# The Synthetic Applications of 1,4-Hydrogen Atom Abstraction via Co(II)-Based Metalloradical Catalysis

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# The Synthetic Applications of 1,4-Hydrogen Atom Abstraction *via* Co(II)-Based Metalloradical Catalysis

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**PhD Advisor:** Prof. X. Peter Zhang

**Abstract:** Radical reactions have attracted continuous research interest in recent year considering their diverse reactivities. Hydrogen-atom abstraction (HAA), as one type of the most well-explored radical reactions, has been identified as one of powerful tools for C–H functionalization. Reactions involving 1,4-HAA, which is typically a challenging process both entropically and enthalpically, are rather scarce, while 1,5-HAA have been well demonstrated for variety of synthetic applications. Guided by the concept of metalloradical catalysis (MRC), 1,4-HAA was for the first time utilized as the key step to achieve asymmetric construction of chiral ring structures: cyclobutanones, azetidines and tetrahydropyridines. The design of different $D_2$-symmetric chiral amidoporphyrin as the supporting ligand is the key to all these transformations. The reactions can be conducted under mild conditions, affording corresponding ring structure in good yields with excellent selectivity. Furthermore, The combined computational and experimental studies have shed light on the mechanistic details of these new asymmetric radical intramolecular C–H alkylation processes, which are fundamentally different from existing catalytic systems involving metallocarbenes for concerted C–H insertion. We envision that these asymmetric radical processes via Co(II)-based MRC could become an alternative method for important chiral ring structures synthesis and potentially provide new opportunities for complex molecule construction.

**Committee Member:** Prof. James P. Morken, Prof. Jeffery A. Byers

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# List of Abbreviations

Por: porphyrin

Xanthpos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

MeO: methoxy

Me: methyl

$^{t}$Bu: tert-butyl

Et: ethyl

Ar: aryl

Ph: phenyl

TPP: tetraphenyl porphyrin

TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy

Ts: 4-methylphenyl sulfonyl

Å: angstrom

MRC: metalloradical catalysis

KIE: kinetic isotope effect

ee: enantiomeric excess

es: enantiomeric specificity

de: diastereomeric excess

ds: diastereomeric specificity

dr: diastereomeric ratio

equiv: equivalent(s)

THF: tetrahydrofuran

EtOAc: ethyl acetate

DCM: dichloromenthane

PhMe: toluene

PhF: fluorobenzene

RT: room temperature

HPLC: high performance liquid chromatograph

HRMS: high resolution mass spectrometry

y: yield

IR: infrared spectroscopy

L: ligand

ESI: electrospray ionization

EPR: electron paramagnetic resonance

M: molar or metal

NMR: nuclear magnetic resonance

DART: direct analysis in real time

RA: radical activation

HAA: hydrogen atom abstraction

RS: radical substitution

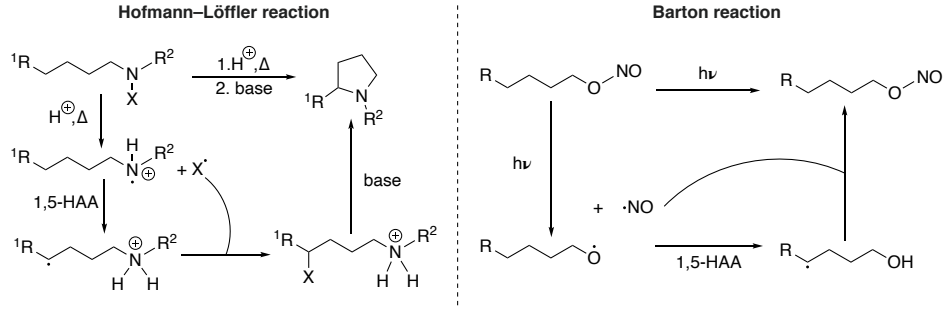
MRC:  metalloradical catalysis

# Chapter 1. Exploration of 1,4-Hydrogen Atom Abstraction through MRC

## 1.1 A Rare Radical Process: 1,4-Hydrogen Atom Abstraction

In the past decades, radical reactions have attracted increasing research interest from synthetic organic chemists in light of their rich reactivities and attractive characteristics. Among different types of classic radical reactions, hydrogen-atom abstraction (HAA), as one of the most well-explored radical reactions, has emerged as a general pathway for C–H functionalization and finds diverse synthetic applications.[1] Since C–H bond is the most ubiquitous motif in organic chemistry, functionalization of specific C–H necessitates a high level of precision. Compared to intermolecular HAA reactions, the applications of intramolecular HAA reactions in radical-mediated C–H functionalization are much more common, presumably due to both entropy reason and easiness of the precise control of the regioselectivity for the reactions. Some early works like Hofmann-Loffler-Freytag reaction[2] and Barton's nitrite photolysis[3] have already started to show the interest of regioselective intramolecular HAA for remote C–H

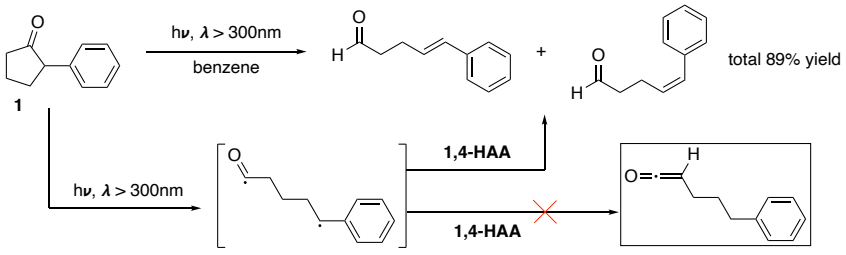
**Scheme 1.1. Hofmann-Loffler-Freytag Reaction and Barton Reaction**




functionalization (Scheme 1.1). Comprehensive computational studies have been done to model the reaction process for HAA and it is currently accepted that the ideal arrangement for HAA reaction involves a linear transition state for those three atoms participating in the

HAA process although small distortion from the linearity (145°-180°) is believed not to affect the process significantly.[4] 1,5-HAA is the most commonly investigated HAA reaction because 1,5-HAA process involves a six-membered transition structure in which a linear transition state can be readily accommodated with less entropic issue compared to 1,6-HAA, although theoretical calculations predict that 1,5-HAA are enthalpically slightly more disfavored than 1,6-HAA. 1,6-HAA was thus found to be the second common HAA, and it can sometimes even compete with 1,5-HAA when both enthalpic and geometric factors are favorable. As for 1,n-HAA when n>6, even though ideal linear geometry can be easily reached as expected, they are rather rare because of even larger entropic penalty than in the case of 1,6-HAA. Moreover, 1,2- and 1,3-HAA encounter the least entropic penalty during the reaction process but their highly strained transition states are highly unfavored considering the enthalpy factor. As a consequence, there is barely any case was reported for 1,2- and 1,3-HAA. Although 1,4-HAA has a less distorted transition state than 1,2- and 1,3-HAA and does not suffer a huge entropy penalty like 1,n-HAA (n>6), it was much less explored than common 1,5-HAA and 1,6-HAA in remote C–H activation. Only a few examples were reported in literature to date. A brief summary for all the cases of 1,4-HAA that were reported in literature are described as follows:

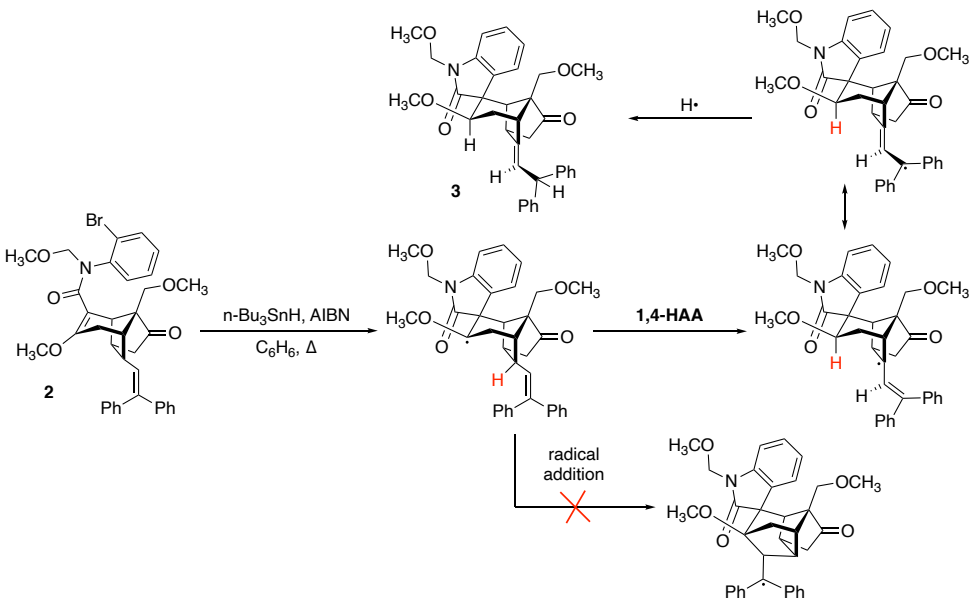
**Scheme 1.2. Photolysis of 2-Phenylcyclopentanone**



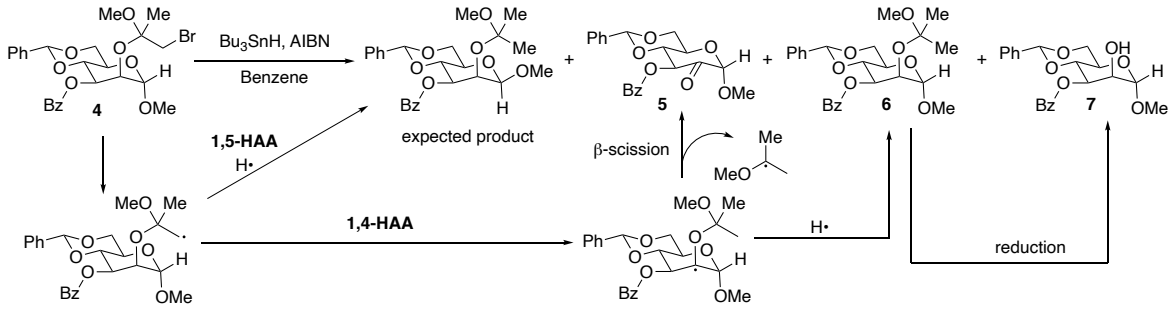
It was reported in 1972 by Baum that 2-phenylcyclopentanone **1** underwent photolysis to generate diradical. Following by intramolecular 1,4-HAA, both *E*- and *Z*-acyclic unsaturated aldehyde were delivered as final product efficiently (Scheme 1.2).[5] After the generation of diradical, only product resulting from 1,4-HAA of acyl radical was observed with no ketene product from 1,4-HAA of benzyl radical identified.

In 1991, David Hart and his co-worker reported their effort toward direct synthesis of Gelsemine through radical cyclization (Scheme 1.3). However, when the optimal reaction condition was applied for **2**, no desired cyclization product was observed. After the generation of radical under reaction condition, it underwent 1,4-HAA instead of radical addition to the double bond to deliver **3** as the product.[6]

**Scheme 1.3. Unexpected Product Resulting from 1,4-HAA during the Synthesis of Gelsemine**

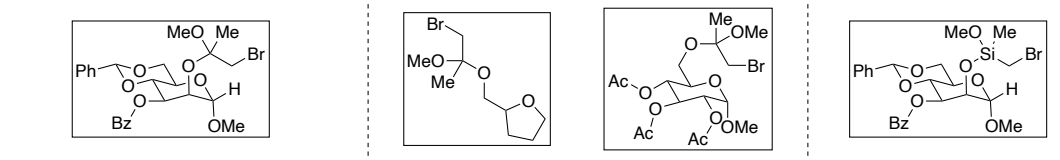


**Scheme 1.4. Unexpected 1,4-HAA Processes during the Investigation of β-O-Mannopyranoside Synthesis**




David Crich and his co-worker disclosed their observation of 1,4-HAA during their investigation in application of 1,5-HAA to the formation of β-O-mannopyranoside (Scheme 1.4). When **4** was treated with $Bu_3SnH$ and AIBN in benzene at reflux over 5 h, in addition to the expected 1,5-HAA product, products **5**, **6** and **7** were also observed and believed to be a result of 1,4-HAA process. It was also concluded by the author that 1,4-HAA was not found in the system that is less conformationally rigid under the same reaction condition and even small change from carbon linkage to silica linkage could result in a dramatic different product distribution (Scheme 1.5).[7]

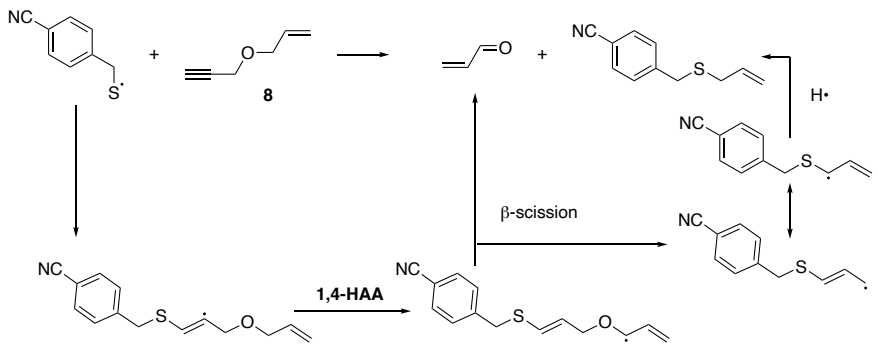
**Scheme 1.5. Different Linkages Result in Different Types of HAA**



Both 1,5-HAA and 1,4-HAA were observed | Only 1,5-HAA was observed | Only 1,4-HAA was observed

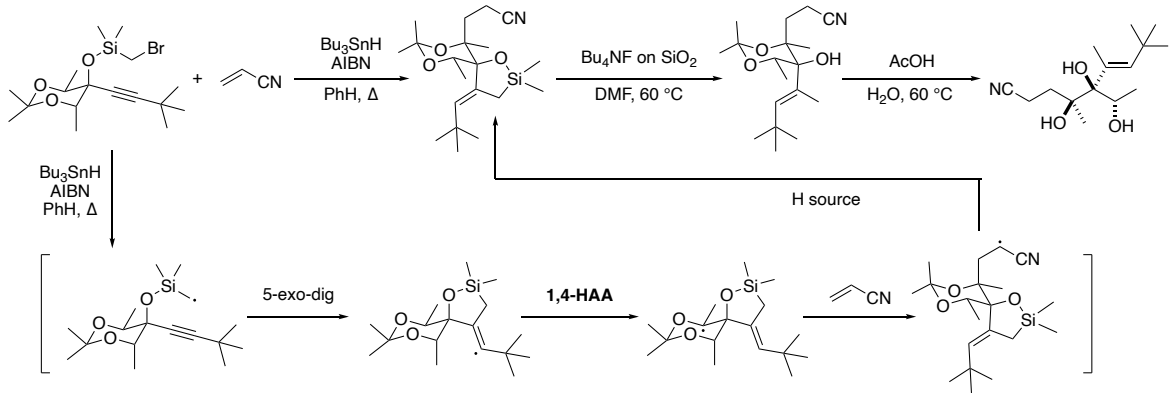
Maria and co-worker have been interested in the exploration of the rearrangement and cyclization of vinyl radicals. An unexpected observation of 1,4-HAA was reported by their group in 1996 during their investigation of 4-cyanophenylmethanesulfanyl radical and its addition to enyne **8** (Scheme 1.6).[8]

**Scheme 1.6. Vinyl Radical Undergo 1,4-HAA as an Unexpected Pathway**



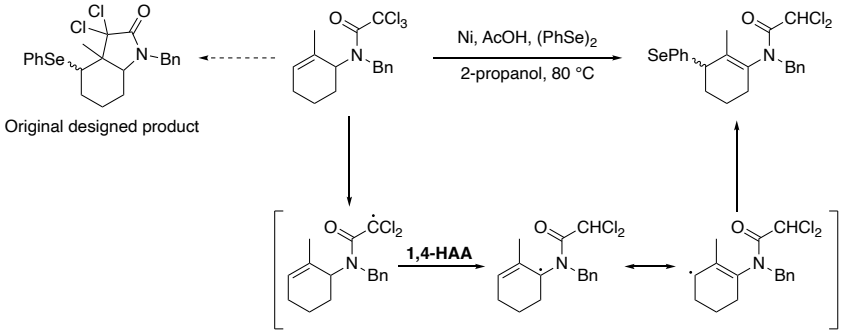

1,4-HAA was first intended to be applied toward designed synthetic application by Max Malacria and co-workers in 2000 (Scheme 1.7). The synthesis of 1,2,3-triol from 1,3-dioxane moiety utilizing 1,4-HAA as the key step was achieved and some mechanistic studies like deuterium labeling experiment and olefin trapping experiments were carried out to further support the existence of 1,4-HAA during the reaction processes.[9]

**Scheme 1.7. First Designed Example for 1,4-HAA towards 1,2,3-triol Synthesis**



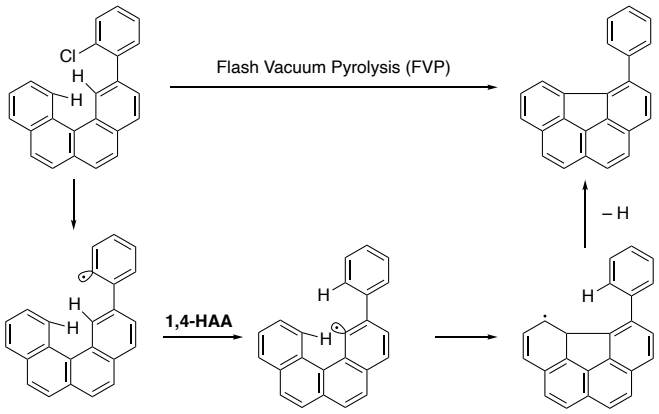

In 2001, Samir Z. Zard reported their interesting observation of 1,4-HAA in the total synthesis towards (–)-Dendrobine (Scheme 1.8). This uncommon results somehow thwarted his original synthetic plan. Their initial expectation for this reaction was to generate the fused ring cyclization product through radical addition, however, unexpected product from 1,4-HAA was obtained instead.[10]

**Scheme 1.8. Competitions between 1,4-HAA and Radical Addition in the Key Step toward (–)-Dendrobine Synthesis**




In 2005, Lawrence T. Scott reported that 1,4-HAA was utilized to synthesis 1-phenylbenzo[*ghi*]fluoranthene at 1100 °C through flash vacuum pyrolysis (FVP) (Scheme 1.9). In this work, a control experiment was conducted to provide evidence for the following proposed pathway in which 1,4-HAA was involved in the ring closing process.[11]

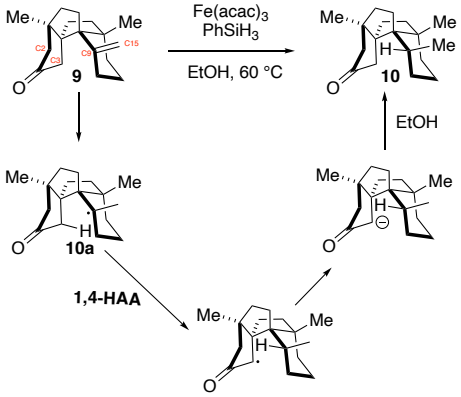
**Scheme 1.9. 1,4-HAA in Flash Vacuum Pyrolysis**




1,4-HAA played an important role in the total synthesis of (+)-Waihoensene by Yang group in 2020 (Scheme 1.10). [12] It was claimed that diastereoselective hydrogenation of olefin **9** was very challenging since the product formation with the opposite stereochemistry of C9 in **10** was generated by common transition metal catalysts such as Pd/C, $PtO_2$ and $Rh(PPh_3)_3Cl$. However, through a carefully designed 1,4-HAA,

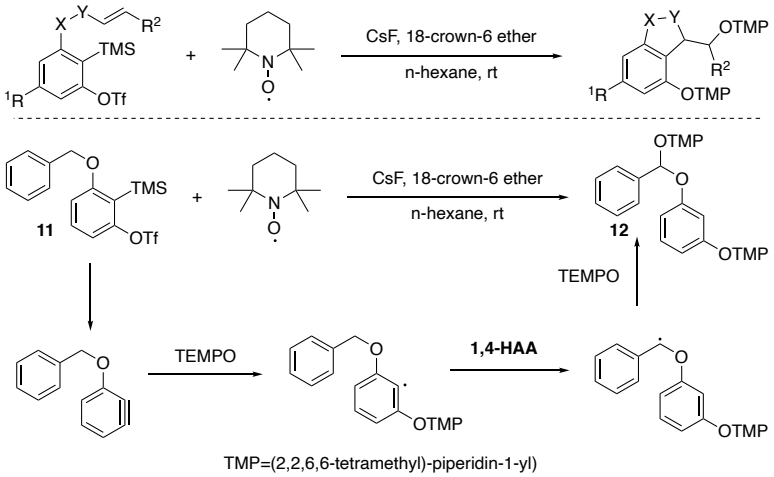
diastereoselective saturation of the C9−C15 double bond was realized in **10**. **10a** which was derived from a radical-mediated reductive reaction of **9** was believed to abstract a hydrogen atom through 1,4-HAA from the C3 due to the close proximity (2.4 Å) between the H atoms of C3 and C9 and their position next to the C2 carbonyl group. After 1,4-HAA, the newly generated carbon radical was reduced to carbon anion and quenched by EtOH allowing for the formation of **10** with desired stereochemistry.

**Scheme 1.10. Smart Design of 1,4-HAA for the Key Selectivity Determined Step for Synthesis of (+)-Waihoensene**




In 2021, the Armido Studer group reported a TEMPO-mediated cascades reaction using *in-situ* generated arynes as the radical acceptors (Scheme 1.11). After various applications of aryl radical generated by TEMPO addition to an aryne toward fuse ring construction through radical addition were demonstrated, the reactivity of the aryl radical intermediate towards intramolecular HAA to further leverage the potential of radical aryne chemistry was also investigated. During the investigation, it was found that when **11** was applied to the reaction condition, product **12** was observed which was observed presumably through 1,4-HAA.[13]

**Scheme 1.11. 1,4-HAA with Aryl Radical**




In addition to the examples that were mentioned above, the mechanistic investigations involving 1,4-HAA have attracted the interest of a number of research groups. 1,4-HAA involved EPR study and KIE study have been intensively reported.[14]

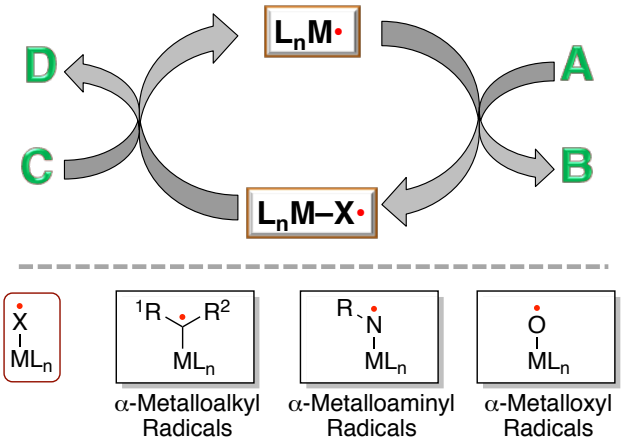
In summary, there are much less cases of 1,4-HAA can be found compared to 1,5-HAA and 1,6-HAA in the literature. For the existing cases, conformation rigidity is the dominated factor that leads to 1,4-HAA. Moreover, in most of the reported examples, vinyl or aryl radicals are the most common radicals that undergo facile 1,4-HAA since stronger C–H bond formed as the thermodynamic driving force. In most of the existing examples, 1,4-HAA was still mentioned as side reaction that was discovered accidentally during the exploration for other reactions. Only one literature claimed that they intended to utilize 1,4-HAA for some synthetic applications. Besides, 1,4-HAA has barely been implemented in catalytic process. Considering both enthalpy and entropy factor that were aforementioned, it was envisioned that the potential of applying 1,4-HAA in remote C–H functionalization was largely underestimated. Like 1,6-HAA being able to compete with 1,5-HAA when

both enthalpic and geometric factors are favorable, 1,4-HAA should find broader application in radical C–H activation with congruous conditions.

### 1.2 Metalloradical Catalysis (MRC)

To investigate the vast potential of radical reactions in stereoselective organic synthesis, metalloradical catalysis(MRC) provides a conceptually new approach to solve existing challenges in the field such as the initiation and the control of reactivity and selectivity of different radical reactions. The main idea of MRC is to catalytic generate as well as subsequently regulate metal-stabilized organic radical, which is detailed in the catalytic cycle shown in Scheme 1.12.

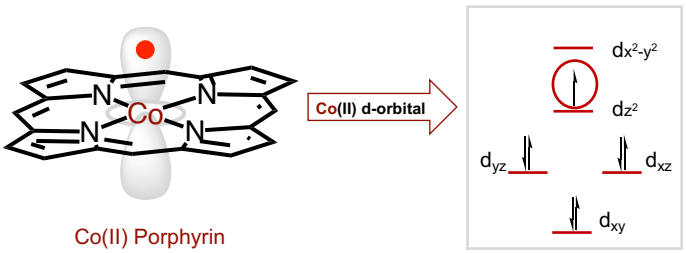
**Scheme 1.12. General Catalytic Cycle for MRC**




A stable metal-centered radical (metalloradical) could work as the catalyst to activate the radical precursor A(also termed as ‘metalloradicophile’) and generate the metal-supported X radical which can be carbon-centered radical, nitrogen-centered radical or oxygen-centered radical etc. depending on the metalloradicophile. These metal-supported X radicals were thus assumed to have the same reactivity as normal organic radicals which could further undergo different types of radical reactions to deliver the final

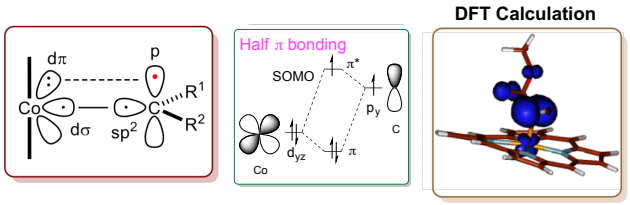
product and regenerate the catalyst. With well tuning of the ligand environment (Ln), MRC is expected to be applied a broad range of transformations.

**Scheme 1.13. *d* Electron Distribution for Co(II) Porphyrin Complexes**



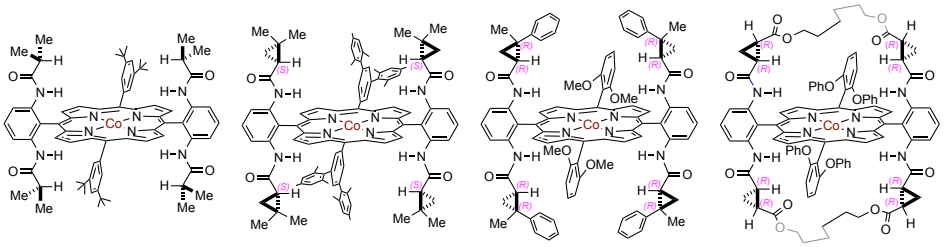

Through years of exploration, cobalt(II) porphyrin was identified as one of the most suitable candidates for MRC and was also the most commonly used catalyst by our group. Cobalt(II) has 7 d electrons, and cobalt(II) porphyrin complex was known to adopt a low-spin ground state with $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$ electron configuration. The unpaired electron located in $d_{z^2}$ orbital that is perpendicular to the porphyrin plane dedicates the radical character of the catalyst, which enables the Co(II) porphyrin as a metalloradical catalyst (Scheme 1.13). It was reported in the literature that diazo compounds have certain portion of diradical resonance,[15] as a result, they can theoretically serve as good radical precursor and be activated by Co(II) porphyrin complexes through radical recombination generating [Co(Por)]-supported carbon-centered radicals (α-Co(III)-alkyl radicals) by releasing nitrogen gas as the driving force and the only byproduct. The dominated bonding interaction is the covalent bond that was formed between Co-$d_{z^2}$ orbital and the C-$sp^2$ orbital. Different from classic metallocarbene complex, additional π-bonding interaction between Co-$d_{xz,yz}$ and p orbitals is only fractional (half π-bonding) somehow due to the fully-filled $d_{xz,yz}$ and singly-filled p orbitals. This so-called half π-bonding interaction was believed to be in favor of stabilizing Co(III) species, meanwhile, make the unpaired electron more reactive by raising its energy (Scheme 1.14).

**Scheme 1.14. Bonding Picture for Co(II) Porphyrin Complexes**




The result from DFT calculation indicates that most of the spin population is located in the α-carbon for α-Co(III)-alkyl species, which further supports the hypothesis of the formation of [Co(Por)]-supported carbon-centered radicals instead of metallocarbene complexes (Scheme 1.14). These newly generated α-Co(III)-alkyl radicals could undergo a variety of classic radical reactions such as radical addition, hydrogen atom abstraction as well as the subsequent radical substitution, which lead to new catalytic processes for stereoselective transformations, for example, cyclopropanation,[16] cyclopropenation,[17] C–H alkylation[18] and even some very challenging radical cascade reactions.[19]

**Scheme 1.15. Representative Examples of Co(II) Complexes of *D*$_2$-Symmetric Amido Porphyrins**

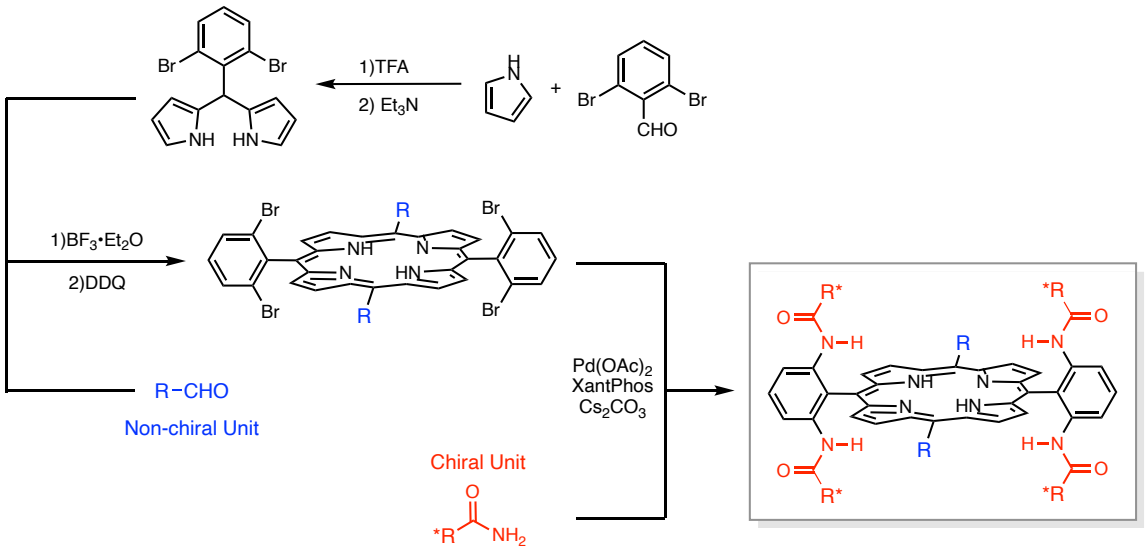



Ligand design has laid the most important foundation for MRC. Series of *D*$_2$-symmetric Co(II) amido porphyrin catalyst with different steric and electronic properties were synthesized and fully characterized in the past decade in the lab (Scheme 1.15). The reactivity and selectivity for different reactions could be easily tuned through different

design of catalysts, which are easily accessed through modular synthesis processes (Scheme 1.16).

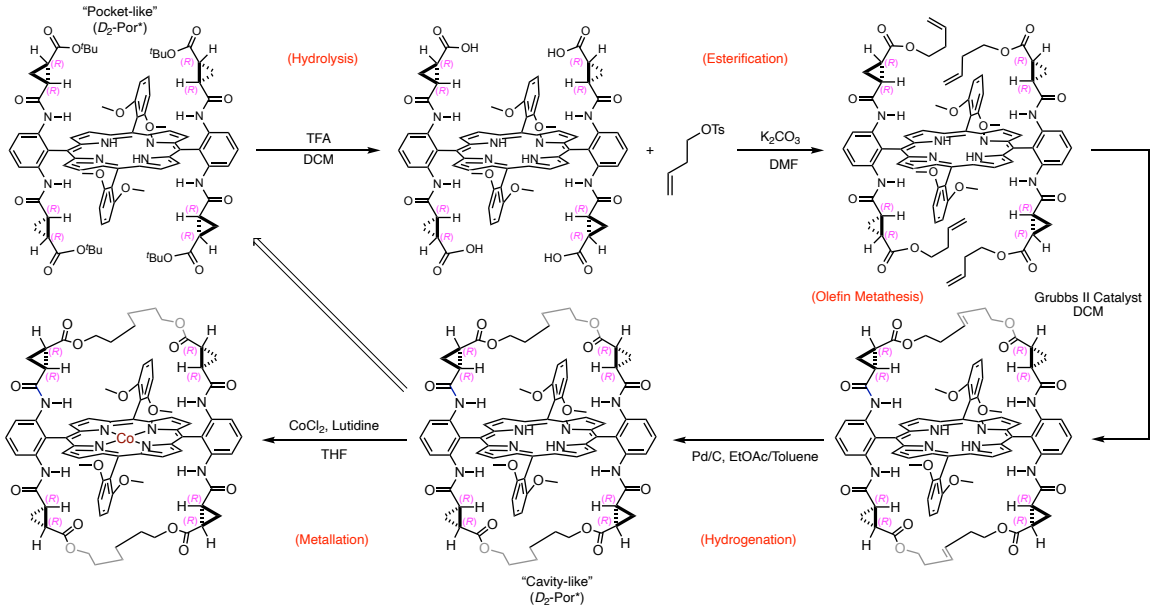
A versatile synthetic protocol has been developed by our group in the early year for the rapid access of $D_2$-symmetric chiral porphyrins via palladium-catalyzed quadruple cross-coupling reactions using 5,15-bis(2',6'-dibromophenyl)porphyrins as synthons.[20] As shown in Scheme 1.16, the tetrabromoporphyrin synthon could be built from 2,2'-((2,6-dibromophenyl)methylene)bis(1H-pyrrole) and any type of aldehydes via MacDonald [2+2] porphyrin synthesis following Lindsey's condition.[21] Those two meso-R groups at the 10- and 20-positions installed in the resulting core structures help to tune the electronic and steric properties of the porphyrin. Upon the formation of tetrabromoporphyrin synthons, the quadruple amidation reactions of the tetrabromoporphyrin synthons with different types of chiral amides could be effectively catalyzed by the combination of $Pd(OAc)_2$ and XantPhos affording a variety of chiral amido-porphyrin in high yield.[16a] Following by the subsequent cobaltlation step, $D_2$-symmetric Co(II) complexes of chiral amido-porphyrins could be obtained as stable purple solids efficiently.

**Scheme 1.16. Modular Synthetic Route for Co(II) Amido Porphyrin Complexes**



In order to address the limitations of existing systems and open windows for discovering new catalytic radical transformations, a novel $D_2$-symmetric chiral amidoporphyrins with alkyl bridges across two chiral amide units on both sides of the porphyrin plane (designated "HuPhyrin") was introduced in 2019. [22] This new type of bridged porphyrin ligand can be efficiently synthesized in a modular fashion through a five-step synthesis featuring double ring-closing olefin metathesis in efficiency (Scheme 1.17). More rigid, cavity-like chiral environment is provided by this new bridged ligand. In addition, the shape and size of this porphyrin ligand can be further adjusted by variation of the bridge length. This type of ligand have been recently showcase to exhibit notably different catalytic reactivity and stereoselectivity from existing non-bridged catalysts in various of catalytic transformation.[23]

**Scheme 1.17. New Generation of Co(II) Amido Porphyrin Complexes and Its Synthetic Route**

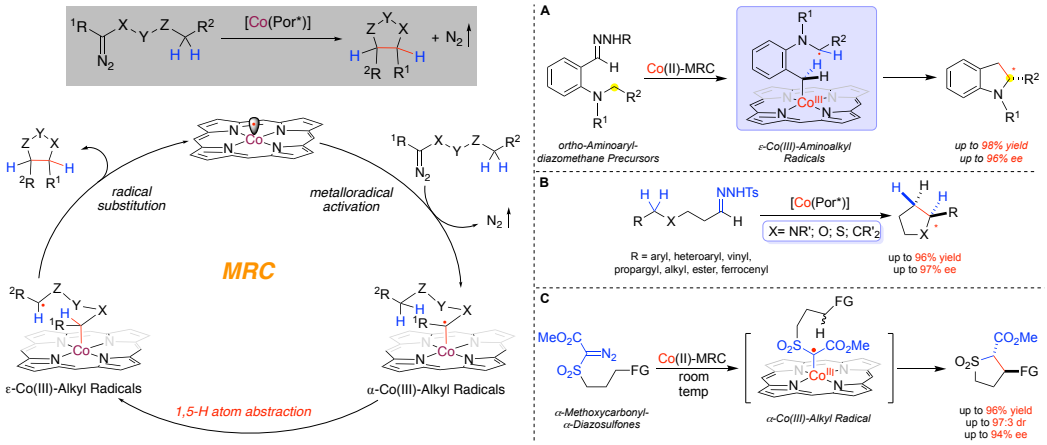


### 1.3 Synthetic Application of 1,4-HAA via Co(II)-Based MRC

Intramolecular C–H alkylation, as an important research direction in the group, aims at utilizing regioselective intramolecular HAA for precise C–H bond activation following by radical substitution to construct different-sized ring structures in a catalytic and stereoselective manner. Given that 1,5-HAA is the most common HAA process, the state of the art in intramolecular C–H alkylation via MRC is that a variety of important five-membered cyclic compounds could be accessed in high yield and excellent selectivity utilizing 1,5-HAA as the fundamental key step following by facile radical substitution (Scheme 1.18).[18]

To seek for more advancement in this research direction, we were intrigued by the possibility of incorporating 1,4-HAA process for intramolecular C–H alkylation through MRC. It would be both fundamentally and practically appealing attribute to the underdevelopment of 1,4-HAA in radical-mediated C–H functionalization and the

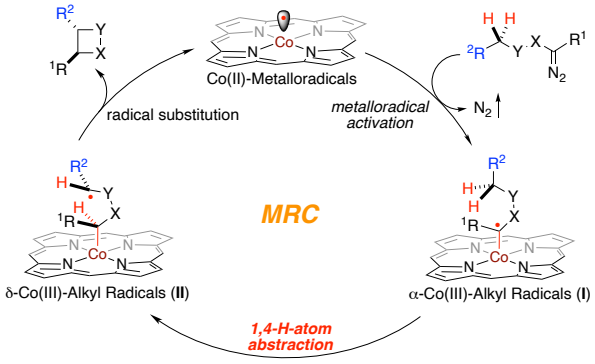
**Scheme 1.18. Reported Examples of Intramolecular C–H Alkylation via Co(II)-Based MRC**




attractiveness of potential chiral four-membered ring product (Scheme 1.19). If succeed, it would become an exciting new application for intramolecular C–H alkylation through MRC. Moreover, it could also potentially provide an alternative pathway for four-

membered ring synthesis in the near future since the field has been long dominated by the classic methods such [2+2] cycloaddition[24] and three-membered ring expansion[25].

**Scheme 1.19. General Catalytic Cycle for 1,4-HAA Involving Intramolecular C–H Alkylation via Co(II)-Based MRC**



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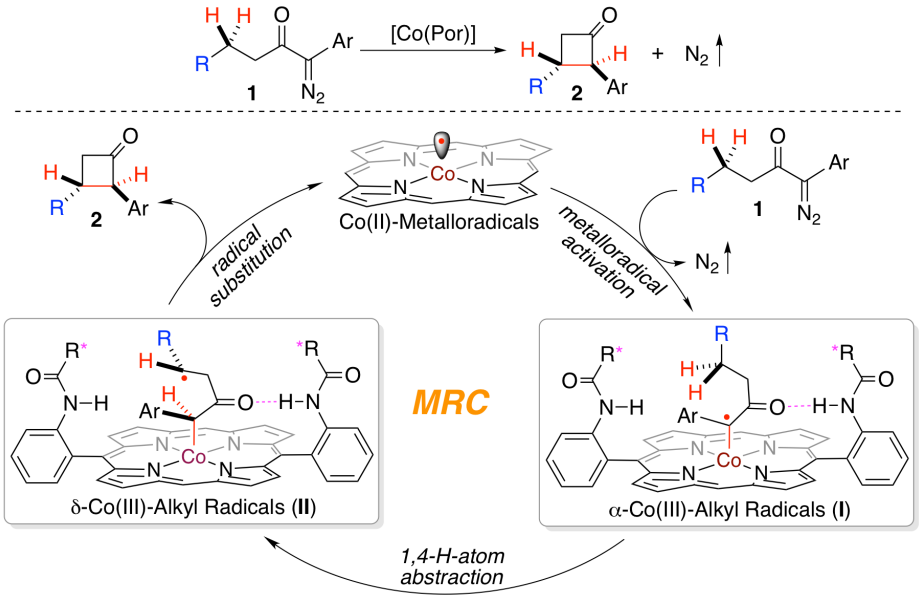
# Chapter 2. Asymmetric Radical Process for Stereoselective Construction of Cyclobutanones via Co(II)-Based Metalloradical Catalysis

## 2.1 Introduction

In the past decades, radical reactions have attracted growing attention of synthetic organic chemists in view of their rich reactivities and attractive characteristics.[1] Notably, hydrogen atom abstraction (HAA) by free radicals has long been recognized as one of the most general pathways for C–H activation,[2] a fundamental radical reaction that can potentially be utilized for direct functionalization of prevalent C–H bonds in organic molecules. However, realization of this immense potential faces longstanding challenges that are associated with governing reactivity as well as controlling selectivity of the departing radicals from HAA for ensuing bond formation. To address this and related challenges, metalloradical catalysis (MRC) provides a conceptually new approach for achieving controllable reactivity and selectivity in radical reactions through catalytic generation as well as subsequent regulation of metal-stabilized organic radical.[3-5] As stable 15e-metalloradicals, Co(II) complexes of $D_2$-symmetric chiral amidoporphyrins [Co($D_2$-Por*)] enjoy the unique capability of activating diazo compounds homolytically to generate α-Co(III)-alkyl radicals.[6] These Co-stabilized C-centered radical intermediates can undergo common radical reactions, such as radical addition and hydrogen atom abstraction as well as following radical substitution, leading to new catalytic processes for stereoselective radical transformations.[7] In particular, Co(II)-based MRC was successfully applied for the development of enantioselective radical C–H alkylation of diazo compounds involving 1,5-HAA as the key step for stereoselective construction of 5-

membered ring structures.[8] To broaden the synthetic applications of Co(II)-MRC for solving more challenging problems, we were intrigued by the possibility of constructing strained 4-membered ring structures such as cyclobutanones through radical 1,4-C–H

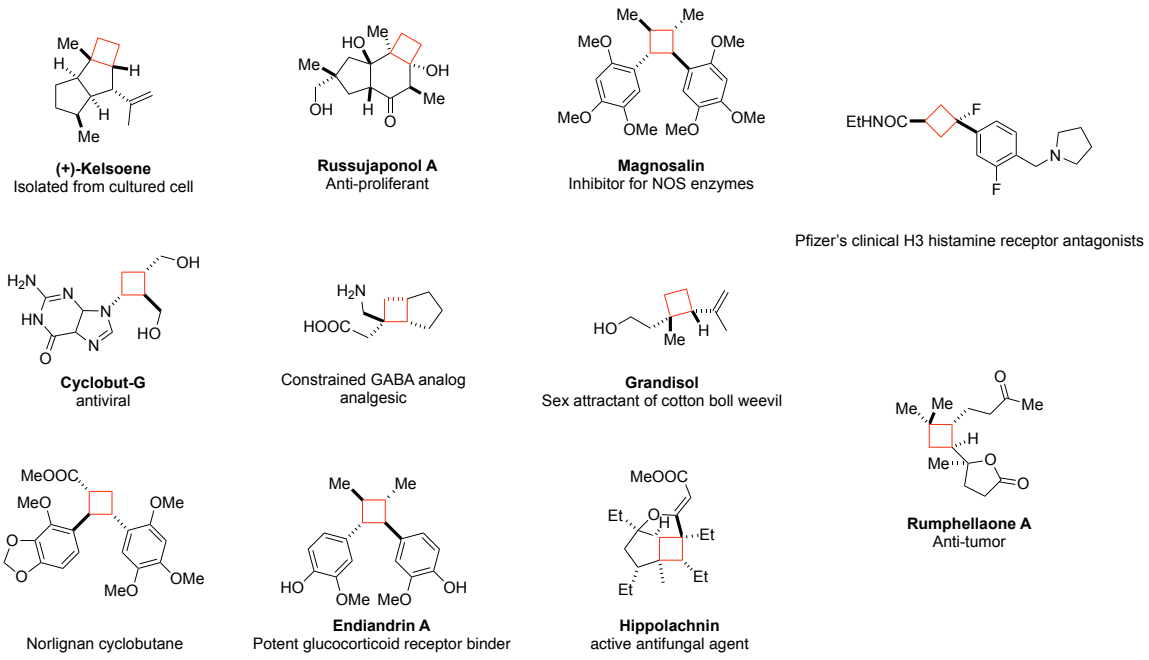
**Scheme 2.1 Working Proposal for Construction of Cyclobutanones by Radical 1,4-C−H Alkylation via Co(II)-MRC**




alkylation of α-aryldiazoketones (Scheme 2.1). However, this proposed radical process presented several potential challenges. In view of their unique electronic and steric properties compared with other types of diazo compounds, it was uncertain whether donor/acceptor-substituted diazo compounds 1 could be effectively activated by [Co($D_2$-Por*)] to generate the corresponding α-Co(III)-alkyl radicals I. Given that 1,4-HAA is known to be an inherently challenging process due to both unfavorable entropic and enthalpic factors,[9] how could the resulting tertiary radical intermediate **I** be promoted for the desired intramolecular hydrogen atom abstraction to form α-Co(III)-alkyl radicals **II**? Apart from the reactivity concerns, could the 1,4-HAA of α-Co(III)-alkyl radicals **I** be rendered enantioselective? Furthermore, the subsequent *4-exo-tet* radical cyclization of the

alkyl radicals **II** via intramolecular radical substitution was expected to be equally challenging in light of the high strain associated with four-membered transition state. What factors could be utilized to facilitate the ring closure for product formation? Additionally, how could the C–C bond formation be achieved with effective diastereoselective control during radical cyclization? We reasoned that all these and related questions could be potentially addressed through optimization of [Co($D_2$-Por$^*$)] catalyst by fine-tuning of the $D_2$-symmetric chiral amidoporphyrin ligand to adopt suitable environments that govern the course of the catalytic radical process (Scheme 2.1). If realized successfully, it would give rise to the first catalytic radical process for asymmetric intramolecular C−H alkylation involving 1,4-HAA as the key step for stereoselective construction of highly-strained cyclobutanone structures, the four-membered carbocycles that are important moieties in natural products and pharmaceuticals (Figure 2.1).[10]

**Figure 2.1. Four-Membered Ring Containing Natural Products and Drugs**



Catalytic asymmetric intramolecular 1,4-C–H alkylation of diazo compounds represents a potentially attractive strategy for stereoselective construction of four-membered cyclic compounds.[11] Due to the high strain associated with four-membered ring structures, catalytic process for 1,4-C–H alkylation has been largely underdeveloped. While there have been a few reports on asymmetric synthesis of β-lactams[12] and β-lactones[13] from α-diazoamides and α-diazoesters, respectively, by Ru, Rh and Ir-based catalytic systems, asymmetric synthesis of cyclobutanones via 1,4-C–H alkylation from α-diazoketones has not been previously realized.[14] The absence of catalytic system for cyclobutanone synthesis is presumably attributed to the augmented challenge of 1,4-C–H alkylation for α-diazoketones because of their relatively higher conformational flexibility than α-diazoamides and α-diazoesters. As an exciting new application of Co(II)-based MRC for stereoselective organic synthesis, we herein report the development of the first catalytic system that is highly effective for asymmetric 1,4-C–H alkylation of α-diazoketones to construct chiral cyclobutanones. Supported by a new-generation $D_2$-symmetric chiral amidoporphyrin ligand, the Co(II)-based metalloradical system, which enjoys operational simplicity and mild conditions, can activate α-aryldiazoketones with varied electronic and steric properties for 1,4-alkylation of C($sp^3$)–H bonds, enabling stereoselective construction of chiral α,β-disubstituted cyclobutanones. We show the importance of catalyst development through fine-tuning of the ligand environments in achieving high reactivity and stereoselectivity in this new radical process. Furthermore, our combined experimental and computational studies on the mechanism of the Co(II)-based metalloradical system have shed light on the underlying stepwise radical pathway, including the key steps of 1,4-HAA and 4-*exo*-*tet*-RS. A series of further transformations

of the resulting enantioenriched α,β-disubstituted cyclobutanones are provided to showcase their synthetic applications.

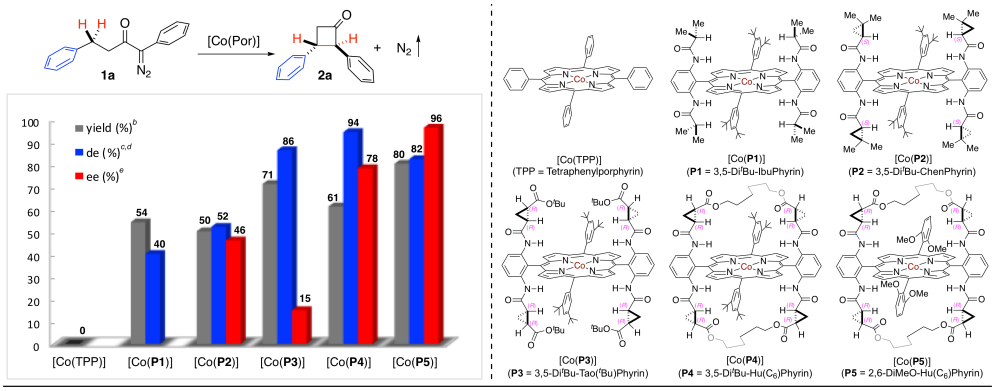
## 2.2 Results and discussion

### 2.2.1 Catalyst Development

At the outset of this research project, 1-diazo-1,4-diphenylbutan-2-one (**1a**) was used as the model substrate to examine the feasibility of the proposed catalytic process for 1,4-C–H alkylation (Scheme 2.2). Simple achiral metalloradical catalyst [Co(TPP)] (TPP = 5,10,15,20-tetraphenylporphyrin) was shown to be incapable of activating **1a** for the intramolecular C–H alkylation reaction, failing to generate any cyclobutanone product. Instead, diazoketone **1a** was thermally decomposed to the carboxylic acid derivative via Wolff rearrangement, followed by nucleophilic reaction of the corresponding ketene intermediate with water. Excitingly, when the achiral amidoporphyrin catalyst [Co(**P1**)] (**P1** = 3,5-Di$^t$Bu-IbuPhyrin)[15] was used, it could productively catalyze the C–H alkylation reaction to deliver the desired product 2,3-diphenylcyclobutan-1-one (**2a**) in 54% yield with 40% de. The dramatic difference in reactivity between [Co(**P1**)] and [Co(TPP)] might be attributed to rate acceleration through the potential hydrogen bonding interaction between amide units of the porphyrin and the carbonyl group of the a-diazoketone. Employment of first-generation chiral metalloradical catalyst [Co(**P2**)] (**P2** = 3,5-Di$^t$Bu-ChenPhyrin)[7a] enabled asymmetric induction in the 1,4-C–H alkylation reaction, affording cyclobutanone **2a** with moderate enantioselectivity (46% ee) without significantly affecting the product yield (50%) and diastereoselectivity (52% de). When second-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di$^t$Bu-TaoPhyrin) bearing chiral amide units with ester moieties was used for the catalytic reaction,[16] it led to the

increase in both product yield (71%) and diastereoselectivity (86% de) but the decrease in enantioselectivity (15% ee). When switching to the new-generation $C_6$-bridged metalloradical catalyst [Co(**P4**)] (**P4** = 3,5-Di$^t$Bu-Hu($C_6$)Phyrin) featuring more rigid cavity-like environments,[16] dramatic improvements in both diastereoselectivity (94% de) and enantioselectivity (78% ee) were observed despite in relatively lower product yield (61%). Subsequent use of analogous catalyst [Co(**P5**)] (**P5** = 2,6-DiMeO-Hu($C_6$)Phyrin),[17] which bears 2,6-dimethoxyphenyl instead of 3,5-di-*tert*-butylphenyl groups as the 5,15-diaryl substituents, further improvements in enantioselectivity (96% ee) as well as yield (80%) were achieved without significantly affecting the diastereoselectivity (82% de). These results demonstrate that the rigidification of ligand environment of chiral metalloradical catalyst [Co($D_2$-Por$^*$)] plays an important role in achieving both high reactivity and stereoselectivity for the 1,4-C−H alkylation process. It should be emphasized that the diastereomeric mixtures of the resulting cyclobutanone **2a** from all the catalytic reactions were isomerized to *trans*-enriched **2a** with 96% de after purification by column chromatography on silica gel as a result of the relative acidity of the tertiary α-C–H bond, regardless the original diastereoselectivities before purification.

**Scheme 2.2 Ligand Effect on Co(II)-Based Catalytic System for Asymmetric 1,4-C–H Alkylation of a-Aryldiazoketone**[a]

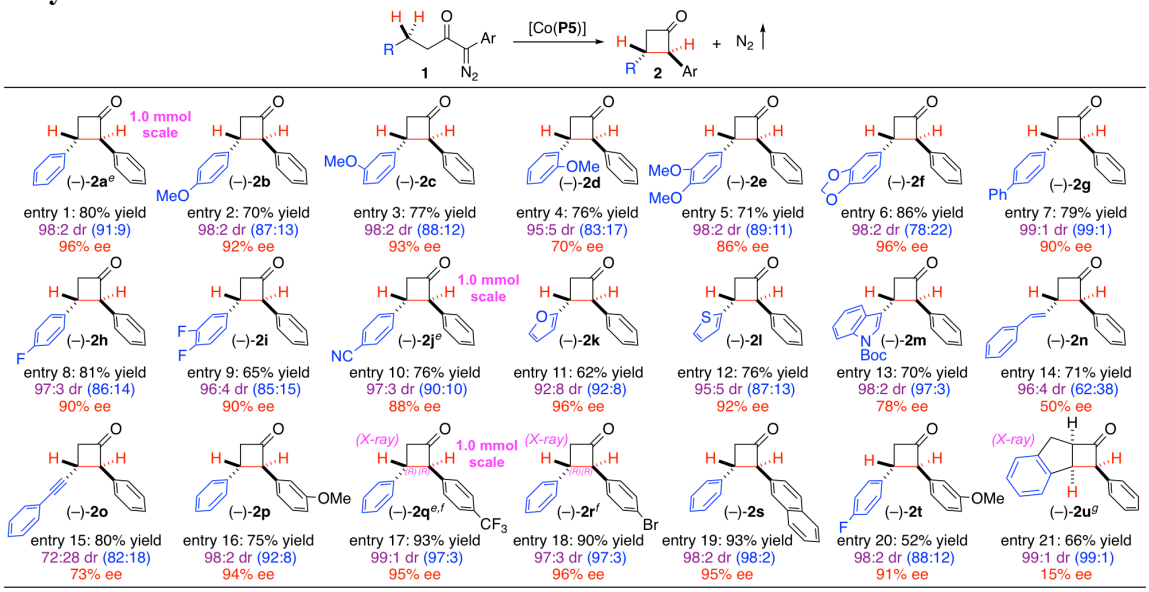


[a]Carried out with **1a** (0.10 mmol) using [Co(Por)] (2 mol %) in *tert*-butyl methyl ether (TBME) (0.5 mL) at 40 ºC for 12 h. [b]Isolated yield. [c]Diastereomeric excess (de) determined by $^1$H NMR analysis of crude reaction mixture before purification. [d]Isomerized to *trans*-enriched products with 96% de after purification by silica gel column chromatography for all catalytic reactions. [e]Enantiomeric excess (ee) of *trans*-diastereomer determined by chiral HPLC after purification

### 2.2.2 Substrate Scope

Under the optimized conditions, the substrate scope of [Co(**P5**)]-catalyzed intramolecular 1,4-C–H alkylation was evaluated with a-aryldiazoketones **1** containing different types of C−H bonds (Table 2.1). Like the parent **1a**, 1,4-diaryl-α-diazoketone derivatives containing 4-aryl substituents with various steric and electronic properties at different positions, including 4-OMe (**1b**), 3-OMe (**1c**), 2-OMe (**1d**), 3,4-di-OMe (**1e**), 1',3'-dioxolane-3,4-fused (**1f**), 4-Ph (**1g**), 4-F (**1h**), 3,4-di-F (**1i**), and 4-CN (**1j**), could be efficiently alkylated by [Co(**P5**)] at the benzylic C−H bonds, delivering the corresponding cyclobutanones **2b**–**2j** in good yields with high enantioselectivities (Table 2.1; entries 2–10). The Co(II)-catalyzed 1,4-C–H alkylation was shown to be compatible with substrates containing heteroarenes, such as furan (**1k**), thiophene (**1l**) and indole (**1m**), allowing for stereoselective construction of a-heteroarylcyclobutanones **2k**–**2m** in similarly good yields with the same high enantioselectivities (Table 2.1; entries 11–13). Furthermore, the Co(II)-based catalytic system could chemoselectively alkylate allylic C–H bonds without affecting the typically more reactive C=C p bonds as demonstrated by the productive formation of a-alkenylcyclobutanone **2n** from the reaction of 4-alkenyl-substituted diazoketone (*Z*)-**1n** in good yield albeit with lower enantioselectivity (Table 2.1; entry 14). It was noted that the olefin configuration was completely isomerized from (*Z*) to (*E*) during the catalytic process.

**Table 2.1. Asymmetric Synthesis of Cyclobutanones by Co(II)-Catalyzed 1,4-C−H Alkylation of a-Diazoketones**[a,b,c,d]

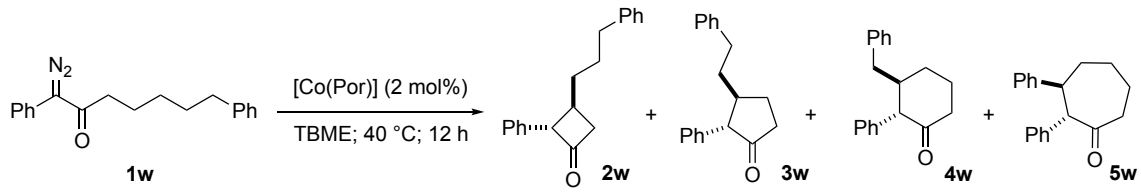



[a]Carried out with **1** (0.10 mmol) and [Co(**P5**)] (2 mol %) in TBME (0.5 mL) at 40 ºC for 12 h. [b]Isolated yield. [c]Diastereomeric ratio (dr) determined by $^1$H NMR analysis: *trans*-enriched products after purification by silica gel column chromatography due to isomerization; value in parathesis determined from reaction mixture before purification. [d]Enantiomeric excess (ee) of *trans*-diastereomer determined by chiral HPLC after purification. [e]Reaction performed in 1.0 mmol scale. [f]Absolute configuration determined by X-ray crystallography. [g]Relative configuration determined by X-ray crystallography.

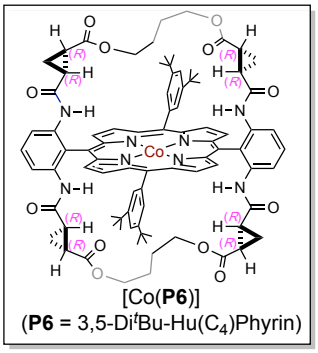
Likewise, propargylic C–H bonds could also be chemoselectively alkylated by [Co(**P5**)] without reacting with the C–C π bonds, as exemplified by the reaction of 4-alkynyl-substituted diazoketone **1o** to generate a-alkynylcyclobutanone **2o** in good yield with better enantioselectivity (Table 2.1; entry 15). In addition to the substrates with different 4-aryl substituents, the Co(II)-based metalloradical system was shown to be applicable to α-diazoketones containing 1-aryl substituents with various steric and electronic properties at different positions. For example, catalytic 1,4-C–H alkylation reactions of 1-aryl-4-phenyl-α-diazoketones, such as those bearing 3-OMe (**1p**), 4-$CF_3$ (**1q**), and 4-Br (**1r**) phenyl groups as well as 2-naphthyl group (**1s**), proceeded smoothly to afford the corresponding

cyclobutanones **2p**–**2s** in good to high yields with excellent enantioselectivities (Table 2.1; entries 16–19). 1,4-Diaryl-α-diazoketones containing both 1- and 4-aryl substituents were found to work equally well as shown with the successful reaction of α-diazoketone **1t** for formation of the desired a,β-bisarylcyclobutanone **2t** with excellent level of enantioselectivity despite in moderate yield (Table 2.1; entry 20). Furthermore, the Co(II)-based catalytic system could be also applicable to cyclic substrates such as 2-indane-derived α-diazoketone **1u**, resulting in asymmetric desymmetrization of the two benzylic C–H sites in the indane ring to deliver cyclobutanone **2u** (Table 2.1; entry 21). It is remarkable that the strained tricyclic structure with fused 4-/5-membered rings could be constructed through catalytic 1,4-C–H alkylation in good yield despite with low enantioselectivity. A new Co(II)-metalloradical catalyst supported by a different type of $D_2$-symmetric chiral amidoporphyrin ligand would likely be needed in order to achieve high enantioselectivity for the asymmetric desymmetrization 1,4-C–H alkylation process. Finally, [Co(**P5**)] was found to be ineffective for 1,4-alkylation of non-benzylic C–H bonds due to the competition from predominant 1,5-C–H alkylation. However, preliminary results from the catalytic reaction of 1-diazo-1,7-diphenylheptane-2-one (**1w**) with C–H bonds at different positions indicated that site-selective 1,4- over 1,5-C–H alkylation could be potentially achieved through fine-tuning of the $D_2$-symmetric chiral amidoporphyrin as the supporting ligand for Co(II)-metalloradical catalyst (Table 2.2). As aforementioned, the diastereomeric mixtures of the resulting cyclobutanones **2**, regardless the original diastereoselectivities from the catalytic reactions, were all further enriched to give *trans*-dominant products with excellent diastereoselectivities after purification by column chromatography on silica gel, which was realized by isomerization as a result

**Table 2.2 Ligand Effect on Selective 1,4-C–H Alkylation**




| [Co] | 2w | 3w | 4w | 5w |
|---|---|---|---|---|
| [Co(TPP)] | 0% yield | 0% yield | 0% yield | 0% yield |
| [Co(**P1**)] | 0% yield | 11% yield; 62:38 dr | 0% yield | 0% yield |
| [Co(**P2**)] | 0% yield | 10% yield; 20:80 dr | 0% yield | 0% yield |
| [Co(**P3**)] | 0% yield | 13% yield; 43:57 dr | 0% yield | 0% yield |
| [Co(**P4**)] | 3% yield | 52% yield; 21:79 dr | 0% yield | 0% yield |
| [Co(**P5**)] | 0% yield | 20% yield; 33:67 dr | 0% yield | 0% yield |
| [Co(**P6**)] | 52% yield; 54:46 dr | 40% yield; 36:64 dr | 0% yield | 0% yield |

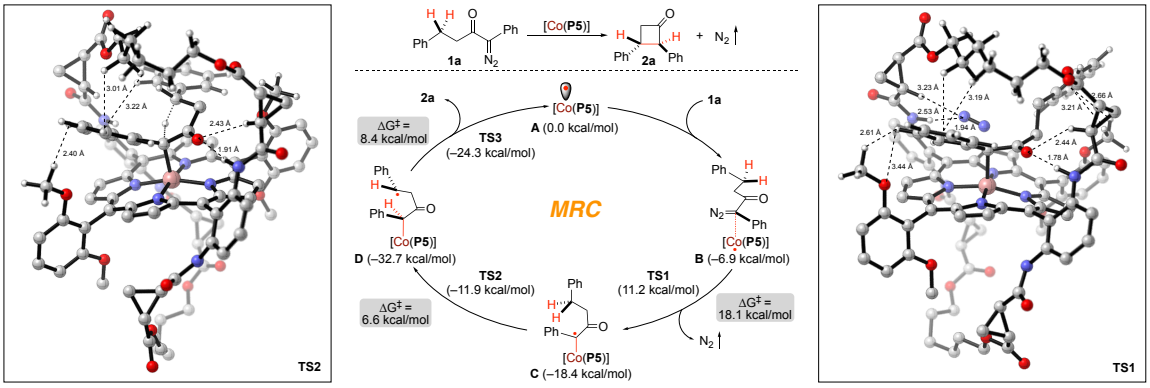



of the relative acidity of the tertiary α-C–H bonds. The only exception was observed for product **2o**, diastereoselectivity of which was decreased after the purification (Table 1; entry 15), which is presumably a result of the less steric hindrance of the alkyne group. It is worth mentioning that the Co(II)-based catalytic process for the synthesis of cyclobutanone derivatives could be readily scaled up under the same condition as exemplified by the stereoselective syntheses of optically active cyclobutanones **2a**, **2j** and **2q** on 1.0 mmol scale in similarly good yields with the same level of high enantioselectivities (Table 1; entries 1, 10 and 17).

### 2.2.3 Mechanistic Studies

To gain insights into this metalloradical process, combined computational and experimental studies were conducted to explore the proposed stepwise radical mechanism for the Co(II)-catalyzed 1,4-C–H alkylation . Firstly, density functional theory (DFT) calculations were performed to elucidate the catalytic pathway for 1,4-C–H alkylation reaction of α-aryldiazoketone **1a** with the use of the actual catalyst [Co(**P5**)]

**Scheme 2.3. DFT Study on Catalytic Pathway for 1,4-C–H Alkylation of Dipheny-α-Diazoketone 1a by [Co(P5)]**[a]



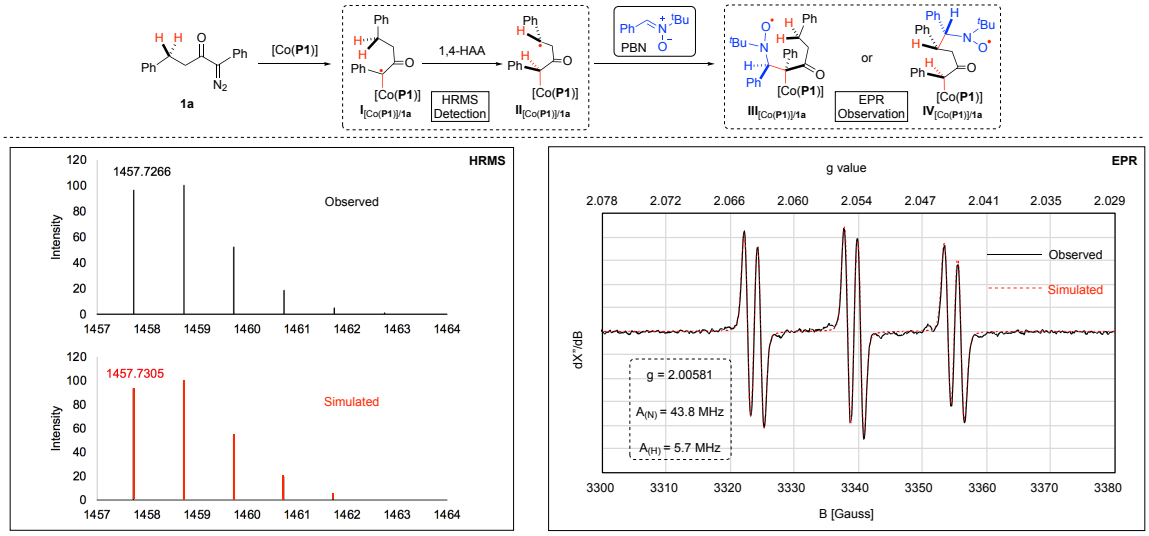

[a]Free energy profile of the [Co(**P5**)]-catalyzed 1,4-C–H alkylation. Density functional theory calculations were performed at SMD(diisopropylether)-BP86-D3(BJ)/def2TZVPP//BP86-D3(BJ)/def2SVP level of theory

(Scheme 2.3; see Experimental Section for details). The computational study reveals the initial formation of intermediate **B** between diazo **1a** and catalyst [Co(**P5**)] through a network of noncovalent attractions, including multiple H-bonds and p-interactions. This complexation process, which is exergonic by 6.9 kcal/mol, places the substrate underneath the bridge of the catalyst and positions the a-carbon atom of diazo **1a** in a close proximity to the Co center of [Co(**P5**)] (C---Co: ~2.70 Å) for further interaction. Upon metalloradical activation (MRA) by [Co(**P5**)], the bound **1a** undergoes the extrusion of dinitrogen to generate a-Co(III)-alkyl radical **C**. The metalloradical activation step, which is exergonic by 11.5 kcal/mol, is found to be associated with a relatively high but accessible activation barrier (**TS1**: $\Delta G^{\ddagger}$ = 18.1 kcal/mol). Subsequent 1,4-HAA of intermediate **C**, which is exergonic by 14.3 kcal/mol, gives rise to the corresponding δ-Co(III)-alkyl radical intermediate **D** with a relatively low activation barrier (**TS2**: $\Delta G^{\ddagger}$ = 6.5 kcal/mol). Such a low barrier for 1,4-HAA revealed by the DFT computation, which is uncommon for free

radical processes,[18] may be attributed to the presence of the multiple noncovalent interactions that stabilize transition state **TS2**. As illustrated by the computed model of **TS2** (Scheme 3A), these cooperative noncovalent attractive interactions orient the reacting substrate within the catalyst cavity in proximity with proper conformation to facilitate the 1,4-HAA. According to the DFT calculations, the final step of *4-exo-tet* cyclization of alkyl radical **D** via intramolecular radical substitution also has a relatively low activation barrier (**TS3**: $\Delta G^{\ddagger}$ = 8.4 kcal/mol), leading to the formation of cyclobutanone **2a** while regenerating catalyst [Co(**P5**)].

To experimentally detect α-Co(III)-alkyl radical **I** and d-Co(III)-alkyl radical **II**, the reaction mixture of a-aryldiazoketone **1a** with catalyst [Co(**P1**)] was analyzed by high-resolution mass spectrometry (HRMS) with electrospray ionization (ESI) in the absence of any additives as electron carriers (Scheme 2.4). The obtained spectrum clearly reveals a signal corresponding to $[(\mathbf{P1})Co–C(C_6H_5)(C(O)CH_2CH_2C_6H_5)]^+$ (m/z = 1457.7266), which resulted from neutral α-Co(III)-alkyl radical intermediate $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ or δ-Co(III)-alkyl radical intermediate $\mathbf{II}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ 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 from the formula $[C_{92}H_{102}CoN_8O_5]^+$ (see Experimental Section for details). In addition to the HRMS detection, we made multiple attempts to observe $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ and $\mathbf{II}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ by electron paramagnetic resonance (EPR) without success. This negative outcome of EPR observation was attributed to the fleeting nature of the alkyl radical intermediates as a result of facile 1,4-HAA and RS steps, as revealed from DFT calculations. Accordingly, the common spin trap phenyl *N-tert*-butyl-α-phenylnitrone(PBN) was employed to trap $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ or $\mathbf{II}_{[Co(\mathbf{P1})]/\mathbf{1a}}$, which resulted in the

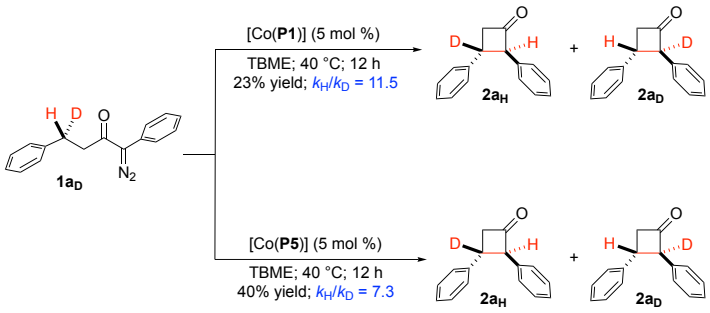
**Scheme 2.4. Detection of Co(III)-Alkyl Radical Intermediates by HRMS and Trapping by Spin Trap PBN for EPR Observation**




generation of radicals $\mathbf{III}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1a}}$ or $\mathbf{IV}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1a}}$ that could be successfully observed by EPR at room temperature (Scheme 2.3B; see Experimental Section for details). The observed triplet of doublet signals in the isotropic EPR spectrum could be fittingly simulated on the basis of hyperfine couplings by $^{14}$N ($I$ = 1) and $^{1}$H ($I$ = 1/2): g = 2.00581; $A_{(N)}$ = 43.9 MHz; $A_{(H)}$ = 5.7 MHz.

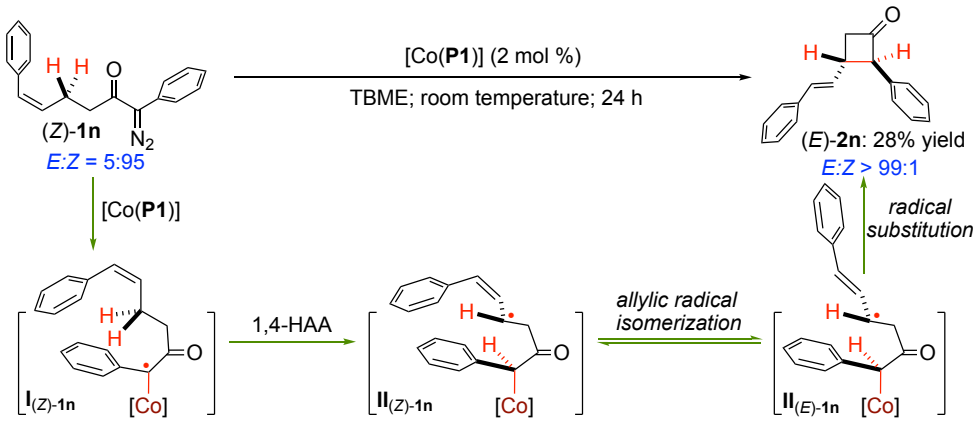
To further study the 1,4-HAA step in the catalytic process, monodeuterated diazo $\mathbf{1a_D}$ was prepared as the substrate for the study of kinetic isotopic effect (KIE) using both achiral catalyst [Co(**P1**)] and chiral catalyst [Co(**P5**)] (Scheme 2.5). The KIE values for the

**Scheme 2.5. Determination of Kinetic Isotope Effects**



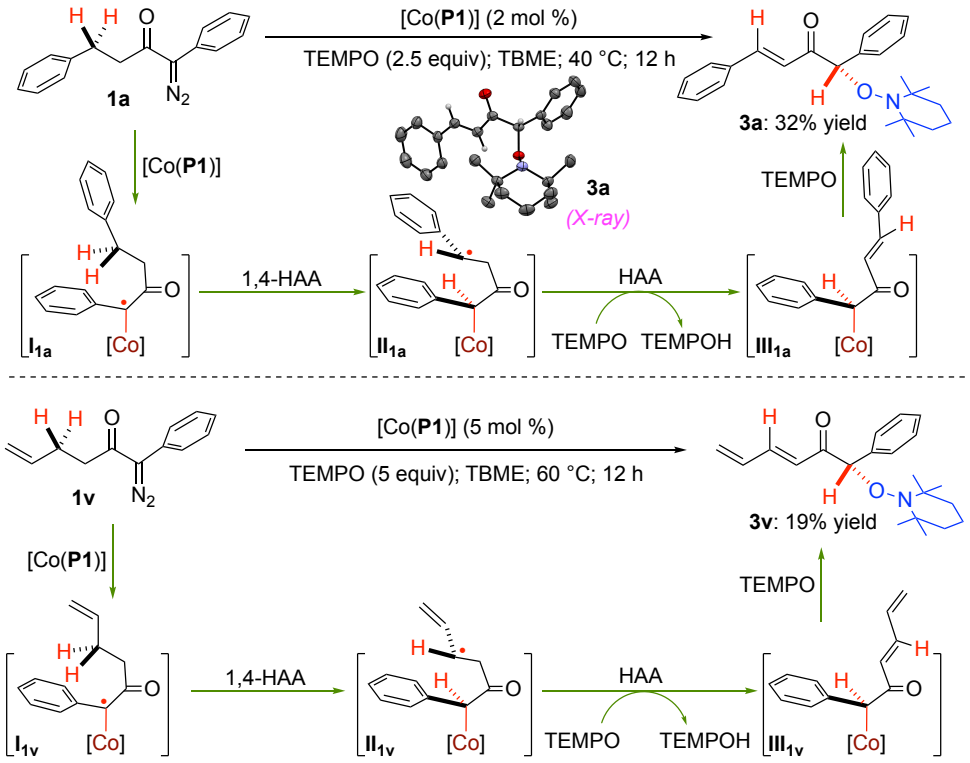
catalytic reaction of diazo **1a$_D$** by [Co(**P1**)] and [Co(**P5**)] were determined to be 11.5 and 7.3, respectively. These large values of primary KIE are in good agreement with the proposed step of homolytic C–H bond cleavage via intramolecular H-atom abstraction by α-Co(III)-alkyl radical intermediate **I**. In general, primary KIE for nonlinear transition state (TS) are lower than those for more linear TS. The results from our experiment indicate that a more bent TS was encountered when bridged catalyst [Co(**P5**)] was applied for the reaction since a smaller KIE value was observed.

**Scheme 2.6. Probing of δ-Co(III)-Allylic Radical Intermediate via Olefin Isomerization**




To further probe the existence of d-Co(III)-alkyl radical intermediate **II**, (*Z*)-**1n** was employed as the substrate for 1,4-C–H alkylation reaction using [Co(**P1)**] as the catalyst (Scheme 2.6). Like the catalytic reaction by [Co(**P5)**] (Table 1; entry 14), it was found that (*E*)-**2n** was generated as the only product, indicating isomerization of the olefin configuration during the catalytic process. The formation of (*E*)-**2n** from (*Z*)-**1n** implies the involvement of δ-Co(III)-allylic radical **II**$_{(E)\text{-}1n}$, which could be generated through isomerization of δ-Co(III)-allylic radical **II**$_{(Z)\text{-}1n}$.

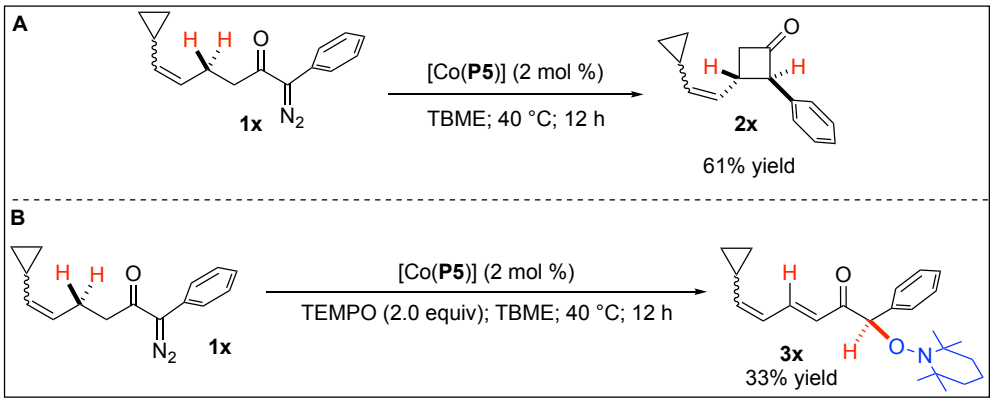
**Scheme 2.7. Trapping and Hydrogen-Atom Abstracting of Alkyl Radical Intermediates by TEMPO**




To directly trap the alkyl radical intermediate, the catalytic reaction of **1a** using [Co(**P1**)] as the catalyst was conducted in the presence of TEMPO (Scheme 2.7). Interestingly, TEMPO-trapping product **3a** was isolated in 32% yield, the structure of which was confirmed by X-ray crystallography. Formation of **3a** further implies the initial generation of α-Co(III)-alkyl radical $\mathbf{I_{1a}}$ by MRA, followed by 1,4-HAA to deliver δ-Co(III)-alkyl radical $\mathbf{II_{1a}}$ in the catalytic reaction. Instead of radical recombination with TEMPO, it is presumed to be more favorable for intermediate $\mathbf{II_{1a}}$ to undergo HAA by TEMPO, furnishing Co(III)-alkyl intermediate $\mathbf{V_{1a}}$ with the extended conjugation. Subsequent radical substitution with another molecule of TEMPO delivered the TEMPO-trapping product **3a**. In a similar pathway, the catalytic reaction of allyl diazoketone **1v** by [Co(**P1**)] in the presence of TEMPO could give TEMPO trapping product **3v**, indicating

the involvement of the corresponding radical intermediates $\mathbf{I_{1v}}$, $\mathbf{II_{1v}}$ and $\mathbf{V_{1v}}$. Furthermore, catalytic reactions of allyl diazoketone bearing a cyclopropyl ring as radical-clock substrate were performed with [Co(**P5**)] in both absence and presence of TEMPO to probe the life time of the corresponding δ-Co(III)-alkyl radical intermediate (Scheme 2.8). Since there was no evidence for formation of ring-opening product in both reactions, it was concluded that the radical substitution step and the TEMPO trapping process were all faster than the ring-opening of cyclopropane (with a rate-constant of $8.6\times10^{7}$ $s^{-1}$ at 298 K) [19] within the cavity-like ligand environment of the catalyst (see Experimental Section for details).

**Scheme 2.8. Radical Clock Reactions in Absence and Presence of TEMPO**

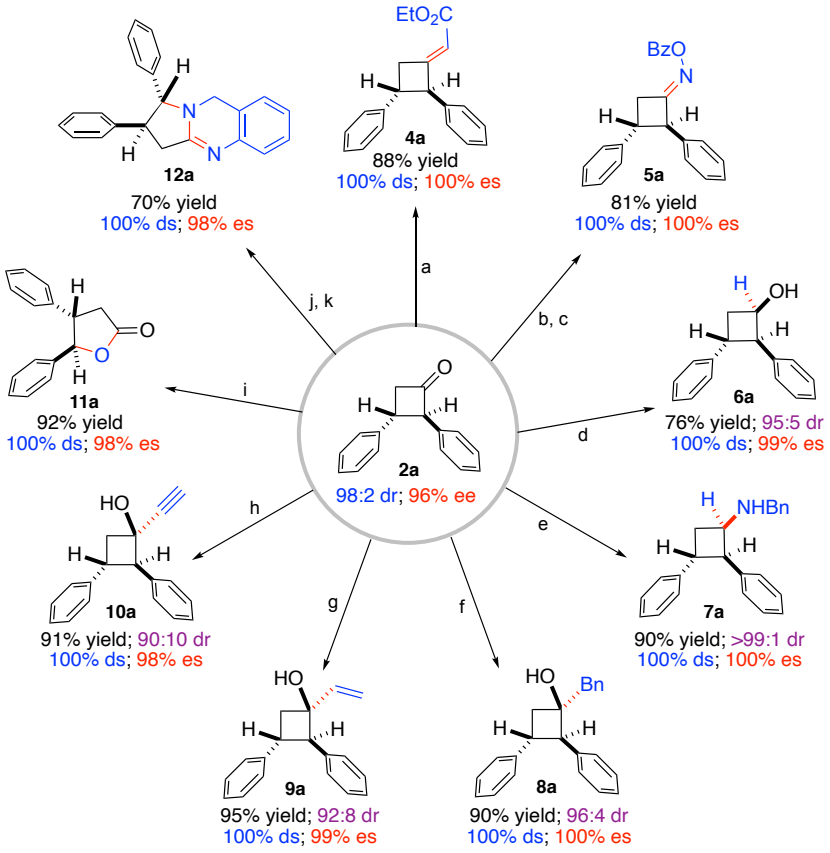



### 2.2.4 Synthetic Applications

Considering that the resulting enantioenriched cyclobutanones contain both versatile carbonyl group and strained four-membered structure, they may serve as useful intermediates for stereoselective organic synthesis (Scheme 2.8). To demonstrate the synthetic utility of this methodology, we carried out a series of synthetic transformations using enantioenriched cyclobutanone **2a** (96% ee) as the model reactant. For example, cyclobutanone **2a** could undergo efficient Horner-Wadsworth-Emmons reaction to provide the corresponding chiral methylenecyclobutane **4a** in high yield without the loss of either

the diastereopurity or the enantiopurity. Cyclobutanone **2a** could also be stereospecifically converted to the corresponding *O*-benzoyl oxime **5a**, which are known to undergo various ring-opening transformations.[20] In addition, **2a** could undergo both efficient reduction and reductive amination, allowing for the production of chiral cyclobutanol **6a** and cyclobutanamine **7a**, respectively, with excellent diastereoselectivities. Moreover, the ketone functionality in cyclobutanone **2a** could undergo nucleophilic addition with Grignard reagents such as benzylmagnesium chloride, vinylmagnesium bromide and ethynylmagnesium bromide to provide corresponding cyclobutanols **8a**, **9a** and **10a**

**Scheme 2.9. Synthetic Transformations of Resulting Chiral Cyclobutanones from Co(II)-Catalyzed 1,4-C–H Alkylation**




(a) Triethyl Phosphonoacetate (1.5 equiv); Sodium Hydride (1.2 equiv); THF; RT; 12 h. (b) Hydroxylamine Hydrochloride (2.0 equiv); Pyridine; RT; 2 h. (c) Benzoyl Chloride (1.5 equiv); Triethylamine (2.0 equiv);

DCM; 0 ºC; 6 h. (d) Sodium Borohydride (1.0 equiv); MeOH; –78 ºC; 10 h. (e) Benzylamine (1.1 equiv); Sodium Triacetoxyborohydride (2.0 equiv); DCM; RT; 12 h. (f) Benzylmagnesium Chloride (1.5 equiv); THF; 0 ºC; 1 h. (g) Vinylmagnesium Bromide (1.5 equiv); THF; 0 ºC; 1 h. (h) Ethynylmagnesium Bromide (1.5 equiv); THF; 0 ºC; 1 h. (i) *m*-CPBA; DCM; 0 ºC; 2 h. (j) *o*-Aminobenzylamine (1.1 equiv); $CHCl_3$; 60 ºC; 9 h. (k) NCS (1.5 equiv); DCM; 0 ºC; 2 h.

bearing a newly-formed quaternary stereogenic center in excellent yields with effective control of diastereoselectivities. It is worth mentioning that tertiary cyclobutanols such as **8a**, **9a** and **10a** can be potentially employed for downstream functionalization via C–C bond cleavage.[21] In view of the wide applications of the chiral γ-lactone scaffold,[22] it was shown that γ-lactone **11a** could be efficiently generated from cyclobutanone **2a** through Baeyer-Villiger oxidation with the retention of the original stereochemical purity. Gratifyingly, chiral dihydroquinazoline **12a**, as a family of heterocycles with interesting biological activities,[23] could be synthesized from the reaction of **2a** with *o*-aminobenzylamine through simple two-step transformation.[24]

## 2.3 Conclusion

In summary, we have demonstrated the first catalytic system for asymmetric radical 1,4-C–H alkylation via Co(II)-based MRC that involves the typically challenging 1,4-hydrogen atom abstraction. The key to the successful development is the judicious modulation of $D_2$-symmetric chiral amidoporphyrin ligand to adopt desired steric, electronic and chiral environments around the Co(II)-metalloradical center that maximize a network of noncovalent attractive interactions in catalytic intermediates. With the bridged $D_2$-symmetric chiral amidoporphyrin 2,6-DiMeO-Hu($C_6$)Phyrin as the optimal supporting ligand, the Co(II)-based metalloradical system, which operates under mild conditions, can catalyze asymmetric 1,4-C–H alkylation of α-aryldiazoketones with varied electronic and

steric properties to construct chiral a,β-disubstituted cyclobutanones in good yields with high diastereoselectivities and enantioselectivities. The combined computational and experimental studies have shed light on the working details of this new catalytic process that proceeds through a stepwise radical mechanism, which is fundamentally different from the concerted C–H insertion by the existing catalytic systems involving metallocarbenes. As showcased with several enantiospecific transformations to other types of cyclic structures from the resulting enantioenriched a,β-disubstituted cyclobutanones, this Co(II)-based metalloradical system for asymmetric 1,4-C−H alkylation should find broad applications in organic synthesis. We envision that catalytic radical processes incorporating 1,4-H-atom abstraction as the key step may offer a general strategy for asymmetric construction of highly strained four-membered cyclic structures.

## 2.4 Experimental Section

### 2.4.1 General Consideration

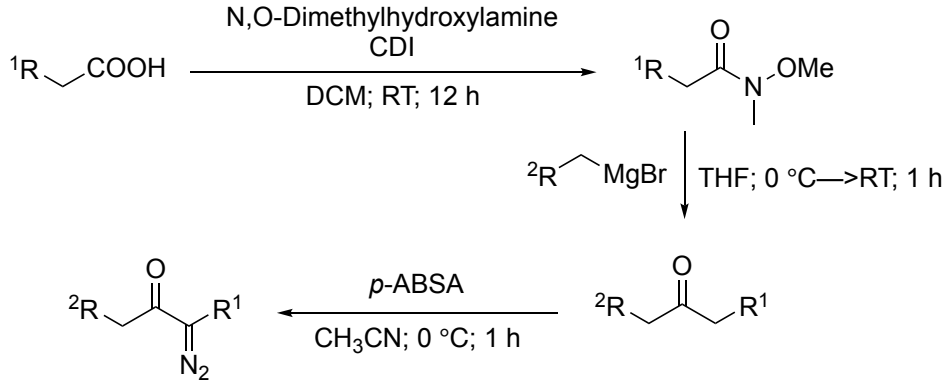
$^{1}H$ NMR, $^{13}C$ NMR and $^{19}F$ NMR were acquired using Varian Inova 400 MHz, Bruke 500 MHz and Varian 600 MHz spectrometer. Spectra were processed using MNova software (Mestrelab). For $^{1}H$ NMR spectra, chemical shifts are internally referenced to residual $CHCl_3$ signal (δ 7.26 ppm). Data are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), and coupling constants (Hz). For $^{13}C$ NMR spectra, chemical shifts are reported in ppm with residual $CHCl_3$ as the internal standard (δ 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart at the Mass Spectrometry Facility, Boston College. 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 ChiralPak Immobilized columns: OD-H, OJ-H, AD-H, IA, IB, IC and IE. Infrared (IR) spectra were recorded on a Termo-Scientific Nicolet Is5 System. X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin).

Unless otherwise noted, all reactions were conducted in oven-dried glassware under an inert atmosphere of dry nitrogen with standard vacuum line techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Anhydrous solvents as well as other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, Strem, Oakwood Products Inc., TCI, or Matrix Scientific and used as received unless otherwise stated. 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).

### 2.4.2 Substrate Synthesis

**General Procedure I for Substrate Synthesis**

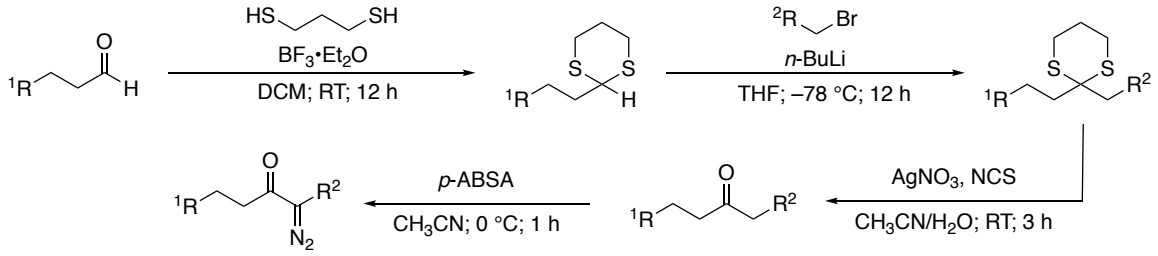



A 20-mL vial was charged with acid (1.0 equiv) and DCM, then carbonyldiimidazole (CDI) (1.2 equiv) was added portionwisely. After the solution was stirred at room temperature for 1 h, N,O-dimethylhydroxylamine (1.5 equiv) was added. Then the solution was stirred for another 12 h for completion. Water was added to the resulting solution and the aqueous layer was extracted with DCM. The combined organic layers were dried over $Na_2SO_4$. After concentrated under vacuum, the resulting Weinreb amide was used without further purification.

To a solution of Weinreb amide (1.0 equiv) in THF, the corresponding Grignard reagent (1.1 equiv) was added dropwisely at 0 °C. The reaction was then warmed up to room temperature and stirred for another 3 h. The reaction was then quenched by saturated $NH_4Cl$ solution. The aqueous layer was extracted with EtOAc. The combined organic layers were then dried over $Na_2SO_4$. After concentrated under vacuum, the resulting ketone product was used without further purification.

A 20-mL vial was charged with ketone (1.0 equiv), 4-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.2 equiv) and $CH_3CN$. The resulting solution was then cool to 0 °C. To the solution 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (1.5 equiv) was added dropwisely at 0 °C. The resulting solution was stirred at 0 °C for 1 hour. After concentrated under vacuum, the resulting diazo product was then purified by flash chromatography (Hexanes/ EtOAc = 10/1).

**General Procedure II for Substrate Synthesis**




Boron trifluoride ethyl ether complex (0.1 equiv) was added dropwisely to a solution of aldehyde (1.0 equiv) and 1,3-propanedithiol (1.5 equiv) in DCM. After 12 h at room temperature the reaction was terminated by addition of $NaHCO_3$ solution and extracted with DCM. The combined organic phases were dried over $Na_2SO_4$, filtered and evaporated under reduced pressure. After concentrated under vacuum, the resulting product was used without further purification.

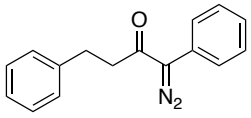
To a solution of dithiane (1.0 equiv) in dry THF, *n*-BuLi (2.5 M, 1.1 equiv) was added at –78 °C. Bromide (1.1 equiv) was then added slowly and reaction continued for 1h. After completion of the reaction, aqueous $NH_4Cl$ was added to the reaction mixture. Solvent THF was evaporated and the residue was extracted with EtOAc. The organic layer was dried over anhydrous $Na_2SO_4$, concentrated and the resulting product was used without further purification.

A 20-mL vial was charged with dithiane (1.0 equiv), *N*-Chlorosuccinimide(NCS) (2.0 equiv) and $AgNO_3$ (5.0 equiv), then a mixture of $CH_3CN$ and water was added as solvent for the reaction. The resulting solution was stirred at room temperature until the reaction complete. After completion, the resulting solution was extracted with EtOAc. The combined organic phases were dried over $Na_2SO_4$, filtered and evaporated under reduced pressure. Then the resulting product was used without further purification.

A 20-mL vial was charged with ketone (1.0 equiv), 4-Acetamidobenzenesulfonyl azide (*p*-ABSA) (1.2 equiv) and $CH_3CN$. The resulting solution was then cool to 0 °C. To the solution 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (1.5 equiv.) was added dropwisely at 0 °C. The resulting solution was stirred at 0 °C for 1 hour. After concentrated under vacuum, the resulting diazo product was then purified by flash chromatography (column condition: Hexanes/ EtOAc = 10/1).

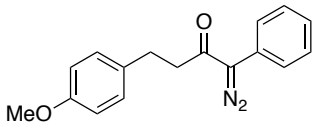
### 2.4.3 Characterization of Diazo Substrates

**1-Diazo-1,4-diphenylbutan-2-one (1a)**



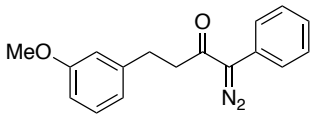

Following **general procedure I**. Orange solid. Yield: 67%. $R_f$ = 0.53 (Hexanes/ EtOAc = 8/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.18 – 7.13 (m, 3H), 2.99 (t, *J* = 7.5, 2H), 2.84 (t, *J* = 7.5 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 192.08, 140.81, 129.18, 128.71, 128.58, 127.25, 126.45, 126.24, 125.58, 72.32, 40.95, 30.85. IR (neat, $cm^{-1}$): 3027.33, 2078.40, 1625.61, 1607.32, 1360.21, 1229.27, 748.57, 686.39. HRMS (DART) ($[M+H]^+$): Calcd. for $C_{16}H_{15}N_2O$: 251.1179, found: 251.1184.

**1-Diazo-4-(4-methoxyphenyl)-1-phenylbutan-2-one (1b)**



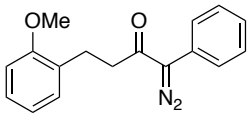
Following **general procedure I**. Orange solid. Yield: 56%. $R_f$ = 0.40 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.28 – 7.23 (m, 1H), 7.14 – 7.09 (m, 2H), 6.86 – 6.80 (m, 2H), 3.78 (s, 3H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 192.15, 158.22, 132.78, 129.49, 129.12, 127.16, 126.25, 125.58, 114.06, 72.41, 55.36, 41.18, 29.97. IR (neat, $cm^{-1}$): 3007.43, 2952.10, 2073.89, 1630.12, 1509.60, 1184.49, 903.97,752.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}N_2O_2$: 281.1284, found: 281.1272.

**1-Diazo-4-(3-methoxyphenyl)-1-phenylbutan-2-one (1c)**



Following **general procedure I**. Orange solid. Yield: 55%. $R_f$ = 0.34 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$) 7.46 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.18 (m, 2H), 6.80 – 6.75 (m, 3H), 3.79 (s, 3H), 3.01 (t, *J* = 7.7 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 191.87, 159.85, 142.39, 129.67, 129.14, 127.19, 126.15, 125.55, 120.87, 114.27, 111.74, 75.01, 57.82, 43.37, 33.41. IR (neat, $cm^{-1}$): 2936.70, 2834.04, 2083.98, 1637.99, 1498.44, 1189.40, 759.14, 690.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}N_2O_2$: 281.1284, found: 281.1290.

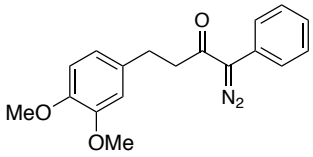
**1-Diazo-4-(2-methoxyphenyl)-1-phenylbutan-2-one (1d)**



Following **general procedure I**. Orange solid. Yield: 56%. $R_f$ = 0.43 (Hexanes/ EtOAc = 8/1). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.21 (td, *J* = 7.9, 1.7 Hz, 1H), 7.17 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.82 (s,

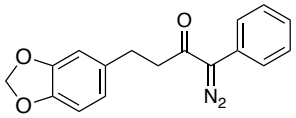
3H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.88 (t, *J* = 7.8 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 192.78, 157.60, 130.40, 129.07, 128.83, 127.85, 126.95, 126.02, 125.81, 120.66, 110.32, 72.30, 55.24, 39.43, 26.60. IR (neat, $cm^{-1}$): 2925.95, 2068.23, 1646.53, 1493.83, 1242.37, 1197.65, 1107.80, 753.85. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}N_2O_2$: 281.1284, found: 281.1295.

**1-Diazo-4-(3,4-dimethoxyphenyl)-1-phenylbutan-2-one (1e)**




Following **general procedure I**. Yellow solid. Yield: 46%. $R_f$ = 0.12 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$):δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.30 – 7.23 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.75 – 6.71 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 192.08, 149.11, 147.73, 133.40, 129.18, 127.25, 126.29, 125.60, 120.43, 111.98, 111.55, 72.56, 56.09, 55.99, 41.17, 30.67. IR (neat, $cm^{-1}$): 3018.34, 2938.95, 2839.59, 2066.40, 1643.45, 1513.39, 1022.46, 752.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{19}N_2O_3$: 311.1390, found: 311.1399.

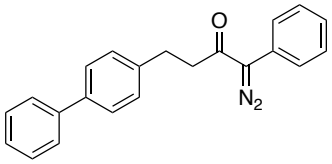
**4-(Benzo[*d*][1,3]dioxol-5-yl)-1-diazo-1-phenylbutan-2-one (1f)**




Following **general procedure I**. Yellow solid. Yield: 76%. $R_f$ = 0.44 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.70 – 6.68 (m, 1H), 6.67 – 6.63 (m, 1H), 5.92 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 191.90, 147.83, 146.14, 134.61, 129.19, 127.26, 126.26, 125.59, 121.39, 109.05, 108.45, 101.00, 72.47, 41.17, 30.57. IR (neat, $cm^{-}$

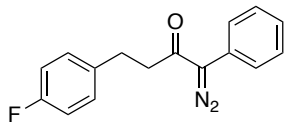
$^{1}$): 3057.42, 2885.14, 2082.94, 1636.77, 1498.51,1186.65, 1041.46, 758.88. HRMS (DART) ($[M+H-N_2]^+$) Calcd. for $C_{17}H_{15}O_3$: 267.1016, found: 267.1018.

**4-([1,1'-Biphenyl]-4-yl)-1-diazo-1-phenylbutan-2-one (1g)**



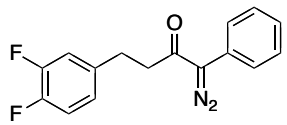
Following **general procedure I**. Yellow solid. Yield: 96%. $R_f$ = 0.44 (Hexanes/ EtOAc = 8/1). $^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 1.5 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.45 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 7.30 – 7.24 (m, 4H), 3.08 (t, *J* = 7.7 Hz, 2H), 2.93 (t, *J* = 7.8 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 191.92, 141.02, 139.90, 139.42, 129.18, 129.00, 128.87, 127.41, 127.27, 127.12, 126.21, 125.56, 124.27, 72.48, 40.84, 30.41. IR (neat, $cm^{-1}$): 3031.46, 2084.30, 1606.75, 1494.90, 1360.88, 1229.23, 1150.80, 750.21. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{19}N_2O$: 327.1492, found: 327.1489.

**1-Diazo-4-(4-fluorophenyl)-1-phenylbutan-2-one (1h)**



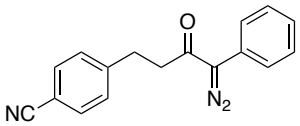
Following **general procedure I**. Orange solid. Yield: 36%. $R_f$ = 0.48 (Hexanes/ EtOAc = 8/1). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.14 (m, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 191.79, 161.64 (d, *J* = 244.2 Hz), 136.43 (d, *J* = 2.7 Hz), 130.01 (d, *J* = 7.8 Hz), 129.21, 127.31, 126.29, 125.48, 115.45 (d, *J* = 21.3 Hz), 72.52, 40.87, 29.96. $^{19}$F NMR (470 MHz, $CDCl_3$) δ –116.93. IR (neat, $cm^{-1}$): 3064.62, 2922.53, 2054.36, 1636.26, 1507,10, 1214.24, 830.13, 750.30. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{14}N_2OF$: 269.1085, found: 269.1032.

**1-Diazo-4-(3,4-difluorophenyl)-1-phenylbutan-2-one (1i)**



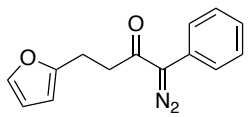
Following **general procedure I**. Orange solid. Yield: 75%. $R_f$ = 0.38 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.09 – 6.97 (m, 2H), 6.94 – 6.89 (m, 1H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.86 (t, *J* = 7.8 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 191.15, 150.20 (dd, *J* = 247.9, 12.8 Hz), 149.01 (dd, *J* = 246.2, 12.6 Hz), 137.81 (m), 129.13, 127.23, 126.13 (m), 125.36, 124.43 (m), 117.33 (d, *J* = 16.9 Hz), 117.12, 72.42, 40.25, 29.59. $^{19}$F NMR (470 MHz, $CDCl_3$): δ –137.98 (m), –141.57 (m). IR (neat, $cm^{-1}$): 3054.17, 3034.35, 2942.05, 2086.78, 1738.66, 1631.48, 1514.97, 1190.53. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{13}N_2OF_2$: 287.0990, found: 287.0980.

**4-(4-Diazo-3-oxo-4-phenylbutyl)benzonitrile (1j)**



Following **general procedure I**. Orange solid. Yield: 65%. $R_f$ = 0.15 (Hexanes/ EtOAc = 8/1). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 190.88, 146.50, 132.42, 129.43, 129.22, 127.42, 126.18, 125.18, 118.99, 110.29, 72.57, 39.78, 30.48. IR (neat, $cm^{-1}$): 3054.26, 2936.59, 2223.37, 2074.22, 1632.17. 1496.38, 1412.87, 1184.01. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{14}N_3O$: 276.1131, found: 276.1135.

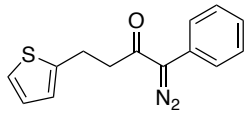
**1-Diazo-4-(furan-2-yl)-1-phenylbutan-2-one (1k)**



Following **general procedure I**. Orange solid. Yield: 68%. $R_f$ = 0.48 (Hexanes/ EtOAc = 8/1). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.30 (m, 1H), 7.29 – 7.23 (m, 1H), 6.28 (d, *J* = 1.7 Hz, 1H), 6.04 (d, *J* = 3.1 Hz, 1H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H).$^{13}$C

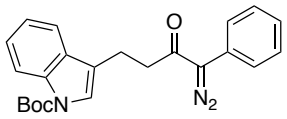
NMR (101 MHz, $CDCl_3$): δ 191.32, 154.28, 141.36, 129.17, 127.22, 126.19, 125.51, 110.42, 105.71, 72.57, 37.39, 23.05. IR (neat, $cm^{-1}$): 3058.16, 2915.59, 2065.94, 1642.38, 1496.23, 1203.19, 1010.16, 729.22. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{13}N_2O_2$: 241.0972, found: 241.0960.

**1-Diazo-1-phenyl-4-(thiophen-2-yl)butan-2-one (1l)**



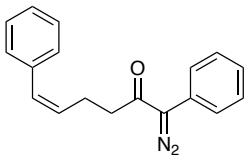
Following **general procedure I**. Orange solid. Yield: 69%. $R_f$ = 0.45 (Hexanes/ EtOAc = 8/1). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.13 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.84 – 6.82 (m, 1H), 3.27 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 191.14, 143.18, 129.06, 127.15, 126.88, 126.61, 126.13, 124.89, 123.57, 71.36, 40.76, 24.63. IR (neat, $cm^{-1}$): 3111.50, 2062.39, 1649.00, 1494.37, 1194.60, 1112.50, 752.60, 690.87. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{13}N_2OS$: 257.0743, found: 257.0752.

***tert*-Butyl 3-(4-diazo-3-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate (1m)**



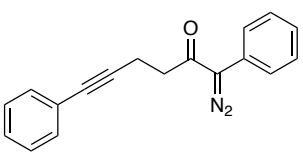
Following **general procedure I**. Orange oil. Yield: 91%. $R_f$ = 0.53 (Hexanes/ EtOAc = 8/1). $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.23 (m, 2H), 3.13 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 1.67 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 191.89, 149.84, 135.63, 130.35, 129.16, 127.26, 126.29, 125.52, 124.54, 122.88, 122.58, 119.54, 118.88, 115.44, 72.55, 38.78, 29.81, 28.32, 19.97. IR (neat, $cm^{-1}$) 3055.79, 2977.46, 2928.71, 2068.50, 1727.61, 1647.05, 1368.39, 747.79. HRMS (DART) ($[M+H-N_2]^+$) Calcd. for $C_{23}H_{24}NO_3$: 362.1751, found: 362.1747.

**(*Z*)-1-Diazo-1,6-diphenylhex-5-en-2-one (1n)**



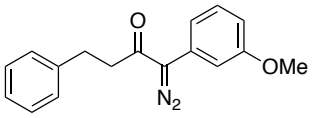
Following **general procedure I**. Orange solid. Yield: 65% (*Z:E* = 95:5). $R_f$ = 0.55 (Hexanes/ EtOAc = 8/1). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.22 (m, 4H), 6.49 (d, *J* = 11.6 Hz, 1H), 5.67 (dt, *J* = 11.6, 6.7 Hz, 1H), 2.79 – 2.70 (m, 4H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 192.05, 142.19, 137.26, 130.43, 129.137, 128.83, 128.38, 127.19, 126.92, 126.18, 125.57, 72.35 39.10, 23.76. IR (neat, $cm^{-1}$): 3079.26, 2909.00, 2070.79, 1655.00, 1496.92, 1367.54, 1193.91, 770.08. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{17}N_2O$: 277.1335, found: 277.1333.

**1-Diazo-1,6-diphenylhex-5-yn-2-one (1o)**



Following **general procedure I**. Orange solid. Yield: 65%. $R_f$ = 0.44 (Hexanes/ EtOAc = 8/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.33 (m, 4H), 7.32 – 7.23 (m, 4H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.82 (t, *J* = 7.3 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 190.84, 131.73, 129.25, 128.35, 127.95, 127.36, 126.28, 125.45, 123.62, 88.32, 81.44, 72.75, 38.04, 15.10. IR (neat, $cm^{-1}$): 3056.82, 2917.54, 2066.77, 1640.53, 1489.93, 1200.84, 1115.09, 751.32. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{15}N_2O$: 275.1179, found: 275.1183.

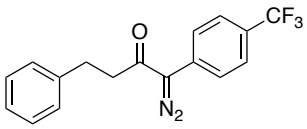
**1-Diazo-1-(3-methoxyphenyl)-4-phenylbutan-2-one (1p)**



Following **general procedure I**. Orange solid. Yield: 28%. $R_f$ = 0.34 (Hexanes/ EtOAc = 8/1). 1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.24 – 7.20 (m, 3H), 7.15 (s, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.82 (s, 3H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.90 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) : δ 191.85, 160.18, 140.77, 130.05, 128.68, 128.54, 126.94, 126.42, 118.18, 112.86, 111.67, 72.55, 55.42, 40.98, 30.78. IR (neat, $cm^{-1}$): 3059.82,

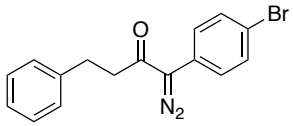
2941.59, 2074.61, 1636.55, 1449.39, 1230.01, 1074.58, 1042.59. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{17}N_2O_2$: 281.1284, found: 281.1272.

**1-Diazo-4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-2-one (1q)**



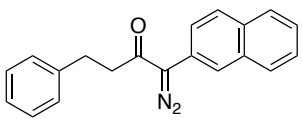
Following **general procedure I**. Yellow solid. Yield: 60%. $R_f$ = 0.50 (Hexanes/ EtOAc = 8/1) $^1$H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.61 (m, 4H), 7.34 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 191.23, 140.53, 129.94, 128.80, 128.58, 128.54(q, *J* = 27.5 Hz), 126.59, 125.99 (q, *J* = 3.7 Hz), 125.17, 124.18 (q, *J* = 271.9 Hz), 72.44, 40.87, 30.70. $^{19}$F NMR (470 MHz, $CDCl_3$) δ –62.62. IR (neat, cm$^{-1}$): 3029.18, 2084.99, 1718.20, 1613.86, 1322.12, 1162.36, 1065.69, 1016.29. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{14}N_2OF_3$: 319.1053, found: 319.1049.

**1-(4-Bromophenyl)-1-diazo-4-phenylbutan-2-one (1r)**



Following **general procedure II**. Orange solid. Yield: 56%. $R_f$ = 0.46 (Hexanes/ EtOAc = 8/1). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.50 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 192.68, 160.97, 143.20, 140.64, 131.29, 128.77.08, 128.58, 126.55, 119.48, 73.00, 40.99, 30.77. IR (neat, cm$^{-1}$): 2928.11, 2065.89, 1645.65, 1488.16, 1370.60, 1201.14, 1111.33, 1005.61. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{14}N_2OBr$: 329.0284, found: 329.0286.

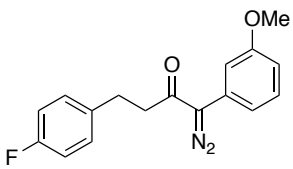
**1-Diazo-1-(naphthalen-2-yl)-4-phenylbutan-2-one (1s)**



Following **general procedure I**. Orange solid. Yield: 46%. $R_f$ = 0.40 (Hexanes/ EtOAc = 8/1). $^1$H NMR (400 MHz, $CDCl_3$):δ

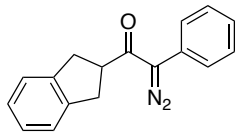
8.04 (s, 1H), 7.88 (d, $J$ = 9.0 Hz, 1H), 7.84 (d, $J$ = 7.1 Hz, 2H), 7.57 – 7.46 (m, 3H), 7.32 (t, $J$ = 7.6 Hz, 2H), 7.25 (d, $J$ = 7.1 Hz, 3H), 3.70 (t, $J$ = 7.7 Hz, 2H), 2.96 (t, $J$ = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 192.22, 140.79, 133.65, 132.22, 128.89, 128.72, 128.59, 127.98, 127.76, 126.78, 126.46, 126.40, 125.28, 123.53, 122.69, 72.85, 41.00, 30.83. IR (neat, cm$^{-1}$): 3054.50, 3024.78, 2944.19, 2082.41, 1628.82, 1226.61, 813.07, 679.26. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{17}N_2O$: 301.1335, found: 301.1332.

**1-Diazo-4-(4-fluorophenyl)-1-(3-methoxyphenyl)butan-2-one (1t)**




Following **general procedure I**. Orange solid. Yield: 64%. $R_f$ = 0.32 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$):δ 7.31 (t, $J$ = 8.1 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.00 – 6.94 (m, 3H), 6.83 – 6.78 (m, 1H), 3.82 (s, 3H), 3.01 (t, $J$ = 7.5 Hz, 2H), 2.86 (t, $J$ = 7.4 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 191.68, 161.65 (d, $J$ = 244.2 Hz), 160.23, 136.41, 130.12, 130.00 (d, $J$ = 7.8 Hz), 126.86, 118.26 (m), 115.46 (d, $J$ = 21.0 Hz), 112.91, 111.96, 72.66, 55.46, 40.95, 29.94. $^{19}$F NMR (470 MHz, $CDCl_3$) δ –116.92 (m). IR (neat, cm$^{-1}$): 3015.40, 2940.66, 2073.61, 1639.49, 1508.18, 1217.77, 822.15, 682.13. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{16}N_2O_2F$: 299.1190, found: 299.1184.

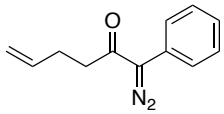
**2-Diazo-1-(2,3-dihydro-1*H*-inden-2-yl)-2-phenylethan-1-one (1u)**




Following **general procedure I**. Orange Solid. Yield: 82%. $R_f$ = 0.55 (Hexanes/ EtOAc = 8/1). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.49 – 7.40 (m, 2H), 7.33 – 7.27 (m, 1H), 7.25 – 7.15 (m, 4H), 3.78 (pd, $J$ = 8.5, 2.9 Hz, 1H), 3.42 (dd, $J$ = 15.7, 8.1 Hz, 2H), 3.18 (dd, $J$ = 15.6, 8.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$):δ 194.27, 141.39, 129.17, 127.23, 126.80, 125.66, 124.66, 124.40, 71.72, 47.41, 36.02. IR (neat, cm$^{-1}$): 3022.66, 2939.59, 2064.19, 1642.90, 1496.12, 1362.85,

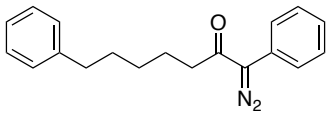
1215.42, 748.07. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{15}N_2O$: 263.1179, found: 263.1170.

**1-Diazo-1-phenylhex-5-en-2-one (1v)**



Following **general procedure I**. Orange oil. Yield: 60%. $R_f$ = 0.44 (Hexanes/ EtOAc = 8/1). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 1H), 5.86 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.49 – 2.43 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 191.90, 136.77, 129.02, 126.98, 125.92, 125.52, 115.72, 72.16, 38.22, 28.54. IR (neat, cm$^{-1}$): 3060.15, 2977.70, 2068.68, 1776.62, 1647.87, 1497.13, 1206.78, 913.14. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{12}H_{13}N_2O$: 201.1022, found 201.1028.

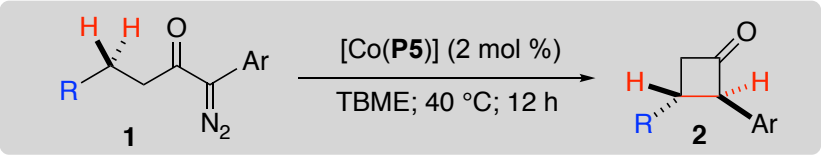
**1-Diazo-1,7-diphenylheptan-2-one (1w)**



Following **general procedure I**. Orange Oil. Yield: 94%. $R_f$ = 0.46 (Hexanes/ EtOAc = 8/1). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.28 (dt, *J* = 16.9, 7.6 Hz, 3H), 7.22 – 7.17 (m, 3H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 2H), 1.46 – 1.39 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 192.91, 142.51, 129.06, 128.45, 128.33, 126.97, 125.90, 125.74, 125.66, 72.04, 39.05, 35.77, 31.25, 28.86, 24.54. IR (neat, cm$^{-1}$): 3025.11, 2931.02, 2856.53, 2066.77, 1643.87, 1496.20, 1210.50, 905.80. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}N_2O$: 293.1648, found: 293.1638.

**2.4.4 Enantioselective Radical Cyclization**

**General Procedure for [Co(P5)]-Catalyzed Enantioselective Radical Cyclization**

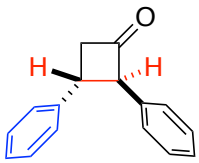



An oven-dried Schlenk tube was charged with diazo compound **1** (0.1 mmol) and [Co(**P5**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, *tert*-butyl methyl ether (TBME) (0.5 mL) was added via a gastight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **2**.

**Characterization of Cyclobutanone Products**

(All the dr value in the parenthesis indicates the dr from crude NMR before purification)

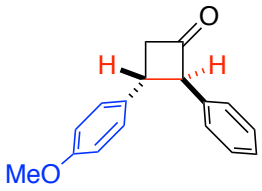
**(2*R*,3*R*)-2,3-Diphenylcyclobutan-1-one (2a) (1.0 mmol Scale)**




known compound.[25] Colorless oil (178 mg, 80% yield). 98:2 dr (91:9). $R_f$ = 0.33 (Hexanes/ EtOAc = 20/1). $[\alpha]_D^{20}$ = (–)-167.98° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 4H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 4H), 4.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.84 (q, *J* = 8.9 Hz, 1H), 3.46 (ddd, *J* = 17.2, 8.9, 1.8 Hz, 1H), 3.40 (ddd, *J* = 17.2, 9.0, 2.1 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 205.27, 142.64, 135.84, 128.97, 128.91, 127.47, 127.21, 127.12, 126.76, 71.65, 51.58, 36.96. IR (neat, $cm^{-1}$): 3027.29, 2929.41, 1779.01, 1681.33, 1495.22, 1073.96, 1030.06, 746.49. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{15}O$: 223.1117, found:

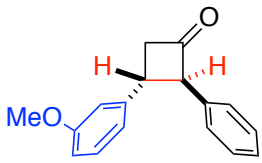
223.1116. HPLC analysis: ee = 96%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 9.82 min, $t_{minor}$ = 11.37 min.

**(2*R*,3*R*)-3-(4-Methoxyphenyl)-2-phenylcyclobutan-1-one (2b)**




Colorless oil (17.6 mg, 70% yield). 98:2 dr (87:13). $R_f$ = 0.32 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-175.36° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.26 (m, 5H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.55 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.77 (q, *J* = 8.9 Hz, 1H), 3.42 (ddd, *J* = 17.2, 8.9, 1.9 Hz, 1H), 3.34 (ddd, *J* = 17.2, 9.0, 2.2 Hz, 1H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 205.50, 158.73, 135.92, 134.71, 128.89, 127.77, 127.41, 127.20, 114.34, 71.78, 55.49, 51.73, 36.38. IR (neat, $cm^{-1}$): 3029.45, 2835.50, 1775.03, 1512.10, 1244.71, 1177.84, 1102.50, 1030.94, 1002.91, 827.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2$: 253.1223, found: 253.1228. HPLC analysis: ee = 92%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 43.14 min, $t_{minor}$ = 35.59 min.

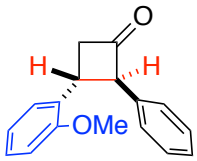
**(2*R*,3*R*)-3-(3-Methoxyphenyl)-2-phenylcyclobutan-1-one (2c)**




Colorless oil (19.4 mg, 77% yield). 98:2 dr (88:12). $R_f$ = 0.32 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-161.56° (c = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 4H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 6.83 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.80 (q, *J* = 8.6, 1H), 3.44 (ddd, *J* = 17.2, 9.0, 1.8 Hz, 1H), 3.38 (ddd, *J* = 17.2, 9.0, 2.0 Hz, 1H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 205.22, 160.12, 144.31, 135.83,130.03, 128.91, 127.46, 127.20, 119.03, 112.97, 112.04, 71.54, 55.41, 51.56, 37.04. IR (neat, $cm^{-1}$): 3027.90, 2936.28, 2835.59, 1779.13, 1600.54, 1489.41, 1157.35, 841.48. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2$: 253.1223, found: 253.1222. HPLC

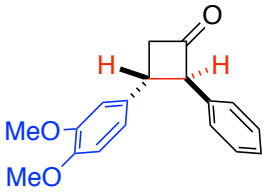
analysis: ee = 93%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 30.99 min, $t_{minor}$ = 29.60 min.

**(2*R*,3*R*)-3-(2-Methoxyphenyl)-2-phenylcyclobutan-1-one (2d)**




Colorless oil (19.1 mg, 76% yield). 95:5 dr (83:17). $R_f$ = 0.36 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-152.97° (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 5H), 7.29 – 7.22 (m, 2H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.92 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.78 (d, *J* = 8.8 Hz, 1H), 3.95 (q, *J* = 8.9 Hz, 1H), 3.81 (s, 3H), 3.41 (d, *J* = 8.9 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 206.90, 157.92, 136.46, 130.22, 128.70, 128.32, 127.66, 127.20, 127.10, 120.75, 110.74, 68.87, 55.29, 50.07, 33.37. IR (neat, $cm^{-1}$): 3027.17, 2922.01, 1776.80, 1600.44, 1492.58, 1462.14, 1244.24, 748.16. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2$: 253.1223, found: 253.1215. HPLC analysis: ee = 70%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 11.10 min, $t_{minor}$ = 12.16 min.

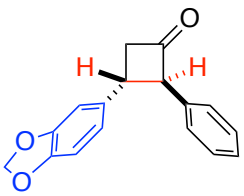
**(2*R*,3*R*)-3-(3,4-Dimethoxyphenyl)-2-phenylcyclobutan-1-one (2e)**




Colorless oil (20.1 mg, 71% yield). 98:2 dr (89:11). $R_f$ = 0.19 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-106.37° (c = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 2H), 7.31 – 7.23 (m, 3H), 6.96 – 6.84 (m, 3H), 4.57 (d, *J* = 8.8 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.76 (q, *J* = 9.2 Hz, 1H), 3.43 (ddd, *J* = 17.2, 8.9, 1.5 Hz, 1H), 3.35 (ddd, *J* = 17.2, 9.2, 1.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 205.39, 149.37, 148.22, 135.94, 135.24, 128.91, 127.45, 127.18, 118.61, 111.54, 110.12, 71.66, 56.14, 56.10, 51.72, 36.91. IR (neat, $cm^{-1}$): 3059.75, 2931.33, 1777.39, 1514.75, 1463.16, 1235.74, 1024.82, 697.25. HRMS (DART) ($[M+H]^+$)

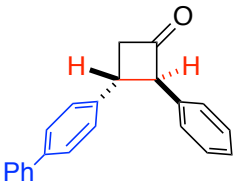
Calcd. for $C_{18}H_{19}O_3$: 283.1329, found: 283.1341. HPLC analysis: ee = 86%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 51.88 min, $t_{minor}$ = 40.52 min.

**(2*R*,3*R*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenylcyclobutan-1-one (2f)**



Colorless oil (23.0 mg, 86% yield). 98:2 dr (78:22). $R_f$ = 0.31 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-211.35° (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 3H), 6.86 – 6.83 (m, 1H), 6.82 – 6.78 (m, 2H), 5.97 (s, 2H), 4.53 (d, *J* = 8.9 Hz, 1H), 3.75 (q, *J* = 8.9 Hz, 1H), 3.41 (ddd, *J* = 17.2, 8.9, 2.0 Hz, 1H), 3.32 (ddd, *J* = 17.2, 9.0, 2.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 205.11, 148.26, 146.69, 136.54, 135.76, 128.92, 127.47, 127.18, 119.85, 108.54, 107.14, 101.28, 71.81, 51.71, 36.93. IR (neat, $cm^{-1}$): 3060.39, 2919.35, 1778.18, 1503.27, 1442.98, 1037.22, 932.39, 714.93. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{15}O_3$: 267.1016, found: 267.1018. HPLC analysis: ee = 96%. IC (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 18.03 min, $t_{minor}$ = 19.32 min.

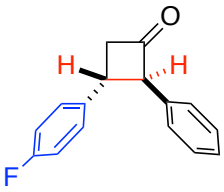
**(2*R*,3*R*)-3-([1,1'-Biphenyl]-4-yl)-2-phenylcyclobutan-1-one (2g)**



Colorless oil (23.5 mg, 79% yield). 99:1 dr (99:1). $R_f$ = 0.42 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-144.98° (c = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, CDCl3): δ 7.63 – 7.58 (m, 4H), 7.48 – 7.43 (m, 4H), 7.39 – 7.35 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 4.65 (d, *J* = 8.7 Hz, 1H), 3.88 (q, *J* = 8.9 Hz, 1H), 3.49 (ddd, *J* = 17.2, 8.9, 1.8 Hz, 1H), 3.43 (ddd, *J* = 17.2, 9.0, 2.0 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 205.17, 141.67, 140.77, 140.16, 135.81, 128.98, 128.95, 127.69, 127.52, 127.51, 127.23, 127.22, 127.18, 71.73, 51.65, 36.76. IR (neat, $cm^{-1}$): 3057.56, 2921.77, 1776.92, 1600.23, 1494.93, 1447.73, 1102.93, 763.10. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{19}O$: 299.1430, found: 299.1434. HPLC analysis:

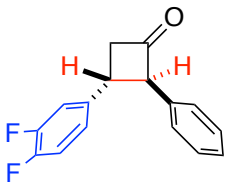
ee = 90%. IE (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 38.85 min, $t_{minor}$ = 35.42 min.

**(2*R*,3*R*)-3-(4-Fluorophenyl)-2-phenylcyclobutan-1-one (2h)**




Colorless oil (14.5 mg, 81% yield). 97:3 dr (86:14). $R_f$ = 0.40 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-113.17° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 4H), 7.30 – 7.24 (m, 3H), 7.06 (t, *J* = 8.5 Hz, 2H), 4.54 (d, *J* = 8.7 Hz, 1H), 3.80 (q, *J* = 8.9 Hz, 1H), 3.44 (ddd, *J* = 17.2, 8.9, 2.0 Hz, 1H), 3.34 (ddd, *J* = 17.2, 9.0, 2.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 204.62, 161.79 (d, *J* = 245.6 Hz), 138.17 (d, *J* = 3.3 Hz), 135.47, 128.82, 128.11 (d, *J* = 8.0 Hz), 127.42, 127.02, 115.65 (d, *J* = 21.5 Hz), 71.75, 51.53, 36.28. $^{19}$F NMR (564 MHz, $CDCl_3$) δ –115.71 (tt, *J* = 8.6, 5.1 Hz). IR (neat, $cm^{-1}$): 3030.45, 2923.39, 1780.35, 1603.10, 1509.86, 1223.97, 1157.83, 831.25. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{14}OF$: 241.1023, found: 241.1023. HPLC analysis: ee = 90%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 14.80 min, $t_{minor}$ = 17.06 min.

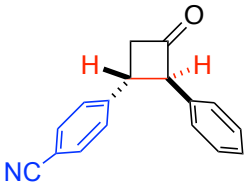
**(2*R*,3*R*)-3-(3,4-Difluorophenyl)-2-phenylcyclobutan-1-one (2i)**




Colorless oil (16.8 mg, 65% yield). 96:4 dr (85:15). $R_f$ = 0.40 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-132.17° (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$ δ 7.38 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 7.19 – 7.10 (m, 2H), 7.08 – 7.04 (m, 1H), 4.52 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.78 (q, *J* = 8.9 Hz, 1H), 3.45 (ddd, *J* = 17.2, 8.9, 2.0 Hz, 1H), 3.32 (ddd, *J* = 17.2, 9.0, 2.2 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 204.08, 150.43 (dd, *J* = 249.1, 12.8 Hz), 149.33 (dd, *J* = 247.9, 12.6 Hz), 139.45 (dd, *J* = 5.5, 3.8 Hz), 135.11, 128.90, 127.58, 126.98, 122.57 (dd, *J* = 6.3, 3.6 Hz), 117.58 (dd, *J* = 17.5, 0.8 Hz), 115.65 (d, *J* = 17.4 Hz),

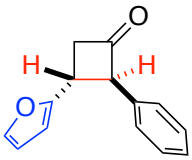
71.91, 51.56, 36.43. $^{19}$F NMR (376 MHz, $CDCl_3$) δ –136.86 (ddd, $J$ = 20.2, 11.2, 8.0 Hz), –140.06 (m). IR (neat, $cm^{-1}$): 3028.93, 2969.93, 1781.45, 1518.50, 1365.08, 1216.41, 1114.55, 1038.74. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{13}OF_2$: 259.0929, found: 259.0930. HPLC analysis: ee = 90%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 31.00 min, $t_{minor}$ = 36.54 min.

**4-((1*R*,2*R*)-3-Oxo-2-phenylcyclobutyl)benzonitrile (2j) (1.0 mmol Scale)**




Colorless oil (189 mg, 76% yield). 97:3 dr (90:10). $R_f$ = 0.37 (Hexanes/ EtOAc = 3/1). $[\alpha]_D^{20}$ = (–)-194.75° ($c$ = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 2H), 7.49 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.28 – 7.23 (m, 2H), 4.58 (d, $J$ = 8.8 Hz, 1H), 3.88 (q, $J$ = 8.9 Hz, 1H), 3.50 (ddd, $J$ = 17.2, 9.0, 2.0 Hz, 1H), 3.40 (ddd, $J$ = 17.2, 8.9, 2.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 203.47, 147.92, 135.09, 132.83, 129.12, 127.87, 127.65, 127.14, 118.72, 111.19, 71.93, 51.33, 37.25. IR (neat, $cm^{-1}$): 3060.44, 2926.23, 2226.86, 2076.42, 1780.73, 1607.70, 1497.11, 832.40. HRMS (DART) ([M+H]$^+$) Calcd. For $C_{17}H_{14}NO$: 248.1070, found: 248.1073. HPLC analysis: ee = 88%. ODH (80% hexanes : 20% isopropanol, 0.8 mL/min): $t_{major}$ = 19.86 min, $t_{minor}$ = 25.22 min.

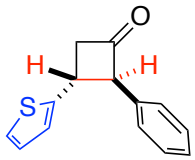
**(2*R*,3*R*)-3-(Furan-2-yl)-2-phenylcyclobutan-1-one (2k)**




Colorless oil (13.2 mg, 62% yield). 92:8 dr (92:8). $R_f$ = 0.53 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-165.57° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, $J$ = 1.9 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 6.37 – 6.36 (m, 1H), 6.23 (d, $J$ = 3.2 Hz, 1H), 4.73 (d, $J$ = 8.3 Hz, 1H), 3.79 (q, $J$ = 8.6 Hz, 1H), 3.50 (ddd, $J$ = 17.4, 8.4, 2.5 Hz, 1H), 3.35 (ddd, $J$ = 17.4, 9.0, 2.1 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 203.87, 154.31, 141.13, 134.53, 127.88, 126.47, 125.99,

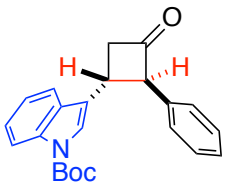
109.63, 104.97, 68.87, 49.23, 29.98. IR (neat, $cm^{-1}$): 2926.98, 1780.88, 1601.48, 1497.02, 1449.13, 1392.05, 1105.39, 747.06. HRMS (DART) ($[M+H]^+$) Calcd. For $C_{14}H_{13}O_2$: 213.0910, found: 213.0900. HPLC analysis: ee = 96%. IC (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 14.83 min, $t_{minor}$ = 15.62 min.

**(2*R*,3*R*)-2-Phenyl-3-(thiophen-2-yl)cyclobutan-1-one (2l)**




Colorless oil (17.3 mg, 76% yield). 95:5 dr (87:13). $R_f$ = 0.56 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-167.17° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.22 (m, 4H), 6.99 (d, *J* = 4.1 Hz, 2H), 4.65 (d, *J* = 8.3 Hz, 1H), 4.00 (q, *J* = 8.7 Hz, 1H), 3.51 (ddd, *J* = 17.3, 8.9, 1.9 Hz, 1H), 3.44 (ddd, *J* = 17.4, 8.7, 2.2 Hz, 1H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 204.58, 146.65, 135.35, 128.95, 127.61, 127.28, 127.09, 124.23, 124.19, 72.93, 53.03, 33.26. IR (neat, $cm^{-1}$): 3061.63, 2921.43, 1780.50, 1495.71, 1395.60, 1105.20, 1044.47, 692.48. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{13}OS$: 229.0682, found: 229.0674. HPLC analysis: ee = 92%. IC (97% hexanes : 3% isopropanol, 0.8 mL/min): $t_{major}$ = 13.13 min, $t_{minor}$ = 14.45 min.

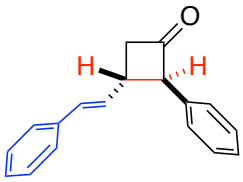
***tert*-Butyl 3-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)-1*H*-indole-1-carboxylate (2m)**




Colorless oil (25.2 mg, 70% yield). 98:2 dr (97:3). $R_f$ = 0.56 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-97.58° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.56 (s, 1H), 7.39 – 7.28 (m, 7H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.70 (d, *J* = 8.4 Hz, 1H), 3.94 (q, *J* = 8.6, 1H), 3.55 (ddd, *J* = 17.3, 9.0, 2.2 Hz, 1H), 3.45 (ddd, *J* = 17.3, 8.6, 2.4 Hz, 1H), 1.69 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 205.64, 149.83, 136.10, 135.91, 129.65, 128.99, 128.59, 127.58, 127.36, 125.00, 122.80, 121.96, 119.50, 115.69, 84.11, 70.61, 50.82, 29.51, 28.37. IR (neat, $cm^{-1}$): 2978.65, 2929.96, 1783.28, 1726.80. 1451.43, 1370.05, 1252.86, 745.69. HRMS (DART) ($[M+H]^+$)

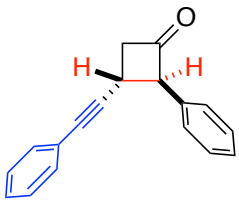
Calcd. for $C_{23}H_{24}NO_3$: 362.1751, found: 362.1745. HPLC analysis: ee = 78%. IC (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 15.07 min, $t_{minor}$ = 16.69 min.

**(2*R*,3*S*)-2-Phenyl-3-((*E*)-styryl)cyclobutan-1-one (2n)**




Colorless oil (17.6 mg, 71% yield). 96:4 dr (62:38). $R_f$ = 0.46 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-43.99° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.39 (m, 3H), 7.38 – 7.32 (m, 3H), 7.31 – 7.28 (m, 3H), 7.27 – 7.26 (m, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.52 (dd, *J* = 15.7, 7.1 Hz, 1H), 4.41 (d, *J* = 8.4 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.26 (ddd, *J* = 17.1, 8.5, 1.8 Hz, 1H), 3.19 (ddd, *J* = 17.1, 8.7, 2.1 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 205.09, 136.76, 135.72, 131.38, 131.12, 128.88, 128.82, 127.82, 127.43, 127.14, 126.39, 70.11, 50.59, 35.88. IR (neat, $cm^{-1}$): 3058.75, 2923.02, 1778.45, 1496.31, 1447.88, 1030.85, 963.74, 746.30. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O$: 249.1274, found: 249.1285. HPLC analysis: ee = 50%. IE (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 11.70 min, $t_{minor}$ = 12.62 min.

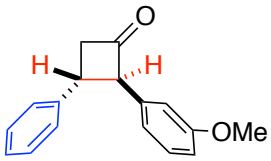
**(2*R*,3*R*)-2-Phenyl-3-(phenylethynyl)cyclobutan-1-one (2o)**




Colorless oil (19.8 mg, 80% yield). 72:28 dr (82:18). $R_f$ = 0.44 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-55.98° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 6H), 4.73 (d, *J* = 7.9 Hz, 1H), 3.54 – 3.49 (m, 1H), 3.48 – 3.40 (m, 2H).$^{13}C$ NMR (151 MHz, $CDCl_3$): δ 204.46, 135.16, 131.80, 128.97, 128.49, 128.38, 127.72, 126.97, 123.11, 90.56, 82.74, 72.05, 52.36, 23.73. IR (neat, $cm^{-1}$):3029.99, 2925.64, 1784.11, 1598.15, 1490.79, 1105.62, 756.33, 692.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{15}O$: 247.1117, found:

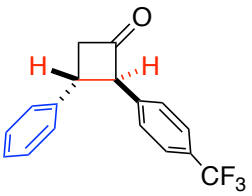
247.1128. HPLC analysis: ee = 73%. IB (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 10.66 min, $t_{minor}$ = 11.54 min.

**(2*R*,3*R*)-2-(3-Methoxyphenyl)-3-phenylcyclobutan-1-one (2p)**

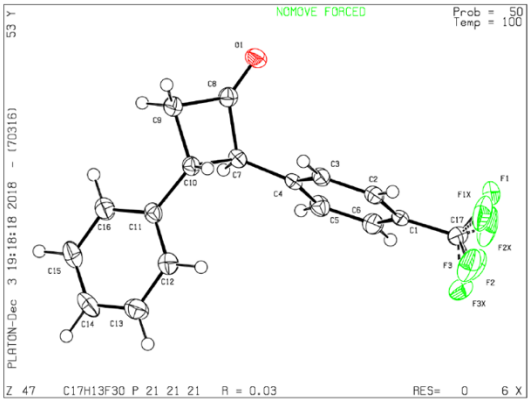



Colorless oil (18.8 mg, 75% yield). 98:2 dr (92:8). $R_f$ = 0.30 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-146.17° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.37 (m, 4H), 7.31 – 7.23 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.84 – 6.82 (m, 1H), 4.57 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.82 (q, *J* = 8.9 Hz, 1H), 3.79 (s, 3H), 3.44 (ddd, *J* = 17.3, 9.0, 1.9 Hz, 1H), 3.37 (ddd, *J* = 17.3, 9.0, 2.1 Hz, 1H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 205.08, 160.01, 142.62, 137.29, 129.92, 128.97, 127.12, 126.75, 119.49, 113.01, 112.82, 71.59, 55.38, 51.52, 36.90. IR (neat, $cm^{-1}$): 3058.93, 2835.31, 1779.14, 1599.54, 1488.71, 1247.75, 1075.65, 1038.30. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2$: 253.1223, found: 253.1216. HPLC analysis: ee = 94%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 18.11 min, $t_{minor}$ = 20.37 min.

**(2*R*,3*R*)-3-Phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutan-1-one (2q) (1.0 mmol Scale)**



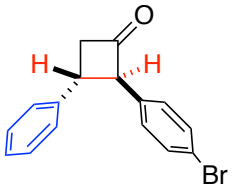

White solid (269 mg, 93% yield). 99:1 dr (97:3). $R_f$ = 0.39 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-134.97° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.39 – 7.36 (m, 3H), 7.31– 7.30 (m, 1H), 4.66 (d, *J* = 8.9 Hz, 1H), 3.84 (q, *J* = 9.0 Hz, 1H), 3.54 – 3.37 (m, 2H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 203.74, 142.02, 139.63,



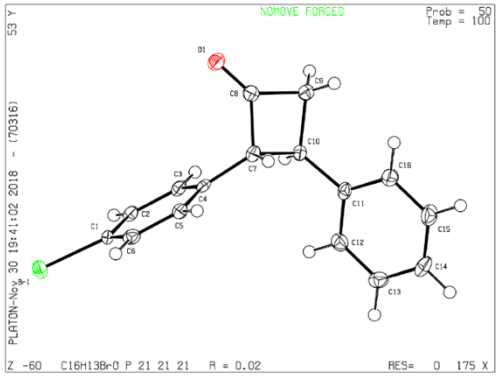
129.68 (q, $J$ = 32.6 Hz), 129.10, 127.48, 127.36, 126.66, 125.82 (q, $J$ = 3.8 Hz), 124.21 (q, $J$ = 273.4 Hz), 70.94, 51.82, 36.86. $^{19}$F NMR (564 MHz, $CDCl_3$) δ –62.53. IR (neat, $cm^{-1}$): 3029.05, 2926.30, 1783.91, 1618.06, 1325.70, 1164.88, 1120.35, 698.67. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{14}OF_3$: 291.0991, found: 291.0983. HPLC analysis: ee = 95%. IC (98.5 % hexanes : 1.5 % isopropanol, 0.8 mL/min): $t_{major}$ = 14.10 min, $t_{minor}$ = 12.92 min. The absolute configuration was assigned as (1*R*, 2*R*) by X-ray crystallography.

| Crystal data and structure refinement for **2q.** | |
|---|---|
| Identification code | **2q** |
| Empirical formula | C17H13F3O |
| Formula weight | 290.27 |
| Temperature/K | 100(2) K |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 6.0821(2) |
| b/Å | 9.8660(4) |
| c/Å | 22.7489(9) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/$Å^3$ | 1365.07(9) |
| Z | 4 |
| $\rho_{calc}$ $Mg/m^3$ | 1.412 |
| μ/$mm^{-1}$ | 0.977 |
| F(000) | 600 |
| Crystal size/$mm^3$ | 0.580 x 0.550 x 0.280 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.886 to 68.217 |
| Index ranges | $-7 \leq h \leq 6$, $-7 \leq k \leq 11$, $-24 \leq l \leq 27$ |
| Reflections collected | 4067 |
| Independent reflections | 2381 [$R_{int}$ = 0.0173] |
| Data/restraints/parameters | 2381 / 3 / 218 |
| Goodness-of-fit on $F^2$ | 1.067 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0305, $wR_2$ = 0.0786 |
| Final R indexes [all data] | $R_1$ = 0.0307, $wR_2$ = 0.0787 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.184/-0.188 |
| Flack parameter | 0.03(4) |

**(2*R*,3*R*)-2-(4-Bromophenyl)-3-phenylcyclobutan-1-one (2r)**



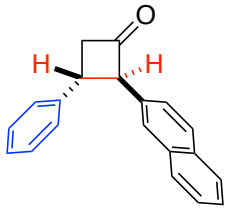

White solid (27.1 mg, 90% yield). 97:3 dr (97:3). $R_f$ = 0.56 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-145.58° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 3.77 (q, *J* = 8.9 Hz, 1H), 3.50 – 3.35 (m, 2H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 204.37, 142.22, 134.77, 132.03, 129.08, 128.88, 127.30, 126.68, 121.46, 70.89, 51.71, 37.09. IR (neat, $cm^{-1}$): 3028.00, 2923.21, 1778.91, 1487.79, 1396.22, 1071.41, 1010.76, 734.82.




HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{14}OBr$: 301.0222, found: 301.0209. HPLC analysis: ee = 96%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 17.66 min, $t_{minor}$ = 19.01 min. The absolute configuration was assigned as (1*R*, 2*R*) by X-ray crystallography.

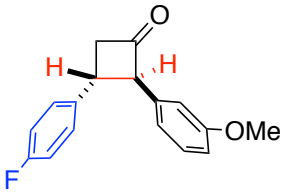
| Crystal data and structure refinement for **2r.** | |
|---|---|
| Identification code | **2r** |
| Empirical formula | C16H13BrO |
| Formula weight | 301.17 |
| Temperature/K | 100(2) K |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 5.8775(4) |
| b/Å | 9.7871(7) |
| c/Å | 21.8520(15) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1257.01(15) |
| Z | 4 |
| $\rho_{calc}$ Mg/m$^3$ | 1.591 |
| μ/mm$^{-1}$ | 4.312 |
| F(000) | 608 |
| Crystal size/mm$^3$ | 0.520 x 0.280 x 0.200 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.046 to 65.930 |
| Index ranges | $-5 \leq h \leq 6$, $-11 \leq k \leq 11$, $-25 \leq l \leq 25$ |
| Reflections collected | 9764 |
| Independent reflections | 2169 [$R_{int}$ = 0.0328] |
| Data/restraints/parameters | 2169 / 0 / 164 |
| Goodness-of-fit on $F^2$ | 1.093 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0205, $wR_2$ = 0.0520 |
| Final R indexes [all data] | $R_1$ = 0.0206, $wR_2$ = 0.0521 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.498/-0.357 |
| Flack parameter | 0.03(2) |

**(2*R*,3*R*)-2-(Naphthalen-2-yl)-3-phenylcyclobutan-1-one (2s)**



Colorless oil (25.3 mg, 93% yield). 98:2 dr (98:2). $R_f$ = 0.50 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-232.96° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.74 (m, 4H), 7.53 – 7.44 (m, 2H), 7.43 – 7.36 (m, 5H), 7.31– 7.28 (m, 1H), 4.76 (d, *J* = 8.8 Hz, 1H), 3.96 (q, *J* = 8.9 Hz, 1H), 3.58 – 3.40 (m, 2H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 205.27, 142.63, 133.56, 133.30, 132.74, 129.00, 128.70, 127.95, 127.81, 127.15, 126.78, 126.42, 126.06, 125.83, 125.41, 71.88, 51.60, 37.09. IR (neat, $cm^{-1}$): 3056.14, 2921.29, 1779.20, 1600.75, 1110.53, 1075.62, 818.00, 699.85. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{17}O$: 273.1274, found: 273.1265. HPLC analysis: ee = 95%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 19.87 min, $t_{minor}$ = 23.11 min.

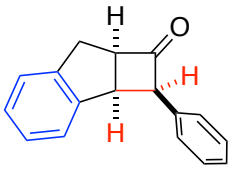
**(2*R*,3*R*)-3-(4-Fluorophenyl)-2-(3-methoxyphenyl)cyclobutan-1-one (2t)**



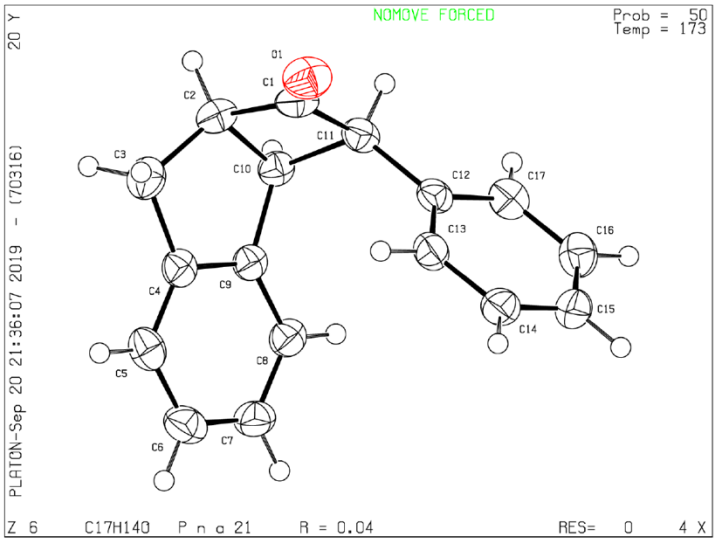
Colorless oil (14.0 mg, 52% yield). 98:2 dr (88:12). $R_f$ = 0.27 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-79.98° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 2H), 7.27 – 7.25 (m, 1H), 7.10 – 7.03 (m, 2H), 6.87– 6.83 (m, 1H), 6.83 – 6.80 (m, 2H), 4.52 (dd, *J* = 8.8, 2.2 Hz, 1H), 3.80 (s, 3H), 3.80 (q, *J* = 9.0 Hz, 1H), 3.44 (ddd, *J* = 17.2, 8.9, 2.0 Hz, 1H), 3.34 (ddd, *J* = 17.2, 9.0, 2.1 Hz, 1H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 203.58, 160.96 (d, *J* = 245.5 Hz), 159.07, 137.33 (d, *J* = 3.4 Hz), 136.07, 129.01, 127.28 (d, *J* = 8.1 Hz), 118.44, 114.82 (d, *J* = 21.5 Hz), 112.05, 111.87, 70.83, 54.40, 50.64, 35.38. $^{19}F$ NMR (564 MHz, $CDCl_3$) δ –115.70 (ddd, *J* = 13.7, 8.7, 5.2 Hz). IR (neat, $cm^{-1}$): 2921.67, 2837.69, 1780.25, 1599.65, 1509.35, 1223.19, 1038.44, 832.16. HRMS (DART) ($[M+H]^+$) Calcd. for

$C_{17}H_{16}O_2F$: 271.1129, found: 271.1118. HPLC analysis: ee = 91%. IB (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 12.92 min, $t_{minor}$ = 14.88 min.

**2-Phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]inden-1-one (2u)**




White solid. (15.5 mg, 66% yield). 99:1 dr (99:1). $R_f$ = 0.38 (Hexanes/ EtOAc = 9/1). $[\alpha]_D^{20}$ = (–)-11.99° (*c* = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 9.4 Hz, 1H), 7.19 – 7.10 (m, 4H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.74 – 6.66 (m, 2H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.02 (dd, *J* = 9.8, 2.3 Hz, 1H), 4.41 (t, *J* = 8.7 Hz, 1H), 4.14 (ddd, *J* = 9.7, 7.6, 1.9 Hz, 1H), 3.41 (d, *J* = 16.6 Hz, 1H), 3.14 (dd, *J* = 16.7, 9.5 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 210.84, 143.11, 138.86, 132.99, 127.99, 127.15, 126.65, 126.40, 125.49, 124.31, 123.39, 69.10, 59.29, 43.88, 32.81. IR (neat, $cm^{-1}$): 3063.89, 2919.14, 2847.94, 1770.75, 1497.47, 1267.82, 1224.89, 756.15, 717.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{15}O$: 235.1117, found: 235.1116. HPLC analysis: ee = 15%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 19.63 min, $t_{minor}$ = 20.62 min.

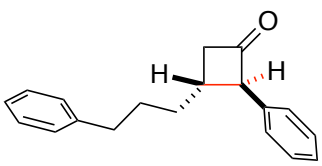


| Crystal data and structure refinement for **2u.** | |
|---|---|
| Identification code | **2u** |
| Empirical formula | C17H14O |
| Formula weight | 234.28 |
| Temperature/K | 173(2) K |
| Crystal system | orthorhombic |
| Space group | $Pna2_1$ |
| a/Å | 12.2267(4) |
| b/Å | 16.9706(5) |
| c/Å | 5.9152(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1227.37(7) |
| Z | 4 |
| $\rho_{calc}$ Mg/m$^3$ | 1.268 |
| μ/mm$^{-1}$ | 0.600 |
| F(000) | 496 |
| Crystal size/mm$^3$ | 0.440 x 0.120 x 0.080 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.457 to 66.677 |
| Index ranges | -13≤ h ≤ 14, -19 ≤ k ≤ 20, -7≤ l ≤ 6 |
| Reflections collected | 21125 |
| Independent reflections | 2124 [R(int) = 0.0481] |
| Data/restraints/parameters | 2124 / 1 / 163 |
| Goodness-of-fit on F$^2$ | 1.091 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0374, $wR_2$ = 0.0956 |
| Final R indexes [all data] | $R_1$ = 0.0432, $wR_2$ = 0.1015 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.180/-0.150 |
| Flack parameter | 0.07(14) |

**Selective 1,4-C–H Alkylation**

An oven-dried Schlenk tube was charged with diazo compound **1w** (0.1 mmol) and [Co(**Por**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, *tert*-butyl methyl ether (TBME) (0.5 mL) was added via a gastight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C for 12 h and then concentrated under reduced pressure. The yield and dr of products were calculated based on crude $^{1}$H NMR with 1,1,2,2-tetrachloroethane as internal standard. Pure products **2w**, **3w** were isolated by PTLC.

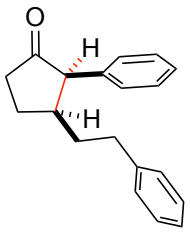
**2-phenyl-3-(3-phenylpropyl)cyclobutan-1-one (2w)**




**2w** was synthesized by [Co(**P6**)] following general procedure and isomerized to *trans*-enriched product (7:93 dr) after purification by silica gel column chromatography. Colorless oil. $R_f$ = 0.35 (Hexanes/ EtOAc = 10/1). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.10 (m, 10H), 4.04 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.13 (dddd, *J* = 17.2, 8.5, 2.4, 0.9 Hz, 1H), 2.81 (dddd, *J* = 17.2, 7.9, 2.5, 0.9 Hz, 1H), 2.67 (m, 2H), 2.59 (m, 1H), 1.92 (m, 1H), 1.77 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 206.54, 142.11, 136.35, 128.83, 128.51, 128.50, 127.33, 127.20, 126.02, 70.29, 50.24, 36.38, 35.87, 32.73, 30.21. IR (neat, $cm^{-1}$): 3026.07, 2928.73, 2854.96, 1775.13, 1496.34, 1452.33, 747.24, 687.50. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}O$: 265.1587, found: 265.1576.

**3-Phenethyl-2-phenylcyclopentan-1-one (3w)**

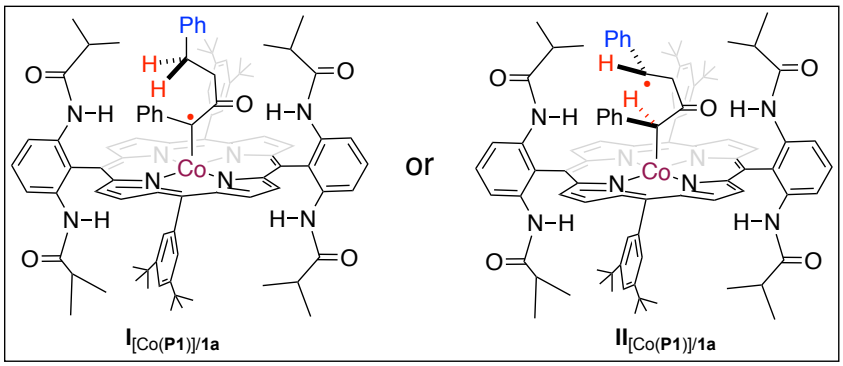
**3w** was synthesized by [Co(**P6**)] following general procedure and isomerized to *trans*-enriched product (1:99 dr) after purification by silica gel column chromatography.



Colorless oil. $R_f$ = 0.23 (Hexanes/ EtOAc = 10/1). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 – 7.07 (dd, *J* = 13.2, 7.7 Hz, 4H), 2.97 (d, *J* = 11.7 Hz, 1H), 2.72 (m, 1H), 2.64 – 2.51 (m, 2H), 2.39 – 2.33 (3H), 1.98 (m, 1H), 1.73 – 1.62 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 217.80, 141.98, 137.94, 128.94, 128.81, 128.49, 128.35, 127.19, 126.01, 63.21, 44.77, 38.65, 36.35, 33.50, 27.45. IR (neat, $cm^{-1}$): 3026.09, 2927.64, 2856.12, 1740.20, 1496.11, 1452.70, 1135.42, 697.46. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}O$: 265.1587, found: 265.1589.

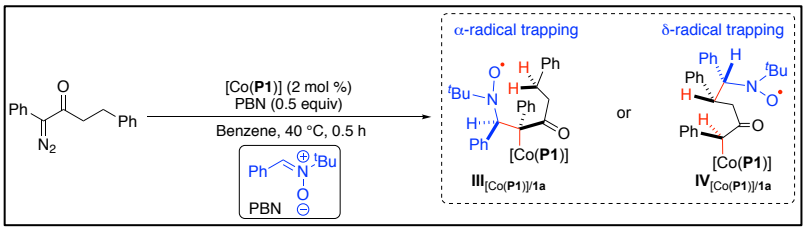
### 2.4.5 Mechanistic Studies of the Proposed Stepwise Radical Mechanism

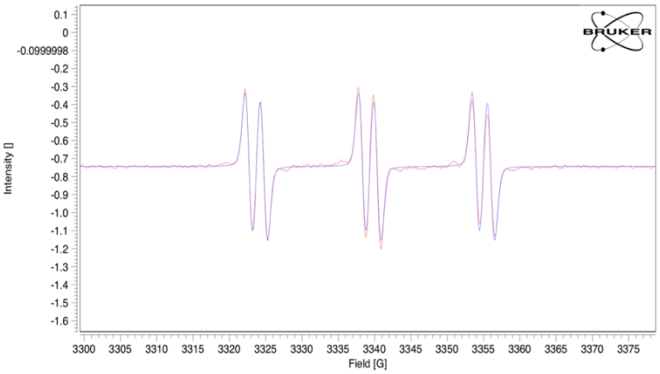
#### 2.4.5.1 Characterization of Co(III)-Alkyl Radical (Intermediate I or II) by HRMS

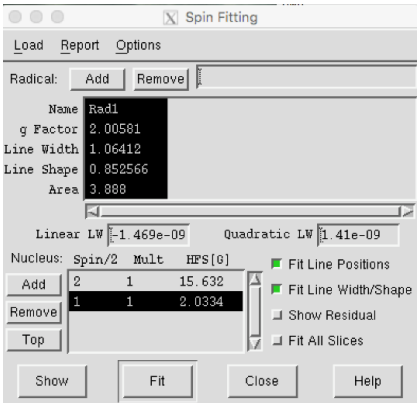



**Procedure for HRMS Experiment:** Diazo **1a** was dissolved in 0.5mL of acetonitrile and added in a HPLC vial (vial A, degassed and backfilled with argon). At the same time, [Co(**P1**)] (2 mol %) was charged into another HPLC vial (vial B, degassed and backfilled with argon) and dissolved in acetonitrile (0.5 mL). After mixing equal amount of solutions from vial A (0.1 mL) and vial B (0.1 mL), 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, which commonly act as electron carriers for ionization, allowing for the detection of the molecular ion signals corresponding to Co(III)-alkyl radical ($C_{92}H_{102}CoN_8O_5^{\cdot}$) by the loss of one electron.

### 2.4.5.2. Characterization of Co(III)-Alkyl Radical (Intermediate I or II) by EPR




The resulting strong EPR signal (in red) has been simulated (in blue) with $g = 2.00581$, $A$N = 43.9 MHz, $A$H = 5.7 MHz, which is assigned to PBN-trapped Co(III)-supported alkyl radical intermediate. The values are consistent with that of the reported similar species. *[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]*

**Procedure for EPR Experiment:** To an oven-dried Schlenk tube, diazo **1a** (0.1 mmol), *N-tert*-butyl-a-phenylnitrone (PBN, 0.5 equiv) and [Co(**P1**)] (2 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, and benzene (0.5 mL) was added via a gastight syringe. The mixture was then stirred at 40 $^{O}$C for 0.5 h. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a gastight 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).

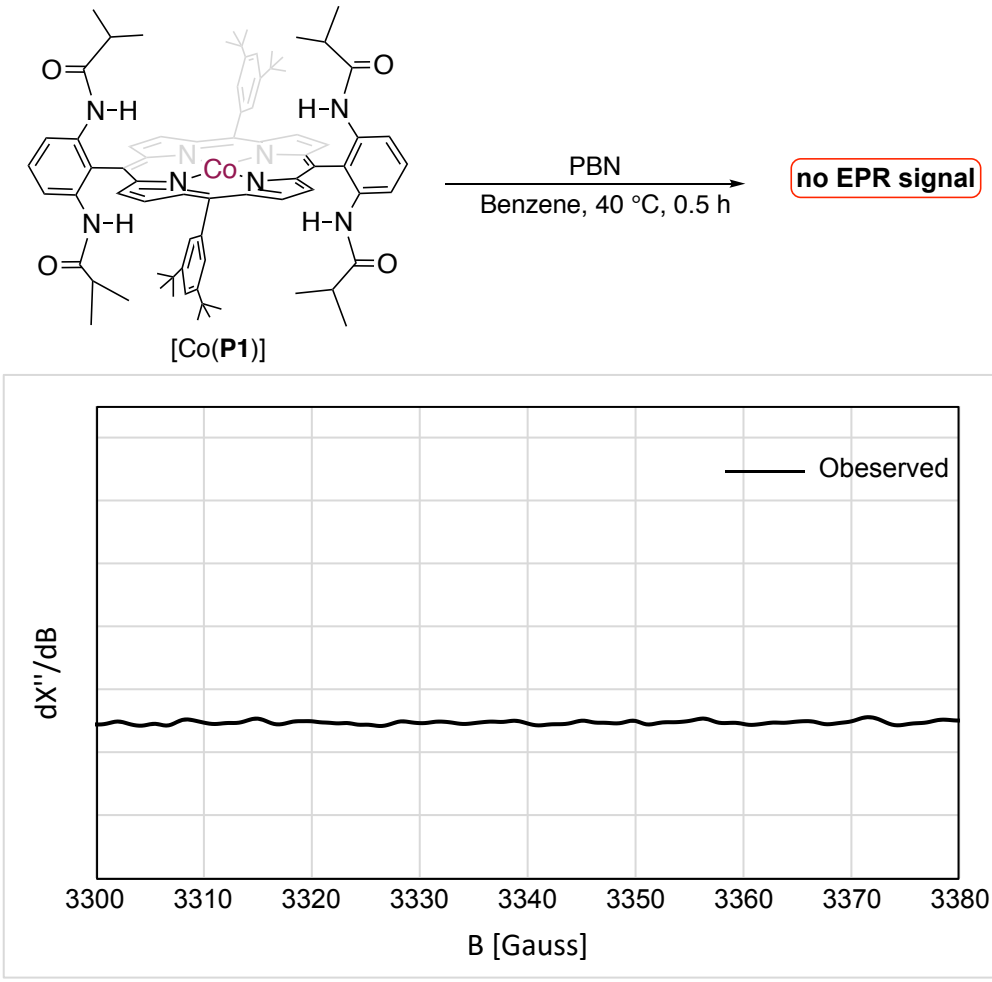
**EPR simulation details:**

g = 2.00581

A(N) = 15.632 x 2.00581 x 1.399611451 = 43.9 MHz

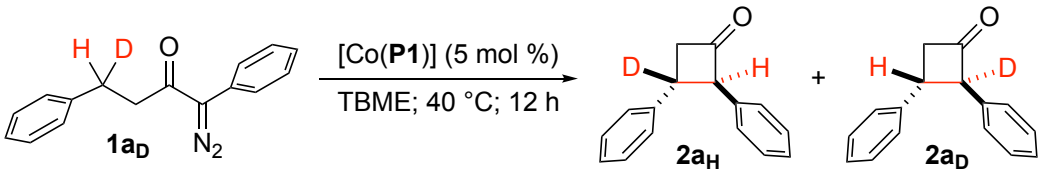
A(H) = 2.0334 x 2.00581 x 1.399611451 = 5.7 MHz

**Procedure for Control Experiment:** To an oven-dried Schlenk tube, *N-tert*-butyl-□-phenylnitrone (PBN, 0.05 mmol) and [Co(**P1**)] (2 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, and benzene (0.5 mL) was added via a gastight syringe. The mixture was then stirred at 40 $^{O}$C for 0.5 h. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a gastight 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).

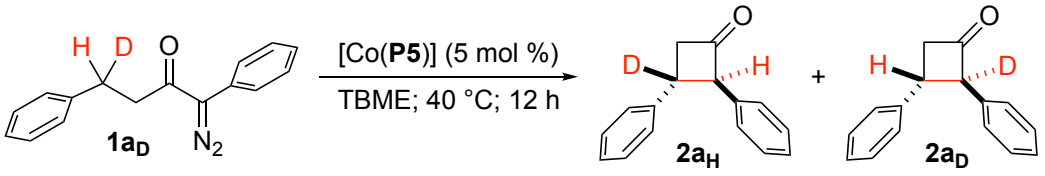



No EPR signal was observed with only [Co(**P1**)] and PBN in the absence of diazo **1a**.

### 2.4.5.3 Determination of Kinetic Isotope Effects




An oven-dried Schlenk tube was charged with diazo compound **1a$_D$** (0.1 mmol) and [Co(**P1**)] (5 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TBME (0.5 mL) was added via a gastight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^{O}$C. After 12 h, the reaction mixture was concentrated and analyzed by NMR. The NMR yield for **2a$_H$** together with **2a$_D$** is 23%. KIE ($k_H/k_D$) was calculated as **11.5** based on $^1$H-NMR analysis.




An oven-dried Schlenk tube was charged with diazo compound **1a$_D$** (0.1 mmol) and [Co(**P5**)] (5 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TBME (0.5 mL) was added via a gastight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^{O}$C. After 12 h, the reaction mixture was concentrated and analyzed by NMR. The NMR yield for **2a$_H$** together with **2a$_D$** is 40%. KIE ($k_H/k_D$) was calculated as **7.3** based on $^1$H-NMR analysis.

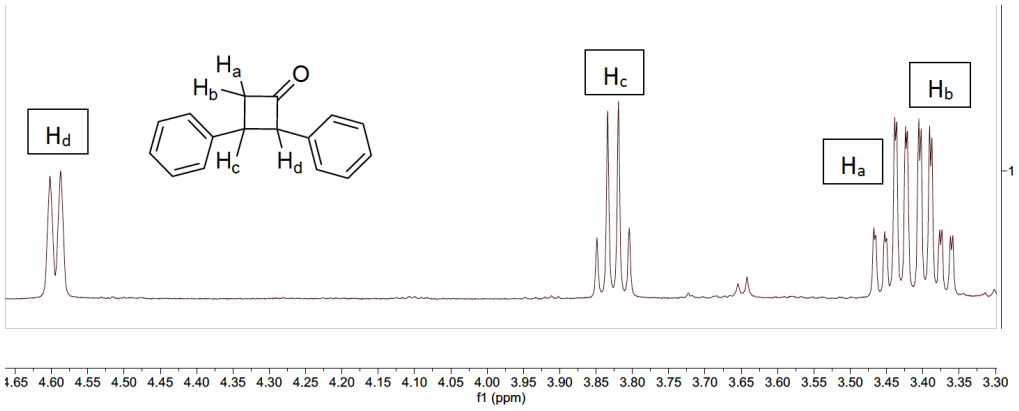
**Determination of KIE:**

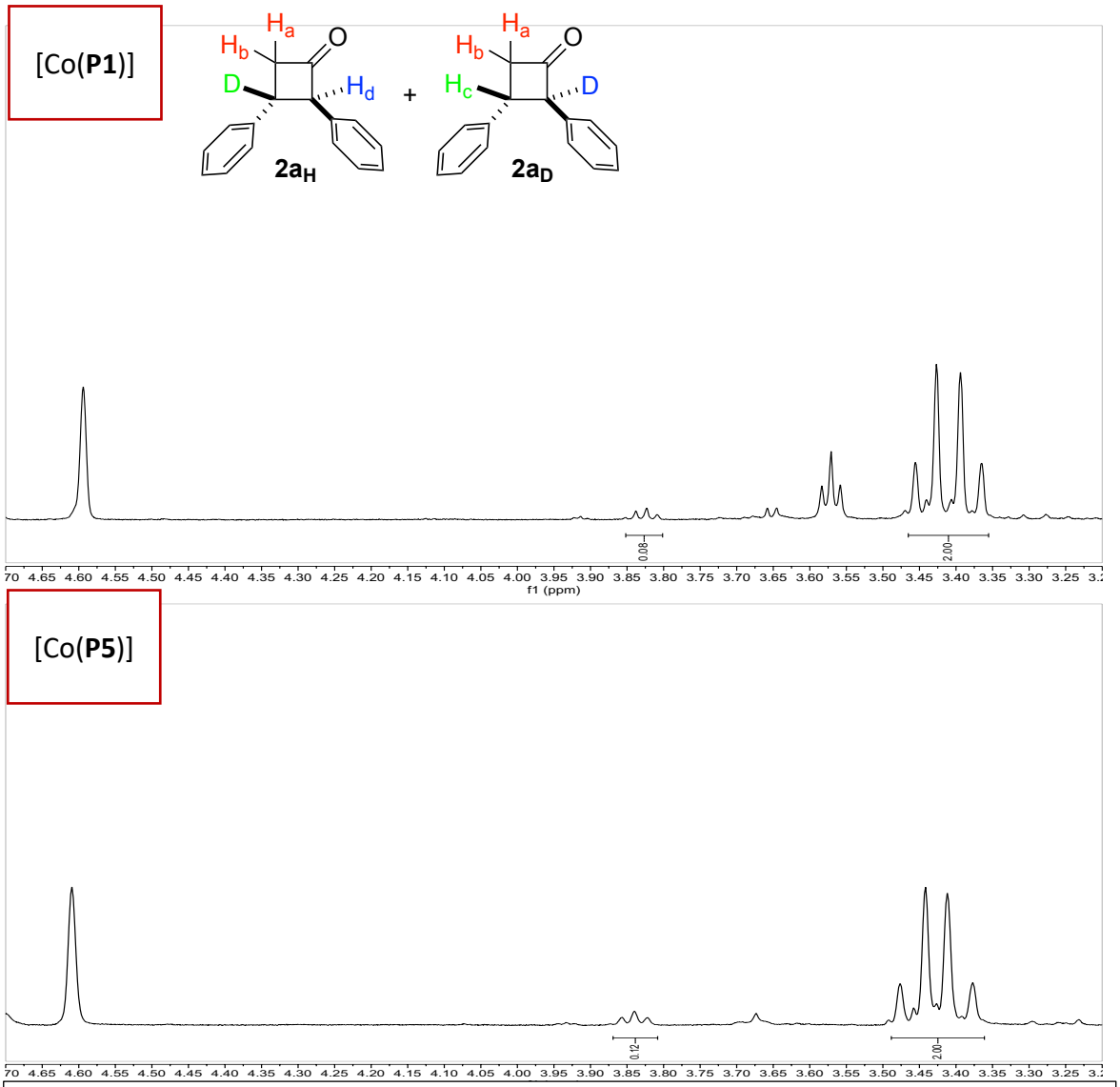
**[Co(P1)]:**

$k_H/k_D$ **= (2/2-0.08)/0.08 = 11.5**

**[Co(P5)]:**

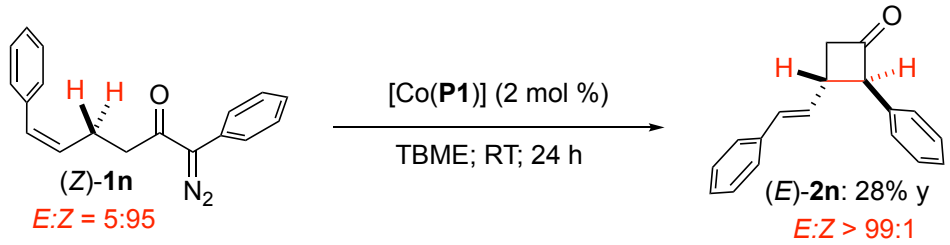
$k_H/k_D$ **= (2/2-0.12)/0.12 = 7.3**



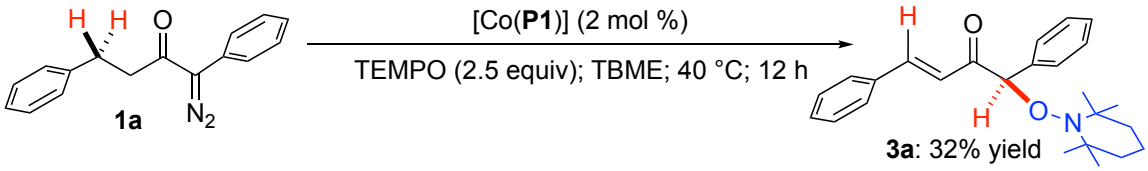

For clarification, only $H_a$, $H_b$ $H_c$ were used for KIE calculation considering the possible H/D exchange at $H_d$ position.

### 2.4.5.4 Probing of δ-Co(III)-Allylic Radical Intermediate via Olefin Isomerization



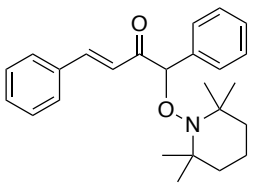

An oven-dried Schlenk tube was charged with diazo compound (*Z*)-**1n** (0.1 mmol) and [Co(**P1**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TBME (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at room temperature. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated to afford the compound (*E*)-**2n**.

### 2.4.5.5 TEMPO Trapping Experiments

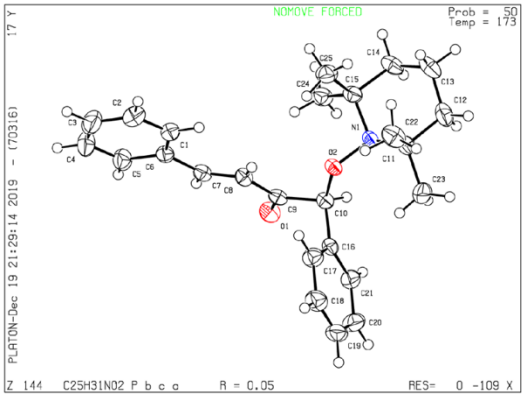



An oven-dried Schlenk tube was charged with diazo compound **1a** (0.1 mmol) and [Co(**P1**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TEMPO (2.5 equiv) and TBME (0.5 mL) was added. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^{o}$C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated to afford the compound **3a**.

**(*E*)-1,4-Diphenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)but-3-en-2-one (3a)**

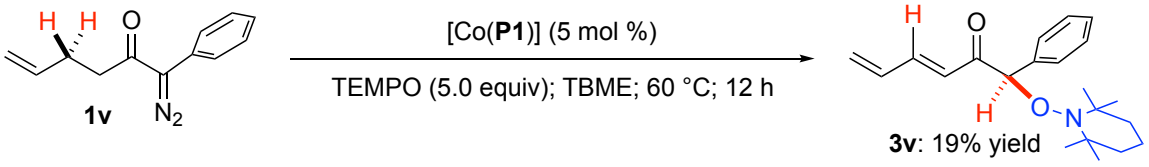



32% yield. pale yellow solid. $R_f$ = 0.34 (Hexanes/ EtOAc = 9/1).$^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.35 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.17 (d, *J* = 16.0 Hz, 1H), 5.31 (s, 1H), 1.52 – 1.28 (m, 6H), 1.24 (s, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 0.77 (s, 3H).$^{13}$C NMR (151 MHz, $CDCl_3$): δ 197.68, 143.66, 138.28, 135.00, 130.59, 129.02, 128.73, 128.57, 127.94, 126.82, 121.65, 95.23, 60.12, 60.00, 40.38, 33.67, 21.20, 20.67, 20.49, 17.21, 14.35. IR (neat,



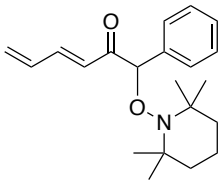
$cm^{-1}$): 2969.45, 2929.25, 1685.97, 1608.36, 1575.94, 1448.83, 1328.17, 989.36. HRMS (DART )($[M+H]^+$) Calcd. for $C_{25}H_{32}NO_2$: 378.2428, found 378.2426.

| Crystal data and structure refinement for **3a.** | |
|---|---|
| Identification code | **3a** |
| Empirical formula | C25H31NO2 |
| Formula weight | 377.51 |
| Temperature/K | 173(2) K |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 9.6013(6) |
| b/Å | 11.3787(7) |
| c/Å | 39.494(2) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/$Å^3$ | 4314.7(5) |
| Z | 8 |
| $\rho_{calc}$ $Mg/m^3$ | 1.162 |
| $\mu/mm^{-1}$ | 0.565 |
| F(000) | 1632 |
| Crystal size/$mm^3$ | 0.480 x 0.280 x 0.160 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 2.237 to 66.652 |
| Index ranges | $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-46 \leq l \leq 43$ |
| Reflections collected | 32470 |
| Independent reflections | 3738 [R(int) = 0.0496] |
| Data/restraints/parameters | 3738 / 0 / 257 |
| Goodness-of-fit on $F^2$ | 1.146 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0450, $wR_2$ = 0.1066 |
| Final R indexes [all data] | $R_1$ = 0.0474, $wR_2$ = 0.1077 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.167/-0.140 |



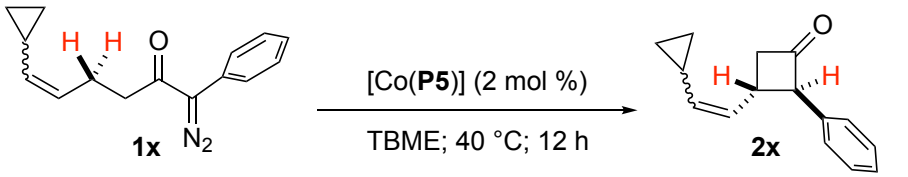

An oven-dried Schlenk tube was charged with diazo compound **1v** (0.1 mmol) and [Co(**P1**)] (5 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TEMPO (5.0 equiv) and TBME (0.5 mL) was added. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 $^{O}$C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated to afford the compound **3v**.

**(*E*)-1-Phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one (3v)**




19% NMR yield. colorless oil. $R_f$ = 0.52 (Hexanes/ EtOAc = 9/1).$^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.38 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 6.58 (d, *J* = 15.4 Hz, 1H), 6.45 (dt, *J* = 17.0, 10.5 Hz, 1H), 5.61 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.50 (d, *J* = 9.9 Hz, 1H), 5.24 (s, 1H), 1.59 – 1.28 (m, 6H), 1.20 (s, 3H), 1.14 (s, 3H), 1.07 (s, 3H), 0.73 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 197.91, 143.61, 138.15, 135.53, 128.66, 127.89, 126.82, 126.76, 125.85, 95.06, 60.06, 59.92, 40.34, 39.73, 33.59, 32.91, 20.57, 20.41, 17.17. IR (neat, cm$^{-1}$): 2970.58, 2930.59, 1777.43, 1688.80, 1618.73, 1589.39, 1264.84, 1132.31. HRMS (DART )([M+H]$^{+}$) Calcd. for $C_{21}H_{30}NO_2$: 328.2271, found 328.2273.

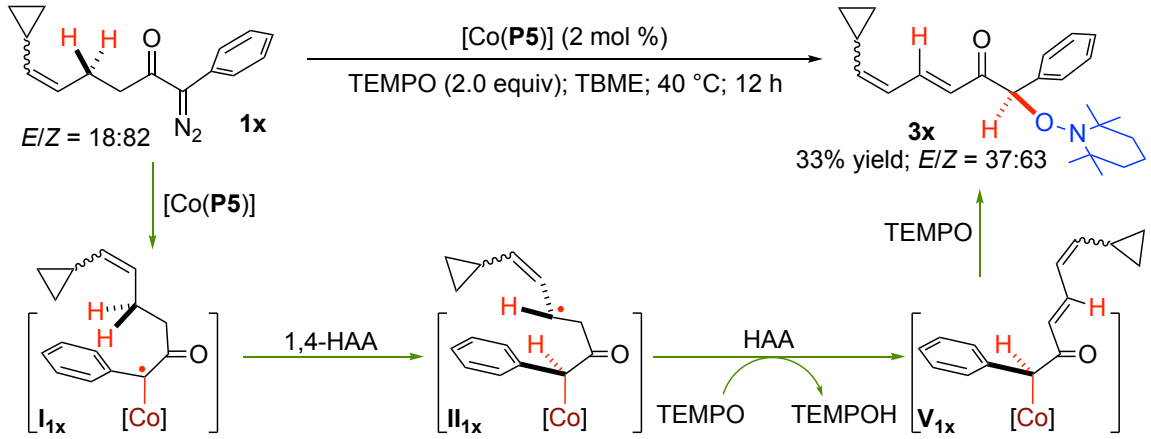
### 2.4.5.6 Radical Clock Experiments




*E*/*Z* = 18:82

61% yield; *E*/*Z* = 22:78

An oven-dried Schlenk tube was charged with diazo compound **1x** (0.1 mmol; *E*/*Z* = 12:82) and [Co(**P5**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, *tert*-butyl methyl ether (TBME) (0.5 mL) was added via a gastight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 °C for 12 h and then concentrated under reduced pressure. The reaction mixture was then purified by flash chromatography to afford the compound **3-(2-Cyclopropylvinyl)-2-phenylcyclobutan-1-one** (**2x**): Colorless oil. 61% yield (*E*/*Z* = 22:78). $R_f$ = 0.34 (Hexanes/EtOAc = 20/1). For major *Z* isomer: $^1$H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 5.59 (ddd, *J* = 10.2, 8.9, 0.9 Hz, 1H), 4.98 – 4.90 (m, 1H), 4.29 (dt, *J* = 8.3, 2.3 Hz, 1H), 3.58 (pd, *J* = 8.5, 1.2 Hz, 1H), 3.27 (ddd, *J* = 17.2, 8.7, 2.1 Hz, 1H), 3.05 (ddd, *J* = 17.2, 8.4, 2.4 Hz, 1H), 1.54 – 1.48 (m, 1H), 0.78 – 0.69 (m, 2H), 0.42 – 0.34 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 205.90, 136.36, 130.47, 129.32, 128.77, 127.25, 127.06, 70.99, 51.60, 31.31, 10.32, 7.40, 7.29. IR (neat, $cm^{-1}$): 3061.72, 3004.05, 2921.15, 1778.46, 1496.60, 1447.93, 1398.95, 1118.73. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{17}O$: 213.1274, found: 213.1272.



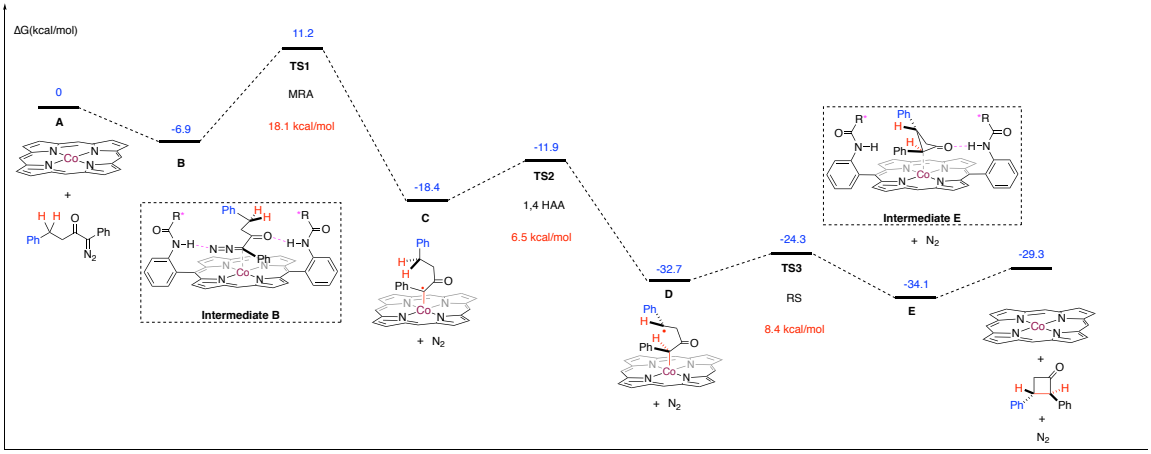

An oven-dried Schlenk tube was charged with diazo compound **1x** (0.1 mmol; *E*/*Z* = 12:82) and [Co(**P5**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, TEMPO (2.0 equiv) and TBME (0.5 mL) was added. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 40 $^{o}$C. After 12 h, the reaction mixture was concentrated and the yield (33%) and *E*/*Z* ratio (37:63) of product **(3*E*)-6-Cyclopropyl-1-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one (3x)** were calculated based on crude $^{1}$H NMR with 1,1,2,2-tetrachloroethane as internal standard. Pure product **3x** was isolated by PTLC: Colorless oil. $R_f$ = 0.22 (Hexanes/ EtOAc = 20/1). *E*/*Z* = 15:85. For major *Z* isomer: $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.77 (ddd, *J* = 15.1, 11.8, 1.1 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.58 (d, *J* = 15.1 Hz, 1H), 6.08 (t, *J* = 11.2 Hz, 1H), 5.24 (s, 1H), 5.20 (d, *J* = 10.6 Hz, 1H), 2.01 – 1.85 (m, 1H), 1.52 – 1.35 (m, 6H), 1.23 (s, 3H), 1.16 (s, 3H), 1.11 (s, 3H), 0.95 – 0.84 (m, 2H), 0.74 (s, 3H), 0.54 – 0.45 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.25, 147.78, 139.24, 138.55, 128.62, 127.80, 126.86, 125.38, 124.32, 95.26, 60.09, 59.90, 40.39, 33.66, 31.72, 20.61, 20.43, 17.22, 15.34, 11.72,

8.68. IR (neat, $cm^{-1}$): 3083.97, 3003.28, 2930.49, 1784.91, 1682.32, 1586.75, 1425.74, 1269.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{34}O_2$: 368.2584, found: 368.2583.

In the catalytic reaction of **1x** with [Co(**P5**)], no ring-opening product was observed. When the reaction of **1x** was further carried out in the presence of TEMPO, there was no evidence for formation of any TEMPO-trapped ring-opening product either. Together, these results indicated that the C–C and related bond formation were faster than the ring-opening of the cyclopropylcarbinyl radical within the cavity-like ligand environment of the catalyst.

### 2.4.5.7 Computational Study

**Figure 2.2. Free-Energy Profile for Overall Reaction**

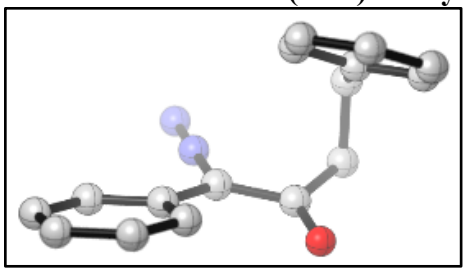



All DFT calculations were performed using the Gaussian 16 C.01[26] program package. For geometry optimization, the BP86[27,28,29,30] functional and the double-ζ def2-SVP[31,32] basis set were used. The D3 correction with Becke-Johnson (BJ)[33,34] damping was applied to include VdW interactions. Vibration frequencies were computed for optimized structures to characterize the stationary points as either equilibrium geometries (zero imaginary frequency) or saddle points (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed with local quadratic approximation (LQA)[35,36] method to ensure the TS found connected the reactant and the product. Subsequent calculations of the solvent effect were conducted with the SMD[37] model and triple-ζ def2-TZVPP basis set using gas phase optimized structures. The software built-in diisopropyl ether was used in the solvent model to best simulate the methyl tert-butyl ether used in the experiment. The energies reported in this paper are relative Gibbs free energies calculated at 298 K in solution and in the gas phase.

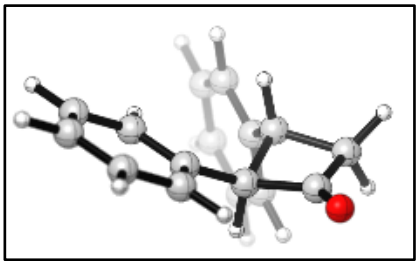
Independent Gradient Model (IGM)[38] analysis was performed with Multiwfn[39] software package using high quality grid option to generate files for further plotting. The

visualization of IGM analysis results were presented with VMD[40] visualization software and rendered with Tachyon[41]. As shown in Scheme S4, the 3D diagrams of optimized structures were generated with CYLview software[42], and the NCI (noncovalent interaction) visual representations of optimized structures were generated with VMD.

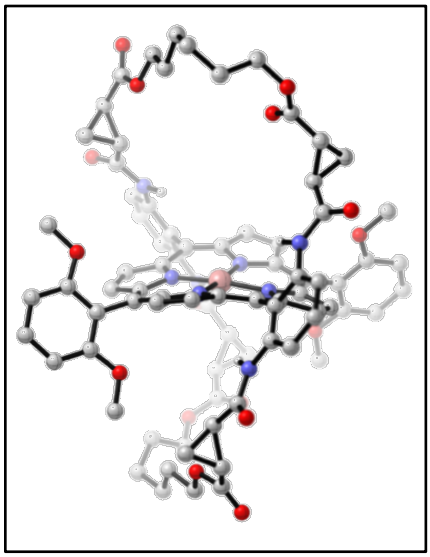
**Figure 2.3. Intermediates and Transition States for the Reaction and Their Non-Covalent Interaction(NCI) Analysis**



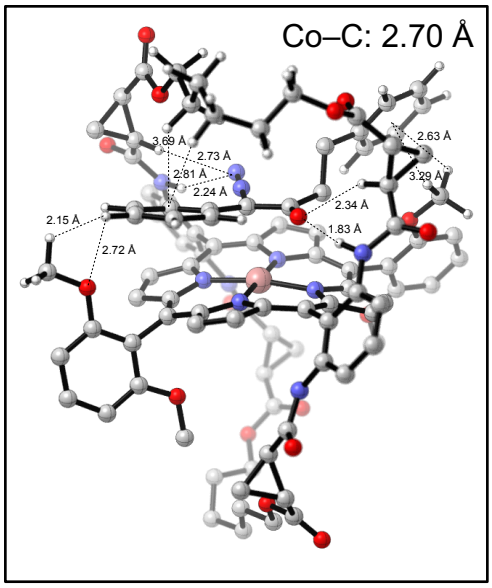
**Substrate Diazo 1a**

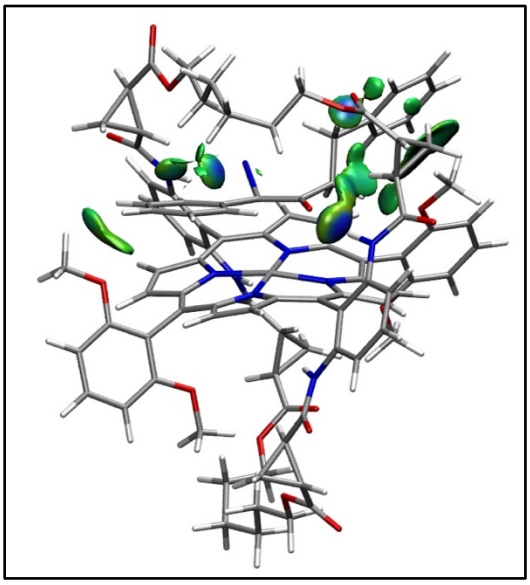


**Cyclobutanone Product 2a**

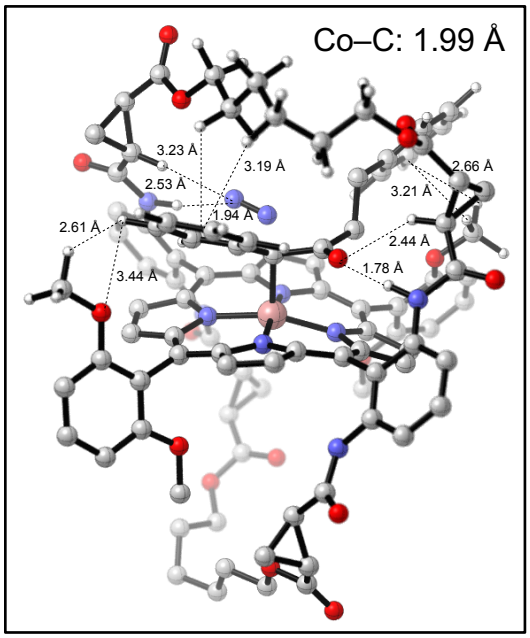


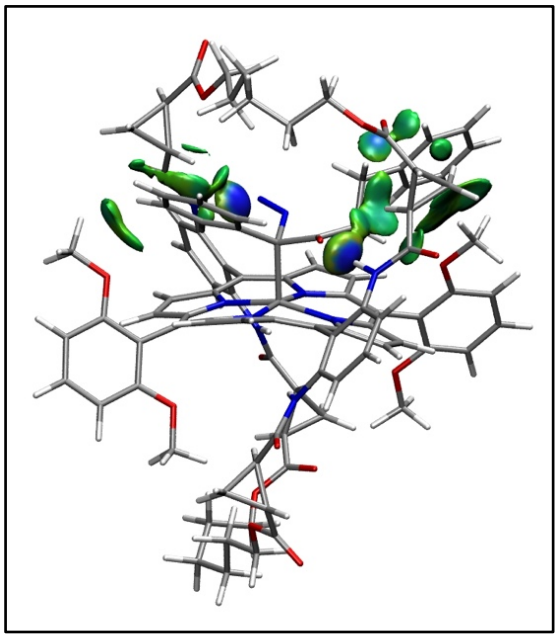
**Catalyst [Co(P5)]**



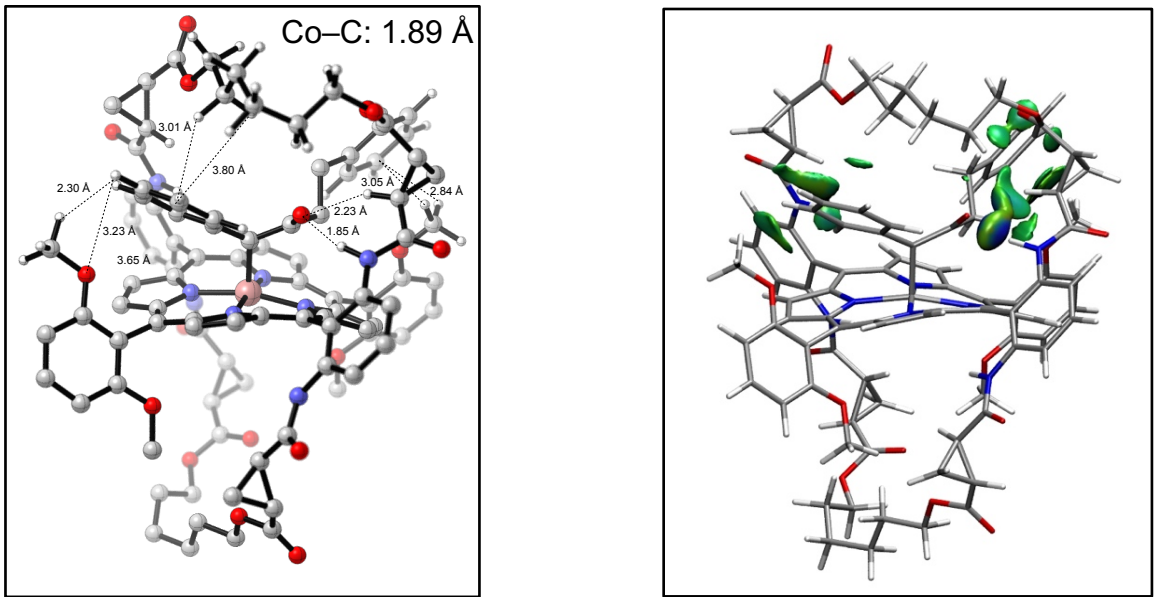



**Intermediate B**

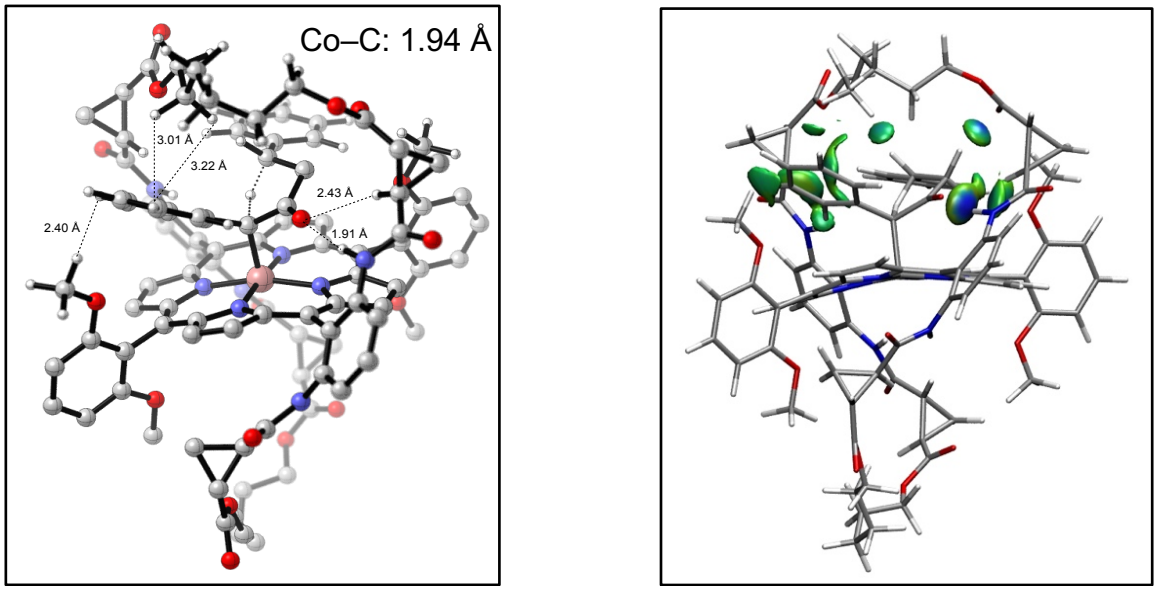


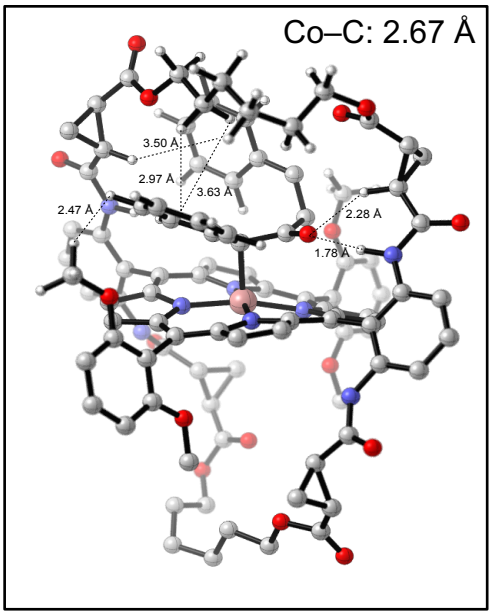
**Transition State of Metalloradical Activation (TS1)**

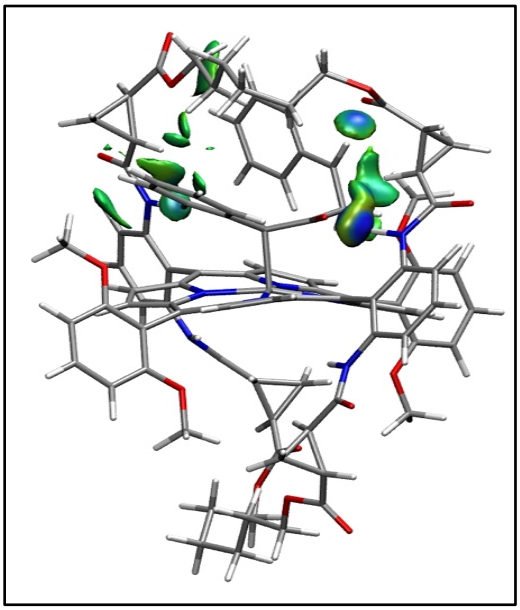



**Intermediate C**

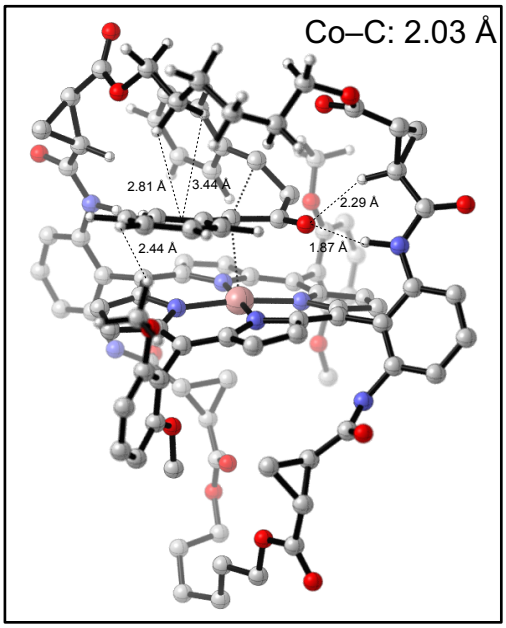


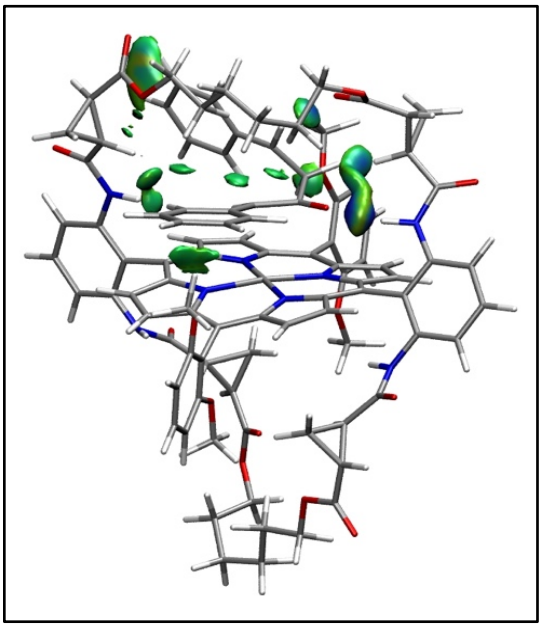

**Transition State of Hydrogen Atom Abstraction (TS2)**



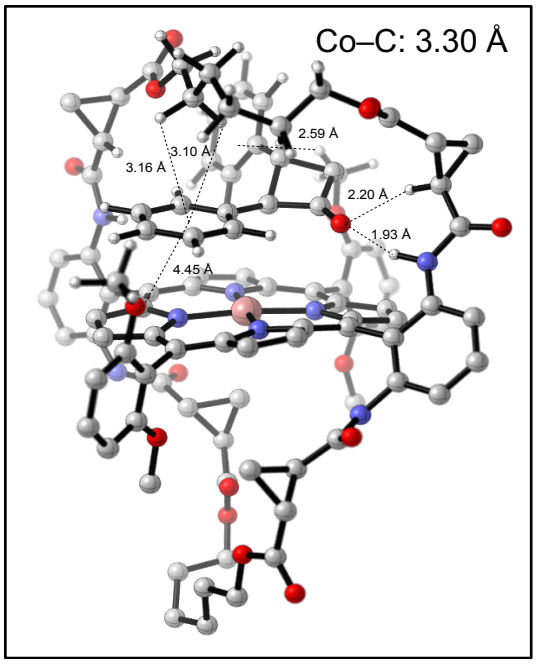



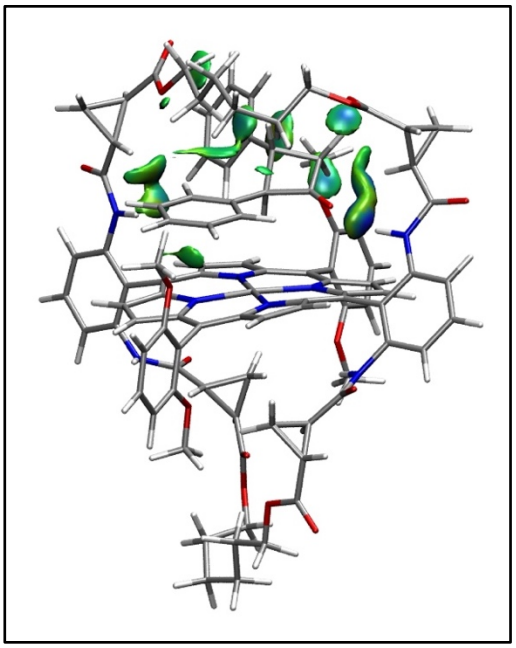
**Intermediate D**



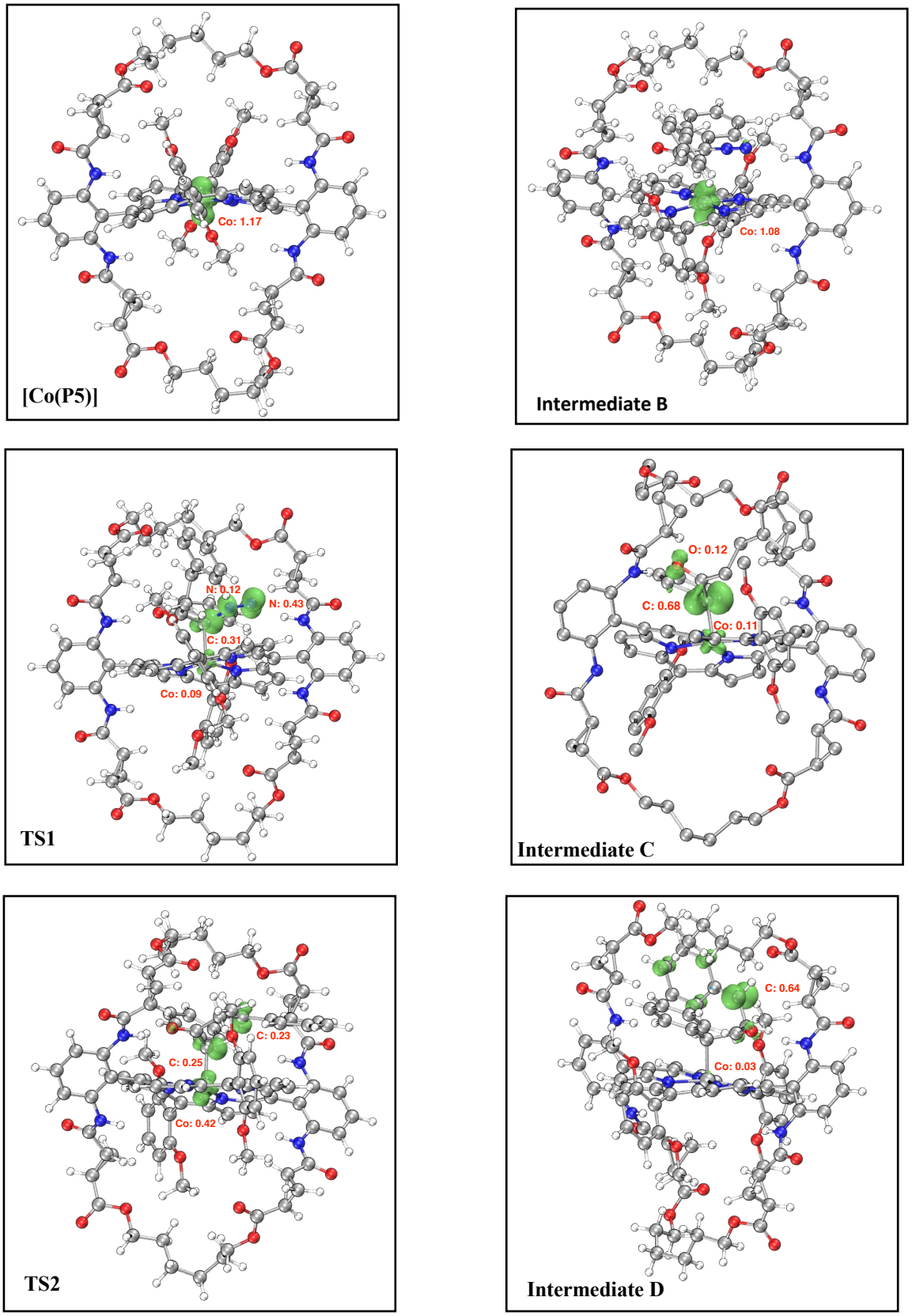
**Transition State for Radical Substitution (TS3)**

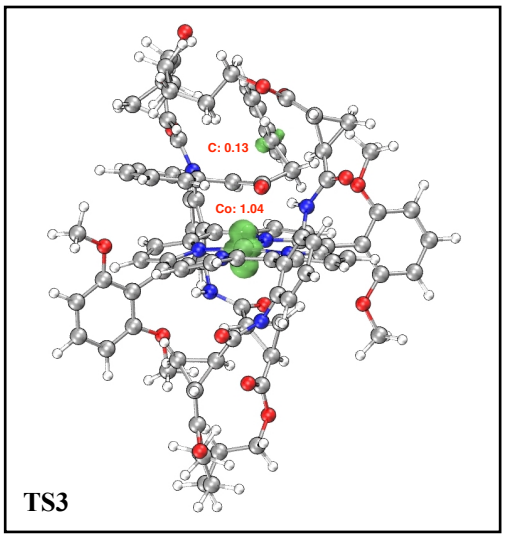


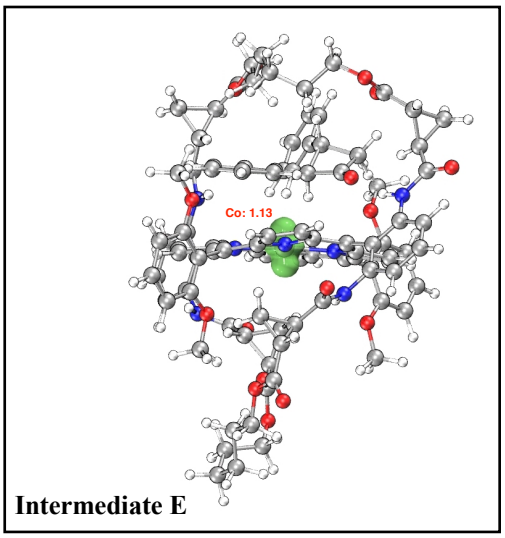



**Intermediate E**

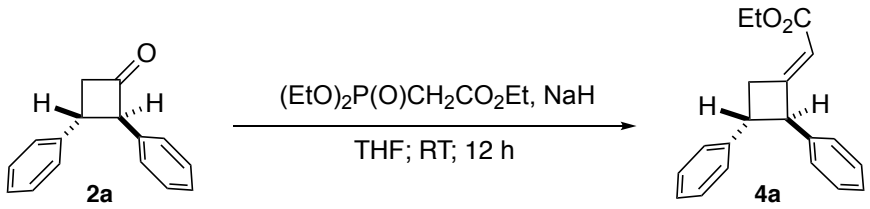
**Figure 2.4. Spin Density Analysis for the Reaction**




C: 0.13
Co: 1.04
TS3

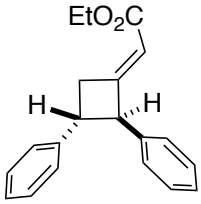

Co: 1.13
Intermediate E

### 2.4.6 Further Transformations

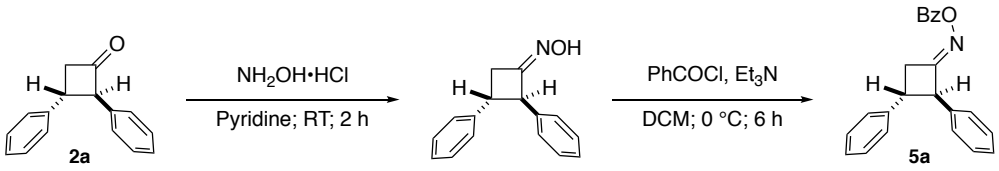



**4a** was prepared through reported procedure.[43] $(EtO)_2P(O)CH_2CO_2Et$ (1.5 equiv) was added dropwisely to a solution of NaH (1.5 equiv) in THF (0.5 mL) at 0 °C. The resulting solution was stirred for 0.5 h. Then **2a** (0.1 mmol) was added to the solution and the solution was stirred for 12 h at room temperature. After the complete consumption of **2a**, the reaction mixture was quenched with water and was extracted with EtOAc. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography.

**Ethyl (*E*)-2-((2*S*,3*R*)-2,3-diphenylcyclobutylidene)acetate (4a)**



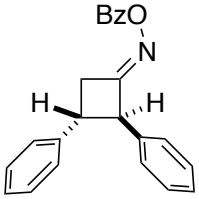

Colorless oil (32.5 mg, 88% yield). $R_f$ = 0.52 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-63.18° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 4H), 7.31 – 7.25 (m, 4H), 7.27 – 7.20 (m, 2H), 5.63 (q, *J* = 2.5 Hz, 1H), 4.24 (dt, *J* = 9.0, 2.5 Hz, 1H), 4.23 – 4.14 (m, 2H), 3.75 (q, *J* = 8.3 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.30 – 3.23 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 166.74, 165.31, 143.31, 139.63, 128.88, 128.68, 127.89, 127.30, 126.75, 126.58, 112.83, 60.01, 58.69, 44.40, 37.89, 14.49. IR (neat, $cm^{-1}$): 3060.55, 3027.90, 2979.85, 1711.82, 1677.48, 1187.43, 1111.37, 1038.99. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}O_2$: 293.1536, found: 293.1540. HPLC analysis: ee = 96%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 7.73 min, $t_{minor}$ = 8.28 min.




**5a** was prepared through reported procedure.[44] To a stirred solution of **2a** in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at room temperature. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

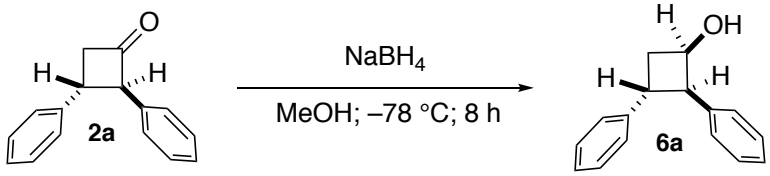
To a mixture of cyclobutanone oxime from last step, $Et_3N$ (2.0 equiv) and DCM (0.5 M) in a 20-mL vial was added benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over $Na_2SO_4$. The solvent was removed under vacuum and the residue was subjected to column chromatography with EtOAc–hexane as eluent to give cyclobutanone *O*-benzoyl oxime **5a**.

**(2*R*,3*R*,*E*)-2,3-Diphenylcyclobutan-1-one *O*-benzoyl oxime (5a)**



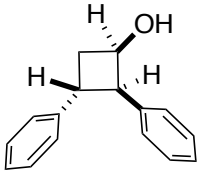

Colorless oil (55.2 mg, 81% overall yield, 0.2 mmol scale). $R_f$ = 0.26 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-5.00° (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.42 – 7.33 (m, 6H), 7.32 – 7.27 (m, 2H), 4.69 (dd, *J* = 7.5, 2.3 Hz, 1H), 3.77 (dt, *J* = 9.6, 7.4 Hz, 1H), 3.70 (ddd, *J* = 16.9, 9.3, 2.4 Hz, 1H), 3.27 (dd, *J* = 16.7, 7.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 168.39, 164.03, 142.22, 137.83, 133.42,

130.32, 129.80, 129.02, 128.91, 128.67, 127.56, 127.45, 127.35, 126.66, 58.26, 42.45, 36.91. IR (neat, $cm^{-1}$): 3060.95, 3028.71, 2926.82, 1741.77, 1688.50, 1600.84, 1450.67, 1245.99. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{20}NO_2$: 342.1489, found: 342.1483. HPLC analysis: ee = 96%. ADH (80% hexanes : 20% isopropanol, 0.8 mL/min): $t_{major}$ = 10.99 min, $t_{minor}$ = 13.76 min.



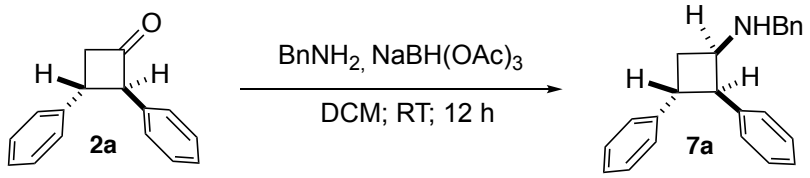

To a stirred solution of compound **2a** (0.1 mmol) in MeOH (2.0 mL) at –78 °C was added $NaBH_4$ (2.0 equiv). The reaction mixture was stirred for 8 h at –78°C. After the complete consumption of **2a**, the reaction mixture was quenched with water and was extracted with EtOAc. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography.

**(1*R*,2*R*)-2,3-Diphenylcyclobutan-1-ol (6a)**



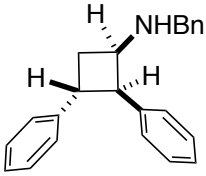

Colorless oil (17.0 mg, 76% yield). 95:5 dr. $R_f$ = 0.28 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-59.66° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 6H), 7.24 – 7.20 (m, 3H), 7.20 – 7.16 (m, 1H), 4.25 (q, *J* = 7.8 Hz, 1H), 3.33 (dd, *J* = 9.9, 7.7 Hz, 1H), 3.08 (td, *J* = 10.1, 7.6 Hz, 1H), 2.78 (dt, *J* = 10.6, 7.3 Hz, 1H), 2.03 (m, 2H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 143.32, 141.60, 128.67, 128.58, 127.12, 126.96, 126.81, 126.46, 70.56, 59.08, 37.36, 37.19. IR (neat, $cm^{-1}$): 3310.95, 3026.07, 2937.83, 1494.87, 1446.53, 1100.73, 750.89, 740.33. HRMS (DART)

([M+H–$H_2O$]$^+$):Calcd. for $C_{16}H_{15}$: 207.1168, found: 207.1162. HPLC analysis: ee = 95%. IA (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 10.30 min, $t_{minor}$ = 11.86 min.

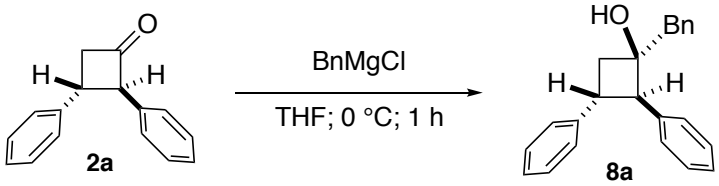



A solution of compound **2a** (0.1 mmol) and benzyl amine (1.5 equiv) in DCM (0.5 mL) was stirred at room temperature for 2h. Then $NaBH(OAc)_3$ (1.5 equiv) was added. The reaction mixture was then stirred for 12 h. After the complete consumption of **2a**, the reaction mixture was quenched with saturated $NaHCO_3$ and was extracted with DCM. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography.

**(1*R*,2*R*)-*N*-Benzyl-2,3-diphenylcyclobutan-1-amine (7a)**

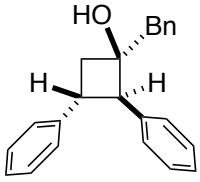



Colorless oil (27.0 mg, 90% yield). >99:1 dr. $R_f$ = 0.26 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-133.78° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): 7.42 – 7.35 (m, 4H), 7.32 – 7.25 (m, 7H), 7.24 – 7.17 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 2H), 4.15 (q, *J* = 8.8 Hz, 1H), 3.80 (t, *J* = 8.1 Hz, 1H), 3.75 (td, *J* = 6.9, 2.7 Hz, 1H), 3.61 (d, *J* = 13.1 Hz, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.40 – 2.25 (m, 2H), 1.39 (s, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 145.03, 140.48, 139.30, 128.59, 128.54, 128.47, 128.42, 128.25, 126.94, 126.70, 126.64, 126.13, 54.39, 51.68, 51.48, 41.71, 33.14. IR (neat, cm$^{-1}$): 3318.59, 3025.04, 2933.20, 2851.27, 1494.33, 1452.23, 1333.27, 1029.40. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{24}N$: 314.1903, found: 314.1899. HPLC analysis: ee = 98%. OJH (80% hexanes : 20% isopropanol, 1.0 mL/min): $t_{major}$ = 18.60 min, $t_{minor}$ = 25.49 min.

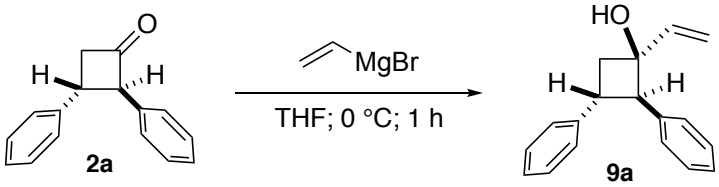



To a stirred solution of compound **2a** (0.1 mmol) in THF (2.0 mL) at 0 °C was added benzyl magnesium chloride solution (1.5 equiv) dropwisely. The reaction mixture was stirred for 1 h at 0°C. After the complete consumption of **2a**, the reaction mixture was quenched with saturated $NH_4Cl$ aqueous solution and was extracted with EtOAc. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography.

**(2*R*)-1-Benzyl-2,3-diphenylcyclobutan-1-ol (8a)**

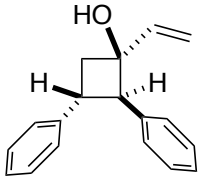



Colorless oil (28.4 mg, 90% yield). 96:4 dr. $R_f$ = 0.32 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-62.78° (c = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 6H), 7.28 – 7.24 (m, 6H), 7.23 – 7.11 (m, 3H), 4.10 (q, *J* = 9.5 Hz, 1H), 3.59 (d, *J* = 10.1 Hz, 1H), 3.01 (s, 2H), 2.40 – 2.27 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 144.32, 137.60, 137.04, 130.22, 128.79, 128.64, 128.56, 128.46, 127.15, 126.78, 126.59, 126.25, 76.59, 56.28, 48.26, 38.89, 38.47. IR (neat, cm$^{-1}$): 3554.87, 3440.19, 2922.73, 2850.21, 1494.63, 1452.51, 1030.60, 696.66. HRMS (DART) ([M+H–$H_2O$]$^+$):Calcd. for $C_{23}H_{21}$: 297.1638, found: 297.1629. HPLC analysis: ee = 96%. IC (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 6.92 min, $t_{minor}$ = 6.51 min.

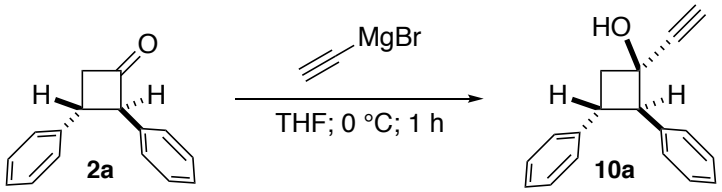


To a stirred solution of compound **2a** (0.1 mmol) in THF (2.0 mL) at 0 °C was added vinyl magnesium bromide solution (0.15 mmol) dropwisely. The reaction mixture was stirred for 1 h at 0°C. After the complete consumption of **2a**, the reaction mixture was quenched with saturated $NH_4Cl$ aqueous solution and was extracted with EtOAc. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated. The residue was purified by column chromatography.

**(2*R*)-2,3-Diphenyl-1-vinylcyclobutan-1-ol (9a)**



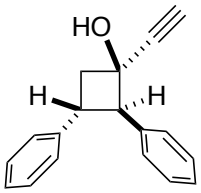

Colorless oil (23.8 mg, 95% yield). 92:8 dr. $R_f$ = 0.36 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-111.99° (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): 7.38 – 7.21 (m, 9H), 7.21 – 7.15 (m, 1H), 6.11 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.24 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.13 (dd, *J* = 10.7, 1.2 Hz, 1H), 4.17 (q, *J* = 9.7 Hz, 1H), 3.68 (d, *J* = 10.3 Hz, 1H), 2.53 (dd, *J* = 11.6, 8.4 Hz, 1H), 2.33 (dd, *J* = 11.6, 9.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 144.12, 143.54, 137.15, 128.78, 128.53, 128.29, 127.30, 126.65, 126.38, 113.14, 76.33, 56.76, 39.49, 38.55. IR (neat, $cm^{-1}$): 3533.20, 3438.05, 3059.40, 3026.34, 2937.87, 1602.21, 1495.31, 1214.36. HRMS (DART) ([M+H–$H_2O$]$^+$) Calcd. for $C_{18}H_{17}$: 233.1325, found: 233.1331. HPLC analysis: ee = 95%. IE (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 9.83 min, $t_{minor}$ = 7.53 min.



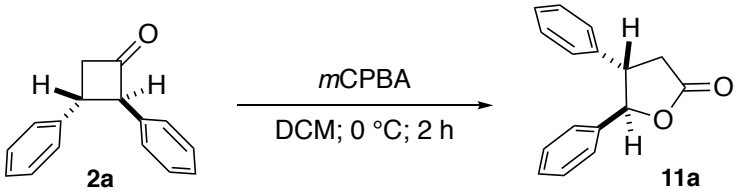

To a stirred solution of compound **2a** (0.1 mmol) in THF (2.0 mL) at 0 °C was added ethynyl magnesium bromide solution (1.5 equiv) dropwisely. The reaction mixture was stirred for 1 h at 0 °C. After the complete consumption of **2a**, the reaction mixture was

quenched with saturated $NH_4Cl$ aqueous solution and was extracted with EtOAc. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by column chromatography.

**(2*R*)-1-Ethynyl-2,3-diphenylcyclobutan-1-ol (10a)**

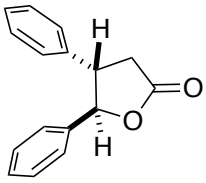



Colorless oil (22.6 mg, 91% yield). 90:10 dr. $R_f$ = 0.32 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-24.40° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.35 (m, 4H), 7.32 – 7.26 (m, 3H), 7.25 – 7.16 (m, 3H), 4.16 (td, *J* = 10.2, 8.4 Hz, 1H), 3.91 (d, *J* = 10.3 Hz, 1H), 2.71 (dd, *J* = 11.7, 8.4 Hz, 1H), 2.66 (s, 1H), 2.58 (dd, *J* = 11.7, 10.0 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 143.17, 136.26, 128.92, 128.62, 128.35, 127.75, 126.69, 126.66, 86.38, 72.96, 67.57, 58.70, 41.05, 39.10. IR (neat, $cm^{-1}$): 3532.47, 3418.20, 3282.97, 3027.04, 2945.15, 1601.88, 1495.37, 1095.89. HRMS (DART) ($[M+H–H_2O]^+$) Calcd. for $C_{18}H_{15}$: 231.1168, found: 231.1171. HPLC analysis: ee = 94%. IE (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 10.31 min, $t_{minor}$ = 9.56 min.

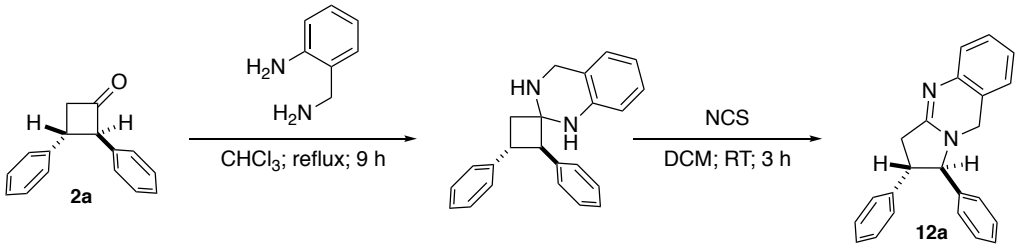



**11a** was prepared through reported procedure.[25] To a stirred solution of compound **2a** (0.1 mmol) in anhydrous DCM (2.0 mL) at 0 °C were added *m*-chloroperoxybenzoic acid (*m*CPBA) (2.0 equiv) and $NaHCO_3$ (2.0 equiv). The reaction mixture was stirred for 2 h at 0 °C. After the complete consumption of **2a**, the reaction mixture was quenched with water and was extracted with DCM. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by column chromatography.

**(4*S*,5*R*)-4,5-Diphenyldihydrofuran-2(3*H*)-one (11a)**



Colorless oil (21.9 mg, 92% yield). $R_f$ = 0.24 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-90.97° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 6H), 7.23 – 7.16 (m, 4H), 5.44 (d, *J* = 8.4 Hz, 1H), 3.60 (dt, *J* = 10.7, 8.5 Hz, 1H), 3.07 (dd, *J* = 17.6, 8.5 Hz, 1H), 2.93 (dd, *J* = 17.6, 10.7 Hz, 1H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 175.40, 138.13, 137.92, 129.25, 129.04, 128.79, 128.03, 127.49, 125.76, 87.56, 50.70, 37.26. IR (neat, $cm^{-1}$): 3032.83, 2924.92, 2145.63, 1780.86, 1455.47, 1269.27, 1193.73, 698.11. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{15}O_2$: 239.1067, found 239.1068. HPLC analysis: ee = 94%. IB (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 28.83 min, $t_{minor}$ = 35.86 min. The experimental data are in accordance with the literature values.[25]



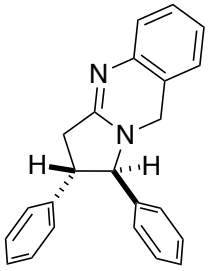

**12a** was prepared through reported procedure.[24] Under $N_2$, a solution of cyclobutanone **2a** (0.3 mmol) and *o*-aminobenzylamine (1.3 equiv) in $CHCl_3$ was stirred under reflux for 9 h. The resulting solution was cooled to room temperature and concentrated. The residue was purified by $SiO_2$ column chromatography (Hexane/ EtOAc = 1/1 with 1% $Et_3N$) to give aminal intermediate.

Under $N_2$, NCS(1.1 equiv) was added to a solution of aminal intermediate in DCM at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and allowed to warm to room temperature. After stirring for 1.5 h, $Na_2S_2O_3$ aq. and 10% NaOH aq. were added to the

reaction mixture and the solution was extracted with DCM. The organic layer was dried over $Na_2SO_4$ and evaporated in vacuo. The residue was purified by $SiO_2$ column chromatography (EtOAc to EtOAc /triethylamine = 10/1) to give quinazoline **12a**.

**(1*R*,2*S*)-1,2-Diphenyl-1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazoline (12a)**

Colorless oil (68.5 mg, 70% overall yield, 0.3 mmol scale). $R_f$ = 0.58 (EtOAc/$Et_3N$ = 8/1).




$[\alpha]_D^{20}$ = (–)-12.80° (*c* = 0.25, MeOH). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 3H), 7.33 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.17 (m, 3H), 7.17 – 7.12 (m, 3H), 6.98 (td, *J* = 7.4, 1.4 Hz, 1H), 6.82 (dd, *J* = 7.5, 1.4 Hz, 1H), 4.37 (d, *J* = 7.5 Hz, 1H), 4.35 (d, *J* = 13.5 Hz, 1H), 4.29 (d, *J* = 13.5 Hz, 1H), 3.34 (dd, *J* = 8.8, 9.1 Hz, 1H), 3.19 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.02 (dd, *J* = 16.9, 9.3 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 162.05, 142.98, 138.10, 129.17, 128.95, 128.68, 128.59, 127.58, 127.45, 127.02, 126.19, 124.39, 124.34, 123.33, 119.94, 74.77, 49.52, 45.50, 38.66. IR (neat, $cm^{-1}$): 3061.29, 3030.19, 2924.21, 1678.47, 1625.99, 1596.86, 1492.20, 1171.92. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{21}N_2$: 325.1699, found 325.1690. HPLC analysis: ee = 94 %. IB (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 18.14 min, $t_{minor}$ = 21.48 min

### 2.4.7 X-ray Crystallographic Information

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using APEX2[45] (Difference Vectors method). Data integration and reduction were performed using SaintPlus[46]. Absorption correction was performed by multi-scan method implemented in SADABS[47]. Space groups were determined using XPREP implemented in APEX2. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.[48,49,50] program.

## 2.5 References

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# Chapter 3. Stereoselective Construction of Chiral Azetidines by Enantioselective 1,4-C–H Radical Alkylation of In Situ-Generated Alkyldiazomethames from Aminoacetaldehyde-Derived Hydrazones

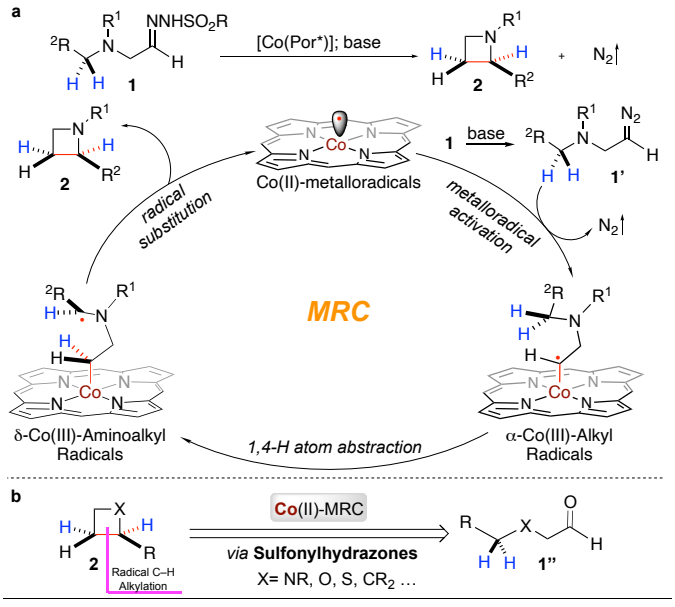
## 3.1 Introduction

Radical reaction has attracted increasing research interest in past decade attribute to its inherent synthetic advantages.[1] Radical C–H functionalization which was achieved through hydrogen atom abstraction (HAA) has emerged as a novel research area.[2] However, the development of HAA-based radical C–H functionalization faces long-standing challenges in controlling the reactivity and selectivity of the outgoing radicals for ensuing effective and accurate bond formation. To address the existing challenges in the field, metalloradical catalysis (MRC) provides a new approach for achieving controllable reactivity and selectivity in radical reactions through catalytic generation as well as subsequent regulation of metal-stabilized organic radical.[3,4,5] As stable 15e-metalloradicals, Co(II) complexes of $D_2$-symmetric chiral amidoporphyrins [Co($D_2$-Por*)] enjoy unique capability of homolytically activating different types of diazo compounds as radical precursors to generate a-Co(III)-alkyl radicals.[6] Upon generation, the a-metalloalkyl radicals can undergo various classic radical reactions such as radical addition (RA) and HAA, following by RS to afford a broad range of chiral products.[7] In particular, Co(II)-based MRC was successfully applied for the development of intramolecular C–H alkylation of diazo compounds involving facile 1,5-HAA as the fundamental key step following by sequent RS for stereoselective construction of different type of five-

membered cyclic compounds.[8] Recently, as an exciting new application for intramolecular C–H alkylation via MRC, we were also able to achieve chiral four-membered cyclobutanone synthesis[9] through 1,4-HAA, which was believed to be much more rare than 1,5-HAA presumably due to enthalpy and entropy reason.[10] To further explore the generality of this 1,4-HAA involved radical cyclization via Co(II)-MRC, we were intrigued if linear aliphatic diazo compounds without providing a-carbonyl as potential H-bonding acceptor for stabilizing the intermediates could still be utilized for the synthesis of different types of four-membered structures, specifically, those saturated nitrogen containing four-membered-ring (Scheme 3.1a). As α-alkyldiazomethanes are commonly generated in situ from corresponding aldehyde derived hydrazone in the presence of base, it would be essential to match the rates between diazo generation and sequential catalytic step avoiding the cumulation of the excess amount of diazo which might cause additional concern for other competitive side reactions. Besides the concern of the efficiency of metalloradical activation of alkyldiazomethanes, additional issues might arise from the regio-and chemoselectivity of the newly formed α-Co(III) alkyl radical **I**. Since 1,4-HAA is known to be inherently challenging, upon the generation of corresponding α-Co(III)-alkyl radicals **I**, how to ensure that intermediate **I** can only proceed desired 1,4- HAA to generate δ-Co(III)-aminoalkyl radicals **II** without the assistance of any obvious non-covalent interaction as a strong handle, for example the potential hydrogen bonding interaction between the a-carbonyl group of the substrate and the amide units of the porphyrin catalyst in the previous study? Can intermediate **I** keep away from other common undesired catalytic pathway such as β-H atom shift, dimerization or addition to the phenyl ring? Furthermore, will the stabilization provided by the adjacent nitrogen to δ-Co(III)-

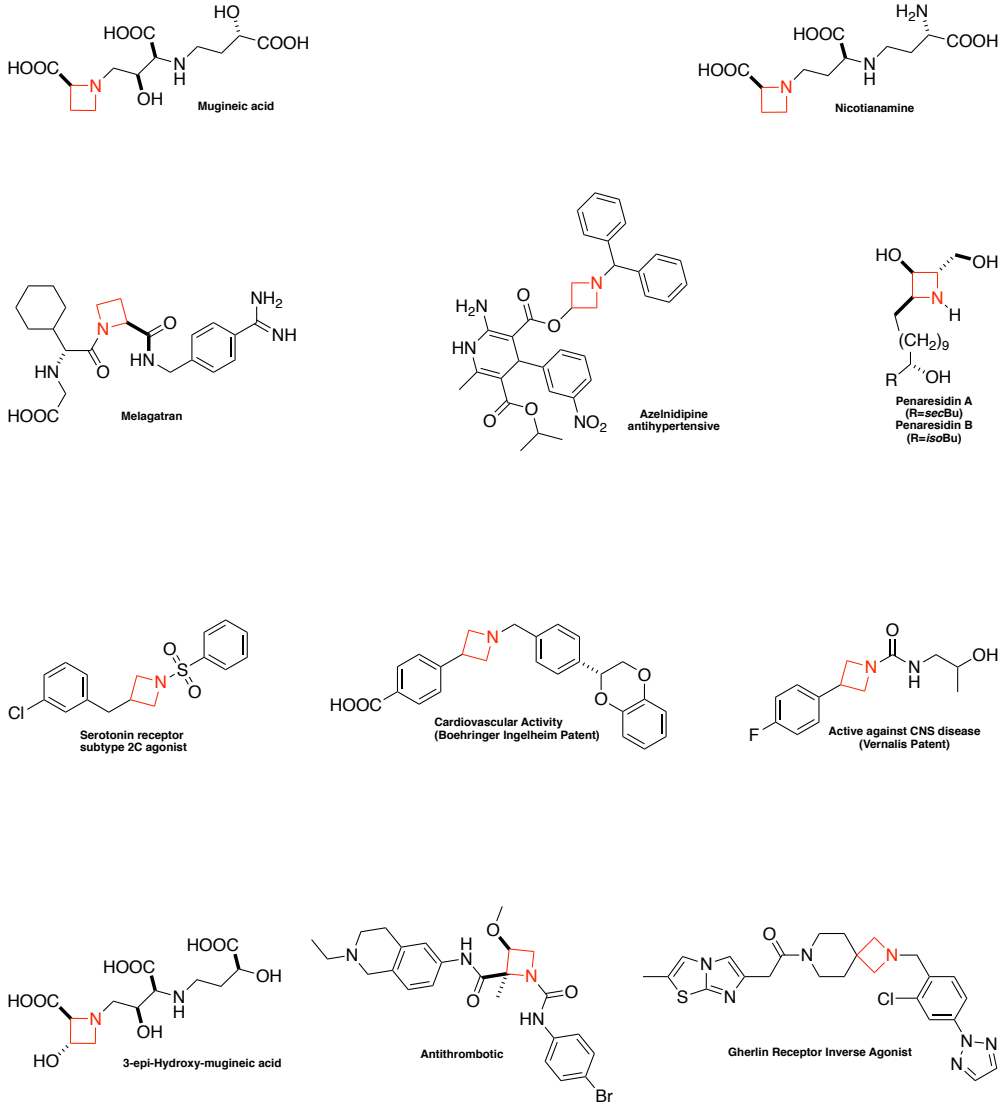
aminoalkyl radicals **II** pose extra challenges in the subsequent *4-exo-tet* radical substitution, which was believed to be equally challenging considering the high strain associated with four-membered transition state. In addition, what factors could be utilized to control the enantioselectivity of radical substitution step considering the flexible nature of linear alkyl chain? We envision that these and related challenges could be addressed through engineering of $D_2$-symmetric chiral amidoporphyrin catalyst that provides the suitable chiral environments for productive catalytic process. If realized, Co(II)-based 1,4-C−H alkylation would become a fundamental new strategy for the preparation of enantioenriched azetidines from aliphatic aldehyde derive hydrazone. With this catalytic system as the demonstration, we also hope that this mode of radical cyclization based on metalloradical C–H alkylation could potentially serve as an alternative retrosynthetic paradigm for construction of four-membered ring structures where C–C bond can be disconnected as common C=O and C–H units of open chain aldehydes (Scheme 3.1b).

**Scheme 3.1. Proposed Mechanism for Construction of Chiral Azetidines by Radical 1,4-C–H Alkylation via Co(II)-MRC**



Azetidines are ubiquitous structures that are widely existing in numerous of natural products and pharmaceuticals (Figure 3.1)[11] and they were believed to have enhanced metabolic stability and potency compared to its 5- and 6-membered ring analogues, pyrrolidines and piperidines.[12] Therefore, tremendous efforts have been devoted to azetidines synthesis.[13] However, there is lack of robust synthetic method allowing for the efficient access of enantioenriched azetidine,[14] which prevents this important moiety from being further investigated in medicinal chemistry. Catalytic asymmetric 1,4-C–H alkylation of diazo compounds represents one potentially promising approach for stereoselective synthesis of four-membered cyclic compounds. Owing to the inherent high strain associated with four-membered ring structures, catalytic process for 1,4-C–H alkylation has not been well explored. While there have been a few reported examples on asymmetric synthesis of carbonyl containing four-membered ring compounds such as β-lactams, β-lactones and cyclobutanones through 1,4-C–H alkylation of donor/acceptor- and acceptor/acceptor-substituted diazo compounds,[9, 15] asymmetric construction of four-membered ring without carbonyl group like azetidine through 1,4-C–H alkylation of diazo compounds has never been demonstrated before. This underdevelopment is presumably attributed to inefficient 1,4-C–H alkylation of those aliphatic diazo without carbonyl group as assistant helping it to go through a highly strained transition state. As an appealing new implementation of Co(II)-based MRC for asymmetric catalysis, we herein report the development of the first catalytic system that is highly effective for enantioselective 1,4-C–H alkylation of aliphatic diazo compounds to construct chiral azetidines. Supported by a new-generation $D_2$-symmetric chiral amidoporphyrin ligand, the Co(II)-based metalloradical system, which enjoys operational simplicity and mild conditions, can

**Figure 3.1. Azetidine-Containing Natural Products and Bioactive Compounds**




activate aliphatic diazo compounds with varied electronic and steric properties for 1,4-alkylation of C($sp^3$)–H bonds, enabling stereoselective construction of chiral azetidines. We show the importance of catalyst development through fine-tuning of the ligand environments in achieving high reactivity and stereoselectivity in this new radical process. Furthermore, our combined experimental and computational studies on the mechanism of the Co(II)-based metalloradical system have shed light on the underlying stepwise radical pathway, including the key steps of 1,4-HAA and *4-exo-tet*-RS. A series of further

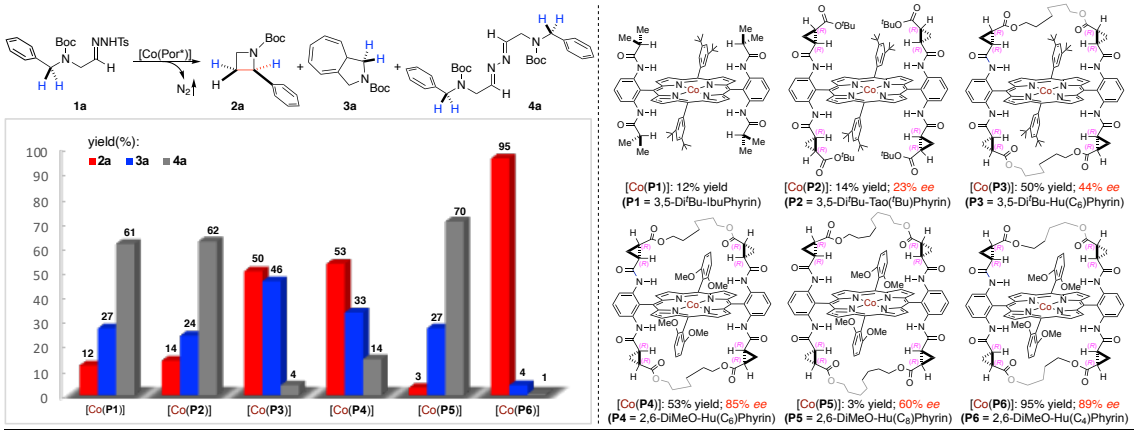
transformations of the resulting enantioenriched azetidines showcase their synthetic applications.

## 3.2 Results and Discussion

### 3.2.1 Reaction Optimization

To test the feasibility of the proposed catalytic process, aliphatic aldehyde-derived tosyl hydrazone **1a** was used as the model substrate to conduct the reactions (Scheme 3.2). When simple achiral metalloradical catalyst [Co(TPP)] (TPP = 5,10,15,20-tetraphenylporphyrin) was applied for the reaction, it will lead to the exclusive formation of **3a**, which resulted from dearomatization of the phenyl ring, as the only catalytic product, incapable of generating the desired azetidine product **2a**. To our delight, when the achiral amidoporphyrin catalyst [Co(**P1**)] (**P1** = 3,5-Di$^t$Bu-IbuPhyrin)[16] was used, it could successfully catalyze the reaction to deliver the alkylation product 2-phenylazetidine **2a** in

**Scheme 3.2. Ligand Effect on Co(II)-Catalyzed 1,4-C–H Alkylation for Construction of Azetidine**[a]



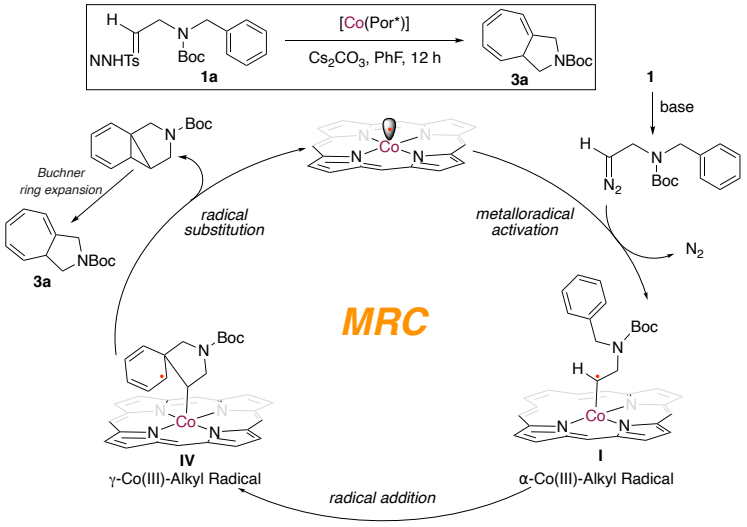

[a]Carried out with **1a** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(Por)] (2 mol %) in PhF (1.0 mL) at 60 ºC for 12 h; isolated yield; ee was determined by chiral HPLC.

significant yield (12%) despite azine **4a** as the major catalytic product. Employment of chiral catalyst [Co(**P2**)] (**P2** = 3,5-Di$^t$Bu-TaoPhyrin)[17] allowed to achieve asymmetric induction for the 1,4-C–H alkylation reaction, affording azetidine 2a in a similar yield (14%) as [Co(**P1**)] with a relatively low but appreciable enantioselectivity (23% ee). Considering the thermodynamically unfavored transition state for 1,4-HAA and 4-*exo*-*tet* RS, a more rigid chiral environment might be desirable. To reduce conformational freedom of the Co(III)-alkyl radical intermediates and promote 1,4 HAA and 4-*exo*-*tet* RS, we decided to rigidify the environment of ligand pocket. Therefore, new-generation $D_2$-symmetric chiral amidoporphyrin with alkyl bridges across two chiral amide units on both side of the porphyrin plane [Co(**P3**)] (**P3** = 3,5-Di$^t$Bu-Hu($C_6$)Phyrin)[17] was utilized for further improve the reactivity and selectivity of the reaction. As expected, it dramatically improved the reactivity compared to [Co(**P2**)] and shift the azetidine **2a** from minor product to major product. In addition, the enantioselectivity of **2a** was increased from 23% to 44%. Subsequent use of analogous catalyst [Co(**P5**)] (P5 = 2,6-DiMeO-Hu($C_6$)Phyrin), which bears 2,6-dimethoxyphenyl instead of 3,5-di-*tert*-butylphenyl groups as the 5,15-diaryl substituents, allowed for the desired azetidine 2a formation in similar 53% yield with further improvement of enantioselectivities (85% ee). To continue improving the system, the effect by changing the carbon chain length of the bridge part for the porphyrin was explored. Applying the catalyst with longer methylene bridge for the reaction [Co(**P5**)][17] which essentially provides a larger chiral pocket for the reaction, will result in a much lower yield and relatively lower enantiomeric induction for the reaction. In contrast, catalyst [Co(**P6**)][17] with a shorter bridge carbon chain which indicate a much rigid chiral

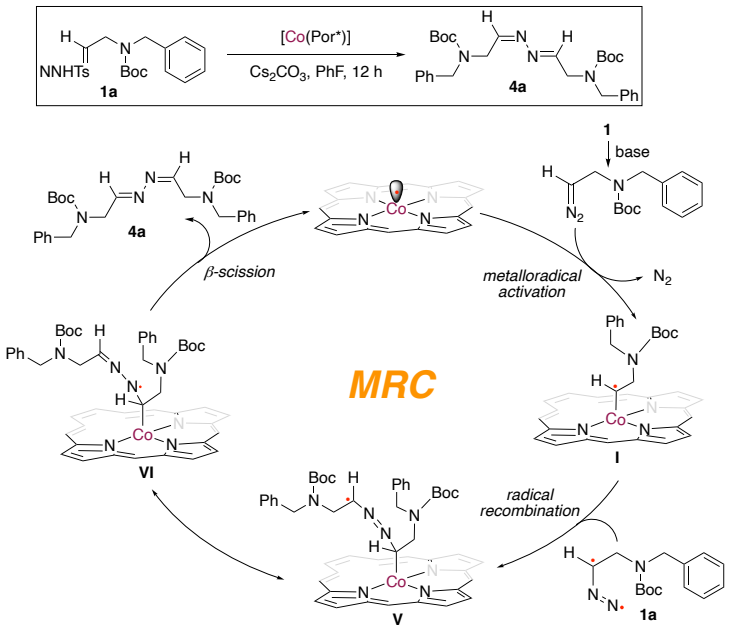
environment will boost the yield for the reaction from 53% to 95%. The enantioselectivity for the reaction was also slightly increase to 89%.

Both side products **3a** and **4a** were also catalytic products and believed to form through the following mechanism. **3a** formed through Buchener ring expansion after catalytic process and **4a** was resulted from dimerization of two molecules of diazo **1a**.

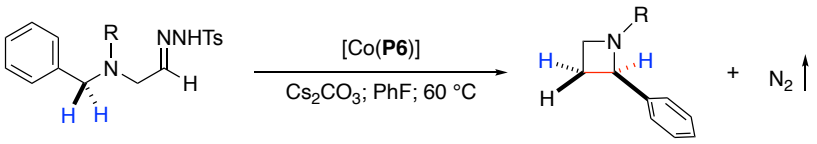
**Scheme 3.3. Proposed Catalytic Cycle for the Formation of 3a**




**Scheme 3.4. Proposed Catalytic Cycle for the Formation of 4a**



**Scheme 3.5. Effect of N-Protecting group[a]**




| Entry | R | yield (%) | ee(%) | [Co(**P6**)] |
|---|---|---|---|---|
| **1** | **Boc** | **95** | **89** | |
| 2 | Cbz | 38 | 92 | |
| 3 | Ac | trace | - | |
| 4 | Ts | 0 | - | |
| 5 | Bn | 0 | - | |

[a]Carried out with **1a** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(Por)] (2 mol %) in PhF (1.0 mL) at 60 ºC for 12 h; isolated yield; ee was determined by chiral HPLC.

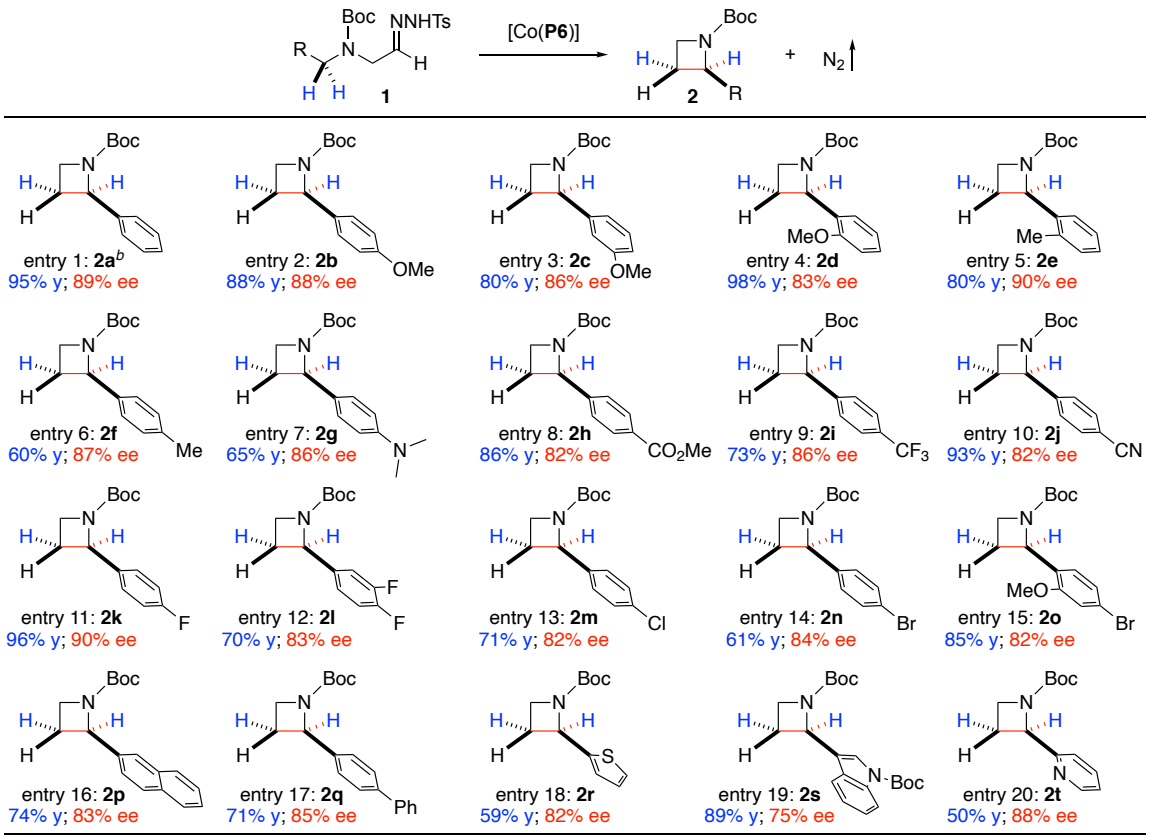
Besides, as shown in Scheme 3.5, the effect of the N-protecting group on the reactivity and selectivity for this catalytic reaction was also investigated. As a result, this reaction is very sensitive to the N-protecting group. When the N-protecting group was changed from Boc to other group such as Cbz, Ac, Ts or Bn, the yield of the product will dramatically decrease. We envisioned that bulkier Boc-protecting group through interacting with the rigid catalyst might be able to force two flexible carbon chains tethered by nitrogen closer enough (similar as Thorpe–Ingold effect) and facilitate the 1,4-HAA and 4-exo-tet radical cyclization steps.

