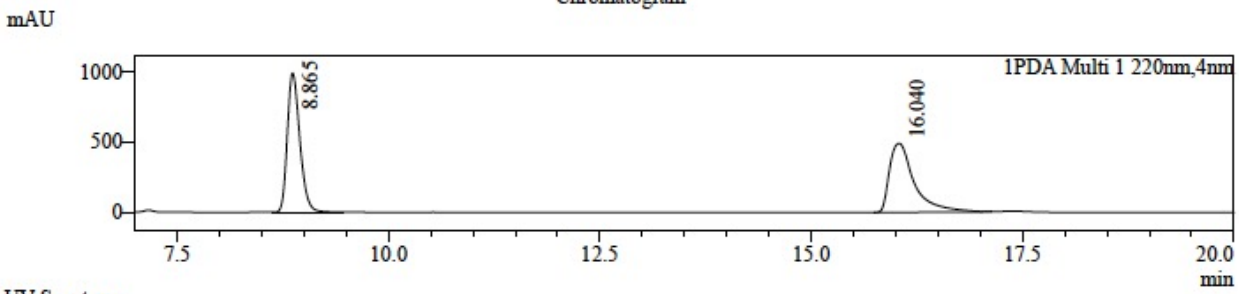


(±)-3h

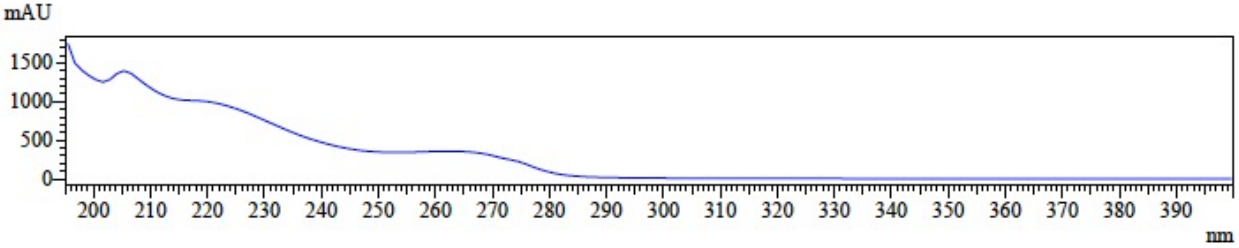
Sample Information

Sample Name	: XXW-0957-n2-ID-5%-0.8mL
Sample ID	: XXW-0957-n2-ID-5%-0.8mL
Data File	: XXW-0957-n2-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

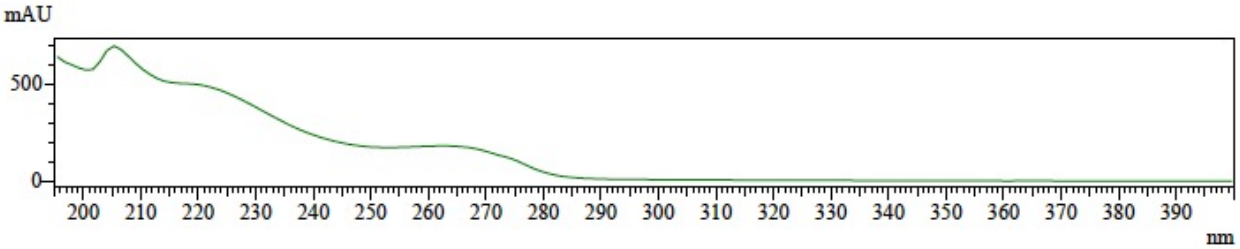
Chromatogram



UV Spectrum
Retention time = 8.865



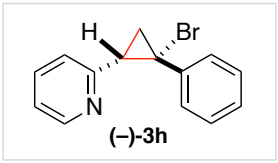
UV Spectrum
Retention time = 16.040



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.865	10205296	50.507
2	16.040	10000384	49.493
Total		20205680	100.000

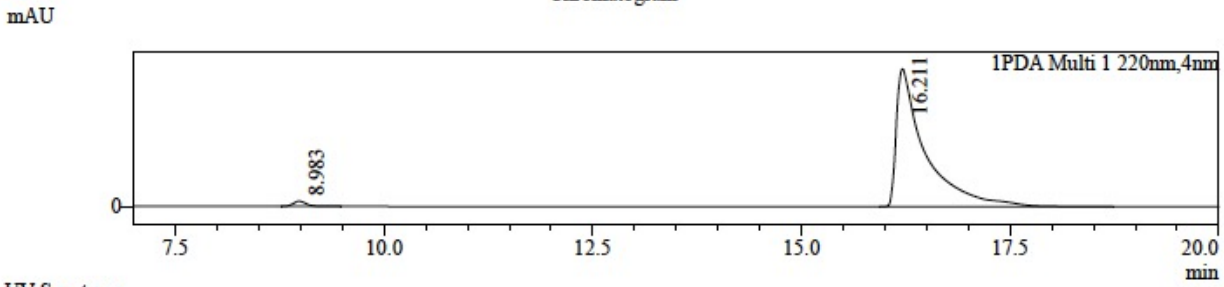


(–)-3h

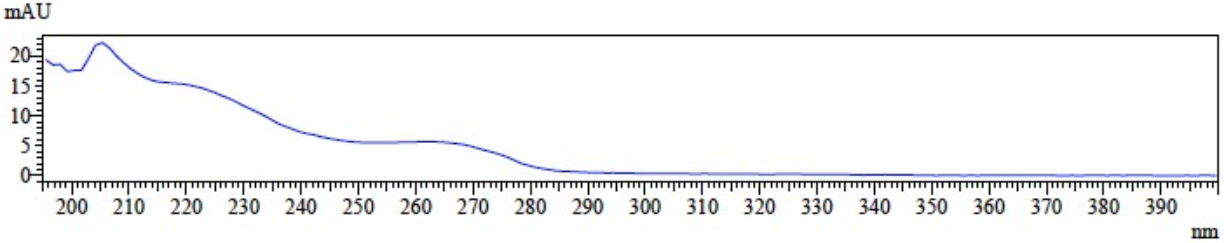
Sample Information

Sample Name	: XXW-1042-ID-5%-0.8mL
Sample ID	: XXW-1042-ID-5%-0.8mL
Data File	: XXW-1042-ID-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

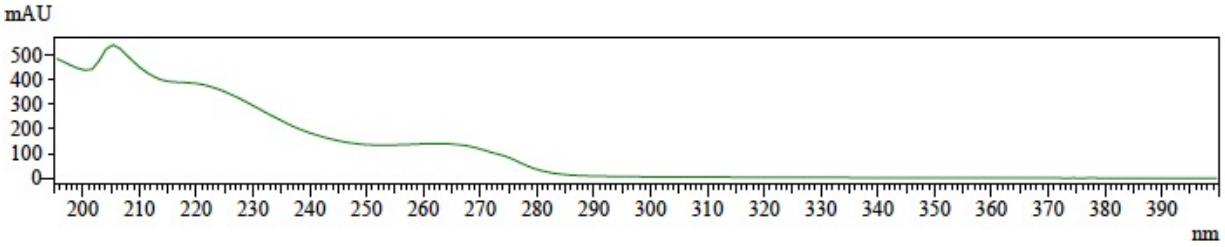
Chromatogram



UV Spectrum
Retention time = 8.983



UV Spectrum
Retention time = 16.211

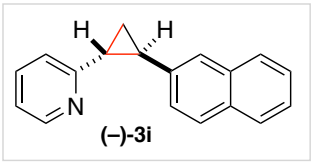


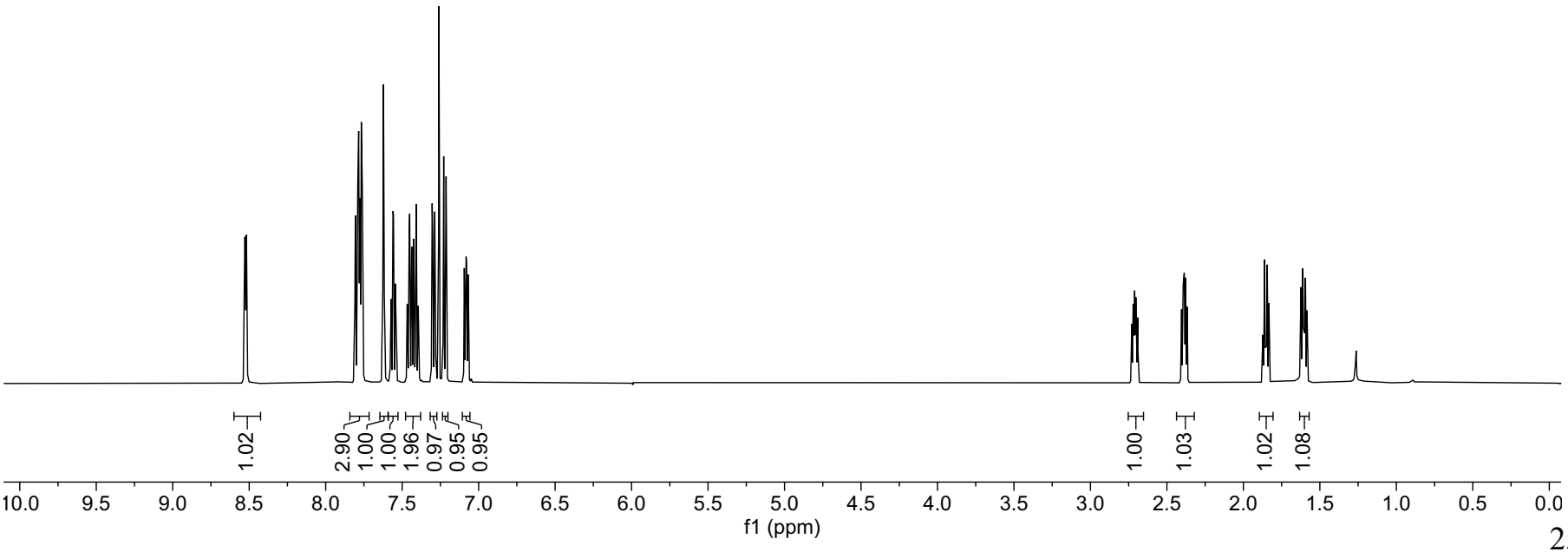
Peak Table

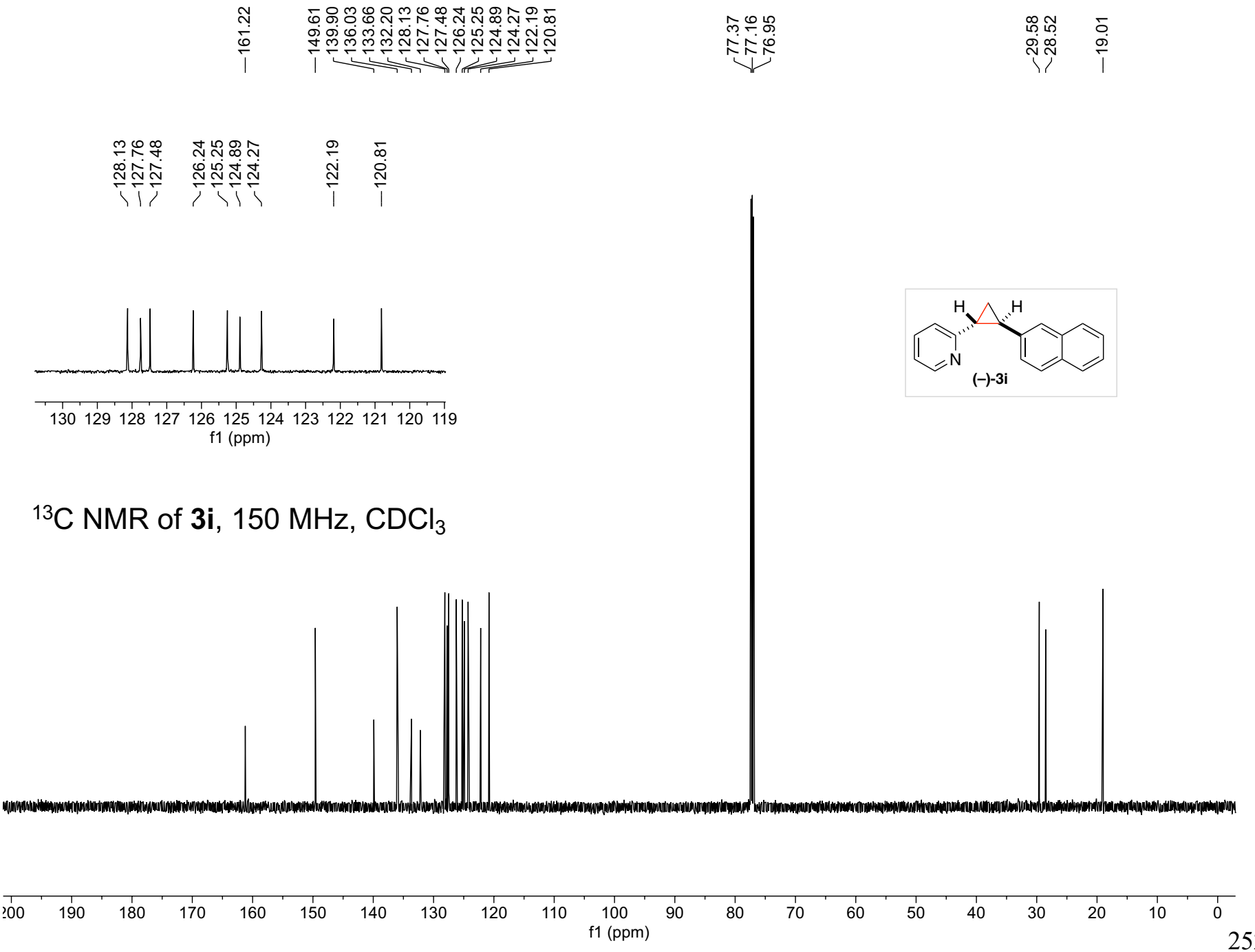
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.983	149588	1.607
2	16.211	9161389	98.393
Total		9310977	100.000

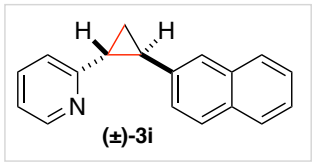
^{1}H NMR of **3i**, 500 MHz, $CDCl_3$







^{13}C NMR of **3i**, 150 MHz, $CDCl_3$

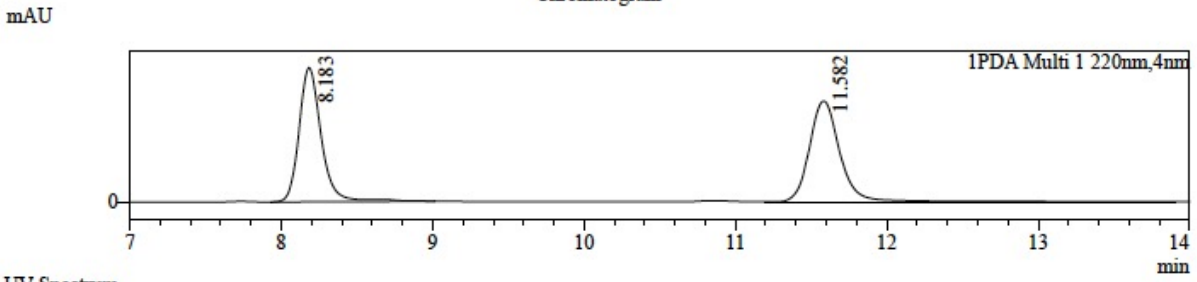


(±)-3i

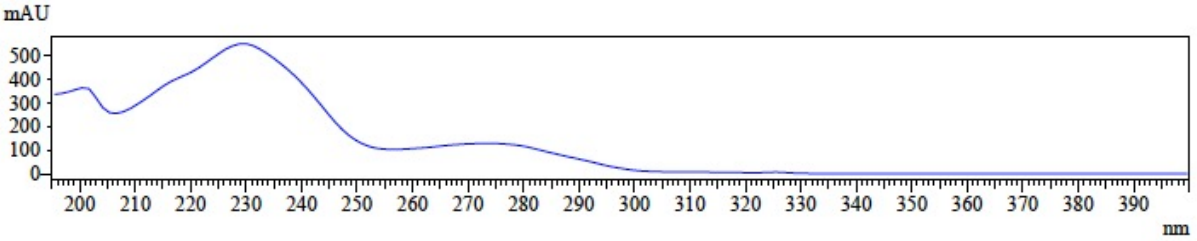
Sample Information

Sample Name	: XXW-0959-IA-5%-0.8mL
Sample ID	: XXW-0959-IA-5%-0.8mL
Data File	: XXW-0959-IA-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

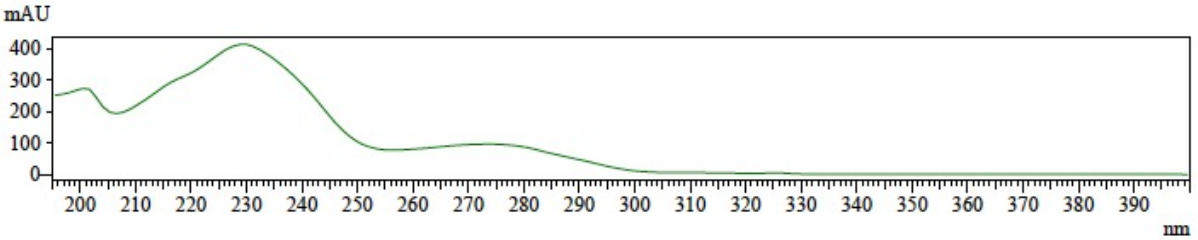
Chromatogram



UV Spectrum
Retention time = 8.183



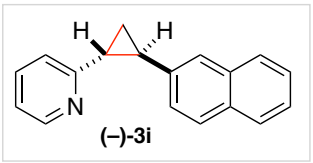
UV Spectrum
Retention time = 11.582



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.183	4454549	49.102
2	11.582	4617443	50.898
Total		9071993	100.000

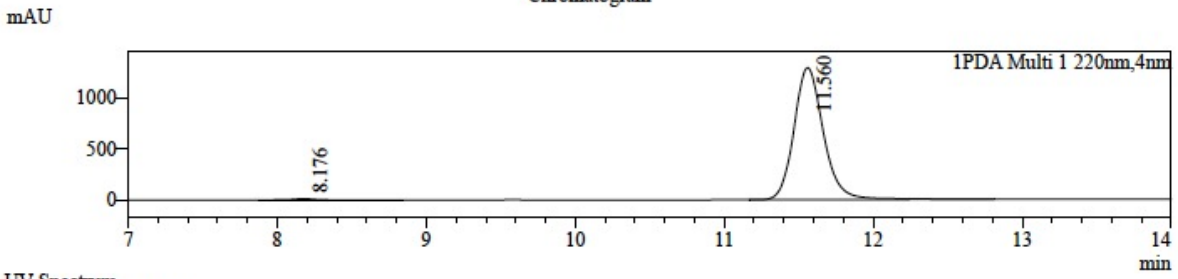


(–)-3i

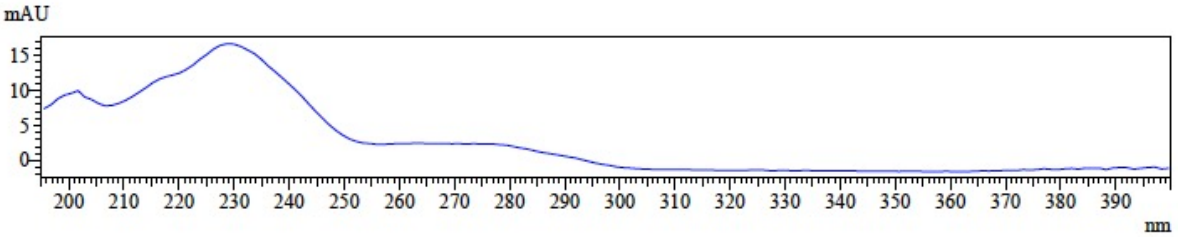
Sample Information

Sample Name	: XXW-1052-IA-5%-0.8mL
Sample ID	: XXW-1052-IA-5%-0.8mL
Data File	: XXW-1052-IA-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

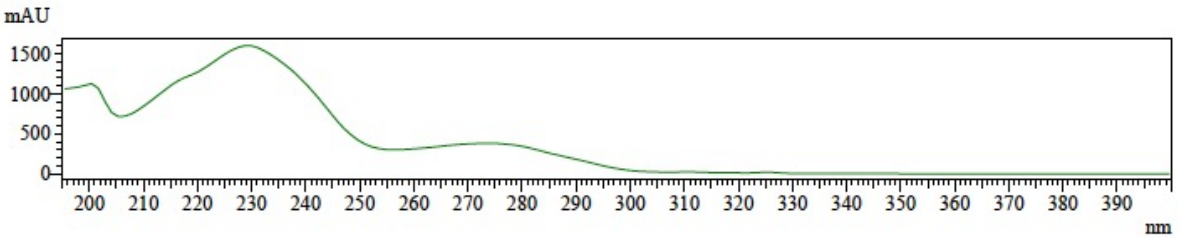
Chromatogram



UV Spectrum
Retention time = 8.176



UV Spectrum
Retention time = 11.560

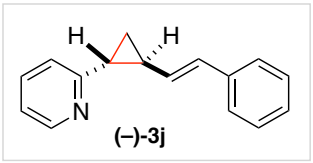


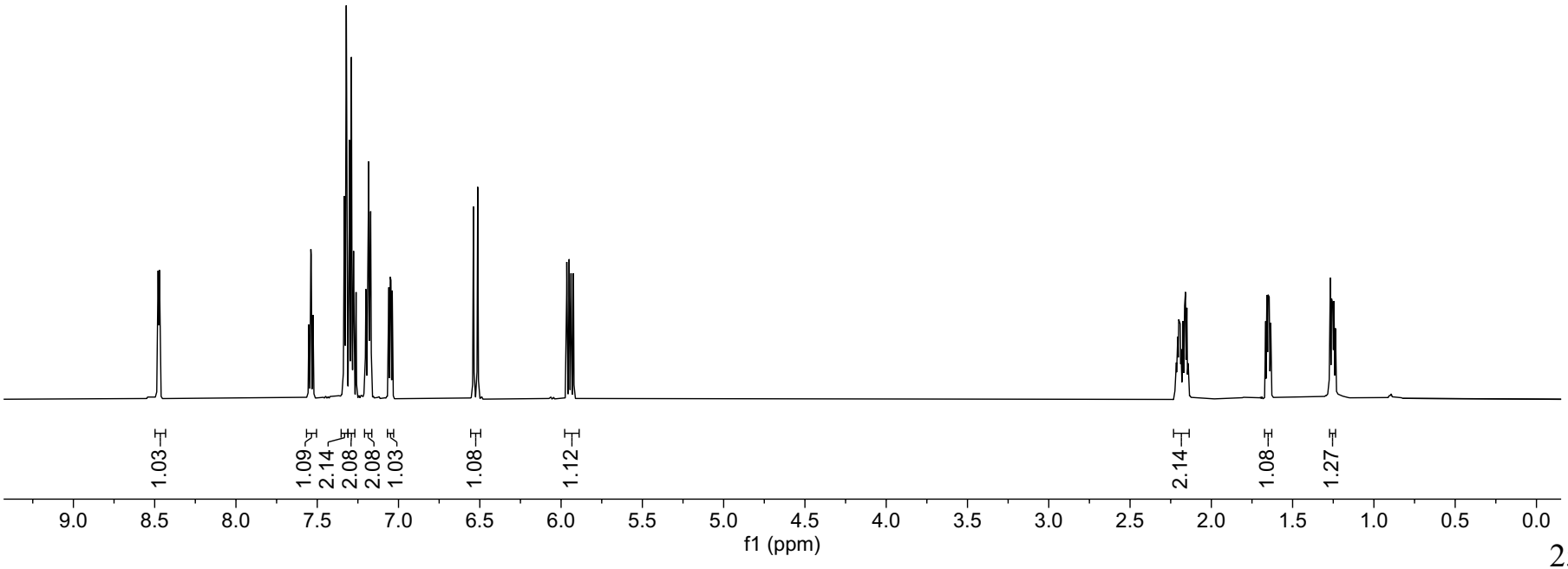
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.176	147035	0.821
2	11.560	17754835	99.179
Total		17901870	100.000

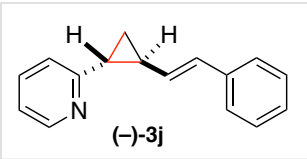
^{1}H NMR of **3j**, 600 MHz, $CDCl_3$

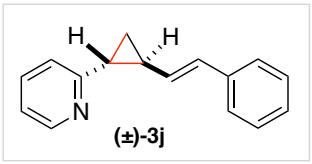




161.06
149.51
137.63
135.96
132.59
128.88
128.64
126.94
125.84
122.02
120.69
77.37
77.16
76.95
27.69
27.33
17.77

^{13}C NMR of **3j**, 150 MHz, $CDCl_3$



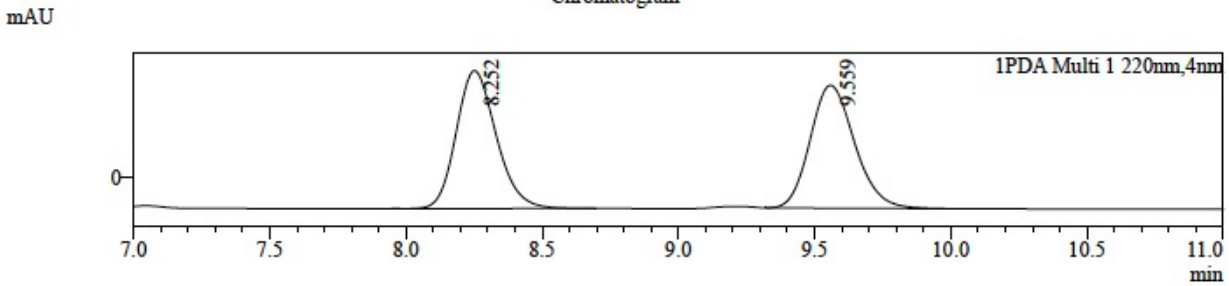


(±)-3j

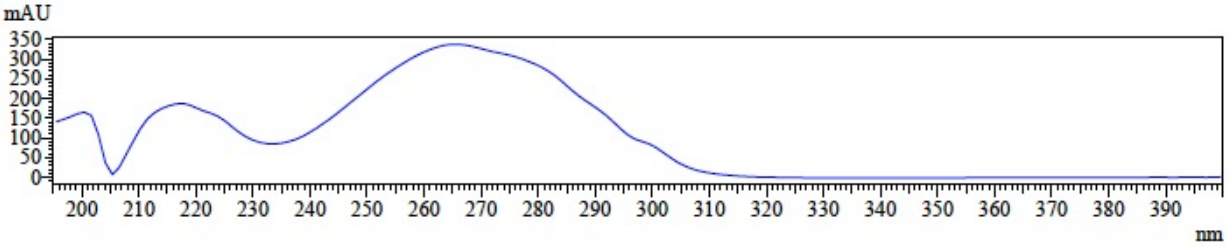
Sample Information

Sample Name	: XXW-0892-ID-5%--0.8mL
Sample ID	: XXW-0892-ID-5%--0.8mL
Data File	: XXW-0892-ID-5%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

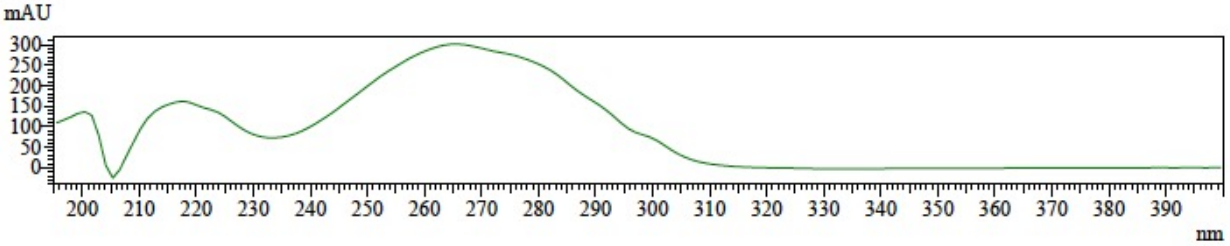
Chromatogram



UV Spectrum
Retention time = 8.252



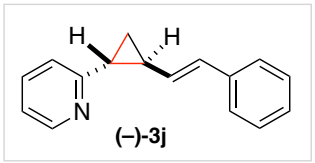
UV Spectrum
Retention time = 9.559



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.252	2304869	50.321
2	9.559	2275441	49.679
Total		4580311	100.000

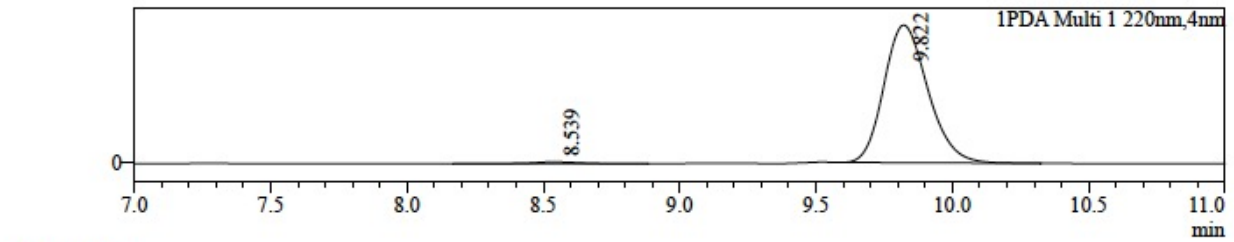


(–)-3j

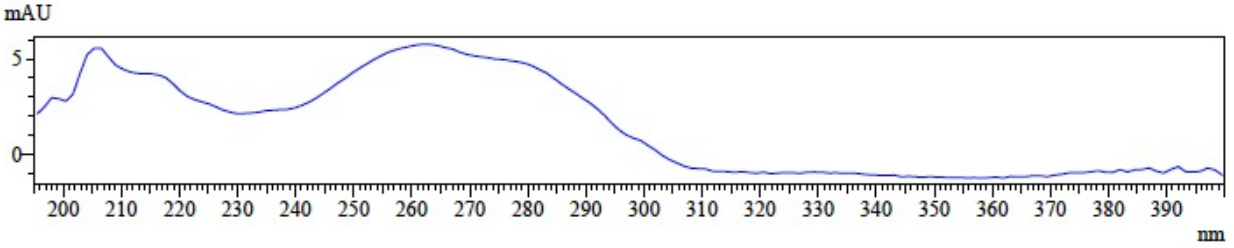
Sample Information

Sample Name	: XXW-1092-ID-5%--0.8mL
Sample ID	: XXW-1092-ID-5%--0.8mL
Data File	: XXW-1092-ID-5%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

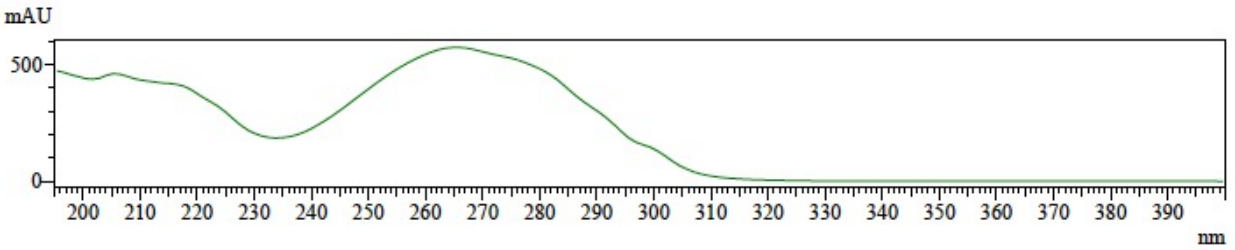
Chromatogram



UV Spectrum
Retention time = 8.539



UV Spectrum
Retention time = 9.822

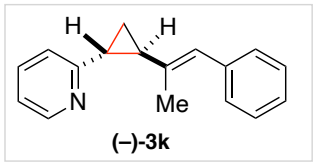


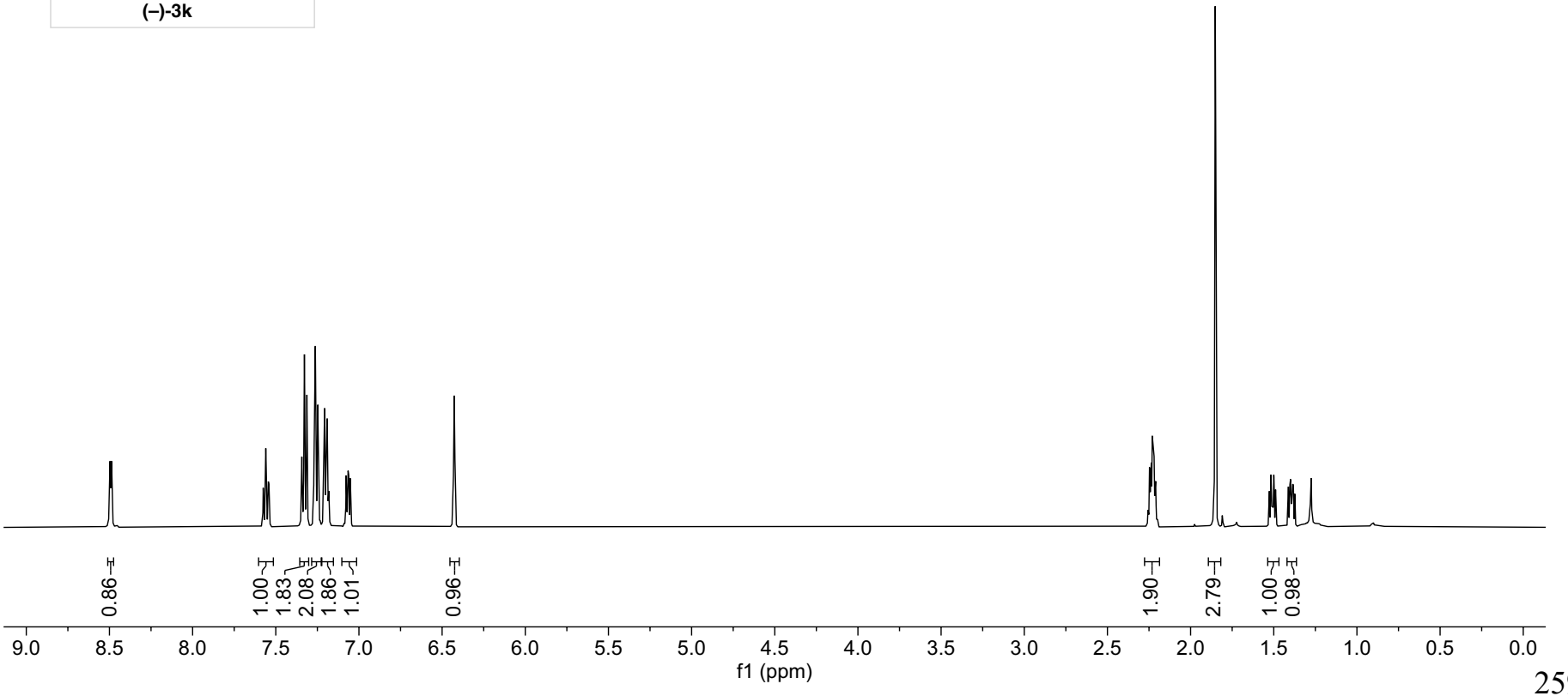
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.539	47863	1.135
2	9.822	4169169	98.865
Total		4217032	100.000

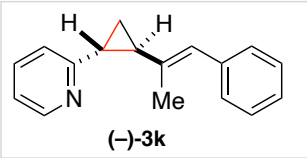
^{1}H NMR of **3k**, 500 MHz, $CDCl_3$



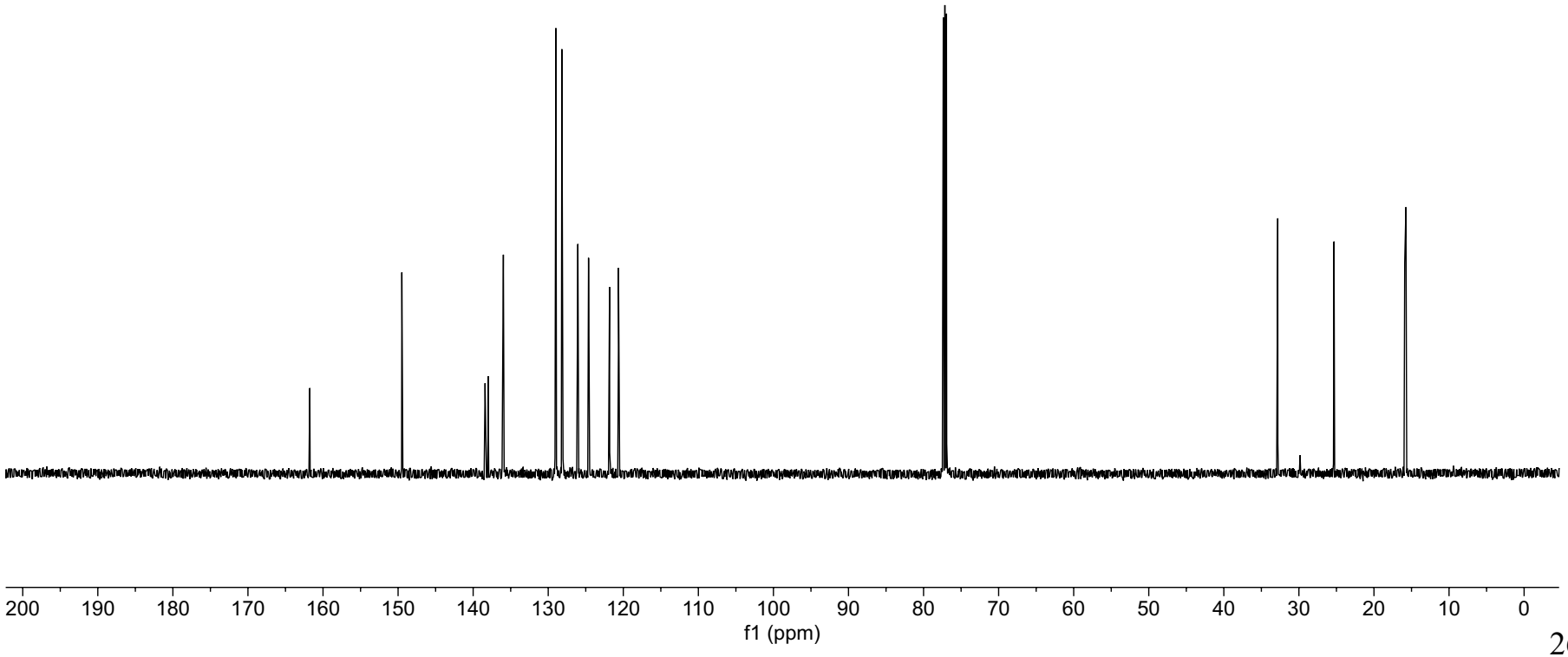


161.76
149.50
138.41
138.01
135.97
128.98
128.18
126.05
124.63
121.83
120.64
77.37
77.16
76.95
32.82
25.32
15.90
15.74

^{13}C NMR of **3k**, 150 MHz, $CDCl_3$



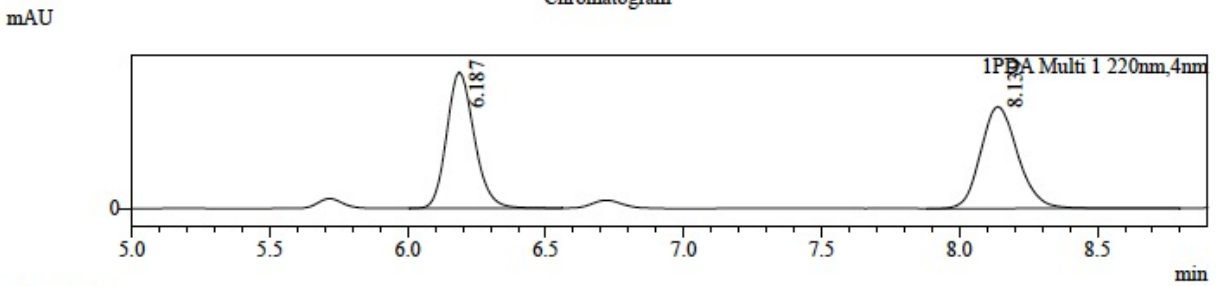
(–)-3k



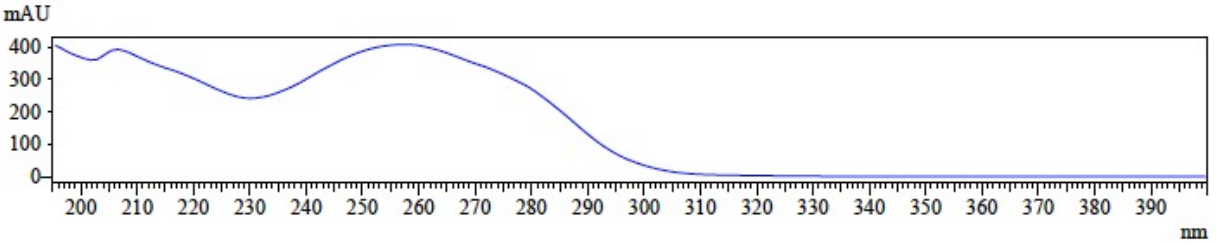
Sample Information

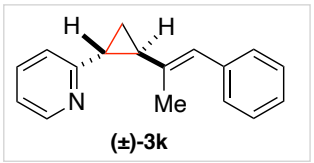
Sample Name	: XXW-0969-ID-10%-0.8mL
Sample ID	: XXW-0969-ID-10%-0.8mL
Data File	: XXW-0969-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



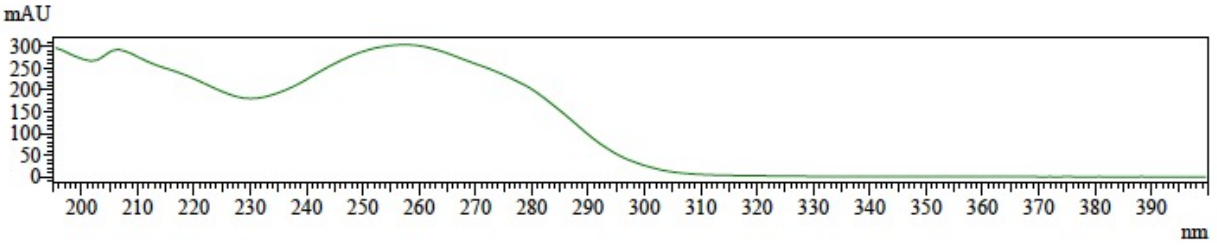
UV Spectrum
Retention time = 6.187





(±)-3k

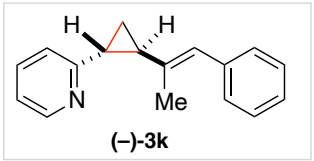
UV Spectrum
Retention time = 8.139



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.187	2088519	49.785
2	8.139	2106594	50.215
Total		4195113	100.000

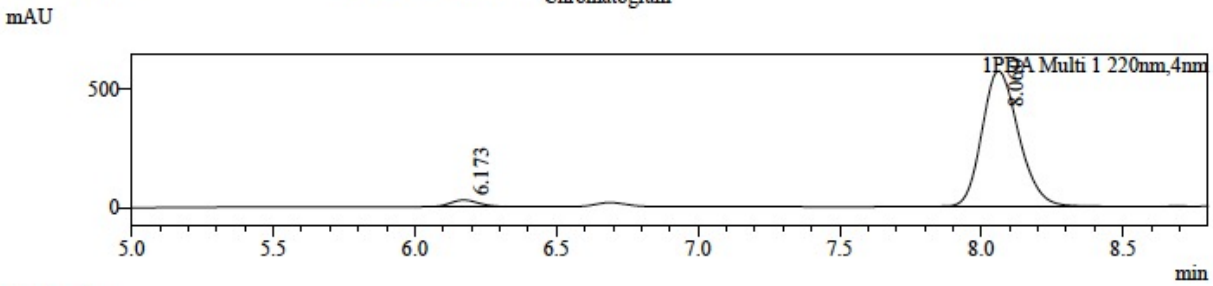


(–)-3k

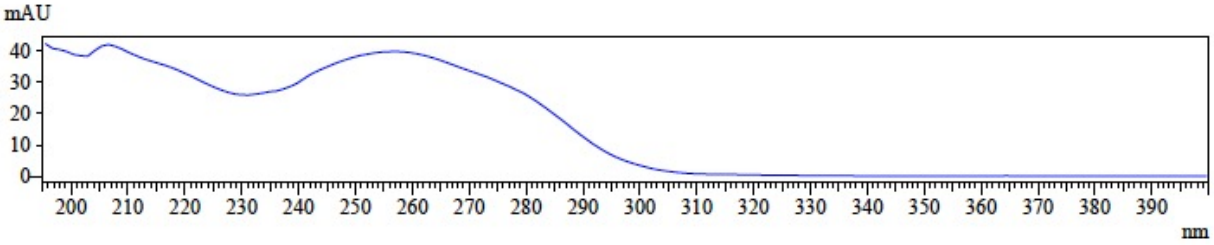
Sample Information

Sample Name	: XXW-1051-ID-10%-0.8mL
Sample ID	: XXW-1051-ID-10%-0.8mL
Data File	: XXW-1051-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

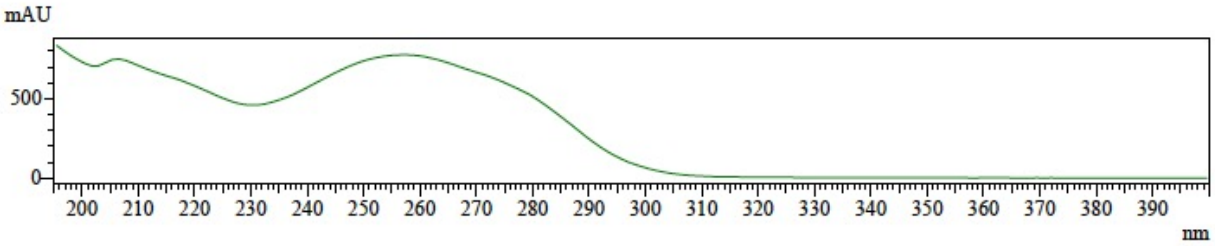
Chromatogram



UV Spectrum
Retention time = 6.173



UV Spectrum
Retention time = 8.060

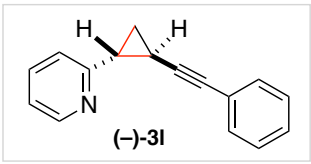


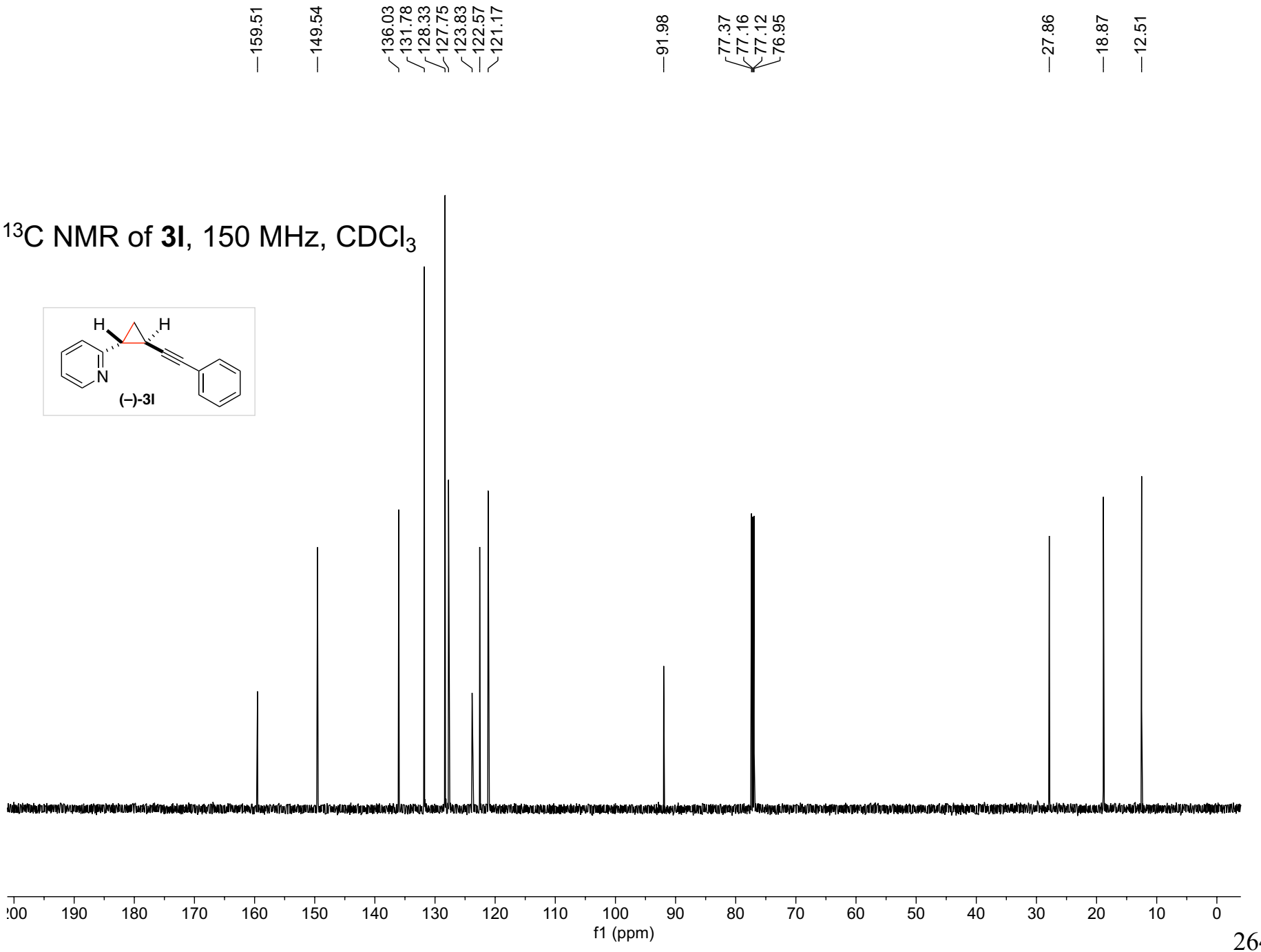
Peak Table

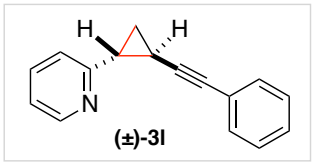
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.173	192058	3.561
2	8.060	5201880	96.439
Total		5393938	100.000

^{1}H NMR of **3l**, 600 MHz, $CDCl_3$




159.51
149.54
136.03
131.78
128.33
127.75
123.83
122.57
121.17
91.98
77.37
77.16
77.12
76.95
27.86
18.87
12.51
13C NMR of 3l, 150 MHz, CDCl3
H
H
N
(–)-3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

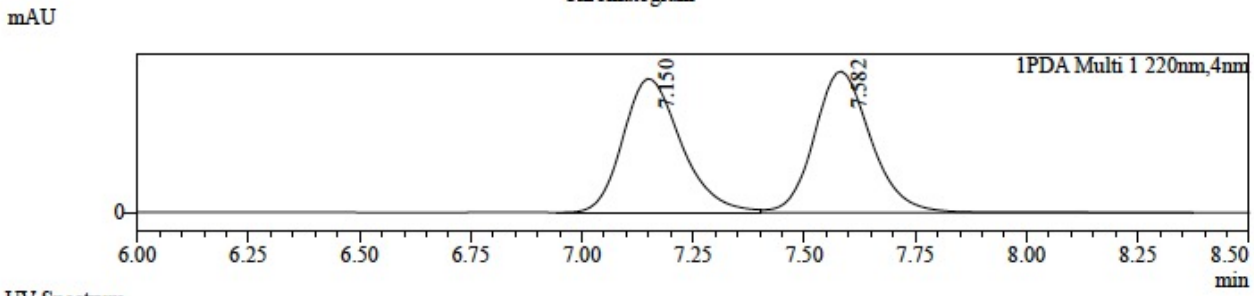


(±)-3l

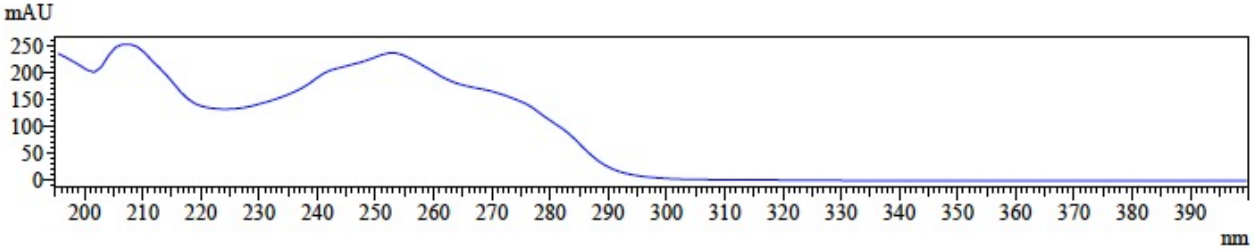
Sample Information

Sample Name	: XXW-0970-n1-ID-5%-0.8mL
Sample ID	: XXW-0970-n1-ID-5%-0.8mL
Data File	: XXW-0970-n1-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

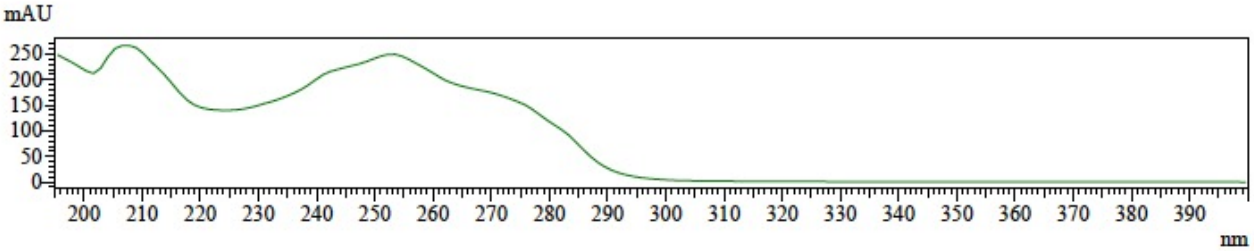
Chromatogram



UV Spectrum
Retention time = 7.150



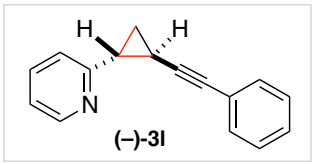
UV Spectrum
Retention time = 7.582



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.150	1308983	49.385
2	7.582	1341604	50.615
Total		2650587	100.000

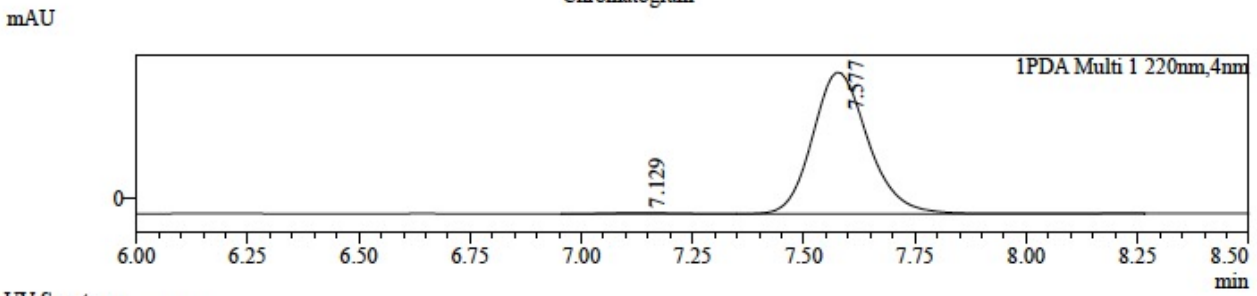


(–)-3l

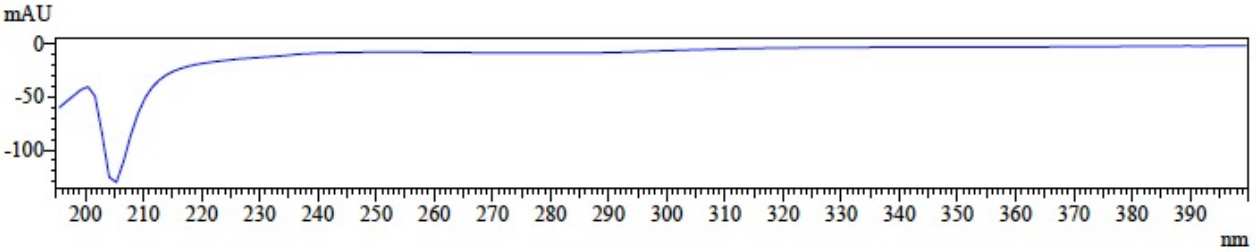
Sample Information

Sample Name	: XXW-1054-ID-5%-0.8mL
Sample ID	: XXW-1054-ID-5%-0.8mL
Data File	: XXW-1054-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

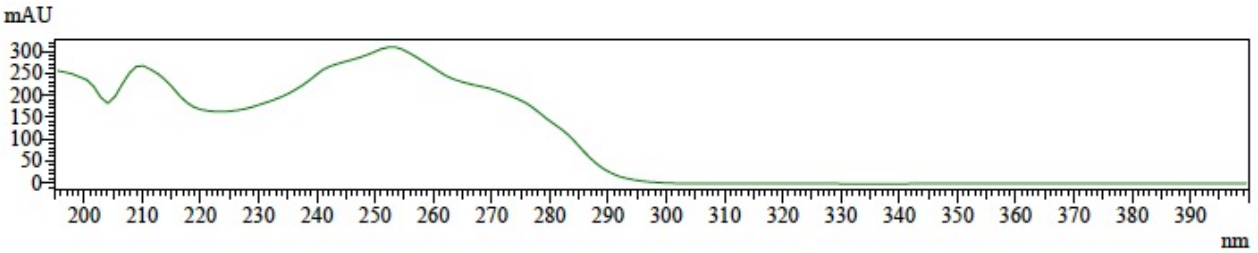
Chromatogram



UV Spectrum
Retention time = 7.129



UV Spectrum
Retention time = 7.577

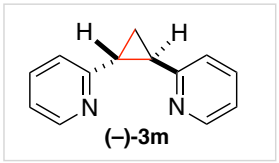


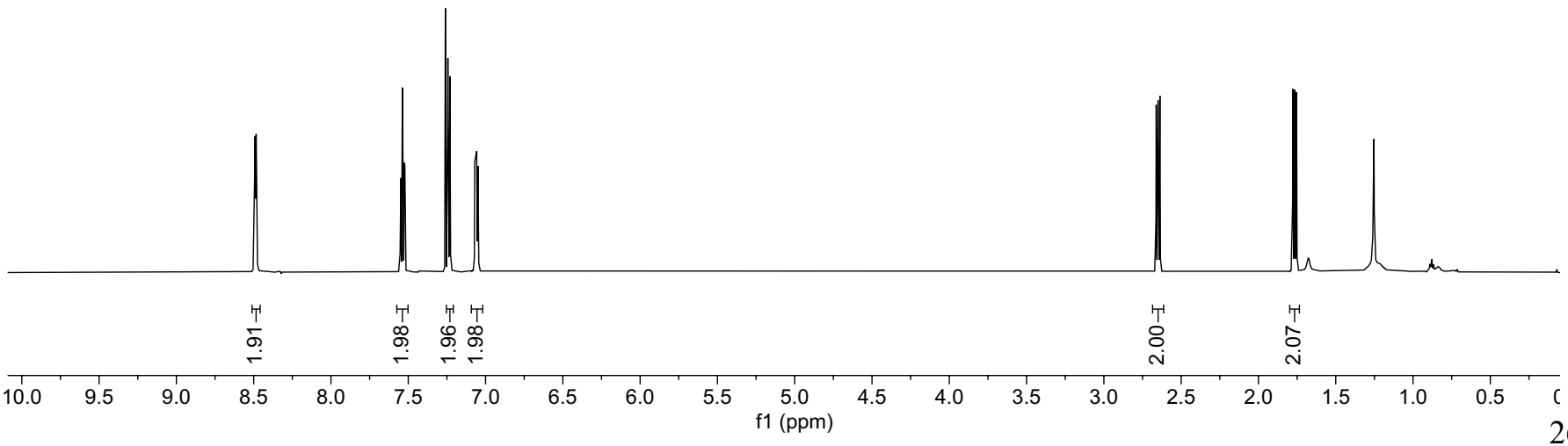
Peak Table

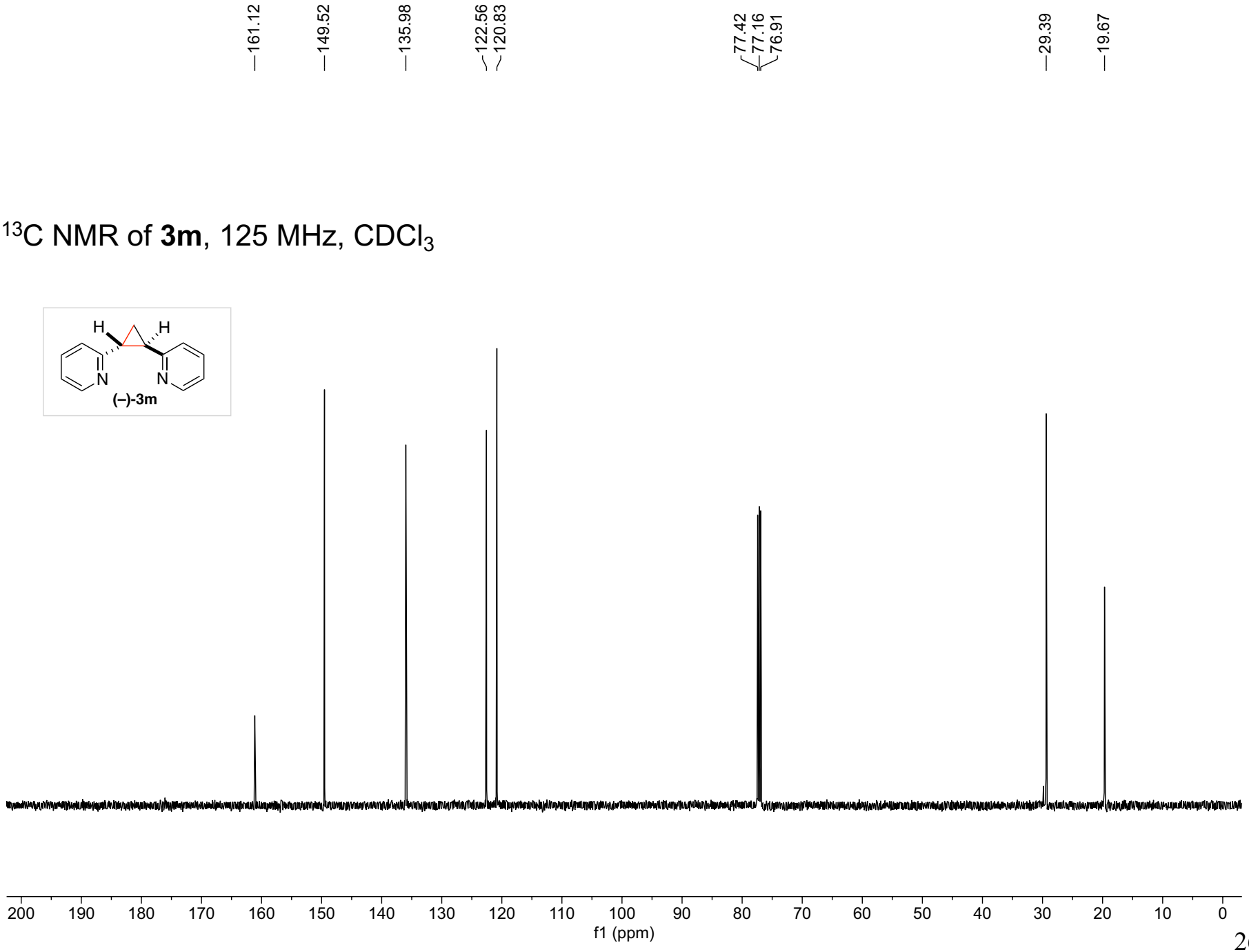
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.129	14047	0.828
2	7.577	1681990	99.172
Total		1696037	100.000

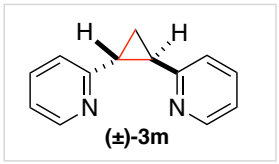
^{1}H NMR of **3m**, 600 MHz, $CDCl_3$







^{13}C NMR of **3m**, 125 MHz, $CDCl_3$

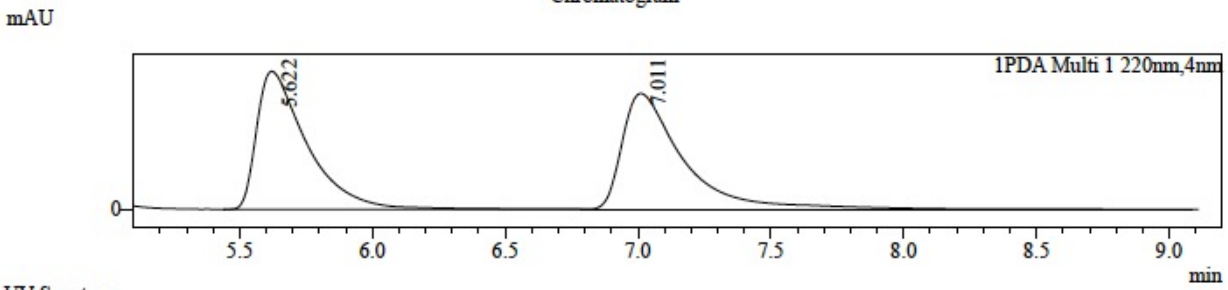


(±)-3m

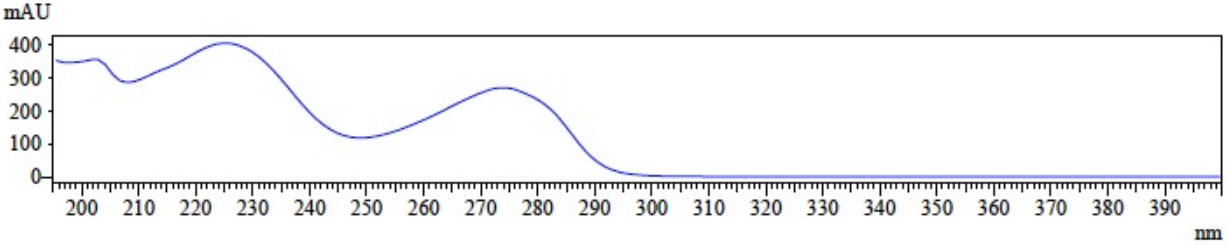
Sample Information

Sample Name	: XXW-0890-n1-ADH-30%-0.8mL
Sample ID	: XXW-0890-n1-ADH-30%-0.8mL
Data File	: XXW-0890-n1-ADH-30%-0.8mL.lcd
Method File	: XXW-30%.0.8.mL.lcm

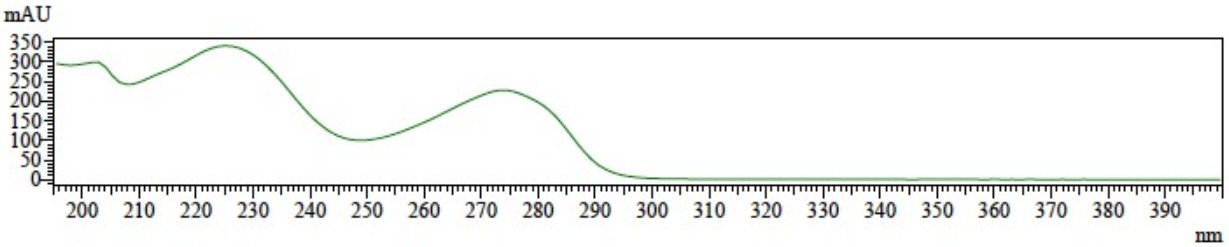
Chromatogram



UV Spectrum
Retention time = 5.622



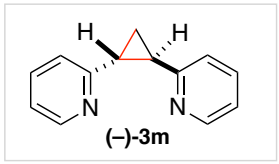
UV Spectrum
Retention time = 7.011



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.622	4966083	49.435
2	7.011	5079643	50.565
Total		10045726	100.000

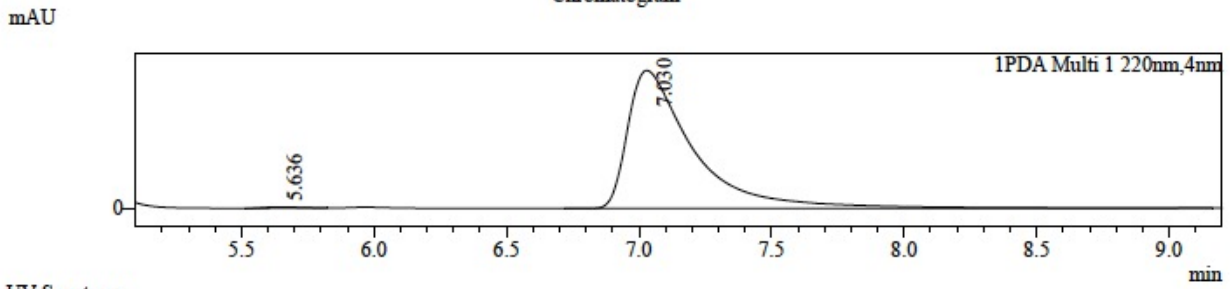


(–)-3m

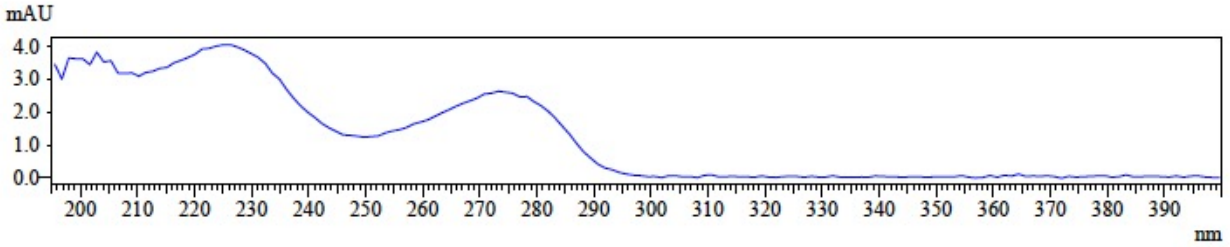
Sample Information

Sample Name	: XXW-1058-ADH-30%-0.8mL
Sample ID	: XXW-1058-ADH-30%-0.8mL
Data File	: XXW-1058-ADH-30%-0.8mL.lcd
Method File	: XXW-30%.0.8.mL.lcm

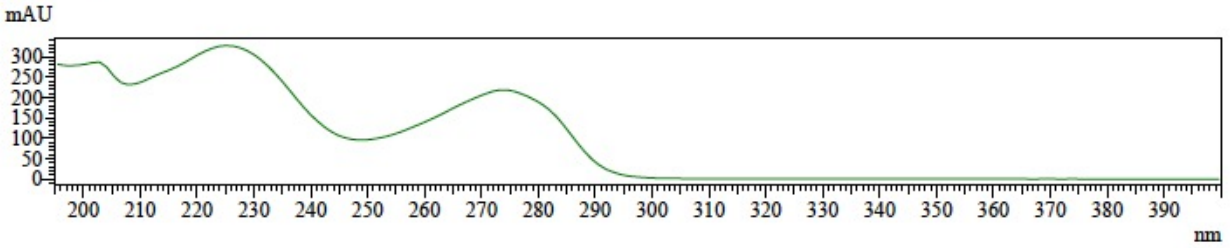
Chromatogram



UV Spectrum
Retention time = 5.636



UV Spectrum
Retention time = 7.030

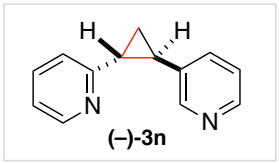


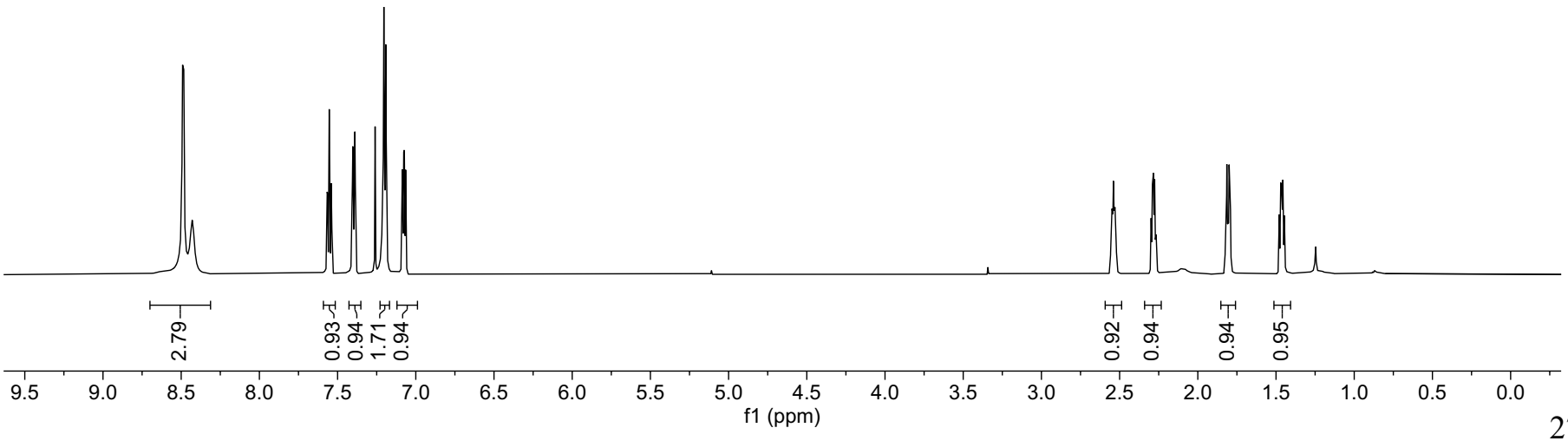
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.636	22806	0.435
2	7.030	5216556	99.565
Total		5239362	100.000

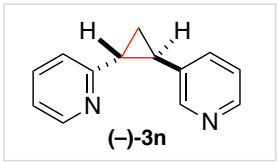
^{1}H NMR of **3n**, 600 MHz, $CDCl_3$



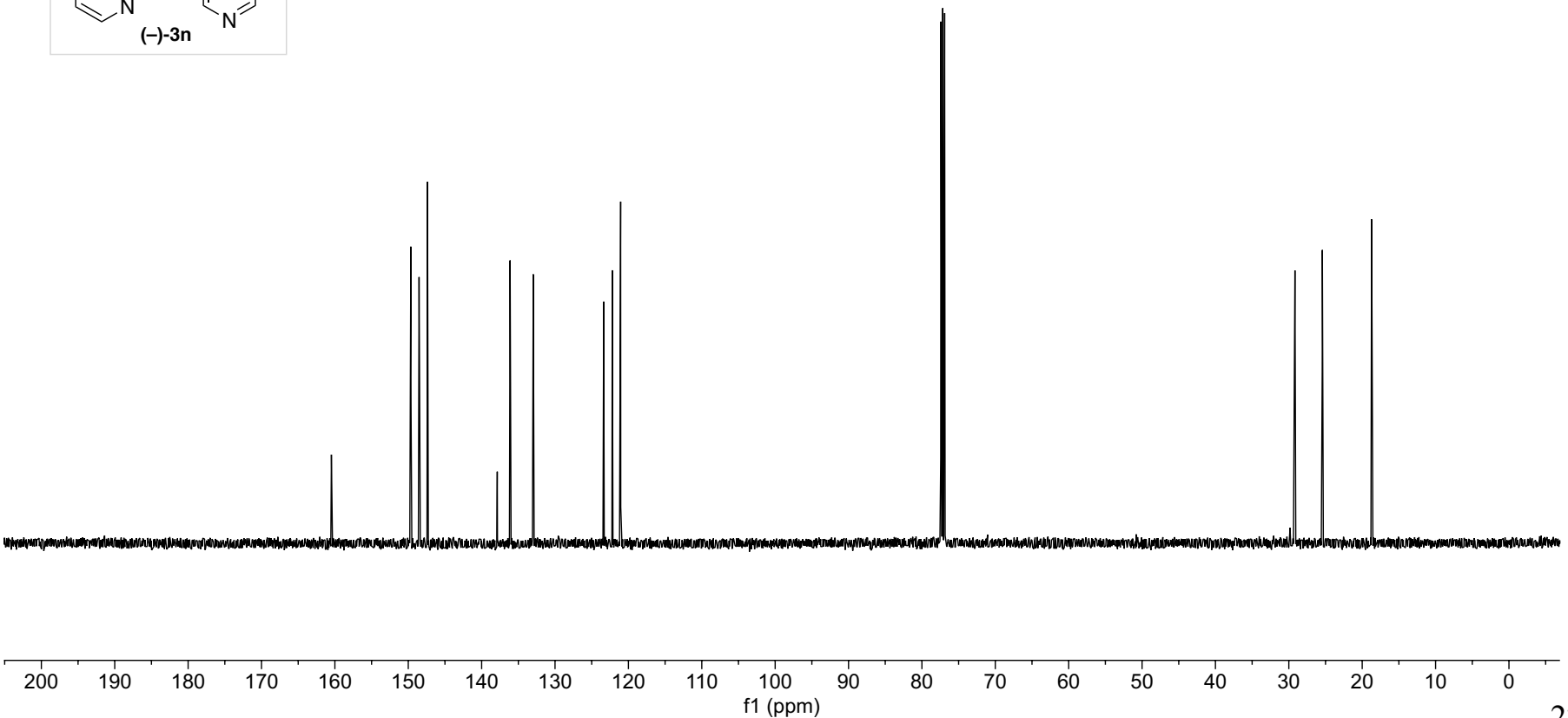


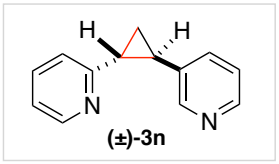
160.48
149.65
148.53
147.38
137.87
136.12
132.97
123.37
122.20
121.06
77.42
77.16
76.91
29.17
25.43
18.72

^{13}C NMR of **3n**, 125 MHz, $CDCl_3$



(–)-3n



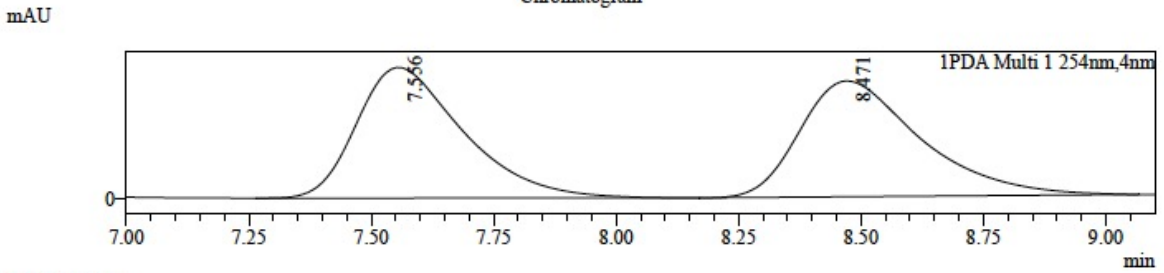


(±)-3n

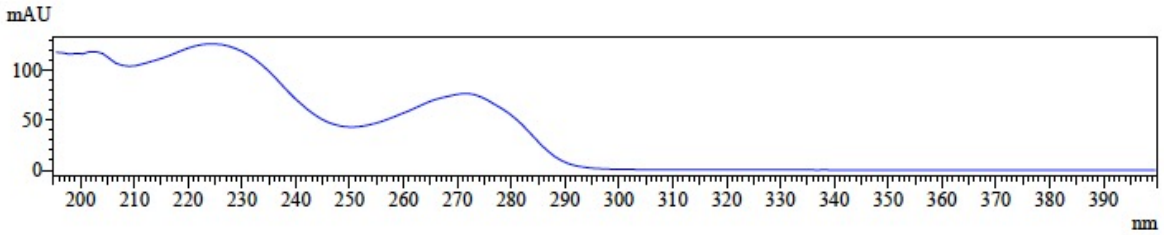
Sample Information

Sample Name	: XXW-1071-ODH-30%-0.8mL
Sample ID	: XXW-1071-ODH-30%-0.8mL
Data File	: XXW-1071-ODH-30%-0.8mL001.lcd
Method File	: XXW-30%.0.8.mL.lcm

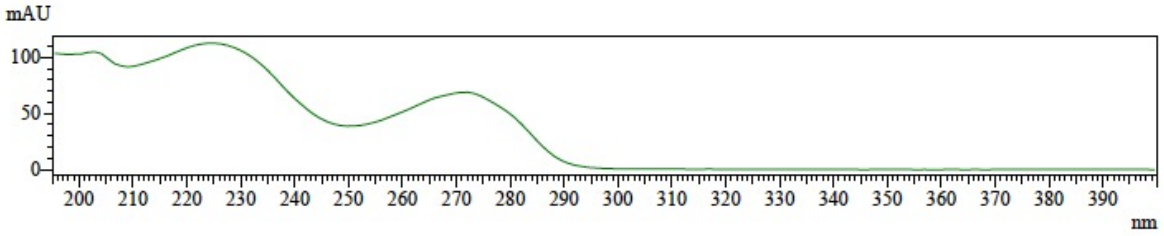
Chromatogram



UV Spectrum
Retention time = 7.556



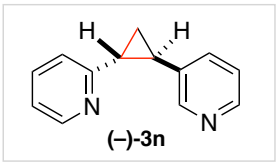
UV Spectrum
Retention time = 8.471



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.556	698282	49.984
2	8.471	698734	50.016
Total		1397015	100.000

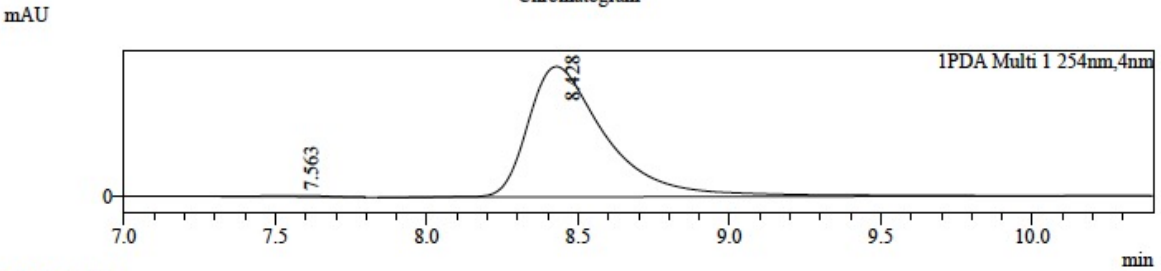


(–)-3n

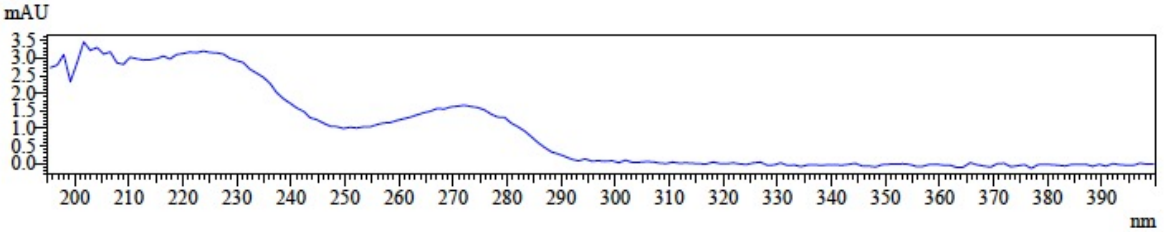
Sample Information

Sample Name	: XXW-1072-ODH-30%-0.8mL
Sample ID	: XXW-1072-ODH-30%-0.8mL
Data File	: XXW-1072-ODH-30%-0.8mL001.lcd
Method File	: XXW-30%.0.8.mL.lcm

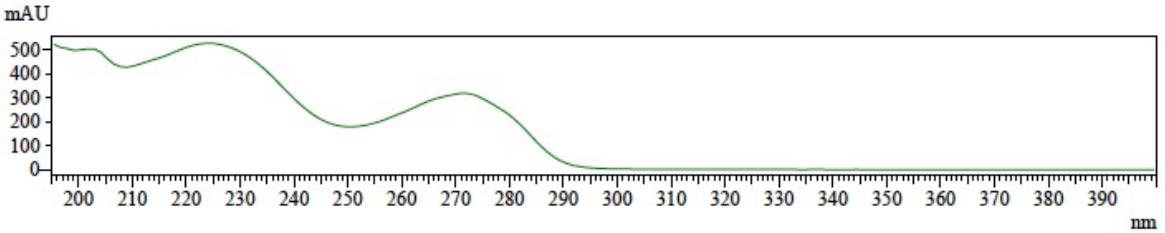
Chromatogram



UV Spectrum
Retention time = 7.563



UV Spectrum
Retention time = 8.428

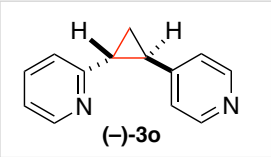


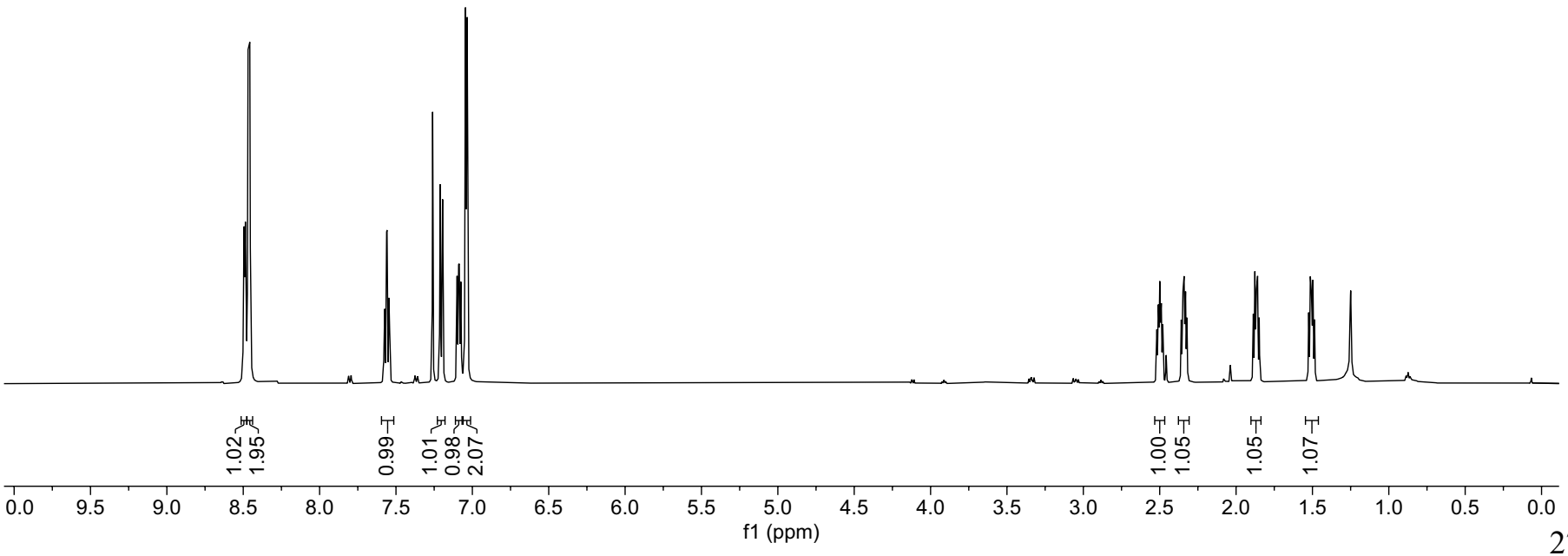
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.563	26403	0.748
2	8.428	3502542	99.252
Total		3528945	100.000

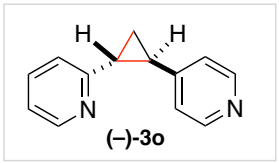
^{1}H NMR of **3o**, 500 MHz, $CDCl_3$



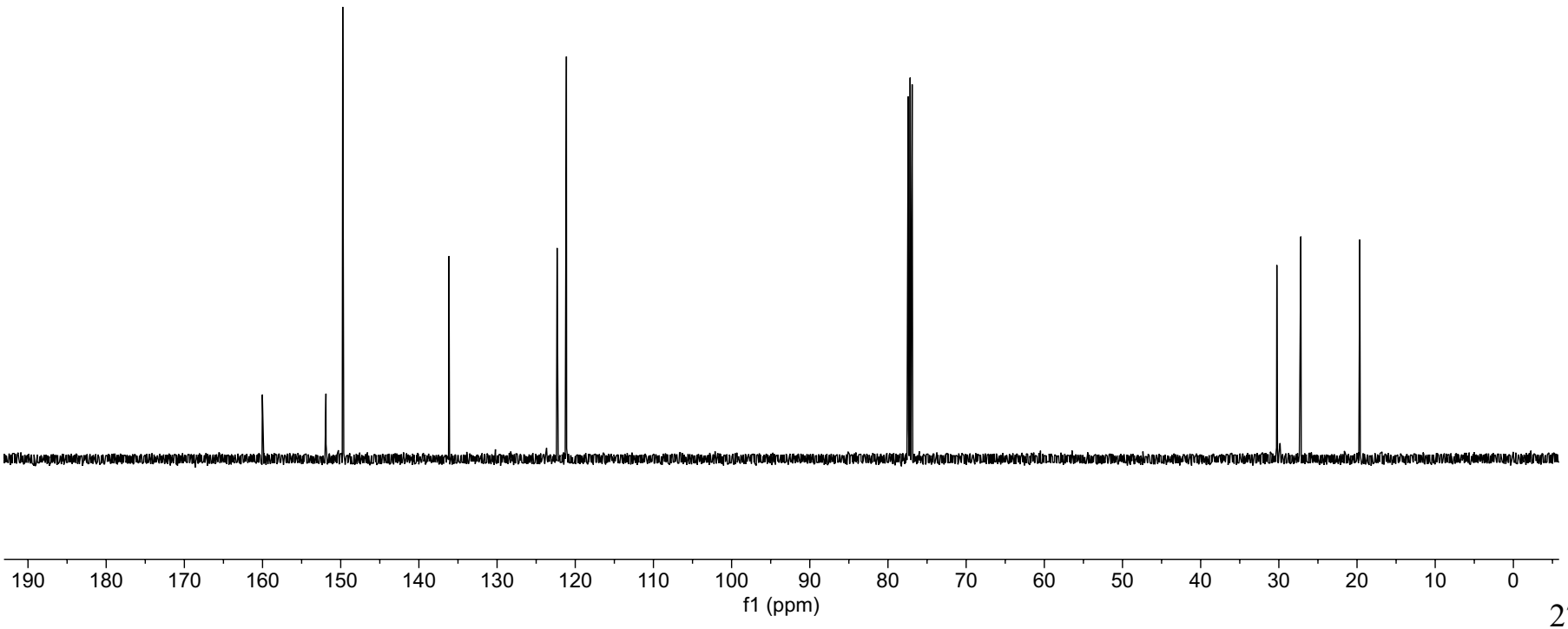


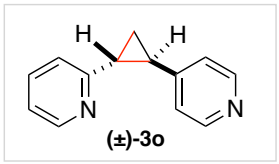
160.02
151.89
149.74
149.67
136.15
122.32
121.20
121.13
77.41
77.16
76.91
30.26
27.19
19.65

^{13}C NMR of **3o**, 125 MHz, $CDCl_3$



(–)-3o



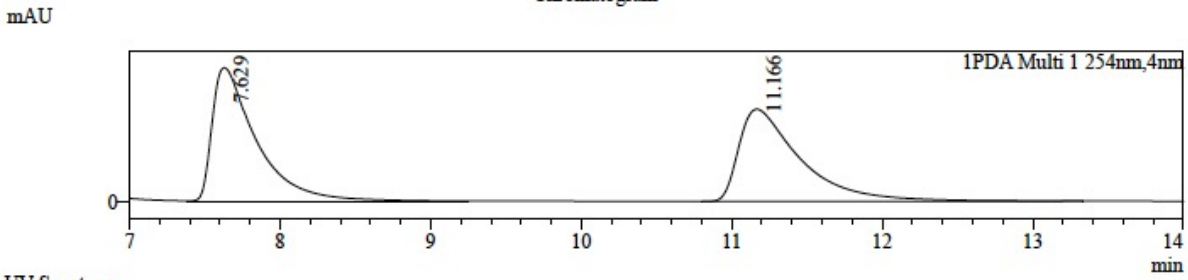


(±)-3o

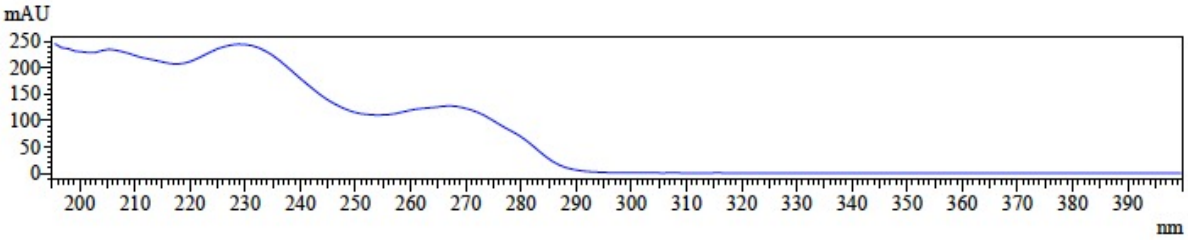
Sample Information

Sample Name	: XXW-0972--ADH-30%-0.8mL
Sample ID	: XXW-0972--ADH-30%-0.8mL
Data File	: XXW-0972--ADH-30%-0.8mL.lcd
Method File	: XXW-30%.0.8.mL.lcm

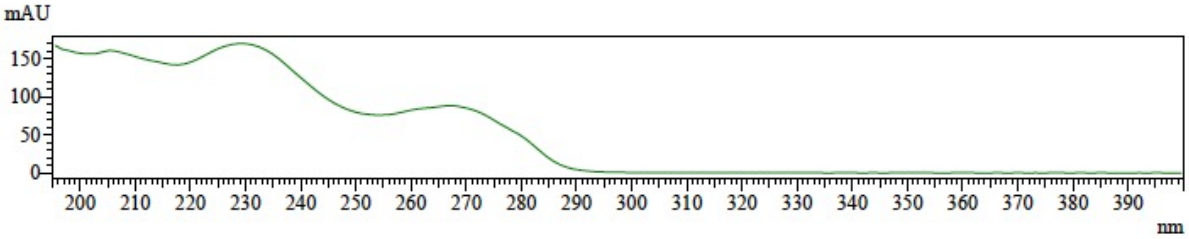
Chromatogram



UV Spectrum
Retention time = 7.629



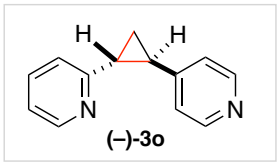
UV Spectrum
Retention time = 11.166



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.629	2241011	50.686
2	11.166	2180382	49.314
Total		4421393	100.000

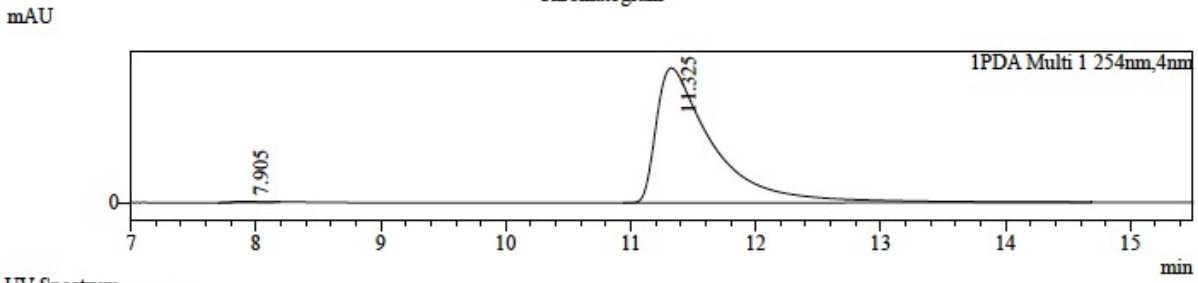


(–)-3o

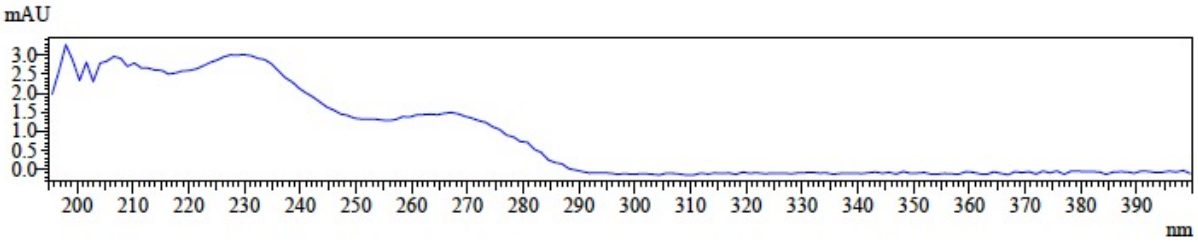
Sample Information

Sample Name	: XXW-1059--ADH-30%-0.8mL
Sample ID	: XXW-1059--ADH-30%-0.8mL
Data File	: XXW-1059--ADH-30%-0.8mL.lcd
Method File	: XXW-30%.0.8.mL.lcm

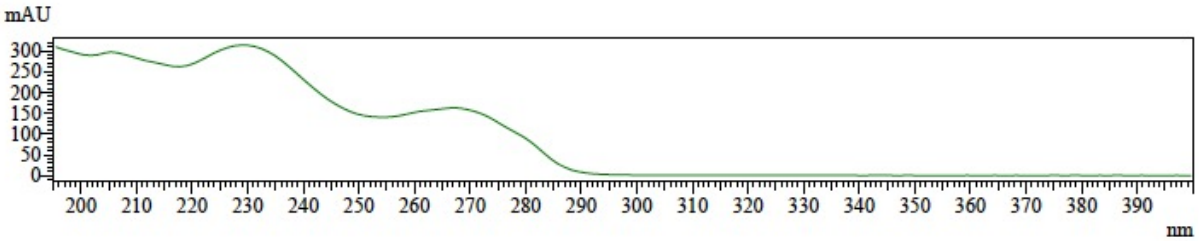
Chromatogram



UV Spectrum
Retention time = 7.905



UV Spectrum
Retention time = 11.325

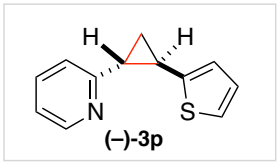


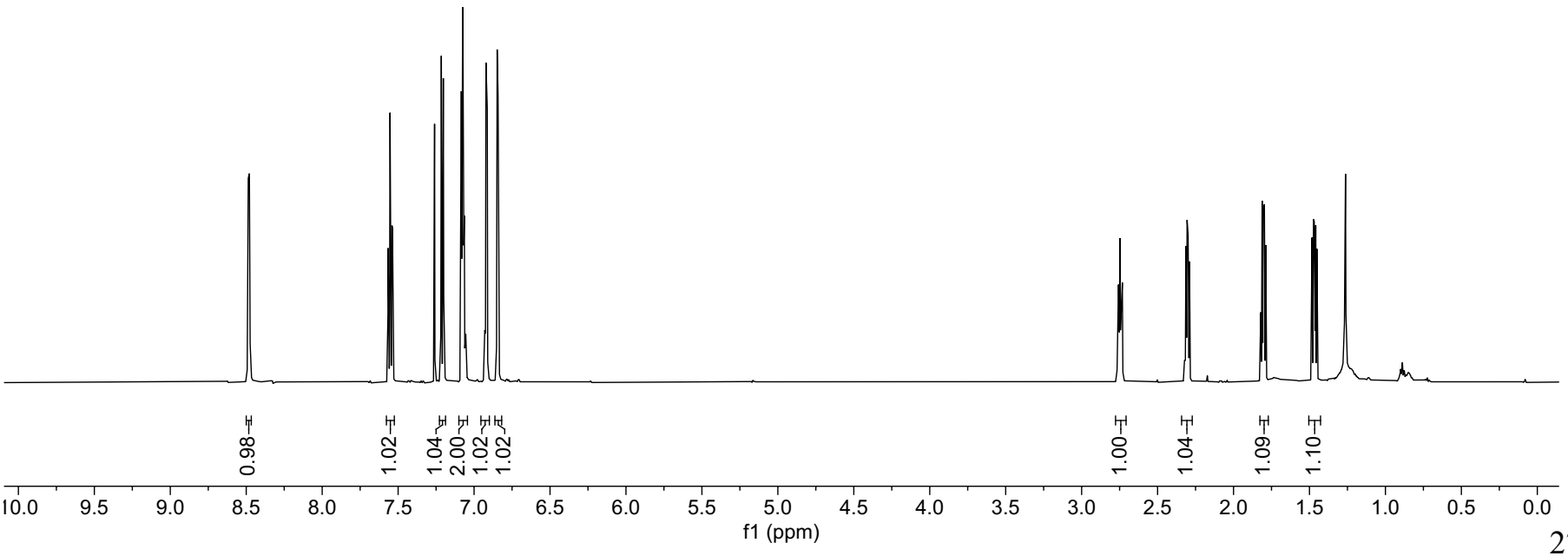
Peak Table

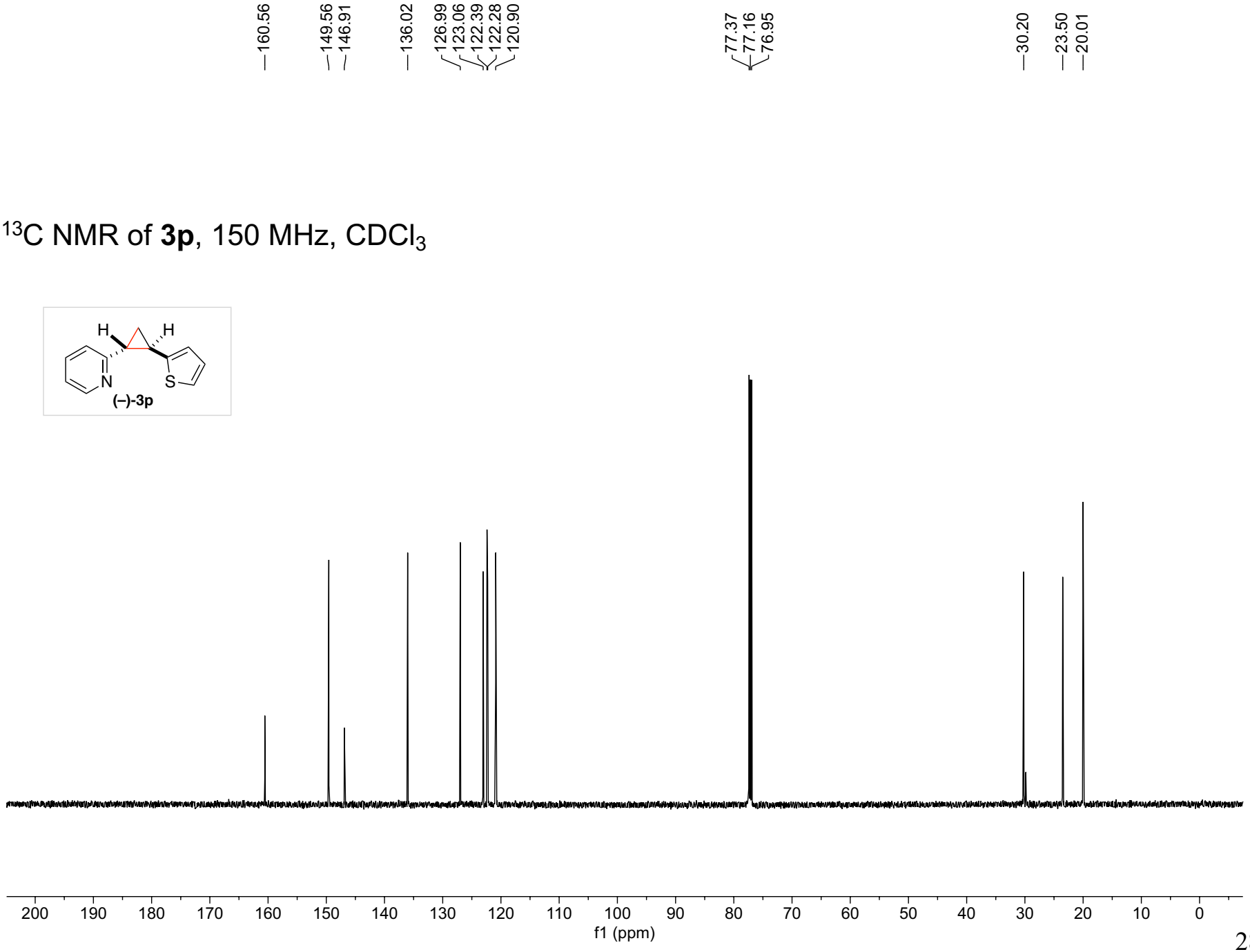
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.905	15271	0.340
2	11.325	4473401	99.660
Total		4488672	100.000

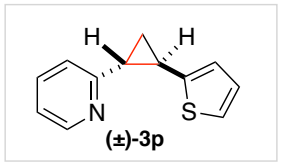
^{1}H NMR of **3p**, 600 MHz, $CDCl_3$







^{13}C NMR of **3p**, 150 MHz, $CDCl_3$

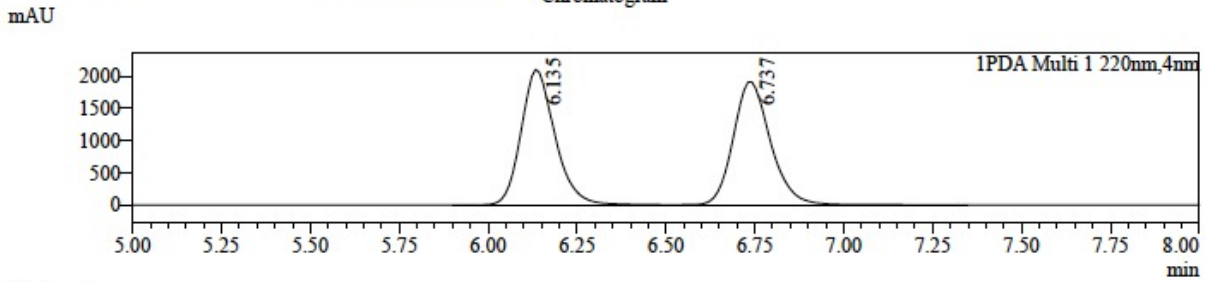


(±)-3p

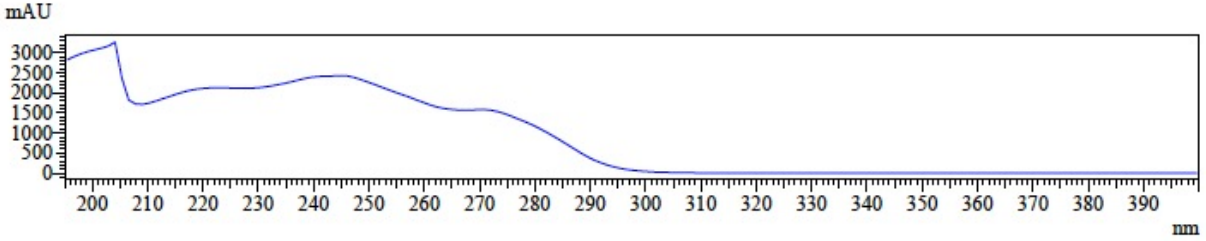
Sample Information

Sample Name	: XXW-1069-ID-10%-0.8mL
Sample ID	: XXW-1069-ID-10%-0.8mL
Data File	: XXW-1069-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

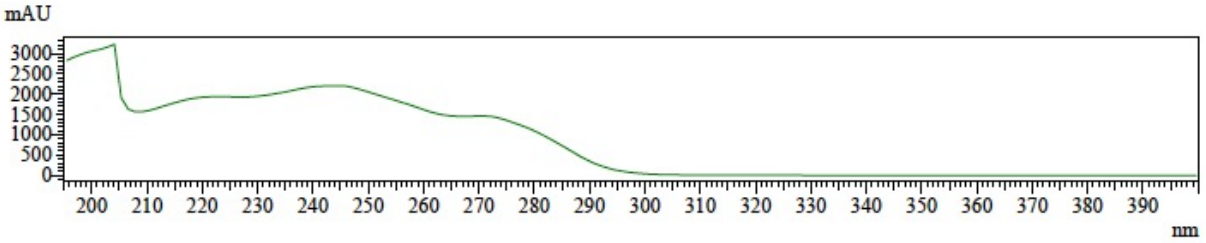
Chromatogram



UV Spectrum
Retention time = 6.135



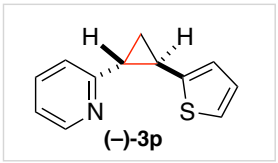
UV Spectrum
Retention time = 6.737



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.135	13894627	49.999
2	6.737	13895237	50.001
Total		27789864	100.000

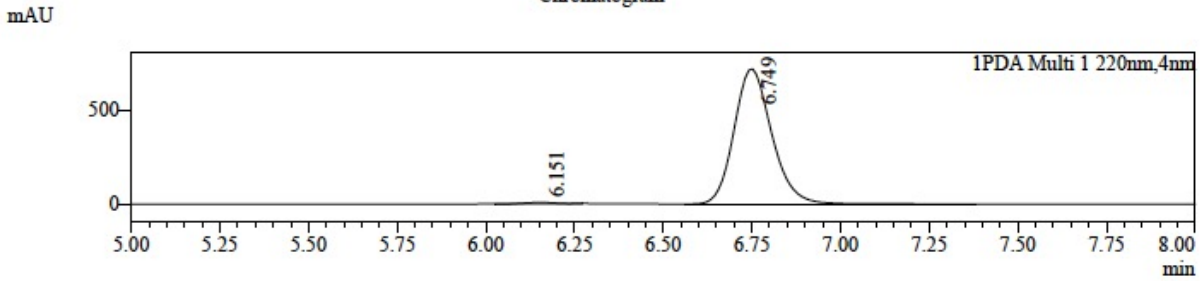


(–)-3p

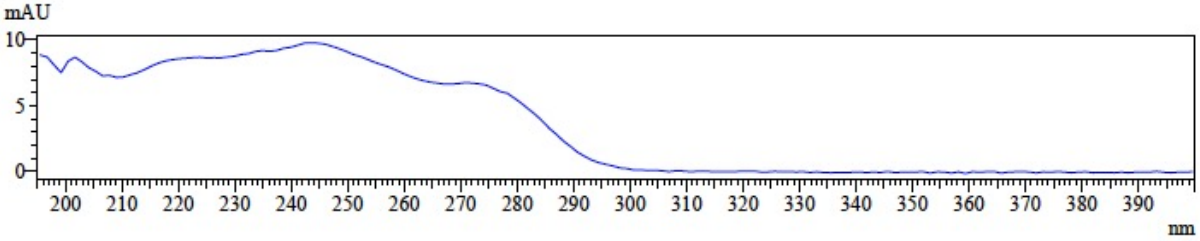
Sample Information

Sample Name	: XXW-1070-ID-10%-0.8mL
Sample ID	: XXW-1070-ID-10%-0.8mL
Data File	: XXW-1070-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

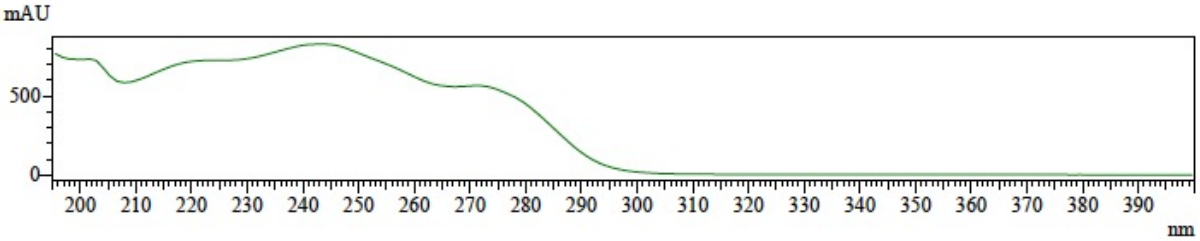
Chromatogram



UV Spectrum
Retention time = 6.151



UV Spectrum
Retention time = 6.749

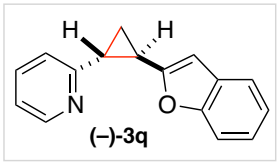


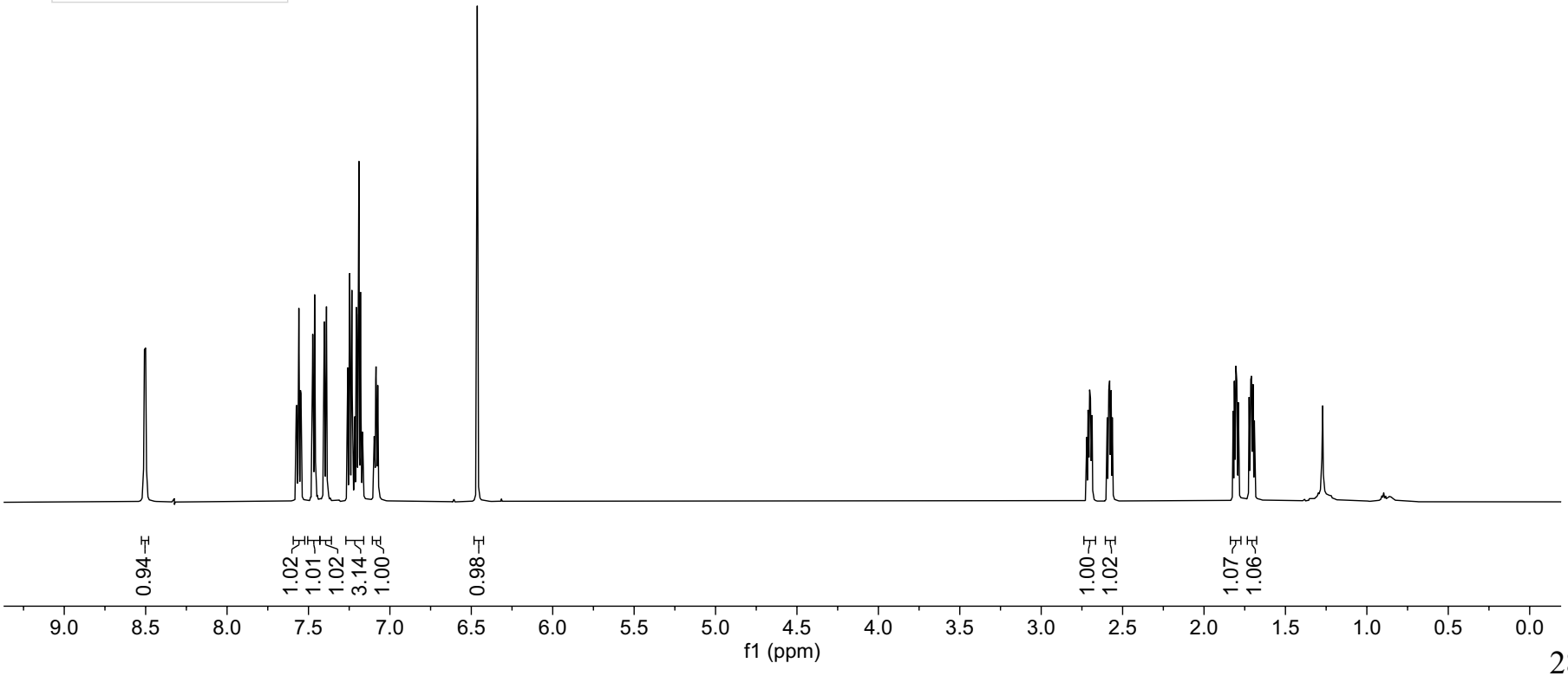
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.151	45485	0.851
2	6.749	5299273	99.149
Total		5344758	100.000

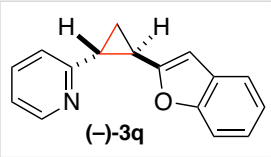
^{1}H NMR of **3q**, 600 MHz, $CDCl_3$



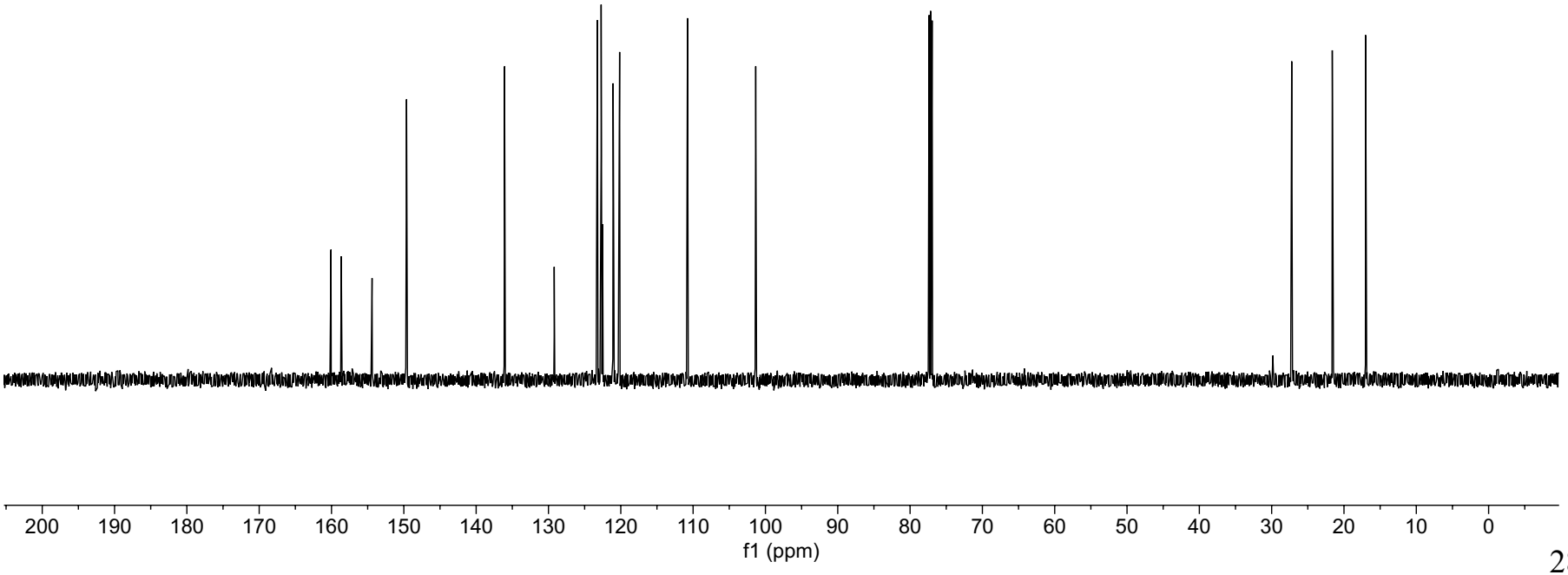


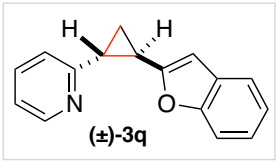
160.07
158.65
154.39
149.62
136.07
129.21
123.24
122.72
122.52
121.06
120.16
110.78
101.34
77.37
77.16
76.95
27.23
21.62
17.01

^{13}C NMR of **3q**, 150 MHz, $CDCl_3$



(–)-3q



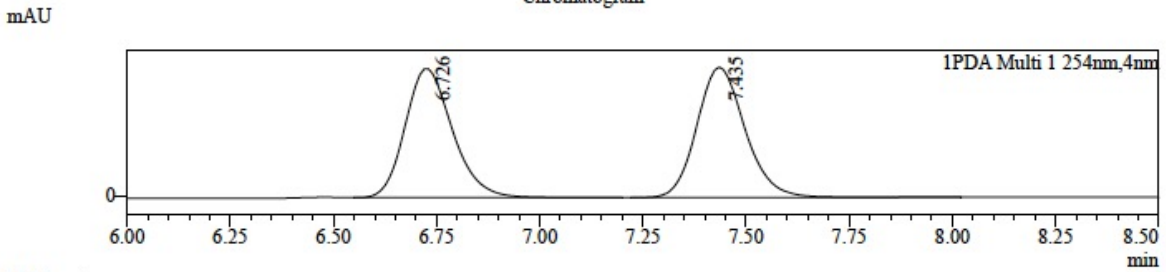


(±)-3q

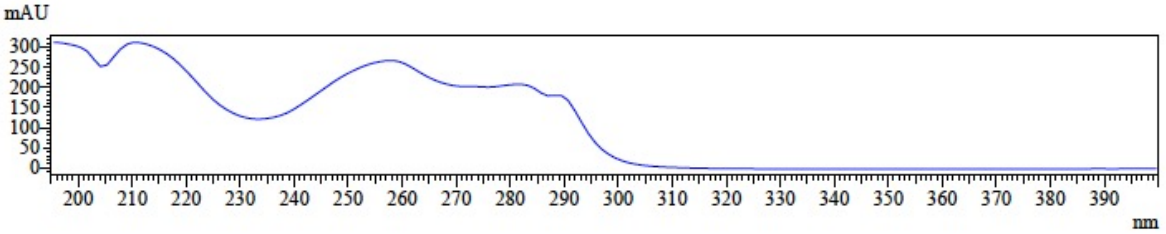
Sample Information

Sample Name : XXW-0888-n1-ID-10%-0.8mL
Sample ID : XXW-0888-n1-ID-10%-0.8mL
Data File : XXW-0888-n1-ID-10%-0.8mL.lcd
Method File : XXW-10%.0.8.mL.lcm

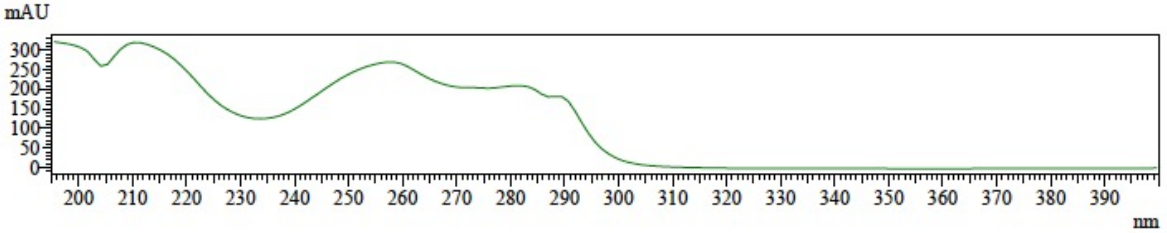
Chromatogram



UV Spectrum
Retention time = 6.726



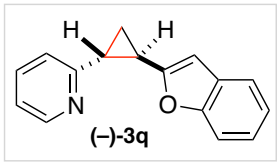
UV Spectrum
Retention time = 7.435



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.726	2089095	49.356
2	7.435	2143591	50.644
Total		4232687	100.000

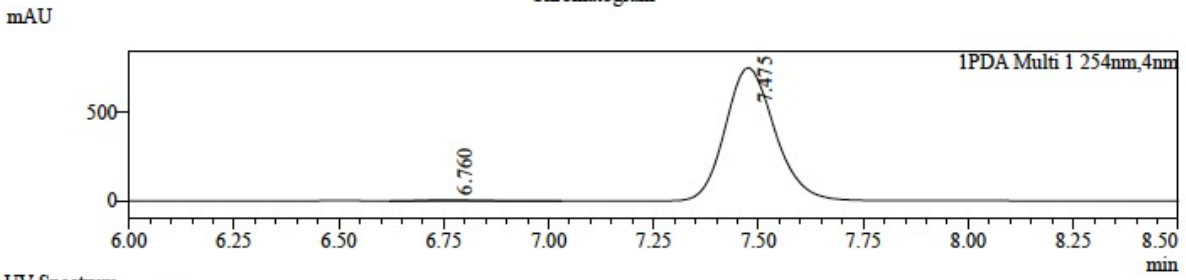


(–)-3q

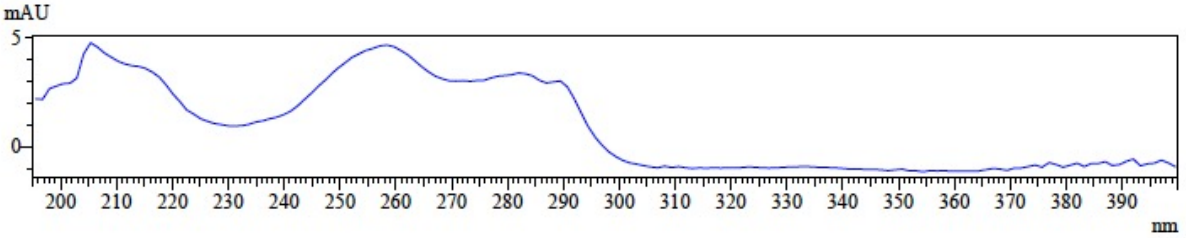
Sample Information

Sample Name	: XXW-1063-ID-10%-0.8mL
Sample ID	: XXW-1063-ID-10%-0.8mL
Data File	: XXW-1063-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

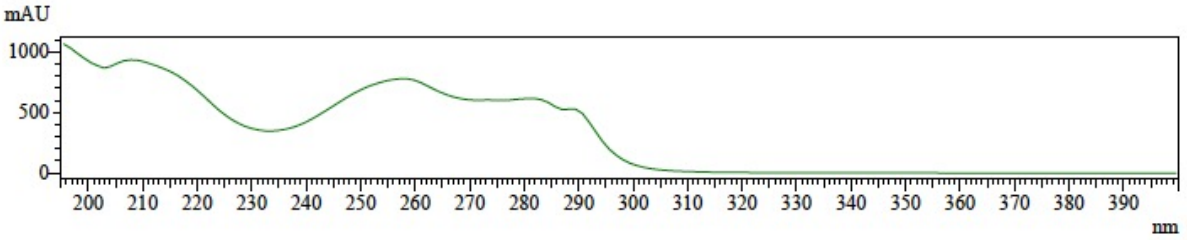
Chromatogram



UV Spectrum
Retention time = 6.760



UV Spectrum
Retention time = 7.475

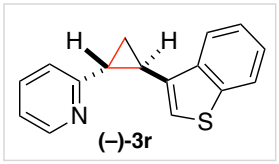


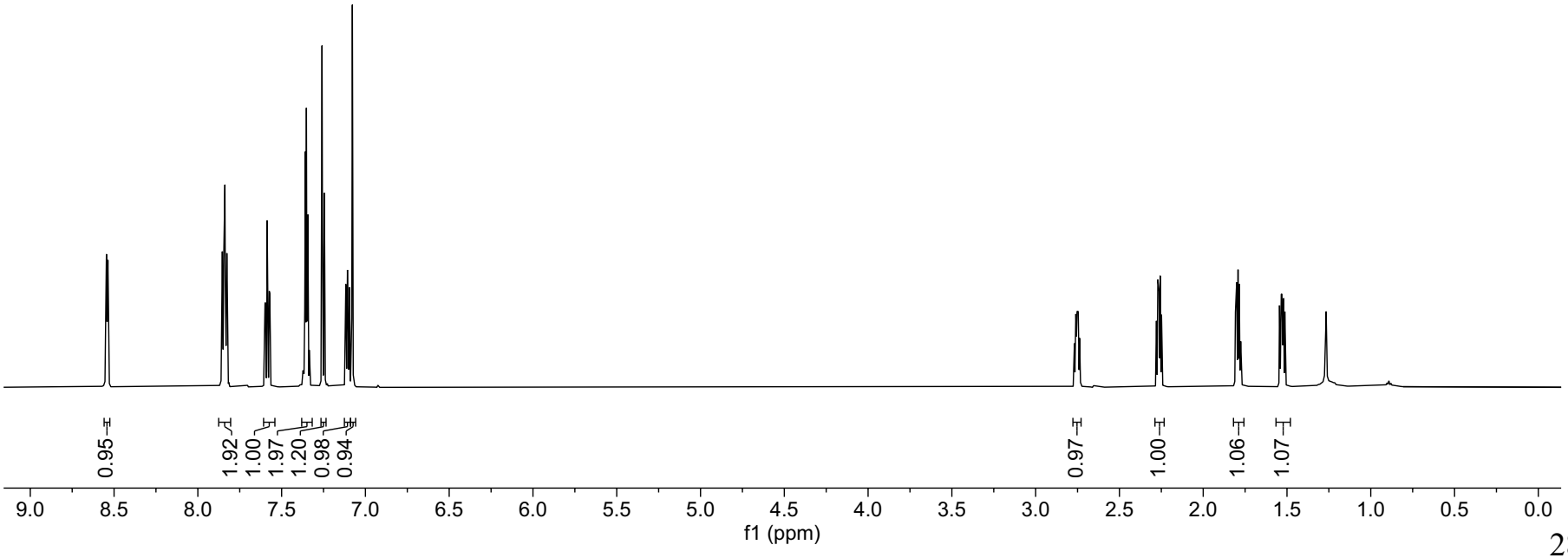
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.760	42711	0.679
2	7.475	6248775	99.321
Total		6291486	100.000

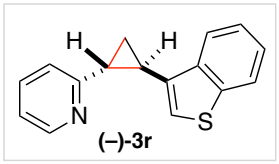
^{1}H NMR of **3r,** 600 MHz, $CDCl_3$

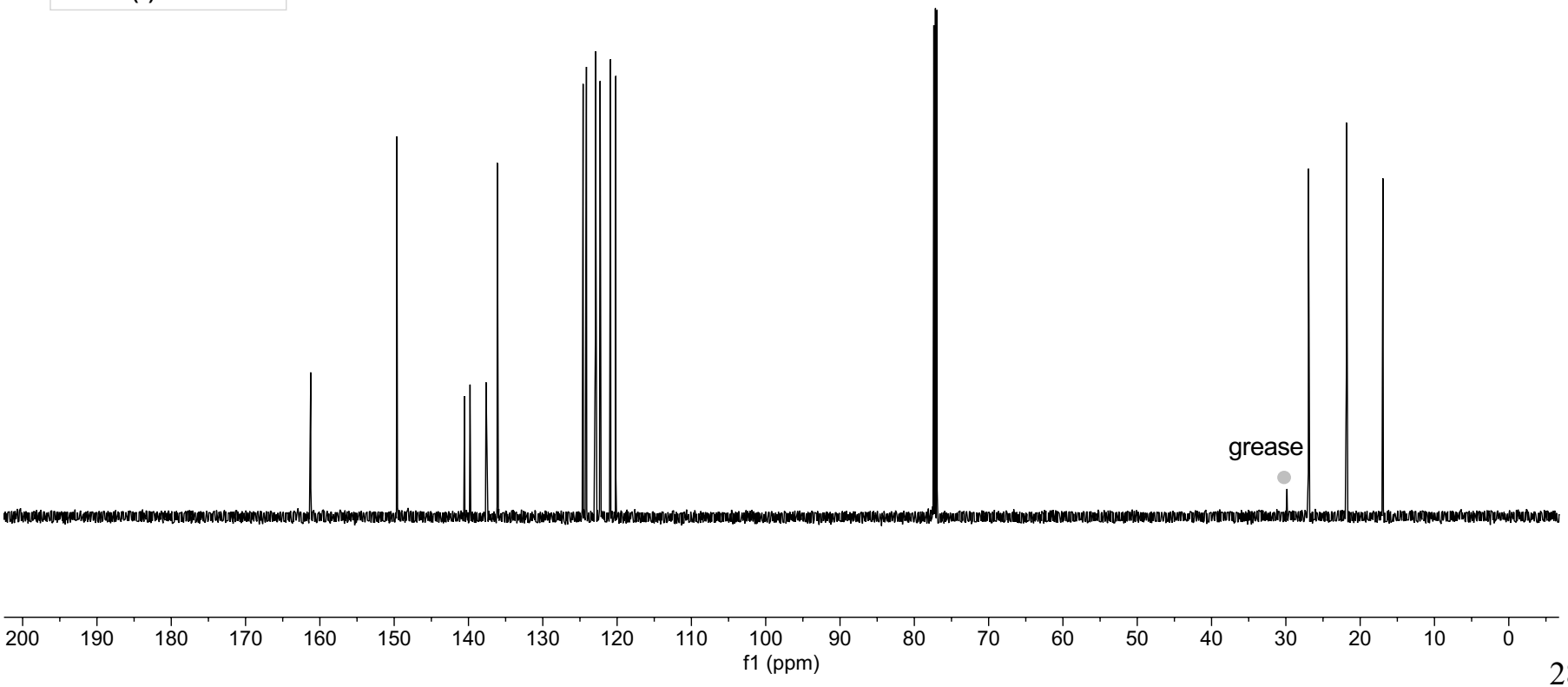


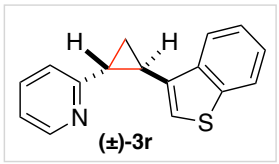


161.23
149.64
140.53
139.79
137.64
136.12
124.57
124.13
122.92
122.28
122.22
120.89
120.17
77.37
77.16
76.95
26.96
21.84
16.94

^{13}C NMR of **3r**, 150 MHz, $CDCl_3$





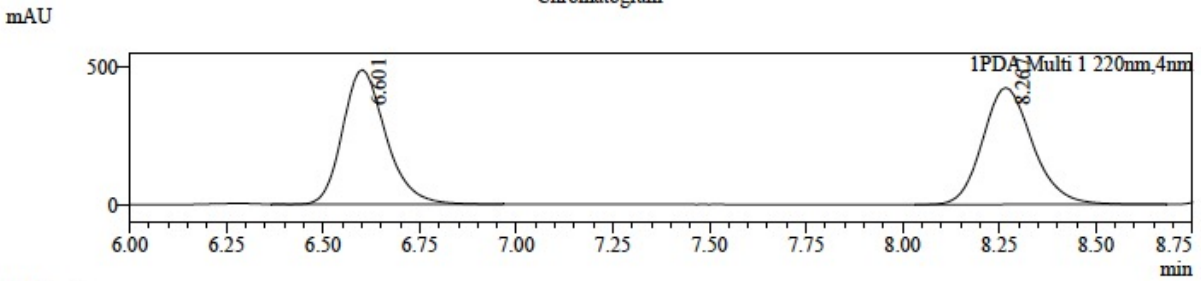


(±)-3r

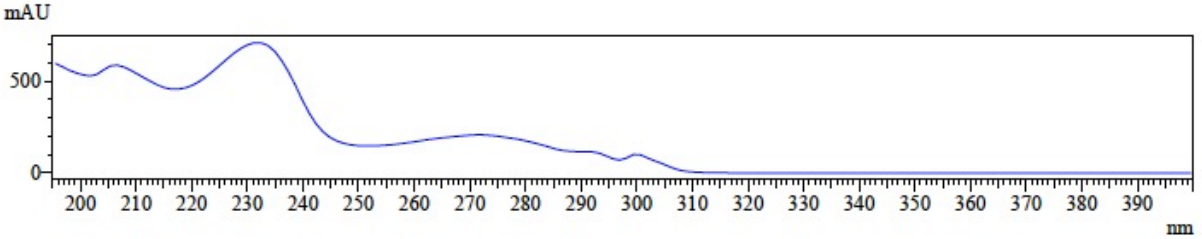
Sample Information

Sample Name	: XXW-1077-ID-10-%--0.8mL
Sample ID	: XXW-1077-ID-10-%--0.8mL
Data File	: XXW-1077-ID-10-%--0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

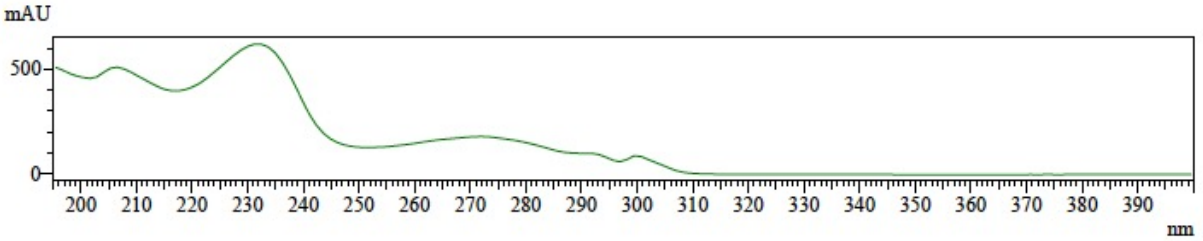
Chromatogram



UV Spectrum
Retention time = 6.601



UV Spectrum
Retention time = 8.267



Peak Table

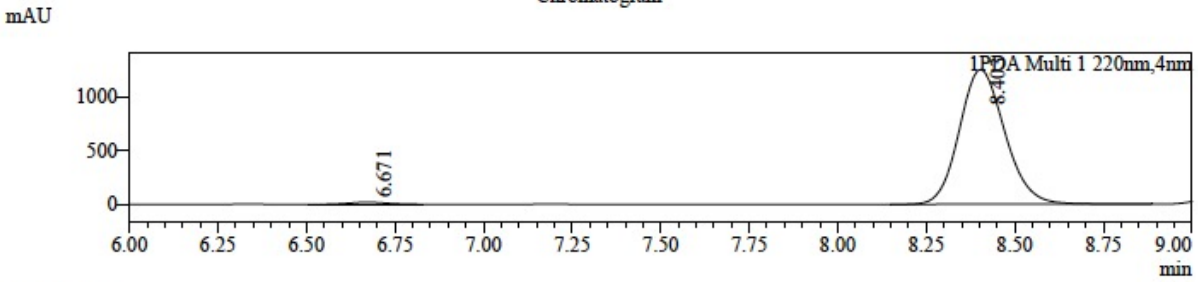
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.601	3784539	49.899
2	8.267	3799875	50.101
Total		7584414	100.000

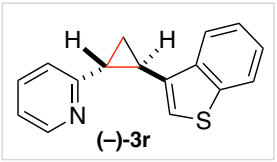
Sample Information

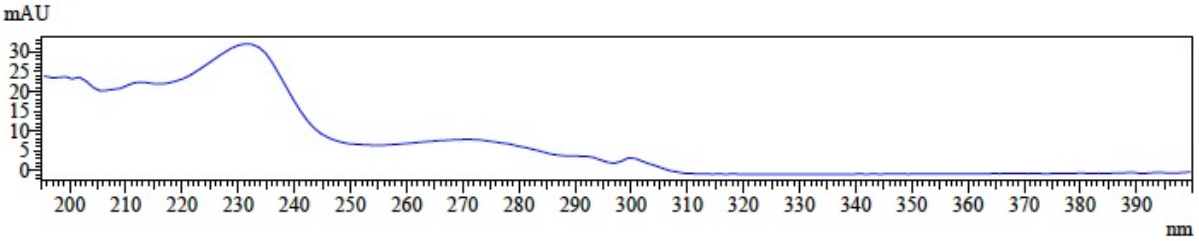
Sample Name	: XXW-1078-ID-10-%--0.8mL
Sample ID	: XXW-1078-ID-10-%--0.8mL
Data File	: XXW-1078-ID-10-%--0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram

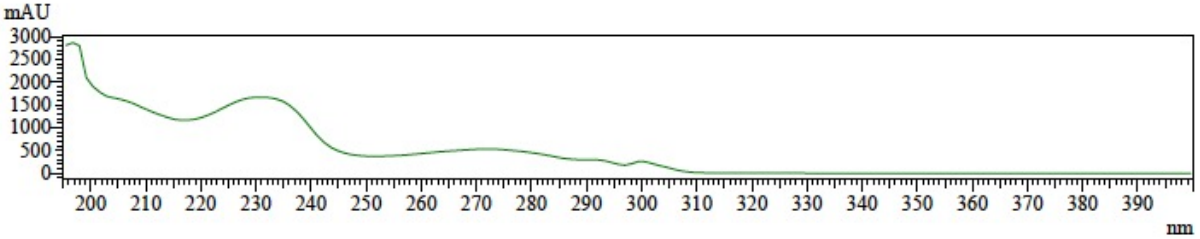


UV Spectrum
Retention time = 6.671





UV Spectrum
Retention time = 8.403

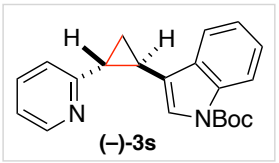


Peak Table

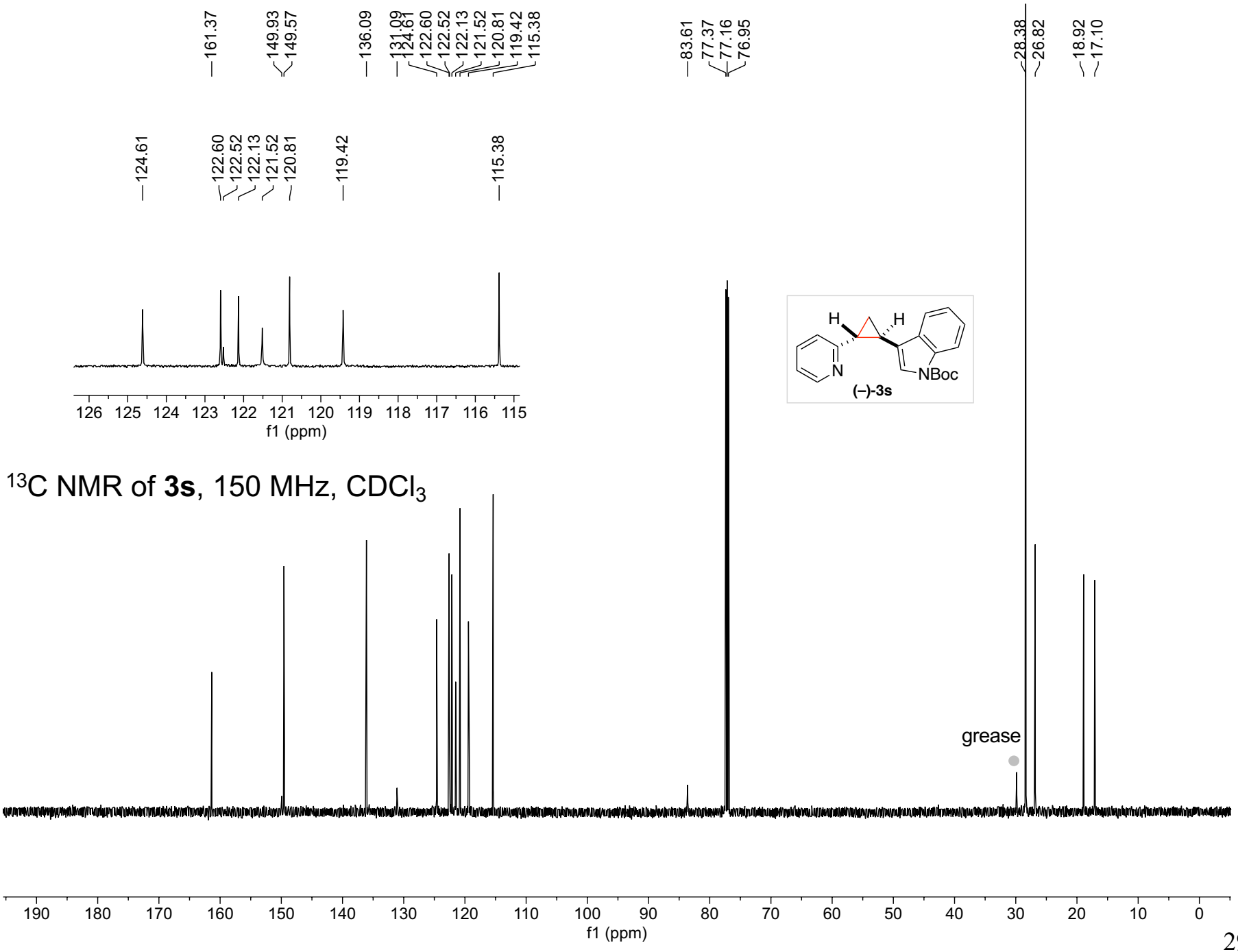
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.671	137884	1.222
2	8.403	11149098	98.778
Total		11286982	100.000

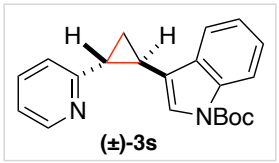
^{1}H NMR of **3s**, 600 MHz, $CDCl_3$



(–)-3s



^{13}C NMR of **3s**, 150 MHz, $CDCl_3$

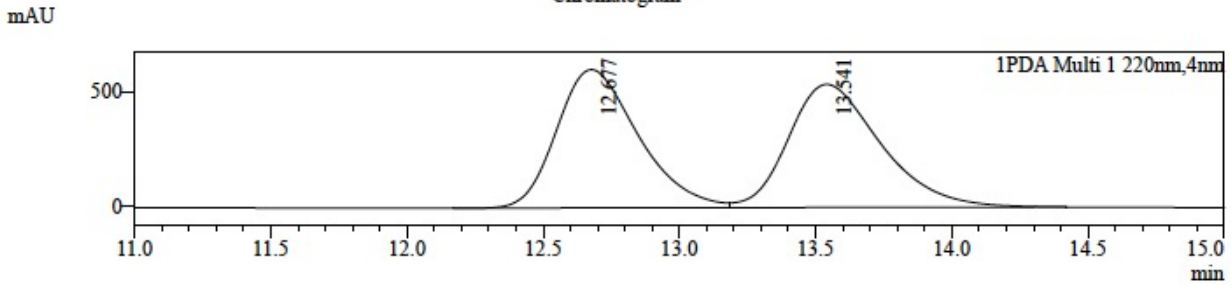


(±)-3s

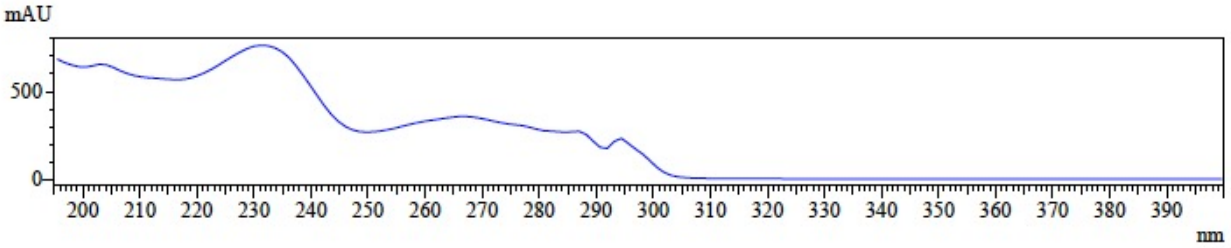
Sample Information

Sample Name	: XXW-1089-ODH-2-%--0.5mL
Sample ID	: XXW-1089-ODH-2-%--0.5mL
Data File	: XXW-1089-ODH-2-%--0.5mL.lcd
Method File	: XXW-2%.0.5.mL.lcm

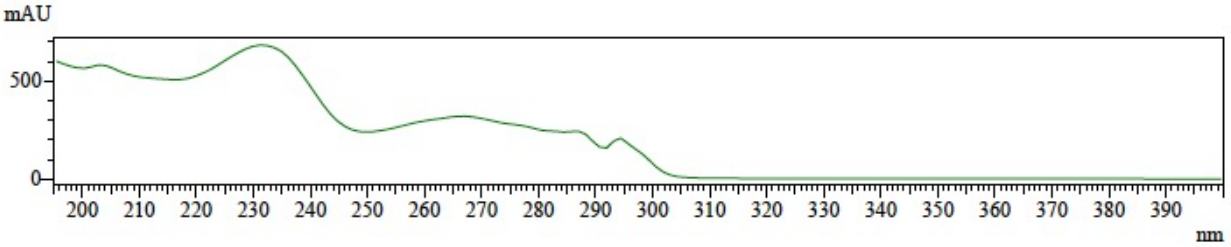
Chromatogram



UV Spectrum
Retention time = 12.677



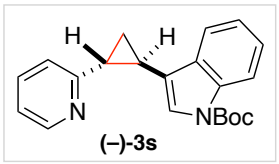
UV Spectrum
Retention time = 13.541



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.677	12589114	49.792
2	13.541	12694305	50.208
Total		25283419	100.000

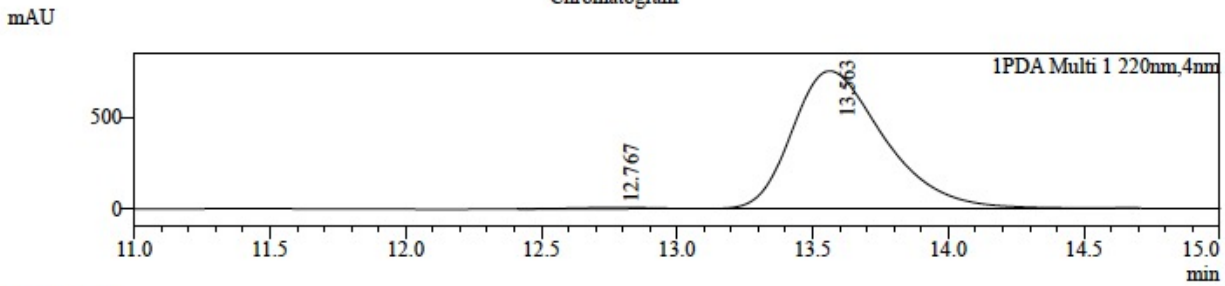


(–)-3s

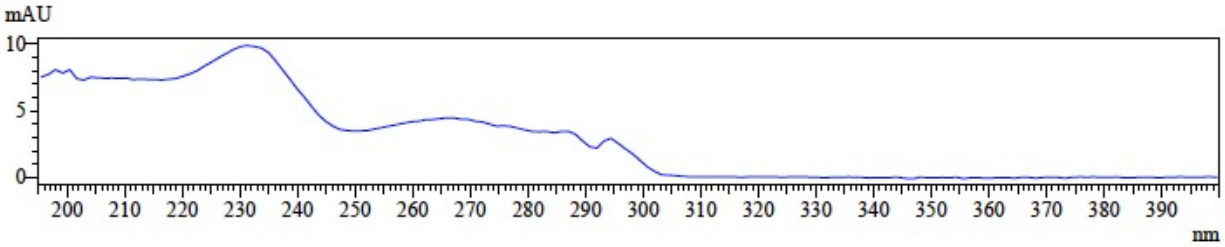
Sample Information

Sample Name	: XXW-1090-ODH-2-%--0.5mL
Sample ID	: XXW-1090-ODH-2-%--0.5mL
Data File	: XXW-1090-ODH-2-%--0.5mL.lcd
Method File	: XXW-2%.0.5.mL.lcm

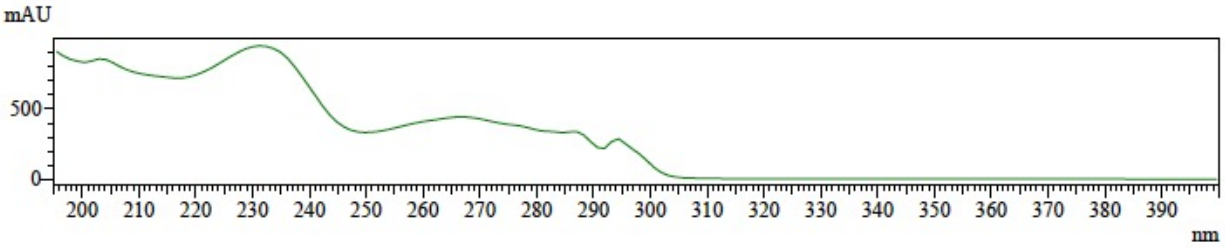
Chromatogram



UV Spectrum
Retention time = 12.767



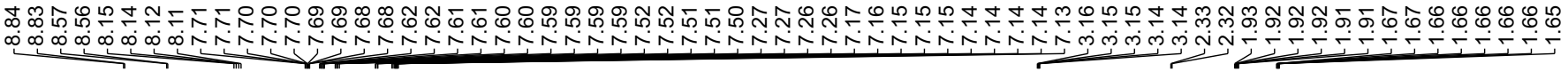
UV Spectrum
Retention time = 13.563



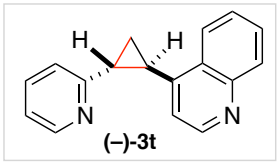
Peak Table

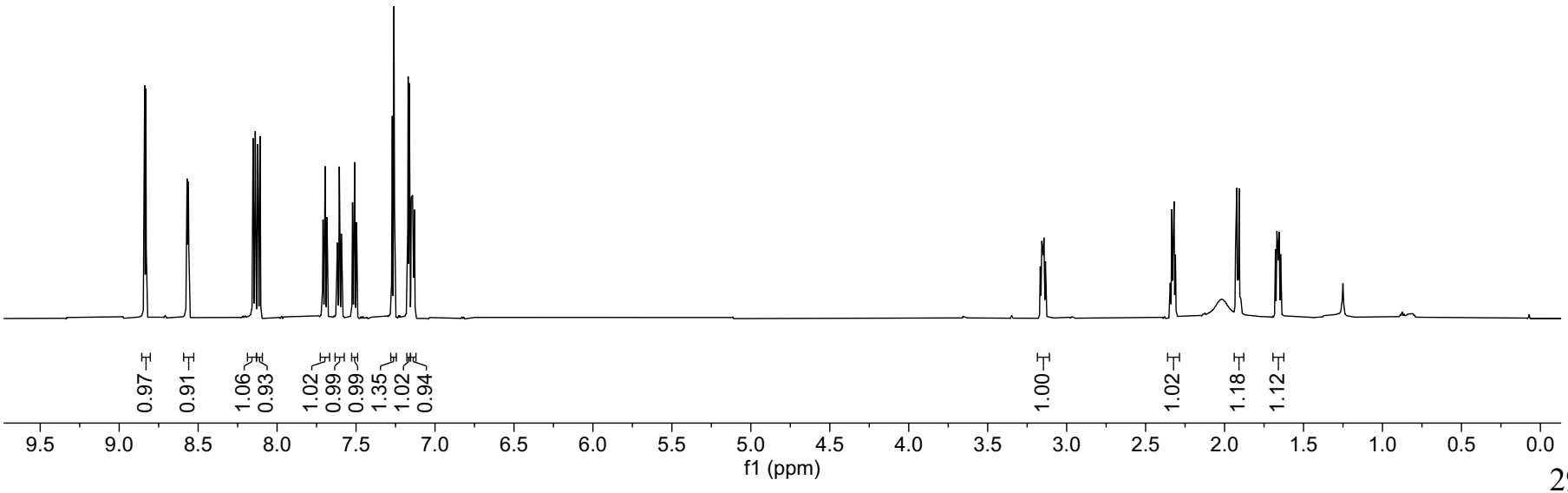
PDA Ch1 220nm

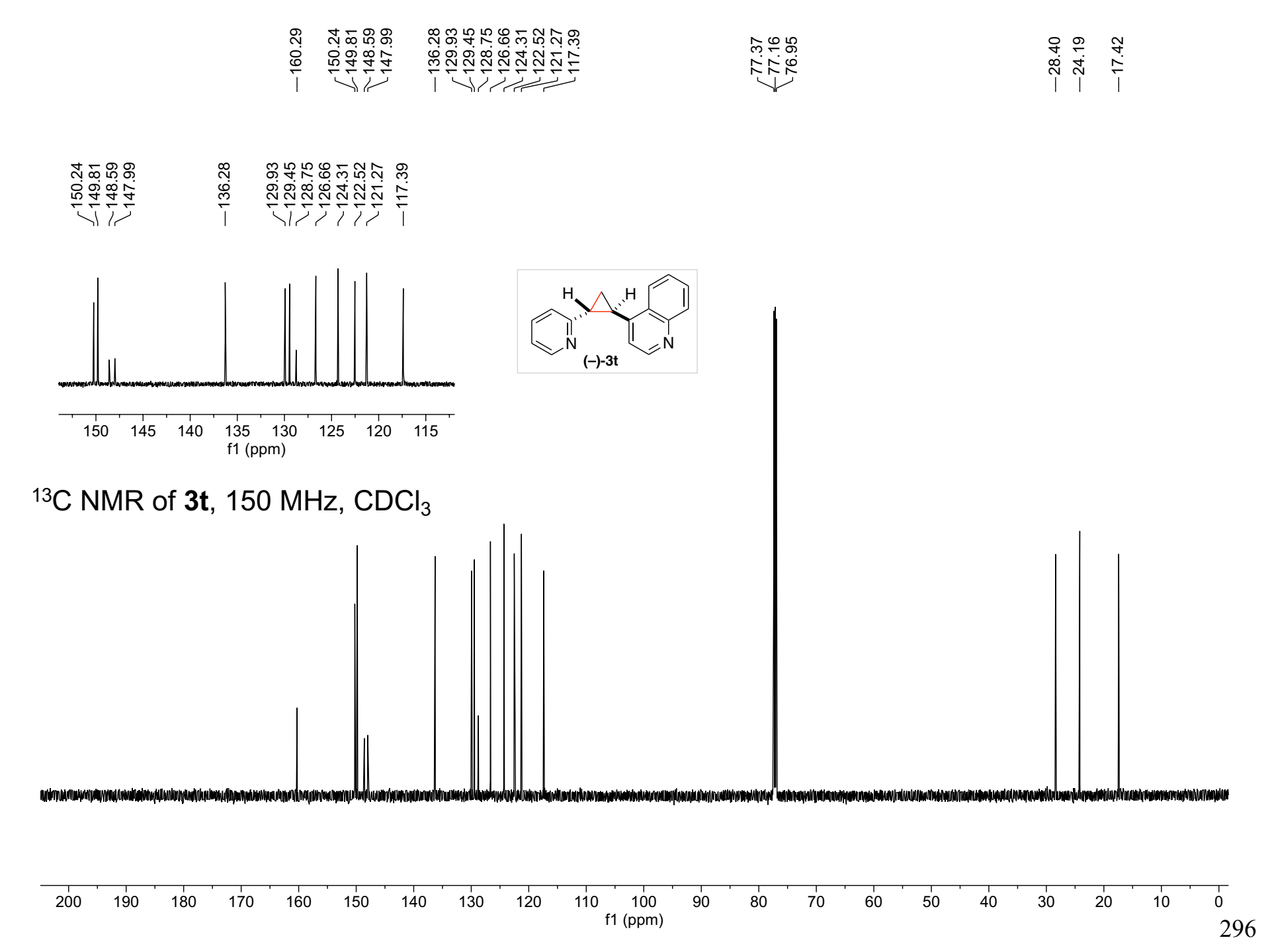
Peak#	Ret. Time	Area	Area%
1	12.767	127494	0.713
2	13.563	17765923	99.287
Total		17893417	100.000



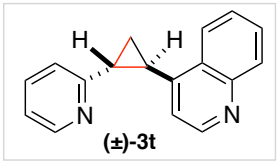
^{1}H NMR of **3t**, 600 MHz, $CDCl_3$







^{13}C NMR of **3t**, 150 MHz, $CDCl_3$

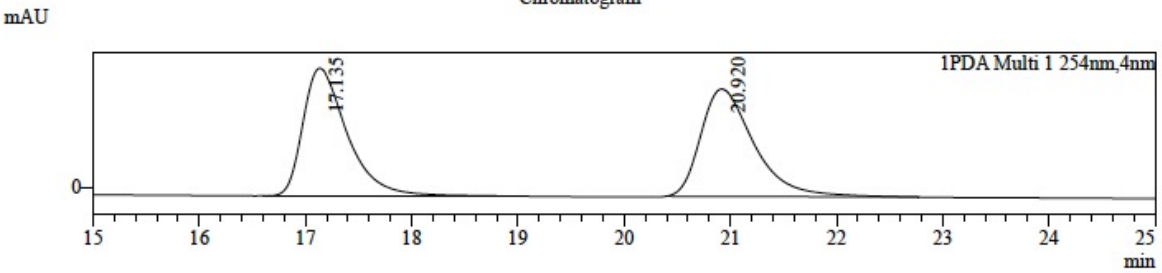


(±)-3t

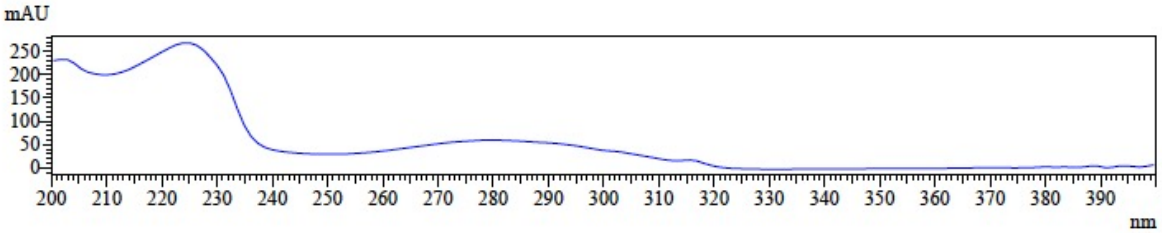
Sample Information

Data File	: XXW-1084-IC-20-%-0.8mL.lcd
Sample Name	: XXW-1084-IC-20-%-0.8mL
Sample ID	: XXW-1084-IC-20-%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

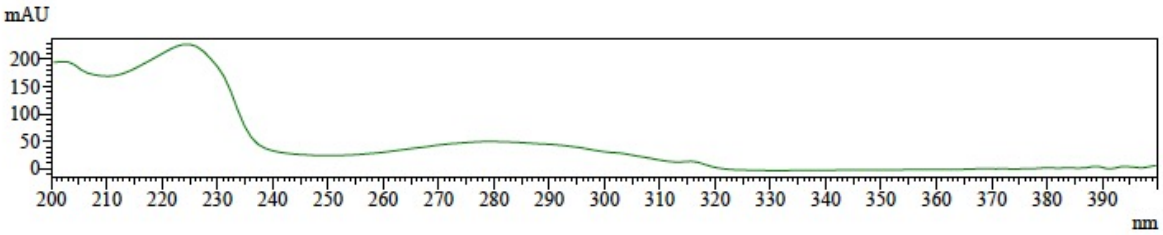
Chromatogram



UV Spectrum
Retention time = 17.135



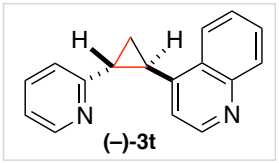
UV Spectrum
Retention time = 20.920



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.135	951266	49.772
2	20.920	959987	50.228
Total		1911253	100.000

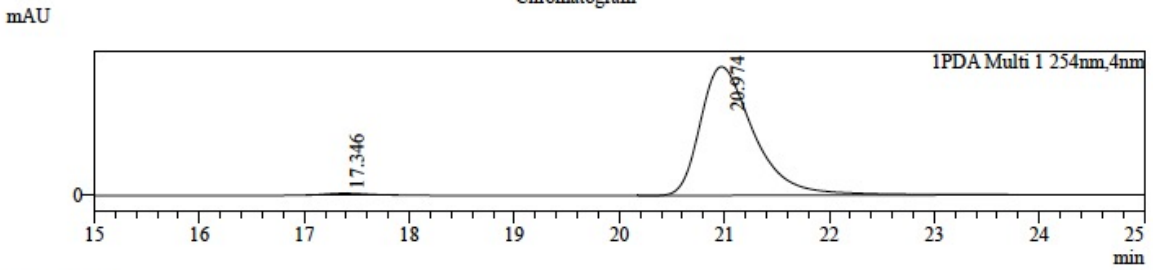


(–)-3t

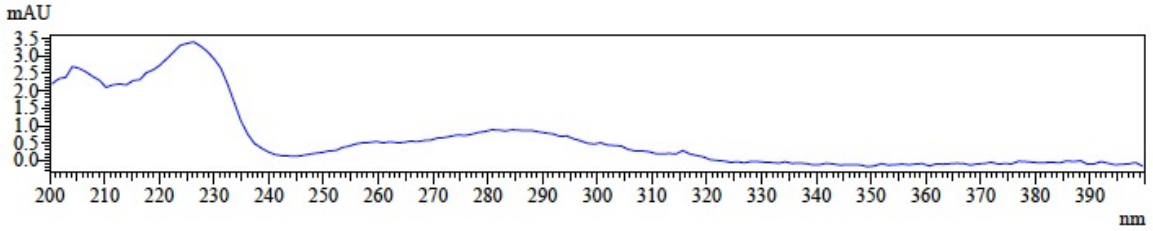
Sample Information

Data File	: XXW-1116-IC-20-%-0.8mL002.lcd
Sample Name	: XXW-1116-IC-20-%-0.8mL
Sample ID	: XXW-1116-IC-20-%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

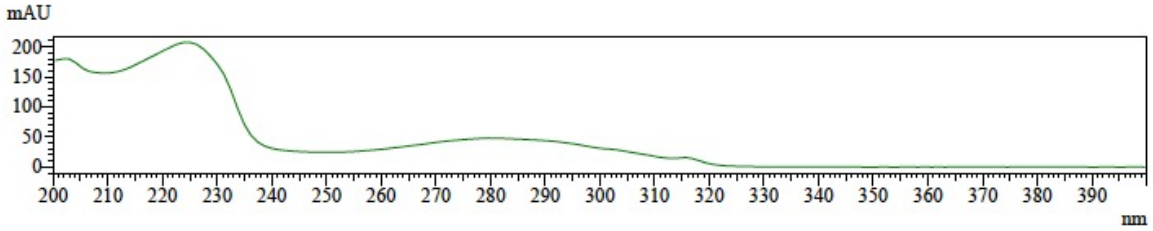
Chromatogram



UV Spectrum
Retention time = 17.346



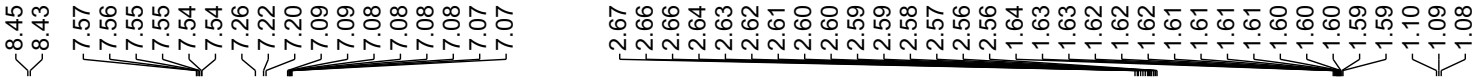
UV Spectrum
Retention time = 20.974



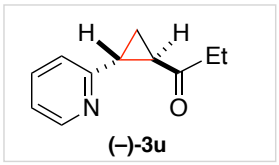
Peak Table

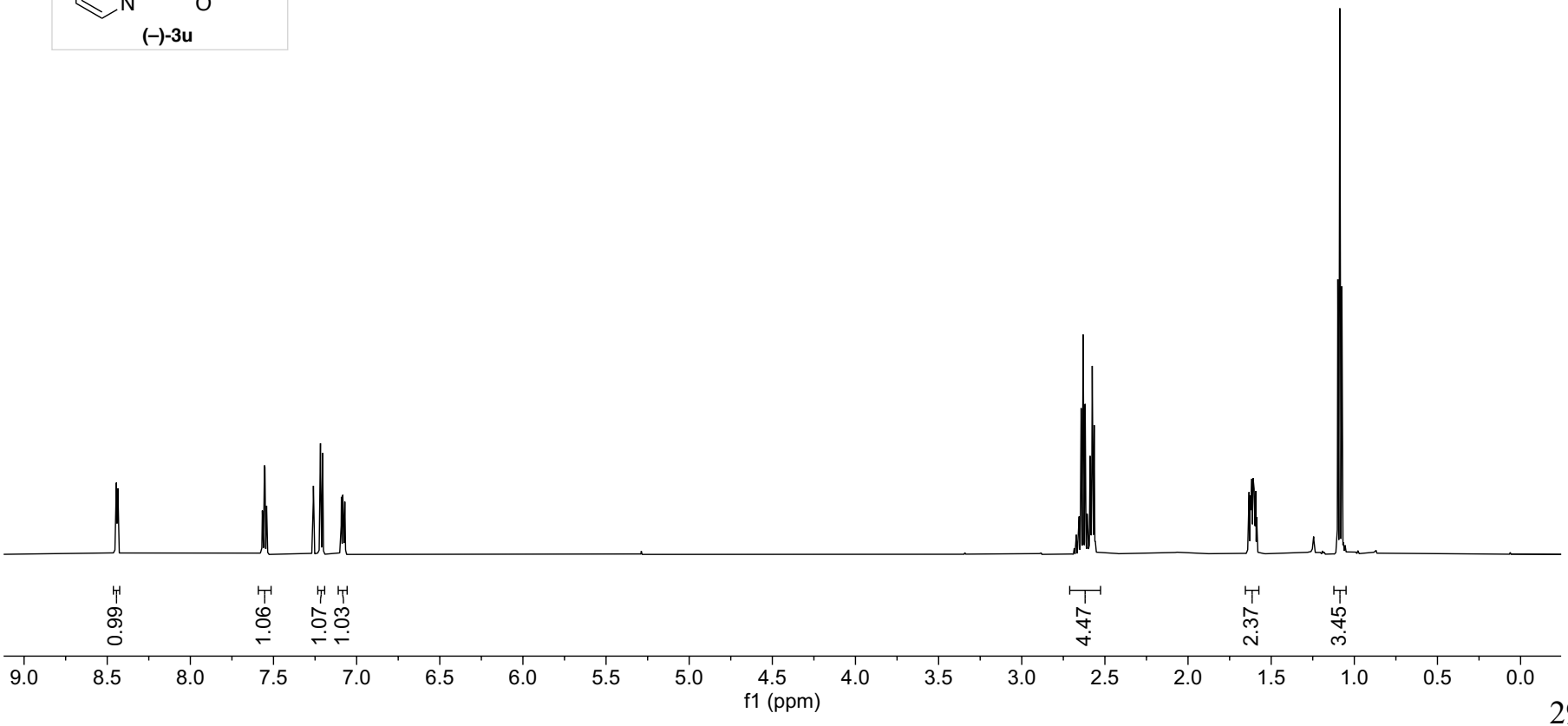
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.346	9379	1.018
2	20.974	911905	98.982
Total		921284	100.000



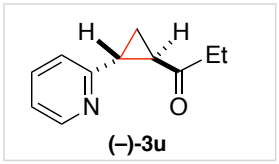
^{1}H NMR of **3u**, 600 MHz, $CDCl_3$



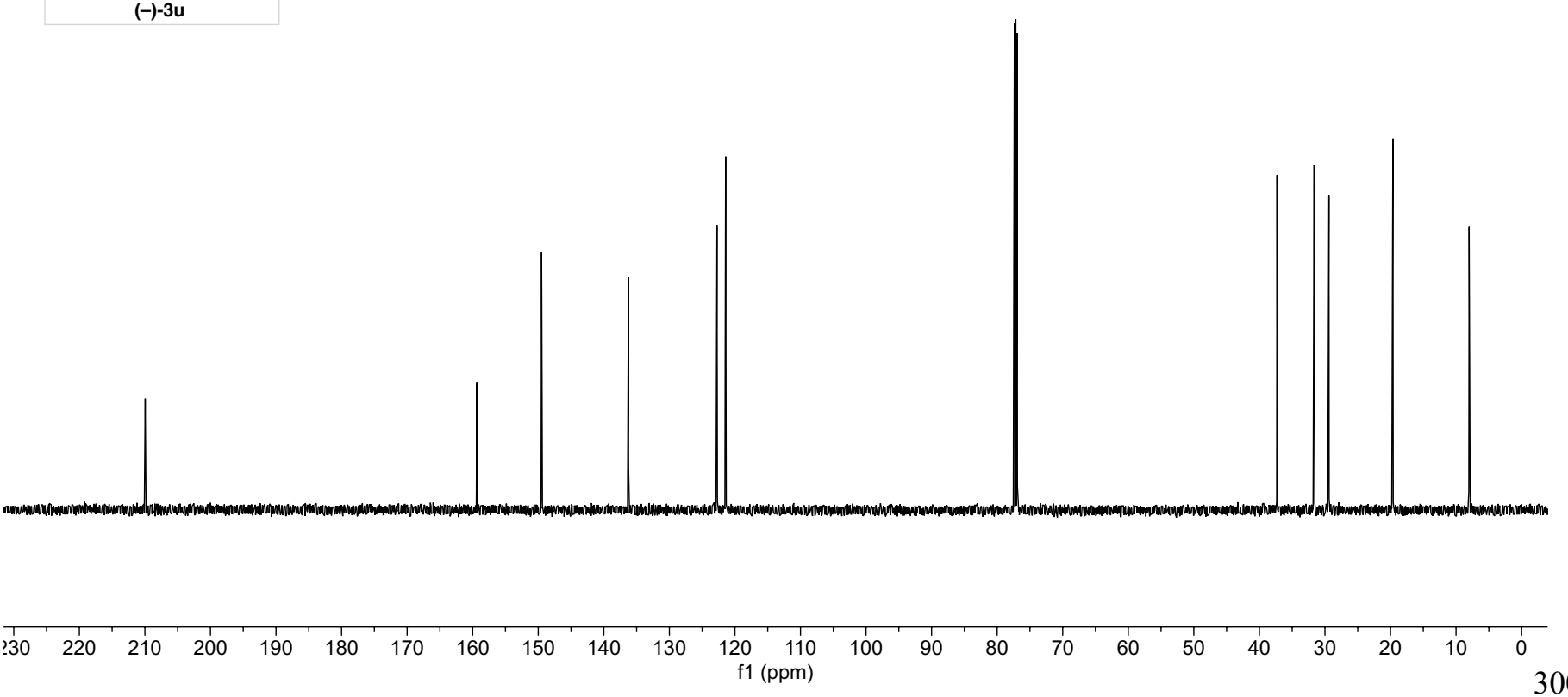


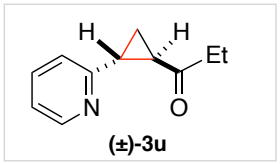
209.95
159.37
149.49
136.24
122.74
121.42
77.37
77.16
76.95
37.31
31.65
29.39
19.63
8.01

^{13}C NMR of **3u**, 150 MHz, $CDCl_3$



(–)-3u



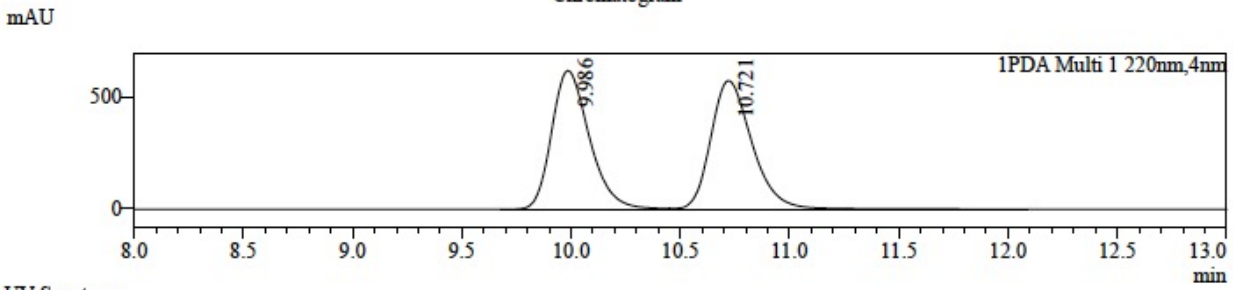


(±)-3u

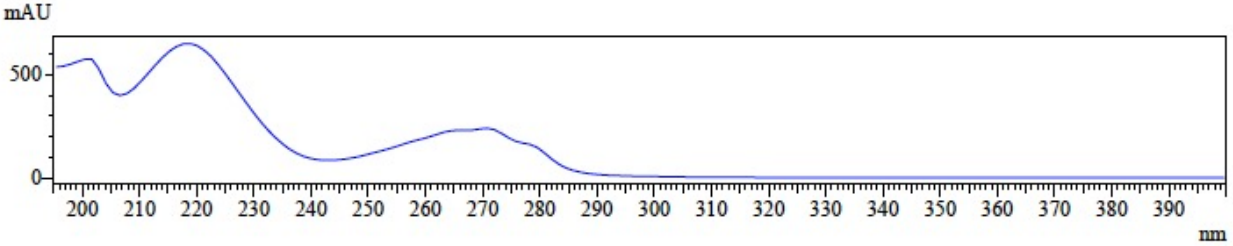
Sample Information

Sample Name	: XXW-0889-IF-5%-0.8mL
Sample ID	: XXW-0889-IF-5%-0.8mL
Data File	: XXW-0889-IF-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

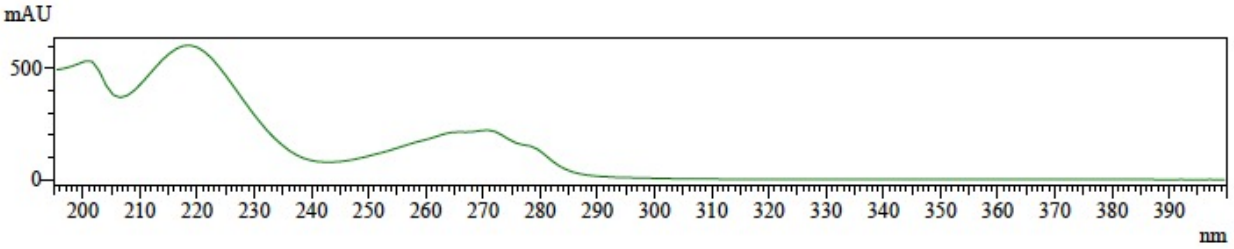
Chromatogram



UV Spectrum
Retention time = 9.986



UV Spectrum
Retention time = 10.721



Peak Table

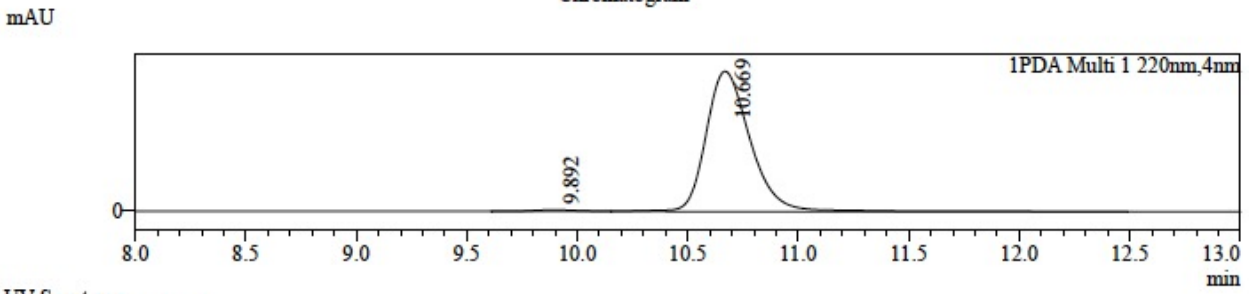
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	9.986	7526371	49.653
2	10.721	7631620	50.347
Total		15157991	100.000

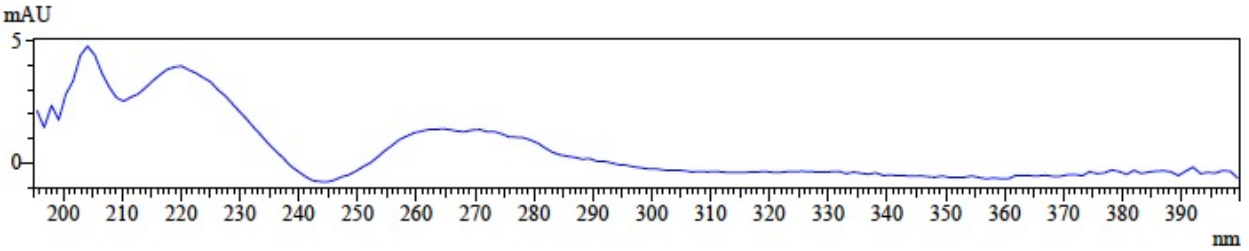
Sample Information

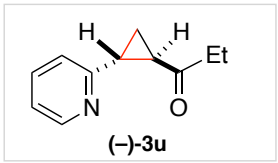
Sample Name	: XXW-1043-IF-5%-0.8mL
Sample ID	: XXW-1043-IF-5%-0.8mL
Data File	: XXW-1043-IF-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram



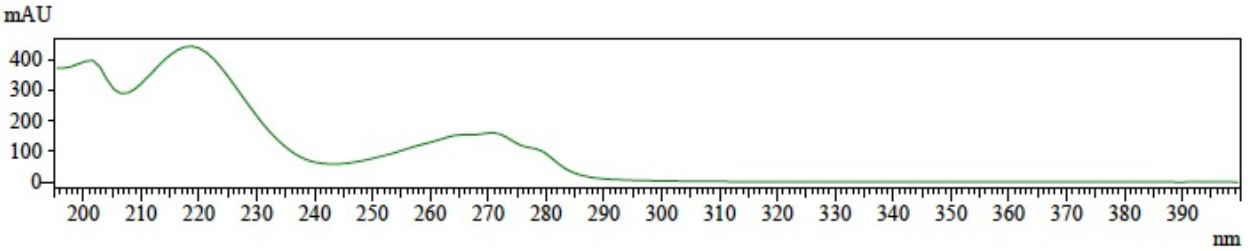
UV Spectrum
Retention time = 9.892





(–)-3u

UV Spectrum
Retention time = 10.669

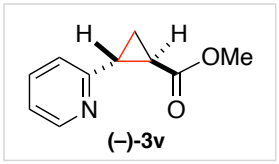


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	9.892	59588	1.002
2	10.669	5887987	98.998
Total		5947575	100.000

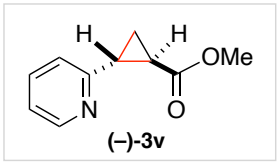
^{1}H NMR of **3v**, 500 MHz, $CDCl_3$



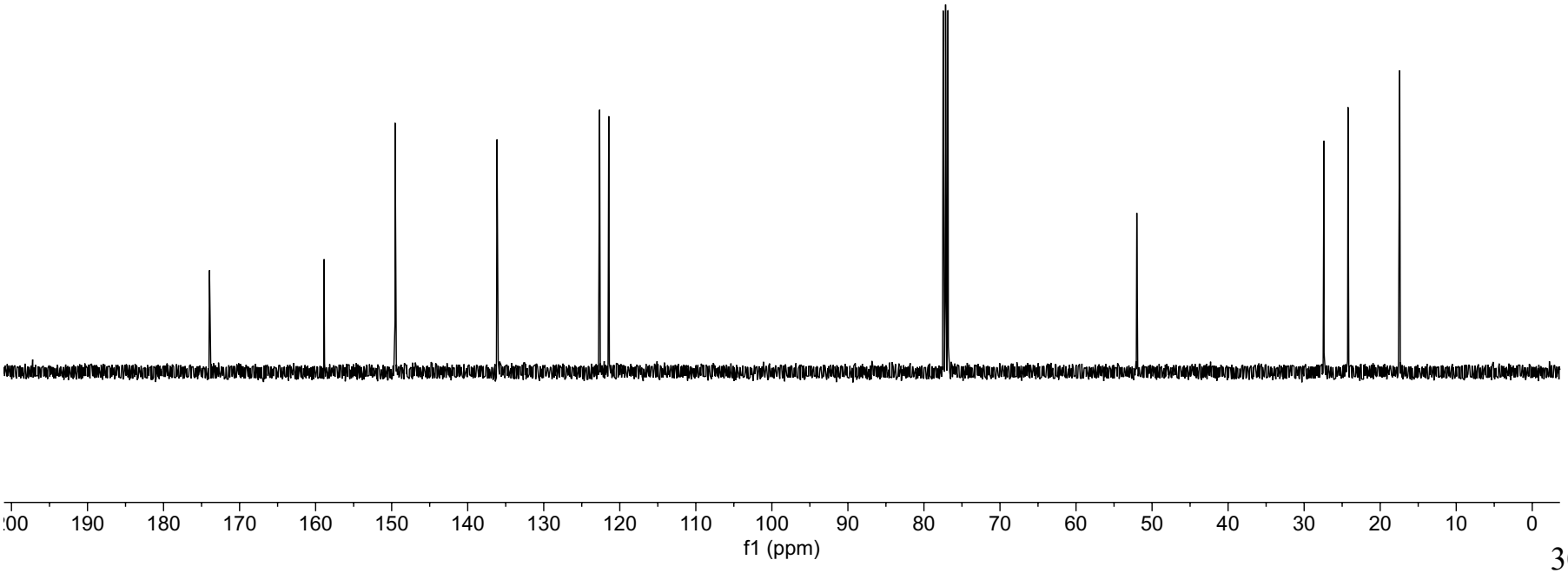
(–)-3v

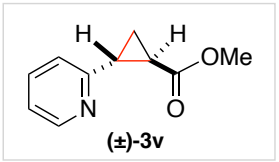
173.96
158.89
149.55
136.15
122.65
121.45
77.47
77.16
76.84
52.01
27.40
24.24
17.43

^{13}C NMR of **3v**, 100 MHz, $CDCl_3$



(–)-3v



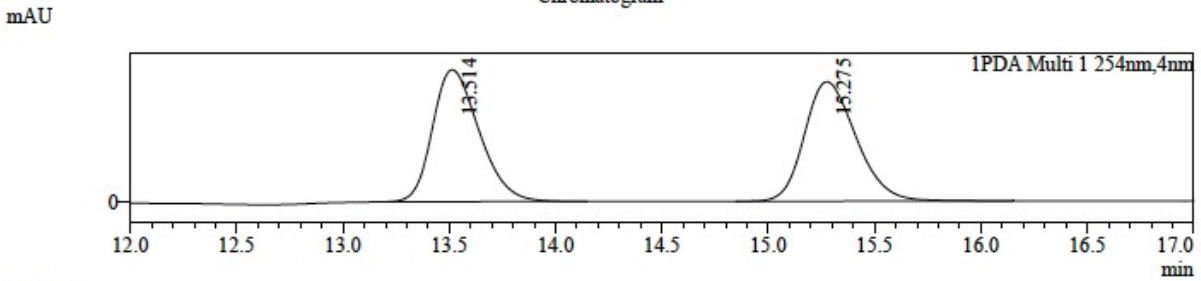


(±)-3v

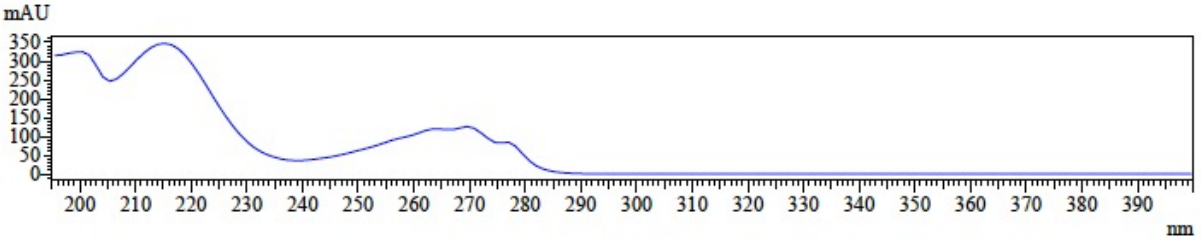
Sample Information

Sample Name	: XXW-0967-IE-5%-0.8mL
Sample ID	: XXW-0967-IE-5%-0.8mL
Data File	: XXW-0967-IE-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

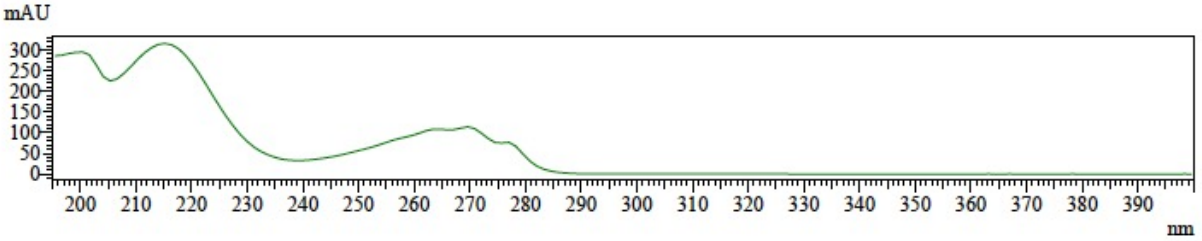
Chromatogram



UV Spectrum
Retention time = 13.514



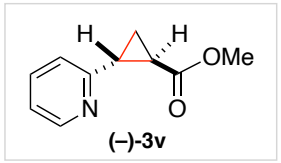
UV Spectrum
Retention time = 15.275



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.514	1214750	49.820
2	15.275	1223534	50.180
Total		2438284	100.000

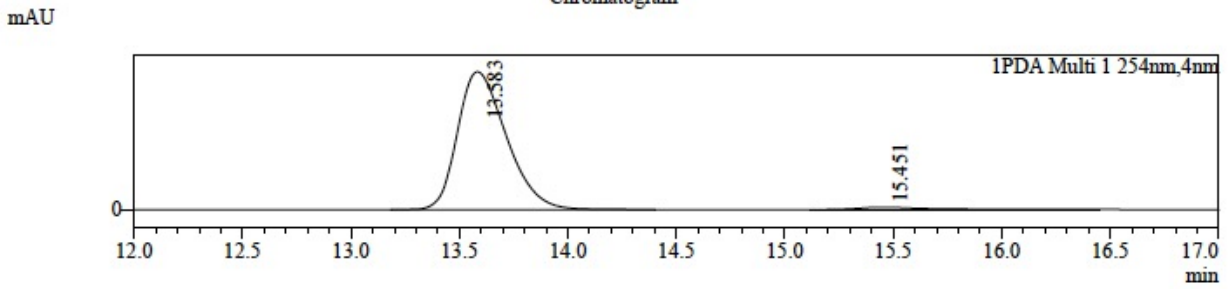


(–)-3v

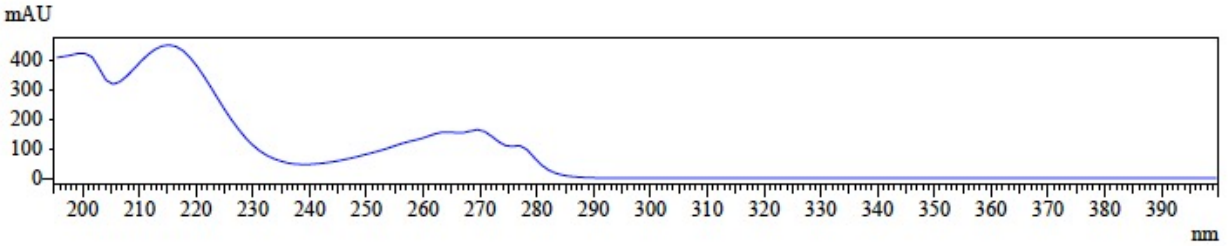
Sample Information

Sample Name	: XXW-1044-IE-5%-0.8mL
Sample ID	: XXW-1044-IE-5%-0.8mL
Data File	: XXW-1044-IE-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

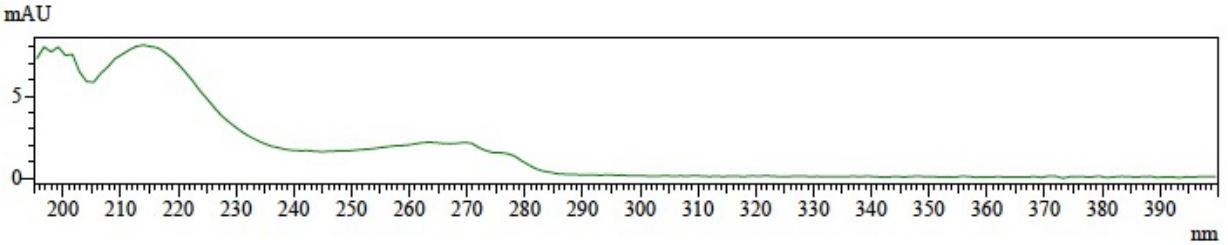
Chromatogram



UV Spectrum
Retention time = 13.583



UV Spectrum
Retention time = 15.451

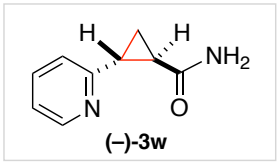


Peak Table

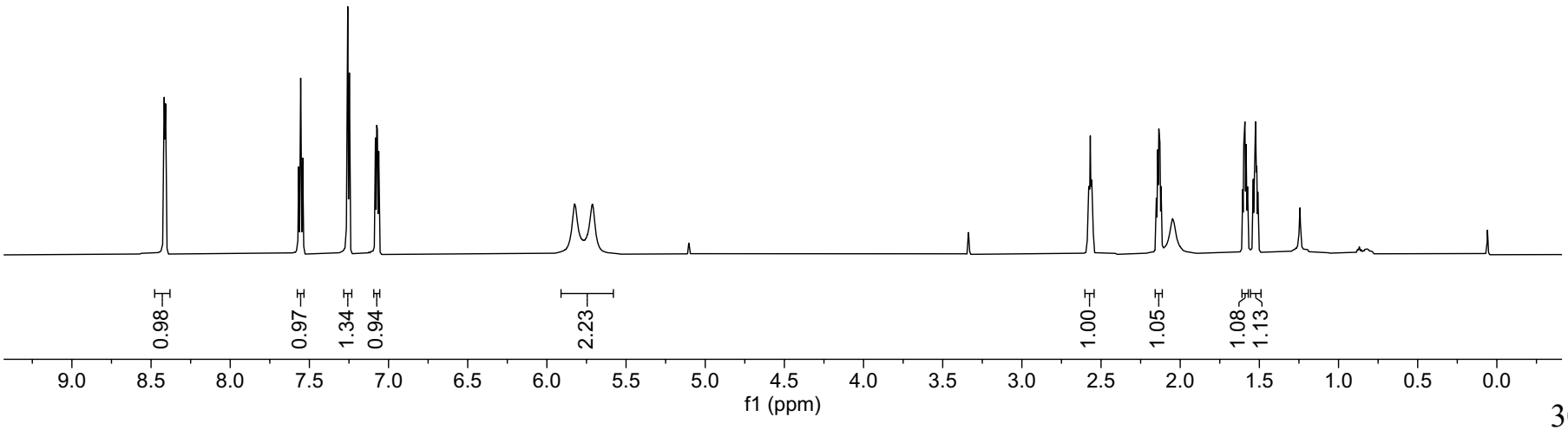
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.583	1633261	97.626
2	15.451	39711	2.374
Total		1672972	100.000

^{1}H NMR of **3w**, 600 MHz, $CDCl_3$

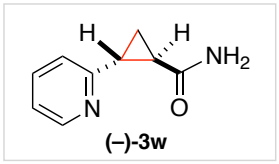


(–)-3w

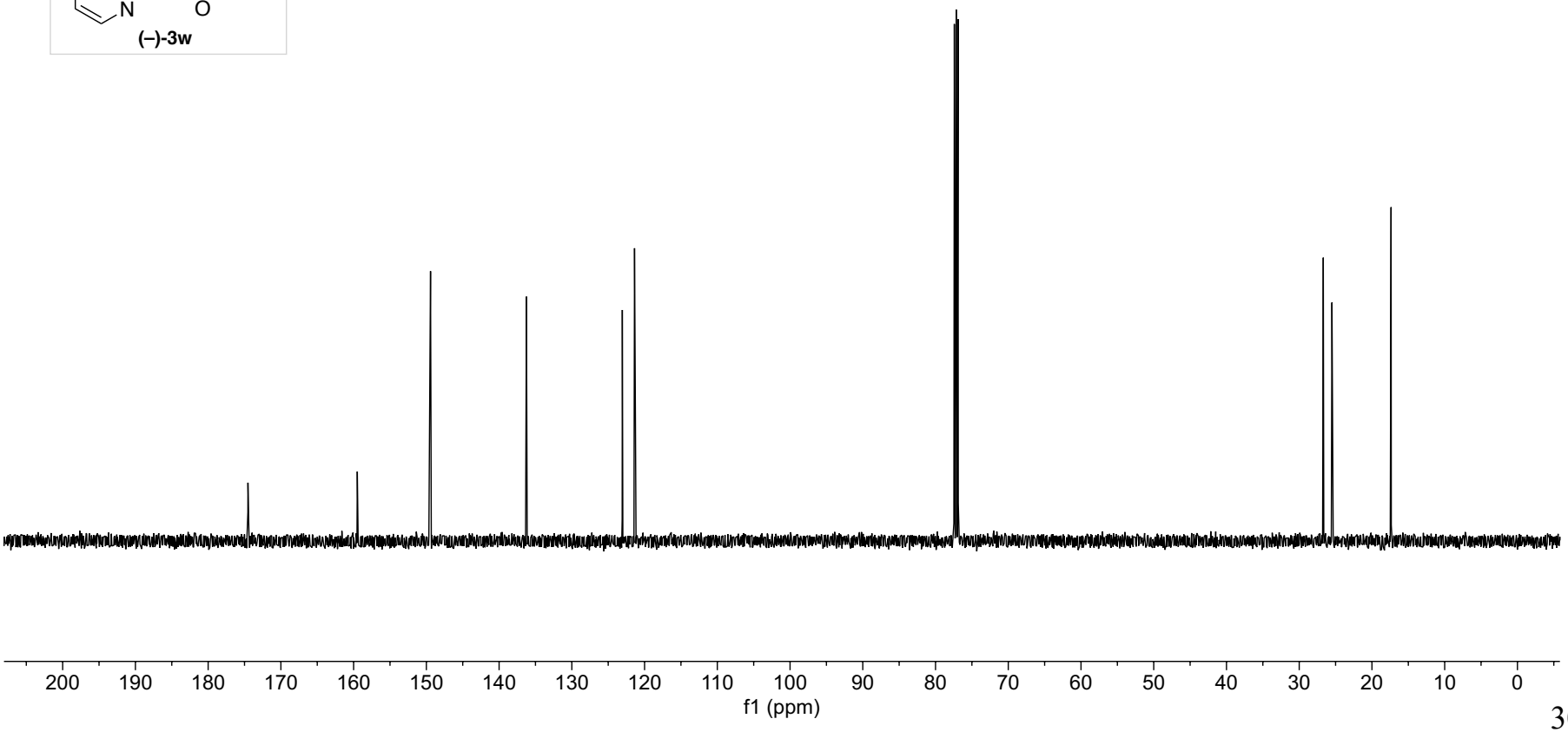


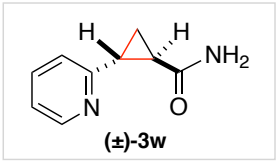
174.53
159.49
149.43
136.24
123.06
121.38
77.42
77.16
76.91
26.69
25.50
17.37

^{13}C NMR of **3w**, 125 MHz, $CDCl_3$



(–)-3w



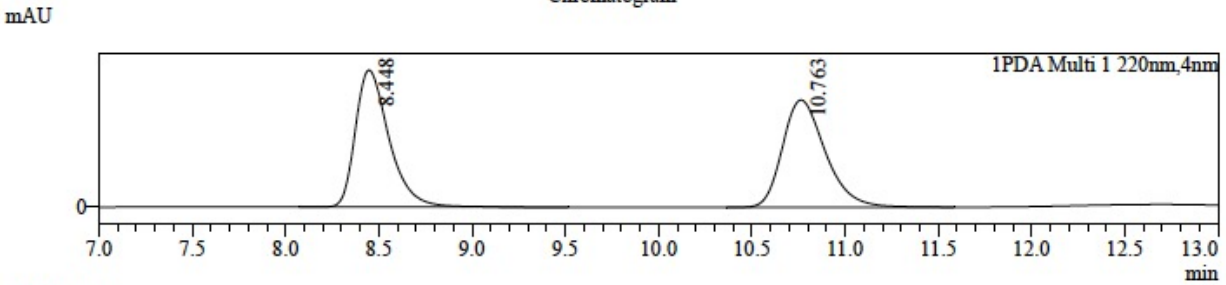


(±)-3w

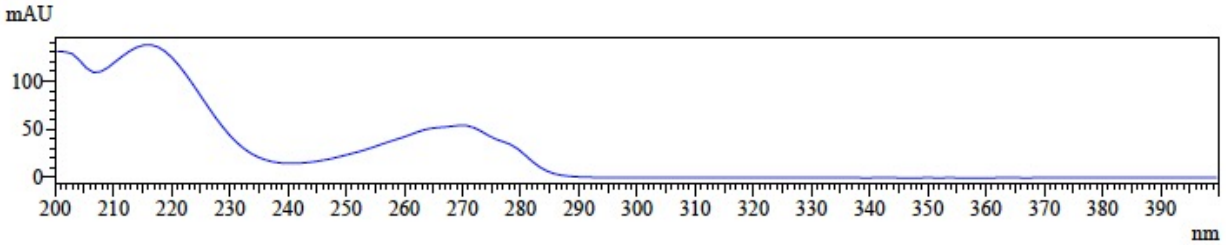
Sample Information

Data File : XXW-1091-ID-30-%--0.8mL.lcd
Sample Name : XXW-1091-ID-30-%--0.8mL
Sample ID : XXW-1091-ID-30-%--0.8mL
Method File : XXW-30%.0.8.mL.lcm

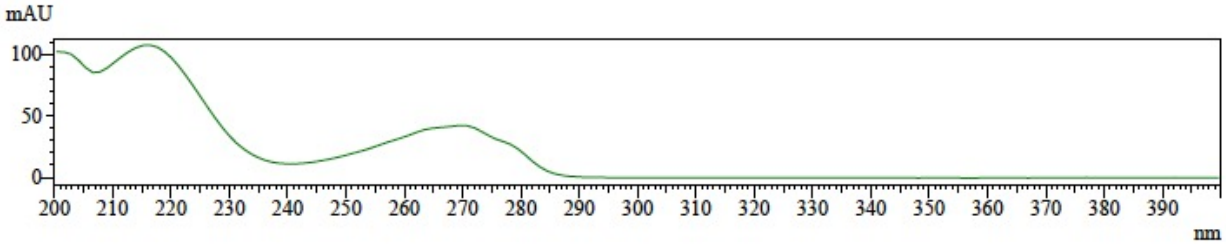
Chromatogram



UV Spectrum
Retention time = 8.448



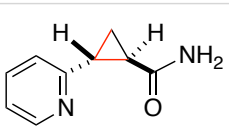
UV Spectrum
Retention time = 10.763



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.448	1520686	50.026
2	10.763	1519119	49.974
Total		3039804	100.000

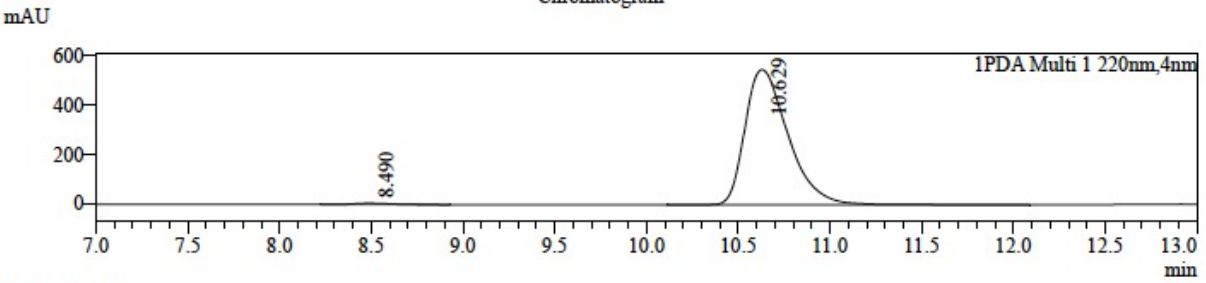


(–)-3w

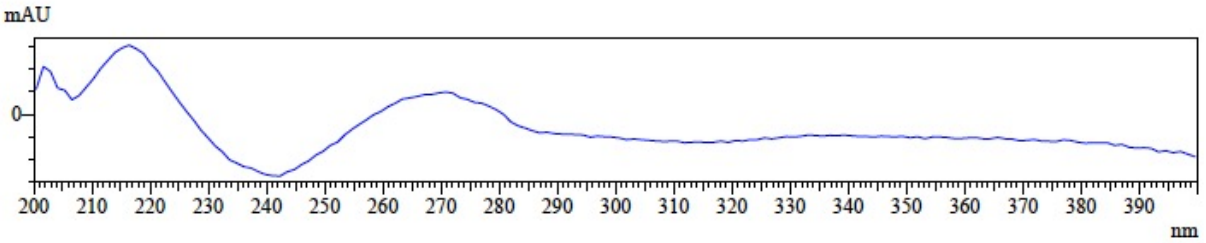
Sample Information

Data File	: XXW-1117-ID-30%-0.8mL.lcd
Sample Name	: XXW-1117-ID-30%-0.8mL
Sample ID	: XXW-1117-ID-30%-0.8mL
Method File	: XXW-30%.0.8.mL.lcm

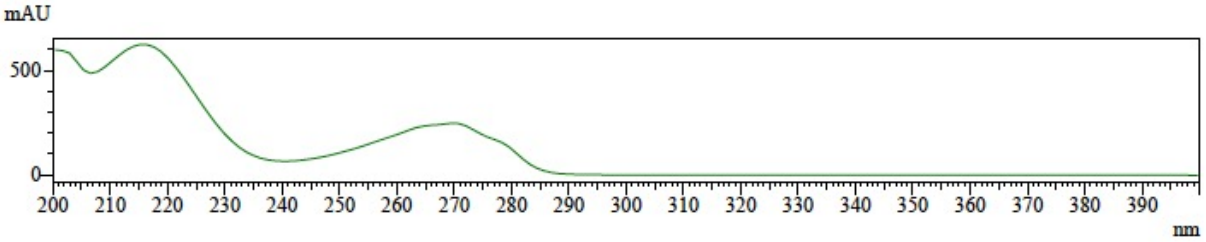
Chromatogram



UV Spectrum
Retention time = 8.490



UV Spectrum
Retention time = 10.629

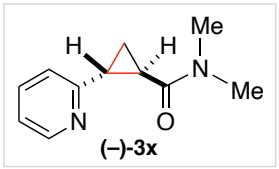


Peak Table

PDA Ch1 220nm

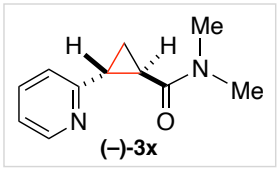
Peak#	Ret. Time	Area	Area%
1	8.490	71499	0.792
2	10.629	8957428	99.208
Total		9028927	100.000

^{1}H NMR of **3x**, 600 MHz, $CDCl_3$



172.12
160.09
149.48
136.10
122.99
121.17
77.37
77.16
76.95
37.49
35.97
26.58
23.06
17.59

^{13}C NMR of **3x**, 150 MHz, $CDCl_3$

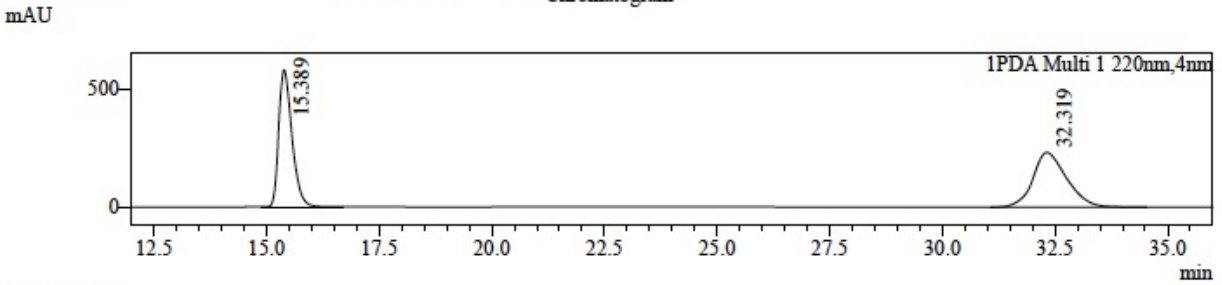


(–)-3x

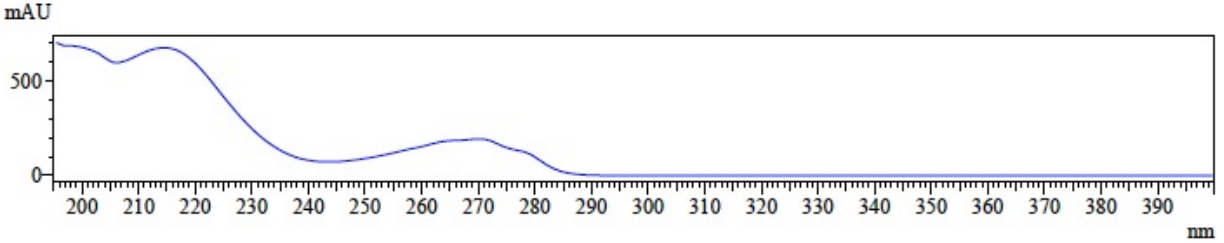
Sample Information

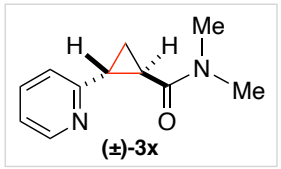
Sample Name	: XXW-0968-ID-20%-0.8mL
Sample ID	: XXW-0968-ID-20%-0.8mL
Data File	: XXW-0968-ID-20%-0.8mL002.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram

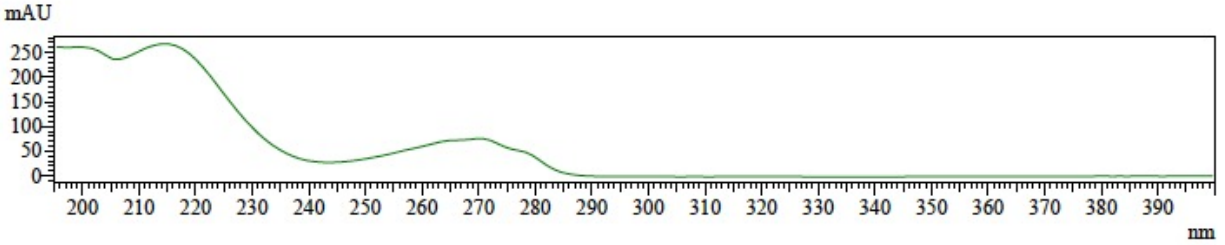


UV Spectrum
Retention time = 15.389





UV Spectrum
Retention time = 32.319



Peak Table

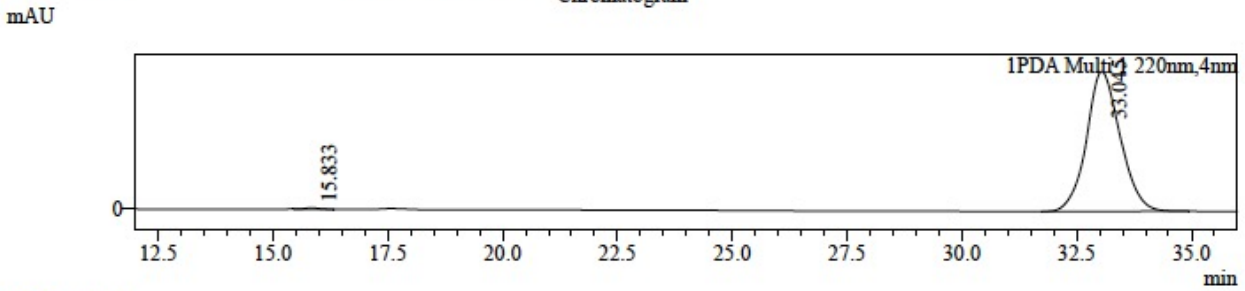
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.389	11890586	49.790
2	32.319	11991076	50.210
Total		23881662	100.000

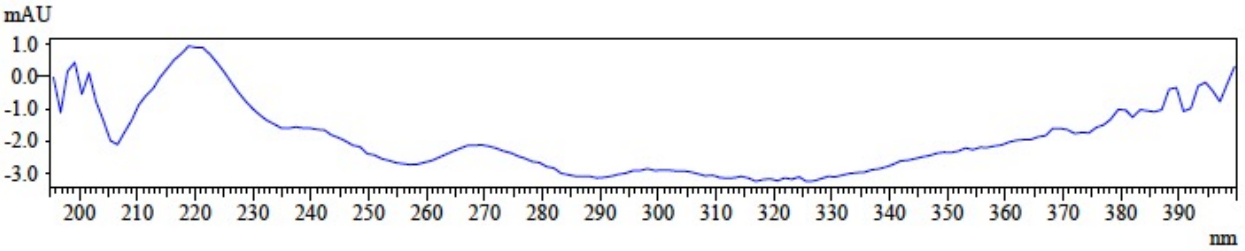
Sample Information

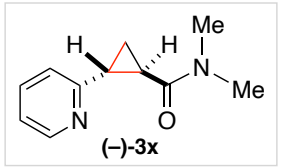
Sample Name	: XXW-1045-ID-20%-0.8mL
Sample ID	: XXW-1045-ID-20%-0.8mL
Data File	: XXW-1045-ID-20%-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram

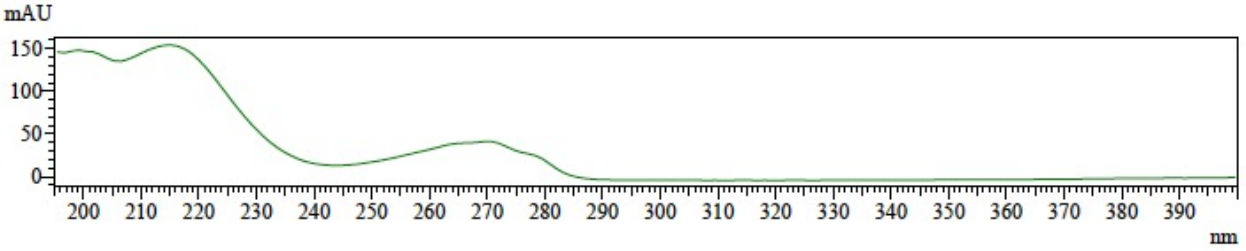


UV Spectrum
Retention time = 15.833





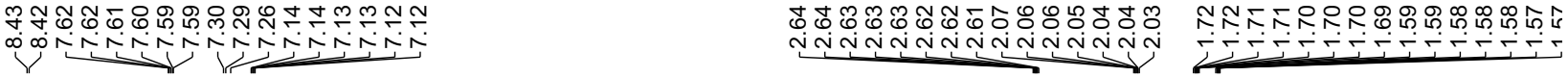
UV Spectrum
Retention time = 33.045



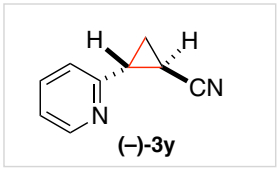
Peak Table

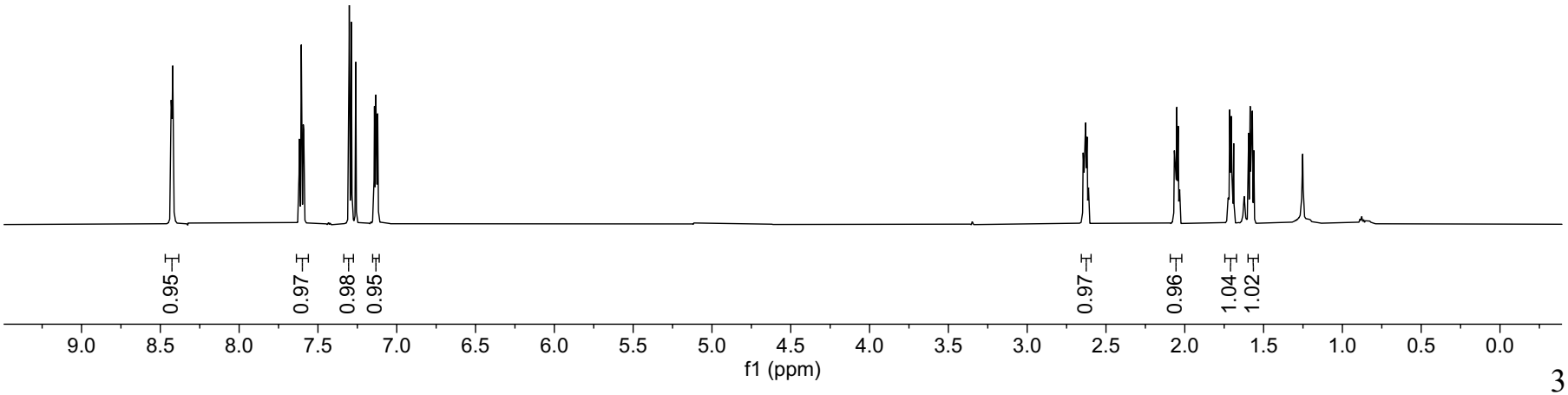
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.833	25940	0.373
2	33.045	6928239	99.627
Total		6954178	100.000



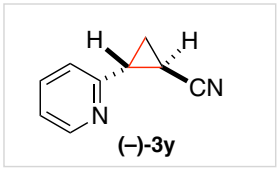
^{1}H NMR of **3y**, 600 MHz, $CDCl_3$



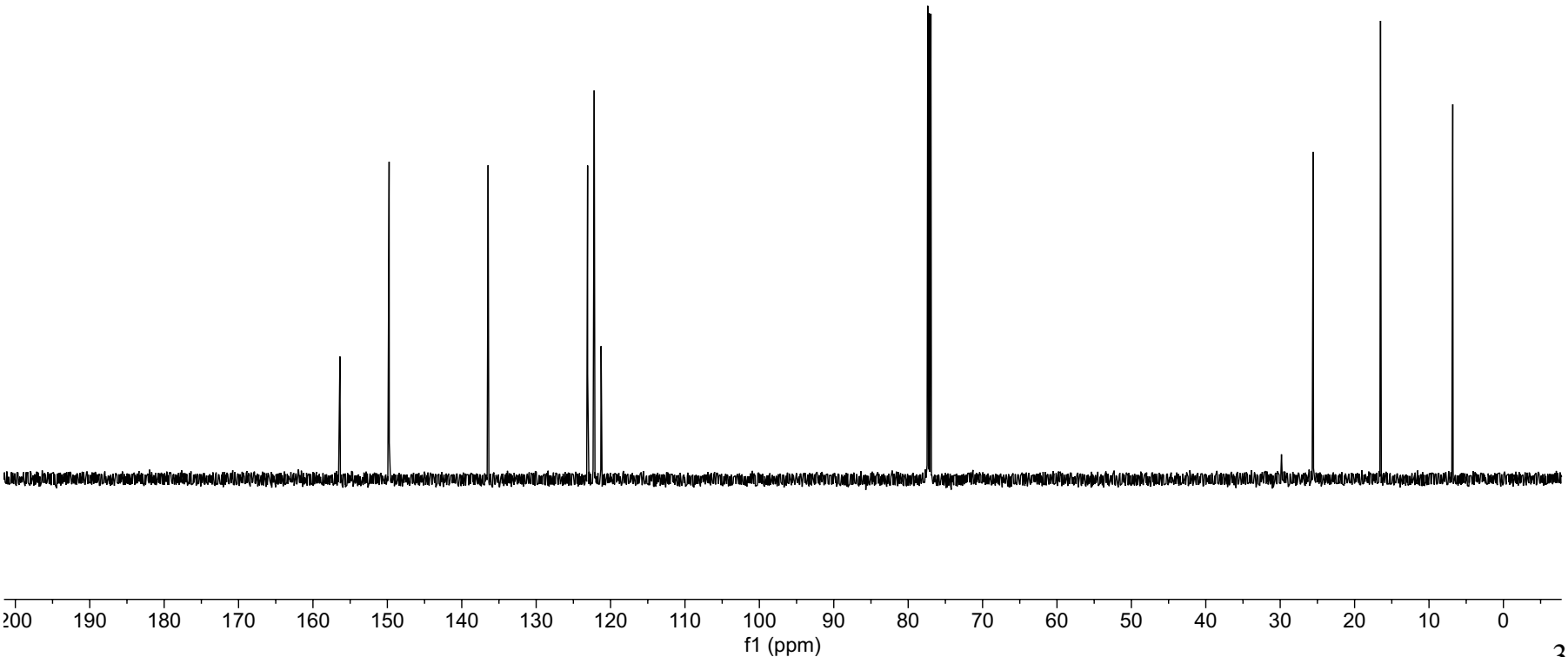


156.37
149.76
136.46
123.09
122.19
121.27
77.37
77.16
76.95
25.56
16.52
6.81

^{13}C NMR of **3y**, 150 MHz, $CDCl_3$



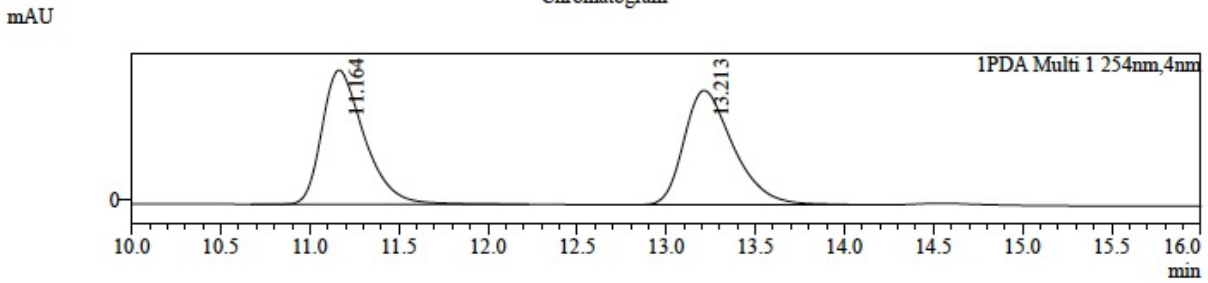
(–)-3y

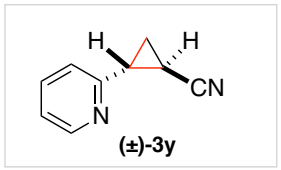


Sample Information

Sample Name : XXW-0962-ODH-5%-0.8mL
Sample ID : XXW-0962-ODH-5%-0.8mL
Data File : XXW-0962-ODH-5%-0.8mL.lcd
Method File : XXW-5%.0.8.mL.lcm

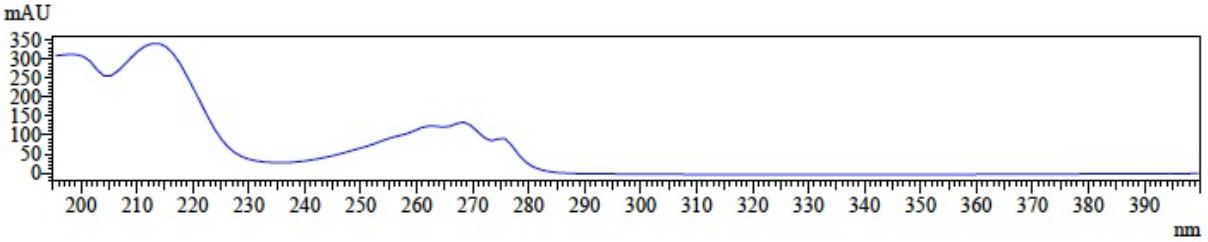
Chromatogram



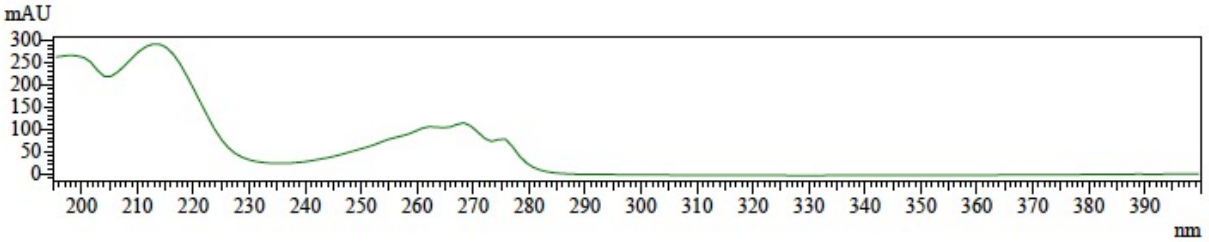


(±)-3y

UV Spectrum
Retention time = 11.164



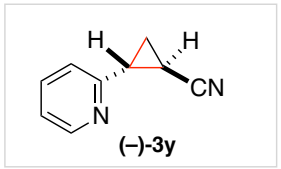
UV Spectrum
Retention time = 13.213



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.164	1460645	50.049
2	13.213	1457808	49.951
Total		2918453	100.000

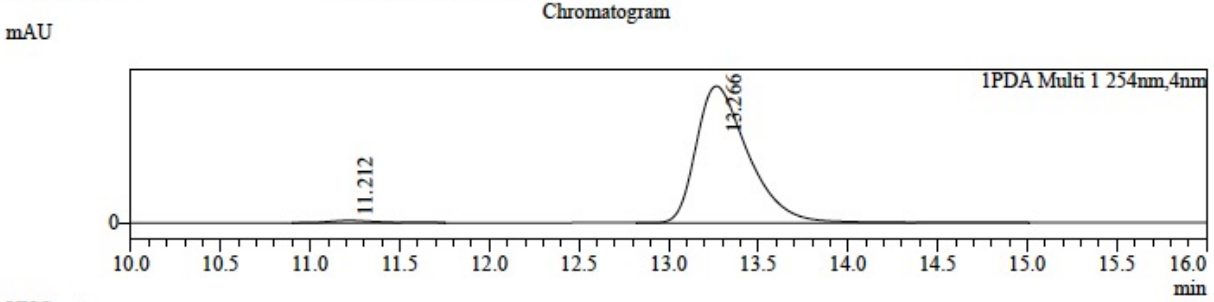


(–)-3y

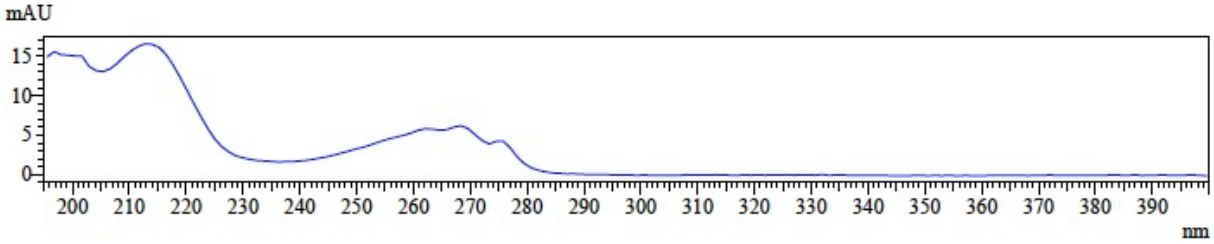
Sample Information

Sample Name	: XXW-1057-ODH-5%-0.8mL
Sample ID	: XXW-1057-ODH-5%-0.8mL
Data File	: XXW-1057-ODH-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

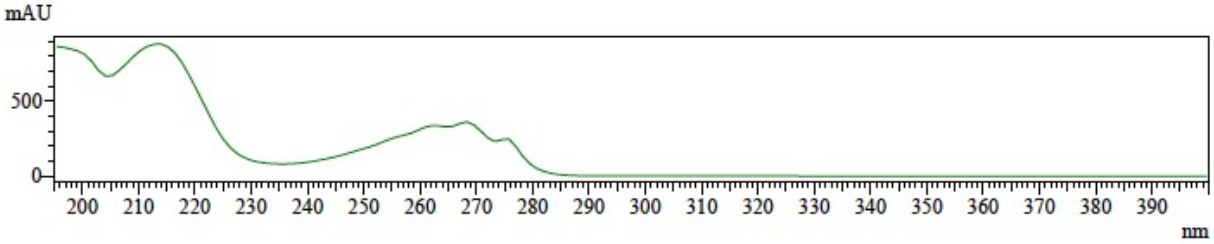
Chromatogram



UV Spectrum
Retention time = 11.212



UV Spectrum
Retention time = 13.266

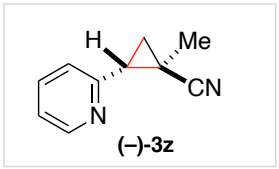


Peak Table

PDA Ch1 254nm

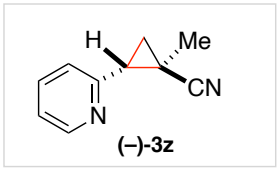
Peak#	Ret. Time	Area	Area%
1	11.212	68385	1.416
2	13.266	4762678	98.584
Total		4831063	100.000

^{1}H NMR of **3z**, 500 MHz, $CDCl_3$

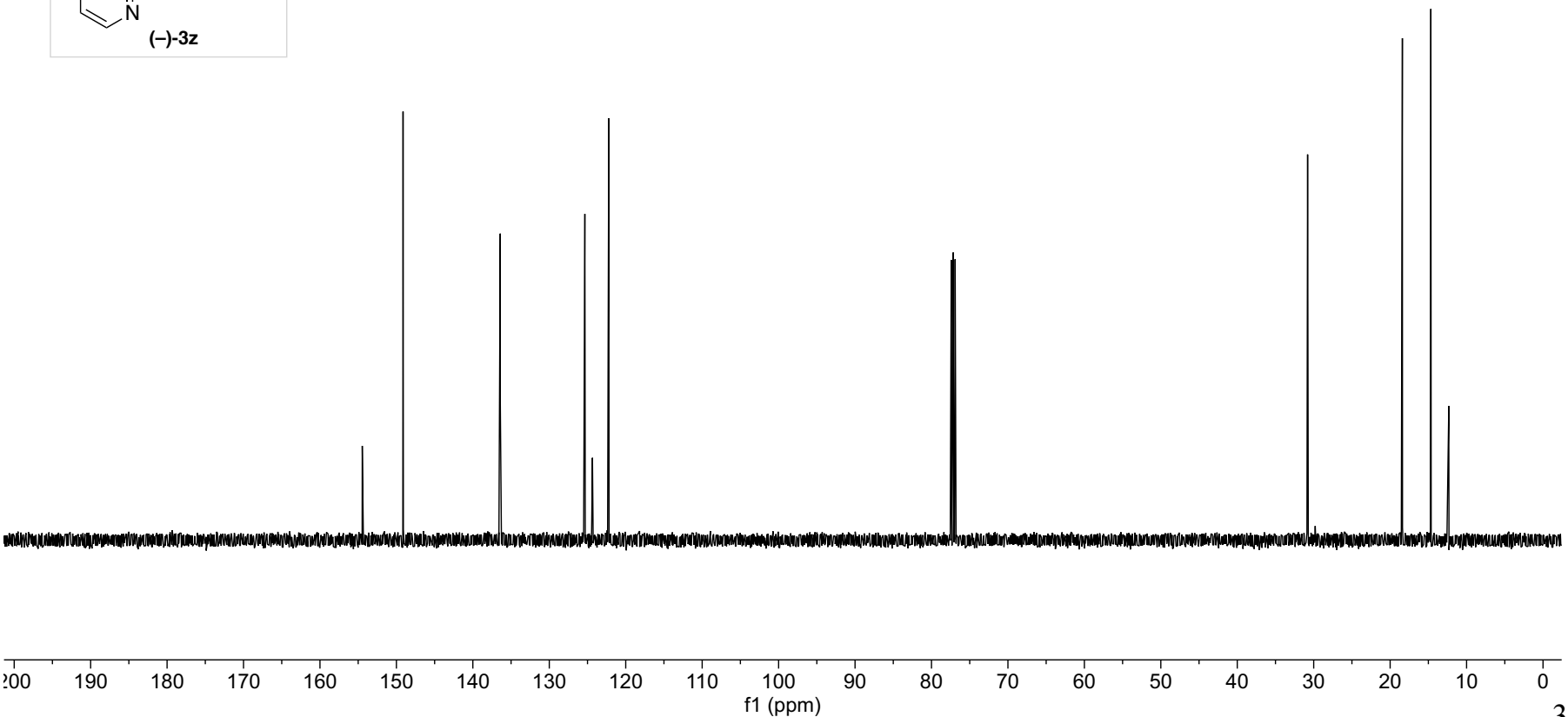


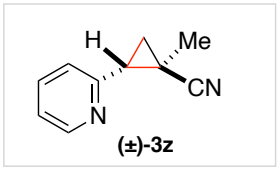
154.47
149.13
136.41
125.35
124.35
122.22
77.41
77.16
76.91
30.80
18.40
14.67
12.33

^{13}C NMR of **3z**, 125 MHz, $CDCl_3$



(–)-3z



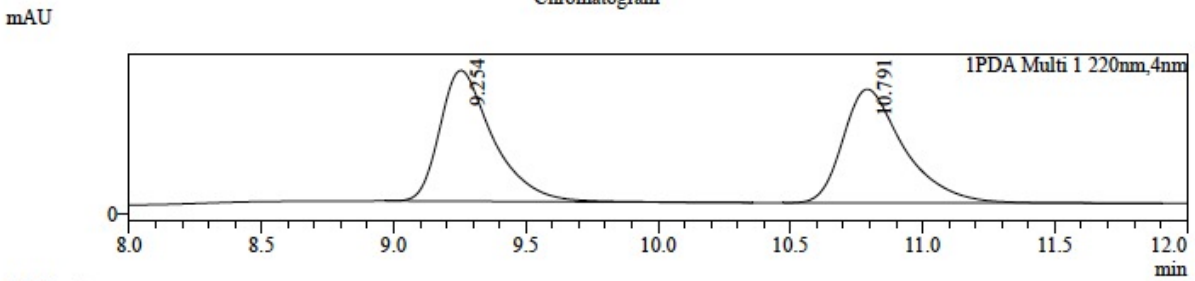


(±)-3z

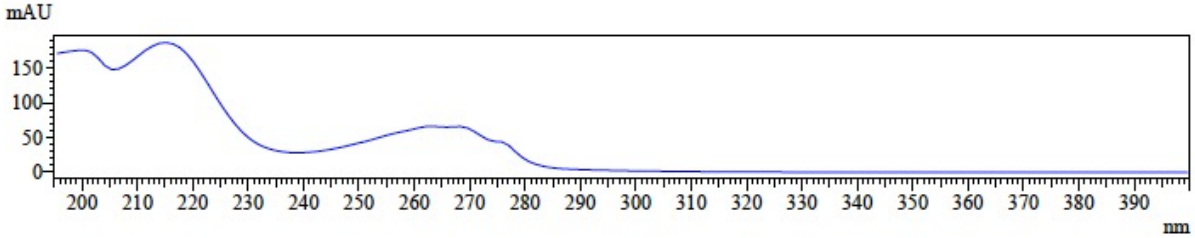
Sample Information

Sample Name	: XXW-1271--ODH-5%--0.8mL
Sample ID	: XXW-1271--ODH-5%--0.8mL
Data File	: XXW-1271--ODH-5%--0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

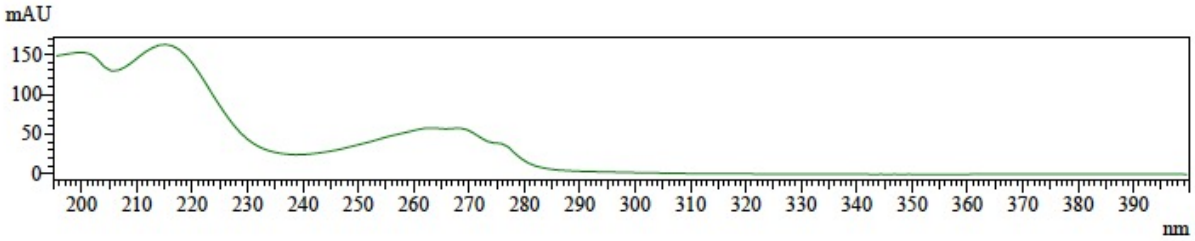
Chromatogram



UV Spectrum
Retention time = 9.254



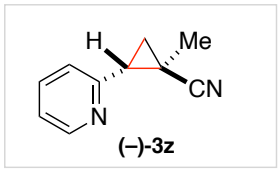
UV Spectrum
Retention time = 10.791



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	9.254	1969724	50.081
2	10.791	1963318	49.919
Total		3933042	100.000

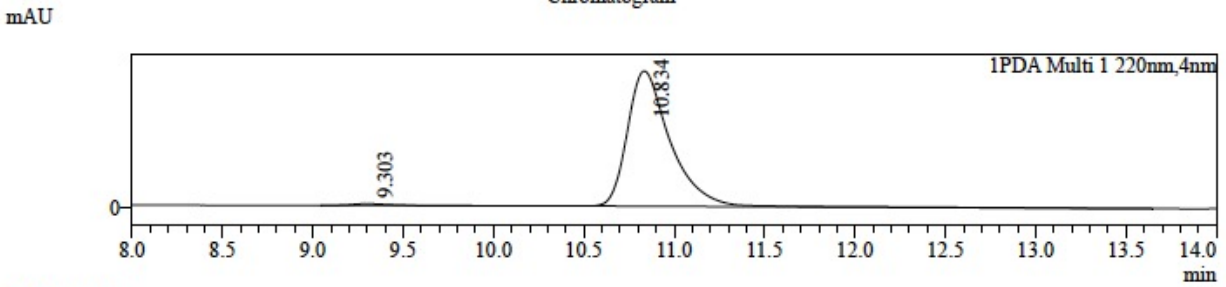


(–)-3z

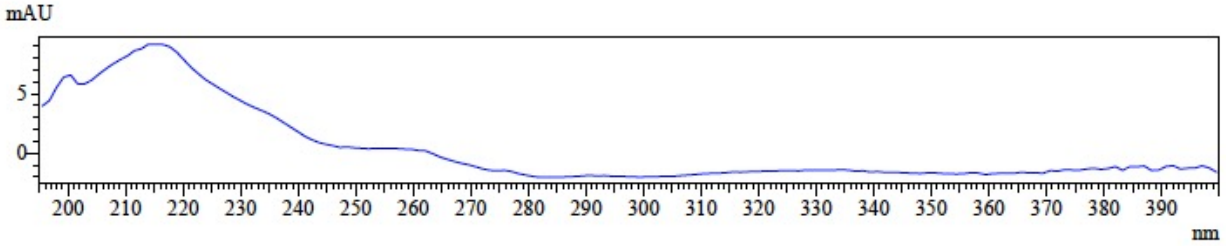
Sample Information

Sample Name	: XXW-1274--ODH-5%--0.8mL
Sample ID	: XXW-1274--ODH-5%--0.8mL
Data File	: XXW-1274--ODH-5%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

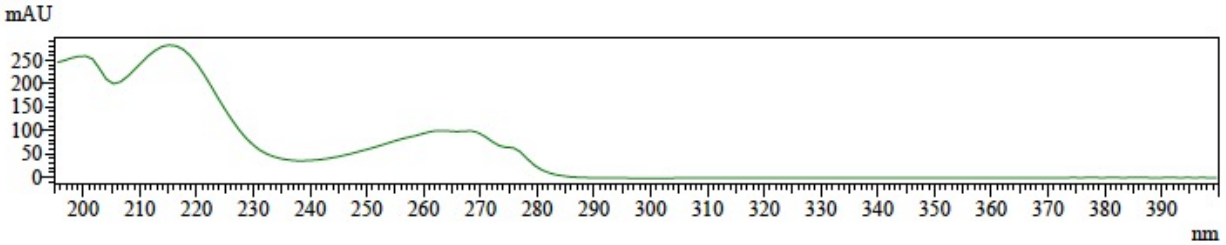
Chromatogram



UV Spectrum
Retention time = 9.303



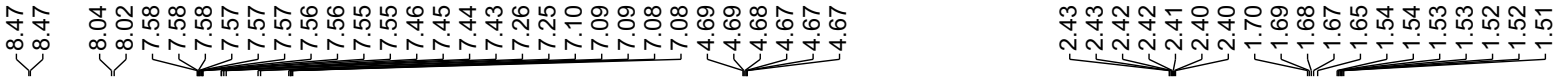
UV Spectrum
Retention time = 10.834



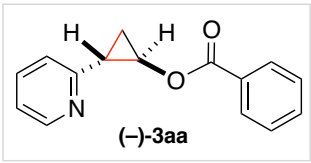
Peak Table

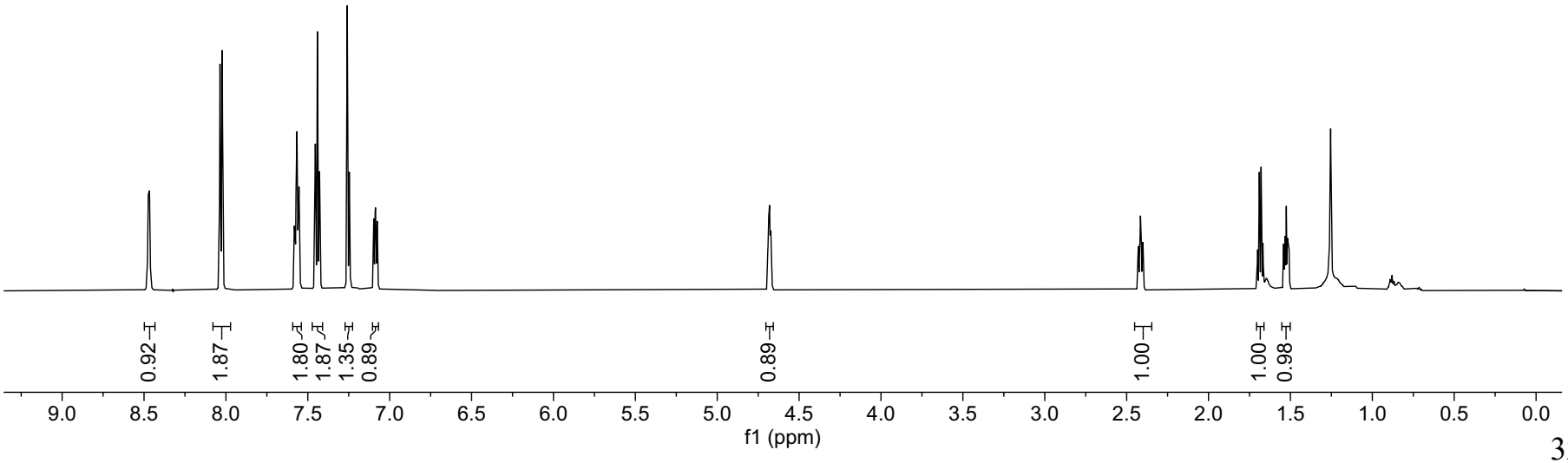
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	9.303	43373	1.112
2	10.834	3855380	98.888
Total		3898752	100.000



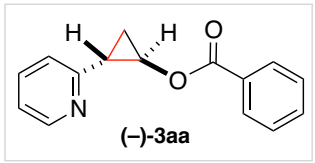
^{1}H NMR of **3aa**, 600 MHz, $CDCl_3$



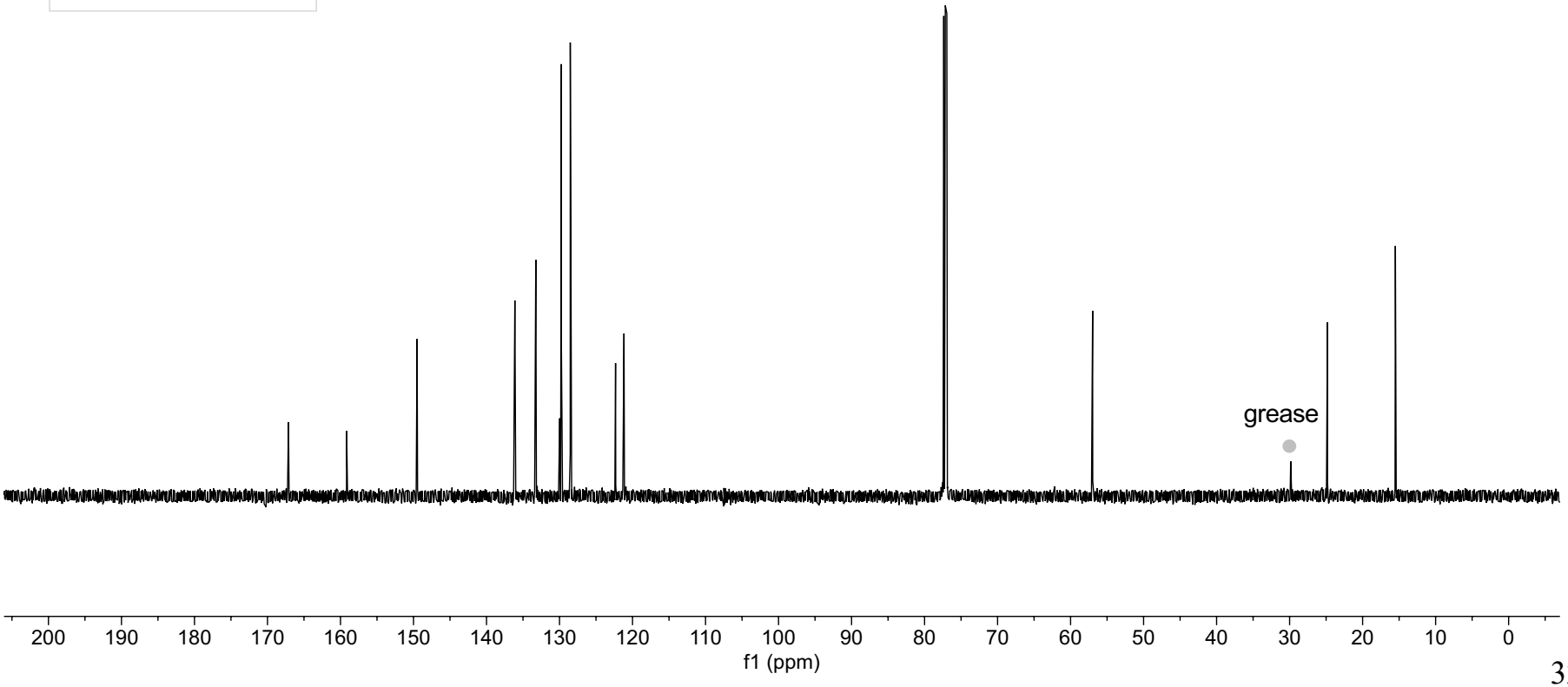


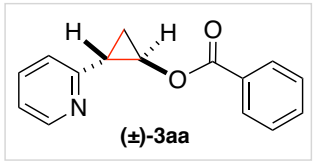
167.12
159.16
149.51
136.12
133.25
129.97
129.74
128.52
122.32
121.17
77.37
77.16
76.95
56.98
24.81
15.51

^{13}C NMR of **3aa**, 150 MHz, $CDCl_3$



(–)-3aa



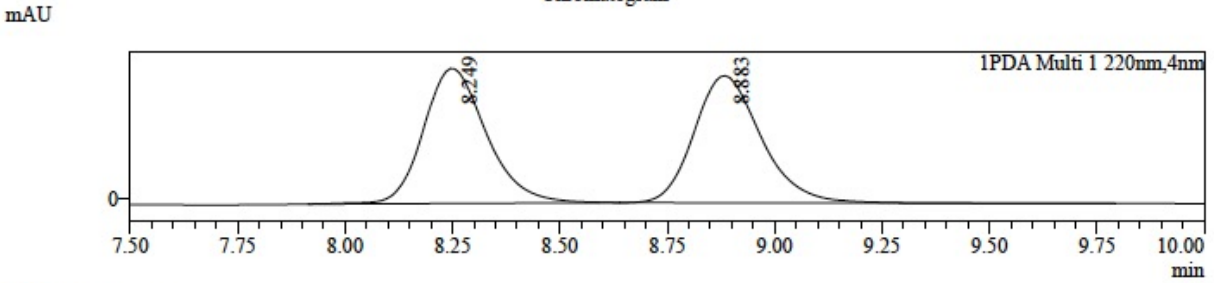


(±)-3aa

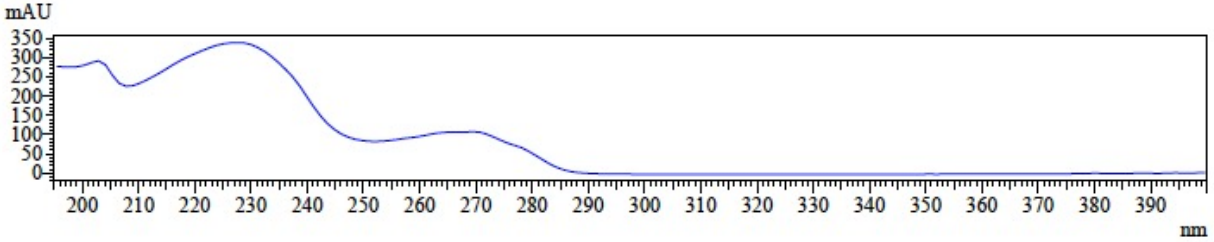
Sample Information

Sample Name	: XXW-1064--IF-20%-0.8mL
Sample ID	: XXW-1064--IF-20%-0.8mL
Data File	: XXW-1064--IF-20%-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

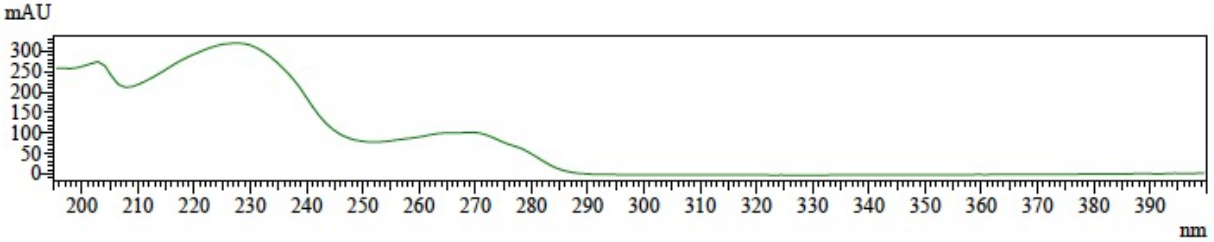
Chromatogram



UV Spectrum
Retention time = 8.249



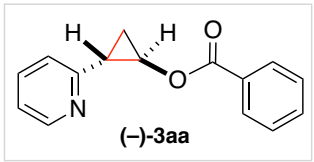
UV Spectrum
Retention time = 8.883



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.249	3263979	49.905
2	8.883	3276359	50.095
Total		6540338	100.000

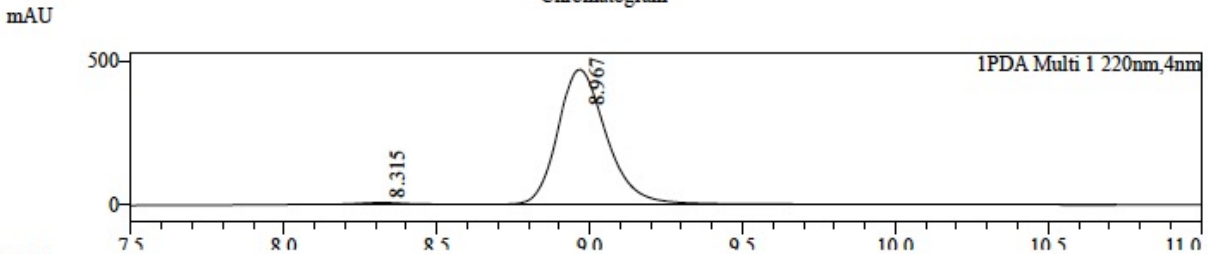


(–)-3aa

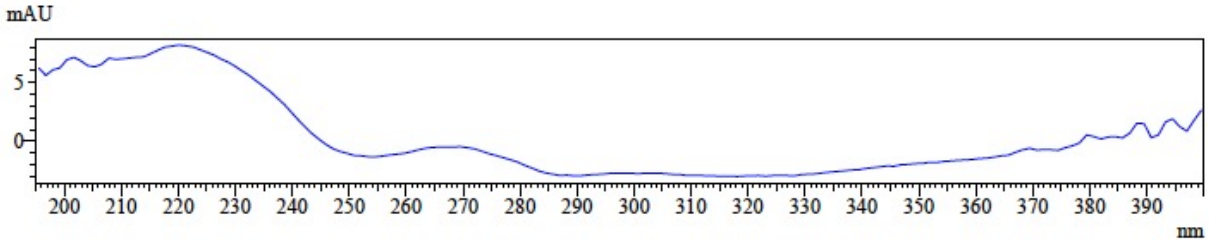
Sample Information

Sample Name	: XXW-I060-IF-20%-0.8mL
Sample ID	: XXW-I060-IF-20%-0.8mL
Data File	: XXW-I060-IF-20%-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

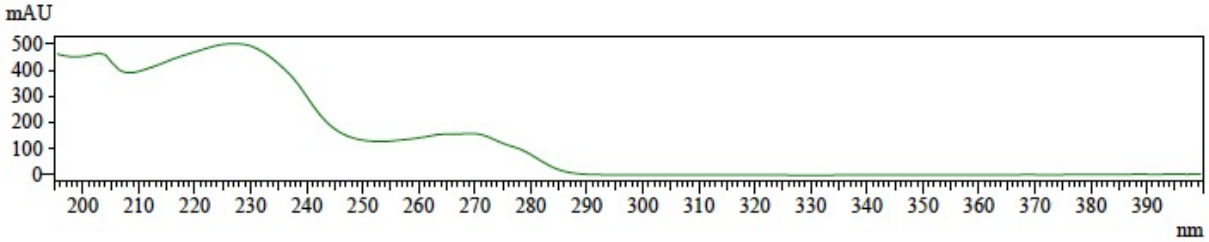
Chromatogram



UV Spectrum
Retention time = 8.315



UV Spectrum
Retention time = 8.967

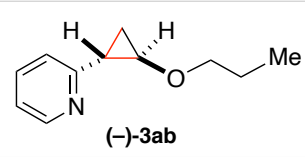


Peak Table

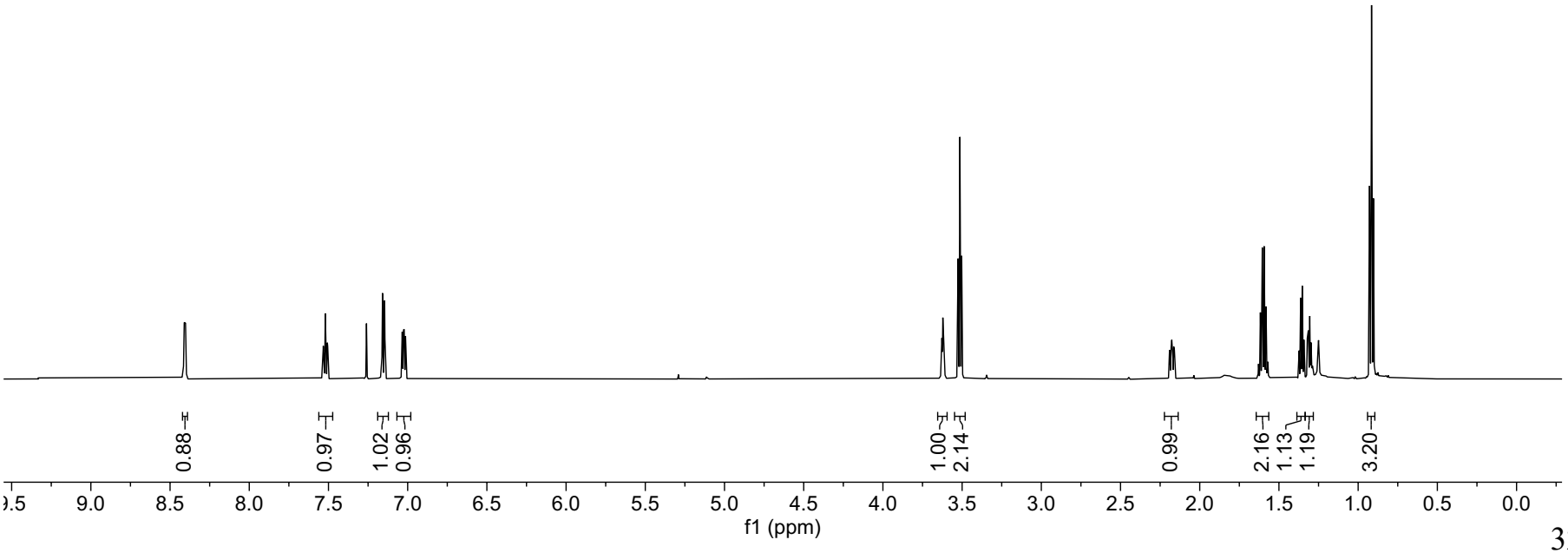
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.315	52965	1.003
2	8.967	5227203	98.997
Total		5280168	100.000

^{1}H NMR of **3ab**, 600 MHz, $CDCl_3$

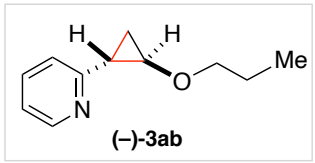


(–)-3ab

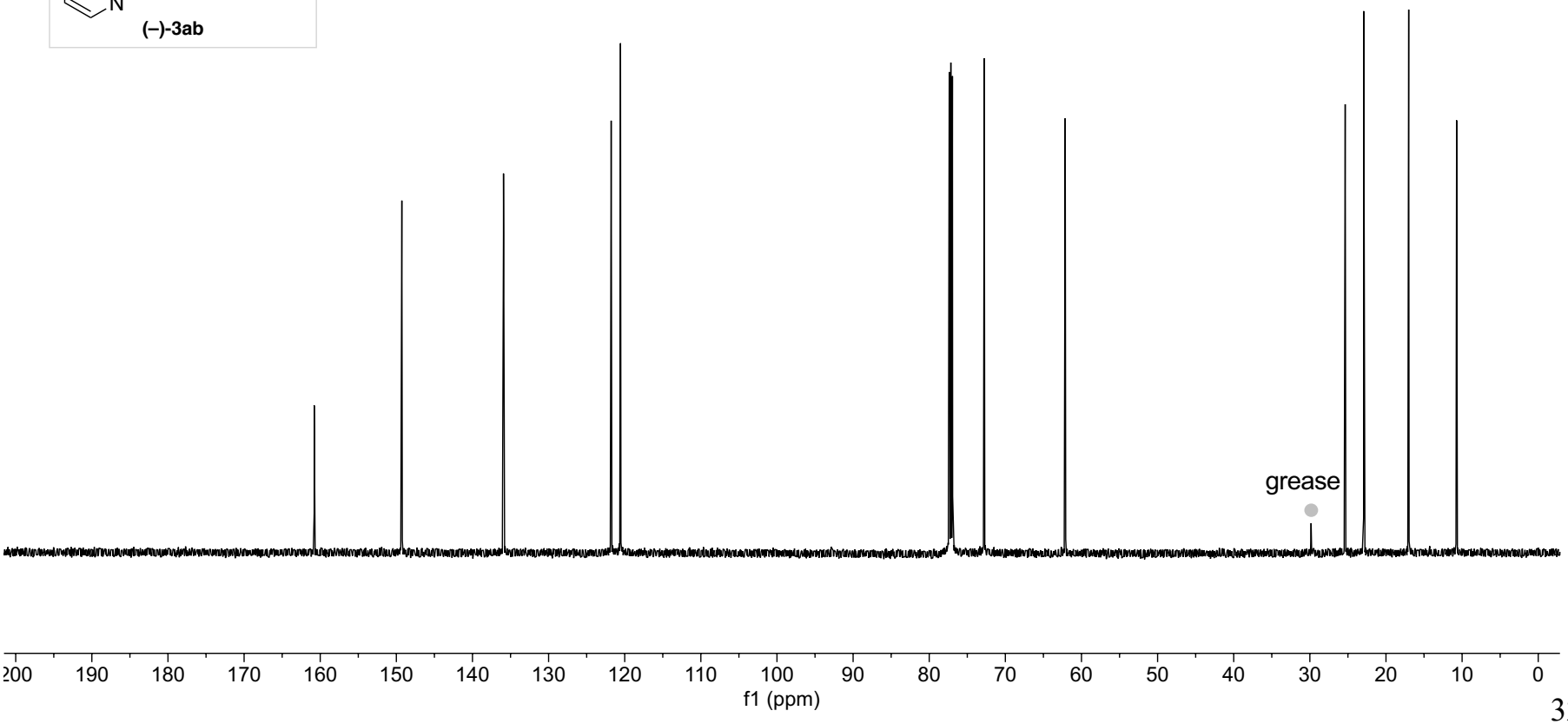


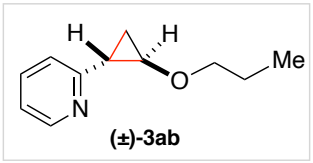
160.79
149.28
135.92
121.78
120.55
77.37
77.16
76.95
72.77
62.13
25.36
22.93
17.02
10.72

^{13}C NMR of **3ab**, 150 MHz, $CDCl_3$



(–)-3ab



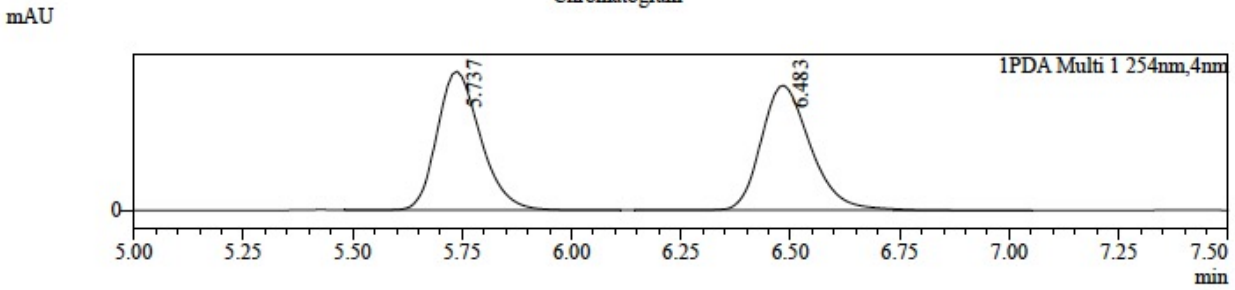


(±)-3ab

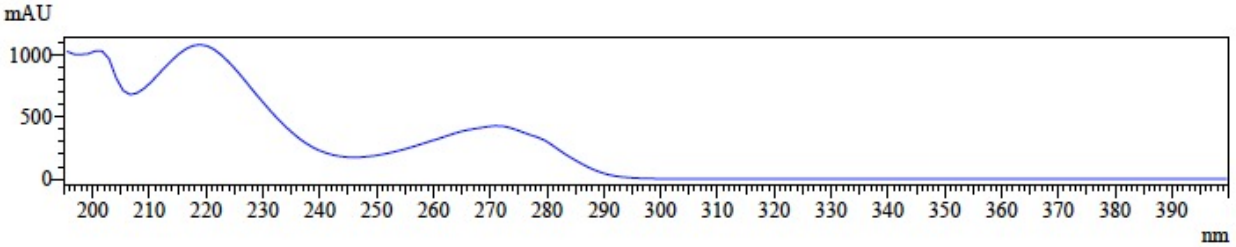
Sample Information

Sample Name	: XXW-905-ID-10%-0.8mL
Sample ID	: XXW-905-ID-10%-0.8mL
Data File	: XXW-905-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

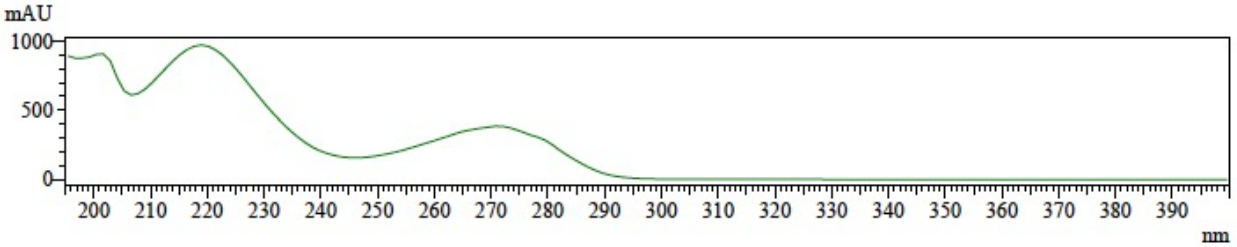
Chromatogram



UV Spectrum
Retention time = 5.737



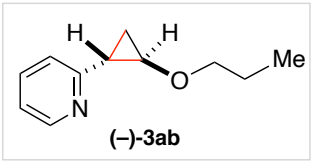
UV Spectrum
Retention time = 6.483



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.737	1608473	49.338
2	6.483	1651624	50.662
Total		3260097	100.000

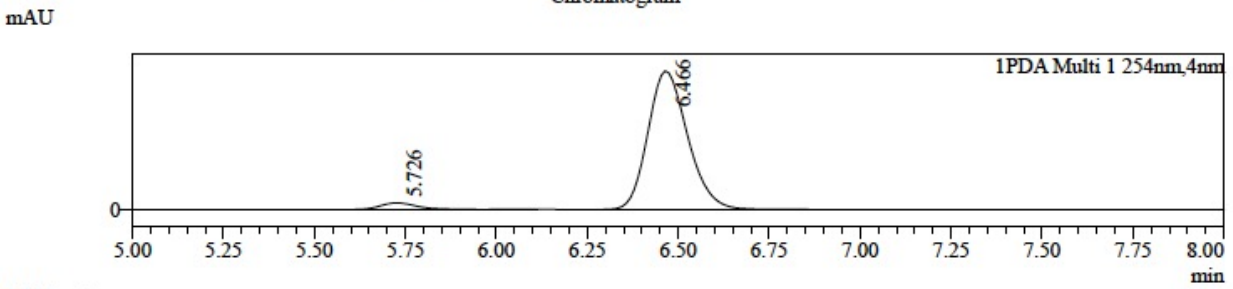


(–)-3ab

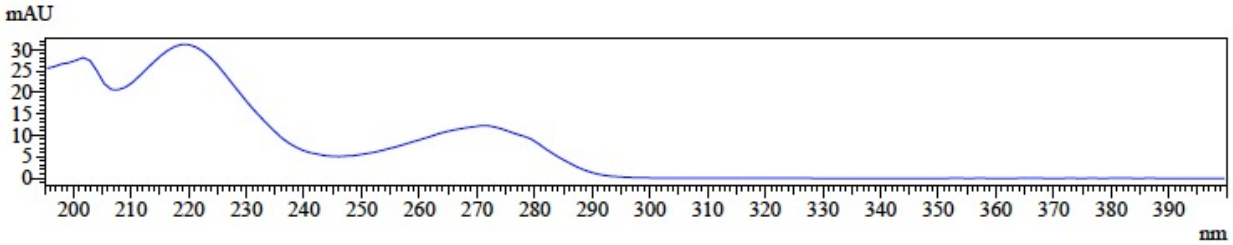
Sample Information

Sample Name	: XXW-1079-ID-10%-0.8mL
Sample ID	: XXW-1079-ID-10%-0.8mL
Data File	: XXW-1079-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

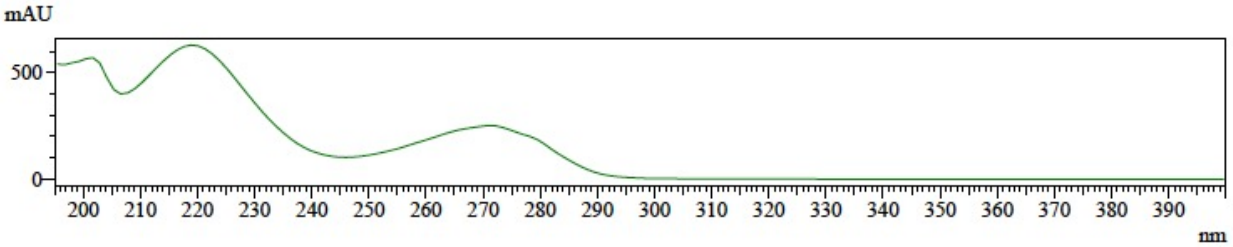
Chromatogram



UV Spectrum
Retention time = 5.726



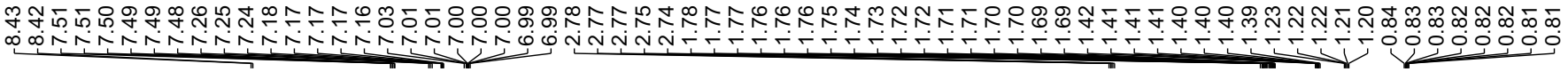
UV Spectrum
Retention time = 6.466



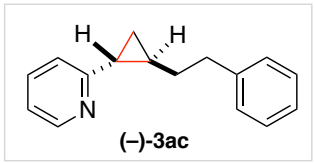
Peak Table

PDA Ch1 254nm

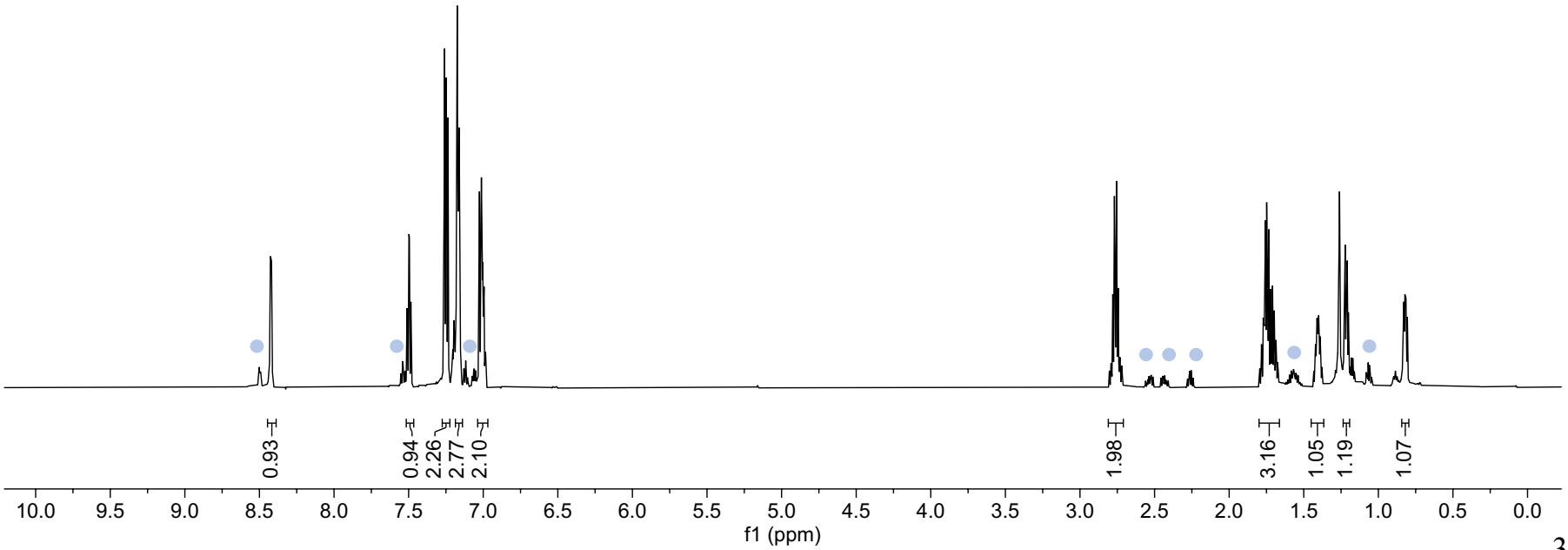
Peak#	Ret. Time	Area	Area%
1	5.726	47907	4.368
2	6.466	1048805	95.632
Total		1096711	100.000

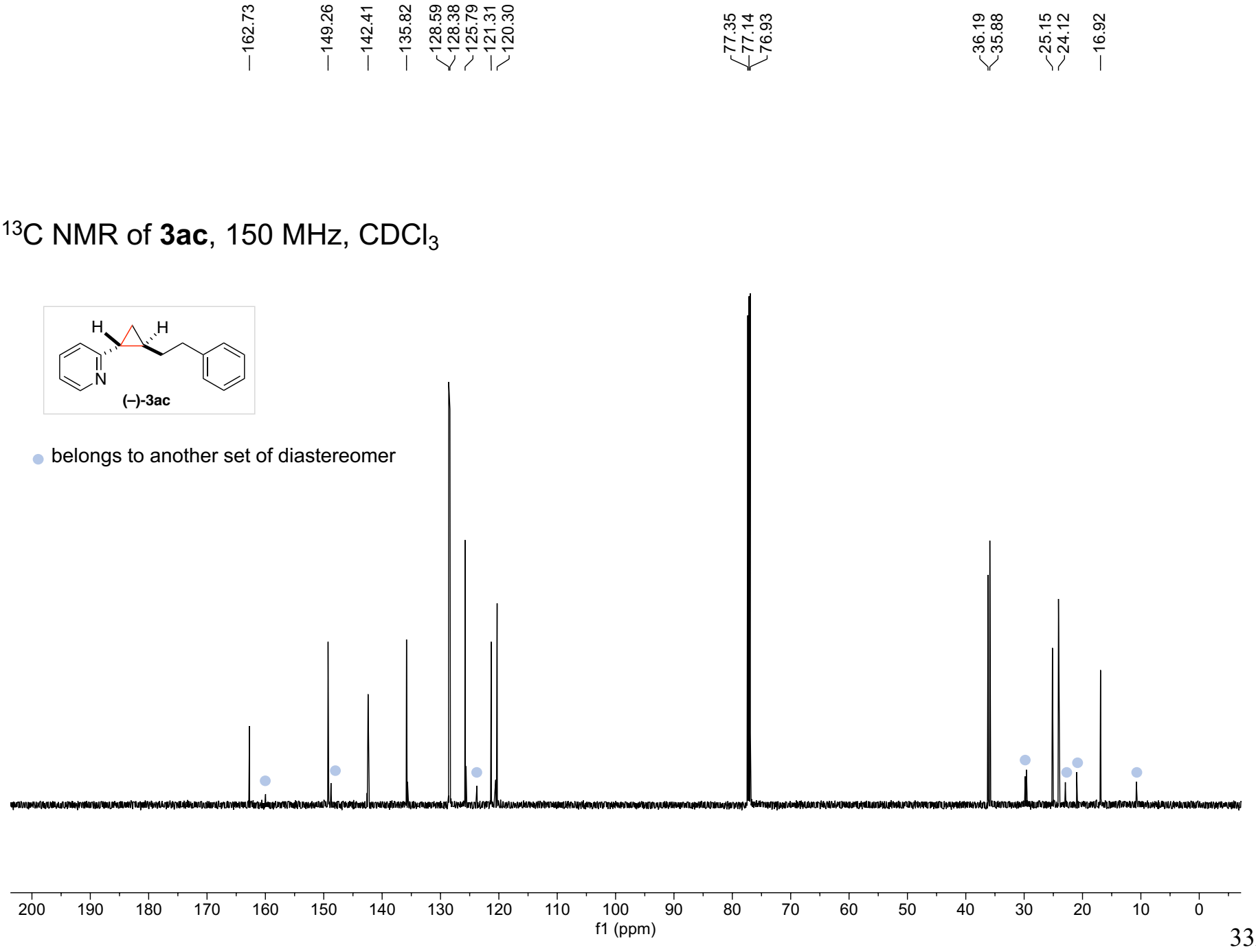


^{1}H NMR of **3ac**, 600 MHz, $CDCl_3$



● belongs to another set of diastereomer



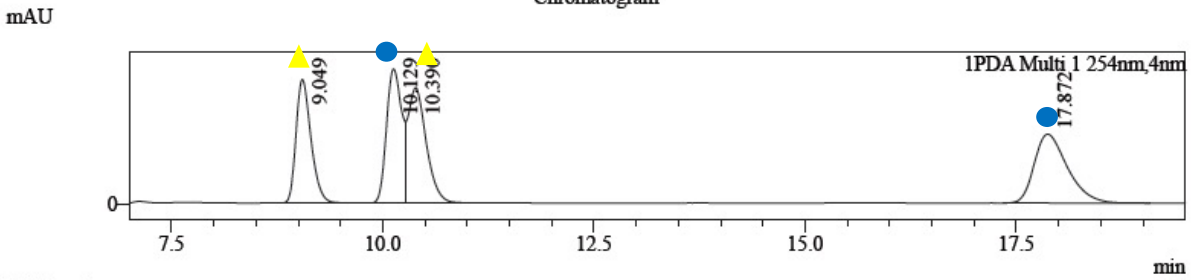


^{13}C NMR of **3ac**, 150 MHz, $CDCl_3$

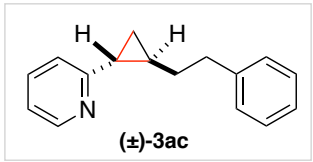
Sample Information

Sample Name	: XXW-0897-ODH-2%-0.8mL
Sample ID	: XXW-0897-ODH-2%-0.8mL
Data File	: XXW-0897-ODH-2%-0.8mL001.lcd
Method File	: XXW-2%.0.8.mL.lcm

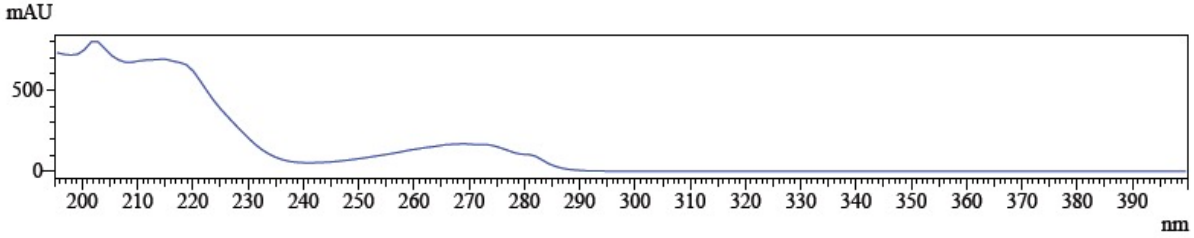
Chromatogram



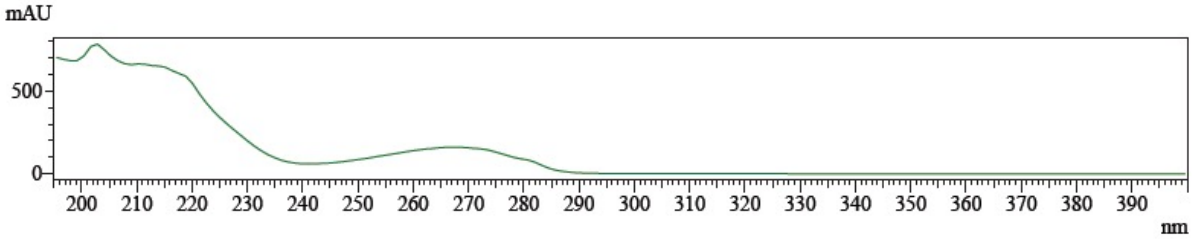
UV Spectrum
Retention time = 9.049



(±)-3ac



UV Spectrum
Retention time = 10.129



Peak Table

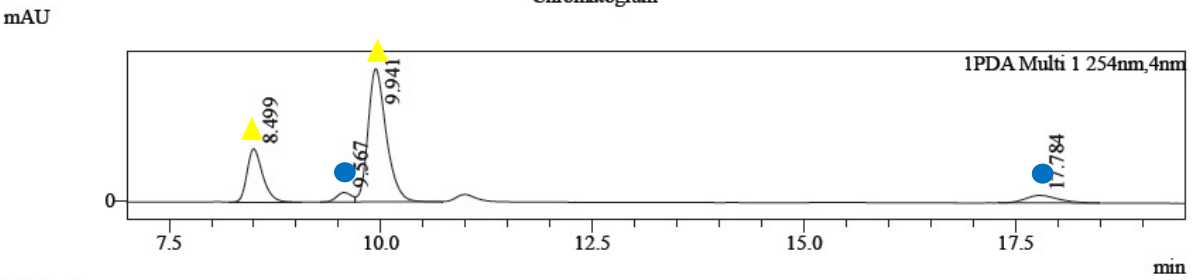
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.049	1212243	22.315
2	10.129	1367649	25.175
3	10.390	1353103	24.908
4	17.872	1499517	27.603
Total		5432512	100.000

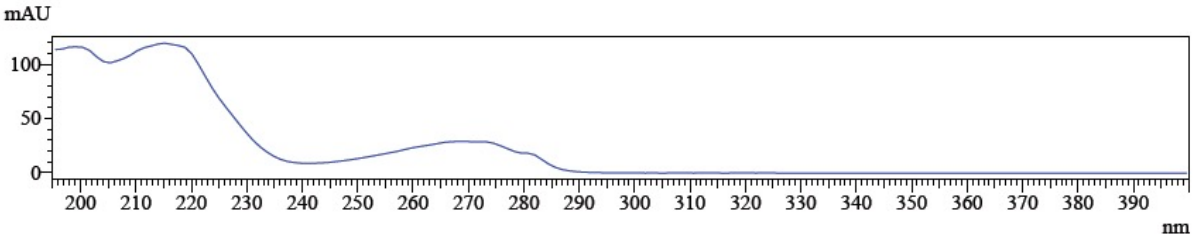
Sample Information

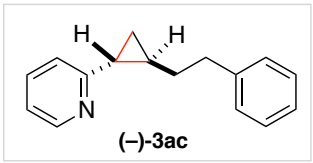
Sample Name	: XXW-1081-ODH-2%-0.8mL
Sample ID	: XXW-1081-ODH-2%-0.8mL
Data File	: XXW-1081-ODH-2%-0.8mL.lcd
Method File	: XXW-2%.0.8.mL.lcm

Chromatogram



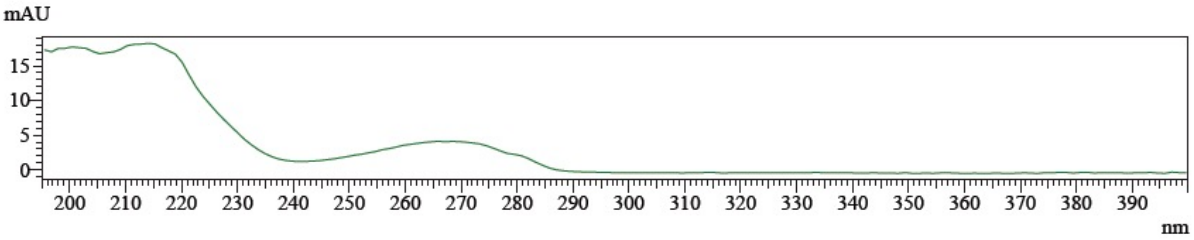
UV Spectrum
Retention time = 8.499





(–)-3ac

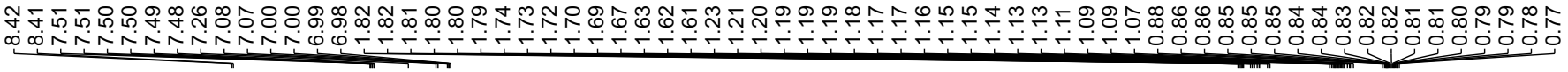
UV Spectrum
Retention time = 9.567



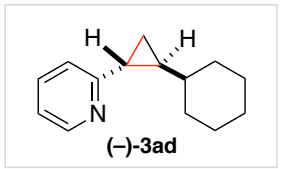
Peak Table

PDA Ch1 254nm

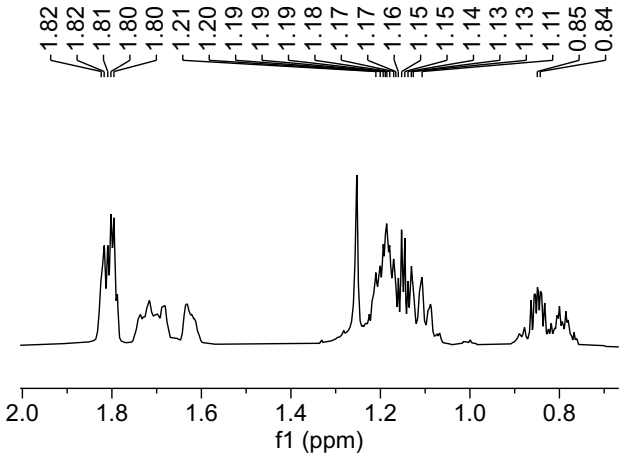
Peak#	Ret. Time	Area	Area%
1	8.499	218784	22.645
2	9.567	37294	3.860
3	9.941	644757	66.736
4	17.784	65291	6.758
Total		966127	100.000

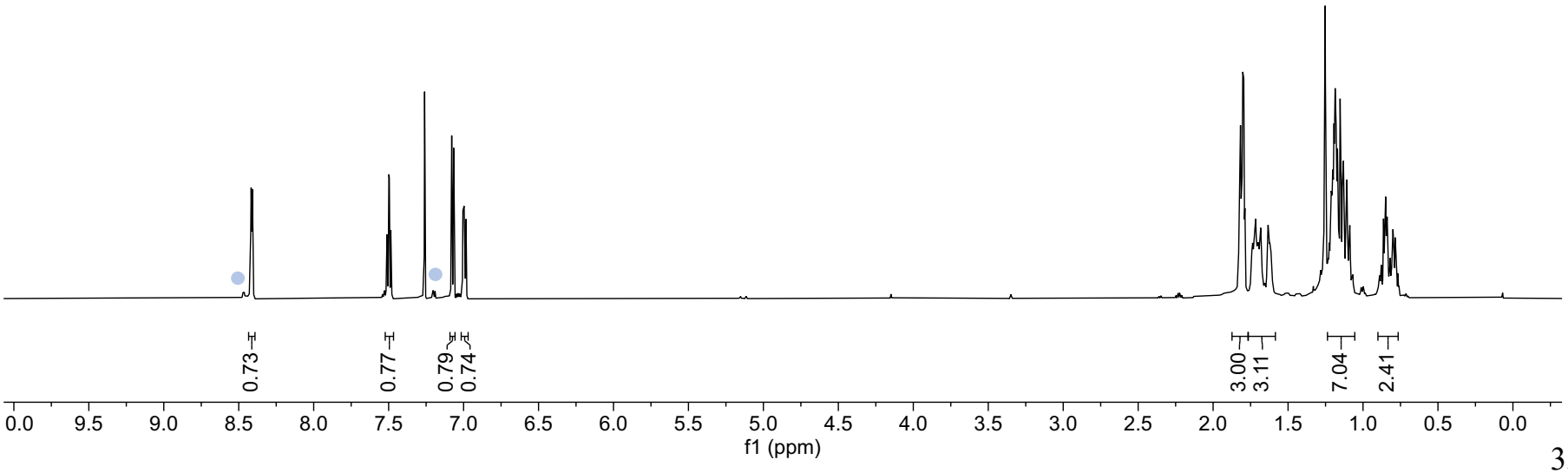


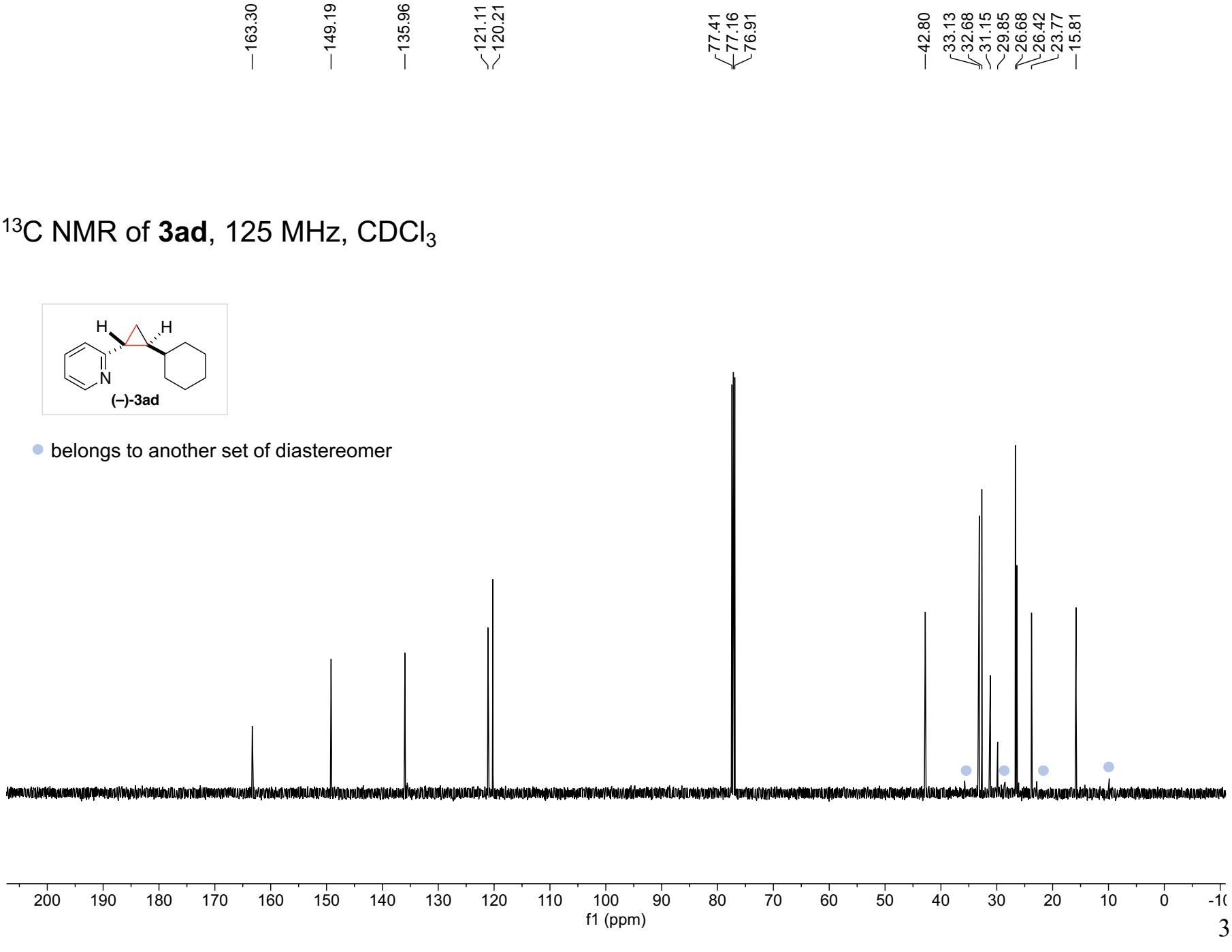
^{1}H NMR of **3ad**, 600 MHz, $CDCl_3$



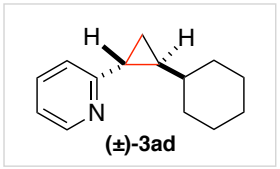
- belongs to another set of diastereomer







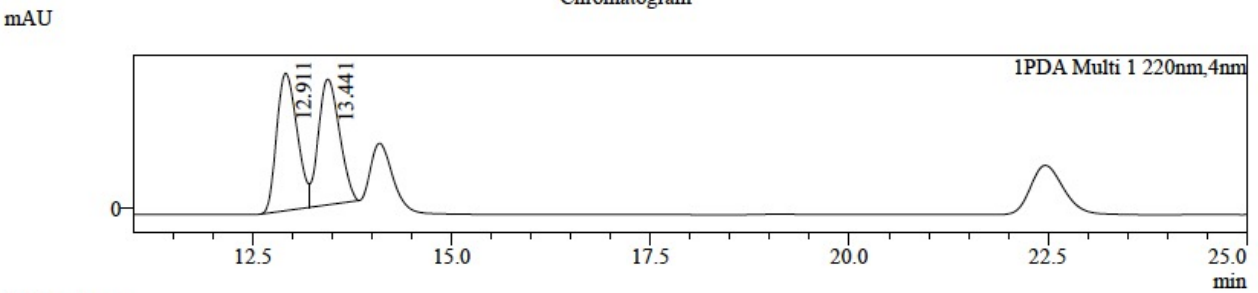
^{13}C NMR of **3ad**, 125 MHz, $CDCl_3$



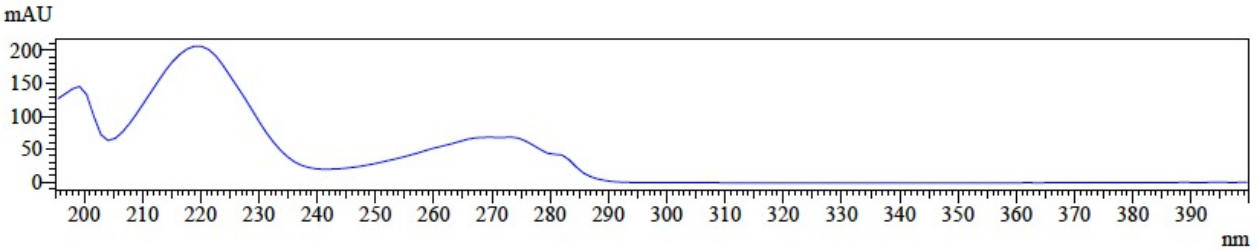
Sample Information

Sample Name	: XXW-1001-1%-IC-0.5mL
Sample ID	: XXW-1001-1%-IC-0.5mL
Data File	: XXW-1001-1%-IC-0.5mL.lcd
Method File	: XXW-1%.0.5.mL.lcm

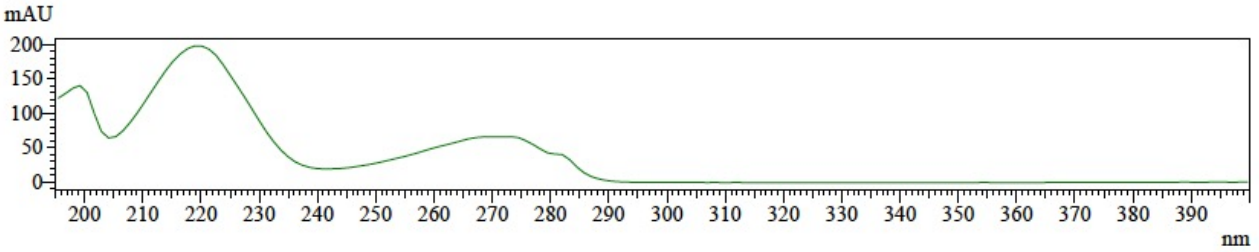
Chromatogram



UV Spectrum
Retention time = 12.911



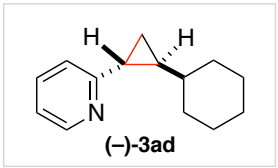
UV Spectrum
Retention time = 13.441



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.911	3588140	51.362
2	13.441	3397896	48.638
Total		6986036	100.000

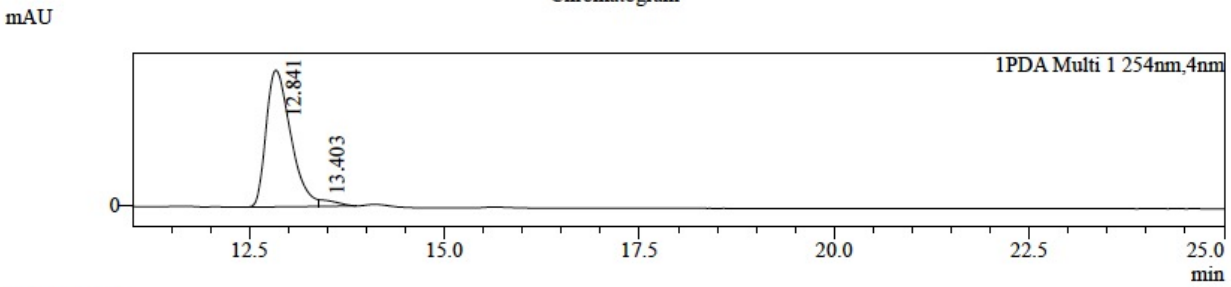


(–)-3ad

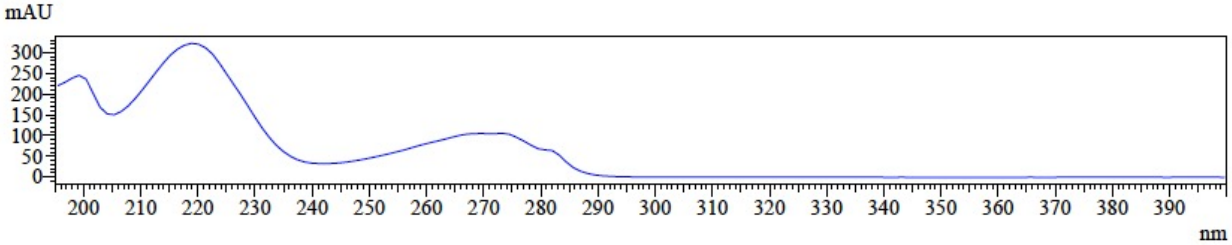
Sample Information

Sample Name : XXW-1118-IC-1-%-0.5mL
Sample ID : XXW-1118-IC-1-%-0.5mL
Data File : XXW-1118-IC-1-%-0.5mL.lcd
Method File : XXW-1%.0.5.mL.lcm

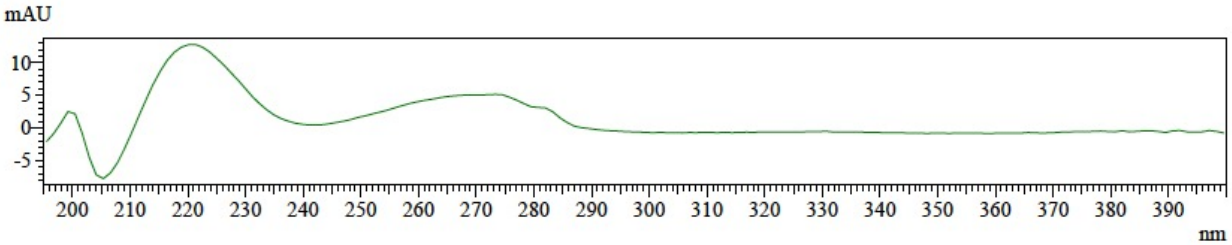
Chromatogram



UV Spectrum
Retention time = 12.841



UV Spectrum
Retention time = 13.403

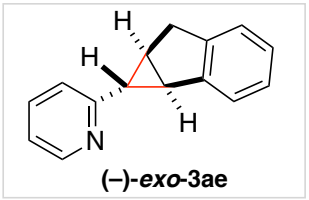


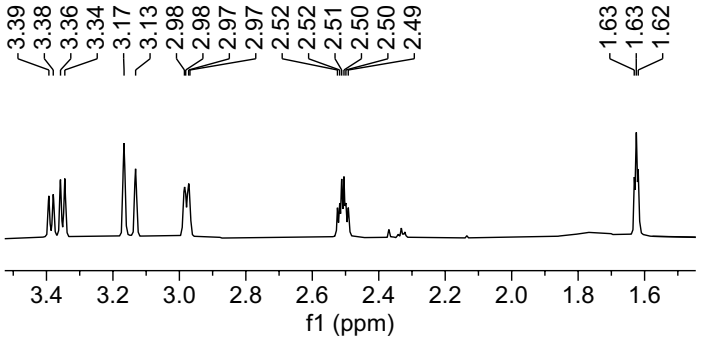
Peak Table

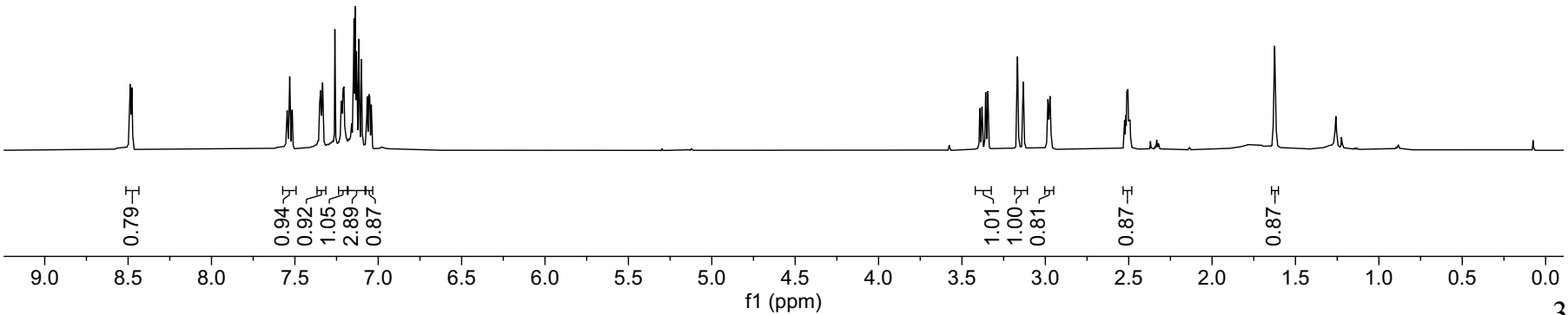
PDA Ch1 254nm

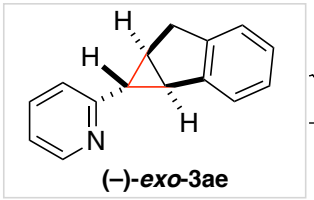
Peak#	Ret. Time	Area	Area%
1	12.841	1291644	96.879
2	13.403	41618	3.121
Total		1333261	100.000

^{1}H NMR of *exo*-**3ae**, 500 MHz, $CDCl_3$



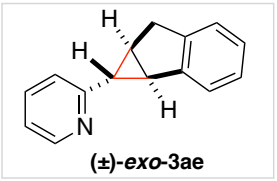






(–)-*exo*-3ae

^{13}C NMR of *exo*-**3ae**, 125 MHz, $CDCl_3$

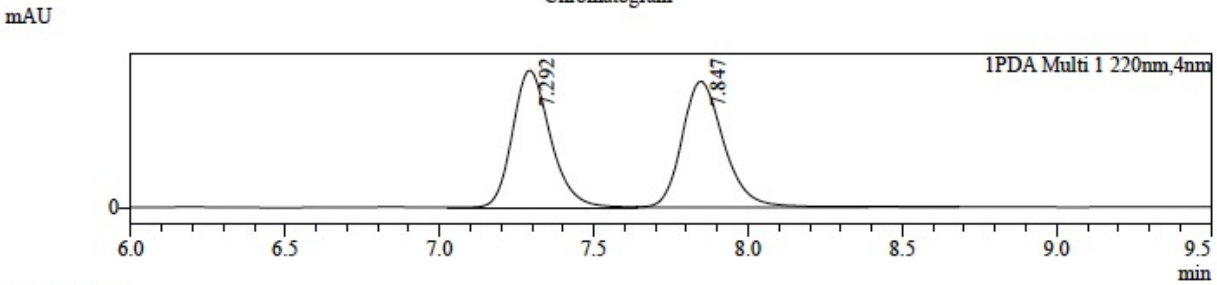


(±)-*exo*-3ae

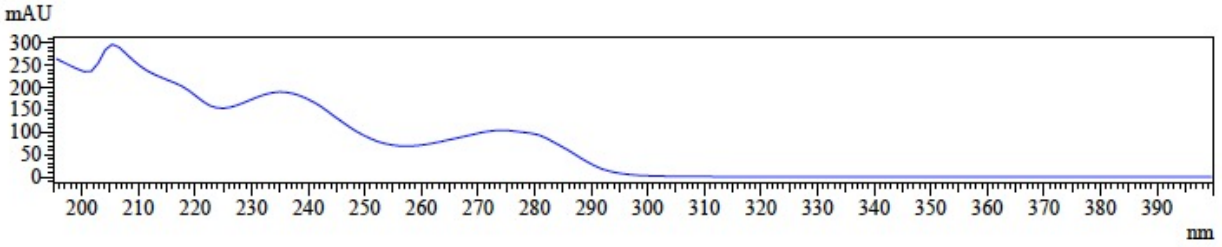
Sample Information

Sample Name	: XXW-0979-n1-ID-5%-0.8mL
Sample ID	: XXW-0979-n1-ID-5%-0.8mL
Data File	: XXW-0979-n1-ID-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

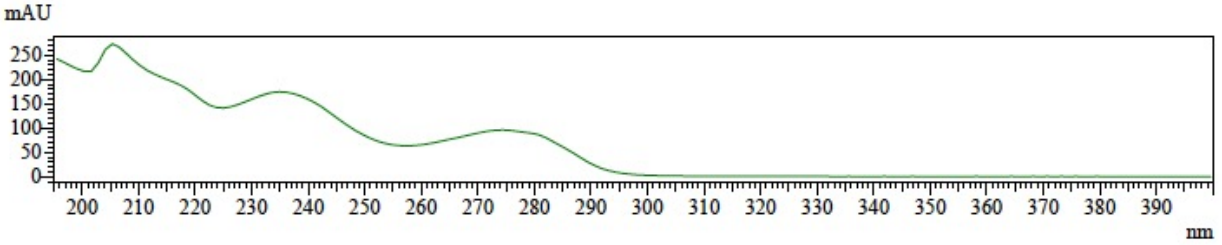
Chromatogram



UV Spectrum
Retention time = 7.292



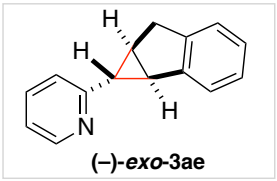
UV Spectrum
Retention time = 7.847



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.292	1553872	49.551
2	7.847	1582019	50.449
Total		3135891	100.000

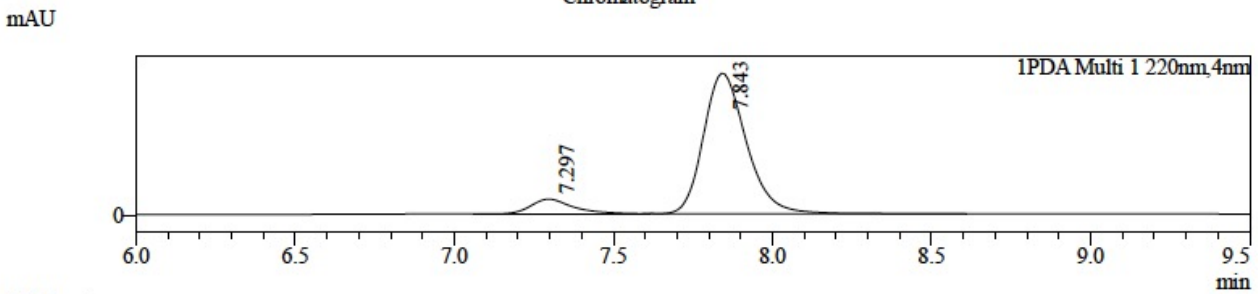


(–)-*exo*-3ae

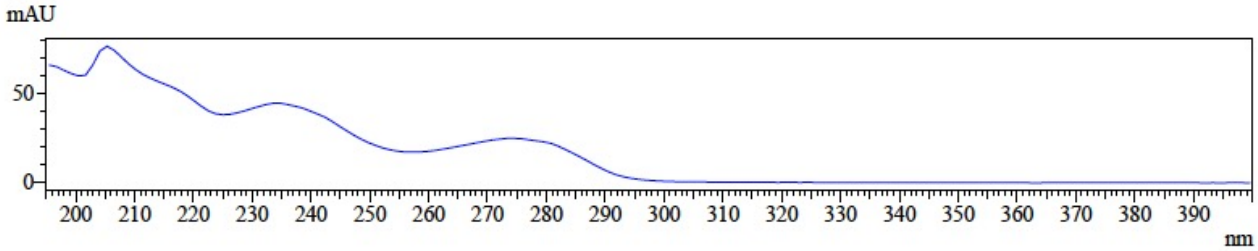
Sample Information

Sample Name	: XXW-0997-n1-ID-5%-0.8mL
Sample ID	: XXW-0997-n1-ID-5%-0.8mL
Data File	: XXW-0997-n1-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

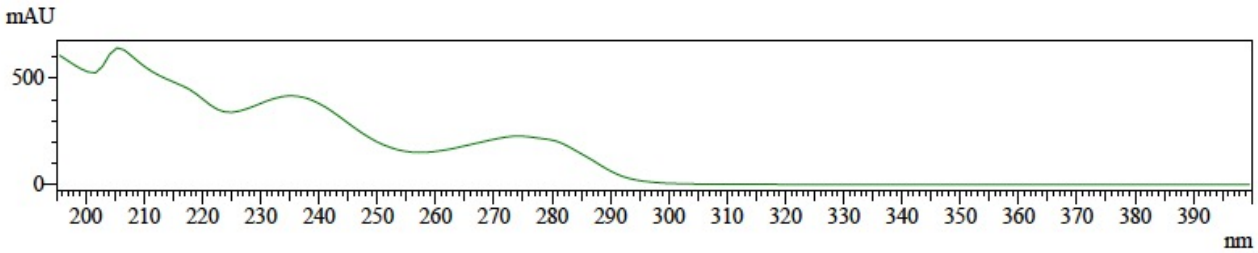
Chromatogram



UV Spectrum
Retention time = 7.297



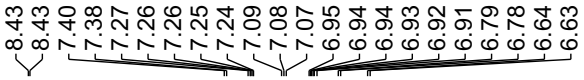
UV Spectrum
Retention time = 7.843

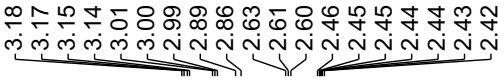


Peak Table

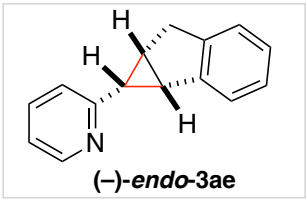
PDA Ch1 220nm

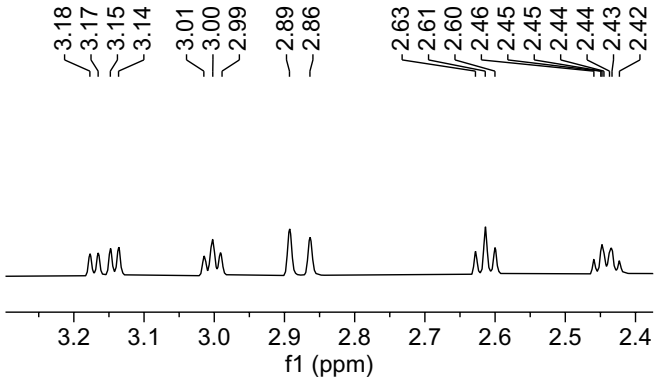
Peak#	Ret. Time	Area	Area%
1	7.297	384322	9.296
2	7.843	3749799	90.704
Total		4134121	100.000

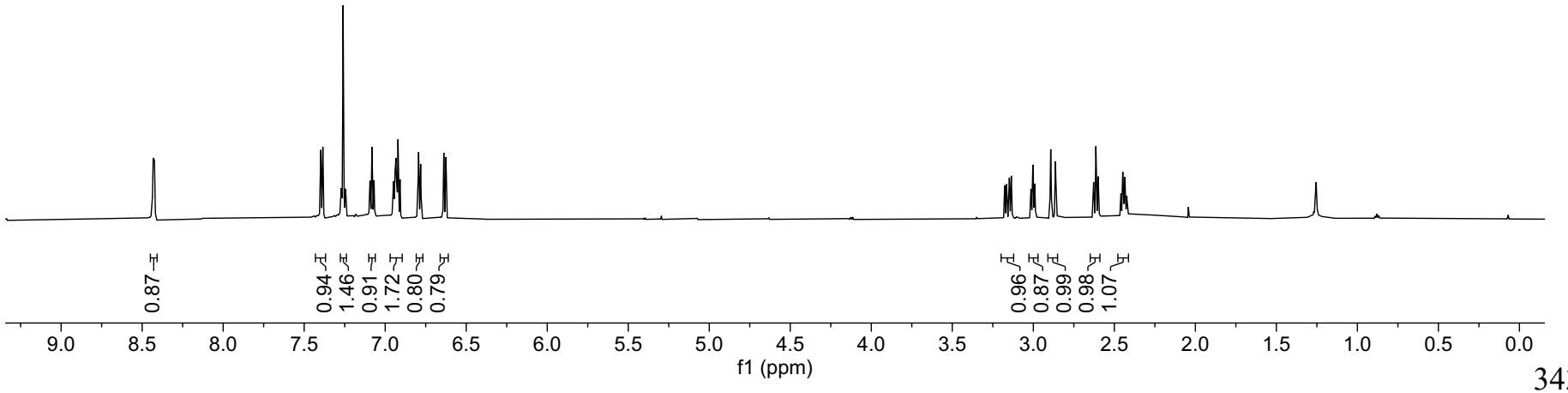


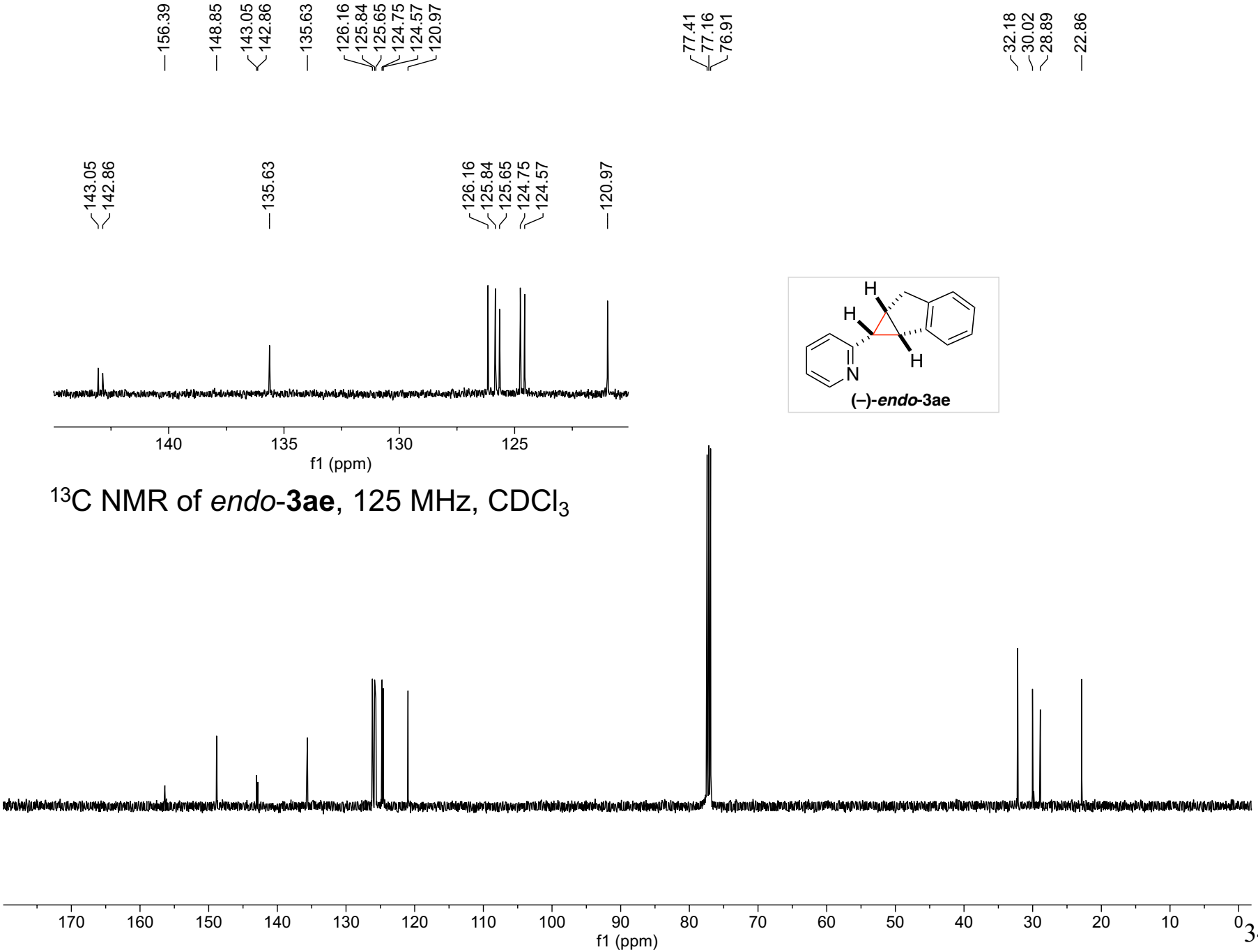


^{1}H NMR of *endo*-**3ae**, 600 MHz, $CDCl_3$







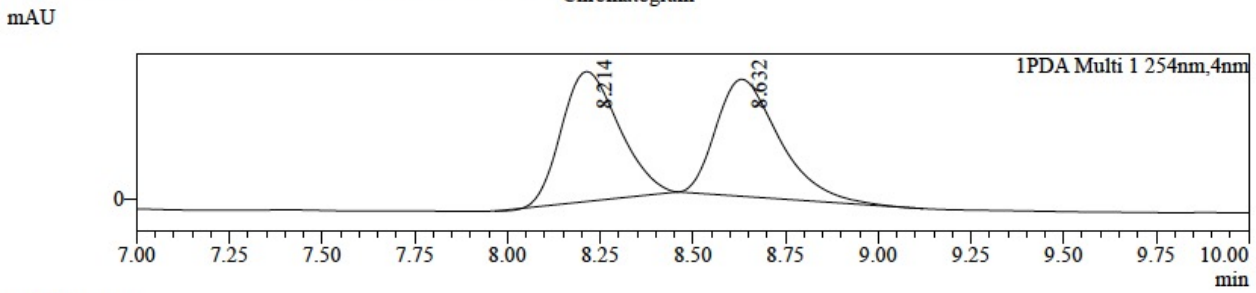


^{13}C NMR of *endo*-**3ae**, 125 MHz, $CDCl_3$

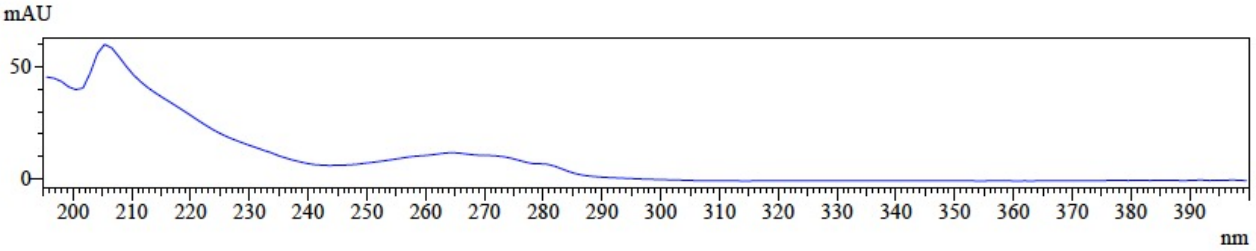
Sample Information

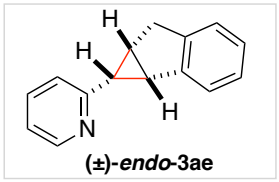
Sample Name : XXW-0979-n3-IA-5%-0.8mL
Sample ID : XXW-0979-n3-IA-5%-0.8mL
Data File : XXW-0979-n3-IA-5%-0.8mL.lcd
Method File : XXW-5%.0.8.mL.lcm

Chromatogram



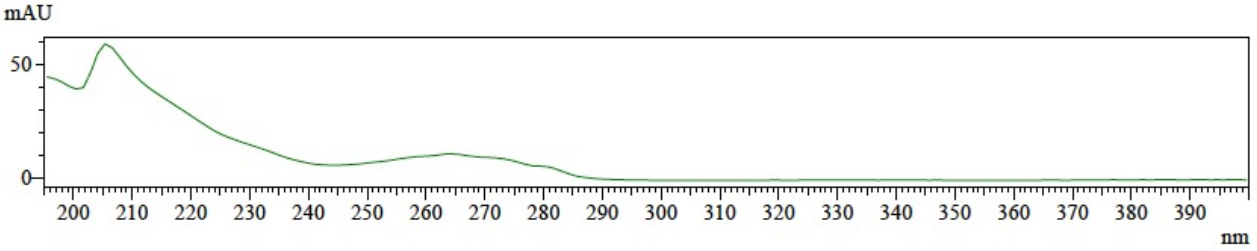
UV Spectrum
Retention time = 8.214





(±)-*endo*-3ae

UV Spectrum
Retention time = 8.632



Peak Table

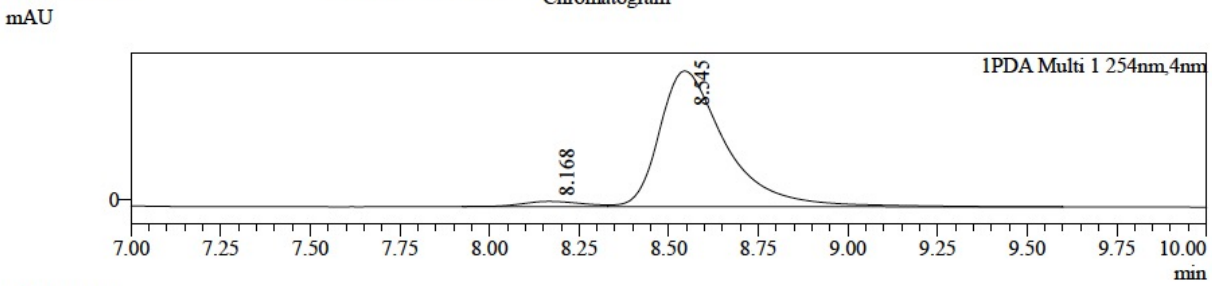
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.214	94861	50.359
2	8.632	93509	49.641
Total		188370	100.000

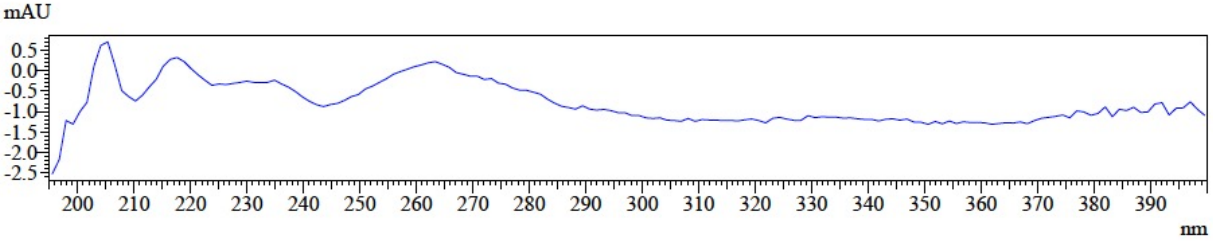
Sample Information

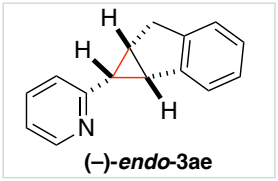
Sample Name	: XXW-0997-n3-IA-5%-0.8mL
Sample ID	: XXW-0997-n3-IA-5%-0.8mL
Data File	: XXW-0997-n3-IA-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram



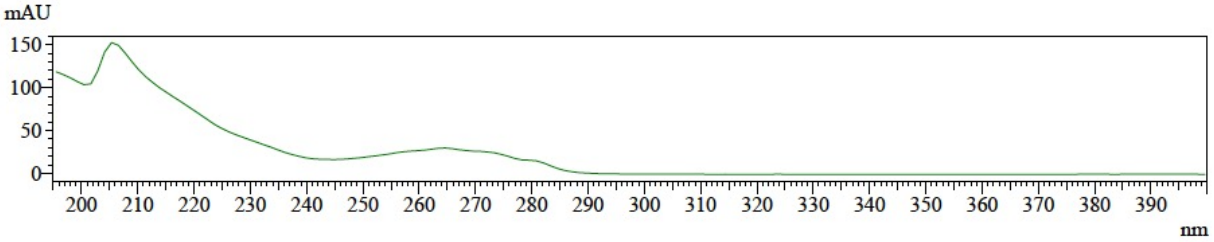
UV Spectrum
Retention time = 8.168





(–)-*endo*-3ae

UV Spectrum
Retention time = 8.545

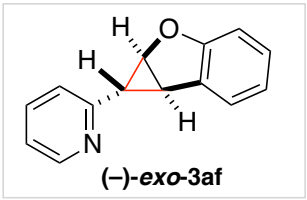


Peak Table

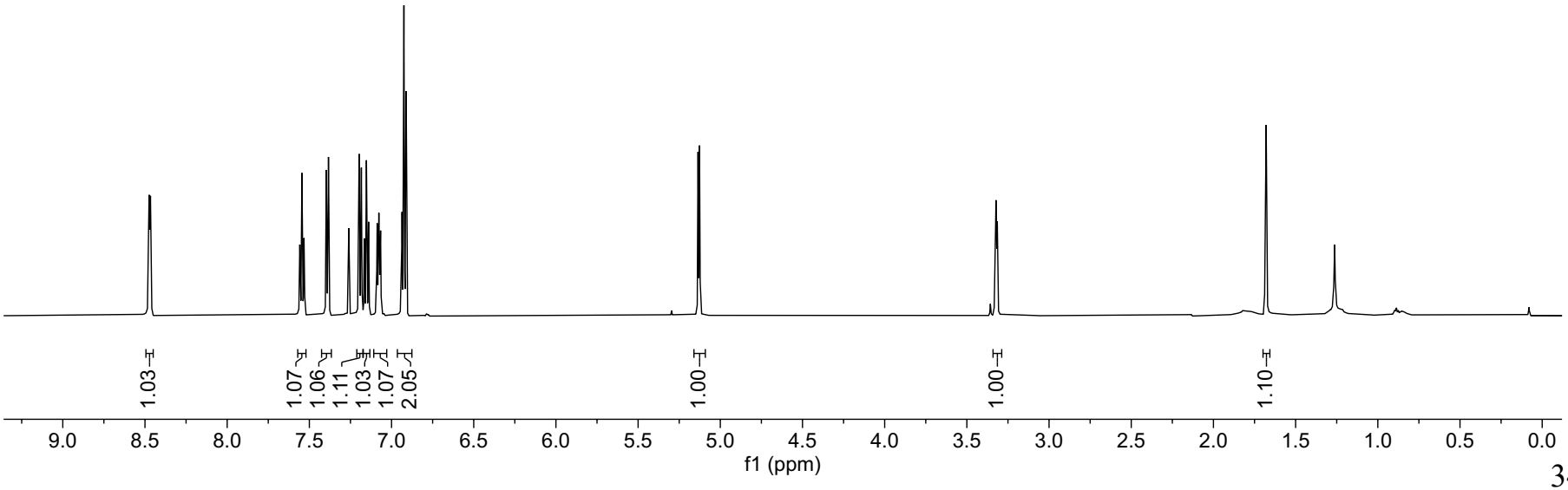
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.168	10443	3.365
2	8.545	299928	96.635
Total		310371	100.000

^{1}H NMR of **3af**, 600 MHz, $CDCl_3$

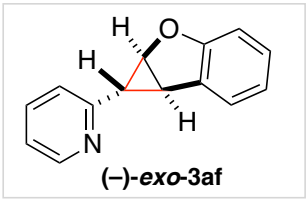


(–)-*exo*-3af

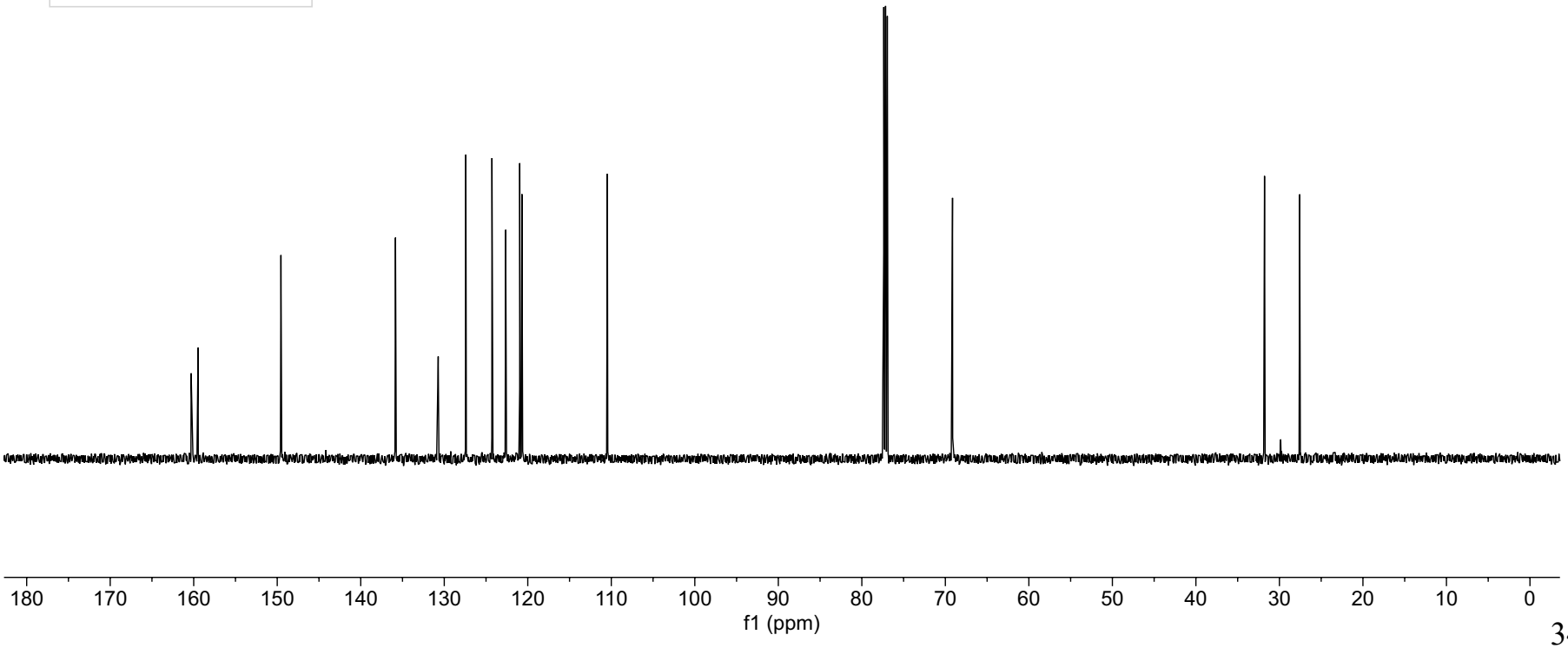


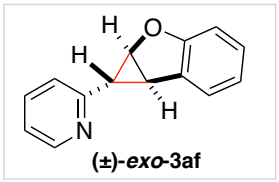
160.31
159.47
149.56
135.84
130.72
127.42
124.29
122.65
120.96
120.70
110.47
77.37
77.16
76.95
69.14
31.78
27.57

^{13}C NMR of *exo*-**3af**, 150 MHz, $CDCl_3$



(–)-*exo*-3af



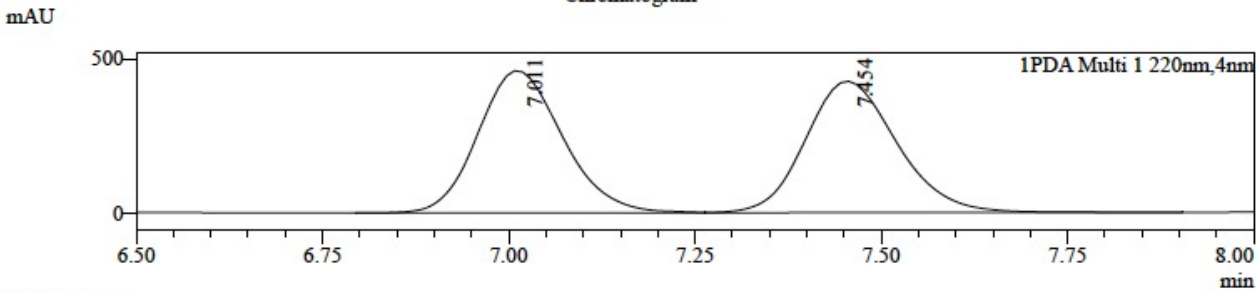


(±)-*exo*-3af

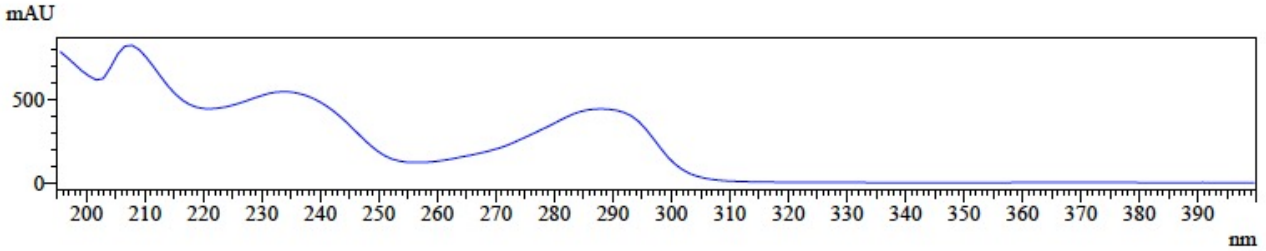
Sample Information

Sample Name	: XXW-1135-n1-ID-10%-0.8mL
Sample ID	: XXW-1135-n1-ID-10%-0.8mL
Data File	: XXW-1135-n1-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

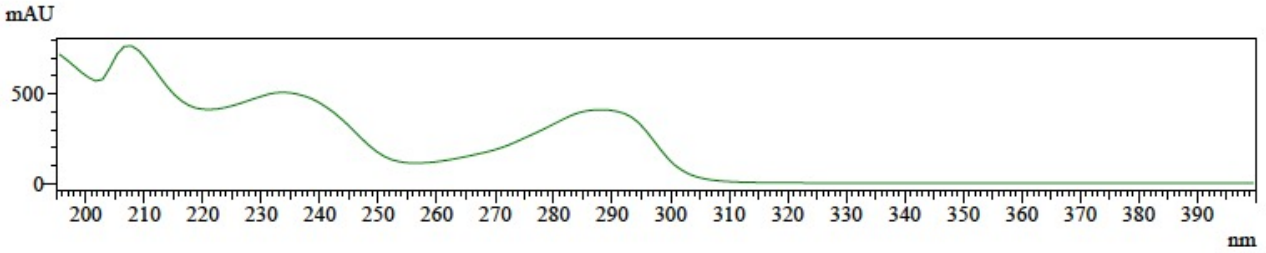
Chromatogram



UV Spectrum
Retention time = 7.011



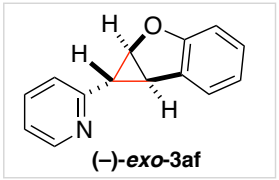
UV Spectrum
Retention time = 7.454



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.011	3647322	50.033
2	7.454	3642545	49.967
Total		7289867	100.000

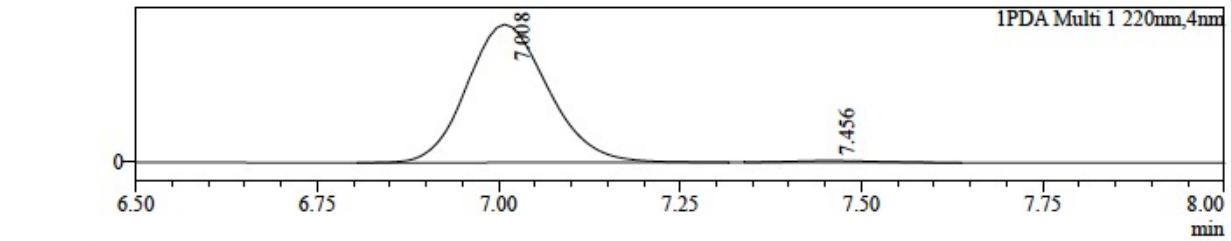


(–)-*exo*-3af

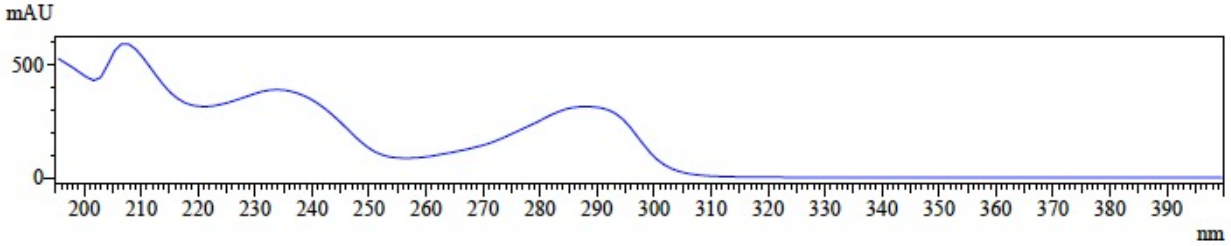
Sample Information

Sample Name	: XXW-1167-1-ID-10%-0.8mL
Sample ID	: XXW-1167-1-ID-10%-0.8mL
Data File	: XXW-1167-1-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

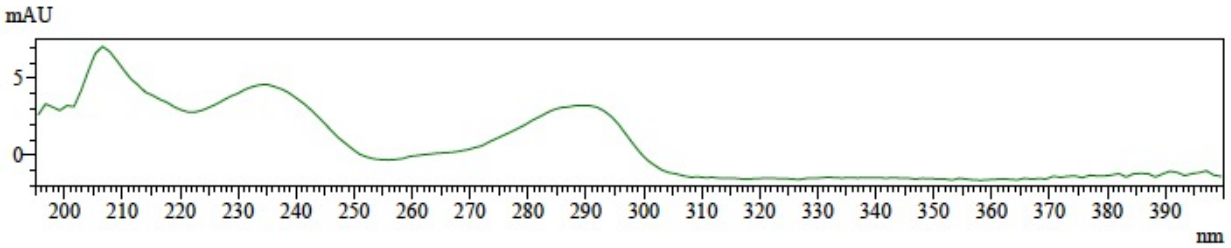
Chromatogram



UV Spectrum
Retention time = 7.008



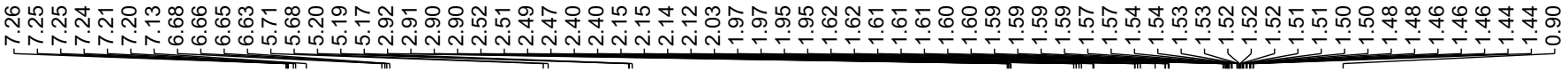
UV Spectrum
Retention time = 7.456



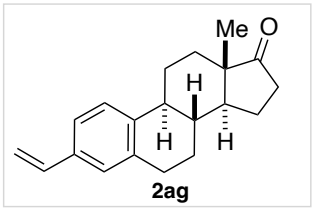
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.008	2544105	98.734
2	7.456	32630	1.266
Total		2576735	100.000

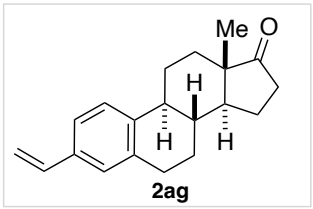


^{1}H NMR of **2ag**, 600 MHz, $CDCl_3$

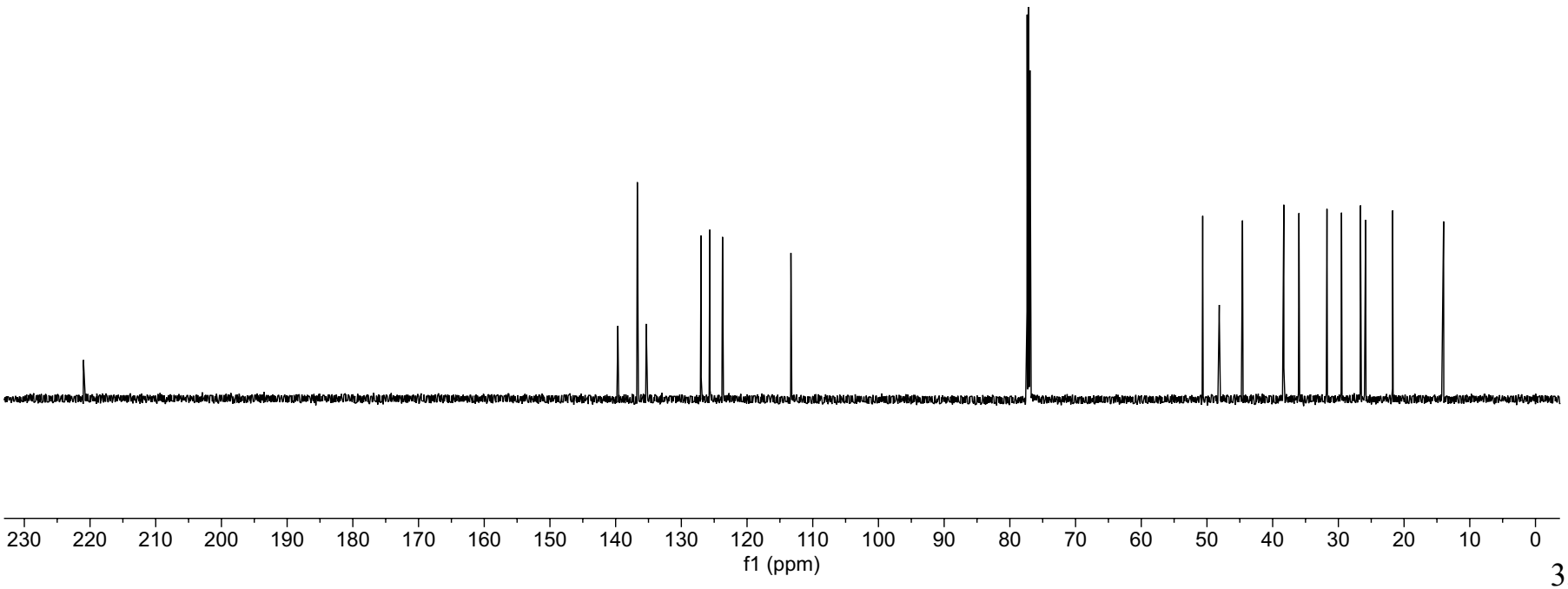


221.01
139.66
136.70
135.35
127.01
125.67
123.74
113.32
77.37
77.16
76.95
50.65
48.13
44.59
38.30
36.00
31.73
29.52
26.64
25.86
21.73
13.98

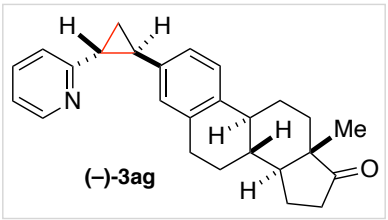
^{13}C NMR of **2g**, 150 MHz, $CDCl_3$

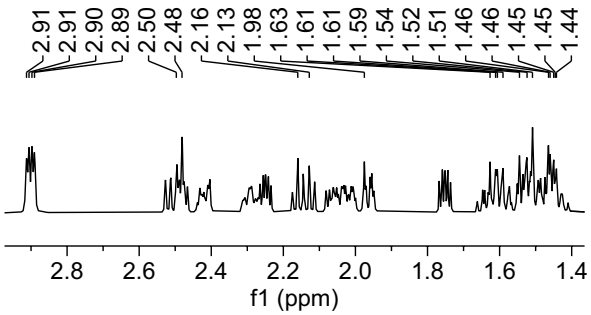


2ag



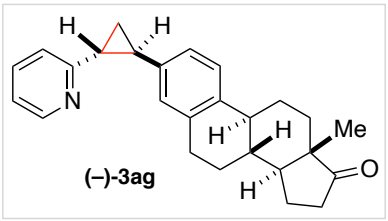
^{1}H NMR of **3ag**, 600 MHz, $CDCl_3$

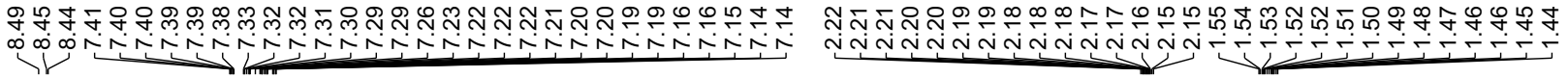




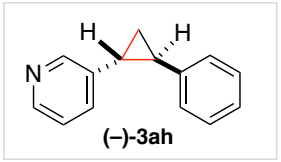
221.01
161.31
149.46
139.87
137.51
136.60
136.02
126.77
125.56
123.42
122.11
120.70
77.37
77.16
76.95
50.60
48.12
44.42
38.37
35.99
31.72
29.54
29.38
27.92
26.66
25.90
21.71
18.79
13.96

^{13}C NMR of **3ag**, 150 MHz, $CDCl_3$

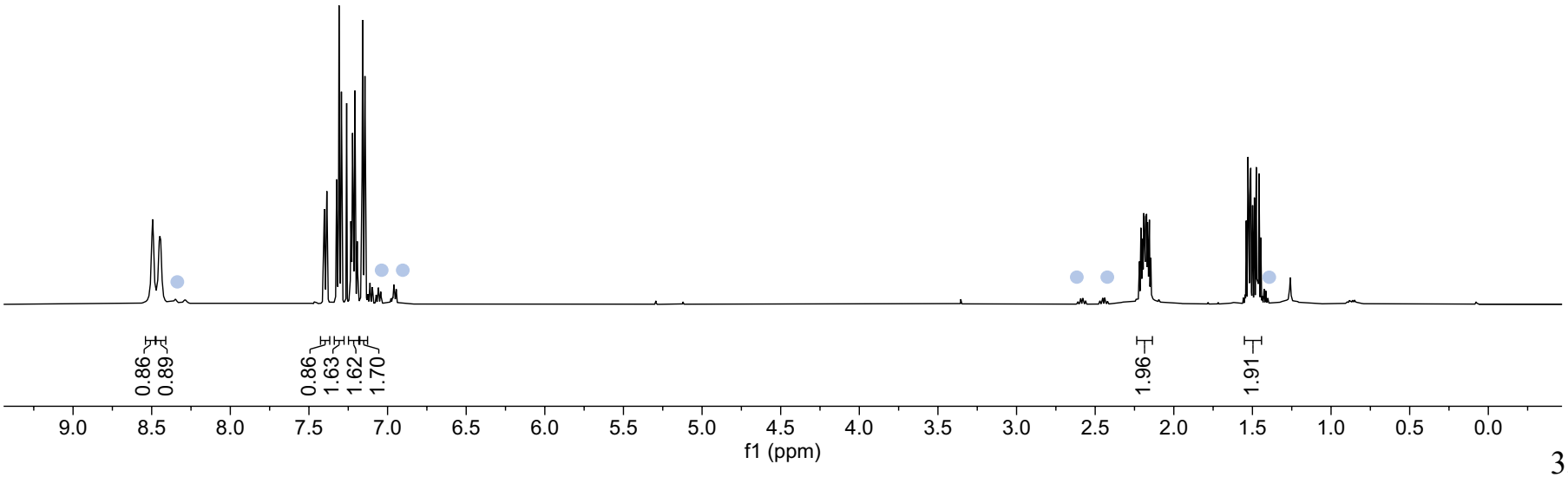




^{1}H NMR of **3ah**, 500 MHz, $CDCl_3$

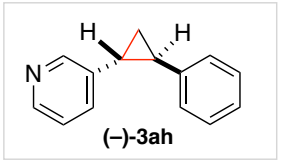


● belongs to another set of diastereomer



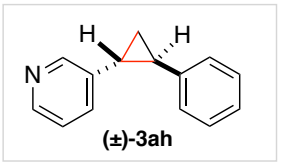
148.36
147.26
141.81
132.84
129.26
128.64
126.23
125.95
123.48
77.42
77.16
76.91
27.96
25.37
17.98

^{13}C NMR of **3ah**, 125 MHz, $CDCl_3$



(–)-3ah

belongs to another set of diastereomer

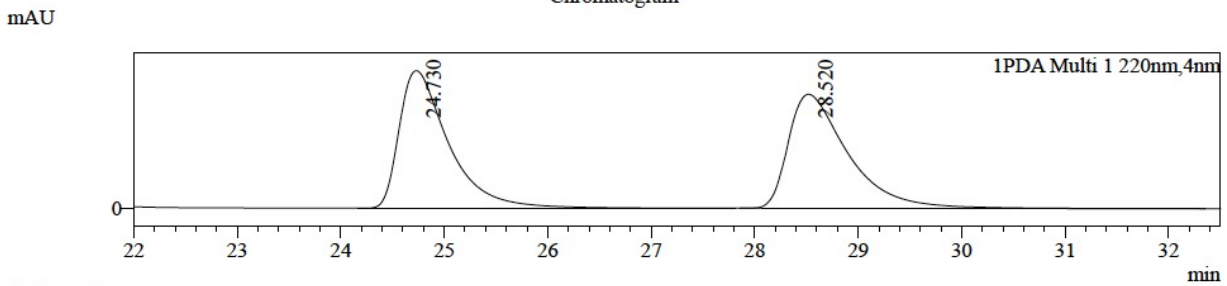


(±)-3ah

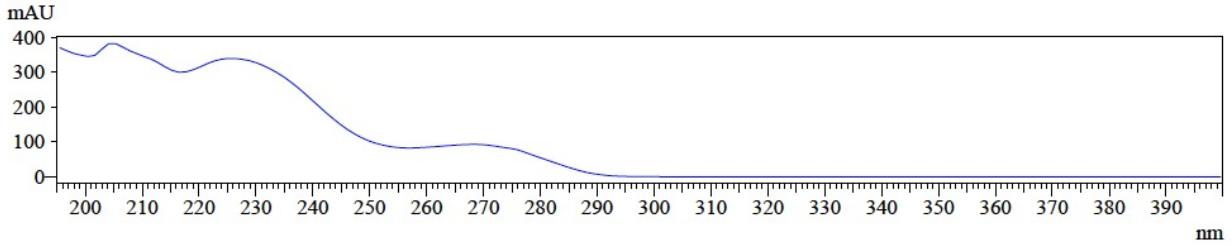
Sample Information

Sample Name	: XXW-0218-rac-ID-5%--0.8mL
Sample ID	: XXW-0218-rac-ID-5%--0.8mL
Data File	: XXW-0218-rac-ID-5%--0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

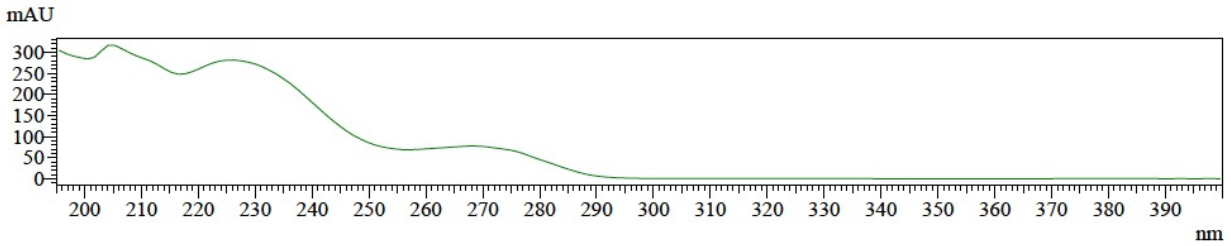
Chromatogram



UV Spectrum
Retention time = 24.730



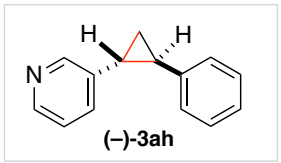
UV Spectrum
Retention time = 28.520



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.730	10564697	49.963
2	28.520	10580295	50.037
Total		21144992	100.000

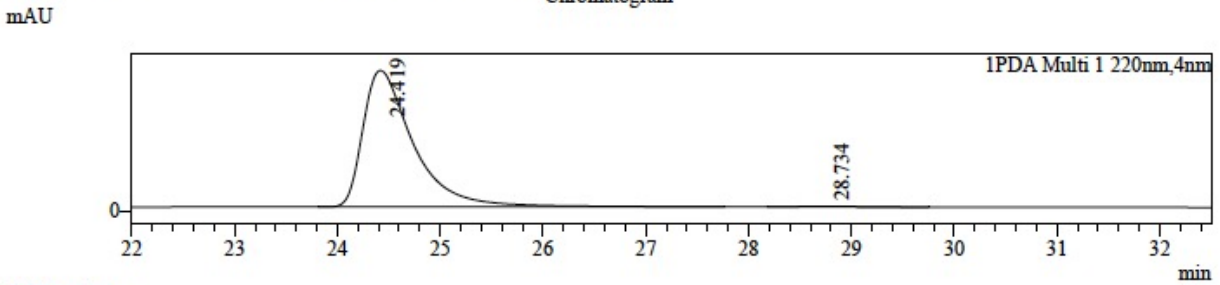


(–)-3ah

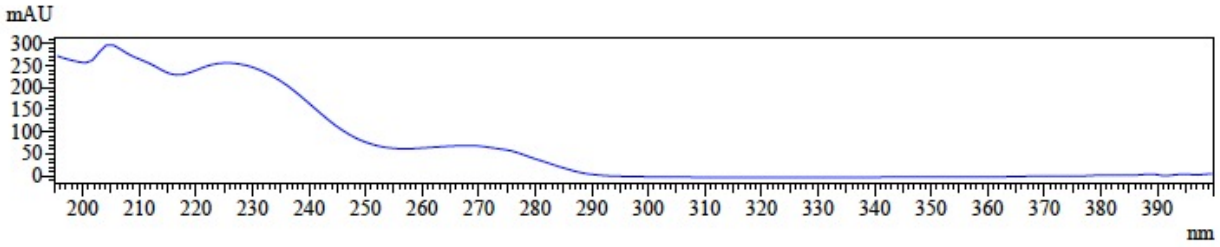
Sample Information

Sample Name	: XXW-1233--ID-5%--0.8mL
Sample ID	: XXW-1233--ID-5%--0.8mL
Data File	: XXW-1233--ID-5%--0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

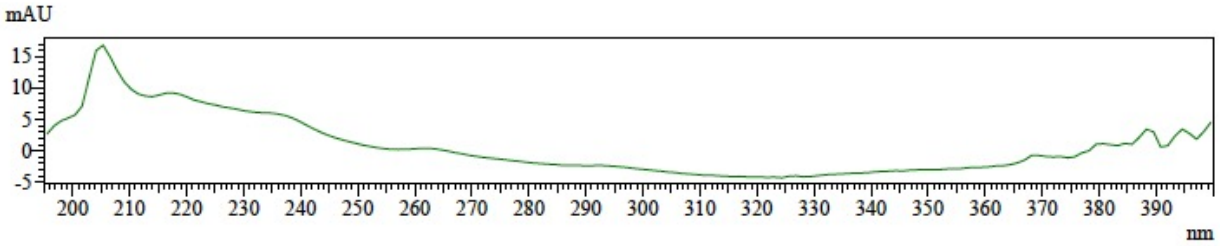
Chromatogram



UV Spectrum
Retention time = 24.419



UV Spectrum
Retention time = 28.734

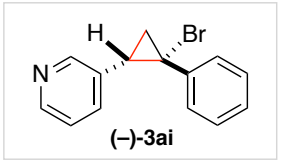


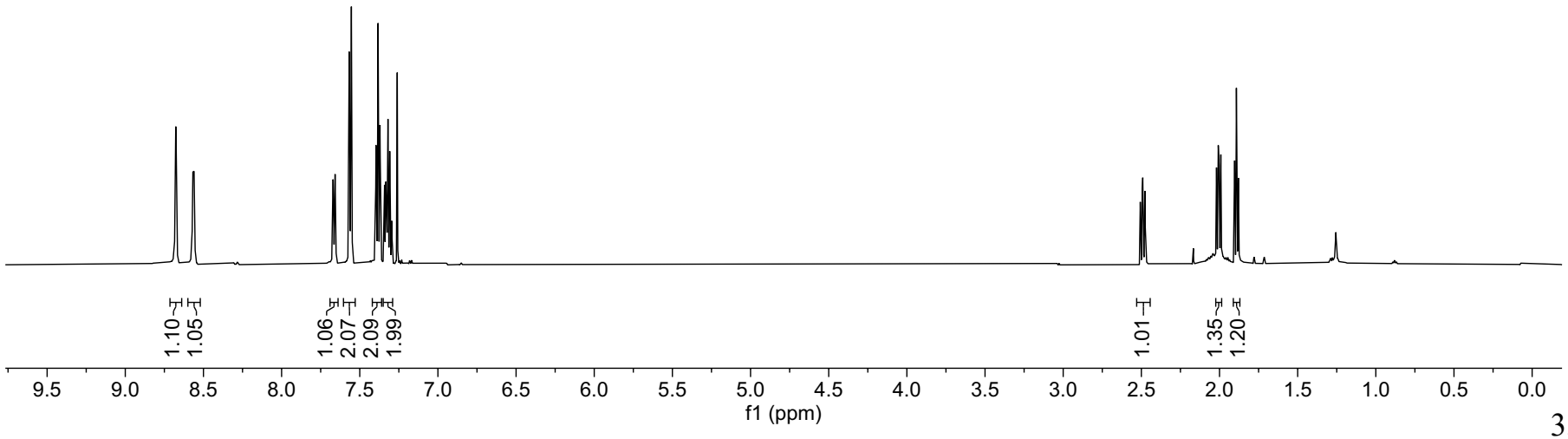
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.419	7952276	99.370
2	28.734	50392	0.630
Total		8002668	100.000

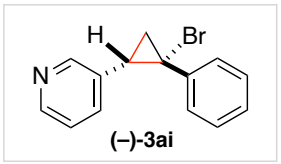
^{1}H NMR of **3ai**, 600 MHz, $CDCl_3$



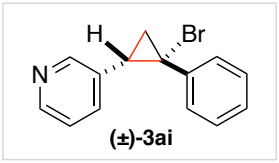


150.96
148.24
143.77
136.69
133.88
128.91
128.62
128.43
123.09
77.37
77.16
76.95
41.24
28.61
21.22

^{13}C NMR of **3ai**, 150 MHz, $CDCl_3$



(–)-3ai

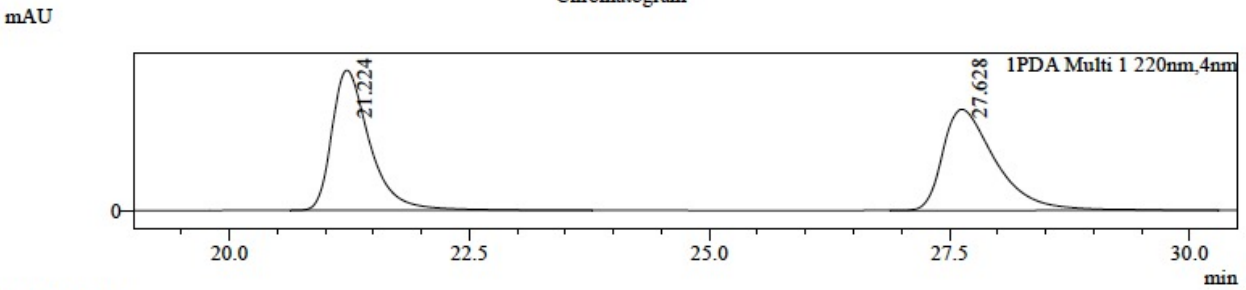


(±)-3ai

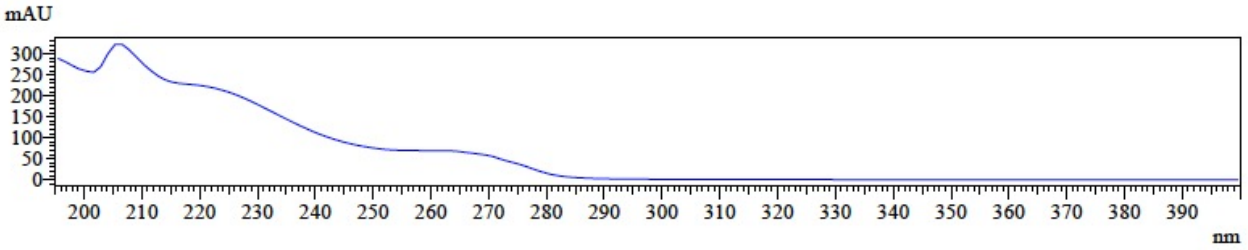
Sample Information

Sample Name	: XXW-1281-IE-10%--0.8mL
Sample ID	: XXW-1281-IE-10%--0.8mL
Data File	: XXW-1281-IE-10%--0.8mL002.lcd
Method File	: XXW-10%.0.8.mL.lcm

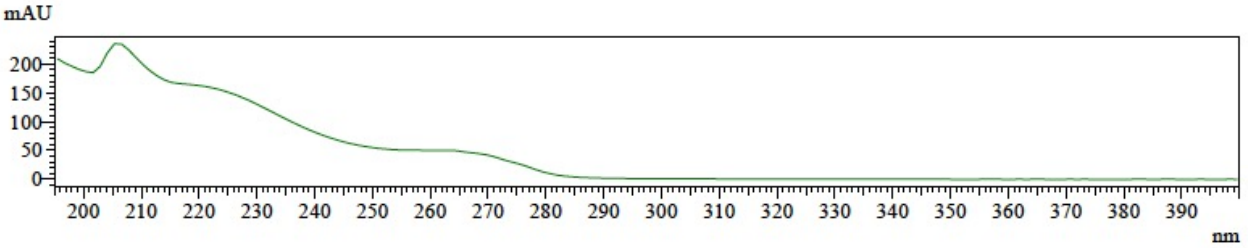
Chromatogram



UV Spectrum
Retention time = 21.224



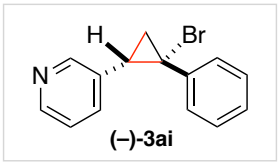
UV Spectrum
Retention time = 27.628



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	21.224	6168831	49.913
2	27.628	6190289	50.087
Total		12359120	100.000

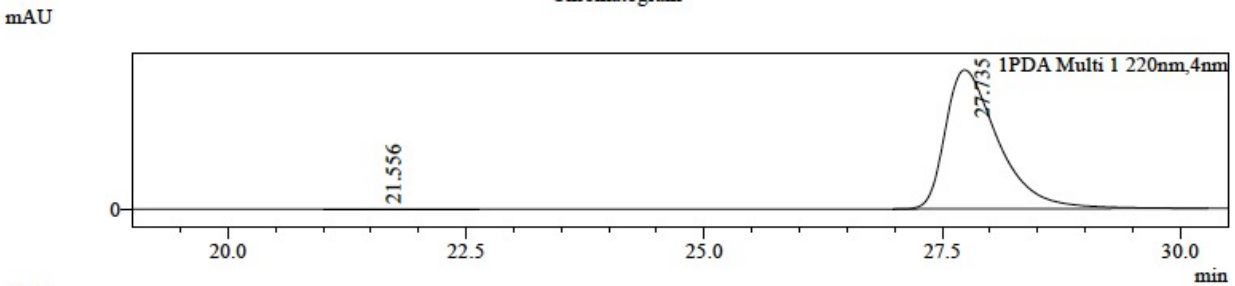


(–)-3ai

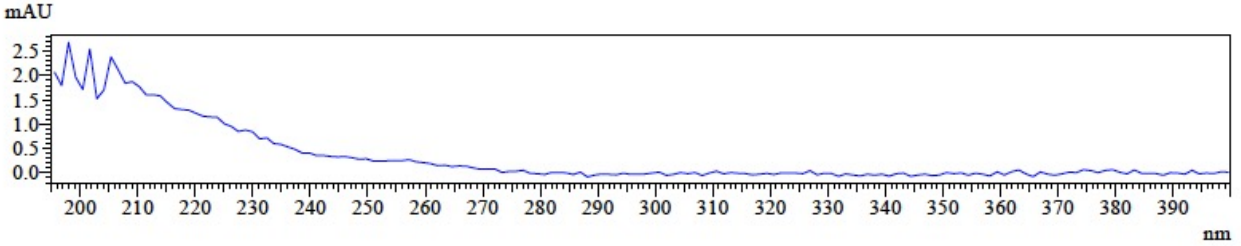
Sample Information

Sample Name	: XXW-1282-IE-10%--0.8mL
Sample ID	: XXW-1282-IE-10%--0.8mL
Data File	: XXW-1282-IE-10%--0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

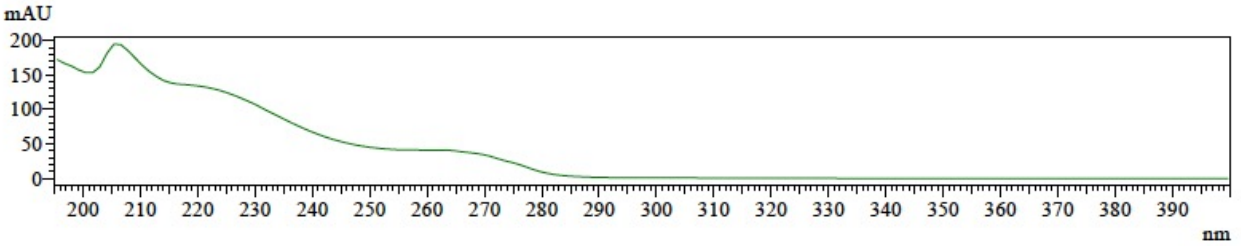
Chromatogram



UV Spectrum
Retention time = 21.556



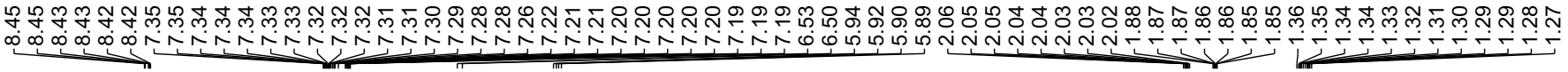
UV Spectrum
Retention time = 27.735



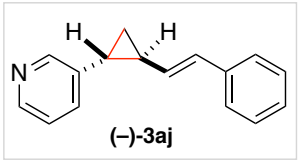
Peak Table

PDA Ch1 220nm

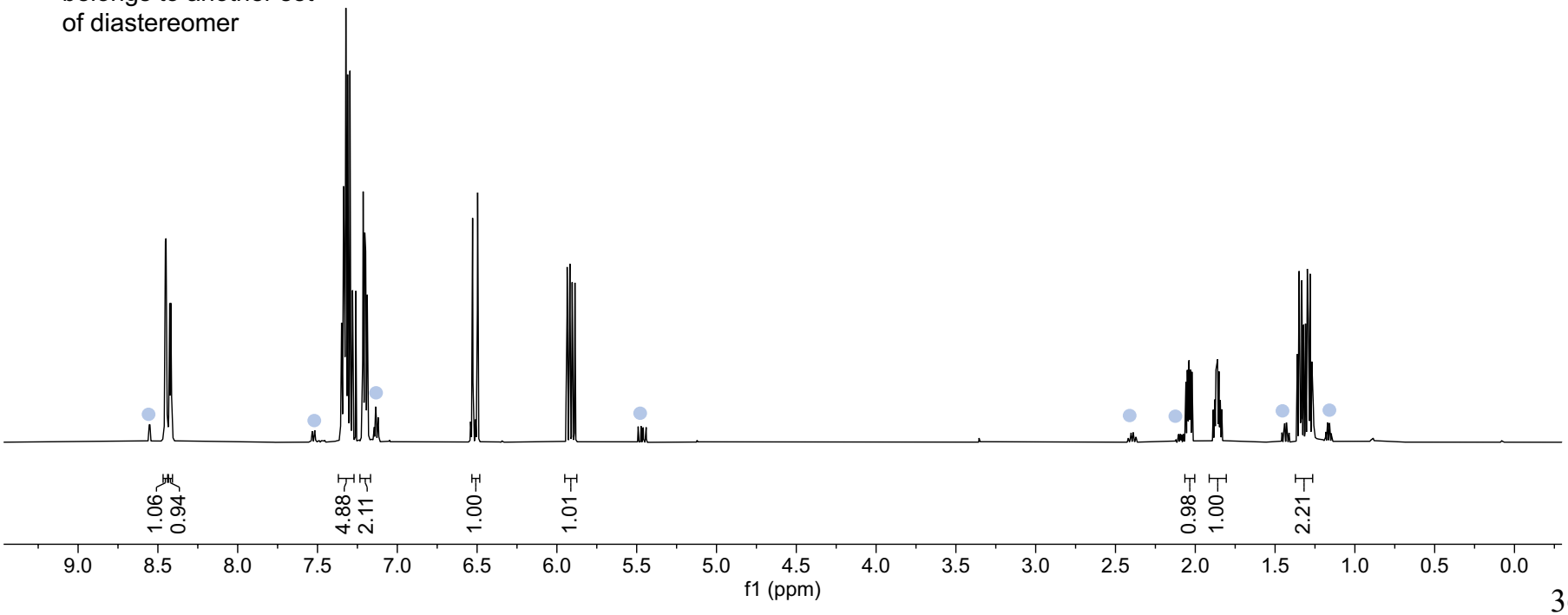
Peak#	Ret. Time	Area	Area%
1	21.556	5719	0.112
2	27.735	5102140	99.888
Total		5107860	100.000



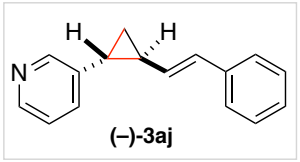
^{1}H NMR of **3aj**, 500 MHz, $CDCl_3$



belongs to another set of diastereomer

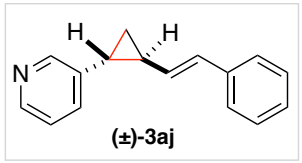


^{13}C NMR of **3aj**, 125 MHz, $CDCl_3$



(–)-3aj

● belongs to another set of diastereomer

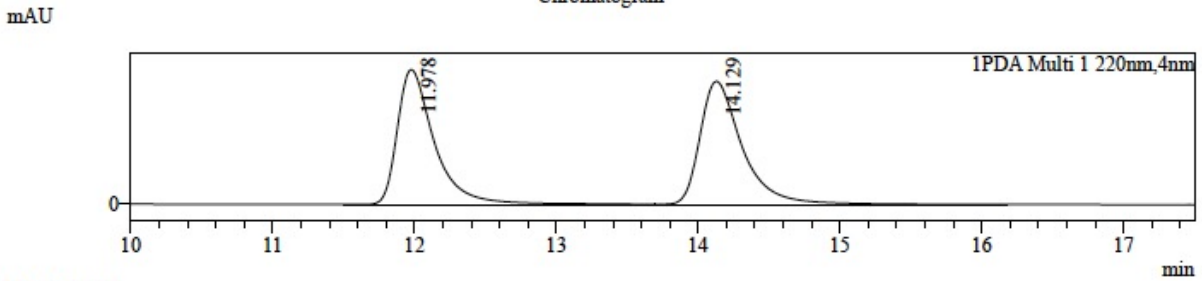


(±)-3aj

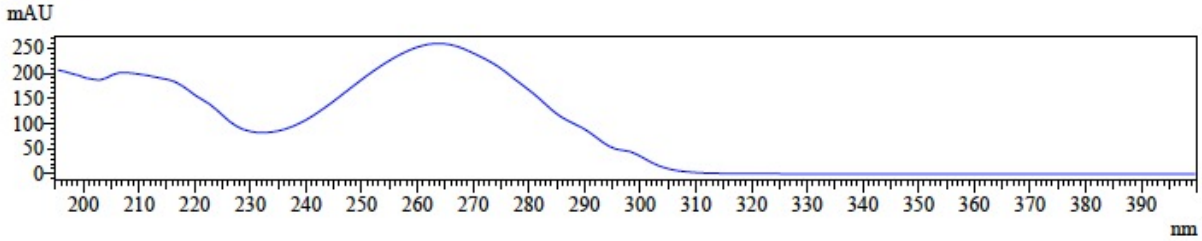
Sample Information

Sample Name	: XXW-0877-ID-20%--0.8mL
Sample ID	: XXW-0877-ID-20%--0.8mL
Data File	: XXW-0877-ID-20%--0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

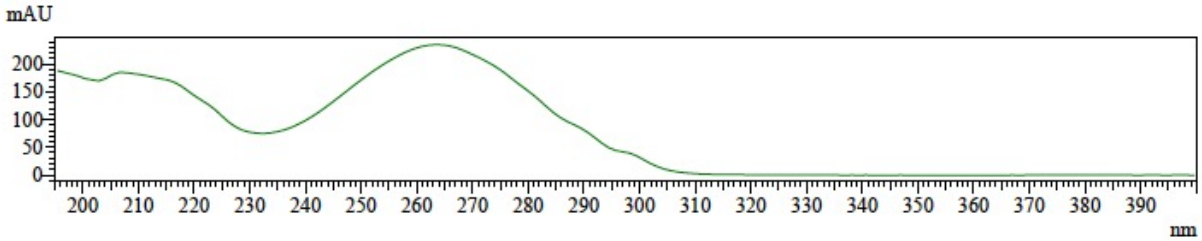
Chromatogram



UV Spectrum
Retention time = 11.978



UV Spectrum
Retention time = 14.129



Peak Table

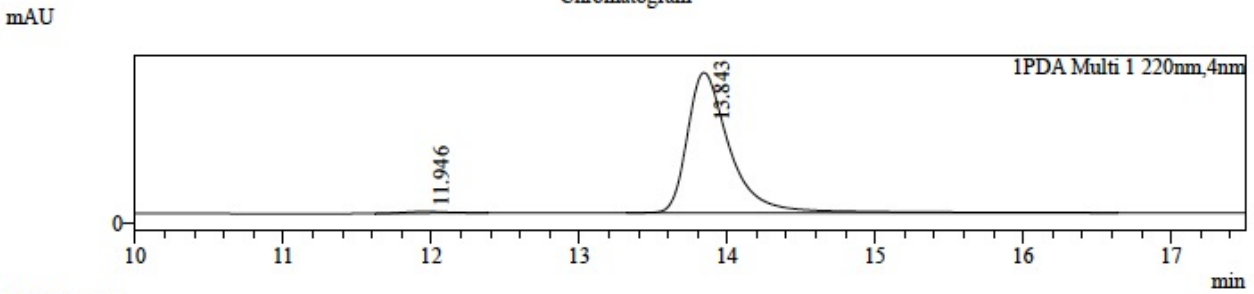
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	11.978	2883411	49.182
2	14.129	2979325	50.818
Total		5862737	100.000

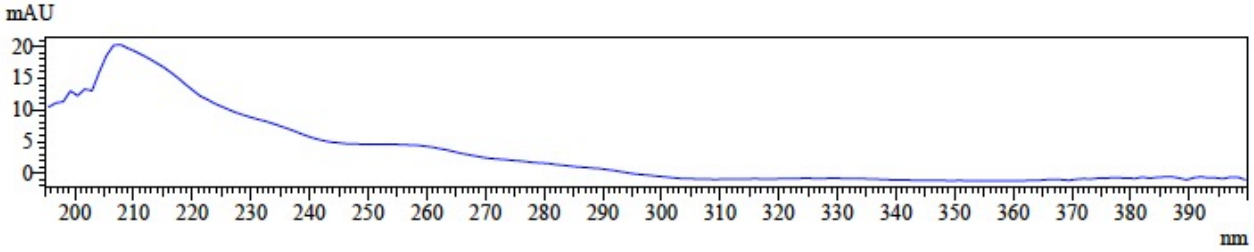
Sample Information

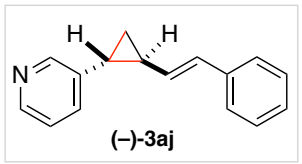
Sample Name	: XXW-1331-ID-20%-0.8mL
Sample ID	: XXW-1331-ID-20%-0.8mL
Data File	: XXW-1331-ID-20%-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram

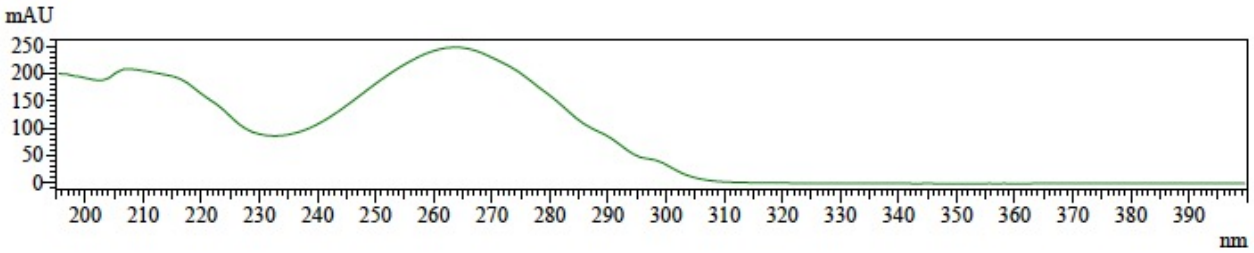


UV Spectrum
Retention time = 11.946





UV Spectrum
Retention time = 13.843

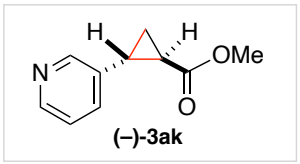


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	11.946	32571	1.066
2	13.843	3023249	98.934
Total		3055820	100.000

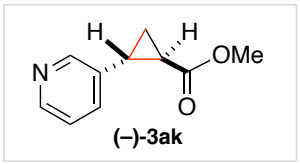
^{1}H NMR of **3ak**, 500 MHz, $CDCl_3$



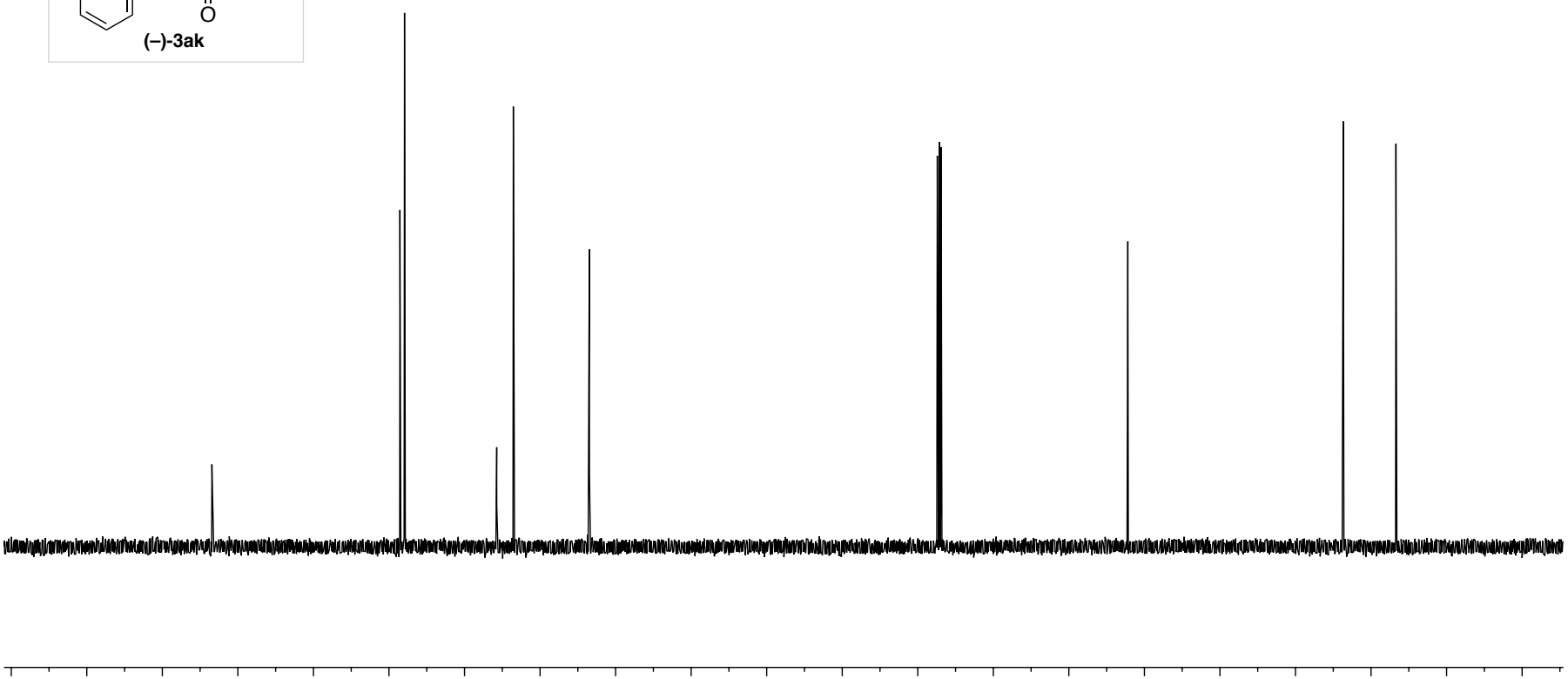
(–)-3ak

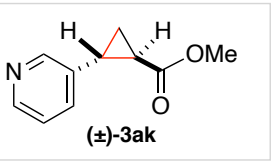
173.44
148.55
147.94
135.74
133.54
123.47
77.41
77.16
76.91
52.19
23.70
23.67
16.70

^{13}C NMR of **3ak**, 125 MHz, $CDCl_3$



(–)-3ak



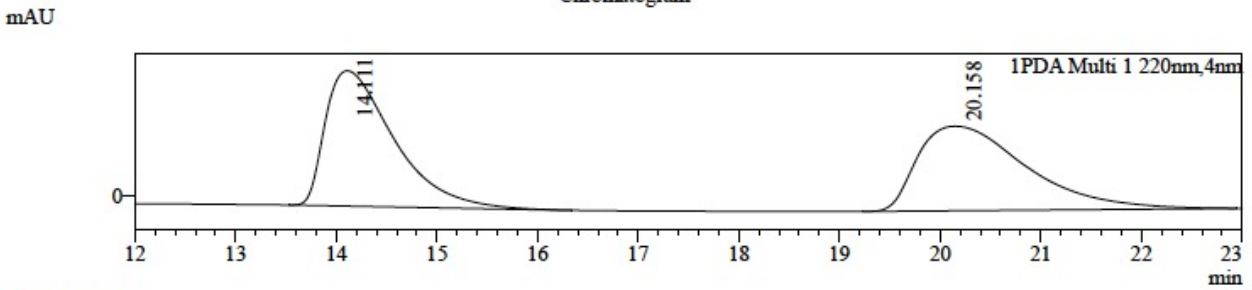


(±)-3ak

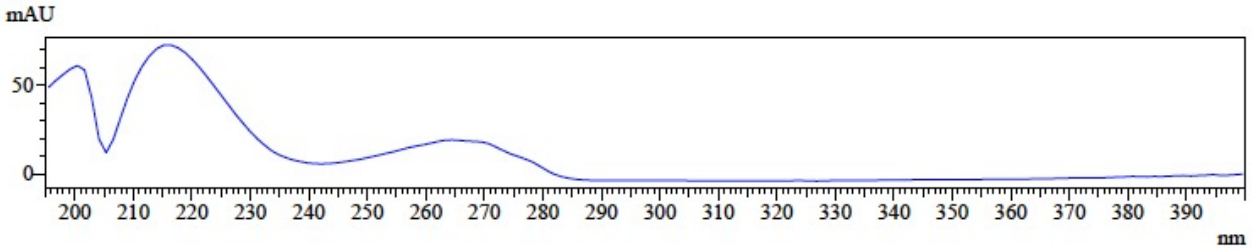
Sample Information

Sample Name	: XXW-0816-ASH-10%-0.8mL
Sample ID	: XXW-0816-ASH-10%-0.8mL
Data File	: XXW-0816-ASH-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

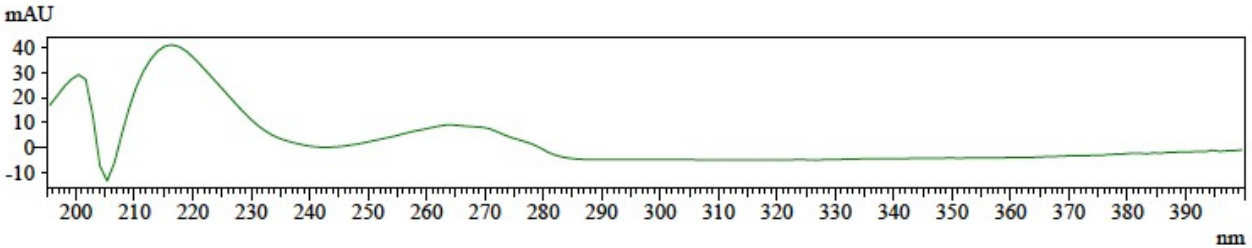
Chromatogram



UV Spectrum
Retention time = 14.111



UV Spectrum
Retention time = 20.158



Peak Table

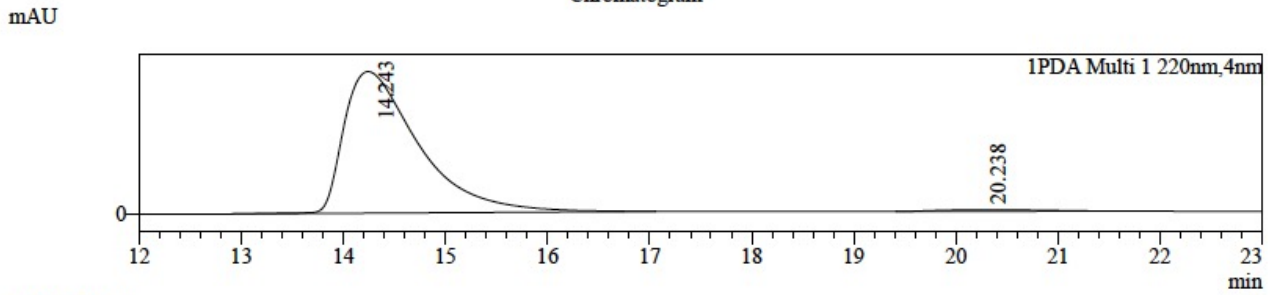
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.111	3211098	50.082
2	20.158	3200552	49.918
Total		6411650	100.000

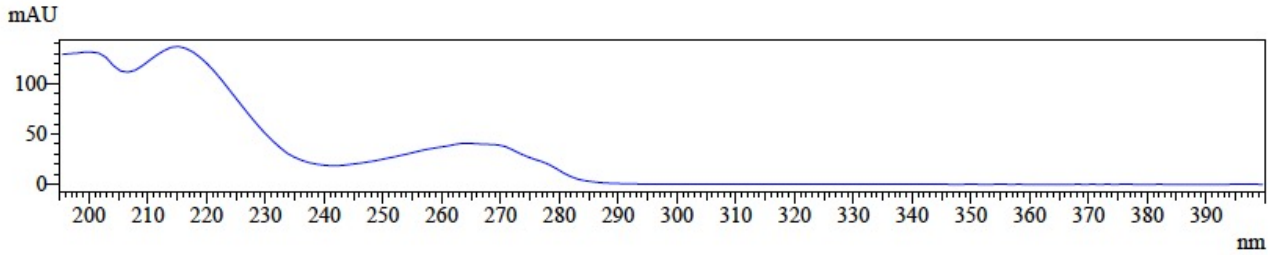
Sample Information

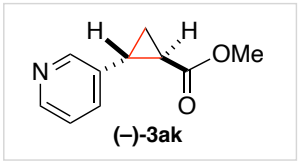
Sample Name	: XXW-0859-ASH-10%-0.8mL
Sample ID	: XXW-0859-ASH-10%-0.8mL
Data File	: XXW-0859-ASH-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram

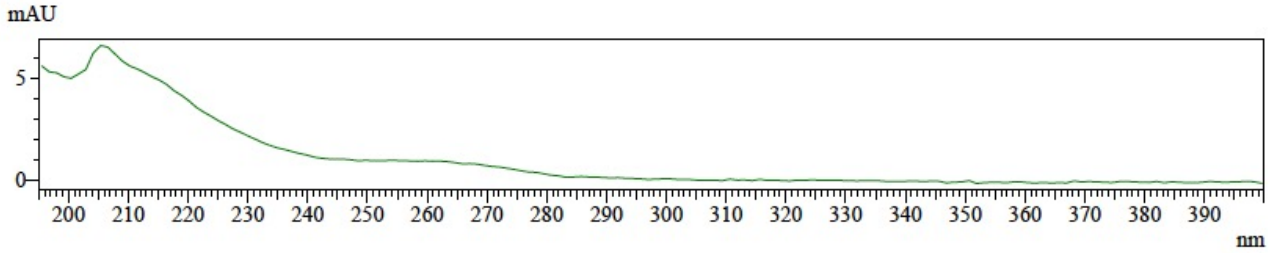


UV Spectrum
Retention time = 14.243





UV Spectrum
Retention time = 20.238

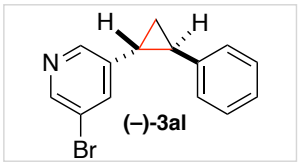


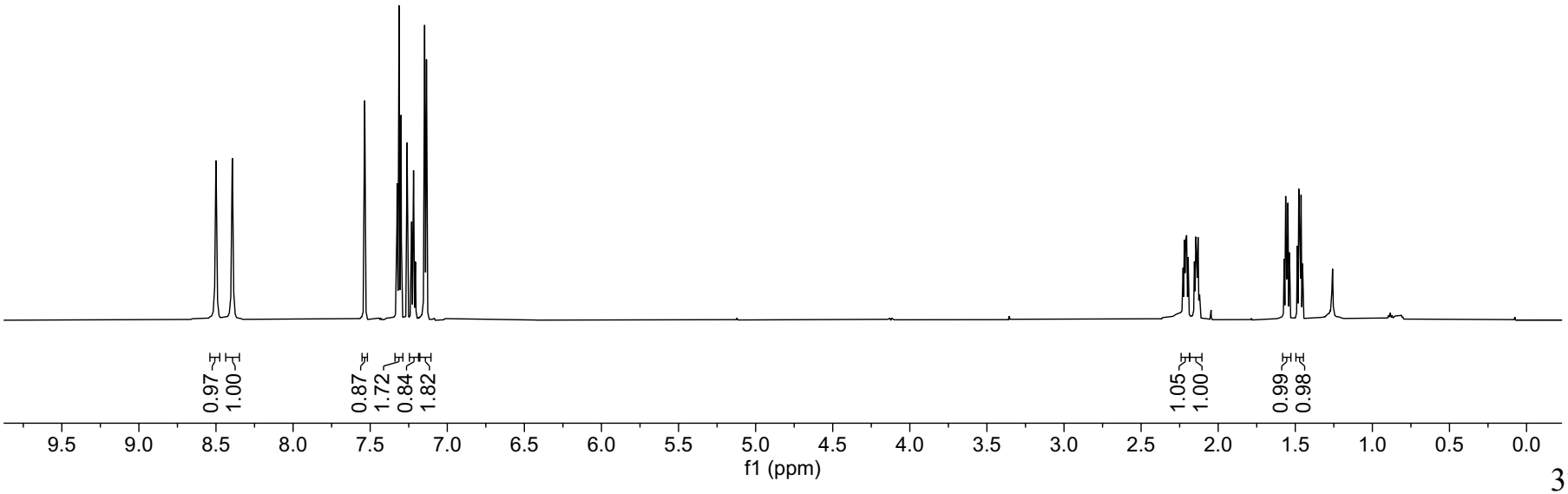
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.243	5950037	98.496
2	20.238	90830	1.504
Total		6040867	100.000

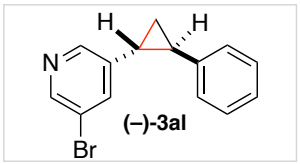
^{1}H NMR of **3al**, 600 MHz, $CDCl_3$



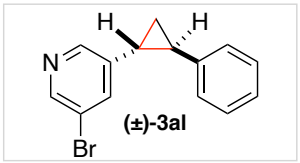


148.17
146.45
141.21
140.25
135.49
128.71
126.46
125.96
120.96
77.37
77.16
76.95
28.36
24.88
18.15

^{13}C NMR of **3al**, 150 MHz, $CDCl_3$



(–)-3al

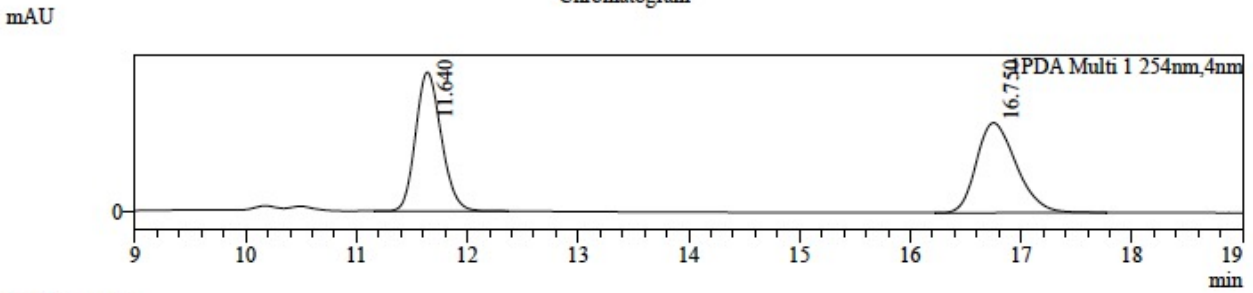


(±)-3al

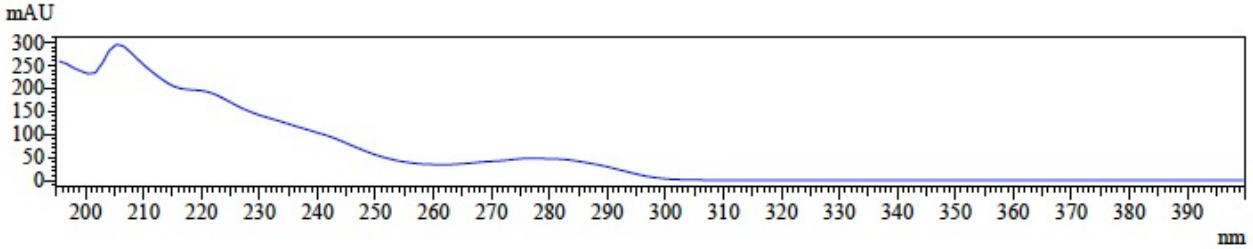
Sample Information

Sample Name	: XXW-0288-ODH--5%-0.8mL
Sample ID	: XXW-0288-ODH--5%-0.8mL
Data File	: XXW-0288-ODH--5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

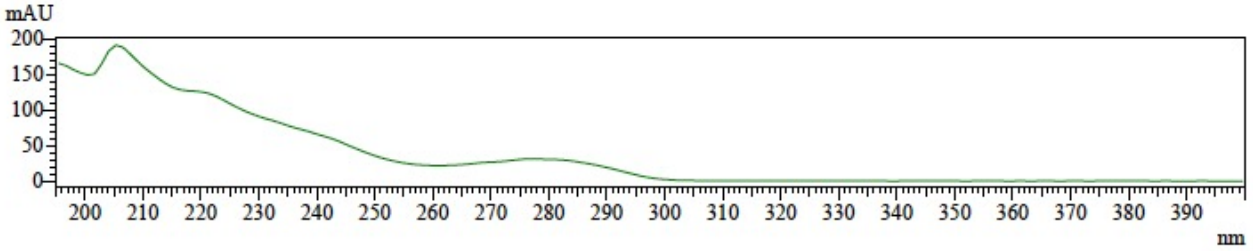
Chromatogram



UV Spectrum
Retention time = 11.640



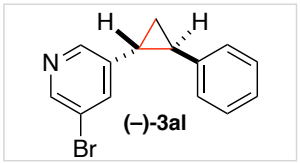
UV Spectrum
Retention time = 16.750



Peak Table

PDA Ch1 254nm

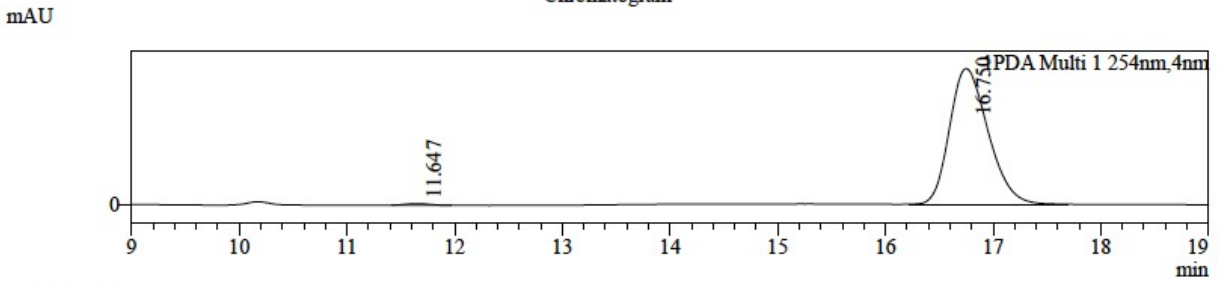
Peak#	Ret. Time	Area	Area%
1	11.640	691467	50.042
2	16.750	690315	49.958
Total		1381782	100.000



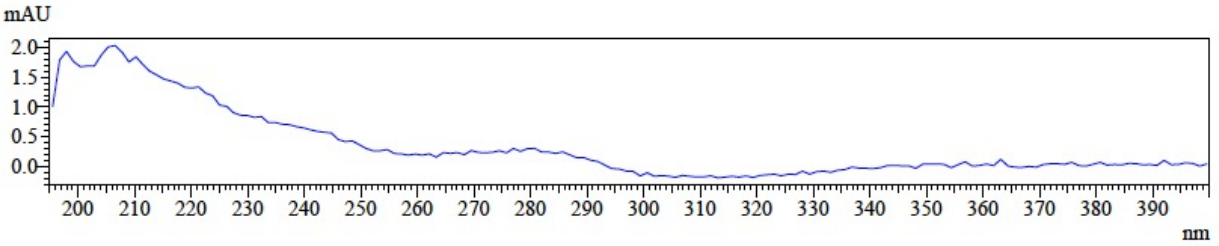
Sample Information

Sample Name	: XXW-0903-ODH--5%-0.8mL
Sample ID	: XXW-0903-ODH--5%-0.8mL
Data File	: XXW-0903-ODH--5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

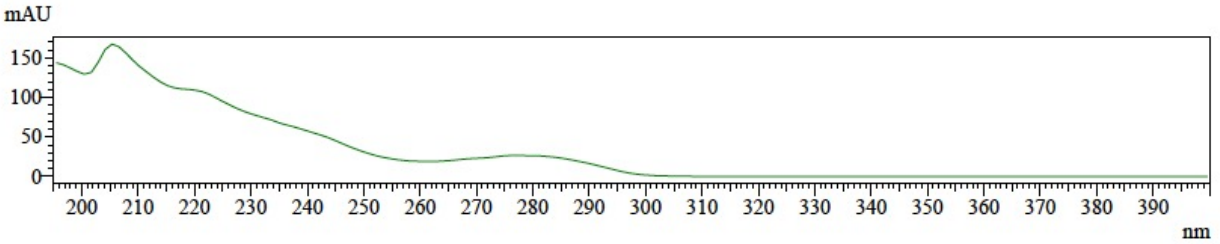
Chromatogram



UV Spectrum
Retention time = 11.647



UV Spectrum
Retention time = 16.750



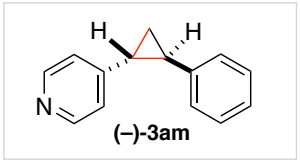
Peak Table

PDA Ch1 254nm

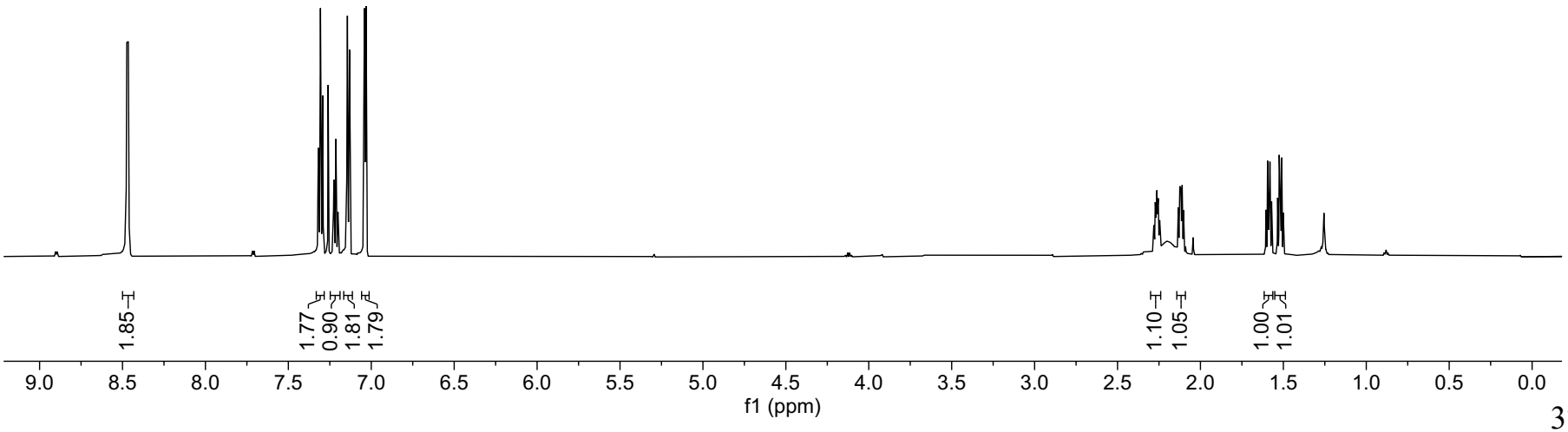
Peak#	Ret. Time	Area	Area%
1	11.647	4294	0.719
2	16.750	592974	99.281
Total		597268	100.000

8.47
8.47
7.32
7.31
7.29
7.26
7.23
7.21
7.20
7.14
7.13
7.04
7.03
2.28
2.27
2.27
2.26
2.26
2.26
2.25
2.25
2.13
2.12
2.12
2.11
2.10
1.61
1.60
1.59
1.59
1.58
1.57
1.53
1.53
1.52
1.52
1.51
1.50

^{1}H NMR of **3am**, 600 MHz, $CDCl_3$

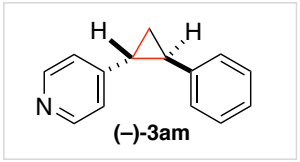


(–)-3am

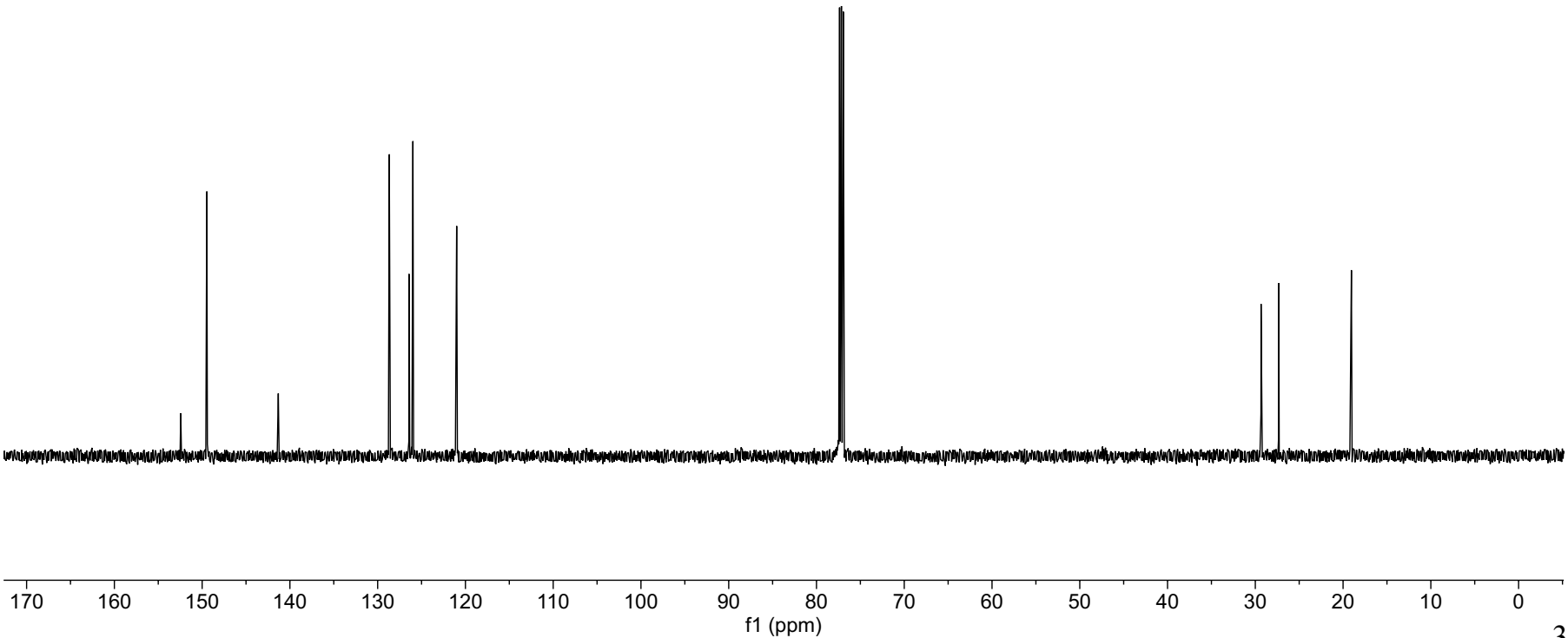


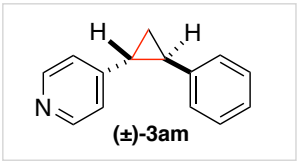
152.44
149.47
141.32
128.68
126.42
125.98
121.00
77.37
77.16
76.95
29.35
27.33
19.05

^{13}C NMR of **3am**, 150 MHz, $CDCl_3$



(–)-3am



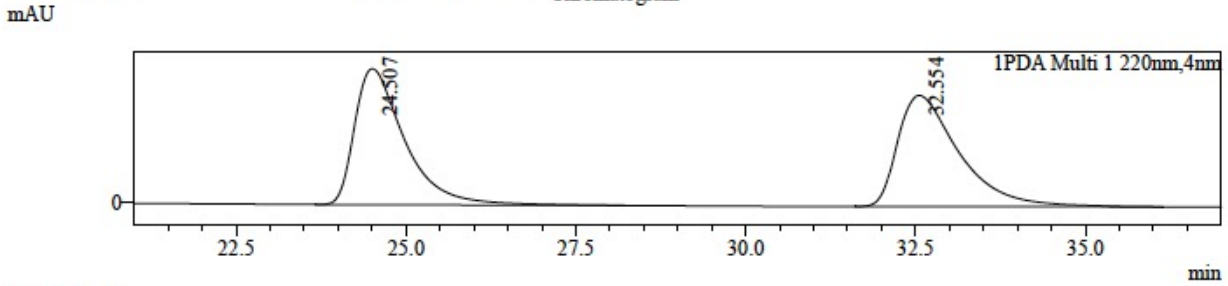


(±)-3am

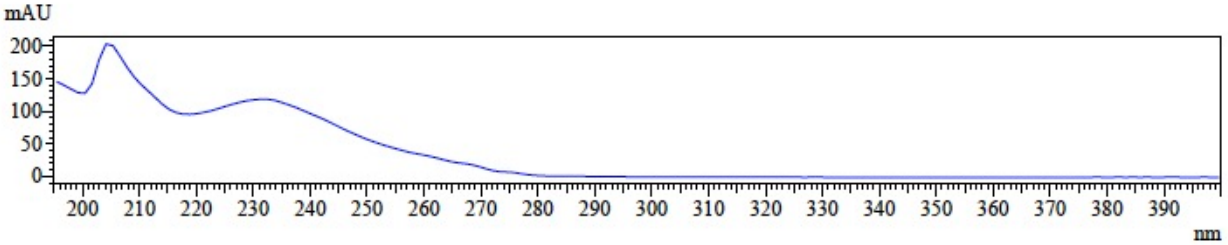
Sample Information

Sample Name	: XXW-0901-rac-ODH--5%-0.8mL
Sample ID	: XXW-0901-rac-ODH--5%-0.8mL
Data File	: XXW-0901-rac-ODH--5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