### 3.2.2 Substrate Scope

Under the optimized reaction conditions, the substrate scope of [Co(**P6**)]-catalyzed radical alkylation was evaluated for different types of benzylic C−H bonds with nitrogen-containing aliphatic tosylhydrazone substrates **1**. Like parent **1a**, benzylic C–H bond with

MeO substituents at the *para*-, *meta*-, and *ortho*-positions could be alkylated to afford 2-arylazetidines **2b**–**2d** in high yields with good enantioselectivities (Table 3.1; entries 2–4). In addition to MeO group, other electron-rich substituents like 2-Me, 4-Me and 4-dimethylamino could be well tolerated in the system and deliver corresponding 2-arylazetidines **2e**-**2g** in good yields and same level of enantioselectivities (Table 3.1, entries 5–7). Besides, those aliphatic tosylhydrazone with electron-withdrawing group such as 4-$CO_2Me$, 4-$CF_3$ and 4-CN could serve as suitable substrates for this alkylation system, affording four-membered *N*-heterocycles **2h**–**2j** with good enantioselectivities (Table 3.1, entries 8–10). Furthermore, substrates with fluorinated benzylic C–H bond could be used for delivering fluorinated azetidines **2k** and **2l** in high yield and high level of enantioselectivities (Table 3.1, entries 11 and 12). Other halogenated benzylic C–H bond could be also effectively alkylated to generate the halogenated azetidines **2m**–**2o** in high yields with good enantioselectivities (Table 3.1; entries 13–15), which may be potentially transformed to other azetidine derivatives by cross-coupling and related reactions. Moreover, the alkylation reaction by [Co(**P6**)] could be applied to benzylic C–H substrates with expanded aromatic system as shown by the construction of azetidines **2p** and **2q** in high yields and high enantioselectivities (Table 3.1; entries 16 and 17). The Co(II)-catalyzed 1,4-C–H alkylation was also demonstrated to be compatible with substrates containing heteroarenes, such as thiophene (**1r**), indole (**1s**), pyridine (**1t**), allowing for stereoselective construction of 2-heteroarylazetidine **2r**–**2t** in moderate to good yields with the same high enantioselectivities (Table 3.1; entries 17–19).

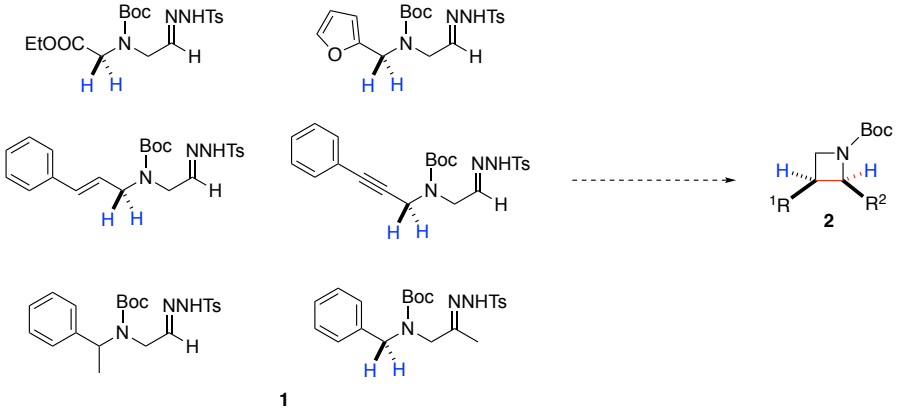
**Table 3.1. Asymmetric Radical 1,4-C–H Alkylation by Co(II)-Based Metalloradical System for Construction of Azetidines**[a]




[a]Carried out with **1a** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %) in PhF (1.0 mL) at 60 ºC for 12 h; isolated yield; ee was determined by chiral HPLC. [b] Absolute configuration of **2a** was *R* which was reported in the literature[18]

Additional substrates were tried out for the Co(II)-catalyzed 1,4-C–H alkylation for azetidine formation, however, providing no desired azetidine product under the optimized reaction condition (Scheme 3.6). For the ketone base substrates, starting material totally remained, which mean under the optimized reaction temperature, hydrazone failed to be deprotonated and deliver diazo compound for catalytic reaction.

**Scheme 3.6. Substrates that Failed to Work for [Co(P6)]-Catalyzed Azetidine Formation**[a]

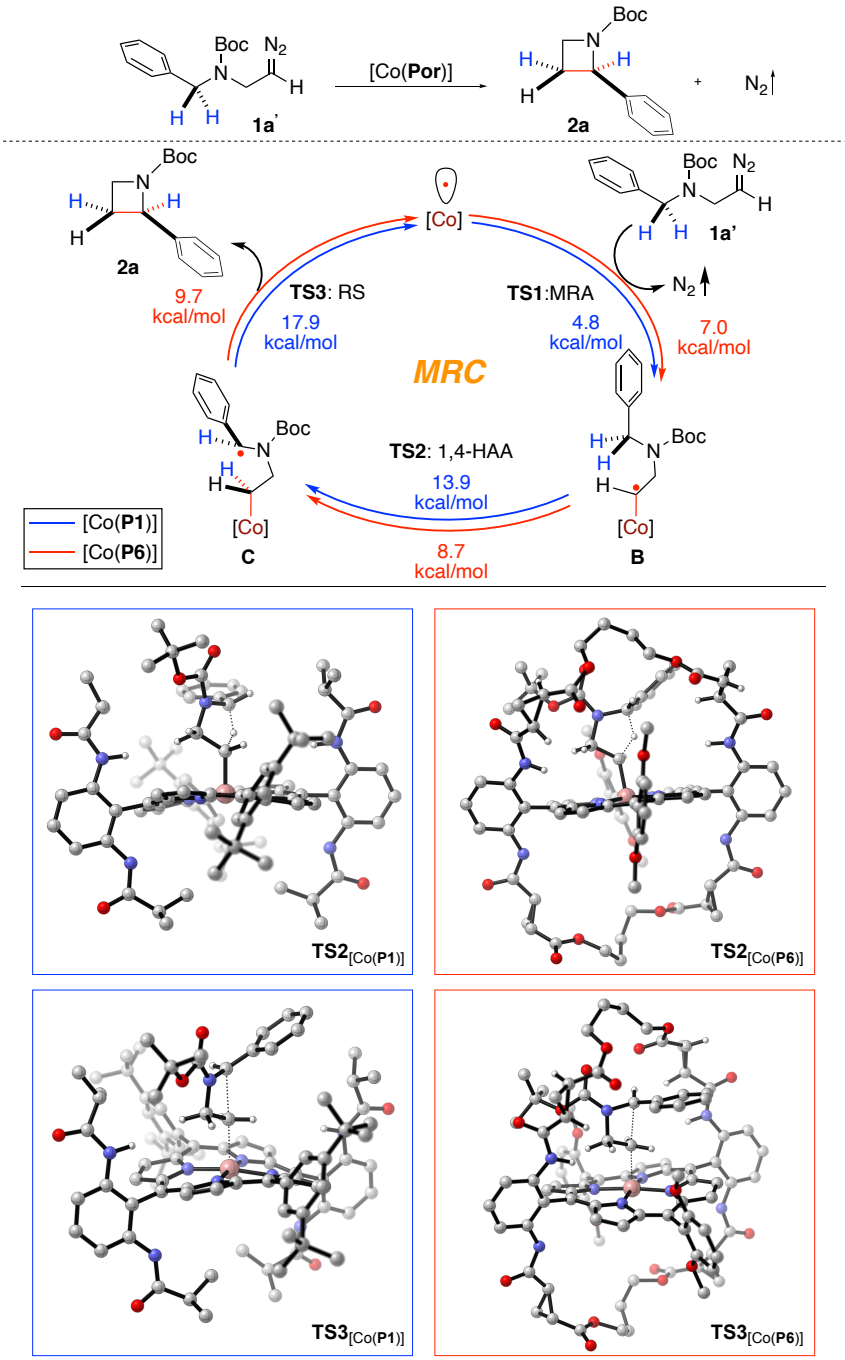



### 3.2.3 Mechanistic Studies

To gain insights into this catalytic process, combined computational and experimental studies were conducted to explore the proposed stepwise radical mechanism for the Co(II)-catalyzed 1,4-C–H alkylation. First, to elucidate the dramatic ligand effect in term of reactivity for desired azetidine formation, density functional theory (DFT) calculations were performed for 1,4-C–H alkylation reaction of **1a'** by both [Co(**P1**)] (12% yield of azetidine **2a**) and the optimized catalyst [Co(**P6**)] (95% yield of azetidine **2a**). (Scheme 3.7; see Experimental Section for details). Upon metalloradical activation (MRA), **1a'** undergoes the extrusion of dinitrogen to generate α-Co(III)-alkyl radical **B**. The metalloradical activation step, which is exergonic by 16.1 kcal/mol for [Co(**P1**)] and 6.7 kcal/mol for [Co(**P6**)], is found to be associated with a relatively low activation barrier (**TS1**$_{[Co(P1)]}$: $\Delta G^{\ddagger}$ = 4.8 kcal/mol, **TS1**$_{[Co(P6)]}$: $\Delta G^{\ddagger}$ = 7.0 kcal/mol). The results reveal the fact that the activation of this donor type of diazo is much more facile than the donor/acceptor in the cyclobutanone case. The higher activation energy for [Co(**P6**)] might attribute to the rigidity of the catalyst which could increase the difficulty for the substrate

to get into the reaction pocket. Subsequent 1,4-HAA of intermediate **B**, which is exergonic by 12.3 kcal/mol for [Co(**P1**)] and 9.4 kcal/mol for [Co(**P6**)], gives rise to the corresponding δ-Co(III)-alkyl radical intermediate **C** with a higher energy barrier (**TS2**$_{[Co(P1)]}$: $\Delta G^{\ddagger}$ = 13.9 kcal/mol, **TS2**$_{[Co(P6)]}$: $\Delta G^{\ddagger}$ = 8.7 kcal/mol). For the transition state of 1,4-HAA, the angle of hydrogen atom transfer was measured. The C1–H–C2 angle in TS2 for [Co(**P1**)] and [Co(**P6**)] was 128.20° and 127.31° respectively, which means the transition state for 1,4-HAA is more linear with [Co(**P1**)]. According to the DFT calculations, the final step (*4-exo-tet* radical substitution) has the highest energy barrier (**TS3**$_{[Co(P1)]}$: $\Delta G^{\ddagger}$ = 17.9 kcal/mol, **TS3**$_{[Co(P6)]}$: $\Delta G^{\ddagger}$ = 9.7 kcal/mol) and is believed to be the rate determining step for this catalytic process. The experimental results can be well explained by DFT calculation. Since [Co(**P1**)] is associated with a low activation energy barrier but much higher energy barrier for both 1,4-HAA and 4-exo-tet RS steps, after facile activation, intermediate B would peruse through other catalytic pathways to generate side products (**3a** and **4a)** in high yield. However, a much lower energy barrier for both 1,4-HAA and 4-exo-tet RS steps for [Co(**P6**)] make the azetidine formation favorable pathway, thus allowing for the desired azetidine formation in 95% yield. It was believed that the lower energy barrier for both 1,4-HAA and 4-exo-tet RS steps for [Co(**P6**)] may be attributed to the presence of the multiple noncovalent interactions that stabilize transition state **TS2**$_{[Co(P6)]}$ and **TS3**$_{[Co(P6)]}$. As illustrated by the computed model of **TS2**$_{[Co(P6)]}$ and **TS3**$_{[Co(P6)]}$ (Scheme 3.7), the highly rigid chiral environment that was provided [Co(**P6**)] might help to orient the reacting substrate within the catalyst cavity in proximity with proper conformation to facilitate those two key reaction steps.

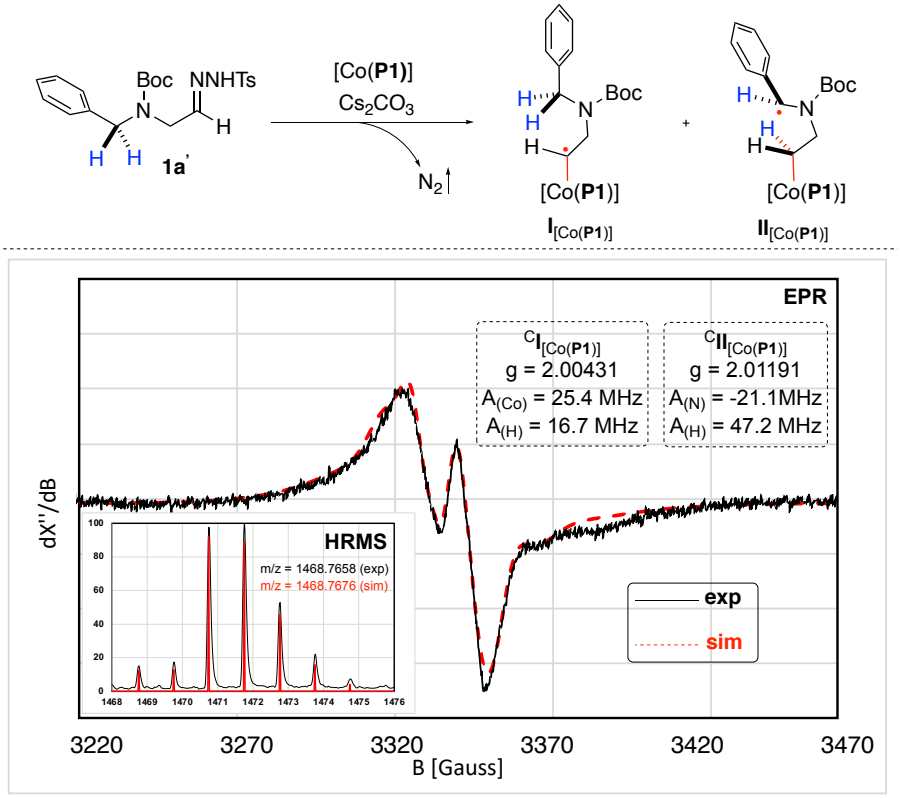
**Scheme 3.7. DFT Calculation of Azetidine with [Co(P1)] and [Co(P6)]**




To experimentally detect α-Co(III)-alkyl radical **I** and δ-Co(III)-alkyl radical **II**, the isotropic X-band electron paramagnetic resonance (EPR) spectrum was recorded at room temperature for the reaction mixture of [Co(**P1**)] with hydrazone **1a** and $Cs_2CO_3$ in

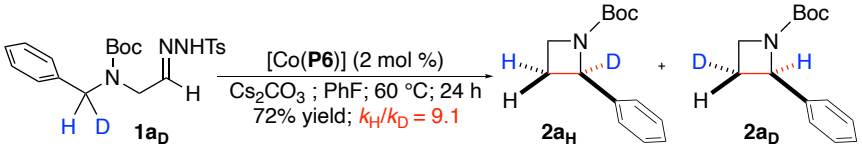
benzene (Scheme 3.8). The spectrum displays notable signals that are characteristic of mixture of α-Co(III)-alkyl radical and δ-Co(III)-alkyl radical. The observed isotropic g-values of three species is all around 2.00, which is consistent with the generation of organic radical **I** and **II**. The observed signals were broad and could be fittingly simulated by two proposed species: **I** and **II** on the basis of couplings by $^{59}Co$ (I = 7/2), $^{14}N$ (I = 1) and $^{1}H$ (I =1/2): 65% of α-Co(III)-alkyl radical **I** (g: 2.00431; $A_{(Co)}$: 25.4 MHz; $A_{(H)}$: 16.7 MHz) and 35% of d-Co(III)-alkyl radical radical **II** (g: 2.01191; $A_{(N)}$: -21.1 MHz; $A_{(H)}$: 47.2 MHz). In addition to EPR, the reaction mixture of hydrozone **1a**, $Cs_2CO_3$ and catalyst [Co(**P1**)] was also analyzed by high-resolution mass spectrometry (HRMS) with electrospray ionization (ESI) in the absence of any additives as electron carriers (Scheme 3B). The obtained spectrum clearly reveals a signal corresponding to [(**P1**)Co–$CHCH_2NCO_2C_4H_{10}CH_2C_6H_5$)]$^+$ (m/z = 1468.765747), which resulted from neutral α-Co(III)-alkyl radical intermediate $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ or δ-Co(III)-alkyl radical intermediate $\mathbf{II}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ 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 from the formula $[C_{90}H_{107}CoN_9O_6]^+$ (see Experimental Section for details).

**Scheme 3.8. Generation and Detection of Co(III)-Alkyl Radical Intermediates by EPR and HRMS**

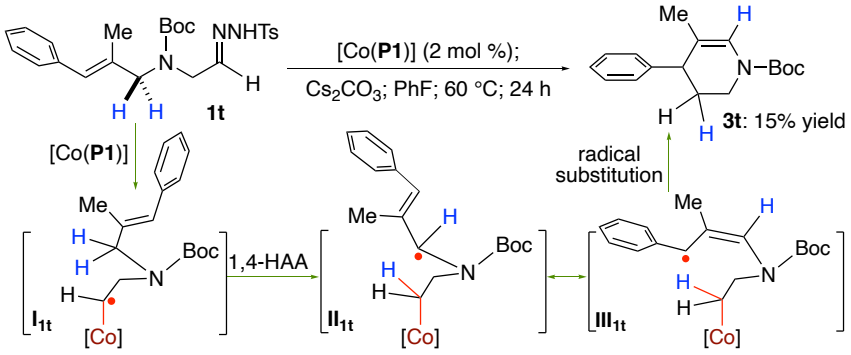



To continue the exploration on the 1,4-HAA step in the catalytic process, monodeuterated diazo **1a$_D$** was prepared as the substrate for the study of kinetic isotopic effect (KIE) using chiral catalyst [Co(**P6**)] (Scheme 3.9). The KIE values for the catalytic reaction of diazo **1a$_D$** by [Co(**P6**)] were determined to be 9.1. This large values of primary KIE are in good agreement with the proposed step of homolytic C–H bond cleavage via intramolecular H-atom abstraction by α-Co(III)-alkyl radical intermediate **I**.

**Scheme 3.9. Kinetic Isotope Effect for Azetidine Synthesis**

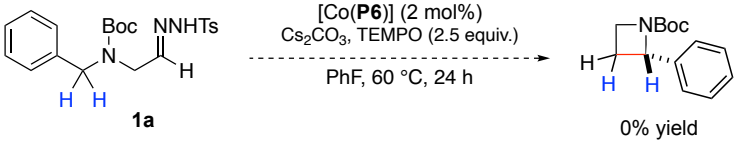


**Scheme 3.10. Probing of Allylic Radical Intermediate through chain walking process**




To further probe the existence of δ-Co(III)-alkyl radical intermediate **II**, **1t** was employed as the substrate for 1,4-C–H alkylation reaction using [Co(**P1**)] as the catalyst (Scheme 3.10). It was found that six membered tetrahydropyridine **3t** was generated as the only product without the observation of azetidine product, indicating isomerization of the olefin configuration during the catalytic process. The formation of **3t** from **1t** implies the involvement of both δ-Co(III)-allylic radical $\mathbf{II}_{1t}$ and its resonance ζ-Co(III)-allylic radical $\mathbf{III}_{1t}$. No azetidine product formation was observed might be due to *6-exo-tet* is much facile than *4-exo-tet* cyclization under [Co(**P1**)] catalytic environment.

**Scheme 3.11. Radial Scavenger Effect for Azetidine Synthesis**

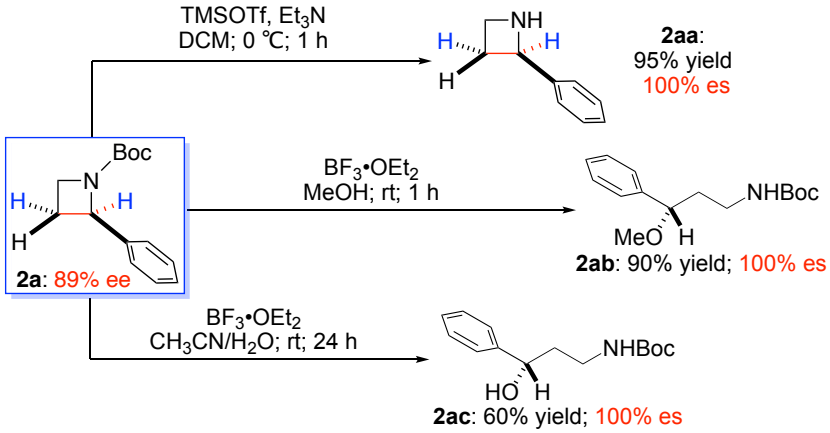



Besides, the effect of radical scavenger TEMPO on the Co(II)-catalyzed azetidine formation was tested with the model substate **1a** (Scheme 3.11). In the presence of 2.5 equiv. of TEMPO, the catalytic reaction was totally shut down and resulting in no azetidine product formation. However, no TEMPO trapping product was obtained presumably due the instability of the potential TEMPO trapping product.

### 3.2.4 Synthetic Applications

Co(II)-catalyzed C–H alkylation allowed for asymmetric construction of azetidine. By taking advantage of product's inherent ring strain, azetidine **2a** could be further transformed to several equally important compounds (Scheme 4). Product **2a** which was derived from model substrate can be efficiently deprotected to generate corresponding N–H azetidine **2aa** in 95% yield without erosion of its optical purity. In addition to N-deprotection, product **2a** was shown to undergo facile ring opening reaction using methanol and water as the nucleophiles in the present of boron trifluoride diethyl etherate as the Lewis acid to generate 1,3-amino ether **2ab** in 90% yield and 1,3-amino alcohol **2ac** in 60% yield with preservation of the high enantiomeric purity. Both of the resulting chiral products are important motif in natural products and drug molecules.[19]

**Scheme 3.12. Further Transformation for Chiral Azetidine**



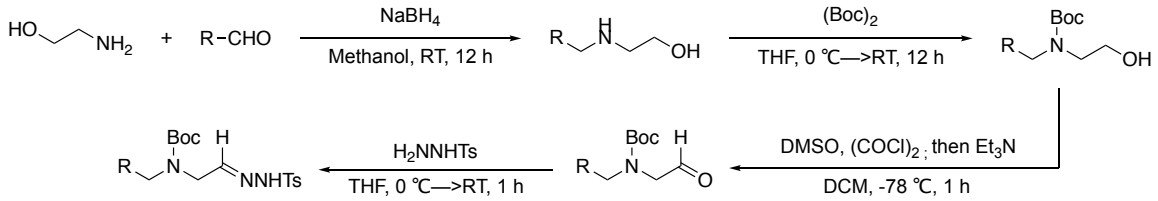

## 3.3 Conclusion

In summary, we have for the first time showcased chiral azetidine synthesis through a fundamental new method, asymmetric radical 1,4-C–H alkylation, via Co(II)-based MRC. The judicious modulation of $D_2$-symmetric chiral amidoporphyrin ligand to adopt desired steric, electronic and chiral environments around the Co(II)-metalloradical center that

maximize a network of noncovalent attractive interactions in catalytic intermediates is the key to the success of this transformation. With the bridged $D_2$-symmetric chiral amidoporphyrin 2,6-DiMeO-Hu($C_4$)Phyrin as the optimal supporting ligand, the Co(II)-based metalloradical system can catalyze asymmetric 1,4-C–H alkylation of in situ generated donor- type diazo compound with varied electronic and steric properties to construct chiral 2-azetidine in good yields with high enantioselectivities. The combined computational and experimental studies have shed light on the working details of this new catalytic process that proceeds through a stepwise radical mechanism. As a demonstration of its broad synthetic application of this Co(II)-based metalloradical system for asymmetric 1,4-C−H alkylation, we have performed several enantiospecific transformations from the resulting enantioenriched 2-azetidine. We envision that this work further reveals the generality of this 1,4-HAA following by radical substitution (RS) reaction pattern in asymmetric construction of strained four-membered ring product and with the hope that it can be soon utilized as a routine method for the asymmetric construction of different kinds of four-membered ring structures.

## 3.4 Experimental Section

### 3.4.1 General Procedure for Substrate Synthesis




**Step 1:** To a solution of aldehyde (10 mmol) in anhydrous methanol (20.0 mL) was added Ethanolamine (10 mmol) dropwise at room temperature. The reaction was stirred overnight. After that, the reaction mixture was cooled down to 0 °C in an ice bath. Sodium borohydride (15 mmol) was added portionwise. After the bubbling stopped, the solvent was then evaporated. The resulting residue was then partitioned between $H_2O$ (30 mL) and EtOAc (30 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were then dried and concentrated under vacuum. The obtained raw compound was directly used without further purification.

**Step 2:** To a solution of resulting alcohol from last step (5 mmol) and triethylamine (1.5 equiv.) in DCM (30.0 mL), di-tert-butyl dicarbonate (1.1 equiv.) was added portionwise at 0 $^{O}$C. The reaction was then stirred at room temperature and monitored by TLC. After the reaction was completed, the mixture was filtrated through a short pad of silica and eluted with ethyl acetate. The filtrate was then evaporated and concentrated under vacuum. The obtained raw compound was directly used without further purification.

**Step 3:** (Swern oxidation): To a solution of oxalyl chloride (1.5 equiv.) in DCM (30 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 Boc protected alcohol in DCM (5.0 mL) was added dropwisely. The solution was then stirred for 30 min at -78 °C, followed by the dropwise

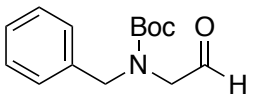
addition of triethylamine (4.5 equiv.). After 10 min, the reaction mixture was warmed up to room temperature, poured into brine (30 mL) and stirred for another 10 min. The layers were then separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under vacuum. The oxidized product was further purified by flash chromatography.

**Step 4:** To a stirred solution of pure tosylhydrazide (1 mmol) in THF (2.0 mL) at room temperature, aldehyde was added dropwise (or portionwise if solid). The reaction was completed within 0.5 h. After that, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by flash chromatography.

### 3.4.2 Characterization of Aldehyde Substrates

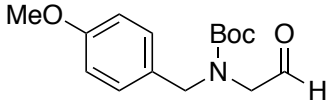
**Characterization of Aldehyde Substrates**

***tert*-Butyl benzyl(2-oxoethyl)carbamate s-1a**




Colorless Oil. Yield: 80%. $R_f$ = 0.44 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.39 – 7.19 (m, 5H), 4.56 (s, 2H), 3.79 (s, 2H), 1.48 (s, 9H).$^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.55, 155.28, 137.04, 128.60, 127.98, 127.59, 77.20, 56.27, 51.36, 28.16. IR (neat, $cm^{-1}$): 2976.92, 2930.77, 1734.86, 1688.47, 1496.02, 1391.85, 1241.05,1162.08. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{20}NO_3$: 250.14377, found 250.14478.

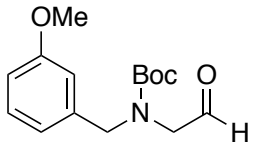
***tert*-Butyl (4-methoxybenzyl)(2-oxoethyl)carbamate s-1b**




Colorless Oil. Yield: 85%. $R_f$ = 0.33 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.34 (s, 1H), 7.14 (d, $J$ = 8.1 Hz, 2H), 6.82

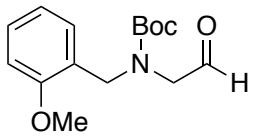
(d, $J$ = 8.5, 2H), 4.43 (s, 2H), 3.73 (s, 3H), 3.72 (s, 2H) 1.42 (s, 9H).$^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.72, 159.02, 155.19, 129.34, 128.99, 128.82, 80.66, 55.01, 50.69, 32.19, 28.14. IR (neat, $cm^{-1}$): 2975.99, 2932.67, 2836.61, 1734.36, 1688.19, 1512.44, 1237.17, 1161.01. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_4$: 280.15433, found 280.15549.

***tert*-Butyl (3-methoxybenzyl)(2-oxoethyl)carbamate s-1c**



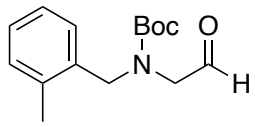

Colorless Oil. Yield: 77%. $R_f$ = 0.13 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.20 (t, $J$ = 7.2 Hz, 1H), 6.81 – 6.71 (m, 3H), 4.47 (s, 2H), 3.75 (s, 2H), 3.74 (s, 3H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 198.50, 159.79, 155.25, 138.64, 129.60, 120.13, 113.41, 113.00, 80.81, 54.96, 51.28, 28.03. IR (neat, $cm^{-1}$): 3004.75, 2970.09, 2940.32, 1736.95, 1688.61, 1366.82, 1236.62, 1161.76. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_4$: 280.15433, found 280.15472.

***tert*-Butyl (2-methoxybenzyl)(2-oxoethyl)carbamate s-1d**



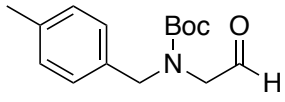

Colorless Oil. Yield: 83%. $R_f$ = 0.35 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.36 – 7.17 (m, 2H), 6.92 (m, 1H), 6.84 (m, 1H), 4.47 (s, 2H), 3.83 (s, 2H), 3.78 (s, 3H), 1.43 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 199.92, 157.38, 155.18, 129.78, 128.92, 125.34, 120.38, 110.24, 80.58, 57.23, 55.05, 47.43, 28.27. IR (neat, $cm^{-1}$): 2975.20, 2933.69, 2837.97, 1734.10, 1686.76, 1456.85, 1238.22, 1159.23. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_4$: 280.15433, found 280.15532.

***tert*-Butyl (2-methylbenzyl)(2-oxoethyl)carbamate s-1e**



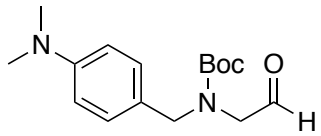

Colorless Oil. Yield: 80%. $R_f$ = 0.44 (Hexane/ EtOAc: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.21 – 7.06 (m, 4H), 4.55 (s, 2H), 3.82 (s, 2H), 2.29 (s, 3H), 1.47 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.69, 155.27, 137.13, 134.69, 130.91, 129.02, 128.05, 126.28, 81.10, 55.94, 49.46, 28.36, 19.16. IR (neat, $cm^{-1}$): 2975.62, 2929.51, 1735.10, 1689.87, 1391.69, 1365.79, 1238.40, 1130.12. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{22}NO_3$: 264.15942, found 264.15986.

***tert*-Butyl (4-methylbenzyl)(2-oxoethyl)carbamate s-1f**




Colorless Oil. Yield: 87%. $R_f$ = 0.45 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.16 – 7.07 (m, 4H), 4.49 (s, 2H), 3.75 (s, 2H), 2.31 (s, 3H), 1.45 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.75, 155.27, 137.28, 133.95, 129.29, 128.05, 80.77, 56.16, 51.09, 28.09, 20.93. IR (neat, $cm^{-1}$): 2976.33, 2926.42, 2813.38, 1735.23, 1689.04, 1391.33, 1365.87,1239.66. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{22}NO_3$: 264.15942, found 264.16000.

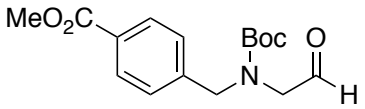
***tert*-Butyl (4-(dimethylamino)benzyl)(2-oxoethyl)carbamate s-1g**




Colorless Oil. Yield: 90%. $R_f$ = 0.30 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.24 – 6.92 (m, 3H), 6.63 (d, $J$ = 8.1 Hz, 1H), 4.35 (s, 2H), 3.76 (s, 2H), 2.88 (s, 6H), 1.42 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 199.20, 155.17, 150.01, 130.08, 129.26, 128.05, 119.97, 112.41, 80.91, 77.20, 55.77, 50.37, 28.02. IR (neat, $cm^{-1}$): 2976.55, 2931.54, 2832.52, 1734.74, 1687.98, 1523.01,

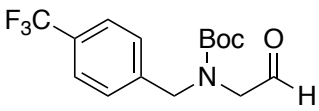
1240.17,1161.68. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{25}N_2O_3$: 293.18597, found 293.18561.

**Methyl 4-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)benzoate s-1h**



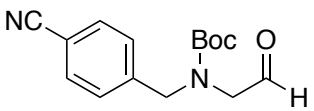

Colorless Oil. Yield: 75%. $R_f$ = 0.23 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.97 – 7.89 (m, 2H), 7.26 – 7.20 (m, 2H), 4.51 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H), 3.81 (s, 3H), 1.38 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ δ 197.88, 166.46, 155.18, 142.35, 129.81, 129.36, 127.63, 81.03, 77.20, 51.88, 51.16, 27.97. IR (neat, cm$^{-1}$): 2978.74, 2953.29, 1716.92, 1690.51, 1278.81, 1243.17, 1162.20, 908.75. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{22}NO_5$: 308.14925, found 308.14967.

***tert*-Butyl (2-oxoethyl)(4-(trifluoromethyl)benzyl)carbamate s-1i**




Colorless Oil. Yield: 90%. $R_f$ = 0.36 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.58 – 7.50 (m, 2H), 7.32 (dd, *J* = 13.0, 7.8 Hz, 2H), 4.54 (s, 2H), 3.81 (s, 2H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 197.76, 155.29, 141.41, 129.76 (q, *J* = 32.1 Hz), 128.03, 125.55, 122.61, 81.23, 56.69, 51.12, 28.01. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.59, -62.60. IR (neat, cm$^{-1}$): 2979.23, 2932.57, 2819.54, 1736.60, 1690.90, 1322.94, 1244.01, 1159.97. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{19}NO_3F_3$: 318.13115, found 318.13233.

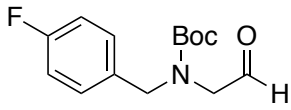
***tert*-Butyl (4-cyanobenzyl)(2-oxoethyl)carbamate s-1j**




Colorless Oil. Yield: 88%. $R_f$ = 0.15 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was

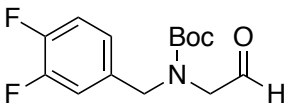
reported. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.72 – 7.43 (m, 2H), 7.35 – 7.26 (m, 2H), 4.50 (s, 2H), 3.82 (s, 2H), 1.38 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 197.35, 155.12, 142.80, 132.25, 128.19, 118.38, 111.19, 81.21, 56.90, 51.18, 27.90. IR (neat, $cm^{-1}$): 2978.05, 2931.79, 2821.33, 2228.92, 1735.15, 1690.35, 1243.81. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{19}N_2O_3$: 275.13902, found 275.14032.

***tert*-Butyl (4-fluorobenzyl)(2-oxoethyl)carbamate s-1k**




Colorless Oil. Yield: 91%. $R_f$ = 0.33 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.22 – 7.14 (m, 2H), 7.03 – 6.92 (m, 2H), 4.47 (s, 2H), 3.77 (s, 2H), 1.44 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.30, 162.19 (d, $J$ = 245.5 Hz), 155.27, 132.95, 129.70 (d, $J$ = 8.2 Hz), 115.42, 77.24, 56.35, 50.74, 28.09. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -114.66. IR (neat, $cm^{-1}$): 2977.67, 2931.61, 2818.83, 1735.21, 1688.04, 1509.42, 1366.62,1154.60. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{19}NO_3F$: 268.13435, found 268.13471.

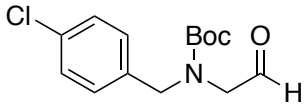
***tert*-Butyl (3,4-difluorobenzyl)(2-oxoethyl)carbamate s-1l**




Colorless Oil. Yield: 85%. $R_f$ = 0.43 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.40 (s, 1H), 7.02 (t, $J$ = 10.7 Hz, 2H), 6.91 (d, $J$ = 9.6 Hz, 1H), 4.40 (s, 2H), 3.78 (s, 2H), 1.39 (s, 9H).$^{13}$C NMR (101 MHz, $CDCl_3$): δ 197.73, 155.16, 150.19 (dd, $J$ = 249.3, 13.1 Hz), 149.54 (d, $J$ = 247.5 Hz), 134.39, 123.76, 117.23 (d, $J$ = 17.3 Hz), 116.66 (d, $J$ = 17.5 Hz), 81.13, 56.54, 50.51, 27.92. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -137.22, -139.48. IR (neat, $cm^{-1}$): 2978.73, 2931.61, 2820.99, 1735.81,

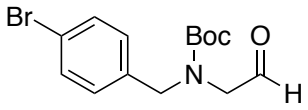
1690.10, 1517.90, 1281.88, 1162.07. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{18}NO_3F_2$: 286.12493, found 286.12582.

***tert*-Butyl (4-chlorobenzyl)(2-oxoethyl)carbamate s-1m**



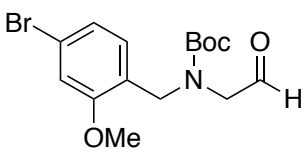

Colorless Oil. Yield: 87%. $R_f$ = 0.32 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.39 (s, 1H), 7.25 – 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 4.44 (s, 2H), 3.75 (s, 2H), 1.41 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.08, 155.20, 135.67, 133.36, 129.28, 128.72, 81.02, 56.43, 50.78, 28.03. IR (neat, cm$^{-1}$): 2976.91, 2930.94, 2816.34, 1735.24, 1689.00, 1240.58, 1160.80, 1128.88. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{19}NO_3Cl$: 284.10480, found 284.10486.

***tert*-Butyl (4-bromobenzyl)(2-oxoethyl)carbamate s-1n**




Colorless Oil. Yield: 80%. $R_f$ = 0.33 (Hexane/EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.40 (s, 1H), 7.49 – 7.29 (m, 2H), 7.08 (m, 2H), 4.44 (s, 2H), 3.76 (s, 2H), 1.42 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.08, 155.23, 136.18, 131.72, 129.65, 121.52, 77.21, 56.46, 50.88, 28.07. IR (neat, cm$^{-1}$): 2976.49, 2930.21, 2816.62, 1735.24, 1687.49, 1391.37, 1240.79, 1160.89. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{19}NO_3Br$: 328.05428, found 328.05365.

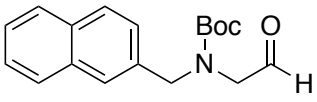
***tert*-Butyl (4-bromo-2-methoxybenzyl)(2-oxoethyl)carbamate s-1o**




Colorless Oil. Yield: 78%. $R_f$ = 0.43 (Hexane/EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.18 – 6.97 (m, 2H), 6.92 (d, $J$ = 5.7 Hz, 1H), 4.34 (d, $J$ = 4.1 Hz, 2H), 3.80 (d, $J$ = 3.8 Hz, 2H), 3.72

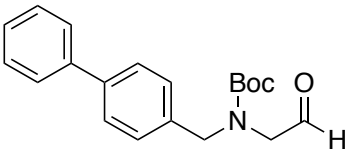
(d, $J$ = 5.0 Hz, 3H), 1.37 (d, $J$ = 4.7 Hz, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 199.28, 157.84, 155.00, 130.68, 124.57, 123.29, 121.92, 113.83, 77.20, 57.40, 55.33, 46.47, 28.03. IR (neat, $cm^{-1}$): 2975.50, 2935.05, 2831.40, 1734.35, 1687.75, 1488.53, 1238.38, 1160.96 HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{21}N_2O_4Br$: 358.06485, found 358.06632.

***tert*-Butyl (naphthalen-2-ylmethyl)(2-oxoethyl)carbamate s-1p**



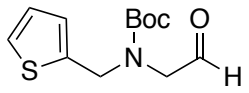

White solid. Yield: 83%. $R_f$ = 0.43 (Hexane/EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.81 (dd, $J$ = 11.7, 8.6 Hz, 3H), 7.63 (d, $J$ = 14.2 Hz, 1H), 7.53 – 7.31 (m, 3H), 4.70 (s, 2H), 3.81 (s, 2H), 1.50 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 198.55, 155.45, 134.56, 133.20, 132.85, 128.70, 127.65, 126.99, 126.28, 126.01, 125.94, 125.35, 81.04, 56.26, 51.62, 28.18. IR (neat, $cm^{-1}$): 3054.87, 2976.75, 2930.51, 2815.57, 1734.78, 1687.85, 1240.15, 1161.85. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{22}N_2O_3$: 300.15942, found 300.16026.

***tert*-Butyl ([1,1'-biphenyl]-4-ylmethyl)(2-oxoethyl)carbamate s-1q**



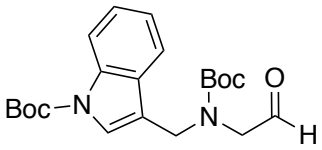

White solid. Yield: 90%. $R_f$ = 0.33 (Hexane/EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.57 (q, $J$ = 8.2, 7.6 Hz, 4H), 7.42 (td, $J$ = 8.0, 2.7 Hz, 2H), 7.36 – 7.27 (m, 3H), 4.58 (s, 2H), 3.82 (s, 2H), 1.49 (s, 9H).$^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.38, 155.23, 140.36, 140.30, 136.03, 128.59, 128.33, 127.79, 127.20, 126.79, 80.79, 56.32, 51.02, 28.02. IR (neat, $cm^{-1}$): 3055.57, 2976.35, 2816.07, 1734.95, 1687.83, 1453.06, 1391.29, 1161.31. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_3$: 326.17507, found 326.17644.

***tert*-Butyl (2-oxoethyl)(thiophen-2-ylmethyl)carbamate s-1r**



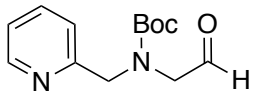

Colorless Oil. Yield: 60%. $R_f$ = 0.30 (Hexane/ EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.20 (s, 2H), 6.94 – 6.84 (m, 4H), 4.58 (s, 2H), 3.80 (s, 2H), 1.41 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.59, 154.75, 139.64, 126.61, 126.32, 125.60, 77.20, 55.98, 46.68, 28.11. IR (neat, $cm^{-1}$): 2976.52, 2930.51, 2816.56, 1733.83, 1688.43, 1452.96, 1365.75, 1148.42. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{12}H_{18}NO_3S$: 358.0648, found 358.0663.

***tert*-Butyl 3-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)-1*H*-indole-1-carboxylate s-1s**




Colorless Oil. Yield: 75%. $R_f$ = 0.20 (Hexane/EtOAc: 4/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.08 (d, *J* = 10.8 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.30 – 7.12 (m, 1H), 4.62 (s, 2H), 3.74 (s, 2H), 1.60 (s, 9H), 1.42 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 201.39, 157.81, 152.04, 138.47, 131.90, 127.62, 127.44, 125.51, 122.32, 119.10, 117.93, 83.51, 80.17, 58.29, 45.15, 30.81, 30.73. IR (neat, $cm^{-1}$): 2977.50, 2932.33, 1731.94, 1691.34, 1450.96, 1366.16, 1251.31, 1151.66. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{28}N_2O_5$: 388.19927, found 388.19934.

***tert*-Butyl (2-oxoethyl)(pyridin-2-ylmethyl)carbamate s-1t**

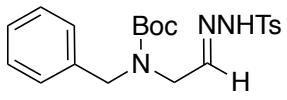



Colorless Oil. Yield: 55%. $R_f$ = 0.25 (Hexane/EtOAc: 1/2). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 8.35 (dt, *J* = 14.0, 7.1 Hz, 1H), 7.53 (dtd, *J* = 9.6, 7.7, 1.8 Hz, 1H), 7.17 (dd, *J* = 33.6, 7.9 Hz, 1H), 7.04 (q, *J* = 6.3 Hz, 1H), 4.50 (s, 2H),

3.86 (s, 2H), 1.30 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): $^{13}$C NMR (126 MHz, $CDCl_3$) δ 198.66, 157.22, 155.15, 149.05, 136.79, 122.43, 122.23, 77.50, 57.56, 53.34, 28.08. IR (neat, $cm^{-1}$): 2976.34, 2931.32, 1734.38, 1688.50, 1592.08, 1454.63, 1244.03, 1162.90. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{19}N_2O_3$: 251.13902, found 251.13895.

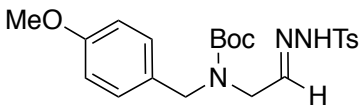
### 3.4.3 Characterization of Hydrozone Substrates

***tert*-Butyl (*Z*)-benzyl(2-(2-tosylhydrazineylidene)ethyl)carbamate 1a**



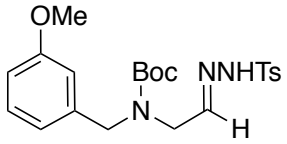

White solid. Yield: 78%. $R_f$ = 0.53 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.09 (s, 1H), 7.93 – 7.66 (m, 2H), 7.44 – 7.18 (m, 5H), 7.13 – 6.53 (m, 3H), 4.28 (s, 2H), 3.80 (s, 2H), 2.36 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.47, 146.54, 143.90, 136.82, 135.33, 129.49, 128.67, 128.42, 127.80, 127.27, 80.63, 50.03, 47.13, 28.14, 21.43. IR (neat, $cm^{-1}$): 3191.81, 2976.27, 2929.88, 1693.50, 1664.55, 1365.87, 1246.17, 1163.70. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{28}N_3O_4S$: 418.17950, found 418.18018.

***tert*-Butyl (*Z*)-(4-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1b**



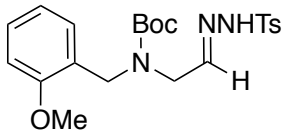

White solid. Yield: 86%. $R_f$ = 0.43 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.02 (s, 1H), 7.93 – 7.63 (m, 2H), 7.34 – 7.12 (m, 2H), 7.06 – 6.40 (m, 5H), 4.15 (s, 2H), 3.73 (s, 5H), 2.33 (s, 3H), 1.38 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 158.77, 155.35, 146.66, 143.74, 135.30, 129.37, 128.75, 127.86, 127.74, 113.77, 80.50, 55.09, 49.27, 46.78, 28.13, 21.38. IR (neat, $cm^{-1}$): 3056.81, 2979.47, 2932.01, 1689.25, 1667.75, 1596.64, 1263.32, 1159.36. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{30}N_3O_5S$: 448.19007, found 448.19136.

***tert*-Butyl (*Z*)-(3-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1c**



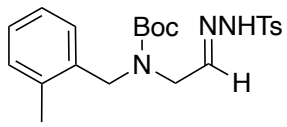

White solid. Yield: 84%. $R_f$ = 0.37 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.46 – 8.17 (m, 1H), 7.88 – 7.68 (m, 3H), 7.33 – 7.26 (m, 1H), 7.24 – 7.19 (m, 1H), 7.15 – 7.03 (m, 1H), 6.91 – 6.51 (m, 3H), 4.27 (s, 2H), 3.82 – 3.68 (m, 5H), 2.38 (s, 3H), 1.42 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 159.86, 147.79, 146.97, 144.31, 138.52, 134.75, 129.78, 128.03, 120.57, 116.77, 113.34, 111.58, 80.79, 55.30, 50.32, 47.31, 28.52, 21.69. IR (neat, $cm^{-1}$): 3188.81, 2976.21, 2931.78, 1691.90, 1663.73, 1454.81, 1244.55, 1047.95. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{30}N_3O_5S$: 448.19007, found 448.19062.

***tert*-Butyl (*Z*)-(2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1d**




White solid. Yield: 81%. $R_f$ = 0.50 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.76 – 8.90 (s, 1H), 7.77 (m, *J* = 17.0, 8.1 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.07 (m, *J* = 21.4, 6.1 Hz, 2H), 6.92 – 6.40 (m, 2H), 4.31 (s, 2H), 3.87 – 3.77 (m, 2H), 3.73 (s, 3H), 2.35 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 157.28, 155.79, 147.29, 143.67, 135.46, 129.39, 128.44, 127.78, 125.48, 124.80, 120.41, 110.19, 77.36, 55.08, 47.74, 45.67, 28.17, 21.39. IR (neat, $cm^{-1}$): 3199.35, 2975.81, 2930.31, 1693.05, 1664.04, 1459.31, 1243.06, 1165.13. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{30}N_3O_5S$: 448.19007, found 448.19100.

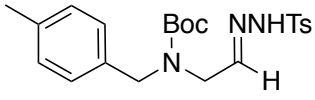
***tert*-Butyl (*Z*)-(2-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1e**




White solid. Yield: 62%. $R_f$ = 0.34 (Hexane/EtOAc: 2/1). Mixture of amide rotamers. Chemical shift for major isomer was reported.

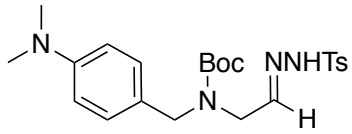
$^1$H NMR (600 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.85 – 7.69 (m, 2H), 7.33 – 7.26 (m, 2H), 7.21 – 6.18 (m, 5H), 4.35 (s, 2H), 3.89 – 3.63 (m, 2H), 2.41 (s, 3H), 2.13 (s, 3H), 1.43 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ δ 146.75, 144.38, 136.73, 134.42, 130.99, 130.58, 129.78, 128.14, 128.06, 127.42, 126.46, 126.14, 80.74, 56.01, 42.16, 21.72, 19.10. IR (neat, cm$^{-1}$): 3194.26, 2976.09, 2928.32, 1667.53, 1455.72, 1366.03, 1245.15, 1160.48. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{30}N_3O_4S$: 432.19515, found 432.19609.

***tert*-Butyl (4-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1f**




White solid. Yield: 90%. $R_f$ = 0.70 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.67 – 8.65 (m, 1H), 7.81 (t, *J* = 7.7 Hz, 2H), 7.43 – 6.45 (m, 7H), 4.26 (s, 2H), 3.87 – 3.72 (m, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 1.43 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.59, 146.80, 144.09, 137.07, 135.42, 134.40, 133.79, 129.63, 129.24, 127.97, 80.73, 49.91, 47.11, 28.37, 21.59, 21.11. IR (neat, cm$^{-1}$): 3164.97, 2976.33, 2925.37, 1693.10, 1664.93, 1365.85, 1245.37, 1163.42. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{30}N_3O_4S$: 432.19515, found 432.19458.

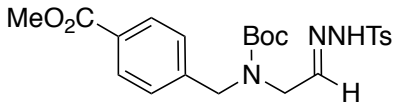
***tert*-Butyl (4-(dimethylamino)benzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1g**




White solid. Yield: 80%. $R_f$ = 0.47 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.05 – 8.71 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.25 (dt, *J* = 11.9, 8.1 Hz, 2H), 7.17 – 6.86 (m, 3H), 6.66 – 6.43 (m, 2H), 4.07 (s, 2H), 3.87 – 3.65 (m, 2H), 2.86 (s, 6H), 2.37 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 155.35, 149.98, 147.02, 143.95, 135.41, 129.54, 128.95, 127.87, 124.97, 112.55, 80.50, 49.50, 46.68, 43.71, 40.58, 28.29, 21.53. IR (neat, cm$^{-1}$): 3193.92, 2978.24, 2800.21,

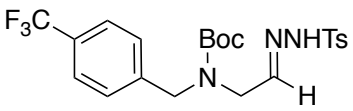
1663.82, 1523.01, 1365.97, 1245.04, 1161.18. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{33}N_4O_4S$: 461.22170, found 461.22108.

**Methyl 4-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)benzoate 1h**



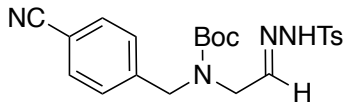

White solid. Yield: 79%. $R_f$ = 0.34 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.03 (s, 0H), 7.97 – 7.60 (m, 1H), 7.24 – 6.54 (m, 1H), 4.26 (s, 0H), 3.91 – 3.72 (m, 1H), 2.33 (s, 0H), 1.31 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 166.85, 155.35, 146.15, 143.98, 142.37, 135.29, 129.74, 129.52, 127.80, 127.05, 80.77, 52.07, 50.03, 47.68, 28.14, 21.45. IR (neat, cm$^{-1}$): 3556.91, 3184.97, 2978.36, 1719.50, 1693.98, 1669.82, 1278.67, 1161.01. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{30}N_3O_6S$: 476.18498, found 432.18548.

***tert*-Butyl (2-(2-tosylhydrazineylidene)ethyl)(4-(trifluoromethyl)benzyl)carbamate 1i**



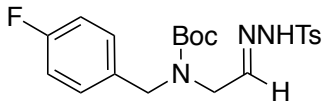

White solid. Yield: 93%. $R_f$ = 0.62 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.58 – 8.96 (s, 1H), 7.87 – 7.62 (m, 2H), 7.48 (q, $J$ = 8.0 Hz, 2H), 7.30 – 6.59 (m, 5H), 4.31 (s, 2H), 3.91 – 3.78 (m, 2H), 2.37 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.44, 146.21, 144.13, 141.31, 135.32, 129.61, 127.90, 125.39, 123.05, 120.89, 81.02, 49.95, 47.65, 28.19, 21.44. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -62.52. IR (neat, cm$^{-1}$): 3181.31, 2978.97, 1694.39, 1667.25, 1456.74, 1323.39, 1159.65, 1122.38. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{27}N_3O_4F_3S$: 486.16689, found 486.16783.

***tert*-Butyl (4-cyanobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1j**



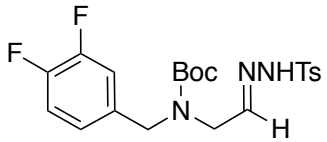

White solid. Yield: 83%. $R_f$ = 0.52 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.89 – 7.62 (m, 2H), 7.59 – 7.43 (m, 2H), 7.31 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 7.13 – 7.04 (m, 1H), 4.35 (s, 2H), 3.98 – 3.77 (m, 2H), 2.40 (s, 3H), 1.38 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.30, 145.96, 142.71, 135.30, 132.56, 132.35, 129.68, 128.40, 127.94, 118.77, 111.06, 77.36, 50.27, 47.94, 28.23, 21.60. IR (neat, $cm^{-1}$): 3188.13, 2976.38, 2929.80, 2228.30, 1692.89, 1669.02, 1404.16, 1136.03. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{27}N_4O_4S$: 443.17475, found 443.17620.

***tert*-Butyl (4-fluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1k**




White solid. Yield: 93%. $R_f$ = 0.66 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 7.75 (t, $J$ = 7.2 Hz, 2H), 7.32 – 7.17 (m, 2H), 7.09 – 6.94 (m, 3H), 6.95 – 6.47 (m, 2H), 4.23 (s, 2H), 3.95 – 3.71 (m, 2H), 2.36 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 162.04 (d, $J$ = 245.4 Hz), 155.42, 146.49, 144.14, 135.31, 133.28, 129.72, 129.28 (m), 127.89, 115.31 (d, $J$ = 21.4 Hz), 80.88, 49.50, 47.23, 21.52, 8.95. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.06. IR (neat, $cm^{-1}$): 3187.98, 2978.10, 2930.36, 1666.41, 1509.49, 1406.30, 1366.54, 1155.49. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{27}N_3O_4FS$: 436.17008, found 436.17100.

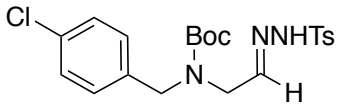
***tert*-Butyl (3,4-difluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1l**




White solid. Yield: 79%. $R_f$ = 0.64 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.97 (s, 1H), 7.76

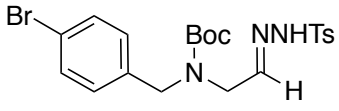
(dd, $J$ = 8.3, 2.2 Hz, 2H), 7.35 – 6.52 (m, 6H), 4.23 (s, 2H), 3.92 – 3.74 (m, 2H), 2.38 (s, 3H), 1.39 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.34, 150.22 (dd, $J$ = 248.5, 12.8 Hz), 149.55 (dd, $J$ = 247.4, 13.0 Hz), 146.19, 135.27, 134.24 (m), 129.65, 127.86, 123.47, 117.50 (m), 117.23 (d, $J$ = 17.2 Hz), 116.55 (m), 81.05, 49.29, 47.35, 28.23, 21.49. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -137.45 (dt, J = 20.4, 9.5 Hz), -139.68 – -139.85 (m). IR (neat, $cm^{-1}$): 3181.91, 2980.98, 1694.25, 1666.94, 1518.21, 1407.17, 1275.75, 1162.39. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{26}N_3O_4F_2S$: 454.16066, found 454.16159.

***tert*-Butyl (4-chlorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1m**




White solid. Yield: 87%. $R_f$ = 0.62 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.84 – 7.69 (m, 2H), 7.36 – 7.14 (m, 4H), 7.10 – 6.52 (m, 3H), 4.23 (s, 2H), 3.94 – 3.68 (m, 2H), 2.40 (s, 3H), 1.41 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 155.45, 146.44, 144.33, 135.34, 133.23, 129.75, 129.59, 129.05, 128.75, 128.03, 81.03, 49.81, 47.52, 28.38, 21.68. IR (neat, $cm^{-1}$): 3188.18, 2977.17, 2929.19, 1693.83, 1667.36, 1403.11, 1246.95, 1164.69. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{27}N_3O_4SCl$: 452.14053, found 452.14121.

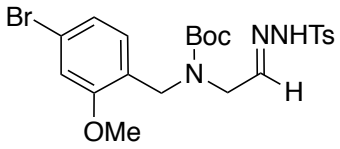
***tert*-Butyl (4-bromobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1n**




White solid. Yield: 73%. $R_f$ = 0.69 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.84 – 7.65 (m, 2H), 7.43 – 7.27 (m, 3H), 7.15 – 7.00 (m, 2H), 7.00 – 6.52 (m, 2H), 4.23 (s, 2H), 3.87 – 3.65 (m, 2H), 2.39 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.37, 146.31, 136.69, 135.35, 131.58, 129.63, 129.19, 127.92, 126.34, 121.17, 77.41, 49.70, 47.48, 28.28, 21.59. IR (neat,

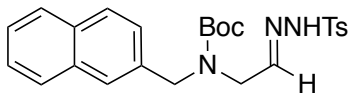
$cm^{-1}$): 3196.60, 2977.90, 1691.22, 1664.48, 1400.54, 1366.42, 1245.68, 1160.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{27}N_3O_4SBr$: 496.09002, found 496.08515.

***tert*-Butyl (4-bromo-2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1o**



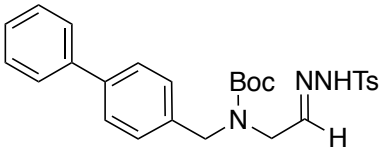

White solid. Yield: 74%. $R_f$ = 0.50 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.93 – 7.63 (m, 3H), 7.41 – 7.26 (m, 2H), 7.18 – 6.95 (m, 2H), 6.86 – 6.51 (m, 2H), 4.29 (s, 2H), 3.99 – 3.69 (m, 2H), 2.42 (s, 3H), 1.41 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 156.46, 150.10, 147.22, 143.37, 132.56, 131.95, 129.78, 129.57, 128.08, 127.42, 112.39, 112.17, 82.30, 55.66, 48.44, 43.55, 28.43, 21.73. IR (neat, $cm^{-1}$): 3188.67, 3005.12, 2987.22, 1691.01, 1665.48, 1458.03, 1275.37, 1260.41, 1163.15. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{29}N_3O_5SBr$: 526.10058, found 526.10051.

***tert*-Butyl (naphthalen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1p**



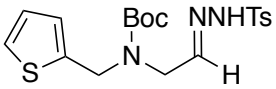

White solid. Yield: 89%. $R_f$ = 0.46 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (600 MHz, $CDCl_3$): δ 9.30 (s, 1H), 7.95 – 7.65 (m, 5H), 7.50 – 7.38 (m, 2H), 7.30 – 6.47 (m, 5H), 4.42 (s, 2H), 3.96 – 3.72 (m, 2H), 2.29 (s, 3H), 1.44 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 155.44, 146.36, 143.70, 135.24, 134.74, 134.20, 133.02, 132.50, 129.35, 128.16, 127.65, 127.43, 126.46, 126.01, 125.65, 125.32, 80.55, 50.04, 47.02, 28.07, 21.21. IR (neat, $cm^{-1}$): 3181.35, 3053.57, 2970.85, 1737.30, 1691.50, 1664.45, 1455.57, 1243.81, 1160.73. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{30}N_3O_4S$: 468.19515, found 468.19469.

***tert*-Butyl ([1,1'-biphenyl]-4-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1q**



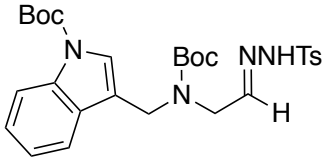

White solid. Yield: 90%. $R_f$ = 0.52 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.88 – 7.78 (m, 2H), 7.61 – 7.49 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 – 6.59 (m, 6H), 4.36 (s, 2H), 3.98 – 3.68 (m, 2H), 2.40 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.65, 146.77, 144.26, 140.78, 140.47, 136.66, 135.90, 129.74, 128.90, 128.07, 127.62, 127.45, 127.36, 127.13, 80.91, 50.13, 47.42, 28.39, 21.67. IR (neat, $cm^{-1}$): 3190.02, 2976.25, 2928.44, 1691.81, 1665.42, 1404.61, 1246.24, 1164.66. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{27}H_{32}N_3O_4S$: 494.21080, found 494.21027.

***tert*-Butyl (thiophen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1r**



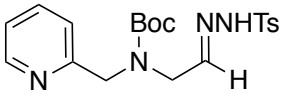

White solid. Yield: 77%. $R_f$ = 0.48 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NM (600 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.86 – 7.69 (m, 2H), 7.30 – 7.19 (m, 2H), 7.18 – 6.95 (m, 2H), 6.87 – 6.63 (m, 2H), 4.36 (s, 2H), 3.86 – 3.74 (m, 2H), 2.37 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 154.98, 146.64, 144.12, 140.06, 135.34, 129.62, 127.91, 126.69, 126.52, 125.46, 81.23, 66.26, 47.05, 45.07, 28.35, 21.56. IR (neat, $cm^{-1}$): 3189.15, 2978.20, 1667.14, 1454.63, 1408.92, 1366.14, 1251.23, 1160.96. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{22}N_3O_4S$: 424.13255, found 424.13628.

***tert*-Butyl 3-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)-1*H*-indole-1-carboxylate 1s**



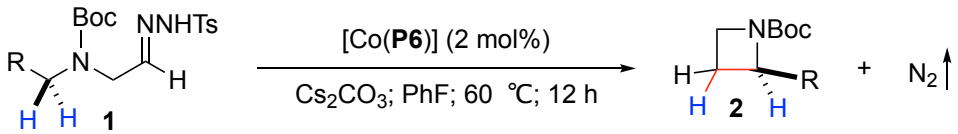
Light Yellow solid. Yield: 82%. $R_f$ = 0.71 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.36 – 7.87 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.37 (m, 2H), 7.35 – 7.12 (m, 4H), 7.08 – 6.44 (m, 1H), 4.37 (s, 2H), 3.87 – 3.62 (m, 2H), 2.38 (s, 3H), 1.68 (s, 9H), 1.47 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.34, 149.68, 146.73, 144.40, 135.77, 135.26, 129.77, 129.51, 128.05, 125.15, 124.78, 122.82, 116.58, 115.36, 84.05, 46.42, 40.89, 28.49, 28.32, 21.66. IR (neat, $cm^{-1}$): 3170.65, 2977.78, 2931.09, 1732.34, 1692.58, 1666.32, 1451.35, 1250.56. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{28}H_{37}N_4O_6S$: 557.24283, found 557.24115.

***tert*-Butyl (pyridin-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate 1t**



Light Yellow solid. Yield: 84%. $R_f$ = 0.11 (Hexane/EtOAc: 1/1). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.90 – 7.54 (m, 3H), 7.47 – 6.70 (m, 6H), 4.27 (s, 2H), 4.03 – 3.85 (m, 2H), 2.40 – 2.31 (m, 3H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.61, 149.19, 146.98, 143.76, 137.75, 136.10, 135.44, 129.48, 127.86, 123.27, 120.91, 80.68, 52.45, 48.79, 28.25, 21.59. IR (neat, $cm^{-1}$): 3221.54, 2970.67, 2928.27, 1737.73, 1672.02, 1596.45, 1328.21, 1158.32. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{27}N_4O_4S$: 419.17475, found 419.17502.

### 3.4.4 General Procedure for [Co(P6)]-Catalyzed Enantioselective Radical Cyclization

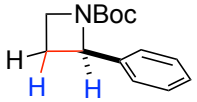



An oven-dried Schlenk tube was charged with hydrazone **1** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with

nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **2**.

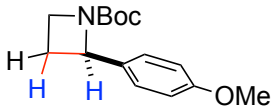
### 3.4.5 Characterization of Azetidine Products

***tert*-Butyl (*R*)-2-phenylazetidine-1-carboxylate (2a)**




Colorless oil (22 mg, 95% yield). Hexanes/ EtOAc = 4:1, $R_f$ = 0.43. $[\alpha]_D^{20}$ = 47.39 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.30 – 7.25 (m, 1H), 5.19 (t, *J* = 7.6 Hz, 1H), 4.01 (t, *J* = 7.7 Hz, 2H), 2.63 (ddt, *J* = 11.3, 8.4, 7.0 Hz, 1H), 2.14 (dtd, *J* = 11.3, 8.1, 6.3 Hz, 1H), 1.33 (s, 9H).$^{13}C$ NMR (151 MHz, $CDCl_3$) δ 157.95, 142.58, 128.35, 127.29, 125.87, 79.40, 64.40, 46.50, 28.28, 25.41.IR (neat, $cm^{-1}$): 3353.21, 2974.16, 2929.71, 1697.30, 1363.74, 1248.43, 1130.13, 697.29. HPLC analysis: *ee* = 89%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 14.89 min, $t_{minor}$ = 16.91 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{20}NO_2$: 234.14886, found 234.14864.

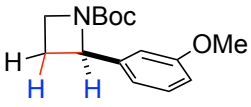
***tert*-Butyl (*R*)-2-(4-methoxyphenyl)azetidine-1-carboxylate (2b)**




Colorless oil (23 mg, 88% yield). Hexanes/ EtOAc = 4:1, $R_f$ = 0.35. $[\alpha]_D^{20}$ =83.99 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 6.91 – 6.85 (m, 2H), 5.18 – 5.07 (m, 1H), 3.97 (dd, *J* = 8.6, 6.7 Hz, 2H), 3.81 (d, *J* = 0.8 Hz, 3H), 2.66 – 2.50 (m, 1H), 2.22 – 2.06 (m, 1H), 1.46 – 1.20 (m, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 158.89, 156.56, 134.79, 127.25, 113.72, 79.32, 63.86,

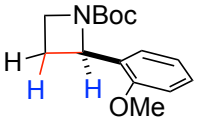
55.26, 46.41, 28.30, 25.48. IR (neat, $cm^{-1}$): 3349.34, 2973.02, 2934.10, 1698.32, 1602.21, 1365.08, 1259.21, 1132.03. HPLC analysis: *ee* = 88%. ID (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 27.38 min, $t_{minor}$ = 29.50 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_3$: 264.15942, found 264.15915.

***tert*-Butyl (*R*)-2-(3-methoxyphenyl)azetidine-1-carboxylate (2c)**




Colorless oil (21 mg, 80% yield). Hexanes/ EtOAc = 4:1, $R_f$ = 0.53. $[\alpha]_D^{20}$ = 55.59 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 1H), 6.99 – 6.87 (m, 2H), 6.84 – 6.74 (m, 1H), 5.15 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.98 (dd, *J* = 8.5, 6.8 Hz, 2H), 3.81 (s, 3H), 2.61 (ddt, *J* = 11.4, 9.0, 6.9 Hz, 1H), 2.11 (dtd, *J* = 11.4, 7.8, 6.2 Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.74, 156.55, 144.33, 129.42, 118.12, 112.76, 111.30, 79.46, 64.12, 55.20, 46.54, 28.30, 25.44. IR (neat, $cm^{-1}$): 3349.34, 2973.02, 2934.10, 1698.32, 1602.21, 1365.08, 1259.21, 1132.03. HPLC analysis: *ee* = 86%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 24.67 min, $t_{minor}$ = 26.95 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_3$: 264.15942, found 264.15981.

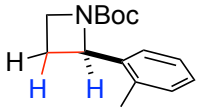
***tert*-Butyl (*R*)-2-(2-methoxyphenyl)azetidine-1-carboxylate (2d)**




Colorless oil (26 mg, 98% yield). Hexanes/ EtOAc =4:1, $R_f$ =0.46. $[\alpha]_D^{20}$ = 2.999 (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.42 (t, *J* = 7.6 Hz, 1H), 3.97 (td, *J* = 8.7, 6.8 Hz, 1H), 3.92 (td, *J* = 8.8, 5.4 Hz, 1H), 3.79 (s, 3H), 2.63 (dtd, *J* = 11.3, 9.0, 5.4 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.35 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.81, 156.06, 130.66, 127.95, 126.06, 120.37, 109.98, 79.24, 60.21, 55.24, 46.45, 28.32, 24.87. IR (neat, $cm^{-1}$):3367.55, 2970.38, 2890.33, 1697.78, 1364.66,

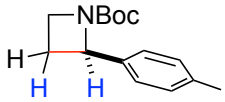
1243.74, 1131.12, 752.72. HPLC analysis: *ee* = 83%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 20.69 min, $t_{minor}$ = 18.32 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_3$: 264.15942, found 264.15984.

***tert*-Butyl (*R*)-2-(*o*-tolyl)azetidine-1-carboxylate (2e)**




Colorless oil (20 mg, 80% yield). Hexanes/EtOAc = 8:1, $R_f$ = 0.23. $[\alpha]_D^{20}$ = 133.20 (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 5.37 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.02 (q, *J* = 8.2 Hz, 1H), 3.94 (td, *J* = 8.7, 5.1 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.22 (s, 3H), 1.97 (td, *J* = 10.0, 5.1 Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.93, 140.51, 133.89, 130.09, 126.98, 126.18, 124.68, 79.66, 62.00, 46.59, 28.49, 25.00, 18.87. IR (neat, cm$^{-1}$):3377.16, 2976.17, 2894.13, 1646.85, 1367.94, 1258.00, 1164.10, 833.99. HPLC analysis: *ee* = 90%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 6.51 min, $t_{minor}$ = 11.33 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_2$: 248.16451, found 248.16422.

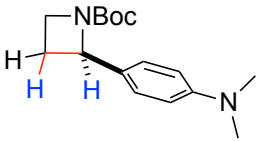
***tert*-Butyl (*R*)-2-(*p*-tolyl)azetidine-1-carboxylate (2f)**




Colorless oil (15 mg, 60% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.44. $[\alpha]_D^{20}$ = 71.39 (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.20 – 5.09 (m, 1H), 3.97 (dd, *J* = 8.4, 6.9 Hz, 2H), 2.64 – 2.49 (m, 1H), 2.33 (s, 3H), 2.17 – 2.02 (m, 1H), 1.32 (s, 9H). $^{13}$C NMR (151 MHz, CDCl3) δ 159.21, 142.27, 139.57, 131.68, 128.52, 82.00, 66.64, 49.18, 30.95, 28.12, 23.77. IR (neat, cm$^{-1}$): 3355.02, 3003.47, 2970.81, 1698.66, 1364.66, 1179.70, 1132.18, 815.01. HPLC analysis: *ee* = 87%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$

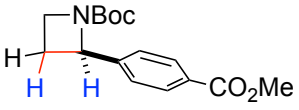
= 15.56 min, $t_{minor}$ = 18.00 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{22}NO_2$: 248.16451, found 248.16445.

***tert*-Butyl (*R*)-2-(4-(dimethylamino)phenyl)azetidine-1-carboxylate (2g)**



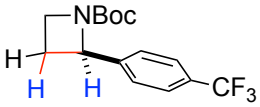

Colorless oil (18 mg, 65% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.39. $[\alpha]_D^{20}$ = 82.36 (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 0.9 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 5.09 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.96 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.79 (s, 6H), 2.64 – 2.50 (m, 1H), 2.10 (dq, *J* = 11.4, 7.7 Hz, 1H), 1.35 (s, 9H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.54, 149.50, 137.69, 128.32, 125.00, 119.82, 79.60, 63.30, 46.74, 43.81, 28.30, 25.26. IR (neat, cm$^{-1}$): 3193.92, 2978.24, 2928.85, 2800.21, 1663.82, 1455.54, 1245.04, 1161.18. HPLC analysis: *ee* = 86%. IC (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 11.99 min, $t_{minor}$ = 14.33 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{25}N_2O_2$: 277.19105, found 277.19102.

***tert*-Butyl (*R*)-2-(4-(methoxycarbonyl)phenyl)azetidine-1-carboxylate (2h)**



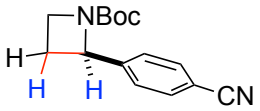

Colorless oil (25 mg, 86% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.25. $[\alpha]_D^{20}$ = 83.78 (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 5.21 (t, *J* = 7.7 Hz, 1H), 4.04 – 3.95 (m, 2H), 3.90 (s, 3H), 2.63 (dtd, *J* = 11.4, 8.9, 5.3 Hz, 1H), 2.09 (dddd, *J* = 11.3, 9.1, 7.1, 6.4 Hz, 1H), 1.31 (s, 9H). $^{13}$C NMR (151 MHz, CDCl3) δ 166.94, 156.40, 147.69, 129.81, 129.14, 115.30, 79.74, 63.86, 52.04, 46.63, 28.25, 25.28. IR (neat, cm$^{-1}$):3399.04, 2974.88, 2891.85, 1721.28, 1699.57, 1390.11, 1365.29, 1277.15. HPLC analysis: *ee* = 82%. ODH (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 7.77 min, $t_{minor}$ = 9.67 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{22}NO_4$: 292.15433, found 292.15394.

***tert*-Butyl (*R*)-2-(4-(trifluoromethyl)phenyl)azetidine-1-carboxylate (2i)**



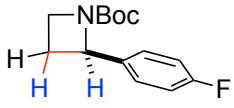

Colorless oil (22 mg, 73% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.38. $[\alpha]_D^{20}$ = 71.19 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.24 (dd, *J* = 8.9, 6.4 Hz, 1H), 4.08 – 3.94 (m, 2H), 2.65 (dtd, *J* = 11.4, 8.9, 5.2 Hz, 1H), 2.17 – 2.03 (m, 1H), 1.35 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 156.51, 146.53, (129.69, 129.37), 126.04, (125.44, 125.41), 122.82, 79.85, 63.46, 46.79, 28.26, 25.30. $^{19}F$ NMR (564 MHz, $CDCl_3$) δ -62.47. IR (neat, cm-1):3460.93, 2970.42, 2936.12, 1737.57, 1700.35, 1365.88, 1323.59, 1122.86. HPLC analysis: *ee* = 86%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 11.44 min, $t_{minor}$ = 15.52 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{19}NO_2F_3$: 302.13624, found 302.13595.

***tert*-Butyl (*R*)-2-(4-cyanophenyl)azetidine-1-carboxylate (2j)**




Colorless oil (24 mg, 93% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.20. $[\alpha]_D^{20}$ = 86.99 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.21 (t, *J* = 7.7 Hz, 1H), 4.01 (td, *J* = 8.8, 7.0 Hz, 1H), 3.95 (td, *J* = 8.8, 5.0 Hz, 1H), 2.64 (dtd, *J* = 11.5, 9.0, 5.0 Hz, 1H), 2.07 (ddt, *J* = 11.4, 9.2, 6.8 Hz, 1H), 1.33 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 159.09, 150.53, 135.02, 129.11, 121.51, 113.76, 82.69, 66.13, 49.11, 30.91, 27.85. IR (neat, $cm^{-1}$):3512.17, 2974.89,2931.73, 2227.64, 1697.07, 1364.87, 1133.50, 839.11. HPLC analysis: *ee* = 82%. ID (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 13.96 min, $t_{minor}$ = 16.35 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{19}N_2O_2$: 259.14410, found 259.14375.

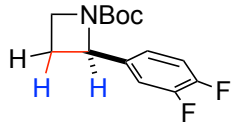
***tert*-Butyl (*R*)-2-(4-fluorophenyl)azetidine-1-carboxylate (2k)**




Colorless oil (24 mg, 96% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.36. $[\alpha]_D^{20}$ = 75.39 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$) δ δ 7.35

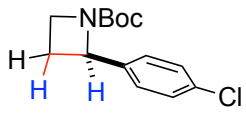
– 7.27 (m, 2H), 7.06 – 6.97 (m, 2H), 5.14 (dd, $J$ = 8.7, 6.4 Hz, 1H), 4.01 – 3.93 (m, 2H), 2.59 (dtd, $J$ = 11.4, 8.5, 5.9 Hz, 1H), 2.16 – 2.01 (m, 1H), 1.32 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.07 (d, $J$ = 245.1 Hz), 156.50, 138.35 (d, $J$ = 3.1 Hz) , 127.55 (d, $J$ = 8.1 Hz), 115.18 (d, $J$ = 21.4 Hz), 79.55, 63.90, 46.35, 28.27, 25.47. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.54. IR (neat, cm$^{-1}$): 2974.67, 2931.42, 2891.41, 1695.64, 1509.94, 1364.09, 1221.37, 1130.23. HPLC analysis: *ee* = 90%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 9.29 min, $t_{minor}$ = 9.72 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H19NO_2F$: 252.13943, found 252.13897.

***tert*-Butyl (R)-2-(3,4-difluorophenyl)azetidine-1-carboxylate (2l)**




Colorless oil (19 mg, 70% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.33. $[\alpha]_D^{20}$ = 46.19 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.00 (m, 3H), 5.12 (t, $J$ = 7.6 Hz, 1H), 4.03 – 3.86 (m, 2H), 2.66 – 2.51 (m, 1H), 2.07 (ddt, $J$ = 11.4, 8.9, 7.0 Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.45, 150.38 (dd, $J$ = 247.6, 12.6 Hz),149.55 (dd, $J$ = 247.6, 12.6 Hz), 139.72, 129.54, 121.74 (q, $J$ = 4.0 Hz), 117.12 (d, $J$ = 17.4 Hz), 114.85 (d, $J$ = 17.8 Hz), 79.84, 63.09, 46.69, 28.27, 25.37. $^{19}$F NMR (376 MHz,$CDCl_3$) δ -137.83, -140.04. IR (neat, cm$^{-1}$): ): 2975.91, 2932.01, 2894.38, 1697.12, 1518.81, 1390.10, 1365.02, 1149.53. HPLC analysis: *ee* = 83%. ID (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 11.28 min, $t_{minor}$ = 12.42 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{18}NO_2F_2$: 270.13001, found 270.13068.

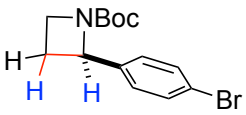
***tert*-Butyl (*R*)-2-(4-chlorophenyl)azetidine-1-carboxylate (2m)**




Colorless oil (19 mg, 71% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.40. $[\alpha]_D^{20}$= 73.99 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 5.16 – 5.11 (m, 1H), 3.97 (pd, $J$ = 8.5, 6.1 Hz, 2H), 2.59 (dtd, $J$ = 11.4, 8.9,

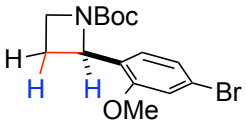
5.3 Hz, 1H), 2.07 (dddd, $J$ = 11.4, 9.1, 7.1, 6.3 Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.41, 141.10, 132.97, 128.53, 127.26, 79.66, 63.66, 46.51, 28.27, 25.37. IR (neat, $cm^{-1}$):3351.00, 3002.91, 2974.51, 1697.82, 1491.93, 1364.96, 1133.04, 828.46. HPLC analysis: *ee* = 82%. ID (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 12.78 min, $t_{minor}$ = 15.61 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{19}NO_2Cl$: 268.10988, found 268.10906.

**_tert_-Butyl (_R_)-2-(4-bromophenyl)azetidine-1-carboxylate (2n)**




Colorless oil (19 mg, 61% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.47. $[\alpha]_D^{20}$ = 76.39 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 8.4 Hz, 2H), 5.14 (dd, $J$ = 8.8, 6.3 Hz, 1H), 4.09 – 3.89 (m, 2H), 2.70 – 2.51 (m, 1H), 2.09 (ddt, $J$ = 11.4, 9.1, 6.8 Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.50, 141.65, 131.50, 127.62, 121.09, 79.68, 63.77, 46.17, 28.29, 25.33. IR (neat, $cm^{-1}$): 3330.93, 2973.99, 2929.25, 1696.12, 1487.39, 1364.11, 1131.15, 1010.26. HPLC analysis: *ee* = 84%. ODH (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 10.91 min, $t_{minor}$ = 11.91 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{19}NO_2Br$: 312.05937, found 312.05873.

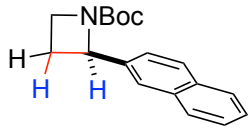
**_tert_-Butyl (_R_)-2-(4-bromo-2-methoxyphenyl)azetidine-1-carboxylate (2o)**




Colorless oil (29 mg, 85% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.52. $[\alpha]_D^{20}$ = 103.98 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, $J$ = 2.5, 0.8 Hz, 1H), 7.30 (dd, $J$ = 8.6, 2.5 Hz, 1H), 6.69 (d, $J$ = 8.6 Hz, 1H), 5.36 (t, $J$ = 7.6 Hz, 1H), 3.97 (td, $J$ = 8.7, 6.8 Hz, 1H), 3.90 (td, $J$ = 8.8, 5.2 Hz, 1H), 3.77 (s, 3H), 2.61 (dtd, $J$ = 11.3, 9.0, 5.3 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.37 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.71, 155.07, 132.91, 130.51, 129.13, 112.97, 111.75, 79.64, 59.72,

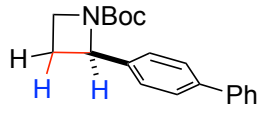
55.51, 46.68, 28.32, 24.77.IR (neat, $cm^{-1}$):3350.15, 3002.79, 2973.21, 1697.92, 1486.95, 1364.91, 1246.55, 1133.21. HPLC analysis: *ee* = 82%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 20.38 min, $t_{minor}$ = 19.59 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{21}NO_3Br$: 342.06993, found 342.06866.

***tert*-Butyl (*R*)-2-(naphthalen-2-yl)azetidine-1-carboxylate (2p)**




Colorless oil (21 mg, 74% yield). Hexanes/EtOAc = 4:1, $R_f$ = 0.45. $[\alpha]_D^{20}$ = 79.39 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 4H), 7.57 – 7.41 (m, 3H), 5.46 – 5.32 (m, 1H), 4.08 (dd, *J* = 8.7, 6.6 Hz, 2H), 2.81 – 2.60 (m, 1H), 2.27 – 2.12 (m, 1H), 1.33 (s, 9H). $^{13}C$ NMR (151 MHz, CDCl3) δ 156.61, 139.91, 133.29, 132.87, 128.29, 127.91, 127.64, 126.05, 125.69, 124.66, 123.90, 79.50, 64.62, 47.16, 28.28, 25.40. IR (neat, $cm^{-1}$):3338.17, 2973.74, 1695.12, 1508.77, 1389.67, 1364.53, 1171.73, 1133.86. HPLC analysis: *ee* = 83%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 19.29 min, $t_{minor}$ = 23.25 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{22}NO_2$: 284.16451, found 284.16396.

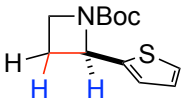
***tert*-Butyl (*R*)-2-([1,1'-biphenyl]-4-yl)azetidine-1-carboxylate (2q)**




Colorless oil (22 mg, 71% yield). Hexanes/EtOAc = 4:1, $R_f$ =0.40. $[\alpha]_D^{20}$ = 68.79 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 4H), 7.38 – 7.32 (m, 1H), 5.24 (t, *J* = 7.5 Hz, 1H), 4.03 (t, *J* = 7.6 Hz, 2H), 2.65 (ddt, *J* = 11.4, 8.8, 7.2 Hz, 1H), 2.18 (dtd, *J* = 11.4, 8.0, 6.2 Hz, 1H), 1.36 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 156.57, 141.62, 140.93, 140.23, 128.71, 127.18, 127.13, 127.05, 126.33, 79.48, 64.01, 46.54, 28.30, 25.42. IR (neat, $cm^{-1}$):3367.52, 3002.64, 2973.86, 1695.71, 1389.13, 1363.96, 1131.24, 762.46. HPLC analysis: *ee* = 85%.

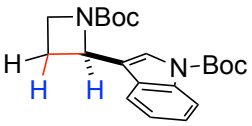
IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 23.61 min, $t_{minor}$ = 30.86 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_2$: 310.18016, found 310.17973.

***tert*-Butyl (*R*)-2-(thiophen-2-yl)azetidine-1-carboxylate (2r)**



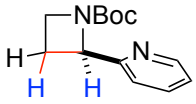

Colorless oil (14 mg, 59% yield). Hexanes/EtOAc = 4:1, $R_f$ =0.42. $[\alpha]_D^{20}$ = 28.79 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, $J$ = 5.0, 1.2 Hz, 1H), 7.00 – 6.98 (m, 1H), 6.94 (dd, $J$ = 5.1, 3.5 Hz, 1H), 5.37 (t, $J$ = 7.5 Hz, 1H), 4.01 – 3.87 (m, 2H), 2.67 – 2.58 (m, 1H), 2.30 (ddt, $J$ = 11.5, 9.1, 6.6 Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.59, 146.72, 126.74, 124.82, 124.58, 79.89, 59.81, 46.33, 28.46, 26.24. IR (neat, cm$^{-1}$): 3340.64, 2975.25, 2930.70, 1699.03, 1390.96, 1365.68, 1248.29, 1132.92. HPLC analysis: *ee* = 82%. IC (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 10.41 min, $t_{minor}$ = 11.39 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{12}H_{18}NO_2S$: 240.10528, found 240.10586.

***tert*-Butyl (*R*)-3-(1-(*tert*-butoxycarbonyl)azetidin-2-yl)-1*H*-indole-1-carboxylate (2s)**




Colorless oil (33 mg, 89% yield). Hexanes/EtOAc = 4:1, $R_f$ =0.40. $[\alpha]_D^{20}$ = 37.19 ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.54 (s, 1H), 7.31 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.24 – 7.19 (m, 1H), 5.41 (dd, J = 8.7, 6.5 Hz, 1H), 4.13 – 4.01 (m, 2H), 2.63 (dtd, J = 11.3, 8.9, 5.3 Hz, 1H), 2.34 (ddt, J = 11.3, 8.9, 6.7 Hz, 1H), 1.65 (s, 9H), 1.34 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 156.58, 149.66, 136.03, 128.26, 124.41, 122.95, 122.47, 121.81, 119.17, 115.45, 83.52, 79.55, 57.48, 46.89, 28.33, 28.19, 23.82. IR (neat, cm$^{-1}$): 3368.14, 2976.38, 2930.64, 1702.05, 1450.87, 1365.91, 1249.38, 1152.61. HPLC analysis: *ee* = 75%. IC (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 25.09 min, $t_{minor}$ = 17.74 min. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{29}N_2O_4$: 373.21218, found 373.21067.

***tert*-Butyl (*R*)-2-(pyridin-2-yl)azetidine-1-carboxylate (2t)**




Colorless oil (12 mg, 50% yield). Hexanes/EtOAc = 1:1, $R_f$ =0.16. $[\alpha]_D^{20}$ = 75.18 (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 8.59 (d, J = 4.3 Hz, 1H), 7.69 (td, J = 7.7, 1.8 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.21 – 7.13 (m, 1H), 5.27 (s, 1H), 4.02 (ddd, J = 8.9, 6.5, 4.1 Hz, 2H), 2.71 – 2.57 (m, 1H), 2.30 (s, 1H), 1.35 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 161.25, 156.82, 149.20, 137.02, 122.46, 121.02, 79.81, 64.73, 46.98, 28.45, 23.67. IR (neat, $cm^{-1}$): 3380.43, 2974.07, 2929.49, 1700.28, 1476.29, 1390.87, 1365.80, 1134.20. HPLC analysis: *ee* = 88%. IC (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 33.26 min, $t_{minor}$ = 17.74 min. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{19}N_2O_2$: 235.14410, found 235.14409.

### 3.4.6 Mechanistic Studies

#### 3.4.6.1 DFT Calculation

All DFT calculations were performed using the Gaussian 16 C.01 program package. For geometry optimization, the BP86 functional and the Lanl2dz basis set were used. Vibration frequencies were computed for optimized structures to characterize the stationary points as either equilibrium geometries (zero imaginary frequency) or saddle points (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed with local quadratic approximation (LQA) method to ensure the TS found connected the reactant and the product. Subsequent calculations of the solvent effect were conducted with the SMD model and def2-TZVP basis set using gas phase optimized structures. The software built-in chlorobenzene was used in the solvent model to best simulate the fluorobenzene that was used in the experiments. The energies reported in this paper are relative Gibbs free energies calculated at 298 K in solution and in the gas phase.

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

**Figure 3.2. Free-Energy Profile of Overall Reaction with [Co(P1)]**

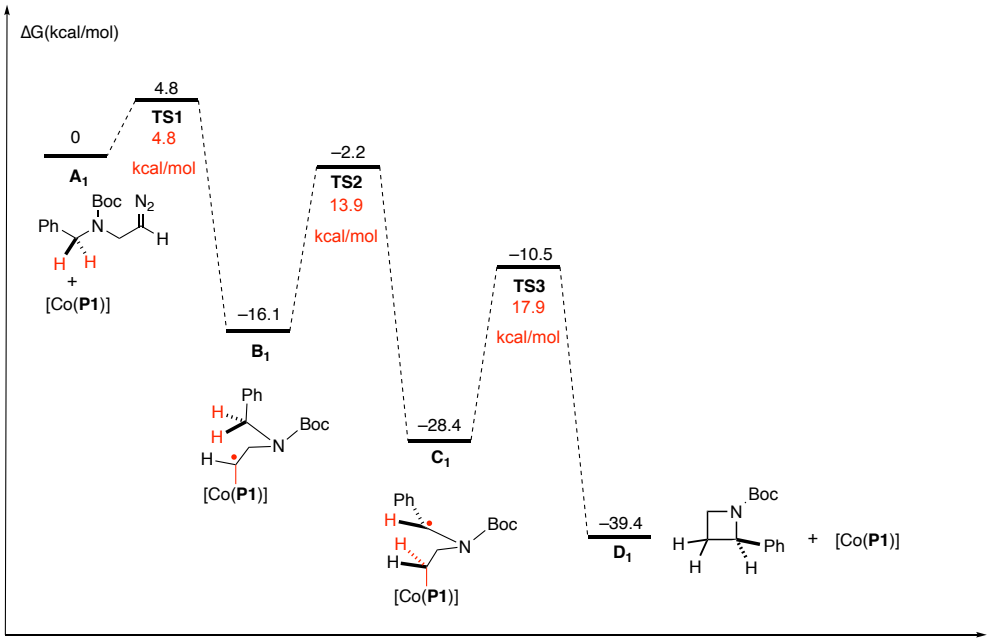



**Figure 3.3. Free-Energy Profile of Overall Reaction with [Co(P6)]**

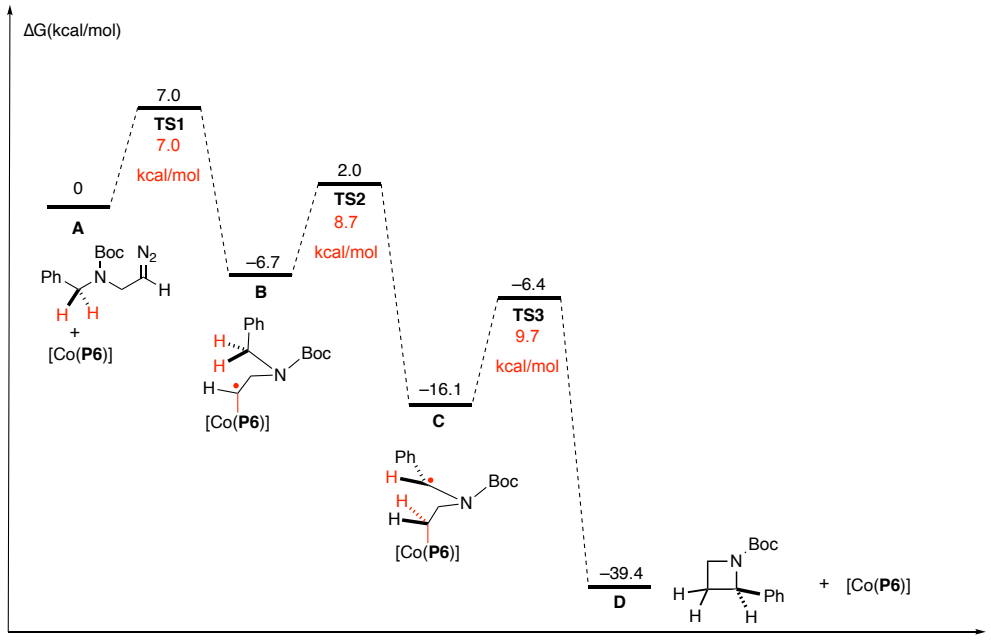
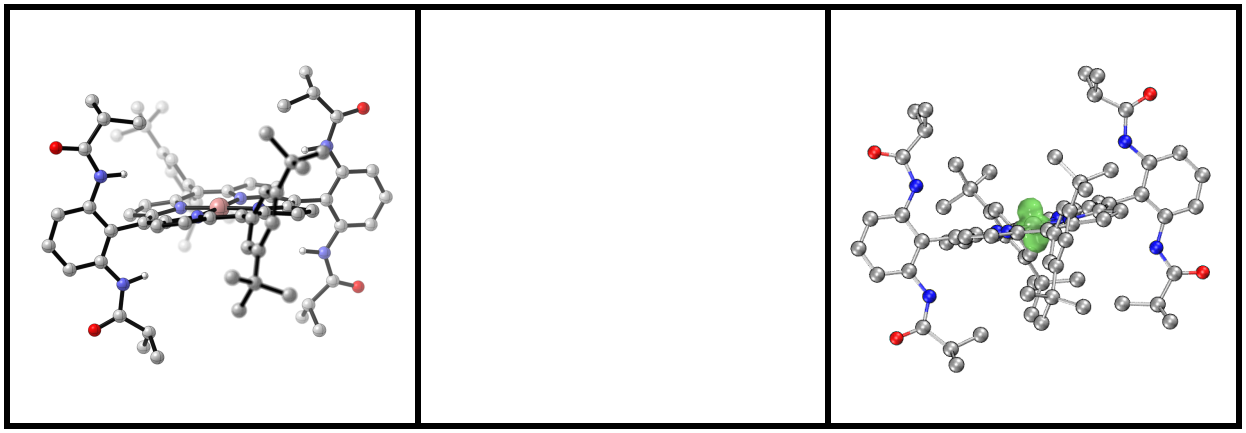
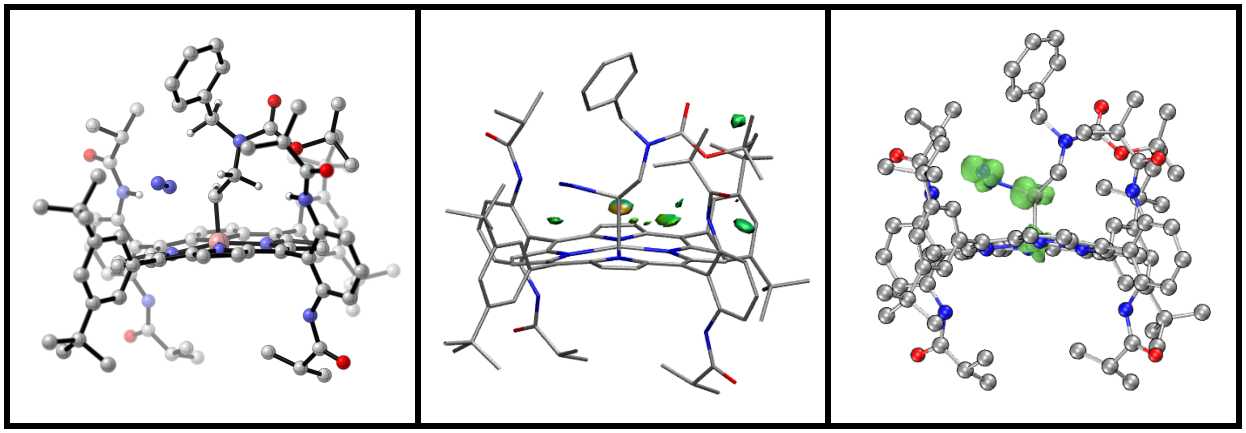


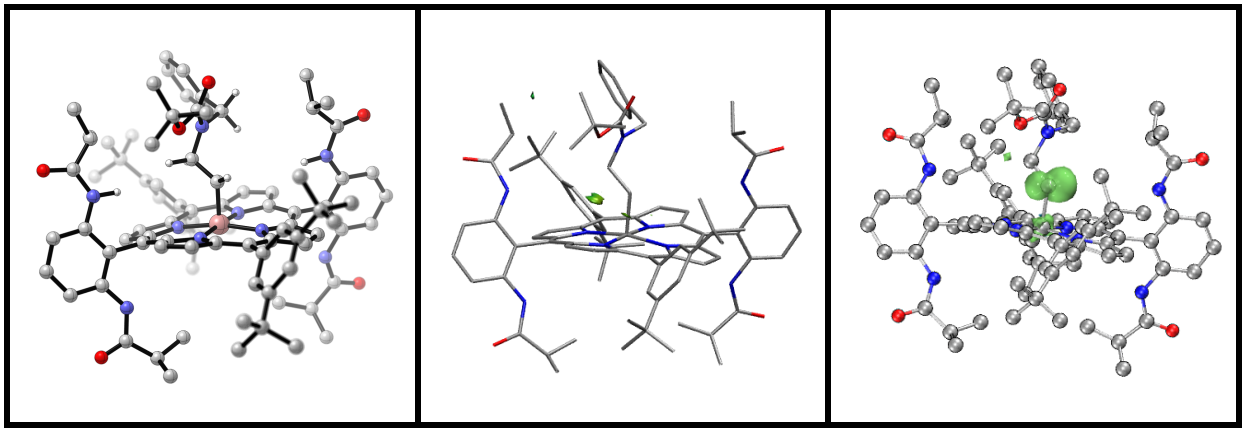
**Figure 3.4. NCI Plots and Spin Density Graph for Each Intermediates**



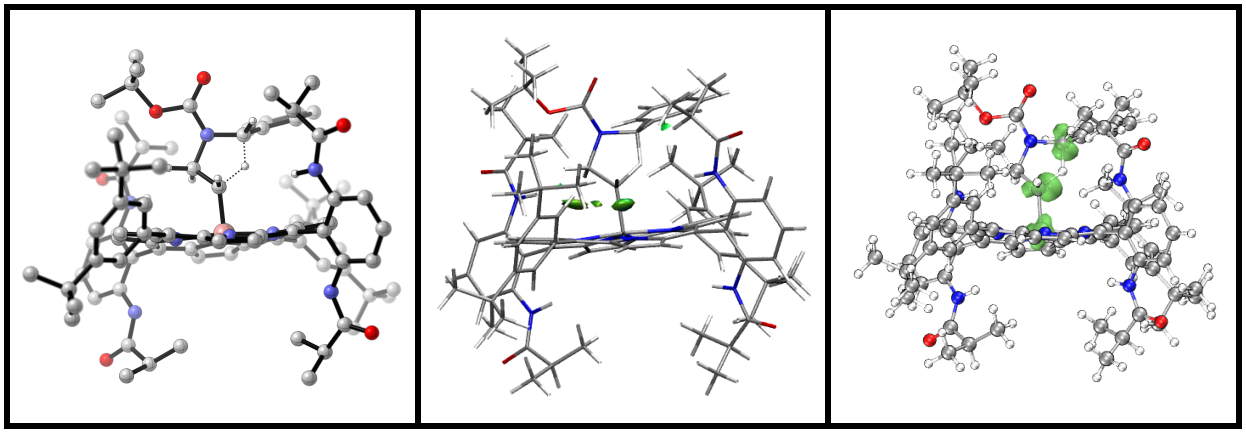
[Co(**P1**)]



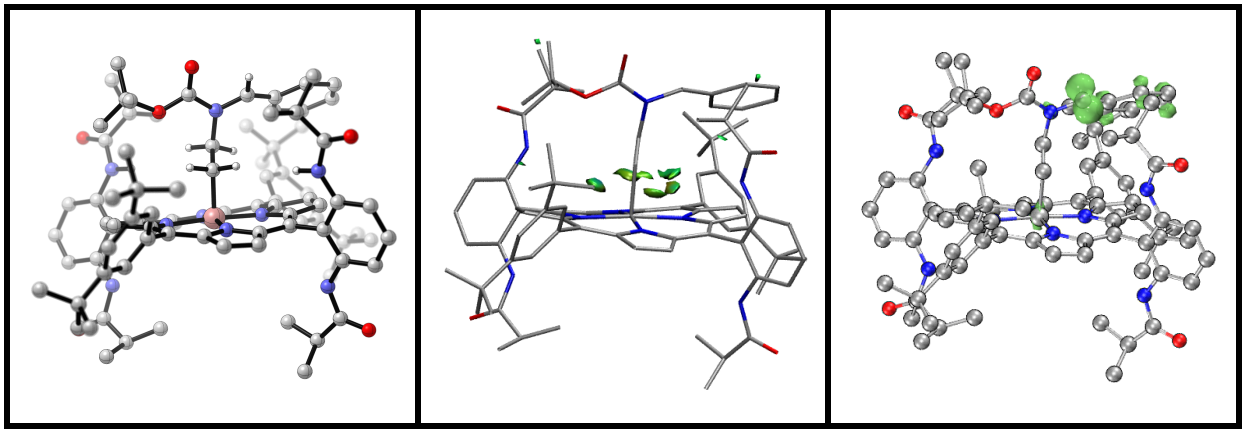
**TS1**$_{[Co(\mathbf{P1})]}$



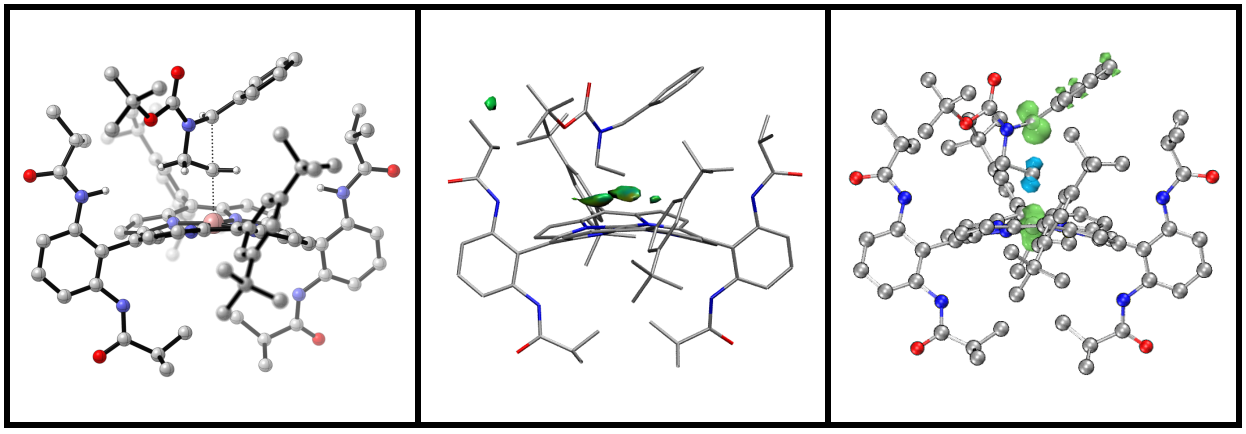
**Intermediate B**$_{[Co(\mathbf{P1})]}$



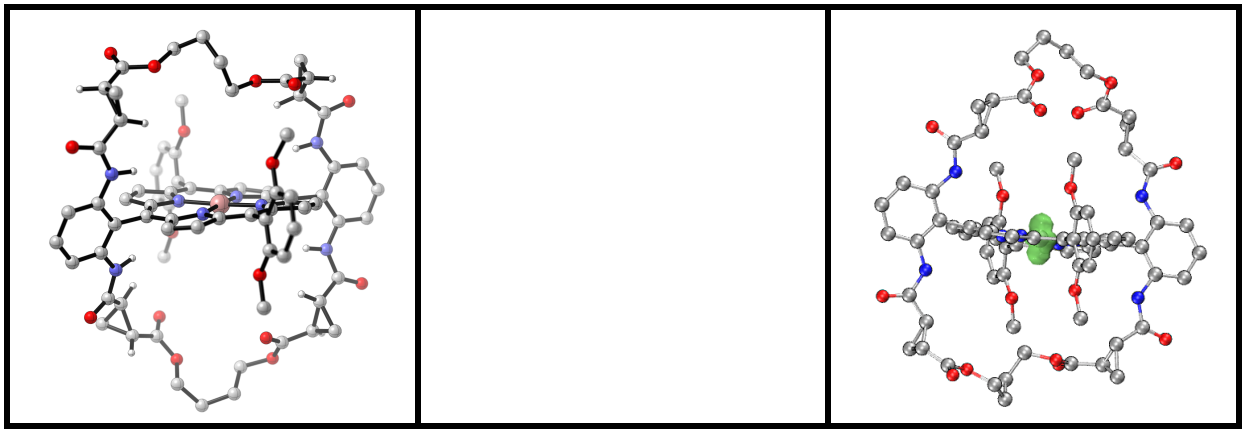
**TS2**$_{[Co(\mathbf{P1})]}$



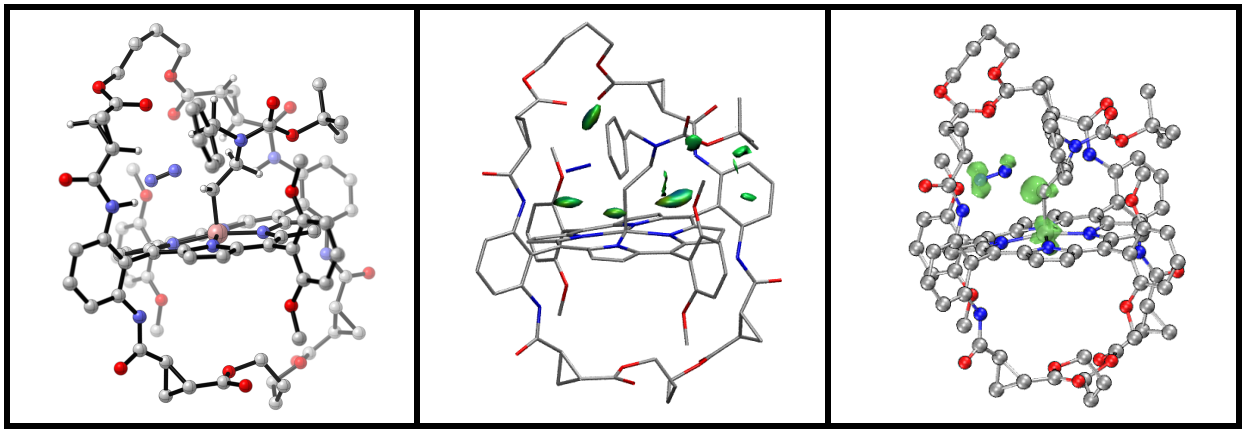
**Intermediate C**$_{[Co(\mathbf{P1})]}$



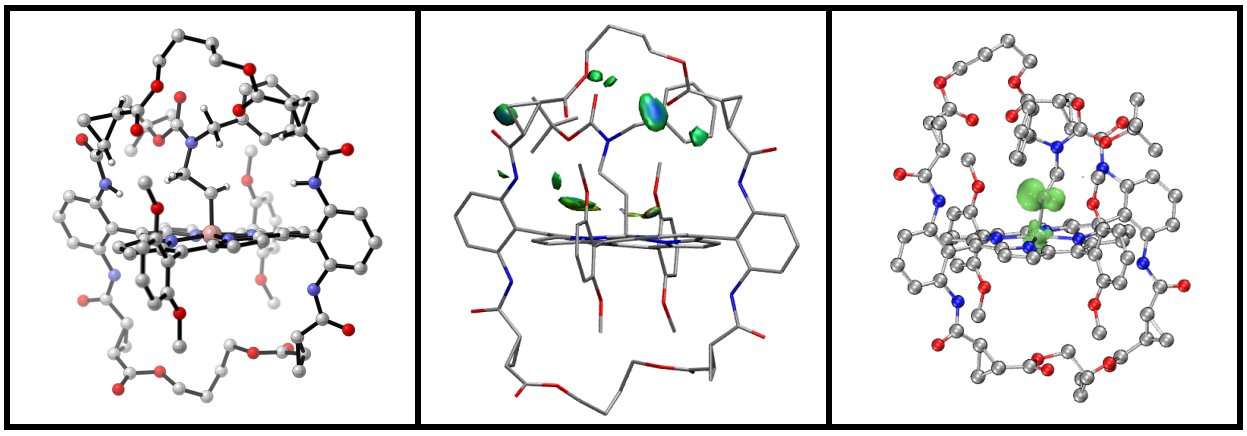
**TS3**$_{[Co(\mathbf{P1})]}$



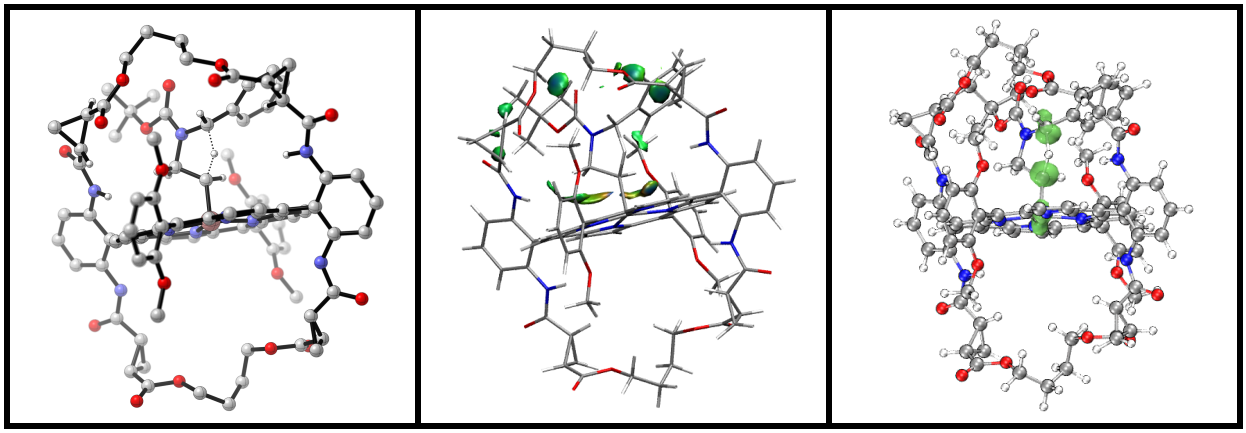
[Co(**P6**)]



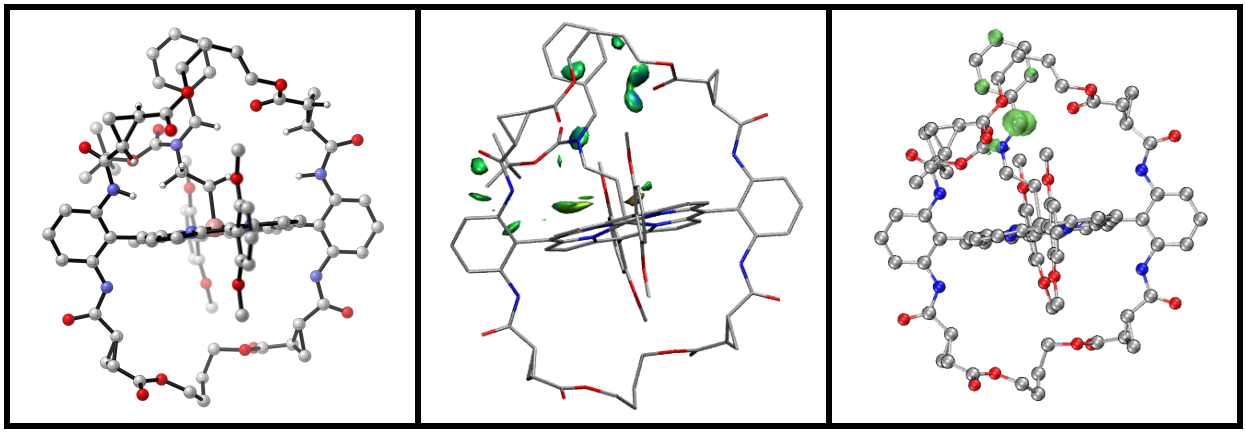
**TS1**[Co(**P6**)]



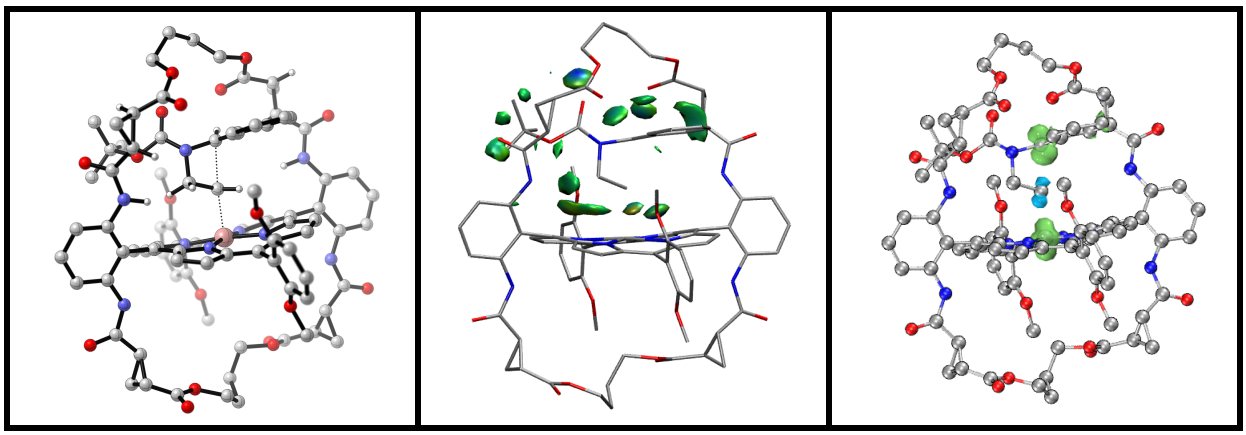
**Intermediate B**[Co(**P6**)]



**TS2**$_{[Co(\mathbf{P6})]}$



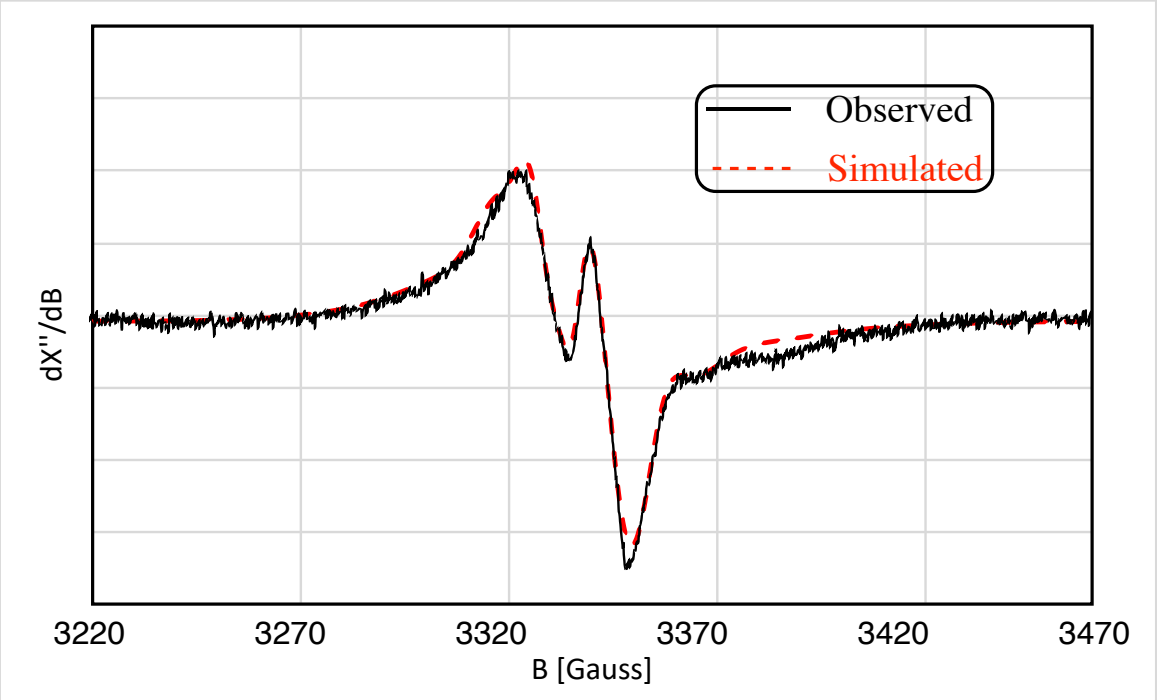
**Intermediate C**$_{[Co(\mathbf{P6})]}$



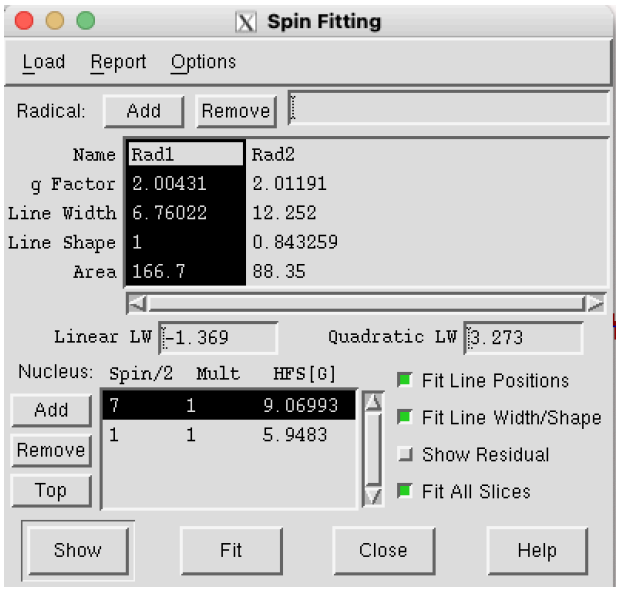
**TS3**$_{[Co(\mathbf{P6})]}$

### 3.4.6.2. Characterization of Co(III)-Alkyl Radical by EPR

**Procedure for EPR Experiment:** To an over-dried Schlenk tube, [Co(**P1**)] (2 mol %), **1a** (0.1 mmol) and $Cs_2CO_3$ (0.15 mmol) was 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 (1 mL) were added via a gas-tight syringe. The mixture was then stirred at 60 °C for 2 hour and transferred into a degassed EPR tube (filled with argon) through a gas tight 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). X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit in Xenon.



**EPR simulation details:**

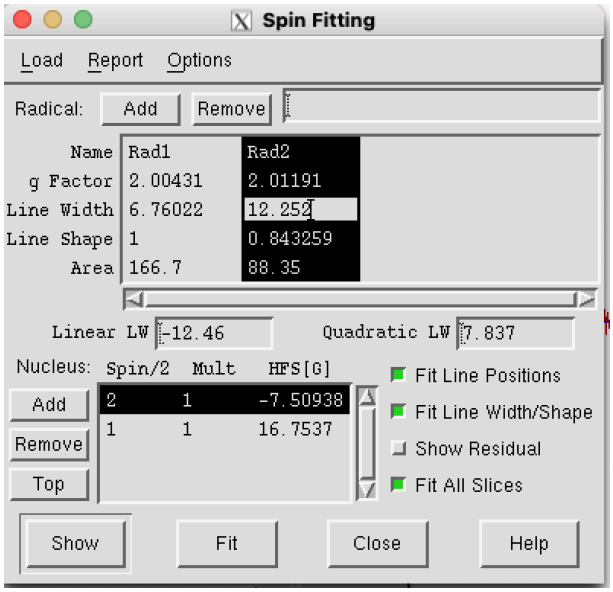



166.7/(166.7+88.35)*100%=65%

g = 2.00431

A(Co) = 9.06993 x 2.00431 x 1.399611451 = 25.4 MHz

A(H) = 5.9483 x 2.00431 x 1.399611451 = 16.7 MHz




88.35/(166.7+88.35)*100%=35%

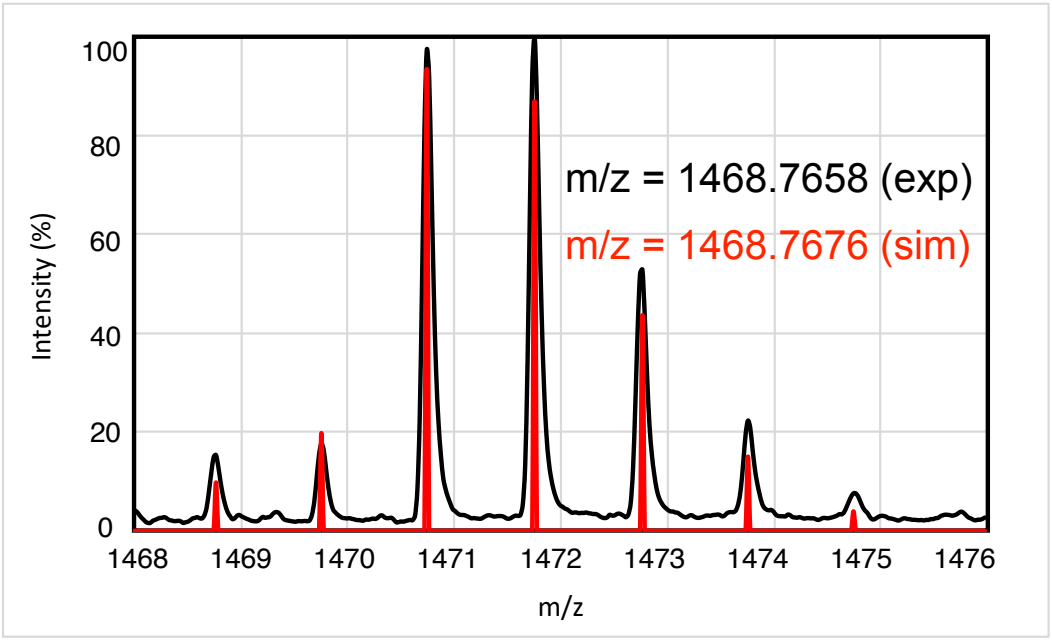
g = 2.01191

A(N) = -7.50938 x 2.01191 x 1.399611451 = -21.1 MHz

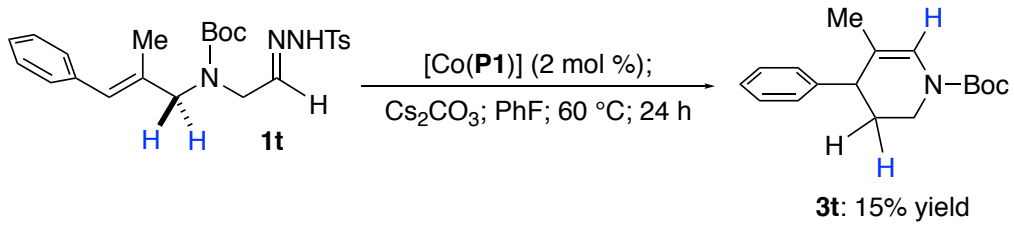
A(H) = 16.7537 x 2.01191 x 1.399611451 = 47.2 MHz

### 3.4.6.3. Characterization of Co(III)-Alkyl Radical by HRMS

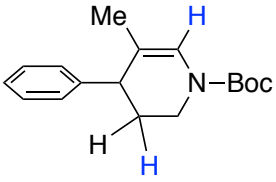
**Procedure for HRMS Experiment:** To an over-dried Schlenk tube, [Co(**P1**)] (2 mol %), **1a** (0.1 mmol) and $Cs_2CO_3$ (0.15 mmol) was added. The Schlenk tube was then evacuated and backfilled with nitrogen 3 times. The Teflon screw cap was replaced with a rubber septum, and PhF (1 mL) were added via a gas-tight syringe. The mixture was then stirred at 60 °C for 2 hour and transferred into a degassed vial (filled with argon) through a gas tight syringe. The sample was further diluted with CH3CN and immediately injected into HRMS instrument. The HRMS experiment was carried out in the absence of any additives such as formic acid, which commonly act as electron carriers for ionization, allowing for the detection of the molecular ion signals corresponding to Co(III)-alkyl radical ($C_{90}H_{107}CoN_9O_6^{\cdot}$) by the loss of one electron.



### 3.4.6.4. Probing of Allylic Radical Intermediate through chain walking process

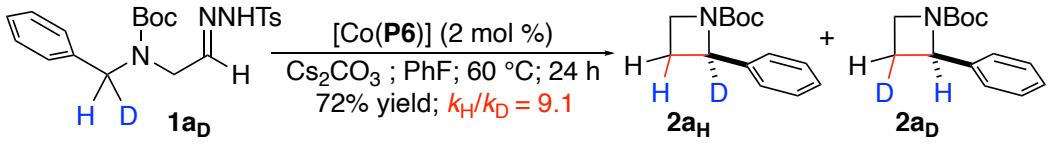



An oven-dried Schlenk tube was charged with hydrazone **1t** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P1**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **3t**.



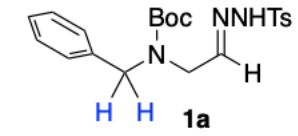

15% yield. Colorless oil. $R_f$ = 0.22 (Hexanes/EtOAc = 20/1). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, $J$ = 7.6 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.17 (d, $J$ = 7.6 Hz, 2H), 6.76 (s, 1H), 3.66 (dd, $J$ = 11.7, 6.5 Hz, 1H), 3.28 (t, $J$ = 5.2 Hz, 1H), 3.25 – 3.16 (m, 1H), 2.14 – 2.04 (m, 1H), 1.83 – 1.74 (m, 1H), 1.55 (s, 3H), 1.51 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.86, 146.65, 138.38, 131.02, 128.97, 125.04, 116.62, 83.19, 45.45, 40.16, 33.60, 31.06, 22.48. IR (neat, $cm^{-1}$): 3060.83, 2975.01, 2929.41, 1697.60, 1670.71, 1392.74, 1366.49, 1157.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{24}NO_2^+$: 274.18016, found: 274.18103.

### 3.4.6.5. Kinetic Isotope Effect

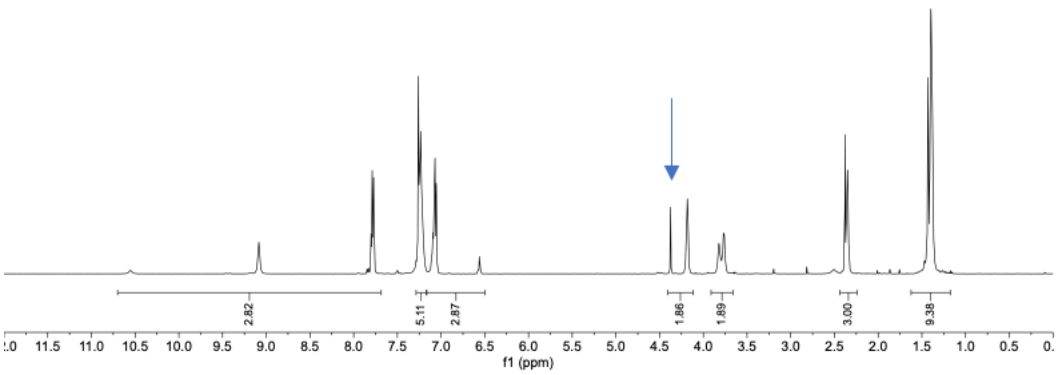


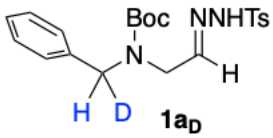

An oven-dried Schlenk tube was charged with hydrazone **1a$_D$** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was filtered and concentrated. The KIE value was determined by crude NMR.

**Figure 3.5. NMR for Monodeuterated Standard Substrate $1a_D$ and Standard Substrate 1a**




**1a**




**$1a_D$**

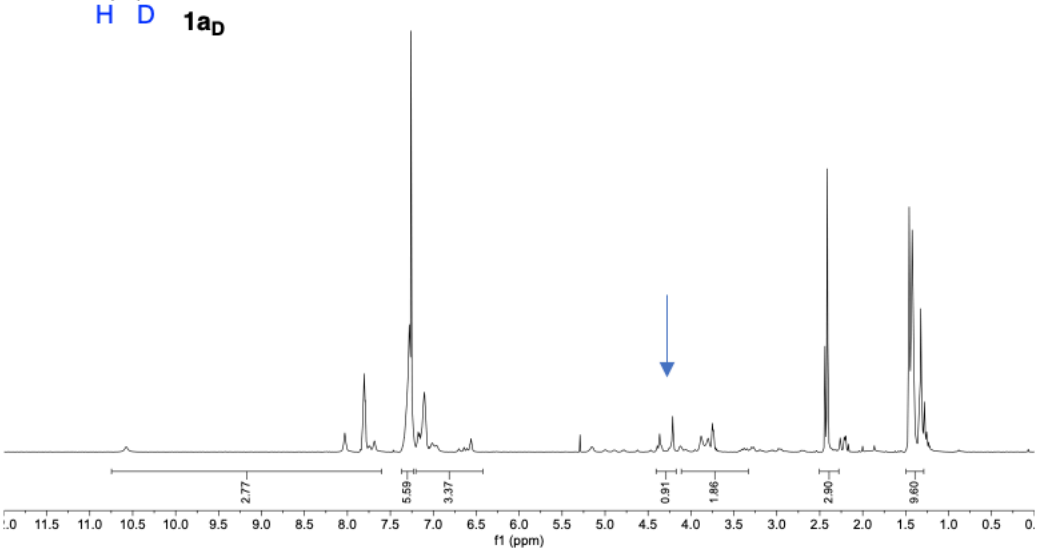
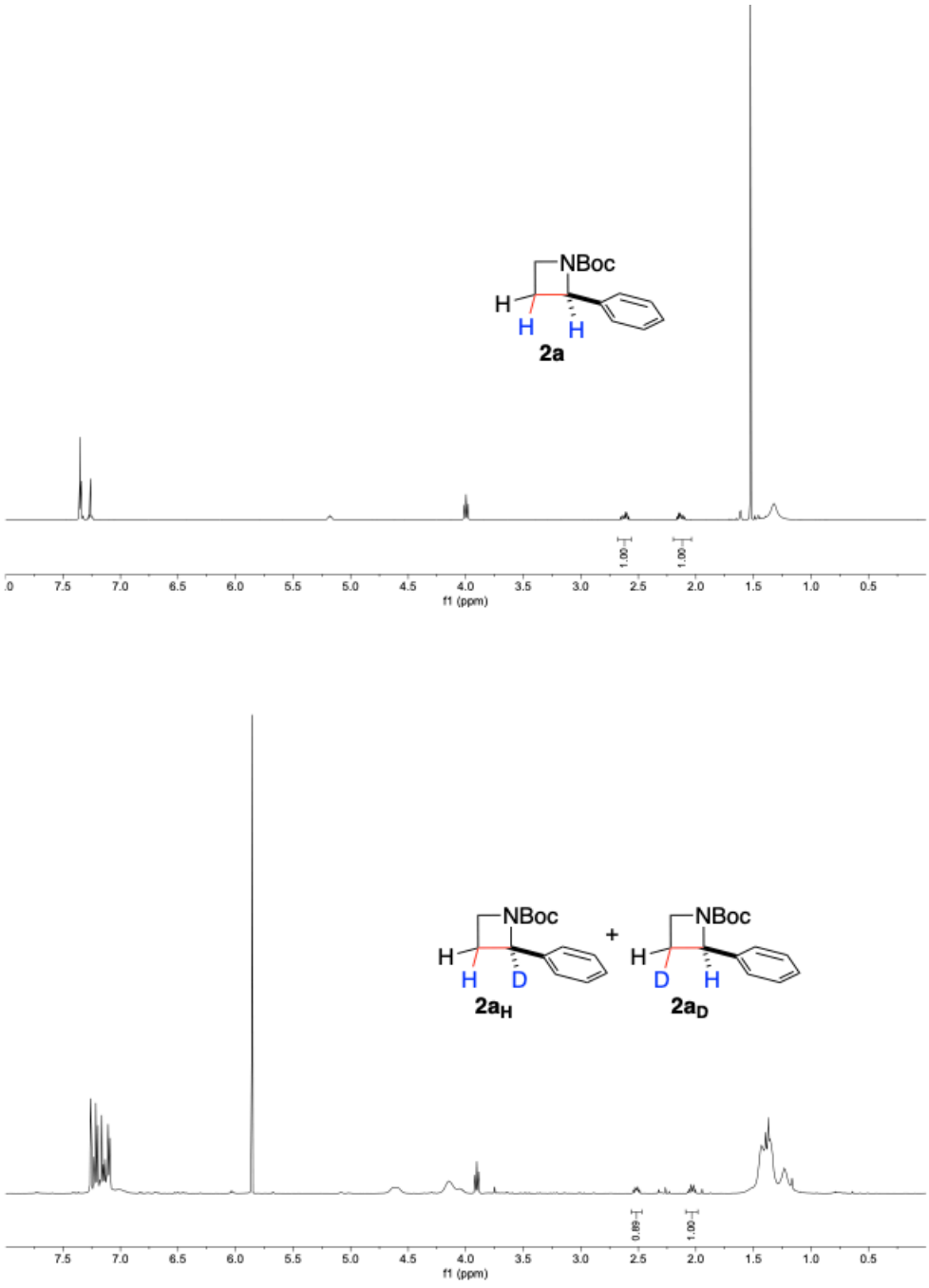


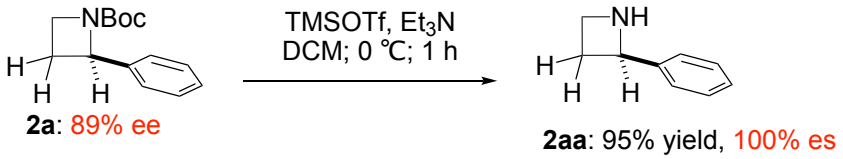
**Figure 3.6. NMR for KIE Study**




**Calculation of KIE:**

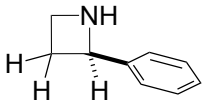
1/(1-0.89)=9.1

### 3.4.7 Further Transformations

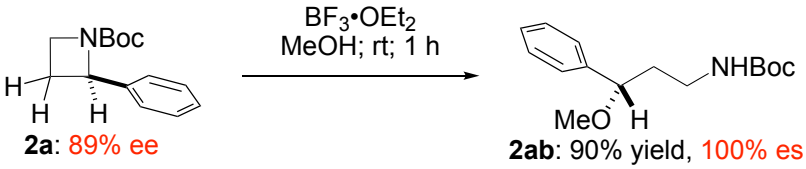



To a solution of *N*-Boc Azetidine **2a** (0.1 mmol) in DCM (1.0 mL) was added $Et_3N$ and TMSOTf. After 2 hours of stirring at room temperature, $H_2O$ (3 mL) were added. The two layers were separated and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated. The product can not be purified through column due to its instability.

**(*R*)-2-phenylazetidine 2aa**

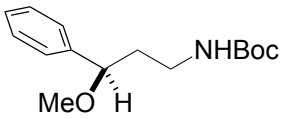



NMR Yield: 95%. HRMS (DART) ($[M+H]^+$) Calcd. for $C_9H_{12}N$: 134.09643, found 134.09722.



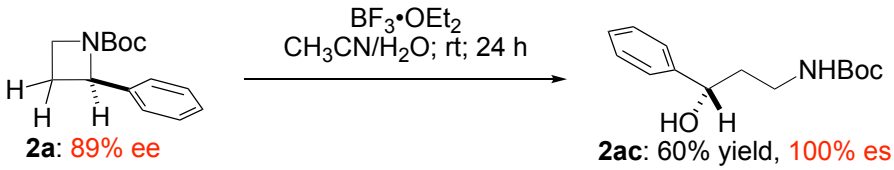

MeOH (1.0 mL, 0.1 M) was added to N-Boc Azetidine **2a** (0.10 mmol) and the mixture was stirred. $BF_3{\cdot}(OEt)_2$ (0.01 mmol) was added and the mixture was stirred at room temperature for 1 h. After the reaction finished, the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel to afford pure products.

***tert*-Butyl (3-methoxy-3-phenylpropyl)carbamate 2ab**



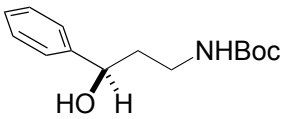

Yield: 90%. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 1H), 7.30 – 7.24 (m, 2H), 4.84 (s, 0H), 4.19 (dd, $J$ = 8.2, 4.7 Hz, 1H),

3.21 (s, 3H), 1.97 – 1.79 (m, 1H), 1.44 (s, 5H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.84, 144.22, 128.46, 127.43, 125.62, 79.62, 71.74, 46.21, 39.66, 37.64, 28.38. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{24}NO3$: 266.17507, found 266.17499.




A mixture of $H_2O$ and $CH_3CN$ (1:1) (1.0 mL, 0.1 M) was added to N-Boc Azetidine **2a** (0.10 mmol) and the mixture was stirred. $BF_3{\cdot}(OEt)_2$ (0.01 mmol) was added and the mixture was stirred at room temperature for 12 h. After the reaction finished, the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel to afford pure products.

***tert*-Butyl (*R*)-(3-hydroxy-3-phenylpropyl)carbamate 2ac**




Yield: 60%. $R_f$ = 0.21 (Hexane/EA: 4/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.29 – 7.22 (m, 2H), 4.75 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.51 – 3.40 (m, 1H), 3.17 (dt, *J* = 14.1, 5.5 Hz, 1H), 1.91 – 1.78 (m, 2H), 1.45 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.94, 141.60, 128.50, 127.70, 126.46, 82.72, 56.66, 38.15, 28.42, 27.40. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{14}H_{22}N_2O_3$: 252.15942, found 252.15988.

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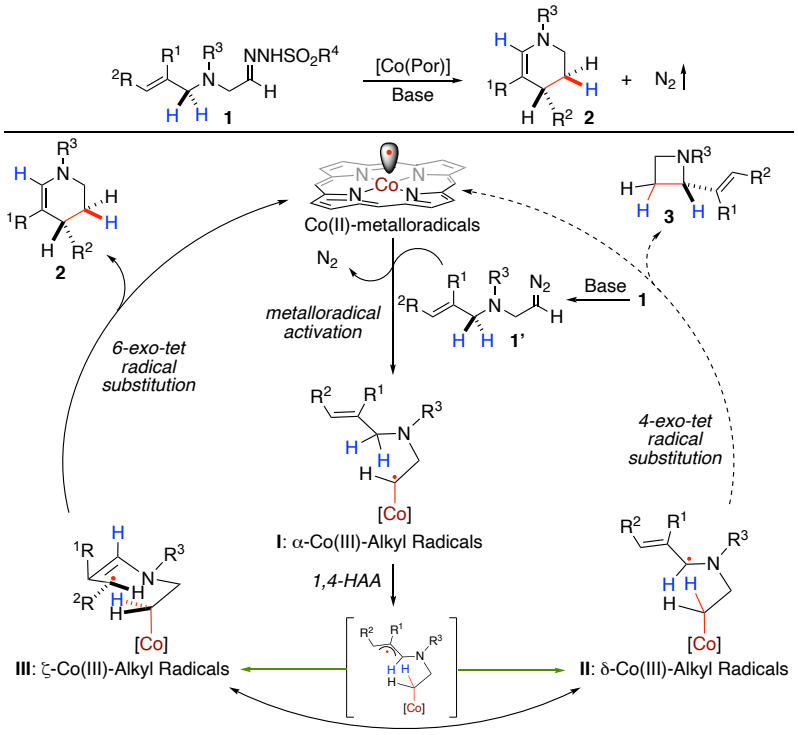
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# Chapter 4. Novel Radical Approach for Asymmetric Synthesis of Chiral Tetrahydropyridine via Co(II)-Based Metalloradical Catalysis

## 4.1 Introduction

Radical reactions which involve the open-shell intermediates have attracted increasing research interest in the past decade in view of their rich reactivities and attractive inherent synthetic advantages.[1] Despite tremendous advancements, the issue of controlling chemo-, regio- as well as stereoselective in radical transformation continue to present formidable challenges while offering exciting research opportunities in modern synthetic chemistry.[2] As a fundamentally new approach to address the existing challenges in the field, metalloradical catalysis (MRC) can achieve effective initiation and sequential regulation of radicals transformations by utilizing ligand-stabilized metalloradical as working catalysts.[3,4,5] With the employment of $D_2$-symmetric chiral amidoporphyrins as the supporting ligands, Co(II) complexes is capable of homolytically activating diazo compounds as radical precursors to generate a-Co(III)-alkyl radicals.[6] After generation, the α-metalloalkyl radicals can undergo common radical reactions such as radical addition and hydrogen atom abstraction, following by radical substitution to afford a board range of chiral products.[7] In particular, Co(II)-based MRC was recently applied for 1,4-HAA involving intramolecular C–H alkylation of diazo compounds to efficiently construct different four-membered rings.[8] To further explore the synthetic applications of this rare 1,4-HAA process beyond four member ring synthesis in MRC system, we were intrigued by the possibility of constructing 6-membered heterocycle structures by utilizing allylic C–H source for 1,4-HAA reaction (Scheme 4.1), since 6-membered heterocycles, especially piperidine, widely exist in a number of natural products and pharmaceutically relevant

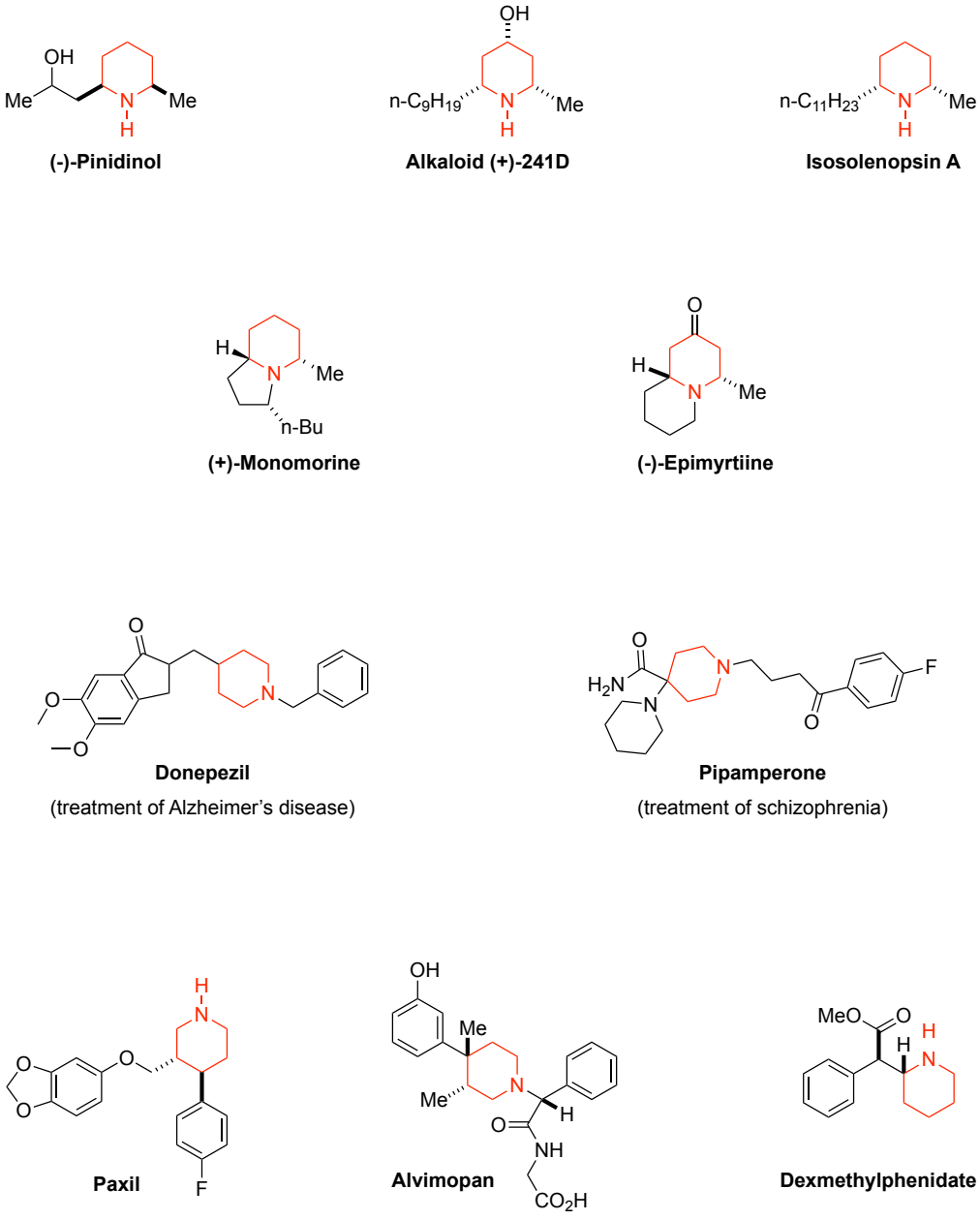
**Scheme 4.1. Working Proposal for Construction of Tetrahydropyridines via Co(II)-MRC**




small molecules. However, this proposed radical process show several potential challenges. In view of their unique steric properties, it was uncertain whether sterically-hindered diazo compounds **1** could be effectively activated by [Co($D_2$-Por$^*$)] to generate the corresponding α-Co(III)-alkyl radicals **I**. Given the fact that 1,4-HAA and *4-exo-tet* radical substitution are both relatively facile process in MRC system from our previous DFT calculation, how could we achieve the formation of six-membered ring with effective control of regioselectivity? Besides the concern of regioselectivity, could this process be rendered in an enantioselective fashion? We reasoned that these and related questions could be potentially addressed through optimization of [Co($D_2$-Por$^*$)] catalyst by fine-tuning of the $D_2$-symmetric chiral amidoporphyrin ligand to adopt suitable environments that govern the course of the catalytic radical process (Scheme 4.1). If realized, it would give rise to the

first asymmetric radical process to catalyze intramolecular C−H alkylation involving 1,4-HAA as the key step for asymmetric construction of tetrahydropyridine structures, which are valuable synthetic intermediates to chiral multi-substituted piperidine, most common motif in drugs and natural products.[9] (Figure 4.1.).

**Figure 4.1. Piperidine-Containing Natural Products and Bioactive Compounds**



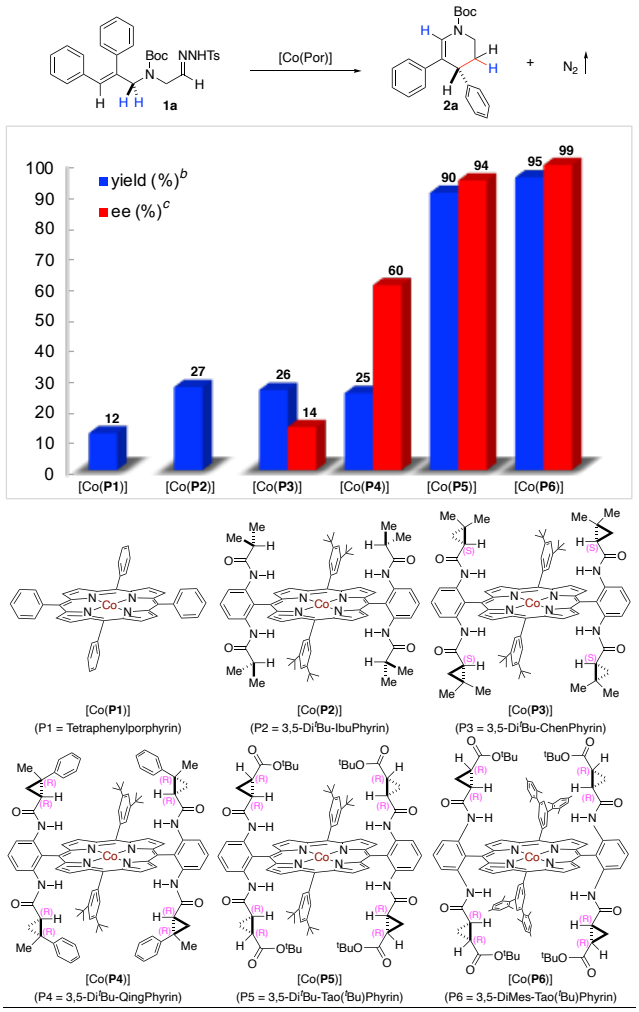
Tetrahydropyridines and piperidines are present as ubiquitous moiety in many bioactive natural products and therefore attract tremendous research interest. 1,4-HAA involving radical cyclization of allylic C–H bond containing diazo compounds represents a brand new strategy for stereoselective construction of six-membered cyclic compounds. While there have been enormous efforts made towards asymmetric synthesis of nitrogen-containing six-membered ring structure because of their biological importance, no example was shown that six-membered ring can be accessed through the proposed approach (Scheme 4.1). This underdevelopment is mainly attributed to the entropically and enthalpically unfavored 1,4-HAA process in radical reaction. And combining this rare reaction process with allylic C–H substrate to generate highly regioselective product is even unprecedented. As an exciting new application of Co(II)-based MRC for stereoselective organic synthesis, we herein report the development of the first catalytic system that is highly effective for asymmetric construction of tetrahydropyridines utilizing facile 1,4-HAA as the key step. Supported by a new-generation $D_2$-symmetric chiral amidoporphyrin ligand, the Co(II)-based metalloradical system, which enjoys operational simplicity and mild conditions, can activate in situ-generated nitrogen-containing aliphatic diazo compounds with varied electronic and steric properties, enabling enantioselective construction of chiral 3,4-disubstituted tetrahydropyridines. We show the importance of catalyst development through fine-tuning of the ligand environments in achieving high reactivity and enantioselectivity in this new radical process. Furthermore, our combined experimental and computational studies on the mechanism of the Co(II)-based metalloradical system have shed light on the underlying stepwise radical pathway, including the key steps of 1,4-HAA and 6-*exo*-*tet*-RS. A series of further transformations

of the resulting enantioenriched tetrahydropyridines are provided to showcase their synthetic applications.

## 4.2 Results and Discussion

### 4.2.1 Reaction Optimization

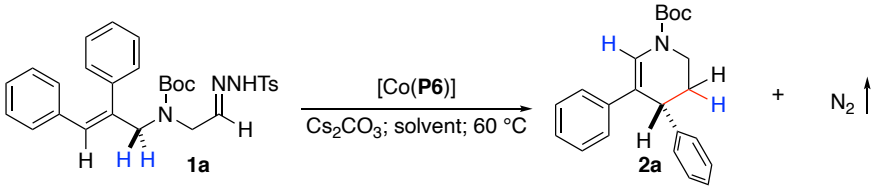
**Scheme 4.2. Ligand Effect on Co(II)-Based Catalytic System for Construction of Tetrahydropyridine[a]**



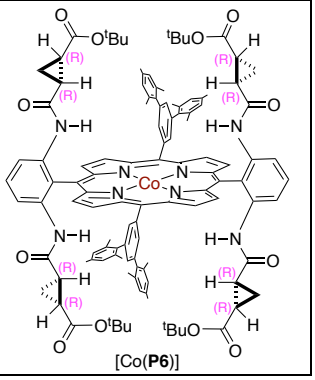

[a] Carried out with 1a (0.10 mmol), $Cs_2CO_3$ (1.5 equiv) using [Co(Por)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification.

At the outset of this project, aliphatic aldehyde-derived tosylhydrazone **1a** was investigated as the representative substrate to conduct the reactions (Scheme 4.2). To our delight, commercial available [Co(**P1**)] (**P1** = tetraphenylporphyrin) could successfully catalyze the reaction to deliver the desired product 2a in low but significant 12% yield. Excitingly, when the achiral amidoporphyrin catalyst [Co(**P2**)] (P**2** = 3,5-Di$^t$Bu-IbuPhyrin)[10] was used, it could double the product yield to 27%. Employment of the chiral catalyst [Co(**P3**)] (P3 = 3,5-Di$^t$Bu-ChenPhyrin)[7a] allowed to achieve asymmetric induction for this novel transformation, affording tetrahydropyridine 2a in a similar 26% yield like [Co(**P3**)] with a relatively low but significant enantioselectivity (14% ee). When second-generation chiral metalloradical catalyst [Co(**P4**)] (**P4** = 3,5-DitBu-QingPhyrin)[7e] was used for the catalytic reaction, it led to very similar product yield (25%) but significant increase in enantioselectivity (60% ee). When switching to [Co(**P5**)] (**P5** = 3,5-Di$^t$Bu-TaoPhyrin)[11] bearing chiral amide units with ester moieties for the catalytic reaction, it led to increase in both product yield (90%) and enantioselectivity (94% ee). Subsequent use of analogous catalyst [Co(**P6**)] (**P6** = 3,5-DiMes-TaoPhyrin), which bears 3,5-di-mesitylphenyl instead of 3,5-di-*tert*-butyphenyl groups as the 5,15-diaryl substituents, further improvements in enantioselectivity (99% ee) as well as yield (95%) were achieved. These results demonstrate the vital role of rigid chiral environment in achieving high enantioselectivity in this transformation.

**Scheme 4.3. Solvent Effect on Co(II)-Based Catalytic System for Construction of Tetrahydropyridine**[a]




| entry | solvent | yield (%) [b] | ee (%) [c] |
|---|---|---|---|
| **1** | **PhF** | **95** | **99** |
| 2 | Toluene | 97 | 97 |
| 3 | Dioxane | 93 | 95 |
| 4 | Hexanes | 80 | 94 |

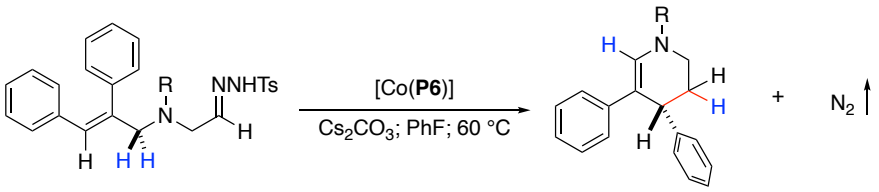



[a] Carried out with 1a (0.10 mmol), $Cs_2CO_3$ (1.5 equiv) using [Co(Por)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification.

Further investigation on solvent effect for the reaction indicates that no obvious difference was observed in terms of both reactivity and enantioselectivity for the reaction with different solvents (Scheme 4.3). Overall, fluorobenzene was still considered as the optimized solvent for the reaction.

In addition, as shown in Scheme 4.4, this reaction is also very sensitive to the N-protecting group of the substrate. When the N-protecting group was change from Boc to Ts, the reactivity and enantioselectivity of the reaction will both dramatically decrease. That might be attributed to the bulkier Boc-protecting group have a positive effect for the ring closure. Besides, stronger interactions between the bulkier Boc-group and catalyst might exist to help tuning the selectivity for the reaction.

**Scheme 4.4. Effect of N-Protecting group**[a]



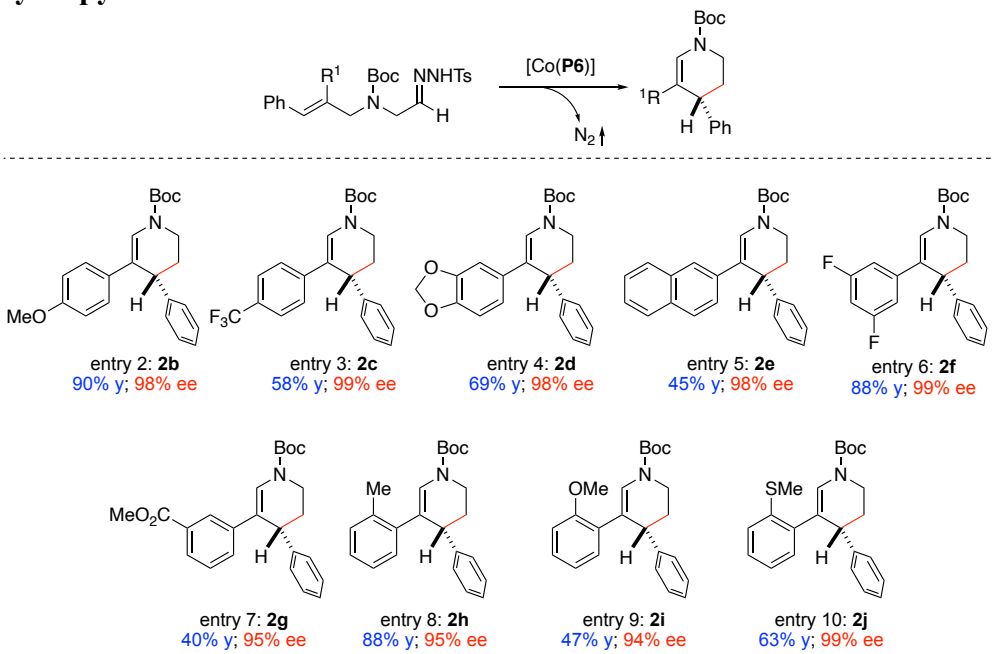

| entry | R | yield (%) [b] | ee (%) [c] |
|---|---|---|---|
| **1** | **Boc** | **95** | **99** |
| 2 | Ts | 70 | 50 |

[a] Carried out with 1a (0.10 mmol), $Cs_2CO_3$ (1.5 equiv) using [Co(Por)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification.

### 4.2.2 Substrate Scope

Under the optimized conditions, the substrate scope of [Co(**P6**)]-catalyzed intramolecular 1,4-C–H alkylation was evaluated with in-situ generated olefin containing aliphatic diazo compounds **1** bearing different functionalities (Table 4.1). Like the parent **1a**, *tert*-butyl (*E*)-(2-diazoethyl)(2,3-diphenylallyl)carbamate derivatives containing 2-aryl substituents with various steric and electronic properties at different positions, including 4-OMe (**1b**), 4-$CF_3$ (**1c**), 1',3'-dioxolane-3,4-fused (**1d**), 2-Naph (**1e**), 3,5-di-F (**1f**), 3-$CO_2$Me(**1g**), 2-Me (**1h**), 2-OMe(**1i**) and 2-SMe (**1j**), could be efficiently activated by [Co(**P6**)] and deliver the corresponding tetrahydropyridines **2b**–**2j** in good yields with high enantioselectivities (Table 4.1; entries 2–10).

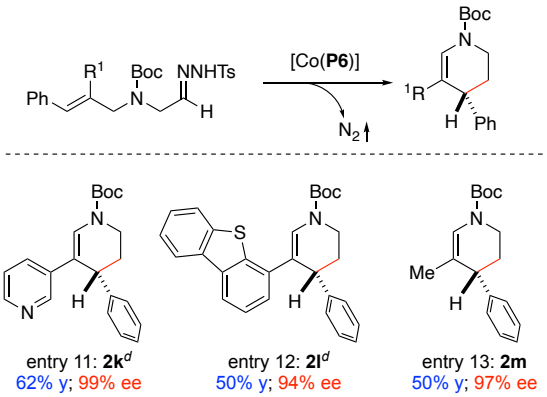
**Table 4.1. Asymmetric Radical C–H Alkylation for Construction of Tetrahydropyridines**[a,b,c]




[a] Carried out with 1 (0.10 mmol) and $Cs_2CO_3$ (1.5 equiv) using [Co(**P6**)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification.

The Co(II)-catalyzed tetrahydropyridine formation was shown to be compatible with substrates containing heteroarenes, such as pyridine (**1k**) and dibenzo[*b*,*d*]thiophene (**1l**), allowing for enantioselective construction of heteroaryl tetrahydropyridine **2k** and **2l** in similarly good yields with the same high enantioselectivities (Table 4.2; entries 11 and 12). Furthermore, the Co(II)-based catalytic system could work for the aliphatic group containing substrate (**1m**) in moderate yield but still with excellent level of enantioselectivity (Table 4.2; entry 13).

**Table 4.2. Asymmetric Radical C–H Alkylation for Construction of Tetrahydropyridines**[a,b,c]

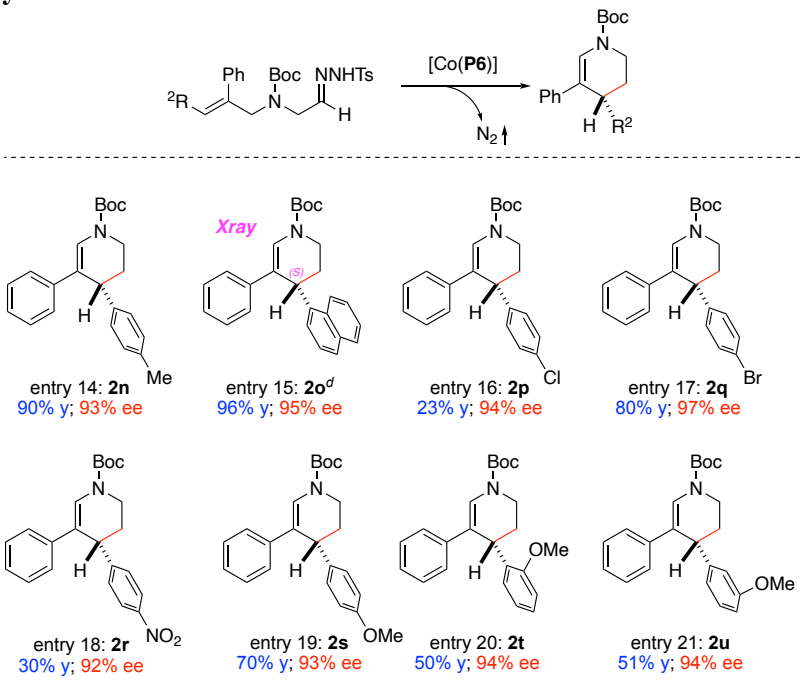



[a] Carried out with 1 (0.10 mmol) and $Cs_2CO_3$ (1.5 equiv) using [Co(**P6**)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification. [d] Using aldehyde and tosyl hydrazine as the starting materials instead of hydrazone

In addition to the substrates with different 2-aryl substituents, the Co(II)-based metalloradical system was shown to be applicable to α-diazoketones containing 3-aryl substituents with various steric and electronic properties at different positions. For example, catalytic sixmembered ring cyclization reactions of (*E*)-(2-diazoethyl)(2,3-diarylallyl)carbamate, such as those bearing 4-Me (**1n**), 1-Naph (**1m**), 4-Cl (**1p**), 4-Br (**1q**), 4-$NO_2$ (**1r**), 4-OMe (**1s**), 2-OMe (**1t**) and 3-OMe (**1u**) proceeded smoothly to afford the corresponding tetrahydropyridine **2n**–**2u** in moderate to good yields with excellent enantioselectivities (Table 4.3; entries 14–21).

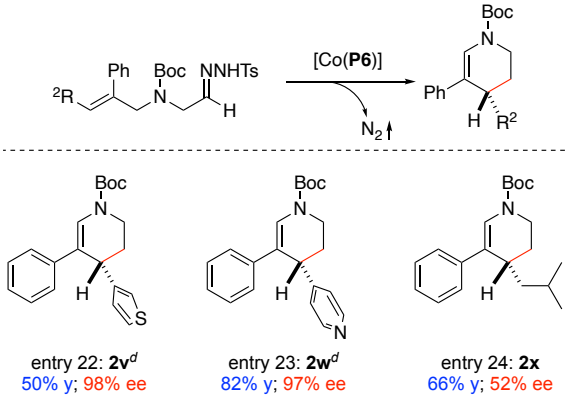
Besides aryl rings with different substituents, heteroaryl group can also be tolerate when it is at 3-position as shown by **1v** and **1w**. (Table 4.4; entries 22 and 23). Gratifyingly, aliphatic substrate **1x** could also undergo the selective 1,4-HAA in the presence of other activated C–H bond and deliver the desired product **2x** in good yield but with a lower enantioselectivity than other cases.

**Table 4.3. Asymmetric Radical C–H Alkylation for Construction of Tetrahydropyridines**[a,b,c]




[a] Carried out with 1 (0.10 mmol) and $Cs_2CO_3$ (1.5 equiv) using [Co(**P6**)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification. [d] Absolute configuration was determined as *S* by X-ray crystallography.

**Table 4.4. Asymmetric Radical C–H Alkylation for Construction of Tetrahydropyridines**[a,b,c]

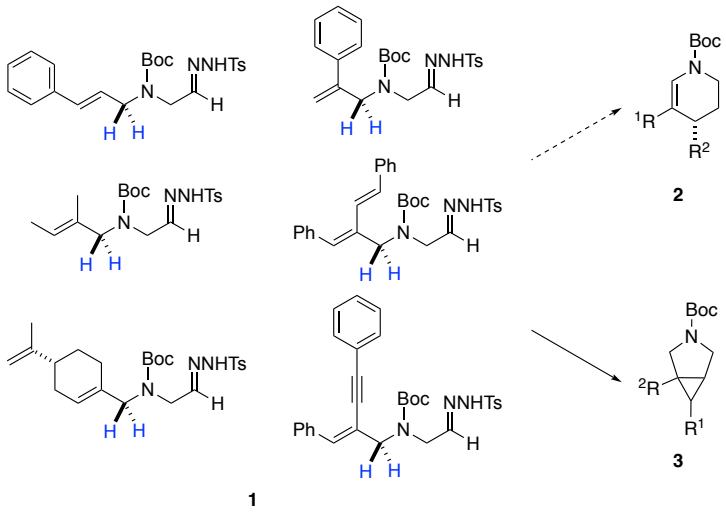



[a] Carried out with 1 (0.10 mmol) and $Cs_2CO_3$ (1.5 equiv) using [Co(**P6**)] (2 mol %) in fluorobenzene (1.0 mL) at 60 ºC for 12 h. [b] Isolated yield. [c] Enantiomeric excess (ee) of product determined by chiral HPLC after purification. [d] Using aldehyde and tosyl hydrazine as the starting materials instead of hydrazone

It is worth to mention that the Co(II)-based catalytic process for the synthesis of tetrahydropyridine derivatives could be readily scaled up under the same condition as exemplified by the enantioselective syntheses of optically active tetrahydropyridine **2a** on 2.0 mmol scale in similarly good yields with the same level of high enantioselectivities.

In addition, the substrates shown in Scheme 4.5 were also investigated for the tetrahydropyridine formation under optimized condition. However, intramolecular cyclopropanation propanation product was observed as the major product in all these cases instead of tetrahydropyridine formation. The cyclopropane products were resulted from radical addition after metalloradical activation following by radical substitution, which means that radical addition, as a competition pathway, is much more facile than 1,4-HAA in these specific cases.

**Scheme 4.5. Substrates that Failed to Work for [Co(P6)]-Catalyzed Tetrahydropyridine Formation**

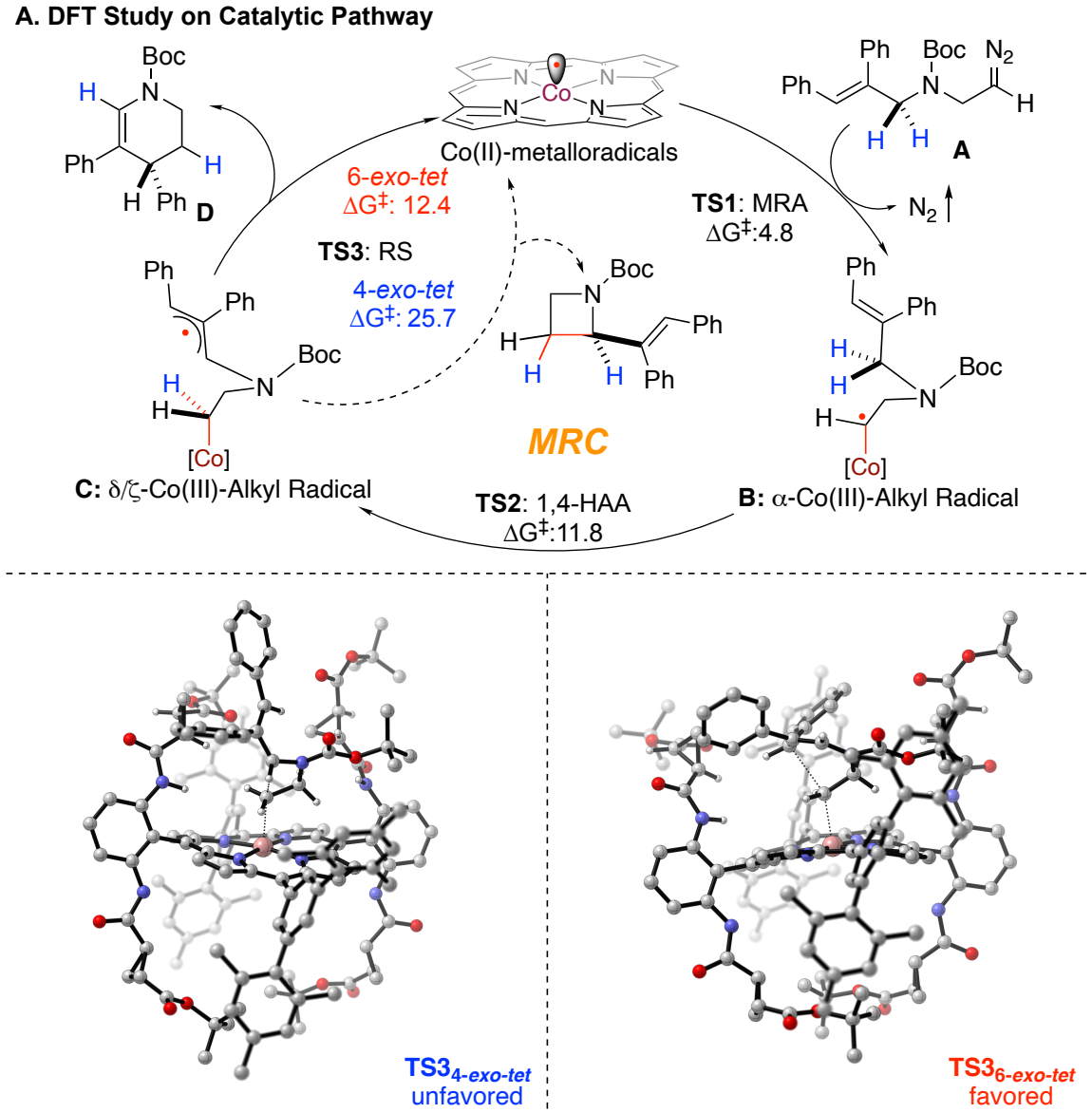



### 4.2.3 Mechanistic Studies

To gain insights into this metalloradical process, combined computational and experimental studies were conducted to explore the proposed stepwise radical mechanism

for this Co(II)-catalyzed tetrahydropyridine synthesis. Firstly, density functional theory (DFT) calculations were performed to elucidate the catalytic pathway for the reaction of in-situ generated aliphatic diazo **A** with the use of the actual catalyst [Co(**P6**)] (Scheme 4.6; see Experimental Section for details). Upon metalloradical activation (MRA) by [Co(**P6**)], **1a** undergoes the extrusion of dinitrogen to generate α-Co(III)-alkyl radical **B**. The metalloradical activation step, which is exergonic by 18.9 kcal/mol, is found to be associated with a low activation barrier (**TS1**: $\Delta G^{\ddagger}$ = 4.8 kcal/mol). This low activation energy is consistent with the azetidine case since similar type of diazo compound was used as the substrate and this calculation result further confirms the facile activation of this donor type diazo compounds. Subsequent 1,4-HAA of intermediate **B**, which is exergonic by 10.0 kcal/mol, gives rise to the corresponding δ/ζ-Co(III)-alkyl radical intermediate **C** with a higher energy barrier (**TS2**: $\Delta G^{\ddagger}$ = 11.8 kcal/mol). The radical cyclization of alkyl radical **C** via 6-*exo*-*tet* radical substitution, the final step of the catalytic reaction, has the highest energy barrier (**TS3**$_{\textbf{6-exo-tet}}$: $\Delta G^{\ddagger}$ = 12.4 kcal/mol), which was considered as the rate-determining step for this reaction. The undesired pathway for the generation of vinyl azetidine was also calculated. The result indicates that 4-*exo*-*tet* radical substitution is associated with a surprisingly high energy barrier (25.7 kcal/mol). That might be due to the fact that the bulky diphenyl substituted vinyl group largely increase the difficulty for the high-strained four-membered ring closure. The results from DFT calculation well match with the experimental observation that six-membered ring is the only observed product since the energy input requirement for vinyl azetidine formation is too high .

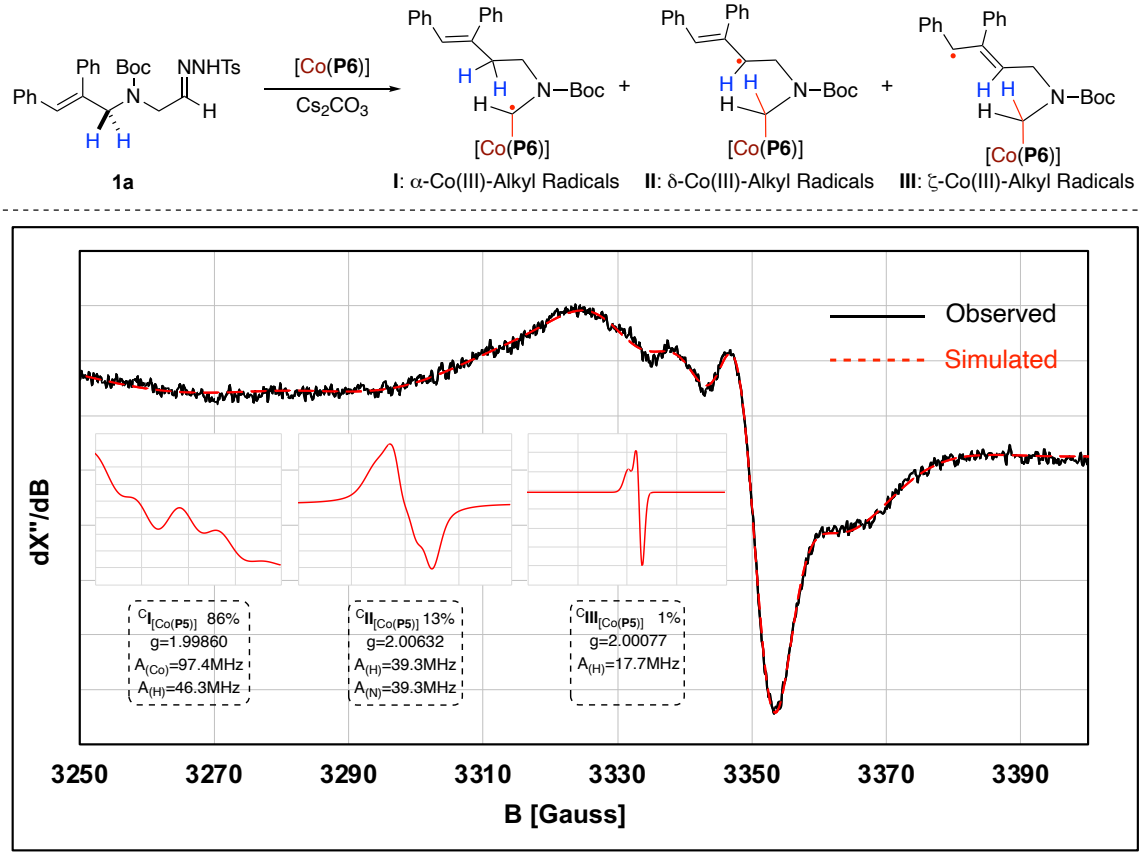
**Scheme 4.6. DFT Study on Catalytic Pathway**




To direct detect radical intermediates, the isotropic X-band electron paramagnetic resonance (EPR) spectrum was recorded at room temperature for the reaction mixture of [Co(**P6**)] with hydrazone **1a** and $Cs_2CO_3$ in benzene (Scheme 4.7). The spectrum displays notable signals that are characteristic of mixture of α-Co(III)-alkyl radical, d-Co(III)-alkyl radical and z-Co(III)-alkyl radical. The observed isotropic g-values of three species is all around 2.00, which is consistent with the generation of organic radical **I**, **II** and **III**. The

observed signals were broad and could be fittingly simulated by three proposed species: **I**, **II** and **III** on the basis of couplings by $^{59}$Co (I = 7/2), $^{14}$N (I = 1) and $^{1}$H (I =1/2): 86% of α-Co(III)-alkyl radical **I** (g: 1.99860; $A_{(Co)}$: 97.4 MHz; $A_{(H)}$: 46.3 MHz), 13% of δ-Co(III)-alkyl radical **II** (g: 2.00632; $A_{(N)}$: 39.3 MHz; $A_{(H)}$: 39.3 MHz) and 1% of ζ-Co(III)-alkyl radical radical **III** (g: 2.00077; $A_{(H)}$: 17.7 MHz).

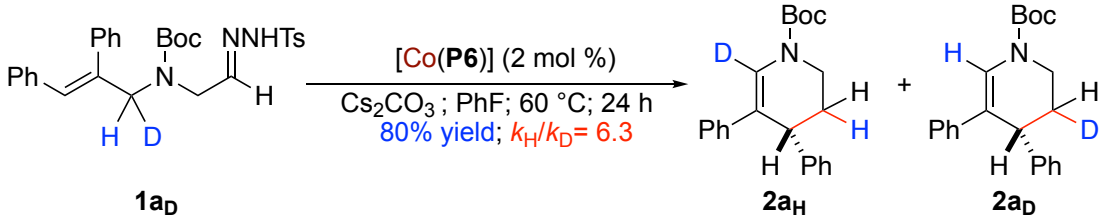
**Scheme 4.7. Detection of Radical Intermediates by EPR**




In addition, monodeuterated diazo **1a$_D$** was prepared as the substrate for the study of kinetic isotopic effect (KIE) using optimized catalyst [Co(**P6**)] (Scheme 4.8). The KIE values for the catalytic reaction of diazo **1a$_D$** by [Co(**P6**)] were determined to be 6.3. This large value of primary KIE is in good agreement with the proposed step of homolytic C–

H bond cleavage via intramolecular H-atom abstraction by α-Co(III)-alkyl radical intermediate **I**.

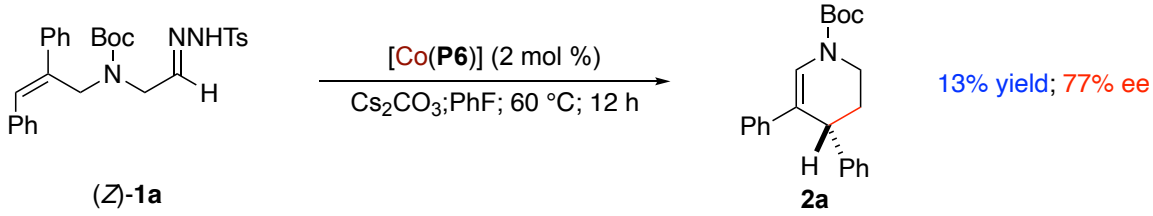
**Scheme 4.8. Determination of Kinetic Isotope Effect**




**1a$_D$** **2a$_H$** **2a$_D$**

Besides, (*Z*)-**1a** was employed as the substrate for the reaction using [Co(**P6**)] as the catalyst (Scheme 4.9). Different from the catalytic reaction by (*E*)-**1a** and [Co(**P6**)] (Table 1; entry 1), it was found that even though (*Z*)-**1a** is much less reactive towards product formation but still lead to the same major enantiomer, implying the involvement of ζ-Co(III)-allylic radical **III$_{1a}$** during the reaction.

**Scheme 4.9. Probing of δ-Co(III)-Allylic Radical Intermediate via Olefin Isomerization**

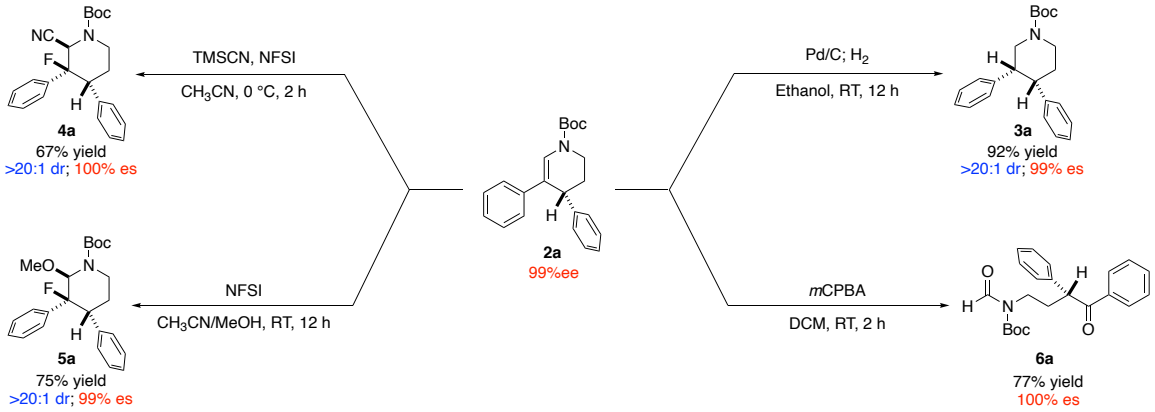



(*Z*)-**1a** **2a**

### 4.2.4 Synthetic Applications

Considering that the resulting enantioenriched tetrahydropyrdine contains versatile enamine moiety, they may serve as useful precursor for further functionalized piperidines. To demonstrate the synthetic utility of this methodology, we carried out a series of synthetic transformations using enantioenriched tetrahydropyridine **2a** (99% ee) as the model reactant (Scheme 4.8). Tetrahydropyridine **2a** can undergo efficient hydrogenation

**Scheme 4.8. Synthetic Transformations**




reaction to generate corresponding disubstituted piperidine **3a** in 92% yield without erosion of its optical purity. In addition to hydrogenation reaction, enamine double bond in product **2a** can be further functionalized with different nucleophile such as MeOH and TMSCN in the present of NFSI to deliver trisubstituted piperidine **4a** and **5a** in good yield with preservation of the high enantiomeric purity and well control of the diastereoselectivity (>20:1).[12] Both of the resulting chiral products might be important motif in bioactive molecules but hard to accessed through other methods. Furthermore, Tetrahydropyridine **2a** will proceed smoothly ring opening reaction with the treatment of *m*CPBA to provide chiral acyclic *tert*-butyl formyl carbamate **6a** in 77% yield and with fully retention of the enantiopurity.

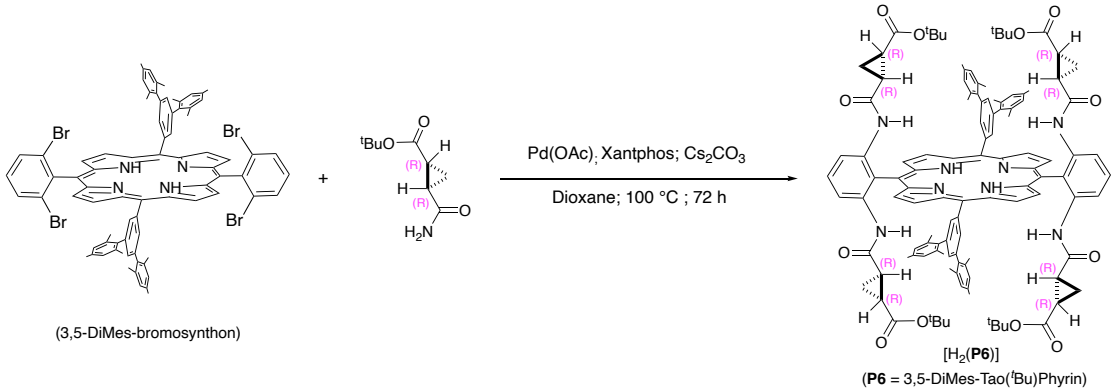
## 4.3 Conclusion

In summary, we have for the first time demonstrated chiral tetrahydropyridine synthesis through Co(II)-based MRC. The judicious modulation of $D_2$-symmetric chiral amidoporphyrin ligand to adopt desired steric, electronic and chiral environments around the Co(II)-metalloradical center that maximize a network of noncovalent attractive interactions in catalytic intermediates is the key to the success of this transformation. With

the $D_2$-symmetric chiral amidoporphyrin 3,5-DiMes-Tao($^t$Bu)Phyrin as the optimal supporting ligand, the Co(II)-based metalloradical system can catalyze asymmetric construction of tetrahydropyridine from aliphatic aldehyde with varied electronic and steric properties in good yields with high enantioselectivities. The combined computational and experimental studies have shed light on the working details of this new catalytic process that proceeds through a stepwise radical mechanism. To showcase its broad synthetic application of this Co(II)-based metalloradical system for asymmetric tetrahydropyridine construction, we have performed several enantiospecific transformations from the resulting enantioenriched tetrahydropyridine to multi-functionalized piperidine. This work further reveals the general synthetic application of this rare 1,4-HAA process. We envision that it would find broader synthetic applications beyond the four-membered ring and six-membered ring synthesis.

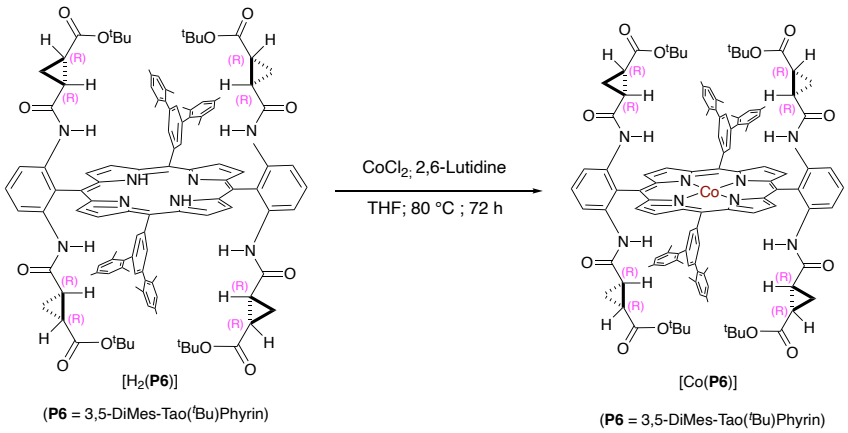
## 4.4 Experimental Section

### 4.4.1 Synthesis and Characterization of Catalyst



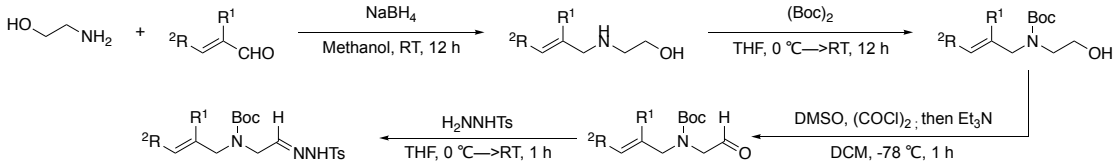

**3,5-DiMes-Tao(ᵗBu)Phyrin** was synthesized according to our previous reported procedure.[7a] 3,5- DiMes-bromosynthon (200 mg, 0.142 mmol, 1.0 equiv), the chiral amide (1R,2R)-*tert*-butyl-2-carbamoylcyclopropane-1-carboxylate3 (422 mg, 2.28 mmol, 16.0 equiv), Pd(OAc)2 (14 mg, 0.064 mmol, 0.45 equiv), Xantphos (74 mg, 0.128 mmol, 0.9 equiv) and Cs2CO3 (743 mg, 2.28 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 screwcap. After stirring at 100 °C for 72 h, the resulting mixture was cooled down to room temperature, diluted with EtOAc, filtered through a silica pad and concentrated under vacuum. The crude mixture was further purified by flash column chromatography (4:1 to 2:1 Hexanes/EtOAc) to afford the title compound (261 mg, 77% yield). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, $J$ = 4.8 Hz, 4H), 8.95 (d, $J$ = 4.8 Hz, 4H), 8.63 (d, $J$ = 8.5 Hz, 4H), 8.12 (d, $J$ = 1.6 Hz, 4H), 7.92 (t, $J$ = 8.5 Hz, 2H), 7.51 (d, $J$ = 1.6 Hz, 2H), 7.09 (d, $J$ = 5.4 Hz, 8H), 6.72 (s, 4H), 2.47 (d, $J$ = 3.1 Hz, 24H), 2.41 (s, 12H), 1.86 (dt, $J$ = 9.1, 4.7 Hz, 4H), 1.03 (s, 40H), 0.66 – 0.43 (m, 8H), -2.38 (s, 2H). $^{13}$C NMR

(126 MHz, $CDCl_3$) δ 170.67, 168.84, 161.36, 158.11, 147.34, 146.26, 141.37, 140.10, 139.21, 138.45, 136.93, 135.97, 135.93, 134.15, 133.90, 133.19, 130.57, 130.48, 128.43, 128.39, 121.79, 121.01, 117.15, 107.70, 80.78, 27.70, 24.18, 23.03, 21.31, 21.27, 21.17, 15.18. UV-vis ($CHCl_3$), lmax nm (log e): 422 (5.51), 515 (4.22), 551 (3.70), 590 (3.68), 644 (3.40). HRMS (ESI) ([M+Na]+) Calcd. For $C_{116}H_{122}N_8O_{12}Na^+$: 1841.907992, Found: 1841.901733.




[Co(**P6**)] was synthesized according to our previous reported procedure.[7a] Free base porphyrin [$H_2$(**P6**)] (261 mg) 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 (4.0 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 12 h prior to being cooled down to room temperature. The reaction mixture was diluted with EtOAc, washed with water 2 times and concentrated under vacuum. The compound [Co(P6)] was isolated (248 mg, 93% yield) as a purple solid after purification by flash column chromatography (5:1 to 2:1 Hexanes/EtOAc). UV-vis ($CHCl_3$), lmax nm (log e): 414 (5.38), 527 (4.08). HRMS (ESI) ([M+Na]+) Calcd. For C116H120N8O12CoNa+: 1898.825539, Found: 1898.820801.

### 4.4.2 General Procedure for Substrate Synthesis




**Step 1:** To a solution of aldehyde (10 mmol) in anhydrous methanol (20.0 mL) was added Ethanolamine (10 mmol) dropwise at room temperature. The reaction was stirred overnight. After that, the reaction mixture was cooled down to 0 °C in an ice bath. Sodium borohydride (15 mmol) was added portionwise. After the bubbling stopped, the solvent was then evaporated. The resulting residue was then partitioned between $H_2O$ (30 mL) and EtOAc (30 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic extracts were then dried and concentrated under vacuum. The obtained raw compound was directly used without further purification.

**Step 2:** To a solution of resulting alcohol from last step (5 mmol) and triethylamine (1.5 equiv.) in DCM (30.0 mL), di-tert-butyl dicarbonate (1.1 equiv.) was added portionwise at 0 $^{O}$C. The reaction was then stirred at room temperature and monitored by TLC. After the reaction was completed, the mixture was filtrated through a short pad of silica and eluted with ethyl acetate. The filtrate was then evaporated and concentrated under vacuum. The obtained raw compound was directly used without further purification.

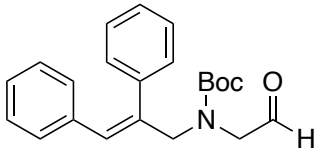
**Step 3:** (Swern oxidation): To a solution of oxalyl chloride (1.5 equiv.) in DCM (30 mL) at -78 °C was added dimethyl sulfoxide (3.0 equiv.) dropwise via syringe. After stirring for 20 min at -78 °C, a solution of Boc protected alcohol in DCM (5.0 mL) was added dropwisely. The solution was then stirred for 30 min at -78 °C, followed by the dropwise addition of triethylamine (4.5 equiv.). After 10 min, the reaction mixture was warmed up to room temperature, poured into brine (30 mL) and stirred for another 10 min. The layers

were then separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under vacuum. The oxidized product was further purified by flash chromatography.

**Step 4:** To a stirred solution of pure tosylhydrazide (1 mmol) in THF (2.0 mL) at room temperature, aldehyde was added dropwise (or portionwise if solid). The reaction was completed within 0.5 h. After that, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by flash chromatography.

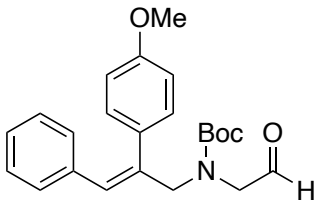
### 4.4.3 Characterization of Aldehyde Substrates

***tert*-Butyl (*E*)-(2,3-diphenylallyl)(2-oxoethyl)carbamate (1a')**




Colorless Oil. Yield: 92%. $R_f$ = 0.40 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.21 (d, *J* = 3.7 Hz, 1H), 7.36 – 6.85 (m, 10H), 6.49 (d, *J* = 3.7 Hz, 1H), 4.35 (d, *J* = 3.8 Hz, 2H), 3.78 (d, *J* = 3.7 Hz, 2H), 1.40 – 1.28 (m, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.73, 155.30, 138.17, 137.68, 136.00, 129.13, 128.96, 128.60, 128.51, 127.77, 127.46, 126.87, 80.34, 56.09, 55.82, 55.00, 27.90. IR (neat, $cm^{-1}$): 3055.73, 2976.44, 2929.26, 1733.79, 1686.48, 1447.93, 1366.50,1162.69. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{26}NO_3$: 352.19072, found 352.19096.

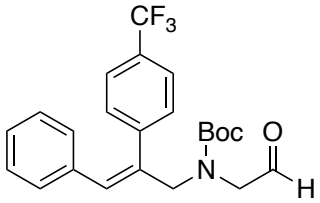
***tert*-Butyl (E)-(2-(4-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate(1b')**




Colorless Oil. Yield: 77%. $R_f$ = 0.38 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 7.13 – 6.94 (m, 7H), 6.81 (dd, *J* = 13.3, 8.3 Hz, 2H), 6.46 (s, 1H), 4.35 (s, 2H), 3.92 – 3.64 (m, 5H), 1.45 – 1.31 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.34, 159.22, 155.71, 137.50,

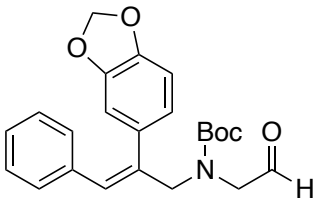
136.37, 130.02, 129.61, 129.25, 128.54, 128.11, 127.03, 114.32, 80.80, 56.42, 55.86, 55.28, 28.29. IR (neat, $cm^{-1}$): 3007.59, 2977.02, 2836.72, 1733.49, 1685.60, 1511.34, 1243.72,1162.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_4$: 382.20128, found 382.20076.

***tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)carbamate (1c')**




Colorless Oil. Yield: 84%. $R_f$ = 0.48 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 1H), 7.63 – 7.51 (m, 2H), 7.36 – 7.26 (m, 2H), 7.20 – 7.11 (m, 3H), 7.02 – 6.90 (m, 2H), 6.60 (s, 1H), 4.40 (s, 2H), 3.87 (s, 2H), 1.35 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 198.59, 154.98, 141.74, 136.42, 135.44, 130.49, 129.41, 128.31, 127.62, 125.79, 122.78, 81.30, 56.18, 54.98, 28.15. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -62.60 (d, $J$ = 8.6 Hz). IR (neat, $cm^{-1}$): 2970.22, 2937.85, 1736.84, 1689.36, 1366.83, 1322.14, 1240.58,1161.30. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{25}NO_3F_3$: 420.17810, found 420.17821.

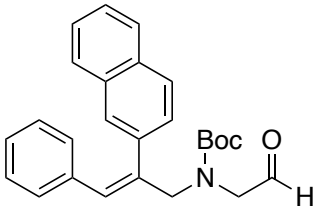
***tert*-Butyl (*E*)-(2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1d')**




Colorless Oil. Yield: 91%. $R_f$ = 0.45 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (600 MHz, $CDCl_3$): δ 9.30 (s, 1H), 7.17 – 6.94 (m, 5H), 6.77 – 6.57 (m, 3H), 6.52 – 6.31 (m, 1H), 5.92 (s, 2H), 4.32 (s, 2H), 3.80 (s, 2H), 1.52 – 1.31 (m, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 199.19, 155.64, 148.00, 147.18, 137.40, 136.12, 131.76, 129.25, 128.84, 128.15, 127.19, 122.40, 109.20, 108.84, 101.16, 80.86, 56.28, 55.32, 28.27. IR (neat, $cm^{-1}$): 2977.30, 2898.00, 1733.42, 1685.07, 1488.55,

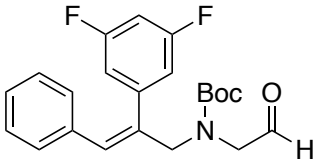
1448.41, 1236.95,1162.91. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{26}NO_5$: 396.18055, found 396.17931.

**tert-Butyl (E)-(2-(naphthalen-2-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1e')**




Colorless Oil. Yield: 81%. $R_f$ = 0.40 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 7.88 – 7.66 (m, 4H), 7.52 – 7.42 (m, 2H), 7.32 – 7.25 (m, 1H), 7.13 – 6.96 (m, 5H), 6.63 (s, 1H), 4.51 (s, 2H), 3.86 (s, 2H), 1.42 – 1.24 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.11, 155.08, 137.65, 136.02, 135.87, 133.56, 129.33, 129.26, 129.01, 128.54, 128.16, 127.98, 127.91, 127.82, 127.71, 127.26, 126.26, 126.17, 80.82, 56.54, 55.23, 28.18. IR (neat, cm$^{-1}$): 3058.05, 2978.80, 2930.24, 1733.72, 1685.70, 1453.11, 1242.60, 1163.40. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{28}NO_3$: 402.20637, found 402.20501.

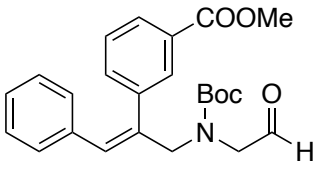
***tert*-butyl (E)-(2-(3,5-difluorophenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1f')**




Colorless Oil. Yield: 71%. $R_f$ = 0.50 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.41 (s, 1H), 7.17 – 7.09 (m, 3H), 7.01 – 6.93 (m, 2H), 6.76 – 6.65 (m, 3H), 6.55 (s, 1H), 4.33 (s, 2H), 3.85 (s, 2H), 1.37 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.49, 163.21 (d, $J$ = 249.9 Hz), 155.35, 142.42 – 141.22 (m), 135.54, 135.19, 130.51, 129.21, 128.36, 127.79, 112.17 – 111.89 (m), 103.54 – 103.01 (m), 81.15, 56.03, 55.85, 28.17. $^{19}$F NMR (564 MHz, $CDCl_3$) δ -108.96 (t, $J$ = 7.9 Hz), -109.21 (t, $J$ = 8.0 Hz). IR (neat, cm$^{-1}$): 2979.65, 2932.40, 1735.03, 1687.68,

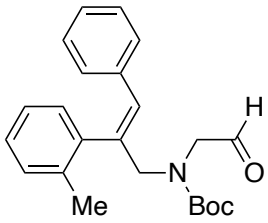
1618.84, 1588.09, 1244.08,1119.06. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{24}NO_3F_2$: 388.17188, found 388.17273.

**Methyl (*E*)-3-(3-((*tert*-butoxycarbonyl)(2-oxoethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g')**



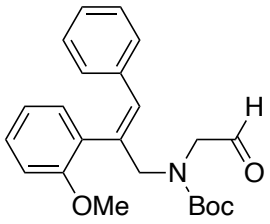

Colorless Oil. Yield: 21%. $R_f$ = 0.33 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.00 – 7.87 (m, 2H), 7.41 – 7.28 (m, 2H), 7.15 – 7.06 (m, 3H), 6.94 (m, 2H), 6.57 (s, 1H), 4.40 (s, 2H), 3.97 – 3.74 (m, 5H), 1.35 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.84, 166.75, 155.54, 138.80, 136.88, 135.66, 133.84, 130.85, 129.98, 129.77, 129.29, 129.00, 128.23, 127.43, 81.01, 56.18, 55.27, 52.24, 28.14. IR (neat, cm$^{-1}$): 2976.41, 2952.09, 2929.57, 1720.15, 1687.60, 1438.42, 1366.79, 1161.79. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{24}H_{28}NO_5$: 410.19620, found 410.19444.

***tert*-butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(*o*-tolyl)allyl)carbamate (1h')**



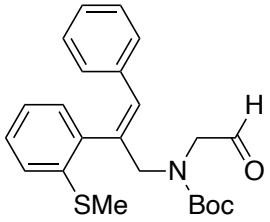

Colorless Oil. Yield: 76%. $R_f$ = 0.59 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.24 – 7.15 (m, 3H), 7.14 – 6.97 (m, 4H), 6.90 (ddd, J = 15.0, 7.1, 3.6 Hz, 2H), 6.51 (s, 1H), 4.49 – 4.03 (m, 2H), 4.01 – 3.69 (m, 2H), 2.13 (s, 3H), 1.37 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$): δ 198.84, 155.69, 138.00, 136.74, 136.16, 135.48, 130.56, 128.66, 128.23, 127.83, 127.25, 126.54, 124.63, 80.71, 56.93, 56.55, 28.10, 19.20. IR (neat, cm$^{-1}$): 3005.20, 2987.70, 2970.18, 1738.00, 1365.85, 1275.36, 1260.50,1162.35. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{28}NO_3$: 366.20637, found 366.20561.

***tert*-Butyl (*E*)-(2-(2-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1i')**



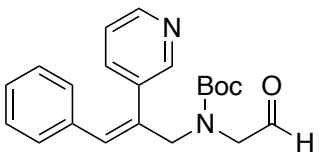

Colorless Oil. Yield: 69%. $R_f$ = 0.53 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 1H), 7.36 – 7.28 (m, 1H), 7.10 (dt, *J* = 5.2, 2.6 Hz, 3H), 7.04 – 6.79 (m, 5H), 6.54 (s, 1H), 4.35 (s, 2H), 3.84 (s, 2H), 3.75 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 199.88, 157.07, 155.96, 136.49, 135.47, 130.55, 129.31, 128.81, 128.09, 127.39, 127.08, 121.28, 111.10, 80.53, 56.73, 55.80, 55.44. IR (neat, $cm^{-1}$): 3004.44, 2977.04, 2835.69, 1734.16, 1685.83, 1454.51, 1275.44, 1162.00. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_4$: 382.20218, found 382.20222.

***tert*-butyl (*E*)-(2-(2-(methylthio)phenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1j')**




Colorless Oil. Yield: 73%. $R_f$ = 0.50 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.39 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.16 – 7.04 (m, 4H), 7.00 – 6.91 (m, 3H), 6.54 (s, 1H), 5.11 – 3.41 (m, 4H), 2.39 (s, 3H), 1.51 – 1.29 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 199.17, 157.77, 155.79, 137.32, 136.97, 135.90, 129.95, 129.23, 129.07, 128.64, 128.47, 128.18, 127.36, 125.29, 80.57, 56.78, 55.29, 15.21. IR (neat, $cm^{-1}$): 3056.40, 2976.15, 2922.41, 1733.54, 1685.26, 1448.01, 1243.62,1161.79. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{27}NO_4S$: 397.17062, found 397.17078.

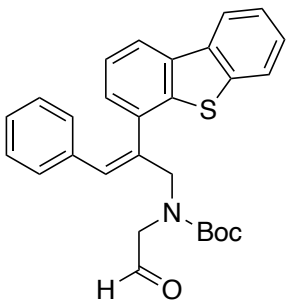
***tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(pyridin-3-yl)allyl)carbamate (1k')**




Colorless Oil. Yield: 64%. $R_f$ = 0.19 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was

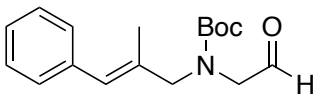
reported. $^{1}$H NMR (500 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.68 – 8.34 (m, 2H), 7.51 – 7.30 (m, 2H), 7.20 – 7.12 (m, 3H), 6.97 – 6.90 (m, 2H), 6.71 (s, 1H), 4.41 (s, 2H), 3.94 (s, 2H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 198.50, 155.47, 153.25, 149.88, 136.88, 135.43, 134.36, 132.19, 131.30, 129.35, 128.58, 128.46, 123.61, 81.30, 56.07, 54.83, 28.18. IR (neat, $cm^{-1}$): 3005.93, 2976.61, 2931.46, 1772.21, 1690.42, 1454.19, 1366.68,1162.35. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{25}N_2O_3$: 353.18597, found 353.18644.

***tert*-Butyl (*E*)-(2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1l')**




Colorless Oil. Yield: 53%. $R_f$ = 0.32 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.20 – 8.07 (m, 2H), 7.82 – 7.67 (m, 1H), 7.51 – 7.39 (m, 3H), 7.37 – 7.18 (m, 1H), 7.08 – 6.87 (m, 4H), 6.70 (s, 1H), 4.44 (s, 2H), 3.85 (s, 2H), 1.65 – 1.17 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.95, 155.68, 139.51, 138.91, 136.21, 135.86, 135.75, 133.69, 130.62, 128.70, 128.32, 127.71, 127.04, 126.95, 126.90, 125.33, 124.56, 122.99, 121.84, 121.03, 80.85, 56.77, 55.55, 28.13. IR (neat, $cm^{-1}$): 3054.97, 2827.56, 2711.06, 1679.45, 1441.73, 1387.39, 1303.83, 1128.51. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{28}NO_3S$: 458.17844, found 458.17717.

***tert*-Butyl (*E*)-(2-methyl-3-phenylallyl)(2-oxoethyl)carbamate (1m')**

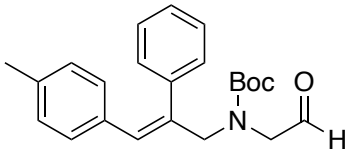



Colorless Oil. Yield: 64%. $R_f$ = 0.59 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^{1}$H NMR (600 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.31 (t, $J$ = 7.7 Hz, 2H), 7.24 – 7.17 (m, 3H), 6.30 (s, 1H), 4.10 – 3.79 (m, 4H), 1.82 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR (151 MHz,

$CDCl_3$): δ 198.70, 155.41, 137.13, 134.04, 128.87, 128.33, 128.22, 126.74, 80.81, 56.62, 56.04, 28.24, 15.73.

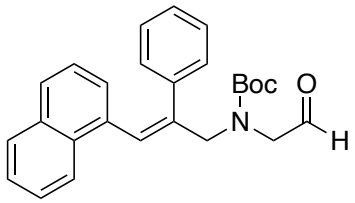
IR (neat, $cm^{-1}$): 2977.76, 2930.49, 2816.43, 1735.71, 1686.47, 1367.00, 1243.49, 1162.56. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{24}NO_3$: 290.17507, found 290.17650.

***tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(*p*-tolyl)allyl)carbamate (1n')**




Colorless Oil. Yield: 63%. $R_f$ = 0.50 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (600 MHz, $CDCl_3$): δ 9.24 (s, 1H), 7.35 – 7.26 (m, 3H), 7.21 – 7.14 (m, 2H), 6.96 – 6.81 (m, 5H), 6.47 (s, 1H), 4.36 (s, 2H), 3.80 (s, 2H), 2.24 (s, 3H), 1.35 (s, 10H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 199.29, 155.68, 138.64, 137.04, 136.92, 133.18, 129.34, 129.17, 129.02, 128.85, 128.83, 128.81, 127.68, 80.76, 56.31, 55.37, 28.22, 21.20. IR (neat, $cm^{-1}$): 3007.00, 2976.47, 2836.57, 1733.21, 1685.17, 1510.11, 1244.97, 1163.52. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_3$: 366.19909, found 366.17112.

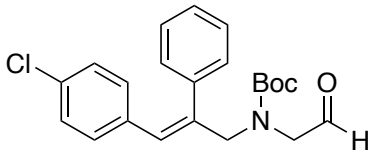
***tert*-Butyl (*E*)-(3-(naphthalen-1-yl)-2-phenylallyl)(2-oxoethyl)carbamate (1o')**




Colorless Oil. Yield: 87%. $R_f$ = 0.52 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (600 MHz, $CDCl_3$): δ 9.29 (s, 1H), 8.08 (dd, $J$ = 16.4, 8.3 Hz, 1H), 7.82 (dd, $J$ = 8.4, 3.0 Hz, 1H), 7.65 (dd, $J$ = 8.2, 5.4 Hz, 1H), 7.58 – 7.44 (m, 1H), 7.19 – 7.06 (m, 6H), 7.04 – 6.96 (m, 1H), 4.59 (s, 2H), 3.93 (s, 2H), 1.54 – 1.29 (m, 9H). $^3C$ NMR (151 MHz, $CDCl_3$): δ 199.20, 155.05, 139.76, 137.74, 134.05, 133.44, 132.12, 129.03, 128.60, 128.26, 127.84, 127.53, 127.44, 127.07, 126.15, 125.87, 125.33, 124.36, 80.98, 56.17, 54.52, 28.15. IR (neat, $cm^{-1}$): 3016.50, 2977.84,

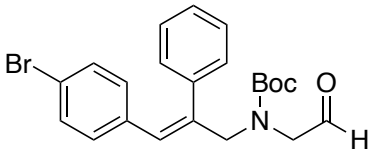
2930.41, 1733.24, 1686.80, 1391.86, 1242.34, 1162.65. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{28}NO_3$: 402.20637, found 402.20630.

***tert*-Butyl (*E*)-(3-(4-chlorophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1p')**



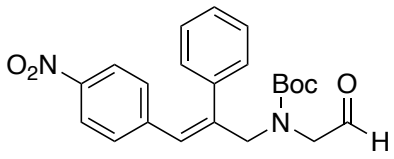

Colorless Oil. Yield: 87%. $R_f$ = 0.42 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.26 (s, 1H), 7.36 – 7.24 (m, 3H), 7.20 – 6.99 (m, 4H), 6.95 – 6.83 (m, 2H), 6.43 (s, 1H), 4.36 (s, 2H), 3.81 (s, 2H), 1.41 – 1.30 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 199.00, 155.58, 138.78, 138.02, 134.57, 132.82, 130.44, 128.85, 128.23, 127.97, 127.43, 126.51, 80.86, 56.45, 55.29, 28.19. IR (neat, cm$^{-1}$): 2978.46, 2928.53, 1733.88, 1685.08, 1453.53, 1367.40, 1244.62, 1162.74. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{25}NO_3Cl$: 386.15175, found 386.15314.

***tert*-Butyl (*E*)-(3-(4-bromophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1q')**



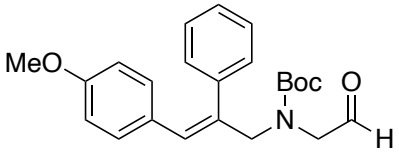

Colorless Oil. Yield: 76%. $R_f$ = 0.42 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.08 (m, 4H), 6.81 (dd, *J* = 21.5, 8.1 Hz, 2H), 6.42 (s, 1H), 4.34 (s, 2H), 3.79 (s, 2H), 1.35 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.01, 155.57, 138.94, 137.99, 135.02, 131.24, 130.76, 129.04, 128.85, 128.01, 127.45, 121.00, 80.88, 56.46, 55.30, 28.21. IR (neat, cm$^{-1}$): 2977.84, 2929.66, 1733.72, 1685.43, 1452.65, 1244.12, 1162.82, 1132.04. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{25}NO_3Br$: 430.10123, found 430.10273.

***tert*-Butyl (*E*)-(3-(4-nitrophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1r')**



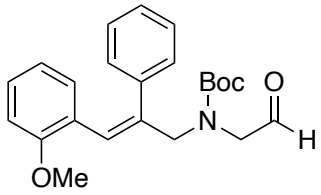

Colorless Oil. Yield: 77%. $R_f$ = 0.30 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.32 (s,1H), 8.21 – 7.71 (m, 2H), 7.38 – 7.30 (m, 3H), 7.18 – 7.03 (m, 4H), 6.56 (s, 1H), 4.39 (s, 2H), 3.85 (s, 2H), 1.38 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.83, 155.59, 146.45, 143.25, 143.00, 137.05, 129.85, 129.19, 128.74, 128.62, 126.25, 123.44, 81.27, 56.85, 55.52, 28.31. IR (neat, $cm^{-1}$): 2970.31, 2930.22, 1769.09, 1735.91, 1689.43, 1515.68, 1341.31, 1162.18. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{25}N_2O_5$: 397.17580, found 397.17475.

***tert*-butyl (*E*)-(3-(4-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1s')**




Colorless Oil. Yield: 76%. $R_f$ = 0.38 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.08 (m, 4H), 6.81 (dd, $J$ = 21.5, 8.1 Hz, 2H), 6.42 (s, 1H), 4.34 (s, 2H), 3.79 (s, 2H), 1.35 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.01, 155.57, 138.94, 137.99, 135.02, 131.24, 130.76, 129.04, 128.85, 128.01, 127.45, 121.00, 80.88, 56.46, 55.30, 28.21. IR (neat, $cm^{-1}$): 3021.08, 2978.20, 2921.99, 1733.61, 1685.02, 1243.87, 1163.22, 1132.24. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_4$: 382.20128, found 382.20176.

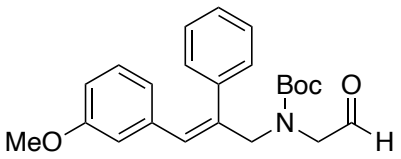
***tert*-Butyl (*E*)-(3-(2-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1t')**




Colorless Oil. Yield: 81%. $R_f$ = 0.40 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.22 (s, 1H), 7.26 –

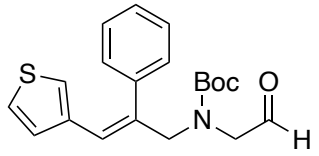
7.18 (m, 4H), 7.17 – 7.07 (m, 2H), 7.01 – 6.49 (m, 4H), 4.45 (s, 2H), 4.07 – 3.50 (m, 5H), 1.46 – 1.31 (m, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 199.59, 157.46, 155.75, 138.51, 137.36, 130.26, 128.94, 128.57, 128.41, 127.51, 124.55, 123.23, 119.92, 110.35, 80.78, 56.05, 55.44, 28.19. IR (neat, $cm^{-1}$): 2974.99, 2930.49, 2836.21, 1734.28, 1686.27, 1456.08, 1242.28, 1161.04. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_4$: 382.20128, found 382.20164.

***tert*-Butyl (*E*)-(3-(3-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1u')**




Colorless Oil. Yield: 96%. $R_f$ = 0.40 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.37 – 7.26 (m, 3H), 7.25 – 7.13 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.71 – 6.50 (m, 3H), 6.44 (s, 1H), 4.37 (s, 2H), 3.82 (s, 2H), 3.49 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 199.14, 159.15, 155.66, 138.60, 138.16, 137.33, 129.87, 129.04, 128.97, 128.80, 127.79, 122.14, 113.76, 113.70, 80.84, 56.41, 55.42, 54.85. IR (neat, $cm^{-1}$): 2975.72, 2930.40, 2833.94, 1733.58, 1685.95, 1598.20, 1243.32, 1159.47. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_4$: 382.20128, found 382.20017.

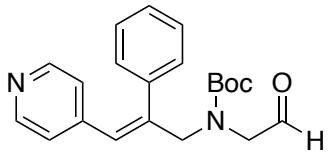
***tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(thiophen-3-yl)allyl)carbamate (1v')**




Colorless Oil. Yield: 37%. $R_f$ = 0.45 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.40 – 7.27 (m, 3H), 7.24 – 7.12 (m, 2H), 7.03 – 6.95 (m, 1H), 6.84 (s, 1H), 6.56 – 6.41 (m, 2H), 4.31 (s, 2H), 3.81 (s, 2H), 1.33 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.17, 155.67, 138.99, 137.65, 136.60, 129.07, 128.88, 128.71, 127.94, 124.95, 124.53, 123.19, 80.81, 56.58, 56.33, 28.18. IR (neat, $cm^{-}$

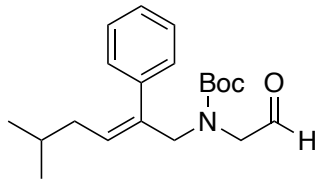
[1]): 2975.36, 2925.83, 1733.35, 1685.26, 1453.59, 1365.94, 1243.54, 1159.67. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_3S$: 358.14714, found 358.14820.

***tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(pyridin-4-yl)allyl)carbamate (1w')**




Colorless Oil. Yield: 76%. $R_f$ = 0.17 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.33 – 8.23 (m, 2H), 7.31 – 7.20 (m, 3H), 7.13 – 7.00 (m, 2H), 6.85 – 6.70 (m, 2H), 6.38 (s, 1H), 4.31 (s, 2H), 3.79 (s, 2H), 1.32 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.50, 155.36, 149.50, 149.45, 143.58, 143.09, 137.36, 129.02, 128.43, 128.29, 125.61, 123.44, 80.89, 56.63, 55.27, 28.07. IR (neat, cm$^{-1}$): 2976.09, 1733.33, 1687.34, 1594.14, 1452.72, 1242.78, 1162.28, 1131.16. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{25}N_2O_3$: 353.18597, found 353.18544.

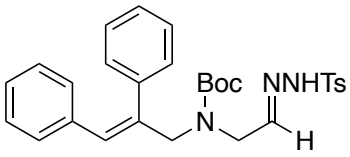
***tert*-butyl (*E*)-(5-methyl-2-phenylhex-2-en-1-yl)(2-oxoethyl)carbamate (1x')**




Colorless Oil. Yield: 84%. $R_f$ = 0.62 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 1H), 7.33 – 7.28 (m, 2H), 7.24 – 7.20 (m, 1H), 7.17 – 7.03 (m, 2H), 5.66 – 5.47 (m, 1H), 4.22 (s, 2H), 3.72 (s, 2H), 2.00 – 1.78 (m, 2H), 1.66 – 1.51 (m, 1H), 1.30 (s, 9H), 0.81 (d, *J* = 3.7 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 199.60, 155.67, 138.50, 137.00, 130.24, 128.82, 128.33, 127.20, 80.56, 77.48, 77.16, 76.84, 55.89, 28.77, 28.15, 22.42. IR (neat, cm$^{-1}$): 2956.01, 2928.62, 2869.75, 1734.91, 1687.46, 1366.14, 1242.03, 1164.74. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{30}NO_3$: 332.22202, found 332.22282.

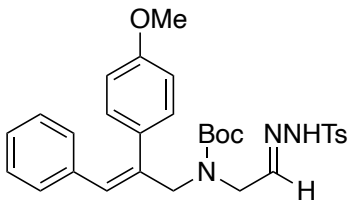
### 4.4.4 Characterization of Hydrozone Substrates

***tert*-butyl ((*E*)-2,3-diphenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1a)**



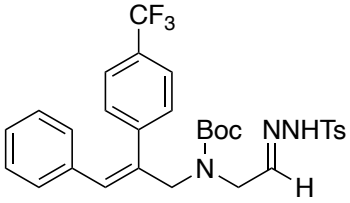

Colorless Oil. Yield: 85%. $R_f$ = 0.35 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.86 – 7.55 (m, 3H), 7.38 – 7.19 (m, 5H), 7.19 – 7.04 (m, 5H), 7.01 – 6.71 (m, 3H), 6.40 (s, 1H), 4.29 – 3.71 (m, 4H), 2.39 (s, 3H), 1.33 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 160.84, 156.08, 147.14, 144.41, 143.28, 137.82, 137.61, 136.30, 135.37, 129.26, 129.00, 128.72, 128.20, 128.10, 127.62, 127.07, 80.60, 76.91, 57.36, 42.87, 28.33, 21.71. IR (neat, $cm^{-1}$): 3055.64, 2976.26, 2929.87, 1691.53, 1663.76, 1454.80, 1247.97, 1165.24. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{29}H_{34}N_3O_4S$: 520.22645, found 520.22641.

***tert*-Butyl ((*E*)-2-(4-methoxyphenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1b)**



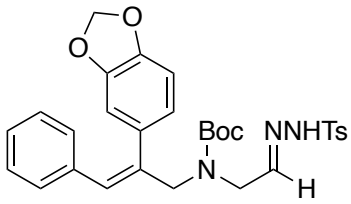

Colorless Oil. Yield: 71%. $R_f$ = 0.24 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.84 – 7.60 (m, 3H), 7.45 – 7.16 (m, 4H), 7.16 – 6.51 (m, 8H), 6.32 (s, 1H), 4.24 – 3.60 (m, 7H), 2.39 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 158.62, 155.52, 148.29, 147.25, 144.34, 143.56, 135.37, 130.52, 129.77, 129.02, 128.92, 128.42, 128.03, 127.47, 126.58, 113.56, 80.49, 63.44, 55.29, 42.68, 28.29, 21.68. IR (neat, $cm^{-1}$): 3199.25, 2970.17, 2931.82, 1738.42, 1690.21, 1510.63, 1366.07, 1165.21. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{30}H_{36}N_3O_5S$: 550.23702, found 550.23322.

***tert*-Butyl ((*E*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1c)**




Colorless Oil. Yield: 76%. $R_f$ = 0.30 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.92 – 8.22 (m, 1H), 7.98 – 7.41 (m, 4H), 7.34 – 7.01 (m, 7H), 6.88 (d, *J* = 12.9 Hz, 2H), 6.48 (s, 1H), 4.28 – 3.77 (m, 4H), 2.37 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.22, 146.46, 143.06 (q, *J* = 100.4Hz), 136.24, 133.24, 130.68, 129.76, 129.55, 129.29, 128.59 (q, *J* = 258.6 Hz), 128.27, 127.43, 126.50, 125.69, 122.75, 80.76, 54.23, 42.98, 28.18, 21.63. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.53. IR (neat, cm$^{-1}$): 3191.70, 2978.31, 2930.96, 1667.15, 1454.34, 1322.65, 1125.25, 1067.90. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{30}H_{32}N_3O_4SF_3Na$: 610.196333, found 610.193787

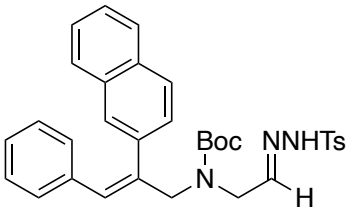
***tert*-Butyl ((*E*)-2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1d)**




Colorless Oil. Yield: 88%. $R_f$ = 0.20 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.46 (d, *J* = 913.0 Hz, 1H), 7.78 (dd, *J* = 8.1, 4.1 Hz, 2H), 7.23 – 6.87 (m, 7H), 6.80 – 6.44 (m, 4H), 6.33 (s, 1H), 5.94 (s, 2H), 4.21 – 3.67 (m, 4H), 2.38 (s, 3H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 155.43, 146.96, 144.24, 137.24, 137.05, 136.32, 135.88, 135.38, 132.13, 129.50, 129.23, 128.18, 128.10, 127.99, 127.00, 126.49, 122.32, 108.77, 101.14, 80.55, 54.70, 42.80, 28.28, 21.64. IR (neat, cm$^{-1}$): 3201.52, 2971.03, 2927.77, 1738.05, 1666.62,

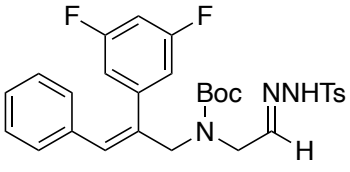
1488.69, 1448.92, 1236.81. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{30}H_{33}N_3O_6SNa$: 586.198779, found 586.199219.

***tert*-Butyl ((*E*)-2-(naphthalen-2-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1e)**




Colorless Oil. Yield: 76%. $R_f$ = 0.60 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.89 – 7.67 (m, 5H), 7.61 (s, 3H), 7.32 (dd, *J* = 8.6, 4.3 Hz, 1H), 7.25 – 6.77 (m, 8H), 6.50 (d, *J* = 43.6 Hz, 1H), 4.37 – 3.68 (m, 4H), 2.37 (s, 3H), 1.27 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 166.24, 156.43, 146.97, 144.31, 143.49, 137.34, 136.30, 135.79, 133.60, 132.78, 129.74, 129.51, 129.34, 128.64, 128.46, 128.23, 128.15, 127.99, 127.83, 127.46, 127.10, 126.24, 80.59, 54.87, 42.78, 28.25, 21.59. IR (neat, cm$^{-1}$): 3205.29, 3055.25, 2977.54, 1663.80, 1453.99, 1366.42, 1247.64, 1163.48. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{33}H_{35}N_3O_4SNa$: 592.224599, found 592.225098.

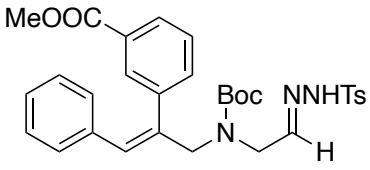
***tert*-Butyl ((*E*)-2-(3,5-difluorophenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1f)**




Colorless Oil. Yield: 76%. $R_f$ = 0.34 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.42 (d, *J* = 871.1 Hz, 1H), 7.79 (t, *J* = 8.2 Hz, 2H), 7.30 – 7.20 (m, 2H), 7.18 – 7.11 (m, 3H), 7.09 – 6.85 (m, 3H), 6.77 – 6.56 (m, 3H), 6.44 (s, 1H), 4.21 – 3.72 (m, 4H), 2.37 (s, 3H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 163.14 (d, *J* = 248.3 Hz), 155.03, 146.38, 144.40, 136.26 – 134.59 (m), 130.84, 129.78, 129.55, 129.25, 128.42, 128.33, 128.18, 128.02,

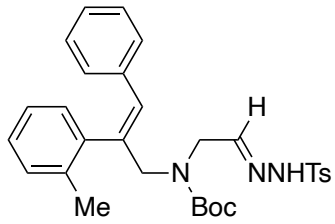
127.62, 111.88, 103.26 (d, $J$ = 24.5 Hz), 80.86, 53.95, 46.74, 28.22, 21.65. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -108.67, -109.08. IR (neat, $cm^{-1}$): 3084.95, 2978.21, 2929.69, 1667.25, 1618.51, 1587.32, 1246.24, 1162.13. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{29}H_{32}N_3O_4F_2S$: 556.20761, found 556.20855.

**Methyl 3-((*E*)-3-((*tert*-butoxycarbonyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g)**




Colorless Oil. Yield: 95%. $R_f$ = 0.50 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.79 – 7.60 (m, 5H), 7.37 – 7.30 (m, 1H), 7.27 – 7.18 (m, 3H), 7.14 – 7.06 (m, 3H), 6.96 – 6.75 (m, 3H), 6.47 (s, 1H), 4.58 – 3.51 (m, 7H), 2.38 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 167.00, 163.05, 155.34, 146.86, 144.41, 142.99, 138.52, 136.53, 135.42, 134.04, 130.74, 129.78, 129.54, 129.35, 129.08, 128.86, 128.33, 128.07, 127.31, 80.72, 56.83, 52.39, 42.63, 28.25, 21.69. IR (neat, $cm^{-1}$): 3186.38, 2970.19, 2951.00, 1722.82, 1698.46, 1366.38, 1266.66, 1165.07. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{31}H_{35}N_3O_6SNa$: 600.214429, found 600.215088.

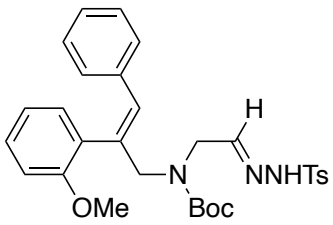
***tert*-Butyl ((*E*)-3-phenyl-2-(*o*-tolyl)allyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1h)**




Colorless Oil. Yield: 92%. $R_f$ = 0.23 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 10.99 – 7.53 (m, 3H), 7.39 – 7.29 (m, 1H), 7.25 – 7.16 (m, 4H), 7.15 – 7.02 (m, 3H), 6.95 – 6.63 (m, 4H), 6.38 (s, 1H), 4.57 – 2.93 (m, 4H), 2.41 (s, 3H), 2.07 (s, 3H), 1.31

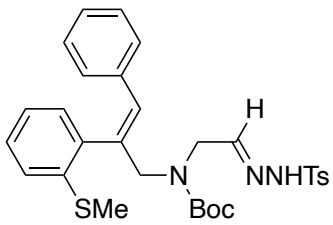
(s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 155.63, 152.99, 146.81, 143.17, 138.43, 136.66, 136.32, 135.60, 135.34, 130.55, 129.79, 128.91, 128.60, 128.34, 128.07, 127.53, 127.23, 126.59, 80.61, 54.70, 47.77, 28.11, 21.70, 19.22. IR (neat, $cm^{-1}$): 3200.45, 3064.31, 2976.24, 2926.12, 1689.10, 1664.04, 1454.92, 1163.06. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_4SNa$: 556.225098, found 556.224599.

***tert*-Butyl ((*E*)-2-(2-methoxyphenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1i)**




Colorless Oil. Yield: 87%. $R_f$ = 0.17 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.96 – 7.58 (m, 3H), 7.42 – 7.01 (m, 6H), 7.02 – 6.57 (m, 6H), 6.41 (d, *J* = 17.3 Hz, 1H), 4.30 – 3.45 (m, 7H), 2.38 (s, 3H), 1.28 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 157.23, 147.69, 143.92, 143.56, 136.18, 135.37, 134.97, 130.28, 129.75, 129.49, 129.00, 128.91, 128.78, 128.10, 127.25, 125.63, 121.14, 111.09, 80.25, 56.40, 55.45, 42.98, 28.10, 21.68. IR (neat, $cm^{-1}$): 3003.39, 2969.99, 2837.29, 1738.45, 1654.77, 1455.08, 1365.83, 1161.48. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_5SNa$: 572.219514, found 572.218201.

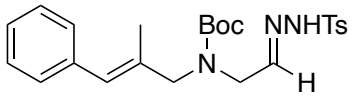
***tert*-Butyl ((*E*)-2-(2-(methylthio)phenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1j)**




Colorless Oil. Yield: 67%. $R_f$ = 0.17 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 11.13 – 7.62 (m, 3H), 7.35 – 7.15 (m, 3H), 7.17 – 7.04 (m, 4H), 7.03 – 6.70 (m,

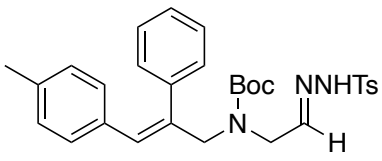
5H), 6.39 (s, 1H), 4.71 – 3.57 (m, 4H), 2.50 – 2.10 (m, 6H), 1.31 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 156.68, 155.04, 147.20, 143.61, 137.64, 137.38, 136.67, 136.19, 135.41, 129.74, 129.12, 128.72, 128.30, 128.12, 127.63, 125.44, 125.13, 123.22, 81.78, 56.00, 47.48, 28.23, 21.69, 15.23. IR (neat, $cm^{-1}$): 3054.84, 2970.13, 2924.96, 1738.50, 1685.16, 1455.15, 1365.73, 1160.64. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_4S_2Na$: 588.196671, found 588.197205.

***tert*-Butyl ((*E*)-2-methyl-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1m)**




Colorless Oil. Yield: 82%. $R_f$ = 0.38 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.85 – 7.75 (m, 2H), 7.39 – 7.29 (m, 2H), 7.29 – 7.16 (m, 5H), 7.16 – 6.74 (m, 1H), 6.24 (s, 1H), 4.12 – 3.55 (m, 4H), 2.39 (s, 3H), 1.71 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 156.76, 155.75, 146.89, 143.22, 137.44, 135.39, 133.79, 129.72, 128.94, 128.26, 128.01, 126.64, 80.60, 54.59, 47.08, 28.37, 21.66, 15.68. IR (neat, $cm^{-1}$): 3025.15, 2970.18, 2941.41, 1738.44, 1693.47, 1661.85, 1365.78, 1161.69. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{32}N_3O_4S$: 458.21080, found 458.21055.

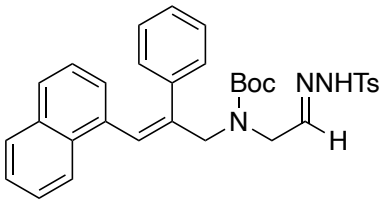
***tert*-Butyl ((*E*)-2-phenyl-3-(*p*-tolyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1n)**




Colorless Oil. Yield: 84%. $R_f$ = 0.67 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.95 – 7.52 (m, 3H), 7.40 – 7.18 (m, 4H), 7.18 – 7.00 (m, 3H), 6.96 – 6.65 (m, 5H), 6.35 (s, 1H),

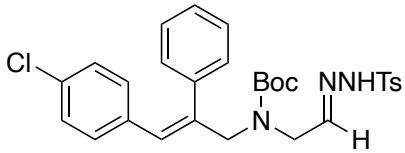
4.36 – 3.55 (m, 4H), 2.38 (s, 3H), 2.23 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 166.90,162.53, 147.20, 144.42, 138.62, 136.89, 135.35, 133.55, 132.50, 129.79, 129.50, 129.18, 128.90, 128.61, 128.07, 127.51, 80.53, 57.42, 42.79, 28.31, 21.70, 21.25. IR (neat, $cm^{-1}$): 2976.96, 2925.08, 1689.35, 1664.63, 1454.65, 1247.40, 1162.95, 1094.04. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_4SNa$: 556.224599, found 556.225281.

***tert*-Butyl ((*E*)-3-(naphthalen-1-yl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1o)**




Colorless Oil. Yield: 77%. $R_f$ = 0.59 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 10.71 – 7.92 (m, 2H), 7.87 – 7.34 (m, 6H), 7.19 – 6.74 (m, 10H), 4.76 – 3.55 (m, 4H), 2.39 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 156.50, 155.40, 144.35, 143.59, 139.40, 135.34, 134.28, 133.48, 132.25, 129.74, 129.00, 128.55, 128.23, 127.98, 127.71, 127.35, 126.66, 126.33, 125.98, 125.31, 124.77, 124.20, 80.76, 53.47, 46.84, 28.35, 21.59. IR (neat, $cm^{-1}$): 2970.30, 2930.01, 1738.34, 1685.20, 1366.35, 1246.15, 1160.97, 905.37. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{33}H_{35}N_3O_4SNa$: 592.224599, found 592.225220.

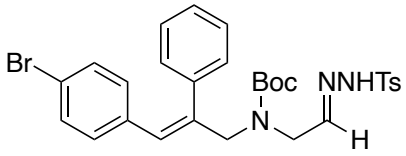
***tert*-Butyl ((*E*)-3-(4-chlorophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1p)**




Colorless Oil. Yield: 96%. $R_f$ = 0.59 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.66 – 7.58 (m, 3H), 7.42 – 7.15 (m, 6H), 7.12 – 6.66 (m, 6H), 6.31 (s, 1H), 4.35 – 3.11 (m, 4H), 2.38 (s, 3H), 1.29 (s, 9H). $^{13}$C

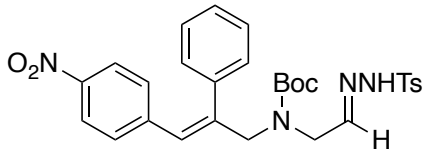
NMR (101 MHz, $CDCl_3$) δ 165.19, 155.88, 155.40, 146.91, 144.69, 144.02, 138.42, 135.19, 132.84, 130.49, 129.79, 129.03, 128.76, 128.31, 128.02, 127.79, 80.61, 56.22, 46.19, 28.27, 21.68. IR (neat, $cm^{-1}$): 3217.16, 2977.42, 2927.96, 1668.82, 1366.57, 1247.77, 1159.57, 1091.49. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{29}H_{32}N_3O_4SClNa$: 576.169977, found 576.170471.

***tert*-Butyl ((*E*)-3-(4-bromophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1q)**




Colorless Oil. Yield: 86%. $R_f$ = 0.37 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$) δ 11.03 – 7.51 (m, 3H), 7.43 – 7.14 (m, 7H), 7.14 – 6.69 (m, 5H), 6.32 (s, 1H), 4.59 – 3.53 (m, 4H), 2.41 (s, 3H), 1.33 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 156.44, 155.42, 146.89, 144.36, 138.61, 135.34, 131.76, 131.24, 130.76, 129.77, 129.48, 129.00, 128.76, 128.01, 127.84, 120.93, 80.66, 54.82, 43.01, 28.30, 21.70. IR (neat, $cm^{-1}$): 3194.75, 2976.98, 2928.60, 1690.35, 1366.47, 1247.41, 1163.18, 1009.45. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{29}H_{32}N_3O_4SBrNa$: 620.119460, found 620.119080.

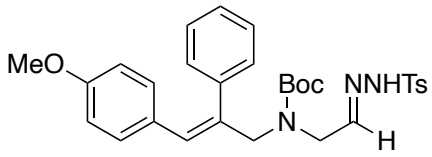
***tert*-Butyl ((*E*)-3-(4-nitrophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1r)**




Colorless Oil. Yield: 68%. $R_f$ = 0.52 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$) δ 10.61 – 7.69 (m, 5H), 7.39 – 7.16 (m, 5H), 7.14 – 6.68 (m, 5H), 4.26 – 3.59 (m, 4H), 2.39 (s, 3H), 1.33 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 159.59, 155.30, 146.54, 144.36,

142.46, 137.73, 135.39, 129.75, 129.55, 129.17, 128.68, 128.34, 127.96, 126.51, 125.78, 123.39, 80.84, 54.56, 47.51, 28.14, 21.66. IR (neat, $cm^{-1}$): 3188.97, 3020.66, 2976.72, 2929.48, 1671.03, 1594.77, 1515.04, 1340.05. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{29}H_{32}N_4O_6SNa$: 587.194028, found 587.194275.

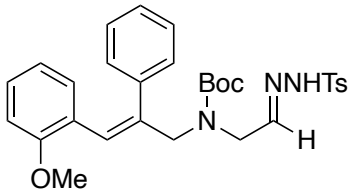
***tert*-Butyl ((*E*)-3-(4-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1s)**




Colorless Oil. Yield: 68%. $R_f$ = 0.23 (Hexane/EA: 121). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.74 – 7.48 (m, 2H), 7.39 – 7.18 (m, 5H), 7.17 – 6.97 (m, 3H), 6.94 – 6.53 (m, 5H), 6.32 (s, 1H), 4.38 – 3.49 (m, 7H), 2.39 (s, 3H), 1.31 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 158.60, 147.19, 143.53, 140.06, 139.10, 138.42, 135.38, 130.50, 129.75, 128.90, 128.02, 127.46, 126.56, 123.82, 113.96, 113.55, 80.46, 57.47, 55.28, 42.71, 28.28.

IR (neat, $cm^{-1}$): 2975.60, 2932.09, 1688.85, 1664.33, 1510.65, 1249.71, 1166.09, 1033.47. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_5SNa$: 572.219514, found 572.219116.

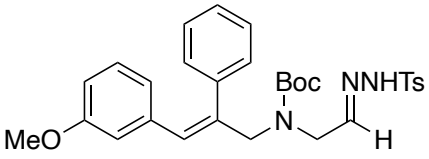
***tert*-Butyl ((*E*)-3-(2-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1t)**




Colorless Oil. Yield: 52%. $R_f$ = 0.61 (Hexane/EA: 1/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$) δ 9.88 – 7.50 (m, 1H), 7.33 – 7.07 (m, 12H), 6.89 (s, 1H), 6.85 – 6.71 (m, 2H), 4.52 – 3.91 (m, 2H), 3.91 (s, 3H), 3.85 – 2.95 (m, 2H), 2.32 – 1.94 (m, 3H), 1.54 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 156.75, 154.37, 147.99, 144.82, 142.98, 140.99, 131.69, 129.75, 128.46, 127.55, 125.93,

125.04, 120.32, 117.68, 116.89, 114.56, 112.26, 110.36, 79.77, 55.48, 50.45, 37.54, 32.97, 28.53. IR (neat, $cm^{-1}$): 3208.24, 2976.08, 1658.28, 1597.97, 1459.08, 1338.71, 1246.19, 1164.47. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_5SNa$: 572.219514, found 572.220520.

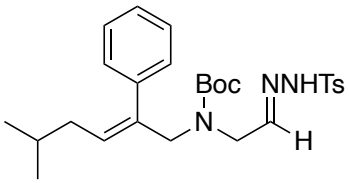
***tert*-Butyl ((*E*)-3-(3-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1u)**




Colorless Oil. Yield: 81%. $R_f$ = 0.42 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.92 – 7.55 (m, 3H), 7.43 – 7.15 (m, 5H), 7.13 – 6.71 (m, 4H), 6.72 – 6.22 (m, 4H), 4.33 – 3.58 (m, 4H), 3.47 (s, 3H), 2.37 (s, 3H), 1.30 (s, 9H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 159.13, 155.46, 146.97, 144.32, 143.48, 138.96, 137.96, 137.81, 137.07, 135.37, 129.75, 129.01, 128.88, 128.70, 127.99, 127.60, 122.15, 113.63, 80.58, 57.39, 54.88, 47.29, 28.26, 21.67. IR (neat, $cm^{-1}$): 3189.03, 2975.91, 2932.20, 1666.60, 1597.95, 1366.30.77, 1246.49, 1160.12. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{30}H_{35}N_3O_5SNa$: 572.219514, found 572.219727.

***tert*-Butyl ((*E*)-5-methyl-2-phenylhex-2-en-1-yl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1x)**

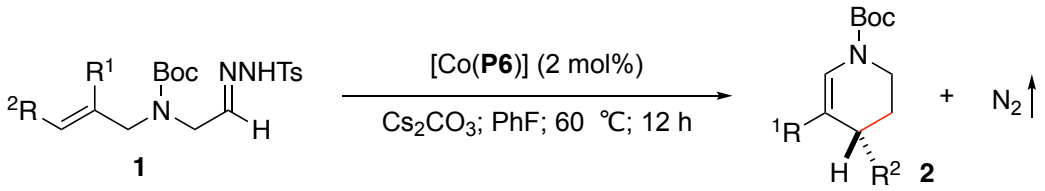



Colorless Oil. Yield: 75%. $R_f$ = 0.34 (Hexane/EA: 2/1). a mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$) δ 10.79 – 7.65 (m, 3H), 7.35 – 7.19 (m, 5H), 7.16 – 6.70 (m, 3H), 5.62 – 5.40 (m, 1H), 4.11 – 3.67 (m, 4H), 2.41 (s, 3H), 1.89 – 1.74 (m, 2H), 1.64 – 1.51 (m, 1H), 1.27 (s, 9H), 0.82 (d, $J$ = 6.4 Hz,

6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.41, 147.34, 143.62, 138.28, 136.96, 135.35, 129.71, 129.40, 128.93, 128.35, 128.05, 127.01, 80.29, 56.33, 46.84, 42.41, 37.67, 28.82, 28.05, 22.44. IR (neat, $cm^{-1}$): 3194.44, 2955.50, 2927.50, 2869.13, 1689.88, 1662.62, 1246.45, 1162.90. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{27}H_{37}N_3O_4SNa$: 522.240249, found 522.240601.

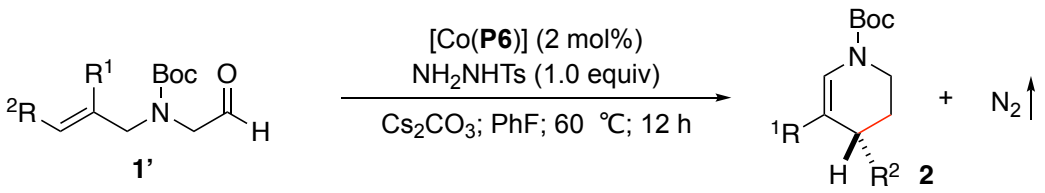
### 4.4.5 General Procedure for [Co(P6)]-Catalyzed Enantioselective Radical Cyclization

**General Procudure I:**




An oven-dried Schlenk tube was charged with hydrazone **1** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **2**.

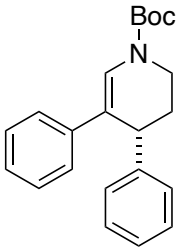
**General Procudure II:**



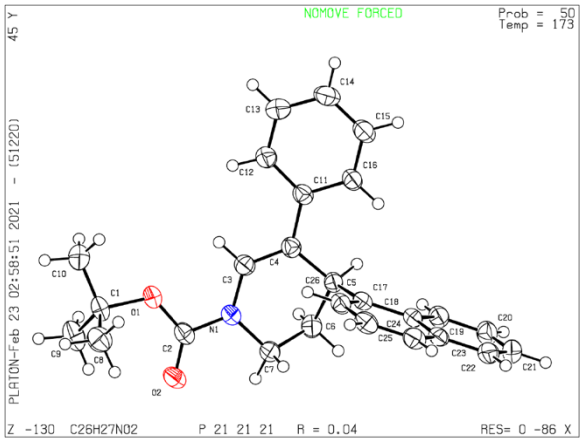
An oven-dried Schlenk tube was charged with aldehyde **1'** (0.1 mmol), $NH_2NHTs$ (0.1mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **2**.

### 4.4.6 Characterization of Tetrahydropyridine Products

***tert*-Butyl (*R*)-4,5-diphenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2a)**



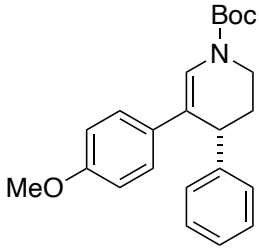

Following **general procedure I**. 95% yield; 99% ee. White solid. $R_f$ = 0.48 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = – 42.19° (*c* = 1.0, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.34 – 7.04 (m, 10H), 4.03 (dd, *J* = 5.4, 2.6 Hz, 1H), 3.88 (m, 1H), 3.07 (td, *J* = 12.9, 3.2 Hz, 1H), 2.21 (tt, *J* = 13.1, 4.7 Hz, 1H), 1.99 (t, *J* = 13.5 Hz, 1H), 1.58 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 152.87, 144.03, 139.81, 128.43, 128.35, 126.33, 125.84, 125.00, 124.78, 124.37, 116.64, 81.33, 39.66, 36.99, 30.43, 28.35. IR (neat, $cm^{-1}$): 3082.13, 2976.42, 2929.87, 1698.66, 1637.33, 1382.75, 1249.47, 1153.37. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{26}NO2^+$:



336.19581, found: 336.19559. HPLC analysis: *ee* = 99%. IA (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 6.74 min, $t_{minor}$ = 7.33 min.

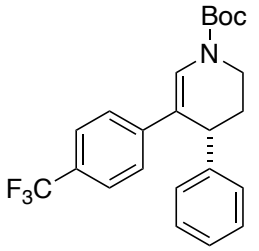
| Crystal data and structure refinement for **2a** | | |
|---|---|---|
| Identification code | C22H25NO2 | |
| Empirical formula | C22 H25 N O2 | |
| Formula weight | 335.43 | |
| Temperature | 173(2) K | |
| Wavelength | 1.54178 ≈ | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 5.9516(3) ≈ | α= 90∞. |
| | b = 16.6683(8) ≈ | β= 90∞. |
| | c = 37.8707(18) ≈ | γ = 90∞. |
| Volume | 3756.9(3) ≈$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.186 Mg/m$^3$ | |
| Absorption coefficient | 0.591 mm$^{-1}$ | |
| F(000) | 1440 | |
| Crystal size | 0.380 x 0.160 x 0.100 mm$^3$ | |
| Theta range for data collection | 2.333 to 66.838∞. | |
| Index ranges | 0<=h<=7, 0<=k<=19, 0<=l<=45 | |
| Reflections collected | 3953 | |
| Independent reflections | 3953 [R(int) = ?] | |
| Completeness to theta = 66.838∞ | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7528 and 0.5442 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3953 / 0 / 453 | |
| Goodness-of-fit on $F^2$ | 1.037 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0618, wR2 = 0.1490 | |
| R indices (all data) | R1 = 0.0762, wR2 = 0.1702 | |
| Extinction coefficient | 0.0075(8) | |
| Largest diff. peak and hole | 0.301 and -0.310 e.≈$^{-3}$ | |

***tert*-Butyl (*R*)-5-(4-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2b)**




Following **general procedure I**. 90% yield; 98% ee. Colorless oil. $R_f$ = 0.08 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –62.39° (*c* = 1.0, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.30 – 7.12 (m, 7H), 6.74 (t, *J* = 8.3 Hz, 2H), 3.97 (dd, *J* = 5.4, 2.5 Hz, 1H), 3.95 – 3.75 (m, 1H), 3.73 (s, 3H), 3.04 (td, *J* = 13.0, 3.2 Hz, 1H), 2.20 (tt, *J* = 13.2, 4.7 Hz, 1H), 1.98 (d, *J* = 11.9 Hz, 1H), 1.56 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.96, 157.84, 152.28, 144.11, 128.41, 128.26, 126.30, 126.12, 123.06, 116.21, 113.72, 80.96, 55.18, 39.49, 36.88, 30.48, 28.34. IR (neat, $cm^{-1}$): 3082.15, 2975.71, 2931.90, 1699.13, 1639.13, 1513.38, 1384.48, 1249.47. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_3^+$: 366.20637, found: 366.20601. HPLC analysis: *ee* = 98%. IA (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 15.27 min, $t_{minor}$ = 26.82 min.

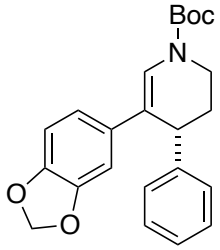
***tert*-Butyl (*R*)-4-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)**




Following **general procedure I**. 58% yield; 99% ee. Colorless oil. $R_f$ = 0.16 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –47.99° (*c* = 1.0, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.49 – 7.15 (m, 9H), 4.01 (dd, *J* = 5.3, 2.6 Hz, 1H), 3.89 (m, 1H), 3.07 (td, *J* = 12.9, 3.3 Hz, 1H), 2.21 (tt, *J* = 13.1, 4.7 Hz, 1H), 2.01 (s, 1H), 1.52 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.61, 152.78, 143.52, 143.04, 128.61, 128.09, 126.61, 126.17, 125.27, 124.62, 122.96, 115.23, 81.76, 39.13, 38.07, 30.34, 28.28. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.36. IR (neat, $cm^{-1}$):

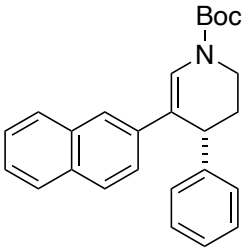
3061.00, 2931.27, 1705.62, 1637.49, 1610.24, 1322.85, 1250.49, 1156.79. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{24}NO_2F_3^+$: 403.17537, found: 403.17592. HPLC analysis: *ee* = 99%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 6.99 min, $t_{minor}$ = 7.36 min.

***tert*-butyl (*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2d)**




Following **general procedure I**. 69% yield; 98% ee. Colorless oil. $R_f$ = 0.13 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –86.19° (*c* = 1.0, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.12 (m, 3H), 6.83 – 6.76 (m, 1H), 6.76 – 6.59 (m, 1H), 6.64 (t, *J* = 9.5 Hz, 1H), 5.87 (s, 2H), 3.98 – 3.73 (m, 2H), 3.03 (td, *J* = 12.9, 3.2 Hz, 1H), 2.25 – 2.13 (m, 1H), 1.95 (t, *J* = 14.2 Hz, 1H), 1.56 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.39, 147.82, 145.92, 144.13, 134.49, 128.61, 128.38, 126.53, 124.22, 118.78, 116.60, 108.34, 105.75, 100.95, 81.45, 40.28, 38.09, 30.64, 28.47. IR (neat, cm$^{-1}$): 2975.82, 2885.83, 1700.73, 1641.23, 1490.97, 1387.72, 1222.93, 1162.42. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{26}NO_4^+$: 380.18563, found: 380.18427. HPLC analysis: *ee* = 98%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 24.82 min, $t_{minor}$ = 22.22 min.

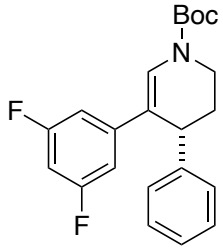
***tert*-Butyl (*R*)-5-(naphthalen-2-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2e)**




Following **general procedure I**. 45% yield; 97% ee. Colorless oil. $R_f$ = 0.16 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –9.99° (*c* = 1.0, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.76 – 7.48 (m, 5H), 7.41 – 7.26 (m,

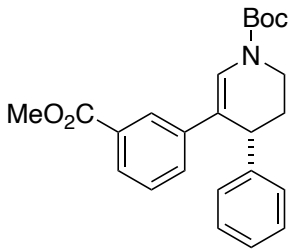
5H), 7.23 – 7.10 (m, 1H), 4.18 (dd, $J$ = 5.4, 2.6 Hz, 1H), 3.98 (d, $J$ = 13.3 Hz, 1H), 3.10 (td, $J$ = 12.9, 3.2 Hz, 1H), 2.27 (tt, $J$ = 13.0, 4.7 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.59 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.94, 151.72, 143.98, 137.02, 133.59, 131.91, 128.48, 128.24, 127.80, 127.72, 127.37, 126.38, 125.88, 125.04, 124.95, 123.49, 116.69, 81.47, 39.19, 38.12, 30.50, 28.32. IR (neat, $cm^{-1}$): 3016.23, 2970.17, 1738.24, 1686.47, 1366.94, 1216.00, 1156.11, 1124.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{28}NO_2^+$: 386.21146, found: 386.21161. HPLC analysis: *ee* = 97%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 18.03 min, $t_{minor}$ = 12.59 min.

***tert*-Butyl (*R*)-5-(3,5-difluorophenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2f)**



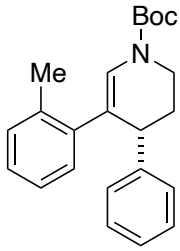

Following **general procedure I**. 88% yield; 98% ee. Colorless oil. $R_f$= 0.54 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –450.16° (*c* = 0.5, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.35 – 7.23 (m, 2H), 7.24 – 7.11 (m, 3H), 6.85 – 6.66 (m, 3H), 4.00 – 3.75 (m, 2H), 3.05 (td, $J$ = 12.9, 3.2 Hz, 1H), 2.26 – 2.10 (m, 1H), 2.05 – 1.87 (m, 1H), 1.52 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.01 (d, $J$ = 246.3 Hz), 164.24, 161.79, 143.29, 128.33 (d, $J$ = 59.7 Hz), 126.67, 126.43, 126.30, 114.59, 107.38 (m), 100.84 (m), 81.66, 39.14, 37.01, 30.25, 28.26. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -110.77. IR (neat, $cm^{-1}$): 3083.84, 2970.19, 2931.38, 1708.01, 1615.93, 1383.13, 1318.34, 1153.82. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{23}NO_2F_2^+$: 371.16914, found: 371.16979. HPLC analysis: *ee* = 98%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 7.55 min, $t_{minor}$ = 9.67 min.

***tert*-Butyl (*R*)-5-(3-(methoxycarbonyl)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2g)**




Following **general procedure I**. 40% yield; 95% ee. Colorless oil. $R_f$ = 0.26 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –78.400° (*c* = 0.5, $CHCl_3$). Mixture of amide rotamers. Chemical shift for major isomer was reported. $^1$H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.86 – 7.37 (m, 3H), 7.31 – 7.13 (m, 5H), 4.05 (dd, *J* = 5.4, 2.7 Hz, 1H), 3.86 (m, 4H), 3.08 (td, *J* = 12.9, 3.1 Hz, 1H), 2.21 (tt, *J* = 13.1, 4.7 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.54 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 167.32, 153.01, 143.79, 140.02, 130.35, 129.45, 128.65, 128.54, 128.36, 127.00, 126.62, 125.97, 125.41, 115.97, 81.51, 52.17, 39.37, 38.25, 30.61, 28.46. IR (neat, $cm^{-1}$): 2970.07, 2949.31, 1737.18, 1724.10, 1638.62, 1381.61, 1366.22, 1158.14. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{27}NO_4^+$: 393.19346, found: 393.19205. HPLC analysis: *ee* = 95%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 13.18 min, $t_{minor}$ = 5.97 min.

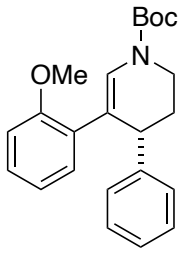
***tert*-Butyl (*R*)-4-phenyl-5-(o-tolyl)-3,4-dihydropyridine-1(2H)-carboxylate (2h)**




Following **general procedure I**. 88% yield; 95% ee. Colorless oil. $R_f$ = 0.36 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –80.988° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 5H), 7.12 – 6.95 (m, 4H), 3.91 – 3.74 (m, 2H), 3.36 (q, *J* = 15.0, 14.0 Hz, 1H), 2.38 (s, 3H), 2.32 – 2.22 (m, 1H), 2.01 – 1.87 (m, 1H), 1.53 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.50, 143.67, 140.58, 136.07, 130.39, 130.12, 128.57, 128.32, 126.60, 126.44, 126.04, 125.53, 117.93, 81.22, 77.41, 77.16, 76.91, 42.40, 37.80, 30.74, 28.53, 20.66. IR (neat, $cm^{-1}$): 3015.81, 2970.09, 2947.18, 1738.26, 1702.93, 1380.57, 1366.18, 1158.27. HRMS (DART) ($[M+H]^+$)

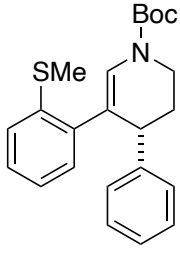
Calcd. for $C_{23}H_{28}NO_2^+$: 350.21146, found: 350.21170. HPLC analysis: *ee* = 95%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 5.08 min, $t_{minor}$ = 4.73 min.

***tert*-Butyl (*R*)-5-(2-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2i)**




Following **general procedure I**. 47% yield; 94% ee. Colorless oil. $R_f$ = 0.37 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –77.600° (*c* = 0.5, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.17 (dt, J = 14.7, 7.7 Hz, 4H), 7.08 (tdd, J = 12.8, 10.1, 6.7 Hz, 3H), 6.88 – 6.71 (m, 2H), 4.14 (t, J = 5.2 Hz, 1H), 3.81 – 3.66 (m, 4H), 3.37 – 3.27 (m, 1H), 2.28 – 2.21 (m, 1H), 1.95 – 1.86 (m, 1H), 1.50 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 157.27, 144.50, 130.39, 129.68, 128.16, 127.51, 126.76, 126.11, 120.64, 117.23, 116.56, 115.25, 110.74, 81.12, 55.41, 40.99, 38.21, 31.08, 28.52. IR (neat, $cm^{-1}$): 3058.12, 2975.16, 2932.32, 1697.46, 1643.26, 1382.94, 1366.31, 1247.33. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{28}NO_3^+$: 366.20637, found: 366.20479. HPLC analysis: *ee* = 98%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 8.20 min, $t_{minor}$ = 5.45 min.

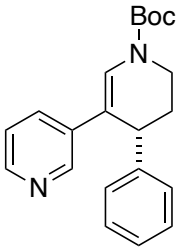
***tert*-Butyl (*R*)-5-(2-(methylthio)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2j)**




Following **general procedure I**. 63% yield; 99% ee. Colorless oil. $R_f$ = 0.39 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –29.200° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 4H), 7.22 – 7.07 (m, 4H), 7.06 – 7.02 (m, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 4.08 (s, 1H), 3.84 (dd, *J* = 47.5, 12.9 Hz, 1H), 3.34 – 3.23 (m, 1H), 2.45 (s, 3H), 2.39 – 2.25 (m, 1H), 2.01 – 1.87 (m, 1H), 1.52 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.47, 143.75, 139.77, 138.30, 130.39, 128.26,

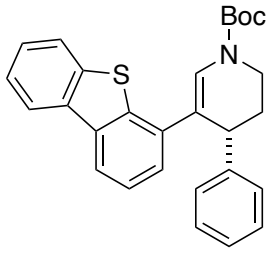
127.36, 127.01, 126.37, 125.14, 124.42, 119.77, 116.97, 81.29, 41.45, 37.65, 30.47, 28.51, 16.24.IR (neat, $cm^{-1}$): 2976.80, 2920.28, 1700.78, 1646.43, 1381.70, 1306.79, 1157.25, 1115.76. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_2S^+$: 382.18353, found: 382.18325. HPLC analysis: *ee* = 99%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 6.47 min, $t_{minor}$ = 8.10 min.

***tert*-Butyl (*R*)-4-phenyl-5,6-dihydro-[3,3'-bipyridine]-1(4*H*)-carboxylate (2k)**




Following **general procedure II**. 62% yield; 99% ee. Colorless oil. $R_f$ = 0.38 (Hexanes/EtOAc = 1/1). $[\alpha]_D^{20}$ = –272.42° (*c* = 0.5, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 8.60 – 8.53 (m, 1H), 8.30 (s, 1H), 7.57 (s, 1H), 7.56 – 7.42 (m, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 7.10 – 7.06 (m, 1H), 3.97 (dd, *J* = 5.3, 2.8 Hz, 1H), 3.95 – 3.78 (m, 1H), 3.09 (t, *J* = 12.8 Hz, 1H), 2.21 (dq, *J* = 12.5, 6.6, 4.8 Hz, 1H), 2.00 (d, *J* = 15.3 Hz, 1H), 1.55 (s, 9H). IR (neat, $cm^{-1}$): 3026.34, 2975.77, 2929.48, 1700.26, 1635.82, 1382.30, 1254.26, 1154.10. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{25}N_2O_2^+$: 337.19105, found: 337.19280. HPLC analysis: *ee* = 99%. ID (90% hexanes : 10% isopropanol, 0.8 mL/min): $t_{major}$ = 33.93 min, $t_{minor}$ = 39.26 min.

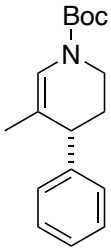
***tert*-Butyl (*R*)-5-(dibenzo[*b*,*d*]thiophen-4-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2l)**




Following **general procedure II**. 50% yield; 94% ee. Colorless oil. $R_f$ = 0.30 (Hexanes/EtOAc = 1/1). $[\alpha]_D^{20}$ = –272.42° (*c* = 0.5, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 8.13 – 7.81 (m, 4H), 7.45 (q, *J* = 7.0, 6.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 3H), 7.24 – 7.09 (m, 4H), 4.22 (t, *J* = 4.6 Hz, 1H), 3.91 (dd, *J* = 51.0, 13.0 Hz, 1H), 3.31 (td, *J* = 12.1, 3.3 Hz,

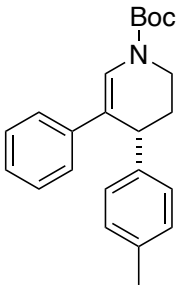
1H), 2.36 (ddd, $J$ = 12.9, 8.2, 4.8 Hz, 1H), 2.11 – 1.97 (m, 1H), 1.57 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.24, 143.80, 139.40, 138.04, 135.98, 128.19, 127.70, 127.40, 126.60, 126.39, 125.63, 124.70, 124.30, 122.51, 121.57, 119.43, 117.16, 116.64, 81.45, 41.12, 37.56, 30.94, 28.38. IR (neat, $cm^{-1}$): 3061.53, 2975.61, 2927.70, 1700.46, 1638.58, 1442.25, 1379.03, 1155.85. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{28}NO_2S^+$: 442.18353, found: 442.18231. HPLC analysis: *ee* = 94%. IA (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 5.79 min, $t_{minor}$ = 2.89 min.

***tert*-Butyl (*R*)-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2m)**




Following **general procedure I**. 50% yield; 97% ee. Colorless oil. $R_f$ = 0.22 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –85.99° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, $J$ = 7.6 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.17 (d, $J$ = 7.6 Hz, 2H), 6.76 (s, 1H), 3.66 (dd, $J$ = 11.7, 6.5 Hz, 1H), 3.28 (t, $J$ = 5.2 Hz, 1H), 3.25 – 3.16 (m, 1H), 2.14 – 2.04 (m, 1H), 1.83 – 1.74 (m, 1H), 1.55 (s, 3H), 1.51 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.86, 146.65, 138.38, 131.02, 128.97, 125.04, 116.62, 83.19, 45.45, 40.16, 33.60, 31.06, 22.48. IR (neat, $cm^{-1}$): 3060.83, 2975.01, 2929.41, 1697.60, 1670.71, 1392.74, 1366.49, 1157.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{24}NO_2^+$: 274.18016, found: 274.18103. HPLC analysis: *ee* = 98%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 7.09 min, $t_{minor}$ = 7.66 min.

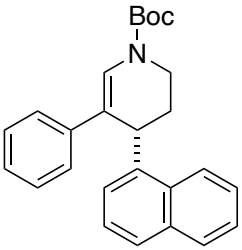
***tert*-Butyl (*R*)-5-phenyl-4-(*p*-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2n)**



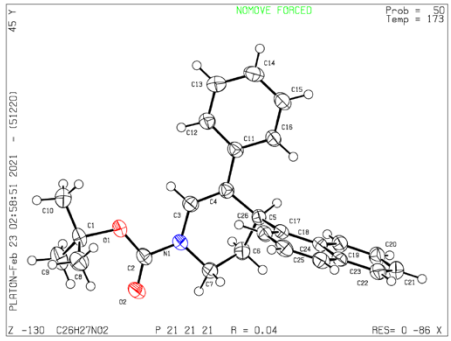

Following **general procedure I**. 90% yield; 94% ee. Colorless oil. $R_f$ = 0.43 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –443.10° ($c$ = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 2H), 7.12 – 7.04 (m, 5H), 3.97 (t, $J$ = 3.8 Hz, 1H), 3.79 (d, $J$ = 12.9 Hz,

1H), 3.05 (td, $J$ = 13.0, 3.2 Hz, 1H), 2.29 (s, 3H), 2.22 – 2.14 (m, 1H), 1.99 – 1.90 (m, 1H), 1.56 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.94, 143.69, 142.56, 138.48, 131.80, 131.01, 130.77, 128.47, 127.67, 127.34, 119.31, 83.94, 41.94, 40.71, 33.16, 31.03, 23.63. IR (neat, cm$^{-1}$): 2976.40, 2926.56, 1701.95, 1638.78, 1384.21, 1367.85, 1250.51, 1157.94. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{28}NO_2^+$: 350.21146, found: 350.21091. HPLC analysis: *ee* = 94%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 12.53 min, $t_{minor}$ = 6.16 min.

***tert*-Butyl (*R*)-4-(naphthalen-1-yl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2o)**



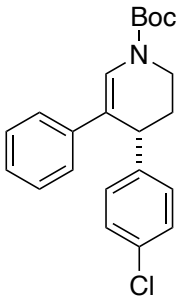

Following **general procedure I**. 96% yield; 94% ee. White Solid. $R_f$ = 0.14 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –77.185° (*c* = 1.0, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, $J$ = 8.5 Hz, 1H), 7.95 (s, 1H), 7.91 (d, $J$ = 8.2 Hz, 1H), 7.72 (t, $J$ = 4.6 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.53 (t, $J$ = 7.4 Hz, 1H), 7.38 – 7.26 (m, 4H), 7.22 – 7.02 (m, 3H), 4.83 (s, 1H), 3.90 (dd, $J$ = 59.8, 13.2 Hz, 1H), 3.01 (t, $J$ = 14.6 Hz, 1H), 2.30 (tt, $J$ = 13.1, 4.8 Hz, 1H), 2.20 – 2.07 (m, 1H), 1.60 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.44, 139.73, 138.78, 134.50, 130.93, 129.40, 128.49, 127.37, 126.66, 126.37, 125.92, 125.63, 125.50, 125.03, 124.92, 123.00, 116.38, 81.34, 37.44, 35.52, 29.86, 28.41. IR (neat, cm$^{-1}$): 3057.51, 2976.30, 2930.50, 1698.30, 1639.22, 1596.60, 1383.92, 1117.44. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{27}NO_2^+$: 385.20363, found: 385.20462. HPLC



analysis: *ee* = 94%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 10.03 min, $t_{minor}$ = 11.27 min.

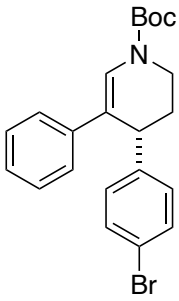
| Crystal data and structure refinement for **2o** | | |
|---|---|---|
| Identification code | C26H27NO2 | |
| Empirical formula | C26 H27 N O2 | |
| Formula weight | 385.48 | |
| Temperature | 173(2) K | |
| Wavelength | 1.54178 ≈ | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 6.5687(5) ≈ | a= 90∞. |
| | b = 14.1677(10) ≈ | b= 90∞. |
| | c = 22.4156(15) ≈ | g = 90∞. |
| Volume | 2086.1(3) $≈^3$ | |
| Z | 4 | |
| Density (calculated) | 1.227 $Mg/m^3$ | |
| Absorption coefficient | 0.601 $mm^{-1}$ | |
| F(000) | 824 | |
| Crystal size | 0.380 x 0.120 x 0.080 $mm^3$ | |
| Theta range for data collection | 3.691 to 66.675∞. | |
| Index ranges | -7<=h<=7, -16<=k<=16, -26<=l<=26 | |
| Reflections collected | 45805 | |
| Independent reflections | 3667 [R(int) = 0.0991] | |
| Completeness to theta = 66.675∞ | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7528 and 0.6672 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3667 / 0 / 266 | |
| Goodness-of-fit on $F^2$ | 1.087 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0420, wR2 = 0.0939 | |
| R indices (all data) | R1 = 0.0512, wR2 = 0.0982 | |
| Absolute structure parameter | 0.11(15) | |
| Extinction coefficient | 0.0036(4) | |
| Largest diff. peak and hole | 0.164 and -0.156 $e.≈^{-3}$ | |

***tert*-Butyl (*R*)-4-(4-chlorophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2p)**




Following **general procedure I**. 23% yield; 92% ee. Colorless Oil. $R_f$ = 0.20 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –80.789° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.25 – 7.15 (m, 8H), 7.15 – 7.05 (m, 1H), 4.00 (dd, *J* = 5.4, 2.7 Hz, 1H), 3.88 (dd, *J* = 49.9, 13.0 Hz, 1H), 3.02 (td, *J* = 12.9, 3.2 Hz, 1H), 2.21 (tt, *J* = 13.1, 4.7 Hz, 1H), 1.95 (s, 1H), 1.56 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 152.34, 142.73, 139.35, 132.29, 129.74, 128.77, 128.56, 126.15, 125.21, 124.88, 116.17, 81.47, 39.26, 37.06, 30.54, 28.47. IR (neat, $cm^{-1}$): 2977.92, 2929.98, 1694.89, 1637.67, 1488.19, 1383.99, 1367.52, 1154.78. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{24}NO_2Cl^+$: 369.14901, found: 369.14880. HPLC analysis: *ee* = 92%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 18.08 min, $t_{minor}$ = 5.91 min.

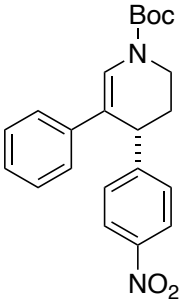
***tert*-Butyl (*R*)-4-(4-bromophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2q)**




Following **general procedure I**. 80% yield; 97% ee. Colorless Oil. $R_f$ = 0.20 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –67.589° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 17.6 Hz, 4H), 7.15 – 7.07 (m, 3H), 3.98 (dd, *J* = 5.5, 2.7 Hz, 1H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.02 (td, *J* = 12.9, 3.2 Hz, 1H), 2.27 – 2.16 (m, 1H), 1.95 (d, *J* = 13.5 Hz, 1H), 1.56 (s, 9H). $^{13}C$ NMR (151 MHz, , $CDCl_3$) δ 152.15, 143.12, 139.45, 131.56, 129.99, 128.44, 125.89, 124.71, 124.65, 120.22, 115.90, 81.49, 39.16,

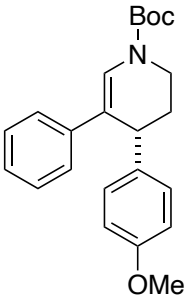
36.88, 30.32, 28.33. IR (neat, $cm^{-1}$): 2976.10, 1698.09, 1636.88, 1484.35, 1382.21, 1336.18, 1249.38, 1153.66. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{25}NO_2Br^+$: 414.10632, found: 414.10507. HPLC analysis: *ee* = 97%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 18.52 min, $t_{minor}$ = 1.79 min.

***tert*-Butyl (*R*)-4-(4-nitrophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2r)**




Following **general procedure I**. 30% yield; 92% ee. Colorless Oil. $R_f$ = 0.08 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –61.189° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 1H), 7.44 – 7.35 (m, 2H), 7.24 – 7.17 (m, 4H), 7.13 – 7.06 (m, 1H), 4.14 (d, *J* = 4.3 Hz, 1H), 3.89 (dd, *J* = 69.5, 13.1 Hz, 1H), 3.02 (td, *J* = 12.8, 3.2 Hz, 1H), 2.34 – 2.24 (m, 1H), 2.04 – 1.95 (m, 1H), 1.56 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 152.80, 152.06, 146.86, 139.16, 129.24, 128.72, 126.42, 125.80, 125.08, 123.96, 115.43, 81.75, 39.82, 38.13, 30.43, 28.45. IR (neat, $cm^{-1}$): 2969.99, 2942.32, 1738.47, 1519.20, 1365.95, 1346.47, 1228.67, 1158.08. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{24}N_2O_4^+$: 380.17306, found: 380.17199. HPLC analysis: *ee* = 92%. IB (80% hexanes : 20% isopropanol, 0.8 mL/min): $t_{major}$ = 13.48 min, $t_{minor}$ = 6.66 min.

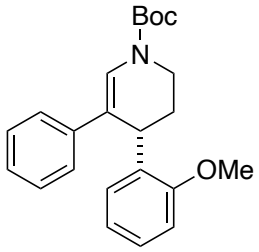
***tert*-Butyl (*R*)-4-(4-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2s)**




Following **general procedure I**. 70% yield; 94% ee. Colorless Oil. $R_f$ = 0.50 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –485.42° (*c* = 0.5, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 2H), 7.14 – 7.04 (m, 5H), 4.00 – 3.96 (m, 1H), 3.94 – 3.77 (m, 1H), 3.05 (td, *J* = 13.0, 3.2 Hz, 1H), 2.29 (s, 3H), 2.21 – 2.14 (m, 1H), 1.99 –

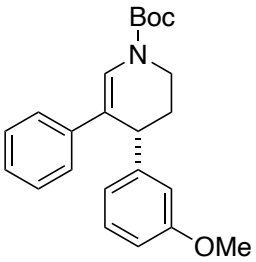
1.90 (m, 1H), 1.56 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.65, 152.41, 141.18, 140.05, 135.97, 129.29, 128.49, 125.83, 125.15, 124.84, 116.80, 81.22, 39.43, 38.19, 30.66, 28.51, 21.12. IR (neat, $cm^{-1}$): 2975.97, 2931.36, 2834.80, 1699.83, 1638.00, 1508.36, 1383.54, 1156.89. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_3^+$: 366.20637, found: 366.20568. HPLC analysis: *ee* = 94%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 13.72 min, $t_{minor}$ = 7.96 min.

***tert*-Butyl (*R*)-4-(2-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2t)**



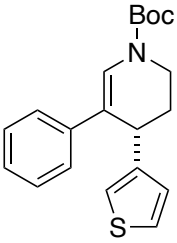

Following **general procedure I**. 50% yield; 95% ee. Colorless Oil. $R_f$ = 0.43 (Hexanes/EtOAc = 20/1). $[\alpha]_D^{20}$ = –415.09° (*c* = 0.5, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.33 – 7.24 (m, 2H), 7.23 – 7.12 (m, 3H), 7.11 – 7.03 (m, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.76 (m, 1H), 4.43 (s, 1H), 3.91 (s, 3H), 3.98 – 3.74 (m, 1H), 3.08 – 2.95 (m, 1H), 2.15 – 1.95 (m, 2H), 1.57 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.75, 147.07, 142.98, 131.69, 129.82, 128.46, 127.55, 125.84, 124.85, 120.32, 116.89, 112.23, 110.36, 81.34, 55.48, 37.54, 32.97, 28.53, 27.90. IR (neat, $cm^{-1}$): 2975.44, 2933.21, 2836.51, 1786.24, 1700.97, 1639.24, 1384.66, 1158.35. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_3^+$: 366.20637, found: 366.20610. HPLC analysis: *ee* = 95%. IB (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 6.07 min, $t_{minor}$ = 5.34 min.

***tert*-Butyl (*R*)-4-(3-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2u)**



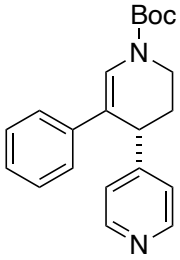

Following **general procedure I**. 51% yield; 93% ee. Colorless Oil. $R_f$ = 0.35 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –52.000° (*c* = 0.1, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 7.10 (d, *J* = 9.2 Hz, 1H), 6.90 – 6.70 (m, 3H), 4.04 – 3.80 (m, 2H), 3.77 (s, 3H), 3.09 (s, 1H), 2.20 (tt, *J* = 13.1, 4.6 Hz, 1H), 1.99 (t, *J* = 14.4 Hz, 1H), 1.55 (d, *J* = 21.1 Hz, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 159.83, 153.02, 145.99, 140.00, 129.54, 128.50, 126.00, 124.96, 124.56, 120.89, 116.53, 114.65, 111.36, 81.49, 55.29, 39.53, 37.24, 30.50, 28.50. IR (neat, $cm^{-1}$): 2975.18, 2931.86, 2834.31, 1701.66, 1638.07, 1597.47, 1484.11, 1384.04. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{28}NO_3^+$: 366.20637, found: 366.20513. HPLC analysis: *ee* = 93%. IB (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 10.29 min, $t_{minor}$ = 6.11 min.

***tert*-Butyl (*S*)-5-phenyl-4-(thiophen-3-yl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2v)**



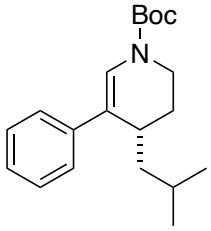

Following **general procedure II**. 50% yield; 98% ee. Colorless Oil. $R_f$ = 0.47 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –540.62° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.35 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.06 (m, 1H), 6.97 (s, 1H), 6.93 – 6.88 (m, 1H), 4.06 (s, 1H), 3.90 (dd, *J* = 77.5, 12.9 Hz, 1H), 3.04 (q, *J* = 12.4, 11.9 Hz, 1H), 2.16 – 1.96 (m, 2H), 1.54 (s, 9H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 152.36, 145.01, 139.67, 128.49, 127.54, 126.09, 125.87, 124.84, 123.77, 122.29, 117.45, 81.49, 37.44, 35.35, 29.56, 28.50. IR (neat, $cm^{-1}$): 3100.65, 2975.56, 2928.27, 2885.76, 1699.35, 1637.41, 1382.82, 1156.03. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_2S^+$: 342.15223, found: 342.15068. HPLC analysis: *ee* = 99%. IA (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 6.28 min, $t_{minor}$ = 6.93 min.

***tert*-Butyl (*R*)-5-phenyl-3,4-dihydro-[4,4'-bipyridine]-1(2*H*)-carboxylate (2w)**




Following **general procedure II**. 82% yield; 97% ee. Colorless Oil. $R_f$= 0.25 (Hexanes/EtOAc = 1/1). $[\alpha]_D^{20}$ = –332.86° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.51 – 8.46 (m, 2H), 7.55 (s, 1H), 7.23 – 7.14 (m, 6H), 7.13 – 7.06 (m, 1H), 4.00 (dd, *J* = 5.5, 2.8 Hz, 1H), 3.97 – 3.78 (m, 1H), 2.99 (td, *J* = 12.9, 3.2 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.02 – 1.91 (m, 1H), 1.55 (s, 9H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 153.36, 152.23, 150.06, 138.96, 128.67, 126.34, 125.72, 125.03, 123.74, 114.97, 81.81, 39.34, 37.09, 29.95, 28.45**.** IR (neat, $cm^{-1}$): 2976.45, 1701.85, 1638.62, 1596.12, 1385.34, 1368.26, 1251.31, 1157.67. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{25}N_2O_2^+$: 337.19105, found: 337.19090. HPLC analysis: *ee* = 97%. ODH (80% hexanes : 20% isopropanol, 0.8 mL/min): $t_{major}$ = 18.12 min, $t_{minor}$ = 9.03 min.

***tert*-Butyl (*S*)-4-isobutyl-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2x)**




Following **general procedure I**. 66% yield; 51% ee. Colorless Oil. $R_f$= 0.57 (Hexanes/EtOAc = 8/1). $[\alpha]_D^{20}$ = –338.72° (*c* = 1.0, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.24 – 7.14 (m, 1H), 7.05 (s, 1H), 3.91 (dd, *J* = 70.9, 12.7 Hz, 1H), 3.33 – 3.17 (m, 1H), 2.83 (d, *J* = 8.0 Hz, 1H), 1.97 – 1.81 (m, 2H), 1.73 – 1.58 (m, 1H), 1.52 (s, 9H), 1.23 – 1.15 (m, 2H), 0.90 (dd, *J* = 10.2, 6.4 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (151 MHz, $cdcl_3$) δ 152.51, 140.46, 128.58, 126.19, 125.83, 123.09, 122.02, 81.10, 42.55, 37.54, 30.50, 28.50, 25.26, 24.06, 21.38. IR (neat, $cm^{-1}$): 2954.10, 2927.98, 2869.09, 1703.43, 1639.59, 1385.80, 1317.96, 1162.27. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{29}NO_2^+$: 315.21928, found: 315.22027. HPLC analysis: *ee* = 51%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 10.04 min, $t_{minor}$ = 12.90 min.

### 4.4.7 Mechanistic Studies

#### 4.4.7.1 DFT Calculations

All DFT calculations were performed using the Gaussian 16 C.01 program package. For geometry optimization, the BP86 functional and the Lanl2dz basis set were used. Vibration frequencies were computed for optimized structures to characterize the stationary points as either equilibrium geometries (zero imaginary frequency) or saddle points (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed with local quadratic approximation (LQA) method to ensure the TS found connected the reactant and the product. Subsequent calculations of the solvent effect were conducted with the SMD model and def2-TZVP basis set using gas phase optimized structures. The software built-in chlorobenzene was used in the solvent model to best simulate the fluorobenzene that was used in the experiments. The energies reported in this paper are relative Gibbs free energies calculated at 298 K in solution and in the gas phase.

Independent Gradient Model (IGM) analysis was performed with Multiwfn software package using high quality grid option to generate files for further plotting. The visualization of IGM analysis results were presented with VMD visualization software and rendered with Tachyon17. As shown the 3D diagrams of optimized structures were generated with CYLview software, and the NCI (noncovalent interaction) visual representations of optimized structures were generated with VMD.

**Figure 4.2. Free-Energy Profile of Overall Reaction with [Co(P6)]**

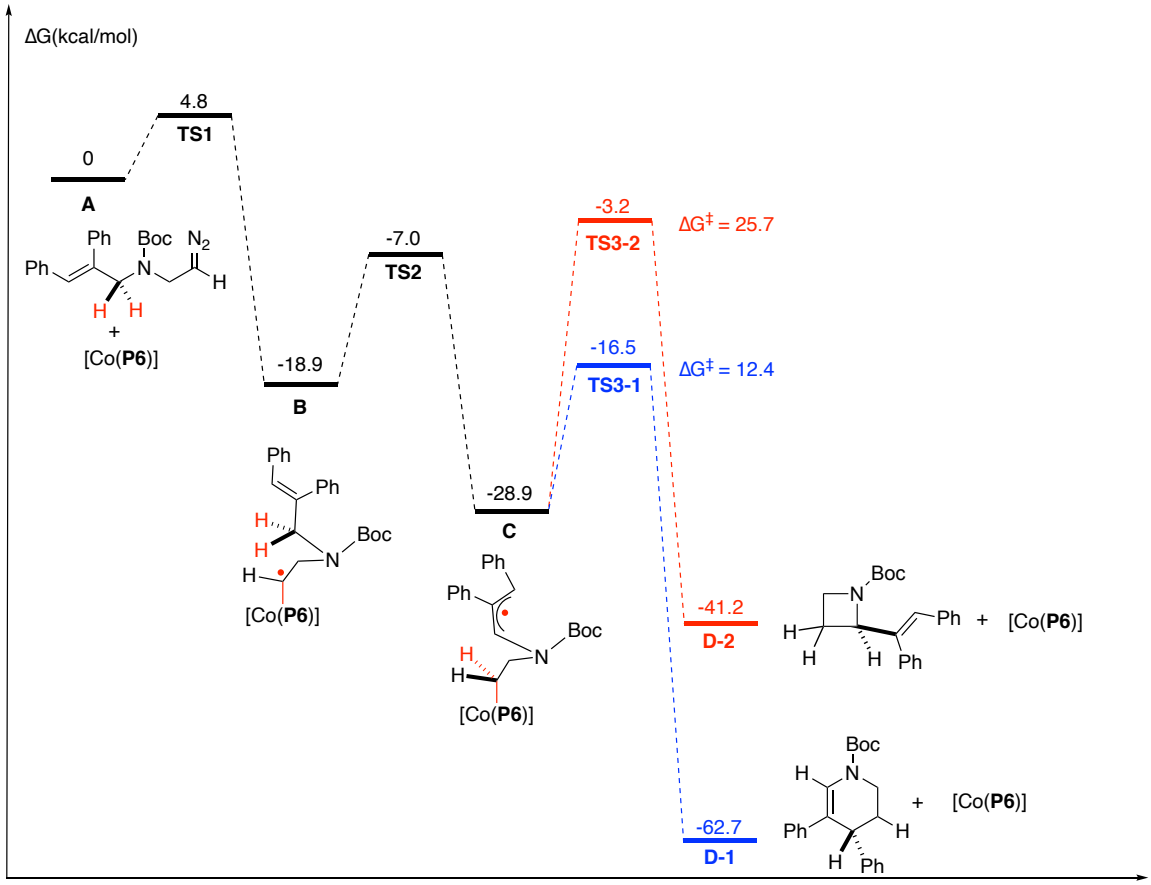
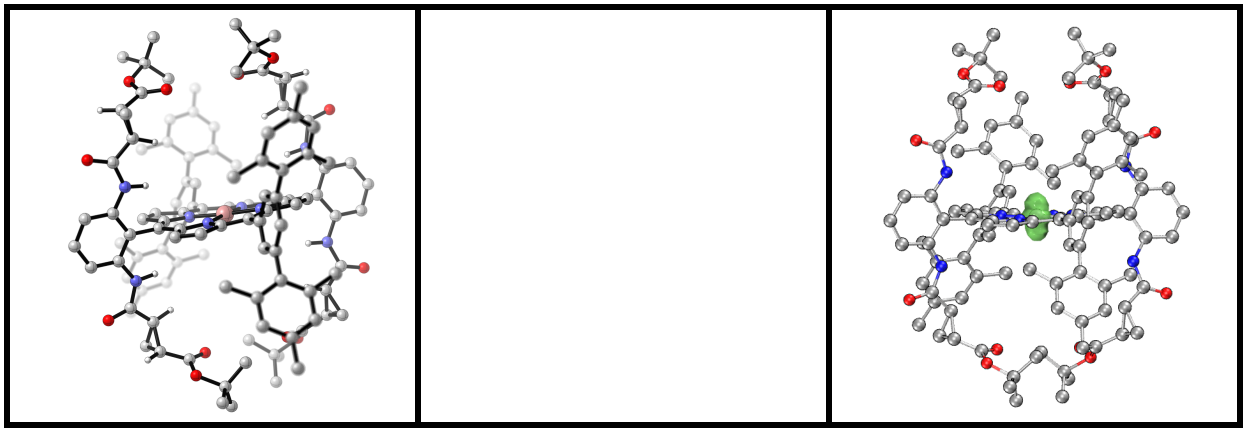
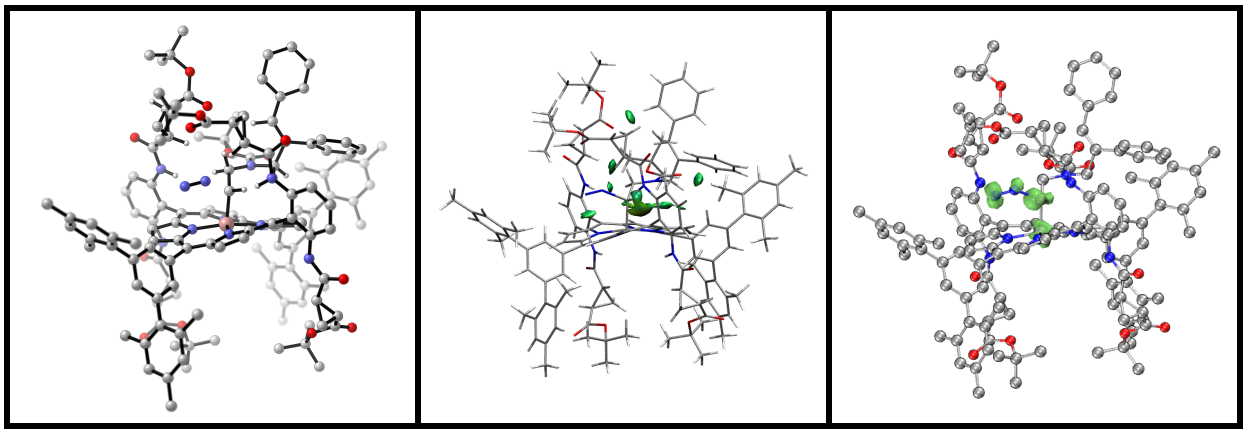


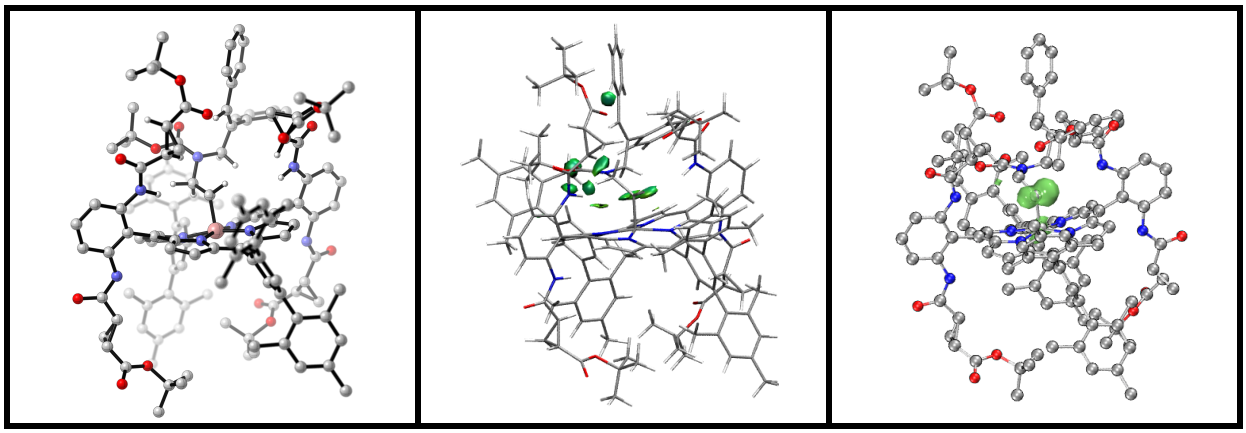
**Figure 4.3. NCI Plot and Spin Density Graph for Each intermediates and Transition States**



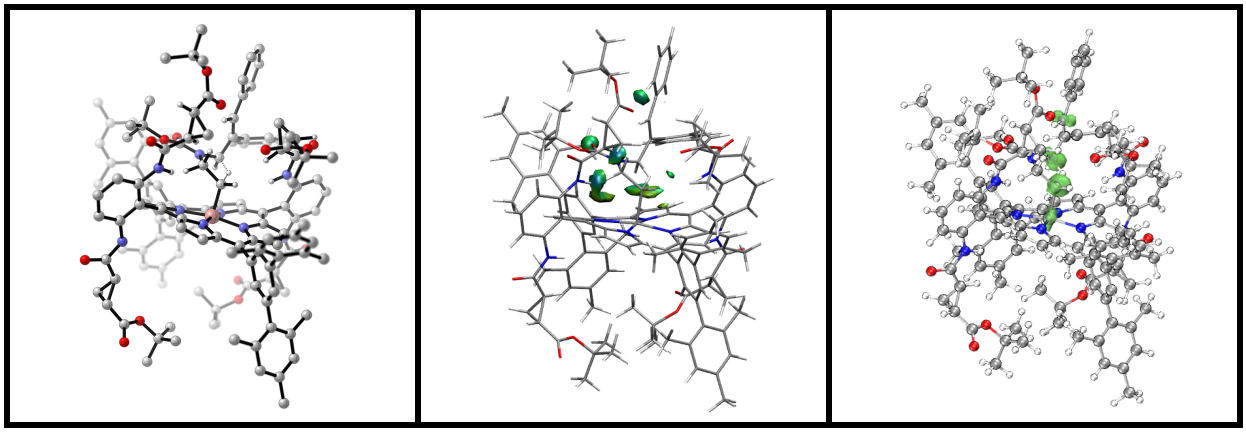
[Co(**P6**)]



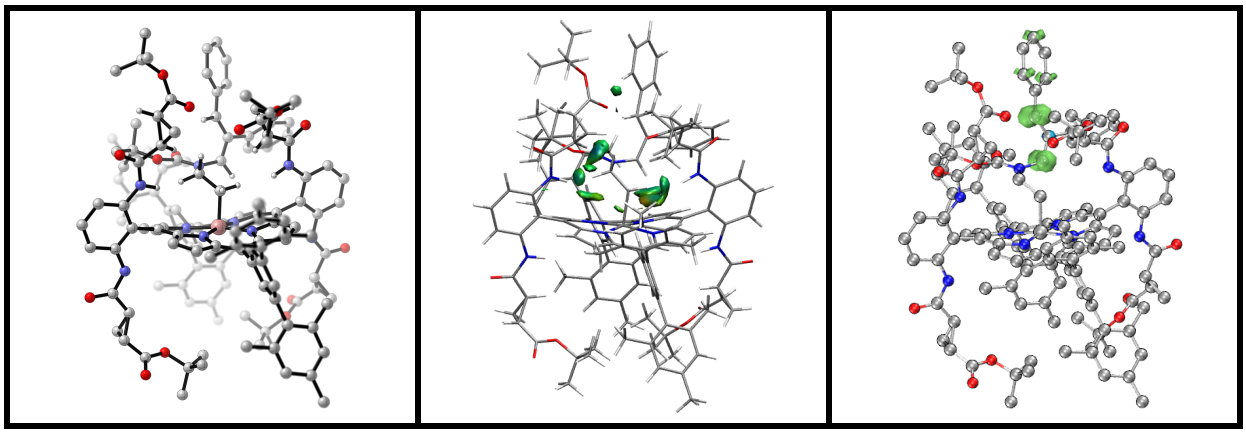
**TS1**$_{[Co(\mathbf{P6})]}$



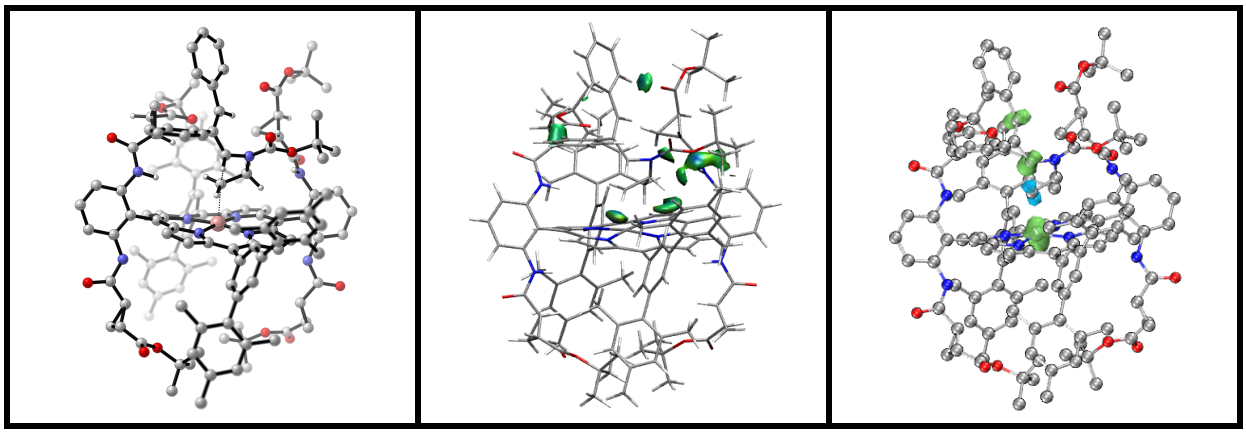
**Intermediate B**$_{[Co(\mathbf{P6})]}$



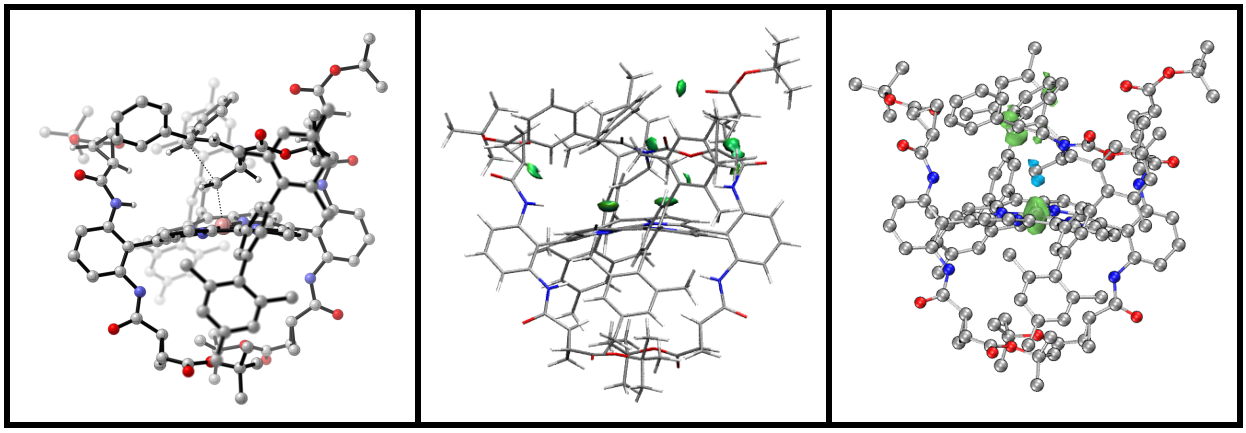
**TS2**$_{[Co(\mathbf{P6})]}$



**Intermediate C**$_{[Co(\mathbf{P6})]}$



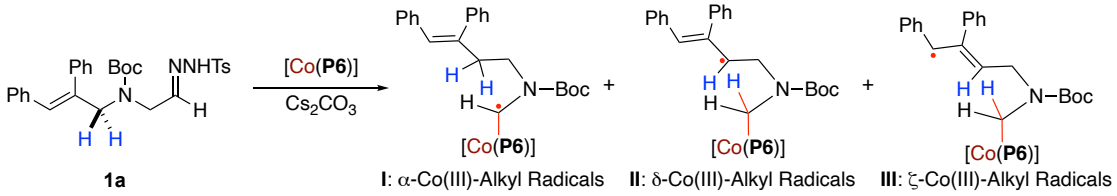
**TS3**$_{[Co(\mathbf{P6})](Azetidine)}$

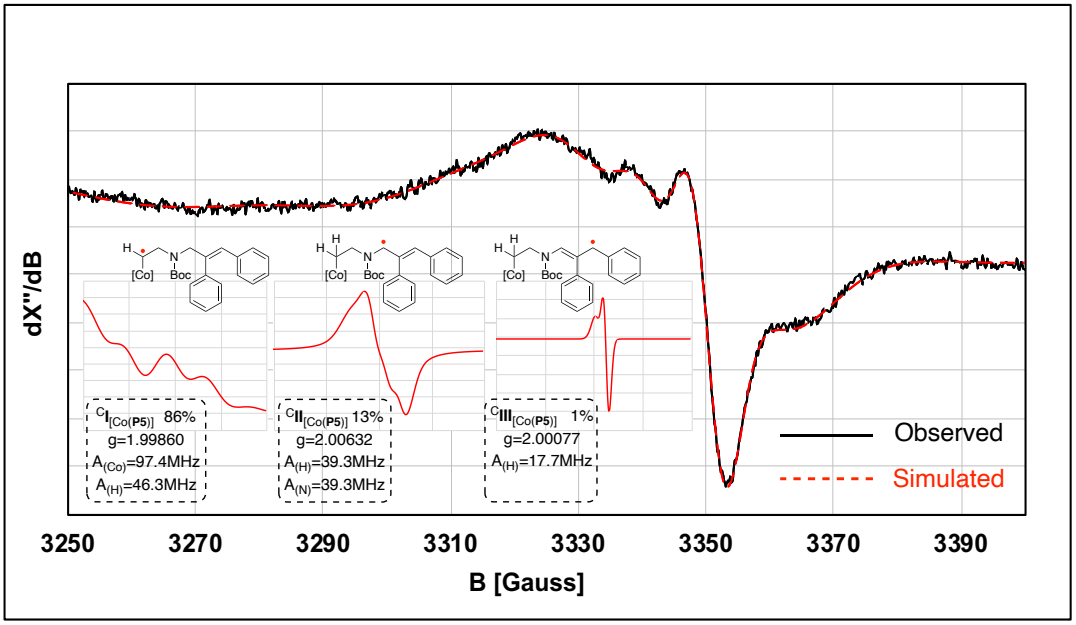


**TS3**[Co(**P6**)](Tetrahydropyridine)

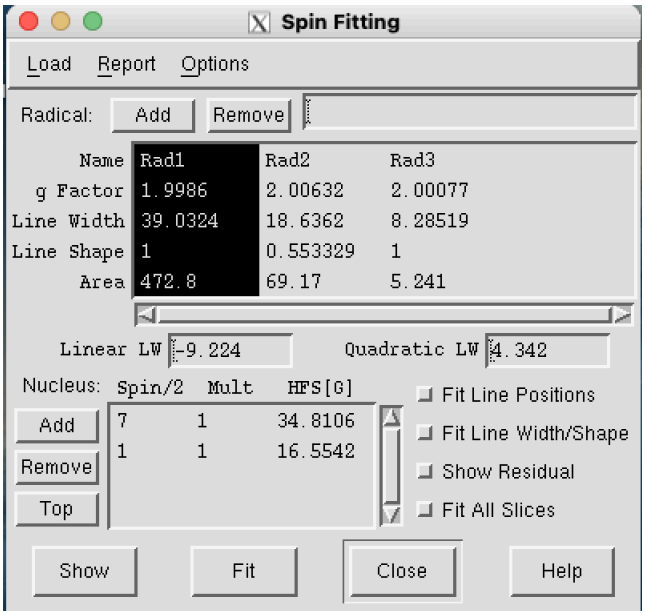
### 4.4.7.2 Characterization of Co(III)-Alkyl Radical (Intermediate I or II) by EPR

**Procedure for EPR Experiment:** To an over-dried Schlenk tube, [Co(**P6**)] (2 mol %), **1a** (0.1 mmol) and $Cs_2CO_3$ (0.15 mmol) was 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 (1 mL) were added via a gas-tight syringe. The mixture was then stirred at 60 °C for 2 hour and transferred into a degassed EPR tube (filled with argon) through a gas tight 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). X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit in Xenon.



**EPR simulation details:**

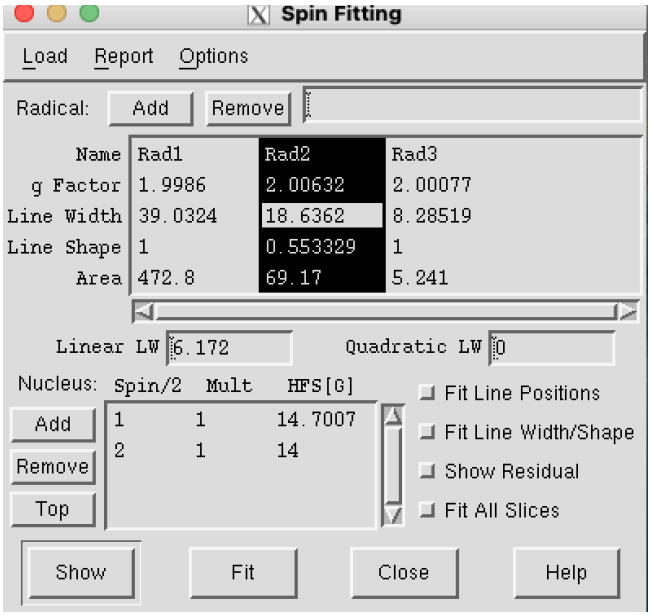



472.8/(472.8+69.17+5.241)*100%=86%

g = 1.9986

A(Co) = 34.8106 x 1.9986 x 1.399611451 = 97.4 MHz

A(H) = 16.5542 x 1.9986 x 1.399611451 = 46.3 MHz

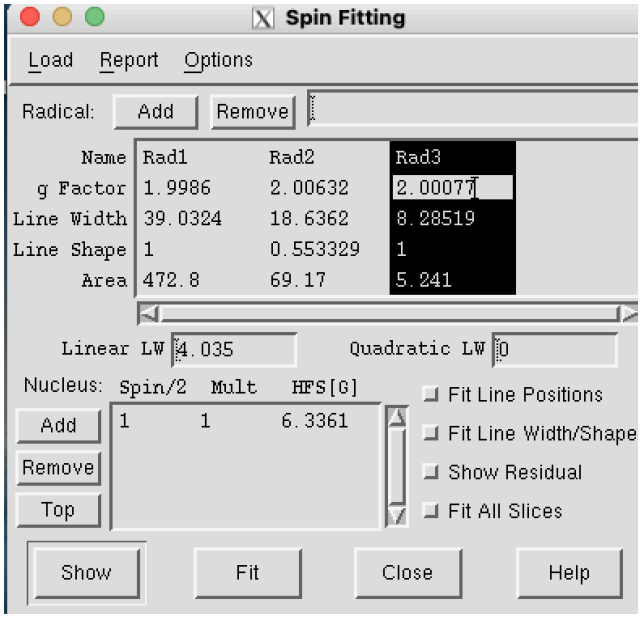



69.17/(472.8+69.17+5.241)*100%=13%

g = 2.00632

A(N) = 14.0000 x 2.00632 x 1.399611451 = 39.3 MHz

A(H) = 14.7007 x 2.00632 x 1.399611451 = 39.3 MHz

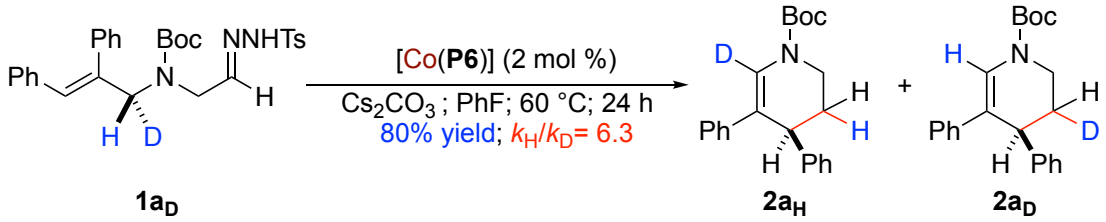



5.241/(472.8+69.17+5.241)*100%=1%

g = 2.00077

A(H) = 6.3361 x 2.00077 x 1.399611451 = 17.7 MHz

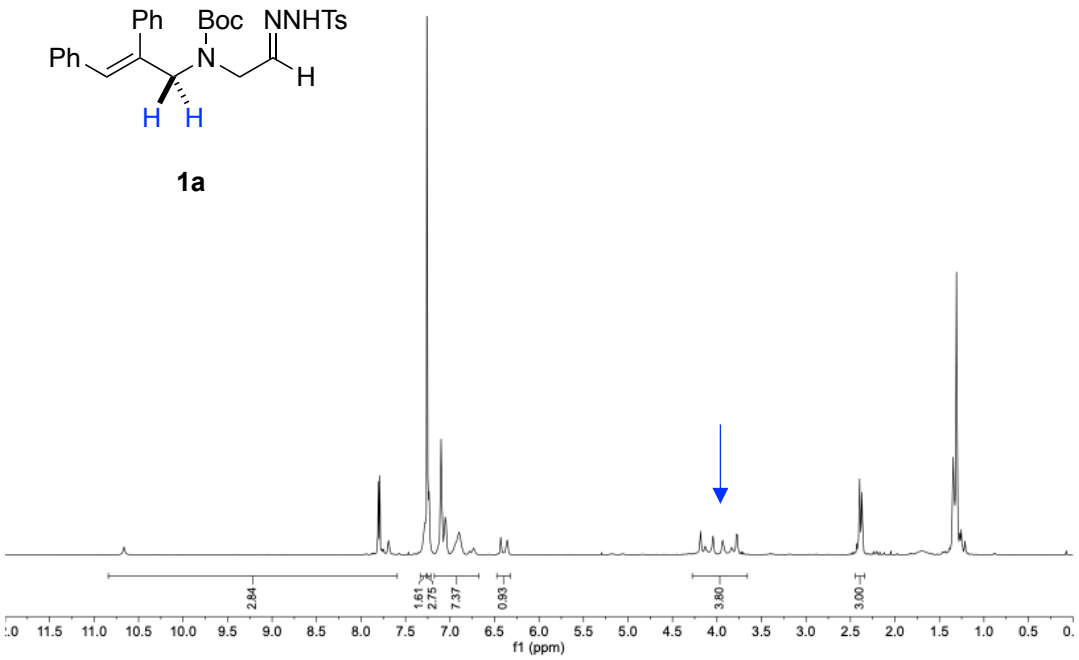
### 4.4.7.3 Kinetic Isotope Effect




**1a$_D$** **2a$_H$** **2a$_D$**

An oven-dried Schlenk tube was charged with hydrazone **1a$_D$** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (0.5 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was filtered and concentrated. The KIE value was determined by crude NMR.

**Figure 4.4. NMR for Monodeuterated Standard Substrate $1a_D$ and Standard Substrate 1a**



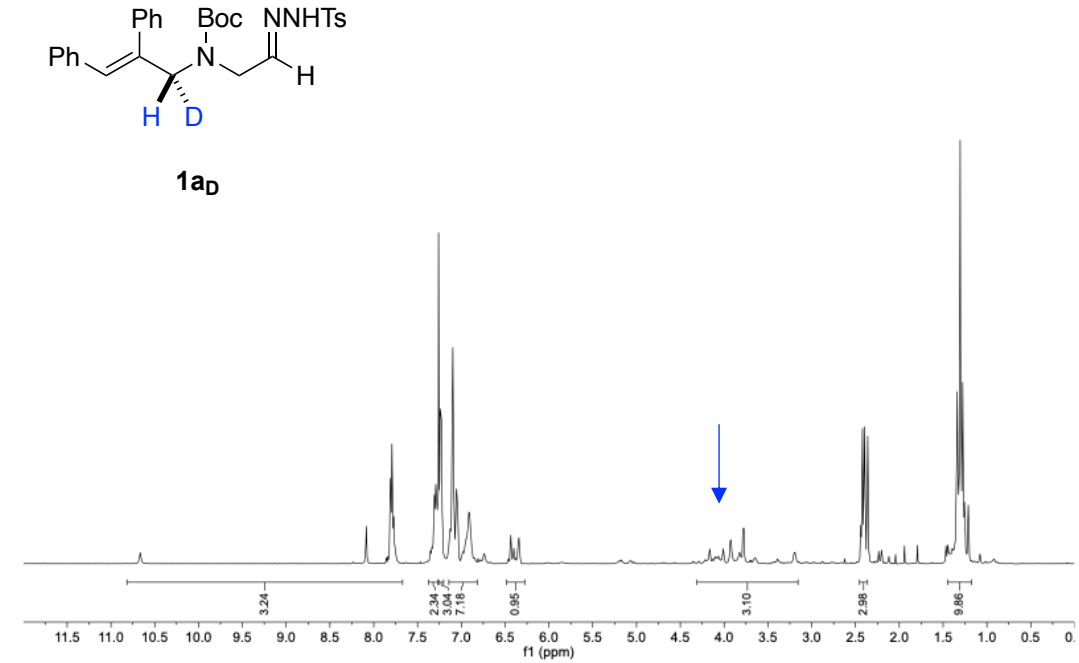
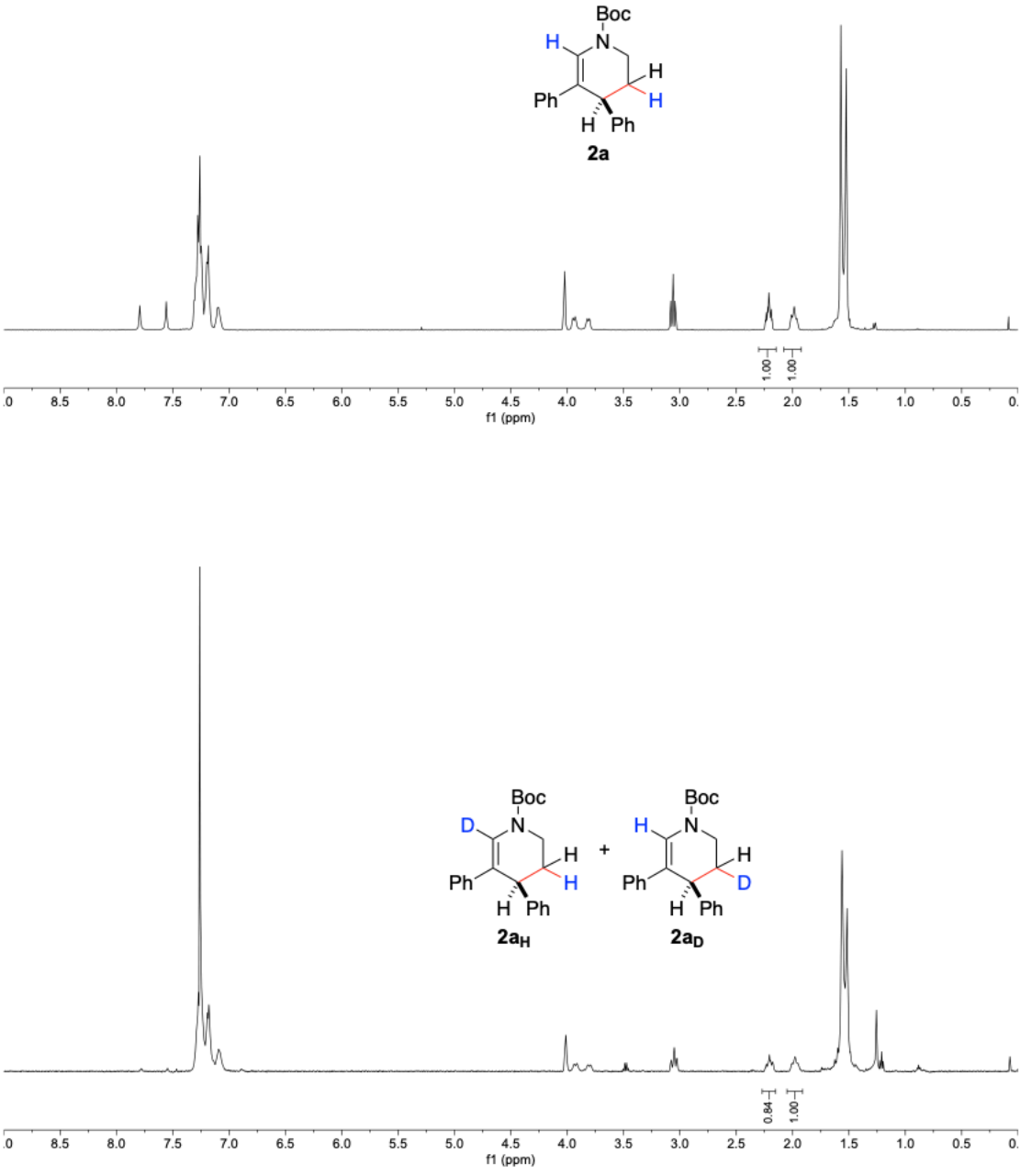



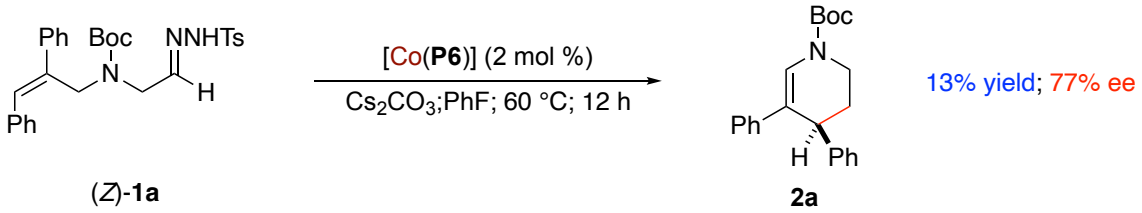
**Figure 4.5. NMR for KIE Study**




**Calculation of KIE:**

1/(1-0.84)=6.3

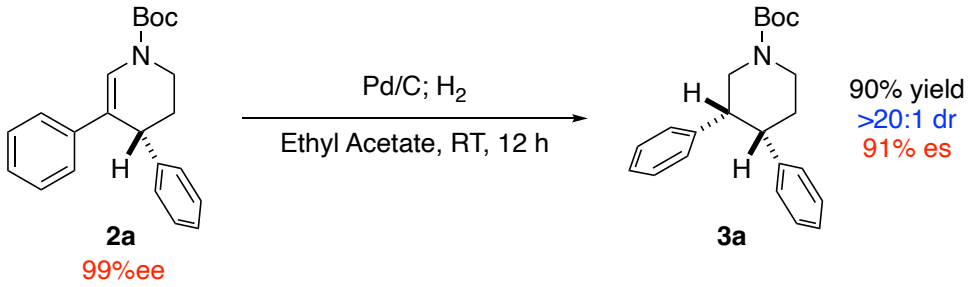
### 4.4.7.4 Probing of δ-Co(III)-Allylic Radical Intermediate via Olefin Isomerization




(*Z*)-**1a** **2a**

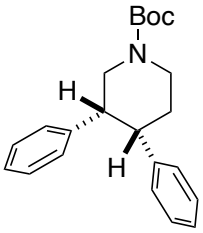
An oven-dried Schlenk tube was charged with hydrazone (*Z*)-**1a** (0.1 mmol), $Cs_2CO_3$ (0.15 mmol) and [Co(**P6**)] (2 mol %). The Schlenk tube was then evacuated and backfilled with nitrogen for 3 times. The Teflon screw cap was replaced with a rubber septum, Fluorobenzene (1.0 mL) was added via a gas-tight syringe. The tube was then purged with nitrogen for 30 s and the rubber septum was replaced with a Teflon screw cap. The mixture was then stirred at 60 °C. After 12 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the desired compound **2a**.

### 4.4.8 Further Transformations

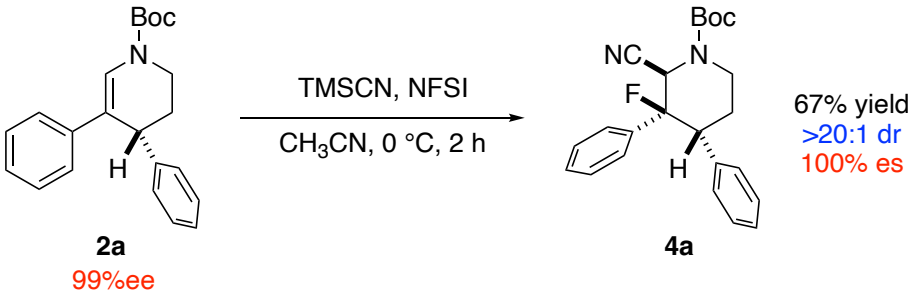



To a 100 mL round bottom flask was added Pd/C (30 mg), **2a** (0.1 mmol) and EtOAc. The reaction mixture was allowed to stir at RT under hydrogen atmosphere (with hydrogen gas filled balloon) for until starting material was all consumed. Then the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography.

***tert*-Butyl (*3S,4R*)-3,4-diphenylpiperidine-1-carboxylate (3a)**

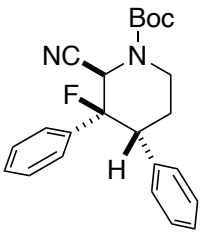



Colorless oil (90% yield). $R_f$ = 0.40 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-93.600° (*c* = 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.18 – 7.01 (m, 6H), 6.90 – 6.76 (m, 4H), 4.62 – 4.34 (m, 2H), 3.45 – 3.34 (m, 1H), 3.19 (dt, *J* = 12.6, 4.1 Hz, 1H), 3.13 – 2.92 (m, 2H), 2.17 (qd, *J* = 12.7, 4.4 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.47 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$): δ 155.18, 143.34, 140.73, 129.69, 128.01, 127.98, 127.48, 126.34, 126.27, 79.88, 48.93, 46.50, 45.65, 43.91, 28.63, 25.34. IR (neat, $cm^{-1}$): 3059.77, 3027.23, 2855.36, 1688.94, 1424.10, 1245.53, 1159.82, 1106.89. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{28}NO_2$: 338.21146, found 338.21108. HPLC analysis: ee = 98%. IF (95% hexanes : 5% isopropanol, 0.8 mL/min): $t_{major}$ = 11.12 min, $t_{minor}$ = 7.90 min.

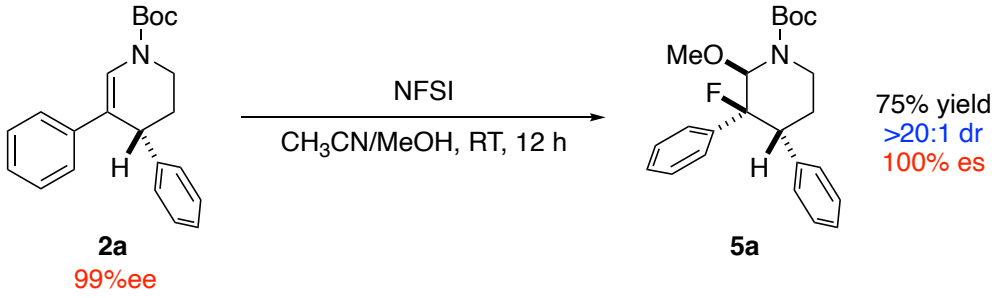



**4a** was synthesized following a previously reported literature. To a 20 mL vial was added NFSI (1.1 equiv), TMSCN (0.02 mL, 10 equiv) and MeCN. After the mixture was cooled to 0 °C, pyridine (1.2 equiv) and **2a** (0.10 mmol) were added. The reaction mixture was allowed to stir at 0 °C for 1 hour. Upon completion, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl ether three times. The combined organic layer was washed with brine, dried with $Na_2SO4$ and was concentrated *in vacuo*. The residue was purified by column chromatography.

***tert*-Butyl (2*R*,3*S*,4*R*)-2-cyano-3-fluoro-3,4-diphenylpiperidine-1-carboxylate (4a)**

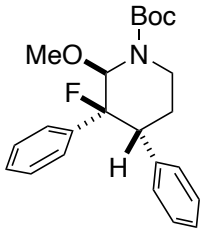



Colorless oil (67% yield). $R_f$ = 0.41 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-205.13° (*c* = 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.10 (m, 4H), 7.04 – 6.95 (m, 2H), 6.82 – 6.78 (m, 2H), 5.97 – 5.48 (m, 1H), 4.62 – 4.23 (m, 1H), 3.64 (td, J = 13.2, 3.7 Hz, 1H), 3.35 (s, 1H), 2.18 – 2.08 (m, 1H), 1.90 (d, J = 14.0 Hz, 1H), 1.53 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 153.21, 136.66, 129.39, 128.78, 127.88, 127.74, 127.66, 125.95, 125.87, 115.20, 92.42 (d, *J* = 186.7 Hz), 83.01, 58.58, 48.60, 41.10, 28.36, 26.45. $^{19}$F NMR (470 MHz, $CDCl_3$) δ -140.54. IR (neat, $cm^{-1}$): 2978.35, 1704.30, 1496.08, 1394.22, 1367.90, 1285.25, 1157.90, 1031.14. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{26}N_2O_2F$: 381.19728, found 381.19693. HPLC analysis: ee = 99%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 10.68 min, $t_{minor}$ = 20.70 min.

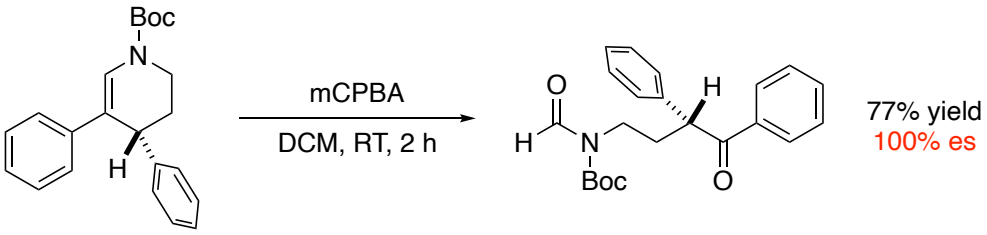



**4a** was synthesized following a previously reported literature. A 20 mL vial was charged with **2a** (0.1 mmol), NFSI (1.1 equiv) and 1:1 mixture of $CH_3CN$ and MeOH as solvent. The reaction mixture was stirred at RT for 12 hours. Upon completion, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl ether three times. The combined organic layer was washed with brine, dried with $Na_2SO4$ and was concentrated *in vacuo*. The residue was purified by column chromatography.

***tert*-Butyl (2*R*,3*S*,4*S*)-3-fluoro-2-methoxy-3,4-diphenylpiperidine-1-carboxylate (5a)**




Colorless oil (75% yield). $R_f$ = 0.45 (Hexanes/ EtOAc = 8/1). $[\alpha]_D^{20}$ = (–)-59.992° (*c* = 0.1, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.23 – 6.98 (m, 8H), 6.78 (d, J = 7.4 Hz, 2H), 5.47 (s, 1H), 4.37 – 4.06 (m, 1H), 3.85 – 3.61 (m, 1H), 3.45 (s, 3H), 3.22 (dt, J = 16.6, 9.5 Hz, 1H), 2.12 (qd, J = 13.6, 5.0 Hz, 1H), 1.76 (d, J = 14.0 Hz, 1H), 1.50 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 154.80, 138.25, 137.60, 132.19, 129.58, 127.93, 127.45, 126.98, 126.47, 95.46 (d, $J$ = 187.3 Hz), 86.35 (d, $J$ = 22.8 Hz), 81.34, 55.74, 45.35 (d, $J$ = 22.9 Hz), 37.76, 28.47, 27.08. $^{19}F$ NMR (470 MHz, $CDCl_3$) δ -149.34. IR (neat, $cm^{-1}$): 3061.22, 2975.07, 2932.47, 2878.88, 1700.75, 1495.50, 1165.44, 1076.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{29}NO_3F$: 386.21260, found 386.21238. HPLC analysis: ee = 98%. IF (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 9.68 min, $t_{minor}$ = 12.14 min.

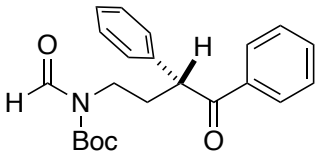



**2a**
99%ee

**6a**

To a stirred solution of compound **2a** (0.1 mmol) in anhydrous DCM (2.0 mL) at 0 °C were added *m*-chloroperoxybenzoic acid (*m*CPBA) (2.0 equiv). The reaction mixture was stirred for 2 h at 0 °C. After the complete consumption of **2a**, the reaction mixture was quenched with water and was extracted with DCM. The combined extract was dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by column chromatography.

***tert*-Butyl formyl(4-oxo-3,4-diphenylbutyl)carbamate (6a)**




Colorless oil (77% yield). $R_f$ = 0.27 (Hexanes/ EtOAc = 5/1). $[\alpha]_D^{20}$ = (–)-99.985° (*c* = 0.1, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 9.12 (s, 1H), 7.98 – 7.87 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.28 (m, 4H), 7.20 (dtd, *J* = 8.7, 5.3, 2.6 Hz, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.69 (ddd, *J* = 13.9, 8.5, 5.7 Hz, 1H), 3.53 (ddd, *J* = 13.3, 8.3, 6.3 Hz, 1H), 2.45 (dtd, *J* = 13.6, 8.0, 5.7 Hz, 1H), 2.07 (ddt, *J* = 13.4, 8.7, 6.5 Hz, 1H), 1.49 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 198.78, 163.25, 152.54, 139.04, 136.56, 133.03, 129.21, 128.91, 128.63, 128.29, 127.41, 84.19, 51.52, 39.36, 32.33, 28.12. IR (neat, $cm^{-1}$): 3060.81, 2977.85, 2933.12, 1735.60, 1683.53, 1448.17, 1340.72, 1149.03. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{26}NO_4$: 368.18563, found 368.18455. HPLC analysis: ee = 99%. IC (98% hexanes : 2% isopropanol, 0.8 mL/min): $t_{major}$ = 25.40 min, $t_{minor}$ = 19.96 min.

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# Chapter 5. Cartesian Coordinates for DFT Calculation

## 5.1 Cartesian Coordinates for DFT Calculation in Chapter 2

**Substrate Diazo 1a**

Electronic energy in diisopropyl ether= -803.197306
Thermal correction to Enthalpy= 0.273145
Enthalpy in diisopropyl ether= -802.924161
Thermal correction to Gibbs Free Energy= 0.207894
Gibbs Free Energy in diisopropyl ether= -802.989412

0 1

| | | | |
|---|---|---|---|
| C | 2.12615700 | 0.02123000 | -1.45680000 |
| C | 1.24452500 | -1.02718800 | -2.04899600 |
| C | 3.14947100 | -0.19687700 | -0.40751500 |
| C | 0.53550900 | -0.69630600 | -3.36023800 |
| O | 1.16730300 | -2.14388600 | -1.54555300 |
| C | 3.61736700 | -1.50184300 | -0.12018000 |
| C | 3.70919600 | 0.89972400 | 0.29211500 |
| C | 1.55382500 | -0.56329200 | -4.53087500 |
| H | -0.16086500 | -1.53683600 | -3.54622000 |
| H | -0.06749600 | 0.23328600 | -3.27218800 |
| C | 4.61835200 | -1.69043300 | 0.84449200 |
| H | 3.18275300 | -2.35779200 | -0.65033400 |
| C | 4.71135800 | 0.69960600 | 1.25137400 |
| H | 3.35538300 | 1.92290200 | 0.08799300 |
| C | 2.60378800 | -1.65446900 | -4.48920700 |
| H | 2.04863200 | 0.42933600 | -4.49327500 |
| H | 0.98915300 | -0.59523800 | -5.48669500 |
| C | 5.17180800 | -0.59818500 | 1.53422900 |
| H | 4.97139200 | -2.71211100 | 1.05599400 |
| H | 5.13175100 | 1.56624400 | 1.78532000 |
| C | 3.87231400 | -1.40393400 | -3.92526900 |
| C | 2.29978200 | -2.96673300 | -4.90685400 |
| H | 5.95703000 | -0.75638200 | 2.28970500 |
| C | 4.81108800 | -2.43770400 | -3.77318100 |
| H | 4.12583100 | -0.38461000 | -3.59269400 |
| C | 3.23726400 | -4.00155900 | -4.76360200 |
| H | 1.31055700 | -3.18166900 | -5.34364000 |
| C | 4.49478400 | -3.74108300 | -4.19080100 |
| H | 5.79256300 | -2.22188700 | -3.32303000 |
| H | 2.98295200 | -5.02051300 | -5.09555700 |
| H | 5.22761500 | -4.55444000 | -4.07158800 |
| N | 2.00117100 | 1.24040900 | -1.94251800 |

| | | | |
|---|---|---|---|
| N | 1.87573400 | 2.29939900 | -2.37981500 |

**Cyclobutanone Product 2a**

Electronic energy in diisopropyl ether= -693.6561417
Thermal correction to Enthalpy= 0.261116
Enthalpy in diisopropyl ether= -693.395026
Thermal correction to Gibbs Free Energy= 0.202987
Gibbs Free Energy in diisopropyl ether= -693.453155

0 1

| | | | |
|---|---|---|---|
| C | 2.63763400 | 0.00257300 | 0.13732000 |
| C | 2.72463700 | 0.28370200 | -1.33988800 |
| C | 2.48456000 | 1.13901800 | 1.16930500 |
| C | 3.49631600 | -0.55553900 | -2.17236700 |
| C | 2.04488100 | 1.38137200 | -1.90935000 |
| C | 3.47817800 | 0.46828000 | 2.12926400 |
| O | 1.90134400 | 2.19961500 | 1.16893200 |
| C | 3.58390800 | -0.30383900 | -3.55093200 |
| H | 4.02705300 | -1.41622200 | -1.73483100 |
| C | 2.13710000 | 1.63139100 | -3.28895000 |
| H | 1.45746600 | 2.04371000 | -1.25589500 |
| H | 2.95016700 | -0.08926400 | 2.93300100 |
| C | 3.91578000 | -0.45330100 | 0.94012800 |
| H | 4.24077600 | 1.12270400 | 2.59788900 |
| H | 4.18731600 | -0.96766300 | -4.19030600 |
| C | 2.90395400 | 0.79068100 | -4.11378900 |
| H | 1.60639200 | 2.49405200 | -3.72218700 |
| C | 4.12895700 | -1.92568500 | 1.17629300 |
| H | 4.81047700 | -0.02119300 | 0.44791900 |
| H | 2.97347700 | 0.98857700 | -5.19501500 |
| C | 3.14315600 | -2.71628300 | 1.80746400 |
| C | 5.31837100 | -2.55387300 | 0.75112700 |
| C | 3.34005900 | -4.09129700 | 2.00608100 |
| H | 2.20276600 | -2.25267100 | 2.14977400 |
| C | 5.51950900 | -3.93080500 | 0.94698500 |
| H | 6.09746400 | -1.94939500 | 0.25825700 |
| C | 4.53030600 | -4.70484100 | 1.57556500 |
| H | 2.55831900 | -4.68970300 | 2.49999400 |
| H | 6.45572800 | -4.40070300 | 0.60660000 |
| H | 4.68471800 | -5.78403300 | 1.73048500 |
| H | 1.81627900 | -0.72653100 | 0.34340800 |

**Catalyst [Co(P5)]**

Electronic energy in diisopropyl ether= -6121.376843

Thermal correction to Enthalpy= 1.504906
Enthalpy in diisopropyl ether= -6119.871937
Thermal correction to Gibbs Free Energy= 1.263796
Gibbs Free Energy in diisopropyl ether= -6120.113047

0 2

| | | | |
|---|---|---|---|
| N | -1.56460100 | -1.39916800 | 0.73637300 |
| N | 1.07180200 | 0.02461800 | -1.75572900 |
| N | 1.17791700 | -1.60835900 | 0.47362600 |
| N | -1.58824900 | 0.56119800 | -1.21143600 |
| C | -1.47145100 | 1.37120100 | -2.33175100 |
| C | -2.83497800 | 0.86626600 | -0.67081100 |
| C | -2.90074700 | -1.04630000 | 0.86233600 |
| C | -1.41652700 | -2.53806700 | 1.52195100 |
| C | 1.02578800 | -2.55668500 | 1.47562100 |
| C | 2.55429700 | -1.44694600 | 0.33397200 |
| C | 2.43382700 | -0.24262000 | -1.79951600 |
| C | 0.79196500 | 0.68133100 | -2.95057000 |
| C | 1.97406000 | 0.74219300 | -3.78477400 |
| C | -0.40253800 | 1.35262400 | -3.23824100 |
| C | -2.62316300 | 2.23846100 | -2.45800000 |
| C | -3.49544900 | 0.09734300 | 0.30102800 |
| C | 3.00090100 | 0.19133700 | -3.06056300 |
| C | 3.17953600 | -0.83925800 | -0.76824600 |
| C | 3.26139500 | -2.22312200 | 1.33407100 |
| C | -3.61012100 | -2.00342700 | 1.68695000 |
| C | -0.19319400 | -3.10104900 | 1.89780600 |
| C | 2.31054500 | -2.93829800 | 2.02003600 |
| C | -3.45779300 | 1.94896800 | -1.40651100 |
| C | -2.69122600 | -2.94664600 | 2.07307400 |
| Co | -0.22509400 | -0.60512100 | -0.43925900 |
| C | -0.18183800 | -4.27558800 | 2.81400500 |
| C | -0.20472700 | -6.51126200 | 4.51279200 |
| C | -0.40876500 | -4.11556300 | 4.20188400 |
| C | 0.03136700 | -5.57330200 | 2.28760600 |
| C | 0.01920100 | -6.69972000 | 3.14059000 |
| C | -0.42068800 | -5.23689400 | 5.06024800 |
| C | -4.88710800 | 0.44010800 | 0.72588200 |
| C | -7.49861700 | 0.95349900 | 1.62203800 |
| C | -5.99710100 | 0.21104700 | -0.13093600 |
| C | -5.11433600 | 0.93470800 | 2.03883500 |
| C | -6.42604200 | 1.18155700 | 2.49591500 |
| C | -7.30944500 | 0.48096200 | 0.31536500 |
| C | -0.52737500 | 2.12193800 | -4.50752400 |
| C | -0.77144300 | 3.56133700 | -6.91324600 |
| C | -1.39787400 | 1.66867200 | -5.53061500 |

| | | | |
|---|---|---|---|
| C | 0.20982700 | 3.31601900 | -4.70904500 |
| C | 0.09485600 | 4.03728000 | -5.91772600 |
| C | -1.52250600 | 2.38906500 | -6.73905900 |
| C | 4.65714700 | -0.97512600 | -0.95509200 |
| C | 7.40316400 | -1.21472400 | -1.50560100 |
| C | 5.50663700 | 0.15903100 | -0.87884700 |
| C | 5.21509500 | -2.23594400 | -1.31250100 |
| C | 6.59532000 | -2.35814400 | -1.57904800 |
| C | 6.88448000 | 0.04132300 | -1.16407700 |
| N | -5.71823900 | -0.31544600 | -1.40528200 |
| C | -6.57318900 | -0.51395600 | -2.46871500 |
| N | 4.32554800 | -3.31901900 | -1.41706600 |
| C | 4.57788900 | -4.63356800 | -1.74637500 |
| O | -7.78050800 | -0.26894200 | -2.45687000 |
| O | 5.68808000 | -5.09933800 | -2.00690700 |
| C | -5.89103500 | -1.09293400 | -3.68356200 |
| C | -6.70694700 | -2.16157000 | -4.42662500 |
| C | -6.50459600 | -0.78775900 | -5.02453200 |
| C | 3.32066500 | -5.46479900 | -1.81568600 |
| C | 3.15492500 | -6.24938100 | -3.13164800 |
| C | 3.45859800 | -6.95793800 | -1.83299300 |
| C | -6.04625800 | -3.37148400 | -4.99239300 |
| C | 1.77990000 | -6.29729700 | -3.70247400 |
| O | 1.83610000 | -6.15411900 | -5.05008100 |
| O | -4.77744900 | -3.12329600 | -5.44567100 |
| C | 0.59735600 | -6.10845800 | -5.79374300 |
| C | -4.12484000 | -4.26411100 | -6.04950900 |
| C | -2.69681300 | -3.89600400 | -6.41865900 |
| C | 0.46033300 | -4.74201400 | -6.46706200 |
| C | -2.02153200 | -5.02861300 | -7.20655500 |
| C | -0.56625500 | -4.73811900 | -7.61189900 |
| O | -6.57000300 | -4.46828000 | -5.06179200 |
| O | 0.74567000 | -6.42691700 | -3.06115200 |
| O | 0.22205900 | -5.63197300 | 0.94069700 |
| O | -2.06842500 | 0.51250800 | -5.25904800 |
| O | 1.00209800 | 3.69335400 | -3.66756800 |
| O | -0.61111300 | -2.83110100 | 4.61069300 |
| C | 0.28878900 | -6.90919800 | 0.31656000 |
| C | -0.95036800 | -2.59428600 | 5.96715100 |
| C | -2.96132600 | 0.00193900 | -6.23578300 |
| C | 1.86580100 | 4.80600400 | -3.83345700 |
| H | -0.62866200 | -7.50584700 | 0.51900100 |
| H | 0.17964000 | -7.71072200 | 2.74448700 |
| H | -0.21260500 | -7.38815500 | 5.17914700 |
| H | -0.59224200 | -5.12428100 | 6.13868000 |
| H | 1.17458700 | -7.48707000 | 0.66531000 |

| | | | |
|---|---|---|---|
| H | 0.37369300 | -6.72289600 | -0.77120800 |
| H | -1.87791400 | -3.13548900 | 6.26028000 |
| H | -0.12786000 | -2.88723200 | 6.65813900 |
| H | -1.12610300 | -1.50603200 | 6.05460400 |
| H | 2.44538900 | -3.66145200 | 2.83219200 |
| H | 4.35131500 | -2.23984600 | 1.44909600 |
| H | -2.83662700 | -3.83056500 | 2.70367700 |
| H | -4.67840300 | -1.94526800 | 1.92401200 |
| H | -6.57433200 | 1.53939400 | 3.52138300 |
| H | -8.52367800 | 1.15100800 | 1.97288300 |
| H | -8.14760700 | 0.30342500 | -0.36803000 |
| H | -4.42961800 | 2.39020800 | -1.15694600 |
| H | -2.75354700 | 2.97924100 | -3.25481200 |
| H | -4.72914300 | -0.52654200 | -1.56917800 |
| H | 3.34832100 | -3.08543800 | -1.21784100 |
| H | 6.99511600 | -3.34106000 | -1.85399000 |
| H | 8.47878000 | -1.30642800 | -1.72330300 |
| H | 7.51742900 | 0.93463700 | -1.12562000 |
| H | 2.00230900 | 1.18324400 | -4.78709600 |
| H | 4.05438800 | 0.07562400 | -3.33904500 |
| H | -2.18994200 | 2.04347300 | -7.53895600 |
| H | -0.86592000 | 4.12341000 | -7.85559600 |
| H | 0.66241700 | 4.96270300 | -6.08069200 |
| H | -3.78118500 | 0.72137000 | -6.45881800 |
| H | -3.39544600 | -0.92376700 | -5.81428300 |
| H | -2.43490000 | -0.24471400 | -7.18576600 |
| H | 1.29923900 | 5.75285000 | -3.98259800 |
| H | 2.45486400 | 4.87876500 | -2.90058800 |
| H | 2.56168600 | 4.66262200 | -4.69021100 |
| H | -5.82768100 | -0.70202600 | -5.88622600 |
| H | -7.38561600 | -0.12729900 | -5.01291800 |
| H | -7.70062400 | -2.37208100 | -4.00337500 |
| H | -4.80127300 | -1.25084600 | -3.64381600 |
| H | 2.39261300 | -5.04432300 | -1.39308300 |
| H | 3.97462600 | -6.14488700 | -3.85778000 |
| H | 4.48340300 | -7.34707400 | -1.73128700 |
| H | 2.64614000 | -7.54483600 | -1.38105700 |
| H | -4.70846700 | -4.57250500 | -6.94478700 |
| H | -0.23992200 | -6.33663100 | -5.10399500 |
| H | 1.45632800 | -4.46434800 | -6.87317200 |
| H | 0.66708300 | -6.91371100 | -6.55638500 |
| H | 0.21324700 | -3.97422400 | -5.70154400 |
| H | -2.07331400 | -5.97367300 | -6.62007100 |
| H | -0.52413200 | -3.75413000 | -8.12884600 |
| H | -0.24965600 | -5.48982000 | -8.36911000 |
| H | -4.16077400 | -5.11851300 | -5.34048800 |

| | | | |
|---|---|---|---|
| H | -2.61539900 | -5.22128900 | -8.12730900 |
| H | -2.70198100 | -2.97217900 | -7.03750700 |
| H | -2.12602000 | -3.65481600 | -5.49556900 |
| N | 4.92413000 | 1.37958700 | -0.48080800 |
| C | 5.41777900 | 2.65334000 | -0.68473100 |
| H | 3.98349000 | 1.30149500 | -0.08276800 |
| O | 6.45765700 | 2.90262900 | -1.29605300 |
| C | 4.58440100 | 3.74723000 | -0.06440400 |
| C | 5.40490800 | 4.95969000 | 0.39837200 |
| C | 4.50065100 | 5.05926900 | -0.80740800 |
| H | 3.72197800 | 3.46668500 | 0.56113100 |
| C | 5.09844900 | 5.66674500 | 1.67561700 |
| H | 6.48319200 | 4.87797300 | 0.19518800 |
| H | 3.57203400 | 5.63784700 | -0.69114700 |
| H | 5.00403200 | 5.10387800 | -1.78593000 |
| O | 3.75887900 | 5.76182700 | 1.91518400 |
| O | 5.94570200 | 6.13093100 | 2.41778500 |
| C | 3.40791100 | 6.52157600 | 3.09410800 |
| C | 1.89897100 | 6.70505400 | 3.13660800 |
| H | 3.93836800 | 7.49775400 | 3.05483200 |
| H | 3.78670300 | 5.99170300 | 3.99504600 |
| C | 1.49293800 | 7.69255800 | 4.24140900 |
| H | 1.55532200 | 7.08598100 | 2.14905100 |
| H | 1.41029100 | 5.71873700 | 3.28958400 |
| C | -0.01231400 | 8.00859400 | 4.28733200 |
| H | 1.83297300 | 7.30358900 | 5.22771000 |
| H | 2.04738500 | 8.64619900 | 4.09585800 |
| C | -0.92939600 | 6.79701100 | 4.51690300 |
| H | -0.30813300 | 8.49765100 | 3.33308400 |
| H | -0.19635500 | 8.76401300 | 5.08378400 |
| C | -0.66583000 | 6.08719000 | 5.84356200 |
| H | -1.99171800 | 7.12130900 | 4.49552000 |
| H | -0.80924400 | 6.06071300 | 3.69327200 |
| O | -1.60812200 | 5.00758100 | 6.03149000 |
| H | 0.36179700 | 5.67368300 | 5.88783000 |
| H | -0.82468100 | 6.76874600 | 6.70383100 |
| C | -1.23785500 | 3.79331300 | 5.55055600 |
| C | -2.35090600 | 2.81438300 | 5.70916900 |
| O | -0.15082100 | 3.55067400 | 5.04566400 |
| C | -2.47273000 | 1.74852400 | 4.61295900 |
| C | -2.03658200 | 1.36614400 | 6.00208200 |
| H | -3.30310100 | 3.20573000 | 6.09696900 |
| C | -3.88220200 | 1.44784800 | 4.17362900 |
| H | -1.68028800 | 1.77930500 | 3.84707100 |
| H | -2.77154000 | 0.83183800 | 6.62393900 |
| H | -0.97541500 | 1.10193800 | 6.13009900 |

| | | | |
|---|---|---|---|
| N | -3.97387300 | 1.18802400 | 2.82173400 |
| O | -4.83592200 | 1.47142200 | 4.95260600 |
| H | -3.08796900 | 1.10671600 | 2.31364400 |

**Intermediate B**

Electronic energy in diisopropyl ether= -6924.621036
Thermal correction to Enthalpy= 1.780863
Enthalpy in diisopropyl ether= -6922.840173
Thermal correction to Gibbs Free Energy= 1.507518
Gibbs Free Energy in diisopropyl ether= -6923.113518

0 2

| | | | |
|---|---|---|---|
| N | -1.33232500 | -1.01976600 | 0.85220500 |
| N | 1.33534900 | 0.46873800 | -1.61044600 |
| N | 1.41356300 | -1.37351000 | 0.46172000 |
| N | -1.33226800 | 1.03733200 | -0.98692900 |
| C | -1.22189200 | 1.86071600 | -2.09800600 |
| C | -2.58826800 | 1.31617200 | -0.44957100 |
| C | -2.66850400 | -0.66328100 | 0.98635200 |
| C | -1.20205100 | -2.20279600 | 1.57688000 |
| C | 1.23827400 | -2.35850600 | 1.42899300 |
| C | 2.78963300 | -1.33516200 | 0.23111300 |
| C | 2.67961900 | 0.12370500 | -1.73578400 |
| C | 1.04325900 | 1.20549400 | -2.75495200 |
| C | 2.20499900 | 1.29942200 | -3.61231700 |
| C | -0.16721000 | 1.85364300 | -3.02231700 |
| C | -2.38184800 | 2.71621900 | -2.21741300 |
| C | -3.26385300 | 0.50296100 | 0.47781300 |
| C | 3.22935100 | 0.65238000 | -2.96814100 |
| C | 3.41575400 | -0.66873900 | -0.83732900 |
| C | 3.48169800 | -2.22902500 | 1.13597400 |
| C | -3.39233900 | -1.66232700 | 1.74689400 |
| C | 0.00410800 | -2.82694700 | 1.90383100 |
| C | 2.51520600 | -2.87944700 | 1.86526000 |
| C | -3.21155100 | 2.41091200 | -1.16661700 |
| C | -2.48407700 | -2.62700800 | 2.09675700 |
| Co | 0.04146200 | -0.15845400 | -0.26124700 |
| C | -0.00838100 | -3.99109500 | 2.83259000 |
| C | 0.01968700 | -6.19097400 | 4.58375100 |
| C | -0.32488800 | -3.82081800 | 4.20435300 |
| C | 0.27156500 | -5.29221200 | 2.34426300 |
| C | 0.29248000 | -6.39794800 | 3.22292600 |
| C | -0.29625900 | -4.92078500 | 5.08881200 |
| C | -4.68549700 | 0.79065500 | 0.84943500 |
| C | -7.37858400 | 1.27373500 | 1.54167000 |

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|---|---|---|---|
| C | -5.72120100 | 0.68362500 | -0.12482000 |
| C | -5.04701600 | 1.08708200 | 2.19731800 |
| C | -6.39781900 | 1.32167600 | 2.53831700 |
| C | -7.06356400 | 0.95847900 | 0.21447300 |
| C | -0.42406900 | 2.40035300 | -4.39051100 |
| C | -0.98289500 | 3.23753800 | -7.02921200 |
| C | -1.21489100 | 1.59940300 | -5.25940100 |
| C | 0.09977400 | 3.61796400 | -4.88703800 |
| C | -0.18731300 | 4.04379000 | -6.20426500 |
| C | -1.49671100 | 2.01394800 | -6.57857200 |
| C | 4.86705800 | -0.92101400 | -1.12009900 |
| C | 7.56442800 | -1.35585400 | -1.82176800 |
| C | 5.83185500 | 0.11618400 | -0.98670100 |
| C | 5.29710200 | -2.19121100 | -1.60326500 |
| C | 6.64859000 | -2.40735000 | -1.95166600 |
| C | 7.18074600 | -0.09713800 | -1.34368200 |
| N | -5.36775200 | 0.21895800 | -1.40812800 |
| C | -6.15837800 | 0.13616600 | -2.53471100 |
| N | 4.32693900 | -3.20252600 | -1.73016200 |
| C | 4.49450500 | -4.51823600 | -2.10809400 |
| O | -7.30374800 | 0.58276600 | -2.62469000 |
| O | 5.55974000 | -5.02074600 | -2.47091900 |
| C | -5.52539800 | -0.62420800 | -3.67365000 |
| C | -6.48924900 | -1.61656500 | -4.34989400 |
| C | -6.05202600 | -0.35361100 | -5.05620400 |
| C | 3.21806100 | -5.31994900 | -2.06838000 |
| C | 2.96288900 | -6.17083300 | -3.32542300 |
| C | 3.35505600 | -6.81502400 | -2.01722100 |
| C | -6.03342400 | -2.96617600 | -4.78529800 |
| C | 1.55052700 | -6.27077800 | -3.78684300 |
| O | 1.50346900 | -6.25856700 | -5.14235300 |
| O | -4.75184200 | -2.96810600 | -5.26805800 |
| C | 0.21177200 | -6.31854000 | -5.78744500 |
| C | -4.30739500 | -4.24794700 | -5.77206700 |
| C | -2.92122000 | -4.09494800 | -6.37732100 |
| C | 0.09050000 | -5.14885700 | -6.76154700 |
| C | -2.48076800 | -5.38089800 | -7.09177700 |
| C | -1.08740100 | -5.30080200 | -7.73802200 |
| O | -6.72355100 | -3.96829500 | -4.74000900 |
| O | 0.56933800 | -6.34584400 | -3.05901600 |
| O | 0.48410700 | -5.37996700 | 1.00141400 |
| O | -1.64938100 | 0.42007500 | -4.73111800 |
| O | 0.89156100 | 4.32669400 | -4.03137600 |
| O | -0.66237000 | -2.55703200 | 4.57791000 |
| C | 0.51840100 | -6.67093600 | 0.40391400 |
| C | -1.14345700 | -2.33673700 | 5.89834100 |

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|---|---|---|---|
| C | -2.32737600 | -0.48952100 | -5.58174900 |
| C | 1.46790900 | 5.53439400 | -4.49973700 |
| H | -0.38331800 | -7.26379000 | 0.67516700 |
| H | 0.51684400 | -7.40739300 | 2.85481800 |
| H | 0.04518000 | -7.05032000 | 5.27214800 |
| H | -0.51417700 | -4.78886700 | 6.15622900 |
| H | 1.42556100 | -7.23974100 | 0.71002600 |
| H | 0.53028500 | -6.51081300 | -0.69136700 |
| H | -2.03531500 | -2.96651800 | 6.11041500 |
| H | -0.35405700 | -2.52811200 | 6.65558800 |
| H | -1.43070300 | -1.27149300 | 5.94373200 |
| H | 2.63676300 | -3.65532700 | 2.62908500 |
| H | 4.56994800 | -2.35282200 | 1.17088400 |
| H | -2.64427200 | -3.54584700 | 2.67064500 |
| H | -4.46493400 | -1.61697000 | 1.96518700 |
| H | -6.64927100 | 1.52622400 | 3.58494200 |
| H | -8.42759300 | 1.47493300 | 1.80987500 |
| H | -7.82938200 | 0.89805400 | -0.56646100 |
| H | -4.18424400 | 2.84556000 | -0.91059500 |
| H | -2.51594300 | 3.46530100 | -3.00559600 |
| H | -4.40466900 | -0.11867300 | -1.49469100 |
| H | 3.38176400 | -2.92923000 | -1.44499400 |
| H | 6.94326700 | -3.39437200 | -2.32479800 |
| H | 8.61636300 | -1.52570100 | -2.09986000 |
| H | 7.89094800 | 0.73124600 | -1.24343100 |
| H | 2.22149000 | 1.81811900 | -4.57662100 |
| H | 4.26654500 | 0.51317400 | -3.29280100 |
| H | -2.10625400 | 1.39472000 | -7.24885600 |
| H | -1.20370500 | 3.57043600 | -8.05539200 |
| H | 0.20700300 | 4.99260900 | -6.58904200 |
| H | -3.26481900 | -0.05254100 | -5.98879000 |
| H | -2.58946100 | -1.36845600 | -4.96637000 |
| H | -1.68396800 | -0.81480900 | -6.43025500 |
| H | 0.69321600 | 6.28870100 | -4.76379700 |
| H | 2.08426900 | 5.92931000 | -3.67070900 |
| H | 2.12287700 | 5.36487400 | -5.38340400 |
| H | -5.35434600 | -0.46597400 | -5.89854900 |
| H | -6.81262500 | 0.43857400 | -5.13595500 |
| H | -7.51055500 | -1.62281200 | -3.94065900 |
| H | -4.47809400 | -0.94785700 | -3.57001800 |
| H | 2.32555500 | -4.87061900 | -1.60168300 |
| H | 3.72924000 | -6.10869800 | -4.11210200 |
| H | 4.38533300 | -7.19904700 | -1.96501200 |
| H | 2.57572700 | -7.37748700 | -1.48423300 |
| H | -5.04231500 | -4.60767100 | -6.52451000 |
| H | -0.57486300 | -6.31732300 | -5.00618100 |

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|---|---|---|---|
| H | 1.03714500 | -5.08236900 | -7.33897400 |
| H | 0.16962100 | -7.28799000 | -6.33066900 |
| H | 0.01380100 | -4.20059600 | -6.18568900 |
| H | -2.52169900 | -6.23425800 | -6.37779400 |
| H | -1.06820100 | -4.45096100 | -8.45542400 |
| H | -0.92597600 | -6.21600200 | -8.35019900 |
| H | -4.31635800 | -4.98891600 | -4.94361700 |
| H | -3.22528200 | -5.62281300 | -7.88202700 |
| H | -2.93180700 | -3.25153700 | -7.10317200 |
| H | -2.19693100 | -3.81960200 | -5.58017100 |
| N | 5.38475200 | 1.34628000 | -0.47573500 |
| C | 6.03368600 | 2.56544200 | -0.45509900 |
| H | 4.44088900 | 1.32169200 | -0.07982100 |
| O | 7.16988900 | 2.76691700 | -0.88603600 |
| C | 5.19689300 | 3.66304300 | 0.14039700 |
| C | 5.93269500 | 4.73831200 | 0.94050900 |
| C | 5.36347800 | 5.04871900 | -0.42924900 |
| H | 4.19976700 | 3.40750900 | 0.52518200 |
| C | 5.27771200 | 5.32447200 | 2.14772100 |
| H | 7.02527300 | 4.63437000 | 1.01715800 |
| H | 4.46573300 | 5.68336200 | -0.47150600 |
| H | 6.09704500 | 5.15352500 | -1.24372800 |
| O | 3.91786000 | 5.24556700 | 2.05721600 |
| O | 5.86228800 | 5.84242400 | 3.08106000 |
| C | 3.17267700 | 5.95049200 | 3.07117000 |
| C | 1.69083400 | 5.83143800 | 2.74548600 |
| H | 3.50369900 | 7.01271400 | 3.07420800 |
| H | 3.42444800 | 5.53652100 | 4.07134800 |
| C | 0.86493600 | 6.87956200 | 3.50374300 |
| H | 1.55299100 | 5.96998100 | 1.65118800 |
| H | 1.33533500 | 4.80233300 | 2.96935900 |
| C | -0.64683500 | 6.79497000 | 3.23757400 |
| H | 1.06778000 | 6.80443700 | 4.59632000 |
| H | 1.22433100 | 7.88979000 | 3.20683100 |
| C | -1.36236400 | 5.60010900 | 3.88450600 |
| H | -0.81222100 | 6.75775300 | 2.13919900 |
| H | -1.13204200 | 7.73270200 | 3.58993900 |
| C | -1.37992000 | 5.66336200 | 5.41386700 |
| H | -2.41704100 | 5.56875900 | 3.53659400 |
| H | -0.90334400 | 4.63991200 | 3.56354200 |
| O | -2.31772900 | 4.68795100 | 5.92225200 |
| H | -0.38155400 | 5.47038200 | 5.85511000 |
| H | -1.75572400 | 6.64452000 | 5.76863500 |
| C | -1.83639100 | 3.44959000 | 6.18697000 |
| C | -2.96109400 | 2.48507100 | 6.30322400 |
| O | -0.64329900 | 3.17147100 | 6.22926000 |

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|---|---|---|---|
| C | -2.87844300 | 1.34583100 | 5.25958100 |
| C | -2.74535300 | 1.05974900 | 6.72802300 |
| H | -3.96275800 | 2.92062400 | 6.43358900 |
| C | -4.17400600 | 1.08691000 | 4.53804900 |
| H | -1.96405900 | 1.34812500 | 4.65006900 |
| H | -3.60786800 | 0.57183500 | 7.20742300 |
| H | -1.74280400 | 0.78976700 | 7.09397100 |
| N | -4.03100100 | 1.15683200 | 3.16618400 |
| O | -5.23275700 | 0.90409900 | 5.14288700 |
| H | -3.06230600 | 1.27833000 | 2.82378700 |
| C | 0.73337100 | 1.88633000 | 1.36101500 |
| C | -0.22496900 | 1.34828800 | 2.36210800 |
| C | 0.55050300 | 3.08668900 | 0.50407900 |
| C | 0.27433500 | 0.31099100 | 3.33692500 |
| O | -1.36337900 | 1.82981800 | 2.43688800 |
| C | -0.61480700 | 3.88108800 | 0.57471900 |
| C | 1.58820400 | 3.46866000 | -0.37591100 |
| C | 1.05085900 | 0.95121800 | 4.51354600 |
| H | -0.60017500 | -0.25251500 | 3.71130400 |
| H | 0.90839700 | -0.42468400 | 2.80736800 |
| C | -0.71319200 | 5.04361700 | -0.20520600 |
| H | -1.43655100 | 3.57349100 | 1.22968800 |
| C | 1.49333200 | 4.64460500 | -1.12236300 |
| H | 2.47224400 | 2.82949200 | -0.50256200 |
| C | 1.43353600 | -0.05924400 | 5.57620400 |
| H | 0.44488000 | 1.75489600 | 4.97702000 |
| H | 1.97548800 | 1.44040700 | 4.13430400 |
| C | 0.34142600 | 5.44437700 | -1.03971800 |
| H | -1.63657100 | 5.64092700 | -0.15494800 |
| H | 2.32287000 | 4.91389800 | -1.79044500 |
| C | 1.16307400 | 0.21095900 | 6.93414600 |
| C | 2.06491000 | -1.27514100 | 5.23840400 |
| H | 0.25714300 | 6.36412600 | -1.63834600 |
| C | 1.51822500 | -0.71288800 | 7.93313900 |
| H | 0.67454600 | 1.16343900 | 7.19663600 |
| C | 2.41103700 | -2.20303300 | 6.23242100 |
| H | 2.27804400 | -1.50915400 | 4.18345300 |
| C | 2.13927300 | -1.92499100 | 7.58516500 |
| H | 1.30429000 | -0.48497200 | 8.98949200 |
| H | 2.89196300 | -3.15234000 | 5.94891400 |
| H | 2.41303100 | -2.65250200 | 8.36549800 |
| N | 3.08858700 | 1.21006700 | 1.70773200 |
| N | 1.99506200 | 1.51428700 | 1.54435100 |

**Transition State of Metalloradical Activation (TS1)**
Imaginary Frequency: -383.97 $cm^{-1}$

Electronic energy in diisopropyl ether= -6924.592370
Thermal correction to Enthalpy= 1.778143
Enthalpy in diisopropyl ether= -6922.814227
Thermal correction to Gibbs Free Energy= 1.507801
Gibbs Free Energy in diisopropyl ether= -6923.084569

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|---|---|---|---|
| N | -0.67783100 | 0.81702700 | 2.91790300 |
| N | 1.93260900 | 2.23899000 | 0.41203300 |
| N | 2.06801800 | 0.47484600 | 2.51396800 |
| N | -0.71880700 | 2.84433600 | 1.06760100 |
| C | -0.60154700 | 3.70146300 | -0.01718700 |
| C | -1.96211700 | 3.13404500 | 1.62509400 |
| C | -2.02475100 | 1.14767600 | 3.04530600 |
| C | -0.53105200 | -0.35821600 | 3.65471100 |
| C | 1.90823300 | -0.48842900 | 3.50558500 |
| C | 3.43990700 | 0.50050200 | 2.26096500 |
| C | 3.27918900 | 1.90825100 | 0.27136200 |
| C | 1.62648800 | 2.98254500 | -0.72599600 |
| C | 2.76752000 | 3.05693900 | -1.61050900 |
| C | 0.43709400 | 3.67987700 | -0.95562900 |
| C | -1.74668400 | 4.57817800 | -0.10366700 |
| C | -2.63237200 | 2.30899000 | 2.54554300 |
| C | 3.80211700 | 2.41348000 | -0.98026600 |
| C | 4.04654200 | 1.15974200 | 1.18143000 |
| C | 4.14521000 | -0.37307000 | 3.17255100 |
| C | -2.73354100 | 0.13756300 | 3.80065400 |
| C | 0.68163300 | -0.96443100 | 3.98956100 |
| C | 3.19009300 | -1.00377300 | 3.93231800 |
| C | -2.57618800 | 4.25251200 | 0.94180700 |
| C | -1.80773500 | -0.80613700 | 4.16337500 |
| Co | 0.70779100 | 1.75812700 | 1.86504300 |
| C | 0.68238400 | -2.13036300 | 4.91672300 |
| C | 0.74427400 | -4.33955200 | 6.65364900 |
| C | 0.37702900 | -1.96924100 | 6.29288300 |
| C | 0.96666800 | -3.42657600 | 4.41724900 |
| C | 1.00336600 | -4.53719500 | 5.28876200 |
| C | 0.42533600 | -3.07488000 | 7.16975200 |
| C | -4.05829200 | 2.58236500 | 2.90605700 |
| C | -6.76234900 | 3.03592700 | 3.56363100 |
| C | -5.07972500 | 2.46078100 | 1.91813100 |
| C | -4.43498200 | 2.89059400 | 4.24771000 |
| C | -5.79379900 | 3.10808900 | 4.57022100 |
| C | -6.42916200 | 2.71762900 | 2.24148200 |
| C | 0.20024400 | 4.30312100 | -2.29350300 |
| C | -0.29771900 | 5.30827500 | -4.87967100 |

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|---|---|---|---|
| C | -0.58567200 | 3.56689000 | -3.21970900 |
| C | 0.74627100 | 5.54478900 | -2.69838100 |
| C | 0.48921300 | 6.05425400 | -3.99193400 |
| C | -0.83510400 | 4.06562900 | -4.51617200 |
| C | 5.49864900 | 0.94306900 | 0.87928200 |
| C | 8.17823600 | 0.56094800 | 0.08653400 |
| C | 6.43155300 | 2.01938100 | 0.93124200 |
| C | 5.95062600 | -0.33278900 | 0.42768900 |
| C | 7.29432300 | -0.52416200 | 0.04018700 |
| C | 7.76991500 | 1.82636900 | 0.52195200 |
| N | -4.70513300 | 2.00287800 | 0.63795100 |
| C | -5.48338700 | 1.91283300 | -0.49774200 |
| N | 5.00667100 | -1.37484500 | 0.35254800 |
| C | 5.20229800 | -2.69788100 | 0.01492400 |
| O | -6.63405100 | 2.34244200 | -0.59674900 |
| O | 6.27999600 | -3.19403100 | -0.31778900 |
| C | -4.82872000 | 1.16530100 | -1.63269800 |
| C | -5.76499800 | 0.14025700 | -2.29989300 |
| C | -5.36846500 | 1.41169600 | -3.01450700 |
| C | 3.93478800 | -3.51363400 | 0.04728300 |
| C | 3.70700200 | -4.37297200 | -1.20984200 |
| C | 4.07871200 | -5.00686100 | 0.10938000 |
| C | -5.26973400 | -1.19661500 | -2.73125100 |
| C | 2.30454700 | -4.47302200 | -1.69977800 |
| O | 2.28731500 | -4.46793100 | -3.05592200 |
| O | -3.99071800 | -1.16187400 | -3.21977700 |
| C | 1.00967000 | -4.50909900 | -3.72961900 |
| C | -3.51347500 | -2.42983400 | -3.72473000 |
| C | -2.12756100 | -2.24587000 | -4.32156500 |
| C | 0.90013500 | -3.30278700 | -4.66015800 |
| C | -1.66408900 | -3.51918600 | -5.04472500 |
| C | -0.25922000 | -3.42198500 | -5.66287200 |
| O | -5.92923700 | -2.21873200 | -2.67931600 |
| O | 1.30748700 | -4.53845400 | -0.99272400 |
| O | 1.16726000 | -3.50466800 | 3.07185800 |
| O | -1.04736700 | 2.36546800 | -2.76878600 |
| O | 1.52268400 | 6.18476000 | -1.78087600 |
| O | 0.03203200 | -0.71267300 | 6.67525200 |
| C | 1.21317600 | -4.79332700 | 2.46892900 |
| C | -0.39162300 | -0.48881100 | 8.01523200 |
| C | -1.71859000 | 1.51755000 | -3.68762300 |
| C | 2.13297900 | 7.40859200 | -2.15935400 |
| H | 0.31655300 | -5.39467900 | 2.73802200 |
| H | 1.23028200 | -5.54291400 | 4.91243800 |
| H | 0.78357000 | -5.20258100 | 7.33672400 |
| H | 0.21859700 | -2.95091500 | 8.24031800 |

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|---|---|---|---|
| H | 2.12515200 | -5.35456400 | 2.77392200 |
| H | 1.22512700 | -4.63070100 | 1.37408000 |
| H | -1.26376900 | -1.12910100 | 8.27285400 |
| H | 0.43586500 | -0.66196900 | 8.73545100 |
| H | -0.68939500 | 0.57356600 | 8.06582300 |
| H | 3.32046000 | -1.76522100 | 4.70898300 |
| H | 5.23350000 | -0.49972300 | 3.18927600 |
| H | -1.95227000 | -1.72764800 | 4.73698100 |
| H | -3.80924700 | 0.16237200 | 4.00648000 |
| H | -6.05770200 | 3.32209800 | 5.61187900 |
| H | -7.81711200 | 3.22287100 | 3.81931300 |
| H | -7.18569400 | 2.64326500 | 1.45292000 |
| H | -3.54512500 | 4.68637100 | 1.21274100 |
| H | -1.87737700 | 5.34583800 | -0.87422500 |
| H | -3.74003700 | 1.67002600 | 0.55960300 |
| H | 4.05391200 | -1.11680300 | 0.62465900 |
| H | 7.60638700 | -1.51713500 | -0.30155700 |
| H | 9.22399100 | 0.41265300 | -0.22526700 |
| H | 8.45559000 | 2.68050400 | 0.55096600 |
| H | 2.76251200 | 3.56233700 | -2.58197900 |
| H | 4.83177700 | 2.26523600 | -1.32328500 |
| H | -1.43845700 | 3.49761000 | -5.23547000 |
| H | -0.49428900 | 5.70583500 | -5.88759700 |
| H | 0.89955400 | 7.02114900 | -4.30891000 |
| H | -2.63426500 | 1.99799700 | -4.09591000 |
| H | -2.01632100 | 0.61076500 | -3.13111900 |
| H | -1.05642900 | 1.22838500 | -4.53467100 |
| H | 1.37758200 | 8.19398000 | -2.38493500 |
| H | 2.74126400 | 7.73278900 | -1.29585600 |
| H | 2.79867300 | 7.28093100 | -3.04183600 |
| H | -4.67111800 | 1.31483100 | -3.85852400 |
| H | -6.15252300 | 2.18059000 | -3.09464700 |
| H | -6.78428000 | 0.10387400 | -1.88723000 |
| H | -3.77171500 | 0.87366200 | -1.52930700 |
| H | 3.03048100 | -3.06636500 | 0.49277700 |
| H | 4.48814100 | -4.31181100 | -1.98190100 |
| H | 5.10977400 | -5.38561500 | 0.18158300 |
| H | 3.29333600 | -5.57100700 | 0.63170300 |
| H | -4.23591300 | -2.80346200 | -4.48252600 |
| H | 0.20717500 | -4.54189900 | -2.96543100 |
| H | 1.85689500 | -3.21032400 | -5.21696800 |
| H | 0.98686700 | -5.45666600 | -4.31072200 |
| H | 0.80816100 | -2.37793200 | -4.04949400 |
| H | -1.71284900 | -4.38250600 | -4.34333200 |
| H | -0.22569800 | -2.55089500 | -6.35376400 |
| H | -0.08736500 | -4.31840100 | -6.29949500 |

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|---|---|---|---|
| H | -3.51115700 | -3.17313900 | -2.89848700 |
| H | -2.39244100 | -3.75483200 | -5.85169000 |
| H | -2.14909700 | -1.39767500 | -5.04140700 |
| H | -1.41207500 | -1.96395100 | -3.51861900 |
| N | 5.98355700 | 3.25860600 | 1.41690200 |
| C | 6.61018300 | 4.48852000 | 1.32540100 |
| H | 5.12167400 | 3.24153200 | 1.98034000 |
| O | 7.67828300 | 4.69811200 | 0.74716500 |
| C | 5.84928500 | 5.58091000 | 2.02435100 |
| C | 6.68033900 | 6.53309300 | 2.89557200 |
| C | 6.08934800 | 6.99777600 | 1.58066400 |
| H | 4.85519800 | 5.34032200 | 2.42798800 |
| C | 6.10391700 | 7.01084800 | 4.18751100 |
| H | 7.76618600 | 6.35876700 | 2.92554700 |
| H | 5.23638600 | 7.69090100 | 1.62885500 |
| H | 6.80594400 | 7.13011600 | 0.75503400 |
| O | 4.74324300 | 7.07505800 | 4.12738100 |
| O | 6.75136600 | 7.32540900 | 5.16985300 |
| C | 4.07678400 | 7.62422900 | 5.28160500 |
| C | 2.59794200 | 7.75458400 | 4.94836600 |
| H | 4.53237600 | 8.61096900 | 5.51902900 |
| H | 4.25967100 | 6.96881900 | 6.16081500 |
| C | 1.86033400 | 8.66414400 | 5.93990800 |
| H | 2.50759200 | 8.17716900 | 3.92457100 |
| H | 2.13000900 | 6.74742500 | 4.89638300 |
| C | 0.35781000 | 8.81152500 | 5.63701500 |
| H | 2.00768400 | 8.29465900 | 6.98002400 |
| H | 2.33583800 | 9.66957500 | 5.91360800 |
| C | -0.51954800 | 7.63922100 | 6.10570000 |
| H | 0.22917900 | 8.94548200 | 4.54120600 |
| H | -0.02444200 | 9.74779500 | 6.10210000 |
| C | -0.70794200 | 7.62316700 | 7.62429700 |
| H | -1.52501900 | 7.70971600 | 5.63829800 |
| H | -0.08871700 | 6.66834100 | 5.77672100 |
| O | -1.70263400 | 6.64033700 | 7.99168800 |
| H | 0.23722100 | 7.39690800 | 8.15749600 |
| H | -1.11002900 | 8.59246700 | 7.98264000 |
| C | -1.25467500 | 5.39354800 | 8.27420300 |
| C | -2.39345700 | 4.43934700 | 8.34470300 |
| O | -0.06959900 | 5.10022100 | 8.37929200 |
| C | -2.29709500 | 3.29113000 | 7.31406300 |
| C | -2.18520600 | 3.01767300 | 8.78735300 |
| H | -3.39534400 | 4.88024200 | 8.45501400 |
| C | -3.58630300 | 3.00383200 | 6.59260100 |
| H | -1.37755300 | 3.28242300 | 6.71161800 |
| H | -3.05510600 | 2.53198000 | 9.25534200 |

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|---|---|---|---|
| H | -1.18788800 | 2.75325600 | 9.17090900 |
| N | -3.42897300 | 2.99573700 | 5.22078900 |
| O | -4.65089400 | 2.85168600 | 7.19628500 |
| H | -2.45569700 | 3.12520700 | 4.88316100 |
| C | 1.16108200 | 3.27021700 | 3.07628200 |
| C | 0.26610900 | 3.01977800 | 4.26138500 |
| C | 1.21561000 | 4.62989800 | 2.46850800 |
| C | 0.72416000 | 2.10361800 | 5.37176100 |
| O | -0.82959200 | 3.59955700 | 4.35424000 |
| C | 0.23416000 | 5.62574500 | 2.72958400 |
| C | 2.29375700 | 4.98898400 | 1.61970200 |
| C | 1.47837600 | 2.86938600 | 6.48379300 |
| H | -0.17324500 | 1.60901700 | 5.78960000 |
| H | 1.37794000 | 1.31262000 | 4.97246700 |
| C | 0.34382800 | 6.90960800 | 2.17842300 |
| H | -0.62521700 | 5.36944200 | 3.35748500 |
| C | 2.41829600 | 6.28204200 | 1.10583500 |
| H | 3.05167600 | 4.24522500 | 1.35445600 |
| C | 1.97705700 | 1.94814600 | 7.57860100 |
| H | 0.83703900 | 3.65623600 | 6.92736400 |
| H | 2.34619400 | 3.39367800 | 6.02910700 |
| C | 1.44280700 | 7.25437200 | 1.37683300 |
| H | -0.44485100 | 7.64938600 | 2.38726500 |
| H | 3.28614900 | 6.51441500 | 0.47217500 |
| C | 1.71878900 | 2.24638000 | 8.93320200 |
| C | 2.71218700 | 0.78272800 | 7.27046000 |
| H | 1.53136100 | 8.26967000 | 0.95926000 |
| C | 2.17462900 | 1.39425500 | 9.95509400 |
| H | 1.16187100 | 3.16644500 | 9.17336400 |
| C | 3.16277000 | -0.07192100 | 8.28793400 |
| H | 2.93011800 | 0.53510200 | 6.21962600 |
| C | 2.89271400 | 0.22874600 | 9.63638200 |
| H | 1.96571400 | 1.64355800 | 11.00775700 |
| H | 3.72818300 | -0.98062700 | 8.02726800 |
| H | 3.24709900 | -0.44173600 | 10.43524800 |
| N | 3.76332700 | 3.26214000 | 3.36907700 |
| N | 2.73805600 | 2.90402700 | 3.76563800 |

**Intermediate C**

Electronic energy in diisopropyl ether= -6815.049480
Thermal correction to Enthalpy= 1.769054
Enthalpy in diisopropyl ether= -6813.280426
Thermal correction to Gibbs Free Energy= 1.500541
Gibbs Free Energy in diisopropyl ether= -6813.548939

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|---|---|---|---|
| N | -0.68629400 | 0.82875400 | 2.89741800 |
| N | 1.93525900 | 2.12915200 | 0.34172400 |
| N | 2.04034600 | 0.48167100 | 2.52770300 |
| N | -0.74661100 | 2.68689600 | 0.88215200 |
| C | -0.62422600 | 3.46242300 | -0.25685400 |
| C | -1.95402000 | 3.07086600 | 1.46714300 |
| C | -1.99937300 | 1.24365500 | 3.08842700 |
| C | -0.56541300 | -0.34181700 | 3.64393300 |
| C | 1.86082800 | -0.53647900 | 3.45439700 |
| C | 3.42109100 | 0.59427500 | 2.37626900 |
| C | 3.30142100 | 1.87025200 | 0.29598800 |
| C | 1.64726800 | 2.77771800 | -0.85646200 |
| C | 2.82819200 | 2.84305400 | -1.69155600 |
| C | 0.44163700 | 3.41511200 | -1.16858700 |
| C | -1.75412700 | 4.35592300 | -0.38725400 |
| C | -2.58899100 | 2.38243000 | 2.51525600 |
| C | 3.86226900 | 2.31034600 | -0.96425200 |
| C | 4.05201300 | 1.24057600 | 1.30190000 |
| C | 4.10834600 | -0.30328300 | 3.28139000 |
| C | -2.71550400 | 0.30561400 | 3.92714800 |
| C | 0.62807900 | -1.01216400 | 3.91888500 |
| C | 3.13603000 | -1.03378700 | 3.92149700 |
| C | -2.56006700 | 4.14208400 | 0.70417600 |
| C | -1.83255700 | -0.69377900 | 4.24545300 |
| Co | 0.68401000 | 1.68046900 | 1.77343200 |
| C | 0.61693200 | -2.20137300 | 4.81417400 |
| C | 0.63866700 | -4.44758500 | 6.49558100 |
| C | 0.42897300 | -2.04857600 | 6.21050200 |
| C | 0.80170200 | -3.49591400 | 4.27041000 |
| C | 0.81114700 | -4.62850800 | 5.11433100 |
| C | 0.44591800 | -3.17710800 | 7.05928300 |
| C | -3.97799100 | 2.74038400 | 2.93347700 |
| C | -6.62131100 | 3.29397200 | 3.74638700 |
| C | -5.06768500 | 2.59007500 | 2.02338700 |
| C | -4.25688500 | 3.12034700 | 4.27780200 |
| C | -5.58291200 | 3.39415500 | 4.67833300 |
| C | -6.38560000 | 2.89525500 | 2.42422100 |
| C | 0.25466200 | 4.05569300 | -2.50263600 |
| C | -0.17718700 | 5.19043700 | -5.04786500 |
| C | -0.64609900 | 3.45435600 | -3.42182100 |
| C | 0.93848700 | 5.23570000 | -2.89102300 |
| C | 0.72099600 | 5.80611600 | -4.16557900 |
| C | -0.86331900 | 4.01926300 | -4.69718900 |
| C | 5.51974400 | 1.03328800 | 1.08260500 |
| C | 8.24521900 | 0.64036700 | 0.52148400 |

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|---|---|---|---|
| C | 6.45926000 | 2.06866200 | 1.32859400 |
| C | 5.97913500 | -0.21267200 | 0.56766400 |
| C | 7.34743900 | -0.40876200 | 0.28343500 |
| C | 7.82897400 | 1.87239100 | 1.04128200 |
| N | -4.78975000 | 2.05515900 | 0.74920800 |
| C | -5.64498200 | 1.88288100 | -0.31895200 |
| N | 5.01601100 | -1.21725300 | 0.36036000 |
| C | 5.19703000 | -2.52330800 | -0.04546600 |
| O | -6.81903300 | 2.25593100 | -0.34986300 |
| O | 6.27354900 | -3.01410600 | -0.38848400 |
| C | -5.02850300 | 1.13463500 | -1.47555700 |
| C | -5.94314700 | 0.04739300 | -2.06787700 |
| C | -5.66448300 | 1.32570800 | -2.82528600 |
| C | 3.91953900 | -3.32473000 | -0.05254300 |
| C | 3.70030800 | -4.17987900 | -1.31248000 |
| C | 4.04982400 | -4.82034000 | 0.00992400 |
| C | -5.39489400 | -1.26495400 | -2.51217400 |
| C | 2.30129600 | -4.27866200 | -1.81404100 |
| O | 2.29020900 | -4.28459900 | -3.17009400 |
| O | -4.15047900 | -1.16035200 | -3.07559400 |
| C | 1.01190700 | -4.35047400 | -3.84179800 |
| C | -3.62262400 | -2.40254000 | -3.59559500 |
| C | -2.27400300 | -2.14050600 | -4.24675900 |
| C | 0.80164600 | -3.08216100 | -4.66687700 |
| C | -1.76274000 | -3.38148300 | -4.99338600 |
| C | -0.38039100 | -3.19858700 | -5.64391500 |
| O | -5.98641500 | -2.32404300 | -2.41091200 |
| O | 1.29988200 | -4.34184700 | -1.11288200 |
| O | 0.94974500 | -3.54288600 | 2.91699700 |
| O | -1.25148200 | 2.31217900 | -2.98878600 |
| O | 1.79419100 | 5.75805500 | -1.97109800 |
| O | 0.23269400 | -0.77329600 | 6.63469800 |
| C | 0.98079900 | -4.81453600 | 2.27917400 |
| C | -0.03648300 | -0.53854300 | 8.01189600 |
| C | -2.12337400 | 1.63507400 | -3.88057400 |
| C | 2.56940700 | 6.88739600 | -2.33946800 |
| H | 0.06511800 | -5.40377900 | 2.50910400 |
| H | 0.95034100 | -5.63754500 | 4.70549700 |
| H | 0.65148000 | -5.32908300 | 7.15576200 |
| H | 0.31340200 | -3.06788300 | 8.14324800 |
| H | 1.87204900 | -5.40513100 | 2.59089300 |
| H | 1.02804000 | -4.61856200 | 1.19089500 |
| H | -0.95734300 | -1.06998800 | 8.33855000 |
| H | 0.82269500 | -0.83609200 | 8.64945200 |
| H | -0.18486800 | 0.55093100 | 8.10897600 |
| H | 3.24941700 | -1.83947900 | 4.65506700 |

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|---|---|---|---|
| H | 5.19804900 | -0.38821400 | 3.36098900 |
| H | -1.99881100 | -1.59101700 | 4.85090500 |
| H | -3.76933200 | 0.40553300 | 4.20914500 |
| H | -5.77724300 | 3.66704500 | 5.72166400 |
| H | -7.65173800 | 3.52168400 | 4.06102700 |
| H | -7.19627900 | 2.78839100 | 1.69501300 |
| H | -3.50342600 | 4.63336100 | 0.96737000 |
| H | -1.88393400 | 5.06965400 | -1.20804000 |
| H | -3.82647200 | 1.73573300 | 0.61496200 |
| H | 4.05955000 | -0.95383100 | 0.61401500 |
| H | 7.67001200 | -1.37579600 | -0.11843900 |
| H | 9.31298600 | 0.49001500 | 0.29774200 |
| H | 8.53043500 | 2.69230500 | 1.22955700 |
| H | 2.84756400 | 3.26705200 | -2.70080900 |
| H | 4.91551800 | 2.19442100 | -1.24368900 |
| H | -1.55445000 | 3.55522100 | -5.41201700 |
| H | -0.34639600 | 5.63632900 | -6.04045500 |
| H | 1.24067800 | 6.72381400 | -4.46843300 |
| H | -2.97885200 | 2.27882300 | -4.18315100 |
| H | -2.51255700 | 0.75232600 | -3.34172700 |
| H | -1.58829800 | 1.29602100 | -4.79625500 |
| H | 1.93259600 | 7.77786800 | -2.53950500 |
| H | 3.22813500 | 7.10216000 | -1.47951900 |
| H | 3.19605400 | 6.68062000 | -3.23559300 |
| H | -5.01638900 | 1.25528200 | -3.70996500 |
| H | -6.49467500 | 2.04790600 | -2.86598600 |
| H | -6.93208800 | -0.04132100 | -1.59374600 |
| H | -3.95198100 | 0.90368500 | -1.43476300 |
| H | 3.01203100 | -2.87632300 | 0.38530600 |
| H | 4.49037800 | -4.12452700 | -2.07591200 |
| H | 5.07596100 | -5.20947500 | 0.09556900 |
| H | 3.25161300 | -5.37504700 | 0.52318400 |
| H | -4.35226700 | -2.81950400 | -4.32347100 |
| H | 0.22061600 | -4.50132000 | -3.08046100 |
| H | 1.73291700 | -2.88431300 | -5.23926800 |
| H | 1.05365700 | -5.24392800 | -4.50115000 |
| H | 0.66983700 | -2.21700400 | -3.98071000 |
| H | -1.74679100 | -4.25318800 | -4.30109600 |
| H | -0.40172900 | -2.29416700 | -6.29106300 |
| H | -0.19057000 | -4.05457500 | -6.32926700 |
| H | -3.54550700 | -3.13997600 | -2.76788800 |
| H | -2.49763200 | -3.64763000 | -5.78473600 |
| H | -2.37315300 | -1.29618100 | -4.96403400 |
| H | -1.54585300 | -1.81513100 | -3.47215700 |
| N | 5.96937700 | 3.26896300 | 1.87524000 |
| C | 6.64652400 | 4.46077600 | 2.07289300 |

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|---|---|---|---|
| H | 4.98435900 | 3.24897400 | 2.15703000 |
| O | 7.83179400 | 4.64255100 | 1.79142500 |
| C | 5.79146700 | 5.54942000 | 2.65591100 |
| C | 6.49309200 | 6.51723600 | 3.61167300 |
| C | 6.10968400 | 6.95774700 | 2.21461100 |
| H | 4.73906100 | 5.32886500 | 2.89076400 |
| C | 5.74216300 | 7.08775400 | 4.77079100 |
| H | 7.56079200 | 6.33315500 | 3.80260300 |
| H | 5.26289500 | 7.65376000 | 2.12022400 |
| H | 6.93809700 | 7.06634300 | 1.49739100 |
| O | 4.40322600 | 7.10642400 | 4.52185800 |
| O | 6.25173800 | 7.52589800 | 5.78572300 |
| C | 3.58564400 | 7.84374700 | 5.45422300 |
| C | 2.12994900 | 7.69043900 | 5.03604200 |
| H | 3.90568900 | 8.90979500 | 5.42568400 |
| H | 3.77735100 | 7.47877600 | 6.48545200 |
| C | 1.26283800 | 8.81793500 | 5.61225000 |
| H | 2.07288000 | 7.70628100 | 3.92641900 |
| H | 1.75195700 | 6.69329200 | 5.34759400 |
| C | -0.23963700 | 8.66277600 | 5.32806700 |
| H | 1.43428100 | 8.90195300 | 6.70958500 |
| H | 1.61155800 | 9.78558100 | 5.18737300 |
| C | -0.91512100 | 7.48030500 | 6.03841200 |
| H | -0.38961100 | 8.55197400 | 4.23189000 |
| H | -0.76069100 | 9.60343400 | 5.61620400 |
| C | -0.83413400 | 7.57105300 | 7.56389700 |
| H | -1.98849100 | 7.44043800 | 5.75436700 |
| H | -0.47504300 | 6.51452500 | 5.70660700 |
| O | -1.65783600 | 6.53476600 | 8.14309600 |
| H | 0.20385700 | 7.45544700 | 7.93481800 |
| H | -1.25300100 | 8.52794300 | 7.93652900 |
| C | -1.06559100 | 5.32882000 | 8.33037700 |
| C | -2.10579100 | 4.27135400 | 8.43265500 |
| O | 0.14504700 | 5.14548200 | 8.30143500 |
| C | -1.98488500 | 3.26718600 | 7.26119700 |
| C | -1.75388700 | 2.83327200 | 8.68062200 |
| H | -3.12844600 | 4.60973400 | 8.65596000 |
| C | -3.27759300 | 2.97625800 | 6.55684100 |
| H | -1.10870500 | 3.43094600 | 6.61698200 |
| H | -2.54686000 | 2.22157500 | 9.13744700 |
| H | -0.71461800 | 2.61105200 | 8.96742600 |
| N | -3.19624700 | 3.22312000 | 5.19572600 |
| O | -4.29540200 | 2.61429300 | 7.14907400 |
| H | -2.25689900 | 3.46878000 | 4.83355700 |
| C | 0.92751700 | 3.22497700 | 2.84114700 |
| C | 0.34961500 | 3.15417100 | 4.18656600 |

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|---|---|---|---|
| C | 1.15671900 | 4.53288200 | 2.21461400 |
| C | 0.87987600 | 2.17522400 | 5.20437200 |
| O | -0.50676100 | 4.00557400 | 4.53871200 |
| C | 0.19127000 | 5.57867200 | 2.25950700 |
| C | 2.39848300 | 4.81582500 | 1.59025000 |
| C | 1.81706000 | 2.92516000 | 6.18450700 |
| H | 0.03764700 | 1.71601800 | 5.76116700 |
| H | 1.43510700 | 1.36090700 | 4.71610400 |
| C | 0.47278200 | 6.83839200 | 1.71331200 |
| H | -0.77663100 | 5.38107800 | 2.73224500 |
| C | 2.68215900 | 6.08043800 | 1.06663300 |
| H | 3.15206900 | 4.02106000 | 1.52509300 |
| C | 2.32368500 | 2.03451800 | 7.29929500 |
| H | 1.28808500 | 3.79666200 | 6.62101500 |
| H | 2.67596300 | 3.33012800 | 5.60299900 |
| C | 1.71982400 | 7.10307700 | 1.12305600 |
| H | -0.29878100 | 7.62386000 | 1.74957500 |
| H | 3.66733300 | 6.26041700 | 0.61084400 |
| C | 2.09683700 | 2.38126700 | 8.64831700 |
| C | 3.01885200 | 0.83922100 | 7.01574100 |
| H | 1.93667800 | 8.09827900 | 0.70425800 |
| C | 2.55348200 | 1.55105500 | 9.68808100 |
| H | 1.56147700 | 3.31874600 | 8.87034100 |
| C | 3.47279800 | 0.00851900 | 8.05147600 |
| H | 3.20281100 | 0.55110400 | 5.96928000 |
| C | 3.24071700 | 0.36079200 | 9.39429400 |
| H | 2.37183700 | 1.83942800 | 10.73584700 |
| H | 4.01117100 | -0.92179600 | 7.80943600 |
| H | 3.59941900 | -0.28931200 | 10.20805200 |

**Transition State of Hydrogen Atom Abstraction (TS2)**

Imaginary Frequency: -1363.70 $cm^{-1}$

Electronic energy in diisopropyl ether= -6815.033532

Thermal correction to Enthalpy= 1.762687

Enthalpy in diisopropyl ether= -6813.270845

Thermal correction to Gibbs Free Energy= 1.495070

Gibbs Free Energy in diisopropyl ether= -6813.538462

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|---|---|---|---|
| N | -0.31844000 | -1.18247900 | 1.88521200 |
| N | 0.92381100 | 0.29743900 | -1.52994100 |
| N | 0.52473200 | 1.34070200 | 1.02424800 |
| N | -0.26289600 | -2.10614100 | -0.73351300 |
| C | -0.05424200 | -2.44586700 | -2.06475300 |
| C | -0.95279300 | -3.18491200 | -0.18836400 |
| C | -0.70686400 | -2.49108600 | 2.14687400 |

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|---|---|---|---|
| C | -0.23200000 | -0.58334600 | 3.13665000 |
| C | 0.35815200 | 1.66280100 | 2.36479000 |
| C | 0.93887300 | 2.52707900 | 0.42516700 |
| C | 1.44824400 | 1.56349700 | -1.77265800 |
| C | 1.16031200 | -0.41695200 | -2.69735400 |
| C | 1.86524600 | 0.39722900 | -3.66500000 |
| C | 0.72128100 | -1.71638600 | -2.97473200 |
| C | -0.67408800 | -3.71729100 | -2.36776300 |
| C | -1.10341300 | -3.42940700 | 1.18501500 |
| C | 2.04091700 | 1.63098400 | -3.09333200 |
| C | 1.41679800 | 2.65401500 | -0.88825000 |
| C | 0.99442100 | 3.60281000 | 1.39213700 |
| C | -0.77411800 | -2.73427000 | 3.57353400 |
| C | 0.02735000 | 0.76594400 | 3.38194700 |
| C | 0.64871000 | 3.05981100 | 2.60175300 |
| C | -1.26961200 | -4.15687700 | -1.21375100 |
| C | -0.49341200 | -1.54198000 | 4.18889500 |
| C | 0.00157600 | 1.25419100 | 4.78941500 |
| C | -0.01401700 | 2.12604400 | 7.45500900 |
| C | -1.21290400 | 1.62541100 | 5.40910500 |
| C | 1.20922000 | 1.31098800 | 5.52665800 |
| C | 1.20479300 | 1.74874600 | 6.86937200 |
| C | -1.22608400 | 2.07207800 | 6.74809600 |
| C | -1.64107800 | -4.75163700 | 1.62419700 |
| C | -2.66384700 | -7.28084700 | 2.31383600 |
| C | -0.91271000 | -5.93350100 | 1.33020200 |
| C | -2.87595600 | -4.85765500 | 2.32364400 |
| C | -3.37835500 | -6.12954100 | 2.67653600 |
| C | -1.43318200 | -7.20213400 | 1.64565800 |
| C | 1.21760100 | -2.38466100 | -4.21549400 |
| C | 2.27758300 | -3.68639500 | -6.48501500 |
| C | 2.59424900 | -2.72968800 | -4.28266800 |
| C | 0.38397500 | -2.71628400 | -5.31098100 |
| C | 0.91331200 | -3.36648400 | -6.44881900 |
| C | 3.12940700 | -3.37838300 | -5.41471200 |
| C | 2.07855900 | 3.93737700 | -1.29126900 |
| C | 3.39044200 | 6.29715200 | -2.08939300 |
| C | 1.48952800 | 4.80380900 | -2.24970800 |
| C | 3.33594700 | 4.29414200 | -0.72560700 |
| C | 3.99297400 | 5.47768500 | -1.12563400 |
| C | 2.14975800 | 5.98295200 | -2.65907700 |
| N | 0.37049700 | -5.78256500 | 0.75835000 |
| C | 0.85429100 | -6.46194400 | -0.34718400 |
| N | 3.87826900 | 3.42460000 | 0.23777500 |
| C | 4.94421400 | 3.63009600 | 1.08874100 |
| O | 0.28360200 | -7.41226000 | -0.87761200 |

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|---|---|---|---|
| O | 5.70181800 | 4.60101300 | 1.05199100 |
| C | 2.15931300 | -5.89616800 | -0.83601900 |
| C | 3.05067100 | -6.83107400 | -1.66035100 |
| C | 2.35519700 | -5.65895600 | -2.31181800 |
| C | 5.12967000 | 2.51165900 | 2.08266000 |
| C | 6.58064100 | 2.01288200 | 2.21912300 |
| C | 5.92711200 | 2.80468000 | 3.32228500 |
| C | 4.50623900 | -6.87586100 | -1.34913700 |
| C | 6.75851600 | 0.53960100 | 2.35774600 |
| O | 7.77794900 | 0.13179900 | 1.56123100 |
| O | 5.02733800 | -5.63149700 | -1.09518400 |
| C | 8.07137400 | -1.27918600 | 1.46202300 |
| C | 6.35855700 | -5.62960600 | -0.53631700 |
| C | 6.96566400 | -4.24027600 | -0.65337900 |
| C | 8.46868100 | -1.55413000 | 0.01386200 |
| C | 8.28899100 | -4.15204500 | 0.12372700 |
| C | 9.14098700 | -2.91680300 | -0.20966200 |
| O | 5.16195100 | -7.89914100 | -1.27635800 |
| O | 6.07975200 | -0.20366800 | 3.05266600 |
| O | 2.31640600 | 0.90804900 | 4.84492500 |
| O | 3.32940200 | -2.41376200 | -3.17625500 |
| O | -0.93044700 | -2.37963400 | -5.18084200 |
| O | -2.32917100 | 1.51039500 | 4.62645200 |
| C | 3.55090300 | 0.79198000 | 5.54003700 |
| C | -3.60659100 | 1.77767000 | 5.19744600 |
| C | 4.73343800 | -2.62541600 | -3.20198200 |
| C | -1.83502800 | -2.81866300 | -6.18108700 |
| H | 3.46952800 | 0.08676300 | 6.39732300 |
| H | 2.13357100 | 1.79659900 | 7.45285900 |
| H | -0.02060300 | 2.47234000 | 8.50041900 |
| H | -2.16174000 | 2.37272300 | 7.23702600 |
| H | 3.90063600 | 1.77826900 | 5.92083300 |
| H | 4.28313700 | 0.39813600 | 4.80873800 |
| H | -3.78450900 | 1.14206100 | 6.09254500 |
| H | -3.70857600 | 2.84736800 | 5.48587700 |
| H | -4.35359100 | 1.53120800 | 4.41830000 |
| H | 0.58487900 | 3.54615600 | 3.58032000 |
| H | 1.26487900 | 4.63675100 | 1.15446700 |
| H | -0.45639400 | -1.30996000 | 5.25874800 |
| H | -1.02123200 | -3.70061400 | 4.02696700 |
| H | -4.32133300 | -6.18752800 | 3.23264100 |
| H | -3.07310200 | -8.26915400 | 2.57532400 |
| H | -0.86365300 | -8.10121900 | 1.37855000 |
| H | -1.82089400 | -5.08833900 | -1.04541200 |
| H | -0.65276900 | -4.20125400 | -3.34816100 |
| H | 0.82447900 | -4.88660600 | 0.95796000 |

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|---|---|---|---|
| H | 3.31877600 | 2.58506200 | 0.41463400 |
| H | 4.95722600 | 5.72581900 | -0.66784400 |
| H | 3.90541400 | 7.21793700 | -2.40526900 |
| H | 1.67143400 | 6.62285200 | -3.40902500 |
| H | 2.16456900 | 0.05281200 | -4.66081300 |
| H | 2.52735500 | 2.52021700 | -3.50938200 |
| H | 4.19075600 | -3.65475500 | -5.45827600 |
| H | 2.68779100 | -4.19437900 | -7.37166300 |
| H | 0.27196000 | -3.61865500 | -7.30278800 |
| H | 4.98563900 | -3.70835400 | -3.24236700 |
| H | 5.12099900 | -2.20884000 | -2.25424300 |
| H | 5.21132300 | -2.09844700 | -4.05729700 |
| H | -1.79659800 | -3.92308400 | -6.31345400 |
| H | -2.84200500 | -2.53136900 | -5.83059700 |
| H | -1.63751300 | -2.33054100 | -7.16203100 |
| H | 2.94251800 | -4.77221900 | -2.58323800 |
| H | 1.51252600 | -5.90491900 | -2.97527100 |
| H | 2.61460800 | -7.82444200 | -1.84572600 |
| H | 2.68783300 | -5.19794000 | -0.16784600 |
| H | 4.34704600 | 1.73831800 | 2.15798000 |
| H | 7.31806100 | 2.53137700 | 1.58869200 |
| H | 6.27520600 | 3.84271000 | 3.43647200 |
| H | 5.65218700 | 2.25791600 | 4.23509800 |
| H | 6.97333000 | -6.39394300 | -1.05556100 |
| H | 7.18709800 | -1.85772100 | 1.80068300 |
| H | 9.16891200 | -0.75059700 | -0.29925700 |
| H | 8.91155500 | -1.50359800 | 2.15662300 |
| H | 7.57076900 | -1.44451900 | -0.63329200 |
| H | 8.07506200 | -4.19155100 | 1.21563300 |
| H | 9.45613800 | -2.97682700 | -1.27483700 |
| H | 10.08081900 | -2.95855400 | 0.38491200 |
| H | 6.28789900 | -5.94364500 | 0.52975600 |
| H | 8.89686100 | -5.05921500 | -0.09067300 |
| H | 7.13898000 | -4.00425400 | -1.72697600 |
| H | 6.23820900 | -3.48939500 | -0.27558400 |
| N | 0.22313300 | 4.44064100 | -2.73844600 |
| C | -0.55974000 | 5.07734500 | -3.67989400 |
| H | -0.19450700 | 3.63452400 | -2.26313100 |
| O | -0.22141300 | 6.07233300 | -4.32300400 |
| C | -1.92350800 | 4.46006100 | -3.81984500 |
| C | -3.08839600 | 5.45879400 | -3.79520800 |
| C | -2.70941700 | 4.73156100 | -5.07070900 |
| H | -2.11933600 | 3.50448700 | -3.31072000 |
| C | -4.34867600 | 5.11886500 | -3.07324300 |
| H | -2.81881300 | 6.52420300 | -3.74109200 |
| H | -3.38281800 | 3.93565000 | -5.42241800 |

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|---|---|---|---|
| H | -2.20683300 | 5.34153000 | -5.83731500 |
| O | -4.49733600 | 3.76898400 | -2.93576500 |
| O | -5.16252100 | 5.93056400 | -2.67354800 |
| C | -5.75651000 | 3.33318000 | -2.38196200 |
| C | -5.75916800 | 1.81402300 | -2.32845500 |
| H | -6.57619700 | 3.71873000 | -3.02801100 |
| H | -5.89516000 | 3.79454500 | -1.38061600 |
| C | -7.17853700 | 1.26230100 | -2.14693700 |
| H | -5.31841900 | 1.41701600 | -3.26743500 |
| H | -5.09002500 | 1.46156900 | -1.51400700 |
| C | -7.22596100 | -0.25480900 | -1.90712500 |
| H | -7.68741400 | 1.79448500 | -1.31104500 |
| H | -7.77261600 | 1.50774300 | -3.05483200 |
| C | -6.75705900 | -0.70903800 | -0.51683100 |
| H | -6.60717000 | -0.76165300 | -2.67914600 |
| H | -8.26762000 | -0.61492400 | -2.06173000 |
| C | -7.62481200 | -0.15531000 | 0.61836600 |
| H | -6.80495400 | -1.81729400 | -0.46054200 |
| H | -5.69295700 | -0.44202700 | -0.33878000 |
| O | -7.46386800 | -0.98513100 | 1.78865000 |
| H | -7.37516000 | 0.89260300 | 0.88006700 |
| H | -8.70175800 | -0.21863900 | 0.35754800 |
| C | -6.61039000 | -0.57714500 | 2.75766400 |
| C | -6.32119700 | -1.71211500 | 3.67110800 |
| O | -6.10157300 | 0.53799000 | 2.81113000 |
| C | -4.80740900 | -1.99967300 | 3.79600500 |
| C | -5.59662800 | -1.52266600 | 4.97635900 |
| H | -6.96558500 | -2.59606600 | 3.55576400 |
| C | -4.42925000 | -3.45165800 | 3.67820900 |
| H | -4.16089000 | -1.27744600 | 3.27361600 |
| H | -5.81079700 | -2.27650600 | 5.74953200 |
| H | -5.42353000 | -0.49082400 | 5.31322200 |
| N | -3.55398700 | -3.66832600 | 2.63307700 |
| O | -4.88551600 | -4.32425900 | 4.41902100 |
| H | -3.28391000 | -2.83006300 | 2.09379000 |
| Co | 0.04136300 | -0.36043600 | 0.12343100 |
| C | -1.77242200 | 0.17760600 | -0.32417700 |
| C | -2.25104900 | -0.03017200 | -1.71150900 |
| C | -2.77349300 | -0.12359100 | 0.76031000 |
| C | -1.83544700 | 0.85090200 | -2.73998800 |
| C | -3.16783300 | -1.06029000 | -2.04069200 |
| C | -3.20706900 | 1.16729100 | 1.43744200 |
| O | -3.20931100 | -1.24625900 | 1.03446600 |
| C | -2.34899000 | 0.74493500 | -4.03618100 |
| H | -1.09870200 | 1.62976400 | -2.49638700 |
| C | -3.67101100 | -1.17452000 | -3.34465200 |

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|---|---|---|---|
| H | -3.47315800 | -1.76875700 | -1.25765800 |
| H | -2.60318600 | 1.25812300 | 2.36942000 |
| C | -2.85712700 | 2.24794600 | 0.43514200 |
| H | -4.27139000 | 1.11918900 | 1.74786200 |
| H | -2.01963600 | 1.45090300 | -4.81360500 |
| C | -3.28218500 | -0.26206200 | -4.34011600 |
| H | -4.38178300 | -1.98258000 | -3.58023100 |
| C | -2.39543100 | 3.58745800 | 0.82336600 |
| H | -3.52751000 | 2.26737200 | -0.44631600 |
| H | -3.69782700 | -0.33596100 | -5.35709100 |
| C | -2.21620100 | 3.98067900 | 2.17206500 |
| C | -2.11634600 | 4.53702600 | -0.19454900 |
| C | -1.79766200 | 5.28313200 | 2.48343500 |
| H | -2.40369900 | 3.25857000 | 2.97935100 |
| C | -1.65589500 | 5.82025600 | 0.11560200 |
| H | -2.28427500 | 4.24892400 | -1.24205300 |
| C | -1.50108300 | 6.20342000 | 1.46329800 |
| H | -1.68059300 | 5.57588800 | 3.53893900 |
| H | -1.43125900 | 6.53202600 | -0.69401100 |
| H | -1.15397500 | 7.21785200 | 1.71344100 |
| H | -1.86463200 | 1.56579400 | -0.11080000 |

**Intermediate D**

Electronic energy in diisopropyl ether= -6815.072258
Thermal correction to Enthalpy= 1.768466
Enthalpy in diisopropyl ether= -6813.303792
Thermal correction to Gibbs Free Energy= 1.500612
Gibbs Free Energy in diisopropyl ether= -6813.571646

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|---|---|---|---|
| N | -0.94884500 | 1.10970200 | 1.58184200 |
| N | -0.19881900 | -1.39109600 | -1.33082500 |
| N | -0.29527100 | -1.59857600 | 1.41852400 |
| N | -0.62505600 | 1.36178300 | -1.13377800 |
| C | -0.64533800 | 1.27175300 | -2.51795500 |
| C | -0.64157700 | 2.72827100 | -0.86056300 |
| C | -1.10797200 | 2.49104500 | 1.52502800 |
| C | -1.28028500 | 0.77078500 | 2.89392000 |
| C | -0.63048100 | -1.58523200 | 2.76917100 |
| C | 0.19857500 | -2.88096600 | 1.18887200 |
| C | 0.17464500 | -2.73007900 | -1.25332700 |
| C | -0.42093600 | -1.15906600 | -2.68378000 |
| C | -0.25237300 | -2.37846000 | -3.44608400 |
| C | -0.67239900 | 0.08753700 | -3.26538000 |
| C | -0.63309600 | 2.58762800 | -3.11911100 |

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|---|---|---|---|
| C | -0.87488800 | 3.29764000 | 0.40136500 |
| C | 0.15156800 | -3.34722500 | -2.56347600 |
| C | 0.44291300 | -3.44026900 | -0.07490100 |
| C | 0.20571800 | -3.65769200 | 2.41108000 |
| C | -1.56694800 | 3.01239700 | 2.79446600 |
| C | -1.14390600 | -0.49198500 | 3.47332900 |
| C | -0.33726300 | -2.85999100 | 3.38558200 |
| C | -0.58930900 | 3.49383400 | -2.08967700 |
| C | -1.68325400 | 1.94065200 | 3.64169500 |
| Co | -0.35104100 | -0.09976000 | 0.13508600 |
| C | -1.44555800 | -0.65172300 | 4.92416300 |
| C | -1.98592700 | -0.90102500 | 7.66677000 |
| C | -0.38354500 | -0.69679600 | 5.85976800 |
| C | -2.78144600 | -0.72864500 | 5.38309100 |
| C | -3.05824500 | -0.85186500 | 6.76197300 |
| C | -0.65036400 | -0.82805100 | 7.23945400 |
| C | -1.02231200 | 4.78030100 | 0.54670100 |
| C | -1.37491800 | 7.55677800 | 0.87368900 |
| C | -2.14665000 | 5.44342000 | -0.02463200 |
| C | -0.09618700 | 5.53959400 | 1.32163600 |
| C | -0.28454100 | 6.93077400 | 1.48776000 |
| C | -2.30944600 | 6.83801500 | 0.11751800 |
| C | -1.04099500 | 0.17213100 | -4.70845100 |
| C | -1.85785900 | 0.33307300 | -7.40043700 |
| C | -2.39093100 | 0.46528400 | -5.03898400 |
| C | -0.11463700 | -0.05567600 | -5.75532100 |
| C | -0.52109900 | 0.02982700 | -7.10609000 |
| C | -2.80292700 | 0.54705200 | -6.38670700 |
| C | 0.64548700 | -4.92531300 | -0.13270900 |
| C | 0.90858200 | -7.71859300 | 0.00108800 |
| C | 1.90488400 | -5.53113300 | -0.36653600 |
| C | -0.48163100 | -5.74804700 | 0.13774500 |
| C | -0.35383400 | -7.14589000 | 0.22009200 |
| C | 2.03335700 | -6.93847500 | -0.30266600 |
| N | -3.11186200 | 4.64949400 | -0.67840600 |
| C | -4.16846600 | 5.06163400 | -1.46234300 |
| N | -1.71074300 | -5.08704400 | 0.34988300 |
| C | -2.56257200 | -5.29681100 | 1.42642900 |
| O | -4.40635600 | 6.23354400 | -1.76085500 |
| O | -2.59388600 | -6.32698800 | 2.09386600 |
| C | -5.07327000 | 3.94121900 | -1.91319600 |
| C | -6.56765000 | 4.29703100 | -1.84736400 |
| C | -5.85854000 | 4.17344100 | -3.17662300 |
| C | -3.41681000 | -4.09387600 | 1.71341000 |
| C | -4.81921400 | -4.33829900 | 2.29210400 |
| C | -3.72242800 | -3.77156700 | 3.15348000 |

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|---|---|---|---|
| C | -7.58983100 | 3.30427600 | -1.41376300 |
| C | -5.87335200 | -3.44281700 | 1.73891300 |
| O | -6.91847300 | -4.17537300 | 1.27383700 |
| O | -7.28330500 | 2.02190900 | -1.78378700 |
| C | -7.90491900 | -3.46290800 | 0.49460400 |
| C | -8.31146800 | 1.05380500 | -1.47224700 |
| C | -7.80445400 | -0.35070600 | -1.75721400 |
| C | -7.47704300 | -3.42032700 | -0.97280600 |
| C | -8.94366300 | -1.37235700 | -1.61179000 |
| C | -8.54371300 | -2.82773500 | -1.90656500 |
| O | -8.60911300 | 3.59506700 | -0.81396300 |
| O | -5.80004900 | -2.22340900 | 1.65634700 |
| O | -3.72917300 | -0.68212600 | 4.40407700 |
| O | -3.22988300 | 0.63477300 | -3.97740100 |
| O | 1.15330100 | -0.36473100 | -5.36688500 |
| O | 0.86391100 | -0.60293600 | 5.31881000 |
| C | -5.10579000 | -0.72506100 | 4.76289900 |
| C | 2.00119200 | -0.67297300 | 6.16672200 |
| C | -4.61025500 | 0.83986700 | -4.23294400 |
| C | 2.07921800 | -0.77177000 | -6.36071200 |
| H | -5.39544900 | 0.16862700 | 5.35882700 |
| H | -4.09140900 | -0.91125200 | 7.12820900 |
| H | -2.19825700 | -0.99878900 | 8.74292800 |
| H | 0.16557700 | -0.86440300 | 7.97312800 |
| H | -5.34883200 | -1.64431700 | 5.34121100 |
| H | -5.66135300 | -0.74617000 | 3.80730400 |
| H | 2.01470900 | 0.16017000 | 6.90420200 |
| H | 2.04708900 | -1.64265100 | 6.71037200 |
| H | 2.88073000 | -0.58657900 | 5.50092700 |
| H | -0.53240500 | -3.09866000 | 4.43605900 |
| H | 0.53605100 | -4.69915500 | 2.48652800 |
| H | -1.99943400 | 1.92474300 | 4.69002900 |
| H | -1.77859100 | 4.06947600 | 2.98859000 |
| H | 0.43055000 | 7.48571600 | 2.10554800 |
| H | -1.50804000 | 8.64322300 | 0.99569500 |
| H | -3.17005100 | 7.32214000 | -0.35664500 |
| H | -0.56313000 | 4.58816800 | -2.13592600 |
| H | -0.63639200 | 2.77182900 | -4.19898000 |
| H | -2.98756500 | 3.63883600 | -0.57025000 |
| H | -1.73348400 | -4.13480500 | -0.02595900 |
| H | -1.23341200 | -7.75416900 | 0.46384900 |
| H | 1.02150000 | -8.81222100 | 0.06266200 |
| H | 3.01751100 | -7.38470800 | -0.48470600 |
| H | -0.41029500 | -2.45890200 | -4.52621000 |
| H | 0.39123100 | -4.39965600 | -2.75370200 |
| H | -3.84502800 | 0.77105900 | -6.64796400 |

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|---|---|---|---|
| H | -2.17397700 | 0.40133200 | -8.45312000 |
| H | 0.19484000 | -0.13246100 | -7.92186700 |
| H | -4.78398200 | 1.76257200 | -4.82955200 |
| H | -5.10414100 | 0.95226900 | -3.24993600 |
| H | -5.05985100 | -0.02502700 | -4.77124800 |
| H | 2.33737200 | 0.06081000 | -7.05319900 |
| H | 2.98937100 | -1.08731900 | -5.82059200 |
| H | 1.69169800 | -1.62905600 | -6.95543100 |
| H | -6.09942900 | 3.29671000 | -3.79364700 |
| H | -5.65757500 | 5.11944700 | -3.70298900 |
| H | -6.78789200 | 5.31819700 | -1.50199000 |
| H | -4.80061900 | 2.90570200 | -1.65415900 |
| H | -3.32270000 | -3.22613400 | 1.03977200 |
| H | -5.08716500 | -5.39780500 | 2.42071700 |
| H | -3.29567900 | -4.45660600 | 3.90159100 |
| H | -3.76076600 | -2.70171800 | 3.40766500 |
| H | -9.21095000 | 1.29030800 | -2.08318600 |
| H | -8.02958500 | -2.44489100 | 0.91584400 |
| H | -7.23780800 | -4.45684700 | -1.29303500 |
| H | -8.84758700 | -4.03232800 | 0.62367100 |
| H | -6.53059100 | -2.84237300 | -1.04715400 |
| H | -9.37546600 | -1.29614300 | -0.58833900 |
| H | -8.17475300 | -2.89782000 | -2.95370100 |
| H | -9.45631900 | -3.46347100 | -1.86534900 |
| H | -8.61199400 | 1.17385900 | -0.41003900 |
| H | -9.77045400 | -1.08796800 | -2.29989300 |
| H | -7.39207300 | -0.39593700 | -2.78983600 |
| H | -6.96836700 | -0.58799600 | -1.06424100 |
| N | 2.98748100 | -4.67723800 | -0.63885900 |
| C | 4.27710600 | -5.00855900 | -1.01102200 |
| H | 2.77710300 | -3.67758500 | -0.55493000 |
| O | 4.70302900 | -6.16145600 | -1.09826400 |
| C | 5.11867000 | -3.81470200 | -1.36251600 |
| C | 6.62884600 | -3.96929300 | -1.19976700 |
| C | 6.00436300 | -3.95830700 | -2.57928900 |
| H | 4.72277800 | -2.81133400 | -1.14600600 |
| C | 7.42952300 | -2.78952500 | -0.75884300 |
| H | 6.98304200 | -4.93779600 | -0.81687800 |
| H | 6.16227700 | -3.06150700 | -3.19664100 |
| H | 5.96580400 | -4.92692700 | -3.10134000 |
| O | 6.84654500 | -1.63076200 | -1.16490300 |
| O | 8.47699800 | -2.84554600 | -0.13708100 |
| C | 7.57342700 | -0.40761100 | -0.93228900 |
| C | 6.64250300 | 0.76095900 | -1.22978900 |
| H | 8.45987900 | -0.40202900 | -1.60612200 |
| H | 7.95968800 | -0.40046800 | 0.10851100 |

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|---|---|---|---|
| C | 7.42222900 | 2.02705900 | -1.60737000 |
| H | 5.97530200 | 0.47637200 | -2.07069900 |
| H | 5.97461900 | 0.93890000 | -0.36000800 |
| C | 6.53179100 | 3.24858600 | -1.88719600 |
| H | 8.16540500 | 2.26802600 | -0.81342600 |
| H | 8.02671700 | 1.81109400 | -2.51665000 |
| C | 5.77869800 | 3.79831300 | -0.66666900 |
| H | 5.78893200 | 2.97911200 | -2.66898500 |
| H | 7.15811800 | 4.06029700 | -2.32089600 |
| C | 6.71794500 | 4.25871200 | 0.44908800 |
| H | 5.15530200 | 4.66506000 | -0.97376700 |
| H | 5.07577500 | 3.03847300 | -0.26207000 |
| O | 5.97231400 | 4.95696400 | 1.47100800 |
| H | 7.25335600 | 3.40674700 | 0.91399400 |
| H | 7.45704100 | 4.99574800 | 0.07476700 |
| C | 5.37709500 | 4.18433100 | 2.41102900 |
| C | 4.38569400 | 4.98028100 | 3.18134500 |
| O | 5.58242700 | 2.98229000 | 2.53917000 |
| C | 2.97058000 | 4.36414600 | 3.14109600 |
| C | 3.74745600 | 4.42352300 | 4.42457200 |
| H | 4.42729400 | 6.07256000 | 3.05783700 |
| C | 1.85413400 | 5.33544000 | 2.87200100 |
| H | 2.90976200 | 3.39974900 | 2.61804300 |
| H | 3.41291000 | 5.16905500 | 5.16220200 |
| H | 4.14609300 | 3.47237800 | 4.80992000 |
| N | 0.99962600 | 4.87354000 | 1.88948700 |
| O | 1.76965300 | 6.42032700 | 3.45241000 |
| H | 1.22435300 | 3.92811200 | 1.51965000 |
| C | 1.67050400 | 0.13243800 | 0.15517200 |
| C | 1.79703800 | 1.22101400 | 1.15589700 |
| C | 2.31440000 | 0.30611000 | -1.17050600 |
| C | 1.99458200 | 0.78412400 | 2.61583800 |
| O | 1.87414800 | 2.42187500 | 0.84051300 |
| C | 2.45289100 | 1.54929800 | -1.83533000 |
| C | 2.88017100 | -0.83605800 | -1.78648300 |
| C | 3.45861000 | 0.49076400 | 2.68126900 |
| H | 1.69476400 | 1.61656400 | 3.28176900 |
| H | 1.37493200 | -0.09607900 | 2.85524000 |
| C | 3.15909500 | 1.63805000 | -3.04314700 |
| H | 2.01701100 | 2.44693300 | -1.38230500 |
| C | 3.58492400 | -0.75101400 | -2.99129100 |
| H | 2.75792400 | -1.80973000 | -1.29078700 |
| C | 4.03479700 | -0.79805200 | 2.49545900 |
| C | 3.73839700 | 0.49657700 | -3.62158100 |
| H | 3.25296000 | 2.61629500 | -3.54011900 |
| H | 4.02234100 | -1.66110700 | -3.42952300 |

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|---|---|---|---|
| C | 3.25770400 | -2.00255300 | 2.47783500 |
| C | 5.45129200 | -0.92041200 | 2.30490000 |
| H | 4.30290700 | 0.58029600 | -4.56334900 |
| C | 3.85782800 | -3.24162300 | 2.24769100 |
| H | 2.17919900 | -1.95634700 | 2.67840600 |
| C | 6.04203300 | -2.16536700 | 2.08278100 |
| H | 6.06150700 | -0.00317300 | 2.32710500 |
| C | 5.25060400 | -3.33441800 | 2.03851600 |
| H | 3.23675100 | -4.15089900 | 2.24169700 |
| H | 7.12946600 | -2.24188500 | 1.93330300 |
| H | 5.72022400 | -4.31270900 | 1.85462600 |
| H | 4.14969000 | 1.35164800 | 2.71157800 |
| H | 1.93585200 | -0.84643100 | 0.58901700 |

**Transition State for Radical Substitution (TS3)**

Imaginary Frequency: -164.35 $cm^{-1}$

Electronic energy in diisopropyl ether= -6815.057849

Thermal correction to Enthalpy= 1.767171

Enthalpy in diisopropyl ether= -6813.290678

Thermal correction to Gibbs Free Energy= 1.499505

Gibbs Free Energy in diisopropyl ether= -6813.558344

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| | | | |
|---|---|---|---|
| N | -0.59651400 | 0.99217400 | 1.94413000 |
| N | -0.36446700 | -0.94467600 | -1.47871000 |
| N | -0.16023000 | -1.67007000 | 1.20730200 |
| N | -0.58264500 | 1.72862000 | -0.73978600 |
| C | -0.80086000 | 1.90587000 | -2.10033600 |
| C | -0.53315600 | 3.01589700 | -0.21846400 |
| C | -0.72371100 | 2.36293300 | 2.13702300 |
| C | -0.66924300 | 0.44554400 | 3.22222000 |
| C | -0.26264600 | -1.88251600 | 2.57830100 |
| C | 0.07526300 | -2.93152800 | 0.67093700 |
| C | -0.09701300 | -2.29220800 | -1.69169900 |
| C | -0.71434000 | -0.45017600 | -2.72660600 |
| C | -0.67585100 | -1.49263200 | -3.72729400 |
| C | -1.00115000 | 0.88409700 | -3.03145800 |
| C | -0.82106800 | 3.31239300 | -2.44136200 |
| C | -0.63275800 | 3.34367900 | 1.14015500 |
| C | -0.25744200 | -2.63649200 | -3.09023200 |
| C | 0.15292500 | -3.24131200 | -0.69401900 |
| C | 0.11705600 | -3.93726800 | 1.71201000 |
| C | -0.91906500 | 2.67093900 | 3.53926800 |
| C | -0.50172200 | -0.90261800 | 3.54477000 |
| C | -0.09649600 | -3.28308900 | 2.89830900 |
| C | -0.60122400 | 4.00358400 | -1.27865200 |

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|---|---|---|---|
| C | -0.87879800 | 1.47781800 | 4.21391200 |
| Co | -0.34929700 | 0.03698800 | 0.23363500 |
| C | -0.52272300 | -1.32057600 | 4.97545200 |
| C | -0.53813900 | -2.14242700 | 7.66022600 |
| C | 0.69458100 | -1.54100900 | 5.66232300 |
| C | -1.74756000 | -1.53405900 | 5.64868700 |
| C | -1.76084800 | -1.94280200 | 7.00045300 |
| C | 0.69274300 | -1.95222900 | 7.01261100 |
| C | -0.74878700 | 4.78090700 | 1.52990500 |
| C | -0.99791500 | 7.49482000 | 2.21691900 |
| C | -1.91395000 | 5.50889900 | 1.18049300 |
| C | 0.29403100 | 5.43486900 | 2.24458900 |
| C | 0.15423600 | 6.79485000 | 2.60315300 |
| C | -2.03404800 | 6.87306000 | 1.50493700 |
| C | -1.73496800 | 1.18957600 | -4.29479600 |
| C | -3.34230200 | 1.79231200 | -6.52673200 |
| C | -3.12371800 | 0.88526900 | -4.29216900 |
| C | -1.17321900 | 1.81166700 | -5.43158700 |
| C | -1.97625400 | 2.11010400 | -6.55636500 |
| C | -3.93311000 | 1.18593900 | -5.40819800 |
| C | 0.15037500 | -4.69928400 | -1.03390800 |
| C | 0.03027400 | -7.48837400 | -1.25931700 |
| C | 1.33970900 | -5.43980200 | -1.23558700 |
| C | -1.09796800 | -5.36505300 | -1.02349500 |
| C | -1.16585400 | -6.76302500 | -1.11751800 |
| C | 1.27743500 | -6.84822100 | -1.33985100 |
| N | -2.95541100 | 4.82149900 | 0.50830600 |
| C | -3.54631400 | 5.25754700 | -0.66646100 |
| N | -2.25561500 | -4.53720100 | -0.91044500 |
| C | -2.91376200 | -4.32731200 | 0.29730100 |
| O | -3.35446100 | 6.37035600 | -1.15331300 |
| O | -2.92005900 | -5.13205100 | 1.22279500 |
| C | -4.44565500 | 4.23349400 | -1.30957800 |
| C | -5.52979500 | 4.80602500 | -2.23305700 |
| C | -4.35175400 | 4.05542300 | -2.80540900 |
| C | -3.57902100 | -2.97635200 | 0.36377400 |
| C | -4.79761600 | -2.83725000 | 1.28219300 |
| C | -3.47330100 | -2.21377700 | 1.65890500 |
| C | -6.91841500 | 4.27010900 | -2.17213000 |
| C | -5.88685100 | -1.96027900 | 0.77565400 |
| O | -7.10474600 | -2.50419800 | 1.01911300 |
| O | -6.96483700 | 2.90351900 | -2.09332500 |
| C | -8.24003600 | -1.78564100 | 0.48070700 |
| C | -8.28883400 | 2.35871600 | -1.88969300 |
| C | -8.21739800 | 0.84036900 | -1.91911300 |
| C | -8.41709700 | -2.07619200 | -1.00897800 |

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|---|---|---|---|
| C | -9.55242700 | 0.20673000 | -1.49912800 |
| C | -9.59785300 | -1.32582000 | -1.64825000 |
| O | -7.91905100 | 4.96490300 | -2.16255800 |
| O | -5.72043200 | -0.89224500 | 0.19524600 |
| O | -2.86417600 | -1.32938500 | 4.89281900 |
| O | -3.58623900 | 0.32571000 | -3.14102400 |
| O | 0.15640900 | 2.11037300 | -5.34858000 |
| O | 1.82311800 | -1.33647900 | 4.92181900 |
| C | -4.13654300 | -1.55846200 | 5.47789500 |
| C | 3.08924700 | -1.60904800 | 5.50395800 |
| C | -4.98421100 | 0.10858300 | -2.98584900 |
| C | 0.75434900 | 2.81361000 | -6.42404000 |
| H | -4.32464300 | -0.87403200 | 6.33533000 |
| H | -2.70568300 | -2.10977900 | 7.53385200 |
| H | -0.54461000 | -2.46105100 | 8.71434900 |
| H | 1.63156200 | -2.12049600 | 7.55618500 |
| H | -4.24745900 | -2.61094600 | 5.82266900 |
| H | -4.87989500 | -1.35873800 | 4.68385600 |
| H | 3.29549300 | -0.94206300 | 6.37058400 |
| H | 3.16907300 | -2.66919100 | 5.83174800 |
| H | 3.83763900 | -1.42133400 | 4.71128900 |
| H | -0.16010500 | -3.69898500 | 3.90922400 |
| H | 0.24762300 | -5.00971100 | 1.53753700 |
| H | -0.97467800 | 1.29046900 | 5.28896500 |
| H | -1.05891800 | 3.68196300 | 3.93725700 |
| H | 0.96077800 | 7.27241700 | 3.17223900 |
| H | -1.09164200 | 8.55884900 | 2.48496000 |
| H | -2.93399400 | 7.42345100 | 1.20343400 |
| H | -0.54667500 | 5.08735800 | -1.12818300 |
| H | -0.95709500 | 3.70097800 | -3.45523100 |
| H | -3.00254700 | 3.81428600 | 0.68821700 |
| H | -2.20536900 | -3.70112100 | -1.50310000 |
| H | -2.14382100 | -7.26202700 | -1.08024000 |
| H | -0.00784700 | -8.58674200 | -1.32747100 |
| H | 2.20915900 | -7.40882700 | -1.48239300 |
| H | -0.90922600 | -1.33633300 | -4.78636500 |
| H | -0.07985200 | -3.63536200 | -3.50653300 |
| H | -5.00707200 | 0.95855000 | -5.40446400 |
| H | -3.96652300 | 2.02946900 | -7.40244000 |
| H | -1.54744000 | 2.58801600 | -7.44644100 |
| H | -5.55469600 | 1.05647400 | -3.08826500 |
| H | -5.12181800 | -0.27702000 | -1.95818000 |
| H | -5.36770000 | -0.63502700 | -3.72087600 |
| H | 0.25397300 | 3.79073800 | -6.60828900 |
| H | 1.80381100 | 2.99889200 | -6.12897900 |
| H | 0.74272400 | 2.22036300 | -7.36614900 |

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|---|---|---|---|
| H | -4.50931300 | 3.04226800 | -3.20002900 |
| H | -3.60068500 | 4.66514700 | -3.32993900 |
| H | -5.49802500 | 5.90249600 | -2.32316700 |
| H | -4.71576800 | 3.33945900 | -0.72495300 |
| H | -3.59788200 | -2.36677300 | -0.55470400 |
| H | -5.09929000 | -3.75678900 | 1.80582200 |
| H | -2.92097500 | -2.69298300 | 2.47993300 |
| H | -3.38625200 | -1.11921400 | 1.58635800 |
| H | -8.97234400 | 2.76266500 | -2.66663000 |
| H | -8.09332500 | -0.70214200 | 0.66642700 |
| H | -8.54687300 | -3.17086300 | -1.14620800 |
| H | -9.10835400 | -2.13909500 | 1.07177500 |
| H | -7.47461000 | -1.80225300 | -1.52798600 |
| H | -9.77028000 | 0.49337600 | -0.44545300 |
| H | -9.62443200 | -1.58666100 | -2.72911300 |
| H | -10.55589400 | -1.70043900 | -1.22401200 |
| H | -8.67277300 | 2.72430500 | -0.91138900 |
| H | -10.38117900 | 0.64491000 | -2.09847700 |
| H | -7.94370900 | 0.50016000 | -2.94282900 |
| H | -7.40338200 | 0.50433400 | -1.24194100 |
| N | 2.52522200 | -4.69576300 | -1.34692000 |
| C | 3.75760000 | -5.10413100 | -1.82108300 |
| H | 2.39457500 | -3.68741200 | -1.21195200 |
| O | 4.09664900 | -6.28061600 | -1.95359100 |
| C | 4.61331000 | -3.95289400 | -2.27106000 |
| C | 6.12235600 | -4.16143200 | -2.34303900 |
| C | 5.29449000 | -4.12801600 | -3.61017400 |
| H | 4.28911400 | -2.93382900 | -2.01050100 |
| C | 7.01079300 | -3.00603200 | -2.02314200 |
| H | 6.49652000 | -5.13936000 | -2.00557300 |
| H | 5.38433200 | -3.23751300 | -4.24917300 |
| H | 5.14049400 | -5.09513400 | -4.11322200 |
| O | 6.45301800 | -1.83510900 | -2.43619400 |
| O | 8.09364800 | -3.08690000 | -1.46724400 |
| C | 7.23633700 | -0.63332700 | -2.28732600 |
| C | 6.29960400 | 0.56647700 | -2.27911900 |
| H | 7.94248700 | -0.58059300 | -3.14659500 |
| H | 7.85131000 | -0.71116000 | -1.36616400 |
| C | 7.06153800 | 1.86421300 | -2.57869800 |
| H | 5.50768200 | 0.41362300 | -3.04299600 |
| H | 5.77079800 | 0.62501500 | -1.30319000 |
| C | 6.19353200 | 3.13105100 | -2.52776100 |
| H | 7.92486700 | 1.96424100 | -1.88177100 |
| H | 7.51314600 | 1.78193500 | -3.59252500 |
| C | 5.65255200 | 3.49708400 | -1.13809400 |
| H | 5.33389000 | 3.00529900 | -3.22032100 |

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|---|---|---|---|
| H | 6.78688600 | 3.98767200 | -2.91906900 |
| C | 6.76218100 | 3.71673600 | -0.10898700 |
| H | 5.06033900 | 4.43434700 | -1.20901400 |
| H | 4.95267800 | 2.71928200 | -0.76529300 |
| O | 6.24346900 | 4.38773200 | 1.05977200 |
| H | 7.23120700 | 2.76154700 | 0.20291100 |
| H | 7.54472400 | 4.39625000 | -0.50421400 |
| C | 5.68364100 | 3.60696000 | 2.01462400 |
| C | 4.98622000 | 4.44802200 | 3.02298600 |
| O | 5.70628000 | 2.38122000 | 2.00144200 |
| C | 3.55975400 | 3.95448000 | 3.33674500 |
| C | 4.63072200 | 3.89292900 | 4.38051500 |
| H | 5.11243300 | 5.53616400 | 2.92347700 |
| C | 2.48971200 | 5.01116500 | 3.37298700 |
| H | 3.29555900 | 3.02462900 | 2.81467900 |
| H | 4.56427800 | 4.63371200 | 5.19229400 |
| H | 5.02699200 | 2.89768500 | 4.63435800 |
| N | 1.44487300 | 4.68678900 | 2.53194100 |
| O | 2.58255700 | 6.03786000 | 4.04939400 |
| H | 1.56394800 | 3.79874400 | 2.00603600 |
| C | 2.29719700 | 0.20379500 | -0.07532100 |
| C | 2.49530600 | 0.49493300 | -1.48460400 |
| C | 2.20252800 | 1.16345400 | 1.02669800 |
| C | 2.65460800 | -0.59481300 | -2.37879800 |
| C | 2.54247500 | 1.81353000 | -2.00775200 |
| C | 2.65404000 | 0.40200300 | 2.27654900 |
| O | 2.17060400 | 2.40200100 | 0.91846900 |
| C | 2.87626400 | -0.38760600 | -3.74246600 |
| H | 2.57756700 | -1.61748100 | -1.98197300 |
| C | 2.75770500 | 2.01598500 | -3.37649000 |
| H | 2.37661000 | 2.65613500 | -1.32332000 |
| H | 1.91804100 | -0.34037500 | 2.63287800 |
| C | 3.82045600 | -0.20395100 | 1.54452000 |
| H | 2.92460800 | 1.06859400 | 3.11639700 |
| H | 2.98979300 | -1.25045500 | -4.41602600 |
| C | 2.93344500 | 0.92450100 | -4.24637100 |
| H | 2.76477100 | 3.04382900 | -3.77115900 |
| C | 4.14852800 | -1.61380100 | 1.48076000 |
| H | 4.62256900 | 0.51107700 | 1.29090500 |
| H | 3.09680200 | 1.09105600 | -5.32207400 |
| C | 3.24174100 | -2.62051400 | 1.91263800 |
| C | 5.41616700 | -2.01644100 | 0.97464900 |
| C | 3.58337300 | -3.97276500 | 1.81653100 |
| H | 2.26579700 | -2.33876800 | 2.33076200 |
| C | 5.76645700 | -3.37097400 | 0.91607500 |
| H | 6.13057600 | -1.24490400 | 0.64755900 |

| | | | |
|---|---|---|---|
| C | 4.84404600 | -4.35538500 | 1.31831900 |
| H | 2.85595100 | -4.73468000 | 2.13421600 |
| H | 6.76109800 | -3.65920000 | 0.54587000 |
| H | 5.10624500 | -5.42141200 | 1.23762700 |
| H | 2.03120700 | -0.83534700 | 0.16699300 |

**Intermediate E**

Electronic energy in diisopropyl ether= -6815.0770422
Thermal correction to Enthalpy= 1.769308
Enthalpy in diisopropyl ether= -6813.307734
Thermal correction to Gibbs Free Energy= 1.503175
Gibbs Free Energy in diisopropyl ether= -6813.573867

0 2

| | | | |
|---|---|---|---|
| N | -0.31669600 | 0.79833400 | 1.80843100 |
| N | -0.53598900 | -1.00596500 | -1.68920000 |
| N | 0.11873500 | -1.82086600 | 0.90329400 |
| N | -0.74822200 | 1.63995900 | -0.80096300 |
| C | -1.05767400 | 1.87182900 | -2.13493500 |
| C | -0.65432400 | 2.90718800 | -0.23048800 |
| C | -0.53971800 | 2.14474800 | 2.09040400 |
| C | -0.16451400 | 0.19878400 | 3.05435900 |
| C | 0.23099600 | -2.08692800 | 2.26739100 |
| C | 0.25362300 | -3.06404500 | 0.29368900 |
| C | -0.29506100 | -2.34048900 | -1.98360800 |
| C | -1.00476900 | -0.45755600 | -2.87523500 |
| C | -1.06758100 | -1.45730700 | -3.91859200 |
| C | -1.29407000 | 0.88994000 | -3.10010000 |
| C | -1.09577300 | 3.29052000 | -2.41618200 |
| C | -0.63938700 | 3.17768500 | 1.14787100 |
| C | -0.60123400 | -2.62772000 | -3.37007900 |
| C | 0.07669200 | -3.32941800 | -1.06776400 |
| C | 0.46756000 | -4.10546900 | 1.27845900 |
| C | -0.57349300 | 2.37316100 | 3.52042800 |
| C | 0.10033100 | -1.15292900 | 3.29590000 |
| C | 0.45063200 | -3.49663500 | 2.50372900 |
| C | -0.80158800 | 3.93465800 | -1.24203600 |
| C | -0.32119700 | 1.16649600 | 4.11830100 |
| Co | -0.32914600 | -0.09162100 | 0.04172900 |
| C | 0.13268500 | -1.64967200 | 4.70162900 |
| C | 0.09974600 | -2.68593500 | 7.31526700 |
| C | 1.33968800 | -2.02557000 | 5.33599800 |
| C | -1.09360600 | -1.82576700 | 5.39048900 |
| C | -1.11511700 | -2.33662000 | 6.70571600 |
| C | 1.32649700 | -2.54451400 | 6.64986700 |

| | | | |
|---|---|---|---|
| C | -0.87911000 | 4.58224400 | 1.60967100 |
| C | -1.42908200 | 7.24463900 | 2.38813100 |
| C | -2.12312300 | 5.19852800 | 1.29876800 |
| C | 0.08761700 | 5.33654800 | 2.34510900 |
| C | -0.20163600 | 6.66615500 | 2.73172900 |
| C | -2.39625500 | 6.52551700 | 1.67783100 |
| C | -1.94500600 | 1.27365300 | -4.38548900 |
| C | -3.30991400 | 1.98838200 | -6.73597700 |
| C | -3.33851600 | 1.03960200 | -4.50803300 |
| C | -1.24625800 | 1.85898500 | -5.46425600 |
| C | -1.92894500 | 2.22418100 | -6.64616400 |
| C | -4.02899000 | 1.39778000 | -5.68555600 |
| C | -0.02044800 | -4.77162600 | -1.44906700 |
| C | -0.32326300 | -7.54234500 | -1.76861800 |
| C | 1.12410400 | -5.59612500 | -1.58419300 |
| C | -1.31096000 | -5.34935100 | -1.51210800 |
| C | -1.46900700 | -6.73265700 | -1.67300100 |
| C | 0.96744600 | -6.99363500 | -1.73056200 |
| N | -3.11169400 | 4.46857500 | 0.58887300 |
| C | -3.71880100 | 4.95255000 | -0.55999800 |
| N | -2.43523600 | -4.46594500 | -1.37155200 |
| C | -2.79183200 | -3.99789300 | -0.11086300 |
| O | -3.53060600 | 6.08808100 | -0.99502400 |
| O | -2.57673700 | -4.62012700 | 0.92543400 |
| C | -4.64027900 | 3.97909900 | -1.24498600 |
| C | -5.73944200 | 4.64603300 | -2.09070900 |
| C | -4.59389600 | 3.92372400 | -2.75248700 |
| C | -3.45321100 | -2.64359300 | -0.12270900 |
| C | -4.49981100 | -2.39860600 | 0.97425100 |
| C | -3.15740700 | -1.70980500 | 1.02362900 |
| C | -7.13931100 | 4.14141800 | -2.03634800 |
| C | -5.70845900 | -1.63642400 | 0.56660800 |
| O | -6.83380300 | -2.23423400 | 1.03194800 |
| O | -7.22285100 | 2.77958800 | -2.12905900 |
| C | -8.08834800 | -1.65469500 | 0.60257400 |
| C | -8.54840100 | 2.24285600 | -1.91510900 |
| C | -8.46595000 | 0.72467700 | -1.92117900 |
| C | -8.44048800 | -2.10329700 | -0.81590200 |
| C | -9.73576100 | 0.07966700 | -1.34682700 |
| C | -9.72387500 | -1.46096700 | -1.37104900 |
| O | -8.11765600 | 4.85390900 | -1.89449100 |
| O | -5.70702800 | -0.61885200 | -0.11885700 |
| O | -2.20691600 | -1.48881800 | 4.67895100 |
| O | -3.91976300 | 0.47515800 | -3.41464100 |
| O | 0.09604100 | 2.03729000 | -5.27062900 |
| O | 2.47652000 | -1.86660700 | 4.59525300 |

| | | | |
|---|---|---|---|
| C | -3.48170900 | -1.68313600 | 5.26971000 |
| C | 3.68841100 | -2.43279500 | 5.08585200 |
| C | -5.31340200 | 0.18701700 | -3.43146200 |
| C | 0.85192400 | 2.66641300 | -6.29386400 |
| H | -3.61326900 | -1.05836400 | 6.18160900 |
| H | -2.06066300 | -2.47305400 | 7.24644700 |
| H | 0.08960900 | -3.08668900 | 8.34097300 |
| H | 2.25882300 | -2.83211700 | 7.15229700 |
| H | -3.65446200 | -2.75070900 | 5.53291100 |
| H | -4.22259000 | -1.37426600 | 4.50893700 |
| H | 4.02766200 | -1.93082600 | 6.01900000 |
| H | 3.57335500 | -3.52205400 | 5.27411700 |
| H | 4.44216200 | -2.28407900 | 4.29157300 |
| H | 0.55260700 | -3.94984900 | 3.49458900 |
| H | 0.56322600 | -5.17064100 | 1.04758800 |
| H | -0.24732800 | 0.92822700 | 5.18487800 |
| H | -0.75532200 | 3.34607500 | 3.98935400 |
| H | 0.56014600 | 7.21866100 | 3.29301900 |
| H | -1.63612100 | 8.28303200 | 2.69041200 |
| H | -3.36090300 | 6.97389900 | 1.40992100 |
| H | -0.74778400 | 5.01208200 | -1.05090000 |
| H | -1.30847000 | 3.72267500 | -3.39917500 |
| H | -3.12386900 | 3.45421300 | 0.72614300 |
| H | -2.50433100 | -3.76338700 | -2.11774500 |
| H | -2.48185500 | -7.15862900 | -1.70039000 |
| H | -0.43519400 | -8.63229800 | -1.87763300 |
| H | 1.86425400 | -7.62160300 | -1.79676900 |
| H | -1.39360000 | -1.25684200 | -4.94520200 |
| H | -0.45988100 | -3.60573300 | -3.84606600 |
| H | -5.10956400 | 1.22826600 | -5.78090300 |
| H | -3.84237900 | 2.27502100 | -7.65633900 |
| H | -1.39753500 | 2.68428100 | -7.48925500 |
| H | -5.92030400 | 1.10916300 | -3.55987000 |
| H | -5.53753800 | -0.24097500 | -2.43713500 |
| H | -5.56857300 | -0.54244600 | -4.23287200 |
| H | 0.48605600 | 3.69659300 | -6.50260200 |
| H | 1.89152600 | 2.72080800 | -5.91954000 |
| H | 0.83663900 | 2.07943900 | -7.23955600 |
| H | -4.78152800 | 2.94573700 | -3.21324000 |
| H | -3.84533200 | 4.55954700 | -3.24842500 |
| H | -5.68151600 | 5.74496300 | -2.08640800 |
| H | -4.90348700 | 3.04431100 | -0.72427400 |
| H | -3.64855100 | -2.16567400 | -1.09670500 |
| H | -4.65745700 | -3.24908100 | 1.65442800 |
| H | -2.46233800 | -2.06191500 | 1.80018600 |
| H | -3.14163000 | -0.63311000 | 0.78963800 |

| | | | |
|---|---|---|---|
| H | -9.23571300 | 2.63956100 | -2.69317500 |
| H | -8.00871200 | -0.55074700 | 0.67048300 |
| H | -8.53319700 | -3.21008000 | -0.82988700 |
| H | -8.83496600 | -2.00749400 | 1.34154800 |
| H | -7.58462000 | -1.85094800 | -1.47660900 |
| H | -9.87497000 | 0.43942200 | -0.30215900 |
| H | -9.85694700 | -1.81409700 | -2.41720800 |
| H | -10.60857600 | -1.83718400 | -0.81100100 |
| H | -8.92623400 | 2.62142200 | -0.93994600 |
| H | -10.63099500 | 0.43943600 | -1.90093400 |
| H | -8.28563900 | 0.35609000 | -2.95577500 |
| H | -7.58167700 | 0.42783600 | -1.31853600 |
| N | 2.36991600 | -4.94742900 | -1.58605200 |
| C | 3.64041900 | -5.49917300 | -1.60481800 |
| H | 2.30755800 | -3.92376000 | -1.61388200 |
| O | 3.87770400 | -6.69624800 | -1.44135100 |
| C | 4.70407400 | -4.48832300 | -1.92622700 |
| C | 6.07441200 | -4.60769000 | -1.26832000 |
| C | 5.88680100 | -4.98534000 | -2.72491300 |
| H | 4.38124800 | -3.45685000 | -2.12469100 |
| C | 6.85969500 | -3.36702000 | -0.97699500 |
| H | 6.22866900 | -5.42838200 | -0.55293800 |
| H | 6.30116800 | -4.31294300 | -3.49120000 |
| H | 5.89652300 | -6.06317000 | -2.94973600 |
| O | 6.32363800 | -2.29489200 | -1.62460600 |
| O | 7.87107100 | -3.31907200 | -0.30152400 |
| C | 7.04807900 | -1.04958000 | -1.58522200 |
| C | 6.08621300 | 0.05555900 | -1.99538700 |
| H | 7.90977700 | -1.12348500 | -2.28698600 |
| H | 7.46626900 | -0.90132900 | -0.56726000 |
| C | 6.79361000 | 1.35965100 | -2.37953400 |
| H | 5.47542300 | -0.30024500 | -2.85251900 |
| H | 5.36093600 | 0.23019100 | -1.17421700 |
| C | 5.81382700 | 2.53277600 | -2.56630300 |
| H | 7.55856700 | 1.62009500 | -1.61346400 |
| H | 7.36275100 | 1.19810500 | -3.32154000 |
| C | 5.27256200 | 3.13262500 | -1.25862400 |
| H | 4.95471500 | 2.18886700 | -3.18322200 |
| H | 6.31087200 | 3.34063500 | -3.14865200 |
| C | 6.36638600 | 3.79811600 | -0.42135000 |
| H | 4.50248700 | 3.89830800 | -1.49211600 |
| H | 4.76004000 | 2.35735600 | -0.65003200 |
| O | 5.79357200 | 4.62226600 | 0.61637200 |
| H | 7.03958600 | 3.05131100 | 0.04589100 |
| H | 6.96691800 | 4.49499600 | -1.04142000 |
| C | 5.55120100 | 4.03021700 | 1.81238800 |

| | | | |
|---|---|---|---|
| C | 4.83107000 | 4.97120000 | 2.71058900 |
| O | 5.85413000 | 2.87234100 | 2.07608600 |
| C | 3.57892400 | 4.38082100 | 3.39565900 |
| C | 4.78196400 | 4.74599200 | 4.20372000 |
| H | 4.73574200 | 6.00310900 | 2.34143000 |
| C | 2.37546100 | 5.28508800 | 3.37190900 |
| H | 3.39913800 | 3.32079100 | 3.17279500 |
| H | 4.69990000 | 5.65573000 | 4.81818300 |
| H | 5.38665200 | 3.91794400 | 4.60382500 |
| N | 1.32531800 | 4.74351900 | 2.64876700 |
| O | 2.38503800 | 6.39809800 | 3.90236700 |
| H | 1.50831400 | 3.81044000 | 2.24910800 |
| C | 2.88230400 | -0.10360500 | 0.79177500 |
| C | 2.64185800 | -0.05775600 | -0.68752800 |
| C | 2.85413000 | 1.11020800 | 1.69653600 |
| C | 2.85346100 | -1.21964200 | -1.46181700 |
| C | 2.21462400 | 1.12362100 | -1.33137100 |
| C | 3.86871800 | 0.49657200 | 2.65446600 |
| O | 2.37362700 | 2.22576600 | 1.56905500 |
| C | 2.61837400 | -1.21164500 | -2.84248800 |
| H | 3.22053700 | -2.12480800 | -0.95580900 |
| C | 1.99327700 | 1.13365800 | -2.71966900 |
| H | 2.05513300 | 2.03205000 | -0.73491600 |
| H | 3.35243200 | -0.07932500 | 3.45160100 |
| C | 4.26995900 | -0.43524500 | 1.44583700 |
| H | 4.63849600 | 1.17836000 | 3.06191400 |
| H | 2.76807000 | -2.12836600 | -3.43513800 |
| C | 2.17601200 | -0.03461900 | -3.47434900 |
| H | 1.62875100 | 2.04799500 | -3.20841000 |
| C | 4.64271700 | -1.87359900 | 1.68885200 |
| H | 5.07741200 | 0.07874100 | 0.88451800 |
| H | 1.95051400 | -0.03071400 | -4.55088900 |
| C | 3.71245200 | -2.92060400 | 1.53400400 |
| C | 5.95334600 | -2.19575400 | 2.10336600 |
| C | 4.07456900 | -4.25273100 | 1.78712200 |
| H | 2.68490500 | -2.70369900 | 1.21718500 |
| C | 6.31824500 | -3.52582900 | 2.36650100 |
| H | 6.69899700 | -1.39195300 | 2.21346300 |
| C | 5.37886200 | -4.56027700 | 2.20909900 |
| H | 3.32783500 | -5.04967100 | 1.64948700 |
| H | 7.35068900 | -3.75750400 | 2.66730800 |
| H | 5.66714700 | -5.60534100 | 2.40167200 |
| H | 2.15460300 | -0.80726200 | 1.25780800 |

## 5.2 Cartesian Coordinates for DFT Calculation in Chapter 3

$N_2$:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.008229 Hartree
H: -109.481845 Hartree
G_corr: -0.013594 Hartree
G: -109.564778 Hartree
S: 45.930 cal/mol-kelvin

N -3.50606000 1.21746000 0.00000000
N -4.65220000 1.21746000 0.00000000

Diazo **1a'**:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.328331 Hartree
H: -859.158626 Hartree
G_corr: 0.254857 Hartree
G: -859.998907874 Hartree
S: 154.638 cal/mol-kelvin

H 5.386174 0.433157 -0.710762
C 4.305079 0.658447 -0.643849
H 3.978197 1.069964 -1.616265
H 4.147256 1.415847 0.140197
H 4.770700 -1.999116 -1.490260
H 4.948458 -1.509540 1.085921
O 2.057225 1.237411 1.353304
C 3.531946 -0.639160 -0.320416
C 3.709428 -1.695612 -1.429435
H 3.403686 -1.287714 -2.409184
C 3.883082 -1.211621 1.070565
H -0.093275 3.717361 0.276934
H 3.712096 -0.460828 1.858311
N -3.105686 3.573864 -0.688763
N -2.054240 3.300024 -0.199197
C -0.903501 2.989529 0.363908
C 1.439650 0.569678 0.472593
O 2.027713 -0.366292 -0.391512
H 3.099098 -2.590927 -1.216038
H 3.272240 -2.107649 1.284610
C -0.692547 1.652399 1.063528
H -0.112016 1.826080 1.984029
N 0.068690 0.665636 0.251841

H -1.665069 1.202204 1.331296
C -0.637116 -0.003366 -0.868327
H 0.115055 -0.594628 -1.414772
H -1.025344 0.769984 -1.562700
C -1.787436 -0.899131 -0.403018
H -0.587956 -1.967890 1.068285
C -1.577451 -1.879837 0.602974
C -3.072476 -0.783416 -0.991218
H -3.249299 -0.023306 -1.763670
C -2.631018 -2.730943 1.007050
C -4.129340 -1.637297 -0.590839
H -2.457294 -3.484835 1.784234
C -3.911112 -2.613758 0.409465
H -5.118340 -1.535518 -1.052882
H -4.728356 -3.273731 0.723339

Product **2a**:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.317838 Hartree
H: -749.716700 Hartree
G_corr: 0.252497 Hartree
G: -750.480907 Hartree
S: 137.521 cal/mol-kelvin

H 0.502226 3.746377 -0.235188
H 4.144928 0.441551 -0.286791
H 3.145465 -0.498755 1.895919
H -1.619450 3.323095 -1.521909
C -0.208445 3.042447 0.235128
O 2.349292 1.590020 0.893641
C 3.866415 -0.487150 -0.810100
C -1.512439 2.740482 -0.593908
C 1.402199 1.030275 0.268691
N 0.174907 1.614722 0.056508
C 2.867638 -1.423924 1.365547
H 4.724089 -1.185840 -0.783305
H -0.360356 3.336154 1.288594
C -0.993198 1.251166 -0.807381
H 3.645126 -0.252952 -1.867597
O 1.421062 -0.249705 -0.310386
H 3.682009 -2.163080 1.486718
C 2.641955 -1.148906 -0.138195
H 1.951024 -1.841038 1.820908
H -2.443838 2.794582 -0.009865
C 2.203233 -2.423245 -0.887208

H 3.004545 -3.183538 -0.836853
H 1.996429 -2.197679 -1.948452
H 1.286931 -2.841294 -0.435044
H -0.689213 1.047919 -1.852864
C -1.894307 0.130850 -0.311895
C -2.626555 -0.648838 -1.243562
C -2.061288 -0.119016 1.075012
C -3.522175 -1.650649 -0.800142
H -2.491630 -0.475462 -2.319692
C -2.951414 -1.122515 1.521159
H -1.476213 0.463004 1.797700
C -3.688596 -1.889625 0.585262
H -4.081232 -2.247073 -1.531036
H -3.067912 -1.311132 2.595187
H -4.378245 -2.668529 0.931515

[Co(**P1**)]:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.551416 Hartree
H: -3831.391671 Hartree
G_corr: 1.313875 Hartree
G: -5073.05657145 Hartree
S: 499.947 cal/mol-kelvin

H -5.663320 15.044034 -5.404788
C -5.713888 14.160767 -6.068643
H -4.819992 14.181642 -6.720624
H -6.613456 14.271845 -6.703525
H -4.431616 13.726044 -3.680849
H -6.986419 13.852327 -3.654178
C -5.770414 12.868712 -5.207516
C -4.488272 12.820871 -4.315578
H -3.575747 12.777161 -4.939340
H -4.535558 12.261486 -9.872224
C -7.033424 12.948207 -4.291081
H -5.816689 12.573860 -7.997442
H -7.162207 12.379765 -9.840908
H -7.957564 13.000192 -4.897115
C -4.627836 11.248041 -10.303814
H -4.633650 11.348360 -11.406236
C -5.855323 11.606392 -7.486418
C -7.173424 11.361552 -10.271115
H -7.188778 11.459641 -11.373672
C -5.843151 11.580978 -6.070603
H -4.485602 11.939276 -3.648737

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$TS1_{[Co(\mathbf{P1})]}$:
Imaginary Freqency: -262.65 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.878620 Hartree
H: -4690.524905 Hartree
G_corr: 1.597171 Hartree
G: -5933.07622570 Hartree
S: 592.359 cal/mol-kelvin

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Intermediate $B_{[Co(\mathbf{P1})]}$:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.868839 Hartree
H: -4581.055913 Hartree
G_corr: 1.589273 Hartree
G: -5823.52328210 Hartree
S: 588.396 cal/mol-kelvin

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$TS2_{[Co(\mathbf{P1})]}$:
Imaginary Freqency: -1284.94 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.863684 Hartree
H: -4581.035638 Hartree
G_corr: 1.586690 Hartree
G: -5823.49849889 Hartree
S: 582.984 cal/mol-kelvin

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Intermediate $C_{[Co(\mathbf{P1})]}$:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.869057 Hartree
H: -4581.077390 Hartree
G_corr: 1.594668 Hartree
G: -5823.54823096 Hartree
S: 577.501 cal/mol-kelvin

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$TS3_{[Co(\mathbf{P1})]}$:
Imaginary Freqency: -661.50 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.866947 Hartree

H: -4581.052744 Hartree
G_corr: 1.590281 Hartree
G: -5823.51539260 Hartree
S: 582.294 cal/mol-kelvin

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[Co(**P6**)]:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.390327 Hartree
H: -4721.978014 Hartree
G_corr: 1.160297 Hartree
G: -5963.97844226 Hartree
S: 484.138 cal/mol-kelvin

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C -0.426952 4.958914 1.052579
C -1.632206 5.658647 0.744796
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C -8.957583 -1.284526 -1.580583
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H 2.302128 -7.335183 -2.097328
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H -5.489802 4.156226 -3.332818
H 7.038197 -3.585358 -1.683145

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H 1.213717 -1.432227 -4.885594
C 2.713226 1.651830 -4.987119
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H 4.833027 3.316892 -4.623029
H 5.553271 1.660931 -4.777878
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C -1.919747 0.742045 -6.320389
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H -1.691083 -0.009623 -7.100936
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H 2.370478 2.135223 -8.370113

$TS1_{[Co(\mathbf{P6})]}$:
Imaginary Freqency: -261.10 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.716921 Hartree
H: -5581.104028 Hartree
G_corr: 1.443682 Hartree
G: -6823.99468884 Hartree
S: 575.081 cal/mol-kelvin

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O -4.475154 6.416174 0.340180
H -6.576762 5.417178 -0.928091
C -6.138052 3.785652 0.548814

H -9.383479 0.387536 1.164913
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C -6.267085 4.369555 -0.875823
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C -0.490121 8.012630 0.521577
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H -6.477244 0.163263 2.219609
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H 5.729986 1.124600 -5.121783
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H 3.226230 -7.328511 -0.478033
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H 7.408330 -5.220158 -1.203543

Intermediate $B_{[Co(\mathbf{P6})]}$:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.707946 Hartree
H: -5471.627529 Hartree
G_corr: 1.439273 Hartree
G: -6714.43372870 Hartree
S: 565.470 cal/mol-kelvin

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C -4.890512 -4.864630 2.454934
C 0.786766 -7.516037 0.026833
C -0.385247 -6.789566 0.319517
H -3.426221 -1.359016 6.350150
C 2.042678 -6.882058 -0.081901
O -3.249362 -6.036868 0.370023
H 2.961197 -7.446997 -0.250343
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H -3.115921 -3.502681 2.593947
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$TS2_{[Co(\mathbf{P6})]}$:
Imaginary Freqency: -1374.31 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.702820 Hartree
H: -5471.614931 Hartree
G_corr: 1.434086 Hartree
G: -6714.41471262 Hartree
S: 565.598 cal/mol-kelvin

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Intermediate $C_{[Co(\mathbf{P6})]}$:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.707725 Hartree
H: -5471.647077 Hartree
G_corr: 1.440231 Hartree
G: -6714.44976752 Hartree
S: 562.988 cal/mol-kelvin

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H -5.756223 -4.289758 3.695186
C 1.729754 -5.381305 0.936687
C 0.404756 -2.147030 1.777047
C 0.286183 -7.343046 1.083265
H 8.691741 0.156389 -0.786356
H 5.930935 -0.245365 0.568455
H 3.003732 -3.743274 0.825700
C 1.582042 -6.792199 0.991785
C 8.033166 -0.379999 -0.078677
N 3.016647 -4.766366 0.896813
C -0.201644 2.063445 2.572620
O -5.065400 -1.602608 3.862902
H 0.168063 -8.432199 1.108923
H 7.953996 -1.424569 -0.437720
C -0.399859 3.434486 3.014996
H -3.508291 -3.299935 3.155937
H 7.058514 3.741151 1.804455
H 5.212405 -3.350780 0.738673
H 2.473447 -7.421158 0.977797
C -0.055250 -0.341573 3.002853
H -4.896872 1.163927 3.997361
C 4.271484 -5.367722 1.005886
C -0.293137 0.969541 3.441181
C 5.421793 -4.392297 1.003223
C 0.183266 -2.602262 3.143508
O 4.464910 -6.619458 1.122094
C -4.293068 1.330548 4.898352
O -2.894805 1.256421 4.436187
C 8.677552 -0.386071 1.331739
H -0.693253 3.714644 4.025242
C -0.101573 -1.483136 3.897910
H 7.493944 -4.263016 0.138038
C 6.812319 -4.929121 0.670673
H 0.291892 -3.634549 3.476614
H 8.877115 0.652607 1.662695
O 7.333134 -2.363560 1.880250
H 6.928579 -0.457260 2.673698
H 6.866962 -5.995007 0.431765
H -4.506347 2.324356 5.339150
C 7.823574 -1.055398 2.419373
H 9.655887 -0.899439 1.267826
H -4.512750 0.523568 5.619512
C -0.561590 1.215028 4.900140

C 6.494340 -4.593276 2.136331
C -1.886533 1.355030 5.400415
C 7.062912 -3.388849 2.807349
H -0.308666 -1.416754 4.964635
O 1.797411 1.181528 5.248551
H 6.313953 -5.433082 2.812370
C 0.520085 1.319211 5.820264
H 8.393962 -1.243791 3.345857
O 7.274910 -3.274837 4.038101
C -2.129973 1.579853 6.783071
H -3.149269 1.679880 7.164963
H 3.831832 1.126849 5.485781
C 2.960818 1.268529 6.142330
C 0.295305 1.546620 7.203675
C -1.033259 1.671767 7.665568
H 3.016577 2.260351 6.631675
H 2.937755 0.470985 6.910043
H 1.128315 1.626100 7.907464
H -1.215890 1.845303 8.732468

$TS3_{[Co(\mathbf{P6})]}$:
Imaginary Freqency: -704.66 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 1.705945 Hartree
H: -5471.621623 Hartree
G_corr: 1.44009 Hartree
G: -6714.43420518 Hartree
S: 559.539 cal/mol-kelvin

H 2.032040 0.330554 -8.793553
C 1.862024 0.318392 -7.710693
H -0.300717 0.224444 -7.916036
C 0.540725 0.253831 -7.218515
H -2.039412 1.278040 -6.698802
H 3.981647 0.429327 -7.240739
C 2.967507 0.374191 -6.836247
H -2.212389 -0.523786 -6.784357
C -2.108495 0.345460 -6.106210
H 5.098492 1.656092 -5.632961
C 0.331993 0.227858 -5.813920
H 1.299436 2.887053 -4.459758
C 2.740606 0.352962 -5.433146
H -2.973822 0.395159 -5.430167
O -0.943170 0.194933 -5.220295
C 5.122851 0.771038 -4.969085

C 1.423167 0.254282 -4.899441
H 5.566757 -0.091071 -5.503928
C 1.129720 2.748520 -3.393068
H 0.846020 4.788717 -2.544195
O 3.768043 0.442286 -4.482043
C 0.892530 3.706177 -2.429684
H -5.242018 6.339106 -2.428800
H 0.583393 9.097024 0.316410
H -5.386113 4.677077 -3.268365
H -1.569401 7.902313 -0.186607
H -4.740788 -1.361532 -3.900609
C 0.574391 8.003220 0.247149
H 5.702390 1.017872 -4.068156
C -0.641986 7.346940 -0.037093
C -5.154909 5.250789 -2.366719
O -3.480478 6.906030 -0.565830
H -4.172609 4.326176 2.953360
C -3.110666 5.714967 -0.811679
C 1.192365 0.230770 -3.413429
C 1.100555 1.453742 -2.728329
O -5.331140 -0.900243 -1.601401
C 1.780975 7.293206 0.428412
C -4.135445 3.235086 2.856543
C -4.013781 -2.176457 -4.051294
H -4.241974 -2.684301 -5.007577
C -0.659486 5.927702 -0.138633
C -4.027676 4.718560 -1.478190
N -1.832069 5.212821 -0.534278
H 2.730090 7.800819 0.613198
O 6.451812 2.512869 -2.386614
H -4.475836 2.863470 4.983818
C -4.301467 2.411759 4.000316
C -3.938608 2.653995 1.590550
H -3.596328 3.759734 -1.789308
H -3.822738 3.299299 0.714234
H -2.993802 -1.756424 -4.116472
H 6.258912 4.885484 -1.248143
H 1.068029 -2.387981 -4.541991
C 0.746229 3.003059 -1.160262
C 1.751810 5.876805 0.358044
C 0.529448 5.171907 0.102133
H -6.241632 -2.995523 -2.549384
O 4.699034 6.637663 0.563628
H -1.680828 4.213361 -0.710903
C -4.254996 1.003211 3.856758
C -3.883618 1.231660 1.432601

C -5.531231 4.621763 -1.019561
C -4.241068 -1.369111 -1.155162
N 0.886550 1.609563 -1.342881
C 1.004947 -1.001939 -2.763691
C 0.933038 -2.273484 -3.467482
H -5.784432 -4.357102 -3.621362
C -5.500772 -3.795346 -2.710995
C 6.204518 4.065680 -0.527062
C 4.261966 5.445215 0.586785
N 2.918991 5.078964 0.518031
C 6.320666 2.718756 -1.152705
C 0.563110 3.660423 0.075034
H -1.439654 0.775193 -1.023840
C -4.086264 -3.210275 -2.906864
C -4.028319 0.418443 2.595593
C -3.657080 0.674650 0.099489
H -4.425193 0.355064 4.723049
H -4.009274 1.246113 -0.770820
O -5.708981 2.334991 -1.830000
H -5.850205 5.285782 -0.213194
N -3.517948 -0.761031 -0.130644
H 2.737737 4.069597 0.513154
O -3.614769 -2.532038 -1.602656
C -6.076444 3.225058 -1.014838
C 5.165357 4.234261 0.642782
H 5.363190 0.392858 -1.684185
C -1.479051 0.364338 -0.010010
H -4.021860 -0.669628 2.499595
H 7.882650 0.229125 -1.842205
H -5.503622 -4.503045 -1.863345
C 6.652755 4.380551 0.913769
C 0.647324 -3.244218 -2.530032
N 0.804345 -1.190008 -1.377069
H 7.019125 5.398589 1.076670
H -1.339173 1.021585 0.847447
C -3.038988 -4.324072 -3.086060
H -7.748010 0.717676 -1.555160
H -3.255192 -4.882387 -4.016288
O 6.194281 1.679536 -0.215680
C 5.996996 0.300728 -0.784677
C 0.640776 2.963671 1.301678
C -2.084115 -1.034101 0.167714
Co 0.741562 0.193134 0.028691
H 4.707246 3.291998 0.961544
C 7.322470 -0.396969 -1.123719
H -2.026294 -3.891836 -3.160778

O -6.980523 3.014042 0.016414
H 0.517293 -4.314904 -2.681715
H 7.063453 -1.337740 -1.647621
C 0.593479 -2.581999 -1.232396
C -8.276695 0.892017 -0.601796
H -1.689734 -1.784129 -0.529643
H -9.134411 1.564610 -0.802006
H 0.484451 4.684396 2.759369
C 0.648385 3.618811 2.604384
N 0.856992 1.573006 1.444598
H 7.142312 3.585751 1.481067
H 5.435907 -0.219438 0.008521
H -7.061513 -1.599943 -0.645367
H -3.073231 -5.028268 -2.238112
H -9.589851 -0.820154 -0.780796
C -7.319144 1.581139 0.383217
H -1.952724 -1.383010 1.207427
C -8.838333 -0.454284 -0.051396
C 8.227027 -0.738539 0.087598
C -7.825171 -1.597880 0.152303
H -6.371953 1.026982 0.465863
H 8.524329 0.191656 0.612562
C 0.456655 -3.270777 -0.005008
H 9.155795 -1.209191 -0.287802
H 6.943337 -4.433180 -1.681077
C 0.917333 2.644691 3.542763
C 1.031836 1.380195 2.830700
N 0.830462 -1.222694 1.404531
H 4.787514 -3.654251 -0.623243
H -8.348935 -2.571776 0.209330
H -6.100985 -3.645193 0.264468
H -7.767101 1.697929 1.382908
C 6.329489 -5.187065 -1.183787
H 2.616583 -4.038583 -0.337541
C 5.007156 -4.725774 -0.575829
C 0.218267 -4.762773 -0.029027
C 0.658632 -2.614583 1.226160
N 2.604408 -5.060223 -0.429231
H -9.377516 -0.289683 0.902915
O -4.027921 -5.659019 -0.074583
O 7.024793 -2.854897 0.403349
C 7.581606 -1.667227 1.126375
O -7.143304 -1.364155 1.476959
C 1.310986 -5.648429 -0.316396
H 6.335569 -6.194682 -1.609180
C 3.842264 -5.684765 -0.580159

C -1.073525 -5.332768 0.204089
C -3.505918 -4.764878 0.666229
N -2.131140 -4.503652 0.706462
C -5.778722 -3.488343 1.295811
H 6.735950 -1.187477 1.654446
H 1.005550 2.750392 4.623109
C 1.103348 -1.074276 2.783192
C 1.232736 0.144663 3.471313
C 1.105175 -7.044643 -0.464949
O 4.010804 -6.940716 -0.688795
C -1.284347 -6.728287 0.029578
H -1.833465 -3.645517 1.181048
C -6.240227 -2.262905 2.044706
C -0.200097 -7.558892 -0.314563
C 6.217447 -5.115522 0.348069
C -4.338286 -3.993231 1.666749
H 1.957929 -7.689206 -0.685103
C 6.888881 -4.047393 1.142610
H -2.285706 -7.140414 0.164195
H 8.307978 -2.019735 1.879737
H -2.650202 -1.050820 5.732153
C 0.830595 -3.321904 2.489440
O -0.711228 -0.479726 5.402850
H -0.369592 -8.633802 -0.444581
H -5.776961 -5.700010 1.716459
C -5.578828 -4.731396 2.183562
C 1.139294 -2.371884 3.441149
C 1.547459 0.131863 4.940916
O -5.841506 -2.027207 3.215600
C -1.771290 -0.837451 6.356580
H -3.813256 -3.360045 2.389968
H 6.116521 -6.064103 0.881891
O 3.790377 0.724615 4.381321
H -1.992271 0.003493 7.042076
H 0.771354 -4.404204 2.604049
C 0.560118 -0.183037 5.918219
O 7.283113 -4.166058 2.327386
H 5.696950 1.243027 3.841052
C 2.861756 0.439328 5.397144
H -5.822944 -4.617167 3.242623
C 5.166025 1.048998 4.784594
H 1.359288 -2.518727 4.497233
H -1.497371 -1.737478 6.940781
H 5.194957 1.953762 5.422274
C 0.865815 -0.185021 7.305597
C 3.186058 0.439970 6.779825

H 0.102051 -0.420769 8.051562
H 5.638449 0.199295 5.314671
C 2.178658 0.127885 7.717429
H 4.197545 0.672094 7.123886
H 2.421100 0.127285 8.786398

## 5.3 Cartesian Coordinates for DFT Calculation in Chapter 4

$N_2$:

Temperature: 298.15 Kelvin

Pressure: 1.0 atm
H_corr: 0.008229 Hartree
H: -109.481845 Hartree
G_corr: -0.013594 Hartree
G: -109.564778 Hartree
S: 45.930 cal/mol-kelvin

N -3.50606000 1.21746000 0.00000000
N -4.65220000 1.21746000 0.00000000

Diazo **1a'**:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.447290 Hartree
H: -1167.443741 Hartree
G_corr: 0.356822 Hartree
G: -1168.59155023 Hartree
S: 190.405 cal/mol-kelvin

H -5.716517 -0.675500 1.240214
H -4.630610 -1.101421 2.602266
C -5.120889 -1.488761 1.691544
N -1.707807 4.796686 -1.374426
H -2.627010 1.283351 1.010602
H -5.805466 -2.307007 1.981282
N -2.197671 3.757902 -1.056136
C -2.732520 2.614075 -0.677965
C -1.968876 1.626560 0.198620
H -0.377815 1.558637 -1.885922
O -3.247533 -0.757384 0.415553
C -4.072428 -2.015256 0.690750
H -3.732632 2.385203 -1.053857
N -1.507721 0.418376 -0.535496
H -5.322548 -1.676518 -1.076521
H 1.464692 2.907601 -1.379707
H -1.091824 2.127075 0.645128
C -0.352636 0.532276 -1.472182
C -2.144629 -0.814255 -0.453715
C -4.731816 -2.492888 -0.622118
C 1.680601 2.651304 -0.334807

H -2.668000 -2.692286 2.230113
C 1.002676 0.242994 -0.808775
C -3.169820 -3.093314 1.330632
C 1.586556 -0.977945 -1.047365
H 0.981803 -1.682337 -1.638852
H 2.251226 4.687946 0.180997
H -5.416778 -3.334036 -0.404198
C 2.135004 3.660806 0.546041
C 2.906553 -1.514267 -0.640379
C 3.073026 -2.932162 -0.625306
H -3.790806 -3.956030 1.637484
C 1.531775 1.305179 0.108039
H 2.217784 -3.570063 -0.883876
O -1.772549 -1.842601 -1.091659
C 4.040227 -0.704954 -0.327829
C 4.307819 -3.522472 -0.276747
H -0.523032 -0.177003 -2.299047
H 3.955826 0.385330 -0.366575
C 5.277449 -1.295031 0.010112
C 5.418258 -2.705142 0.046065
H 4.406483 -4.614450 -0.264310
C 2.436827 3.346862 1.893613
H -3.969943 -2.830597 -1.342421
C 1.835234 1.005138 1.467805
H 6.137431 -0.654176 0.238986
H 6.381069 -3.158260 0.310259
H -2.406142 -3.440099 0.616621
H 2.783364 4.129476 2.578596
C 2.283286 2.013960 2.350147
H 1.714091 -0.024196 1.823526
H 2.508329 1.762246 3.393384

Tetrahydropyridine Product **2a**:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.438391 Hartree
H: -1058.044148 Hartree
G_corr: 0.359394 Hartree
G: -1059.11564608 Hartree
S: 166.262 cal/mol-kelvin

H 5.537689 1.248894 -1.439261
H 0.032890 0.262147 -2.793067
C 5.660786 1.169998 -0.344553
H -5.768475 -1.586023 0.127614
C -4.752409 -1.998904 0.121656

H 5.251475 2.083535 0.121689
H 6.740574 1.110611 -0.115371
H -3.845727 -0.085283 -0.338070
C -3.657524 -1.148893 -0.154685
H -1.073043 0.994277 1.550097
C -4.544510 -3.370784 0.397460
H 2.008965 1.239047 -1.622428
H -5.393187 -4.030940 0.611178
H 5.286257 -1.285737 -1.604420
C -0.141701 0.991795 -1.978599
H -1.808038 2.960489 2.919804
C -2.317897 -1.642930 -0.163099
C -1.621630 1.816499 1.075343
C 0.105955 -1.069225 -0.100515
H 0.348652 -1.988197 0.439506
C -3.222340 -3.881888 0.384157
C 1.089343 1.034518 -1.054236
N 1.247051 -0.275479 -0.360988
C 2.492151 -0.730958 0.105308
C -2.045485 2.923560 1.849757
C -1.176922 -0.733948 -0.461613
O 2.657592 -1.823736 0.715921
O 3.490968 0.195147 -0.203233
H -0.272099 1.989549 -2.437059
C -2.130174 -3.035423 0.101201
C 4.944309 -0.083347 0.195394
C 5.431717 -1.367086 -0.511777
H -3.044490 -4.946422 0.579544
H 6.512280 -1.502967 -0.317187
C -1.435582 0.582989 -1.202460
C -1.922862 1.742608 -0.309414
H -1.123991 -3.468612 0.058312
C -2.779777 3.975246 1.252004
H 0.974233 1.834558 -0.297109
H 4.890286 -2.251619 -0.140593
C 5.039640 -0.175043 1.734181
H -3.111016 4.830243 1.853163
C -2.667671 2.801866 -0.897830
H 4.626231 0.737076 2.201709
H 6.102062 -0.263167 2.029817
H -2.221512 0.401602 -1.963880
C -3.092455 3.909209 -0.128304
H -2.920575 2.754479 -1.966163
H 4.492425 -1.053654 2.111032
H -3.669462 4.714016 -0.599698

Azetidine Product:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 0.436857 Hartree
H: -1058.003592 Hartree
G_corr: 0.353647 Hartree
G: -1059.07562083 Hartree
S: 175.130 cal/mol-kelvin

H -2.629653 -2.672412 -2.315737
H -0.008783 2.893292 -2.129202
H -4.664933 -3.826661 -1.435560
C -3.046595 -2.373729 -1.344570
H -0.744139 -1.328073 -1.994971
H 0.911556 -0.042028 -2.420538
C 0.830169 2.224210 -2.372871
C -4.195233 -3.028208 -0.848952
C 0.715106 0.786354 -1.712378
C -1.201184 -0.711173 -1.203371
H 0.985710 2.200440 -3.462619
C -2.413424 -1.322885 -0.612997
H 2.062700 3.305509 -0.790878
C -0.553775 0.466269 -0.921486
C 2.130811 2.484887 -1.526129
N 1.950841 1.134086 -0.925672
C -4.733750 -2.658263 0.407375
H 0.626441 1.335668 1.424333
H -5.622488 -3.166074 0.800145
H 1.310409 -2.992355 1.081297
C -0.300235 1.870626 1.194874
H 2.380139 -1.265937 2.633667
C -1.043150 1.515367 0.033934
C -2.962105 -0.972178 0.657907
H 3.070325 2.585299 -2.098991
C 2.866328 0.386639 -0.225853
O 2.382519 -0.925312 -0.063215
C -4.105472 -1.632985 1.157398
C 2.302101 -3.199010 0.642285
C 3.368058 -1.461333 2.177744
C -0.760136 2.892244 2.060332
O 3.969124 0.839015 0.200339
C 3.200265 -1.948155 0.720688
H -0.178025 3.147023 2.953959
C -2.251543 2.218342 -0.241437
H 2.159918 -3.509892 -0.407963
H -2.484735 -0.194445 1.260245

H 3.973303 -0.541192 2.215735
H -2.831930 1.950825 -1.132448
H 2.770129 -4.033049 1.197278
H -4.505377 -1.351285 2.138849
H 3.873102 -2.245509 2.772888
C -1.963967 3.581625 1.777816
C -2.708854 3.240016 0.621940
C 4.555090 -2.176895 0.012961
H -2.317612 4.373715 2.448423
H 4.393922 -2.462064 -1.042907
H 5.174672 -1.266607 0.048868
H -3.642479 3.767977 0.393789
H 5.097764 -3.000981 0.513801

[Co(**P6**)]:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.204788 Hartree
H: -5975.815992 Hartree
G_corr: 1.846247 Hartree
G: -7219.40288937 Hartree
S: 754.613 cal/mol-kelvin

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C -9.274644 4.268366 -0.324170
C -8.438336 2.832133 1.598601
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H -11.110567 -5.918764 2.097670
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H -9.769100 -6.369524 3.183806
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C -10.016507 -6.088027 2.144783
H -7.383846 2.700905 1.906591
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C -7.950159 -2.813010 2.263473

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$TS1_{[Co(\mathbf{P6})]}$:
Imaginary Freqency: -271.14 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.650240 Hartree
H: -7143.216548 Hartree
G_corr: 2.235693 Hartree
G: -8388.01937906 Hartree
S: 872.488 cal/mol-kelvin

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Intermediate B:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.639855 Hartree
H: -7033.729790 Hartree
G_corr: 2.226047 Hartree
G: -8278.46912676 Hartree
S: 870.932 cal/mol-kelvin

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H -4.486738 9.088149 -3.222690
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H -4.645527 6.922626 -4.114190
H -4.244240 11.690408 -0.568169
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H 7.515229 -6.318867 0.690915
H 9.956410 -7.027066 2.444394

TS2:
Imaginary Freqency: -1375.76 Hz

Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.635822 Hartree
H: -7033.733574 Hartree
G_corr: 2.231337 Hartree
G: -8278.45553164 Hartree
S: 851.310 cal/mol-kelvin

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H -4.240546 7.298871 -3.814709
H -3.693886 11.791830 0.054163
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C -4.346792 6.691088 -2.899011
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H -8.234690 2.421821 3.544664
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H -5.229401 6.035444 -3.021374
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H -10.206406 1.777062 2.438168
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Intermediate C:
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.640608 Hartree
H: -7033.772248 Hartree
G_corr: 2.234300 Hartree

G: -8278.49334257 Hartree
S: 855.148 cal/mol-kelvin

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$TS3_{4\text{-exo-tet}}$:
Imaginary Freqency: -586.77 Hz
Temperature: 298.15 Kelvin
Pressure: 1.0 atm
H_corr: 2.639497 Hartree
H: -7033.739835 Hartree
G_corr: 2.230931 Hartree
G: -8278.44894972 Hartree
S: 859.898 cal/mol-kelvin

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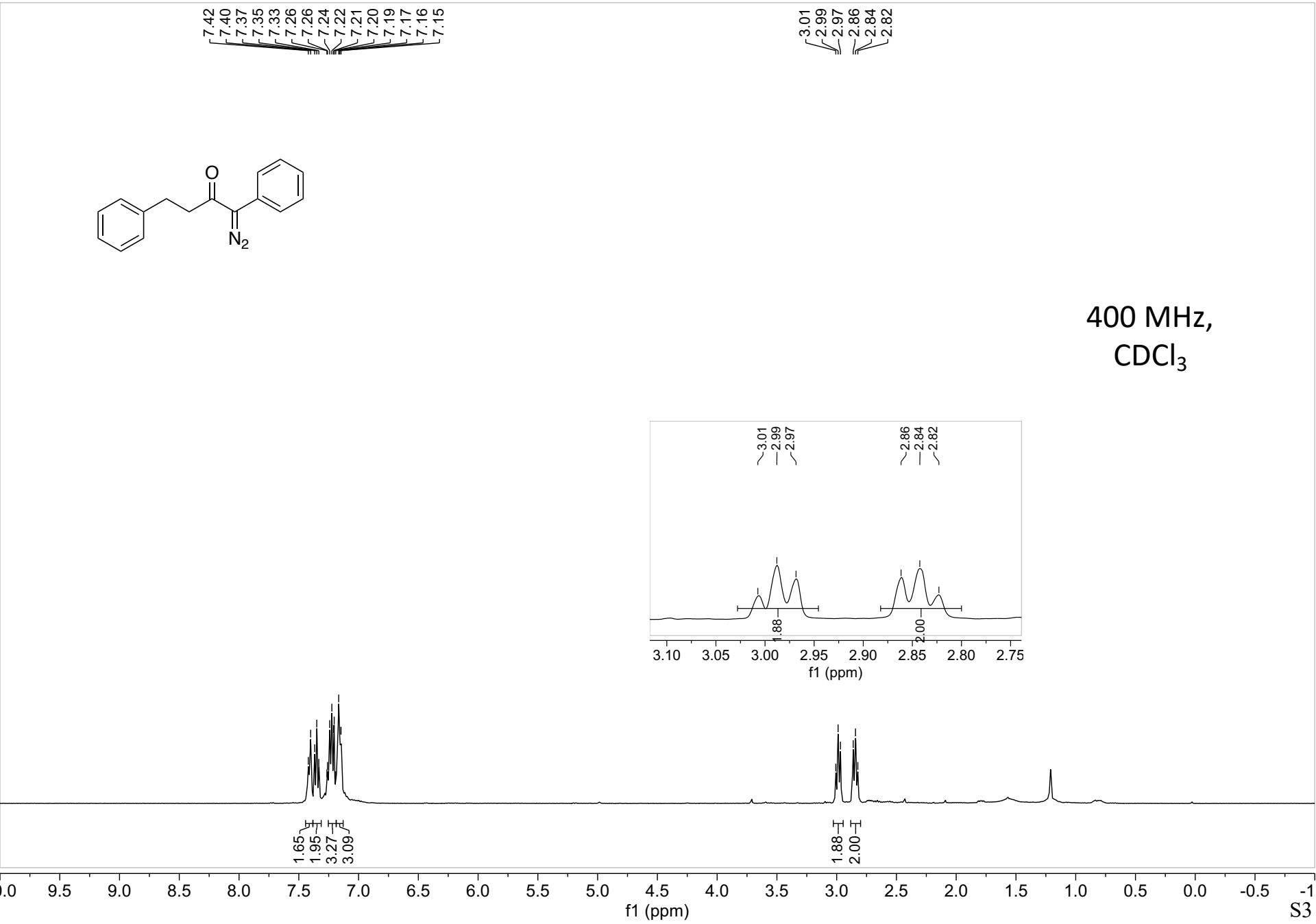
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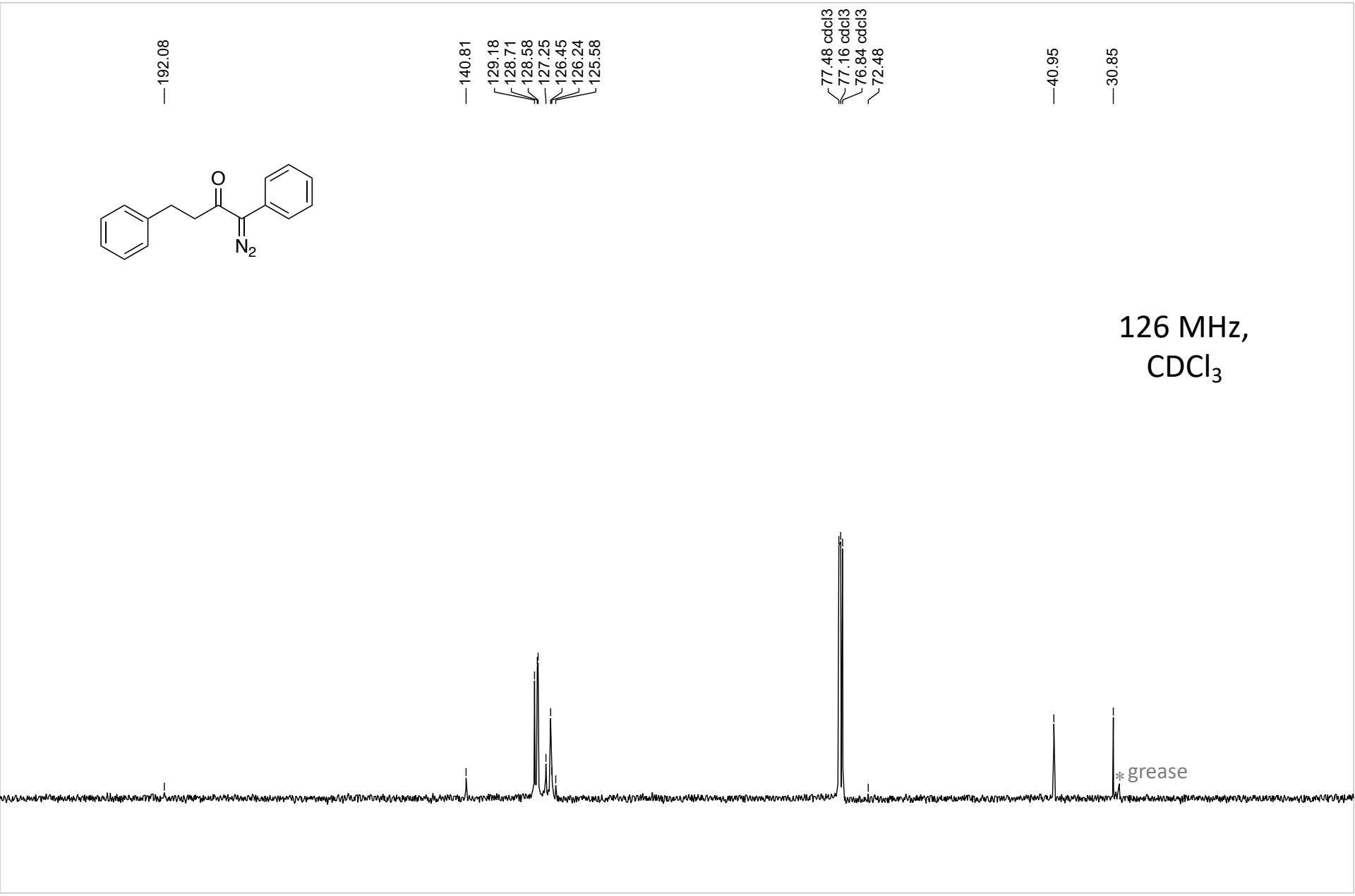
# NMR and HPLC Spectrum

# Spectral Data for Chapter 2

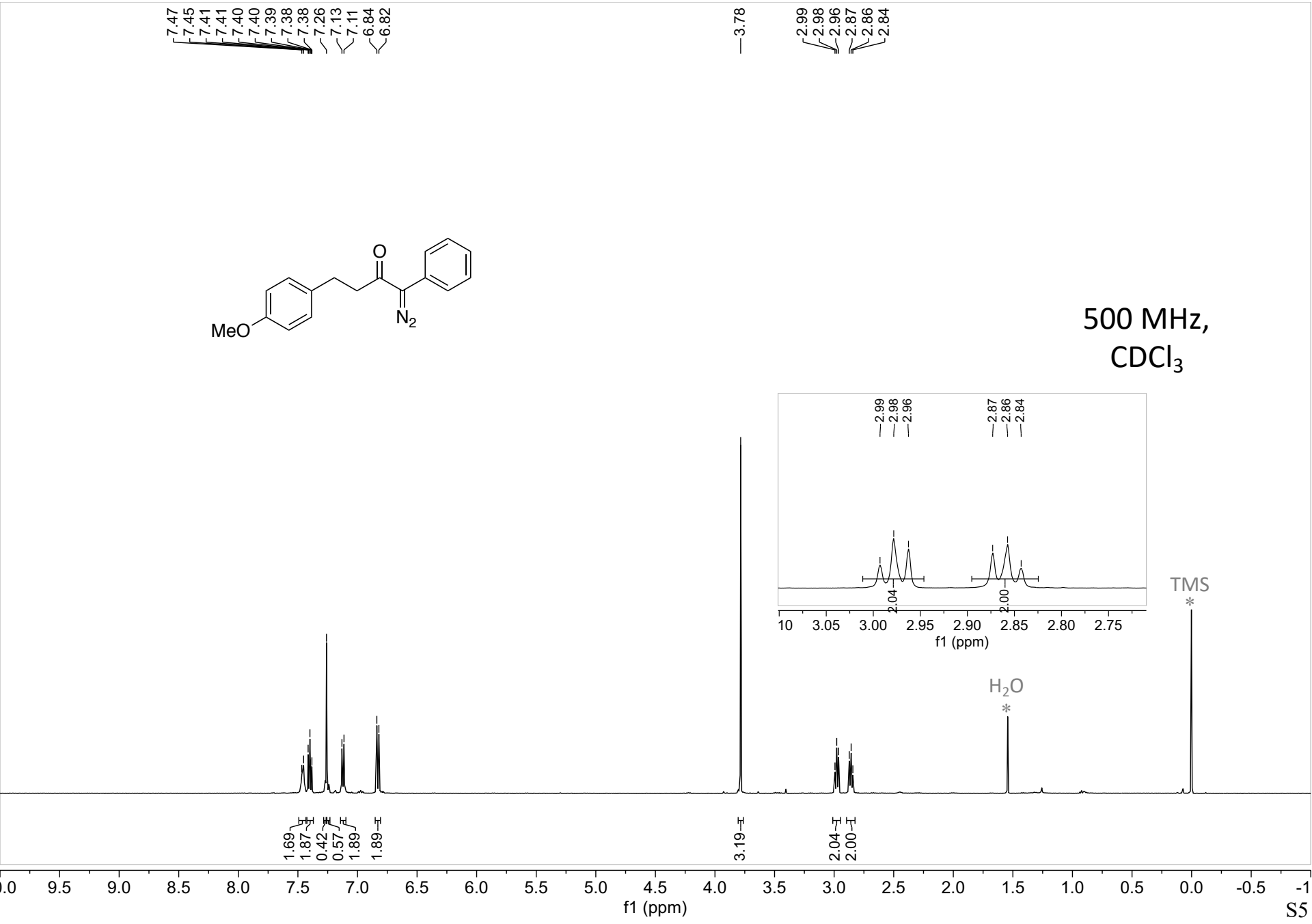
# $^{1}$H NMR 1-diazo-1,4-diphenylbutan-2-one **(1a)**



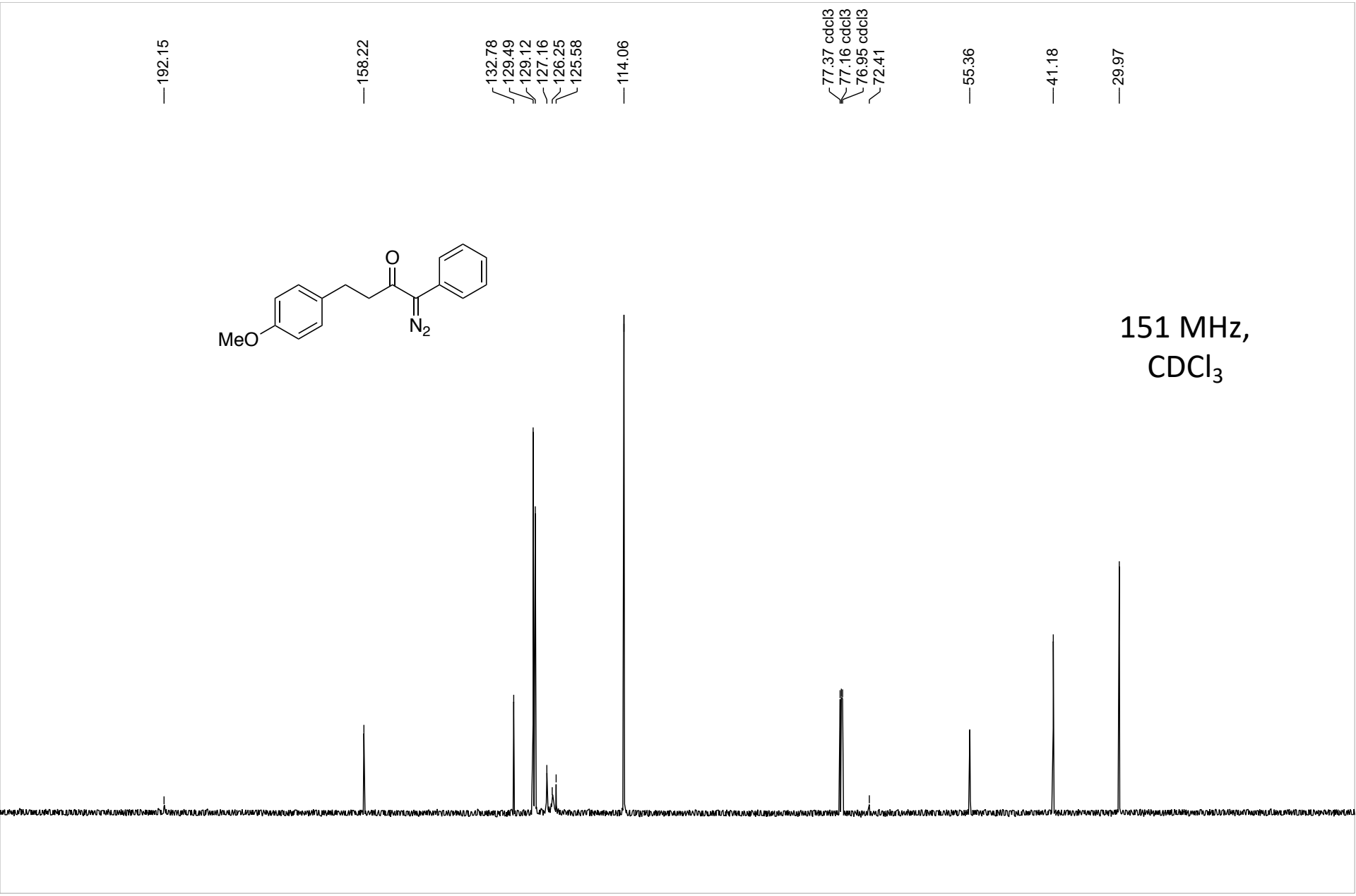
# $^{13}$C NMR 1-diazo-1,4-diphenylbutan-2-one **(1a)**



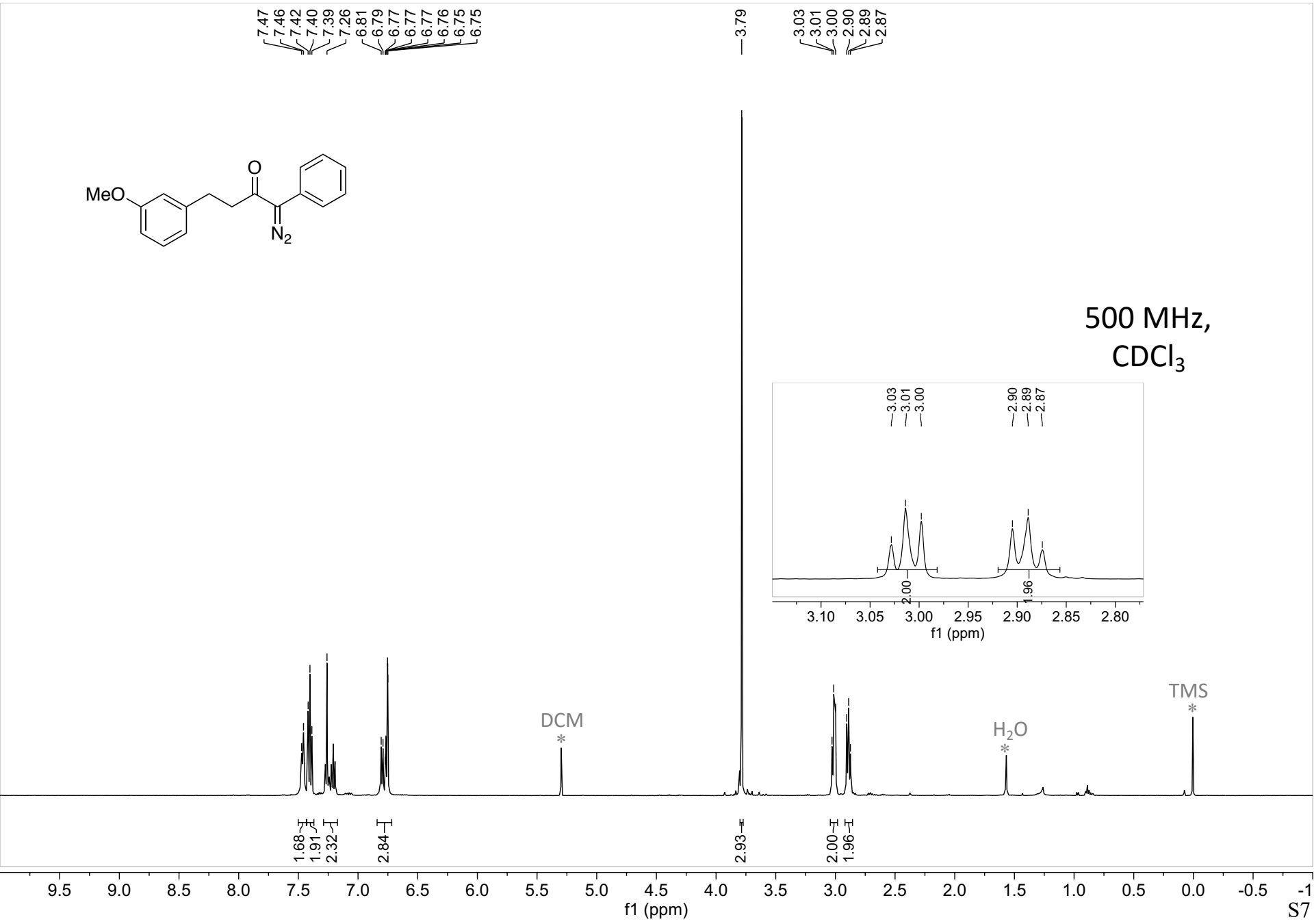
# **$^1$H NMR** 1-diazo-4-(4-methoxyphenyl)-1-phenylbutan-2-one **(1b)**



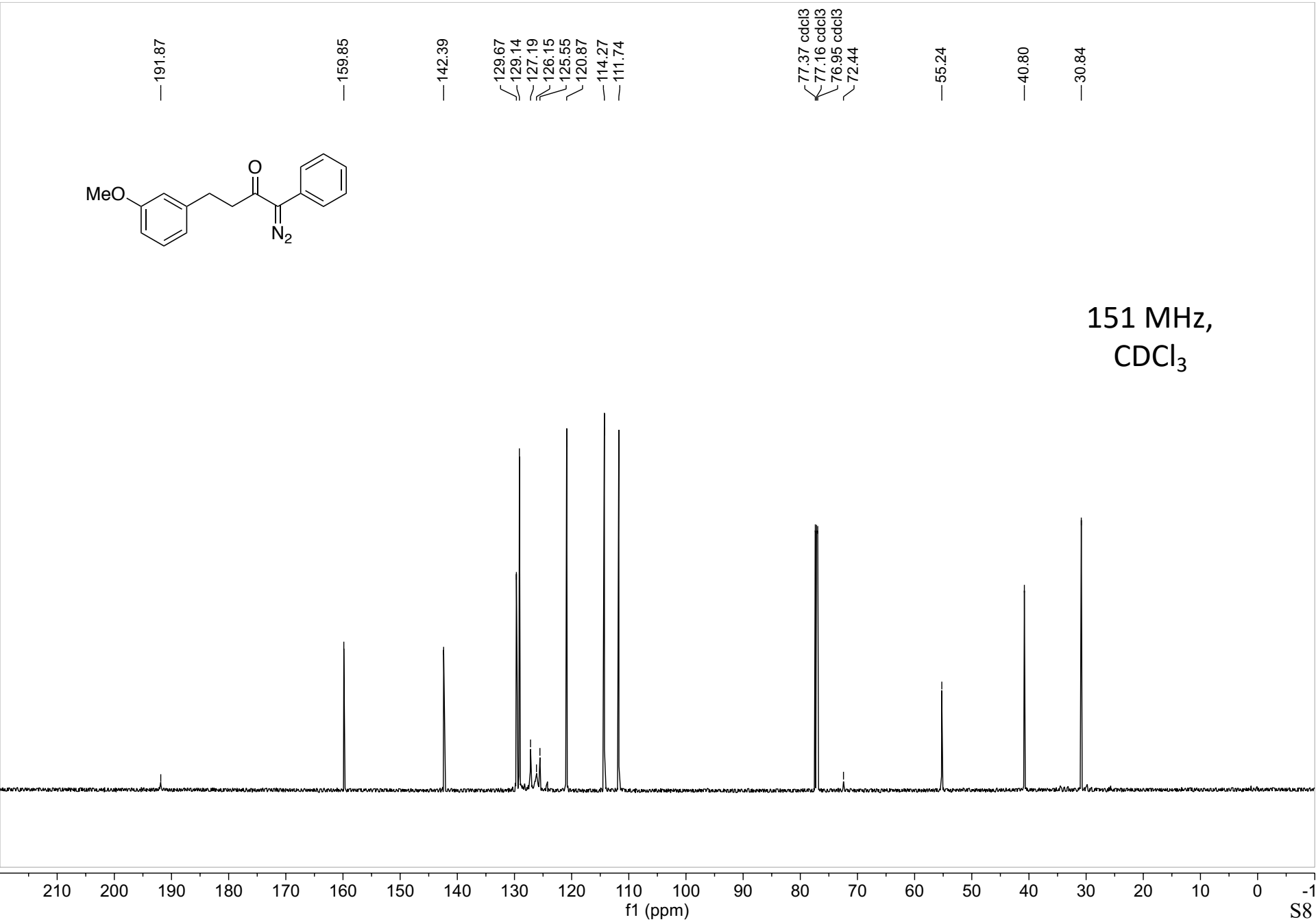
# $^{13}$C NMR 1-diazo-4-(4-methoxyphenyl)-1-phenylbutan-2-one **(1b)**



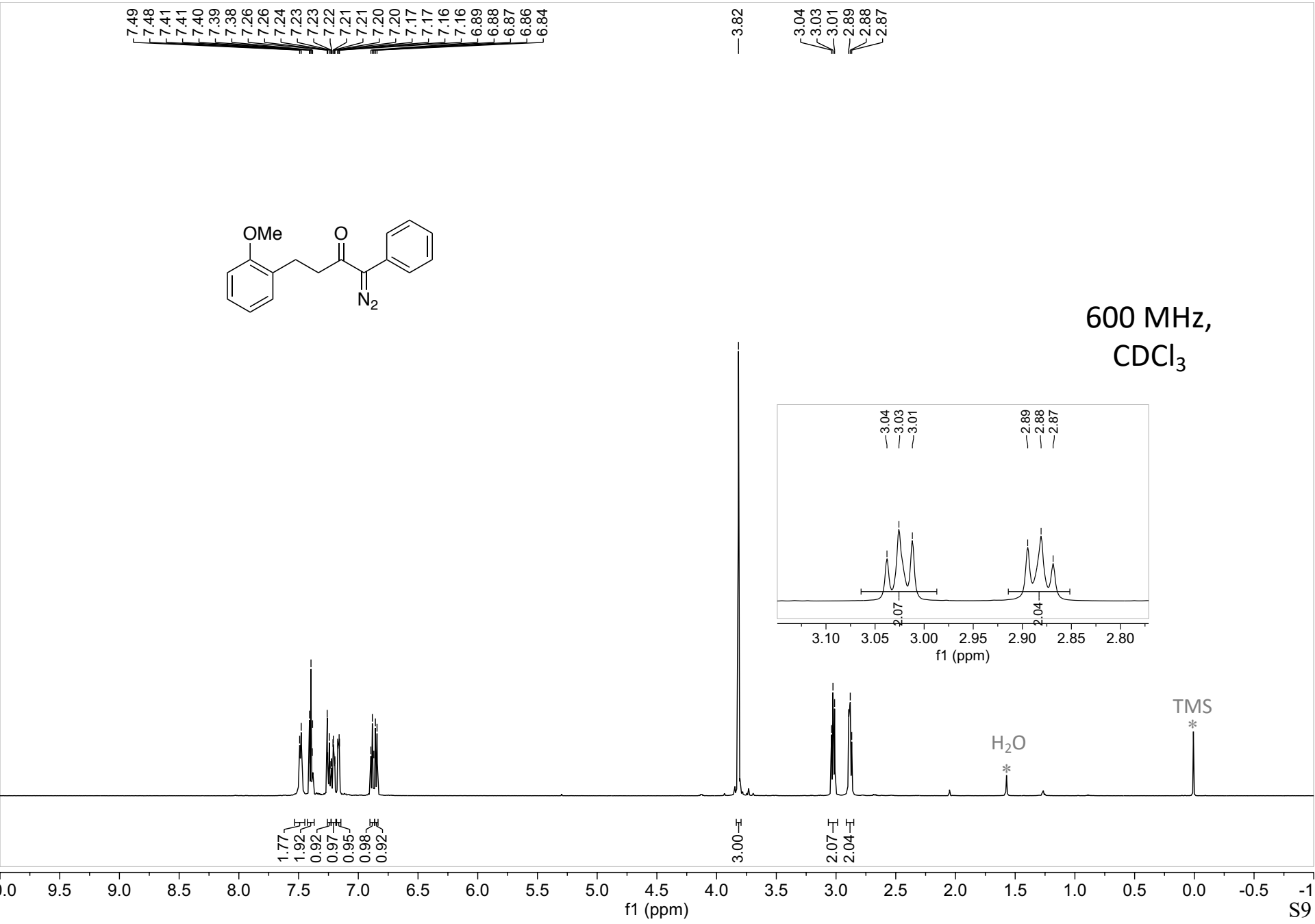
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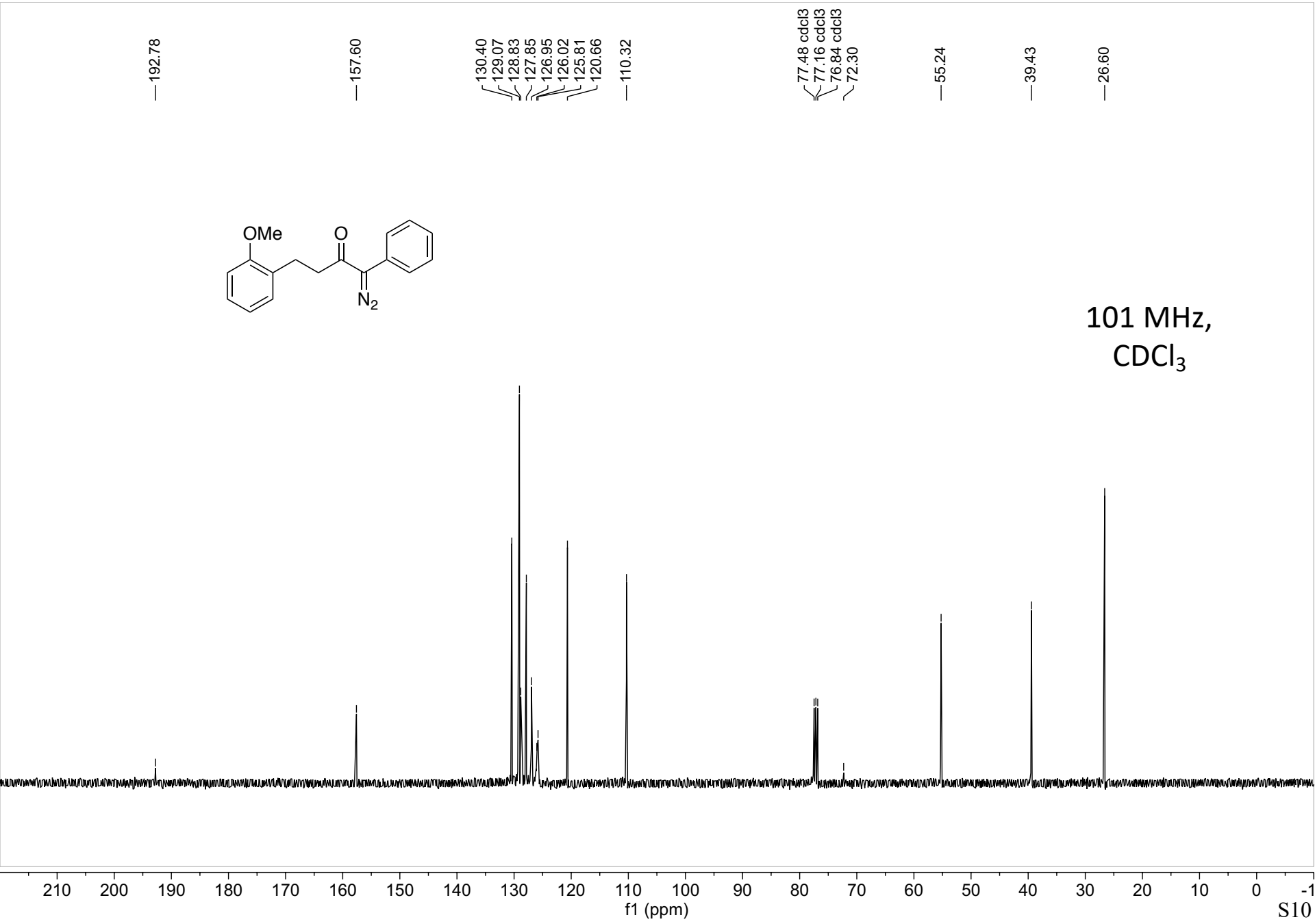
# $^{13}$C NMR 1-diazo-4-(3-methoxyphenyl)-1-phenylbutan-2-one **(1c)**