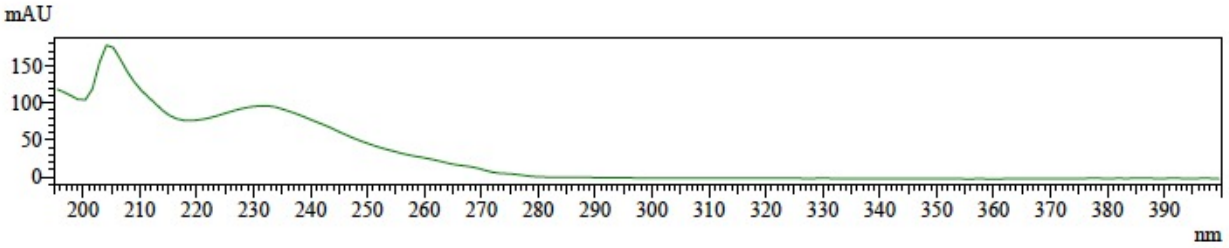
Chromatogram



UV Spectrum
Retention time = 24.507



UV Spectrum
Retention time = 32.554



Peak Table

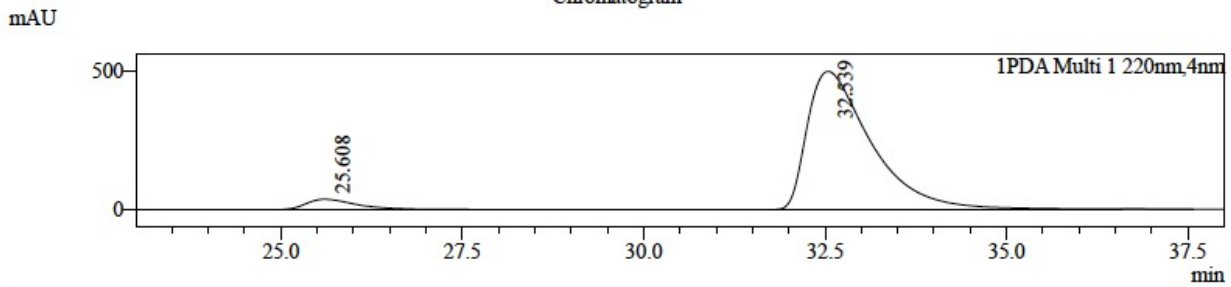
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.507	5135162	49.946
2	32.554	5146268	50.054
Total		10281430	100.000

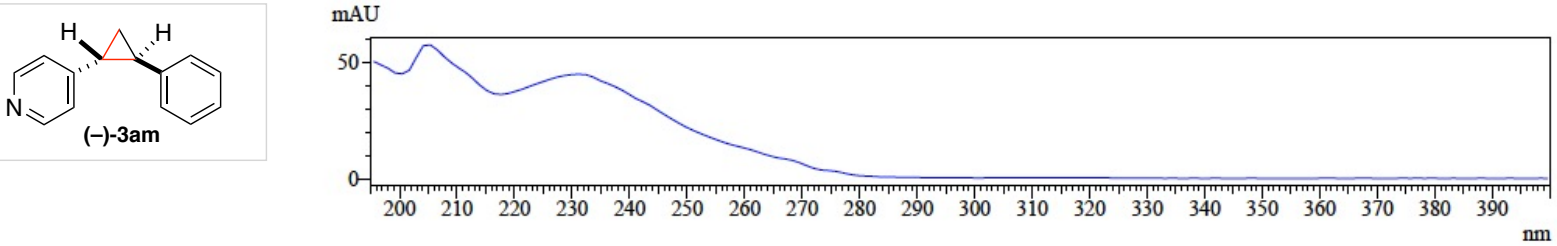
Sample Information

Sample Name	: XXW-0864-ODH--5%-0.8mL
Sample ID	: XXW-0864-ODH--5%-0.8mL
Data File	: XXW-0864-ODH--5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

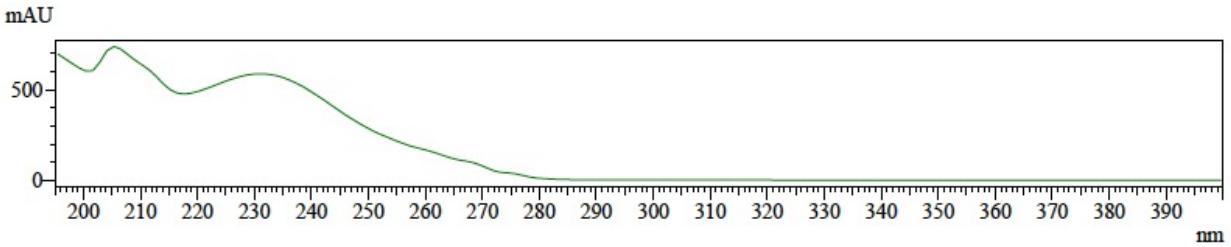
Chromatogram



UV Spectrum
Retention time = 25.608



UV Spectrum
Retention time = 32.539

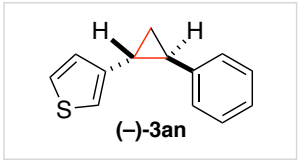


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	25.608	1797606	5.560
2	32.539	30536272	94.440
Total		32333878	100.000

^{1}H NMR of **3an**, 600 MHz, $CDCl_3$



(–)-3an

belongs to another set of diastereomer

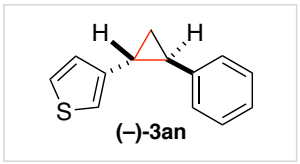
H_2O

2.05 1.25 0.98 2.08 0.89 0.94 0.97 1.01 2.25

f1 (ppm)

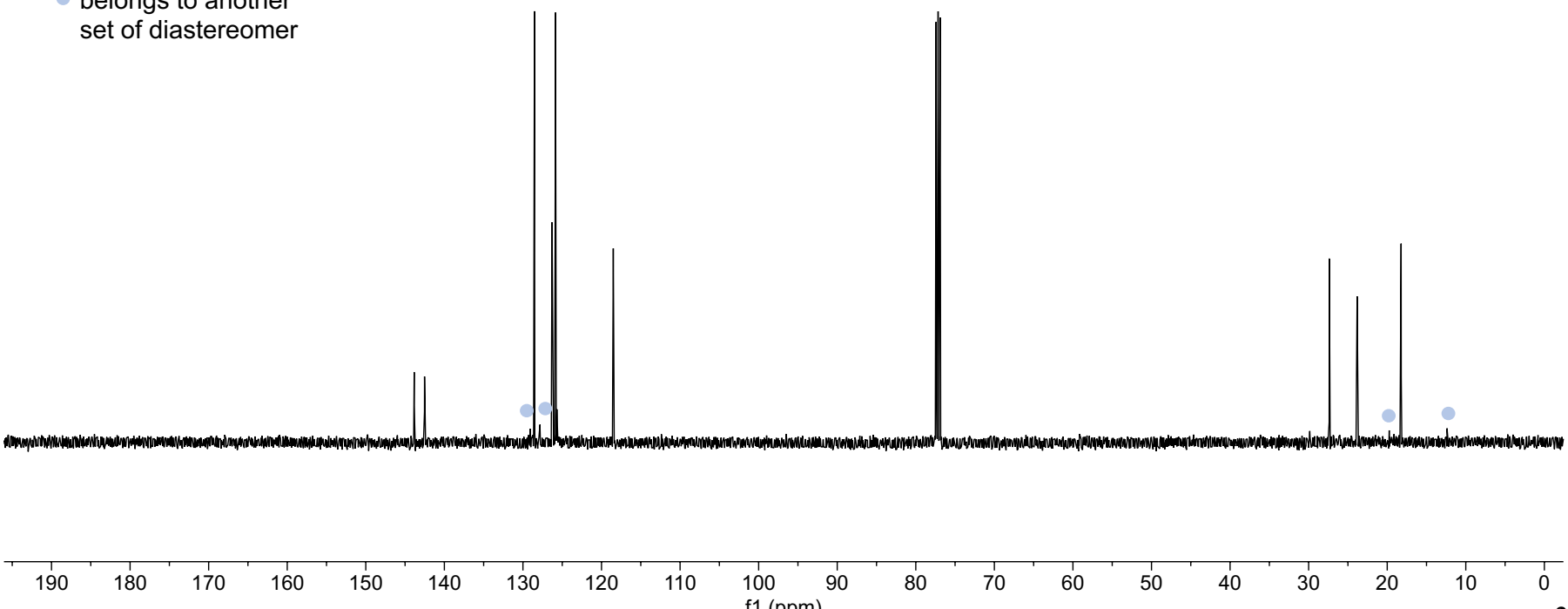
143.84
142.53
128.53
126.30
125.89
125.86
125.70
118.50
77.41
77.16
76.90
27.37
23.83
18.23

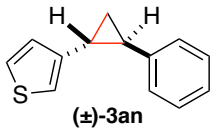
^{13}C NMR of **3an**, 125 MHz, $CDCl_3$



(–)-3an

● belongs to another set of diastereomer



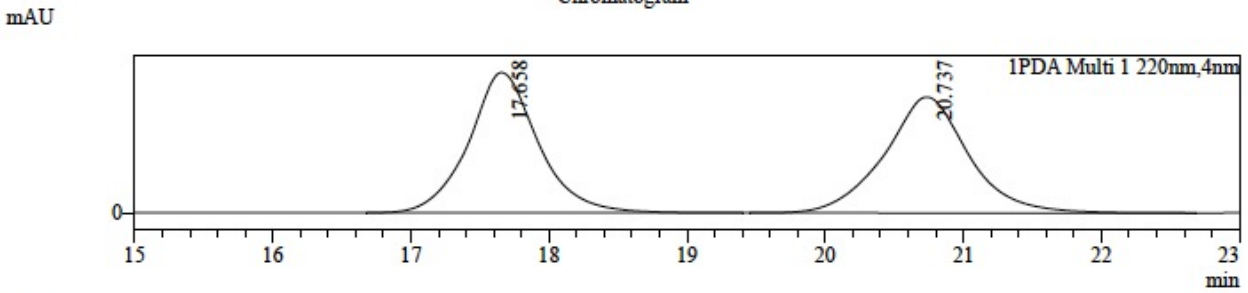


(±)-3an

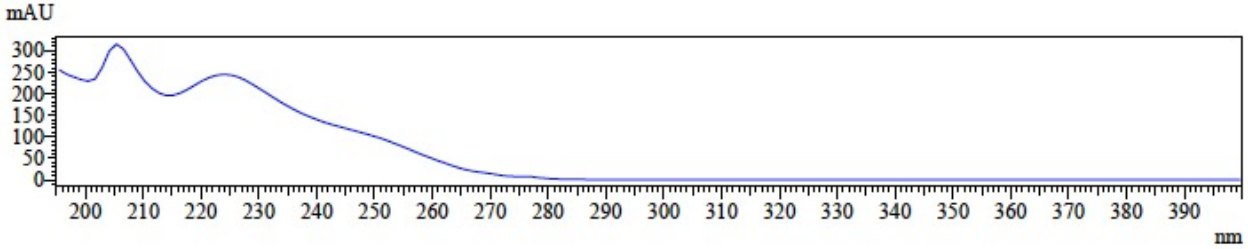
Sample Information

Sample Name	: XXW-1334--OJH5%-0.8mL001
Sample ID	: XXW-1334--OJH5%-0.8mL001
Data File	: XXW-1334--OJH5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

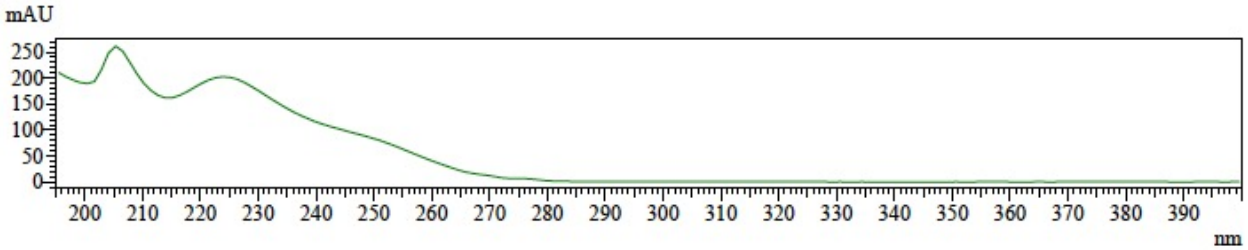
Chromatogram



UV Spectrum
Retention time = 17.658



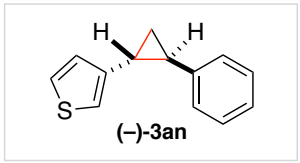
UV Spectrum
Retention time = 20.737



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.658	7963820	49.990
2	20.737	7966978	50.010
Total		15930798	100.000

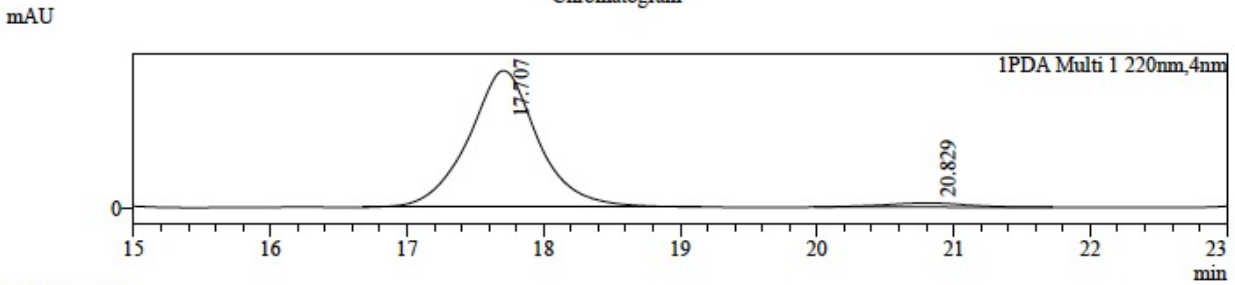


(–)-3an

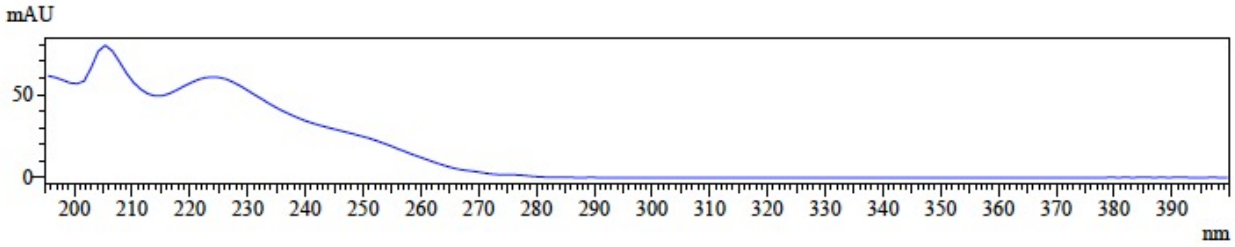
Sample Information

Sample Name	: XXW-1332--OJH5%-0.8mL
Sample ID	: XXW-1332--OJH5%-0.8mL
Data File	: XXW-1332--OJH5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

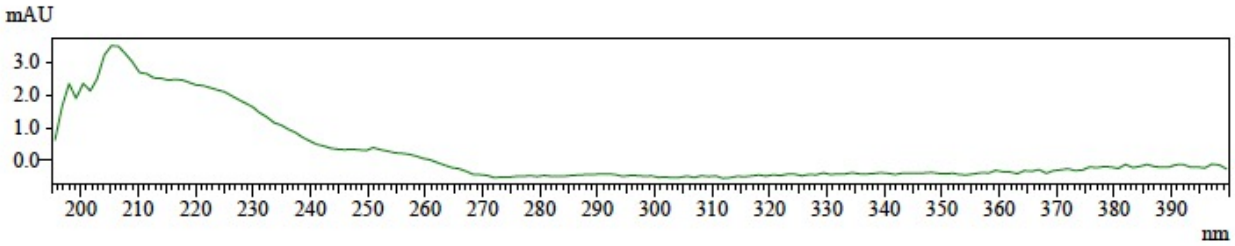
Chromatogram



UV Spectrum
Retention time = 17.707



UV Spectrum
Retention time = 20.829

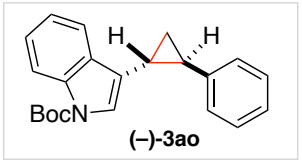


Peak Table

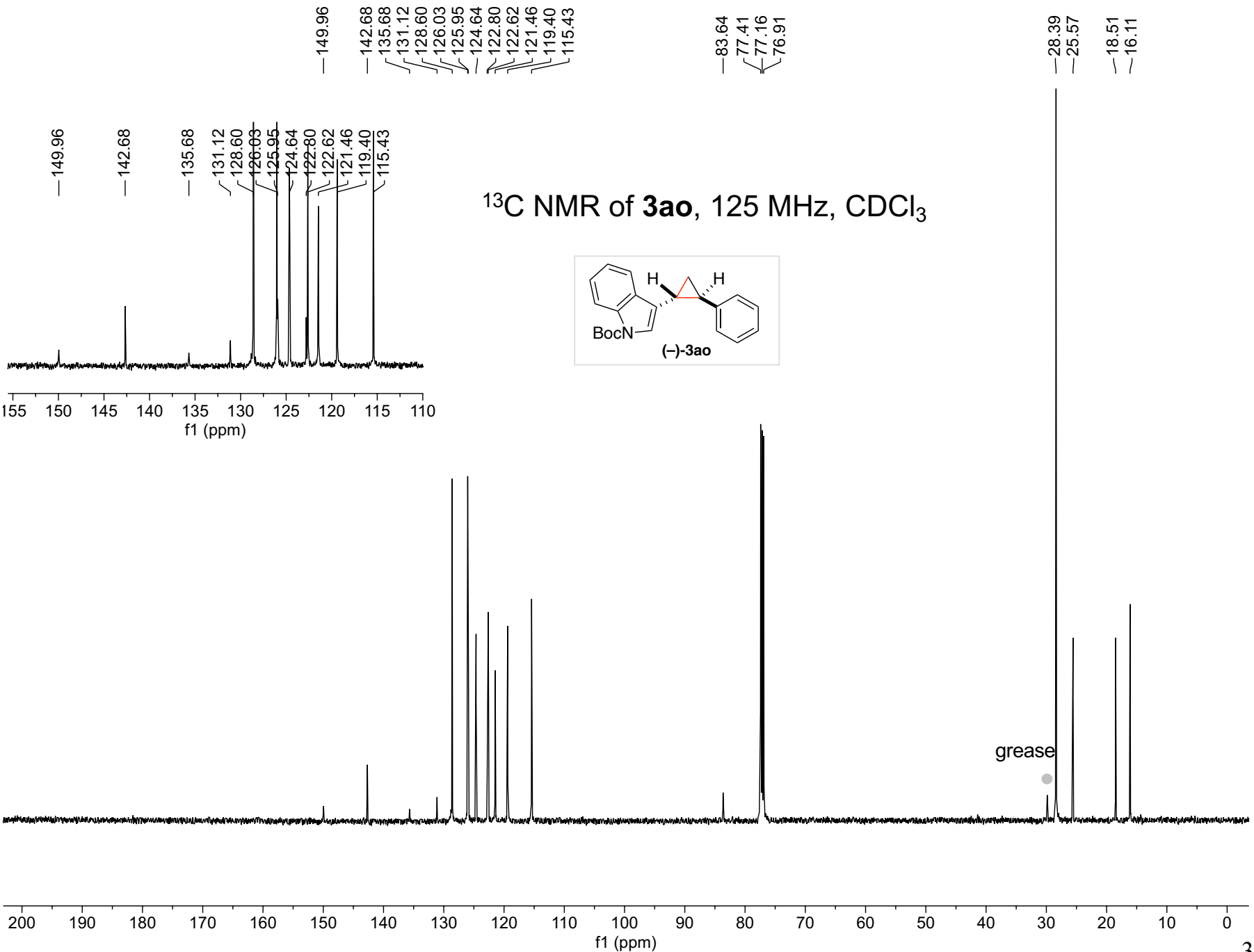
PDA Ch1 220nm

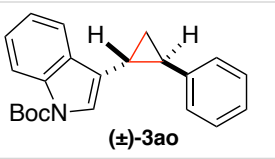
Peak#	Ret. Time	Area	Area%
1	17.707	1974865	96.571
2	20.829	70131	3.429
Total		2044996	100.000

^{1}H NMR of **3ao**, 600 MHz, $CDCl_3$



(–)-3ao


149.96
142.68
135.68
131.12
128.60
126.03
125.95
124.64
122.80
122.62
121.46
119.40
115.43
83.64
77.41
77.16
76.91
28.39
25.57
18.51
16.11
^{13}C NMR of **3ao**, 125 MHz, $CDCl_3$
H
H
BocN
(–)-3ao
grease
f1 (ppm)

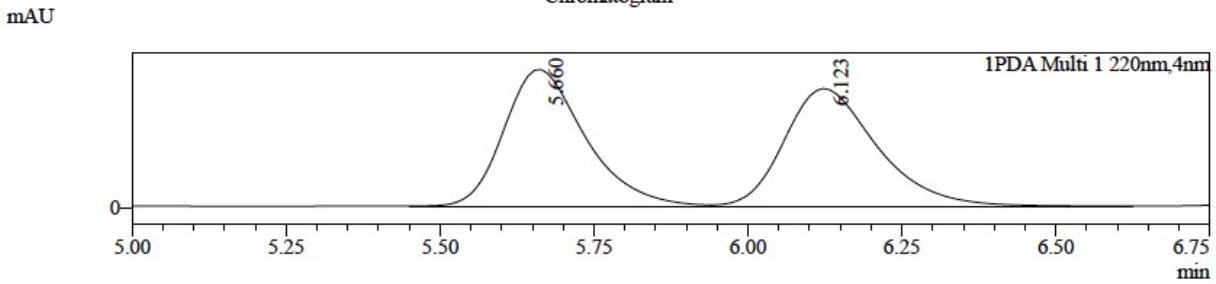


(±)-3ao

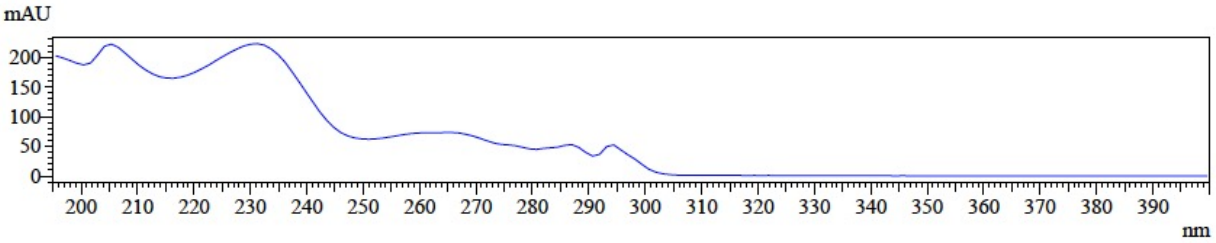
Sample Information

Sample Name	: XXW-0499-ODH-5%-0.8mL
Sample ID	: XXW-0499-ODH-5%-0.8mL
Data File	: XXW-0499-ODH-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

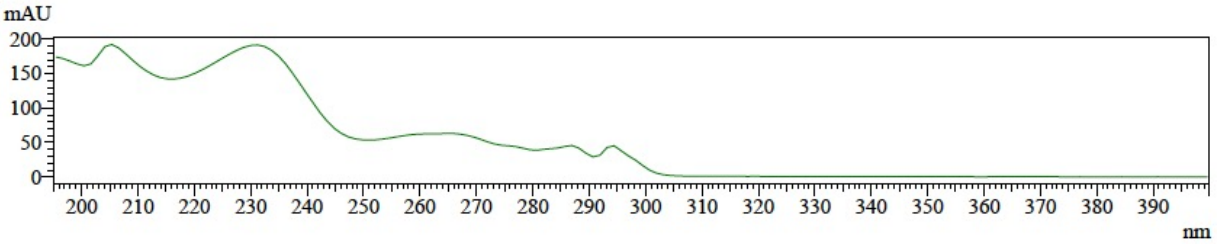
Chromatogram



UV Spectrum
Retention time = 5.660



UV Spectrum
Retention time = 6.123



Peak Table

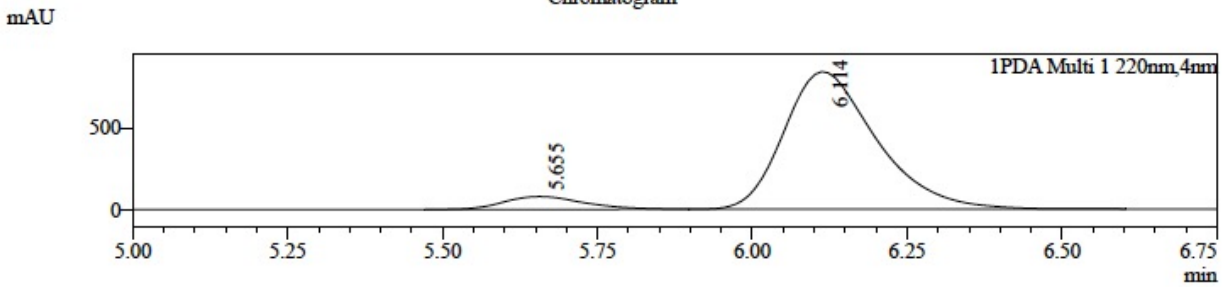
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.660	1601673	50.479
2	6.123	1571307	49.521
Total		3172980	100.000

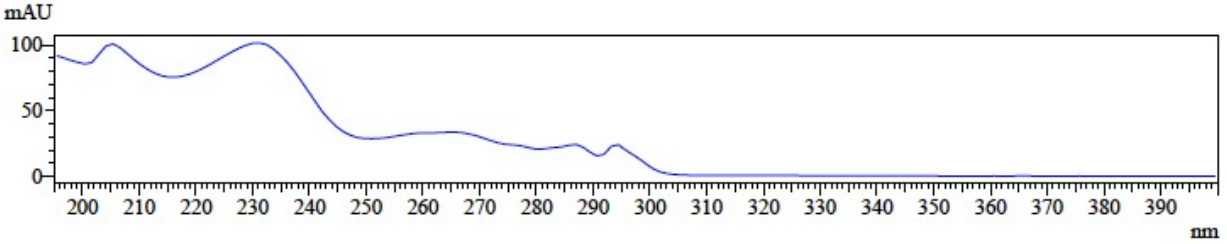
Sample Information

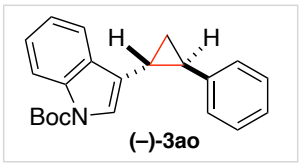
Sample Name	: XXW-0865-ODH-5%-0.8mL
Sample ID	: XXW-0865-ODH-5%-0.8mL
Data File	: XXW-0865-ODH-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram

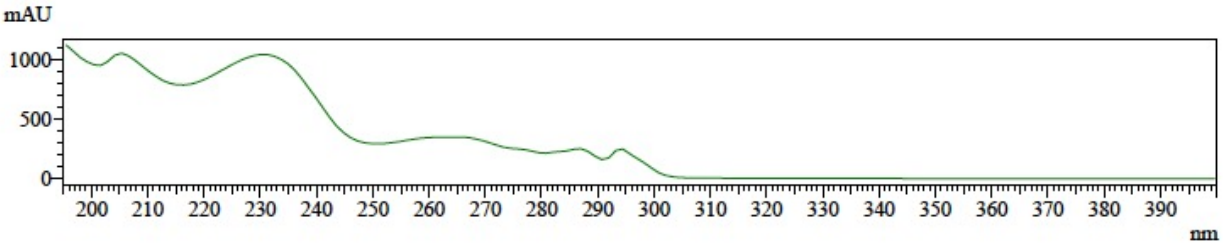


UV Spectrum
Retention time = 5.655





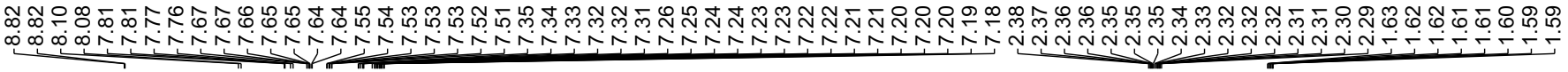
UV Spectrum
Retention time = 6.114



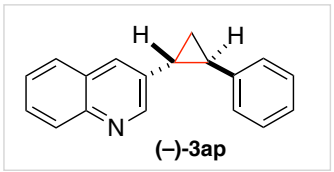
Peak Table

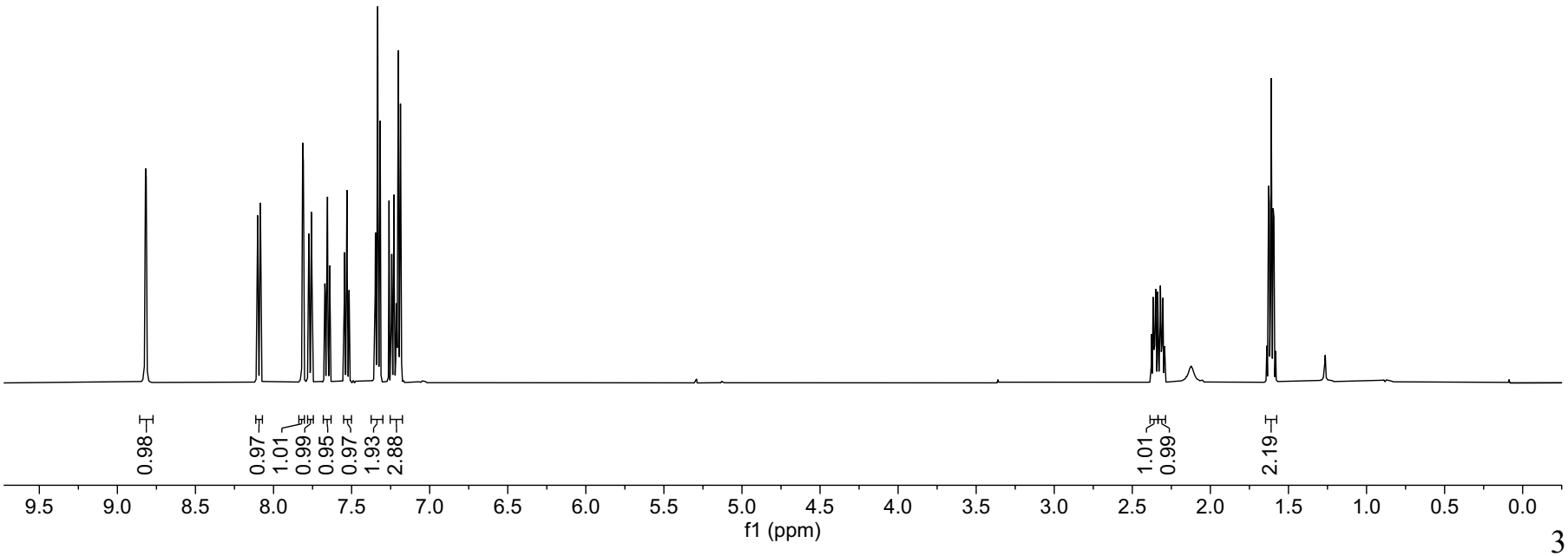
PDA Ch1 220nm

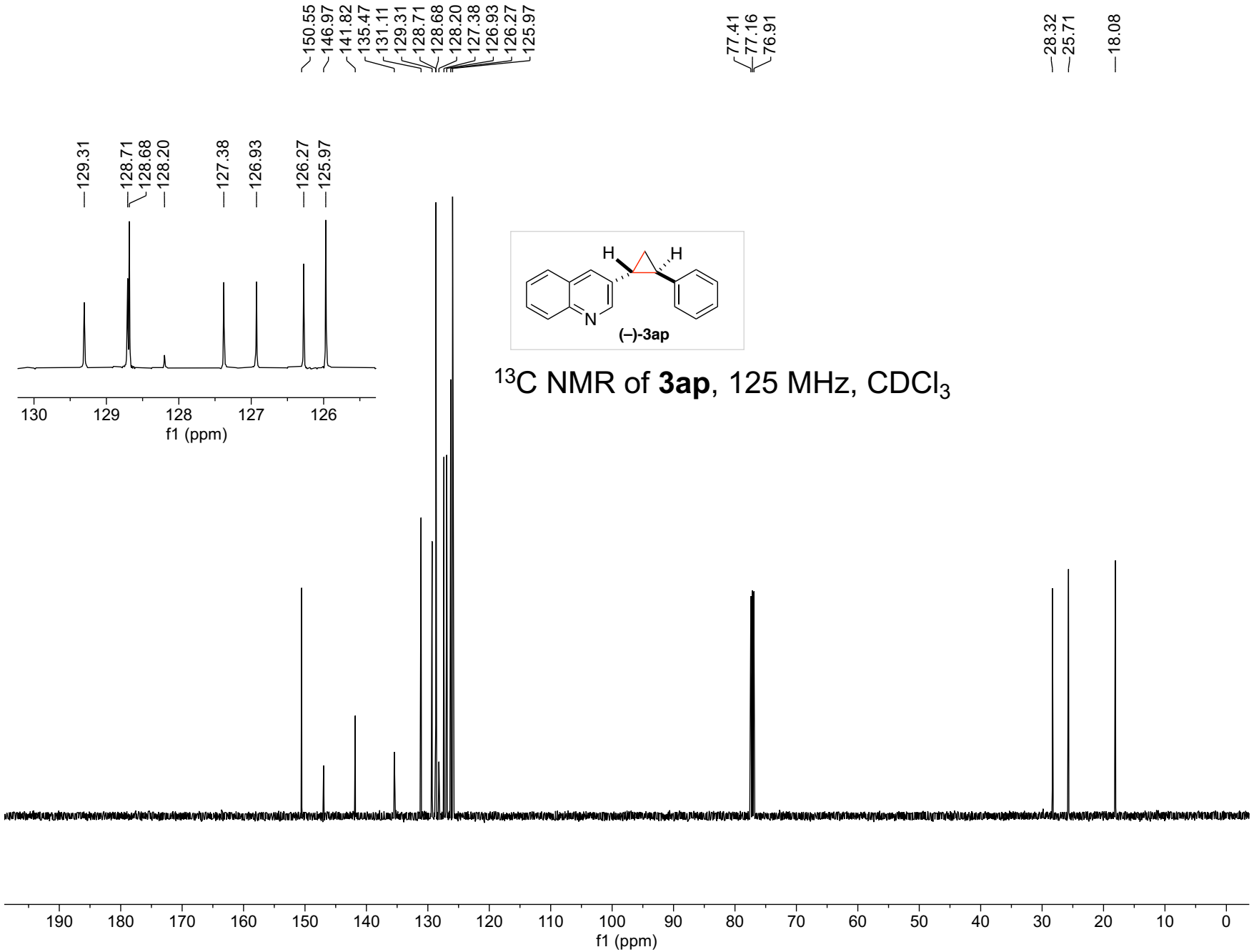
Peak#	Ret. Time	Area	Area%
1	5.655	707705	7.458
2	6.114	8780960	92.542
Total		9488664	100.000



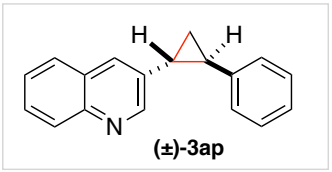
^{1}H NMR of **3ap**, 500 MHz, $CDCl_3$







^{13}C NMR of **3ap**, 125 MHz, $CDCl_3$

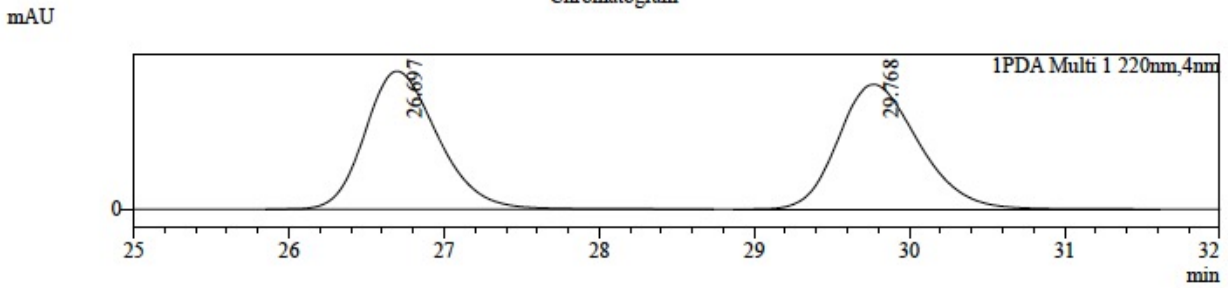


(±)-3ap

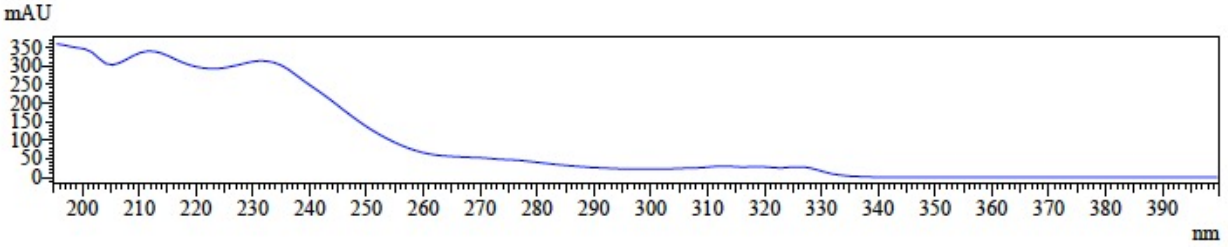
Sample Information

Sample Name	: XXW-0360-ID-5%-0.8mL
Sample ID	: XXW-0360-ID-5%-0.8mL
Data File	: XXW-0360-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

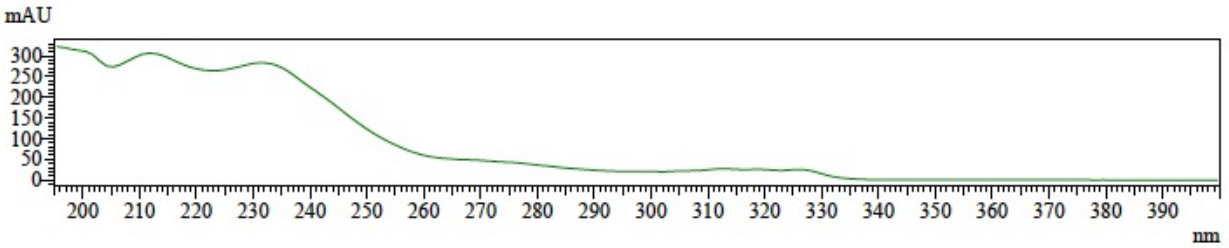
Chromatogram



UV Spectrum
Retention time = 26.697



UV Spectrum
Retention time = 29.768



Peak Table

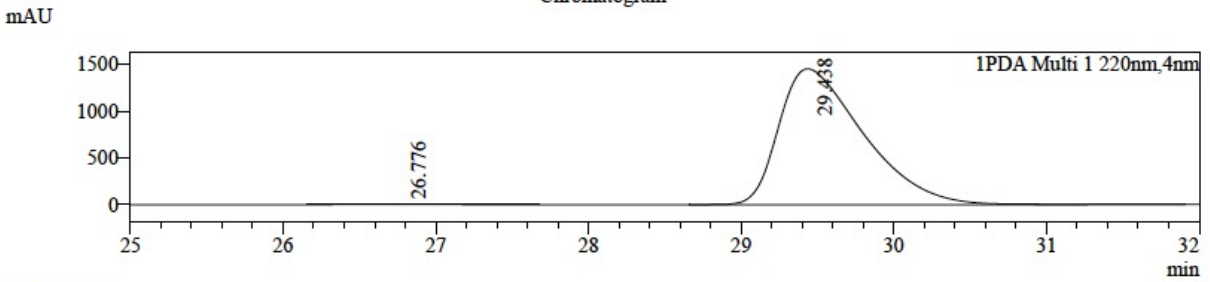
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	26.697	9808145	50.009
2	29.768	9804518	49.991
Total		19612663	100.000

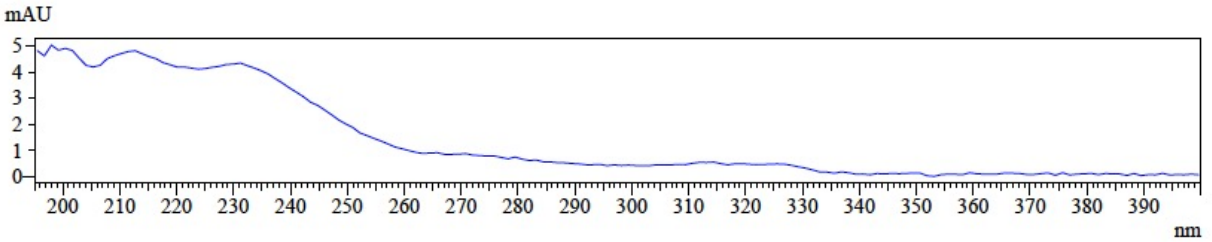
Sample Information

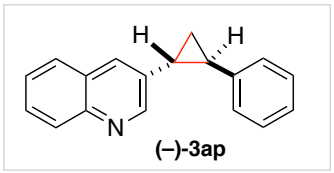
Sample Name	: XXW-0854-ID-5%-0.8mL
Sample ID	: XXW-0854-ID-5%-0.8mL
Data File	: XXW-0854-ID-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram

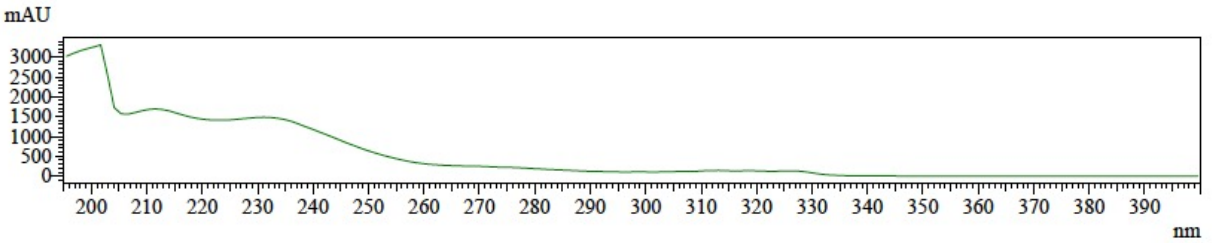


UV Spectrum
Retention time = 26.776





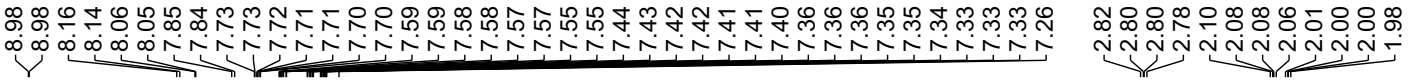
UV Spectrum
Retention time = 29.438



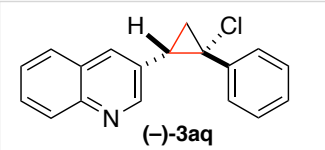
Peak Table

PDA Ch1 220nm

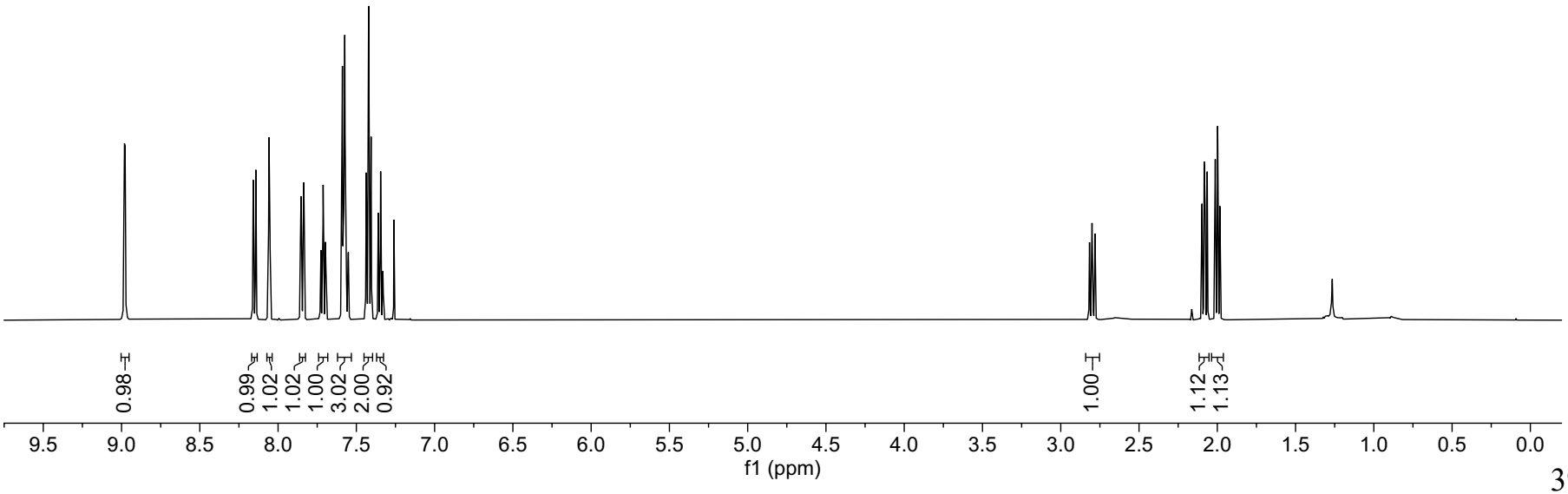
Peak#	Ret. Time	Area	Area%
1	26.776	124178	0.223
2	29.438	55656271	99.777
Total		55780449	100.000

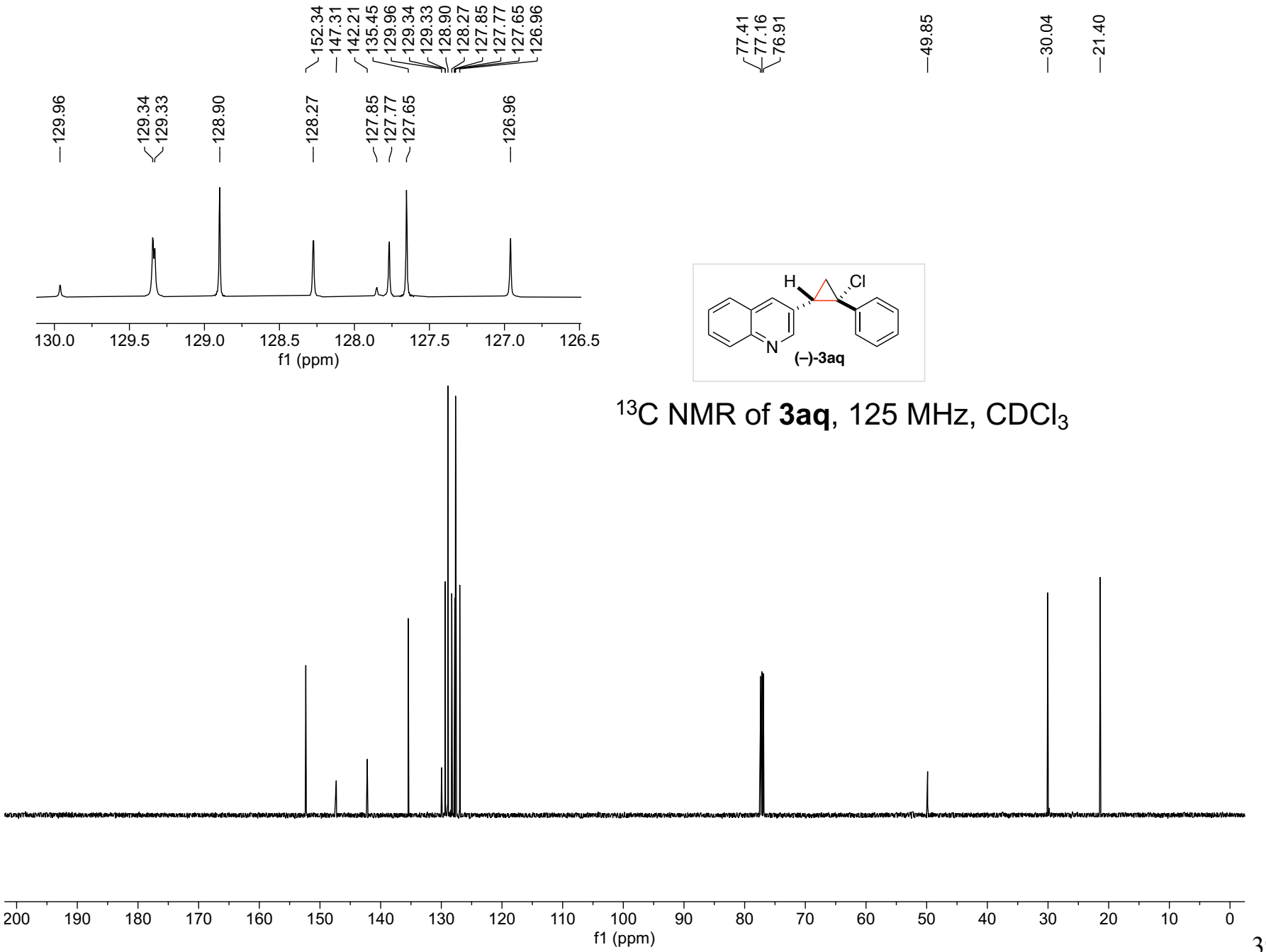


^{1}H NMR of **3aq**, 500 MHz, $CDCl_3$

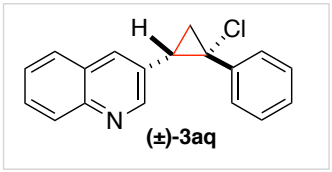


(–)-3aq





^{13}C NMR of **3aq**, 125 MHz, $CDCl_3$

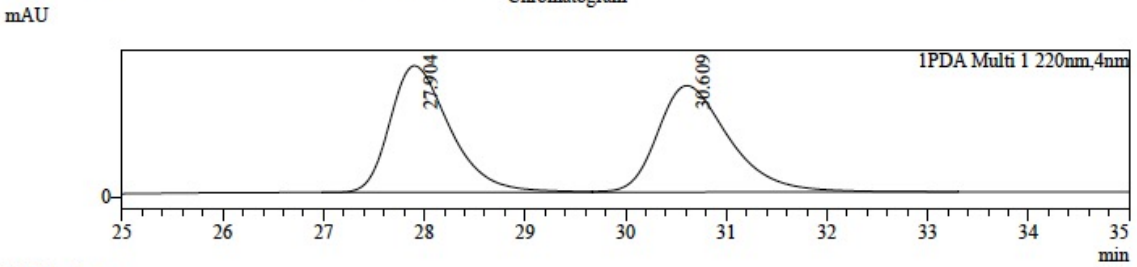


(±)-3aq

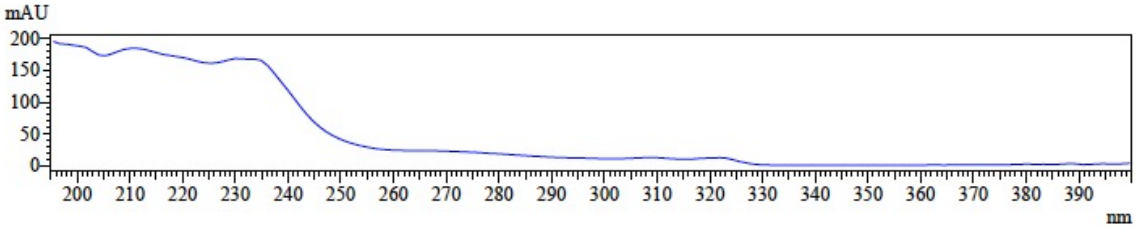
Sample Information

Sample Name	: XXW-0434-IF--5%--0.8mL-1
Sample ID	: XXW-0434-IF--5%--0.8mL-1
Data File	: XXW-0434-IF--5%--0.8mL-2.lcd
Method File	: XXW-5%.0.8.mL.lcm

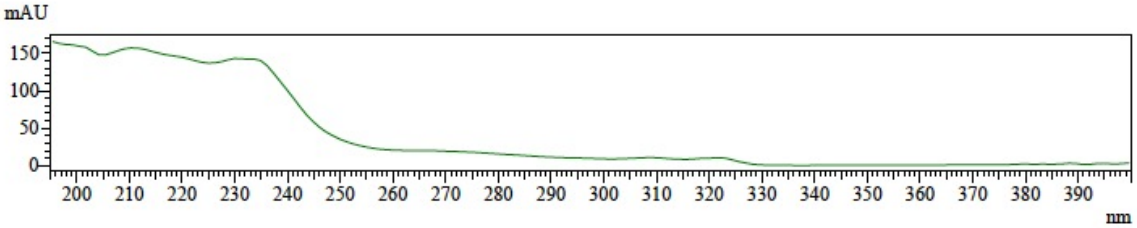
Chromatogram



UV Spectrum
Retention time = 27.904



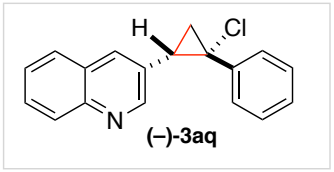
UV Spectrum
Retention time = 30.609



Peak Table

PDA Ch1 220nm

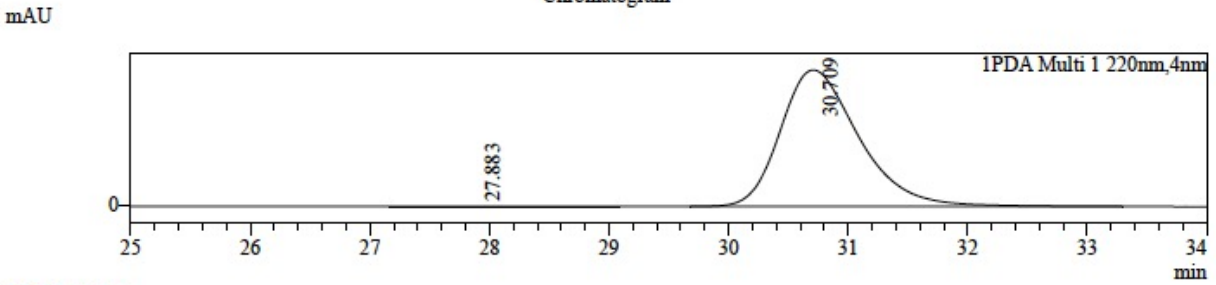
Peak#	Ret. Time	Area	Area%
1	27.904	6764417	49.895
2	30.609	6793009	50.105
Total		13557426	100.000



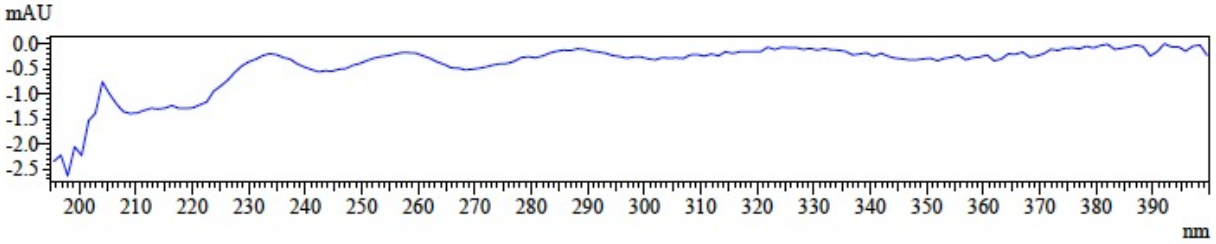
Sample Information

Sample Name	: XXW-1330-IF-5%-0.8mL
Sample ID	: XXW-1330-IF-5%-0.8mL
Data File	: XXW-1330-IF-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

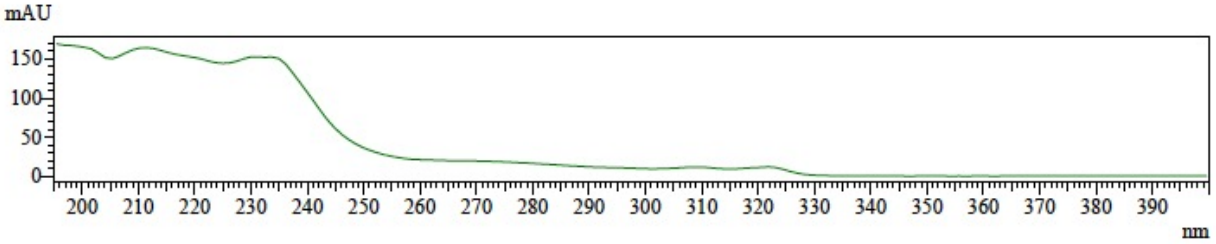
Chromatogram



UV Spectrum
Retention time = 27.883



UV Spectrum
Retention time = 30.709

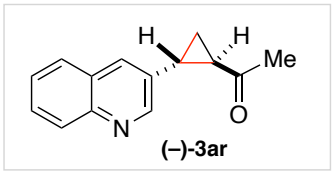


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	27.883	582	0.008
2	30.709	6943317	99.992
Total		6943900	100.000

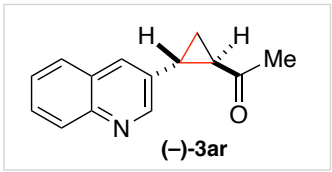
^{1}H NMR of **3ar**, 600 MHz, $CDCl_3$



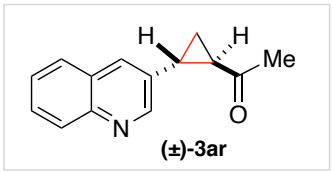
(–)-3ar

206.36
150.19
147.32
133.27
132.01
129.42
129.15
127.92
127.42
127.14
77.37
77.16
76.95
32.58
31.10
26.52
18.91

^{13}C NMR of **3ar**, 150 MHz, $CDCl_3$



(–)-3ar

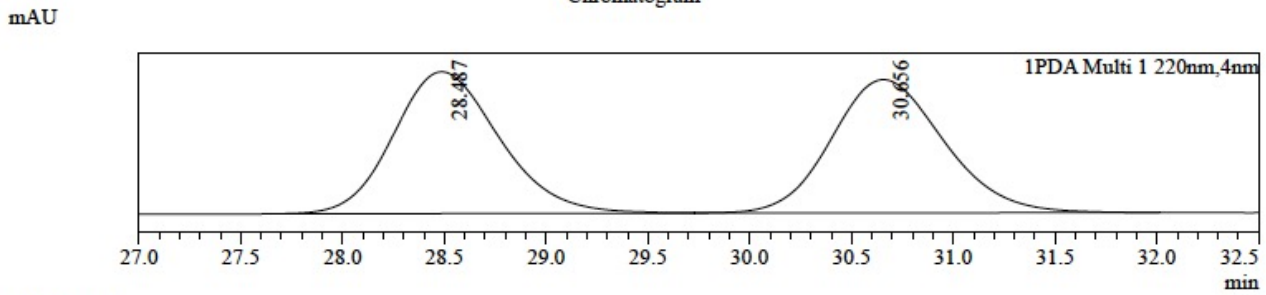


(±)-3ar

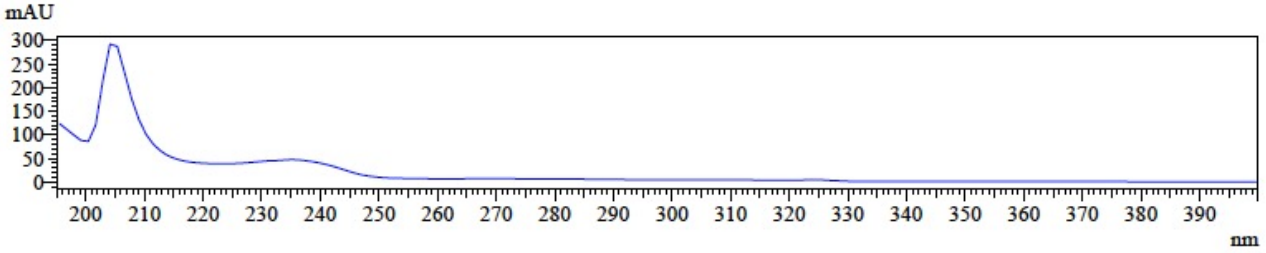
Sample Information

Sample Name	: XXW-0506-20%-IE-0.8mL
Sample ID	: XXW-0506-20%-IE-0.8mL
Data File	: XXW-0506-20%-IE-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

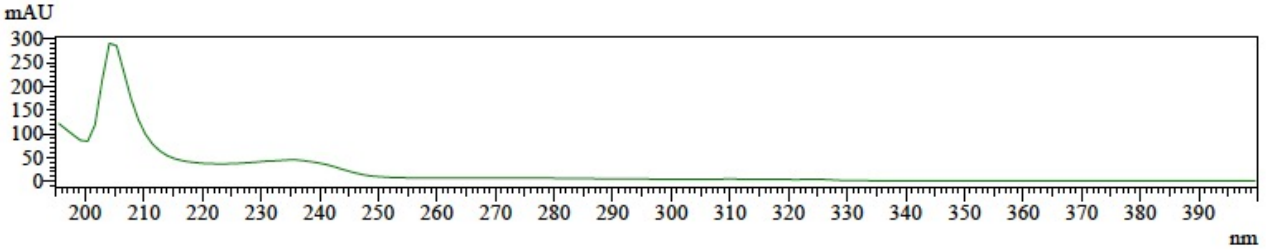
Chromatogram



UV Spectrum
Retention time = 28.487



UV Spectrum
Retention time = 30.656



Peak Table

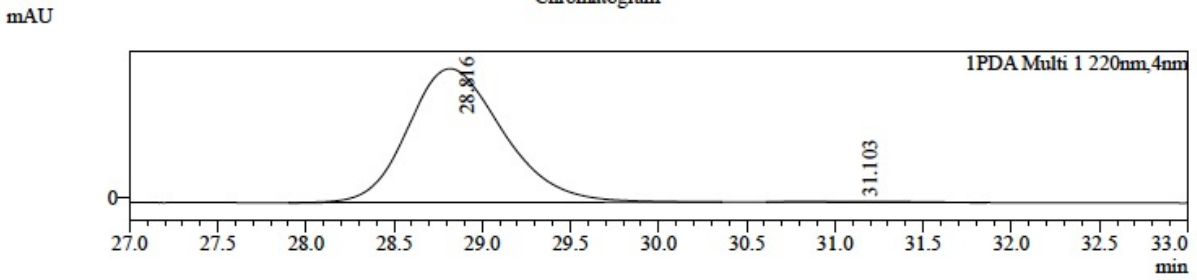
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	28.487	1211416	50.016
2	30.656	1210651	49.984
Total		2422068	100.000

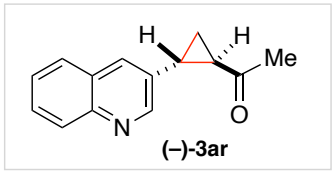
Sample Information

Sample Name	: XXW-1327-IE-20%-0.8mL
Sample ID	: XXW-1327-IE-20%-0.8mL
Data File	: XXW-1327-IE-20%-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

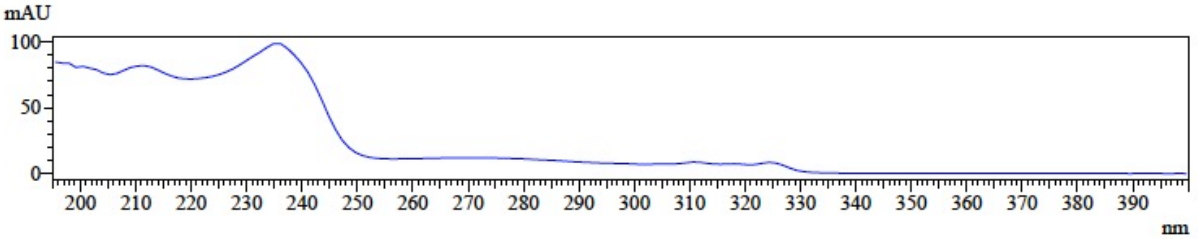
Chromatogram



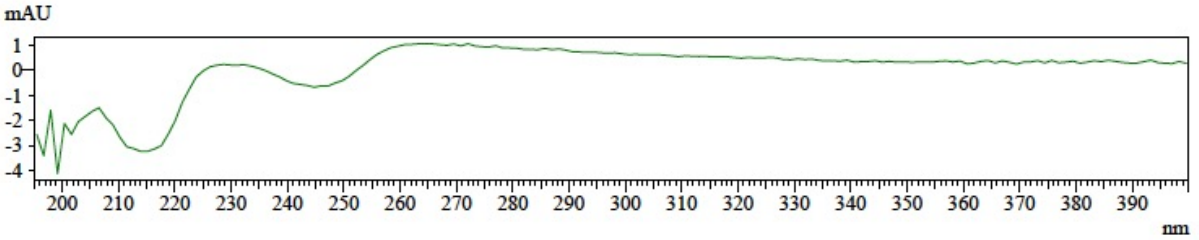
UV Spectrum
Retention time = 28.816



(–)-3ar



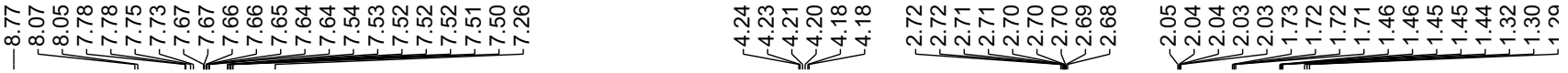
UV Spectrum
Retention time = 31.103



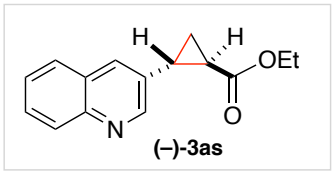
Peak Table

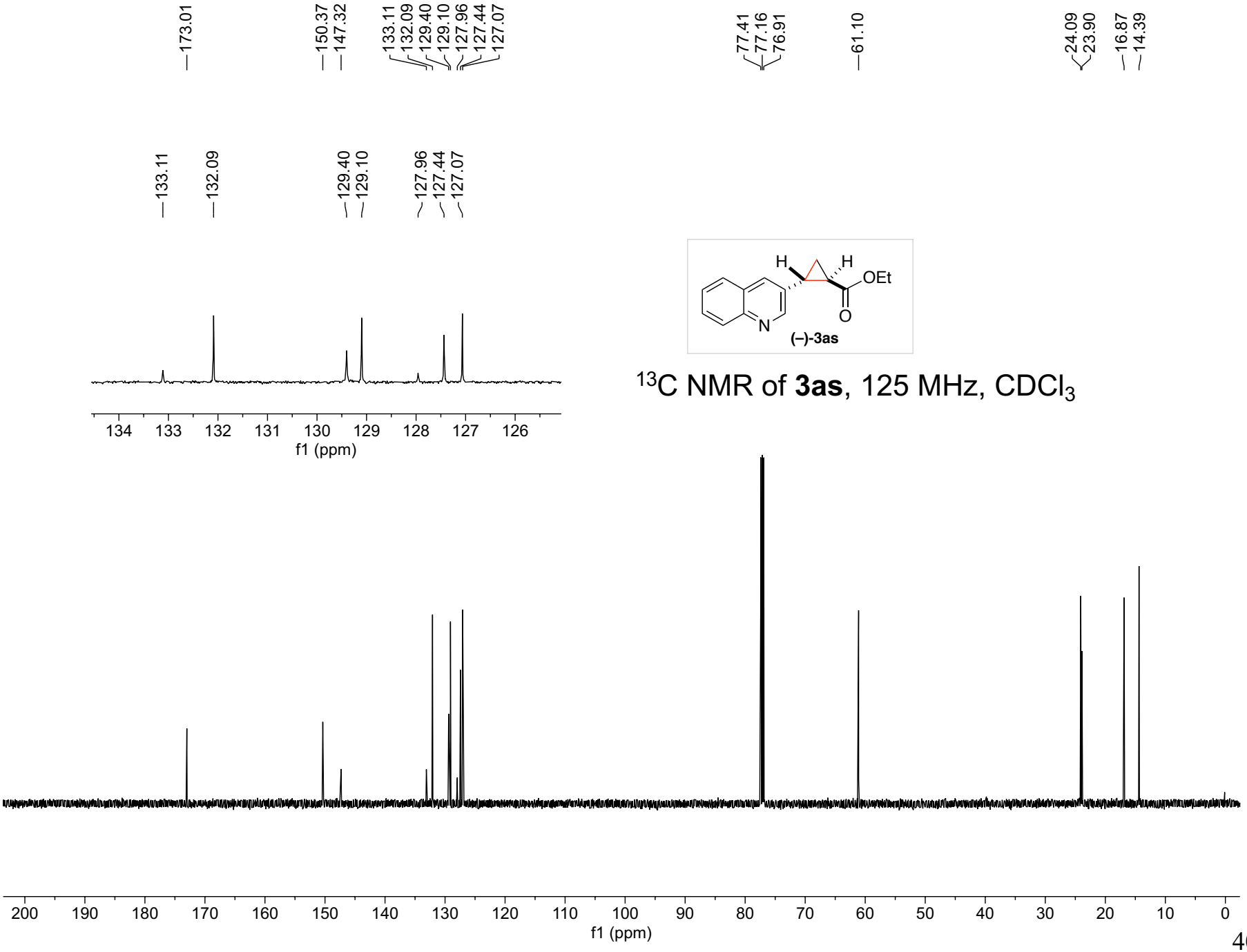
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	28.816	2833027	99.236
2	31.103	21823	0.764
Total		2854850	100.000



^{1}H NMR of **3as**, 500 MHz, $CDCl_3$



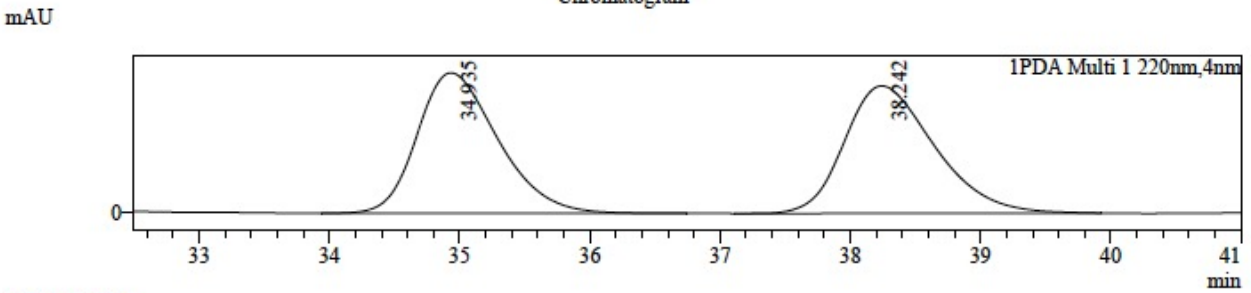


^{13}C NMR of **3as**, 125 MHz, $CDCl_3$

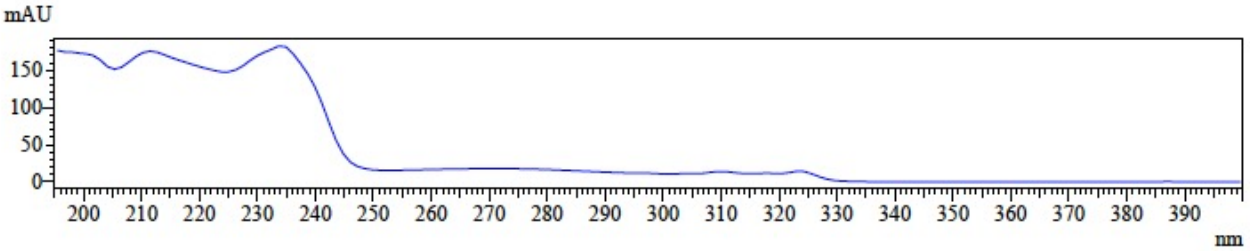
Sample Information

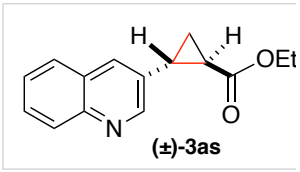
Sample Name	: XXW-0502-IE-10%-0.8mL
Sample ID	: XXW-0502-IE-10%-0.8mL
Data File	: XXW-0502-IE-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



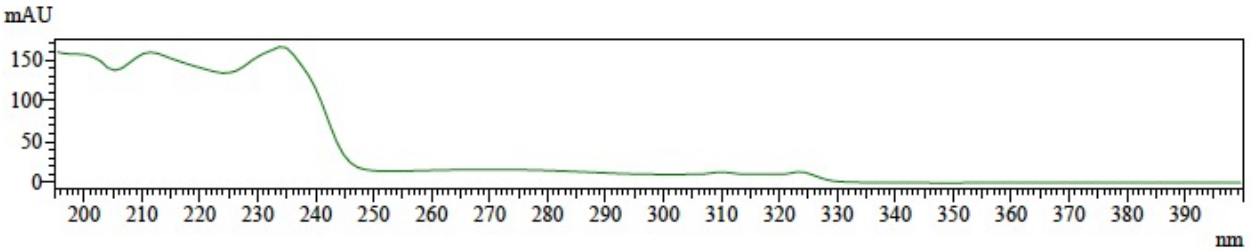
UV Spectrum
Retention time = 34.935





(±)-3as

UV Spectrum
Retention time = 38.242



Peak Table

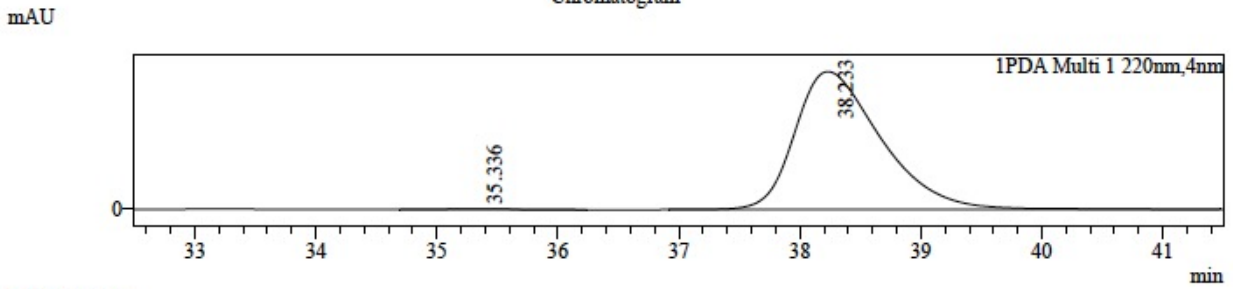
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	34.935	6709239	49.637
2	38.242	6807392	50.363
Total		13516630	100.000

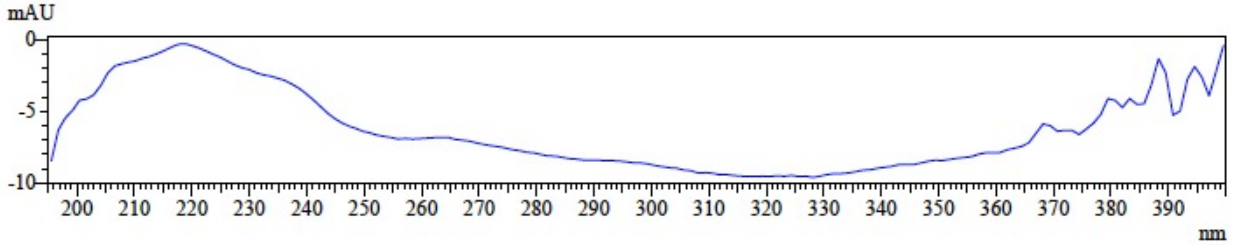
Sample Information

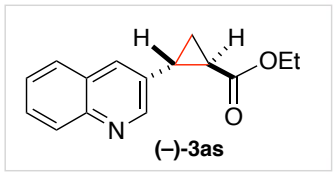
Sample Name	: XXW-1328-IE-10%-0.8mL
Sample ID	: XXW-1328-IE-10%-0.8mL
Data File	: XXW-1328-IE-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



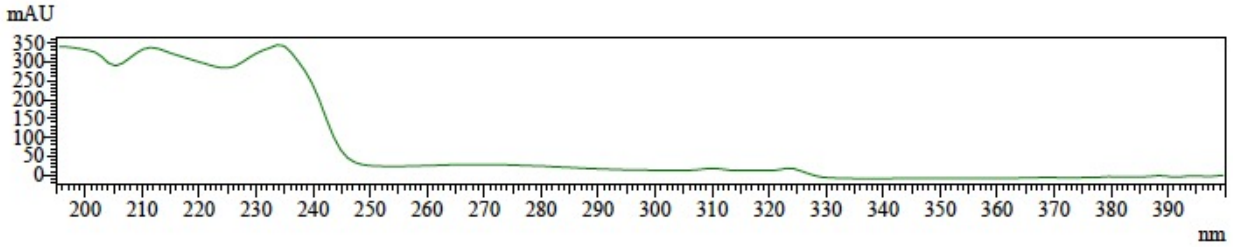
UV Spectrum
Retention time = 35.336





(–)-3as

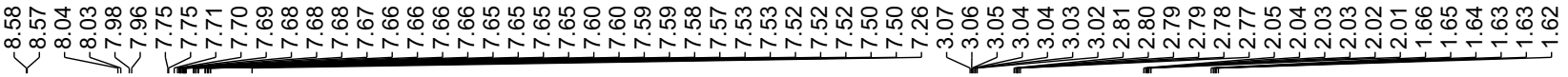
UV Spectrum
Retention time = 38.233



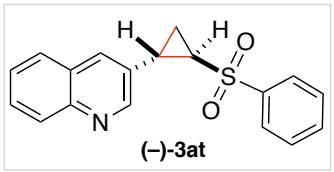
Peak Table

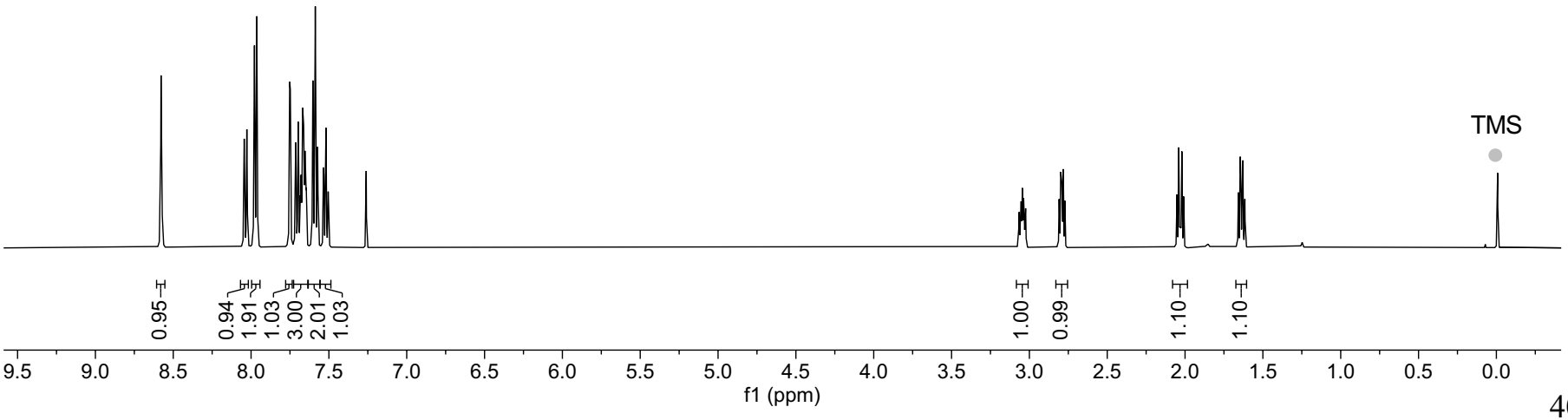
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	35.336	54117	0.362
2	38.233	14908033	99.638
Total		14962150	100.000

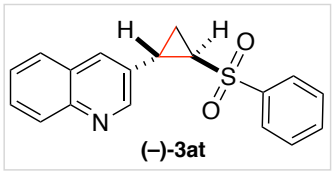


^{1}H NMR of **3at**, 500 MHz, $CDCl_3$

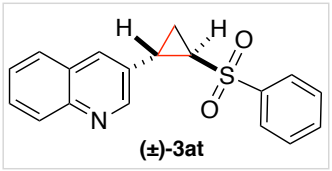




^{13}C NMR of **3at**, 125 MHz, $CDCl_3$



(–)-3at

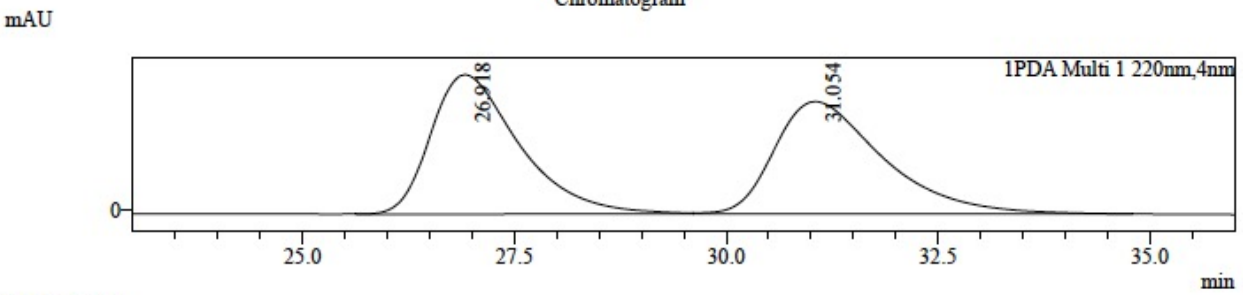


(±)-3at

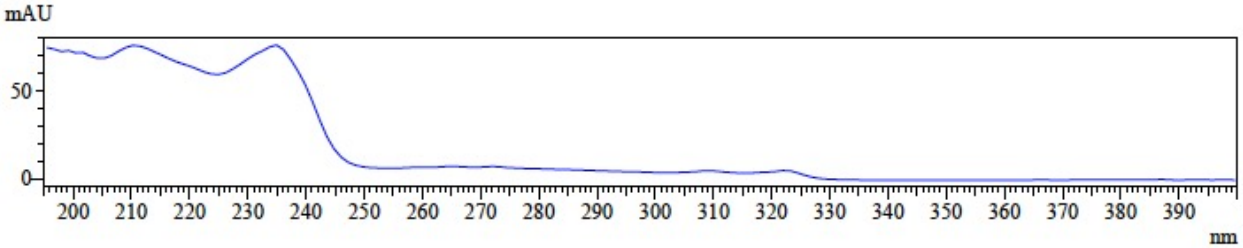
Sample Information

Sample Name	: XXW-0543-20%-ODH---0.8mL
Sample ID	: XXW-0543-20%-ODH---0.8mL
Data File	: XXW-0543-20%-ODH---0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

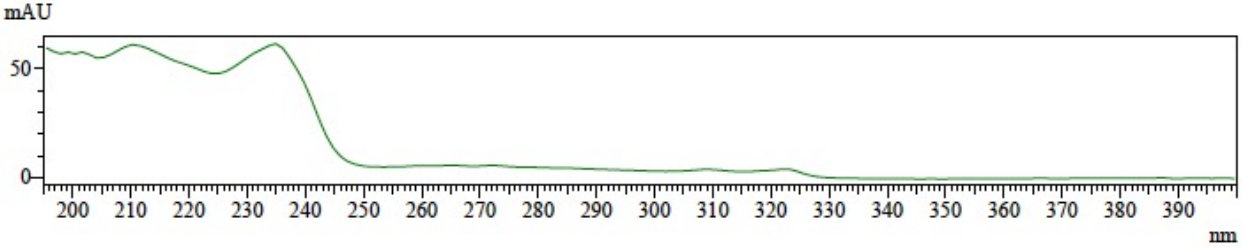
Chromatogram



UV Spectrum
Retention time = 26.918



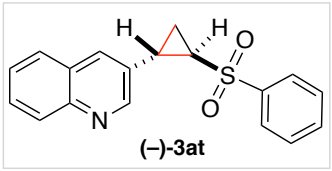
UV Spectrum
Retention time = 31.054



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	26.918	4788624	50.285
2	31.054	4734386	49.715
Total		9523010	100.000

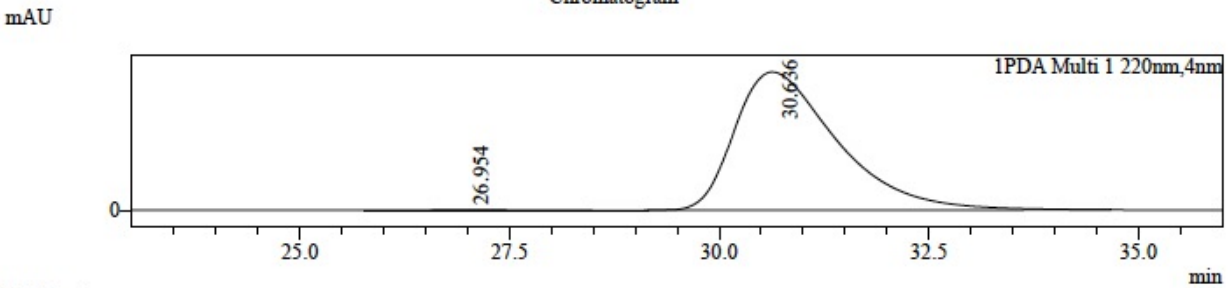


(–)-3at

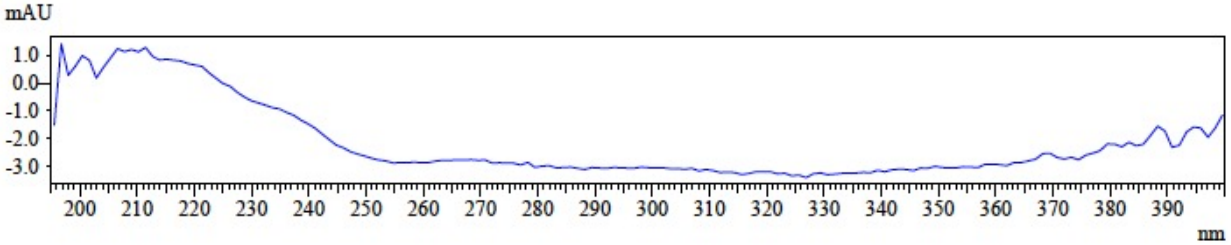
Sample Information

Sample Name	: XXW-1329-ODH-20%-0.8mL
Sample ID	: XXW-1329-ODH-20%-0.8mL
Data File	: XXW-1329-ODH-20%-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

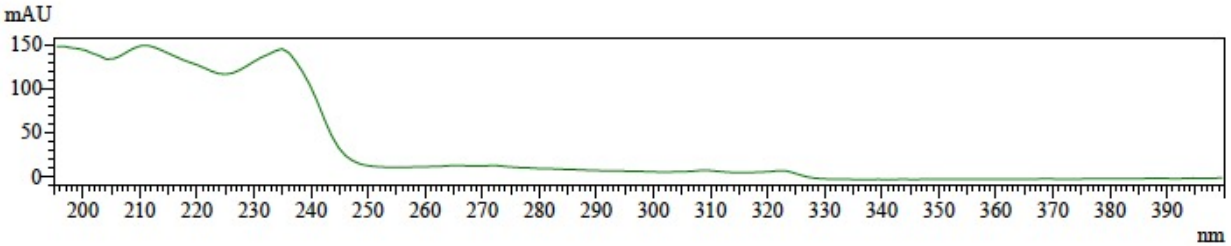
Chromatogram



UV Spectrum
Retention time = 26.954



UV Spectrum
Retention time = 30.636

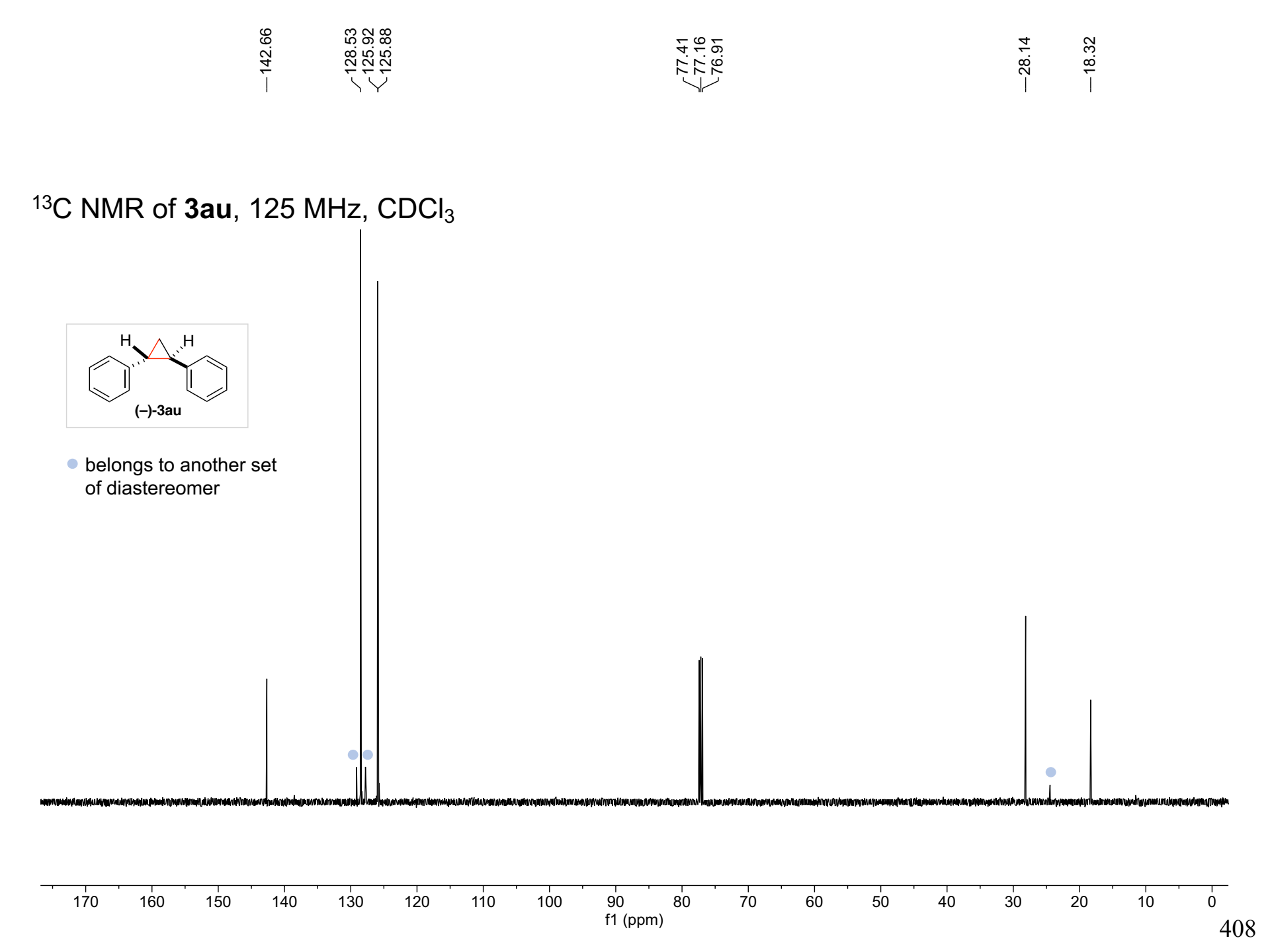


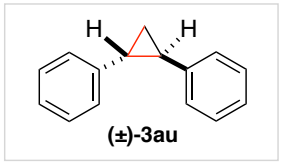
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	26.954	40610	0.377
2	30.636	10741180	99.623
Total		10781790	100.000

^{1}H NMR of **3au**, 500 MHz, $CDCl_3$

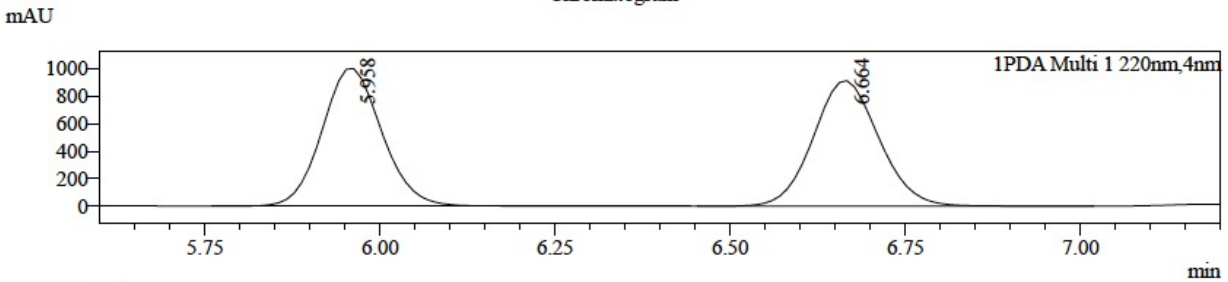

142.66
128.53
125.92
125.88
77.41
77.16
76.91
28.14
18.32
13C NMR of 3au, 125 MHz, CDCl3
H
H
(–)-3au
belongs to another set of diastereomer
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



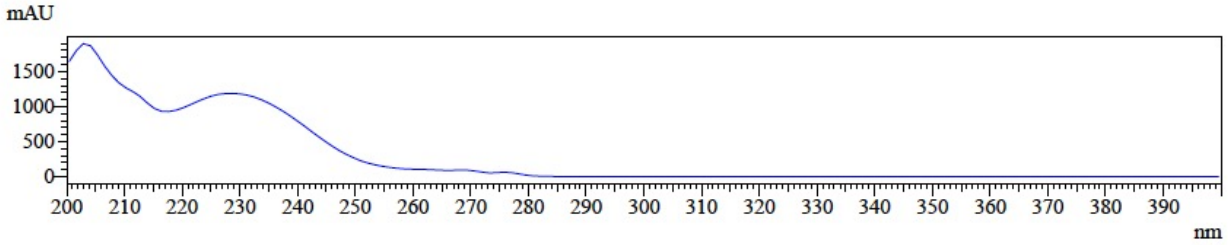
Sample Information

Data File	: XXW-1569--IA-0.5%-0.8mL001.lcd
Sample Name	: XXW-1569--IA-0.5%-0.8mL
Sample ID	: XXW-1569--IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

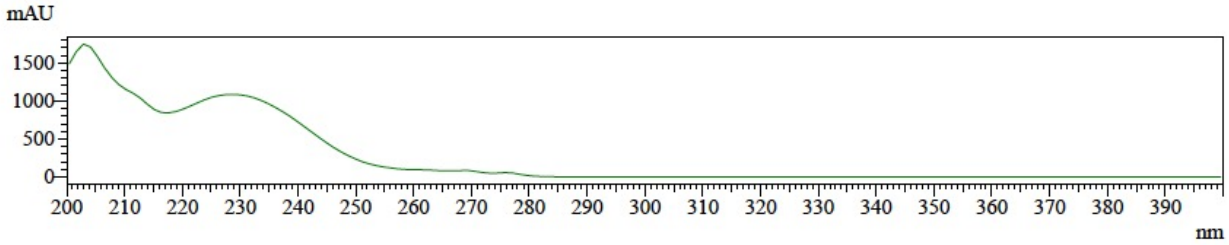
Chromatogram



UV Spectrum
Retention time = 5.958



UV Spectrum
Retention time = 6.664



Peak Table

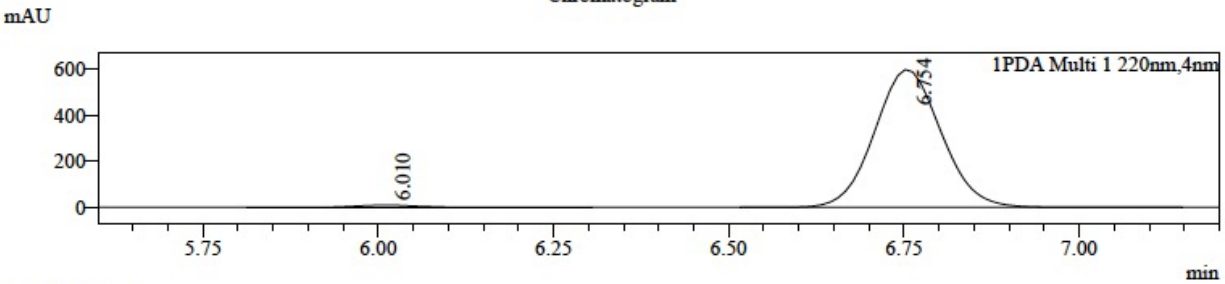
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.958	5970983	49.998
2	6.664	5971534	50.002
Total		11942518	100.000

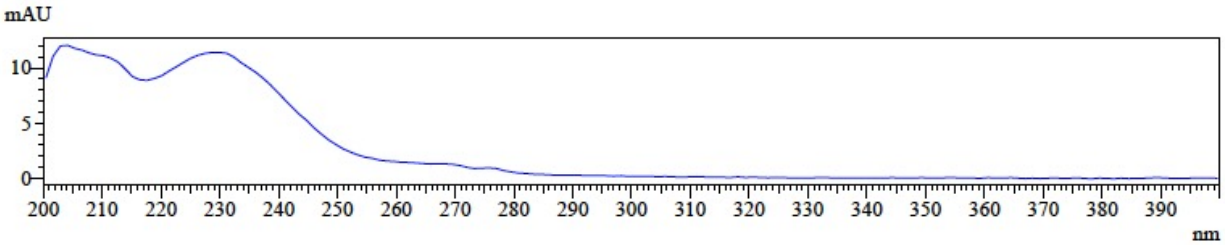
Sample Information

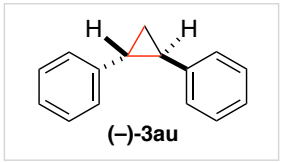
Data File	: XXW-1570--IA-0.5%-0.8mL001.lcd
Sample Name	: XXW-1570--IA-0.5%-0.8mL
Sample ID	: XXW-1570--IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

Chromatogram

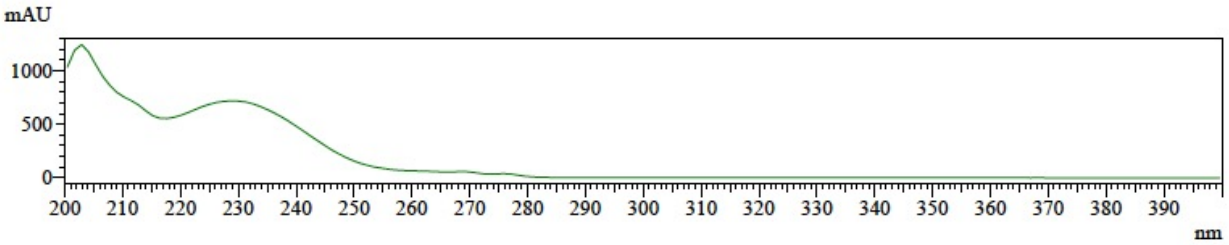


UV Spectrum
Retention time = 6.010





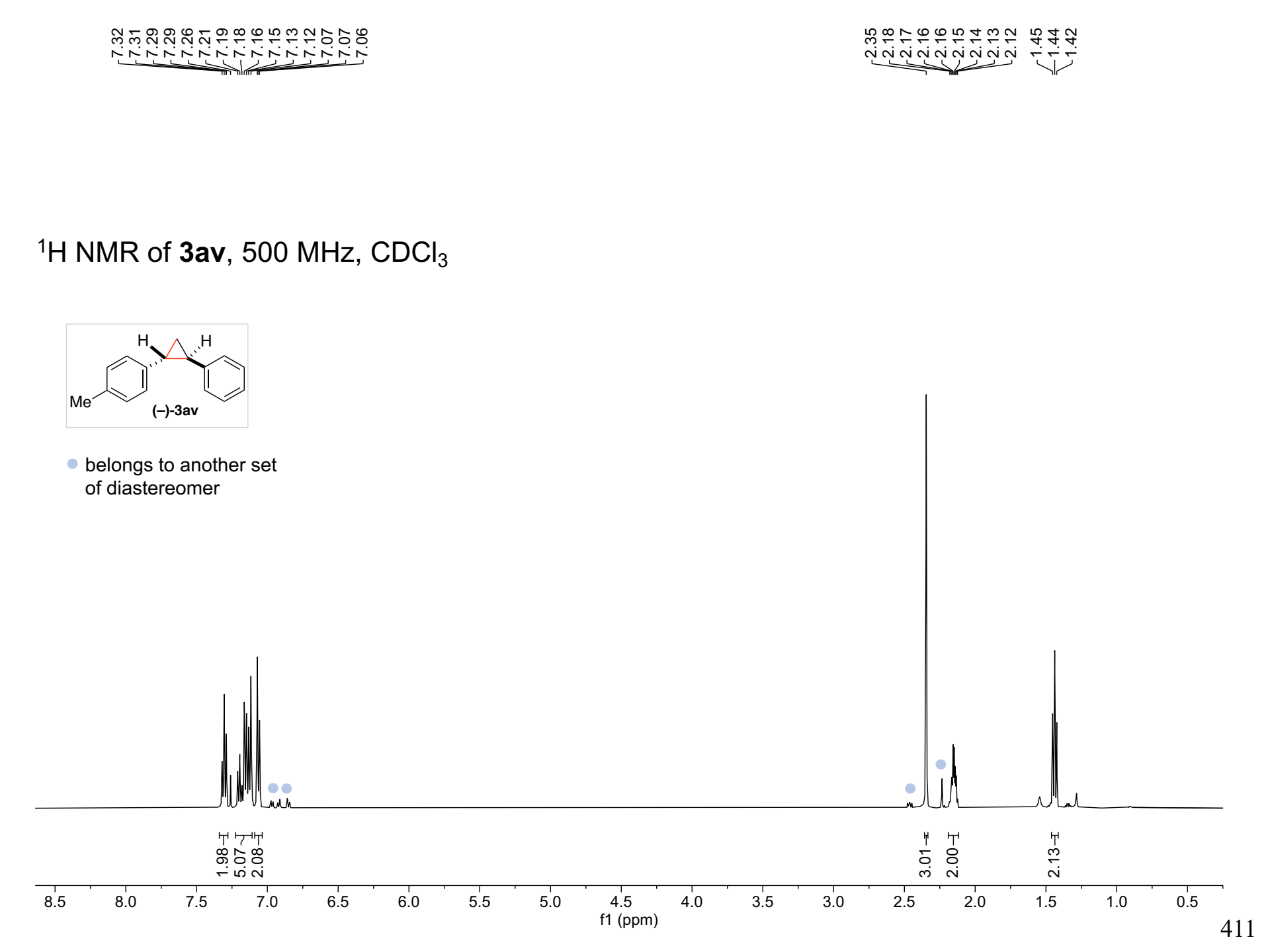
UV Spectrum
Retention time = 6.754



Peak Table

PDA Ch1 220nm

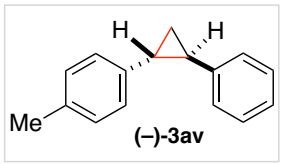
Peak#	Ret. Time	Area	Area%
1	6.010	60687	1.504
2	6.754	3973479	98.496
Total		4034167	100.000



^{1}H NMR of **3av**, 500 MHz, $CDCl_3$

142.83
139.59
135.42
129.21
128.51
125.89
125.86
125.80
77.41
77.16
76.91
27.96
27.85
21.11
18.13

^{13}C NMR of **3av**, 125 MHz, $CDCl_3$

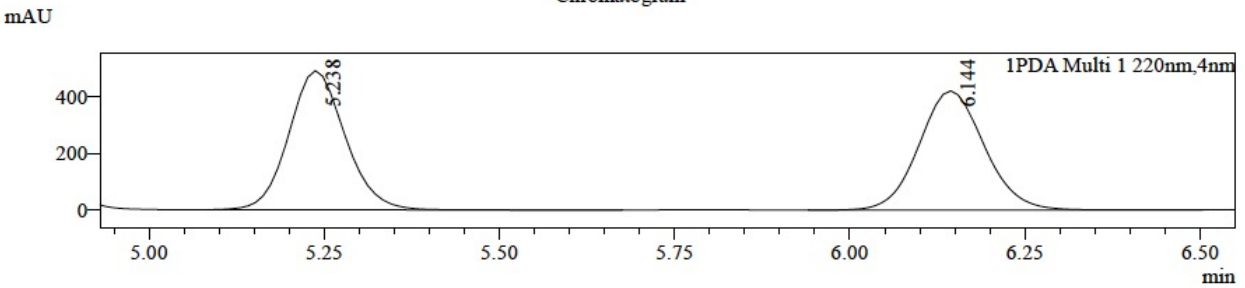


belongs to another set of diastereomer

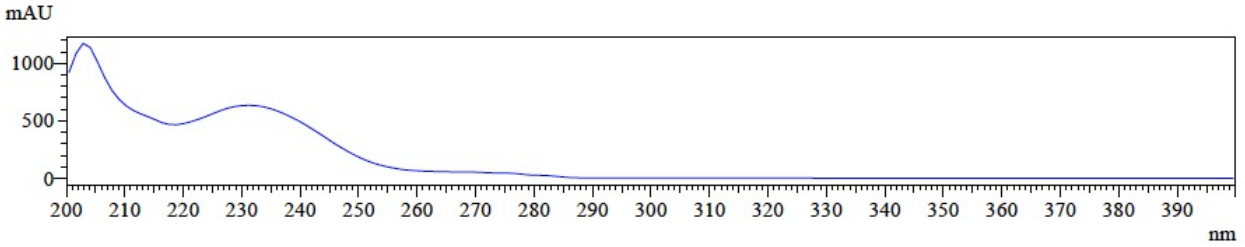
Sample Information

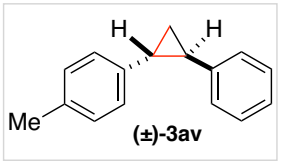
Data File	: XXW-1583-IA-0.5%-0.8mL001.lcd
Sample Name	: XXW-1583-IA-0.5%-0.8mL
Sample ID	: XXW-1583-IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

Chromatogram

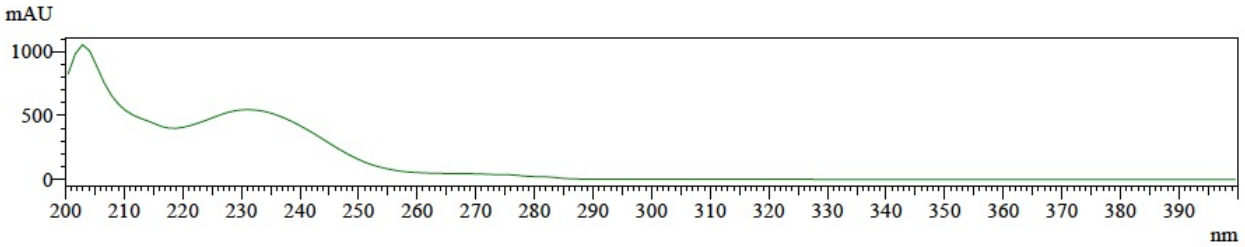


UV Spectrum
Retention time = 5.238





UV Spectrum
Retention time = 6.144



Peak Table

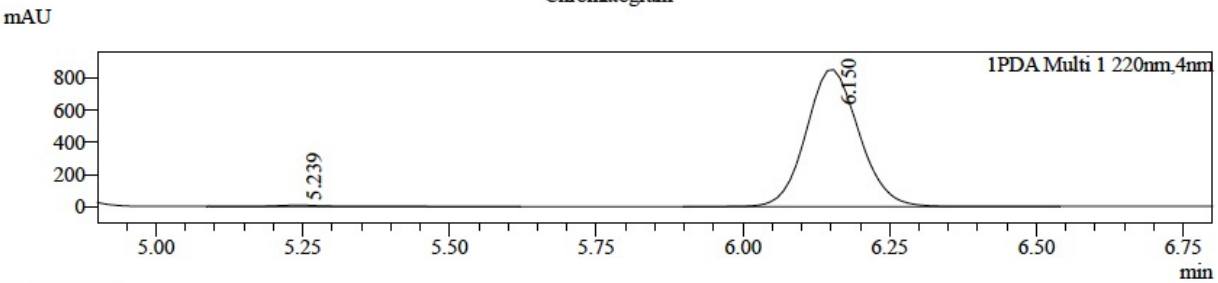
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.238	2738669	50.110
2	6.144	2726664	49.890
Total		5465333	100.000

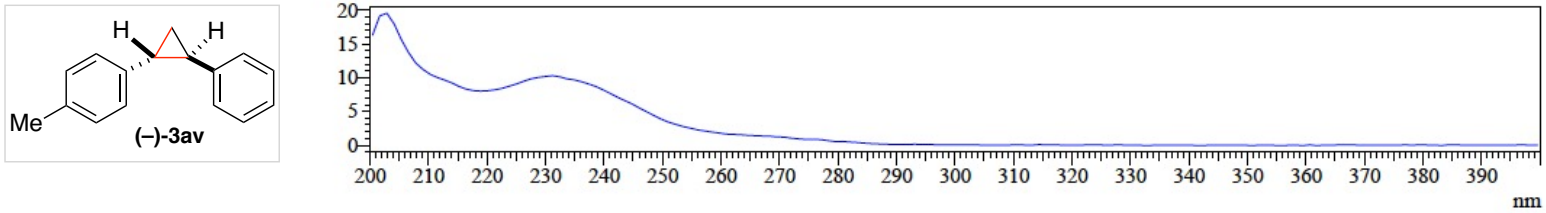
Sample Information

Data File	: XXW-1584-IA-0.5%-0.8mL001.lcd
Sample Name	: XXW-1584-IA-0.5%-0.8mL
Sample ID	: XXW-1584-IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

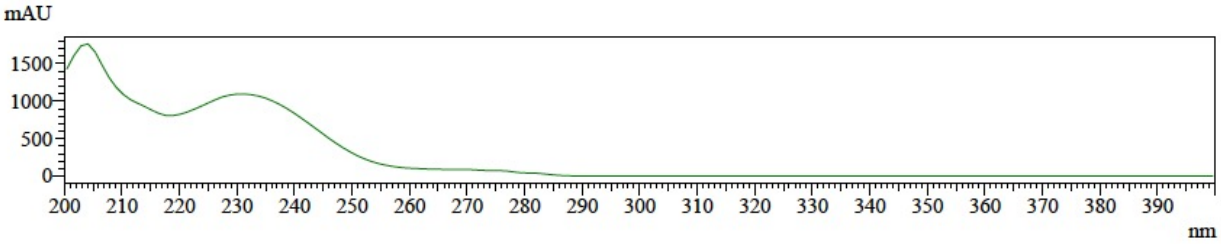
Chromatogram



UV Spectrum
Retention time = 5.239



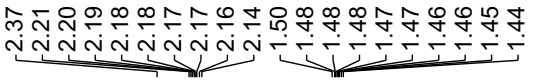
UV Spectrum
Retention time = 6.150



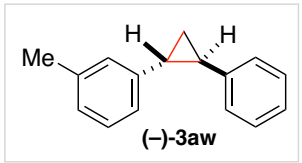
Peak Table

PDA Ch1 220nm

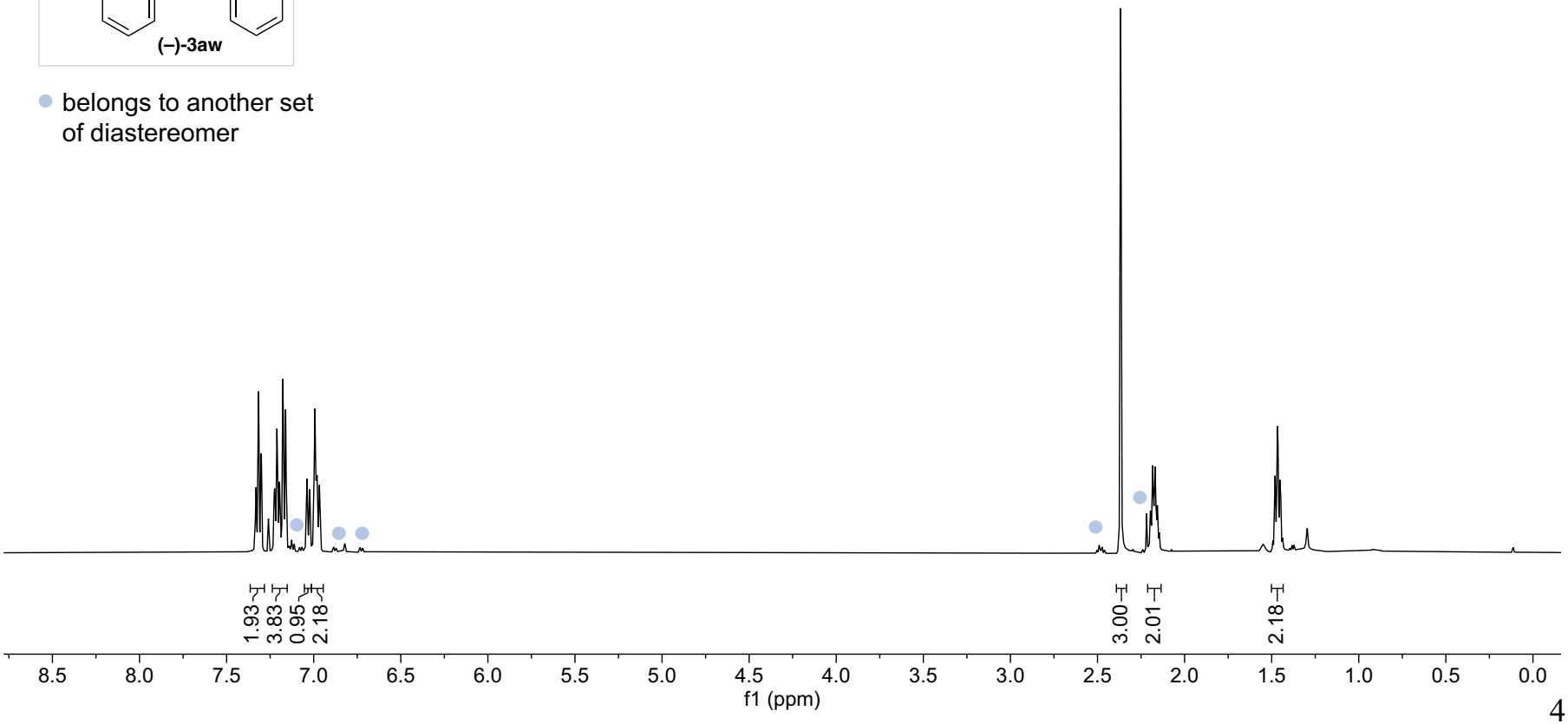
Peak#	Ret. Time	Area	Area%
1	5.239	48107	0.888
2	6.150	5370510	99.112
Total		5418617	100.000



^{1}H NMR of **3aw**, 500 MHz, $CDCl_3$

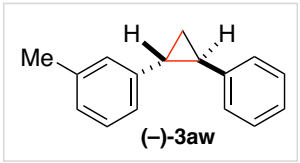


● belongs to another set of diastereomer



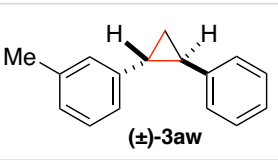
142.75
142.61
138.11
128.51
128.45
126.72
126.67
125.91
125.84
122.92
77.41
77.16
76.91
28.11
28.06
21.57
18.24

^{13}C NMR of **3aw**, 125 MHz, $CDCl_3$



(–)-3aw

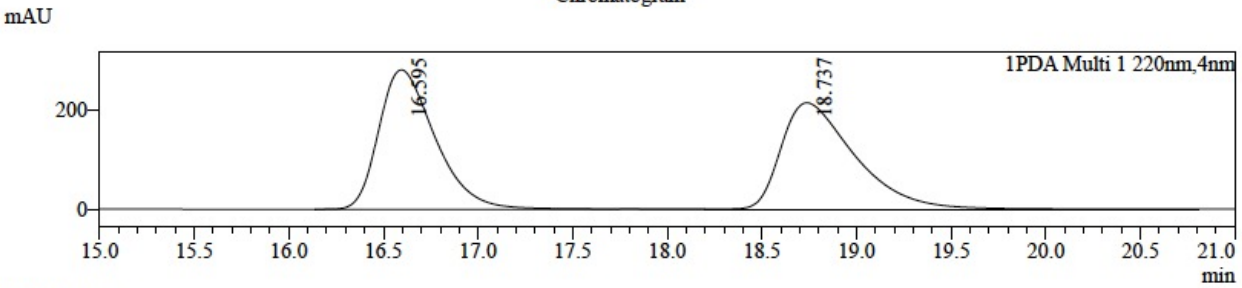
● belongs to another set of diastereomer



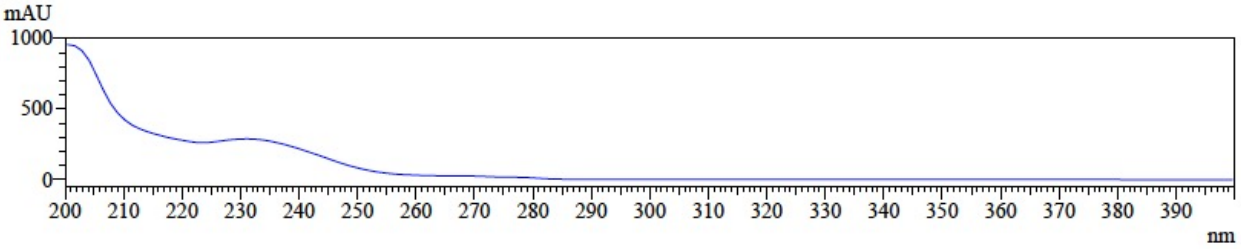
Sample Information

Data File : XXW-1612-rac-IF--0%-0.5mL001.lcd
Sample Name : XXW-1612-rac-IF--0%-0.5mL
Sample ID : XXW-1612-rac-IF--0%-0.5mL
Method File : XXW-0%-0.5mL.lcm

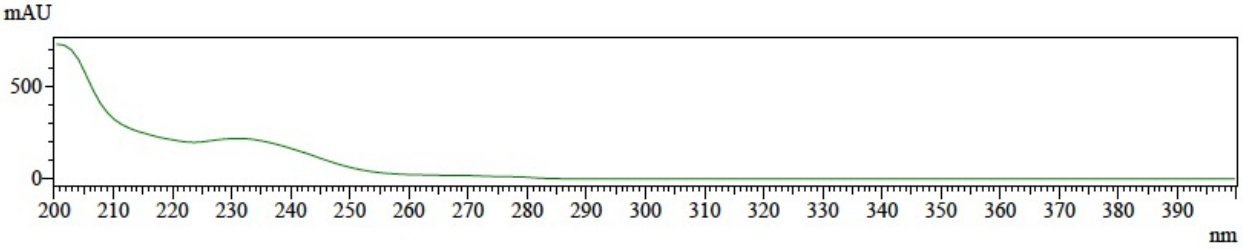
Chromatogram



UV Spectrum
Retention time = 16.595



UV Spectrum
Retention time = 18.737



Peak Table

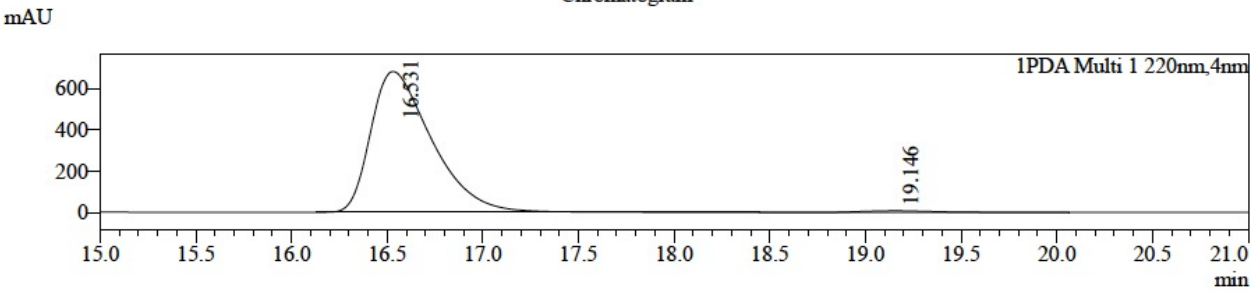
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	16.595	5843564	50.111
2	18.737	5817743	49.889
Total		11661307	100.000

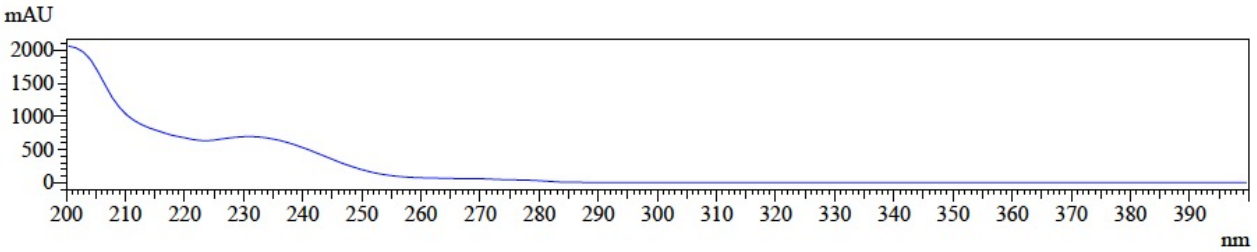
Sample Information

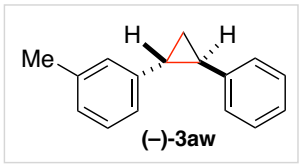
Data File	: XXW-1613-chiral-IF--0%-0.5mL001.lcd
Sample Name	: XXW-1613-chiral-IF--0%-0.5mL
Sample ID	: XXW-1613-chiral-IF--0%-0.5mL
Method File	: XXW-0%-0.5mL.lcm

Chromatogram

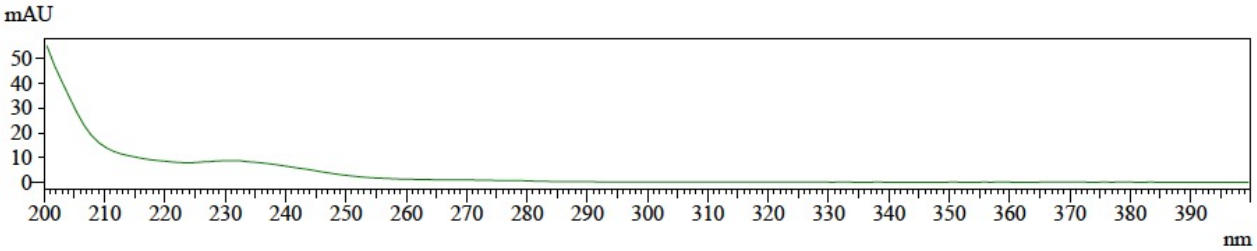


UV Spectrum
Retention time = 16.531





UV Spectrum
Retention time = 19.146

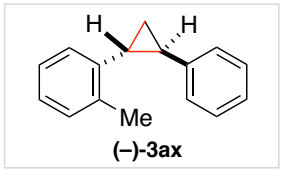


Peak Table

PDA Ch1 220nm

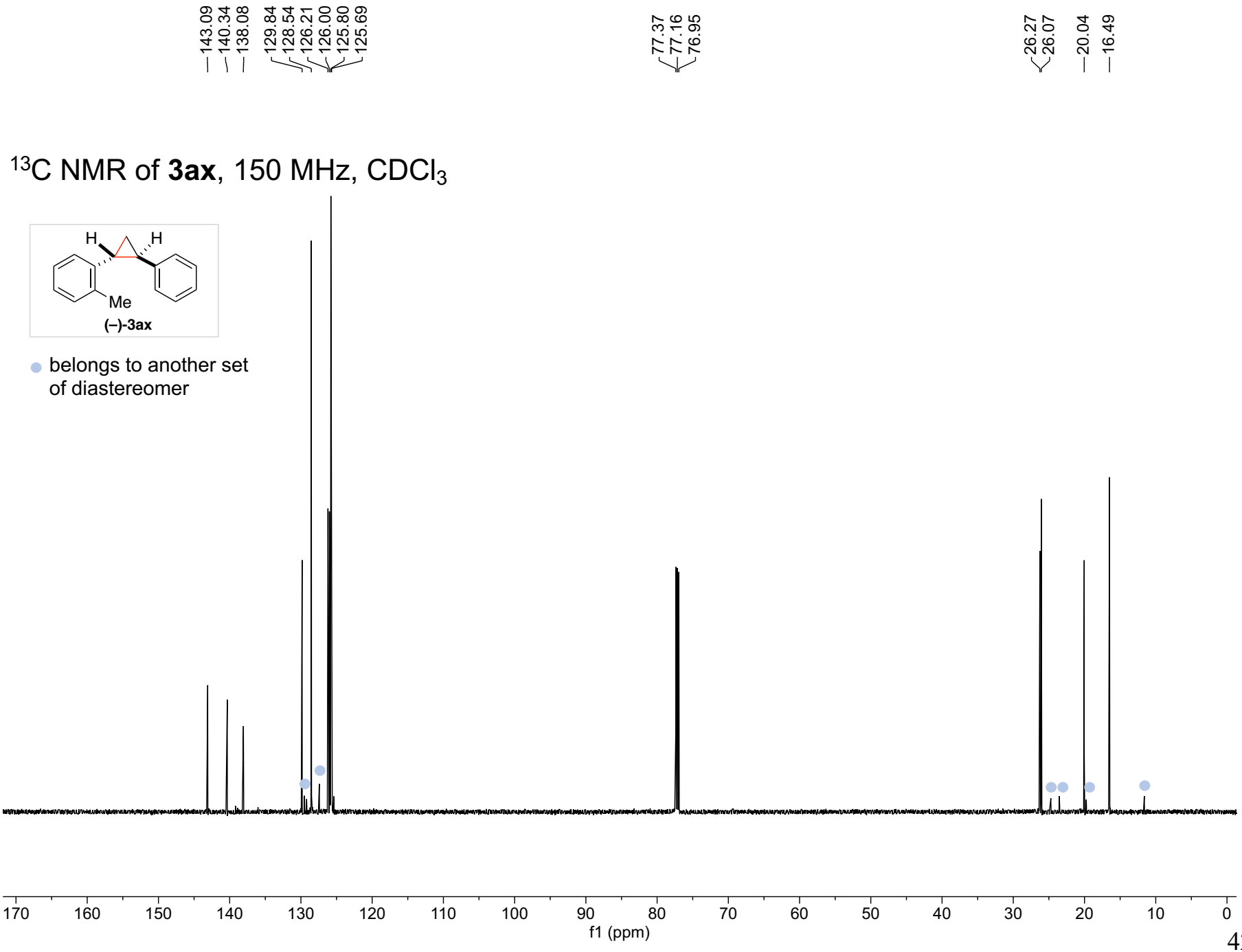
Peak#	Ret. Time	Area	Area%
1	16.531	15165667	98.574
2	19.146	219367	1.426
Total		15385034	100.000

^{1}H NMR of **3ax**, 600 MHz, $CDCl_3$



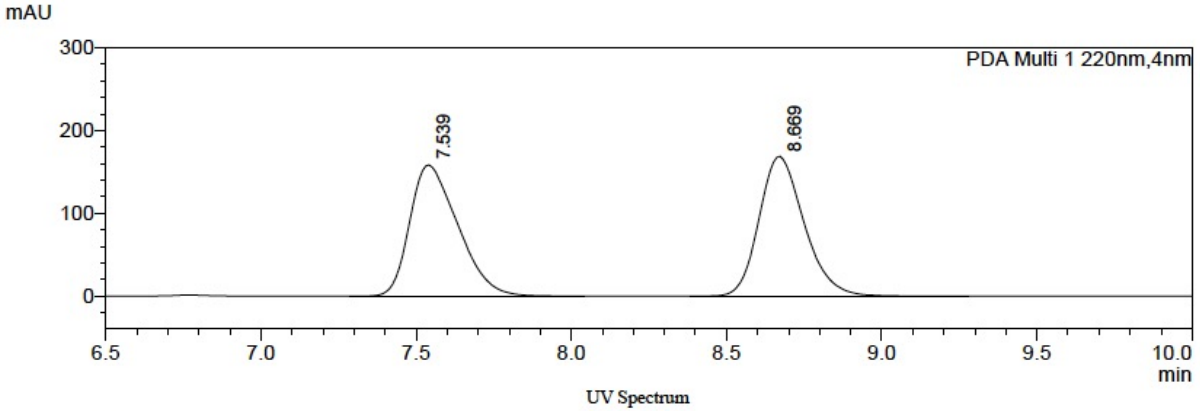
(–)-3ax

belongs to another set of diastereomer

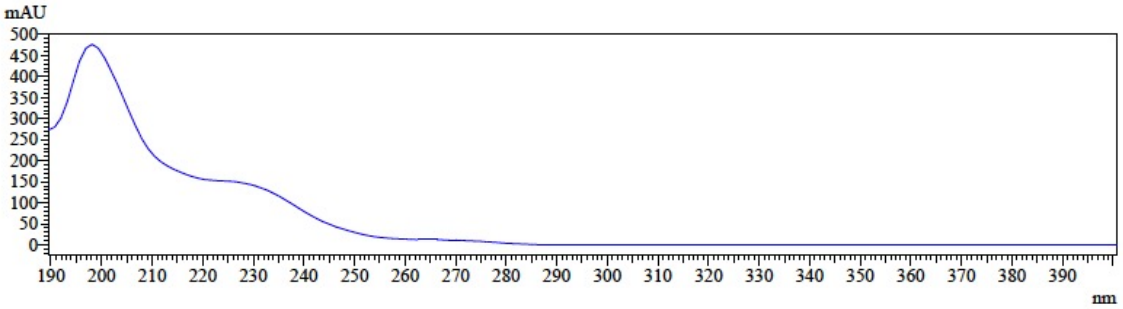


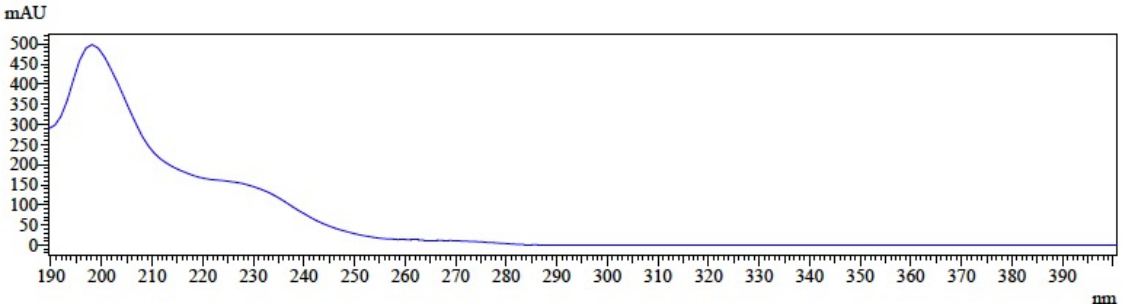
^{13}C NMR of **3ax**, 150 MHz, $CDCl_3$

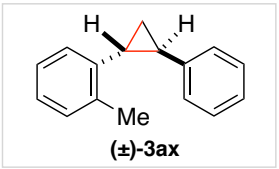
XXW-1595-rac-IB-0.1%0.8mL
XXW-0.1%-0.8mL.lcm



UV Spectrum







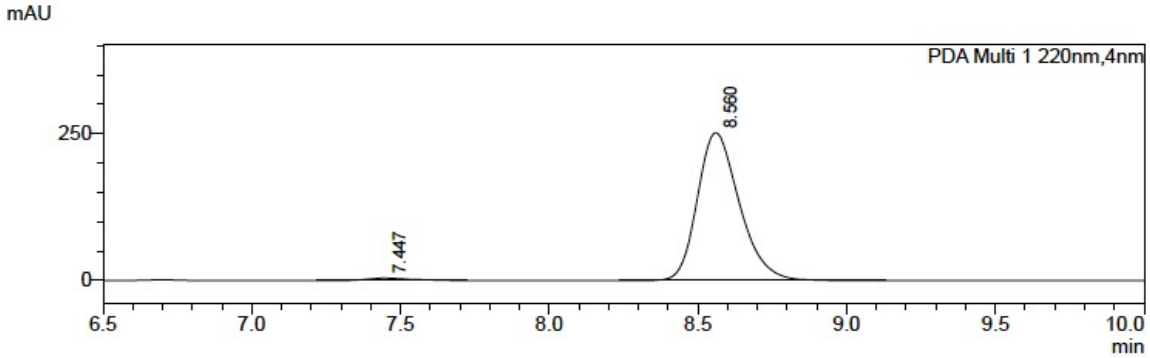
(±)-3ax

Peak Table

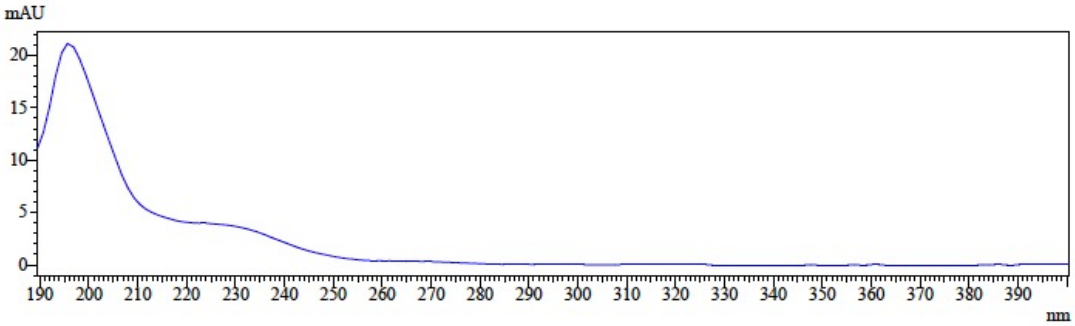
PDA Ch1 220nm

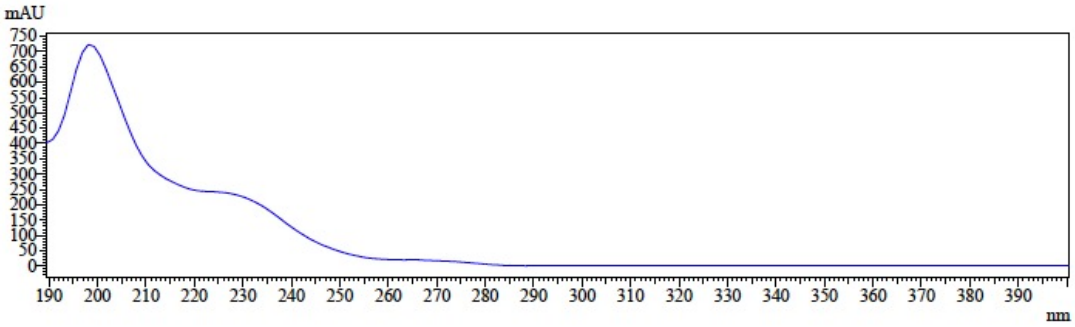
Peak#	Ret. Time	Area%
1	7.539	49.983
2	8.669	50.017
Total		100.000

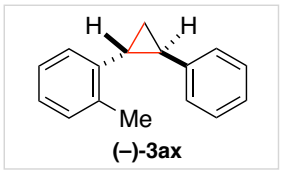
XXW--1596-chiral-IB-0.1%0.8mL
XXW-0.1%-0.8mL.lcm



UV Spectrum





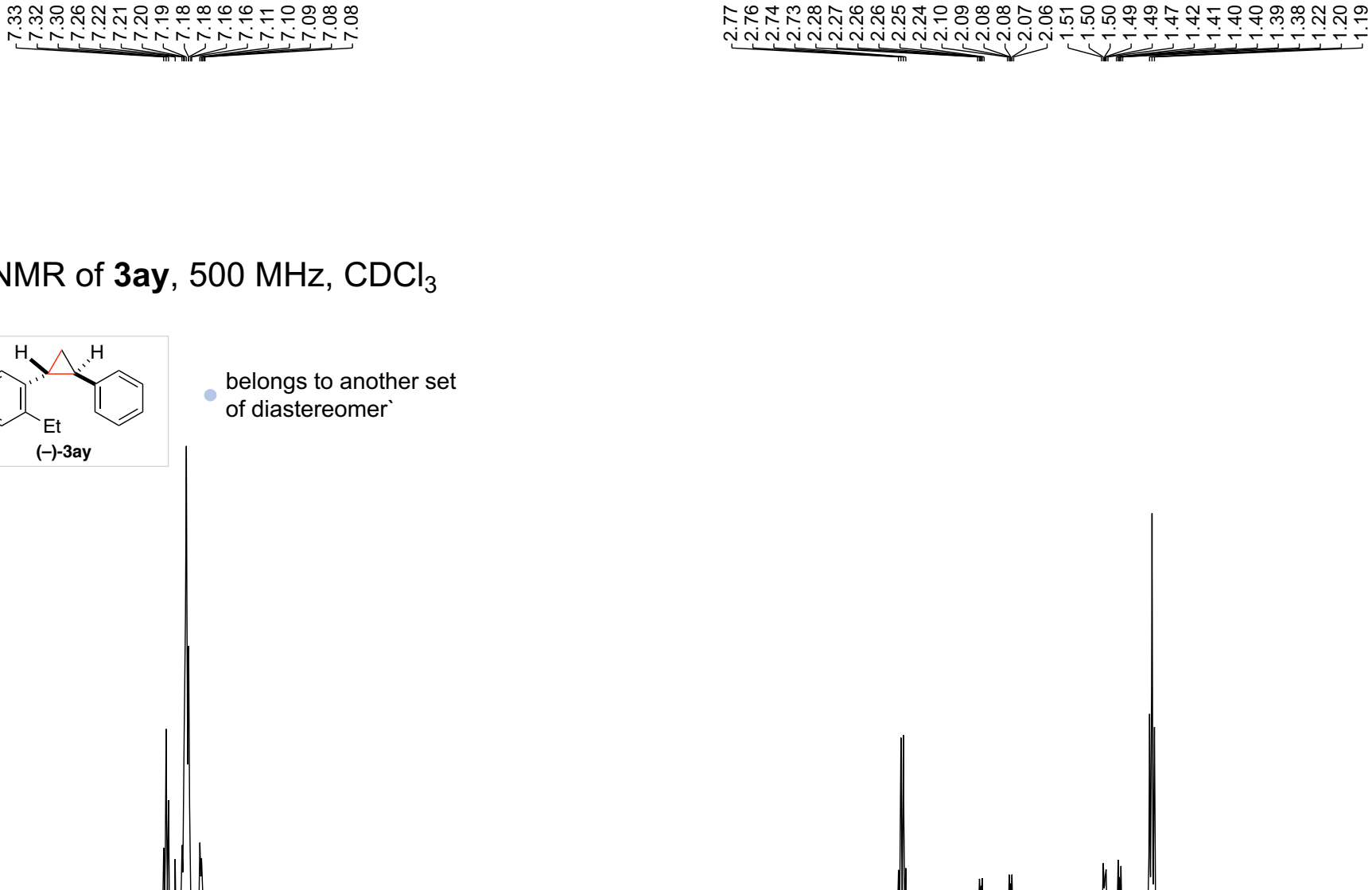


(–)-3ax

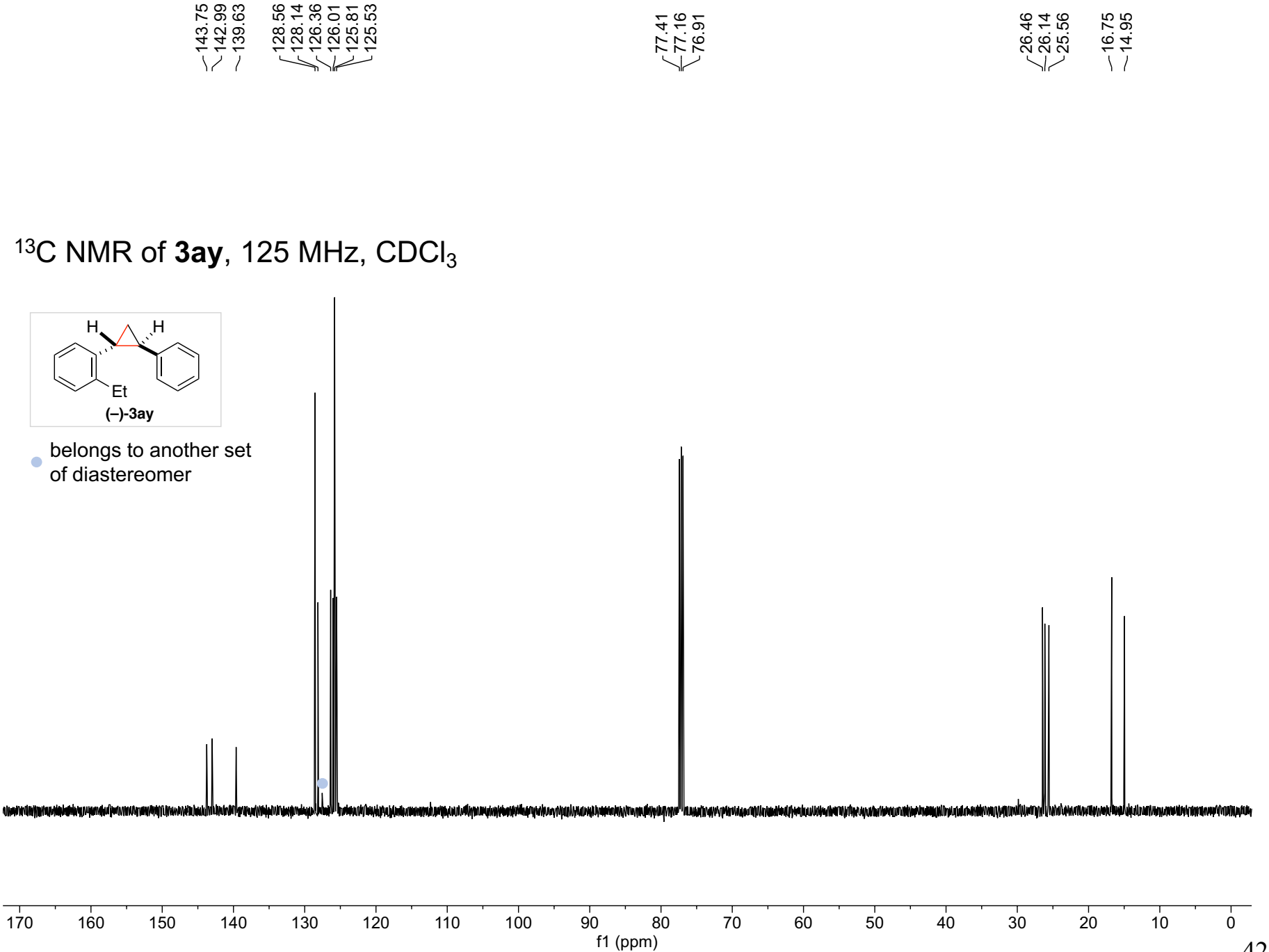
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area%
1	7.447	1.555
2	8.560	98.445
Total		100.000



^{1}H NMR of **3ay**, 500 MHz, $CDCl_3$

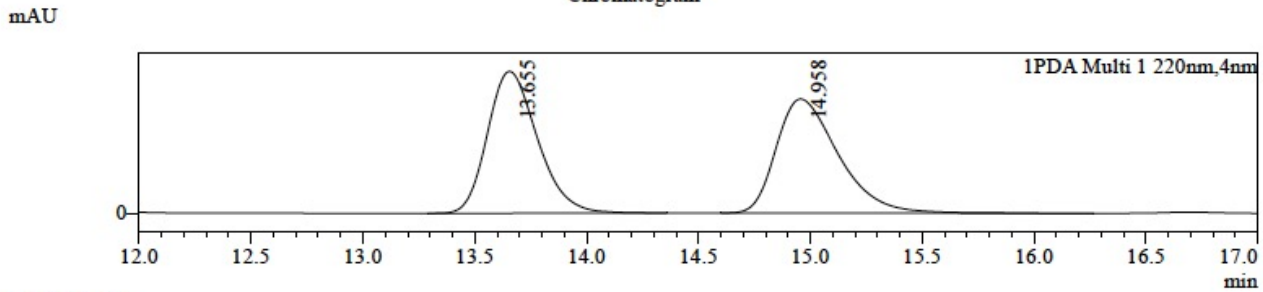


^{13}C NMR of **3ay**, 125 MHz, $CDCl_3$

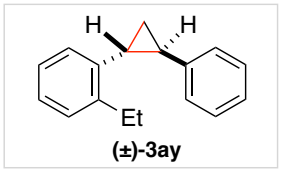
Sample Information

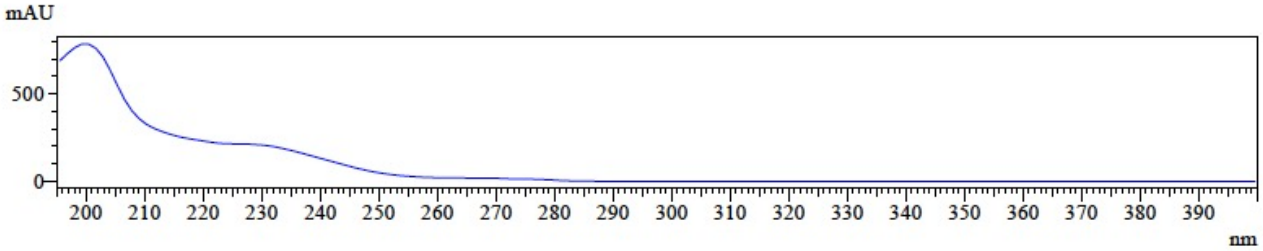
Sample Name	: XXW-1601-IF-0%-0.5mL
Sample ID	: XXW-1601-IF-0%-0.5mL
Data File	: XXW-1601-IF-0%-0.5mL001.lcd
Method File	: XXW-0%-0.5mL.lcm

Chromatogram

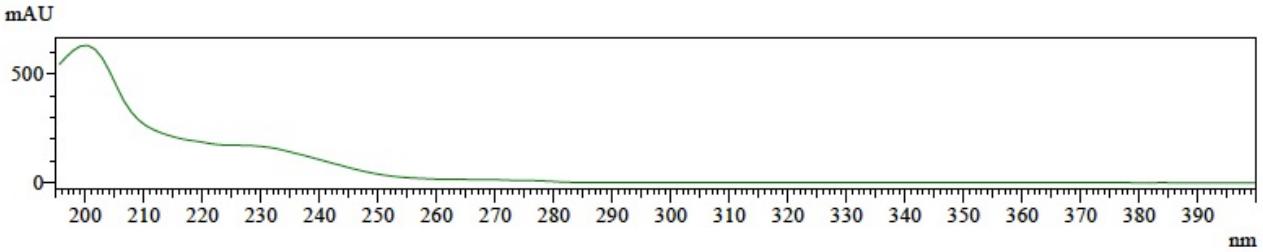


UV Spectrum
Retention time = 13.655





UV Spectrum
Retention time = 14.958



Peak Table

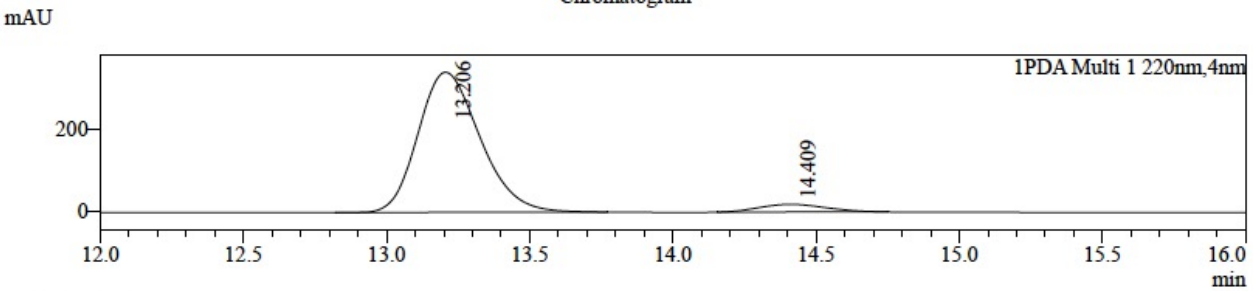
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	13.655	3596346	49.997
2	14.958	3596797	50.003
Total		7193144	100.000

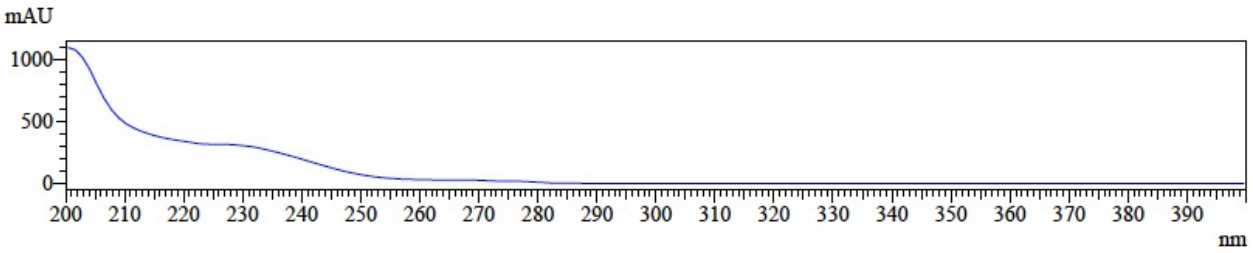
Sample Information

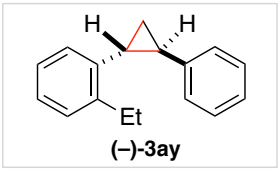
Data File : XXW-1602-IF-0%-0.5mL001.lcd
Sample Name : XXW-1602-IF-0%-0.5mL
Sample ID : XXW-1602-IF-0%-0.5mL
Method File : XXW-0%-0.5mL.lcm

Chromatogram

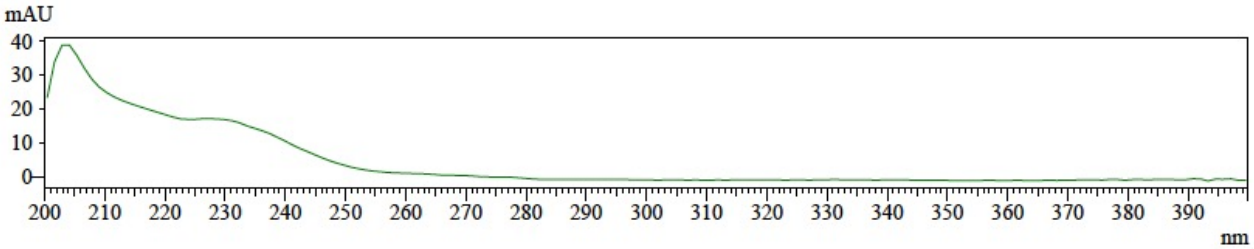


UV Spectrum
Retention time = 13.206





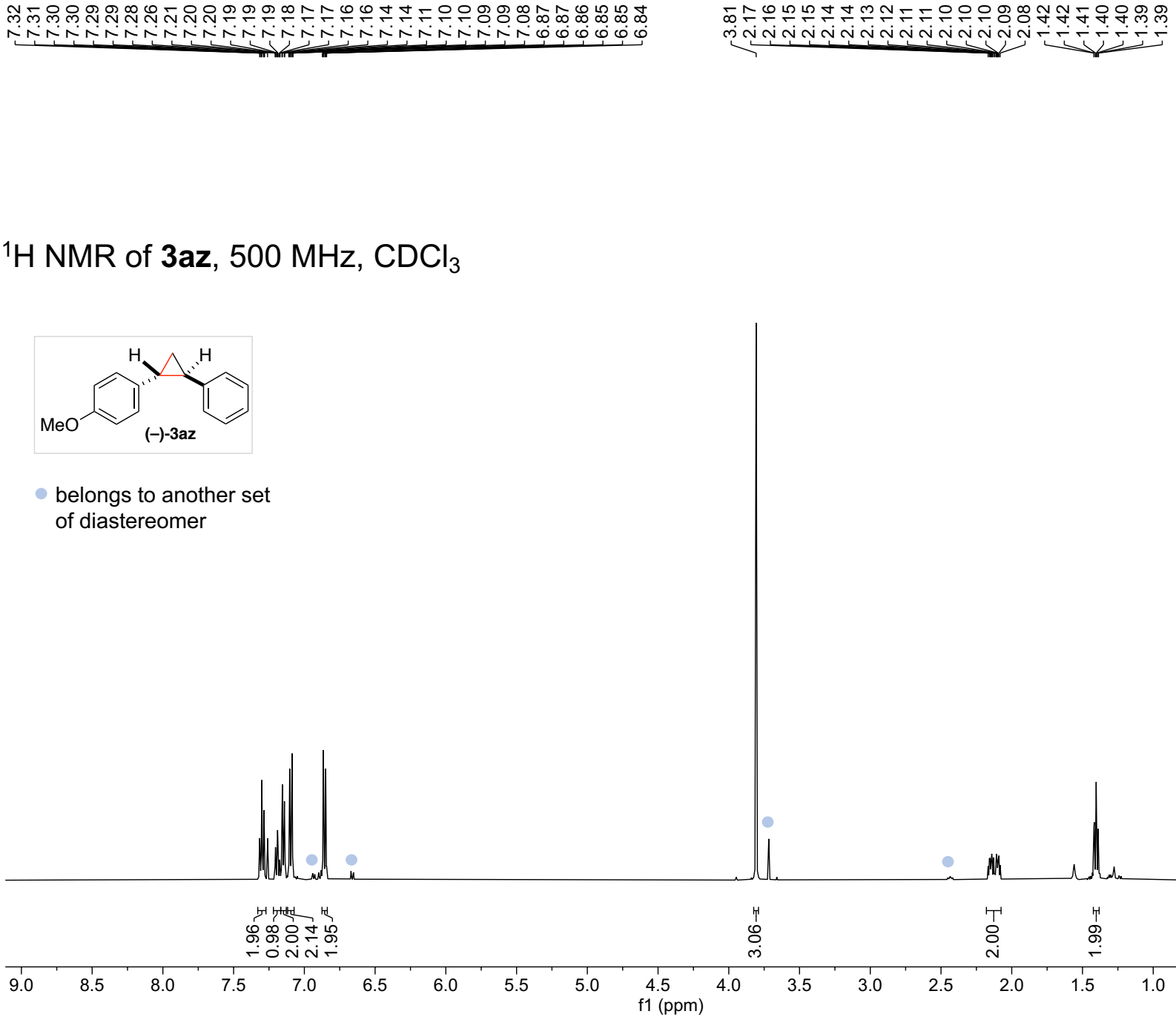
UV Spectrum
Retention time = 14.409



Peak Table

PDA Ch1 220nm

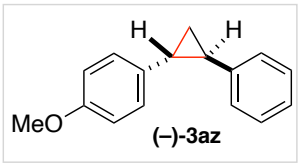
Peak#	Ret. Time	Area	Area%
1	13.206	5142912	94.402
2	14.409	304946	5.598
Total		5447858	100.000



^{1}H NMR of **3az**, 500 MHz, $CDCl_3$

158.02
142.88
134.67
128.51
127.07
125.86
125.78
114.02
77.41
77.16
76.91
55.48
27.63
27.45
17.92

^{13}C NMR of **3az**, 125 MHz, $CDCl_3$



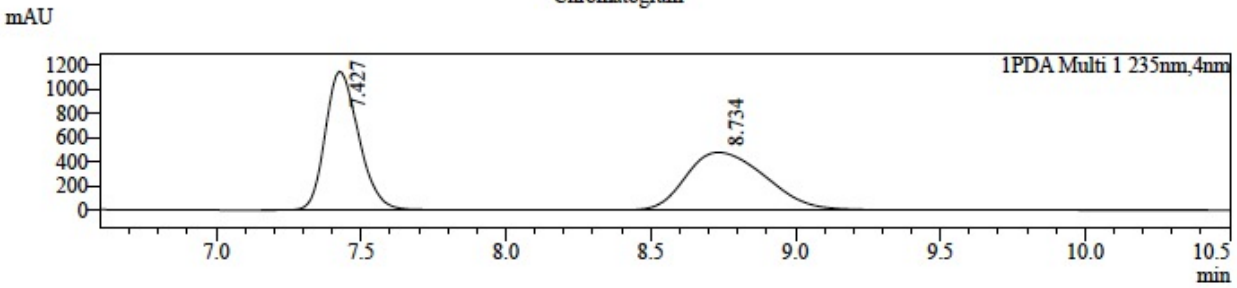
(–)-3az

belongs to another set of diastereomer

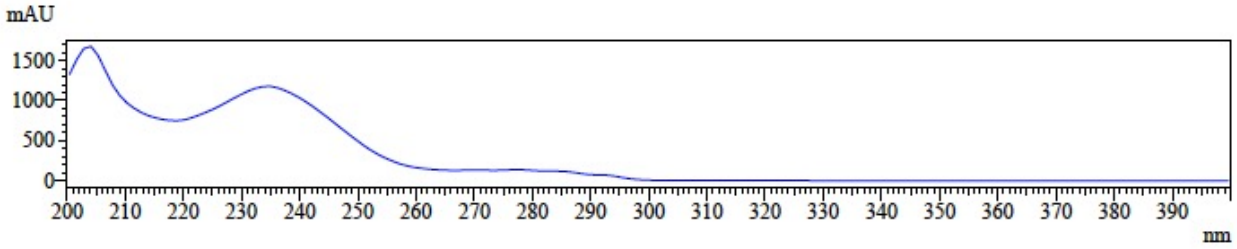
Sample Information

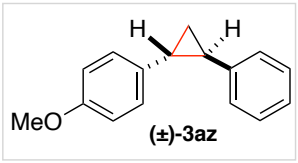
Data File	: XXW-1581-IA--0.5%-0.8mL.lcd
Sample Name	: XXW-1581-IA--0.5%-0.8mL
Sample ID	: XXW-1581-IA--0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

Chromatogram

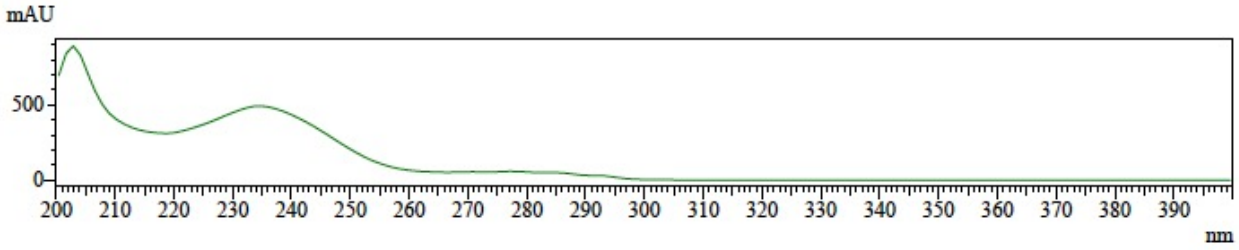


UV Spectrum
Retention time = 7.427





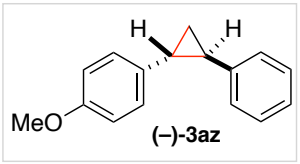
UV Spectrum
Retention time = 8.734



Peak Table

PDA Ch1 235nm

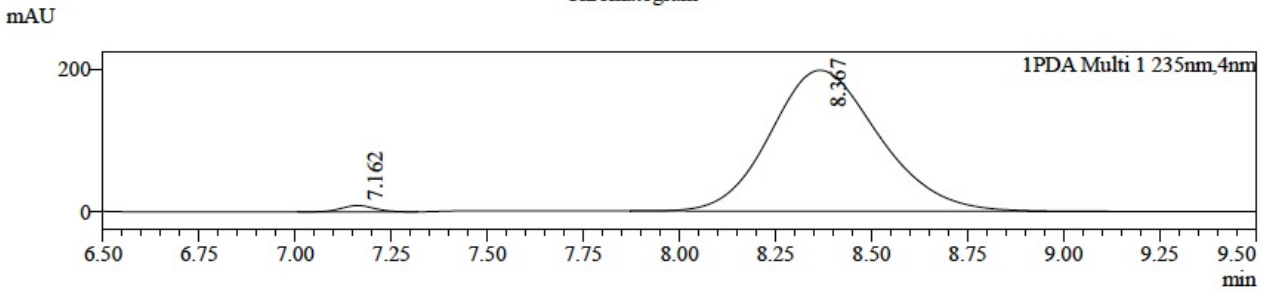
Peak#	Ret. Time	Area	Area%
1	7.427	9240579	50.174
2	8.734	9176390	49.826
Total		18416969	100.000



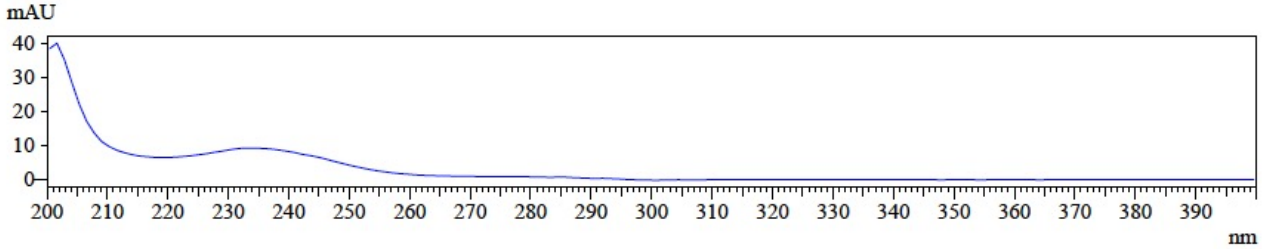
Sample Information

Data File : XXW-1582-IA--0.5%-0.8mL001.lcd
Sample Name : XXW-1582-IA--0.5%-0.8mL
Sample ID : XXW-1582-IA--0.5%-0.8mL
Method File : XXW-0.5%.0.8.mL.lcm

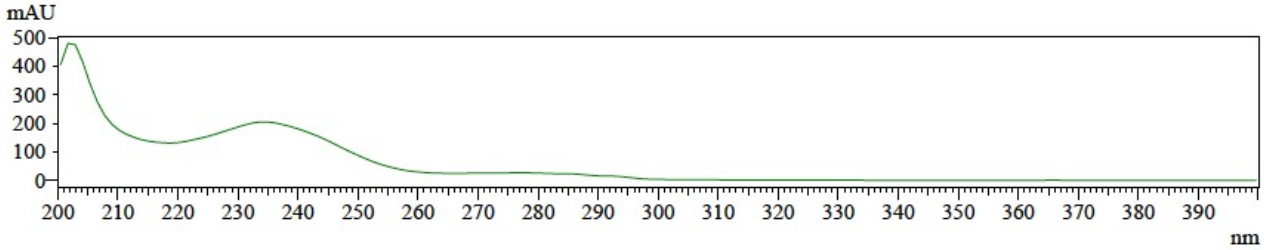
Chromatogram



UV Spectrum
Retention time = 7.162



UV Spectrum
Retention time = 8.367

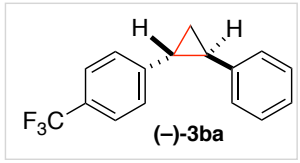


Peak Table

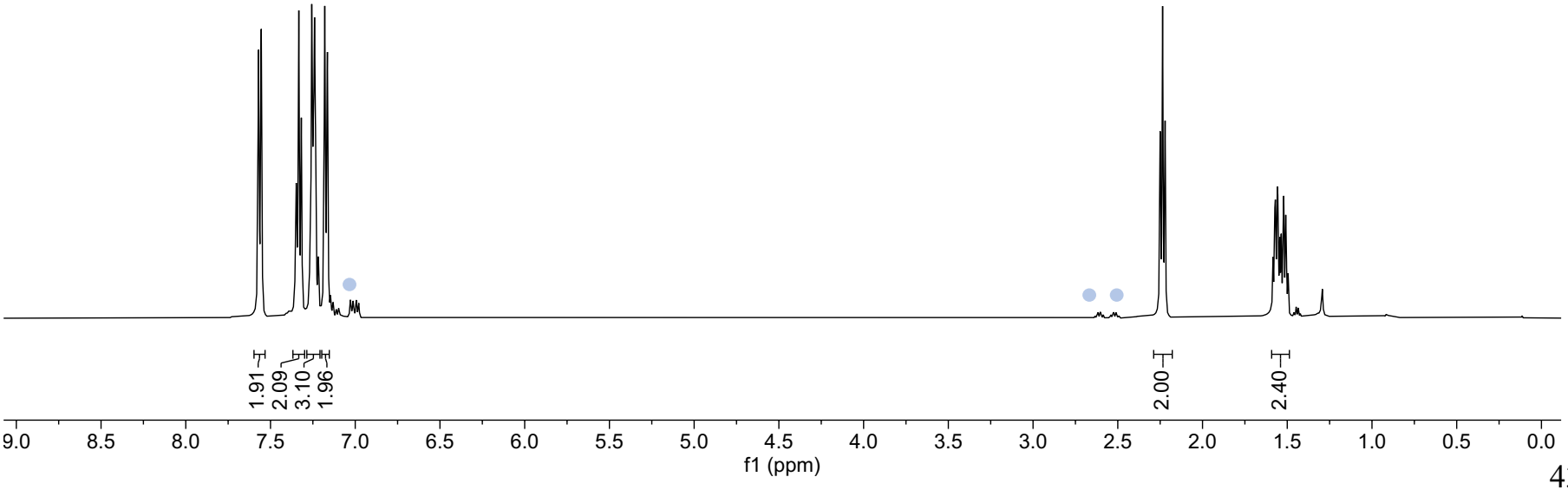
PDA Ch1 235nm

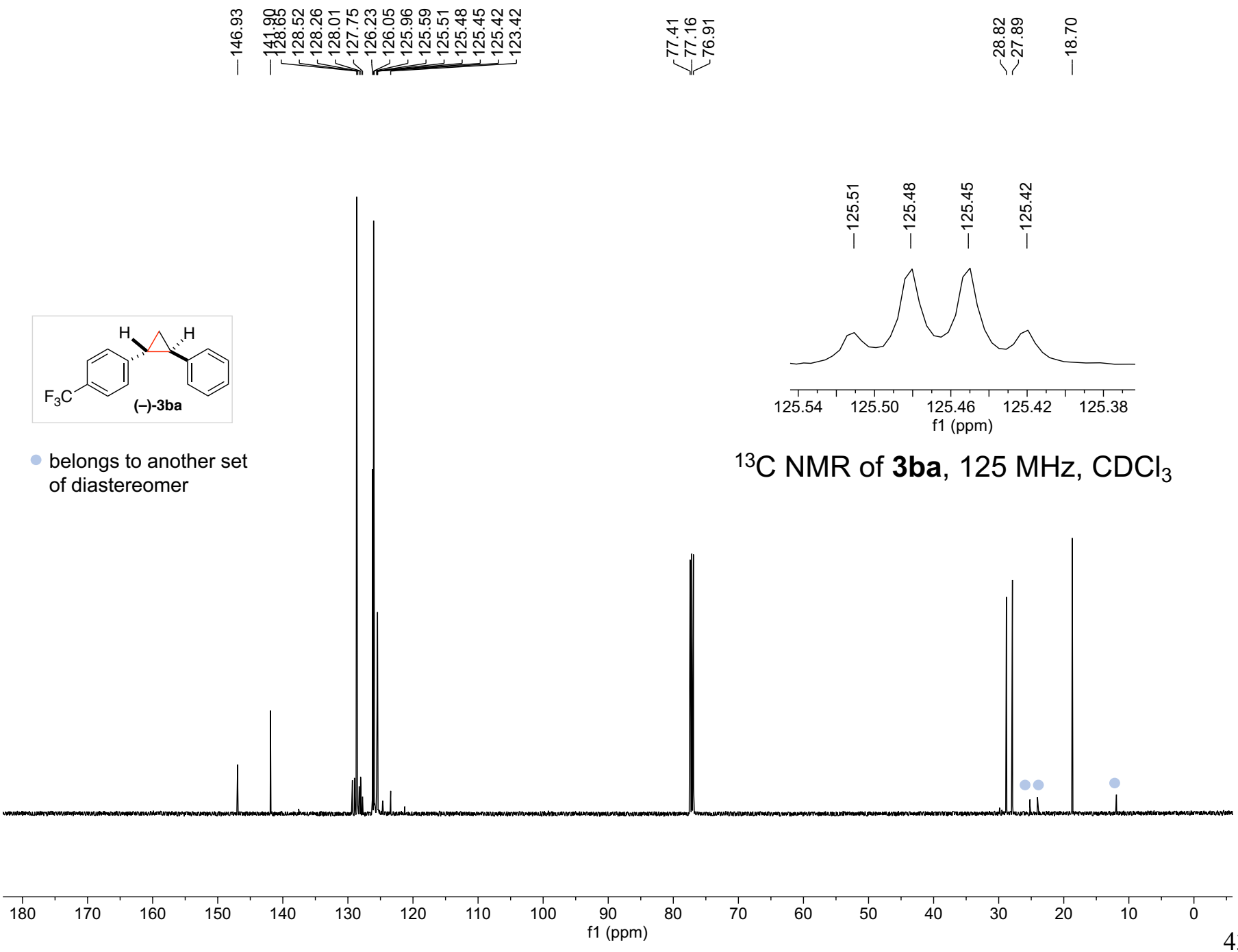
Peak#	Ret. Time	Area	Area%
1	7.162	52997	1.340
2	8.367	3900841	98.660
Total		3953838	100.000

^{1}H NMR of **3ba**, 500 MHz, $CDCl_3$



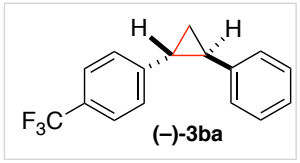
● belongs to another set of diastereomer

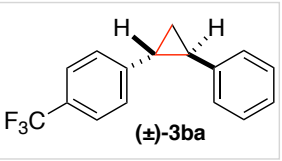




^{13}C NMR of **3ba**, 125 MHz, $CDCl_3$

^{19}F NMR of **3ba**, 470 MHz, $CDCl_3$



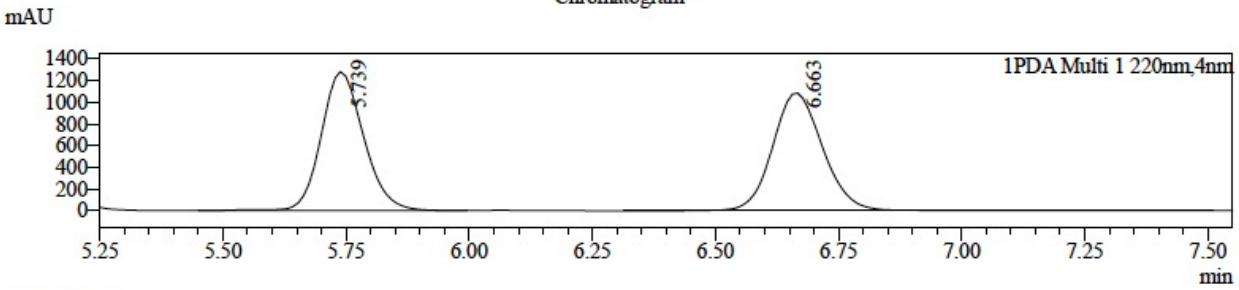


(±)-3ba

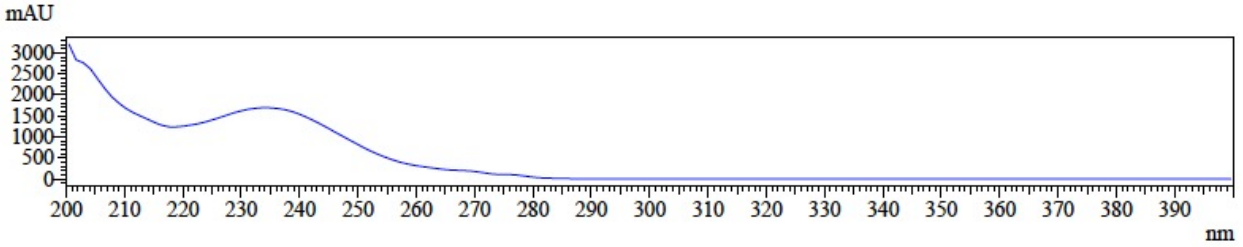
Sample Information

Data File	: XXW-1585-IA-0.5%-0.8mL.lcd
Sample Name	: XXW-1585-IA-0.5%-0.8mL
Sample ID	: XXW-1585-IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

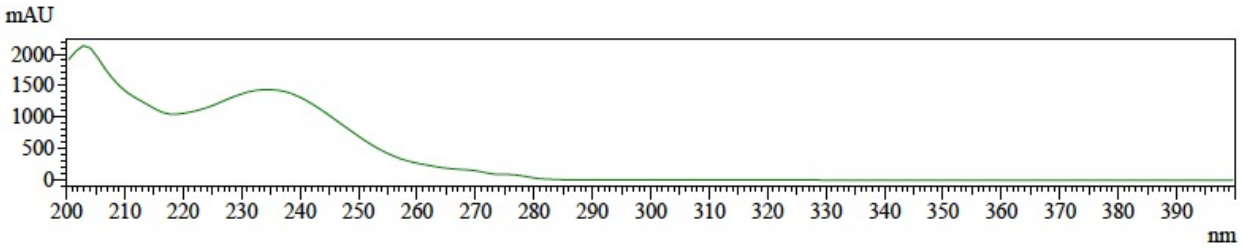
Chromatogram



UV Spectrum
Retention time = 5.739



UV Spectrum
Retention time = 6.663



Peak Table

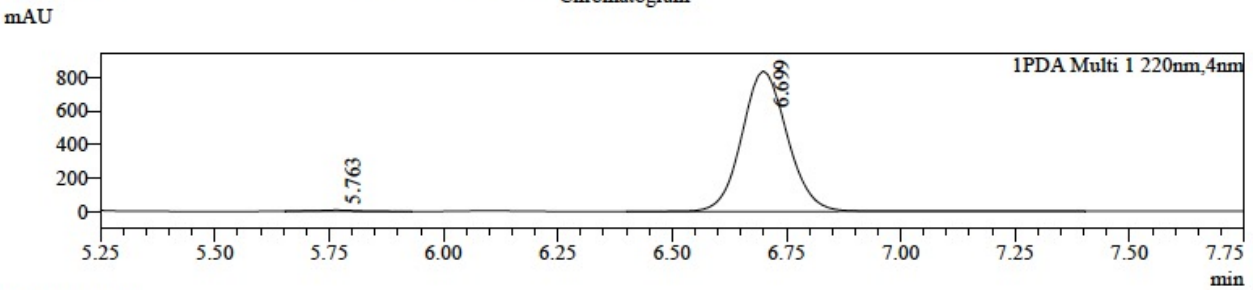
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	5.739	7671092	50.039
2	6.663	7659156	49.961
Total		15330249	100.000

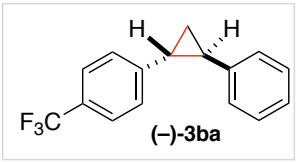
Sample Information

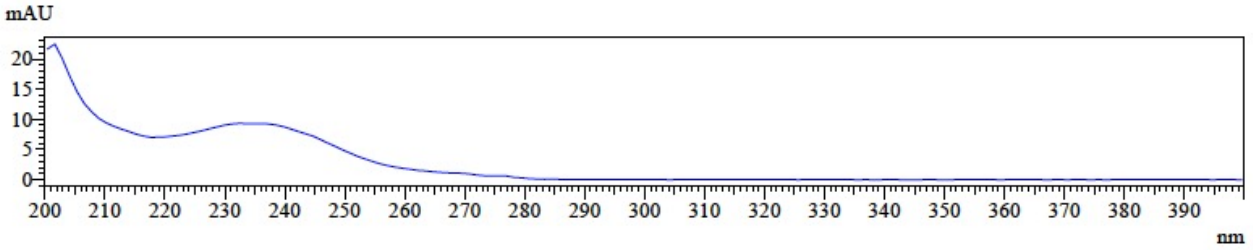
Data File	: XXW-1586-IA-0.5%-0.8mL002.lcd
Sample Name	: XXW-1586-IA-0.5%-0.8mL
Sample ID	: XXW-1586-IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

Chromatogram

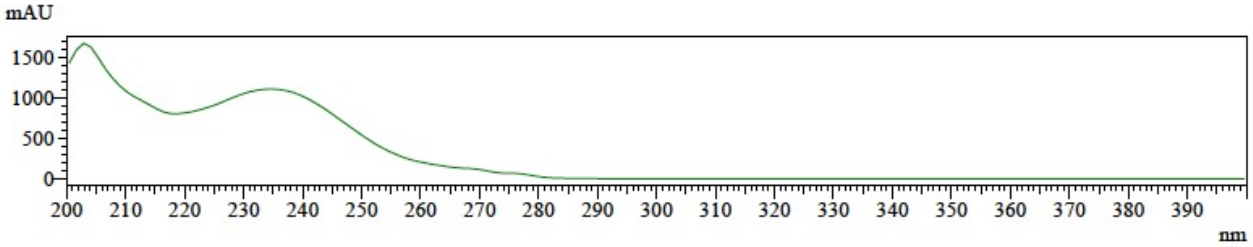


UV Spectrum
Retention time = 5.763





UV Spectrum
Retention time = 6.699

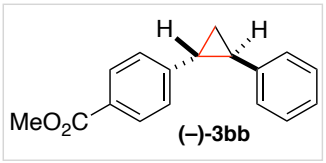


Peak Table

PDA Ch1 220nm

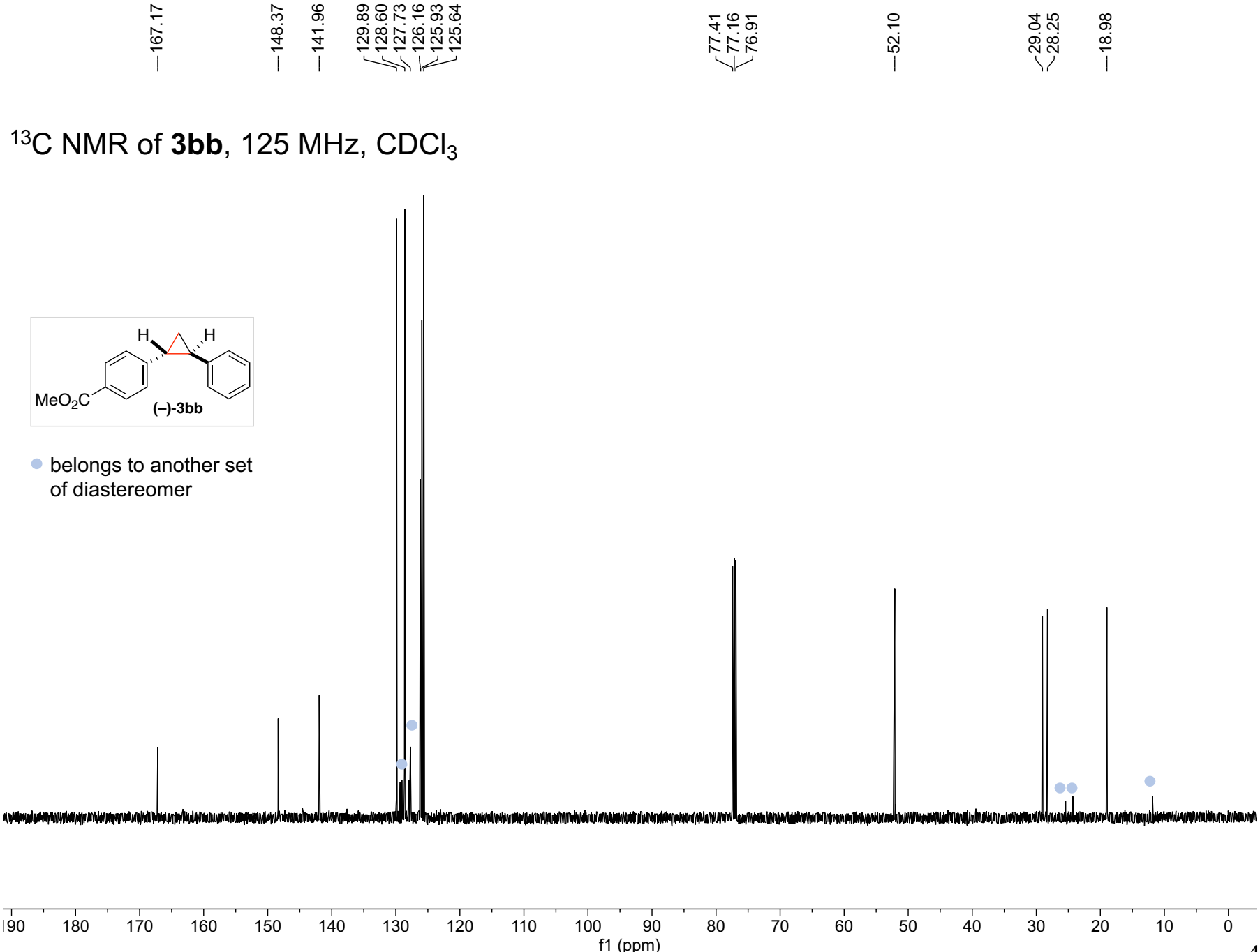
Peak#	Ret. Time	Area	Area%
1	5.763	39966	0.684
2	6.699	5807209	99.316
Total		5847175	100.000

^{1}H NMR of **3bb**, 500 MHz, $CDCl_3$

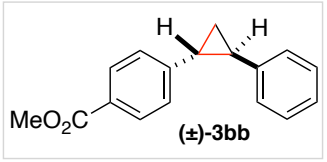


(–)-3bb

● belongs to another set of diastereomer



^{13}C NMR of **3bb**, 125 MHz, $CDCl_3$

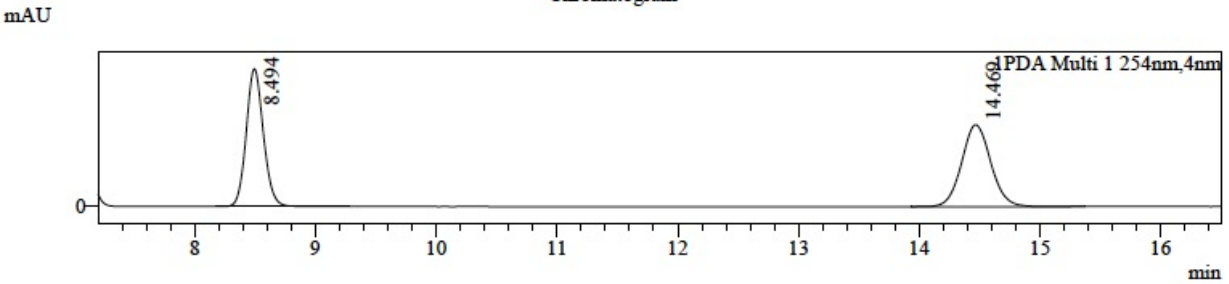


(±)-3bb

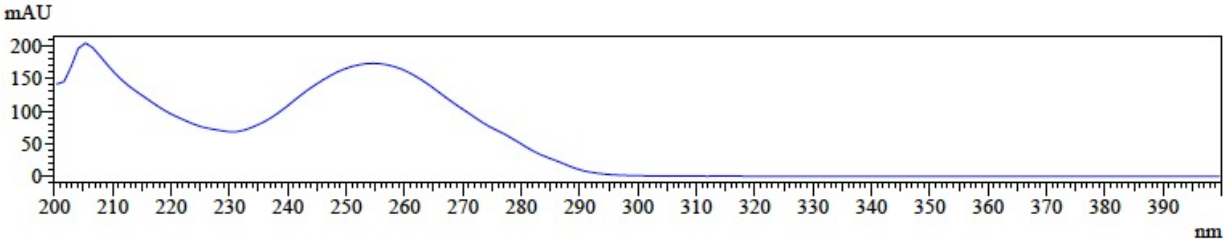
Sample Information

Data File	: XXW-1608--IA-5%-0.8mL.lcd
Sample Name	: XXW-1608--IA-5%-0.8mL
Sample ID	: XXW-1608--IA-5%-0.8mL
Method File	: XXW-5%.0.8.mL.lcm

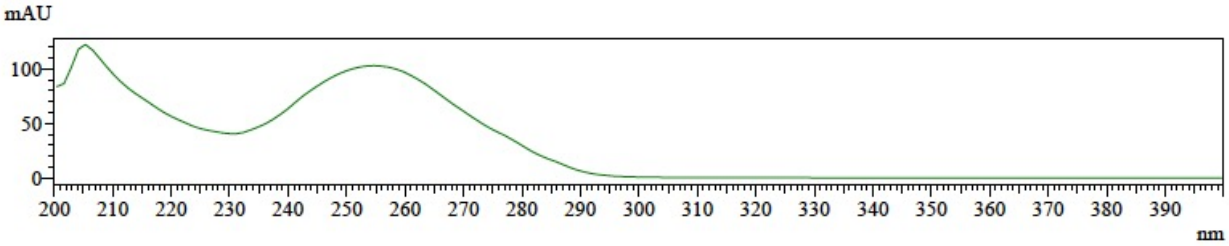
Chromatogram



UV Spectrum
Retention time = 8.494



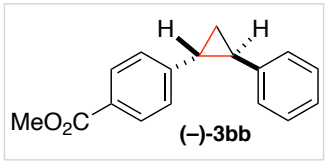
UV Spectrum
Retention time = 14.469



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.494	1705435	49.778
2	14.469	1720681	50.222
Total		3426116	100.000

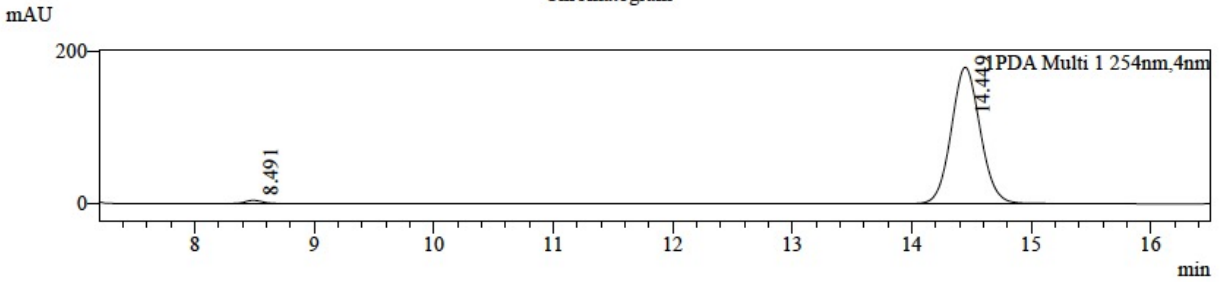


(–)-3bb

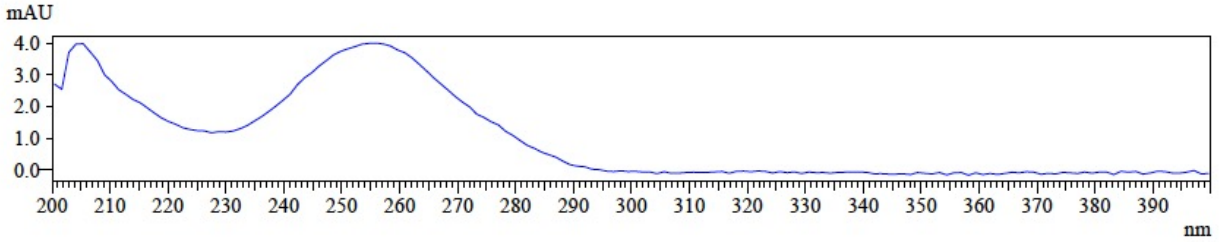
Sample Information

Data File	: XXW-1609-IA-5%-0.8mL.lcd
Sample Name	: XXW-1609-IA-5%-0.8mL
Sample ID	: XXW-1609-IA-5%-0.8mL
Method File	: XXW-5%.0.8.mL.lcm

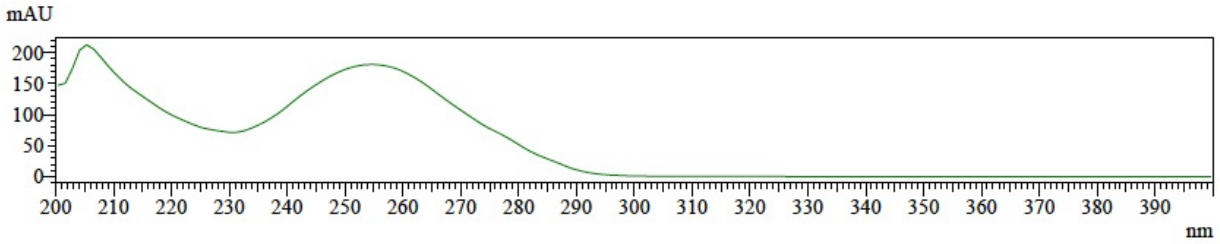
Chromatogram



UV Spectrum
Retention time = 8.491



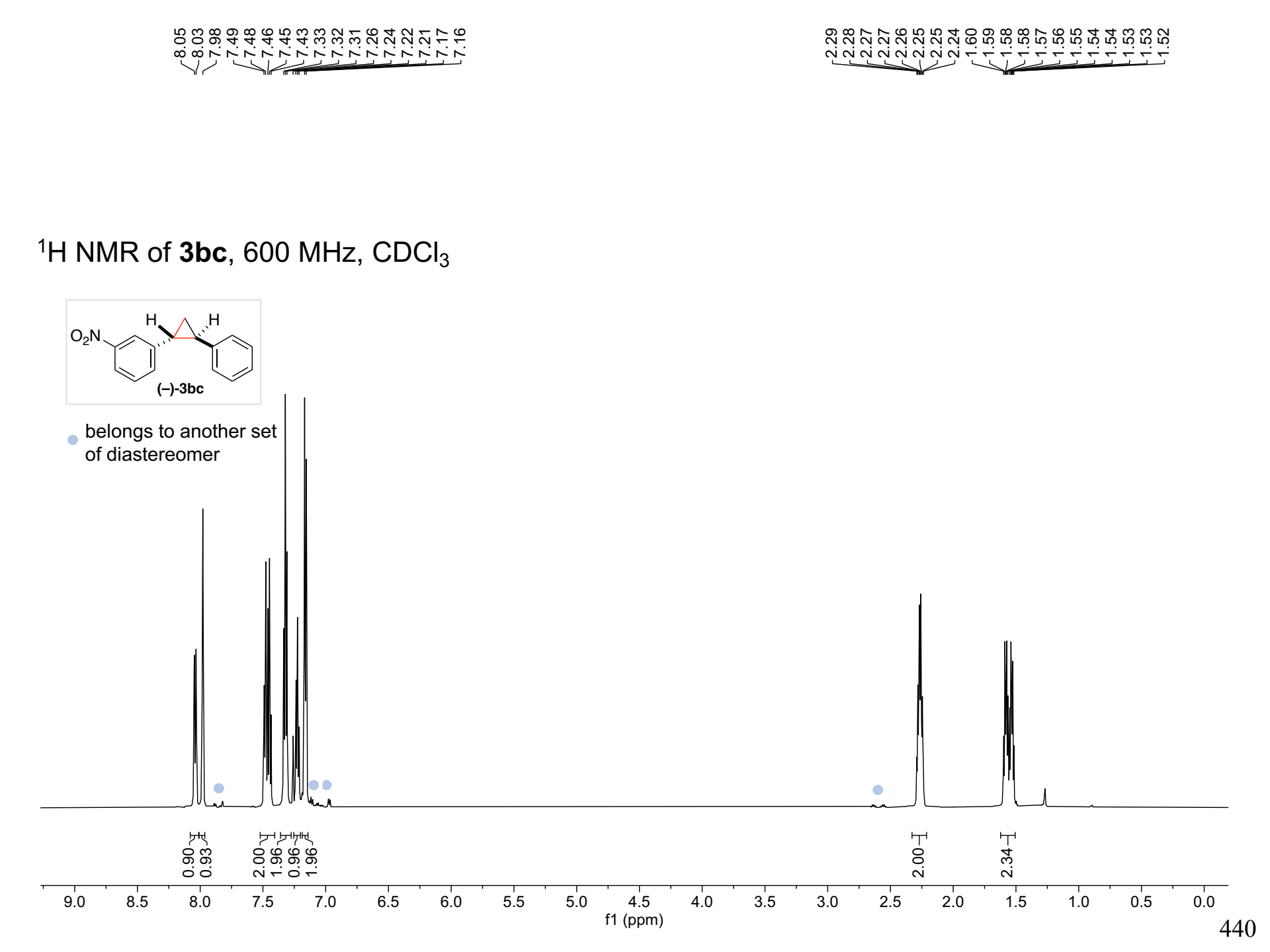
UV Spectrum
Retention time = 14.449



Peak Table

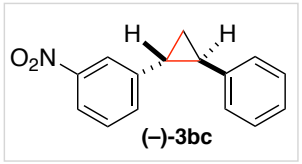
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.491	41813	1.358
2	14.449	3037232	98.642
Total		3079045	100.000


8.05
8.03
7.98
7.49
7.48
7.46
7.45
7.43
7.33
7.32
7.31
7.26
7.24
7.22
7.21
7.17
7.16
2.29
2.28
2.27
2.27
2.26
2.25
2.25
2.24
1.60
1.59
1.58
1.58
1.57
1.56
1.55
1.54
1.54
1.53
1.53
1.52
^{1}H NMR of **3bc**, 600 MHz, $CDCl_3$
H
H
O_2N
(–)-3bc
belongs to another set of diastereomer
0.90
0.93
2.00
1.96
0.96
1.96
2.00
2.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

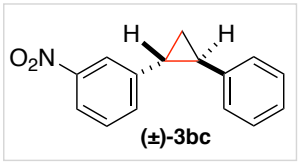
148.64
144.96
141.48
132.36
129.34
128.68
126.36
125.94
125.93
120.92
120.49
77.37
77.16
76.95
28.79
27.52
18.68

^{13}C NMR of **3bc**, 150 MHz, $CDCl_3$



(–)-3bc

● belongs to another set of diastereomer

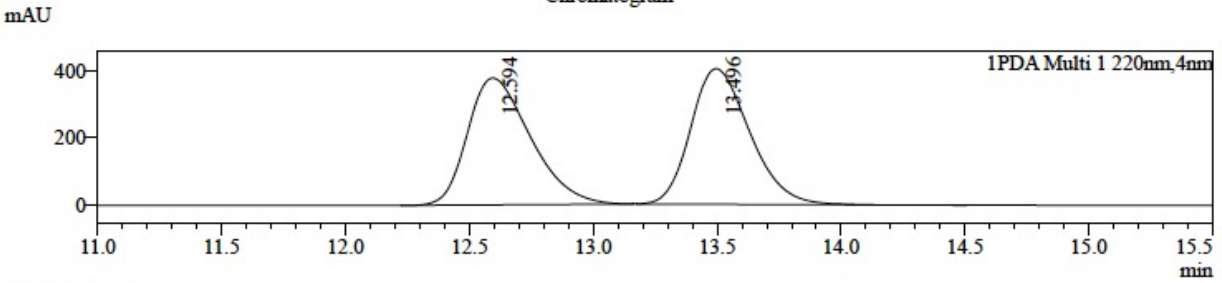


(±)-3bc

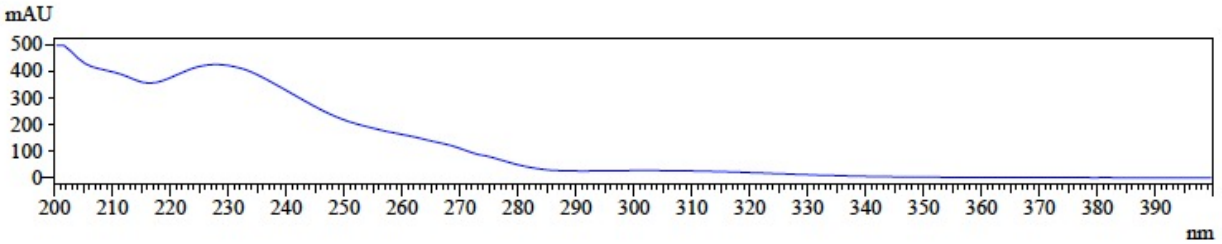
Sample Information

Data File	: XXW-1588--IA-0.5%-0.8mL001.lcd
Sample Name	: XXW-1588--IA-0.5%-0.8mL
Sample ID	: XXW-1588--IA-0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

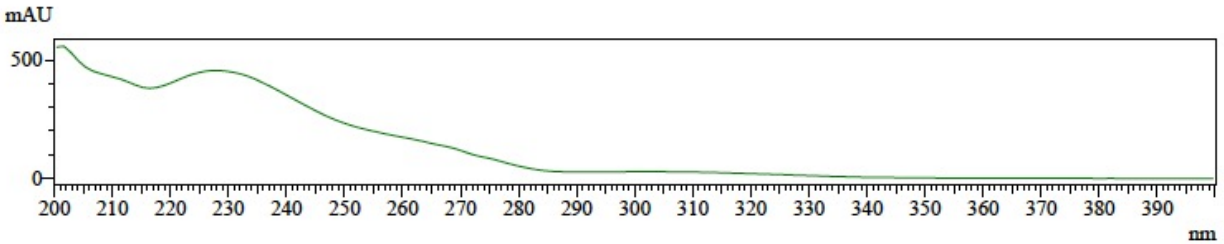
Chromatogram



UV Spectrum
Retention time = 12.594



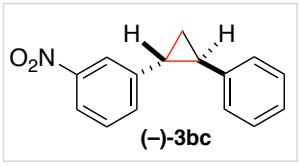
UV Spectrum
Retention time = 13.496



Peak Table

PDA Ch1 220nm

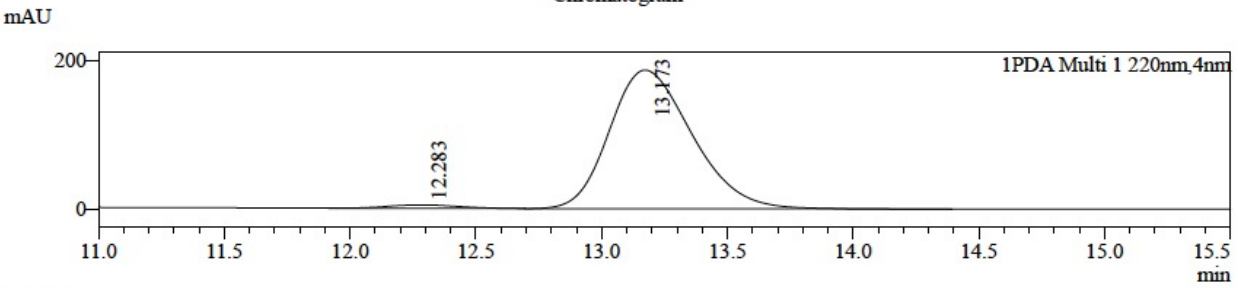
Peak#	Ret. Time	Area	Area%
1	12.594	6668980	49.943
2	13.496	6684175	50.057
Total		13353156	100.000



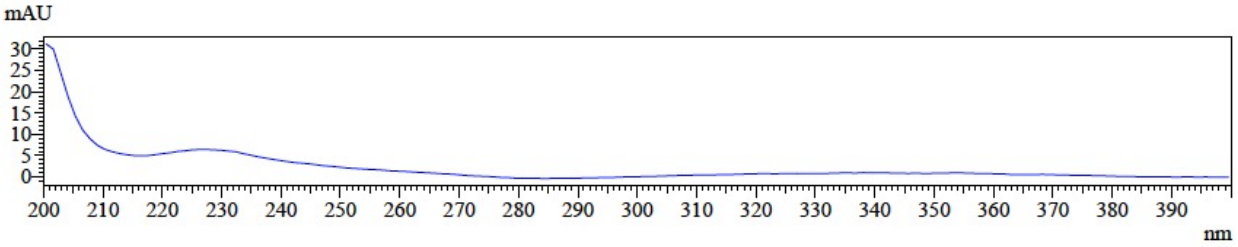
Sample Information

Data File	: XXW-1593-IA--0.5%-0.8mL001.lcd
Sample Name	: XXW-1593-IA--0.5%-0.8mL
Sample ID	: XXW-1593-IA--0.5%-0.8mL
Method File	: XXW-0.5%.0.8.mL.lcm

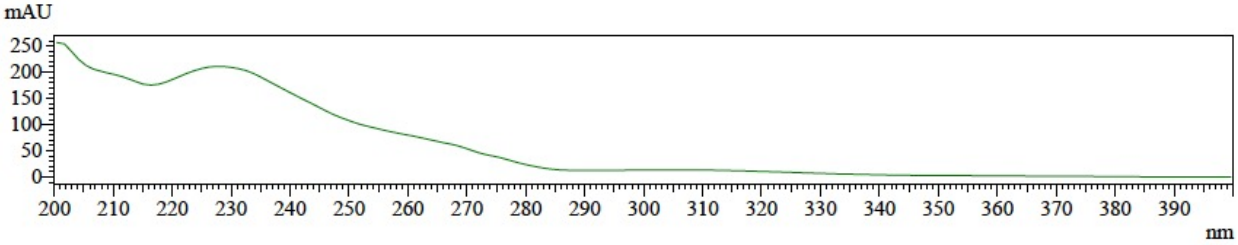
Chromatogram



UV Spectrum
Retention time = 12.283



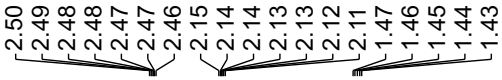
UV Spectrum
Retention time = 13.173



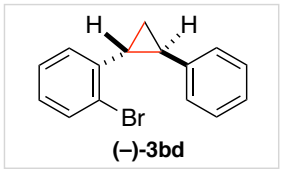
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.283	91039	2.085
2	13.173	4275851	97.915
Total		4366890	100.000