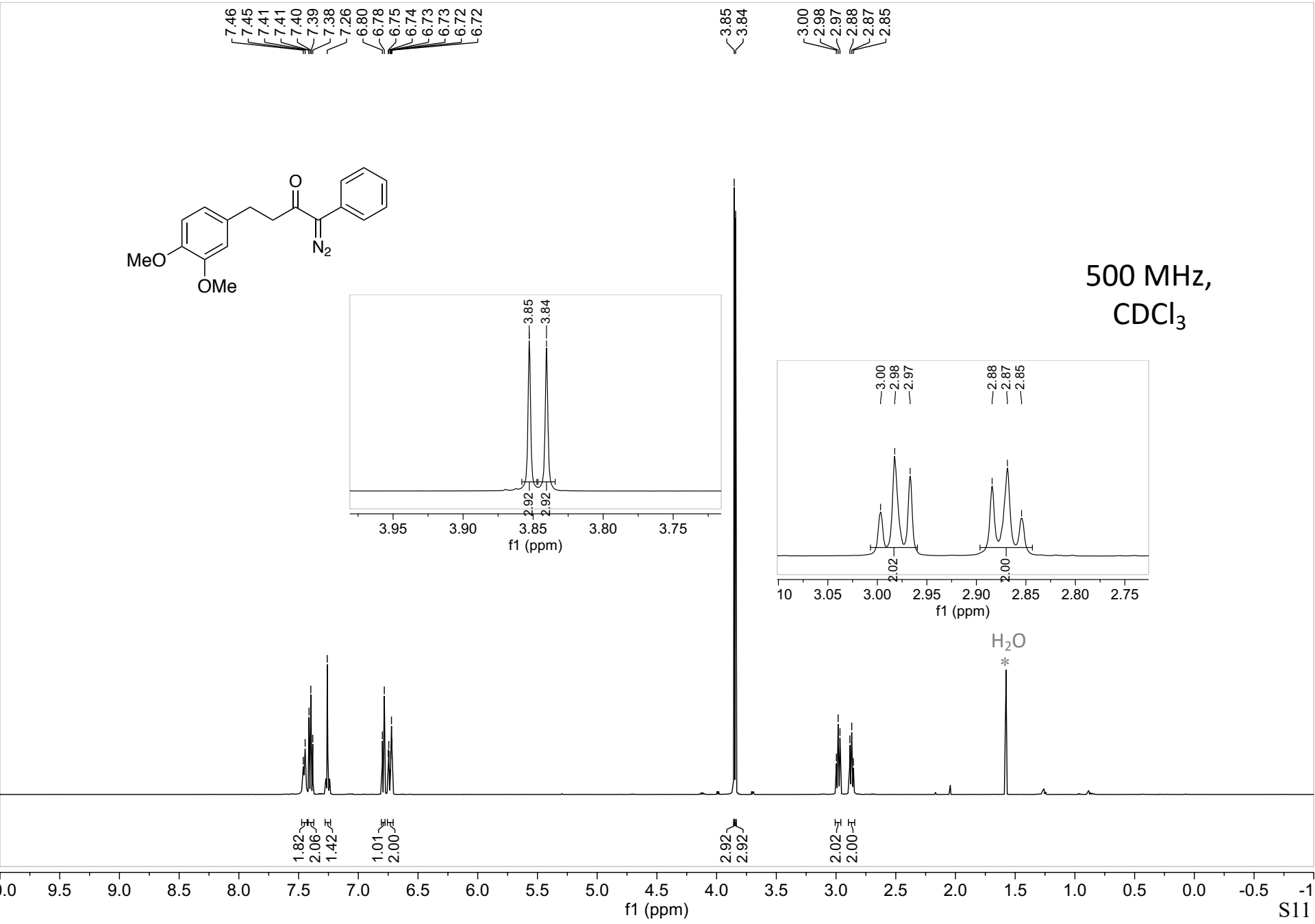
# $^{1}$H NMR 1-diazo-4-(2-methoxyphenyl)-1-phenylbutan-2-one **(1d)**



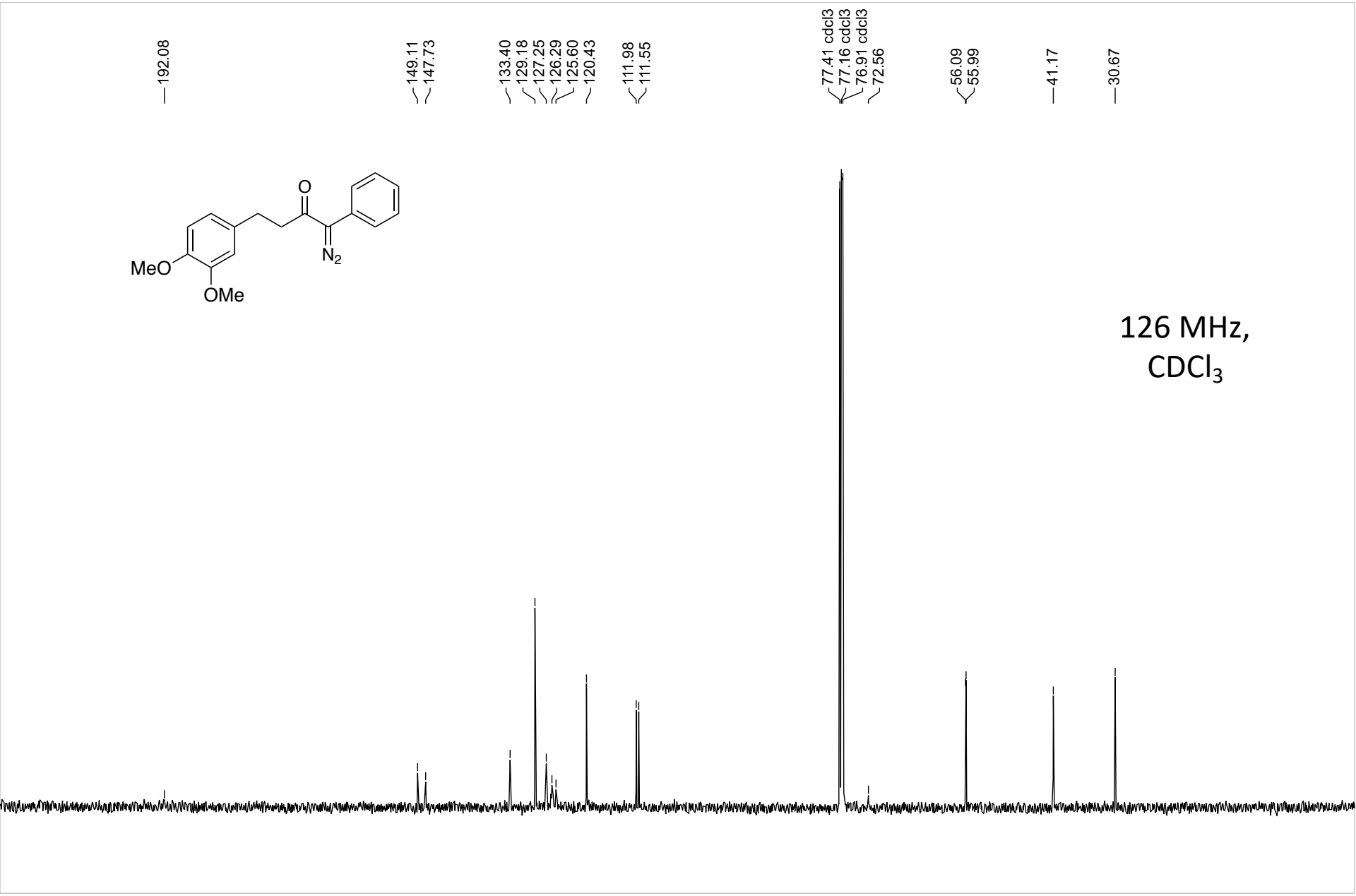
# $^{13}$C NMR 1-diazo-4-(2-methoxyphenyl)-1-phenylbutan-2-one **(1d)**



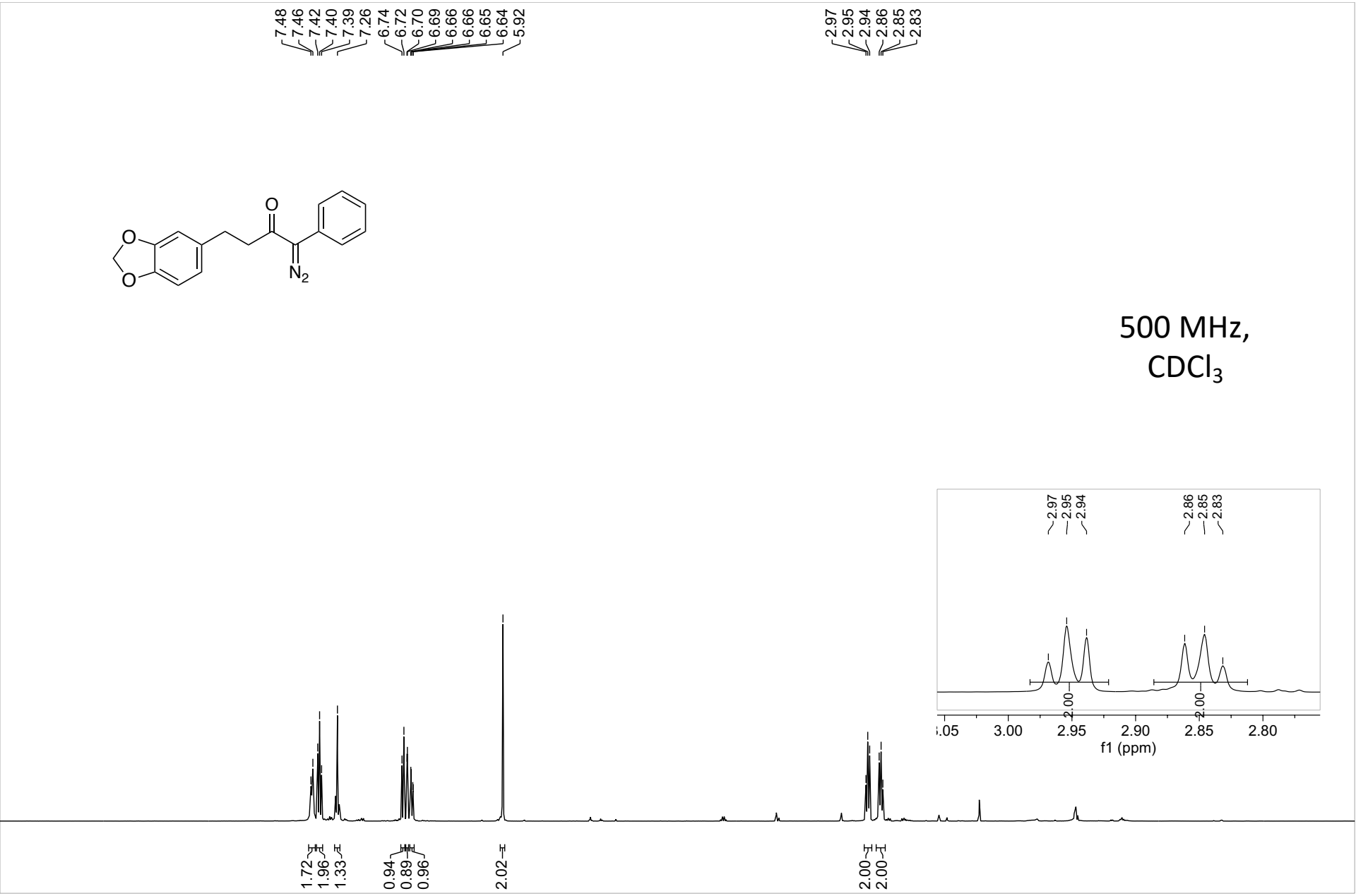
# $^{1}$H NMR 1-diazo-4-(3,4-dimethoxyphenyl)-1-phenylbutan-2-one **(1e)**



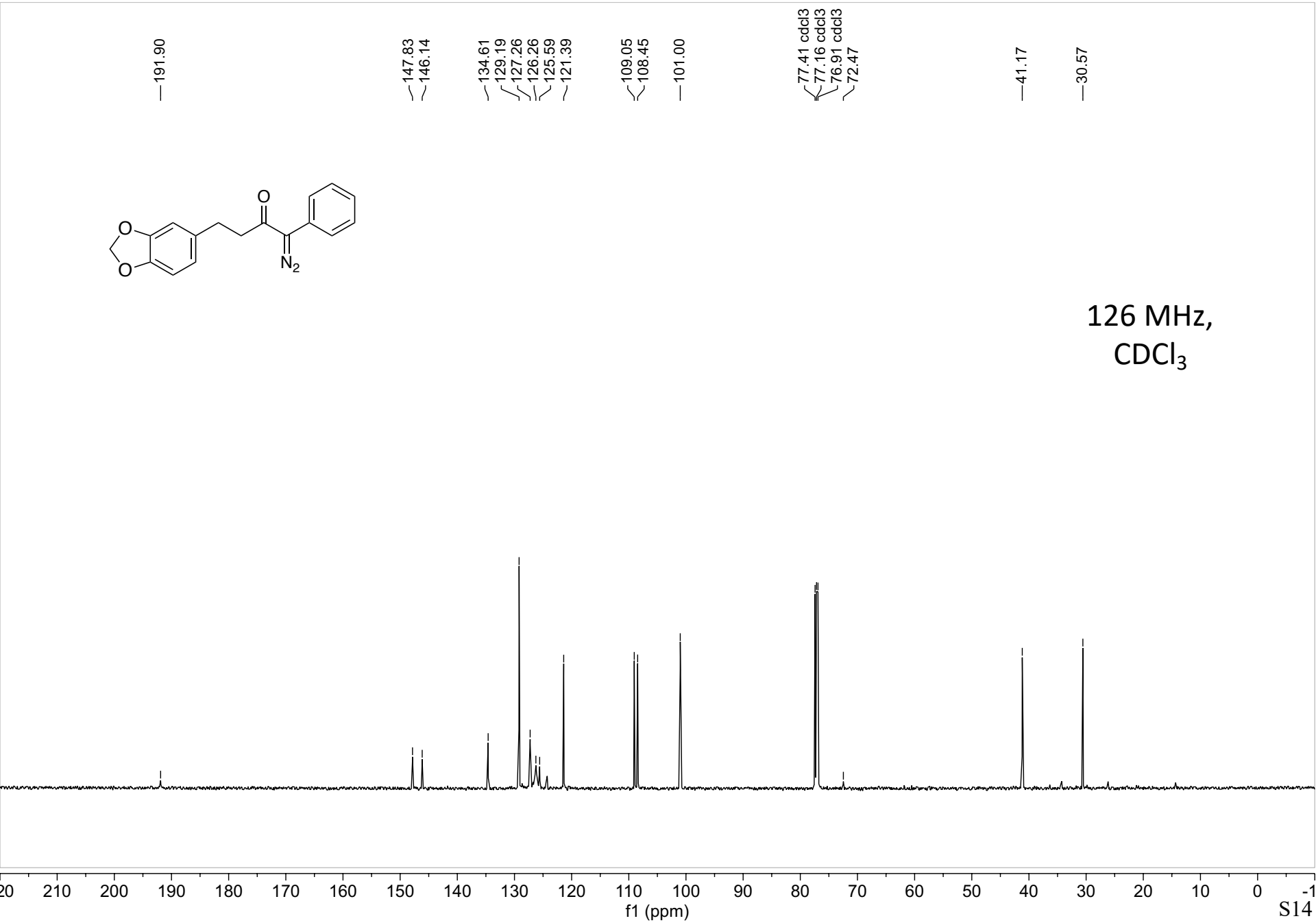
# $^{13}$C NMR 1-diazo-4-(3,4-dimethoxyphenyl)-1-phenylbutan-2-one **(1e)**



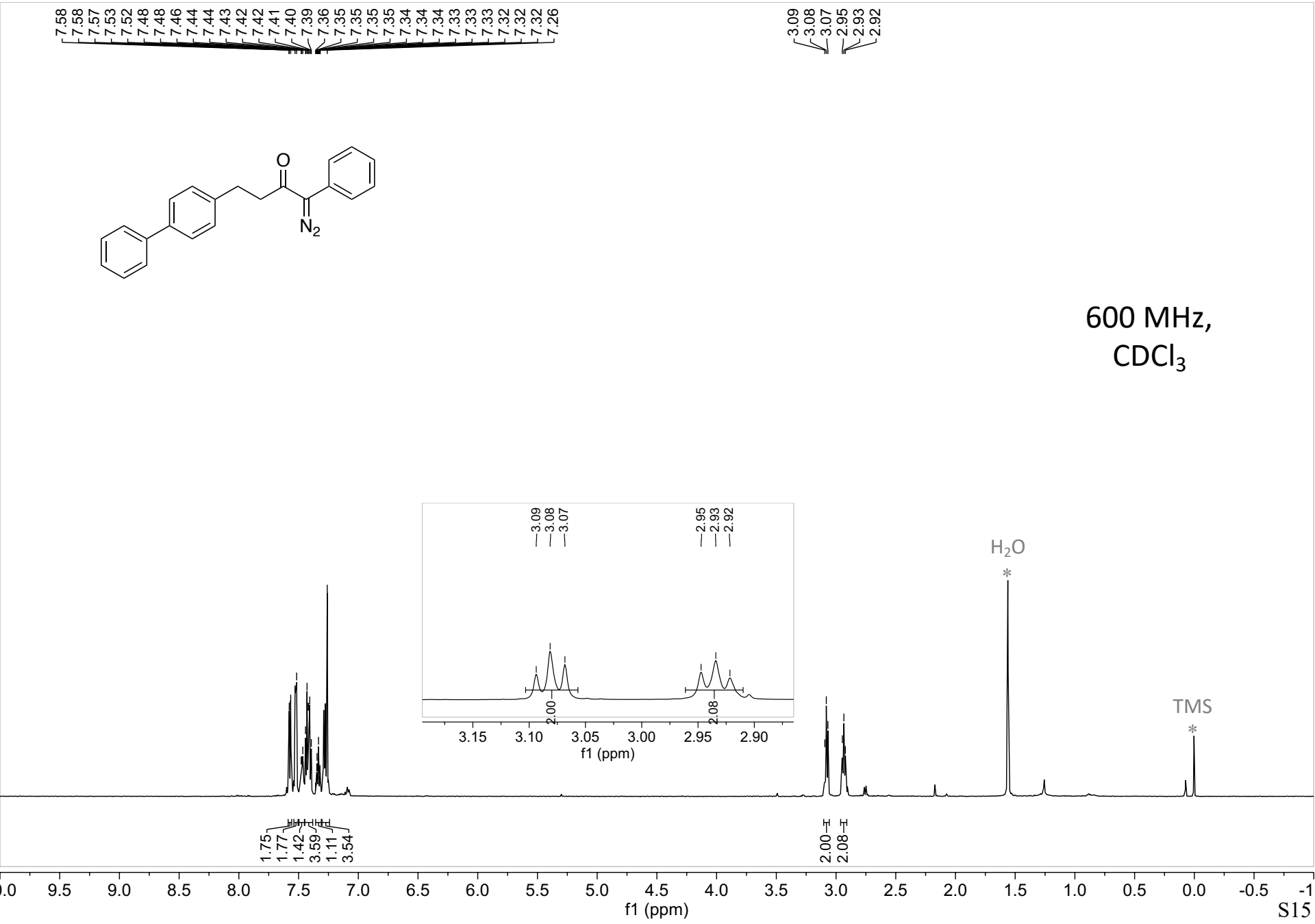
# $^1$H NMR 4-(benzo[*d*][1,3]dioxol-5-yl)-1-diazo-1-phenylbutan-2-one **(1f)**



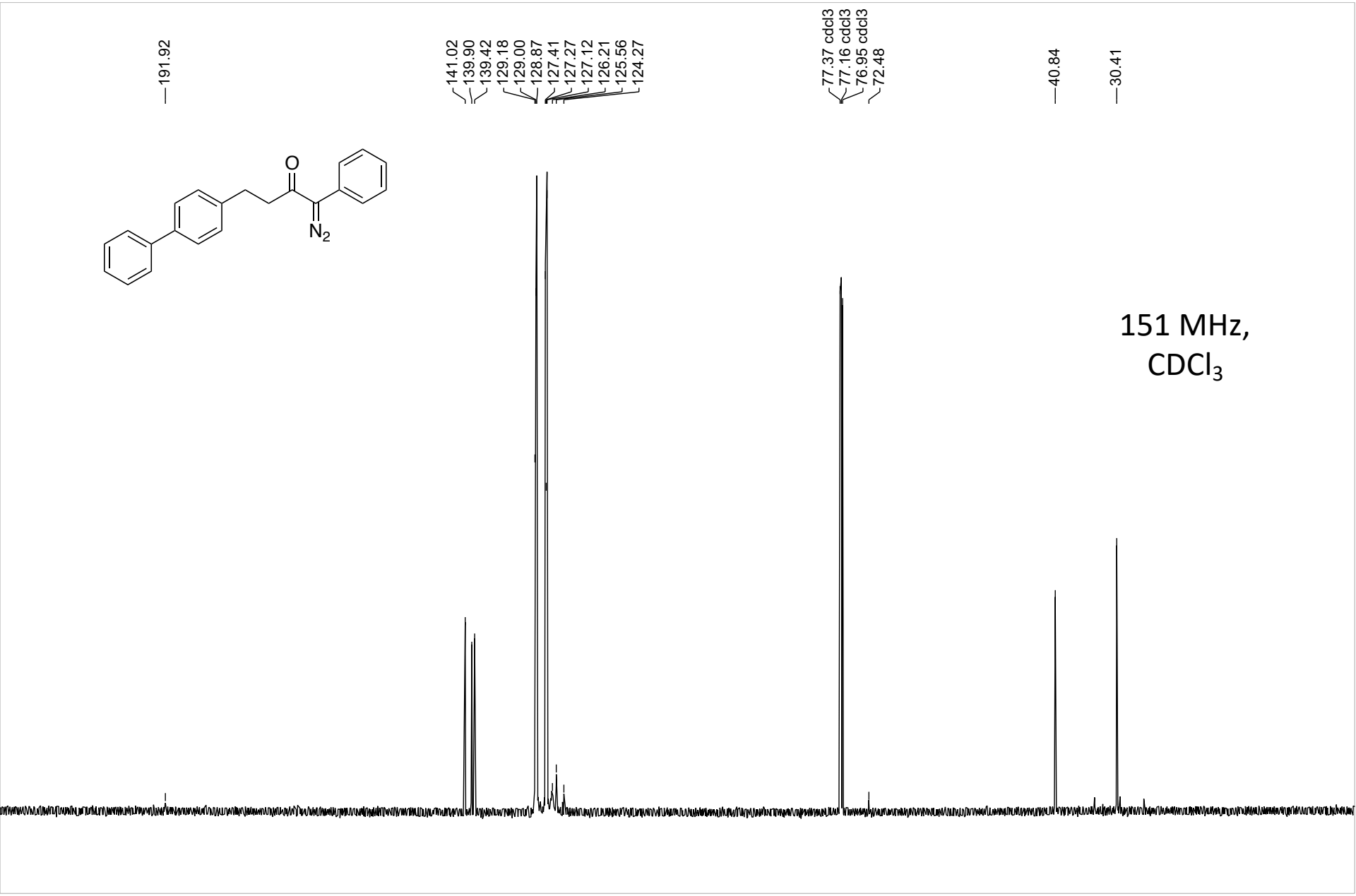
# $^{13}$C NMR 4-(benzo[*d*][1,3]dioxol-5-yl)-1-diazo-1-phenylbutan-2-one **(1f)**



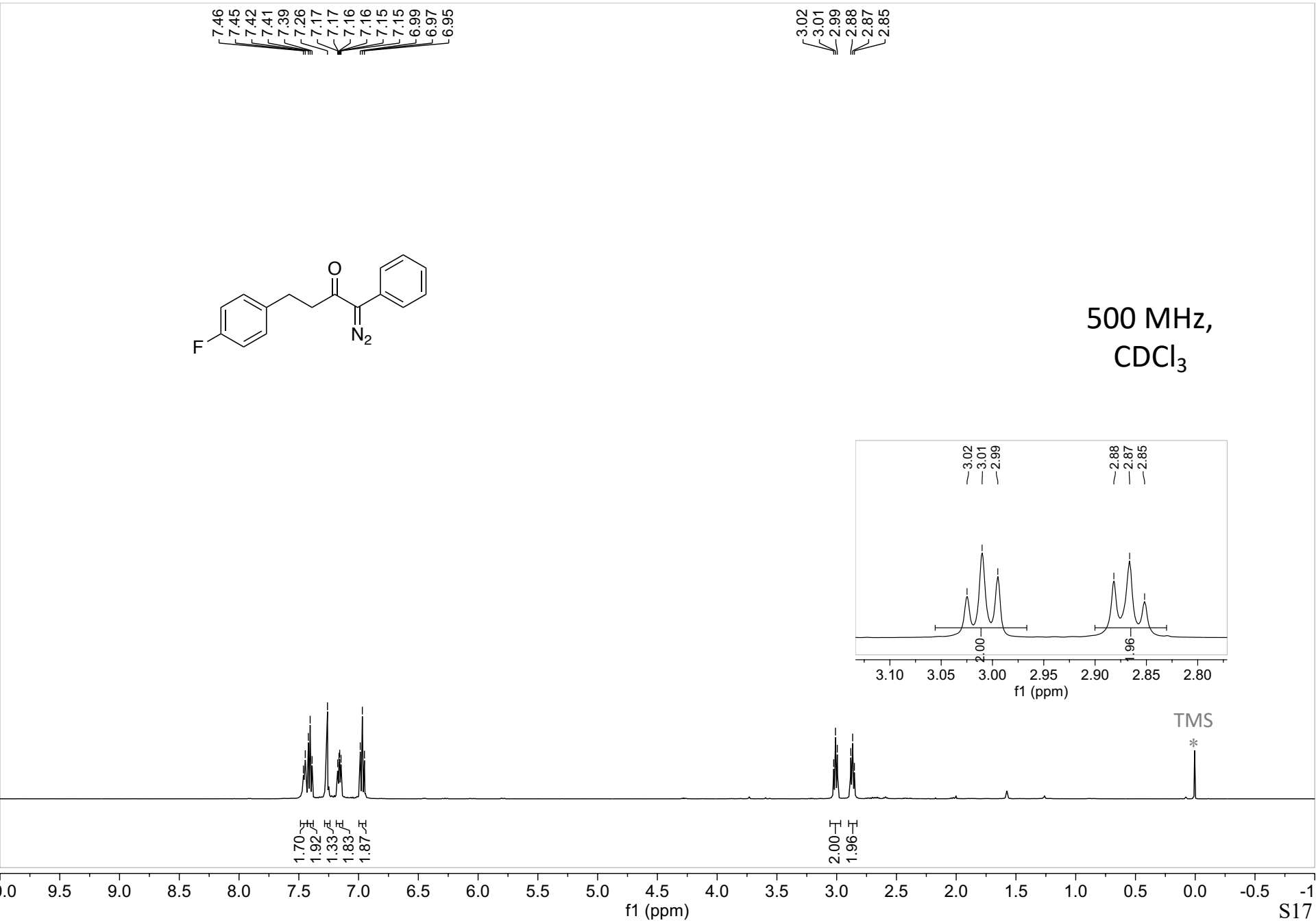
# $^{1}$H NMR 4-([1,1'-biphenyl]-4-yl)-1-diazo-1-phenylbutan-2-one **(1g)**



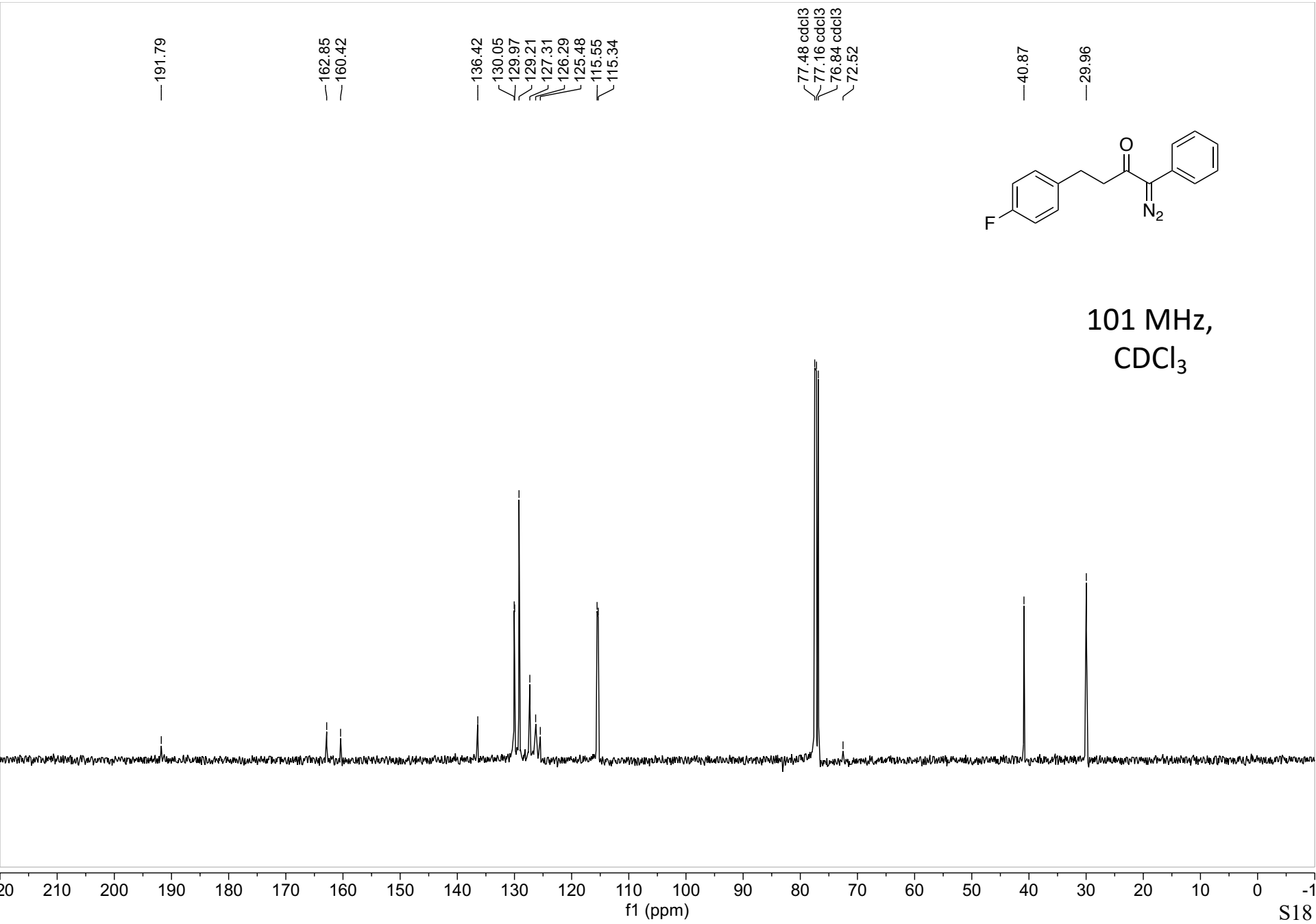
# $^{13}$C NMR 4-([1,1'-biphenyl]-4-yl)-1-diazo-1-phenylbutan-2-one **(1g)**



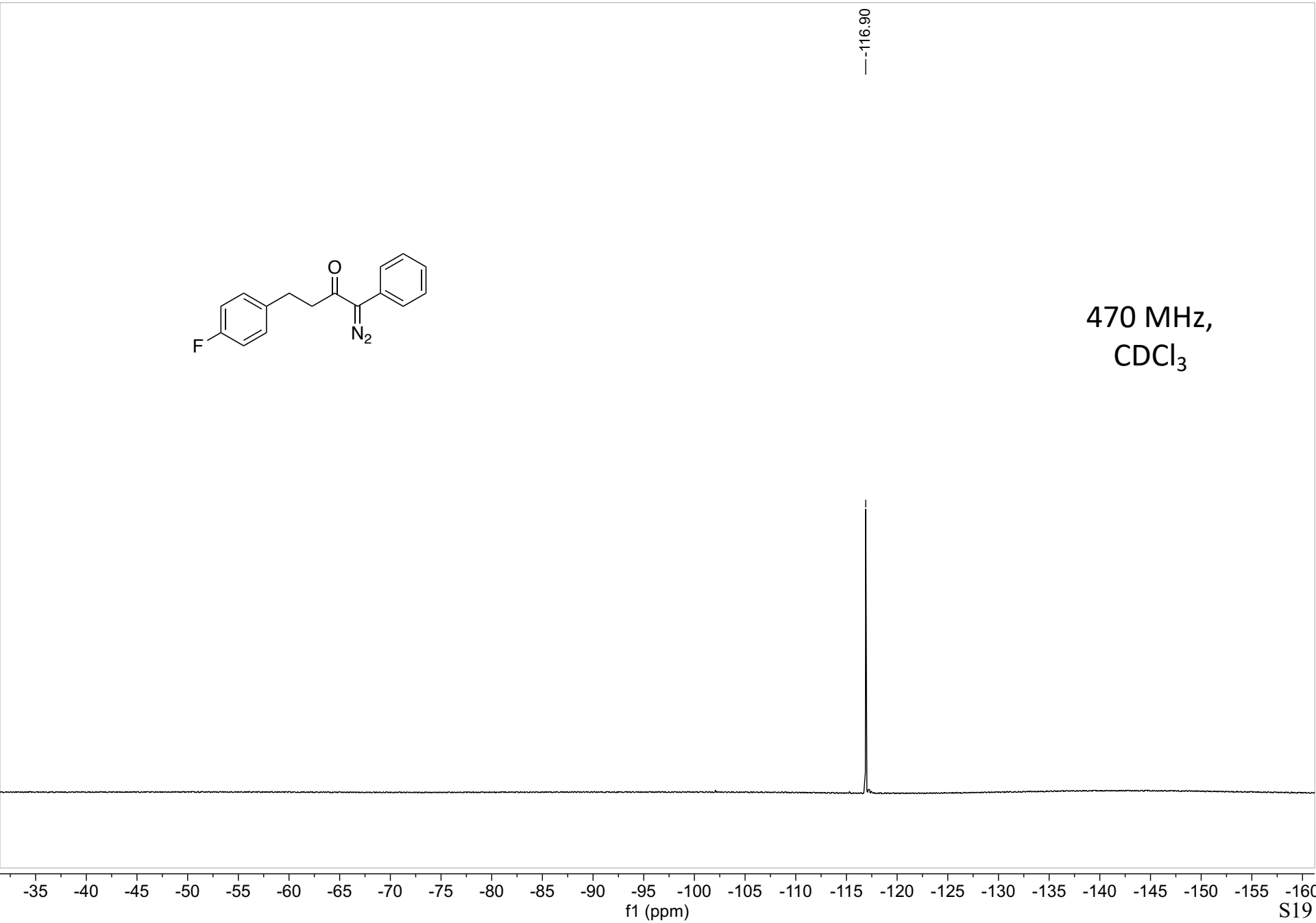
# $^{1}$H NMR 1-diazo-4-(4-fluorophenyl)-1-phenylbutan-2-one **(1h)**



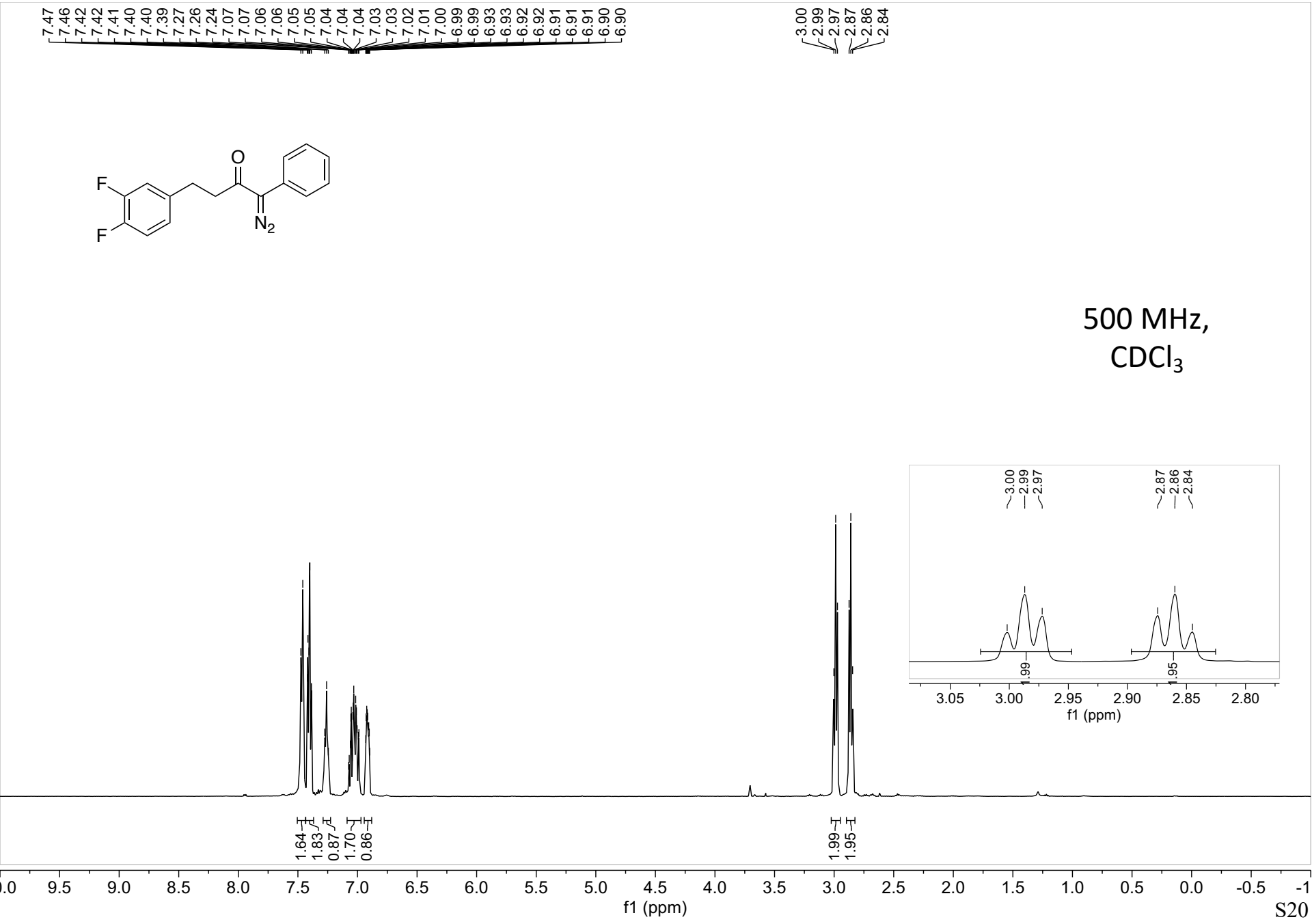
# $^{13}$C NMR 1-diazo-4-(4-fluorophenyl)-1-phenylbutan-2-one **(1h)**



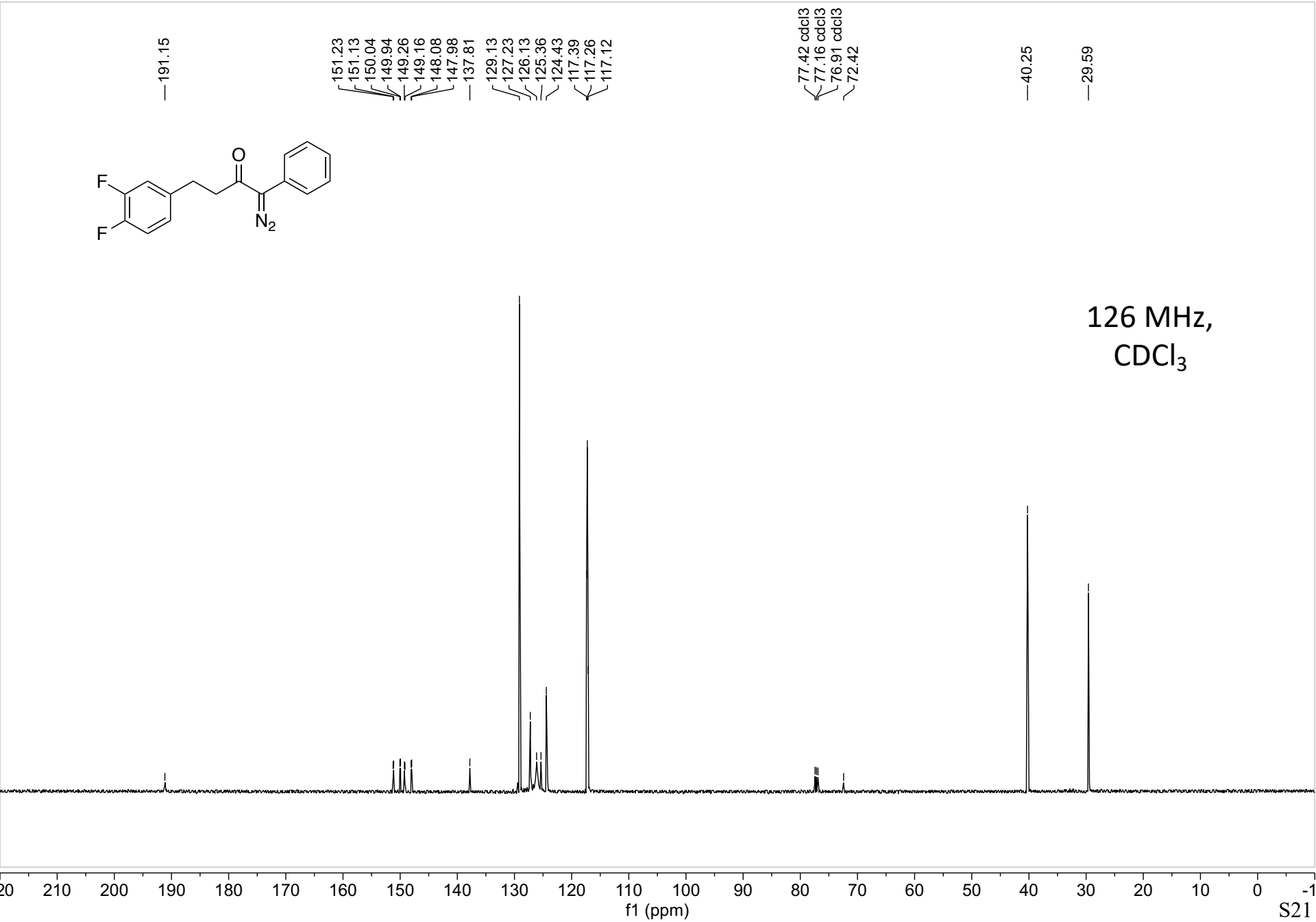
# $^{19}$F NMR 1-diazo-4-(4-fluorophenyl)-1-phenylbutan-2-one **(1h)**



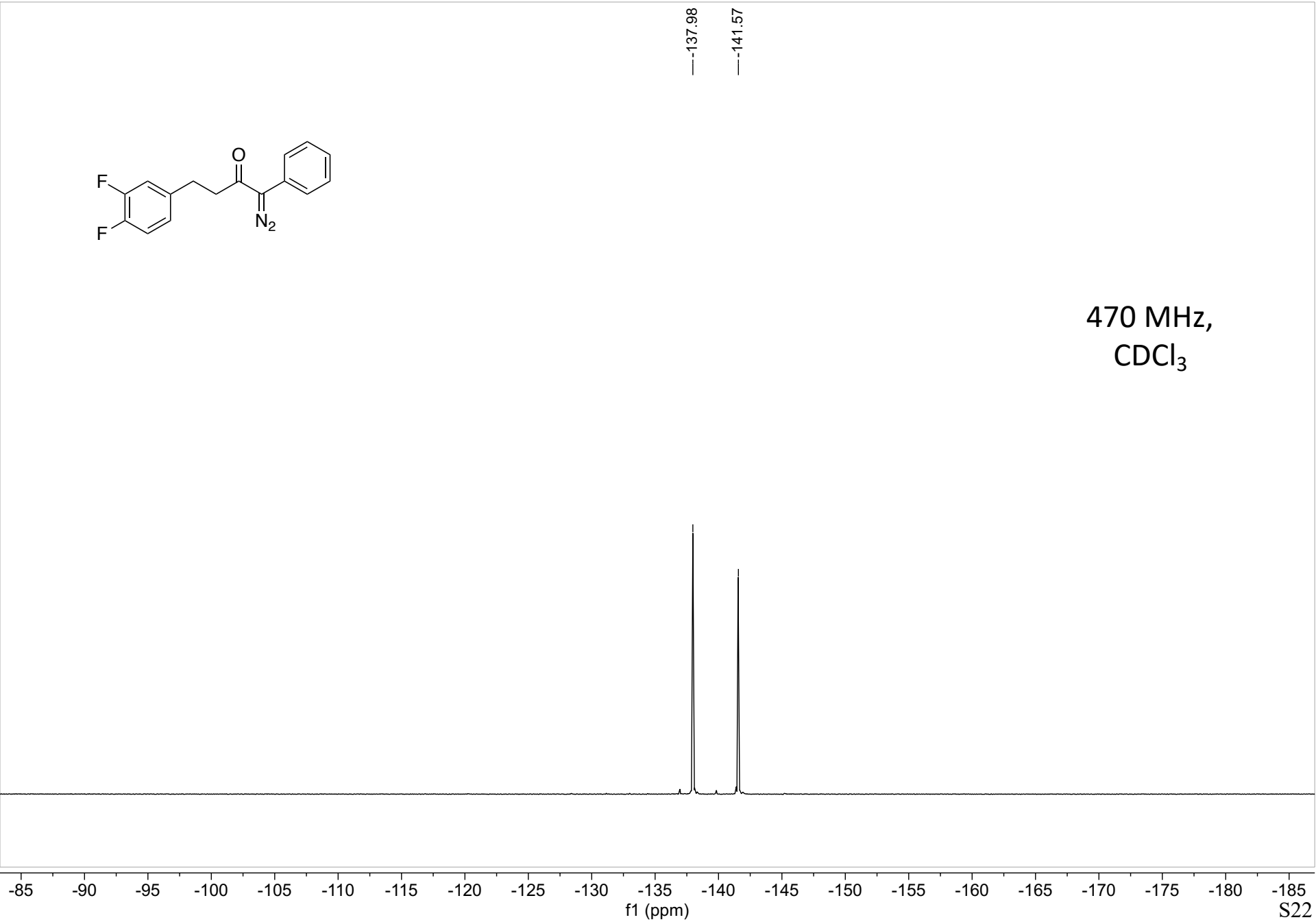
# $^{1}$H NMR 1-diazo-4-(3,4-difluorophenyl)-1-phenylbutan-2-one **(1i)**



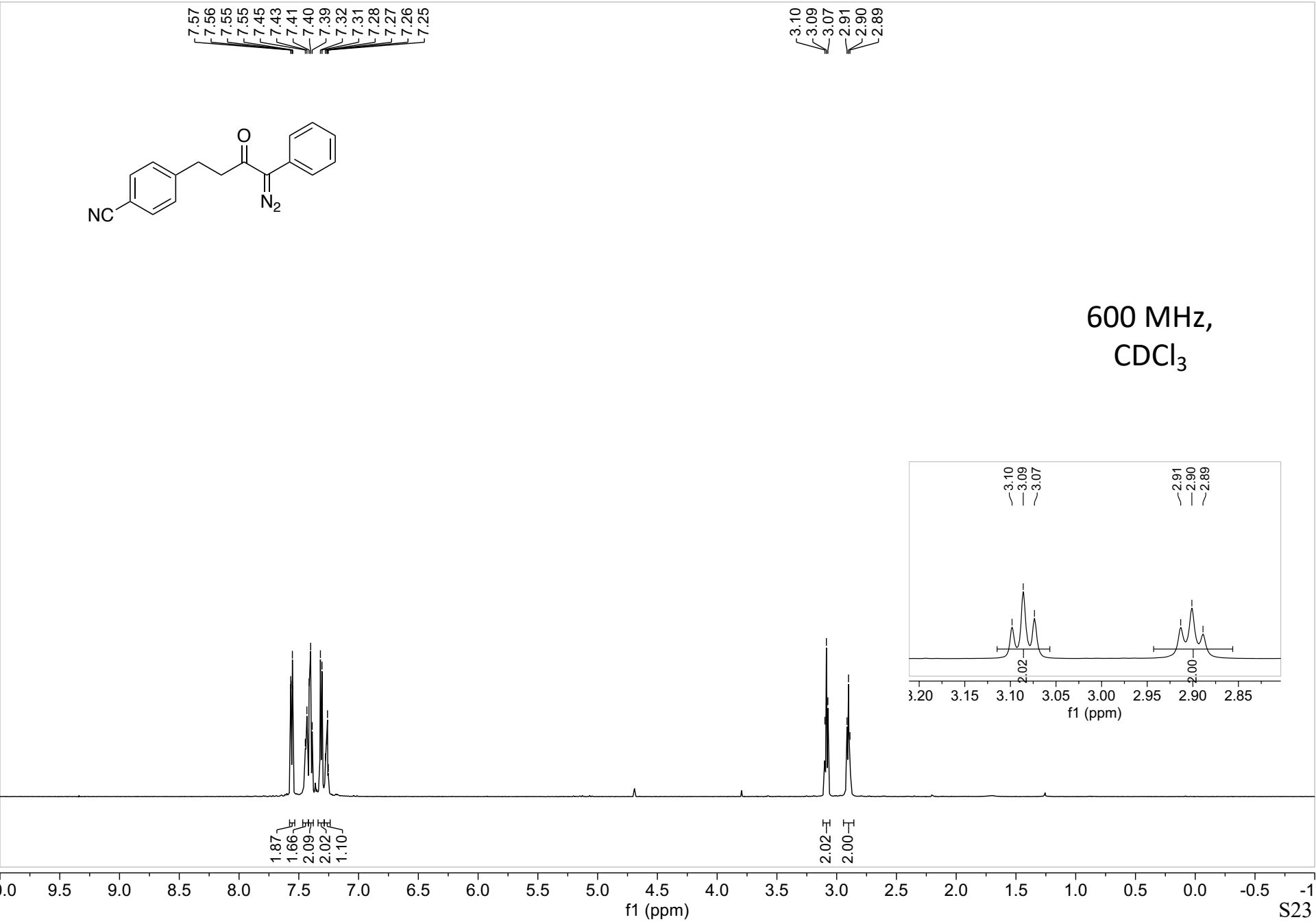
# $^{13}$C NMR 1-diazo-4-(3,4-difluorophenyl)-1-phenylbutan-2-one **(1i)**



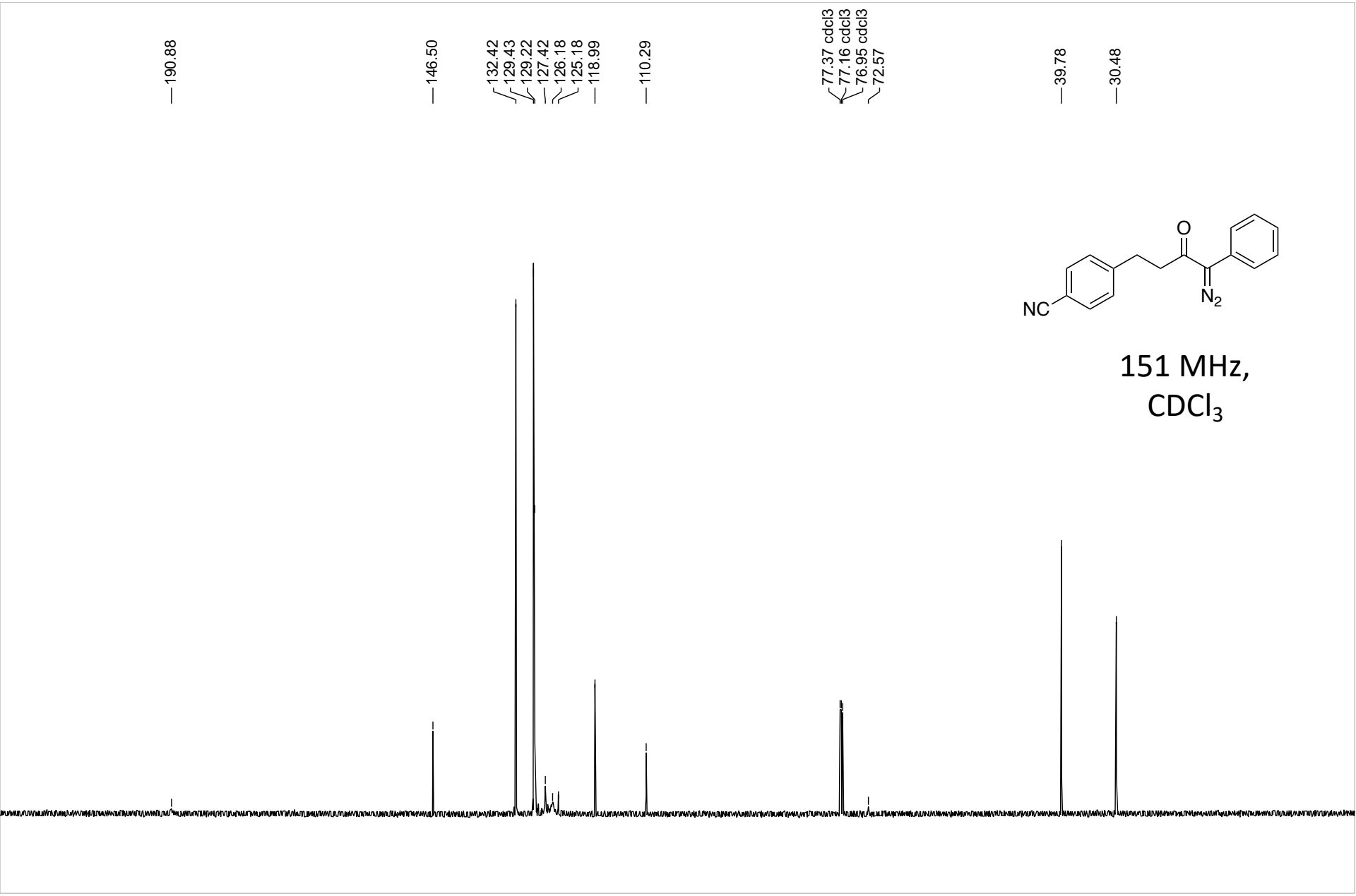
# $^{19}$F NMR 1-diazo-4-(3,4-difluorophenyl)-1-phenylbutan-2-one **(1i)**



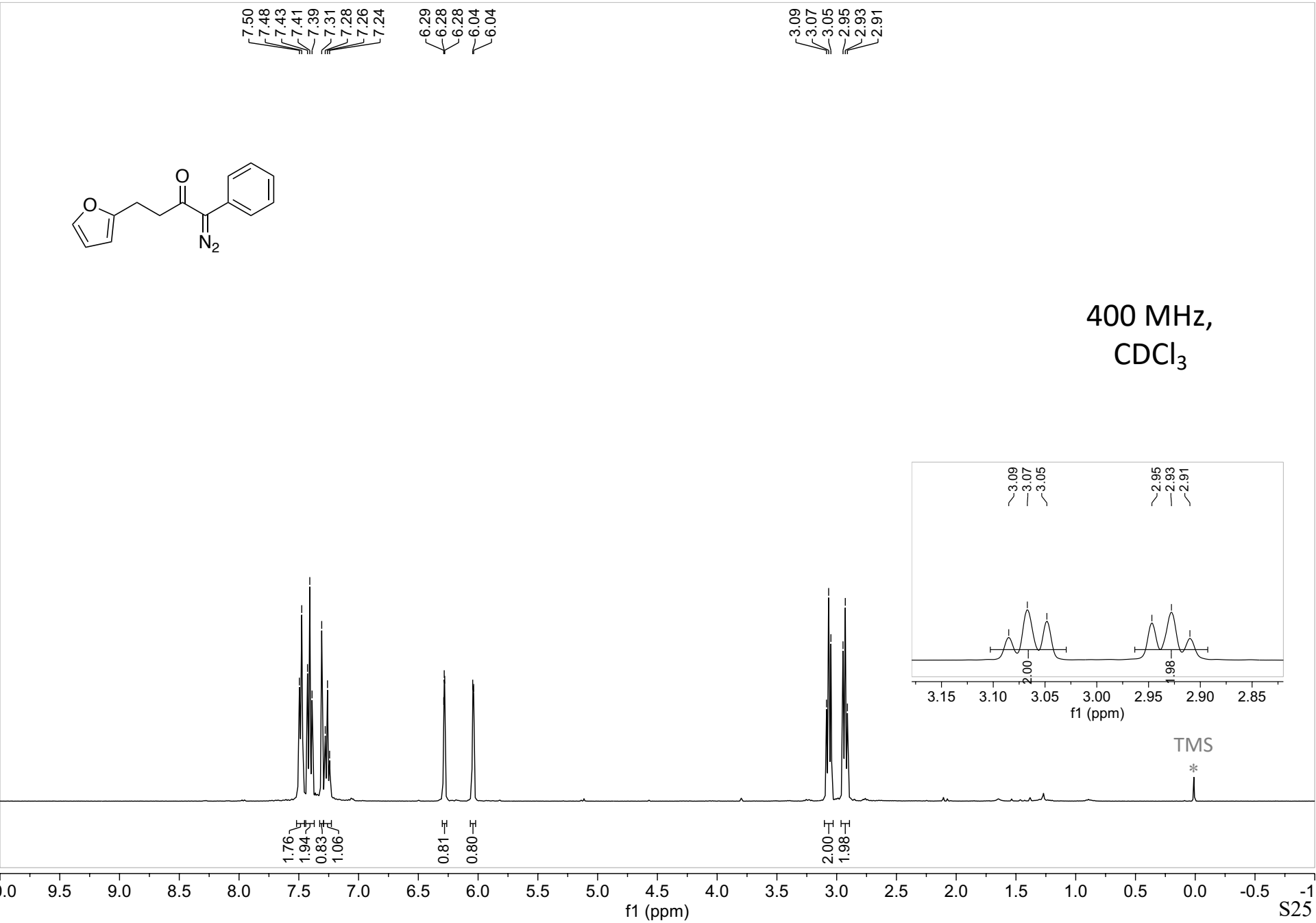
# $^1$H NMR 4-(4-diazo-3-oxo-4-phenylbutyl)benzonitrile **(1j)**



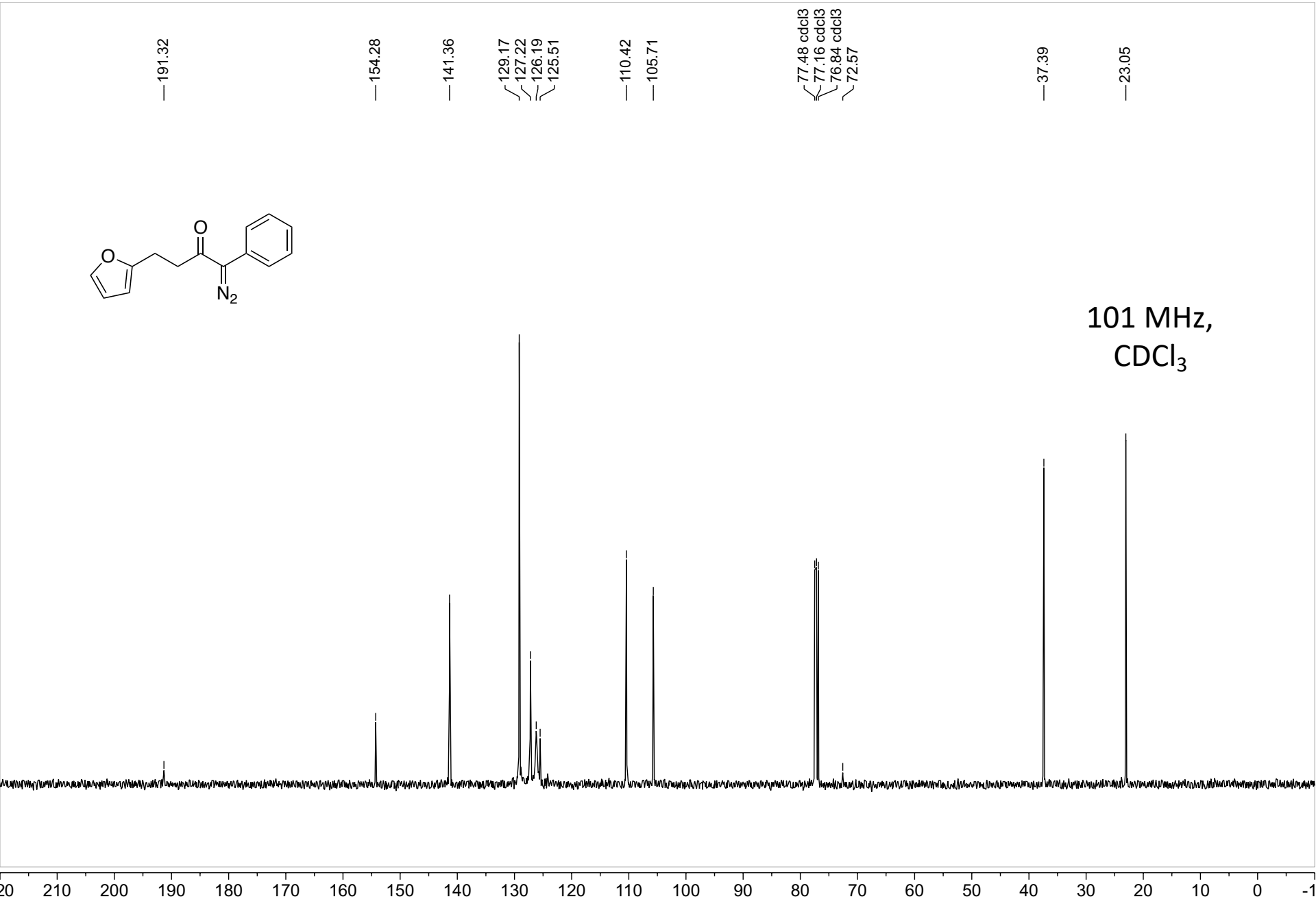
# $^{13}$C NMR 4-(4-diazo-3-oxo-4-phenylbutyl)benzonitrile **(1j)**



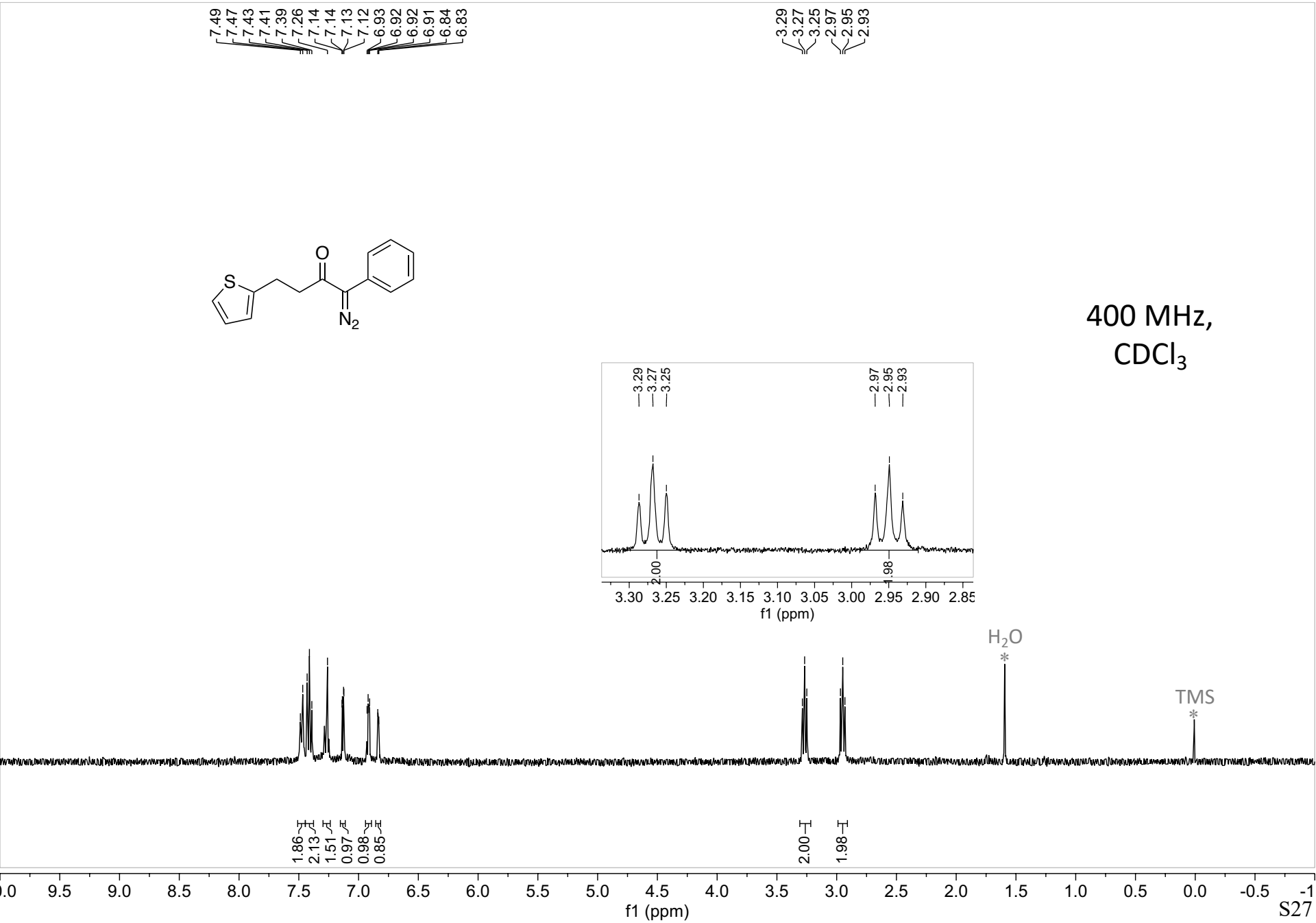
# $^{1}$H NMR 1-diazo-4-(furan-2-yl)-1-phenylbutan-2-one **(1k)**



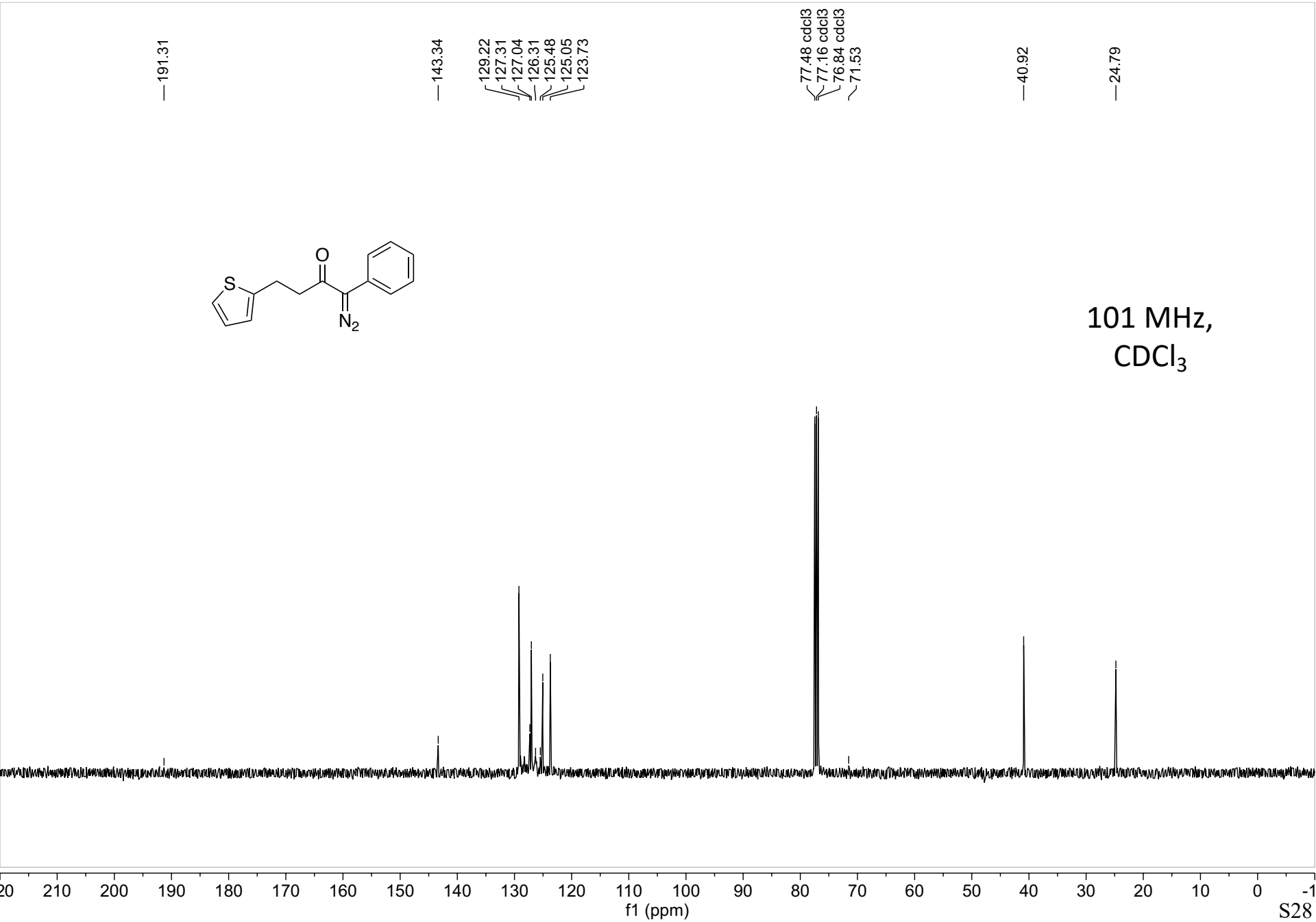
# $^{13}$C NMR 1-diazo-4-(furan-2-yl)-1-phenylbutan-2-one **(1k)**



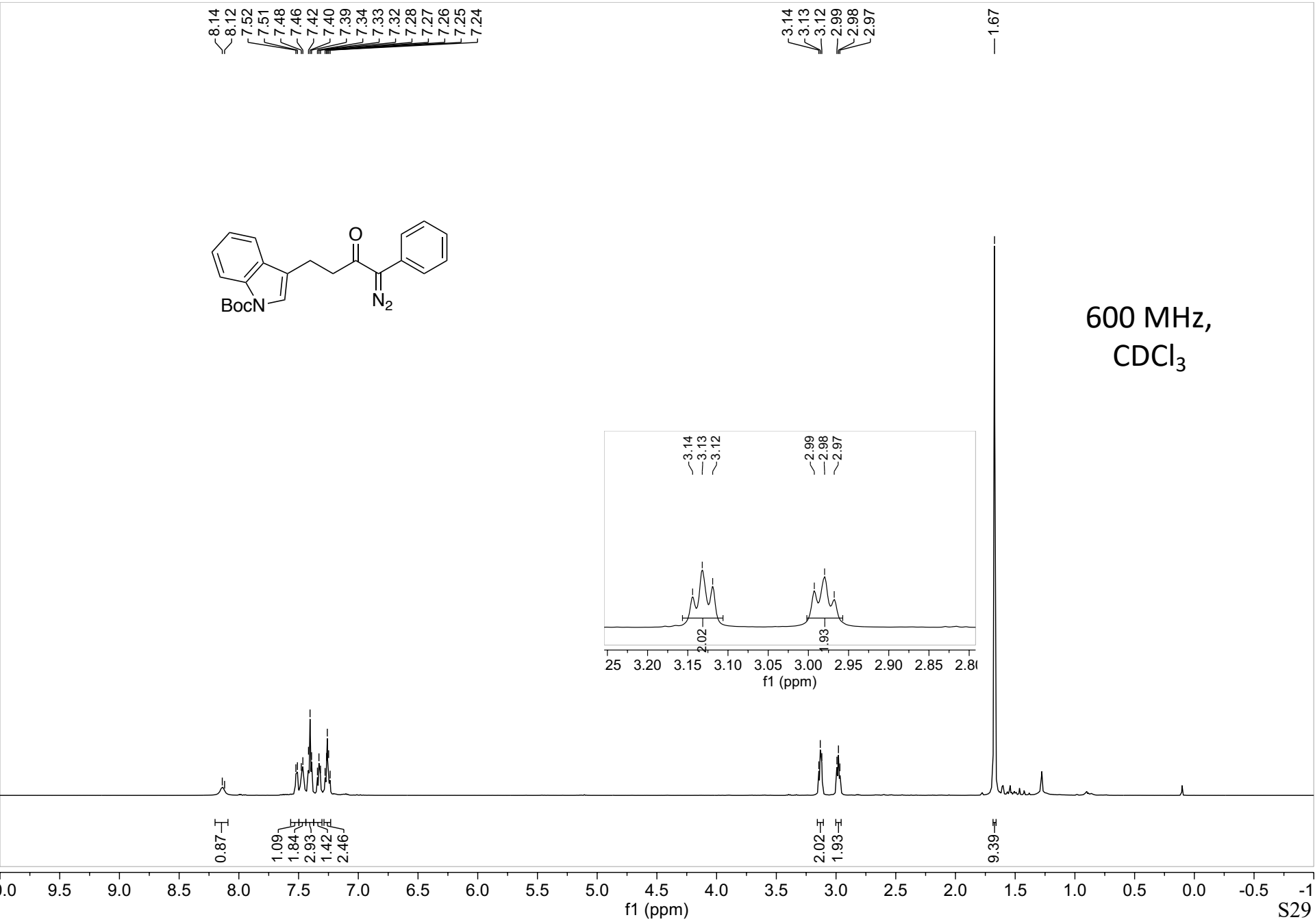
# $^{1}$H NMR 1-diazo-1-phenyl-4-(thiophen-2-yl)butan-2-one **(1l)**



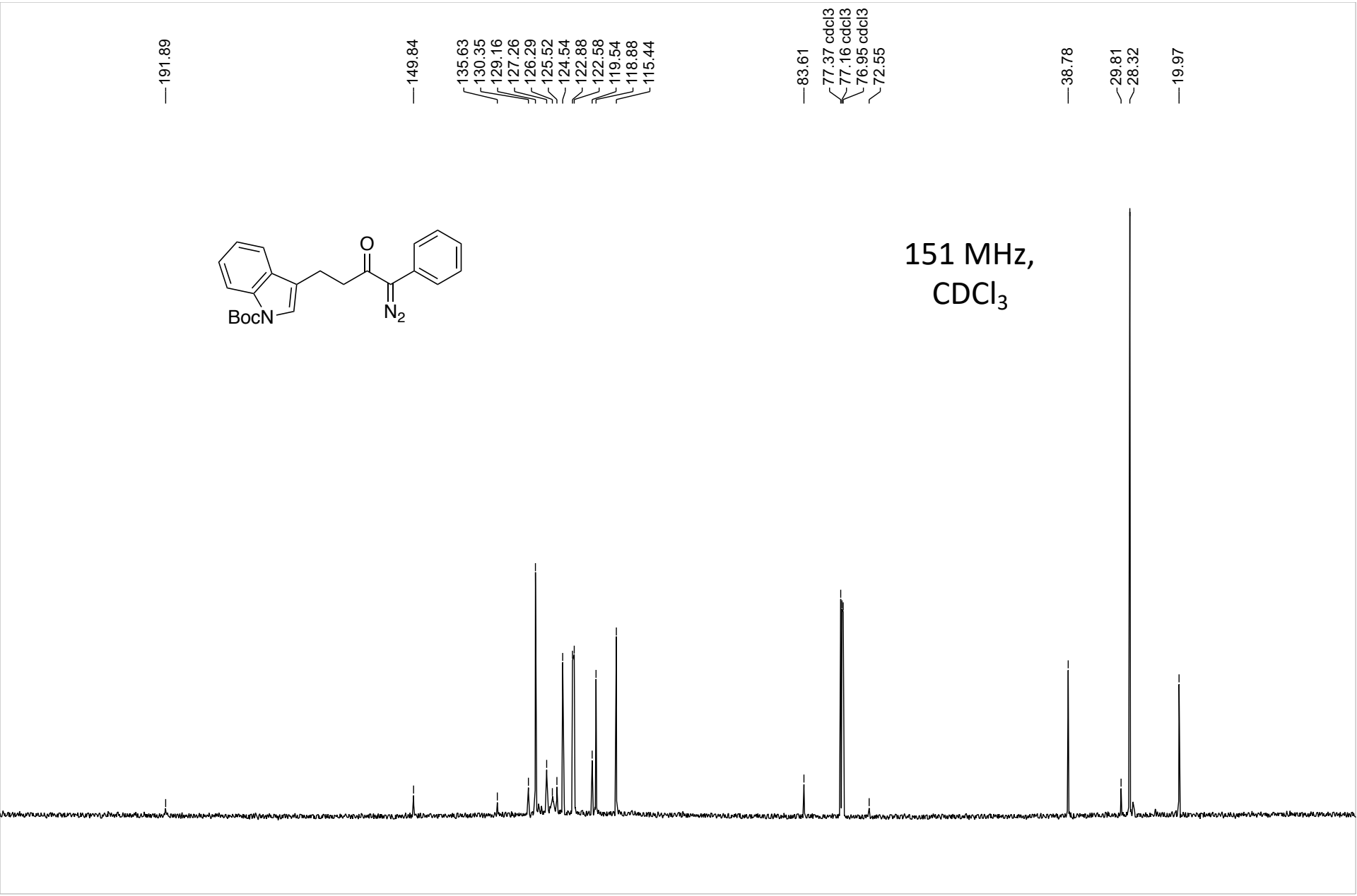
# $^{13}$C NMR 1-diazo-1-phenyl-4-(thiophen-2-yl)butan-2-one **(1l)**



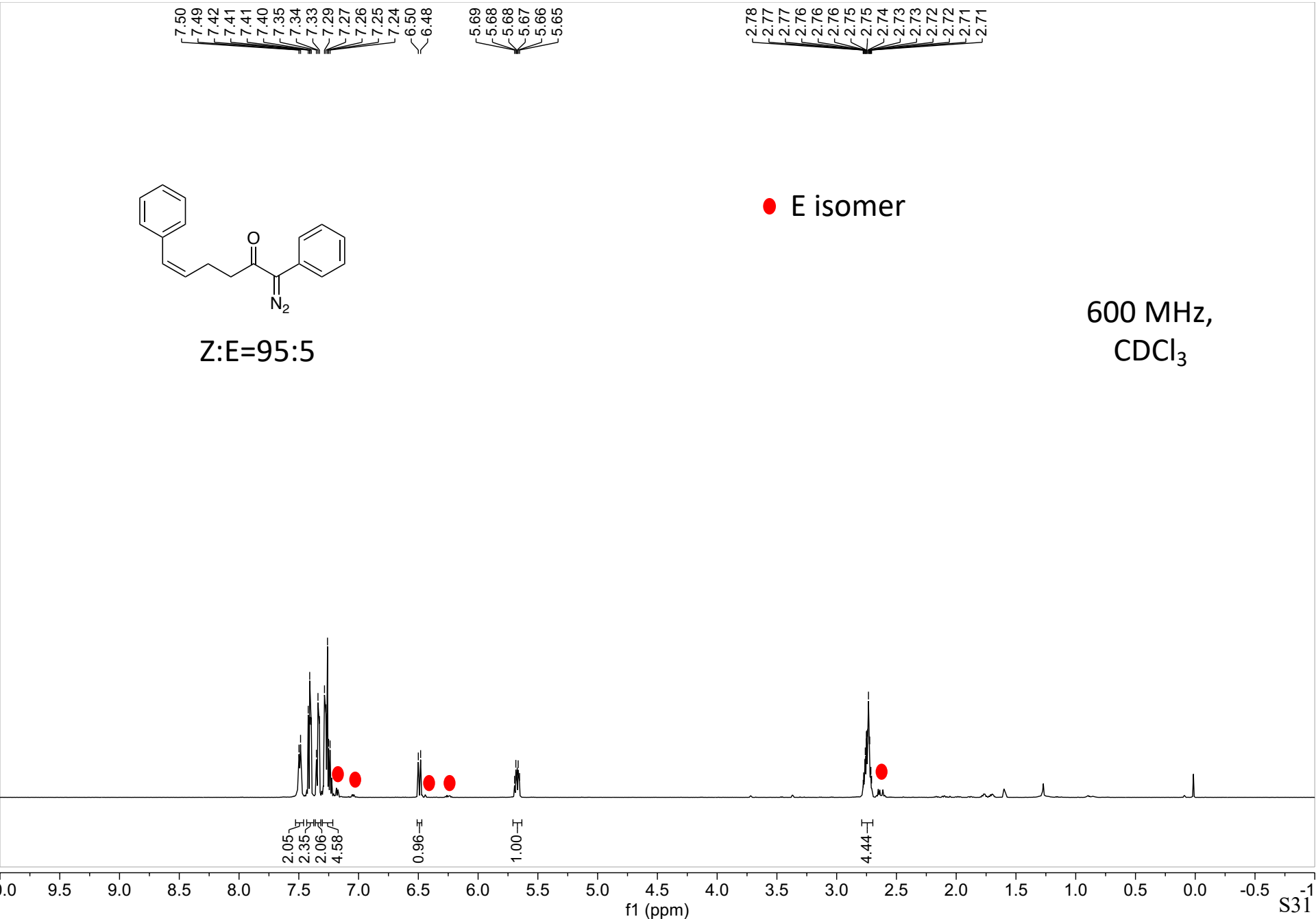
**$^1$H NMR** *tert*-butyl 3-(4-diazo-3-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate **(1m)**



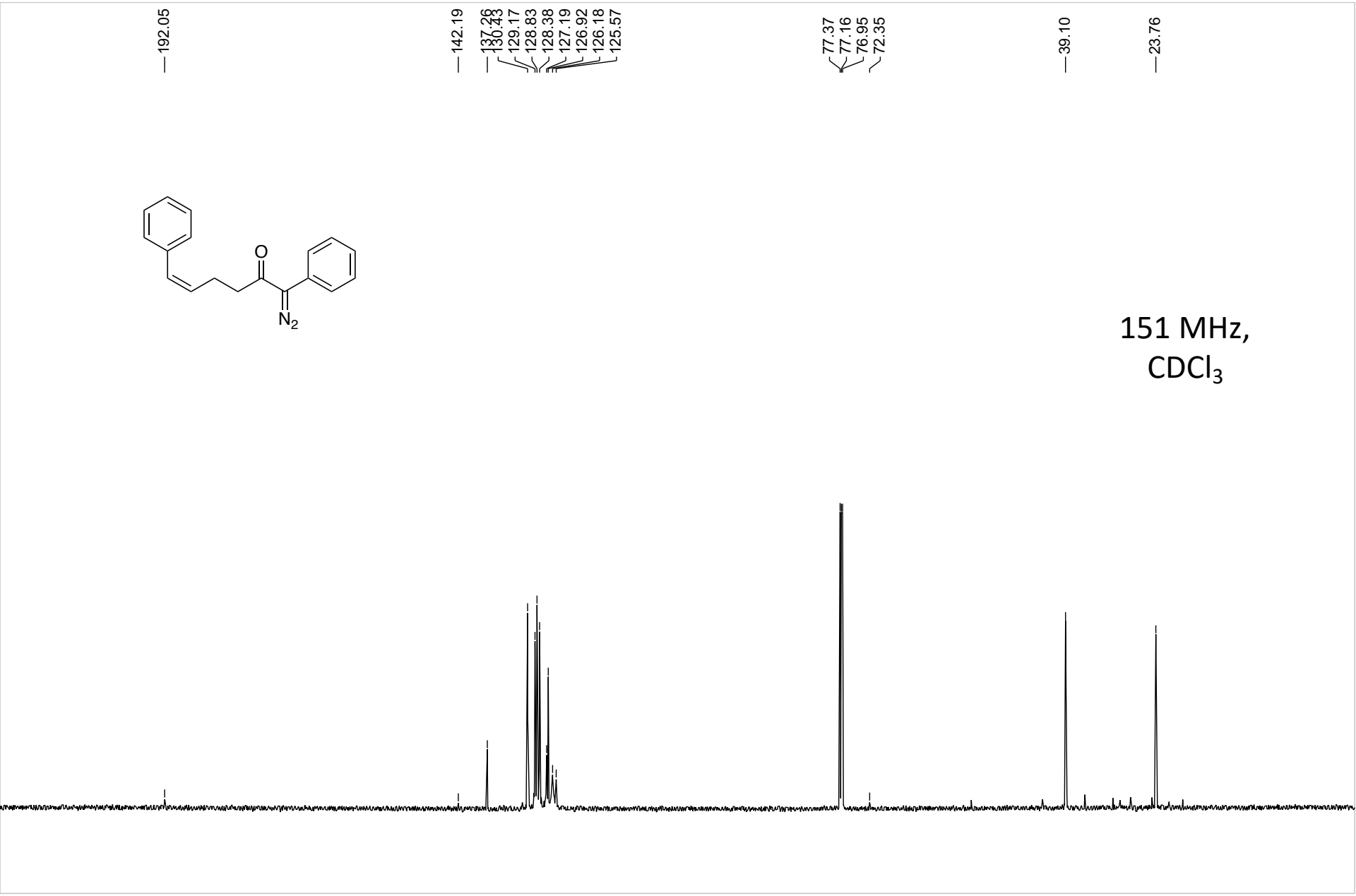
# $^{13}$C NMR *tert*-butyl 3-(4-diazo-3-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate **(1m)**



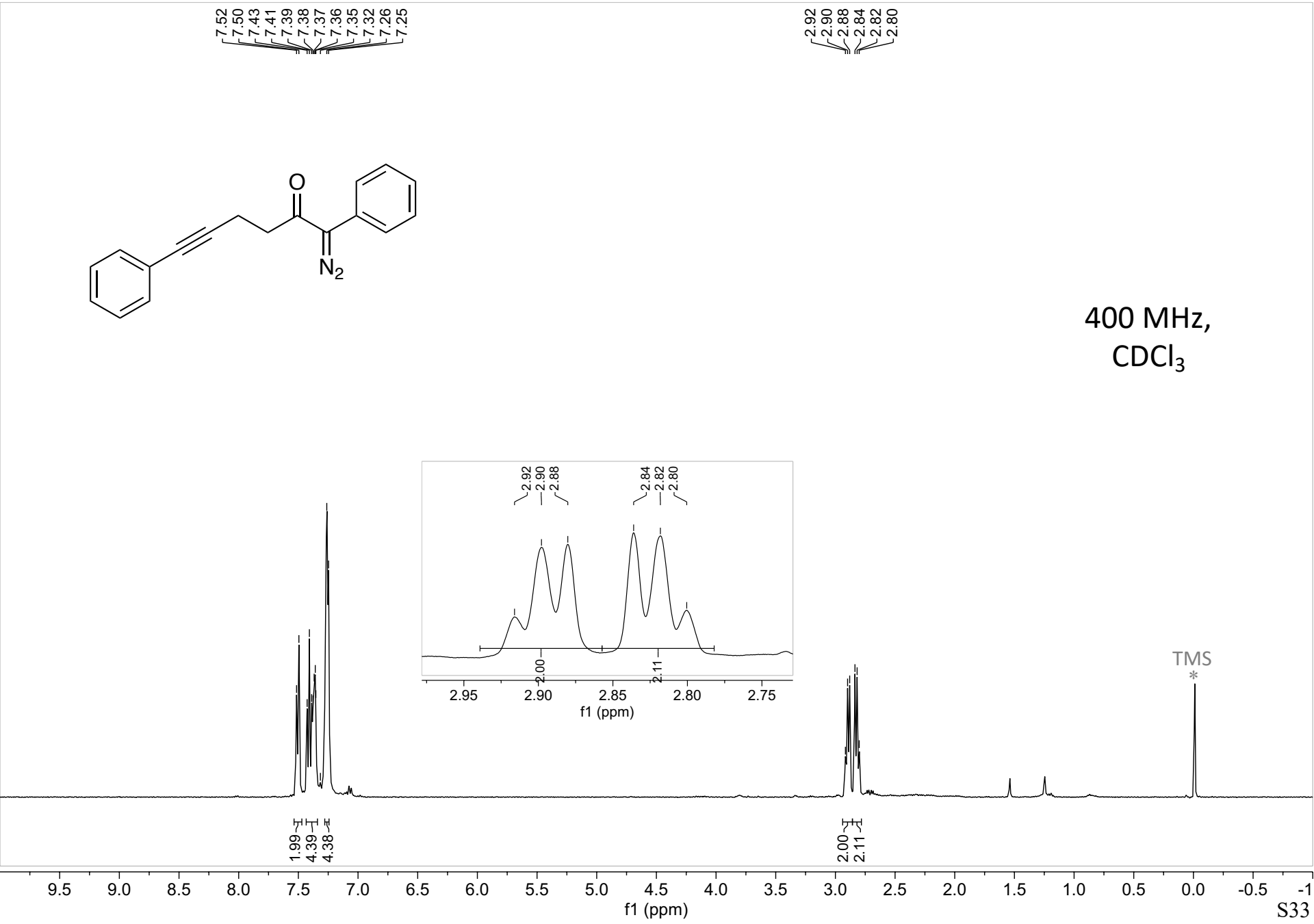
# $^1$H NMR (*Z*)-1-diazo-1,6-diphenylhex-5-en-2-one **(1n)**



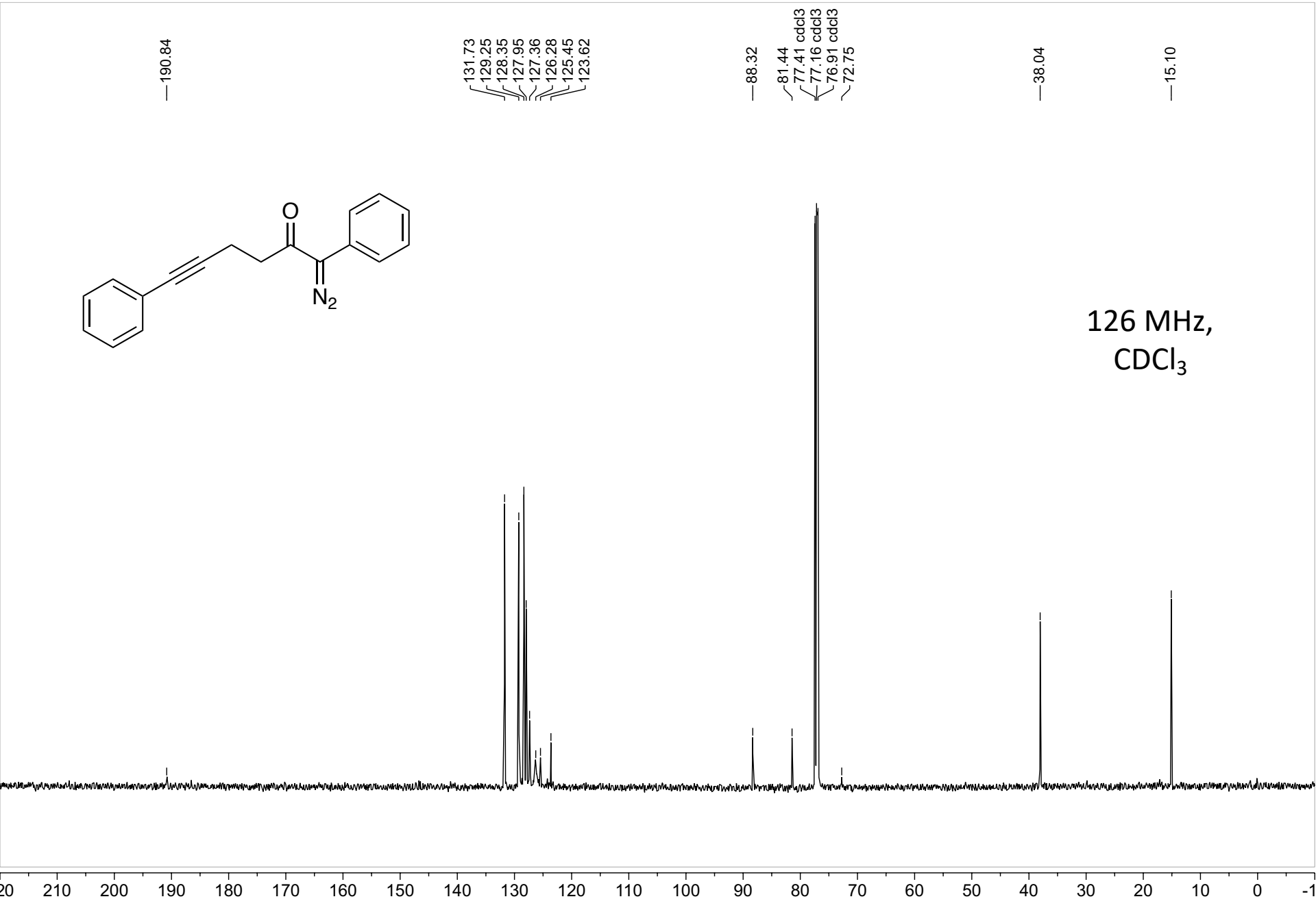
# $^{13}$C NMR (*Z*)-1-diazo-1,6-diphenylhex-5-en-2-one **(1n)**



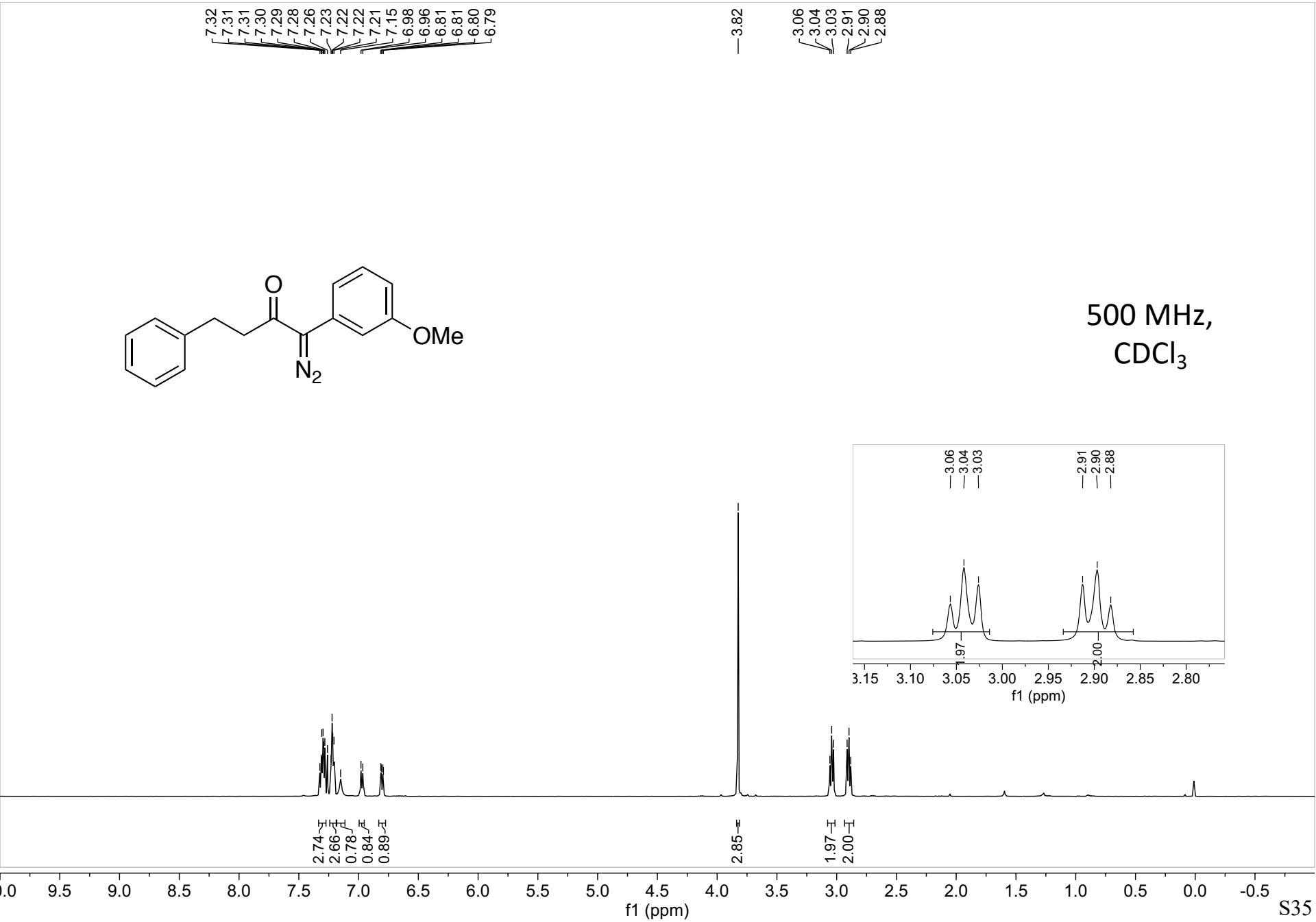
# $^{1}$H NMR 1-diazo-1,6-diphenylhex-5-yn-2-one (**1o**)



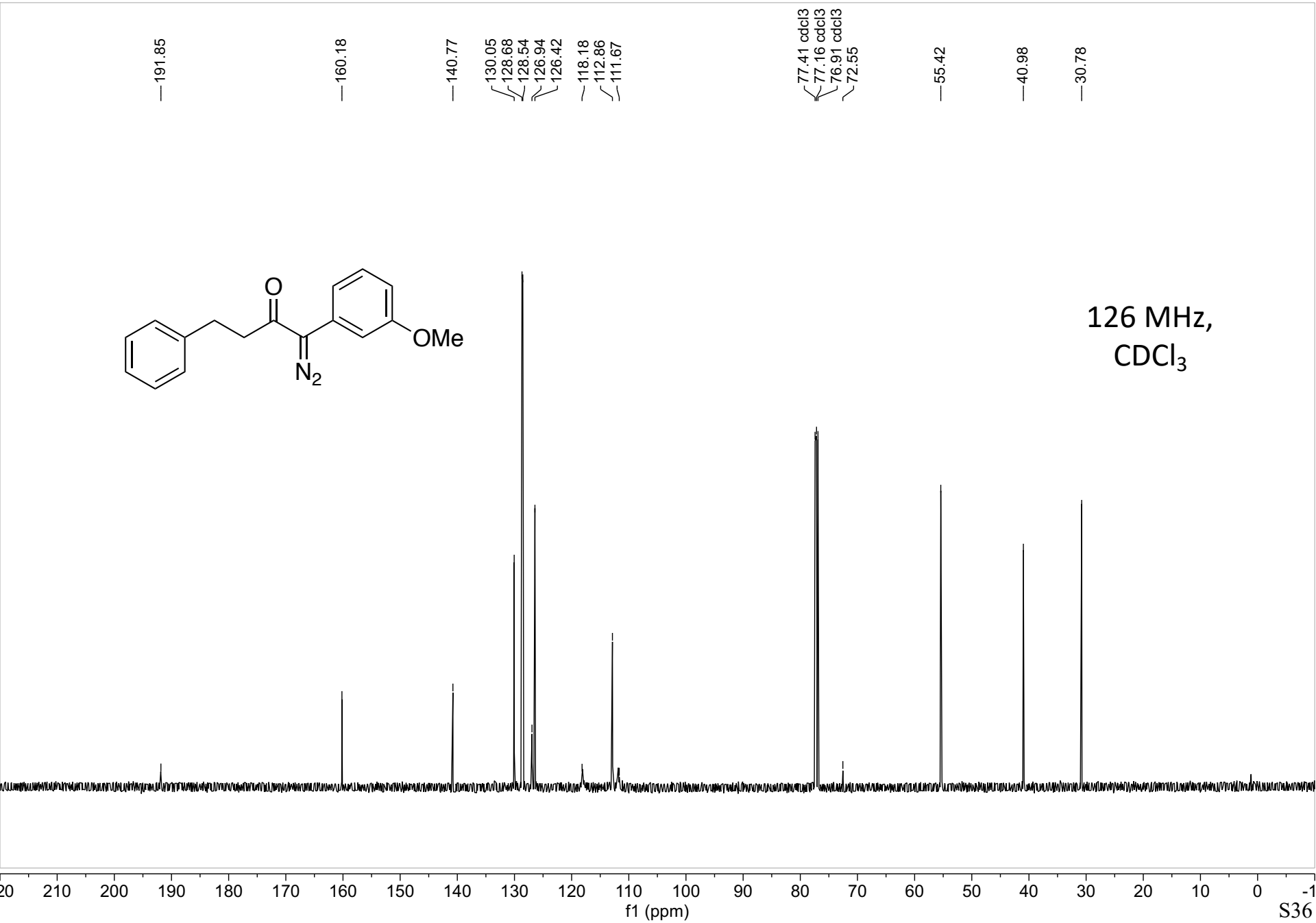
# $^{13}$C NMR 1-diazo-1,6-diphenylhex-5-yn-2-one **(1o)**



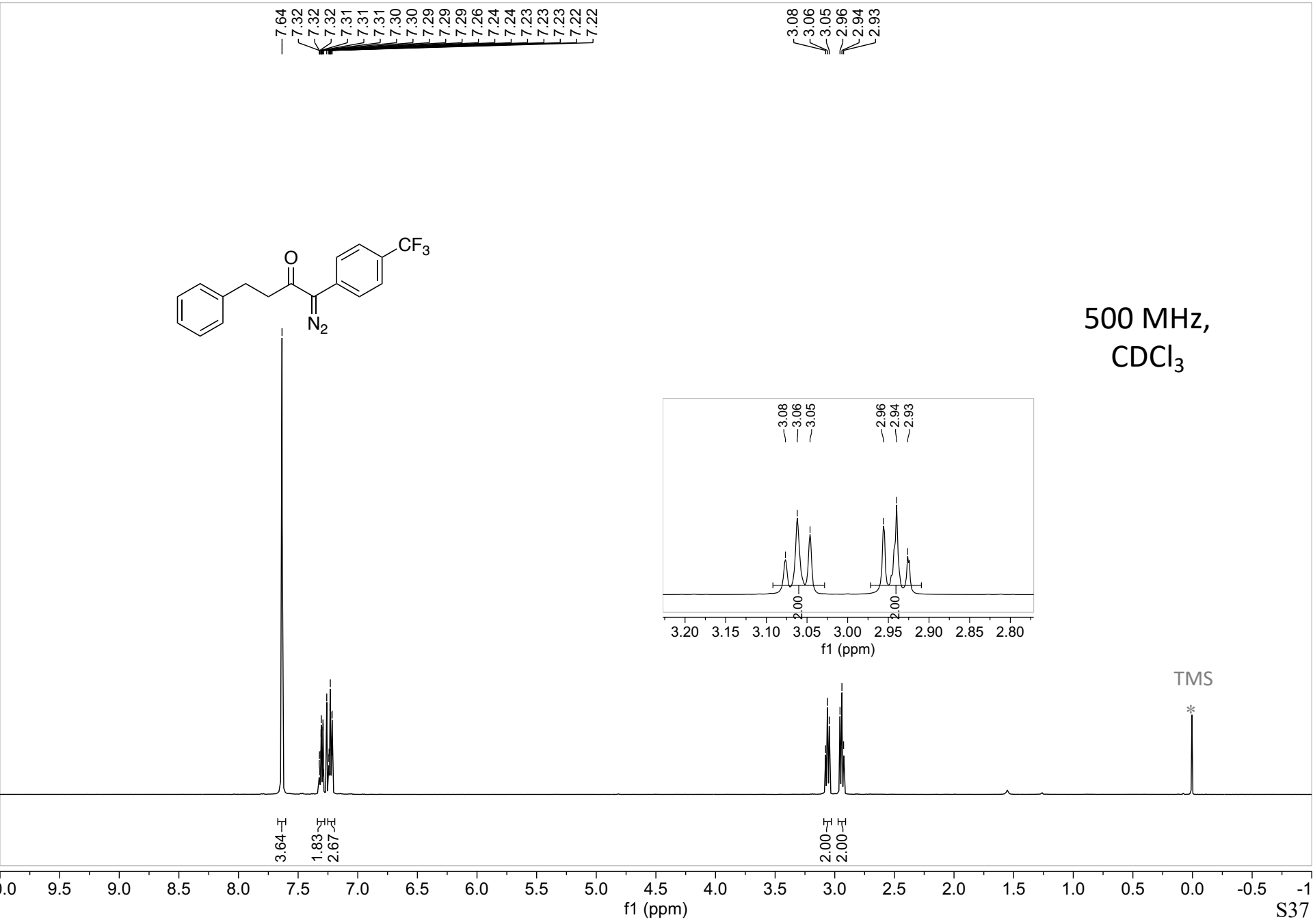
# $^{1}$H NMR 1-diazo-1-(3-methoxyphenyl)-4-phenylbutan-2-one **(1p)**



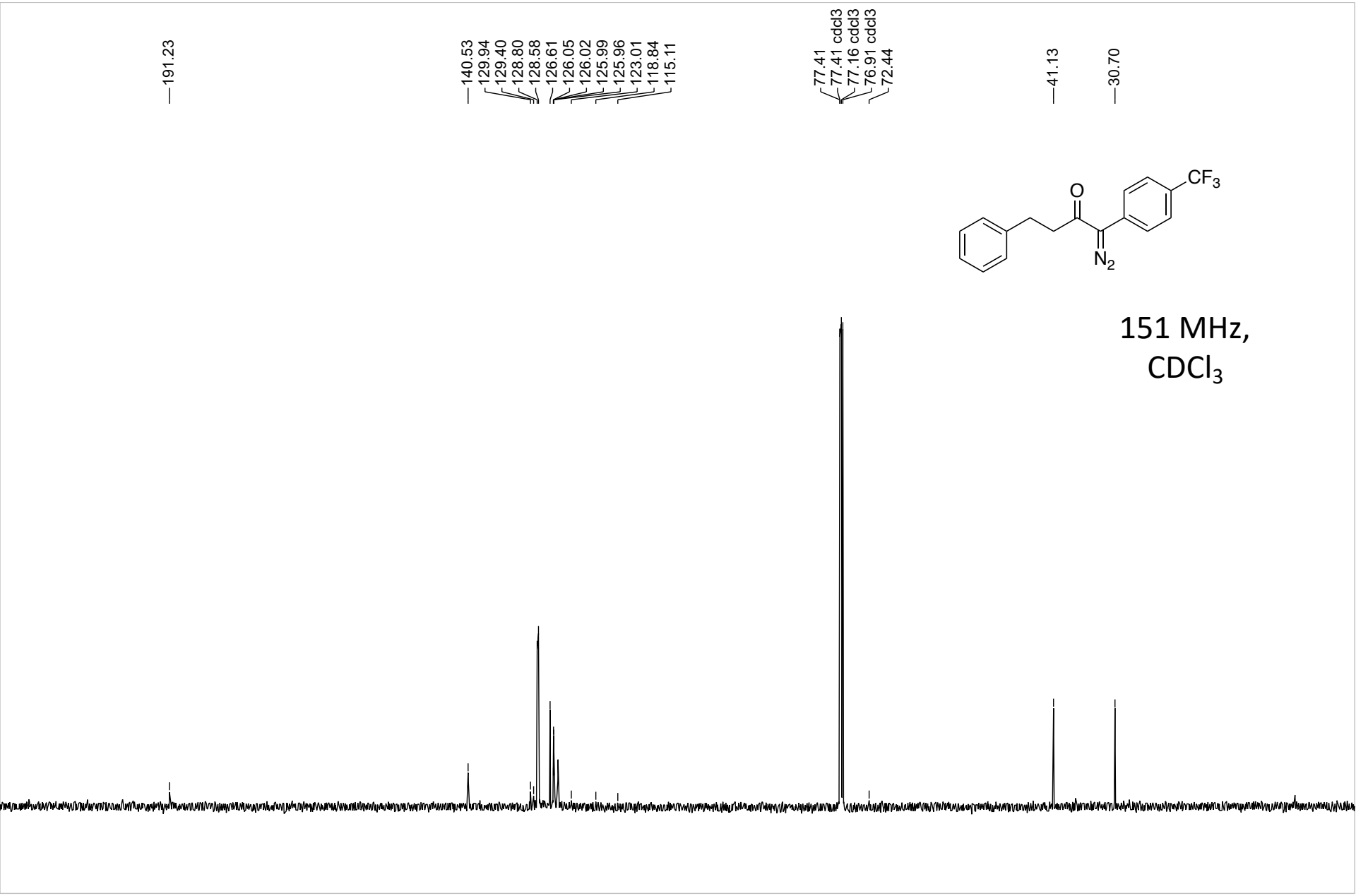
# $^{13}$C NMR 1-diazo-1-(3-methoxyphenyl)-4-phenylbutan-2-one **(1p)**



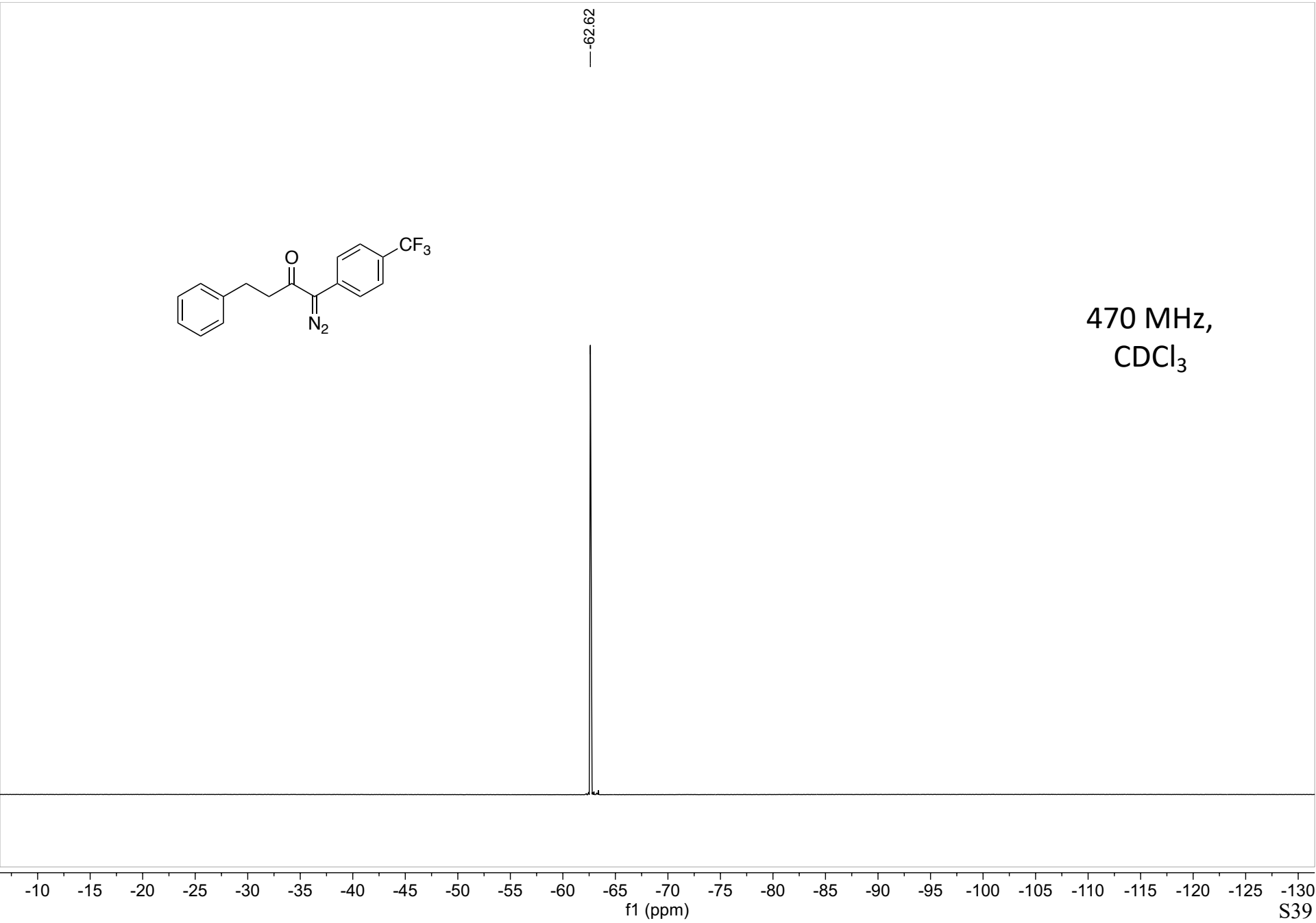
# $^{1}$H NMR 1-diazo-4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-2-one **(1q)**



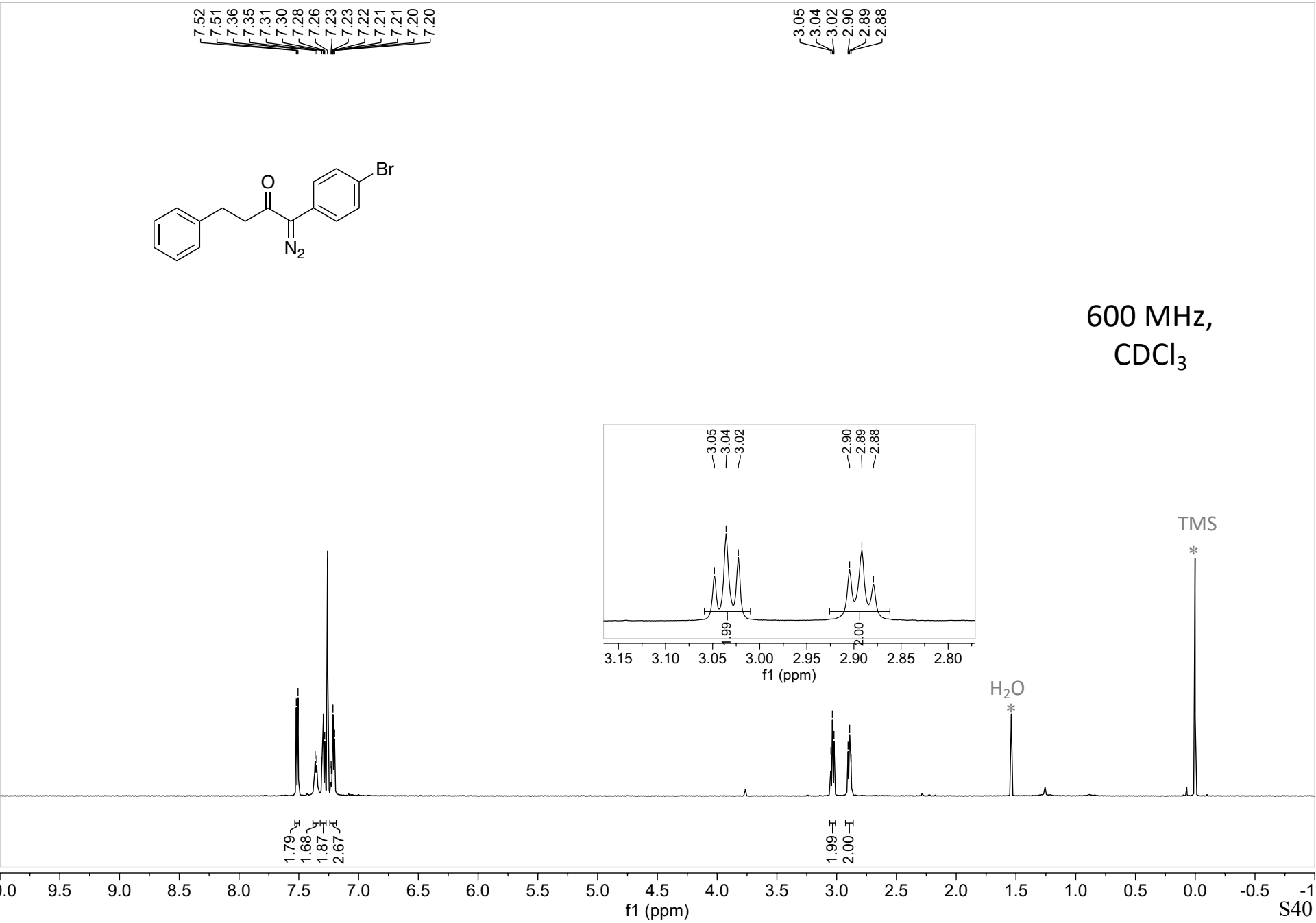
# $^{13}$C NMR 1-diazo-4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-2-one **(1q)**



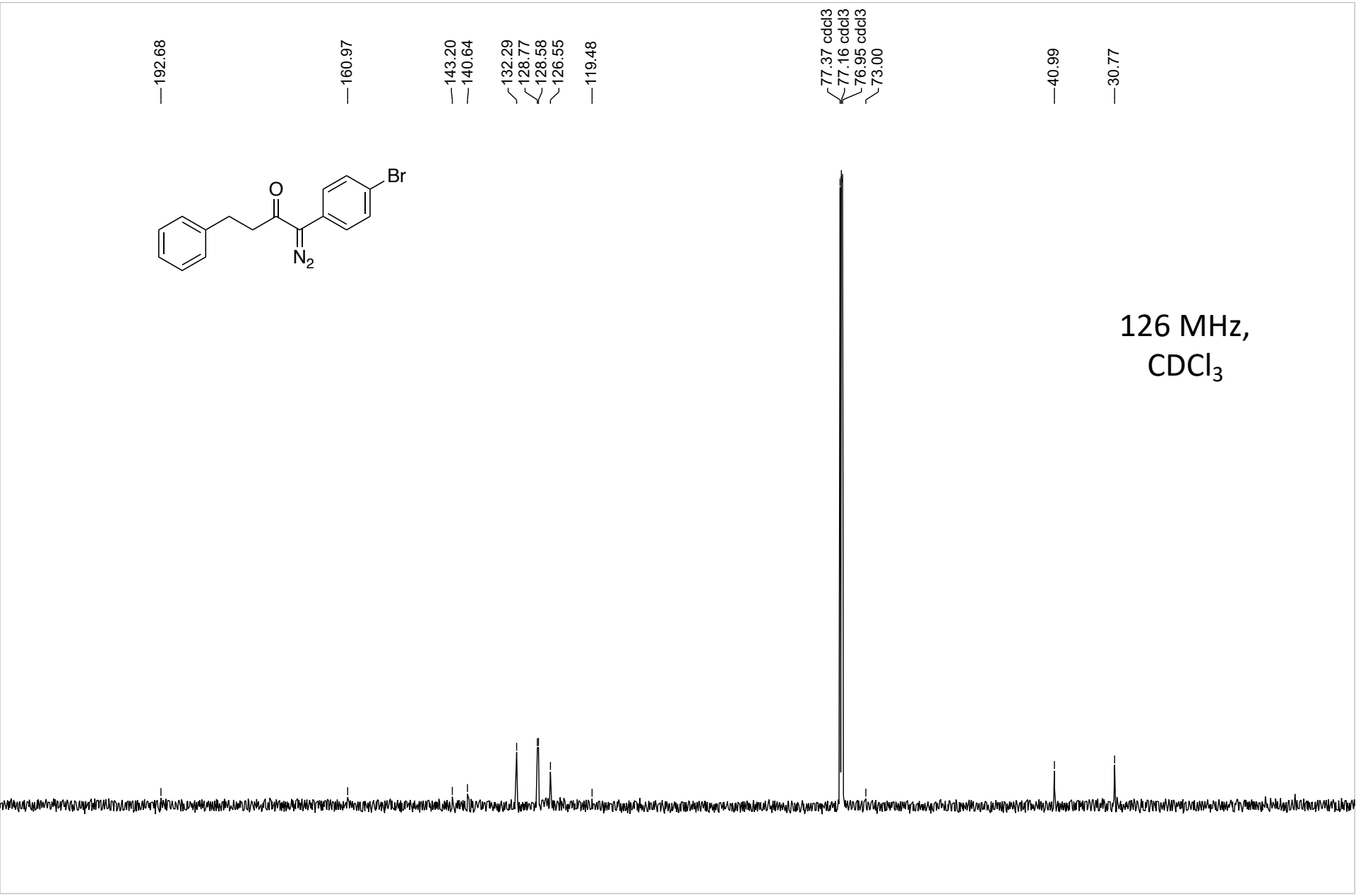
**$^{19}$F NMR** 1-diazo-4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-2-one **(1q)**



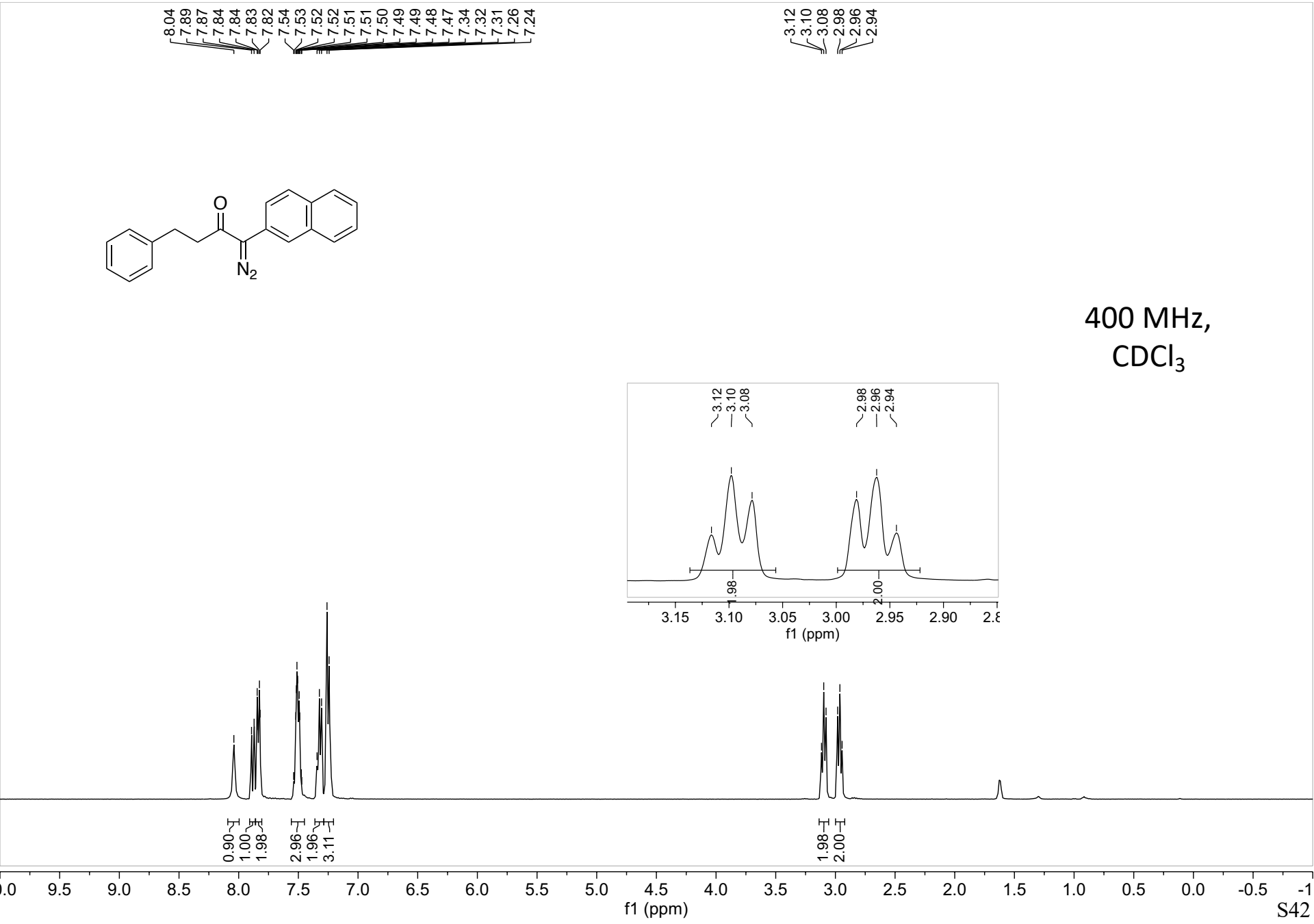
# $^{1}$H NMR 1-(4-bromophenyl)-1-diazo-4-phenylbutan-2-one **(1r)**



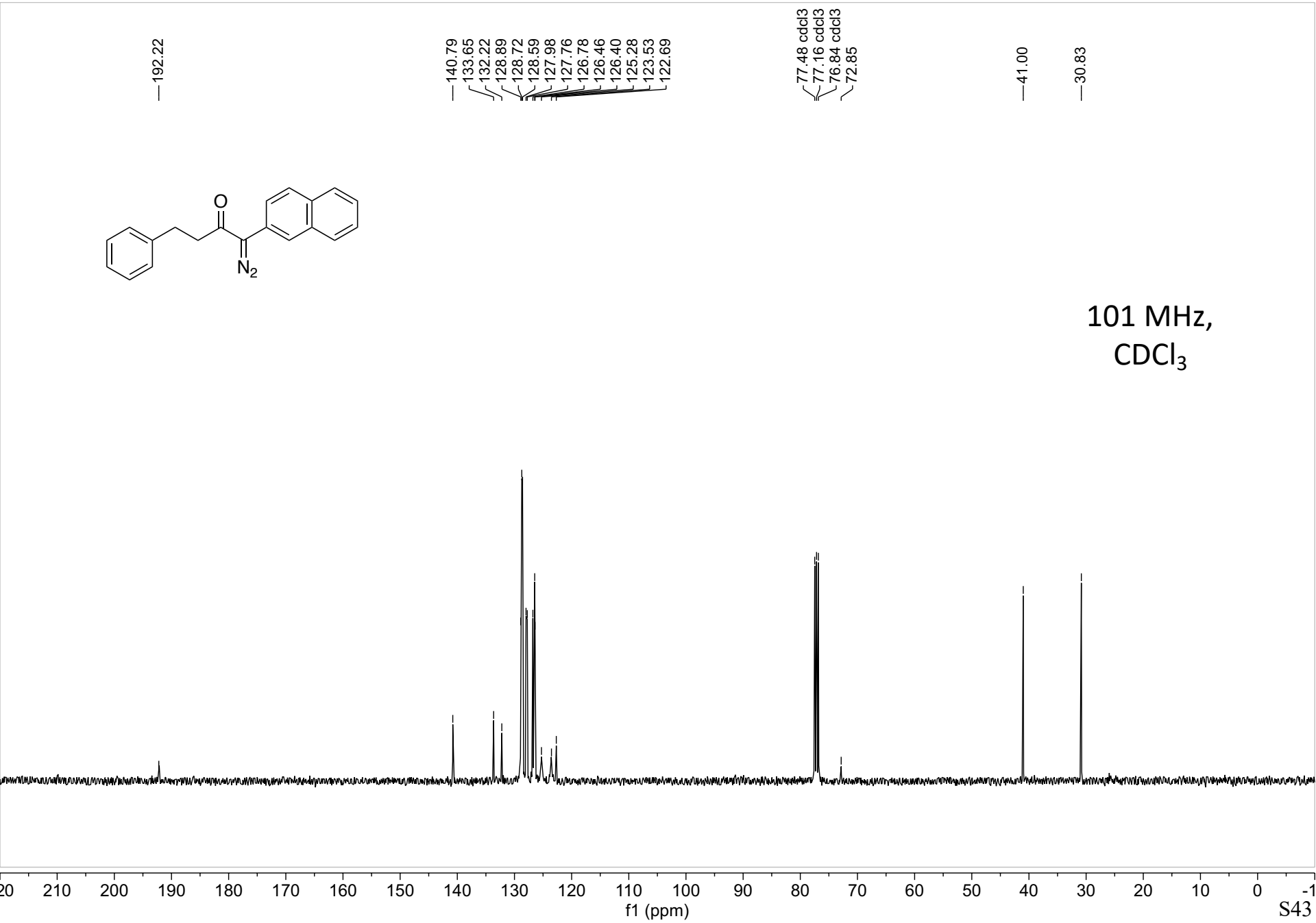
# $^{13}$C NMR 1-(4-bromophenyl)-1-diazo-4-phenylbutan-2-one **(1r)**



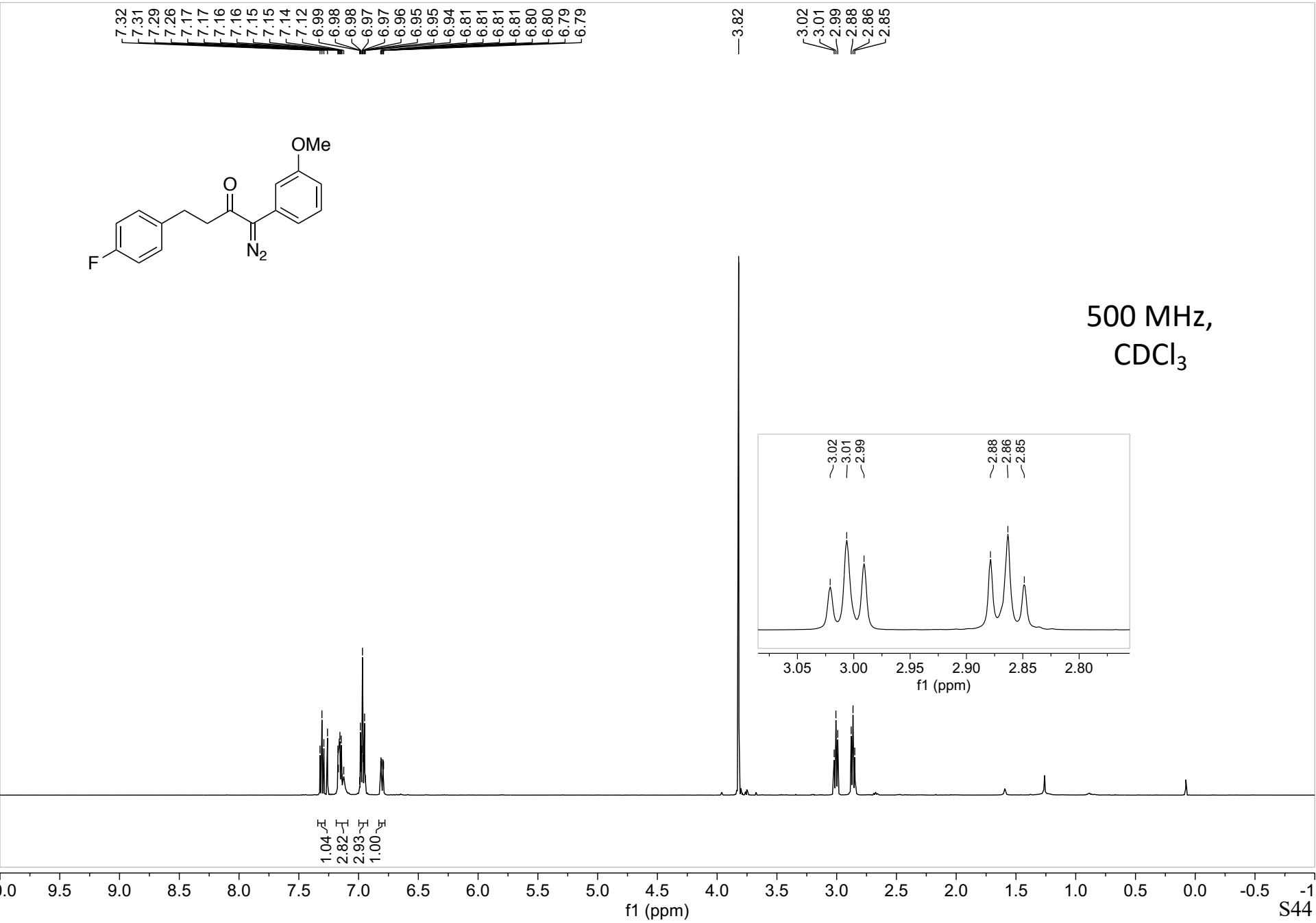
# $^{1}$H NMR 1-diazo-1-(naphthalen-2-yl)-4-phenylbutan-2-one **(1s)**



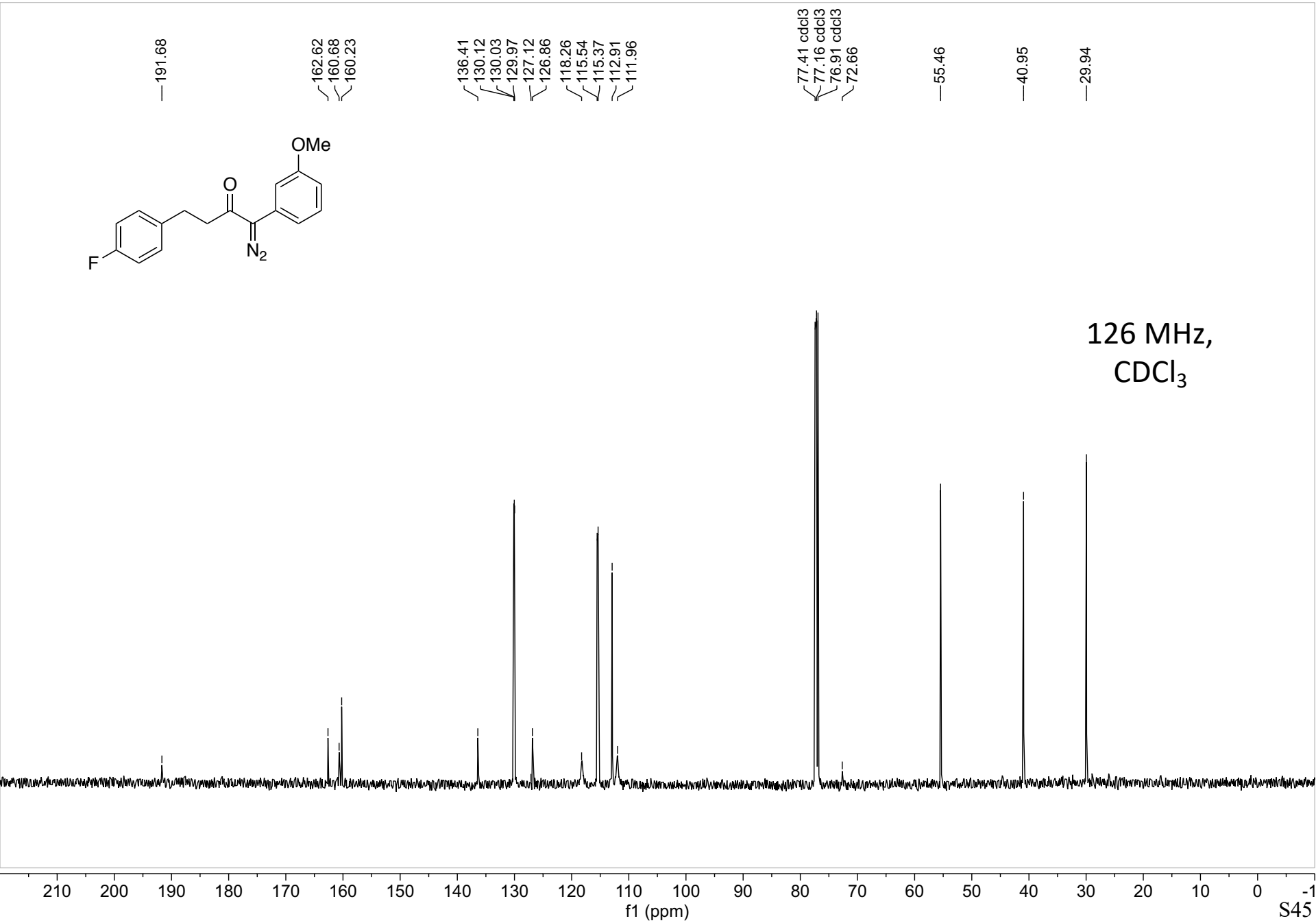
# $^{13}$C NMR 1-diazo-1-(naphthalen-2-yl)-4-phenylbutan-2-one **(1s)**



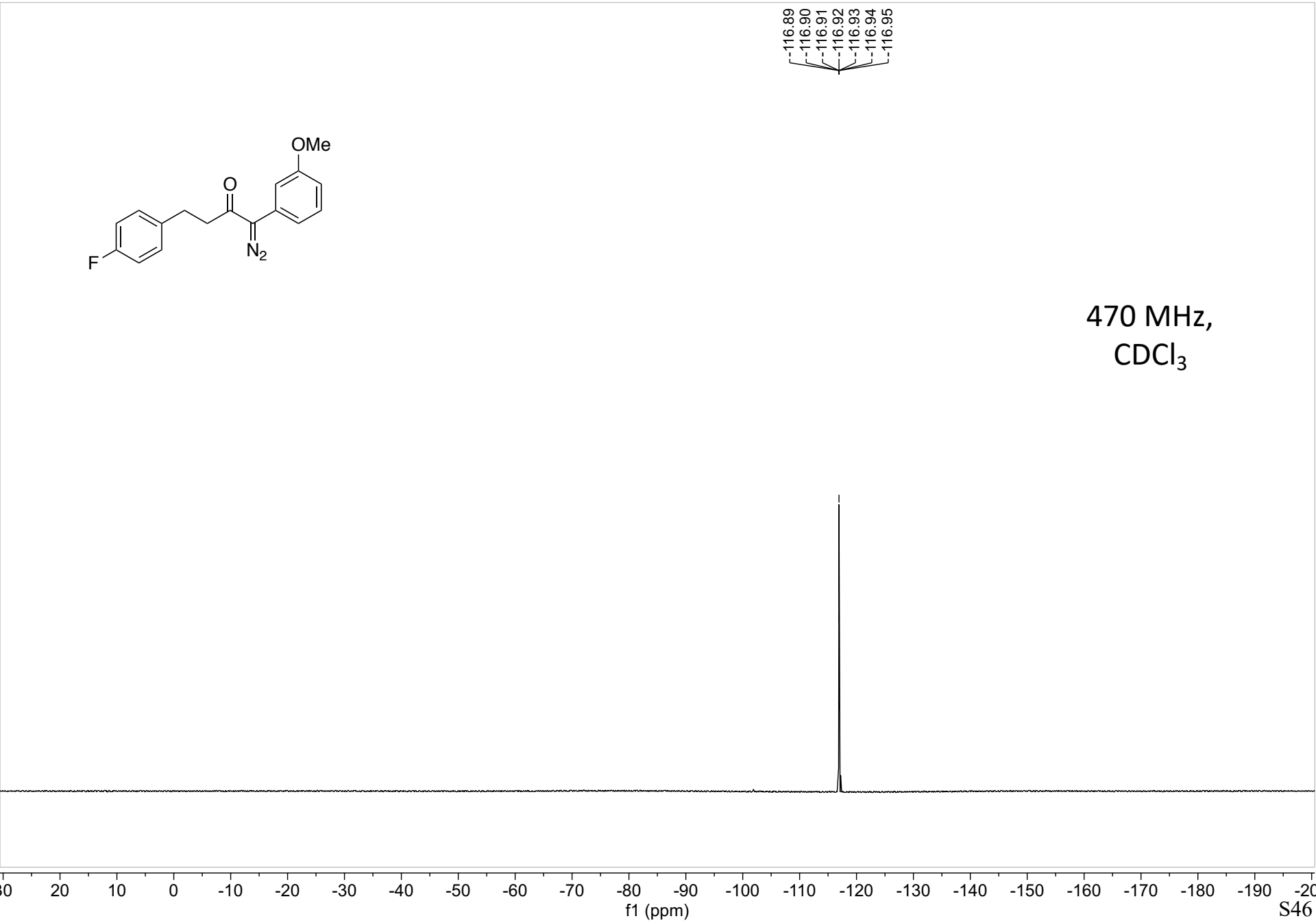
# $^{1}$H NMR 1-diazo-4-(4-fluorophenyl)-1-(3-methoxyphenyl)butan-2-one **(1t)**



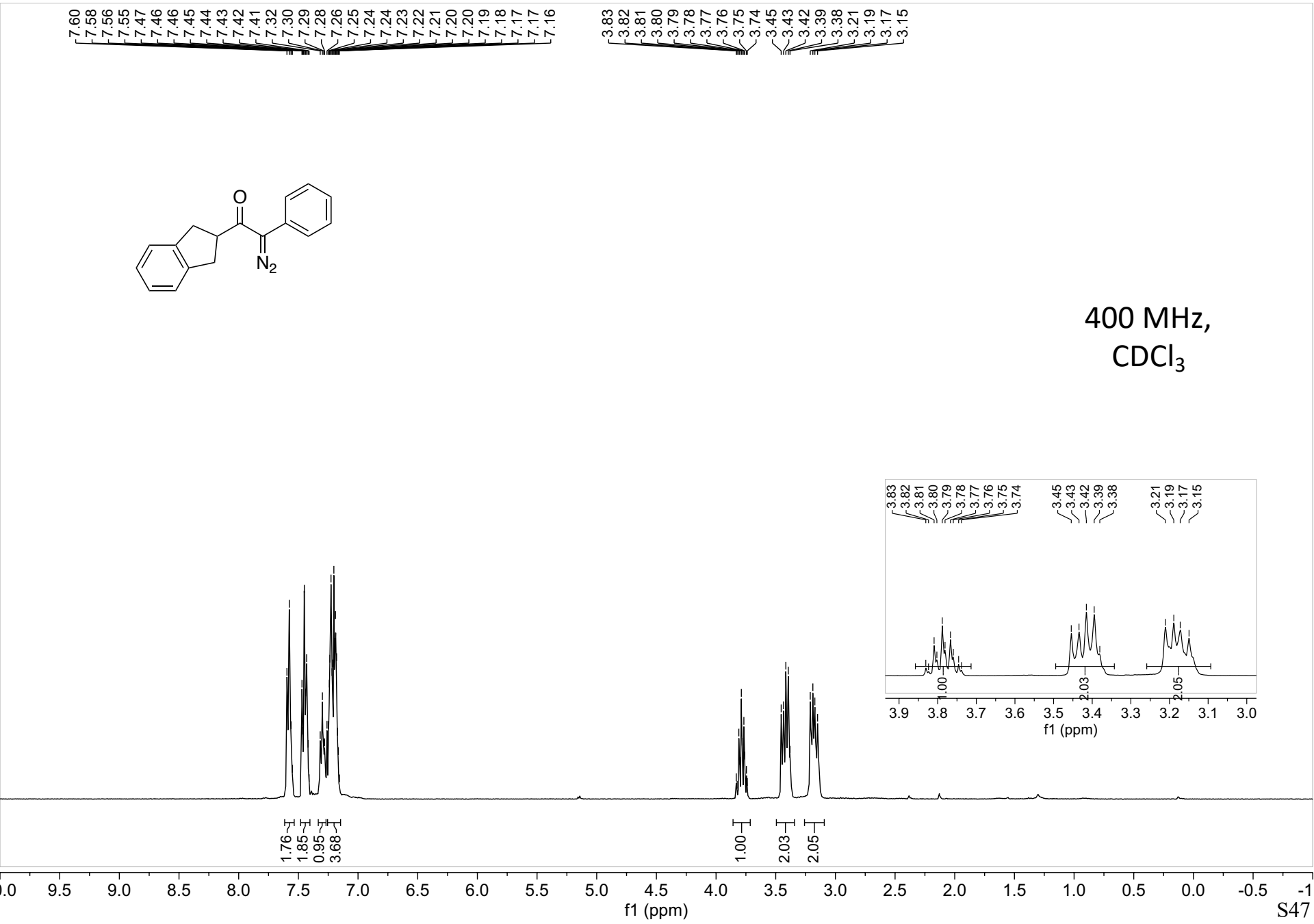
# $^{13}$C NMR 1-diazo-4-(4-fluorophenyl)-1-(3-methoxyphenyl)butan-2-one **(1t)**



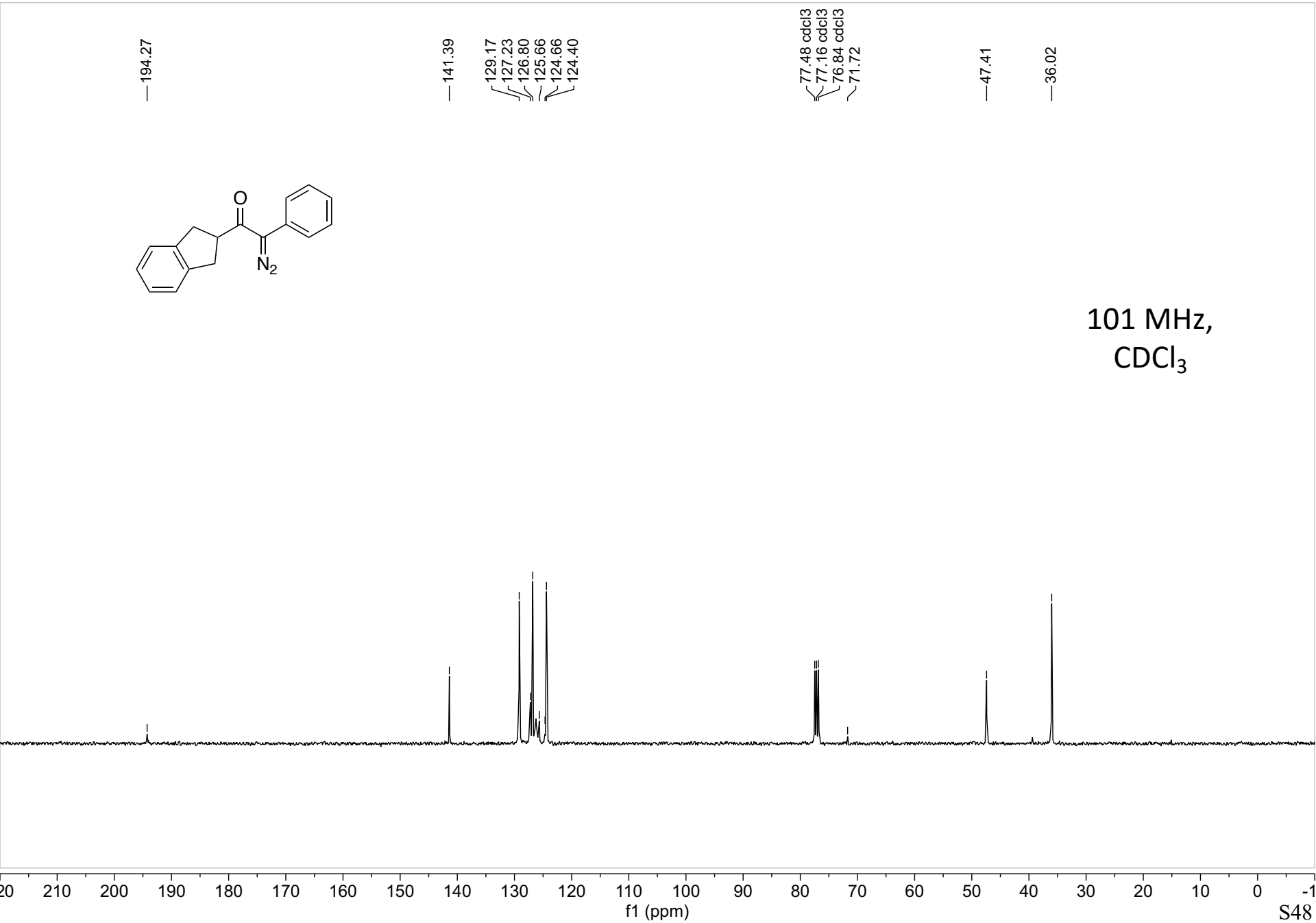
# $^{19}$F NMR 1-diazo-4-(4-fluorophenyl)-1-(3-methoxyphenyl)butan-2-one **(1t)**



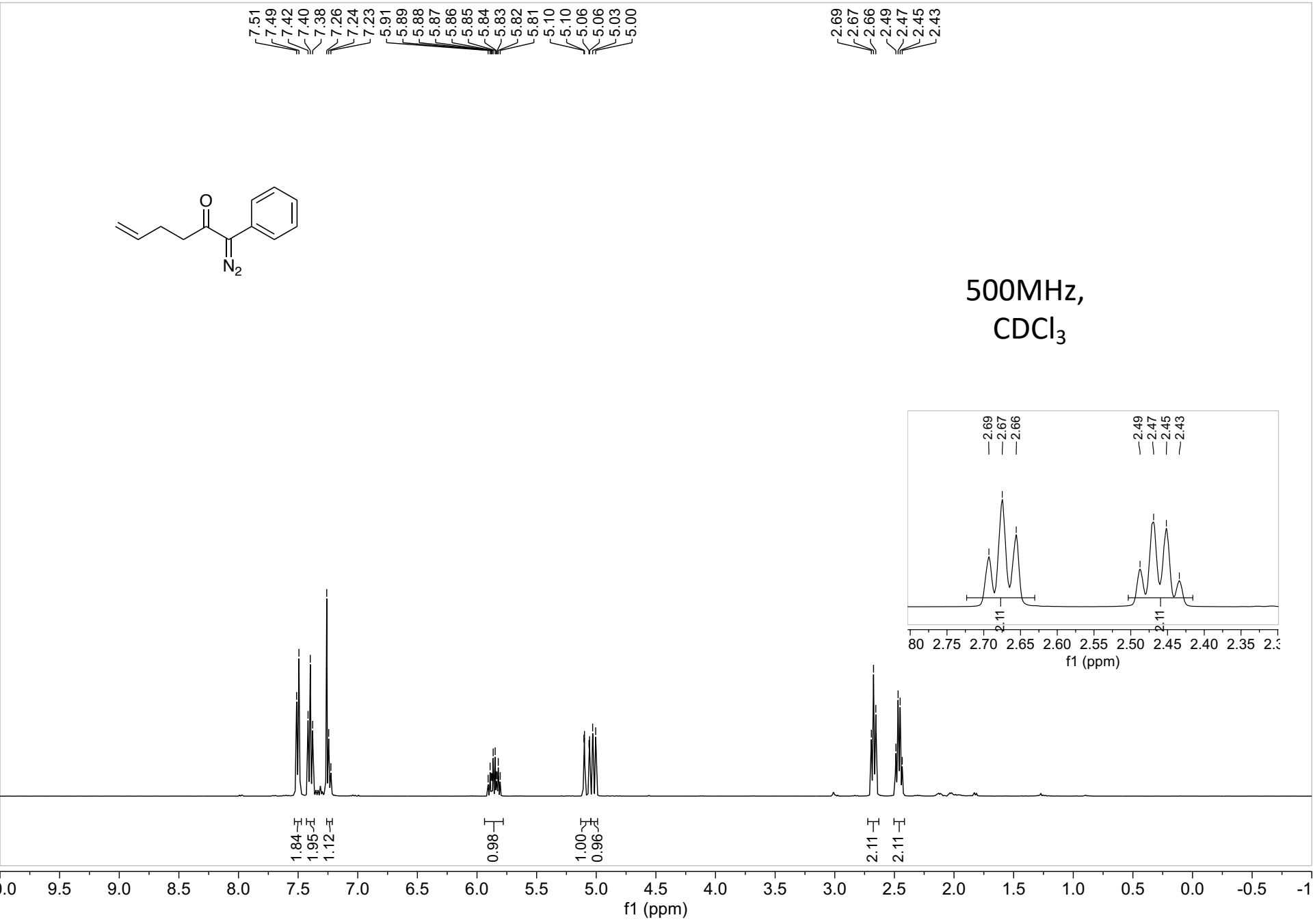
# $^{1}$H NMR 2-diazo-1-(2,3-dihydro-1*H*-inden-2-yl)-2-phenylethan-1-one **(1u)**



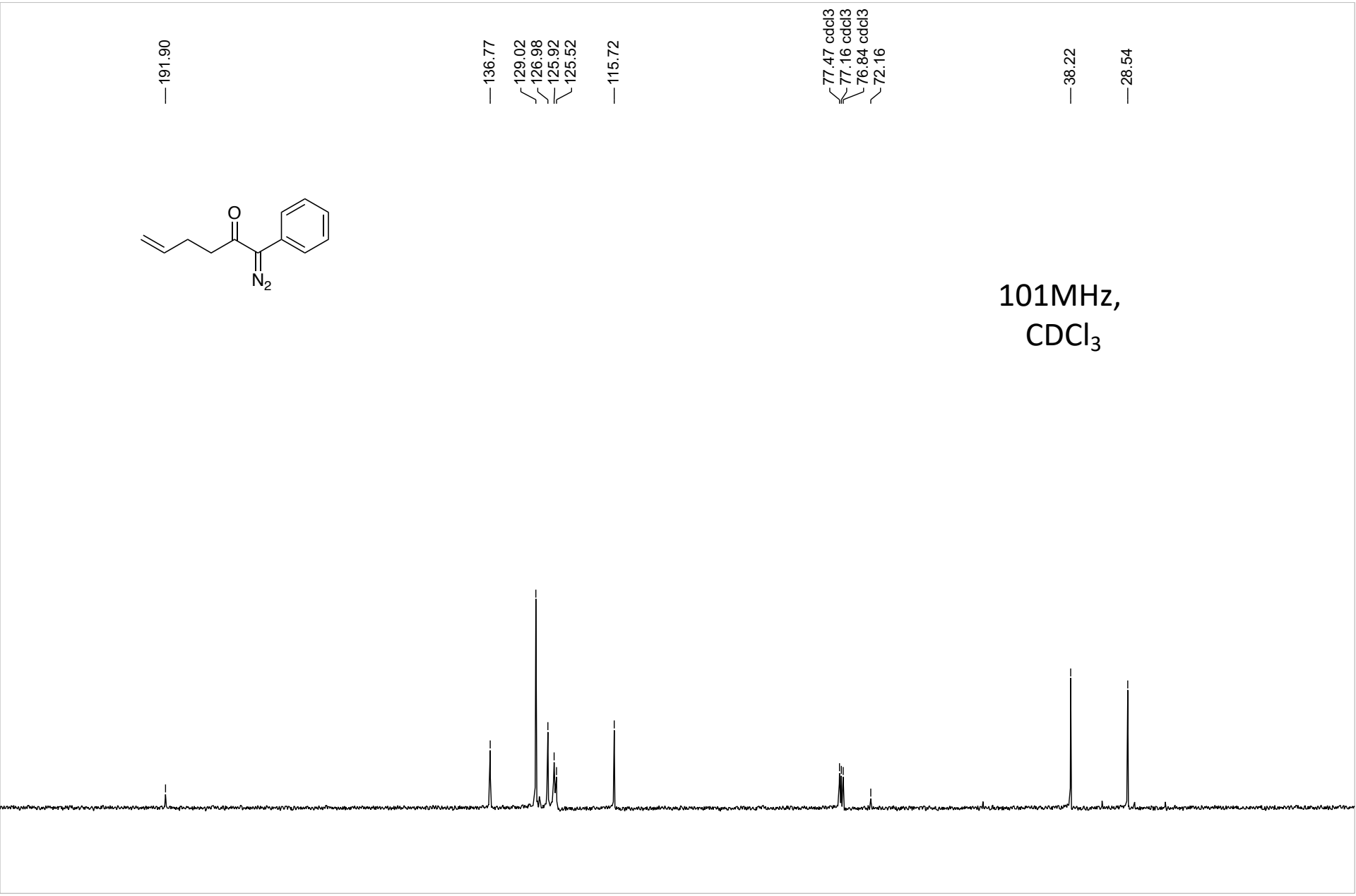
# $^{13}$C NMR 2-diazo-1-(2,3-dihydro-1*H*-inden-2-yl)-2-phenylethan-1-one **(1u)**



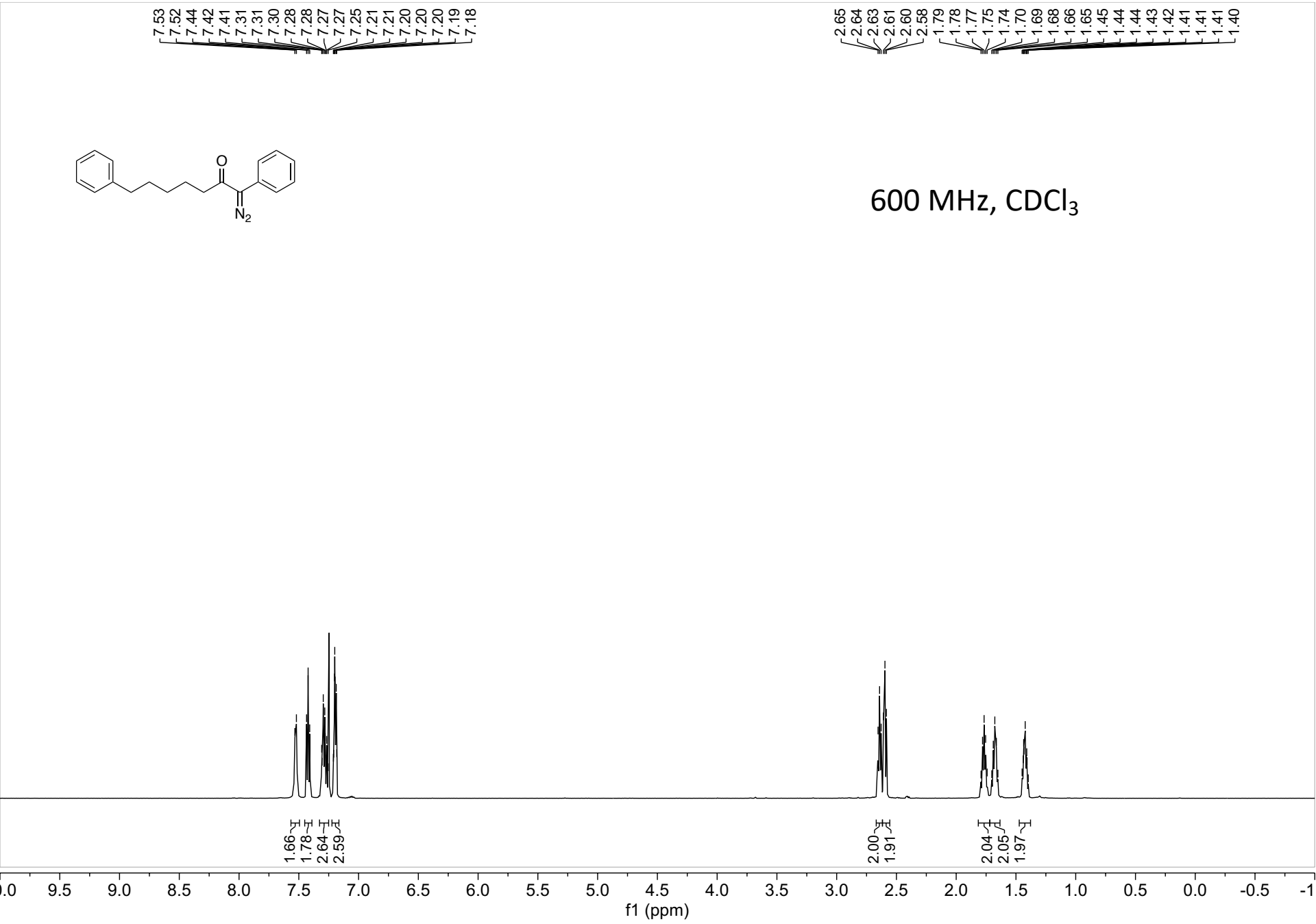
# $^{1}$H NMR 1-Diazo-1-phenylhex-5-en-2-one **(1v)**



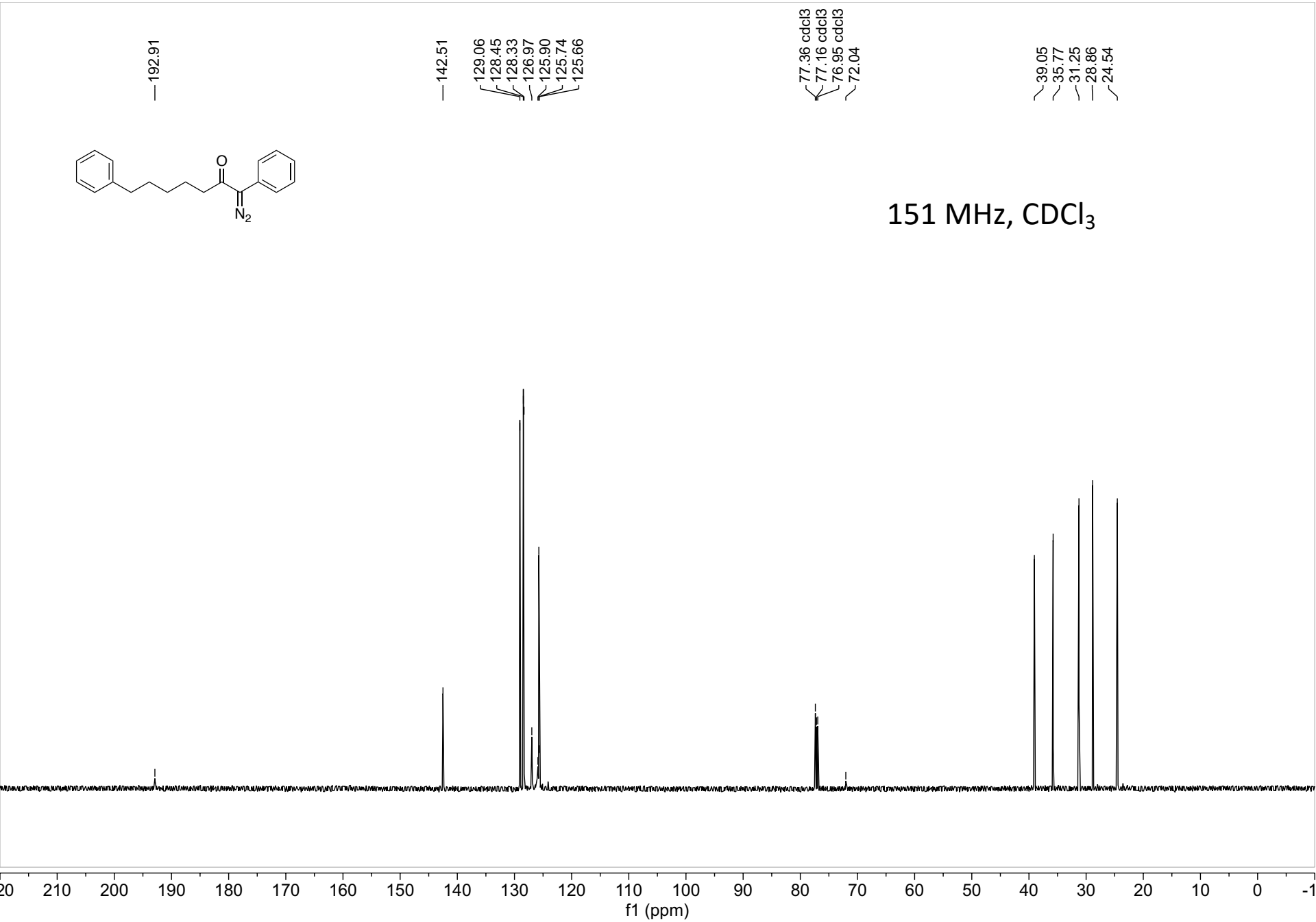
# $^{13}$C NMR 1-Diazo-1-phenylhex-5-en-2-one **(1v)**



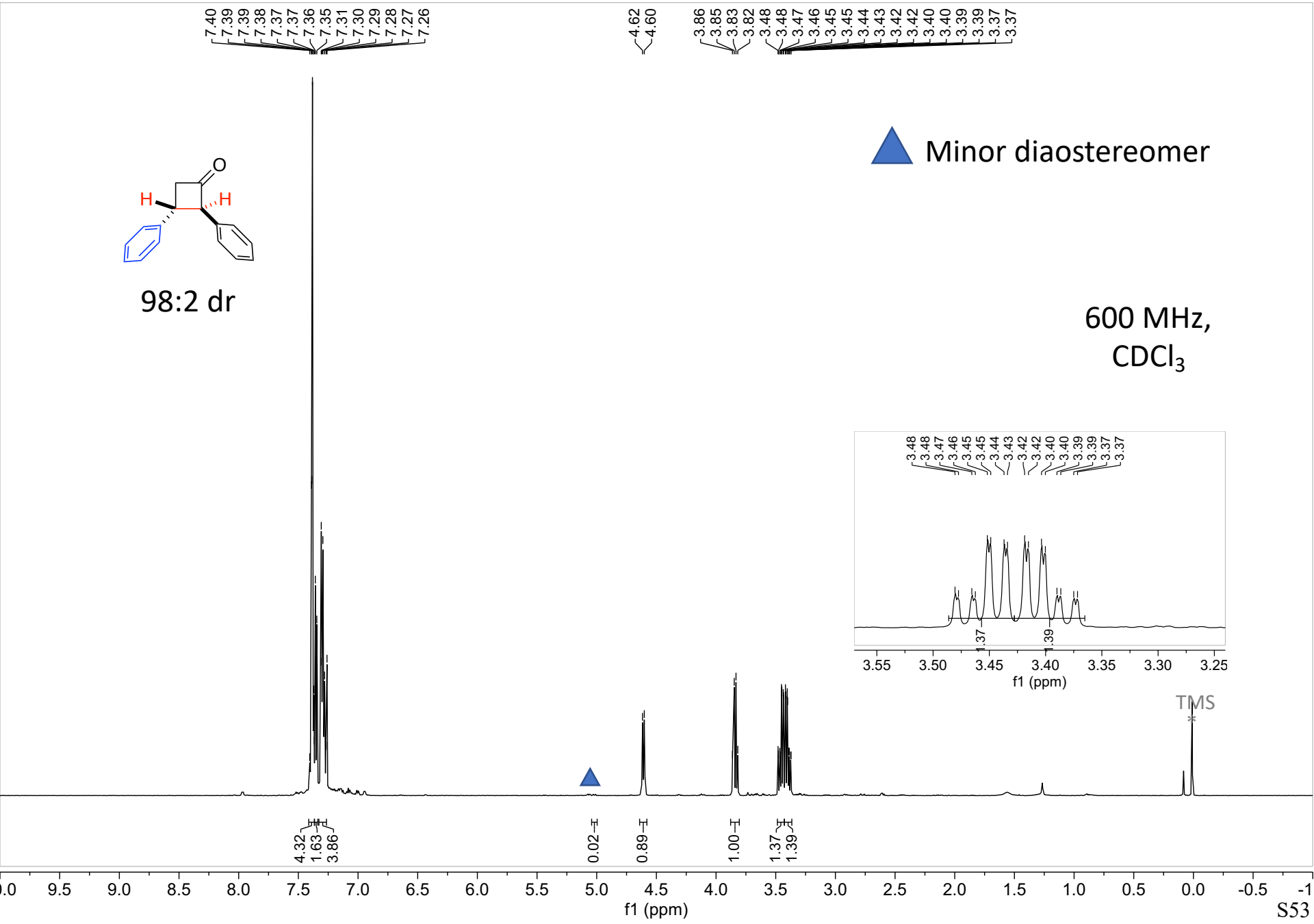
# $^{1}$H NMR 1-Diazo-1,7-diphenylheptan-2-one **(1w)**



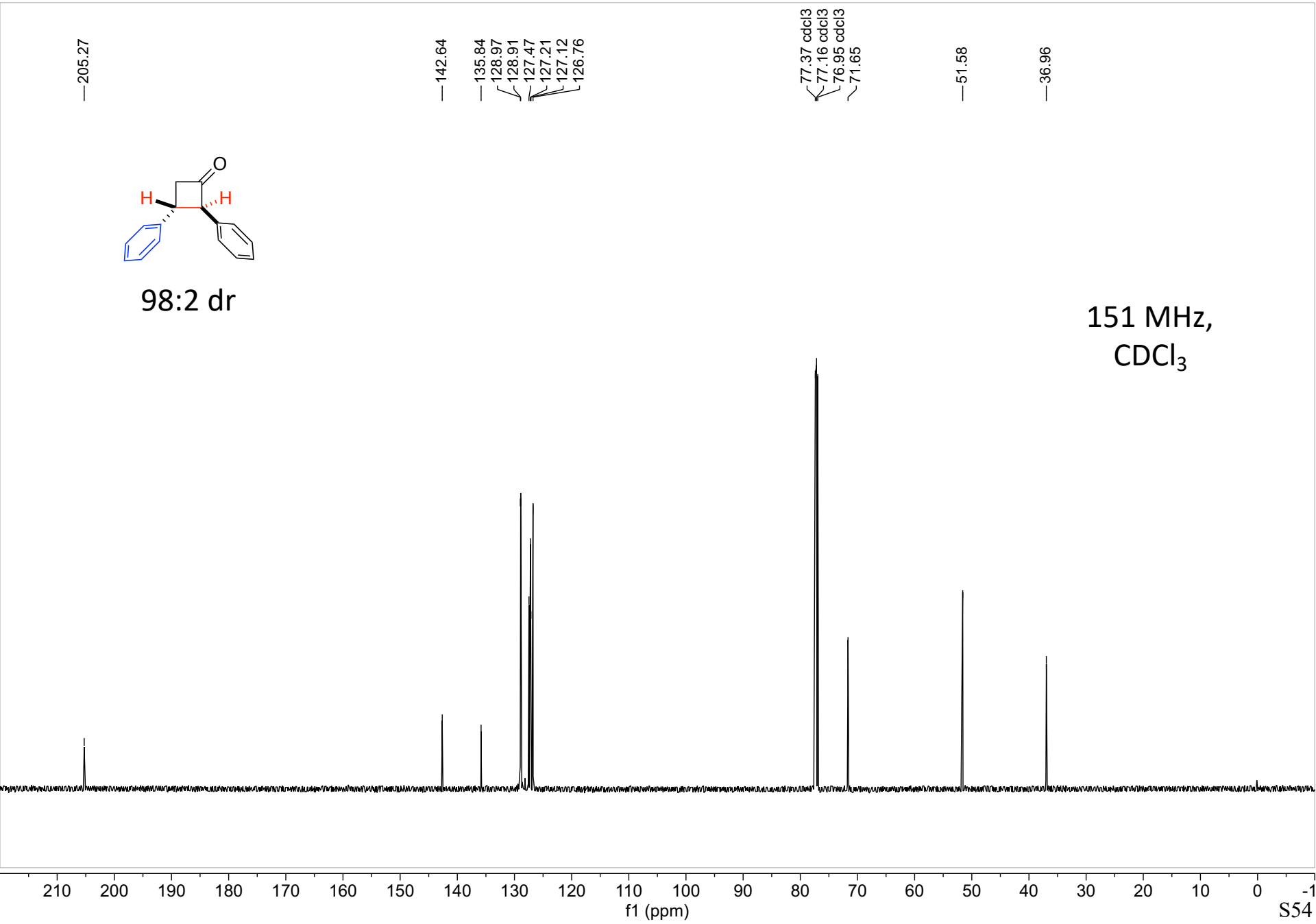
# $^{13}$C NMR 1-Diazo-1,7-diphenylheptan-2-one **(1w)**

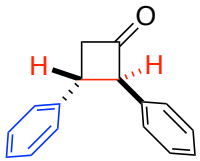


# $^1$H NMR (2*R*,3*R*)-2,3-diphenylcyclobutan-1-one **(2a)**

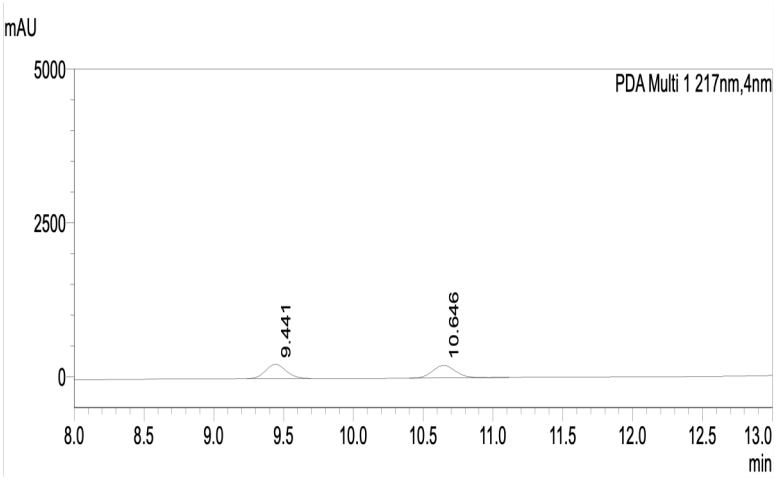


# $^{13}$C NMR (2*R*,3*R*)-2,3-diphenylcyclobutan-1-one **(2a)**



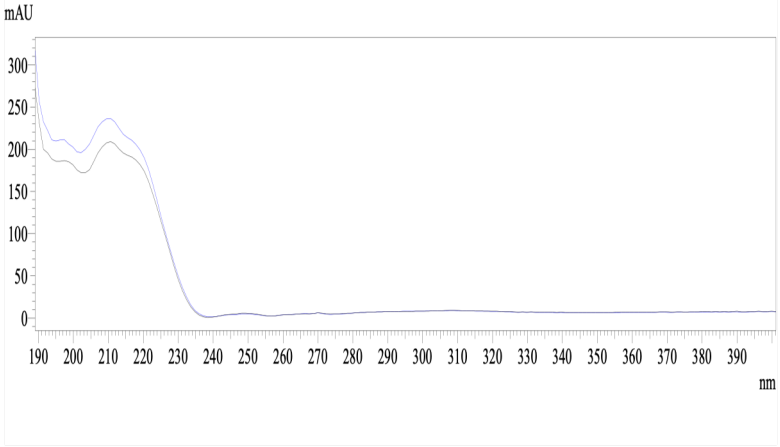


# **HPLC** (2*R*,3*R*)-2,3-diphenylcyclobutan-1-one **(2a)**




UV Spectrum

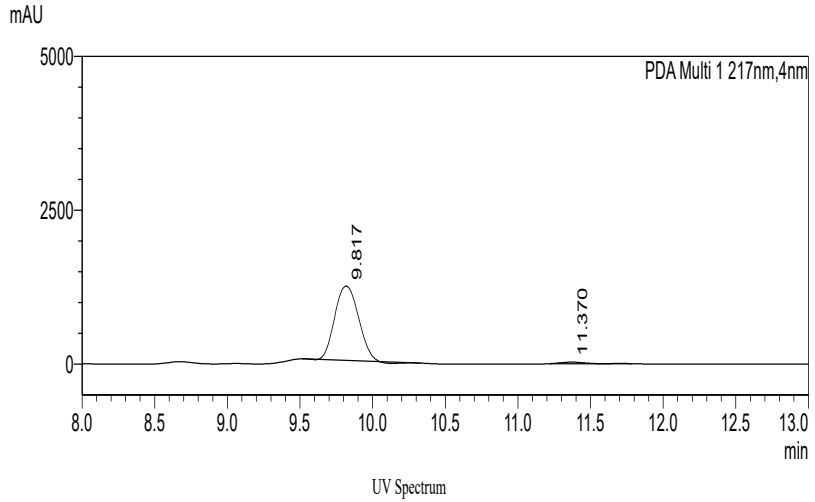
JJX-modelcyclobutanone-IC-2%0.8mL_001.lcd




Peak Table

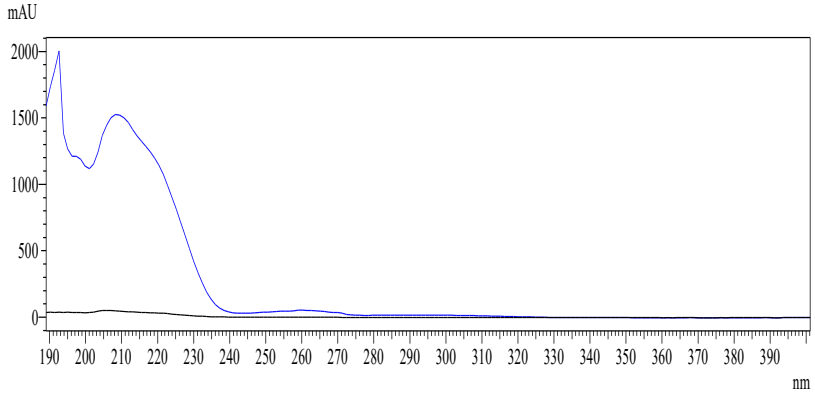
PDA Ch1 217nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.441 | 50.139 |
| 2 | 10.646 | 49.861 |
| Total | | 100.000 |




UV Spectrum

JJX-modelcyclobutanone-c-IC-2%0.8mL_001.lcd

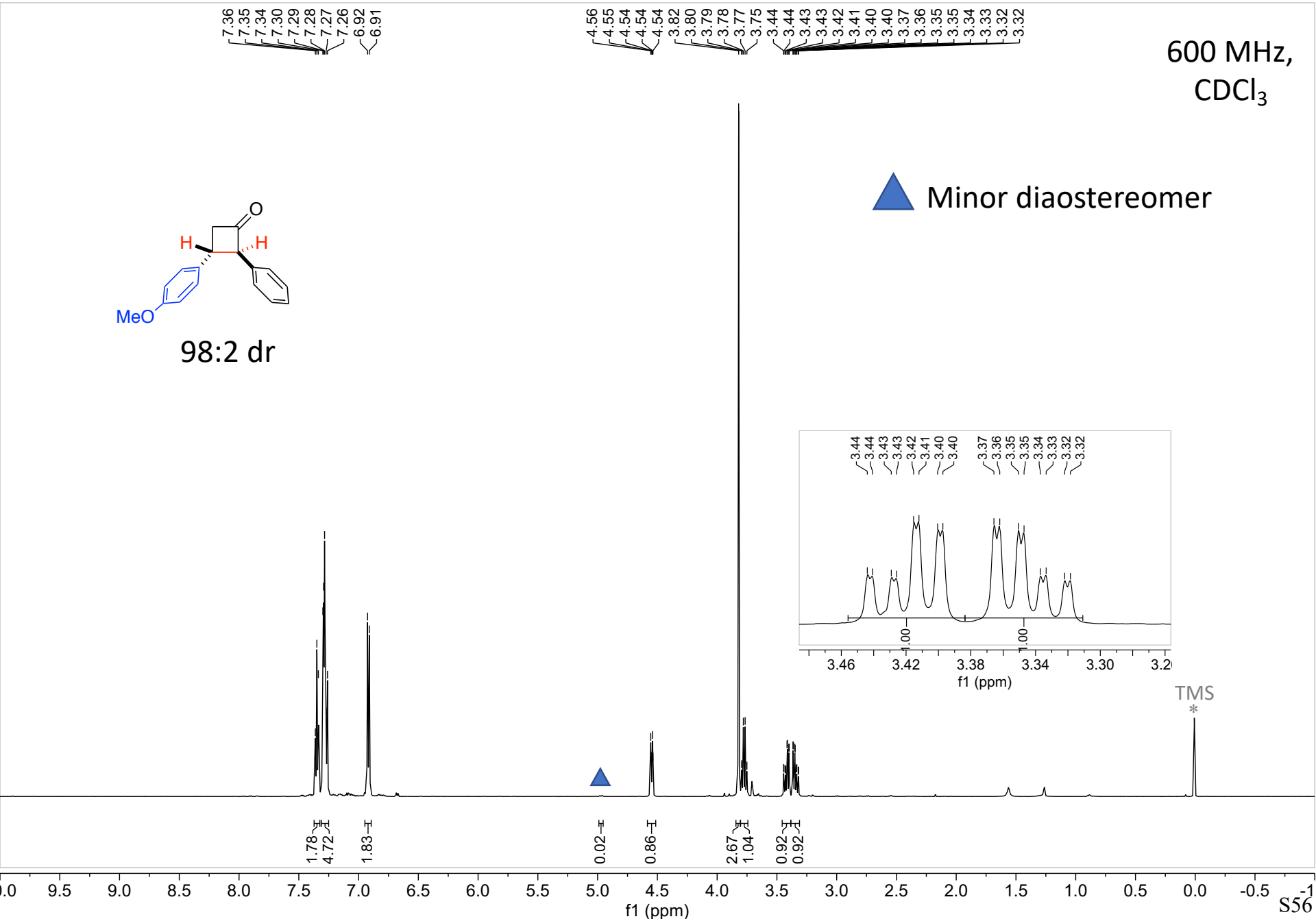



Peak Table

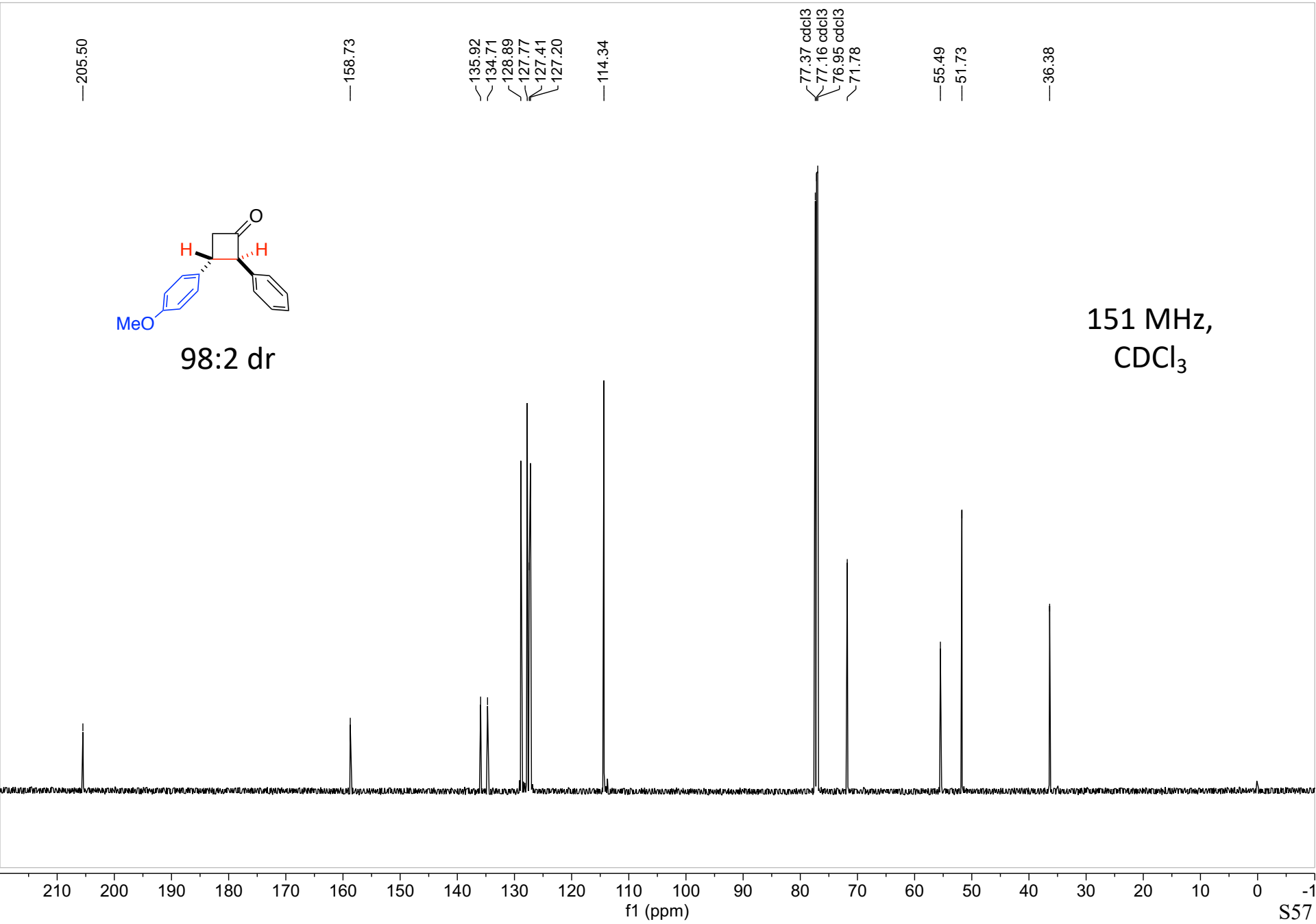
PDA Ch1 217nm

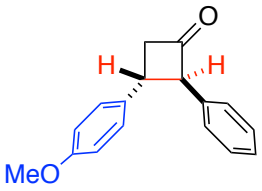
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.817 | 98.052 |
| 2 | 11.370 | 1.948 |
| Total | | 100.000 |

# $^1$H NMR (2*R*,3*R*)-3-(4-methoxyphenyl)-2-phenylcyclobutan-1-one (**2b**)

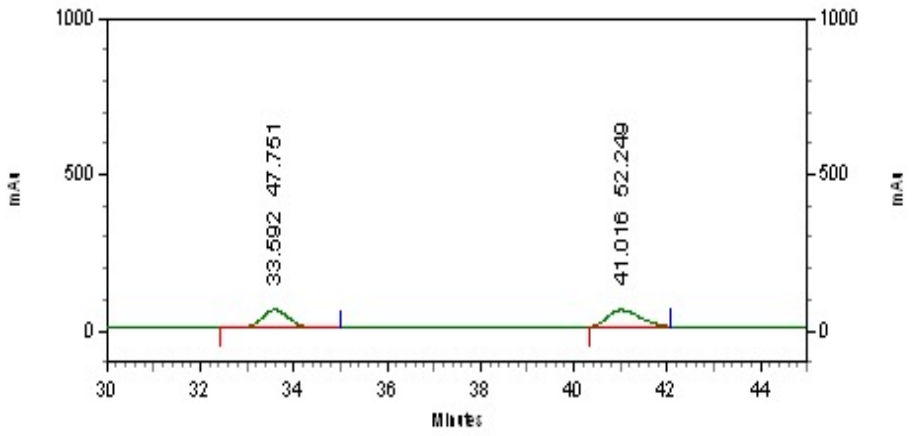


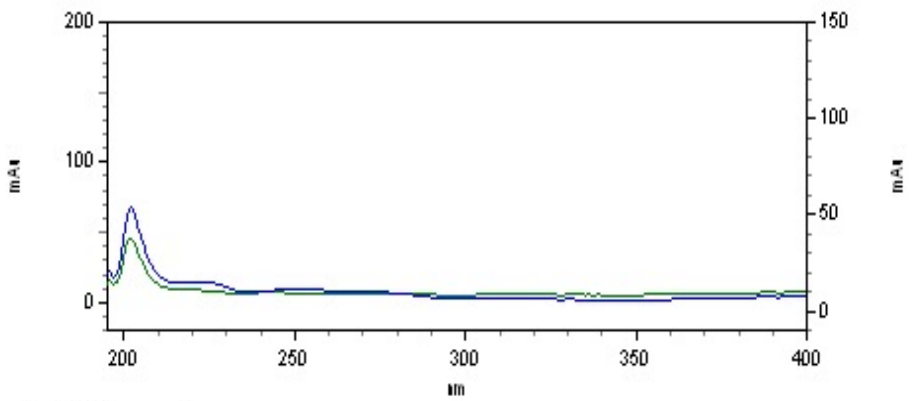
# $^{13}$C NMR (2*R*,3*R*)-3-(4-methoxyphenyl)-2-phenylcyclobutan-1-one **(2b)**






# **HPLC** (2*R*,3*R*)-3-(4-methoxyphenyl)-2-phenylcyclobutan-1-one **(2b)**

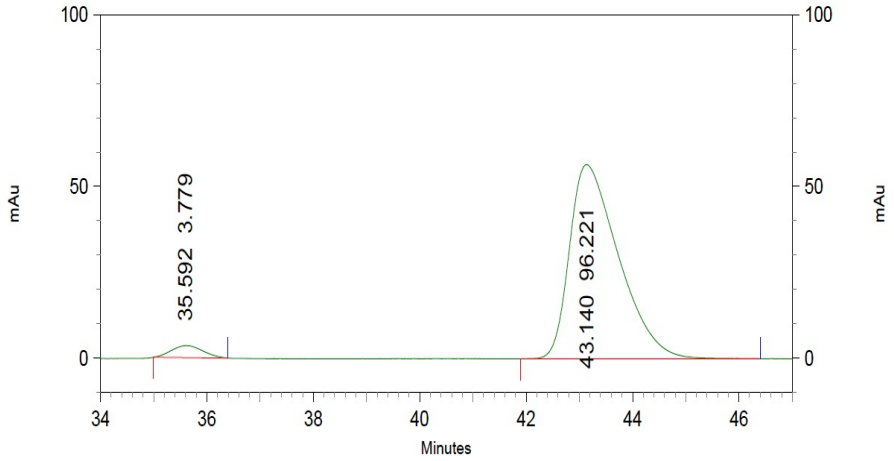


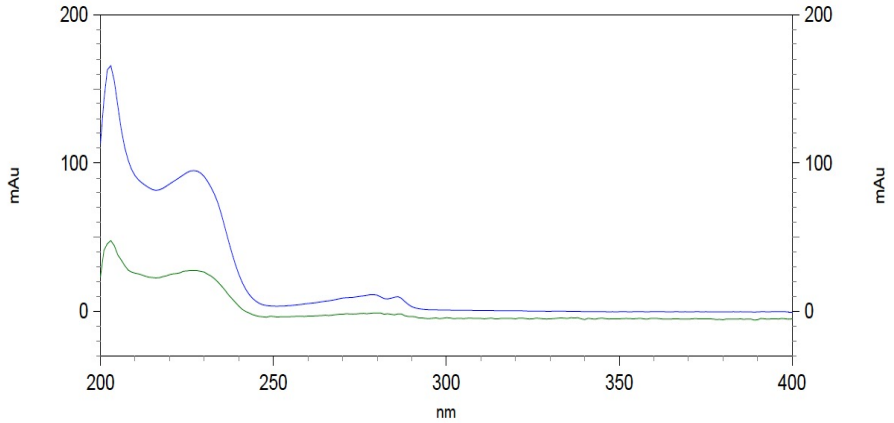




2: 236 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 33.592 | 47.751 |
| 2 | 41.016 | 52.249 |

| Totals | | 100.000 |
|---|---|---|



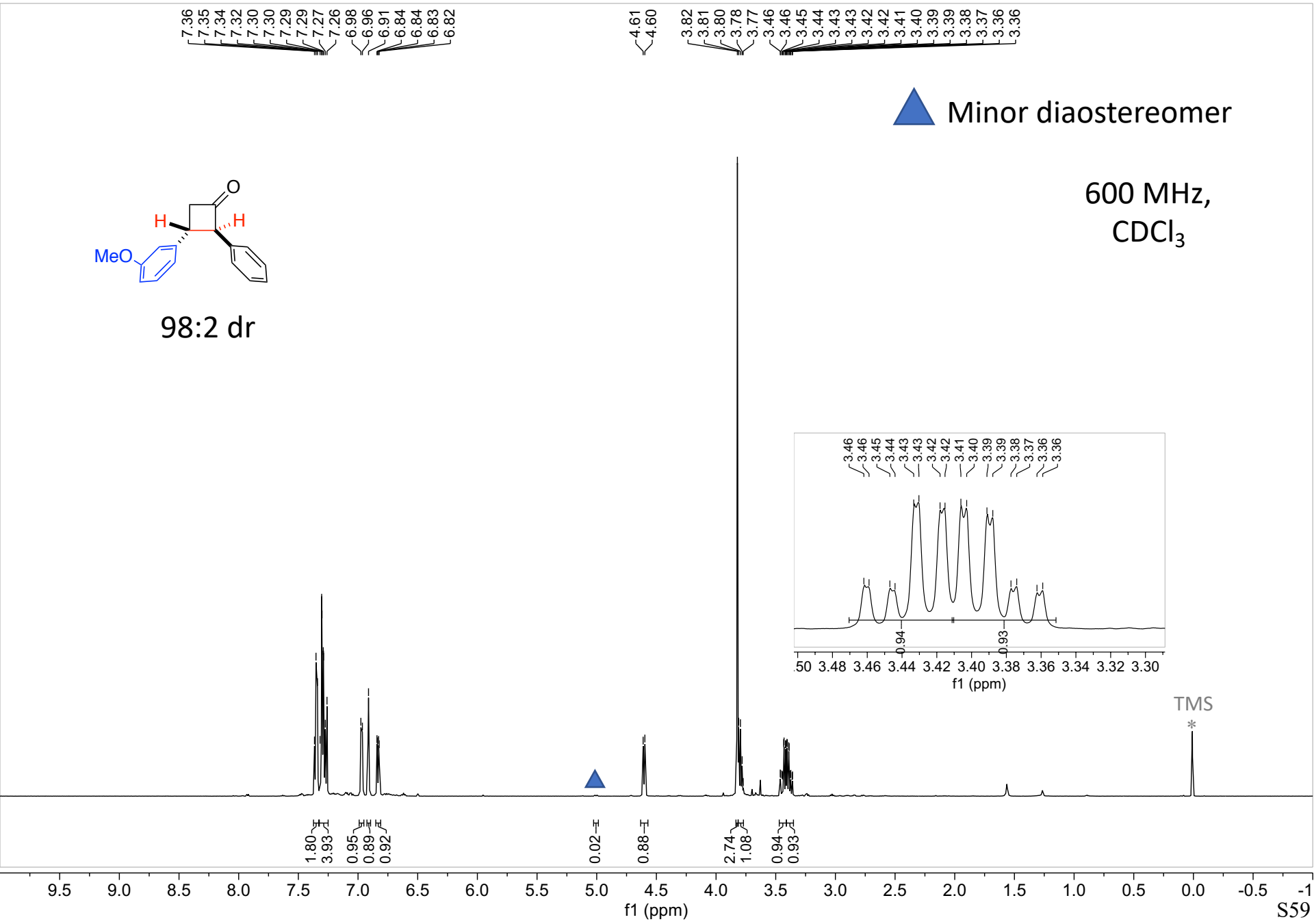




2: 236 nm, 4
nm Results

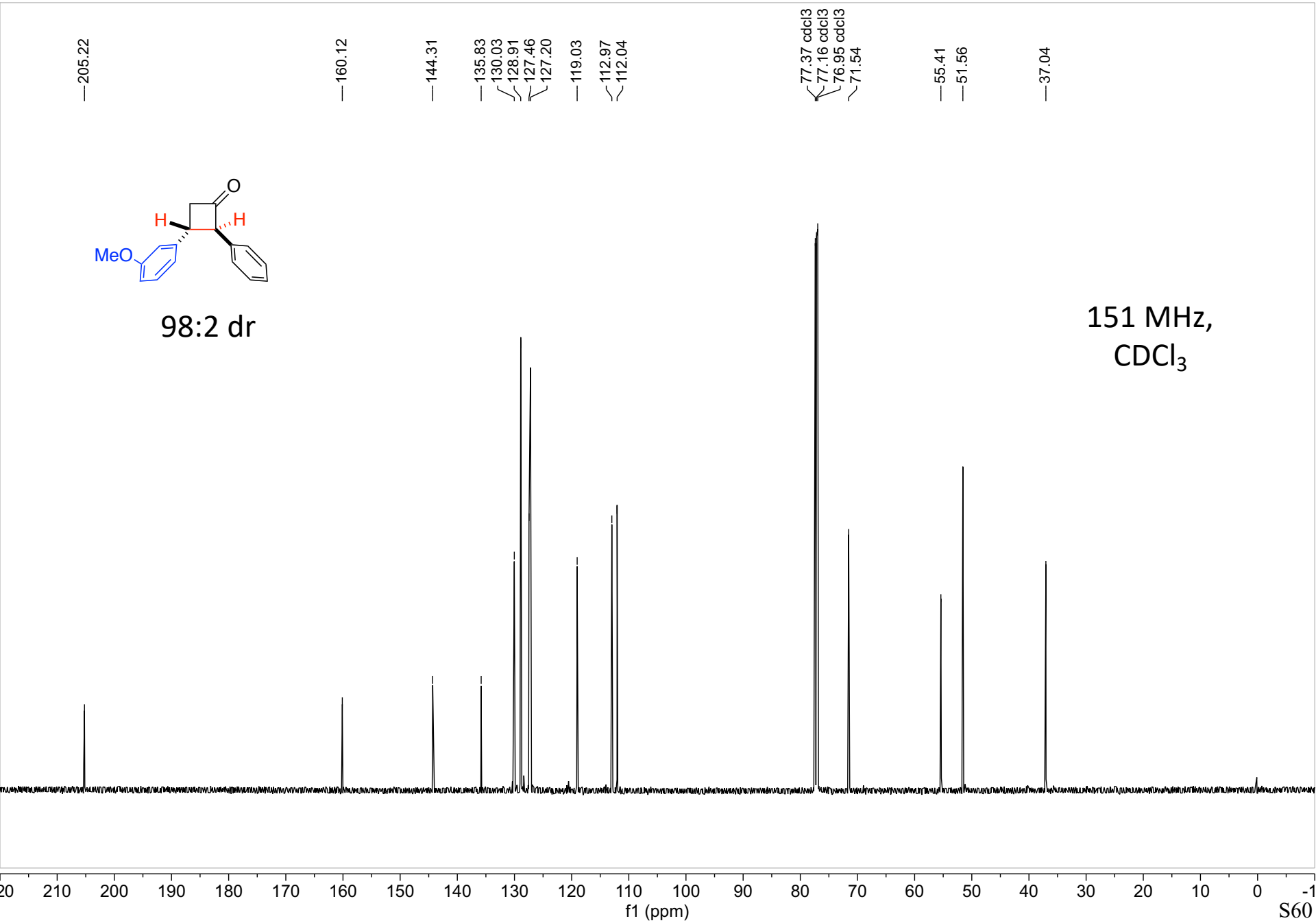
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 35.592 | 3.779 |
| 2 | 43.140 | 96.221 |

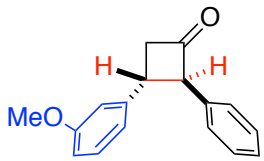
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-3-(3-methoxyphenyl)-2-phenylcyclobutan-1-one **(2c)**

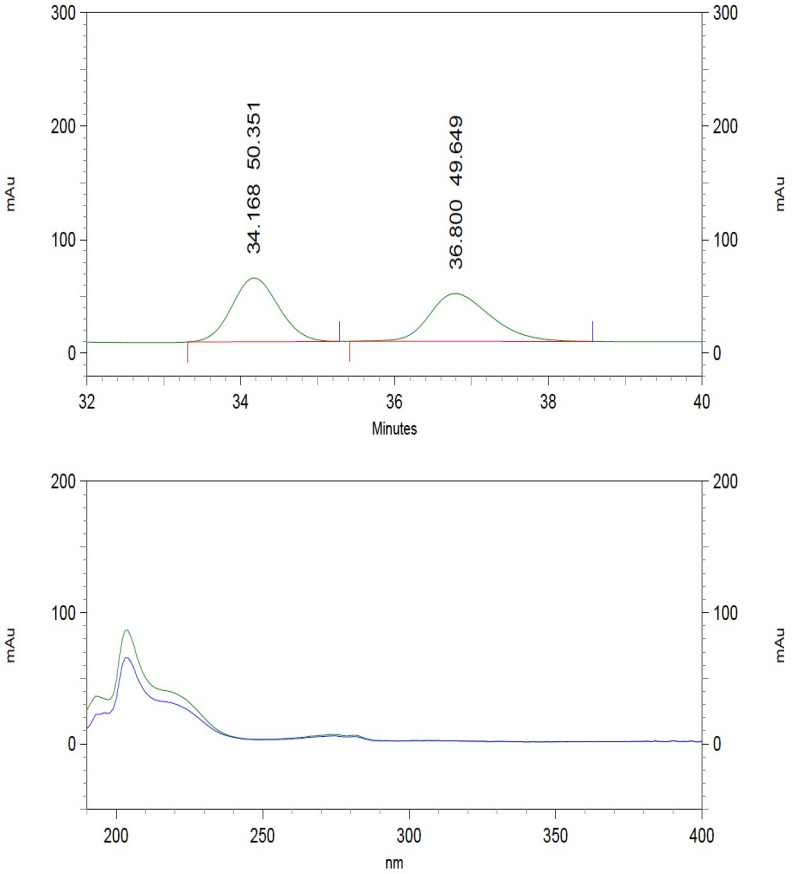


# $^{13}$C NMR (2*R*,3*R*)-3-(3-methoxyphenyl)-2-phenylcyclobutan-1-one **(2c)**





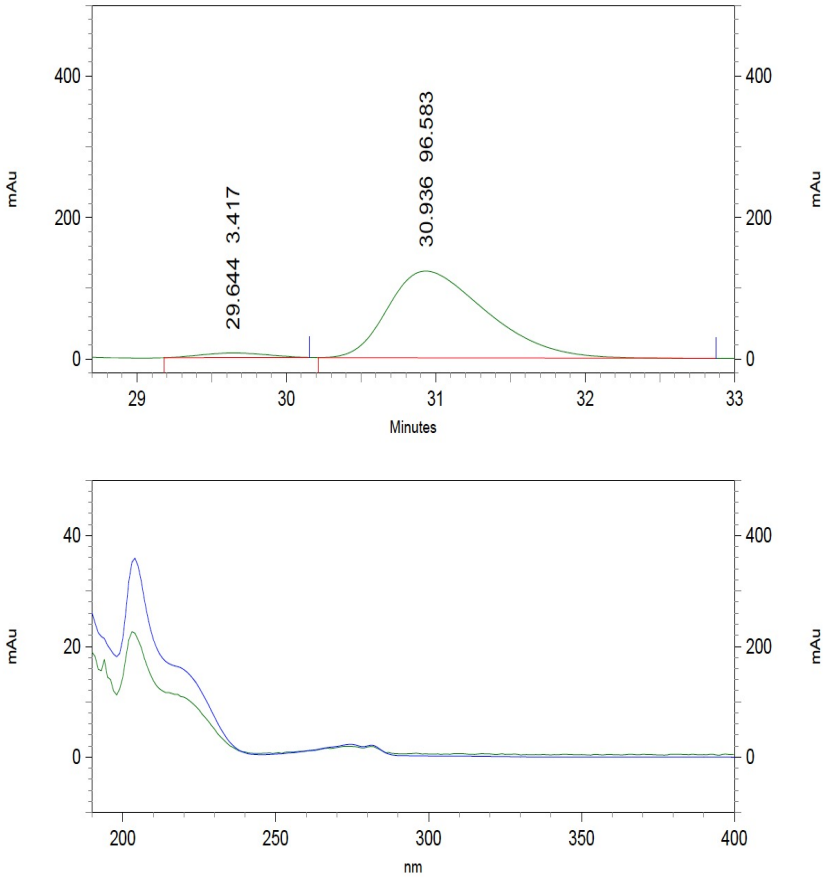

# **HPLC** (2*R*,3*R*)-3-(3-methoxyphenyl)-2-phenylcyclobutan-1-one **(2c)**




4: 224 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 34.168 | 50.351 |
| 2 | 36.800 | 49.649 |

| Totals | | 100.000 |
|---|---|---|

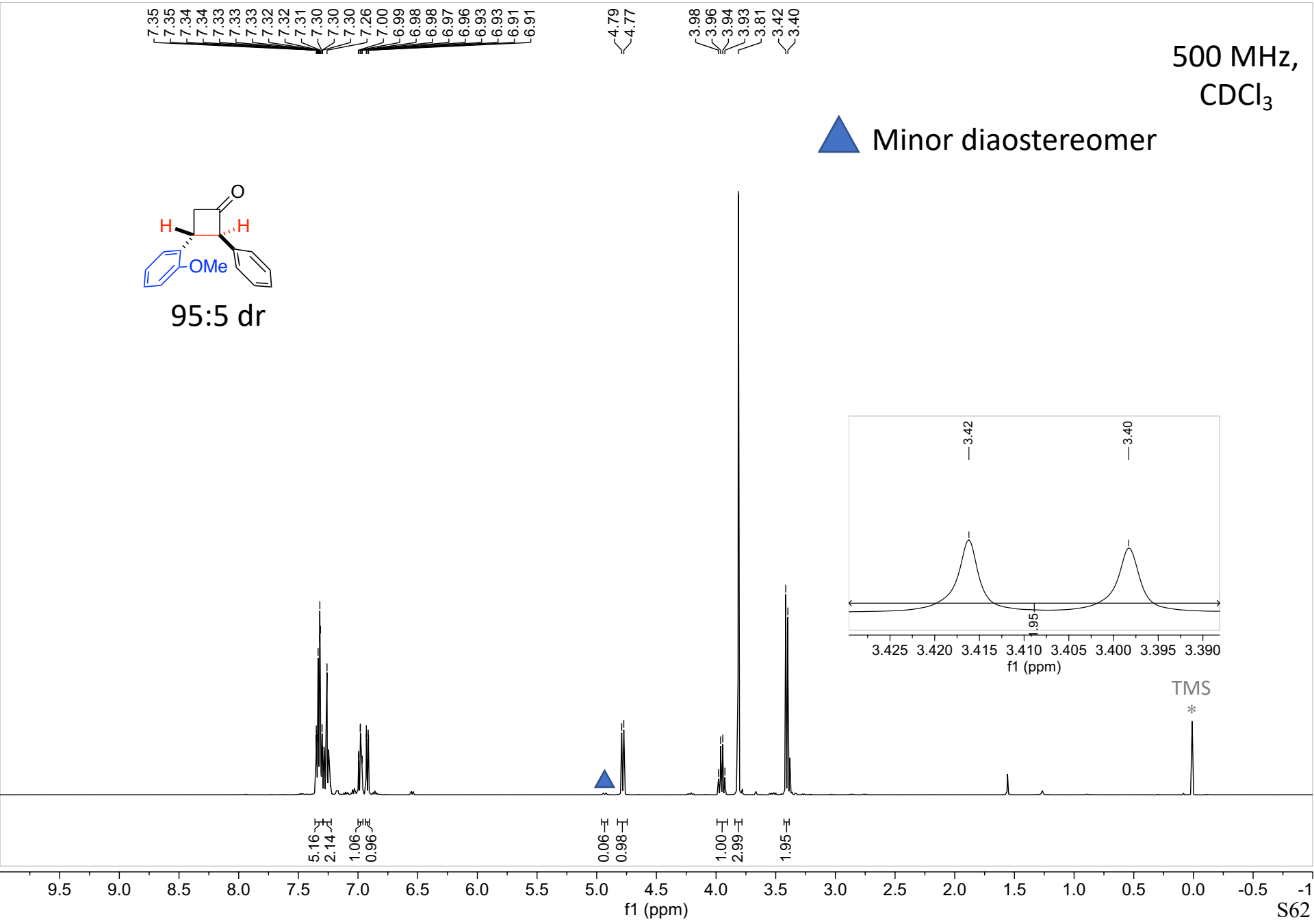



3: 225 nm, 4
nm Results

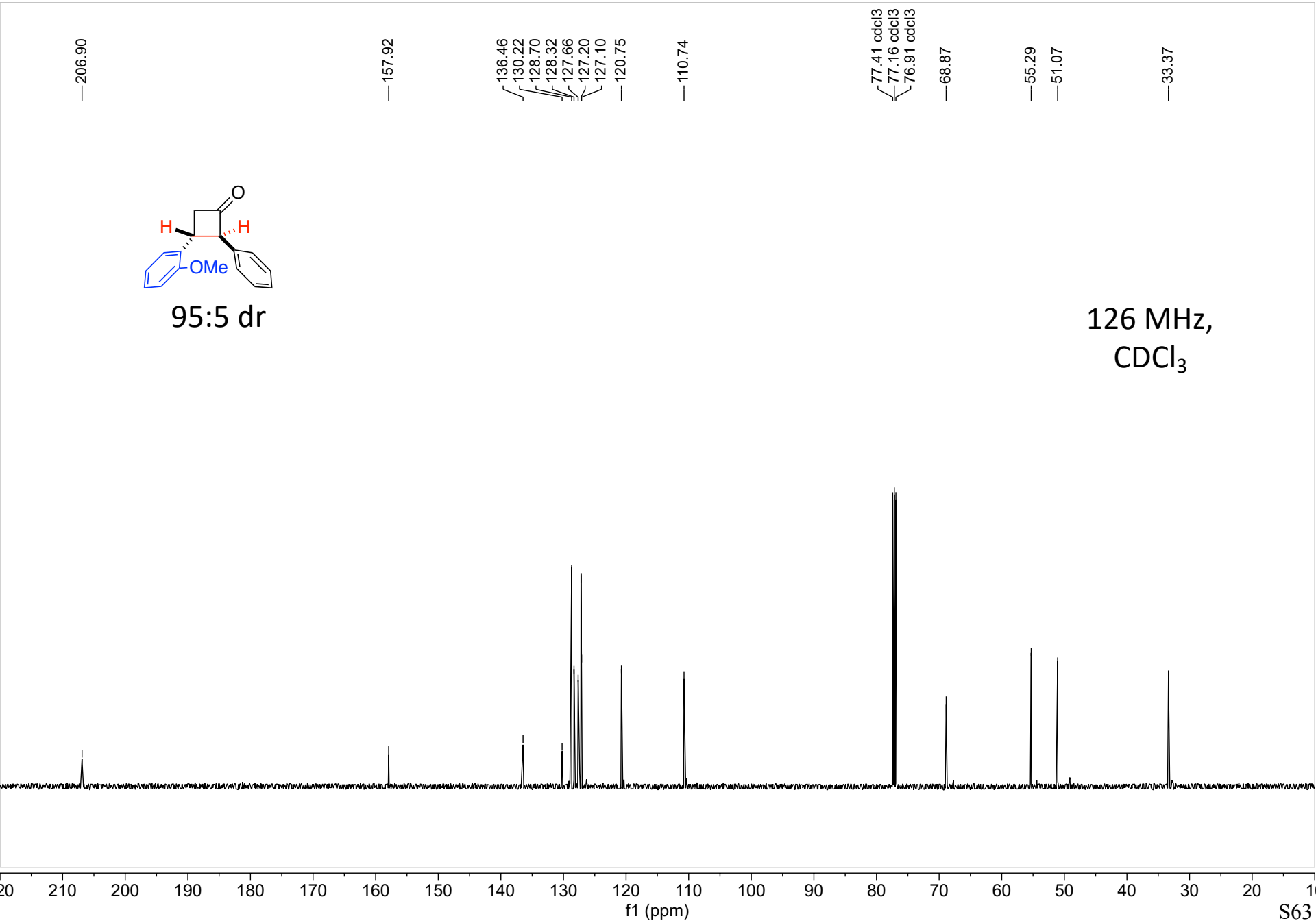
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 29.644 | 3.417 |
| 2 | 30.936 | 96.583 |

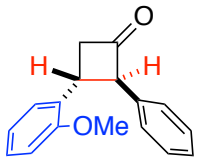
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-3-(2-methoxyphenyl)-2-phenylcyclobutan-1-one **(2d)**

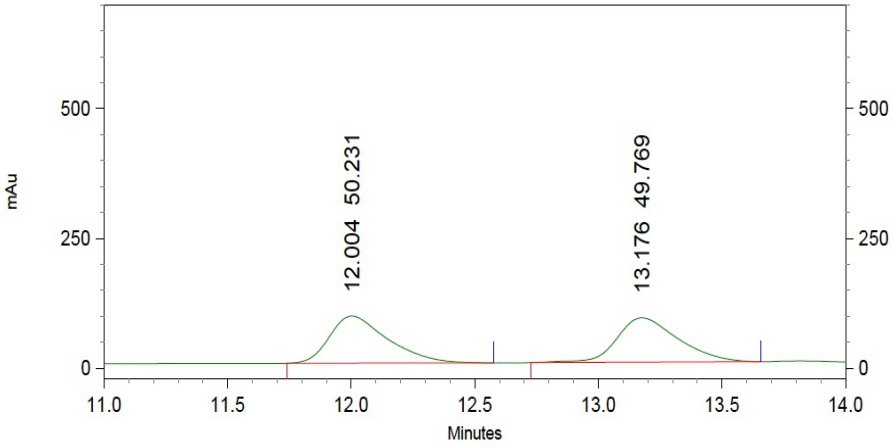


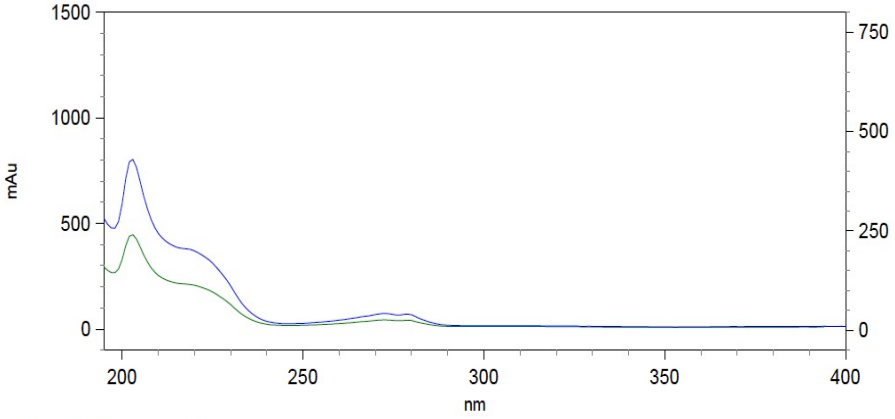
# $^{13}$C NMR (2*R*,3*R*)-3-(2-methoxyphenyl)-2-phenylcyclobutan-1-one **(2d)**





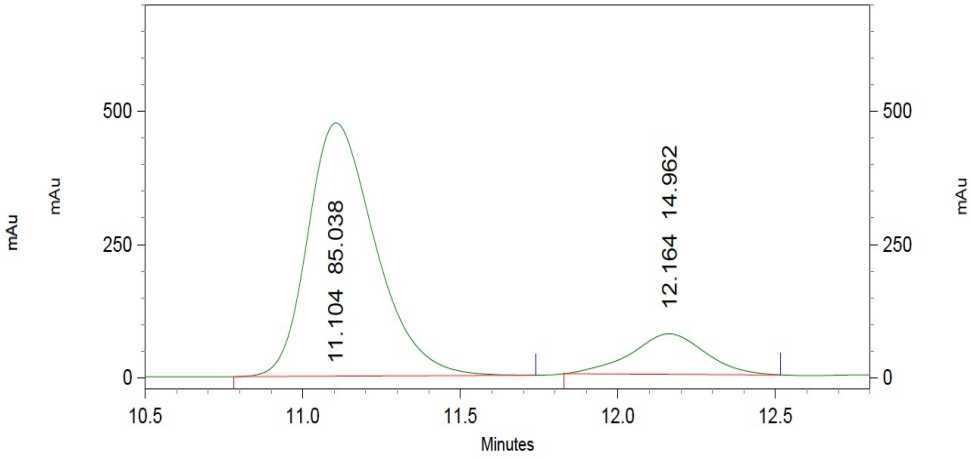

# **HPLC** (2*R*,3*R*)-3-(2-methoxyphenyl)-2-phenylcyclobutan-1-one **(2d)**

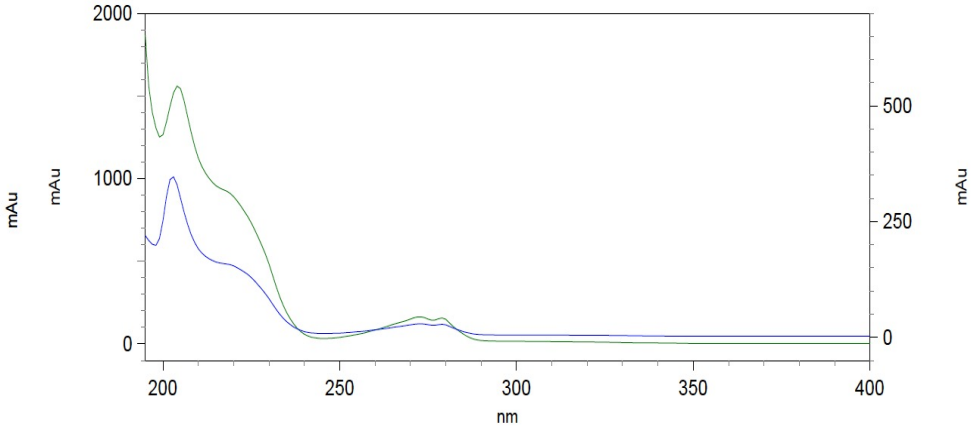



4: 231 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.004 | 50.231 |
| 2 | 13.176 | 49.769 |
| Totals | | 100.000 |

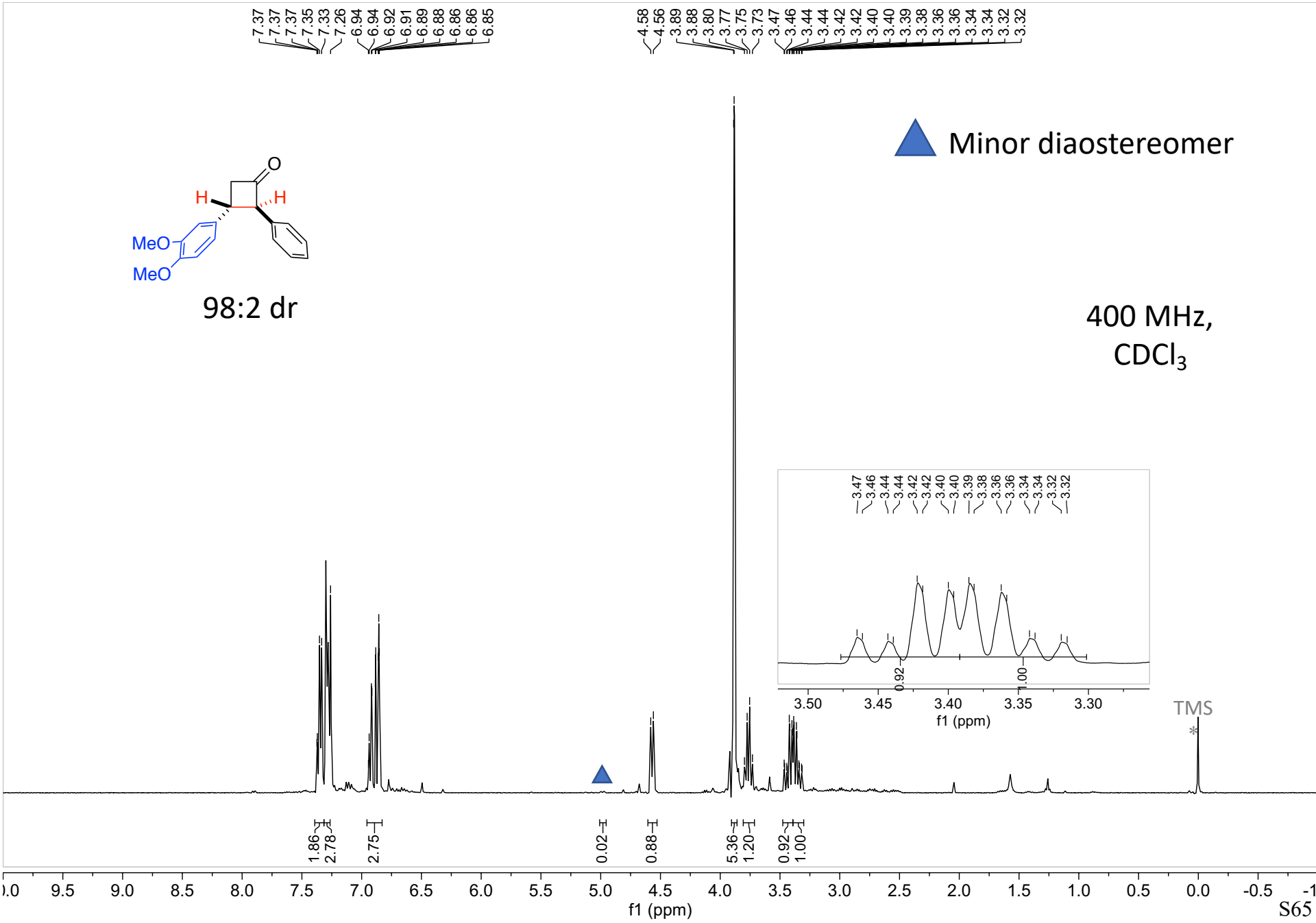


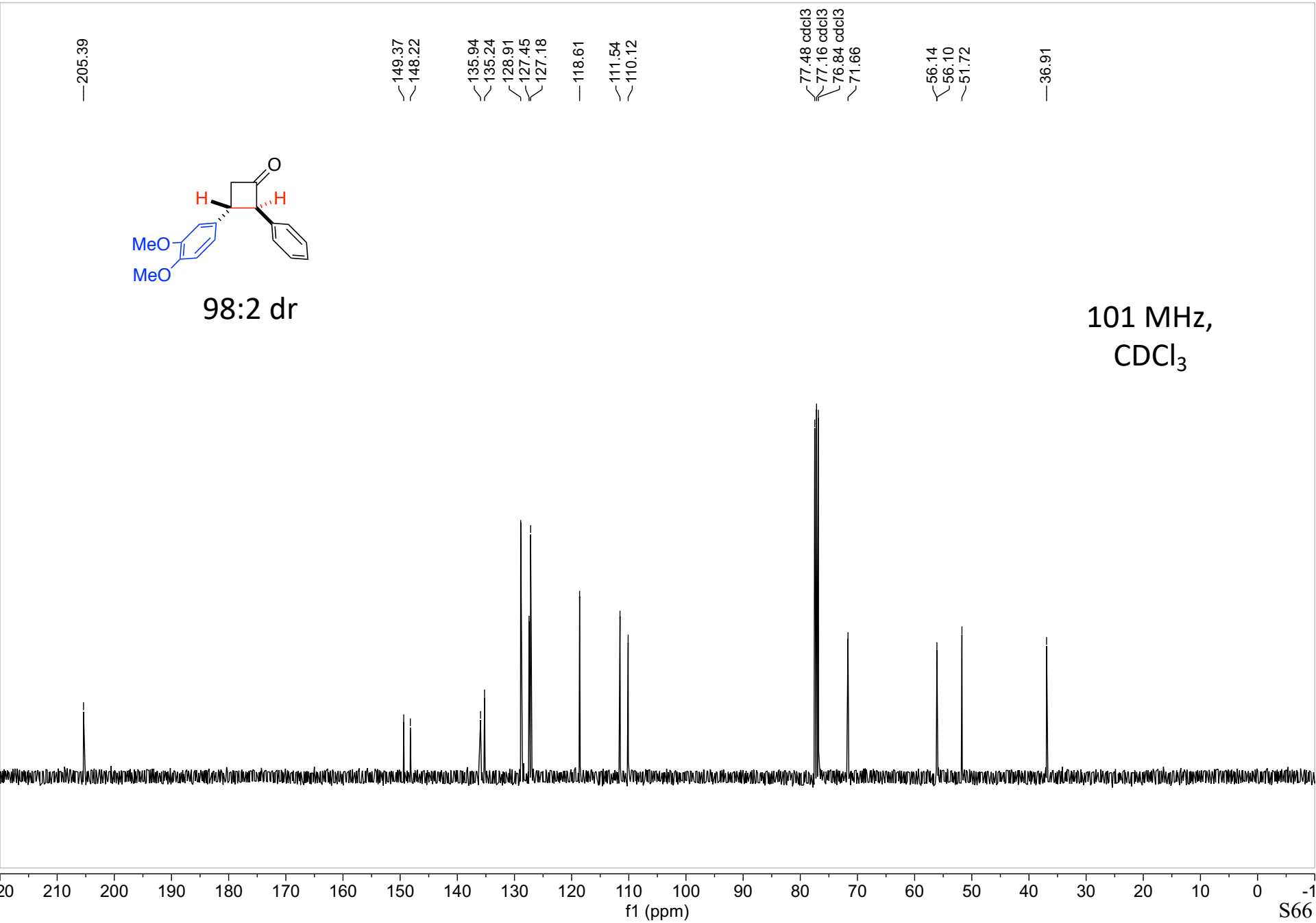

4: 230 nm, 4 nm Results

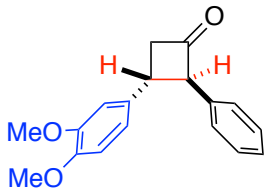
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.104 | 85.038 |
| 2 | 12.164 | 14.962 |
| Totals | | 100.000 |

# $^1$H NMR (2*R*,3*R*)-3-(3,4-dimethoxyphenyl)-2-phenylcyclobutan-1-one **(2e)**

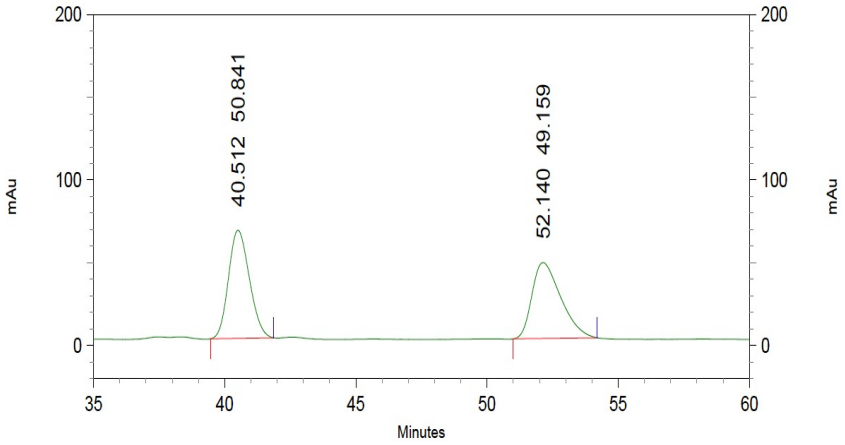


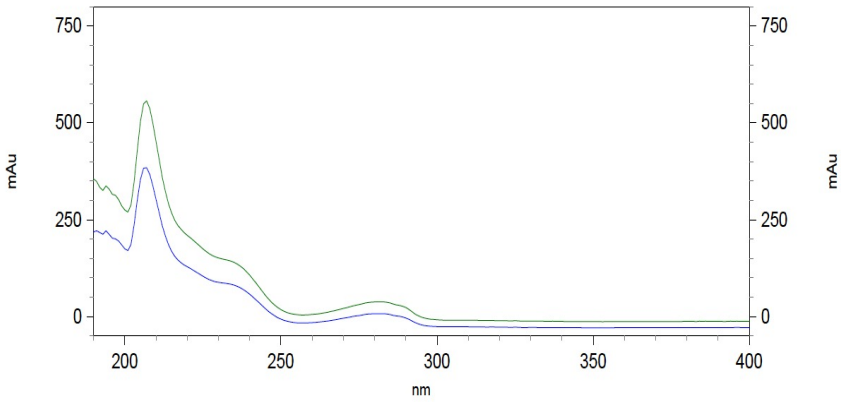
# $^{13}$C NMR (2*R*,3*R*)-3-(3,4-dimethoxyphenyl)-2-phenylcyclobutan-1-one **(2e)**






# **HPLC** (2*R*,3*R*)-3-(3,4-dimethoxyphenyl)-2-phenylcyclobutan-1-one **(2e)**

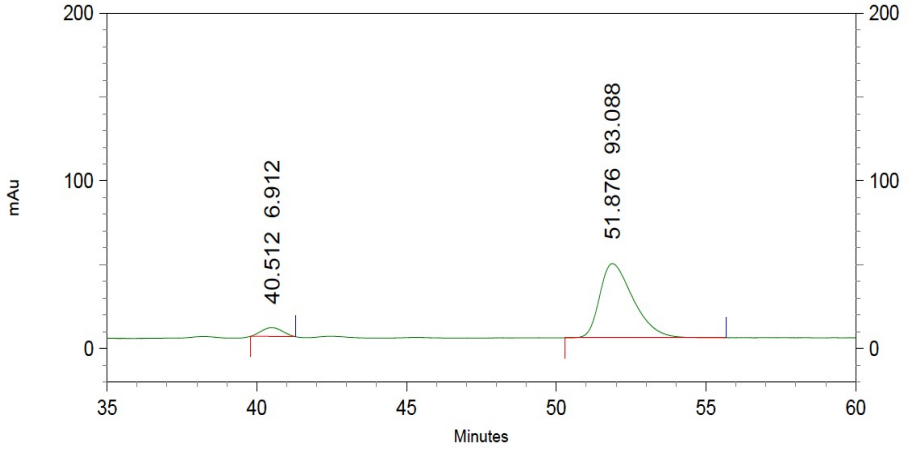


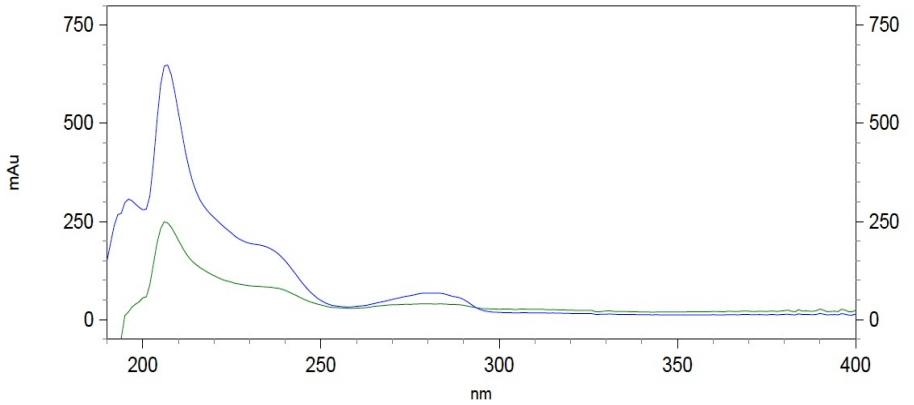




4: 241 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 40.512 | 50.841 |
| 2 | 52.140 | 49.159 |

| Totals | | 100.000 |
|---|---|---|



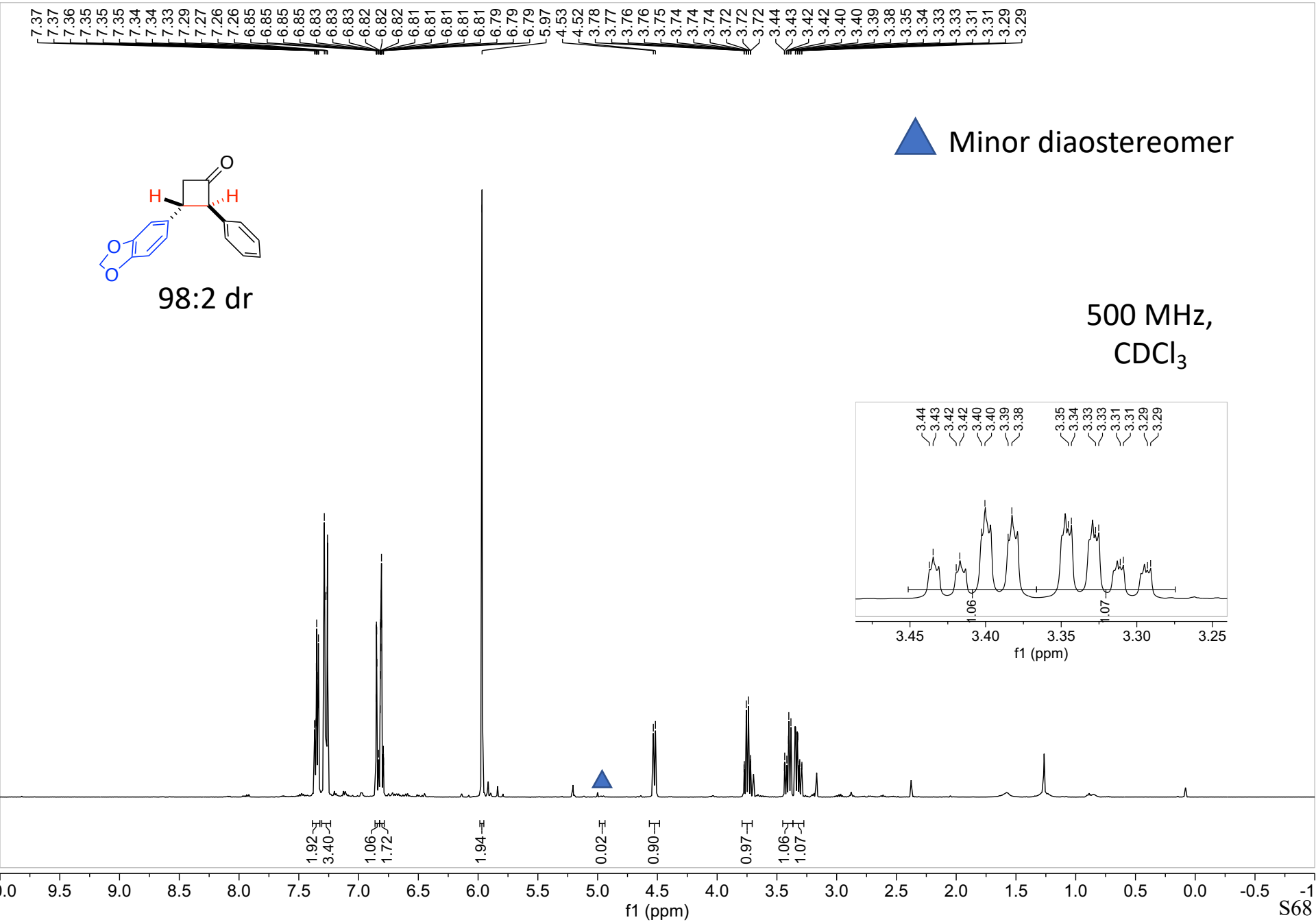




4: 241 nm, 4 nm Results

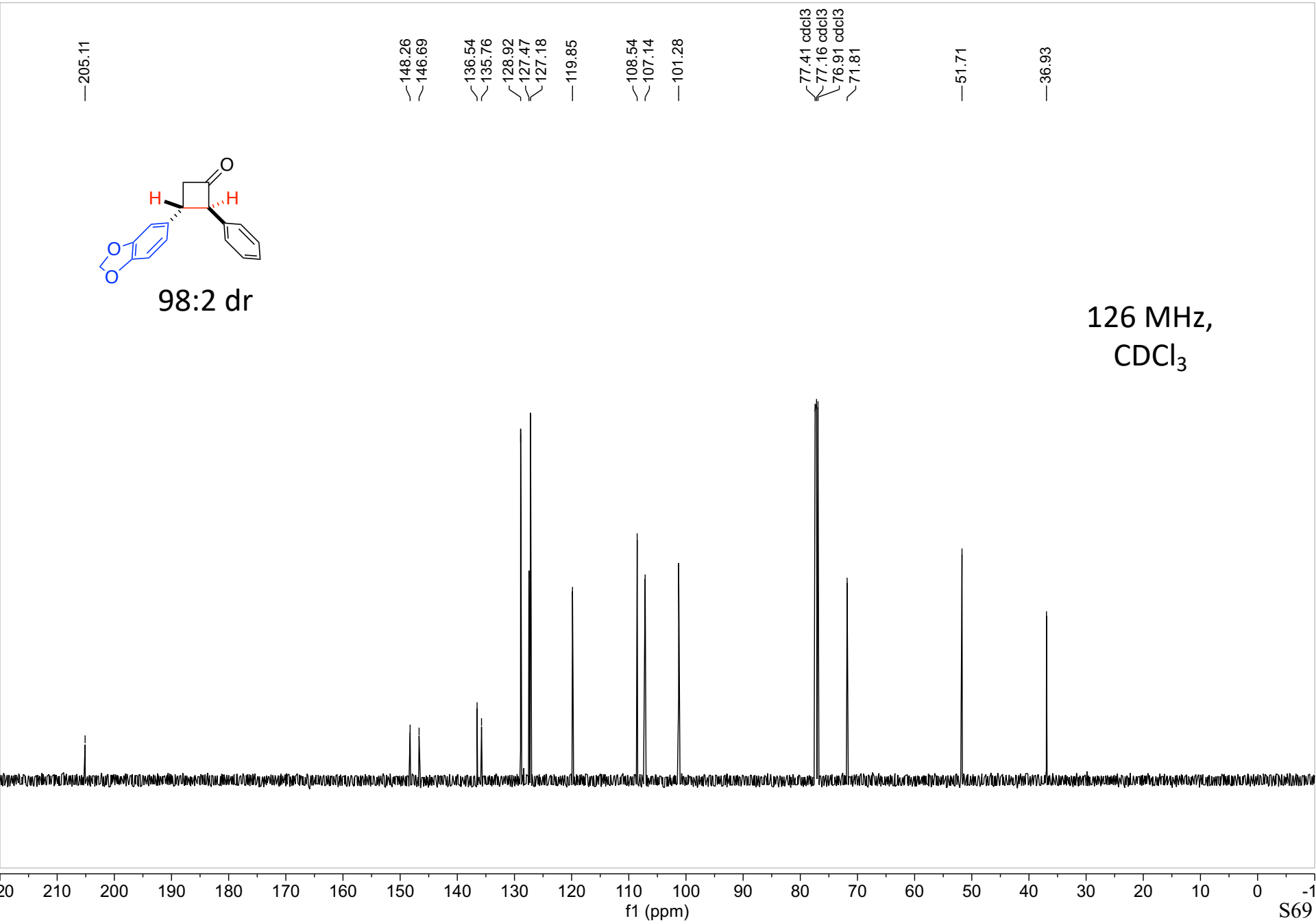
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 40.512 | 6.912 |
| 2 | 51.876 | 93.088 |

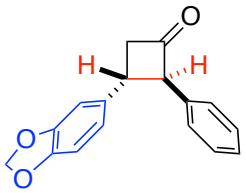
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-3-(benzo[*d*][1,3]dioxol-5-yl)-2-phenylcyclobutan-1-one **(2f)**

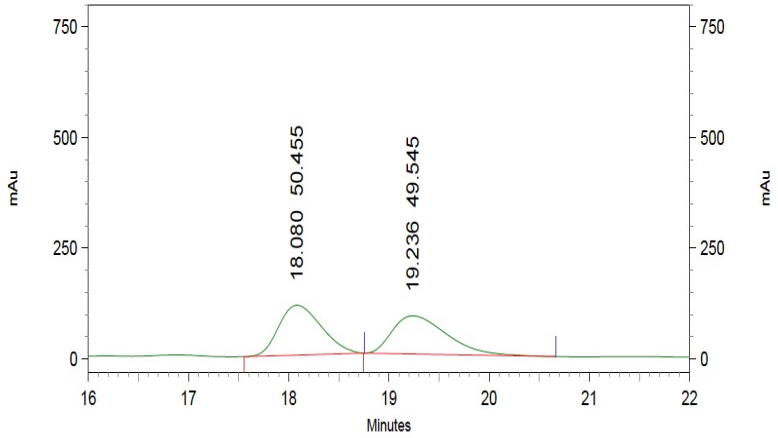


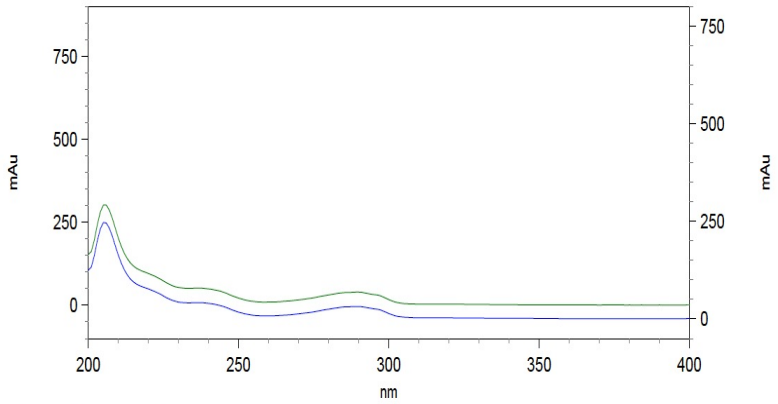
# $^{13}$C NMR (2*R*,3*R*)-3-(benzo[*d*][1,3]dioxol-5-yl)-2-phenylcyclobutan-1-one **(2f)**





# **HPLC** (2*R*,3*R*)-3-(benzo[*d*][1,3]dioxol-5-yl)-2-phenylcyclobutan-1-one **(2f)**

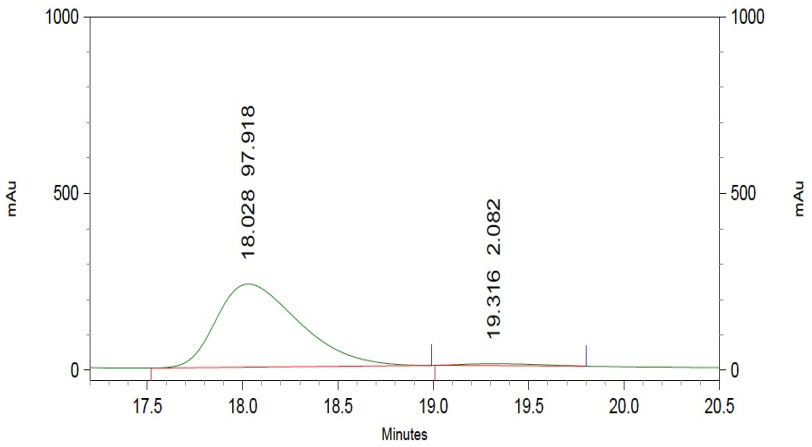


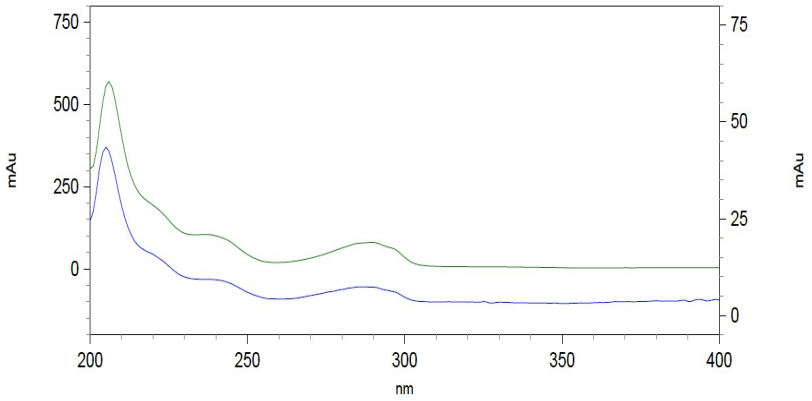




4: 215 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 18.080 | 50.455 |
| 2 | 19.236 | 49.545 |

| Totals | | 100.000 |
|---|---|---|



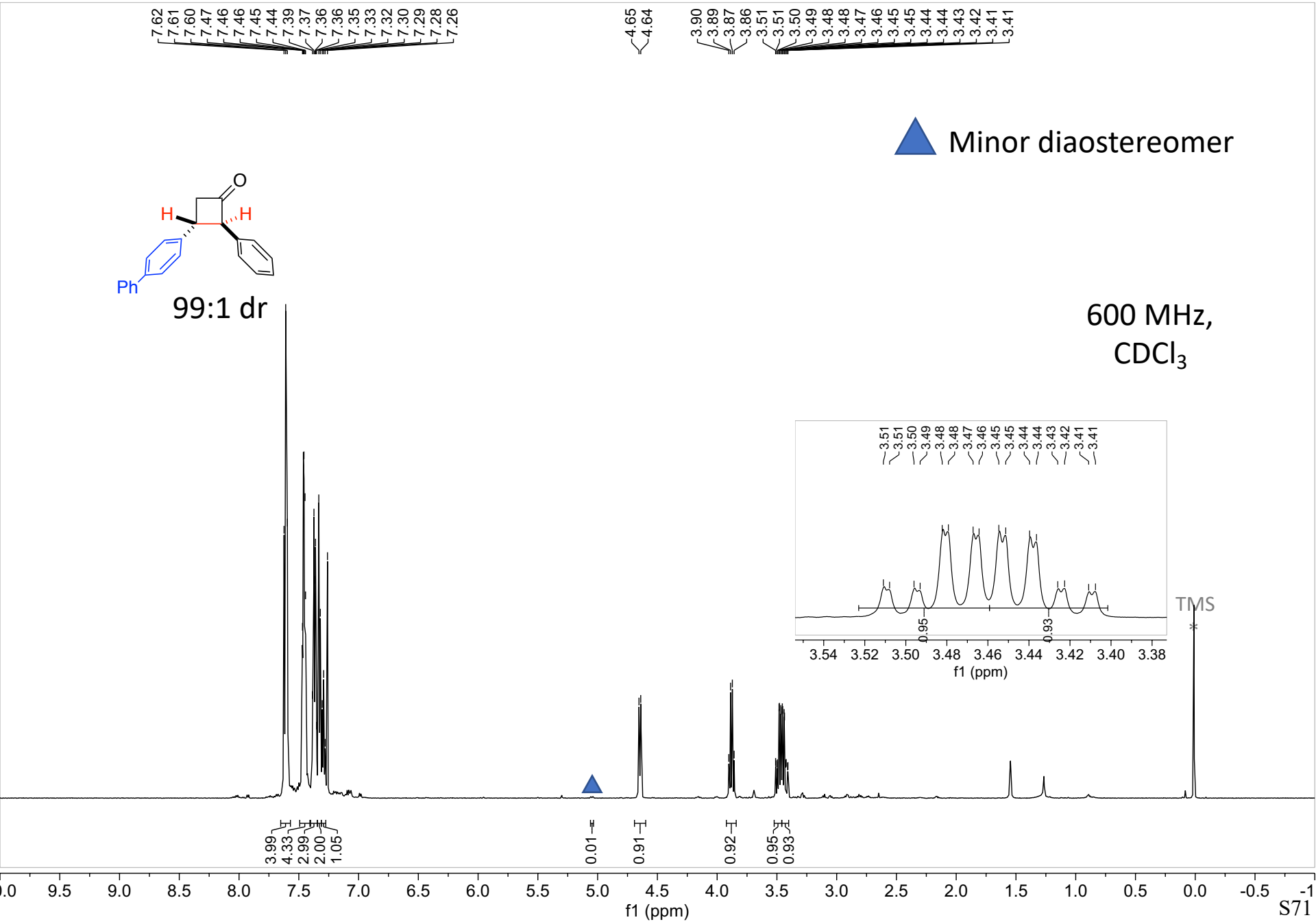




4: 215 nm, 4
nm Results

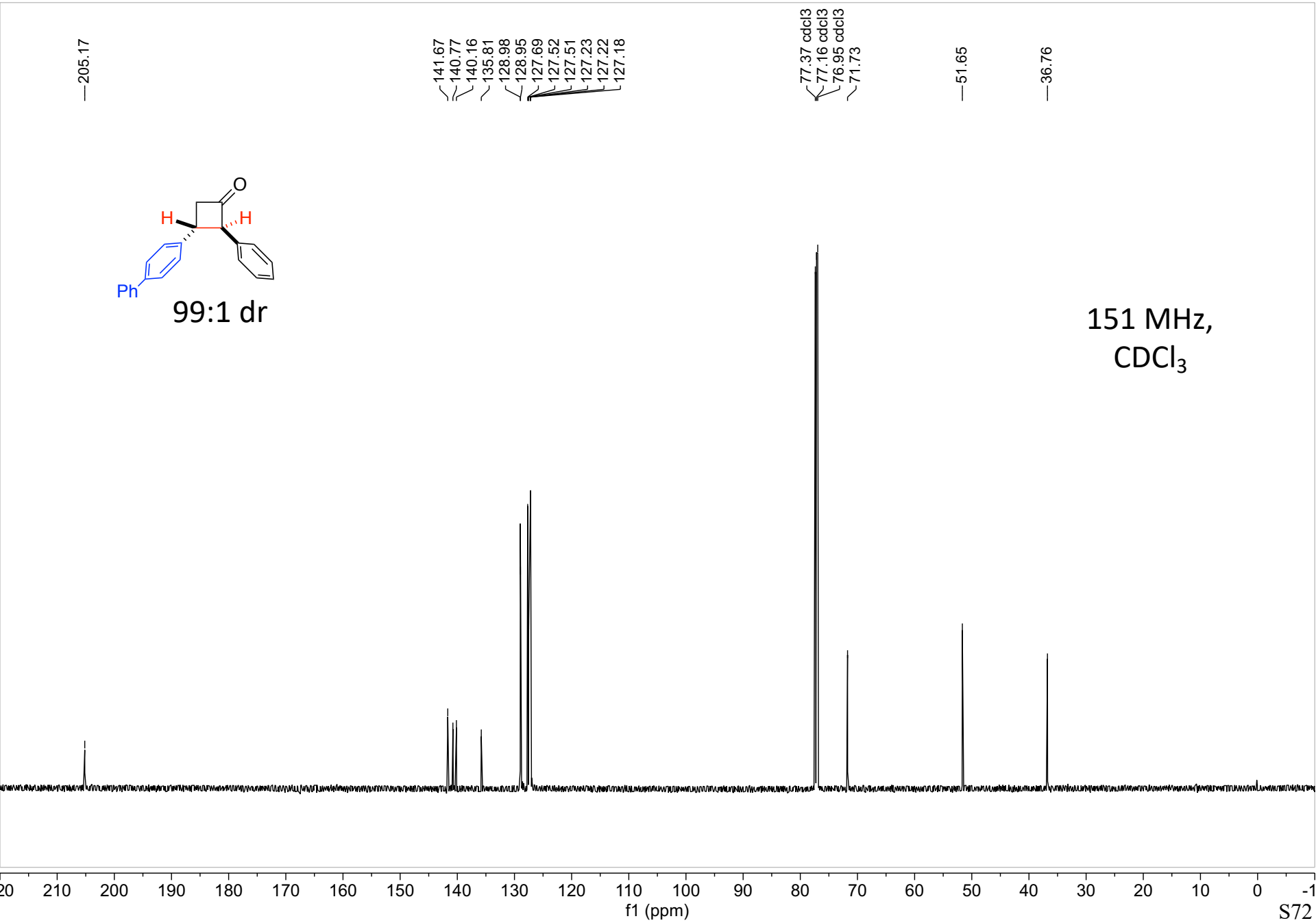
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 18.028 | 97.918 |
| 2 | 19.316 | 2.082 |

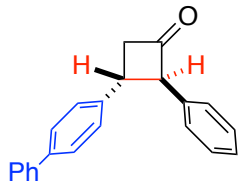
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-3-([1,1'-biphenyl]-4-yl)-2-phenylcyclobutan-1-one **(2g)**