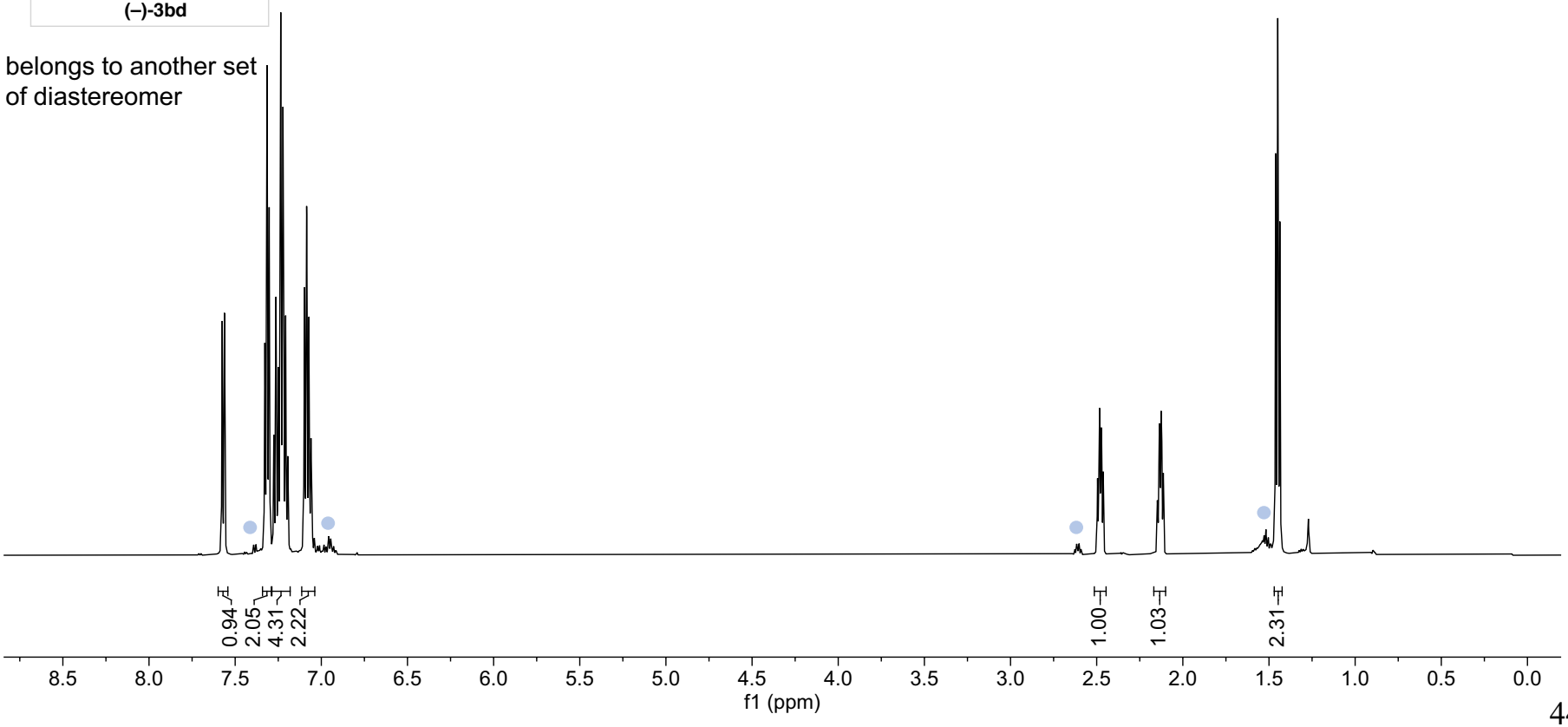


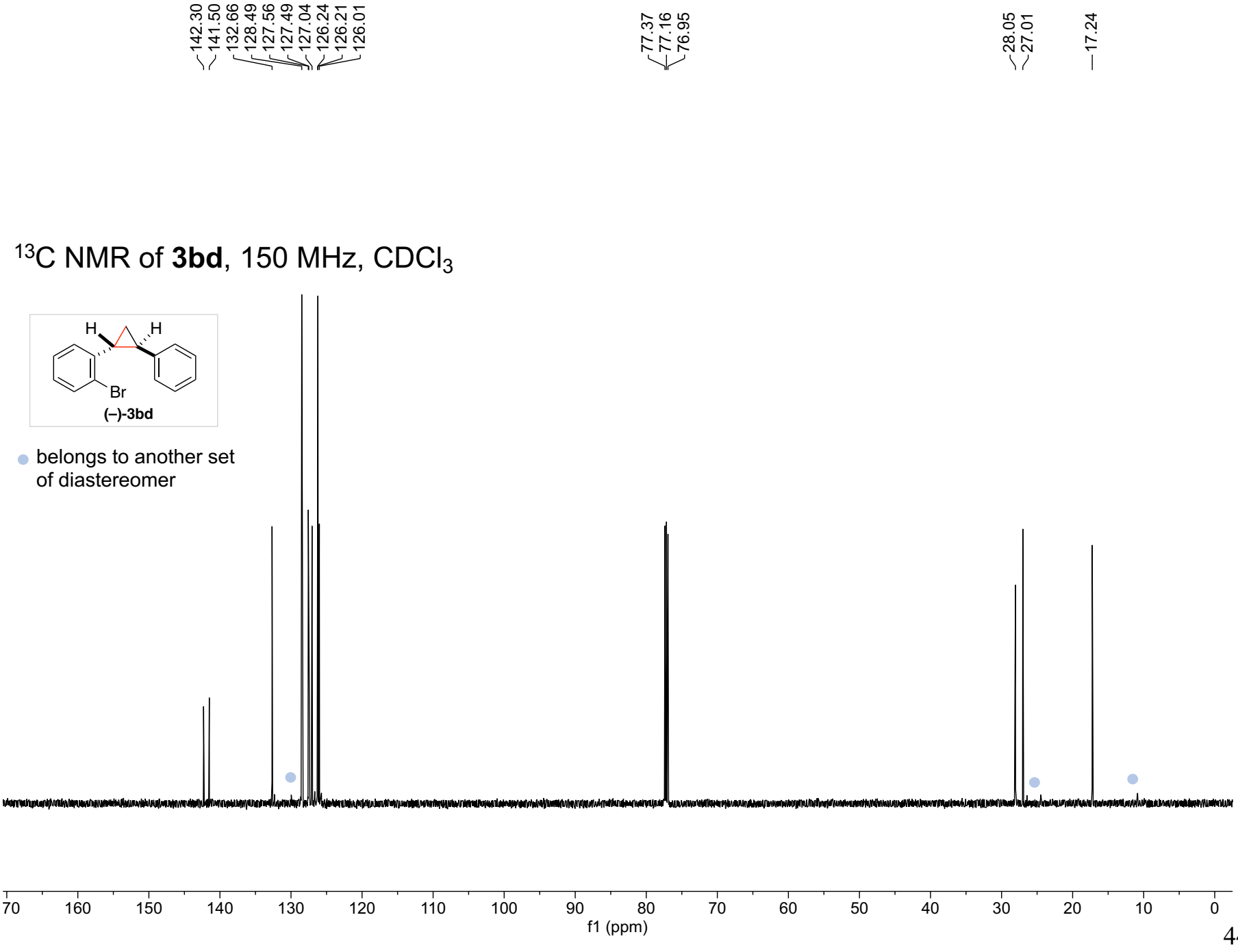
^{1}H NMR of **3bd**, 600 MHz, $CDCl_3$



(–)-3bd

belongs to another set of diastereomer

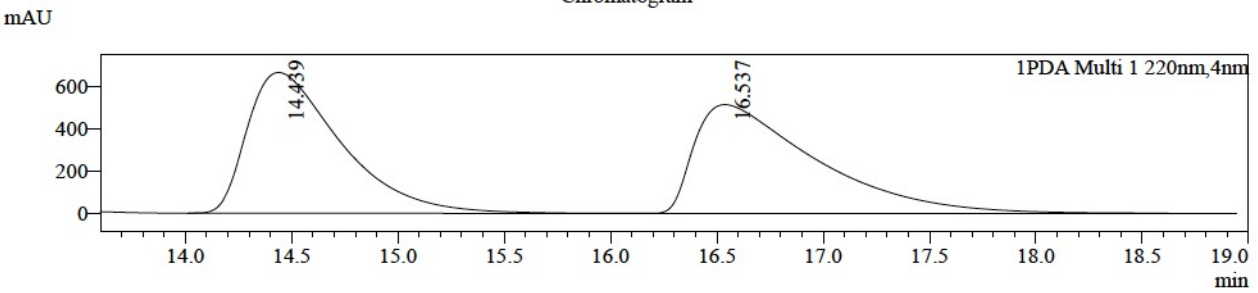



142.30
141.50
132.66
128.49
127.56
127.49
127.04
126.24
126.21
126.01
77.37
77.16
76.95
28.05
27.01
17.24
^{13}C NMR of **3bd**, 150 MHz, $CDCl_3$
H
H
Br
(–)-3bd
belongs to another set of diastereomer
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

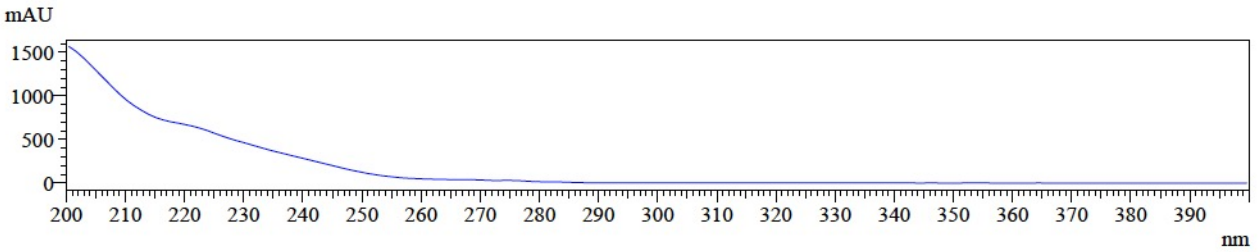
Sample Information

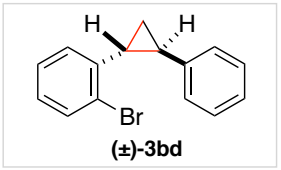
Data File	: XXW-1606-ADH-rac--0%-0.5mL.lcd
Sample Name	: XXW-1606-ADH-rac--0%-0.5mL
Sample ID	: XXW-1606-ADH-rac--0%-0.5mL
Method File	: XXW-0%-0.5mL.lcm

Chromatogram



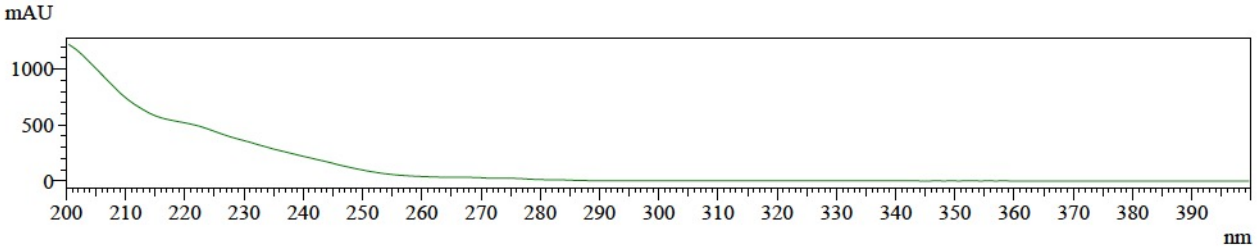
UV Spectrum
Retention time = 14.439





(±)-3bd

UV Spectrum
Retention time = 16.537



Peak Table

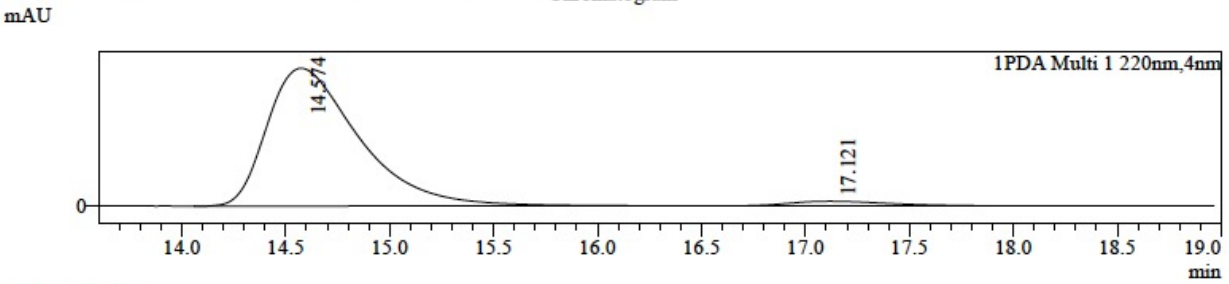
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.439	20353407	49.857
2	16.537	20470032	50.143
Total		40823439	100.000

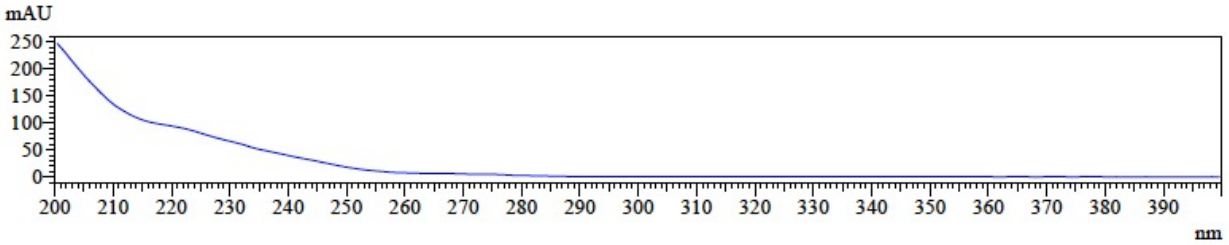
Sample Information

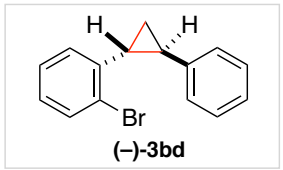
Data File	: XXW-1607-ADH--chiral-0%-0.5mL001.lcd
Sample Name	: XXW-1607-ADH--chiral-0%-0.5mL
Sample ID	: XXW-1607-ADH--chiral-0%-0.5mL
Method File	: XXW-0%-0.5mL.lcm

Chromatogram

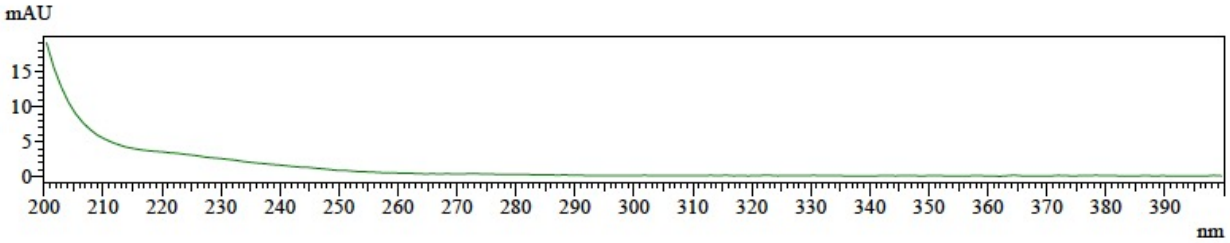


UV Spectrum
Retention time = 14.574





UV Spectrum
Retention time = 17.121

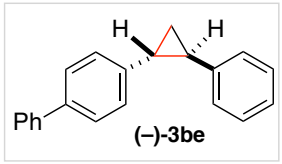


Peak Table

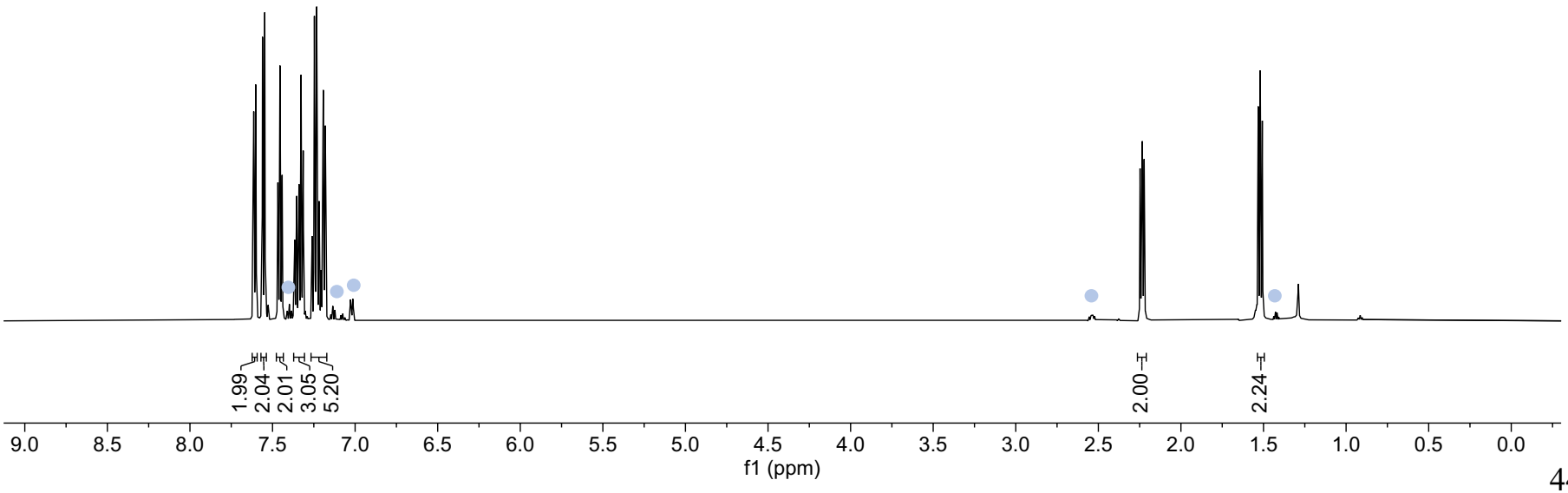
PDA Ch1 220nm

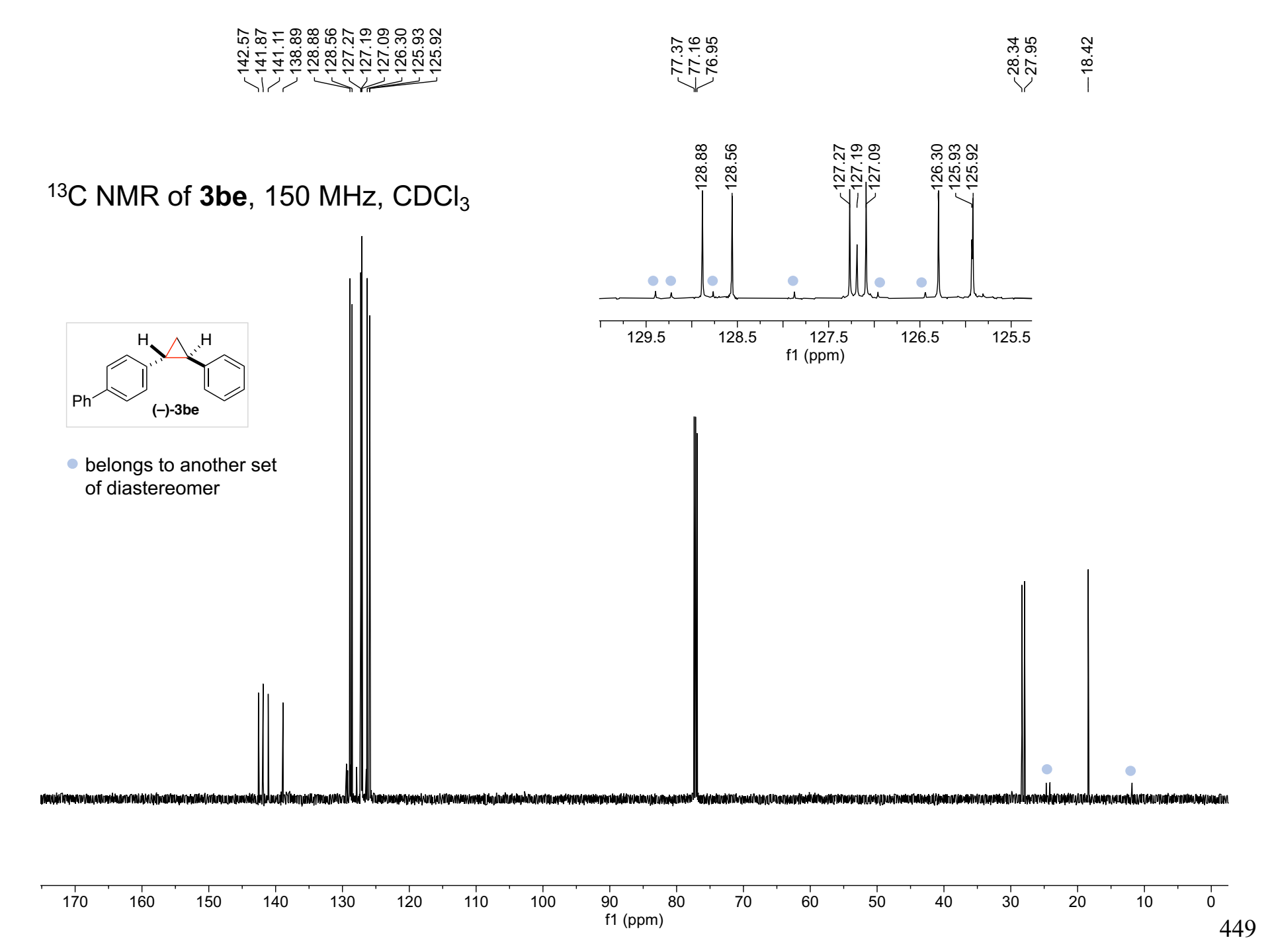
Peak#	Ret. Time	Area	Area%
1	14.574	2880627	96.646
2	17.121	99983	3.354
Total		2980610	100.000

^{1}H NMR of **3be**, 600 MHz, $CDCl_3$



● belongs to another set of diastereomer

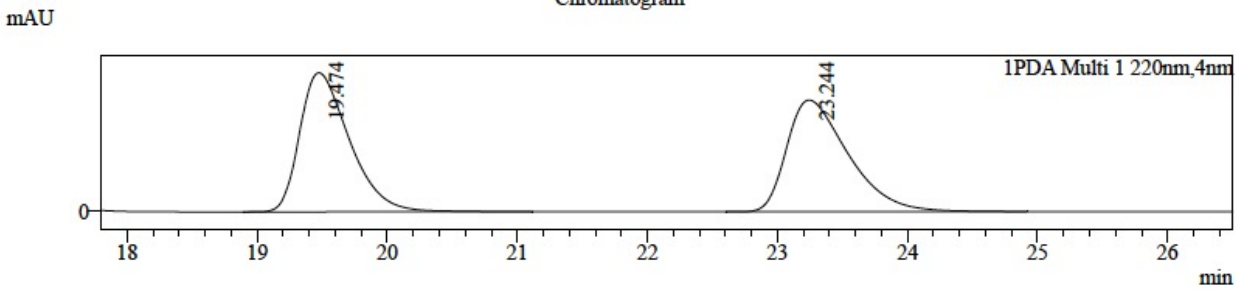



142.57
141.87
141.11
138.89
128.88
128.56
127.27
127.19
127.09
126.30
125.93
125.92
77.37
77.16
76.95
28.34
27.95
18.42
128.88
128.56
127.27
127.19
127.09
126.30
125.93
125.92
129.5
128.5
127.5
126.5
125.5
f1 (ppm)
^{13}C NMR of **3be**, 150 MHz, $CDCl_3$
H
H
Ph
(–)-3be
belongs to another set of diastereomer
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

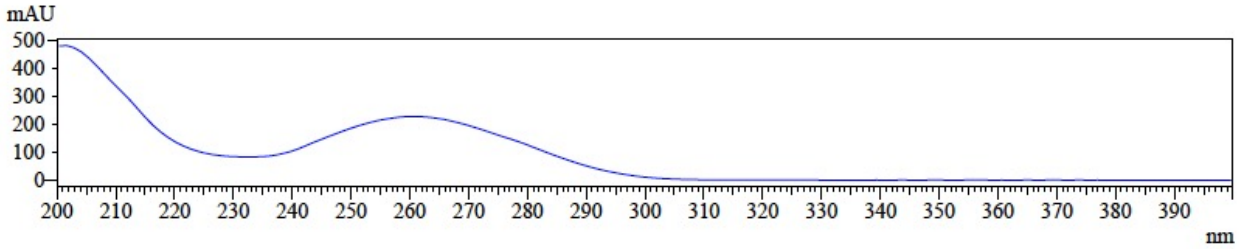
Sample Information

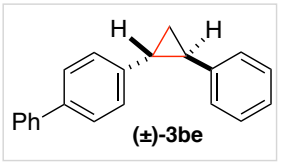
Data File	: XXW-1598-rac-IF--0.1%-0.8mL.lcd
Sample Name	: XXW-1598-rac-IF--0.1%-0.8mL
Sample ID	: XXW-1598-rac-IF--0.1%-0.8mL
Method File	: XXW-0.1%.0.8.mL.lcm

Chromatogram

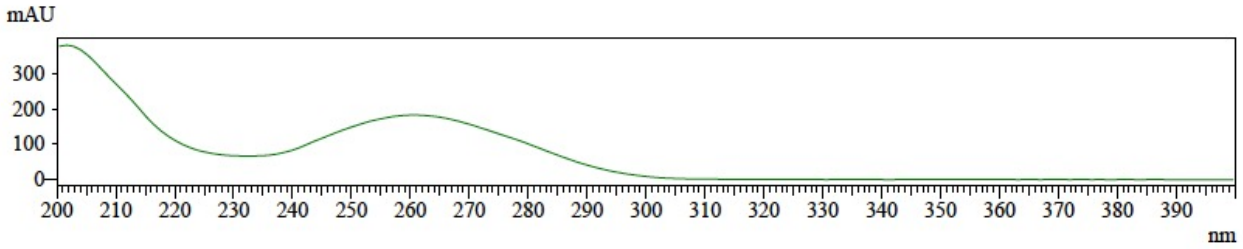


UV Spectrum
Retention time = 19.474





UV Spectrum
Retention time = 23.244



Peak Table

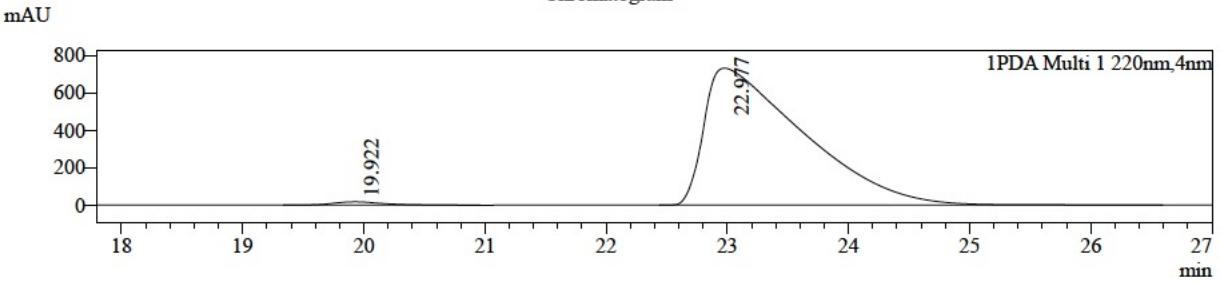
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	19.474	3782776	50.107
2	23.244	3766621	49.893
Total		7549397	100.000

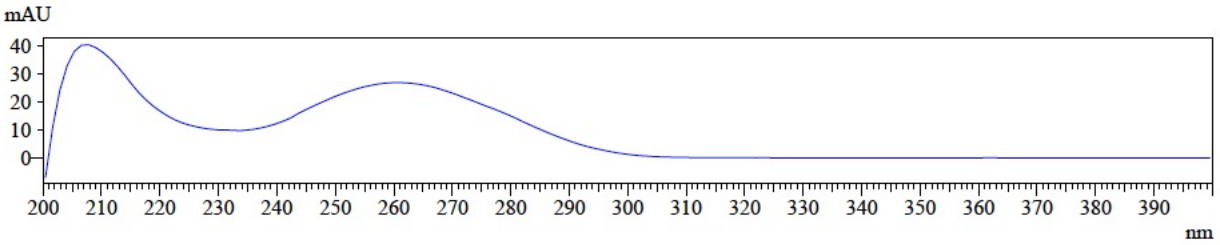
Sample Information

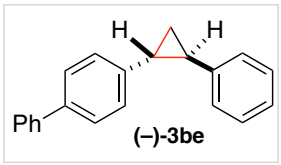
Data File : XXW-1599-IF--0.1%-0.8mL.lcd
Sample Name : XXW-1599-IF--0.1%-0.8mL
Sample ID : XXW-1599-IF--0.1%-0.8mL
Method File : XXW-0.1%.0.8.mL.lcm

Chromatogram

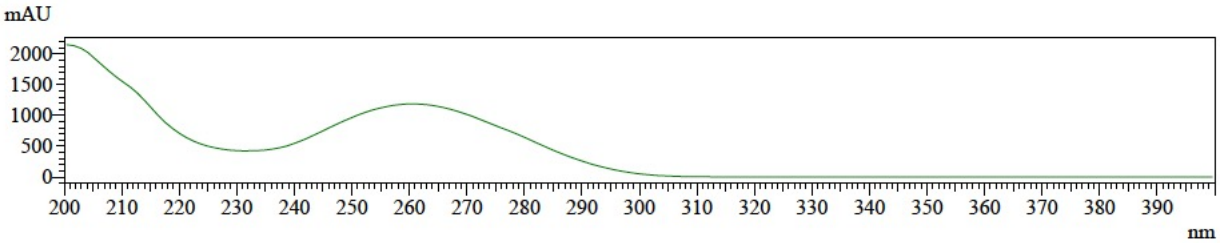


UV Spectrum
Retention time = 19.922





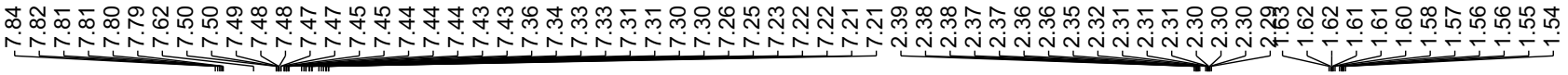
UV Spectrum
Retention time = 22.977



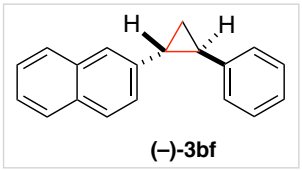
Peak Table

PDA Ch1 220nm

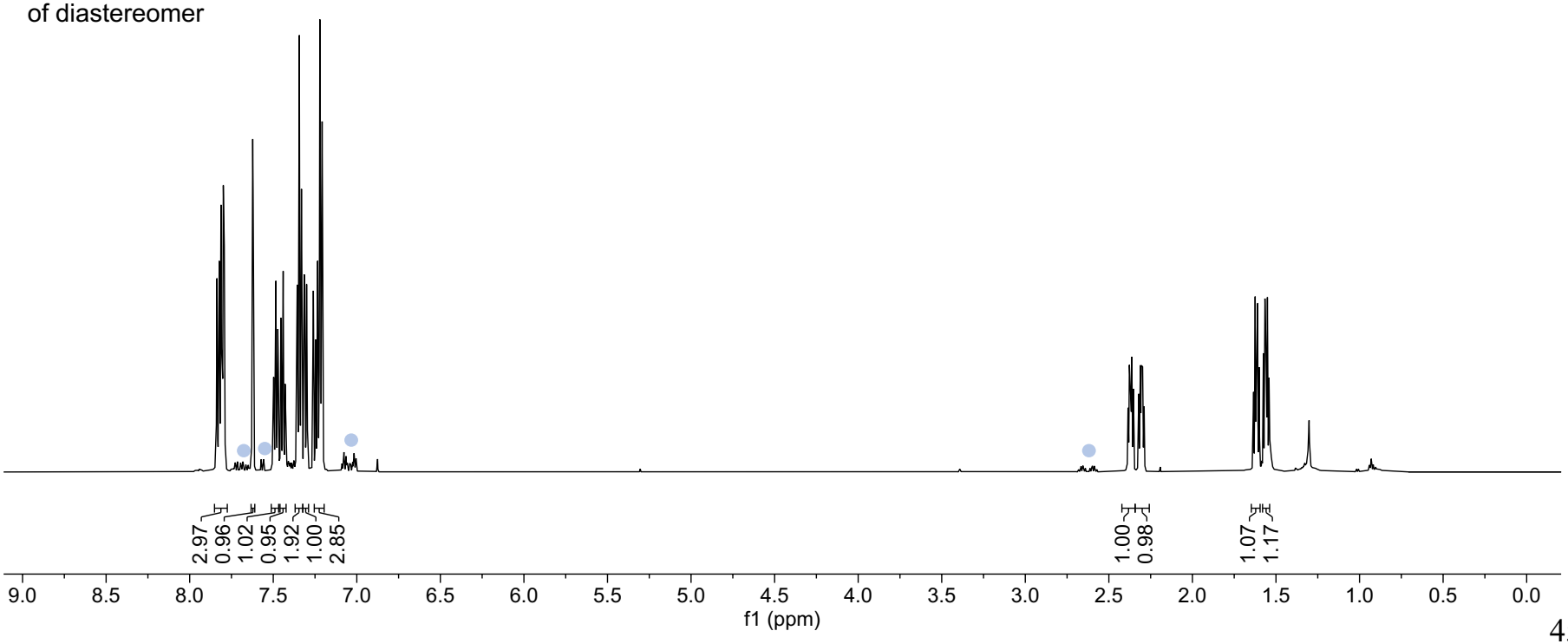
Peak#	Ret. Time	Area	Area%
1	19.922	461588	1.102
2	22.977	41436145	98.898
Total		41897732	100.000

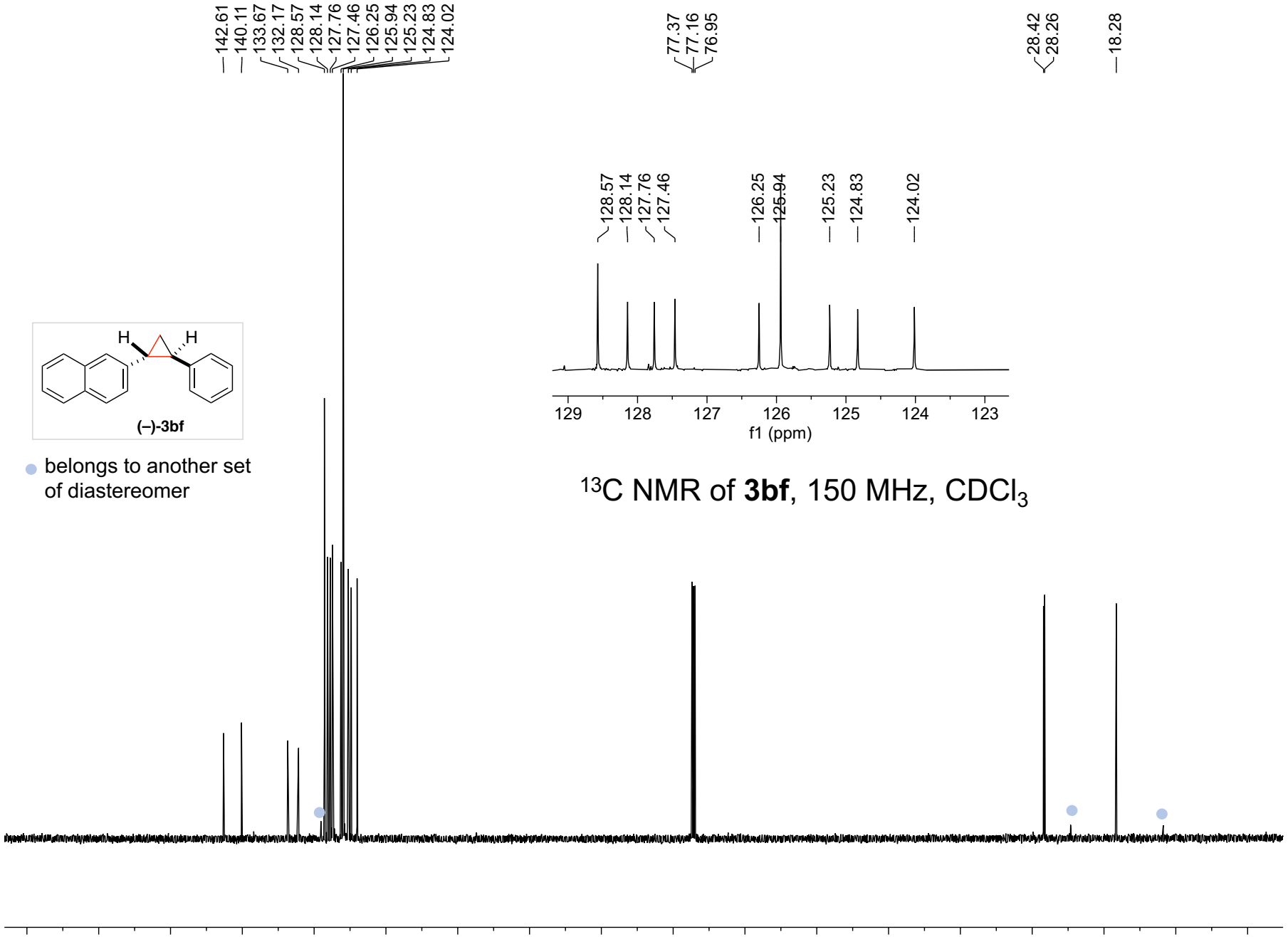


^{1}H NMR of **3bf**, 600 MHz, $CDCl_3$



● belongs to another set of diastereomer





^{13}C NMR of **3bf**, 150 MHz, $CDCl_3$

Sample Information

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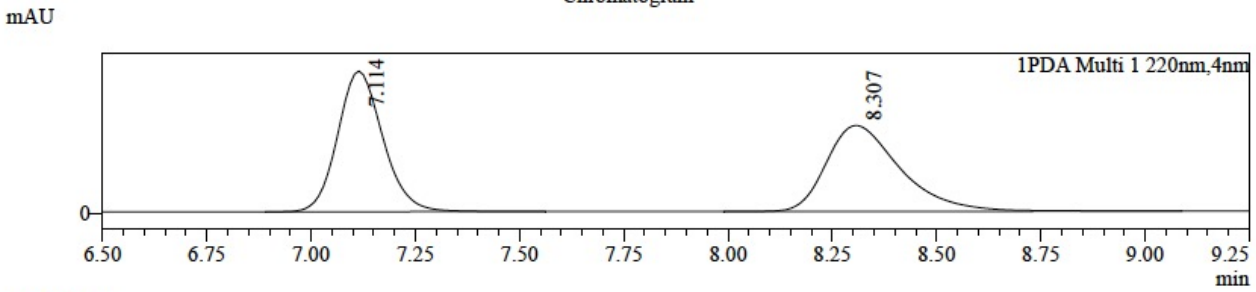
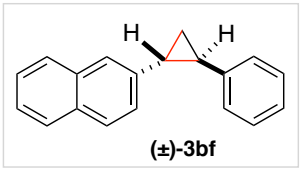
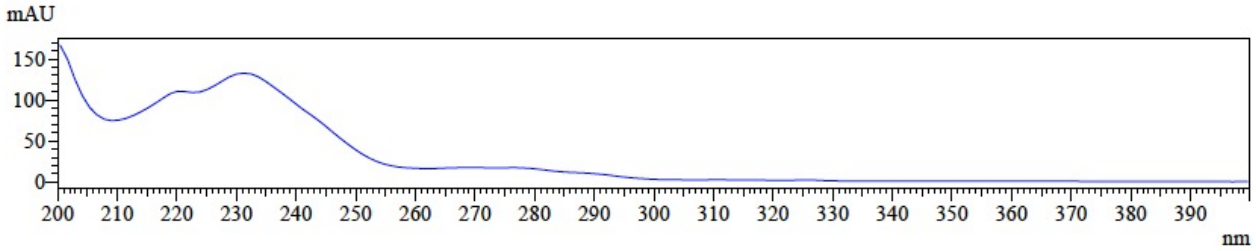
Sample Name : XXW-1589---IA-0.5%-0.8mL
Sample ID : XXW-1589---IA-0.5%-0.8mL
Method File : XXW-0.5%.0.8.mL.lcm

Chromatogram

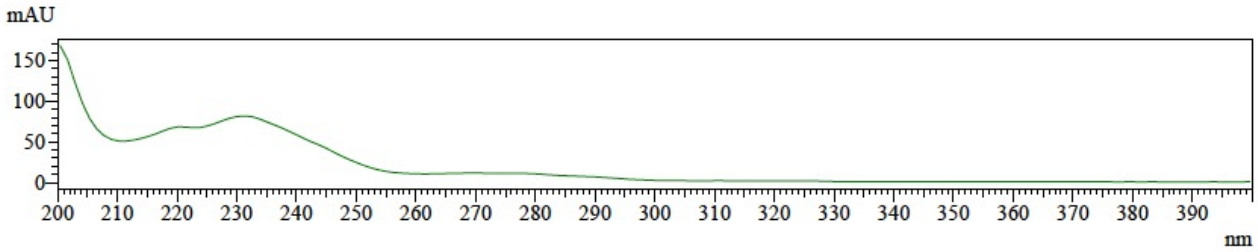


UV Spectrum
Retention time = 7.114





UV Spectrum
Retention time = 8.307



Peak Table

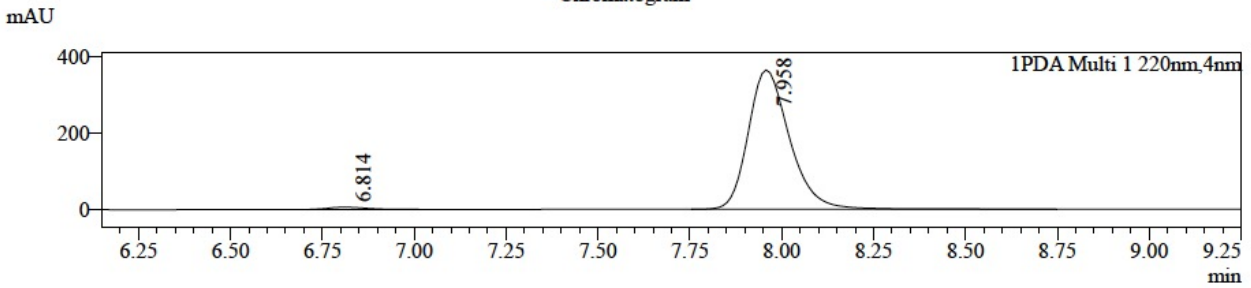
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.114	794998	50.130
2	8.307	790866	49.870
Total		1585864	100.000

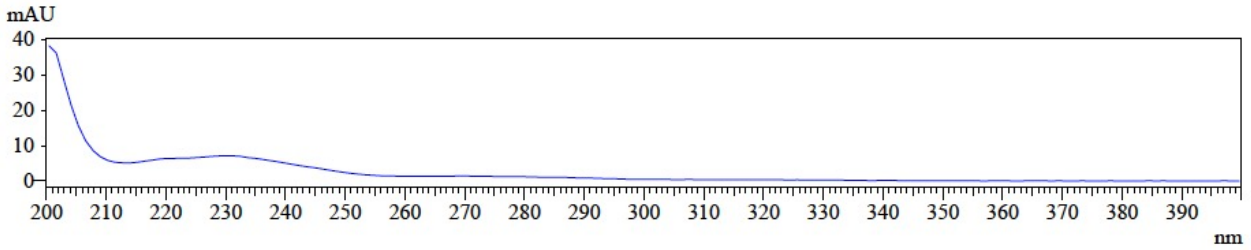
Sample Information

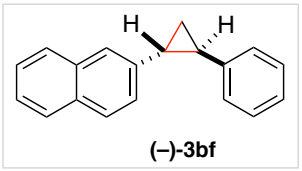
Data File : XXW-1594--IA-0.5%-0.8mL003.lcd
Sample Name : XXW-1594--IA-0.5%-0.8mL
Sample ID : XXW-1594--IA-0.5%-0.8mL
Method File : XXW-0.5%.0.8.mL.lcm

Chromatogram

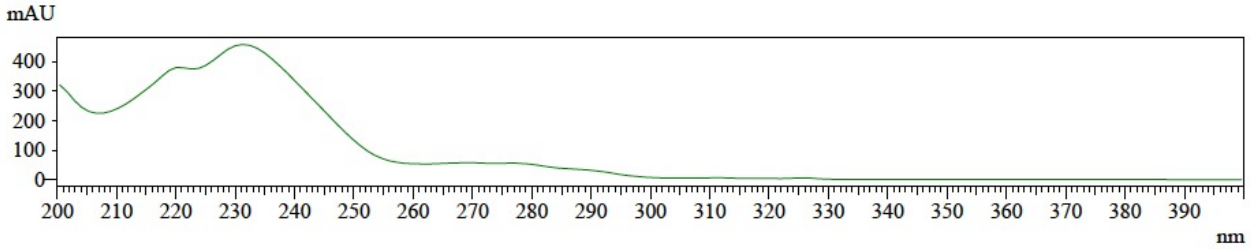


UV Spectrum
Retention time = 6.814





UV Spectrum
Retention time = 7.958



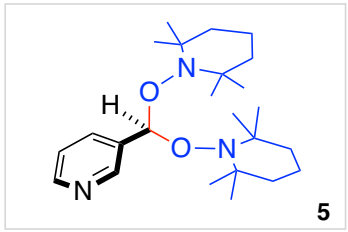
Peak Table

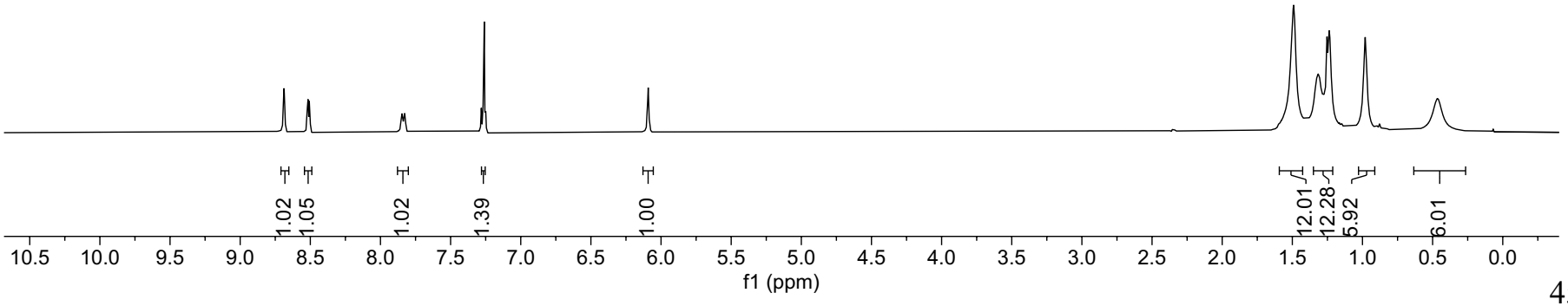
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	6.814	46015	1.582
2	7.958	2862933	98.418
Total		2908948	100.000

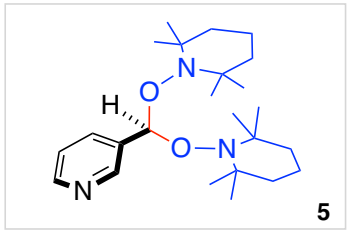
8.69
8.68
8.52
8.52
8.51
8.50
7.85
7.83
7.28
7.27
7.26
7.25
6.09
1.49
1.32
1.25
1.24
0.98
0.47

^{1}H NMR of **5**, 400 MHz, $CDCl_3$

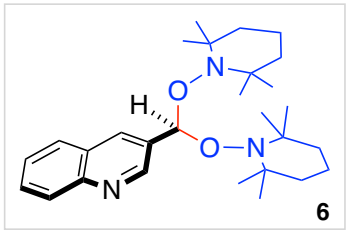




^{13}C NMR of **5**, 100 MHz, $CDCl_3$

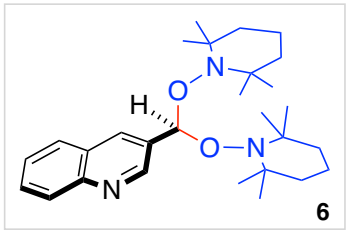


^{1}H NMR of **6**, 500 MHz, $CDCl_3$



151.73
147.75
135.18
133.50
129.35
129.30
128.28
127.51
126.43
107.86
77.41
77.16
76.91
60.82
60.32
40.77
40.11
34.60
33.55
21.41
20.87
17.32

^{13}C NMR of **6**, 125 MHz, $CDCl_3$



6

CHAPTER 3

ENANTIOSELECTIVE METALLORADICAL 1,6-C–H ALKYLATION OF IN SITU-GENERATED ALKYLDIAZOMETHANES FOR SYNTHESIS OF CHIRAL PIPERIDINES

3.1. INTRODUCTION

The past decades have witnessed renaissance in radical reactions owing to their rich reactivities and unique attributes.[1] In particular, hydrogen atom abstraction (HAA) by free alkyl radicals has been demonstrated with the potential for direct functionalization of ubiquitous C(sp^3)–H bond in organic molecules, offering a new strategy for C–C bond formation.[2] Despite significant advancements, development of HAA-mediated C–H alkylation have been hampered by several longstanding challenges that are associated with controlling reactivity and stereoselectivity of highly reactive radical intermediates. To address this enduring issue, metalloradical catalysis (MRC) offers a conceptually new approach for governing reactivity and controlling selectivity of radical processes through

[1] (a) Zard, S. Z. *Radical Reactions in Organic Synthesis*; Oxford University Press, 2003. (b) Chatgilialoglu, C.; Studer, A., *Encyclopedia of Radicals in Chemistry, Biology, and Materials*; John Wiley & Sons, 2012. For selected reviews, see: (c) Zard, S. Z. *Chem. Soc. Rev.* **2008**, *37*, 1603–1618. (d) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, *40*, 102–113. (e) Quiclet-Sire, B.; Zard, S. Z. *Pure Appl. Chem.* **2011**, *83*, 519–551. (f) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322–5363. (g) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58–102.

[2] (a) Choi, G. J.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. *Nature* **2016**, *539*, 268–271. (b) Chu, J. C. K.; Rovis, T. *Nature* **2016**, *539*, 272–275. (c) Zhang, W.; Wang, F.; McCann, S. D.; Wang, D.; Chen, P.; Stahl, S. S.; Liu, G. *Science* **2016**, *353*, 1014–1018. (d) Hu, X.-Q.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2017**, *56*, 1960–1962. (e) Lu, Q.; Glorius, F. *Angew. Chem., Int. Ed.* **2017**, *56*, 49–51. (f) Burg, F.; Gicquel, M.; Breitenlechner, S.; Pöthig, A.; Bach, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 2953–2957. (g) Stateman, L. M.; Nakafuku, K. M.; Nagib, D. A. *Synthesis* **2018**, *50*, 1569–1586. (h) Nakafuku, K. M.; Zhang, Z.; Wappes, E. A.; Stateman, L. M.; Chen, A. D.; Nagib, D. A. *Nat. Chem.* **2020**, *12*, 697–704. (i) Sarkar, S.; Cheung, K. P. S.; Gevorgyan, V. *Chem. Sci.* **2020**, *11*, 12974–12993. (j) Zhang, C.; Li, Z. L.; Gu, Q. S.; Liu, X. Y. *Nat. Commun.* **2021**, *12*, 475.

catalytic initiation and regulation of metal-stabilized organic radicals.[3,4,5] As stable 15e metalloradicals, Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] exhibit unique capability of homolytically activating diazo compounds as radial precursors to generate α-Co(III)-alkyl radicals.[6] These Co-stabilized C-centered radicals can serve as key catalytic intermediates to engage in radical addition and hydrogen atom abstraction as well as subsequent radical substitution, leading to the development of novel catalytic

[3] For selected reviews and highlights on Co(II)-based MRC, see: (a) Lu, H. J.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899–1909. (b) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775–2823. (c) Demarteau, J.; Debuigne, A.; Detrembleur, C. *Chem. Rev.* **2019**, *119*, 6906–6955. (d) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626–4638. (e) Singh, R.; Mukherjee, A. *ACS Catal.* **2019**, *9*, 3604–3617.

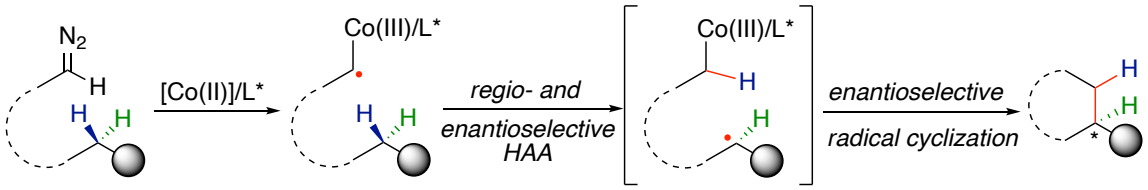
[4] For selected examples of Ti(III)-based radical processes, see: (a) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561–8562. (b) Rajanbabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986–997. (c) Gansäuer, A.; Hildebrandt, S.; Michelmann, A.; Dahmen, T.; von Laufenberg, D.; Kube, C.; Fianu, G. D.; Flowers II, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7003–7006. (d) Funken, N.; Mühlhaus, F.; Gansäuer, A. *Angew. Chem., Int. Ed.* **2016**, *55*, 12030–12034. (e) Hao, W.; Wu, X.; Sun, J. Z.; Siu, J. C.; MacMillan, S. N.; Lin, S. *J. Am. Chem. Soc.* **2017**, *139*, 12141–12144. (f) Yao, C. B.; Dahmen, T.; Gansäuer, A.; Norton, J. *Science* **2019**, *364*, 764–767. (g) Ye, K. Y.; McCallum, T.; Lin, S. *J. Am. Chem. Soc.* **2019**, *141*, 9548–9554. (f) Roy, S.; Das, S. K.; Khatua, H.; Das, S.; Chattopadhyay, B. *Acc. Chem. Res.* **2021**, *54*, 4395–4409.

[5] For selected examples of metalloradical-mediated radical processes, see: (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944. (b) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897–7898. (c) Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 2051–2061. (d) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920–6922. (e) Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662–14665. (f) Kuo, J. L.; Hartung, J.; Han, A.; Norton, J. R. *J. Am. Chem. Soc.* **2015**, *137*, 1036–1039. (g) Roy, S.; Khatua, H.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2019**, *58*, 11439–11443. (h) Das, S. K.; Roy, S.; Khatua, H.; Chattopadhyay, B. *J. Am. Chem. Soc.* **2020**, *142*, 16211–16217. (i) Zhang, Z.; Gevorgyan, V. *Org. Lett.* **2020**, *22*, 8500–8504. (j) Roy, S.; Das, S. K.; Khatua, H.; Das, S.; Singh, K. N.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2021**, *60*, 8772–8780.

[6] (a) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902. (b) Belof, J. L.; Cioce, C. R.; Xu, X.; Zhang, X. P.; Space, B.; Woodcock, H. L. *Organometallics* **2011**, *30*, 2739–2746. (c) Lu, H.; Dzik, W. I.; Xu, X.; Wojtas, L.; de Bruin, B.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521. (d) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2017**, *139*, 1049–1052. (e) Lee, W.-C. C.; Wang, D.-S.; Zhang, C.; Xie, J.; Li, B.; Zhang, X. P. *Chem* **2021**, *7*, 1588–1601. (f) Wang, X.; Ke, J.; Zhu, Y.; Deb, A.; Xu, Y.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11121–11129. (g) Xie, J.; Xu, P.; Zhu, Y.; Wang, J.; Lee, W.-C. C.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11670–11678. (h) Zhang, C.; Wang, D.-S.; Lee, W.-C. C.; McKillop, A. M.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11130–11140. (i) Zhou, M.; Wolzak, L. A.; Li, Z.; de Zwart, F. J.; Mathew, S.; de Bruin, B. *J. Am. Chem. Soc.* **2021**, *143*, 20501–20512.

processes for stereoselective radical transformations.[6d-h,7] Specifically, Co(II)-based MRC has been demonstrated as a potentially general strategy for stereoselective synthesis of cyclic molecules via new radical cyclization pathway that is based on asymmetric intramolecular radical C–H alkylation of diazo compounds (Scheme 3.1).[6g,8]

Scheme 3.1. Enantioselective Radical C–H Alkylation via Co(II)-MRC



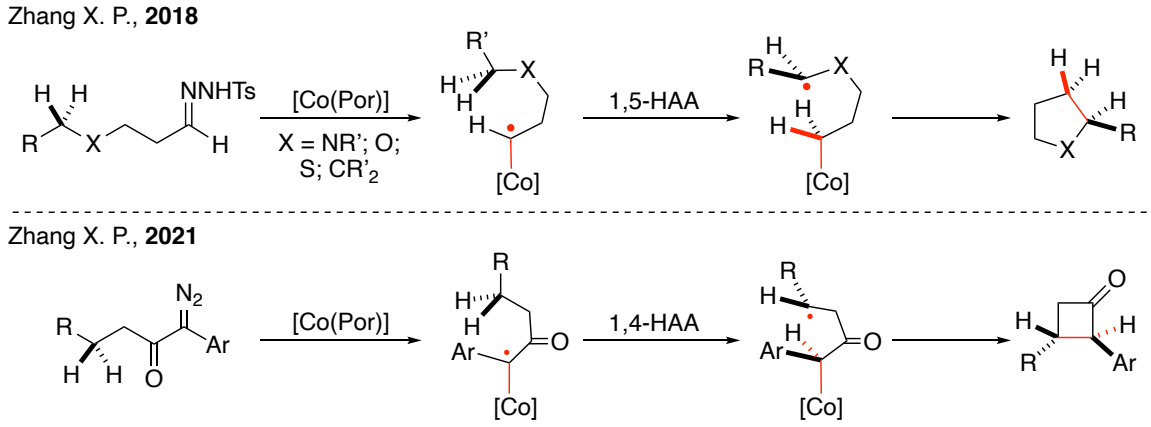
To harness the potential of this new radical cyclization strategy beyond synthesis of 5-membered[8] and 4-membered[6g] cyclic compounds (Scheme 3.2), we sought to explore the possibility of constructing 6-membered ring structures, such as the important *N*-heterocyclic compound piperidines **2**, by asymmetric 1,6-C–H alkylation of linear α-alkyldiazomethanes **1'** through in situ-generation from the corresponding 4-aminobutanal-derived hydrazones **1** in the presence of base (Scheme 3.3).

---

[7] (a) Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719. (b) Caselli, A.; Gallo, E.; Ragaini, F.; Ricatto, F.; Abbiati, G.; Cenini, S. *Inorg. Chim. Acta.* **2006**, *359*, 2924–2932. (c) Chen, Y.; Ruppel, J. V.; Zhang, X. P. *J. Am. Chem. Soc.* **2007**, *129*, 12074–12075. (d) Fantauzzi, S.; Gallo, E.; Rose, E.; Raoul, N.; Caselli, A.; Issa, S.; Ragaini, F.; Cenini, S. *Organometallics* **2008**, *27*, 6143–6151. (e) Zhu, S.; Ruppel, J. V.; Lu, H.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043. (f) Zhu, S.; Xu, X.; Perman, J. A.; Zhang, X. P. *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799. (g) Xu, X.; Lu, H. J.; Ruppel, J. V.; Cui, X.; de Mesa, S. L.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 15292–15295. (h) Paul, N. D.; Mandal, S.; Otte, M.; Cui, X.; Zhang, X. P.; de Bruin, B. *J. Am. Chem. Soc.* **2014**, *136*, 1090–1096. (i) Reddy, A. R.; Hao, F.; Wu, K.; Zhou, C. Y.; Che, C. M. *Angew. Chem., Int. Ed.* **2016**, *55*, 1810–1815. (j) Chirila, A.; Gopal Das, B.; Paul, N. D.; de Bruin, B. *ChemCatChem* **2017**, *9*, 1413–1421. (k) Roy, S.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2018**, *57*, 2238–2243.

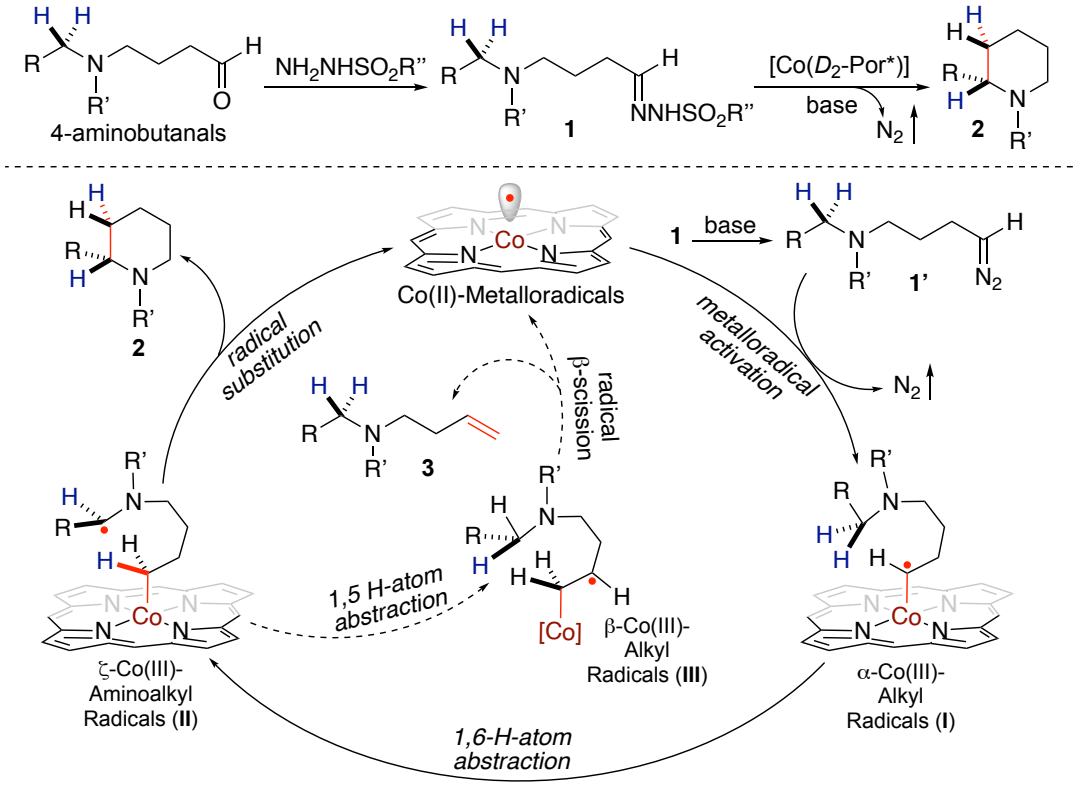
[8] (a) Cui, X.; Xu, X.; Jin, L.-M.; Wojtas, L.; Zhang, X. P. *Chem. Sci.* **2015**, *6*, 1219–1224. (b) Wang, Y.; Wen, X.; Cui, X.; Zhang, X. P. *J. Am. Chem. Soc.* **2018**, *140*, 4792–4796. (c) Wen, X.; Wang, Y.; Zhang, X. P. *Chem. Sci.* **2018**, *9*, 5082–5086.

Scheme 3.2. Co(II)-Based Metalloradical 1,4- and 1,5-C–H Alkylation



However, the intended synthesis of piperidines **2** by Co(II)-based catalytic system presented several potential challenges. In addition to the prerequisite for matching the rates between metalloradical activation of alkyldiazomethanes **1'** and their in situ-generation from hydrazones **1**, it was uncertain whether the resulting α-Co(III)-alkyl radicals **I** with C–H bonds at various positions could undergo competitive 1,6-HAA to generate the desired ζ-Co(III)-aminoalkyl radical **II** over potential 1,2, 1,3- and 1,4-HAA that lead to side reactions. This uncertainty came from the consideration that the 7-memebred cyclic transition state associated with 1,6-HAA is entropically less favorable. Additional challenges could arise in the subsequent step of radical substitution of ζ-Co(III)-alkyl radicals **II** for formation of piperidines **2**. If the 6-*exo*-*tet* radical cyclization of ζ-Co(III)-alkyl radicals **II** fails to compete with typically facile 1,5-HAA, it would result in the generation of β-Co(III)-alkyl radicals **III**, which would lead to formation of olefin **3** as side products via radical β-scission. Besides the concerns with controlling of reactivity, whether the ensuing C–C bond formation during radical cyclization could be rendered enantioselective is another unanswered question.

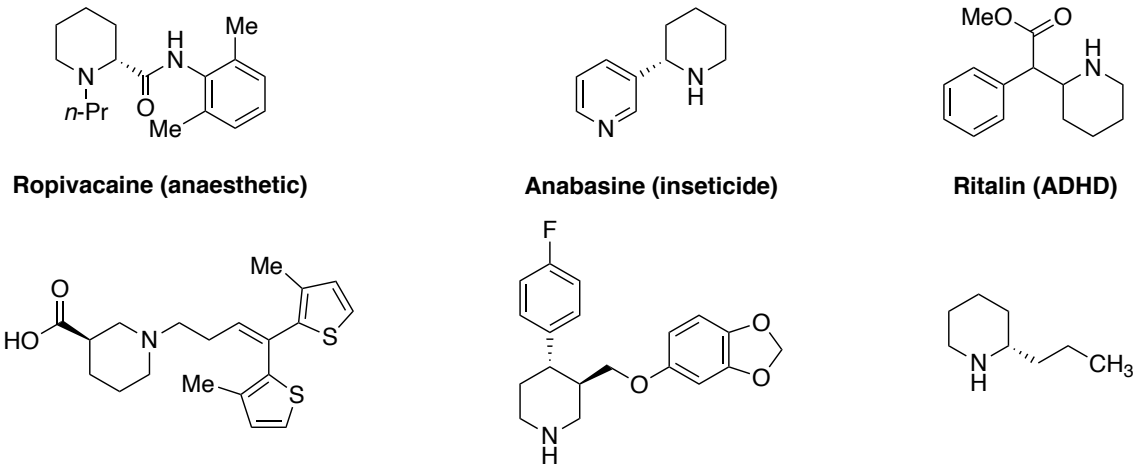
Scheme 3.3. Working Proposal for Stereoselective Synthesis of Piperidines by Metalloradical 1,6-C–H Alkylation



In view of the conformational flexibility associated with the linear methylene chain in ζ-Co(III)-alkyl radicals **II**, what elements could be exploited to differentiate the two prochiral radical faces at the remote ζ-position in order to induce high asymmetry during the course of 6-*exo*-*tet* radical cyclization? We reasoned that the key to address these and related challenges is to identify a suitable D_2- symmetric chiral amidoporphyrin ligand (D_2-Por*) with proper electronic, steric, and chiral environments that could govern the stereochemical course of the Co(II)-based radical processes as proposed. If realized, it would lead to the development of a new catalytic method for enantioselective synthesis of

piperidines,[9] which exist ubiquitously in natural products and bioactive compounds (Figure 3.1), from readily accessible 4-aminobutanal derivatives.

Figure 3.1. Selected Examples of Bioactive Compounds Containing Piperidines

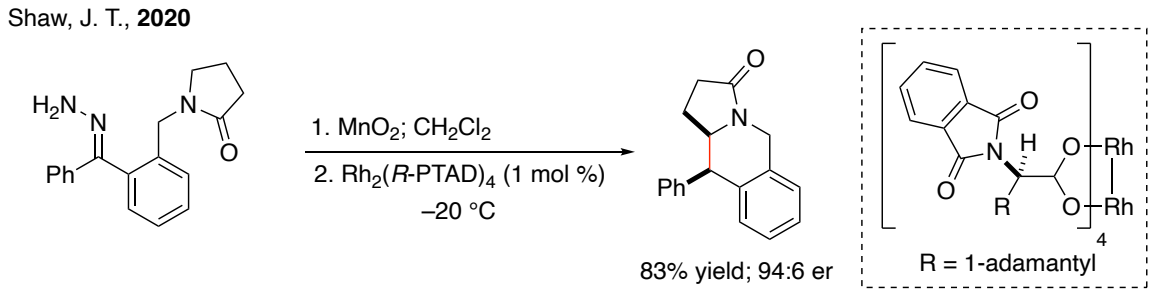


Catalytic asymmetric intramolecular 1,6-C–H alkylation of diazo compounds represents an attractive approach for stereoselective construction of chiral 6-membered cyclic compounds.[10] Despite considerable advancements, there have been only a few reports on

[9] (a) Fujita, K.-i.; Fujii, T.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 3525–3528. (b) Pastine, S. J.; Gribkov, D. V.; Sames, D. *J. Am. Chem. Soc.* **2006**, *128*, 14220–14221. (c) Coldham, I.; Leonori, D. *Org. Lett.* **2008**, *10*, 3923–3925. (d) Beng, T. K.; Gawley, R. E. *J. Am. Chem. Soc.* **2010**, *132*, 12216–12217. (e) Stead, D.; Carbone, G.; O'Brien, P.; Campos, K. R.; Coldham, I.; Sanderson, A. *J. Am. Chem. Soc.* **2010**, *132*, 7260–7261. (f) Yoshikai, N.; Mieczkowski, A.; Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2010**, *132*, 5568–5569. (g) Cui, Z.; Yu, H.-J.; Yang, R.-F.; Gao, W.-Y.; Feng, C.-G.; Lin, G.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 12394–12397. (h) McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* **2011**, *334*, 1114–1117. (i) Qu, B.; Mangunuru, H. P. R.; Tcyrulnikov, S.; Rivalti, D.; Zatolochnaya, O. V.; Kurouski, D.; Radomkit, S.; Biswas, S.; Karyakarte, S.; Fandrick, K. R.; Sieber, J. D.; Rodriguez, S.; Desrosiers, J.-N.; Haddad, N.; McKellop, K.; Pennino, S.; Lee, H.; Yee, N. K.; Song, J. J.; Kozlowski, M. C.; Senanayake, C. H. *Org. Lett.* **2018**, *20*, 1333–1337. (j) Boddy, A. J.; Affron, D. P.; Cordier, C. J.; Rivers, E. L.; Spivey, A. C.; Bull, J. A. *Angew. Chem. Int. Ed.* **2019**, *58*, 1458–1462.

[10] (a) Lee, E.; Choi, I.; Song, S. Y. *J. Chem. Soc., Chem. Commun.* **1995**, 321–322. (b) Rosales, A.; Rodríguez-García, I.; López-Sánchez, C.; Álvarez-Corral, M.; Muñoz-Dorado, M. *Tetrahedron* **2011**, *67*, 3071–3075. (c) Taber, D. F.; Paquette, C. M.; Gu, P.; Tian, W. *J. Org. Chem.* **2013**, *78*, 9772–9780. (d) Bergstrom, B. D.; Nickerson, L. A.; Shaw, J. T.; Souza, L. W. *Angew. Chem. Int. Ed.* **2021**, *60*, 6864–6878.

Scheme 3.4. Rh_2-Catalyzed Asymmetric 1,6-C–H Alkylation for Synthesis of Tetrahydroisoquinolines

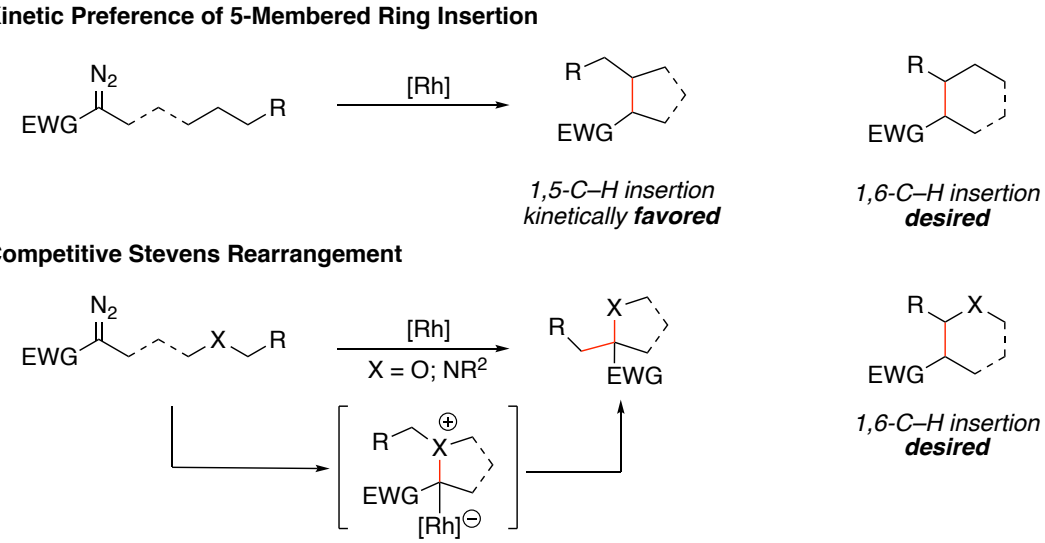


metal-based catalytic systems for asymmetric 1,6-C–H alkylation.[11] In addition to moderate enantioselectivity, the existing catalytic systems has been largely limited to the formation of oxygen-containing ring structures. To date, Shaw and coworkers reported the only notable example of asymmetric 1,6-C–H alkylation to form nitrogen-containing 6-membered heterocycles based on a Rh_2-catalytic system involving donor/donor-substituted diazo compounds (Scheme 3.4).[12]

[11] (a) McCarthy, N.; McKervey, M. A.; Ye, T.; McCann, M.; Murphy, E.; Doyle, M. P. *Tetrahedron Lett.* **1992**, *33*, 5983–5986. (b) McKervey, M. A.; Ye, T. *J. Chem. Soc., Chem. Commun.* **1992**, 823–824. (c) Ye, T.; García, C. F.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. I* **1995**, 1373–1379. (d) Slattery, C. N.; Clarke, L.-A.; O'Neill, S.; Ring, A.; Ford, A.; Maguire, A. R. *Synlett* **2012**, *23*, 765–767. (e) Ito, M.; Kondo, Y.; Nambu, H.; Anada, M.; Takeda, K.; Hashimoto, S. *Tetrahedron Lett.* **2015**, *56*, 1397–1400. (f) Anada, M.; Hashimoto, S.; Ito, M.; Kondo, Y.; Namie, R.; Natori, Y.; Takeda, K.; Nambu, H.; Yamamoto, Y. *Heterocycles* **2021**, *103*, 1078–1098.

[12] Nickerson, L. A.; Bergstrom, B. D.; Gao, M.; Shiue, Y.-S.; Laconsay, C. J.; Culberson, M. R.; Knauss, W. A.; Fettinger, J. C.; Tantillo, D. J.; Shaw, J. T. *Chem. Sci.* **2020**, *11*, 494–498.

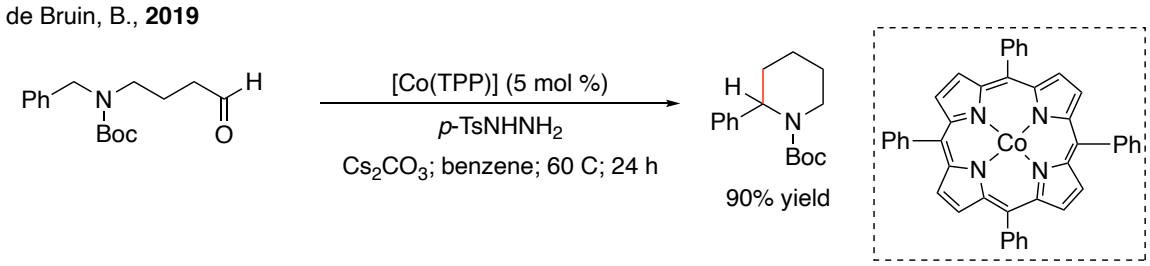
Scheme 3.5. Potential Challenges of Intramolecular 1,6-C–H Alkylation Involving Electrophilic Metallocarbenes



This underdevelopment is presumably attributed to the kinetic preference for 1,5-C–H alkylation and inherent propensity of electrophilic metallocarbene intermediate toward the formation of cyclic ylide by nucleophilic attack of the Lewis basic nitrogen atom (Scheme 3.5).[12,13,14] Evidently, a new catalytic system that is fundamentally different from the existing ionic systems involving electrophilic metallocarbene intermediates would be highly appealing to allow selective C–H alkylation without complication by the heteroatoms. To circumvent the problem, de Bruin and coworkers recently disclosed a [Co(TPP)]-catalyzed (TPP = 5,10,15,20-tetraphenylporphyrin) metalloradical alkylation of α-alkyldiazomethanes for synthesis of 6-membered *N*-heterocyclic piperidines (Scheme 3.6).[15] However, the enantioselective control of this transformation remains to be addressed.

[13] Estevan, F.; Herbst, K.; Lahuerta, P.; Barberis, M.; Pérez-Prieto, J. *Organometallics* **2001**, *20*, 950–957.
[14] Doyle, M. P.; Ene, D. G.; Forbes, D. C.; Tedrow, J. S. *Tetrahedron Lett.* **1997**, *38*, 4367–4370.
[15] Lankelma, M.; Olivares, A. M.; de Bruin, B. *Chem. Eur. J.* **2019**, *25*, 5658–5663.

Scheme 3.6. [Co(TPP)]-Catalyzed Formation of Substituted Piperidines



As an exciting application of Co(II)-MRC, we herein report the development of the first catalytic system that is highly efficient for asymmetric 1,6-C–H alkylation of α-alkyldiazomethanes to construct chiral piperidines. Supported by an optimal D_2-symmetric chiral amidoporphyrin ligand, the Co(II)-based metalloradical system can activate a wide array of α-alkyldiazomethanes with varied steric and electronic properties for intramolecular radical 1,6-C–H alkylation, enabling the synthesis of α-substituted piperidines in good to high yields with excellent enantioselectivities. Furthermore, the radical alkylation process features high degree of functional group tolerance as well as compatibility of heteroaryl units. We also present detailed computational and experimental studies that have shed light on the underlying stepwise radical mechanism that consists of facile 1,6-HAA and 6-*exo*-*tet* radical substitution (RS) as the key steps.

3.2. RESULTS AND DISCUSSION

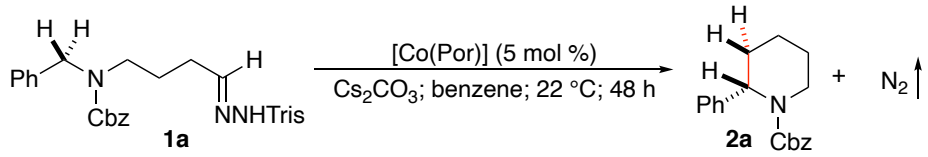
3.2.1. Condition Optimization for Co(II)-Catalyzed 1,6-C–H Alkylation of α-Alkyldiazomethanes

At the outset of this project, 4-aminobutanal-derived trishydrazone (**1a**) was chosen as the model substrate to examine the feasibility of the proposed radical 1,6-C–H alkylation process by Co(II)-based metalloradical catalysts [Co(Por)] (Figure 3.2). It was gratifying to find that first-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-

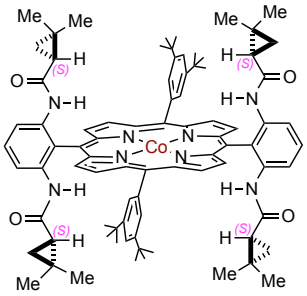
ChenPhyrin)[7a] could effectively catalyze the C–H alkylation reaction, even at room temperature, affording the desired 2-phenylpiperidine (**2a**) in high yield (84%) with a low but significant level of asymmetric induction (9% ee) (Figure 3.2; entry 1). Switching to second-generation metalloradical catalyst [Co(**P6**)] (**P6** = 3,5-Di^{t}Bu-QingPhyrin)[7g] containing phenyl groups in the chiral amide units resulted in some improvement in enantioselectivity (24% ee) but led to considerable decrease in reactivity (57% yield) (entry 2). Subsequent employment of naphthyl-substituted metalloradical catalyst [Co(**P7**)] (**P7** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin)[16] gave rise to higher yield (64%) without improving enantioselectivity (21% ee) (entry 3). When we turned our attention to [Co(**P15**)] (**P15** = 3,5-Di^{t}Bu-ZhuPhyrin)[17] bearing rigid tetrahydrofurancarboxamide units, further increase in the yield (67%) of **2a** was attained albeit with lower enantioselectivity (17% ee) (entry 4). Considering the relative flexibility of aliphatic chain in **1a**, we decided to increase the steric bulkiness of the ligand environment by fine-tuning the nonchiral *meso*-aryl substituents of ZhuPhyrin ligand from 3,5-di-*tert*-butylphenyl to more sterically encumbered 2,6-dimethoxyphenyl groups. To our delight, the analogous catalyst [Co(**P5**)] (**P5** = 2,6-DiMeO-ZhuPhyrin)[17] could catalyze the alkylation reaction with substantially enhanced enantioselectivity (79% ee) in higher yield (69%) (entry 5). This ligand buttressing effect promoted us to evaluate [Co(**P16**)] (**P16** = 2,4,6-TriMe-ZhuPhyrin)[8b] containing even more sterically-demanding mesityl groups at achiral *meso*-aryl positions. Excitingly, the use of [Co(**P6**)] led to further improvement in both reactivity and enantioselectivity, allowing for the enantioselective construction of 6-membered *N*-heterocycle **2a** in high yield (78%) with excellent enantioselectivity (92% ee) (entry 6).

[16] Jin, L.-M.; Xu, X.; Lu, H.; Cui, X.; Wojtas, L.; Zhang, X. P. *Angew. Chem. Int. Ed.* **2013**, *52*, 5309–5313.
[17] Zhu, S.; Ruppel, J. V.; Lu, H.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043.

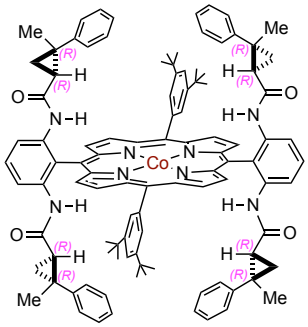
Figure 3.2. Ligand Effect on Co(II)-Based Catalytic System for Enantioselective Construction of α-Piperidines[a]



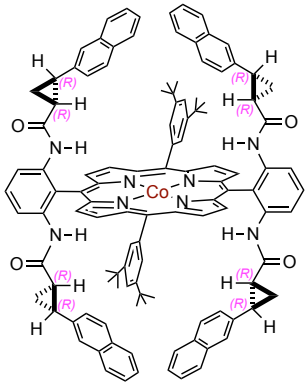
entry	[Co(Por)]	yield (%)	ee (%)
1	[Co(**P3**)]	84	9
2	[Co(**P6**)]	57	24
3	[Co(**P7**)]	64	21
4	[Co(**P15**)]	66	17
5	[Co(**P5**)]	69	79
6	[Co(**P16**)]	78	92



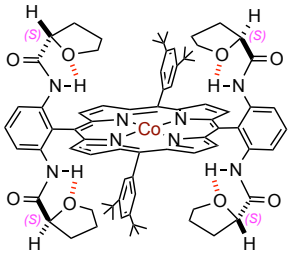
[Co(**P3**)]
(**P3** = 3,5-Di^{t}Bu-ChenPhyrin)



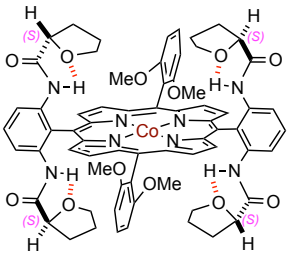
[Co(**P6**)]
(**P6** = 3,5-Di^{t}Bu-QingPhyrin)



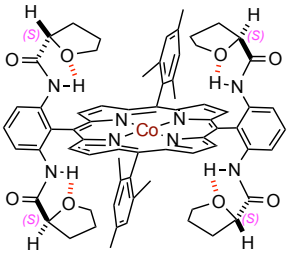
[Co(**P7**)]
(**P7** = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin)



[Co(**P15**)]
(**P15** = 3,5-Di^{t}Bu-ZhuPhyrin)



[Co(**P5**)]
(**P5** = 2,6-DiMeO-ZhuPhyrin)



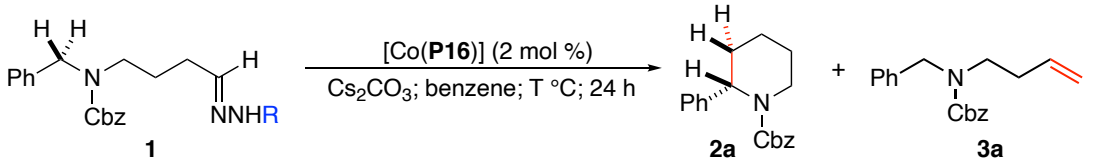
[Co(**P16**)]
(**P16** = 2,4,6-TriMe-ZhuPhyrin)

[a]Carried out with **1a** (0.10 mmol) using [Co(Por)] (5 mol %) in the presence of Cs_2CO_3 (0.20 mmol) in benzene (2.0 mL) at 22 °C for 48 h; Isolated yields; Determined by chiral HPLC analysis; Tris = (2,4,6-triisopropyl)benzene sulfonyl.

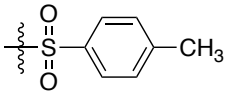
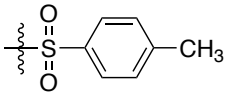
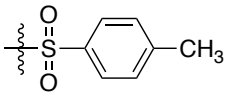
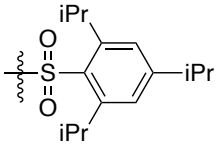
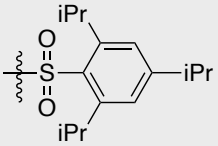
The dramatic difference in catalytic performance between [Co(**P5**)] and [Co(**P16**)] revealed the immense power of judicious tuning of ligand environment in controlling reactivity and enantioselectivity of Co(II)-based metalloradical systems.

During the course of our investigation, we also conducted the C–H alkylation reactions with 4-aminobutanal-derived tosylhydrazone (**1aa**) (Table 3.1). At elevated temperature of 80 °C, the alkylation reaction afforded **2a** in high yield (86%) but with diminished enantioselectivity (78% ee) (Table 3.1; entry 1). When the reaction was carried out 60 °C, a slight improvement in enantioselectivity (82% ee) was observed without affecting the yield (84%) (entry 2). Further lowering the reaction temperature to 40 °C led to significant decrease in yield due to incomplete decomposition of tosylhydrazone **1aa**, forming alkylation product **2a** in 26% yield with 86% ee (entry 3). Subsequent use of the corresponding trishydrazone **1a** allowed the reaction to proceed even at room temperature, resulting in the formation of **2a** in moderate yield (51%) with improved enantioselectivity (92%). When the reaction time was extended to 48 h with 5 mol % of [Co(**P16**)], the desired product **2a** was isolated in 78% yield while maintaining the same high level of enantioselectivity (92%) (entry 5). Along with 2-phenylpiperidine (**2a**), we also observed the formation of linear alkene **3a** as a side product in small amounts (Table 3.1).

Table 3.1. Effect of Different Sulfonyl Hydrazones on Enantioselective Radical 1,6-C–H Alkylation[a]



1 **2a** **3a**

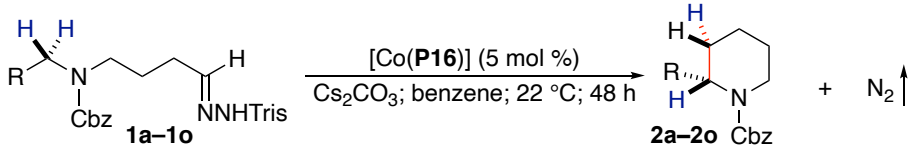
entry	R	T °C	**2a** yield (%)	**2a** ee (%)	**3a** yield (%)
1	 (**1aa**)	80	86	78	14
2	 (**1aa**)	60	84	82	11
3	 (**1aa**)	40	26	86	2
4	 (**1a**)	22	51	92	4
5[b]	 (**1a**)	22	78[c]	92	7

[a]Carried out with **1a** (0.10 mmol) using [Co(**P16**)] (2 mol %) in the presence of Cs_2CO_3 (0.20 mmol) in benzene (2.0 mL) for 24 h; Determined by ^1H NMR yield; Determined by chiral HPLC analysis. [b]Using [Co(**P16**)] (5 mol %) for 48 h. [c]Isolated yield.

3.2.2. Enantioselective Metalloradical 1,6-C–H Alkylation for Synthesis of α-Piperidines

Under the optimized conditions, the scope of the [Co(**P16**)]-catalyzed intramolecular 1,6-C–H alkylation was evaluated by employing 4-aminobutanal-derived trishydrazone **1** containing different types of C–H bonds (Table 3.2). Like **1a** (Table 3.2; entry 1), its derivatives containing various electron-donating substituents at different positions, including *m*-Me (**1b**), *p*-^{t}Bu (**1c**), *m*-OMe (**1d**), *p*-OMe (**1e**), and 1',3'-dioxolane-3,4-fused

Table 3.2. Enantioselective Metalloradical 1,6-C–H Alkylation of Different Benzylic C–H Bonds[a]



-1.0 mmol- entry 1: (–)-**2a**[b] 72% yield; 92% ee	entry 2: (–)-**2b** 74% yield; 94% ee	entry 3: (–)-**2c** 80% yield; 92% ee	entry 4: (–)-**2d** 51% yield; 90% ee
entry 5: (–)-**2e** 81% yield; 90% ee	entry 6: (–)-**2f** 70% yield, 84% ee	entry 7: (–)-**2g** 48% yield; 95% ee	entry 8: (–)-**2h** 83% yield; 94% ee
entry 9: (–)-**2i**[c] 70% yield; 86% ee	X-ray Crystal Structure (–)-**2i**	entry 10: (–)-**2j** 73% yield; 94% ee	entry 11: (–)-**2k** 69% yield; 93% ee
entry 12: (–)-**2l** 67% yield, 94% ee	entry 13: (–)-**2m** 66% yield; 90% ee	entry 14: (–)-**2n** 53% yield; 93% ee	entry 15: (–)-**2o** 78% yield; 91% ee

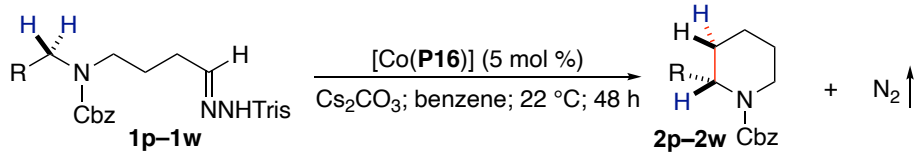
[a]Carried out with **1** (0.10 mmol) using [Co(**P16**)] (5 mol %) in the presence of Cs_2CO_3 (0.20 mmol) in benzene (2.0 mL) at 22 °C for 48 h; Isolated yields; Enantiomeric excess (ee) determined by chiral HPLC; Tris = (2,4,6-triisopropyl)benzenesulfonyl. [b]Performed on 1.0 mmol scale. [c]Absolute configuration determined by X-ray crystallography.

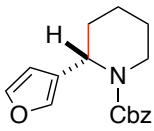
(**1f**) could be efficiently alkylated by [Co(**P16**)] at benzylic C–H bonds, affording the corresponding piperidines **2b**–**2f** in moderate to high yields with excellent enantioselectivities (entries 2–6). Similarly, the Co(II)-catalyzed 1,6-C–H alkylation system was shown to be compatible with substrates containing electron withdrawing aryl

substituents, such as *m*-NO_2 (**1g**), *p*-CN (**1h**), *p*-CO_2Me (**1i**), and *p*-CF_3 (**1j**), allowing for the effective formation of α-piperidines **2g**–**2j** in similarly high enantioselectivities (entries 7–10). Furthermore, halogenated substrates, including *m*-F (**1k**), 3,4-*di*-F (**1l**), *p*-Br (**1m**), and 3,4-*di*-Br (**1n**), could also successfully undergo the radical alkylation as exemplified by the enantioselective formation of **2k**–**2n** in varied yields (entries 11–14). In addition, the Co(II)-based alkylation was highlighted by its applicability to extended aromatic ring system, delivering napthyl-substituted piperidine **2o** in high yield with high enantioselectivity (entry 15). Gratifyingly, the Co(II)-based alkylation system could be readily scaled up under the same reaction condition as demonstrated with the similarly high-yielding synthesis of phenylpiperidine **2a** on 1.0 mmol scale with the same high level of enantioselectivity (entry 1).

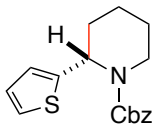
Notably, the catalytic radical alkylation system was equally effective for substrates containing various heteroarenes, leading to the enantioselective construction of a wide array of α-heteroarylpiperidines. For example, furan and thiophene-based precursors **1p**–**1r** could be effectively activated by [Co(**P16**)] for alkylation to furnish the corresponding piperidines **2p**–**2r** with high enantioselectivities despite lower yields (Table 3.3, entries 1–3). Likewise, pyridine-based precursors **1s**–**1u** could serve as suitable C–H substrates as well, enabling convenient access to highly-enantioenriched α-pyridyl piperidine derivatives **2s**–**2u** (entries 4–6). It is noteworthy that the C–H alkylation could be applied to the enantioselective synthesis of naturally-occurring anabasine (**2u**) albeit in a considerably lower yield (entry 6). Moreover, chiral piperidines containing α-benzothiophene (**2v**) and α-quinoline (**2w**) could be effectively constructed in moderate to high yields with excellent enantioselectivities (entries 7–8).

Table 3.3. Enantioselective Metalloradical 1,6-C–H Alkylation of Different Heterobenzylic C–H Bonds[a]

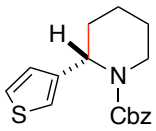




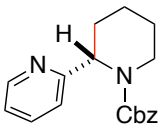
entry 1: (–)-**2p**
30% yield; 91% ee



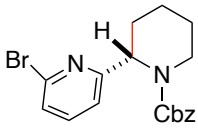
entry 2: (–)-**2q**
53% yield; 92% ee



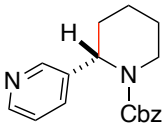
entry 3: (–)-**2r**
77% yield, 92% ee



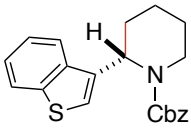
entry 4: (–)-**2s**
87% yield; 92% ee



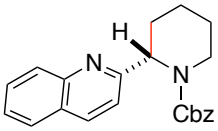
entry 5: (–)-**2t**
72% yield; 96% ee



entry 6: (–)-**2u**
21% yield; 90% ee



entry 7: (–)-**2v**
54% yield; 94% ee



entry 8: (–)-**2w**
75% yield; 95% ee

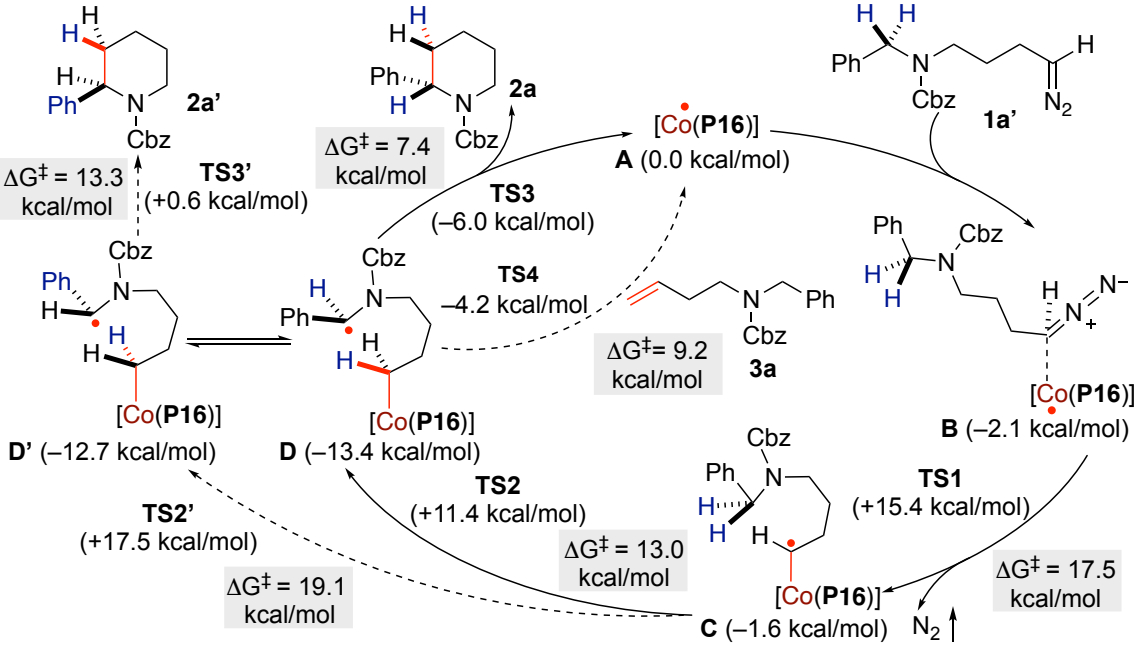
[a]Carried out with **1** (0.10 mmol) using [Co(**P16**)] (5 mol %) in the presence of Cs_2CO_3 (0.20 mmol) in benzene (2.0 mL) at 22 °C for 48 h; Isolated yields; Enantiomeric excess (ee) determined by chiral HPLC; Tris = (2,4,6-triisopropyl)benzenesulfonyl.

3.2.3. Mechanistic Studies on Co(II)-Catalyzed 1,6-C–H Alkylation of α-Alkyldiazomethanes

To gain insights into the proposed stepwise radical mechanism (Scheme 3.3), both computational and experimental studies was conducted. First, density functional theory (DFT) calculations were performed with collaboration of Jing Ke to elucidate the details of the catalytic pathway as well as the origin of asymmetric induction for 1,6-C–H alkylation reaction with alkyldiazomethane (**1a'**) by [Co(**P16**)] (Scheme 3.6; see Experimental Section for details). The geometry optimizations were performed with the

Gaussian 16[18] at the BP86[19,20]/lanl2dz[21,22] level of theory in the gas phase at room temperature. To further improve the accuracy of energies, single point energies were carried out at the B3LYP[23]/def2-tzvp[21,22] level of theory along with Grimme's dispersion correction[24](D3BJ) and SMD[25] solvation model (in benzene).

Scheme 3.6. DFT Study on Catalytic Pathway for 1,6-C–H Alkylation by [Co(P6)][a]



[a]Applied BP86/LANL2DZ for geometry optimization and B3LYP/def2-tzvp for calculations of single point energies (kcal/mol) along with Grimme's dispersion correction and SMD (benzene) solvation model.

The DFT calculations revealed the formation of intermediate **B** between the catalyst and the diazomethane through multiple noncovalent attractive interactions, including H-bonding and π-stacking interactions. The noncovalent complexation, which is exergonic

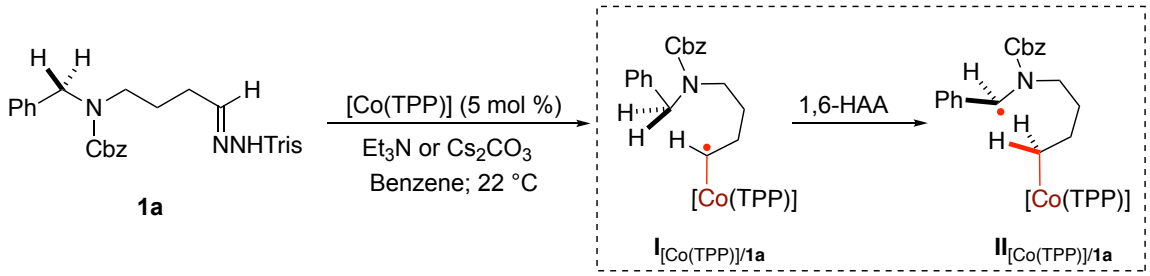
[18] Frisch, M. J. *et al.*, *Gaussian 16*, *Revision A.03*, Gaussian, Inc., Wallingford CT, **2016**.
[19] Schultz, N. E.; Zhao, Yan; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.
[20] Suarez, A. I. O.; Jiang, H.-L.; Zhang, X. P.; de Bruin, B. *Dalton Trans.* **2011**, *40*, 5697–5705.
[21] Lang, K.; Torker, S.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2019**, *141*, 12388–12396.
[22] Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119–124.
[23] Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.
[24] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. **2010**, *132*, 154104.
[25] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys.Chem. B* **2009**, *113*, 6378–6396.

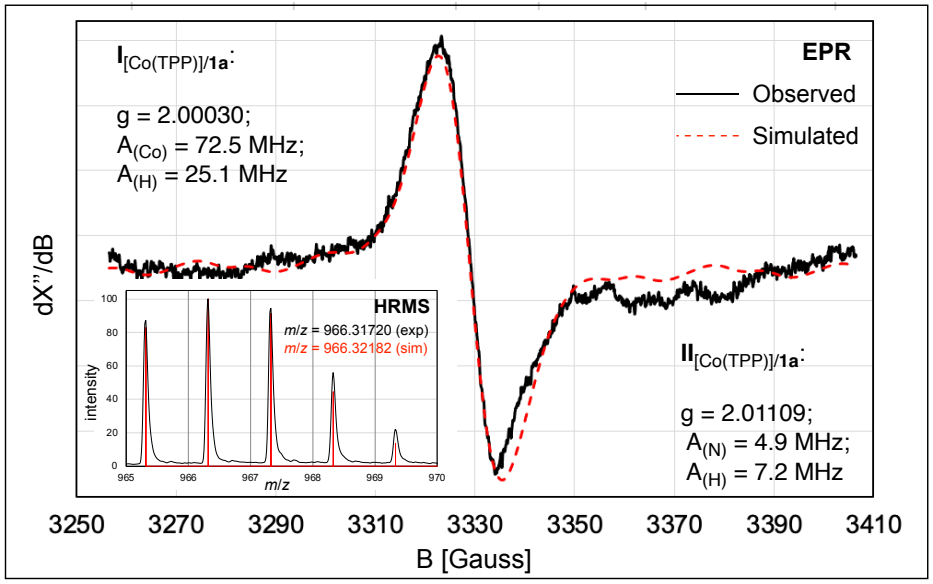
by 2.1 kcal/mol, positions the α-carbon atom of diazo **1a'** in close proximity to the Co(II)-metalloradical center of [Co(**P16**)] (C---Co: ~2.45 Å) for further interactions. The ensuing metalloradical activation, which is slightly endergonic by 0.5 kcal/mol, is found to be associated with a relatively high but accessible activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS1}}$ = 17.5 kcal/mol), affording α-Co(III)-alkyl radical intermediate **C** with release of dinitrogen as the byproduct. Subsequent intramolecular 1,6-HAA of radical intermediate **C**, which is highly exergonic by 11.8 kcal/mol, has a lower activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS2}}$ = 13.0 kcal/mol), delivering ζ-Co(III)-aminoalkyl radical intermediate **D**. The final step of 6-*exo*-*tet* cyclization of radical intermediate **D** via radical substitution exhibits a relatively lower activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS3}}$ = 7.4 kcal/mol), leading to the formation of piperidine product **2a** with regeneration of metalloradical catalyst [Co(**P16**)].

According to the DFT calculations, the H-atom abstraction (HAA) is an enantiodifferentiative process, where abstraction of the *pro*-(*R*) benzylic hydrogen of intermediate **C** is kinetically less favorable, proceeding through a higher activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS2}}$, = 19.1 kcal/mol) than that of the *pro*-(*S*) benzylic hydrogen ($\Delta G^{\ddagger}_{\mathbf{TS2}}$ = 13.0 kcal/mol). Furthermore, the resulting *pro*-(*R*) ζ-Co(III)-aminoalkyl radical intermediate **D'** also undergoes a higher activation barrier in the final step of 6-*exo*-*tet* cyclization ($\Delta G^{\ddagger}_{\mathbf{TS3}}$, = 13.3 kcal/mol vs. $\Delta G^{\ddagger}_{\mathbf{TS3}}$ = 7.4 kcal/mol), implying that radical substitution is likely the stereodetermining step. In addition, the energetics associated with competitive 1,5-HAA of ζ-Co(III)-aminoalkyl radical **D** was also calculated to elucidate the formation of linear alkene **3a**, which reveals a higher activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS4}}$ = 9.2 kcal/mol) than that of the desired cyclization pathway ($\Delta G^{\ddagger}_{\mathbf{TS3}}$ = 7.4 kcal/mol).

To experimentally detect Co(III)-supported alkyl radical intermediates, the reaction solution of [Co(TPP)] with hydrazone **1a** was monitored by electron paramagnetic resonance (EPR) spectroscopy at room temperature (Scheme 3.7, see Experimental Section for details).

Scheme 3.7. Detection of Co(III)-Alkyl Radical Intermediates by EPR and HRMS





The isotropic EPR spectrum displays diagnostic signals at *g*-value of ~2.00 that are characteristic of α-Co(III)-alkyl radicals and related radical species. Consistent with the proposed stepwise radical mechanism involving the key step of 1,6-H-atom abstraction, the observed broad signals (in black) could be fittingly simulated (in red) as a mixture of α-Co(III)-alkyl radical and ζ-Co(III)-aminoalkyl radical on the basis of couplings by ^{59}Co

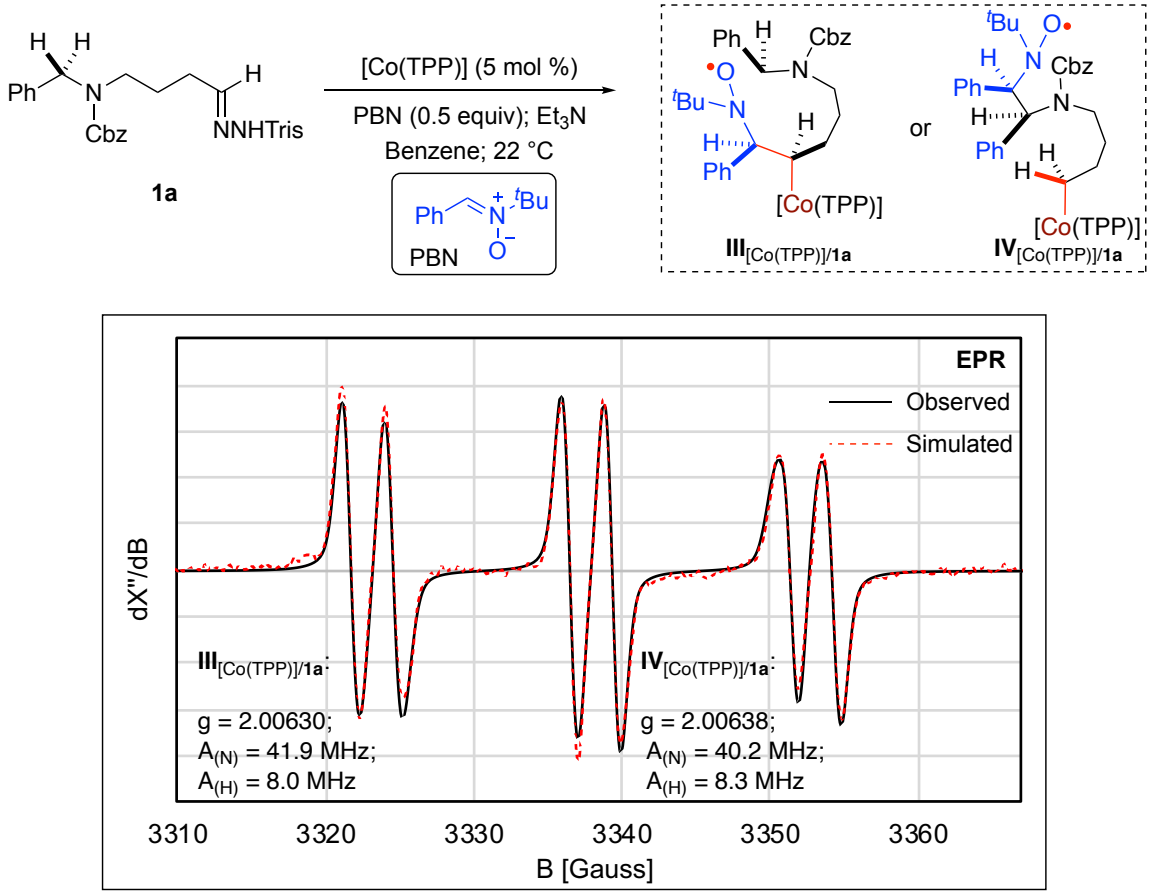
(I = 7/2), ^{14}N (I = 1) and ^{1}H (I = 1/2): 23% of C-centered radical at α-position $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$ (g = 2.00030; $A_{(Co)}$ = 72.5 MHz; $A_{(H)}$ = 25.1 MHz) and 77% of C-centered radical at ζ-position $\mathbf{II}_{[Co(TPP)]/\mathbf{1a}}$ (g = 2.01109; $A_{(N)}$ = 4.9 MHz; $A_{(H)}$ = 7.2 MHz).

Moreover, the corresponding Co(II)-supported alkyl radicals from the reaction solution of hydrazone **1a** with [Co(TPP)] could be directly detected by high resolution mass spectrometry (HRMS) with electrospray ionization (ESI) in the absence of any additives as electron carriers (Scheme 3.7). The observed spectrum evidently reveals a signal corresponding to $[C_{63}H_{49}CoN_5O_2]^+$ (m/z = 966.31720), which resulted from neutral α-Co(III)-alkyl radical intermediate $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$ or ζ-Co(III)-aminoalkyl radical intermediate $\mathbf{II}_{[Co(TPP)]/\mathbf{1a}}$ by the loss of one electron. Both the exact mass and the pattern of isotope distribution determined by ESI-HRMS matches almost perfectly with those calculated as a mixture of three species with the formula of $[C_{63}H_{48}CoN_5O_2]^+$, $[C_{63}H_{49}CoN_5O_2]^+$, and $[C_{63}H_{50}CoN_5O_2]^+$.

In addition, spin trapping reagent PBN (*N-tert*-butyl-α-phenylnitrone) was employed to trap $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$ or $\mathbf{II}_{[Co(TPP)]/\mathbf{1a}}$ for experimental detection by EPR spectroscopy (Scheme 3.8, see Experimental Section for details). The isotropic EPR spectrum exhibits the characteristic triplet of doublet signals at g-value of ~2.00, which was taken as evidence for formation of $\mathbf{III}_{[Co(TPP)]/\mathbf{1a}}$ and $\mathbf{IV}_{[Co(TPP)]/\mathbf{1a}}$ resulting from PBN trapping of the initially generated $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$ and $\mathbf{II}_{[Co(TPP)]/\mathbf{1a}}$.[8b] The observed spectrum (in black) could be fittingly simulated (in red) as a mixture of α-Co(III)-alkyl radical and ζ-Co(III)-aminoalkyl radical on the basis of the hyperfine couplings by ^{14}N (I = 1) and ^{1}H (I = 1/2): 71% of O-centered radical $\mathbf{III}_{[Co(TPP)]/\mathbf{1a}}$ from α-Co(III)-alkyl radical $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$: g = 2.00630; $A_{(N)}$ = 41.9 MHz;

$A_{(H)}$ = 8.0 MHz and 29% O-centered radical **IV**$_{[Co(TPP)]/\mathbf{1a}}$ from ζ-Co(III)-aminoalkyl radical **II**$_{[Co(TPP)]/\mathbf{1a}}$: g = 2.00638; $A_{(N)}$ = 40.2 MHz; $A_{(H)}$ = 8.3 MHz.

Scheme 3.8. Trapping by Spin Trap PBN for EPR Observation



3.3. CONCLUSIONS AND OUTLOOK

In summary, we have demonstrated an effective Co(II)-based alkylation system for asymmetric 1,6-C–H alkylation of α-alkyldiazomethanes, enabling the enantioselective construction of six-membered *N*-heterocyclic compounds. Supported by an optimal D_2-symmetric chiral amidoporphyrin 2,4,6-TriMe-ZhuPhyrin, the Co(II)-catalyzed alkylation system can effectively activate a wide array of α-alkyldiazomethanes containing C(sp^3)–H bonds with varied steric and electronic properties at room temperature, providing access to

chiral α-substituted piperidines in good to high yields with high enantioselectivities. In addition, the metalloradical system is highlighted by its tolerance to different functional groups as well as compatibility with heteroaryl units. Furthermore, our combined computational and experimental studies revealed an underlying stepwise radical mechanism involving 1,6-HAA and 6-*exo*-*tet* radical substitution (RS) as the key steps. Considering the synthetic utility and biological importance of enantioenriched α-piperidines, we envision that the Co(II)-catalyzed asymmetric radical alkylation process incorporating 1,6-HAA will find wide applications in organic synthesis related to drug discovery.

3.4. EXPERIMENTAL SECTION

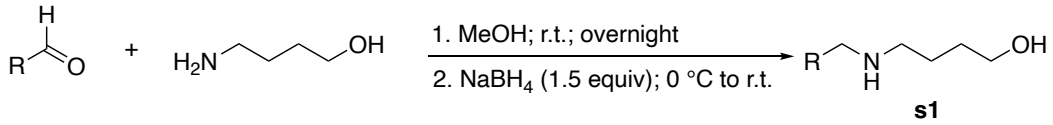
3.4.1. General Considerations

All alkylation reactions were performed in anhydrous solvents under N_2 atmosphere in an oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR spectra were acquired using Varian INOVA 400 (400 MHz), Bruker 500 (500 MHz), or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to residual solvent peak ($CHCl_3$ δ = 7.26 ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, br = broad, m = multiplet), and coupling constants *J* (Hz). ^{13}C NMR spectra were acquired using Varian INOVA 400 (100 MHz), Bruker 500 (125 MHz), or INOVA 600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ δ = 77.16 ppm) as the internal standard. ^{19}F NMR spectrum was acquired using Varian Bruker 500 (470 MHz) or INOVA 600 (564 MHz) spectrometer. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel AD-H, IA, IC, ID, IE, and IF columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected

using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals or TCI and were used without further purification.

3.4.2. Synthesis and Characterization of Substrates

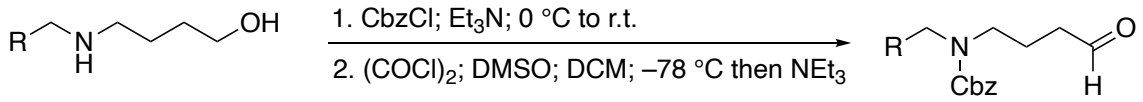
3.4.2.1. Experimental Procedure for Preparation of s1



s1

To a solution of aldehyde (10.0 mmol) in anhydrous methanol (20.0 mL) was added 4-amino-1- propanol (1.0 equiv) dropwise at room temperature. The reaction was stirred at room temperature overnight. After that, the reaction mixture was cooled down to 0 °C in an ice bath. Sodium borohydride (1.5 equiv) was added portionwise. After the bubbling stopped, the solvent was removed under reduced pressure. The resulting residue was then partitioned between H_2O (30.0 mL) and EtOAc (30.0 mL). The aqueous layer was extracted with EtOAc (2 x 20.0 mL). The combined organic extracts were then dried and concentrated under vacuum. The desired product **s1** was used for next step without further purification.

3.4.2.2. Experimental Procedure for Preparation of s2



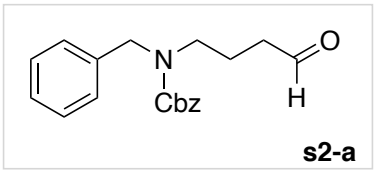
s1 **s2**

General Procedure for Synthesis of Cbz-Protected Amines: To a solution of **s1** (5.0 mmol) and triethylamine (1.5 equiv) in DCM (30.0 mL), benzyl chloroformate (1.1 equiv) was added portionwise at 0 °C. The reaction was then stirred at room temperature and monitored by TLC. After the reaction was completed, the solvent was then evaporated and

concentrated under vacuum. The obtained crude mixture was directly used for next step without further purification.

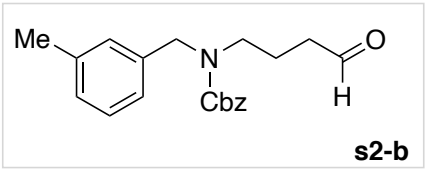
General Procedure for Swern Oxidation: To a solution of oxalyl chloride (1.5 equiv) in DCM (30.0 mL) at –78 °C was added dimethyl sulfoxide (3.0 equiv) dropwise via syringe. After stirring for 20 min at –78 °C, a solution of Cbz-protected **s1** (crude product from previous step) in DCM (5.0 mL) was added dropwise. The solution was then stirred at –78 °C for 30 min, followed by dropwise addition of triethylamine (4.5 equiv). After 10 min, the reaction mixture was warmed up to room temperature, poured into brine (30.0 mL) and stirred for another 10 min. The layers were then separated and the aqueous layer was extracted with DCM (3 x 20.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The aldehyde product **s2** was further purified by flash chromatography.

Benzyl benzyl(4-oxobutyl)carbamate s2-a Yield: 45% over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.65 and 9.54 (s, 1H), 7.47 – 7.05 (m, 10H), 5.19 and 5.17 (s, 2H), 4.50 and 4.48 (s, 2H), 3.35 – 3.15 (m, 2H), 2.49 – 2.15 (m, 2H), 1.92 – 1.68 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.21, 200.97, 156.33, 156.05, 137.51, 136.48, 128.37, 128.25, 127.78, 127.67, 127.18, 127.10, 67.04, 50.27, 50.01, 46.07, 45.12, 40.68, 40.48, 20.31, 19.99. IR (neat, cm^{-1}): 2942.34, 1691.94, 1496.09, 1453.21, 1420.11, 1227.12, 1122.33, 1068.72, 734.08. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{22}NO_3^+$: 312.15942, Found: 312.15854.



s2-a

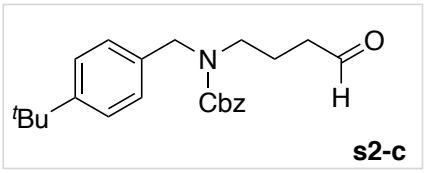
Benzyl (3-methylbenzyl)(4-oxobutyl)carbamate s2-b Yield: 44% over three steps.



s2-b

Hexanes/ethyl acetate = 1:1, R_f = 0.38. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.72 and 9.60 (s, 1H), 7.59 – 6.85 (m, 9H), 5.22 and 5.20 (s, 2H), 4.50 and 4.48 (s, 2H), 3.39 – 3.20 (m, 2H), 2.56 – 2.23 (m, 5H), 1.97 – 1.77 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.43, 201.17, 156.50, 156.27, 138.18, 137.51, 136.64, 128.41, 127.93, 124.92, 124.34, 67.20, 50.34, 50.07, 46.14, 45.16, 40.90, 40.70, 21.31, 20.43, 20.13. IR (neat, cm^{-1}): 2943.14, 1692.23, 1417.82, 1224.47, 1121.54, 1070.15, 768.22, 697.86. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.17507, Found: 326.17535.

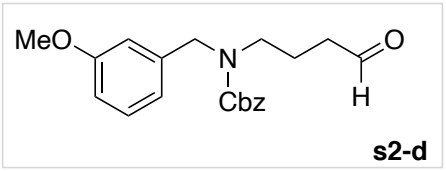
Benzyl (4-(*tert*-butyl)benzyl)(4-oxobutyl)carbamate s2-c Yield: 54% over three steps.



s2-c

Hexanes/ethyl acetate = 1:1, R_f = 0.45. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.70 and 9.58 (s, 1H), 7.47 – 7.11 (m, 9H), 5.22 and 5.20 (br, 2H), 4.51 and 4.49 (br, 2H), 3.35 – 3.26 (m, 2H), 2.47 – 2.31 (m, 2H), 1.95 – 1.79 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.23, 201.00, 156.34, 156.15, 150.14, 136.58, 134.49, 128.31, 127.81, 127.69, 127.53, 126.95, 125.31, 67.05, 49.90, 49.69, 46.02, 45.06, 40.78, 40.58, 34.30, 31.21, 20.36, 20.06. IR (neat, cm^{-1}): 2959.90, 1693.86, 1410.91, 1225.58, 1125.93, 1070.00, 767.39. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{30}NO_3^+$: 368.22202, Found: 368.22204.

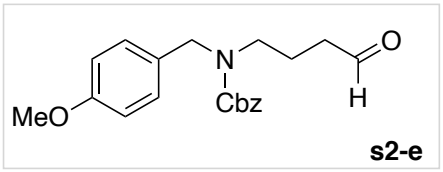
Benzyl (3-methoxybenzyl)(4-oxobutyl)carbamate s2-d Yield: 66% over three steps.



s2-d

Hexanes/ethyl acetate = 1:1, R_f = 0.35. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.59 (s, 1H), 7.49 – 7.12 (m, 6H), 6.94 – 6.62 (m, 3H), 5.18 and 5.16 (br, 2H), 4.47 and 4.45 (br, 2H), 3.76 and 3.70 (s, 3H), 3.36 – 3.18 (m, 2H), 2.47 – 2.27 (m, 2H), 1.97 – 1.68 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.63, 201.34, 159.96, 156.68, 156.39, 139.35, 136.70, 129.69, 128.57, 128.10, 128.01, 120.26, 119.68, 113.46, 113.00, 112.91, 67.41, 55.23, 50.54, 50.30, 46.36, 45.41, 41.09, 40.87, 20.59, 20.27. IR (neat, cm^{-1}): 2941.07, 1692.87, 1600.32, 1418.65, 1260.52, 1121.99, 1048.59, 768.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO^+$: 342.16998, Found: 342.16974.

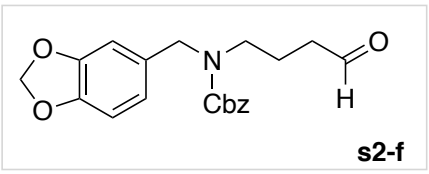
Benzyl (4-methoxybenzyl)(4-oxobutyl)carbamate s2-e Yield: 56% over three steps.



s2-e

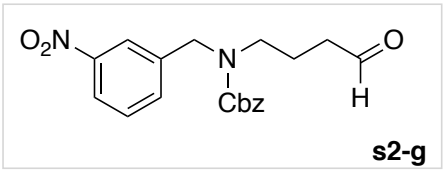
Hexanes/ethyl acetate = 1:1, R_f = 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.69 (s, 1H), 7.51 – 7.00 (m, 7H), 6.85 (d, J = 10.3 Hz, 2H), 5.18 (s, 2H), 4.43 (s, 2H), 3.78 (s, 3H), 3.31 – 3.21 (m, 2H), 2.47 – 2.28 (m, 2H), 1.88 – 1.75 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.65, 201.38, 159.07, 156.60, 156.33, 136.73, 129.72, 129.41, 128.81, 128.55, 128.03, 114.02, 67.34, 55.31, 49.97, 49.69, 46.00, 45.11, 41.05, 40.85, 20.57, 20.23. IR (neat, cm^{-1}): 2935.22, 1694.38, 1611.85, 1512.80, 1417.38, 1246.05, 1032.79. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_4^+$: 342.16998, Found: 342.17007.

Benzyl (benzo[*d*][1,3]dioxol-5-ylmethyl)(4-oxobutyl)carbamate s2-f Yield: 55% over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.31. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.60 (s, 1H), 7.45 – 7.21 (m, 5H), 6.88 – 6.56 (m, 3H), 5.92 (s, 2H), 5.17 (s, 2H), 4.40 and 4.38 (br, 2H), 3.32 – 3.14 (m, 2H), 2.43 – 2.32 (m, 2H), 1.92 – 1.68 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.57, 201.29, 156.55, 156.20, 147.97, 147.01, 136.62, 131.50, 128.54, 128.11, 128.00, 121.33, 120.81, 108.49, 108.17, 107.98, 101.07, 67.38, 50.31, 50.01, 45.96, 45.11, 41.01, 40.81, 20.53, 20.17. IR (neat, cm^{-1}): 2893.04, 1693.50, 1489.39, 1444.37, 1422.23, 1245.49, 1124.73, 1037.88, 926.79, 699.40. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{22}NO_5^+$: 356.14925, Found: 356.15003.



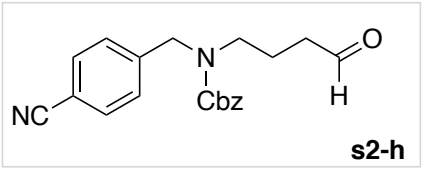
s2-f

Benzyl (3-nitrobenzyl)(4-oxobutyl)carbamate s2-g Yield: 40 % yield over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.40. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.61 (s, 1H), 8.17 – 7.98 (m, 2H), 7.67 – 7.18 (m, 7H), 5.18 and 5.13 (s, 2H), 4.57 and 4.55 (br, 2H), 3.46 – 3.20 (m, 2H), 2.56 – 2.30 (m, 2H), 1.87 – 1.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.21, 200.99, 156.48, 155.96, 148.35, 140.08, 136.24, 133.75, 133.19, 129.55, 128.48, 128.14, 127.97, 122.38, 122.07, 67.53, 49.95, 49.77, 46.78, 45.96, 40.73, 40.59, 20.50, 20.18. IR (neat, cm^{-1}): 2943.83, 1695.41, 1528.09, 1471.91, 1419.10, 1348.18, 1226.18, 1125.53, 731.66. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}N_2O_5^+$: 357.14450, Found: 357.14310.



s2-g

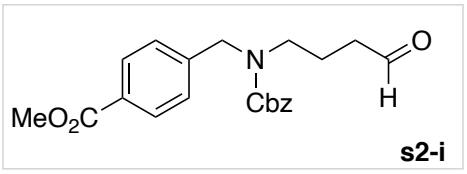
Benzyl (4-cyanobenzyl)(4-oxobutyl)carbamate s2-h Yield: 64% over three steps.



s2-h

Hexanes/ethyl acetate = 1:2, R_f = 0.40. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.65 and 9.56 (s, 1H), 7.61 – 7.12 (m, 9H), 5.13 and 5.08 (s, 2H), 4.48 (s, 2H), 3.31 – 3.20 (m, 2H), 2.40 – 2.25 (m, 2H), 1.91 – 1.71 (m, 2H). ^{13}C NMR (125 MHz, CDl_3) some signals exist as a pair due to the presence of amide rotamers δ 201.26, 201.00, 156.51, 156.03, 143.34, 136.24, 132.36, 128.49, 128.19, 128.01, 127.69, 118.62, 111.20, 67.55, 50.33, 50.14, 46.84, 45.96, 40.78, 40.61, 20.50, 20.19. IR (neat, cm^{-1}): 2945.39, 2228.23, 1696.98, 1473.81, 1412.82, 1230.71, 1125.64, 698.69. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}N_2O_3^+$: 337.15467, Found: 337.15474.

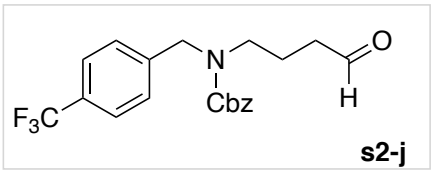
Methyl 4-((((benzyloxy)carbonyl)(4-oxobutyl)amino)methyl)benzoate s2-i Yield: 28% over three steps.



s2-i

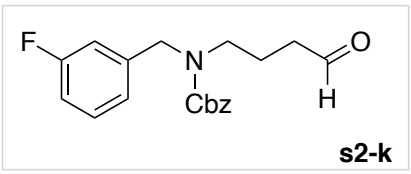
Hexanes/ethyl acetate = 1:1, R_f = 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.68 and 9.57 (s, 1H), 8.00 – 7.94 (m, 2H), 7.35 – 7.20 (m, 7H), 5.17 and 5.13 (s, 2H), 4.53 and 4.50 (br, 2H), 3.86 (s, 3H), 3.37 – 3.17 (m, 2H), 2.37 (m, 2H), 1.92 – 1.70 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.27, 201.00, 166.67, 156.51, 156.15, 143.00, 136.40, 129.85, 129.29, 128.45, 128.08, 127.93, 127.61, 127.03, 67.40, 52.00, 50.33, 50.13, 46.62, 45.69, 40.83, 40.64, 20.49, 20.20. IR (neat, cm^{-1}): 2950.99, 1693.42, 1612.09, 1411.90, 1276.02, 1109.46, 1018.72, 913.18, 731.51. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{24}NO_5^+$: 370.16490, Found: 370.16563.

Benzyl (4-oxobutyl)(4-(trifluoromethyl)benzyl)carbamate s2-j Yield: 56% over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.45. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.73 and 9.62 (s, 1H), 7.69 – 7.11 (m, 9H), 5.18 and 5.14 (s, 2H), 4.54 and 4.52 (br, 2H), 3.31 – 3.24 (m, 2H), 2.51 – 2.34 (m, 2H), 1.94 – 1.78 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.39, 201.10, 156.66, 156.26, 141.98, 136.43, 129.76 (q, J = 31.5 Hz), 128.57, 128.25, 128.08, 127.46, 125.62 (q, J = 4.0 Hz), 124.18 (q, J = 270.0 Hz), 67.56, 50.26, 50.07, 46.77, 45.79, 40.97, 40.75, 20.57, 20.28. ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.49. IR (neat, cm^{-1}): 2942.24, 1697.97, 1415.37, 1325.05, 1163.84, 1122.11, 1066.21, 1017.90, 698.87. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{20}O_3NF_3Na^+$: 402.12930, Found: 402.12970.



s2-j

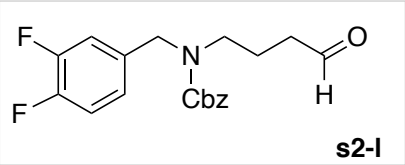
Benzyl (3-fluorobenzyl)(4-oxobutyl)carbamate s2-k Yield: 46% over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.42. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.73 and 9.61 (s, 1H), 7.74 – 7.18 (m, 6H), 7.09 – 6.79 (m, 3H), 5.19 and 5.16 (s, 2H), 4.49 and 4.47 (br, 2H), 3.41 – 3.18 (m, 2H), 2.47 – 2.34 (m, 2H), 1.86 – 1.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.45, 201.18, 163.10 (d, J = 245.0 Hz) 156.65, 156.29, 140.46 (d, J = 7.5 Hz), 136.55, 130.20 (d, J = 8.2 Hz), 128.61, 128.21, 128.07, 123.43, 122.87, 114.78, 114.43 (d, J = 21.8 Hz), 114.14, 67.56, 50.20, 49.97, 46.58, 45.66, 41.01, 40.83, 20.60, 20.29. ^{19}F NMR (564 MHz, $CDCl_3$) δ –



s2-k

112.71. IR (neat, cm^{-1}): 2944.97, 1694.22, 1590.25, 1420.49, 1228.16, 1134.46, 769.94. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}NO_3F^+$: 330.1500, Found: 330.15040.

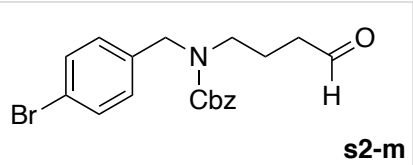
Benzyl (3,4-difluorobenzyl)(4-oxobutyl)carbamate s2-l Yield: 54% over three steps.



s2-l

Hexanes/ethyl acetate = 1:1, R_f = 0.47. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.68 and 9.58 (s, 1H), 7.35 – 7.26 (m, 5H), 7.10 – 6.87 (m, 3H), 5.16 and 5.14 (br, 2H), 4.42 and 4.40 (br, 2H), 3.39 – 3.15 (m, 2H), 2.52 – 2.24 (m, 2H), 1.89 – 1.72 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.22, 200.98, 156.37, 155.91, 150.17 (dd, *J* = 248.6, 12.8 Hz), 149.47 (d, *J* = 248.6 Hz), 136.32, 134.87 (dd, *J* = 4.5, 3.0 Hz), 128.40, 128.03, 127.88, 123.71, 123.16, 117.14 (d, *J* = 17.1 Hz), 116.61 (d, *J* = 18.0 Hz), 116.11 (d, *J* = 15.0 Hz), 67.33, 49.52, 49.25, 46.31, 45.48, 40.68, 40.52, 20.37, 20.03. ^{19}F NMR (470 MHz, $CDCl_3$) δ –137.38, –139.78. IR (neat, cm^{-1}): 2944.28, 1698.37, 1473.99, 1379.57, 1276.69, 1169.19, 1125.96, 903.40, 699.95. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{20}NO_3F_2^+$: 348.14058, Found: 348.14185.

Benzyl (4-bromobenzyl)(4-oxobutyl)carbamate s2-m Yield: 49% over three steps.

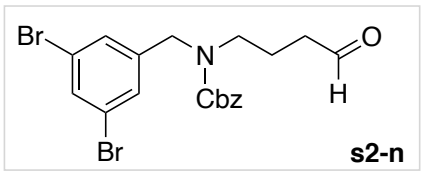


s2-m

Hexanes/ethyl acetate = 1:1, R_f = 0.49. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.72 and 9.61 (s, 1H), 7.74 – 6.79 (m, 9H), 5.18 and 5.16 (br, 2H), 4.43 (s, 2H), 3.25 (dd, *J* = 23.1, 7.8 Hz, 2H), 2.46 – 2.33 (m, 2H), 1.82 (dd, *J* = 23.1, 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.40, 201.14, 156.57, 156.21, 136.81, 136.51, 131.73, 129.67, 129.05, 128.56, 128.18, 128.04, 121.33, 67.48,

50.02, 49.81, 46.46, 45.52, 40.94, 40.77, 20.54, 20.25. IR (neat, cm^{-1}): 2942.06, 1691.46, 1487.26, 1404.15, 1216.03, 1122.63, 1069.73, 1010.63, 697.50. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}NO_3Br^+$: 390.06993, Found: 390.06954.

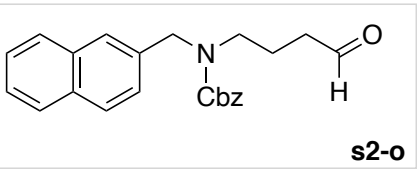
Benzyl (3,5-dibromobenzyl)(4-oxobutyl)carbamate s2-n Yield: 25% over three steps.



s2-n

Hexanes/ethyl acetate = 1:1, R_f = 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.60 (s, 1H), 7.53 (s, 1H), 7.36 – 7.24 (m, 7H), 5.18 and 5.13 (s, 2H), 4.41 and 4.39 (br, 2H), 3.37 – 3.16 (m, 2H), 2.53 – 2.30 (m, 2H), 1.94 – 1.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.14, 200.87, 156.37, 155.88, 141.84, 136.21, 133.00, 129.37, 128.93, 128.54, 128.15, 127.94, 123.08, 67.54, 49.49, 49.27, 46.62, 45.68, 40.75, 40.57, 20.39, 20.09. IR (neat, cm^{-1}): 2942.68, 1693.41, 1584.74, 1556.59, 1415.39, 128.94, 1124.46, 739.85. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{20}NO_3Br_2^+$: 467.98045, Found: 467.98095.

Benzyl (naphthalen-2-ylmethyl)(4-oxobutyl)carbamate s2-o Yield: 61% over three steps.

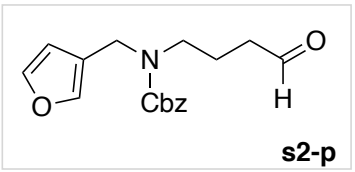


s2-o

Hexanes/ethyl acetate = 1:1, R_f = 0.48. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.72 and 9.59 (s, 1H), 7.89 – 7.55 (m, 4H), 7.52 – 7.22 (m, 8H), 5.26 and 5.24 (s, 2H), 4.70 and 4.67 (s, 2H), 3.45 – 3.23 (m, 2H), 2.54 – 2.30 (m, 2H), 1.98 – 1.78 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.53, 201.25, 156.71, 156.41, 136.66, 135.12, 133.32, 132.83, 128.52, 128.05, 127.76, 127.71, 126.67, 126.29, 126.00, 125.94, 125.42, 67.43, 50.70, 50.44, 46.33, 45.28, 41.01, 40.79, 20.54, 20.26. IR

(neat, cm^{-1}): 2942.23, 1693.93, 1470.78, 1420.14, 1367.16, 1231.17, 1120.19, 957.17, 751.63. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{24}NO_3^+$: 362.17507, Found: 362.17594.

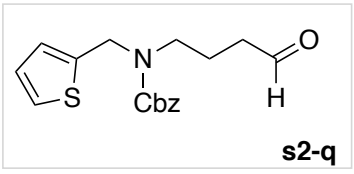
Benzyl (furan-3-ylmethyl)(4-oxobutyl)carbamate s2-p Yield: 51% over three steps.



s2-p

Hexanes/ethyl acetate = 1:1, R_f = 0.35. ^1H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.68 and 9.57 (s, 1H), 7.40 – 7.22 (m, 6H), 6.28 – 6.12 (m, 2H), 5.14 (s, 2H), 4.45 and 4.41 (s, 2H), 3.33 – 3.29 (m, 2H), 2.40 – 2.27 (m, 2H), 1.83 – 1.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.43, 201.19, 155.96, 151.08, 142.06, 136.51, 128.38, 127.92, 127.73, 110.32, 108.42, 107.95, 67.22, 46.39, 45.61, 43.53, 43.44, 40.77, 40.58, 20.52, 20.21. IR (neat, cm^{-1}): 2944.77, 2724.76, 1693.34, 1418.37, 1264.24, 1195.60, 1120.85, 1072.14, 914.85, 734.19, 697.60. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{17}H_{19}O_4NNa^+$: 324.12118, Found: 324.12149.

Benzyl (4-oxobutyl)(thiophen-2-ylmethyl)carbamate s2-q Yield: 47% over three steps.

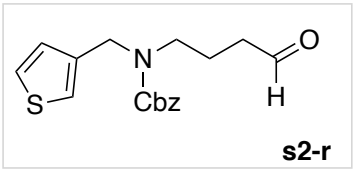


s2-q

Hexanes/ethyl acetate = 1:1, R_f = 0.40. ^1H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.60 (s, 1H), 7.49 – 7.13 (m, 6H), 6.98 – 6.90 (m, 2H), 5.19 (s, 2H), 4.63 and 4.61 (br, 2H), 3.38 – 3.27 (m, 2H), 2.49 – 2.27 (m, 2H), 1.94 – 1.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.49, 201.24, 156.14, 155.86, 140.45, 140.29, 136.51, 128.50, 128.09, 128.03, 126.62, 126.29, 125.51, 125.39, 67.42, 46.14, 45.40, 40.93, 40.75, 20.65, 20.32. IR (neat, cm^{-1}): 2940.73, 1694.38, 1470.32, 1420.33, 1261.69,

1215.64, 976.18, 698.50. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{20}NO_3S^+$: 318.11584, Found: 318.11763.

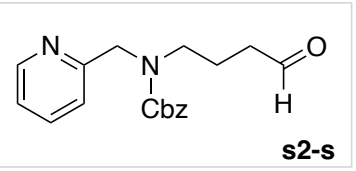
Benzyl (4-oxobutyl)(thiophen-3-ylmethyl)carbamate s2-r Yield: 41% over three steps.



s2-r

Hexanes/ethyl acetate = 1:1, R_f = 0.38. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.71 and 9.6 0 (s, 1H), 7.46 – 6.88 (m, 8H), 5.18 (s, 2H), 4.48 and 4.46 (br, 2H), 3.36 – 3.21 (m, 2H), 2.44 – 2.31 (m, 2H), 1.90 – 1.69 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.61, 201.34, 156.35, 156.14, 138.60, 136.63, 128.56, 128.12, 128.01, 127.72, 127.19, 126.31, 122.86, 122.36, 67.36, 46.25, 45.86, 45.77, 45.40, 40.98, 40.78, 20.63, 20.29. IR (neat, cm^{-1}): 2942.73, 1693.05, 1423.27, 1244.59, 1212.49, 1120.22, 767.91. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{20}NO_3S^+$: 318.11584, Found: 318.11531.

Benzyl (4-oxobutyl)(pyridin-2-ylmethyl)carbamate s2-s Yield: 57% over three steps.

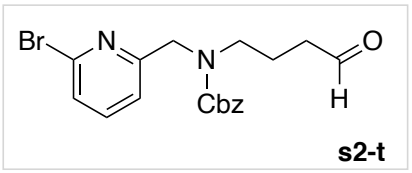


s2-s

100% ethyl acetate, R_f = 0.34. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.64 and 9.52 (s, 1H), 8.45 (d, J = 4.9 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.38 – 6.96 (m, 7H), 5.12 and 5.06 (s, 2H), 4.55 and 4.52 (s, 2H), 3.36 – 3.29 (m, 2H), 2.40 – 2.27 (m, 2H), 1.83 – 1.75 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.40, 201.16, 157.63, 157.54, 156.41, 156.20, 149.11, 149.04, 136.72, 136.62, 136.41, 128.40, 128.27, 128.00, 127.90, 127.83, 127.69, 122.30, 122.16, 121.93, 121.01, 67.30, 67.13, 52.52, 52.22, 47.12, 46.29, 40.84, 40.63, 20.60, 20.31. IR (neat, cm^{-1}): 2942.47, 1695.83, 1592.95, 1474.92,

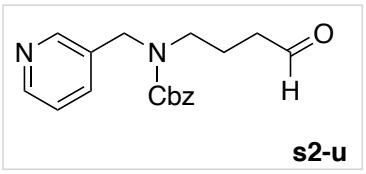
1417.48, 1214.98, 1121.23, 994.27, 752.88. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}N_2O_3^+$: 313.15467, Found: 313.15518.

Benzyl ((6-bromopyridin-2-yl)methyl)(4-oxobutyl)carbamate s2-t Yield: 65% over three steps. 100% ethyl acetate, R_f = 0.35. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.69 and 9.58 (s, 1H), 7.44 – 6.99 (m, 8H), 5.13 and 5.07 (s, 2H), 4.51 and 4.49 (br, 2H), 3.46 – 3.27 (m, 2H), 2.46 – 2.33 (m, 2H), 1.86 – 1.79 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.35, 201.13, 159.35, 159.20, 156.31, 156.03, 141.50, 141.36, 139.03, 138.91, 136.31, 136.26, 128.44, 128.32, 128.05, 127.87, 127.70, 126.56, 126.46, 120.56, 119.67, 67.36, 67.20, 52.27, 51.88, 47.39, 46.71, 40.82, 40.63, 20.72, 20.39. IR (neat, cm^{-1}): 2942.05, 1693.33, 1582.01, 1555.61, 1404.30, 1216.40, 1115.11, 984.68, 768.54, 697.69. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{20}N_2O_3Br^+$: 391.106518, Found: 391.06425.



s2-t

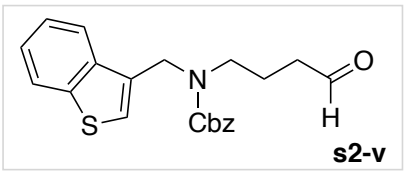
Benzyl (4-oxobutyl)(pyridin-3-ylmethyl)carbamate s2-u Yield: 48% over three steps. 100% ethyl acetate, R_f = 0.25. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.68 and 9.57 (s, 1H), 8.54 – 8.37 (m, 2H), 7.59 – 7.17 (m, 7H), 5.13 and 5.12 (br, 2H), 4.46 and 4.44 (br, 2H), 3.26 – 3.20 (m, 2H), 2.41 – 2.32 (m, 2H), 1.82 – 1.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.28, 201.01, 156.56, 156.27, 149.25, 149.01, 136.38, 135.77, 135.09, 133.32, 128.59, 128.24, 128.09, 123.59, 67.60, 48.22, 48.05, 46.53, 45.67, 40.88, 40.72, 20.56, 20.24. IR (neat, cm^{-1}): 2944.82, 1690.91, 1577.29,



s2-u

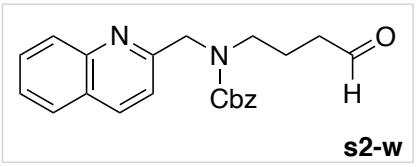
1472.30, 1416.95, 1214.11, 1122.42, 1027.75, 965.12, 760.52. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}N_2O_3^+$: 313.15467, Found: 313.15558.

Benzyl (benzo[*b*]thiophen-3-ylmethyl)(4-oxobutyl)carbamate s2-v Yield: 45% over three steps. Hexanes/ethyl acetate = 1:1, R_f = 0.36. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.69 and 9.56 (s, 1H), 7.95 – 7.61 (m, 2H), 7.46 – 7.14 (m, 8H), 5.24 (s, 2H), 4.79 and 4.74 (s, 2H), 3.33 – 3.23 (m, 2H), 2.41 – 2.28 (m, 2H), 1.84 – 1.74 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.57, 201.30, 156.39, 156.14, 140.66, 138.04, 137.80, 136.62, 132.41, 132.24, 128.61, 128.21, 128.07, 125.17, 124.65, 124.39, 124.29, 124.17, 122.92, 122.31, 121.68, 67.53, 45.92, 44.72, 44.60, 44.49, 40.98, 40.76, 20.38, 20.15. IR (neat, cm^{-1}): 2944.49, 1693.34, 1421.38, 1362.23, 1263.32, 1230.66, 1121.79, 768.27. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{22}NO_3S^+$: 368.13149, Found: 368.13128.



s2-v

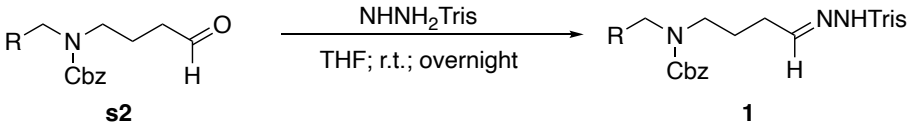
Benzyl (4-oxobutyl)(quinolin-2-ylmethyl)carbamate s2-w Yield: 62% over three steps. 100% ethyl acetate, R_f = 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 9.62 and 9.48 (s, 1H), 8.01 – 7.95 (m, 2H), 7.69 – 7.67 (m, 1H), 7.61 – 7.59 (m, 1H), 7.42 – 7.26 (m, 4H), 7.18 – 7.13 (m, 3H), 5.17 and 5.10 (s, 2H), 4.75 and 4.70 (s, 2H), 3.46 – 3.24 (m, 2H), 2.38 – 2.24 (m, 2H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 201.17, 200.91, 157.88, 156.38, 156.08, 147.36, 136.57, 136.52, 136.35, 136.27, 129.38, 129.30, 128.74, 128.27, 128.06, 127.85, 127.72, 127.61,



s2-w

127.45, 127.33, 127.07, 126.96, 126.05, 119.64, 118.77, 77.36, 67.15, 66.95, 53.18, 52.85, 47.17, 46.18, 40.70, 40.47, 20.49, 20.23. IR (neat, cm^{-1}): 2942.93, 1693.57, 1599.69, 1504.96, 1416.05, 1229.34, 1124.48, 1073.62, 822.13. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{23}N_{23}O_3^+$: 363.17032, Found: 363.16992.

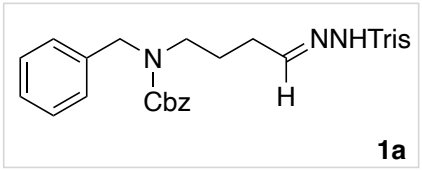
3.4.2.3. Experimental Procedure for Preparation of Sulfonyl Hydrazones



s2 **1**

To a stirred solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (1.0 mmol) in THF (10.0 mL) at room temperature, aldehyde **s2** (1.0 equiv) was added dropwise. After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by flash chromatography.

Benzyl benzyl(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone

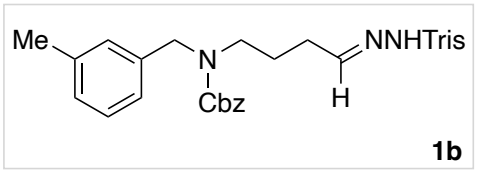


1a

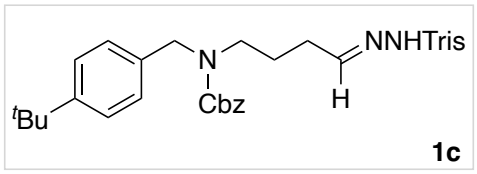
(1a) Yield: 84%. Hexanes/ethyl acetate = 3:1, R_f = 0.35. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.51 – 8.07 (m, 1H), 7.56 – 6.44 (m, 13H), 5.18 and 5.17 (br, 2H), 4.56 – 4.42 (m, 2H), 4.27 – 4.22 (m, 2H), 3.36 – 3.15 (m, 2H), 2.96 – 2.90 (m, 1H), 2.13 (m, 2H), 1.79 – 1.59 (m, 2H), 1.29 (d, J = 6.9 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.68, 156.26, 153.22, 151.33, 149.66, 149.45, 137.66, 136.66, 131.48, 128.66, 128.59, 128.48, 128.08, 127.99, 127.88, 127.39, 127.30, 123.80, 67.49, 67.43, 67.29, 50.58, 50.33, 46.49, 45.47, 34.18, 29.91, 29.88, 29.69, 29.52, 24.90, 24.84, 24.54, 24.18, 23.59. IR (neat, cm^{-1}): 2957.59, 1674.62, 1599.24, 1423.21, 1362.42, 1316.34, 1152.83, 882.15, 751.64. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{34}H_{46}N_3O_4S^+$:

592.32035, Found: 592.31736.

Benzyl (3-methylbenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1b) Yield: 69%. Hexanes/ethyl acetate = 3:1, R_f = 0.42. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.47 – 8.01 (m, 1H), 7.58 – 6.47 (m, 12H), 5.19 and 5.17 (br, 2H), 4.44 and 4.42 (s, 2H), 4.31 – 4.18 (m, 2H), 3.31 – 3.12 (m, 2H), 2.95 – 2.90 (m, 1H), 2.33 and 2.30 (s, 3H), 2.21 – 2.04 (m, 2H), 1.78 – 1.60 (m, 2H), 1.29 (d, J = 6.7 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.69, 156.31, 153.23, 151.34, 149.74, 149.52, 138.27, 137.57, 136.72, 131.48, 128.55, 128.48, 128.12, 128.03, 127.96, 124.95, 124.40, 123.82, 67.48, 67.42, 67.27, 50.45, 50.20, 46.43, 45.37, 34.21, 34.19, 29.93, 29.90, 29.73, 29.55, 24.90, 24.85, 24.54, 24.19, 23.60, 21.42. IR (neat, cm^{-1}): 2958.21, 2868.54, 1695.43, 1600.30, 1461.93, 1421.48, 1228.82, 1153.25, 1008.82. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{35}H_{48}N_3O_4S^+$: 606.33655, Found: 606.33740.

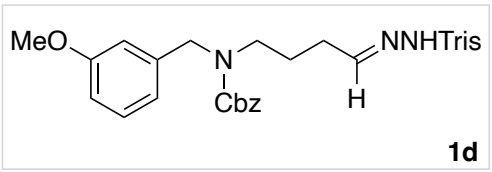


Benzyl (4-(*tert*-butyl)benzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1c) Yield: 79%. Hexanes/ethyl acetate = 3:1, R_f = 0.46. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 7.89 – 6.55 (m, 13H), 5.16 and 5.14 (br, 2H), 4.46 – 4.39 (m, 2H), 4.20 – 4.17 (m, 2H), 3.31 – 3.15 (m, 2H), 2.89 (hept, J = 7.2 Hz, 1H), 2.23 – 1.97 (m, 2H), 1.78 – 1.57 (m, 2H), 1.30 (s, 9H), 1.25 (d, J = 7.0 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide

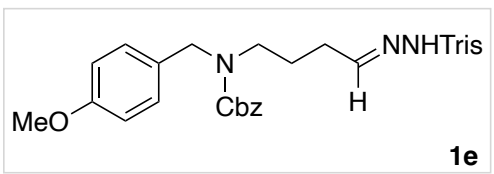


rotamers δ 156.61, 156.33, 153.26, 151.38, 150.38, 149.84, 149.63, 136.77, 134.62, 131.47, 128.61, 128.56, 128.15, 128.03, 127.93, 127.67, 127.11, 125.59, 125.57, 125.52, 123.85, 67.50, 67.40, 67.28, 50.14, 49.94, 46.38, 45.33, 34.54, 34.22, 31.44, 29.96, 29.94, 29.75, 29.56, 24.93, 24.88, 24.56, 24.22, 23.62. IR (neat, cm^{-1}): 2958.89, 1676.29, 1599.36, 1463.57, 1424.97, 1164.31, 1038.92, 882.04, 752.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{38}H_{54}N_3O_4S^+$: 648.38295, Found: 648.38412.

Benzyl (3-methoxybenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1d) Yield: 77%. Hexanes/ethyl acetate = 3:1, R_f = 0.35. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 7.70 – 7.52 (m, 1H), 7.42 – 6.46 (m, 12H), 5.17 and 5.14 (br, 2H), 4.42 and 4.40 (br, 2H), 4.26 – 4.11 (m, 2H), 3.77 and 3.71 (s, 3H), 3.37 – 3.10 (m, 2H), 2.90 (hept, J = 7.0 Hz, 1H), 2.21 – 2.00 (m, 2H), 1.75 – 1.58 (m, 2H), 1.25 (d, J = 6.8 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 159.91, 156.26, 153.28, 151.36, 149.80, 149.59, 139.35, 136.72, 131.46, 129.72, 129.65, 128.58, 128.16, 128.07, 127.98, 120.19, 119.64, 67.55, 67.46, 67.32, 55.22, 50.55, 50.34, 46.52, 45.49, 34.21, 29.95, 29.92, 29.71, 29.54, 24.91, 24.86, 24.59, 24.21, 23.61. IR (neat, cm^{-1}): 2958.54, 1677.85, 1599.51, 1456.17, 1422.72, 1261.60, 1152.46, 1039.35, 907.33, 727.92. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{35}H_{48}O_5N_3S^+$: 622.33147, Found: 622.32867.

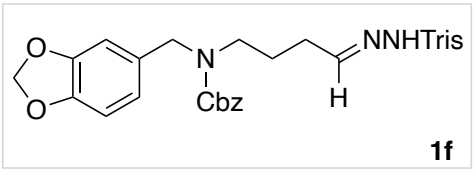


Benzyl (4-methoxybenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1e) Yield: 75%. Hexanes/ethyl acetate = 3:1, R_f = 0.33. ^1H NMR (500 MHz,



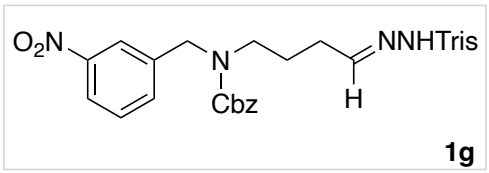
$CDCl_3$) δ 8.12 – 8.04 (m, 1H), 7.44 – 7.23 (m, 5H), 7.22 – 6.39 (m, 7H), 5.16 (s, 2H), 4.45 – 4.35 (m, 2H), 4.25 – 4.19 (m, 2H), 3.78 (s, 3H), 3.26 – 3.09 (m, 2H), 2.91 (hept, J = 7.0 Hz, 1H), 2.22 – 2.03 (m, 2H), 1.76 – 1.58 (m, 2H), 1.27 (d, J = 6.9 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 159.04, 156.22, 153.27, 151.35, 149.81, 149.61, 136.74, 131.48, 129.72, 129.33, 128.78, 128.58, 128.08, 128.03, 123.83, 114.08, 114.01, 67.49, 67.33, 55.30, 50.00, 49.75, 46.17, 45.19, 34.20, 29.94, 29.91, 29.69, 29.55, 24.91, 24.85, 24.57, 24.19, 23.60. IR (neat, cm^{-1}): 2958.76, 2868.93, 1693.21, 1611.57, 1512.88, 1462.59, 1245.64, 1008.78, 753.25. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{35}H_{51}N_4O_5S^+$: 639.35294, Found: 639.35425.

Benzyl (benzo[*d*][1,3]dioxol-5-ylmethyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1f)

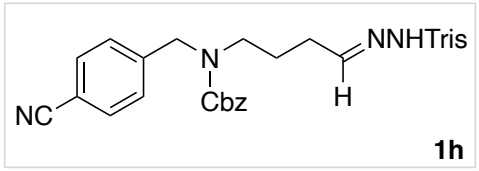


1f

Yield: 70%. Hexanes/ethyl acetate = 3:1, R_f = 0.35. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.12 – 7.95 (m, 1H), 7.45 – 6.93 (m, 8H), 6.79 – 6.56 (m, 3H), 5.92 (s, 2H), 5.15 (s, 2H), 4.35 and 4.32 (br, 2H), 4.28 – 4.15 (m, 2H), 3.26 – 3.07 (m, 2H), 2.91 (hept, J = 7.1 Hz, 1H), 2.23 – 2.01 (m, 2H), 1.75 – 1.57 (m, 2H), 1.26 (d, J = 6.8 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.64, 156.15, 153.31, 151.36, 149.80, 149.58, 147.99, 147.03, 136.67, 131.54, 131.44, 128.61, 128.14, 128.08, 123.86, 121.33, 120.83, 108.48, 108.20, 107.98, 101.09, 67.46, 50.38, 50.10, 46.17, 45.23, 34.21, 29.96, 29.94, 29.71, 29.54, 24.92, 24.86, 24.55, 24.14, 23.61. IR (neat, cm^{-1}): 2957.99, 1675.79, 1599.25, 1489.32, 1423.83, 1363.70, 1244.47, 1164.06, 1037.55, 927.08, 752.84. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{35}H_{46}N_3O_6S^+$: 636.3108, Found: 636.30900.

Benzyl (3-nitrobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1g) 

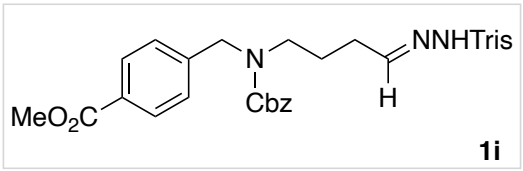
Yield: 79%. Hexanes/ethyl acetate = 1:1, R_f = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.33 – 7.95 (m, 3H), 7.63 – 7.27 (m, 6H), 7.24 – 7.05 (m, 4H), 5.20 and 5.13 (br, 2H), 4.58 and 4.50 (br, 2H), 4.23 – 4.17 (m, 2H), 3.39 – 3.16 (m, 2H), 2.98 – 2.83 (m, 1H), 2.19 – 2.12 (m, 2H), 1.76 – 1.70 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.67, 156.00, 153.35, 151.29, 149.39, 149.17, 148.46, 140.18, 140.04, 136.38, 133.87, 131.38, 129.66, 128.62, 128.28, 128.12, 123.84, 122.48, 122.32, 122.14, 67.67, 50.18, 50.00, 47.11, 46.17, 34.17, 29.92, 29.55, 29.42, 24.87, 24.81, 24.57, 24.19, 23.57. IR (neat, cm^{-1}): 2958.70, 2868.63, 1680.13, 1599.20, 1530.21, 1423.32, 1348.07, 1164.74, 755.45, 731.25. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{34}H_{44}O_6N_4SNa^+$: 659.28793, Found: 659.28851.

Benzyl (4-cyanobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1h) 

Yield: 76%. Hexanes/ethyl acetate = 2:1, R_f = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.05 – 6.85 (m, 13H), 5.13 and 5.09 (br, 2H), 4.47 and 4.45 (br, 2H), 4.19 – 4.14 (m, 2H), 3.34 – 3.11 (m, 2H), 2.96 – 2.82 (m, 1H), 2.17 – 2.03 (m, 2H), 1.77 – 1.66 (m, 2H), 1.23 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.71, 153.48, 151.36, 149.46, 149.20, 143.46, 136.32, 132.51, 131.37, 128.68, 128.39, 128.22, 127.81, 123.93,

118.80, 111.32, 67.88, 67.79, 67.63, 50.61, 50.41, 47.14, 46.10, 34.25, 30.00, 29.98, 29.57, 29.37, 24.93, 24.88, 24.58, 24.22, 23.64. IR (neat, cm^{-1}): 2958.96, 2228.99, 1681.21, 1599.38, 1463.69, 1425.14, 1216.66, 1164.29, 750.53. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{35}H_{45}N_4O_4S^+$: 617.31560, Found: 617.31541.

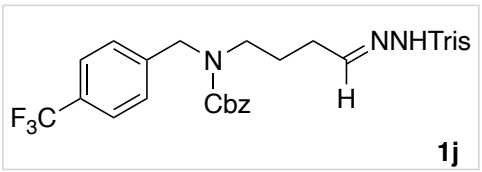
Methyl 4-((((benzyloxy)carbonyl)(4-oxobutyl)amino)methyl)benzoate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1i)



1i

Yield: 74%. Hexanes/ethyl acetate = 1:1, R_f = 0.35. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.06 – 7.60 (m, 3H), 7.45 – 6.83 (m, 10H), 5.14 and 5.11 (br, 2H), 4.48 and 4.45 (br, 2H), 4.19 – 4.14 (m, 2H), 3.90 (s, 3H), 3.28 – 3.14 (m, 2H), 2.98 – 2.85 (m, 1H), 2.25 – 2.00 (m, 2H), 1.78 – 1.57 (m, 2H), 1.23 (d, J = 6.8 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 166.94, 156.72, 153.40, 151.39, 149.64, 149.41, 143.12, 136.50, 131.40, 130.08, 130.02, 129.40, 128.71, 128.61, 128.25, 128.16, 128.08, 127.73, 127.13, 123.91, 67.77, 67.67, 67.52, 52.22, 50.54, 50.36, 46.92, 45.84, 34.25, 30.00, 29.68, 29.46, 24.94, 24.89, 24.59, 24.27, 23.64. IR (neat, cm^{-1}): 2957.28, 2868.81, 1699.10, 1599.56, 1462.50, 1277.67, 1153.42, 1107.80, 752.05. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{36}H_{47}O_6N_3SNa^+$: 672.30833, Found: 672.30878.

Benzyl (4-oxobutyl)(4-(trifluoromethyl)benzyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1j)

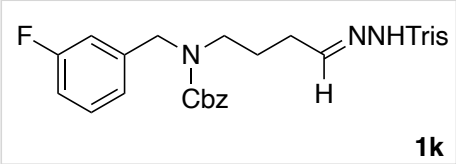


1j

Yield: 76%. Hexanes/ethyl acetate = 3:1, R_f = 0.32. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.22 – 8.08 (m, 1H), 7.54 – 7.52 (m, 2H),

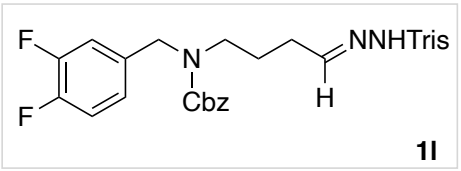
7.36 – 7.18 (m, 10H), 5.17 and 5.13 (br, 2H), 4.50 and 4.48 (br, 2H), 4.23 – 4.18 (m, 2H), 3.37 – 3.13 (m, 2H), 2.93 – 2.88 (m, 1H), 2.19 – 2.11 (m, 2H), 1.81 – 1.63 (m, 2H), 1.26 (d, J = 6.8 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.73, 156.20, 153.41, 151.41, 151.37, 149.53, 149.30, 141.99, 136.42, 131.41, 129.72 (q, J = 33.0 Hz), 128.68, 128.59, 128.21, 128.13, 128.08, 127.45, 125.62 (q, J =4.5 Hz), 124.21 (q, J = 270.0 Hz), 123.90, 67.74, 67.68, 67.54, 50.39, 50.22, 46.98, 45.90, 34.23, 29.98, 29.63, 29.47, 24.91, 24.86, 24.57, 24.23, 23.61. ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.48. IR (neat, cm^{-1}): 2959.34, 2869.47, 1678.02, 1599.40, 1416.09, 1323.45, 1162.70, 1122.76, 1065.84, 1017.69, 754.40. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{35}H_{44}O_4N_3SF_3Na^+$: 682.29023, Found: 682.29071.

Benzyl (3-fluorobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1k) Yield: 77%. Hexanes/ethyl acetate = 3:1, R_f = 0.30. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.22 – 8.08 (m, 1H), 7.41 – 7.14 (m, 9H), 6.88 (m, 3H), 5.15 and 5.13 (br, 2H), 4.43 and 4.40 (br, 2H), 4.31 – 4.14 (m, 2H), 3.34 – 3.10 (m, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 2.16 – 2.07 (m, 2H), 1.72 – 1.62 (m, 2H), 1.25 (d, J = 7.0 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 163.06 (d, J = 246.6 Hz), 156.69, 156.18, 153.32, 151.36, 149.59, 149.36, 140.45, 140.32 (d, J = 7.5 Hz), 131.44, 130.17 (d, J = 9.0 Hz), 128.60, 128.40, 128.17, 128.08, 128.01, 123.86, 123.36, 122.82, 114.66, 114.33 (d, J = 21.0 Hz), 114.07, 67.67, 67.60, 67.47, 50.24, 50.02, 46.76, 45.76, 34.21, 29.95, 29.66, 29.50, 24.91, 24.85, 24.56, 24.19, 23.61. ^{19}F NMR (470 MHz, $CDCl_3$) δ –112.78. IR (neat, cm^{-1}): 2959.08, 1678.22, 1597.05, 1422.68, 1152.82,

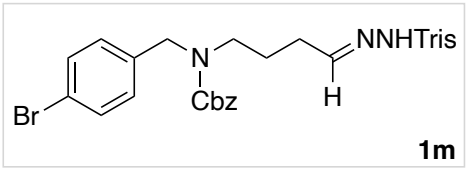


1k

908.21, 729.99. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{34}H_{44}O_4N_3SFNa^+$: 632.29343, Found: 632.29327.

Benzyl (3,4-difluorobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1l) 

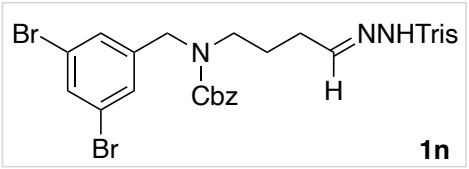
1l Yield: 74%. Hexanes/ethyl acetate = 3:1, R_f = 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.44 – 7.70 (m, 1H), 7.52 – 6.77 (m, 11H), 5.15 and 5.14 (br, 2H), 4.38 and 4.36 (br, 2H), 4.19 (hept, *J* = 6.5 Hz, 2H), 3.30 – 3.12 (m, 2H), 2.97 – 2.85 (m, 1H), 2.21 – 2.06 (m, 2H), 1.76 – 1.60 (m, 2H), 1.25 (d, *J* = 6.9 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.66, 156.09, 153.44, 151.42, 151.39, 149.74 (d, *J* = 250.0 Hz), 136.49, 134.96 (dd, *J* = 3.8, 3.0 Hz), 131.41, 128.68, 128.38, 128.34, 128.20, 123.91, 123.30, 117.44 (d, *J* = 17.5 Hz), 117.38 (d, *J* = 16.3 Hz), 116.80 (d, *J* = 17.5 Hz), 116.30 (d, *J* = 18.8 Hz), 67.79, 67.64, 49.91, 49.66, 46.74, 45.77, 34.25, 29.99, 29.62, 29.48, 24.92, 24.57, 24.20, 23.62. ^{19}F NMR (470 MHz, $CDCl_3$) δ –137.27, –139.70. IR (neat, cm^{-1}): 2959.41, 2869.29, 1694.28, 1599.33, 1518.31, 1281.79, 1212.40, 1114.06, 881.54, 753.33. 2959.39, 2869.41, 1678.69, 1599.67, 1518.54, 1421.93, 1281.89, 1164.52, 1153.16, 908.85, 822.85, 731.12. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{34}H_{43}O_4N_3SF_2Na^+$: 650.28401, Found: 650.28412.

Benzyl (4-bromobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1m) 

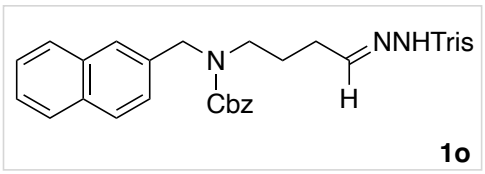
1m Yield: 76%. Hexanes/ethyl acetate = 3:1, R_f = 0.36. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.47 – 8.33 (m, 1H), 7.48 – 6.97 (m, 12H), 5.16 – 5.13 (m,

2H), 4.40 and 4.38 (br, 2H), 4.27 – 4.21 (m, 2H), 3.35 – 3.10 (m, 2H), 2.94 – 2.89 (m, 1H), 2.27 – 2.00 (m, 2H), 1.75 – 1.60 (m, 2H), 1.27 (d, J = 6.7 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.64, 153.25, 151.29, 149.47, 149.23, 136.79, 136.48, 131.66, 131.45, 129.59, 129.02, 128.54, 128.17, 128.01, 123.81, 122.65, 121.30, 121.18, 67.57, 67.51, 67.40, 50.09, 49.88, 46.65, 45.64, 34.16, 29.90, 29.87, 29.59, 29.46, 24.88, 24.82, 24.51, 24.13, 23.58. IR (neat, cm^{-1}): 2958.34, 1676.46, 1598.94, 1463.10, 1424.60, 1316.95, 1153.03, 1011,31, 882.44, 753.78. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{34}H_{45}O_4N_3SBr^+$: 670.23142, Found: 670.23138.

Benzyl (3,5-dibromobenzyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1n) Yield: 71%. Hexanes/ethyl acetate = 3:1, R_f = 0.38. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 7.99 – 7.74 (m, 1H), 7.54 (s, 1H), 7.45 – 6.51 (m, 10H), 5.14 and 5.11 (s, 2H), 4.34 and 4.32 (s, 2H), 4.20 – 4.15 (m, 2H), 3.35 – 3.09 (m, 2H), 2.89 (hept, J = 7.1 Hz, 1H), 2.29 – 2.03 (m, 2H), 1.82 – 1.57 (m, 2H), 1.24 (d, J = 6.7 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.61, 156.00, 153.42, 151.38, 149.50, 149.27, 142.00, 136.32, 133.20, 131.35, 129.48, 129.03, 128.75, 128.37, 128.18, 123.94, 123.91, 123.31, 123.25, 77.36, 67.90, 67.73, 49.77, 49.58, 47.03, 45.95, 34.24, 29.99, 29.62, 29.45, 24.94, 24.90, 24.51, 24.19, 23.64. IR (neat, cm^{-1}): 2958.23, 2868.04, 1681.90, 1585.53, 1463.21, 1418.71, 1315.71, 1217.70, 1153.14, 882.71, 741.03. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{34}H_{44}O_4N_3SBr_2^+$: 748.14193, Found: 748.14630.

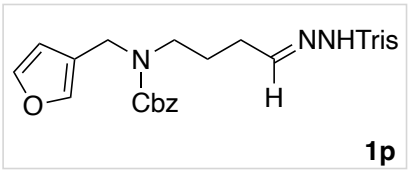


Benzyl (naphthalen-2-ylmethyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1o)



Yield: 72%. Hexanes/ethyl acetate = 3:1, R_f = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.35 – 8.20 (m, 1H), 7.88 – 6.95 (m, 15H), 5.24 and 5.21 (br, 2H), 4.65 and 4.62 (s, 2H), 4.30 – 4.26 (m, 2H), 3.37 – 3.17 (m, 2H), 2.93 (hept, J = 6.6 Hz, 1H), 2.19 – 2.08 (m, 2H), 1.77 – 1.66 (m, 2H), 1.30 (d, J = 6.9 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.32, 153.25, 151.33, 149.68, 149.46, 136.67, 135.13, 133.34, 132.82, 131.48, 128.61, 128.49, 128.12, 128.06, 127.99, 127.81, 127.70, 126.61, 126.28, 125.92, 125.44, 123.83, 67.59, 67.51, 67.38, 50.75, 50.52, 46.50, 45.38, 34.18, 29.94, 29.91, 29.68, 29.50, 24.91, 24.85, 24.55, 24.20, 23.60. IR (neat, cm^{-1}): 2958.51, 1681.93, 1599.51, 1462.44, 1425.01, 1215.77, 1153.11, 750.96, 664.40. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{38}H_{48}O_4N_3S^+$: 642.33655, Found: 642.33630.

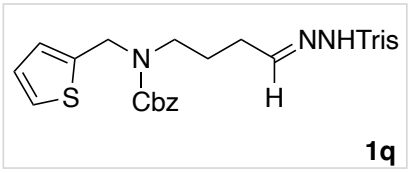
Benzyl (furan-3-ylmethyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1p)



Yield: 70%. Hexanes/ethyl acetate = 3:1, R_f = 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.06 – 7.70 (m, 1H), 7.49 – 6.91 (m, 9H), 6.40 – 5.99 (m, 2H), 5.17 and 5.12 (br, 2H), 4.48 – 4.35 (m, 2H), 4.25 – 4.16 (m, 2H), 3.42 – 3.16 (m, 2H), 2.96 – 2.84 (m, 1H), 2.21 – 1.96 (m, 2H), 1.74 – 1.51 (m, 2H), 1.26 (d, J = 6.9 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.22, 153.33, 151.39, 151.20, 149.96, 149.69, 142.24, 136.68, 131.44, 128.57, 128.23, 128.09,

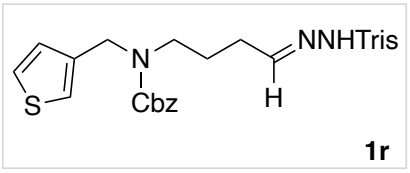
127.95, 123.87, 123.74, 110.45, 67.43, 46.67, 45.81, 43.70, 34.24, 29.98, 29.63, 29.47, 24.93, 24.88, 24.66, 24.34, 23.63. IR (neat, cm^{-1}): 2958.11, 2868.83, 1678.47, 1599.30, 1423.39, 1316.93, 1152.03, 1011.91, 910.23, 730.80. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{32}H_{43}O_5N_3SNa^+$: 604.28211, Found: 604.28229.

Benzyl (4-oxobutyl)(thiophen-2-ylmethyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1q) Yield: 71%. Hexanes/ethyl acetate = 3:1, R_f = 0.33. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 7.51 – 6.48 (m, 12H), 5.18 and 5.15 (br, 2H), 4.56 and 4.53 (s, 2H), 4.21 – 4.16 (m, 2H), 3.34 – 3.16 (m, 2H), 2.95 – 2.82 (m, 1H), 2.22 – 2.04 (m, 2H), 1.77 – 1.61 (m, 2H), 1.26 – 1.24 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.27, 155.83, 153.30, 151.36, 149.77, 149.53, 140.47, 140.32, 136.56, 131.43, 128.59, 128.12, 126.76, 126.66, 126.34, 125.50, 125.37, 123.86, 77.36, 67.49, 46.28, 45.64, 45.48, 34.21, 29.95, 29.92, 29.64, 29.48, 24.93, 24.87, 24.67, 24.27, 23.61. IR (neat, cm^{-1}): 2958.83, 2868.65, 1678.15, 1599.27, 1462.58, 1423.55, 1216.61, 1163.92, 1152.52, 907.97, 729.42. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{32}H_{43}O_4N_3S_2Na^+$: 620.25927, Found: 620.25983.



1q

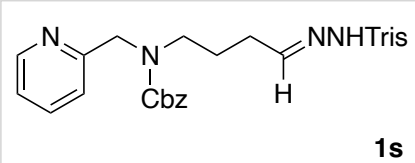
Benzyl (4-oxobutyl)(thiophen-3-ylmethyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1r) Yield: 72%. Hexanes/ethyl acetate = 3:1, R_f = 0.33. ^1H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.29 – 8.13 (m, 1H), 7.40 – 6.85 (m, 11H), 5.19 and 5.15 (br, 2H), 4.42 and 4.40 (br, 2H), 4.22 (hept, J = 7.1 Hz, 2H), 3.41 – 3.10 (m, 2H), 2.95 –



1r

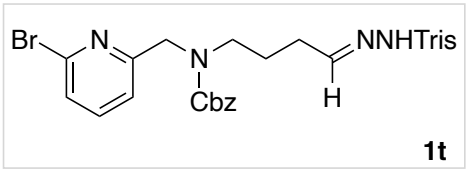
2.83 (m, 1H), 2.16 – 2.06 (m, 2H), 1.69 – 1.62 (m, 2H), 1.27 (d, J = 6.8 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.10, 153.29, 151.36, 149.76, 149.54, 148.43, 138.60, 136.67, 131.49, 128.60, 128.16, 128.06, 127.72, 127.21, 126.48, 126.23, 123.85, 122.83, 122.68, 122.38, 67.56, 67.47, 67.39, 46.39, 45.94, 45.48, 34.21, 29.94, 29.60, 29.46, 24.93, 24.87, 24.63, 24.24, 23.61. IR (neat, cm^{-1}): 2958.18, 2868.40, 1690.79, 1599.19 1461.52, 1426.61, 1214.68, 1083.13, 1009.48, 754.22. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{32}H_{43}O_4N_3S_2Na^+$: 620.25927, Found: 620.26032.

Benzyl (4-oxobutyl)(pyridin-2-ylmethyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1s) Yield: 75%. 100% ethyl acetate, R_f = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.56 – 8.45 (m, 1H), 8.33 – 8.10 (m, 1H), 7.65 – 7.52 (m, 1H), 7.40 – 6.96 (m, 10H), 5.14 and 5.10 (s, 2H), 4.56 and 4.53 (s, 2H), 4.29 – 4.11 (m, 2H), 3.41 – 3.27 (m, 2H), 2.89 (hept, J = 6.9 Hz, 1H), 2.22 – 2.02 (m, 2H), 1.80 – 1.59 (m, 2H), 1.23 (d, J = 7.0 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 157.84, 157.75, 156.62, 156.28, 153.20, 151.34, 149.75, 149.58, 149.24, 149.12, 136.96, 136.82, 136.59, 131.48, 128.63, 128.47, 128.23, 128.16, 128.04, 127.88, 123.84, 122.48, 122.34, 122.15, 121.20, 67.58, 67.54, 67.32, 52.69, 52.47, 47.50, 46.54, 34.19, 29.92, 29.90, 29.77, 29.55, 24.89, 24.50, 23.60. IR (neat, cm^{-1}): 2958.18, 2868.20, 1694.43, 1597.52, 1463.37, 1422.45, 1215.38, 1152.74, 750.48. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{33}H_{45}O_4N_4S^+$: 593.31615, Found: 593.31671.



1s

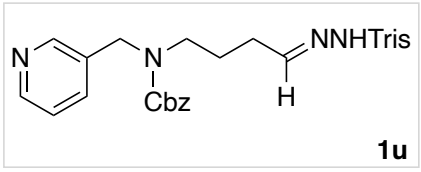
Benzyl ((6-bromopyridin-2-yl)methyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1t)



1t

Yield: 78%. 100% ethyl acetate, R_f = 0.37. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.38 – 7.87 (m, 1H), 7.58 – 6.54 (m, 11H), 5.12 and 5.08 (br, 2H), 4.49 and 4.46 (br, 2H), 4.29 – 4.11 (m, 2H), 3.44 – 3.25 (m, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.24 – 2.03 (m, 2H), 1.80 – 1.63 (m, 2H), 1.23 (d, *J* = 7.1 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 159.55, 159.40, 156.55, 156.13, 153.24, 151.33, 149.67, 149.50, 141.66, 141.50, 139.19, 139.06, 136.49, 136.41, 131.38, 128.66, 128.51, 128.28, 128.15, 128.09, 128.03, 127.90, 126.74, 126.63, 123.83, 120.76, 119.81, 67.65, 67.61, 67.39, 52.43, 52.11, 47.71, 46.90, 34.19, 29.93, 29.70, 29.49, 24.90, 24.51, 23.61. IR (neat, cm^{-1}): 3172.55, 2958.63, 2868.27, 1681.45, 1557.02, 1425.67, 1316.71, 1153.42, 1119.25, 753.70. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{33}H_{44}O_4N_4SBr^+$: 671.22666, Found: 671.22681.

Benzyl (4-oxobutyl)(pyridin-3-ylmethyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1u)

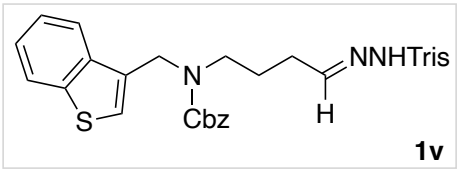


1u

Yield: 84%. 100% ethyl acetate, R_f = 0.31. ^{1}H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.58 – 8.02 (m, 3H), 7.71 – 6.96 (m, 10H), 5.14 and 5.13 (br, 2H), 4.45 and 4.41 (br, 2H), 4.21 – 4.16 (m, 2H), 3.27 – 3.17 (m, 2H), 2.92 – 2.82 (m, 1H), 2.17 – 2.09 (m, 2H), 1.72 – 1.65 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 156.67, 153.32, 151.34, 149.13, 149.01, 148.85, 136.46, 136.08, 135.32, 133.54, 131.53, 128.68, 128.32, 128.19, 123.87, 123.75,

67.84, 67.64, 48.38, 46.78, 45.80, 34.22, 29.95, 29.62, 29.44, 24.93, 24.87, 24.61, 24.24, 23.63. IR (neat, cm^{-1}): 2958.11, 2868.47, 1695.99, 1598.90, 1464.24, 1419.75, 1320.01, 1164.43, 1153.44, 909.16, 730.30. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{33}H_{45}O_4N_4S^+$: 593.31615, Found: 593.31677.

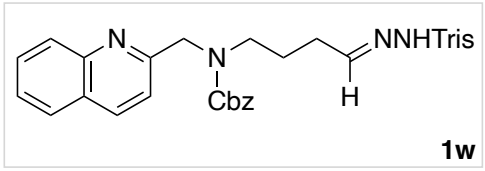
Benzyl (benzo[*b*]thiophen-3-ylmethyl)(4-oxobutyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1v)



1v

Yield: 86%. Hexanes/ethyl acetate = 3:1, R_f = 0.36. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 8.07 – 6.69 (m, 14H), 5.23 and 5.19 (br, 2H), 4.72 and 4.68 (br, 2H), 4.21 – 4.15 (m, 2H), 3.33 – 3.11 (m, 2H), 2.93 – 2.86 (m, 1H), 2.13 – 2.03 (m, 2H), 1.67 – 1.57 (m, 2H), 1.26 (d, J = 6.8 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 153.44, 151.41, 149.91, 149.69, 140.70, 138.11, 137.87, 136.74, 132.51, 132.31, 131.36, 128.73, 128.70, 128.38, 128.31, 128.27, 125.21, 124.85, 124.69, 124.49, 123.94, 122.92, 122.39, 121.76, 67.59, 46.09, 45.13, 44.77, 34.27, 30.02, 29.65, 29.42, 24.97, 24.91, 24.39, 24.13, 23.66. IR (neat, cm^{-1}): 2958.01, 2868.37, 1677.23, 1599.06, 1459.39, 1423.21, 1314.54, 1163.89, 907.36, 728.00. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{36}H_{45}O_4N_3S_2Na^+$: 670.27492, Found: 670.27521.

Benzyl (4-oxobutyl)(quinolin-2-ylmethyl)carbamate 2,4,6-triisopropylbenzenesulfonyl hydrazone (1w)



1w

Yield: 81%. 100% ethyl acetate, R_f = 0.34. ^1H NMR (600 MHz, $CDCl_3$) some signals exist as a

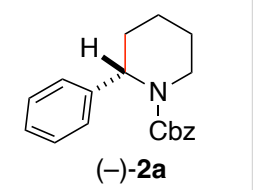
pair due to the presence of amide rotamers. δ 8.26 – 8.00 (m, 2H), 7.80 – 7.69 (m, 3H), 7.60 – 6.71 (m, 10H), 5.18 and 5.13 (s, 2H), 4.75 and 4.71 (s, 2H), 4.24 – 4.16 (m, 2H), 3.43 – 3.30 (m, 2H), 2.89 (hept, J = 7.1 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.76 – 1.66 (m, 2H), 1.24 (d, J = 7.3 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) some signals exist as a pair due to the presence of amide rotamers δ 158.30, 156.84, 156.39, 153.34, 151.40, 150.00, 149.78, 147.72, 137.05, 136.68, 136.59, 131.37, 129.84, 129.09, 128.75, 128.49, 128.38, 128.30, 128.07, 127.93, 127.72, 127.53, 127.40, 126.52, 123.90, 120.11, 119.14, 67.70, 67.43, 53.51, 53.29, 47.60, 46.45, 34.28, 34.26, 30.00, 29.82, 29.52, 24.94, 24.81, 24.58, 23.65. IR (neat, cm^{-1}): 2958.51, 2868.74, 1681.93, 1599.51, 1462.44, 1425.01, 1215.77, 1153.11, 750.96. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{37}H_{47}O_4N_4S^+$: 643.33180, Found: 643.33289.

3.4.3. Synthesis and Characterization of Piperidines

3.4.3.1. Experimental Procedure for [Co(Por)]-Catalyzed Enantioselective Radical Cyclization

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol), [Co(Por)] (2 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, anhydrous benzene (2.0 mL) was added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22 °C for 48 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum and purified by flash column chromatography.

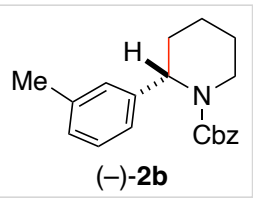
Benzyl (*S*)-2-phenylpiperidine-1-carboxylate (2a) Following general procedure using **1a**



(–)-**2a**

as the starting material. Yield: 78%. Hexanes/ethyl acetate = 8:1, R_f = 0.36. $[\alpha]_D^{20}$ = (–)-70.4° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 7H), 7.26 – 7.22 (m, 3H), 5.53 (s, 1H), 5.20 (s, 2H), 4.14 (d, *J* = 10.9 Hz, 1H), 2.85 (ddd, *J* = 13.6, 11.9, 3.9 Hz, 1H), 2.34 (d, *J* = 15.6 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.66 – 1.46 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.29, 139.95, 137.07, 128.74, 128.57, 128.02, 127.89, 126.67, 126.65, 67.29, 53.67, 40.63, 28.19, 25.59, 19.45. IR (neat, cm^{-1}): 2934.29, 2860.66, 1694.40, 1421.73, 1258.07, 1162.18, 1028.74. HPLC analysis: ee = 92%. ID(95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 23.66 min, t_{minor} = 26.31 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{22}NO_2^+$: 296.16451, Found: 296.16263.

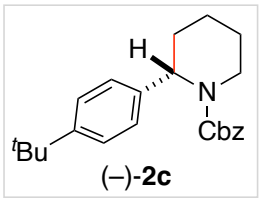
Benzyl (*S*)-2-(*m*-tolyl)piperidine-1-carboxylate (2b) Following general procedure using



(–)-**2b**

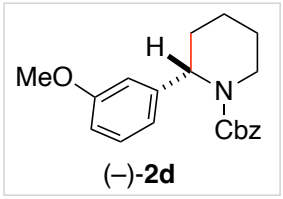
1b as the starting material. Yield: 74%. Hexanes/ethyl acetate = 5:1, R_f = 0.48. $[\alpha]_D^{20}$ = (–)-92.0° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.21 (m, 6H), 7.10 – 7.00 (m, 3H), 5.51 (s, 1H), 5.22 (s, 2H), 4.15 (d, *J* = 12.7 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.35 – 2.33 (m, 4H), 1.95 – 1.87 (m, 1H), 1.59 – 1.47 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.26, 139.91, 138.32, 137.13, 128.61, 128.56, 127.98, 127.85, 127.39, 127.35, 123.67, 67.22, 53.62, 40.63, 28.20, 25.59, 21.75, 19.48. IR (neat, cm^{-1}): 2937.30, 2861.67, 1694.88, 1421.48, 1259.04, 1114.44, 793.52. HPLC analysis: ee = 94%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 12.86 min, t_{minor} = 15.84 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_2^+$: 310.18016, Found: 310.18091.

Benzyl (*S*)-2-(4-(*tert*-butyl)phenyl)piperidine-1-carboxylate (2c) Following general procedure using **1c** as the starting material. Yield: 80%. Hexanes/ethyl acetate = 8:1, R_f = 0.48. $[\alpha]_D^{20}$ = (–)-87.4° (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 7H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 5.20 (s, 2H), 4.14 (d, *J* = 12.4 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 1.93 – 1.88 (m, 1H), 1.66 – 1.50 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.26, 149.44, 137.12, 136.78, 128.55, 127.96, 127.86, 126.36, 125.59, 67.21, 53.40, 40.55, 34.48, 31.49, 28.13, 25.63, 19.47. IR (neat, cm^{-1}): 2949.16, 2865.44, 1696.01, 1421.63, 1254.91, 1163.46, 1104.88, 1029.28, 697.00. HPLC analysis: ee = 92%. IA(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 11.76 min, t_{minor} = 10.55 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{30}NO_2^+$: 352.22711, Found: 352.22837.



(–)-**2c**

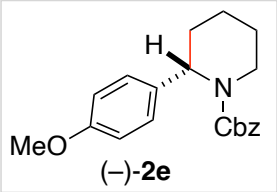
Benzyl (*S*)-2-(3-methoxyphenyl)piperidine-1-carboxylate (2d) Following general procedure using **1d** as the starting material. Yield: 51%. ee: 90%. Hexanes/ethyl acetate = 5:1, R_f = 0.38. $[\alpha]_D^{20}$ = (–)-78.0° (*c* = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 6H), 6.85 – 6.72 (m, 3H), 5.48 (s, 1H), 5.18 (s, 2H), 4.12 (d, *J* = 12.8 Hz, 1H), 3.75 (s, 3H), 2.85 (td, *J* = 12.8, 3.6 Hz, 1H), 2.29 (d, *J* = 14.1 Hz, 1H), 1.88 (ddd, *J* = 13.2, 8.8, 4.8 Hz, 1H), 1.63 – 1.46 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.15, 156.23, 141.83, 137.09, 129.72, 128.58, 128.02, 127.91, 119.01, 112.88, 111.64, 67.27, 55.31, 53.66, 40.72, 28.28, 25.53, 19.51. IR (neat, cm^{-1}): 2938.04, 1695.51, 1489.28, 1422.84, 1256.89, 1170.28, 1140.90, 1034.14. HPLC analysis: ee = 90%. IC(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major}



(–)-**2d**

= 17.17 min, t_{minor} = 19.37 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.17507, Found: 326.17589.

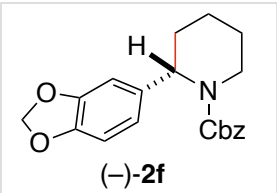
Benzyl (*S*)-2-(4-methoxyphenyl)piperidine-1-carboxylate (2e) Yield: 81 %. Following



(–)-**2e**

general procedure using **1e** as the starting material. Hexanes/ethyl acetate = 5:1, R_f = 0.31. $[\alpha]_D^{20}$ = (–)-91.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.16 – 7.12 (m, 2H), 6.89 – 6.85 (m, 2H), 5.48 (d, *J* = 4.5 Hz, 1H), 5.19 (s, 2H), 4.11 (d, *J* = 13.6 Hz, 1H), 3.80 (s, 3H), 2.82 (ddd, *J* = 13.6, 11.8, 3.8 Hz, 1H), 2.30 (d, *J* = 14.1 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.64 – 1.46 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.36, 156.23, 137.11, 131.83, 128.58, 128.01, 127.88, 127.82, 114.10, 67.25, 55.40, 53.11, 40.43, 28.15, 25.66, 19.41. IR (neat, cm^{-1}): 2937.20, 1693.66, 1610.36, 1511.68, 1422.83, 1248.66, 1162.48, 1035.26. HPLC analysis: ee = 91%. IF(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 15.60 min, t_{minor} = 19.82 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.17507, Found: 326.17450.

Benzyl (*S*)-2-(benzo[*d*][1,3]dioxol-5-yl)piperidine-1-carboxylate (2f) Following general

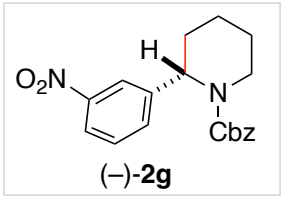


(–)-**2f**

procedure using **1f** as the starting material. Yield: 70%. Hexanes/ethyl acetate = 5:1, R_f = 0.30. $[\alpha]_D^{20}$ = (–)-89.8° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.20 (m, 5H), 6.83 – 6.65 (m, 3H), 5.94 (s, 2H), 5.43 (d, *J* = 4.3 Hz, 1H), 5.19 (s, 2H), 4.11 (d, *J* = 14.2 Hz, 1H), 2.90 – 2.76 (m, 1H), 2.30 – 2.20 (m, 1H), 1.91 – 1.84 (m, 1H), 1.66 – 1.46 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.15, 148.28, 146.27, 137.03, 133.95, 128.59, 128.04, 127.89, 119.70, 108.34, 107.38, 101.12, 67.30, 53.45, 40.50, 28.34, 25.53, 19.39. IR (neat, cm^{-1}): 2938.67, 1691.57, 1489.38, 1421.66, 1352.25, 1236.59, 1167.60, 1035.75, 930.46.

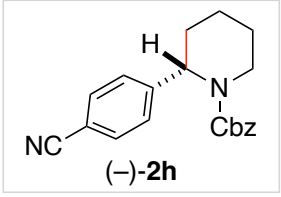
HPLC analysis: ee = 84%. IE(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 22.54 min, t_{minor} = 23.94 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{22}NO_4^+$: 340.15433, Found: 340.15405.

Benzyl (*S*)-2-(3-nitrophenyl)piperidine-1-carboxylate (2g) Following general procedure using **1g** as the starting material. Yield: 48%. Hexanes/ethyl acetate = 5:1, R_f = 0.33. $[\alpha]_D^{20}$ = (–)-103.2° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.10 (m, 2H), 7.55 – 7.49 (m, 2H), 7.37 – 7.30 (m, 5H), 5.56 (s, 1H), 5.20 (d, *J* = 2.9 Hz, 2H), 4.19 (d, *J* = 13.6 Hz, 1H), 2.82 (td, *J* = 12.8, 3.9 Hz, 1H), 2.34 (d, *J* = 14.3 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.72 – 1.53 (m, 3H), 1.45 – 1.36 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.16, 148.92, 142.82, 136.72, 132.97, 129.77, 128.68, 128.25, 128.01, 121.99, 121.74, 67.64, 53.49, 40.79, 28.21, 25.27, 19.34. IR (neat, cm^{-1}): 2941.57, 2863.22, 1695.33, 1528.06, 1419.74, 1348.26, 1257.80, 1162.29, 1034.63. HPLC analysis: ee = 95%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 28.30 min, t_{minor} = 37.22 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}N_2O_4^+$: 341.14958, Found: 341.14983.



(–)-**2g**

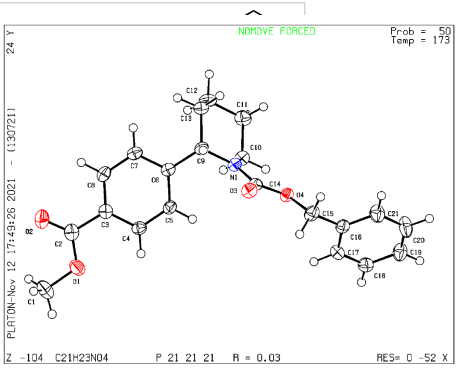
Benzyl (*S*)-2-(4-cyanophenyl)piperidine-1-carboxylate (2h) Following general procedure using **1h** as the starting material. Yield: 83%. Hexanes/ethyl acetate = 3:1, R_f = 0.50. $[\alpha]_D^{20}$ = (–)-110.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.24 (m, 7H), 5.51 (s, 1H), 5.18 (d, *J* = 3.8 Hz, 2H), 4.16 (d, *J* = 14.3 Hz, 1H), 2.79 (ddd, *J* = 13.5, 12.2, 3.8 Hz, 1H), 2.29 (dd, *J* = 14.3, 3.8 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.70 – 1.53 (m, 3H), 1.40 – 1.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.16, 146.10, 136.71, 132.57, 128.65, 128.25, 128.03, 127.48, 118.90, 110.73, 67.59, 53.83, 40.87,



(–)-**2h**

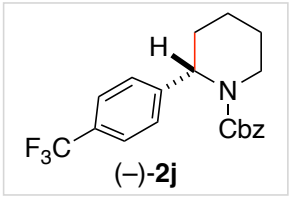
28.19, 25.24, 19.38. IR (neat, cm^{-1}): 2939.15, 2227.71, 1693.85, 1607.69, 1420.47, 1258.31, 1160.44, 1110.70, 1029.40. HPLC analysis: ee = 94%. IC(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 32.13 min, t_{minor} = 40.78 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{21}N_2O_2^+$: 321.15975, Found: 321.15924.

Benzyl (*S*)-2-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (2i) Following



general procedure using **1i** as the starting material. Yield: 70%. Hexanes/ethyl acetate = 5:1, R_f = 0.24. $[\alpha]_D^{20}$ = (–)-96.6° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.24 (m, 7H), 5.53 (s, 1H), 5.19 (s, 2H), 4.16 (d, *J* = 13.5 Hz, 1H), 3.91 (s, 3H), 2.82 (td, *J* = 12.9, 3.7 Hz, 1H), 2.33 (d, *J* = 14.2 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.69 – 1.52 (m, 3H), 1.45 – 1.36 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.01, 156.20, 145.62, 136.87, 130.05, 128.69, 128.61, 128.12, 127.92, 126.69, 67.43, 53.82, 52.19, 40.80, 28.28, 25.40, 19.44. IR (neat, cm^{-1}): 2943.50, 2862.76, 1720.05, 1691.61, 1610.57, 1419.04, 1276.64, 1251.88, 1104.99, 1017.73, 860.77. HPLC analysis: ee = 86%. IA(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 9.98 min, t_{minor} = 8.70 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{24}NO_4^+$: 354.16998, Found: 354.16887. The absolute configuration was assigned as (*S*) by X-ray crystallography.

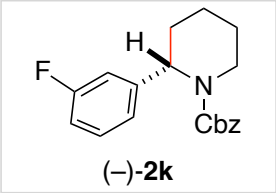
Benzyl (*S*)-2-(4-(trifluoromethyl)phenyl)piperidine-1-carboxylate (2j) Following



general procedure using **1j** as the starting material. Yield: 73%. Hexanes/ethyl acetate = 5:1, R_f = 0.48. $[\alpha]_D^{20}$ = (–)-77.8° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.19 (m, 7H), 5.53 (s, 1H), 5.18 (s, 2H), 4.16 (d, *J* = 14.8 Hz, 1H), 2.82 (td, *J* = 13.0,

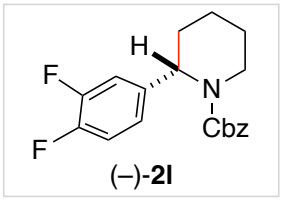
3.7 Hz, 1H), 2.31 (d, J = 12.7 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.70 – 1.52 (m, 3H), 1.42 – 1.35 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.21, 144.48, 136.83, 129.08 (q, J = 31.5 Hz), 128.63, 128.18, 127.98, 127.03, 125.70 (q, J = 3.7 Hz), 124.31 (q, J = 270.0 Hz), 67.49, 53.67, 40.78, 28.29, 25.35, 19.36. ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.48. IR (neat, cm^{-1}): 2939.63, 1697.62, 1619.26, 1420.52, 1327.08, 1257.37, 1162.41, 1120.77, 1068.45. HPLC analysis: ee = 94%. ID(95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 10.62 min, t_{minor} =10.16 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{21}NO_2F_3^+$: 364.15189, Found: 364.15117.

Benzyl (*S*)-2-(3-fluorophenyl)piperidine-1-carboxylate (2k) Following general procedure using **1k** as the starting material. Yield: 69%. Hexanes/ethyl acetate = 5:1, R_f = 0.42. $[\alpha]_D^{20}$ = (–)-82.2° (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 6H), 7.00 (d, J = 7.9 Hz, 1H), 6.97 – 6.90 (m, 2H), 5.49 (s, 1H), 5.19 (s, 2H), 4.14 (d, J = 13.6 Hz, 1H), 2.83 (td, J = 12.9, 3.6 Hz, 1H), 2.28 (d, J = 14.3 Hz, 1H), 1.97 – 1.86 (m, 1H), 1.64 – 1.41 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.49 (d, J = 245.6 Hz), 156.18, 143.02 (d, J = 6.5 Hz), 136.93, 130.22 (d, J = 8.2 Hz), 128.62, 128.11, 127.93, 122.24 (d, J = 2.8 Hz), 113.82 (d, J = 22.3 Hz), 113.60 (d, J = 21.0 Hz), 67.43, 53.47, 40.70, 28.25, 25.45, 19.42. ^{19}F NMR (470 MHz, $CDCl_3$) δ –112.96. IR (neat, cm^{-1}): 2938.49, 1694.30, 1614.17, 1588.45, 1420.29, 1256.44, 1172.63, 1112.17, 1029.46. HPLC analysis: ee = 92%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 14.46 min, t_{minor} = 16.48 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}NO_2F^+$: 314.15508, Found: 314.15596.



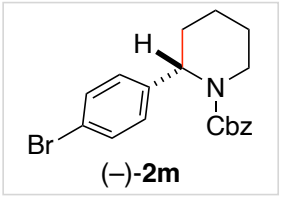
(–)-**2k**

Benzyl (*S*)-2-(3,4-difluorophenyl)piperidine-1-carboxylate (2l) Following general procedure using **1l** as the starting material. Yield: 67%. Hexanes/ethyl acetate = 5:1, R_f = 0.50. $[\alpha]_D^{20}$ = (–)-81.8° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 5H), 7.13 – 7.08 (m, 1H), 7.06 – 6.98 (m, 1H), 6.95 – 6.89 (m, 1H), 5.45 (s, 1H), 5.19 (s, 2H), 4.13 (d, *J* = 13.8 Hz, 1H), 2.79 (td, *J* = 13.0, 4.7 Hz, 1H), 2.23 (d, *J* = 14.4 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.70 – 1.41 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.11, 150.73 (dd, *J* = 243.8, 12.6 Hz), 149.19 (dd, *J* = 246.1, 12.6 Hz), 137.26 (dd, *J* = 4.3, 3.8 Hz), 136.81, 128.64, 128.19, 127.98, 122.57 (dd, *J* = 6.2, 3.5 Hz), 117.42 (d, *J* = 17.2 Hz), 115.88 (d, *J* = 17.9 Hz), 67.50, 53.00, 40.57, 28.14, 25.39, 19.30. ^{19}F NMR (470 MHz, $CDCl_3$) δ –137.46, –141.03. IR (neat, cm^{-1}): 2941.00, 1696.86, 1607.88, 1518.25, 1423.18, 1272.39, 1171.43, 1105.00, 1036.15. HPLC analysis: ee = 94%. ID(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 9.46 min, t_{minor} = 10.57 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{20}NO_2F_2^+$: 332.14566, Found: 332.14627.



(–)-**2l**

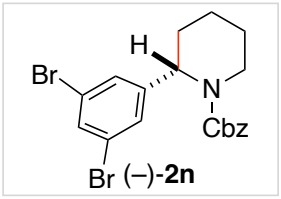
Benzyl (*S*)-2-(4-bromophenyl)piperidine-1-carboxylate (2m) Following general procedure using **1m** as the starting material. Yield: 66%. Hexanes/ethyl acetate = 5:1, R_f = 0.46. $[\alpha]_D^{20}$ = (–)-90.0° (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 5.45 (s, 1H), 5.18 (d, *J* = 2.2 Hz, 2H), 4.13 (d, *J* = 16.5 Hz, 1H), 2.90 – 2.70 (m, 1H), 2.27 (d, *J* = 12.5 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.66 – 1.41 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.19, 139.18, 136.91, 131.82, 128.62, 128.53, 128.13, 127.94, 120.60, 67.41, 53.35, 40.62, 28.14, 25.46, 19.35. IR (neat, cm^{-1}): 2938.34, 1696.36, 1487.97, 1421.06, 1257.63, 1161.38, 1075.21, 1008.36. HPLC



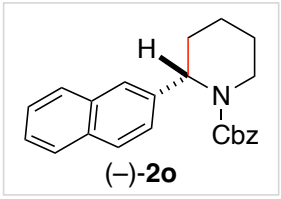
(–)-**2m**

analysis: ee = 91%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 13.09 min, t_{minor} = 14.15 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}NO_2Br^+$: 374.07502, Found: 374.07570.

Benzyl (*S*)-2-(3,5-dibromophenyl)piperidine-1-carboxylate (2n) Following general procedure using **1n** as the starting material. Yield: 53%. Hexanes/ethyl acetate = 8:1, R_f = 0.36. $[\alpha]_D^{20}$ = (–)-74.0° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.38 – 7.21 (m, 7H), 5.42 (s, 1H), 5.21 – 5.13 (m, 2H), 4.13 (d, *J* = 12.3 Hz, 1H), 2.79 (td, *J* = 13.1, 3.4 Hz, 1H), 2.18 (d, *J* = 17.5 Hz, 1H), 1.91 – 1.85 (m, 1H), 1.64 – 1.50 (m, 3H), 1.44 – 1.33 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.04, 144.68, 136.76, 132.54, 128.72, 128.67, 128.22, 127.92, 123.54, 67.59, 53.23, 40.77, 28.20, 25.25, 19.35. IR (neat, cm^{-1}): 2938.22, 2861.49, 1697.13, 1553.30, 1419.67, 1259.82, 1164.53, 740.54. HPLC analysis: ee = 93%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 10.64 min, t_{minor} = 11.32 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{20}NO_2Br_2^+$: 451.98553, Found: 451.98584.

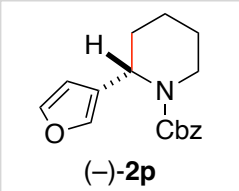


Benzyl (*S*)-2-(naphthalen-2-yl)piperidine-1-carboxylate (2o) Following general procedure using **1o** as the starting material. Yield: 78%. Hexanes/ethyl acetate = 5:1, R_f = 0.50. $[\alpha]_D^{20}$ = (–)-139.8° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 3H), 7.66 (s, 1H), 7.51 – 7.45 (m, 2H), 7.40 – 7.25 (m, 6H), 5.69 (s, 1H), 5.24 (s, 2H), 4.20 (d, *J* = 13.7 Hz, 1H), 3.00 – 2.86 (m, 1H), 2.48 (d, *J* = 17.6 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.71 – 1.52 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.33, 137.52, 137.06, 133.55, 132.37, 128.58, 128.51, 128.02, 127.88, 127.62, 126.20, 125.86, 125.35, 125.02, 67.33, 53.85,



40.78, 28.21, 25.60, 19.51. IR (neat, cm^{-1}): 2935.08, 1693.76, 1421.32, 1316.03, 1257.07, 1175.43, 1108.52, 1029.30. HPLC analysis: ee = 91%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 14.91 min, t_{minor} = 17.19 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{24}NO_2^+$: 346.18016, Found: 346.18022.