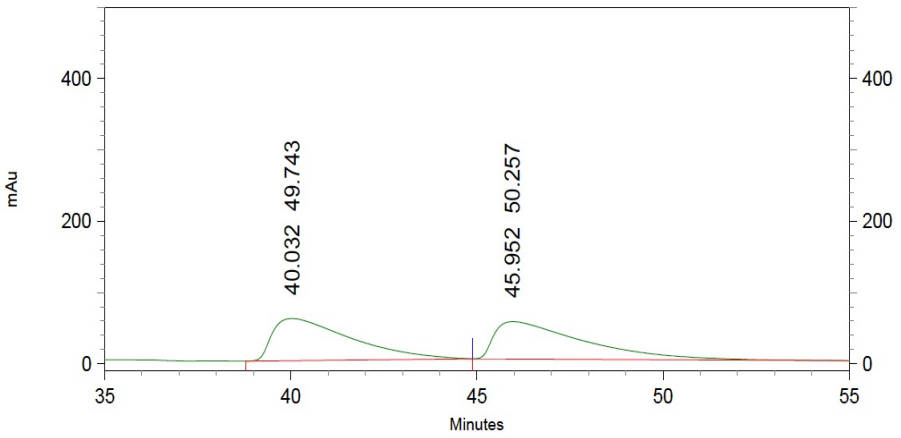


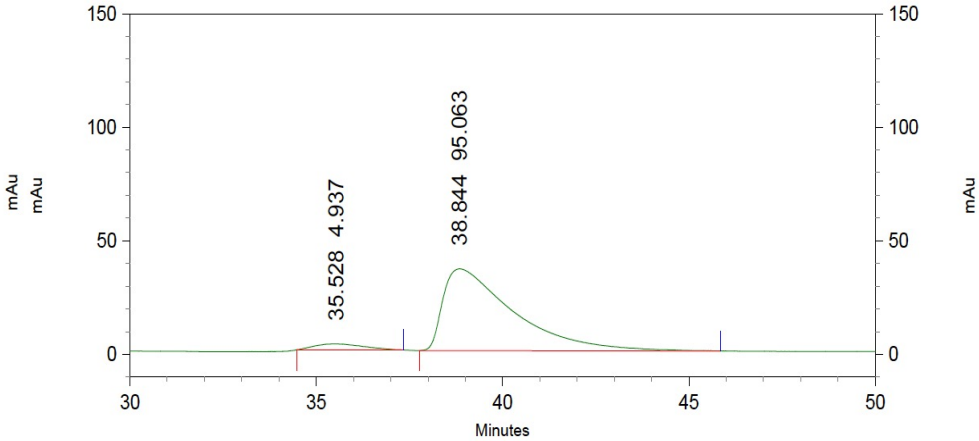
# $^{13}$C NMR (2*R*,3*R*)-3-([1,1'-biphenyl]-4-yl)-2-phenylcyclobutan-1-one **(2g)**

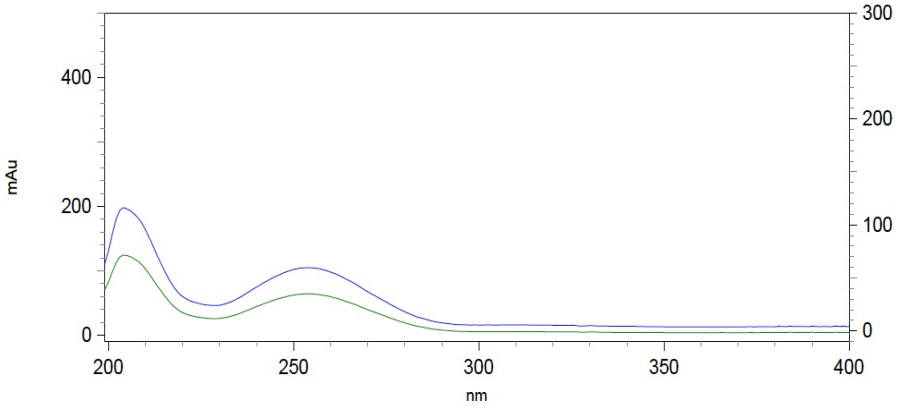


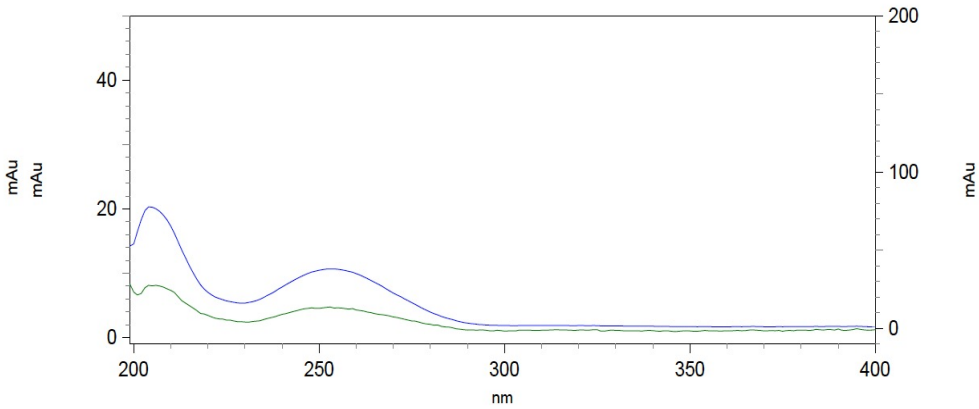



# **HPLC** (2*R*,3*R*)-3-([1,1'-biphenyl]-4-yl)-2-phenylcyclobutan-1-one **(2g)**



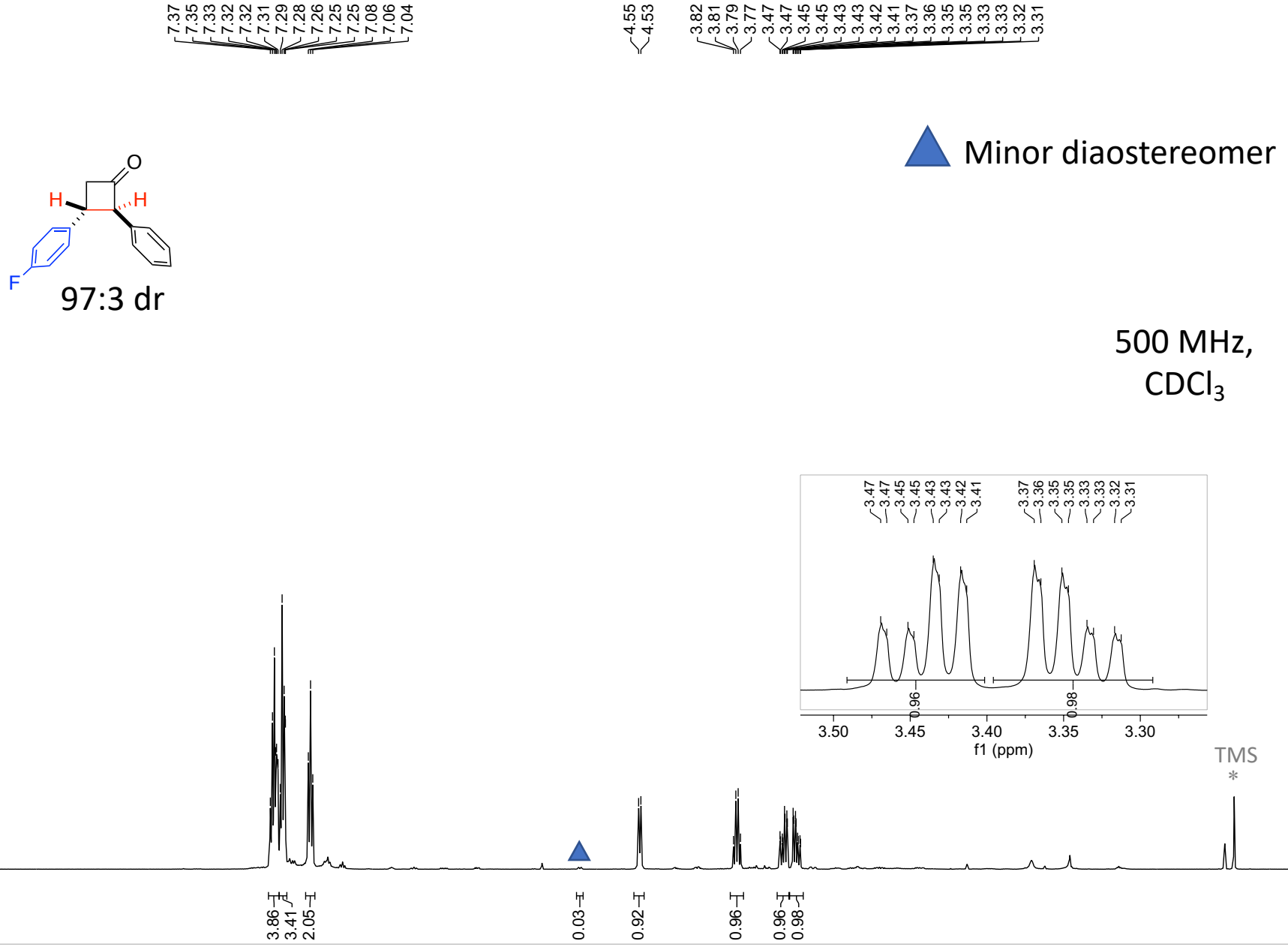

3: 255 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 40.032 | 49.743 |
| 2 | 45.952 | 50.257 |
| Totals | | 100.000 |

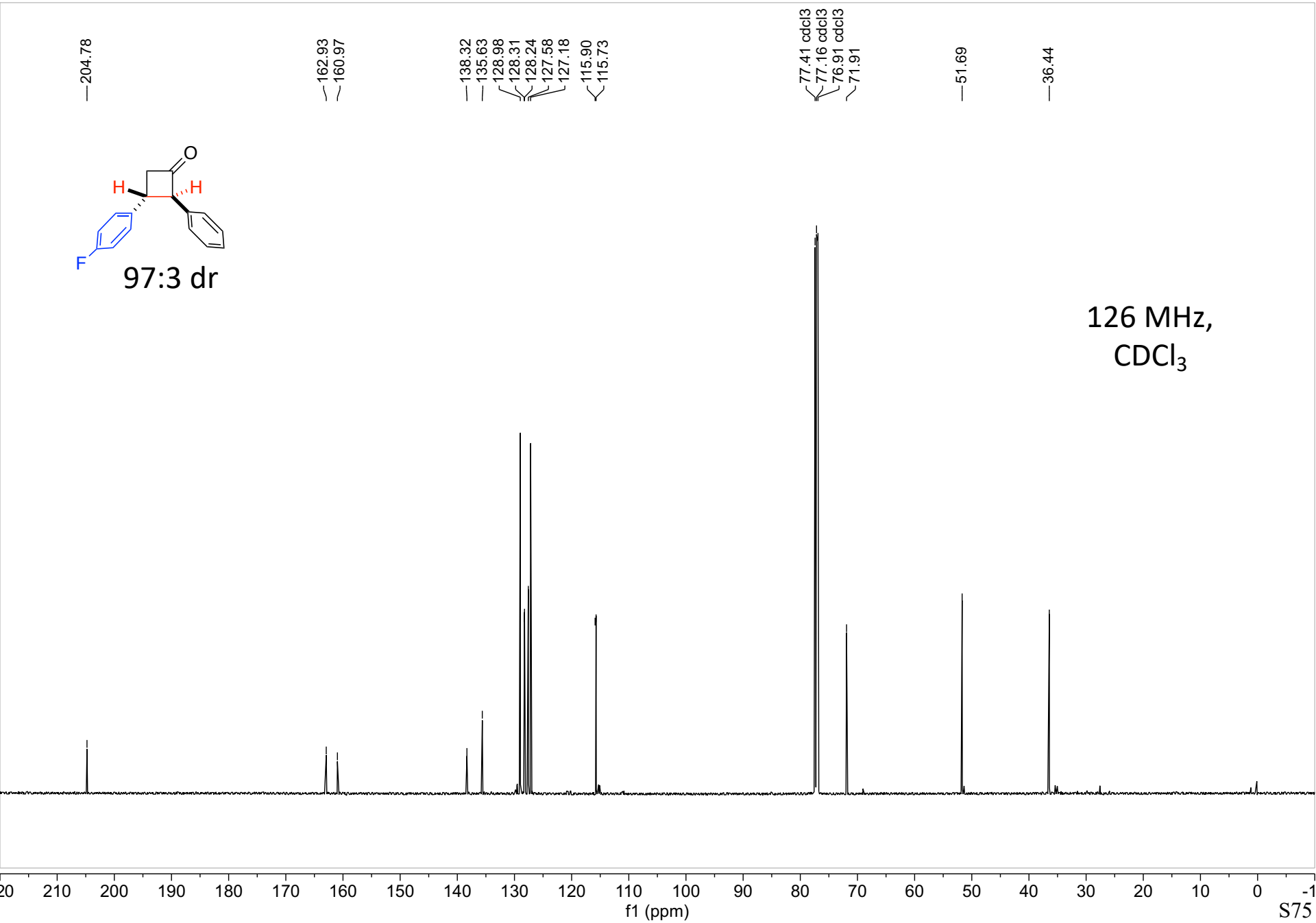
3: 255 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 35.528 | 4.937 |
| 2 | 38.844 | 95.063 |
| Totals | | 100.000 |

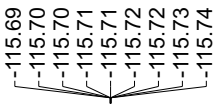
# $^1$H NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-phenylcyclobutan-1-one **(2h)**

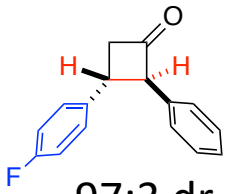


# $^{13}$C NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-phenylcyclobutan-1-one **(2h)**



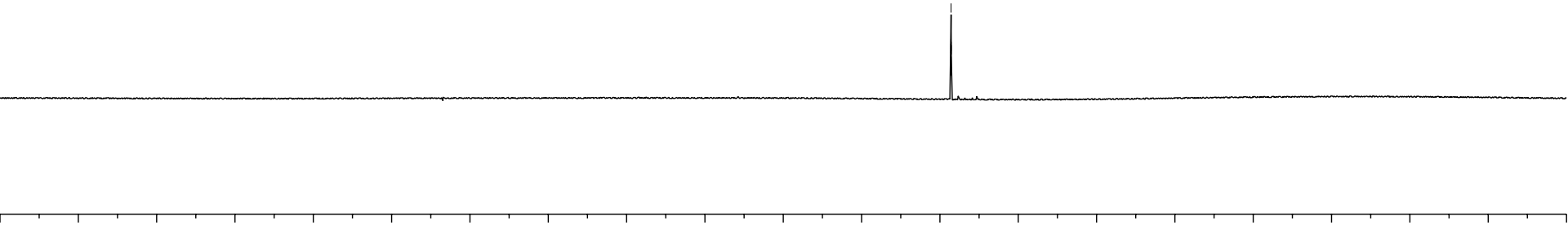
# $^{19}$F NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-phenylcyclobutan-1-one **(2h)**

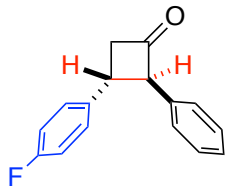


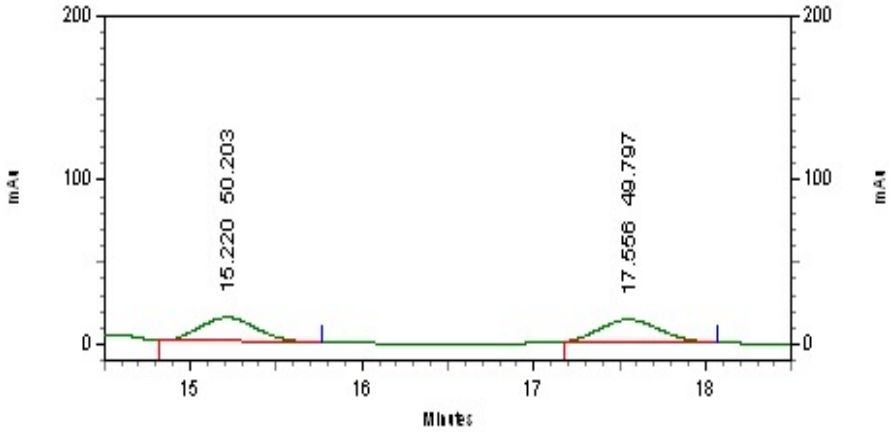

97:3 dr

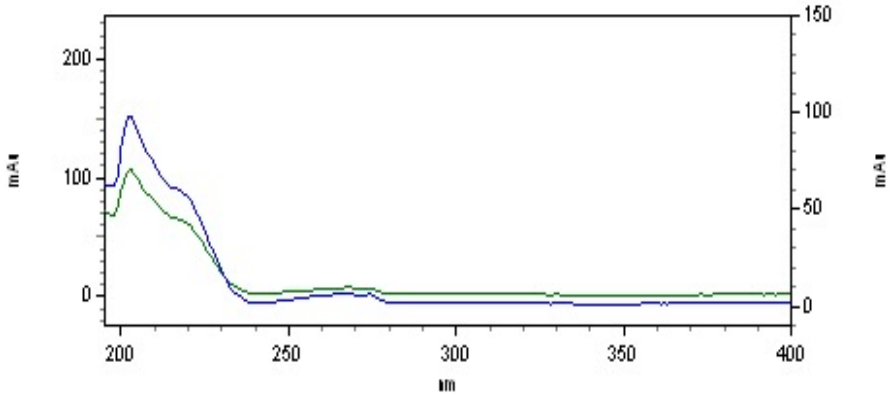
564 MHz,
$CDCl_3$






# **HPLC** (2*R*,3*R*)-3-(4-fluorophenyl)-2-phenylcyclobutan-1-one **(2h)**

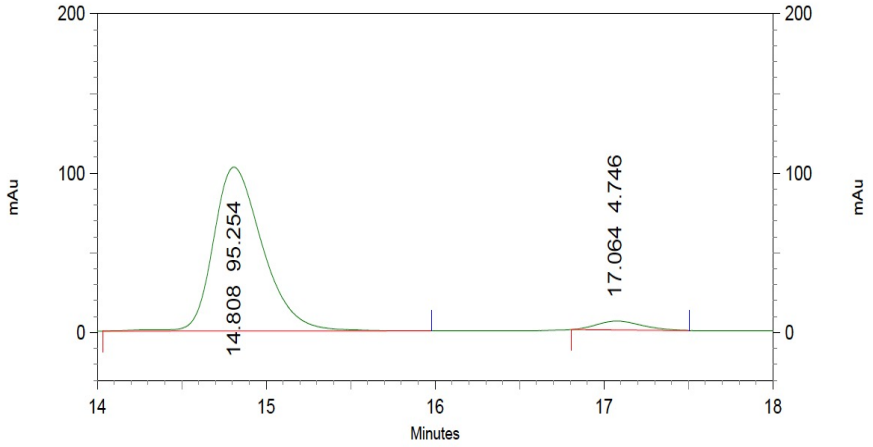


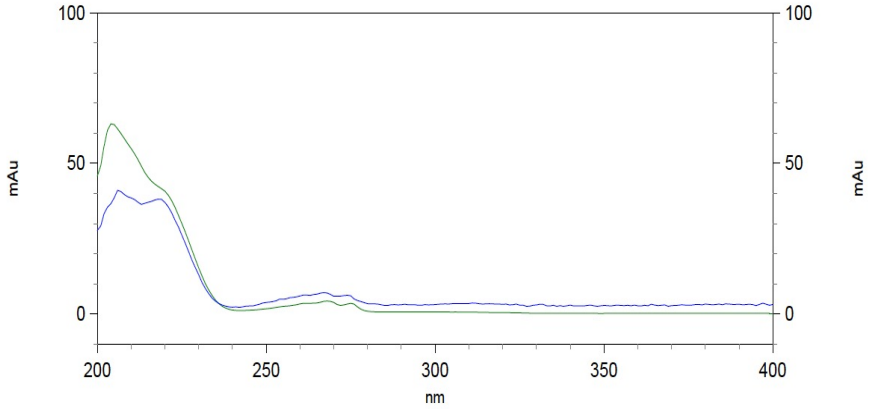




2: 231 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.220 | 50.203 |
| 2 | 17.556 | 49.797 |

| Totals | | 100.000 |
|---|---|---|



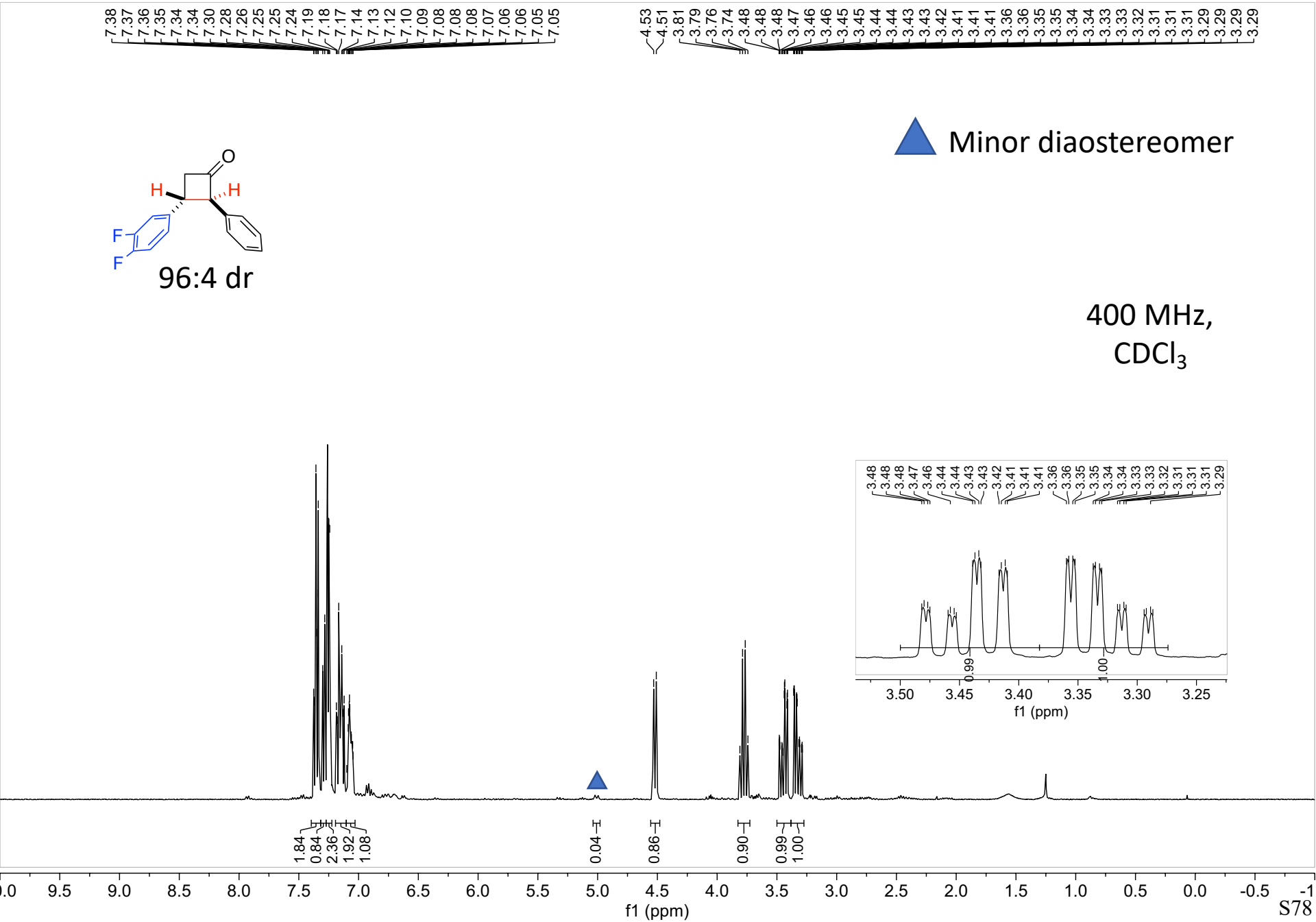




4: 231 nm, 4
nm Results

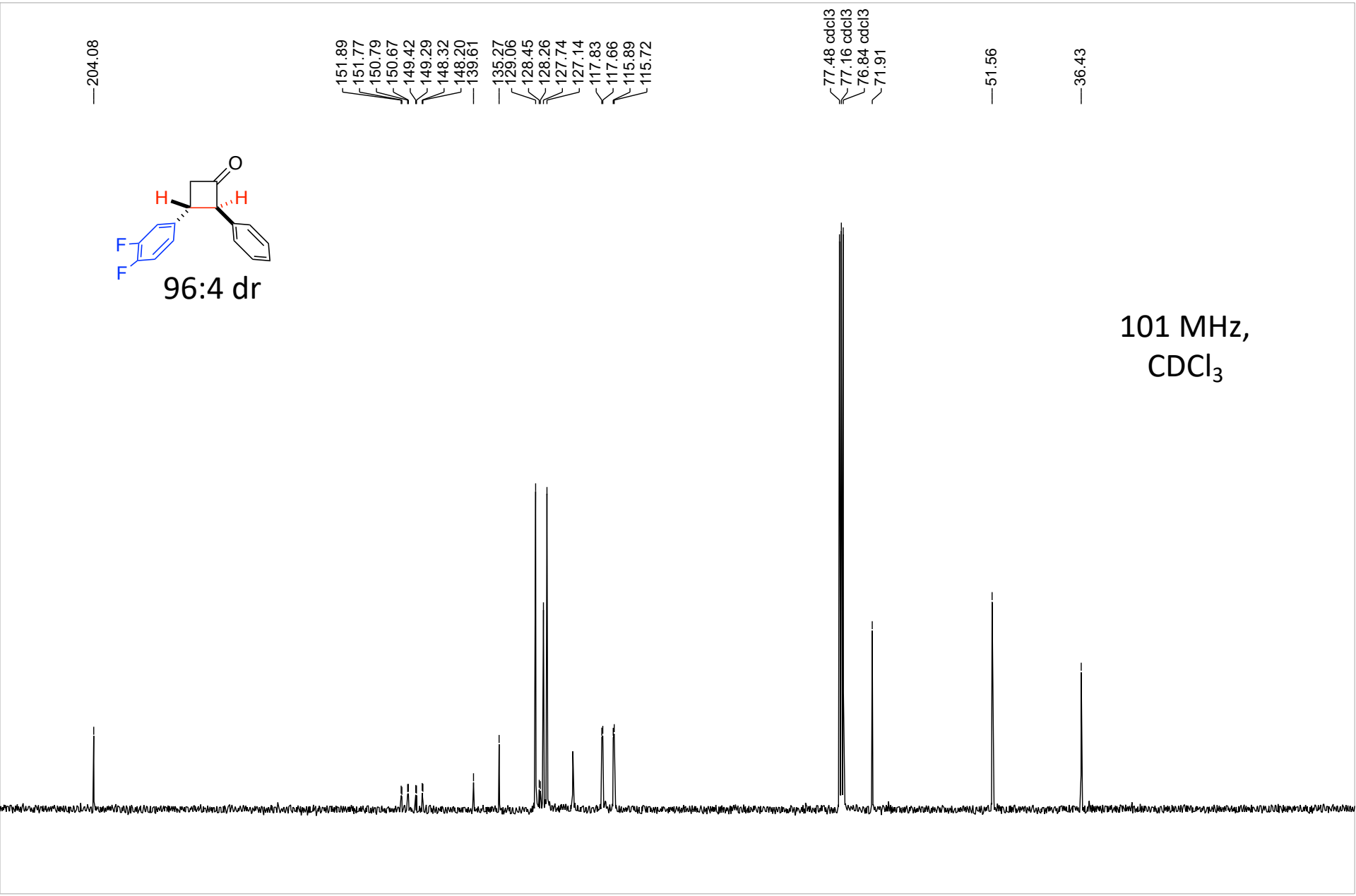
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.808 | 95.254 |
| 2 | 17.064 | 4.746 |

| Totals | | 100.000 |
|---|---|---|

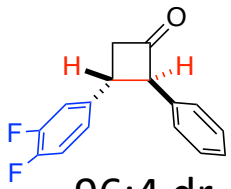
# $^{1}$H NMR (2*R*,3*R*)-3-(3,4-difluorophenyl)-2-phenylcyclobutan-1-one **(2i)**



# $^{13}$C NMR (2*R*,3*R*)-3-(3,4-difluorophenyl)-2-phenylcyclobutan-1-one **(2i)**

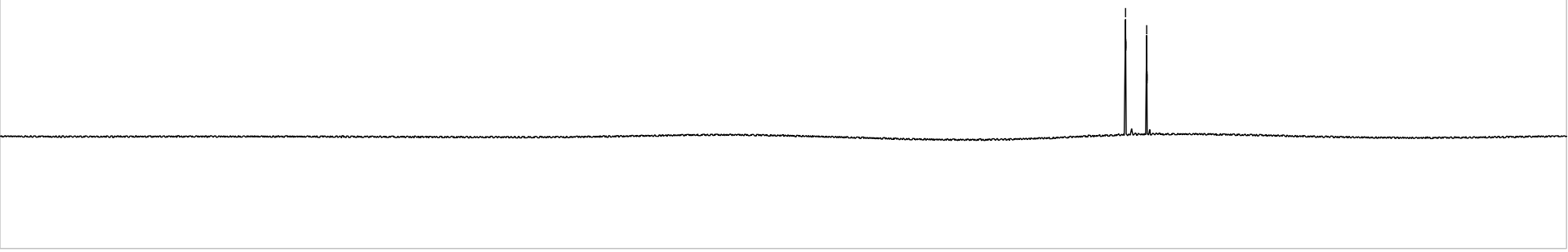


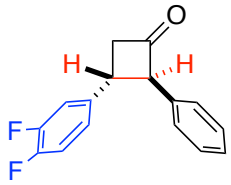
# $^{19}$F NMR (2*R*,3*R*)-3-(3,4-difluorophenyl)-2-phenylcyclobutan-1-one **(2i)**



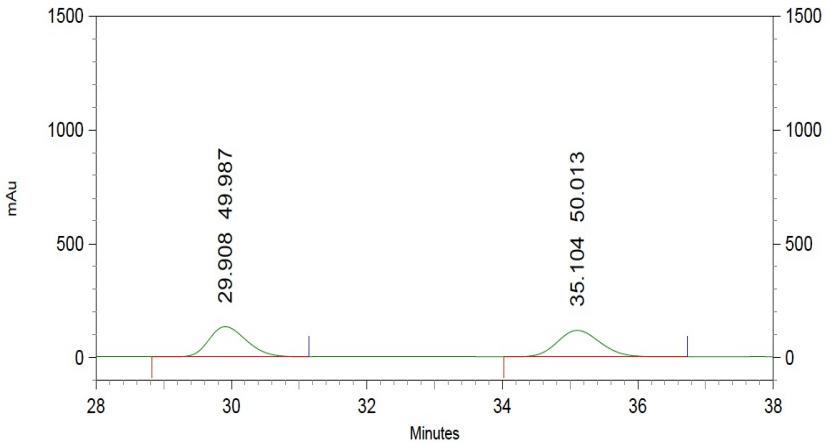

96:4 dr

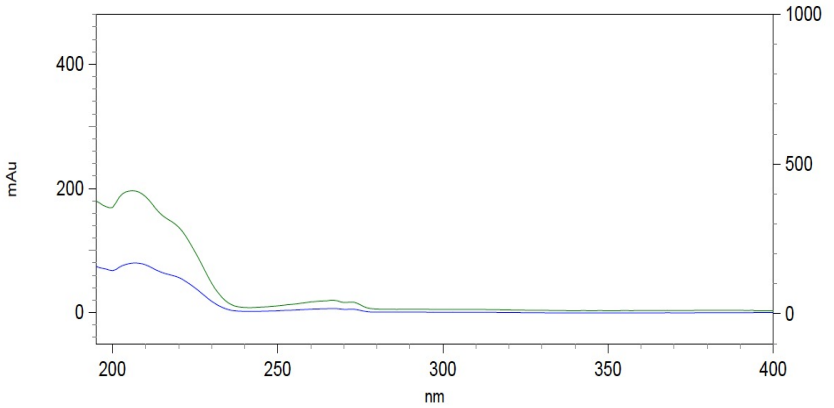
376 MHz,
$CDCl_3$





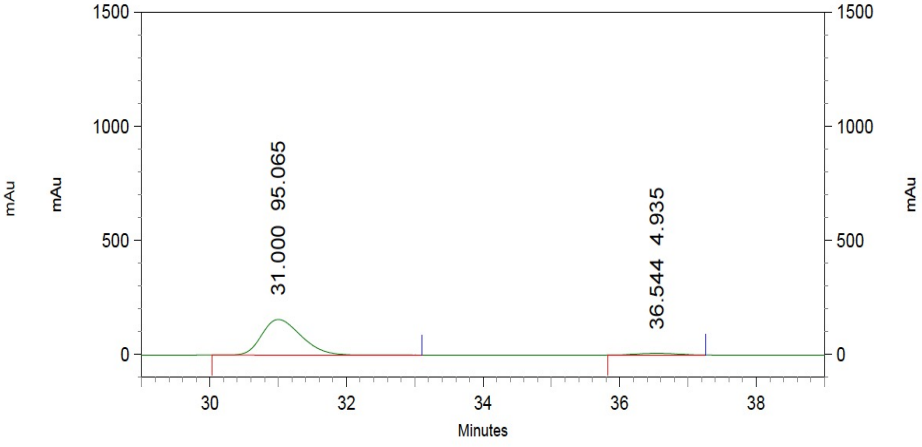

# **HPLC** (2*R*,3*R*)-3-(3,4-difluorophenyl)-2-phenylcyclobutan-1-one **(2i)**

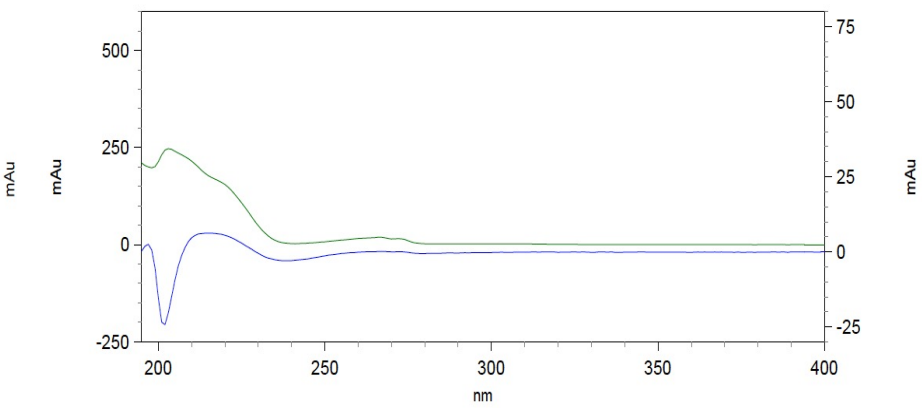



4: 220 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 29.908 | 49.987 |
| 2 | 35.104 | 50.013 |
| Totals | | 100.000 |

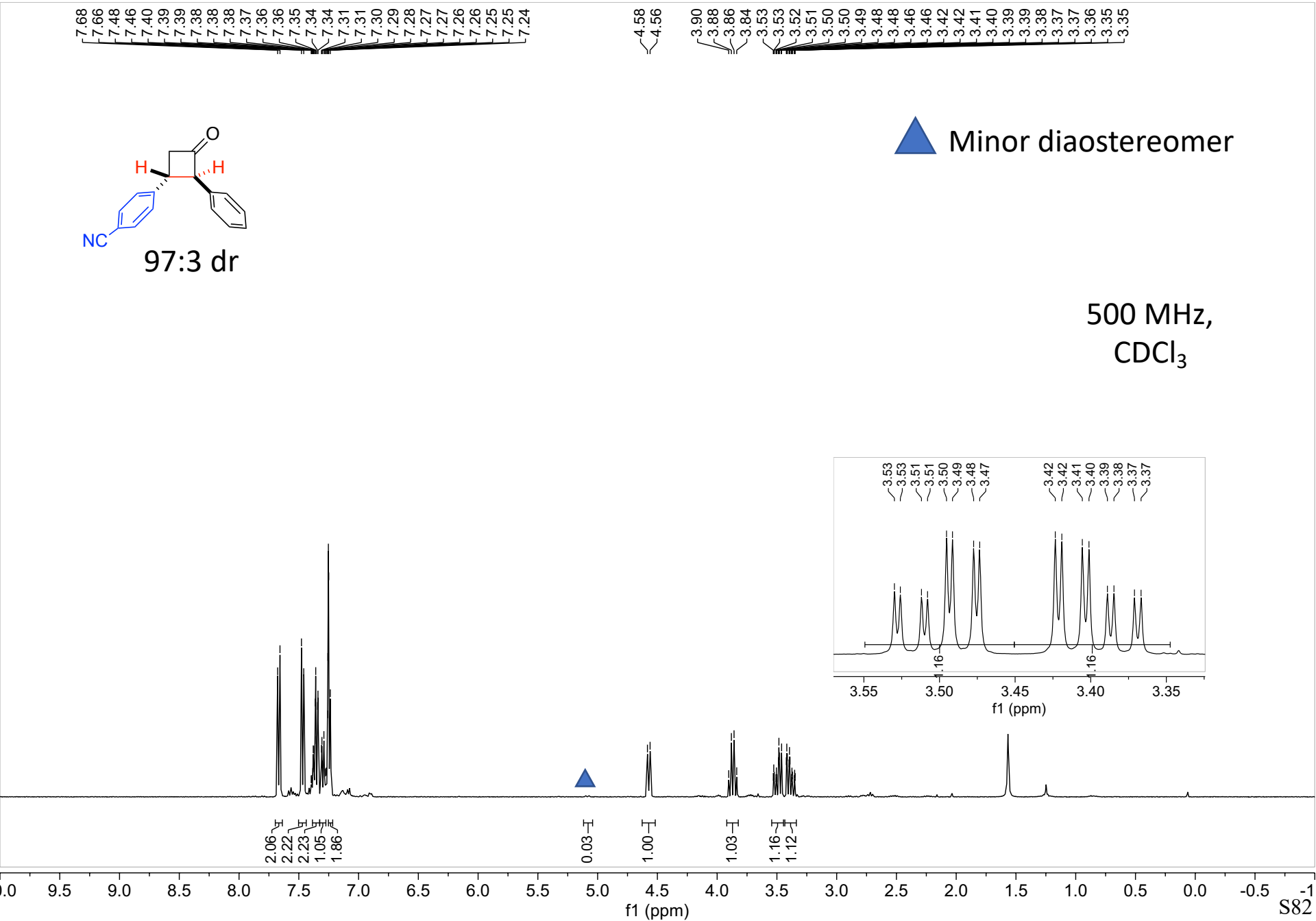


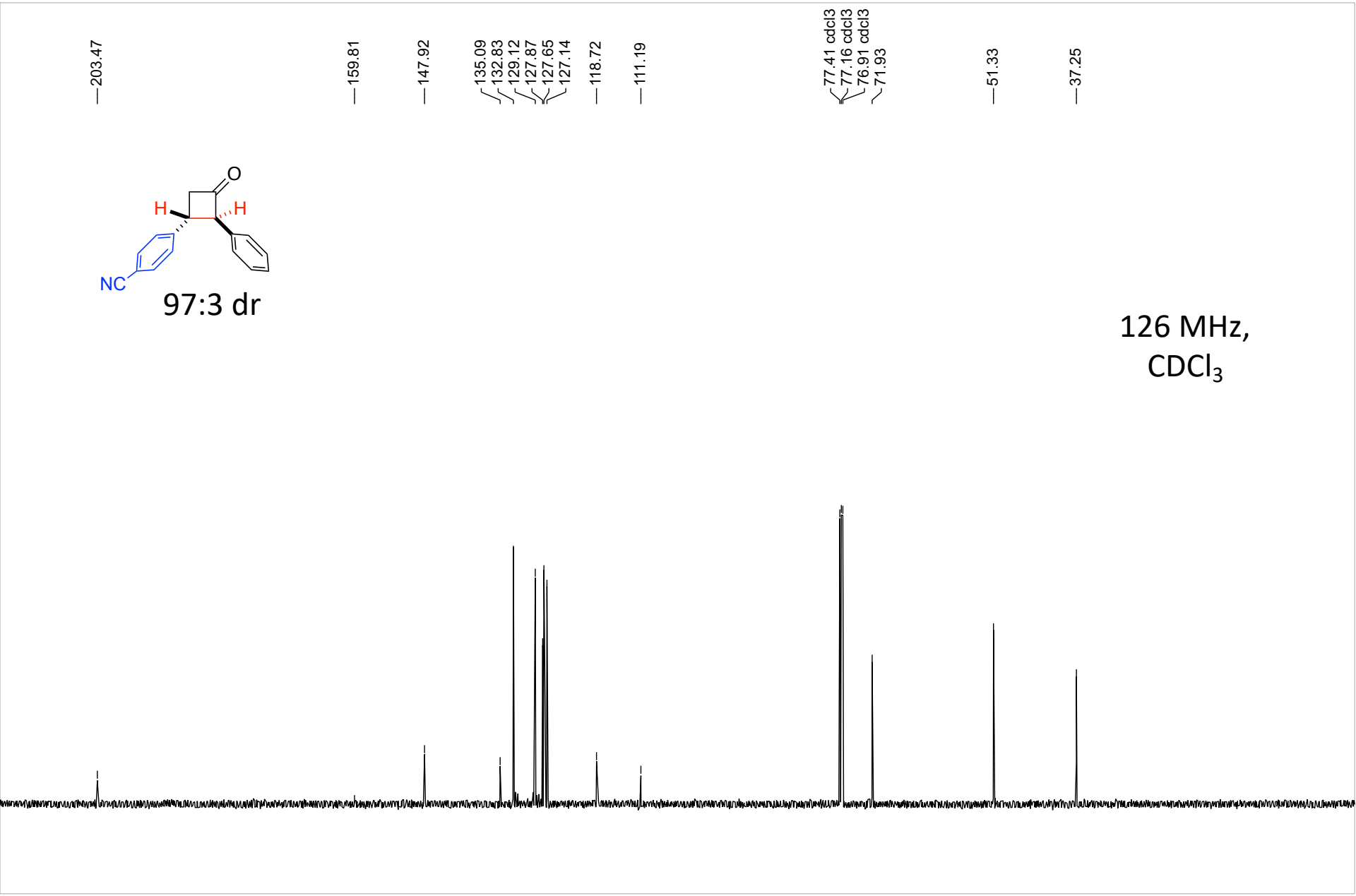

4: 220 nm, 4
nm Results

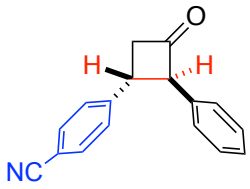
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 31.000 | 95.065 |
| 2 | 36.544 | 4.935 |
| Totals | | 100.000 |

# $^{1}$H NMR 4-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)benzonitrile **(2j)**

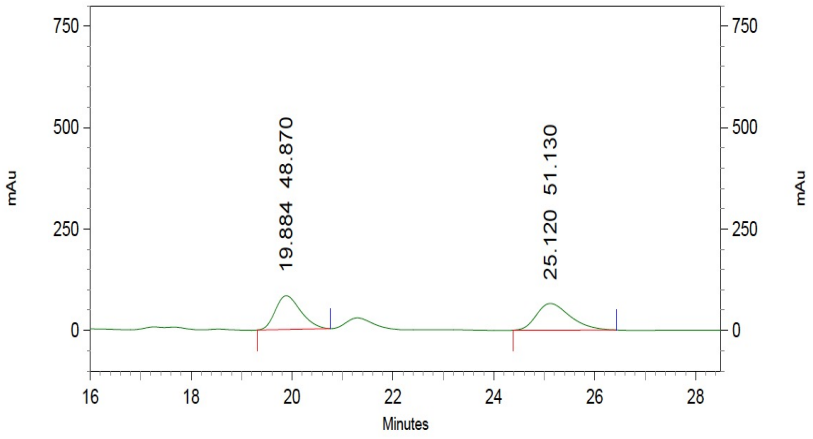


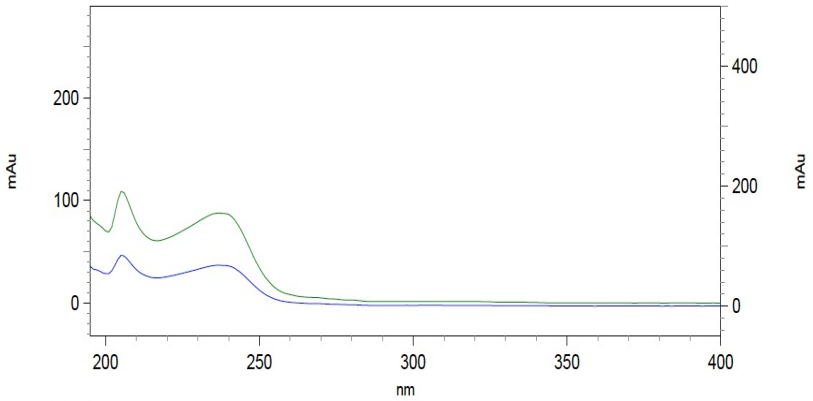
# $^{13}$C NMR 4-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)benzonitrile **(2j)**






# **HPLC** 4-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)benzonitrile **(2j)**

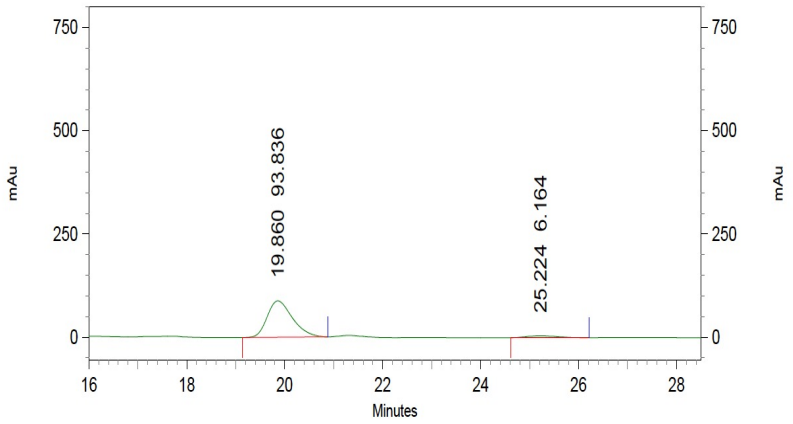


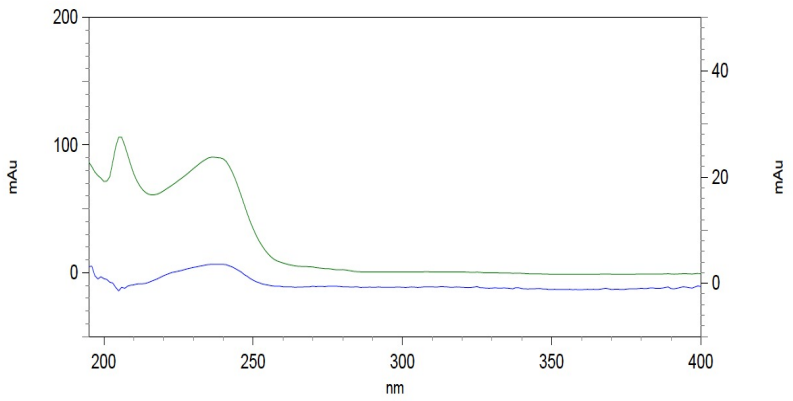




4: 240 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.884 | 48.870 |
| 2 | 25.120 | 51.130 |

| Totals | | 100.000 |
|---|---|---|



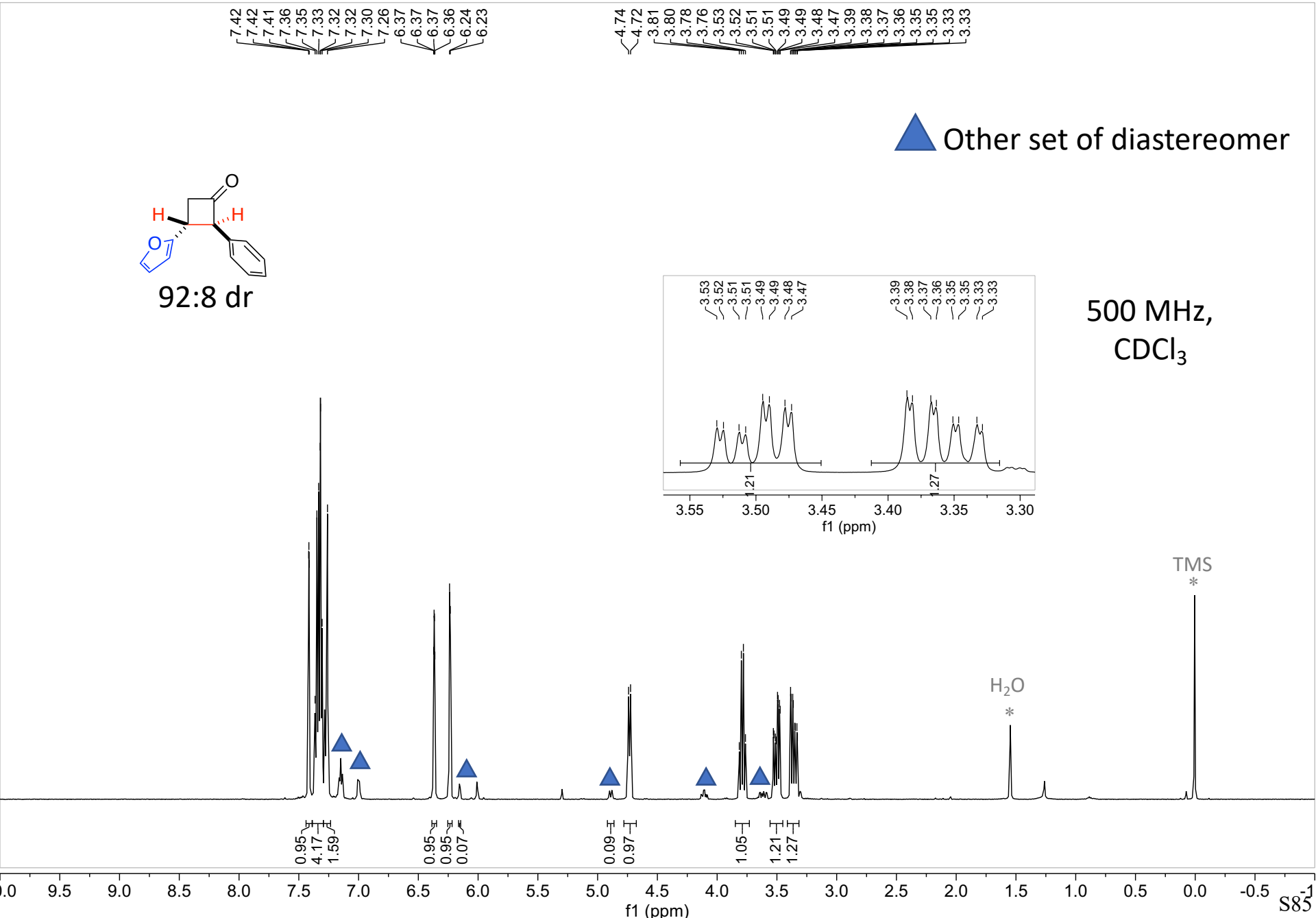




4: 240 nm, 4
nm Results

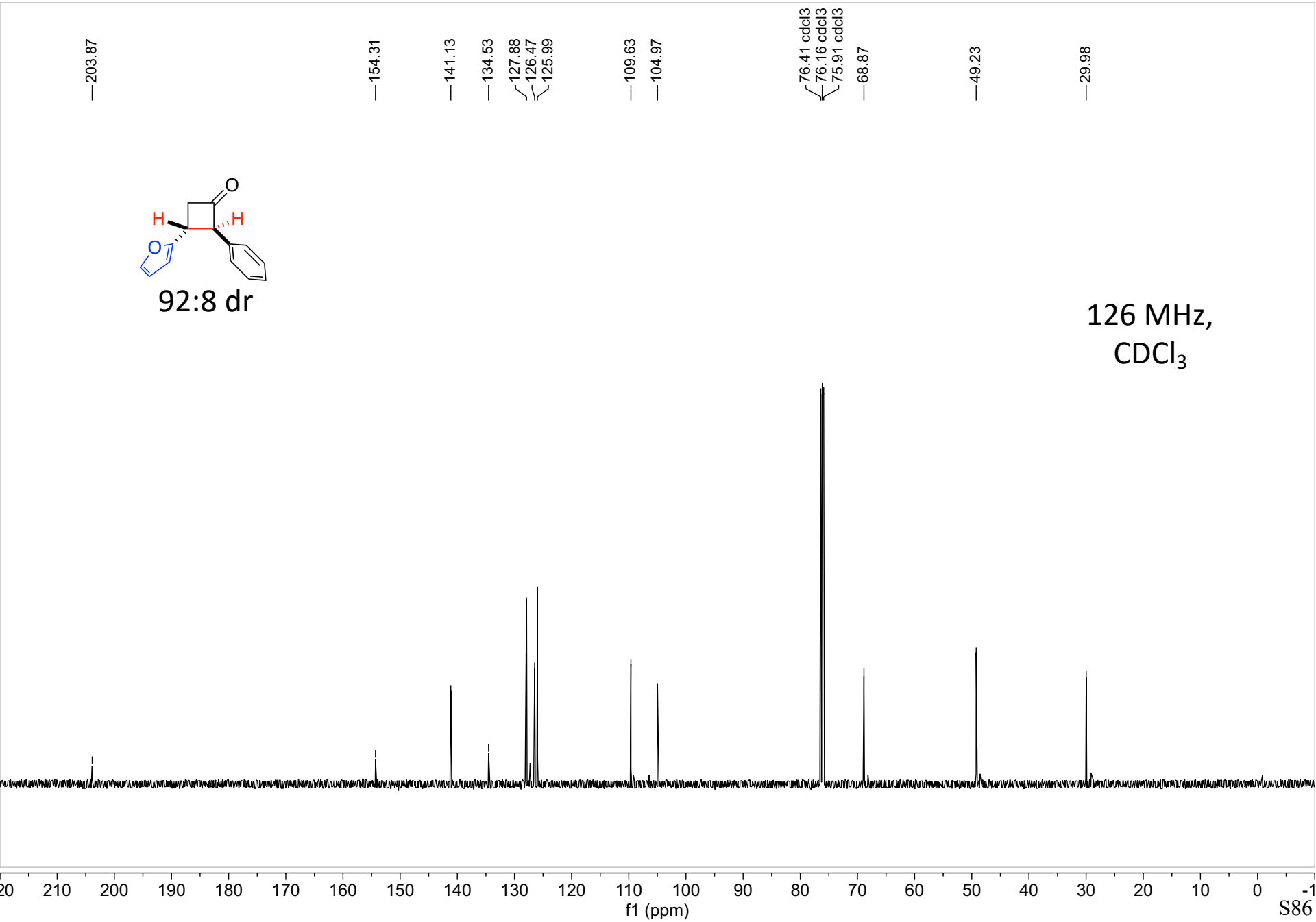
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.860 | 93.836 |
| 2 | 25.224 | 6.164 |

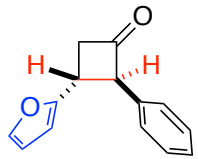
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-3-(furan-2-yl)-2-phenylcyclobutan-1-one **(2k)**

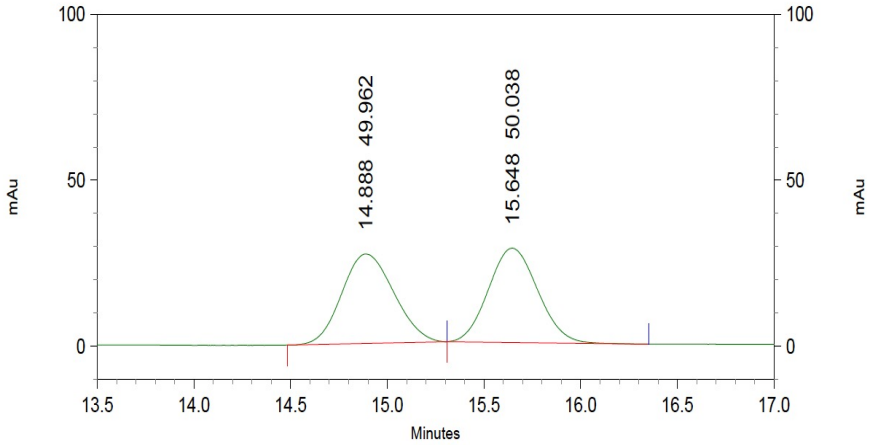


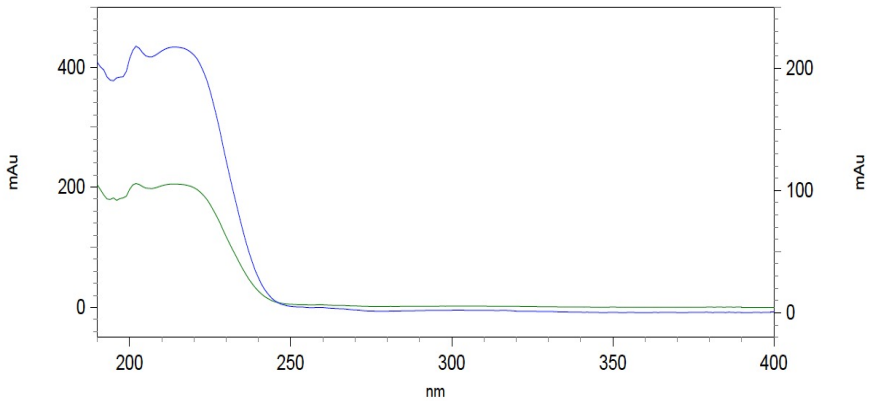
# $^{13}$C NMR (2*R*,3*R*)-3-(furan-2-yl)-2-phenylcyclobutan-1-one **(2k)**





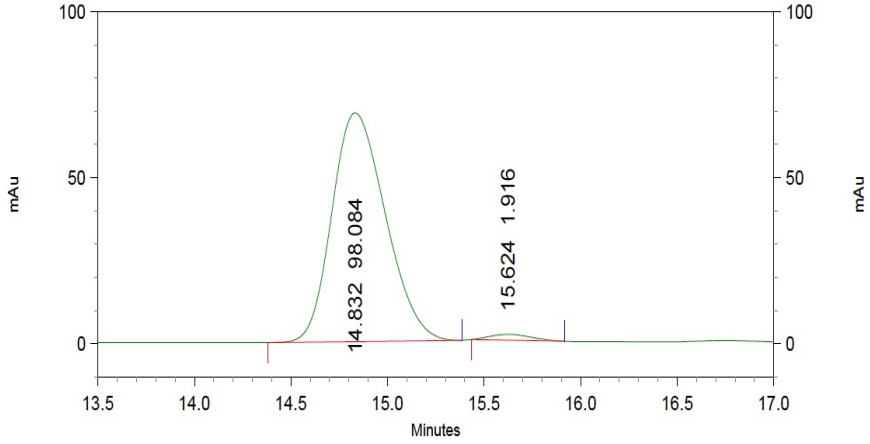

# **HPLC** (2*R*,3*R*)-3-(furan-2-yl)-2-phenylcyclobutan-1-one **(2k)**

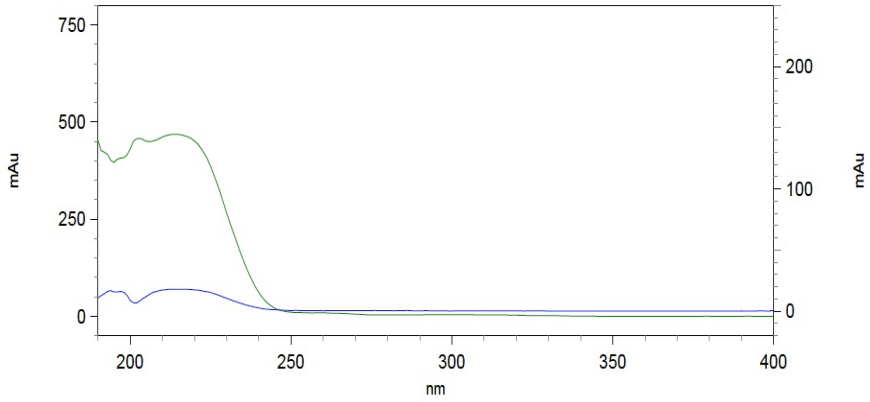



4: 240 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.888 | 49.962 |
| 2 | 15.648 | 50.038 |
| Totals | | 100.000 |

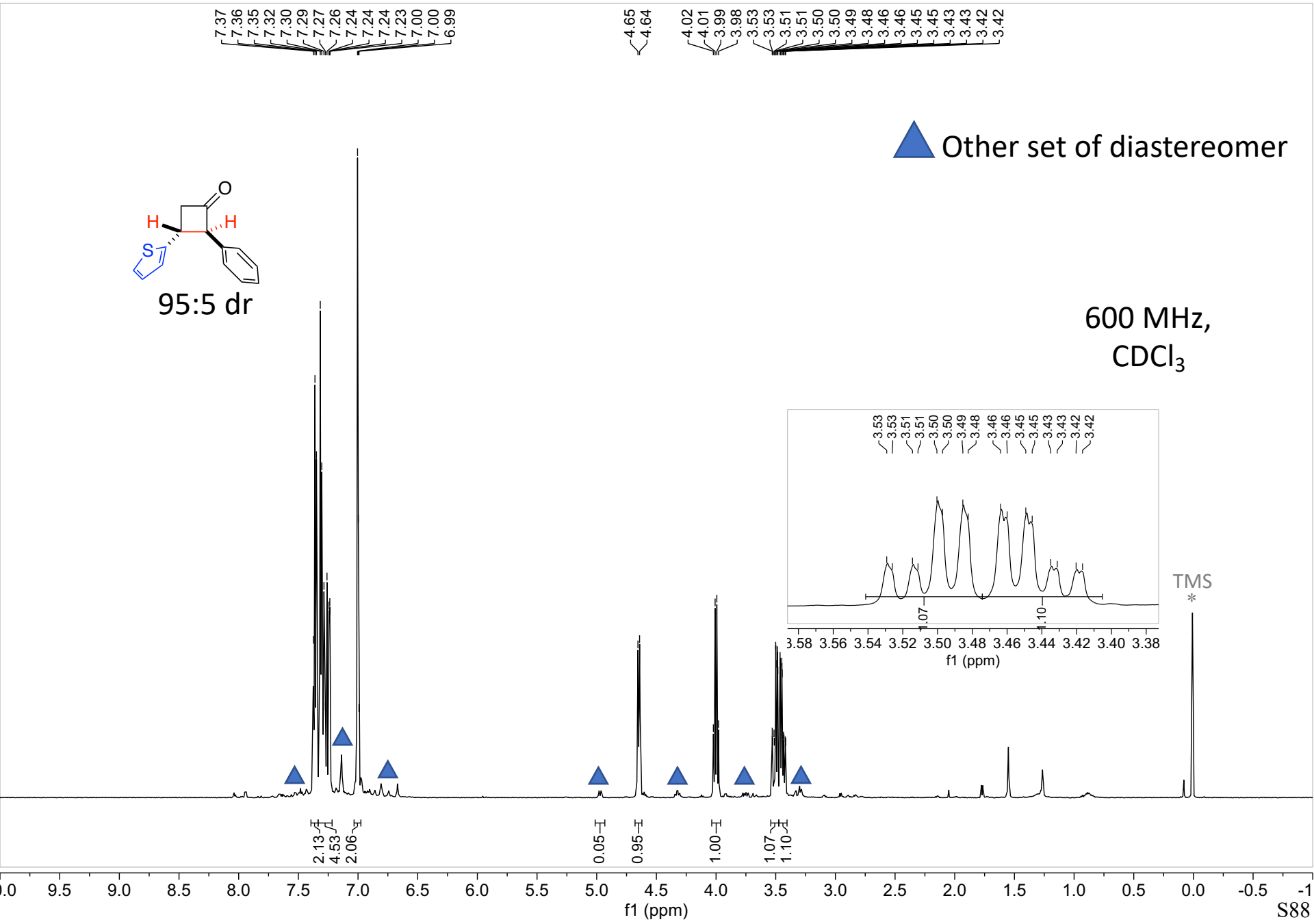


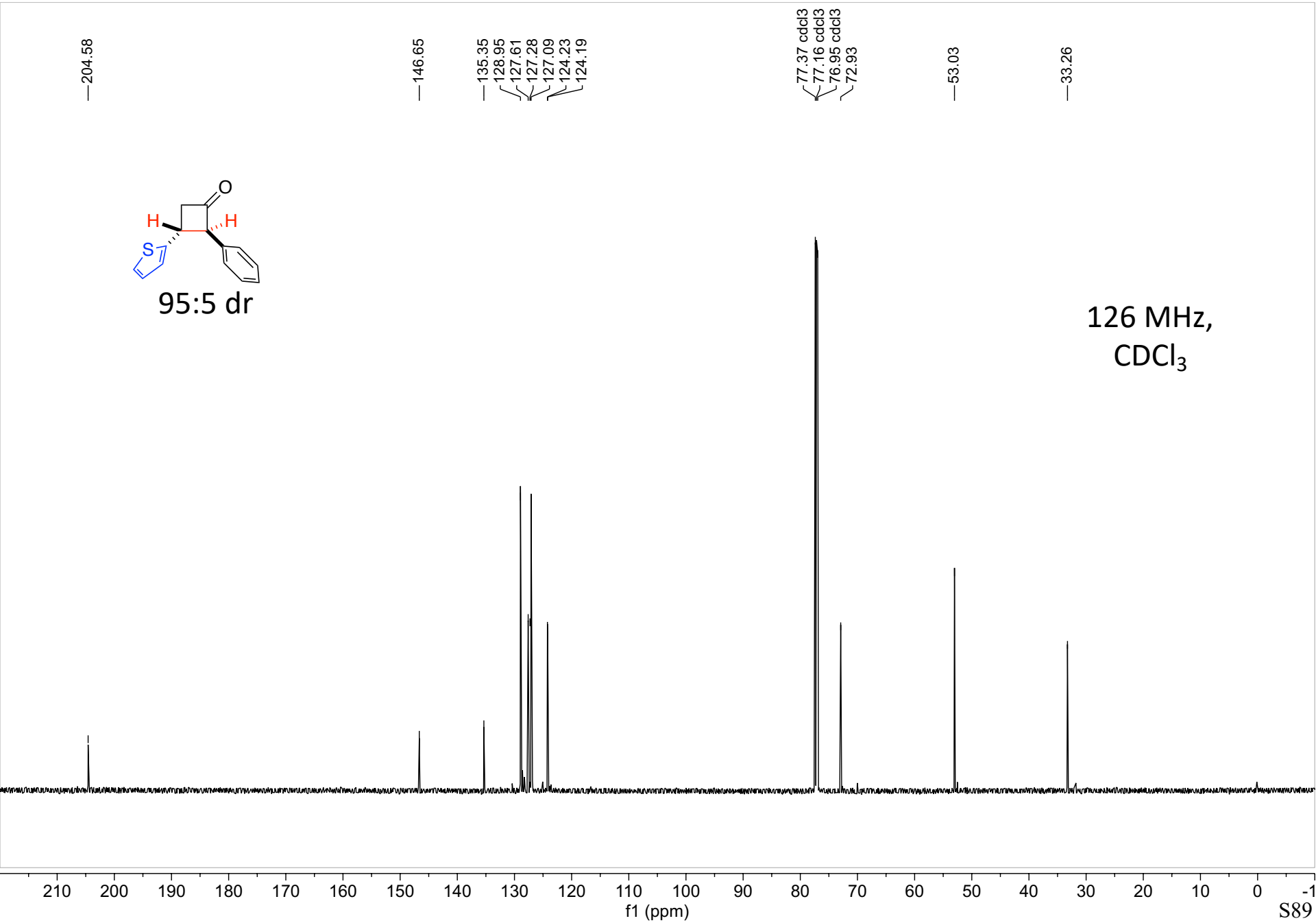

4: 240 nm, 4 nm Results

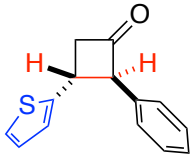
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.832 | 98.084 |
| 2 | 15.624 | 1.916 |
| Totals | | 100.000 |

# $^1$H NMR (2*R*,3*R*)-2-phenyl-3-(thiophen-2-yl)cyclobutan-1-one **(2l)**

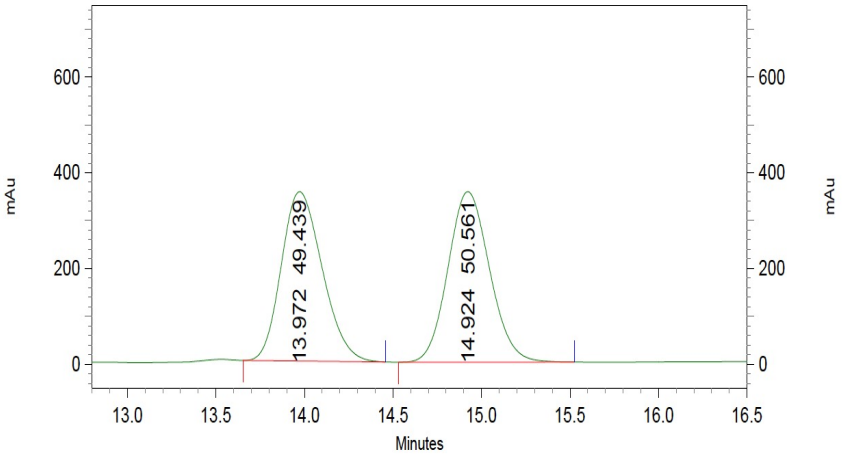


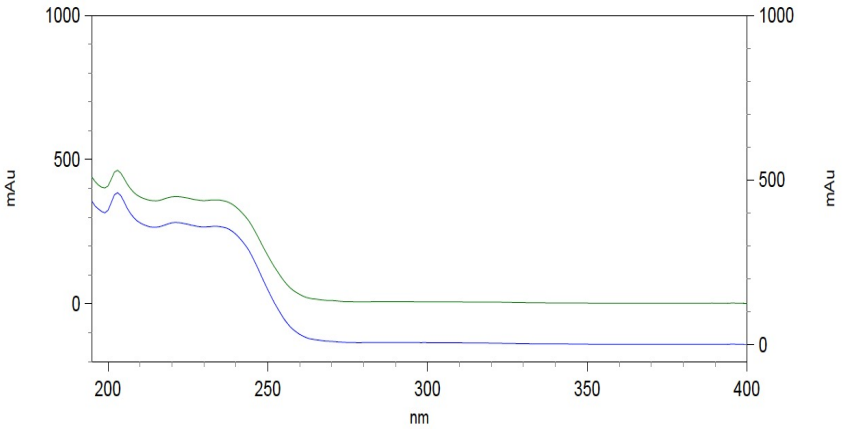
# $^{13}$C NMR (2*R*,3*R*)-2-phenyl-3-(thiophen-2-yl)cyclobutan-1-one **(2l)**






# **HPLC** (2*R*,3*R*)-2-phenyl-3-(thiophen-2-yl)cyclobutan-1-one **(2l)**

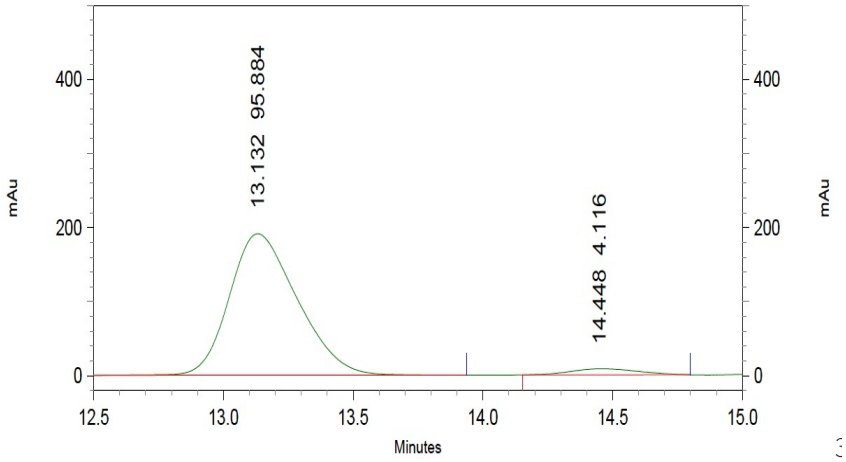


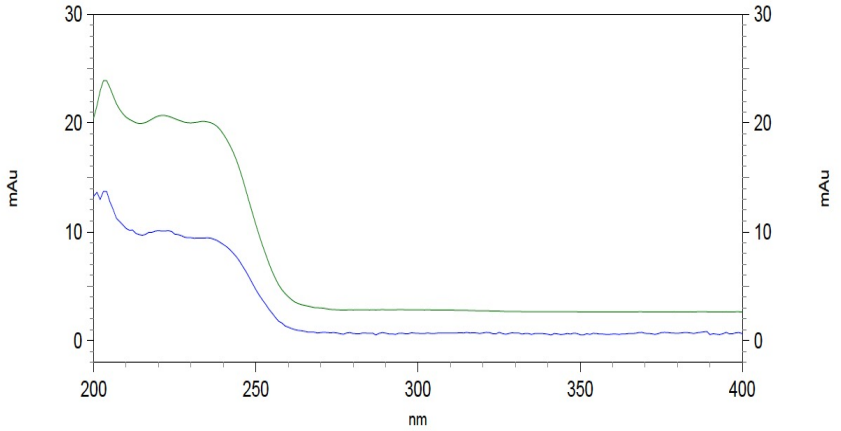




2: 228 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.972 | 49.439 |
| 2 | 14.924 | 50.561 |

| Totals | | 100.000 |
|---|---|---|



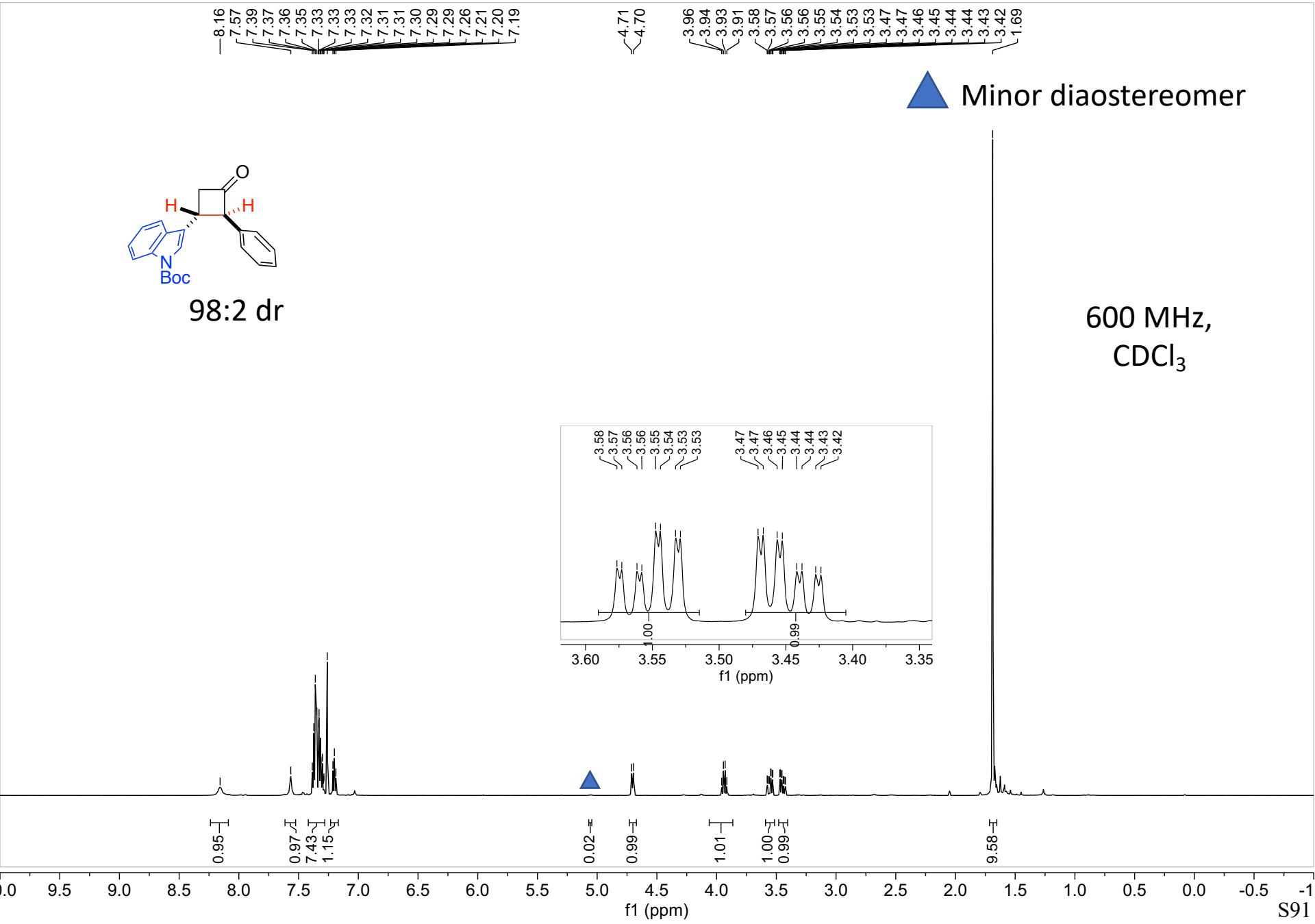




4: 228 nm, 4
nm Results

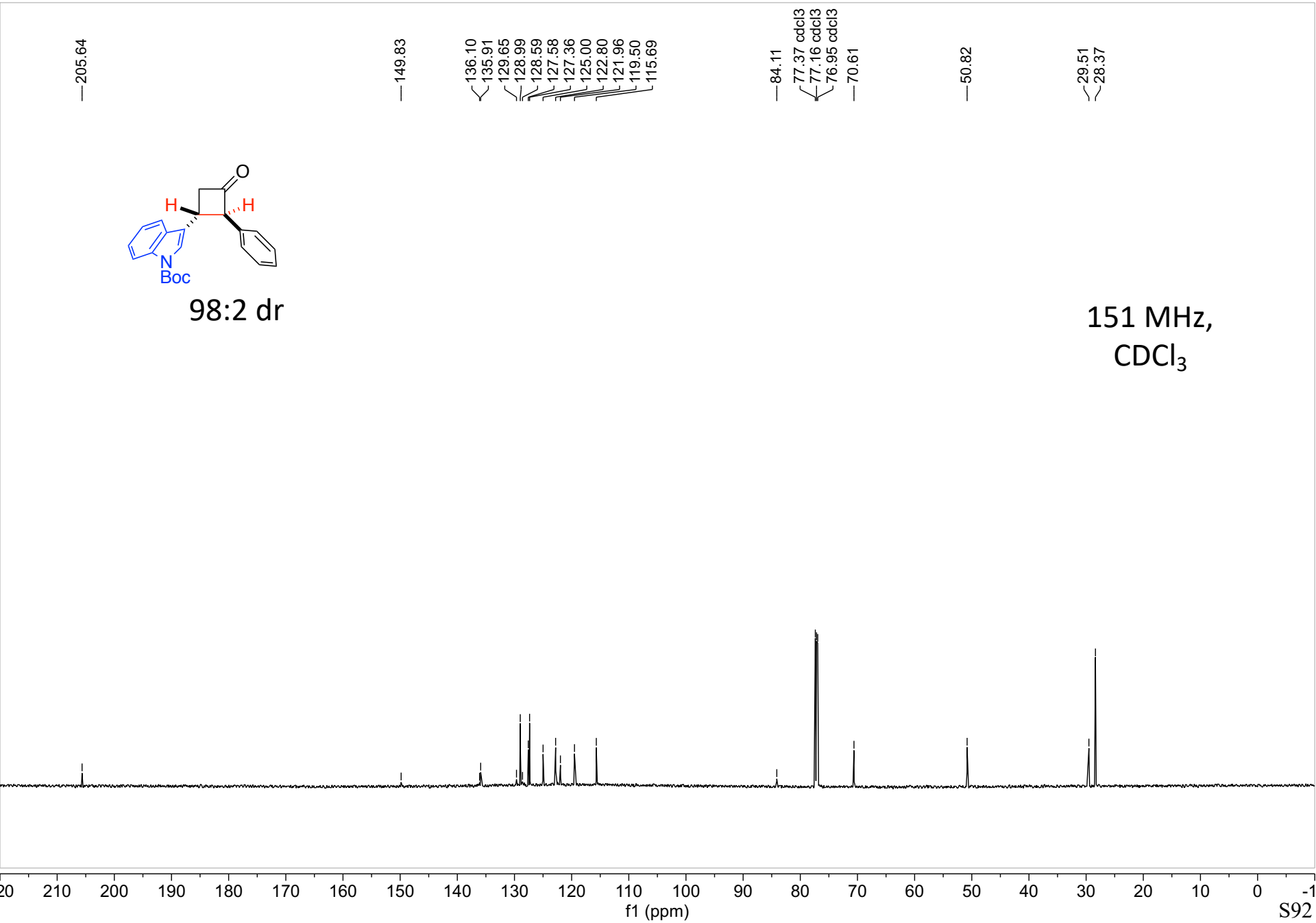
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.132 | 95.884 |
| 2 | 14.448 | 4.116 |

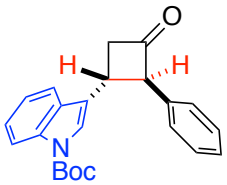
| Totals | | 100.000 |
|---|---|---|

**$^1$H NMR** *tert*-butyl 3-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)-1*H*-indole-1-carboxylate **(2m)**



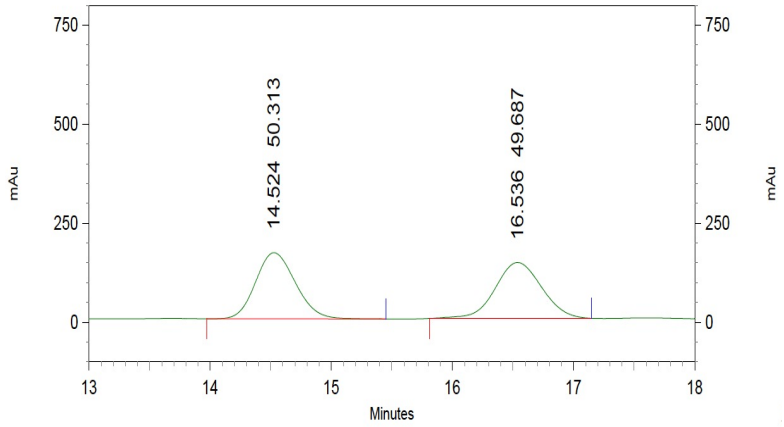
**$^{13}$C NMR** *tert*-butyl 3-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)-1*H*-indole-1-carboxylate **(2m)**

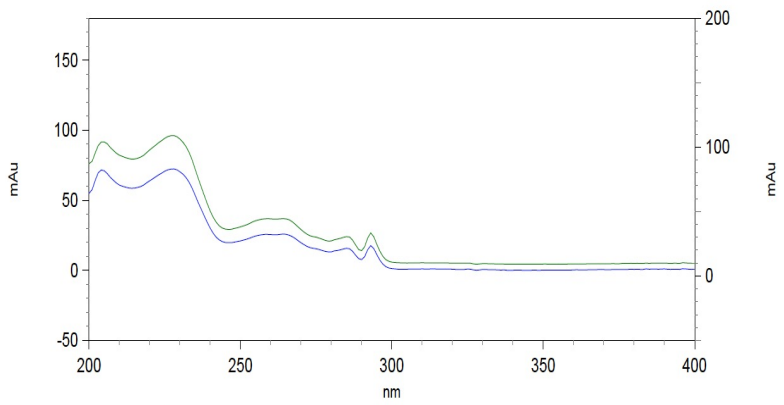





# HPLC

*tert*-butyl 3-((1*R*,2*R*)-3-oxo-2-phenylcyclobutyl)-1*H*-indole-1-carboxylate **(2m)**

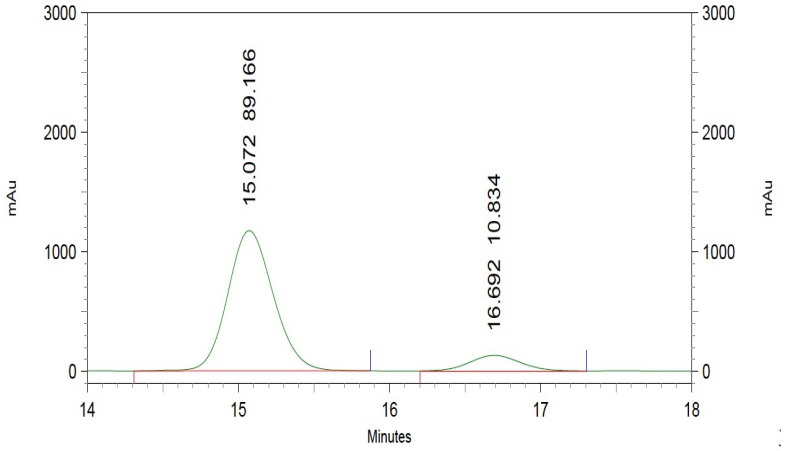


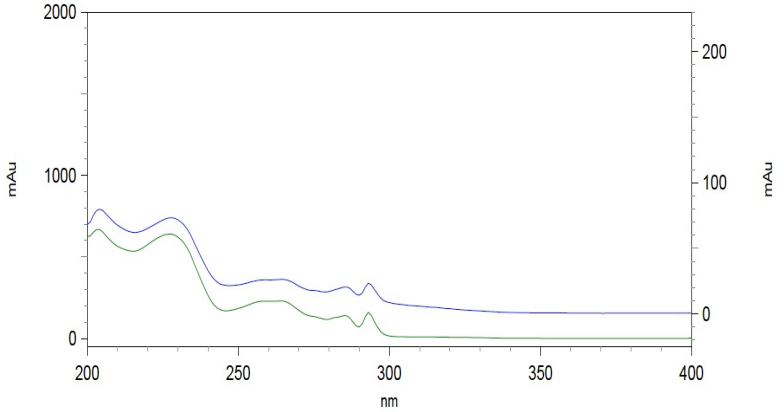




3: 221 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.524 | 50.313 |
| 2 | 16.536 | 49.687 |

| Totals | | 100.000 |
|---|---|---|



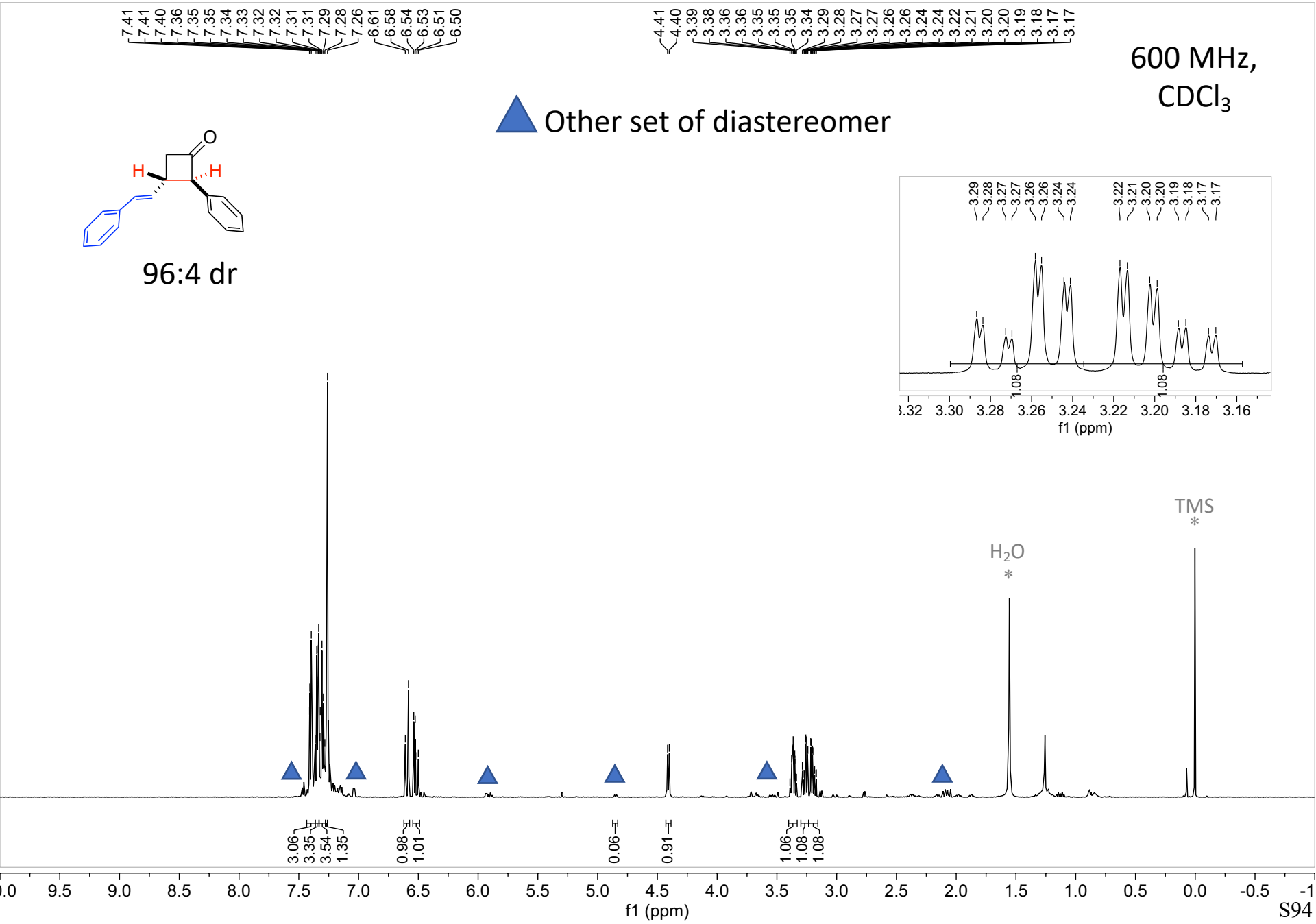




3: 221 nm, 4
nm Results

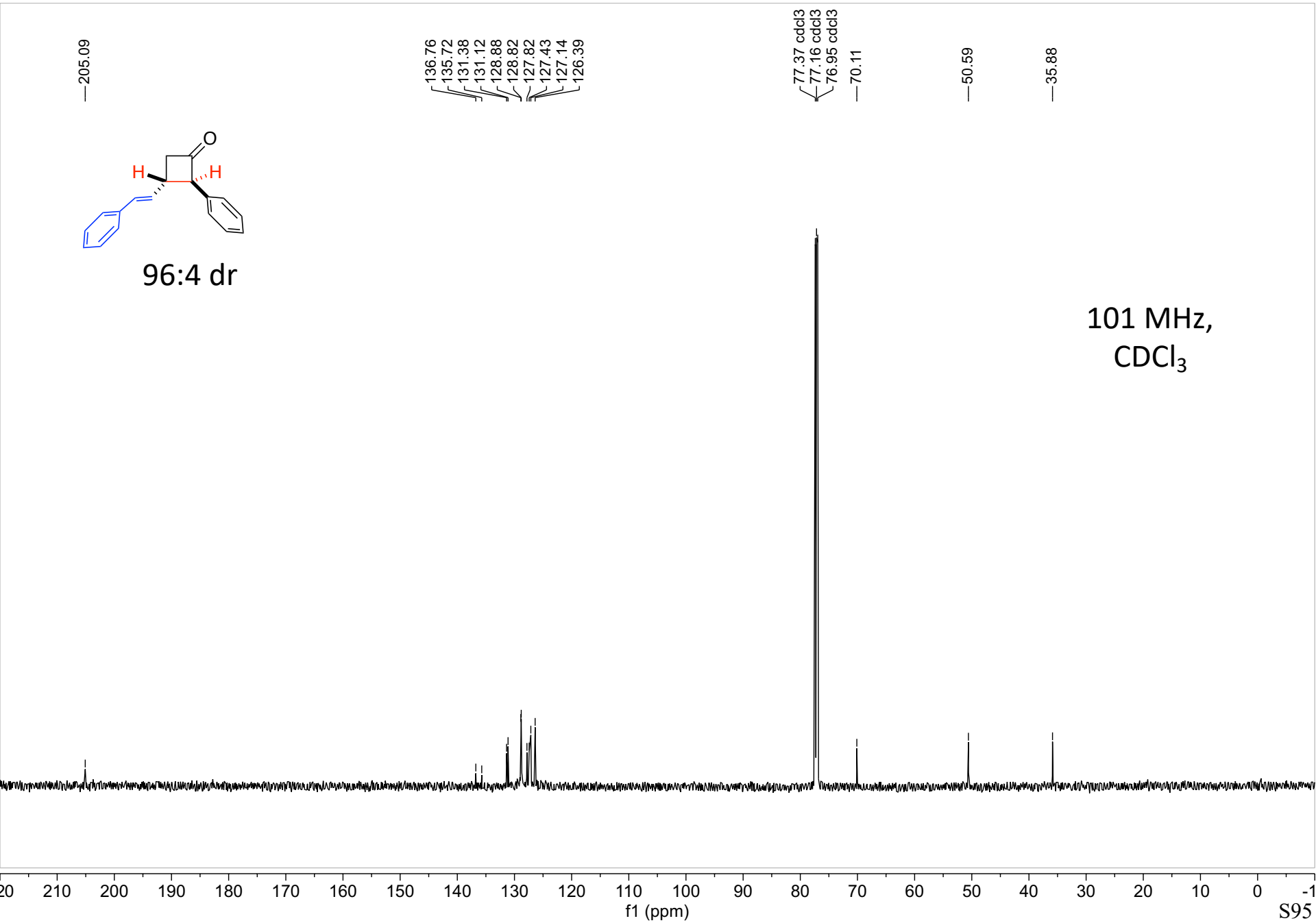
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.072 | 89.166 |
| 2 | 16.692 | 10.834 |

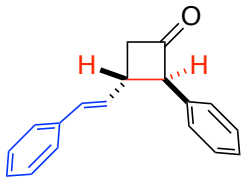
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*S*)-2-phenyl-3-((*E*)-styryl)cyclobutan-1-one **(2n)**



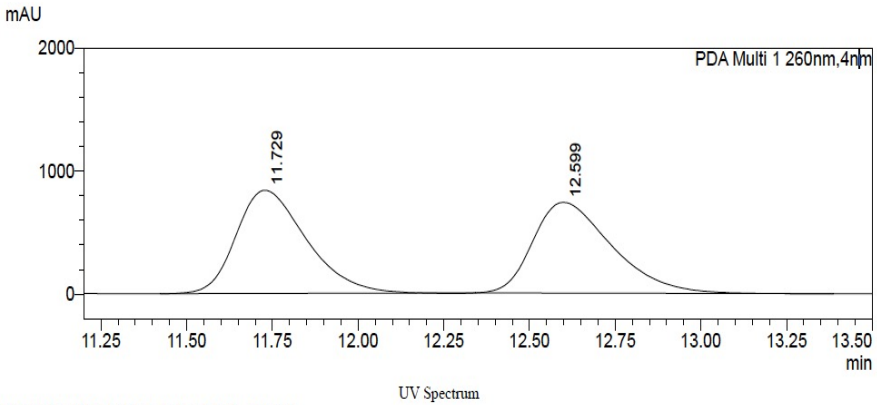
# $^{13}$C NMR (2*R*,3*S*)-2-phenyl-3-((*E*)-styryl)cyclobutan-1-one **(2n)**



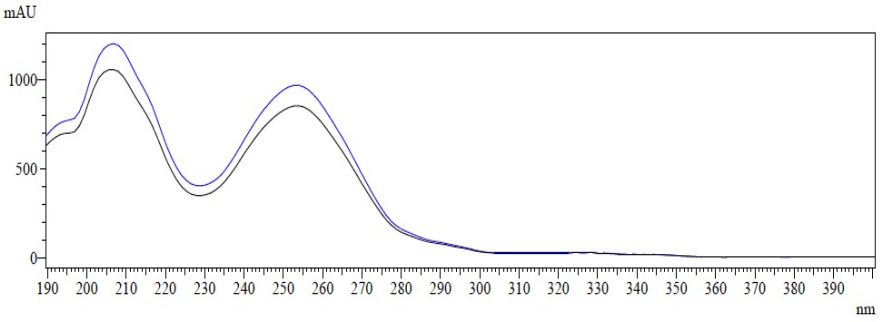



# **HPLC** (2*R*,3*S*)-2-phenyl-3-((*E*)-styryl)cyclobutan-1-one **(2n)**

JJX-REVISION-2N-RAC-IE-2%-0.8mL
JJX-2%-60min0.8mL.lcm



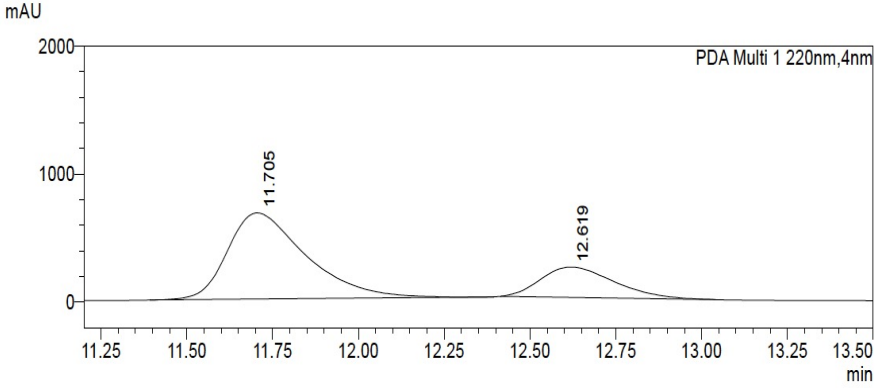

UV Spectrum
JJX-REVISION-2N-RAC-IE-2%-0.8mL_001.lcd



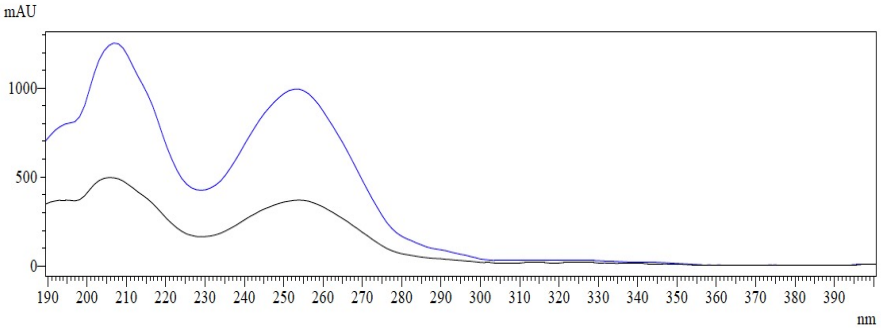

Peak Table
PDA Ch1 260nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 11.729 | 50.256 |
| 2 | 12.599 | 49.744 |
| Total | | 100.000 |

JJX-REVISION-2N-CHIRAL-IE-2%-0.8mL
JJX-2%-60min0.8mL.lcm



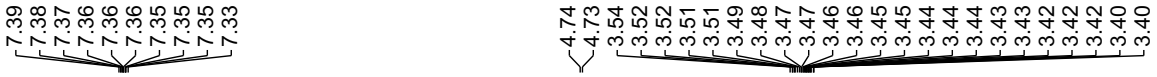

UV Spectrum
JJX-REVISION-2N-CHIRAL-IE-2%-0.8mL_001.lcd




Peak Table
PDA Ch1 220nm

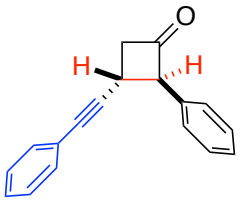
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 11.705 | 75.313 |
| 2 | 12.619 | 24.687 |
| Total | | 100.000 |

# $^{1}$H NMR (2*R*,3*R*)-2-phenyl-3-(phenylethynyl)cyclobutan-1-one **(2o)**

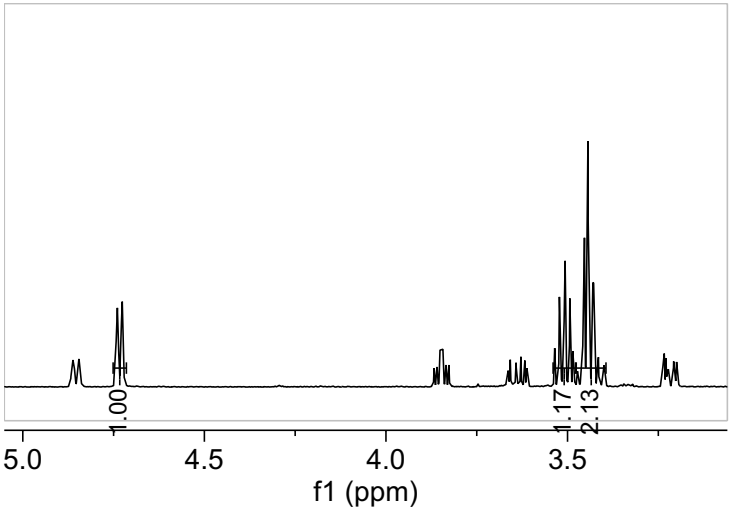


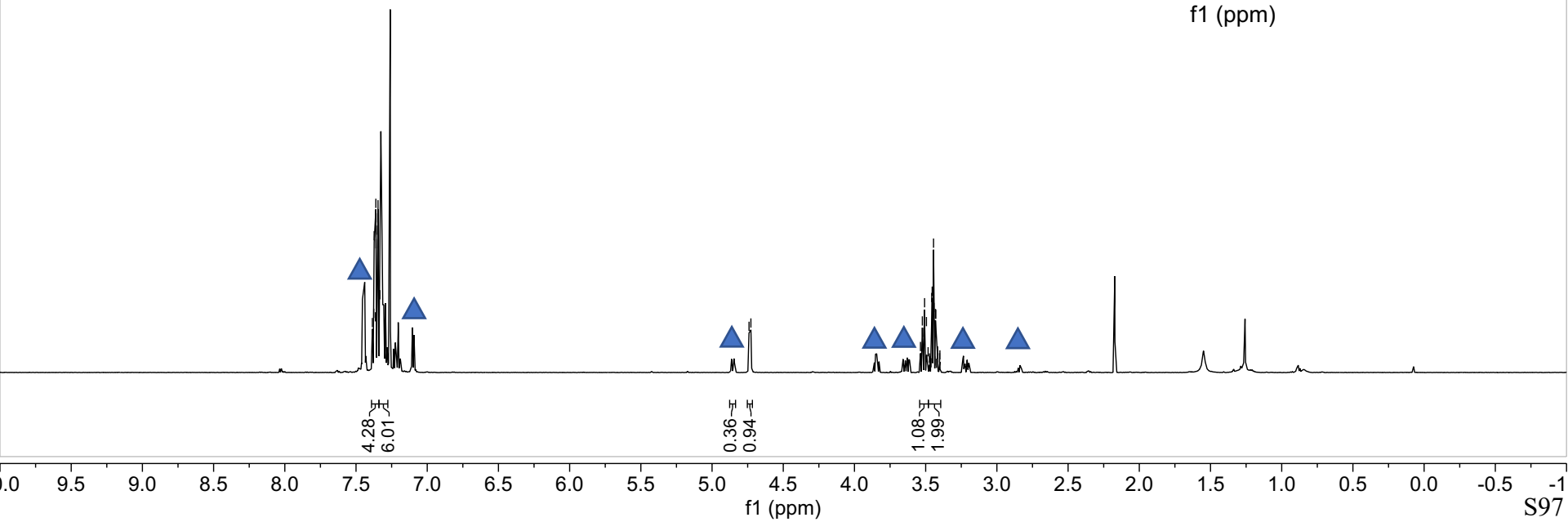

600 MHz, $CDCl_3$

▲ Other set of diastereomer

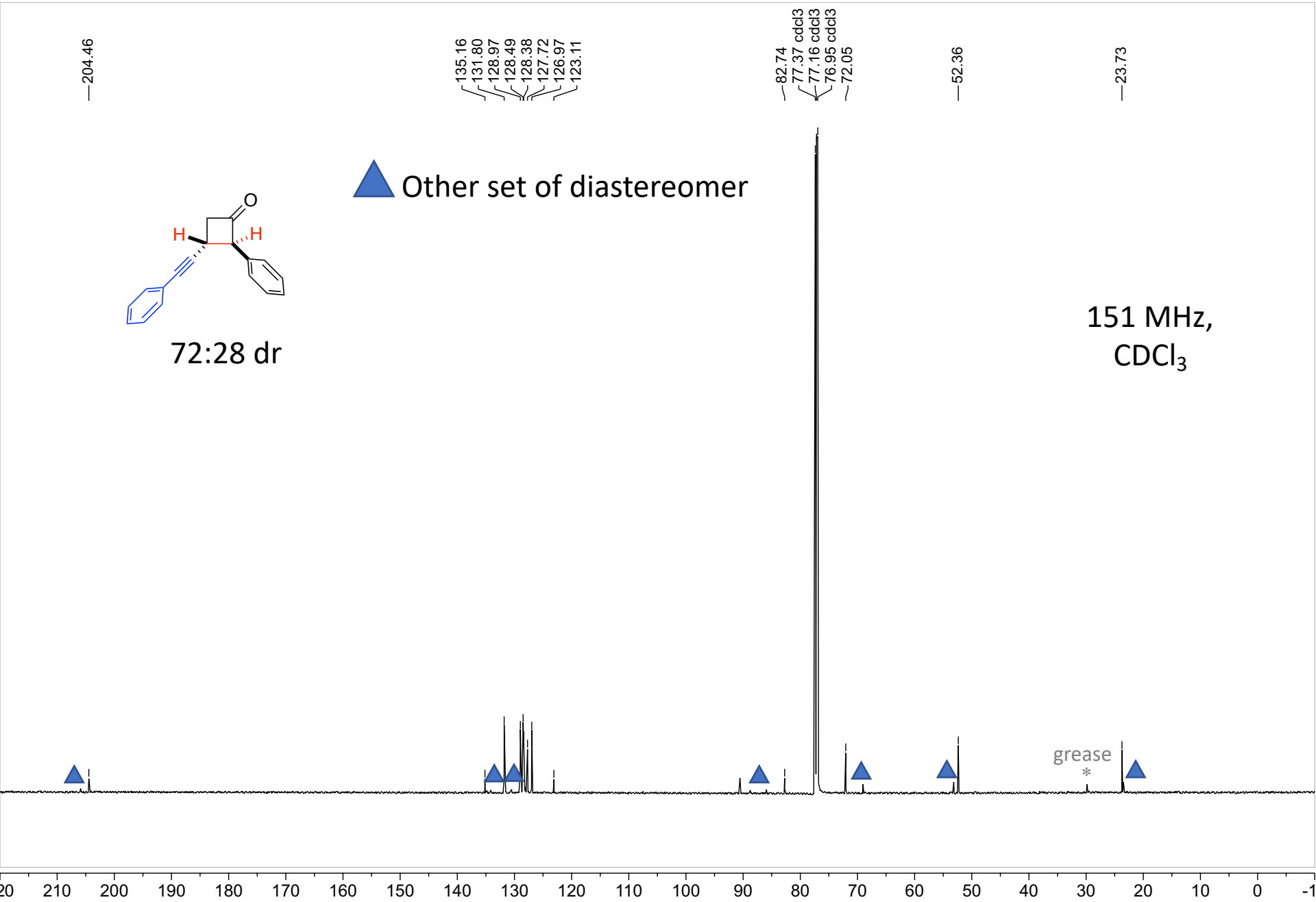


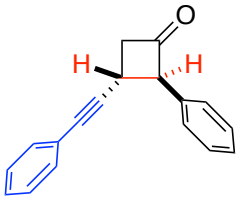

72:28 dr



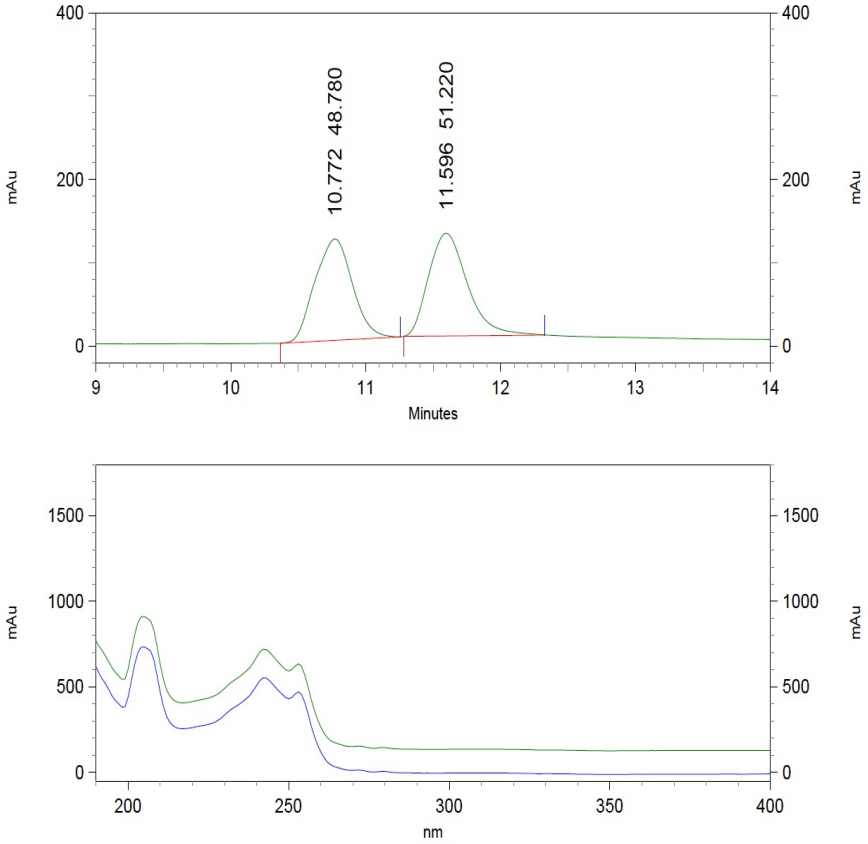



# $^{13}$C NMR (2*R*,3*R*)-2-phenyl-3-(phenylethynyl)cyclobutan-1-one **(2o)**



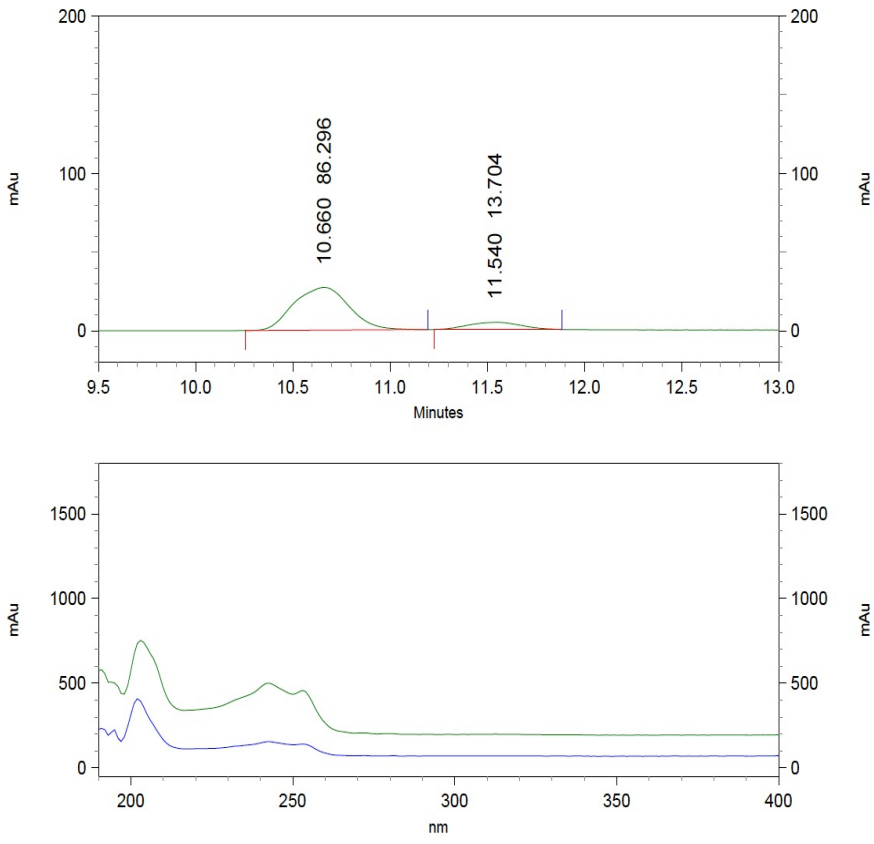



# **HPLC** (2*R*,3*R*)-2-phenyl-3-(phenylethynyl)cyclobutan-1-one **(2o)**




4: 255 nm, 4
nm Results

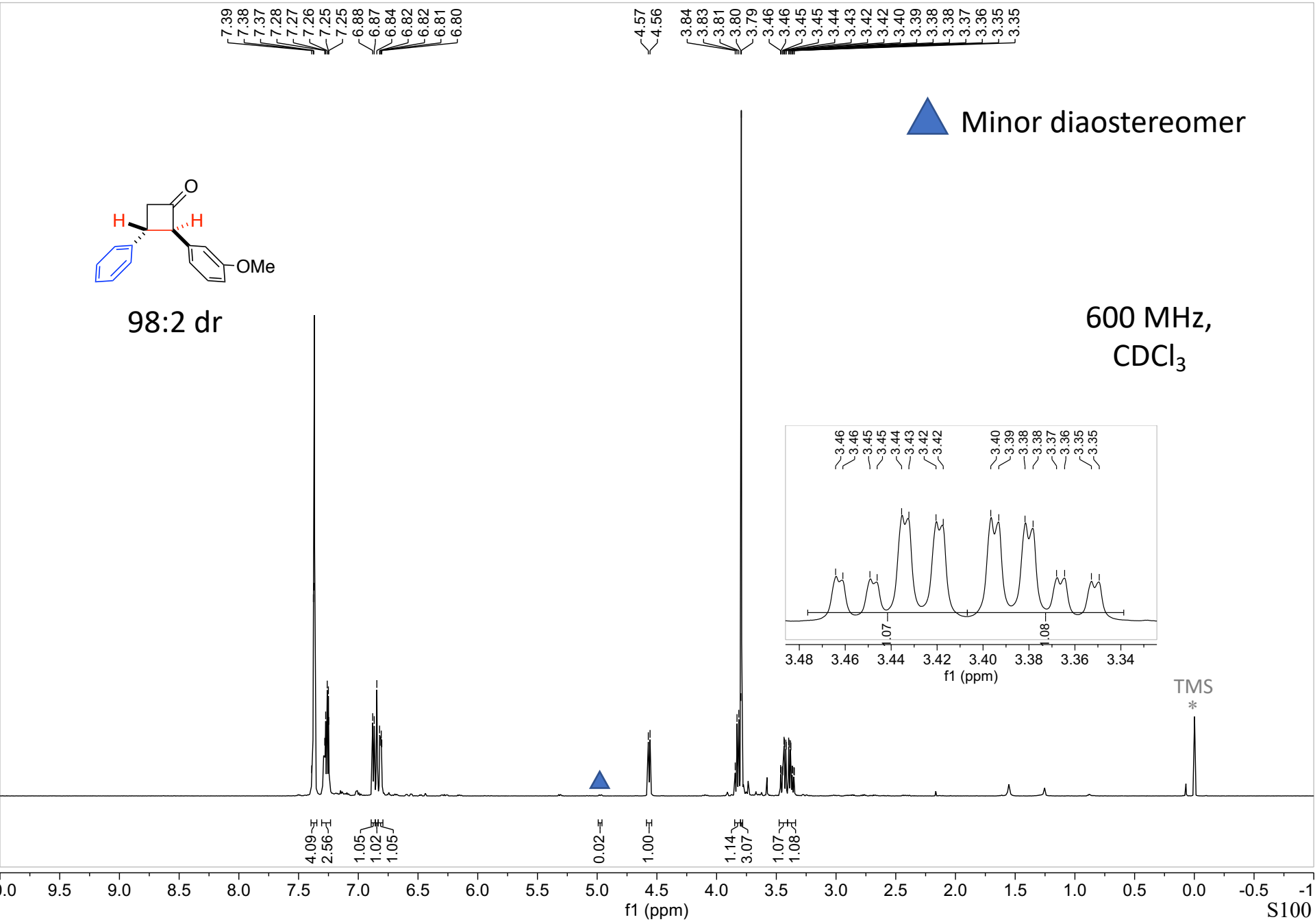
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.772 | 48.780 |
| 2 | 11.596 | 51.220 |
| Totals | | 100.000 |



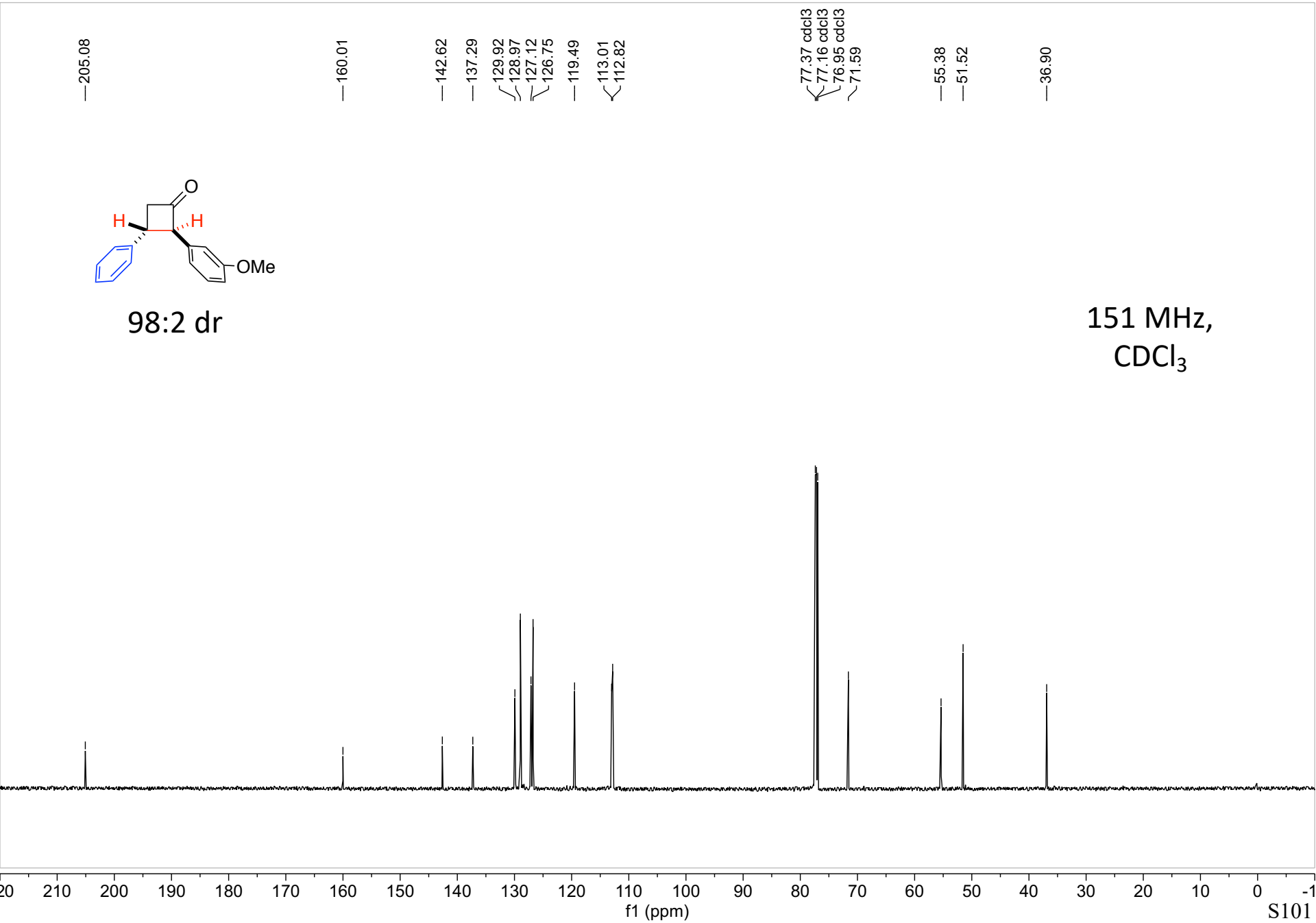

4: 255 nm, 4
nm Results

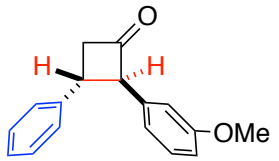
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.660 | 86.296 |
| 2 | 11.540 | 13.704 |
| Totals | | 100.000 |

# $^1$H NMR (2*R*,3*R*)-2-(3-methoxyphenyl)-3-phenylcyclobutan-1-one **(2p)**

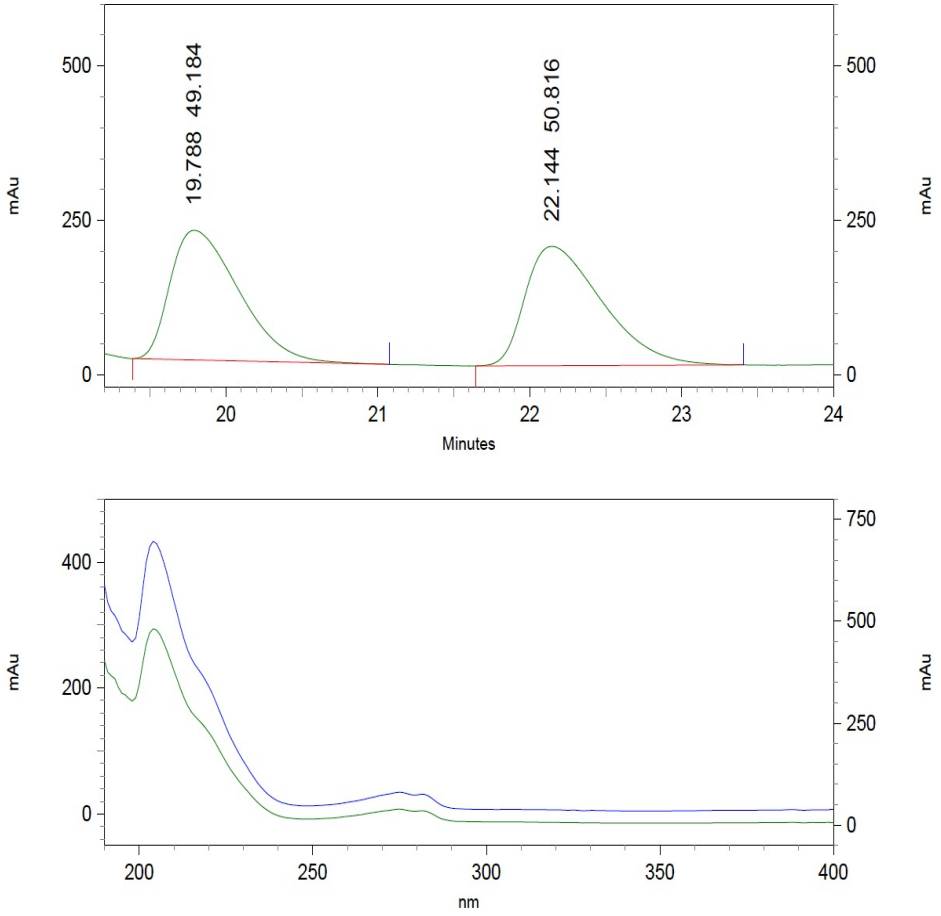


# $^{13}$C NMR (2*R*,3*R*)-2-(3-methoxyphenyl)-3-phenylcyclobutan-1-one **(2p)**





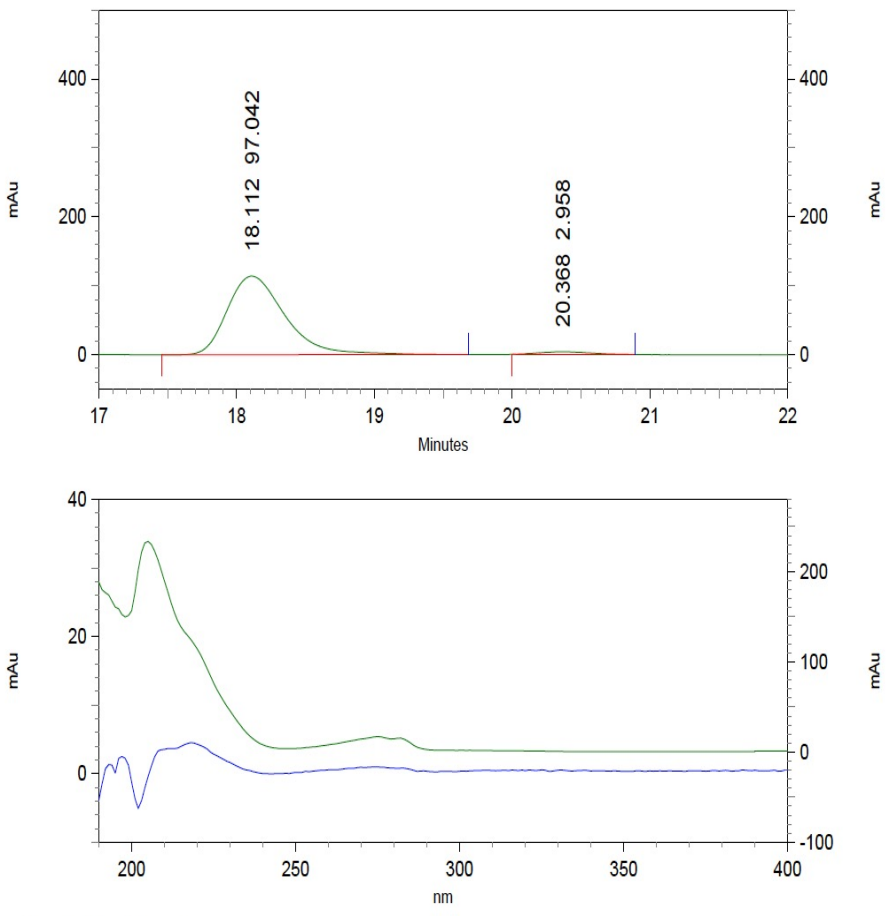

# **HPLC** (2*R*,3*R*)-2-(3-methoxyphenyl)-3-phenylcyclobutan-1-one **(2p)**




4: 228 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.788 | 49.184 |
| 2 | 22.144 | 50.816 |

| Totals | | 100.000 |
|---|---|---|

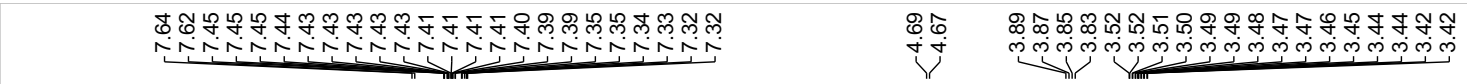



4: 228 nm, 4
nm Results

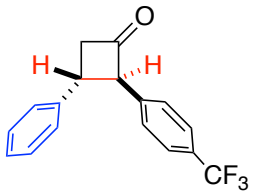
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 18.112 | 97.042 |
| 2 | 20.368 | 2.958 |

| Totals | | 100.000 |
|---|---|---|

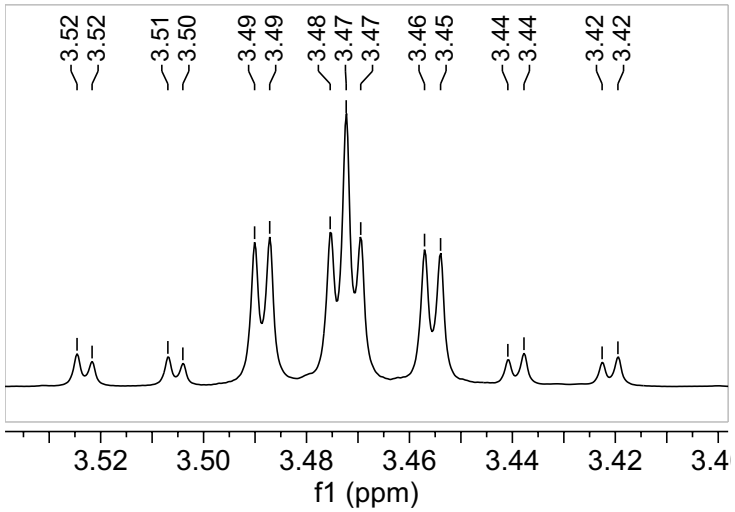
# $^1$H NMR (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutan-1-one **(2q)**



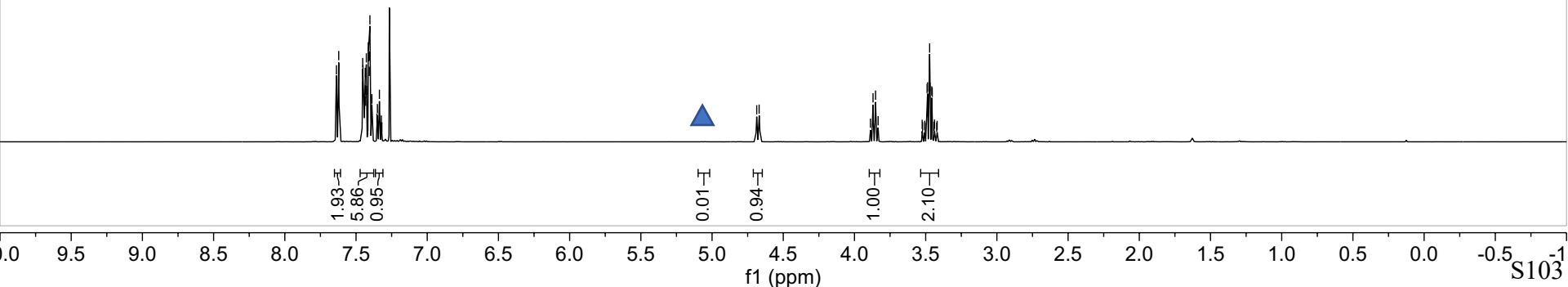

Minor diaostereomer



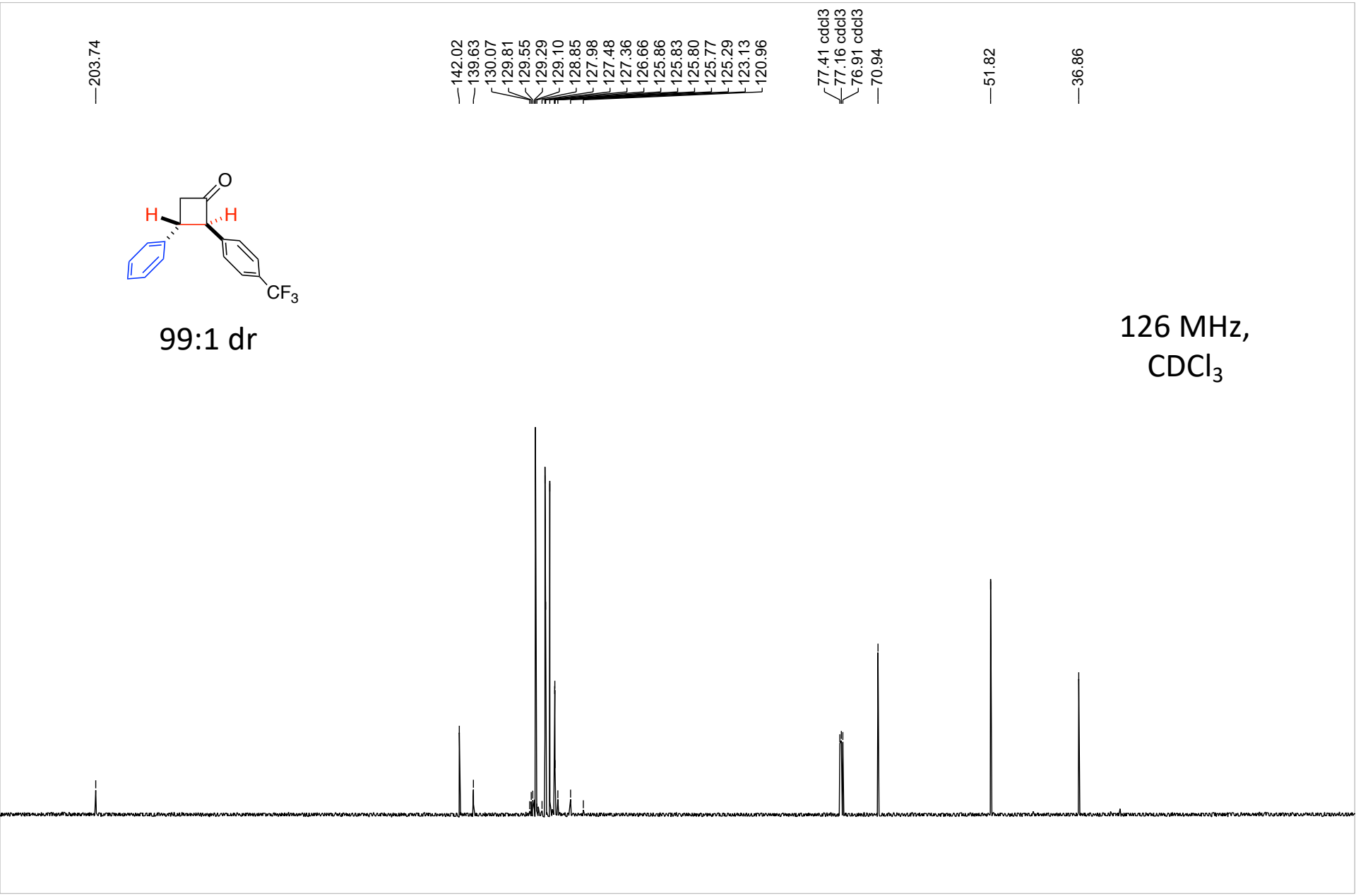

99:1 dr



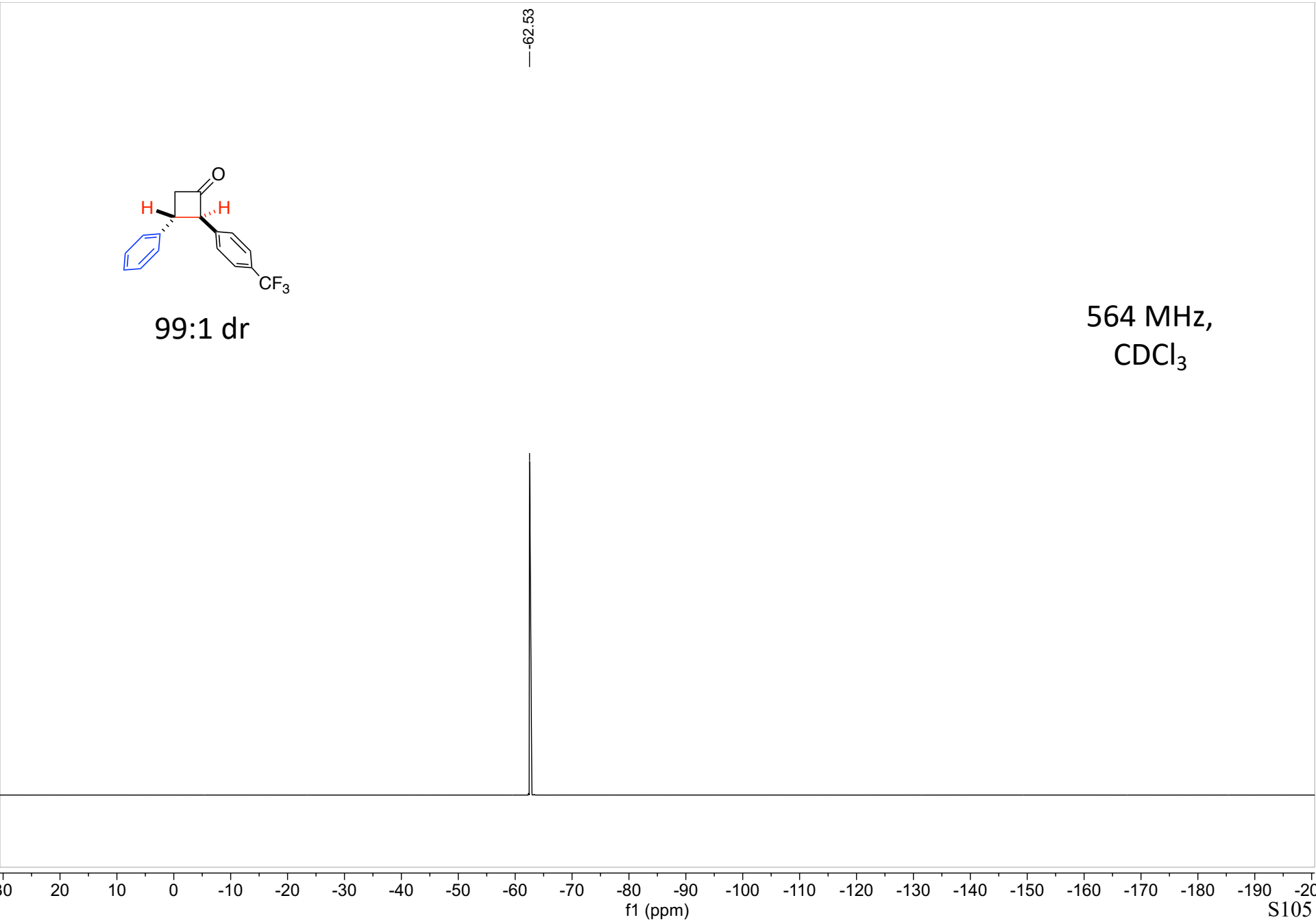

500 MHz, $CDCl_3$

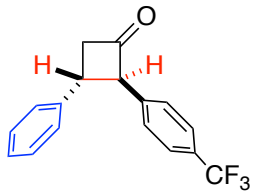


# $^{13}$C NMR (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutan-1-one **(2q)**

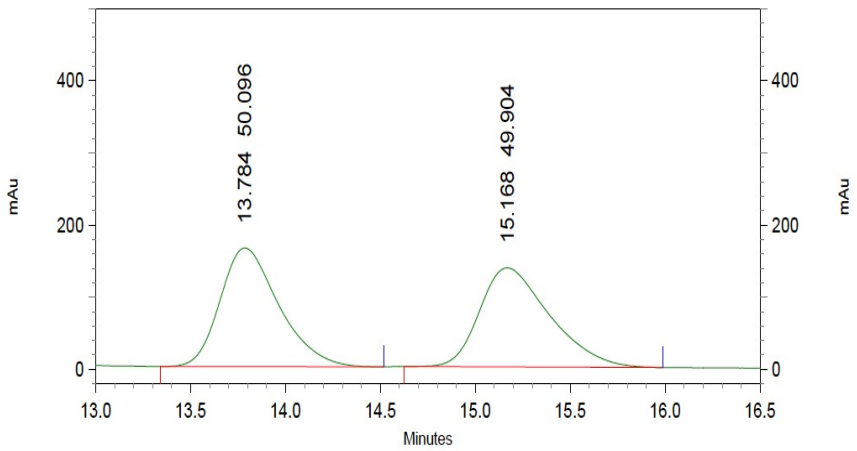


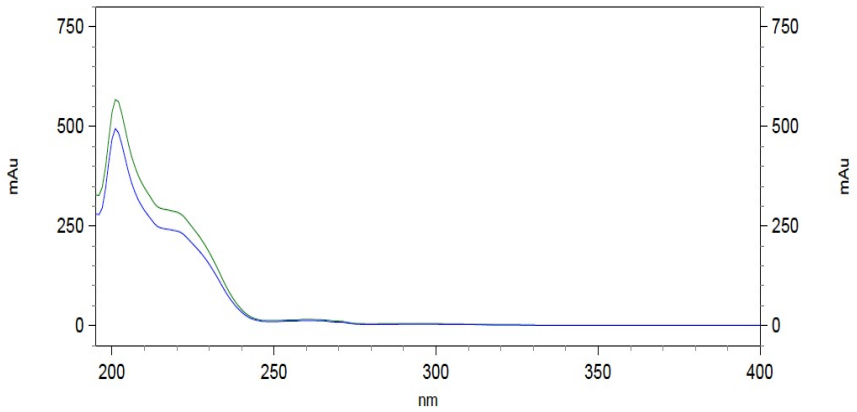
# $^{19}$F NMR (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutan-1-one **(2q)**






# **HPLC** (2*R*,3*R*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutan-1-one **(2q)**

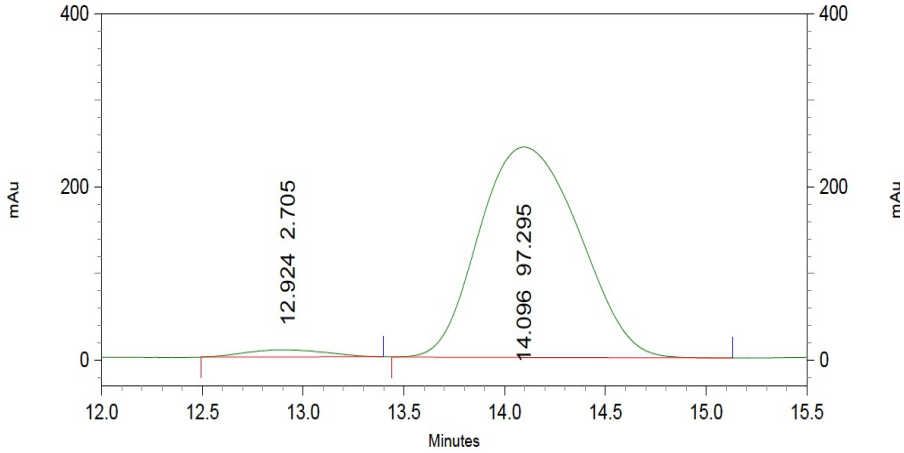


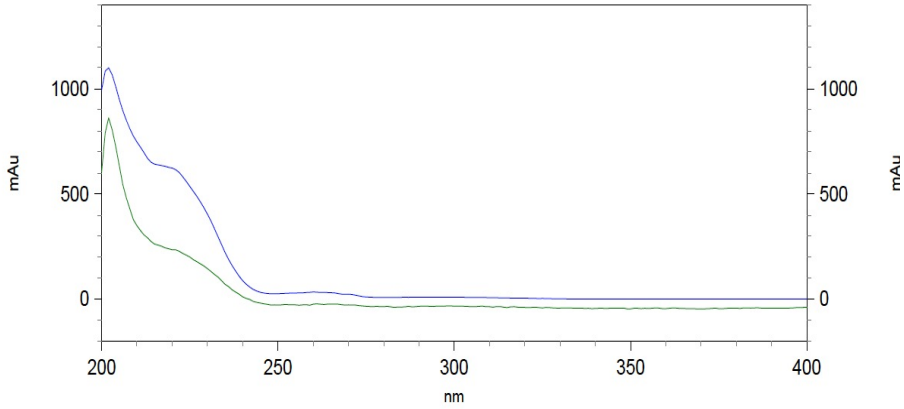




4: 231 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.784 | 50.096 |
| 2 | 15.168 | 49.904 |

| Totals | | 100.000 |
|---|---|---|



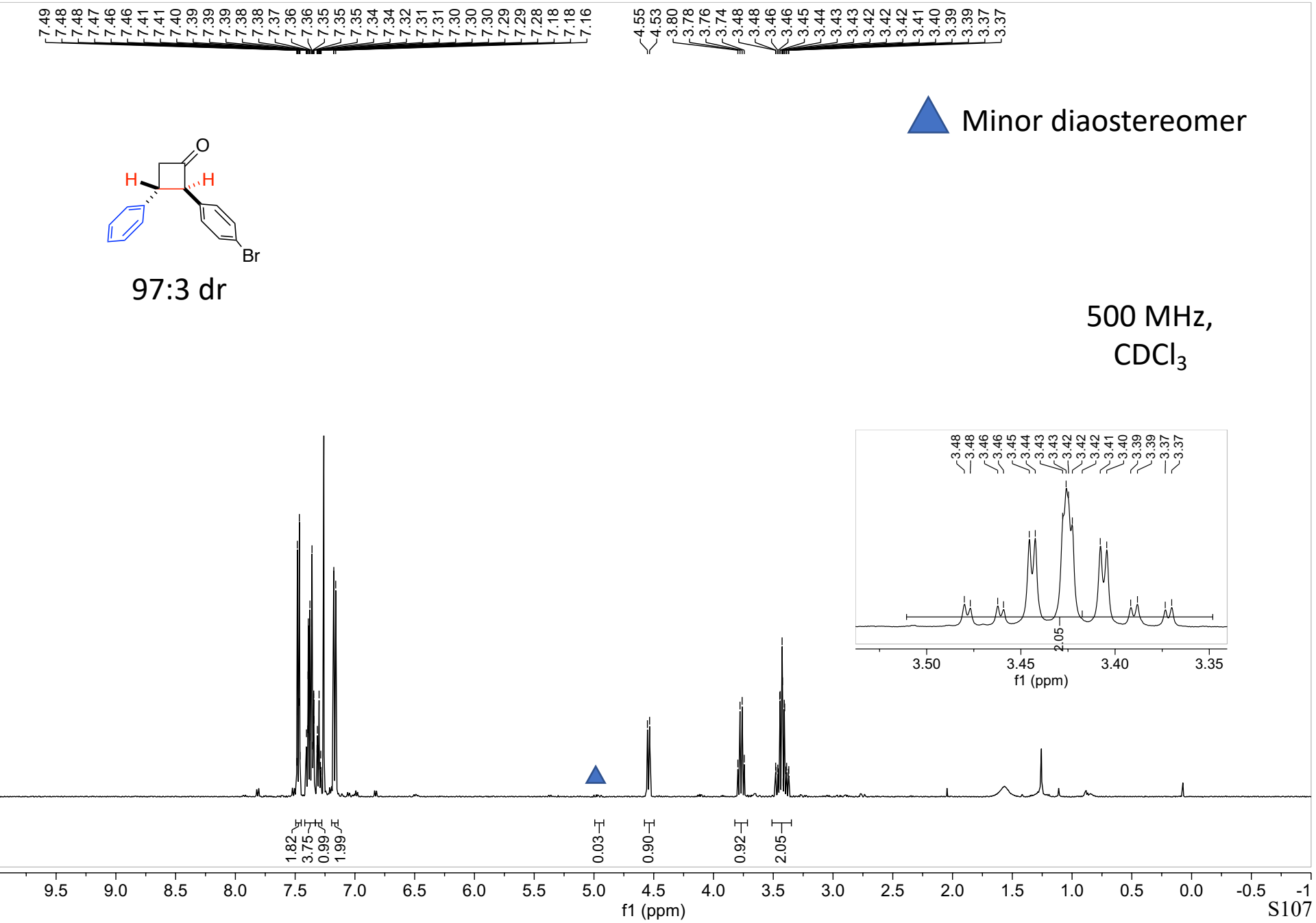




4: 231 nm, 4
nm Results

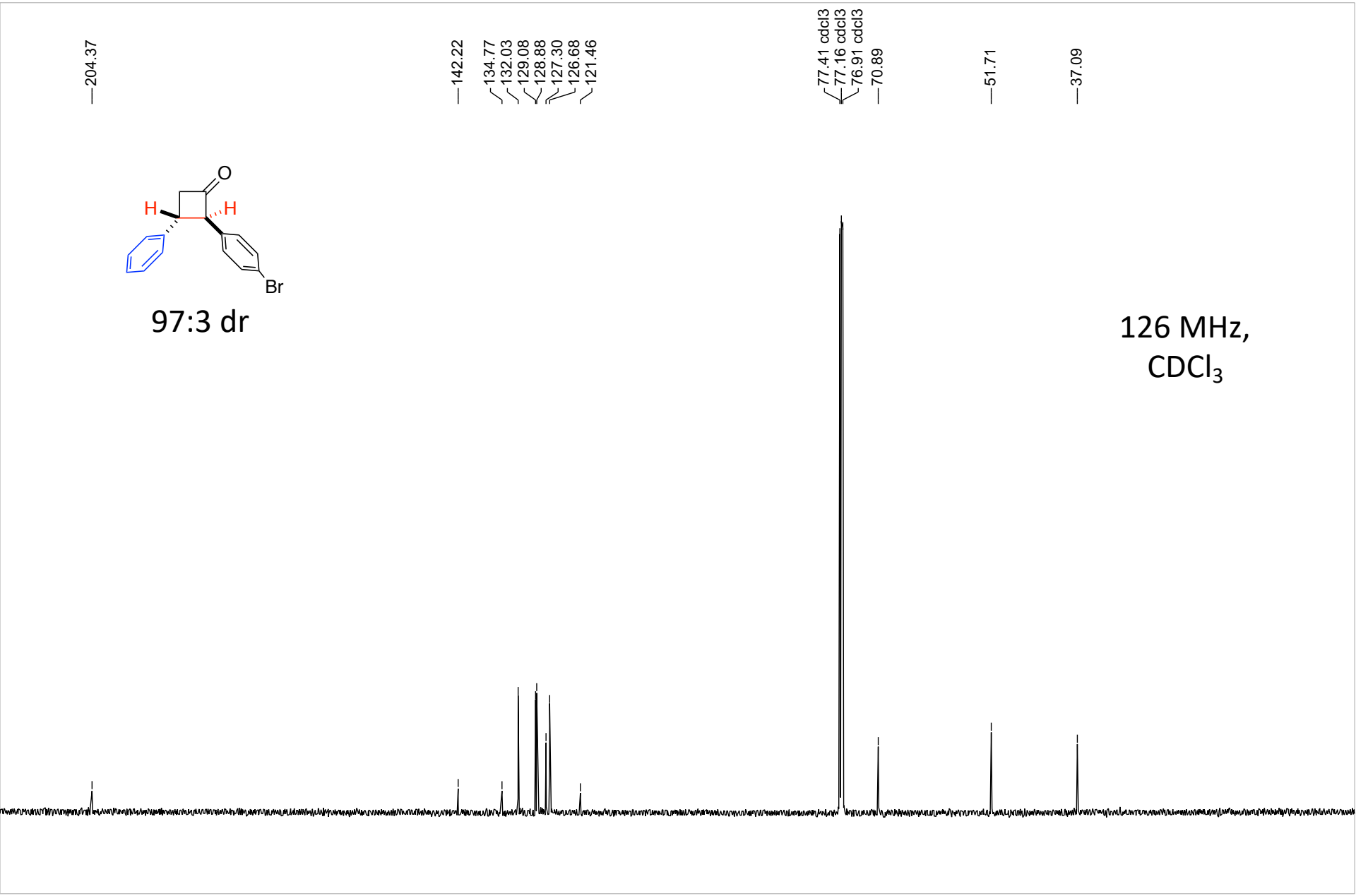
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.924 | 2.705 |
| 2 | 14.096 | 97.295 |

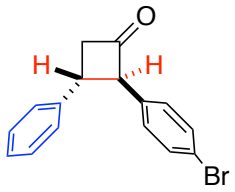
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR (2*R*,3*R*)-2-(4-bromophenyl)-3-phenylcyclobutan-1-one **(2r)**

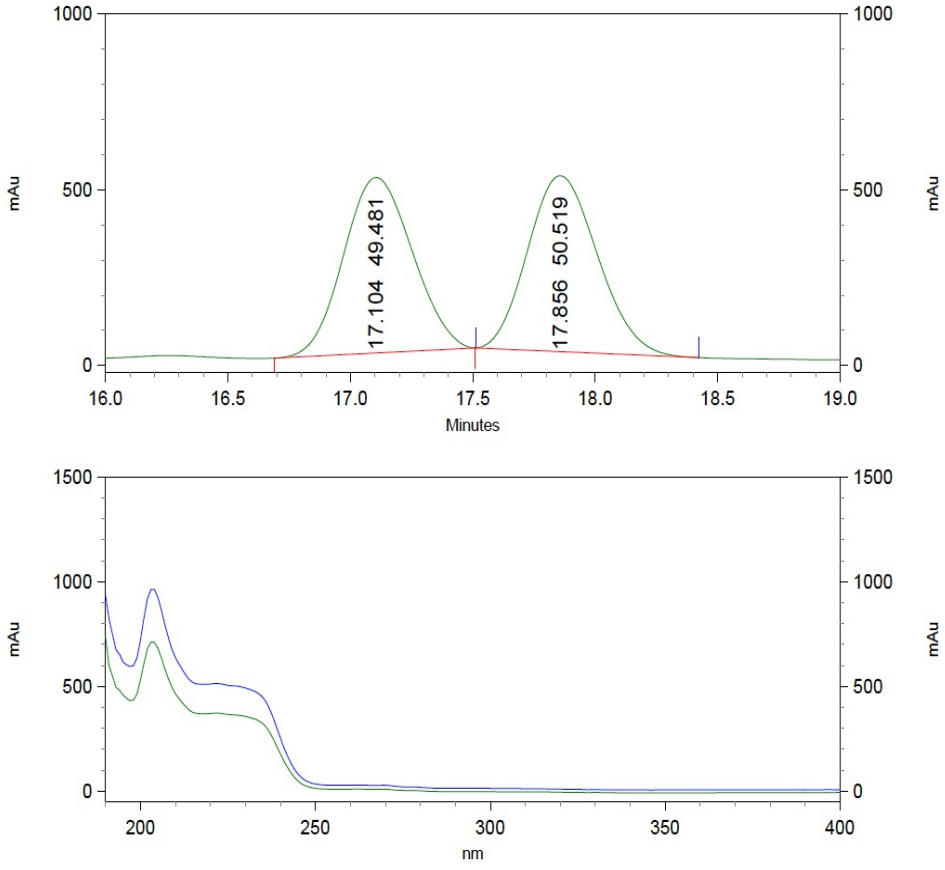


# $^{13}$C NMR (2*R*,3*R*)-2-(4-bromophenyl)-3-phenylcyclobutan-1-one **(2r)**



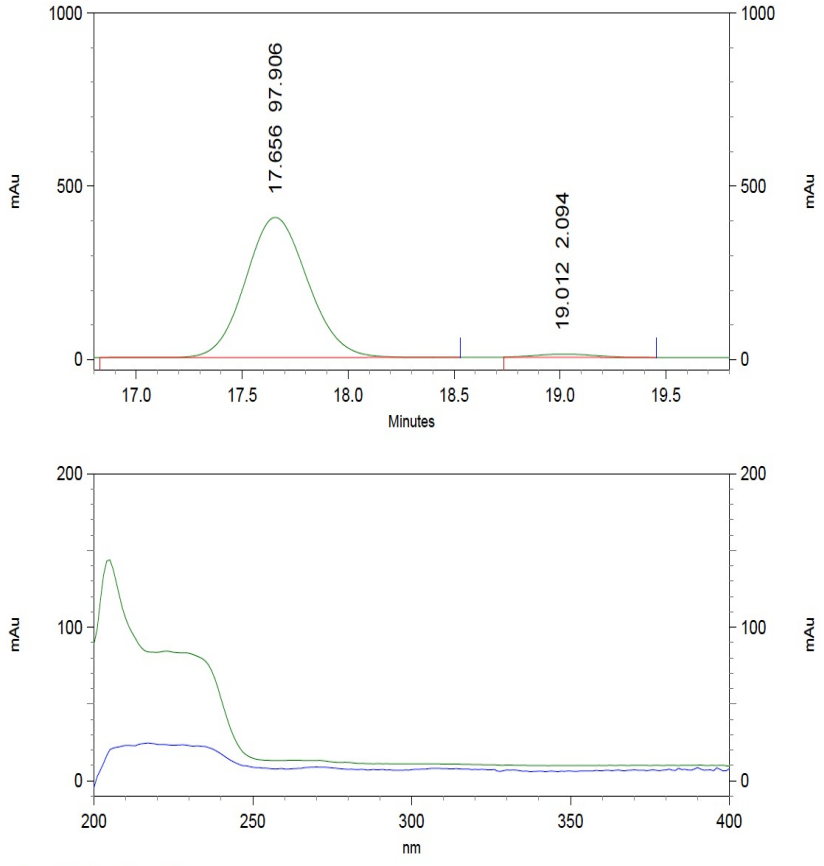



# **HPLC** (2*R*,3*R*)-2-(4-bromophenyl)-3-phenylcyclobutan-1-one **(2r)**




4: 214 nm, 4 nm Results

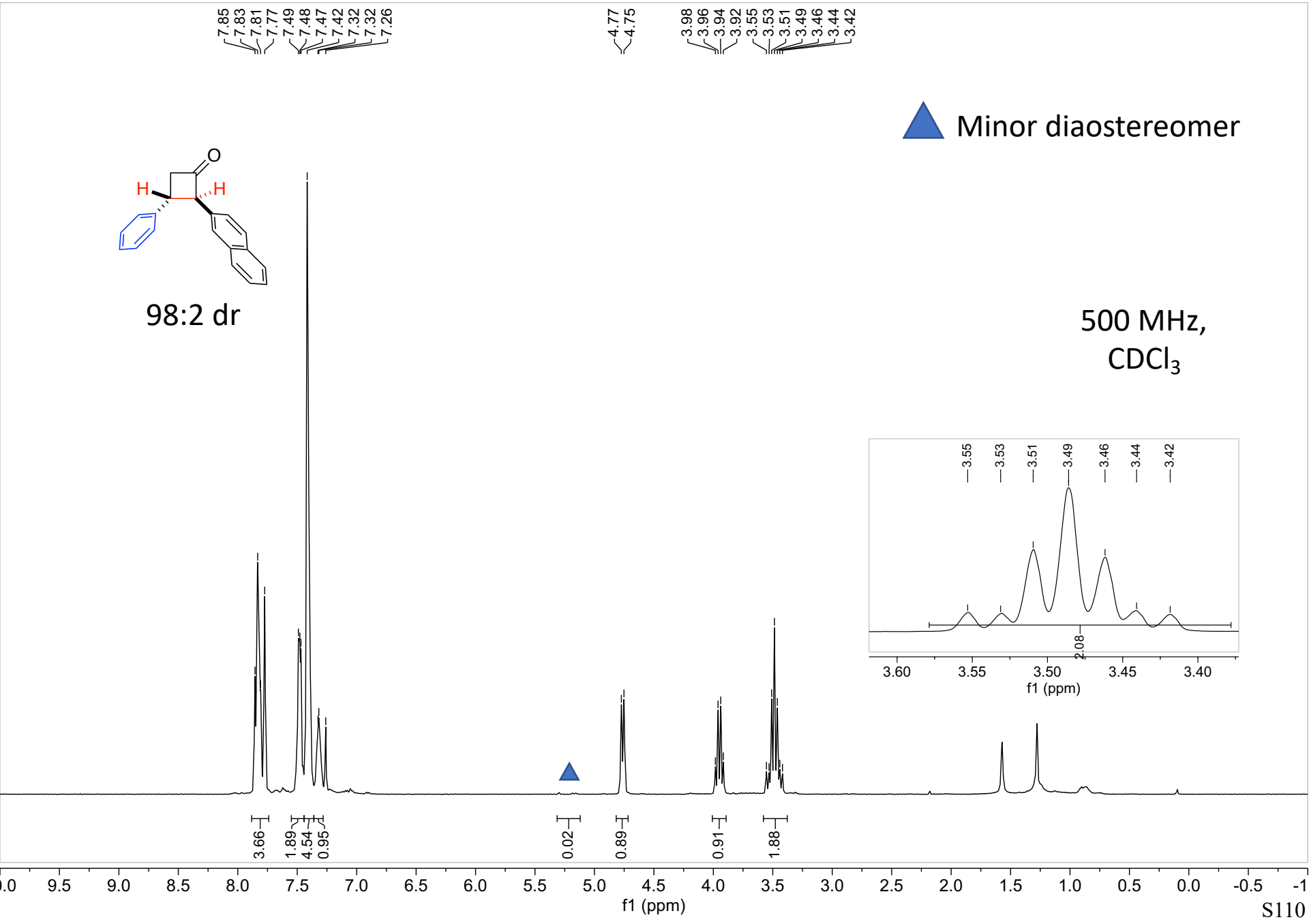
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 17.104 | 49.481 |
| 2 | 17.856 | 50.519 |
| Totals | | 100.000 |



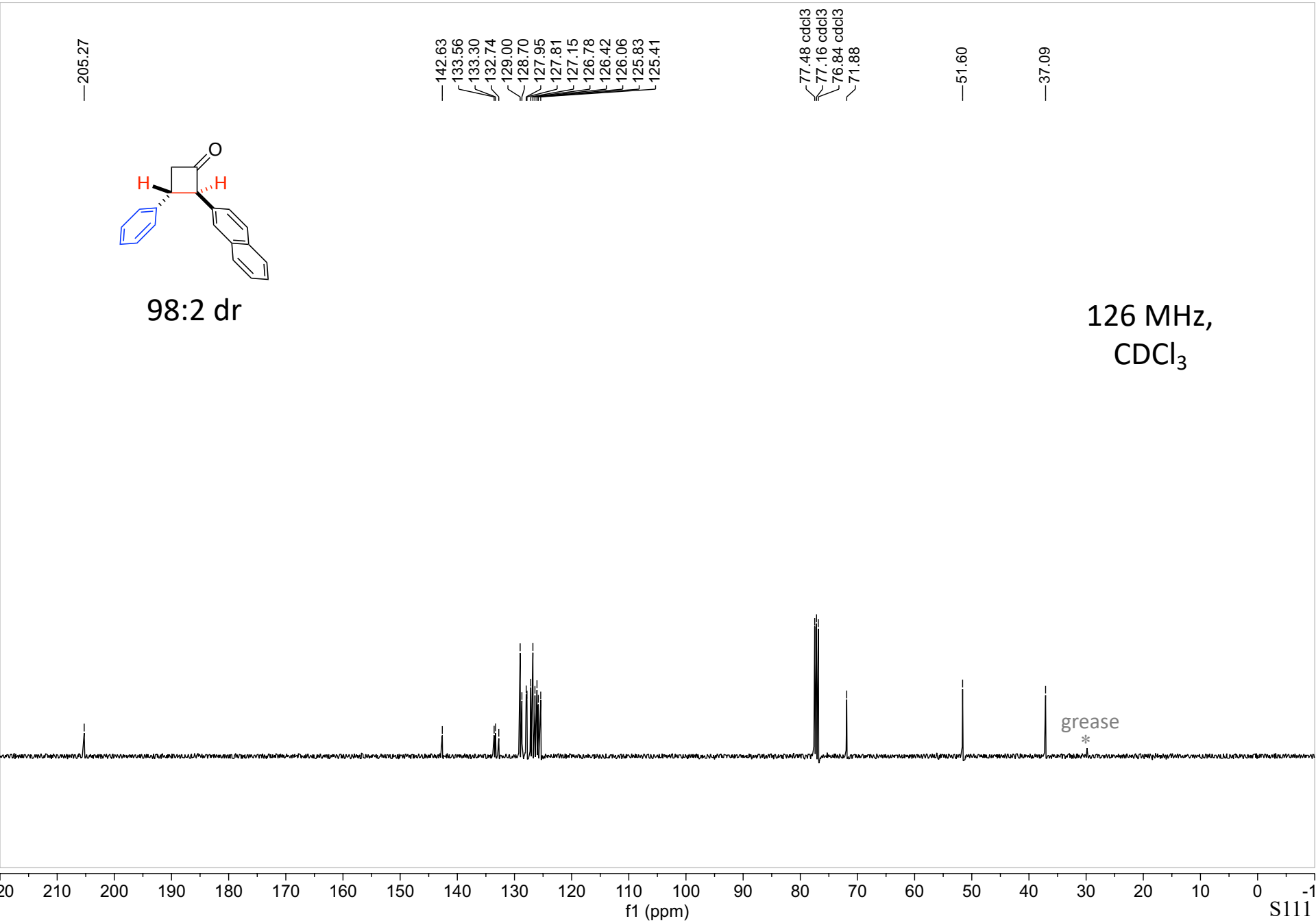

4: 214 nm, 4 nm Results

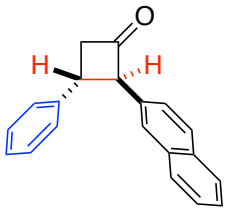
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 17.656 | 97.906 |
| 2 | 19.012 | 2.094 |
| Totals | | 100.000 |

# $^1$H NMR (2*R*,3*R*)-2-(naphthalen-2-yl)-3-phenylcyclobutan-1-one **(2s)**

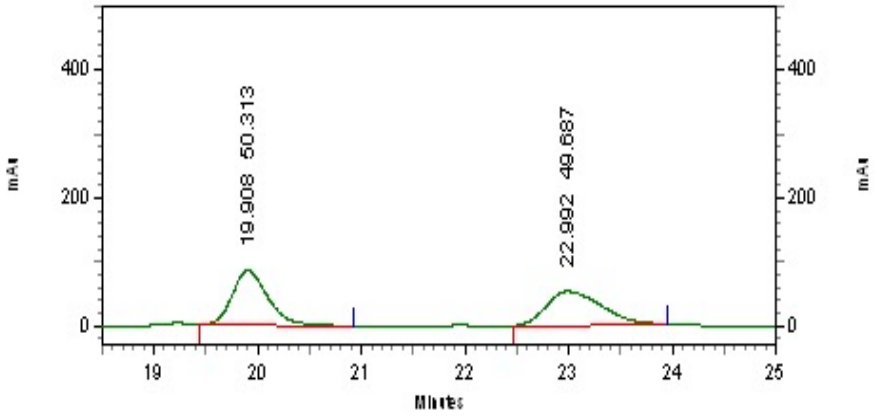


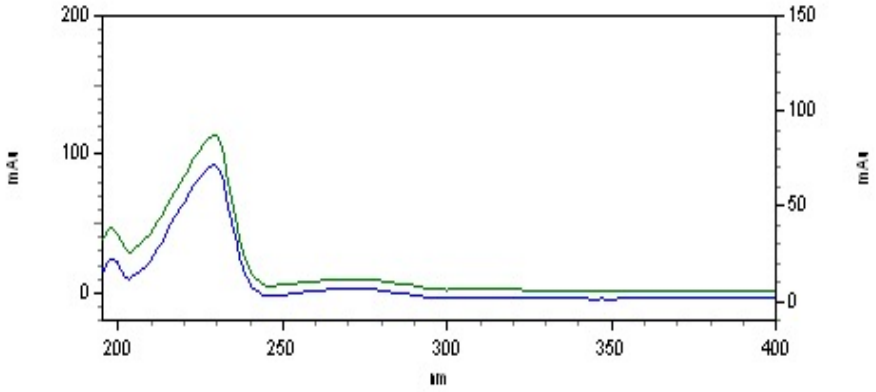
# $^{13}$C NMR (2*R*,3*R*)-2-(naphthalen-2-yl)-3-phenylcyclobutan-1-one **(2s)**






# **HPLC** (2*R*,3*R*)-2-(naphthalen-2-yl)-3-phenylcyclobutan-1-one **(2s)**

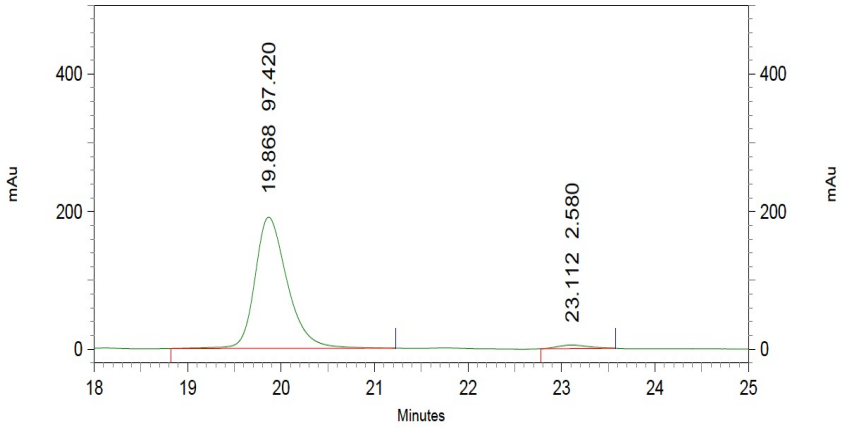


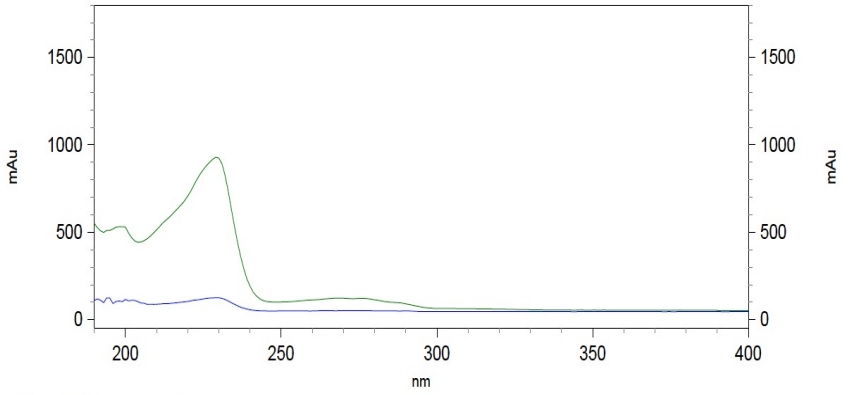




2: 233 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.908 | 50.313 |
| 2 | 22.992 | 49.687 |

| Totals | | |
|---|---|---|
| | | 100.000 |



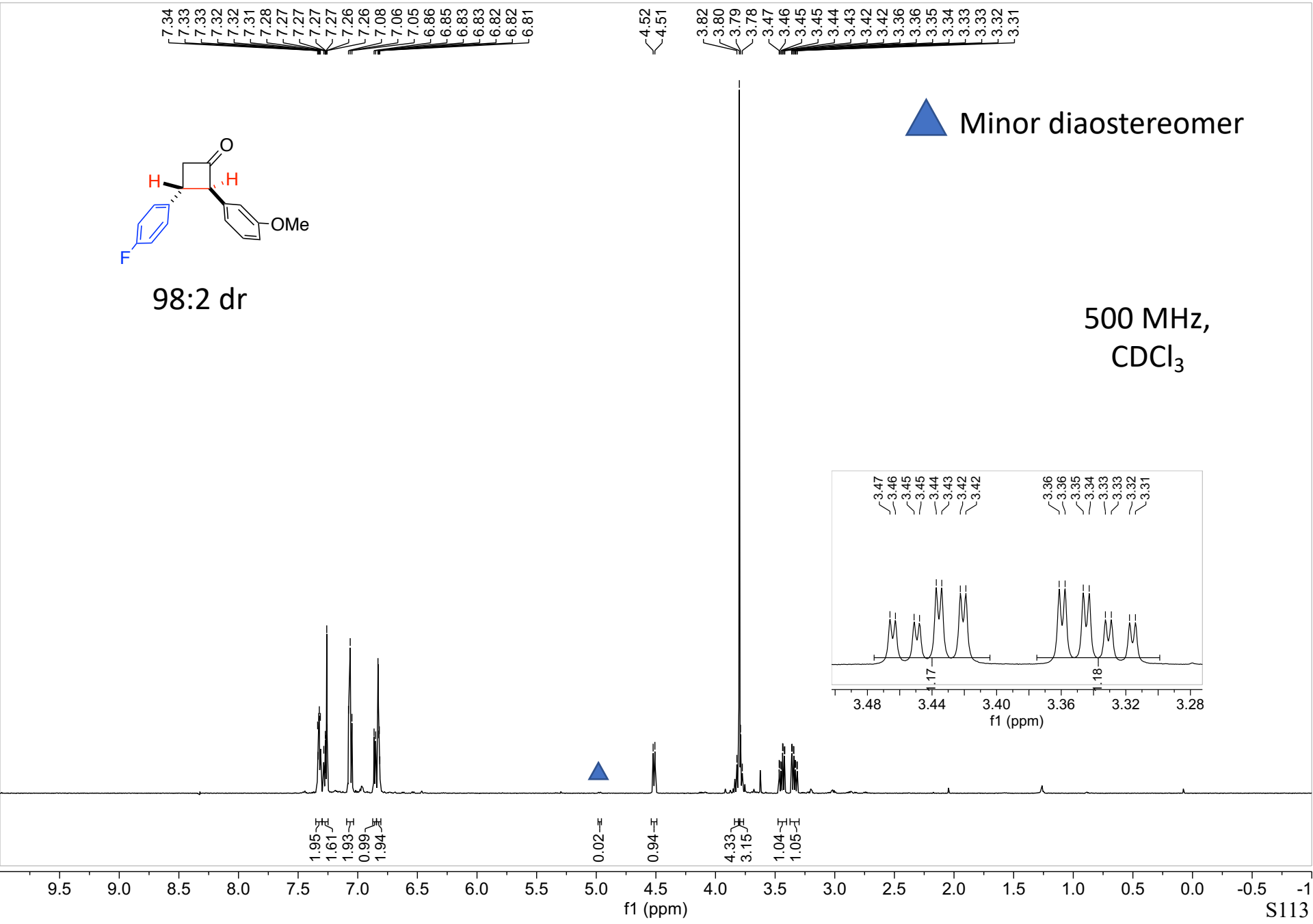




4: 233 nm, 4
nm Results

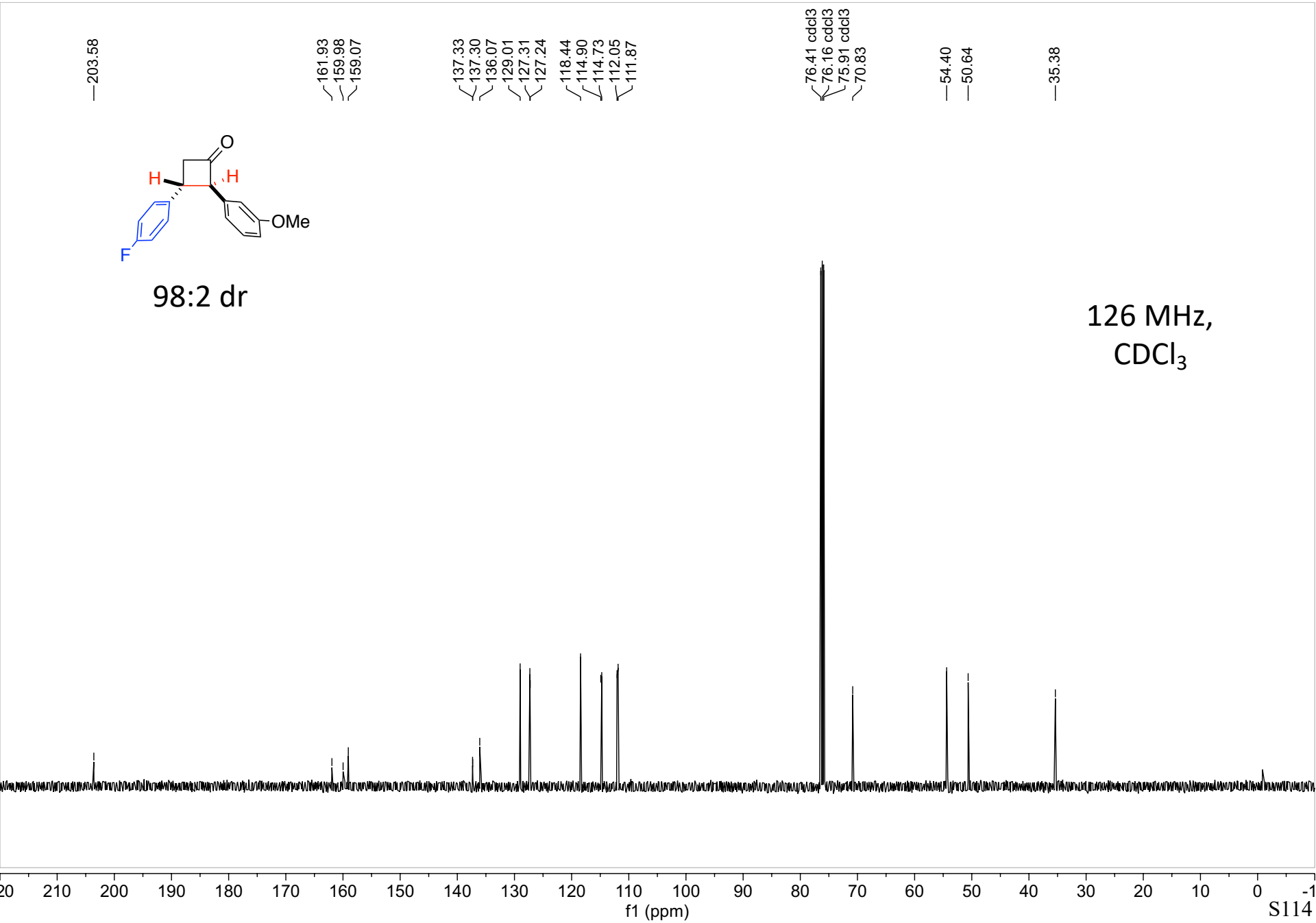
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.868 | 97.420 |
| 2 | 23.112 | 2.580 |

| Totals | | |
|---|---|---|
| | | 100.000 |

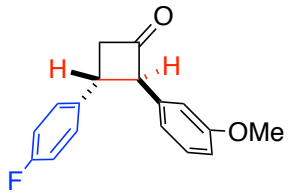
# $^1$H NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-(3-methoxyphenyl)cyclobutan-1-one **(2t)**



# $^{13}$C NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-(3-methoxyphenyl)cyclobutan-1-one **(2t)**

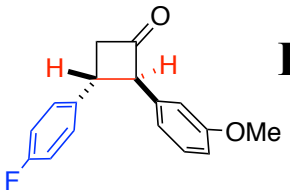


# $^{19}$F NMR (2*R*,3*R*)-3-(4-fluorophenyl)-2-(3-methoxyphenyl)cyclobutan-1-one **(2t)**

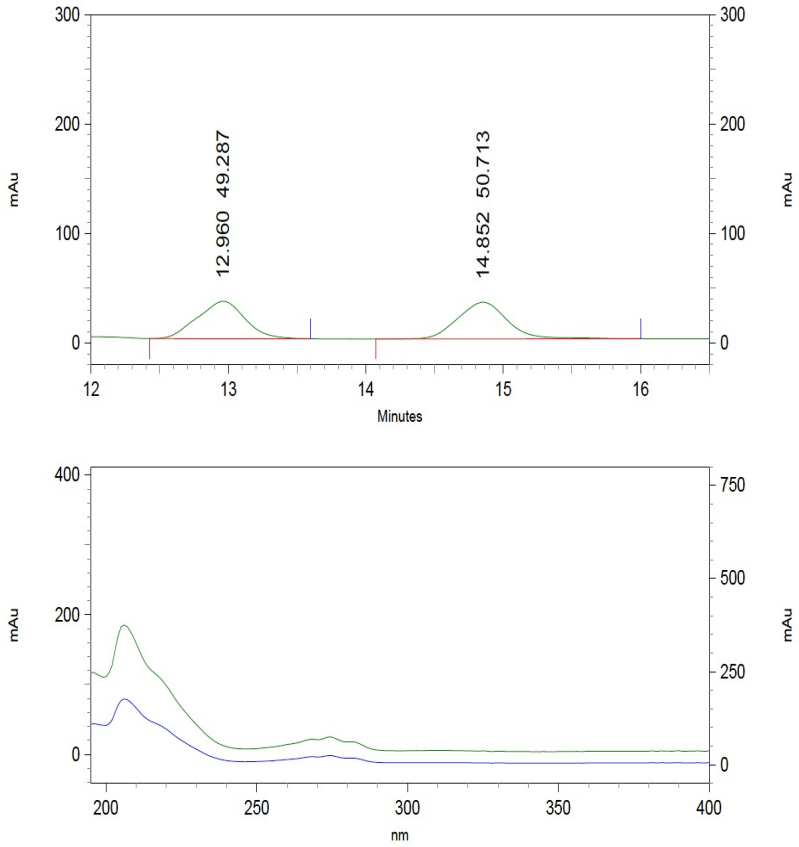



98:2 dr

564 MHz,
$CDCl_3$



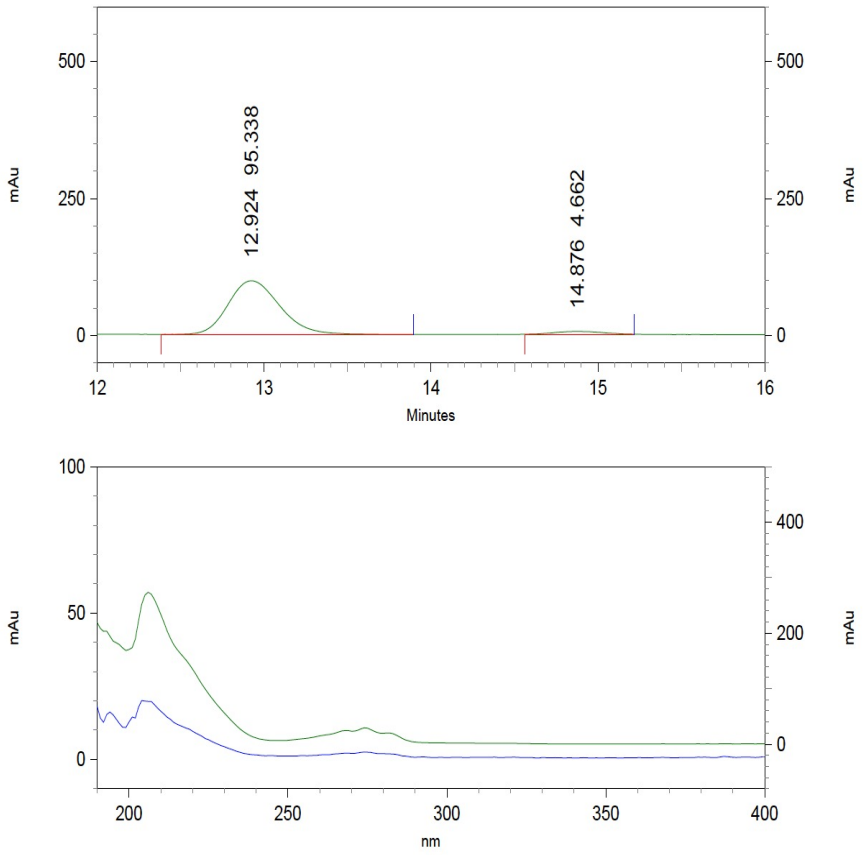

# **HPLC** (2*R*,3*R*)-3-(4-fluorophenyl)-2-(3-methoxyphenyl)cyclobutan-1-one **(2t)**




4: 231 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.960 | 49.287 |
| 2 | 14.852 | 50.713 |

| Totals | | 100.000 |
|---|---|---|

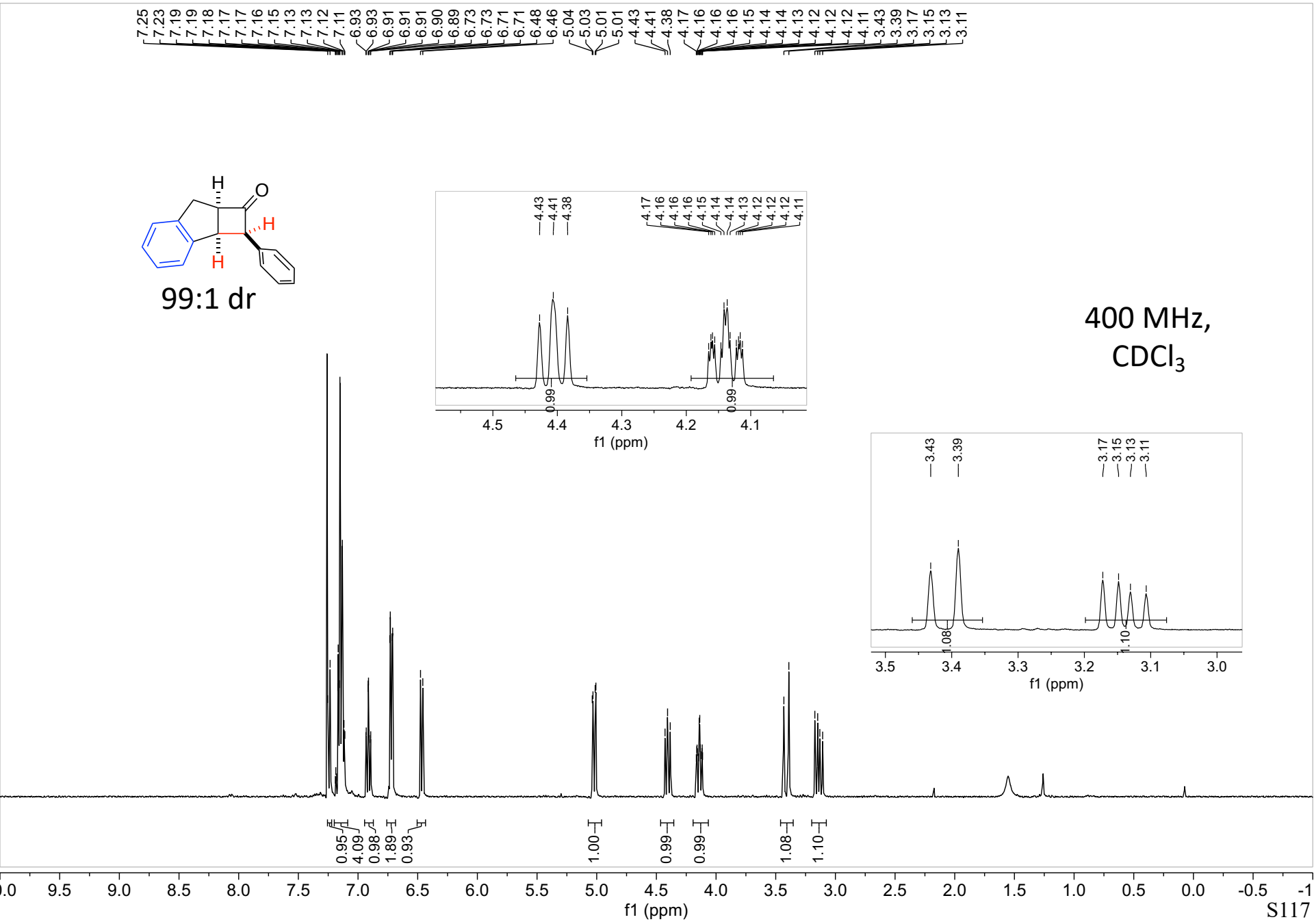



4: 231 nm, 4
nm Results

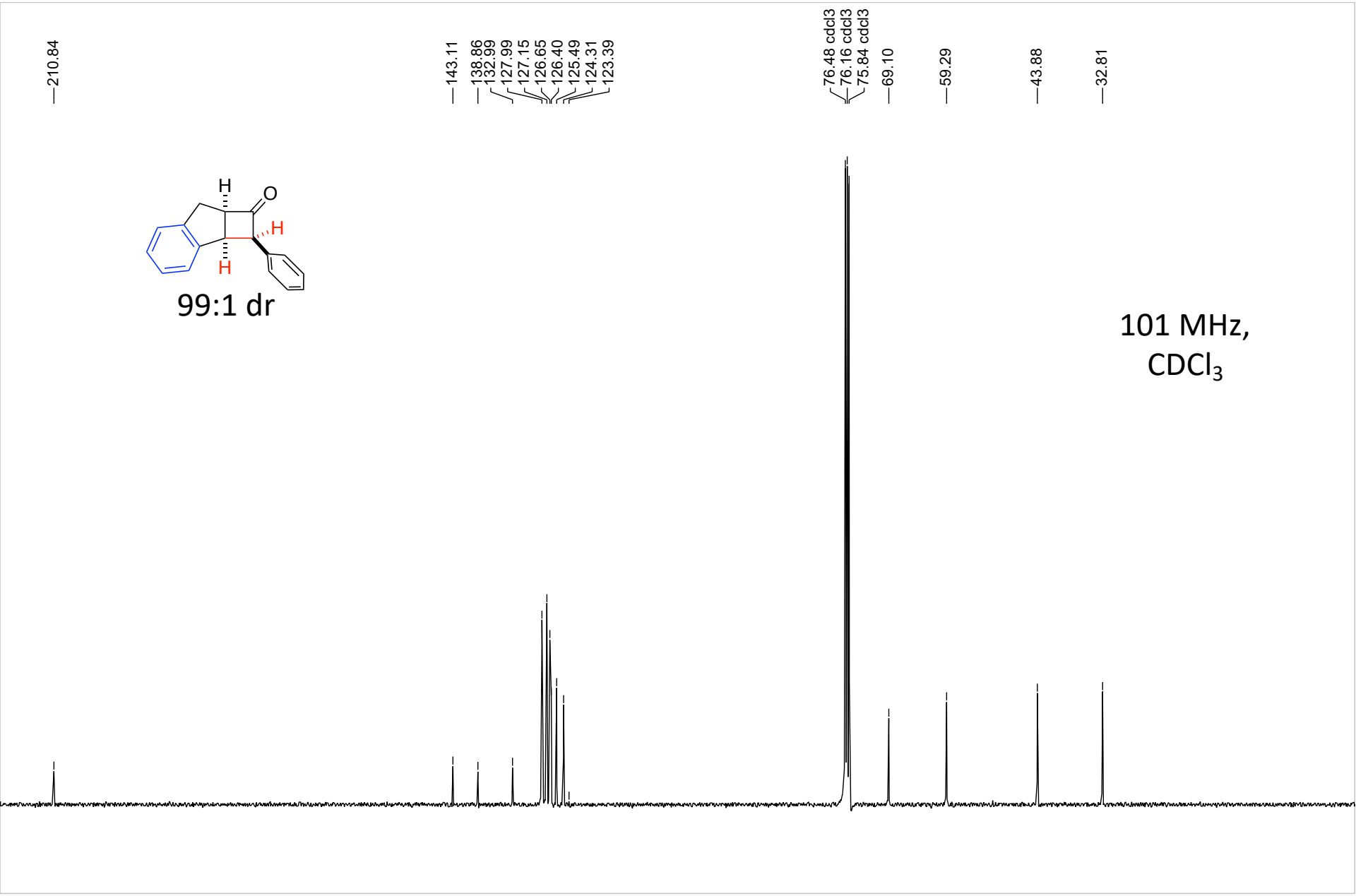
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.924 | 95.338 |
| 2 | 14.876 | 4.662 |

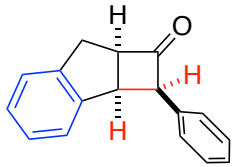
| Totals | | 100.000 |
|---|---|---|

# $^1$H NMR 2-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]inden-1-one **(2u)**

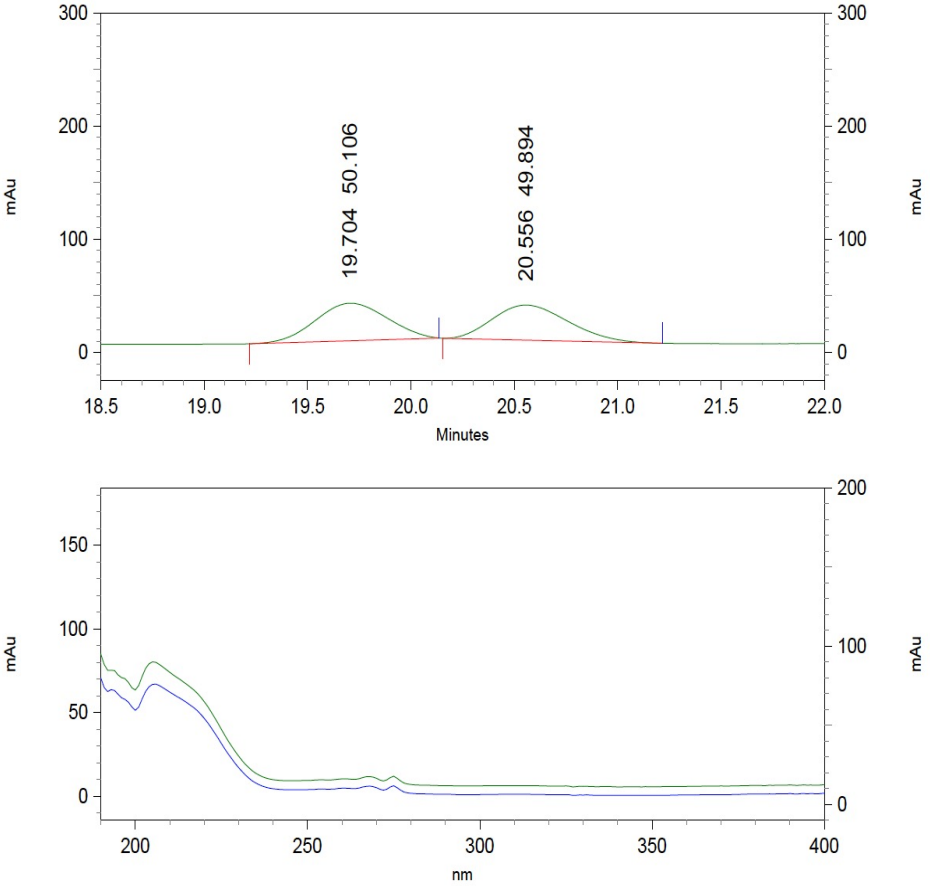


# $^{13}$C NMR 2-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]inden-1-one **(2u)**



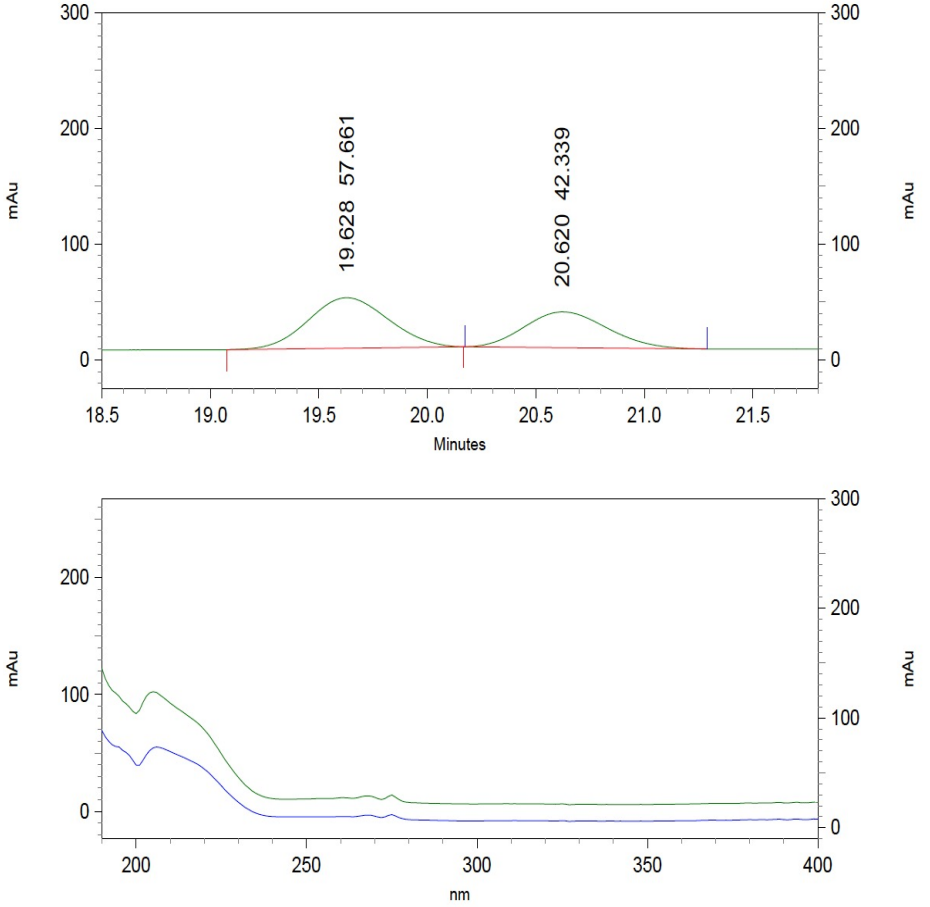



# **HPLC** 2-phenyl-2,2a,7,7a-tetrahydro-1*H*-cyclobuta[*a*]inden-1-one **(2u)**




2: 224 nm, 4
nm Results

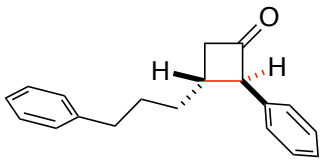
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.704 | 50.106 |
| 2 | 20.556 | 49.894 |
| Totals | | 100.000 |




2: 224 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.628 | 57.661 |
| 2 | 20.620 | 42.339 |
| Totals | | 100.000 |

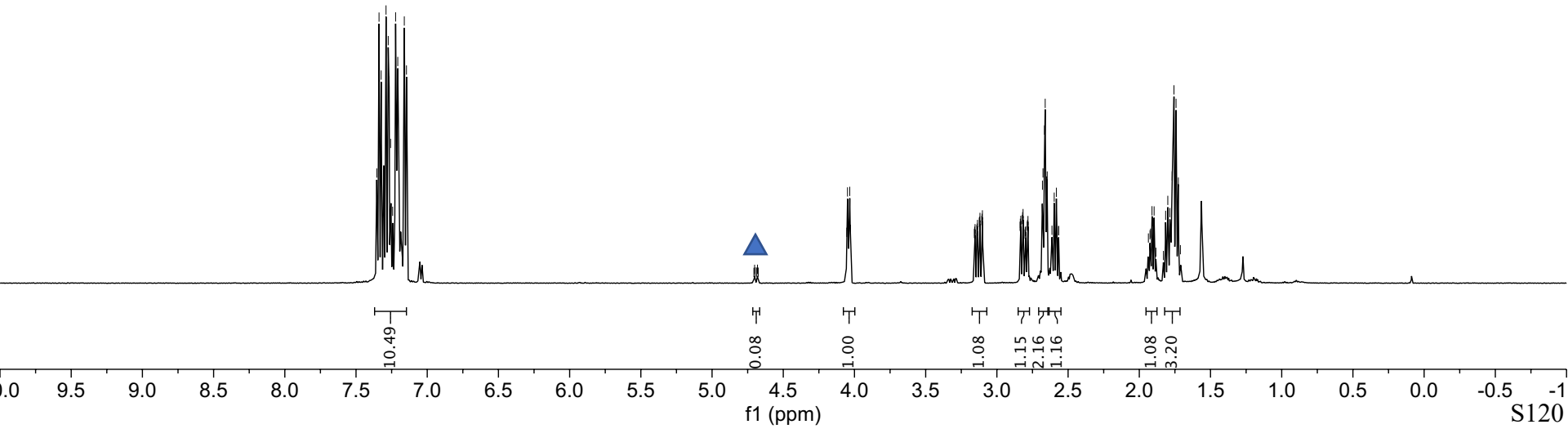
# $^1$H NMR 2-phenyl-3-(3-phenylpropyl)cyclobutan-1-one **(2w)**




93:7 dr

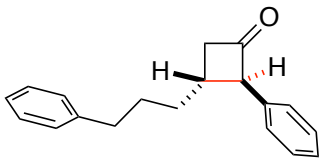
500 MHz, $CDCl_3$

▲ Minor diastereomer



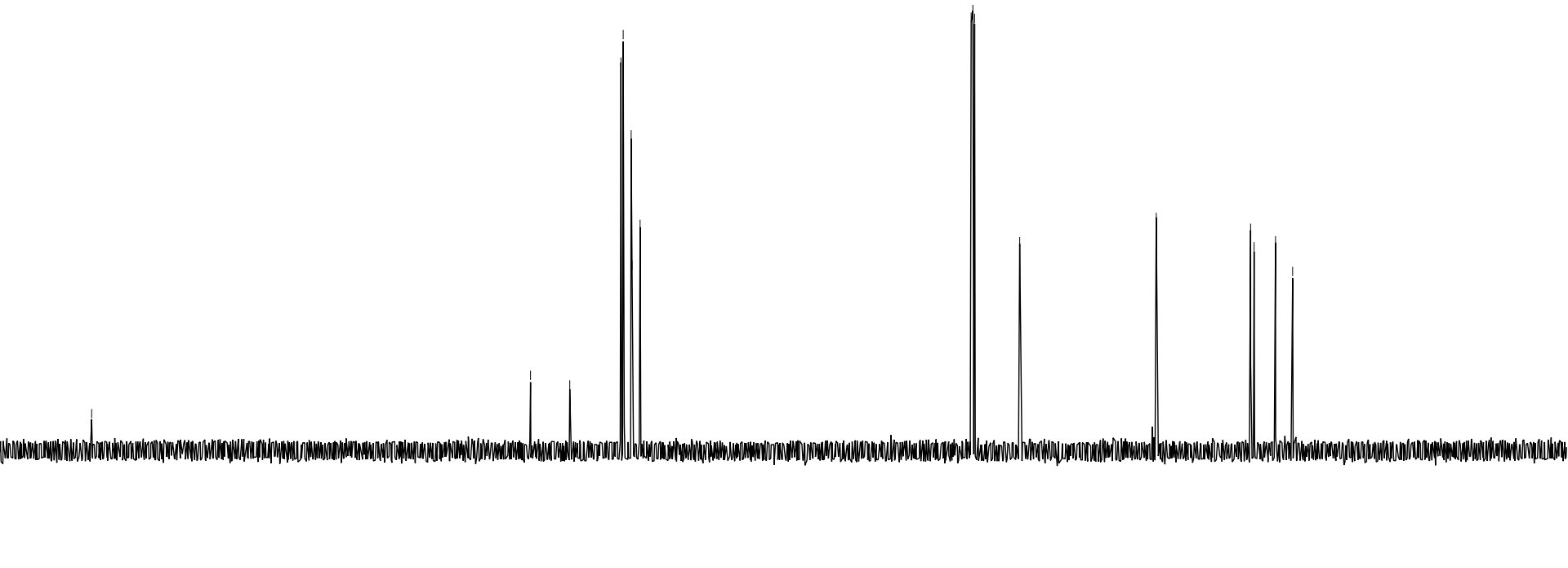
# $^{13}$C NMR 2-phenyl-3-(3-phenylpropyl)cyclobutan-1-one **(2w)**

206.54
142.11
136.35
128.83
128.51
128.50
127.33
127.20
126.02
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
70.29
50.24
36.38
35.87
32.73
30.21

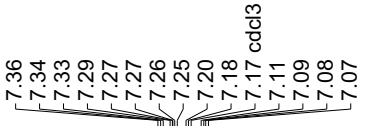


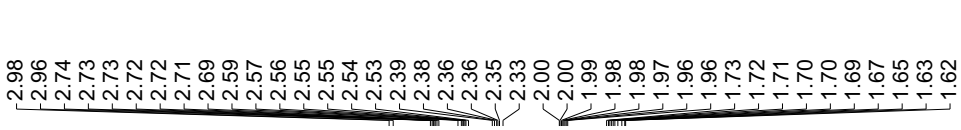

93:7 dr

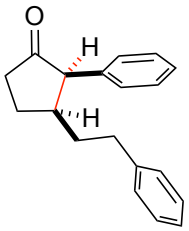
126 MHz, $CDCl_3$



# $^{1}$H NMR 3-Phenethyl-2-phenylcyclopentan-1-one **(3w)**

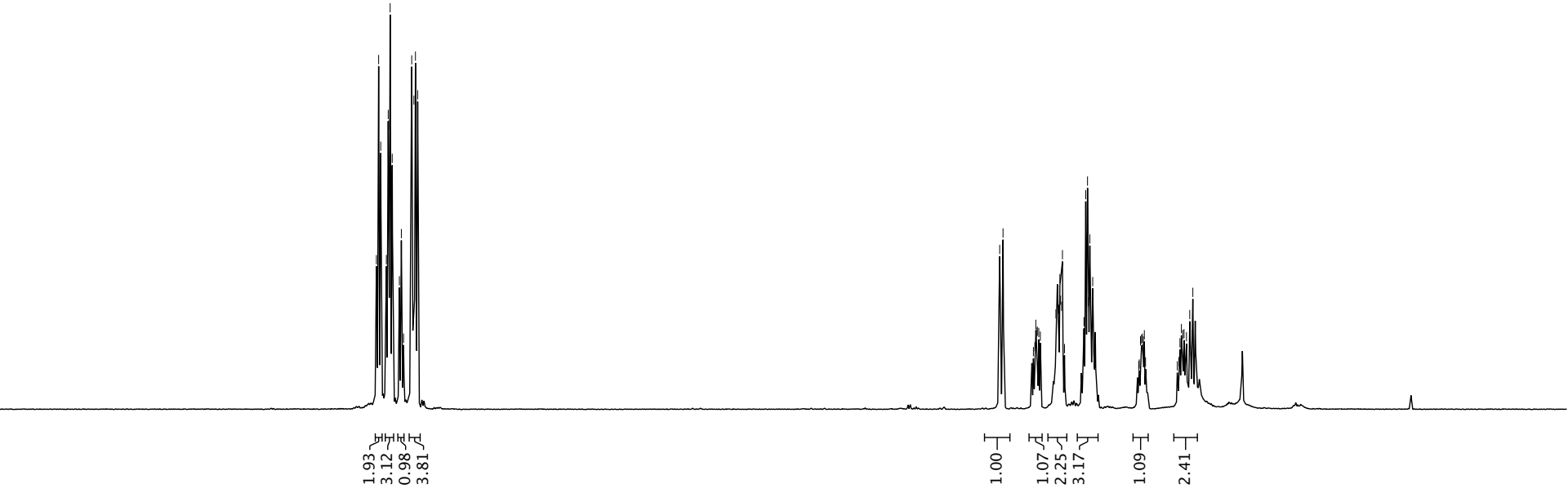


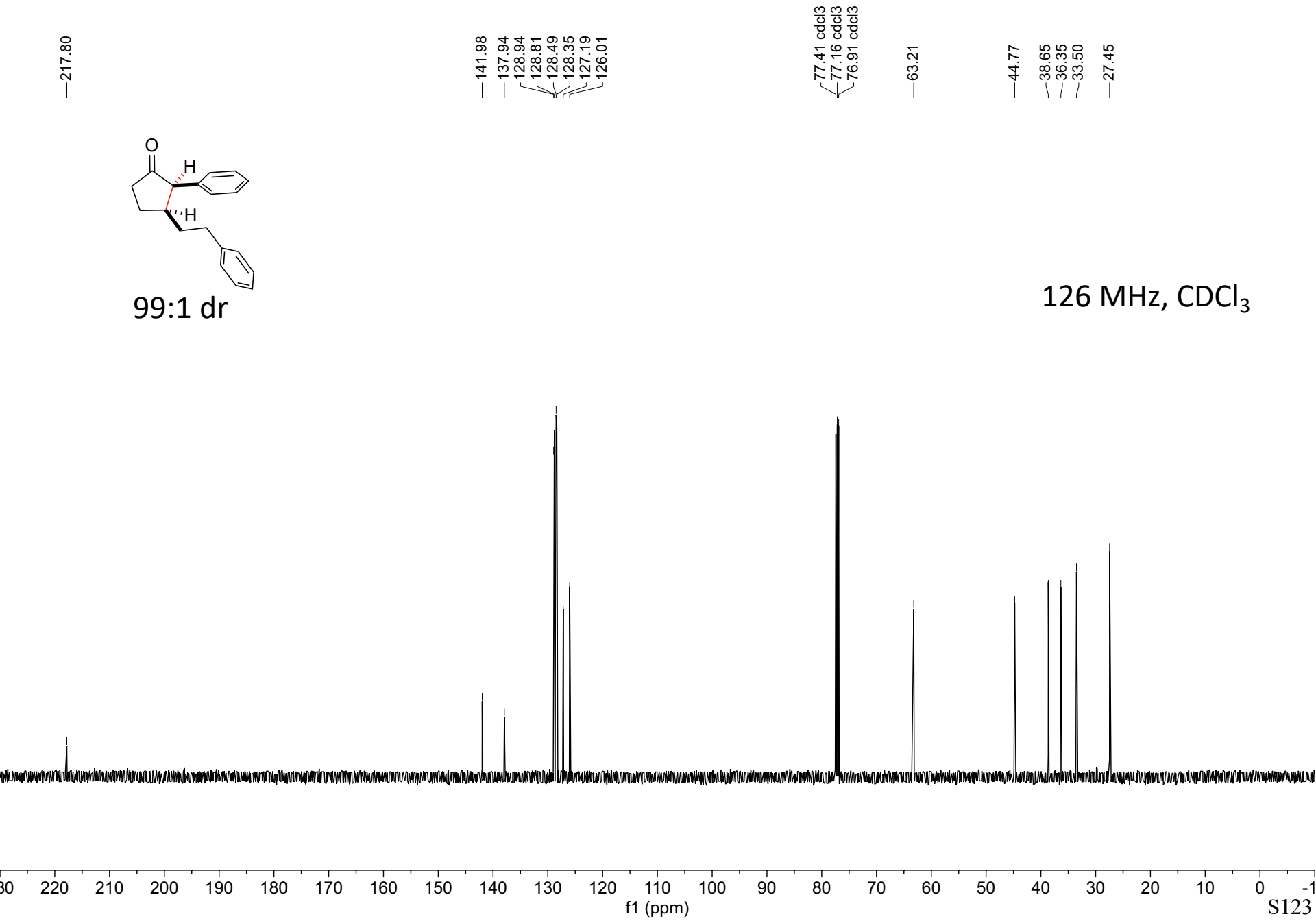




99:1 dr

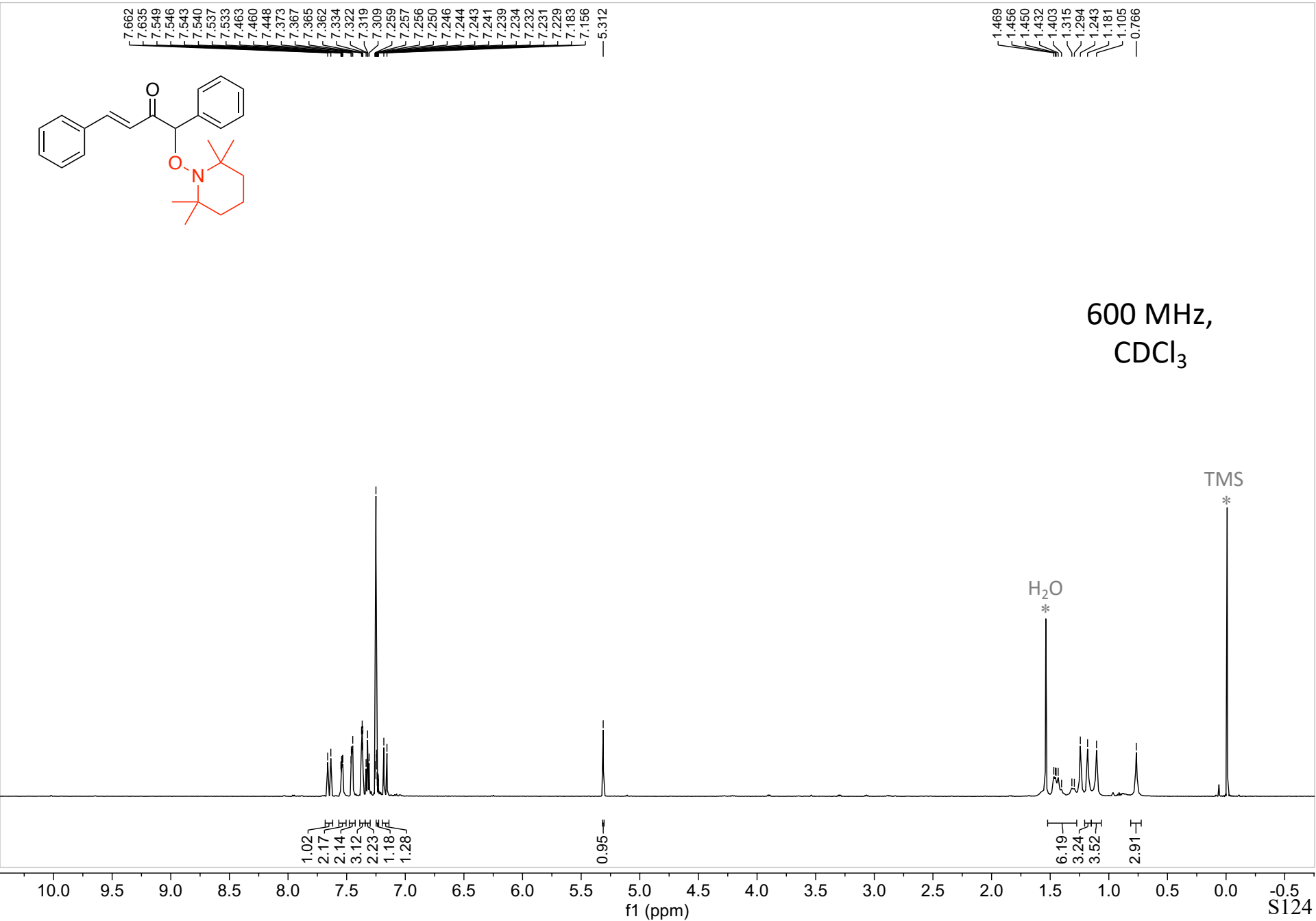
500 MHz, $CDCl_3$



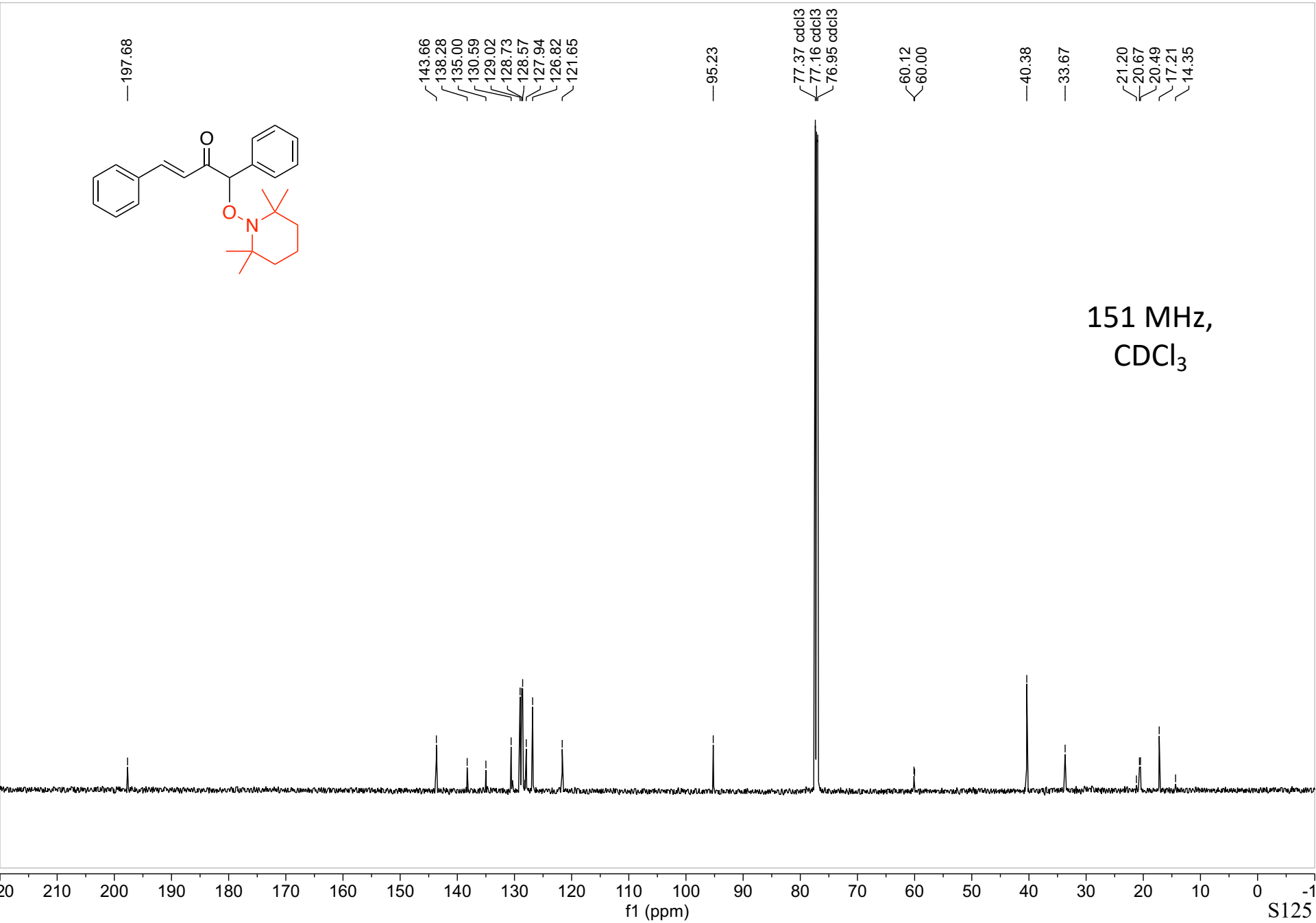
# $^{13}$C NMR 3-Phenethyl-2-phenylcyclopentan-1-one **(3w)**



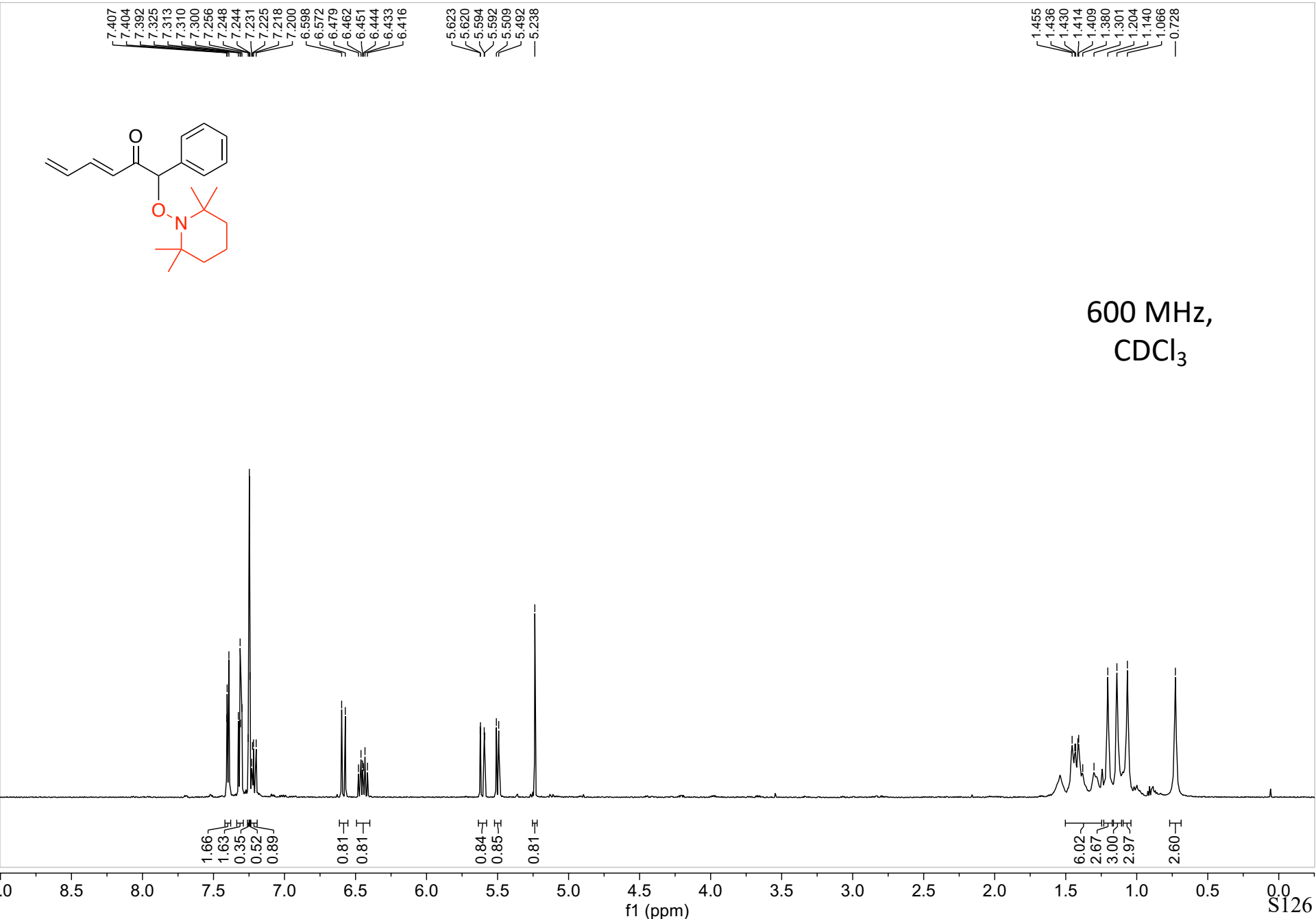
# $^1$H NMR (*E*)-1,4-Diphenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)but-3-en-2-one **(3a)**



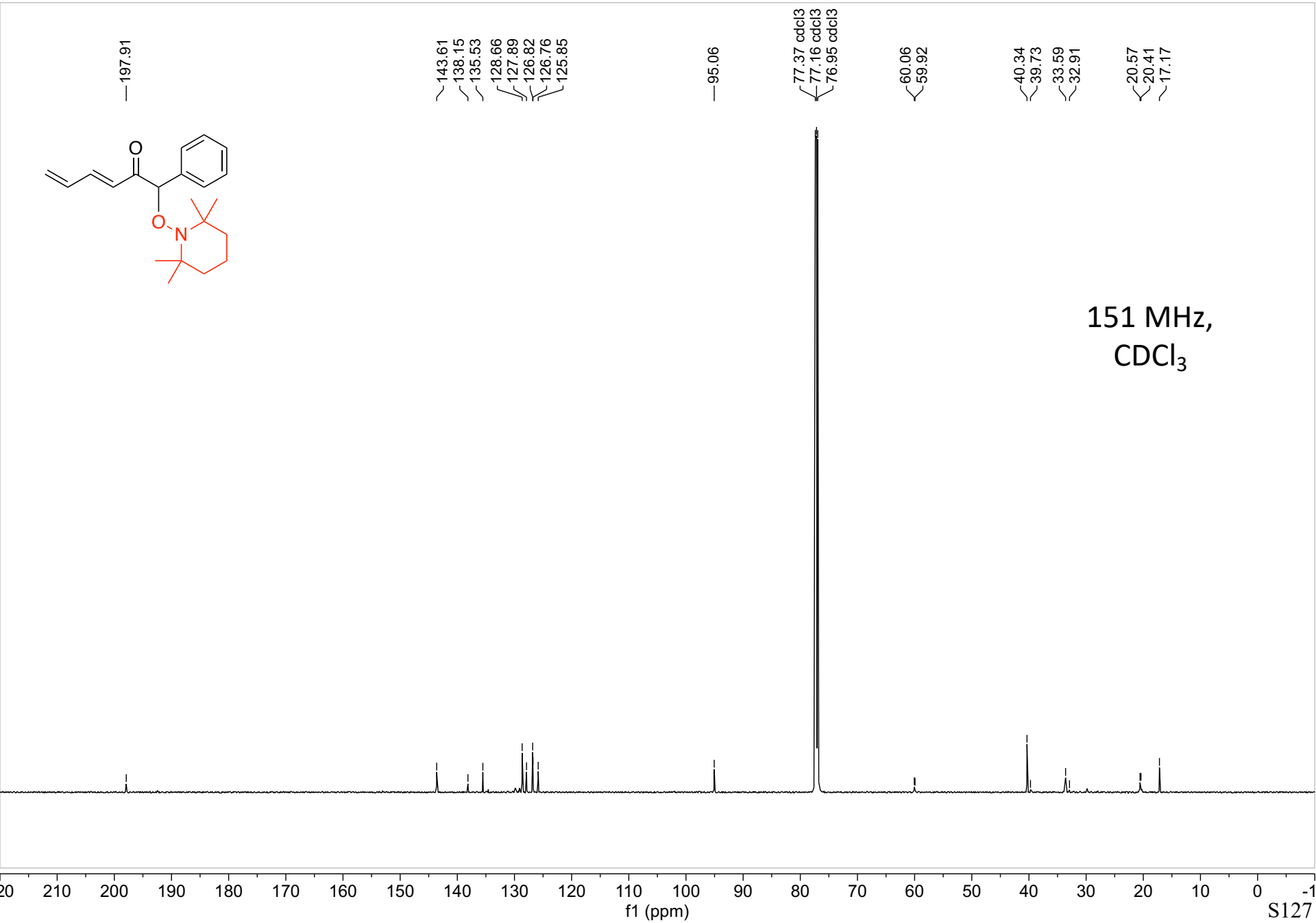
**$^{13}$C NMR** (*E*)-1,4-Diphenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)but-3-en-2-one **(3a)**



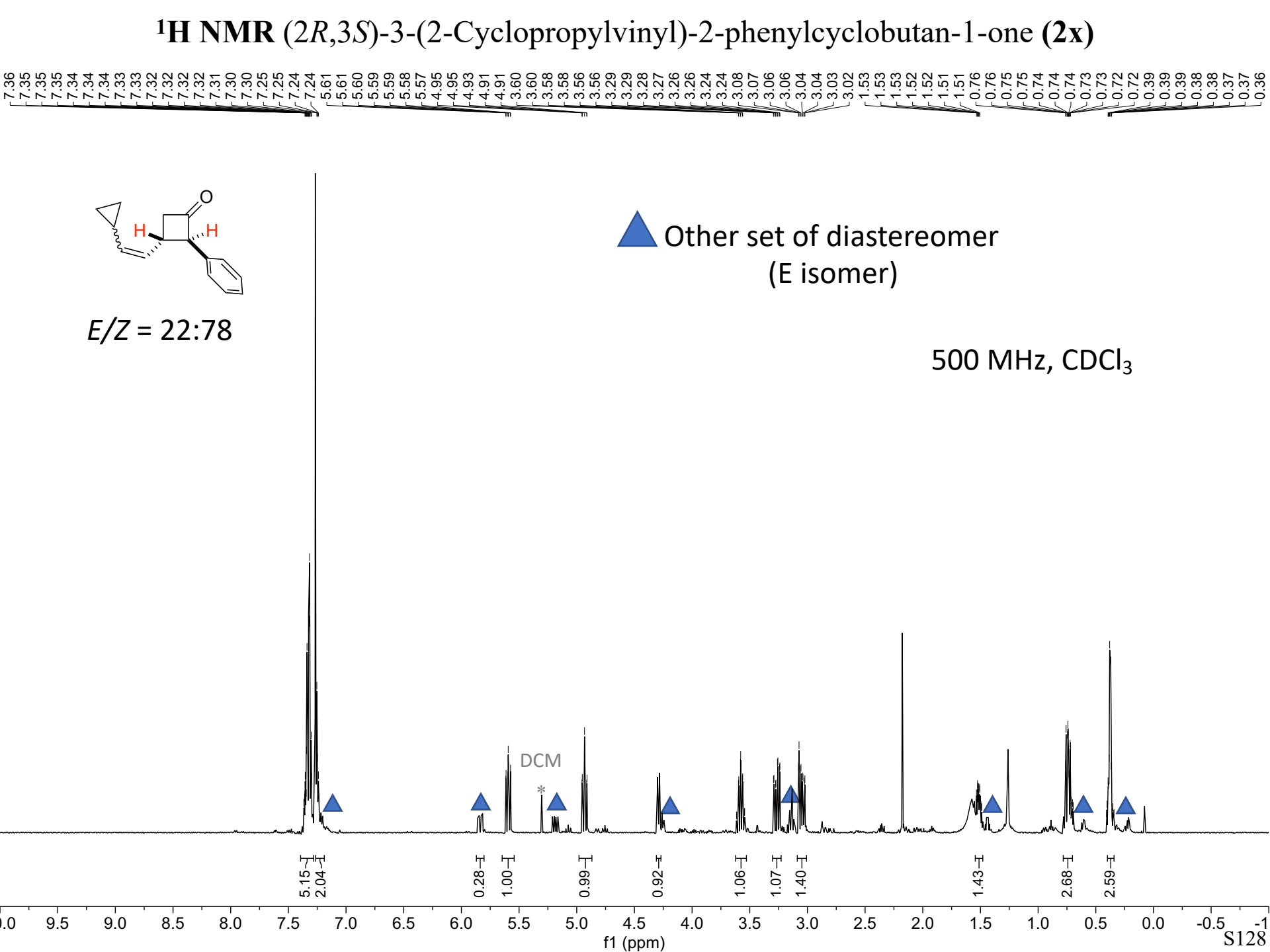
# $^1$H NMR (*E*)-1-Phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one (3v)



# $^{13}$C NMR (*E*)-1-Phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one (3v)

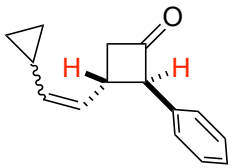


# $^1$H NMR (2*R*,3*S*)-3-(2-Cyclopropylvinyl)-2-phenylcyclobutan-1-one **(2x)**



# $^{13}$C NMR (2*R*,3*S*)-3-(2-Cyclopropylvinyl)-2-phenylcyclobutan-1-one **(2x)**

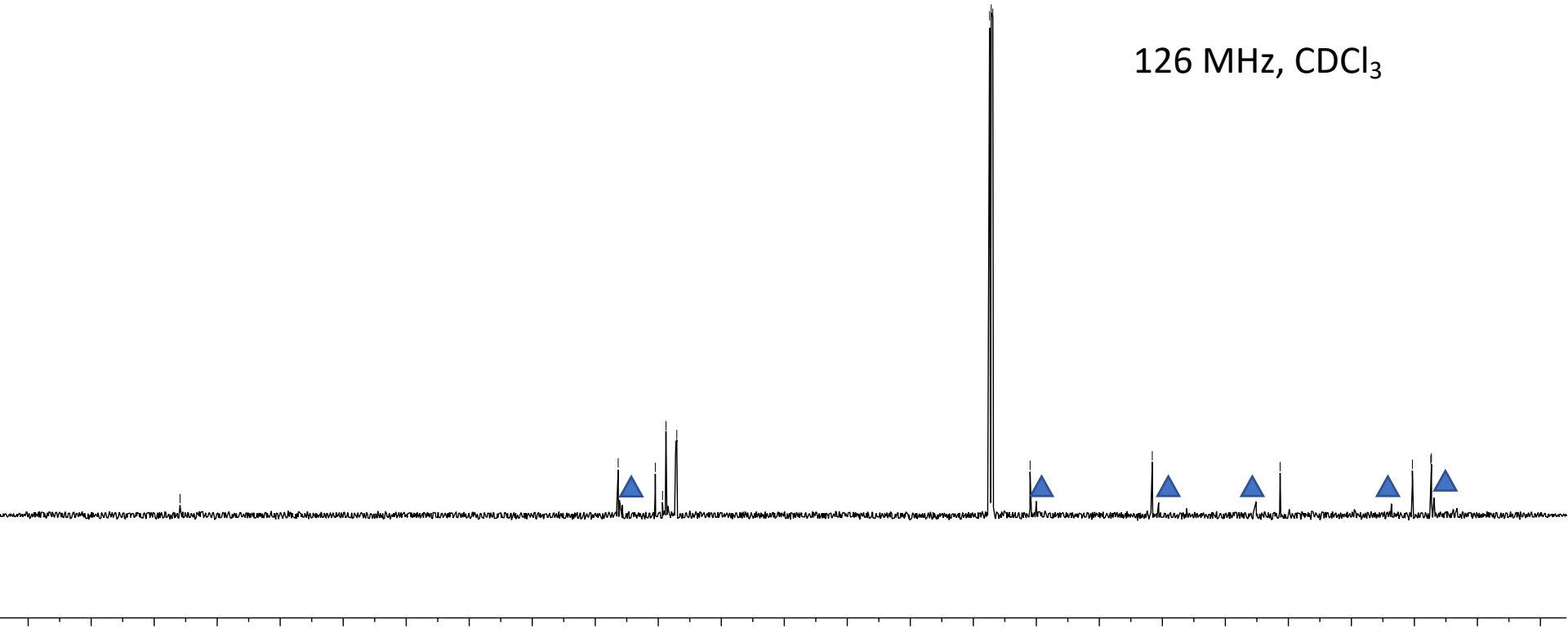
205.90
136.36
130.47
129.32
128.77
127.25
127.06
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
70.99
51.60
31.31
10.32
7.40
7.29



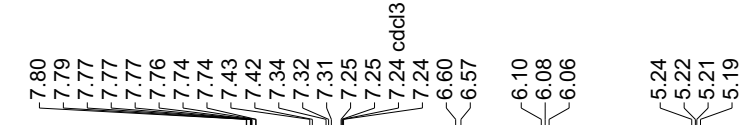

*E*/*Z* = 22:78

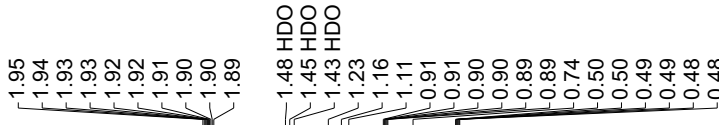
▲ Other set of diastereomer (E isomer)

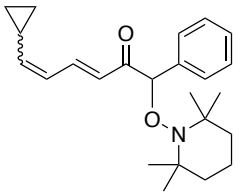
126 MHz, $CDCl_3$



**$^1$H NMR** (3*E*)-6-Cyclopropyl-1-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one **(3x)**



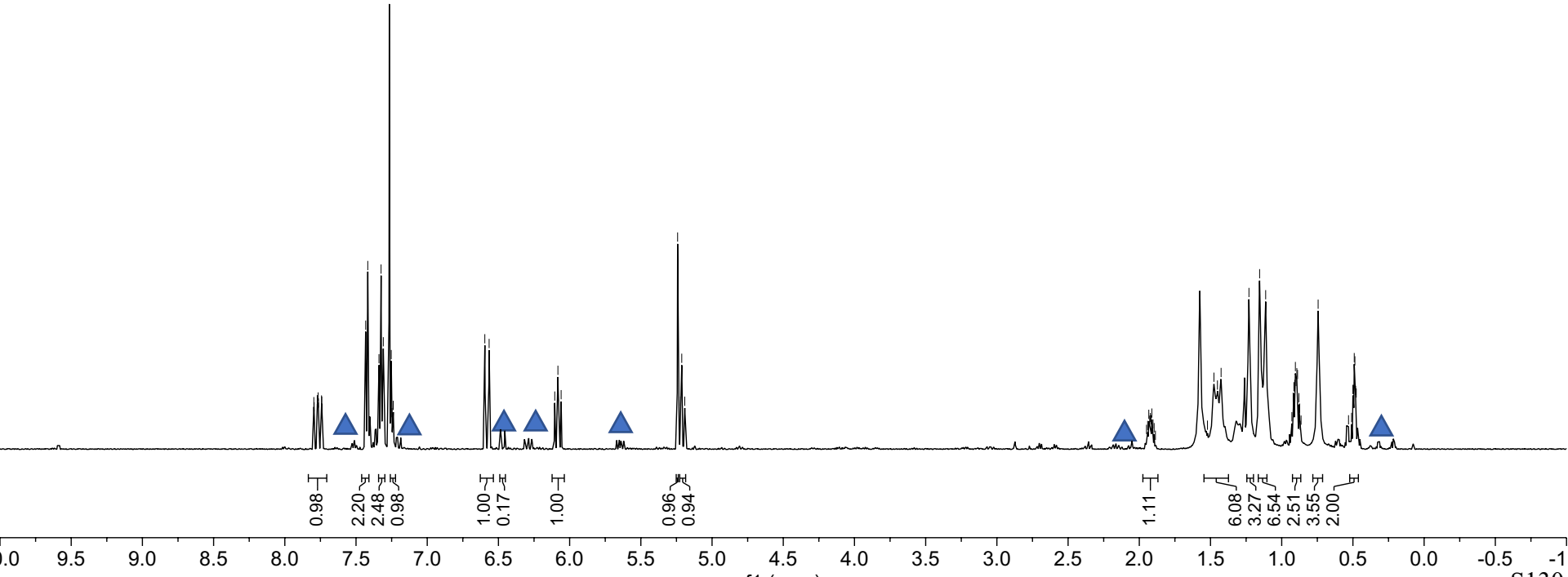



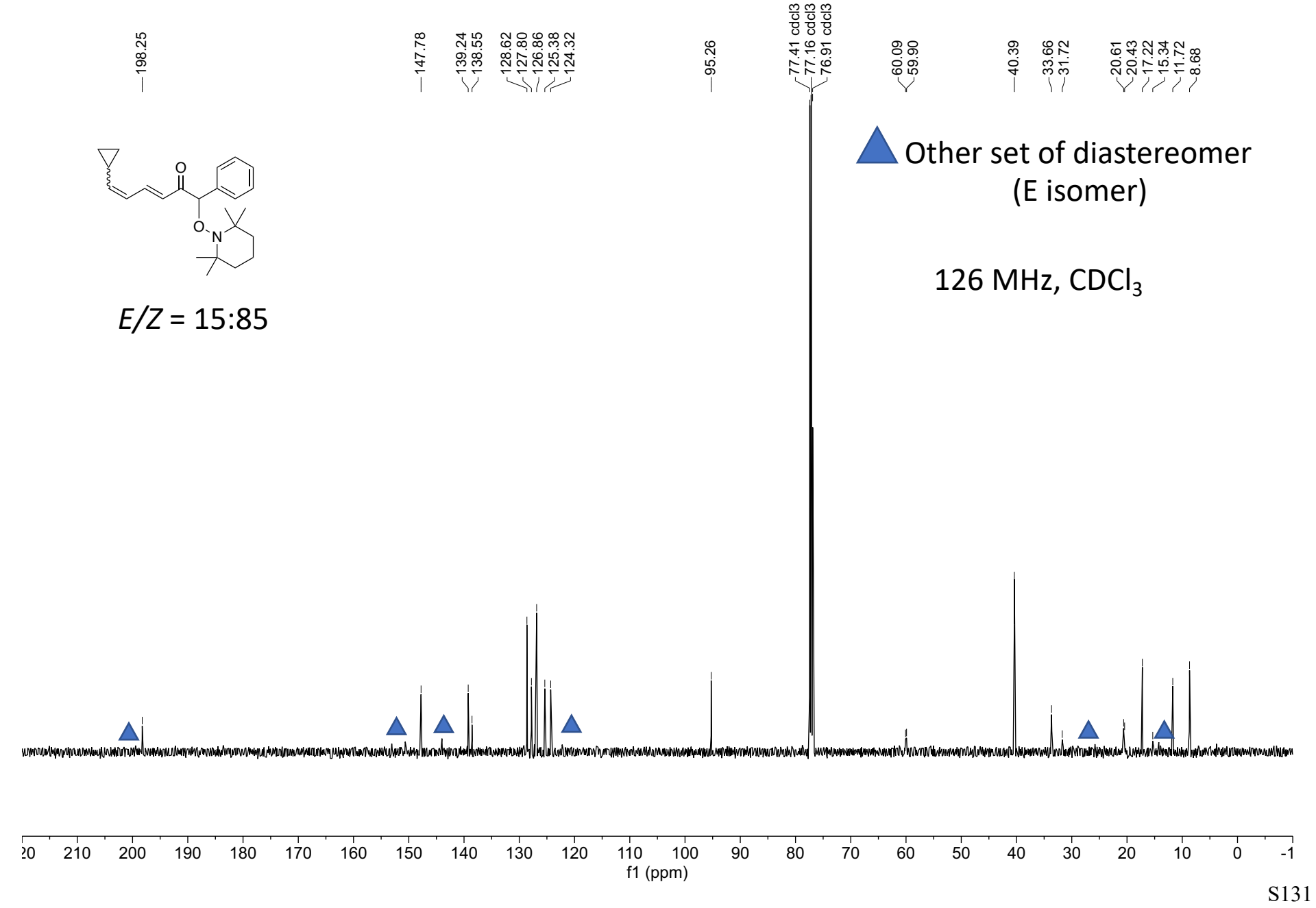

▲ Other set of diastereomer (E isomer)

*E*/*Z* = 15:85

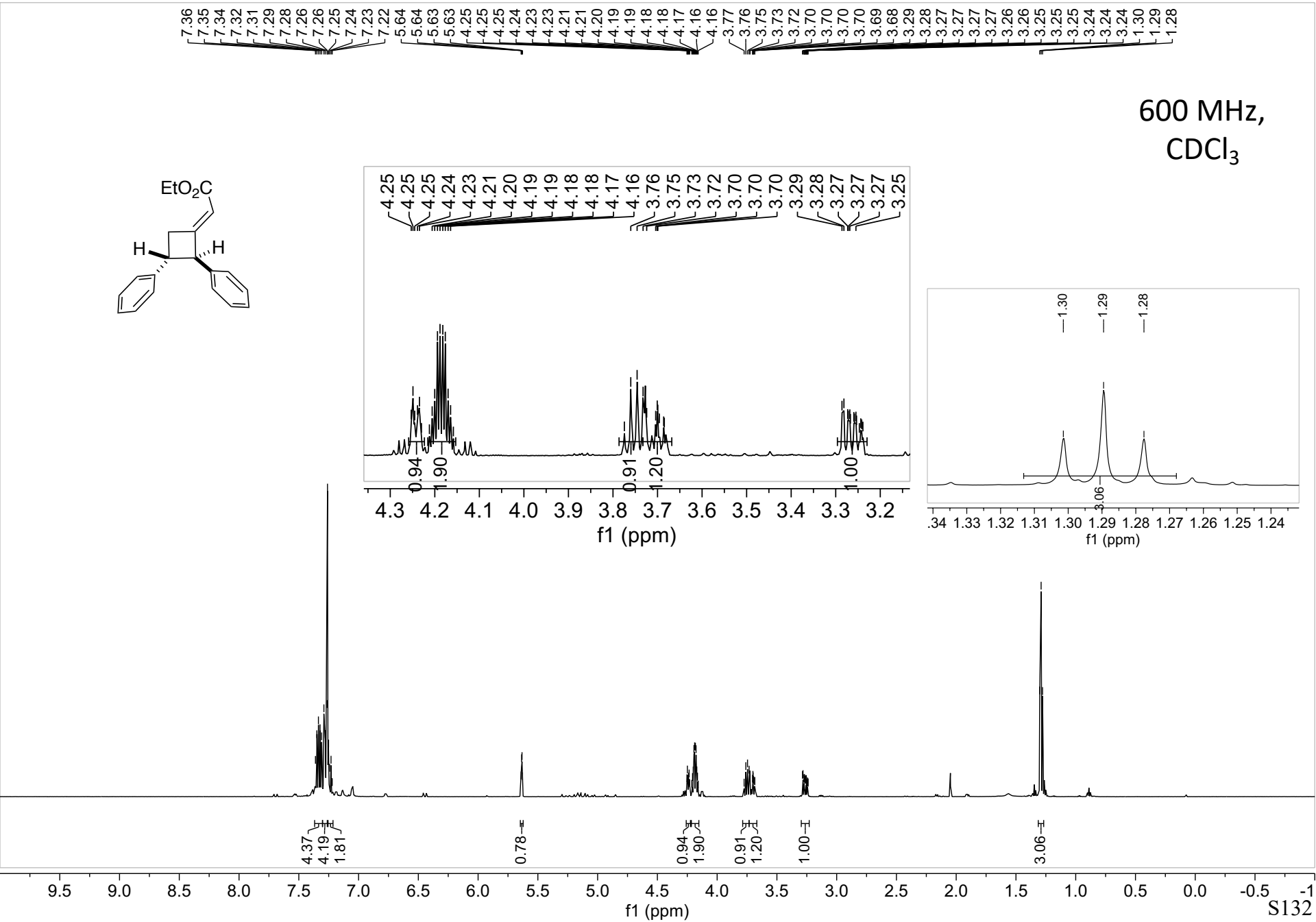
500 MHz, $CDCl_3$



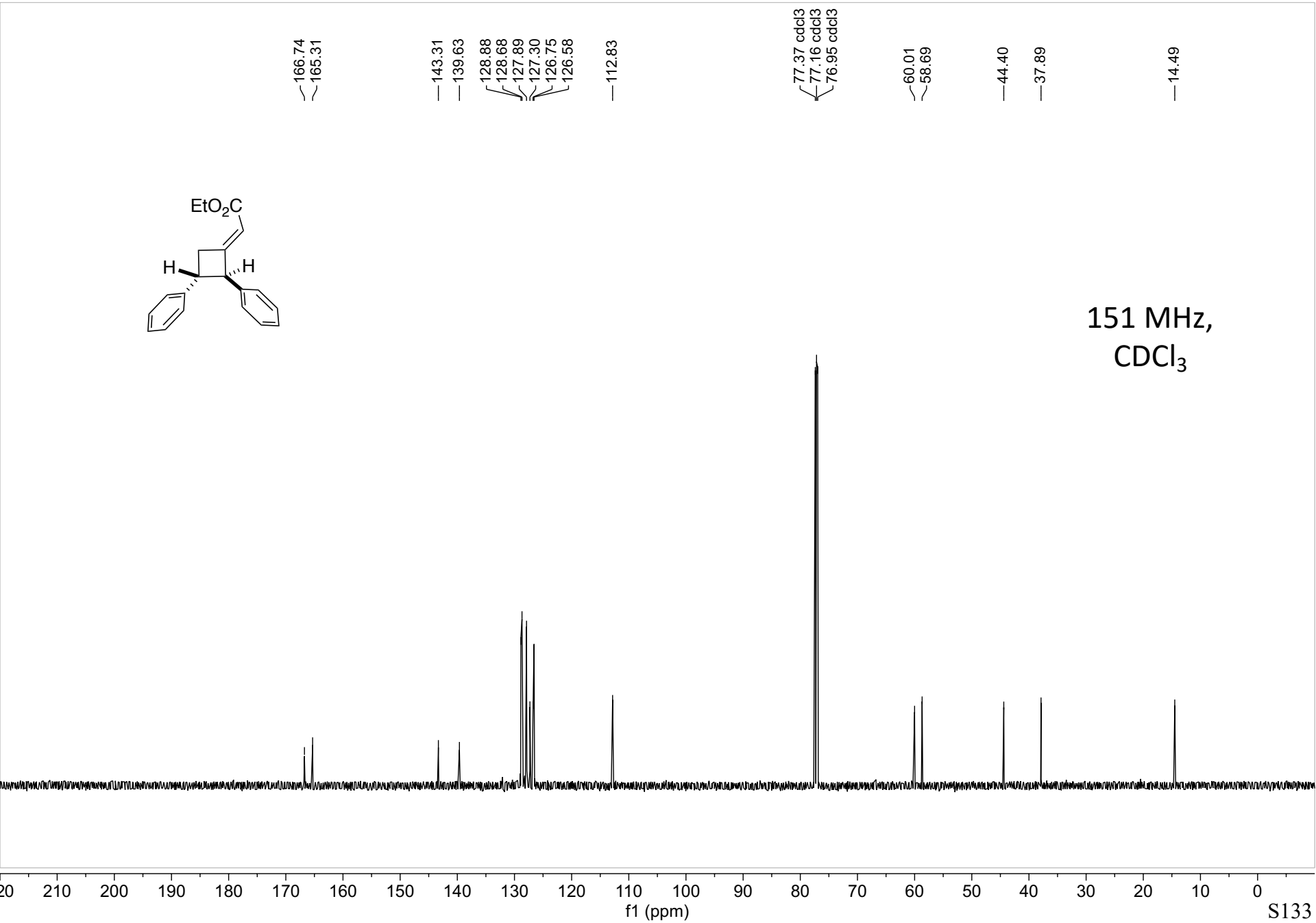
**$^{13}$C NMR** (3*E*)-6-Cyclopropyl-1-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)hexa-3,5-dien-2-one **(3x)**

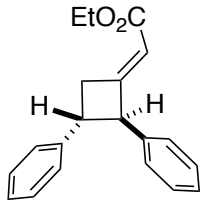


# $^1$H NMR ethyl (*E*)-2-((2*S*,3*R*)-2,3-diphenylcyclobutylidene)acetate (**4a**)

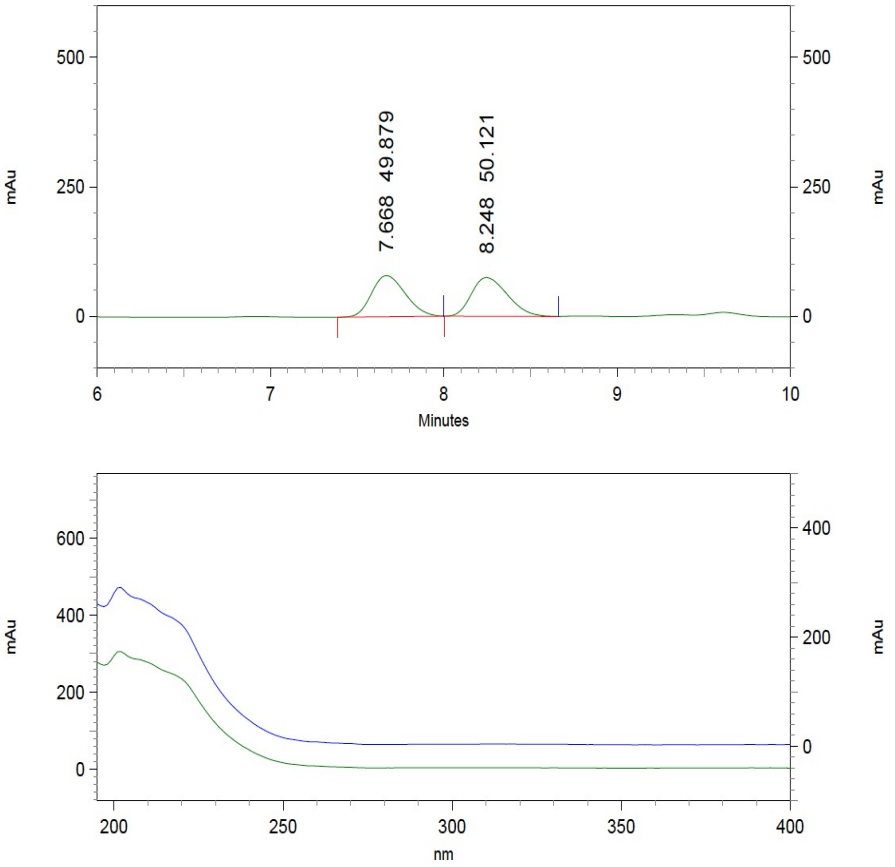


# $^{13}$C NMR ethyl (*E*)-2-((2*S*,3*R*)-2,3-diphenylcyclobutylidene)acetate (**4a**)



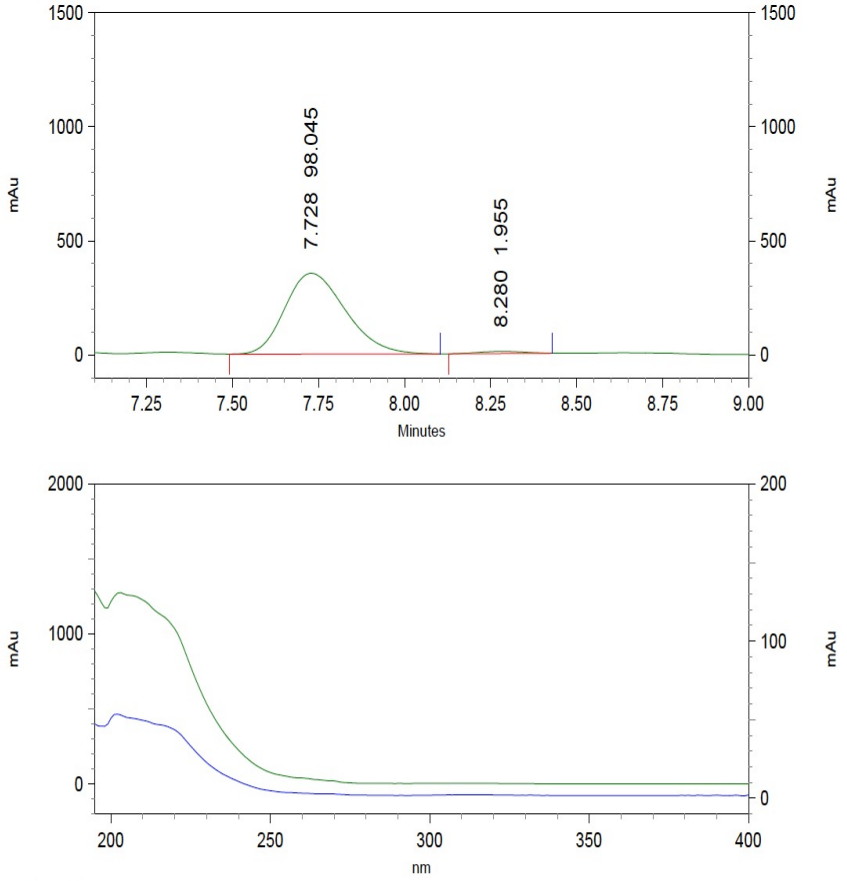



# **HPLC** ethyl (*E*)-2-((2*S*,3*R*)-2,3-diphenylcyclobutylidene)acetate (**4a**)




2: 235 nm, 4
nm Results

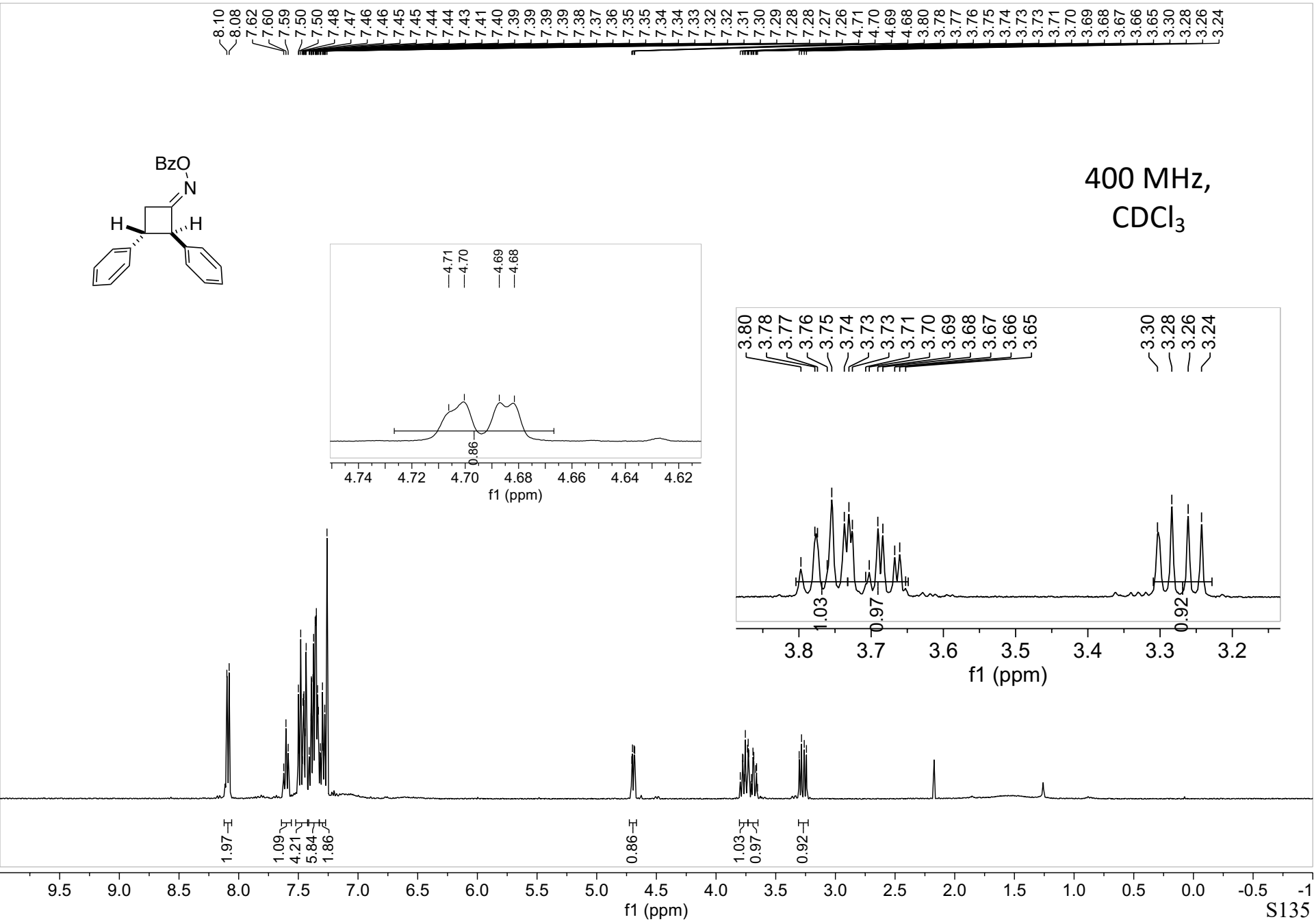
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.668 | 49.879 |
| 2 | 8.248 | 50.121 |
| Totals | | 100.000 |