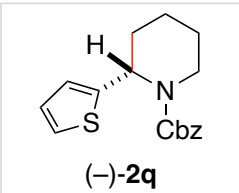
Benzyl (*S*)-2-(furan-3-yl)piperidine-1-carboxylate (2p) Following general procedure



(–)-**2p**

using **1p** as the starting material. Yield: 30%. Hexanes/ethyl acetate = 8:1, R_f = 0.32. $[\alpha]_D^{20}$ = (–)-60.0° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.08 (m, 8H), 6.21 (s, 1H), 5.42 (s, 1H), 5.18 (s, 2H), 4.06 (d, *J* = 11.0 Hz, 1H), 2.83 (t, *J* = 13.3 Hz, 1H), 2.00 (d, *J* = 13.8 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.67 – 1.48 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.75, 143.39, 139.74, 137.04, 128.63, 128.10, 127.96, 125.02, 110.04, 67.28, 47.85, 40.22, 28.61, 25.63, 19.69. IR (neat, cm^{-1}): 2939.37, 1694.72, 1422.43, 1324.70, 1263.71, 1170.34, 1117.41, 1026.33. HPLC analysis: ee = 91%. IE(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 16.80 min, t_{minor} = 15.49 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{20}NO_3^+$: 286.14377, Found: 286.14437.

Benzyl (*S*)-2-(thiophen-2-yl)piperidine-1-carboxylate (2q) Following general procedure

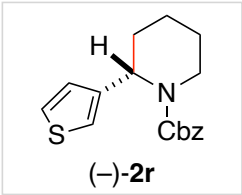


(–)-**2q**

using **1q** as the starting material. Yield: 53%. Hexanes/ethyl acetate = 8:1, R_f = 0.40. $[\alpha]_D^{20}$ = (–)-74.4 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 7.21 (d, *J* = 5.1 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 5.70 (s, 1H), 5.20 (s, 2H), 4.10 (d, *J* = 13.5 Hz, 1H), 2.95 (t, *J* = 13.1 Hz, 1H), 2.19 (d, *J* = 14.0 Hz, 1H), 1.93 (ddd, *J* = 13.7, 11.5, 5.6 Hz, 1H), 1.68 – 1.49 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.68, 144.85, 136.93, 128.61, 128.09, 127.98, 127.04, 124.68, 124.48, 67.42, 51.22, 40.32, 29.85, 25.44, 19.63.

IR (neat, cm^{-1}): 2935.71, 2854.39, 1698.10, 1418.89, 1319.37, 1259.04, 1231.40, 1109.45, 1028.21. HPLC analysis: ee = 92%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 15.12 min, t_{minor} =16.64 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{20}NO_2S^+$: 302.12093, Found: 302.12113.

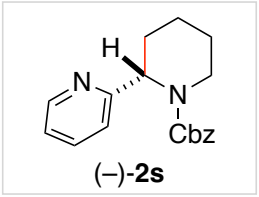
Benzyl (*S*)-2-(thiophen-3-yl)piperidine-1-carboxylate (2r) Following general procedure



(–)-**2r**

using **1r** as the starting material. Yield: 77%. Hexanes/ethyl acetate = 8:1, R_f = 0.38. $[\alpha]_D^{20}$ = (–)-100.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.17 (m, 6H), 6.97 (s, 1H), 6.89 (d, *J* = 5.0 Hz, 1H), 5.50 (s, 1H), 5.18 (s, 2H), 4.09 (d, *J* = 13.5 Hz, 1H), 2.82 (t, *J* = 12.8 Hz, 1H), 2.20 (d, *J* = 13.9 Hz, 1H), 1.90 – 1.86 (m, 1H), 1.67 – 1.48 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.84, 141.77, 137.04, 128.61, 128.07, 127.93, 127.04, 126.07, 121.11, 67.29, 51.42, 40.47, 28.90, 25.64, 19.67. IR (neat, cm^{-1}): 2938.86, 2861.25, 1693.38, 1421.95, 1258.51, 1113.00, 1036.04. HPLC analysis: ee = 93%. IF(95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 17.85 min, t_{minor} = 19.78 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{20}NO_2S^+$: 302.12093, Found: 302.12179.

Benzyl (*S*)-2-(pyridin-2-yl)piperidine-1-carboxylate (2s) Following general procedure

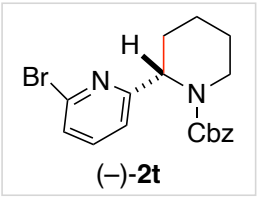


(–)-**2s**

using **1s** as the starting material. Yield: 87%. Hexanes/ethyl acetate = 3:1, R_f = 0.33. $[\alpha]_D^{20}$ = (–)-96.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.3 Hz, 1H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 – 7.09 (m, 7H), 5.50 (s, 1H), 5.18 (s, 2H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.68 – 2.61 (m, 1H), 1.89 – 1.82 (m, 1H), 1.65 – 1.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.06, 156.48, 149.31, 137.01, 136.64, 128.55, 128.00, 127.86, 121.62, 121.30, 67.29, 55.81, 41.28, 27.82, 25.42, 19.75. IR (neat, cm^{-1}): 2937.24, 1694.15,

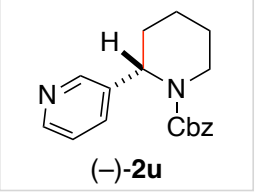
1588.09, 1419.97, 1257.74, 1166.21, 1118.83, 1035.88. HPLC analysis: ee = 92%. IC(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 25.81 min, t_{minor} = 15.35 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}N_2O_2^+$: 297.15975, Found: 297.15999.

Benzyl (*S*)-2-(6-bromopyridin-2-yl)piperidine-1-carboxylate (2t) Following general procedure using **1t** as the starting material. Yield: 72%. Hexanes/ethyl acetate = 5:1, R_f = 0.43. $[\alpha]_D^{20}$ = (–)-80.6° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.24 (m, 6H), 7.10 (d, *J* = 7.7 Hz, 1H), 5.46 (s, 1H), 5.17 (s, 2H), 4.18 (d, *J* = 12.3 Hz, 1H), 2.96 (t, *J* = 13.2 Hz, 1H), 2.59 (d, *J* = 12.8 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.66 – 1.34 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.97, 156.34, 141.83, 138.92, 136.87, 128.60, 128.09, 127.89, 126.03, 120.14, 67.39, 55.51, 41.27, 27.85, 25.26, 19.65. IR (neat, cm^{-1}): 2938.02, 2858.74, 1695.33, 1578.24, 1553.80, 1410.23, 1260.03, 1170.74, 1112.70. HPLC analysis: ee = 96%. IA(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 7.93 min, t_{minor} = 7.46 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{20}N_2O_2Br^+$: 375.07027, Found: 375.07083.



(–)-**2t**

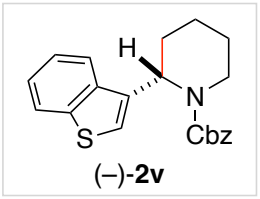
Benzyl (*S*)-2-(pyridin-3-yl)piperidine-1-carboxylate (2u) Following general procedure using **1u** as the starting material. Yield: 21%. Hexanes/ethyl acetate = 1:2, R_f = 0.32. $[\alpha]_D^{20}$ = (–)-64.5° (*c* = 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.49 (d, *J* = 4.9 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.16 (m, 6H), 5.55 (s, 1H), 5.18 (s, 2H), 4.15 (d, *J* = 13.7 Hz, 1H), 2.79 (td, *J* = 13.1, 3.5 Hz, 1H), 2.30 (d, *J* = 12.3 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.74 – 1.37 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.12, 148.47, 148.06, 136.77, 135.57, 134.74, 128.66, 128.20, 128.00, 123.60, 67.55, 52.06, 40.64, 27.90, 25.40, 19.33. IR (neat, cm^{-1}):



(–)-**2u**

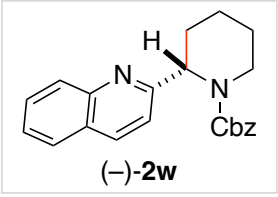
2940.19, 1694.51, 1420.58, 1259.05, 1162.90, 1115.66, 1024.29. HPLC analysis: ee = 90%. ADH(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 17.36 min, t_{minor} = 11.78 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}N_2O_2^+$: 297.15975, Found: 297.16051.

Benzyl (*S*)-2-(benzo[*b*]thiophen-3-yl)piperidine-1-carboxylate (2v) Following general procedure using **1v** as the starting material. Yield: 54%. Hexanes/ethyl acetate = 8:1, R_f = 0.32. $[\alpha]_D^{20}$ = (–)-76.6° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.16 (m, 8H), 5.82 (d, *J* = 5.9 Hz, 1H), 5.31 – 5.16 (m, 2H), 4.09 (d, *J* = 13.6 Hz, 1H), 2.92 (td, *J* = 13.7, 13.2, 3.1 Hz, 1H), 2.30 (d, *J* = 13.9 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.85 – 1.56 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.80, 140.46, 138.36, 137.02, 135.82, 128.59, 128.04, 127.90, 124.48, 124.26, 123.12, 122.80, 67.35, 50.59, 41.23, 28.40, 25.67, 20.15. IR (neat, cm^{-1}): 2937.98, 1689.81, 1419.41, 1311.05, 1249.83, 1168.72, 1026.68, 735.00. HPLC analysis: ee = 94%. ID(90% hexanes: 10% isopropanol, 0.8 mL/min): t_{major} = 21.94 min, t_{minor} = 15.66 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{22}NO_2S^+$: 352.13658, Found: 352.13679.



(–)-**2v**

Benzyl (*S*)-2-(quinolin-2-yl)piperidine-1-carboxylate (2w) Following general procedure using **1w** as the starting material. Yield: 75%. Hexanes/ethyl acetate = 5:1, R_f = 0.47. $[\alpha]_D^{20}$ = (–)-145.4° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 13.0, 8.5 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.26 (m, 6H), 5.65 (s, 1H), 5.21 (s, 2H), 4.22 (d, *J* = 13.4 Hz, 1H), 3.07 (td, *J* = 12.5, 3.8 Hz, 1H), 2.79 (d, *J* = 13.5 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.73 – 1.48 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.58, 156.61, 147.88, 137.06, 136.58, 129.59, 129.39, 128.53, 127.96, 127.80,



(–)-**2w**

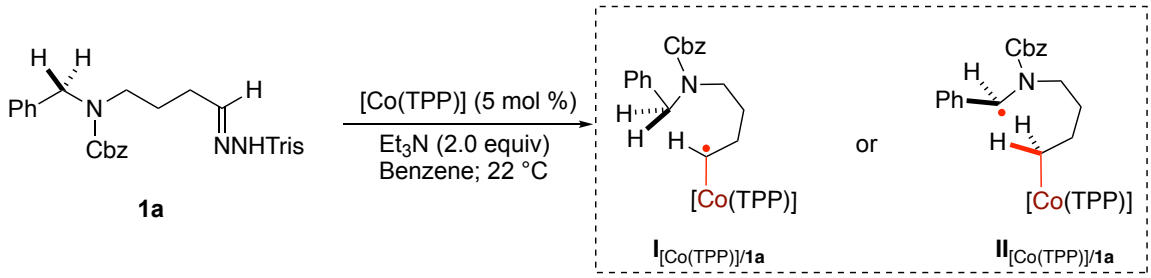
127.53, 126.95, 126.25, 119.33, 67.27, 56.37, 41.70, 27.83, 25.44, 19.82. IR (neat, cm^{-1}): 2936.71, 1693.99, 1600.17, 1502.91, 1421.97, 1253.41, 1168.25, 1120.18, 1072.11. HPLC analysis: ee = 93%. IE(80% hexanes: 20% isopropanol, 0.8 mL/min): t_{major} = 14.99 min, t_{minor} = 13.12 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{23}N_2O_2^+$: 347.17540, Found: 347.17515.

3.4.4. Mechanistic Studies of Proposed Stepwise Radical Mechanism

3.4.4.1. General Procedure of HRMS Experiment

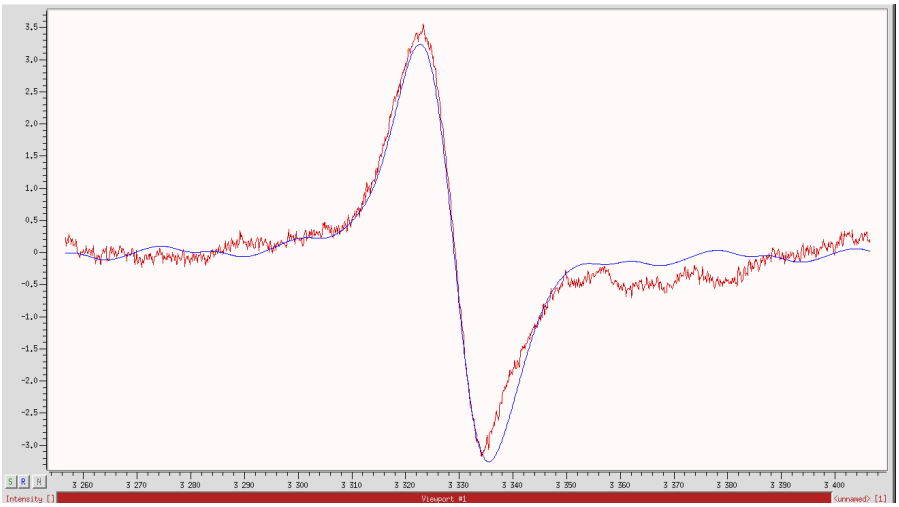
To an over-dried Schlenk tube, sulfonyl hydrazone **1a** (0.10 mmol), [Co(TPP)] (5 mol %), and Cs_2CO_3 (2.0 equiv) were added. The Schlenk tube was then evacuated and backfilled with nitrogen 3 times. The Teflon screw cap was replaced with a rubber septum, and benzene (2.0 mL) was added via a gas-tight syringe. The mixture was stirred at 22 °C for 1 h. The resulting solution was then passed through a short pad of silica gel (to get rid of base and salt) under the flow of nitrogen, and the filtrate was collected in a HPLC vial (degassed and backfilled with argon). The sample was further diluted with CH_3CN and immediately injected into HRMS instrument. The HRMS experiment was carried out in the absence of any additives such as formic acid, commonly act as electron carriers for ionization, allowing the detection of the molecular ion signals corresponding to Co(III)-alkyl radical $[C_{63}H_{49}CoN_5O_2]^+$ (m/z = 966.31720) by the loss of one electron.

3.4.4.2. General Procedure of EPR Experiment

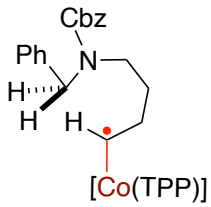


To an oven-dried Schlenk tube, sulfonyl hydrazone **1a** (0.20 mmol, 1.0 equiv) and [Co(TPP)] (5 mol %) were added. The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Et_3N (2.0 equiv) and benzene (2.0 mL) was added via a gastight syringe. The mixture was then stirred at 22 °C for 1.5 h. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for EPR experiment at room temperature (EPR settings: T = 298 K; microwave frequency: 9.37762 GHz; power: 20 mW; modulation amplitude: 1.0 G).

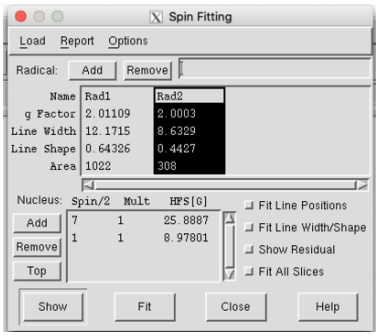
The resulting notable EPR signal (in red) has been simulated (in blue) with 23% C-centered radical at α-position $\mathbf{I}_{[Co(TPP)]/\mathbf{1a}}$: g = 2.00030, $A_{(Co)}$ = 72.5 MHz, $A_{(H)}$ = 25.1 MHz and 77% C-centered at ζ-position $\mathbf{II}_{[Co(TPP)]/\mathbf{1a}}$: g = 2.01109, $A_{(N)}$ = 4.9 MHz, $A_{(H)}$ = 7.2 MHz, which is assigned to Co(III)-supported alkyl radical intermediates. *[The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon]*



EPR Simulation Details:



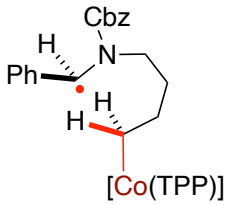
I[Co(TPP)]/**1a**



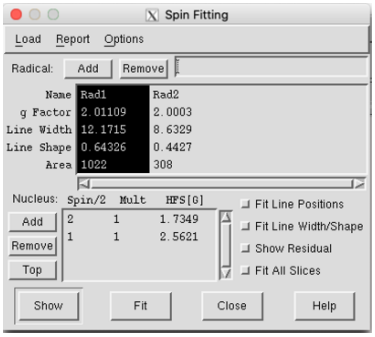
g = 2.00030

$\mathbf{A_{(Co)}}$ = 25.8887 x 2.00030 x 1.39961145 = 72.5 MHz

$\mathbf{A_{(H)}}$ = 8.97801 x 2.00030 x 1.39961145 = 25.1 MHz



II[Co(TPP)]/**1a**

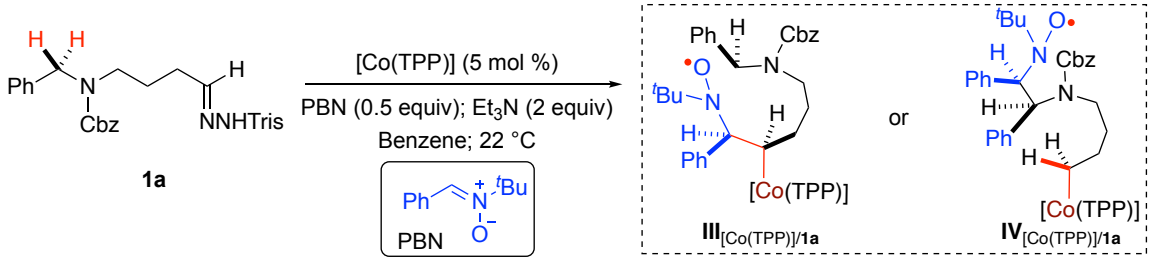


g = 2.01109

$\mathbf{A_{(N)}}$ = 1.7349 x 2.01109 x 1.39961145 = 4.9 MHz

$\mathbf{A_{(H)}}$ = 2.5621 x 2.01109 x 1.39961145 = 7.2 MHz

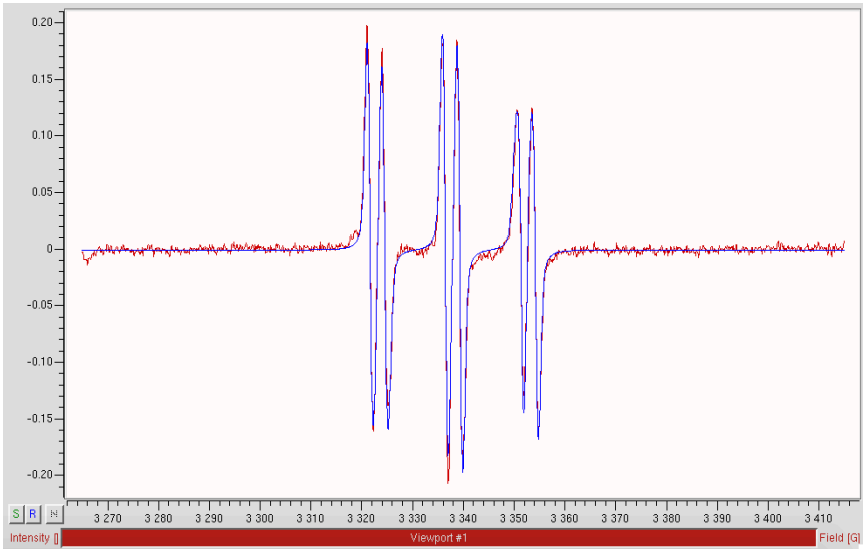
3.4.4.3. Experimental Procedure for Radical Trapping by EPR



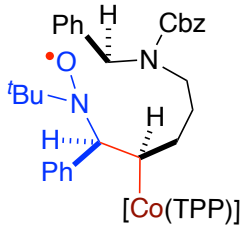
To an oven-dried Schlenk tube, sulfonyl hydrazone **1a** (0.20 mmol, 1.0 equiv), *N-tert*-butyl-α-phenylnitrone (0.5 equiv) and [Co(TPP)] (5 mol %) were added. The Schlenk tube

was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Et_3N (2.0 equiv) and benzene (2.0 mL) was added via a gastight syringe. The mixture was then stirred at 22 °C for 1.5 h. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for EPR experiment at room temperature (EPR settings: T = 298 K; microwave frequency: 9.37762 GHz; power: 20 mW; modulation amplitude: 1.0 G).

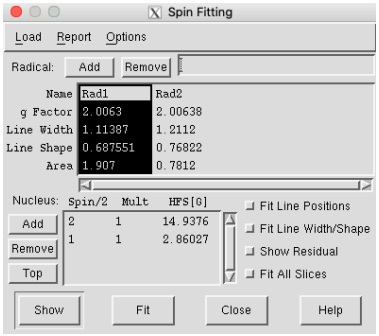
The resulting notable EPR signal (in red) has been simulated (in blue) with 71% O-centered radical $\mathbf{III}_{[Co(TPP)]/1a}$: g = 2.00630, $A_{(N)}$ = 41.9 MHz, $A_{(H)}$ = 8.0 MHz and 29% O-centered $\mathbf{IV}_{[Co(TPP)]/1a}$: g = 2.00638, $A_{(N)}$ = 40.2 MHz, $A_{(H)}$ = 8.3 MHz, which is assigned to PBN-trapped Co(III)-supported alkyl radical intermediates. *[The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon]*



EPR Simulation Details:



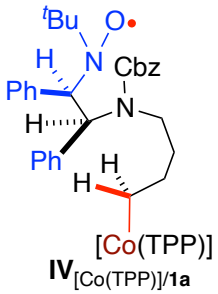
III$_{[Co(TPP)]/\mathbf{1a}}$



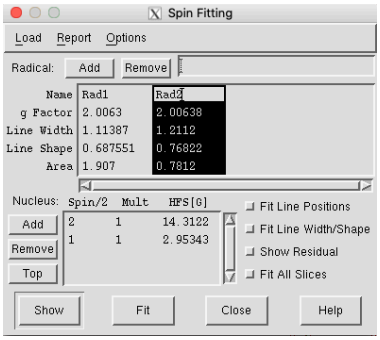
g = 2.00630

$\mathbf{A_{(N)}}$ = 14.93760 x 2.00630 x 1.39961145 = 41.9 MHz

$\mathbf{A_{(H)}}$ = 2.86027 x 2.00630 x 1.39961145 = 8.0 MHz



IV$_{[Co(TPP)]/\mathbf{1a}}$



g = 2.00638

$\mathbf{A_{(N)}}$ = 14.31220 x 2.00638 x 1.39961145 = 40.2 MHz

$\mathbf{A_{(H)}}$ = 2.95343 x 2.00638 x 1.39961145 = 8.3 MHz

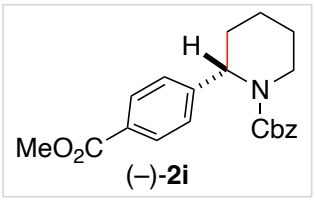
3.4.5. X-Ray Crystallography

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [26] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[27] Absorption correction was performed by multi-scan method implemented in

[26] Bruker (**2012**). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
[27] Bruker (**2012**). SAINT. Data Reduction Software.

SADABS.[28] Space groups were determined using XPREP implemented in APEX2.[18] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[29,30,31] program.

[28] Sheldrick, G. M. (**1996**). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
[29] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837–838.
[30] Sheldrick, G. M. (**2012** Beta) SHELXL-97. Program for the Refinement of Crystal.
[31] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467–473.



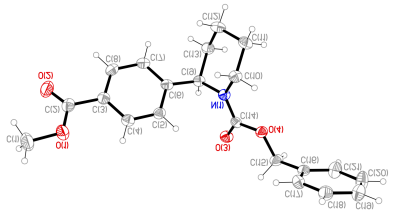


Table S1. Crystal data and structure refinement for (–)-2i

Identification code	C21H23NO4	
Empirical formula	C21 H23 N O4	
Formula weight	353.40	
Temperature	173(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1219(3) ≈	α= 90∞.
	b = 11.7799(6) ≈	β= 90∞.
	c = 24.8215(12) ≈	γ = 90∞.
Volume	1790.01(15) $≈^3$	
Z	4	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.736 mm^{-1}	
F(000)	752	
Crystal size	0.240 x 0.180 x 0.080 mm^3	
Theta range for data collection	3.561 to 66.611∞.	
Index ranges	-7<=h<=7, -13<=k<=13, -28<=l<=29	
Reflections collected	17941	
Independent reflections	3116 [R(int) = 0.0233]	
Completeness to theta = 66.611∞	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.7076	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3116 / 0 / 236	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0667	
R indices (all data)	R1 = 0.0287, wR2 = 0.0680	
Absolute structure parameter	-0.04(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.097 and -0.155 e.$≈^{-3}$	

3.4.6. DFT Calculations

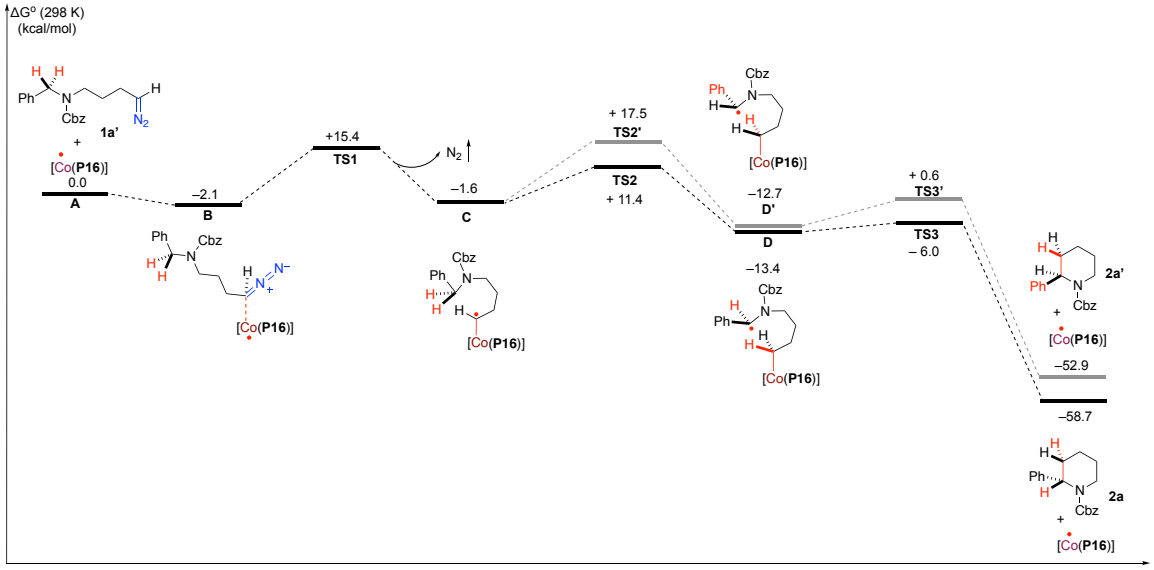
Considering the cost of time and computing resources for the large system with [Co(**P6**)], the geometry optimizations were performed with the Gaussian 16 at the BP86/lanl2dz level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy and thermal corrections (entropy and enthalpy, 298.15 K, 1 Atm) were obtained from these calculations. To further improve the accuracy of energies, single point energies were carried out at the B3LYP/def2-tzvplevel of theory along with Grimme's dispersion correction(D3BJ) and SMD solvation model (in toluene).

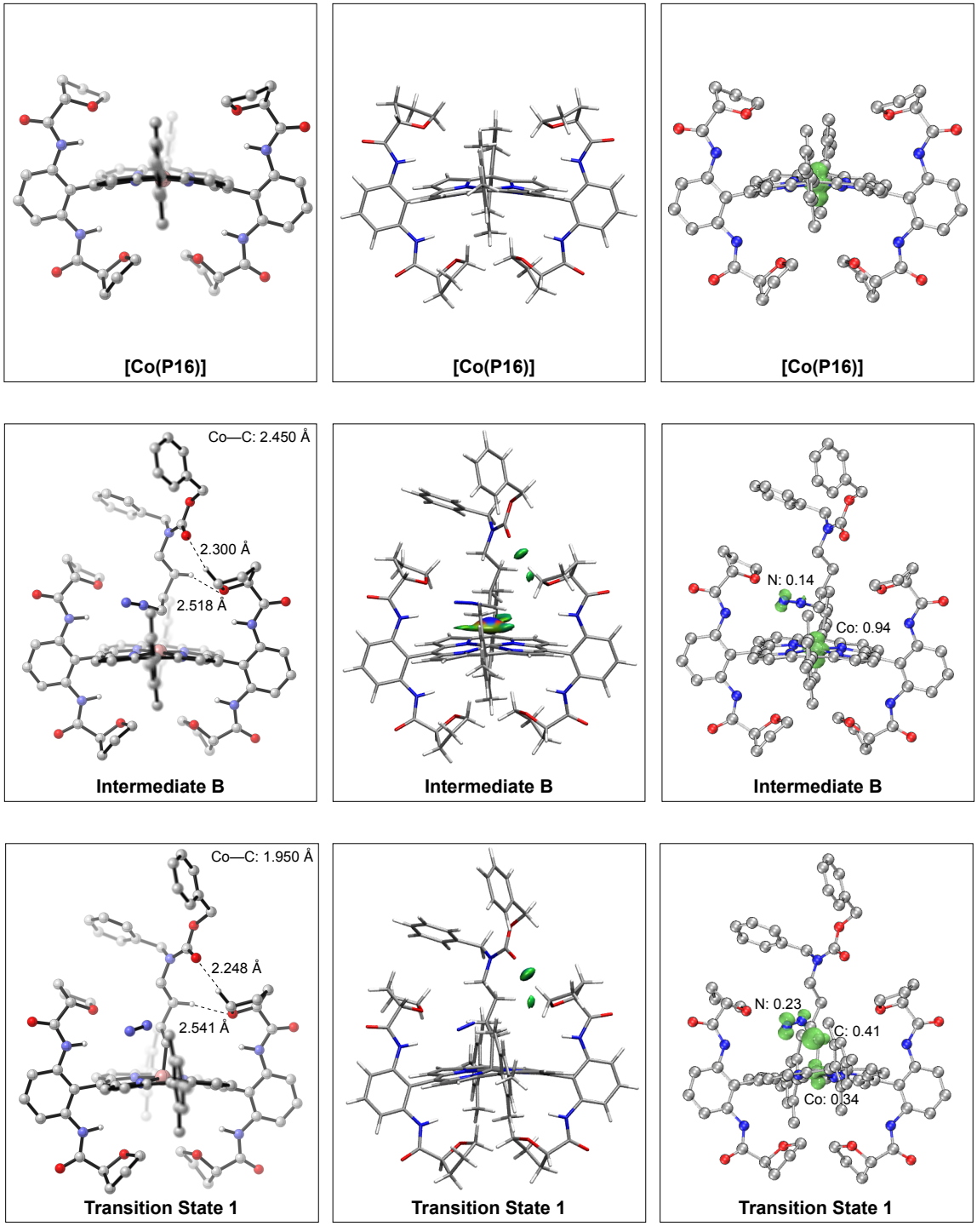
Independent Gradient Model (IGM)[32] analysis was performed with Multiwfn[33] software package using high quality grid option to generate files for further plotting. The visualization of IGM analysis results were presented with VMD[34] visualization software. As shown in Scheme S2, the 3D diagrams of optimized structures were generated with CYLview software. [35] The NCI (noncovalent interaction) visual representations of optimized structures were generated with VMD and rendered with Tachyon.[36]

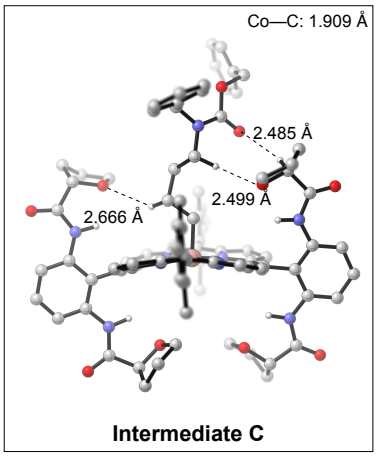
[32] Lefebvre, C.; Rubez, G.; Khartabil, H.; Boisson, J.-C.; Contreras-García, J.; Hénon, E. *Phys. Chem. Chem. Phys.* **2017**, *19*, 17928–17936.
[33] Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580–592.
[34] Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graph.* **1996**, *14*, 33–38.
[35] Legault, C. Y. CYLview, 1.0b (Université de Sherbrooke, Québec, Montreal, Canada, **2009**.
[36] Stone, J. E. Master's Thesis, University of Missouri, **1998**.

Scheme S1. Calculated Energy Diagram for [Co(P16)]-Catalyzed Radical 1,6-C–H Alkylation

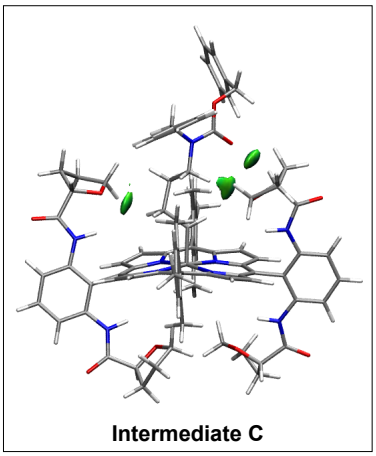


Scheme S2. Optimized Structure Models, NCI Visual Representation and Spin Density Representation of Intermediates and Transition States

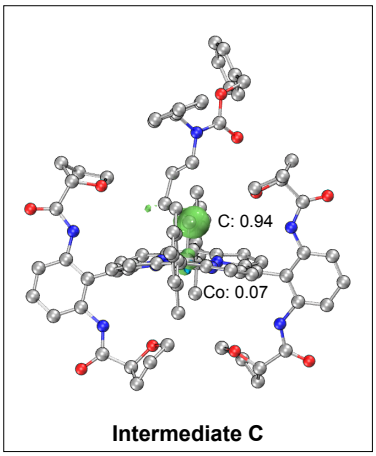




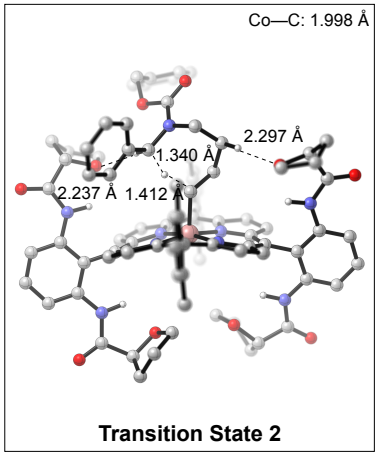
Intermediate C



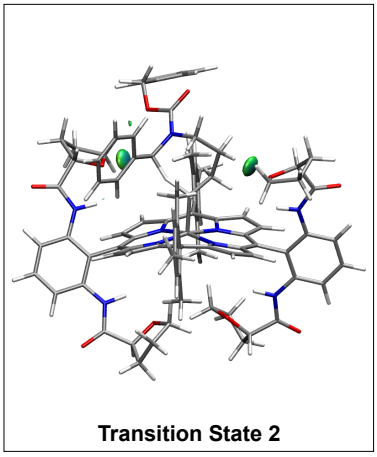
Intermediate C



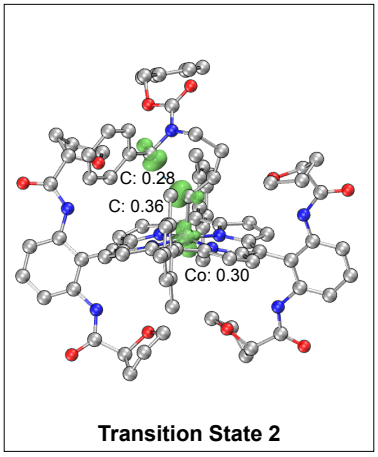
Intermediate C



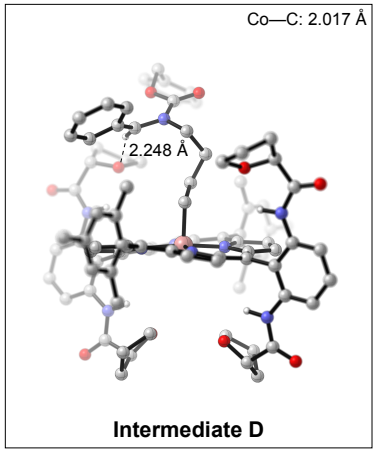
Transition State 2



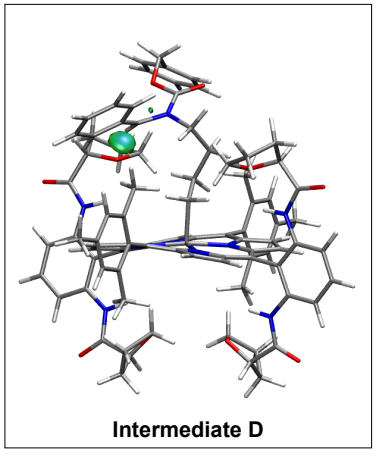
Transition State 2



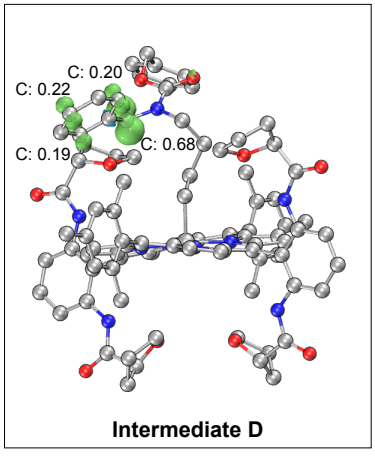
Transition State 2



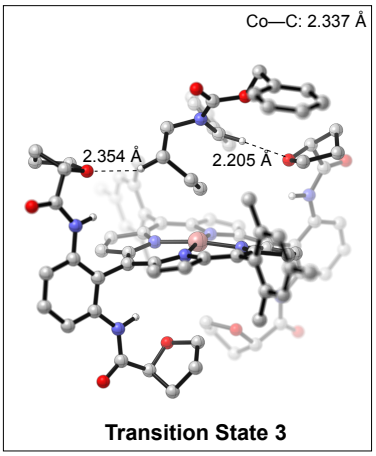
Intermediate D



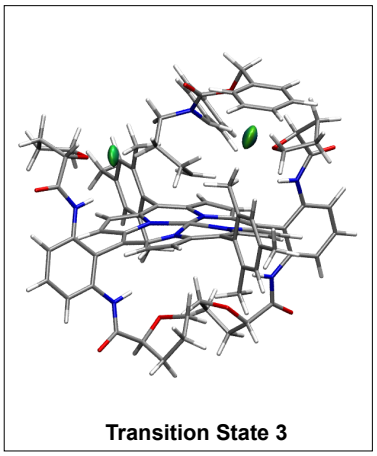
Intermediate D



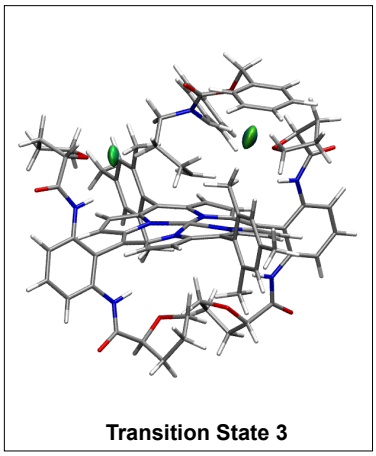
Intermediate D



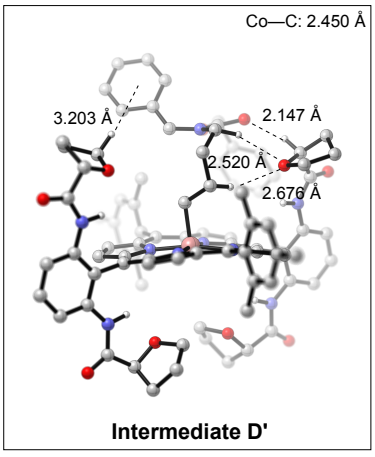
Transition State 3



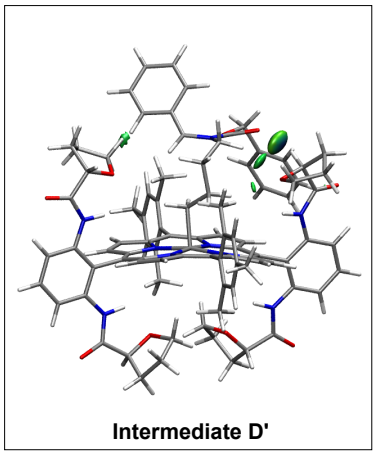
Transition State 3



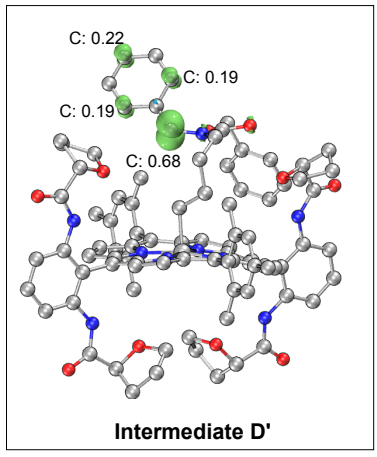
Transition State 3



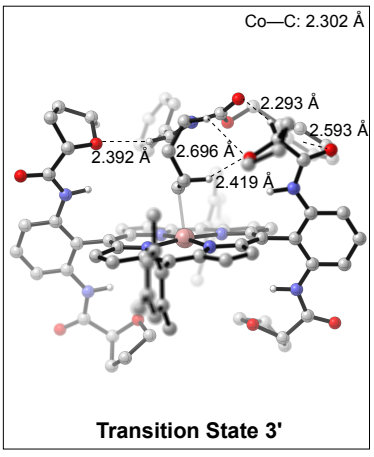
Intermediate D'



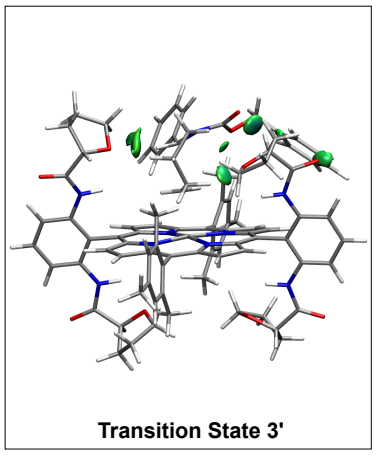
Intermediate D'



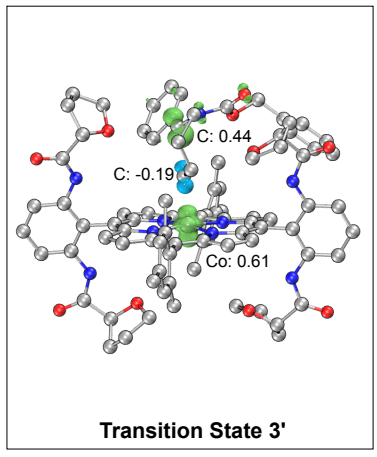
Intermediate D'



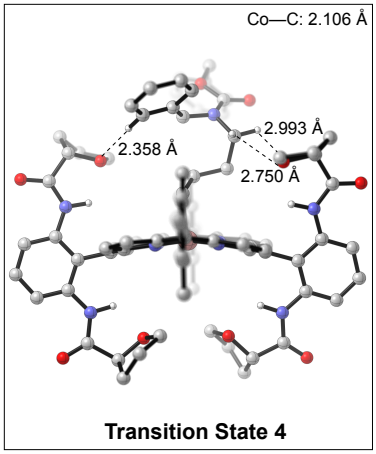
Transition State 3'



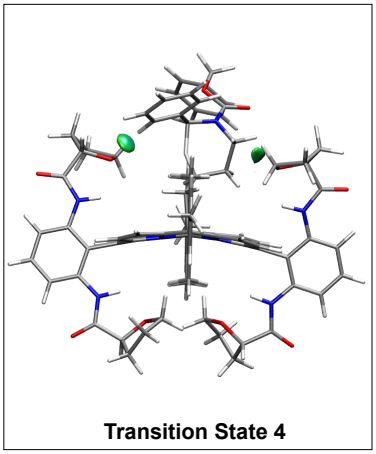
Transition State 3'



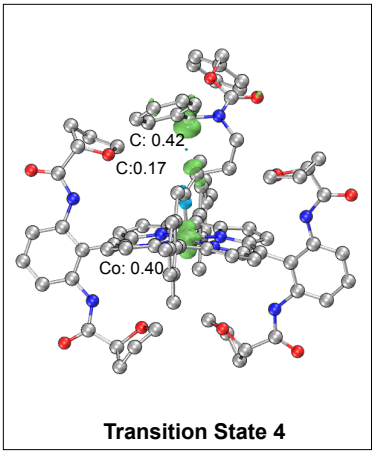
Transition State 3'



Transition State 4



Transition State 4



Transition State 4

Intermediate A

$A_{[Co(II)(P16)]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.102584 Hartree
H_corr: 1.310561 Hartree
SCF: -5133.04 Hartree
S: 437.725 Cal/Mol-Kelvin
H: -5131.726235 Hartree
G: -5131.934212 Hartree

Cartesian Coordinates:

C	-1.38634100	-2.70086500	-0.39155300
C	-2.71235900	-3.30415000	-0.36413600
H	-2.90734000	-4.36309800	-0.52992200
C	-3.60934400	-2.30067000	-0.05657400
H	-4.68882800	-2.36850100	0.07376700
C	-2.84531800	-1.06457400	0.04884000
C	-3.43544200	0.19789200	0.25710400
C	-2.69420900	1.38873500	0.12507000
C	-3.30160800	2.71310700	0.10422900
H	-4.36128200	2.90586700	0.26746000
C	-2.29768300	3.61184000	-0.19450900
H	-2.36628200	4.69235100	-0.31498600
C	-1.06029700	2.85169200	-0.30789300
C	0.27707800	4.92940500	-0.77483500
C	0.17529500	5.40975200	-2.11531200
C	0.25242000	6.80633700	-2.35606300
C	0.42256100	7.73826500	-1.30332100
C	0.51403200	7.23835000	0.02151500
C	0.44395000	5.85219800	0.30486900
C	-4.90669100	0.28320000	0.57634400
C	-5.33489600	0.32142400	1.93985600
C	-6.71541300	0.41770700	2.26451600
H	-7.01390000	0.45223700	3.31443500
C	-7.66048900	0.46996400	1.21799100
H	-8.72591500	0.54270800	1.46524600
C	-7.27279500	0.43201300	-0.13836900
H	-8.00394700	0.47344300	-0.94837200
C	-5.89017300	0.34149800	-0.45819800
C	0.19870900	3.44687400	-0.50925800
Co	-0.00000600	0.00003400	-0.13395800
N	-1.47241900	-1.31067000	-0.15865700
N	-1.30604700	1.47568000	-0.11023900
C	1.38630600	2.70110300	-0.39008500
C	2.71232900	3.30435600	-0.36248500

H	2.90729600	4.36339200	-0.52772200
C	3.60934500	2.30069500	-0.05559700
H	4.68884600	2.36843700	0.07464100
C	2.84532200	1.06455000	0.04921700
C	3.43547500	-0.19803200	0.25668900
C	2.69421900	-1.38880100	0.12411500
C	3.30161300	-2.71316700	0.10252000
H	4.36130500	-2.90600800	0.26553600
C	2.29765700	-3.61174200	-0.19658000
H	2.36623800	-4.69218700	-0.31765400
C	1.06025700	-2.85153100	-0.30943500
C	-0.27717700	-4.92897800	-0.77746800
C	-0.17592600	-5.40859700	-2.11824800
C	-0.25307400	-6.80504900	-2.35971500
C	-0.42281700	-7.73755200	-1.30740600
C	-0.51383600	-7.23835300	0.01772300
C	-0.44366300	-5.85234600	0.30179500
C	4.90678100	-0.28353000	0.57560500
C	5.33523700	-0.32267500	1.93901100
C	6.71581500	-0.41916900	2.26335300
H	7.01449300	-0.45440800	3.31319300
C	7.66069700	-0.47072400	1.21661800
H	8.72616800	-0.54364300	1.46363000
C	7.27275200	-0.43186500	-0.13964500
H	8.00375500	-0.47275000	-0.94981000
C	5.89007100	-0.34113200	-0.45915800
C	-0.19875400	-3.44658800	-0.51111600
N	1.47240400	1.31076600	-0.15797200
N	1.30603000	-1.47562300	-0.11109000
N	5.42822500	-0.31067200	-1.80342500
C	6.15863500	-0.33297300	-2.97804700
H	4.40886100	-0.26996200	-1.97148500
O	7.42416400	-0.37891100	-3.08450400
C	5.26515100	-0.32101800	-4.24869300
O	3.83040700	-0.14057900	-3.88013200
C	5.61548000	0.84646900	-5.20598100
H	5.36560100	-1.30812700	-4.73627800
C	3.37623400	1.20716200	-4.36089000
C	4.66389500	1.97853800	-4.72718500
H	5.38534700	0.56108300	-6.24875900
H	6.68354900	1.10854100	-5.13732000
H	2.79533900	1.66667000	-3.54303200
H	2.72230900	1.05025400	-5.24040800
H	4.48619100	2.73996300	-5.50600600
H	5.08263500	2.48250100	-3.83717400
N	-5.42858300	0.31196600	-1.80257200

C -6.15922700 0.33517500 -2.97702900
H -4.40925000 0.27138800 -1.97085900
O -7.42478000 0.38120600 -3.08319500
C -5.26601600 0.32422900 -4.24786900
O -3.83119100 0.14364500 -3.87972700
C -5.61645900 -0.84258200 -5.20596500
H -5.36668600 1.31168500 -4.73470900
C -3.37687300 -1.20351800 -4.36195800
C -4.66450900 -1.97485700 -4.72839200
H -5.38672500 -0.55633400 -6.24859500
H -6.68445900 -1.10488800 -5.13715700
H -2.79547800 -1.66361200 -3.54479100
H -2.72339400 -1.04563200 -5.24163600
H -4.48694200 -2.73564500 -5.50786700
H -5.08283300 -2.47958500 -3.83861900
N -4.32772800 0.26007900 2.94095400
C -4.44870300 0.36867100 4.31462100
H -3.34767700 0.12448900 2.64125400
O -5.52361200 0.53093300 4.97240000
C -3.08403800 0.25428600 5.05096400
O -1.95872600 0.16011200 4.07842800
C -2.78359000 1.49581600 5.92643600
H -3.09798400 -0.68256800 5.63725500
C -1.21192700 1.47328800 4.07046500
C -2.05271800 2.44293300 4.93308100
H -2.11475800 1.21338000 6.75992400
H -3.70976700 1.92416800 6.34249200
H -1.11514600 1.78713900 3.01652700
H -0.20658900 1.28022800 4.48549600
H -1.42291200 3.18779100 5.44931100
H -2.78924200 2.98390800 4.31142000
N 4.32823400 -0.26204100 2.94031800
C 4.44942800 -0.37162300 4.31388300
H 3.34812500 -0.12634000 2.64086400
O 5.52445100 -0.53427400 4.97138800
C 3.08486400 -0.25792400 5.05051400
O 1.95939600 -0.16329100 4.07820100
C 2.78475300 -1.50010100 5.92518300
H 3.09874200 0.67853500 5.63743600
C 1.21287200 -1.47659500 4.06940800
C 2.05394000 -2.44667800 4.93127400
H 2.11598000 -1.21835700 6.75895200
H 3.71106800 -1.92855600 6.34082600
H 1.11602600 -1.78975000 3.01526800
H 0.20753600 -1.28403800 4.48467100
H 1.42432100 -3.19199900 5.44706400

H	2.79048900	-2.98709500	4.30916000
H	0.17570200	7.17098600	-3.38899600
H	0.64134700	7.94363800	0.85398000
C	-0.01966800	4.44861800	-3.28054100
H	0.77141100	3.67507700	-3.30414000
H	-0.00431800	4.98646300	-4.24463900
H	-0.98453800	3.91152600	-3.20505200
C	0.53643200	5.36660800	1.74544600
H	-0.36468000	4.79235900	2.03446900
H	0.63856800	6.21611100	2.44313300
H	1.40369000	4.69556800	1.89409200
C	0.50441700	9.23342300	-1.57837400
H	0.39868500	9.45294500	-2.65529900
H	1.47290500	9.65124400	-1.24202400
H	-0.29114400	9.78486100	-1.04140400
H	-0.17669300	-7.16916000	-3.39286300
H	-0.64086500	-7.94407700	0.84986100
C	-0.50473900	-9.23255800	-1.58326100
H	-0.39918500	-9.45149000	-2.66032300
H	-1.47318500	-9.65054400	-1.24698900
H	0.29089200	-9.78430900	-1.04671800
C	-0.53574700	-5.36752100	1.74265400
H	0.36560500	-4.79374800	2.03187100
H	-0.63808500	-6.21737000	2.43988900
H	-1.40274800	-4.69625200	1.89178600
C	0.01838500	-4.44678700	-3.28302600
H	-0.77410100	-3.67468000	-3.30708400
H	0.00476700	-4.98437000	-4.24729500
H	0.98220500	-3.90797500	-3.20656100

A_{1a}'
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.298852 Hartree
H_corr: 0.384763 Hartree
SCF: -1051.816529 Hartree
S: 180.814 Cal/Mol-Kelvin
H: -1051.431766 Hartree
G: -1051.517677 Hartree

Cartesian Coordinates:

H	0.08349900	0.96633200	0.12942600
H	0.65846800	2.44208800	-1.83092100
C	-0.69197800	1.21126400	-0.61876100
C	-0.32147400	2.54786900	-1.32566600
C	-0.27813000	3.73422800	-0.37229000

N	0.86026800	4.27074200	0.01753600
N	1.89570000	4.75796700	0.35638800
H	-1.65268500	1.32348100	-0.08226400
H	-1.06722900	2.76410400	-2.11890300
H	-1.18659800	4.14376600	0.07870300
C	-0.79575600	0.04438000	-1.63611300
N	-1.14248400	-1.25871400	-1.01574400
H	-1.58190400	0.26890100	-2.38370700
H	0.16529800	-0.06210700	-2.17111600
C	-2.54926300	-1.74083700	-1.06342700
C	-3.50920300	-0.95216700	-0.17134100
H	-2.52095100	-2.79954200	-0.74991600
H	-2.89126300	-1.69813700	-2.11615400
C	-4.54092300	-0.15938100	-0.73490400
C	-5.43311700	0.56324500	0.09545700
C	-5.29951400	0.49765700	1.50246900
C	-3.38573800	-1.01715200	1.24326900
C	-4.27312700	-0.29662400	2.07407400
H	-2.59712800	-1.63960100	1.68410600
H	-4.17199400	-0.35764000	3.16419100
H	-5.98972100	1.05365200	2.14794700
H	-6.22848700	1.17052000	-0.35289900
H	-4.65248500	-0.11121900	-1.82659600
C	-0.20837400	-2.03645700	-0.35711400
O	1.07840900	-1.45476400	-0.43327200
O	-0.44245600	-3.12914900	0.23700800
C	2.16755000	-2.26031500	0.22025700
C	3.38379900	-1.36873200	0.33477900
H	1.78830400	-2.60238700	1.20018400
H	2.36165400	-3.14851900	-0.40758900
C	3.40397900	-0.29541700	1.26544000
C	4.53855900	0.53988100	1.37423400
C	5.67402100	0.30496000	0.55893600
C	4.52336500	-1.59503400	-0.47876800
C	5.66536300	-0.76579500	-0.36638600
H	2.52682600	-0.11382600	1.89903800
H	4.54096500	1.36941100	2.09066900
H	6.55555700	0.95100500	0.64525800
H	6.54124200	-0.95237000	-0.99871000
H	4.51638100	-2.42001900	-1.20276300

Intermediate B

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.429333 Hartree
H_corr: 1.698588 Hartree

SCF: -6184.884607 Hartree
S: 566.694 Cal/Mol-Kelvin
H: -6183.186019 Hartree
G: -6183.455274 Hartree

Cartesian Coordinates:

H	11.19246000	-0.63280200	3.72759300
H	12.15235500	-1.28491400	1.49723300
C	10.54899300	-1.08562900	2.96394700
C	11.08963600	-1.45287400	1.70760100
H	8.75535500	-1.02813600	4.20526100
C	9.17564200	-1.30870100	3.23231100
C	10.25840900	-2.04052200	0.72512600
C	8.34608500	-1.89817300	2.25048600
H	10.67886000	-2.32352400	-0.24866300
C	8.88116900	-2.26672100	0.98605600
H	7.28087100	-2.06754900	2.44772400
O	1.37036400	-7.17235600	-2.01647800
H	3.52162400	-6.94571900	-0.56320600
C	7.99194600	-2.89552500	-0.06870900
H	2.96966500	-4.84814300	-2.28680500
C	3.55637700	-5.85635500	-0.40034100
H	4.57721500	-5.49144700	-0.61371700
C	1.26806600	-5.98356200	-1.57897500
N	1.70543100	1.27731000	1.93274300
C	2.53711900	-5.12732200	-1.30805300
H	8.57495000	-3.45009300	-0.82168200
O	7.28839300	-1.84826500	-0.89362400
N	1.45108200	0.53610200	1.04819800
N	0.09551700	-5.29825700	-1.31940300
C	-1.25125600	-5.73086700	-1.45808100
H	3.21785000	-0.39899800	-2.72813000
C	3.11181000	-5.42582600	1.02512400
O	2.18032100	-3.86409900	-0.59706300
H	2.25891600	-6.04279600	1.36294300
C	6.01182500	-1.46233500	-0.42476200
H	3.92452300	-5.52005500	1.76542800
H	2.95060700	-1.62724100	-1.45779700
O	5.44455700	-2.01317000	0.56713300
C	2.99730400	-0.53786300	-1.64888400
C	1.03133400	-0.22180800	0.02094600
C	2.68808600	-3.95395700	0.82481300
H	0.26385000	-4.34479400	-0.95856900
H	3.54030000	-3.25688500	0.91223900
C	-2.27480200	-4.77676700	-1.17443700
H	-1.82005200	-5.09599100	1.45992500

C 1.60457500 0.09852400 -1.36446500
N 5.47961500 -0.43412100 -1.17223600
H 0.88342000 -1.27681600 0.28774600
C 4.13721800 0.08901100 -0.80582400
H 0.87831400 -0.29404500 -2.09478500
H -2.22091800 -3.71611800 -3.61839300
C -1.67453000 -4.02722300 1.61344700
H 1.85850100 -3.64322700 1.48453700
H 3.98300700 -0.12464700 0.26480800
C -1.93832800 -3.35468800 -0.80136700
H 1.64213200 1.19637200 -1.49676700
C 6.15535400 0.13876800 -2.36179100
H -1.32059700 -3.75183100 3.79683000
C -2.03204000 -2.71375600 -3.23601200
C -1.42214200 -3.35063000 2.78912700
H 4.15599100 1.18870500 -0.93411100
C -1.72023900 -3.03020300 0.55121300
H 2.35335000 -1.32048600 5.28318500
H 7.01540500 -0.51038500 -2.59416200
C -1.88065800 -2.38741900 -1.82392900
H -1.27515400 -3.37863700 9.32435400
C -1.87980400 -1.53736500 -3.94022300
H 1.28535600 -1.86197100 7.30337900
H -1.92669200 -1.37913900 -5.01709500
H 0.32702300 -2.58977800 9.39529600
C 1.44819100 -1.12280600 4.68278600
C 0.28852600 -1.78372200 6.84945000
C -1.34909900 -1.93289700 2.46000200
C -0.72829500 -2.44173100 9.10599300
N -1.51161200 -1.73493900 1.07023900
C 6.63007200 1.58225700 -2.16867500
C 0.18606100 -1.41107500 5.48361700
H 1.50043900 -1.74749000 3.77049800
C -0.85531500 -2.05430000 7.63914900
N -1.64877300 -1.00515100 -1.65068900
H 5.85792800 2.26557300 -4.09066300
H 7.52360500 1.22075000 -0.21391500
H 1.48511900 -0.06751300 4.35132300
H 0.95201700 -0.20339200 -4.68491100
C -1.65397000 -0.47942400 -2.96476900
C -1.10596800 -1.31062400 4.88534900
C 6.40856900 2.54845500 -3.18318900
C 7.34594900 1.96143700 -1.00260800
C -2.12952600 -1.94565700 7.02476800
C -1.23954000 -0.92201200 3.43299800
C -2.27536200 -1.57855300 5.66443500

H	-1.15016100	-1.65787200	9.76489600
H	-4.44474600	-1.70744200	5.80060400
H	-3.03114100	-2.15082100	7.61780600
C	0.95036600	0.85950100	-4.99540300
Co	-1.40988500	-0.02036700	0.06304600
H	1.19578000	1.45710700	-4.09759600
C	-3.66646000	-1.46902800	5.05461700
C	-0.39757200	1.26153600	-5.57828200
C	-1.51814900	0.87615900	-3.31699500
C	-0.48569900	1.63493500	-6.94485200
H	0.42730500	1.63199000	-7.55517200
H	-2.40951900	1.67505800	-9.58276400
C	-1.57712300	1.26546900	-4.77522900
H	-3.79068200	-2.15738700	4.19727900
C	6.90166800	3.86906800	-3.04409500
C	7.83298200	3.28064400	-0.85764200
H	-4.69493400	-0.66409000	-1.62670000
H	-4.30957800	0.63610100	-4.10269600
C	-1.71495000	2.00717600	-7.54063400
C	-1.33259300	0.43957800	3.09251200
H	1.75810900	0.99811300	-5.73555500
H	-0.79422600	2.42818200	-9.47564000
C	-2.83075400	1.63563000	-5.35856500
C	-1.79504900	2.39667300	-9.01013500
C	-2.87681000	1.99955700	-6.72676300
C	-4.11102100	1.63578900	-4.53426200
N	-1.44145500	0.96773700	1.78588800
C	7.61508700	4.23913100	-1.87904100
H	6.73329800	4.60279100	-3.84157600
H	8.38846100	3.55988700	0.04543900
H	-4.04909500	2.34279400	-3.68548600
H	-3.85782100	-0.44733100	4.67389500
C	-1.44046300	1.88541400	-2.33901400
H	-3.84260400	2.28250400	-7.16699700
N	-1.46421100	1.69401800	-0.93911500
H	-4.42807500	0.85077200	2.11214500
H	-6.60540200	1.00873100	3.89307600
C	-1.37097500	1.50701200	4.08321300
H	-6.05788600	0.26720200	1.61740800
H	-1.30030200	1.34802500	5.15855500
C	-5.48669800	1.13669000	1.99114900
H	1.80140400	4.08337900	-2.10078400
H	-2.26034800	3.39259900	-9.13805600
H	3.48174200	3.41948700	-1.97195600
H	8.00045400	5.25960900	-1.76886400
C	-6.11828000	1.76519400	3.25395400

H	-4.97938400	1.92026500	-5.15393800
C	-1.53691100	2.36160000	1.97650300
C	2.75847700	4.14503900	-1.55310400
C	-1.44379000	3.30640100	-2.66352700
C	-1.52712600	2.99809900	-0.40575000
H	-5.35285600	2.28805400	3.85598000
C	-1.51283500	2.69330200	3.39572300
H	-1.42659600	3.70353300	-3.67789700
O	2.49462700	3.73847100	-0.12765400
C	-1.60116200	3.33372000	0.95929700
O	-5.53869200	2.20859100	0.93109200
H	4.07515000	5.74865300	-2.31126200
C	-1.51754100	3.99438200	-1.46994400
H	-8.06061000	2.27671000	2.35136700
C	3.35244700	5.57204700	-1.49667800
C	-7.13259300	2.78741100	2.66767800
H	-3.98275800	3.45485900	1.07811100
H	0.66151500	4.20018200	0.70626000
H	-1.57417400	3.70584900	3.79226400
H	2.55520300	6.33465300	-1.56453900
C	-6.38339200	3.33319100	1.42579500
H	5.00338300	5.11359400	-0.11499300
H	-7.39380000	3.59963700	3.36514700
C	3.02841300	4.80841500	0.76883300
C	4.02073500	5.61774600	-0.09403600
N	-4.17357900	4.39061500	1.47424000
C	-1.77304000	4.77567200	1.36473200
H	-1.57205100	5.07006900	-1.30483800
N	0.62887300	5.12303000	1.16680200
C	-5.51250900	4.57559500	1.76613000
H	3.51095300	4.30068800	1.62326600
H	-7.07195400	3.62063800	0.61041200
C	-3.07895300	5.27838600	1.65825600
C	1.87656300	5.70241400	1.31312500
C	-0.64882000	5.64291500	1.51581000
H	4.14096200	6.64046600	0.29798400
O	-6.04679300	5.62185900	2.25089300
O	2.12536000	6.83162800	1.84045100
C	-3.25650800	6.61162700	2.11788100
C	-0.81953500	6.97399900	1.98586600
H	-4.26435300	6.96711400	2.34284400
C	-2.12086700	7.43350800	2.28156500
H	0.05888700	7.60888100	2.11791000
H	-2.25338100	8.45906600	2.64533500
H	5.45960100	0.09186600	-3.22325700
H	7.21791900	-3.54158600	0.38012900

C	-3.64271600	-5.17838800	-1.28034000
C	-3.98106600	-6.50027200	-1.67906600
H	-5.03408700	-6.77792400	-1.76121800
C	-2.94395500	-7.41397600	-1.96488600
H	-3.20252400	-8.43288900	-2.27570600
C	-1.58334700	-7.05402900	-1.85851400
H	-0.78044700	-7.76015500	-2.08044900
N	-4.63230500	-4.20488200	-0.97461100
C	-6.00810300	-4.28710200	-1.08786000
H	-4.32005500	-3.28543700	-0.61976300
O	-6.67893800	-5.29148700	-1.48309600
C	-6.73094600	-2.97951700	-0.65758400
O	-5.74728800	-1.92087400	-0.29137700
C	-7.59029800	-2.38340300	-1.80110000
H	-7.32851400	-3.20920100	0.24334500
C	-5.74851900	-0.86303400	-1.36600400
C	-6.58520600	-1.44570700	-2.52780400
H	-8.42805400	-1.80080400	-1.37594400
H	-8.00047900	-3.17627600	-2.44723300
H	-6.19585500	0.05172200	-0.93580700
H	-7.09175900	-0.65629400	-3.10936500
H	-5.94705400	-2.02923800	-3.21624600

Transition State TS1

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -219.5313 cm-1
G_corr: 1.426108 Hartree
H_corr: 1.696261 Hartree
SCF: -6184.853523 Hartree
S: 568.585 Cal/Mol-Kelvin
H: -6183.157262 Hartree
G: -6183.427415 Hartree

Cartesian Coordinates:

H	11.21791200	-0.77947800	3.61022400
H	12.10973200	-1.31832600	1.32199900
C	10.55375400	-1.20338500	2.84762500
C	11.05605000	-1.50697300	1.55884300
H	8.80106200	-1.22098800	4.14733000
C	9.19180700	-1.45241700	3.14939700
C	10.19811400	-2.05732000	0.57765700
C	8.33563300	-2.00461200	2.16873400
H	10.58873800	-2.29048500	-0.42144400
C	8.83224600	-2.30949100	0.87201200
H	7.27872800	-2.19335800	2.39134600

O 1.33291200 -7.27578400 -1.96226400
H 3.45376100 -7.07564500 -0.42804200
C 7.91484200 -2.90002100 -0.18119600
H 3.02066800 -5.02443400 -2.24082200
C 3.51749100 -5.98255500 -0.30268200
H 4.55525200 -5.65714700 -0.49735600
C 1.26167700 -6.07749300 -1.54573600
N 1.47054100 1.45498400 2.18478600
C 2.55003300 -5.25398500 -1.26686200
H 8.47954900 -3.40789300 -0.97983400
O 7.16652700 -1.82760800 -0.92826300
N 1.73446600 0.61023500 1.42688600
N 0.10646500 -5.35212100 -1.31130300
C -1.24962100 -5.75013200 -1.45160800
H 3.10350200 -0.34319800 -2.58898700
C 3.04530200 -5.48648200 1.09249700
O 2.20979700 -3.95898500 -0.61152700
H 2.16459600 -6.06542100 1.42686500
C 5.90067500 -1.48584800 -0.39365200
H 3.83332700 -5.57796000 1.85946300
H 2.73732800 -1.59135100 -1.36944300
O 5.38720400 -2.09070600 0.59558700
C 2.83424900 -0.49888100 -1.52253200
C 0.65892300 -0.27059100 -0.07422500
C 2.67373900 -4.01055400 0.82768400
H 0.30695500 -4.39746100 -0.96773000
H 3.54207900 -3.33436600 0.91426500
C -2.25277700 -4.77095300 -1.17872500
H -1.76502900 -5.08903400 1.45130400
C 1.45763900 0.19577600 -1.28243600
N 5.32248200 -0.43881500 -1.07677200
H 0.91540600 -1.29978300 0.25291200
C 3.98525400 0.05176500 -0.64088300
H 0.82502100 -0.01593400 -2.16695400
H -2.16767300 -3.71481700 -3.62351000
C -1.62117800 -4.01997800 1.60381700
H 1.83563000 -3.64896000 1.44904300
H 3.84505200 -0.24677400 0.40855500
C -1.88952900 -3.35425100 -0.80993700
H 1.57301800 1.29878800 -1.25766800
C 5.95586500 0.20038900 -2.25344000
H -1.28642500 -3.73687700 3.78884100
C -1.96493700 -2.71463200 -3.24282700
C -1.37912900 -3.33990300 2.77876400
H 4.00220300 1.15863200 -0.67782600
C -1.66250800 -3.02571700 0.53923900

H	2.25544500	-1.32302400	5.42842400
H	6.78688000	-0.44893400	-2.57546800
C	-1.82030800	-2.38889700	-1.83146300
H	-1.72356200	-3.22989100	9.35662400
C	-1.78013900	-1.54383600	-3.94861300
H	1.09430500	-1.82623300	7.41309500
H	-1.81047000	-1.38744100	-5.02620900
H	0.00909100	-2.78826100	9.39881800
C	1.37764100	-1.05409800	4.81514600
C	0.12025300	-1.76028000	6.91025400
C	-1.31131600	-1.92236700	2.44676900
C	-0.99695800	-2.43295000	9.11317400
N	-1.46105000	-1.72869300	1.05590300
C	6.48295800	1.61579900	-1.99330400
C	0.08185700	-1.37919700	5.54384300
H	1.45278400	-1.59083200	3.85126500
C	-1.05749600	-2.05407700	7.64002600
N	-1.57300900	-1.00865200	-1.65920100
H	5.83066300	2.37924200	-3.92997700
H	7.26983000	1.16887500	-0.01147600
H	1.44558000	0.02554700	4.58164000
H	1.11996600	-0.19794200	-4.65100500
C	-1.54580500	-0.48773200	-2.97507100
C	-1.17993900	-1.29992800	4.88039200
C	6.35405000	2.61426500	-2.99308800
C	7.16358300	1.93390700	-0.78932700
C	-2.29988100	-1.96603900	6.96168900
C	-1.25172500	-0.91154900	3.42331400
C	-2.38267300	-1.59385200	5.59702900
H	-1.23684700	-1.56380200	9.75739500
H	-4.55293200	-1.76286000	5.62568300
H	-3.22652800	-2.19305000	7.50594400
C	1.11806500	0.85888500	-4.98148500
Co	-1.27274000	-0.03092400	0.04357100
H	1.36011700	1.47447100	-4.09488400
C	-3.74359000	-1.51028400	4.91850000
C	-0.22628400	1.24915200	-5.58031100
C	-1.37803800	0.86329300	-3.33289100
C	-0.30054400	1.61716700	-6.94926800
H	0.61991800	1.61714600	-7.54810800
H	-2.28333000	1.72304300	-9.59219500
C	-1.41656800	1.24732700	-4.79320200
H	-3.81360700	-2.20160400	4.05735700
C	6.90519900	3.90473300	-2.80221000
C	7.70789700	3.22406300	-0.59229200
H	-4.57814500	-0.64091700	-1.70111100

H -4.16379600 0.59842100 -4.16758200
C -1.52417200 1.98032600 -7.56174600
C -1.36345000 0.44568000 3.07599000
H 1.92973800 0.98353400 -5.71966900
H -0.59536700 2.30206500 -9.51179300
C -2.66537500 1.60751200 -5.39330900
C -1.58657500 2.37450800 -9.03074100
C -2.69642000 1.96679600 -6.76295900
C -3.95627400 1.60206500 -4.58568500
N -1.42516300 0.96739200 1.76394100
C 7.58387000 4.21390100 -1.59890300
H 6.80847800 4.66264900 -3.58903200
H 8.23553000 3.45503300 0.34068900
H -3.90443800 2.30041600 -3.72910900
H -3.93568000 -0.49253900 4.52770200
C -1.30296700 1.87415200 -2.35759100
H -3.65848800 2.24143000 -7.21630500
N -1.35476200 1.68414400 -0.95837700
H -4.38211100 0.83435800 2.05479300
H -6.65525900 0.95039400 3.72322100
C -1.47615200 1.51213900 4.06109700
H -5.96223000 0.17812000 1.49737300
H -1.45754500 1.35474700 5.13878600
C -5.44406600 1.07649500 1.87877700
H 1.95229800 4.11865200 -2.03984100
H -1.94553700 3.41476000 -9.15220000
H 3.64866100 3.52468400 -1.81467000
H 8.01455800 5.21092400 -1.44856700
C -6.15431700 1.70898900 3.09746800
H -4.81555900 1.89494300 -5.21390500
C -1.54707900 2.36058500 1.94796300
C 2.87930800 4.23120500 -1.45012700
C -1.29660600 3.29356100 -2.68569500
C -1.43226600 2.98957500 -0.42965800
H -5.43362400 2.25919300 3.72958400
C -1.60584500 2.69424500 3.36504900
H -1.25984600 3.68791500 -3.70051300
O 2.56119600 3.85069800 -0.02938800
C -1.56840300 3.33068200 0.92843400
O -5.48661100 2.12197900 0.79006800
H 4.15985600 5.87020900 -2.19318300
C -1.39726000 3.98317700 -1.49559800
H -8.06302800 2.16175200 2.09583700
C 3.41486100 5.68107300 -1.40176900
C -7.16229700 2.69799300 2.44669300
H -3.95954800 3.40097000 0.96996100

H	0.69983600	4.25249400	0.75127200
H	-1.70586200	3.70620900	3.75494800
H	2.59206100	6.41095800	-1.51327000
C	-6.36748200	3.23995900	1.23259400
H	5.02941000	5.30954400	0.04546600
H	-7.47326700	3.51532700	3.11725600
C	3.03807500	4.94558800	0.86638300
C	4.02916300	5.77759500	0.02271000
N	-4.17915900	4.33652800	1.35083300
C	-1.78160400	4.77145200	1.31941600
H	-1.45894400	5.05880100	-1.33327900
N	0.61934400	5.17992900	1.19738800
C	-5.53097500	4.49964800	1.59491800
H	3.51389900	4.46520600	1.74048500
H	-7.02305300	3.50640300	0.38356700
C	-3.10823400	5.24694300	1.56522700
C	1.84294500	5.80495900	1.36919900
C	-0.68262300	5.66582600	1.50019600
H	4.09830700	6.81070800	0.39962600
O	-6.10059100	5.53928500	2.05249300
O	2.03761700	6.94826400	1.88857900
C	-3.33141800	6.57871500	2.00835900
C	-0.90124600	6.99584700	1.95459900
H	-4.35413400	6.91246700	2.19608400
C	-2.22119100	7.42750700	2.20366600
H	-0.04246900	7.65178600	2.11022400
H	-2.38887200	8.45222000	2.55500800
H	5.21863400	0.22979100	-3.08032000
H	7.16795500	-3.58062500	0.26274100
C	-3.62957400	-5.14171500	-1.28942100
C	-3.99635000	-6.45788500	-1.68128800
H	-5.05505800	-6.71157700	-1.76699900
C	-2.97944100	-7.39728500	-1.95548400
H	-3.25992400	-8.41208400	-2.26061600
C	-1.61184000	-7.06795100	-1.84475100
H	-0.82417400	-7.79387200	-2.05723200
N	-4.60053800	-4.14566700	-0.99495000
C	-5.97735600	-4.20028700	-1.11811000
H	-4.27349200	-3.23063100	-0.64245800
O	-6.66594500	-5.19228300	-1.51344900
C	-6.67601000	-2.87624300	-0.69829400
O	-5.67400800	-1.83282000	-0.33967200
C	-7.52291000	-2.27297600	-1.84660300
H	-7.27784400	-3.08743900	0.20430200
C	-5.63811800	-0.79582000	-1.43597800
C	-6.49595700	-1.37013100	-2.58686900

H	-8.34449500	-1.66448100	-1.42632700
H	-7.95428300	-3.06300500	-2.48232500
H	-6.04847300	0.14227100	-1.02039100
H	-6.98422800	-0.57419800	-3.17514400
H	-5.87757600	-1.97840000	-3.27201100

Intermediate C

$C_{[Co(III)(P16)]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -13.1627 cm-1
G_corr: 1.42143 Hartree
H_corr: 1.685488 Hartree
SCF: -6075.301459 Hartree
S: 555.757 Cal/Mol-Kelvin
H: -6073.615971 Hartree
G: -6073.880029 Hartree

Cartesian Coordinates:

H	8.50365000	1.85854800	-5.74262200
H	6.57686400	0.28756400	-5.36120100
C	8.39191700	1.34892500	-4.77807100
C	7.30616600	0.46486100	-4.56192200
H	10.18191300	2.24750700	-3.91131600
C	9.33746500	1.56792500	-3.74644200
C	7.16526000	-0.19840900	-3.32068400
C	9.19642600	0.90253300	-2.50620100
H	6.32263900	-0.87681500	-3.14234300
C	8.10960700	0.01657500	-2.28094400
H	9.93187300	1.07019200	-1.70854900
O	3.52438600	-6.15223600	-0.41826400
H	5.28016800	-5.30393500	1.24678400
C	7.96216000	-0.69867500	-0.95200600
H	4.23710400	-3.31833600	-0.38976100
C	4.88891600	-4.30244500	1.48870600
H	5.72044100	-3.57522300	1.48360200
C	2.97187300	-5.07330200	-0.03811400
C	3.81228000	-3.86688400	0.46996100
H	7.46847100	-1.67865200	-1.06947300
O	7.15343500	0.10743900	0.03013000
N	1.61098500	-4.80905200	-0.03225100
C	0.52606000	-5.65282300	-0.39276000
H	3.16781000	2.58935400	0.23354000
C	4.11870500	-4.25211000	2.83864600
O	2.93069400	-2.90108000	1.19579300
H	3.51966400	-5.17215900	2.96900200

C	5.75295700	-0.13775700	0.00527900
H	4.79113800	-4.15085900	3.70801700
H	3.01466400	1.28694200	-0.98069100
O	5.23239400	-1.06102100	-0.68831700
C	2.81348100	1.55024800	0.07641800
C	0.66397800	0.18573900	0.02641200
C	3.20184600	-3.01858700	2.66775500
H	1.39614100	-3.86909500	0.33955700
H	3.70383100	-2.08565400	2.98827400
C	-0.76998000	-5.05676900	-0.48081000
H	-0.90993100	-4.86013400	2.21576200
C	1.27697200	1.52484000	0.34104500
N	5.07488000	0.72433600	0.83723800
C	3.60116300	0.57654300	0.99019600
H	0.81480700	2.33545000	-0.26403400
H	-0.41841900	-4.38203200	-3.02146400
C	-0.97240300	-3.77295100	2.17789300
H	2.22739000	-3.11099400	3.17814800
H	3.33213900	-0.47181300	0.77132100
C	-0.93543700	-3.56632700	-0.33313000
H	1.07216200	1.80929000	1.39679300
C	5.74076800	1.82938200	1.57675900
H	-0.90427900	-3.06468400	4.29041900
C	-0.55523100	-3.32188800	-2.81288800
C	-0.96681400	-2.86909500	3.22038500
H	3.35643400	0.77782400	2.05219400
C	-1.05963500	-2.99665100	0.94664200
H	2.34443000	0.30009000	5.20538900
H	6.72594600	1.99238700	1.11094700
C	-0.85697300	-2.77501300	-1.49593300
H	-0.64065100	-1.72546600	9.60037400
C	-0.45634700	-2.25418800	-3.68028700
H	1.35046600	0.00680400	7.33982800
H	-0.23359900	-2.26243800	-4.74657100
H	0.46925600	-0.32740800	9.56186100
C	1.40678300	0.28353500	4.62297500
C	0.37272300	-0.22175700	6.89532100
C	-1.09777300	-1.54025100	2.63561000
C	-0.52851000	-0.68148500	9.24816600
N	-1.17223300	-1.62180400	1.23024900
C	5.90022200	1.55391100	3.07476300
C	0.22599500	-0.13886900	5.48604100
H	1.54187700	-0.39286600	3.75913900
C	-0.70436500	-0.58756600	7.73879000
N	-0.98681200	-1.37224800	-1.55695000
H	4.70320200	3.26533700	3.70001600

H	7.14575600	-0.20826800	2.78483800
H	1.25046300	1.29841600	4.20714400
H	2.15267200	-0.13247900	-3.82517700
C	-0.73270000	-1.05014900	-2.90960900
C	-1.04014400	-0.44072500	4.90006600
C	5.30119800	2.40748000	4.03566700
C	6.67260500	0.44893000	3.52461600
C	-1.95707900	-0.87096300	7.13547400
C	-1.20052700	-0.36530300	3.40233100
C	-2.14425200	-0.80515300	5.73285000
H	-1.28648700	-0.07604100	9.78058400
H	-4.25096100	-1.32010600	5.92893400
H	-2.80867300	-1.14896700	7.77122200
C	1.95035900	0.83604000	-4.32152200
Co	-1.21932100	-0.11564700	-0.05945100
H	1.68618200	1.55106900	-3.51984100
C	-3.51169300	-1.11108500	5.13599400
C	0.83379100	0.70964600	-5.34898000
C	-0.81827300	0.22981700	-3.48317600
C	1.11688700	0.88457600	-6.72736400
H	2.14552100	1.12101400	-7.03125100
H	0.73593400	-0.05239600	-9.64453100
C	-0.50344400	0.40814800	-4.94705100
H	-3.47463200	-1.98906700	4.46319500
C	5.46980600	2.16791300	5.42197700
C	6.84102700	0.20580900	4.90660500
H	-4.07205500	-2.02886500	-2.16506900
H	-3.62105900	-0.10665500	-6.41408200
C	0.11224200	0.75970800	-7.71948400
C	-1.53458300	0.86385200	2.80664500
H	2.88853000	1.17682000	-4.79336600
H	1.28864600	1.61597000	-9.34913900
C	-1.53307700	0.27783300	-5.92927200
C	0.44510400	0.91865300	-9.19648800
C	-1.20726000	0.45871400	-7.29736100
C	-2.96468400	-0.05233500	-5.52803000
N	-1.69620400	1.09744400	1.42357700
C	6.24026500	1.06543600	5.86087900
H	5.00360100	2.83850100	6.15364500
H	7.44500200	-0.64579500	5.24245100
H	-3.01922600	-1.02462400	-5.00157000
H	-3.88612300	-0.26177900	4.53315900
C	-1.27765200	1.32923300	-2.73625400
H	-2.00243400	0.36144900	-8.04865800
N	-1.56563800	1.32739800	-1.35417900
H	-4.33311600	-0.21236200	1.32510400

H	-6.63598900	-0.67505600	2.86699300
C	-1.91198100	2.04376300	3.57337200
H	-5.58975000	-1.36954700	0.74852100
H	-1.86831800	2.10887200	4.66000800
C	-5.39988000	-0.32885900	1.06904000
H	1.02056600	4.32533700	-2.46892100
H	-0.42084100	1.29762600	-9.76875800
H	2.74804400	4.59615600	-2.01026200
H	6.37562200	0.87903200	6.93288700
C	-6.36770400	0.14297600	2.17644600
H	-3.38063900	0.70704200	-4.83899600
C	-2.20136100	2.41238500	1.34237800
C	1.71660200	4.98707300	-1.92509400
C	-1.64492500	2.60453800	-3.33553200
C	-2.12078000	2.60117100	-1.10505500
H	-5.91987900	0.96415300	2.76592800
C	-2.35648500	2.98877700	2.67106200
H	-1.52189700	2.84335700	-4.39136600
O	1.33688000	4.94172100	-0.46915700
C	-2.48295300	3.11463200	0.15449800
O	-5.66913400	0.57173000	-0.11206800
H	2.33257100	6.72105000	-3.15090400
C	-2.20340700	3.37594300	-2.33565900
H	-8.23054700	-0.17784400	1.04977000
C	1.62089800	6.47164900	-2.34537000
C	-7.59145600	0.66458200	1.37201400
H	-4.72033100	2.31593900	0.00941700
H	-0.65695100	4.78294300	-0.01866800
H	-2.73924900	3.98977600	2.86648900
H	0.60145300	6.71501600	-2.69618600
C	-6.93054900	1.32638900	0.13517000
H	3.01694600	7.26327700	-0.83650500
H	-8.21113700	1.38695900	1.92764800
C	1.23736600	6.34060200	0.03878300
C	1.92813400	7.22887400	-1.02319400
N	-5.29481600	3.14810600	0.22557200
C	-3.21956700	4.42724600	0.25288100
H	-2.62691300	4.37774200	-2.40237900
N	-1.12425300	5.67971700	0.19015500
C	-6.63644900	2.83625300	0.35636600
H	1.75008000	6.37435700	1.01768200
H	-7.55955200	1.24298400	-0.77021500
C	-4.64911100	4.40941500	0.33205200
C	-0.24585100	6.74718300	0.26167200
C	-2.54300400	5.68338100	0.31589900
H	1.52772600	8.25505800	-1.00105600

O	-7.58329700	3.64432300	0.61148900
O	-0.54578600	7.95909300	0.49985200
C	-5.38255000	5.61454100	0.50380700
C	-3.27383800	6.89125900	0.48967600
H	-6.47137600	5.56827200	0.57433600
C	-4.68017400	6.83497500	0.58623300
H	-2.73123200	7.83643600	0.55233100
H	-5.24208900	7.76592400	0.72441400
H	5.13890200	2.74759600	1.43261500
H	8.92989700	-0.80954600	-0.43595300
C	-1.89523700	-5.88112400	-0.78678500
C	-1.73021300	-7.27239800	-1.02639300
H	-2.60576500	-7.87975600	-1.26547700
C	-0.43256900	-7.82518000	-0.96240700
H	-0.29989100	-8.89547000	-1.15891600
C	0.69830700	-7.04098600	-0.64776700
H	1.70245100	-7.46831700	-0.60671200
N	-3.16536800	-5.24507400	-0.84670600
C	-4.39493100	-5.77040700	-1.19826300
H	-3.21895000	-4.24046600	-0.60838800
O	-4.64090400	-6.97242500	-1.52914500
C	-5.53910300	-4.71876000	-1.14255200
O	-5.00363800	-3.36584400	-0.81466600
C	-6.26238900	-4.56938600	-2.50405800
H	-6.22659700	-5.01300600	-0.32878500
C	-5.05977300	-2.50787300	-2.05481300
C	-5.42815100	-3.46434400	-3.21158500
H	-7.30159400	-4.22931800	-2.34187600
H	-6.28202000	-5.52539000	-3.05180100
H	-5.82319800	-1.72762600	-1.88364700
H	-5.99696600	-2.95181800	-4.00641200
H	-4.51934900	-3.90251500	-3.66292700
H	1.20874200	-0.50017300	-0.64883500

$C_{[N2]}$
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: -0.013594 Hartree
H_corr: 0.008229 Hartree
SCF: -109.5607783 Hartree
S: 45.93 Cal/Mol-Kelvin
H: -109.5525493 Hartree
G: -109.5743723 Hartree

Cartesian Coordinates:

N	0.00000000	0.00000000	0.57307000

N	0.00000000	0.00000000	-0.57307000

Transition State TS2

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -1200.1007 cm-1
G_corr: 1.428625 Hartree
H_corr: 1.680565 Hartree
SCF: -6075.288033 Hartree
S: 530.253 Cal/Mol-Kelvin
H: -6073.607468 Hartree
G: -6073.859408 Hartree

Cartesian Coordinates:

H	7.31121000	-6.31563900	-0.66179100
H	5.60401100	-6.74221100	1.13569300
C	7.05257300	-5.52294000	0.05046000
C	6.09202300	-5.76300100	1.06513300
H	8.43575600	-4.07051500	-0.81009600
C	7.68643200	-4.25955200	-0.03233200
C	5.76665600	-4.74792300	1.99378400
C	7.35893800	-3.24366000	0.89717100
H	5.02345600	-4.92045900	2.78077100
C	6.39755000	-3.47584900	1.91601000
H	7.86516800	-2.27059600	0.84064900
O	-4.66177100	-6.12691400	2.56459200
H	-4.66062700	-5.65778400	5.06463300
C	6.08565600	-2.39624400	2.93508200
H	-2.24212500	-5.20133700	3.79092900
C	-3.96356700	-4.80761700	5.13564400
H	-3.25892400	-4.98770000	5.96771200
C	-4.03119200	-5.02389900	2.57489200
C	-3.18319000	-4.62122900	3.81300500
H	6.00213200	-2.81937900	3.95139300
O	4.80025500	-1.65910000	2.64939100
N	-3.99089800	-4.08784000	1.55363500
C	-4.70601000	-4.09088500	0.32059700
H	0.79260900	-3.64368500	2.91806600
C	-4.67459700	-3.43547100	5.30388300
O	-2.81836400	-3.17609500	3.75179600
H	-5.58741100	-3.40037200	4.68150400
C	3.66879900	-2.17351200	3.32362900
H	-4.96116000	-3.23294900	6.35007200
H	-0.60632000	-2.65520100	3.41653100
O	3.68675300	-3.26052700	3.97485700
C	0.40373600	-2.60722000	2.96593700

C	0.14583200	-0.54824000	1.36611400
C	-3.61789500	-2.43368900	4.78600900
H	-3.42695800	-3.25593300	1.78830100
H	-2.91895000	-2.12036200	5.58507700
C	-4.40810800	-3.07324900	-0.63975800
H	-5.46607200	-1.32343900	1.18139100
C	0.29196300	-2.06893100	1.50159400
N	2.57101100	-1.34208500	3.21981900
C	1.31198100	-1.77192600	3.89388600
H	-0.58318400	-2.56811500	1.04618800
H	-2.50012900	-4.47171900	-1.89216900
C	-4.56259000	-0.71392000	1.18517500
H	-4.04289100	-1.54342200	4.29272900
H	1.57621600	-2.35494300	4.79260200
C	-3.25823300	-2.10908200	-0.46585300
H	1.16939400	-2.40032300	0.91249200
C	2.53094000	-0.06964700	2.51227300
H	-4.90431900	0.90031900	2.68569700
C	-1.78106100	-3.65801600	-1.80590900
C	-4.27850400	0.40448000	1.94424100
H	0.79668400	-0.84952700	4.21674600
C	-3.39742800	-0.96808600	0.34819400
H	-1.34019400	1.66886800	5.86509600
H	3.30242900	0.00934000	1.72726900
C	-2.04607100	-2.39352700	-1.13184000
H	-6.00888600	4.53324400	6.62695000
C	-0.47917200	-3.60835100	-2.26124500
H	-2.94074300	3.26577600	6.51138500
H	0.07984200	-4.36843300	-2.80595000
H	-4.42921100	5.07451400	7.25391500
C	-1.48244900	1.75074900	4.77336300
C	-3.28836100	3.39995200	5.47835200
C	-2.96565200	0.88128800	1.53121300
C	-5.05929900	5.03164900	6.34776300
N	-2.42184300	0.03455900	0.54111400
C	2.49269900	1.14543500	3.40309200
C	-2.64121700	2.68017100	4.44092500
H	-1.65189300	0.73443800	4.36891200
C	-4.36158900	4.28712400	5.21794300
N	-0.91613600	-1.54851200	-1.19872800
H	2.06480400	2.52084900	1.76554500
H	2.93855100	0.07837000	5.25538700
H	-0.53286800	2.11531000	4.33708800
H	2.51004400	-3.85190900	-0.44656900
C	0.04726200	-2.29554900	-1.91319400
C	-3.08459300	2.85285300	3.09434400

C	2.26365200	2.43161600	2.83862200
C	2.73350000	1.05651900	4.80526400
C	-4.77921700	4.44977900	3.87236600
C	-2.40403800	2.09198100	1.98321500
C	-4.16135500	3.74890700	2.80674200
H	-5.30901000	6.06826500	6.05556700
H	-5.46739600	4.70267000	1.34915800
H	-5.60287300	5.14004000	3.64524800
C	3.37415300	-3.39172900	-0.96477200
Co	-0.64926100	0.19374300	-0.31044600
H	3.43239600	-2.34387900	-0.61708400
C	-4.64192900	3.97006900	1.37865400
C	3.21233000	-3.47855800	-2.47499100
C	1.29188200	-1.81933300	-2.36466300
C	4.06982300	-4.31978200	-3.22792200
H	4.85057900	-4.88318600	-2.69973000
H	4.49765600	-6.43062600	-5.36205500
C	2.19883500	-2.73293000	-3.15191000
H	-5.00198600	3.02965300	0.91964100
C	2.28388200	3.59102900	3.64399900
C	2.75198600	2.21736600	5.61186200
H	-1.89107900	-0.26872700	-3.68557200
H	1.03898700	-2.26494800	-6.40411500
C	3.94501500	-4.45062500	-4.63388000
C	-1.29789900	2.66788500	1.32944400
H	4.28393000	-3.91616200	-0.62735400
H	5.88829500	-5.37177900	-5.01734100
C	2.05676100	-2.84614100	-4.56935500
C	4.85769500	-5.38398300	-5.41723900
C	2.93299400	-3.70178700	-5.28480000
C	0.98768100	-2.06322300	-5.31982800
N	-0.55679600	2.07378700	0.28517300
C	2.52872700	3.49214800	5.03661500
H	2.10813000	4.57016900	3.18411300
H	2.95189200	2.12767200	6.68667200
H	-0.02713500	-2.33260000	-4.96999500
H	-3.82537700	4.34835600	0.73449100
C	1.64689100	-0.46477200	-2.21199000
H	2.82145800	-3.78268100	-6.37436600
N	0.93532700	0.49802500	-1.46737200
H	-2.68520400	2.89646100	-1.69076600
H	-4.66414500	4.83902300	-2.17843800
C	-0.88217600	4.04938900	1.53046400
H	-3.90423100	2.63374100	-2.98949600
H	-1.30085800	4.71286400	2.28623400
C	-3.12294900	3.31671300	-2.61227900

H	5.10351600	0.10758400	-1.21513800
H	4.90153800	-5.10614800	-6.48551300
H	5.75868500	-0.59536200	0.31470500
H	2.54827000	4.39347300	5.66020500
C	-3.60142400	4.77885800	-2.47006300
H	1.10028300	-0.97268200	-5.16804700
C	0.29528000	3.09895600	-0.17902000
C	5.62830600	0.33247000	-0.27150800
C	2.73611800	0.15934300	-2.95264700
C	1.57536600	1.72196900	-1.76257600
H	-3.00195600	5.31680300	-1.71264300
C	0.07477400	4.32663200	0.57541900
H	3.41836100	-0.37965700	-3.60930700
O	4.73378800	1.23849400	0.52478200
C	1.26661300	2.97426400	-1.19623900
O	-2.02366400	3.34904300	-3.64726300
H	7.81875100	0.43578400	-0.56363600
C	2.66662700	1.51603600	-2.70680800
H	-4.14897800	5.09177800	-4.57935500
C	6.95094800	1.10959600	-0.45690900
C	-3.34017200	5.37562900	-3.88146000
H	-0.26731600	3.82170600	-2.86826200
H	3.57363000	2.62323800	-0.30885600
H	0.60415400	5.26160900	0.39533100
H	6.90408300	1.75500300	-1.35325000
C	-2.01766200	4.68665600	-4.30171800
H	7.40404700	1.39185100	1.68179600
H	-3.23668700	6.47285500	-3.88509300
C	5.54823100	2.36746600	1.06534900
C	7.02655600	1.98276900	0.82760200
N	0.09207600	4.77120300	-3.06481600
C	1.99523400	4.22032400	-1.64192700
H	3.28529400	2.31478000	-3.11551800
N	3.96123100	3.58017600	-0.34317600
C	-0.76201900	5.49612900	-3.87720200
H	5.29811900	2.47033200	2.13692500
H	-1.95593400	4.52935100	-5.39437500
C	1.35154200	5.14534900	-2.52509100
C	5.15606900	3.68943700	0.34891100
C	3.29832900	4.54514700	-1.14928500
H	7.65220200	2.88244000	0.71075000
O	-0.59395500	6.68619500	-4.28987700
O	5.88408300	4.72568400	0.44457900
C	1.96390100	6.38461800	-2.85715900
C	3.90966700	5.78791400	-1.47100900
H	1.43887400	7.07385600	-3.52180700

C	3.22801600	6.69137300	-2.31243400
H	4.89056600	6.02025900	-1.05145200
H	3.69717200	7.65118400	-2.55766800
H	1.42422300	-0.09185800	1.75626500
H	6.83823600	-1.59071200	2.91367500
C	-5.19158500	-3.01849100	-1.83849000
C	-6.19897200	-3.98637300	-2.09954500
H	-6.76648000	-3.92311100	-3.03033700
C	-6.42953600	-5.00473500	-1.15260900
H	-7.19657800	-5.76095800	-1.35543900
C	-5.70637200	-5.06709700	0.05592500
H	-5.88662500	-5.85384800	0.79062000
N	-4.93497900	-1.95567700	-2.74509500
C	-5.49478300	-1.71095200	-3.98716500
H	-4.25982300	-1.22201800	-2.47057700
O	-6.35483000	-2.42615700	-4.58998500
C	-4.98081400	-0.39263400	-4.62738900
O	-3.94279000	0.23739300	-3.76589200
C	-4.31159700	-0.62239200	-6.00562100
H	-5.83864800	0.30218600	-4.68829400
C	-2.59937600	0.10546400	-4.44441100
C	-2.82451300	-0.86583200	-5.62478200
H	-4.41048100	0.28693000	-6.62622500
H	-4.77552000	-1.46838400	-6.53827400
H	-2.29556600	1.11866100	-4.76100500
H	-2.13685800	-0.66243300	-6.46363200
H	-2.68098500	-1.91419900	-5.30421800
H	-0.45155100	-0.09585300	2.19102700

Intermediate D

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.427402 Hartree
H_corr: 1.685916 Hartree
SCF: -6075.326268 Hartree
S: 544.09 Cal/Mol-Kelvin
H: -6073.640352 Hartree
G: -6073.898866 Hartree

Cartesian Coordinates:

H	-8.87346500	-4.45222000	0.20428300
H	-6.90892500	-4.89864400	-1.30031700
C	-8.54322700	-3.68851600	-0.50979900
C	-7.43523100	-3.93859800	-1.35818000
H	-10.09096600	-2.25655900	0.05326400

C -9.22799700 -2.45204400 -0.59404500
C -7.01517400 -2.96046600 -2.28859400
C -8.80316600 -1.47079700 -1.52206500
H -6.16414800 -3.14686100 -2.95467700
C -7.69548300 -1.71477700 -2.37591800
H -9.34103100 -0.51608900 -1.59160000
O 4.01155100 -2.67052200 -6.43646300
H 2.77226000 -0.93182100 -7.90433900
C -7.26580100 -0.67413000 -3.39144900
H 1.20759800 -2.36324100 -6.12685800
C 1.98666700 -0.58967600 -7.21172500
H 1.01816200 -0.57728500 -7.74387700
C 3.28497000 -2.08646600 -5.57296700
C 1.89733300 -1.51323200 -5.97428700
H -7.03281300 -1.13544200 -4.36732600
O -6.04190800 0.09017700 -2.95140200
N 3.58181600 -1.90105900 -4.23409800
C 4.74678600 -2.28678100 -3.51424200
H -2.53103800 -1.88898900 -2.90598700
C 2.28374000 0.79671200 -6.57454200
O 1.33256700 -0.67319900 -4.87700600
H 3.35973800 0.88536100 -6.33846800
C -4.82196100 -0.36656100 -3.49528900
H 2.00498800 1.63488700 -7.23586300
H -0.90411300 -1.38025700 -3.41976900
O -4.70806100 -1.43329800 -4.16634300
C -1.81419500 -1.04611100 -2.88115200
C -0.17585500 0.14928100 -1.31179500
C 1.43898000 0.77293900 -5.27978200
H 2.84066500 -1.39383600 -3.72430100
H 0.41090100 1.14594900 -5.44669700
C 4.77647900 -2.01771700 -2.11117100
H 5.26146600 0.59960100 -2.56138100
C -1.43143700 -0.72195700 -1.40121800
N -3.78603300 0.52084400 -3.22730800
C -2.41850500 0.12020400 -3.70308400
H -1.25132000 -1.69224100 -0.90600200
H 3.40860000 -4.25067300 -1.58385600
C 4.38055200 0.91012500 -2.00038600
H 1.90093600 1.31840600 -4.43875500
H -2.49830600 -0.18761500 -4.76176600
C 3.59167900 -1.40691200 -1.40252500
H -2.27898500 -0.24552500 -0.87161800
C -3.97647800 1.69299100 -2.43646200
H 4.27969400 3.13099300 -2.16874200
C 2.63807200 -3.71017400 -1.03549600

C	3.88485400	2.18321600	-1.80452700
H	-1.77995800	1.01687000	-3.63778200
C	3.47885200	-0.00619600	-1.31489500
H	0.30463500	4.86135700	-3.76203300
H	-4.46207700	1.55333400	-1.46289400
C	2.61646700	-2.26424400	-0.85818400
H	4.52062300	8.68616200	-2.42832300
C	1.52140300	-4.21059000	-0.39970200
H	1.54592300	6.83970200	-3.40473800
H	1.19574100	-5.24637300	-0.31242900
H	2.97720800	8.79471300	-3.32388600
C	0.59413900	4.34736600	-2.82956600
C	2.05427200	6.41118800	-2.53079300
C	2.70322500	2.05760200	-0.96196400
C	3.42441400	8.56632100	-2.34034600
N	2.45882800	0.70330900	-0.64437400
C	-3.58664900	2.99796800	-2.88143600
C	1.68516700	5.11189300	-2.09475600
H	0.91857200	3.32078400	-3.08328100
C	3.05391200	7.16638300	-1.87062000
N	1.49409800	-1.86827500	-0.09577600
H	-3.89730000	3.89629500	-0.90555000
H	-3.22351300	2.48240700	-4.98587700
H	-0.31900400	4.25041300	-2.21162100
H	-1.58824900	-4.15272800	-1.44724600
C	0.82513600	-3.07941900	0.19838900
C	2.34433000	4.54670300	-0.96220600
C	-3.62625900	4.09802800	-1.94938500
C	-3.21644400	3.29025000	-4.24484500
C	3.69625300	6.58384000	-0.74760400
C	1.96909600	3.16272300	-0.49323600
C	3.35964800	5.28907500	-0.28174700
H	3.06950800	9.33433500	-1.62527300
H	4.82549700	5.42049400	1.32285300
H	4.47786000	7.14941200	-0.22245600
C	-2.38629800	-4.41019600	-0.72534800
Co	0.93068900	-0.03385600	0.36402300
H	-2.85513800	-3.45771600	-0.41348000
C	4.07870300	4.70918600	0.92879300
C	-1.83280000	-5.17704700	0.46724900
C	-0.29118000	-3.22564800	1.04266900
C	-2.31882400	-6.48007800	0.74836200
H	-3.09095000	-6.90869200	0.09553500
H	-1.65432300	-9.40985600	1.69974400
C	-0.83068500	-4.61043800	1.31197100
H	4.60204700	3.76705200	0.67707700

C -3.32332100 5.40787200 -2.35955700
C -2.91982500 4.60663300 -4.64364000
H 3.31525400 -2.26450500 2.41977300
H 1.03196100 -5.52093900 4.11351800
C -1.83526300 -7.24126700 1.84063600
C 0.95627700 3.01010800 0.46997200
H -3.14703800 -5.00461500 -1.26056600
H -3.33476000 -8.81669800 1.63891100
C -0.32542000 -5.36285600 2.41904200
C -2.34889500 -8.64907200 2.10807900
C -0.83842600 -6.66074400 2.66510300
C 0.75571200 -4.79500700 3.32890700
N 0.50446100 1.78248600 1.00992500
C -2.96837800 5.67678200 -3.71016500
H -3.36485400 6.22791800 -1.63283000
H -2.66612200 4.81115900 -5.69121200
H 1.66948700 -4.54477300 2.75644200
H 3.36770600 4.47345300 1.74356900
C -0.82084200 -2.12839100 1.74713100
H -0.44805900 -7.23120800 3.51865700
N -0.40269600 -0.78353500 1.62698800
H 2.87893700 1.69816900 2.71183800
H 4.80161200 3.16092600 4.16042600
C 0.33428800 4.13408400 1.15591300
H 4.36759100 0.88468900 3.32075400
H 0.51618400 5.17942200 0.90923800
C 3.48127300 1.47740100 3.60946700
H -4.25077200 -1.15841300 0.95394000
H -2.44734000 -8.84515100 3.19157100
H -5.42310200 -0.80594600 -0.38449200
H -2.74348000 6.70097000 -4.02906500
C 3.83093000 2.72440900 4.45231500
H 0.42399700 -3.86344500 3.82537700
C -0.36744700 2.15913300 2.05486300
C -5.12758700 -0.56130400 0.65171400
C -1.81107100 -2.26938300 2.80652600
C -1.12109300 -0.10306200 2.63658700
H 3.05331200 3.50308100 4.34533500
C -0.45805200 3.60948500 2.15594900
H -2.28174300 -3.21187100 3.08407900
O -4.70325800 0.88590200 0.67037200
C -1.08502300 1.28035400 2.89048700
O 2.63251900 0.60555700 4.50596200
H -7.00683700 -1.47635200 1.34758000
C -1.97059100 -1.02455200 3.37950200
H 4.79447400 1.65838900 6.12017000

C	-6.32081200	-0.65868000	1.62512300
C	3.84156400	2.17639500	5.90675400
H	0.71448600	1.14137900	4.46685600
H	-3.47094000	1.44514700	2.16429500
H	-1.06513600	4.13637100	2.89115000
H	-5.97237900	-0.82382800	2.66133600
C	2.67906400	1.15235000	5.89037100
H	-7.60352100	0.78340700	0.57752200
H	3.67902500	2.95195800	6.67268100
C	-5.76523600	1.68399700	1.34730300
C	-6.98498200	0.73943800	1.49172700
N	0.35512600	1.64711900	5.29382300
C	-1.77260700	1.84810500	4.11014100
H	-2.60091500	-0.73574400	4.22010700
N	-3.92213600	1.94468300	2.94832300
C	1.31866500	1.79527100	6.27629400
H	-5.98932300	2.56030300	0.71087800
H	2.85354700	0.30776700	6.58221900
C	-1.00357700	2.06441800	5.29979400
C	-5.26365500	2.20338000	2.71971000
C	-3.15394900	2.21451800	4.11551100
H	-7.60365800	1.02150500	2.35872800
O	1.17604300	2.36425000	7.40363900
O	-6.06437400	2.80534800	3.50204500
C	-1.58828100	2.66489300	6.44767000
C	-3.74064600	2.81860600	5.26238700
H	-0.97125800	2.82614000	7.33403100
C	-2.94679700	3.03922800	6.40632100
H	-4.79416700	3.10255000	5.23073700
H	-3.39942500	3.50806100	7.28767200
H	-0.37309300	1.23497500	-1.32397100
H	-8.02403800	0.11734300	-3.50753500
C	5.94479000	-2.37490700	-1.36755600
C	7.05035700	-3.00030000	-2.00596200
H	7.92473400	-3.27007200	-1.40999700
C	6.98145100	-3.26236600	-3.39019700
H	7.83074300	-3.74823200	-3.88425900
C	5.84956200	-2.91387900	-4.15674200
H	5.79432700	-3.11870100	-5.22773300
N	5.95069100	-2.08248200	0.02292700
C	6.89918100	-2.39865900	0.97952400
H	5.15086000	-1.56080400	0.41915200
O	7.99023700	-3.02219400	0.79188300
C	6.51856300	-1.88907800	2.39721700
O	5.17265600	-1.25097600	2.38616300
C	6.43470500	-3.03798900	3.43279100

H	7.25499500	-1.11625000	2.68361600
C	4.19304400	-2.16637200	3.08138600
C	4.95212900	-3.49214500	3.31691900
H	6.64424600	-2.64586900	4.44478400
H	7.15932300	-3.83597300	3.20349300
H	3.88551300	-1.66581100	4.01643300
H	4.60086400	-4.01342100	4.22401700
H	4.82893800	-4.17406900	2.45573600
H	0.56381000	-0.12657400	-2.08356400

Transition State TS3

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -452.7493 cm-1
G_corr: 1.42995 Hartree
H_corr: 1.685717 Hartree
SCF: -6075.317018 Hartree
S: 538.307 Cal/Mol-Kelvin
H: -6073.631301 Hartree
G: -6073.887068 Hartree

Cartesian Coordinates:

H	7.69208300	-5.20412500	-1.81904700
H	5.83508600	-6.25970100	-0.48937100
C	7.36589900	-4.75258100	-0.87458600
C	6.31934800	-5.34600900	-0.12501000
H	8.81431800	-3.12332400	-0.96536700
C	7.99744900	-3.58005400	-0.39429700
C	5.90695300	-4.77375700	1.10021500
C	7.58163100	-3.00574900	0.83055600
H	5.10018900	-5.22630100	1.68848600
C	6.53473400	-3.59493000	1.58784900
H	8.08420400	-2.10551900	1.20941000
O	-4.39564600	-6.60630100	1.68706500
H	-4.21273700	-6.58655600	4.22433900
C	6.12700500	-3.00075600	2.92171800
H	-1.88820200	-5.90289000	2.89149600
C	-3.51783500	-5.74817600	4.39135300
H	-2.76264400	-6.04778300	5.14049200
C	-3.75322100	-5.52106500	1.84442600
C	-2.82025800	-5.33727300	3.07390600
H	5.94345200	-3.78828700	3.67337600
O	4.87068400	-2.16449600	2.83635500
N	-3.77415100	-4.42228400	1.00139800
C	-4.58211700	-4.20487200	-0.15254100
H	0.99367800	-4.06505000	1.93617900

C	-4.22765400	-4.43258300	4.81842300
O	-2.44365100	-3.90415500	3.24350800
H	-5.17744800	-4.31653200	4.26524500
C	3.68204400	-2.85061400	3.15869300
H	-4.45139300	-4.40402300	5.89858000
H	-0.45401100	-3.08681200	2.28845900
O	3.61923000	-4.09872000	3.34937800
C	0.64362900	-3.04077100	2.16719200
C	0.79137800	-0.63180000	1.21145800
C	-3.21411600	-3.33994600	4.40551100
H	-3.18044900	-3.64423700	1.32838600
H	-2.48562900	-3.12508200	5.21032500
C	-4.35260300	-3.02188100	-0.92137400
H	-5.29008600	-1.61879000	1.21444800
C	1.03105800	-2.11863000	0.97493200
N	2.60647100	-1.97907400	3.29542200
C	1.25811900	-2.58995400	3.51788500
H	0.47317300	-2.47138800	0.09076900
H	-2.54007200	-4.16459500	-2.52341400
C	-4.40208100	-0.98786100	1.25083800
H	-3.68204300	-2.40028200	4.06504200
H	1.36174400	-3.44309500	4.20813500
C	-3.18851400	-2.09568500	-0.65877300
H	2.10111600	-2.26934500	0.72508400
C	2.64936300	-0.59478300	2.96887700
H	-4.71150900	0.43286800	2.94086800
C	-1.82849800	-3.35389000	-2.37179500
C	-4.10959900	0.04247100	2.12090600
H	0.63546600	-1.81708500	3.99771200
C	-3.27865900	-1.09778600	0.32922400
H	-1.51513100	0.56638300	6.06487800
H	3.36116700	-0.29169600	2.19040400
C	-2.03645900	-2.23628100	-1.46075500
H	-5.98704200	4.44777100	6.74744700
C	-0.58969600	-3.17600400	-2.95321400
H	-3.08615800	2.10107400	6.90744600
H	-0.08599500	-3.80626900	-3.68529400
H	-4.97583200	3.44111900	7.82630400
C	-1.66429000	0.77460400	4.99121500
C	-3.32649800	2.47307500	5.90238800
C	-2.82969700	0.60250900	1.70517000
C	-4.94930800	4.13987200	6.97084400
N	-2.30750700	-0.10707000	0.60100300
C	2.28687300	0.39908300	3.97987700
C	-2.67035300	1.89670900	4.78504400
H	-1.99971700	-0.16003300	4.50089300

C	-4.27982700	3.51128700	5.75669400
N	-0.93317600	-1.35449200	-1.48934000
H	2.32948100	2.07040100	2.56974600
H	2.21500000	-0.99986500	5.66207800
H	-0.68004400	1.03119100	4.55860300
H	2.39650600	-3.79880500	-1.57638100
C	-0.04800100	-1.92807600	-2.43286600
C	-2.97182900	2.37732700	3.47464900
C	2.20862700	1.78284200	3.62059600
C	2.10769700	0.04771400	5.35798100
C	-4.58045000	3.95859000	4.44534800
C	-2.28622400	1.76931400	2.27544000
C	-3.94426800	3.41131500	3.30262400
H	-4.40277600	5.04557900	7.30152500
H	-5.15436900	4.63791000	1.97226000
H	-5.33005300	4.74927200	4.30636300
C	3.23898700	-3.24984800	-2.04002000
Co	-0.64243700	0.27298700	-0.39725800
H	3.34727000	-2.30446100	-1.47705700
C	-4.32002700	3.91687800	1.91627500
C	2.98035100	-2.99275400	-3.51727100
C	1.13979100	-1.34557900	-2.91148600
C	3.74944300	-3.67468400	-4.49608700
H	4.53139800	-4.37017000	-4.16334200
H	3.74538600	-4.68593600	-7.69440700
C	1.96327500	-2.08448700	-3.93882100
H	-4.62623700	3.08554100	1.25323500
C	1.96641600	2.76929200	4.59589900
C	1.87086100	1.04202900	6.33015200
H	-2.06955200	0.32400100	-3.58692400
H	0.58283300	-0.91845700	-6.91834600
C	3.53426200	-3.48463600	-5.88261100
C	-1.20256700	2.43931400	1.67765900
H	4.15571400	-3.84558300	-1.88970000
H	4.99530400	-5.00277800	-6.45670000
C	1.72564700	-1.88093000	-5.33471100
C	4.37790800	-4.21288900	-6.91983200
C	2.51275800	-2.58385900	-6.27979700
C	0.63737200	-0.93096200	-5.81563100
N	-0.50348100	2.01759700	0.52322200
C	1.79804500	2.40804200	5.95830800
H	1.90974600	3.82165300	4.29581700
H	1.75925400	0.75526000	7.38283100
H	-0.35459300	-1.22897900	-5.42649900
H	-3.46564400	4.42092400	1.42540000
C	1.51675700	-0.04185700	-2.53701700

H	2.32276000	-2.42510300	-7.35000400
N	0.86425600	0.77018200	-1.58180100
H	-2.61992000	3.35624900	-1.22311000
H	-4.53434900	5.41826600	-1.42616900
C	-0.74059500	3.75278300	2.10527700
H	-3.89147500	3.29393100	-2.49455900
H	-1.11941800	4.27969100	2.98029900
C	-3.06790600	3.89757800	-2.07380400
H	4.61135900	0.07569300	-1.03867000
H	5.06246900	-3.51474600	-7.44058500
H	5.32139700	-0.84807400	0.35061700
H	1.61782800	3.17942700	6.71568100
C	-3.48005400	5.35057900	-1.74513800
H	0.81951400	0.10426700	-5.46930900
C	0.36642100	3.08928300	0.22431800
C	5.22687700	0.14494900	-0.12592200
C	2.59123700	0.69495700	-3.19009000
C	1.53371200	2.01201300	-1.65738700
H	-2.84675600	5.76582100	-0.93974100
C	0.20843800	4.16673700	1.19340200
H	3.23280900	0.28219100	-3.96797800
O	4.48918600	1.03709900	0.83915800
C	1.29410600	3.13178700	-0.83717700
O	-2.00345500	4.00617100	-3.14018000
H	7.38047700	0.07828700	-0.59738400
C	2.58110800	1.97372000	-2.67003600
H	-4.04555200	5.94635000	-3.78838000
C	6.59949600	0.81627900	-0.34682600
C	-3.21462100	6.10655900	-3.07723400
H	-0.20730100	4.28419200	-2.32966500
H	3.47774000	2.59837500	0.10875700
H	0.76742100	5.10155100	1.16994500
H	6.54768800	1.55817100	-1.16460700
C	-1.93161600	5.41874100	-3.60622800
H	7.22956700	0.81039100	1.76435700
H	-3.06188800	7.19018500	-2.94666500
C	5.45238100	2.02959300	1.40607600
C	6.86105900	1.52880200	1.00964500
N	0.18880800	5.23707800	-2.39557000
C	2.05739100	4.41398700	-1.06739900
H	3.21536000	2.82059000	-2.93101500
N	3.95306900	3.51369600	0.16601100
C	-0.63550900	6.10369700	-3.09100600
H	5.30050800	2.05109200	2.50065700
H	-1.88488200	5.40711700	-4.71061200
C	1.45922300	5.48080600	-1.80876600

C	5.15542500	3.44896100	0.84656900
C	3.35872200	4.61337900	-0.51195300
H	7.57113100	2.36832200	0.93695000
O	-0.41420700	7.33064700	-3.33702600
O	5.96746500	4.40546900	1.04591200
C	2.12505900	6.72886100	-1.95332200
C	4.02682700	5.86060400	-0.64768900
H	1.63713600	7.52868200	-2.51443700
C	3.39404700	6.90045300	-1.36138600
H	5.01087200	5.98959000	-0.19224100
H	3.90526100	7.86453700	-1.46504600
H	1.50915100	0.10546100	0.84196200
H	6.87361300	-2.27934800	3.29176200
C	-5.22935900	-2.74284800	-2.02015600
C	-6.26150600	-3.65104700	-2.38050900
H	-6.90196100	-3.41470600	-3.23281700
C	-6.42271900	-4.83440900	-1.63127400
H	-7.20894700	-5.54389600	-1.91400400
C	-5.60656800	-5.12160400	-0.51797600
H	-5.73498100	-6.03462000	0.06618700
N	-5.03797700	-1.52208200	-2.72170200
C	-5.70057900	-1.04169500	-3.83760800
H	-4.33307100	-0.85414600	-2.36679200
O	-6.61928200	-1.62994400	-4.48971200
C	-5.22925700	0.37843300	-4.25513300
O	-4.11078500	0.84114700	-3.38798100
C	-4.68901000	0.41812700	-5.70656700
H	-6.08112500	1.06689300	-4.10470600
C	-2.83372700	0.83614700	-4.19620200
C	-3.17873400	0.10613000	-5.51384100
H	-4.82652400	1.42984300	-6.13021000
H	-5.21249100	-0.31000000	-6.34722000
H	-2.53752300	1.88949000	-4.34708300
H	-2.56426200	0.46495500	-6.35738100
H	-3.02628700	-0.98419200	-5.41157500
H	0.11293500	-0.31085500	2.01053300

Intermediate E

$E_{[Co(II)(P16)]}$=$A_{[Co(II)(P16)]}$

$E_{[(S)\text{-}2a]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.304073 Hartree
H_corr: 0.375911 Hartree
SCF: -942.3408591 Hartree

S: 151.195 Cal/Mol-Kelvin
H: -941.9649481 Hartree
G: -942.0367861 Hartree

Cartesian Coordinates:

H	-5.15112400	-3.33750900	-0.47050100
C	-4.41000300	-2.56170400	-0.24460000
H	-4.43329600	-1.71508100	-2.25407500
H	-4.13616300	-3.18680500	1.82859200
C	-4.00620500	-1.64686500	-1.24620300
C	-3.84000000	-2.47432800	1.04921000
C	-3.04643800	-0.64778300	-0.95600200
C	-2.88183600	-1.47477400	1.33501200
H	-2.72071400	0.04172500	-1.74372900
C	-2.47849200	-0.54726100	0.33879200
H	-2.43410000	-1.42270200	2.33687800
H	-2.31661300	2.48350500	-1.16127100
C	-1.48086100	0.56094900	0.71113100
H	-3.14319300	1.96562900	1.05771200
N	-0.80351700	1.17551000	-0.46629900
H	-0.69235200	0.11553000	1.34770700
C	-1.24188800	2.52552500	-0.89565400
H	-0.67674300	2.78347300	-1.80582300
C	-2.18012100	1.69292400	1.53265500
H	-2.42619500	1.28981900	2.53249700
O	0.58572500	-0.65691400	-0.50302000
C	0.26828900	0.58129300	-1.10256500
H	1.49357200	-2.43794800	-0.97541600
H	-1.69385100	4.42361300	0.06678100
C	-1.01038800	3.56836500	0.23556500
C	1.76414400	-1.37714100	-1.10229100
O	0.89368800	1.05985600	-2.09407500
C	-1.26061800	2.93362200	1.64203300
H	1.80903500	-1.11071300	-2.17250700
H	-0.29602700	2.62066400	2.08856800
H	0.02197000	3.95977000	0.17775500
H	-1.70235200	3.67946300	2.32928100
H	2.96845100	-2.74683100	0.96065300
C	3.05446600	-1.03152000	-0.38359500
C	3.53719600	-1.85457300	0.66777700
H	3.41879900	0.75737800	-1.56583100
C	3.79859000	0.12022100	-0.75837500
C	4.74078100	-1.53336200	1.33896000
H	5.10629300	-2.17726900	2.14774200
C	5.00064300	0.44297500	-0.08724000
C	5.47525600	-0.38269300	0.96211200

H	5.56900100	1.33262800	-0.38354200
H	6.40982100	-0.13368300	1.47905200

Transition State TS2'

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -1198.6029 cm-1
G_corr: 1.425421 Hartree
H_corr: 1.681987 Hartree
SCF: -6075.275085 Hartree
S: 539.989 Cal/Mol-Kelvin
H: -6073.593098 Hartree
G: -6073.849664 Hartree

Cartesian Coordinates:

H	7.83617000	-1.97568200	1.09970900
H	7.41451200	-0.62192500	-0.98950100
C	7.07494900	-2.29705000	0.37882200
C	6.84119700	-1.53469400	-0.79289900
H	6.51231100	-4.07525700	1.51297000
C	6.32803900	-3.47701800	0.61247000
C	5.86736900	-1.95499500	-1.72623300
C	5.34548000	-3.88845300	-0.31931000
H	5.69538600	-1.38205900	-2.64400600
C	5.10435900	-3.13046800	-1.49494400
H	4.77315900	-4.80721200	-0.13768600
O	6.86829900	1.53766500	-2.45345400
H	6.48696900	2.48903000	-4.77920100
C	4.09414200	-3.60614900	-2.51841000
H	4.67105200	0.52180000	-4.05709500
C	5.38660800	2.48499100	-4.83406700
H	5.07478100	2.12950500	-5.83269300
C	5.59910500	1.63214700	-2.42782200
C	4.77948200	1.57693600	-3.74329100
H	4.50711500	-3.54753300	-3.54134800
O	2.80844500	-2.80551200	-2.51593700
N	4.81726300	1.76831200	-1.29181100
C	5.24015700	1.95828700	0.05535900
H	0.21131800	1.65397000	-4.59758300
C	4.75212300	3.86789300	-4.51143100
O	3.39416500	2.09335100	-3.52202200
H	5.31585500	4.36184900	-3.69909200
C	2.68058400	-1.87000100	-3.54857500
H	4.74228300	4.54354400	-5.38399500
H	-0.94182300	0.35562600	-4.23577300
O	3.66575300	-1.43906800	-4.22564300

C 0.09050500 0.70604900 -4.03576200
C -0.41463400 -0.00024400 -1.56278000
C 3.32199500 3.50176200 -4.04379300
H 3.80660200 1.80666100 -1.49181100
H 2.59848400 3.50159800 -4.88102600
C 4.25898500 1.88565700 1.09131400
H 3.21029000 4.23295200 0.35197800
C 0.26596000 1.00163700 -2.51105900
N 1.36409900 -1.48091800 -3.76475200
C 1.14622100 -0.26867200 -4.62170300
H -0.19101500 1.99152800 -2.30836900
H 4.47506300 -0.67918600 1.78606600
C 2.20936900 3.81604100 0.24334700
H 2.94434300 4.14544900 -3.22965200
H 2.11594700 0.24806100 -4.69328000
C 2.83523000 1.45224400 0.82496900
H 1.34281300 1.10585600 -2.28630500
C 0.19071800 -1.99293500 -3.08157800
H 0.86747200 5.52564500 -0.25168400
C 3.40563100 -0.84830300 1.67175700
C 1.03084300 4.46677600 -0.05458100
H 0.84625900 -0.59070200 -5.63993100
C 1.87925000 2.41064600 0.44126700
H -1.54898900 5.35741100 -4.05577000
H 0.07123800 -1.29119400 -1.97054500
C 2.46849800 0.12532800 1.12615500
H -3.99571200 9.49238300 -1.25788000
C 2.67497700 -1.96782800 2.00019700
H -2.19660300 7.43327900 -3.17410000
H 3.02459000 -2.89723600 2.44689800
H -2.44117600 10.06274600 -0.60163300
C -1.46385900 4.80565700 -3.10312300
C -2.16382800 7.05622600 -2.14313500
C -0.02412000 3.46349000 -0.04477000
C -2.89686900 9.37272400 -1.33566300
N 0.49678500 2.18655000 0.26434400
C -0.01332600 -3.47500600 -2.89687700
C -1.80133400 5.70280500 -1.91984000
H -0.43273400 4.40981400 -3.02628400
C -2.48404300 7.93070300 -1.07545800
N 1.16169600 -0.41078900 1.06973000
H 1.44209300 -4.14350500 -4.38313900
H -1.58167900 -3.16858600 -1.41299400
H -2.14024300 3.93099000 -3.15232600
H 2.36116200 -4.07167900 0.22075300
C 1.29282800 -1.70859300 1.61794400

C	-1.75399600	5.20627700	-0.58230600
C	0.66175200	-4.45294800	-3.67948700
C	-1.04962900	-3.90614000	-2.02368200
C	-2.42708000	7.41742900	0.24540600
C	-1.36933500	3.77246900	-0.31028700
C	-2.07002300	6.07201400	0.51085600
H	-2.59866500	9.70351300	-2.34640500
H	-2.30192300	6.36719600	2.65615500
H	-2.66611000	8.07850000	1.08940800
C	1.65425300	-4.90673600	0.37603700
Co	-0.48844400	0.45342600	0.35967000
H	0.79359200	-4.70876300	-0.28676800
C	-2.02705300	5.56700900	1.94683800
C	1.22374800	-5.02478700	1.82907100
C	0.26312400	-2.65193200	1.78563500
C	1.47298600	-6.23000400	2.53645300
H	1.98122200	-7.05136400	2.01376500
H	0.51283400	-8.03044900	5.22989100
C	0.55398600	-3.95323700	2.49632600
H	-1.02002800	5.19809100	2.21890700
C	0.30995200	-5.81907900	-3.58663200
C	-1.40144600	-5.27177900	-1.93073600
H	0.62097800	0.22637800	3.99952800
H	-0.70122700	-3.25590400	5.67274300
C	1.08315600	-6.40496300	3.88627700
C	-2.36944200	2.78560000	-0.30682600
H	2.13545900	-5.84021200	0.03328200
H	2.22870300	-7.56491900	5.33634700
C	0.14698400	-4.11040000	3.86042600
C	1.38249900	-7.69727400	4.63331200
C	0.41892100	-5.32981500	4.52888400
C	-0.56467300	-2.99141400	4.60924900
N	-2.18771100	1.41155000	-0.02535900
C	-0.72260900	-6.23878200	-2.71156700
H	0.83656300	-6.55606300	-4.20543600
H	-2.20026600	-5.57637900	-1.24455500
H	0.00897200	-2.04750200	4.55910700
H	-2.72640000	4.72176900	2.09511000
C	-1.04766200	-2.39756900	1.34077200
H	0.10487100	-5.44065000	5.57572900
N	-1.52292500	-1.19290300	0.78012100
H	-2.93128300	1.86005900	3.28083400
H	-4.54179000	3.15994300	5.17533500
C	-3.76602600	3.06934200	-0.60344300
H	-2.60524100	1.65904400	5.04411300
H	-4.15413200	4.06051000	-0.83488800

C -3.36137800 1.53905100 4.24432600
H -2.79162500 -3.59229100 -4.17745500
H 1.65244200 -8.51263000 3.93890300
H -2.01860800 -2.78528100 -5.59131000
H -0.99285200 -7.29881900 -2.64077600
C -4.69602700 2.22598600 4.60803700
H -1.56137600 -2.77530400 4.18123900
C -3.47626200 0.84944800 -0.17157000
C -2.93127600 -2.83763600 -4.96838600
C -2.11277600 -3.38907700 1.40657800
C -2.88563800 -1.44316300 0.50646800
H -5.27505800 2.46351000 3.69712600
C -4.44872300 1.87357000 -0.52670900
H -1.98562300 -4.39635800 1.80120700
O -3.08672800 -1.49378000 -4.29592000
C -3.82334500 -0.49930500 0.04244100
O -3.67751100 0.07489300 4.12336800
H -4.00136200 -3.64077900 -6.72577400
C -3.24452000 -2.80729300 0.87503000
H -5.03940700 1.11932500 6.47941900
C -4.20288100 -3.04259100 -5.82075200
C -5.42355100 1.13491900 5.44293200
H -4.46164100 -0.44694900 2.36140100
H -4.05719800 -1.18153000 -2.39735200
H -5.51073800 1.68719700 -0.68077800
H -4.99006800 -3.55385800 -5.23716400
C -5.02529500 -0.17413100 4.71239400
H -4.04814000 -1.17673300 -6.98521500
H -6.51820000 1.25694100 5.47287000
C -4.31372200 -0.84192100 -4.84208800
C -4.64421000 -1.58998500 -6.15137900
N -5.47651500 -0.64230700 2.34830800
C -5.27762300 -0.88763200 -0.07485100
H -4.24030600 -3.23400300 0.75962400
N -5.07645700 -1.08792300 -2.51161400
C -6.04557600 -0.55913600 3.60662100
H -4.06760200 0.22365700 -5.00810600
H -4.94064900 -1.03224700 5.40364700
C -6.09402600 -0.93784800 1.10256700
C -5.48723700 -0.91321300 -3.82412100
C -5.89294500 -1.13136100 -1.34063400
H -5.71579300 -1.50431500 -6.39231700
O -7.26272200 -0.76746300 3.90752400
O -6.68741500 -0.77649800 -4.21754600
C -7.48054000 -1.23744700 1.01629400
C -7.28271800 -1.41762900 -1.43020100

H	-8.07479300	-1.26515300	1.93203500
C	-8.05340900	-1.46997800	-0.25090600
H	-7.73413100	-1.57180000	-2.41138700
H	-9.12417000	-1.69305300	-0.32129200
H	-0.69757400	-1.59783000	-3.60464300
H	3.74451100	-4.62820900	-2.29713500
C	4.65787000	2.20807300	2.42992200
C	6.01037200	2.51854100	2.73577300
H	6.28187400	2.74431900	3.76901800
C	6.96226400	2.52350100	1.69587600
H	8.00845700	2.75360700	1.92870700
C	6.59691500	2.25897600	0.36096400
H	7.33148400	2.27559400	-0.44598500
N	3.65249300	2.22235900	3.43486500
C	3.78089300	2.45408700	4.79257500
H	2.66971100	2.07298900	3.15198600
O	4.85808700	2.67817800	5.42930400
C	2.42318100	2.44044700	5.54481000
O	1.30524300	2.12365200	4.61024100
C	2.37808900	1.35592900	6.65208600
H	2.25410200	3.45718900	5.94397000
C	0.76184000	0.76589700	4.95105600
C	1.79991100	0.12526100	5.89930600
H	1.69477000	1.67248900	7.46154200
H	3.37833300	1.18252500	7.08064900
H	-0.21886600	0.90501200	5.44603400
H	1.34219400	-0.61052000	6.58243600
H	2.59304700	-0.38296900	5.32150400
H	-1.47240800	-0.17913700	-1.86892800

Intermediate D'

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.426151 Hartree
H_corr: 1.686746 Hartree
SCF: -6075.32398 Hartree
S: 548.469 Cal/Mol-Kelvin
H: -6073.637234 Hartree
G: -6073.897829 Hartree

Cartesian Coordinates:

H	-7.00919100	-1.35883700	3.07261800
H	-7.08117700	-1.90355100	0.60824200
C	-6.83445700	-0.57218500	2.32872100
C	-6.87915800	-0.88103100	0.94673800
H	-6.54334000	0.99914400	3.81668500

C -6.57079900 0.75547400 2.74780900
C -6.66787000 0.13757200 -0.01067900
C -6.35405000 1.77084400 1.78681900
H -6.70711600 -0.09674100 -1.08013000
C -6.39944600 1.47068800 0.39939800
H -6.15291800 2.79960500 2.11345600
O -6.32208400 -3.24237800 -1.77400000
H -6.27190300 -3.14321900 -4.35281600
C -6.20675000 2.56671400 -0.62854000
H -5.17386200 -0.94091600 -3.06176700
C -5.32181400 -2.61237900 -4.52520900
H -5.47942900 -1.83100800 -5.29046300
C -5.13540400 -2.82914400 -1.97621200
C -4.79950600 -1.96822500 -3.22126400
H -6.78579000 2.36572100 -1.54644900
O -4.75790300 2.74229800 -1.03396200
N -4.04414300 -3.05449000 -1.15365300
C -3.96352000 -3.85602300 0.01936900
H -0.63725500 0.89494800 -4.53758100
C -4.15369400 -3.55580000 -4.92972400
O -3.31705500 -1.85365800 -3.39570600
H -4.21082100 -4.49932900 -4.35655800
C -4.35756800 2.04570600 -2.17728800
H -4.16200300 -3.80426700 -6.00505700
H -0.34585100 2.23319200 -3.42797900
O -5.07664700 1.18225900 -2.76144500
C -0.92744900 1.29711600 -3.54495000
C 0.01443600 0.87952600 -1.16722800
C -2.89762200 -2.74591700 -4.53048500
H -3.18198200 -2.60264200 -1.49702100
H -2.54993400 -2.09212400 -5.35327900
C -2.78212000 -3.75904800 0.81618300
H -1.40784800 -5.01276400 -1.15016500
C -0.50524500 0.24473700 -2.45747400
N -3.06875200 2.41100000 -2.58413200
C -2.44390300 1.58187200 -3.67468600
H 0.29823900 -0.37517400 -2.89312300
H -3.76775100 -1.73548700 2.25616400
C -0.69283200 -4.19520300 -1.23944700
H -2.05949600 -3.36887500 -4.17227600
H -2.99312000 0.62554100 -3.70694300
C -1.71582900 -2.73029100 0.53207400
H -1.35819500 -0.42900900 -2.25896200
C -2.41701900 3.59517500 -2.15013100
H 0.69572700 -4.75106000 -2.89300500
C -2.87739700 -1.13005400 2.09471200

C	0.36400500	-4.06255800	-2.11646300
H	-2.62252000	2.11528200	-4.63165300
C	-0.70480400	-2.99934200	-0.40735800
H	1.45124000	-1.59089500	-6.34533500
H	-0.77274200	1.34627000	-0.55005500
C	-1.76421500	-1.51199000	1.23650100
H	4.46824000	-6.66644700	-6.60198100
C	-2.58763500	0.11931300	2.59900700
H	2.77823700	-3.40553400	-7.00079100
H	-3.18851700	0.73695100	3.26457300
H	3.90583200	-5.44294600	-7.77892200
C	1.57102200	-1.69733400	-5.25282200
C	3.02033400	-3.66377900	-5.96115900
C	1.03103600	-2.80859900	-1.79450600
C	4.46610400	-5.58628500	-6.83788900
N	0.37470200	-2.14851200	-0.73135000
C	-2.99486400	4.90940200	-2.17080900
C	2.47435500	-2.87566200	-4.91524800
H	0.56554600	-1.82028400	-4.80664500
C	3.86760400	-4.76891400	-5.70162700
N	-0.77571100	-0.50362400	1.21713900
H	-4.81397400	4.41586300	-3.30221300
H	-1.32070900	5.79368400	-1.06424800
H	1.98183600	-0.74782200	-4.85973600
H	-2.93214200	3.10555300	1.06832900
C	-1.28066900	0.49773000	2.08149400
C	2.78180000	-3.20542300	-3.56068900
C	-4.25125500	5.21470800	-2.80623200
C	-2.27324100	6.00147600	-1.56783600
C	4.15983200	-5.07932500	-4.34911100
C	2.21352600	-2.38543100	-2.42762800
C	3.63547900	-4.31723300	-3.27560500
H	5.51699600	-5.29163500	-7.02929600
H	4.65948200	-5.56554300	-1.81478500
H	4.81241800	-5.93338800	-4.12298700
C	-2.27970600	3.88554300	1.50494700
Co	0.85530200	-0.41739200	0.11608900
H	-1.32493400	3.84724400	0.94761800
C	3.98862700	-4.68913800	-1.84167900
C	-2.05755000	3.67399000	2.99386100
C	-0.59502100	1.65294300	2.49498000
C	-2.66357300	4.55195300	3.93001600
H	-3.27729500	5.38180900	3.55478100
H	-3.54515900	4.82623200	7.19344300
C	-1.25446100	2.59559400	3.47240900
H	3.08533100	-4.93020100	-1.24970900

C	-4.74696800	6.53052100	-2.82993500
C	-2.78062300	7.31252800	-1.59167700
H	0.48235000	-1.70572800	3.60853400
H	-0.19485000	1.28288700	6.52106400
C	-2.49722100	4.38824400	5.32694100
C	2.94354900	-1.28577200	-1.94289700
H	-2.75598300	4.86056900	1.30389900
H	-3.95183000	5.93208700	5.84791500
C	-1.07573400	2.40823700	4.87880800
C	-3.13294700	5.35652300	6.31501800
C	-1.70093900	3.30530600	5.78000100
C	-0.23528200	1.25880700	5.41789700
N	2.57951700	-0.46224600	-0.85134600
C	-4.02322200	7.59145900	-2.22166700
H	-5.70017900	6.74066900	-3.32995200
H	-2.21445000	8.12395300	-1.11861800
H	-0.65298000	0.28052600	5.11199400
H	4.49684800	-3.85278500	-1.32452200
C	0.73017900	1.89930800	2.09155900
H	-1.56173600	3.15521500	6.85921200
N	1.48105600	1.11706500	1.18638700
H	3.75638200	-2.43144300	1.31834300
H	5.62445300	-4.39333600	2.11375600
C	4.27600100	-0.94638900	-2.42349500
H	3.42769700	-3.48388700	2.74140500
H	4.77113800	-1.44103400	-3.25822600
C	4.14049900	-2.76612500	2.29745400
H	1.15544400	4.83234700	-1.04913300
H	-2.38893000	6.08529700	6.69354000
H	0.58432800	5.14995500	-2.73684400
H	-4.41742200	8.61380200	-2.24189700
C	5.59130800	-3.29862600	2.24972400
H	0.80223200	1.29846200	5.03532200
C	3.70909000	0.36116200	-0.64453100
C	1.46330800	5.13771700	-2.06479300
C	1.53979000	2.98421800	2.62868100
C	2.75246600	1.73000200	1.16125900
H	6.15601100	-2.82968500	1.42325900
C	4.76032600	0.05130900	-1.60409400
H	1.17999000	3.71792200	3.34903900
O	2.41245800	4.09286900	-2.57700000
C	3.83257600	1.36336200	0.33630700
O	4.17682700	-1.55401300	3.19898200
H	1.56214700	7.33801300	-2.25644600
C	2.79707100	2.86558100	2.07292300
H	5.86696100	-3.54823400	4.42058500

C	2.23476400	6.47660600	-2.10473700
C	6.17959900	-2.85452400	3.61880700
H	4.68560800	0.07644200	2.16141100
H	3.70857600	3.20990300	-1.27544800
H	5.72960300	0.54722200	-1.63603700
H	2.79736300	6.63450700	-1.16653500
C	5.52004400	-1.47009400	3.83709200
H	2.70230600	6.43584700	-4.25613800
H	7.27898000	-2.77852500	3.62233000
C	3.60768900	4.78127900	-3.14820700
C	3.21635600	6.27087100	-3.29188200
N	5.65236800	0.42112700	2.28508300
C	5.17024800	2.03621500	0.52305100
H	3.67833600	3.48404400	2.24027000
N	4.65466500	3.62353300	-1.25535300
C	6.35767100	-0.31468000	3.22095000
H	3.82882600	4.30514700	-4.12117300
H	5.36928400	-1.23881500	4.90734700
C	6.07881500	1.53135100	1.50676600
C	4.84633500	4.58601400	-2.23097700
C	5.57746600	3.14127200	-0.28497400
H	4.10622000	6.91875800	-3.24388600
O	7.55599800	-0.11932100	3.59580800
O	5.90604400	5.25760000	-2.43409900
C	7.36278000	2.11657900	1.67839300
C	6.86167000	3.72878000	-0.11753000
H	8.03792600	1.70424900	2.43119900
C	7.73223600	3.20560900	0.86156300
H	7.15113800	4.56501000	-0.75684600
H	8.72291000	3.65686100	0.98975600
H	-1.37396000	3.47167000	-1.83779500
H	-6.45439900	3.56026100	-0.22067500
C	-2.64324900	-4.62261800	1.94917800
C	-3.67838000	-5.52932900	2.30459500
H	-3.54723600	-6.16897300	3.17990800
C	-4.84977000	-5.56922600	1.51943600
H	-5.65458600	-6.26021500	1.79611700
C	-5.00754100	-4.75216200	0.38057100
H	-5.91382300	-4.78530900	-0.22713500
N	-1.43548000	-4.53713800	2.69372200
C	-1.07173800	-5.20130800	3.85166600
H	-0.69187500	-3.90539000	2.35217000
O	-1.77101900	-6.04434900	4.49616400
C	0.36024400	-4.83540200	4.33340300
O	0.95297000	-3.76655800	3.48250900
C	0.36711200	-4.27781500	5.77768200

H	0.99019900	-5.73709700	4.22475100
C	0.94509900	-2.46889600	4.25740400
C	0.14871500	-2.75530200	5.55177400
H	1.35001500	-4.46608100	6.24707400
H	-0.41757000	-4.74905900	6.39145400
H	1.99819700	-2.19391700	4.44517600
H	0.50926300	-2.14906100	6.40043800
H	-0.92658900	-2.54369400	5.40682900
H	0.84546300	1.58374500	-1.35407800

Transition State TS3'

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -512.035 cm-1
G_corr: 1.429097 Hartree
H_corr: 1.6858 Hartree
SCF: -6075.305653 Hartree
S: 540.278 Cal/Mol-Kelvin
H: -6073.619853 Hartree
G: -6073.876556 Hartree

Cartesian Coordinates:

H	7.64612300	-2.33624900	0.32078400
H	7.30677800	-0.61359600	-1.49318000
C	6.89088500	-2.49751100	-0.45756000
C	6.70509600	-1.52893700	-1.47487000
H	6.24967400	-4.42951300	0.33076100
C	6.10330400	-3.67413700	-0.45050200
C	5.73799100	-1.74186800	-2.48279700
C	5.12773400	-3.87783900	-1.45456800
H	5.60616200	-1.00487300	-3.28319500
C	4.93441400	-2.91267100	-2.47727500
H	4.52342600	-4.79410600	-1.45174500
O	6.75930700	1.76904800	-2.35682600
H	6.25563800	3.17637100	-4.42340500
C	3.92409300	-3.15733700	-3.57565800
H	4.49322000	1.08206600	-4.01161700
C	5.15402100	3.16463000	-4.42517400
H	4.79524000	2.99912300	-5.45703600
C	5.49554100	1.87314200	-2.23962000
C	4.60747900	2.05519000	-3.49921900
H	4.31718400	-2.85443100	-4.56212800
O	2.62487300	-2.39767400	-3.36775100
N	4.78104500	1.82970800	-1.05428600
C	5.27872300	1.80112700	0.28137300
H	-0.05143400	2.34796500	-4.20831800

C	4.52477100	4.44989800	-3.81639700
O	3.23288600	2.49725300	-3.11862800
H	5.12116700	4.79027100	-2.95031800
C	2.42326600	-1.29984100	-4.20083000
H	4.46883400	5.27875200	-4.54287600
H	-1.19930400	1.00233500	-4.07878500
O	3.34877000	-0.72079900	-4.84660700
C	-0.14443800	1.28849000	-3.89774200
C	-0.19260400	-0.11292100	-1.67240700
C	3.12121500	3.97740200	-3.36556700
H	3.76157000	1.91103200	-1.18698800
H	2.36161300	4.11869400	-4.15784700
C	4.34925100	1.59435300	1.34800900
H	3.36068800	4.04776400	0.91021800
C	0.18873600	1.19165400	-2.37631800
N	1.08008000	-0.89353000	-4.25149500
C	0.82651600	0.48576900	-4.79716300
H	-0.35520700	2.01708800	-1.88288900
H	4.47635700	-1.02985600	1.81019900
C	2.35021100	3.67192300	0.75100500
H	2.77264500	4.44831500	-2.42966700
H	1.80299700	0.99236100	-4.83870300
C	2.90272400	1.24177000	1.09032100
H	1.26491900	1.39838000	-2.24012400
C	-0.03258800	-1.51471200	-3.64310500
H	1.06150700	5.46026100	0.41901200
C	3.40368800	-1.15691300	1.67369200
C	1.19340100	4.38257200	0.50926200
H	0.43282400	0.39726600	-5.82940900
C	1.97817800	2.26365500	0.80622000
H	-1.31274900	5.73531700	-3.40066200
H	0.56189300	-0.83881600	-1.35352100
C	2.49474700	-0.09723100	1.25623100
H	-2.05521800	10.11128500	0.45778100
C	2.64470000	-2.29254000	1.85149600
H	-1.92887700	7.73042400	-2.32583800
H	2.96842800	-3.28229700	2.17054200
H	-2.30894700	9.90795400	-1.30053200
C	-1.28184000	5.08466200	-2.50890200
C	-1.91143100	7.25432700	-1.33627400
C	0.11060600	3.41338800	0.41110600
C	-2.57353500	9.50375800	-0.30732800
N	0.59155500	2.09746600	0.59749500
C	-0.23320100	-2.96895600	-3.50164400
C	-1.59184000	5.87488000	-1.24461400
H	-0.27997400	4.61709700	-2.45527700

C	-2.20899200	8.03031800	-0.18907000
N	1.17211600	-0.58668500	1.13869200
H	1.17384400	-3.60701900	-5.05487000
H	-1.76334200	-2.71842600	-1.95993200
H	-2.00957300	4.26400200	-2.65818500
H	2.34595200	-4.12933400	-0.28067700
C	1.27113000	-1.95086700	1.50722700
C	-1.56400500	5.24930000	0.03788900
C	0.42043000	-3.93358000	-4.33125000
C	-1.25298500	-3.43319700	-2.61507300
C	-2.17359300	7.38932700	1.07574500
C	-1.22324200	3.78466900	0.16791200
C	-1.85815500	6.01440900	1.20960400
H	-3.66132300	9.65801500	-0.16413200
H	-2.09963700	6.10380800	3.37237000
H	-2.39668000	7.97221300	1.97968100
C	1.53119700	-4.87763100	-0.27726900
Co	-0.44946100	0.39835200	0.55749900
H	0.69476400	-4.43244900	-0.84485900
C	-1.83624700	5.37102800	2.58959900
C	1.11671900	-5.24772700	1.13844700
C	0.22264500	-2.88778300	1.52504800
C	1.34608100	-6.56511600	1.61597900
H	1.81947700	-7.29436000	0.94492000
H	0.31837200	-8.84985500	3.80519000
C	0.49291000	-4.29519200	2.00057400
H	-0.83847100	4.95668800	2.82878500
C	0.06463900	-5.29810000	-4.27226600
C	-1.59834600	-4.79954300	-2.55155800
H	0.85002900	-0.46073700	4.16683300
H	-0.70751500	-4.13885900	5.26970500
C	0.98044400	-6.96389000	2.92424700
C	-2.25198700	2.83236800	0.06999000
H	1.87872400	-5.76829300	-0.83045300
H	1.97717700	-8.38160000	4.25188500
C	0.11250100	-4.67750100	3.32689300
C	1.24360400	-8.37852300	3.42213400
C	0.36391100	-6.00128600	3.76413600
C	-0.54629700	-3.68518600	4.27579800
N	-2.11087100	1.43055900	0.20491700
C	-0.94282800	-5.74385800	-3.38018500
H	0.56670200	-6.01525600	-4.93316000
H	-2.37445600	-5.12437200	-1.84936900
H	0.07873700	-2.78193500	4.40648800
H	-2.55308900	4.52988800	2.65071400
C	-1.08251300	-2.54497900	1.12648700

H	0.07125300	-6.28647600	4.78393100
N	-1.52932000	-1.25979900	0.74962000
H	-2.63261300	1.30639300	3.61955200
H	-4.11161500	2.45960900	5.70384600
C	-3.64093200	3.19169100	-0.18001700
H	-2.29509000	0.85029200	5.33236900
H	-3.99705700	4.21325700	-0.30759700
C	-3.07042000	0.89259500	4.54316400
H	-3.19771000	-2.91057500	-4.57900400
H	1.64380000	-9.02191500	2.61874300
H	-2.36757100	-1.96587100	-5.86786700
H	-1.21249800	-6.80520500	-3.33317300
C	-4.34414300	1.61889200	5.02781800
H	-1.52436300	-3.33548200	3.89627100
C	-3.42317300	0.93250600	0.03269700
C	-3.27375100	-2.02976300	-5.23742900
C	-2.16908400	-3.51180300	1.05411200
C	-2.90186700	-1.43707200	0.45878300
H	-4.92119000	2.01041900	4.17037400
C	-4.36474000	2.01887100	-0.20596300
H	-2.06386800	-4.56892400	1.29496800
O	-3.28583900	-0.79960000	-4.35946500
C	-3.81576600	-0.41810900	0.12176200
O	-3.49869100	-0.51507800	4.23829600
H	-4.43527100	-2.41920500	-7.07599800
C	-3.29158600	-2.83095700	0.63170600
H	-4.73042300	0.30799300	6.75282500
C	-4.57252600	-1.97922900	-6.07348700
C	-5.13283500	0.48298700	5.73809800
H	-4.36758000	-0.71770300	2.45058900
H	-4.16662300	-0.72588500	-2.37416200
H	-5.43503300	1.88568800	-0.35770300
H	-5.38882600	-2.52471000	-5.56615500
C	-4.84496700	-0.74706400	4.83681000
H	-4.29662000	0.04846300	-6.89799400
H	-6.21484500	0.67628800	5.81546600
C	-4.48513500	0.01310500	-4.72215900
C	-4.90380700	-0.46202200	-6.12862000
N	-5.39222500	-0.85350400	2.44886100
C	-5.28631600	-0.74207000	0.00861000
H	-4.29890500	-3.21284500	0.46809400
N	-5.18346800	-0.57970300	-2.43573800
C	-5.91698800	-0.92181000	3.72711500
H	-4.17174100	1.07361200	-4.70063500
H	-4.80443200	-1.68918400	5.41310500
C	-6.06243700	-0.93898900	1.19848200

C	-5.62867200	-0.17717000	-3.68458500
C	-5.95865700	-0.77203500	-1.25135200
H	-5.97102300	-0.25786600	-6.31016500
O	-7.13396500	-1.10989100	4.04237600
O	-6.83372400	0.06887600	-4.00274400
C	-7.46258300	-1.17247800	1.12567000
C	-7.36054900	-0.99358500	-1.32612200
H	-8.02461400	-1.31228200	2.05147900
C	-8.09027700	-1.19383700	-0.13657100
H	-7.85243300	-0.98372900	-2.29992400
H	-9.17120000	-1.36571200	-0.19410300
H	-0.96055500	-0.96358100	-3.82198200
H	3.58823900	-4.20775300	-3.59061000
C	4.82646000	1.70056700	2.69521100
C	6.20218200	1.92969900	2.96874800
H	6.53302400	1.99139000	4.00752300
C	7.09953000	2.06858300	1.89028600
H	8.16304300	2.23583600	2.09687000
C	6.65836500	2.01788600	0.55268500
H	7.35089200	2.13964500	-0.28203300
N	3.87417300	1.58453100	3.74415500
C	4.07932300	1.59451600	5.11202900
H	2.87518900	1.49521300	3.49424200
O	5.19437700	1.69696600	5.71419700
C	2.76332700	1.48098000	5.92771500
O	1.59185700	1.31851800	5.02006500
C	2.75917900	0.24242600	6.86057700
H	2.63295300	2.42740600	6.48363300
C	1.04726500	-0.07196700	5.17974600
C	2.12354500	-0.85593500	5.96326700
H	2.12372700	0.43855600	7.74378400
H	3.77764700	-0.00106500	7.20359100
H	0.09585100	-0.00243900	5.74232100
H	1.69131500	-1.68393700	6.55093900
H	2.87701400	-1.27541200	5.27233200
H	-1.24087100	-0.42680000	-1.67326800

Intermediate E'

$E'_{[Co(II)(P16)]}=A_{[Co(II)(P16)]}$

$E'_{[(R)\text{-}2a]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.304991 Hartree
H_corr: 0.375721 Hartree
SCF: -942.3325619 Hartree

S: 148.864 Cal/Mol-Kelvin
H: -941.9568409 Hartree
G: -942.0275709 Hartree

Cartesian Coordinates:

H	-0.63379100	4.60360300	0.72152600
C	-1.14442600	3.62282500	0.75101500
H	-0.34642900	3.37260100	-1.30708600
H	-0.28326900	3.10972700	2.70633000
H	-2.13187400	3.33228200	-1.21468700
C	-1.19942100	3.02957100	-0.69924100
H	0.62719900	2.48999700	1.31448400
H	-2.16710700	3.80854000	1.13557700
C	-0.39598300	2.65170300	1.70572800
O	0.73651600	1.46828000	-2.08230000
N	-1.11917300	1.54062000	-0.63956200
C	-1.12869600	1.27442900	1.82495800
H	3.18056400	0.86156300	-1.53082400
H	5.33042700	1.09744900	-0.23465000
C	-0.01004300	0.93465000	-1.20895600
H	-2.81450400	1.61852000	0.52053700
H	-1.84469400	1.28592100	2.67036500
C	-1.90518400	0.97883600	0.50729500
C	3.46803700	0.11081500	-0.78530500
C	4.66882100	0.24266100	-0.05023600
H	-0.38986300	0.47575900	2.02001200
O	0.19022200	-0.36471600	-0.70864800
H	1.42922800	-0.77494800	-2.38035500
C	1.31628400	-1.13838700	-1.34426100
C	2.60406200	-0.99453900	-0.55595000
C	5.02217300	-0.72912400	0.91883300
C	-2.41972000	-0.44923300	0.29991100
H	5.95577100	-0.62794500	1.48525400
H	-3.00334700	-0.07441300	-1.76371200
H	-1.97866000	-1.15387400	2.31838000
C	-3.00493900	-0.80482300	-0.94492300
C	-2.42314500	-1.40183900	1.34833600
C	2.96543600	-1.96459700	0.41579700
C	4.16750700	-1.83418100	1.15096500
H	0.93974900	-2.17403500	-1.33129000
C	-3.56547400	-2.08557500	-1.14188100
C	-2.98854700	-2.68611900	1.15600400
H	2.30296500	-2.82113200	0.59663900
H	4.43868500	-2.59049900	1.89716300
H	-4.00709000	-2.34449200	-2.11180400
C	-3.56078500	-3.03481900	-0.08926100

H	-2.98122800	-3.41182900	1.97841600
H	-3.99817000	-4.02915700	-0.23873100

Transition State TS4

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -891.097 cm-1
G_corr: 1.422137 Hartree
H_corr: 1.682058 Hartree
SCF: -6075.306416 Hartree
S: 547.05 Cal/Mol-Kelvin
H: -6073.624358 Hartree
G: -6073.884279 Hartree

Cartesian Coordinates:

H	-9.28691900	-0.91508100	-3.07055200
H	-8.26601500	1.36918700	-2.80247800
C	-8.98131400	-0.56185100	-2.07837700
C	-8.40812200	0.72551200	-1.92649300
H	-9.61932300	-2.38098100	-1.05521500
C	-9.17033800	-1.38707900	-0.94287700
C	-8.02848800	1.18838000	-0.64523700
C	-8.78995000	-0.92283800	0.33846000
H	-7.57941000	2.18052700	-0.51934600
C	-8.21583700	0.36613200	0.49894900
H	-8.94405200	-1.56026000	1.21899500
O	-0.97325800	7.76688300	0.33475700
H	-1.11484200	7.91503900	2.90062600
C	-7.83322600	0.86947200	1.87688900
H	-2.54567500	5.85549800	1.73067400
C	-1.18986300	6.85129300	3.17735000
H	-2.00482900	6.72800100	3.91362000
C	-0.79641600	6.54986100	0.65466400
C	-1.46520500	5.97394900	1.93323900
H	-8.00094500	1.95605600	1.97369300
O	-6.38288400	0.60496700	2.20057700
N	-0.05032000	5.61343900	-0.04059900
C	0.74235200	5.79536300	-1.20930500
H	-2.94549800	1.85161600	-0.20110100
C	0.13918700	6.25661500	3.72179100
O	-0.91702600	4.62385800	2.25459700
H	0.99802800	6.66082700	3.15559100
C	-5.49715200	1.65599300	1.89178900
H	0.29523000	6.47855500	4.79140100
H	-1.42408800	2.36833700	0.57004400
O	-5.84633200	2.73545600	1.33703700

C -2.31598000 1.72960300 0.69956100
C -0.51306700 -0.07496600 1.29055400
C -0.02519400 4.74194000 3.46043600
H -0.03633700 4.68789600 0.41625900
H -0.53245600 4.22834700 4.29950200
C 1.39900400 4.64968000 -1.75654000
H 2.98178500 4.71203300 0.45697500
C -1.88979600 0.25314000 0.86739600
N -4.20387200 1.35466700 2.31299400
C -3.09533300 2.27962400 1.93389700
H -2.25453100 -0.40007600 0.05521000
H -0.69701700 3.93243800 -3.26660000
C 2.77476900 3.66797700 0.69095800
H 0.91986600 4.22486600 3.22168400
H -3.52980200 3.26663600 1.71758600
C 1.17612600 3.25706900 -1.21521600
H -2.63806200 -0.12625800 1.79483100
C -3.80544900 0.05782600 2.78211900
H 3.90335100 3.20909600 2.55859100
C -0.67568400 2.90931000 -2.89325500
C 3.23587300 2.91217100 1.75019400
H -2.41011400 2.37808500 2.79194700
C 1.91509300 2.80224000 -0.10634200
H 1.46852300 1.08004300 6.04037100
H -4.45961500 -0.76157300 2.45728500
C 0.23324800 2.42955000 -1.86004900
H 7.27436100 2.02692300 6.96185100
C -1.47218700 1.84314300 -3.25669000
H 3.60904200 1.31490900 6.98764200
H -2.27147600 1.81312400 -3.99630300
H 5.79495900 1.99881700 7.96695200
C 1.78666800 0.86582800 5.00533400
C 4.10290200 1.16603500 6.01798900
C 2.71165200 1.56391700 1.57306000
C 6.35979800 1.45047700 7.19174700
N 1.88648100 1.49525600 0.42842800
C -3.15035900 -0.08413100 4.09782300
C 3.30209500 0.92251400 4.87280300
H 1.29215300 1.59569800 4.33662900
C 5.51713600 1.21969100 5.94500900
N 0.01218700 1.05940400 -1.59506200
H -2.52664500 -2.14634400 3.70143200
H -3.60999600 1.92905100 4.81201200
H 1.39010300 -0.12973500 4.73009000
H -4.04291600 0.31151100 -1.55660400
C -1.02854700 0.69256800 -2.48020800

C	3.93753900	0.73171800	3.60795000
C	-2.53351400	-1.32908600	4.43672600
C	-3.11218000	0.98117000	5.04871100
C	6.12623300	1.02888900	4.67888900
C	3.09665300	0.47770600	2.38133800
C	5.36254800	0.78315500	3.51002600
H	6.68210600	0.48817800	7.63711500
H	7.16113800	0.66541100	2.28812900
H	7.22074500	1.07126400	4.59752600
C	-4.39248300	-0.66201400	-1.94857000
Co	0.91634100	-0.08505800	-0.25585900
H	-3.97973400	-1.44542800	-1.28374800
C	6.06627600	0.57891900	2.17502300
C	-3.94890900	-0.87078600	-3.38892000
C	-1.50091400	-0.61473300	-2.70427800
C	-4.92451400	-1.09904700	-4.39288800
H	-5.98363000	-1.11738700	-4.10327300
H	-5.92486400	-0.55225600	-7.28407700
C	-2.56739300	-0.84742000	-3.74944600
H	5.73862500	1.32317000	1.42446600
C	-1.91733500	-1.50132900	5.69433000
C	-2.49804400	0.79824100	6.30652500
H	2.02837300	0.23872900	-3.64903500
H	-0.62189300	-1.24320600	-6.61335500
C	-4.56992300	-1.30316800	-5.74921600
C	2.79738100	-0.84698600	2.01503800
H	-5.49211900	-0.68402800	-1.86098700
H	-6.54983100	-1.96439700	-6.39297700
C	-2.18726500	-1.05738300	-5.11237200
C	-5.63409900	-1.51439500	-6.81706700
C	-3.19307000	-1.28267800	-6.08553100
C	-0.72381500	-1.04549600	-5.53191100
N	2.02541400	-1.24330600	0.90001800
C	-1.89686700	-0.44222300	6.63780600
H	-1.44653600	-2.46040500	5.94174300
H	-2.50006900	1.61719000	7.03623100
H	-0.25333100	-0.06714400	-5.31730500
H	5.84357400	-0.42000100	1.75329400
C	-0.89511700	-1.72706400	-2.08770200
H	-2.89241700	-1.44575400	-7.12921100
N	0.13833700	-1.68428400	-1.12494100
H	4.39935600	-1.12160800	-0.84966800
H	7.20511800	-1.37343000	-0.96517300
C	3.34830400	-2.01004800	2.69801000
H	5.31033400	-0.47527800	-2.26081500
H	3.97669900	-1.95951500	3.58651000

C 5.10670700 -1.37723800 -1.65683900
H -2.93217800 -3.48499100 0.06322700
H -5.27116400 -2.17414100 -7.62598000
H -4.13286200 -3.05147400 1.34497100
H -1.42337600 -0.58342500 7.61647700
C 6.38866100 -2.08795400 -1.16747600
H -0.13873100 -1.81001400 -4.98621800
C 2.10236600 -2.65258900 0.89875800
C -3.38521300 -3.79939000 1.01918900
C -1.19379400 -3.10442700 -2.46049500
C 0.48120600 -3.03809500 -0.91374700
H 6.19151500 -2.66103500 -0.24295000
C 2.94114800 -3.12436800 1.99354400
H -1.94594700 -3.39150300 -3.19458600
O -2.29037300 -3.81698600 2.05355200
C 1.42698700 -3.51735300 0.01318400
O 4.40915000 -2.37048200 -2.55688700
H -5.04404000 -5.23228900 0.73408800
C -0.32478500 -3.91309300 -1.75610200
H 7.23783100 -2.51556100 -3.15361600
C -3.97017400 -5.23040200 0.98745300
C 6.72617900 -3.05600800 -2.33629000
H 3.28824200 -3.62255100 -1.49626400
H -0.46093000 -4.38823000 1.32297600
H 3.16109900 -4.17257400 2.19260300
H -3.43877500 -5.85368900 0.24564400
C 5.32476800 -3.51760700 -2.80947800
H -4.45379800 -5.37440900 3.13296500
H 7.34824800 -3.91385400 -2.03350600
C -2.31513400 -5.13827800 2.74666600
C -3.69624800 -5.75588500 2.42442600
N 3.64405700 -4.58715500 -1.38597700
C 1.73700400 -4.99339900 0.07639800
H -0.22390900 -4.99760000 -1.78963400
N -0.22540000 -5.38140800 1.47754600
C 4.83572500 -4.78766100 -2.05992000
H -2.17812300 -4.94675800 3.82663200
H 5.29851700 -3.73946900 -3.89207800
C 2.88716600 -5.50230000 -0.60655000
C -1.14811000 -6.04453600 2.26684400
C 0.93551200 -5.90052800 0.83603100
H -3.66333900 -6.85502900 2.49101900
O 5.50547700 -5.86605800 -2.11689100
O -1.10769000 -7.26542400 2.61820300
C 3.24472300 -6.87463700 -0.50936700
C 1.29026400 -7.27402000 0.93691100

H	4.13505000	-7.22951000	-1.03277400
C	2.44204000	-7.73635000	0.26642700
H	0.66748200	-7.94099200	1.53608400
H	2.71747400	-8.79418900	0.34756300
H	-0.37879600	-1.12296500	1.59731700
H	-8.36115500	0.32176700	2.67422500
C	2.26309900	4.83231200	-2.88413400
C	2.42189900	6.11200700	-3.48225600
H	3.07712300	6.21419500	-4.34984800
C	1.72516700	7.21133600	-2.94003700
H	1.83855100	8.19788200	-3.40406900
C	0.89508900	7.07642900	-1.80810200
H	0.36196000	7.92823200	-1.38162700
N	2.96380100	3.69457800	-3.36751500
C	3.80850500	3.58634100	-4.45833900
H	2.88328900	2.80648500	-2.84414600
O	4.10775300	4.50509000	-5.28380900
C	4.43184900	2.17045900	-4.60020900
O	3.88645400	1.24678700	-3.56769100
C	4.11279800	1.51753200	-5.96797600
H	5.51893500	2.26878900	-4.42457500
C	2.96111600	0.25833800	-4.23839500
C	2.77831800	0.77280400	-5.68443600
H	4.90988900	0.79994100	-6.23555000
H	4.03481100	2.27597500	-6.76378200
H	3.44754700	-0.73180800	-4.18541800
H	2.59753500	-0.05140300	-6.39567400
H	1.92922900	1.47814200	-5.74744700
H	-0.04821600	0.63628200	1.99417700

Intermediate F

$F_{[Co(II)(P16)]}=A_{[Co(II)(P16)]}$

$F_{[3a]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.296938 Hartree
H_corr: 0.373916 Hartree
SCF: -942.313589 Hartree
S: 162.013 Cal/Mol-Kelvin
H: -941.939673 Hartree
G: -942.016651 Hartree

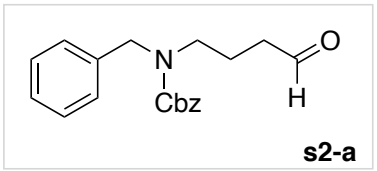
Cartesian Coordinates:

H	-6.40386400	0.29051800	-1.57275400
H	-5.30365600	-1.76473300	-2.51482000

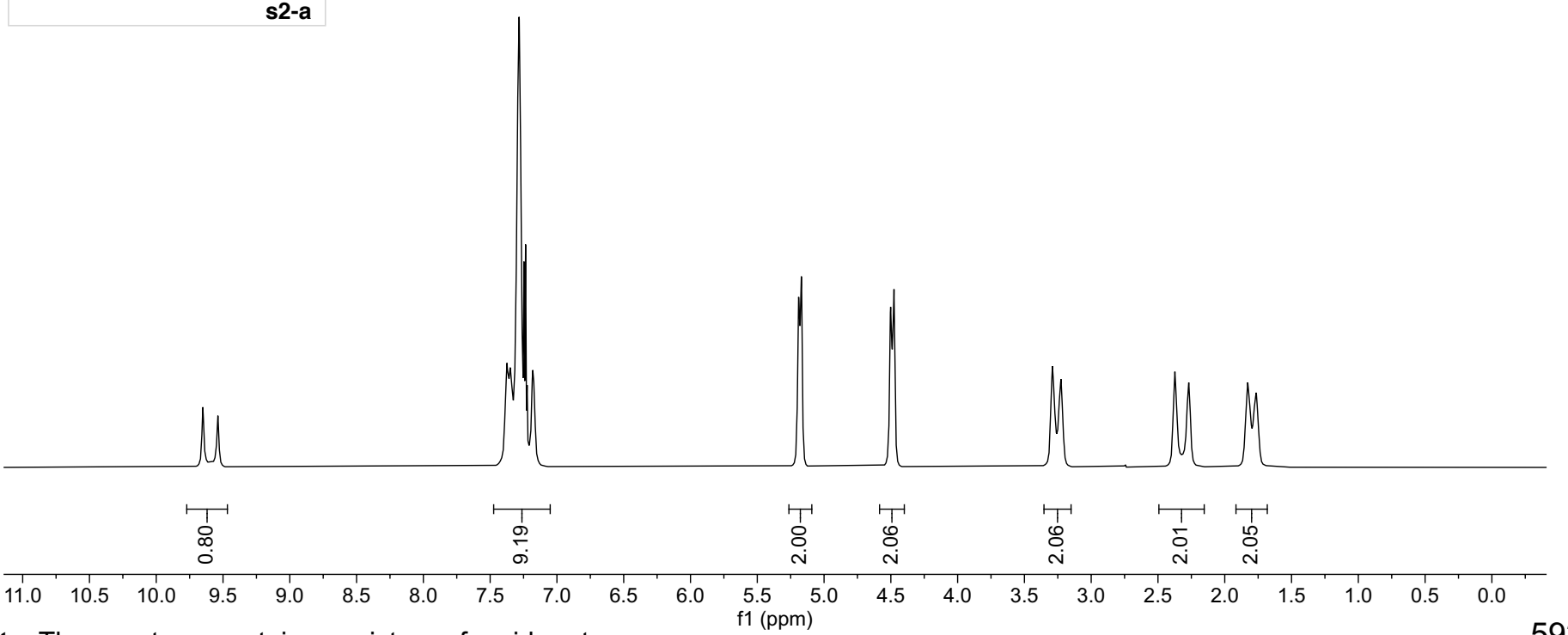
C -5.51880100 -0.13232500 -1.08250300
C -4.89863500 -1.28967800 -1.61346100
C -4.99441300 0.47479800 0.08533000
H -5.47408700 1.36919600 0.50010000
C -3.75894600 -1.83537700 -0.97731200
H -3.27901700 -2.73255800 -1.38972000
C -3.85577100 -0.07216400 0.72108400
C -3.22612700 -1.23153200 0.19232000
H -3.43784800 0.39647800 1.61982800
H -1.86785600 -2.88260900 0.63085900
C -2.00292300 -1.81565600 0.87186500
H -2.02895500 -1.66200700 1.96448000
O -0.72960600 -1.19532700 0.35562400
O -0.85663100 0.37748200 2.11422000
C -0.29888700 -0.04168700 1.05755000
H 0.70660300 -0.66592700 -1.24649100
H 1.98442800 -2.12064300 0.83978900
N 0.80024000 0.54101400 0.46359400
H -0.37980300 2.91993700 1.36728800
C 1.42348200 0.03503000 -0.78835500
H 1.44761000 1.51608600 2.22586700
C 2.87918900 -1.76406700 0.31498200
C 1.40627100 1.71718400 1.14005800
C 0.62197800 3.04523100 0.91136900
H 1.55662300 0.89073100 -1.47772000
C 2.77350600 -0.65165700 -0.56245000
H 4.19141200 -3.26760200 1.18755400
H -0.10330600 2.75174500 -1.17660600
C 4.12151700 -2.40890500 0.50909200
H 1.14371800 3.84593000 1.47185600
C 0.48396200 3.43933900 -0.54676400
H 2.44062000 1.81171900 0.76386000
C 3.93445400 -0.19775000 -1.23839800
C 5.27721200 -1.95120000 -0.17281500
C 1.00002700 4.56490500 -1.10656000
H 3.86435300 0.66318500 -1.91660400
C 5.18075200 -0.84400500 -1.04805600
H 6.24072300 -2.45217500 -0.02173400
H 0.85559100 4.79915000 -2.16818200
H 1.57699000 5.28904200 -0.51586600
H 6.07084700 -0.48271600 -1.57675100

3.5. NMR/HPLC SPECTRAL DATA

^{1}H NMR of **s2-a**, 600 MHz, $CDCl_3$

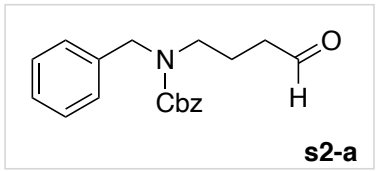


s2-a



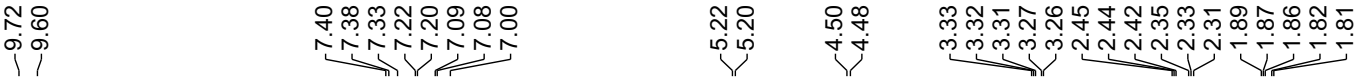
Note: The spectrum contains a mixture of amide rotamers.

^{13}C NMR of **s2-a**, 150 MHz, $CDCl_3$

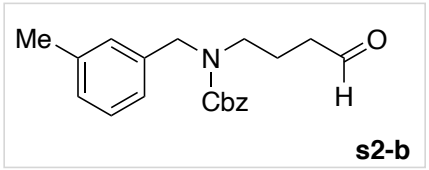


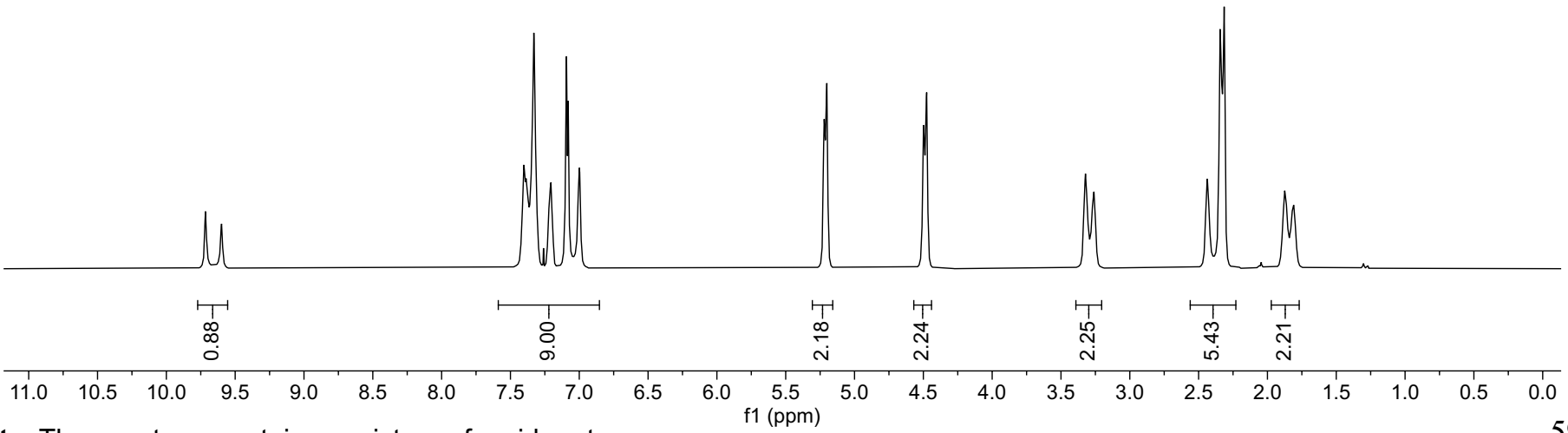
s2-a

Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-b**, 600 MHz, $CDCl_3$

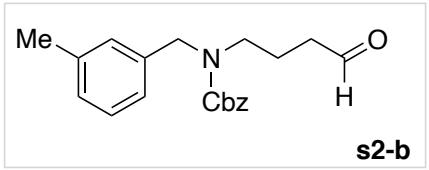




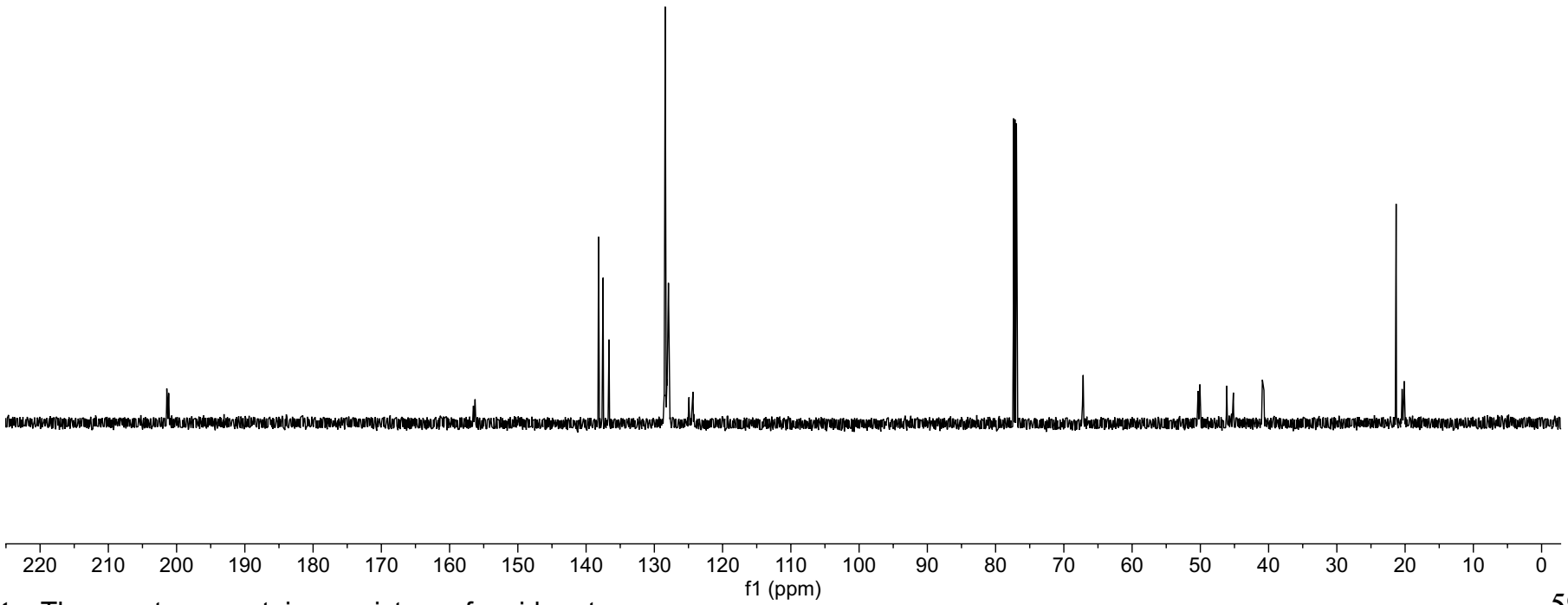
Note: The spectrum contains a mixture of amide rotamers.

201.43
201.17
156.50
156.27
138.18
137.51
136.64
128.41
127.93
124.92
124.34
77.37
77.16
76.95
67.20
50.34
50.07
46.14
45.16
40.90
40.70
21.31
20.43
20.13

^{13}C NMR of **s2-b**, 150 MHz, $CDCl_3$

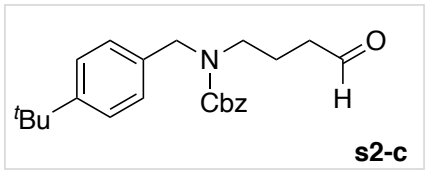


s2-b



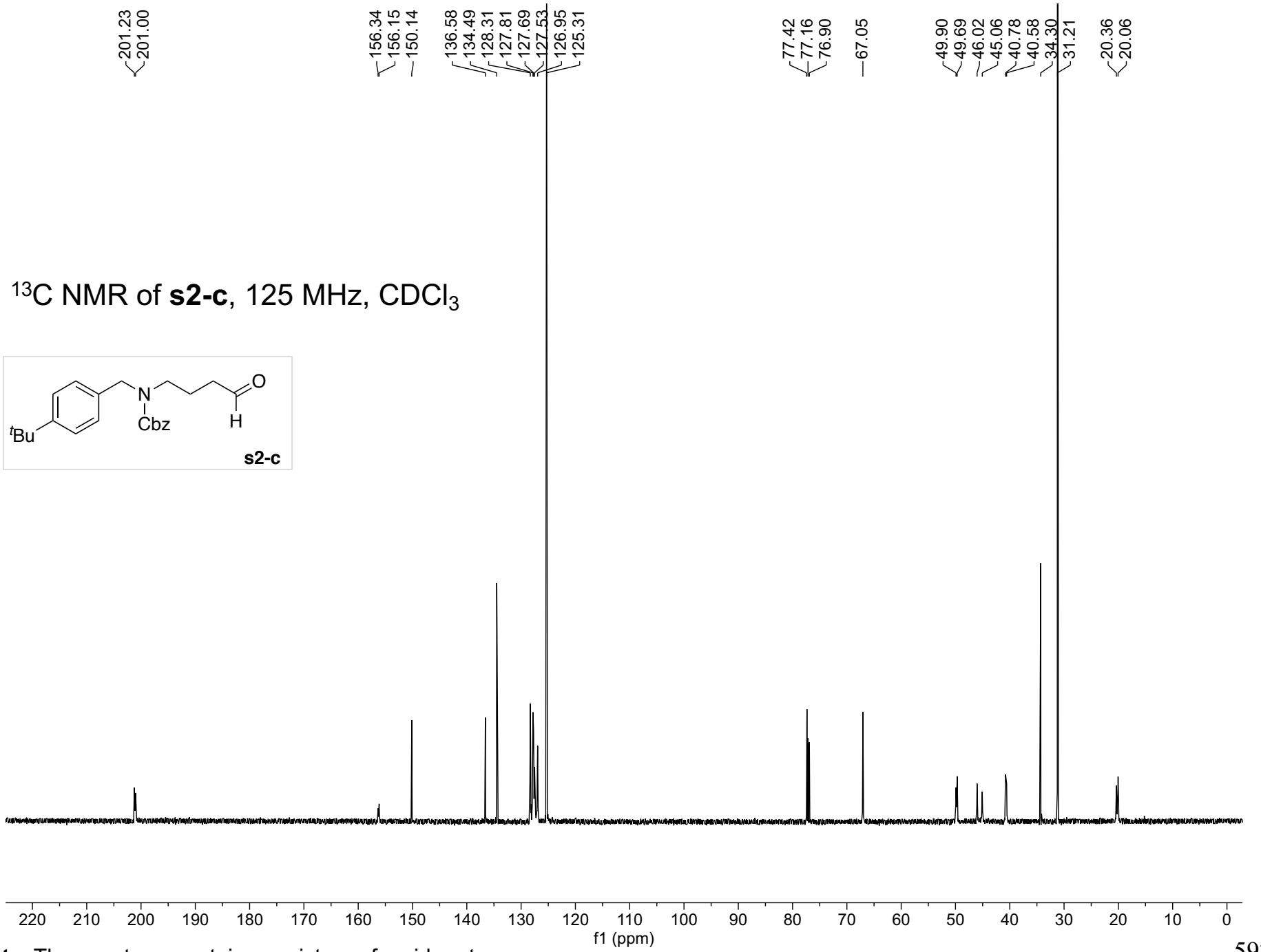
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **s2-c**, 500 MHz, $CDCl_3$



s2-c

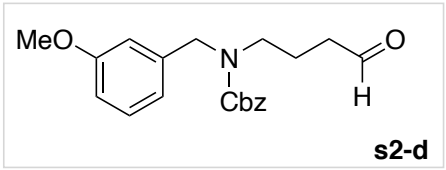
Note: The spectrum contains a mixture of amide rotamers.



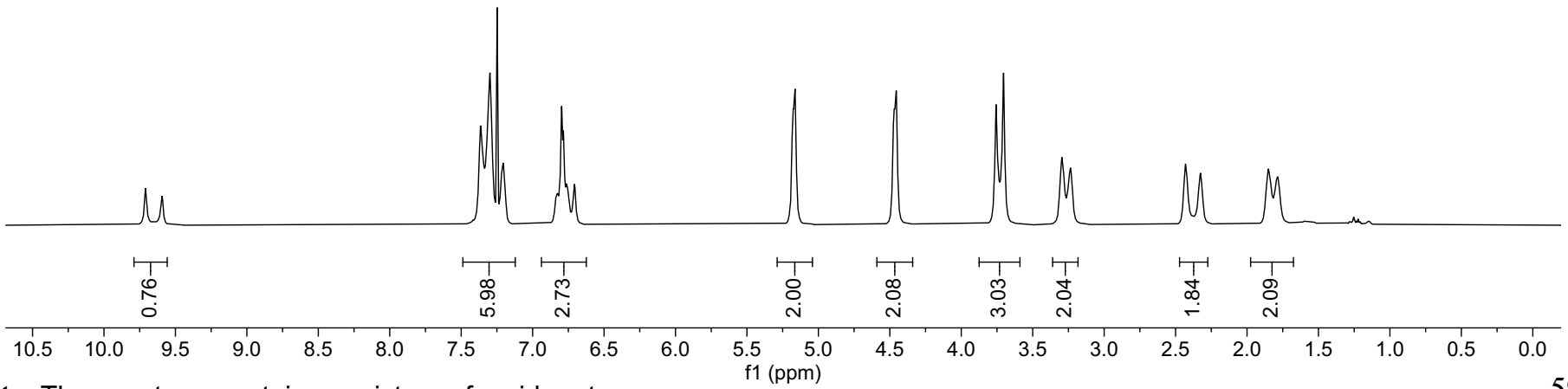
Note: The spectrum contains a mixture of amide rotamers.

9.71
9.59
7.37
7.30
7.25
7.20
6.84
6.80
6.78
6.76
6.71
5.18
5.16
4.47
4.45
3.76
3.70
3.31
3.30
3.23
3.22
2.44
2.43
2.42
2.34
2.33
1.86
1.85
1.84
1.80
1.78

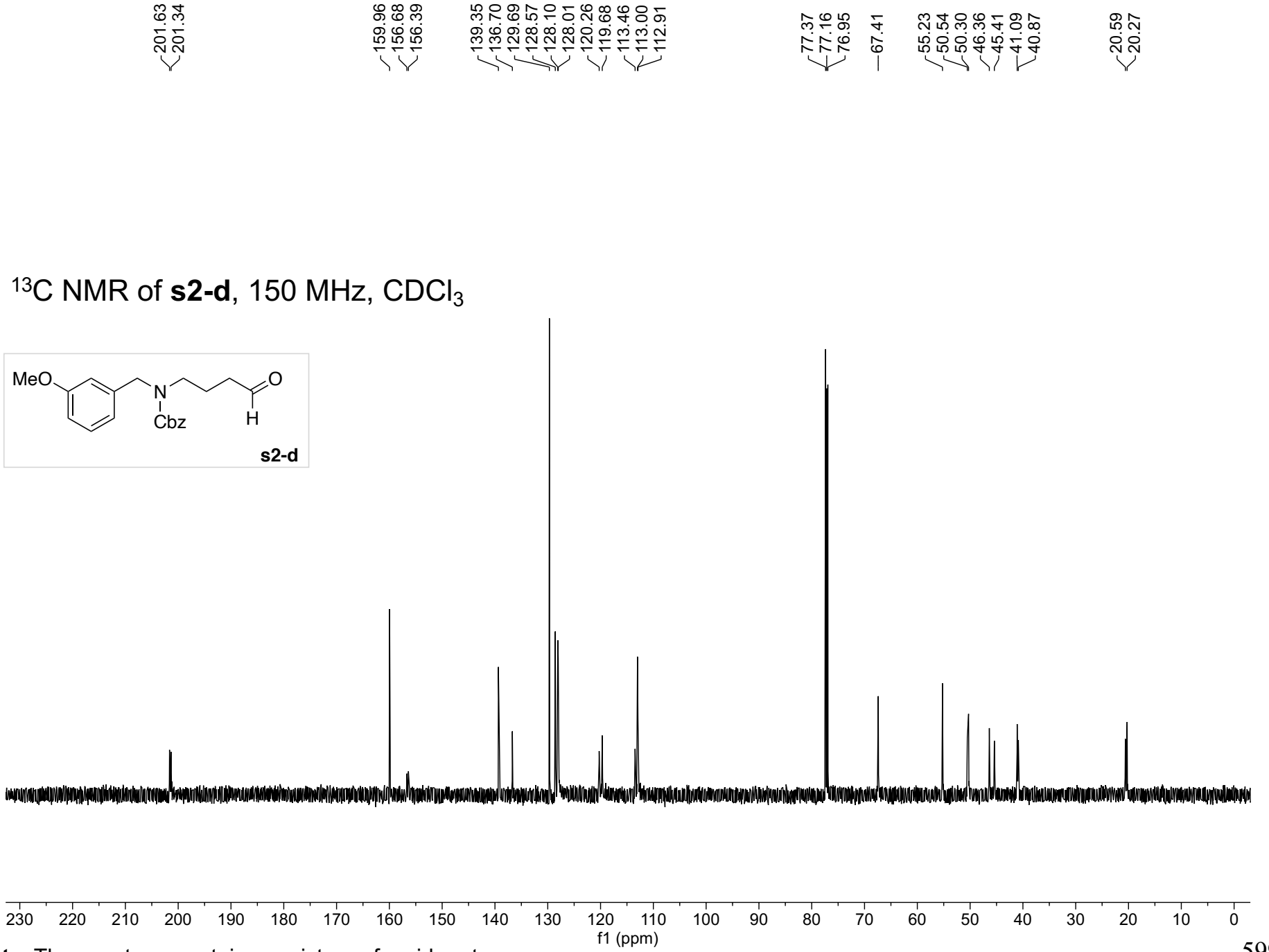
^{1}H NMR of **s2-d**, 600 MHz, $CDCl_3$



s2-d



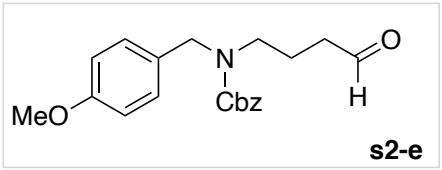
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **s2-d**, 150 MHz, $CDCl_3$

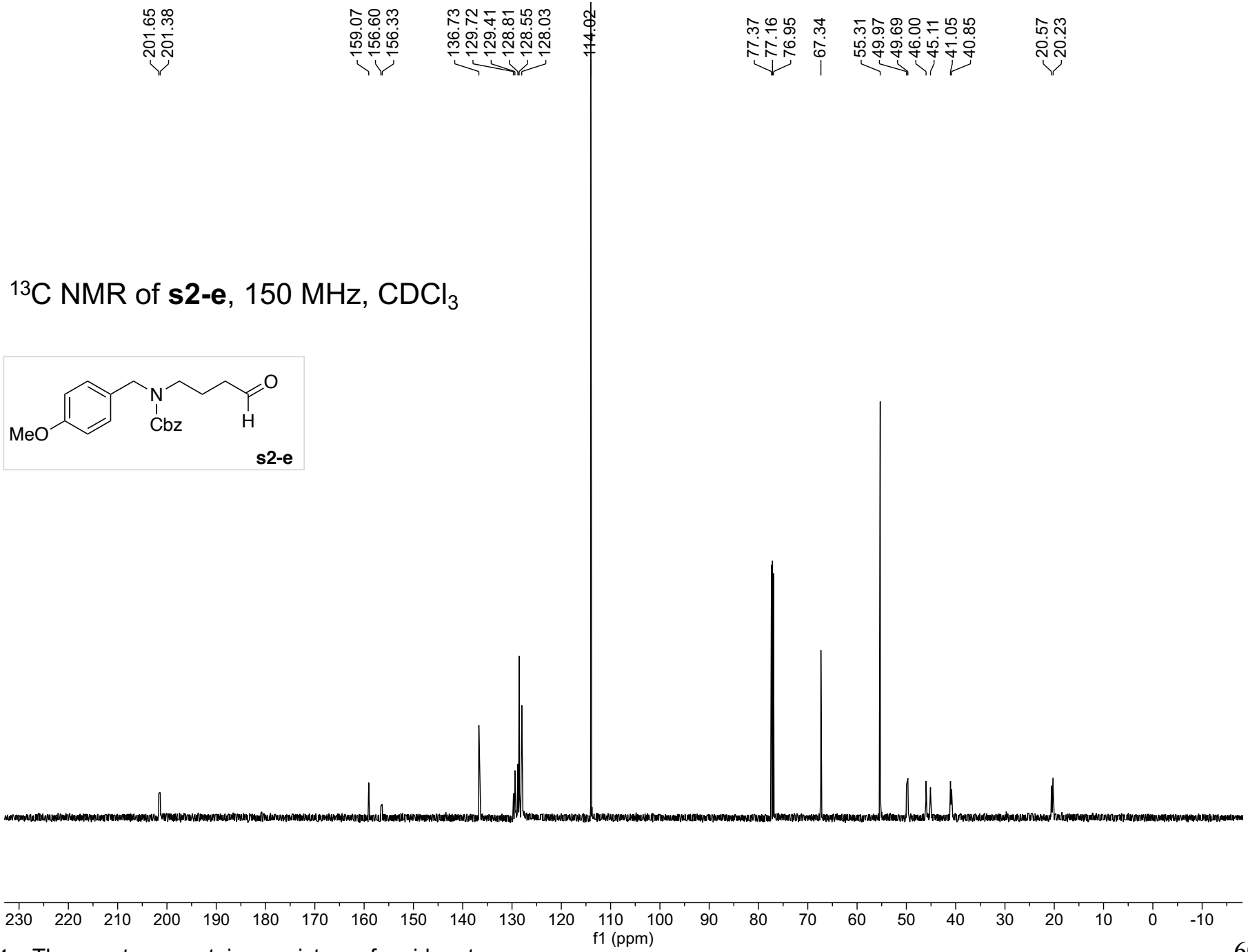
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **s2-e**, 600 MHz, $CDCl_3$



s2-e

Note: The spectrum contains a mixture of amide rotamers.

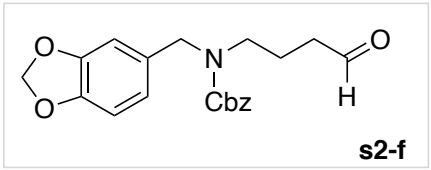


^{13}C NMR of **s2-e**, 150 MHz, $CDCl_3$

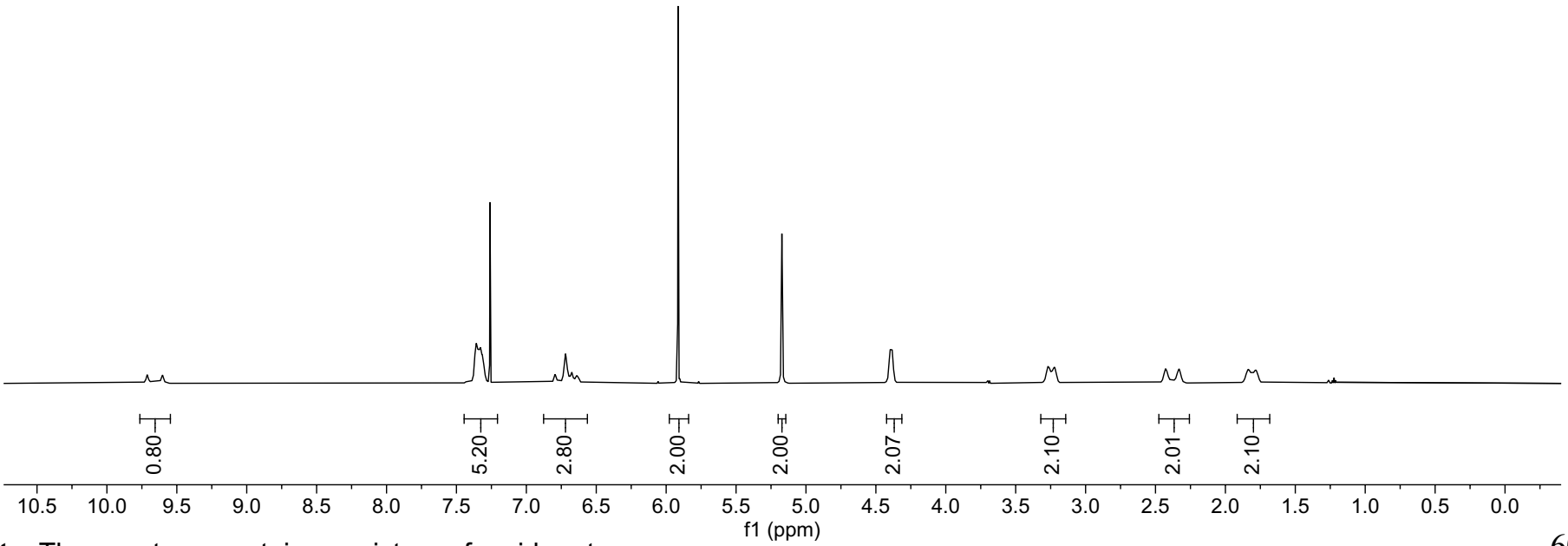
s2-e

Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **s2-f,** 600 MHz, $CDCl_3$



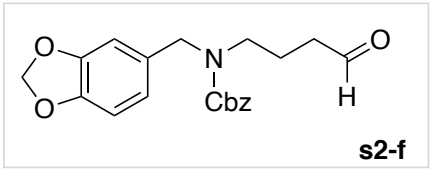
s2-f



Note: The spectrum contains a mixture of amide rotamers.

201.57
201.29
156.55
156.20
147.97
147.01
136.62
131.50
128.54
128.11
128.00
121.33
120.81
108.49
108.17
107.98
101.07
77.37
77.16
76.95
67.38
50.31
50.01
45.96
45.11
41.01
40.81
20.53
20.17

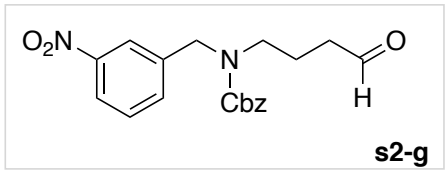
^{13}C NMR of **s2-f**, 150 MHz, $CDCl_3$



s2-f

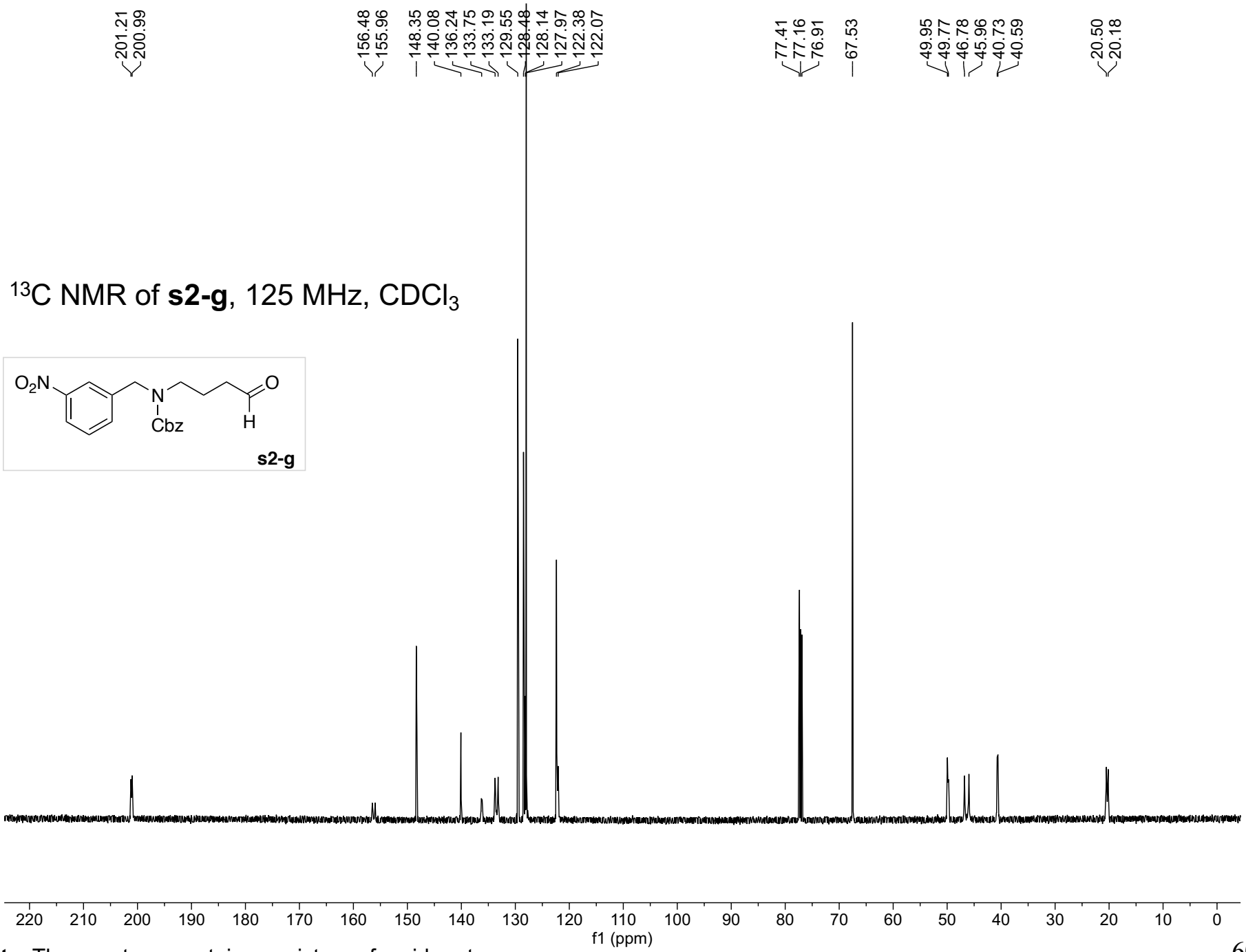
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **s2-g**, 500 MHz, $CDCl_3$

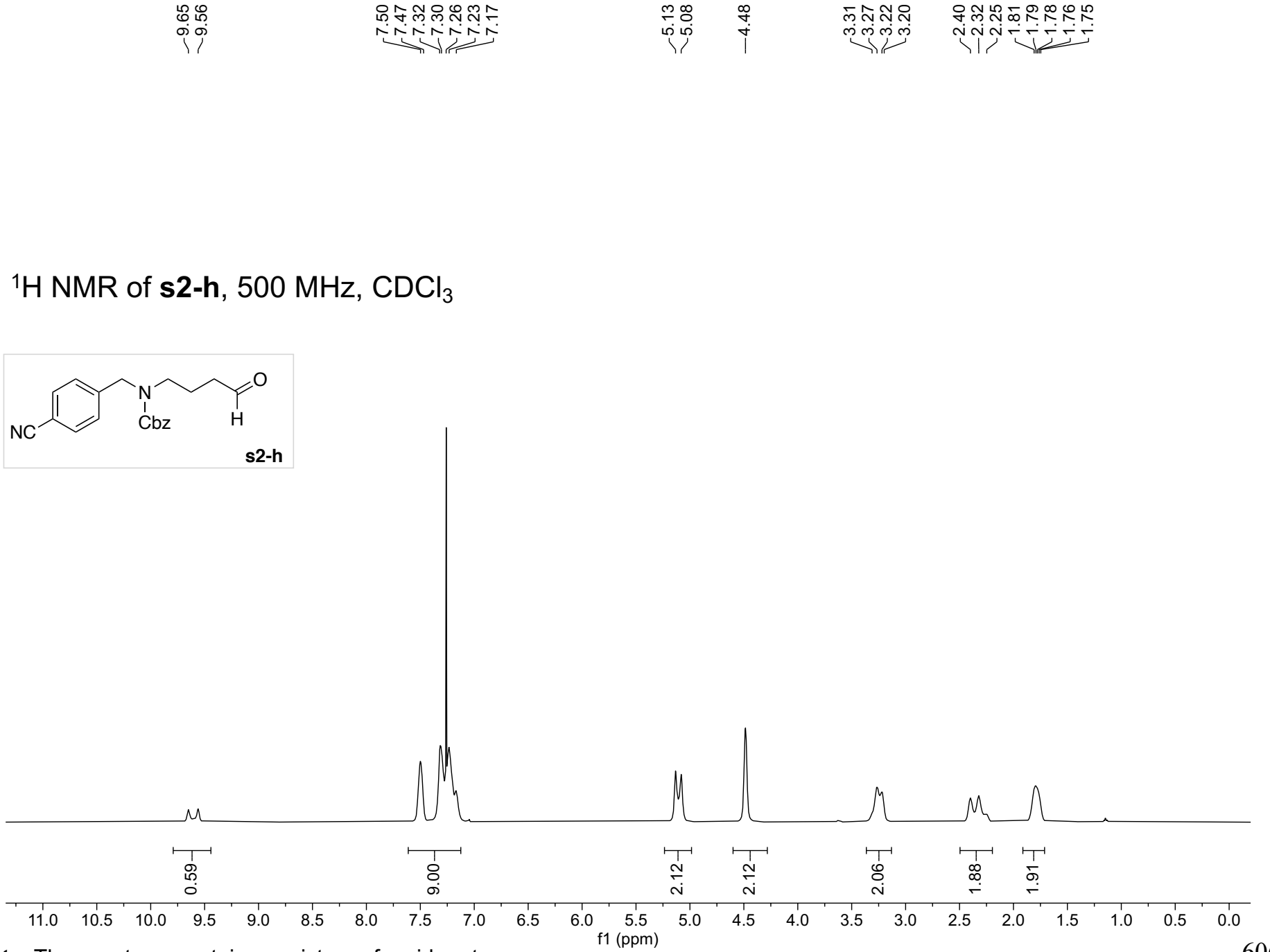


s2-g

Note: The spectrum contains a mixture of amide rotamers.

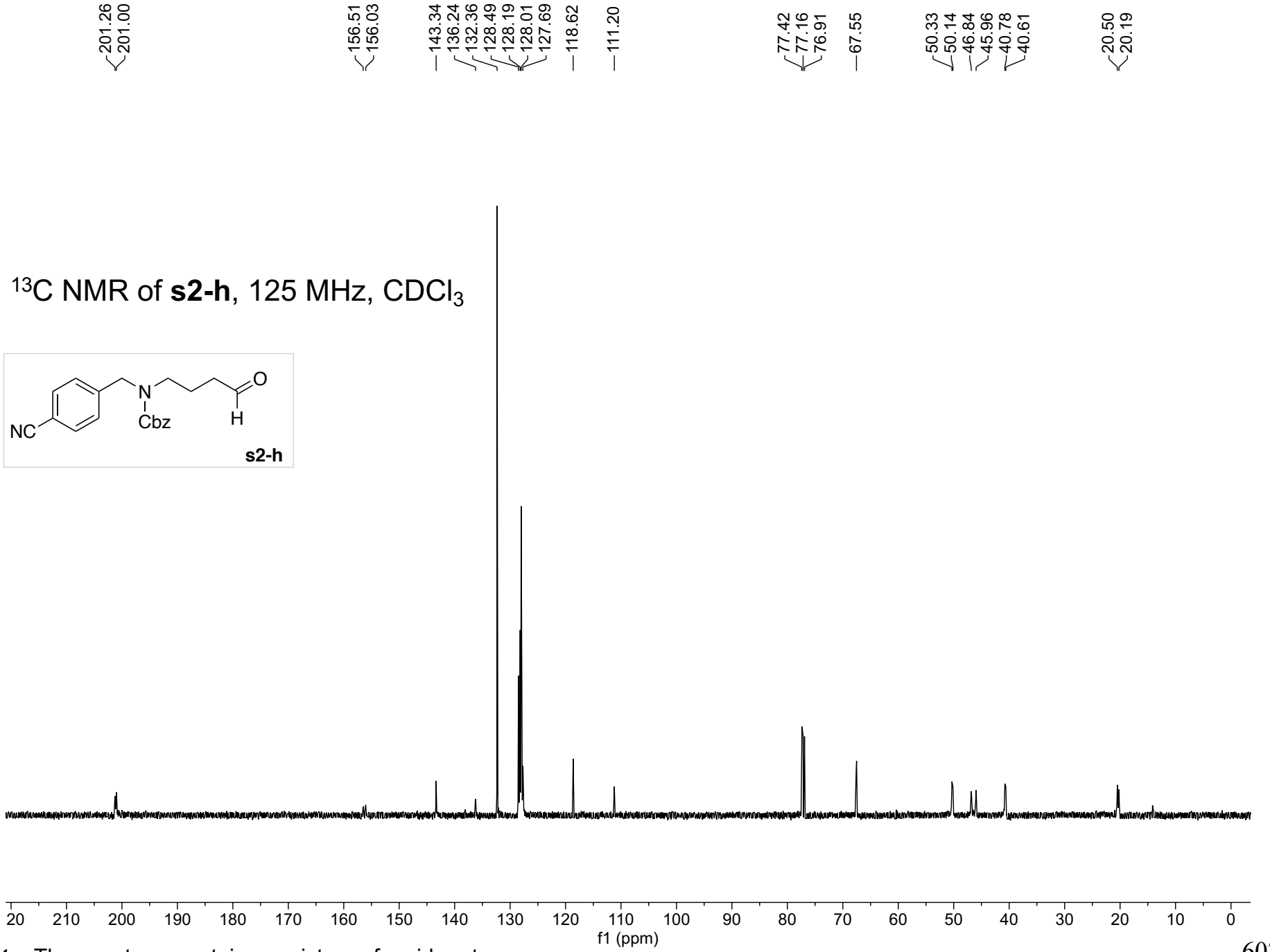


Note: The spectrum contains a mixture of amide rotamers.

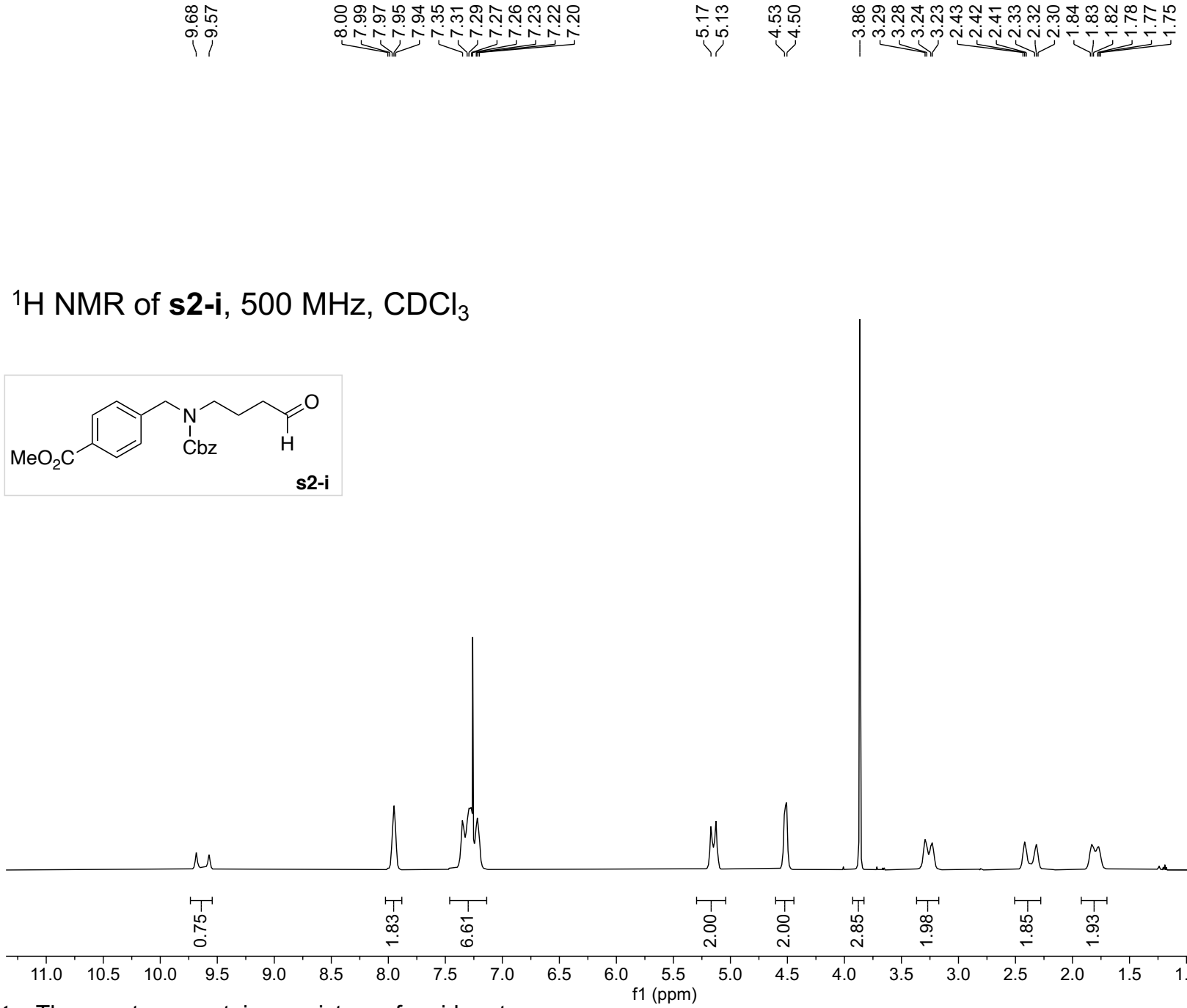


^{1}H NMR of **s2-h**, 500 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

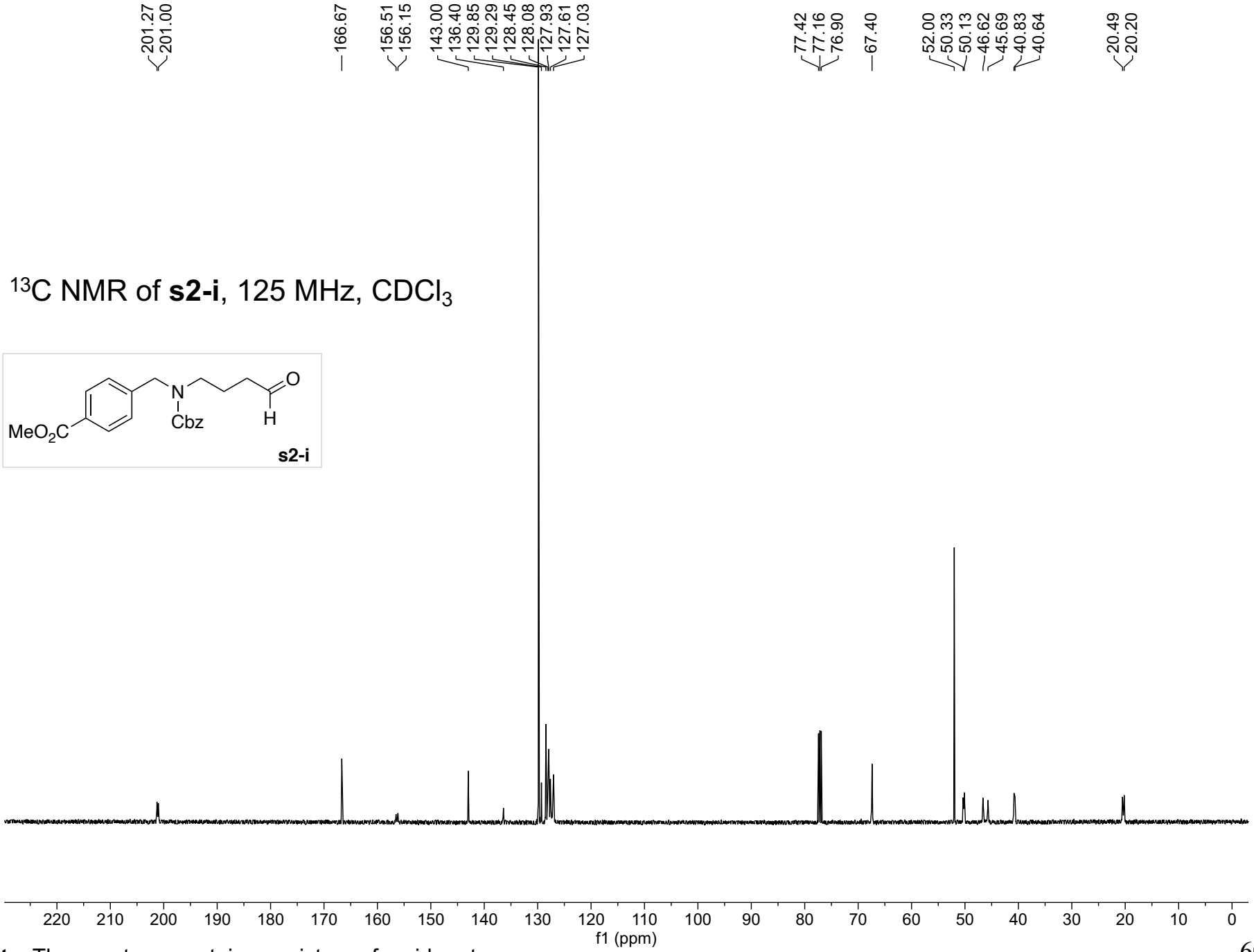


Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-i**, 500 MHz, $CDCl_3$

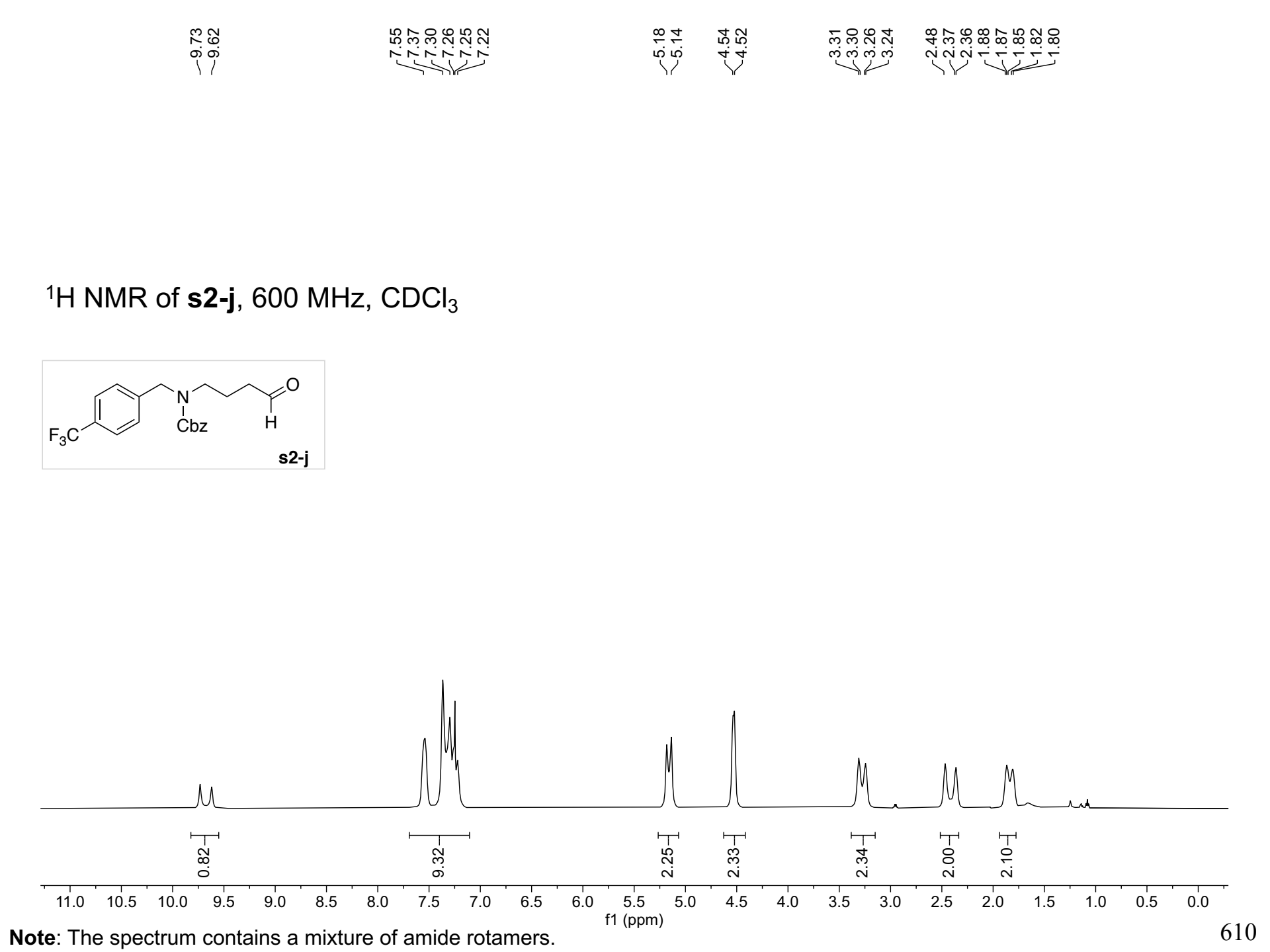
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **s2-i**, 125 MHz, $CDCl_3$

s2-i

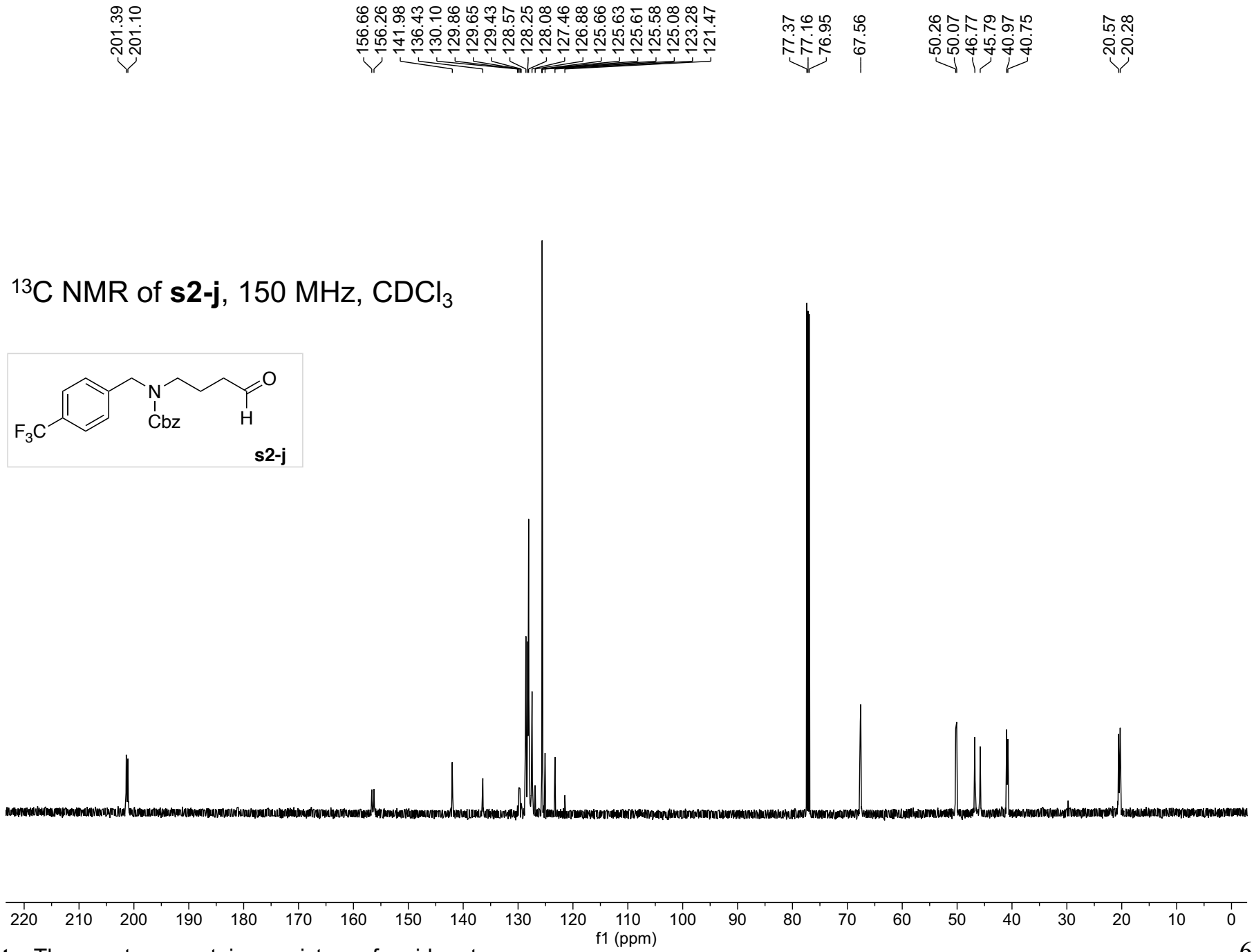
Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-j**, 600 MHz, $CDCl_3$

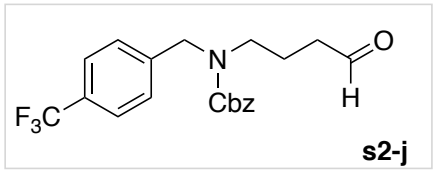
s2-j

Note: The spectrum contains a mixture of amide rotamers.



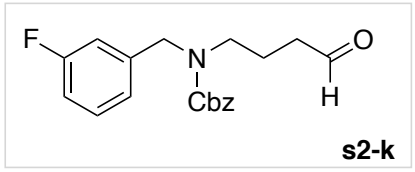
Note: The spectrum contains a mixture of amide rotamers.

^{19}F NMR of **s2-j**, 564 MHz, $CDCl_3$

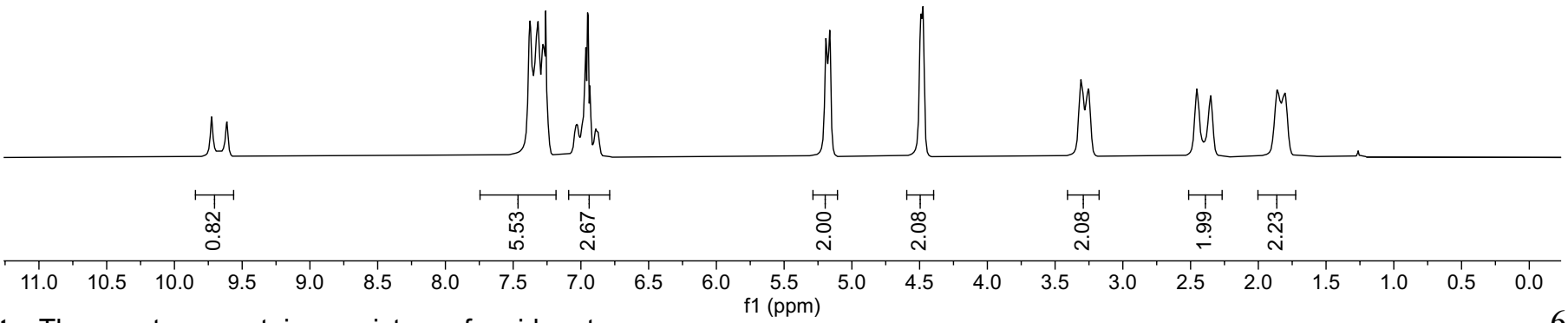


s2-j

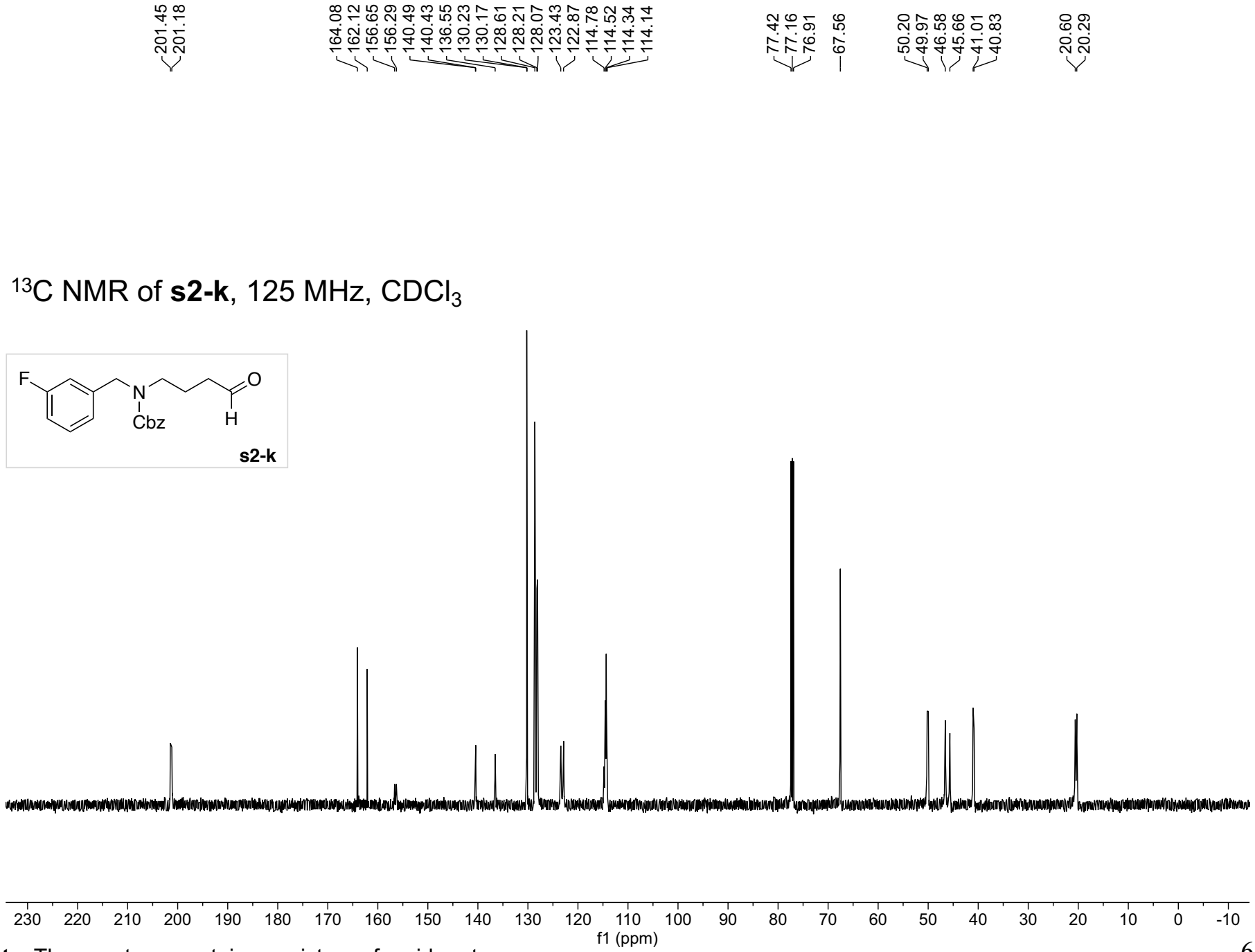
^{1}H NMR of **s2-k**, 500 MHz, $CDCl_3$



s2-k



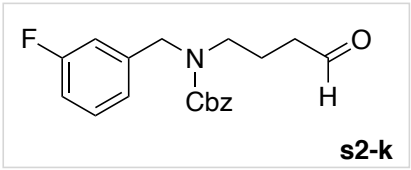
Note: The spectrum contains a mixture of amide rotamers.



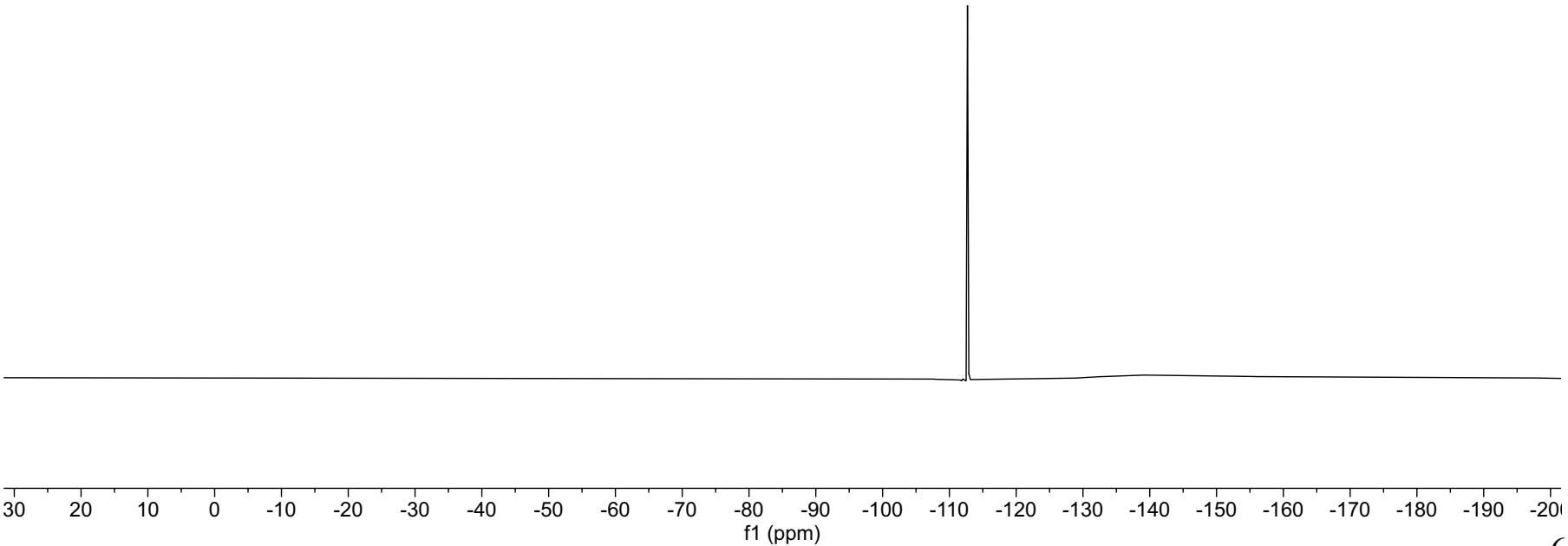
^{13}C NMR of **s2-k**, 125 MHz, $CDCl_3$

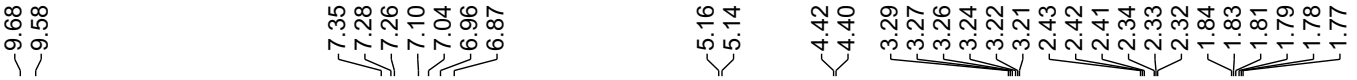
Note: The spectrum contains a mixture of amide rotamers.

^{19}F NMR of **s2-k**, 564 MHz, $CDCl_3$

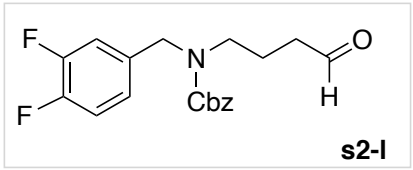


s2-k

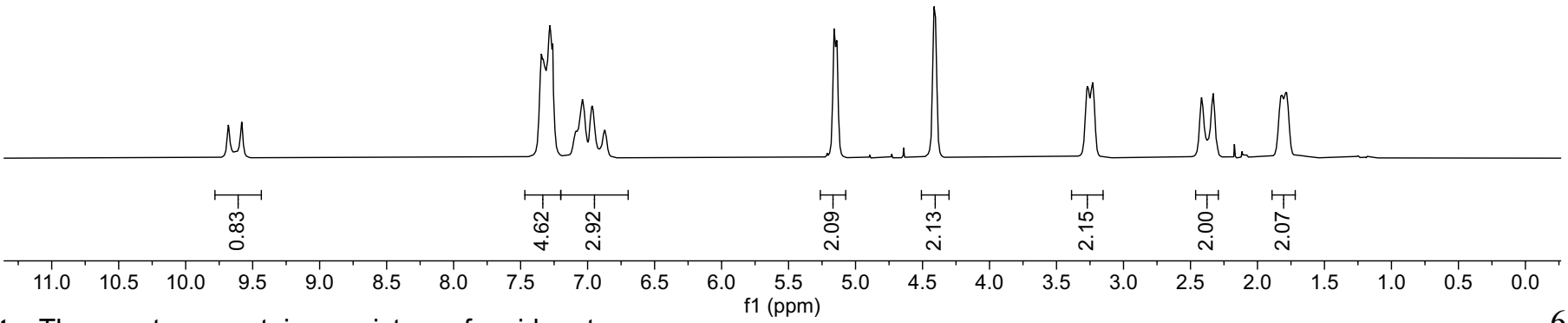




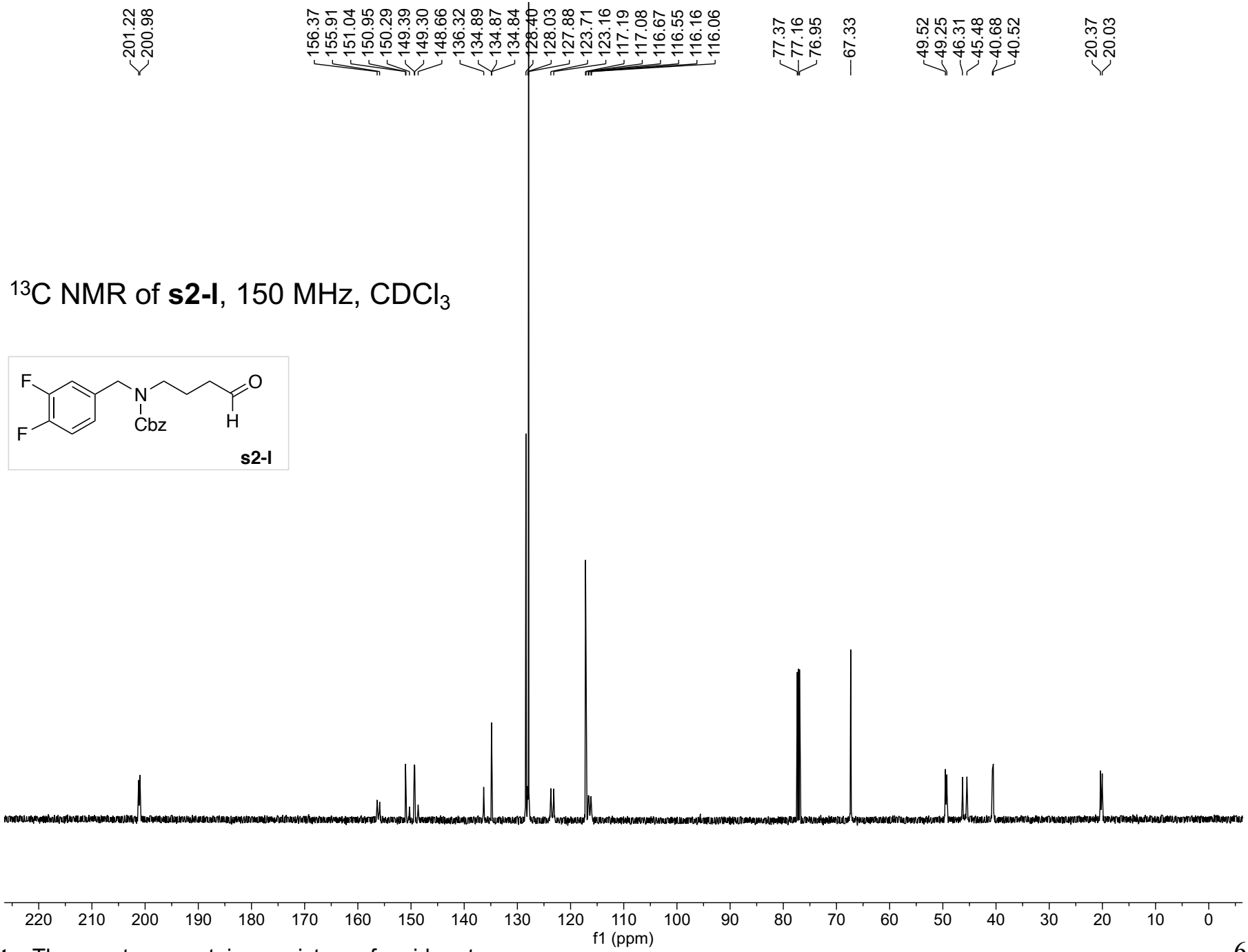
^{1}H NMR of **s2-I**, 600 MHz, $CDCl_3$



s2-I



Note: The spectrum contains a mixture of amide rotamers.



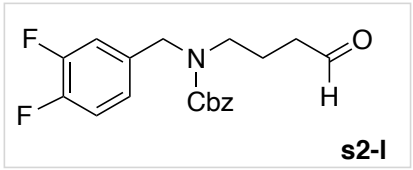
^{13}C NMR of **s2-I**, 150 MHz, $CDCl_3$

s2-I

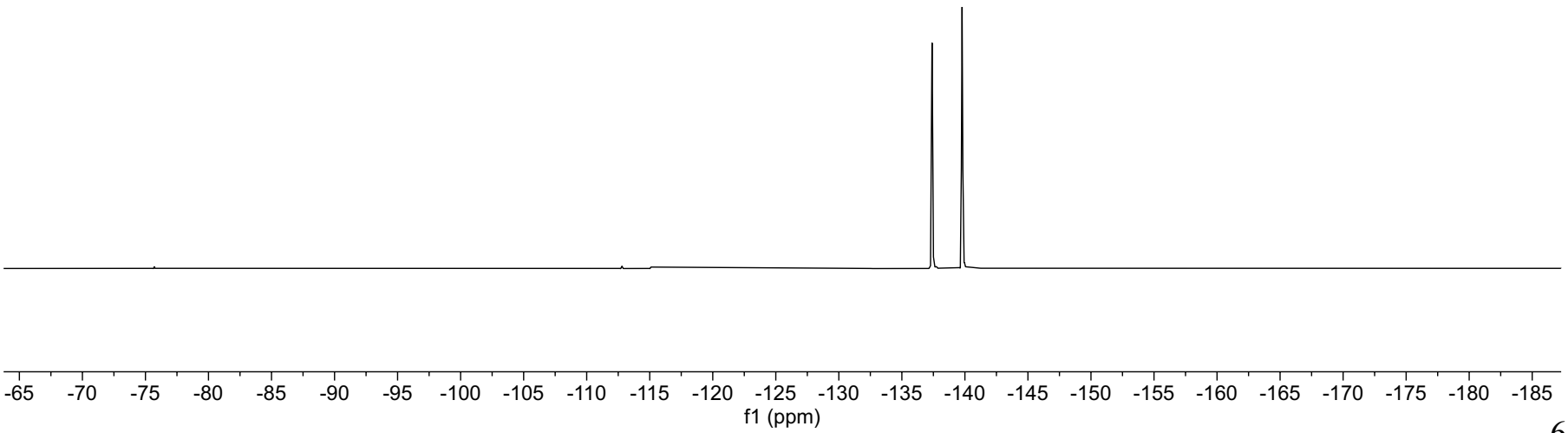
Note: The spectrum contains a mixture of amide rotamers.

-137.38
-139.78

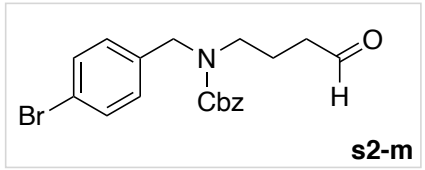
^{19}F NMR of **s2-I**, 470 MHz, $CDCl_3$

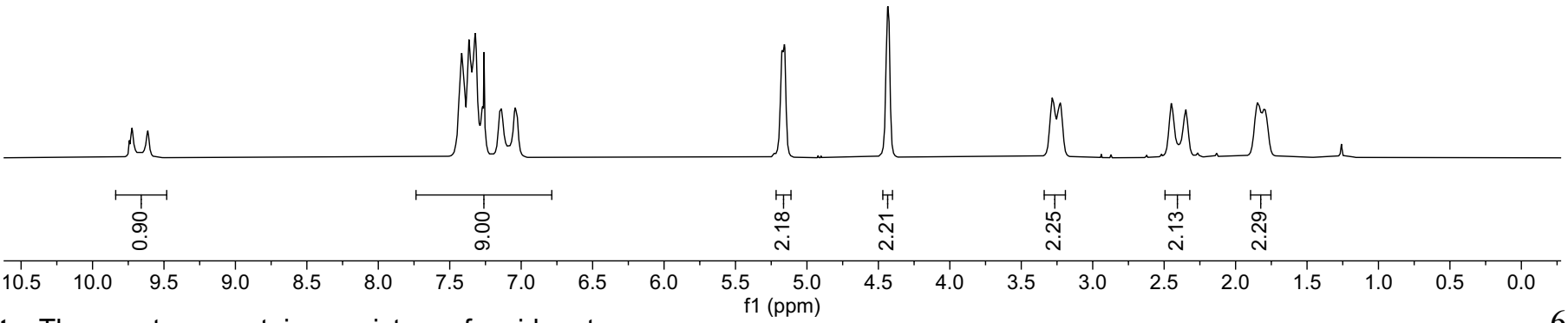


s2-I

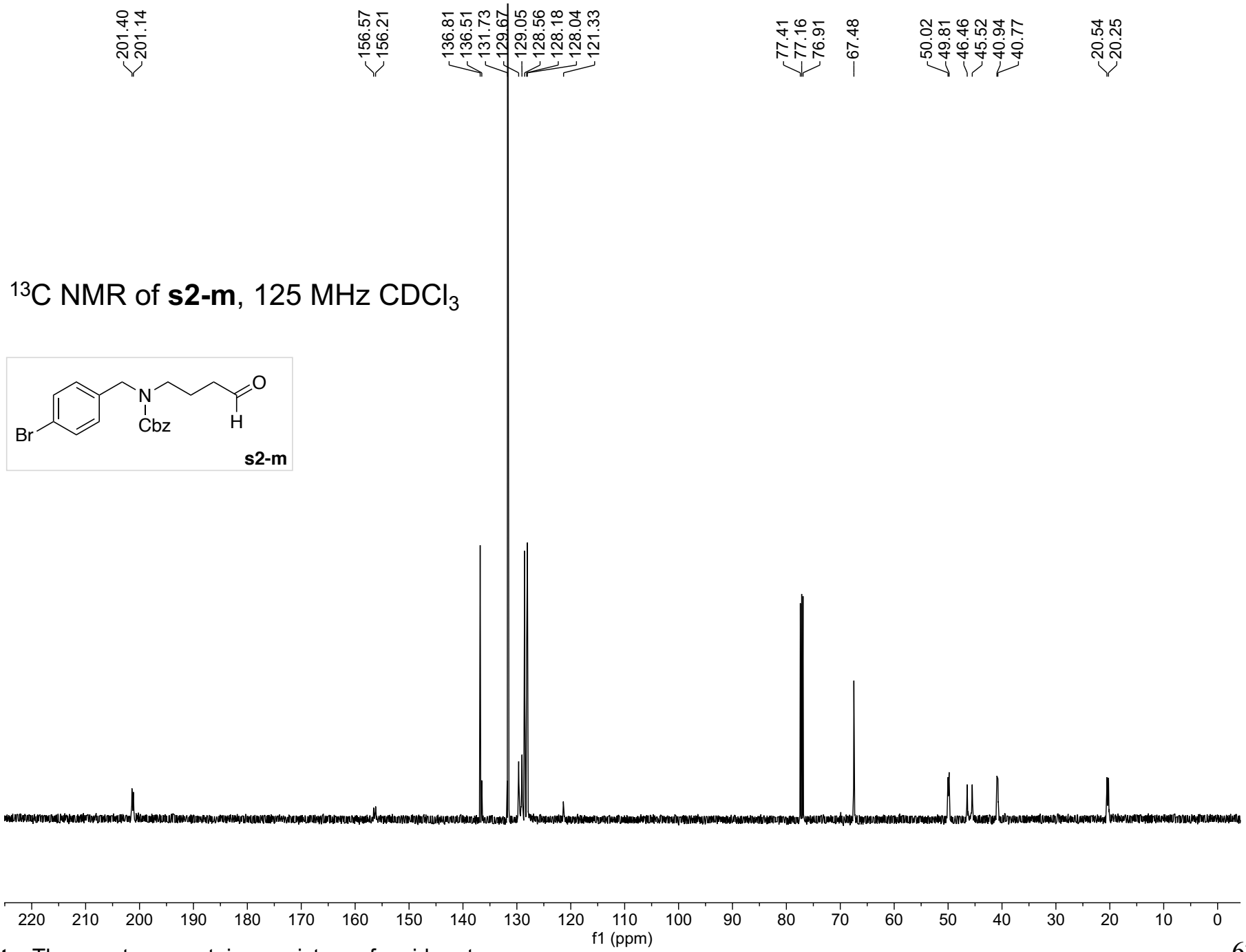


^{1}H NMR of **s2-m**, 500 MHz, $CDCl_3$





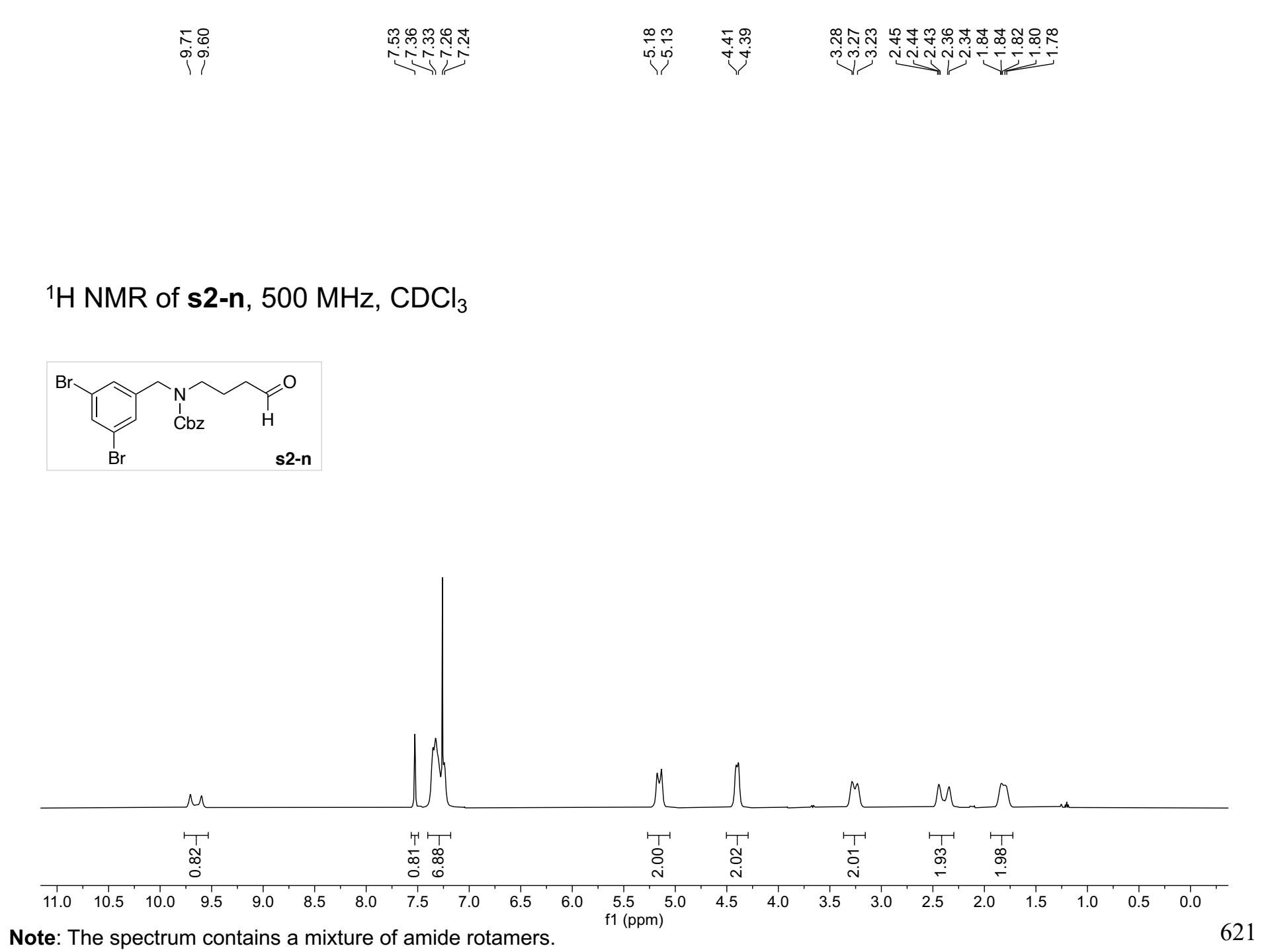
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **s2-m**, 125 MHz $CDCl_3$

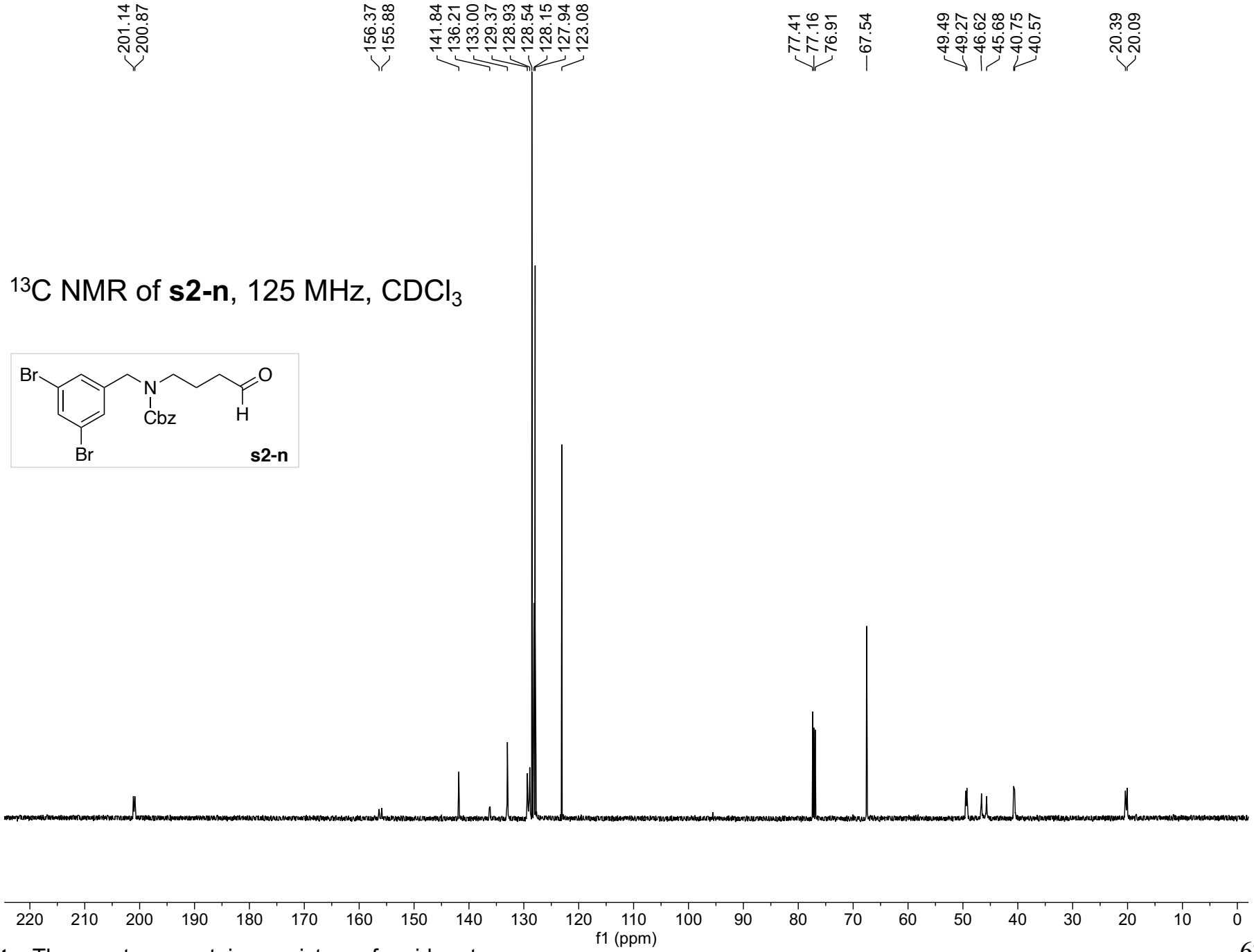
s2-m

Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-n**, 500 MHz, $CDCl_3$

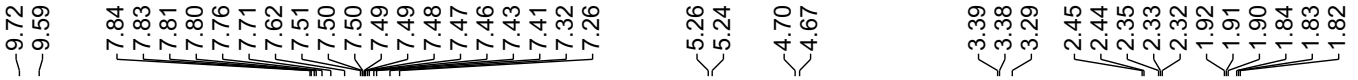
Note: The spectrum contains a mixture of amide rotamers.



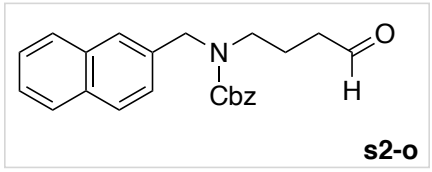
^{13}C NMR of **s2-n**, 125 MHz, $CDCl_3$

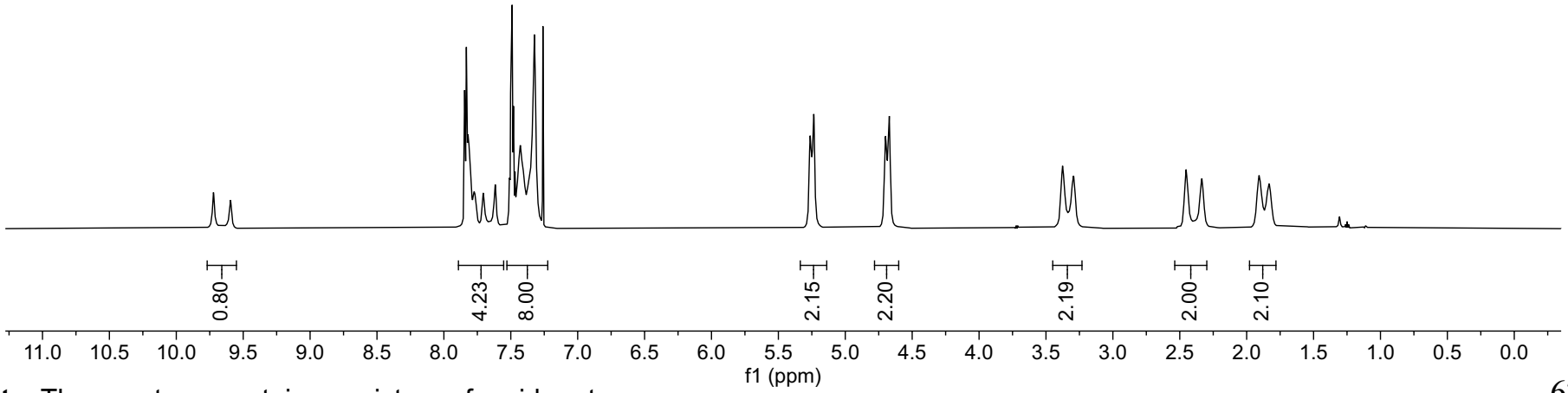
s2-n

Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-o**, 600 MHz, $CDCl_3$

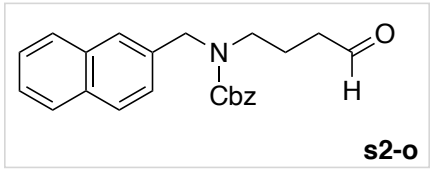




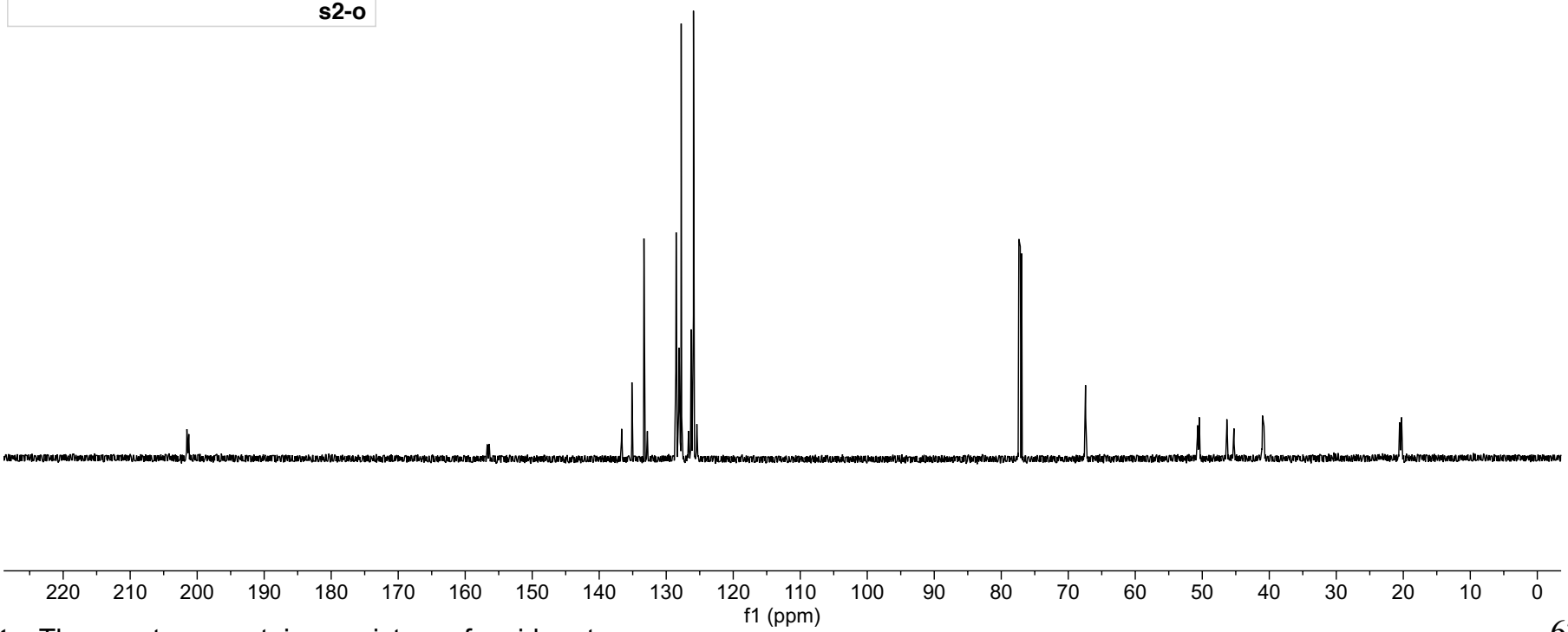
Note: The spectrum contains a mixture of amide rotamers.

201.53
201.25
156.71
156.41
136.66
135.12
133.32
132.83
128.52
128.05
127.76
127.71
126.67
126.29
126.00
125.94
125.42
77.37
77.16
76.95
67.43
50.70
50.44
46.33
45.28
41.01
40.79
20.54
20.26

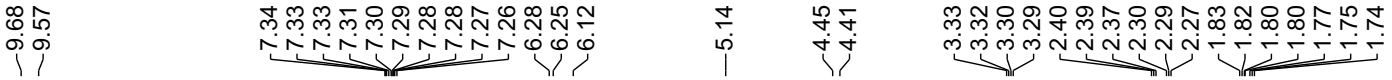
^{13}C NMR of **s2-o**, 150 MHz, $CDCl_3$



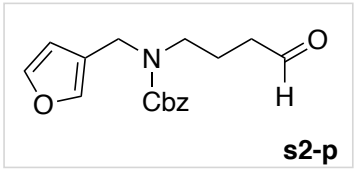
s2-o



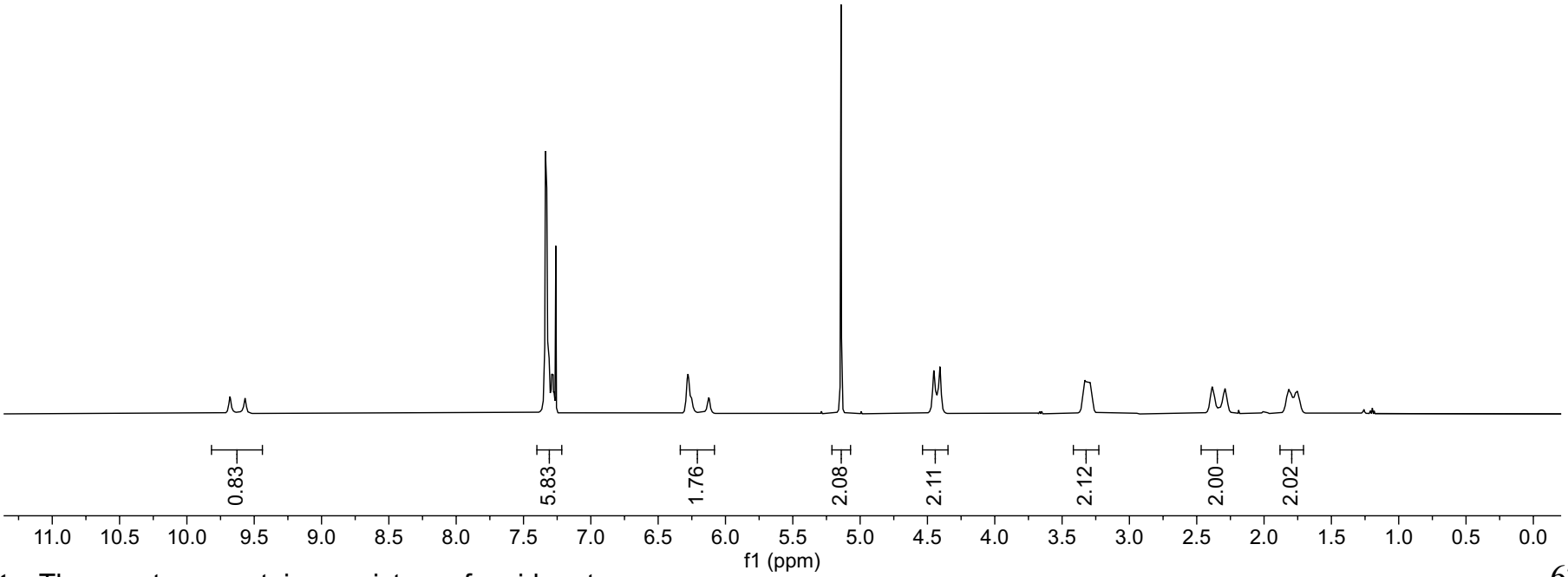
Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-p**, 500 MHz, $CDCl_3$



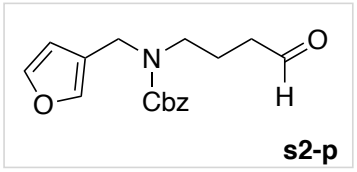
s2-p



Note: The spectrum contains a mixture of amide rotamers.

201.43
201.19
155.96
151.08
142.06
136.51
128.38
127.92
127.73
110.32
108.42
107.95
77.42
77.16
76.90
67.22
46.39
45.61
43.53
43.44
40.77
40.58
20.52
20.21

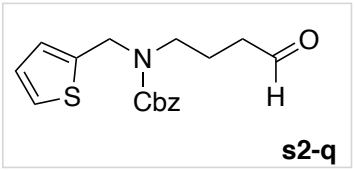
^{13}C NMR of **s2-p**, 125 MHz, $CDCl_3$



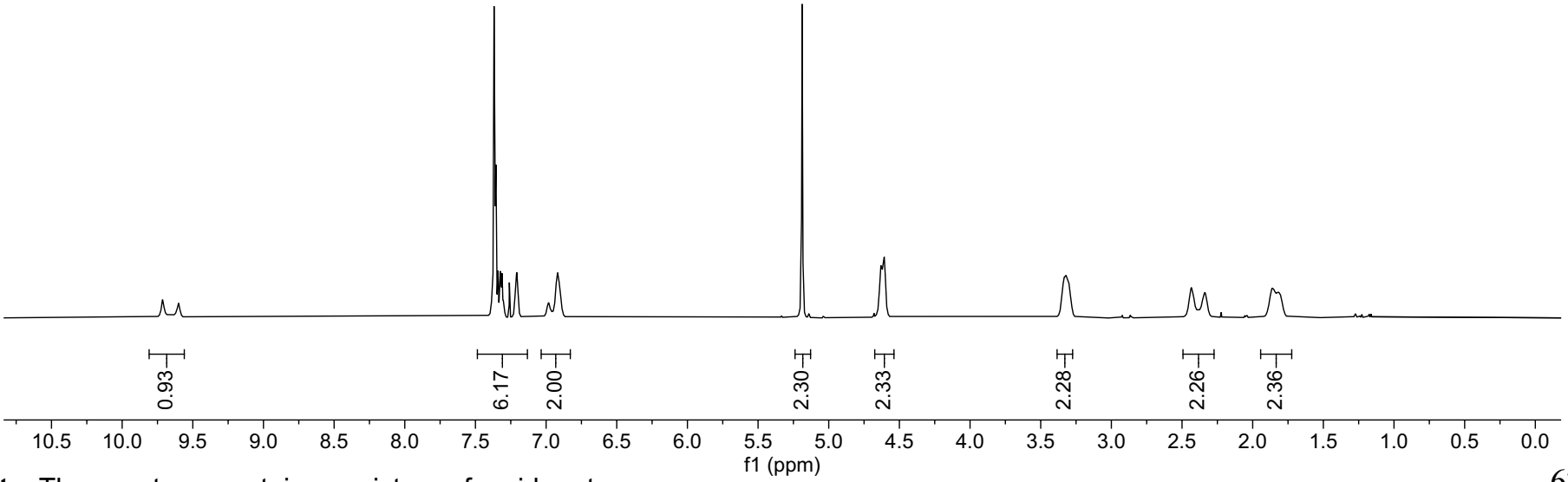
s2-p

Note: The spectrum contains a mixture of amide rotamers.

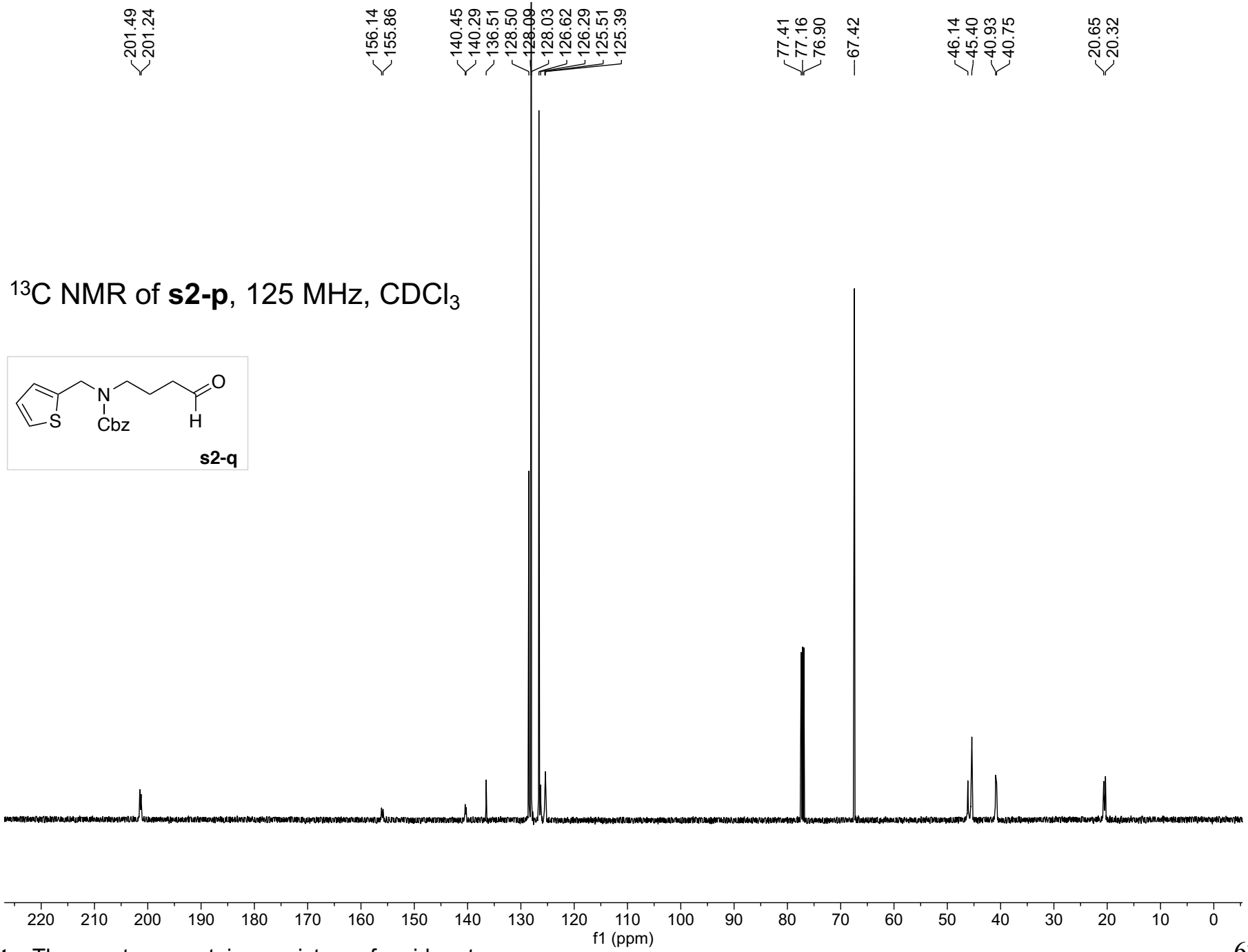
^{1}H NMR of **s2-q**, 500 MHz, $CDCl_3$



s2-q



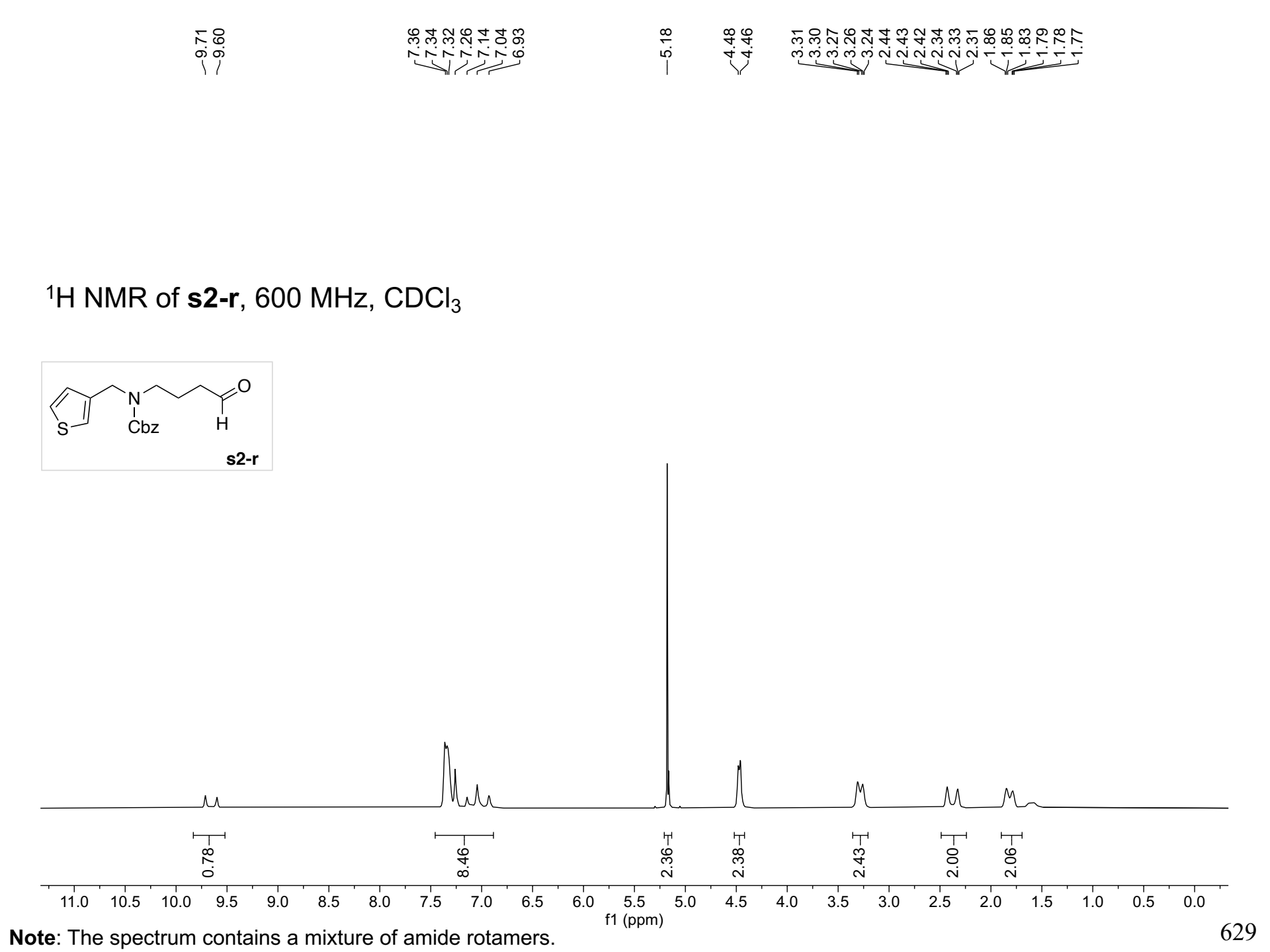
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **s2-p**, 125 MHz, $CDCl_3$

s2-q

Note: The spectrum contains a mixture of amide rotamers.

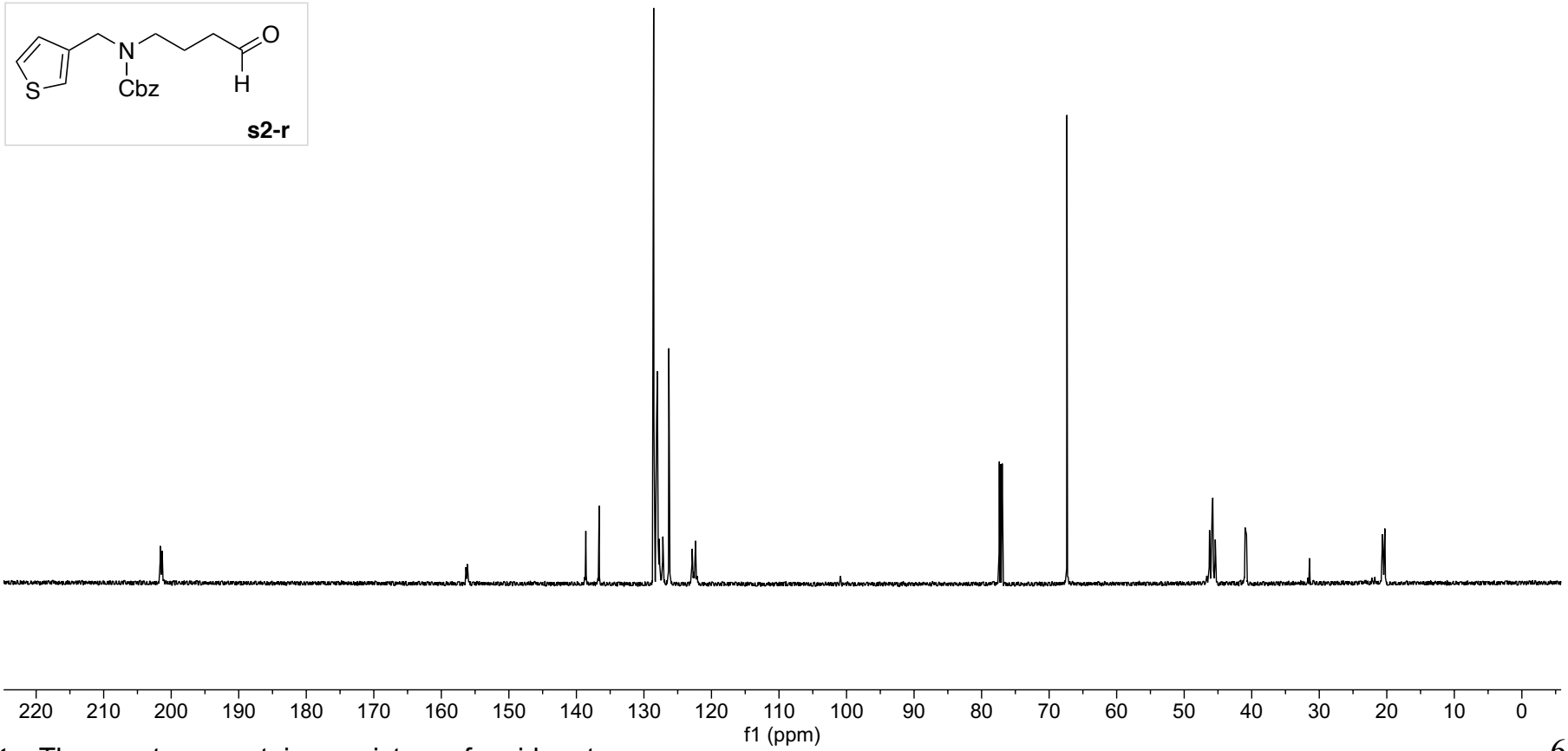


^{1}H NMR of **s2-r**, 600 MHz, $CDCl_3$

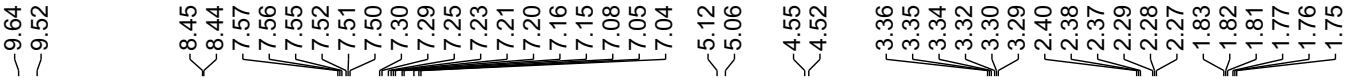
Note: The spectrum contains a mixture of amide rotamers.

201.61
201.34
156.35
156.14
138.60
136.63
128.56
128.12
128.01
127.72
127.19
126.31
122.86
122.36
77.40
77.16
76.94
67.36
46.25
45.86
45.77
45.40
40.98
40.78
20.63
20.29

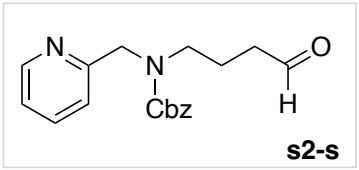
^{13}C NMR of **s2-r**, 150 MHz, $CDCl_3$



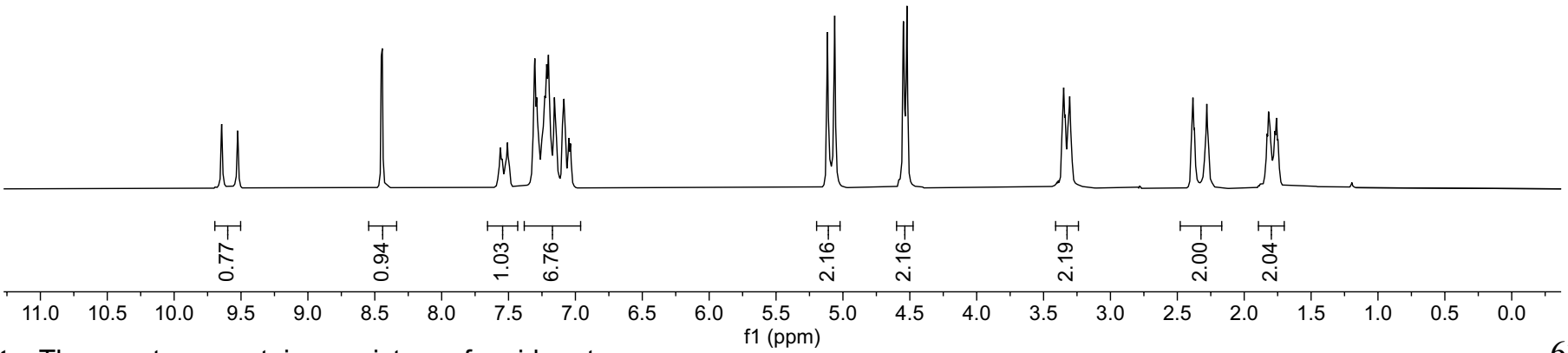
Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **s2-s**, 600 MHz, $CDCl_3$



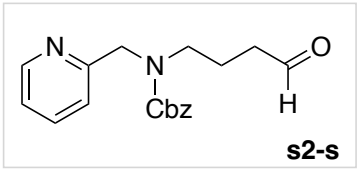
s2-s



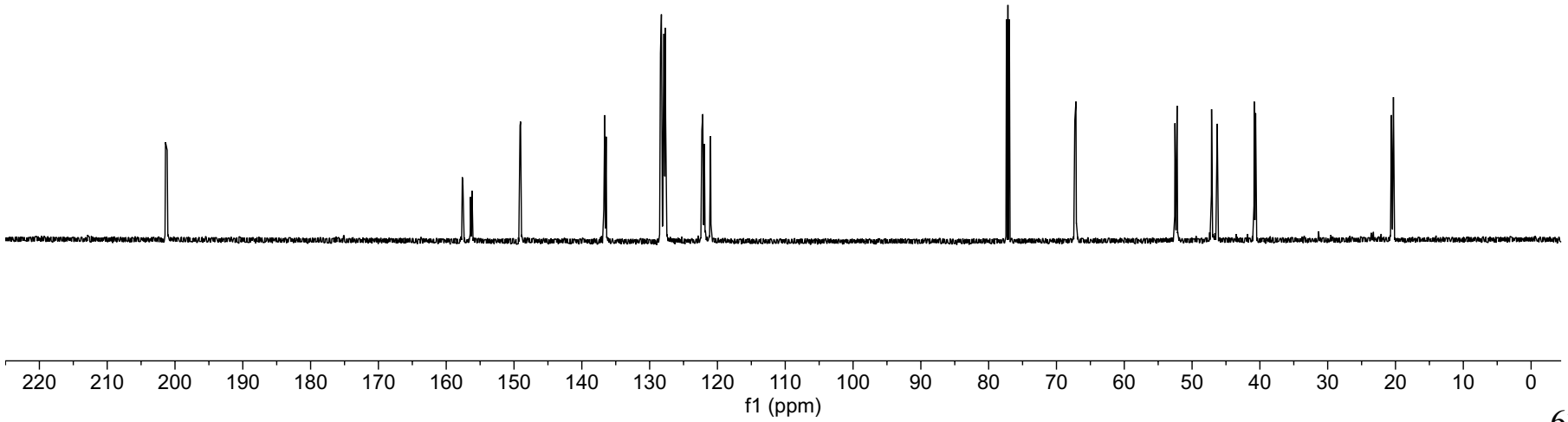
Note: The spectrum contains a mixture of amide rotamers.

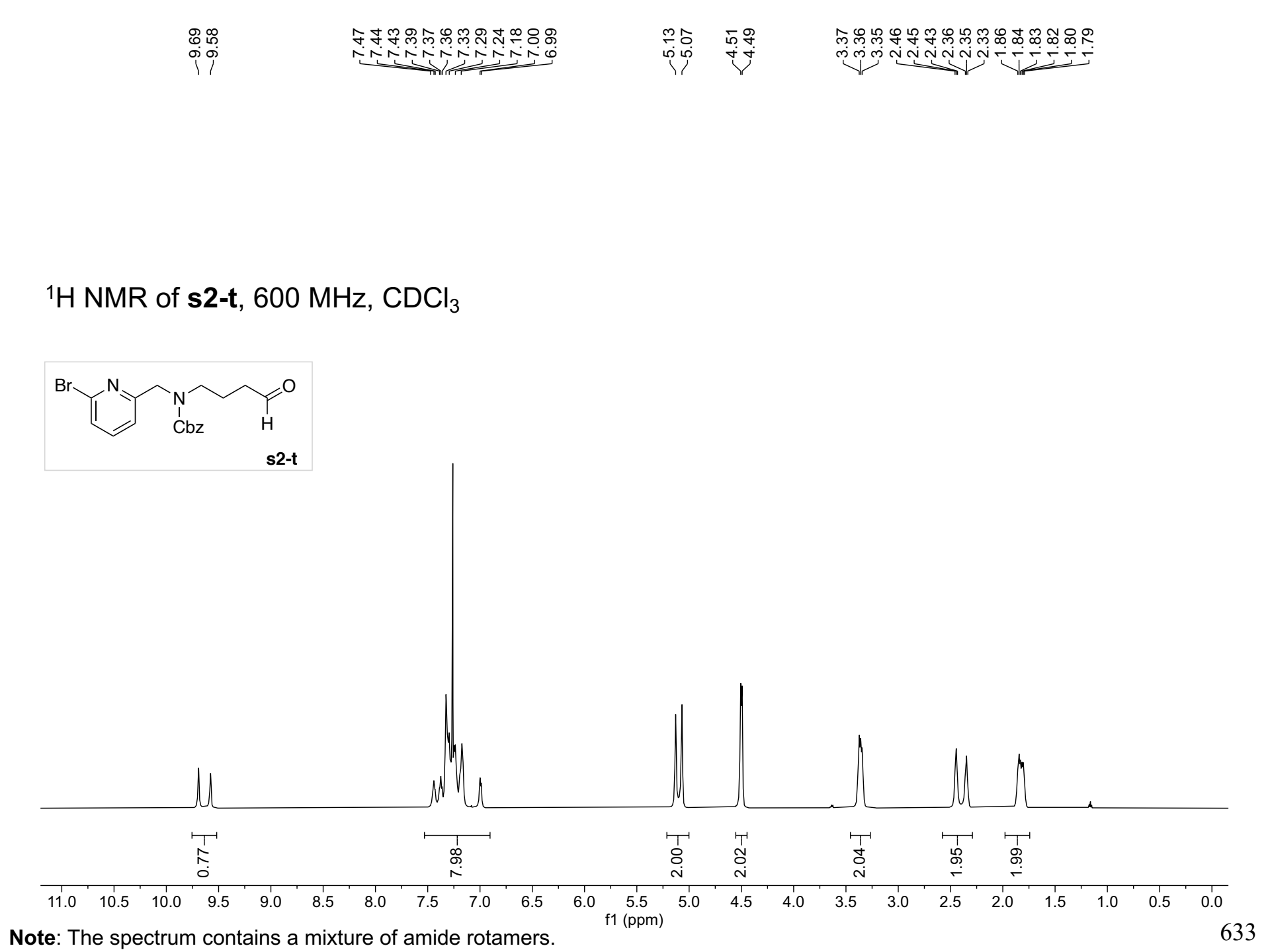
201.40
201.16
157.63
157.54
156.41
156.20
149.11
149.04
136.72
136.62
136.41
128.40
128.27
128.00
127.90
127.83
127.69
122.30
122.16
121.93
121.01
77.37
77.16
76.95
67.30
67.13
52.52
52.22
47.12
46.29
40.84
40.63
20.60
20.31

^{13}C NMR of **s2-s**, 150 MHz, $CDCl_3$



s2-s



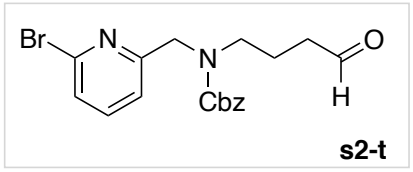


^{1}H NMR of **s2-t**, 600 MHz, $CDCl_3$

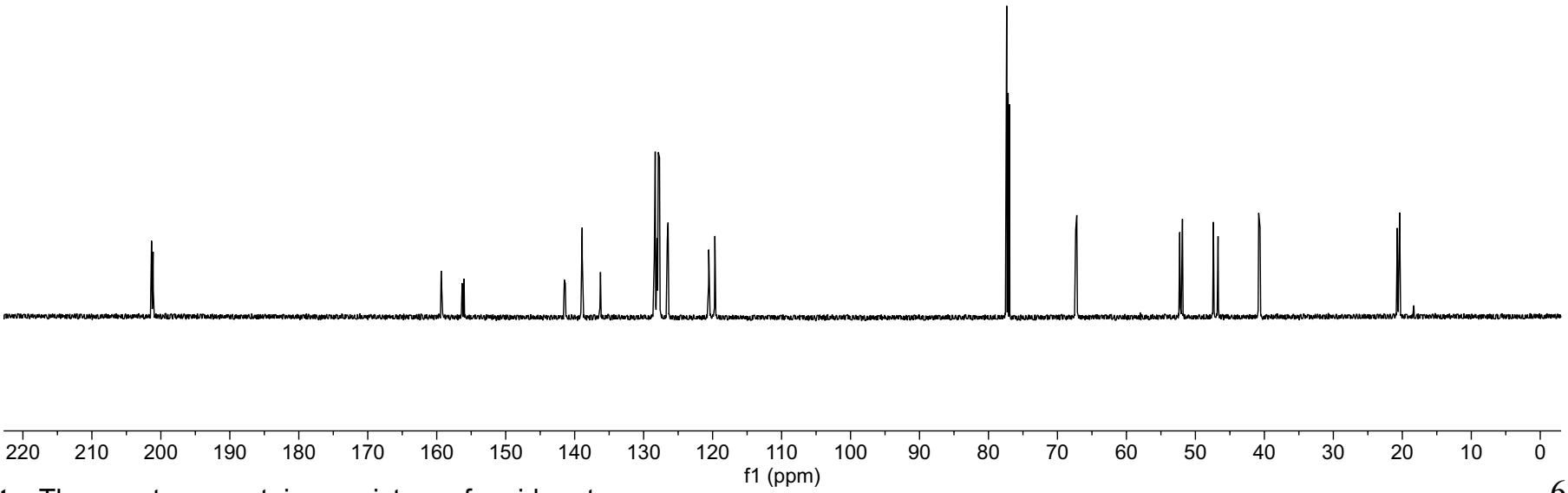
Note: The spectrum contains a mixture of amide rotamers.

201.35
201.13
159.35
159.20
156.31
156.03
141.50
141.36
139.03
138.91
136.31
136.26
128.44
128.32
128.05
127.87
127.70
126.56
126.46
120.56
119.67
77.36
77.16
76.95
67.36
67.20
52.27
51.88
47.39
46.71
40.82
40.63
20.72
20.39

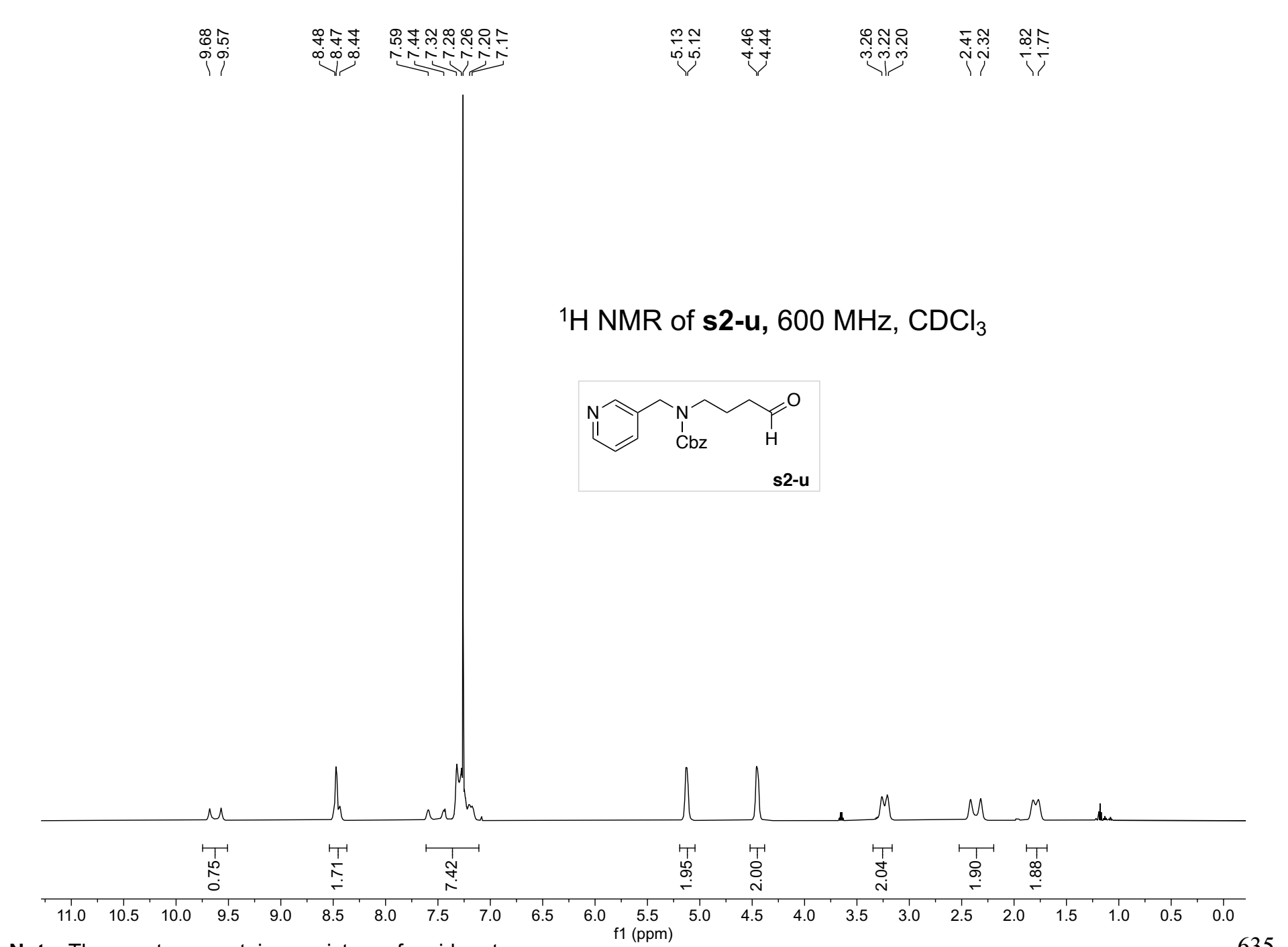
^{13}C NMR of **s2-t**, 150 MHz, $CDCl_3$



s2-t



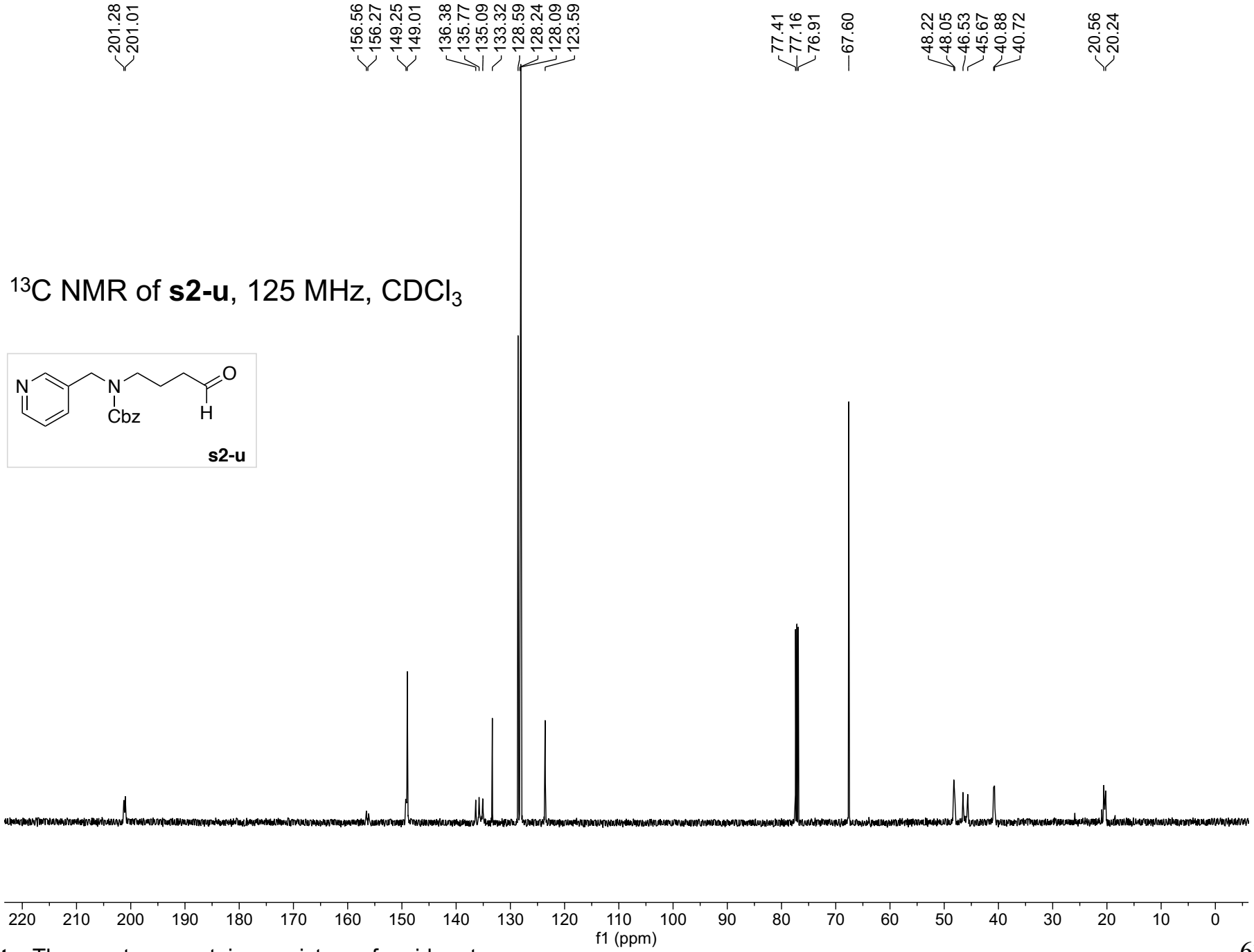
Note: The spectrum contains a mixture of amide rotamers.



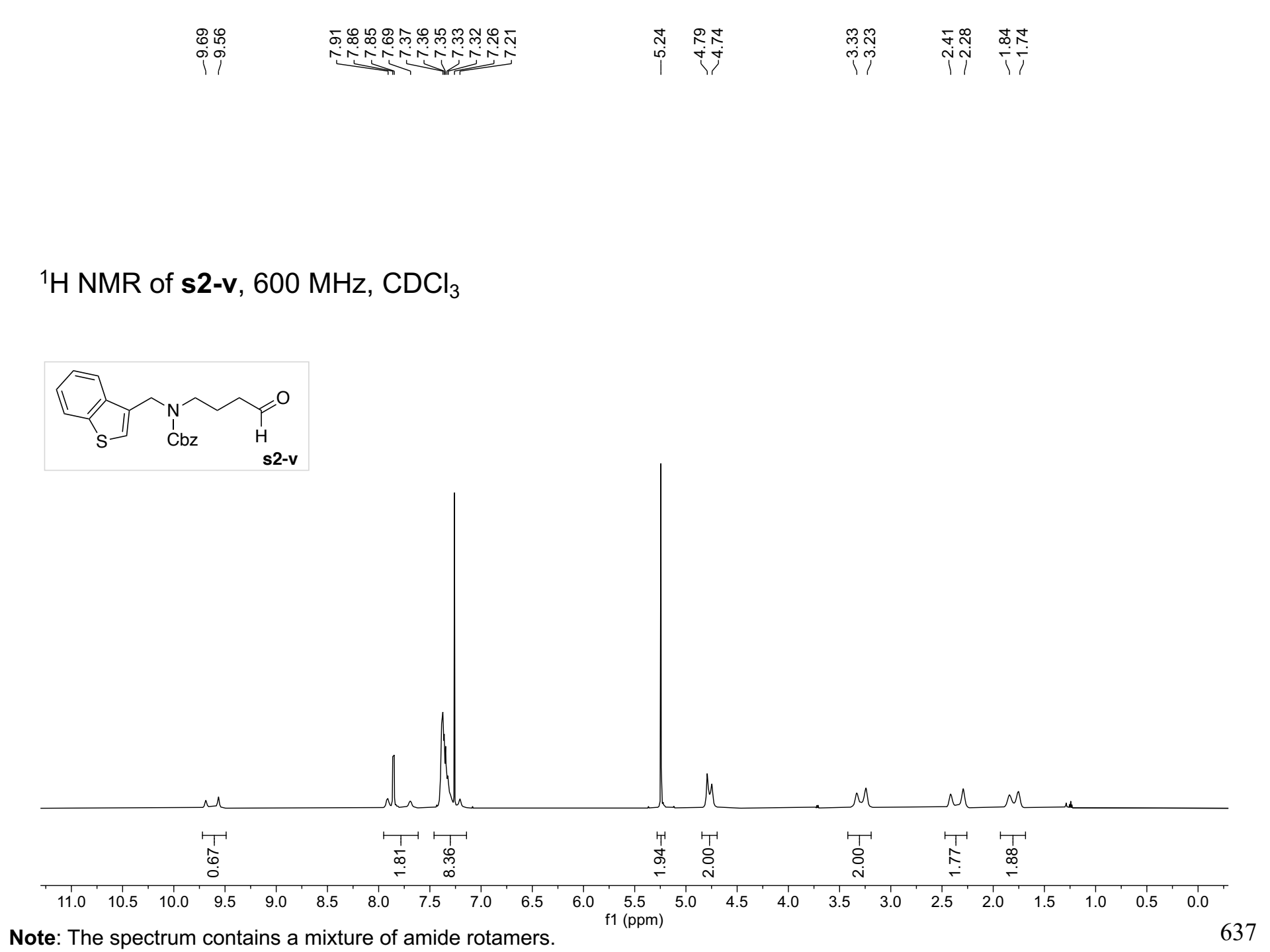
^{1}H NMR of **s2-u,** 600 MHz, $CDCl_3$

s2-u

Note: The spectrum contains a mixture of amide rotamers.

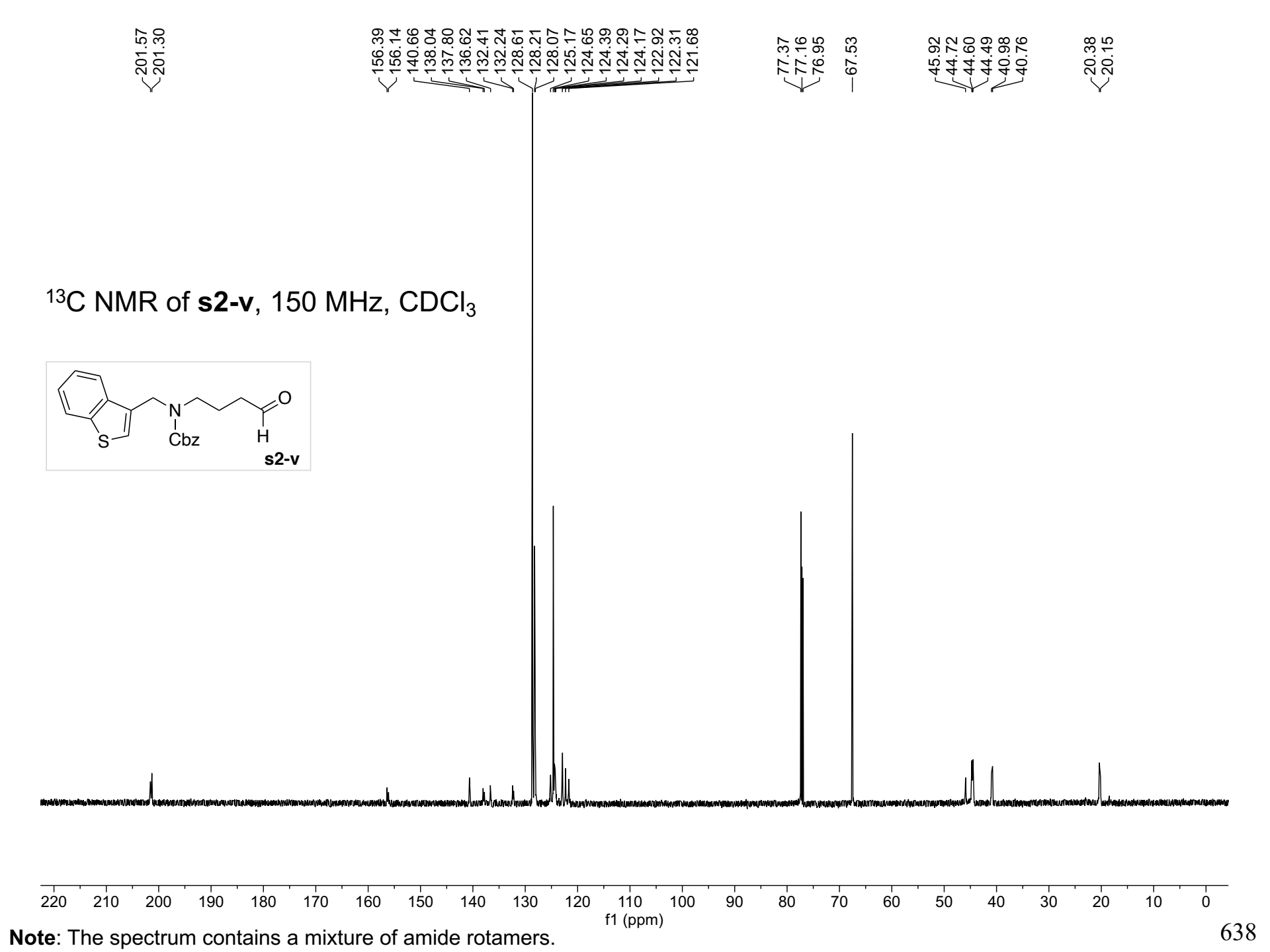


Note: The spectrum contains a mixture of amide rotamers.

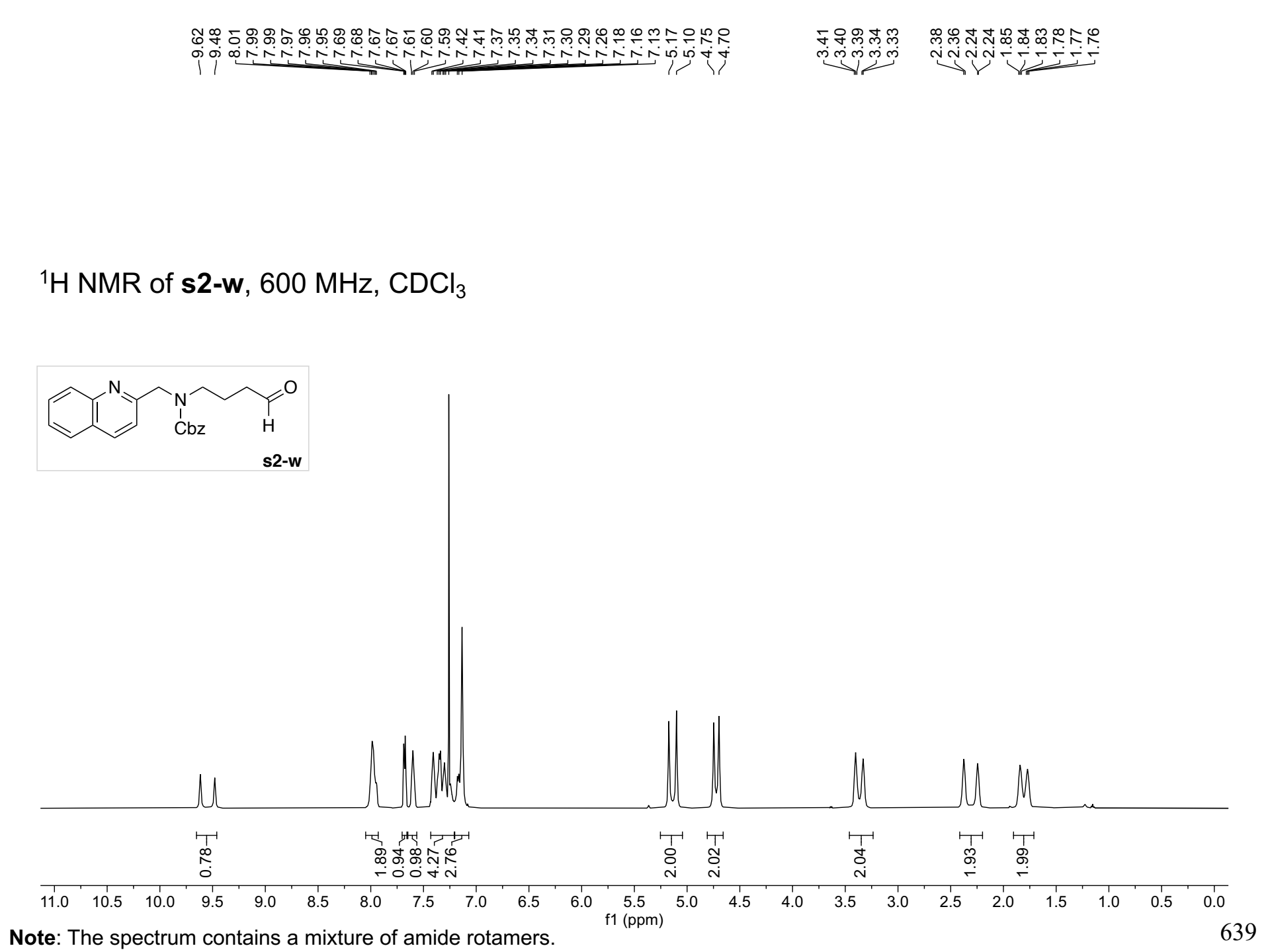


^{1}H NMR of **s2-v**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

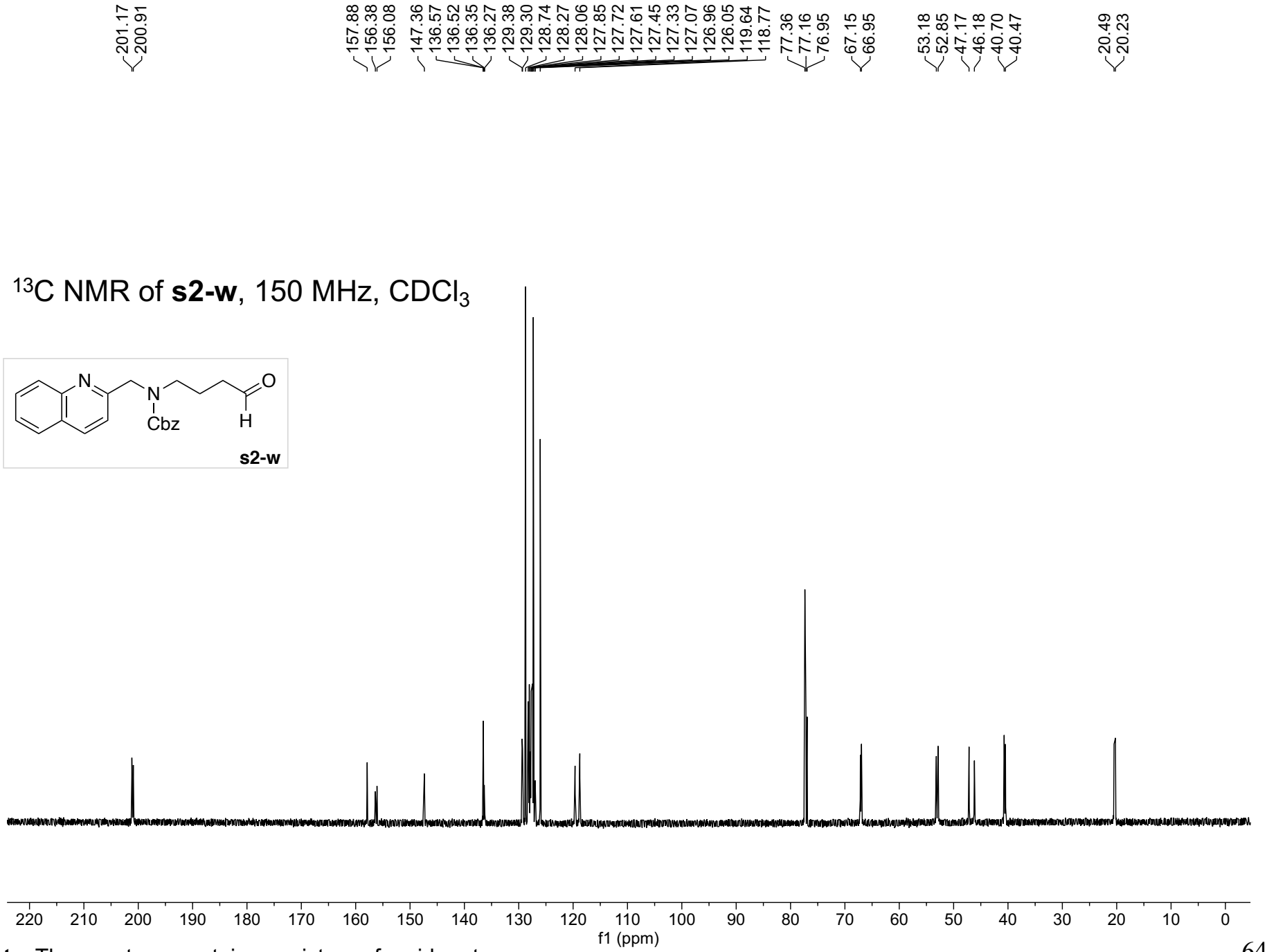


Note: The spectrum contains a mixture of amide rotamers.



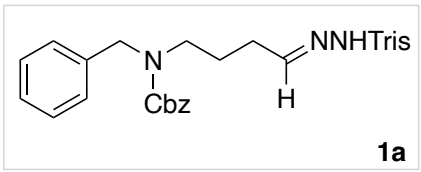
^{1}H NMR of **s2-w**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.



Note: The spectrum contains a mixture of amide rotamers.

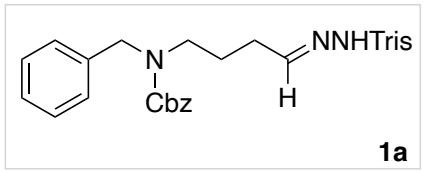
^{1}H NMR of **1a**, 600 MHz, $CDCl_3$



1a

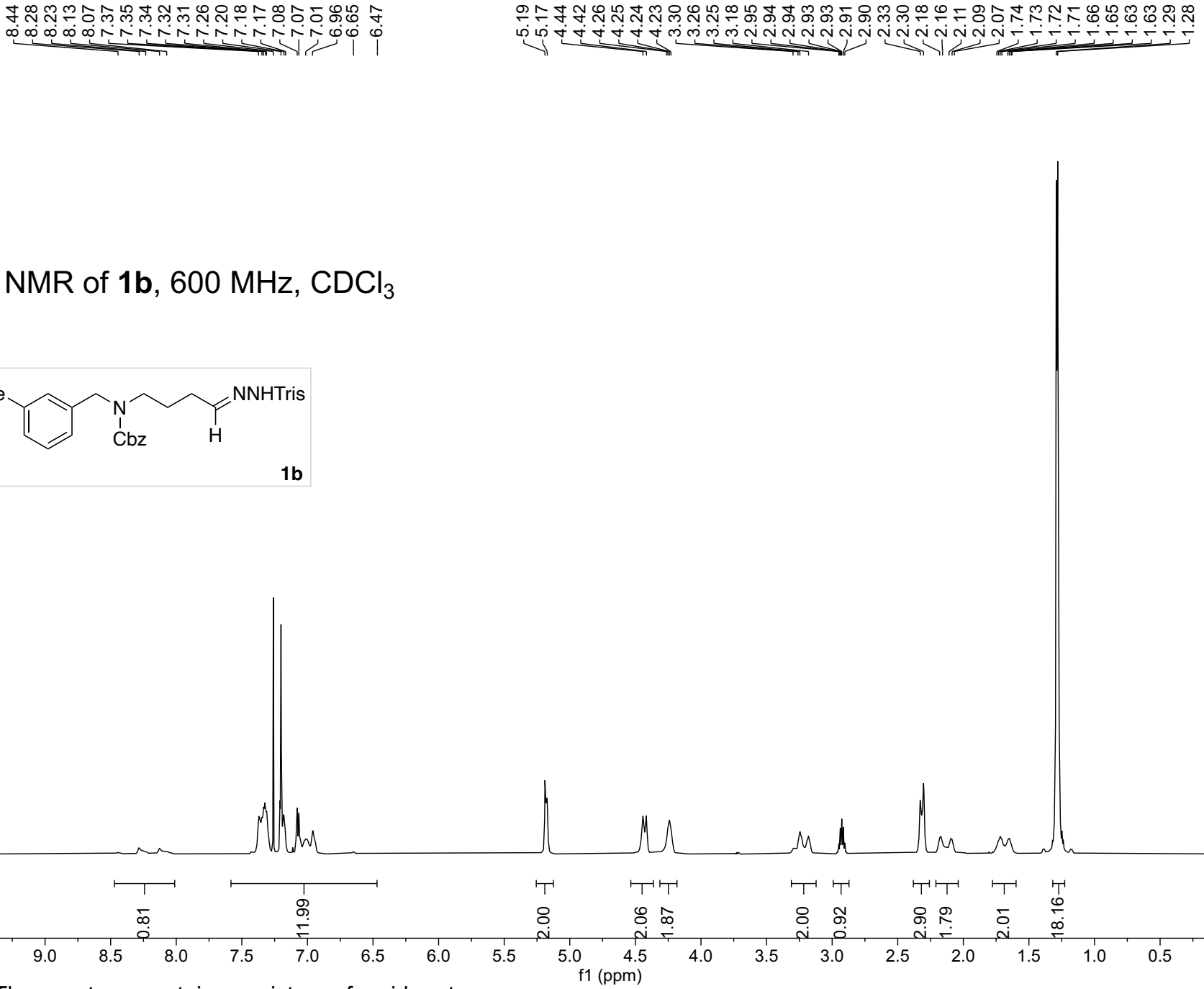
Note: The spectrum contains a mixture of amide rotamers.

^{13}C NMR of **1a**, 150 MHz, $CDCl_3$



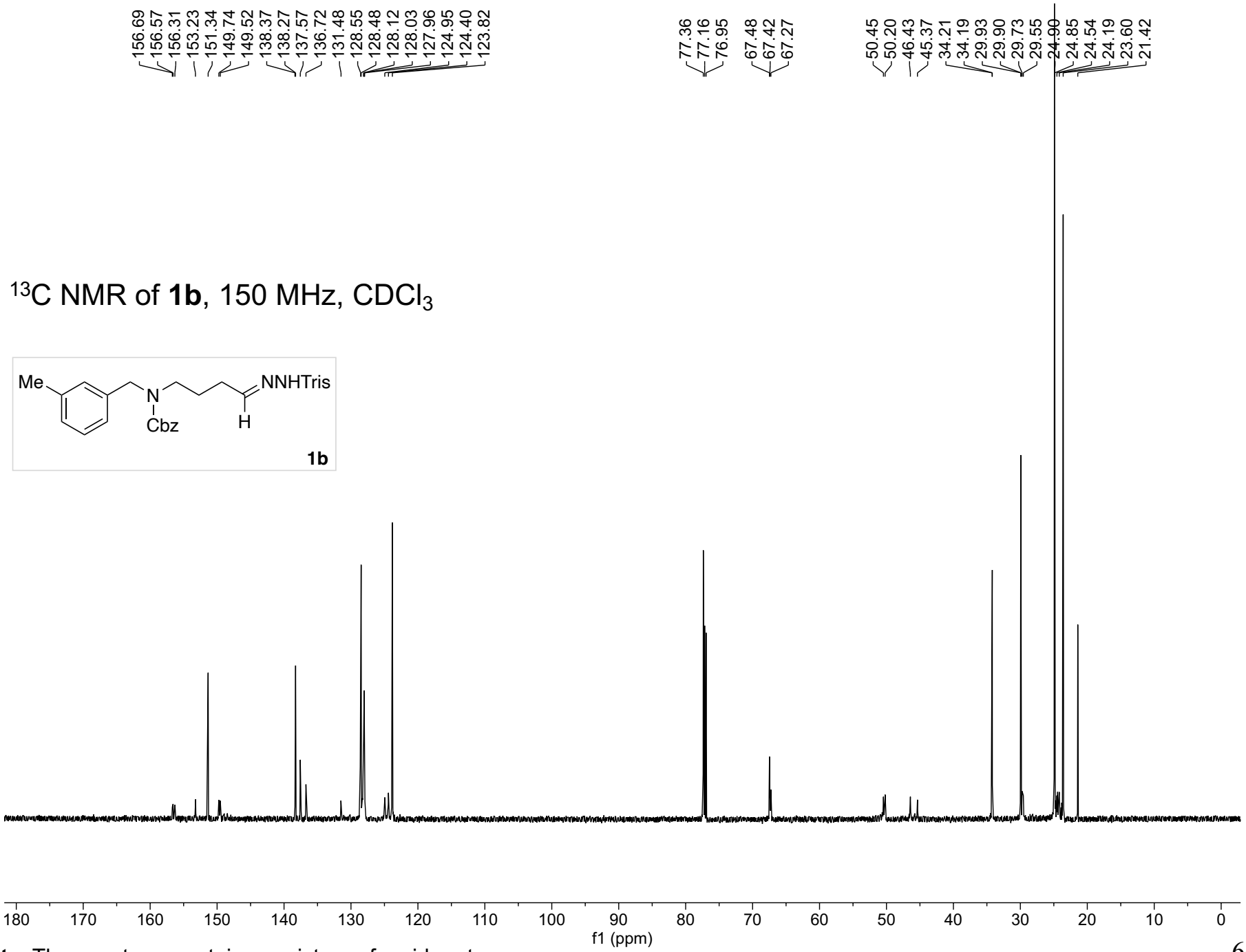
1a

Note: The spectrum contains a mixture of amide rotamers.



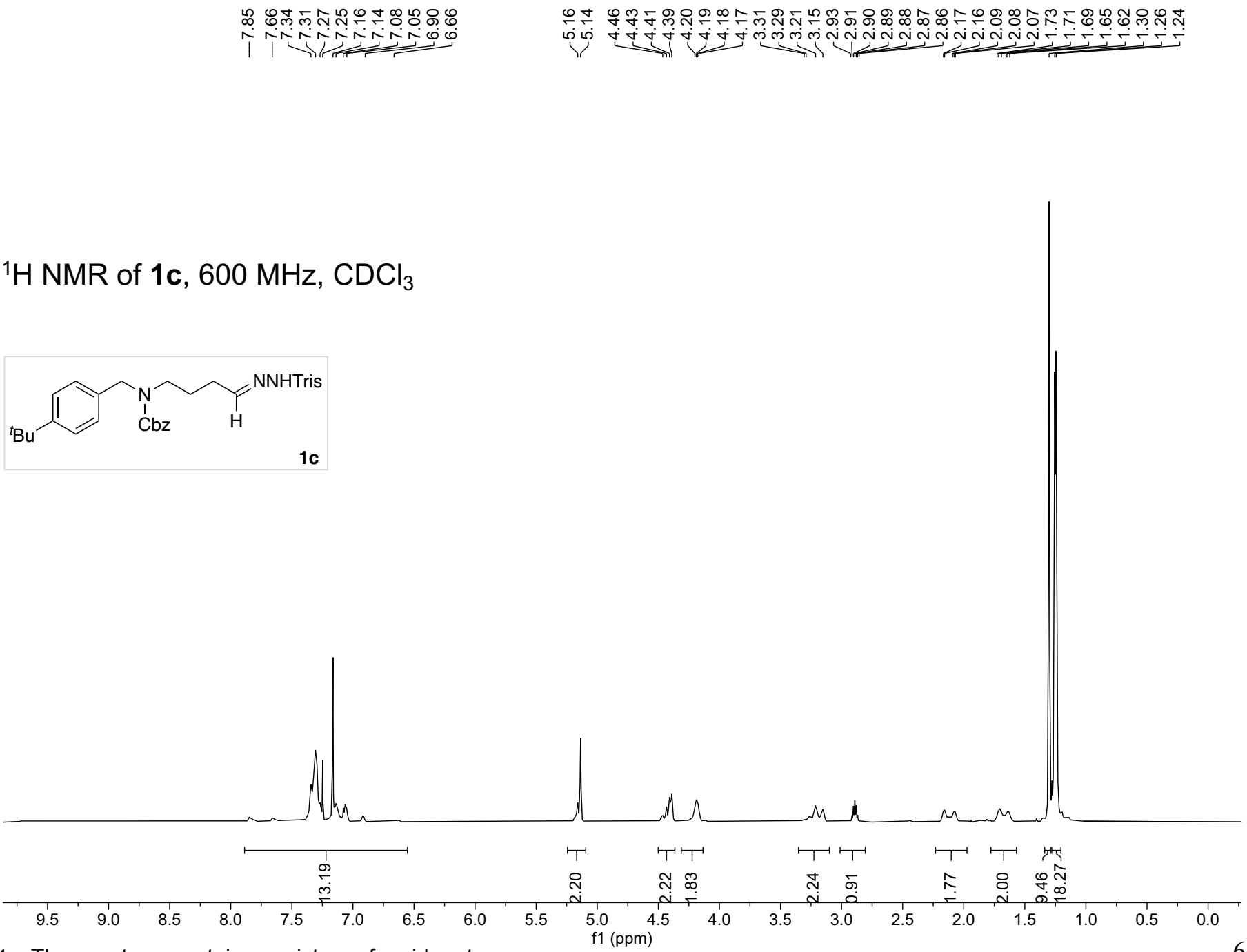
^{1}H NMR of **1b**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.



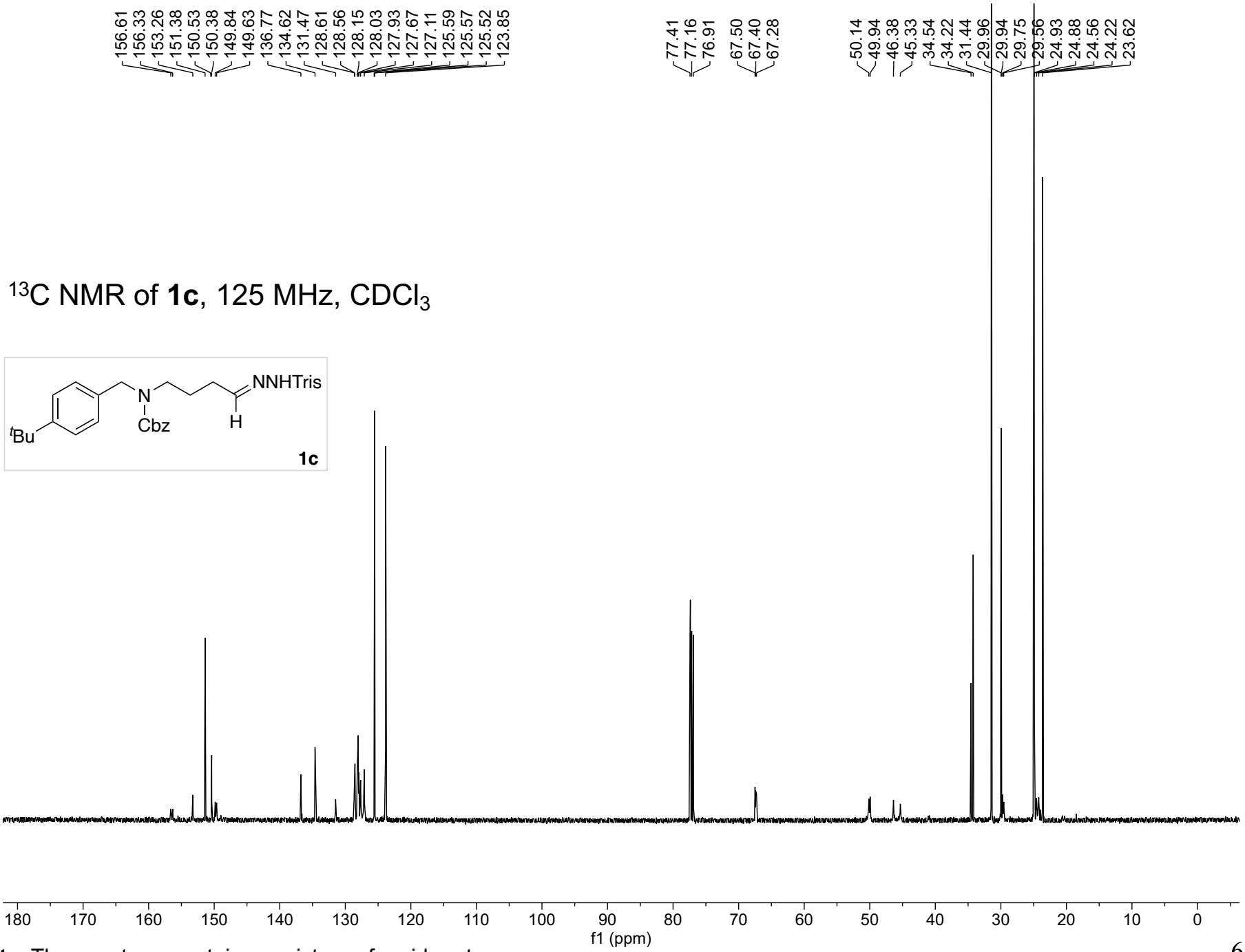
^{13}C NMR of **1b**, 150 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **1c**, 600 MHz, $CDCl_3$

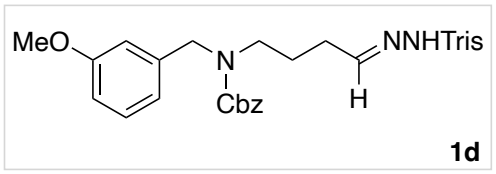
Note: The spectrum contains a mixture of amide rotamers.



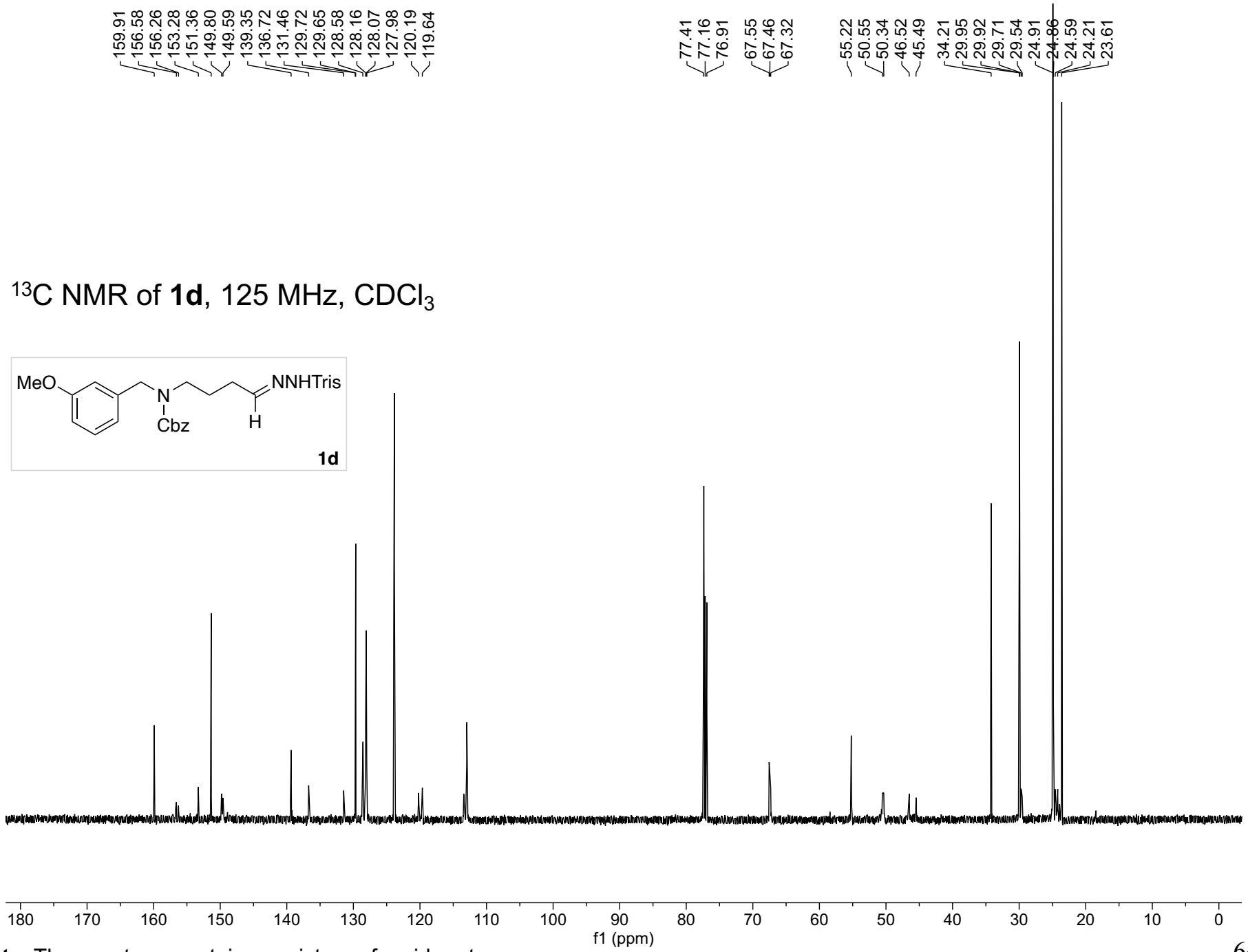
^{13}C NMR of **1c**, 125 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1d**, 600 MHz, $CDCl_3$

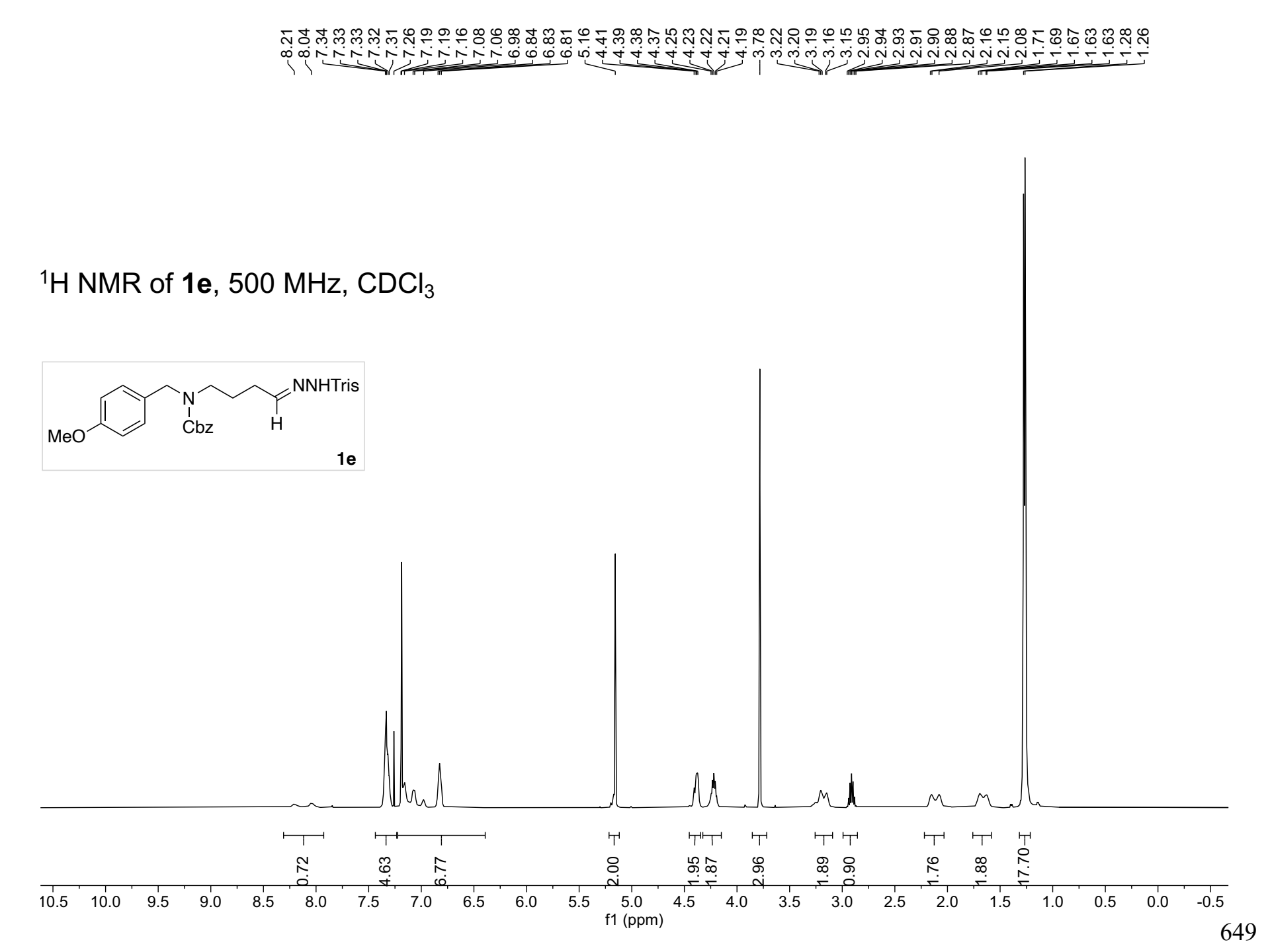


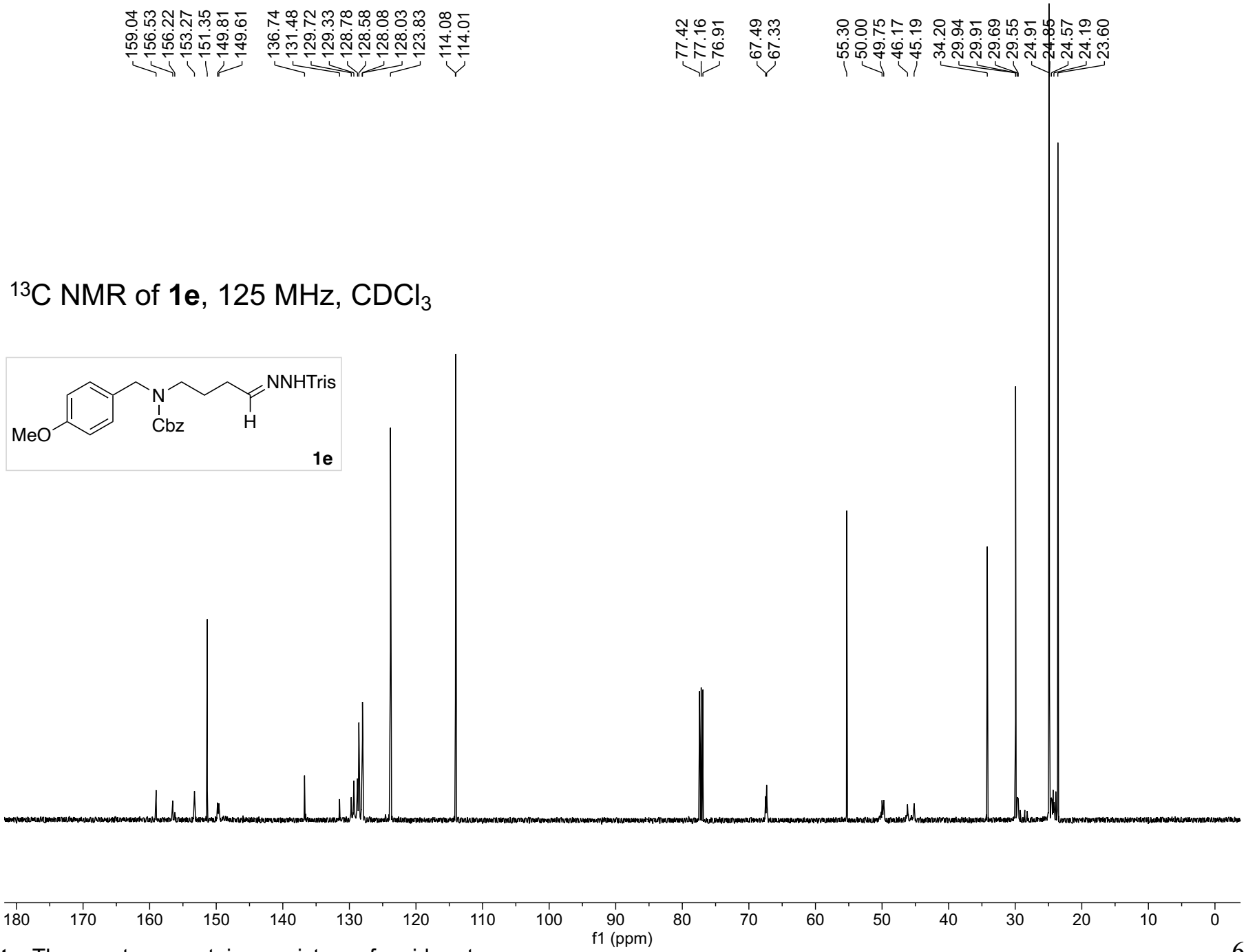
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **1d**, 125 MHz, $CDCl_3$

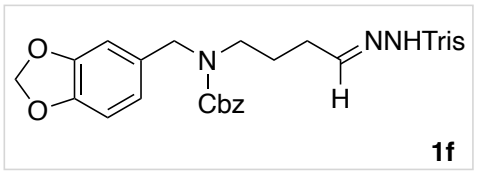
Note: The spectrum contains a mixture of amide rotamers.


8.21
8.04
7.34
7.33
7.33
7.32
7.31
7.26
7.19
7.19
7.16
7.08
7.06
6.98
6.84
6.83
6.81
5.16
4.41
4.39
4.38
4.37
4.25
4.23
4.22
4.21
4.19
3.78
3.22
3.20
3.19
3.16
3.15
2.95
2.94
2.93
2.91
2.90
2.88
2.87
2.16
2.15
2.08
1.71
1.69
1.67
1.63
1.63
1.28
1.26
1H NMR of 1e, 500 MHz, CDCl3
MeO
N
Cbz
NNHTris
H
1e
0.72
4.63
6.77
2.00
1.95
1.87
2.96
1.89
0.90
1.76
1.88
17.70
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



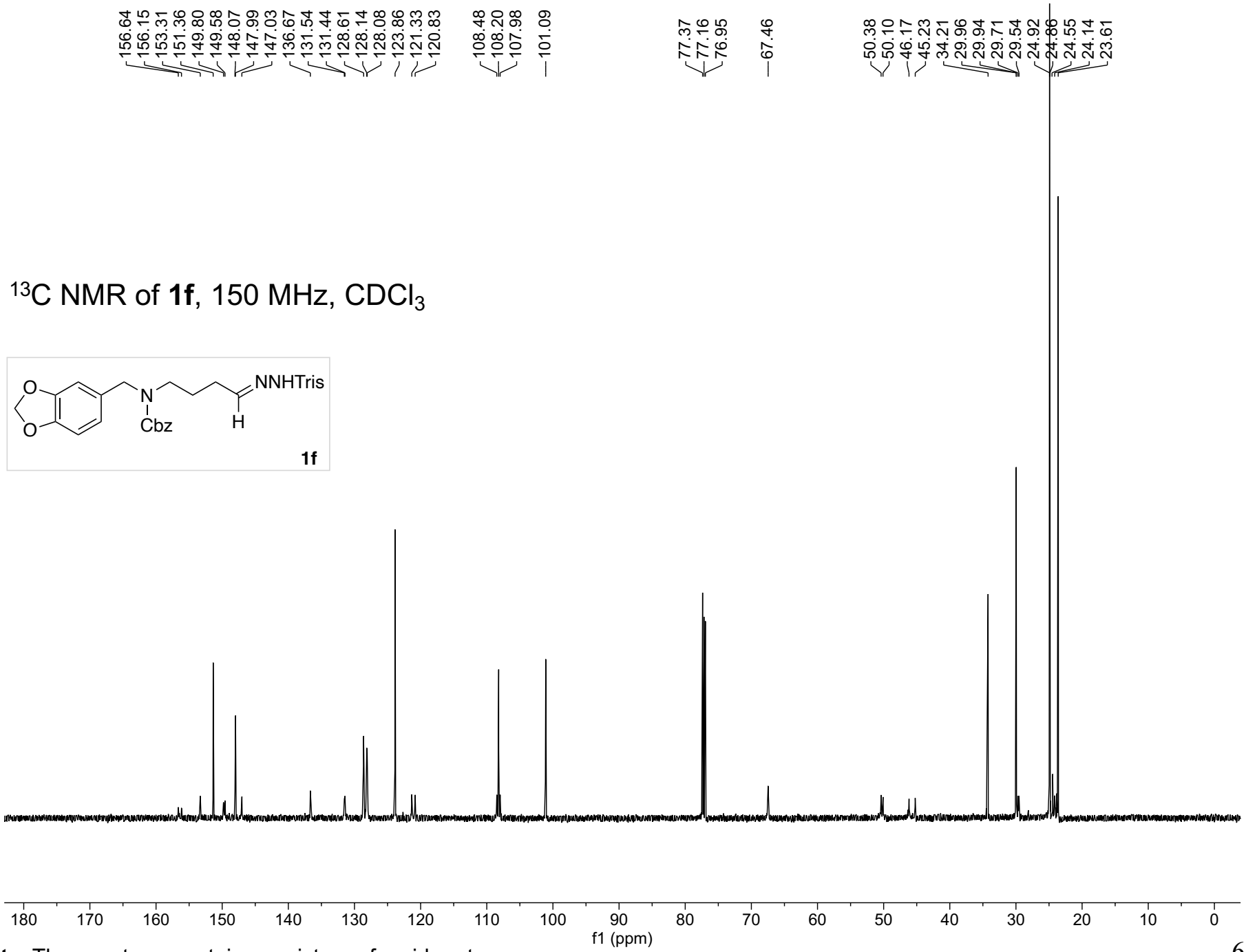
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1f**, 600 MHz, $CDCl_3$



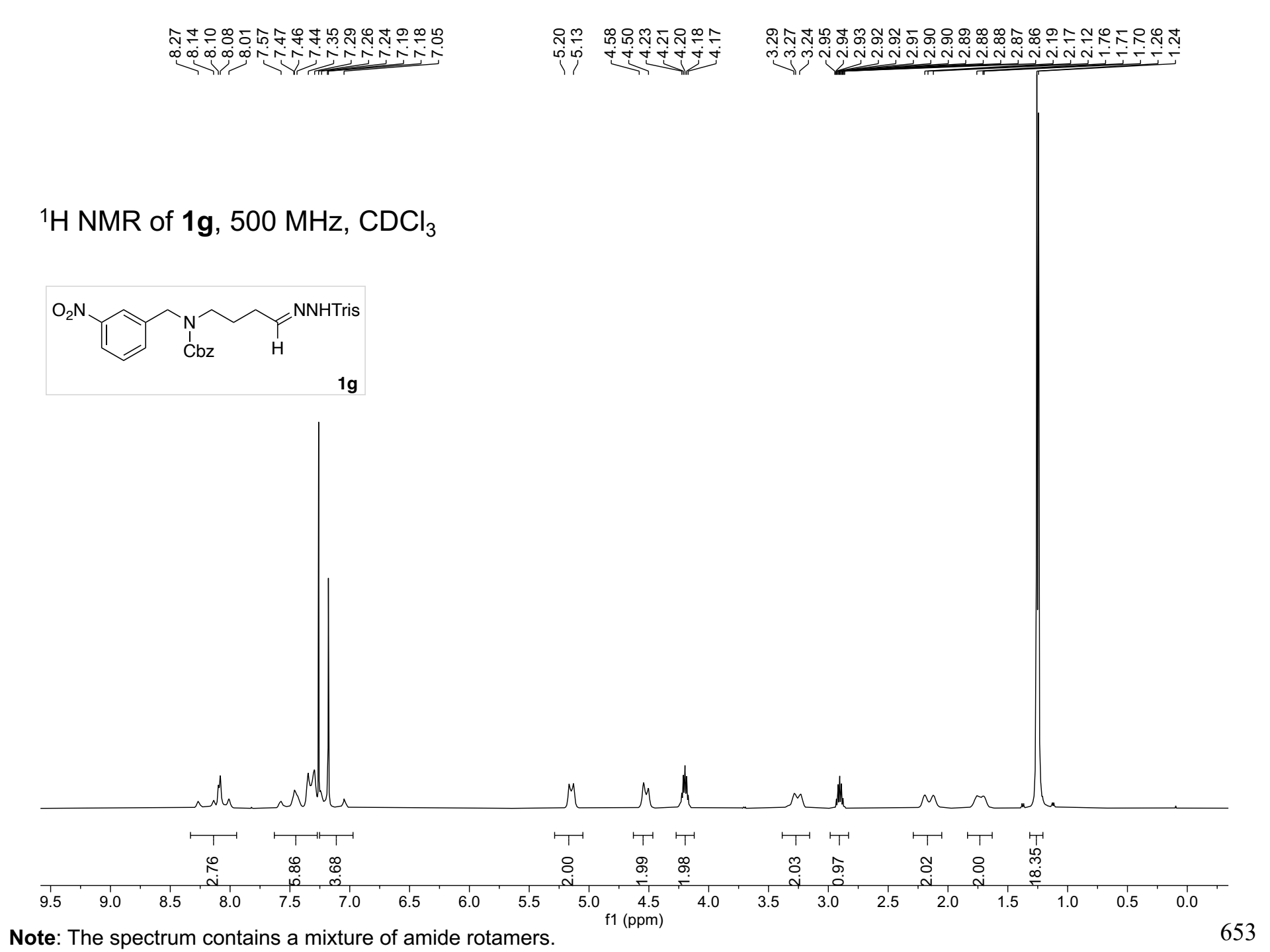
1f

Note: The spectrum contains a mixture of amide rotamers.



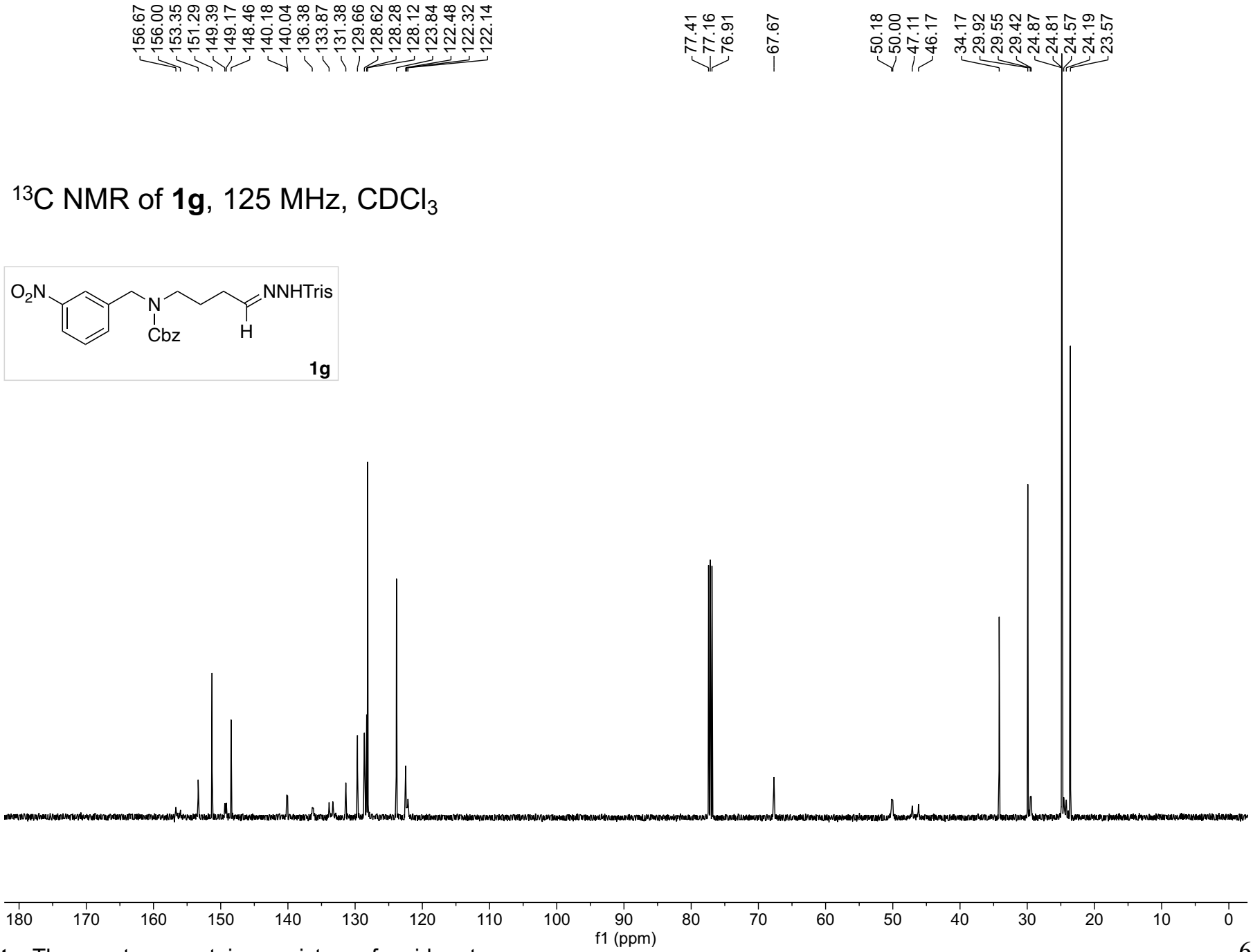
^{13}C NMR of **1f**, 150 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

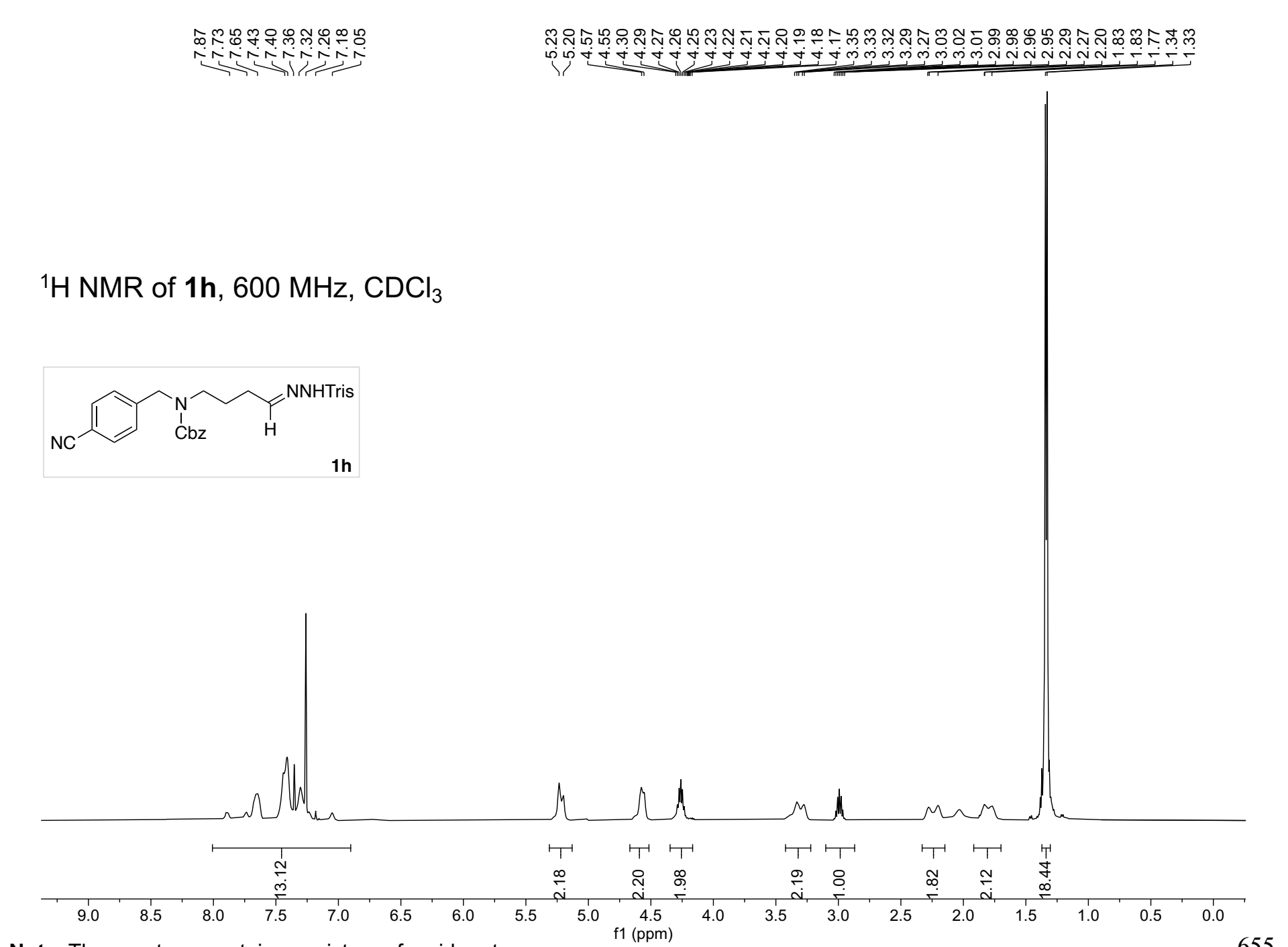


^{1}H NMR of **1g**, 500 MHz, $CDCl_3$

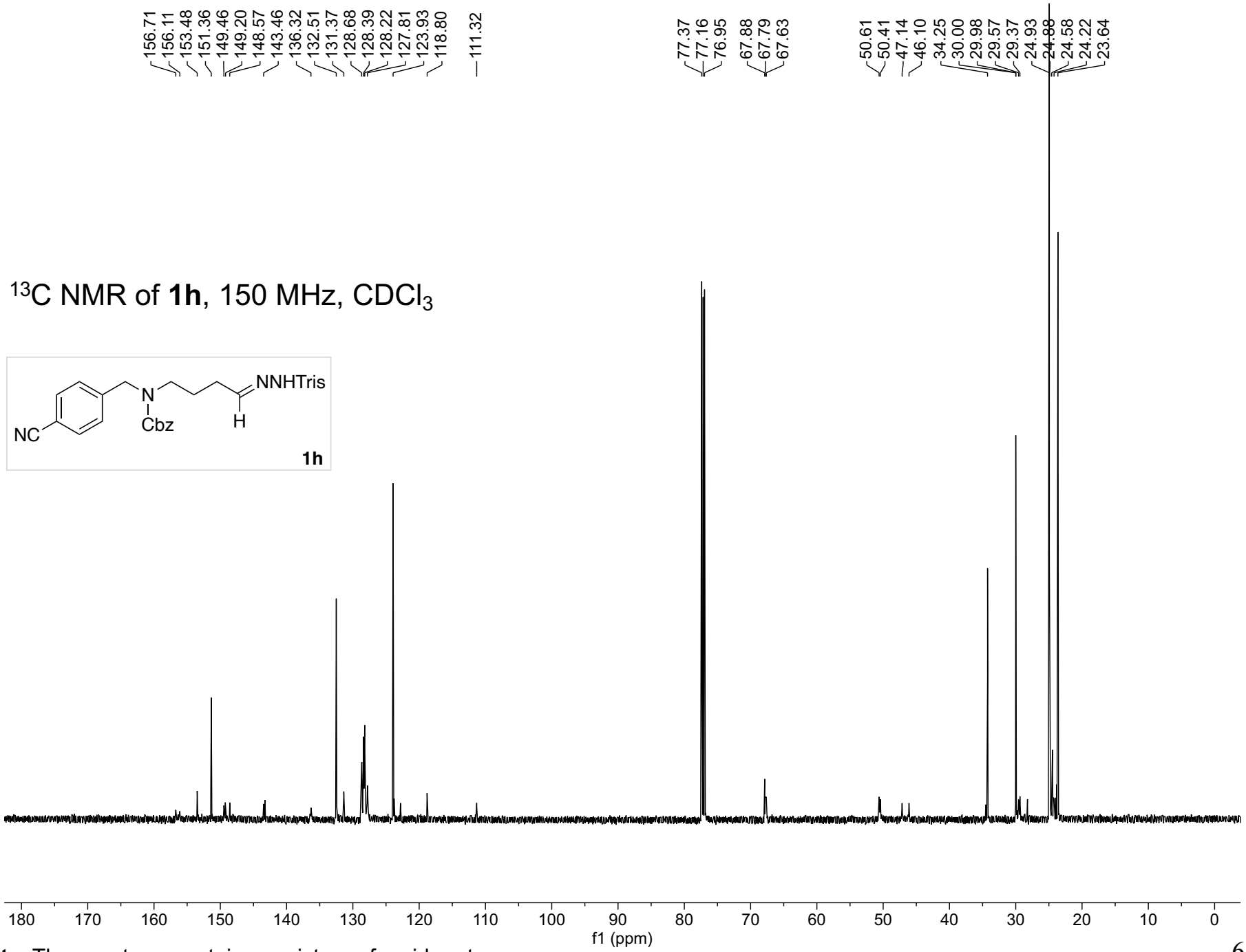
Note: The spectrum contains a mixture of amide rotamers.



Note: The spectrum contains a mixture of amide rotamers.

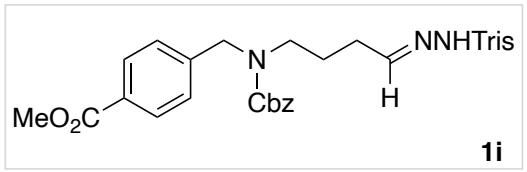


Note: The spectrum contains a mixture of amide rotamers.



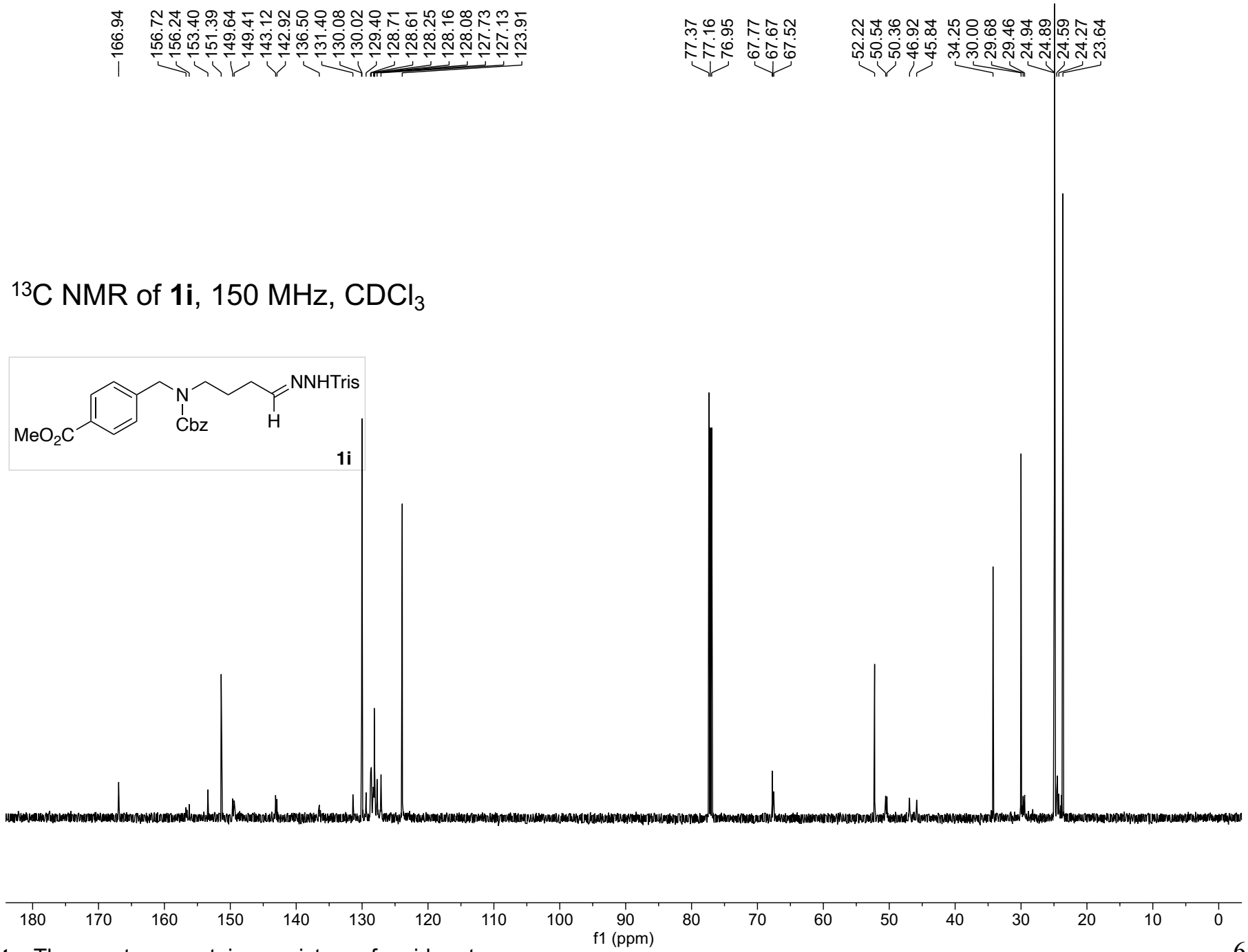
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1i**, 600 MHz, $CDCl_3$



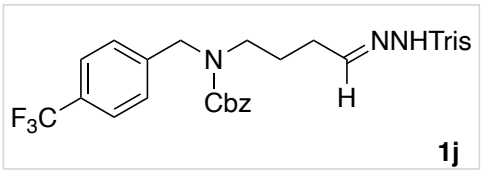
1i

Note: The spectrum contains a mixture of amide rotamers.

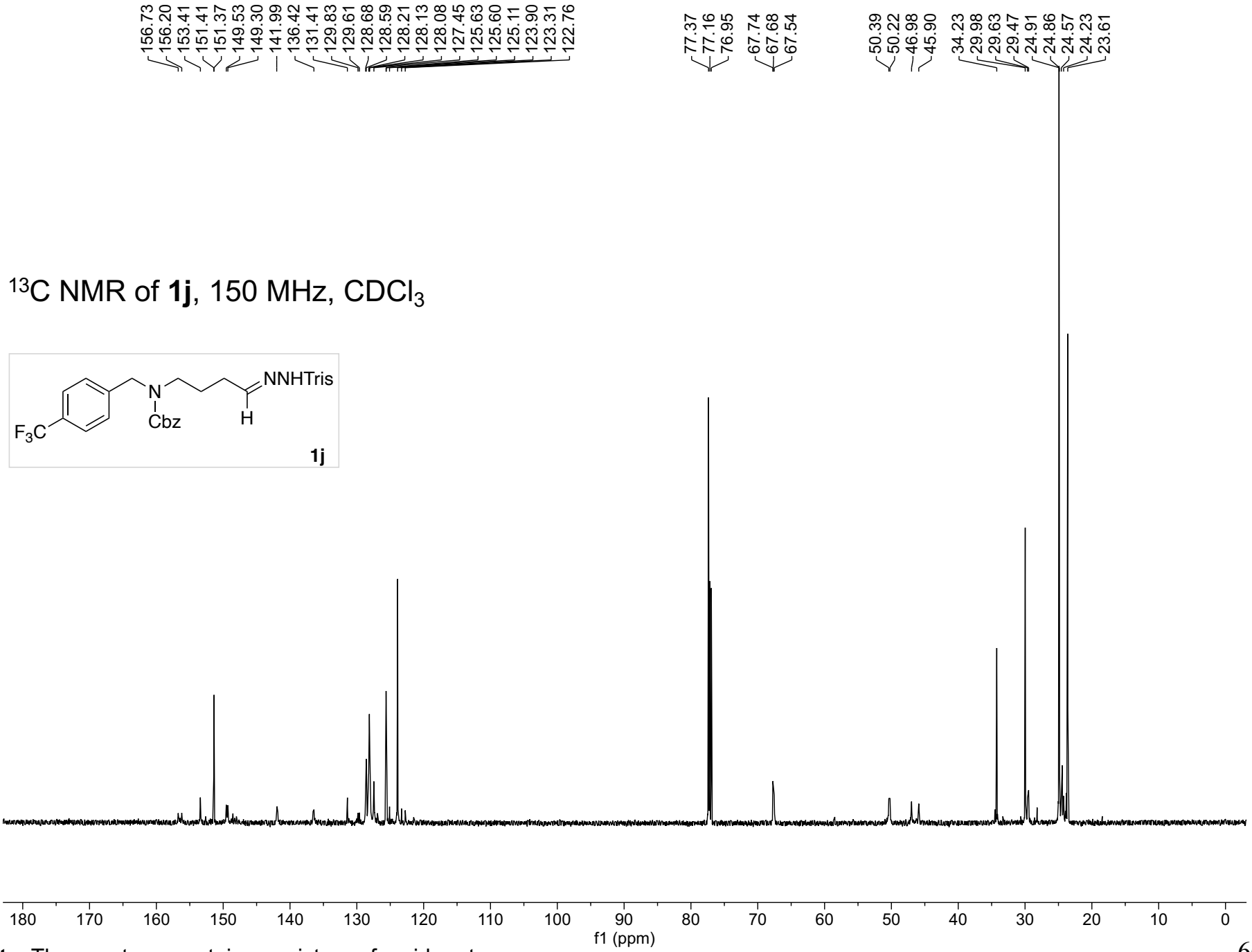


Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1j**, 600 MHz, $CDCl_3$

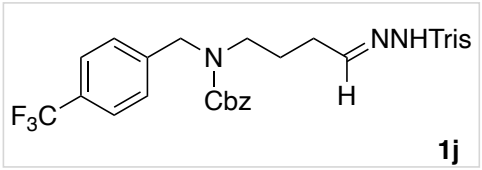


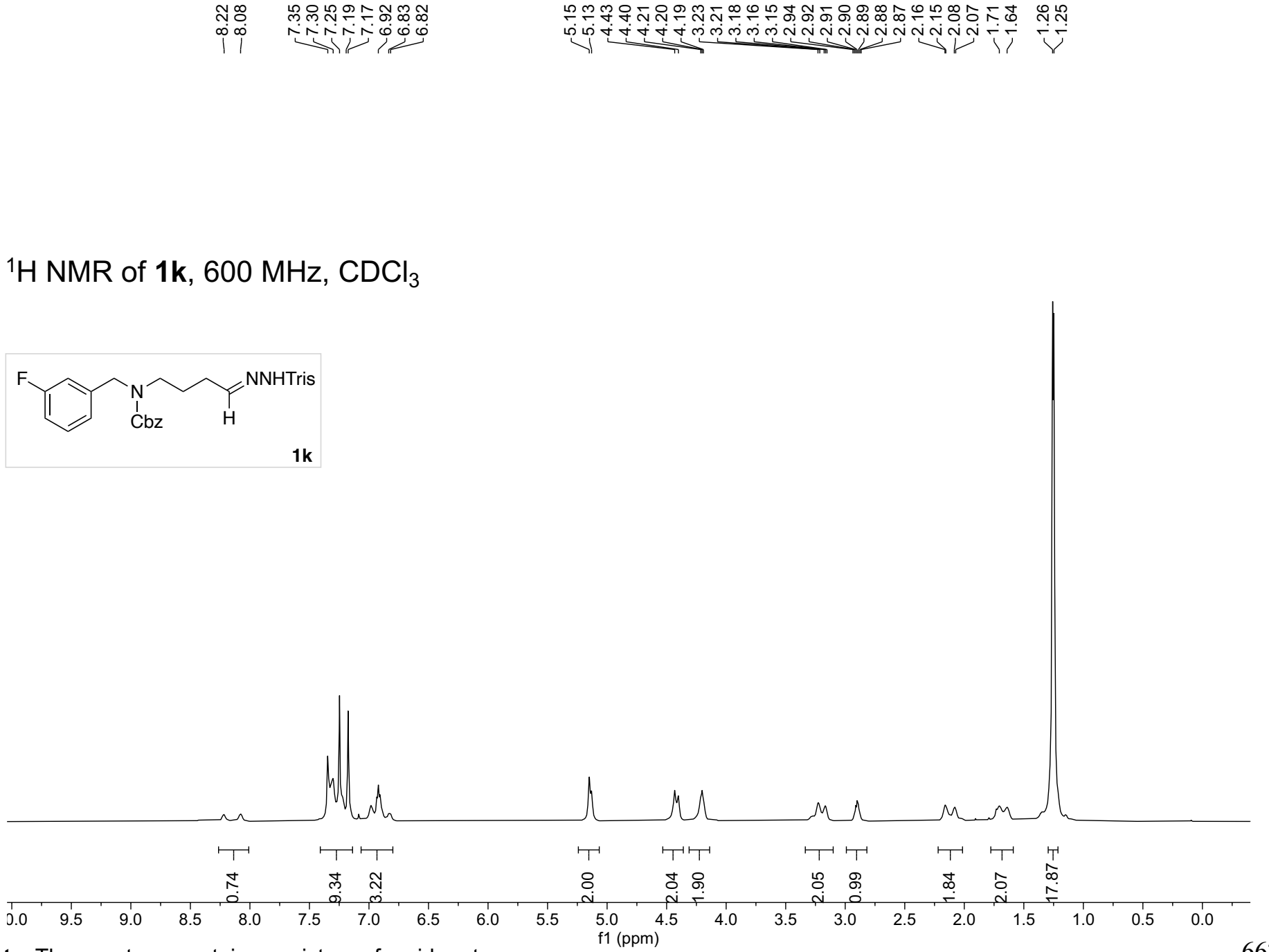
Note: The spectrum contains a mixture of amide rotamers.



Note: The spectrum contains a mixture of amide rotamers.

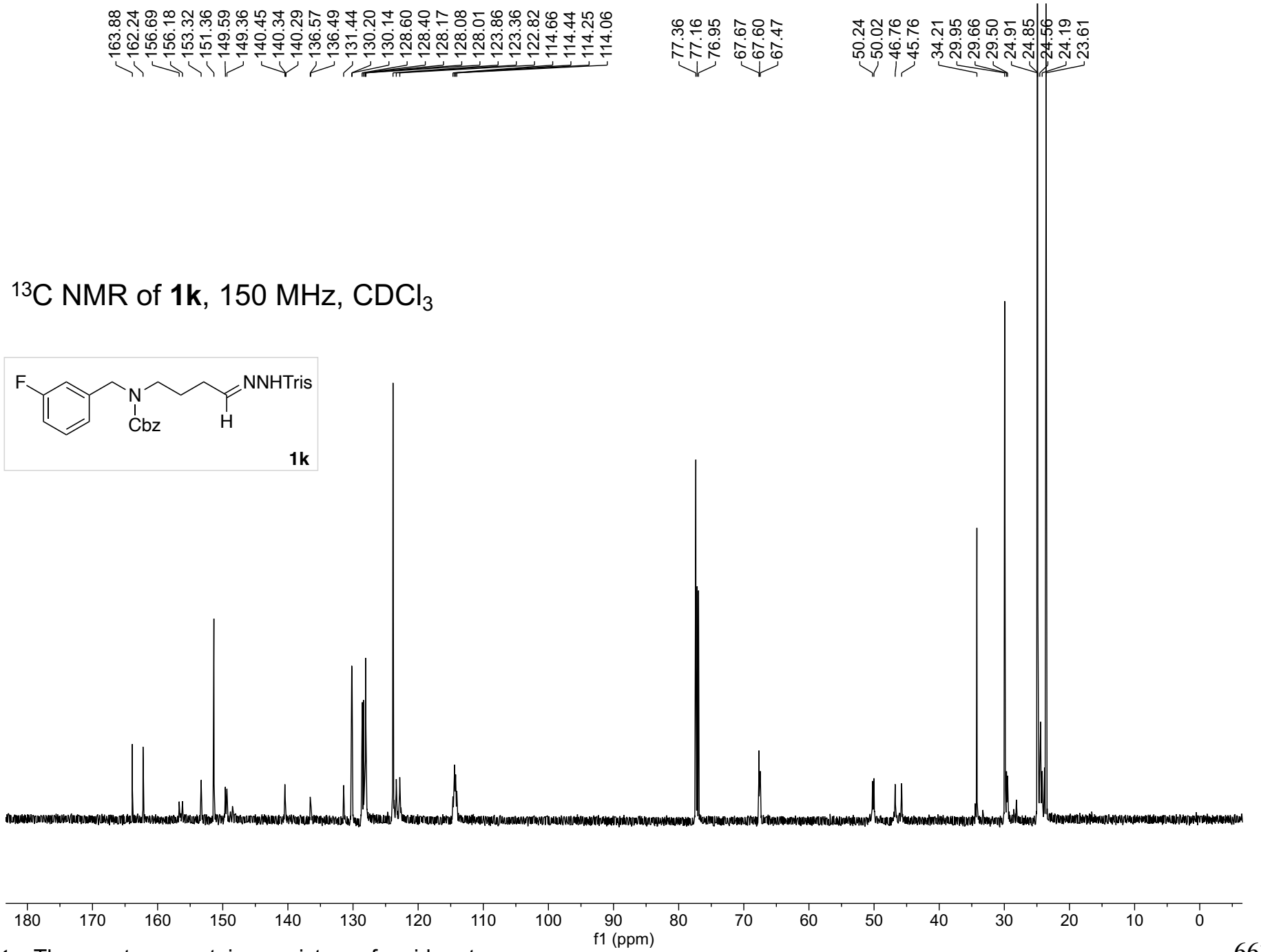
^{19}F NMR of **1j**, 564 MHz, $CDCl_3$





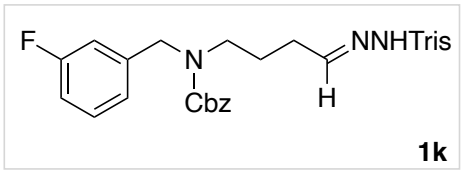
^{1}H NMR of **1k**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

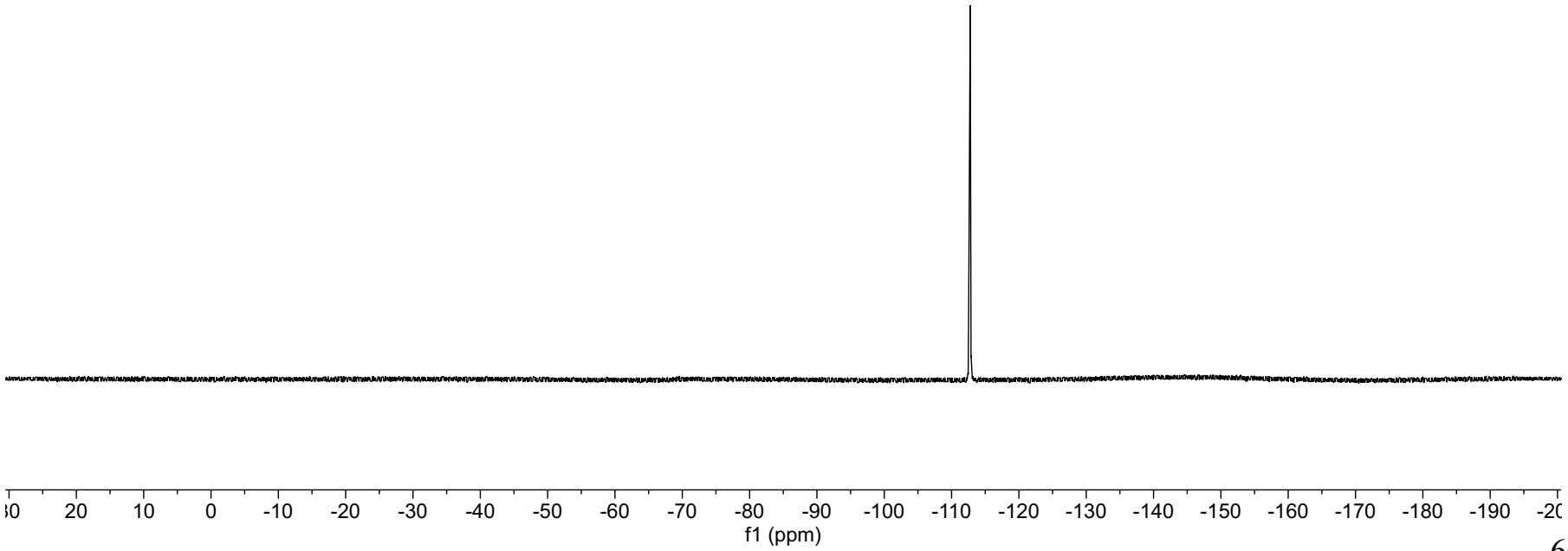


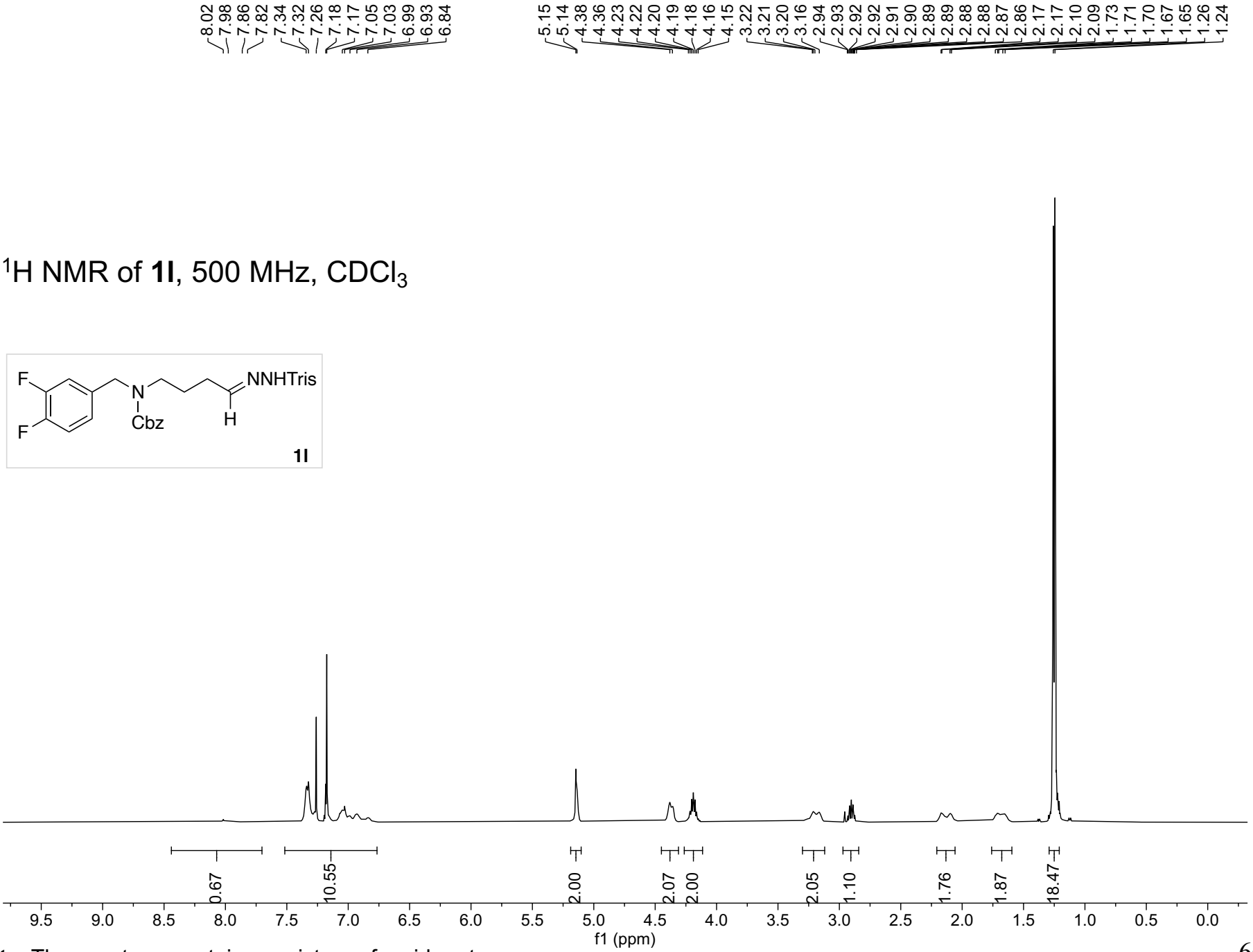
Note: The spectrum contains a mixture of amide rotamers.

^{19}F NMR of **1k**, 470 MHz, $CDCl_3$

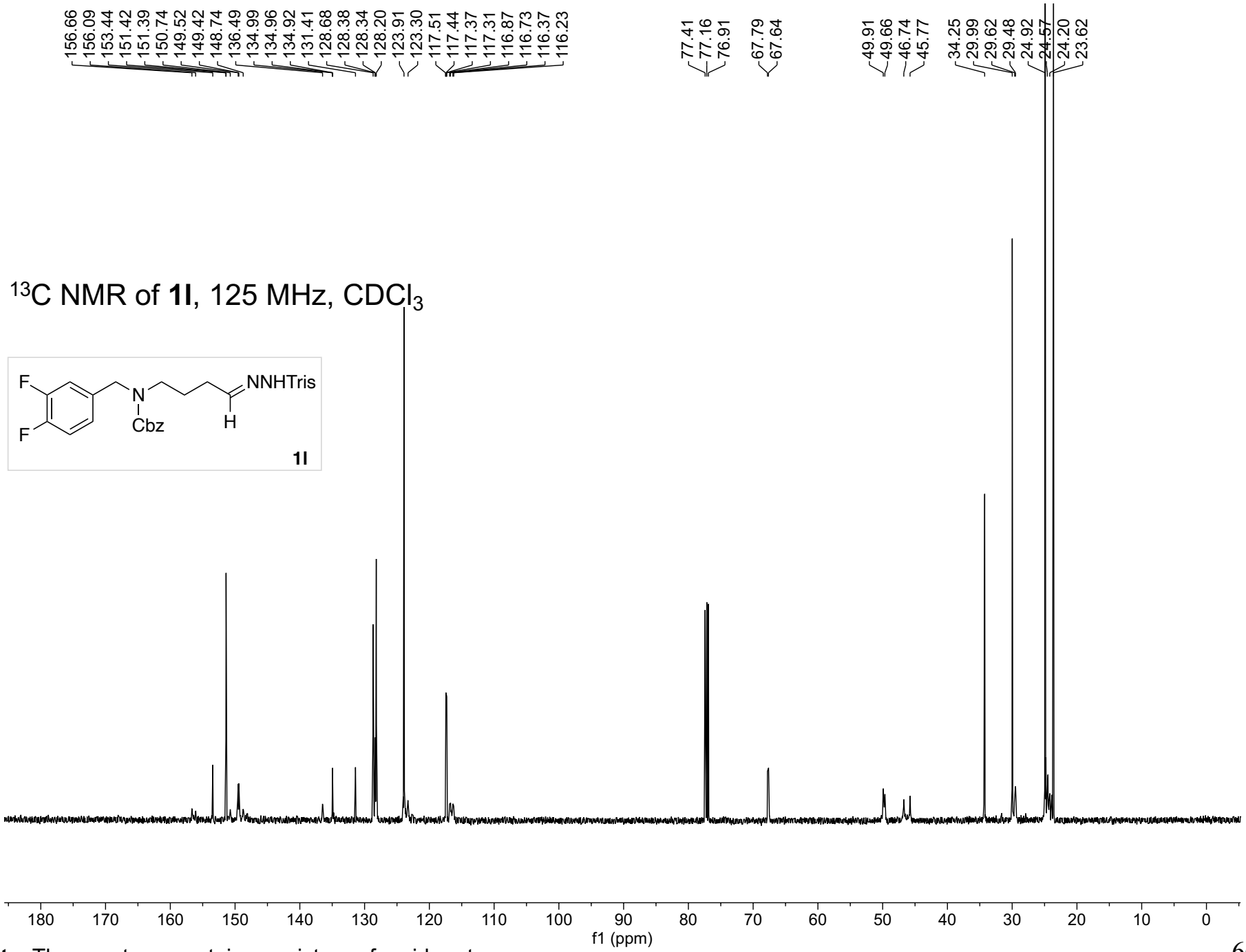


1k



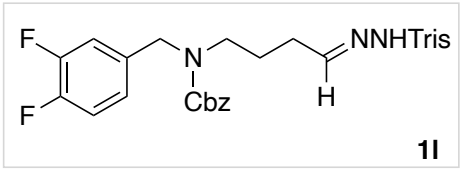


Note: The spectrum contains a mixture of amide rotamers.

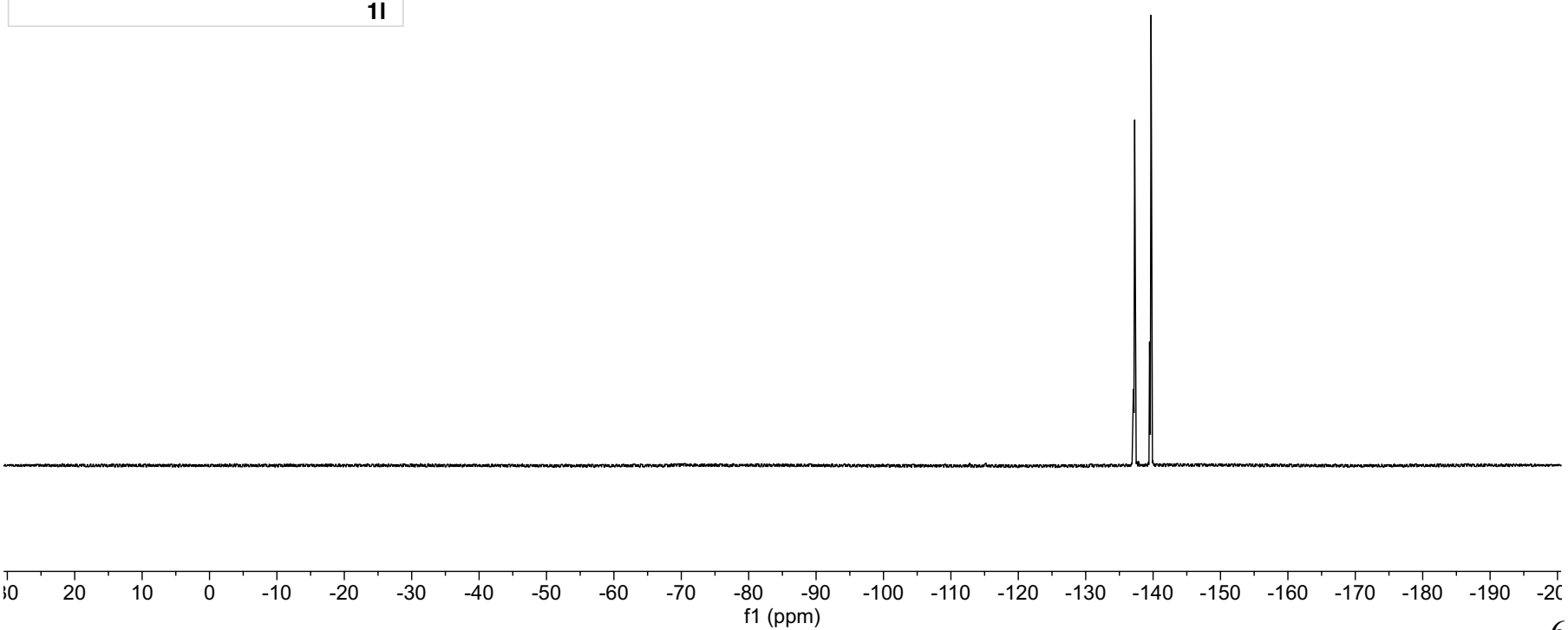


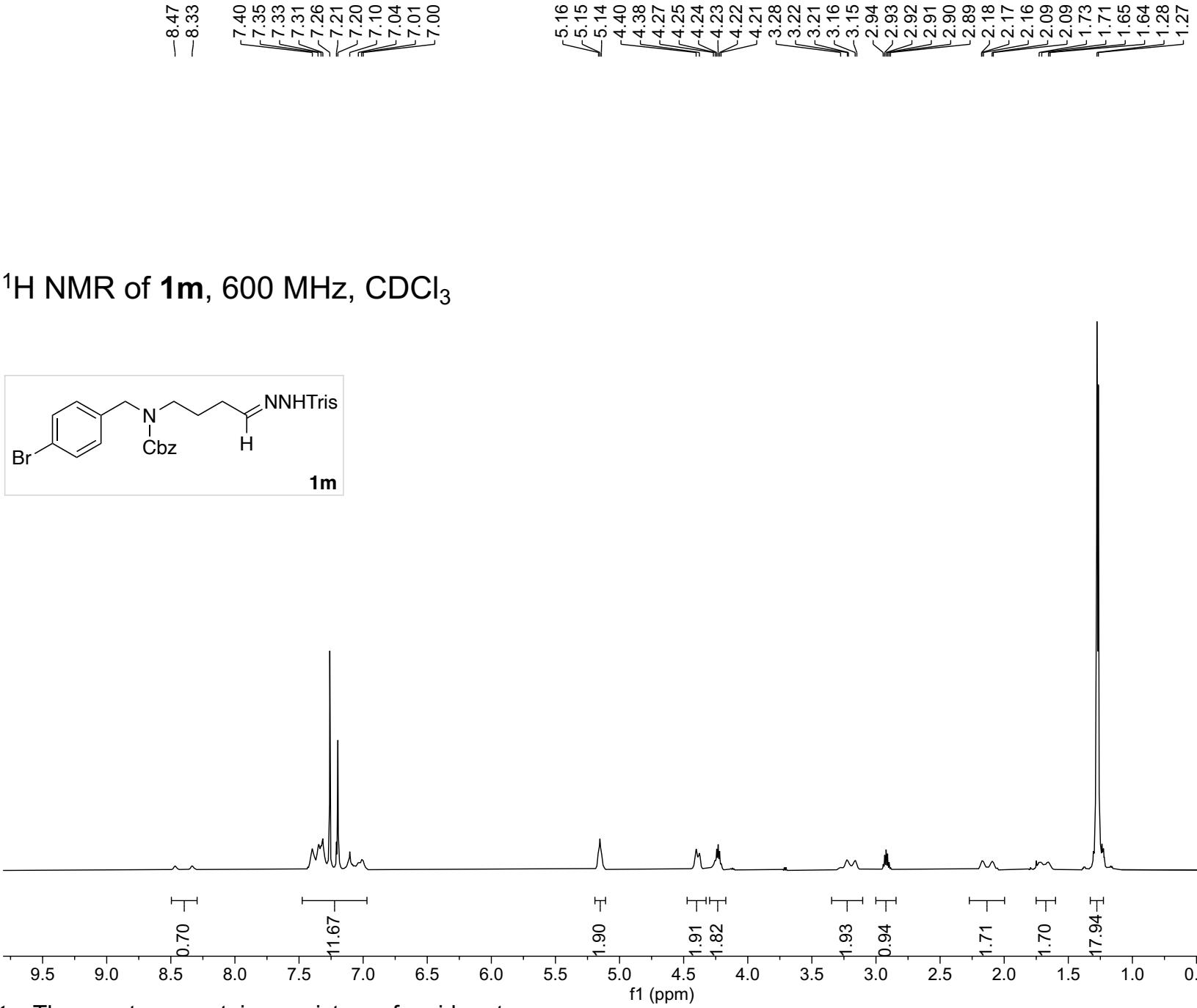
Note: The spectrum contains a mixture of amide rotamers.

^{19}F NMR of **1j**, 470 MHz, $CDCl_3$



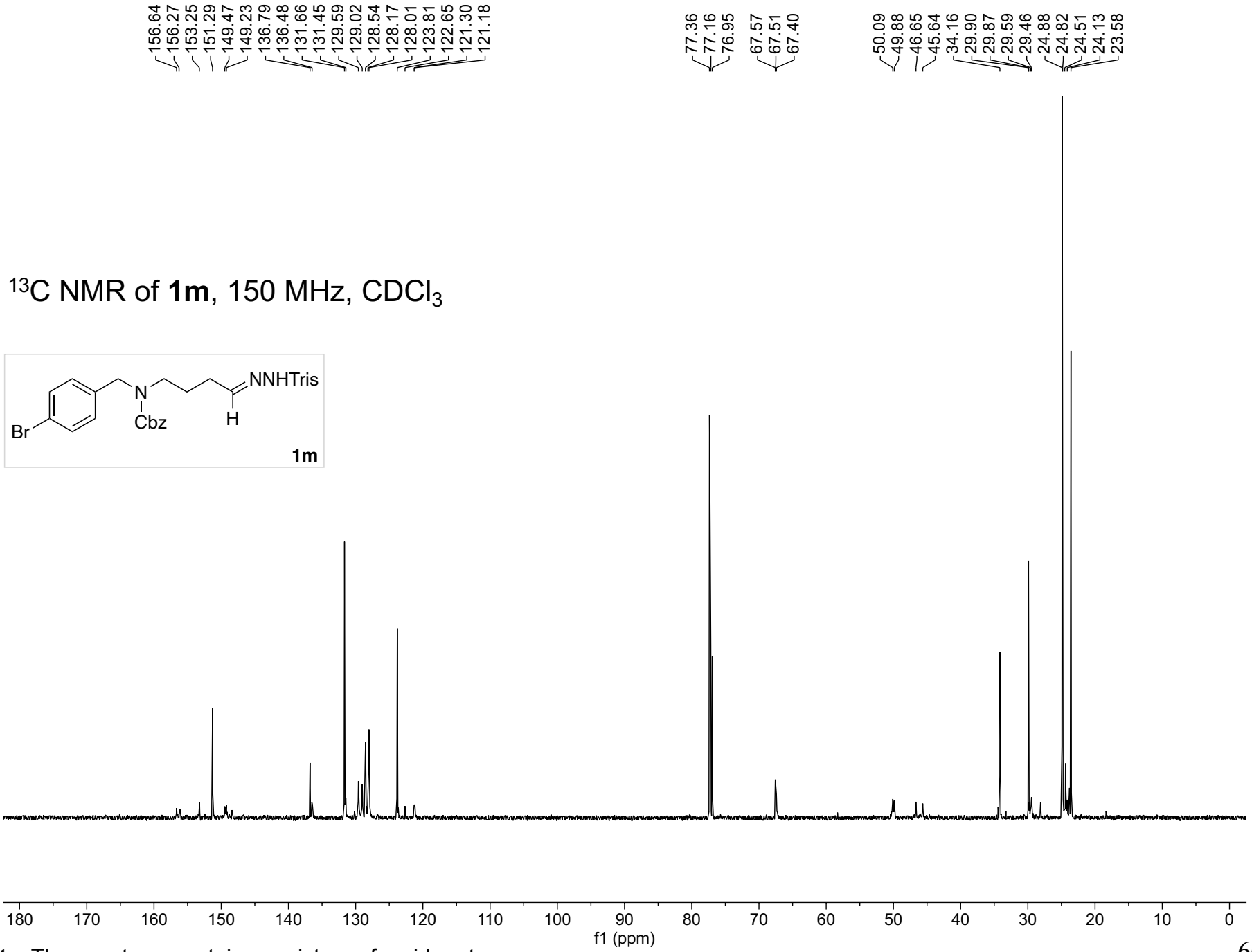
1l



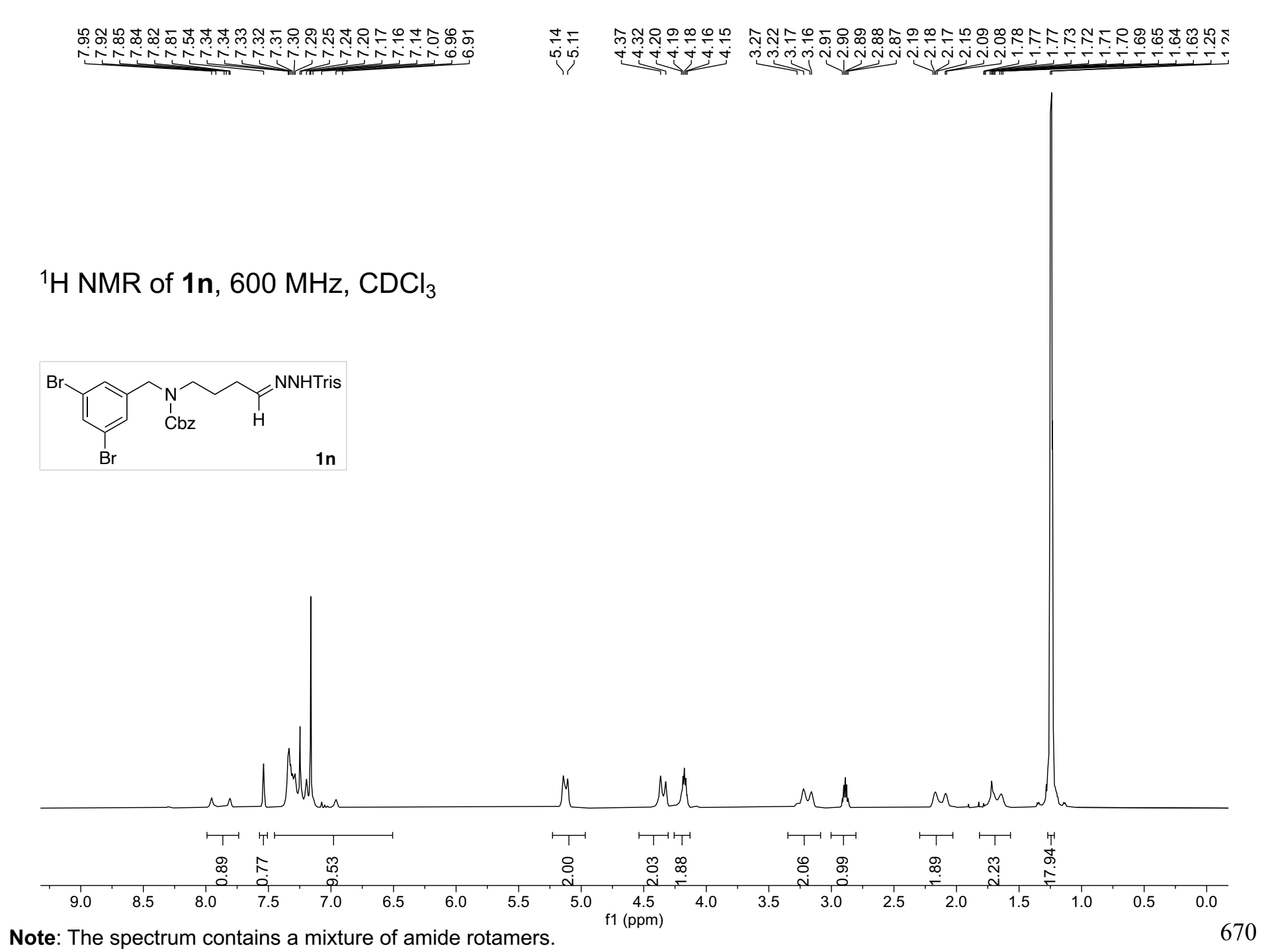


^{1}H NMR of **1m**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

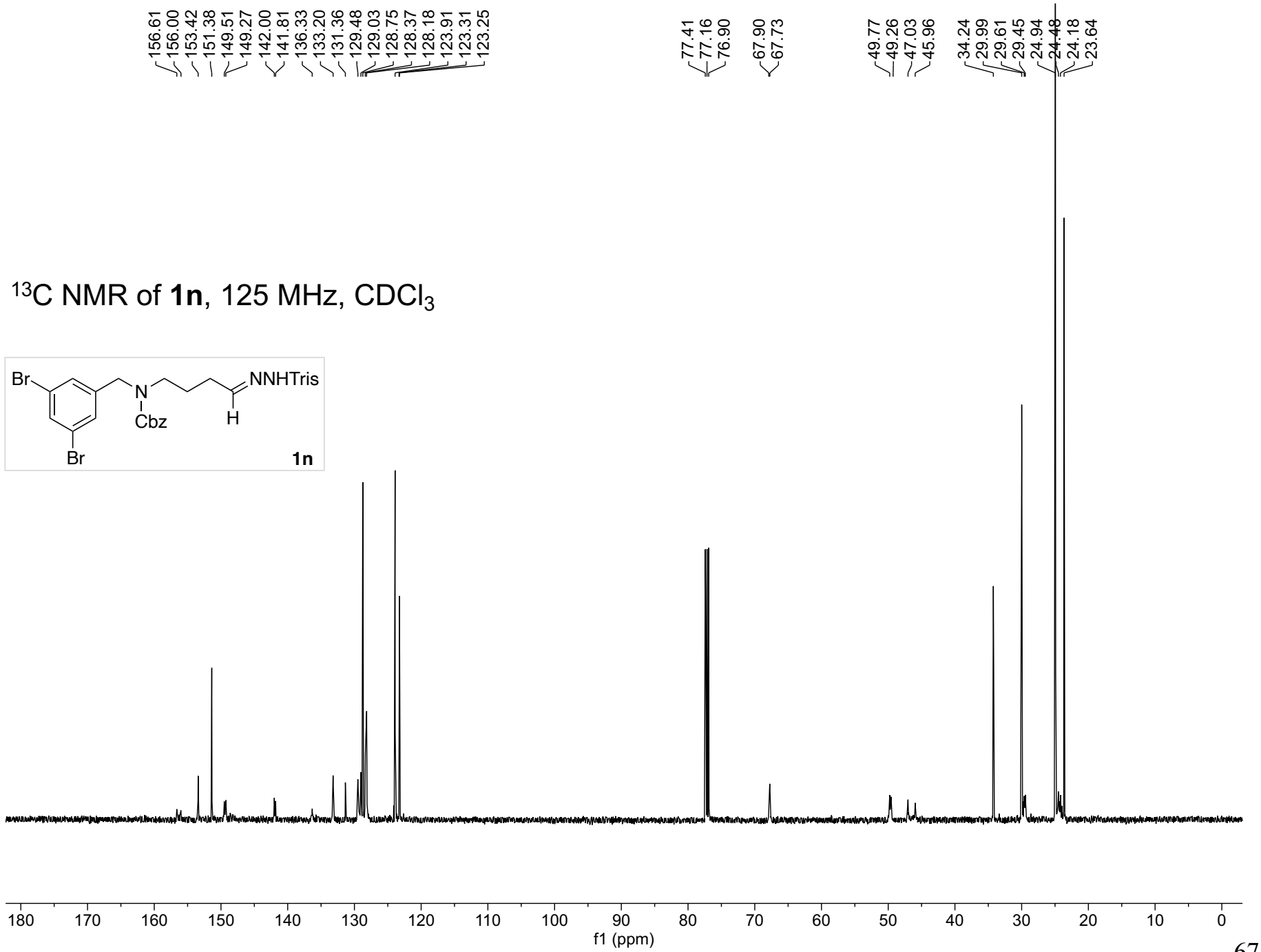


Note: The spectrum contains a mixture of amide rotamers.