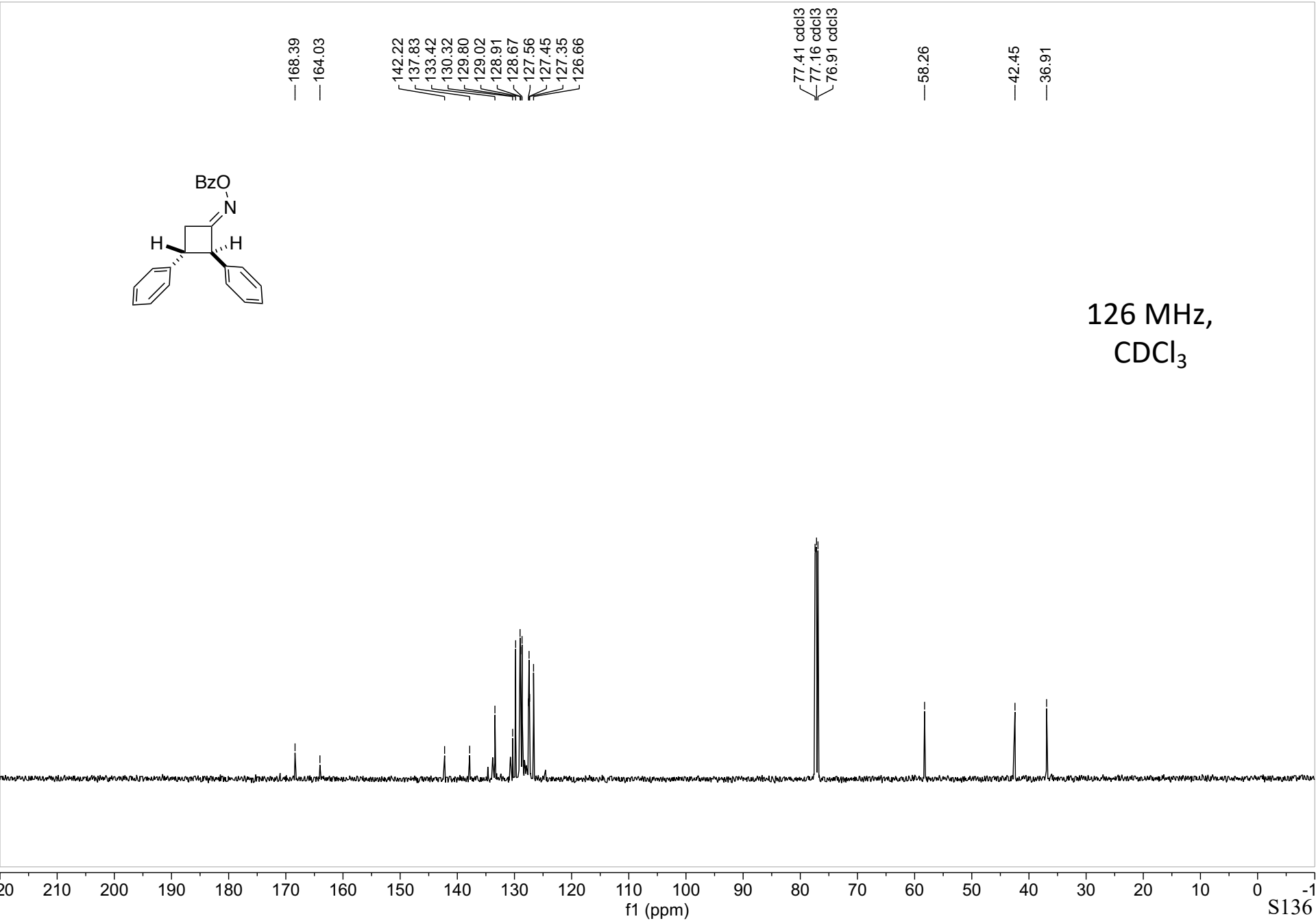

2: 235 nm, 4
nm Results

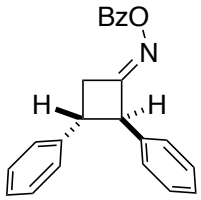
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.728 | 98.045 |
| 2 | 8.280 | 1.955 |
| Totals | | 100.000 |

# $^1$H NMR (2*R*,3*R*,*E*)-2,3-diphenylcyclobutan-1-one *O*-benzoyl oxime (**5a**)



# $^{13}$C NMR (2*R*,3*R*,*E*)-2,3-diphenylcyclobutan-1-one *O*-benzoyl oxime (**5a**)



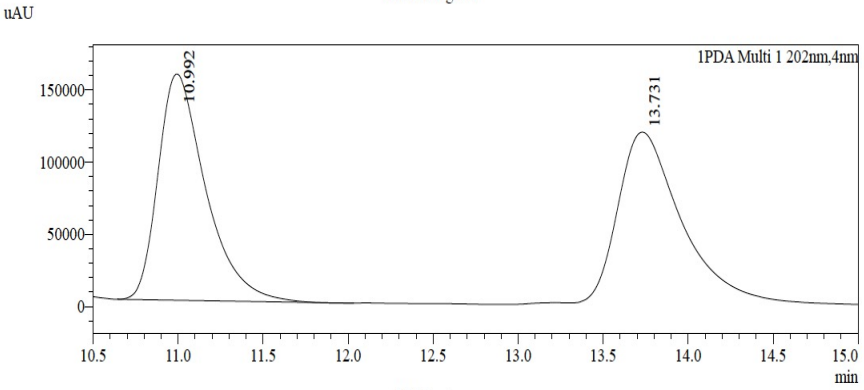



# **HPLC** (2*R*,3*R*,*E*)-2,3-diphenylcyclobutan-1-one *O*-benzoyl oxime (**5a**)

Sample Information

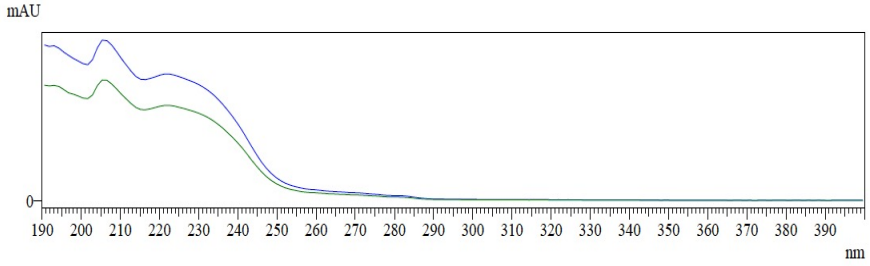
| | |
|---|---|
| Sample Name | : JJX-2728P-ADH-20%-0.8ML-L001 |
| Sample ID | : JJX-2728P-ADH-20%-0.8ML-L001 |
| Data File | : JJX-2728P-ADH-20%-0.8ML-L001.lcd |
| Method File | : dsw-20%0.8mL60MIN.lcm |
| Date Acquired | : 1/21/2021 8:41:15 PM |

Chromatogram




UV Spectrum

JJX-2728P-ADH-20%-0.8ML-L001.lcd




Peak Table

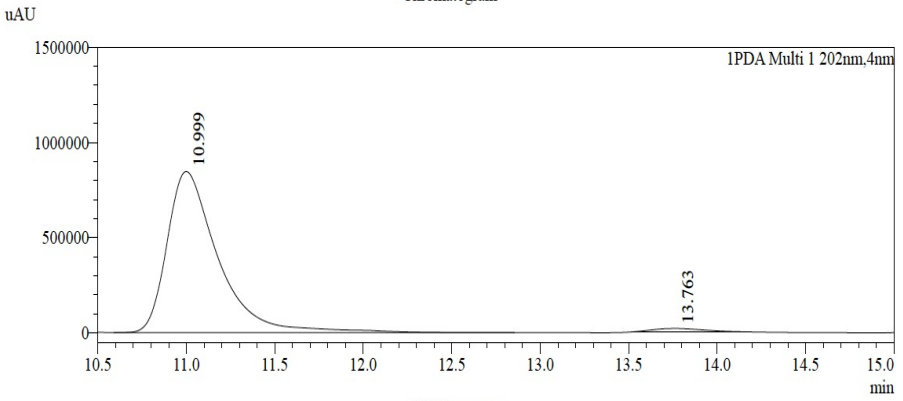
PDA Ch1 202nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 10.992 | 3048423 | 49.565 |
| 2 | 13.731 | 3101937 | 50.435 |
| Total | | 6150360 | 100.000 |

Sample Information

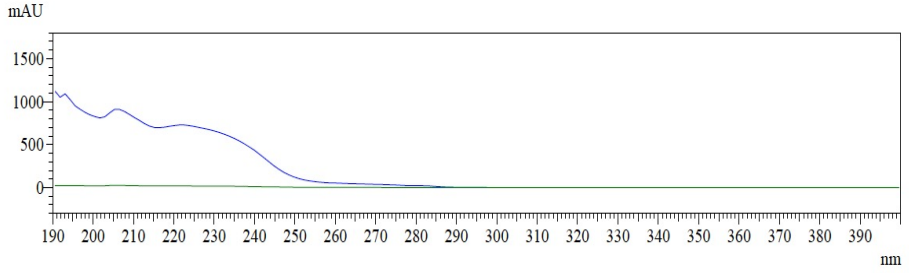
| | |
|---|---|
| Sample Name | : JJX-2735P-ADH-20%-0.8ML-L002 |
| Sample ID | : JJX-2735P-ADH-20%-0.8ML-L002 |
| Data File | : JJX-2735P-ADH-20%-0.8ML-L002.lcd |
| Method File | : dsw-20%0.8mL60MIN.lcm |
| Date Acquired | : 1/21/2021 9:01:41 PM |

Chromatogram




UV Spectrum

JJX-2735P-ADH-20%-0.8ML-L002.lcd

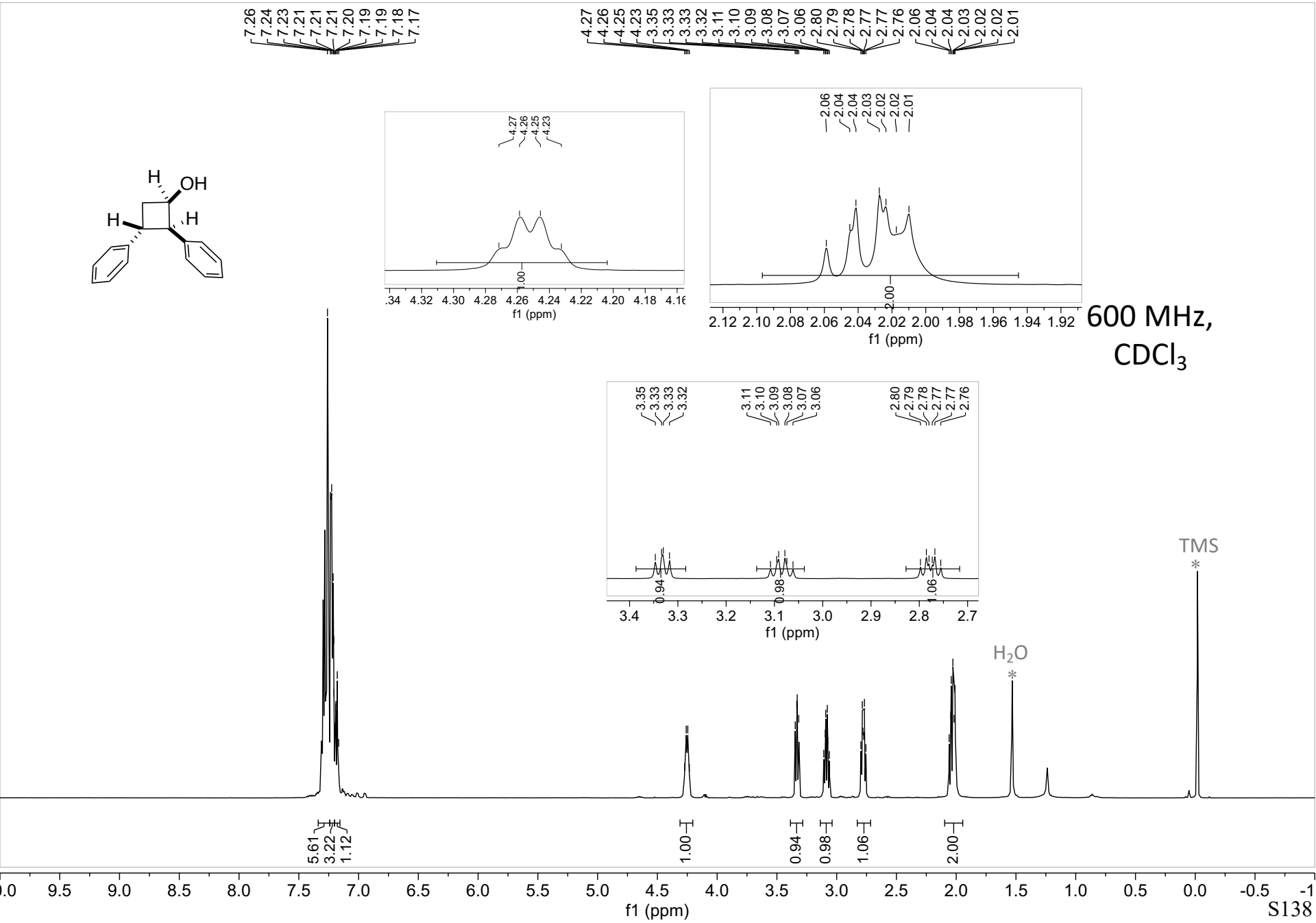



Peak Table

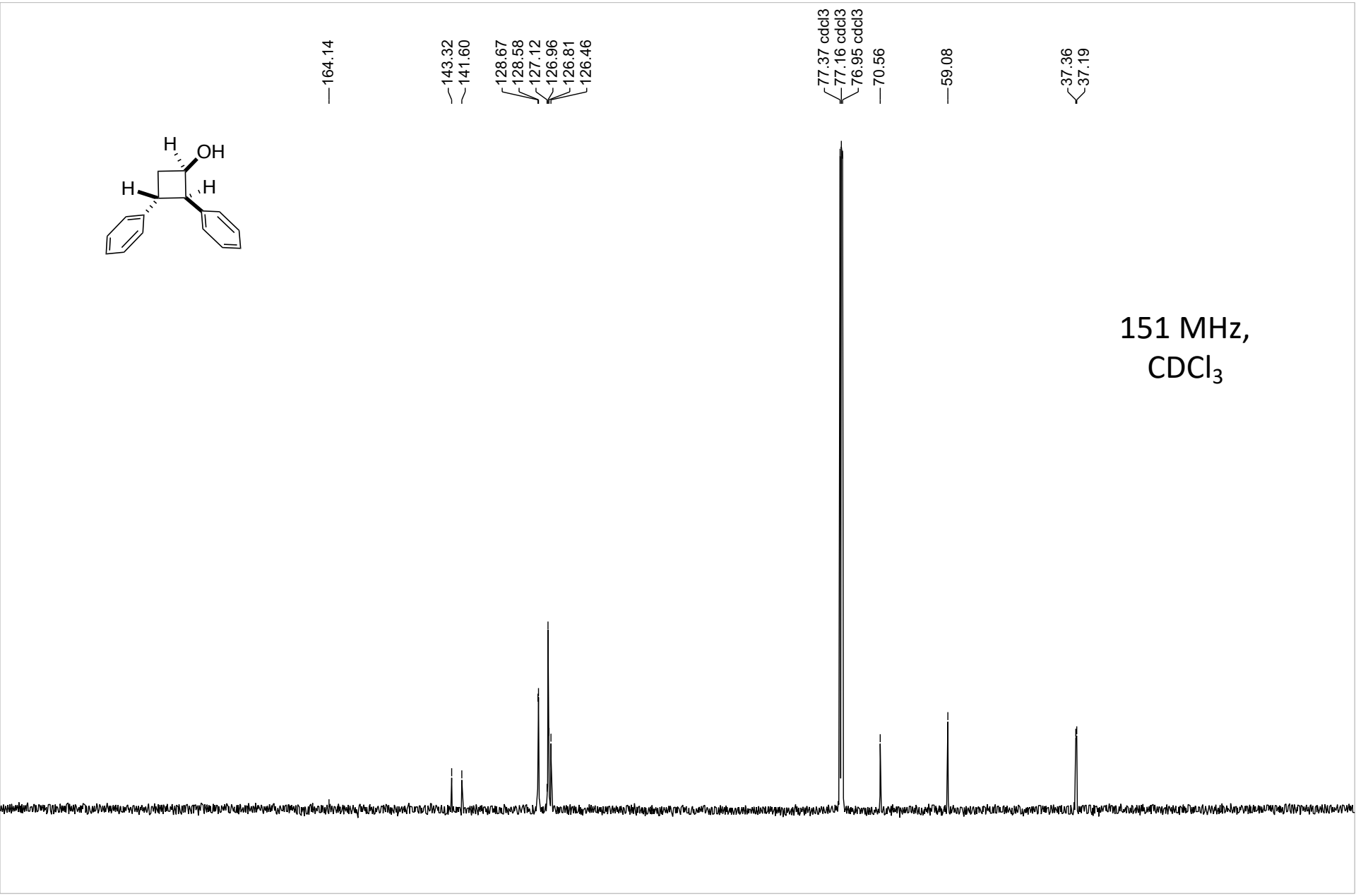
PDA Ch1 202nm

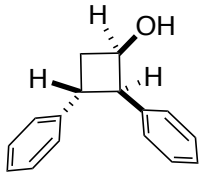
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 10.999 | 17049491 | 97.927 |
| 2 | 13.763 | 360891 | 2.073 |
| Total | | 17410382 | 100.000 |

# $^1$H NMR (1*R*,2*R*,3*R*)-2,3-diphenylcyclobutan-1-ol **(6a)**

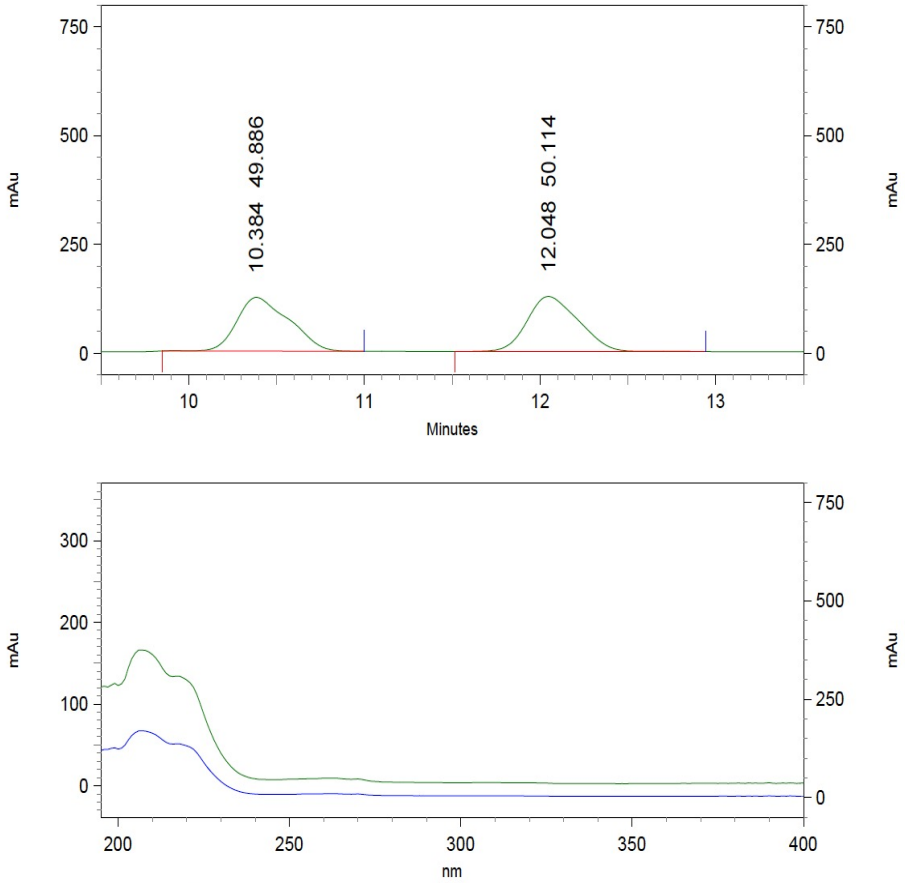


# $^{13}$C NMR (1*R*,2*R*,3*R*)-2,3-diphenylcyclobutan-1-ol **(6a)**



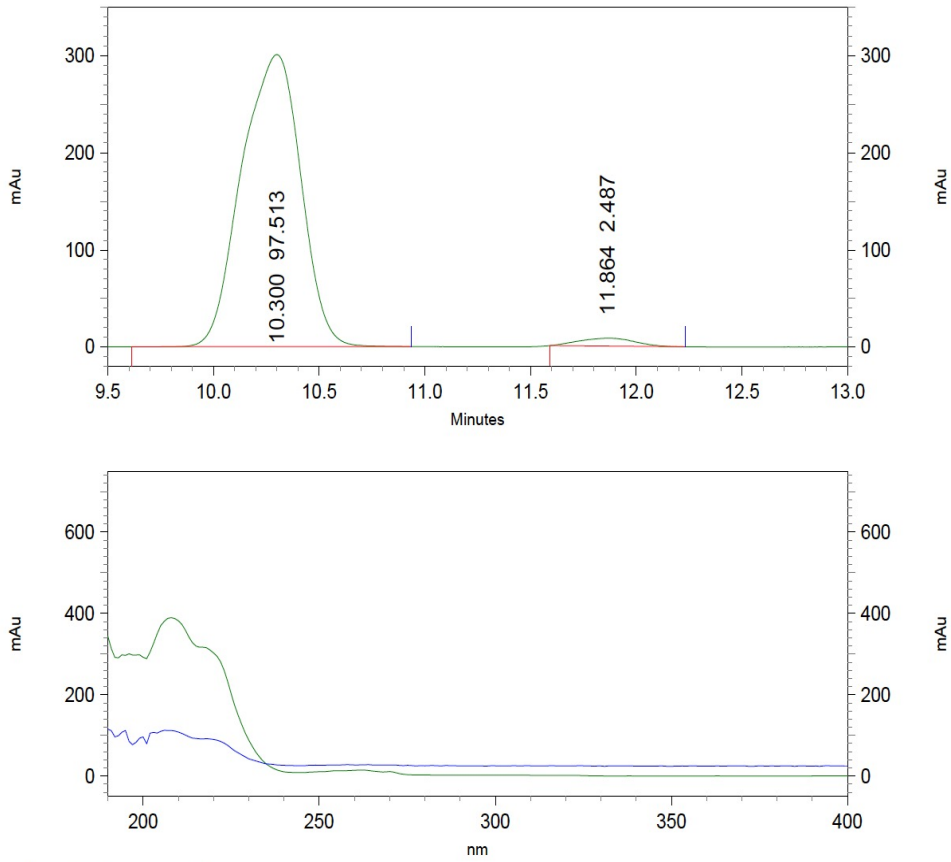



# **HPLC** (1*R*,2*R*,3*R*)-2,3-diphenylcyclobutan-1-ol **(6a)**




4: 220 nm, 4
nm Results

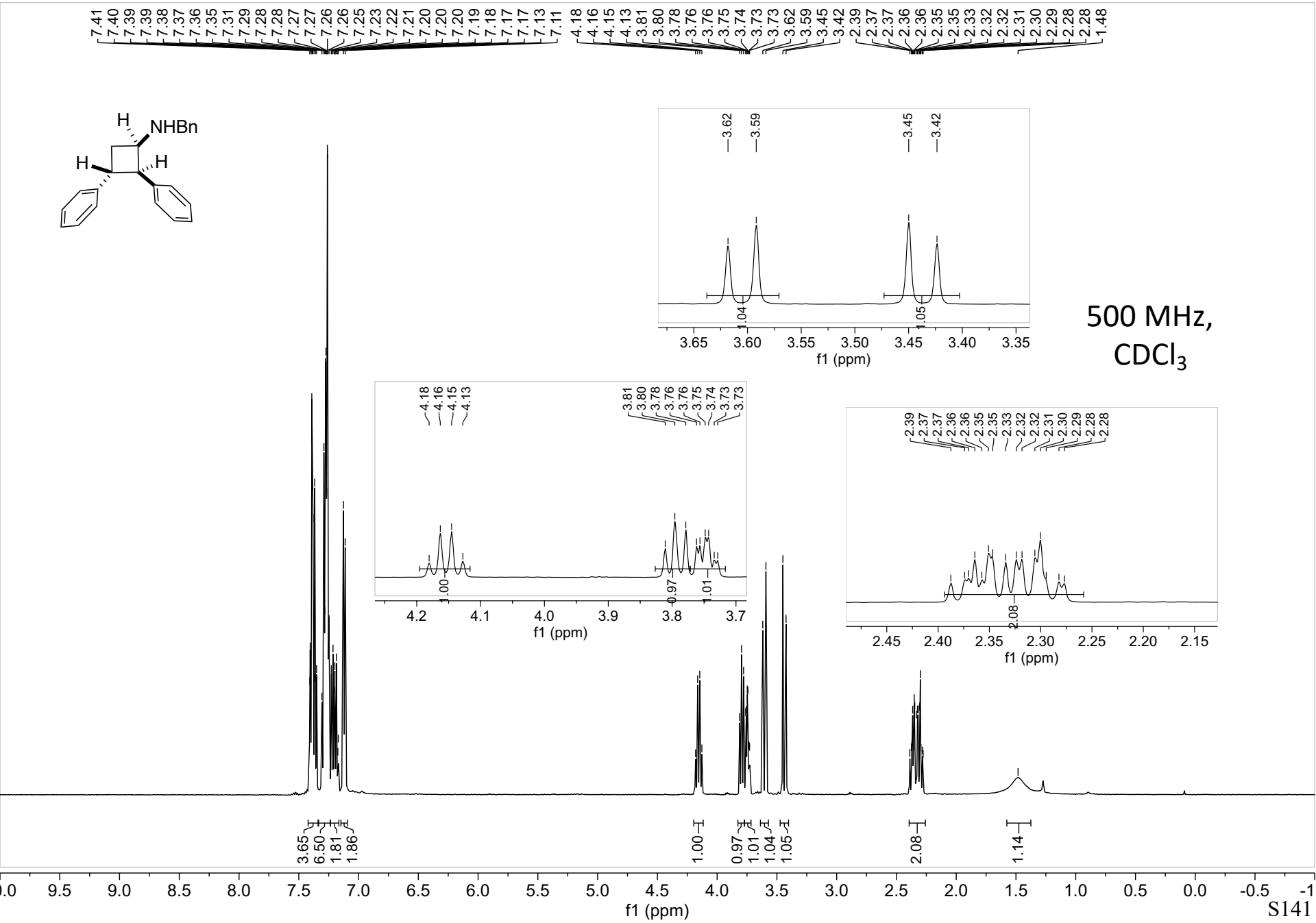
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.384 | 49.886 |
| 2 | 12.048 | 50.114 |
| Totals | | 100.000 |



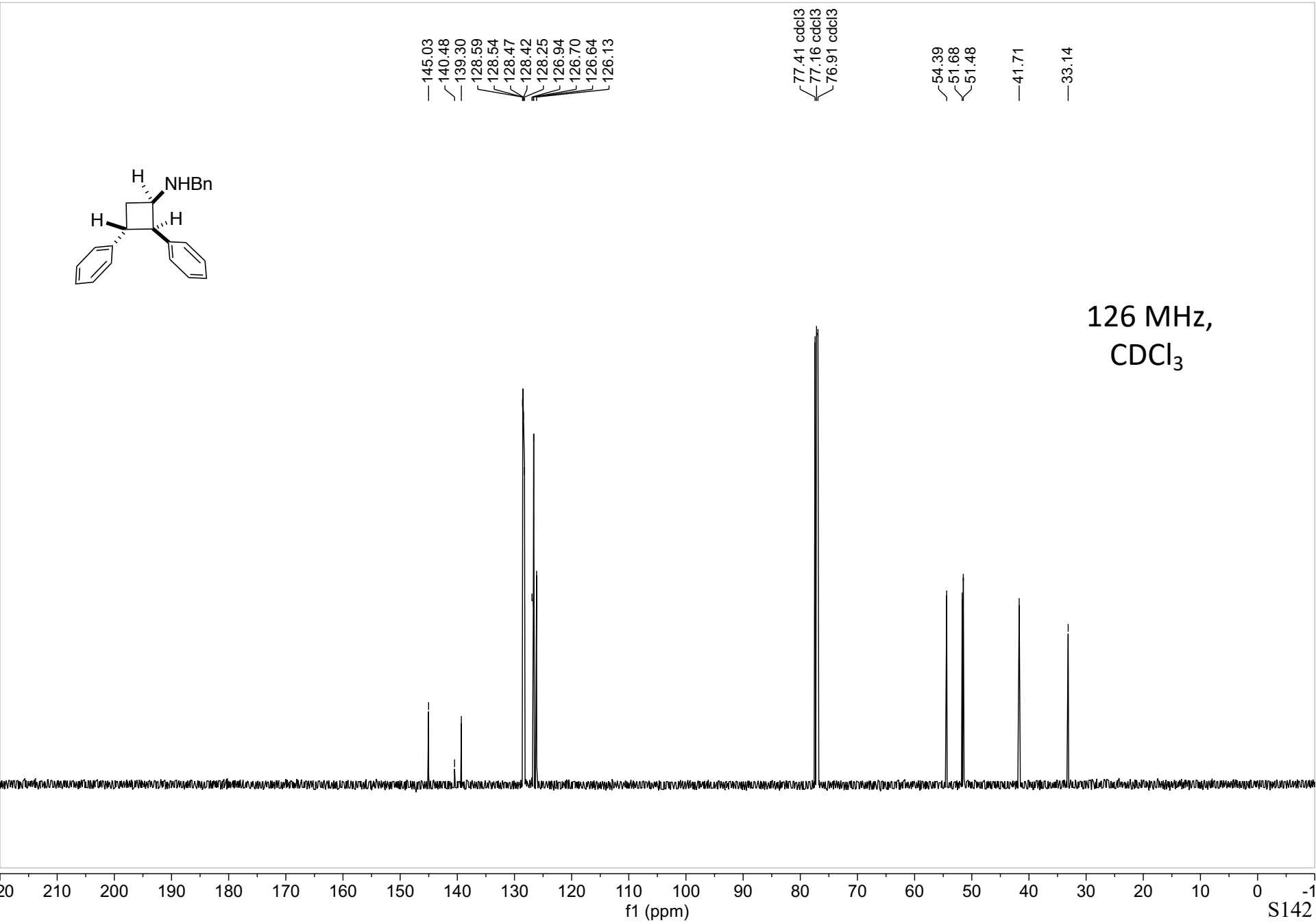

4: 220 nm, 4
nm Results

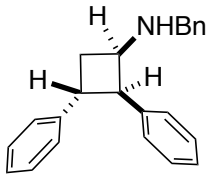
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.300 | 97.513 |
| 2 | 11.864 | 2.487 |
| Totals | | 100.000 |

# $^{1}$H NMR (2*R*,3*R*)-*N*-benzyl-2,3-diphenylcyclobutan-1-amine **(7a)**

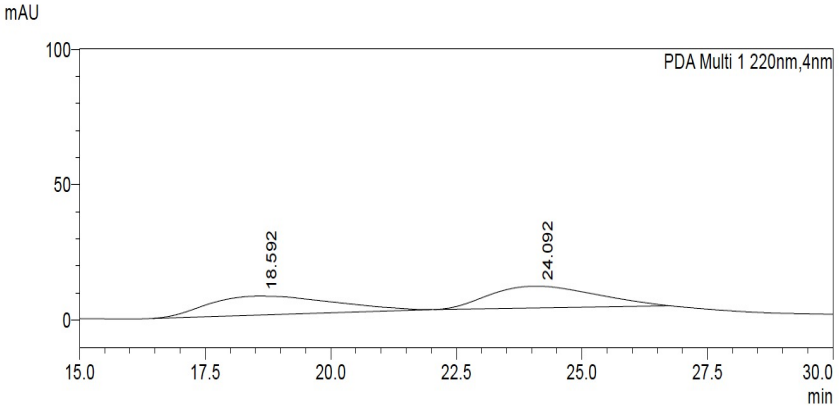


# $^{13}$C NMR (2*R*,3*R*)-*N*-benzyl-2,3-diphenylcyclobutan-1-amine **(7a)**





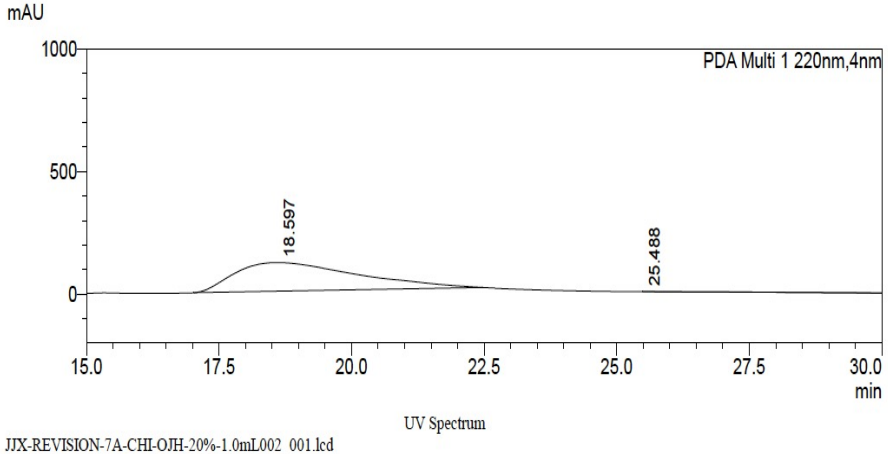

# **HPLC** (2*R*,3*R*)-*N*-benzyl-2,3-diphenylcyclobutan-1-amine **(7a)**




Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 18.592 | 50.269 |
| 2 | 24.092 | 49.731 |
| Total | | 100.000 |

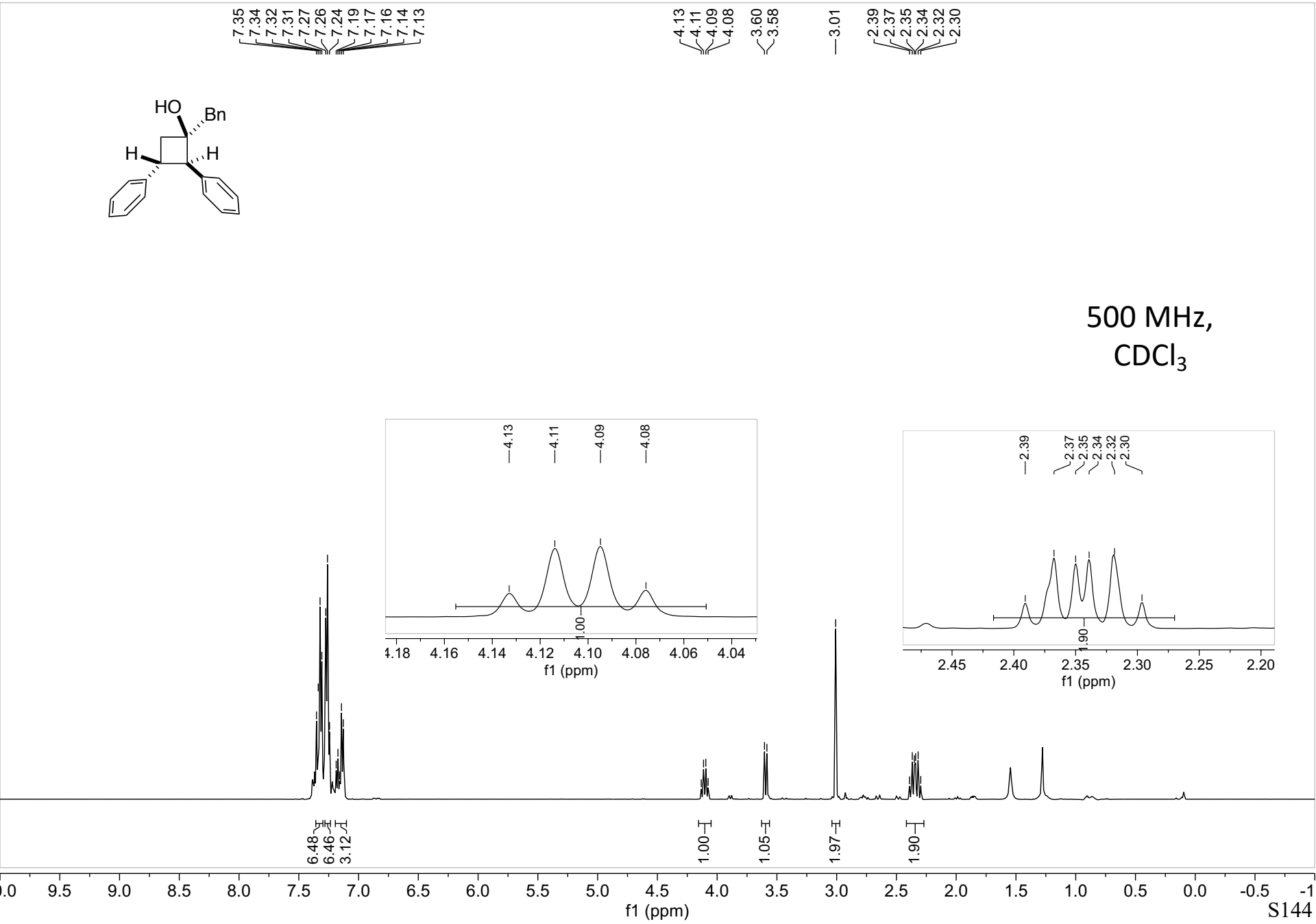



Peak Table

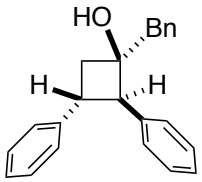
PDA Ch1 220nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 18.597 | 99.021 |
| 2 | 25.488 | 0.979 |
| Total | | 100.000 |

# **$^1$H NMR** (1*R*,2*R*,3*R*)-1-benzyl-2,3-diphenylcyclobutan-1-ol **(8a)**



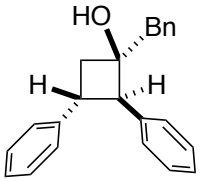
# $^{13}$C NMR (1*R*,2*R*,3*R*)-1-benzyl-2,3-diphenylcyclobutan-1-ol **(8a)**




144.32
137.60
137.04
130.22
128.79
128.64
128.56
128.46
127.15
126.78
126.59
126.25
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
76.59
56.28
48.26
38.89
38.47

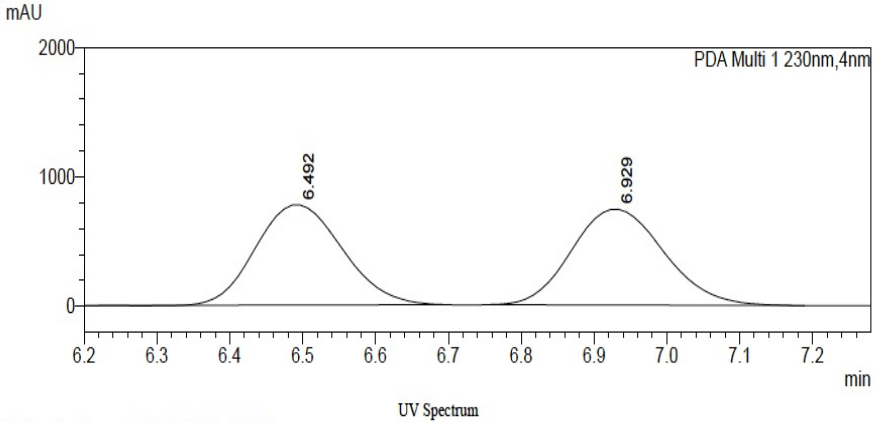
151 MHz,
$CDCl_3$

f1 (ppm)



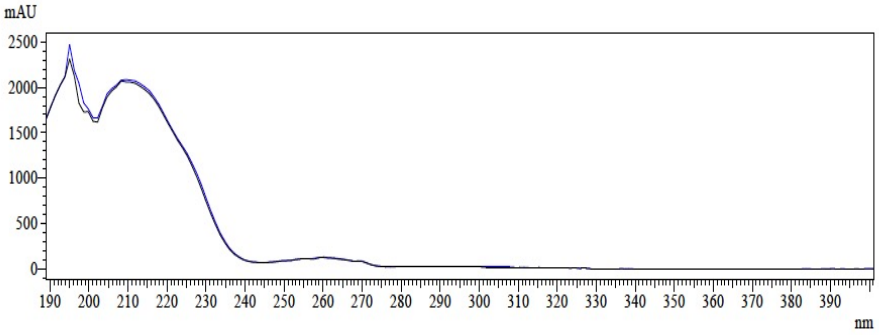

# **HPLC** (1*R*,2*R*,3*R*)-1-benzyl-2,3-diphenylcyclobutan-1-ol **(8a)**

Sample Name : JJX-revision-8a-rac-ic-5%0.8mL001




UV Spectrum

JJX-revision-8a-rac-ic-5%0.8mL001_002.lcd

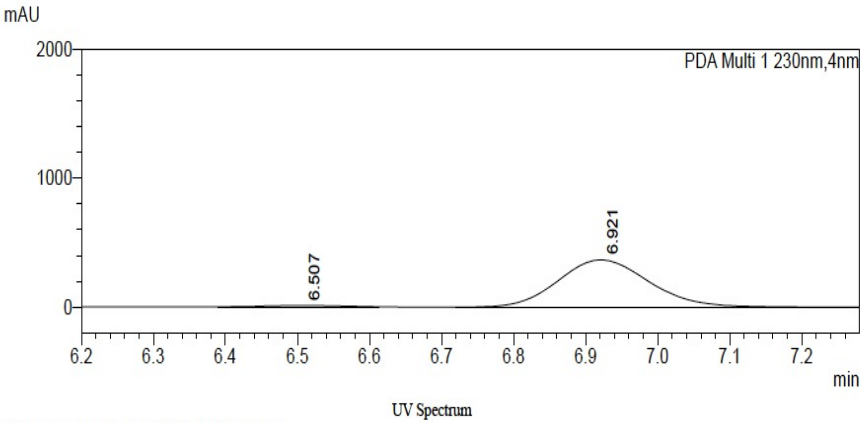



Peak Table

PDA Ch1 230nm

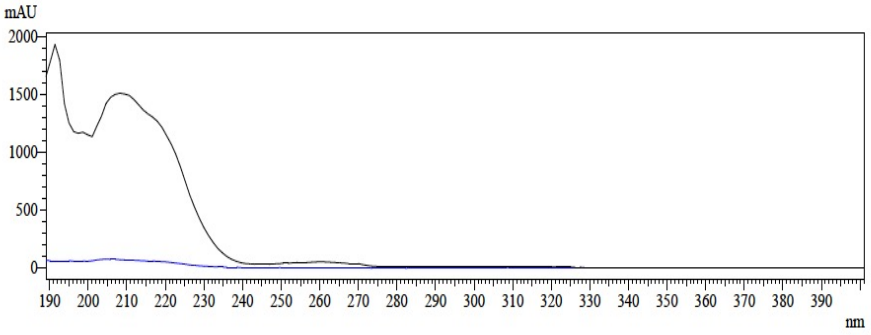
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.492 | 49.448 |
| 2 | 6.929 | 50.552 |
| Total | | 100.000 |

Sample Name : JJX-revision-8a-chiral-ic-5%0.8mL002




UV Spectrum

JJX-revision-8a-chiral-ic-5%0.8mL002_004.lcd

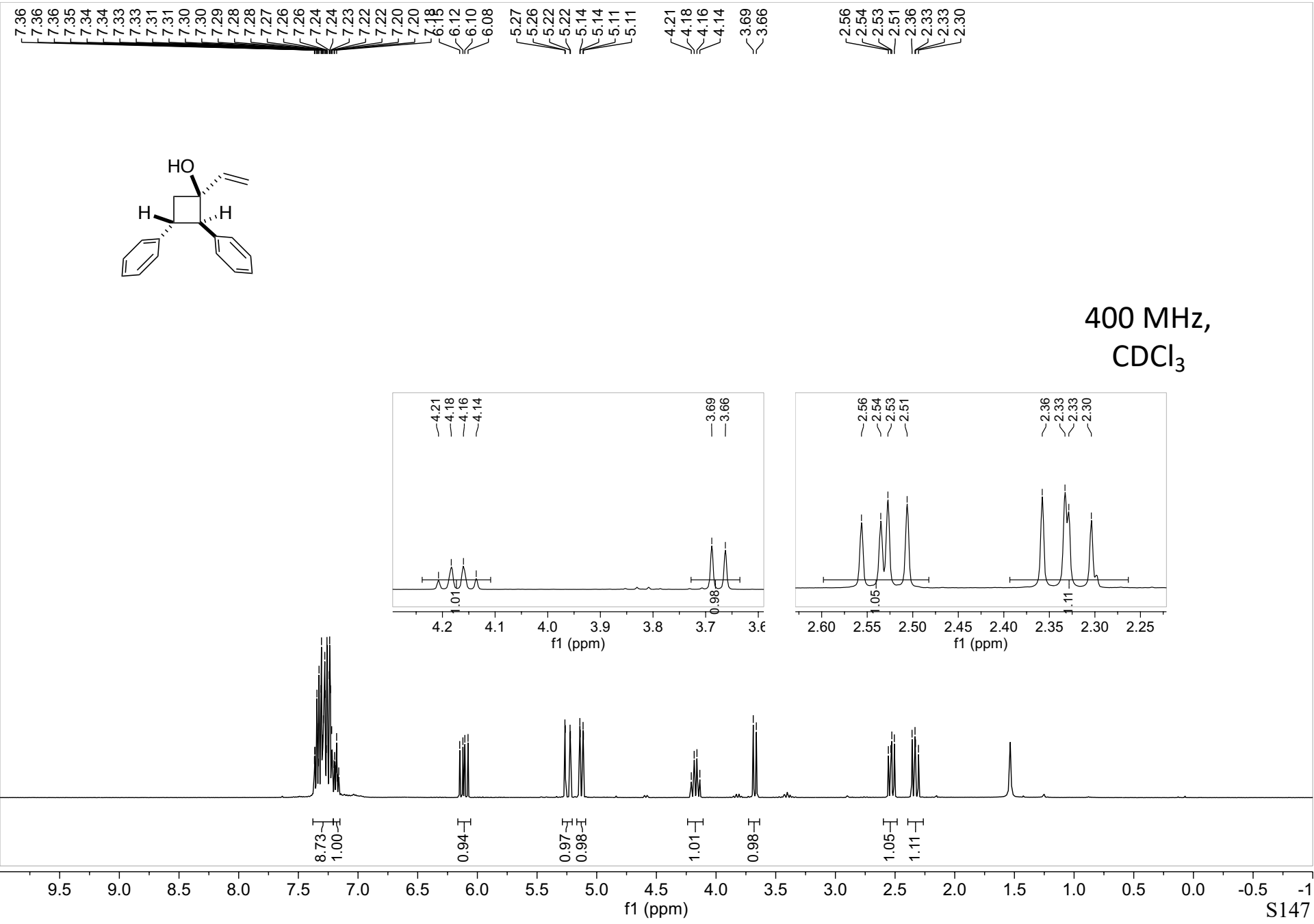



Peak Table

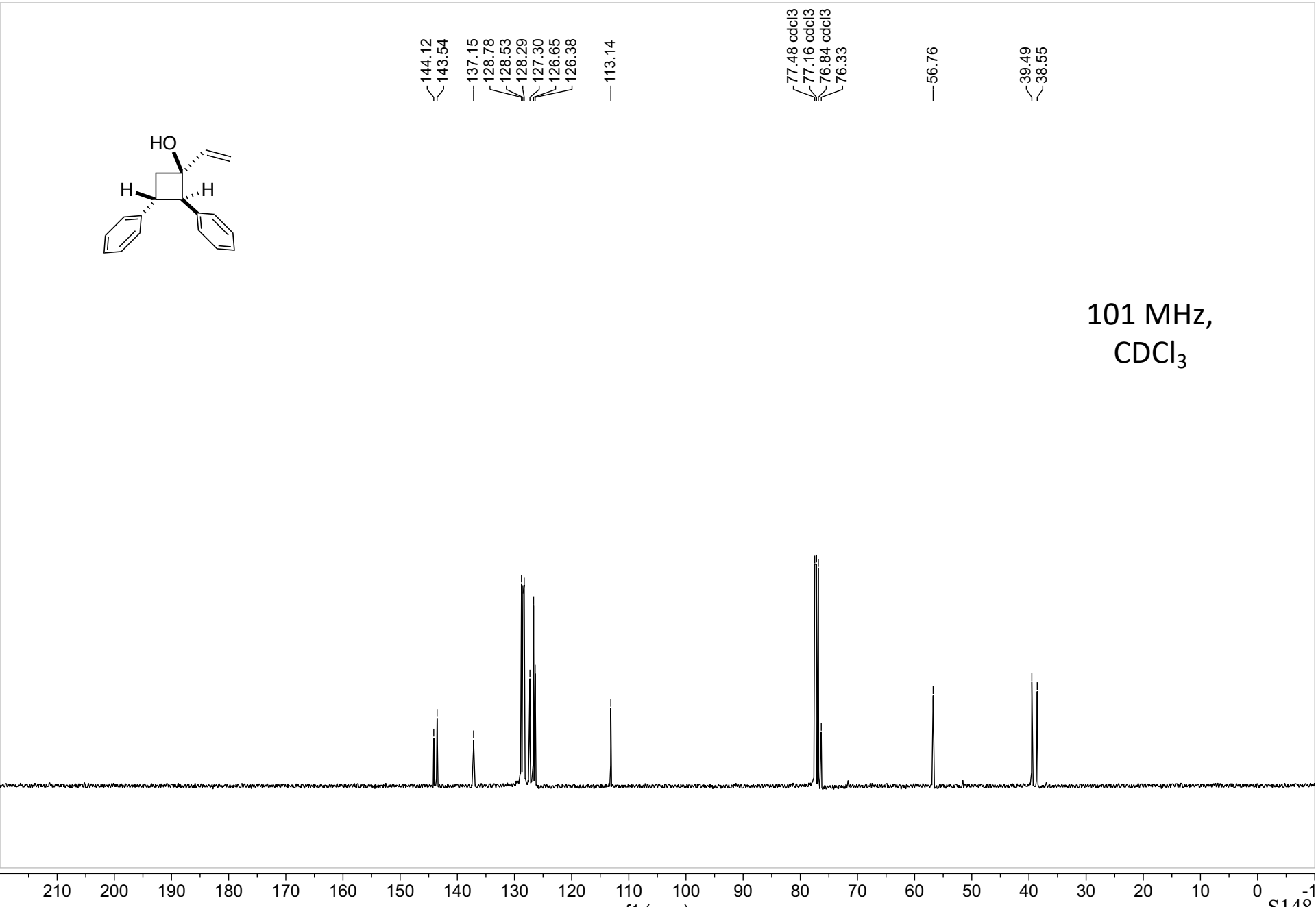
PDA Ch1 230nm

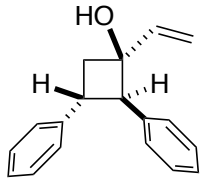
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.507 | 2.298 |
| 2 | 6.921 | 97.702 |
| Total | | 100.000 |

# $^1$H NMR (1*R*,2*R*,3*R*)-2,3-diphenyl-1-vinylcyclobutan-1-ol (**9a**)

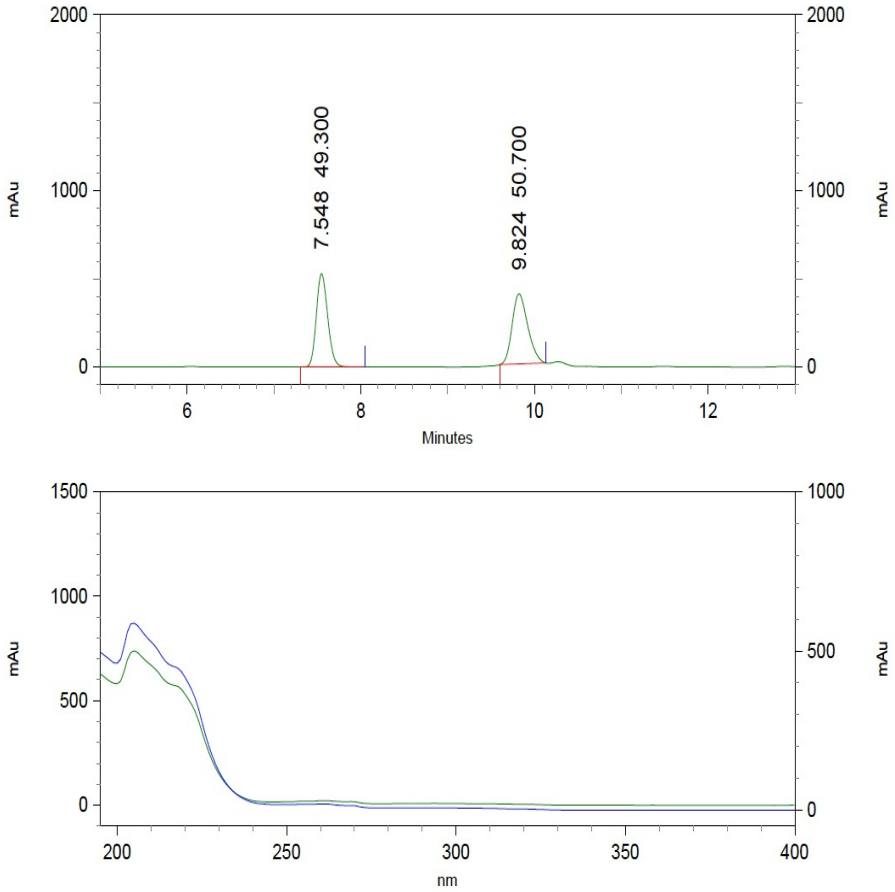


# $^{13}$C NMR (1*R*,2*R*,3*R*)-2,3-diphenyl-1-vinylcyclobutan-1-ol (**9a**)





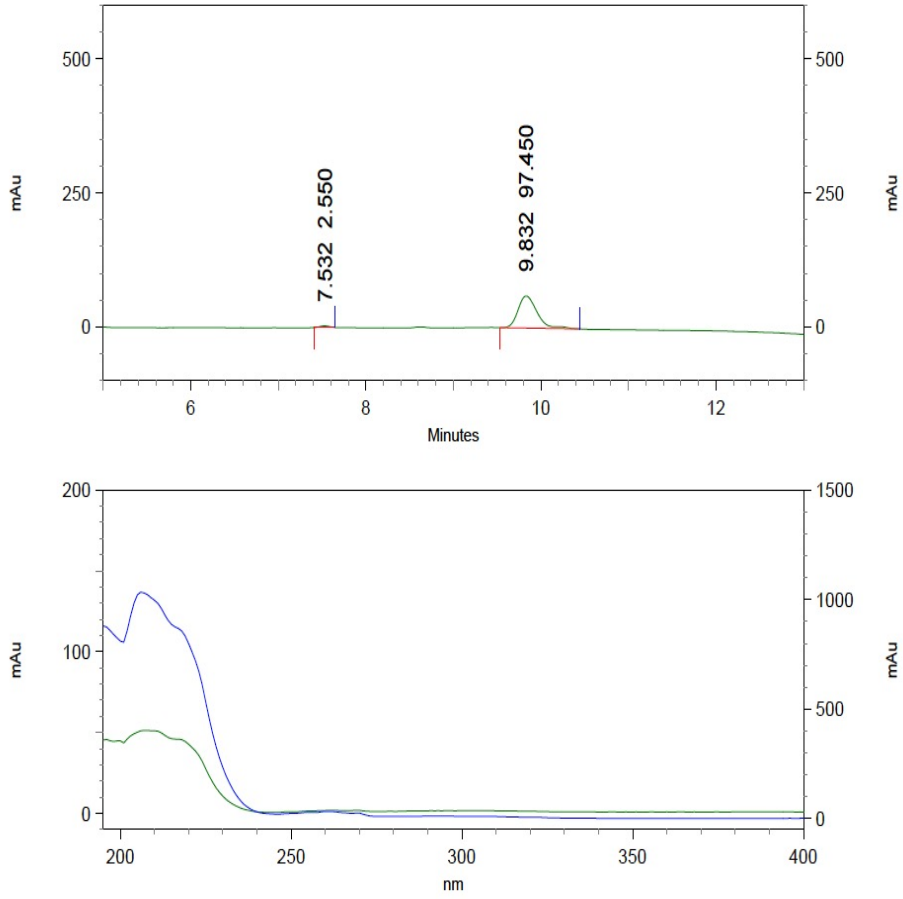

# **HPLC** (1*R*,2*R*,3*R*)-2,3-diphenyl-1-vinylcyclobutan-1-ol (**9a**)




2: 220 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.548 | 49.300 |
| 2 | 9.824 | 50.700 |

| Totals | | 100.000 |
|---|---|---|

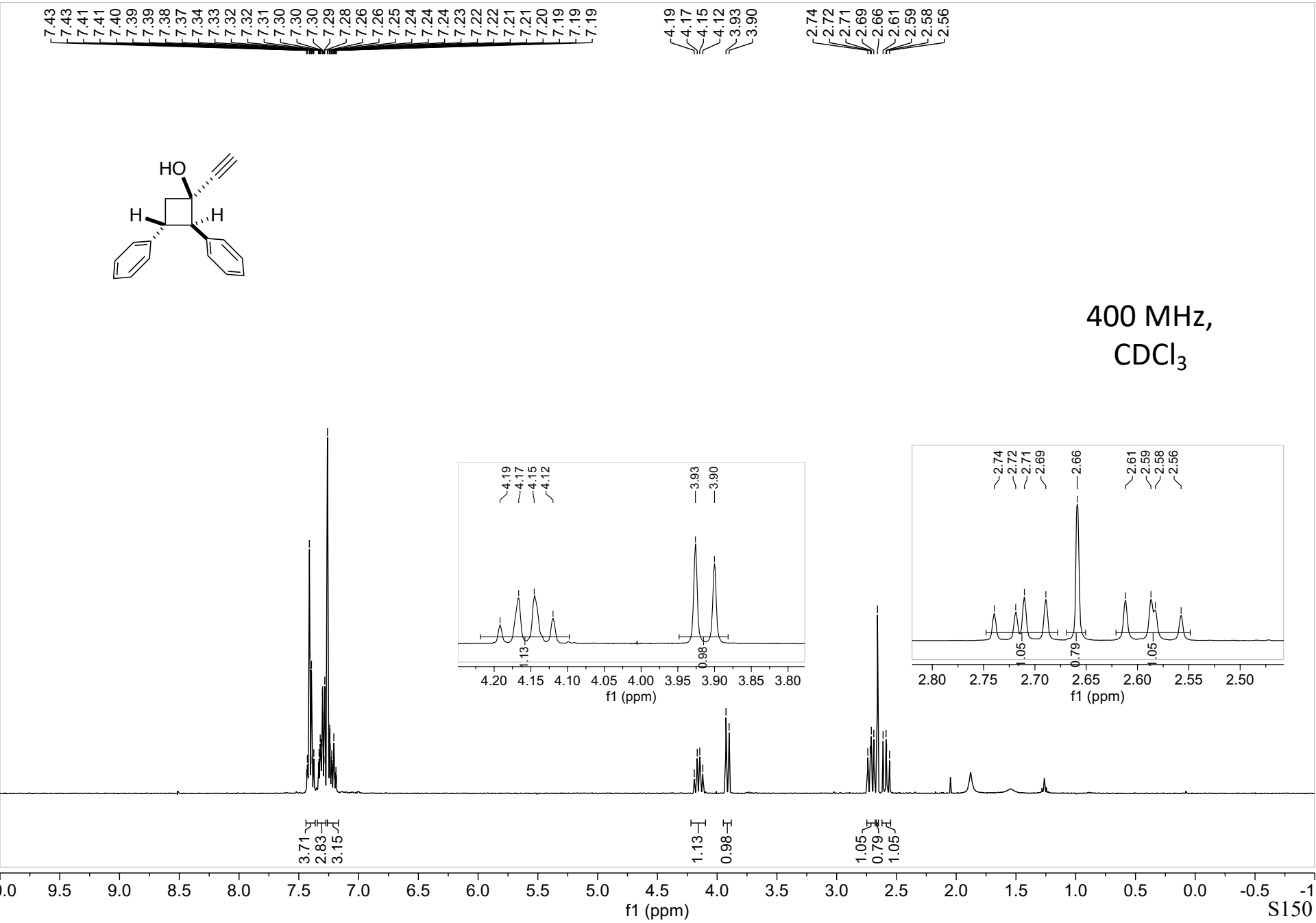



2: 237 nm, 4
nm Results

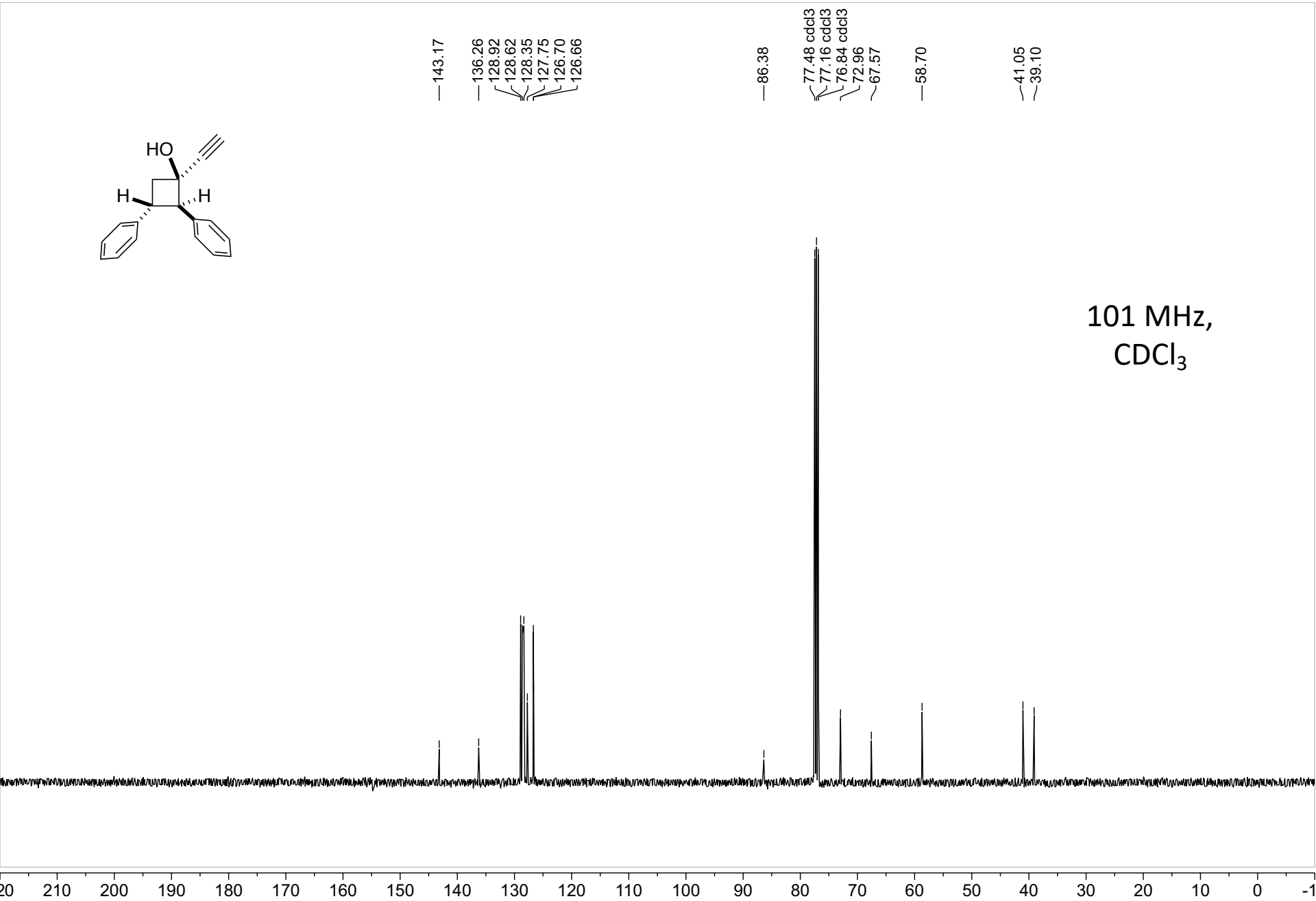
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.532 | 2.550 |
| 2 | 9.832 | 97.450 |

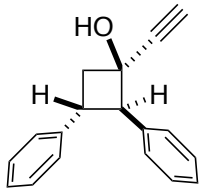
| Totals | 100.000 |
|---|---|

# $^1$H NMR (1*S*,2*R*,3*R*)-1-ethynyl-2,3-diphenylcyclobutan-1-ol (**10a**)

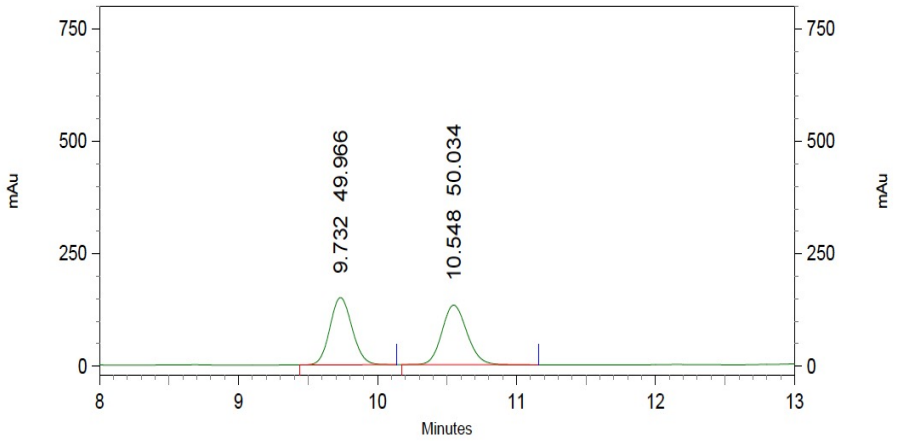


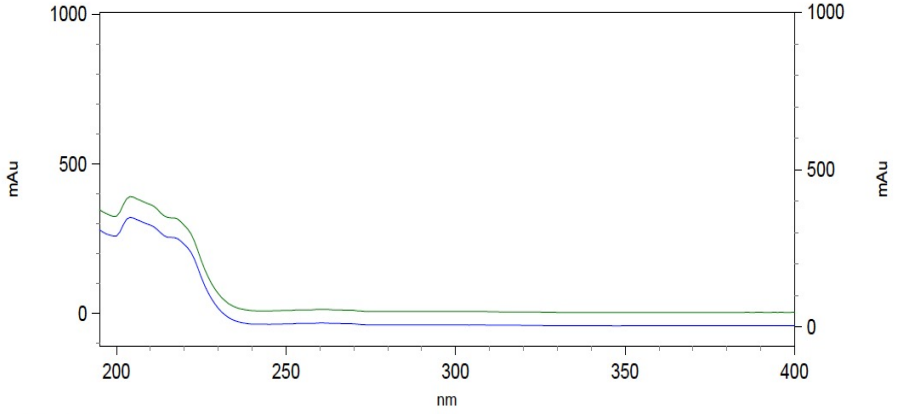
# $^{13}$C NMR (1*S*,2*R*,3*R*)-1-ethynyl-2,3-diphenylcyclobutan-1-ol (**10a**)





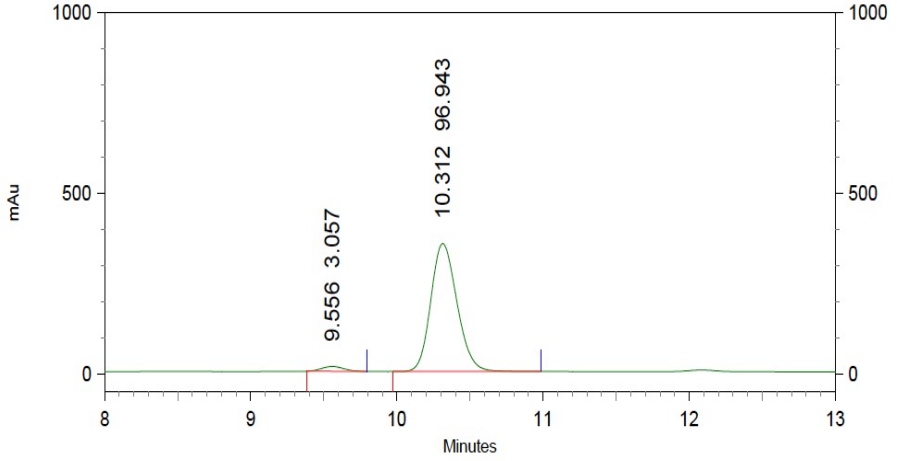

# **HPLC** (1*S*,2*R*,3*R*)-1-ethynyl-2,3-diphenylcyclobutan-1-ol (**10a**)

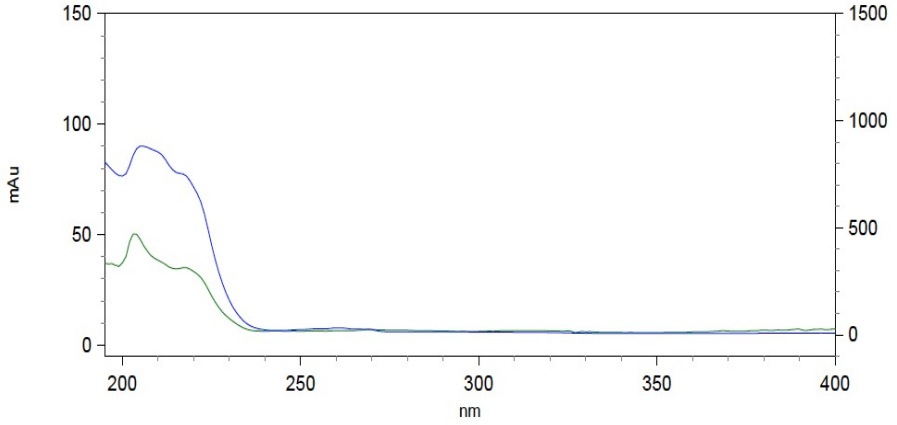



2: 226 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 9.732 | 49.966 |
| 2 | 10.548 | 50.034 |
| Totals | | 100.000 |

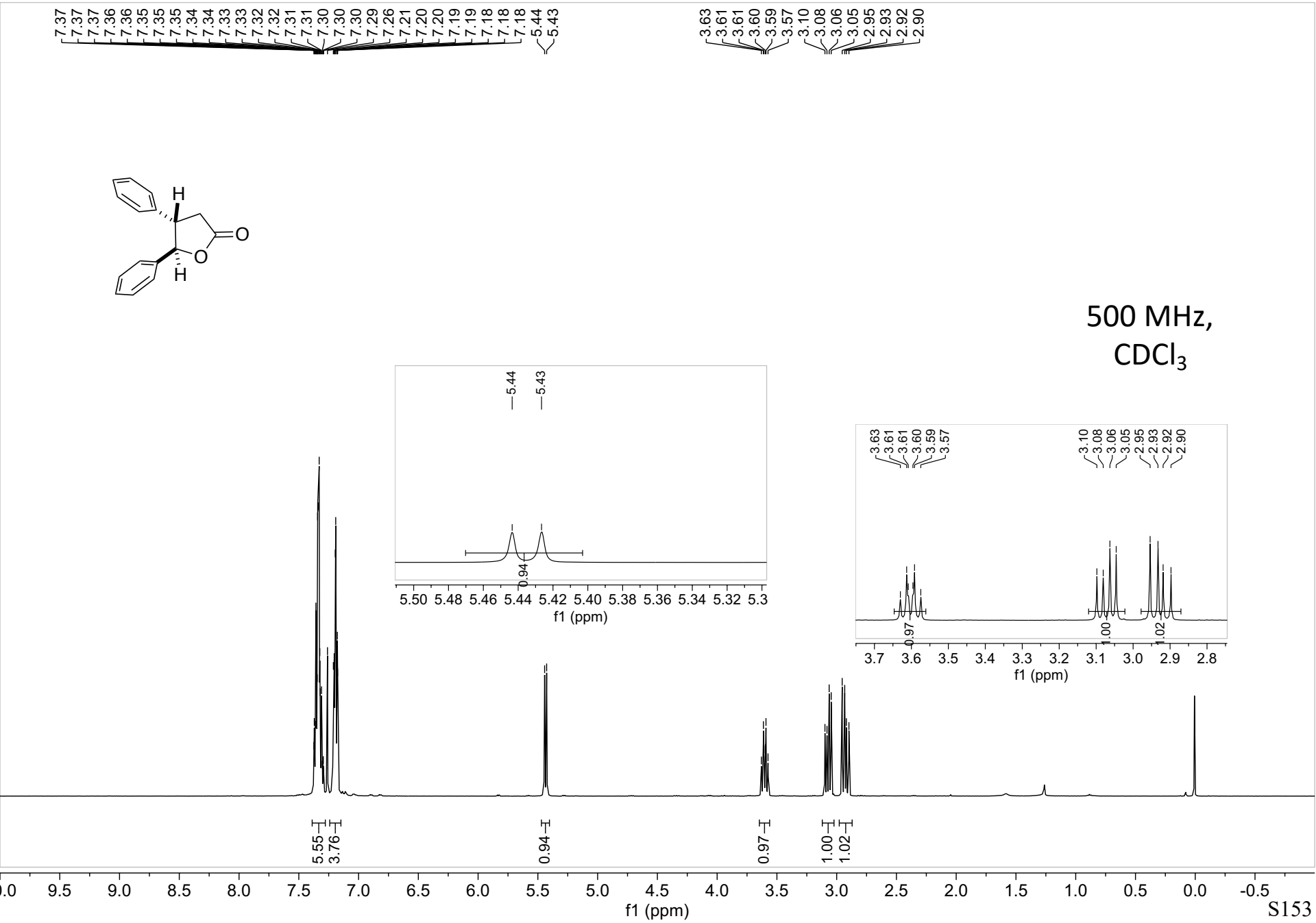


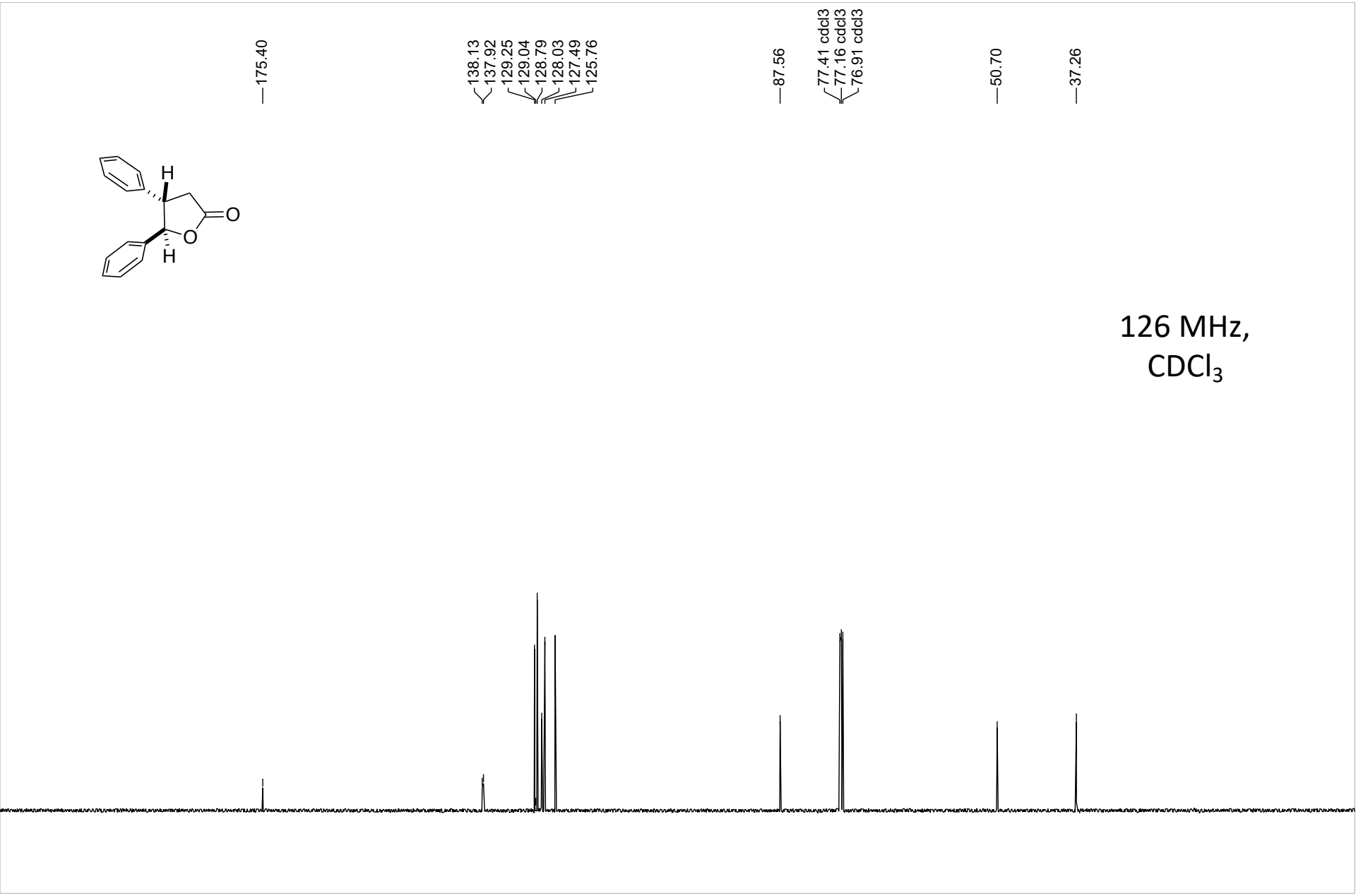

2: 226 nm, 4
nm Results

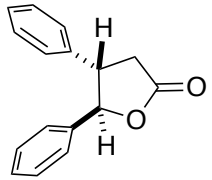
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 9.556 | 3.057 |
| 2 | 10.312 | 96.943 |
| Totals | | 100.000 |

# $^{1}$H NMR (4*S*,5*R*)-4,5-diphenyldihydrofuran-2(3*H*)-one **(11a)**

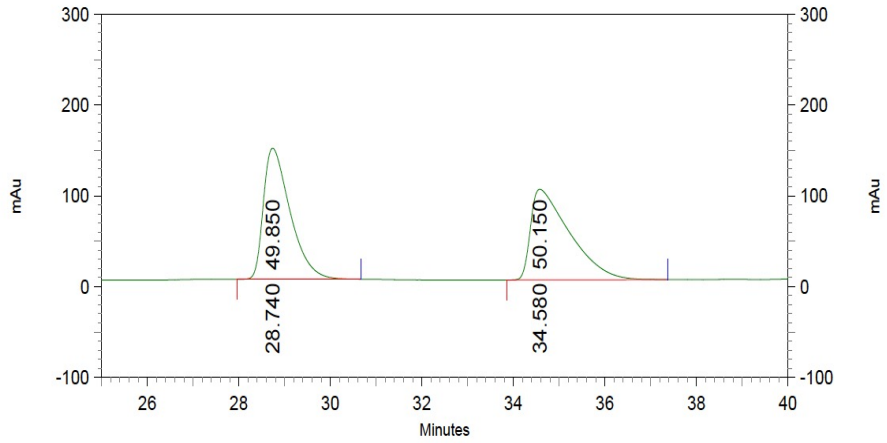


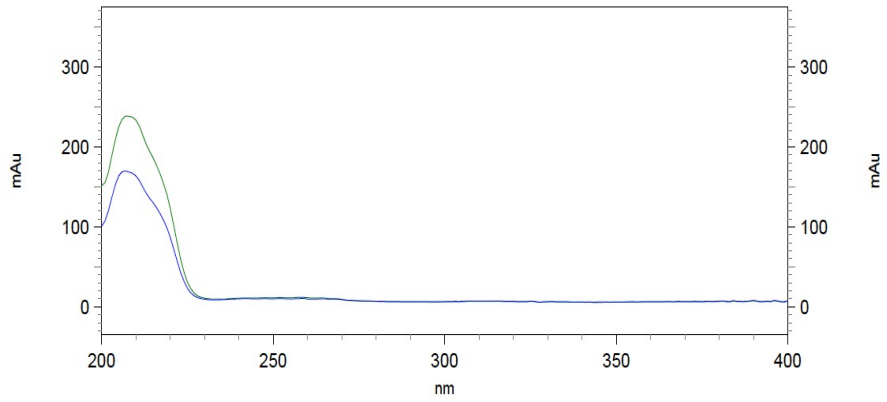
# $^{13}$C NMR (4*S*,5*R*)-4,5-diphenyldihydrofuran-2(3*H*)-one **(11a)**





# **HPLC** (4*S*,5*R*)-4,5-diphenyldihydrofuran-2(3*H*)-one **(11a)**

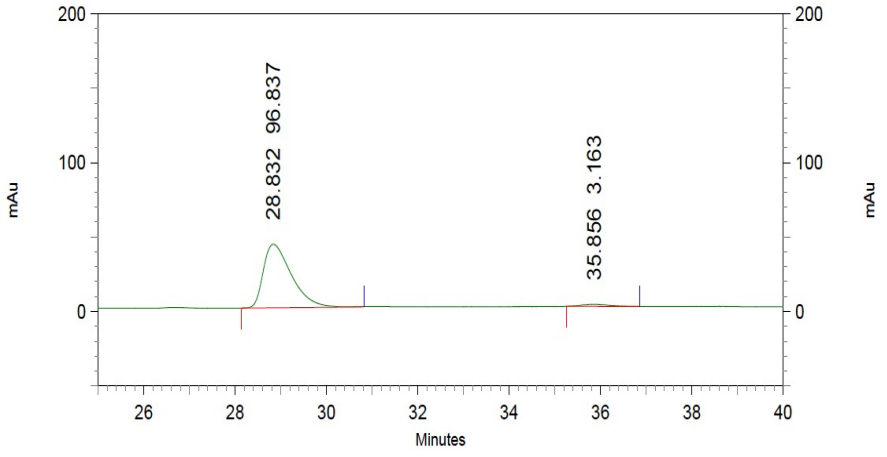


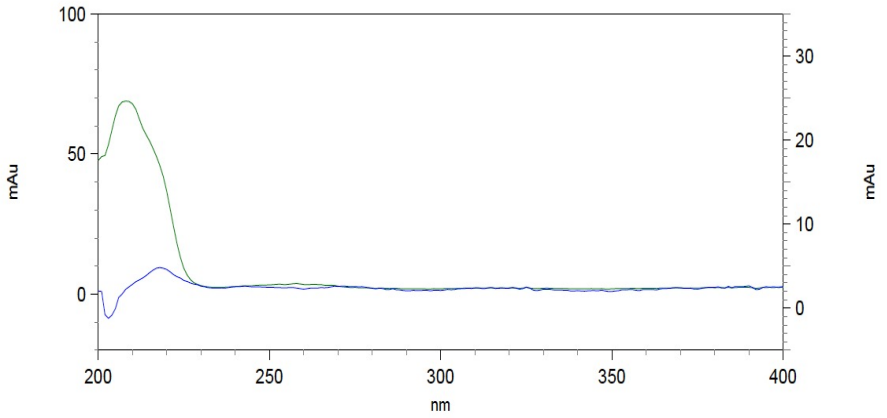




3: 218 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 28.740 | 49.850 |
| 2 | 34.580 | 50.150 |

| Totals | | 100.000 |
|---|---|---|



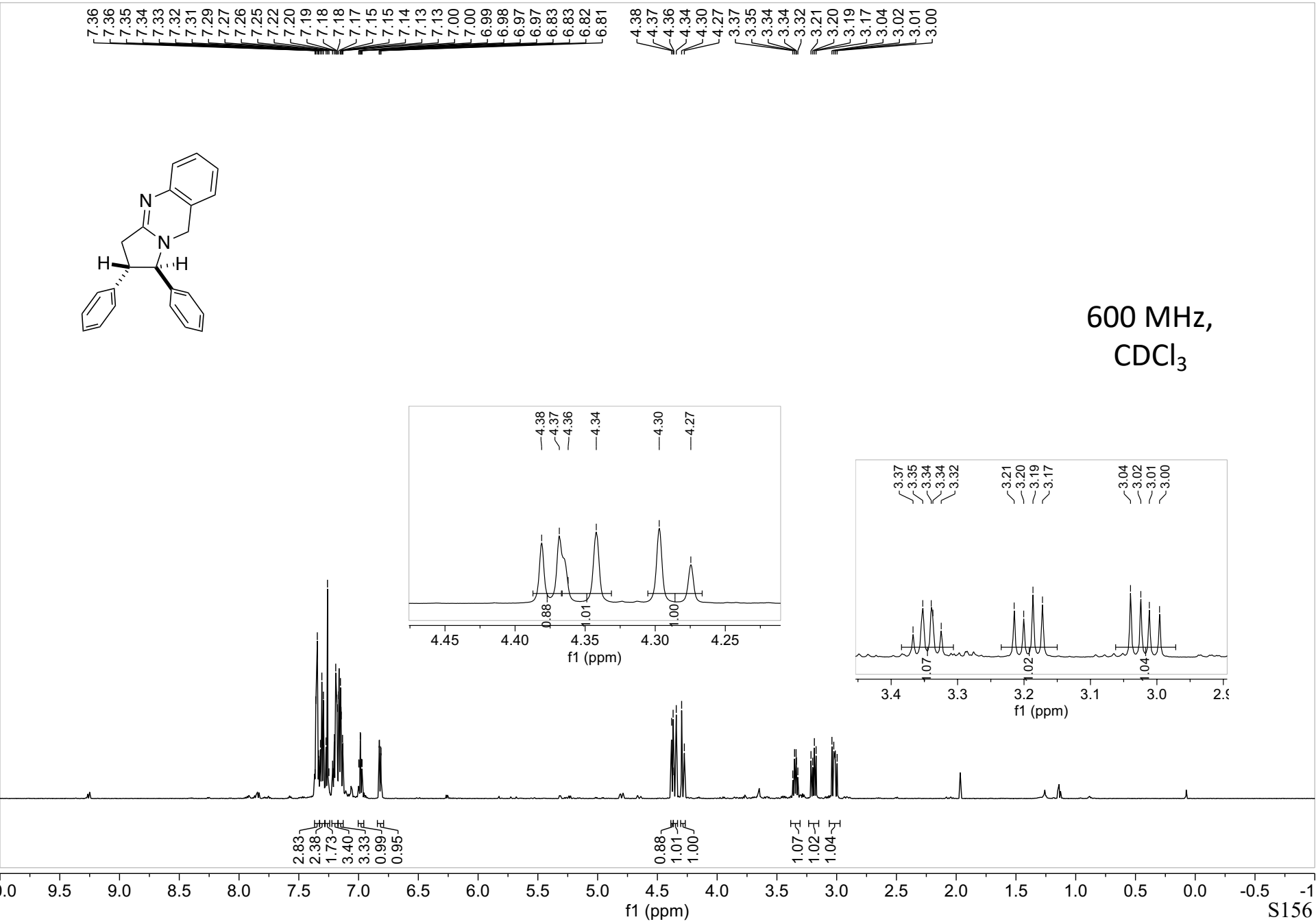




3: 218 nm, 4 nm Results

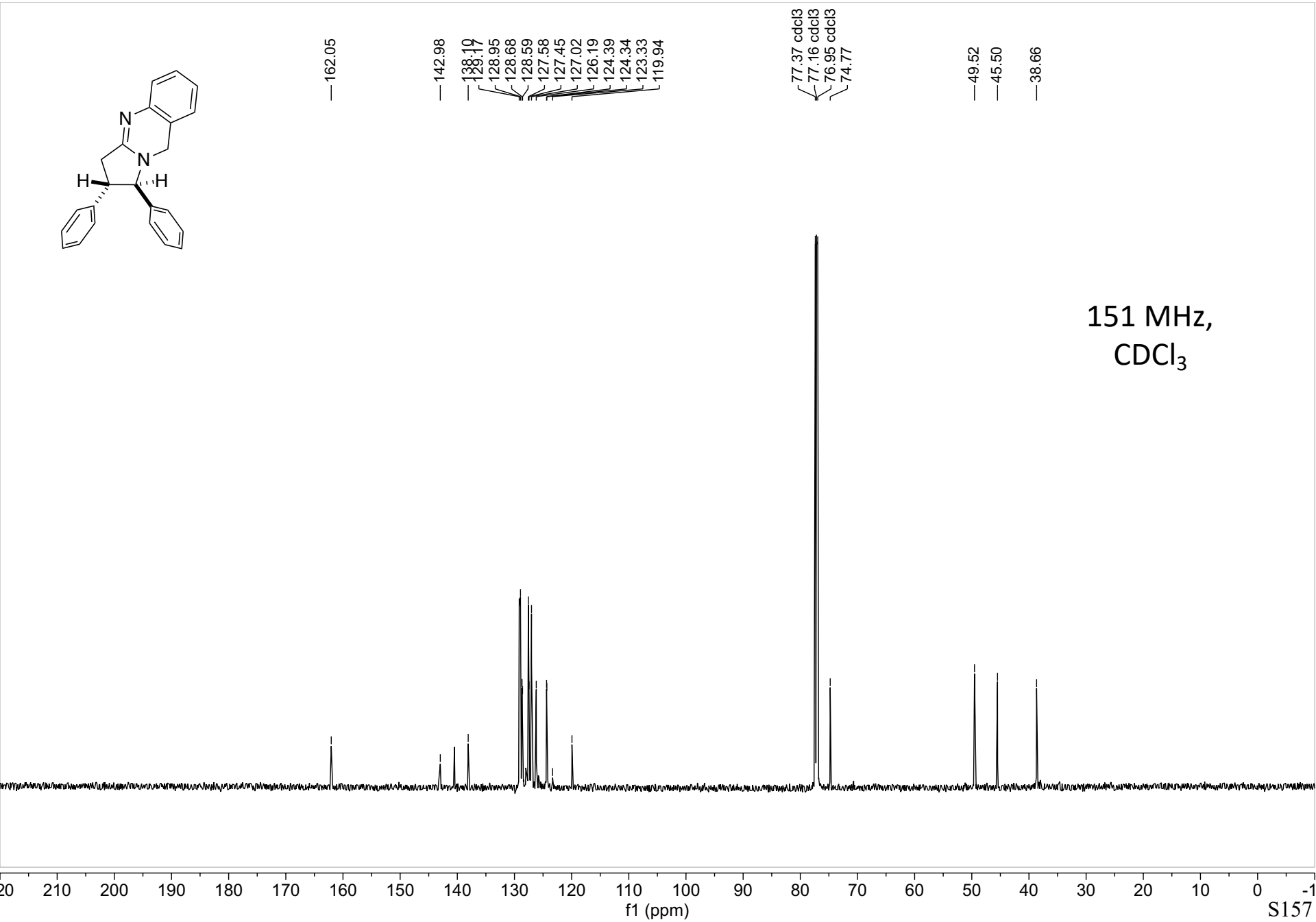
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 28.832 | 96.837 |
| 2 | 35.856 | 3.163 |

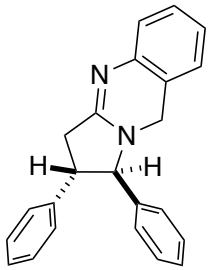
| Totals | | 100.000 |
|---|---|---|

# $^{1}$H NMR (1*S*,2*R*)-1,2-diphenyl-1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazoline (**12a**)



# $^{13}$C NMR (1*S*,2*R*)-1,2-diphenyl-1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazoline (**12a**)



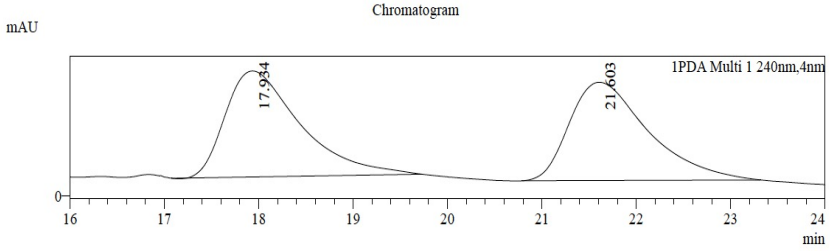


# **HPLC** (1*S*,2*R*)-1,2-diphenyl-1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazoline (**12a**)

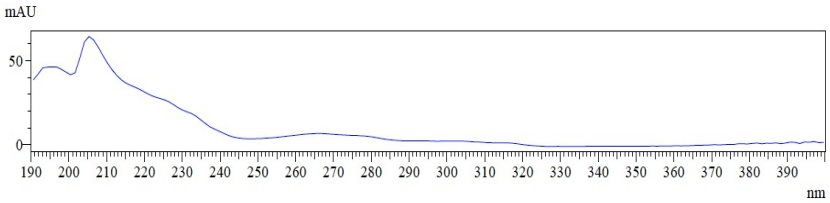
Sample Information

| | |
|---|---|
| Sample Name | : JJX-2741P-1-IB-5%-0.8ML |
| Sample ID | : JJX-2741P-1-IB-5%-0.8ML |
| Data File | : JJX-2741P-1-IB-5%-0.8ML.lcd |
| Method File | : dsw-5%0.8mL.lcm |

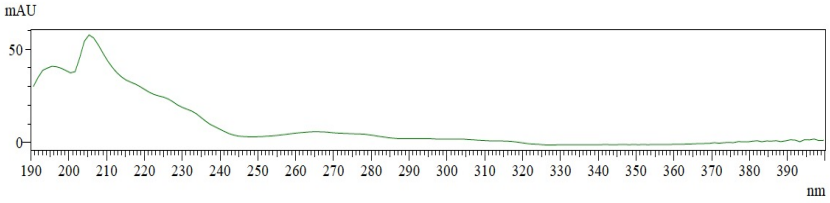
Chromatogram




UV Spectrum
Retention time = 17.934




UV Spectrum
Retention time = 21.603




Peak Table

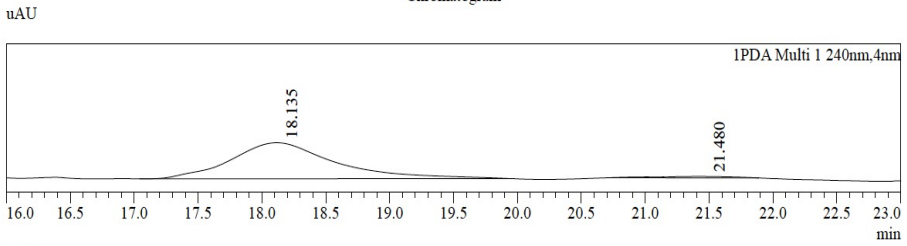
PDA Ch1 240nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 17.934 | 382646 | 50.673 |
| 2 | 21.603 | 372481 | 49.327 |
| Total | | 755127 | 100.000 |

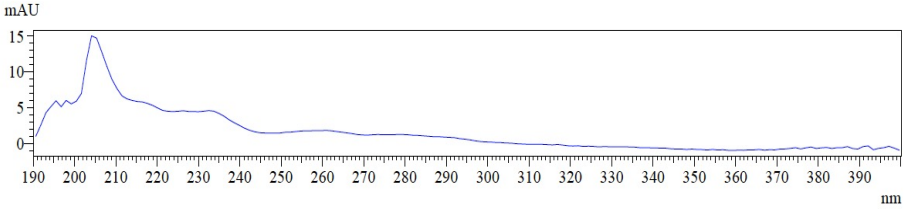
Sample Information

| | |
|---|---|
| Sample Name | : JJX-2741P-chiral-IB-5%-0.8ML001 |
| Sample ID | : JJX-2741P-chiral-IB-5%-0.8ML001 |
| Data File | : JJX-2741P-chiral-IB-5%-0.8ML002.lcd |
| Method File | : dsw-5%0.8mL.lcm |

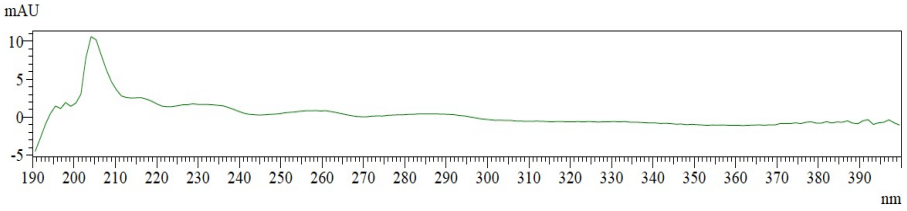
Chromatogram




UV Spectrum
Retention time = 18.135




UV Spectrum
Retention time = 21.480



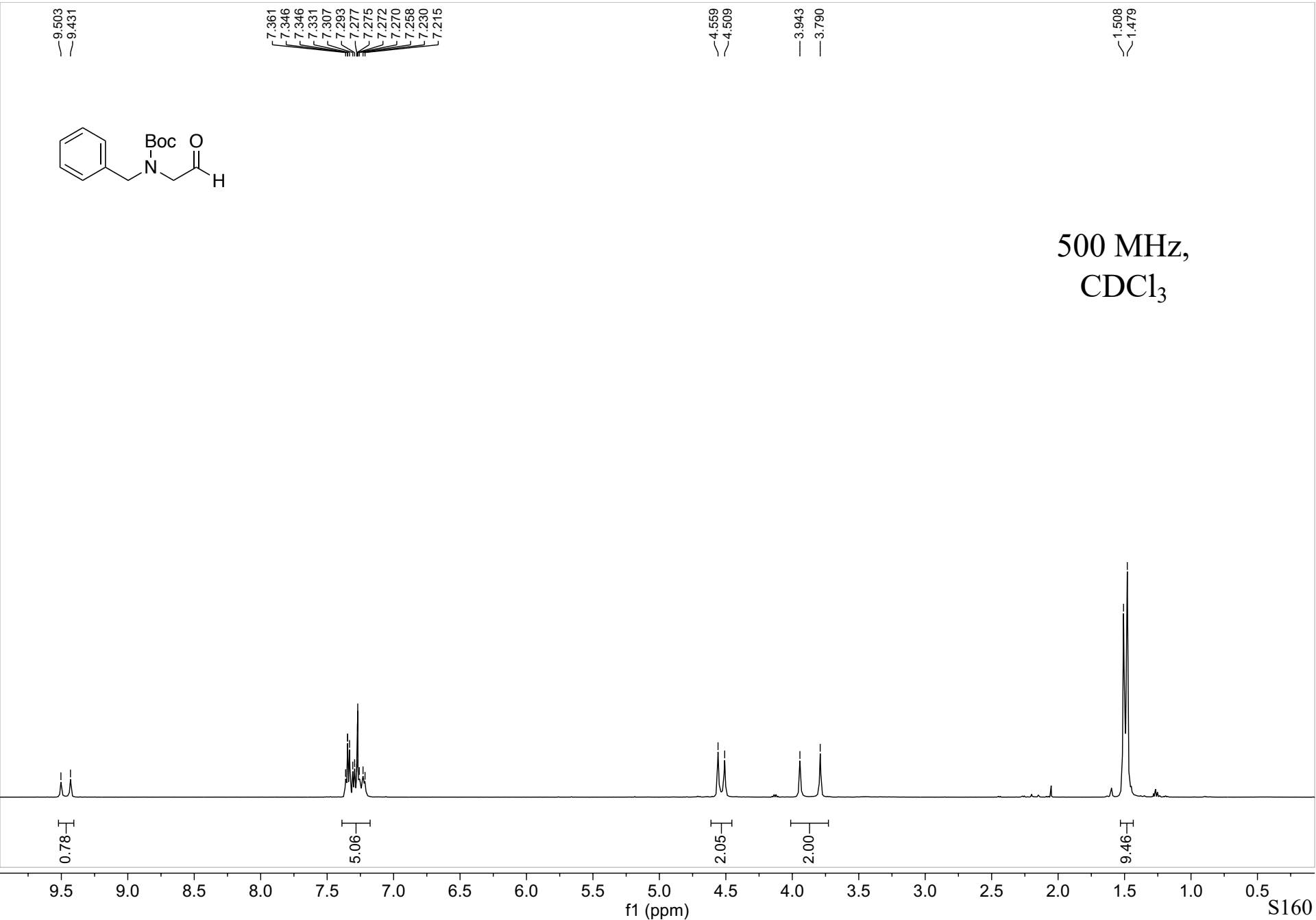

Peak Table

PDA Ch1 240nm

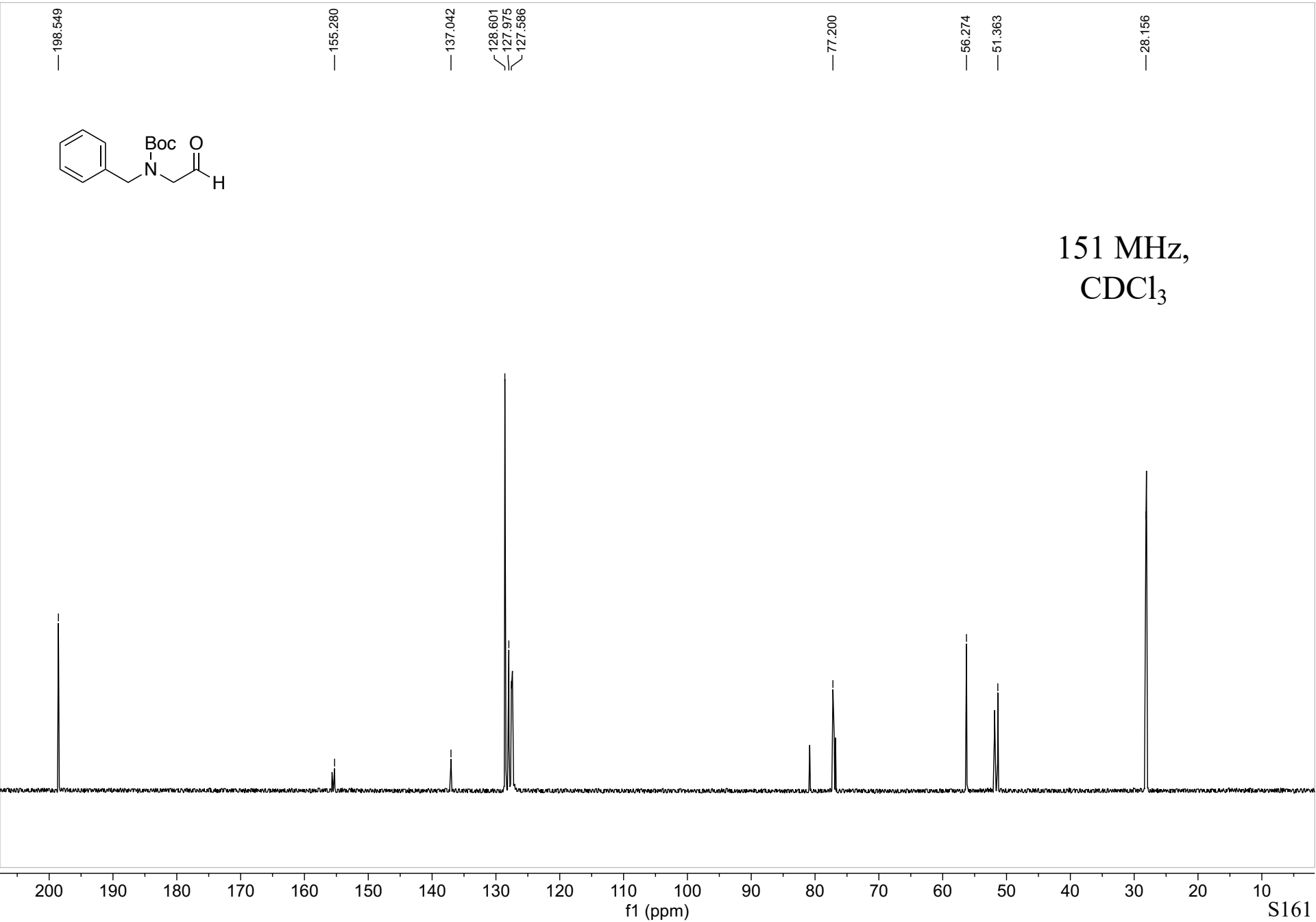
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 18.135 | 110753 | 97.029 |
| 2 | 21.480 | 3391 | 2.971 |
| Total | | 114144 | 100.000 |

# Spectral Data for Chapter 3

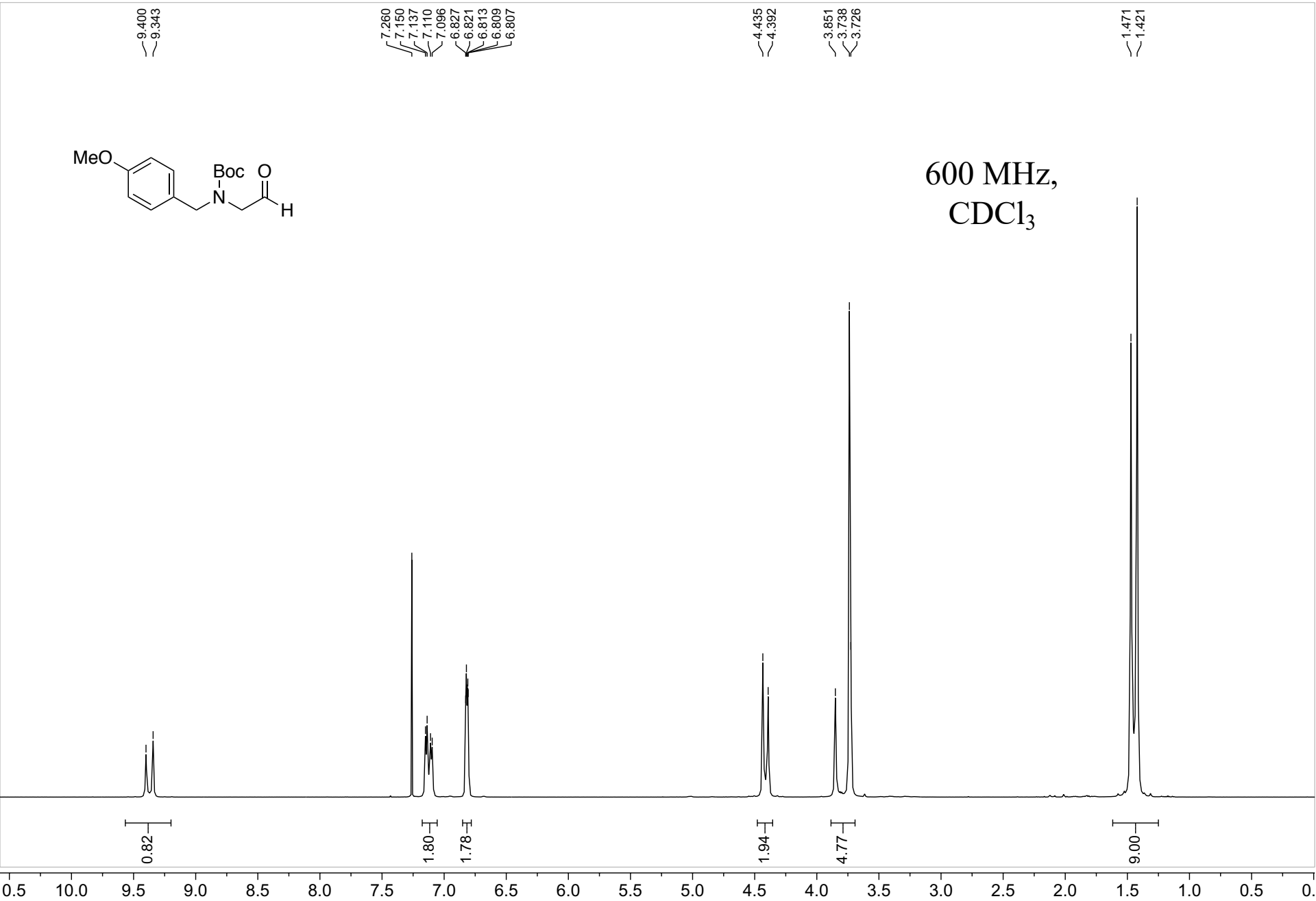
# $^{1}$H NMR *tert*-butyl benzyl(2-oxoethyl)carbamate **s-1a**



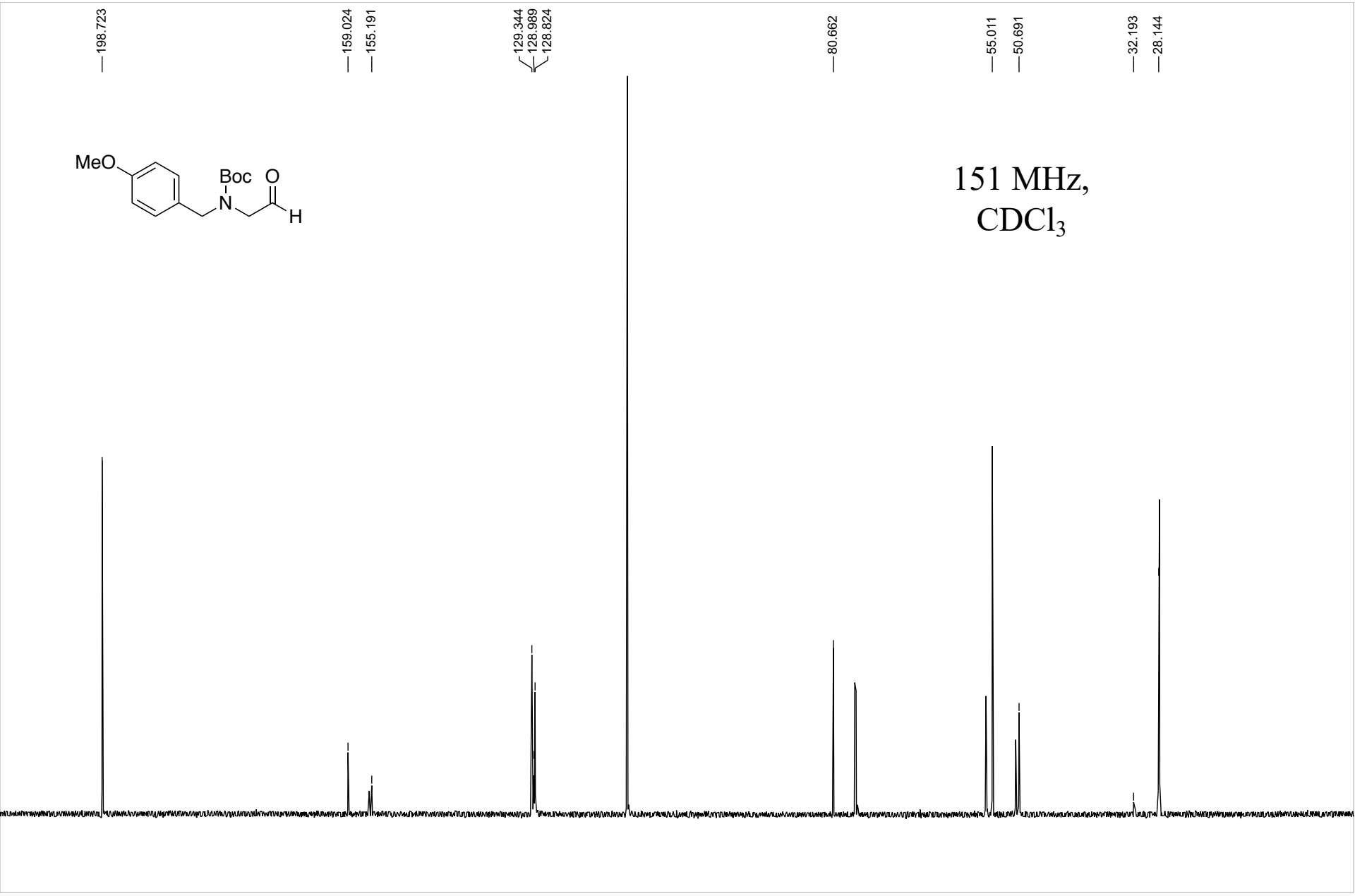
# $^{13}$C NMR *tert*-butyl benzyl(2-oxoethyl)carbamate **s-1a**



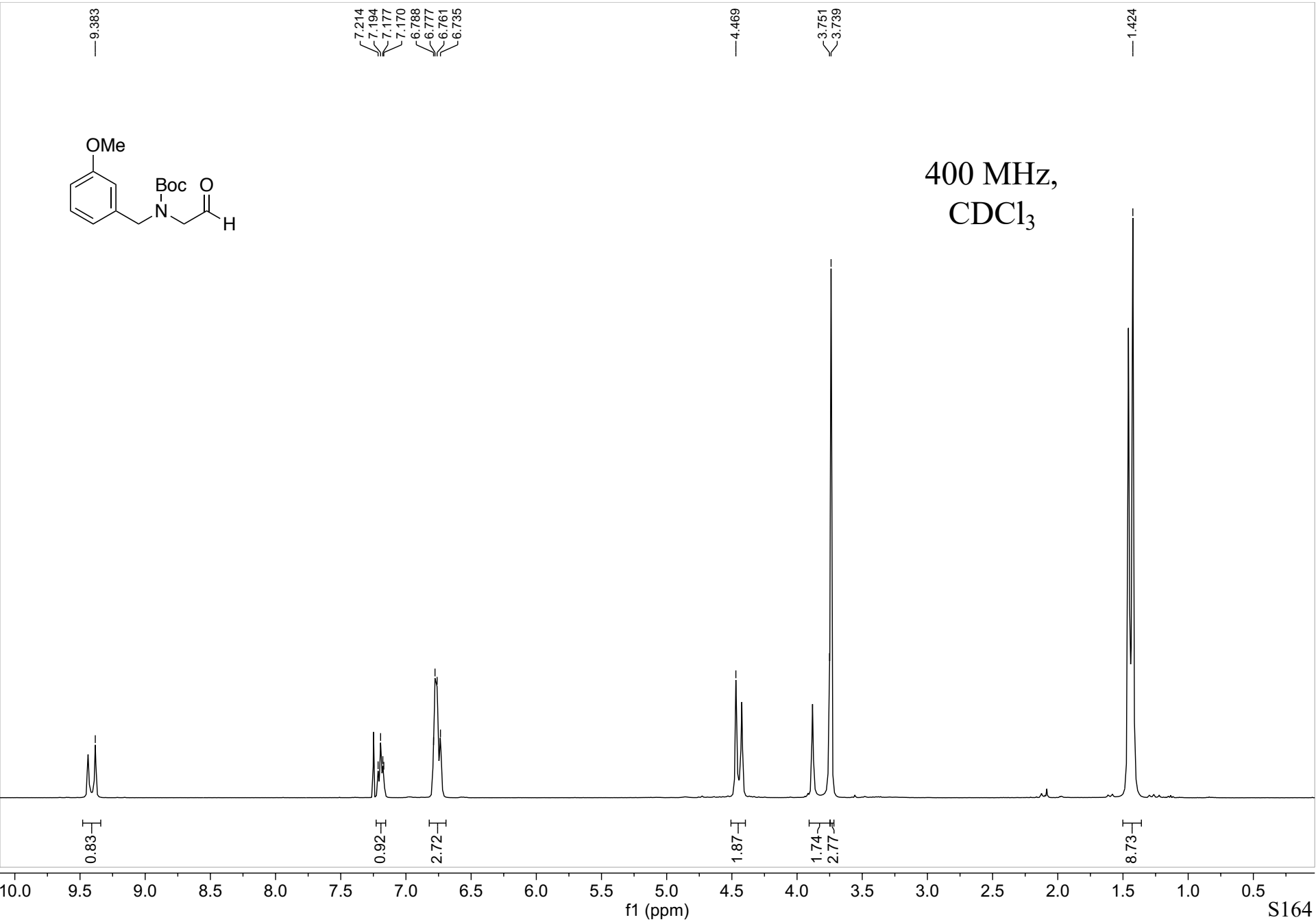
# $^{1}$H NMR *tert*-butyl (4-methoxybenzyl)(2-oxoethyl)carbamate **s-1b**



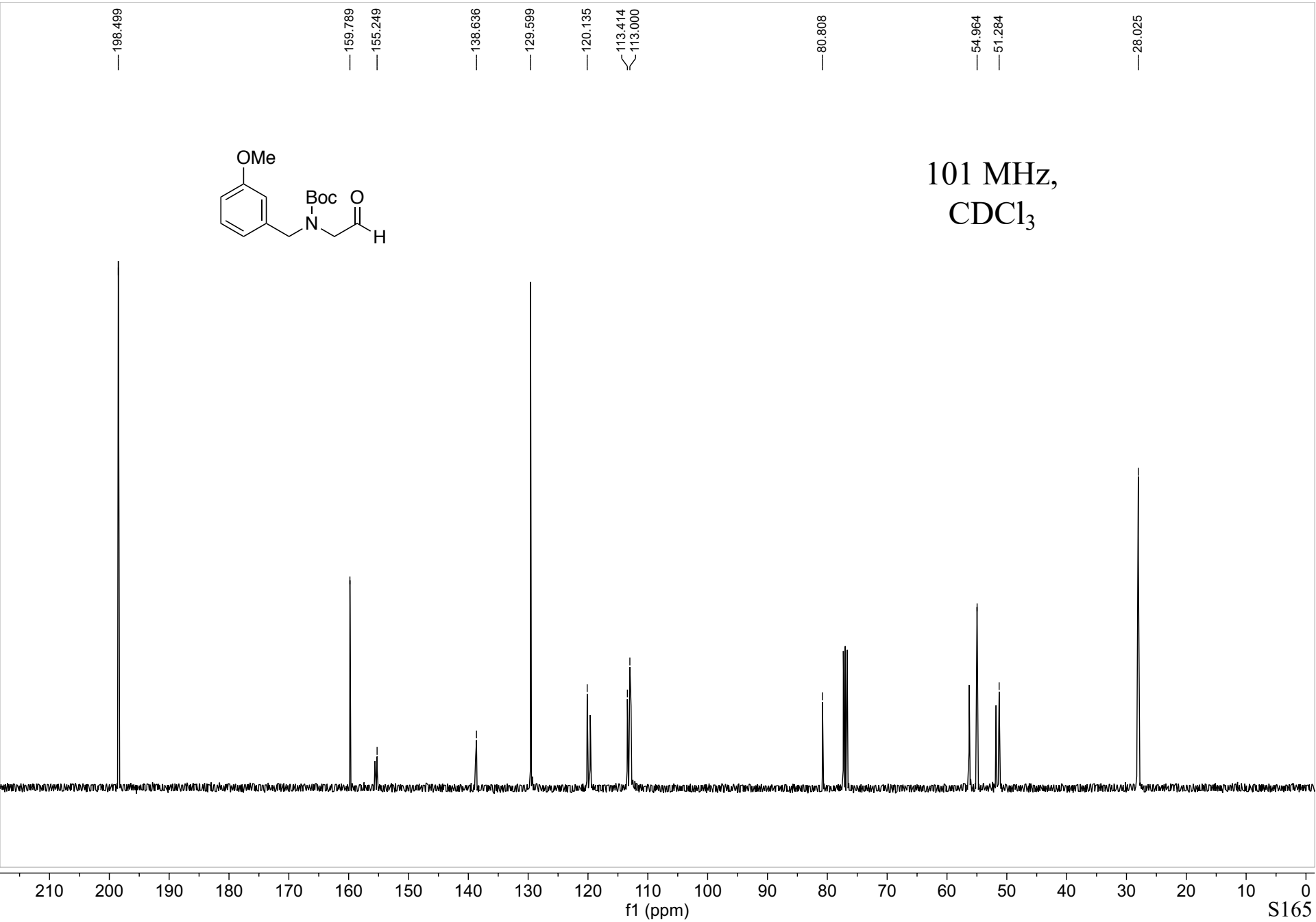
# $^{13}$C NMR *tert*-butyl (4-methoxybenzyl)(2-oxoethyl)carbamate **s-1b**



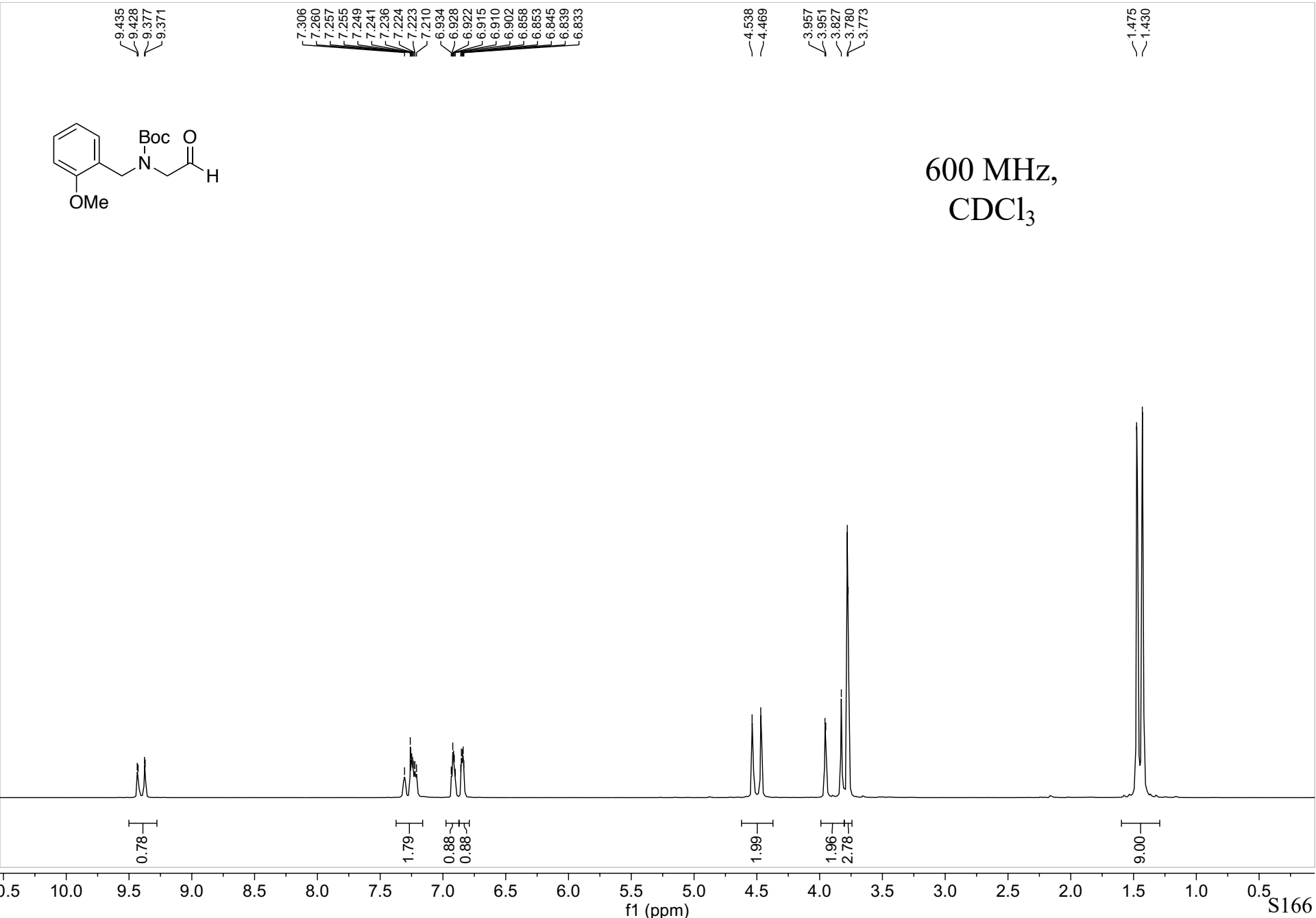
# $^{1}$H NMR *tert*-butyl (3-methoxybenzyl)(2-oxoethyl)carbamate **s-1c**



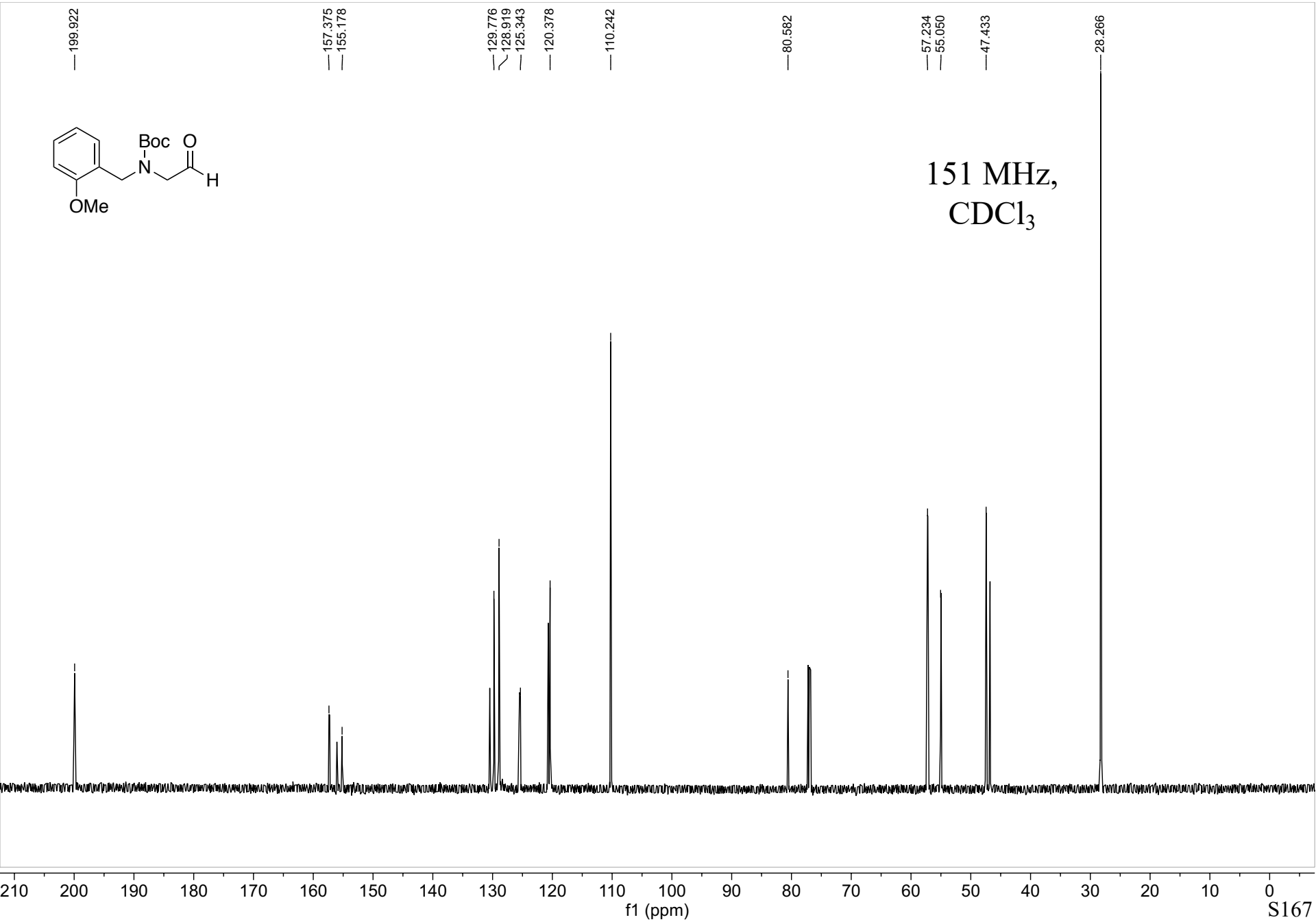
# $^{13}$C NMR *tert*-butyl (3-methoxybenzyl)(2-oxoethyl)carbamate **s-1c**



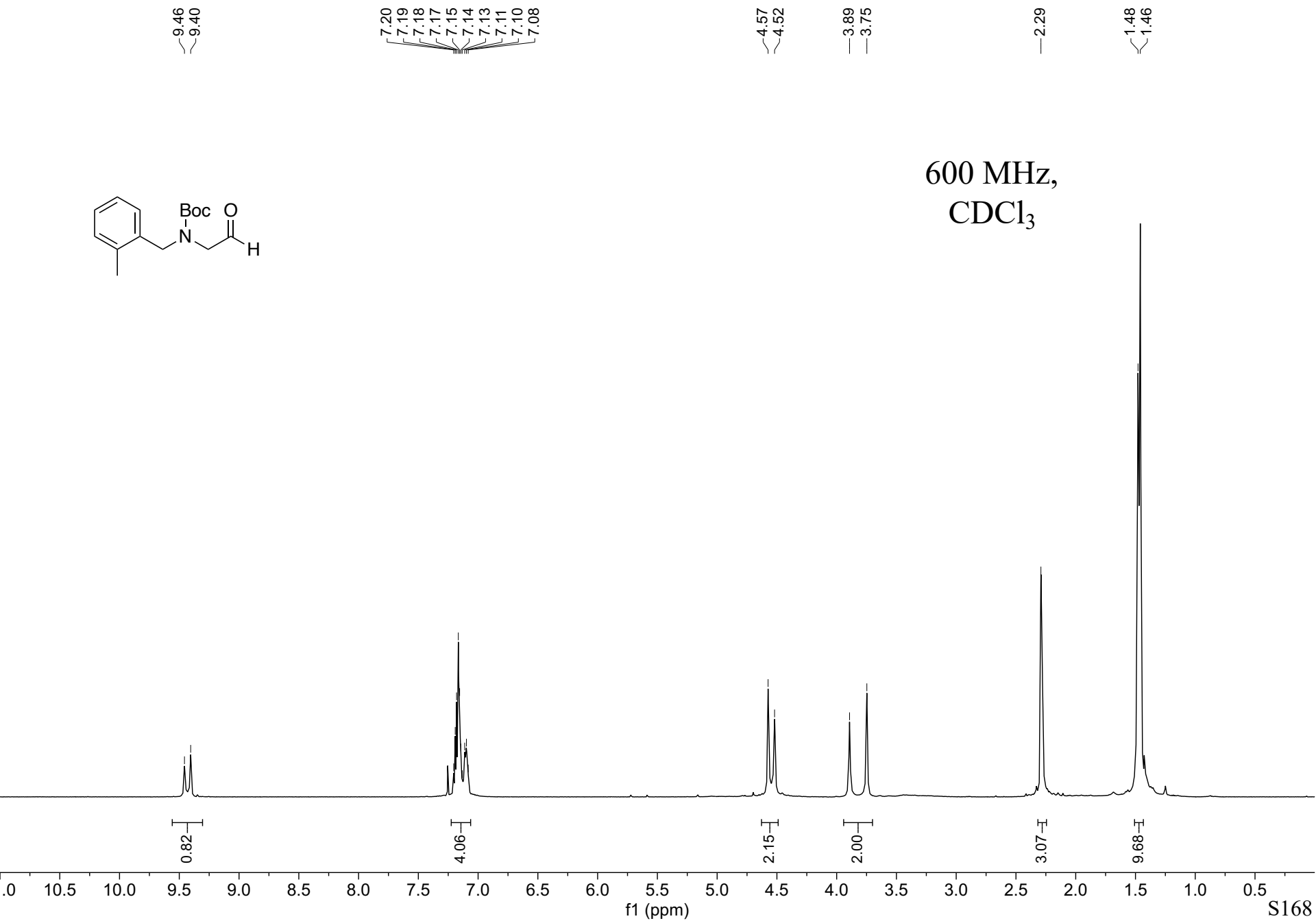
# $^{1}$H NMR *tert*-butyl (2-methoxybenzyl)(2-oxoethyl)carbamate **s-1d**



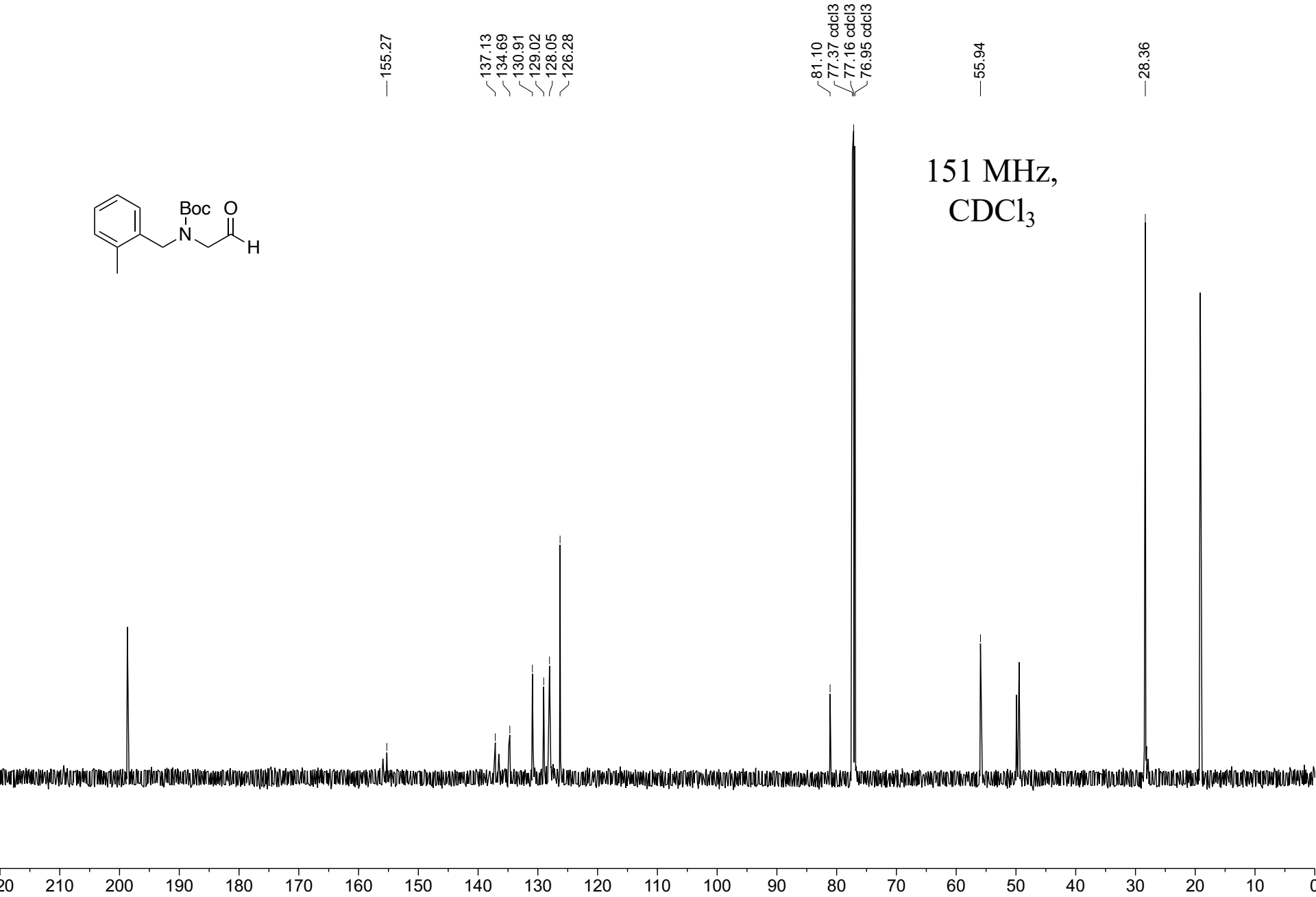
# $^{13}$C NMR *tert*-butyl (2-methoxybenzyl)(2-oxoethyl)carbamate **s-1d**



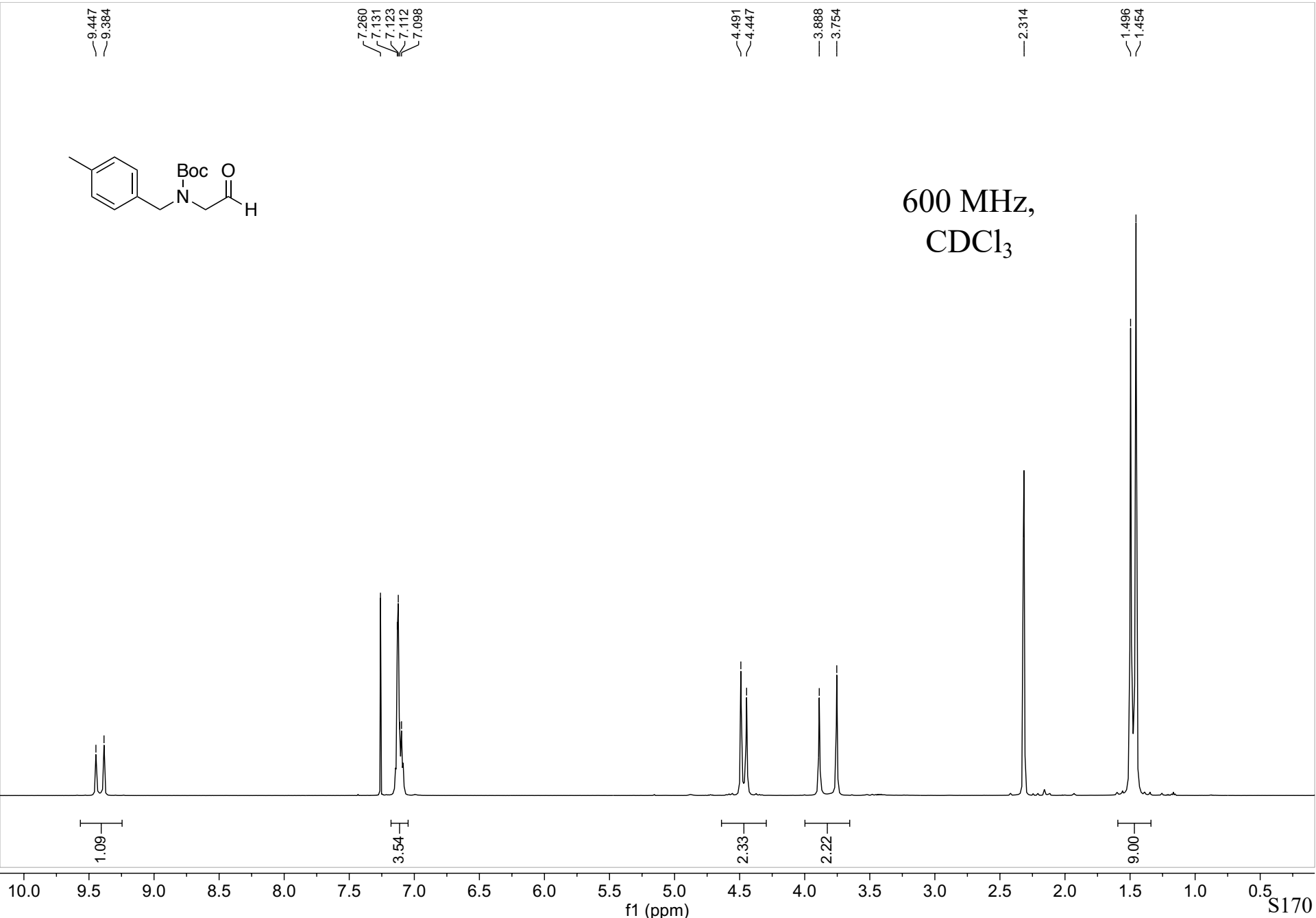
# $^{1}$H NMR *tert*-Butyl (2-methylbenzyl)(2-oxoethyl)carbamate **s-1e**



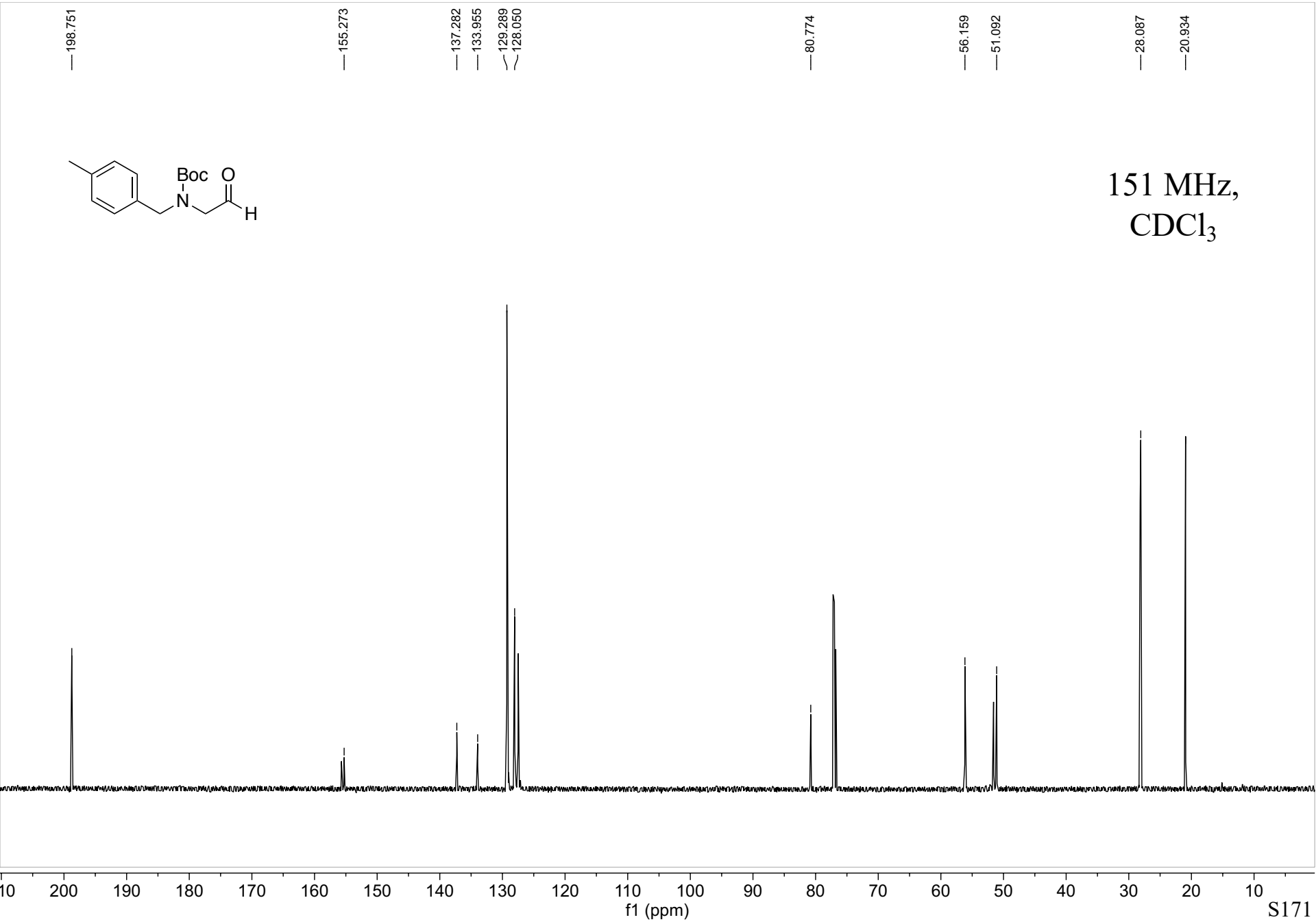
# $^{13}$C NMR *tert*-Butyl (2-methylbenzyl)(2-oxoethyl)carbamate **s-1e**



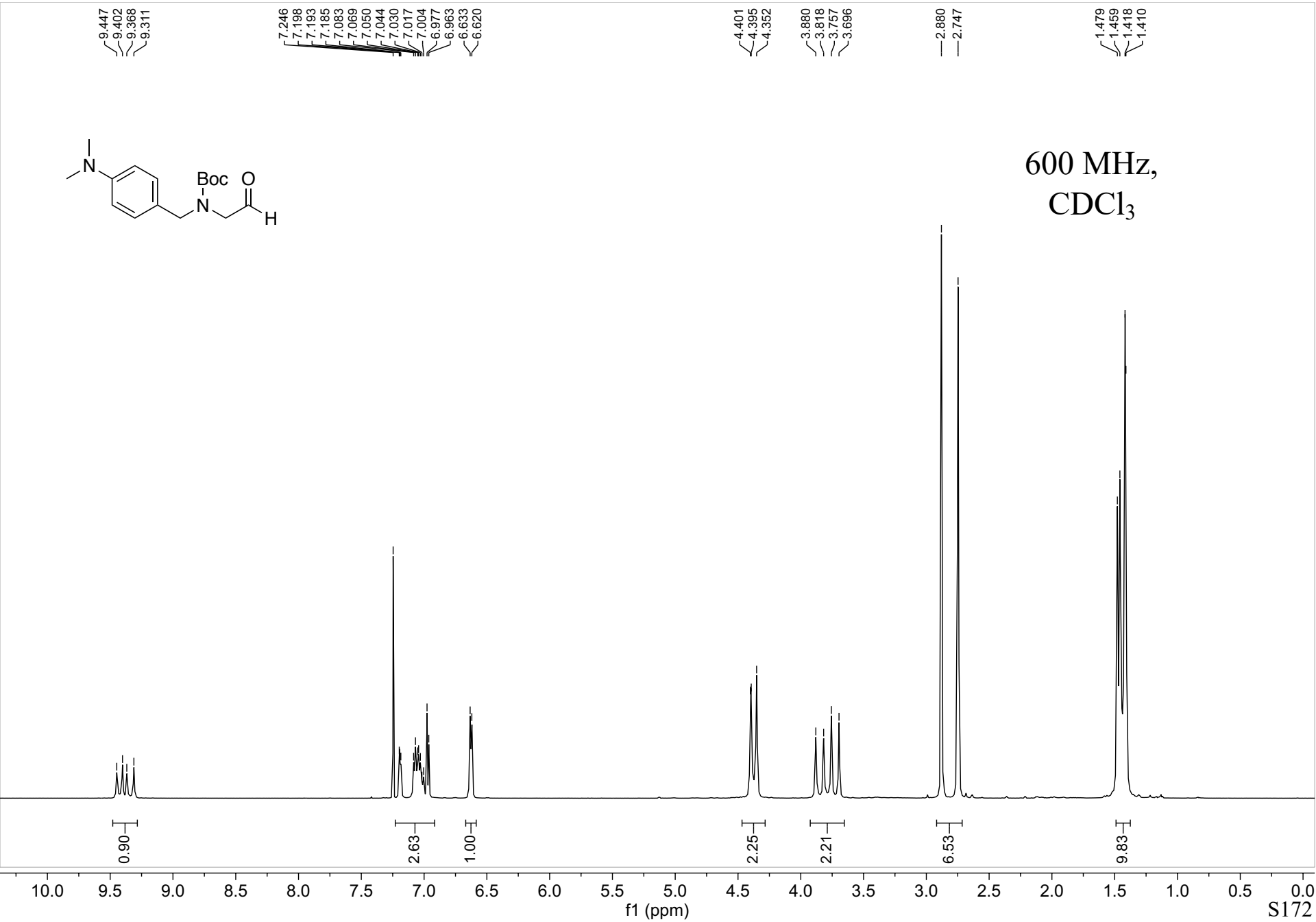
# $^{1}$H NMR *tert*-butyl (4-methylbenzyl)(2-oxoethyl)carbamate **s-1f**



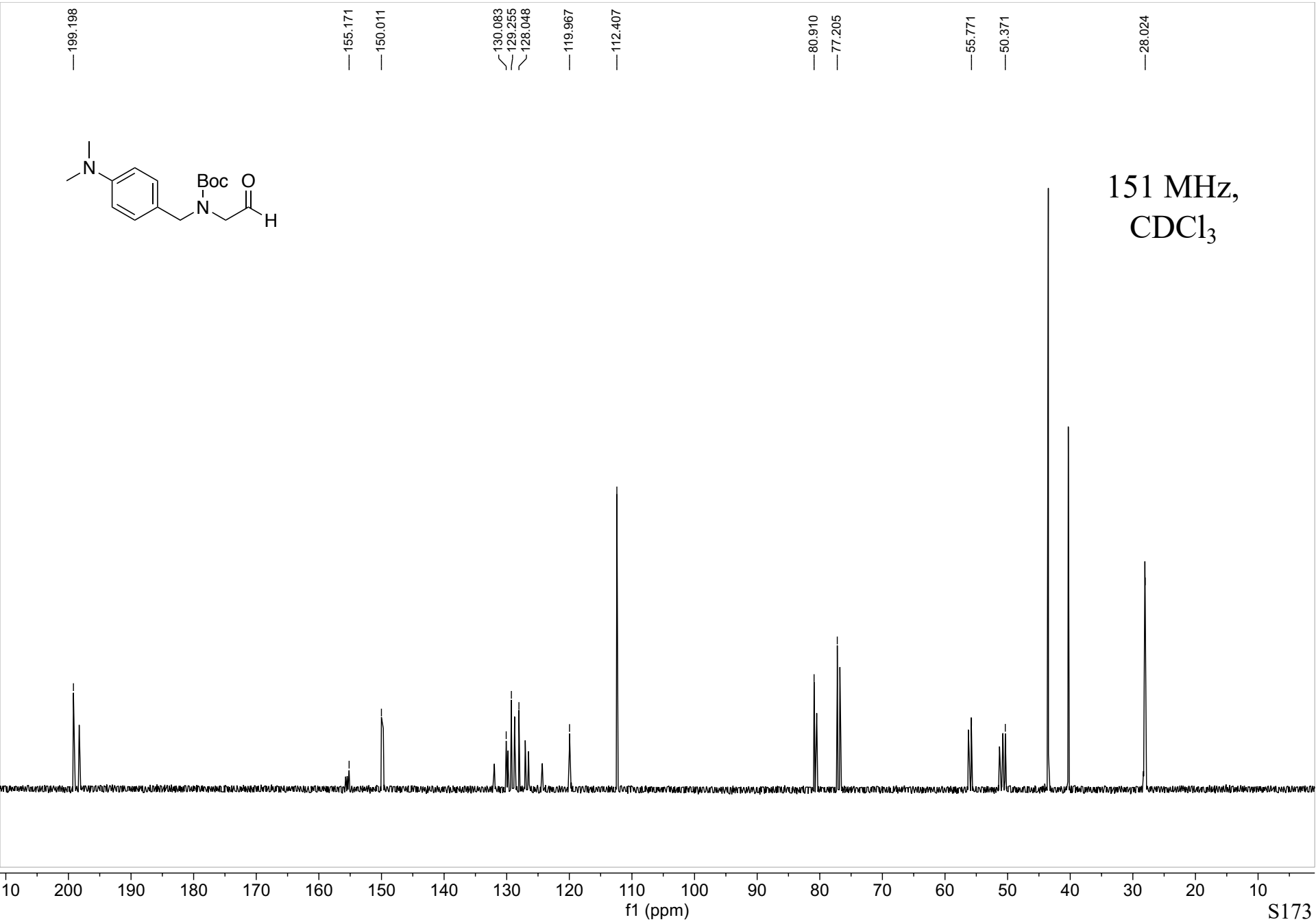
# $^{13}$C NMR *tert*-butyl (4-methylbenzyl)(2-oxoethyl)carbamate **s-1f**



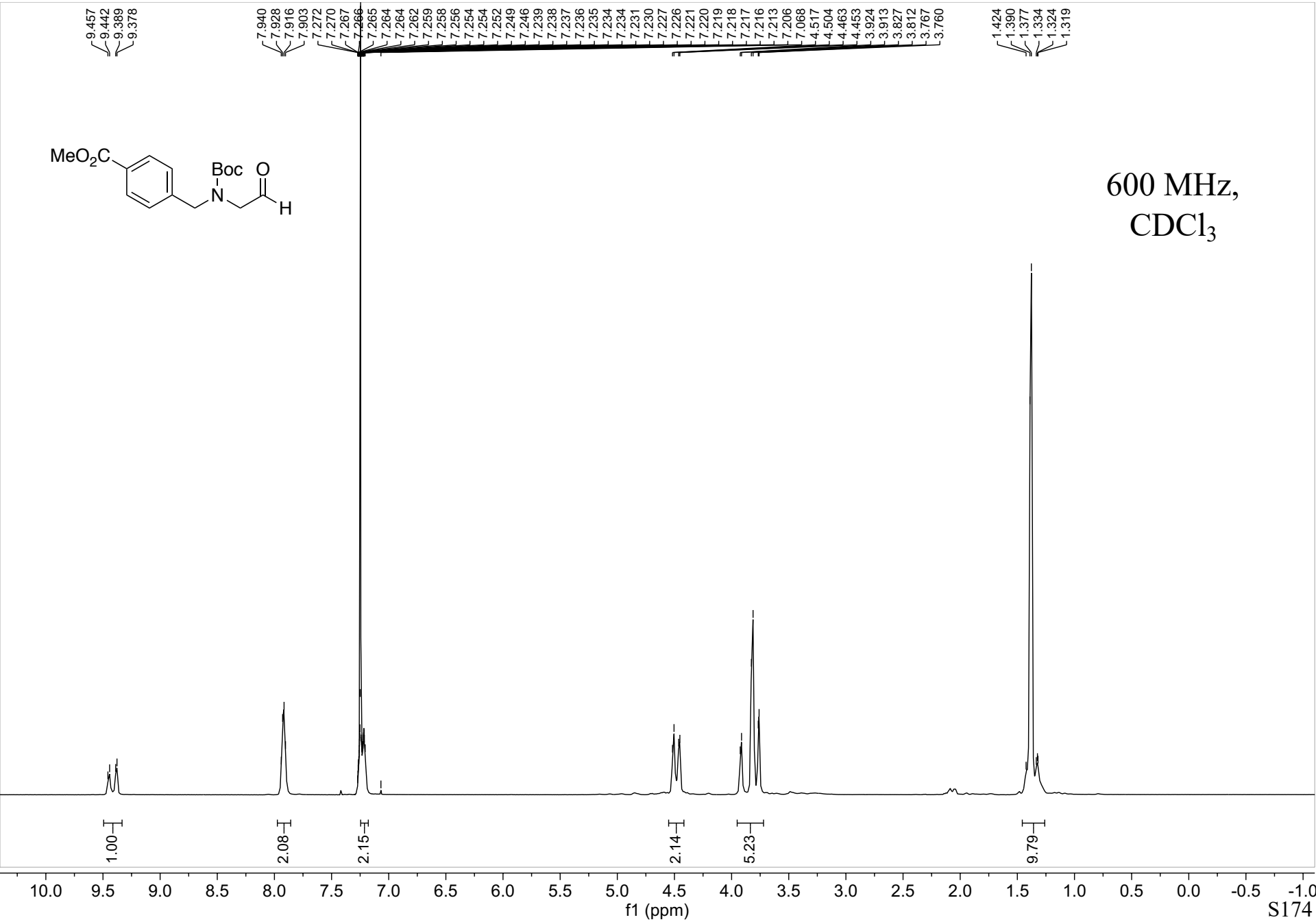
# $^{1}$H NMR *tert*-butyl (4-(dimethylamino)benzyl)(2-oxoethyl)carbamate **s-1g**



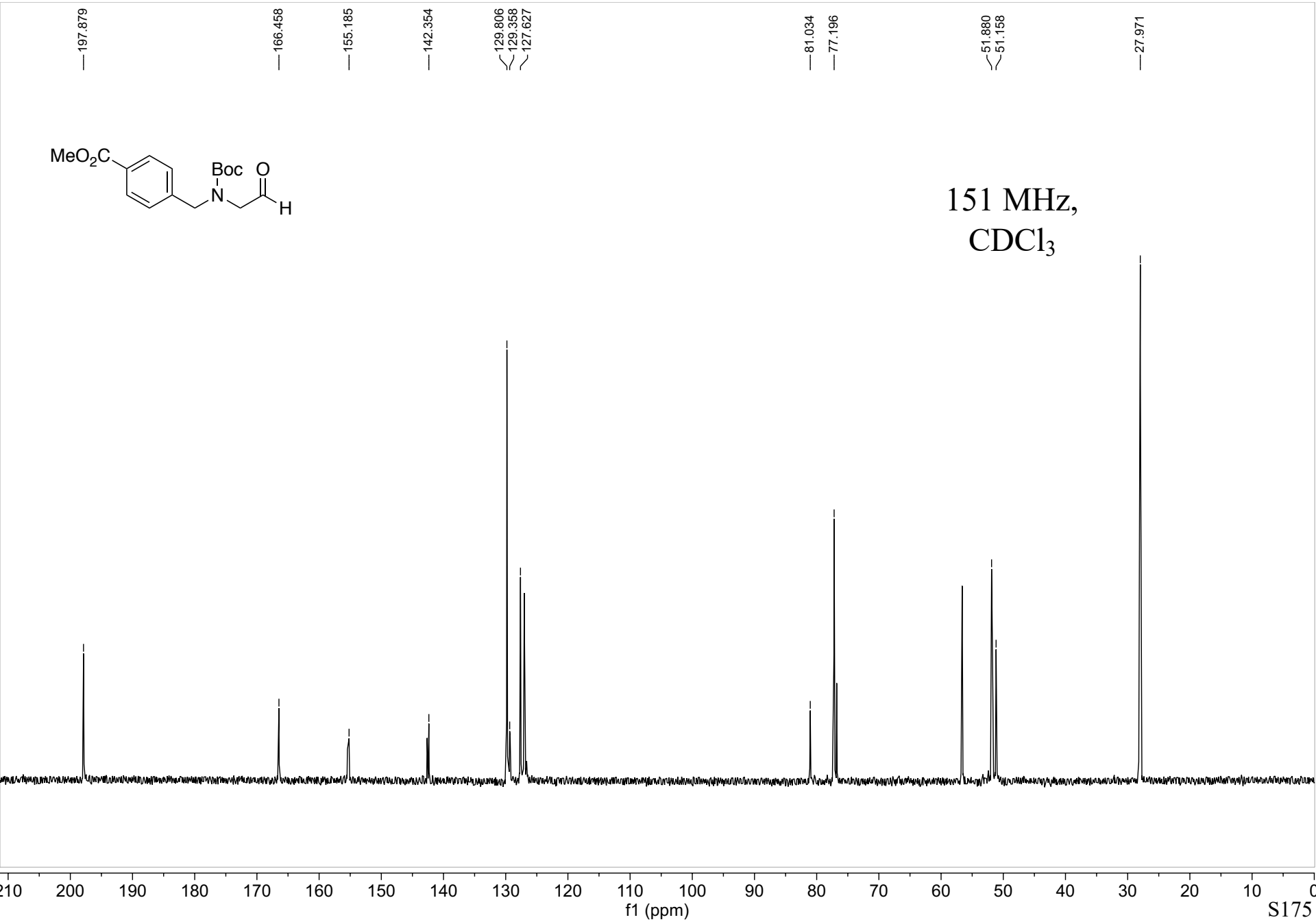
# $^{13}$C NMR *tert*-butyl (4-(dimethylamino)benzyl)(2-oxoethyl)carbamate **s-1g**



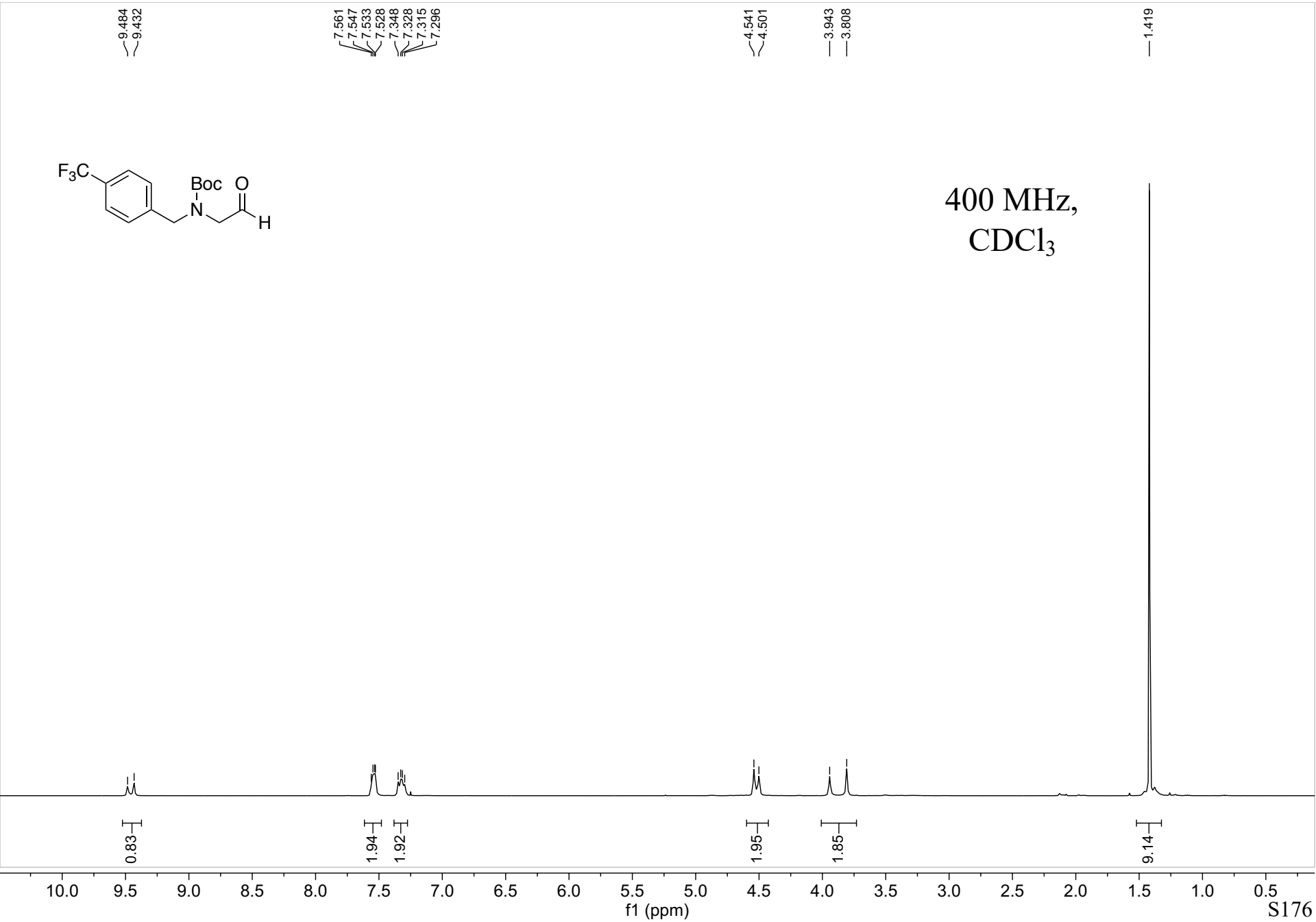
**$^1$H NMR** methyl 4-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)benzoate **s-1h**



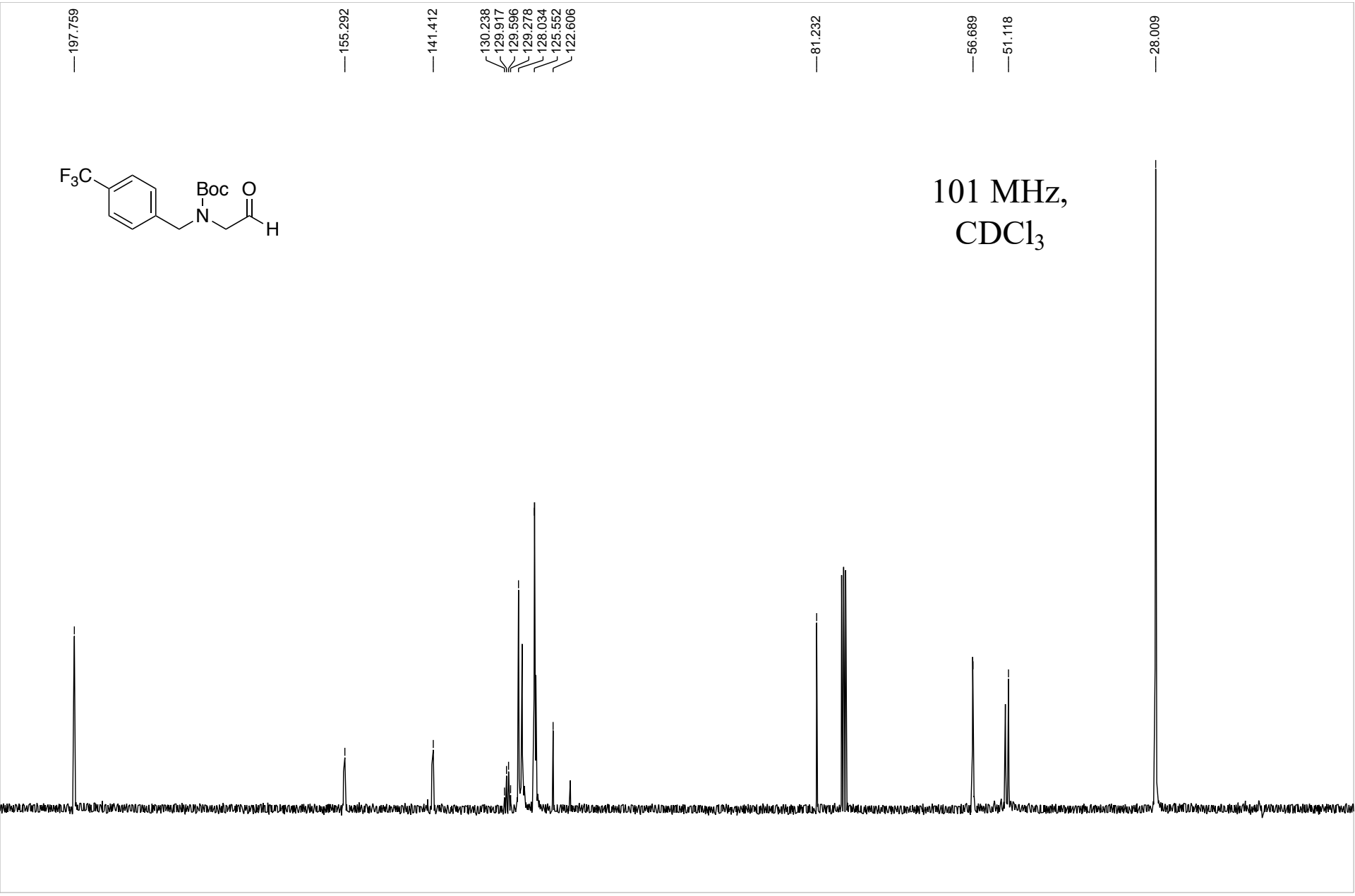
# $^{13}$C NMR methyl 4-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)benzoate **s-1h**



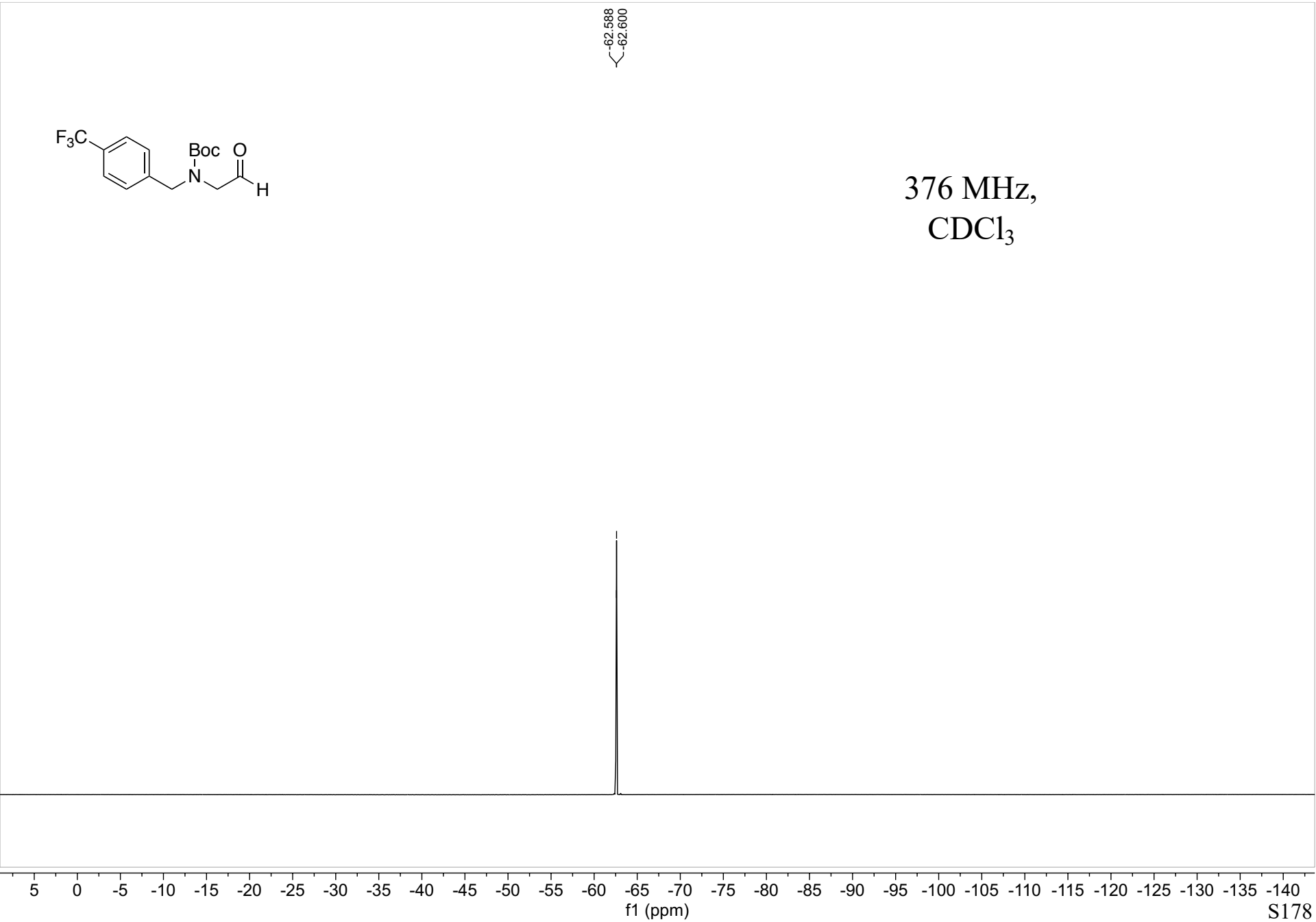
# $^{1}$H NMR *tert*-butyl (2-oxoethyl)(4-(trifluoromethyl)benzyl)carbamate **s-1i**



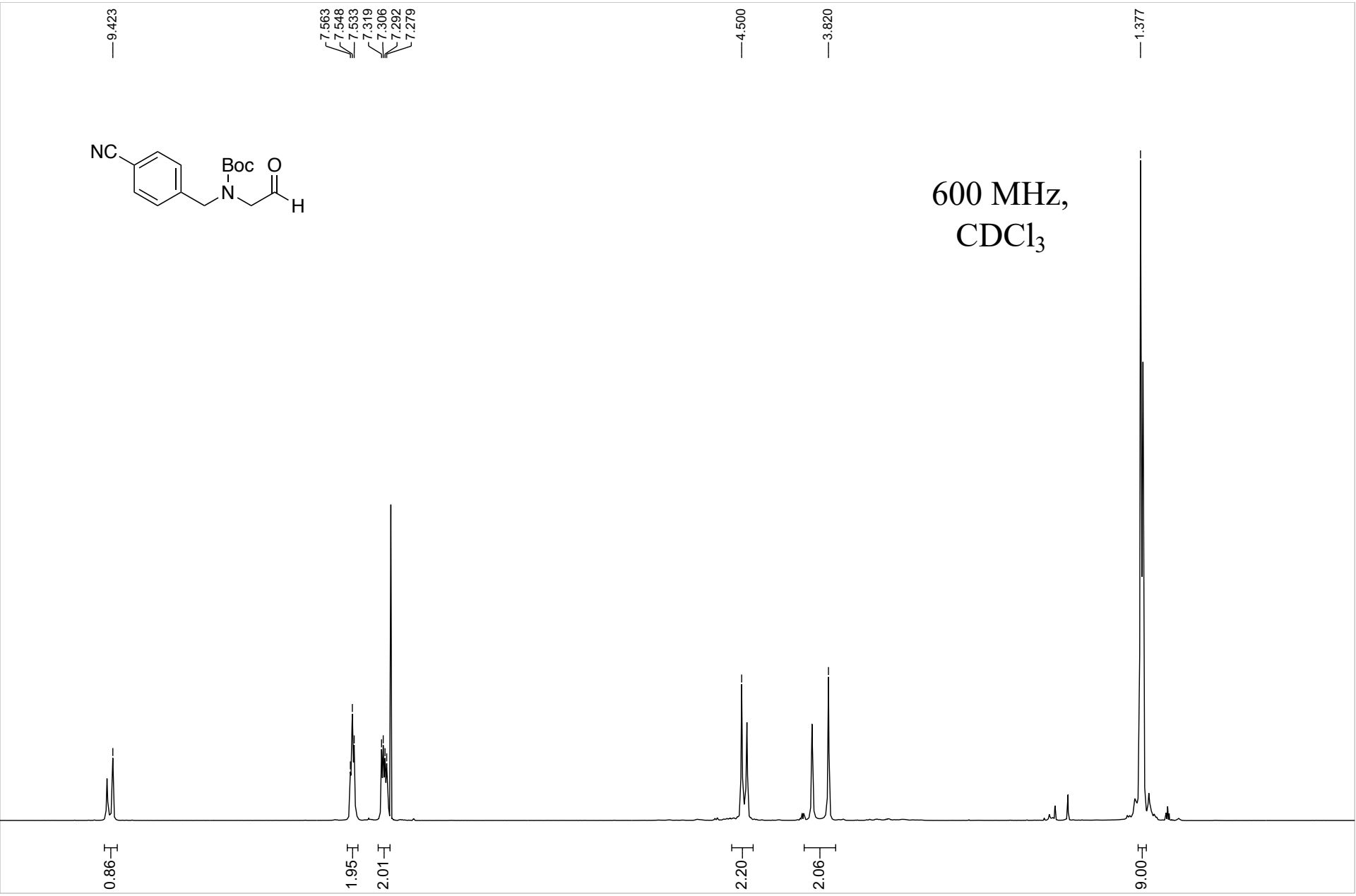
# $^{13}$C NMR *tert*-butyl (2-oxoethyl)(4-(trifluoromethyl)benzyl)carbamate **s-1i**



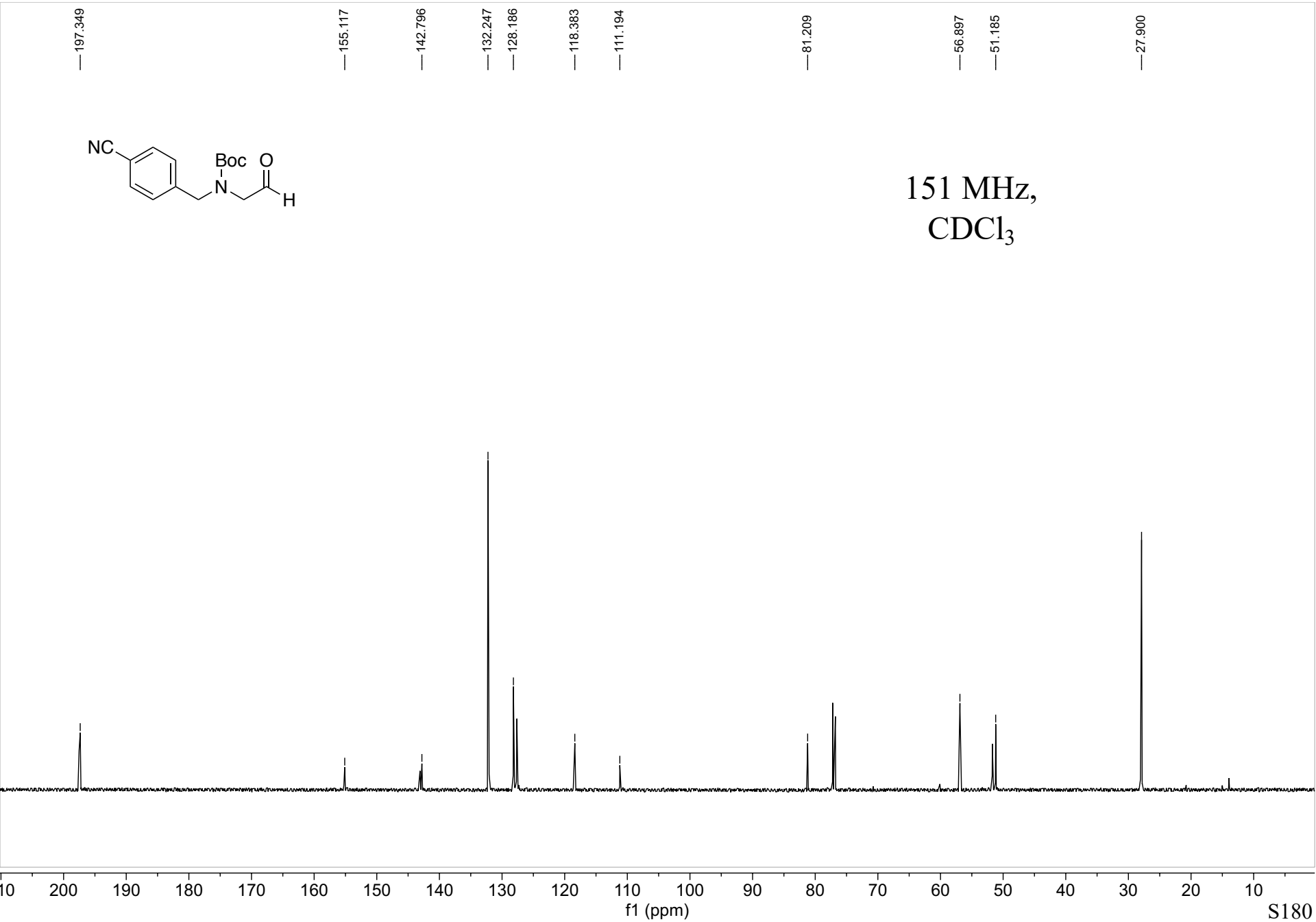
# $^{19}$F NMR *tert*-butyl (2-oxoethyl)(4-(trifluoromethyl)benzyl)carbamate **s-1i**



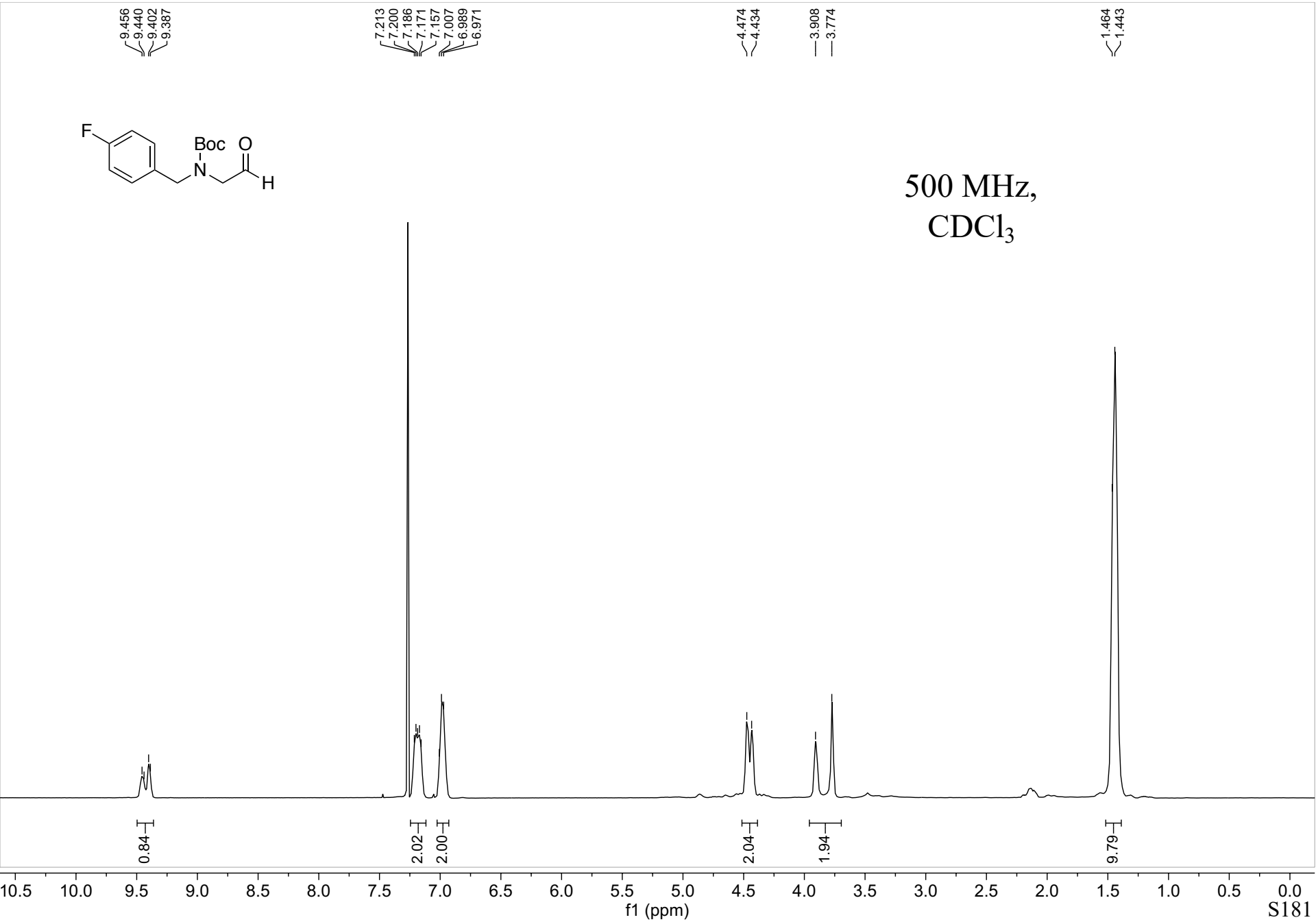
# $^{1}$H NMR *tert*-butyl (4-cyanobenzyl)(2-oxoethyl)carbamate **s-1j**



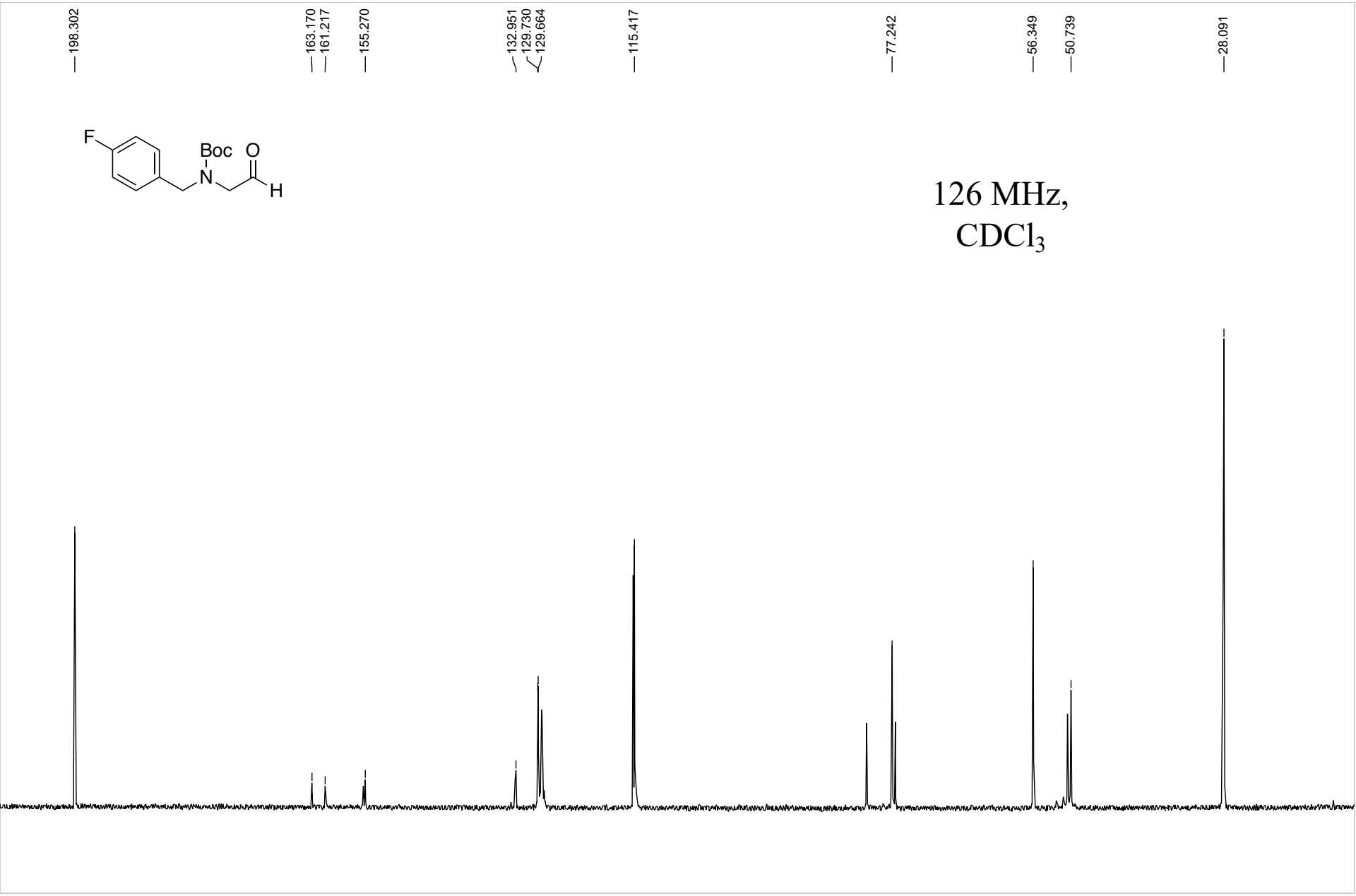
# $^{13}$C NMR *tert*-butyl (4-cyanobenzyl)(2-oxoethyl)carbamate **s-1j**



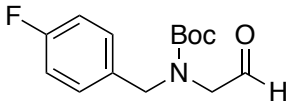
# $^{1}$H NMR *tert*-butyl (4-fluorobenzyl)(2-oxoethyl)carbamate **s-1k**



# $^{13}$C NMR *tert*-butyl (4-fluorobenzyl)(2-oxoethyl)carbamate **s-1k**

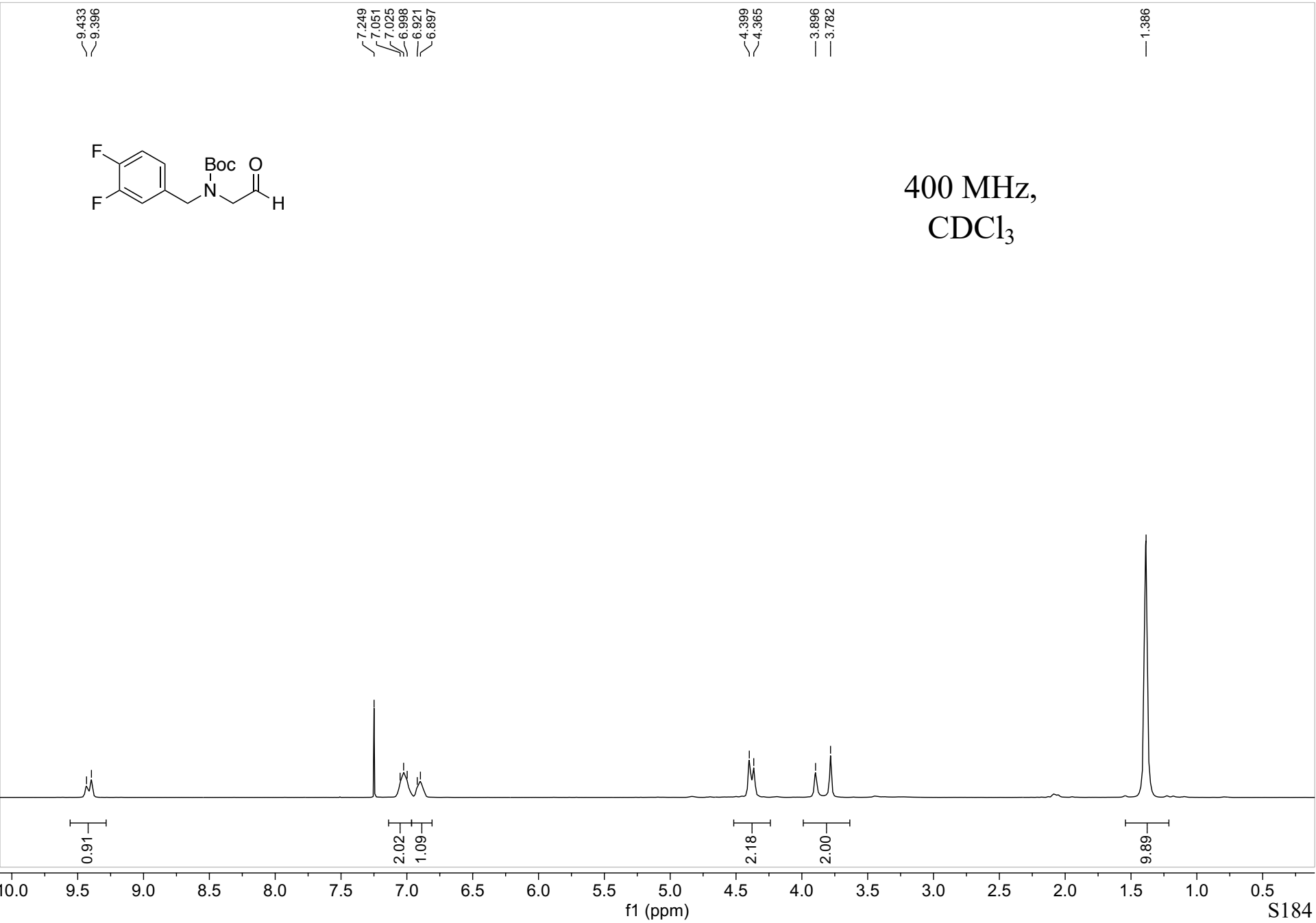


# $^{19}$F NMR *tert*-butyl (4-fluorobenzyl)(2-oxoethyl)carbamate **s-1k**

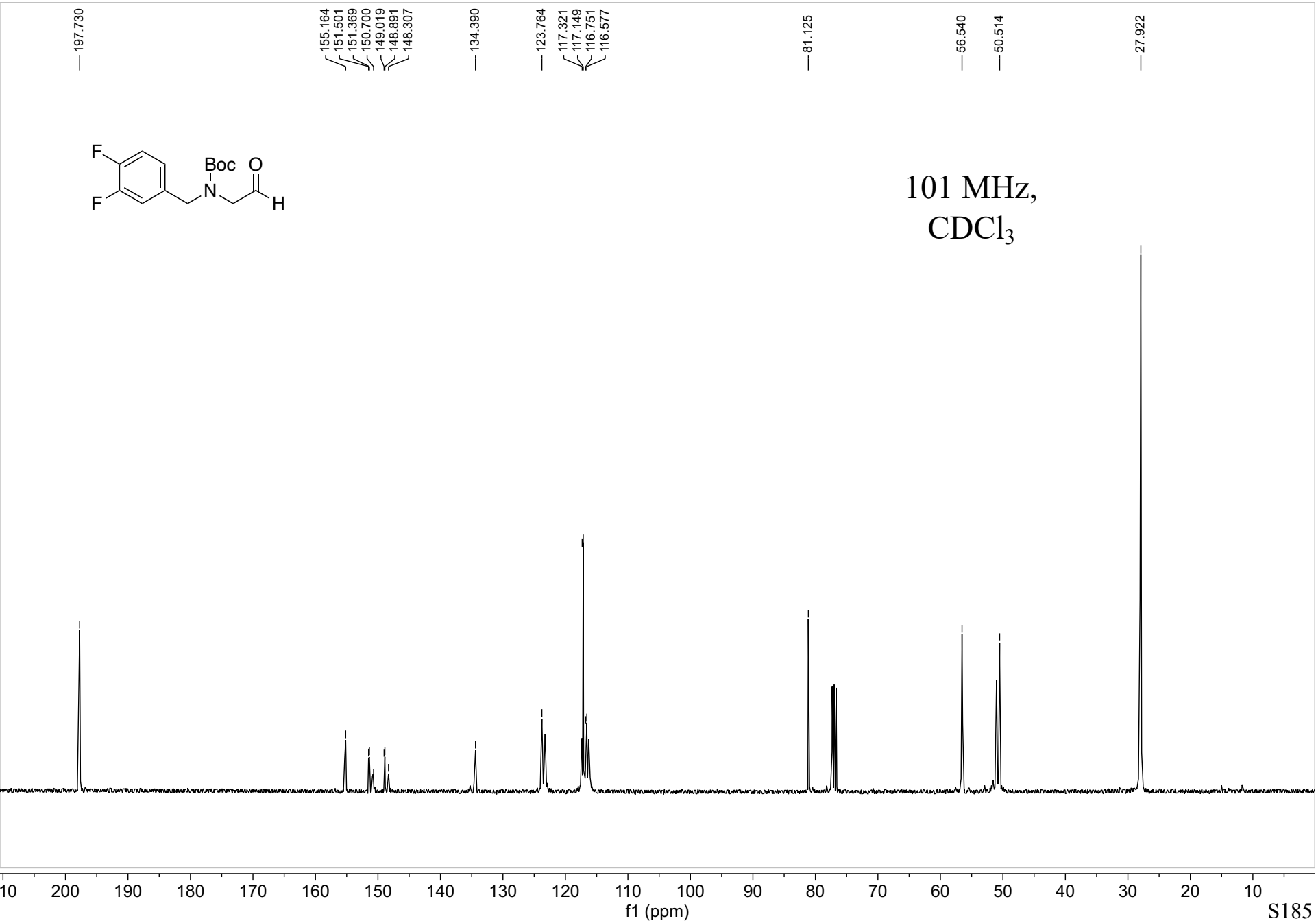



470 MHz,
$CDCl_3$

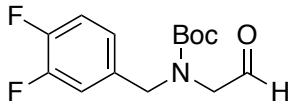
# $^{1}$H NMR *tert*-butyl (3,4-difluorobenzyl)(2-oxoethyl)carbamate **s-1l**



# $^{13}$C NMR *tert*-butyl (3,4-difluorobenzyl)(2-oxoethyl)carbamate **s-1l**

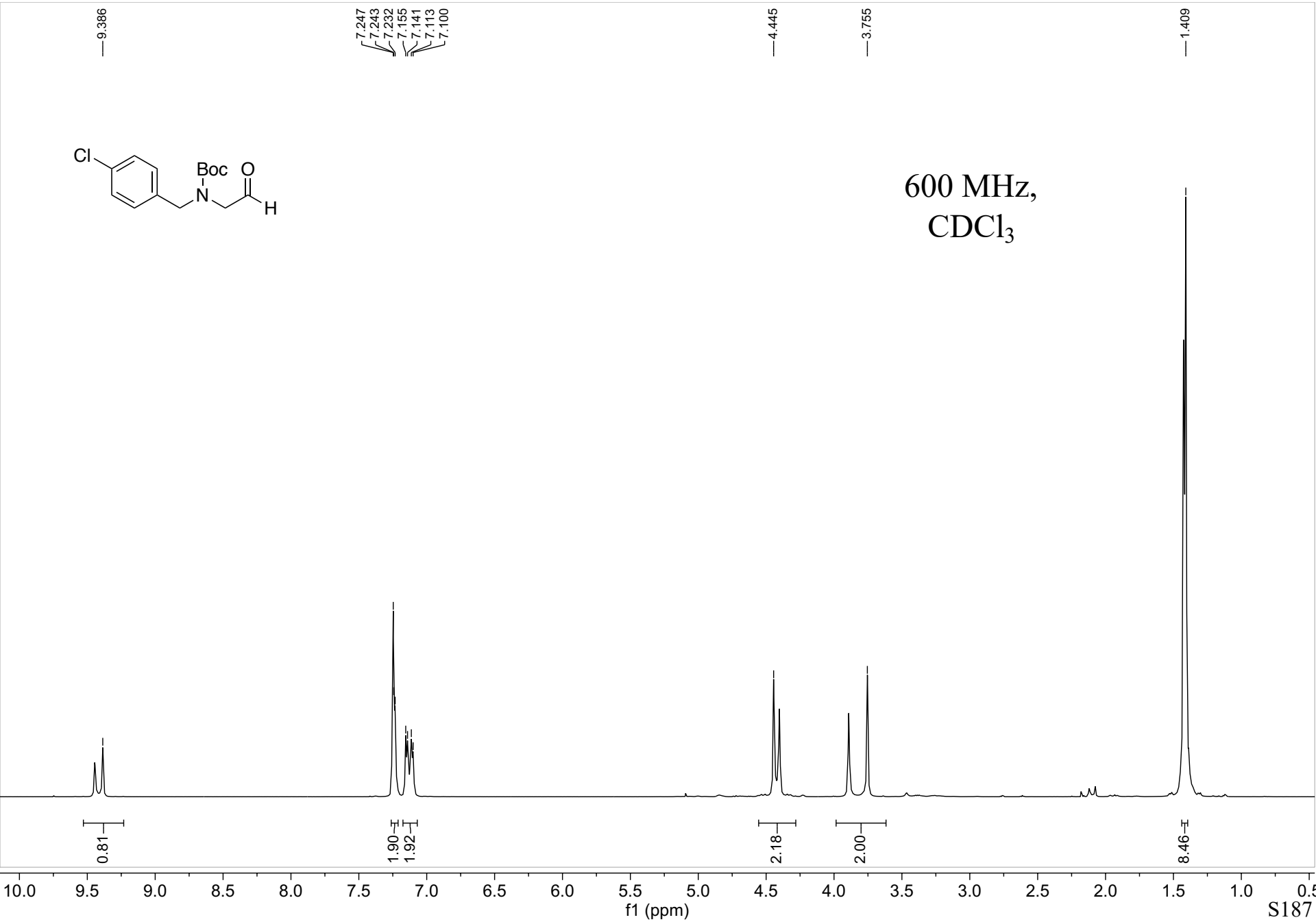


# $^{19}$F NMR *tert*-butyl (3,4-difluorobenzyl)(2-oxoethyl)carbamate **s-1l**

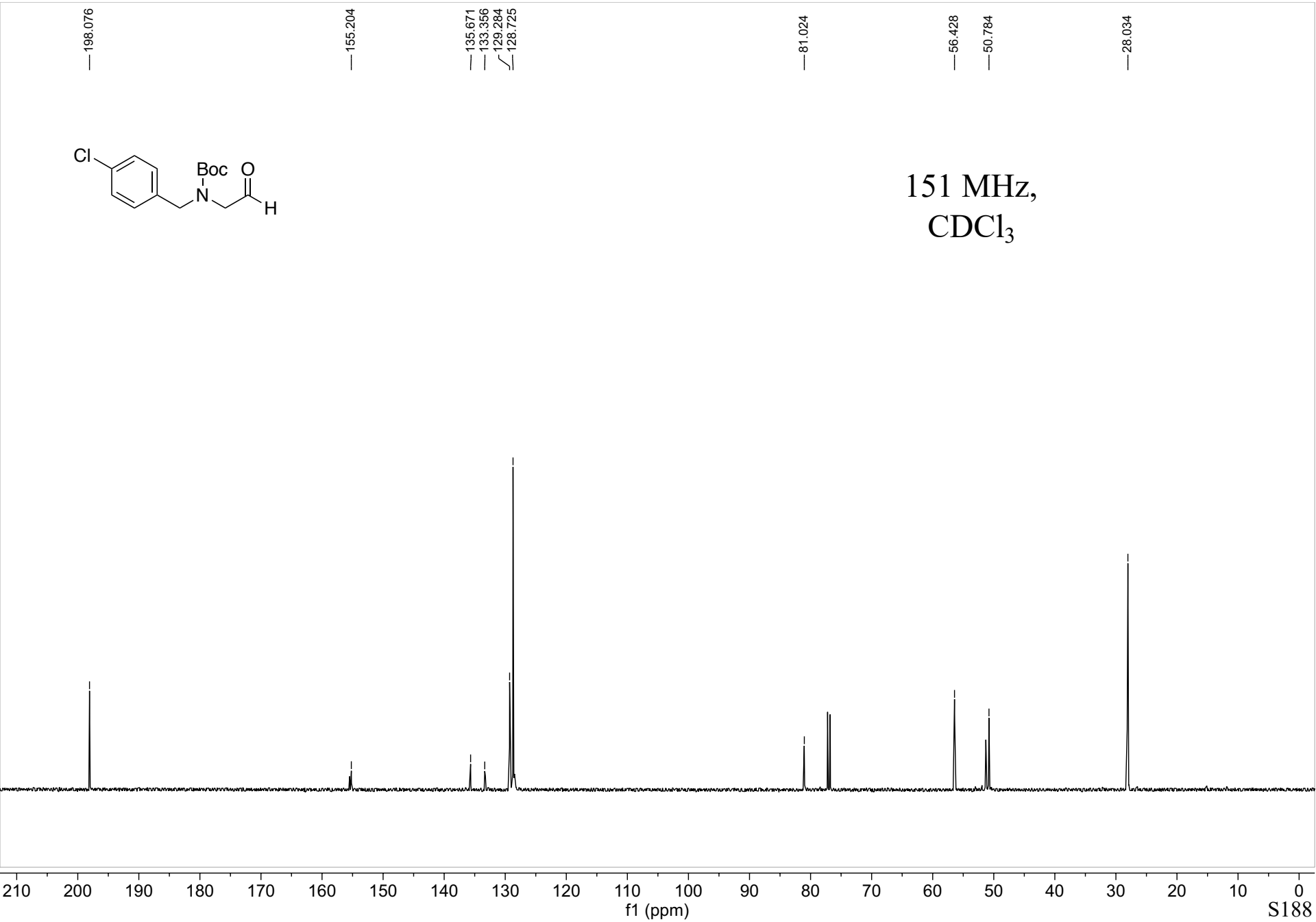



376 MHz,
$CDCl_3$

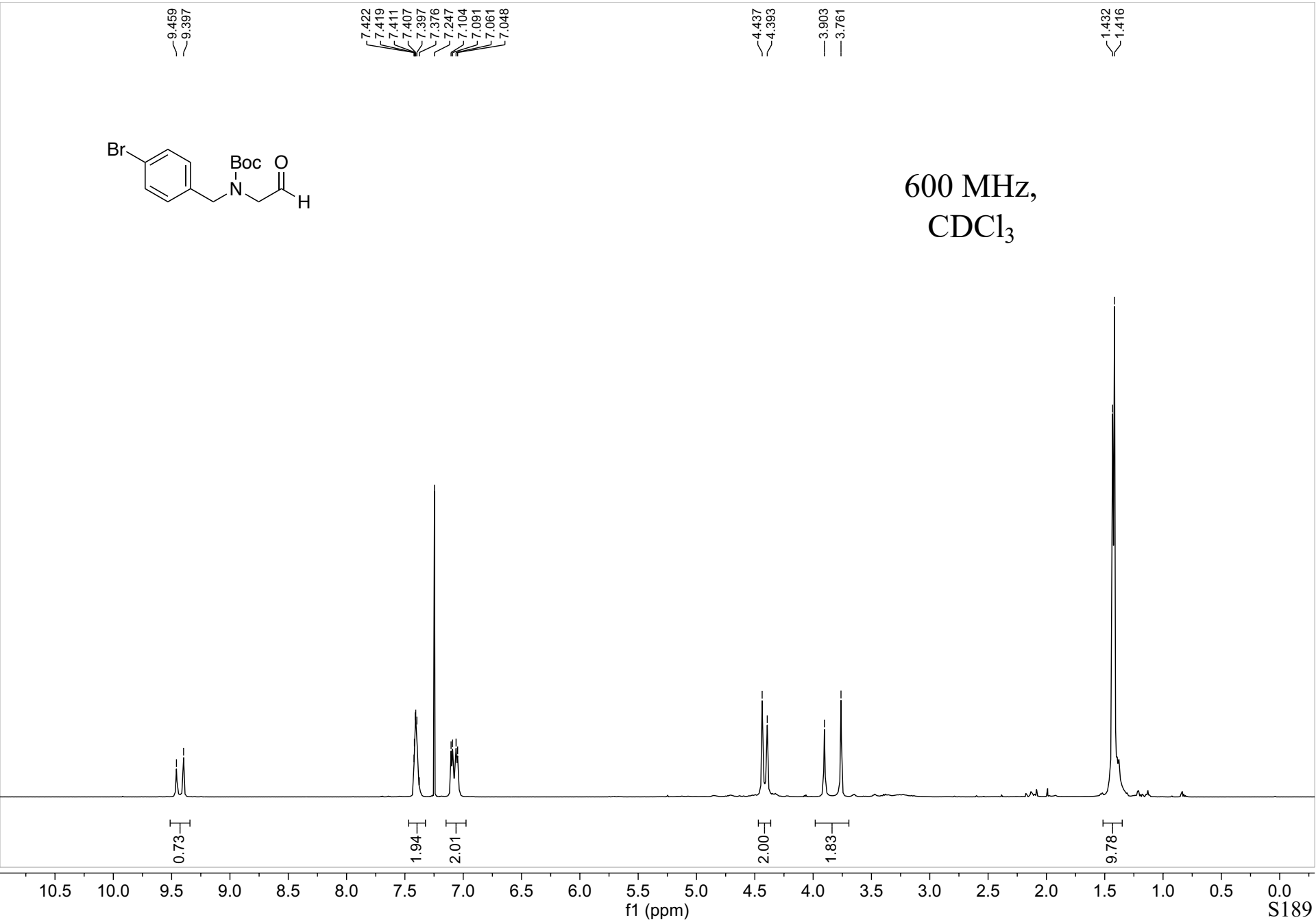
# $^{1}$H NMR *tert*-butyl (4-chlorobenzyl)(2-oxoethyl)carbamate **s-1m**



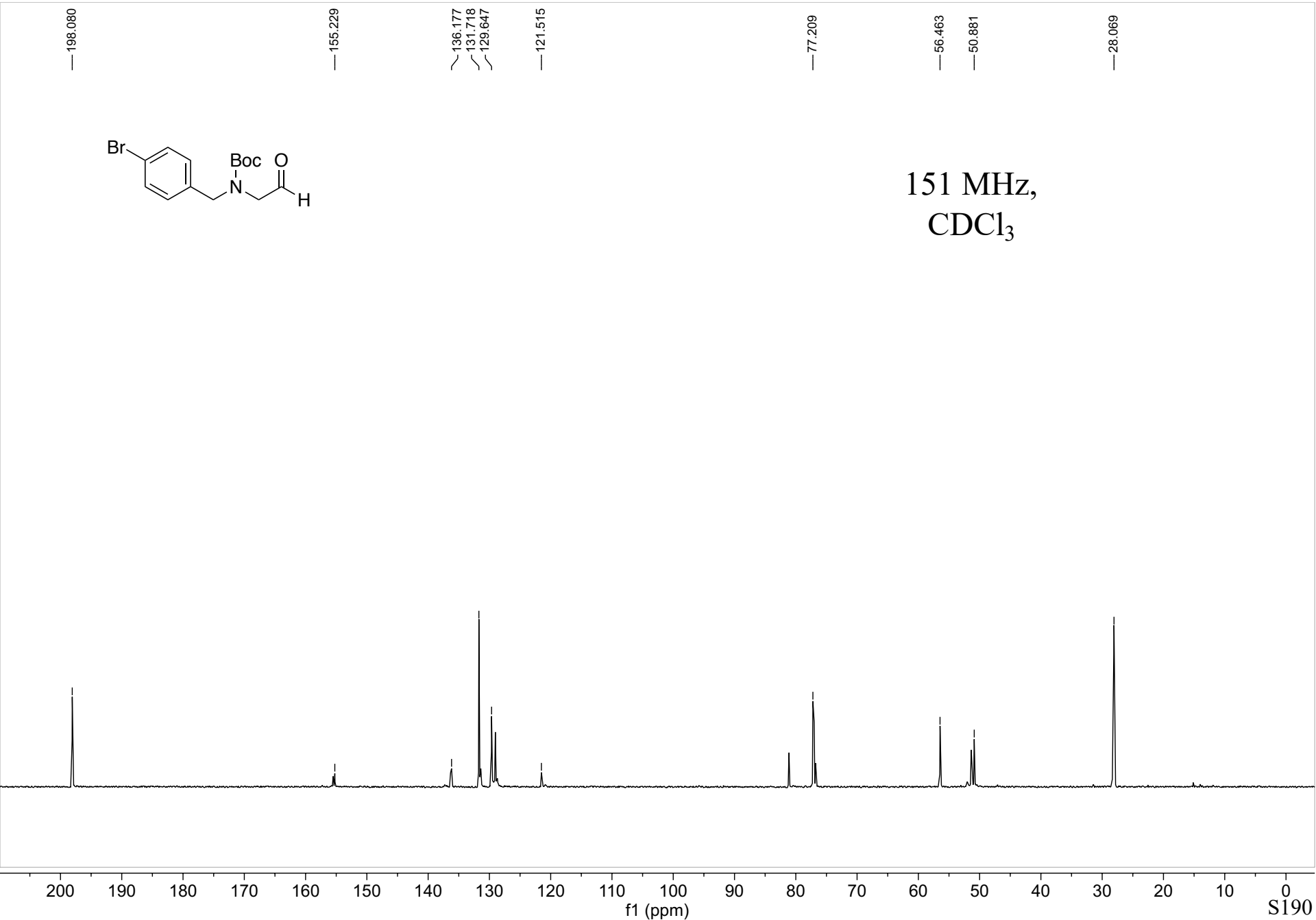
# $^{13}$C NMR *tert*-butyl (4-chlorobenzyl)(2-oxoethyl)carbamate **s-1m**



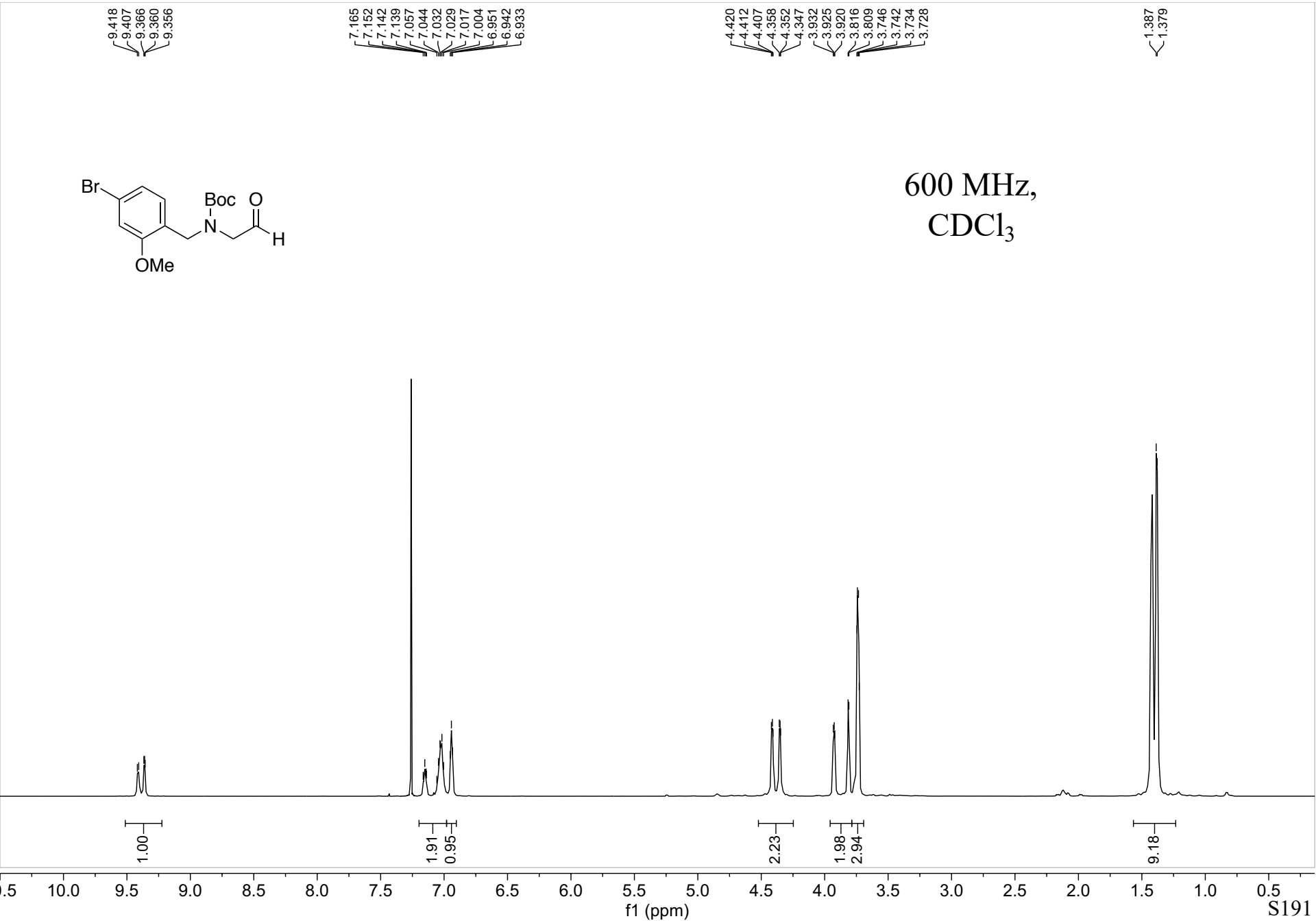
# $^{1}$H NMR *tert*-butyl (4-bromobenzyl)(2-oxoethyl)carbamate **s-1n**



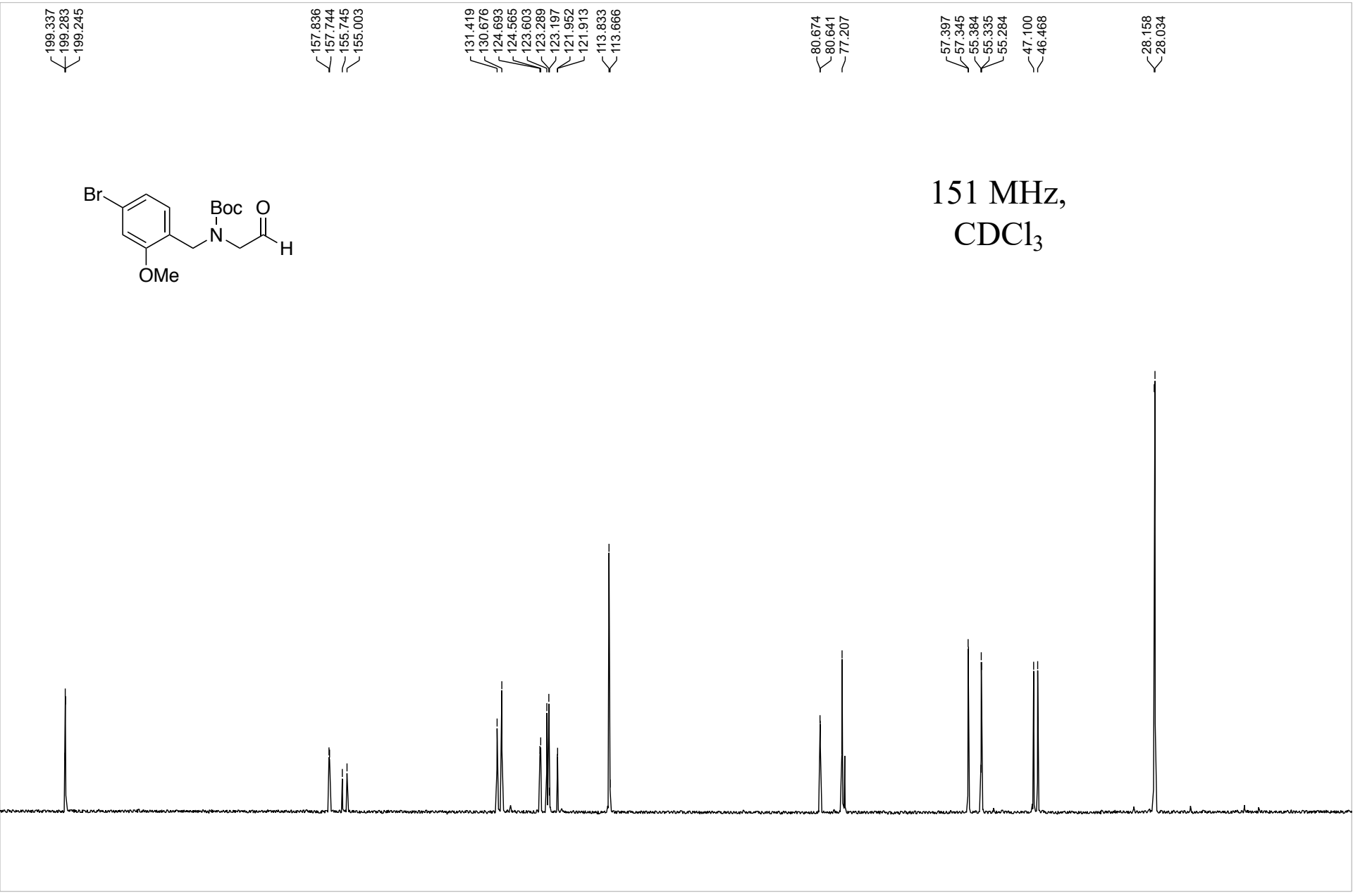
# $^{13}$C NMR *tert*-butyl (4-bromobenzyl)(2-oxoethyl)carbamate **s-1n**



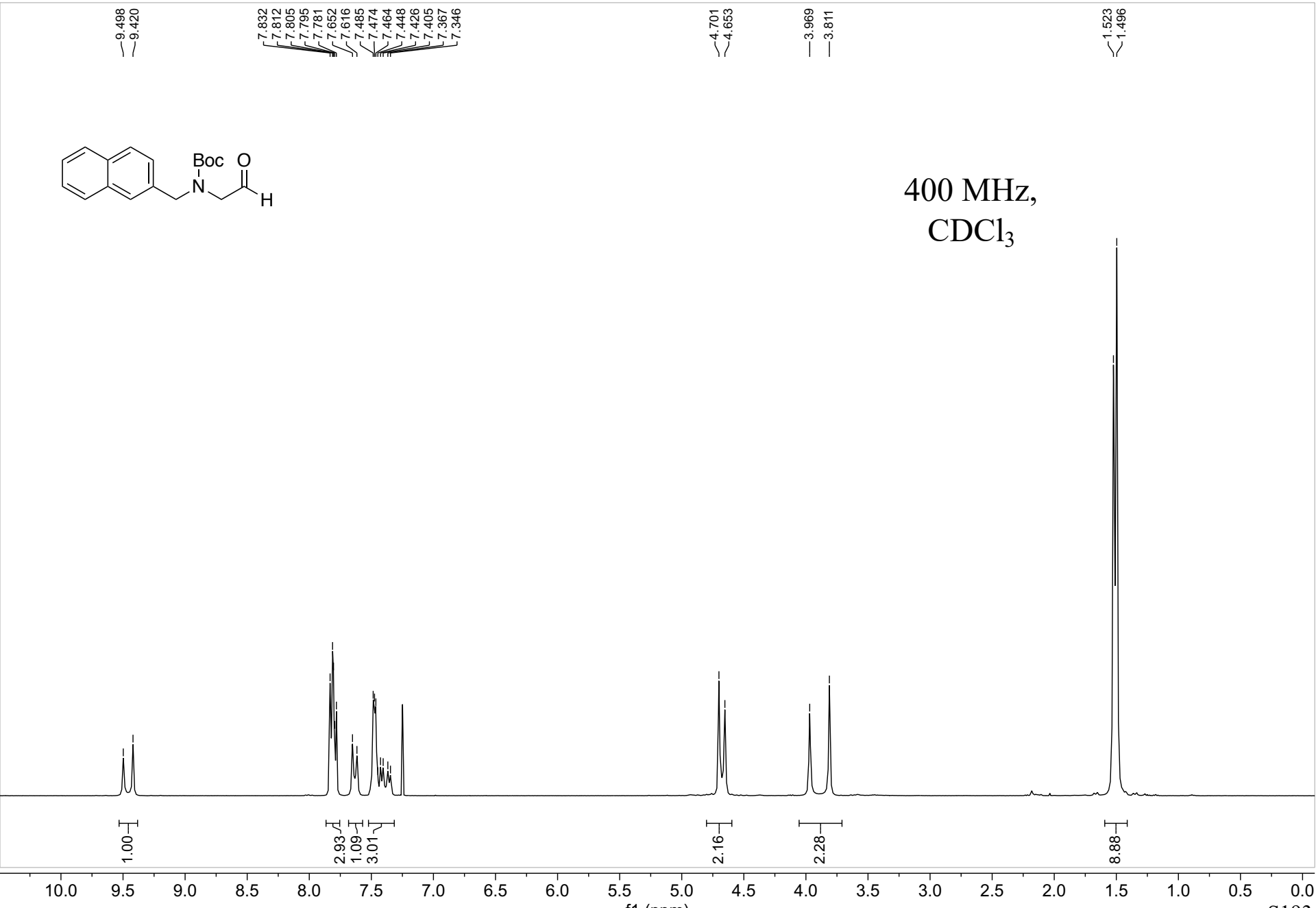
# $^{1}$H NMR *tert*-butyl (4-bromo-2-methoxybenzyl)(2-oxoethyl)carbamate **s-1o**



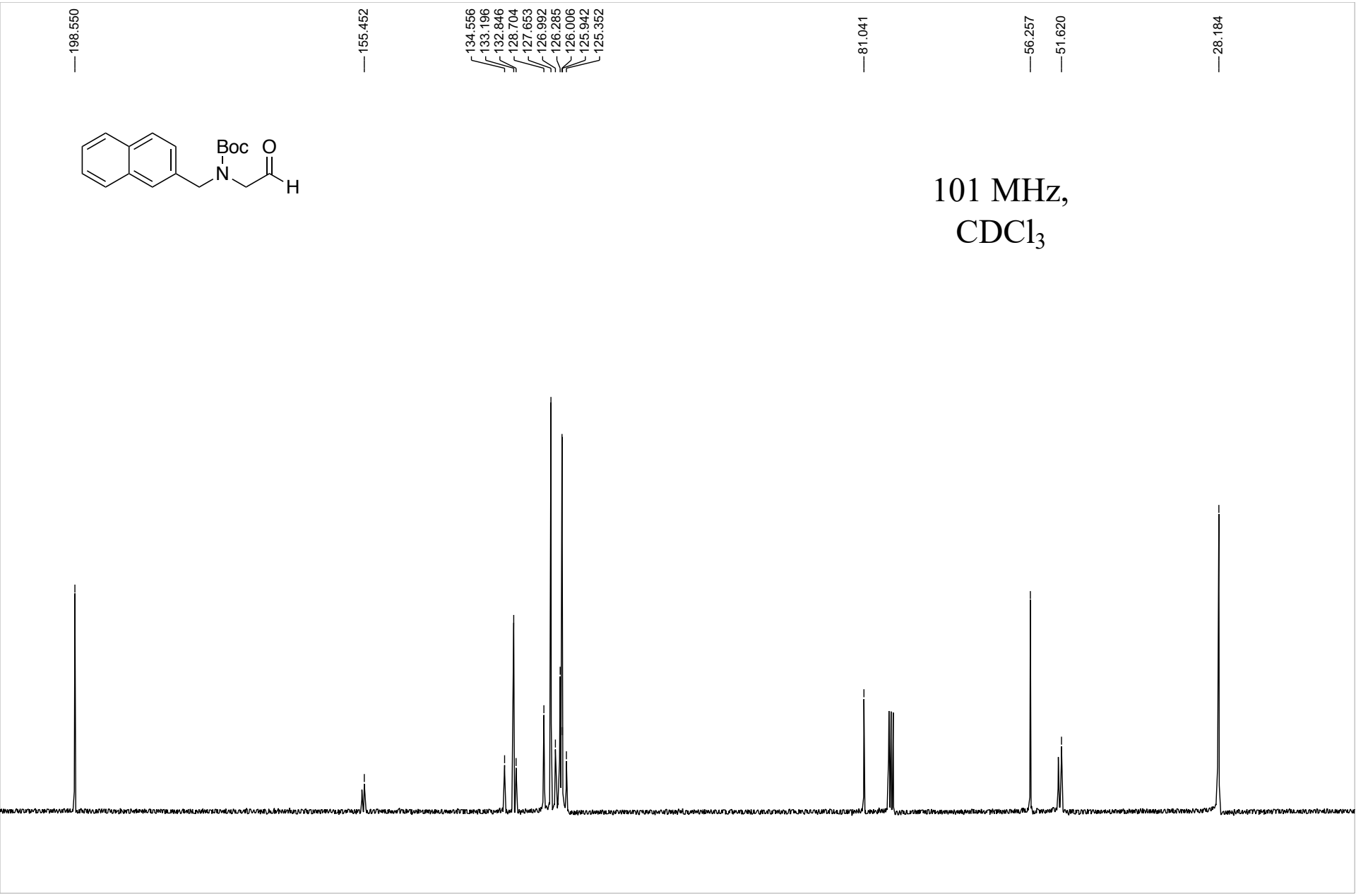
# $^{13}$C NMR *tert*-butyl (4-bromo-2-methoxybenzyl)(2-oxoethyl)carbamate **s-1o**



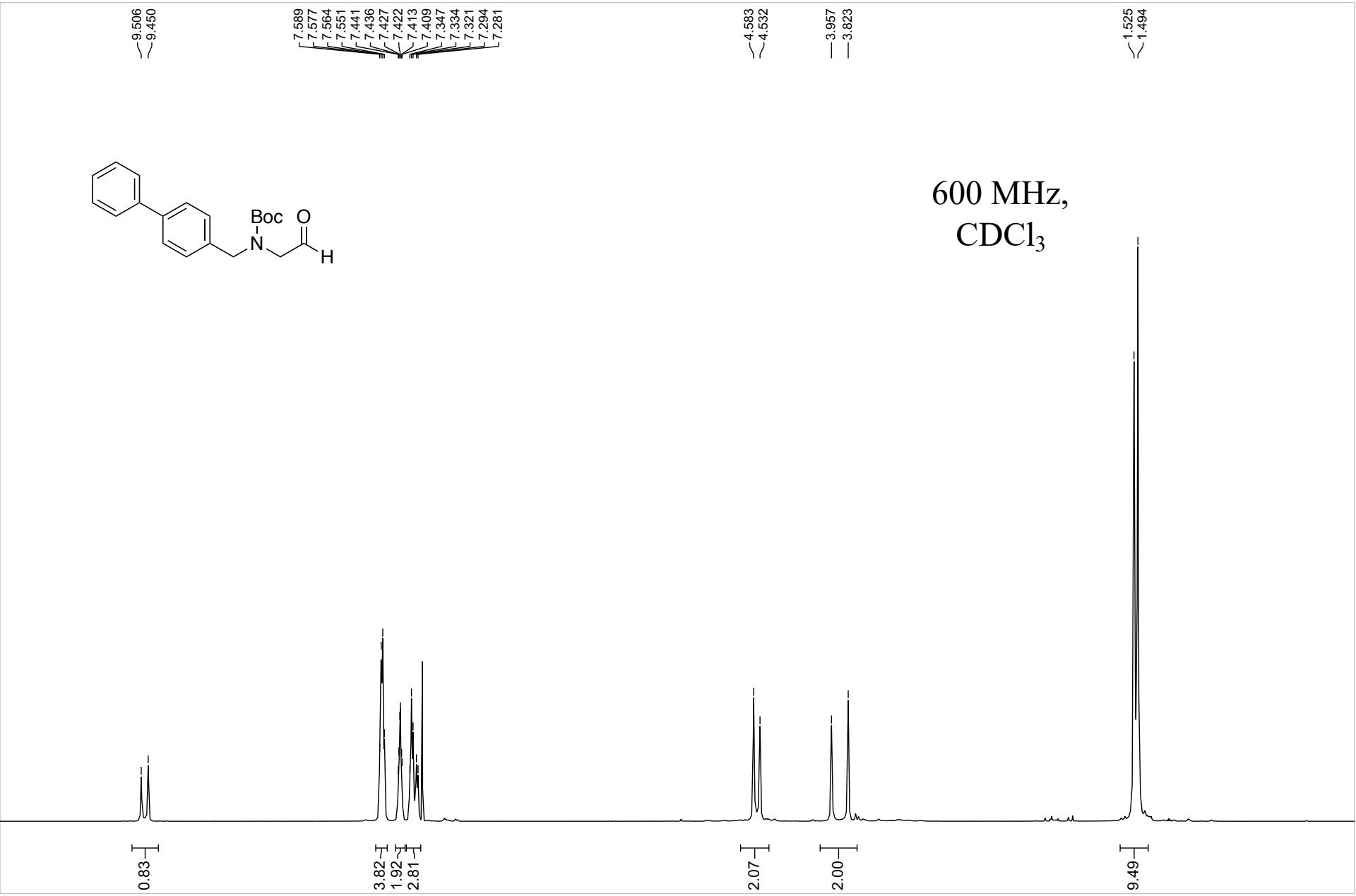
# $^{1}$H NMR *tert*-butyl (naphthalen-2-ylmethyl)(2-oxoethyl)carbamate **s-1p**



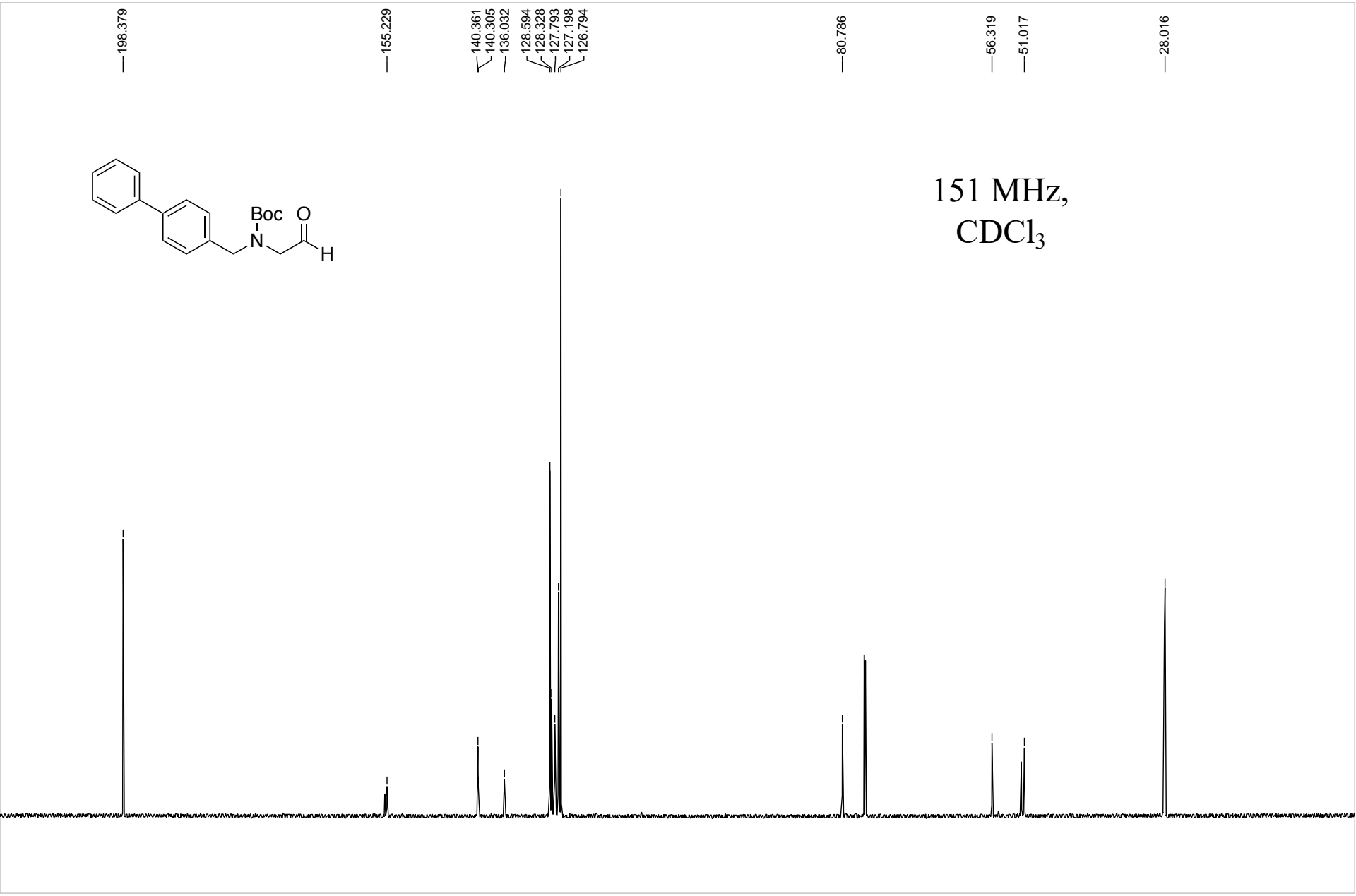
# $^{13}$C NMR *tert*-butyl (naphthalen-2-ylmethyl)(2-oxoethyl)carbamate **s-1p**



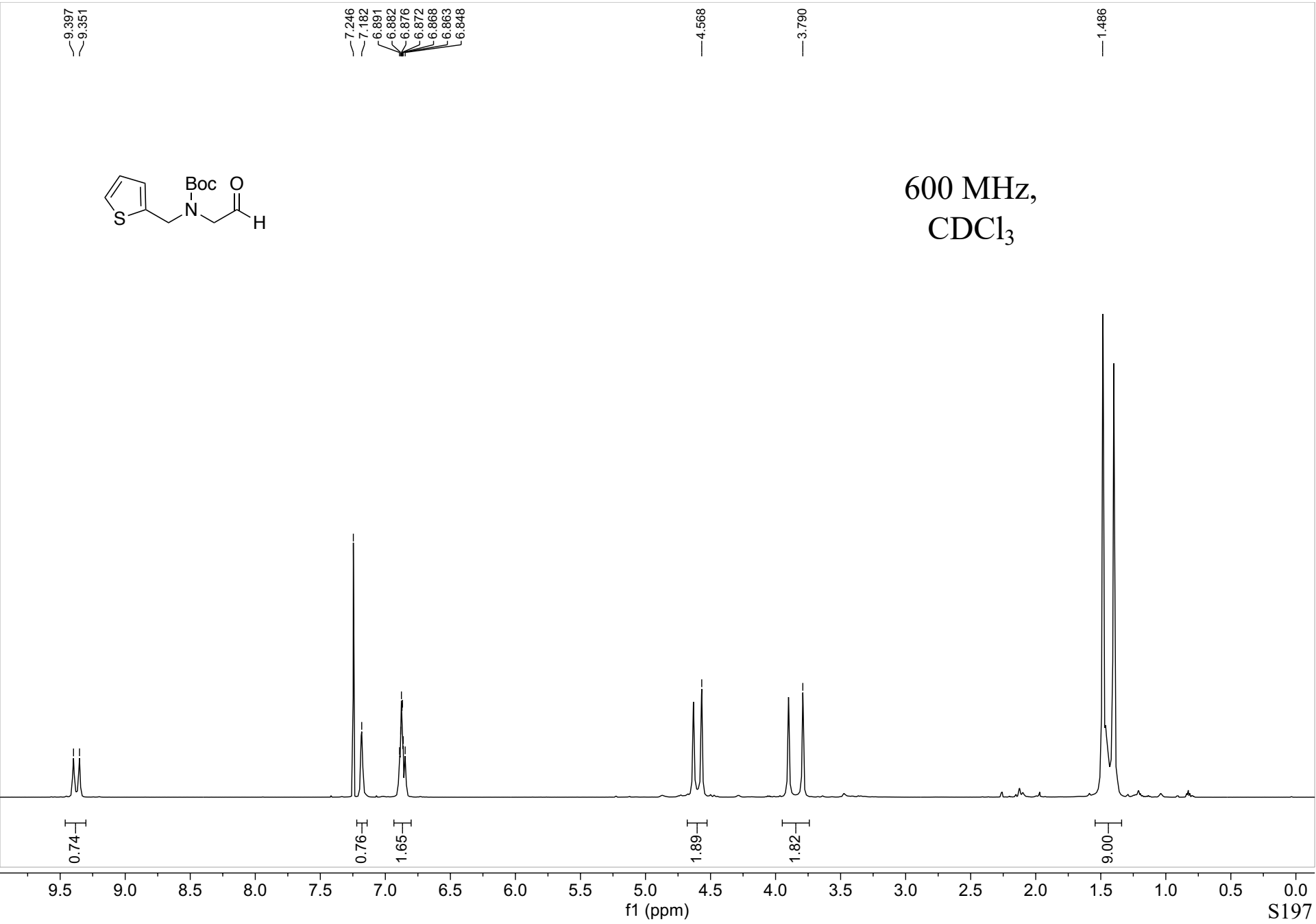
# $^{1}$H NMR *tert*-butyl ([1,1'-biphenyl]-4-ylmethyl)(2-oxoethyl)carbamate **s-1q**



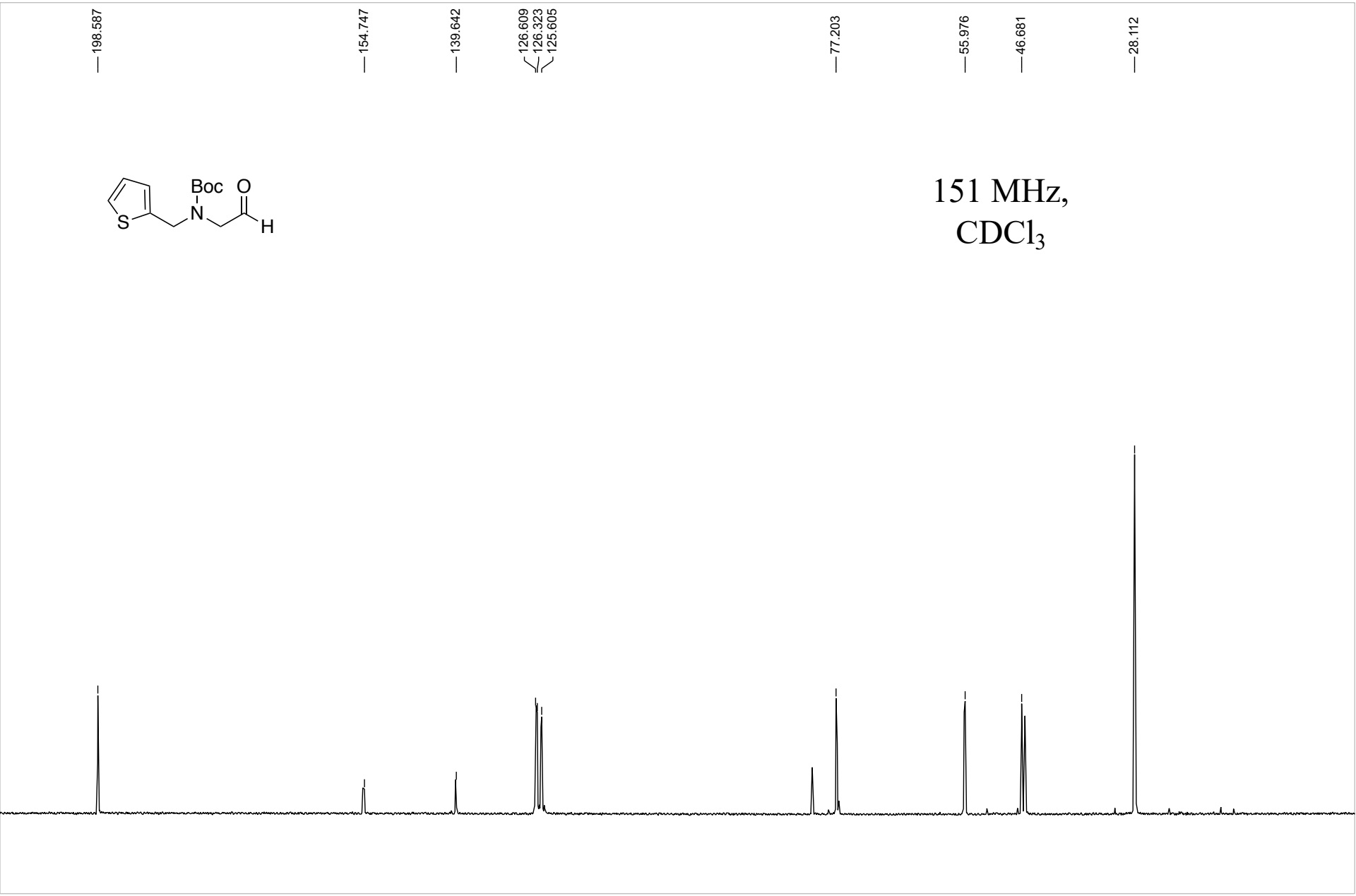
# $^{13}$C NMR *tert*-butyl ([1,1'-biphenyl]-4-ylmethyl)(2-oxoethyl)carbamate **s-1q**



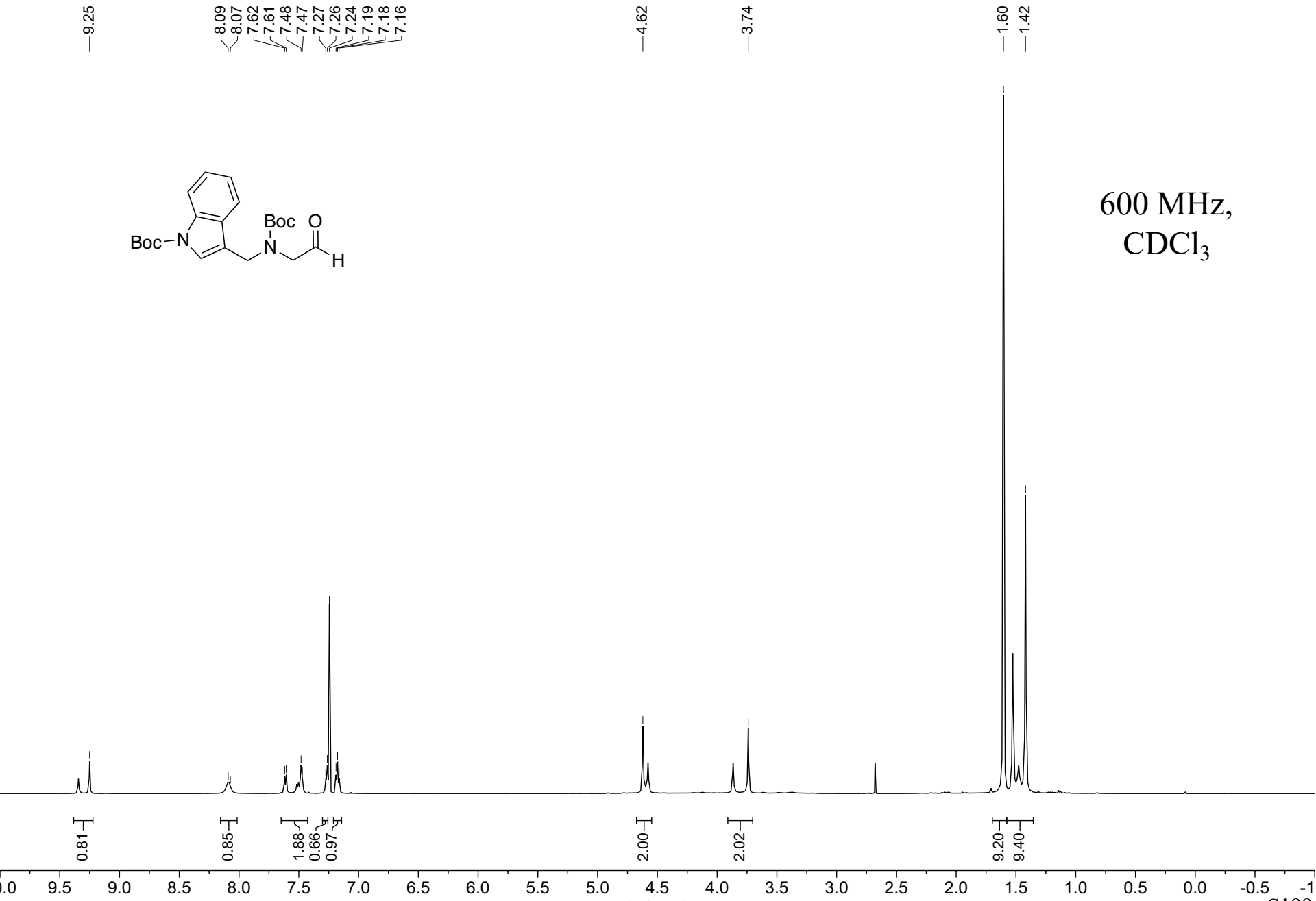
# $^{1}$H NMR *tert*-butyl (2-oxoethyl)(thiophen-2-ylmethyl)carbamate **s-1r**



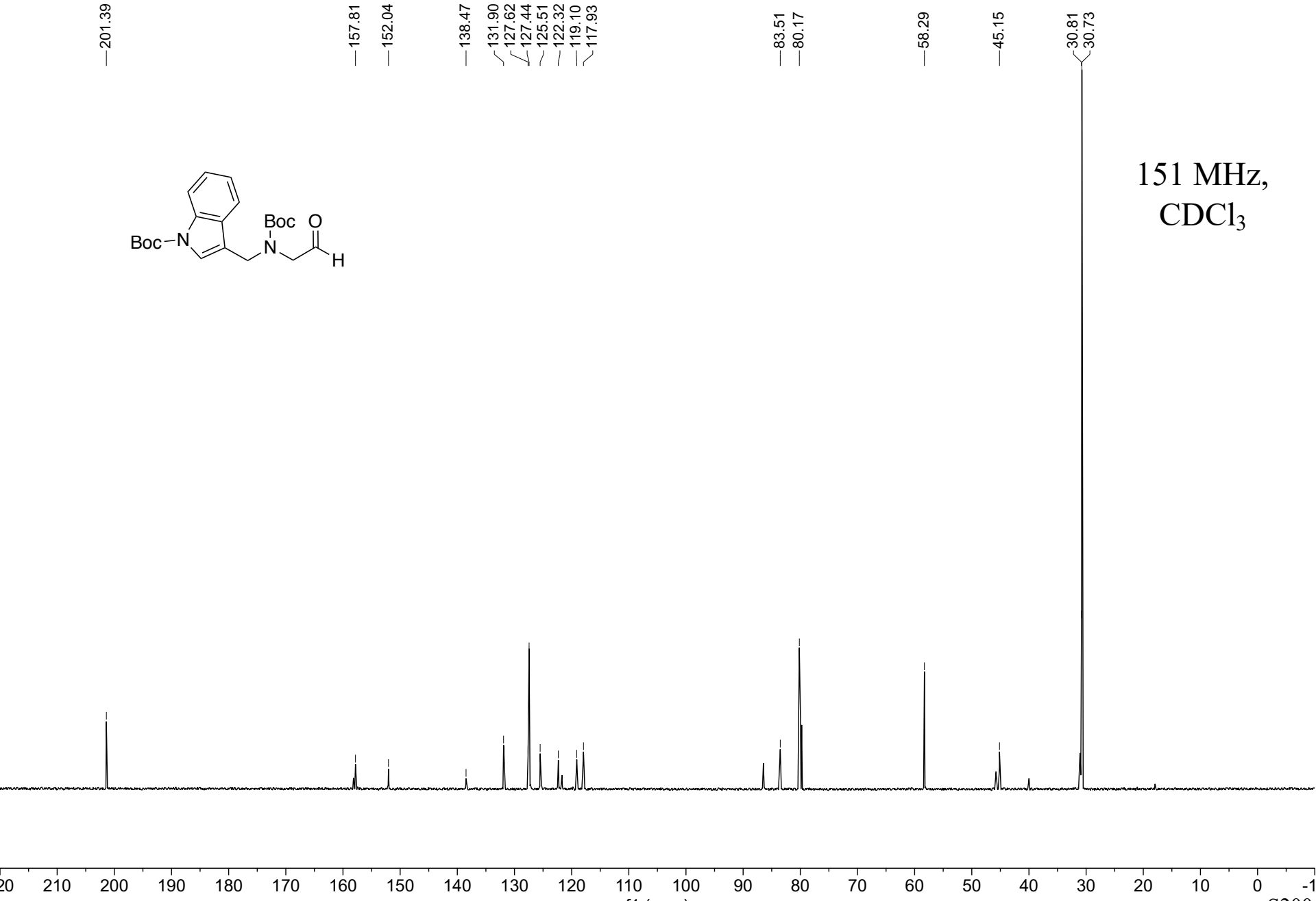
# $^{13}$C NMR *tert*-butyl (2-oxoethyl)(thiophen-2-ylmethyl)carbamate **s-1r**



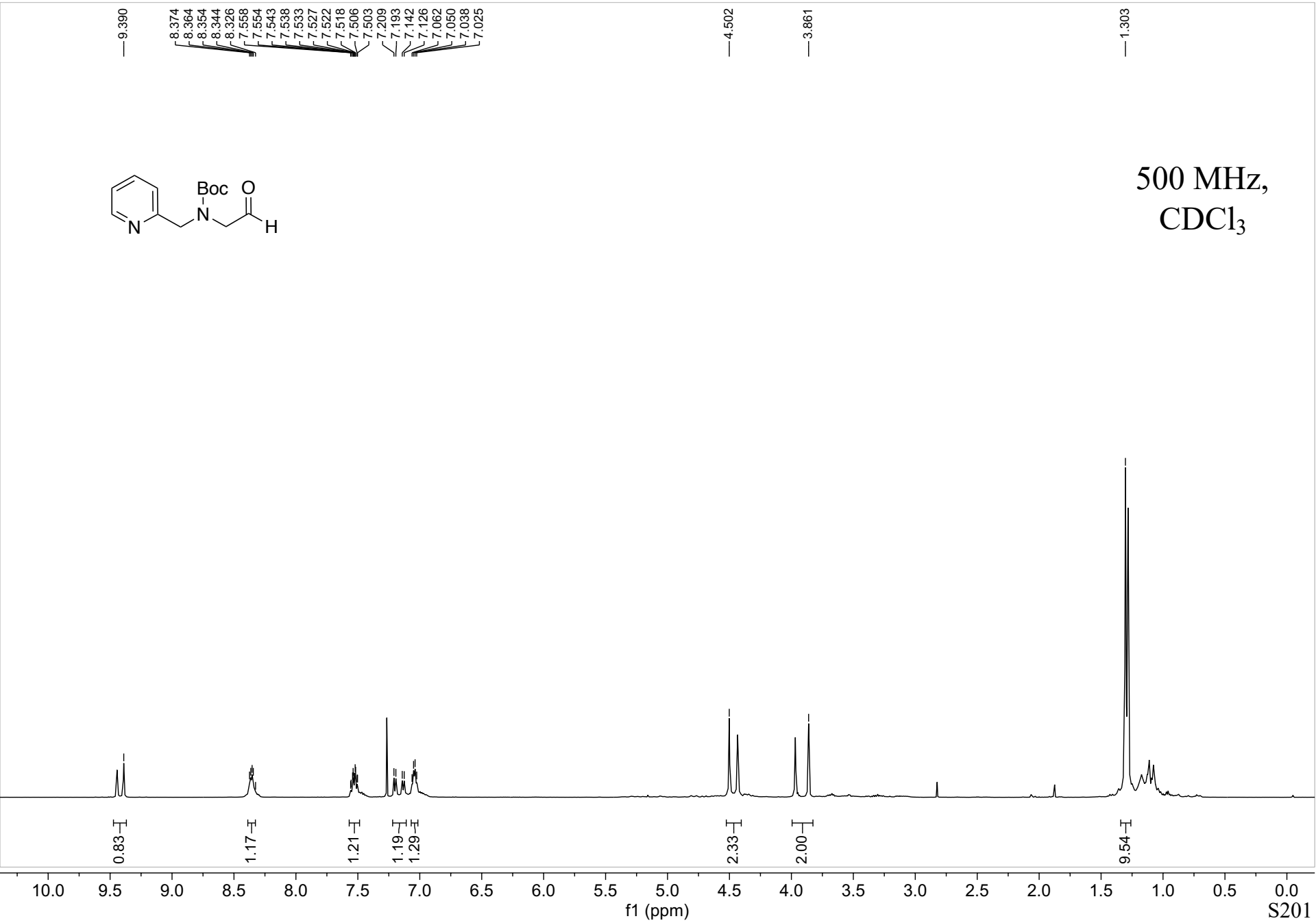
**$^1$H NMR** *tert*-butyl 3-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)-1*H*-indole-1-carboxylate **s-1s**