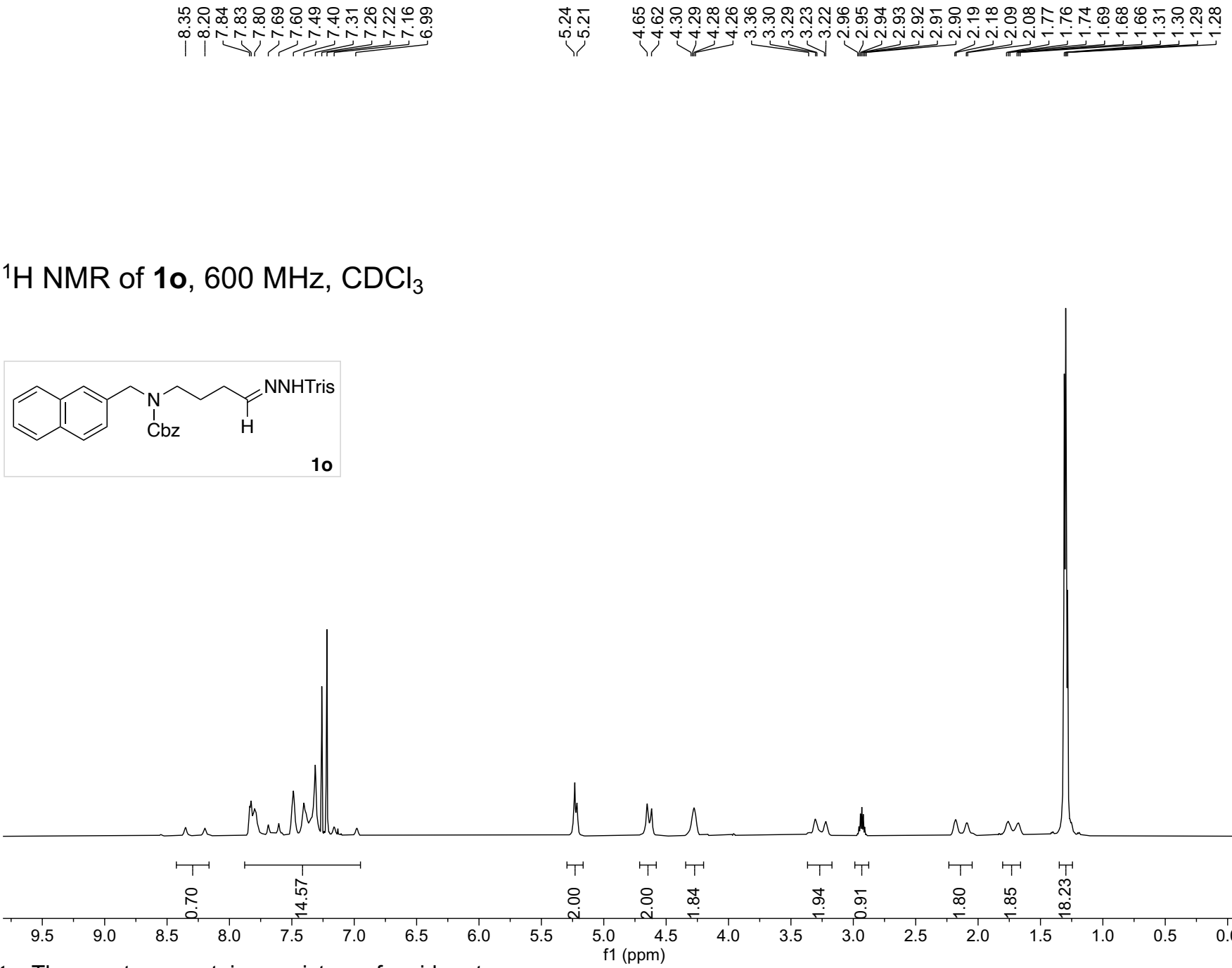


^{1}H NMR of **1n**, 600 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

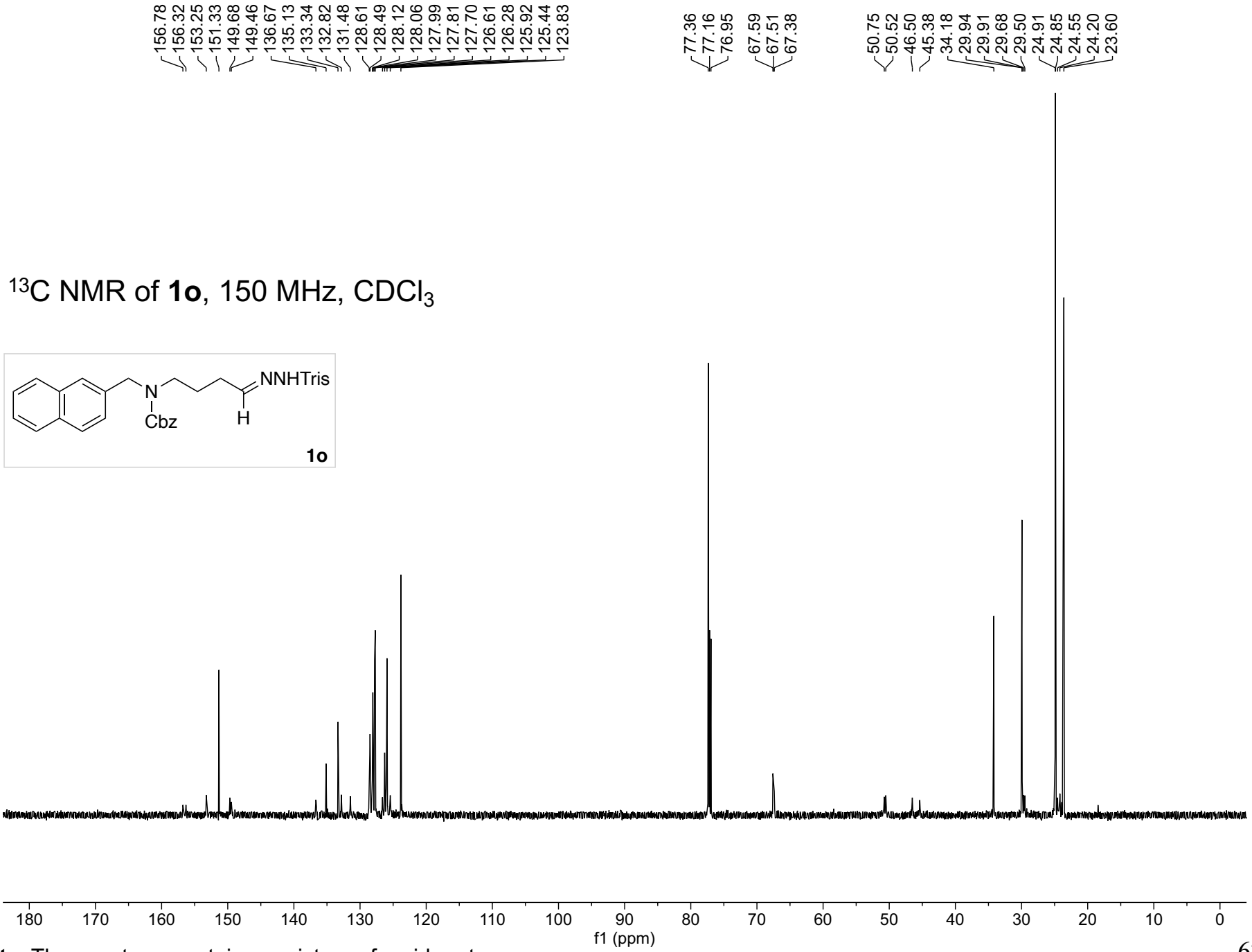


^{13}C NMR of **1n**, 125 MHz, $CDCl_3$

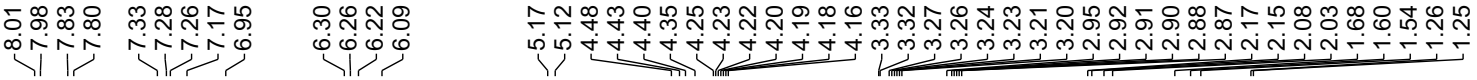


^{1}H NMR of **1o**, 600 MHz, $CDCl_3$

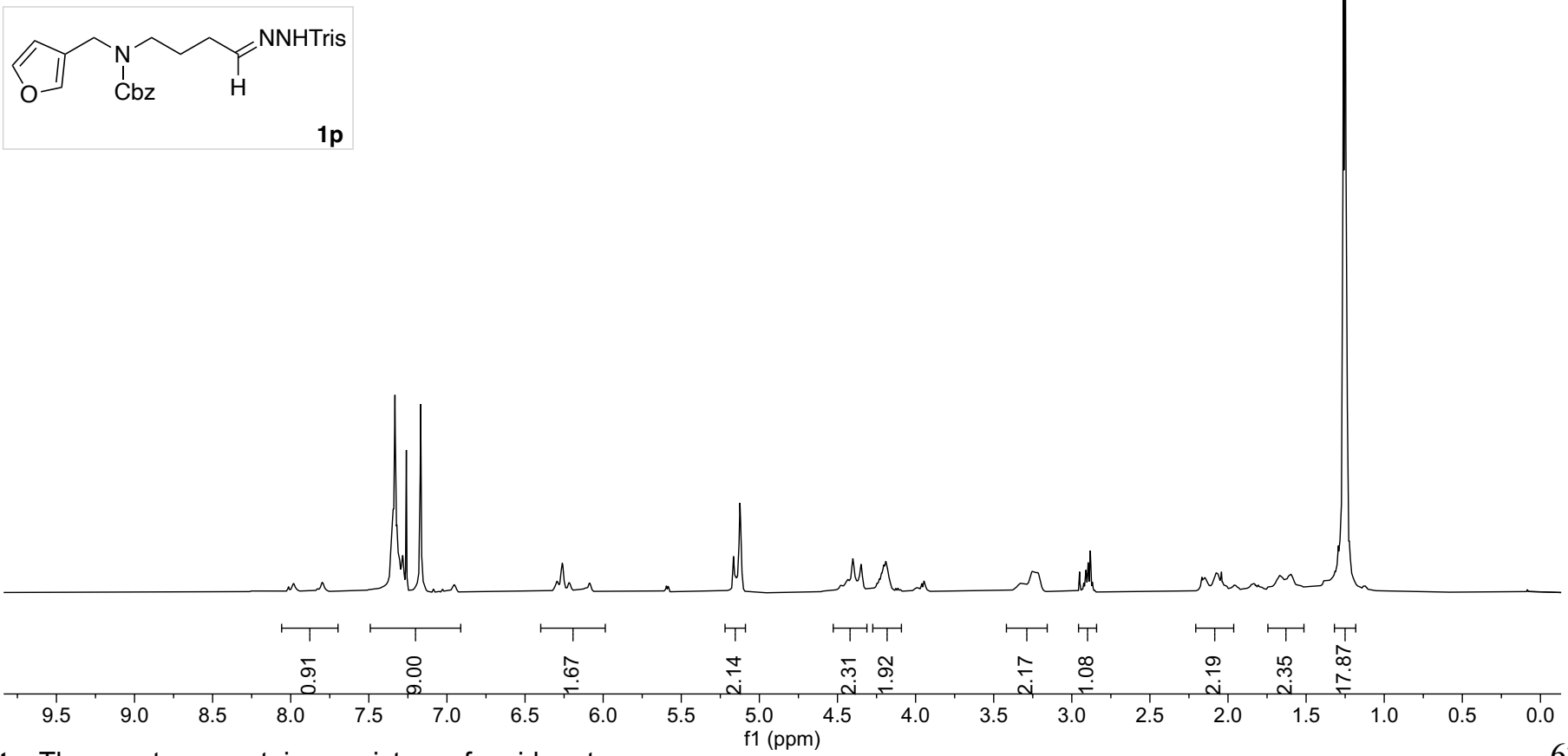
Note: The spectrum contains a mixture of amide rotamers.



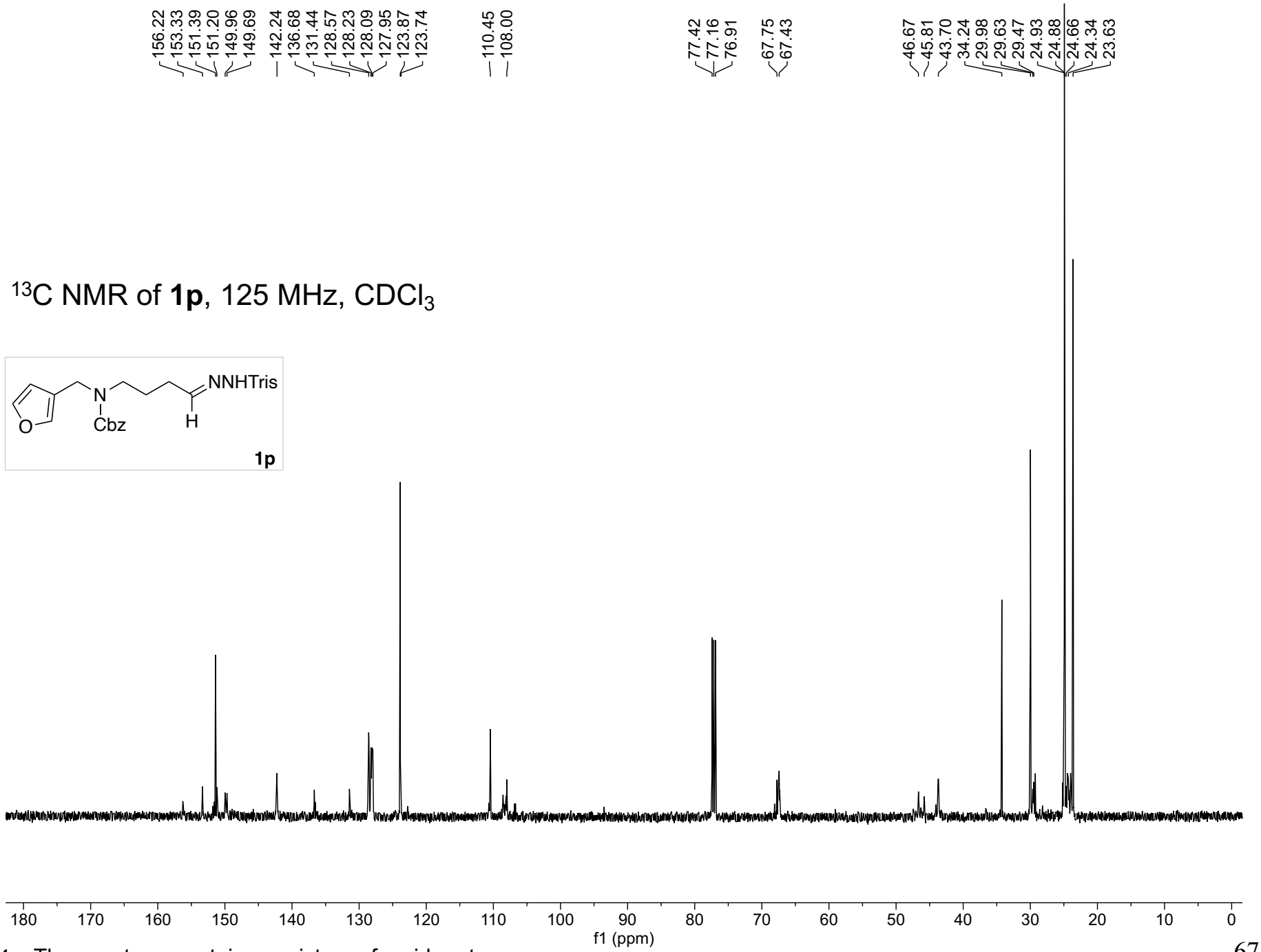
Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **1p**, 500 MHz, $CDCl_3$

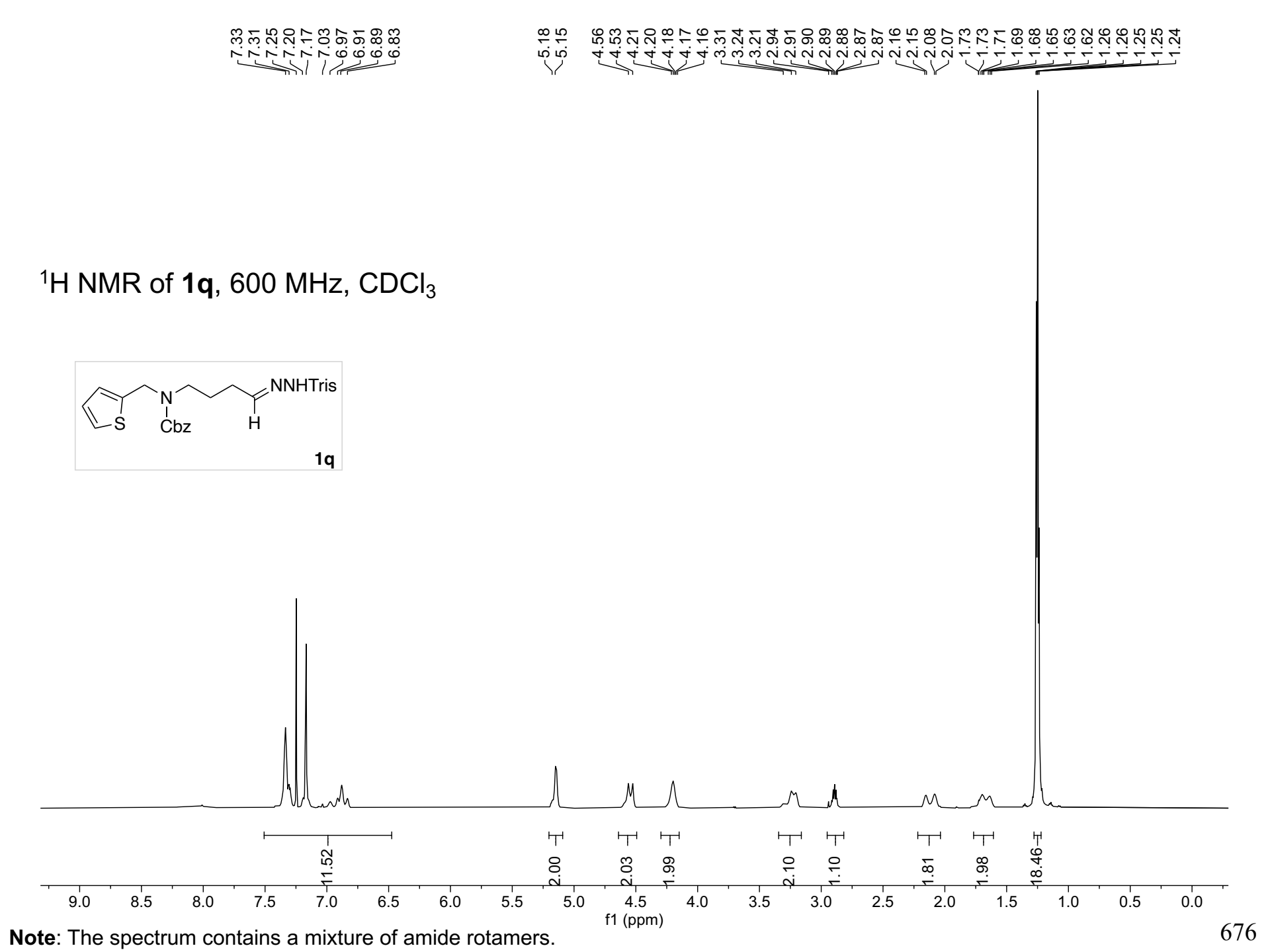


Note: The spectrum contains a mixture of amide rotamers.

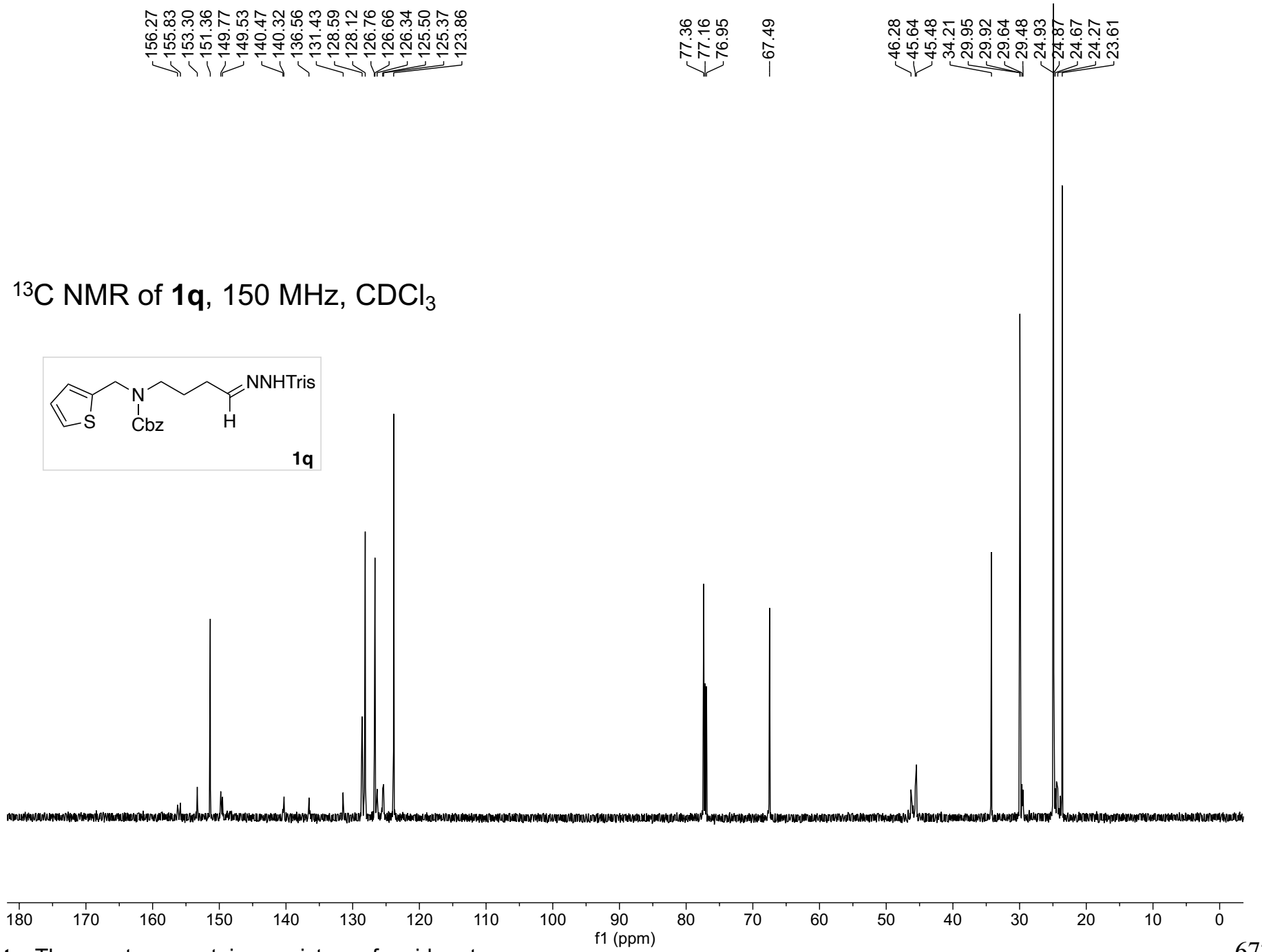


^{13}C NMR of **1p**, 125 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

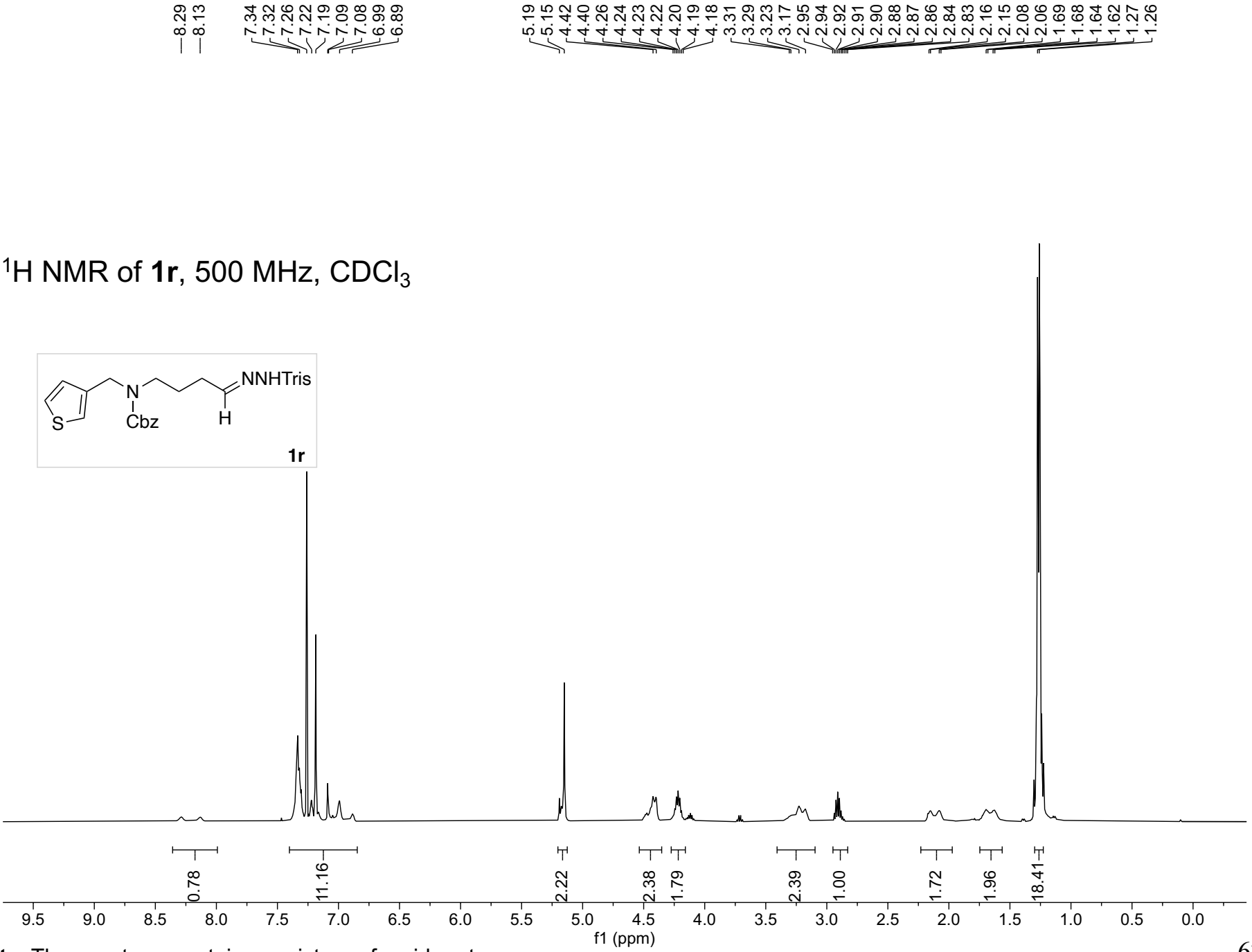


Note: The spectrum contains a mixture of amide rotamers.

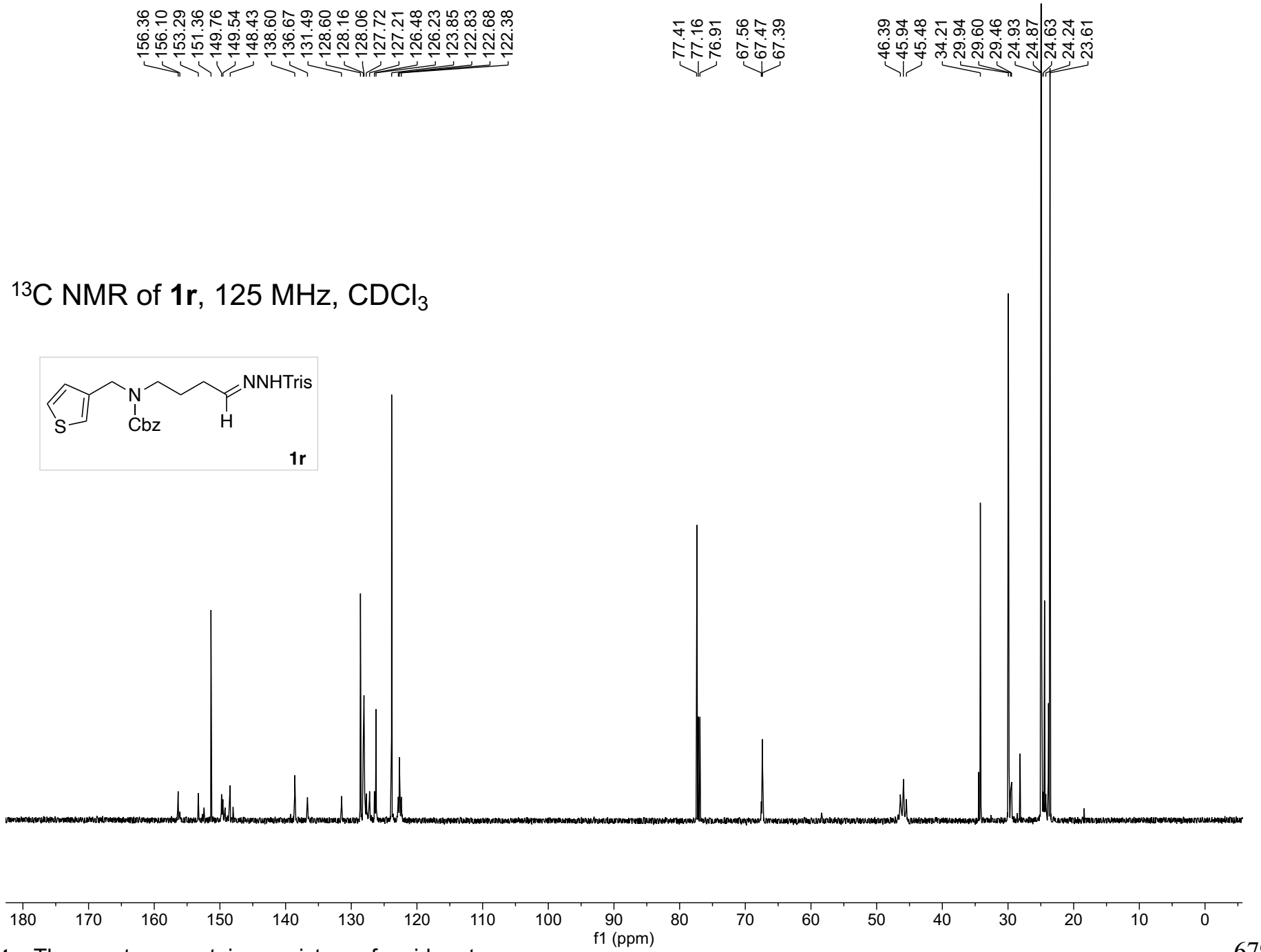


^{13}C NMR of **1q**, 150 MHz, $CDCl_3$

Note: The spectrum contains a mixture of amide rotamers.

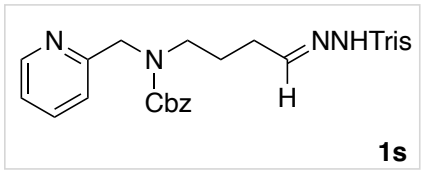


Note: The spectrum contains a mixture of amide rotamers.



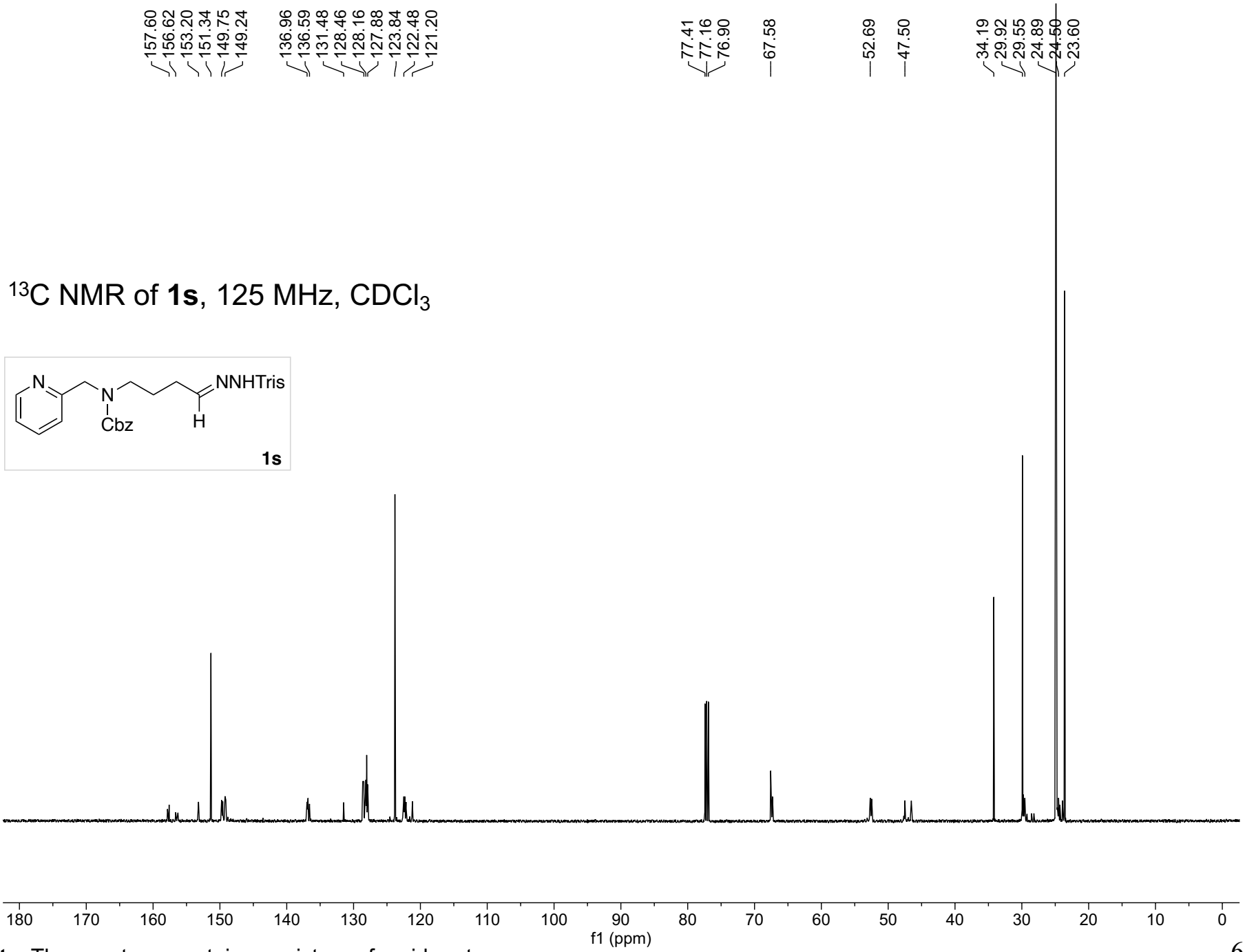
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1s**, 500 MHz, $CDCl_3$

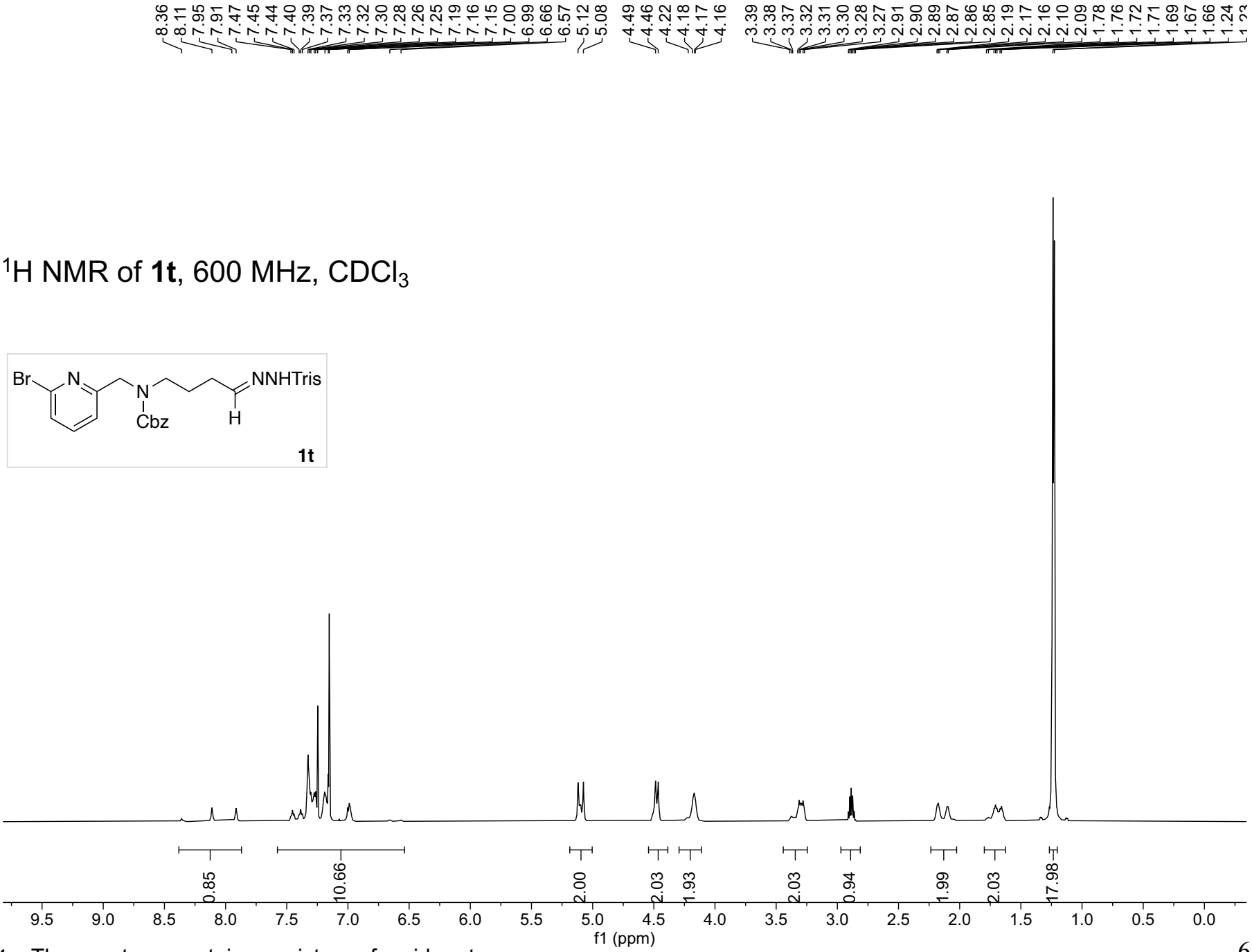


1s

Note: The spectrum contains a mixture of amide rotamers.

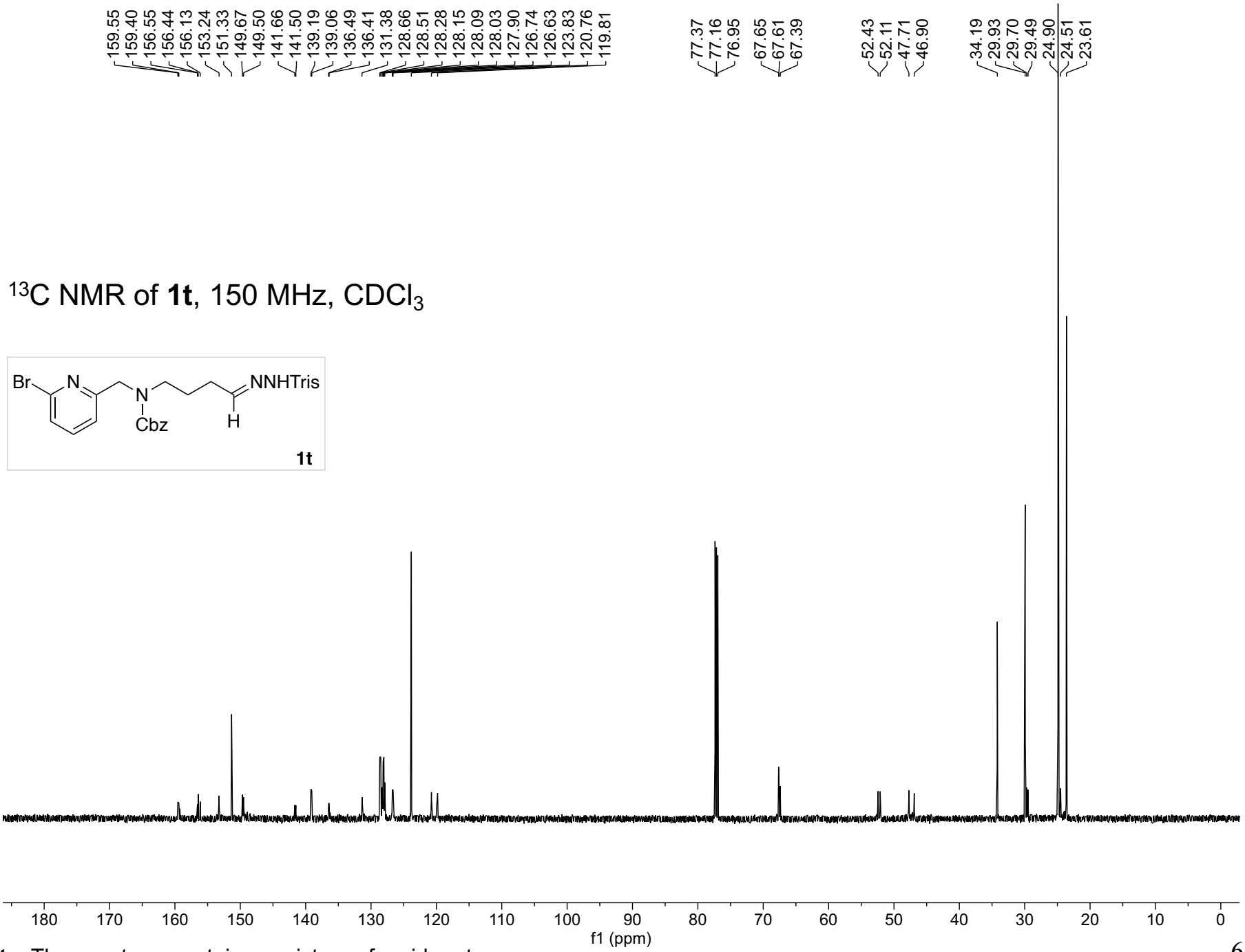


Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **1t**, 600 MHz, $CDCl_3$

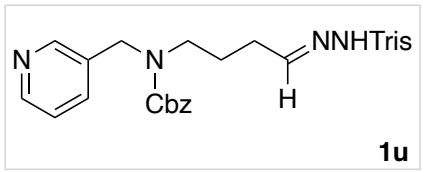
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **1t**, 150 MHz, $CDCl_3$

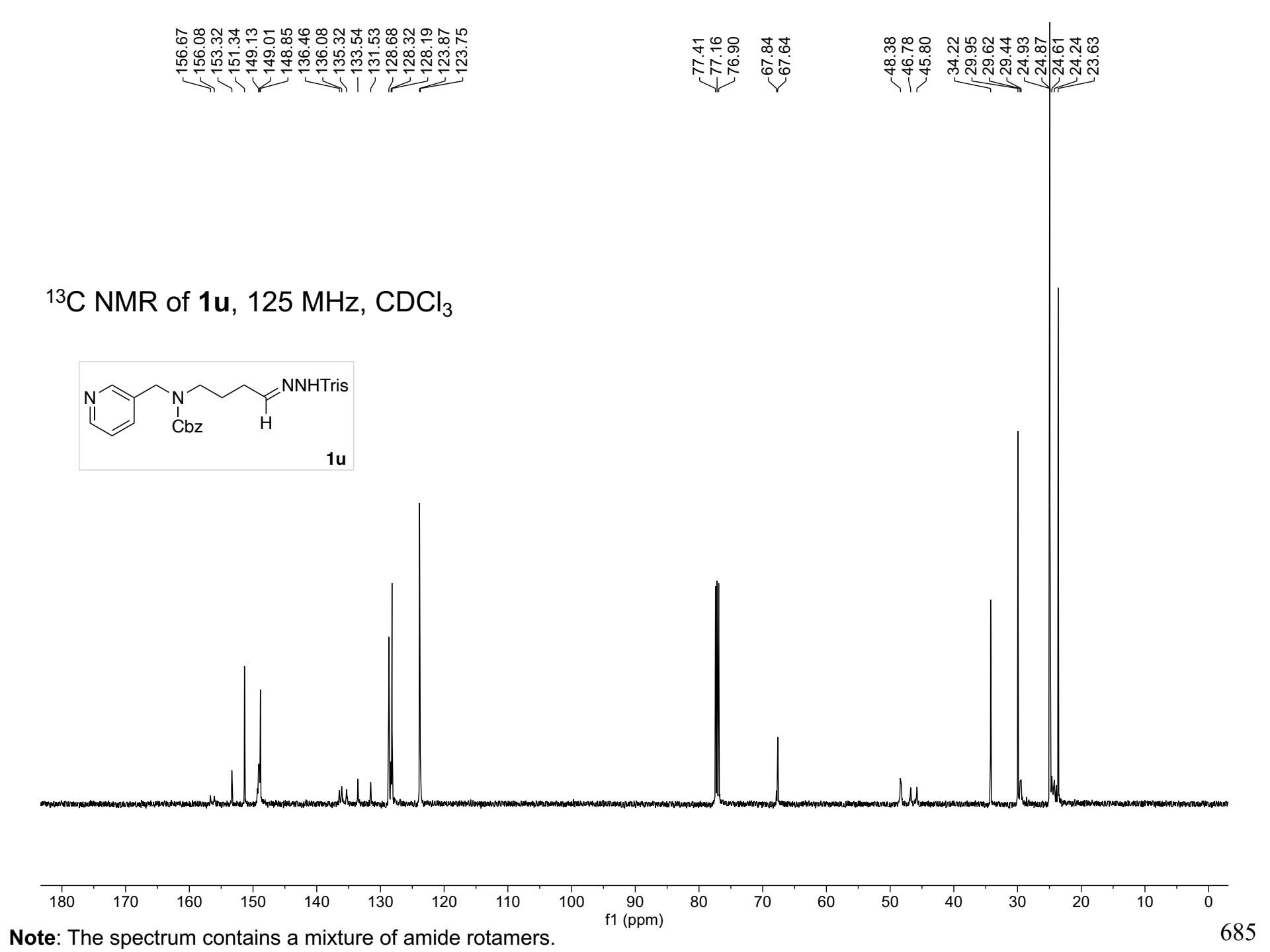
Note: The spectrum contains a mixture of amide rotamers.

^{1}H NMR of **1u**, 600 MHz, $CDCl_3$



1u

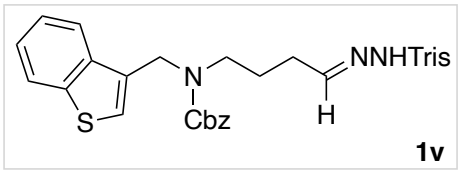
Note: The spectrum contains a mixture of amide rotamers.



^{13}C NMR of **1u**, 125 MHz, $CDCl_3$

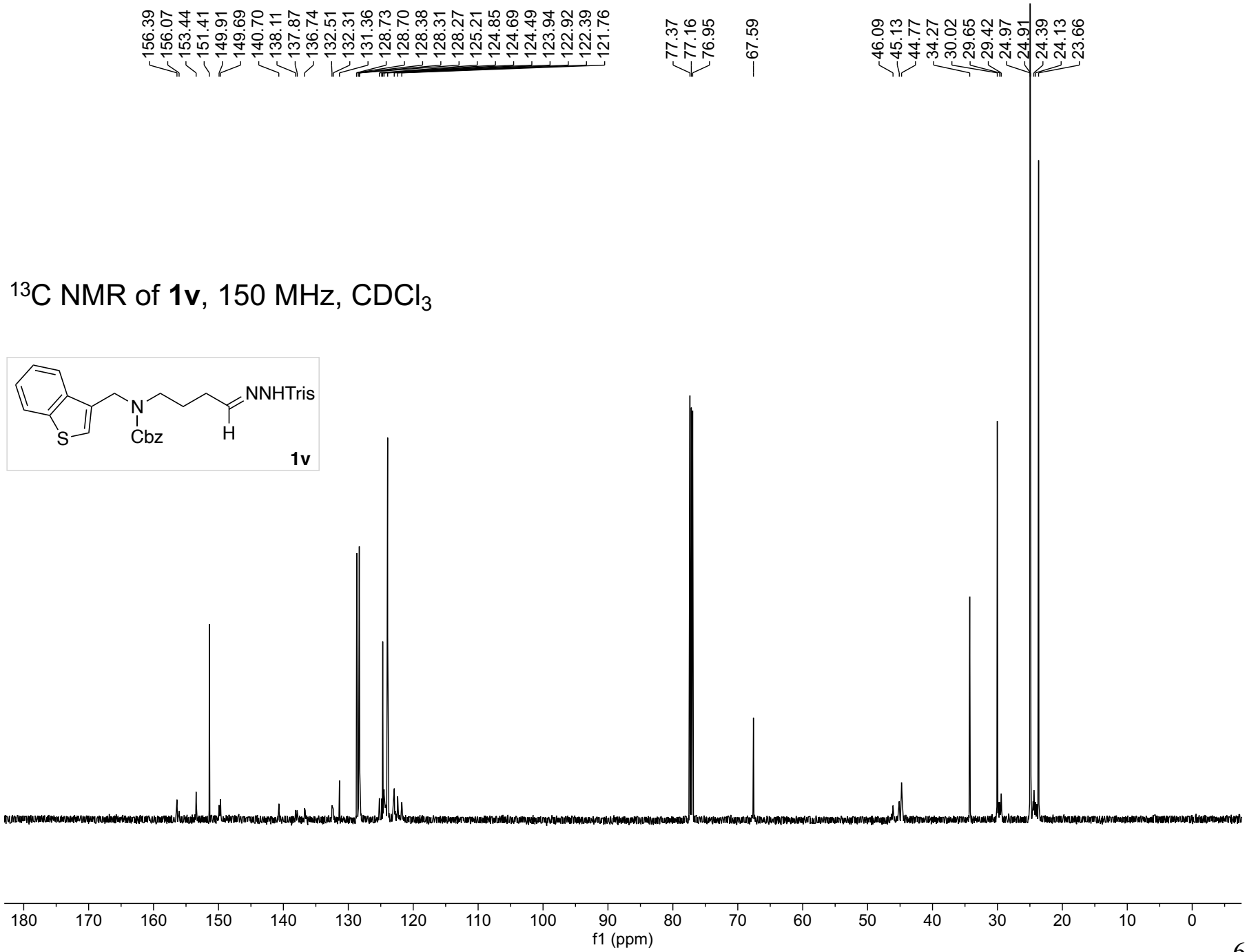
Note: The spectrum contains a mixture of amide rotamers.

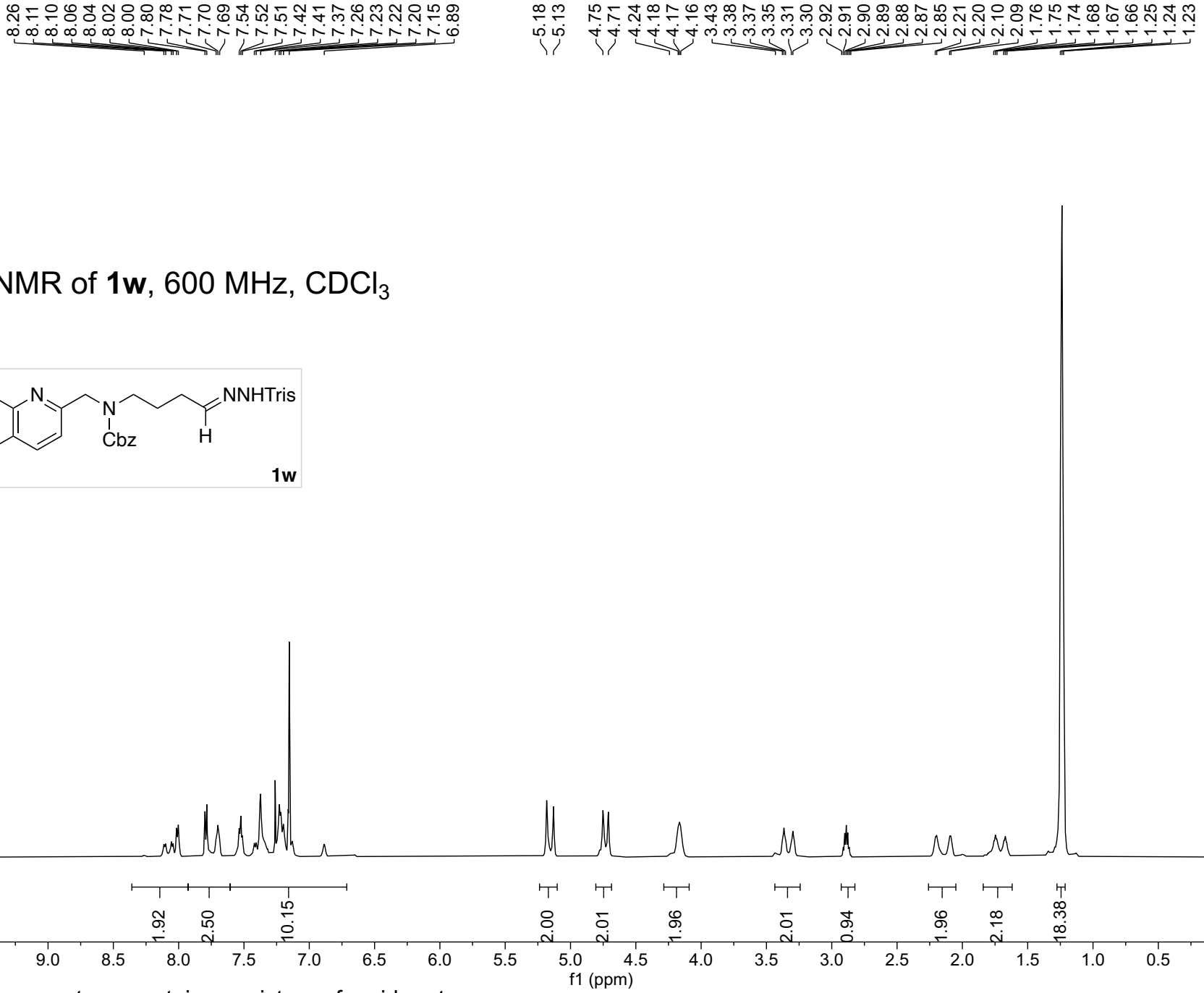
^{1}H NMR of **1v**, 600 MHz, $CDCl_3$



1v

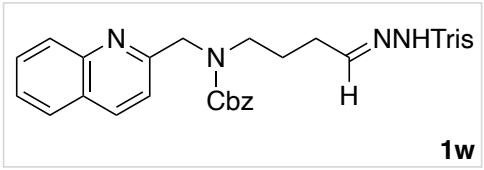
Note: The spectrum contains a mixture of amide rotamers.


156.39
156.07
153.44
151.41
149.91
149.69
140.70
138.11
137.87
136.74
132.51
132.31
131.36
128.73
128.70
128.38
128.31
128.27
125.21
124.85
124.69
124.49
123.94
122.92
122.39
121.76
77.37
77.16
76.95
67.59
46.09
45.13
44.77
34.27
30.02
29.65
29.42
24.97
24.91
24.39
24.13
23.66
^{13}C NMR of **1v**, 150 MHz, $CDCl_3$
NNHTris
N
Cbz
H
S
1v
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Note: The spectrum contains a mixture of amide rotamers.

^{13}C NMR of **1w**, 150 MHz, $CDCl_3$



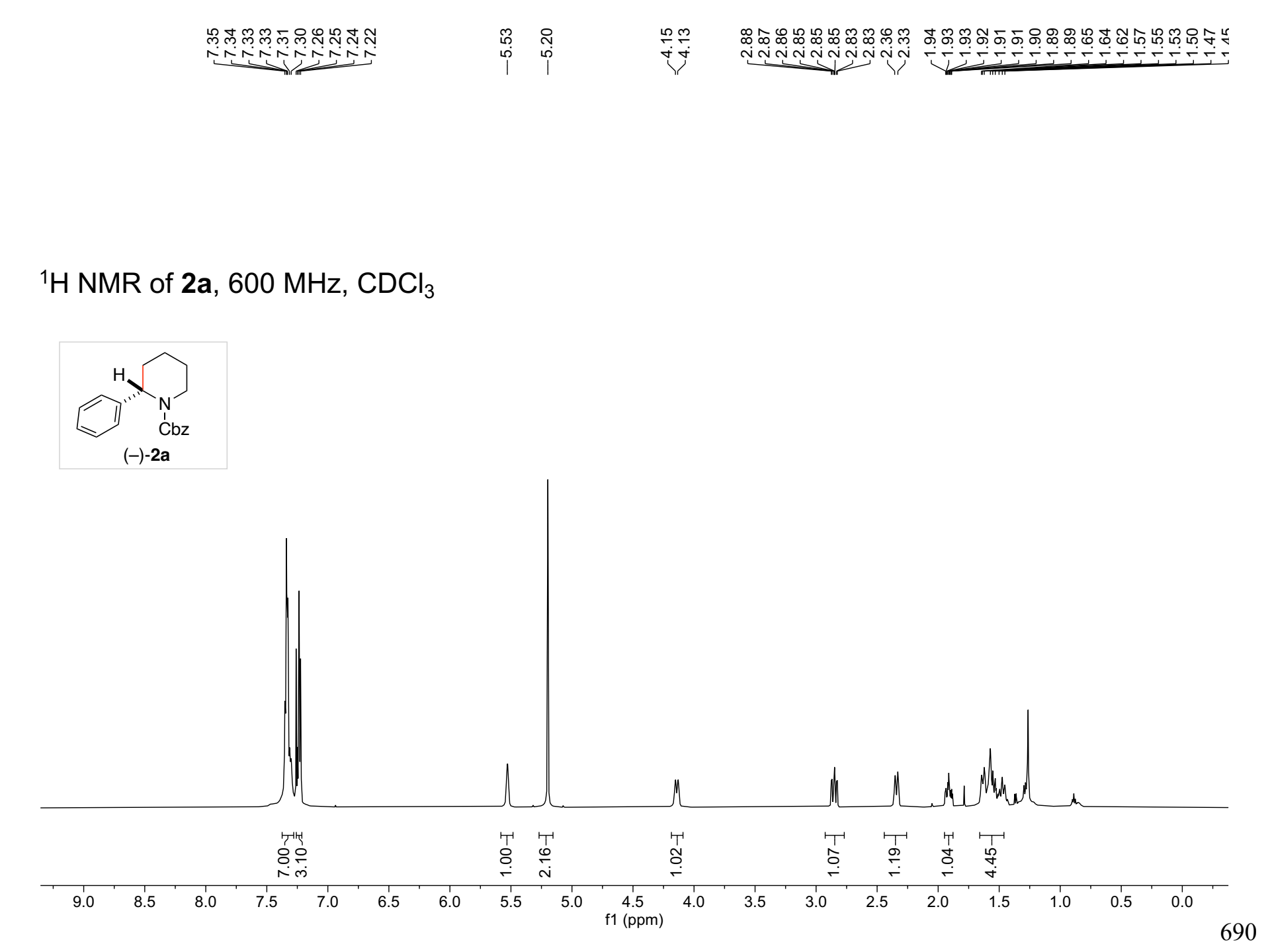
1w

158.30
156.84
156.74
156.39
153.34
151.40
150.00
149.78
147.72
137.05
136.68
136.59
131.37
129.84
129.09
128.75
128.49
128.38
128.30
128.07
127.93
127.72
127.53
127.40
126.61
126.52
123.90
120.11
119.14
77.37
77.16
76.95
67.74
67.70
67.43
53.51
53.29
47.60
46.45
34.28
34.26
30.00
29.82
29.52
24.94
24.81
24.58
23.65

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

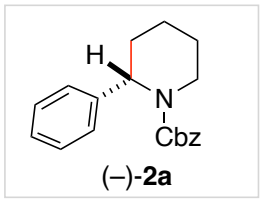
Note: The spectrum contains a mixture of amide rotamers.



^{1}H NMR of **2a**, 600 MHz, $CDCl_3$

156.29
139.95
137.07
128.74
128.57
128.02
127.89
126.67
126.65
77.37
77.16
76.95
67.29
53.67
40.63
28.19
25.59
19.45

^{13}C NMR of (–)-**2a**, 150 MHz, $CDCl_3$

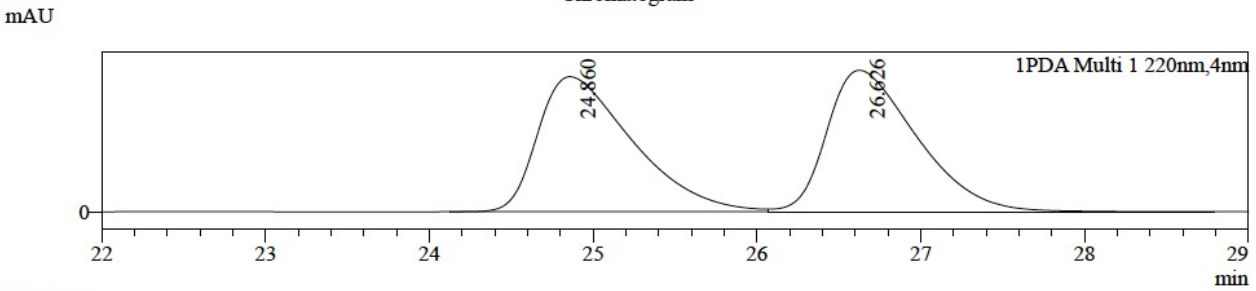


(–)-**2a**

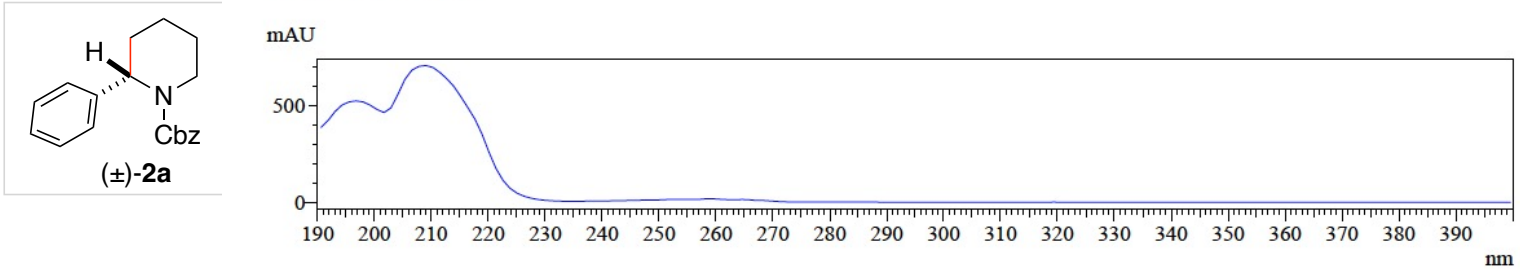
Sample Information

Data File	: XXW-1109-rac-5%-ID-0.8mL001.lcd
Sample Name	: XXW-1109-rac-5%-ID-0.8mL001
Sample ID	: XXW-1109-rac-5%-ID-0.8mL001
Method File	: P0X-5%.0.8.mL-30min.lcm

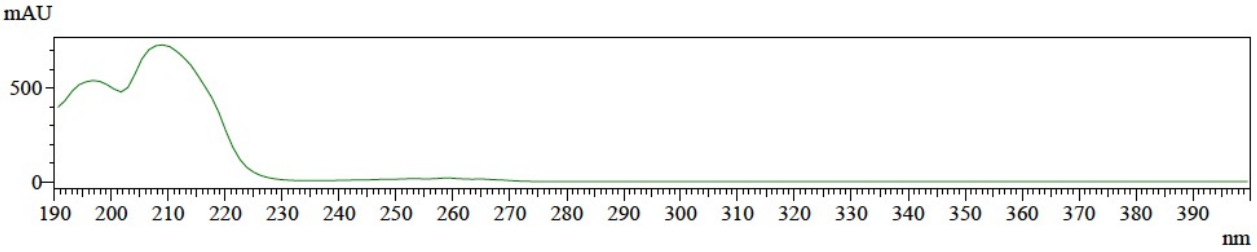
Chromatogram



UV Spectrum
Retention time = 24.860



UV Spectrum
Retention time = 26.626



Peak Table

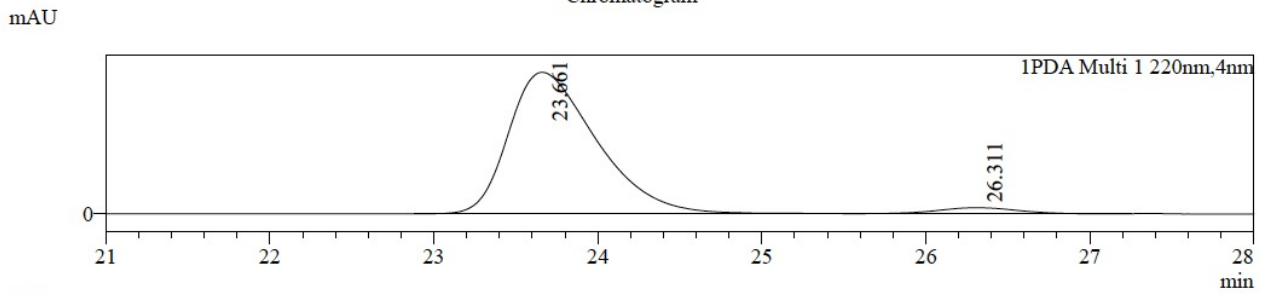
PDA Ch1 220nm

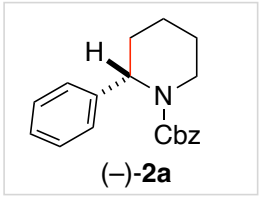
Peak#	Ret. Time	Area	Area%
1	24.860	10797507	50.146
2	26.626	10734683	49.854
Total		21532190	100.000

Sample Information

Data File	: XXW-1492-ID-5%-0.8mL001.lcd
Sample Name	: XXW-1492-ID-5%-0.8mL001
Sample ID	: XXW-1492-ID-5%-0.8mL001
Method File	: XXW-5%.0.8.mL.lcm

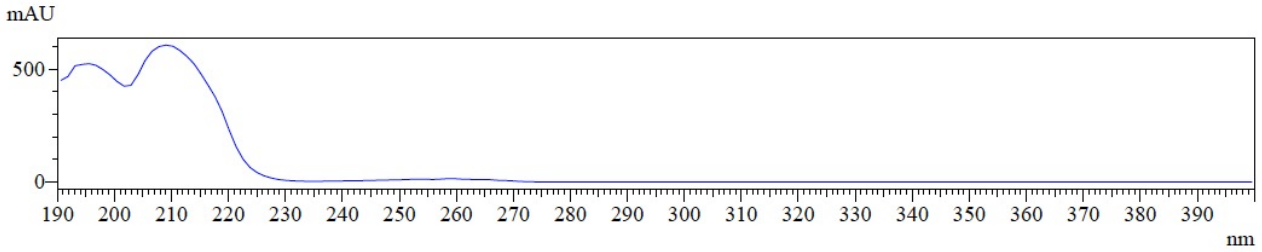
Chromatogram



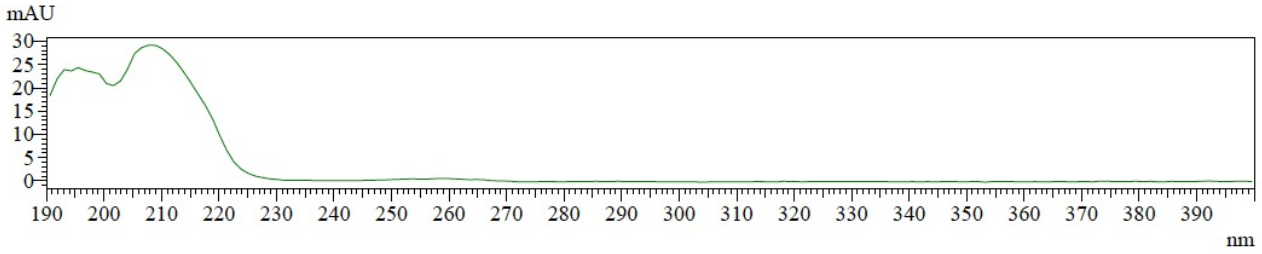


(–)-**2a**

UV Spectrum
Retention time = 23.661



UV Spectrum
Retention time = 26.311

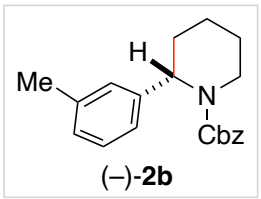


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	23.661	8927216	96.065
2	26.311	365687	3.935
Total		9292902	100.000

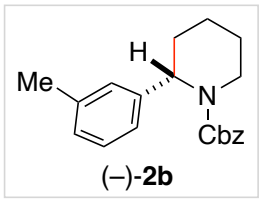
^{1}H NMR of **2b**, 500 MHz, $CDCl_3$



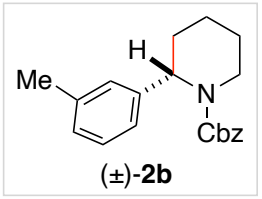
(–)-**2b**

156.26
139.91
138.32
137.13
128.61
128.56
127.98
127.85
127.39
127.35
123.67
77.42
77.16
76.91
67.22
53.62
40.63
28.20
25.59
21.75
19.48

^{13}C NMR of **2b**, 125 MHz, $CDCl_3$



(–)-**2b**

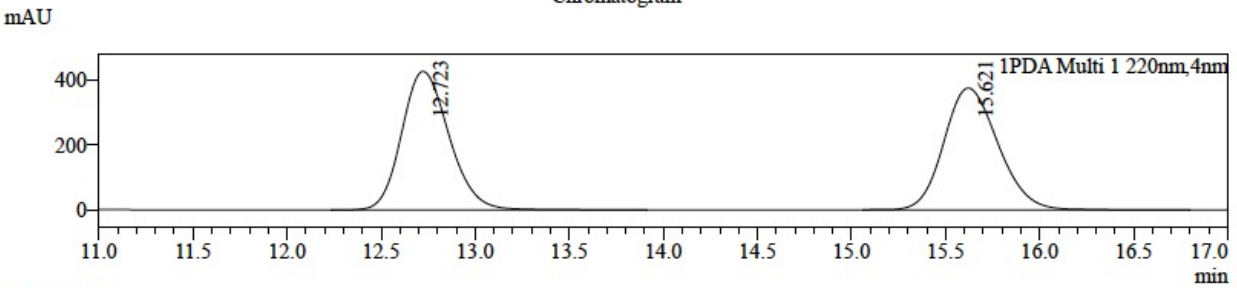


(±)-**2b**

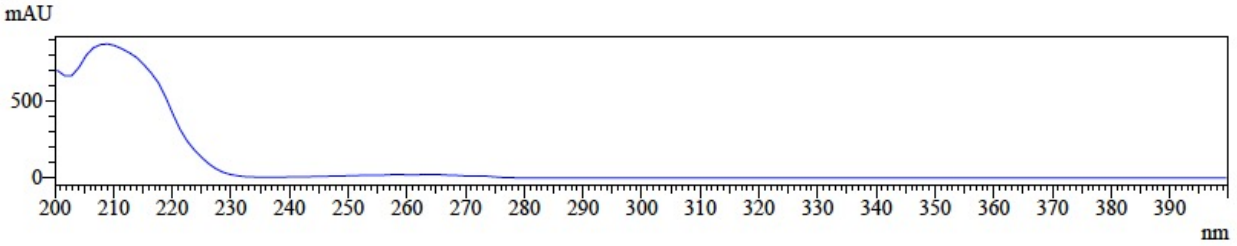
Sample Information

Data File	: XXW-1437-ID-10%-0.8mL002.lcd
Sample Name	: XXW-1437-ID-10%-0.8mL
Sample ID	: XXW-1437-ID-10%-0.8mL
Method File	: XXW-10%.0.8.mL.lcm

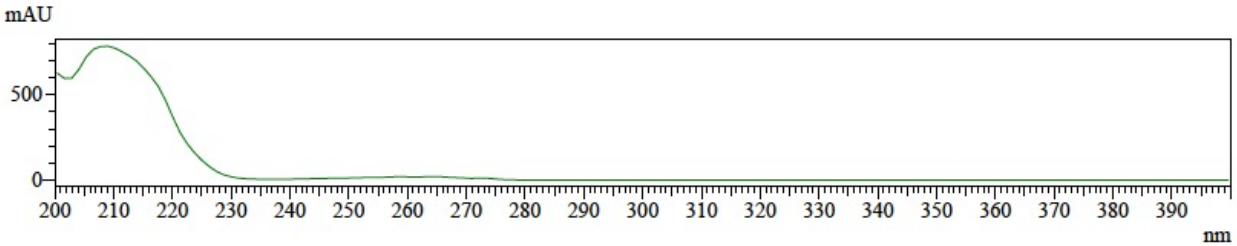
Chromatogram



UV Spectrum
Retention time = 12.723



UV Spectrum
Retention time = 15.621



Peak Table

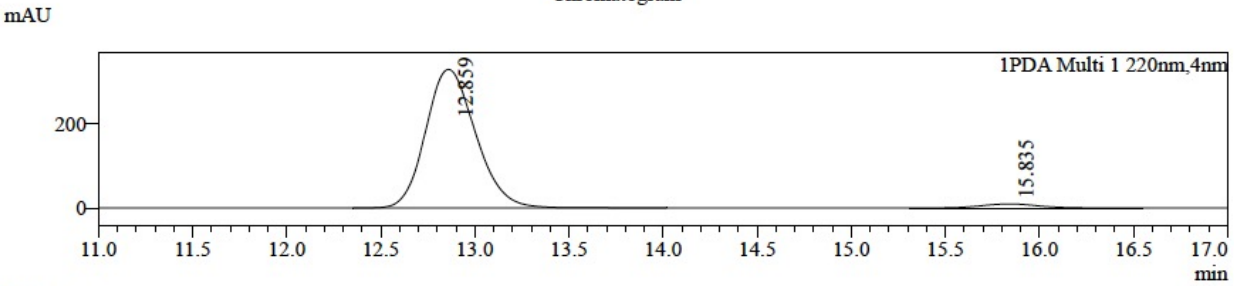
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.723	7502487	49.865
2	15.621	7543044	50.135
Total		15045530	100.000

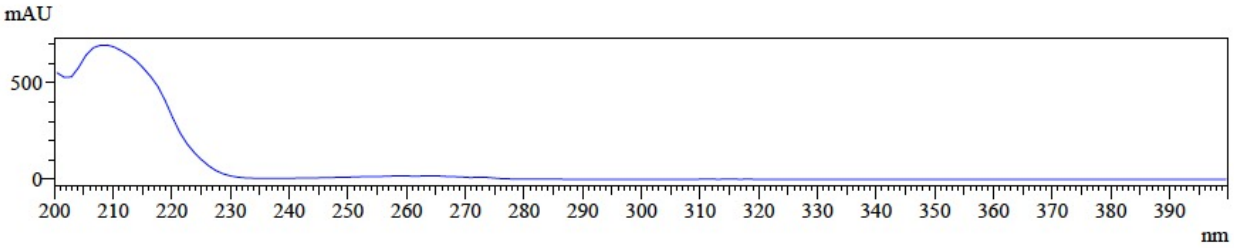
Sample Information

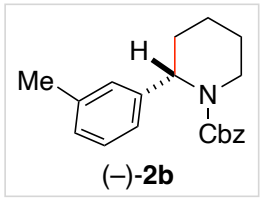
Data File	: XXW-1438-ID-10%-0.8mL.lcd
Sample Name	: XXW-1438-ID-10%-0.8mL
Sample ID	: XXW-1438-ID-10%-0.8mL
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram

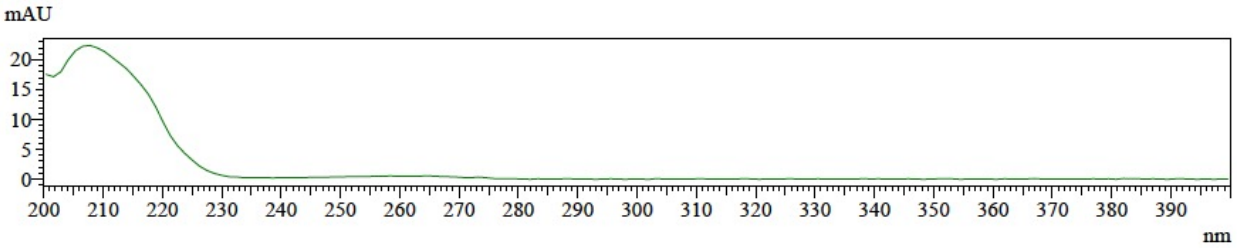


UV Spectrum
Retention time = 12.859





UV Spectrum
Retention time = 15.835

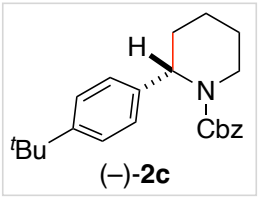


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	12.859	6092003	96.774
2	15.835	203112	3.226
Total		6295115	100.000

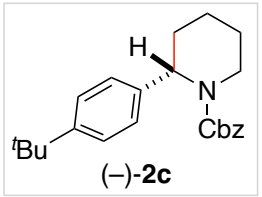
^{1}H NMR of **2c**, 600 MHz, $CDCl_3$



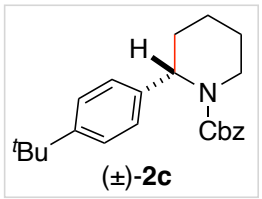
(–)-**2c**

156.26
149.44
137.12
136.78
128.55
127.96
127.86
126.36
125.59
77.37
77.16
76.95
67.21
53.40
40.55
34.48
31.49
28.13
25.63
19.47

^{13}C NMR of **2c**, 150 MHz, $CDCl_3$



(–)-**2c**

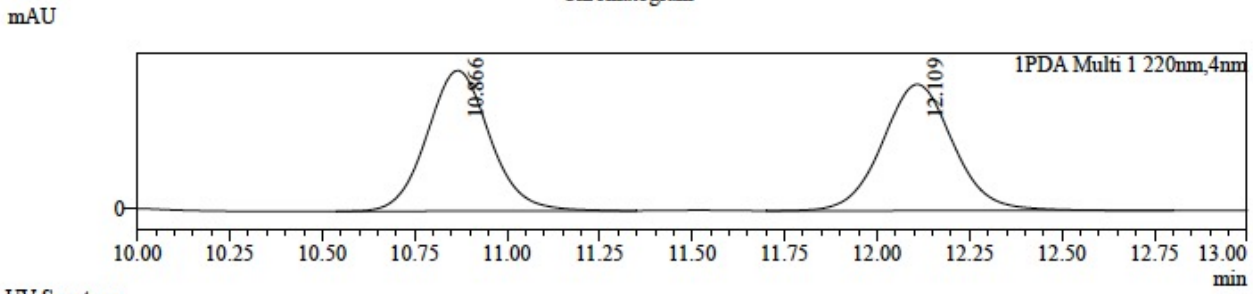


(±)-**2c**

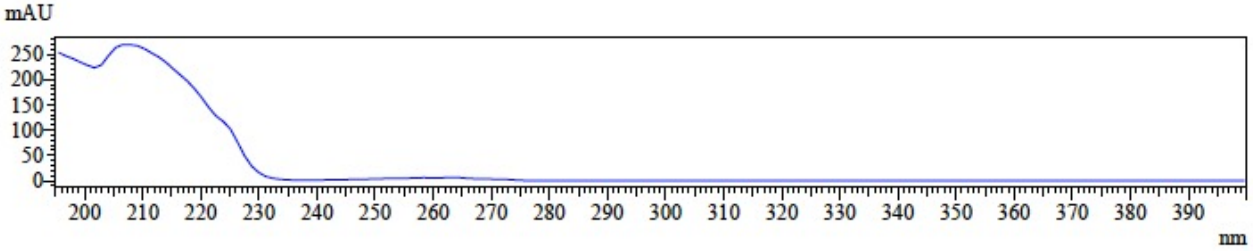
Sample Information

Sample Name	: XXW-1478-IA-10%-0.8mL
Sample ID	: XXW-1478-IA-10%-0.8mL
Data File	: XXW-1478-IA-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

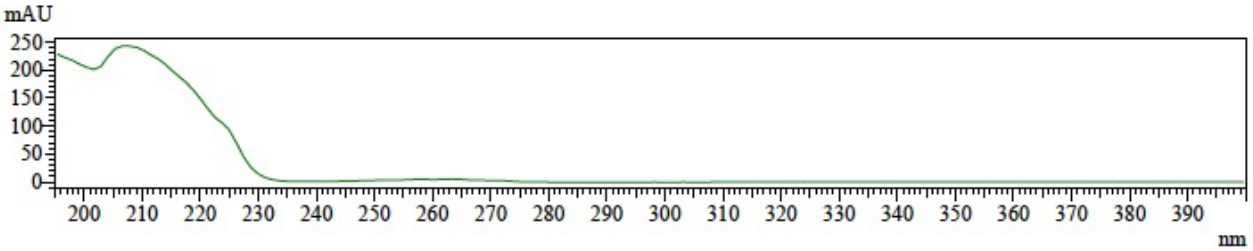
Chromatogram



UV Spectrum
Retention time = 10.866



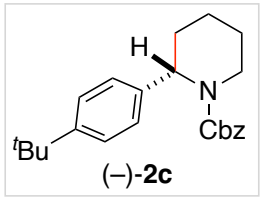
UV Spectrum
Retention time = 12.109



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	10.866	1973567	49.657
2	12.109	2000871	50.343
Total		3974438	100.000

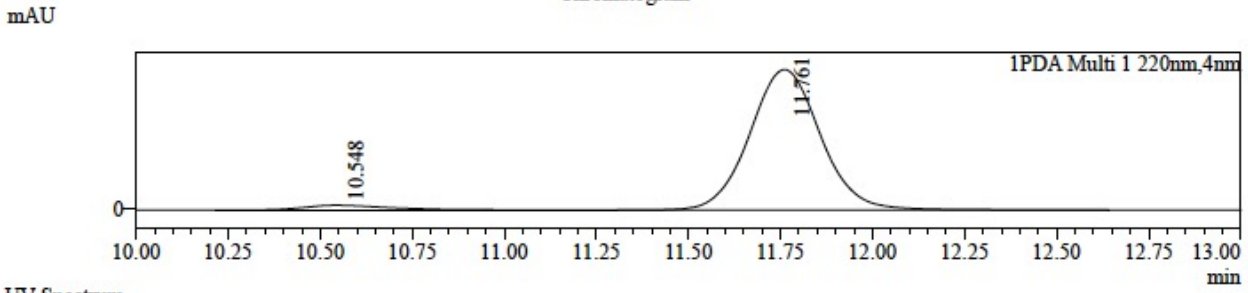


(–)-**2c**

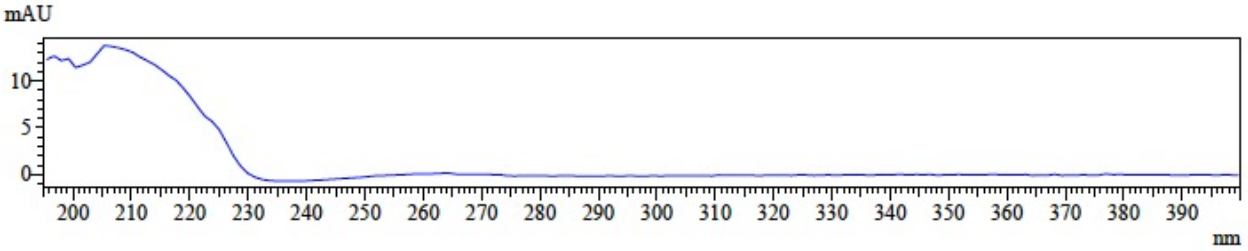
Sample Information

Sample Name	: XXW-1479-IA-10%-0.8mL
Sample ID	: XXW-1479-IA-10%-0.8mL
Data File	: XXW-1479-IA-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

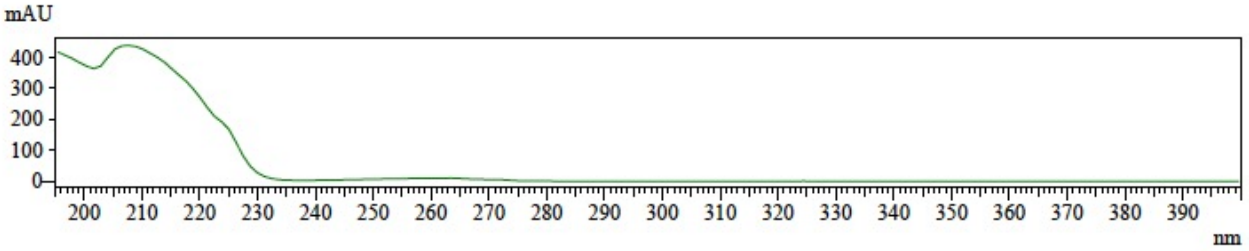
Chromatogram



UV Spectrum
Retention time = 10.548



UV Spectrum
Retention time = 11.761



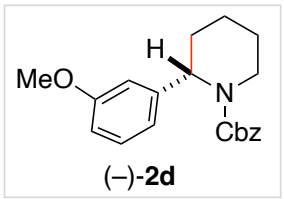
Peak Table

PDA Ch1 220nm

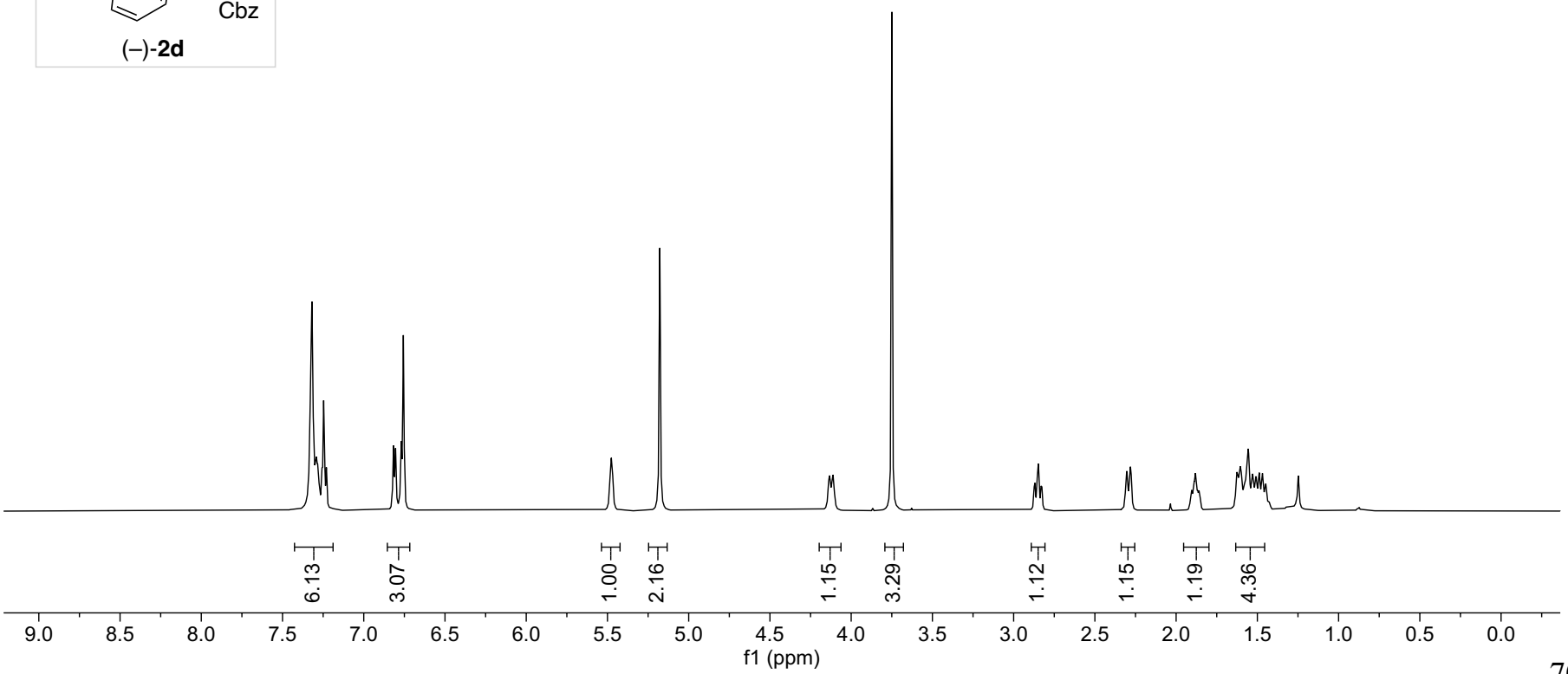
Peak#	Ret. Time	Area	Area%
1	10.548	149550	3.991
2	11.761	3597176	96.009
Total		3746726	100.000

7.32
7.29
7.26
7.25
7.23
6.82
6.80
6.77
6.76
5.48
5.18
4.13
4.11
3.75
2.87
2.87
2.85
2.83
2.83
2.30
2.28
1.90
1.90
1.89
1.88
1.87
1.87
1.86
1.63
1.60
1.58
1.56
1.53
1.51
1.49
1.47
1.47
1.45

^{1}H NMR of **2d**, 600 MHz, $CDCl_3$

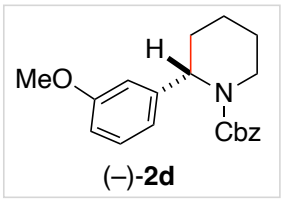


(–)-**2d**

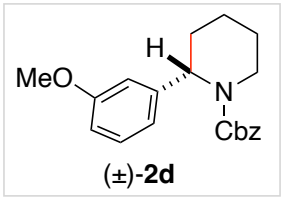


160.15
156.23
141.83
137.09
129.72
128.58
128.02
127.91
119.01
112.88
111.64
77.37
77.16
76.95
67.27
55.31
53.66
40.72
28.28
25.53
19.51

^{13}C NMR of **2d**, 150 MHz, $CDCl_3$



(–)-**2d**

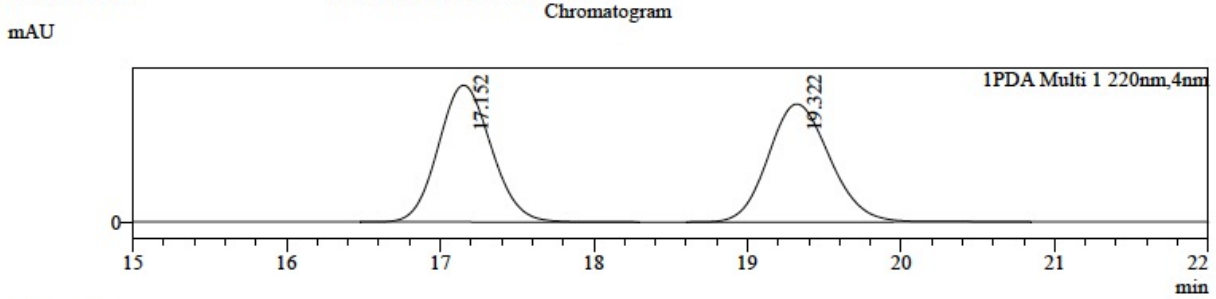


(±)-**2d**

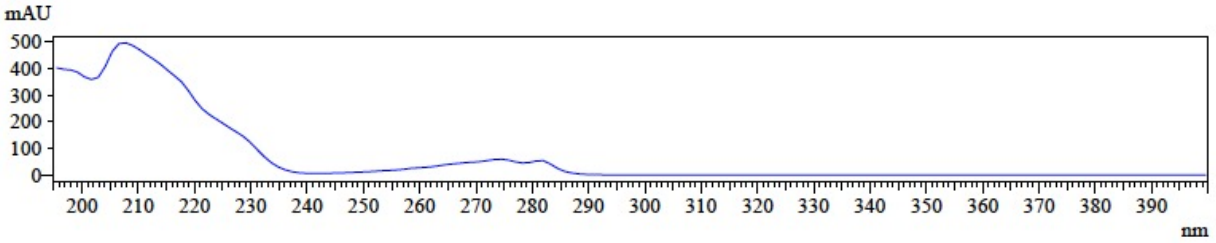
Sample Information

Sample Name	: XXW-1366-10%-IC-0.8mL
Sample ID	: XXW-1366-10%-IC-0.8mL
Data File	: XXW-1366-10%-IC-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

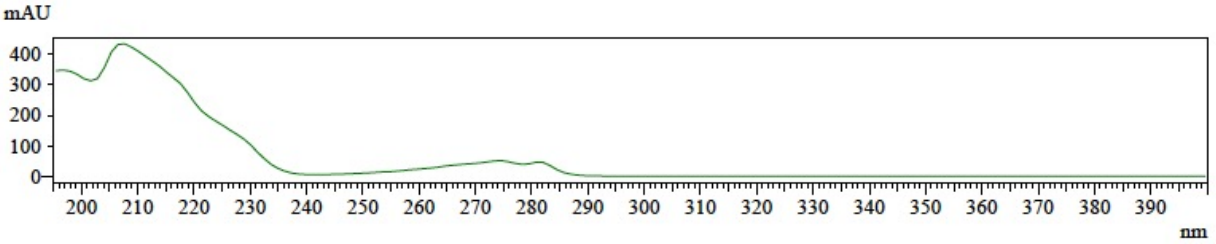
Chromatogram



UV Spectrum
Retention time = 17.152



UV Spectrum
Retention time = 19.322



Peak Table

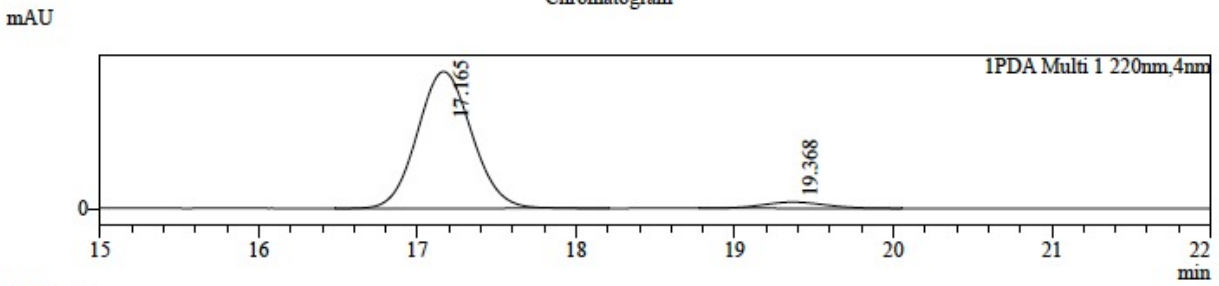
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.152	6877100	49.898
2	19.322	6905106	50.102
Total		13782206	100.000

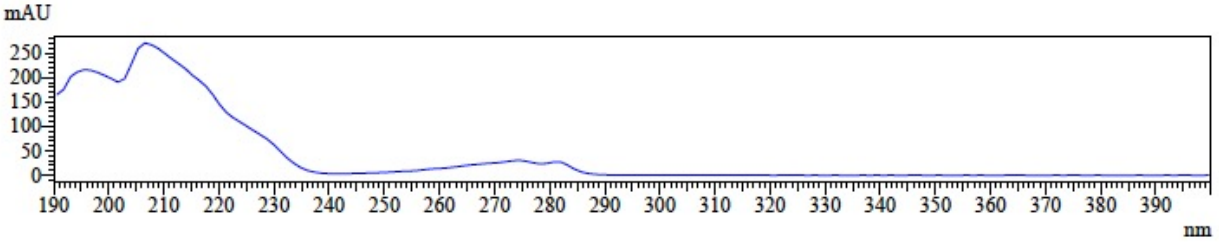
Sample Information

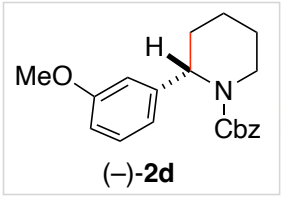
Data File	: XXW-1367-10%-IC-0.8mL.lcd
Sample Name	: XXW-1367-10%-IC-0.8mL
Sample ID	: XXW-1367-10%-IC-0.8mL
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



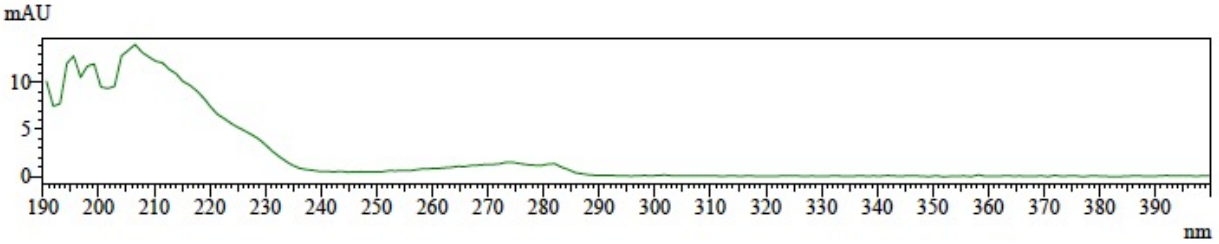
UV Spectrum
Retention time = 17.165





(–)-**2d**

UV Spectrum
Retention time = 19.368

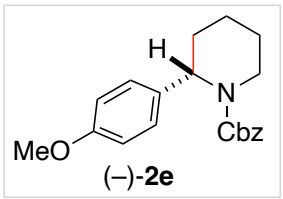


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.165	3546226	95.014
2	19.368	186098	4.986
Total		3732324	100.000

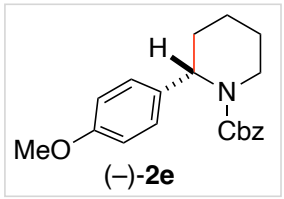
^{1}H NMR of **2e**, 500 MHz, $CDCl_3$



(–)-**2e**

158.36
156.23
137.11
131.83
128.58
128.01
127.88
127.82
114.10
77.41
77.16
76.91
67.25
55.40
53.11
40.43
28.15
25.66
19.41

^{13}C NMR of **2e**, 125 MHz, $CDCl_3$

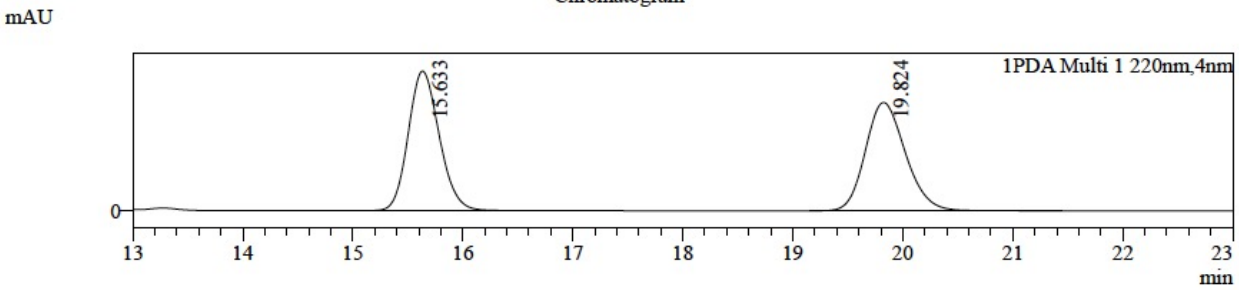


(–)-**2e**

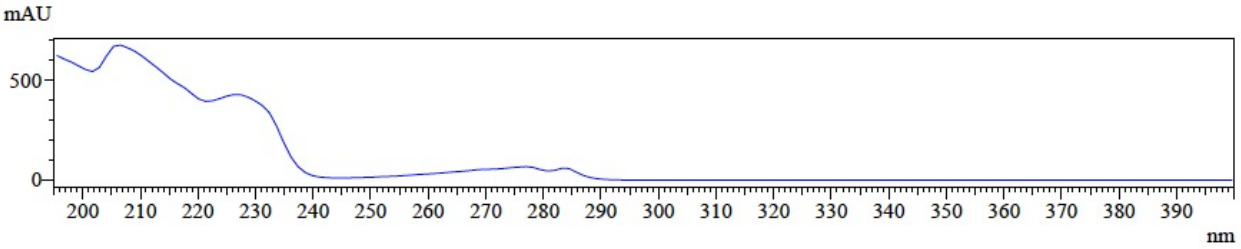
Sample Information

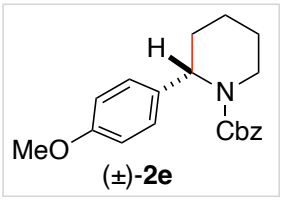
Sample Name	: XXW--1194--10%-IF-0.8mL
Sample ID	: XXW--1194--10%-IF-0.8mL
Data File	: XXW--1194--10%-IF-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



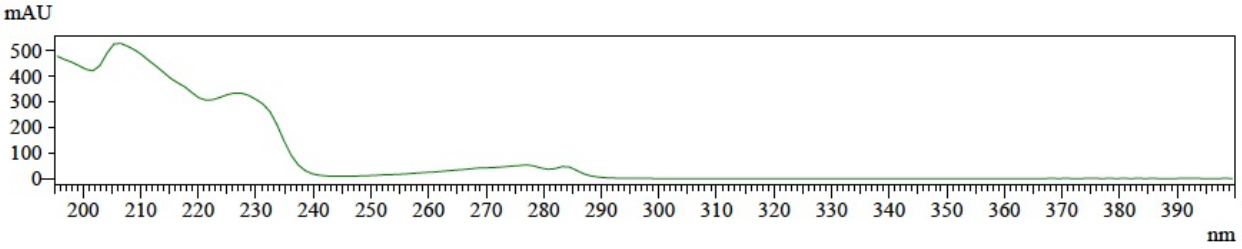
UV Spectrum
Retention time = 15.633





(±)-**2e**

UV Spectrum
Retention time = 19.824



Peak Table

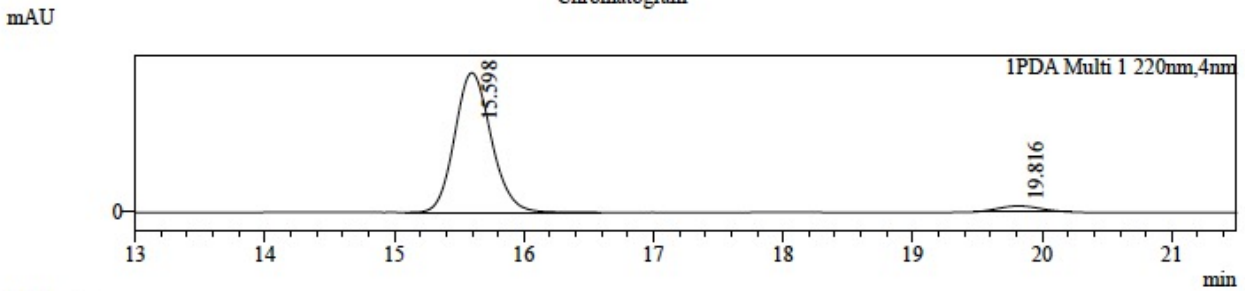
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.633	8380509	49.912
2	19.824	8409976	50.088
Total		16790485	100.000

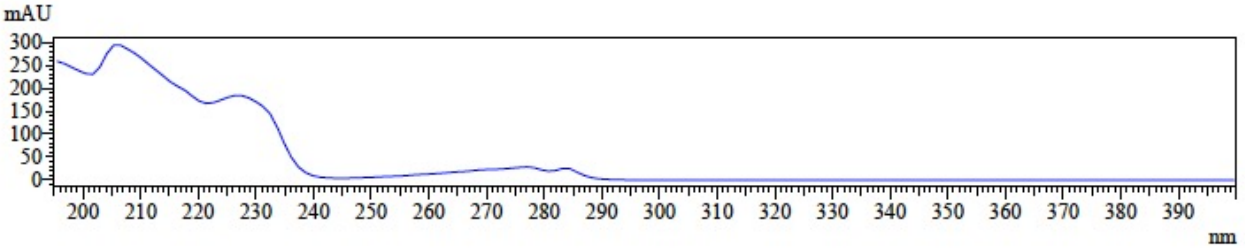
Sample Information

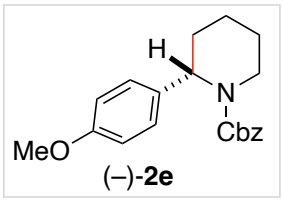
Sample Name	: XXW--1195--10%-IF-0.8mL
Sample ID	: XXW--1195--10%-IF-0.8mL
Data File	: XXW--1195--10%-IF-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



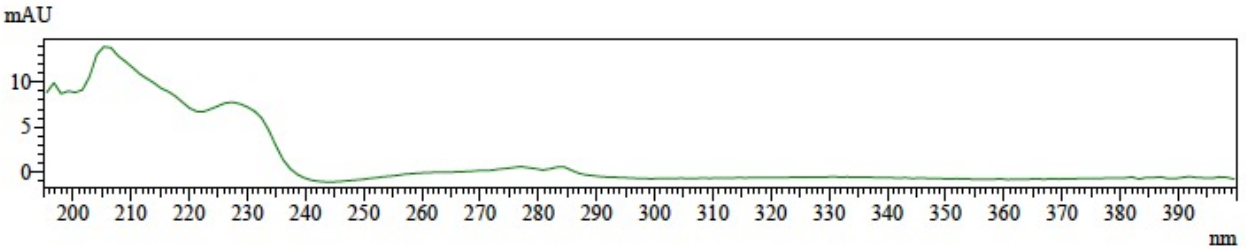
UV Spectrum
Retention time = 15.598





(–)-**2e**

UV Spectrum
Retention time = 19.816

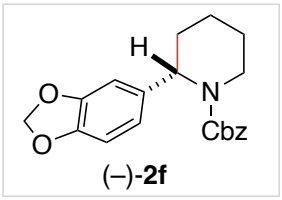


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.598	3566978	95.339
2	19.816	174387	4.661
Total		3741365	100.000

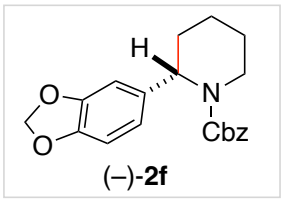
^{1}H NMR of **2f**, 500 MHz, $CDCl_3$



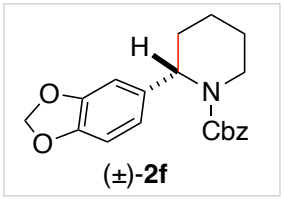
(–)-**2f**

156.15
148.28
146.27
137.03
133.95
128.59
128.04
127.89
119.70
108.34
107.38
101.12
77.41
77.16
76.91
67.30
53.45
40.50
28.34
25.53
19.39

^{13}C NMR of **2f**, 125 MHz, $CDCl_3$



(–)-**2f**

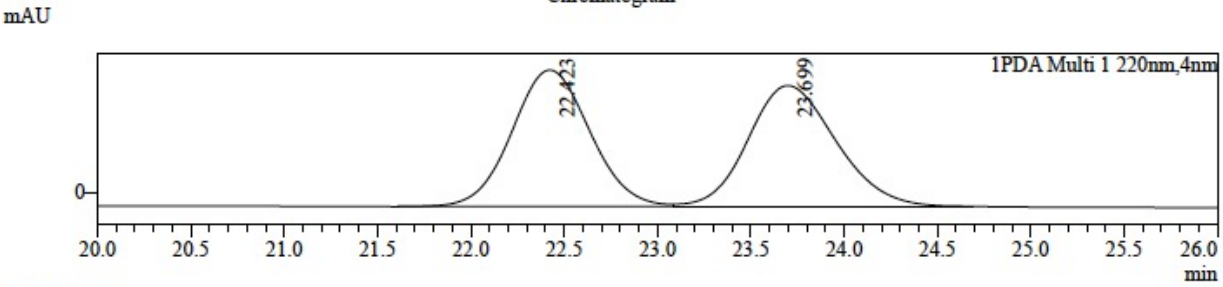


(±)-**2f**

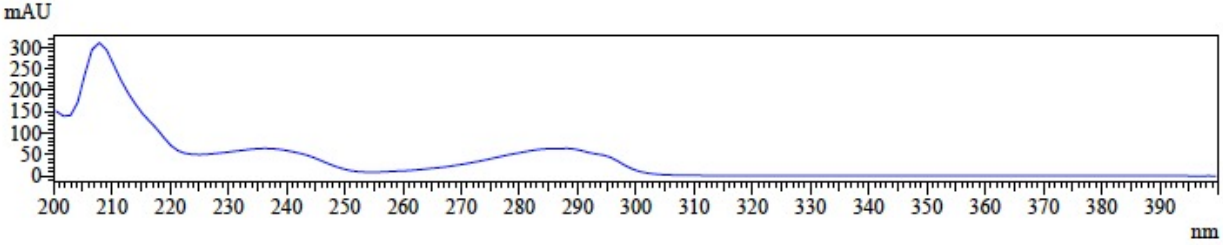
Sample Information

Data File	: XXW-1563--IE-20%-0.8mL001.lcd
Sample Name	: XXW-1563--IE-20%-0.8mL
Sample ID	: XXW-1563--IE-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

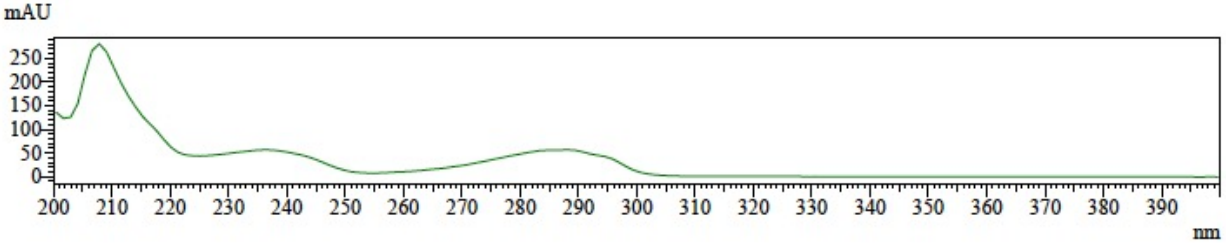
Chromatogram



UV Spectrum
Retention time = 22.423



UV Spectrum
Retention time = 23.699



Peak Table

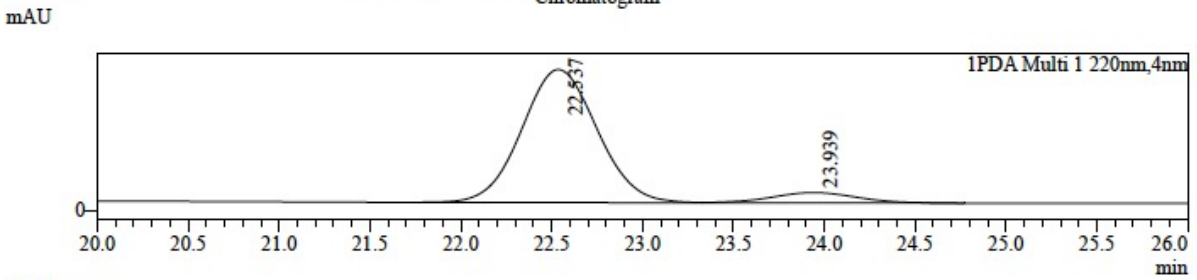
PDA Ch1 220nm

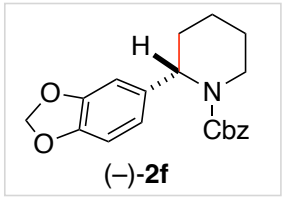
Peak#	Ret. Time	Area	Area%
1	22.423	2609653	49.997
2	23.699	2609949	50.003
Total		5219602	100.000

Sample Information

Data File	: XXW-1564--IE-20%-0.8mL001.lcd
Sample Name	: XXW-1564--IE-20%-0.8mL
Sample ID	: XXW-1564--IE-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

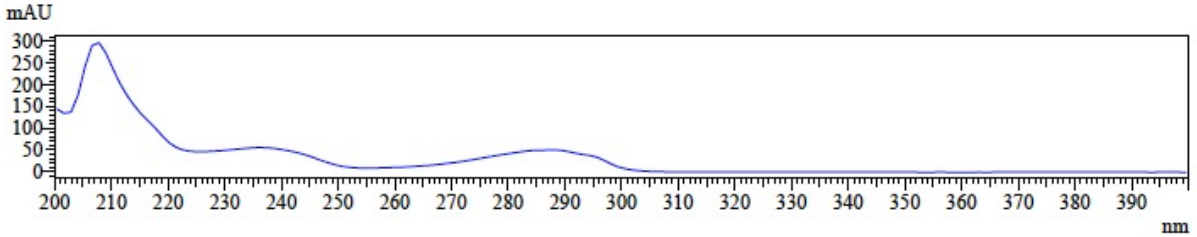
Chromatogram



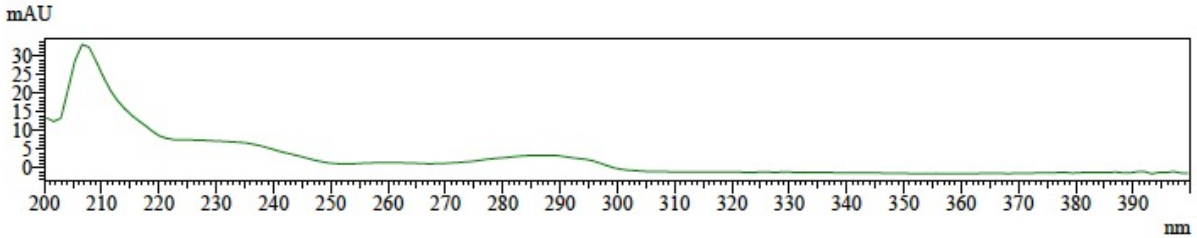


(–)-**2f**

UV Spectrum
Retention time = 22.537



UV Spectrum
Retention time = 23.939

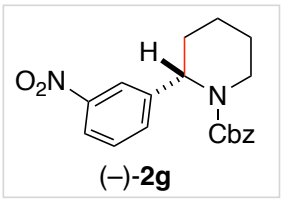


Peak Table

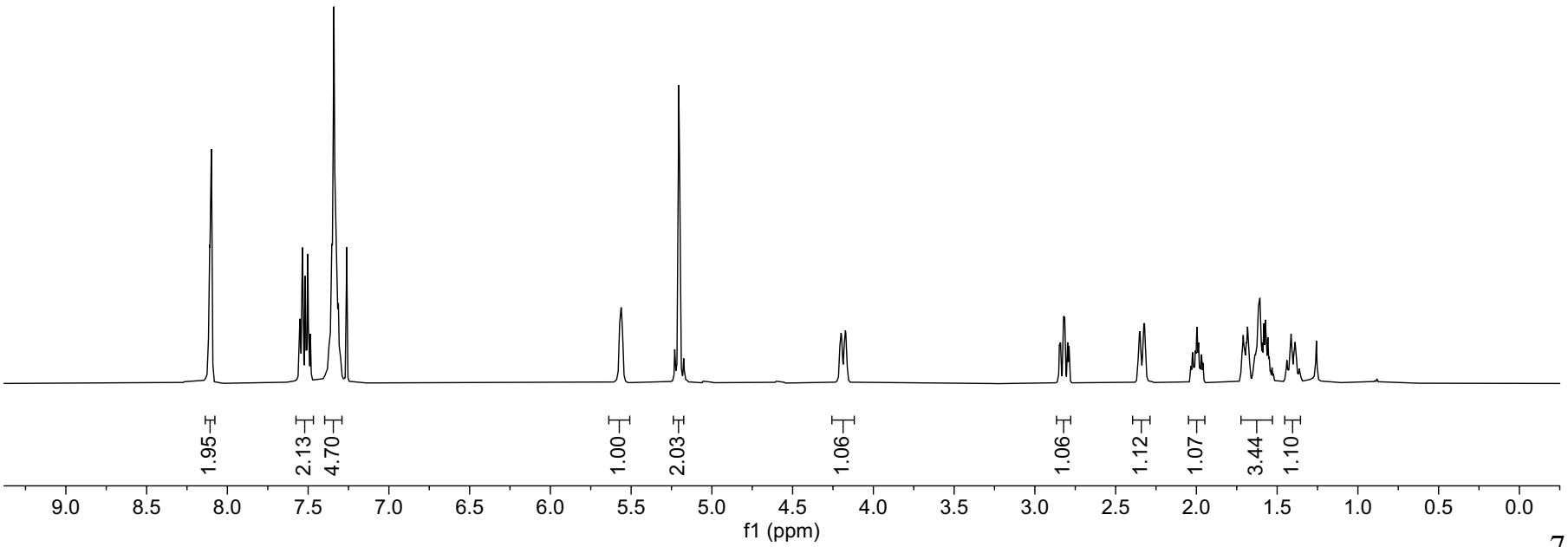
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	22.537	2046103	91.924
2	23.939	179772	8.076
Total		2225875	100.000

^{1}H NMR of **2g**, 500 MHz, $CDCl_3$

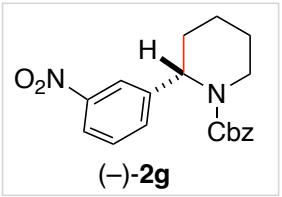


(–)-**2g**

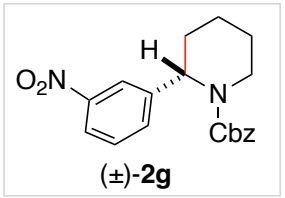


156.16
148.92
142.82
136.72
132.97
129.77
128.68
128.25
128.01
121.99
121.74
77.41
77.16
76.91
67.64
53.49
40.79
28.21
25.27
19.34

^{13}C NMR of **2g**, 125 MHz, $CDCl_3$



(–)-**2g**

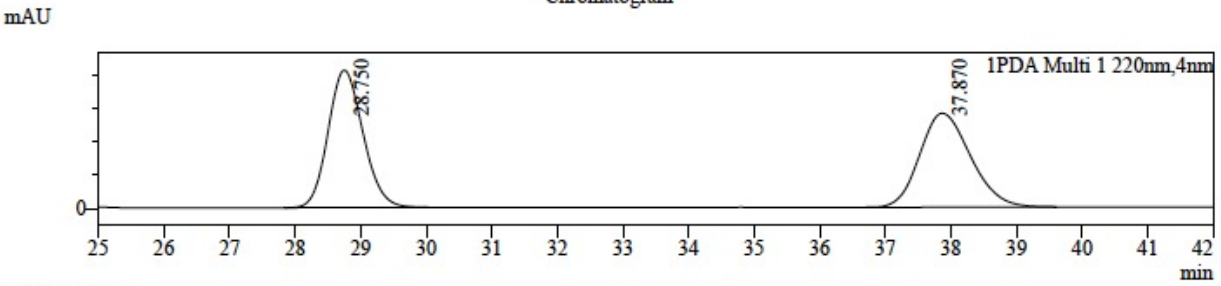


(±)-**2g**

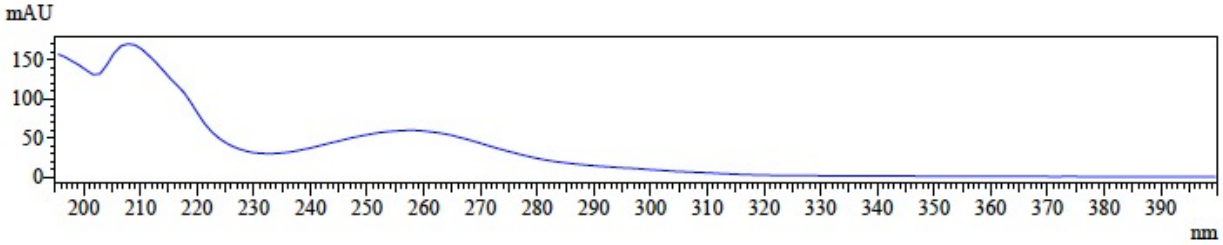
Sample Information

Sample Name	: XXW-1465-ID-10%-0.8mL
Sample ID	: XXW-1465-ID-10%-0.8mL
Data File	: XXW-1465-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

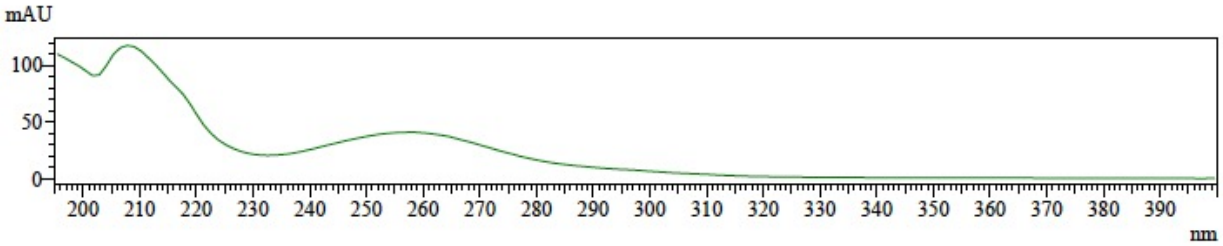
Chromatogram



UV Spectrum
Retention time = 28.750



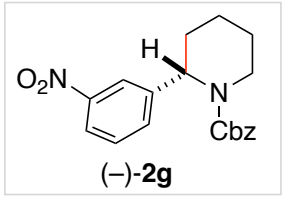
UV Spectrum
Retention time = 37.870



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	28.750	3052678	50.199
2	37.870	3028462	49.801
Total		6081141	100.000

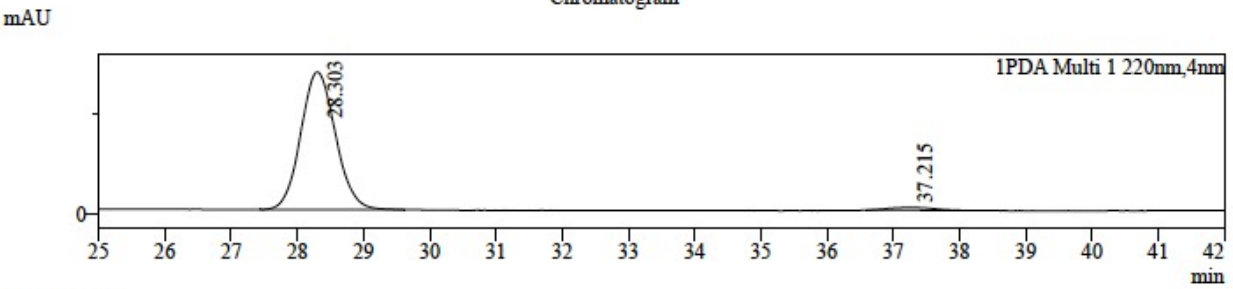


(–)-**2g**

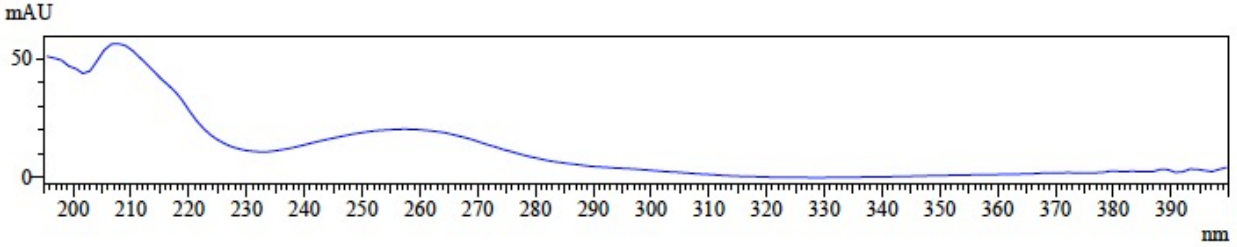
Sample Information

Sample Name	: XXW-1466-ID-10%-0.8mL
Sample ID	: XXW-1466-ID-10%-0.8mL
Data File	: XXW-1466-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

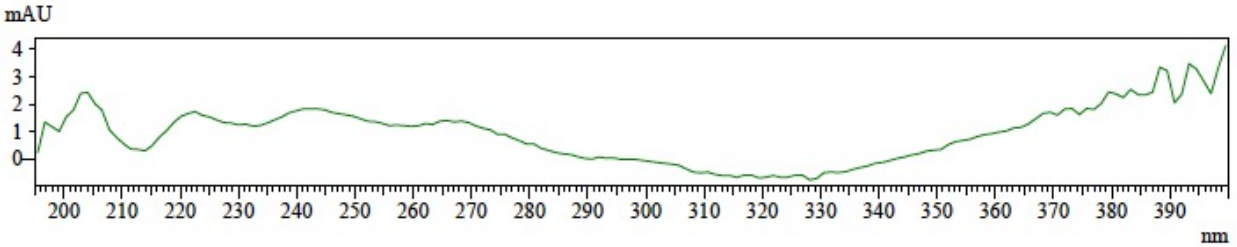
Chromatogram



UV Spectrum
Retention time = 28.303



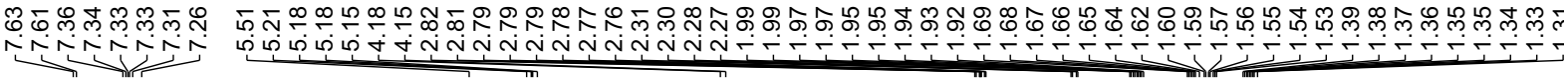
UV Spectrum
Retention time = 37.215



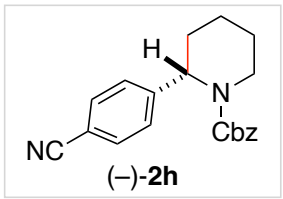
Peak Table

PDA Ch1 220nm

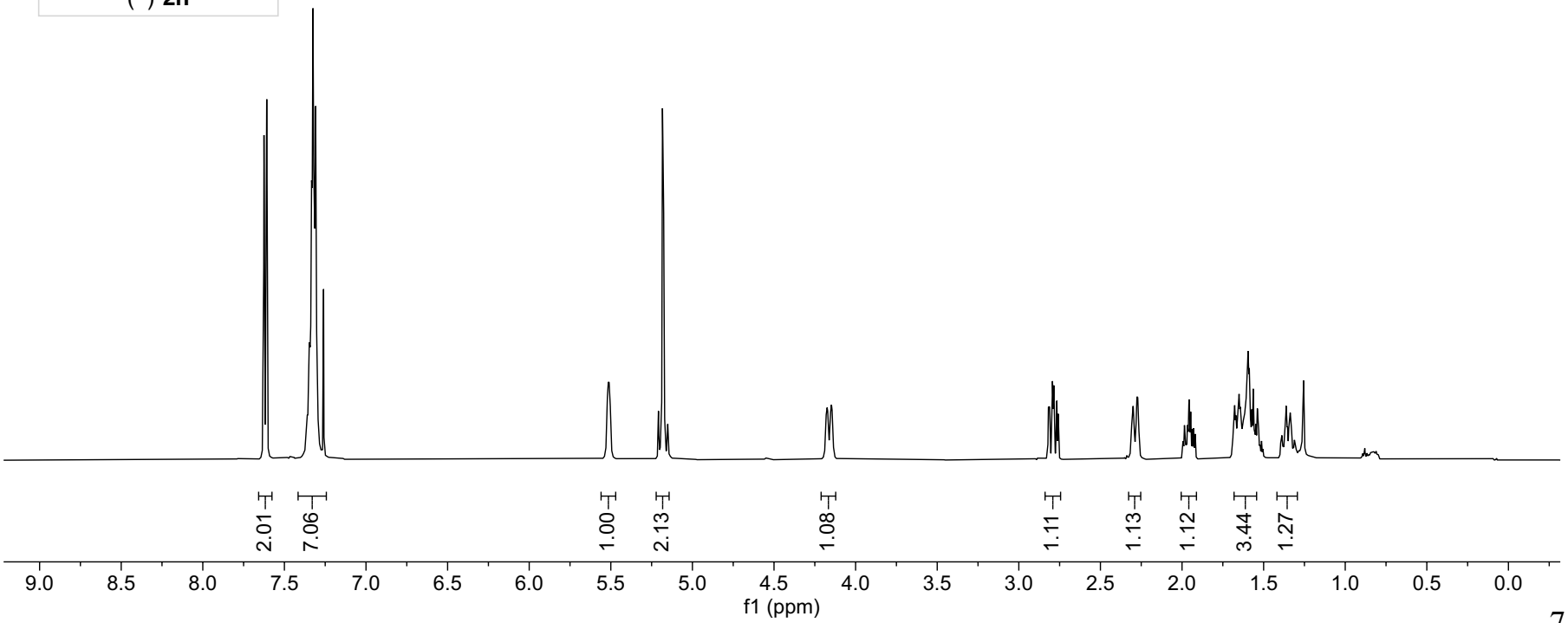
Peak#	Ret. Time	Area	Area%
1	28.303	999921	97.507
2	37.215	25565	2.493
Total		1025486	100.000



^{1}H NMR of **2h**, 500 MHz, $CDCl_3$

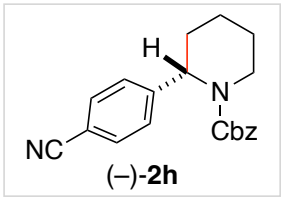


(–)-**2h**



156.16
146.10
136.71
132.57
128.65
128.25
128.03
127.48
118.90
110.73
77.41
77.16
76.91
67.59
53.83
40.87
28.19
25.24
19.38

^{13}C NMR of **2h**, 125 MHz, $CDCl_3$

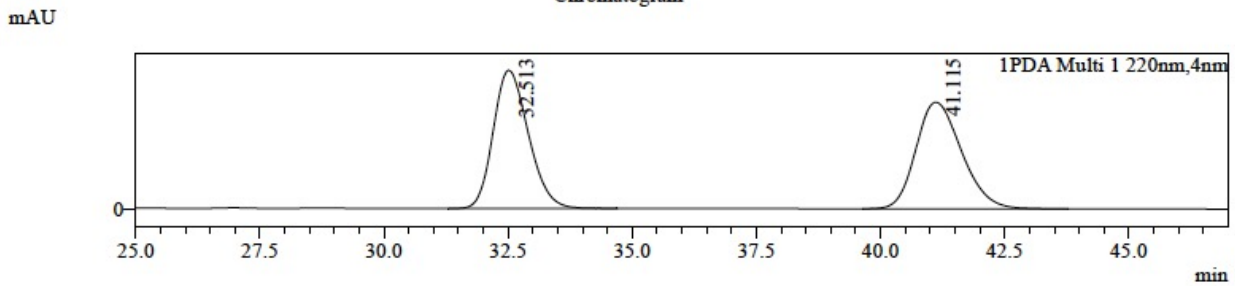


(–)-**2h**

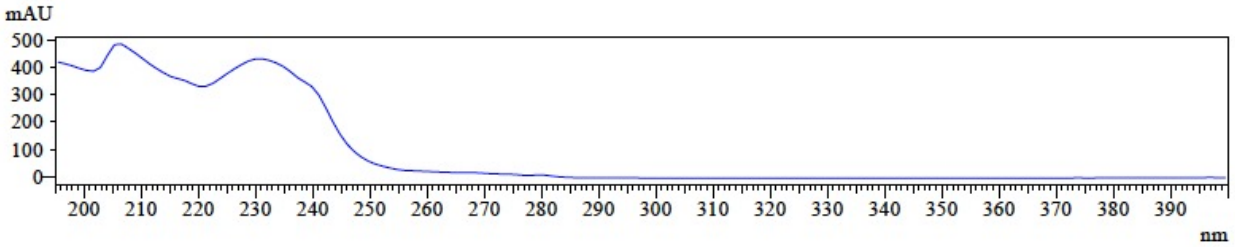
Sample Information

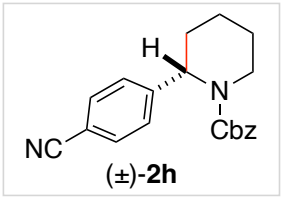
Sample Name	: XXW-1191---20%-IC-0.8mL
Sample ID	: XXW-1191---20%-IC-0.8mL
Data File	: XXW-1191---20%-IC-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram



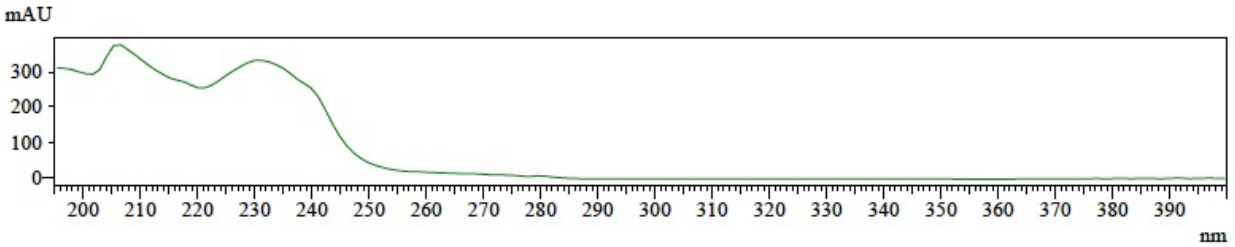
UV Spectrum
Retention time = 32.513





(±)-**2h**

UV Spectrum
Retention time = 41.115



Peak Table

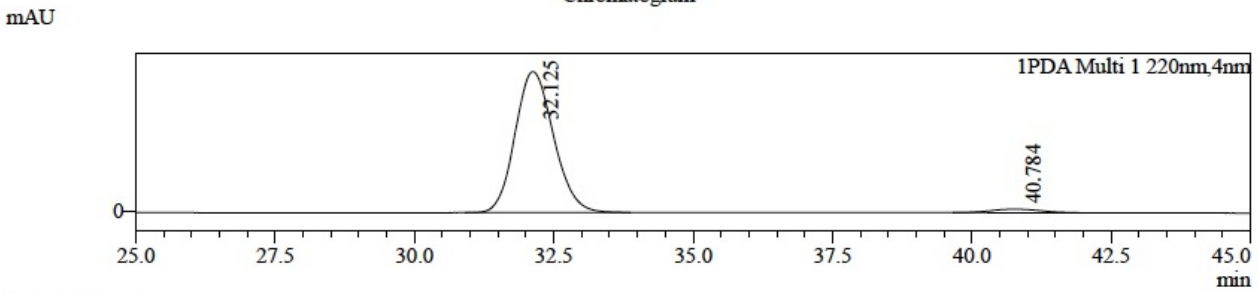
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	32.513	16992358	50.026
2	41.115	16974473	49.974
Total		33966830	100.000

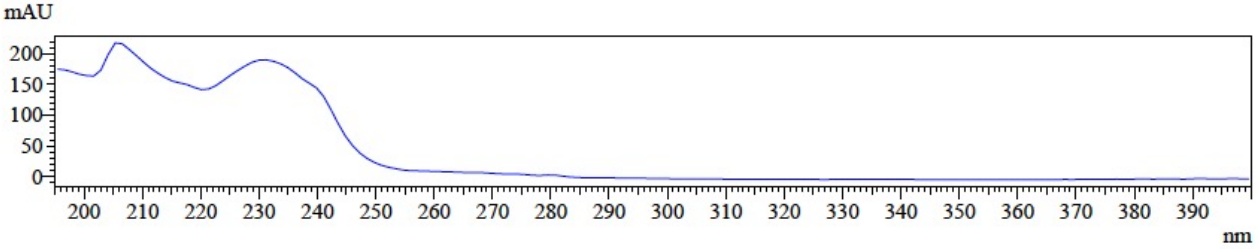
Sample Information

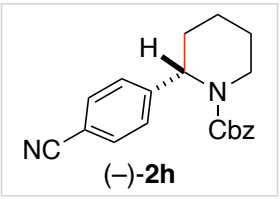
Sample Name	: XXW--1192---20%-IC-0.8mL
Sample ID	: XXW--1192---20%-IC-0.8mL
Data File	: XXW--1192---20%-IC-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram

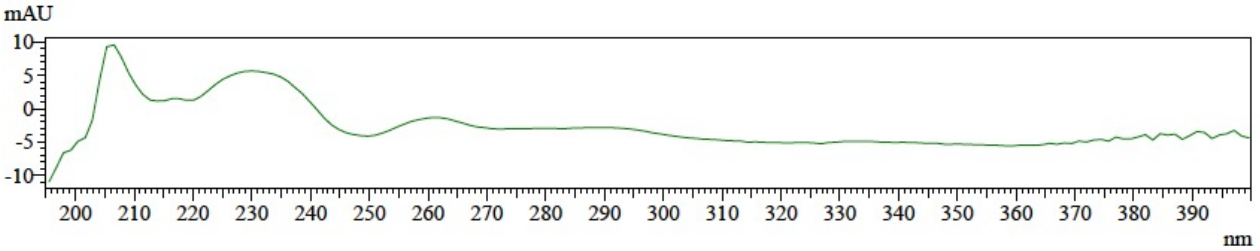


UV Spectrum
Retention time = 32.125





UV Spectrum
Retention time = 40.784

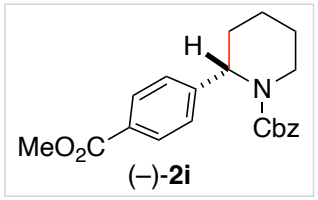


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	32.125	7208016	96.800
2	40.784	238257	3.200
Total		7446274	100.000

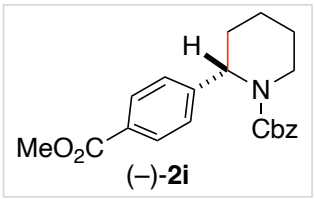
^{1}H NMR of **2i**, 600 MHz, $CDCl_3$



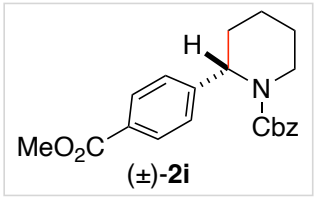
(–)-**2i**

167.01
156.20
145.62
136.87
130.05
128.69
128.61
128.12
127.92
126.69
77.37
77.16
76.95
67.43
53.82
52.19
40.80
28.28
25.40
19.44

^{13}C NMR of **2i**, 150 MHz, $CDCl_3$



(–)-**2i**

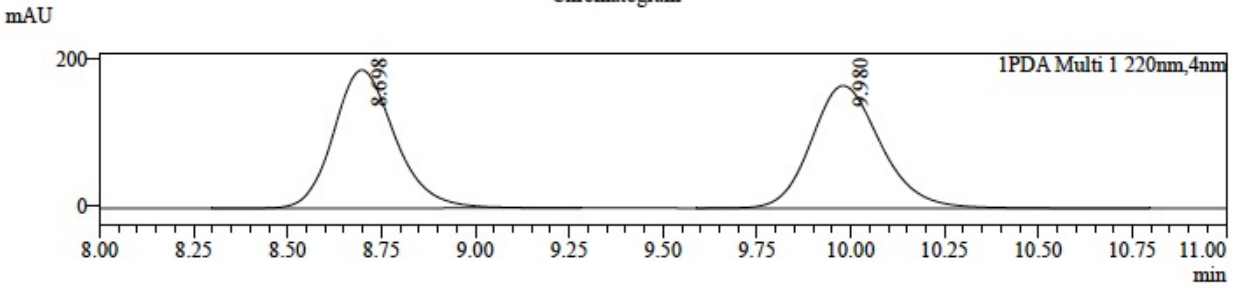


(±)-**2i**

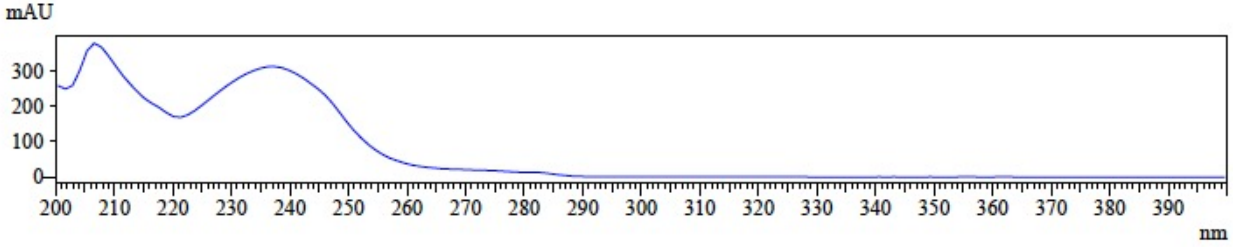
Sample Information

Data File	: XXW-1458-IA-20%-0.8mL001.lcd
Sample Name	: XXW-1458-IA-20%-0.8mL
Sample ID	: XXW-1458-IA-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

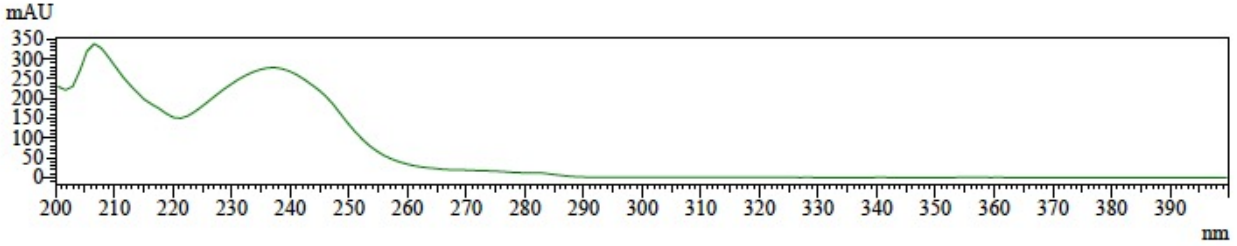
Chromatogram



UV Spectrum
Retention time = 8.698



UV Spectrum
Retention time = 9.980



Peak Table

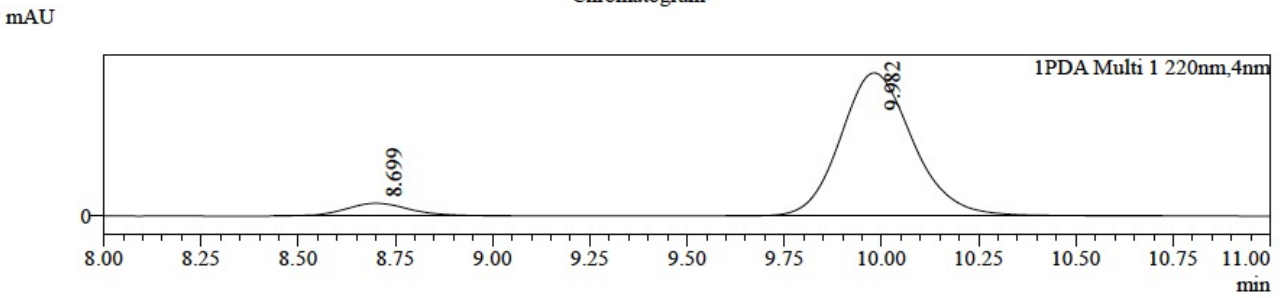
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.698	2151633	49.889
2	9.980	2161248	50.111
Total		4312881	100.000

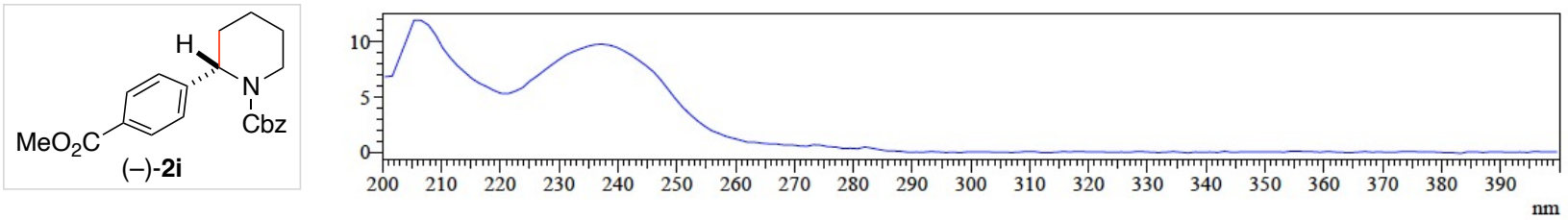
Sample Information

Data File	: XXW-1459-IA-20%-0.8mL002.lcd
Sample Name	: XXW-1459-IA-20%-0.8mL001
Sample ID	: XXW-1459-IA-20%-0.8mL001
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram

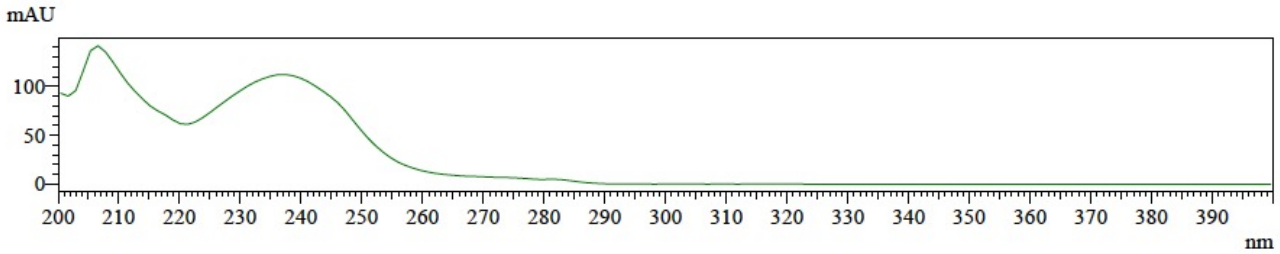


UV Spectrum
Retention time = 8.699



(–)-**2i**

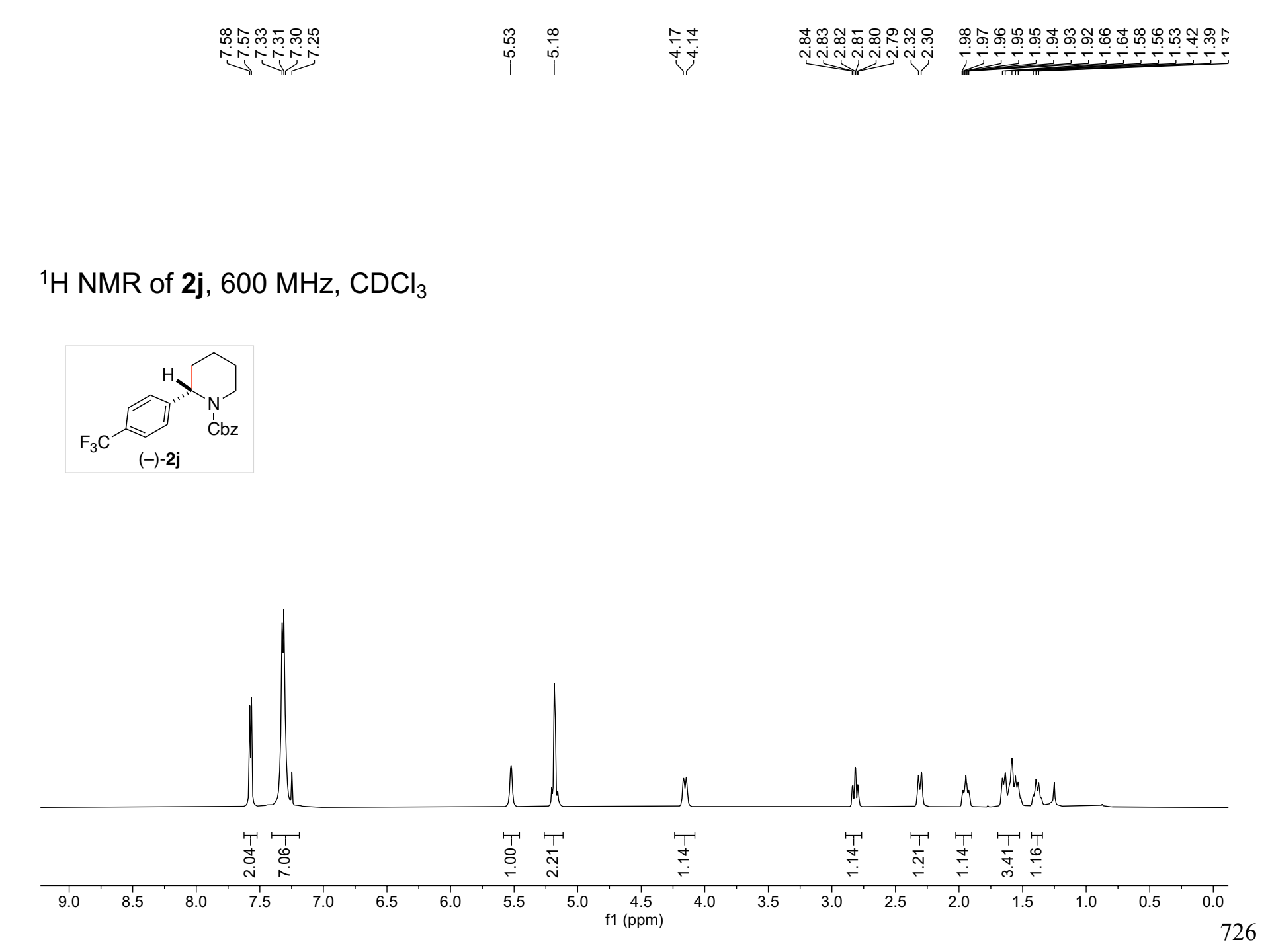
UV Spectrum
Retention time = 9.982



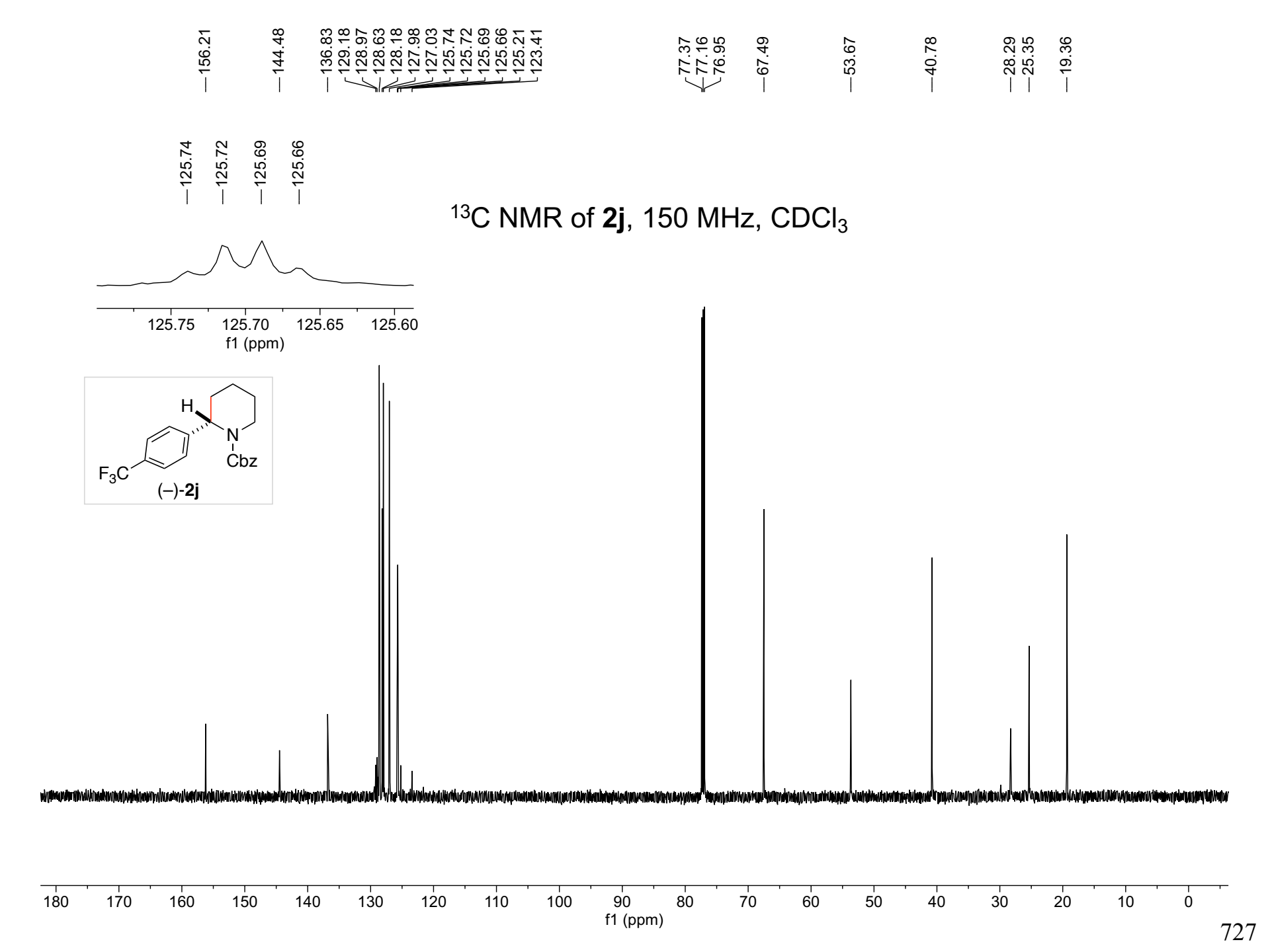
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	8.699	67412	7.190
2	9.982	870110	92.810
Total		937522	100.000

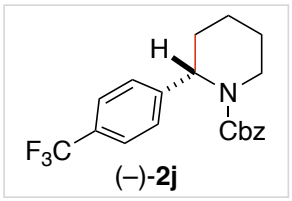


^{1}H NMR of **2j**, 600 MHz, $CDCl_3$



^{13}C NMR of **2j**, 150 MHz, $CDCl_3$

^{19}F NMR of **2j**, 564 MHz, $CDCl_3$

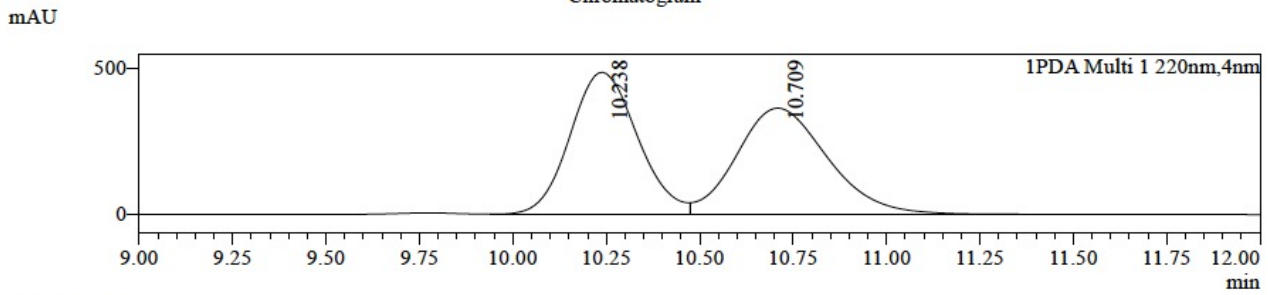


(–)-**2j**

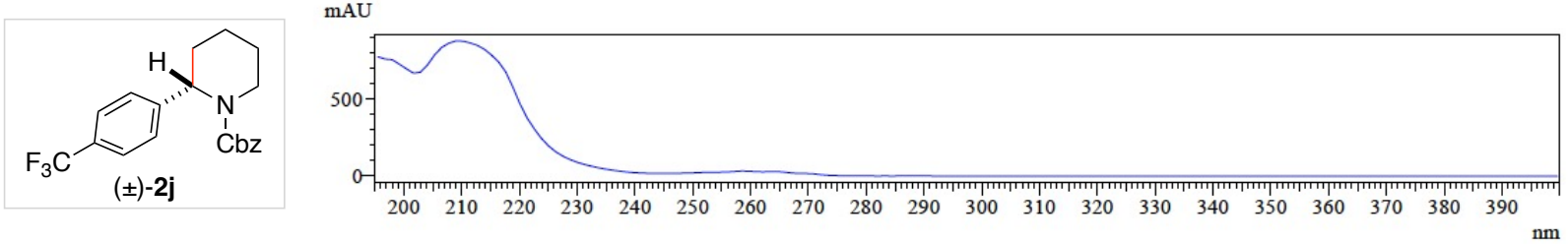
Sample Information

Sample Name	: XXW-1379-ID-5%-0.8mL
Sample ID	: XXW-1379-ID-5%-0.8mL
Data File	: XXW-1379-ID-5%-0.8mL001.lcd
Method File	: XXW-5%.0.8.mL.lcm

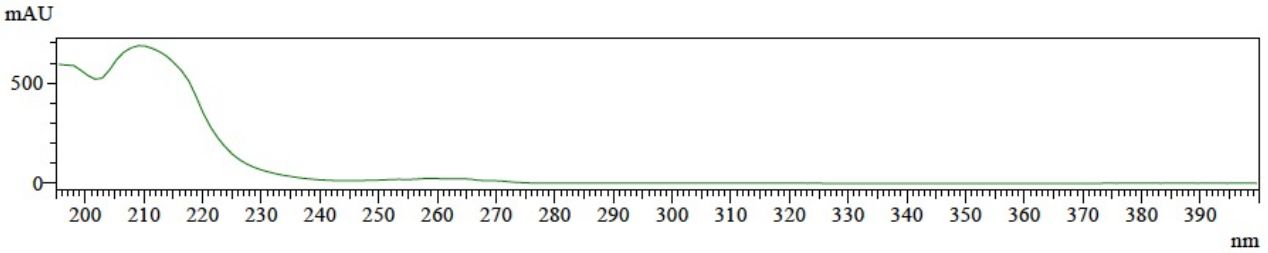
Chromatogram



UV Spectrum
Retention time = 10.238



UV Spectrum
Retention time = 10.709



Peak Table

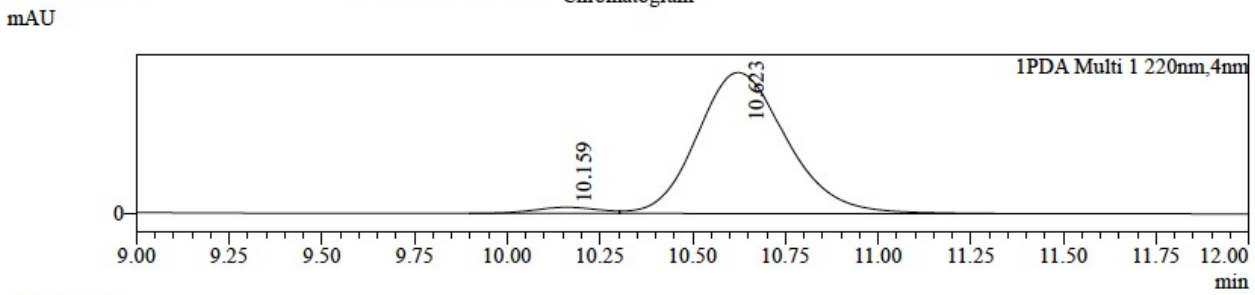
PDA Ch1 220nm

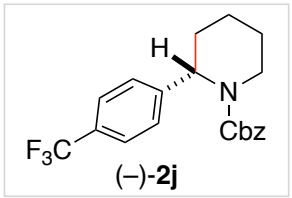
Peak#	Ret. Time	Area	Area%
1	10.238	6123071	49.829
2	10.709	6165160	50.171
Total		12288231	100.000

Sample Information

Sample Name	: XXW-1380-ID-5%-0.8mL
Sample ID	: XXW-1380-ID-5%-0.8mL
Data File	: XXW-1380-ID-5%-0.8mL002.lcd
Method File	: XXW-5%.0.8.mL.lcm

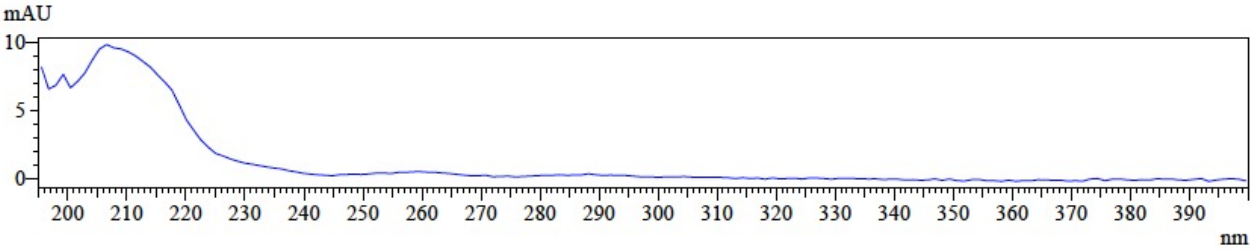
Chromatogram



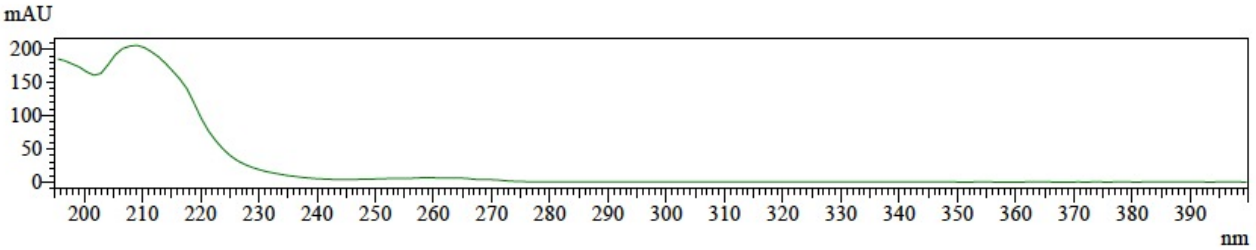


(–)-**2j**

UV Spectrum
Retention time = 10.159



UV Spectrum
Retention time = 10.623

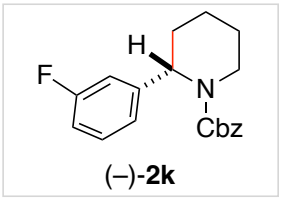


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	10.159	51591	2.986
2	10.623	1675959	97.014
Total		1727550	100.000

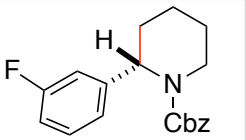
^{1}H NMR of **2k**, 500 MHz, $CDCl_3$



(–)-**2k**

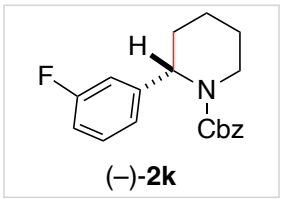
164.47
162.51
156.18
143.00
136.93
130.25
130.19
128.62
128.11
127.93
122.25
122.23
113.91
113.73
113.68
113.52
77.41
77.16
76.91
67.43
53.47
40.70
28.25
25.45
19.42

^{13}C NMR of **2k**, 125 MHz, $CDCl_3$

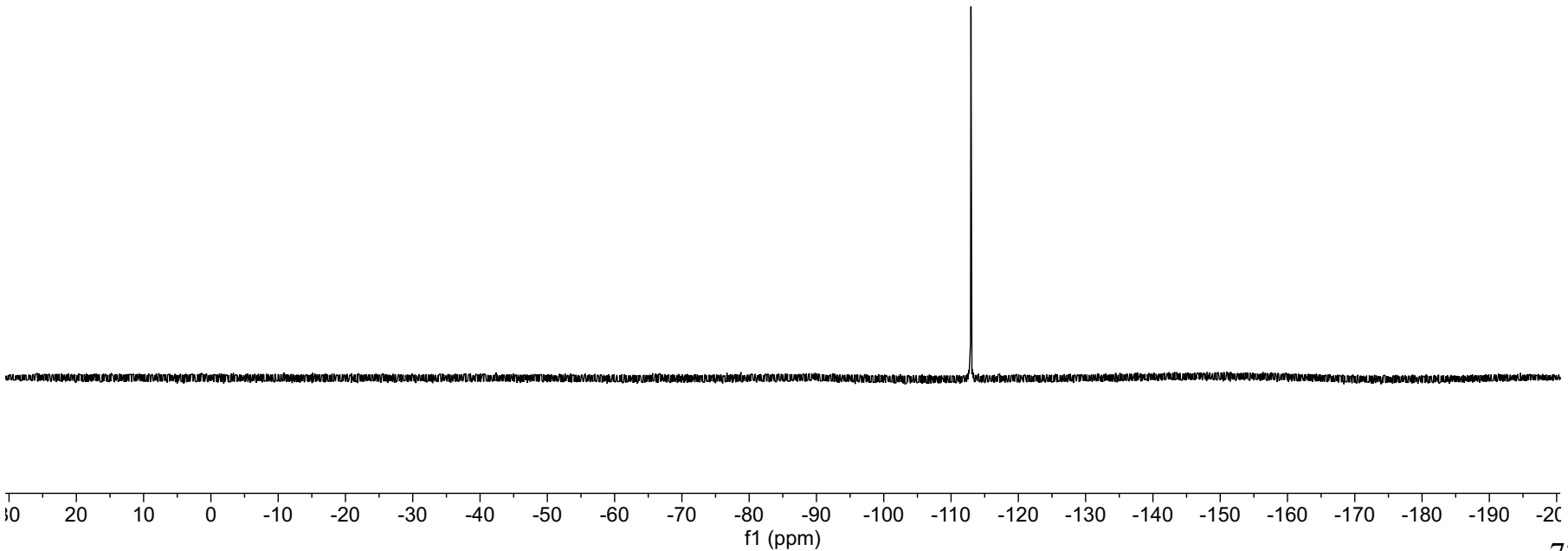


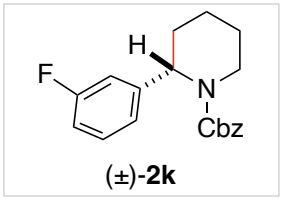
(–)-**2k**

^{19}F NMR of **2k**, 470 MHz, $CDCl_3$



(–)-**2k**



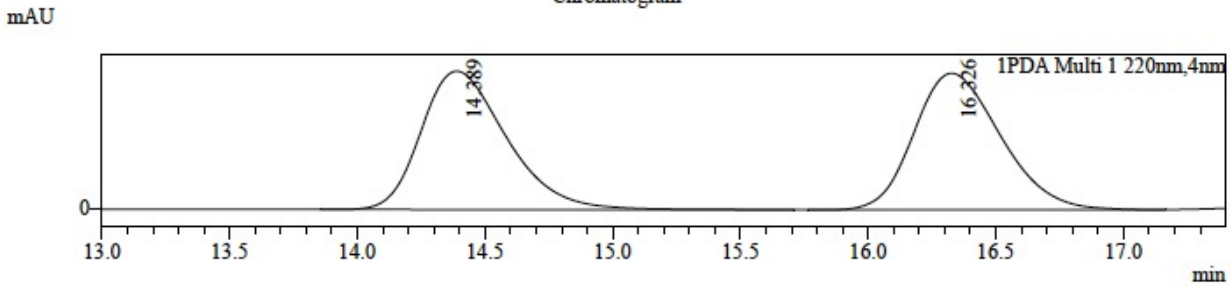


(±)-**2k**

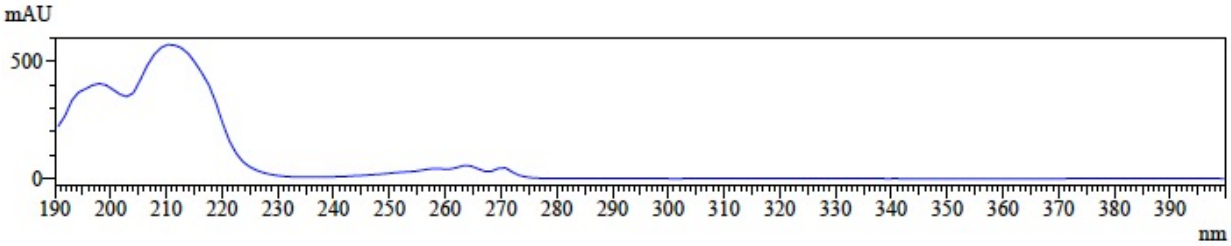
Sample Information

Data File	: XXW-1389-ID-10%-0.8mL001.lcd
Sample Name	: XXW-1389-ID-10%-0.8mL001
Sample ID	: XXW-1389-ID-10%-0.8mL001
Method File	: XXW-10%.0.8.mL.lcm

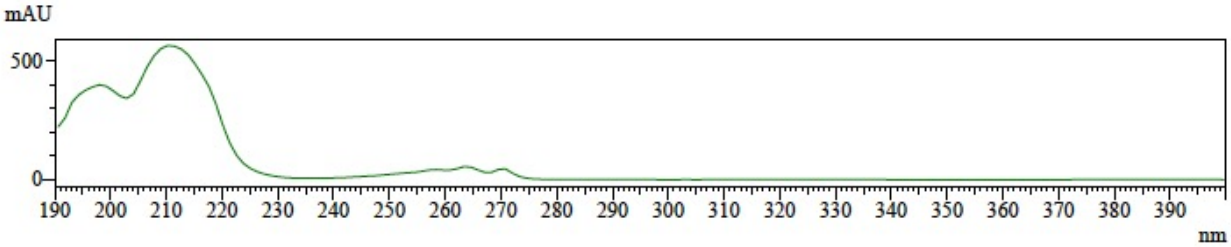
Chromatogram



UV Spectrum
Retention time = 14.389



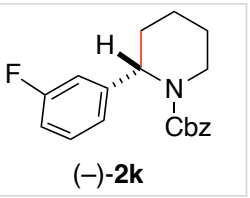
UV Spectrum
Retention time = 16.326



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.389	5839034	50.095
2	16.326	5816784	49.905
Total		11655818	100.000

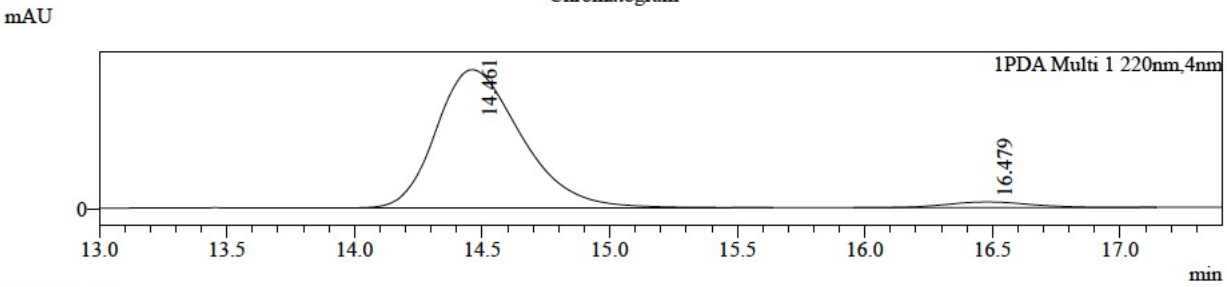


(–)-**2k**

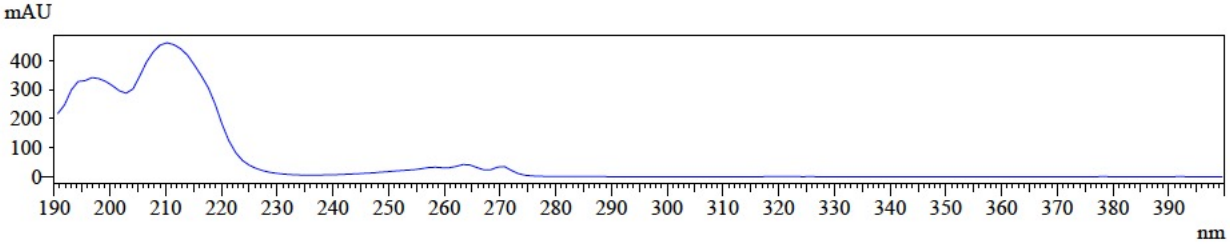
Sample Information

Data File	: XXW-1390-ID-10%-0.8mL002.lcd
Sample Name	: XXW-1390-ID-10%-0.8mL002
Sample ID	: XXW-1390-ID-10%-0.8mL002
Method File	: XXW-10%.0.8.mL.lcm

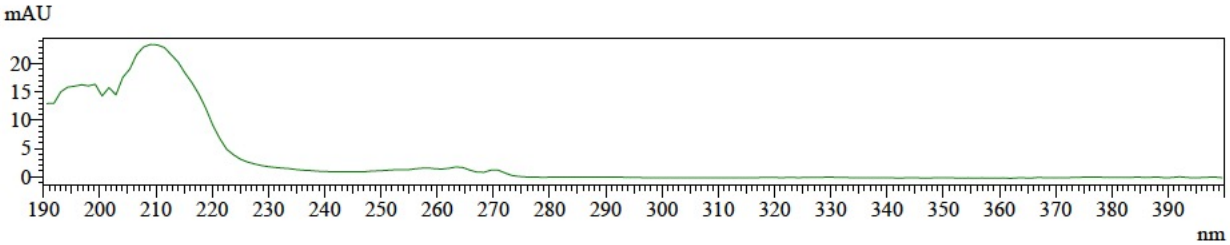
Chromatogram



UV Spectrum
Retention time = 14.461



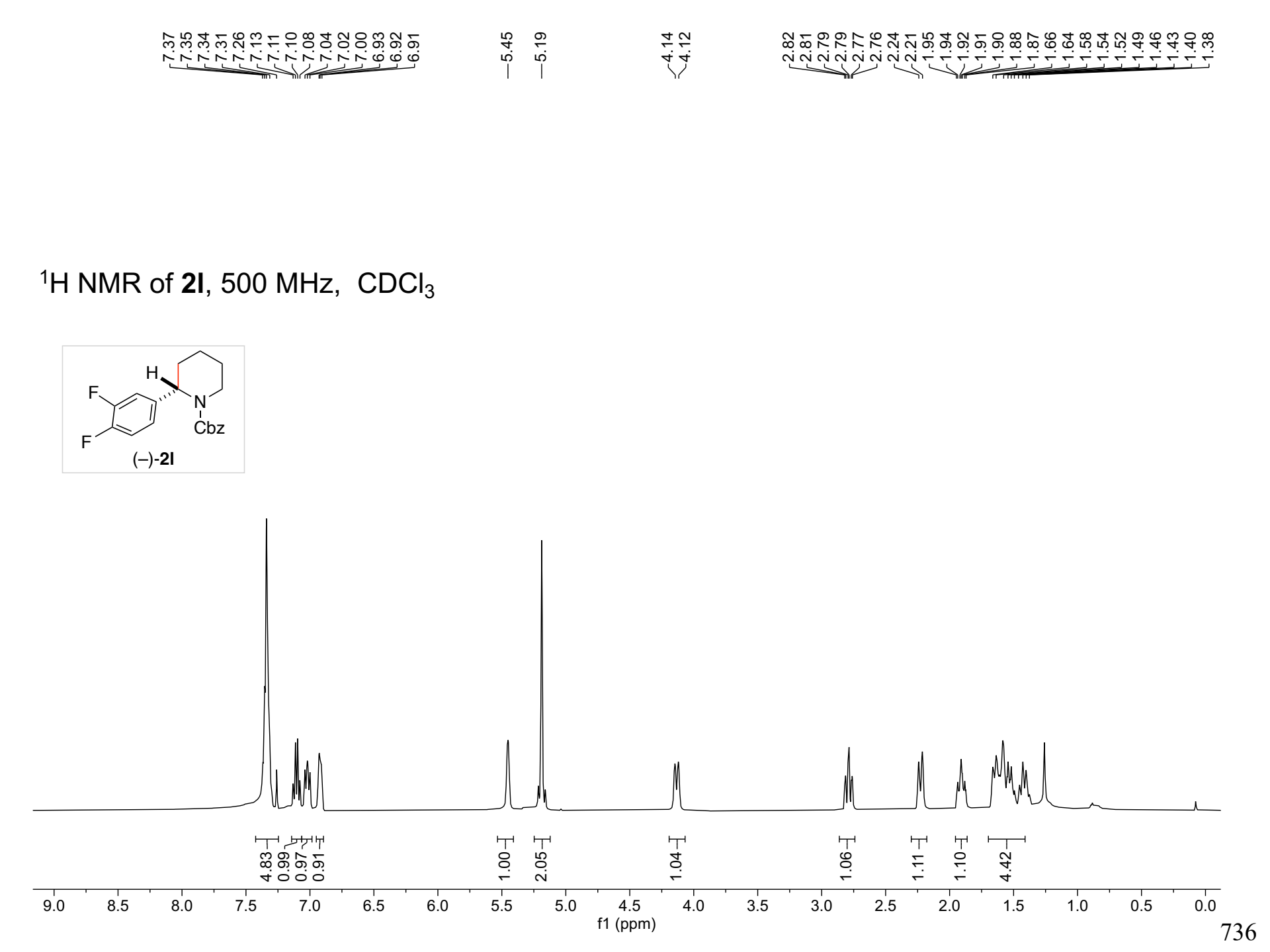
UV Spectrum
Retention time = 16.479



Peak Table

PDA Ch1 220nm

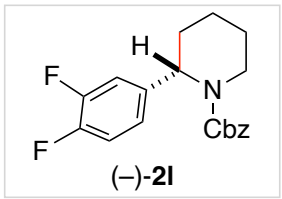
Peak#	Ret. Time	Area	Area%
1	14.461	4437193	96.158
2	16.479	177291	3.842
Total		4614484	100.000



^{1}H NMR of **2l**, 500 MHz, $CDCl_3$

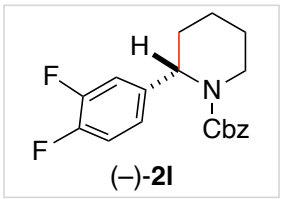
156.11
151.54
151.46
150.01
149.92
149.90
149.82
148.37
148.28
137.29
137.26
137.23
136.81
128.64
128.19
127.98
122.60
122.58
122.56
122.54
117.48
117.37
115.94
115.82
77.37
77.16
76.95
67.50
53.00
40.57
28.14
25.39
19.30

^{13}C NMR of **2l**, 150 MHz, $CDCl_3$

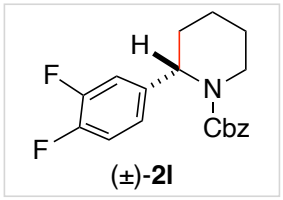


(–)-**2l**

^{19}F NMR of **2l**, 470 MHz, $CDCl_3$



(–)-**2l**

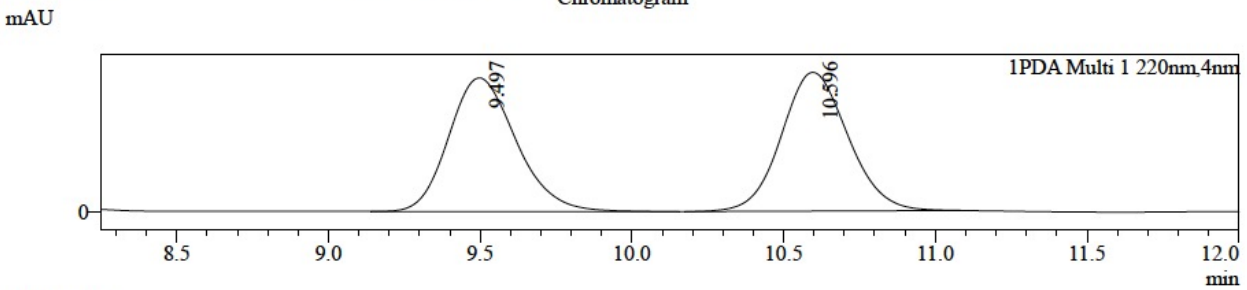


(±)-**2l**

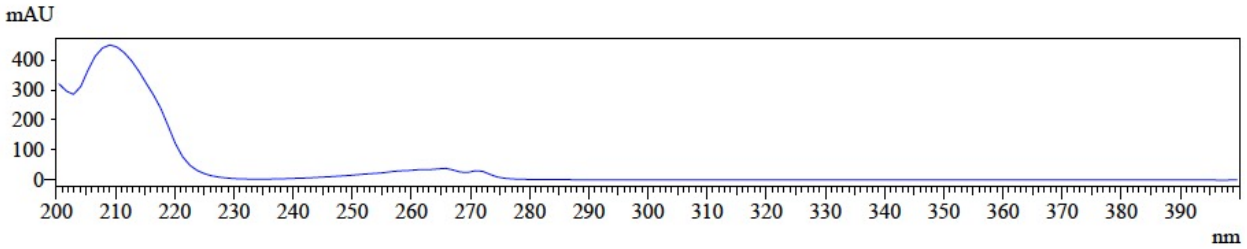
Sample Information

Data File	: XXW-1441-ID-20%-0.8mL.lcd
Sample Name	: XXW-1446-ID-20%-0.8mL
Sample ID	: XXW-1446-ID-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

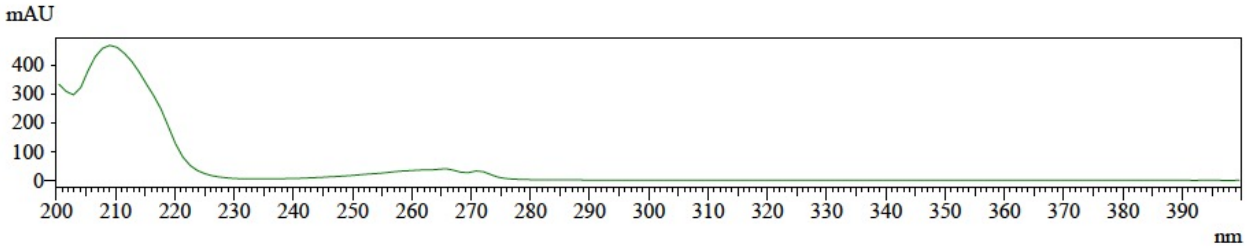
Chromatogram



UV Spectrum
Retention time = 9.497



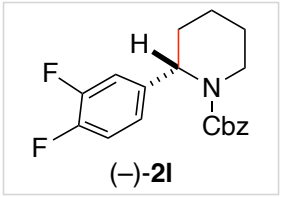
UV Spectrum
Retention time = 10.596



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	9.497	2162800	49.360
2	10.596	2218913	50.640
Total		4381712	100.000

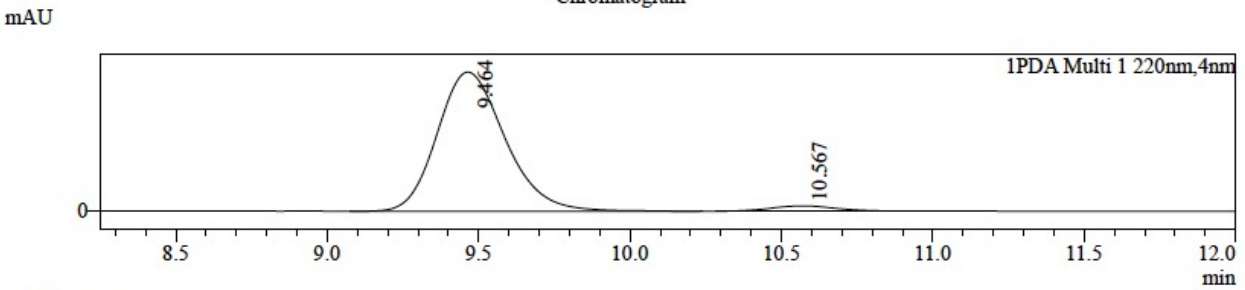


(–)-**2l**

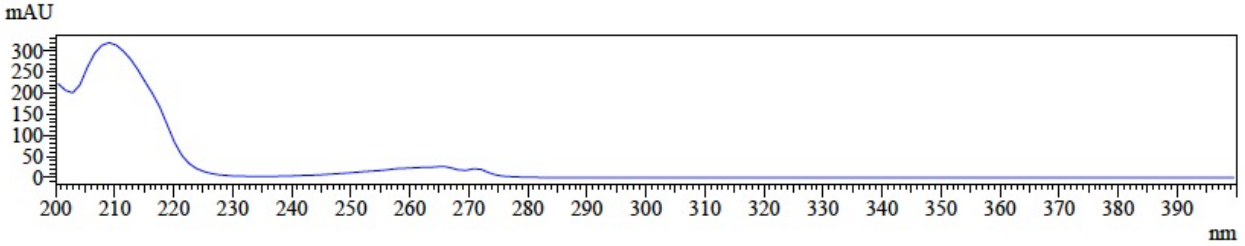
Sample Information

Data File	: XXW-1442-ID-20%-0.8mL001.lcd
Sample Name	: XXW-1442-ID-20%-0.8mL
Sample ID	: XXW-1442-ID-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

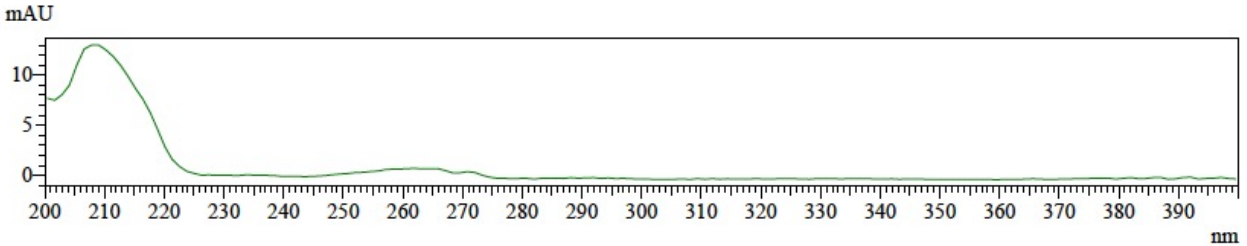
Chromatogram



UV Spectrum
Retention time = 9.464



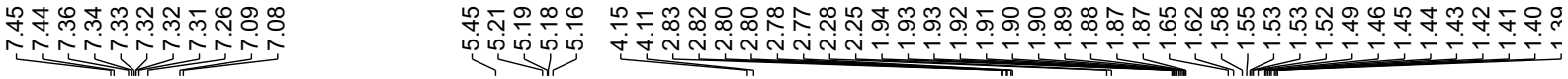
UV Spectrum
Retention time = 10.567



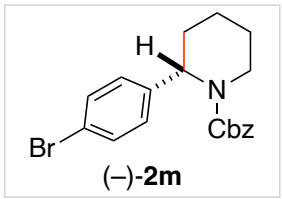
Peak Table

PDA Ch1 220nm

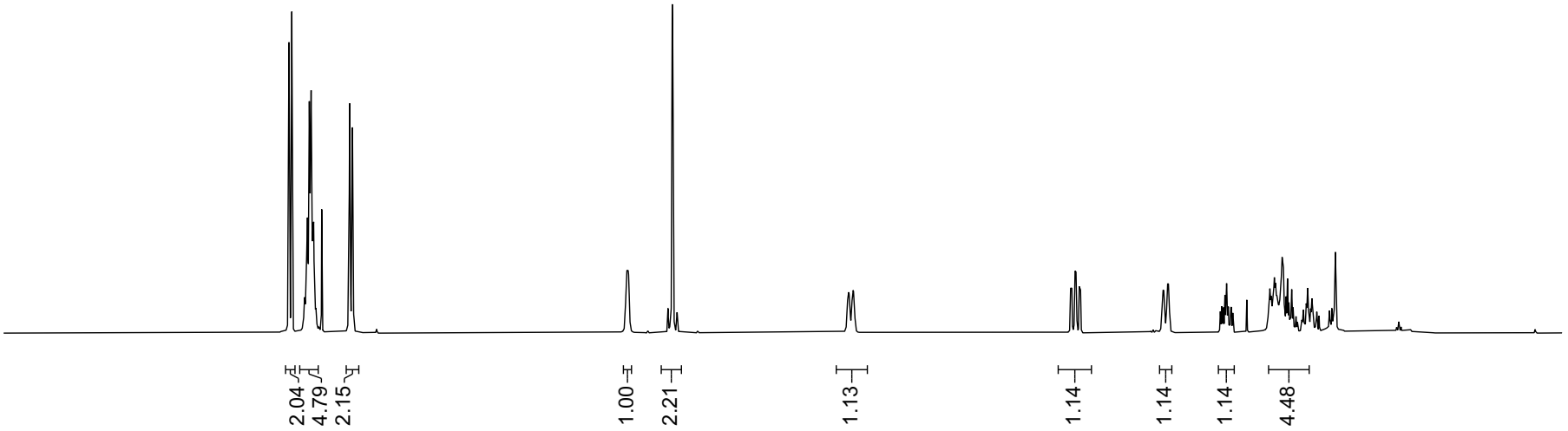
Peak#	Ret. Time	Area	Area%
1	9.464	1529239	96.758
2	10.567	51241	3.242
Total		1580481	100.000



^{1}H NMR of **2m**, 500 MHz, $CDCl_3$

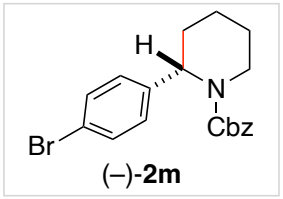


(–)-**2m**



156.19
139.18
136.91
131.82
128.62
128.53
128.13
127.94
120.60
77.41
77.16
76.91
67.41
53.35
40.62
28.14
25.46
19.35

^{13}C NMR of **2m**, 125 MHz, $CDCl_3$

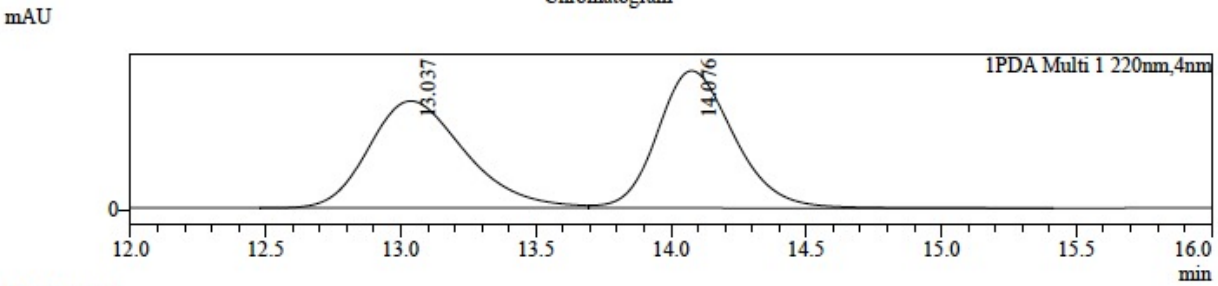


(–)-**2m**

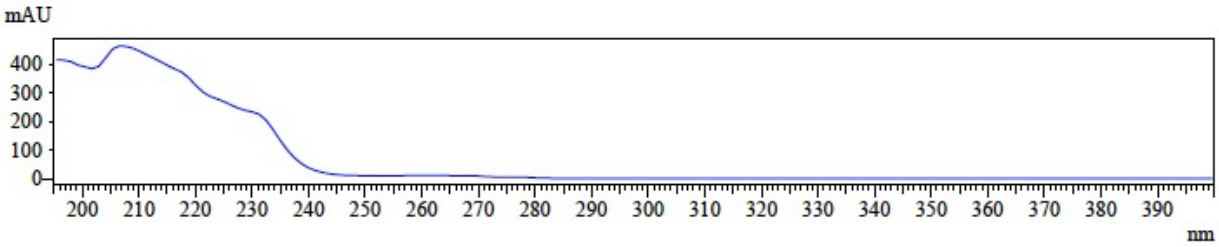
Sample Information

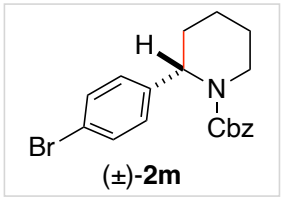
Sample Name : XXW-1340-ID-10%-0.8mL
Sample ID : XXW-1340-ID-10%-0.8mL
Data File : XXW-1340-ID-10%-0.8mL002.lcd
Method File : XXW-10%.0.8.mL.lcm

Chromatogram



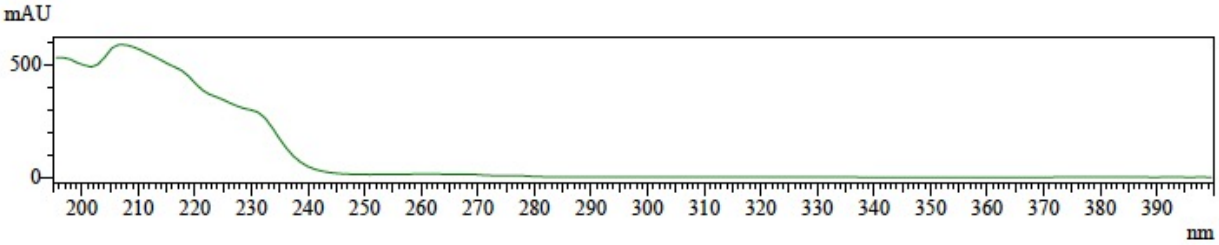
UV Spectrum
Retention time = 13.037





(±)-**2m**

UV Spectrum
Retention time = 14.076



Peak Table

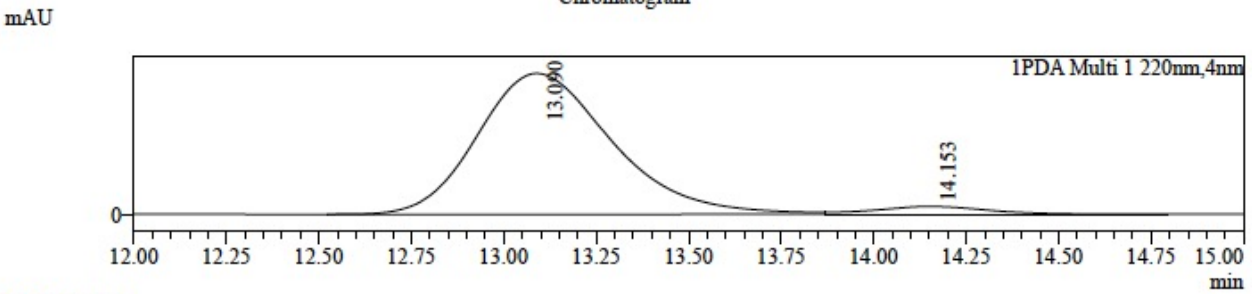
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	13.037	8066614	49.572
2	14.076	8205989	50.428
Total		16272603	100.000

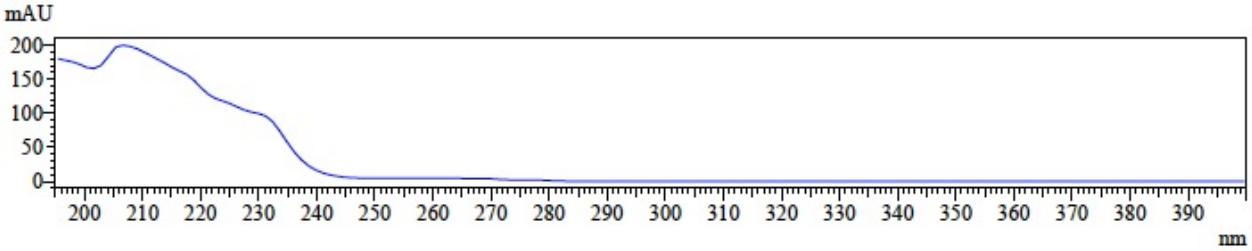
Sample Information

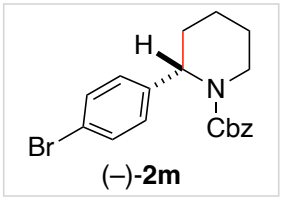
Sample Name	: XXW-1341-ID-10%-0.8mL
Sample ID	: XXW-1341-ID-10%-0.8mL
Data File	: XXW-1341-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



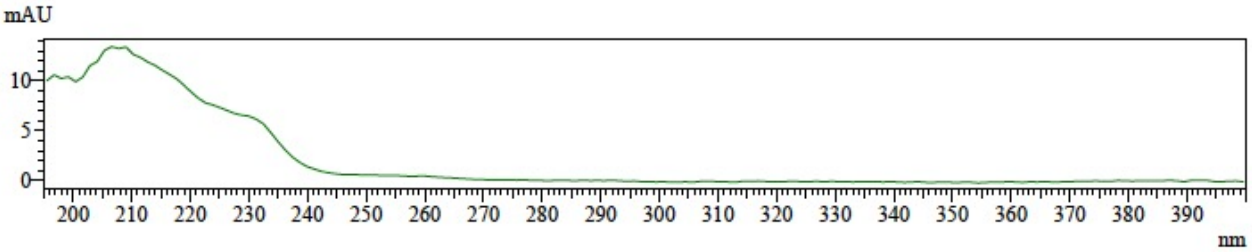
UV Spectrum
Retention time = 13.090





(–)-**2m**

UV Spectrum
Retention time = 14.153



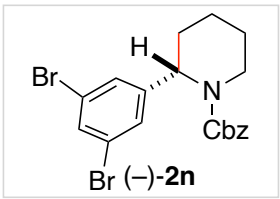
Peak Table

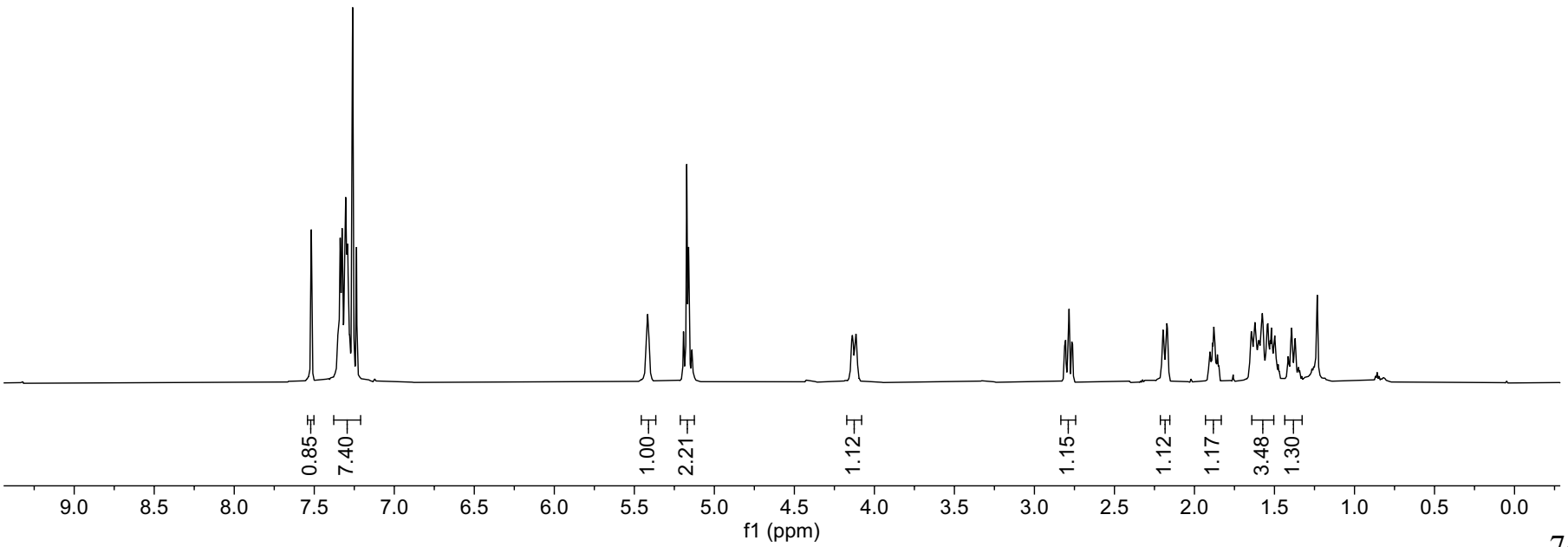
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	13.090	3475373	95.699
2	14.153	156179	4.301
Total		3631552	100.000

7.52 7.35 7.34 7.33 7.30 7.29 7.26 7.24 5.42 5.19 5.17 5.16 5.14 4.14 4.12 2.81 2.80 2.79 2.78 2.77 2.76 2.20 2.17 1.90 1.89 1.89 1.88 1.87 1.64 1.62 1.60 1.58 1.55 1.52 1.50 1.49 1.41 1.39 1.39

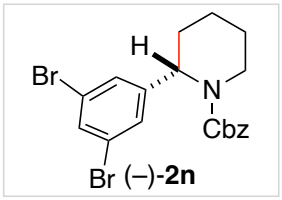
^{1}H NMR of **2n**, 600 MHz, $CDCl_3$





156.04
144.68
136.76
132.54
128.72
128.67
128.22
127.92
123.54
77.37
77.16
76.95
67.59
53.23
40.77
28.20
25.25
19.35

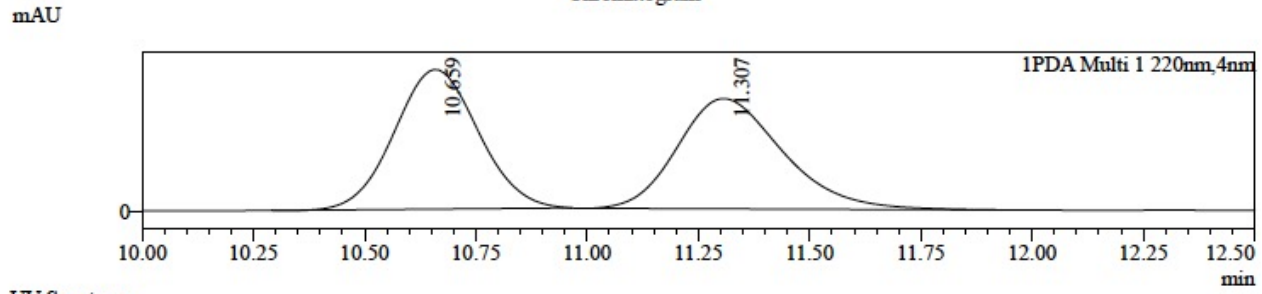
^{13}C NMR of **2n**, 150 MHz, $CDCl_3$



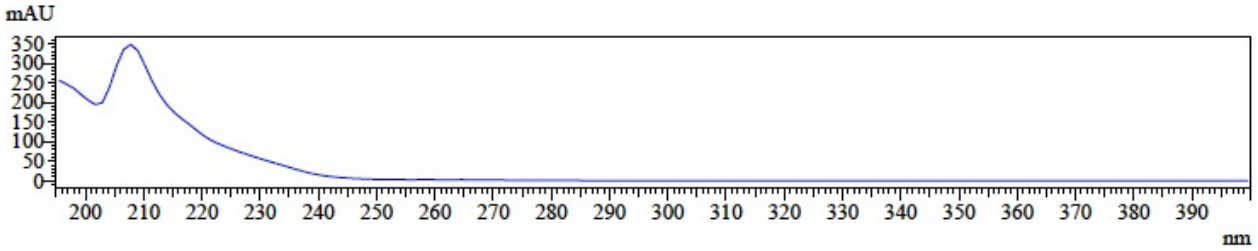
Sample Information

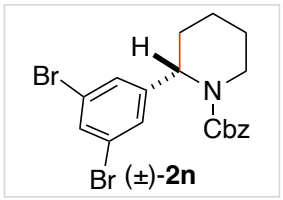
Sample Name	: XXW-1476-ID-10%-0.8mL
Sample ID	: XXW-1476-ID-10%-0.8mL
Data File	: XXW-1476-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram

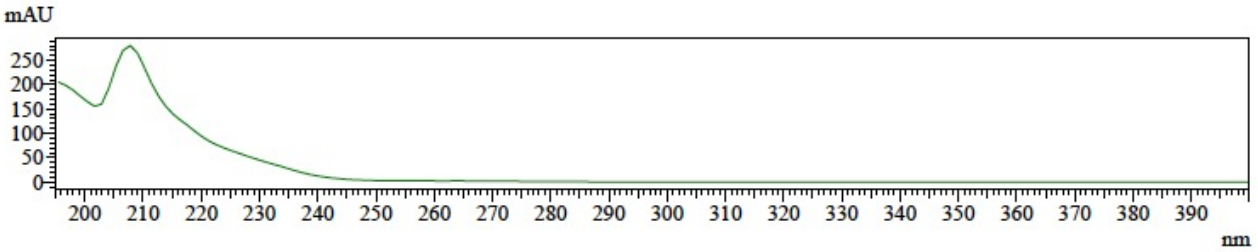


UV Spectrum
Retention time = 10.659





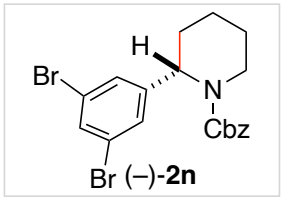
UV Spectrum
Retention time = 11.307



Peak Table

PDA Ch1 220nm

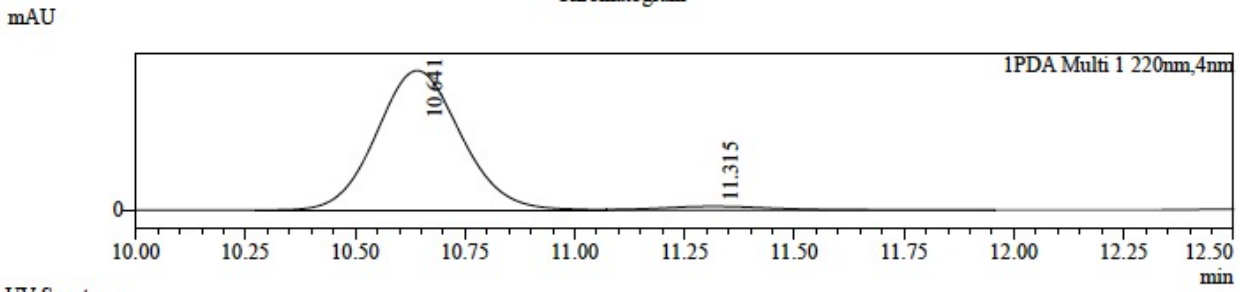
Peak#	Ret. Time	Area	Area%
1	10.659	1561767	50.343
2	11.307	1540479	49.657
Total		3102245	100.000



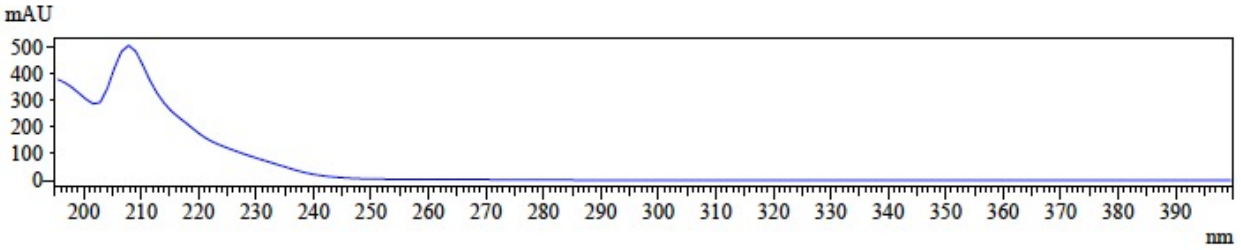
Sample Information

Sample Name	: XXW-1477-ID-10%-0.8mL
Sample ID	: XXW-1477-ID-10%-0.8mL
Data File	: XXW-1477-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

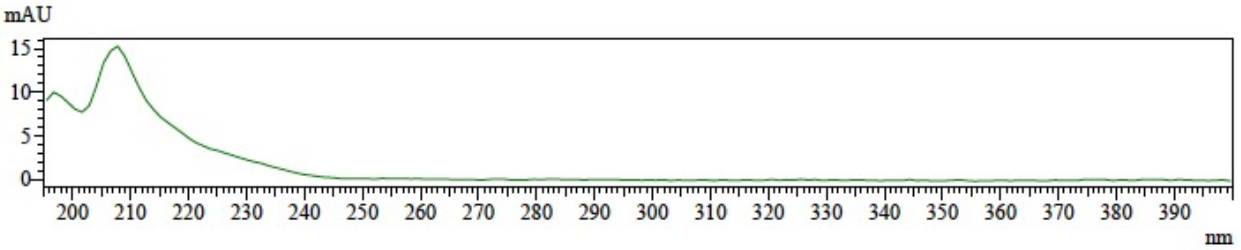
Chromatogram



UV Spectrum
Retention time = 10.641



UV Spectrum
Retention time = 11.315

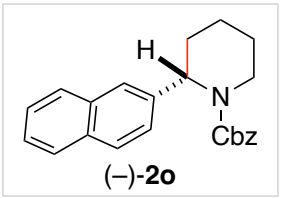


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	10.641	2415278	96.534
2	11.315	86721	3.466
Total		2501999	100.000

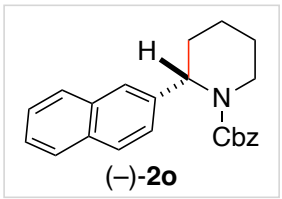
^{1}H NMR of **2o**, 500 MHz, $CDCl_3$



(–)-**2o**

156.33
137.52
137.06
133.55
132.37
128.58
128.51
128.02
127.88
127.62
126.20
125.86
125.35
125.02
77.41
77.16
76.91
67.33
53.85
40.78
28.21
25.60
19.51

^{13}C NMR of **2o**, 125 MHz, $CDCl_3$

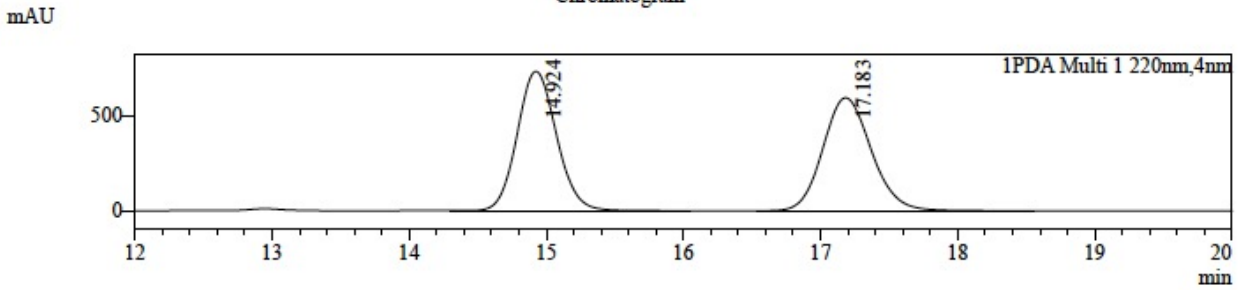


(–)-**2o**

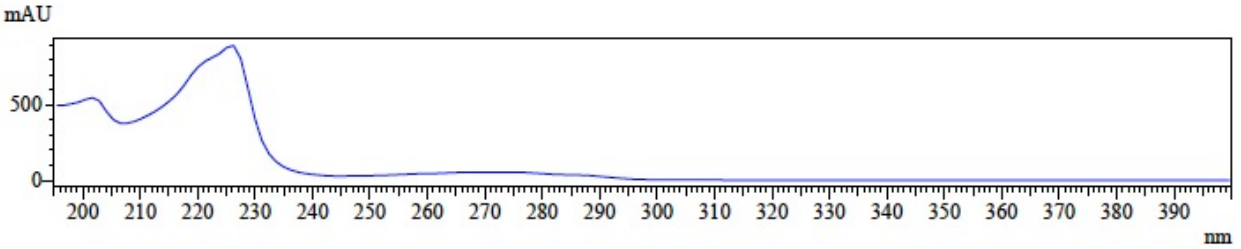
Sample Information

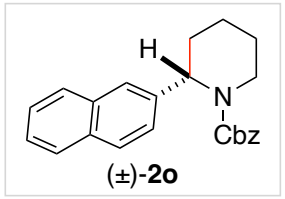
Sample Name	: XXW-1410-ID-10%-0.8mL
Sample ID	: XXW-1410-ID-10%-0.8mL
Data File	: XXW-1410-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



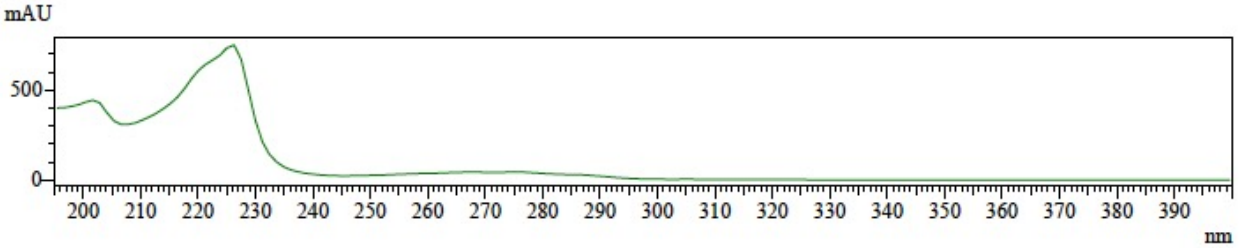
UV Spectrum
Retention time = 14.924





(±)-**2o**

UV Spectrum
Retention time = 17.183



Peak Table

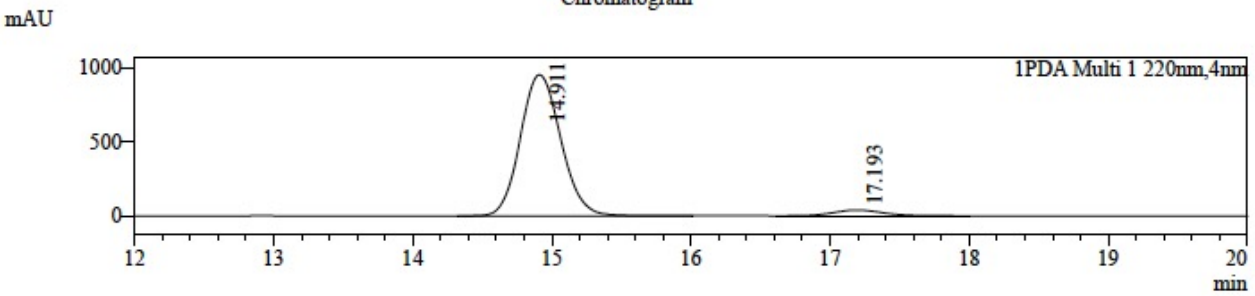
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	14.924	14579106	50.069
2	17.183	14538752	49.931
Total		29117857	100.000

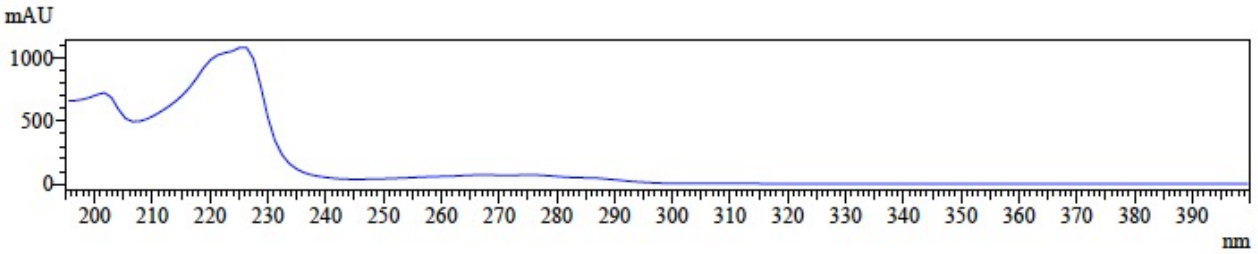
Sample Information

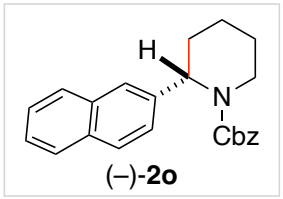
Sample Name	: XXW-1411-ID-10%-0.8mL
Sample ID	: XXW-1411-ID-10%-0.8mL
Data File	: XXW-1411-ID-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



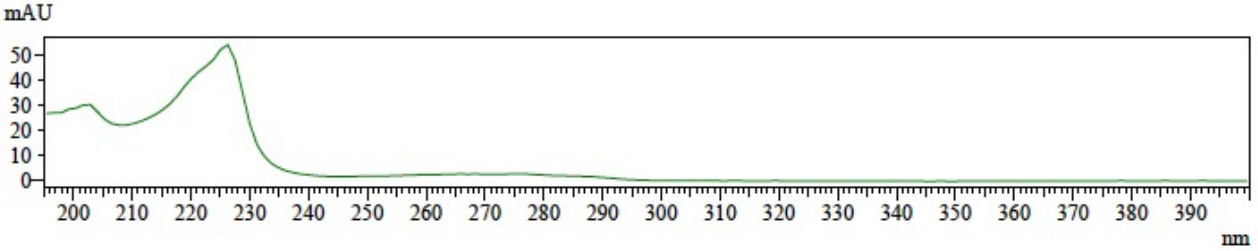
UV Spectrum
Retention time = 14.911





(–)-**2o**

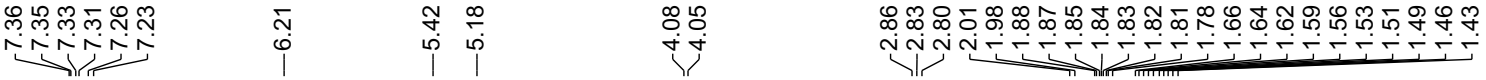
UV Spectrum
Retention time = 17.193



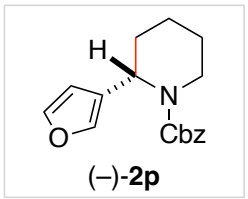
Peak Table

PDA Ch1 220nm

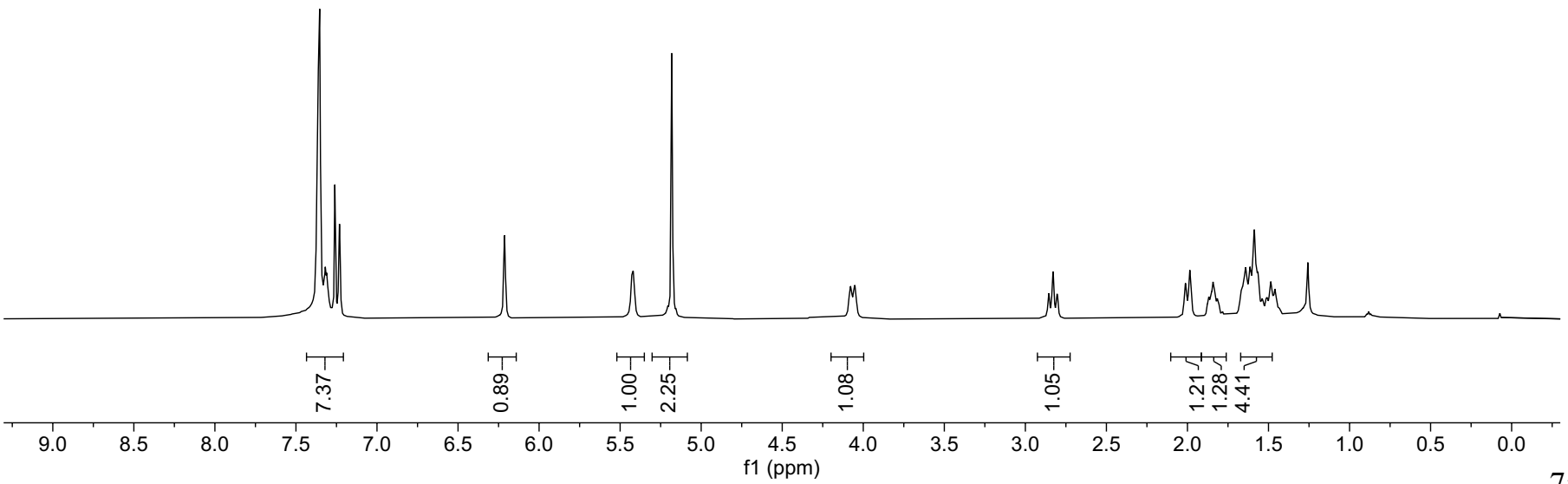
Peak#	Ret. Time	Area	Area%
1	14.911	19221549	95.285
2	17.193	951066	4.715
Total		20172615	100.000



^{1}H NMR of **2p**, 500 MHz, $CDCl_3$

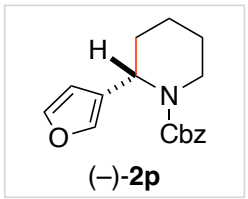


(–)-**2p**



155.75
143.39
139.74
137.04
128.63
128.10
127.96
125.02
110.04
77.41
77.16
76.91
67.28
47.85
40.22
28.61
25.63
19.69

^{13}C NMR of **2p**, 125 MHz, $CDCl_3$

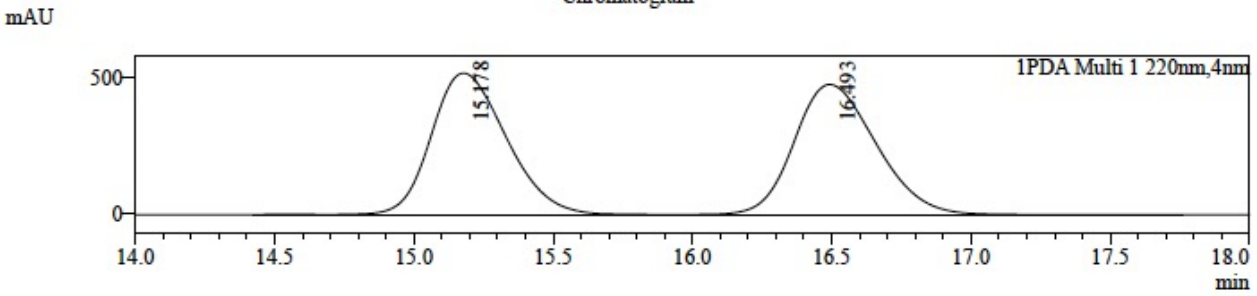


(–)-**2p**

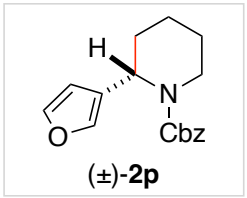
Sample Information

Sample Name	: XXW-1395-IE-10%-0.8mL
Sample ID	: XXW-1395-IE-10%-0.8mL
Data File	: XXW-1395-IE-10%-0.8mL.lcd
Method File	: XXW-10%.0.8.mL.lcm

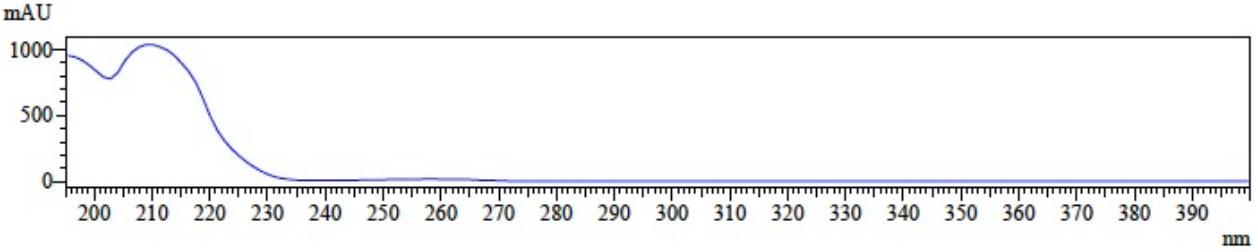
Chromatogram



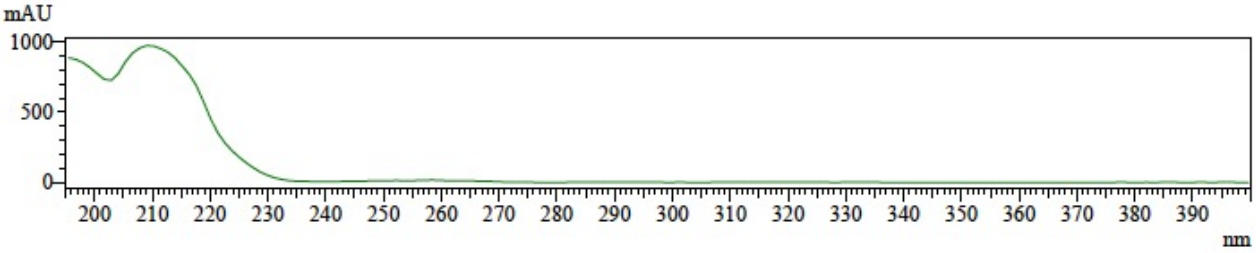
UV Spectrum
Retention time = 15.178



(±)-**2p**



UV Spectrum
Retention time = 16.493



Peak Table

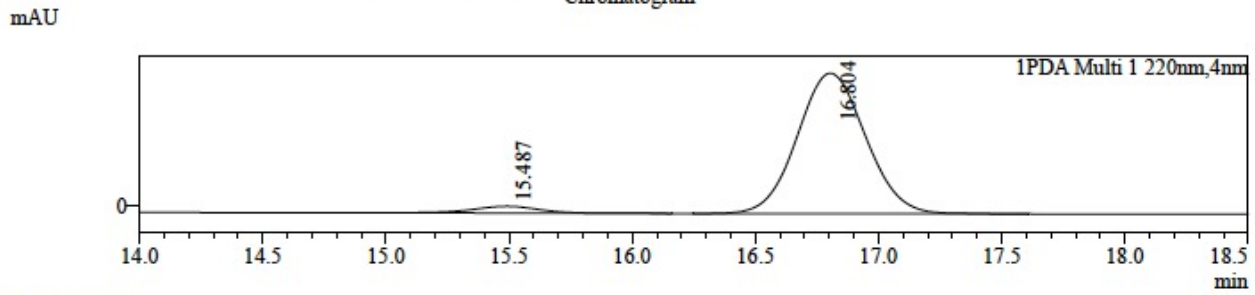
PDA Ch1 220nm

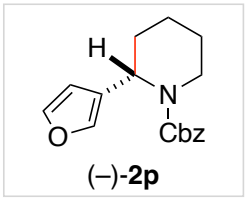
Peak#	Ret. Time	Area	Area%
1	15.178	9796266	49.903
2	16.493	9834169	50.097
Total		19630436	100.000

Sample Information

Sample Name	: XXW-1396-IE-10%-0.8mL
Sample ID	: XXW-1396-IE-10%-0.8mL
Data File	: XXW-1396-IE-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

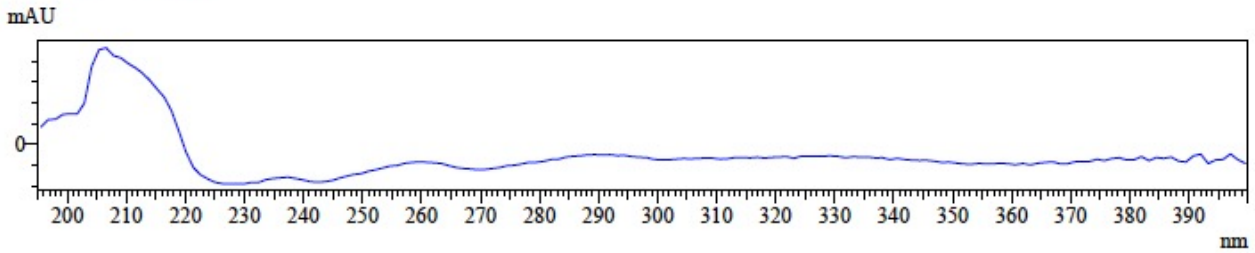
Chromatogram



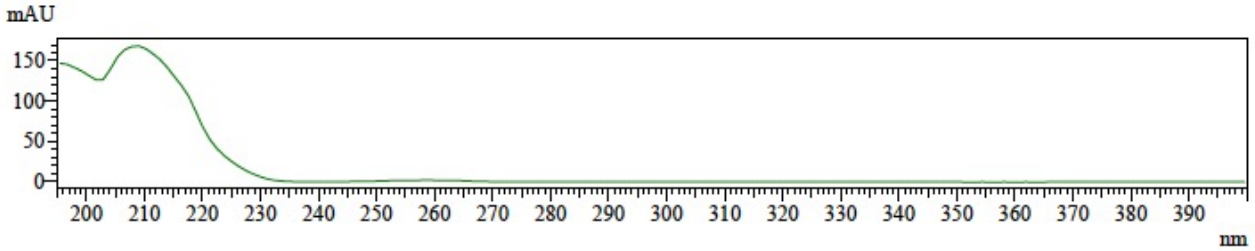


(–)-**2p**

UV Spectrum
Retention time = 15.487



UV Spectrum
Retention time = 16.804

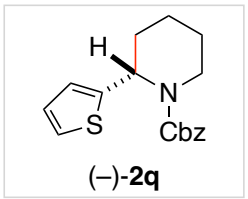


Peak Table

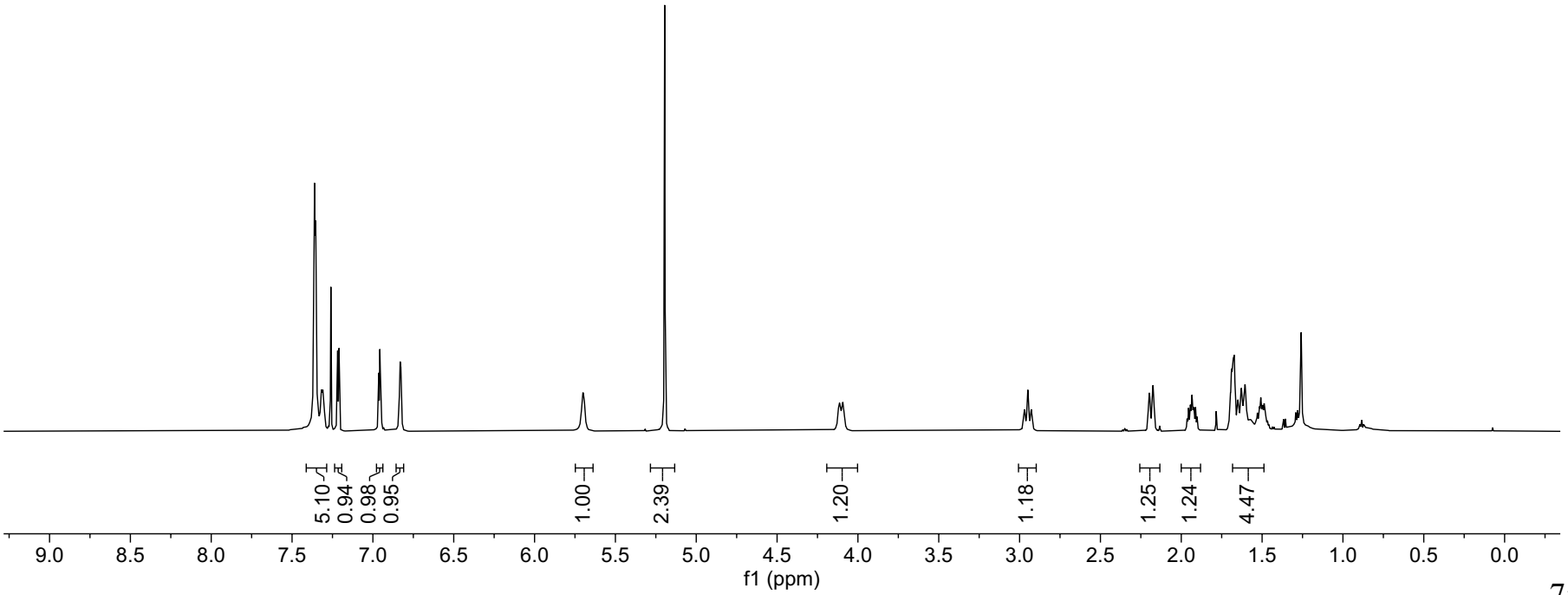
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.487	68087	4.463
2	16.804	1457622	95.537
Total		1525709	100.000

^{1}H NMR of **2q**, 600 MHz, $CDCl_3$

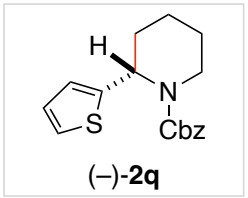


(–)-**2q**

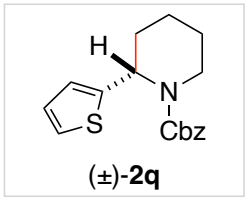


155.68
144.85
136.93
128.61
128.09
127.98
127.04
124.68
124.48
77.37
77.16
76.95
67.42
51.22
40.32
29.85
25.44
19.63

^{13}C NMR of **2q**, 150 MHz, $CDCl_3$



(–)-**2q**

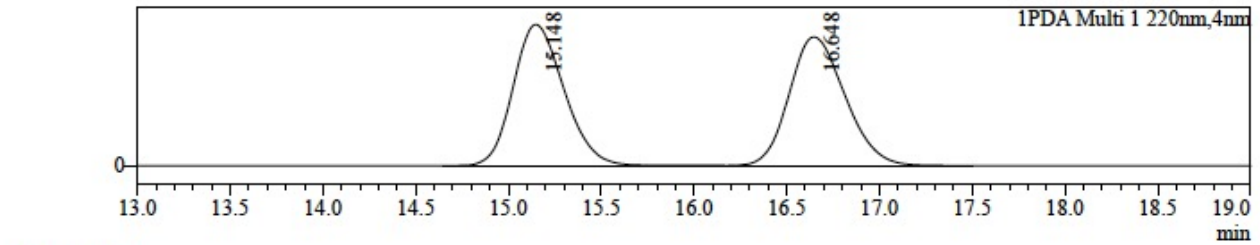


(±)-**2q**

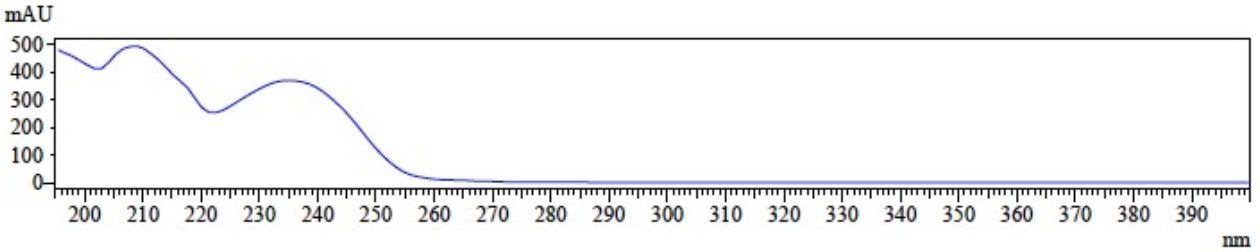
Sample Information

Sample Name	: XXW-1393-ID-10%-0.8mL
Sample ID	: XXW-1393-ID-10%-0.8mL
Data File	: XXW-1393-ID-10%-0.8mL002.lcd
Method File	: XXW-10%.0.8.mL.lcm

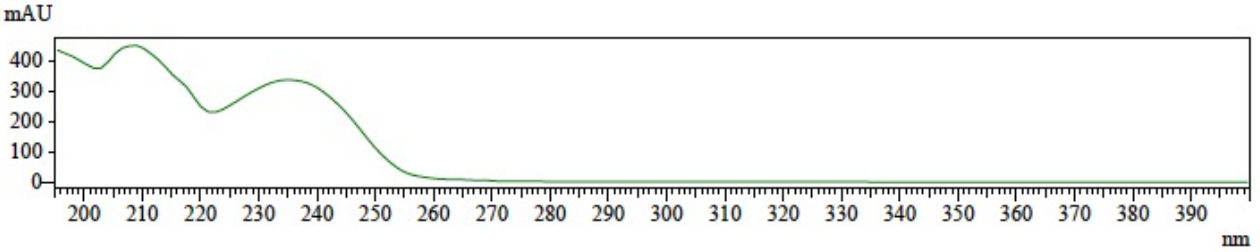
Chromatogram



UV Spectrum
Retention time = 15.148



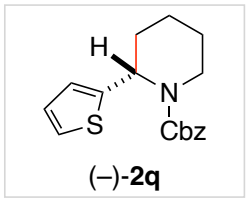
UV Spectrum
Retention time = 16.648



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.148	5611931	50.011
2	16.648	5609361	49.989
Total		11221292	100.000

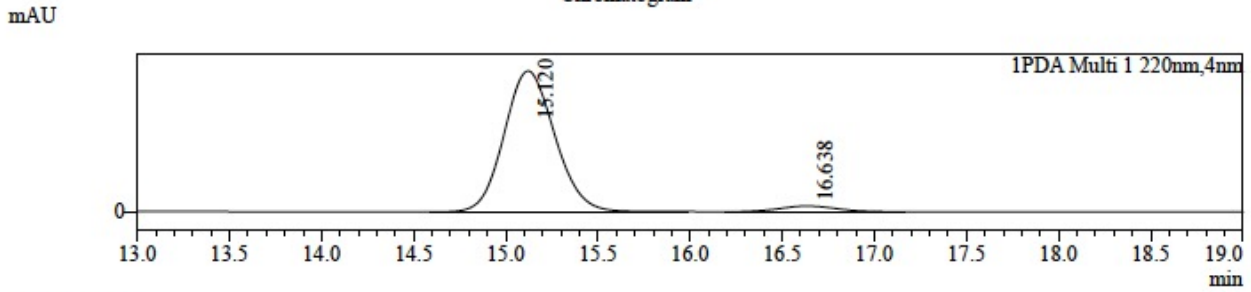


(–)-**2q**

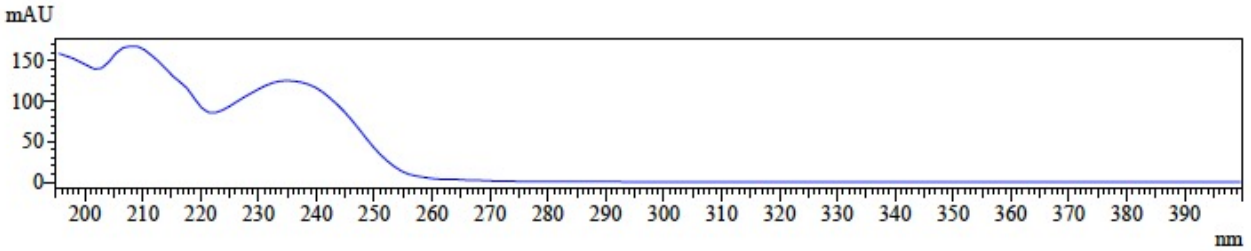
Sample Information

Sample Name	: XXW-1394-ID-10%-0.8mL
Sample ID	: XXW-1394-ID-10%-0.8mL
Data File	: XXW-1394-ID-10%-0.8mL001.lcd
Method File	: XXW-10%.0.8.mL.lcm

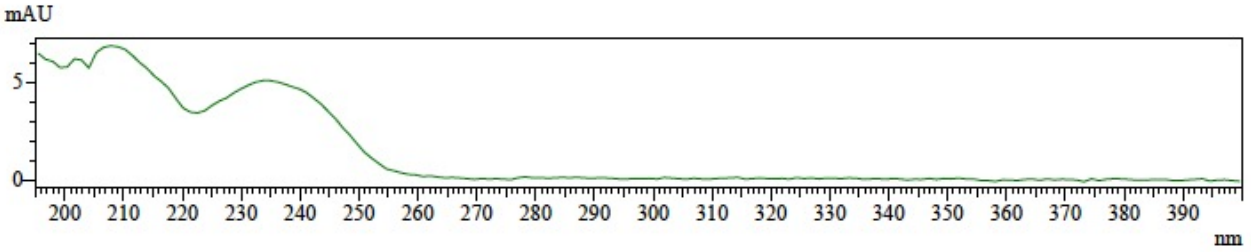
Chromatogram



UV Spectrum
Retention time = 15.120



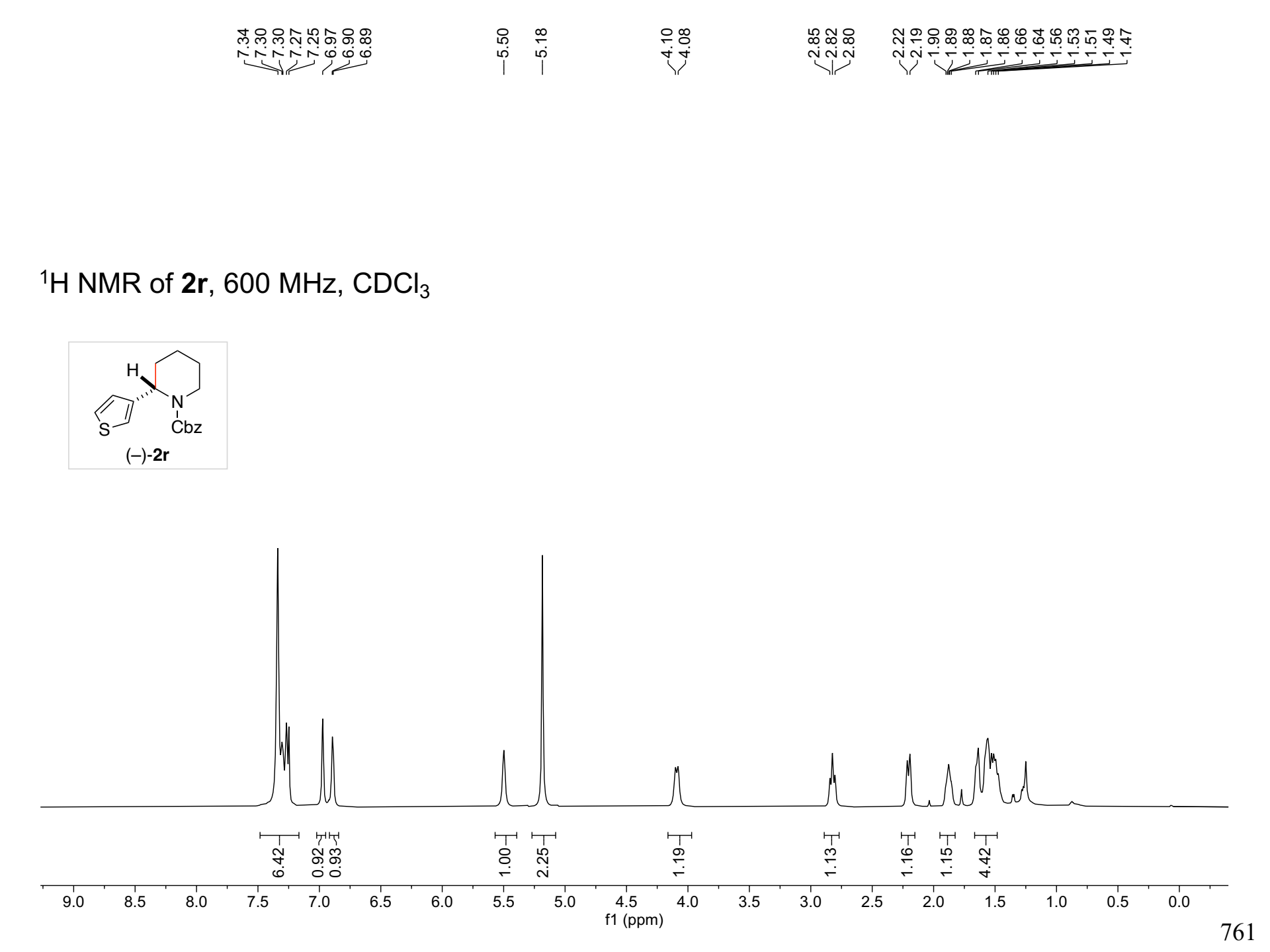
UV Spectrum
Retention time = 16.638



Peak Table

PDA Ch1 220nm

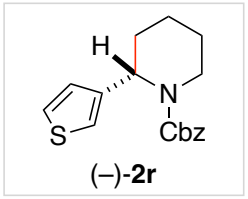
Peak#	Ret. Time	Area	Area%
1	15.120	1906567	95.864
2	16.638	82261	4.136
Total		1988827	100.000



^{1}H NMR of **2r**, 600 MHz, $CDCl_3$

155.84
141.77
137.04
128.61
128.07
127.93
127.04
126.07
121.11
77.37
77.16
76.95
67.29
51.42
40.47
28.90
25.64
19.67

^{13}C NMR of **2r**, 150 MHz, $CDCl_3$

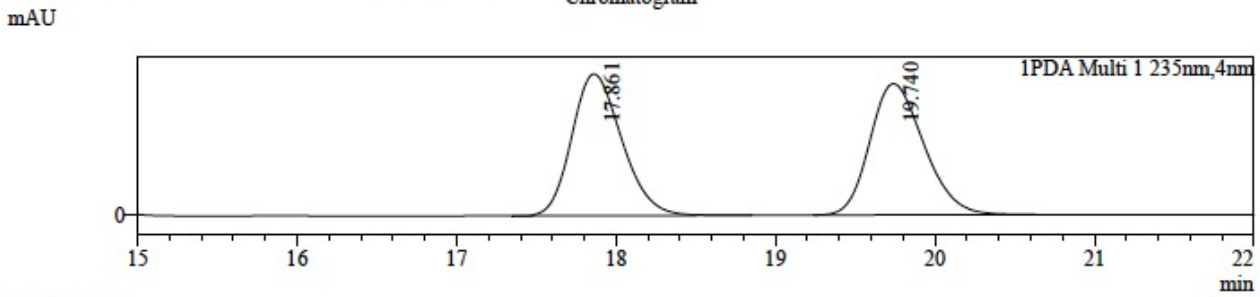


(–)-**2r**

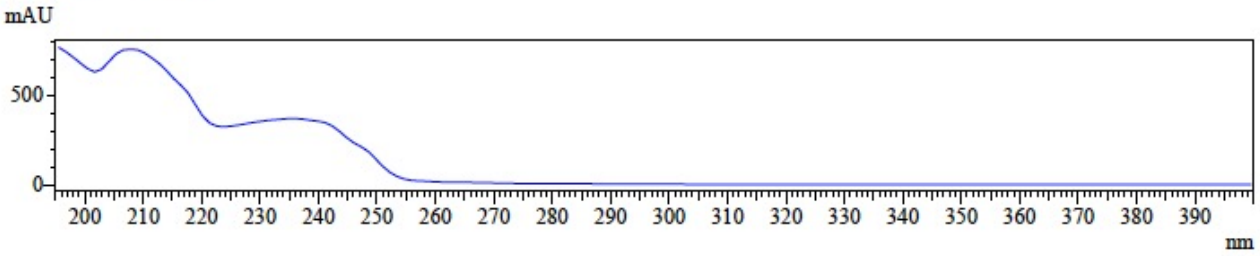
Sample Information

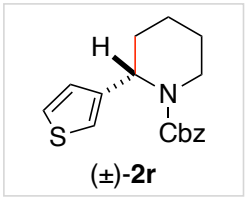
Sample Name	: XXW-1212-IF-5%-0.8mL
Sample ID	: XXW-1212-IF-5%-0.8mL
Data File	: XXW-1212-IF-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram



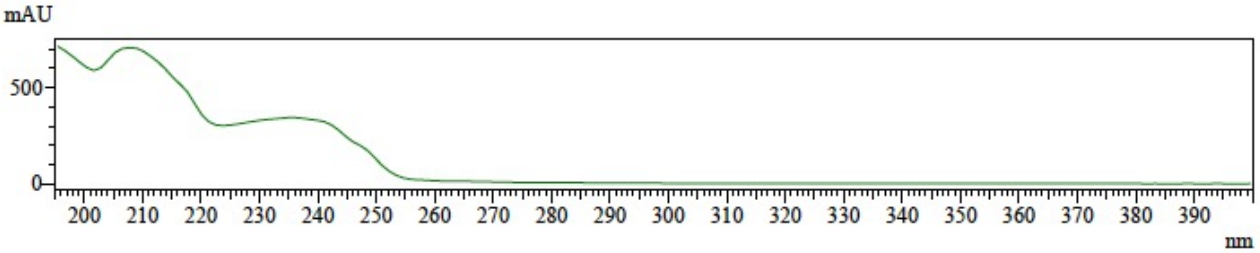
UV Spectrum
Retention time = 17.861





(±)-**2r**

UV Spectrum
Retention time = 19.740



Peak Table

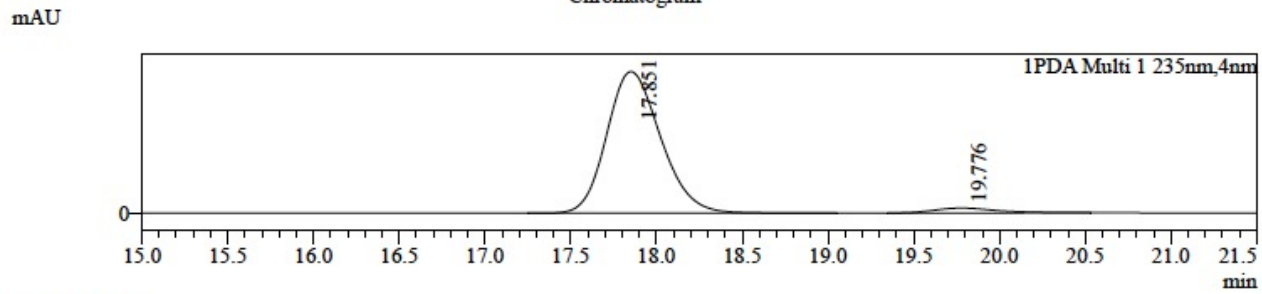
PDA Ch1 235nm

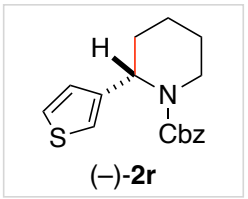
Peak#	Ret. Time	Area	Area%
1	17.861	7968103	50.010
2	19.740	7965054	49.990
Total		15933157	100.000

Sample Information

Sample Name	: XXW-1213-IF-5%-0.8mL
Sample ID	: XXW-1213-IF-5%-0.8mL
Data File	: XXW-1213-IF-5%-0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

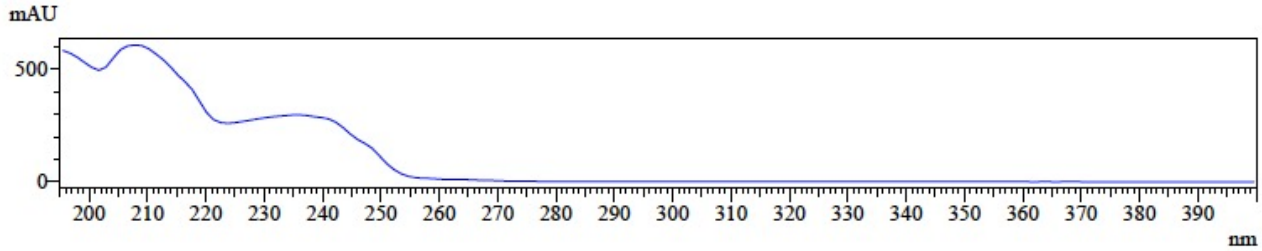
Chromatogram



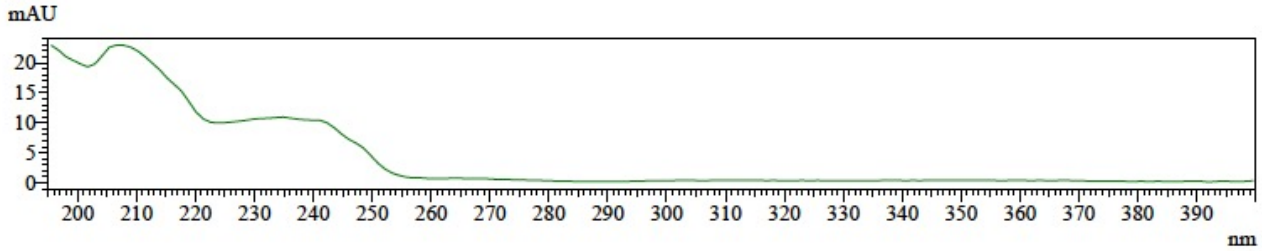


(–)-**2r**

UV Spectrum
Retention time = 17.851



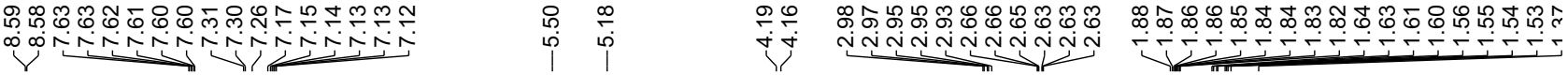
UV Spectrum
Retention time = 19.776



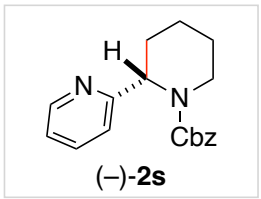
Peak Table

PDA Ch1 235nm

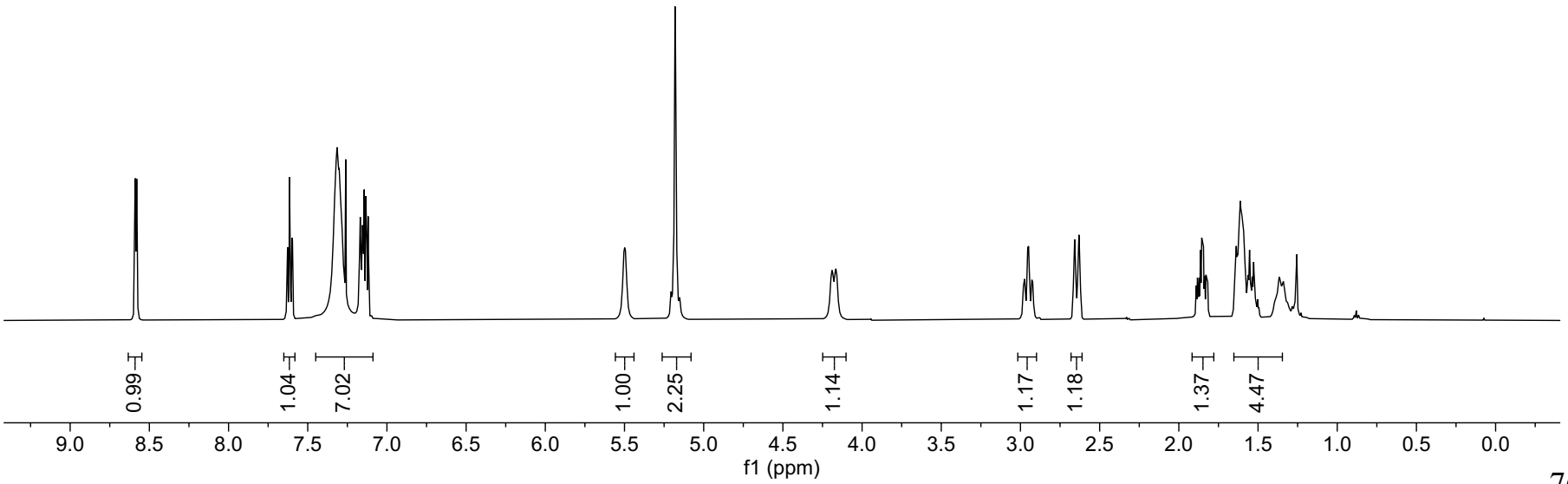
Peak#	Ret. Time	Area	Area%
1	17.851	6402109	96.280
2	19.776	247338	3.720
Total		6649447	100.000



^{1}H NMR of **2s**, 500 MHz, $CDCl_3$

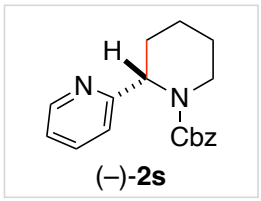


(–)-**2s**



160.06
156.48
149.31
137.01
136.64
128.55
128.00
127.86
121.62
121.30
77.41
77.16
76.91
67.29
55.81
41.28
27.82
25.42
19.75

^{13}C NMR of **2s**, 125 MHz, $CDCl_3$

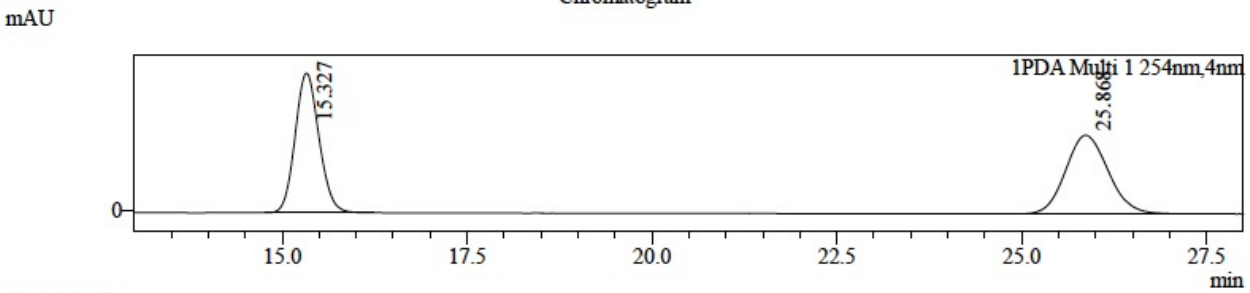


(–)-**2s**

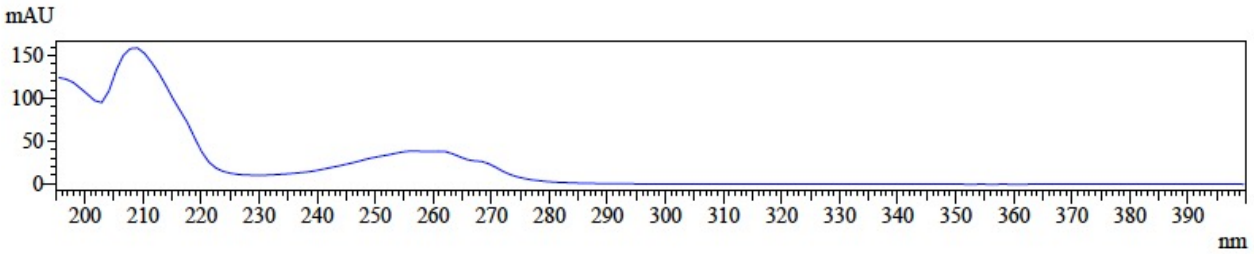
Sample Information

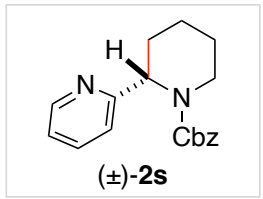
Sample Name	: XXW-1204--20%-IC-0.8mL
Sample ID	: XXW-1204--20%-IC-0.8mL
Data File	: XXW-1204--20%-IC-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram



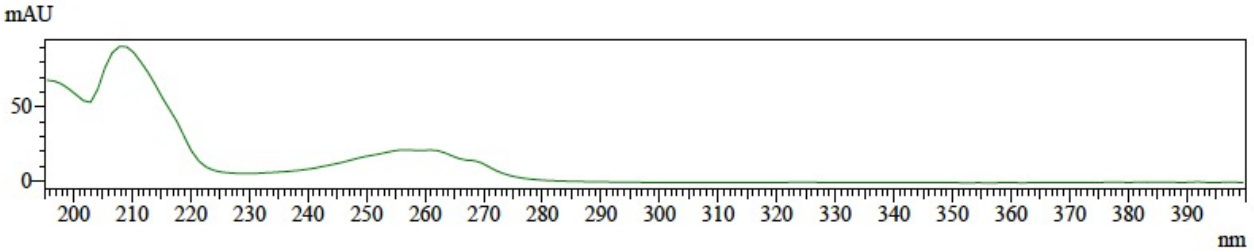
UV Spectrum
Retention time = 15.327





(±)-**2s**

UV Spectrum
Retention time = 25.868



Peak Table

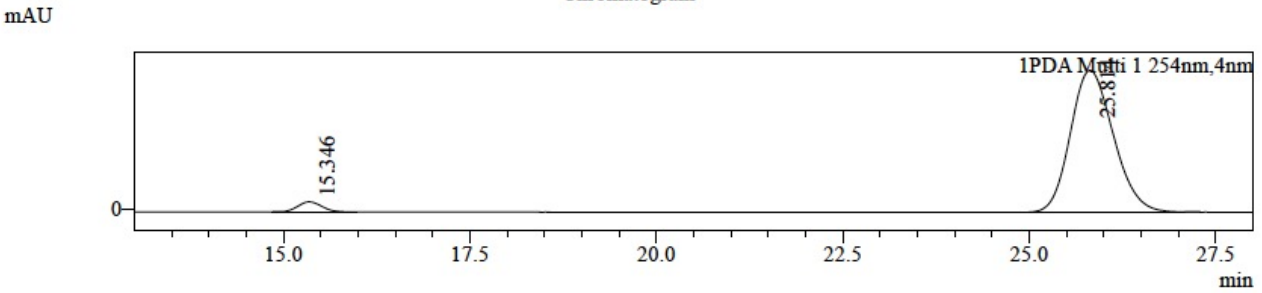
PDA Ch1 254nm

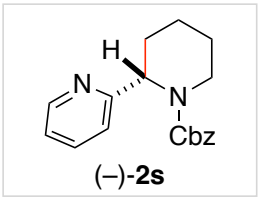
Peak#	Ret. Time	Area	Area%
1	15.327	812418	50.057
2	25.868	810557	49.943
Total		1622975	100.000

Sample Information

Sample Name	: XXW-1203-20%-IC-0.8mL
Sample ID	: XXW-1203-20%-IC-0.8mL
Data File	: XXW-1203-20%-IC-0.8mL.lcd
Method File	: XXW-20%.0.8.mL.lcm

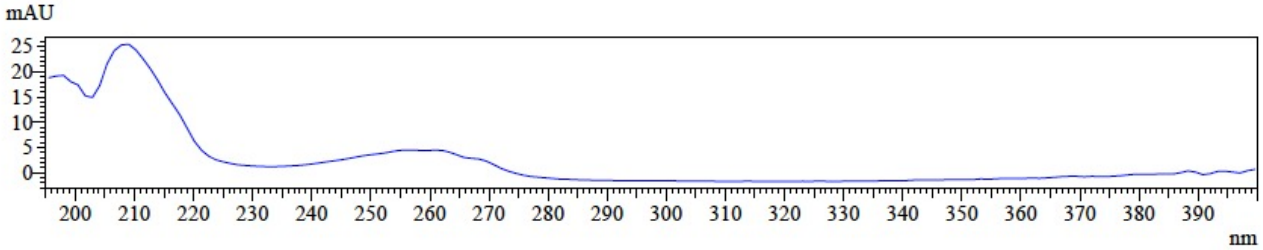
Chromatogram



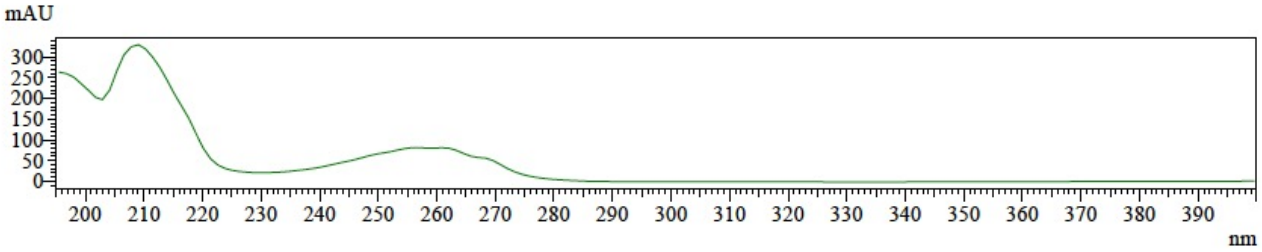


(–)-**2s**

UV Spectrum
Retention time = 15.346



UV Spectrum
Retention time = 25.814

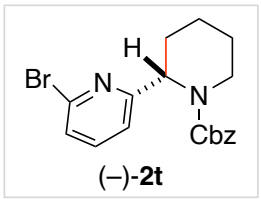


Peak Table

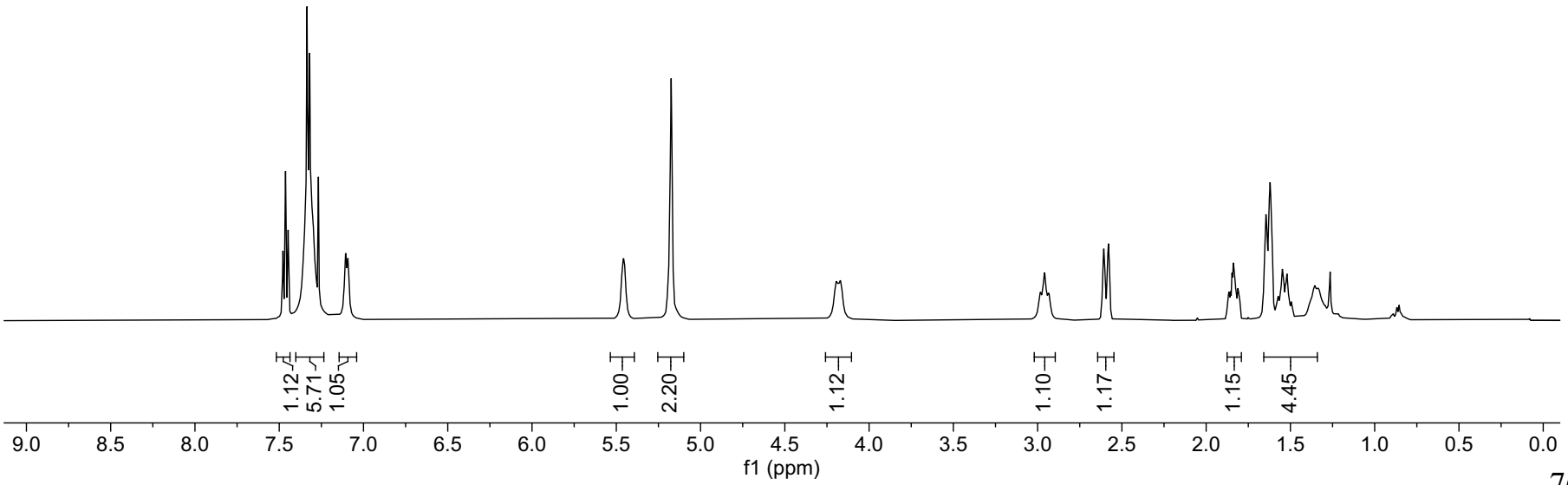
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.346	125314	3.864
2	25.814	3117683	96.136
Total		3242997	100.000

^{1}H NMR of **2t**, 500 MHz, $CDCl_3$

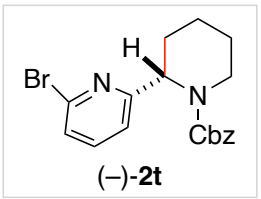


(–)-**2t**

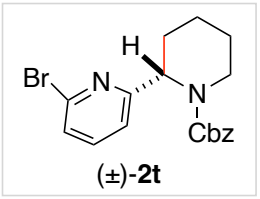


161.97
156.34
141.83
138.92
136.87
128.60
128.09
127.89
126.03
120.14
77.41
77.16
76.91
67.39
55.51
41.27
27.85
25.26
19.65

^{13}C NMR of **2t**, 125 MHz, $CDCl_3$



(–)-**2t**

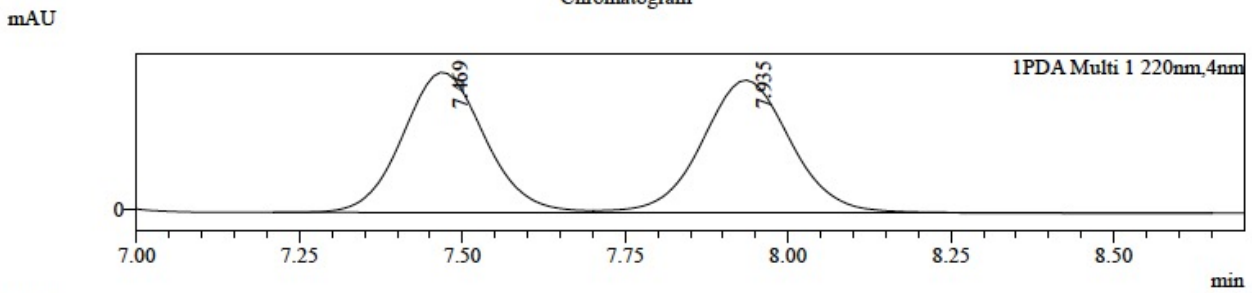


(±)-**2t**

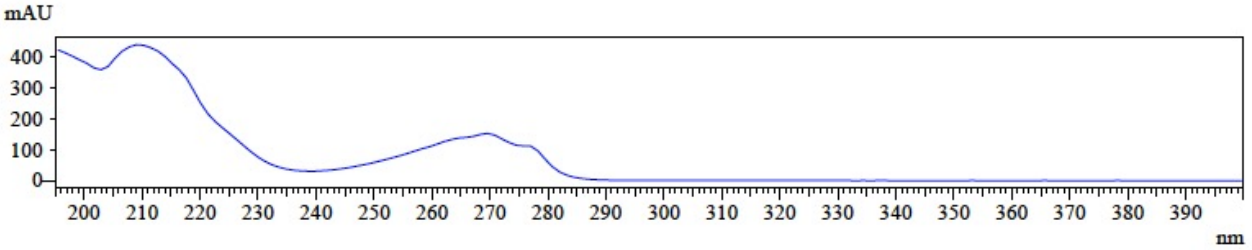
Sample Information

Sample Name	: XXW-1432-IA-20%-0.8mL
Sample ID	: XXW-1432-IA-20%-0.8mL
Data File	: XXW-1432-IA-20%-0.8mL001.lcd
Method File	: XXW-20%.0.8.mL.lcm

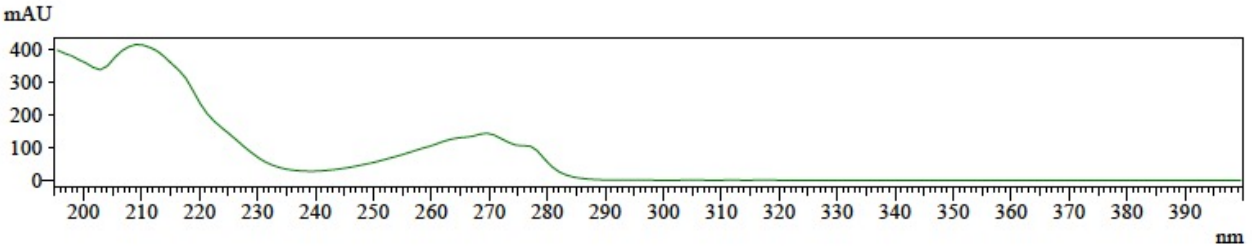
Chromatogram



UV Spectrum
Retention time = 7.469



UV Spectrum
Retention time = 7.935



Peak Table

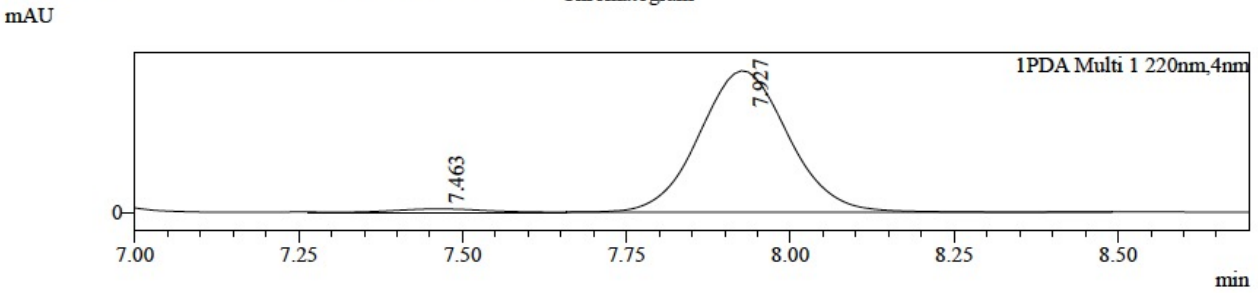
PDA Ch1 220nm

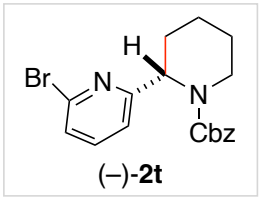
Peak#	Ret. Time	Area	Area%
1	7.469	2335725	49.442
2	7.935	2388422	50.558
Total		4724148	100.000

Sample Information

Sample Name : XXW-1433-IA-20%-0.8mL
Sample ID : XXW-1433-IA-20%-0.8mL
Data File : XXW-1433-IA-20%-0.8mL.lcd
Method File : XXW-20%.0.8.mL.lcm

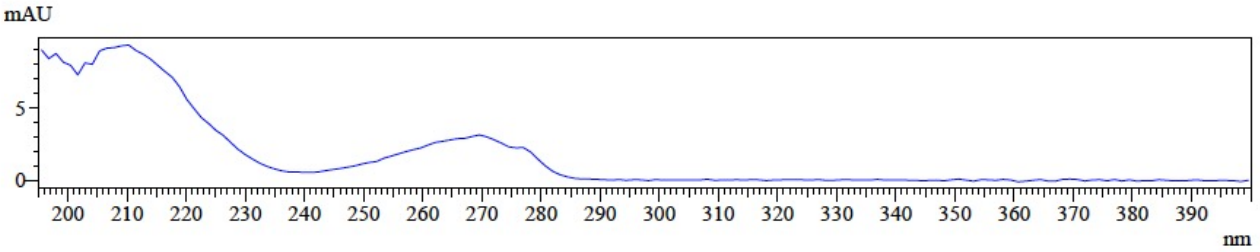
Chromatogram



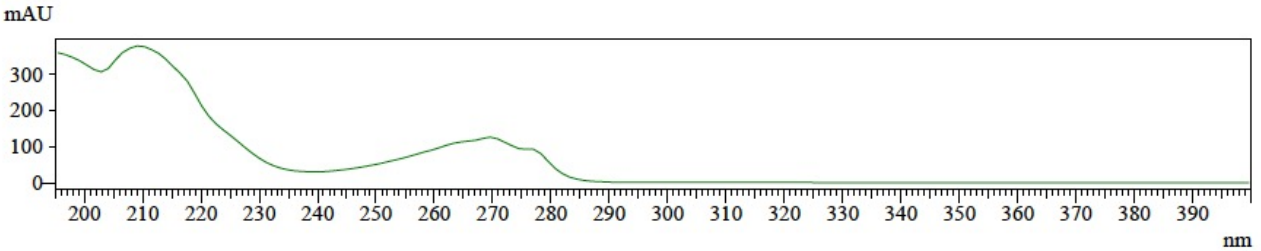


(–)-**2t**

UV Spectrum
Retention time = 7.463



UV Spectrum
Retention time = 7.927

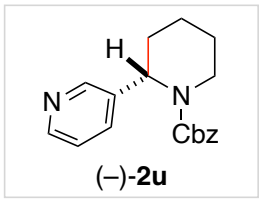


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.463	47650	2.230
2	7.927	2088645	97.770
Total		2136294	100.000

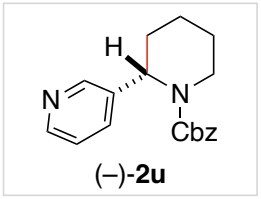
^{1}H NMR of **2u**, 600 MHz, $CDCl_3$



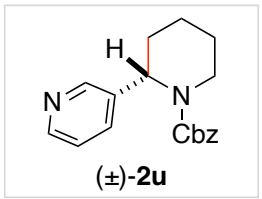
(–)-**2u**

156.12
148.47
148.06
136.77
135.57
134.74
128.66
128.20
128.00
123.60
77.37
77.16
76.95
67.55
52.06
40.64
27.90
25.40
19.33

^{13}C NMR of **2u**, 150 MHz, $CDCl_3$



(–)-**2u**

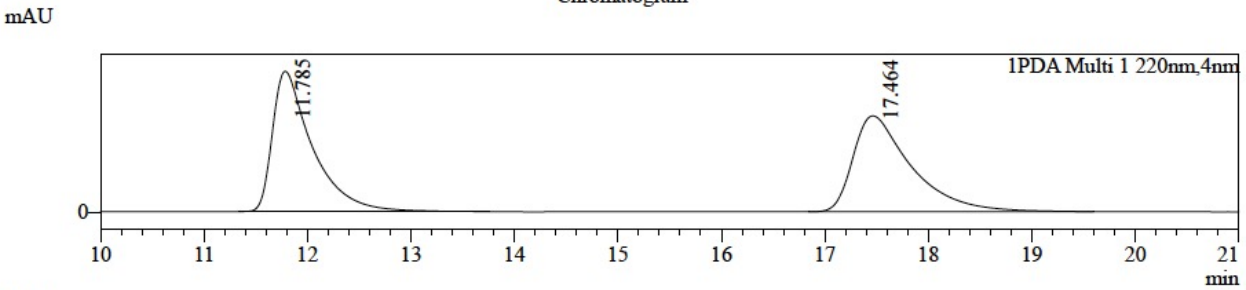


(±)-**2u**

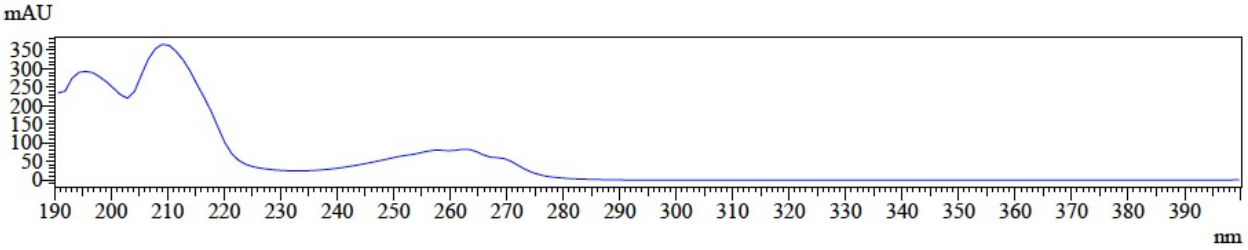
Sample Information

Data File	: XXW-1304--ADH-20%--0.8mL001.lcd
Sample Name	: XXW-1304--ADH-20%--0.8mL
Sample ID	: XXW-1304--ADH-20%--0.8mL
Method File	: XXW-20%.0.8.mL.lcm

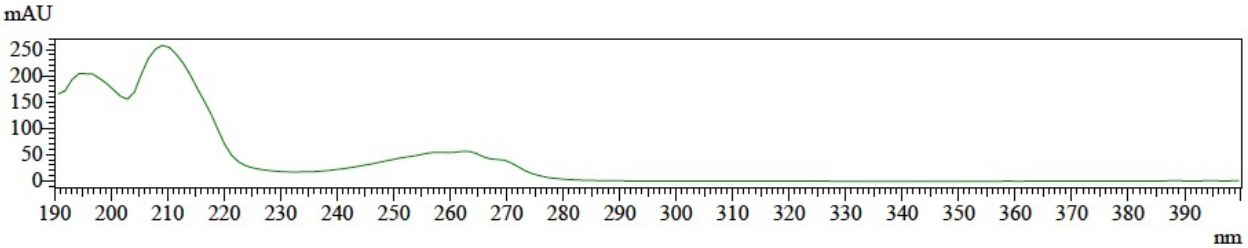
Chromatogram



UV Spectrum
Retention time = 11.785



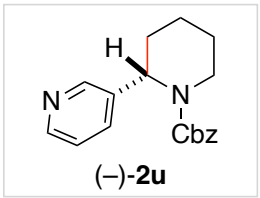
UV Spectrum
Retention time = 17.464



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	11.785	3126871	50.139
2	17.464	3109576	49.861
Total		6236447	100.000

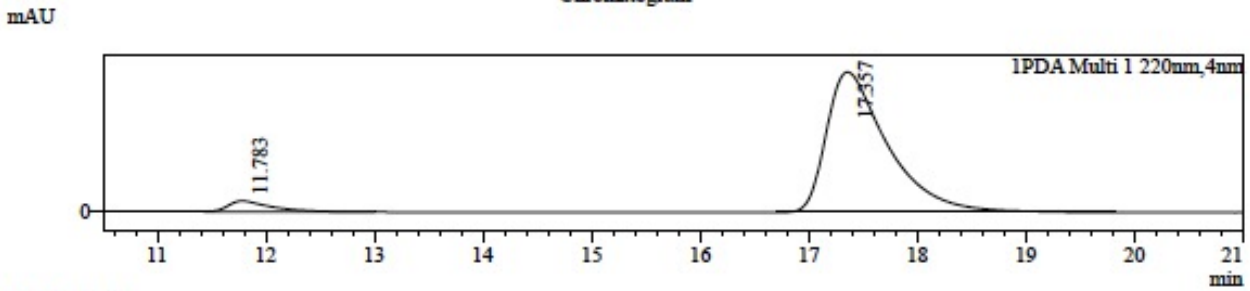


(–)-**2u**

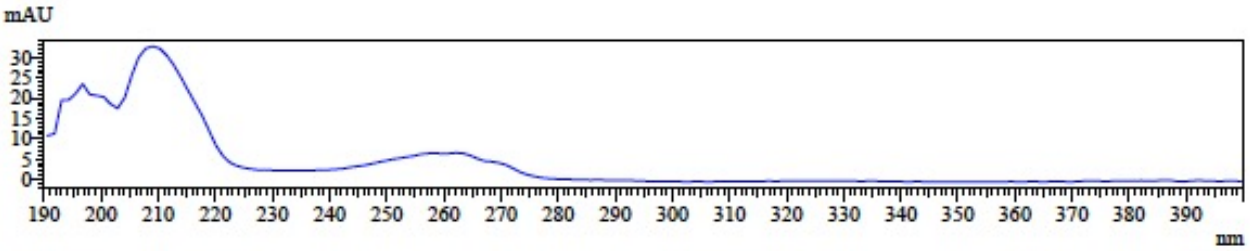
Sample Information

Data File	: XXW-1302--ADH-20%--0.8mL001.lcd
Sample Name	: XXW-1302--ADH-20%--0.8mL
Sample ID	: XXW-1302--ADH-20%--0.8mL
Method File	: XXW-20%.0.8.mL.lcm

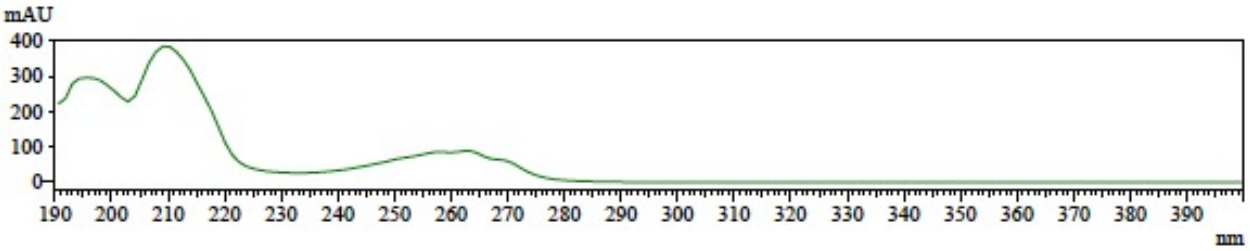
Chromatogram



UV Spectrum
Retention time = 11.783



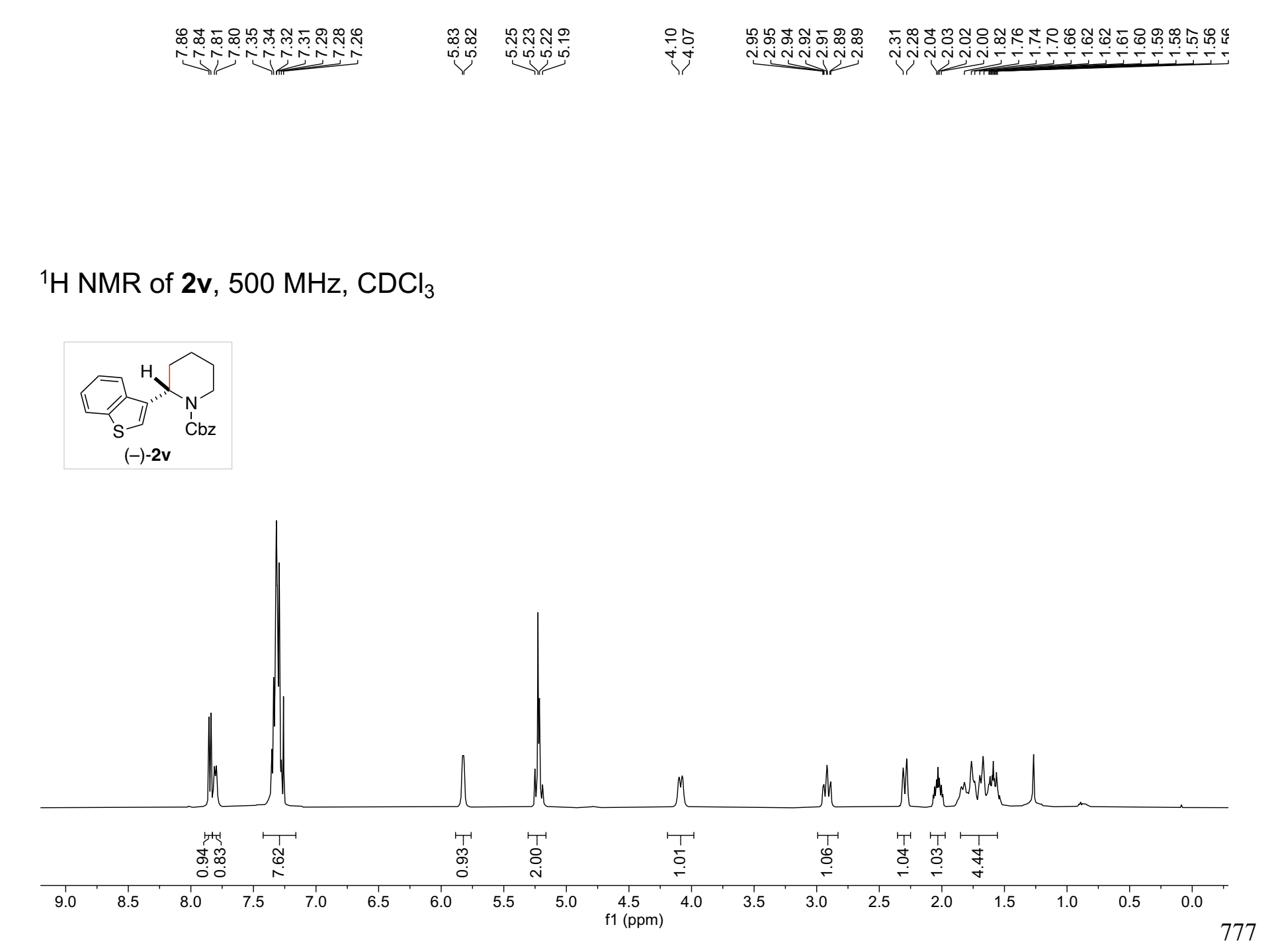
UV Spectrum
Retention time = 17.357



Peak Table

PDA Ch1 220nm

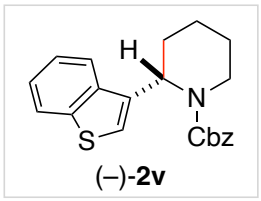
Peak#	Ret. Time	Area	Area%
1	11.783	259636	4.946
2	17.357	4989752	95.054
Total		5249388	100.000



^{1}H NMR of **2v**, 500 MHz, $CDCl_3$

155.80
140.46
138.36
137.02
135.82
128.59
128.04
127.90
124.48
124.26
123.12
122.80
77.41
77.16
76.90
67.35
50.59
41.23
28.40
25.67
20.15

^{13}C NMR of **2v**, 125 MHz, $CDCl_3$

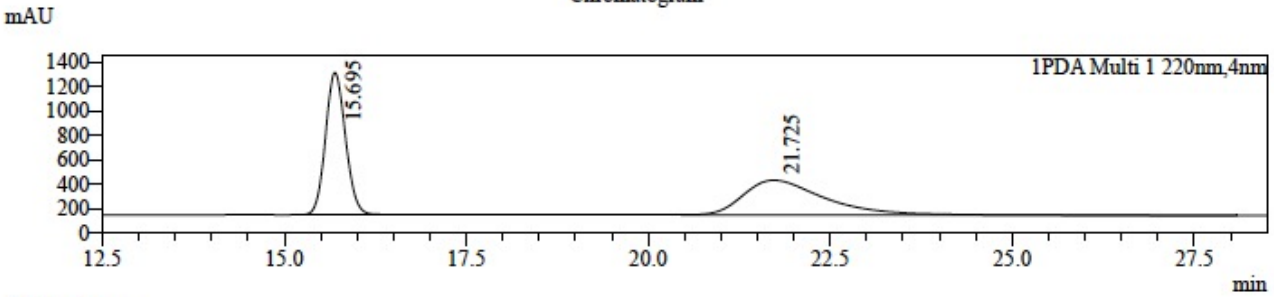


(–)-**2v**

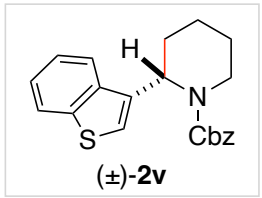
Sample Information

Data File	: XXW-1561--ID-10%-0.8mL001.lcd
Sample Name	: XXW-1561--ID-10%-0.8mL
Sample ID	: XXW-1561--ID-10%-0.8mL
Method File	: XXW-10%.0.8.mL.lcm

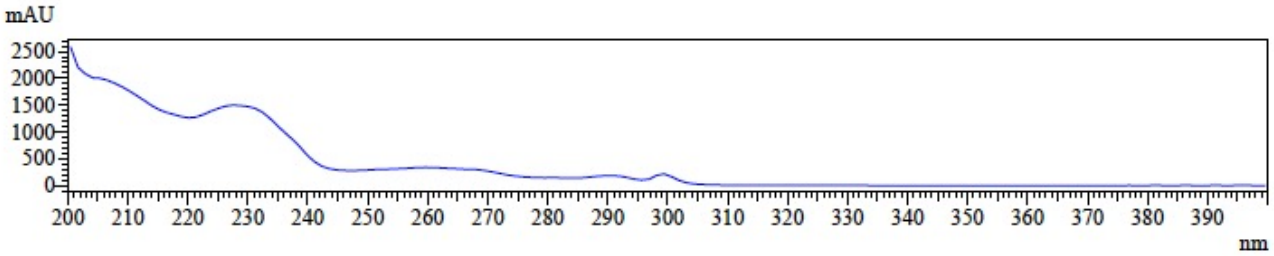
Chromatogram



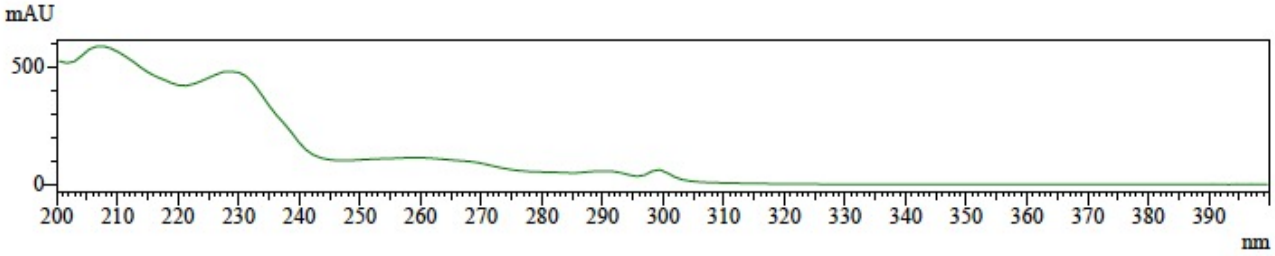
UV Spectrum
Retention time = 15.695



(±)-**2v**



UV Spectrum
Retention time = 21.725



Peak Table

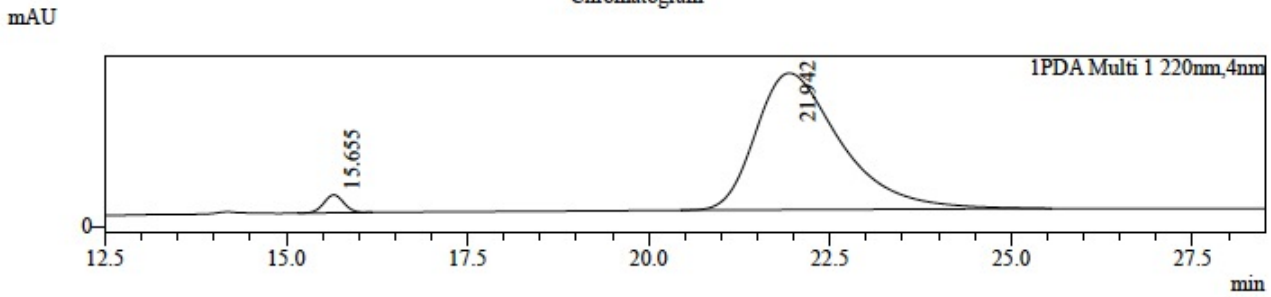
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	15.695	22384674	50.145
2	21.725	22255160	49.855
Total		44639833	100.000

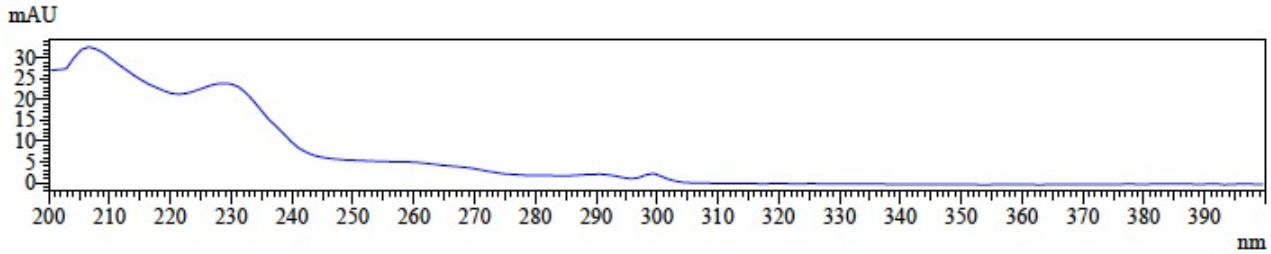
Sample Information

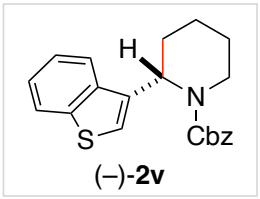
Data File	: XXW-1562--ID-10%-0.8mL.lcd
Sample Name	: XXW-1562--ID-10%-0.8mL
Sample ID	: XXW-1562--ID-10%-0.8mL
Method File	: XXW-10%.0.8.mL.lcm

Chromatogram



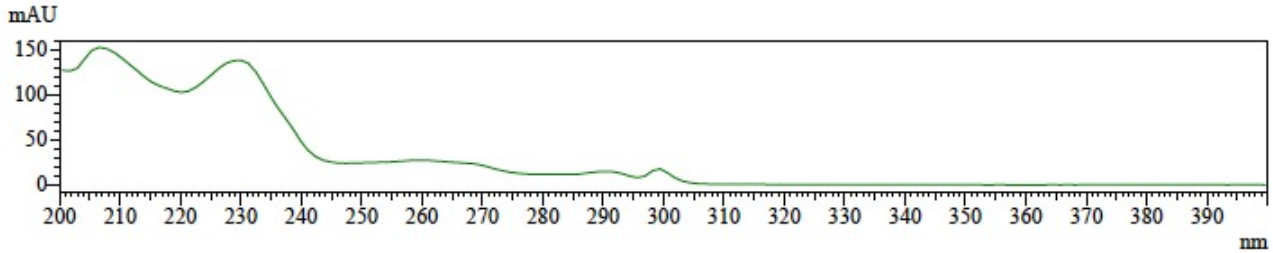
UV Spectrum
Retention time = 15.655





(–)-**2v**

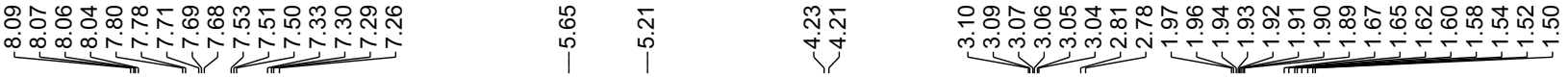
UV Spectrum
Retention time = 21.942



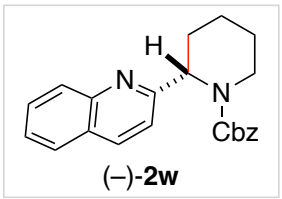
Peak Table

PDA Ch1 220nm

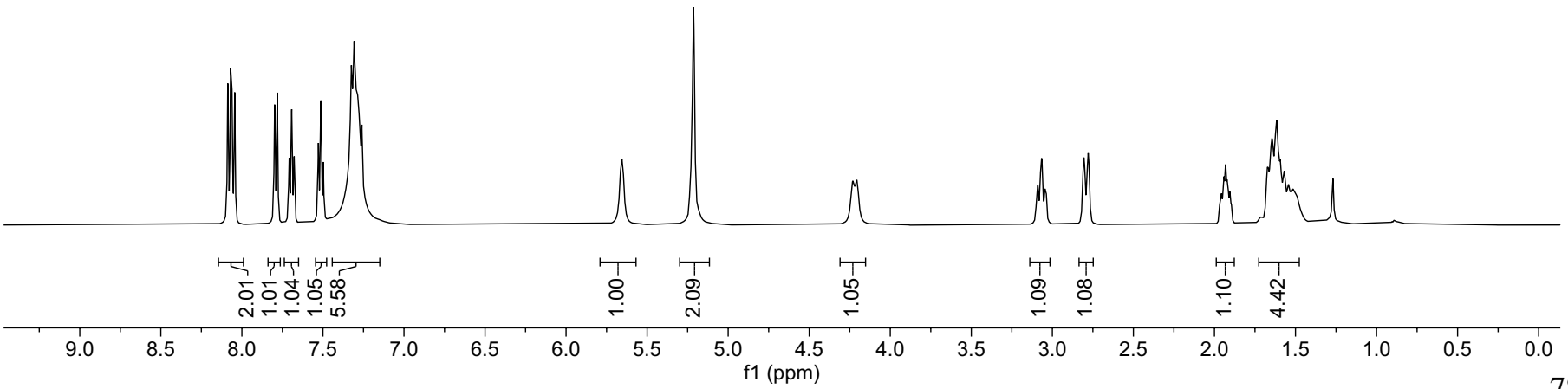
Peak#	Ret. Time	Area	Area%
1	15.655	240903	3.011
2	21.942	7760545	96.989
Total		8001448	100.000



^{1}H NMR of **2w**, 500 MHz, $CDCl_3$

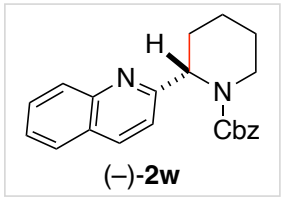


(–)-**2w**



160.58
156.61
147.88
137.06
136.58
129.59
129.39
128.53
127.96
127.80
127.53
126.95
126.25
119.33
77.41
77.16
76.91
67.27
56.37
41.70
27.83
25.44
19.82

^{13}C NMR of **2w**, 125 MHz, $CDCl_3$

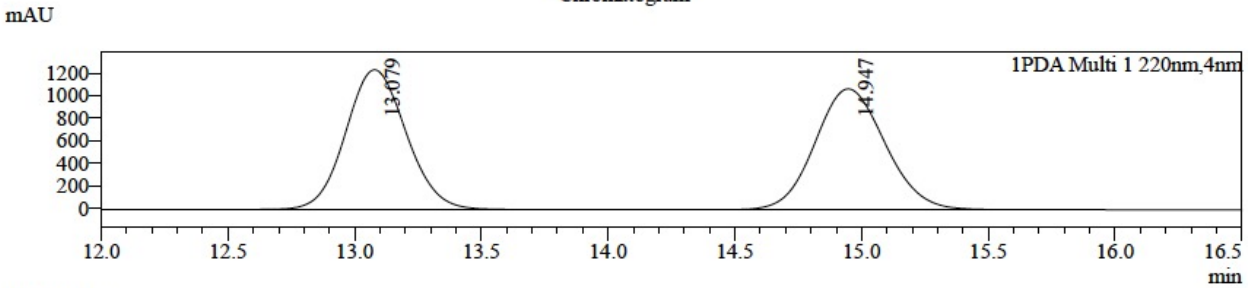


(–)-**2w**

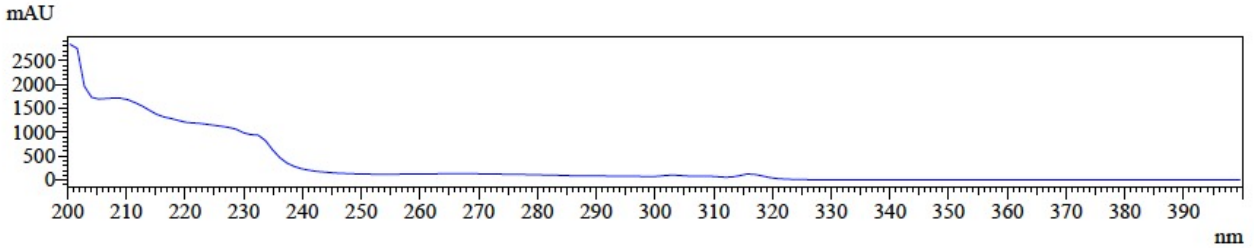
Sample Information

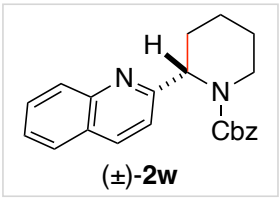
Data File	: XXW-1446-IE-20%-0.8mL001.lcd
Sample Name	: XXW-1446-IE-20%-0.8mL
Sample ID	: XXW-1446-IE-20%-0.8mL
Method File	: XXW-20%.0.8.mL.lcm

Chromatogram



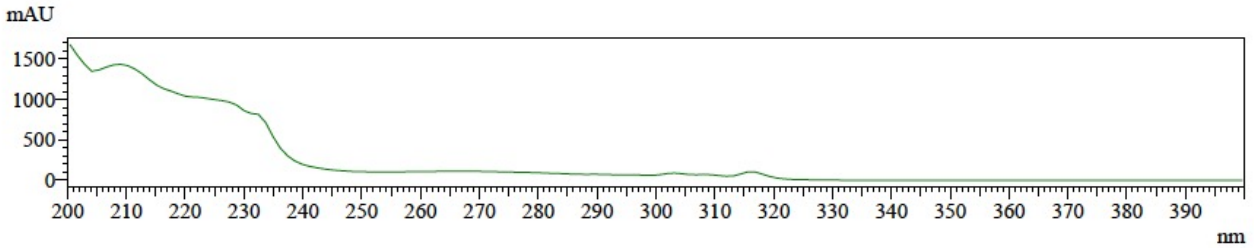
UV Spectrum
Retention time = 13.079





(±)-**2w**

UV Spectrum
Retention time = 14.947



Peak Table

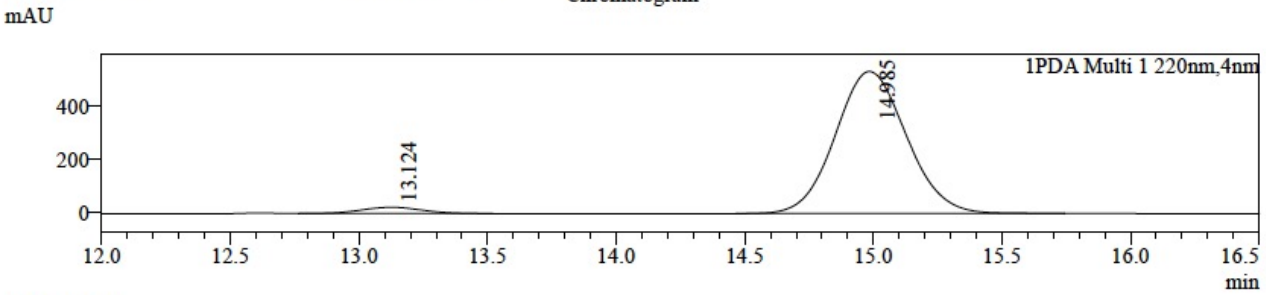
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	13.079	20695279	50.076
2	14.947	20632340	49.924
Total		41327619	100.000

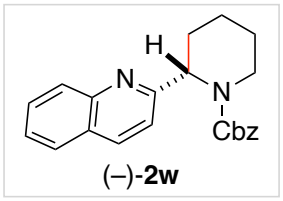
Sample Information

Data File : XXW-1447-IE-20%-0.8mL001.lcd
Sample Name : XXW-1447-IE-20%-0.8mL
Sample ID : XXW-1447-IE-20%-0.8mL
Method File : XXW-20%.0.8.mL.lcm

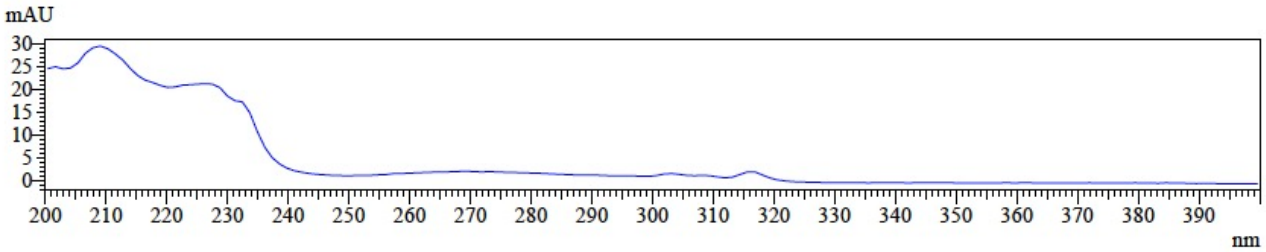
Chromatogram



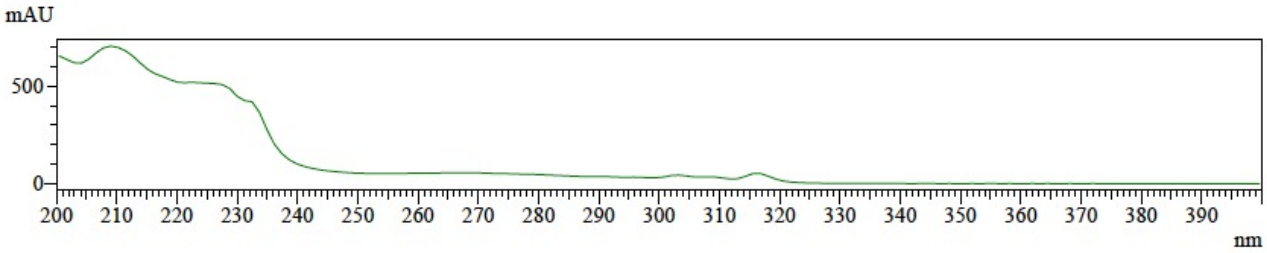
UV Spectrum
Retention time = 13.124



(–)-**2w**



UV Spectrum
Retention time = 14.985



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	13.124	385480	3.610
2	14.985	10292731	96.390
Total		10678211	100.000

CHAPTER 4

DESIGN AND SYNTHESIS OF A NOVEL D_2-SYMMETRIC CHIRAL PORPHYRIN FOR COBALT(II)-BASED METALLORADICAL CATALYSIS

4.1. INTRODUCTION

The past decades have witnessed renaissance of radical reactions in view of their rich reactivities and attractive characteristics.[1] Despite recent advancements, the enduring issues associated with controlling reactivity and stereoselectivity of radical species remain a formidable challenge and largely unaddressed.[2] Among considerable efforts in surmounting this challenge,[3] metalloradical catalysis (MRC) involving catalytic generation and regulation of metal-stabilized organic radicals has emerged as a conceptually different

[1] For selected books, see: (a) Zard, S. Z. *Radical Reactions in Organic Synthesis*; Oxford University Press, 2003. (b) Chatgilialoglu, C.; Studer, A., *Encyclopedia of Radicals in Chemistry, Biology, and Materials*; John Wiley & Sons, 2012. For selected reviews, see: (c) Zard, S. Z. *Chem. Soc. Rev.* **2008**, *37*, 1603–1618. (d) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, *40*, 102–113. (e) Quiclet-Sire, B.; Zard, S. Z. *Pure Appl. Chem.* **2011**, *83*, 519–551. (f) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322–5363. (g) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58–102.

[2] For selected reviews, see: (a) Bar, G.; Parsons, A. F. *Chem. Soc. Rev.* **2003**, *32*, 251–263. (b) Sibi, M. P.; Manyem, S.; Zimmerman, J. *Chem. Rev.* **2003**, *103*, 3263–3295. (c) Brimioulle, R.; Lenhart, D.; Maturi, M. M.; Bach, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 3872–3890.

[3] For selected examples on approaches to controlling radical reactivity and stereoselectivity, see: (a) Du, J. N.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. *Science* **2014**, *344*, 392–396. (b) Huo, H.; Shen, X.; Wang, C.; Zhang, L.; Röse, P.; Chen, L.-A.; Harms, K.; Marsch, M.; Hilt, G.; Meggers, E. *Nature* **2014**, *515*, 100–103. (c) Kainz, Q. M.; Matier, C. D.; Bartoszewicz, A.; Zultanski, S. L.; Peters, J. C.; Fu, G. C. *Science* **2016**, *351*, 681–684. (d) Zhang, W.; Wang, F.; McCann, S. D.; Wang, D. H.; Chen, P. H.; Stahl, S. S.; Liu, G. S. *Science* **2016**, *353*, 1014–1018. (e) Kern, N.; Plesniak, M. P.; McDouall, J. J. W.; Procter, D. J. *Nat. Chem.* **2017**, *9*, 1198–1204. (f) Morrill, C.; Jensen, C.; Just-Baringo, X.; Grogan, G.; Turner, N. J.; Procter, D. J. *Angew. Chem., Int. Ed.* **2018**, *57*, 3692–3696. (g) Proctor, R. S. J.; Davis, H. J.; Phipps, R. J. *Science* **2018**, *360*, 419–422. (h) Biegasiewicz, K. F.; Cooper, S. J.; Gao, X.; Oblinsky, D. G.; Kim, J. H.; Garfinkle, S. E.; Joyce, L. A.; Sandoval, B. A.; Scholes, G. D.; Hyster, T. K. *Science* **2019**, *364*, 1166–1169. (i) Huang, H.-M.; McDouall, J. J. W.; Procter, D. J. *Nat. Catal.* **2019**, *2*, 211–218. (j) Nakafuku, K. M.; Zhang, Z.; Wappes, E. A.; Stateman, L. M.; Chen, A. D.; Nagib, D. A. *Nat. Chem.* **2020**, *12*, 697–704.

approach for the development of stereoselective radical transformations.[4,5,6] To this end, we have demonstrated that Co(II) complexes of porphyrins [Co(Por)] as stable 15e-metalloradicals exhibit unique capability of homolytically activating diazo compounds to generate the fundamentally new α-Co(III)-alkyl radicals[7] as key intermediates for catalytic reactions involving carbon-centered radicals. Through the introduction of modularly-designed D_2-symmetric chiral amidoporphyrins as the supporting ligand system whose environments can be fine-tuned, the initially-formed Co-stabilized C-centered radicals, which are situated inside the confined chiral ligand environment, can be precisely governed to perform subsequent homolytic radical reactions, such as radical addition and H-atom abstraction as well as radical substitution, giving rise to the discovery of new catalytic

[4] For selected reviews and highlights on Co(II)-based MRC, see: (a) Lu, H. J.; Zhang, X. P. *Chem. Soc. Rev.* **2011**, *40*, 1899–1909. (b) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775–2823. (c) Demarteau, J.; Debuigne, A.; Detrembleur, C. *Chem. Rev.* **2019**, *119*, 6906–6955. (d) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626–4638. (e) Singh, R.; Mukherjee, A. *ACS Catal.* **2019**, *9*, 3604–3617.

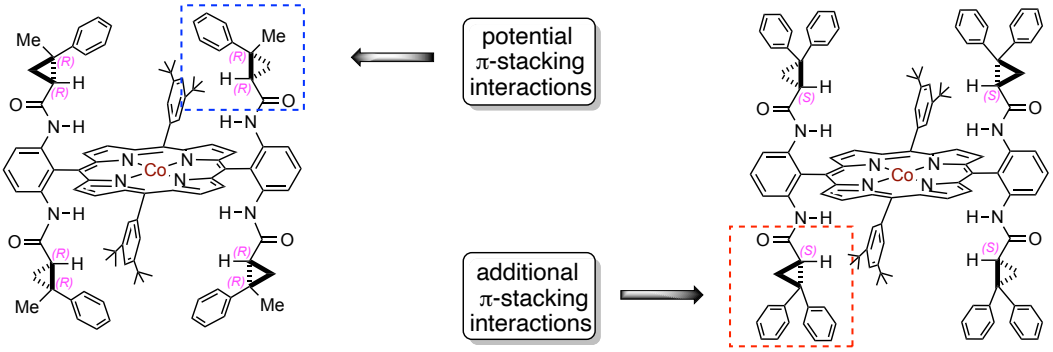
[5] For selected examples of Ti(III)-based radical processes, see: (a) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561–8562. (b) Rajanbabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986–997. (c) Gansäuer, A.; Hildebrandt, S.; Michelmann, A.; Dahmen, T.; von Laufenberg, D.; Kube, C.; Fianu, G. D.; Flowers II, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 7003–7006. (d) Funken, N.; Mühlhaus, F.; Gansäuer, A. *Angew. Chem., Int. Ed.* **2016**, *55*, 12030–12034. (e) Hao, W.; Wu, X.; Sun, J. Z.; Siu, J. C.; MacMillan, S. N.; Lin, S. *J. Am. Chem. Soc.* **2017**, *139*, 12141–12144. (f) Yao, C. B.; Dahmen, T.; Gansäuer, A.; Norton, J. *Science* **2019**, *364*, 764–767. (g) Ye, K. Y.; McCallum, T.; Lin, S. *J. Am. Chem. Soc.* **2019**, *141*, 9548–9554.

[6] For selected examples of metalloradical-mediated radical processes, see: (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944. (b) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897–7898. (c) Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. *J. Am. Chem. Soc.* **2008**, *130*, 2051–2061. (d) Chan, Y. W.; Chan, K. S. *J. Am. Chem. Soc.* **2010**, *132*, 6920–6922. (e) Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662–14665. (f) Kuo, J. L.; Hartung, J.; Han, A.; Norton, J. R. *J. Am. Chem. Soc.* **2015**, *137*, 1036–1039. (g) Roy, S.; Khatua, H.; Das, S. K.; Chattopadhyay, B. *Angew. Chem., Int. Ed.* **2019**, *58*, 11439–11443. (h) Das, S. K.; Roy, S.; Khatua, H.; Chattopadhyay, B. *J. Am. Chem. Soc.* **2020**, *142*, 16211–16217. (i) Zhang, Z.; Gevorgyan, V. *Org. Lett.* **2020**, *22*, 8500–8504.

[7] (a) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902. (b) Belof, J. L.; Cioce, C. R.; Xu, X.; Zhang, X. P.; Space, B.; Woodcock, H. L. *Organometallics* **2011**, *30*, 2739–2746. (c) Lu, H.; Dzik, W. I.; Xu, X.; Wojtas, L.; de Bruin, B.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 8518–8521.

systems for stereoselective radical transformations.[8] The key to the success of controlling reactivity and stereoselectivity in these radical- mediated asymmetric catalytic systems lies in the catalyst

Scheme 4.1. Rational Ligand Design of Novel D_2-Symmetric Chiral Amidoporphyrins Containing Diphenylcyclopropylcarboxamides



[8] (a) Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719. (b) Caselli, A.; Gallo, E.; Ragaini, F.; Ricatto, F.; Abbiati, G.; Cenini, S. *Inorg. Chim. Acta.* **2006**, *359*, 2924–2932. (c) Chen, Y.; Ruppel, J. V.; Zhang, X. P. *J. Am. Chem. Soc.* **2007**, *129*, 12074–12075. (d) Fantauzzi, S.; Gallo, E.; Rose, E.; Raoul, N.; Caselli, A.; Issa, S.; Ragaini, F.; Cenini, S. *Organometallics* **2008**, *27*, 6143–6151. (e) Zhu, S.; Ruppel, J. V.; Lu, H.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2008**, *130*, 5042–5043. (f) Zhu, S.; Xu, X.; Perman, J. A.; Zhang, X. P. *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799. (g) Xu, X.; Lu, H. J.; Ruppel, J. V.; Cui, X.; de Mesa, S. L.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2011**, *133*, 15292–15295. (h) Paul, N. D.; Mandal, S.; Otte, M.; Cui, X.; Zhang, X. P.; de Bruin, B. *J. Am. Chem. Soc.* **2014**, *136*, 1090–1096. (i) Reddy, A. R.; Hao, F.; Wu, K.; Zhou, C. Y.; Che, C. M. *Angew. Chem., Int. Ed.* **2016**, *55*, 1810–1815. (j) Chirila, A.; Gopal Das, B.; Paul, N. D.; de Bruin, B. *ChemCatchem* **2017**, *9*, 1413–1421. (k) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. *J. Am. Chem. Soc.* **2017**, *139*, 1049–1052. (l) Wang, Y.; Wen, X.; Cui, X.; Zhang, X. P. *J. Am. Chem. Soc.* **2018**, *140*, 4792–4796. (m) Wen, X.; Wang, Y.; Zhang, X. P. *Chem. Sci.* **2018**, *9*, 5082–5086. (n) Lee, W.-C. C.; Wang, D.-S.; Zhang, C.; Xie, J.; Li, B.; Zhang, X. P. *Chem* **2021**, *7*, 1588–1601. (o) Wang, X.; Ke, J.; Zhu, Y.; Deb, A.; Xu, Y.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11121–11129. (p) Xie, J.; Xu, P.; Zhu, Y.; Wang, J.; Lee, W.-C. C.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11670–11678. (q) Zhang, C.; Wang, D.-S.; Lee, W.-C. C.; McKillop, A. M.; Zhang, X. P. *J. Am. Chem. Soc.* **2021**, *143*, 11130–11140.

design and development that maximize noncovalent attractive interactions through fine-tuning of the steric, electronic, and chiral environments of D_2-symmetric chiral amidoporphyrin ligands.[8n-8q] While existing D_2-symmetric chiral amidoporphyrin ligands have been successfully applied in a number of catalytic systems, there is an emerging need to design novel [Co(D_2-Por*)] complexes that may address unsolved limitations of the existing systems and also lead to the discovery of new stereoselective radical transformations.

Since the first introduction in 2004,[8a] Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have emerged as a new class of catalysts for controlling reactivity and stereoselectivity in various radical catalytic systems based on Co(II)-MRC. Previous studies have revealed that multiple noncovalent attractive interactions, including H-bonding and π-stacking interactions between the catalyst and the substrates, could be exploited for effective stereochemical control.[8i, 8n–8q] In 2011, our group reported the first construction of [Co(3,5-Di^{t}Bu-QingPhyrin)] based on the Co(II)-catalyzed asymmetric cyclopropanation of alkenes.[8g] The incorporation of phenyl moieties in the chiral amide units significantly enhanced the catalytic reactivity and stereoselectivity as a result of potential π-stacking interactions,[8n-q] enabling the development of a new Co(II)-based catalytic system for asymmetric intramolecular cyclopropanation of diazoacetates. Inspired by the positive outcome of introducing phenyl units in the chiral amides, we sought to develop novel porphyrin catalysts bearing diphenyl moieties that might further rigidify the conformation of radical intermediates through additional π-stacking interactions, allowing for effective control of asymmetric induction (Scheme 4.1). We herein report the design and synthesis of the first example of [Co(D_2-Por*)] complex bearing chiral amides with

diphenyl moieties, ([Co(XPhyrin)]), which could be essentially derived from the corresponding optically pure diphenyl-cyclopropanecarboxamide as a chiral building block. As an initial demonstration, the Co(II) complex of 3,5-Di^{t}Bu-XPhyrin has proven to be an effective catalyst for asymmetric olefin cyclopropanation with in situ-generated α-quinolinyldiazomethane, affording the valuable chiral quinolinyl cyclopropanes in high yield with excellent stereoselectivity.

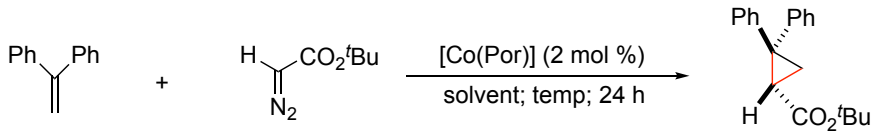
4.2. RESULTS AND DISCUSSION

4.2.1. Synthetic Approach to Construct [Co(XPhyrin)]

For construction of diphenyl porphyrin catalyst [Co(**P18**)], our first endeavor is to identify the optimal catalyst for highly asymmetric radical cyclopropanation of 1,1,-diphenylethylene (**1**) with *tert*-butyl diazoacetate (*t*-BDA) (**2**) (Figure 4.1). It was found that first generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)][8a] could catalyze the formation of *tert*-butyl 2,2-diphenylcyclopropane-1-carboxylate (**3**) in 43% yield with 16% ee (Figure 4.1, entry 1). With the employment of [Co(**P17**)] (**P17** = 3,5-Di^{t}Bu-RuppelPhyrin)][8e] bearing chiral acyclic amide units that possess intramolecular H-bonding interaction, the catalytic cyclopropanation reaction afforded **3** in higher yield (80%) but with diminished enantioselectivity (12%) in favor of the opposite enantiomer (entry 2). To improve the enantioselectivity of the catalytic process, we then applied metalloradical catalyst [Co(**P15**)] (**P15** = 3,5-Di^{t}Bu-ZhuPhyrin),[8e] which is devised to achieve conformational rigidity through intramolecular H-bonding interaction in (*S*)-(–)-2-tetrahydrofurancarboxamide units. To our delight, the catalytic reaction by [Co(**P15**)] indeed delivered the desired chiral diphenyl cyclopropanecarboxylate **3** in excellent yield (98%) with significantly enhanced

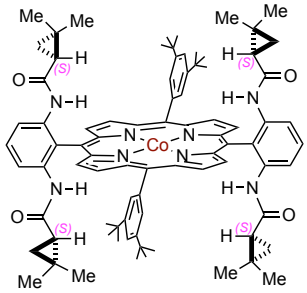
enantioselectivity (94% ee) (entry 3). Using [Co(**P15**)], we then examined the effect of solvent and temperature on the catalytic reaction (entries 4–8). Gratifyingly, we revealed that [Co(**P15**)] could effectively catalyze the asymmetric radical cyclopropanation in $PhCF_3$ even at 4 °C, delivering the corresponding diphenyl cyclopropanecarboxylate **3** in 81% yield with 96% ee (entry 8).

Figure 4.1. Optimization of Asymmetric Radical Cyclopropanation of 1,1-Diphenylethylene with *t*-BDA[a]

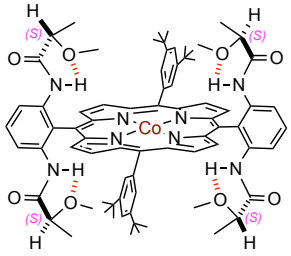


1 **2** **3**

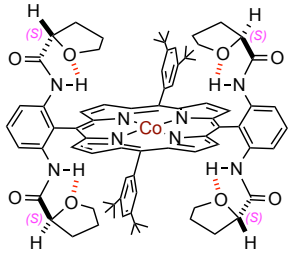
entry	[Co(Por)]	temp (°C)	solvent	yield (%)	ee (%)
1	[Co(**P3**)]	22	$PhCF_3$	43	16
2	[Co(**P17**)]	22	$PhCF_3$	80	–12
3	[Co(**P15**)]	22	$PhCF_3$	98	94
4	[Co(**P15**)]	22	PhCl	99	93
5	[Co(**P15**)]	22	PhH	99	92
6	[Co(**P15**)]	22	$PhCH_3$	43	93
7	[Co(**P15**)]	22	C_6F_6	60	92
8[b]	[Co(**P15**)]	4	$PhCF_3$	81	96



[Co(**P3**)]
(**P3** = 3,5-Di^{t}Bu-ChenPhyrin)



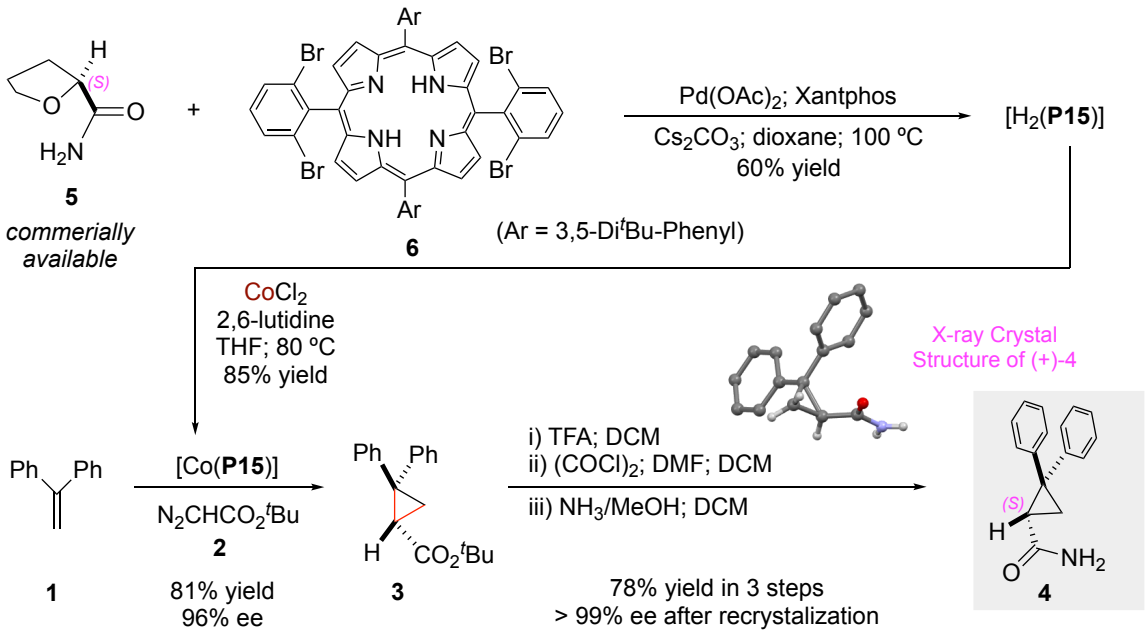
[Co(**P17**)]
(**P17** = 3,5-Di^{t}Bu-RuppelPhyrin)



[Co(**P15**)]
(**P15** = 3,5-Di^{t}Bu-ZhuPhyrin)

[a]Carried out with **1** (0.10 mmol) and **2** (0.12 mmol) by [Co(Por)] (2 mol %) in solvent (1.0 mL) for 24 h; Isolated yields; Enantiomeric excess (ee) determined by chiral HPLC. [b]Reaction performed in 10.0 mmol scale for 72 h.

Scheme 4.2. Synthesis of [Co(P18)]: Asymmetric Synthesis of Diphenyl Cyclopropane Carboxamide 4

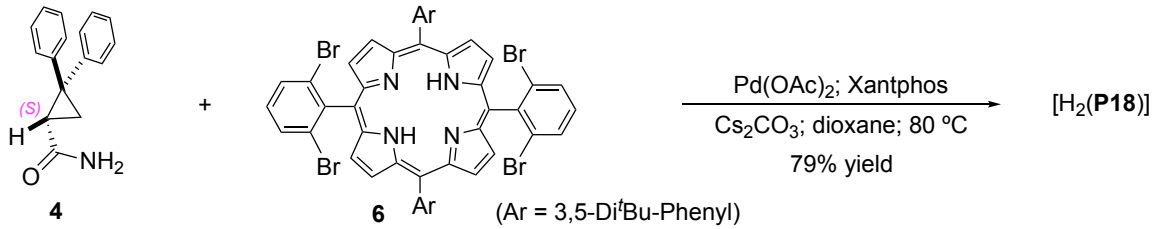


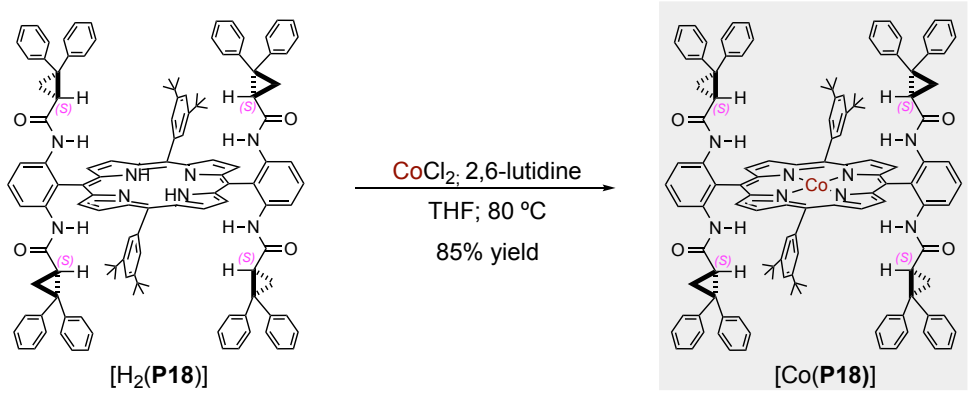
Following the previously established procedures,[8g] the obtained carboxylate **3** could be readily transformed into the corresponding cyclopropanecarboxamide **4** over three steps in 78% yield with retention of the original enantiomeric purity (Scheme 4.2). Further recrystallization of chiral amide **4** from CH_3Cl/pentane led to an improved enantiopurity (>99% ee). The absolute configuration of the newly-generated stereogenic center was established as (*S*) by X-ray crystallography.

With the optically pure chiral amide **4** in hand, it could then be utilized as a chiral building block for the construction of new metalloradical catalyst [Co(**P18**)] (**P18** = 3,5-Di^{t}Bu-XPhyrin) via a two-step procedure (Scheme 4.3). According to our previously reported procedures,[8a] the free-base porphyrin [H_2(**P18**)]) was prepared in 79% yield by the Pd-catalyzed quadruple amidation reaction of tetrabromoporphyrin **6** with chiral amide **4**.

Lastly, metalation of free-base [H_2(**P18**)] was achieved using cobalt(II) chloride in the presence of sterically-hindered base 2,6-lutidine, resulting in the formation of [Co(**P18**)] in 85% yield.

Scheme 4.3. Synthesis of [H_2(P18)] and [Co(P18)]

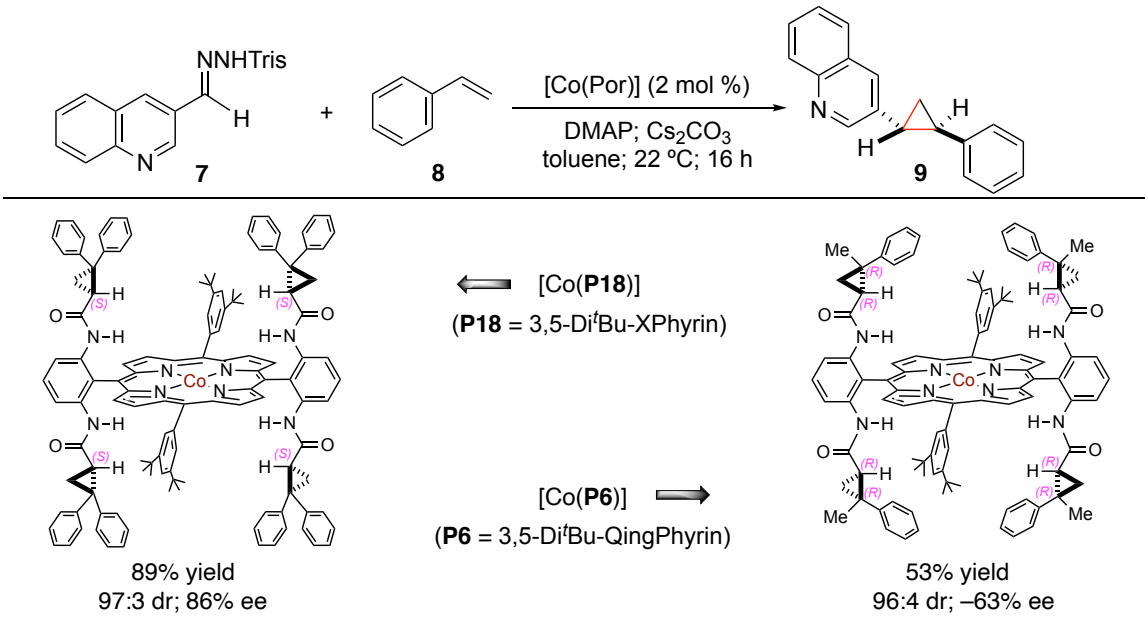




4.2.2. Asymmetric Radical Cyclopropanation Catalyzed by [Co(XPhyrin)]

Chiral heteroaryl cyclopropanes represent a class of prevalent structural motifs in biologically important compounds. However, there remained limited methods for their stereoselective synthesis. In an effort to explore a general synthesis to access these molecules as well as to examine the catalytic performance of the new metalloradical catalyst, [Co(**P18**)], we decided to study the asymmetric cyclopropanation of styrene with in situ-generated α-quinolinyldiazomethane as a model reaction (Scheme 4.4).

Scheme 4.4. Ligand Effect on Co(II)-Catalyzed Asymmetric Olefin Cyclopropanation with 3-Quinolinyldiazomethanes[a]



[a]Carried out with **7** (0.10 mmol), **8** (0.15 mmol), DMAP (0.05 mmol) and Cs_2CO_3 (0.20 mmol) using [Co(Por)] (2 mol %) in toluene (1.0 mL) at 22 °C for 16 h; Isolated yields; Enantiomeric excess (ee) determined by chiral HPLC.

Gratifyingly, [Co(**P18**)] was shown to be an effective catalyst for the cyclopropanation reaction in the presence of DMAP (4-(dimethylamino)pyridine) as an additive, furnishing the cyclopropane product in high yield (89%) with excellent diastereoselectivity (97:3 dr) and enantioselectivity (86% ee). As comparison, the catalytic cyclopropanation reaction was also conducted under the same reaction conditions using [Co(**P6**)] (**P6** = 3,5-Di*t*Bu-QingPhyrin)[8g] as the catalyst, which features one phenyl moiety in the chiral amides. While the reaction with [Co(**P6**)] could afford the desired cyclopropane in a similarly high diastereoselectivity (96:4 dr), both the yield (53%) and enantioselectivity (62% ee) significantly decreased. It is noted that the sense of asymmetric induction also switched in favor of the opposite enantiomer with the use of [Co(**P6**)]. Evidently, the difference in

catalytic performance between [Co(**P18**)] and [Co(**P6**)] implies a positive effect of installing two phenyl groups in the chiral amides, signifying the importance of judicious tuning of ligand environment in controlling reactivity and stereoselectivity of the Co(II)-based metalloradical system.

4.3. CONCLUSIONS AND OUTLOOK

In summary, we have introduced a novel D_2-symmetric chiral amidoporphyrin XPhyrin containing chiral amides with diphenyl moieties for the first time. The newly synthesized metalloradical catalyst, which is derived from optically pure diphenyl cyclopropanecarboxamide, can be effectively constructed based on highly effective Co(II)-catalyzed asymmetric cyclopropanation of diphenyl ethylene with diazoacetate. The optically pure chiral amide was utilized as a chiral building block for Pd-catalyzed amidation and base-assisted metalation, enabling the synthesis of Co(II) complex of 3,5-Di^{t}Bu-XPhyrin in high overall yields. Furthermore, the Co(II) complex of 3,5-Di^{t}Bu-XPhyrin has proven to be an effective catalyst for asymmetric olefin cyclopropanation with in situ-generated α-quinolinyldiazomethane, affording the valuable chiral quinolinyl cyclopropanes in high yield with high stereoselectivity. Considering the modular design of D_2-symmetric chiral amidoporphyrins, we envision the possibilities of rendering chiral diphenyl cyclopropanecarboxamide as a new class of synthon for the synthesis of other chiral catalyst derivatives. Inspired by the successful demonstration of Co(II) complex of 3,5-Di^{t}Bu-XPhyrin for asymmetric radical cyclopropanation, we are currently working to explore new applications in asymmetric radical processes.

4.4. EXPERIMENTAL SECTION

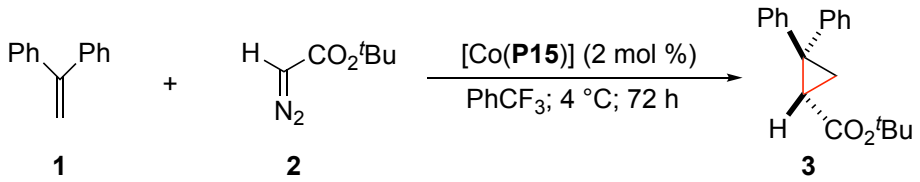
4.4.1. General Considerations

All catalytic reactions were performed under nitrogen in oven-dried glassware following standard Schlenk techniques Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR spectra were acquired using Bruker 500 (500 MHz) or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to residual solvent peak ($CHCl_3$ δ = 7.26 ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, br = broad, m = multiplet), and coupling constants *J* (Hz). ^{13}C NMR spectra were acquired using Bruker 500 (125 MHz) or INOVA 600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ δ = 77.16 ppm) as the internal standard. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel IA, AD-H and ID columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. Anhydrous cobalt(II) chloride, palladium(II) acetate, and 9-dimethyl-4,5-

bis(diphenylphosphino) xanthenes (Xantphos) were purchased from Strem Chemical Co.. Anhydrous cesium carbonate was purchased from Oakwood Chemical.

4.4.2. Synthesis and Characterization of Catalysts

4.4.2.1. Experimental Procedure for Preparation of Diphenylcyclopropanecarboxylate 3

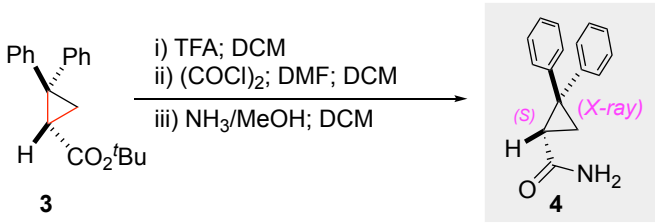


1 **2** **3**

To a 100 mL oven-dried Schlenk tube was charged with [Co(**P15**)] (**P15** = 3,5-Di^{t}Bu-ZhuPhyrin) (2 mol %). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, diphenylethylene **1** (10 mmol, 1.0 equiv), *t*-BDA **2** (1.2 equiv), and anhydrous $PhCF_3$ (0.1 M) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 4 °C for 72 h. Following completion of the reaction, the reaction mixture was concentrated under vacuum and purified by flash column chromatography to give the title compound. Yield: 81%. R_f = 0.30 (1:1 Hexanes/DCM). $[\alpha]_D^{20}$ = (+)-150.2° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.8 Hz, 2H), 7.29 – 7.13 (m, 8H), 2.48 – 2.44 (m, 1H), 2.13 – 2.09 (m, 1H), 1.50 (dd, *J* = 8.8, 5.6 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.78, 145.35, 140.42, 130.18, 128.51, 128.31, 127.70, 126.96, 126.50, 80.40, 77.18, 39.57, 30.21, 27.95, 20.15. IR (neat, cm^{-1}): 3058.40, 2976.40, 1726.91, 1601.45, 1447.15, 1366.87, 1149.49, 847.25. HPLC analysis: ee = 96%. (99.8% hexanes: 0.2% isopropanol, 1.0 mL/min): t_{major} = 7.04 min,

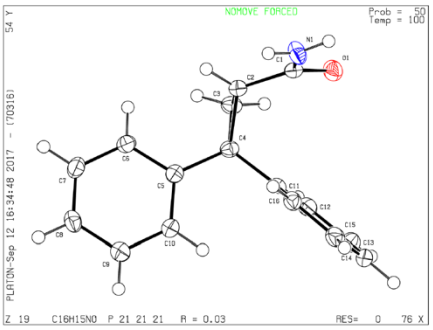
t_{minor} = 10.30 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{23}O_2^+$: 295.16926, Found: 295.16906.

4.4.2.2. Experimental Procedure for Preparation of Diphenylcyclopropanecarboxamide 4

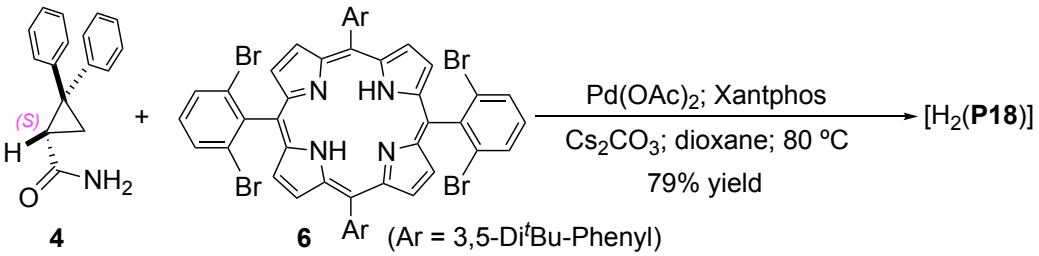


After the asymmetric cyclopropanation reaction, the obtained carboxylate further underwent 3 steps[8g] to afford the corresponding optically pure amide. To a 100-mL round-bottom flask was charged with *tert*-butyl (*S*)-2,2-diphenylcyclopropane-1-carboxylate **3** (10 mmol, 1.0 equiv), trifluoroacetic acid (10.0 equiv) and DCM (40 mL). The reaction was stirred at room temperature overnight. After evaporation of the solvent, the free acid was afforded and used directly for next step without purification. The solution of the free acid and oxalyl chloride (5.0 equiv) in DCM (45 mL) was cooled to 0 °C, then 2-3 drops of DMF was added. The reaction mixture was stirred for 2 h at 0 °C, then 5 h at room temperature. After removal of oxalyl chloride and DCM under reduced pressure, the residue was then dissolved in DCM again and dropwise added to NH_3/MeOH solution (10.0 equiv). After the reaction was completed, the resulting mixture was concentrated under reduced pressure and purified by flash column chromatography to afford with 78% overall yield. The product was recrystallized from $CHCl_3$/pentane to further improve the enantiopurity to >99% ee. R_f = 0.30 (5:1 Hexanes/EtOAc). $[\alpha]_D^{20}$ = (+)-151.0° (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.16 (m, 8H), 5.62 (d, *J* = 33.8 Hz, 2H), 2.36 – 2.29 (m, 1H), 2.16 – 2.09 (m, 1H), 1.62 (dd, *J* = 7.8, 4.4 Hz,

1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.96, 145.29, 140.06, 129.95, 128.55, 128.52, 127.45, 127.13, 126.53, 39.24, 30.65, 20.14. IR (neat, cm^{-1}): 3457.25, 3314.49, 3182.89, 1656.24, 1599.75, 1414.54, 1305.22, 1026.86. HPLC analysis: ee > 99%. (95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 23.84 min, t_{minor} = 17.43 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{16}NO^+$: 238.12264, Found: 238.12247. The absolute configuration of the amide was assigned as (*S*) by X-ray crystallography.



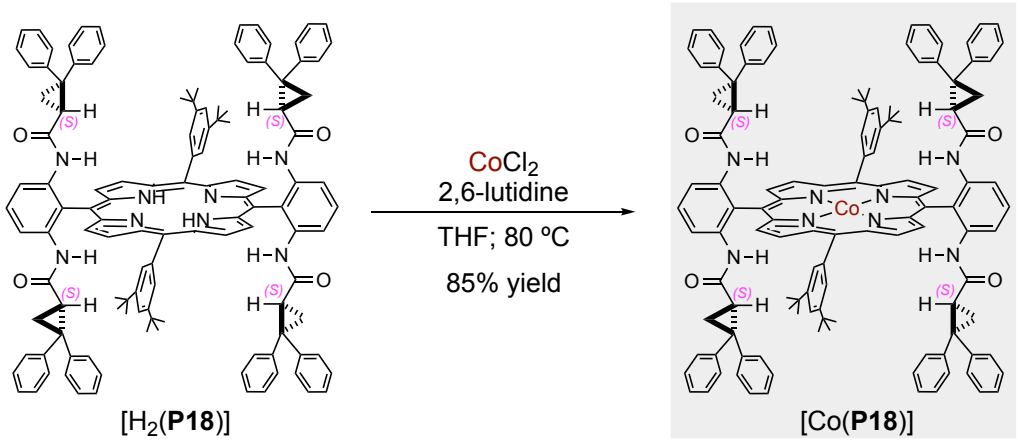
4.4.2.3. Experimental Procedure for Preparation of [H_2(P18)]



[H_2(**P18**)] was synthesized according to our previous reported procedure[8a] with 79% yield. The 5,15-bis(2,6-dibromophenyl)-10,20-bis(3,5-di-*t*-butylphenyl)porphyrin (0.20 mmol), (*S*)-2,2-diphenylcyclopropane-1-carboxamide (3.20 mmol), $Pd(OAc)_2$ (0.08 mmol), Xantphos (0.16 mmol), and Cs_2CO_3 (3.20 mmol) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and dioxane (10 mL) was added via a gastight syringe. The tube was purged with nitrogen for 2 minutes, and then the septum was replaced with the Teflon screwcap. The tube was sealed and stirred at 80 °C for 72 h. The resulting mixture was cooled down to room temperature, diluted in ethyl

acetate, filtrated through a silica pad and concentrated under vacuum. The pure compound was obtained as a purple solid after purification by flash column chromatography (eluent: 4:1 to 3:1 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, J = 4.7 Hz, 4H), 8.92 (d, J = 4.7 Hz, 4H), 8.25 (d, J = 8.4 Hz, 4H), 7.92 (d, J = 1.8 Hz, 4H), 7.80 – 7.79 (m, 2H), 7.66 (t, J = 8.4 Hz, 2H), 7.13 – 7.12 (m, 12H), 6.97 – 6.87 (m, 8H), 6.69 (brs, 4H), 6.46 – 6.43 (m, 4H), 5.96 (brs, 8H), 5.77 (brs, 8H), 1.64 (brs, 4H), 1.30 (s, 36H), 0.78 (brs, 8H), –2.11 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.93, 149.52, 144.37, 139.74, 139.30, 139.06, 130.72, 129.94, 129.50, 128.32, 127.52, 127.07, 126.89, 125.87, 123.62, 122.04, 120.39, 116.68, 108.22, 39.54, 35.04, 31.61, 31.42, 18.86. HRMS (ESI) ([M+H]$^{+}$) Calcd. for $C_{124}H_{115}N_8O_4^{+}$: 238.12264, Found: 1779.90295. UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 425 (5.61), 516 (4.29), 551 (3.85), 590 (3.81), 646 (3.85).

4.4.2.4. Experimental Procedure for Preparation of [Co(P18)]



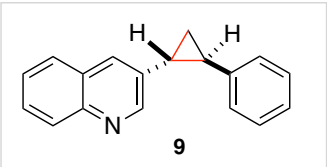
[Co(**P18**)] was synthesized according to our previous reported procedure[8a] with 85% yield. Free base porphyrin [H_2(**P18**)] and anhydrous $CoCl_2$ (8.0 equiv) were placed in an oven-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen. Under nitrogen atmosphere, 2,6-Lutidine (5.0 equiv) and anhydrous dioxane

(0.02 M) were added. The tube was purged with nitrogen for 1 min and sealed with Teflon screw cap. The reaction mixture was stirred at 80 °C for 16 h prior to being cooled down to room temperature. The reaction mixture was diluted with EtOAc, washed with water 2 times and then concentrated under vacuum. The compound [Co(**P18**)] was isolated as a purple solid after purification by flash column chromatography (eluent: 3:1 Hexanes/EtOAc). HRMS (ESI) ([M]$^+$) Calcd. for $C_{124}H_{112}N_8O_4Co^+$, Found: 1835.81384. UV-Vis ($CHCl_3$), λ_{max} nm (log ε): 416 (5.22), 530 (4.06).

4.4.3. Synthesis and Characterization of 3-Quinolinyl Cyclopropanes

4.4.3.1 Experimental Procedure for [Co(Por)]-Catalyzed Asymmetric Cyclopropanation

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol, 1.0 equiv), [Co(Por)] (2 mol %), DMAP (0.5 equiv) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated and backfilled with nitrogen 3 times. Under nitrogen atmosphere, olefin (1.5 equiv) and anhydrous toluene (1.0 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22 °C for 16 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum and purified by flash column chromatography.



9

3-((1*R*,2*R*)-2-Phenylcyclopropyl)quinoline (9) was obtained through the general procedure using 1.5 equiv of styrene (**8**) with 3-quinolinecarboxaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**7**) at 22 °C. R_f = 0.30 (3:1 Hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.3 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* =

2.3 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.65 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.53 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.25 – 7.17 (m, 3H), 2.36 (ddd, J = 8.3, 6.3, 4.5 Hz, 1H), 2.31 (ddd, J = 8.6, 6.5, 4.5 Hz, 1H), 1.65 – 1.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.55, 146.97, 141.82, 135.47, 131.11, 129.31, 128.71, 128.68, 128.20, 127.38, 126.93, 126.27, 125.97, 28.32, 25.71, 18.08. IR (neat, cm^{-1}): 3025.24, 1602.76, 1494.46, 1342.61, 1126.47, 1073.30, 912.98, 786.17. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{16}N^+$: 246.12773, Found: 246.12896. With [Co(**P18**)]: Yield: 89%. dr: 97:3. HPLC analysis (*E*)-isomer: ee = 86%. ID(95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 45.69 min, t_{minor} = 41.15 min. With [Co(**P15**)]: Yield: 53%. dr: 96:4. HPLC analysis (*E*)-isomer: ee = 63%. ID(95% hexanes: 5% isopropanol, 0.8 mL/min): t_{major} = 39.14 min, t_{minor} = 43.63 min.

4.4.4. X-Ray Crystallography

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2*[9] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[10] Absorption correction was performed by multi-scan method implemented in SADABS.[11] Space groups were determined using XPREP implemented in APEX2.[9] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[12,13,14] program.

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[9] Bruker (**2012**). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
[10] Bruker (**2012**). SAINT. Data Reduction Software.
[11] Sheldrick, G. M. (**1996**). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
[12] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837–838.
[13] Sheldrick, G. M. (**2012** Beta) SHELXL-97. Program for the Refinement of Crystal.
[14] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467–473.

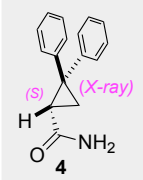
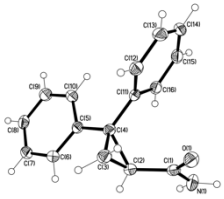


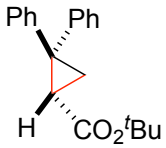
Table S1. Crystal data and structure refinement for 4



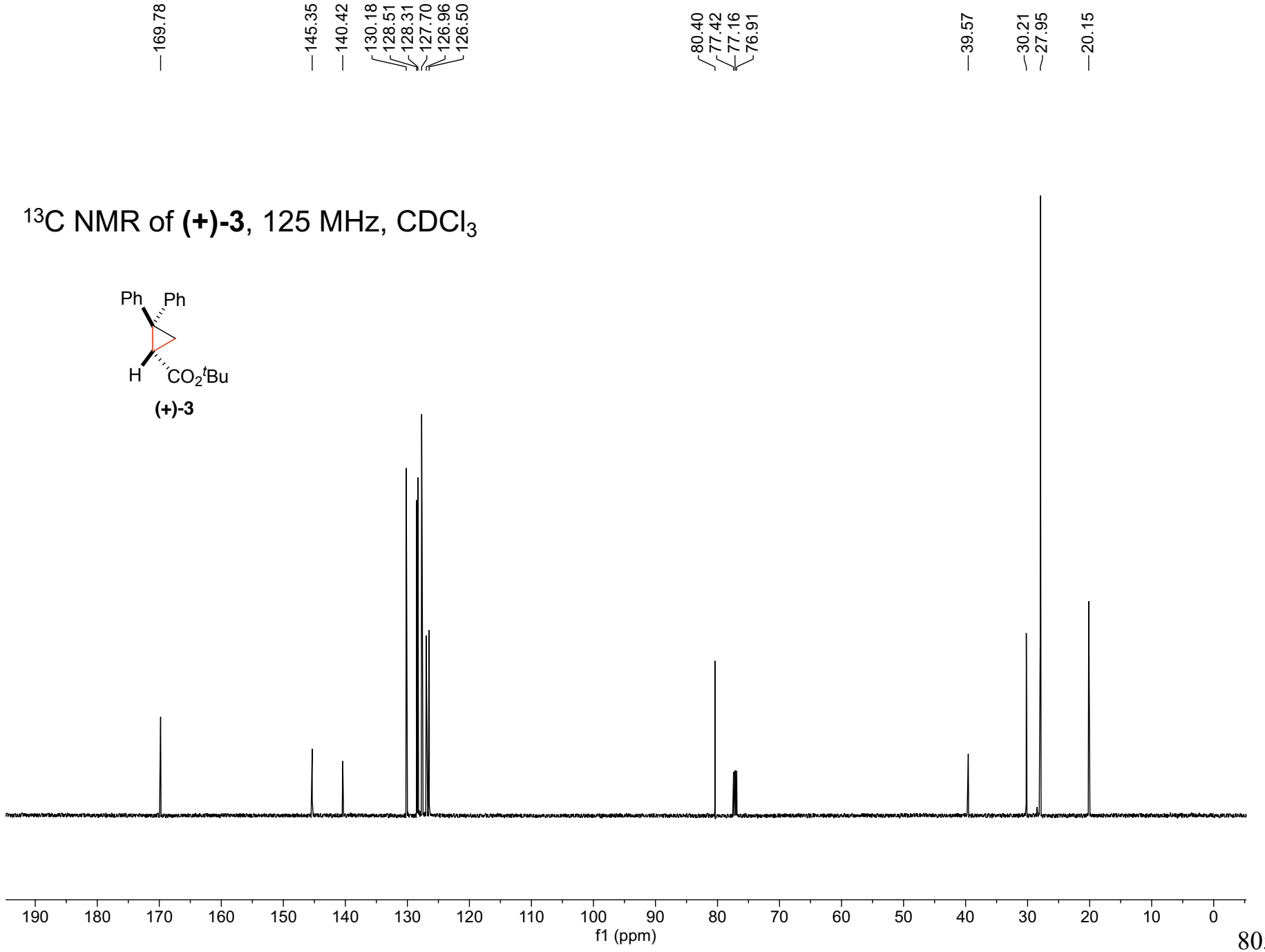
Identification code	C16H15NO	
Empirical formula	C16 H15 N O	
Formula weight	237.29	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.5868(2) ≈	α= 90∞.
	b = 8.9299(3) ≈	β= 90∞.
	c = 21.6132(8) ≈	γ = 90∞.
Volume	1271.28(7) ≈^{3}	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.606 mm^{-1}	
F(000)	504	
Crystal size	0.600 x 0.420 x 0.280 mm^3	
Theta range for data collection	5.360 to 70.612∞.	
Index ranges	-8<=h<=7, -10<=k<=10, -25<=l<=26	
Reflections collected	16879	
Independent reflections	2392 [R(int) = 0.0331]	
Completeness to theta = 67.679∞	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7534 and 0.6671	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2392 / 0 / 163	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0686	
R indices (all data)	R1 = 0.0275, wR2 = 0.0689	
Absolute structure parameter	0.05(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.177 and -0.135 e.≈$^{-3}$	

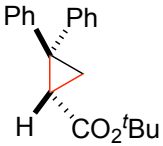
4.5. NMR/HPLC SPECTRAL DATA

^{1}H NMR of **(+)-3**, 500MHz, $CDCl_3$



(+)-3


169.78
145.35
140.42
130.18
128.51
128.31
127.70
126.96
126.50
80.40
77.42
77.16
76.91
39.57
30.21
27.95
20.15
13C NMR of (+)-3, 125 MHz, CDCl3
Ph
Ph
H
CO2tBu
(+)-3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

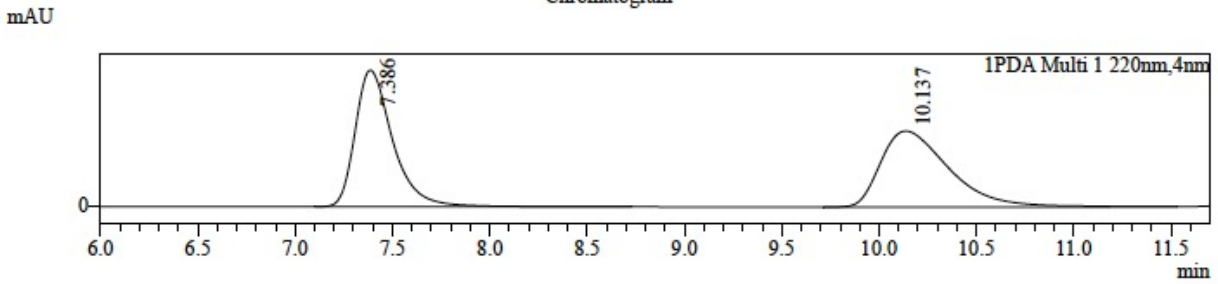


(±)-3

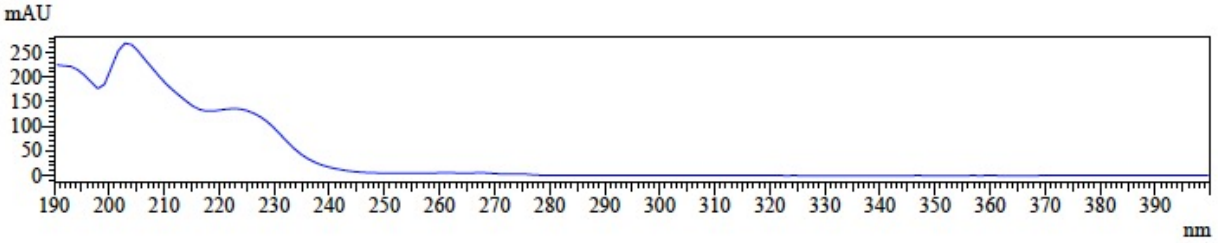
Sample Information

Data File	: XXW-1655-IA-rac-0.2%-1.0mL001.lcd
Sample Name	: XXW-1655-IA-rac-0.2%-1.0mL
Sample ID	: XXW-1655-IA-rac-0.2%-1.0mL
Method File	: XXW-0.2%.1.0.mL-1025.lcm

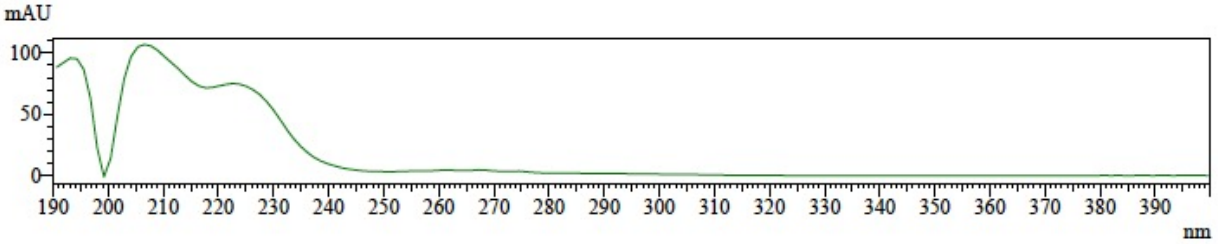
Chromatogram



UV Spectrum
Retention time = 7.386



UV Spectrum
Retention time = 10.137



Peak Table

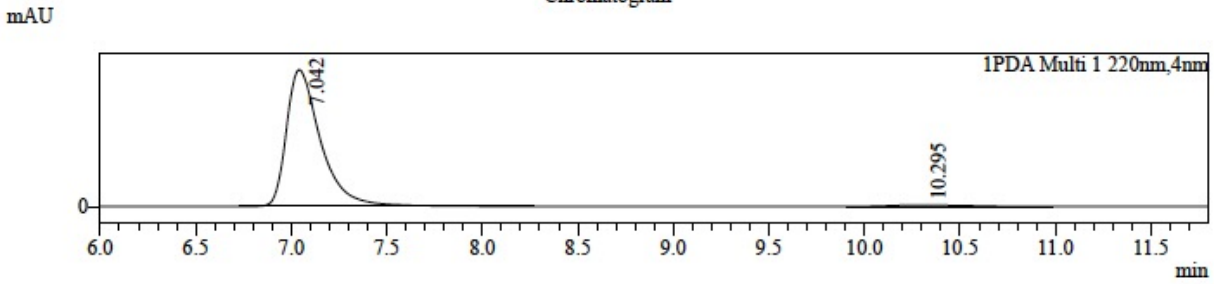
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.386	1810111	49.698
2	10.137	1832085	50.302
Total		3642196	100.000

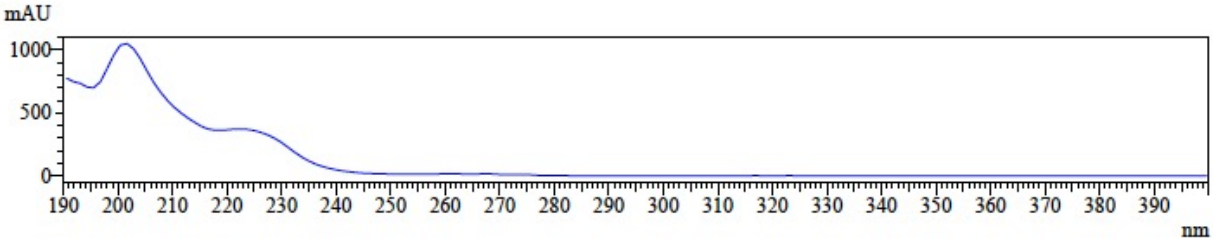
Sample Information

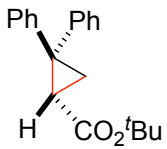
Data File	: XXW-099-IA-0.2%-1.0mL001.lcd
Sample Name	: XXW-099-IA-0.2%-1.0mL001
Sample ID	: XXW-099-IA-0.2%-1.0mL001
Method File	: XXW-0.2%.1.0.mL-1025.lcm

Chromatogram



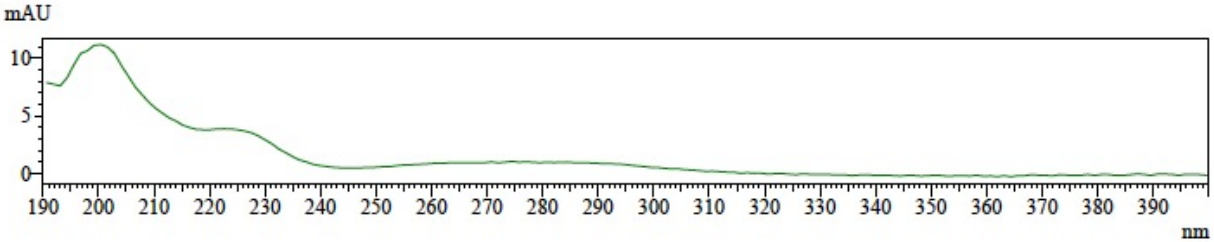
UV Spectrum
Retention time = 7.042





(+)-3

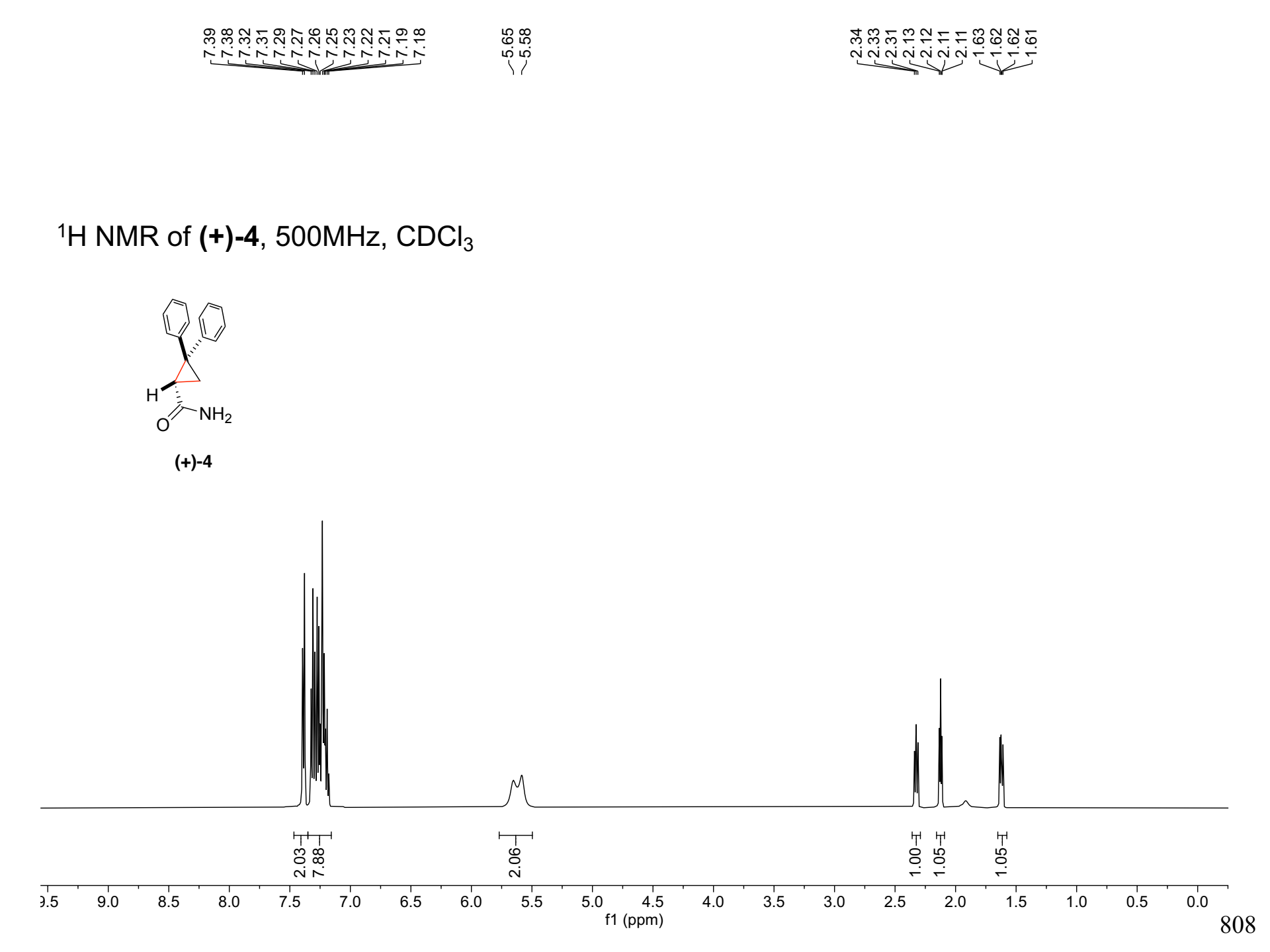
UV Spectrum
Retention time = 10.295



Peak Table

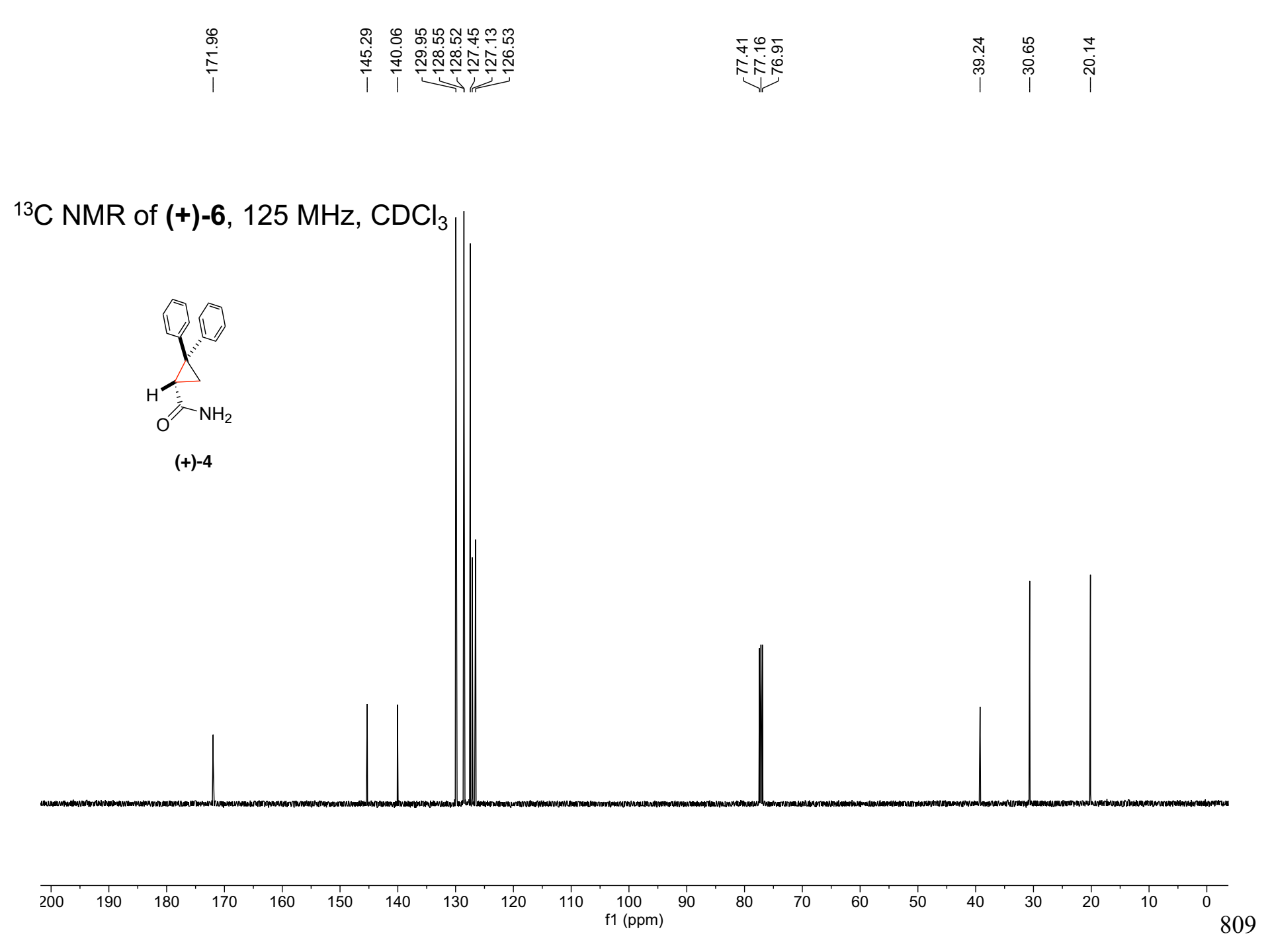
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	7.042	4577135	97.948
2	10.295	95896	2.052
Total		4673031	100.000



^{1}H NMR of **(+)-4**, 500MHz, $CDCl_3$

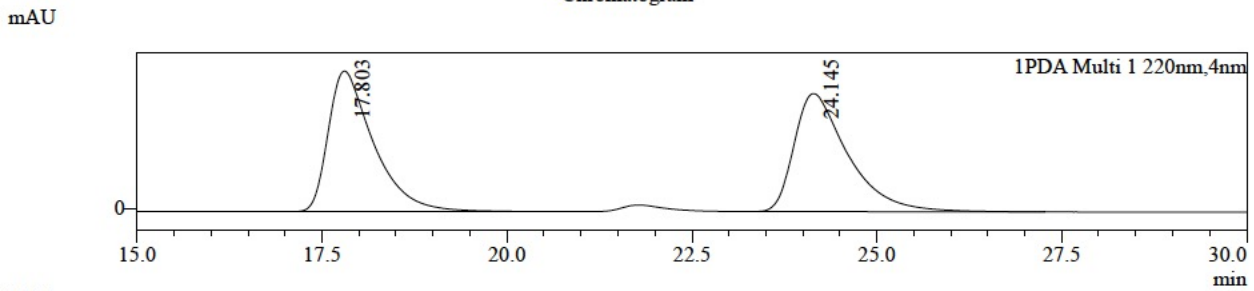
(+)-4


171.96
145.29
140.06
129.95
128.55
128.52
127.45
127.13
126.53
77.41
77.16
76.91
39.24
30.65
20.14
13C NMR of (+)-6, 125 MHz, CDCl3
H
O
NH2
(+)-4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

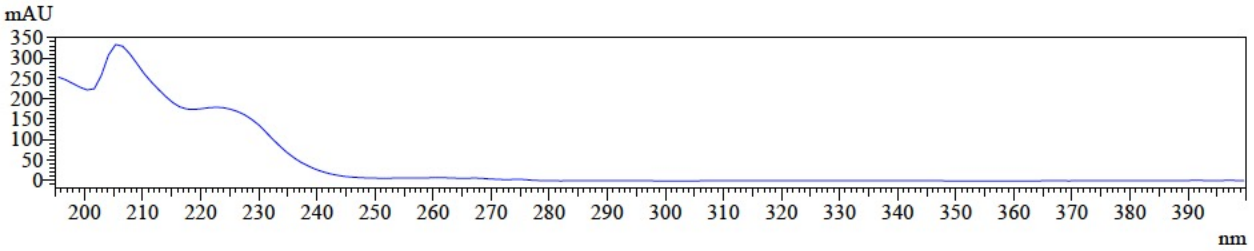
Sample Information

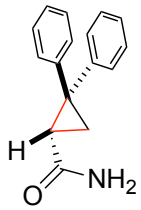
Sample Name	: XXW-0102-racamide-ADH-5%-0.8ml
Sample ID	: XXW-0102-racamide-ADH-5%-0.8ml
Data File	: XXW-0102-racamide-ADH-5%-0.8ml.lcd
Method File	: XXW-5%-0.8mL.lcm

Chromatogram



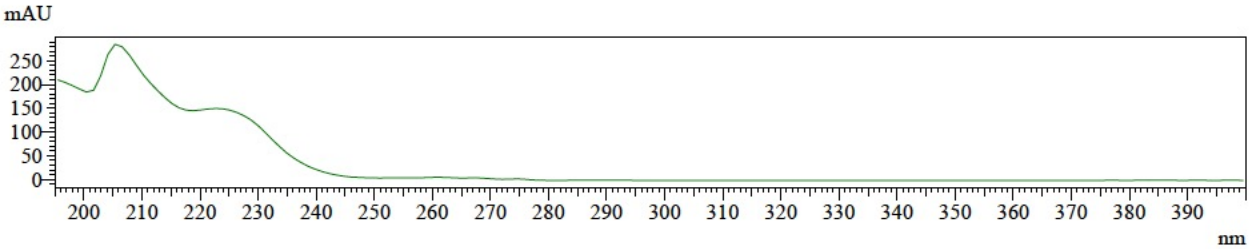
UV Spectrum
Retention time = 17.803





(±)-4

UV Spectrum
Retention time = 24.145



Peak Table

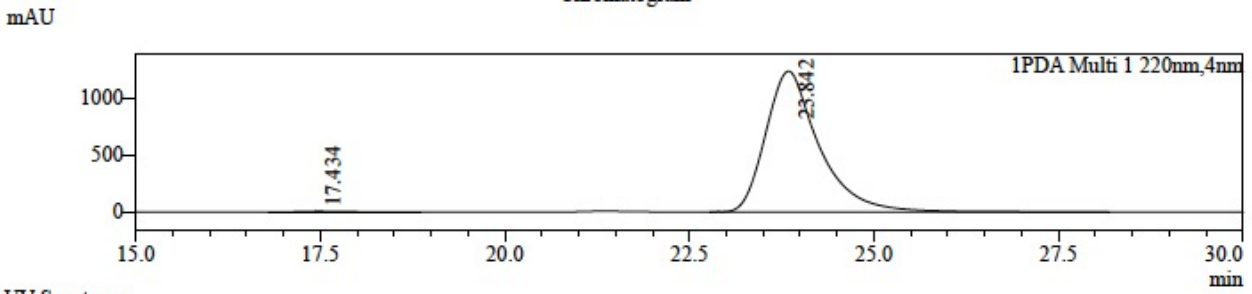
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	17.803	7712958	50.044
2	24.145	7699362	49.956
Total		15412319	100.000

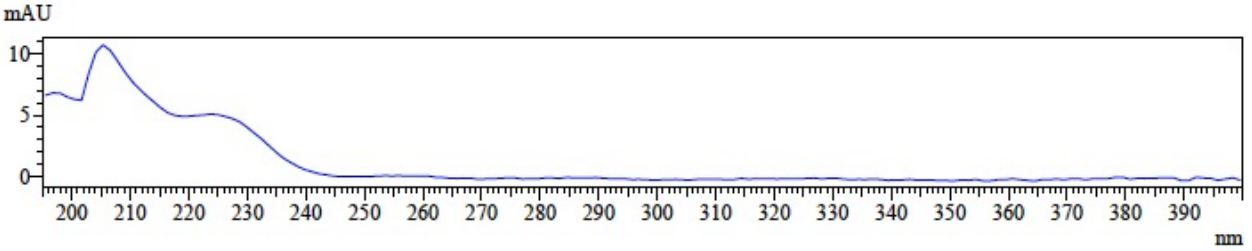
Sample Information

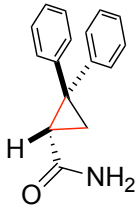
Sample Name	: XXW-0105-chiralamide-recrystal-ADH-5%-0.8ml
Sample ID	: XXW-0105-chiralamide-recrystal-
Data File	: XXW-0105-chiralamide-recrystal-ADH-5%-0.8ml.lcd
Method File	: XXW-5%-0.8mL.lcm

Chromatogram



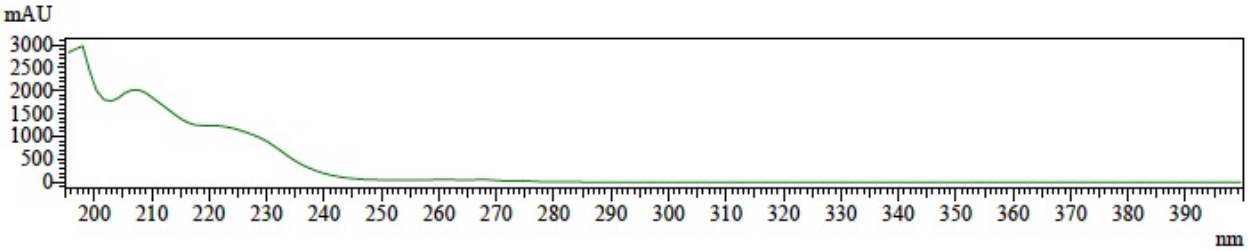
UV Spectrum
Retention time = 17.434





(+)-4

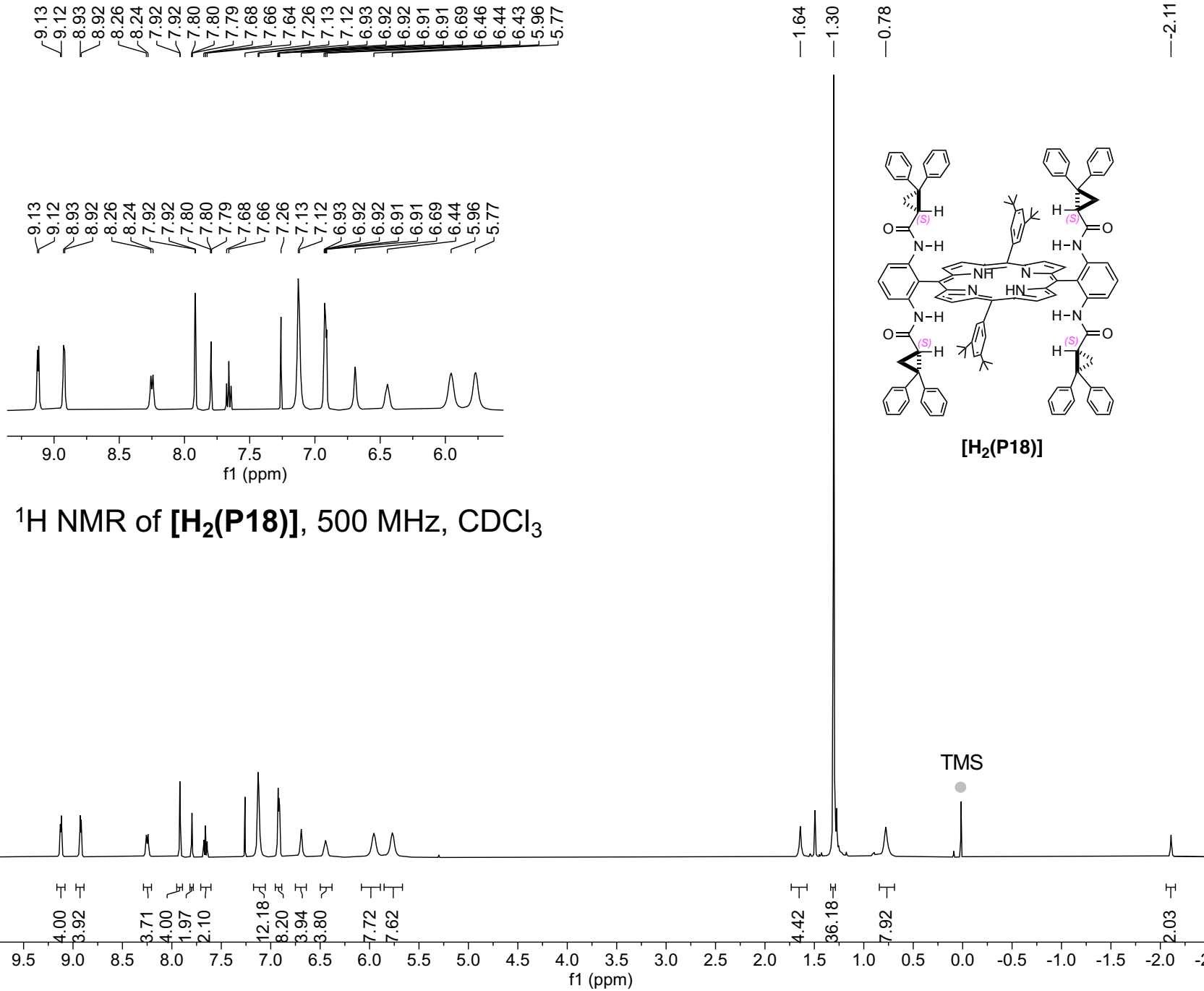
UV Spectrum
Retention time = 23.842



Peak Table

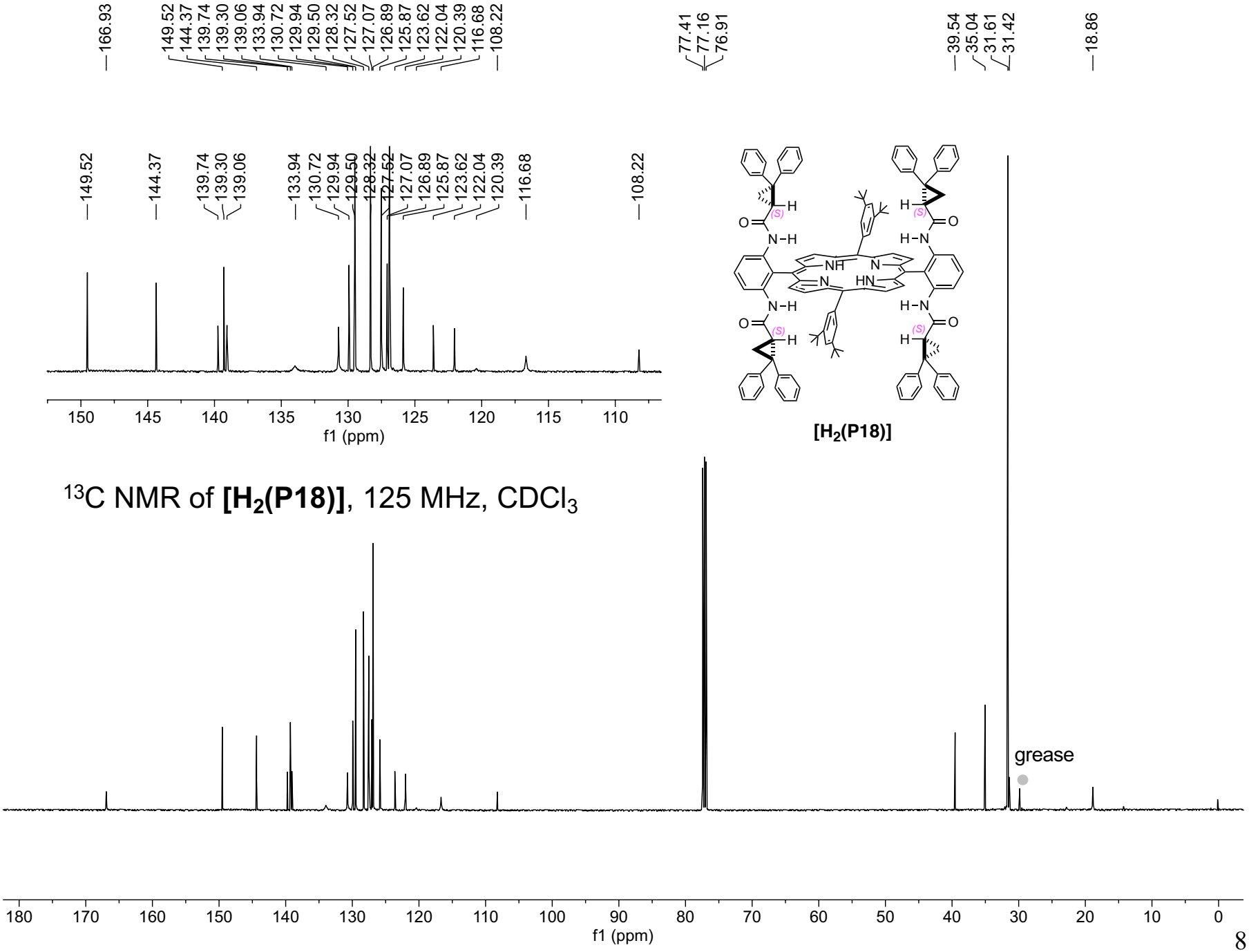
PDA Ch1 220nm

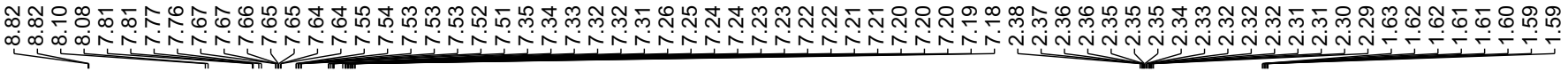
Peak#	Ret. Time	Area	Area%
1	17.434	219939	0.352
2	23.842	62206174	99.648
Total		62426113	100.000



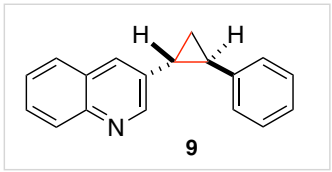
[H_2(P18)]

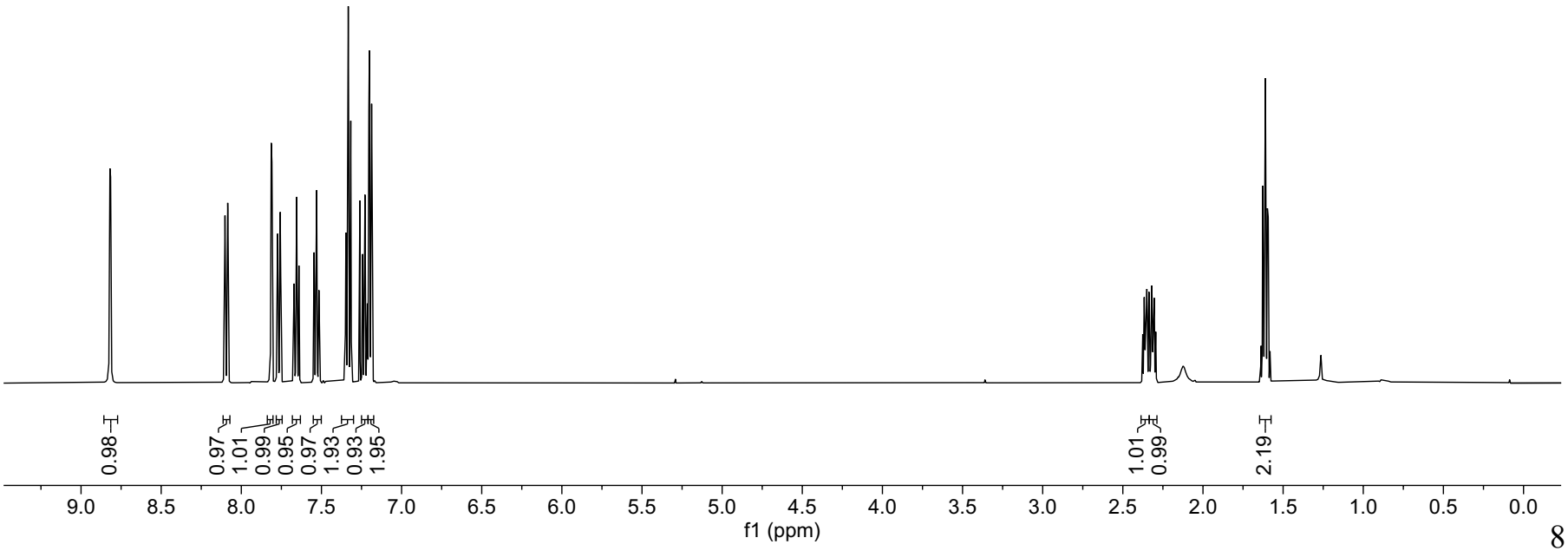
^{1}H NMR of **[H_2(P18)]**, 500 MHz, $CDCl_3$

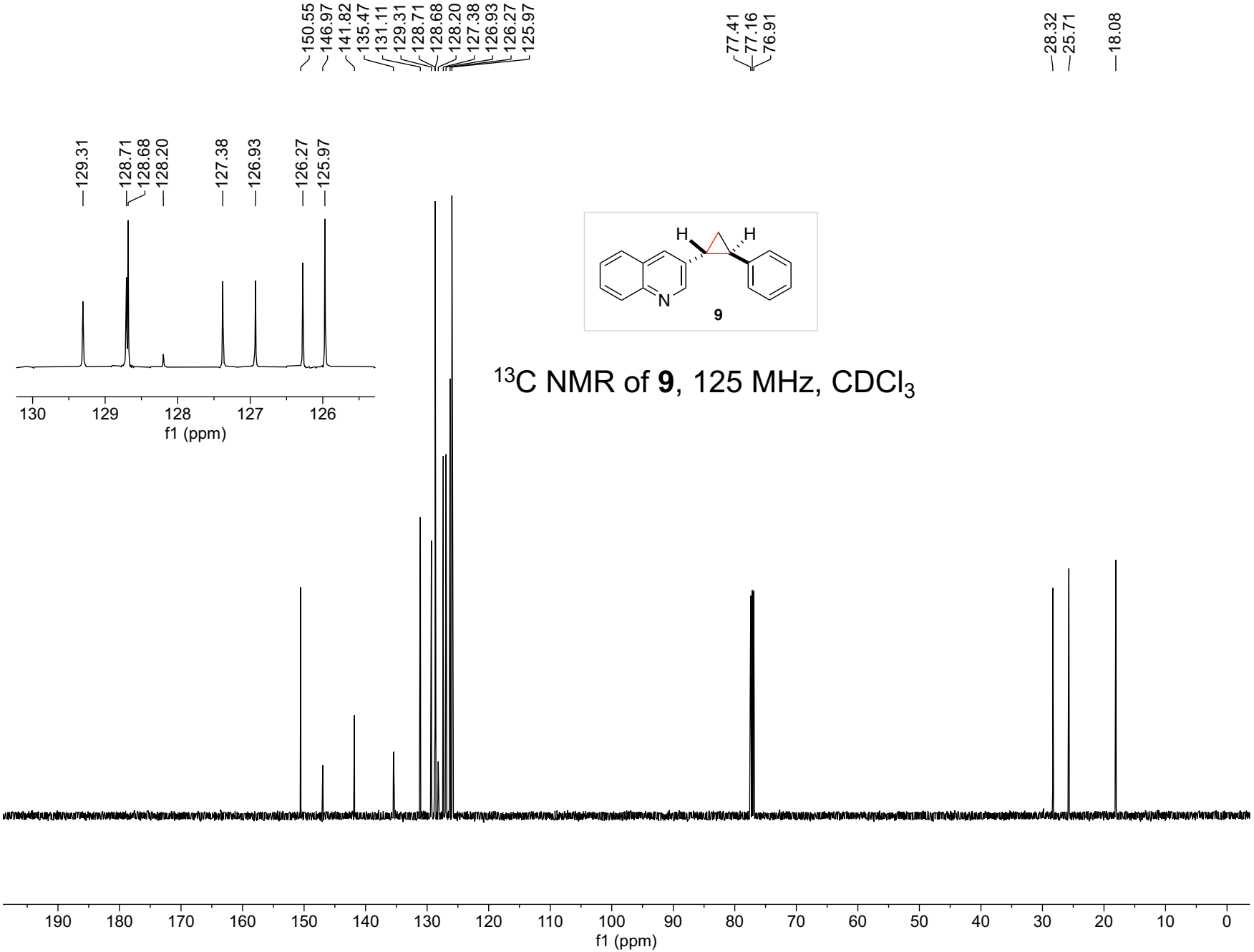

166.93
149.52
144.37
139.74
139.30
139.06
133.94
130.72
129.94
129.50
128.32
127.52
127.07
126.89
125.87
123.62
122.04
120.39
116.68
108.22
77.41
77.16
76.91
39.54
35.04
31.61
31.42
18.86
f1 (ppm)
[H2(P18)]
13C NMR of [H2(P18)], 125 MHz, CDCl3
grease



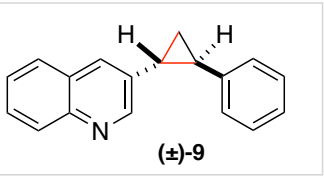
^{1}H NMR of **9**, 500 MHz, $CDCl_3$







^{13}C NMR of **9**, 125 MHz, $CDCl_3$

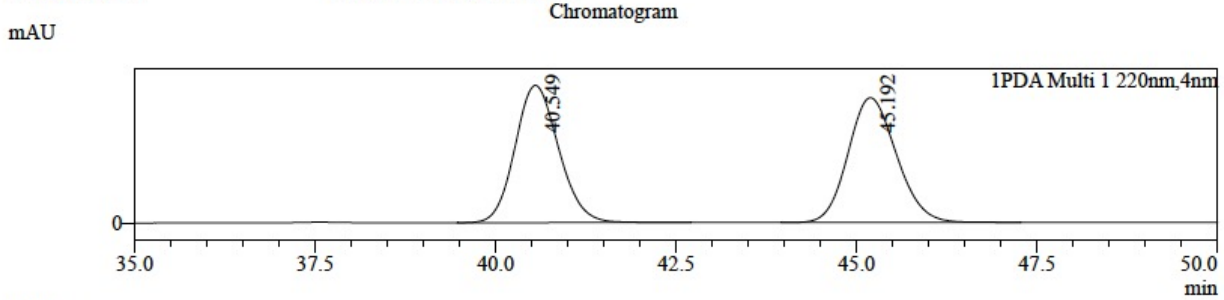


(±)-9

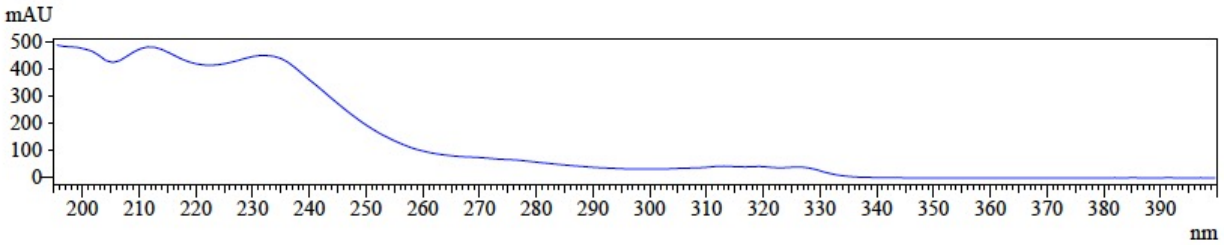
Sample Information

Sample Name : XXW-360-ID-5%0.8mL
Sample ID : XXW-360-ID-5%0.8mL
Data File : XXW-360-ID-5%0.8mL.lcd
Method File : XXW-5%.0.8.mL.lcm

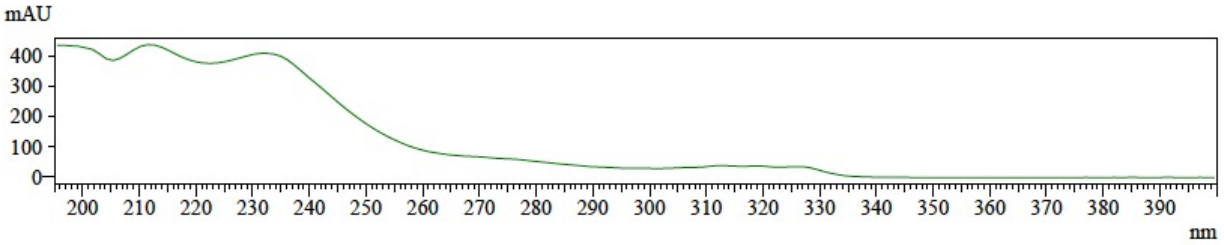
Chromatogram



UV Spectrum
Retention time = 40.549



UV Spectrum
Retention time = 45.192



Peak Table

PDA Ch1 220nm

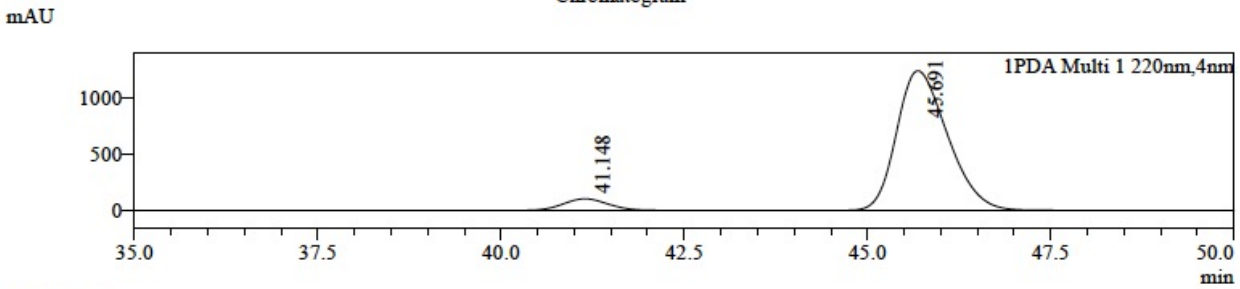
Peak#	Ret. Time	Area	Area%
1	40.549	17696645	49.768
2	45.192	17861769	50.232
Total		35558414	100.000

Sample Information

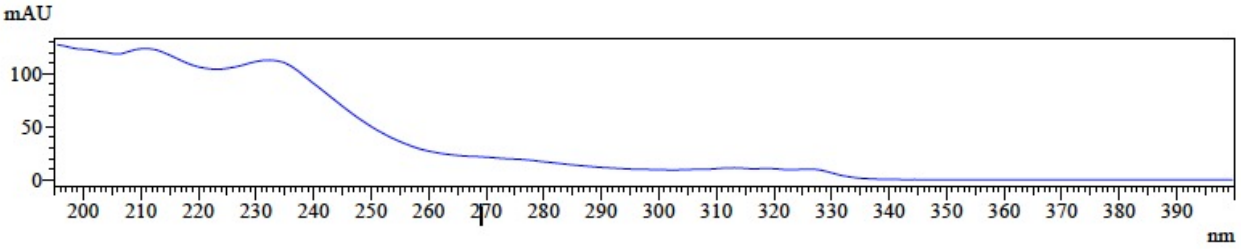
Sample Name	: XXW-396-ID-5%0.8mL
Sample ID	: XXW-396-ID-5%0.8mL
Data File	: XXW-396-ID-5%0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

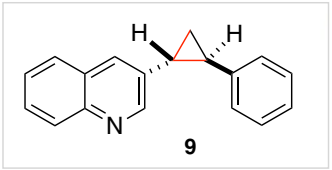
with [Co(**P18**)] (**P18** = 3,5-Di^{t}Bu-Xphyrin)

Chromatogram



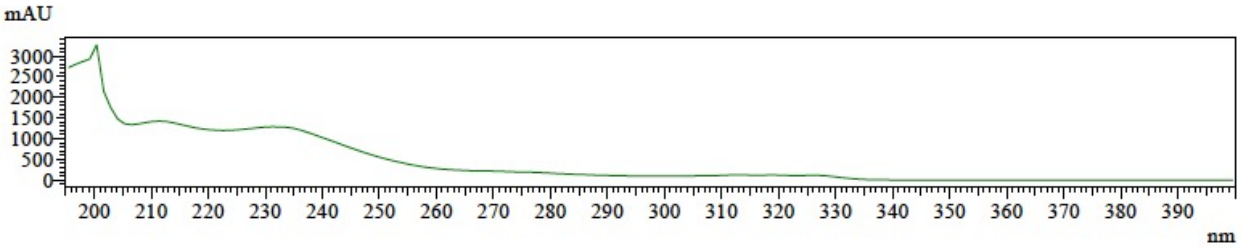
UV Spectrum
Retention time = 41.148





9

UV Spectrum
Retention time = 45.691



Peak Table

PDA Ch1 220nm

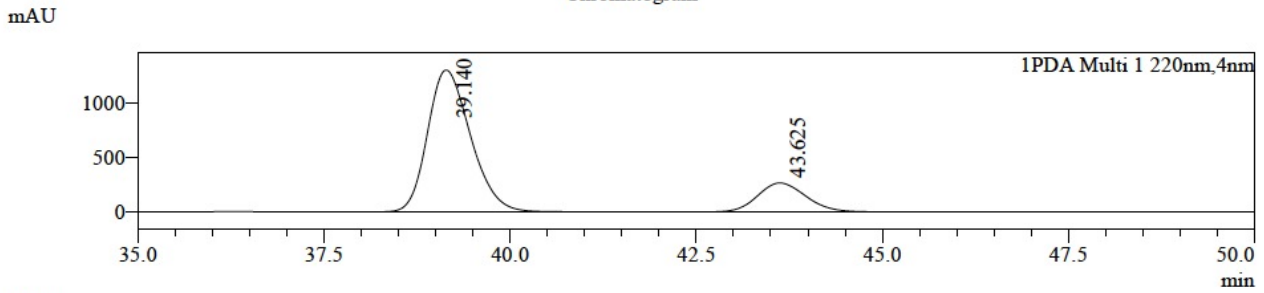
Peak#	Ret. Time	Area	Area%
1	41.148	4456535	6.957
2	45.691	59604662	93.043
Total		64061196	100.000

with [Co(**P6**)] (**P6** = 3,5-Di^{t}Bu-Qingphyrin)

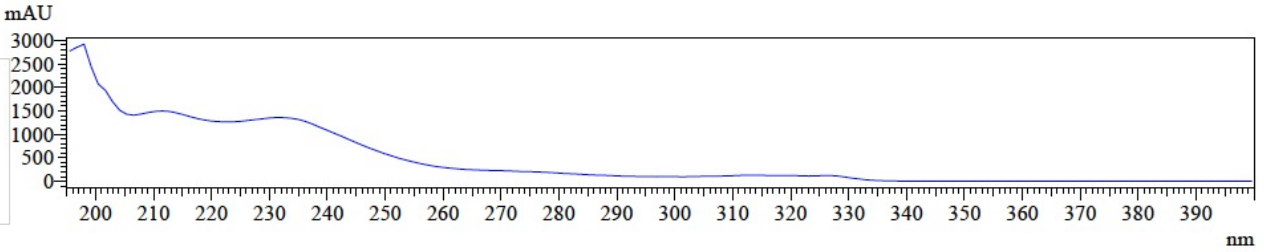
Sample Information

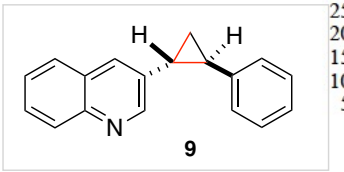
Sample Name	: XXW-474-ID-5%0.8mL
Sample ID	: XXW-474-ID-5%0.8mL
Data File	: XXW-474-ID-5%0.8mL.lcd
Method File	: XXW-5%.0.8.mL.lcm

Chromatogram

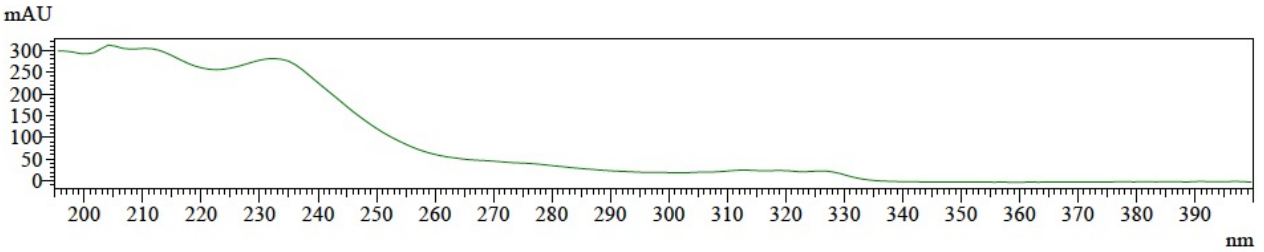


UV Spectrum
Retention time = 39.140





UV Spectrum
Retention time = 43.625



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	39.140	52288930	81.437
2	43.625	11918590	18.563
Total		64207520	100.000