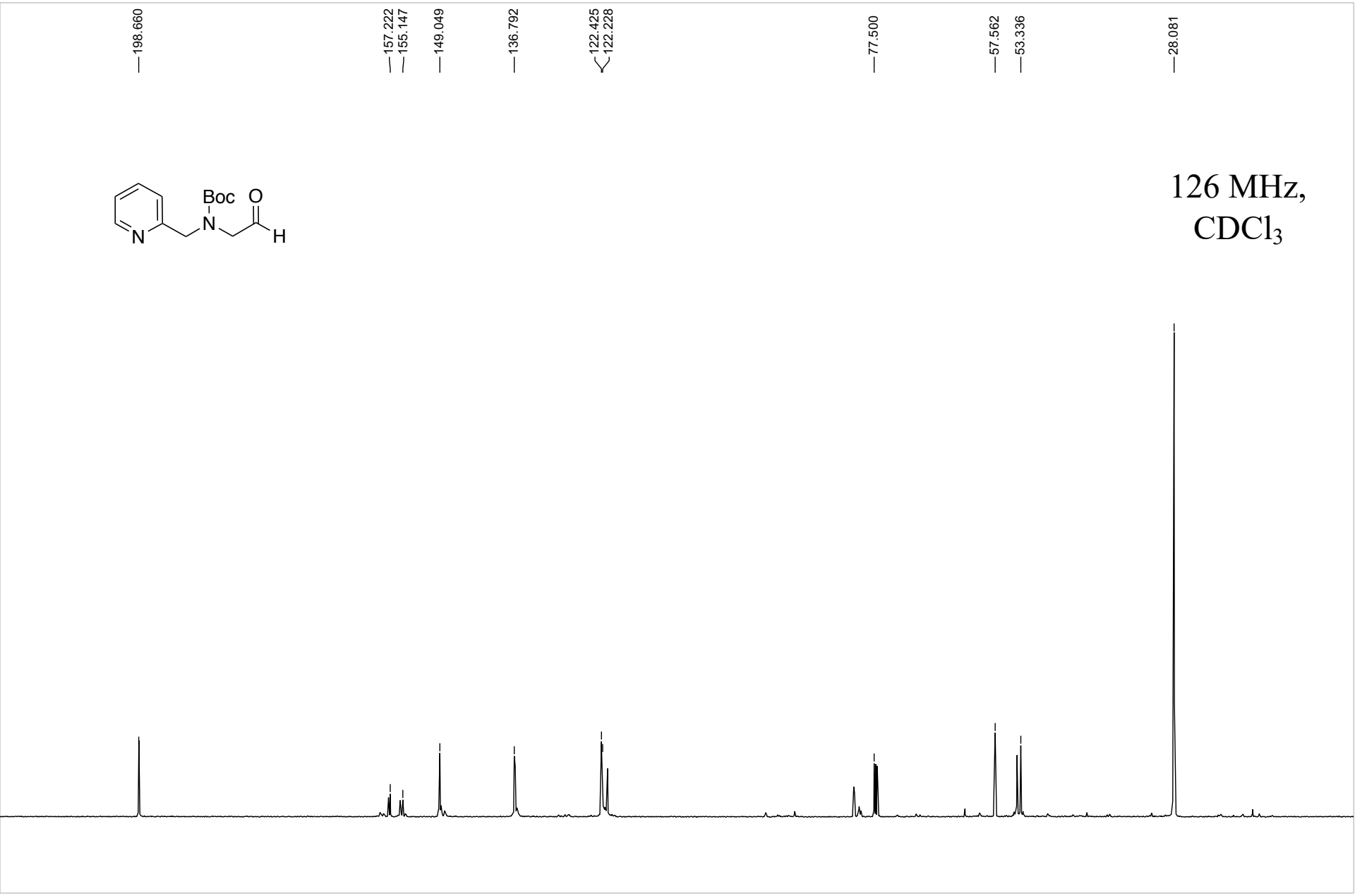
**$^{13}$C NMR** *tert*-butyl 3-(((*tert*-butoxycarbonyl)(2-oxoethyl)amino)methyl)-1*H*-indole-1-carboxylate **s-1s**



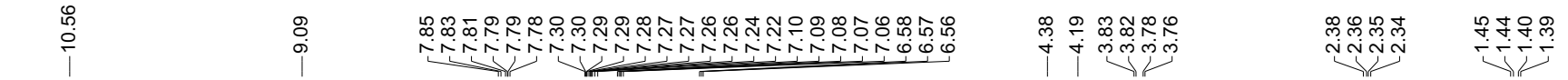
# $^{1}$H NMR *tert*-butyl (2-oxoethyl)(pyridin-2-ylmethyl)carbamate **s-1t**

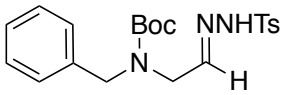


# $^{13}$C NMR *tert*-butyl (2-oxoethyl)(pyridin-2-ylmethyl)carbamate **s-1t**

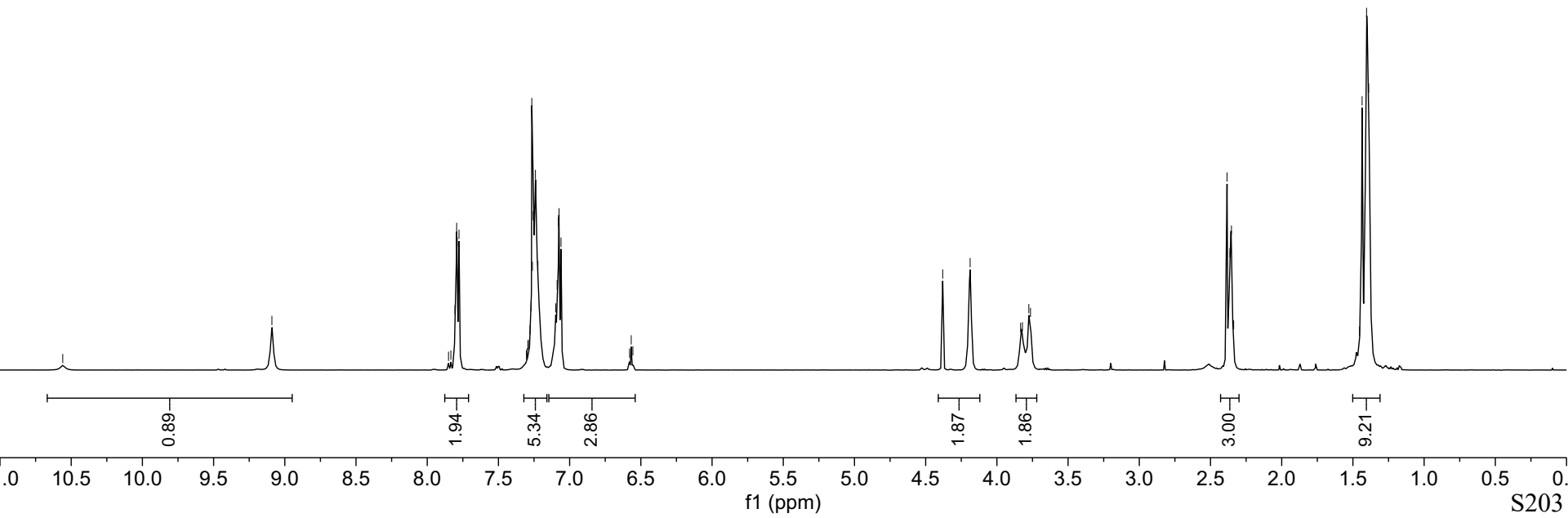


# $^{1}$H NMR *tert*-butyl benzyl(2-(2-tosylhydrazineylidene)ethyl)carbamate **1a**

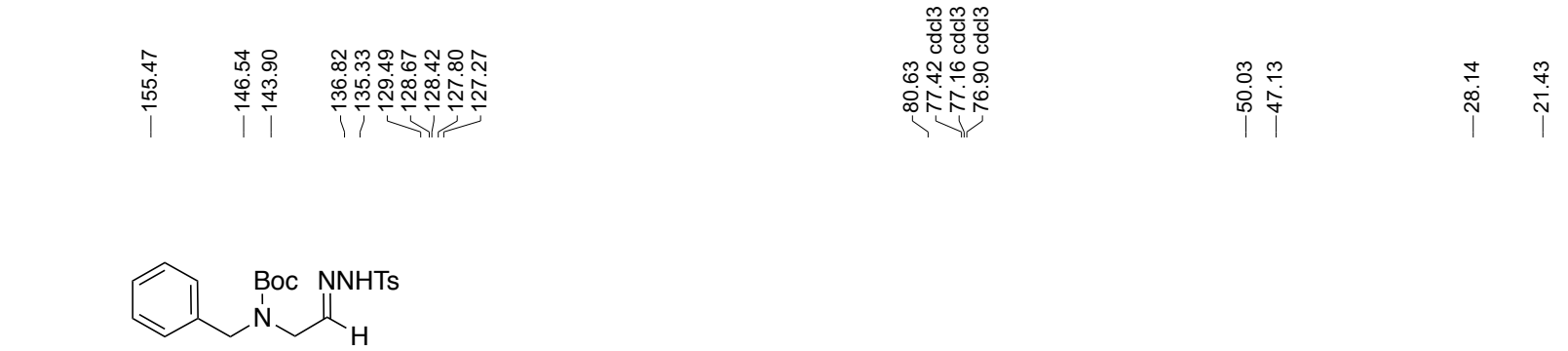



500 MHz,
$CDCl_3$



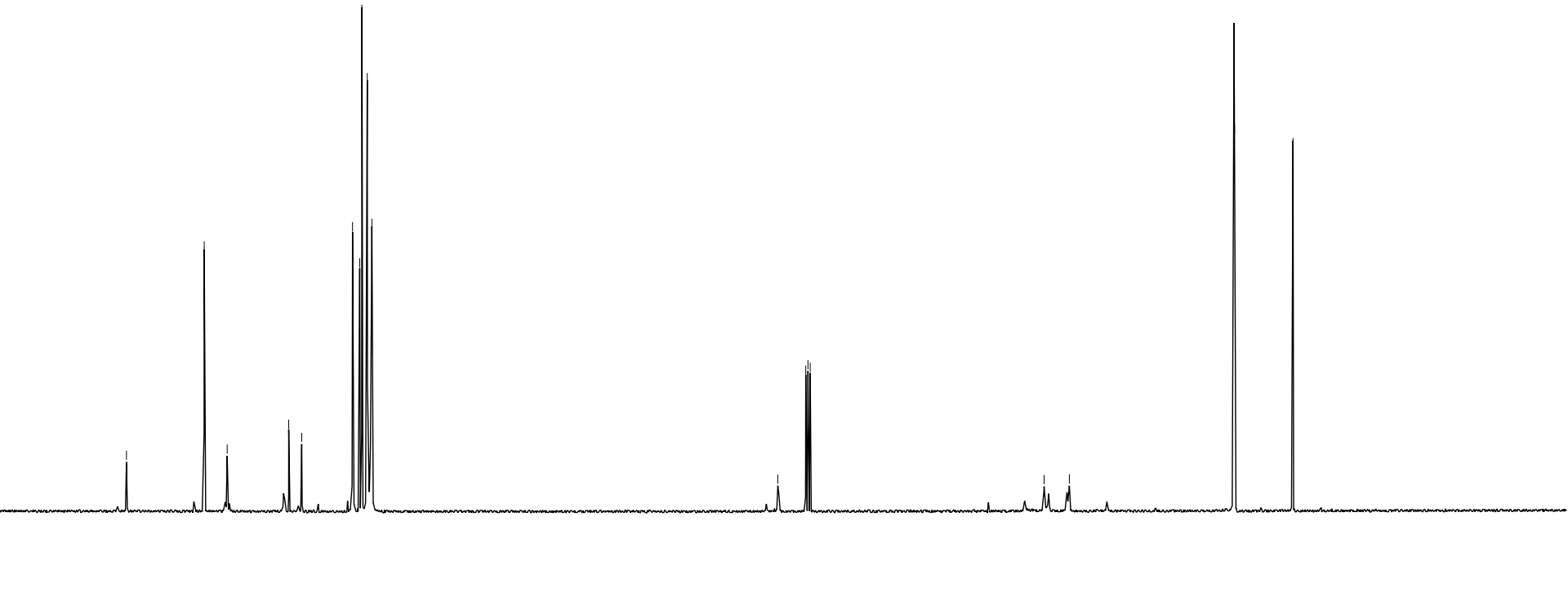
# $^{13}$C NMR *tert*-butyl benzyl(2-(2-tosylhydrazineylidene)ethyl)carbamate **1a**

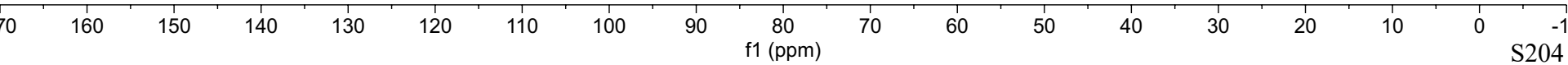




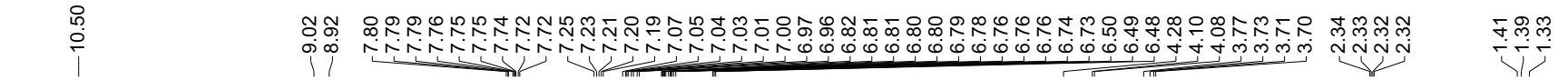


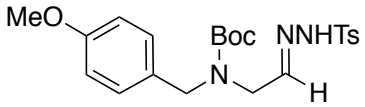
126 MHz,
$CDCl_3$



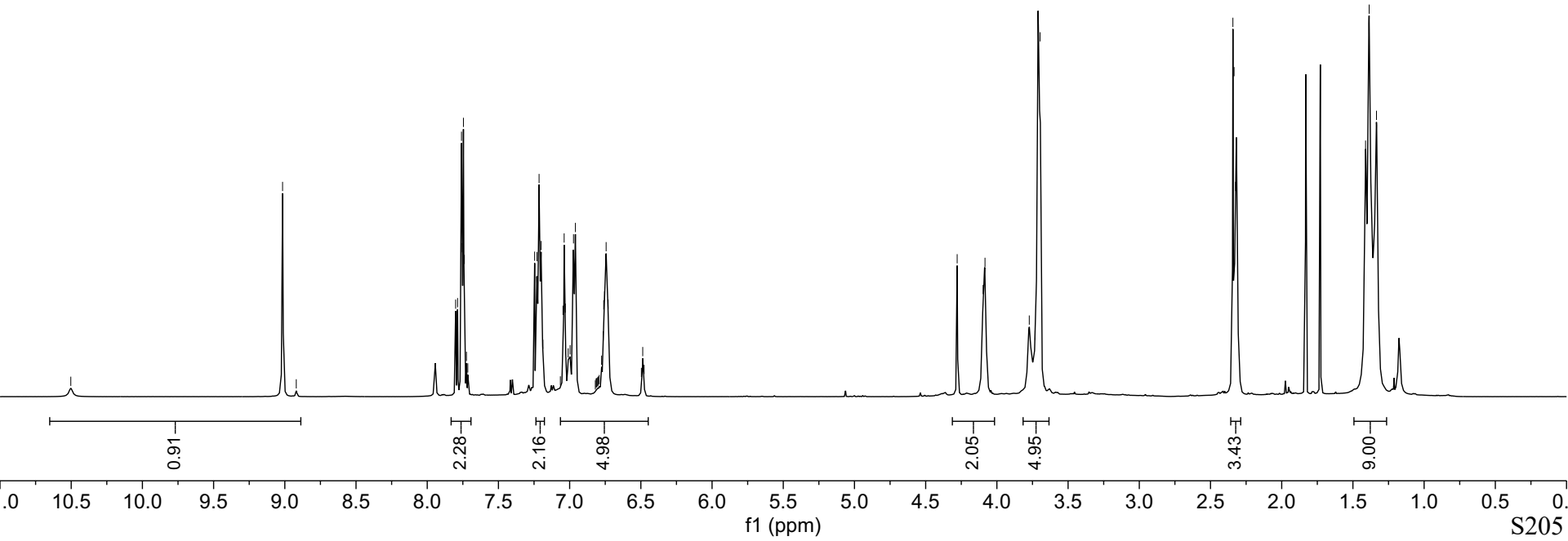


# $^{1}$H NMR *tert*-butyl (4-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1b**

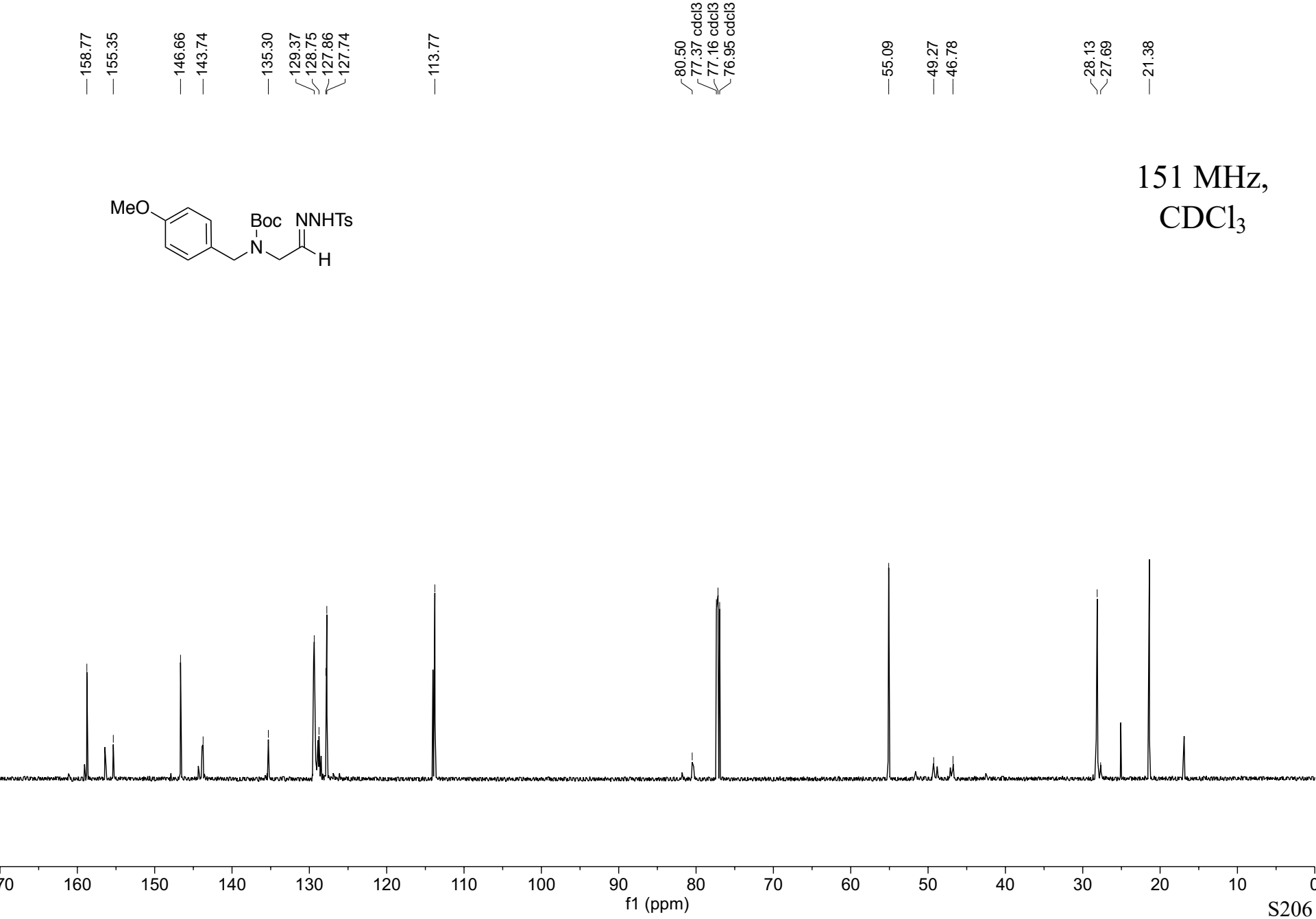


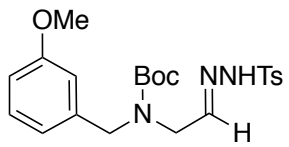

600 MHz,
$CDCl_3$



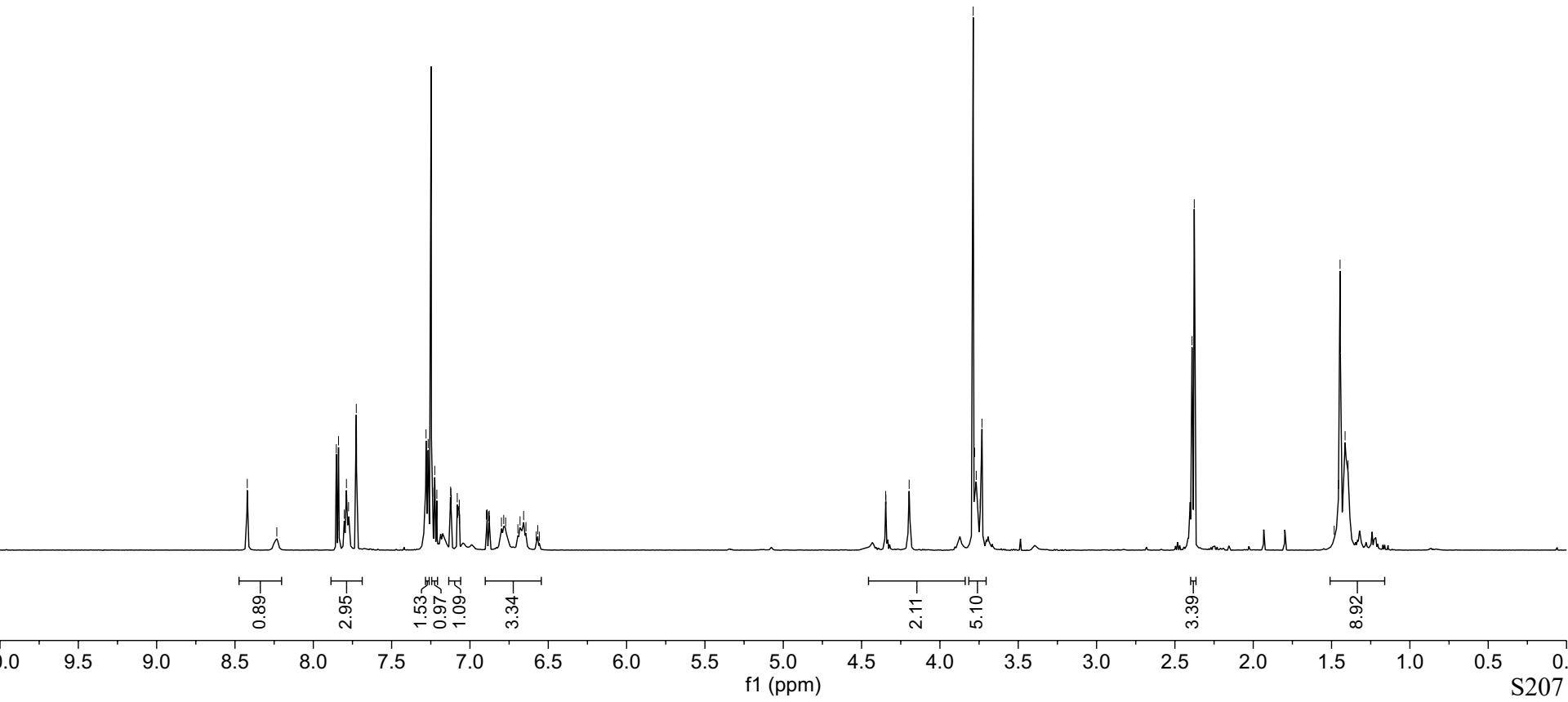
# $^{13}$C NMR *tert*-butyl (4-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1b**



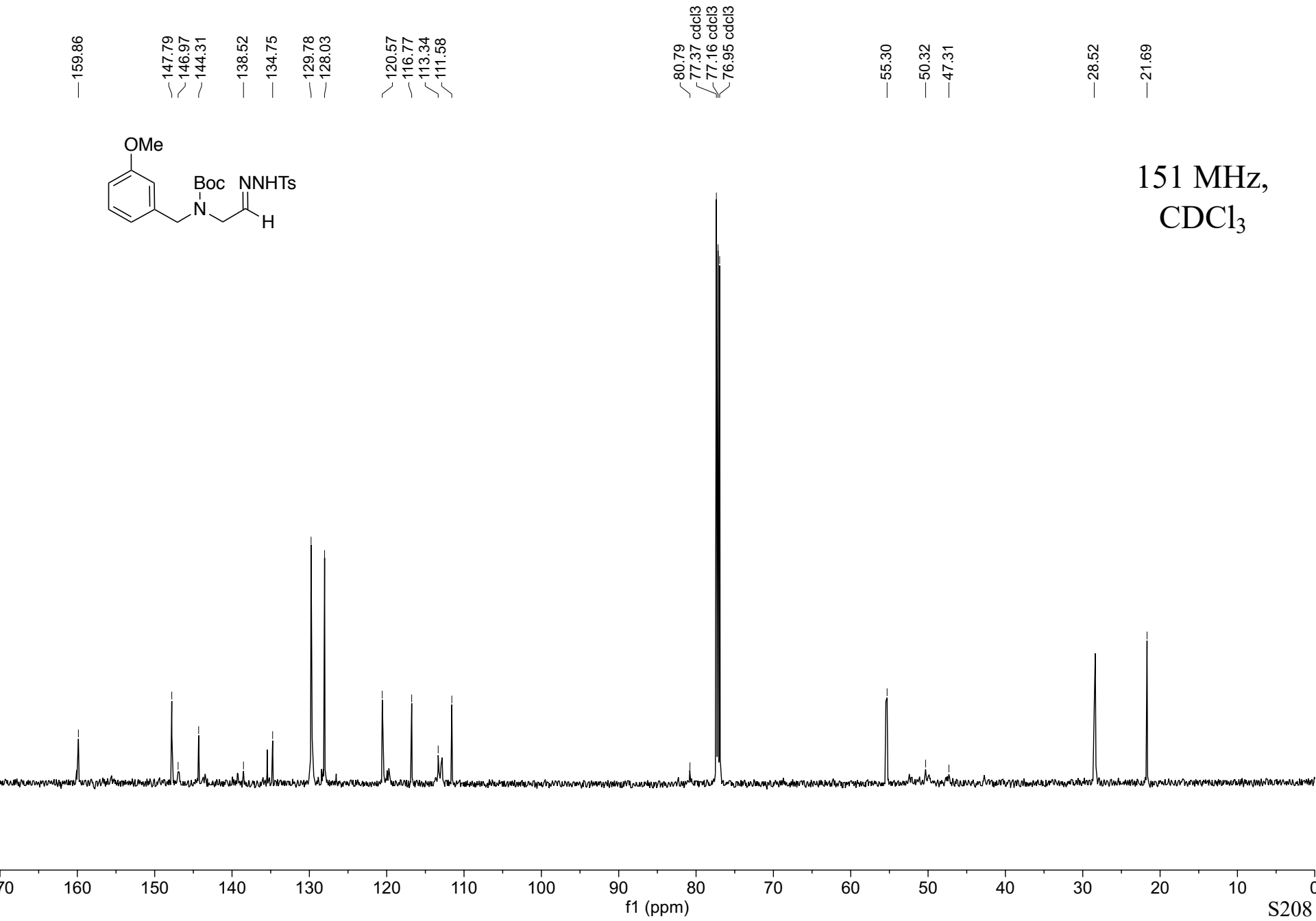
**$^1$H NMR** *tert*-butyl (3-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1c**



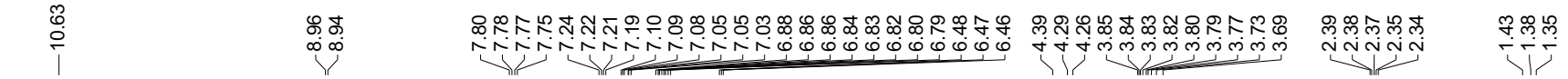

600 MHz,
$CDCl_3$

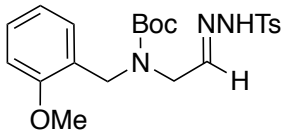


**$^{13}$C NMR** *tert*-butyl (3-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1c**

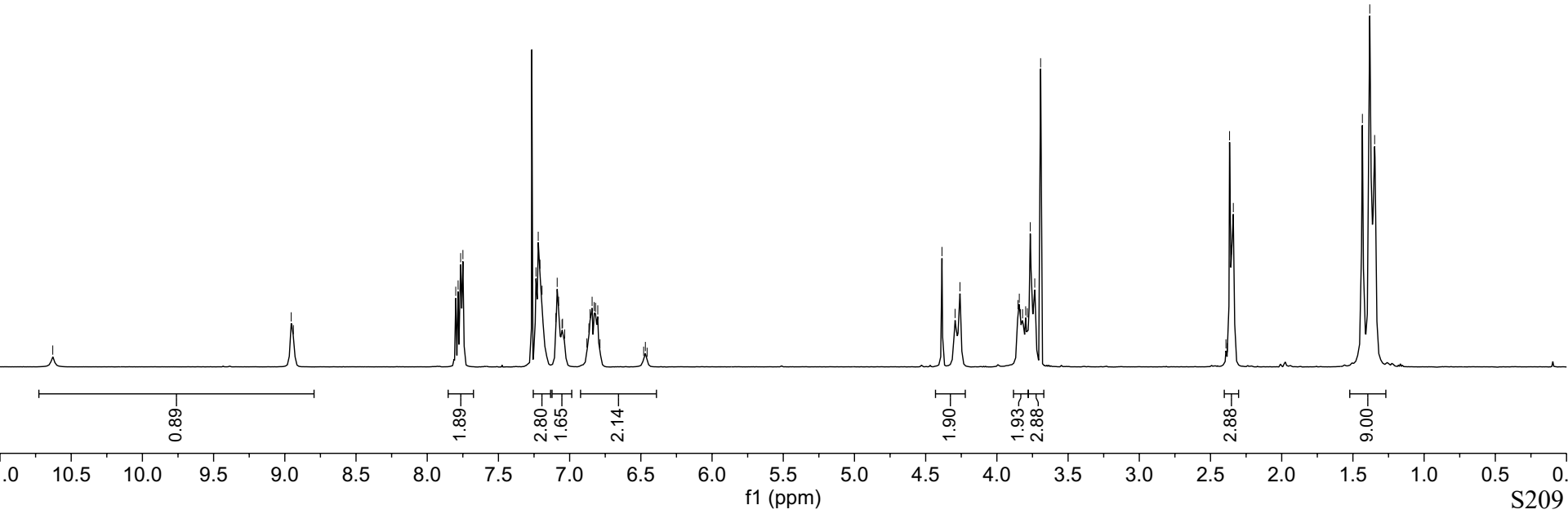


# $^1$H NMR *tert*-butyl (2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1d**

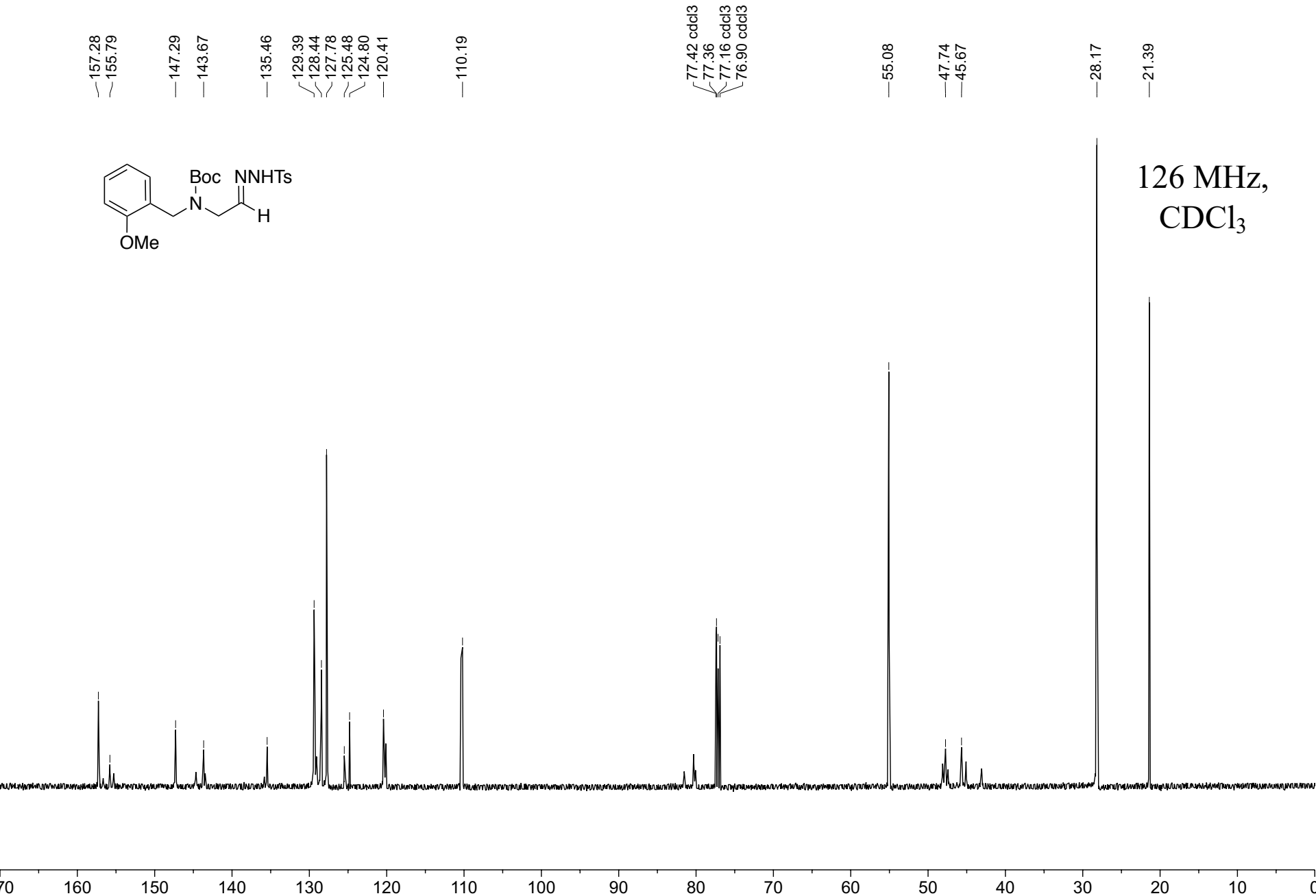


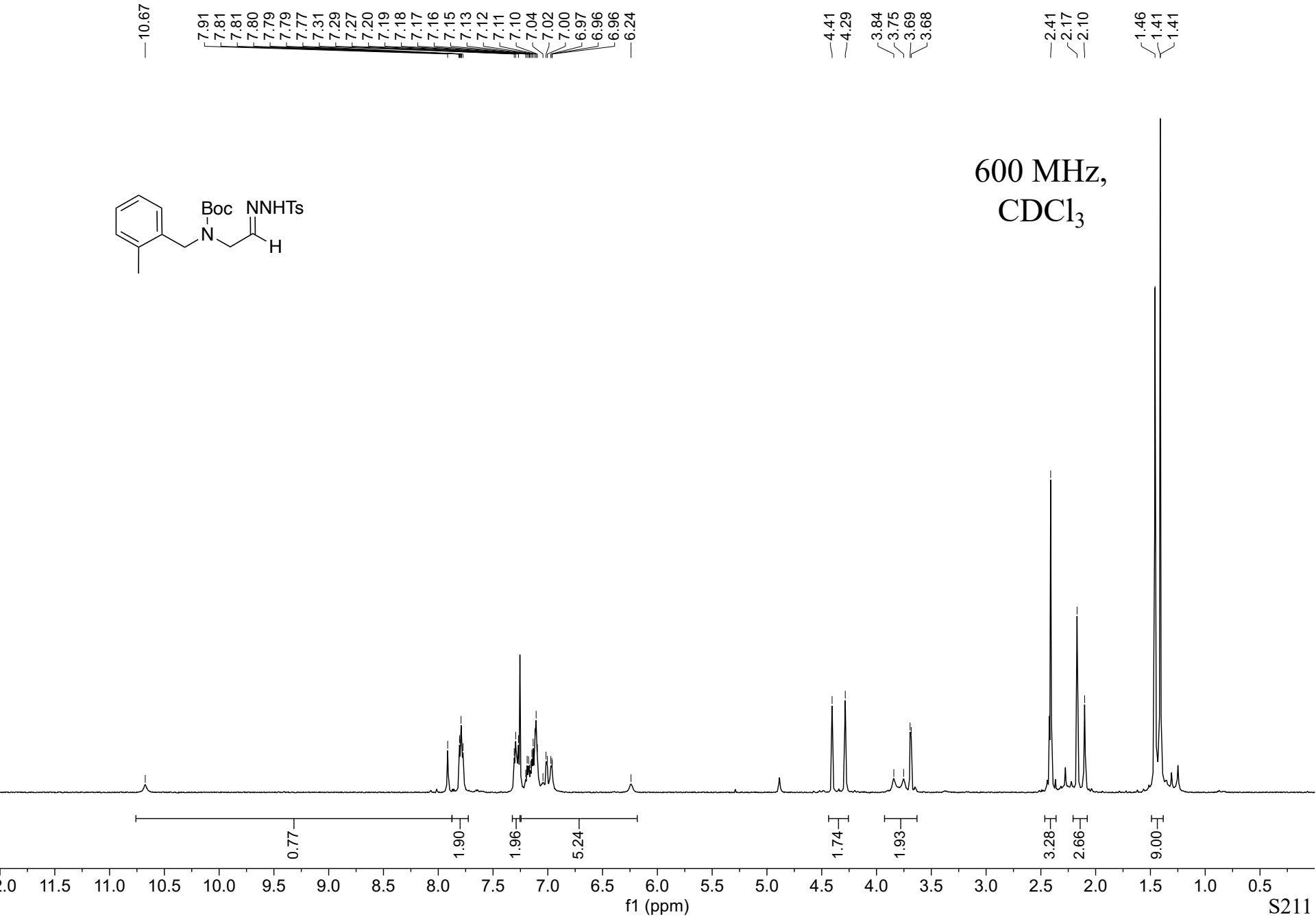

500 MHz,
$CDCl_3$



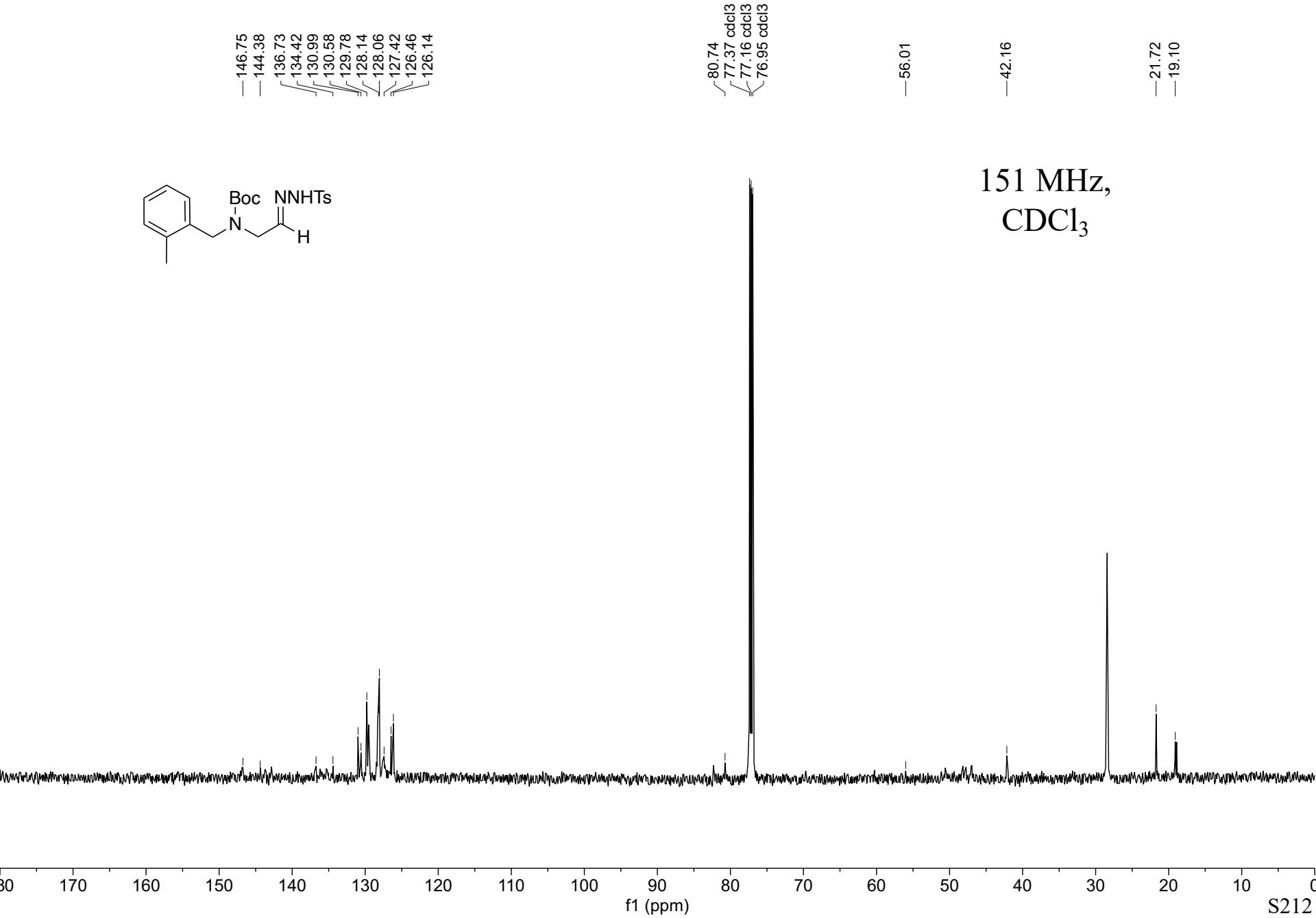
# $^{13}$C NMR *tert*-butyl (2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1d**



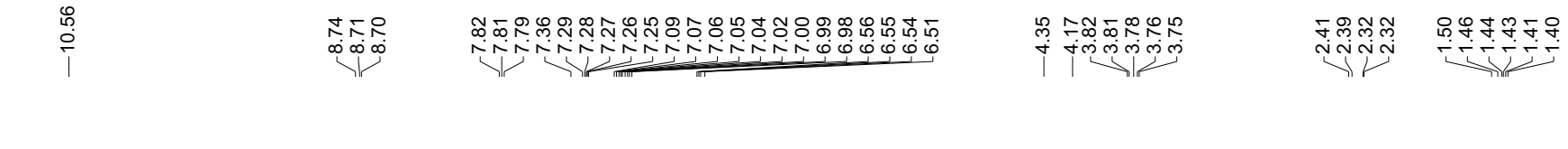
**$^1$H NMR** *tert*-Butyl (*Z*)-(2-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1e**

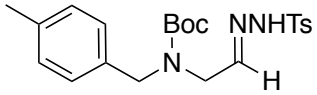


# $^{13}$C NMR *tert*-Butyl (*Z*)-(2-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1e**

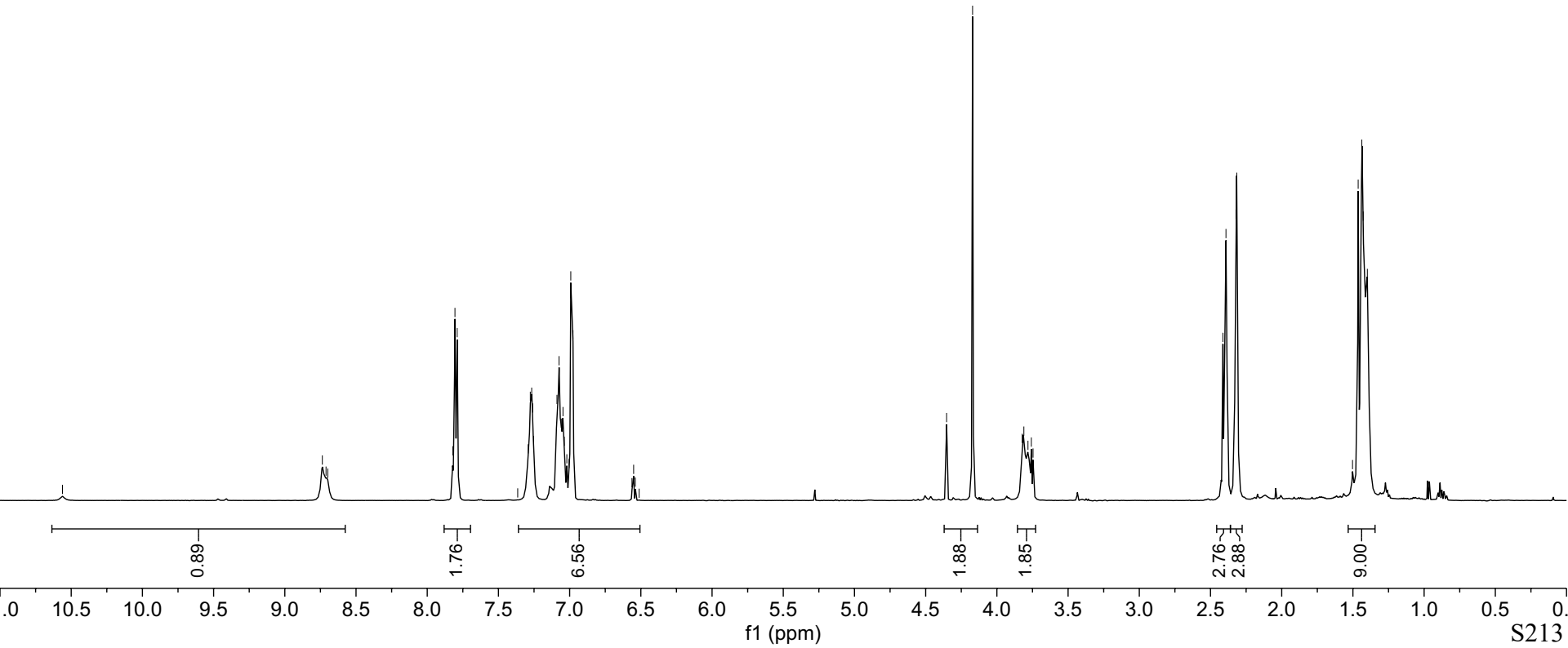


# $^{1}$H NMR *tert*-butyl (4-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1f**

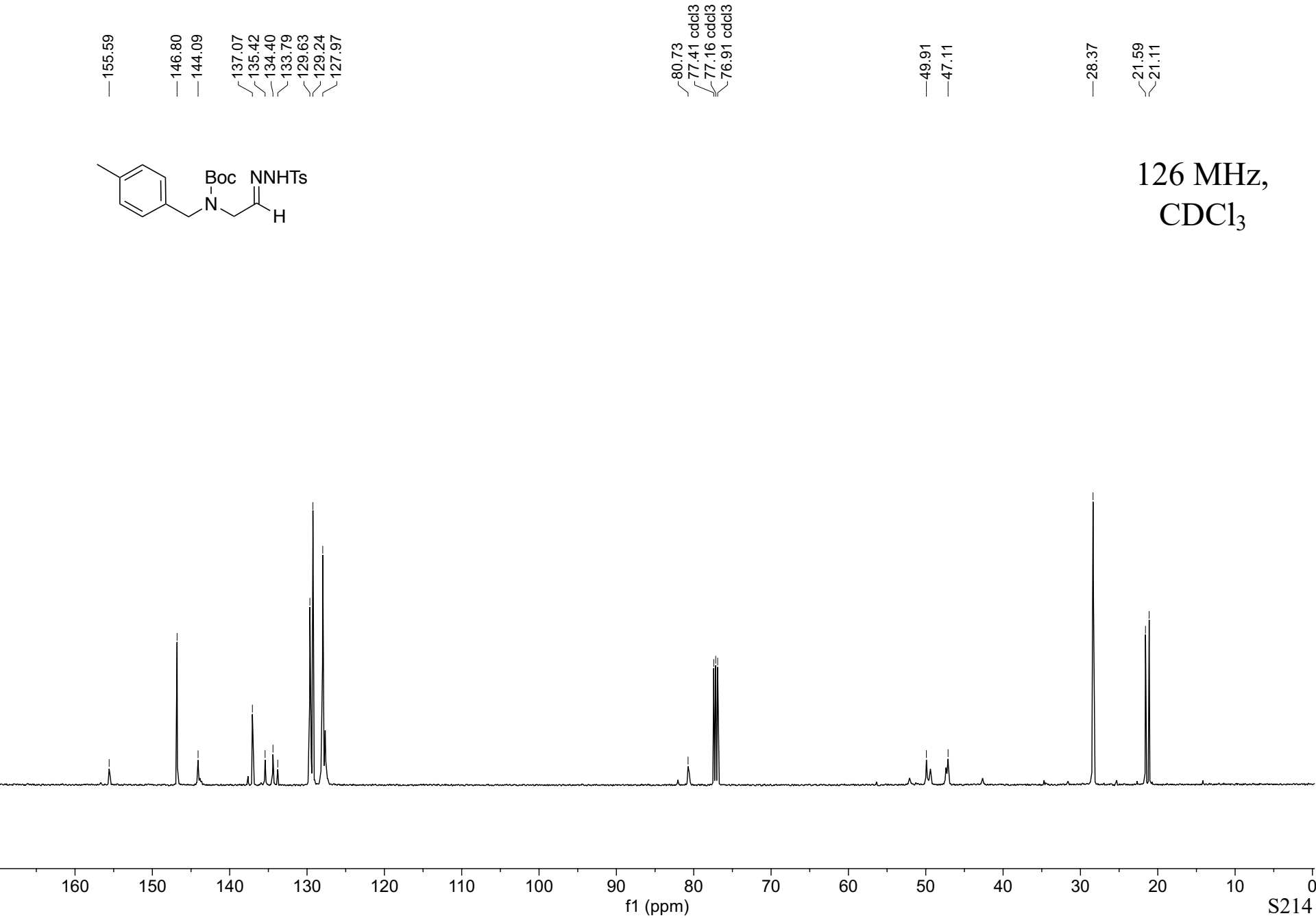


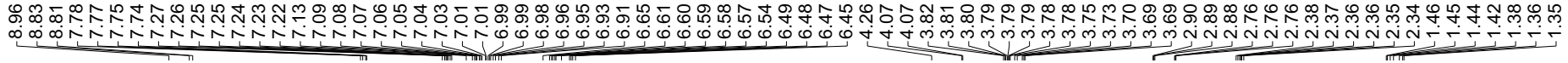

500 MHz,
$CDCl_3$



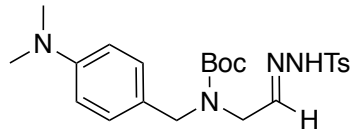
# $^{13}$C NMR *tert*-butyl (4-methylbenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1f**

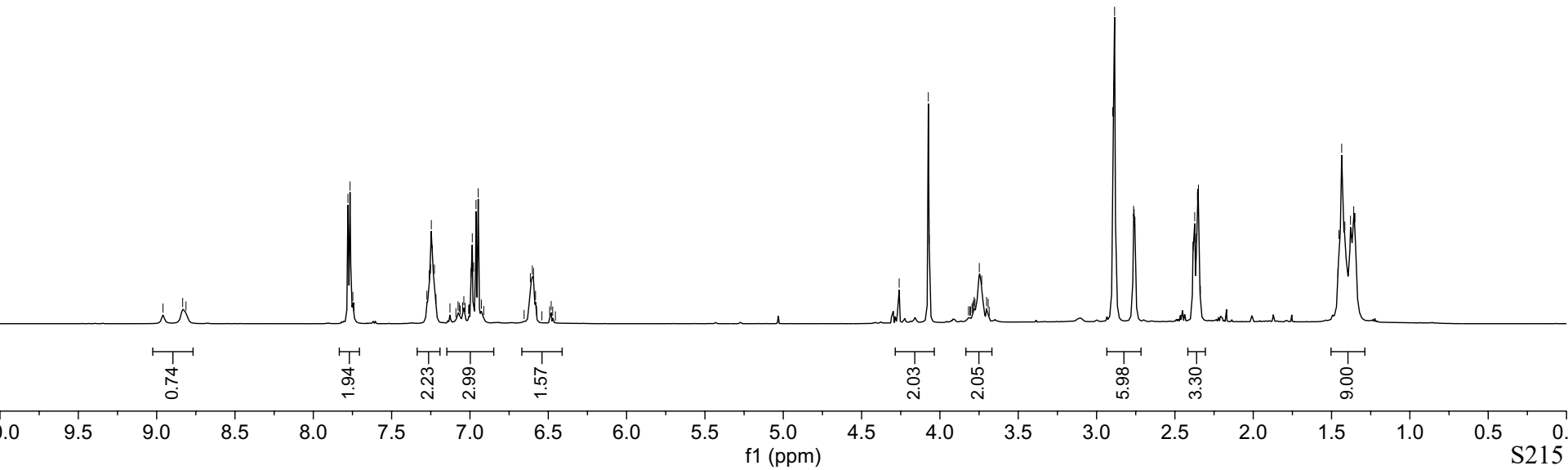


# $^1$H NMR *tert*-butyl (4-(dimethylamino)benzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1g**

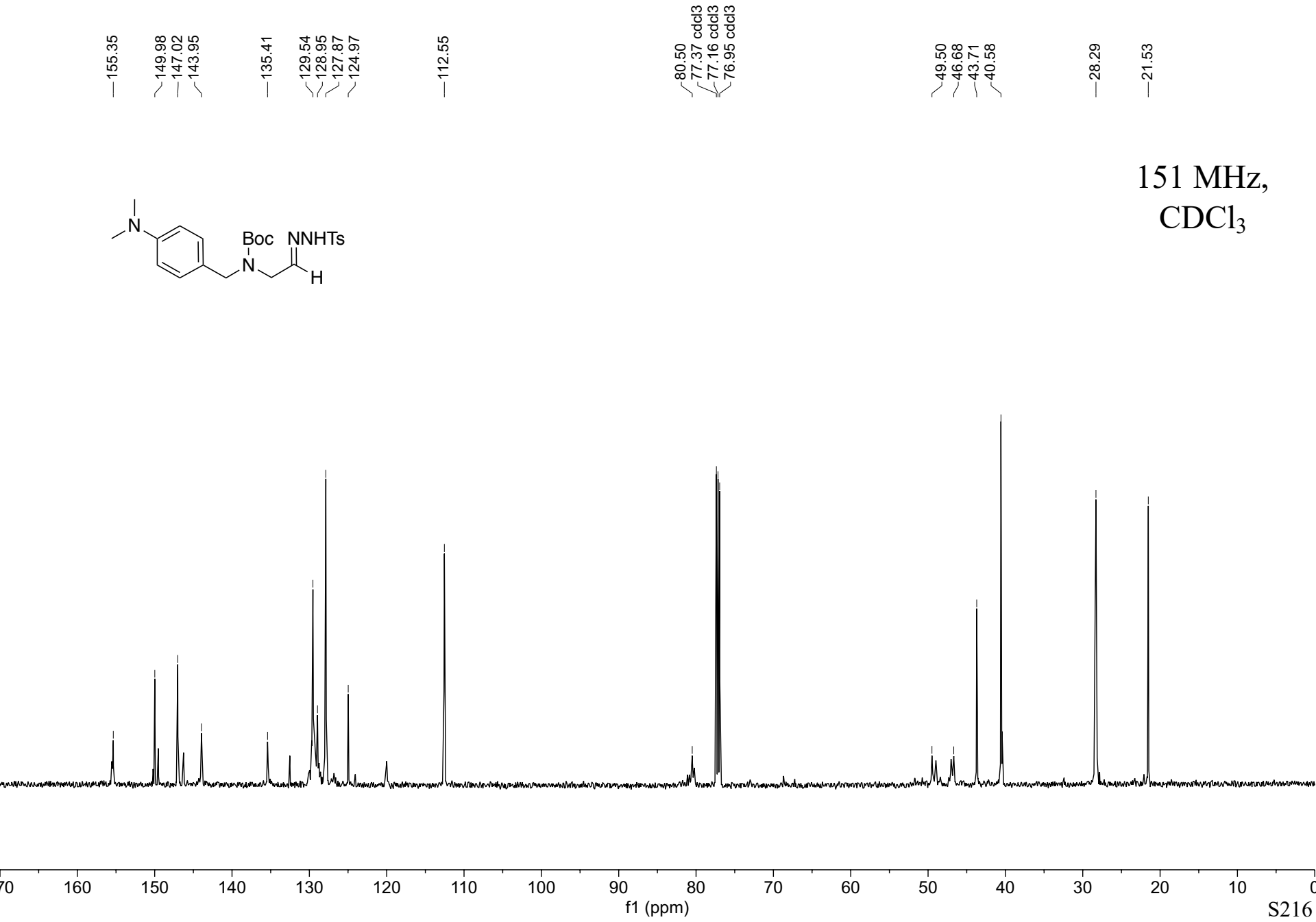



600 MHz,
$CDCl_3$

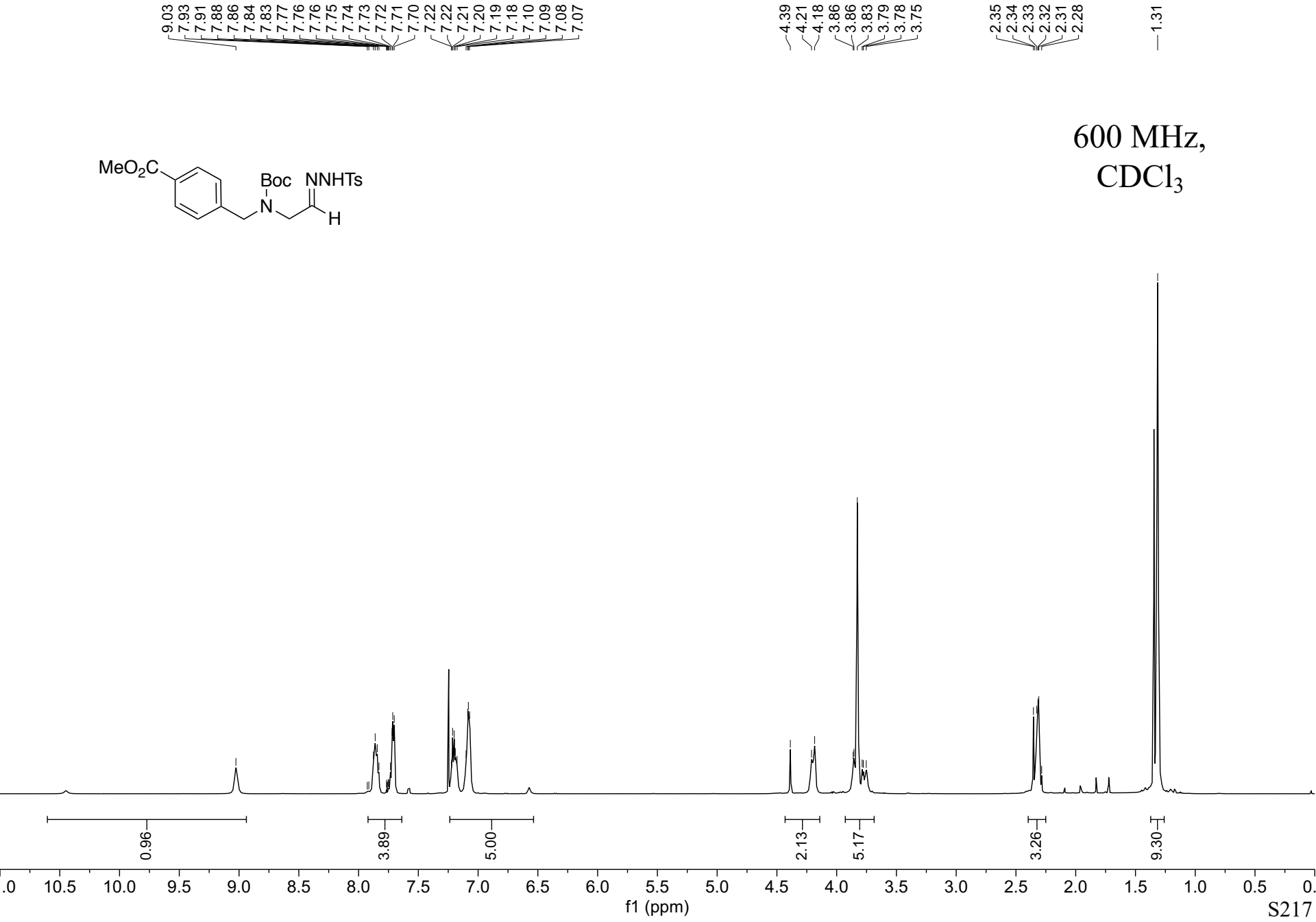


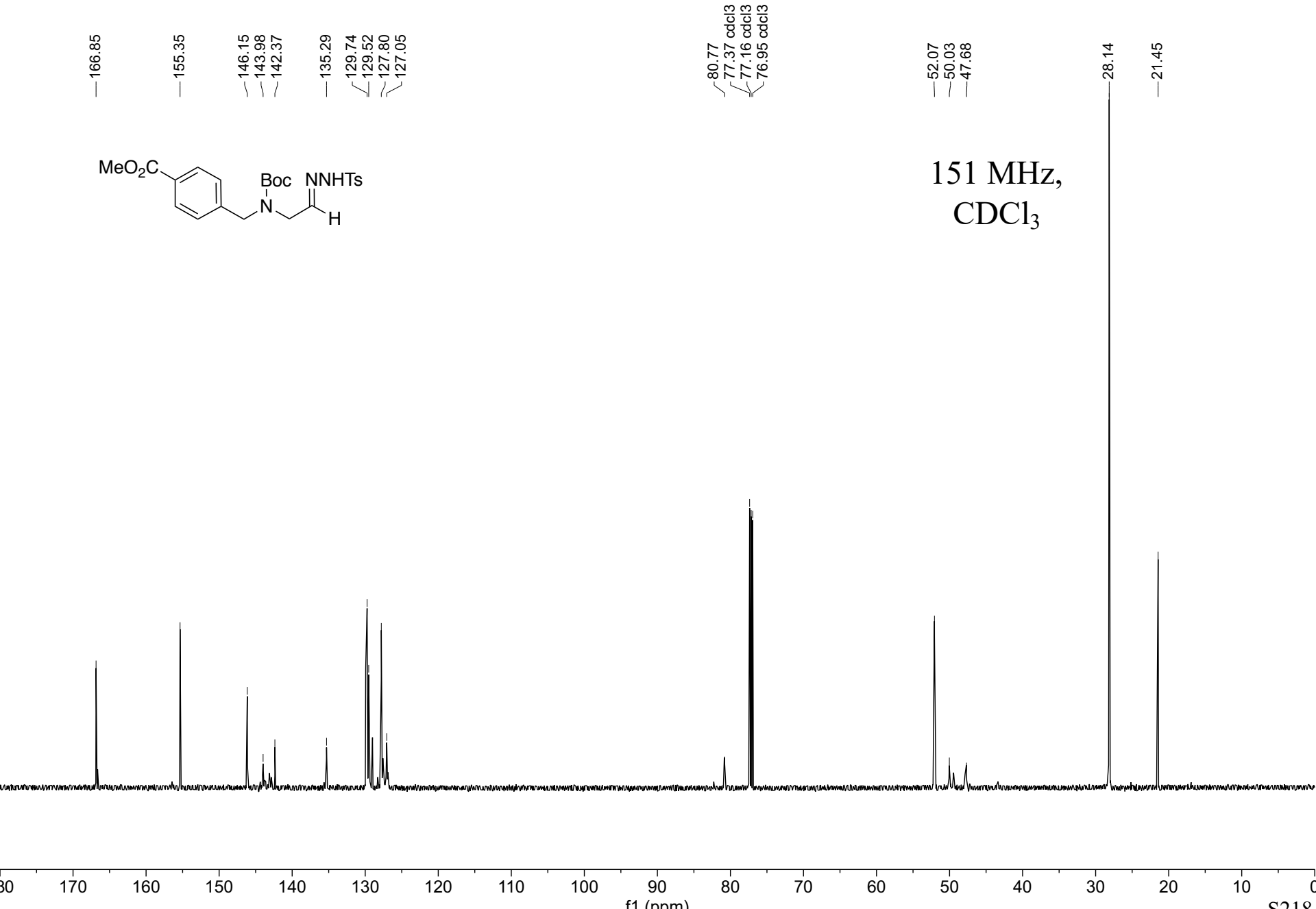
**$^{13}$C NMR** *tert*-butyl (4-(dimethylamino)benzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1g**



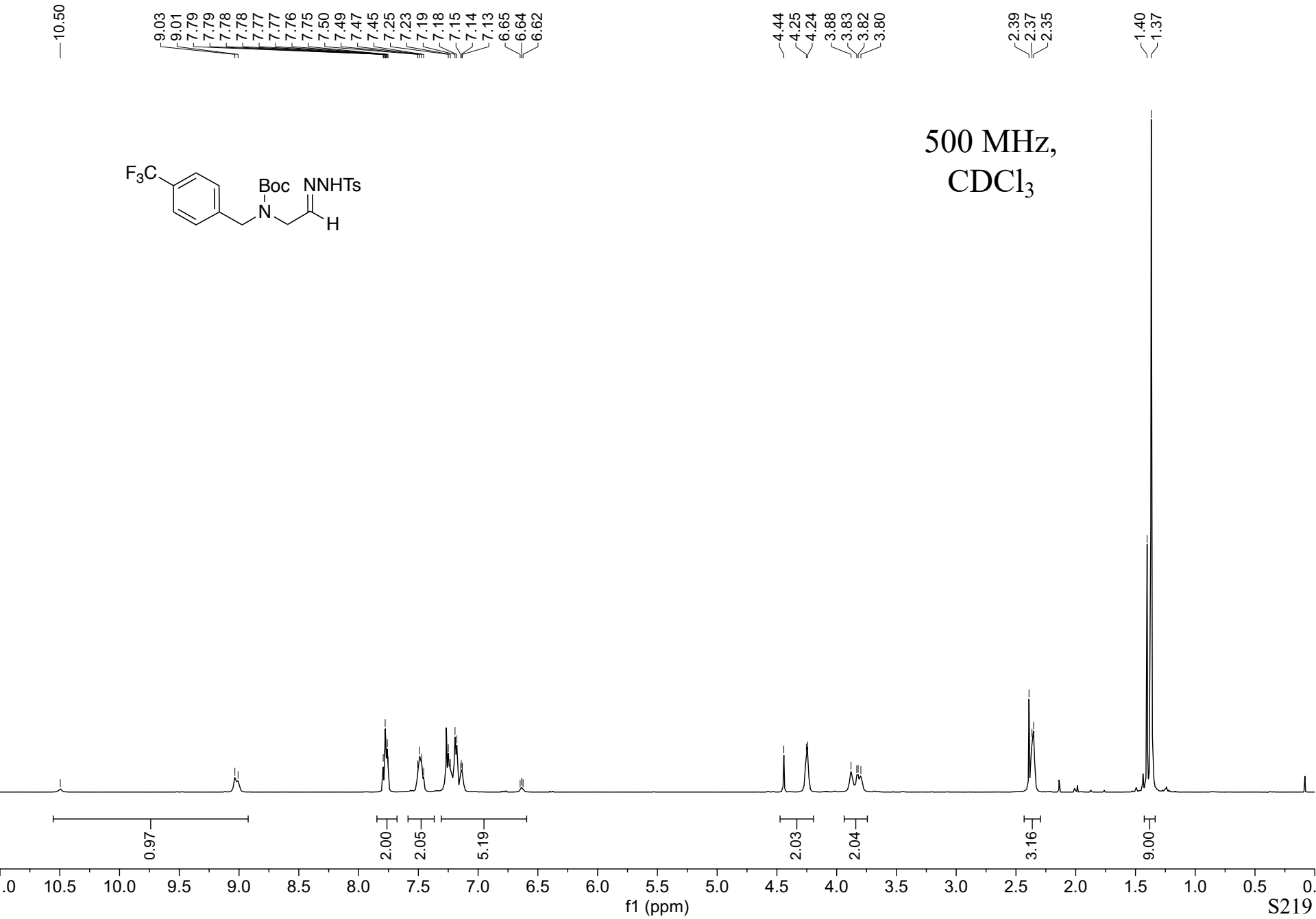
**$^1$H NMR** Methyl 4-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)benzoate **1g**



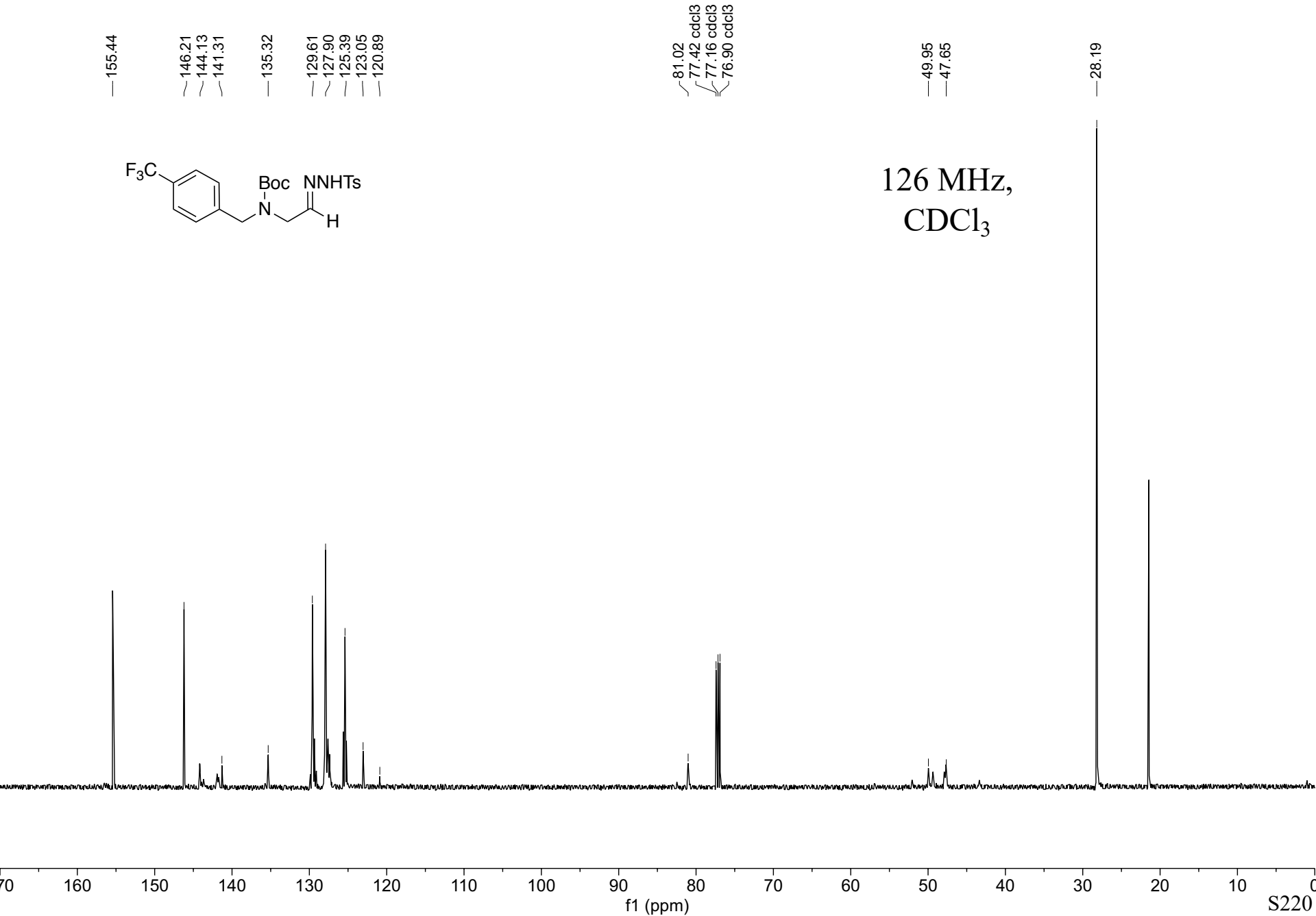
**$^{13}$C NMR** Methyl 4-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)benzoate **1g**



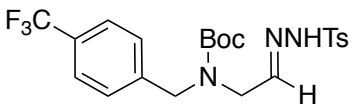
**$^1$H NMR** *tert*-butyl (2-(2-tosylhydrazineylidene)ethyl)(4-(trifluoromethyl)benzyl)carbamate **1h**



# $^{13}$C NMR *tert*-butyl (2-(2-tosylhydrazineylidene)ethyl)(4-(trifluoromethyl)benzyl)carbamate **1h**

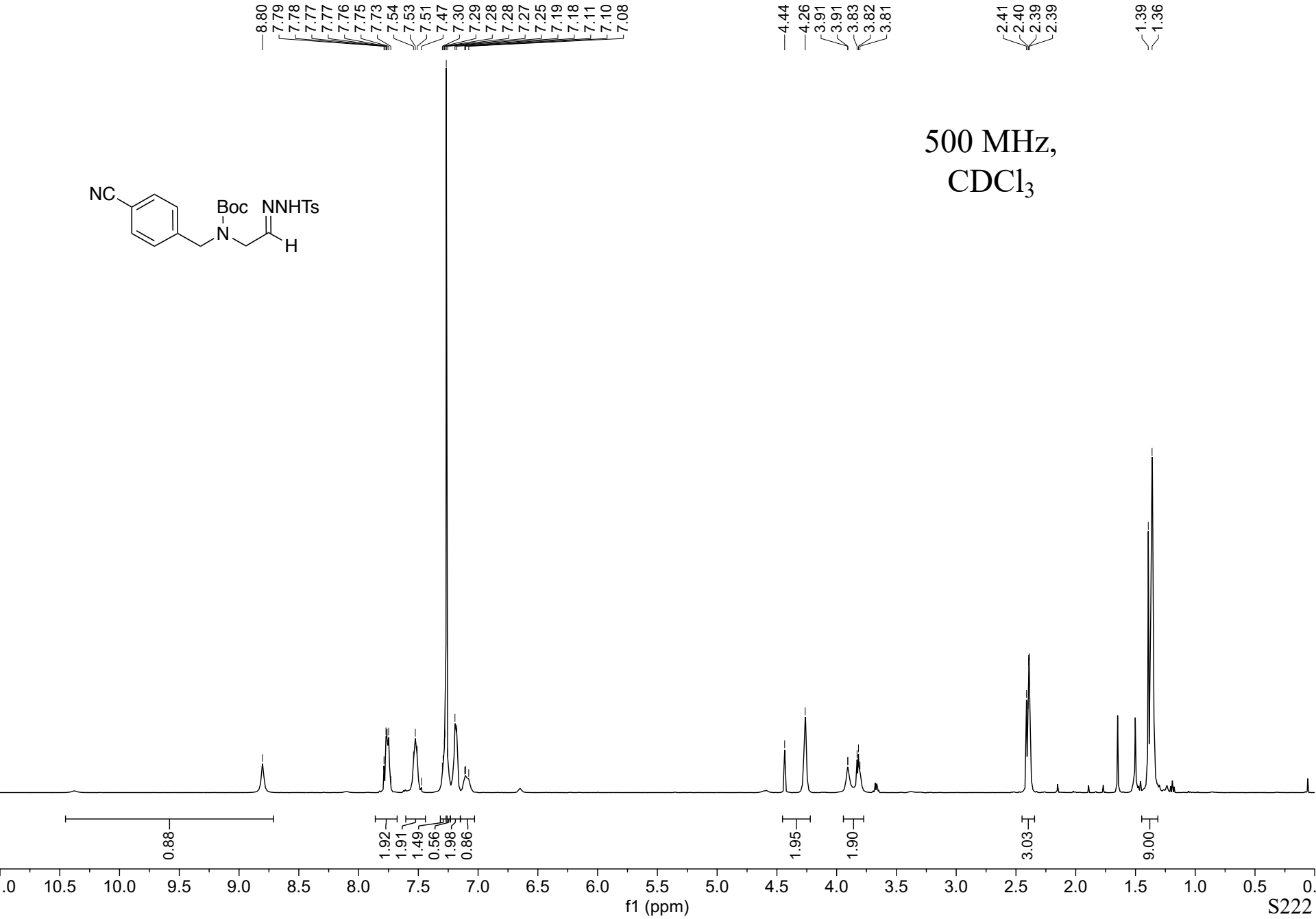


**$^{19}$F NMR** *tert*-butyl (2-(2-tosylhydrazineylidene)ethyl)(4-(trifluoromethyl)benzyl)carbamate **1h**

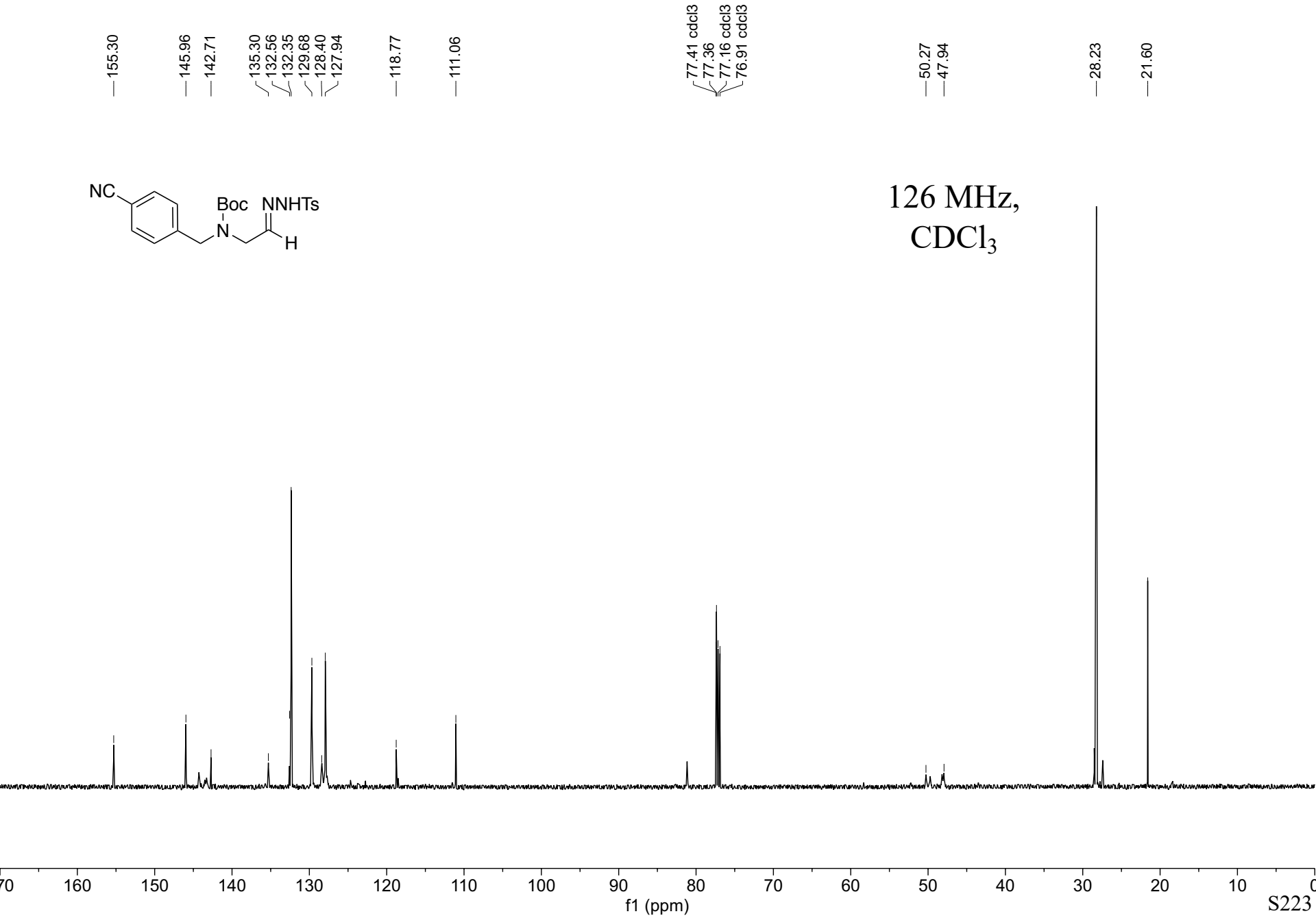



470 MHz,
$CDCl_3$

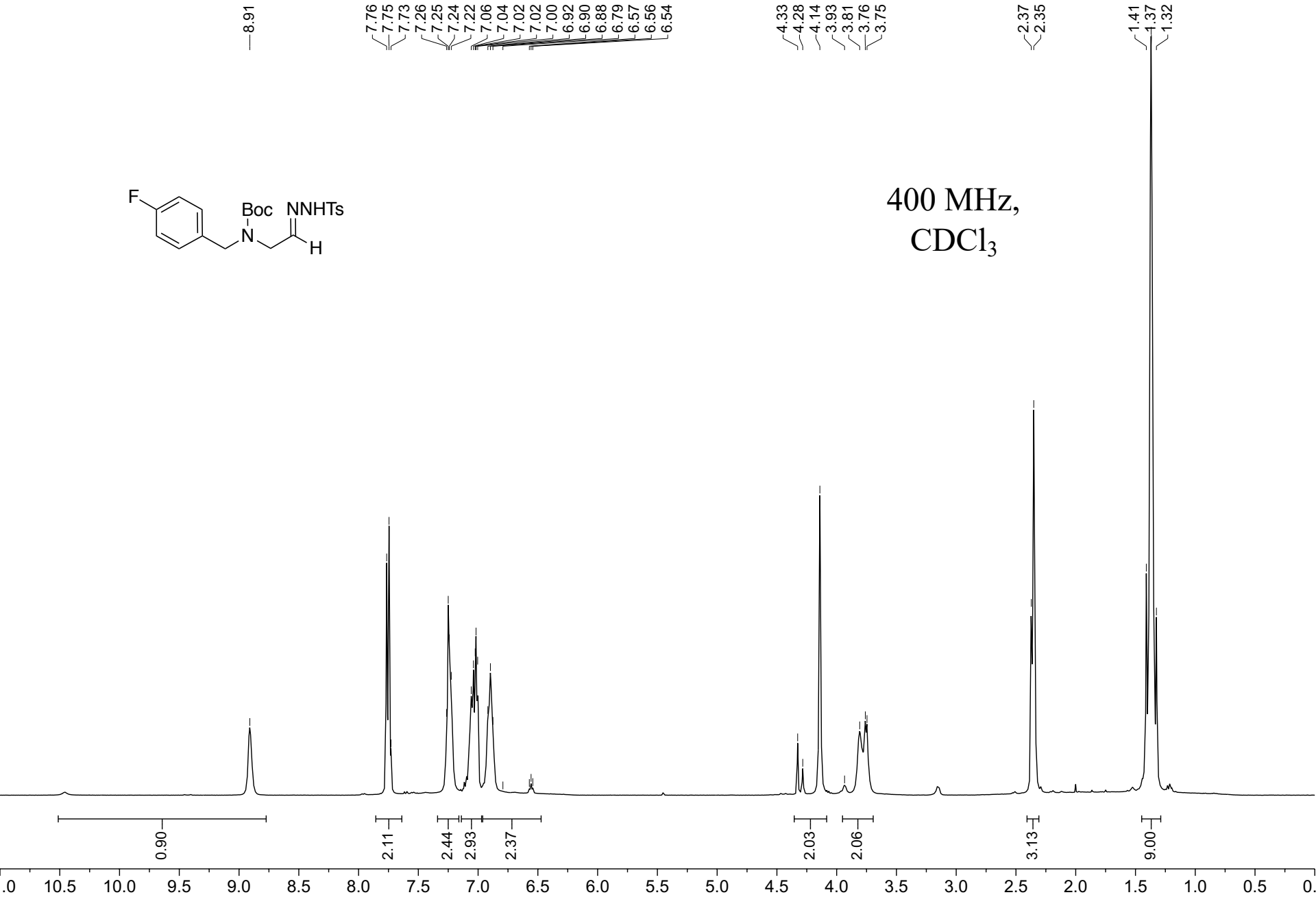
# $^{1}$H NMR *tert*-butyl (4-cyanobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1i**



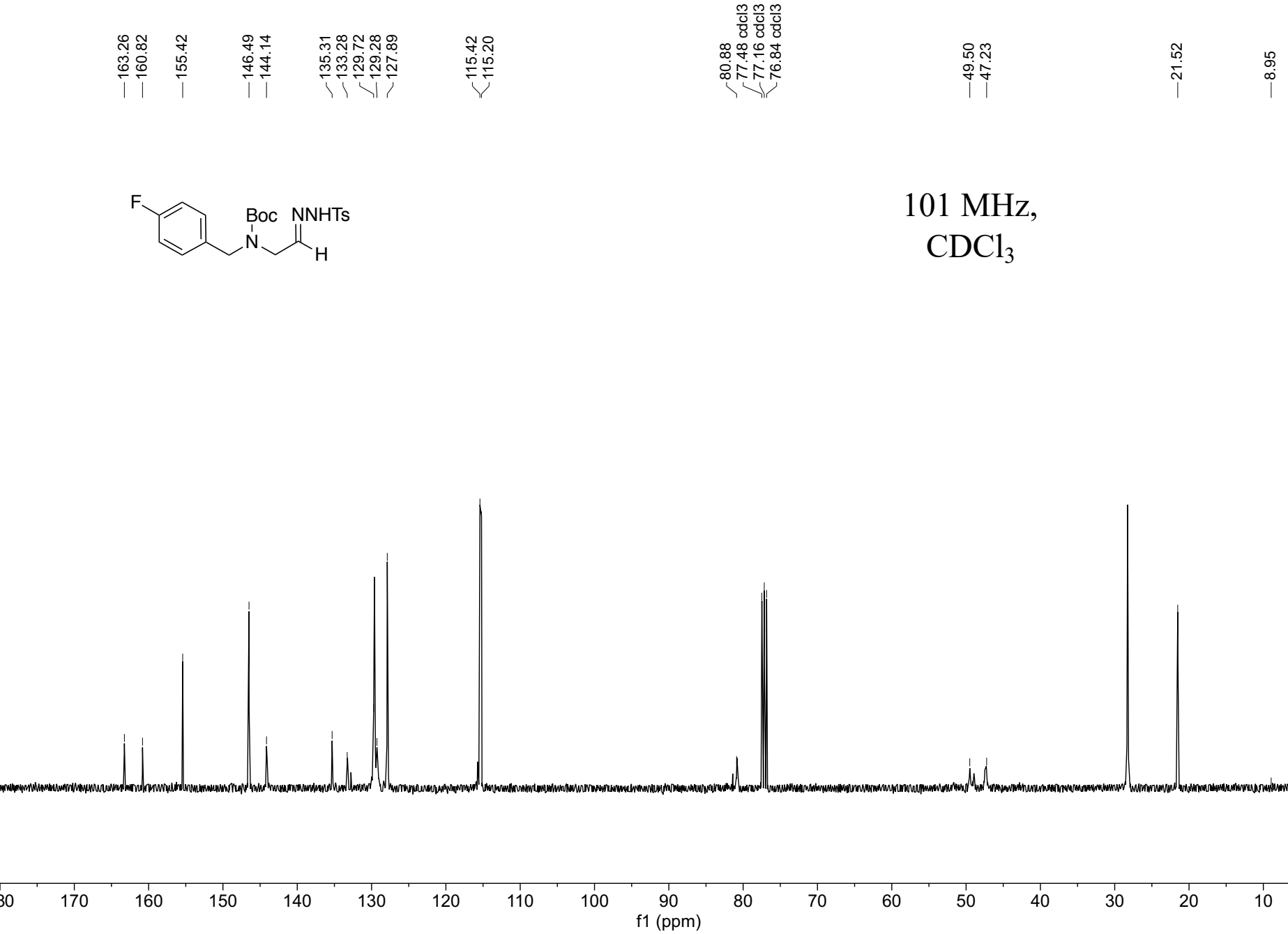
# $^{13}$C NMR *tert*-butyl (4-cyanobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1i**



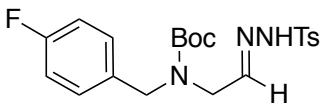
# $^{1}$H NMR *tert*-butyl (4-fluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1j**



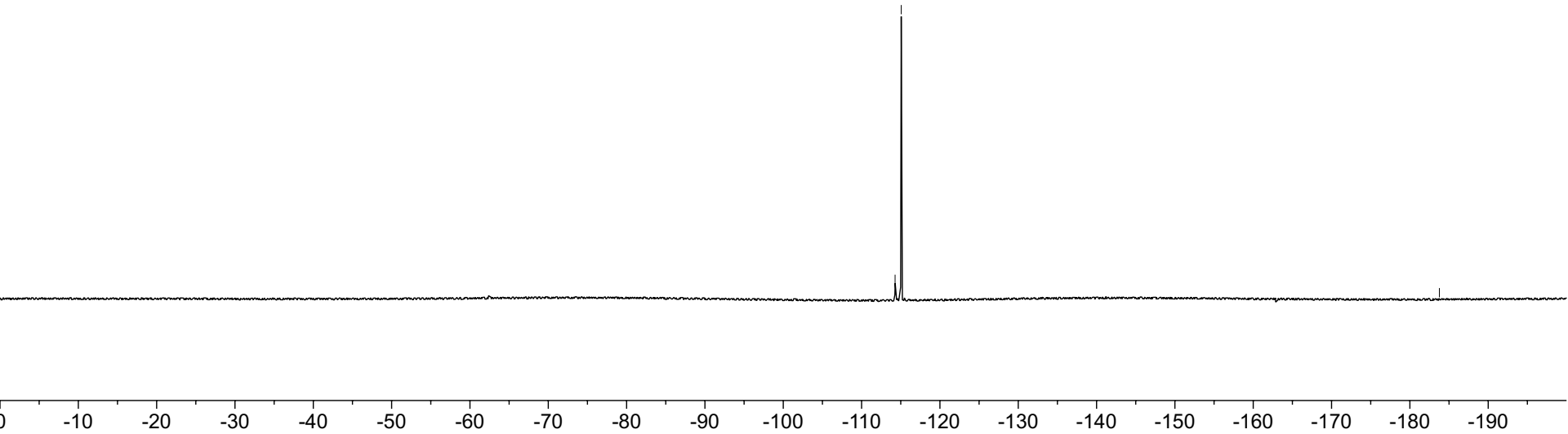
# $^{13}$C NMR *tert*-butyl (4-fluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1j**



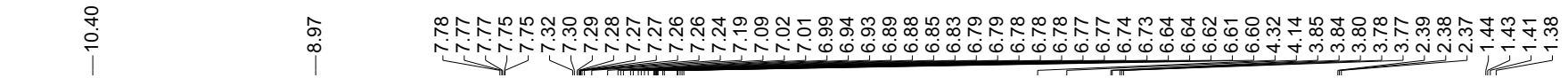
**$^{19}$F NMR** *tert*-butyl (4-fluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1j**

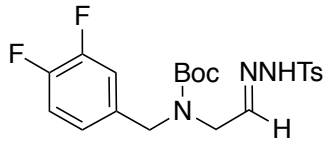



376 MHz,
$CDCl_3$



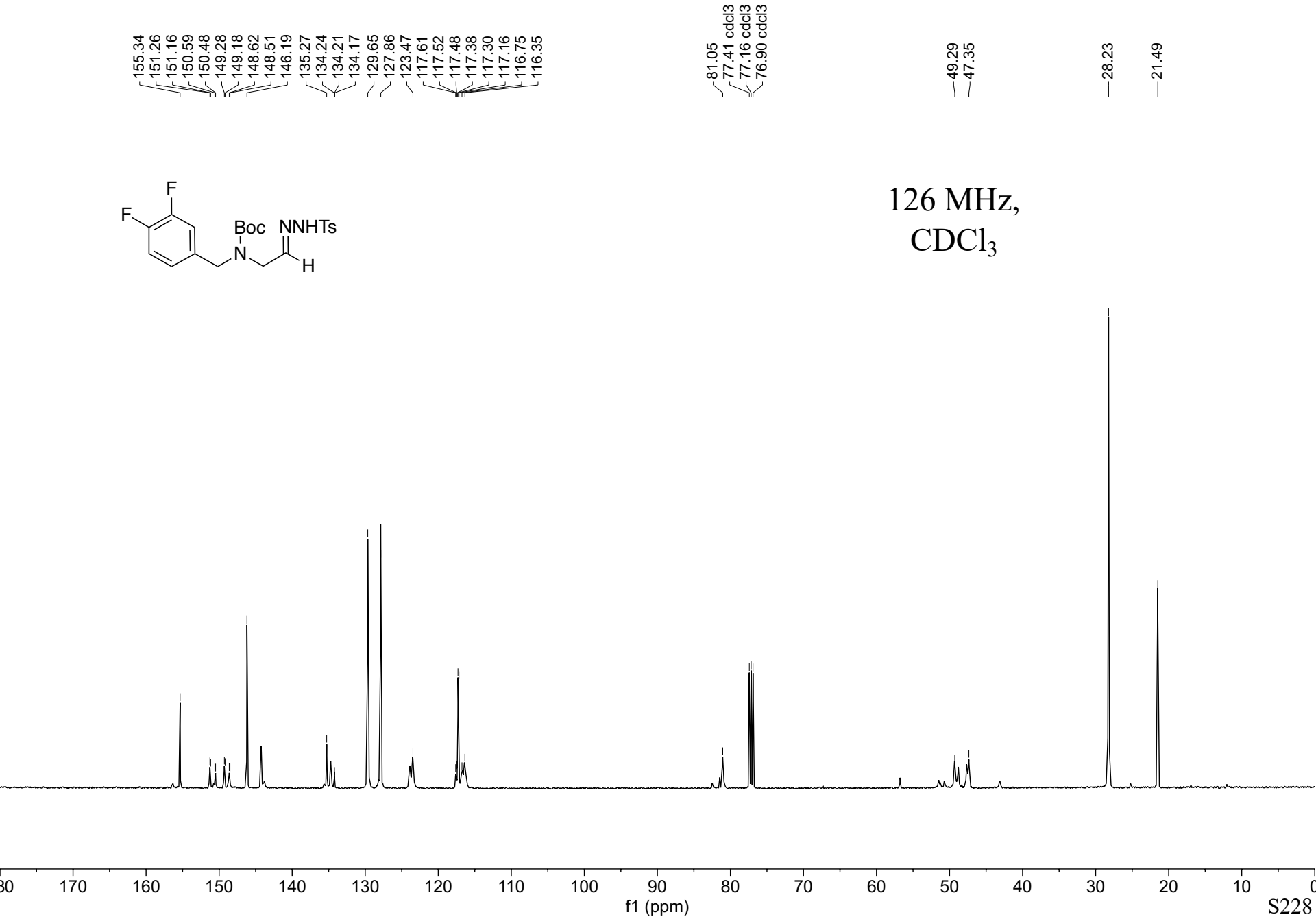
**$^1$H NMR** *tert*-butyl (3,4-difluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1k**



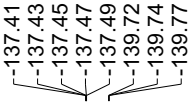



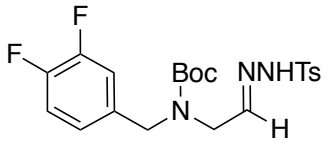

500 MHz,
$CDCl_3$

# $^{13}$C NMR *tert*-butyl (3,4-difluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1k**

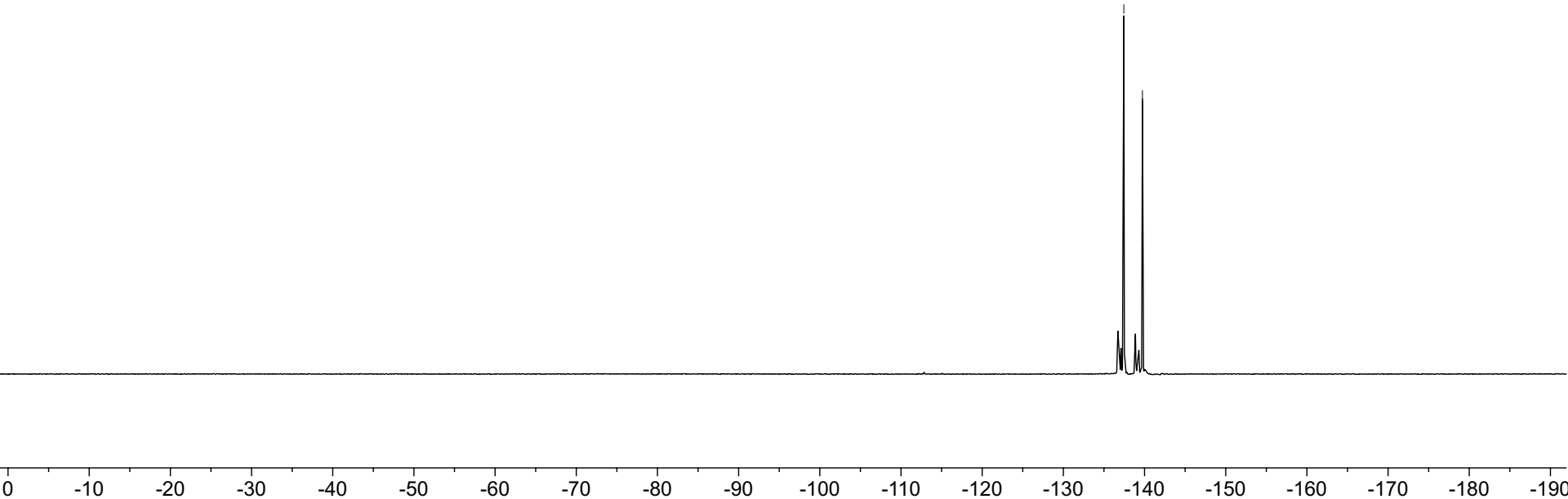


**$^{19}$F NMR** *tert*-butyl (3,4-difluorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1k**

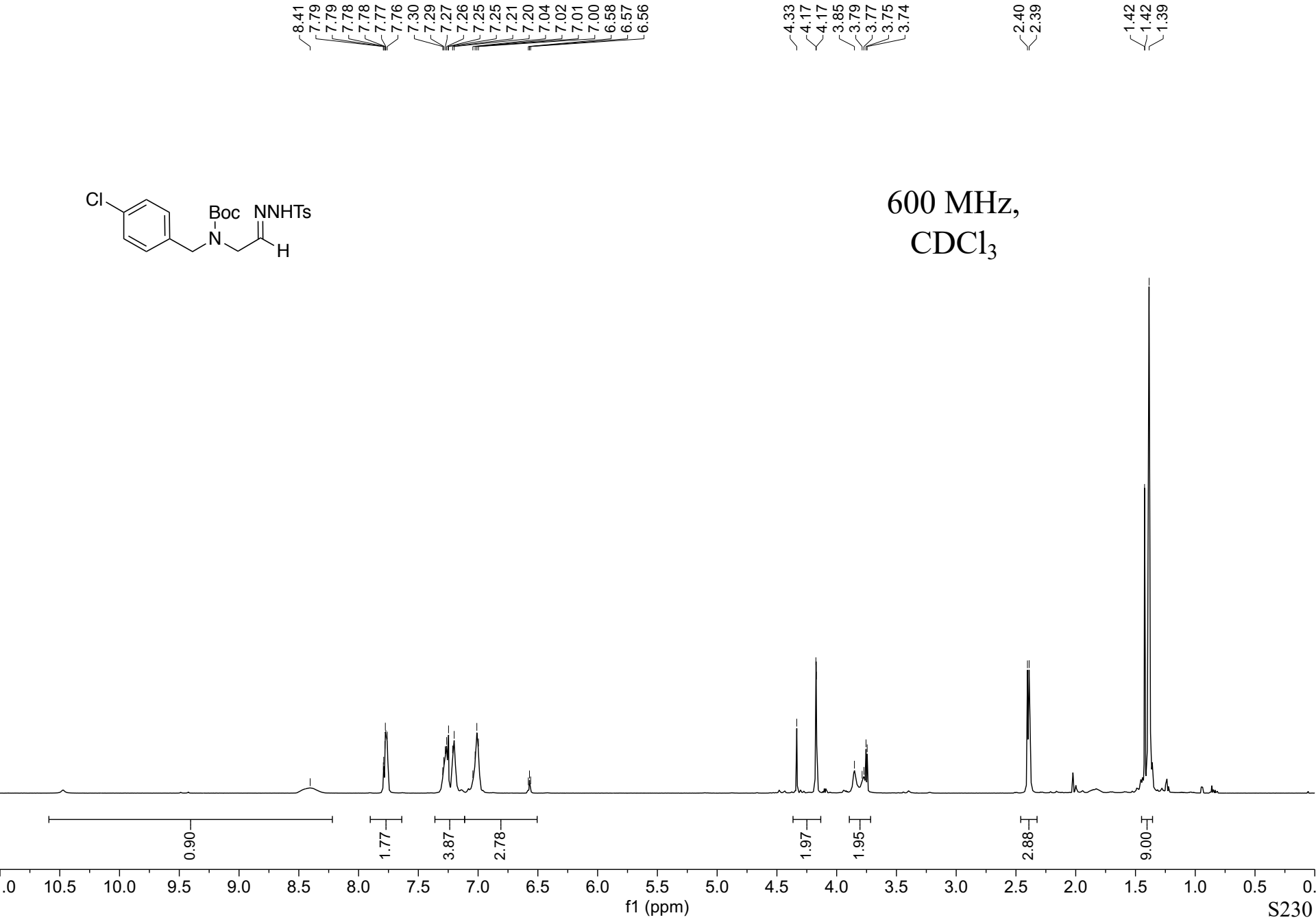



470 MHz,
$CDCl_3$

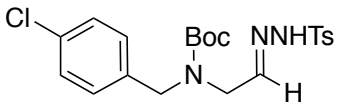


# $^{1}$H NMR *tert*-butyl (4-chlorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1l**

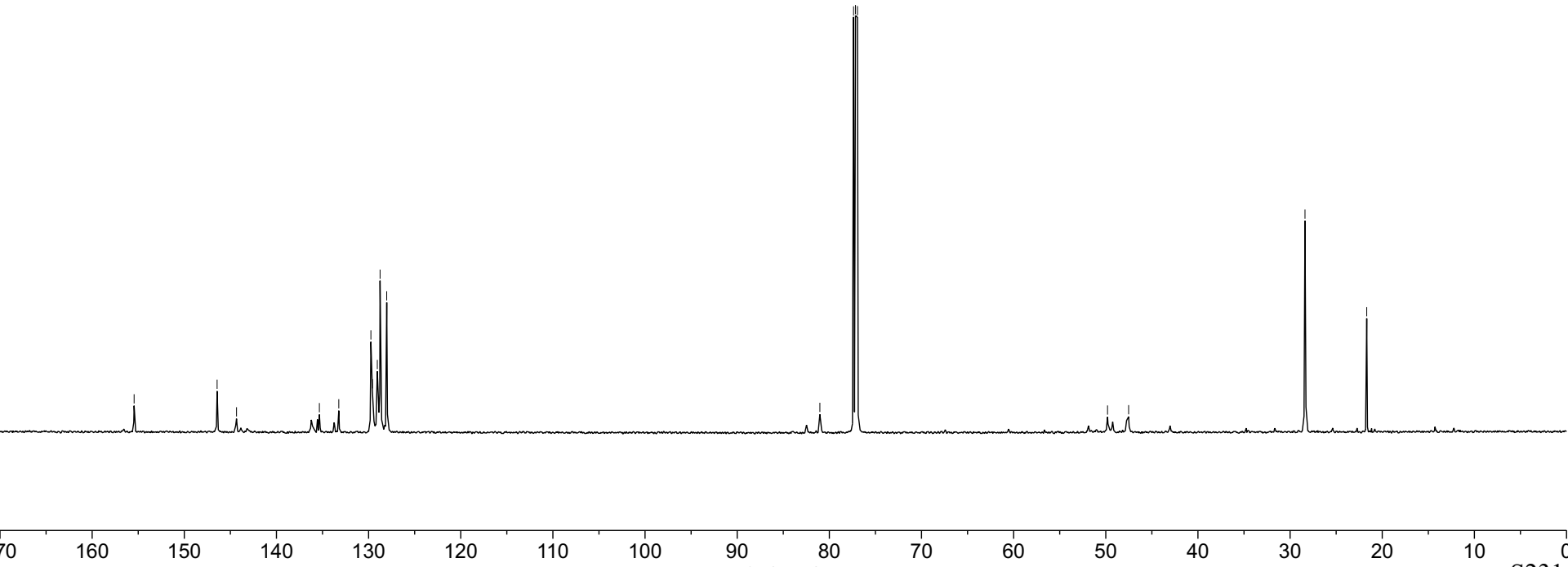


# $^{13}$C NMR *tert*-butyl (4-chlorobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1l**

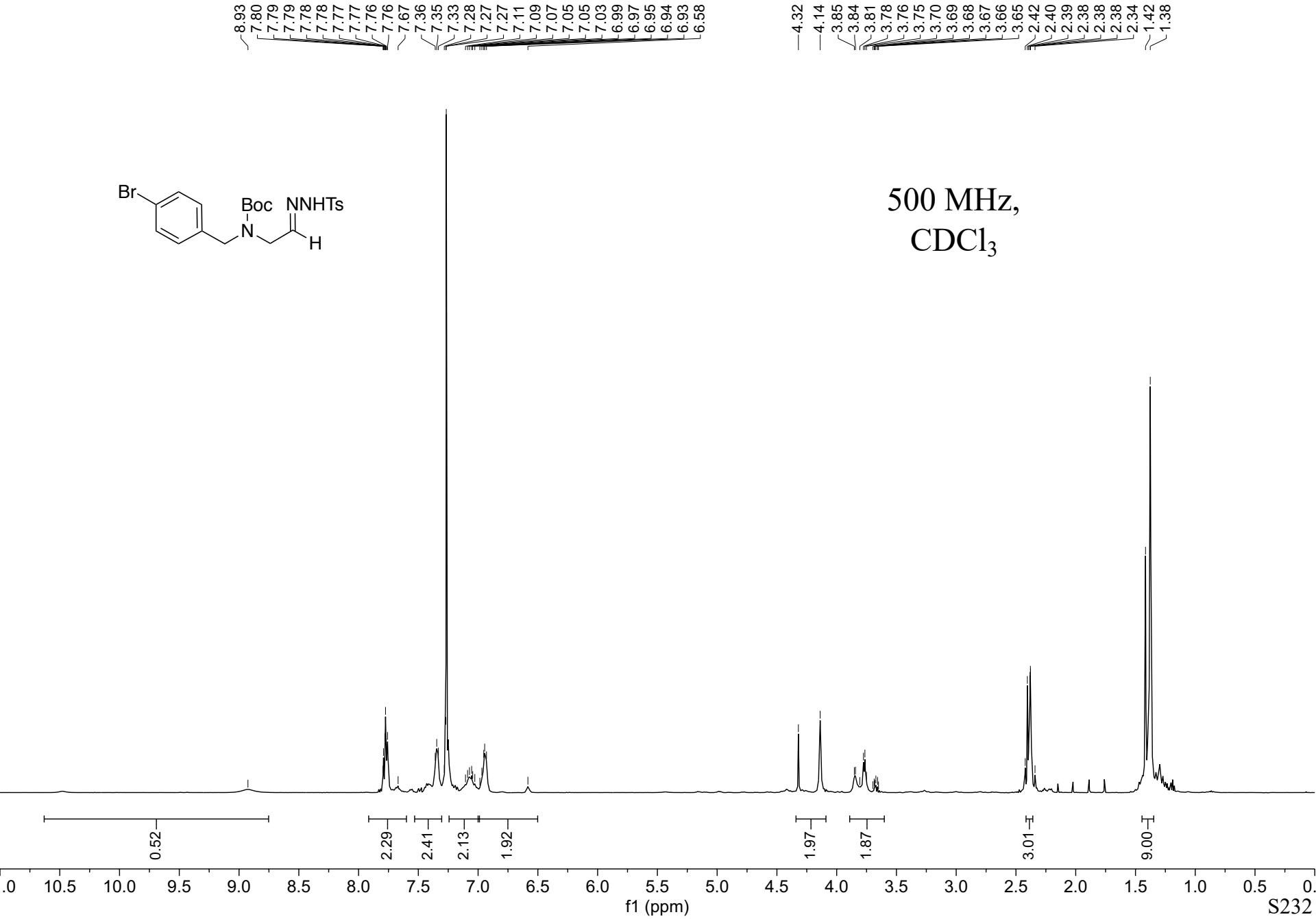


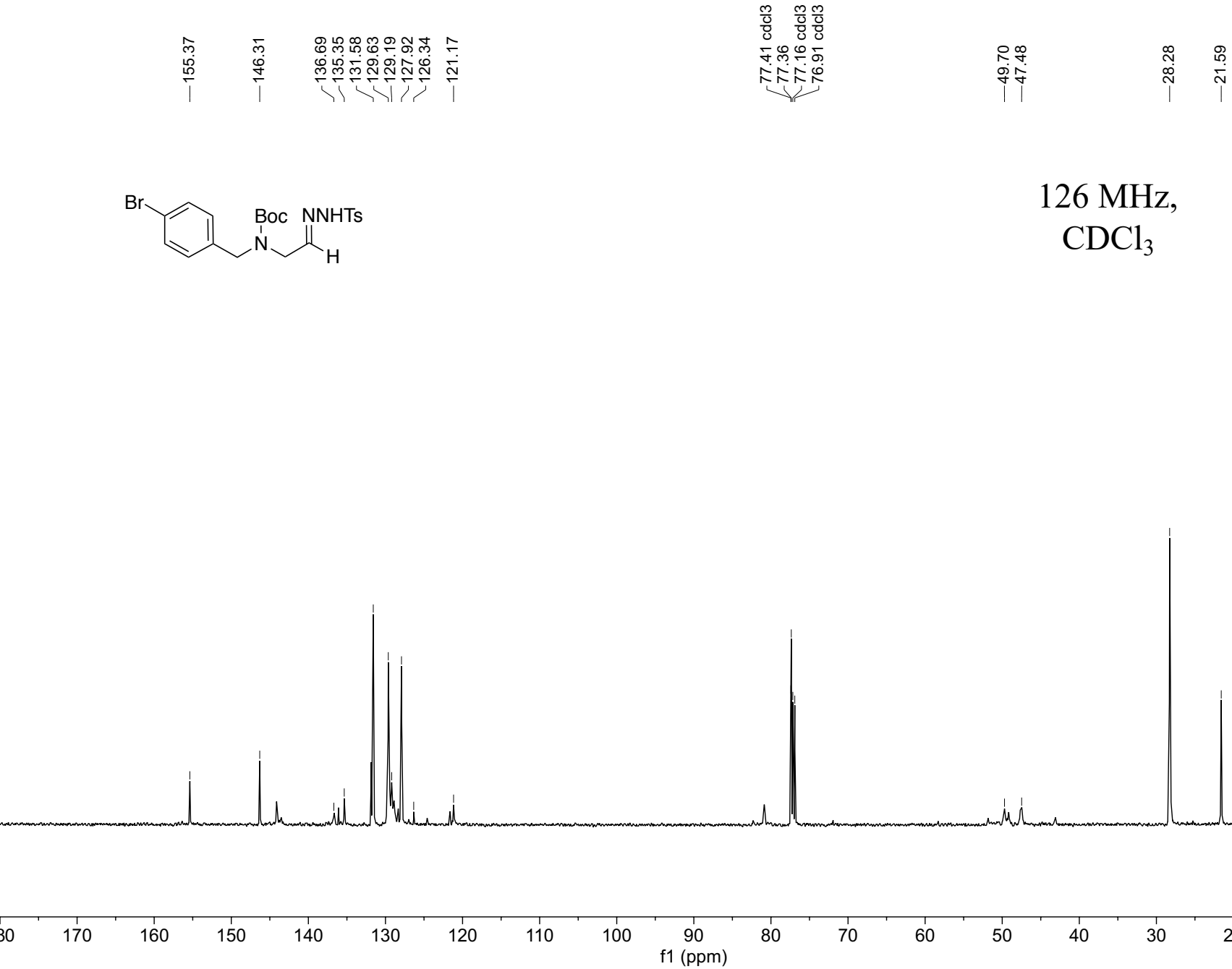

151 MHz,
$CDCl_3$



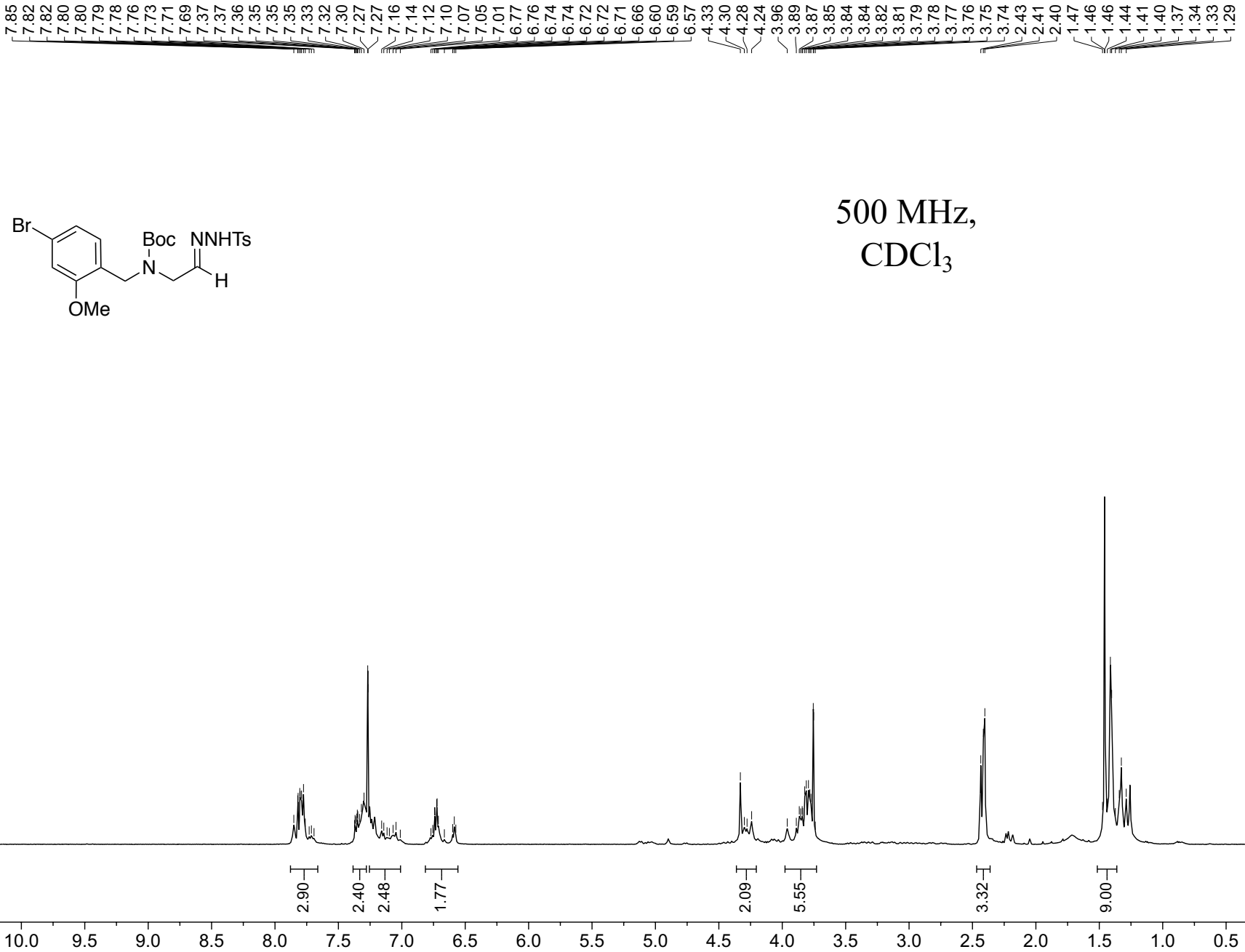
# $^{1}$H NMR *tert*-butyl (4-bromobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1m**



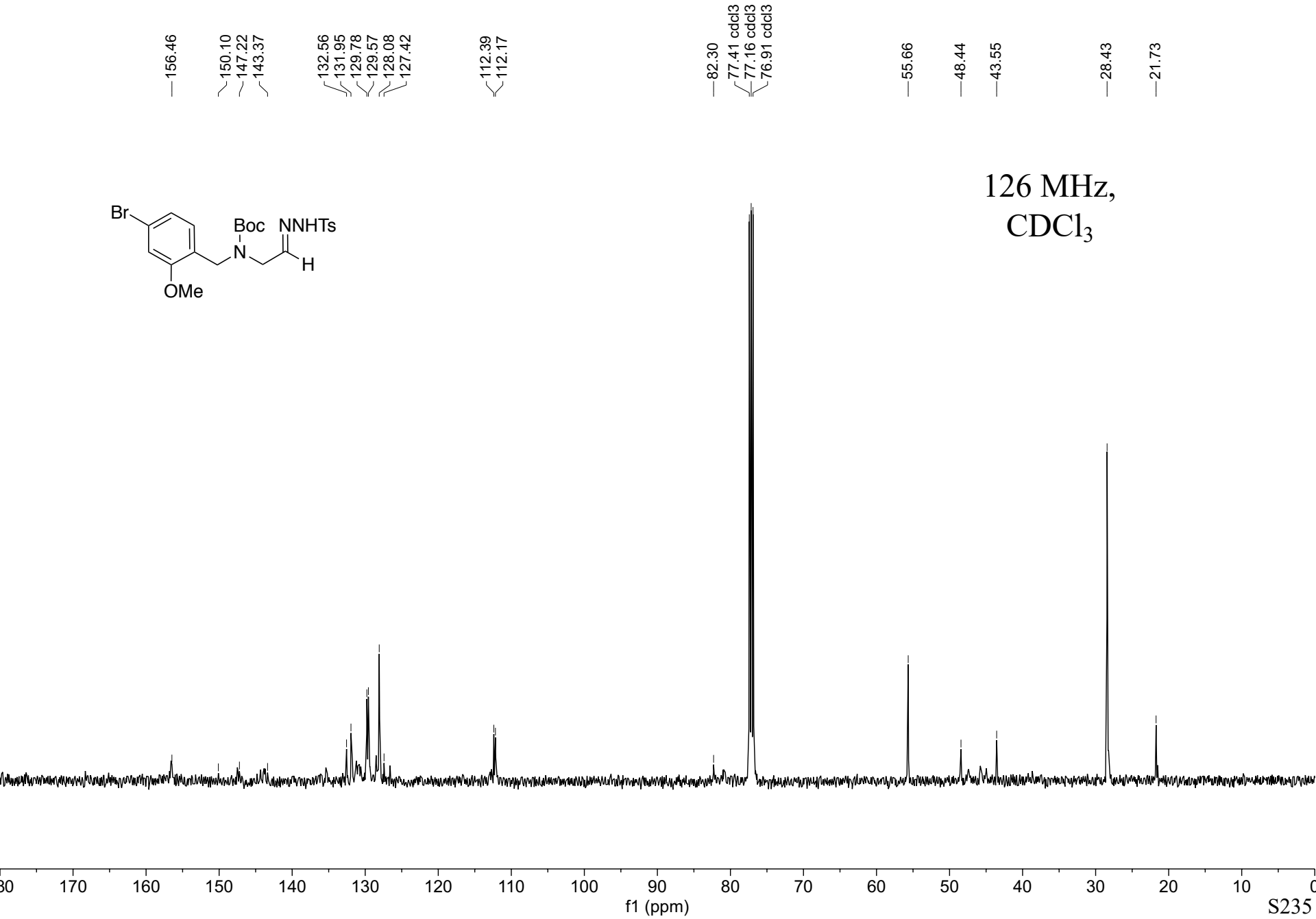
# $^{13}$C NMR *tert*-butyl (4-bromobenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1m**



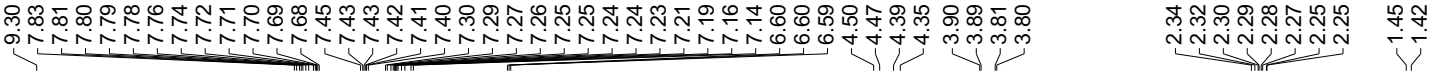
**$^1$H NMR** *tert*-butyl (4-bromo-2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1n**

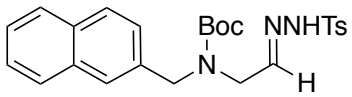


# $^{13}$C NMR *tert*-butyl (4-bromo-2-methoxybenzyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1n**

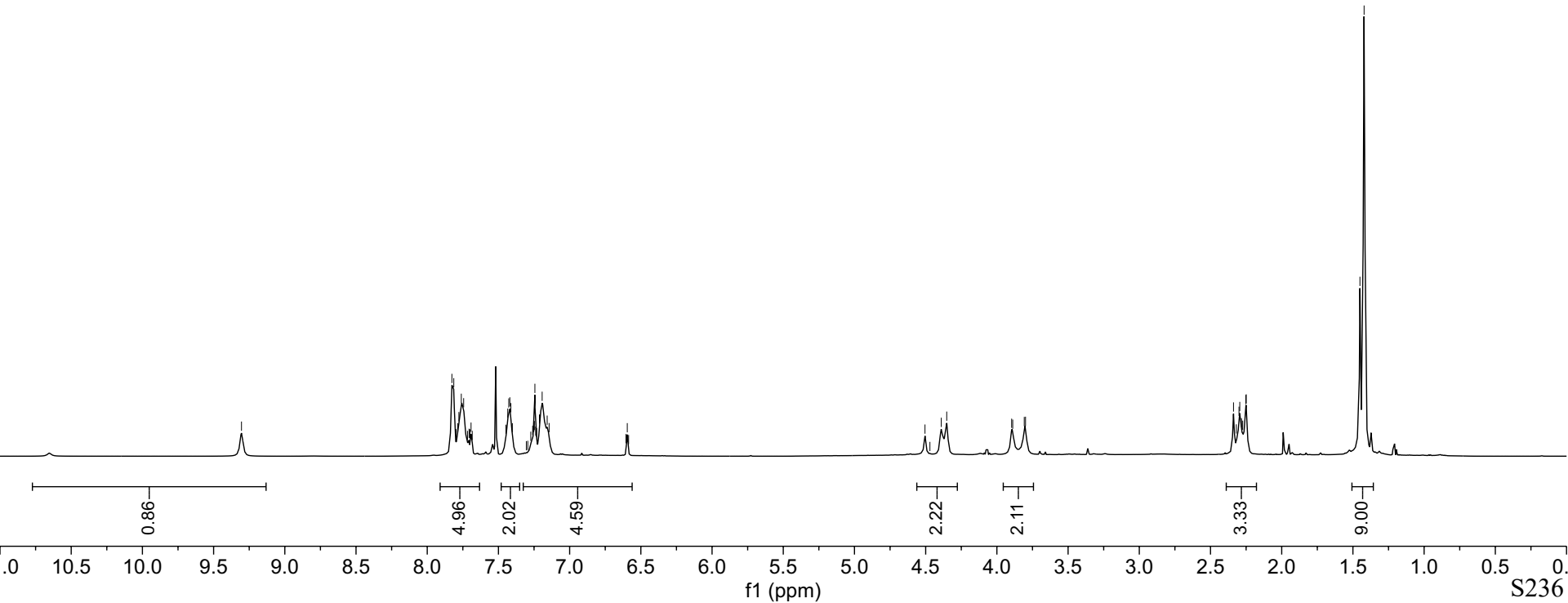


# $^{1}$H NMR *tert*-butyl (naphthalen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1o**

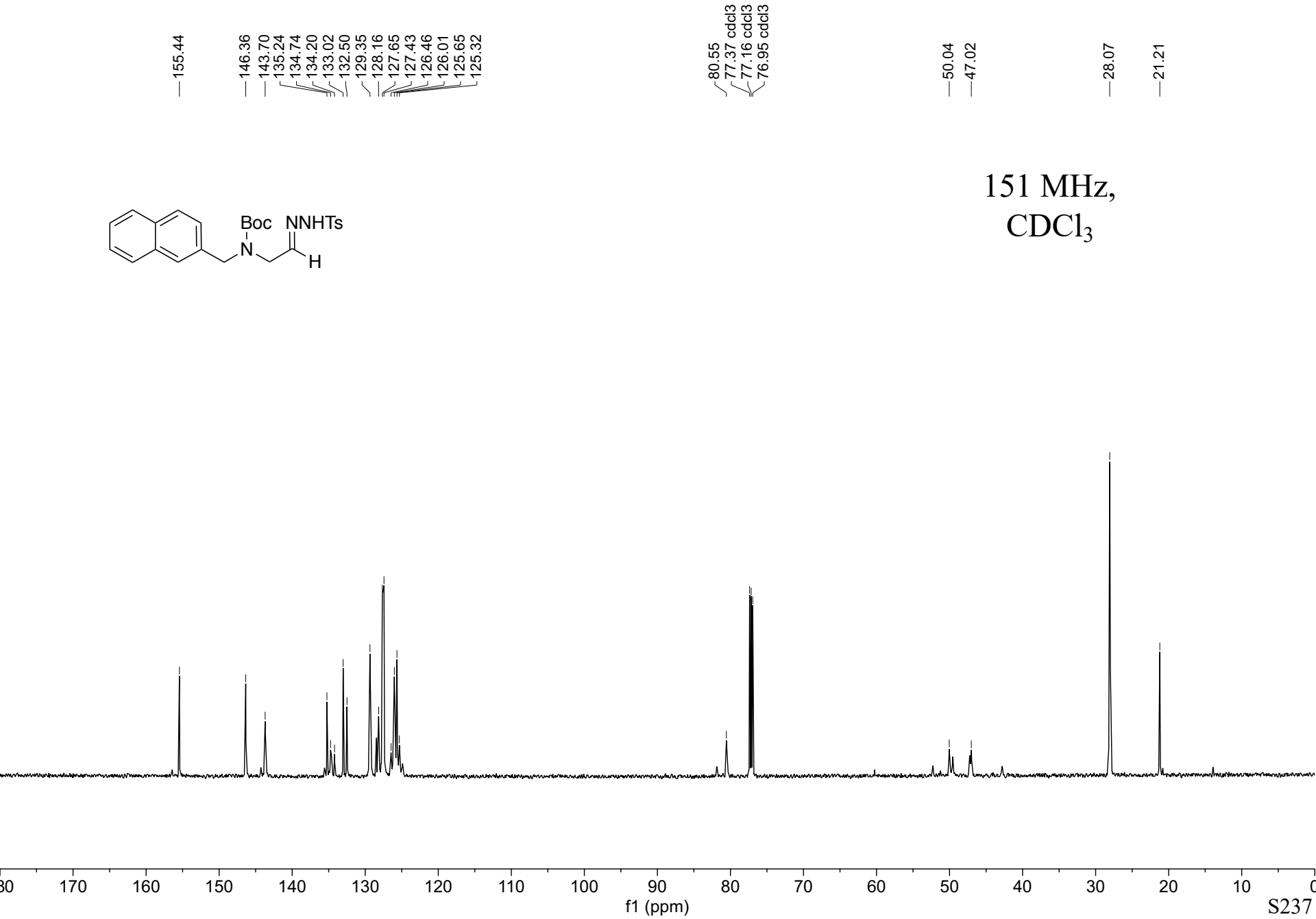


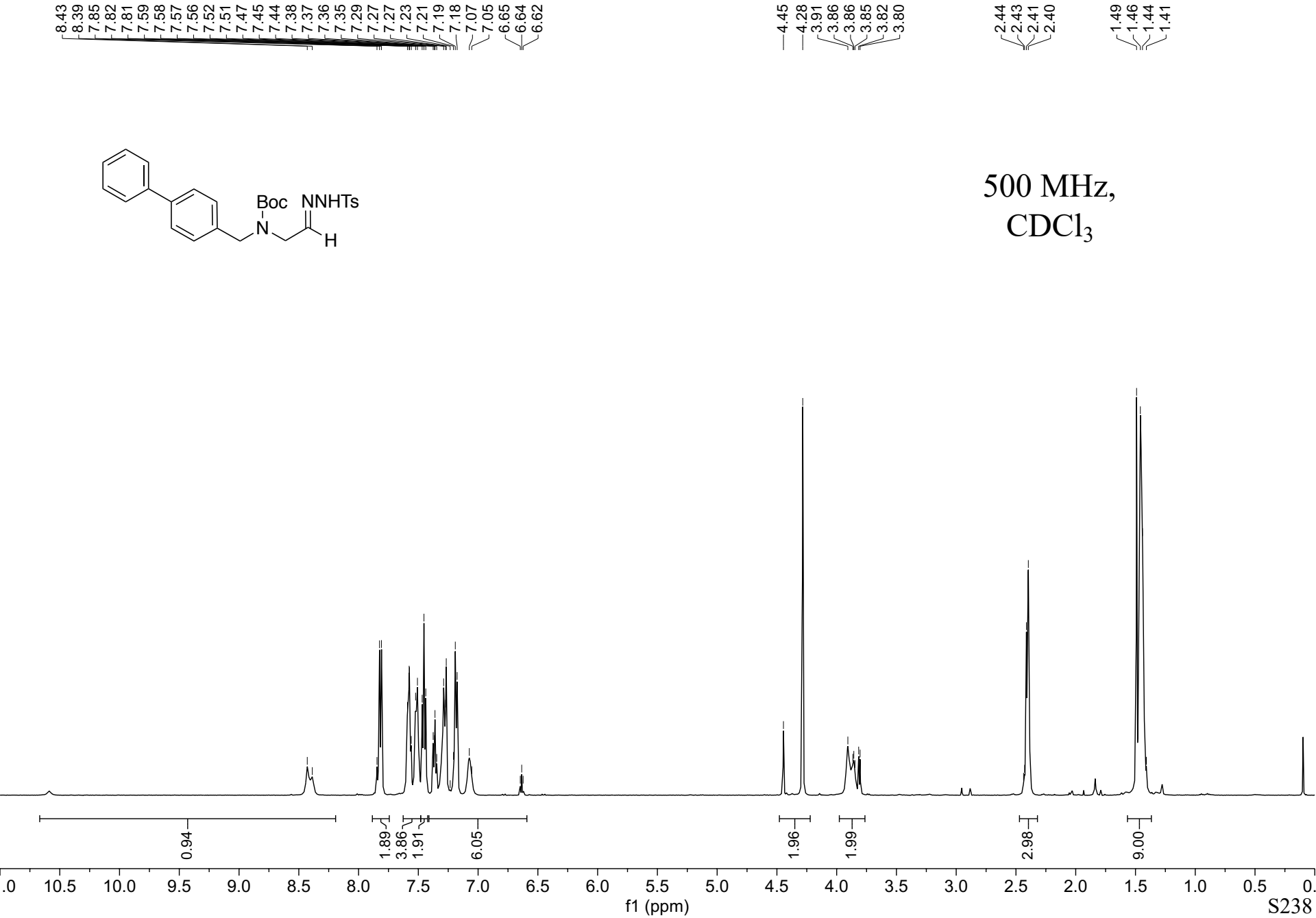

600 MHz,
$CDCl_3$



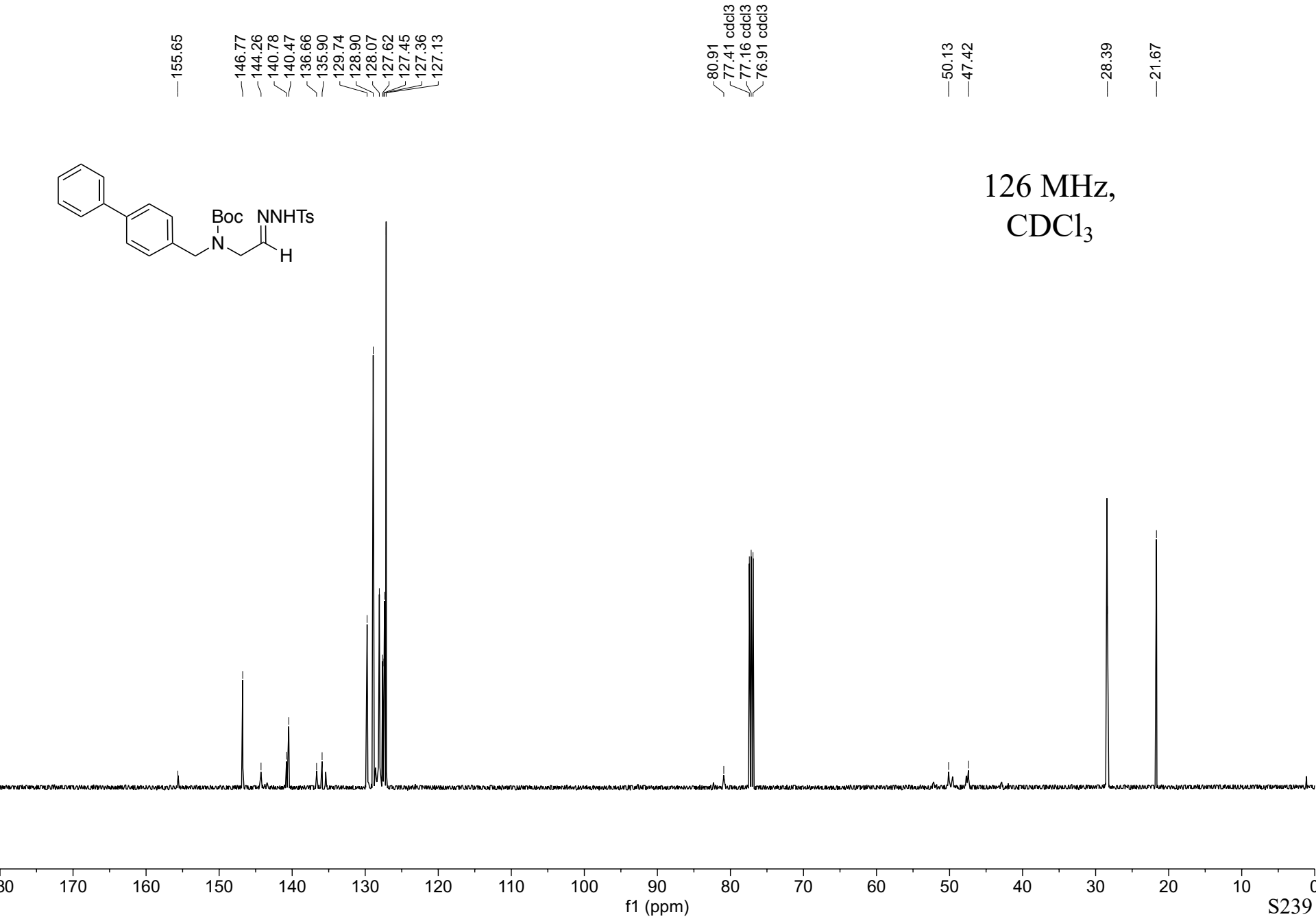
# $^{13}$C NMR *tert*-butyl (naphthalen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1o**



# $^{1}$H NMR *tert*-butyl ([1,1'-biphenyl]-4-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1p**

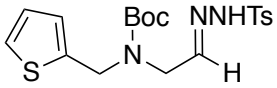


# $^{13}$C NMR *tert*-butyl ([1,1'-biphenyl]-4-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1p**

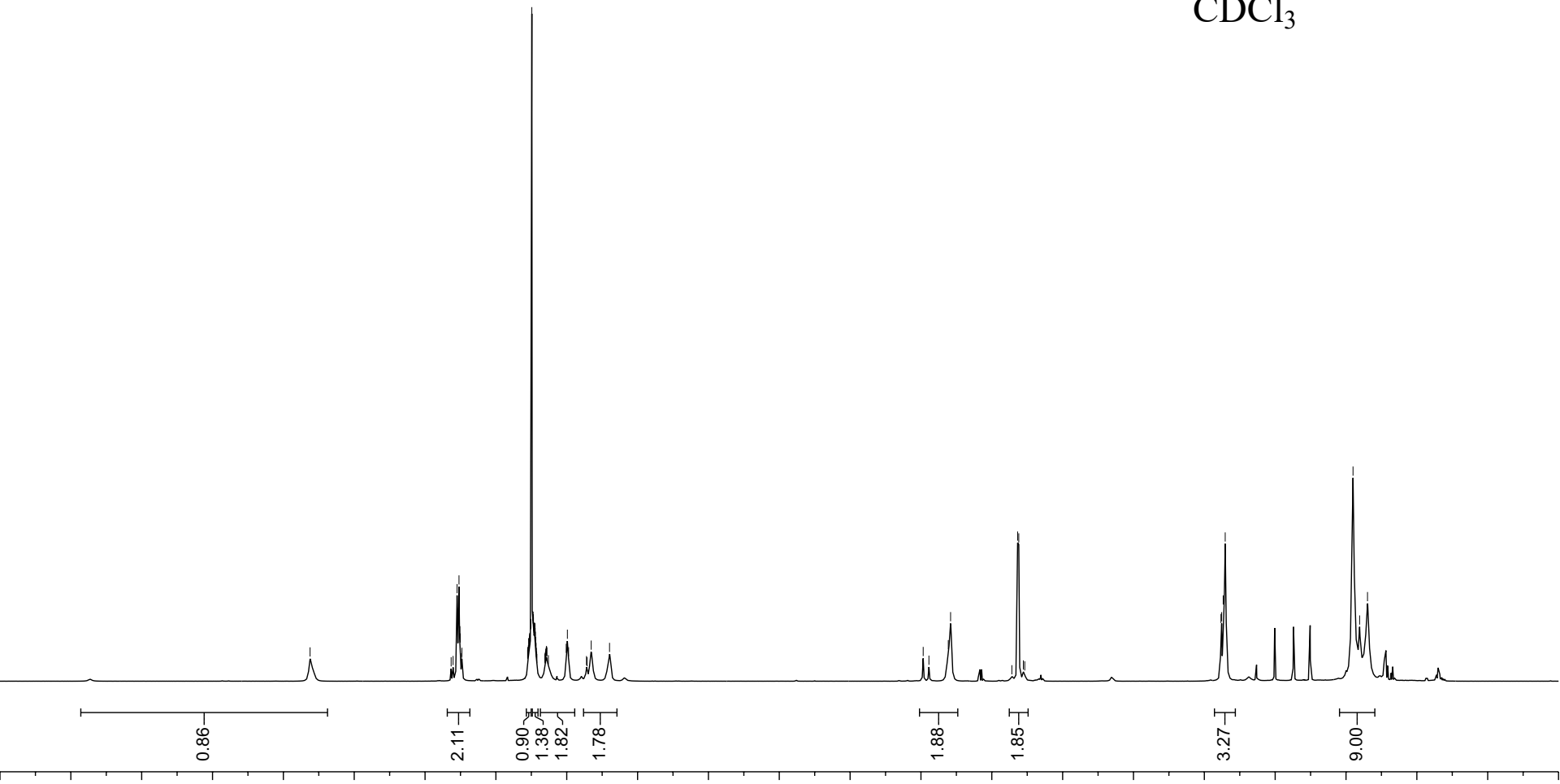


# $^{1}$H NMR *tert*-butyl (thiophen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1q**



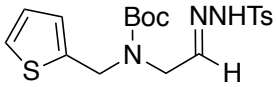




600 MHz,
$CDCl_3$

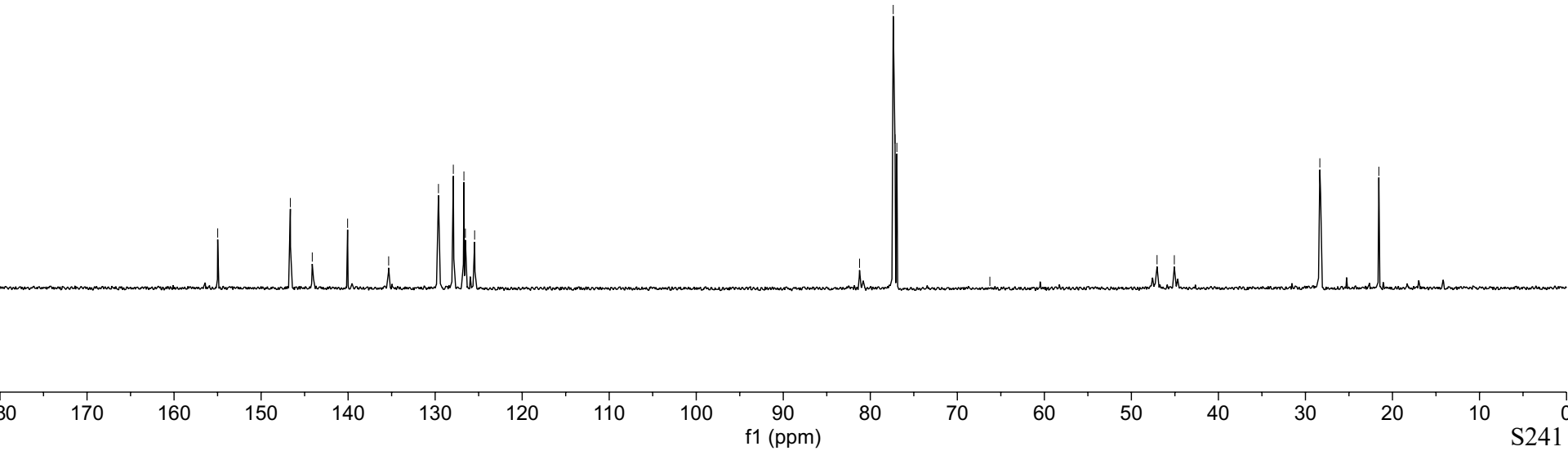


# $^{13}$C NMR *tert*-butyl (thiophen-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1q**

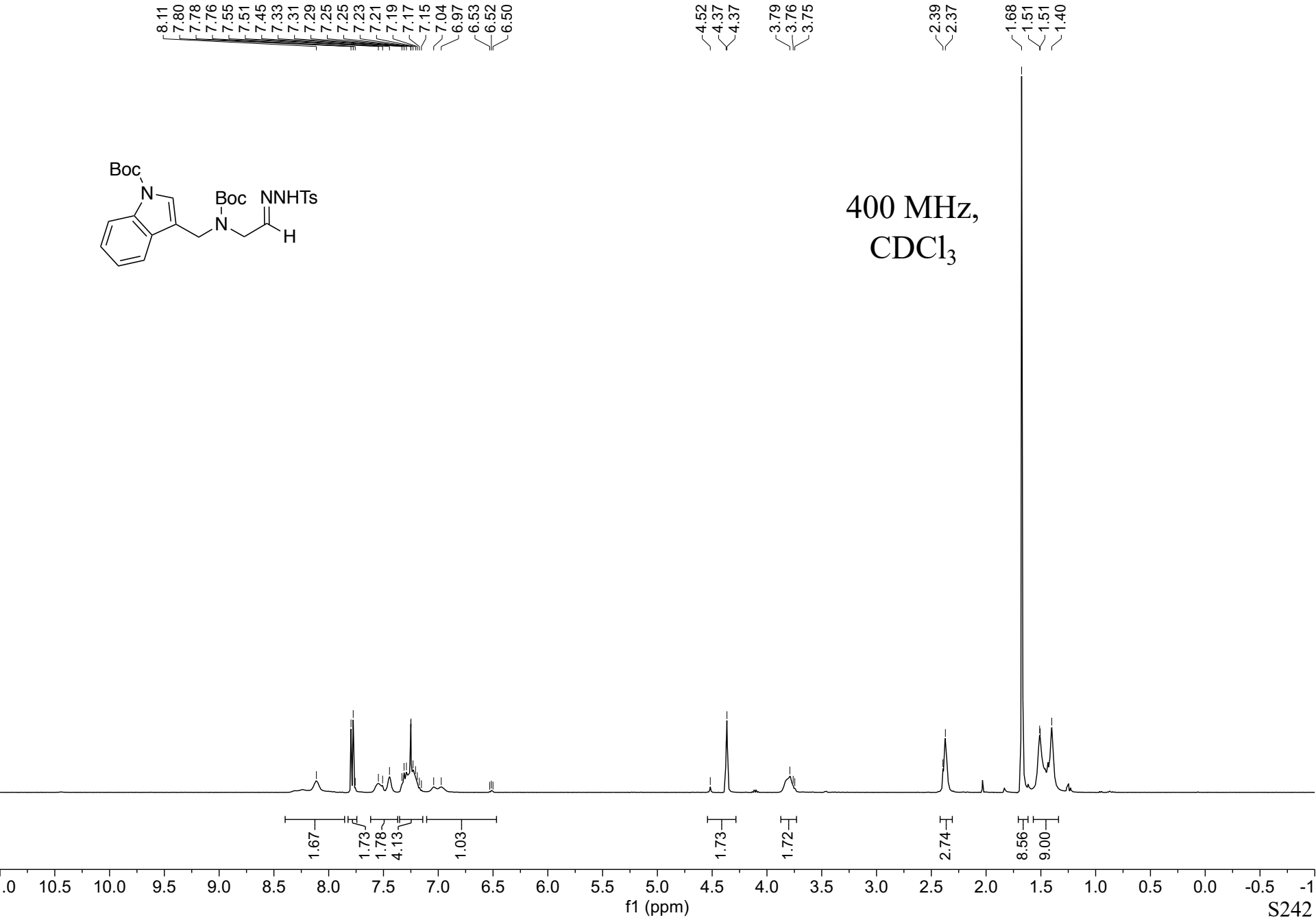


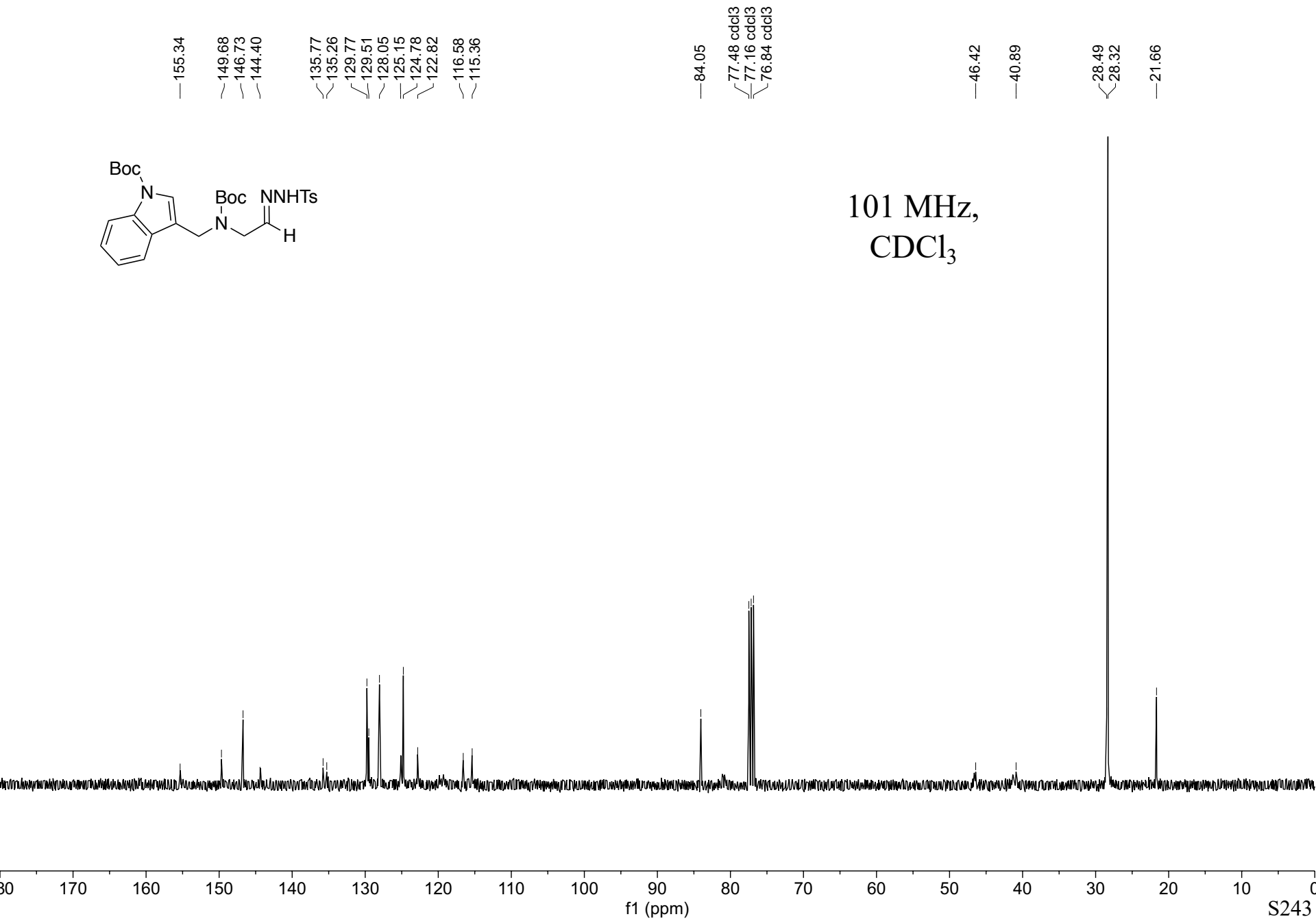

151 MHz,
$CDCl_3$



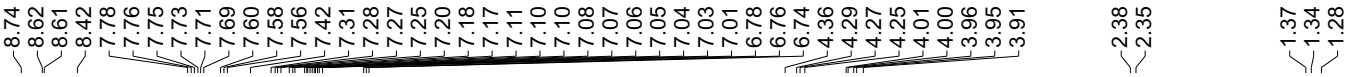
**$^1$H NMR** *tert*-butyl 3-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)-1*H*-indole-1-carboxylate **1r**

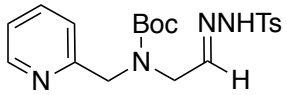


**$^{13}$C NMR** *tert*-butyl 3-(((*tert*-butoxycarbonyl)(2-(2-tosylhydrazineylidene)ethyl)amino)methyl)-1*H*-indole-1-carboxylate **1r**

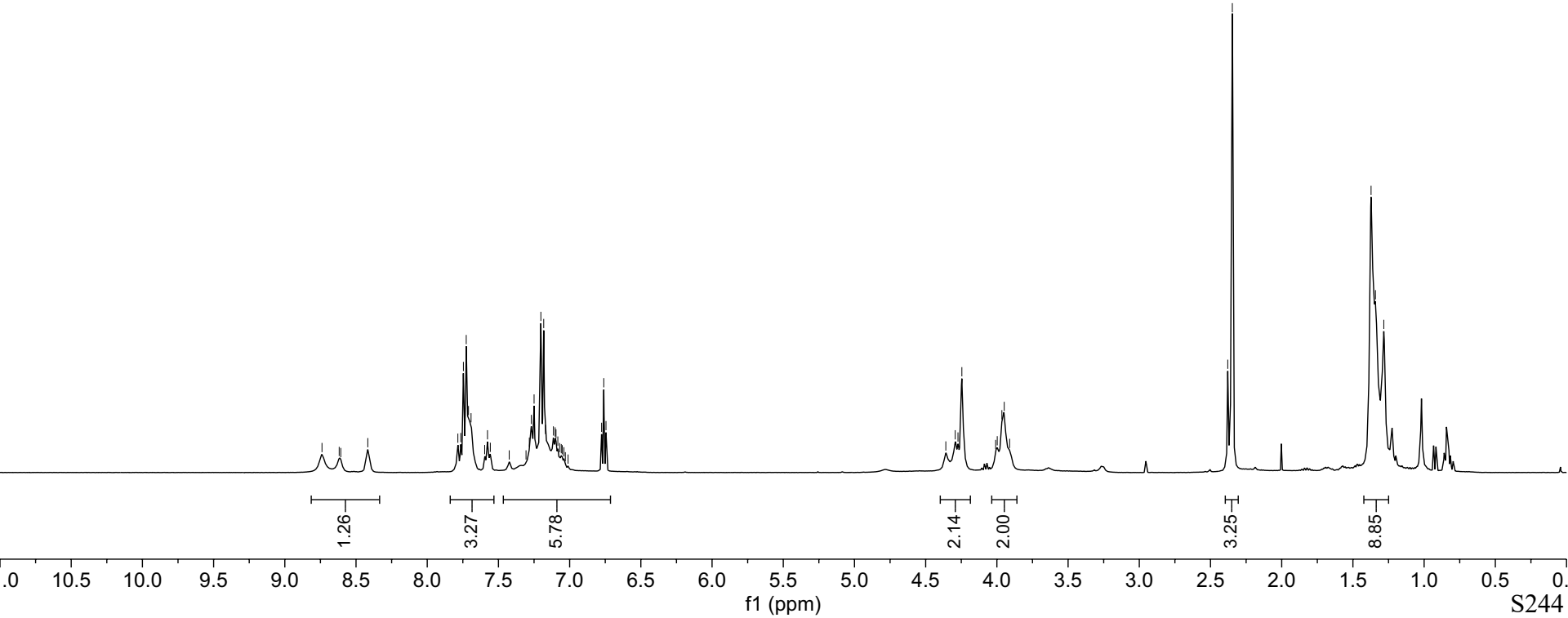


**$^1$H NMR** *tert*-butyl (pyridin-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1s**



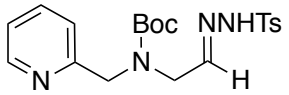




400 MHz,
$CDCl_3$

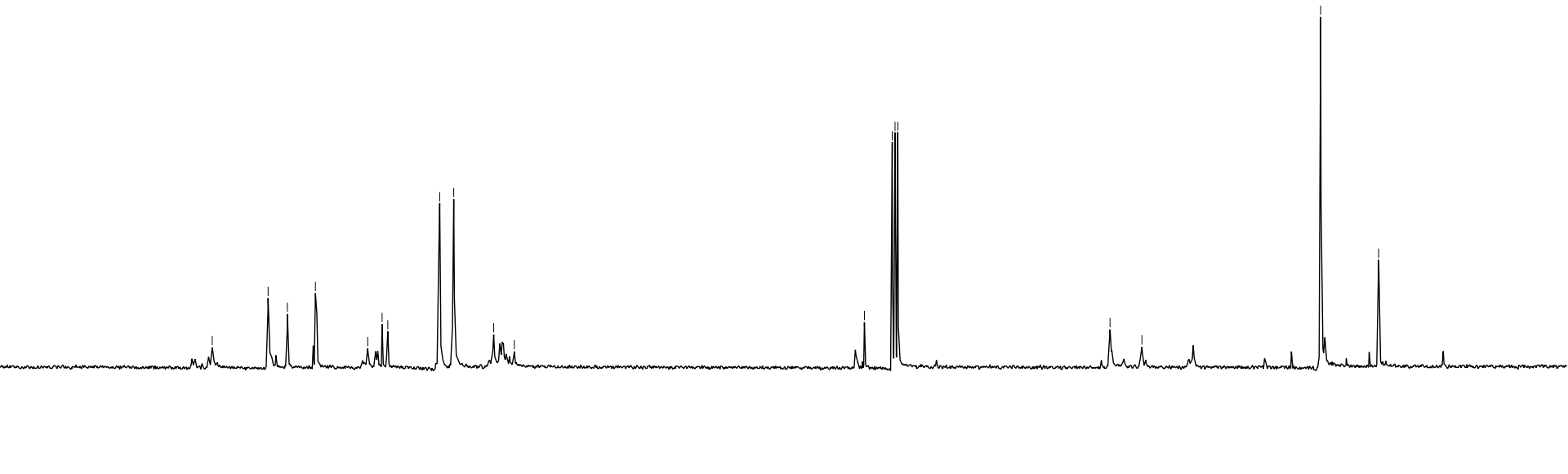


# $^{13}$C NMR *tert*-butyl (pyridin-2-ylmethyl)(2-(2-tosylhydrazineylidene)ethyl)carbamate **1s**

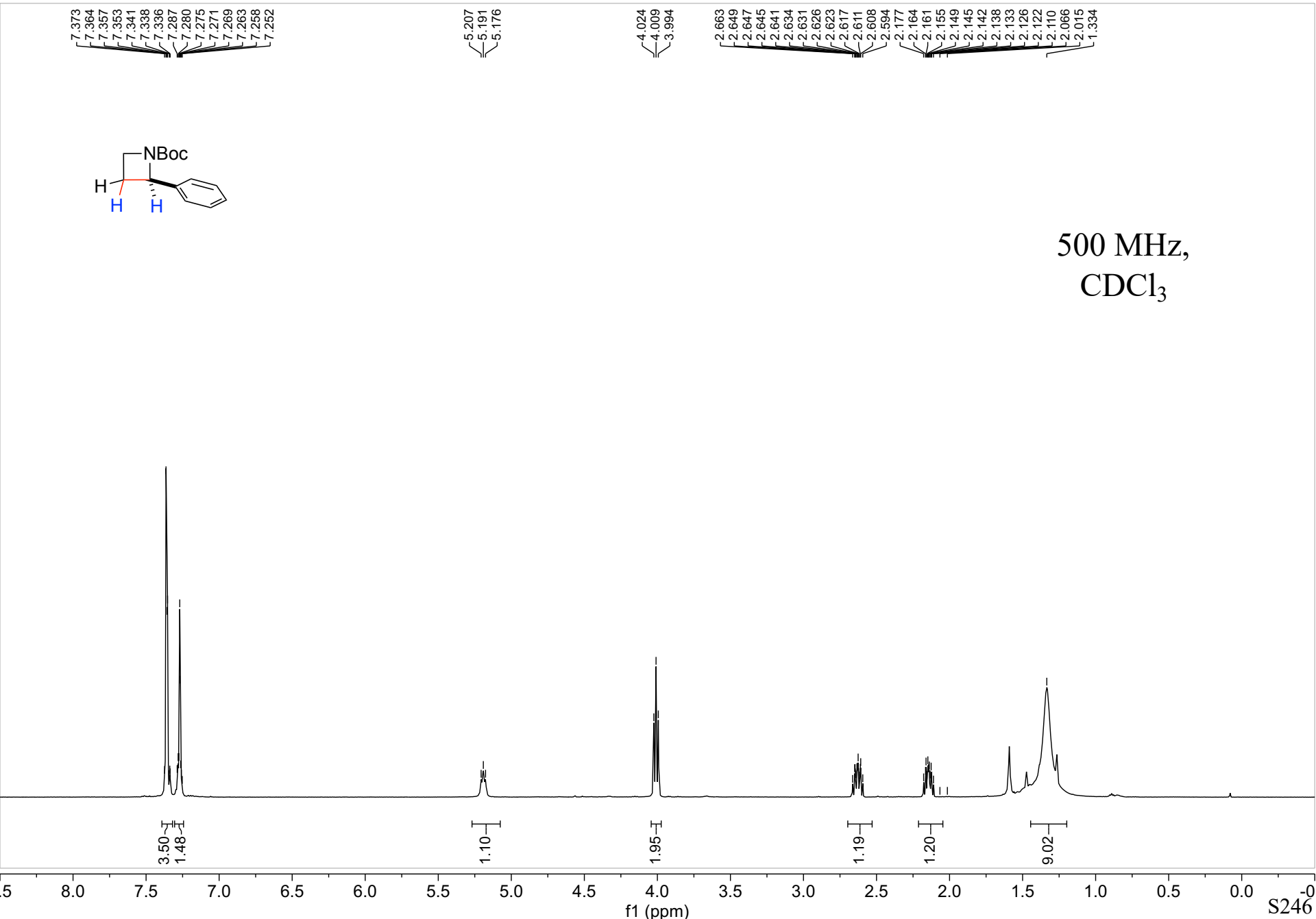
155.61
149.19
146.98
143.76
137.75
136.10
135.44
129.48
127.86
123.27
120.91
80.68
77.48 cdcl3
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48.79
28.25
21.59



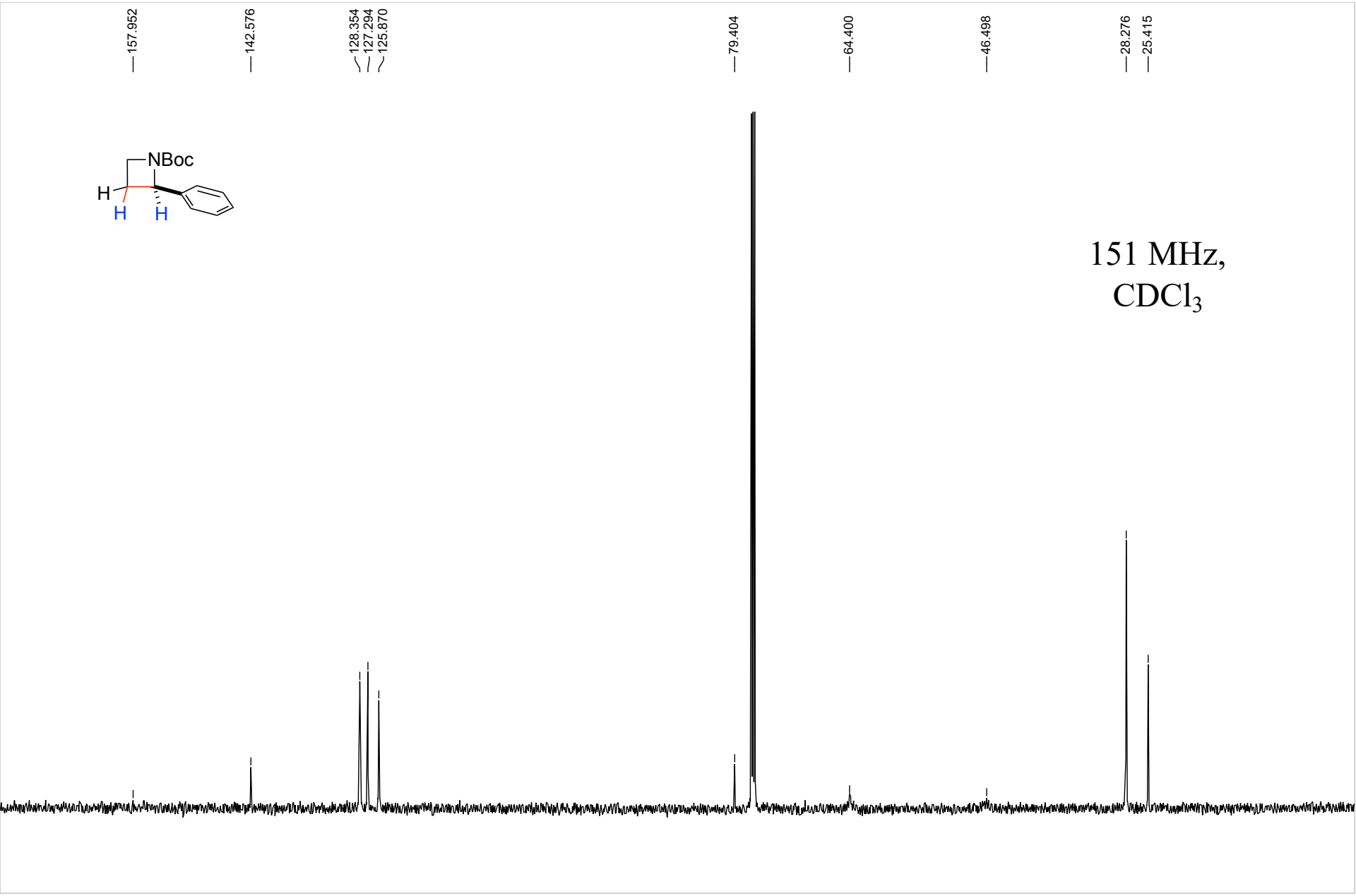

101 MHz,
$CDCl_3$



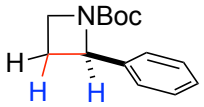
# $^{1}$H NMR *tert*-Butyl (*R*)-2-phenylazetidine-1-carboxylate (**2a**)



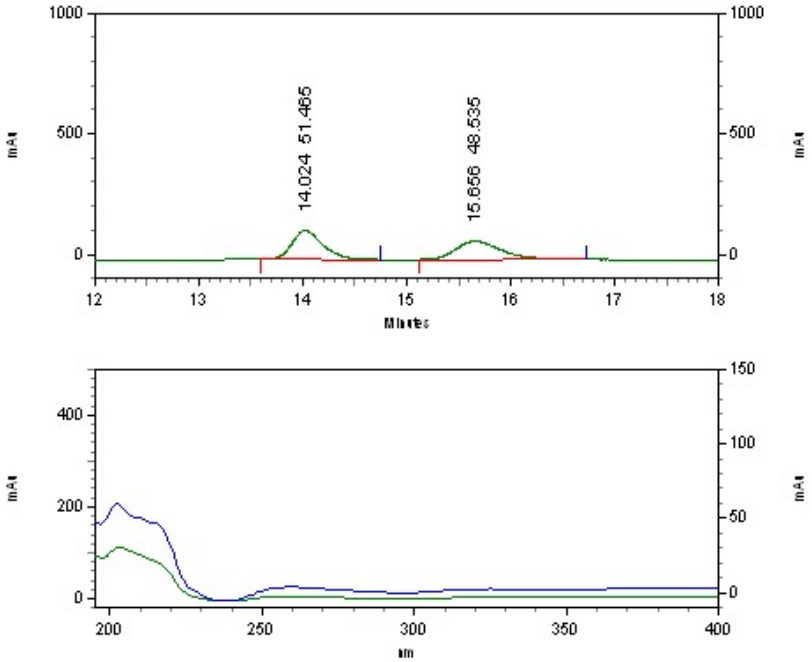
# $^{13}$C NMR *tert*-Butyl (*R*)-2-phenylazetidine-1-carboxylate (**2a**)



# **HPLC** *tert*-Butyl (*R*)-2-phenylazetidine-1-carboxylate (**2a**)



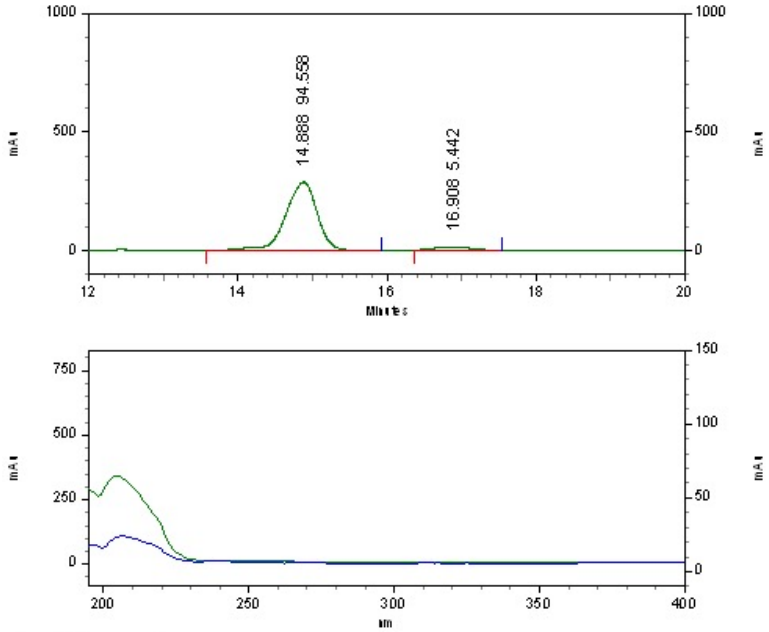

D:\Jingjing HPLC\JJX-1722P-IF-2%-0.8ml-IBu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 200 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.024 | 51.465 |
| 2 | 15.656 | 48.535 |
| Totals | | 100.000 |

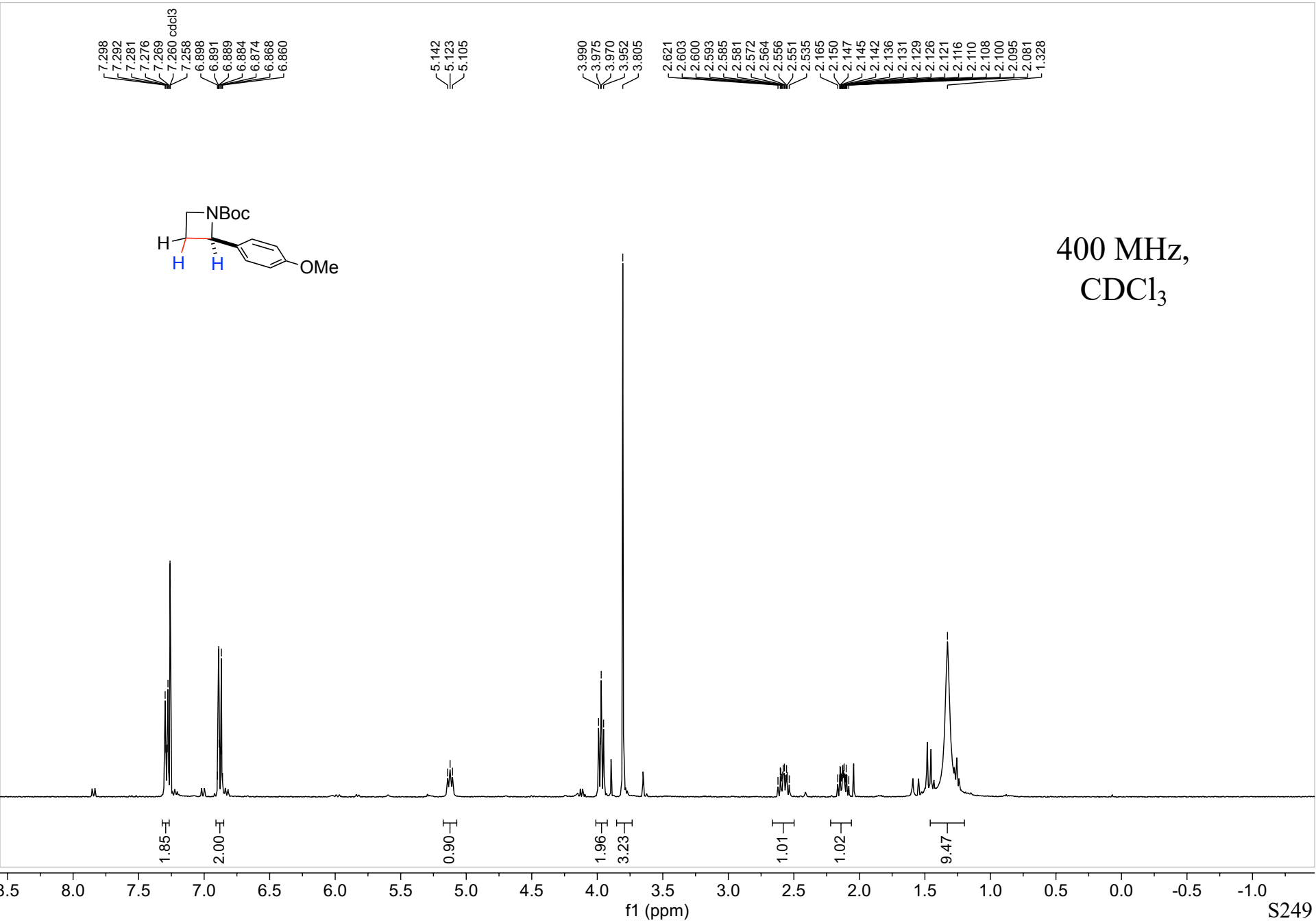
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C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



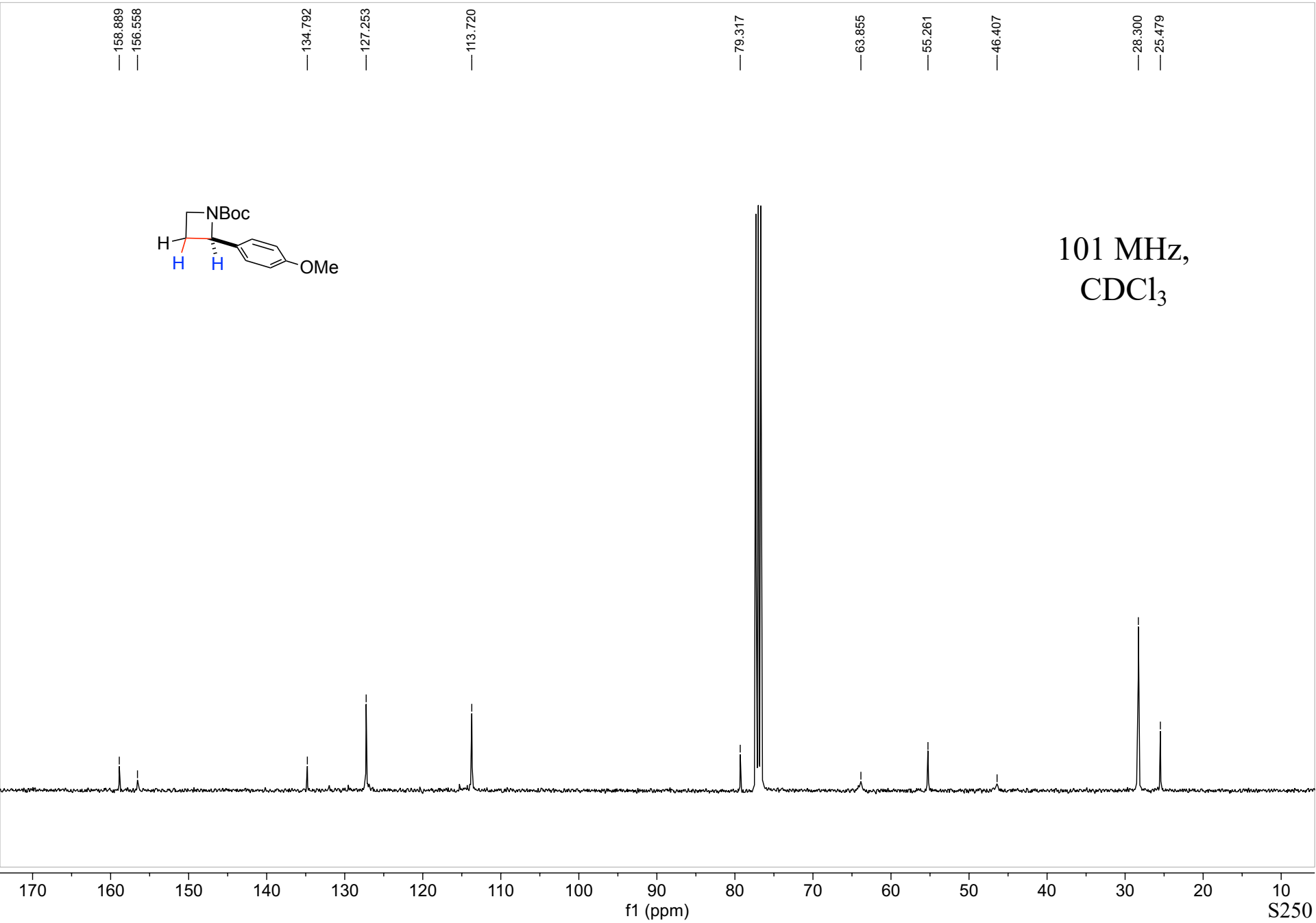

2: 200 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 14.888 | 94.558 |
| 2 | 16.908 | 5.442 |
| Totals | | 100.000 |

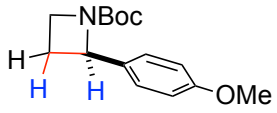
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(4-methoxyphenyl)azetidine-1-carboxylate (**2b**)



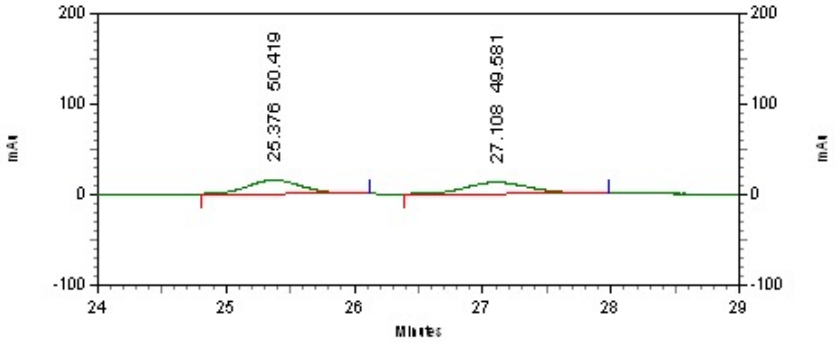
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-methoxyphenyl)azetidine-1-carboxylate (**2b**)

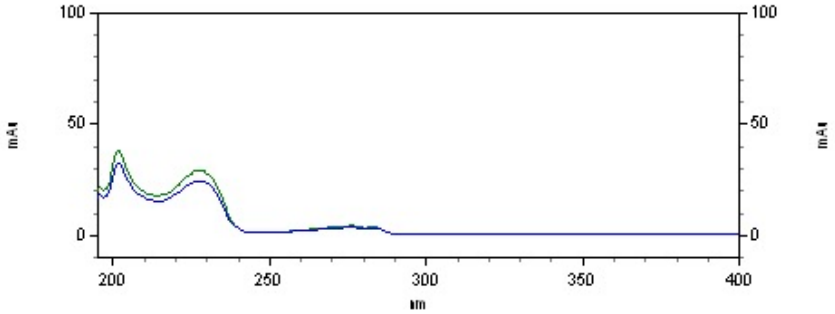


# **HPLC** *tert*-Butyl (*R*)-2-(4-methoxyphenyl)azetidine-1-carboxylate (**2b**)




D:\Jingjing HPLC\JJX-2153P-ID-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

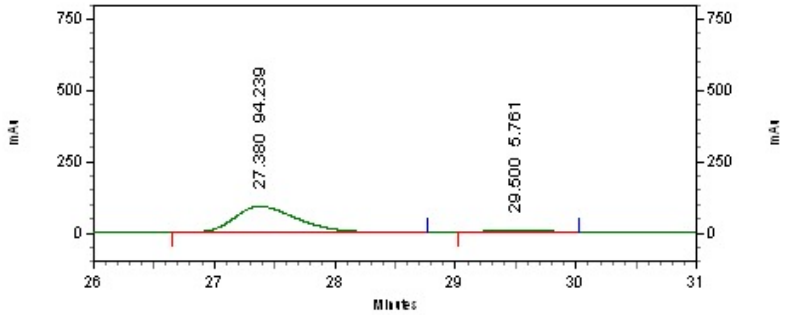


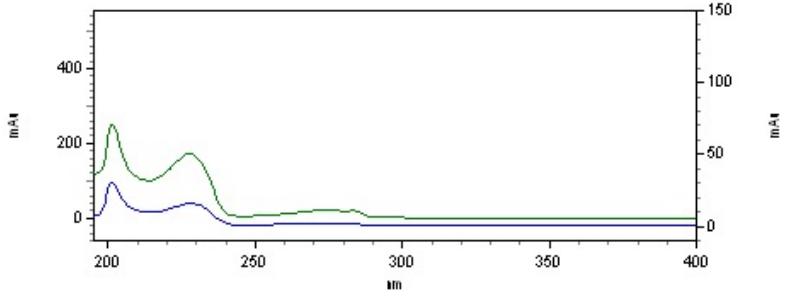




2: 235 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 25.376 | 50.419 |
| 2 | 27.108 | 49.581 |
| Totals | | 100.000 |

D:\Jingjing HPLC\JJX-2159P-ID-2%-0.8ML-C4-2
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

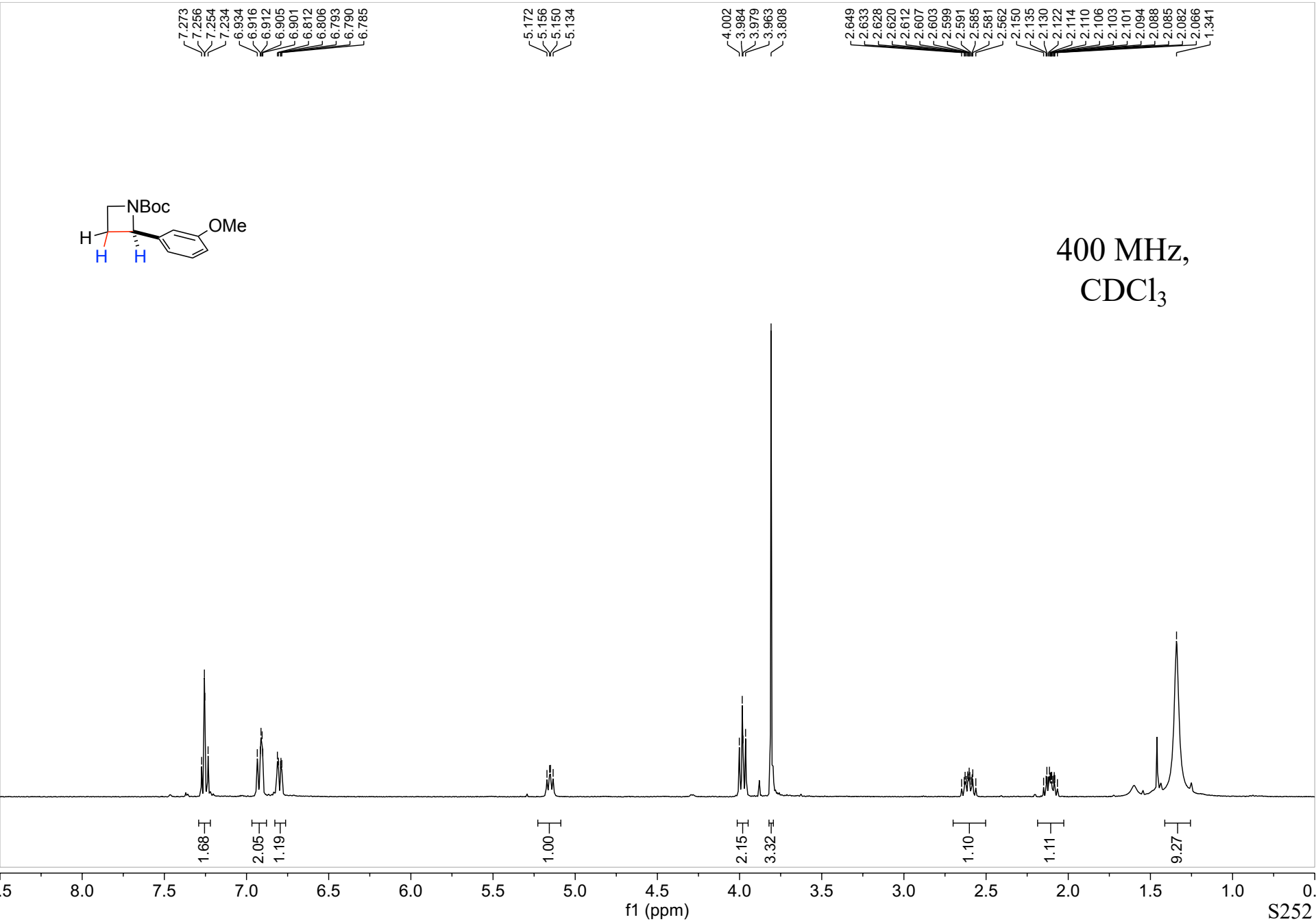


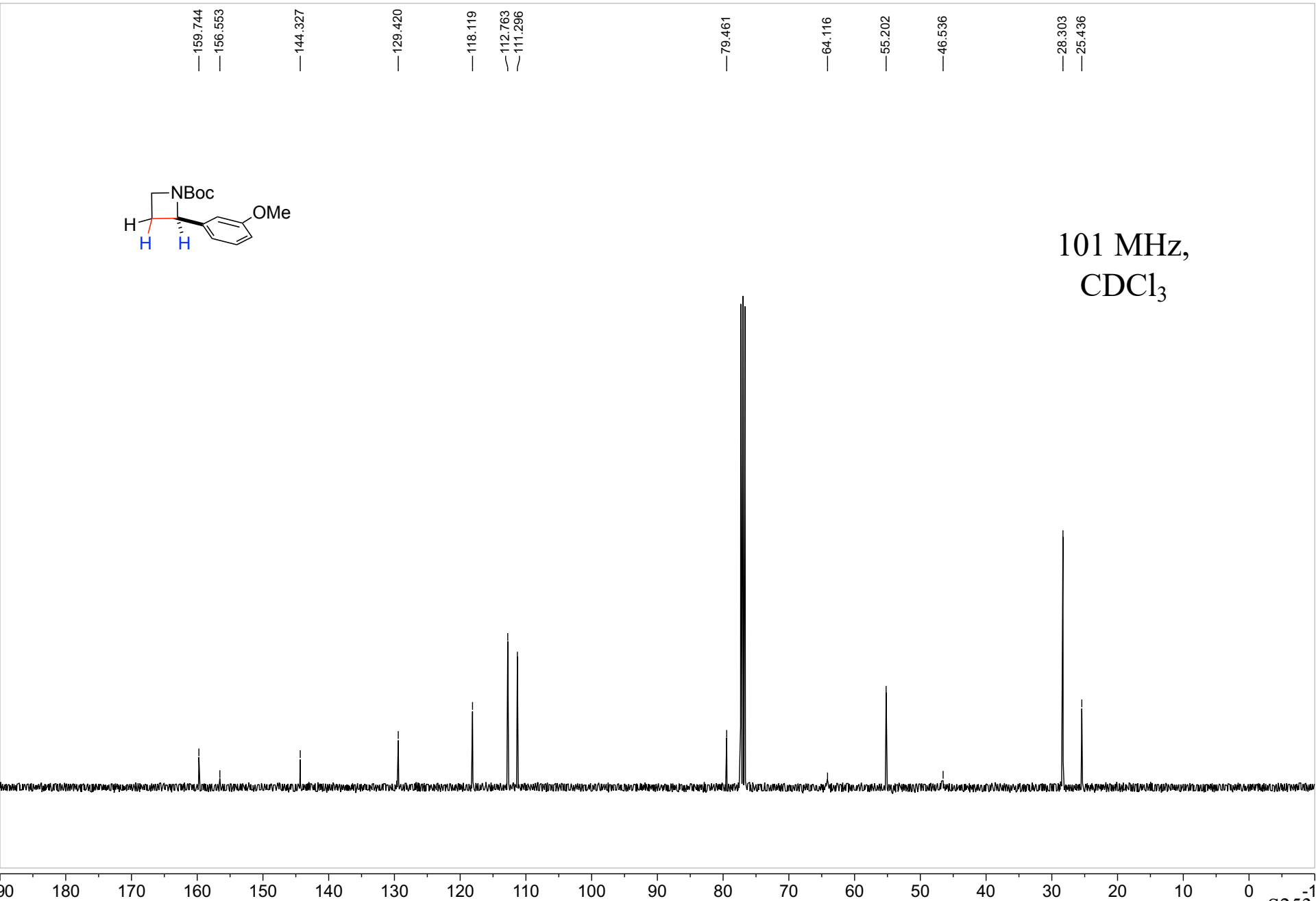

2: 235 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 27.380 | 94.239 |
| 2 | 29.500 | 5.761 |
| Totals | | 100.000 |

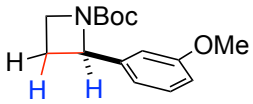
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(3-methoxyphenyl)azetidine-1-carboxylate (**2c**)



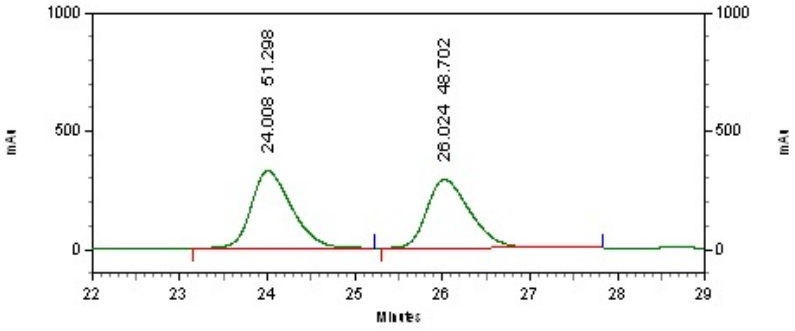
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(3-methoxyphenyl)azetidine-1-carboxylate (**2c**)

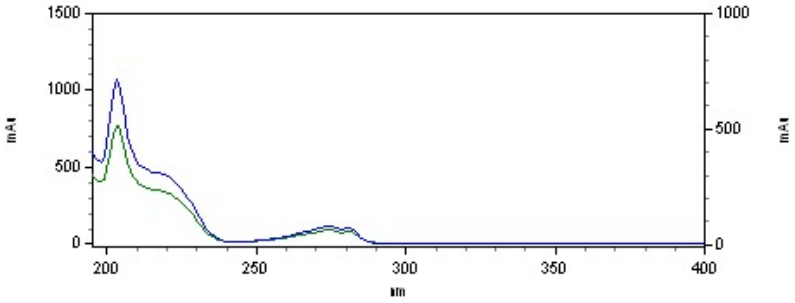


# **HPLC** *tert*-Butyl (*R*)-2-(3-methoxyphenyl)azetidine-1-carboxylate (**2c**)




D:\Jingjing HPLC\JJX-2111P-IF-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



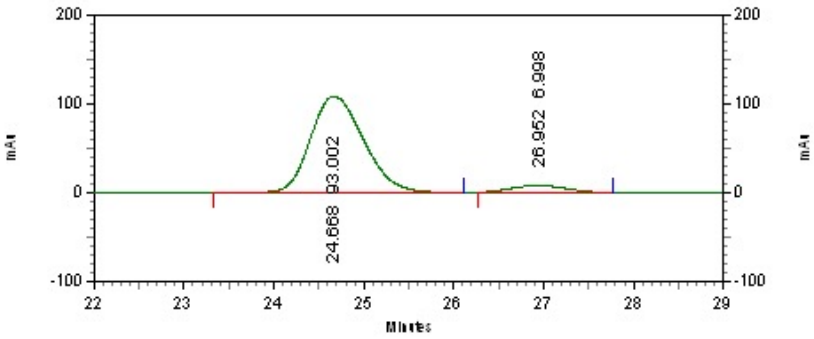



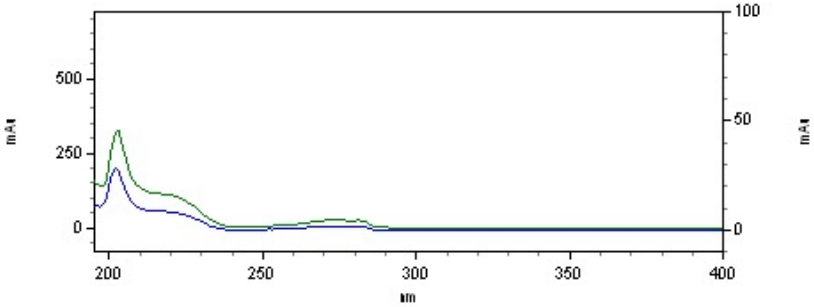

2: 220 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 24.008 | 51.298 |
| 2 | 26.024 | 48.702 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2094P-IF-2%-0.8ML-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



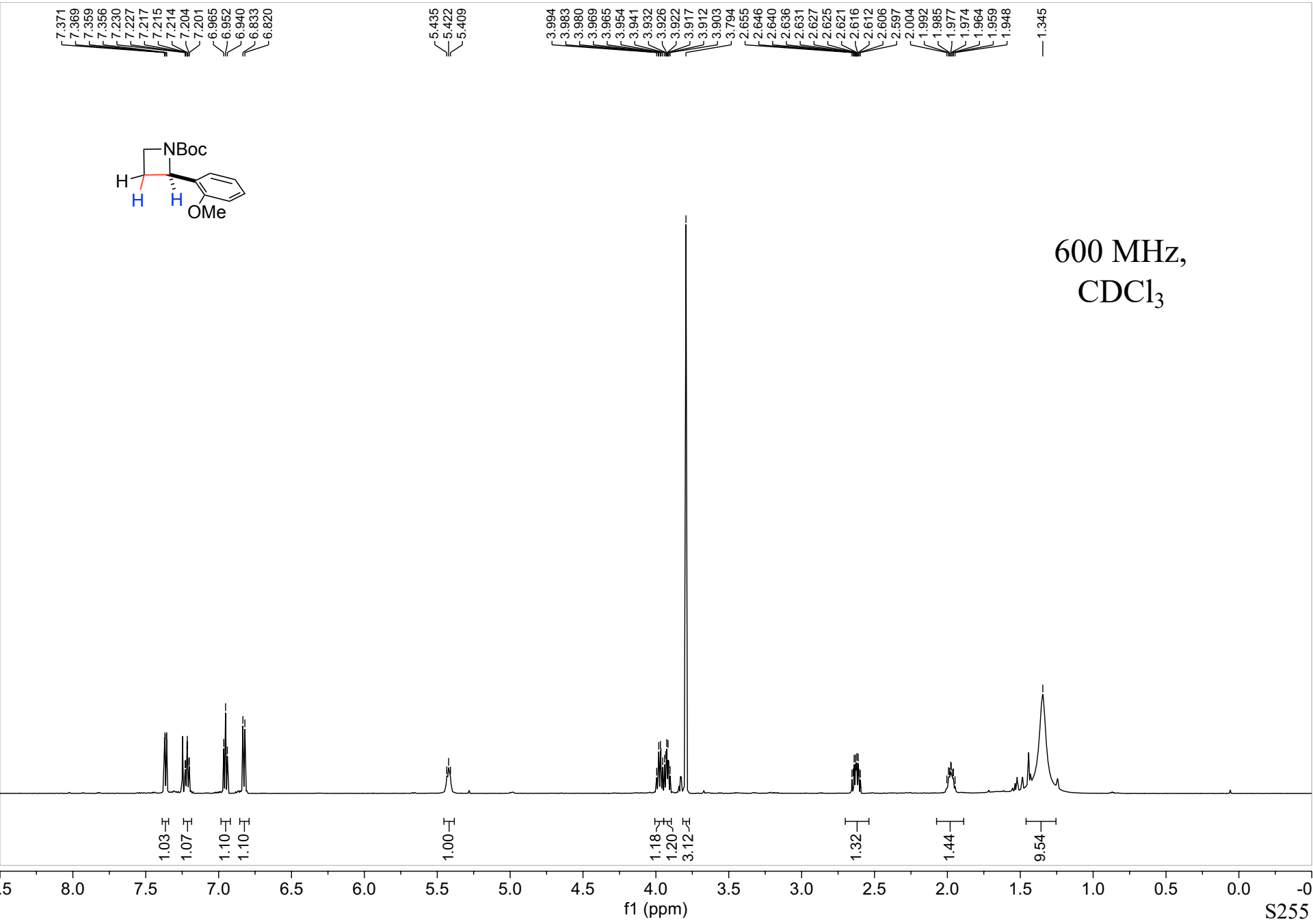




2: 220 nm, 4
nm Results

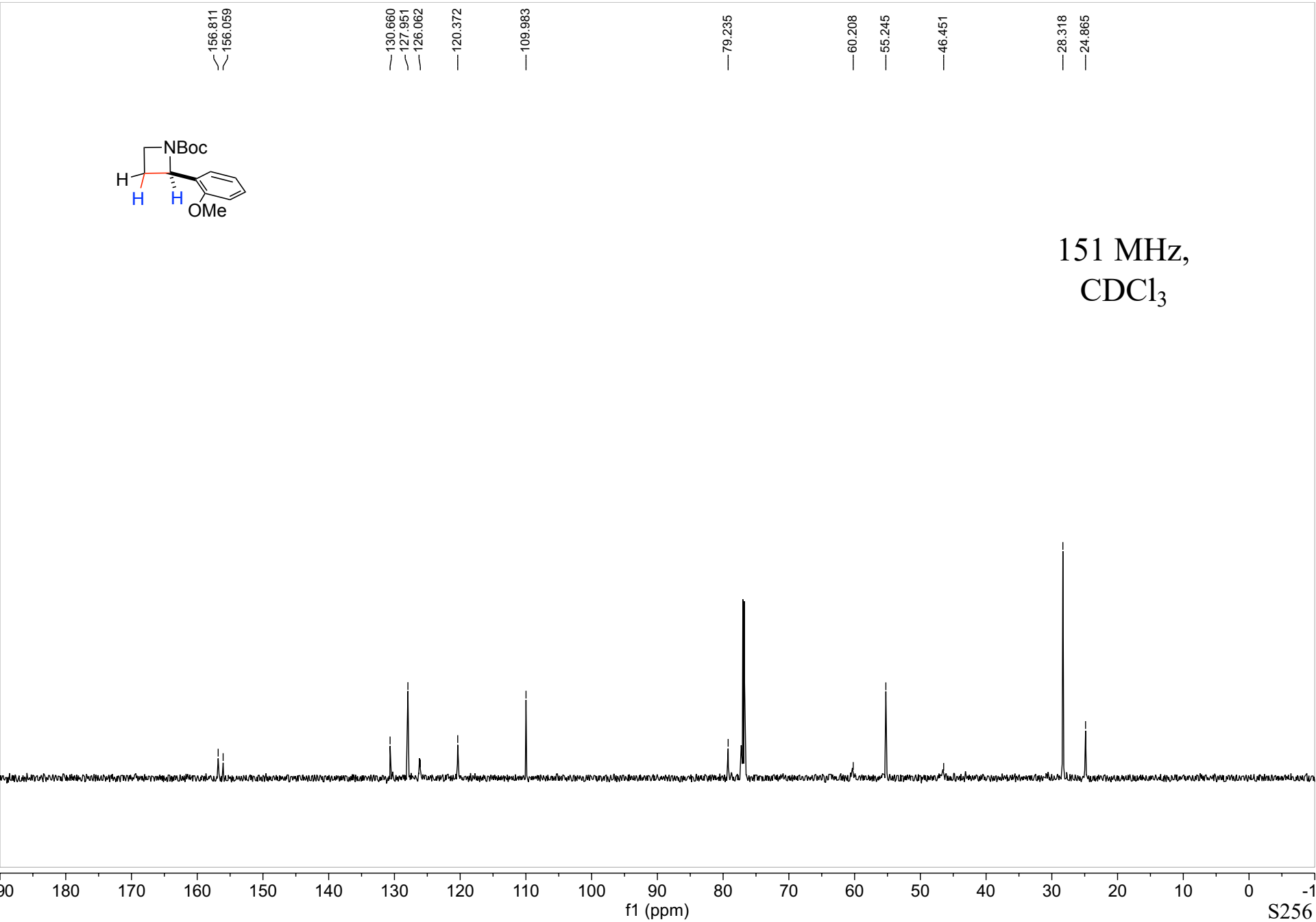
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 24.668 | 93.002 |
| 2 | 26.952 | 6.998 |

| Totals | |
|---|---|
| | 100.000 |

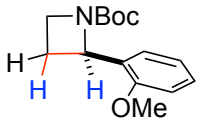
# $^1$H NMR *tert*-Butyl (*R*)-2-(2-methoxyphenyl)azetidine-1-carboxylate (**2d**)



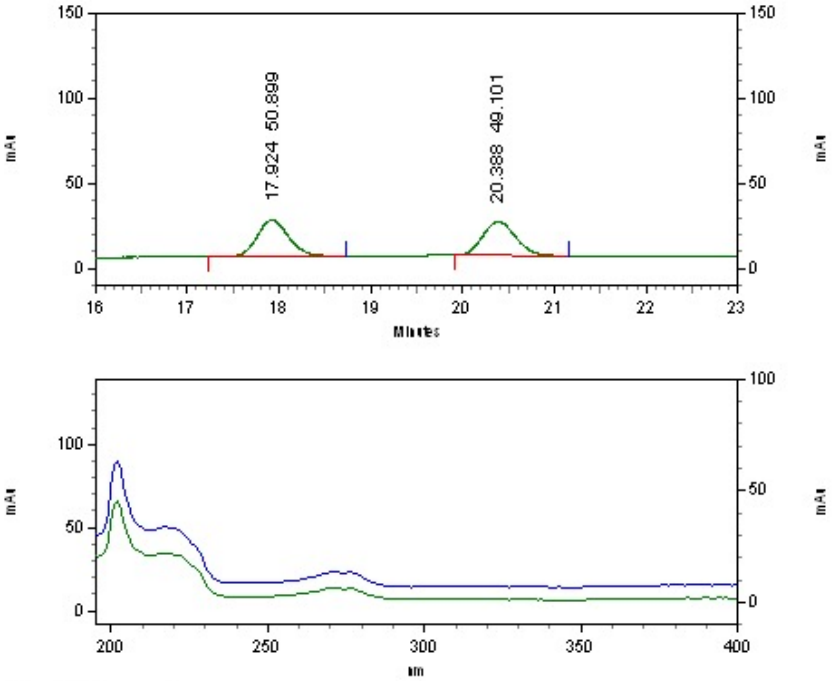
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(2-methoxyphenyl)azetidine-1-carboxylate (**2d**)



# **HPLC** *tert*-Butyl (*R*)-2-(2-methoxyphenyl)azetidine-1-carboxylate (**2d**)



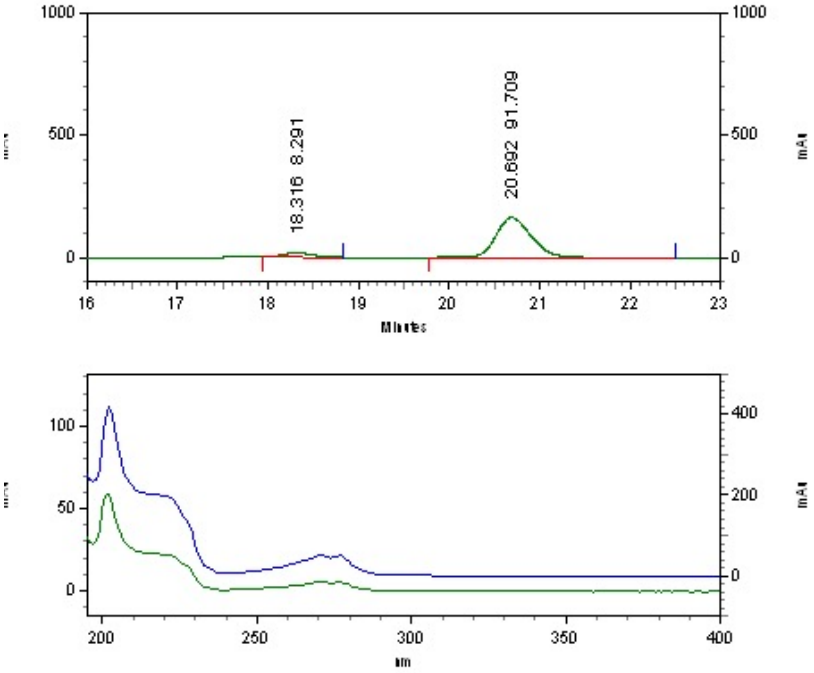

D:\Jingjing HPLC\JJX-2128P-IF-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 225 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 17.924 | 50.899 |
| 2 | 20.388 | 49.101 |
| Totals | | 100.000 |

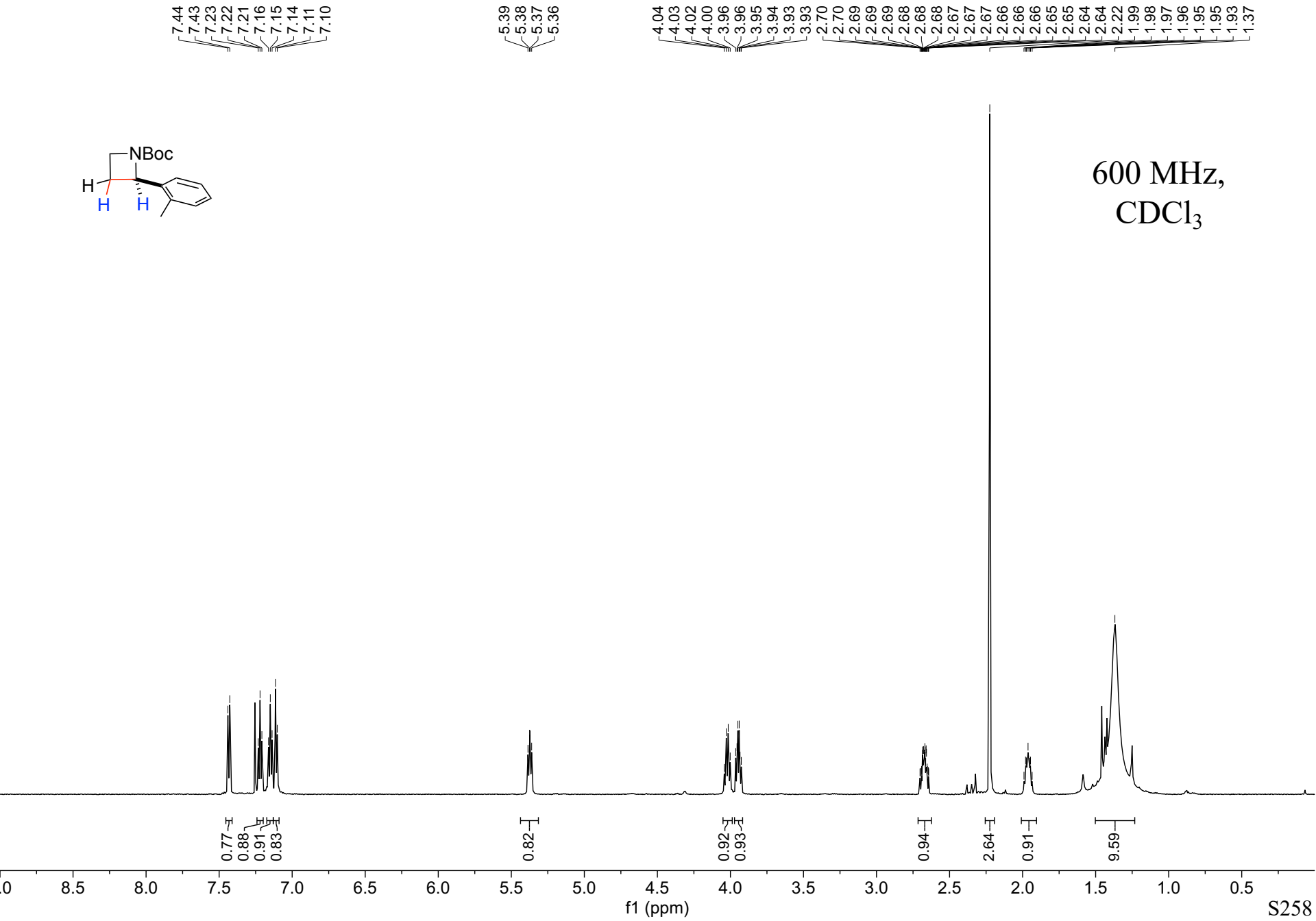
D:\Jingjing HPLC\JJX-2155P-IF-2%-0.8ML-C4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



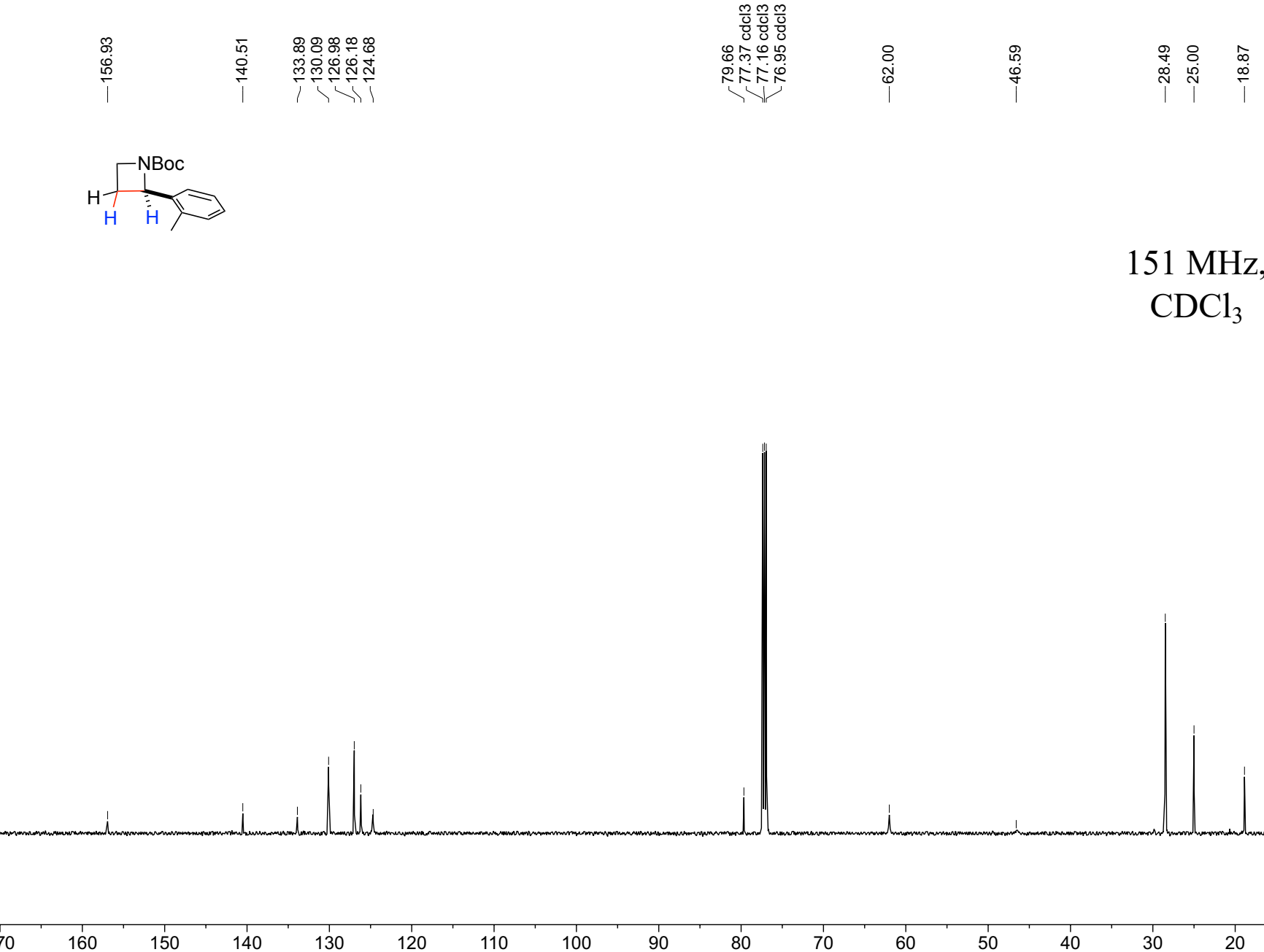

2: 225 nm, 4 nm Results

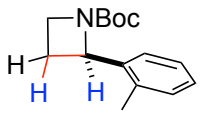
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 18.316 | 8.291 |
| 2 | 20.692 | 91.709 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-Butyl (*R*)-2-(*o*-tolyl)azetidine-1-carboxylate **(2e)**



# $^{13}$C NMR *tert*-Butyl (*R*)-2-(*o*-tolyl)azetidine-1-carboxylate **(2e)**

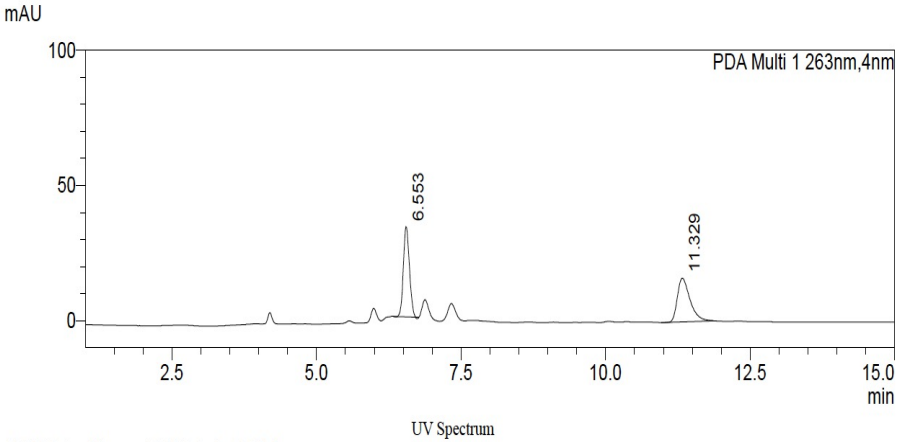





# **HPLC** *tert*-Butyl (*R*)-2-(*o*-tolyl)azetidine-1-carboxylate **(2e)**

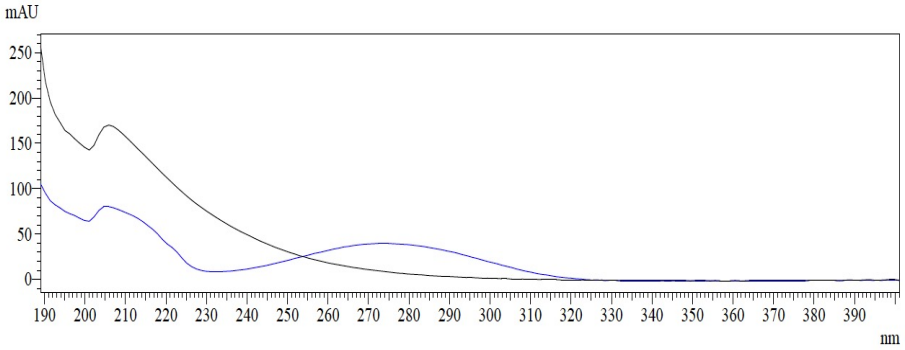
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-2MeAzetidine-rac-IF-2%0.8mL




UV Spectrum

JJX-2MeAzetidine-rac-IF-2%0.8mL_002.lcd



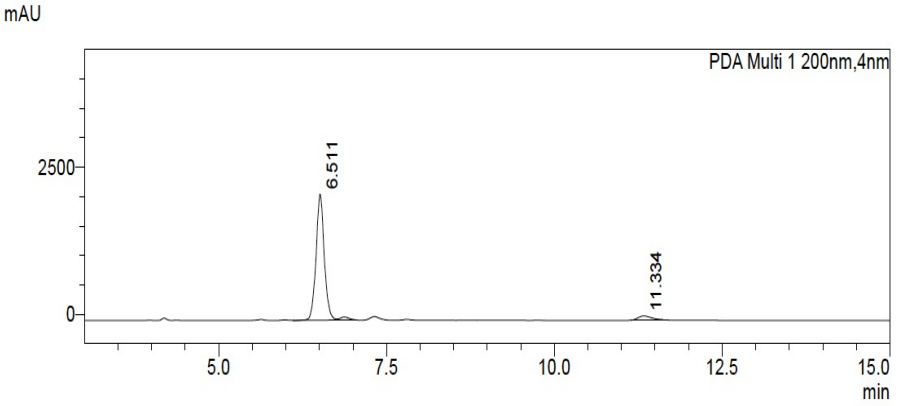

Peak Table

PDA Ch1 263nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.553 | 49.458 |
| 2 | 11.329 | 50.542 |
| Total | | 100.000 |

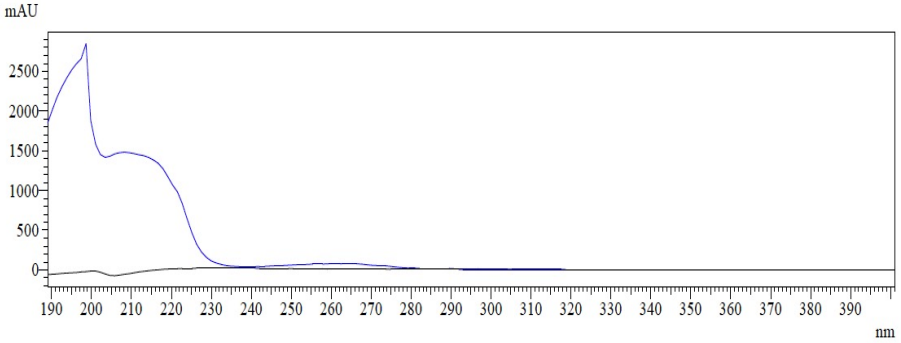
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-2MeAzetidine-chiral-IF-2%0.8mL




UV Spectrum

JJX-2MeAzetidine-chiral-IF-2%0.8mL_001.lcd

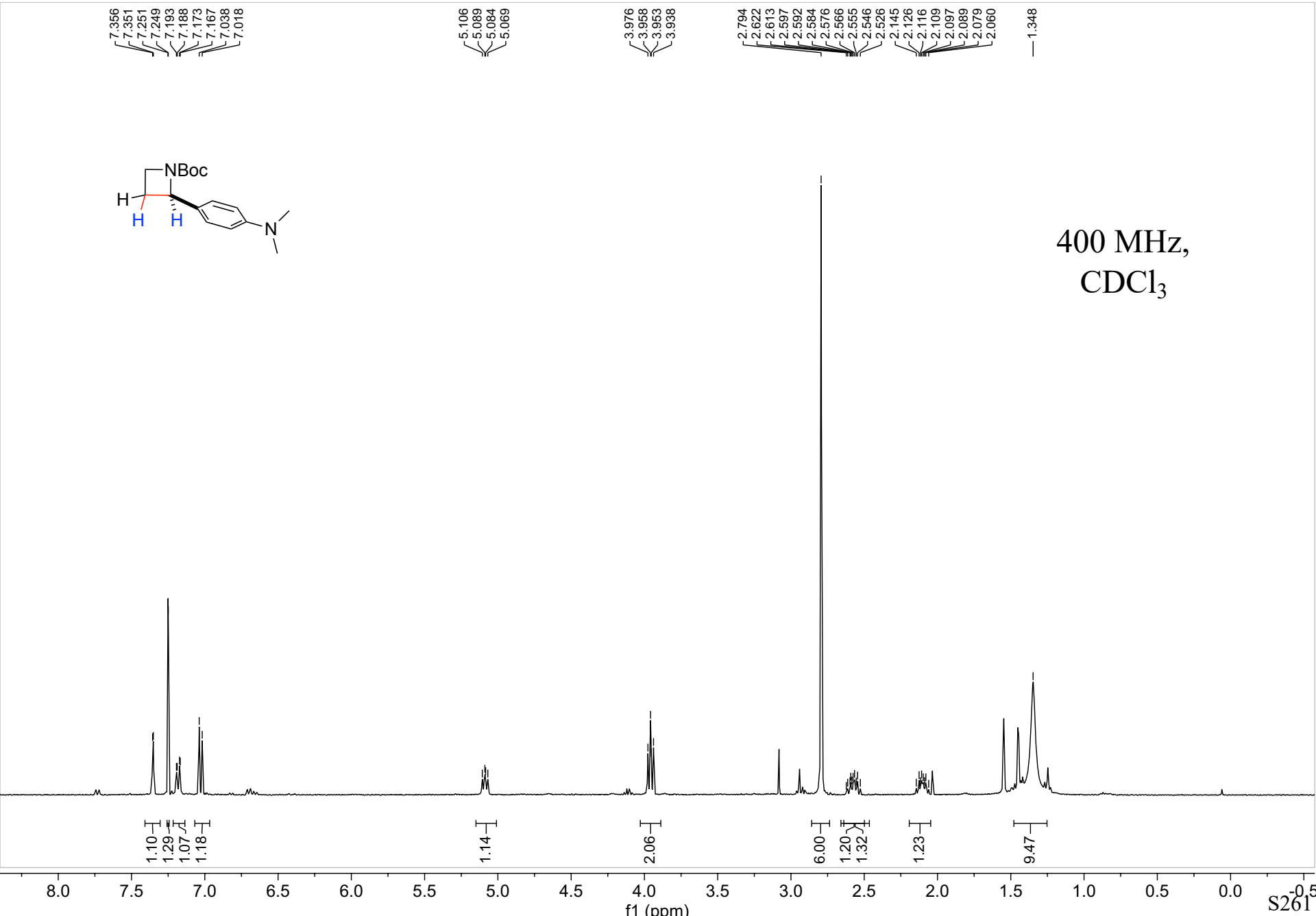



Peak Table

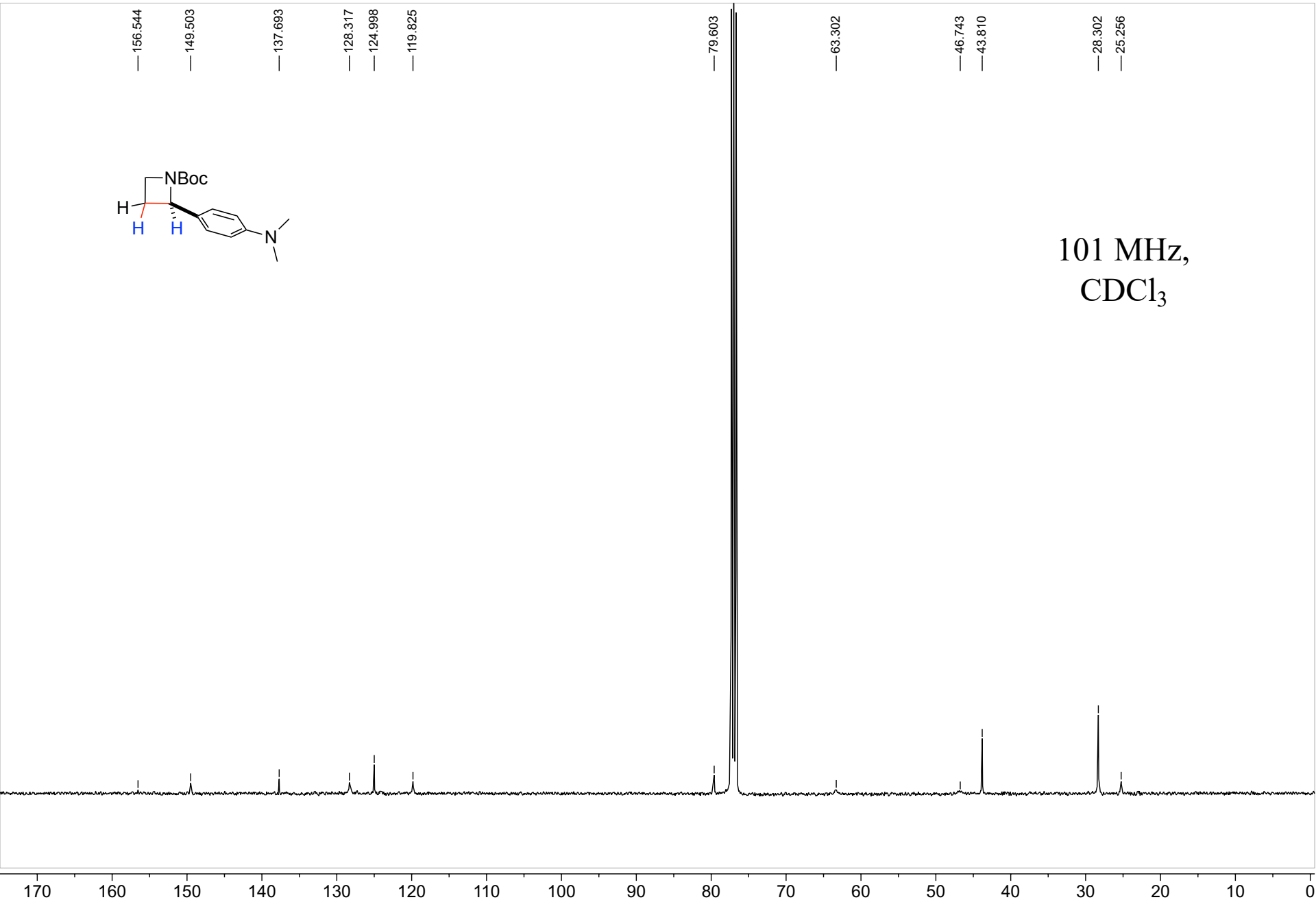
PDA Ch1 200nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.511 | 95.047 |
| 2 | 11.334 | 4.953 |
| Total | | 100.000 |

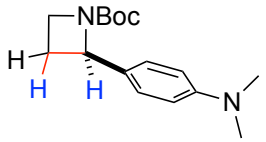
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(4-(dimethylamino)phenyl)azetidine-1-carboxylate (**2e**)



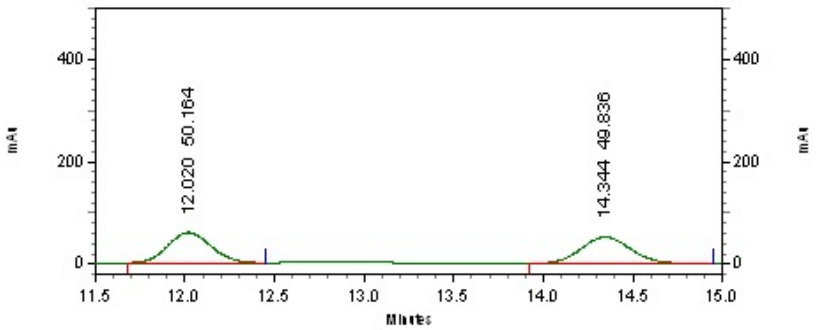
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-(dimethylamino)phenyl)azetidine-1-carboxylate (**2e**)

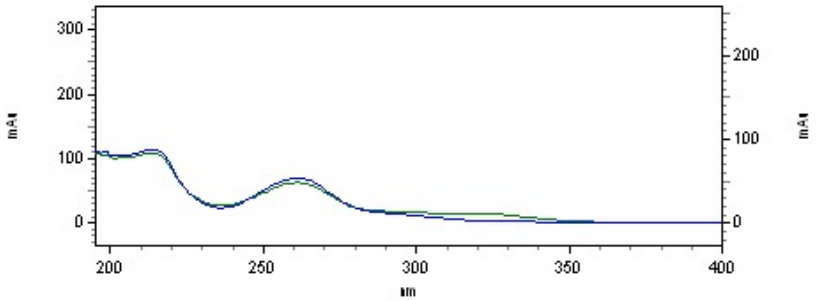


# **HPLC** *tert*-butyl (*R*)-2-(4-(dimethylamino)phenyl)azetidine-1-carboxylate (**2e**)




D:\Jingjing HPLC\JJX-2635-10%-IC-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



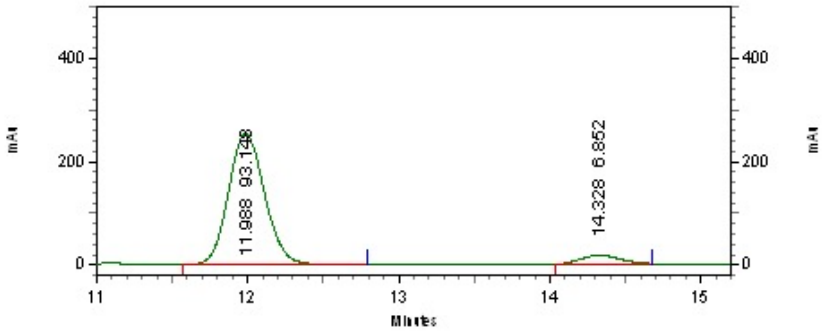



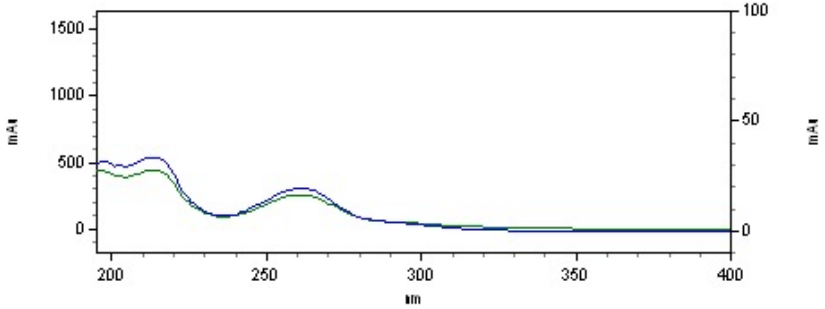

2: 261 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.020 | 50.164 |
| 2 | 14.344 | 49.836 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2636-10%-IC-0.8ml-C4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



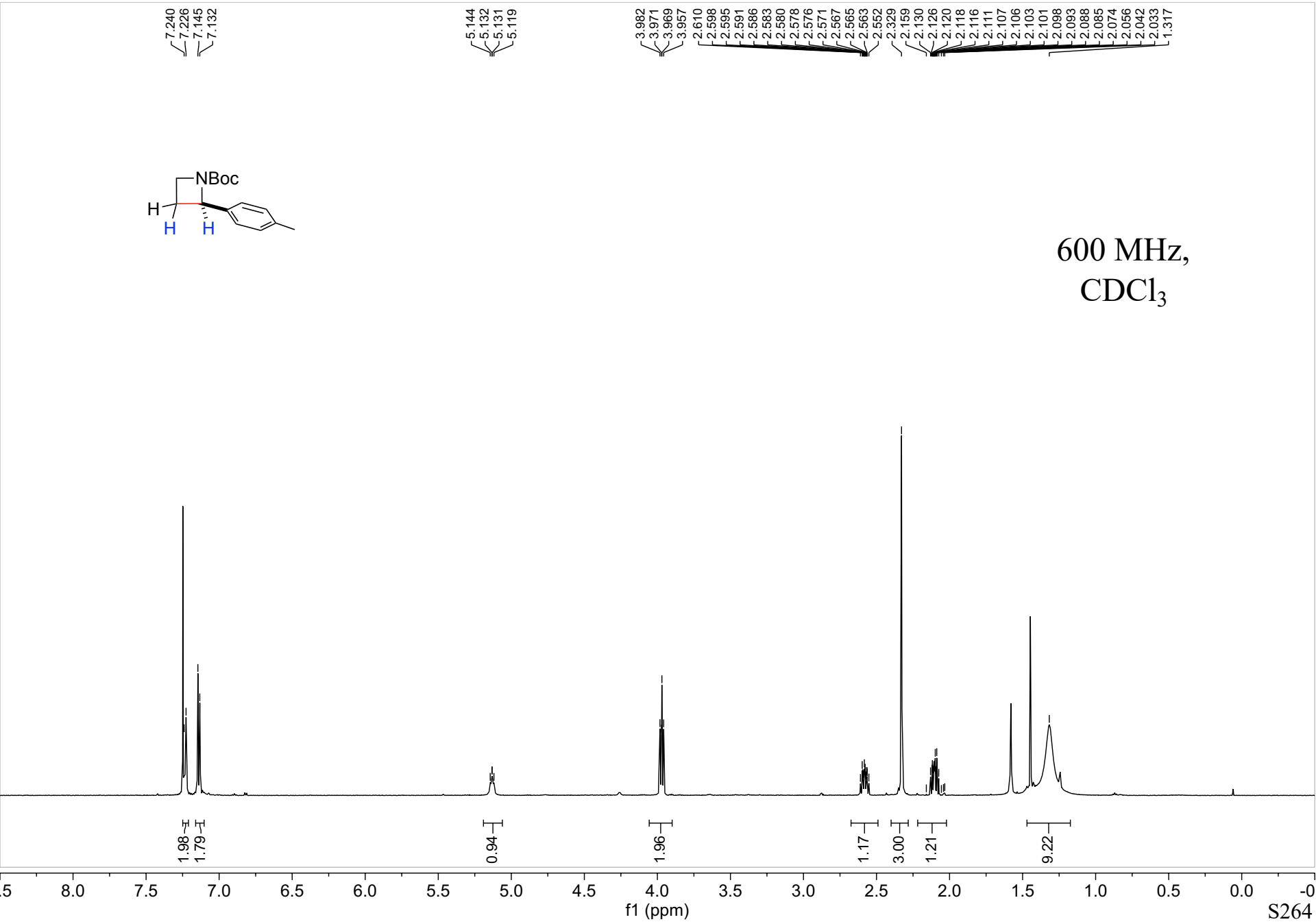




2: 261 nm, 4
nm Results

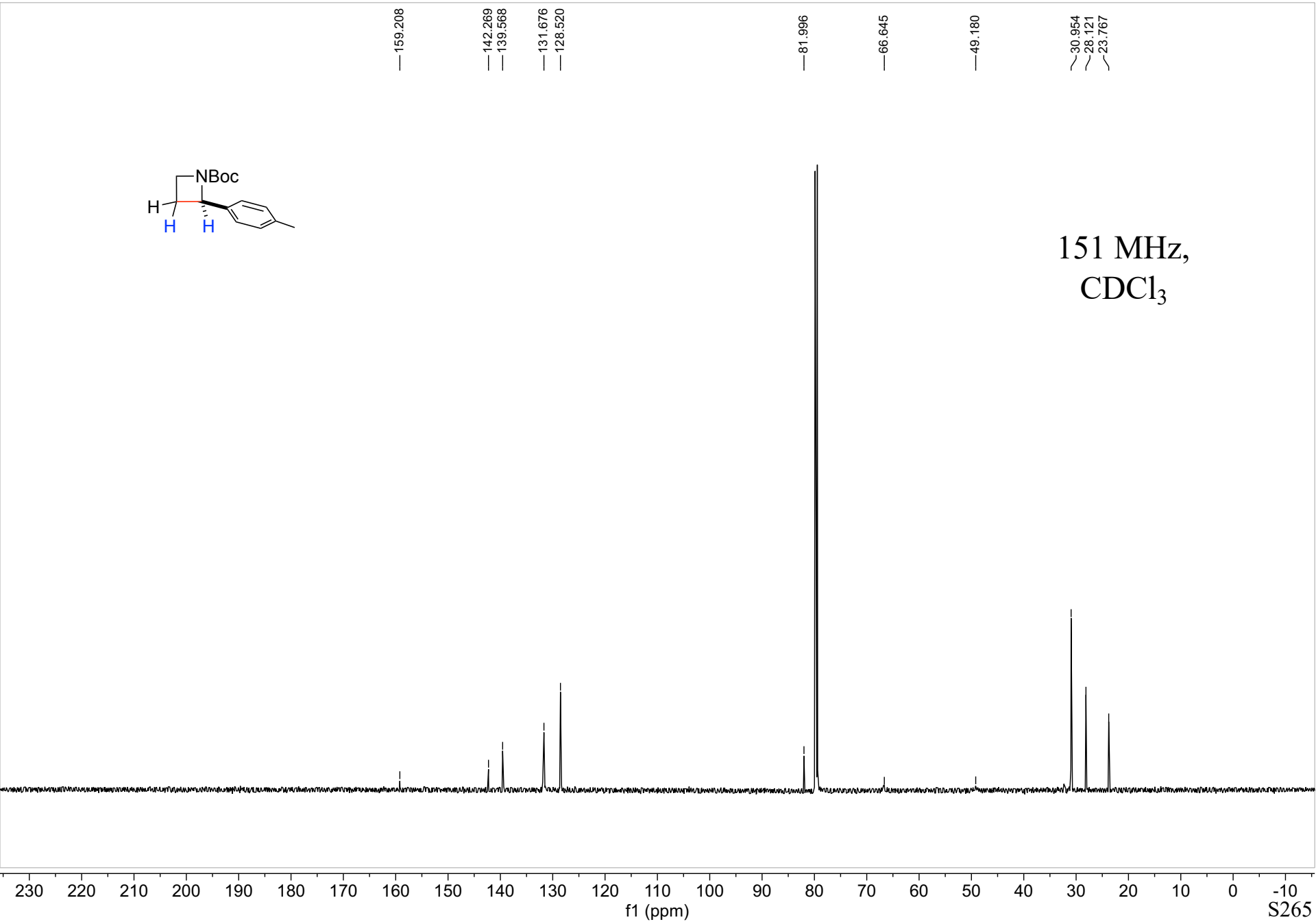
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.988 | 93.148 |
| 2 | 14.328 | 6.852 |

| Totals | |
|---|---|
| | 100.000 |

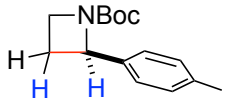
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(*p*-tolyl)azetidine-1-carboxylate (**2f**)



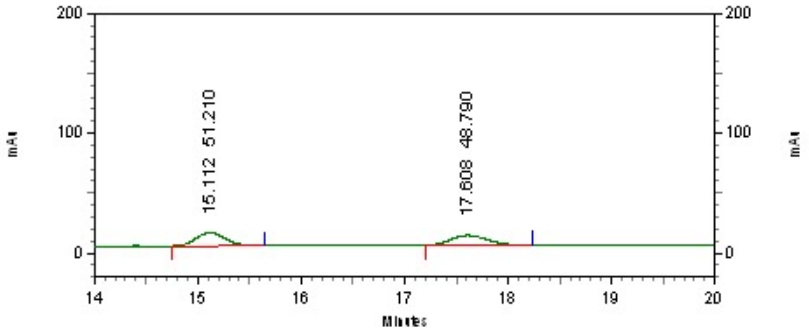
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(*p*-tolyl)azetidine-1-carboxylate (**2f**)

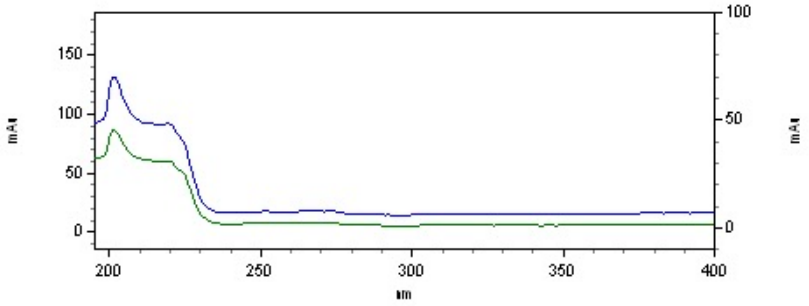


# **HPLC** *tert*-Butyl (*R*)-2-(*p*-tolyl)azetidine-1-carboxylate (**2f**)




D:\Jingjing HPLC\JJX-2142P-IF-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



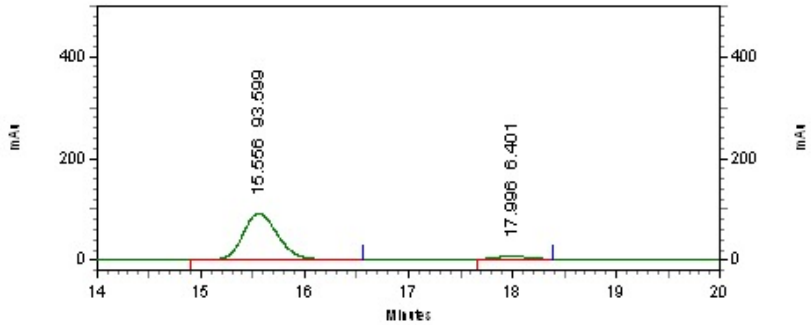



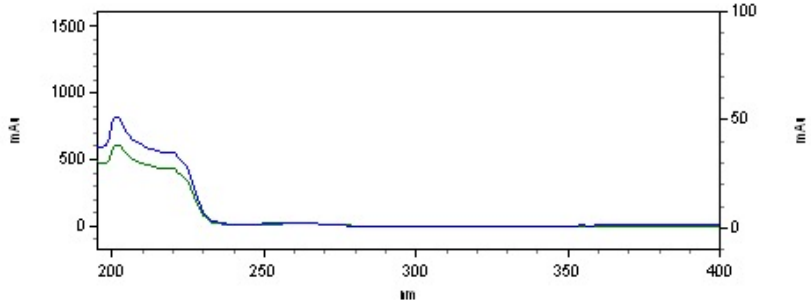

2: 230 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.112 | 51.210 |
| 2 | 17.608 | 48.790 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2156P-IF-2%-0.8ML-C4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



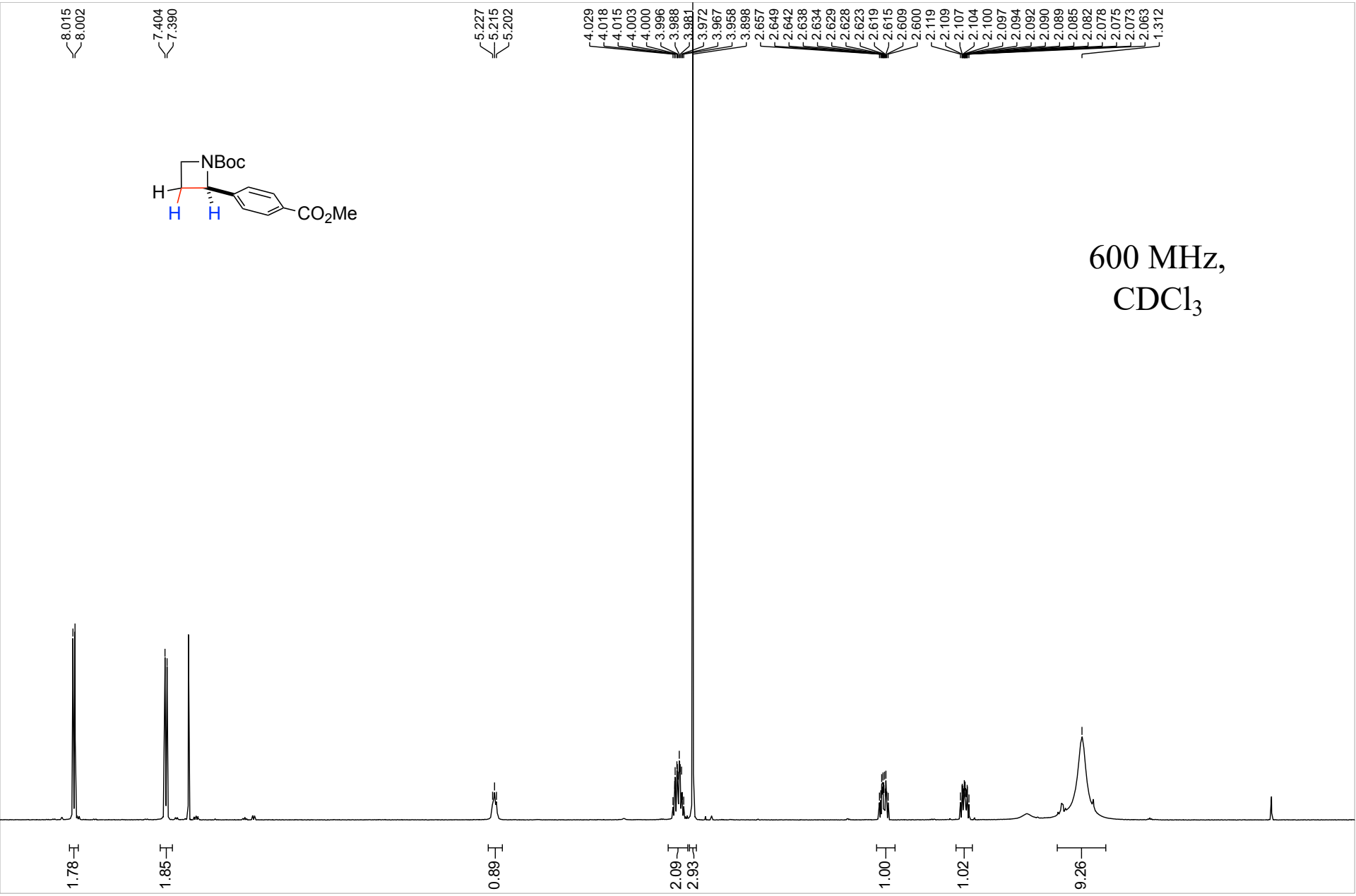




2: 230 nm, 4
nm Results

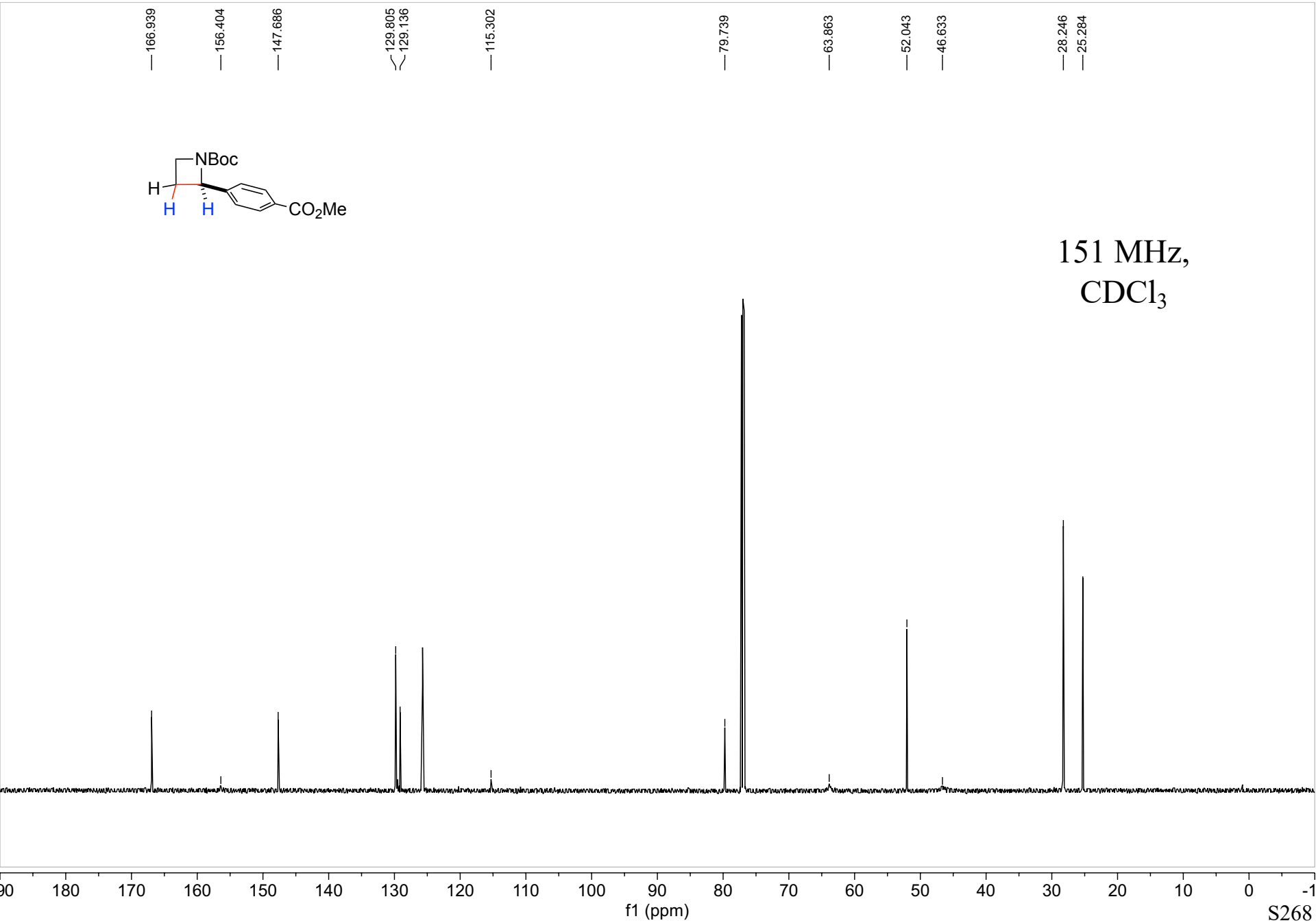
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.556 | 93.599 |
| 2 | 17.996 | 6.401 |

| Totals | |
|---|---|
| | 100.000 |

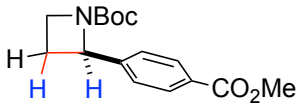
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(4-(methoxycarbonyl)phenyl)azetidine-1-carboxylate (**2g**)



# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-(methoxycarbonyl)phenyl)azetidine-1-carboxylate (**2g**)



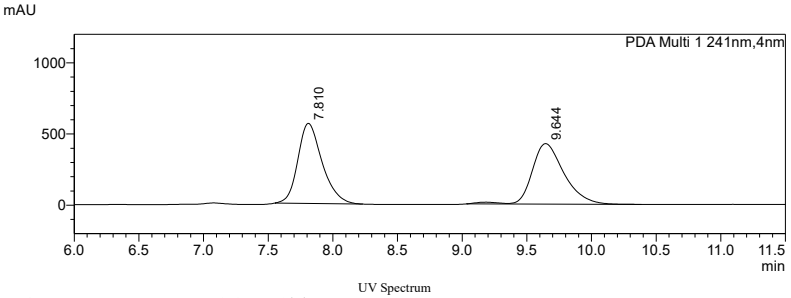
# **HPLC** *tert*-Butyl (*R*)-2-(4-(methoxycarbonyl)phenyl)azetidine-1-carboxylate (**2g**)





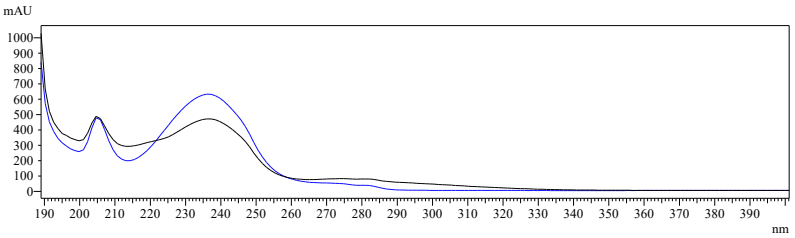

## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-4COOMe-rac-AZETIDINE-ODH-2%0.8mL




UV Spectrum

JJX-4COOMe-rac-AZETIDINE-ODH-2%0.8mL_001.lcd




Peak Table

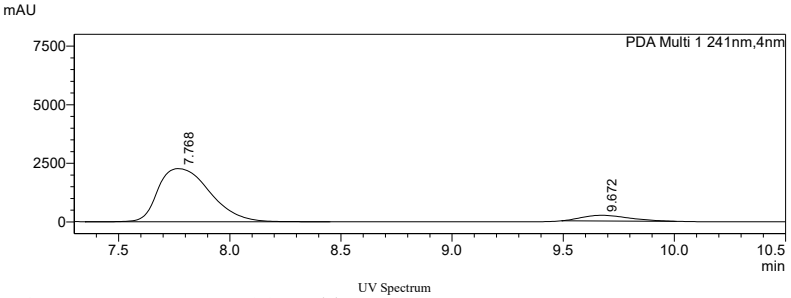
PDA Ch1 241nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 7.810 | 50.108 |
| 2 | 9.644 | 49.892 |
| Total | | 100.000 |



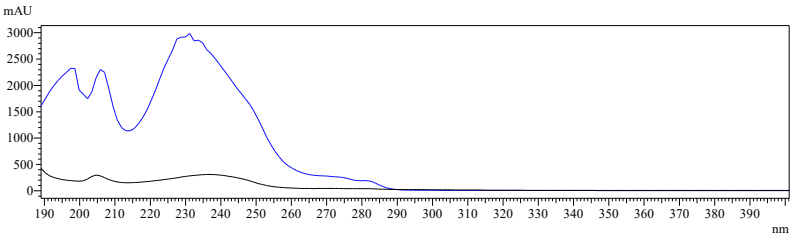
## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-4COOMe-AZETIDINE-CHIRAL-ODH-2%0.8mL




UV Spectrum

JJX-4COOMe-AZETIDINE-CHIRAL-ODH-2%0.8mL_001.lcd

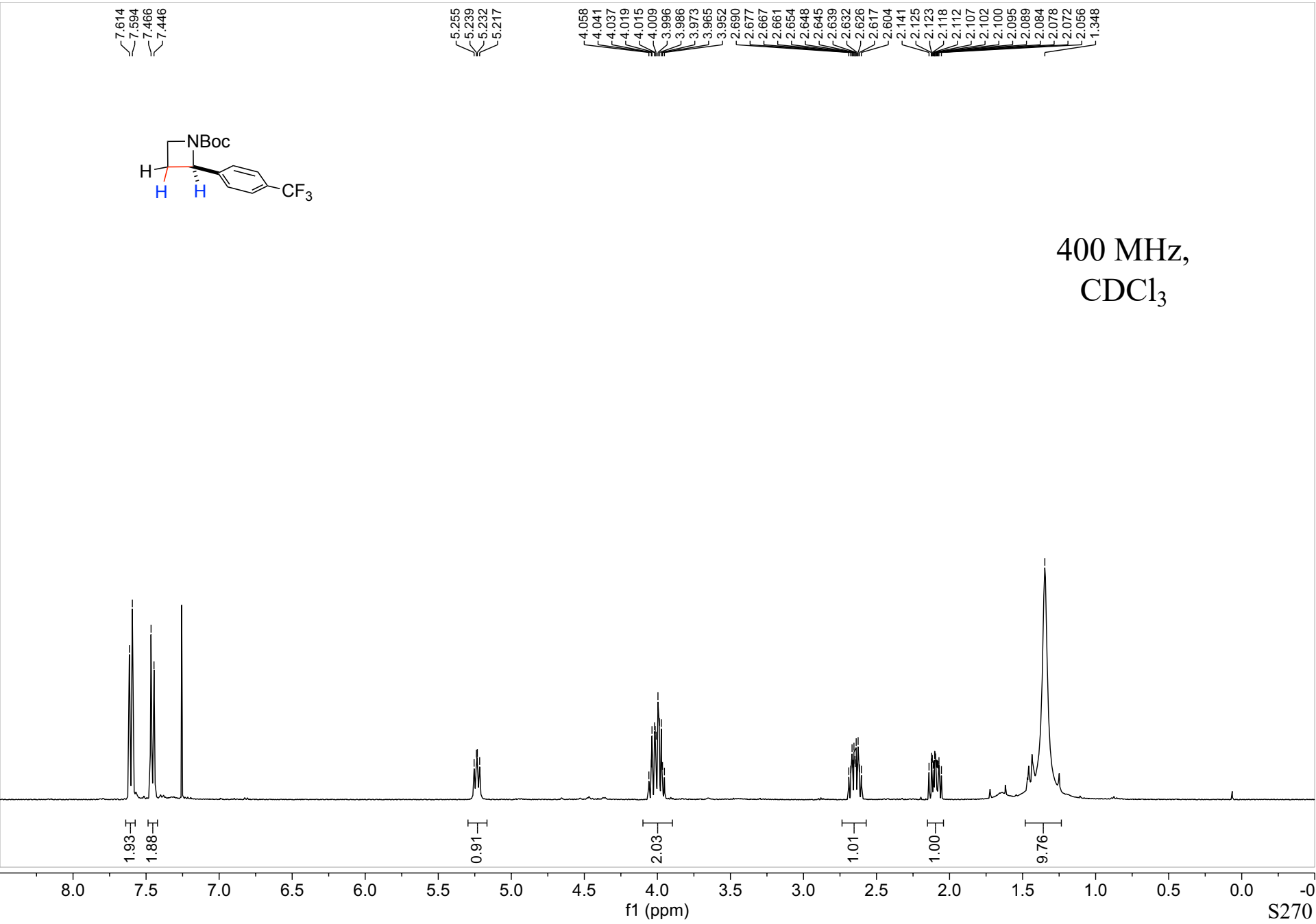



Peak Table

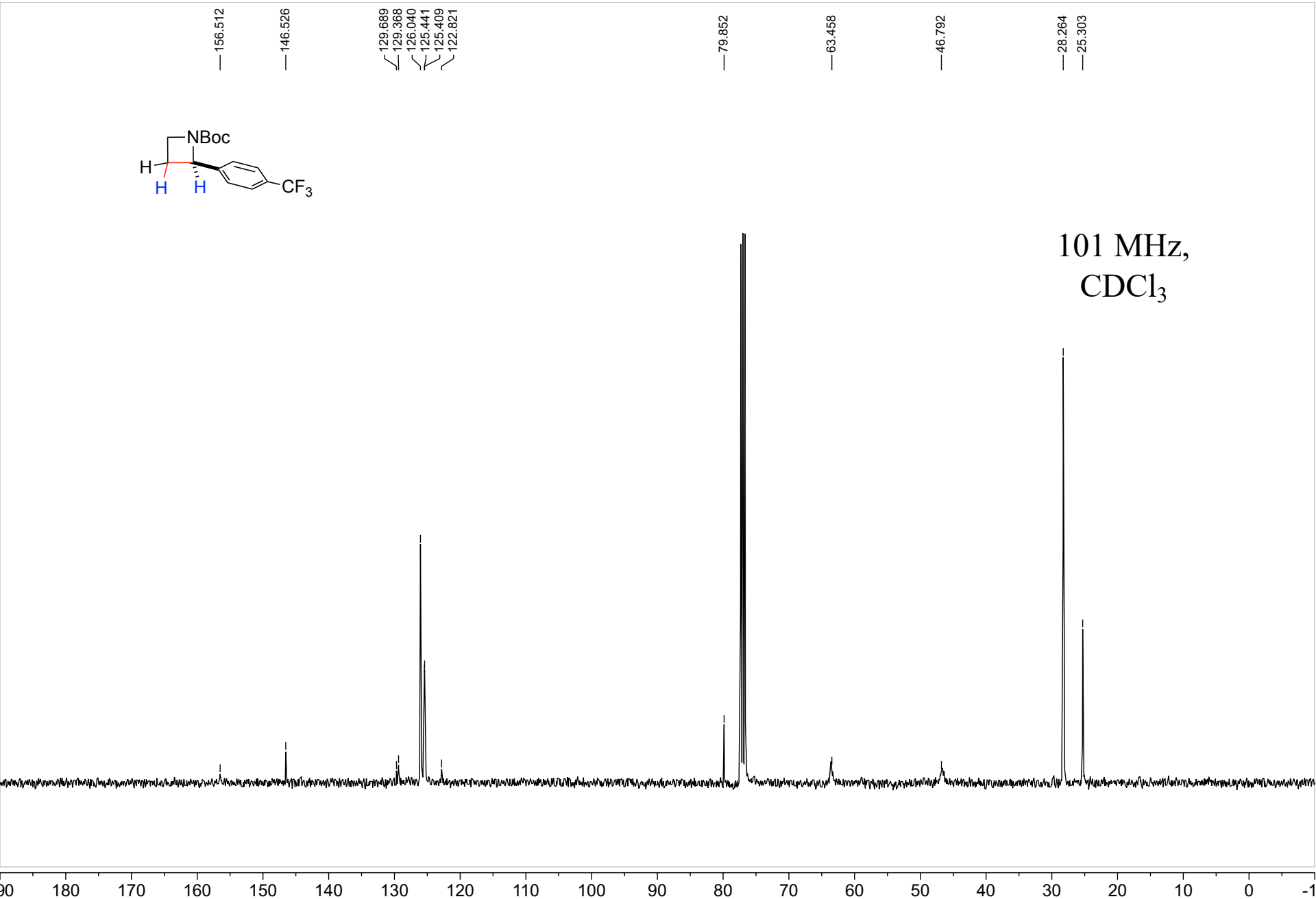
PDA Ch1 241nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 7.768 | 91.182 |
| 2 | 9.672 | 8.818 |
| Total | | 100.000 |

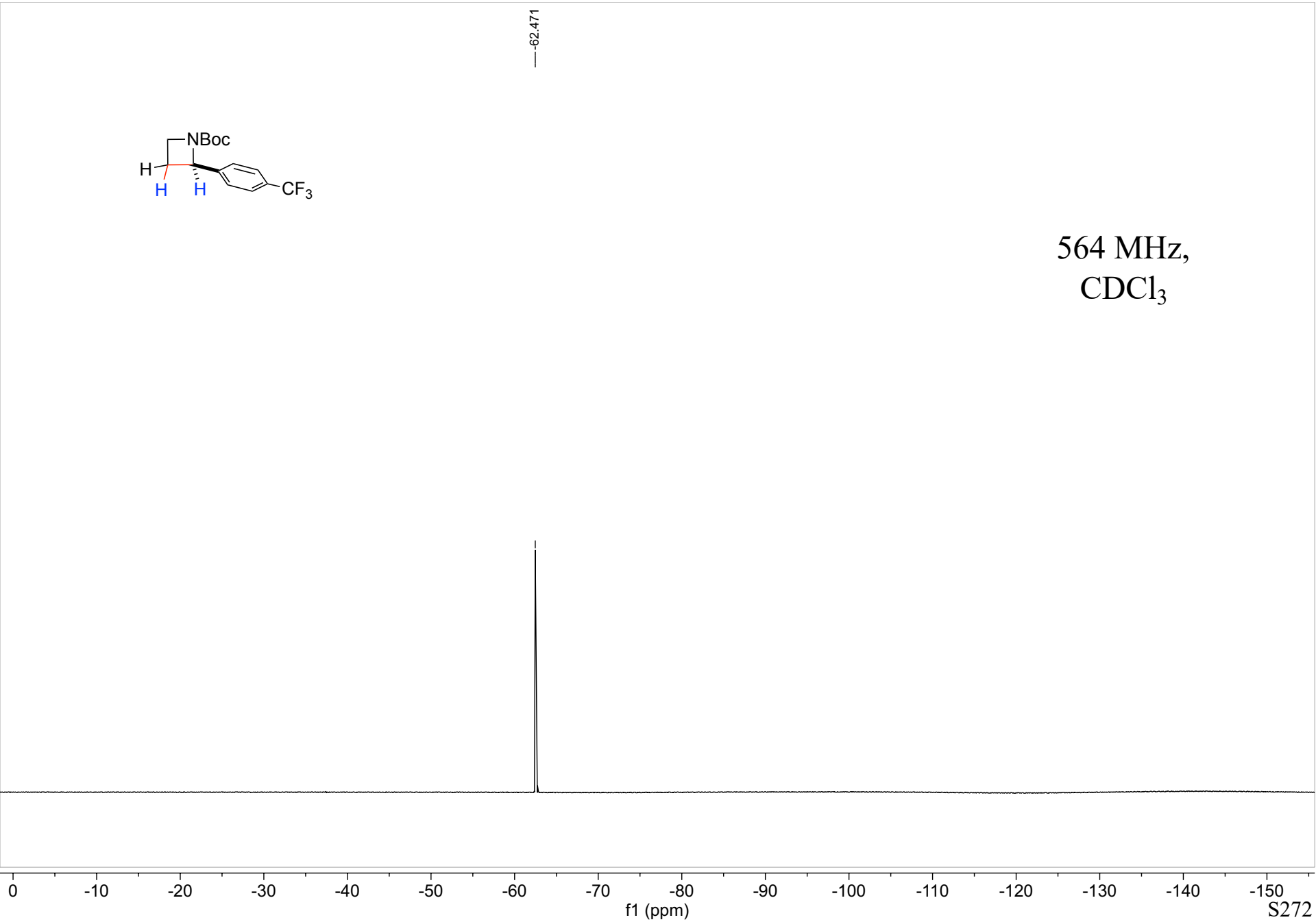
# $^1$H NMR *tert*-Butyl (*R*)-2-(4-(trifluoromethyl)phenyl)azetidine-1-carboxylate (**2h**)



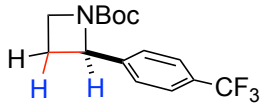
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-(trifluoromethyl)phenyl)azetidine-1-carboxylate (**2h**)



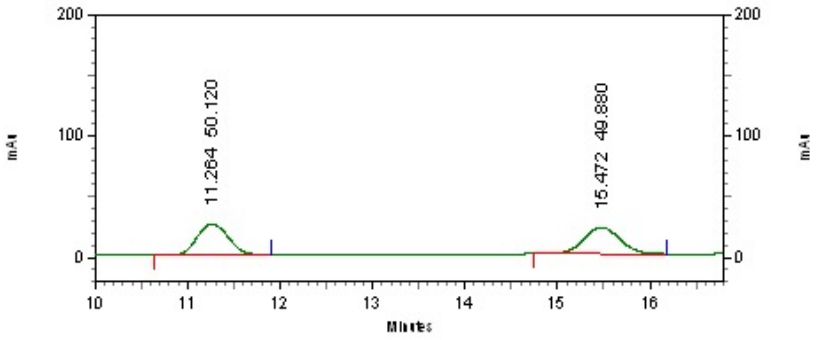
# $^{19}$F NMR *tert*-Butyl (*R*)-2-(4-(trifluoromethyl)phenyl)azetidine-1-carboxylate (**2h**)

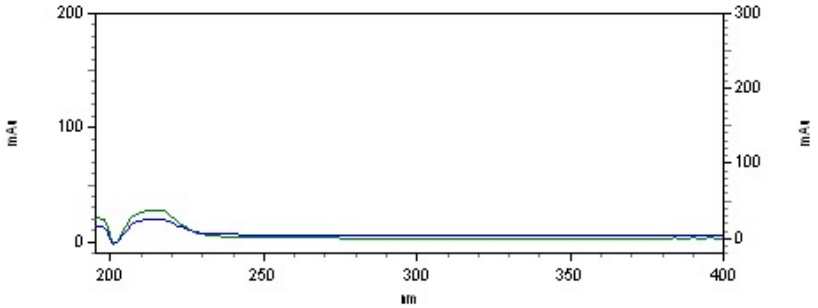


# **HPLC** *tert*-Butyl (*R*)-2-(4-(trifluoromethyl)phenyl)azetidine-1-carboxylate (**2h**)




D:\Jingjing HPLC\JJX-2021P-IF-2%-0.8ml-Ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



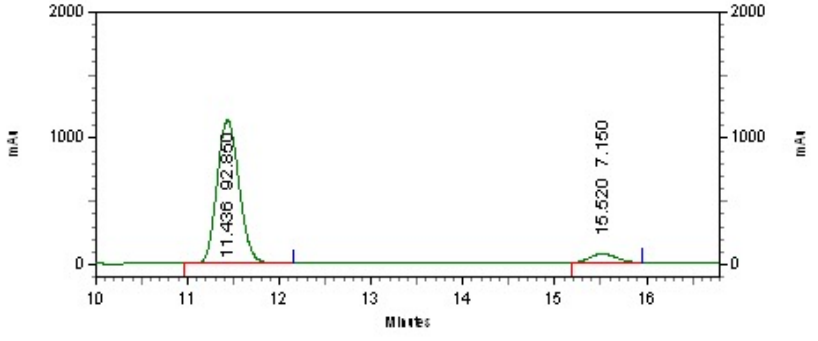



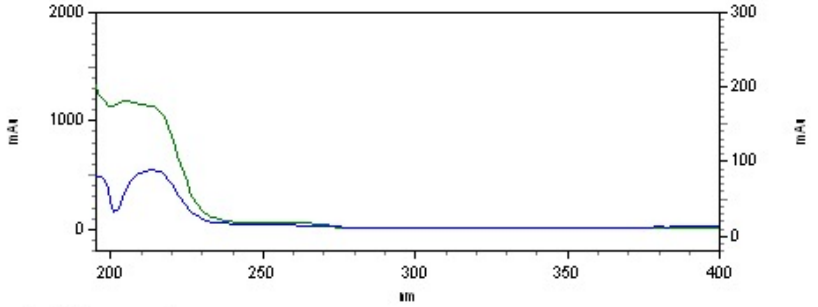

2: 212 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.264 | 50.120 |
| 2 | 15.472 | 49.880 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2022P-IF-2%-0.8ml-c4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



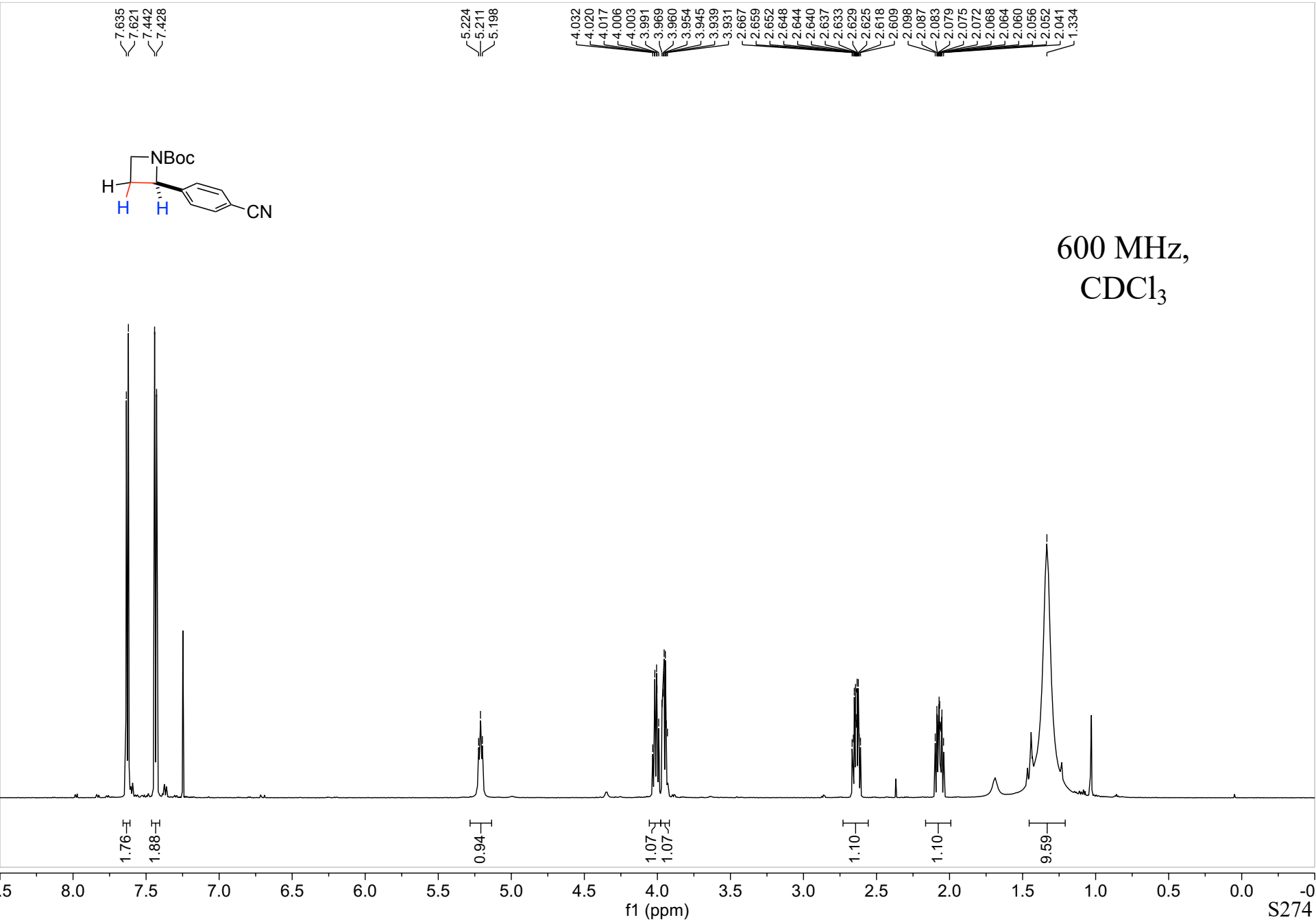




2: 212 nm, 4
nm Results

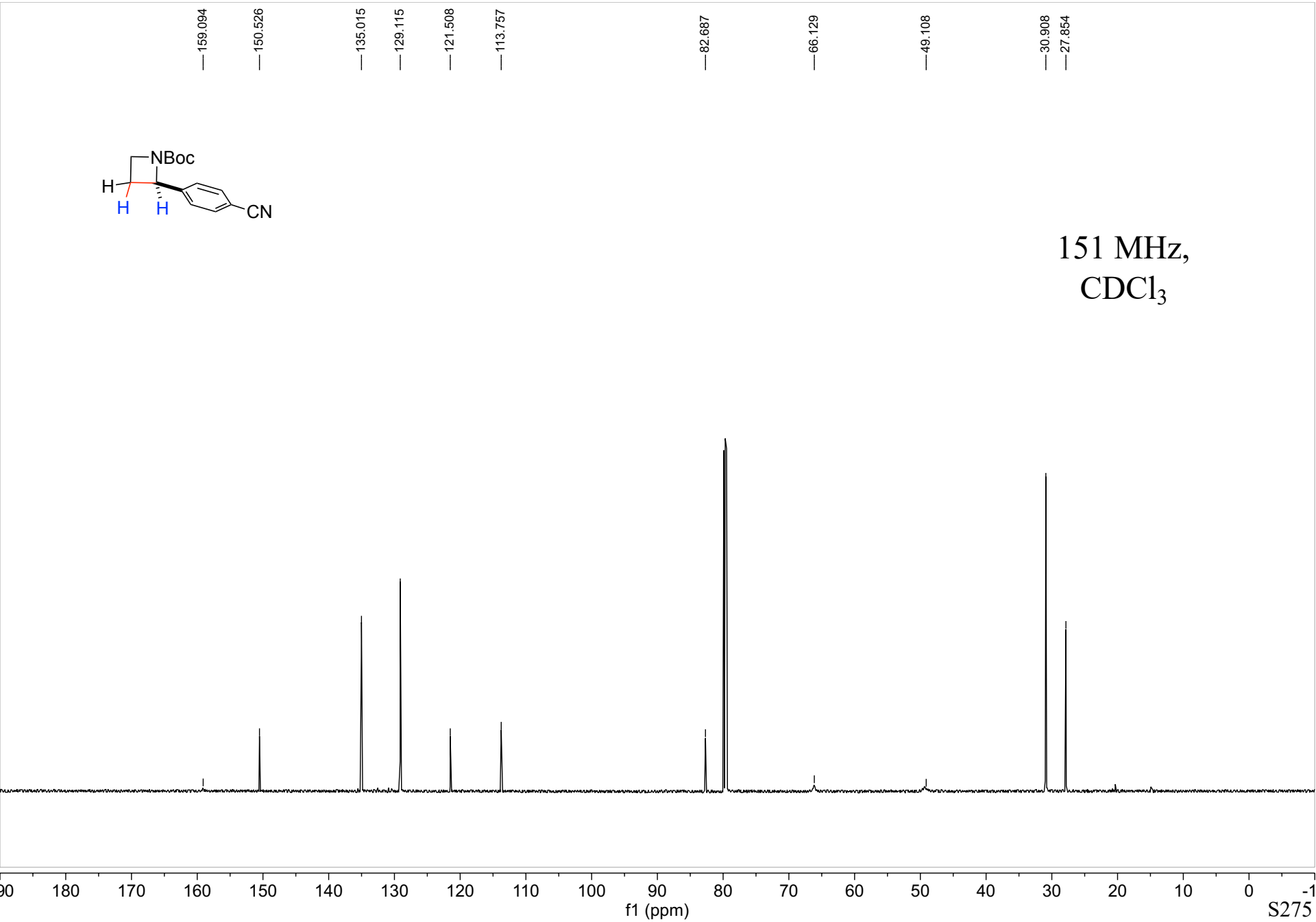
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.436 | 92.850 |
| 2 | 15.520 | 7.150 |

| Totals | |
|---|---|
| | 100.000 |

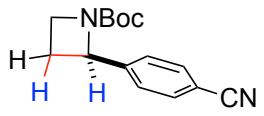
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(4-cyanophenyl)azetidine-1-carboxylate (**2i**)



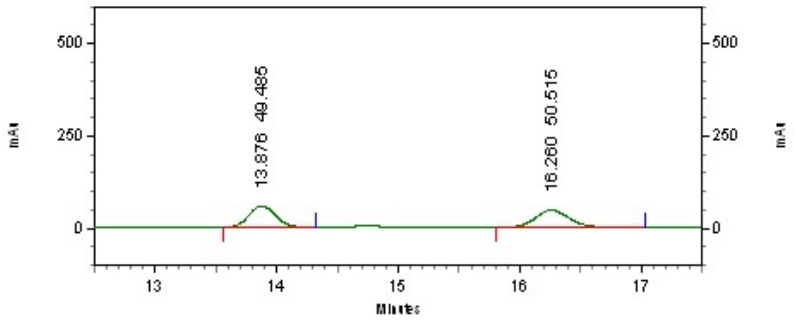
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-cyanophenyl)azetidine-1-carboxylate (**2i**)

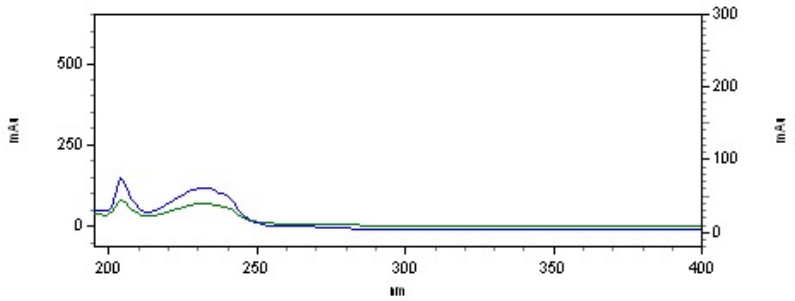


# **HP:LC** *tert*-Butyl (*R*)-2-(4-cyanophenyl)azetidine-1-carboxylate (**2i**)




D:\Jingjing HPLC\JJX-1994P-ID-10%-0.8ml-Ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

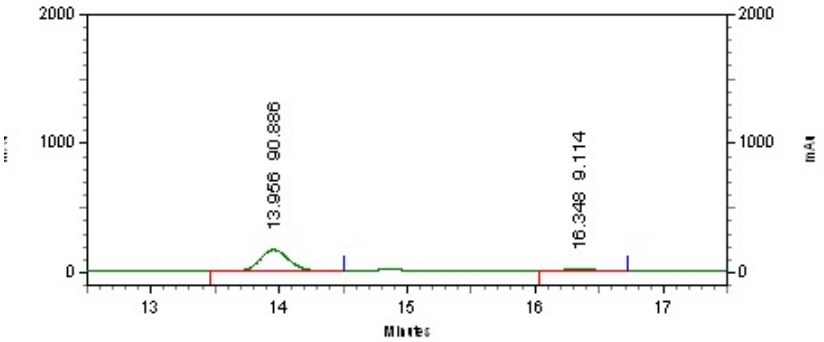


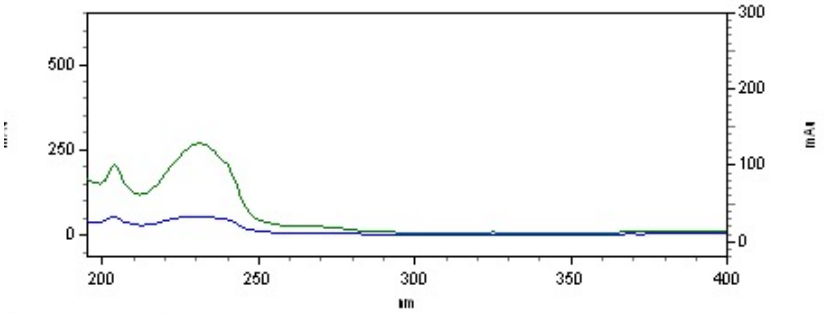




2: 220 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.876 | 49.485 |
| 2 | 16.260 | 50.515 |
| Totals | | 100.000 |

D:\Jingjing HPLC\JJX-1995P-ID-10%-0.8ml-c4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

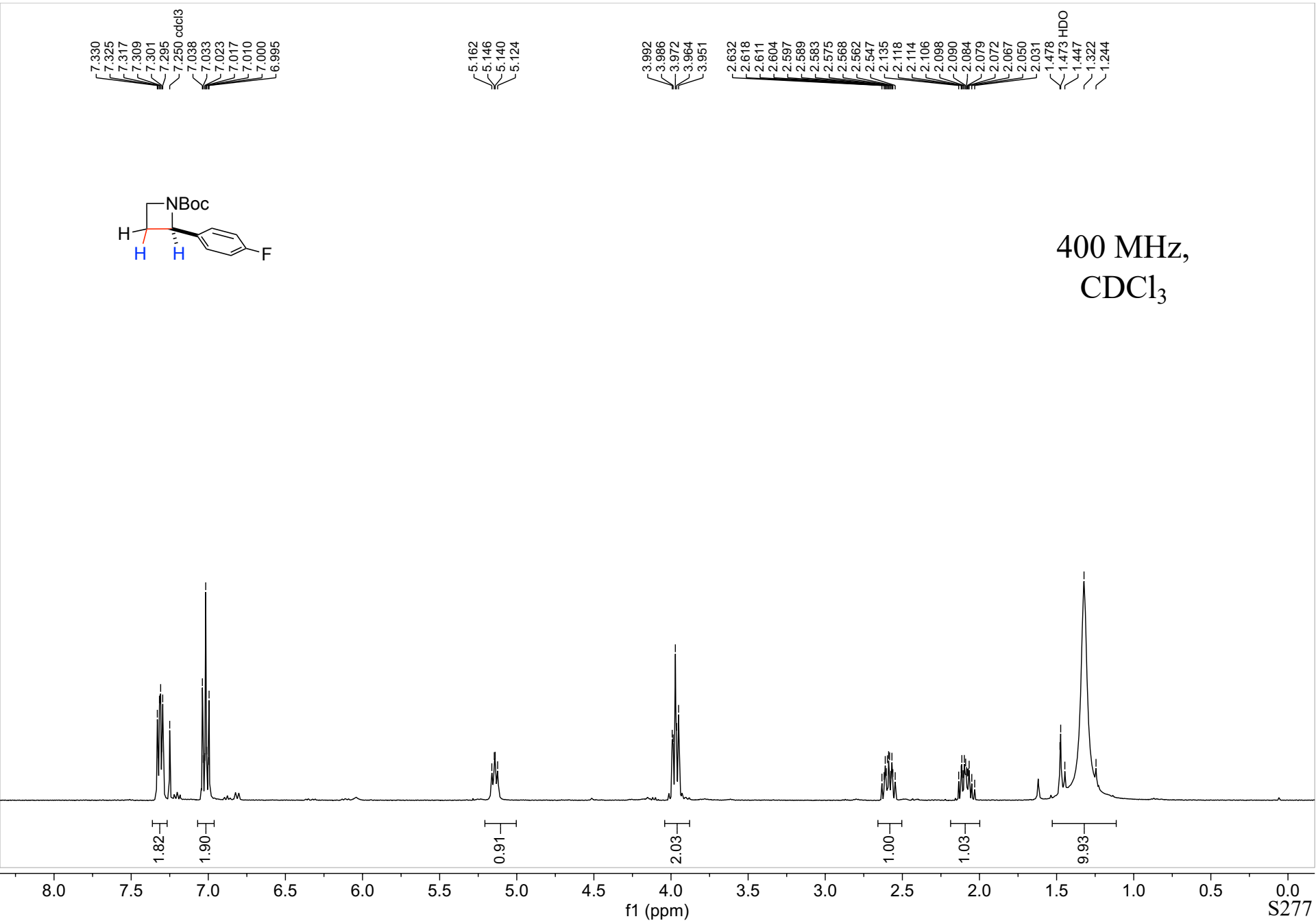


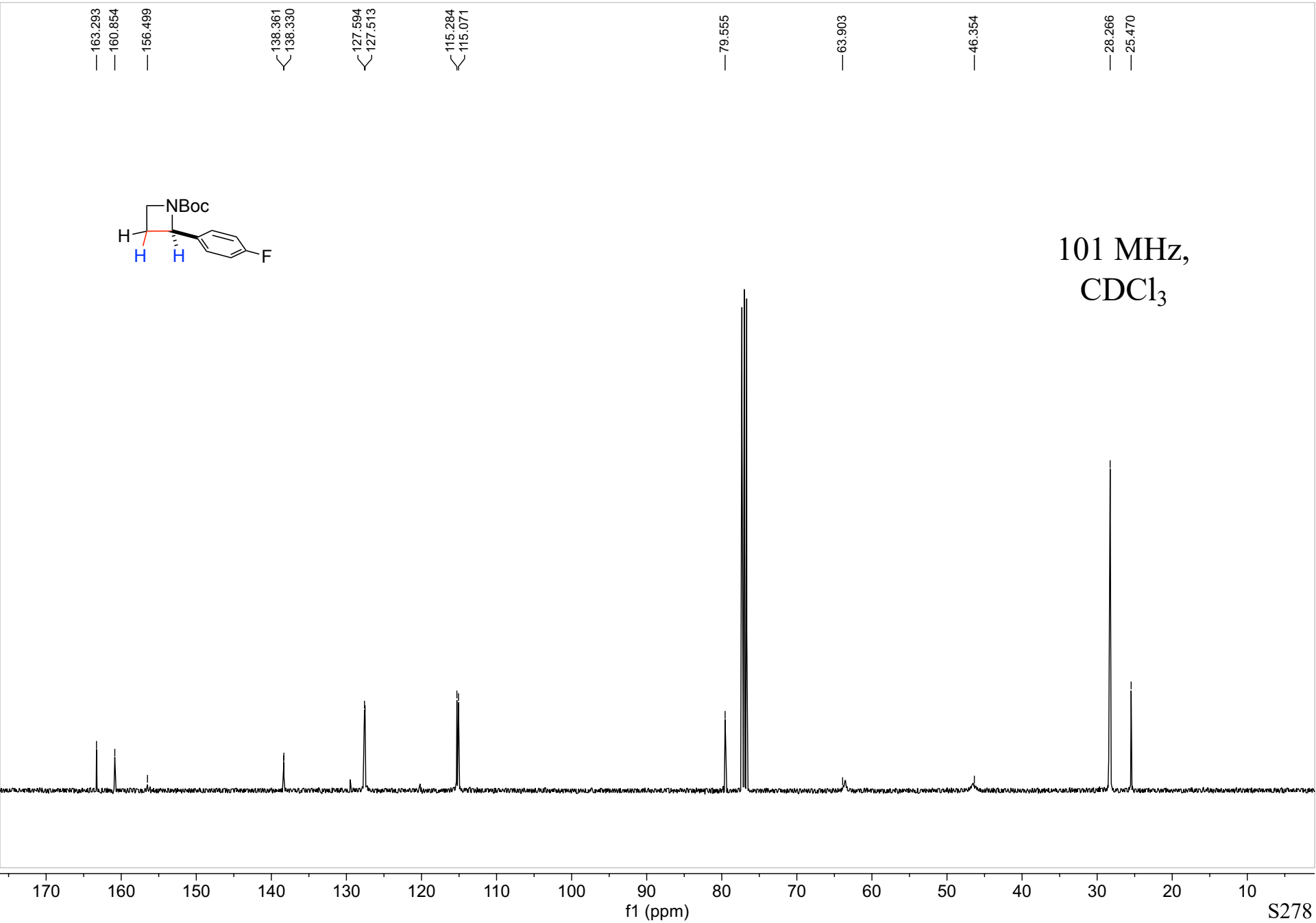

2: 220 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.956 | 90.886 |
| 2 | 16.348 | 9.114 |
| Totals | | 100.000 |

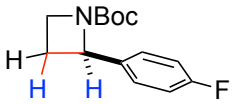
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(4-fluorophenyl)azetidine-1-carboxylate (**2j**)



# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-fluorophenyl)azetidine-1-carboxylate (**2j**)

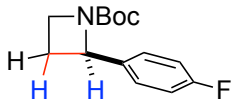


# $^{19}$F NMR *tert*-Butyl (*R*)-2-(4-fluorophenyl)azetidine-1-carboxylate (**2j**)



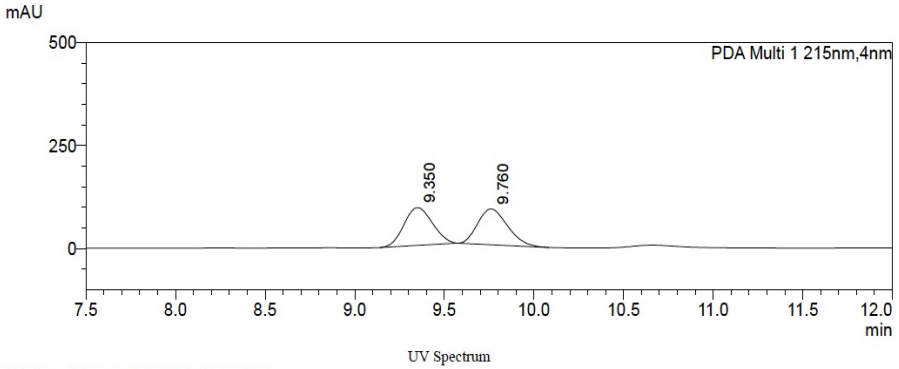

376 MHz,
$CDCl_3$

# **HPLC** *tert*-Butyl (*R*)-2-(4-fluorophenyl)azetidine-1-carboxylate (**2j**)



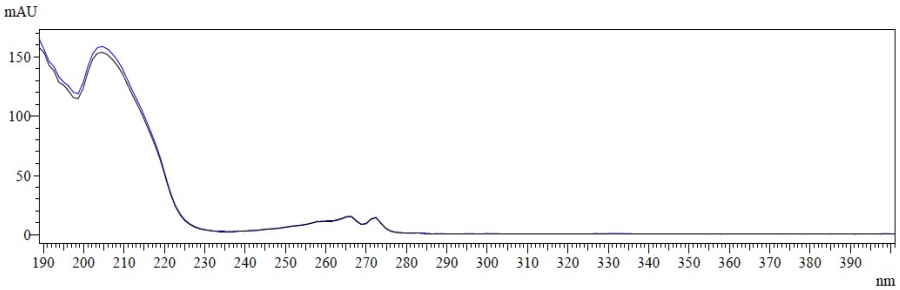

**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-4F-azetidine-rac-IB-2%0.8mL




UV Spectrum

JJX-4F-azetidine-rac-IB-2%0.8mL_001.lcd



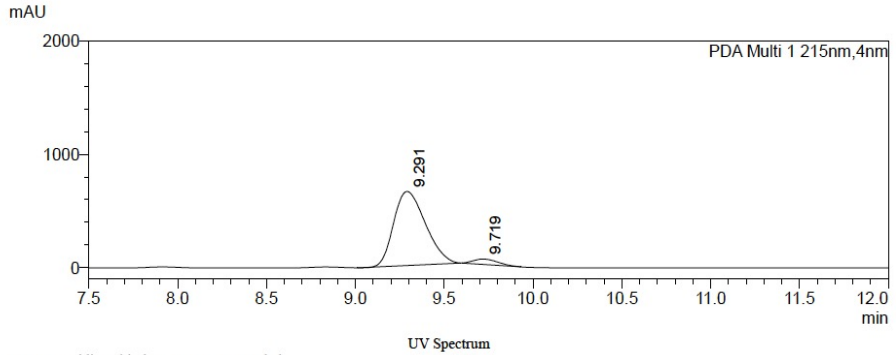

Peak Table

PDA Ch1 215nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.350 | 50.333 |
| 2 | 9.760 | 49.667 |
| Total | | 100.000 |

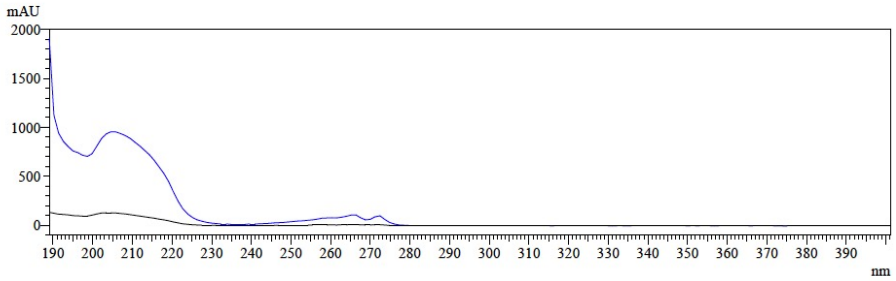
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-4F-azetidine-chiral-IB-2%0.8mL




UV Spectrum

JJX-4F-azetidine-chiral-IB-2%0.8mL_001.lcd

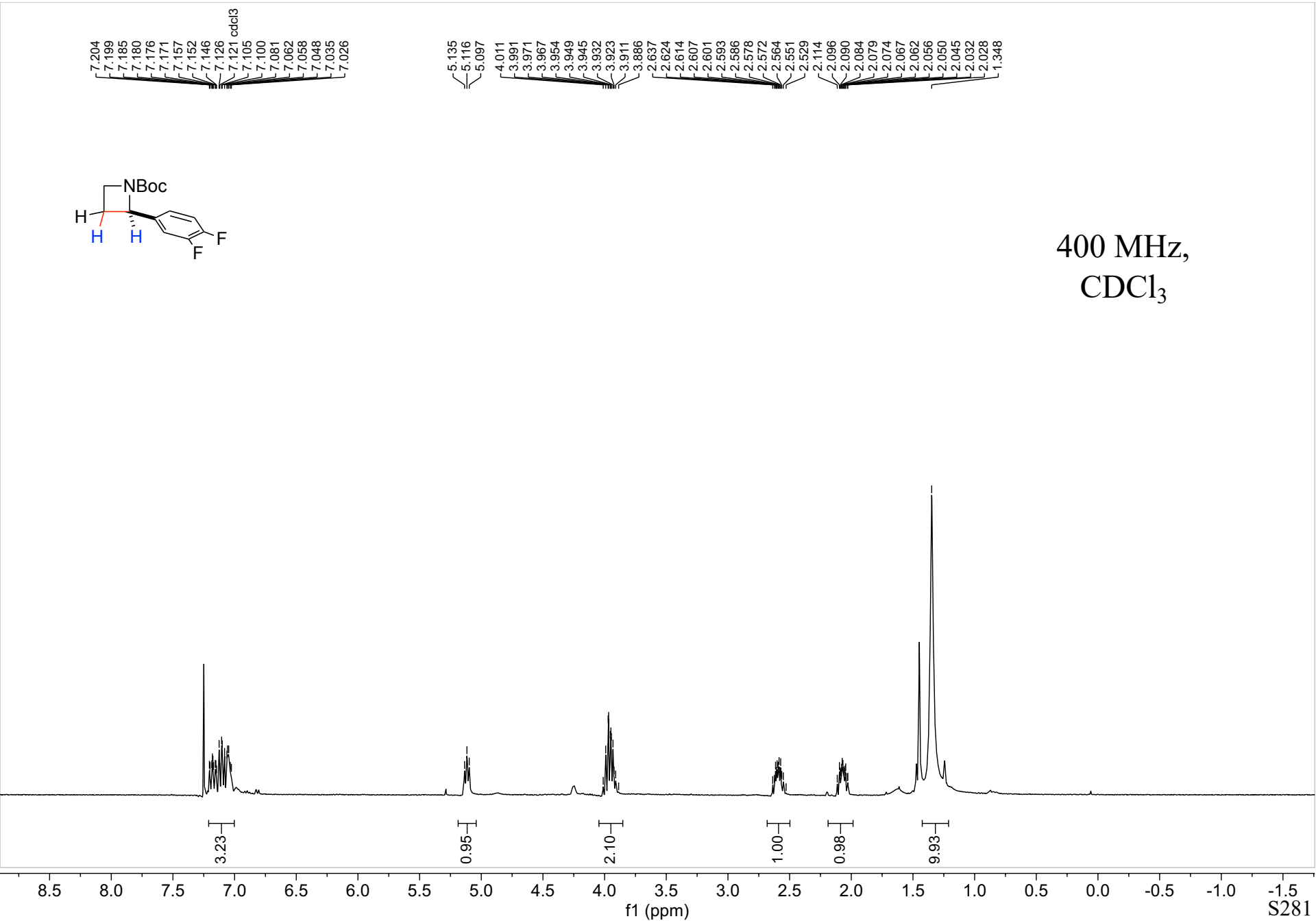



Peak Table

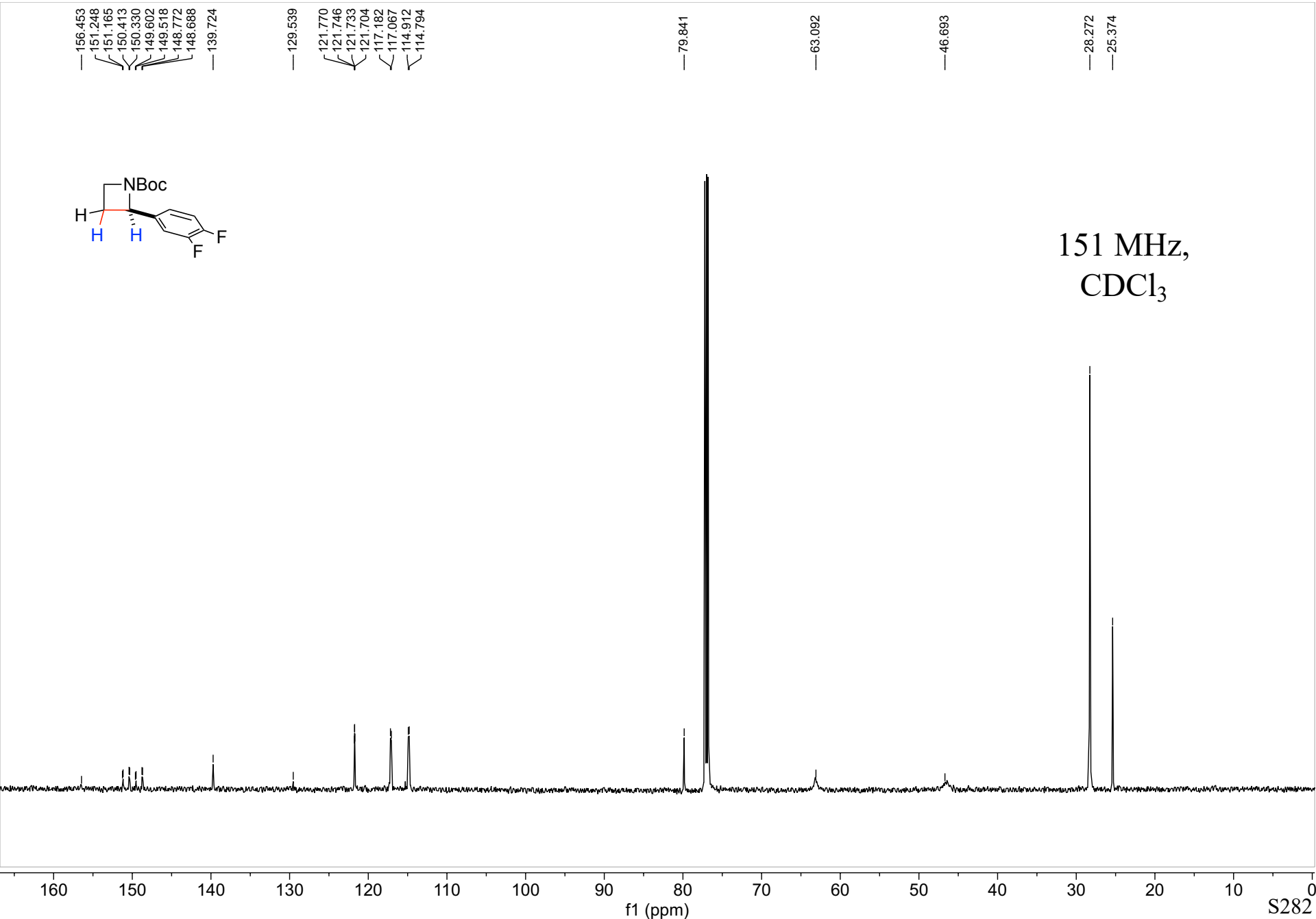
PDA Ch1 215nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.291 | 94.853 |
| 2 | 9.719 | 5.147 |
| Total | | 100.000 |

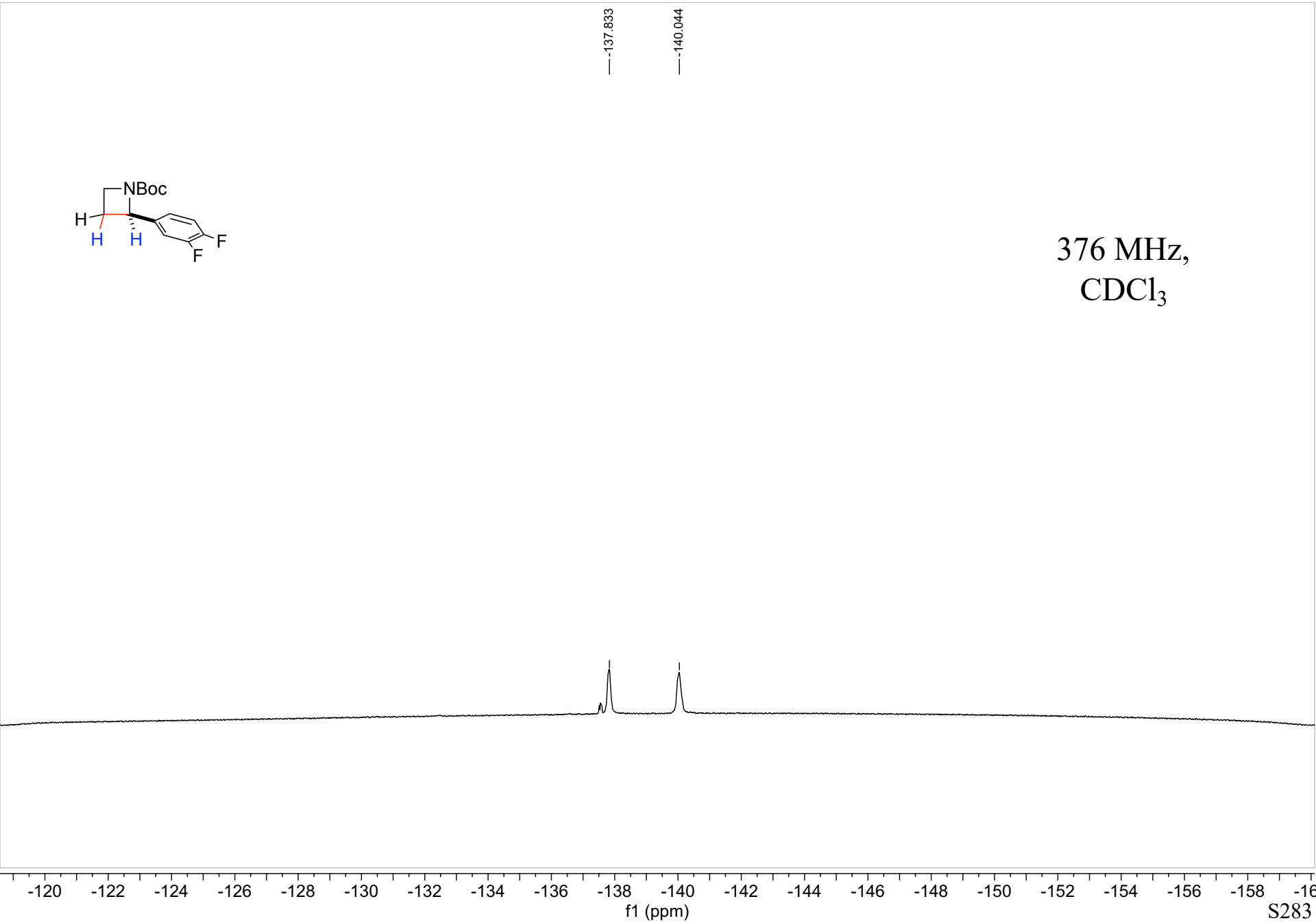
# $^1$H NMR *tert*-Butyl (*R*)-2-(3,4-difluorophenyl)azetidine-1-carboxylate (**2k**)



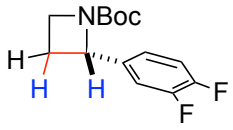
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(3,4-difluorophenyl)azetidine-1-carboxylate (**2k**)



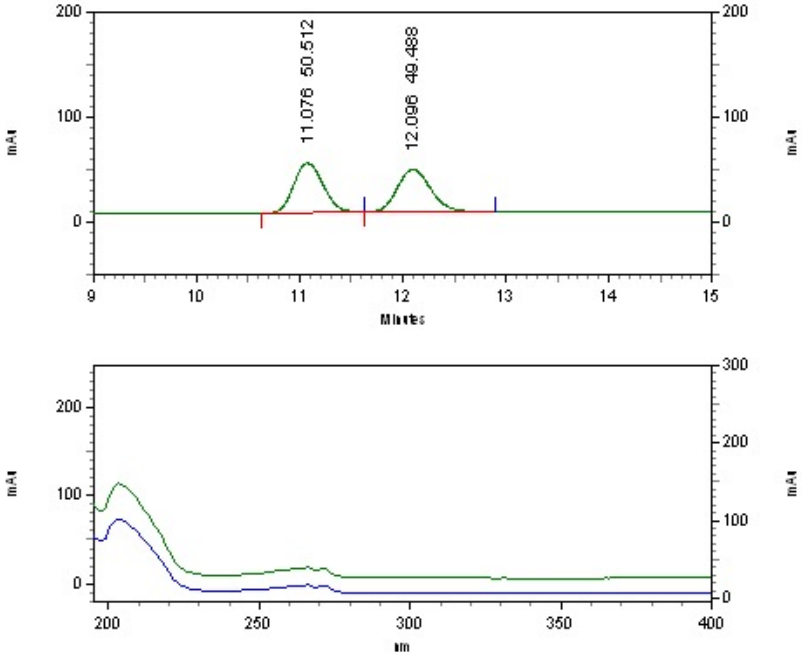
# $^{19}$F NMR *tert*-Butyl (*R*)-2-(3,4-difluorophenyl)azetidine-1-carboxylate (**2k**)



# **HPLC** *tert*-Butyl (*R*)-2-(3,4-difluorophenyl)azetidine-1-carboxylate (**2k**)



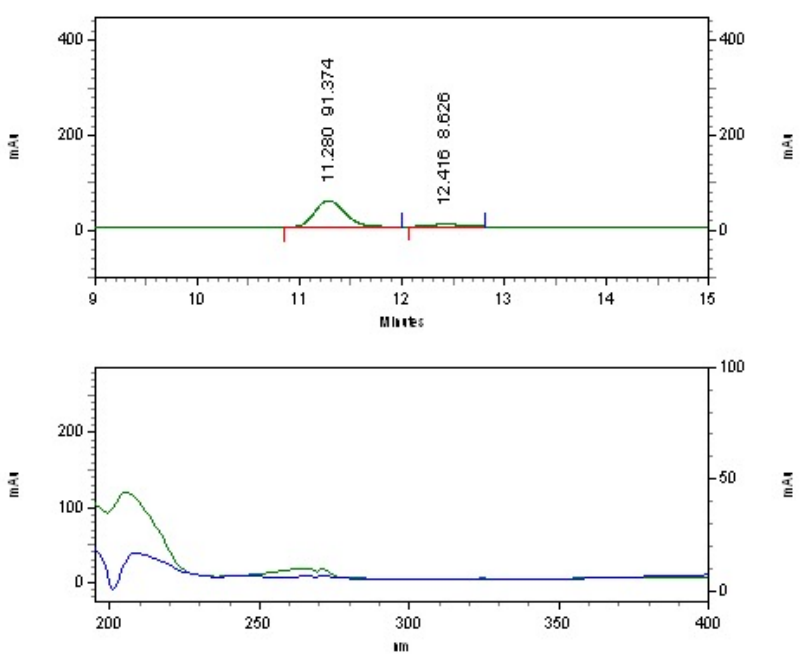

D:\Jingjing HPLC\JJX-2047P-ID-2%-0.8ml-34FIBU-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 217 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.076 | 50.512 |
| 2 | 12.096 | 49.488 |
| Totals | | 100.000 |

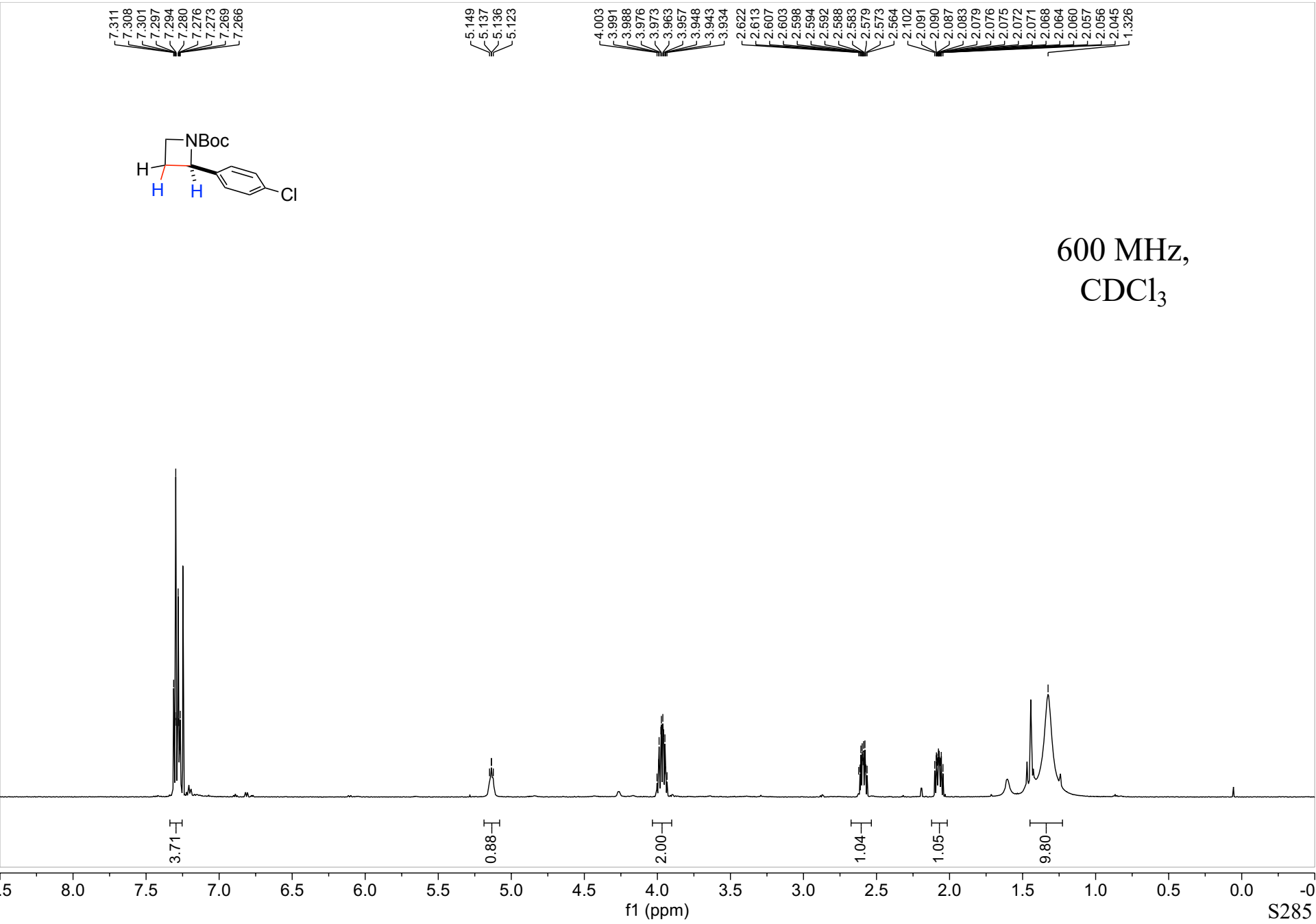
D:\Jingjing HPLC\JJX-2087P-ID-2%-0.8ML-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



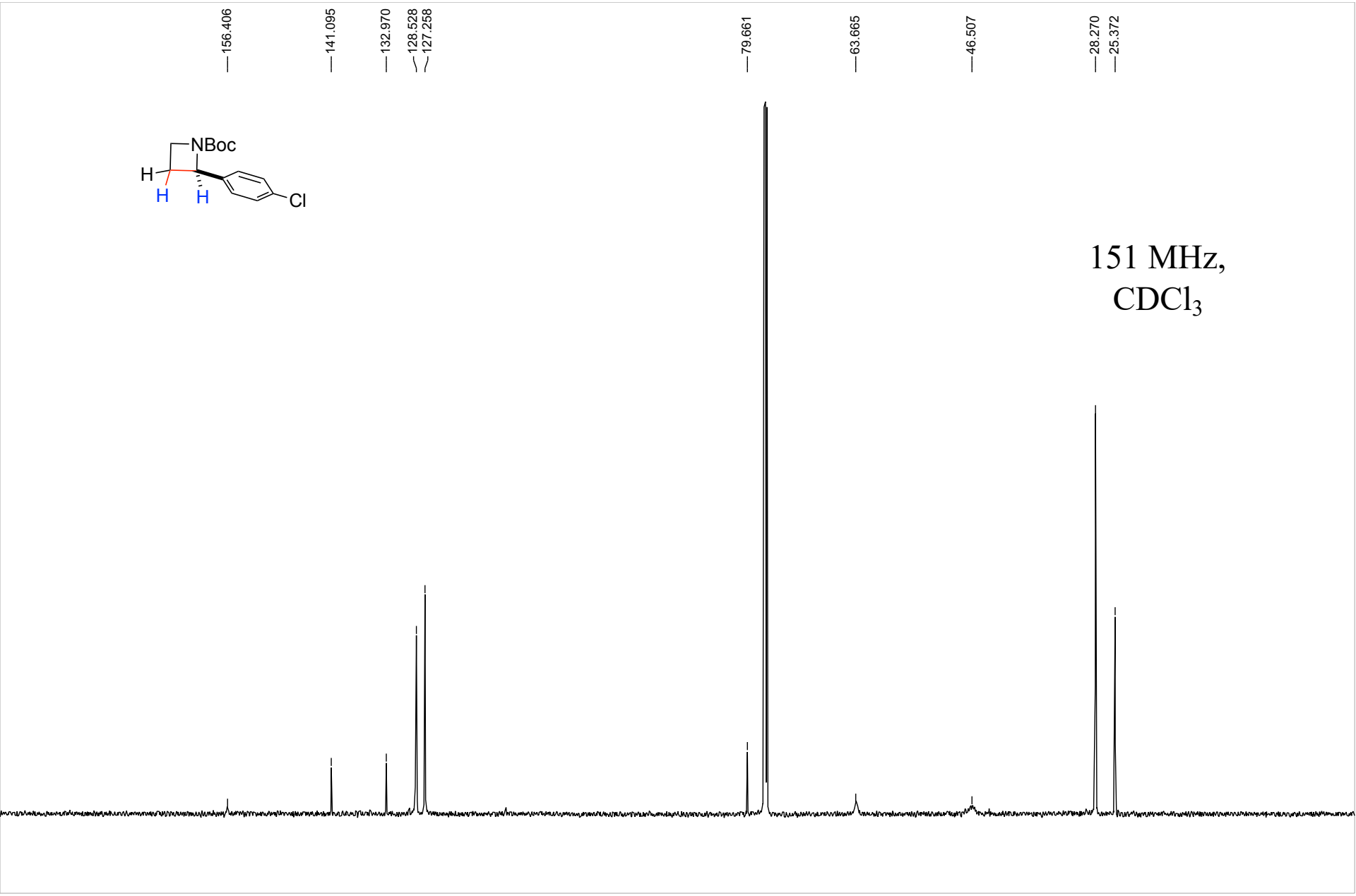

2: 217 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 11.280 | 91.374 |
| 2 | 12.416 | 8.626 |
| Totals | | 100.000 |

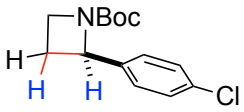
# $^1$H NMR *tert*-Butyl (*R*)-2-(4-chlorophenyl)azetidine-1-carboxylate (**2l**)



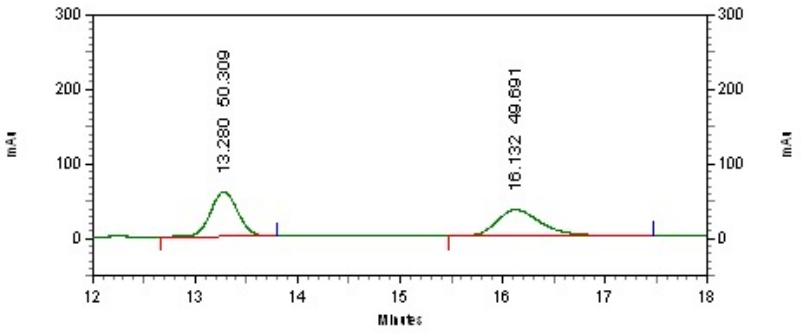
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-chlorophenyl)azetidine-1-carboxylate (**2l**)

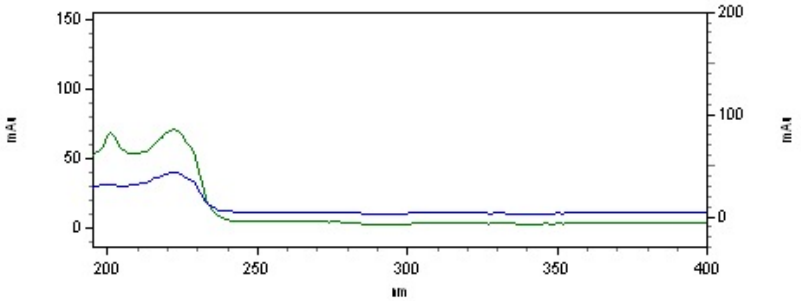


# **HPLC** *tert*-Butyl (*R*)-2-(4-chlorophenyl)azetidine-1-carboxylate (**2l**)




D:\Jingjing HPLC\JJX-2139P-ID-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



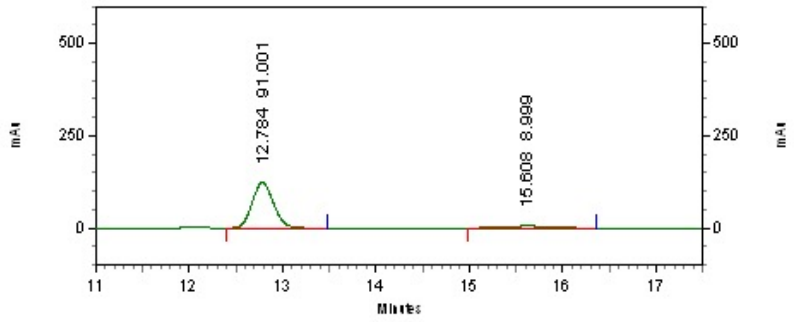



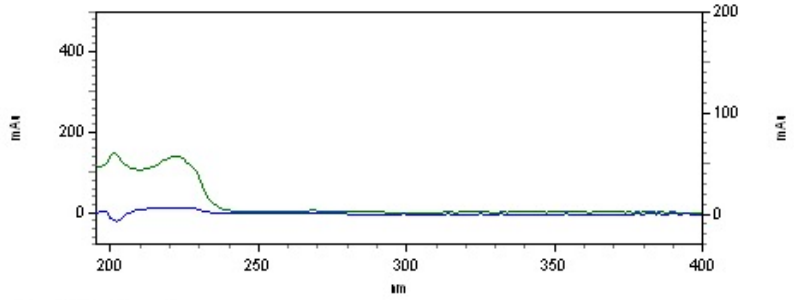

2: 226 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 13.280 | 50.309 |
| 2 | 16.132 | 49.691 |

| Totals | 100.000 |
|---|---|

D:\Jingjing HPLC\JJX-2140P-ID-2%-0.8ML-c4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



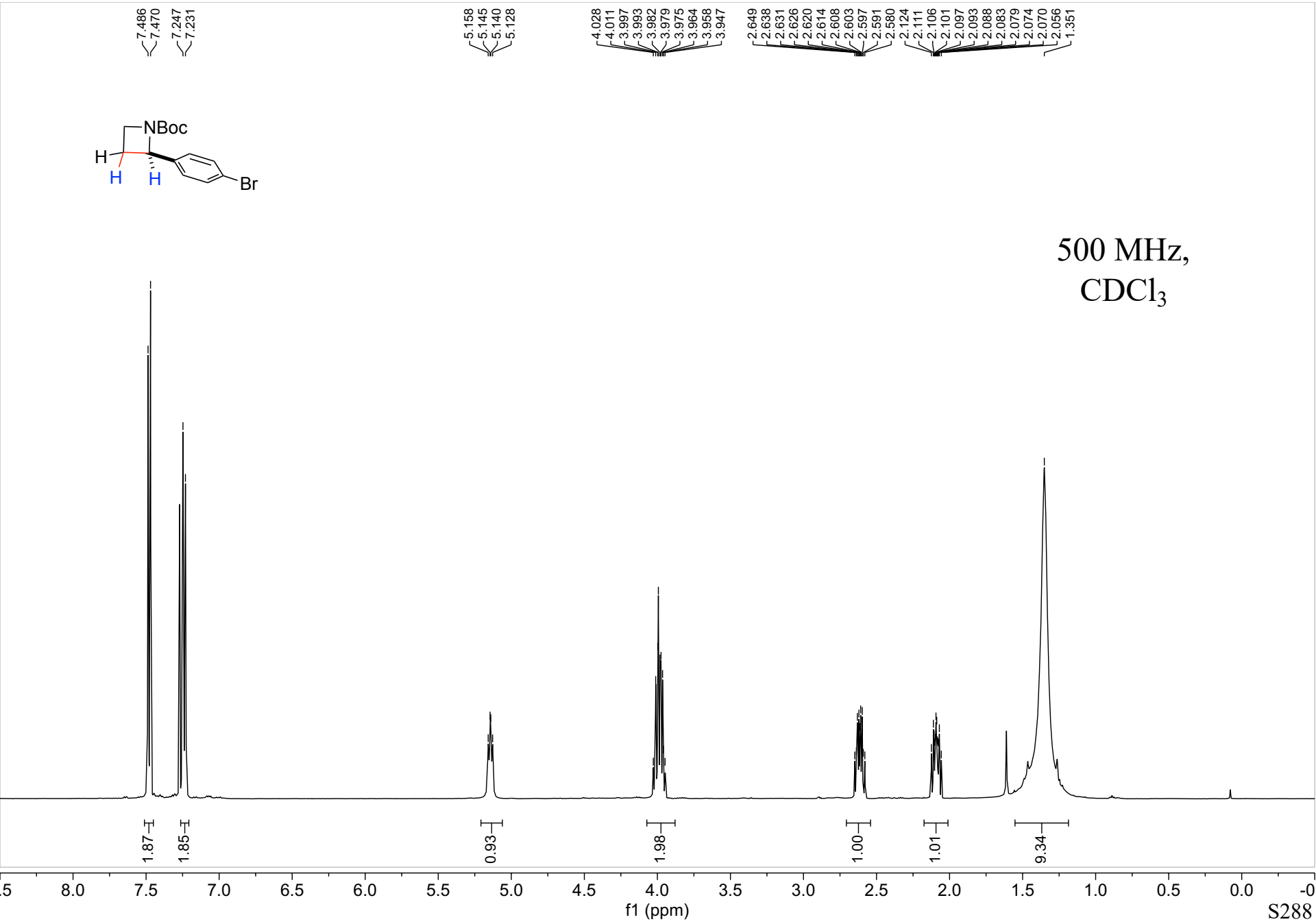




2: 226 nm, 4
nm Results

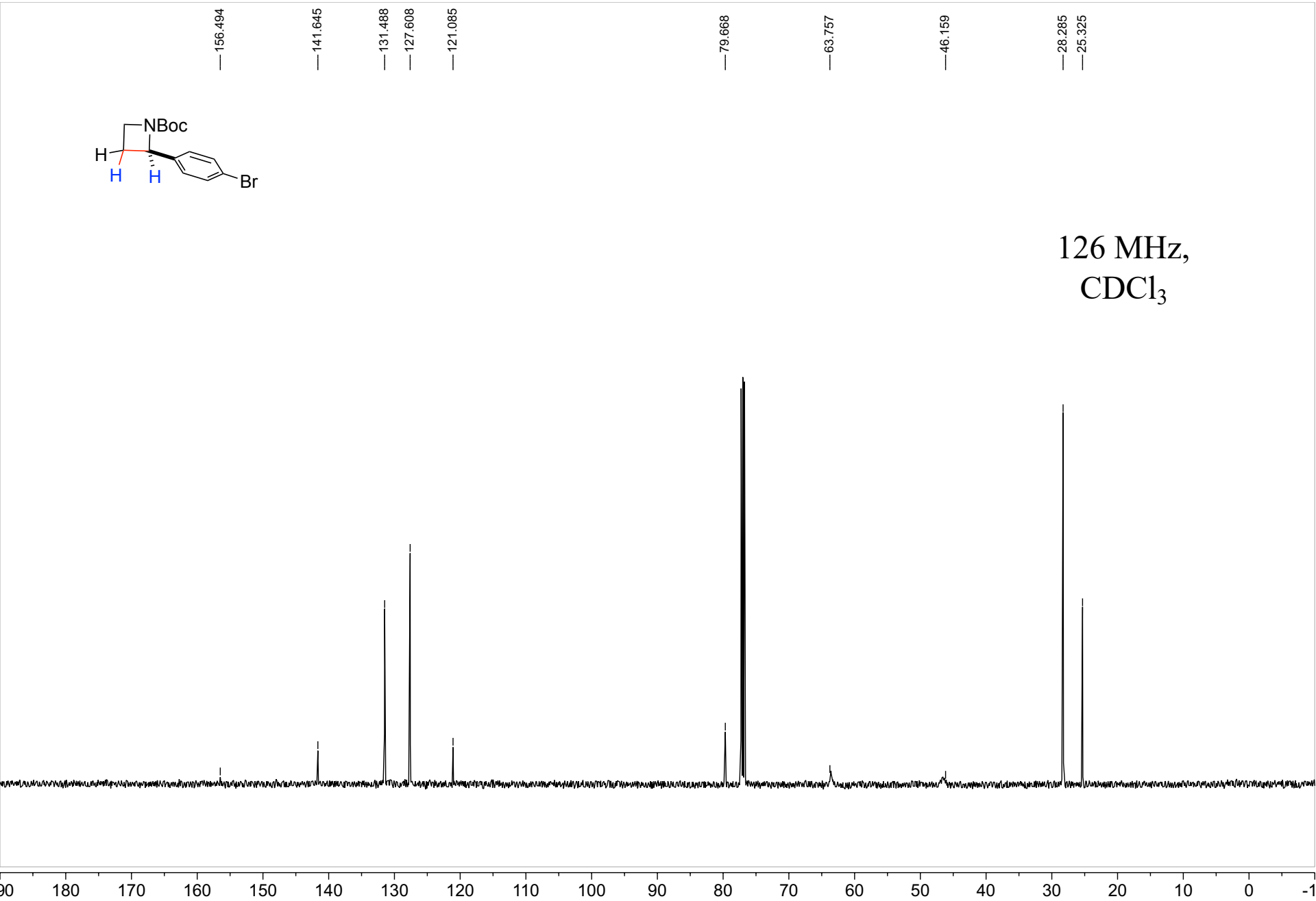
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.784 | 91.001 |
| 2 | 15.608 | 8.999 |

| Totals | 100.000 |
|---|---|

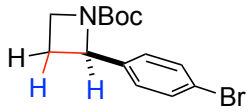
# $^1$H NMR *tert*-Butyl (*R*)-2-(4-bromophenyl)azetidine-1-carboxylate (**2m**)



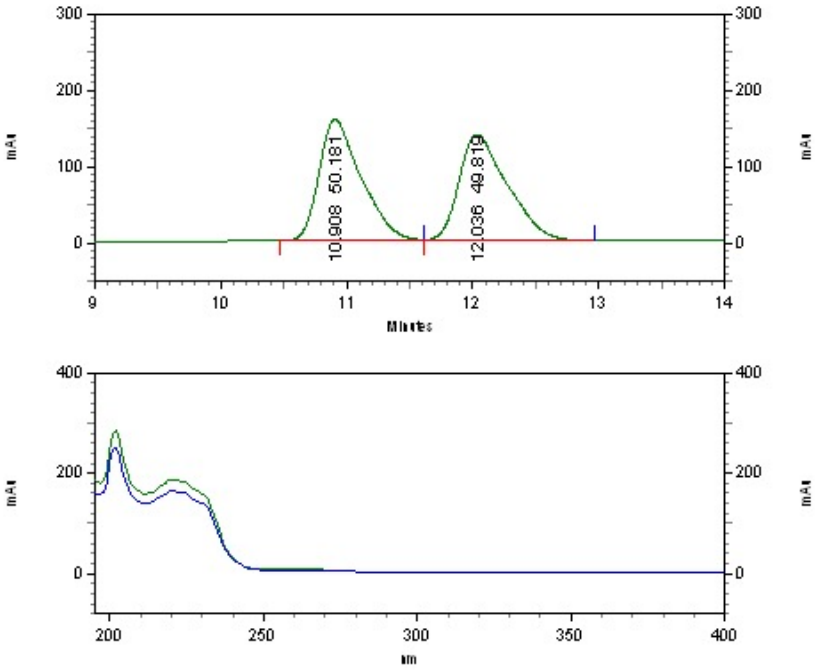
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-bromophenyl)azetidine-1-carboxylate (**2m**)



# HPLC *tert*-Butyl (*R*)-2-(4-bromophenyl)azetidine-1-carboxylate (**2m**)



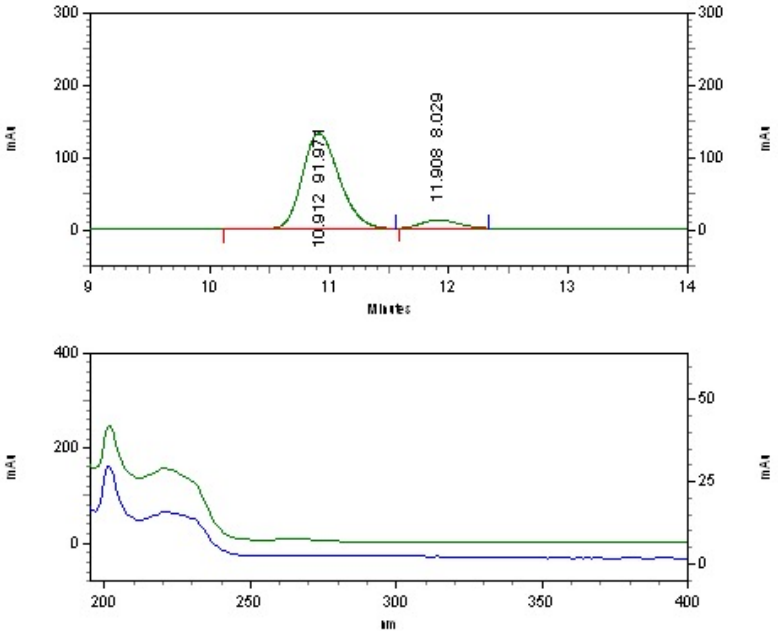

D:\Jingjing HPLC\JJX-1814P-ODH-2%-0.8ml-Ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 229 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.908 | 50.181 |
| 2 | 12.036 | 49.819 |
| Totals | | 100.000 |

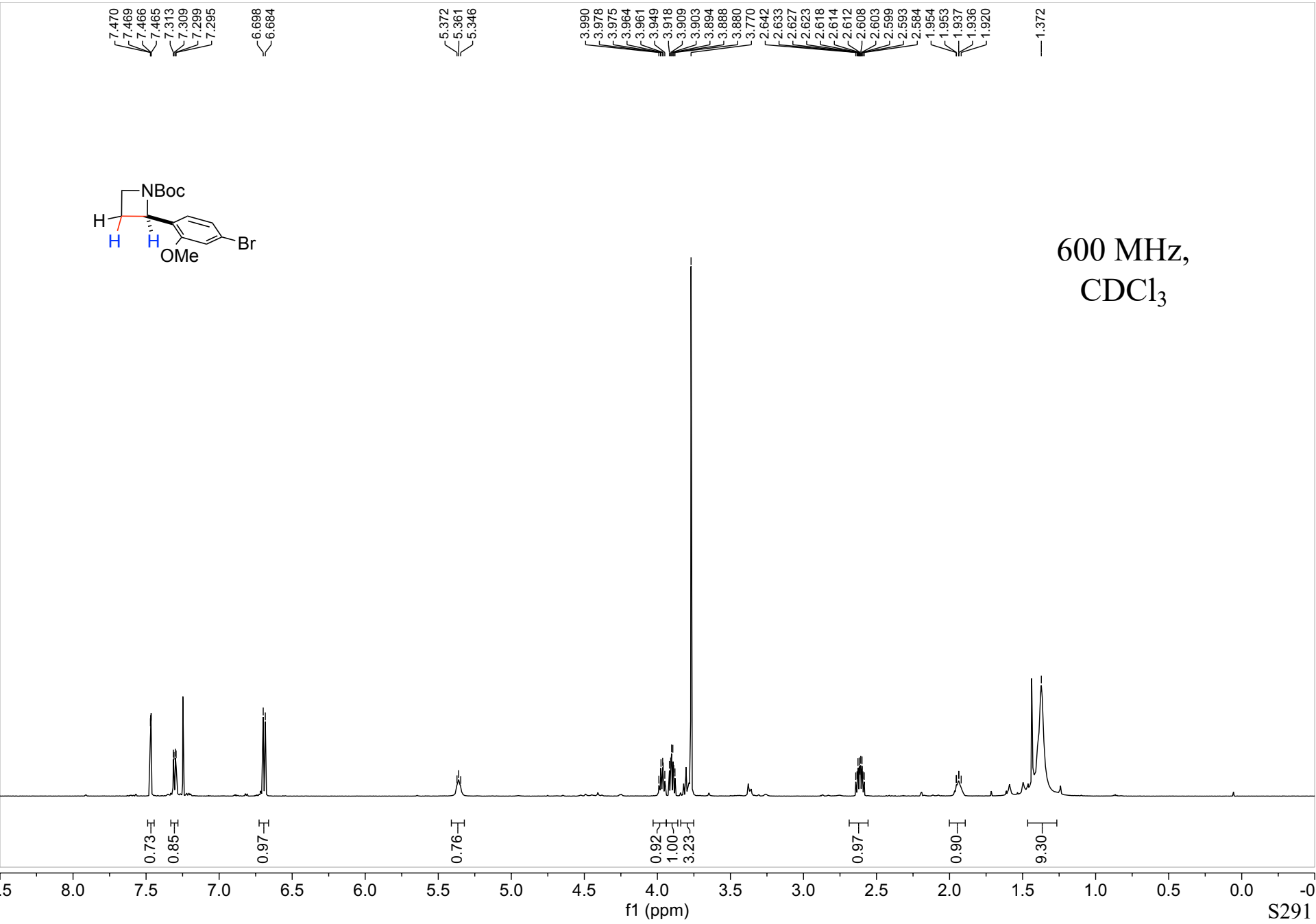
D:\Jingjing HPLC\JJX-1856P-ODH-2%-0.8ml
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



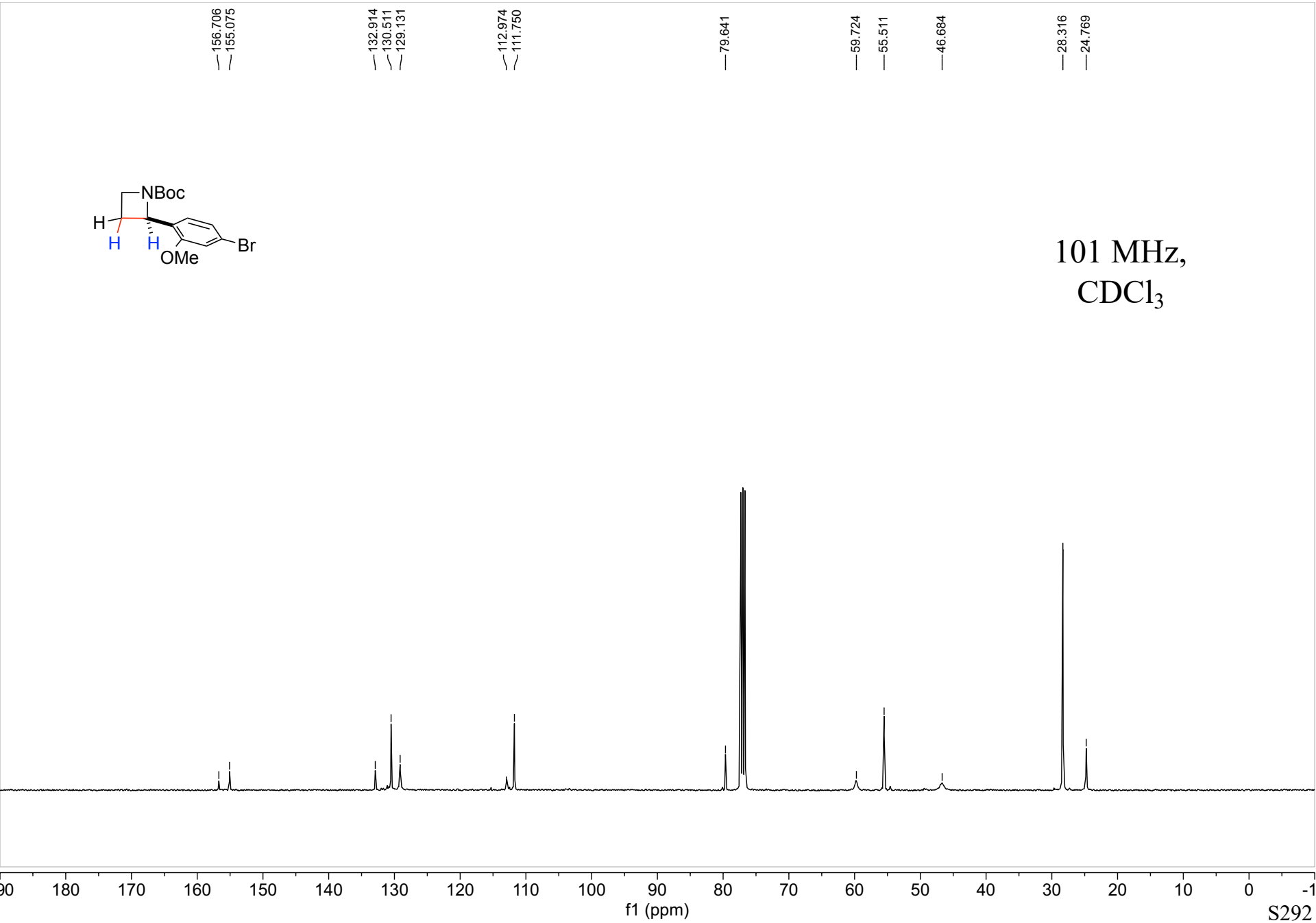

2: 229 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.912 | 91.971 |
| 2 | 11.908 | 8.029 |
| Totals | | 100.000 |

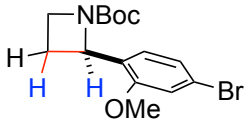
# $^1$H NMR *tert*-Butyl (*R*)-2-(4-bromo-2-methoxyphenyl)azetidine-1-carboxylate (**2n**)



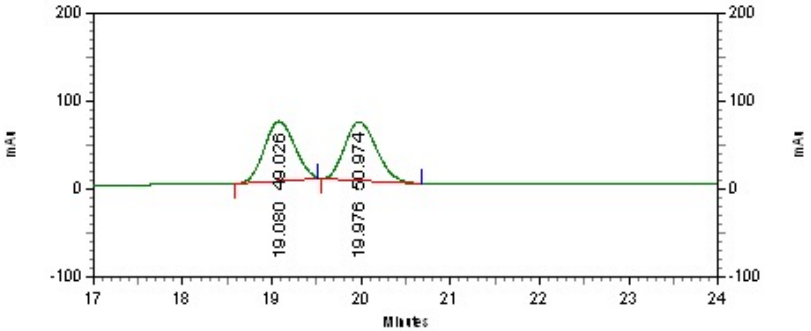
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(4-bromo-2-methoxyphenyl)azetidine-1-carboxylate (**2n**)

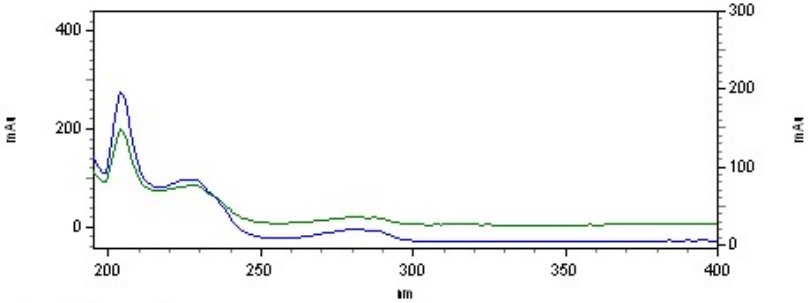


# **HPLC** *tert*-Butyl (*R*)-2-(4-bromo-2-methoxyphenyl)azetidine-1-carboxylate (**2n**)




D:\Jingjing HPLC\JJX-2192P-IF-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



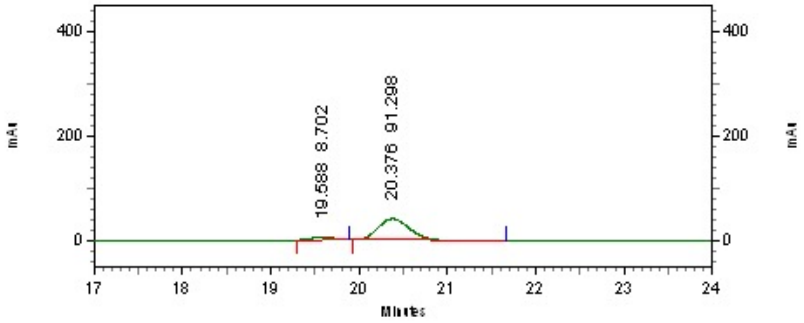



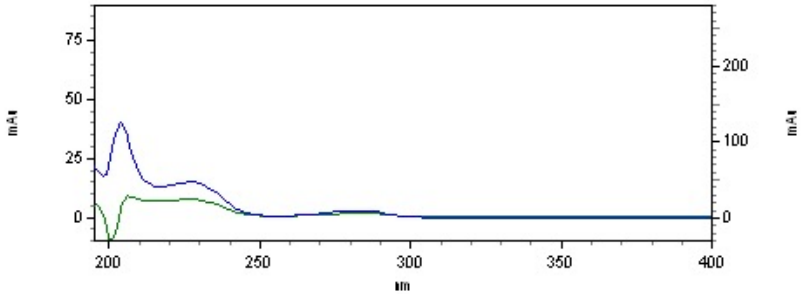

2: 220 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.080 | 49.026 |
| 2 | 19.976 | 50.974 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2194P-IF-2%-0.8ML-C4
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



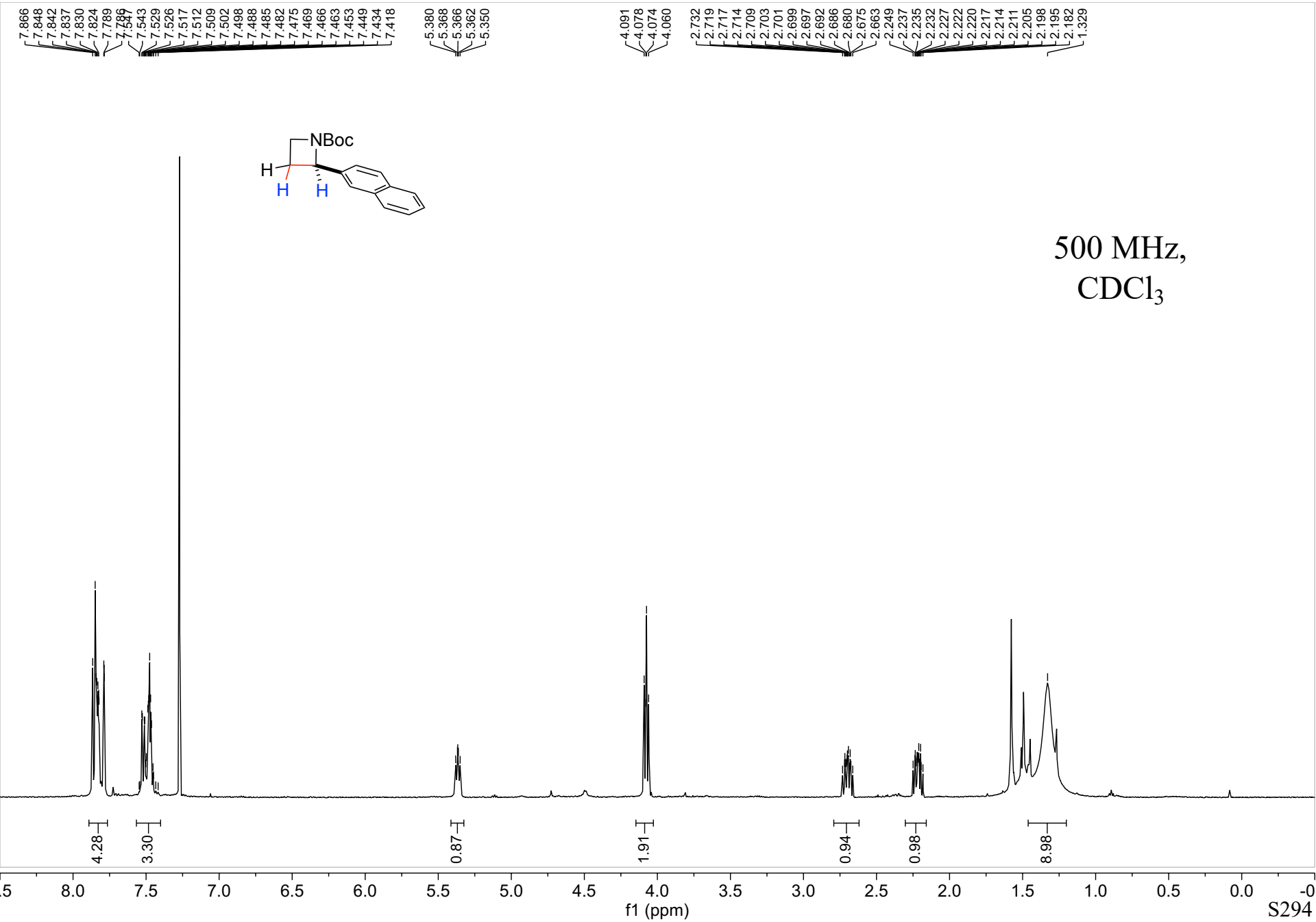




2: 220 nm, 4
nm Results

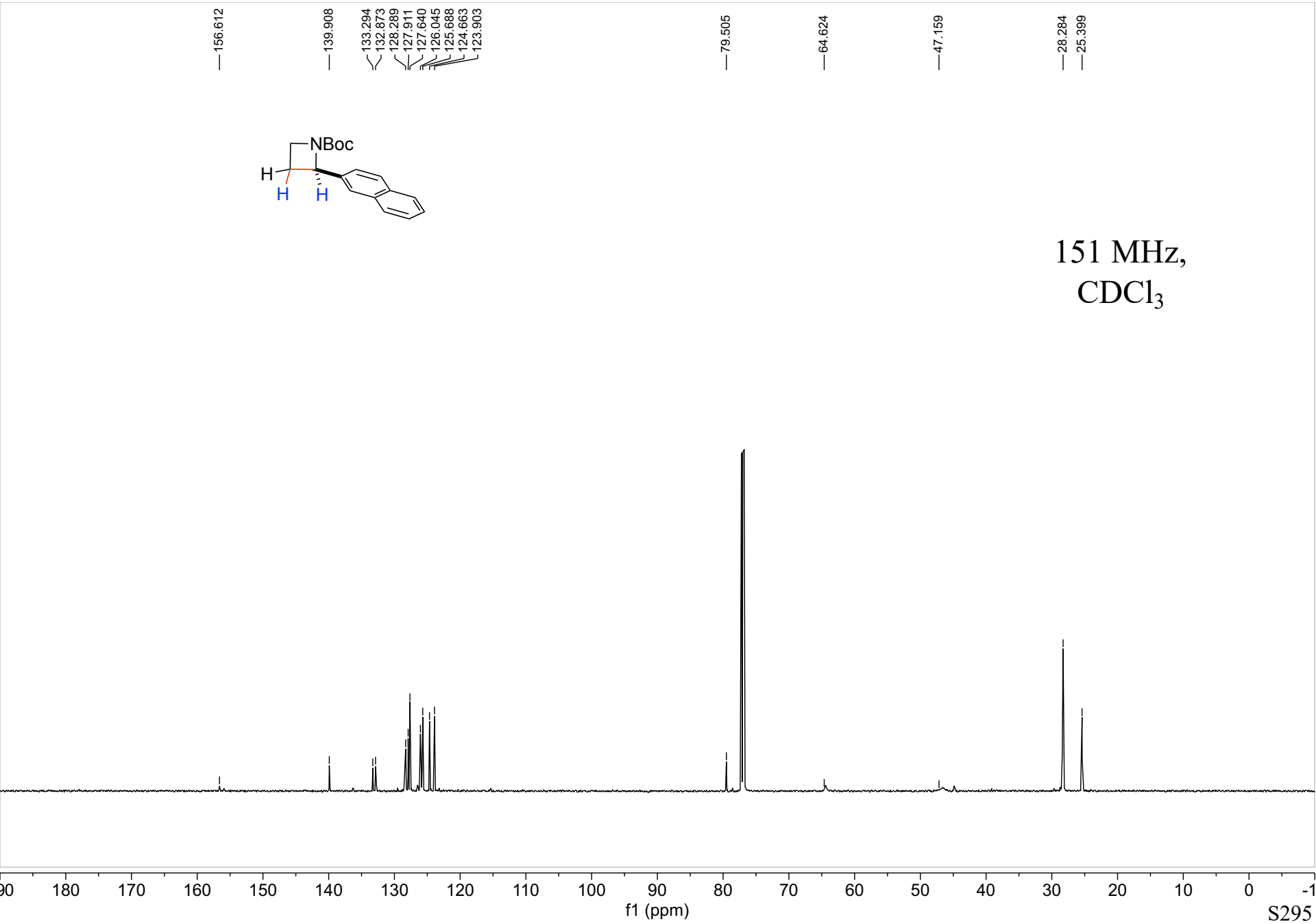
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.588 | 8.702 |
| 2 | 20.376 | 91.298 |

| Totals | |
|---|---|
| | 100.000 |

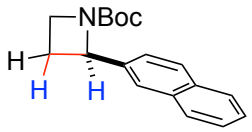
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(naphthalen-2-yl)azetidine-1-carboxylate (**2o**)



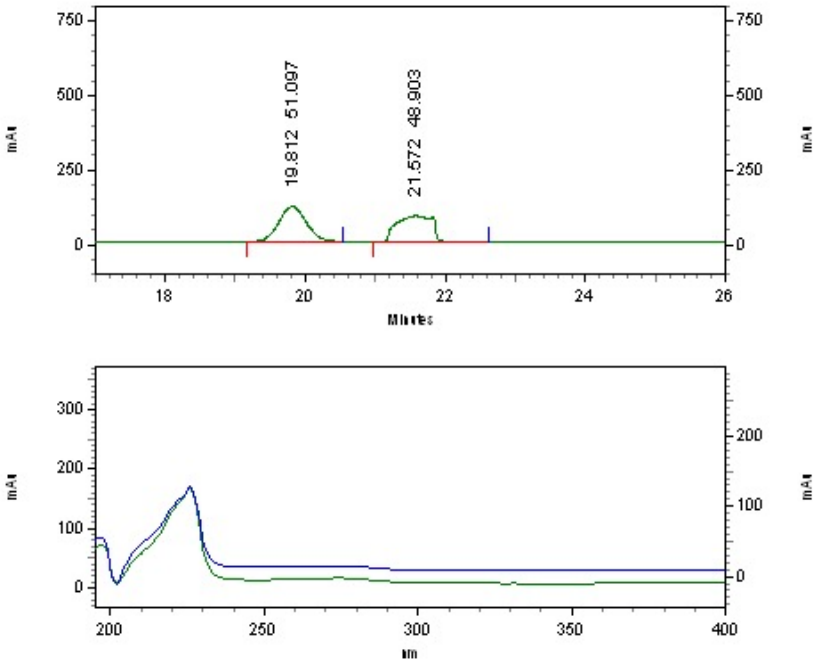
# $^{13}$C NMR *tert*-Butyl (*R*)-2-(naphthalen-2-yl)azetidine-1-carboxylate (**2o**)



# **HPLC** *tert*-Butyl (*R*)-2-(naphthalen-2-yl)azetidine-1-carboxylate (**2o**)




D:\Jingjing HPLC\JJX-1974p-IF-2%-0.8ml-Ibu-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

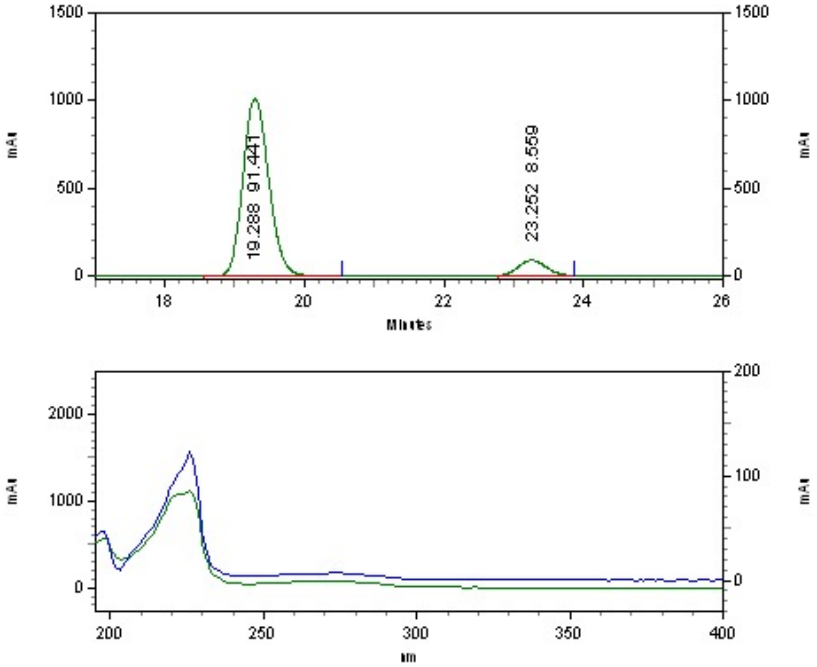



2: 220 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.812 | 51.097 |
| 2 | 21.572 | 48.903 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2364P-IF-2%-0.8ML-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

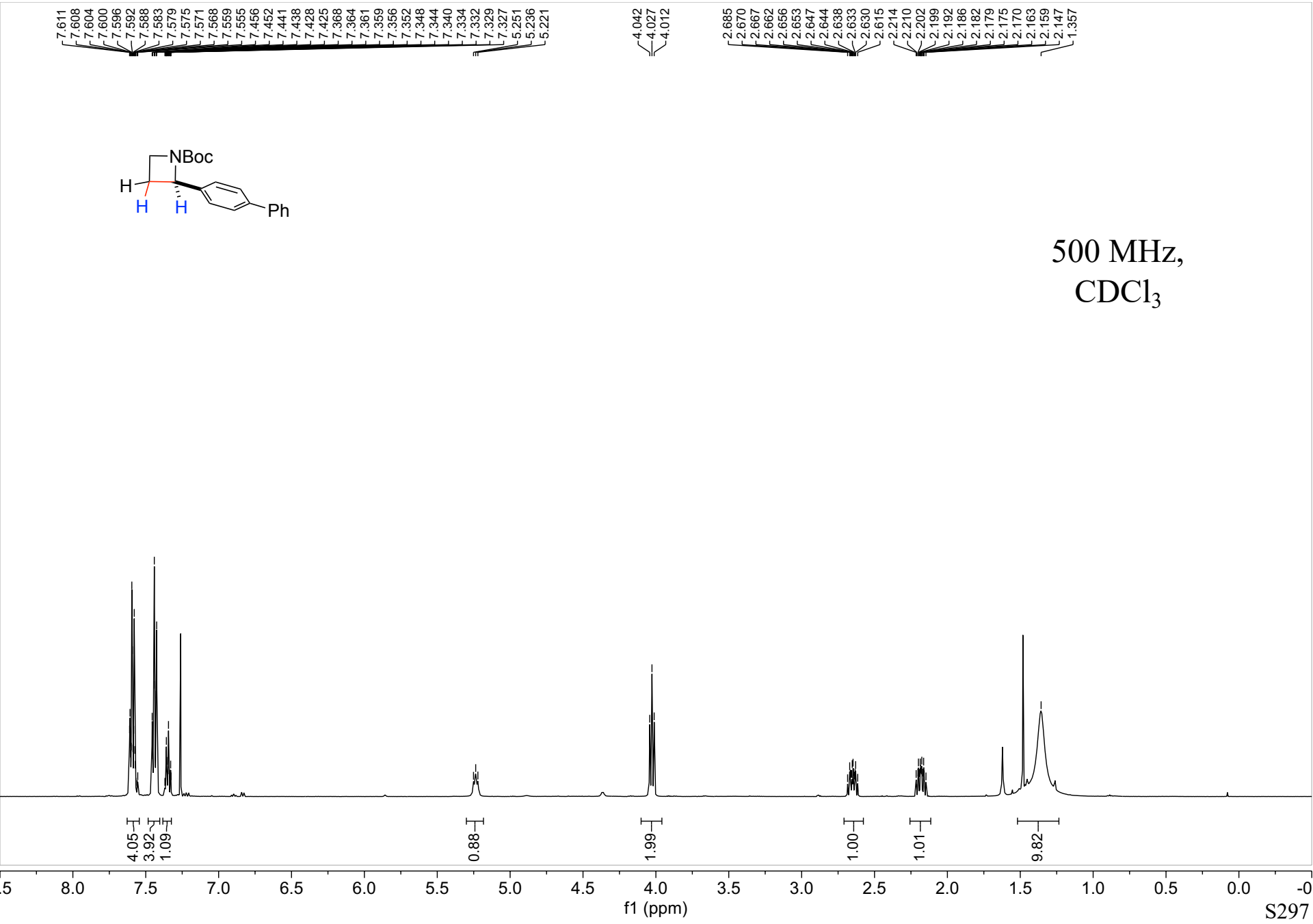



2: 220 nm, 4
nm Results

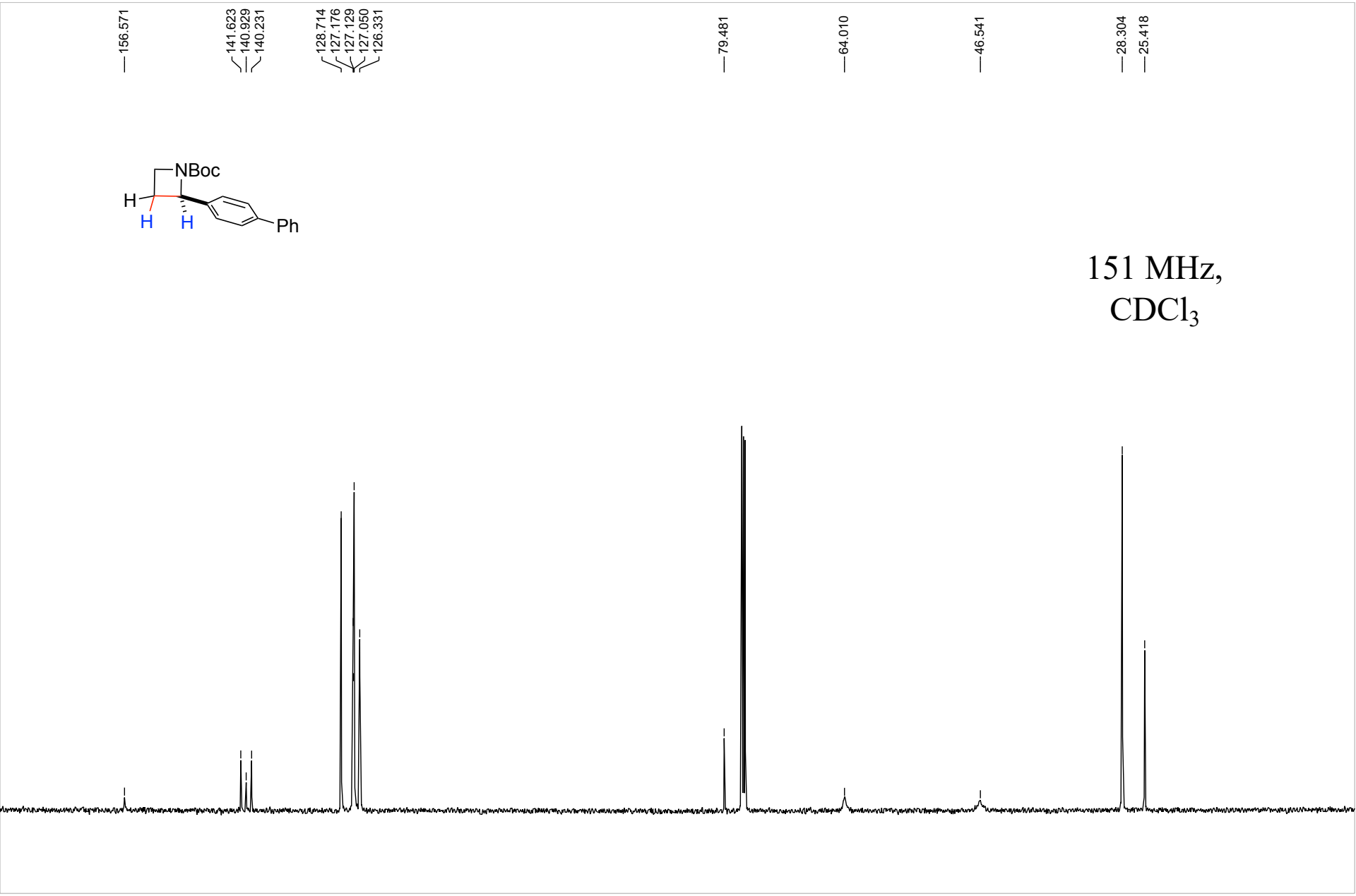
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 19.288 | 91.441 |
| 2 | 23.252 | 8.559 |

| Totals | |
|---|---|
| | 100.000 |

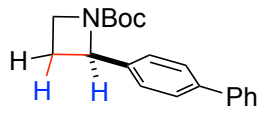
# $^1$H NMR *tert*-Butyl (*R*)-2-([1,1'-biphenyl]-4-yl)azetidine-1-carboxylate (**2p**)



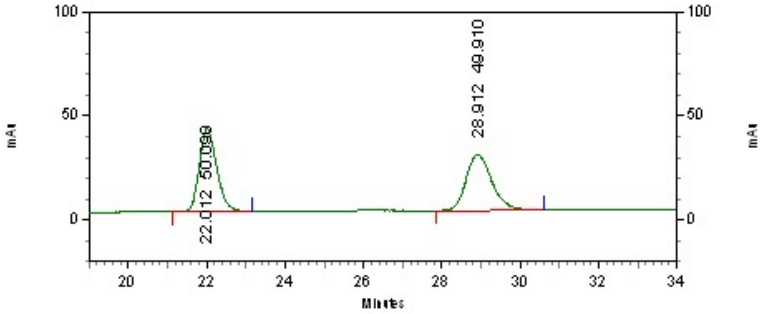
# $^{13}$C NMR *tert*-Butyl (*R*)-2-([1,1'-biphenyl]-4-yl)azetidine-1-carboxylate (**2p**)

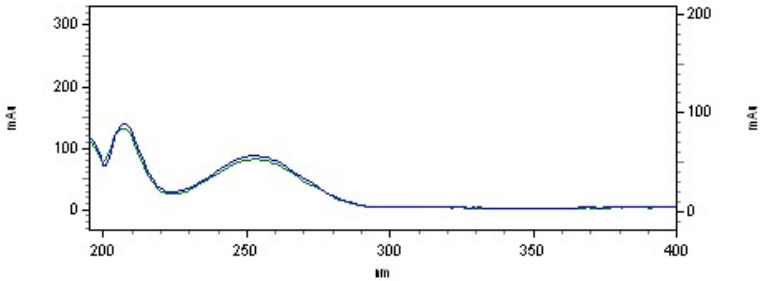


# **HPLC** *tert*-Butyl (*R*)-2-([1,1'-biphenyl]-4-yl)azetidine-1-carboxylate (**2p**)




D:\Jingjing HPLC\JJX-2167P-IF-2%-0.8ML-ibu-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



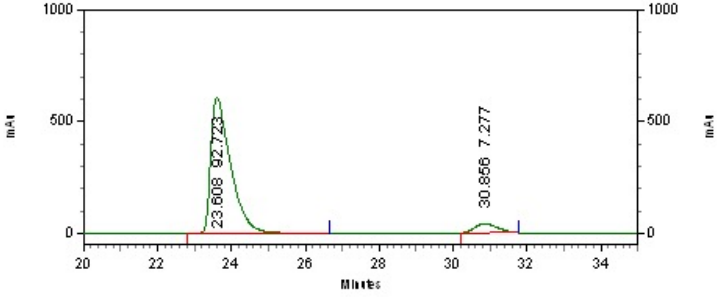



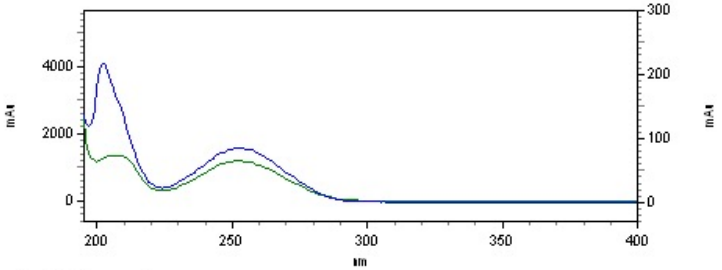

2: 235 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 22.012 | 50.090 |
| 2 | 28.912 | 49.910 |

| Totals | |
|---|---|
| | 100.000 |

D:\Jingjing HPLC\JJX-2172P-IF-2%-0.8ML-C4-1
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



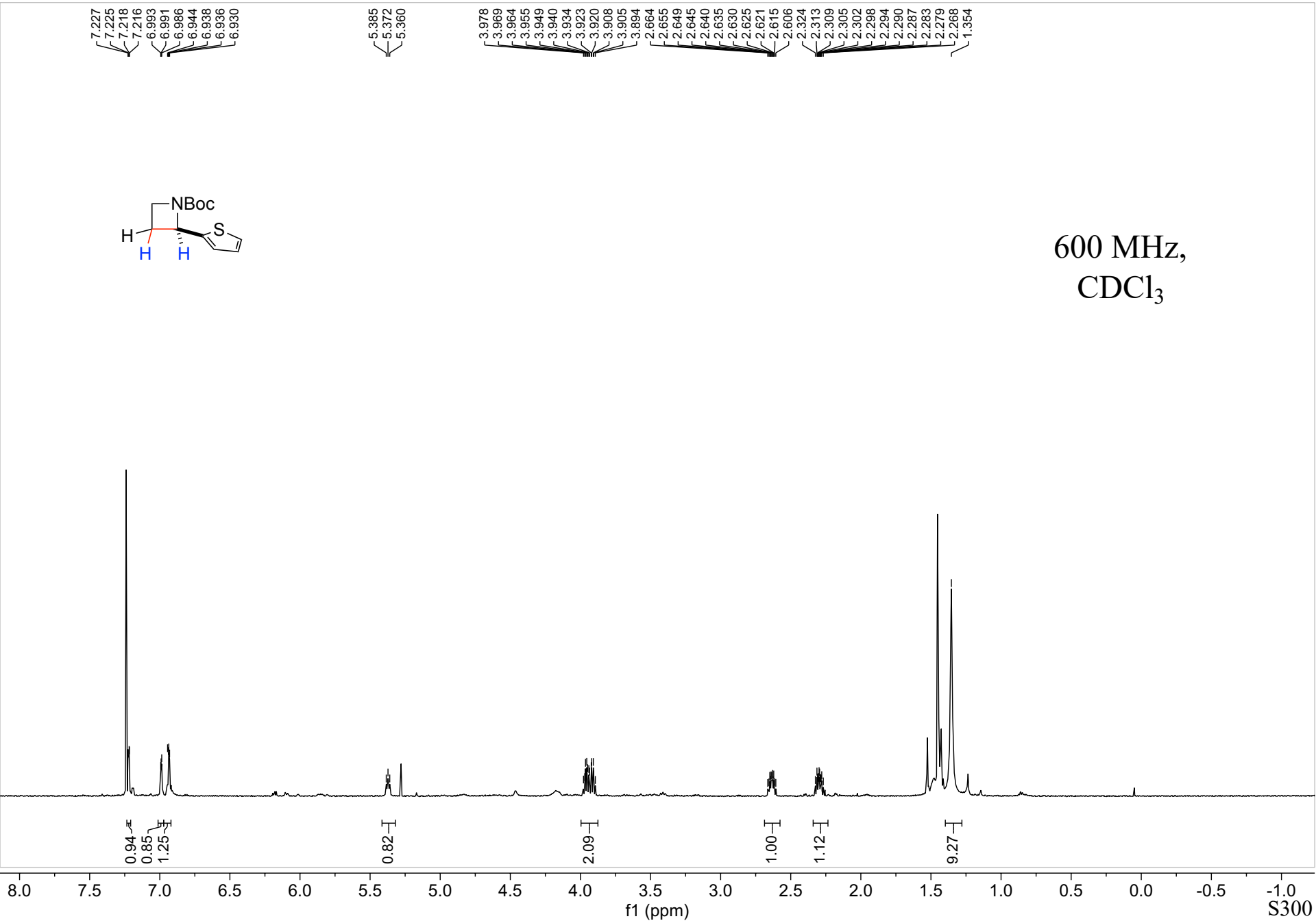




2: 235 nm, 4
nm Results

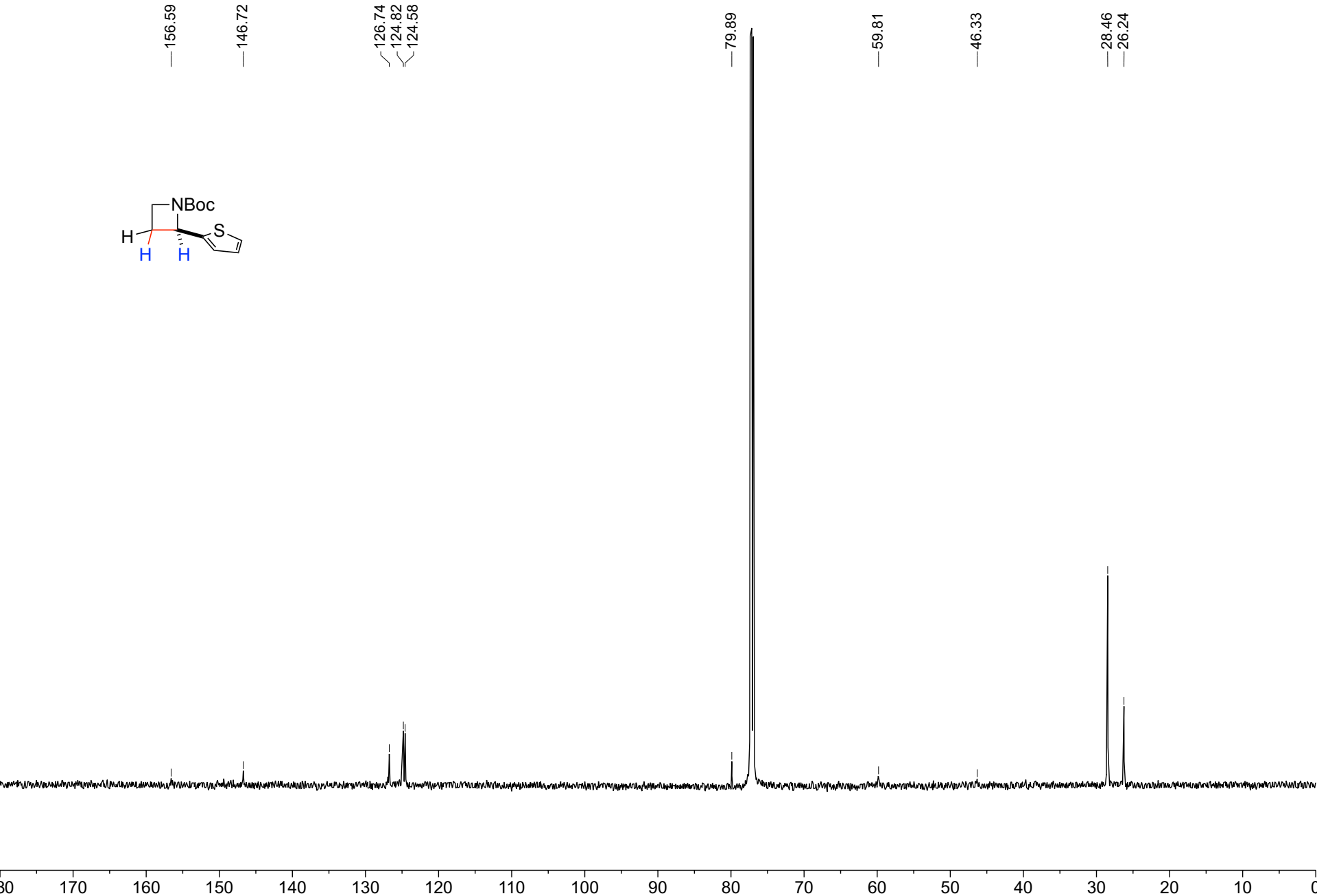
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 23.608 | 92.723 |
| 2 | 30.856 | 7.277 |

| Totals | |
|---|---|
| | 100.000 |

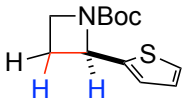
# $^1$H NMR *tert*-Butyl (*R*)-2-(thiophen-2-yl)azetidine-1-carboxylate (**2q**)



# $^{13}$C NMR *tert*-Butyl (*R*)-2-(thiophen-2-yl)azetidine-1-carboxylate (**2q**)



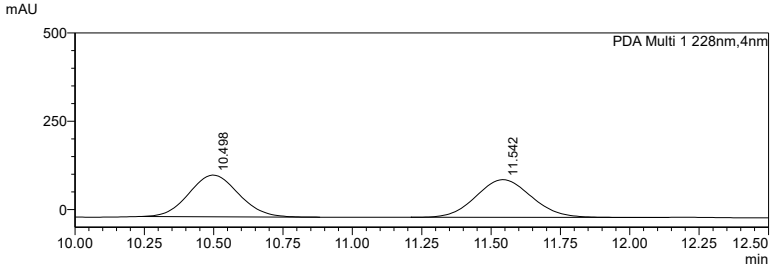
# **HPLC** *tert*-Butyl (*R*)-2-(thiophen-2-yl)azetidine-1-carboxylate (**2q**)





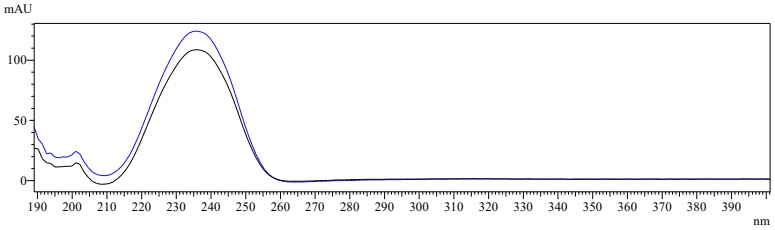

## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-2Thiophen-azetidine-rac-IC-10%0.8mL




UV Spectrum

JJX-2Thiophen-azetidine-rac-IC-10%0.8mL_001.lcd




Peak Table

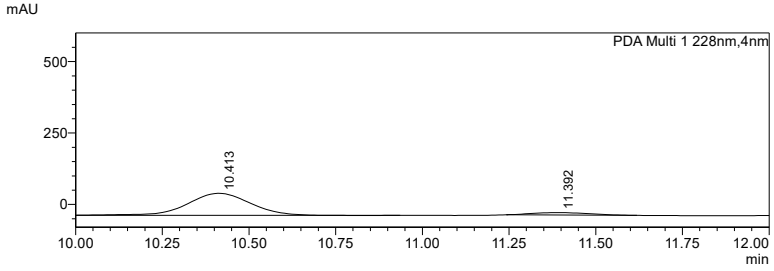
PDA Ch1 228nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 10.498 | 50.025 |
| 2 | 11.542 | 49.975 |
| Total | | 100.000 |



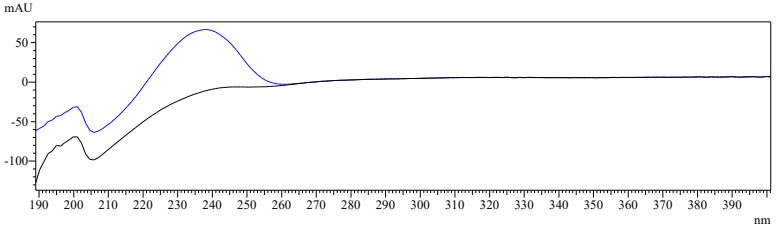
## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-2thiophen-AZETIDINE-chiral-IC-10%0.8mL




UV Spectrum

JJX-2thiophen-AZETIDINE-chiral-IC-10%0.8mL_001.lcd

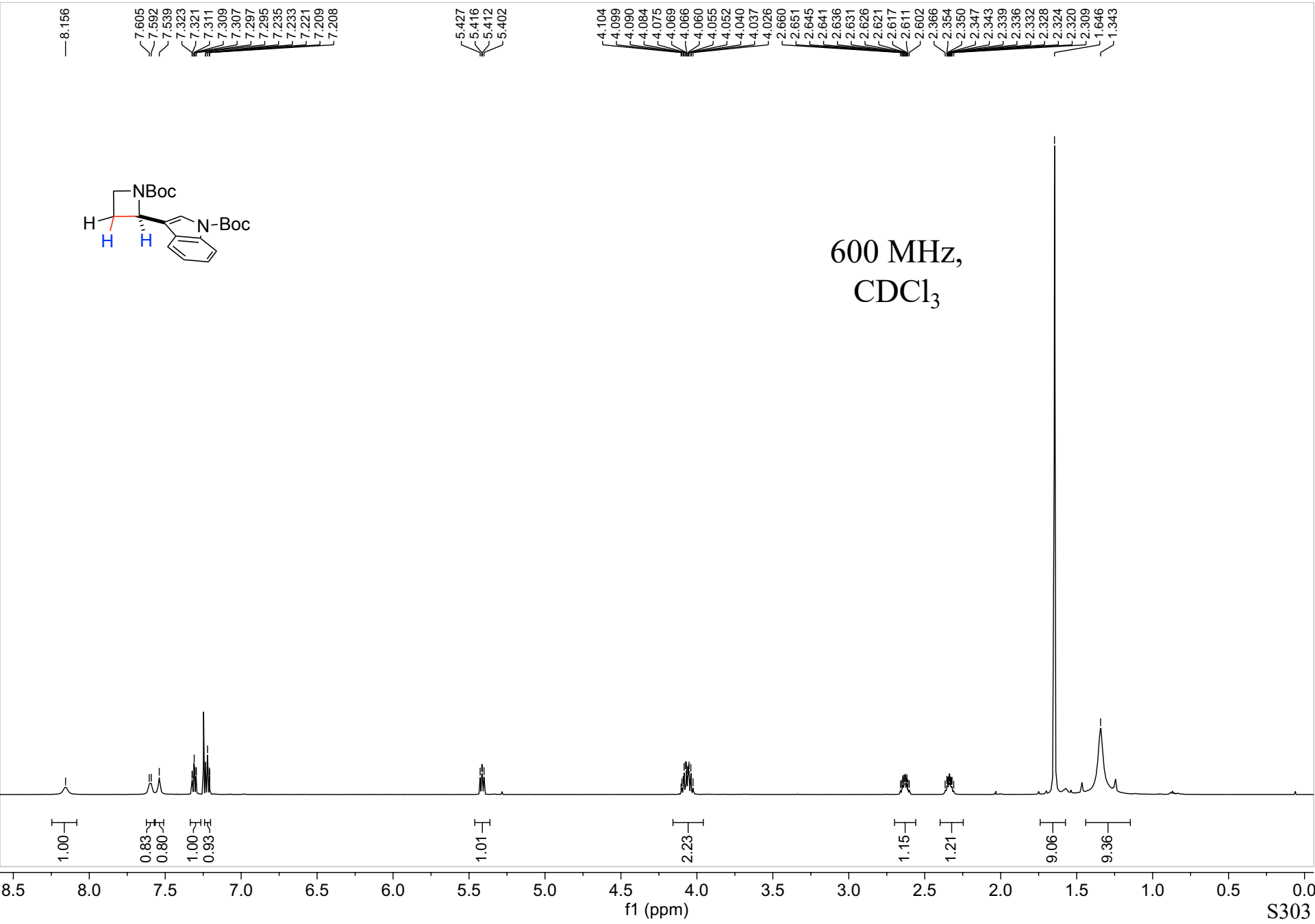



Peak Table

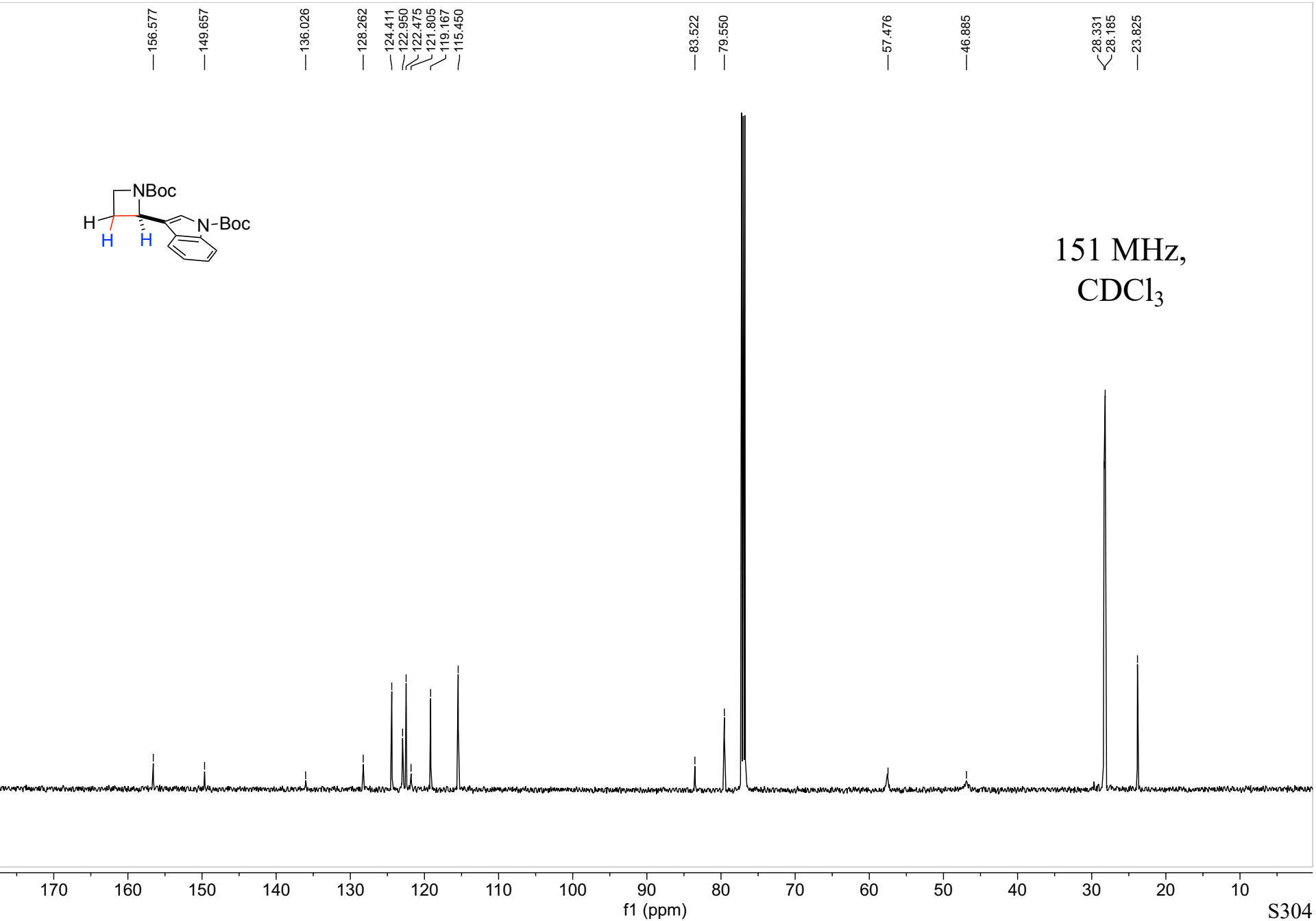
PDA Ch1 228nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 10.413 | 91.074 |
| 2 | 11.392 | 8.926 |
| Total | | 100.000 |

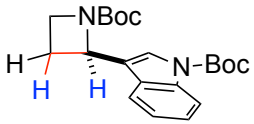
# $^{1}$H NMR *tert*-Butyl (*R*)-3-(1-(*tert*-butoxycarbonyl)azetidin-2-yl)-1*H*-indole-1-carboxylate (**2r**)



**$^{13}$C NMR** *tert*-Butyl (*R*)-3-(1-(*tert*-butoxycarbonyl)azetidin-2-yl)-1*H*-indole-1-carboxylate (**2r**)



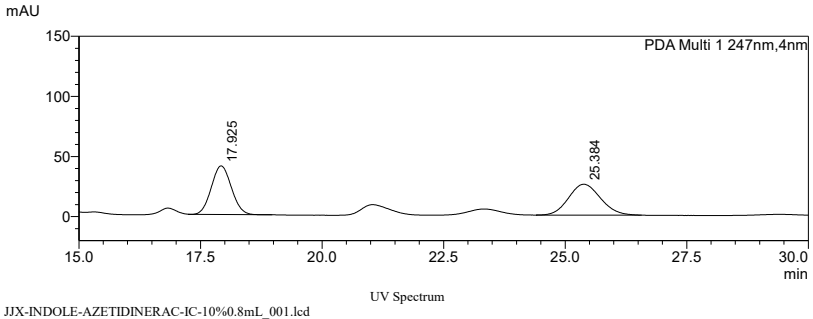
# **HPLC** *tert*-Butyl (*R*)-3-(1-(*tert*-butoxycarbonyl)azetidin-2-yl)-1*H*-indole-1-carboxylate (**2r**)



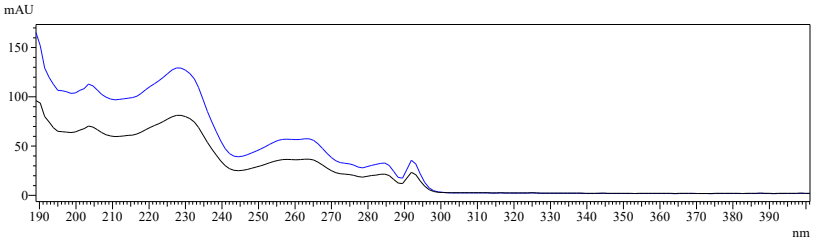



## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-INDOLE-AZETIDINERAC-IC-10%0.8mL




JJX-INDOLE-AZETIDINERAC-IC-10%0.8mL_001.lcd




Peak Table

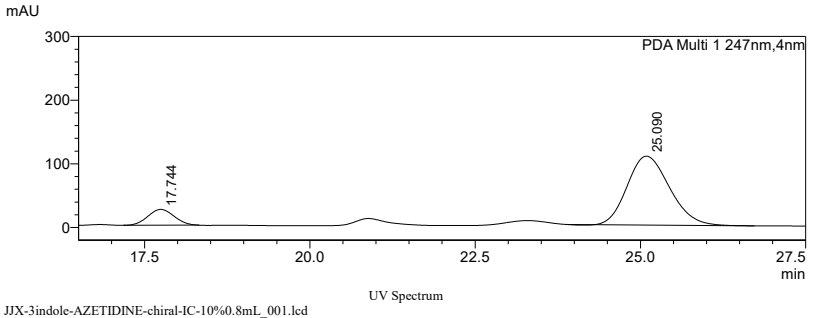
PDA Ch1 247nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 17.925 | 49.754 |
| 2 | 25.384 | 50.246 |
| Total | | 100.000 |

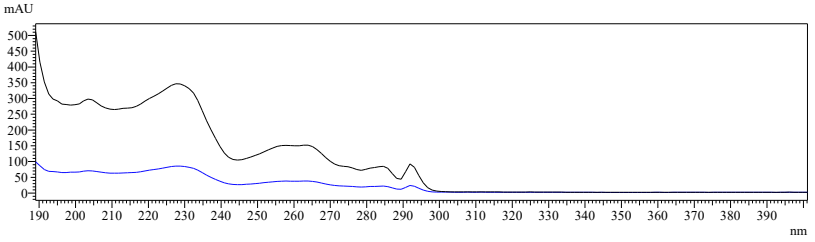


## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-3indole-AZETIDINE-chiral-IC-10%0.8mL




JJX-3indole-AZETIDINE-chiral-IC-10%0.8mL_001.lcd

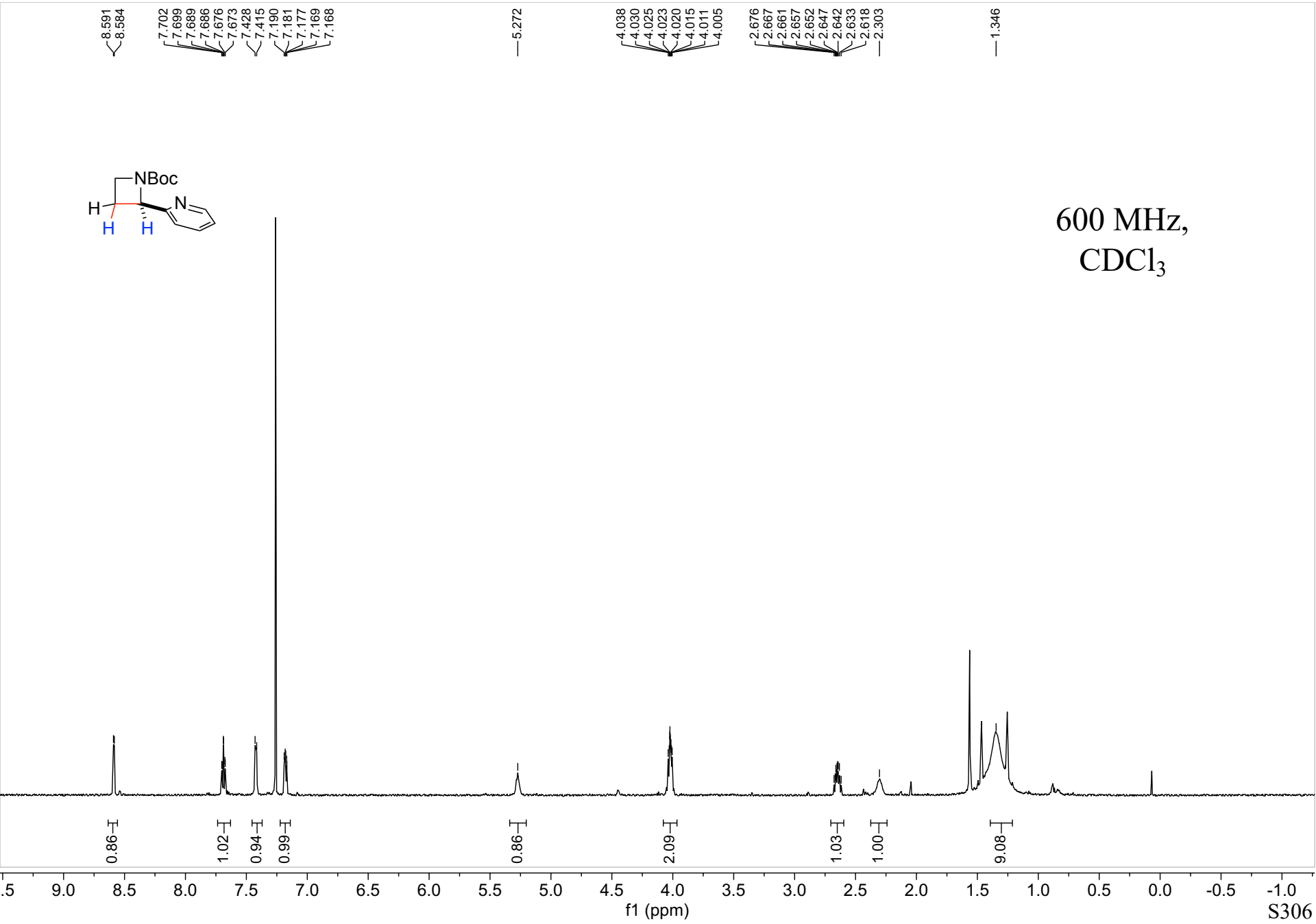



Peak Table

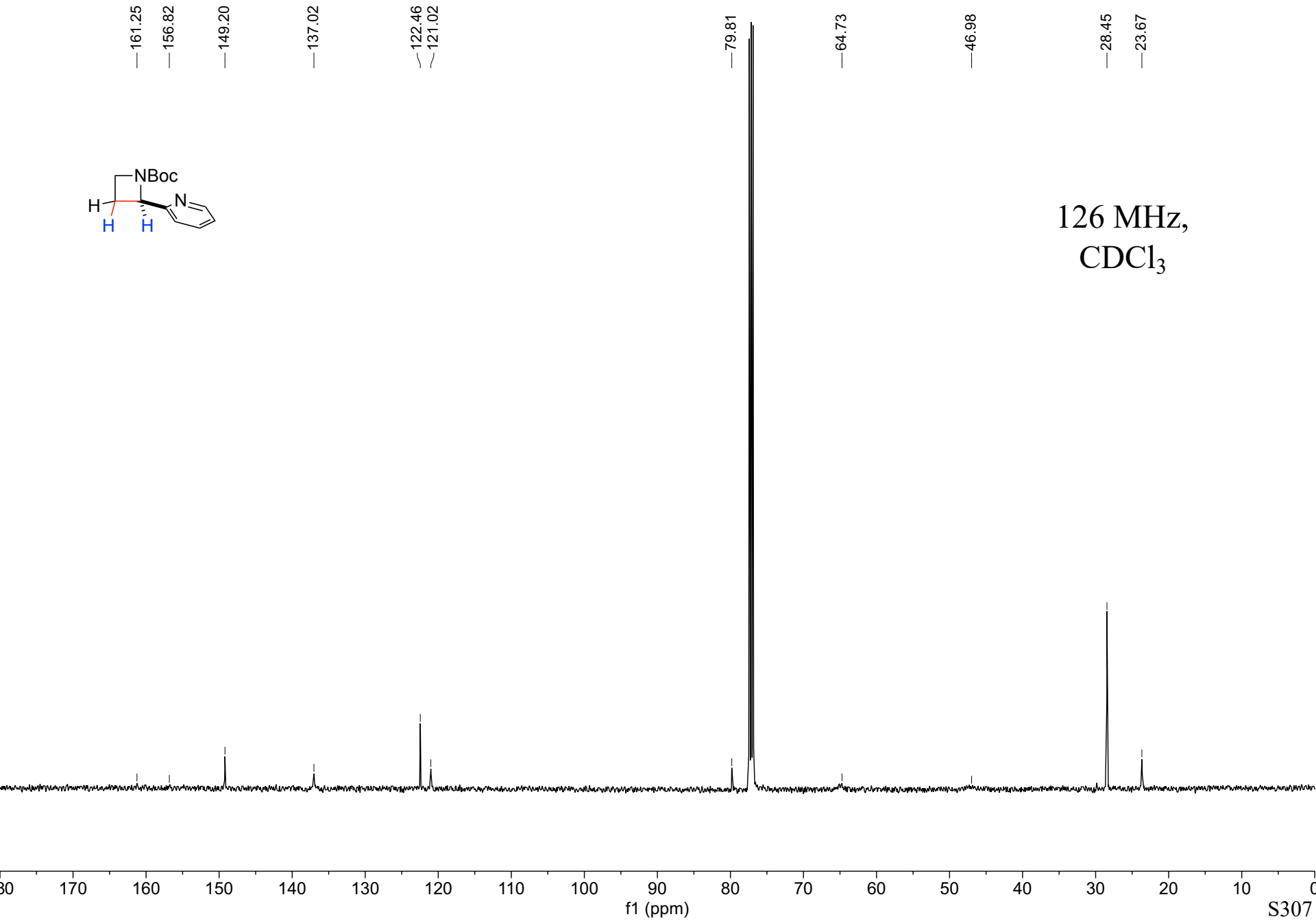
PDA Ch1 247nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 17.744 | 12.507 |
| 2 | 25.090 | 87.493 |
| Total | | 100.000 |

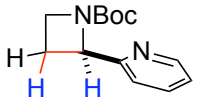
# $^{1}$H NMR *tert*-Butyl (*R*)-2-(pyridin-2-yl)azetidine-1-carboxylate (**2s**)



# $^{13}$C NMR *tert*-Butyl (*R*)-2-(pyridin-2-yl)azetidine-1-carboxylate (**2s**)



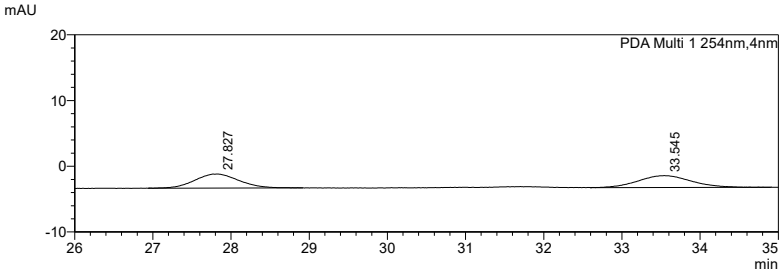
# **HPLC** *tert*-Butyl (*R*)-2-(pyridin-2-yl)azetidine-1-carboxylate (**2s**)





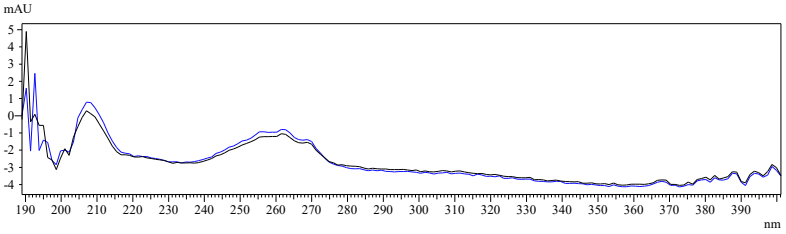

## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-2pyridine-rac-AZETIDINE-IC-10%0.8mL




UV Spectrum

JJX-2pyridine-rac-AZETIDINE-IC-10%0.8mL_001.lcd




Peak Table

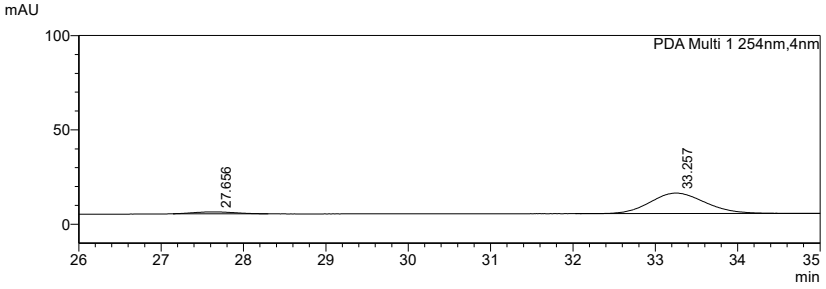
PDA Ch1 254nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 27.827 | 49.614 |
| 2 | 33.545 | 50.386 |
| Total | | 100.000 |



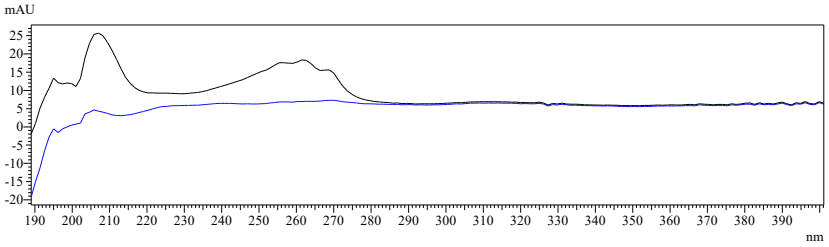
## ==== Shimadzu LabSolutions Analysis Report ====

Sample Name : JJX-2pyridine-chiral-AZETIDINE-IC-10%0.8mL




UV Spectrum

JJX-2pyridine-chiral-AZETIDINE-IC-10%0.8mL_001.lcd

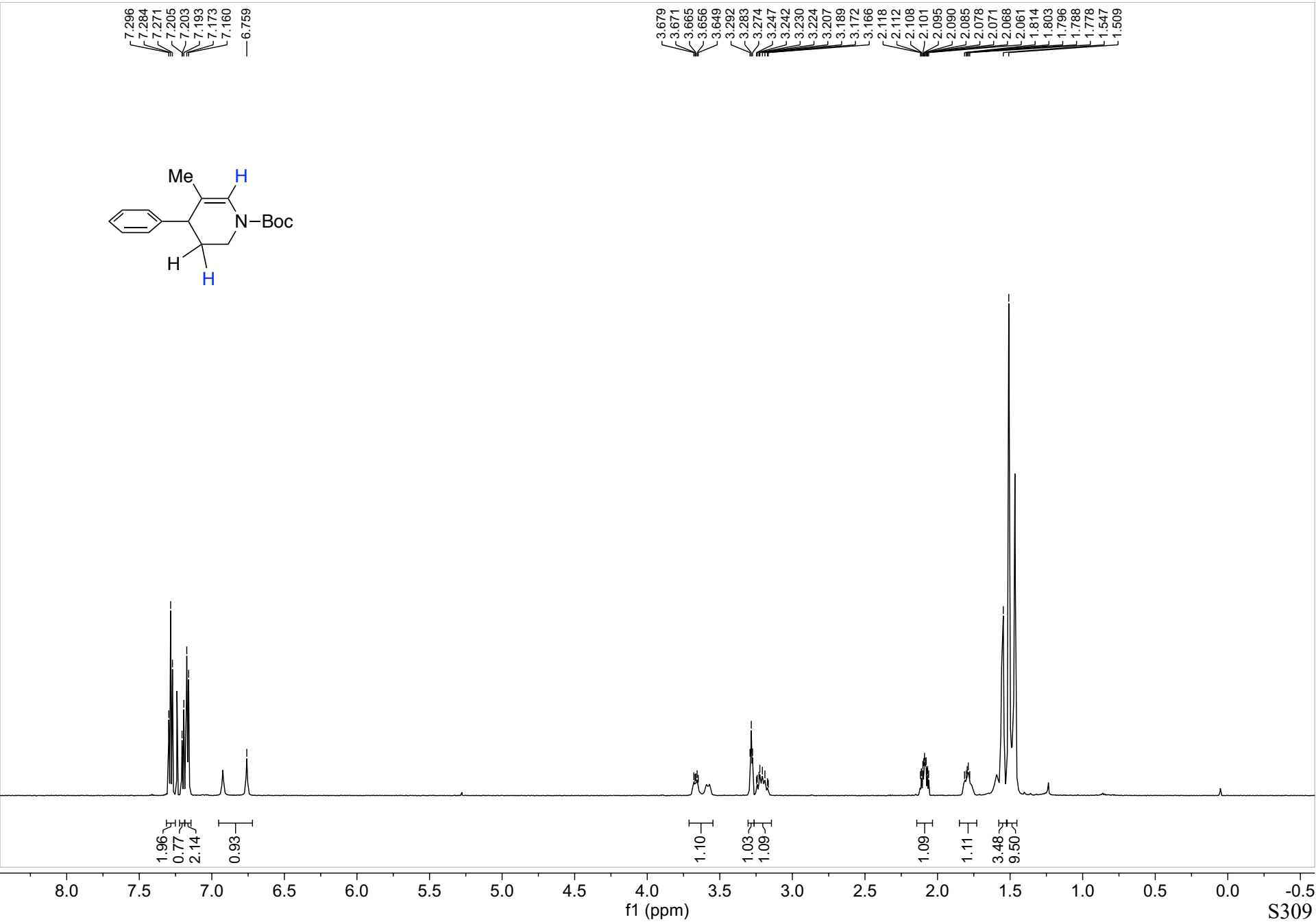



Peak Table

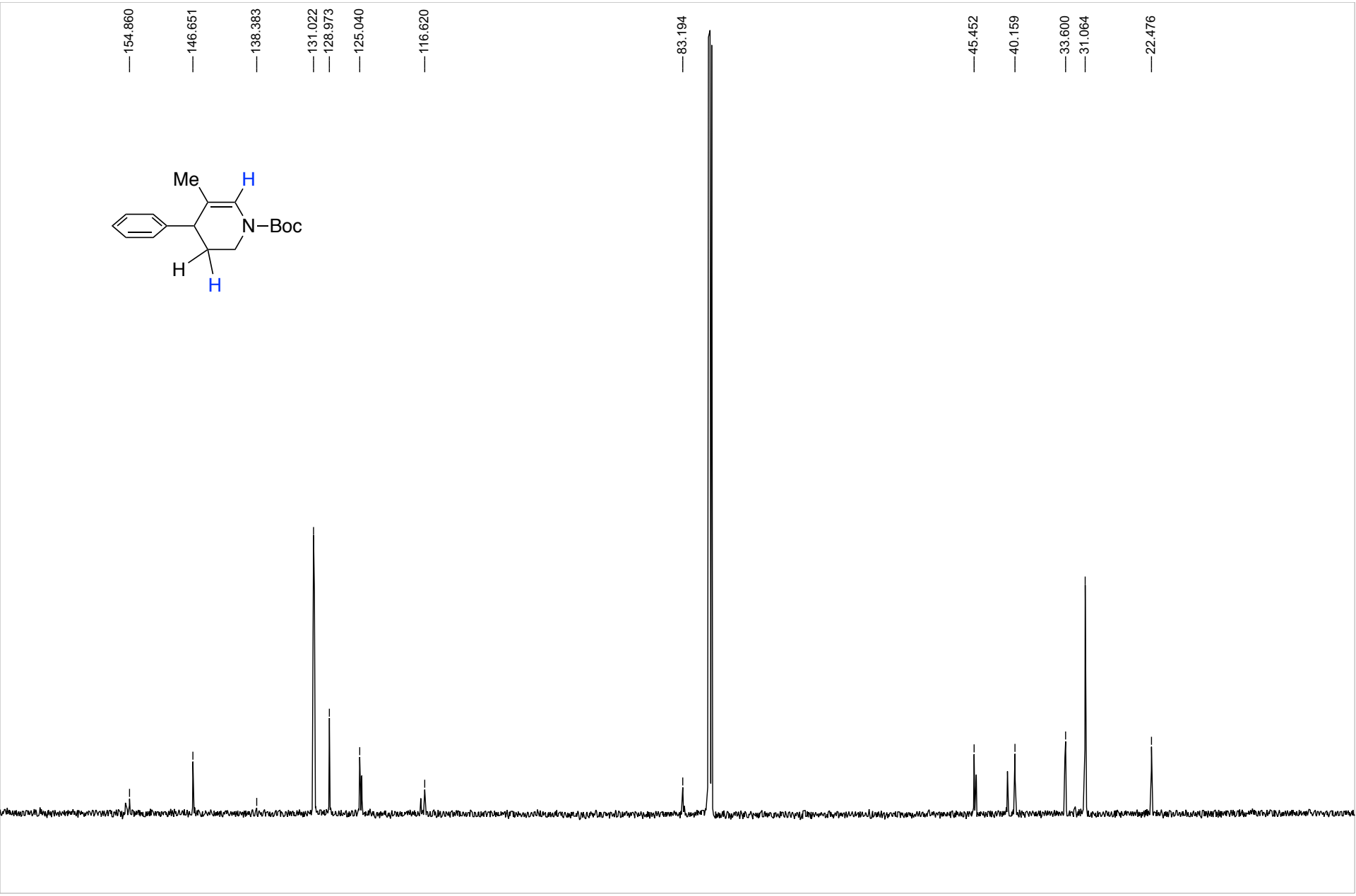
PDA Ch1 254nm

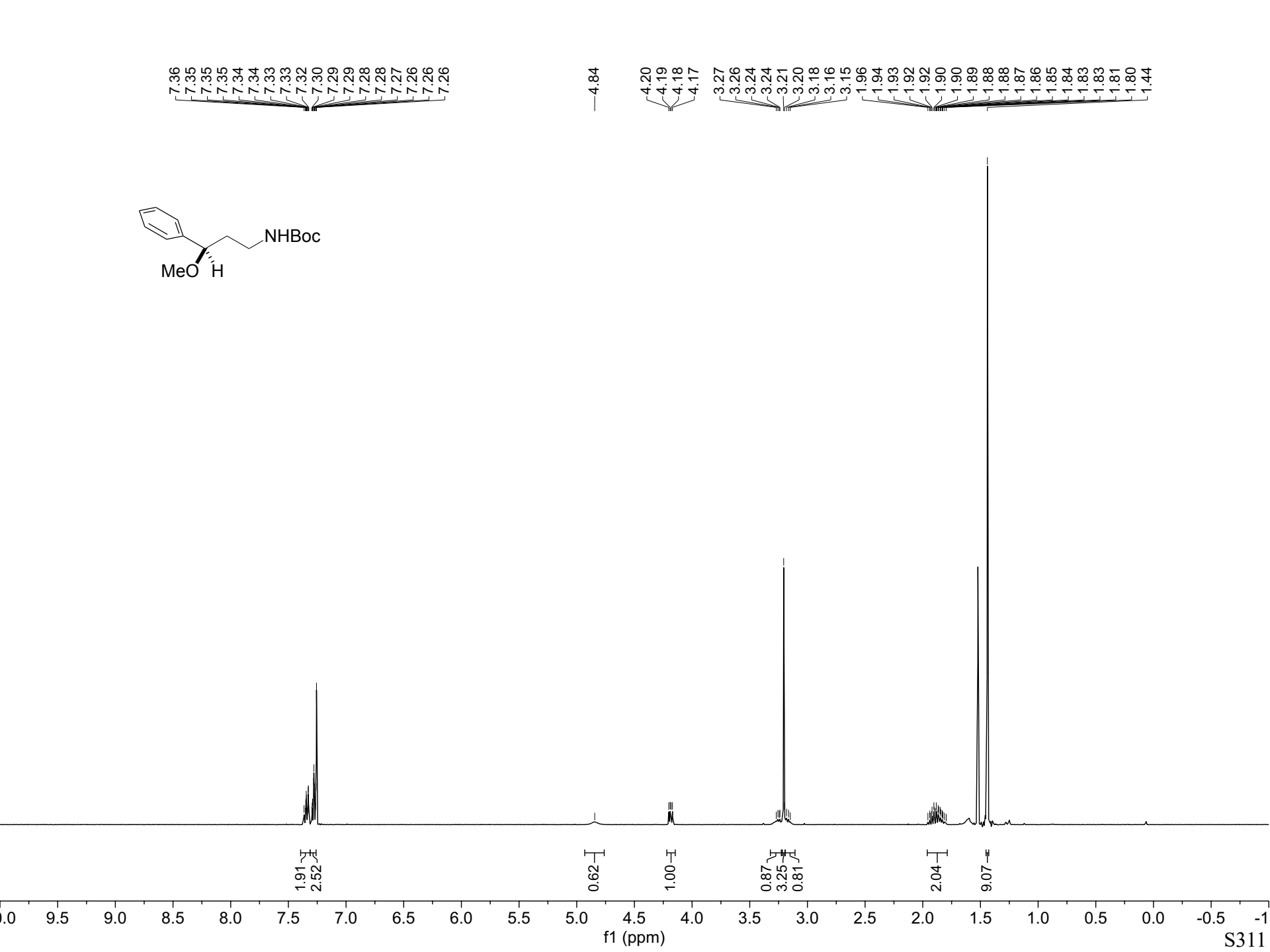
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 27.656 | 6.151 |
| 2 | 33.257 | 93.849 |
| Total | | 100.000 |

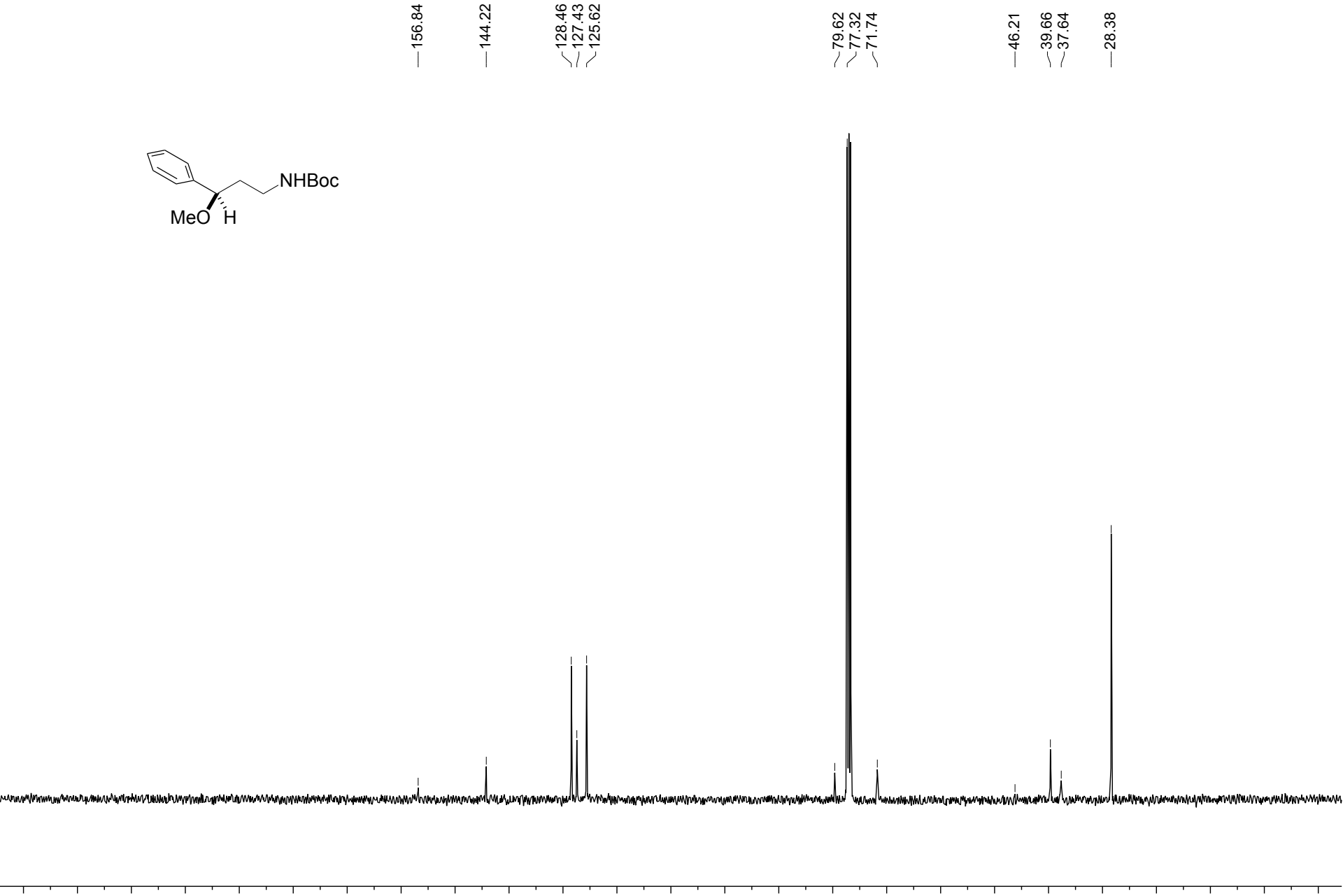
# $^{1}$H NMR *tert*-butyl-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate

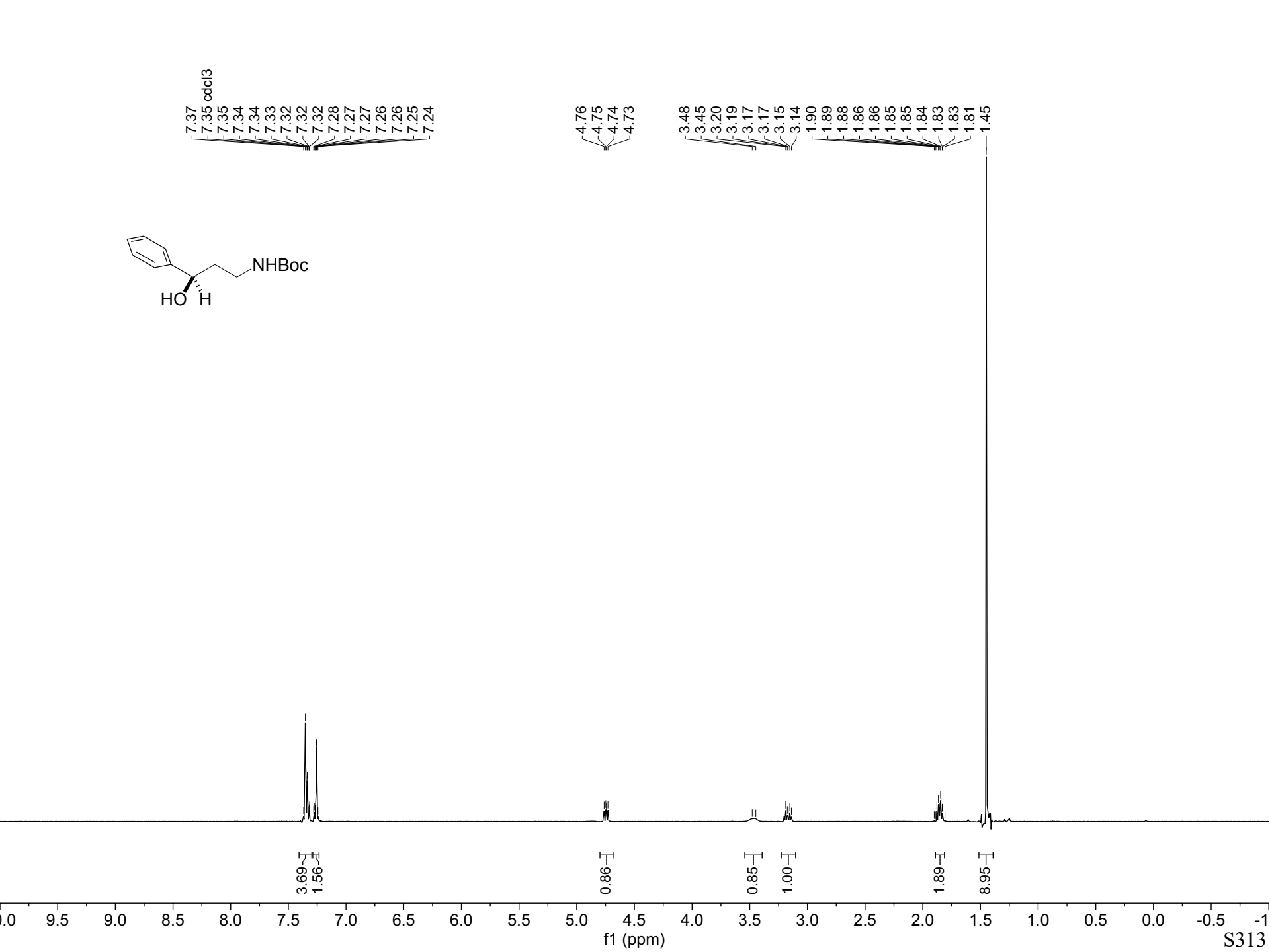


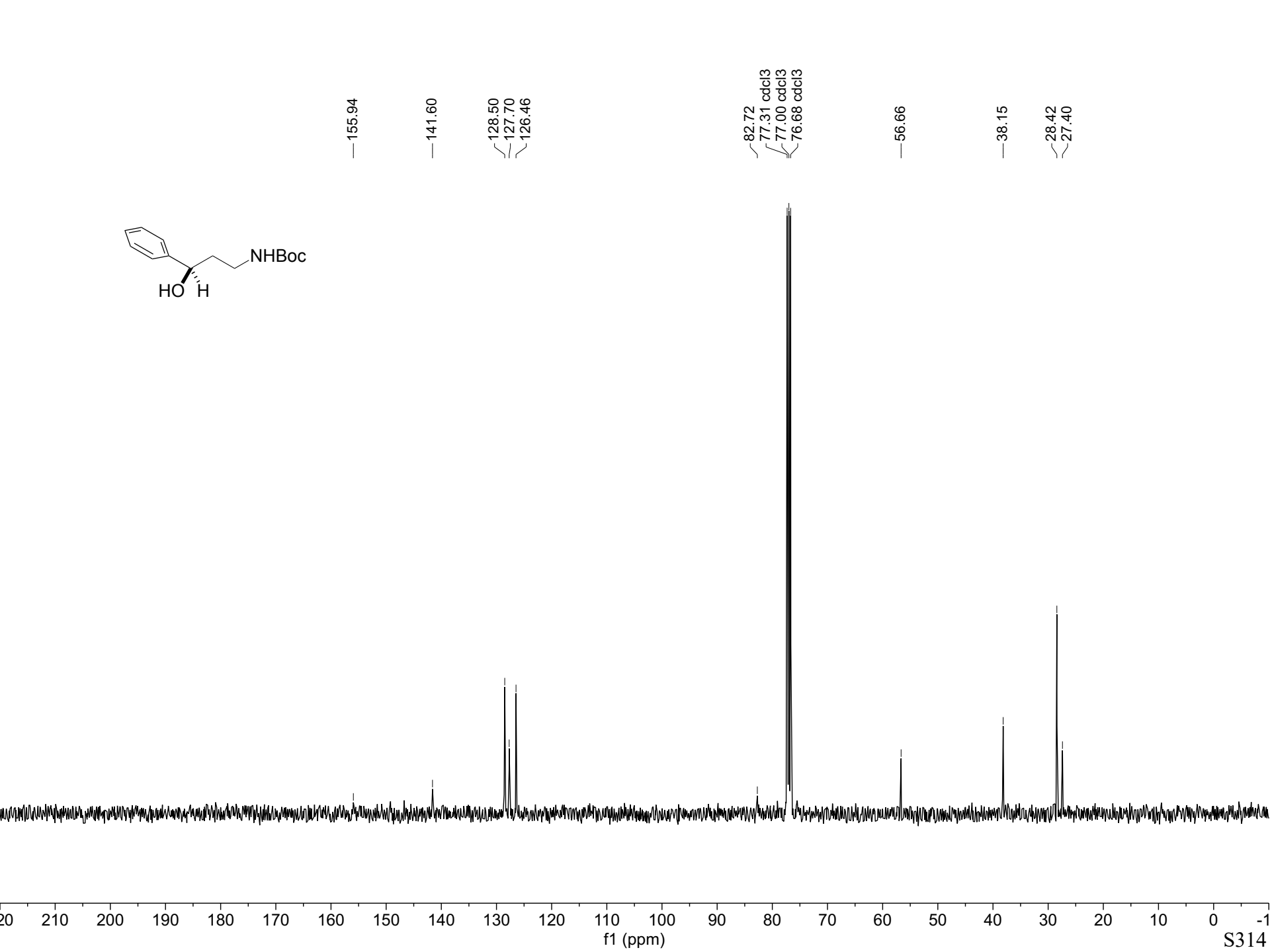
# $^{13}$C NMR *tert*-butyl-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate




7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.26
4.84
4.20
4.19
4.18
4.17
3.27
3.26
3.24
3.24
3.21
3.20
3.18
3.16
3.15
1.96
1.94
1.93
1.92
1.92
1.90
1.90
1.89
1.88
1.88
1.87
1.86
1.85
1.84
1.83
1.83
1.81
1.80
1.44
NHBoc
MeO
H
1.91
2.52
0.62
1.00
0.87
3.25
0.81
2.04
9.07
f1 (ppm)

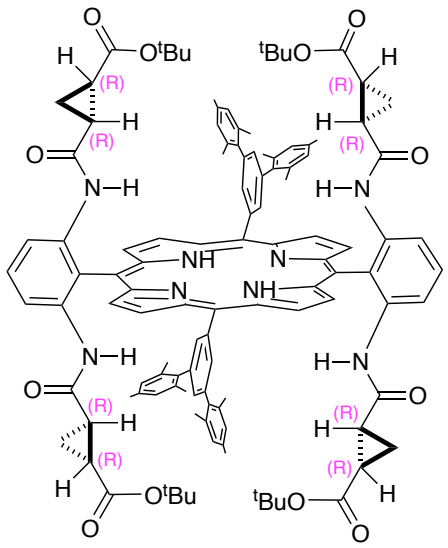

156.84
144.22
128.46
127.43
125.62
79.62
77.32
71.74
46.21
39.66
37.64
28.38
NHBoc
MeO
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37
7.35 cdcl3
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.27
7.27
7.26
7.26
7.25
7.24
4.76
4.75
4.74
4.73
3.48
3.45
3.20
3.19
3.17
3.17
3.15
3.14
1.90
1.89
1.88
1.86
1.86
1.85
1.85
1.84
1.83
1.83
1.81
1.45
NHBoc
HO
H
3.69
1.56
0.86
0.85
1.00
1.89
8.95
f1 (ppm)

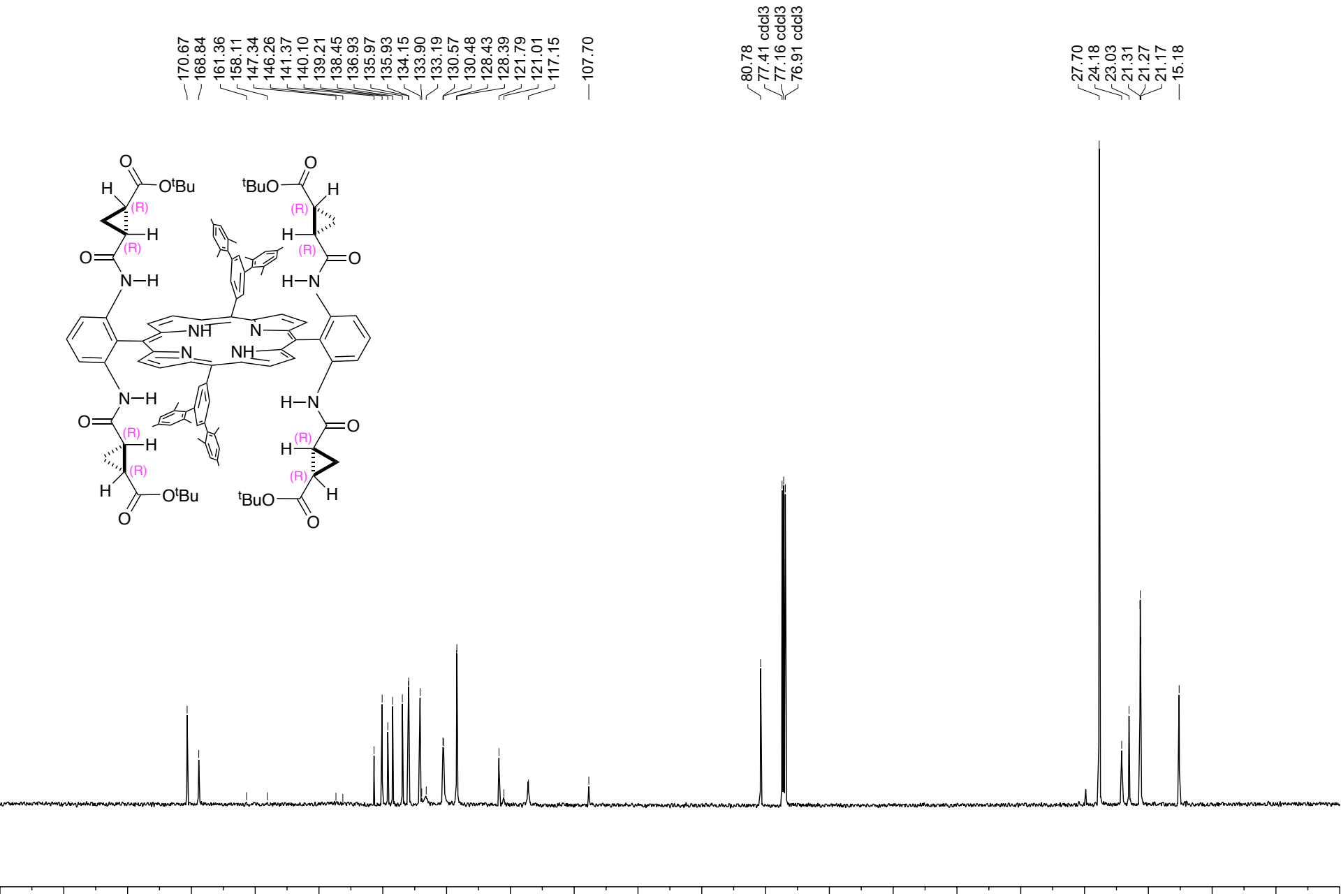

155.94
141.60
128.50
127.70
126.46
82.72
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
56.66
38.15
28.42
27.40
NHBoc
HO
H
f1 (ppm)

# Spectral Data for Chapter 4

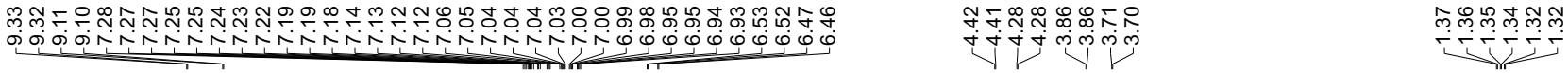
# $^{1}$H NMR 3,5-DiMes-Tao($^{t}$Bu)Phyrin

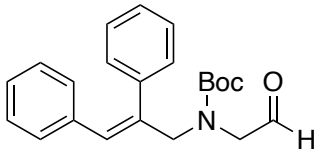


# $^{13}$C NMR 3,5-DiMes-Tao($^t$Bu)Phyrin

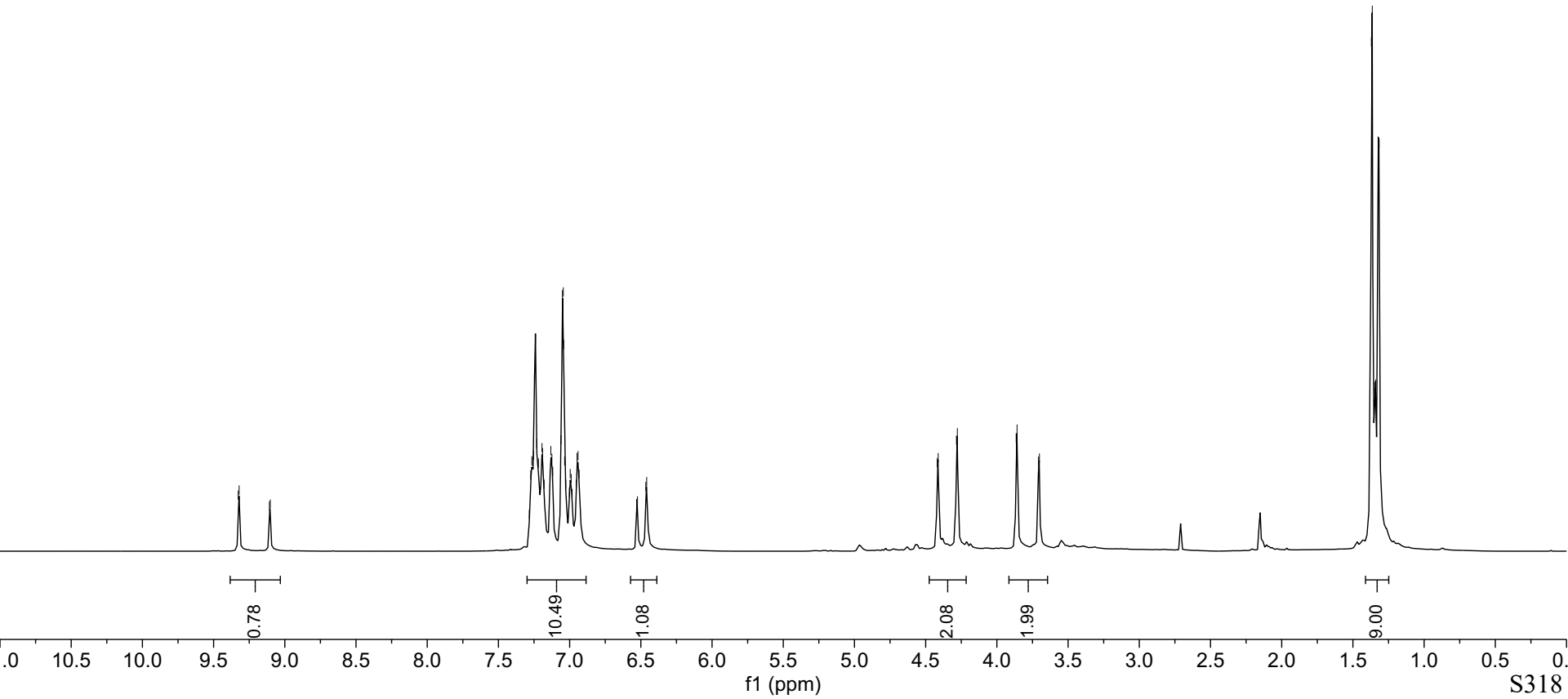


# $^1$H NMR *tert*-Butyl (*E*)-(2,3-diphenylallyl)(2-oxoethyl)carbamate (1a')

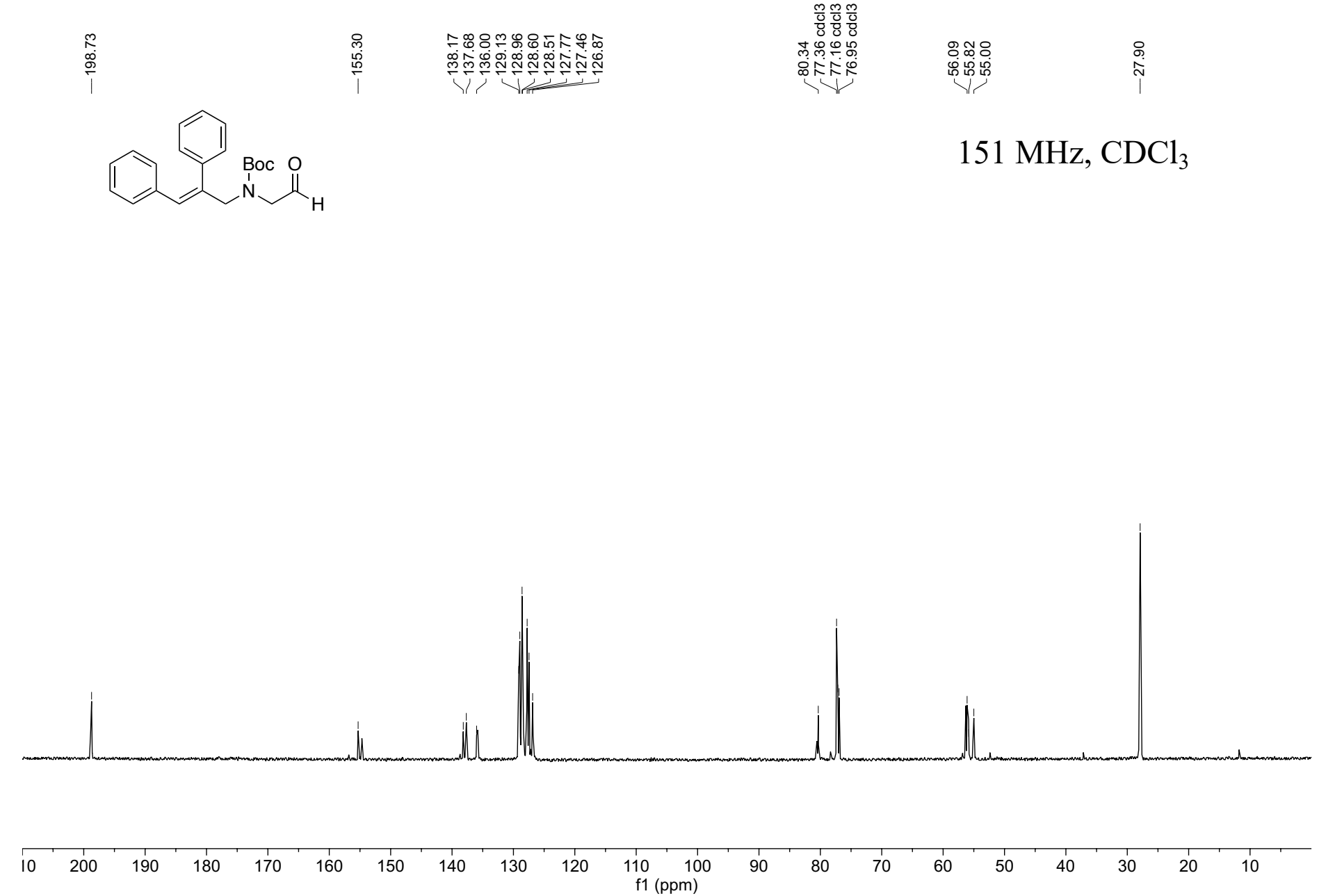


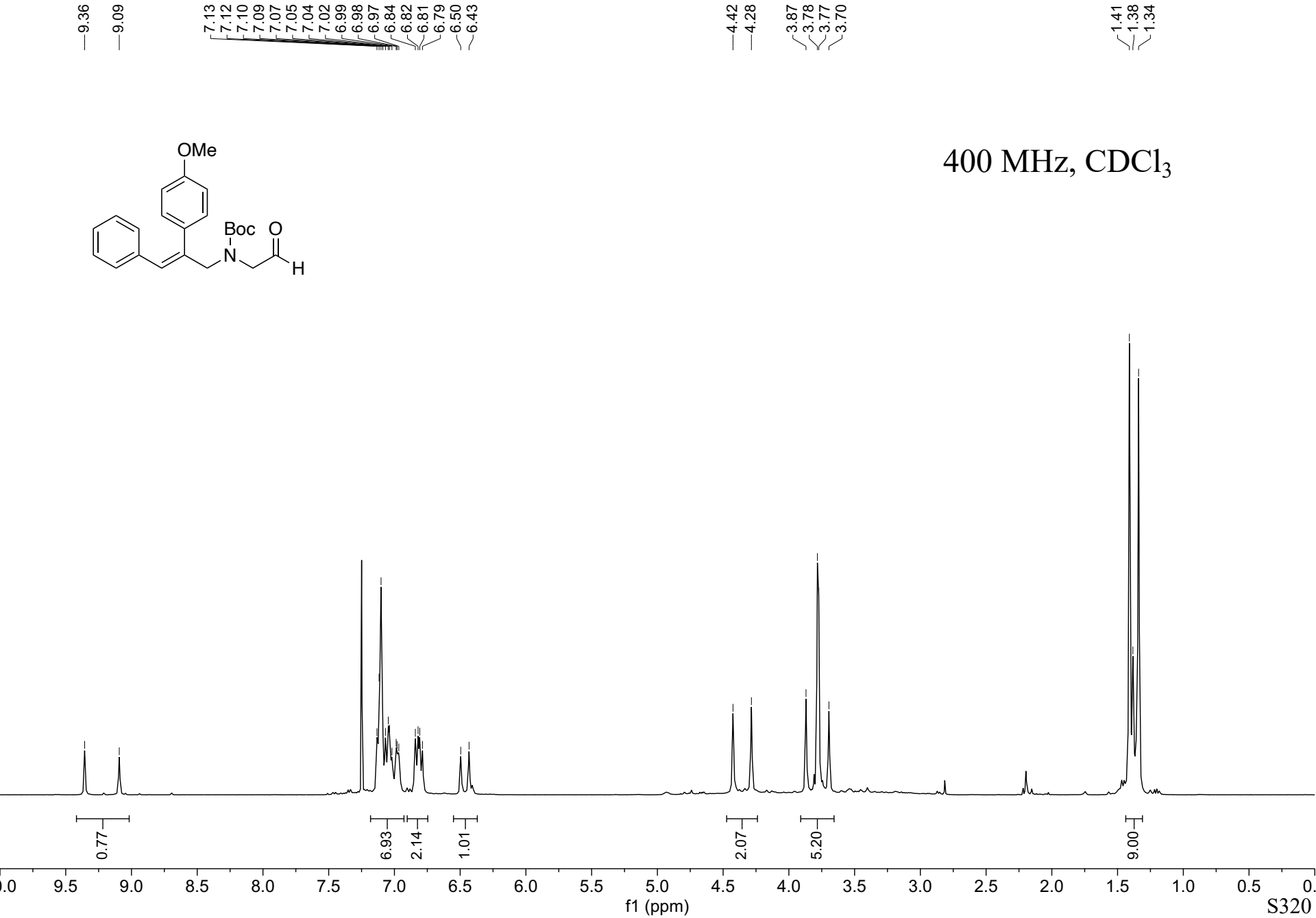

600 MHz, $CDCl_3$



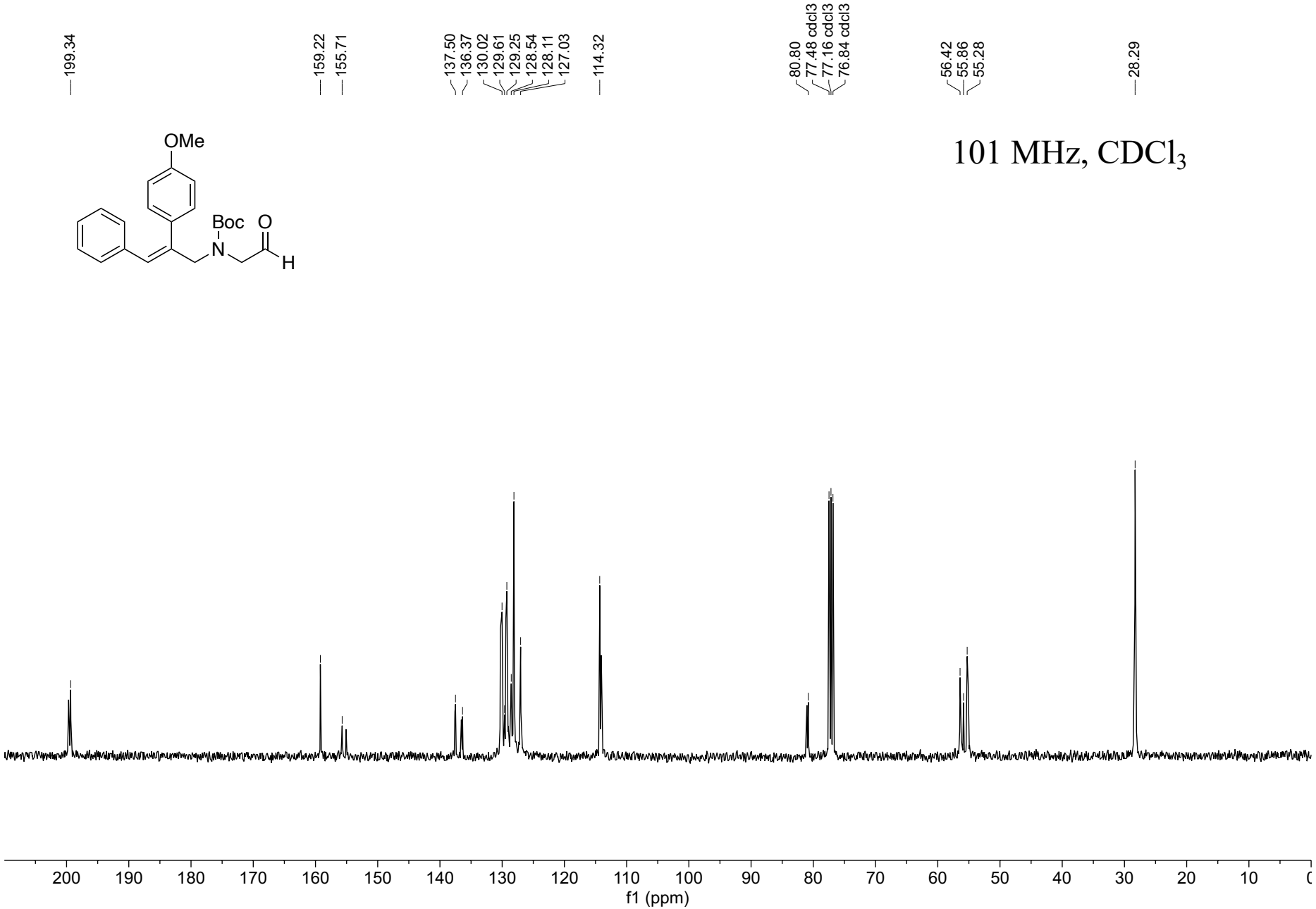
# $^{13}$C NMR *tert*-Butyl (*E*)-(2,3-diphenylallyl)(2-oxoethyl)carbamate (1a')



# $^{1}$H NMR *tert*-Butyl (E)-(2-(4-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate(1b')

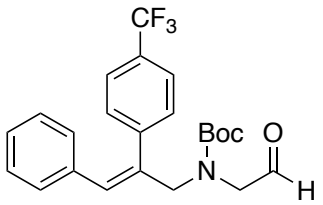


# $^{13}$C NMR *tert*-Butyl (E)-(2-(4-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate(1b')

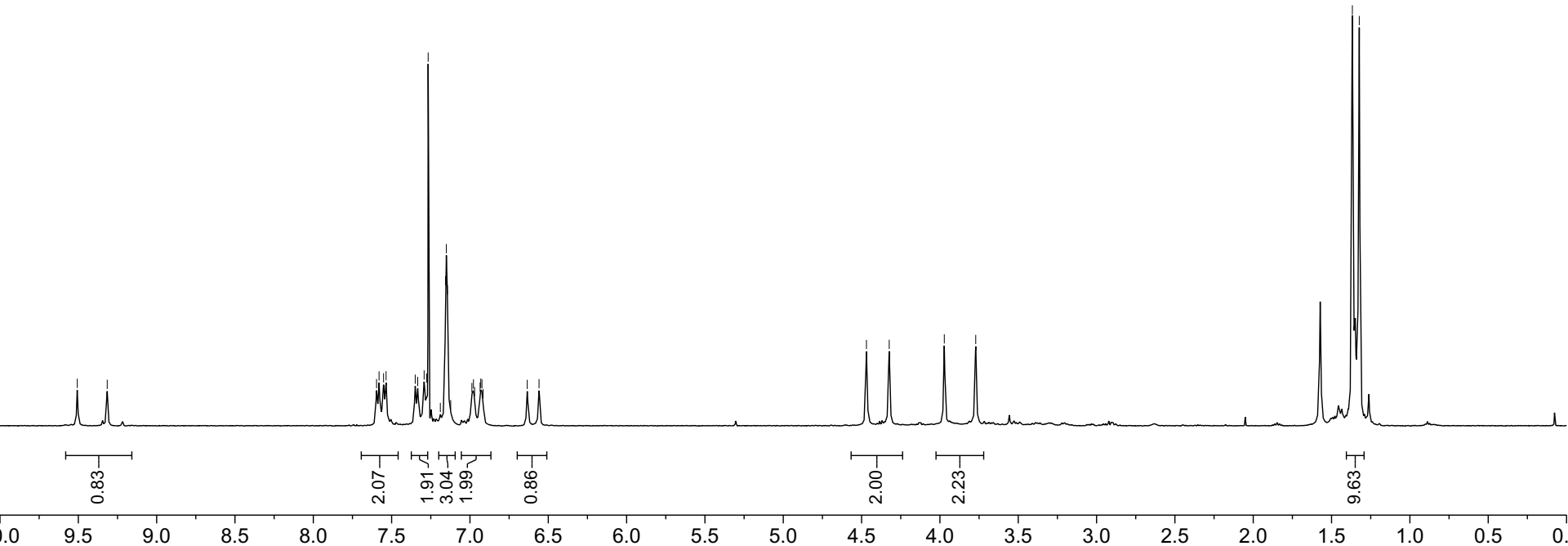


# $^1$H NMR *tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)carbamate (1c')

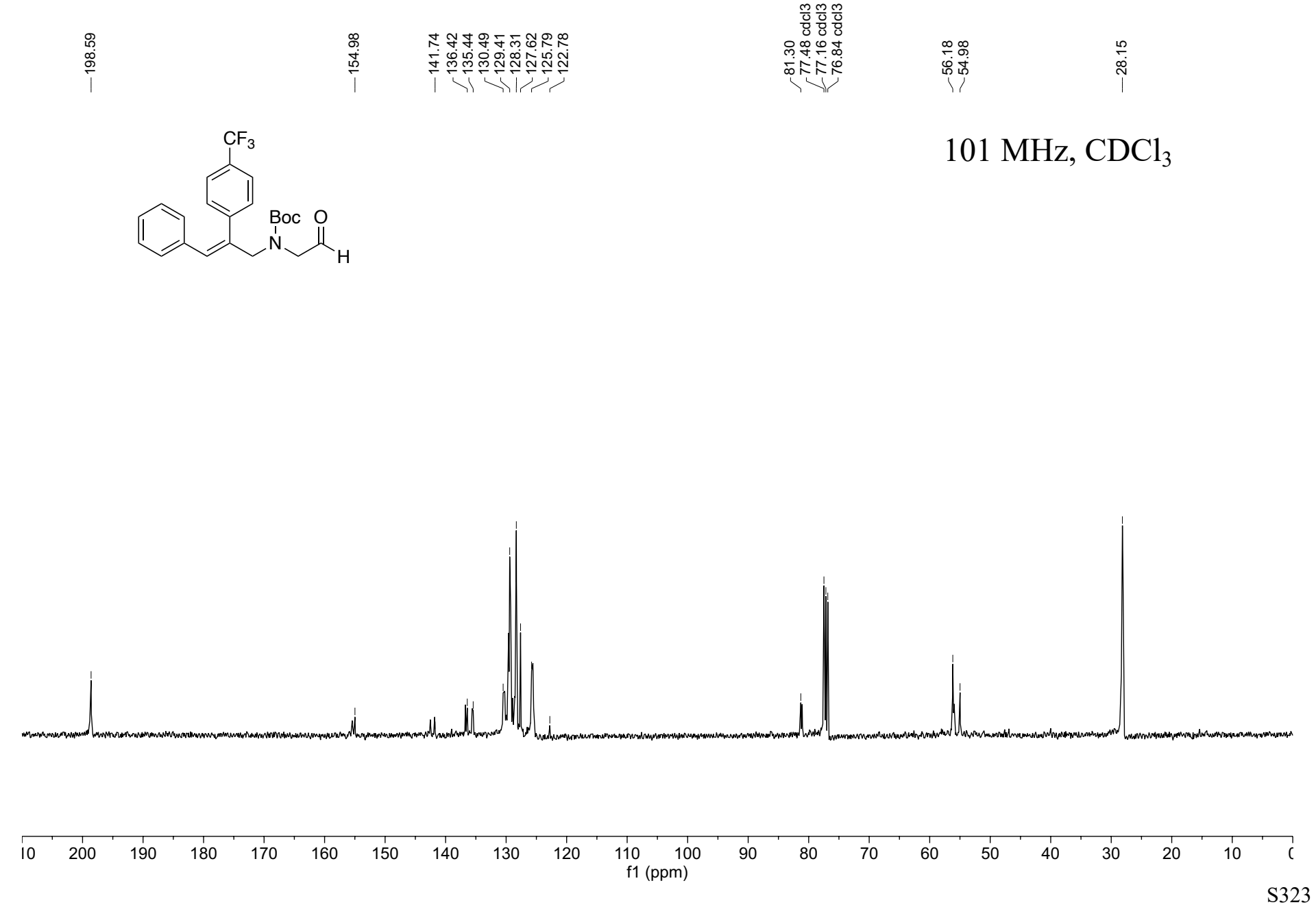


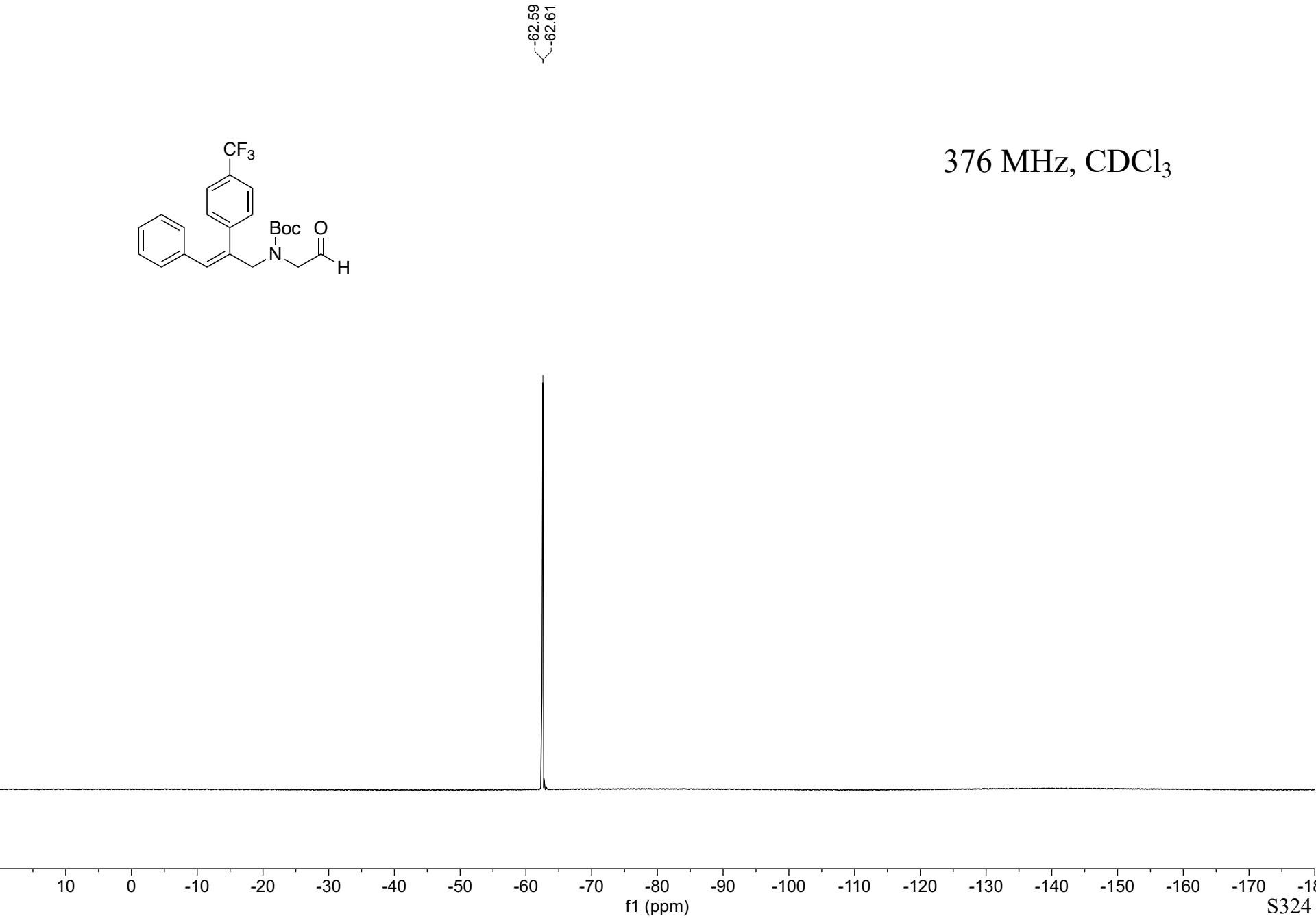

500 MHz, $CDCl_3$



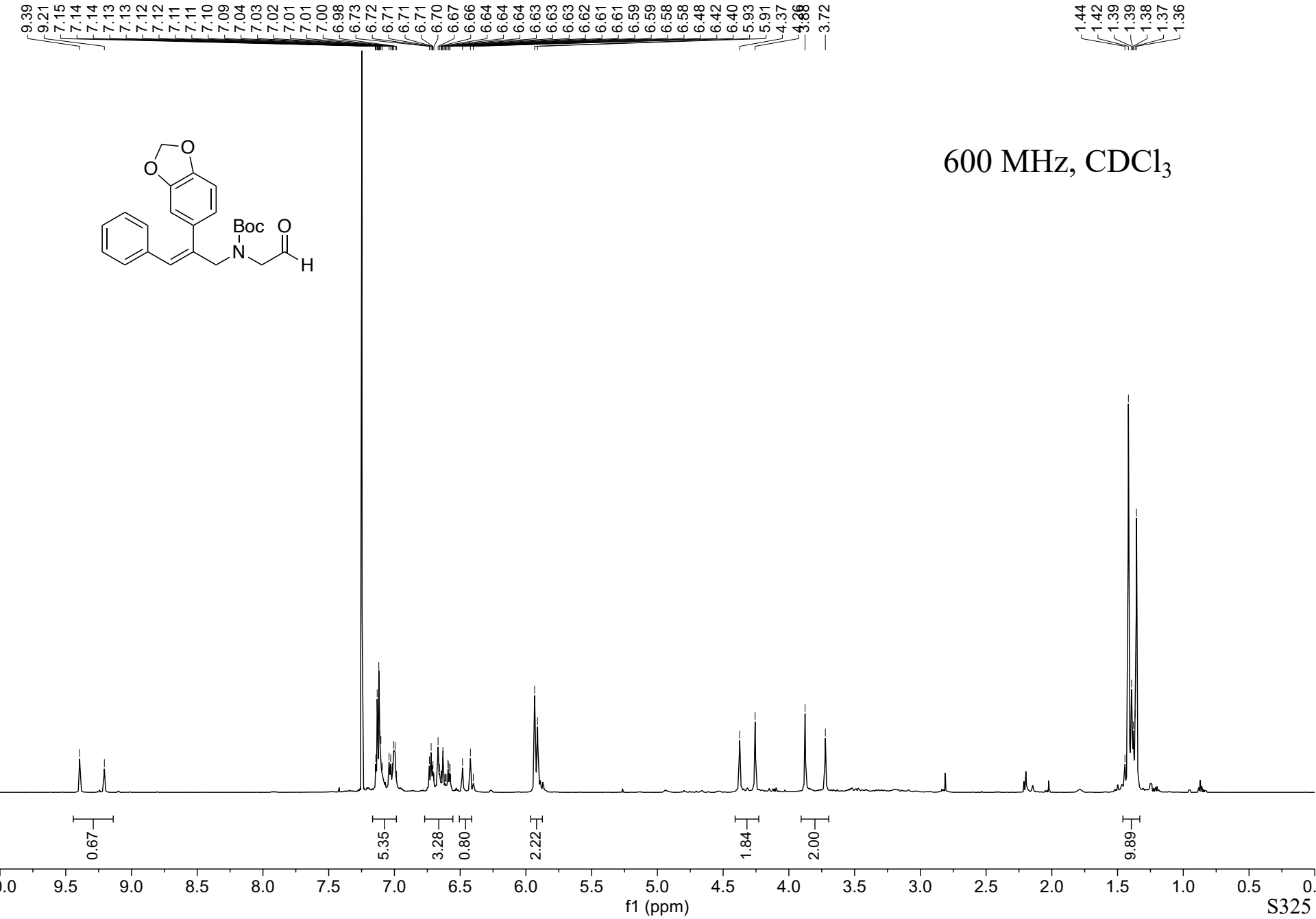
# $^{13}$C NMR *tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)carbamate (1c')



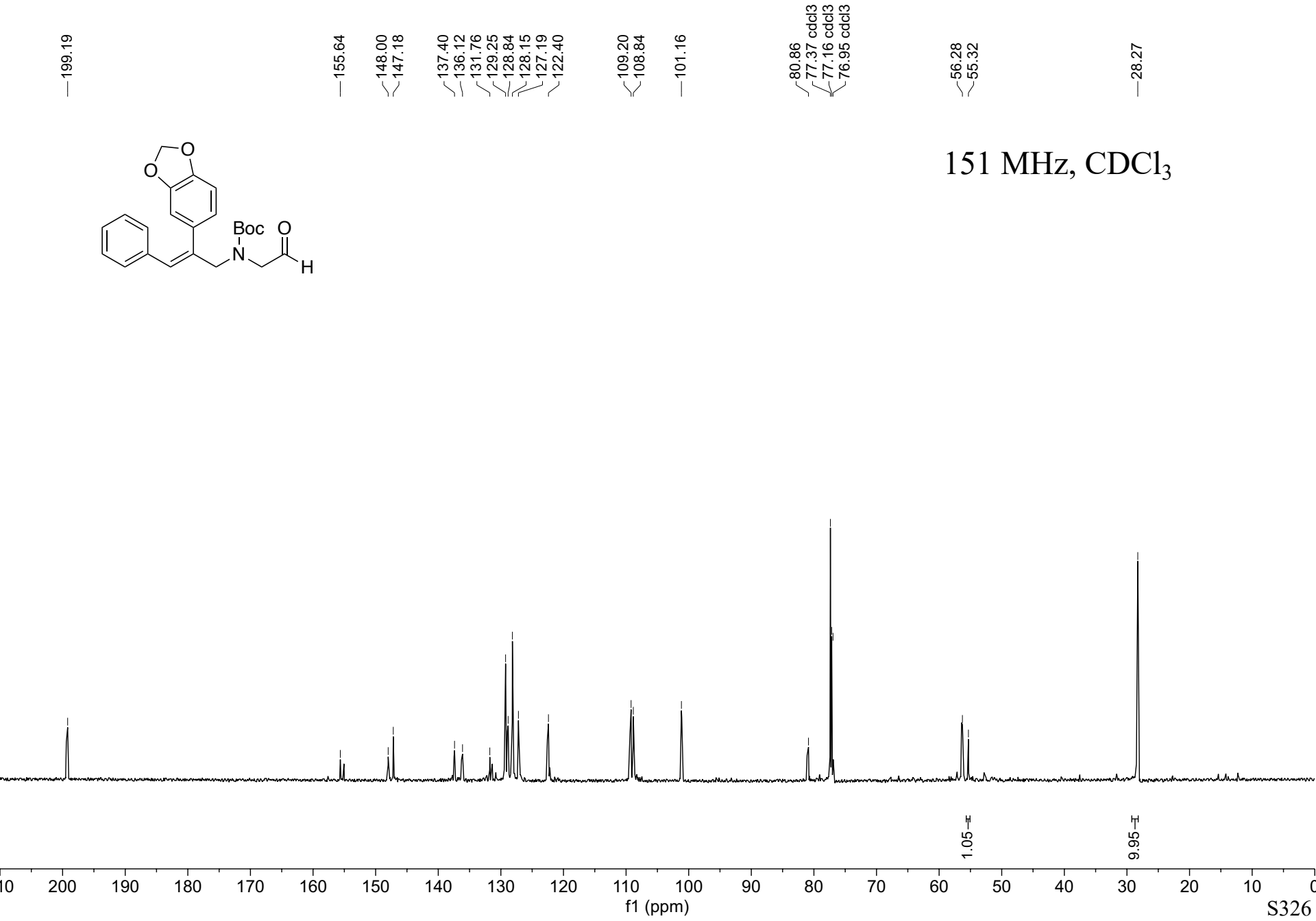
**$^{19}$F NMR *tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)carbamate (1c')**



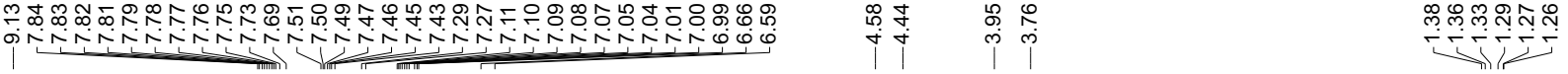
# $^1$H NMR *tert*-Butyl (*E*)-(2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1d')

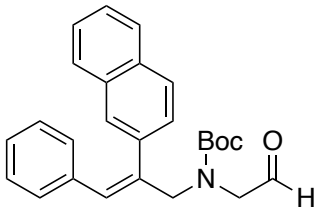


# $^{13}$C NMR *tert*-Butyl (*E*)-(2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1d')

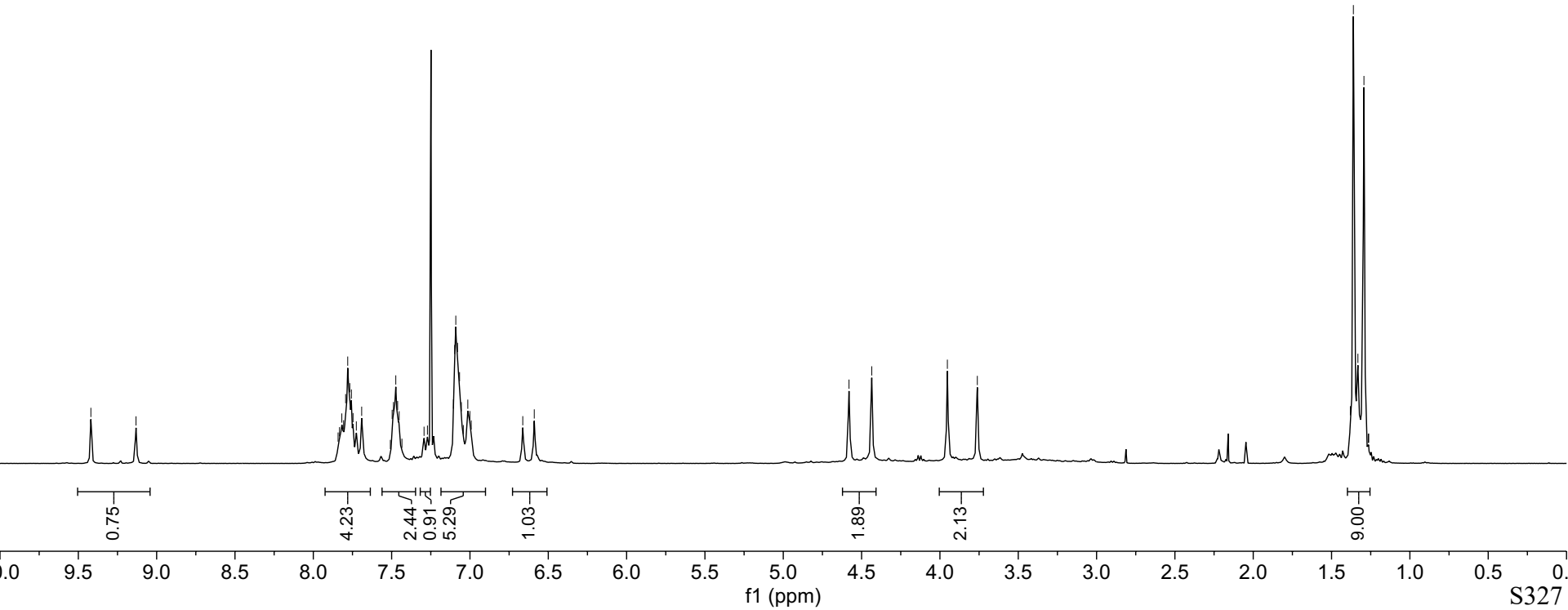


# $^1$H NMR *tert*-Butyl (E)-(2-(naphthalen-2-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1e')

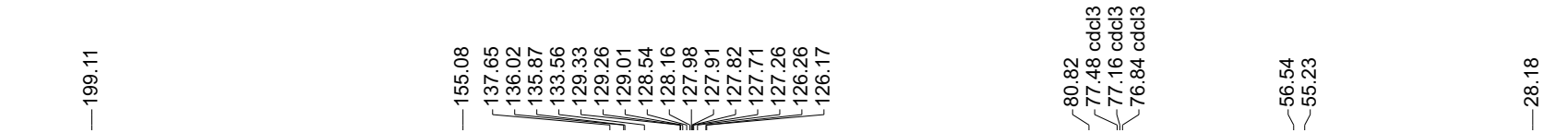


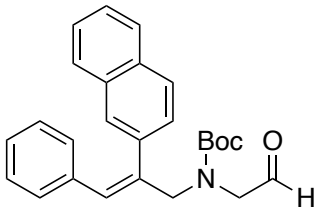




400 MHz, $CDCl_3$

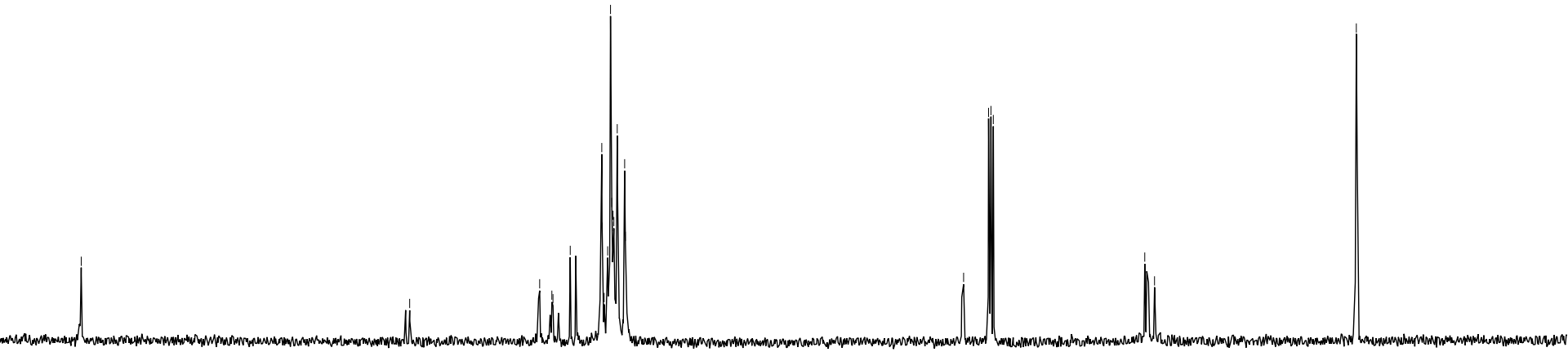


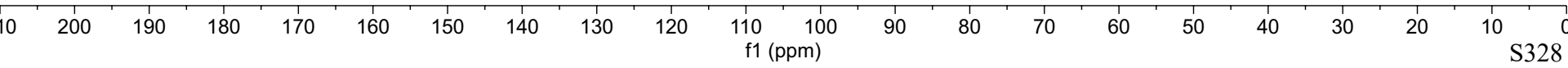
# $^{13}$C NMR *tert*-Butyl (E)-(2-(naphthalen-2-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1e')



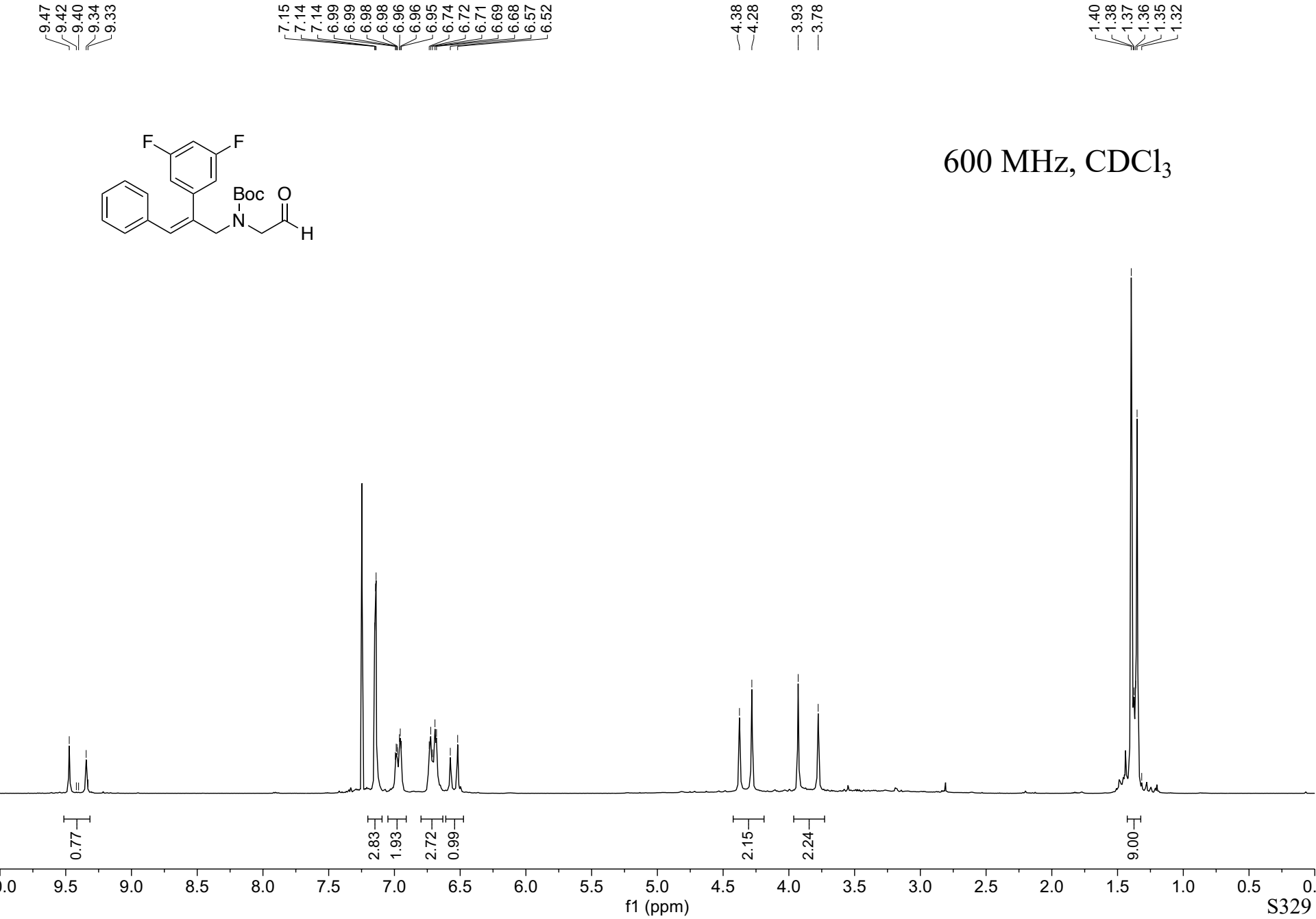




101 MHz, $CDCl_3$

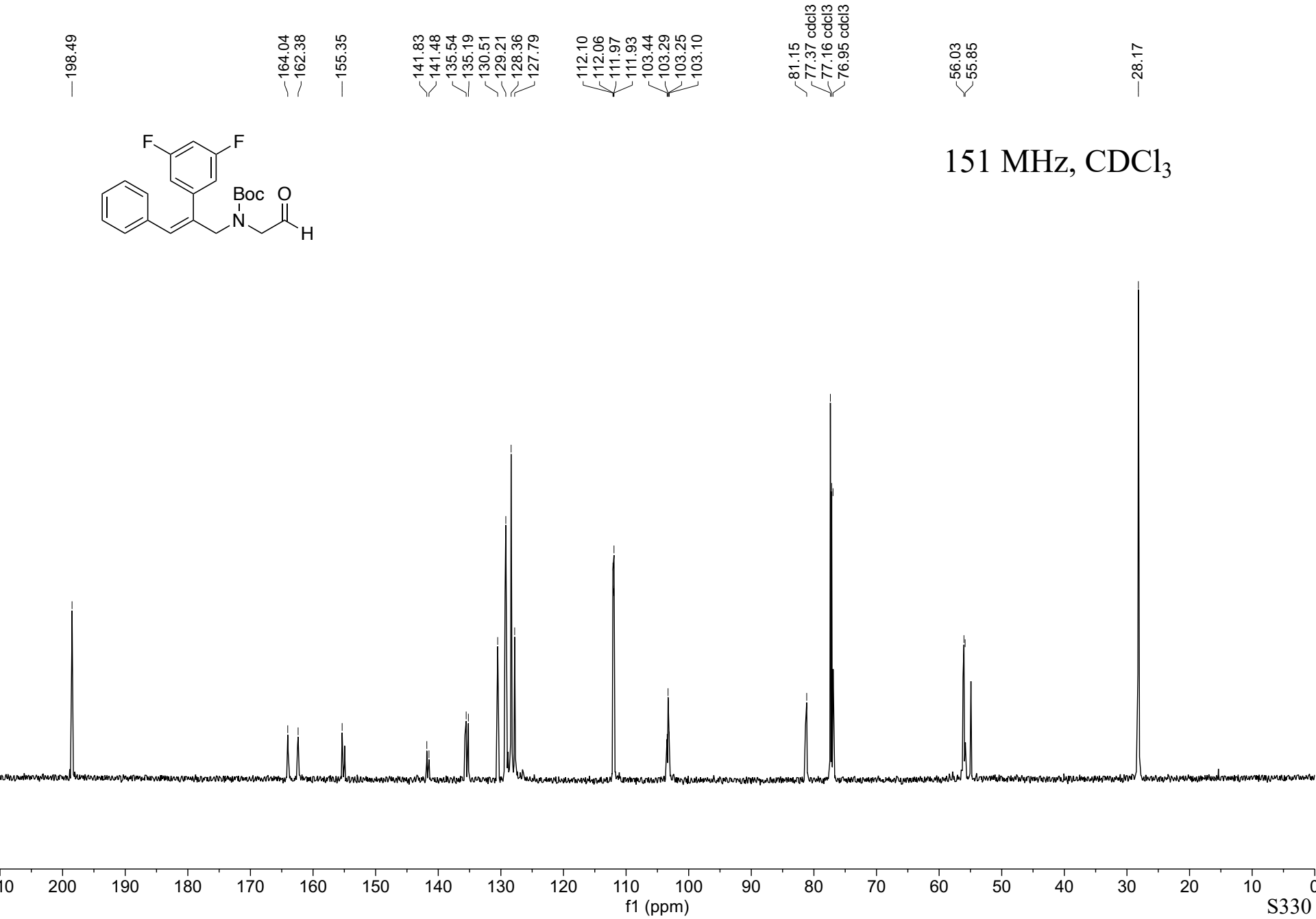




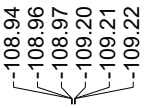
# $^{1}$H NMR *tert*-butyl (E)-(2-(3,5-difluorophenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1f')

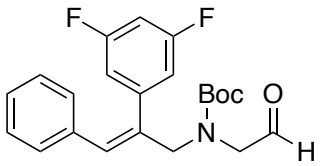


# $^{13}$C NMR *tert*-butyl (E)-(2-(3,5-difluorophenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1f')

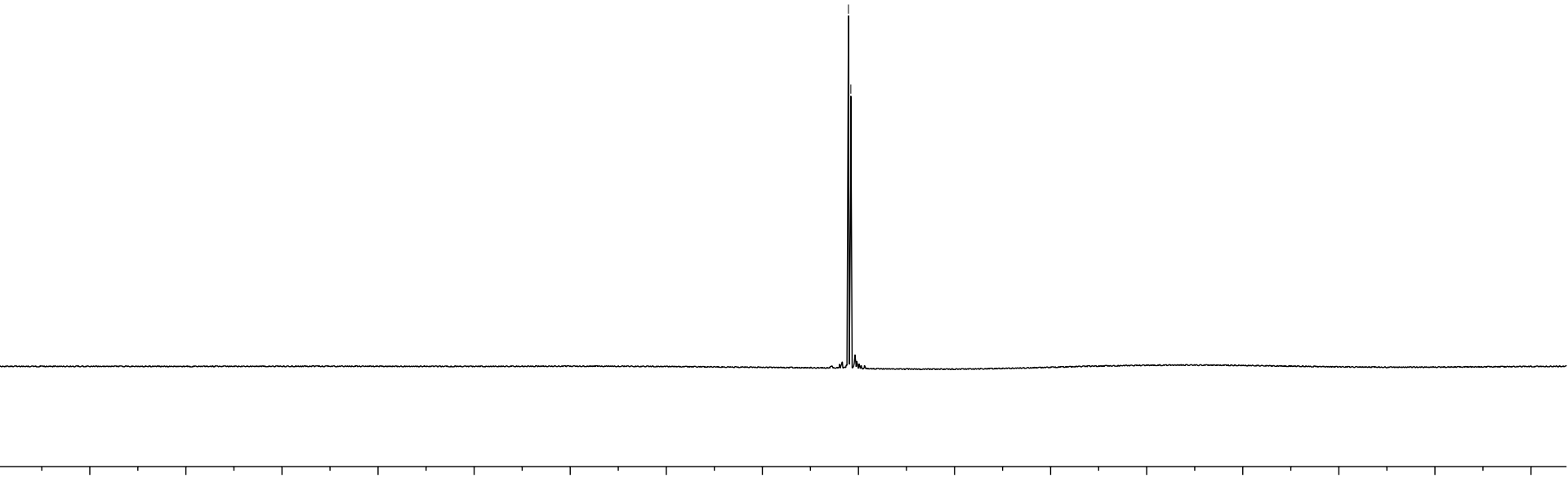


# $^{19}$F NMR *tert*-butyl (E)-(2-(3,5-difluorophenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1f')

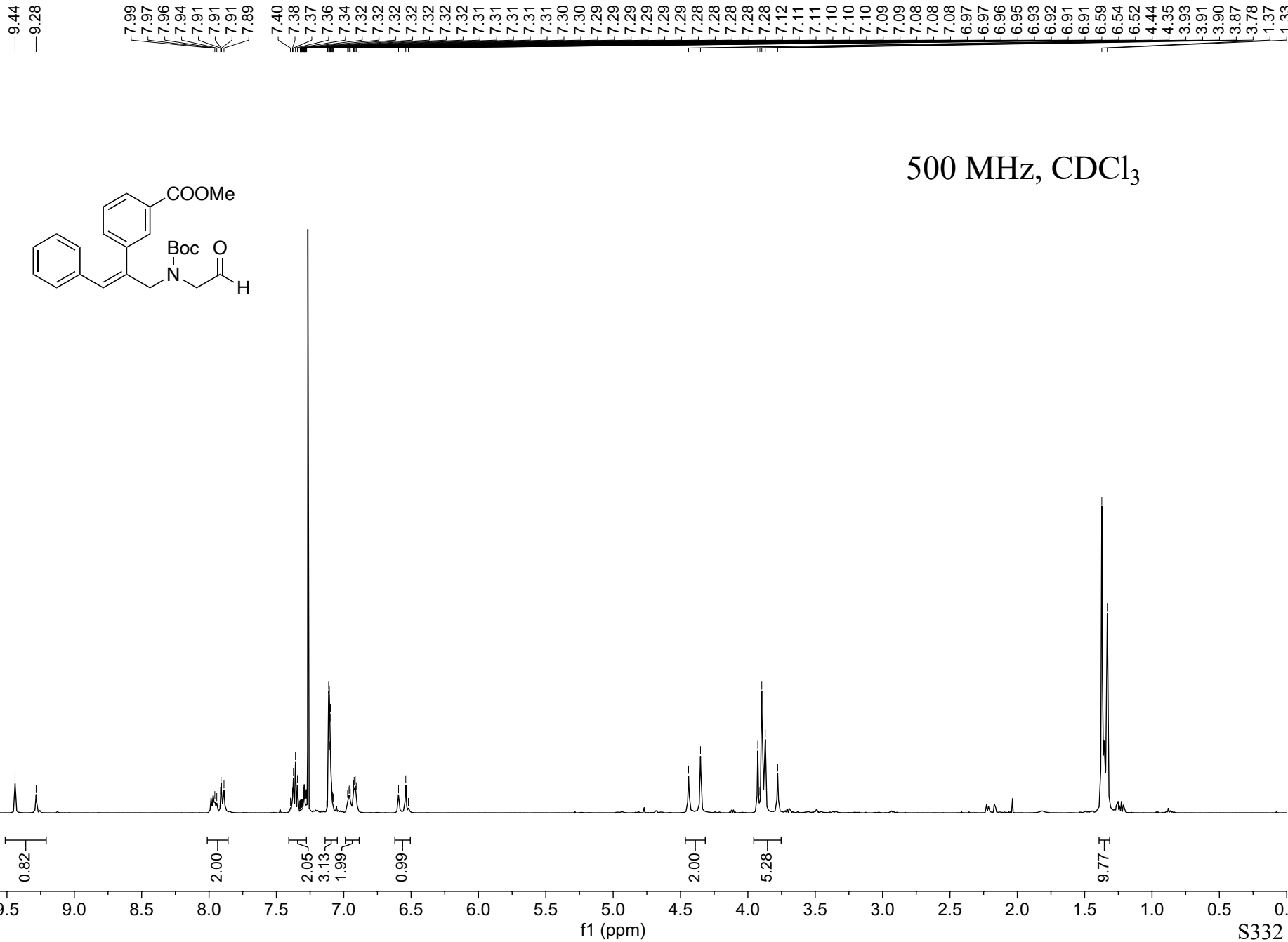


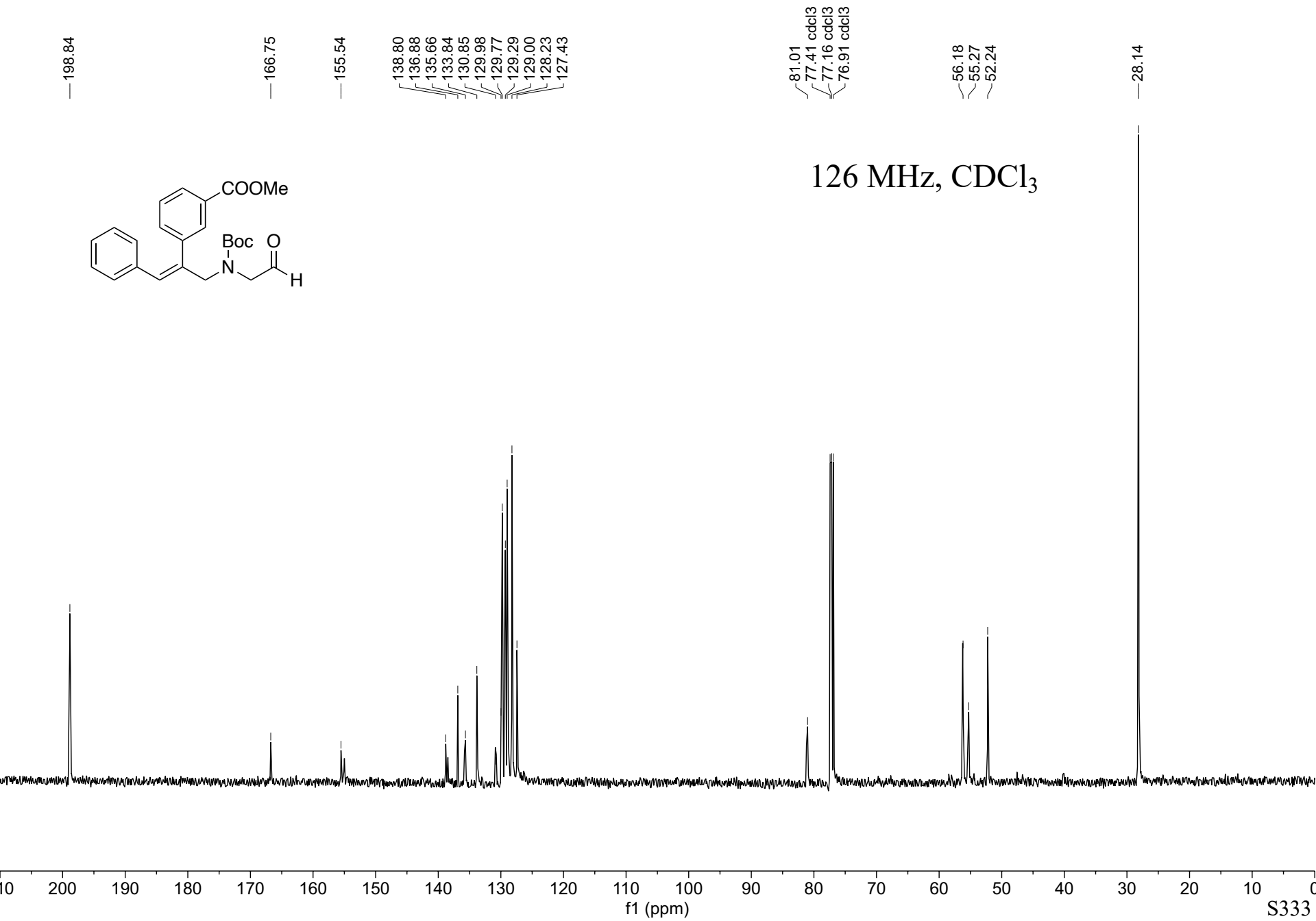

564 MHz, $CDCl_3$



**$^1$H NMR Methyl (*E*)-3-(3-((*tert*-butoxycarbonyl)(2-oxoethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g')**

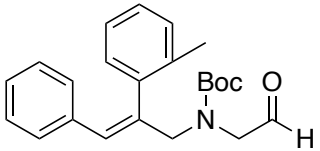


**$^{13}$C NMR Methyl (*E*)-3-(3-((*tert*-butoxycarbonyl)(2-oxoethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g')**

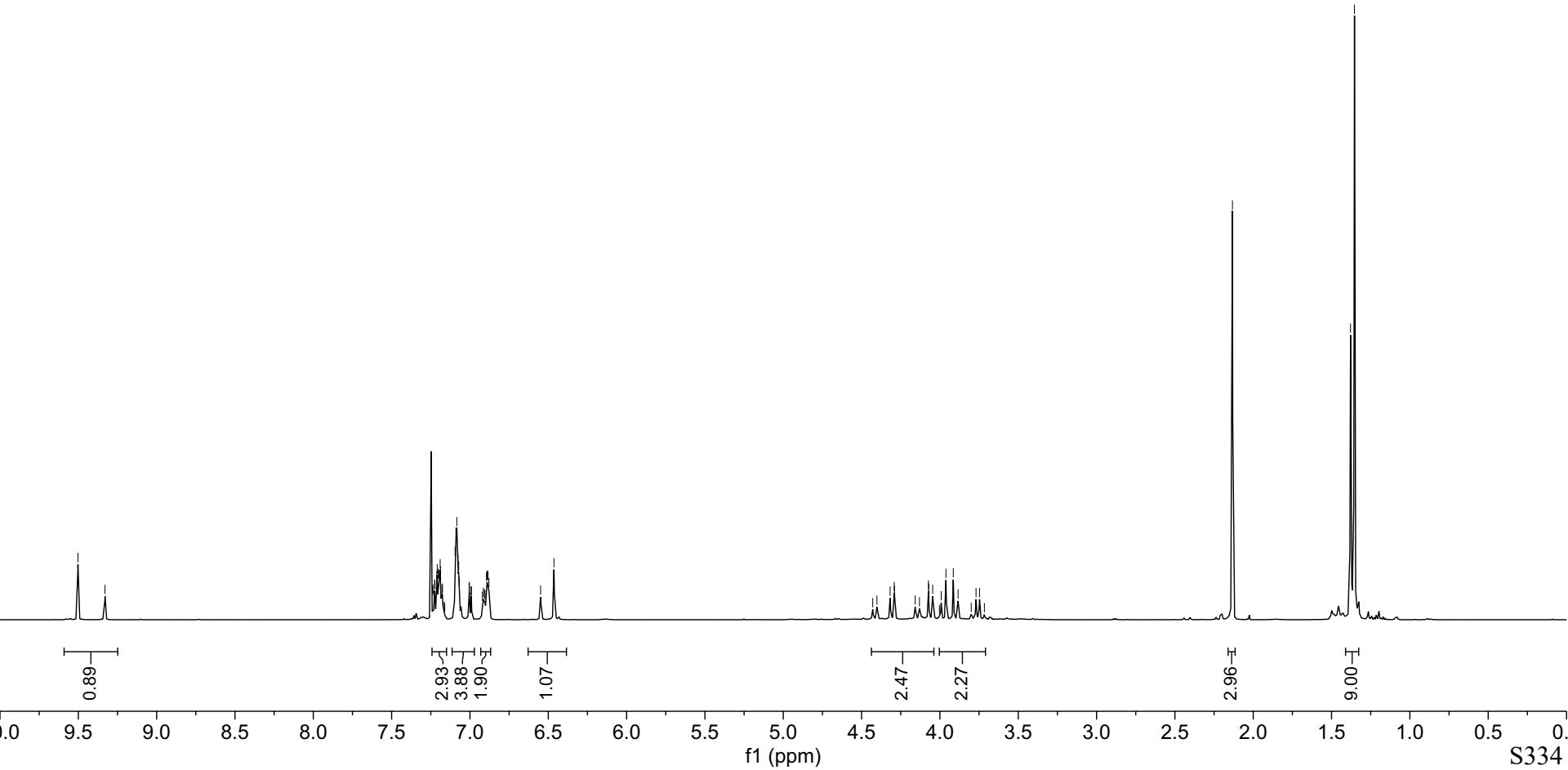


# $^1$H NMR *tert*-butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(*o*-tolyl)allyl)carbamate (1h')

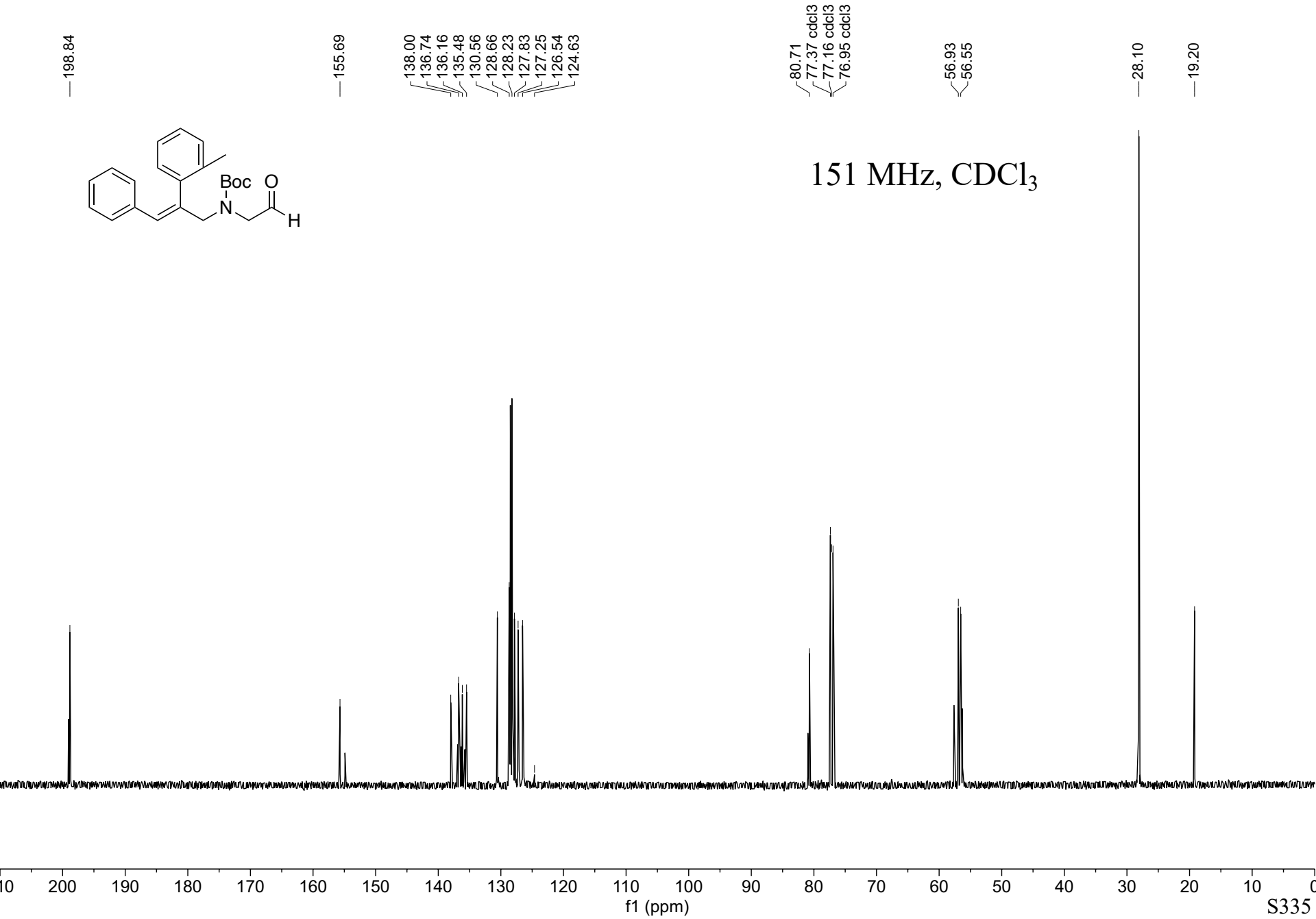


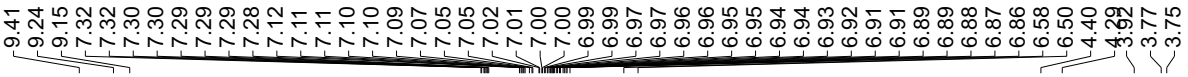

600 MHz, $CDCl_3$

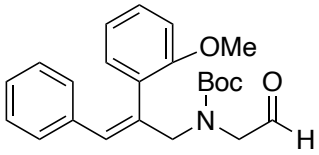


# $^{13}$C NMR *tert*-butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(*o*-tolyl)allyl)carbamate (1h')

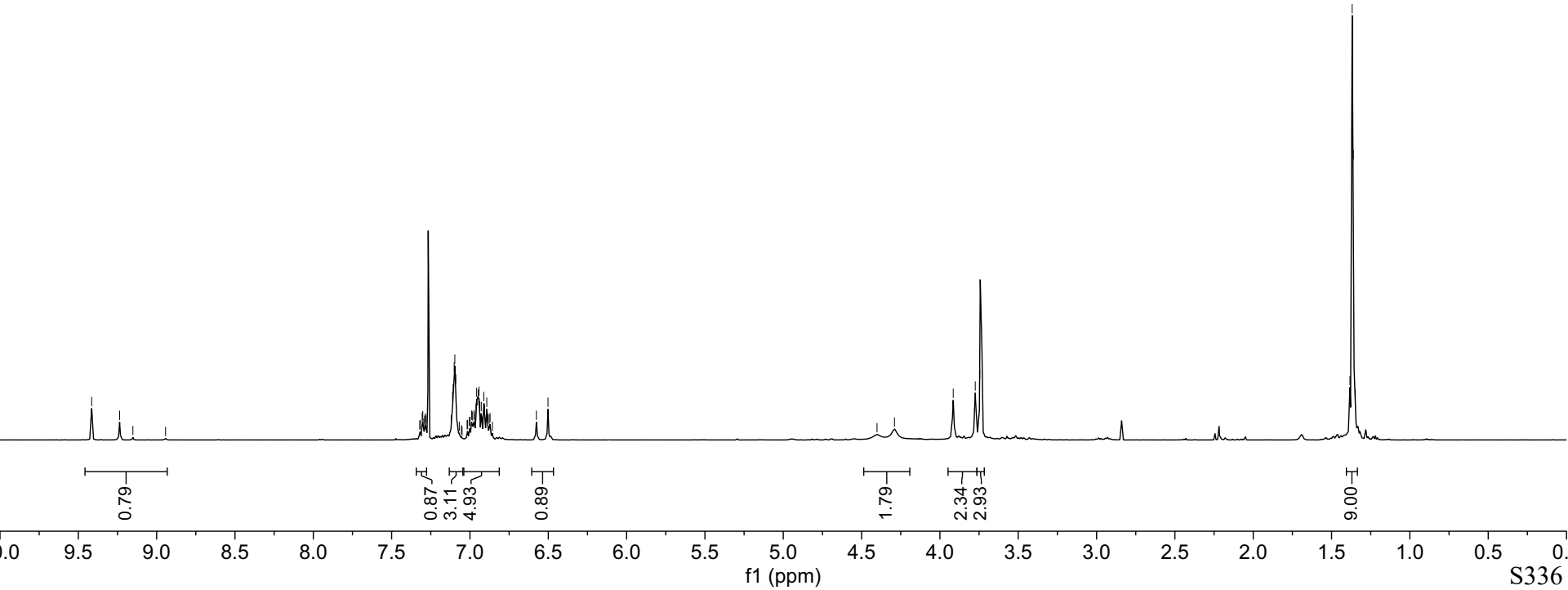


# $^1$H NMR *tert*-Butyl (*E*)-(2-(2-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1i')

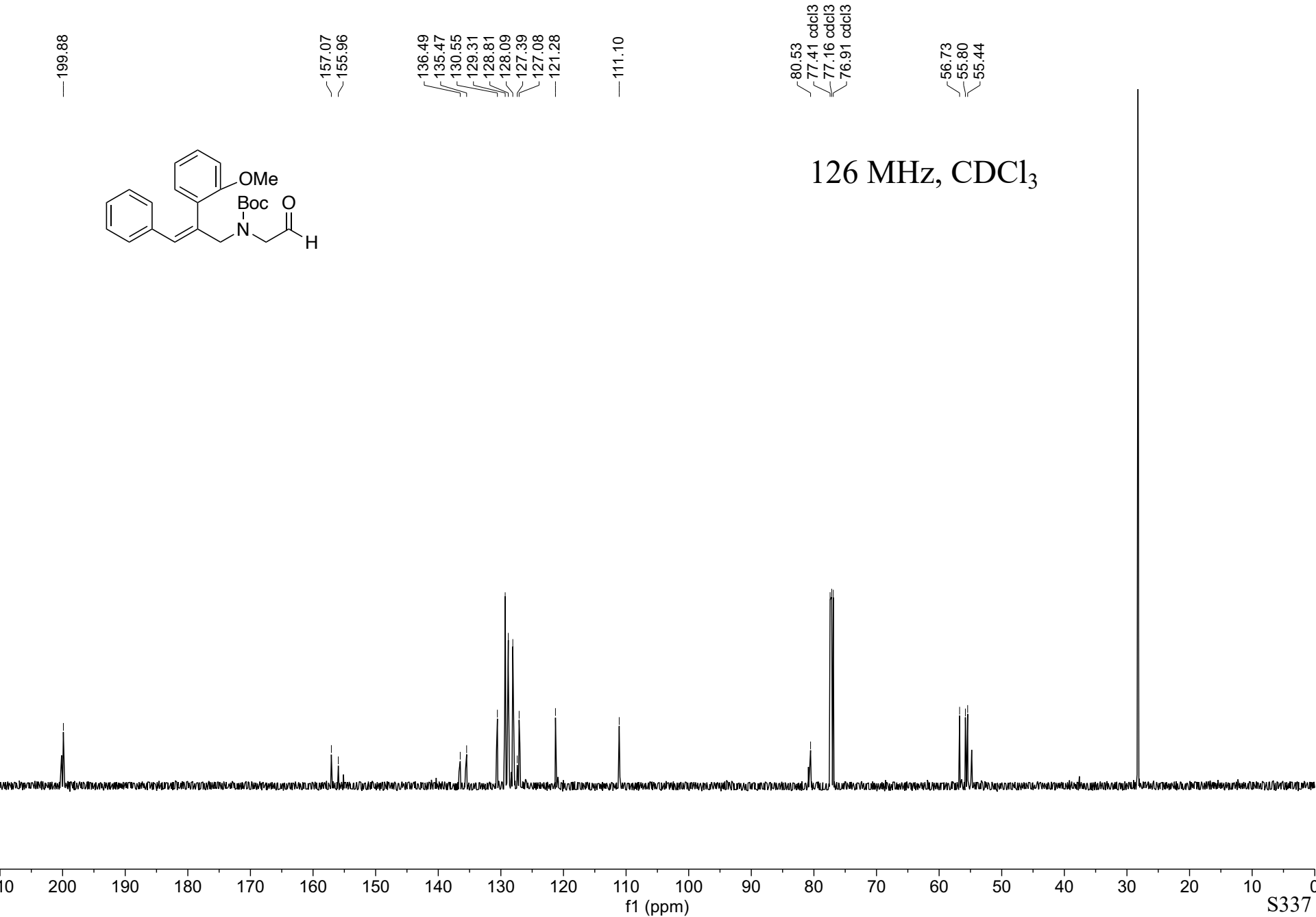


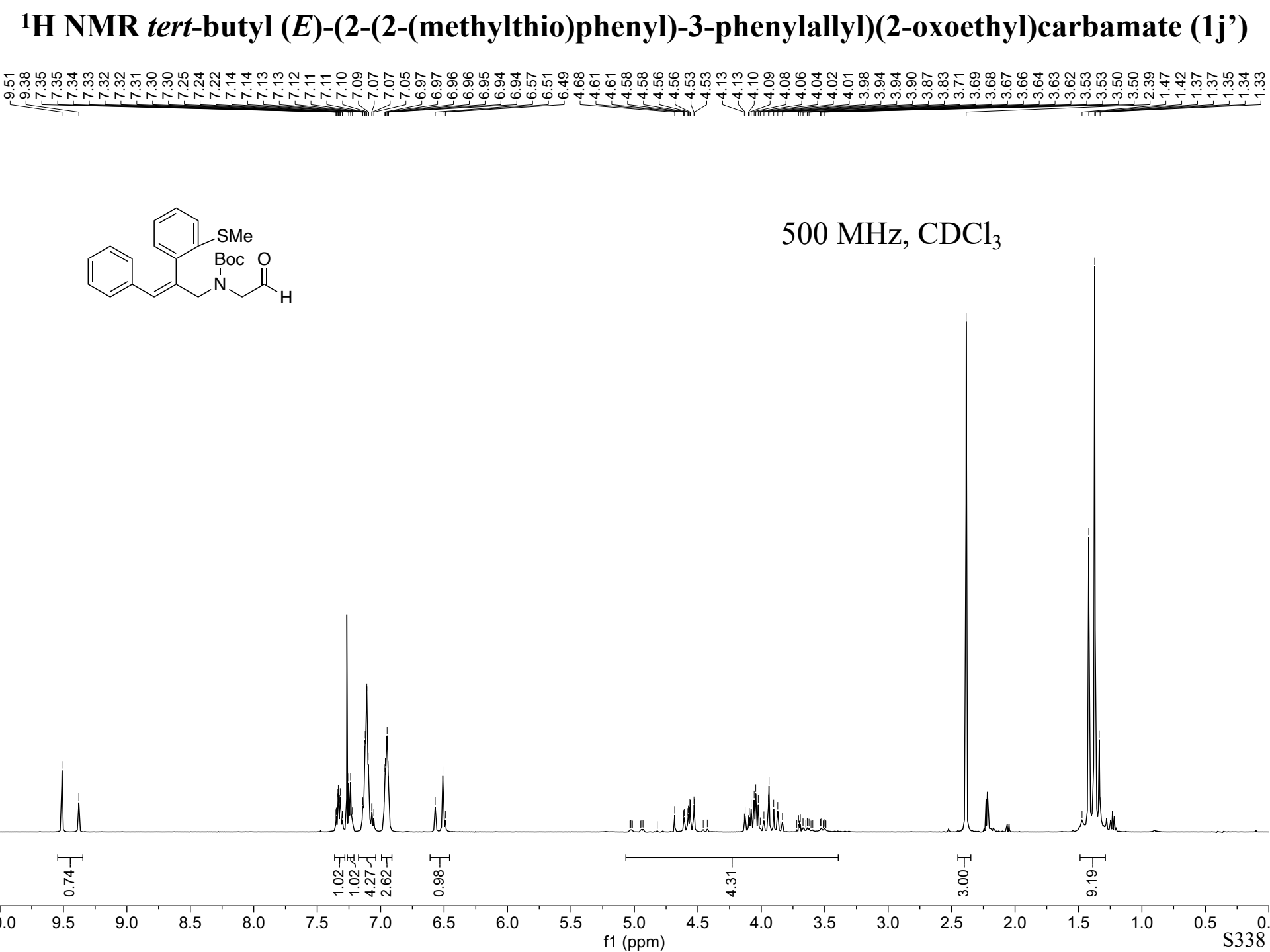

500 MHz, $CDCl_3$



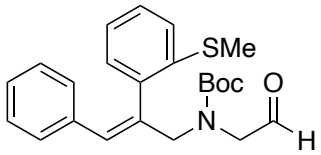
# $^{13}$C NMR *tert*-Butyl (*E*)-(2-(2-methoxyphenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1i')



# $^1$H NMR *tert*-butyl (*E*)-(2-(2-(methylthio)phenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1j')

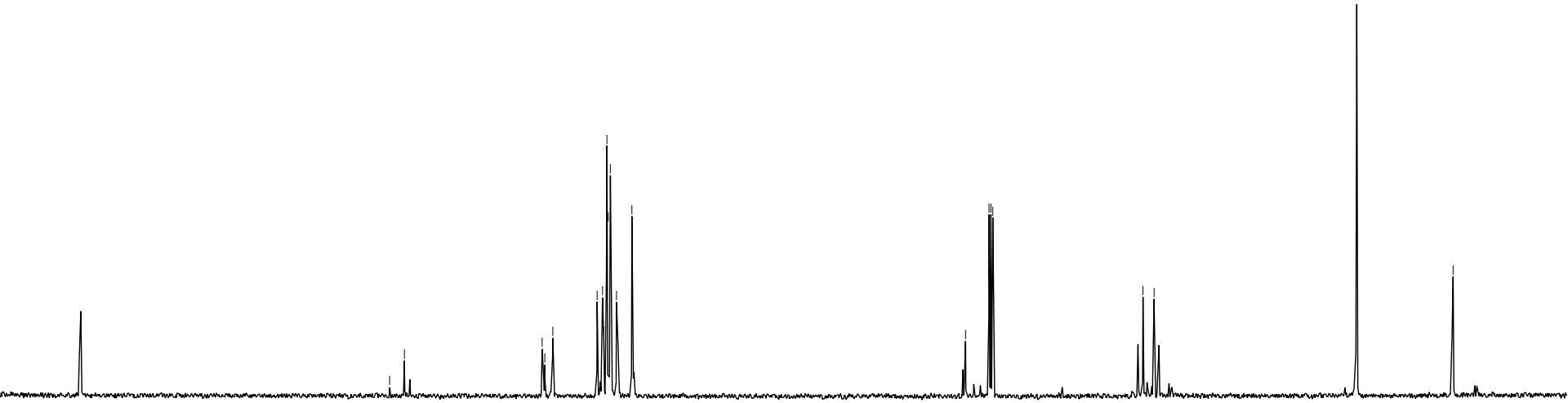


# $^{13}$C NMR *tert*-butyl (*E*)-(2-(2-(methylthio)phenyl)-3-phenylallyl)(2-oxoethyl)carbamate (1j')




126 MHz, $CDCl_3$

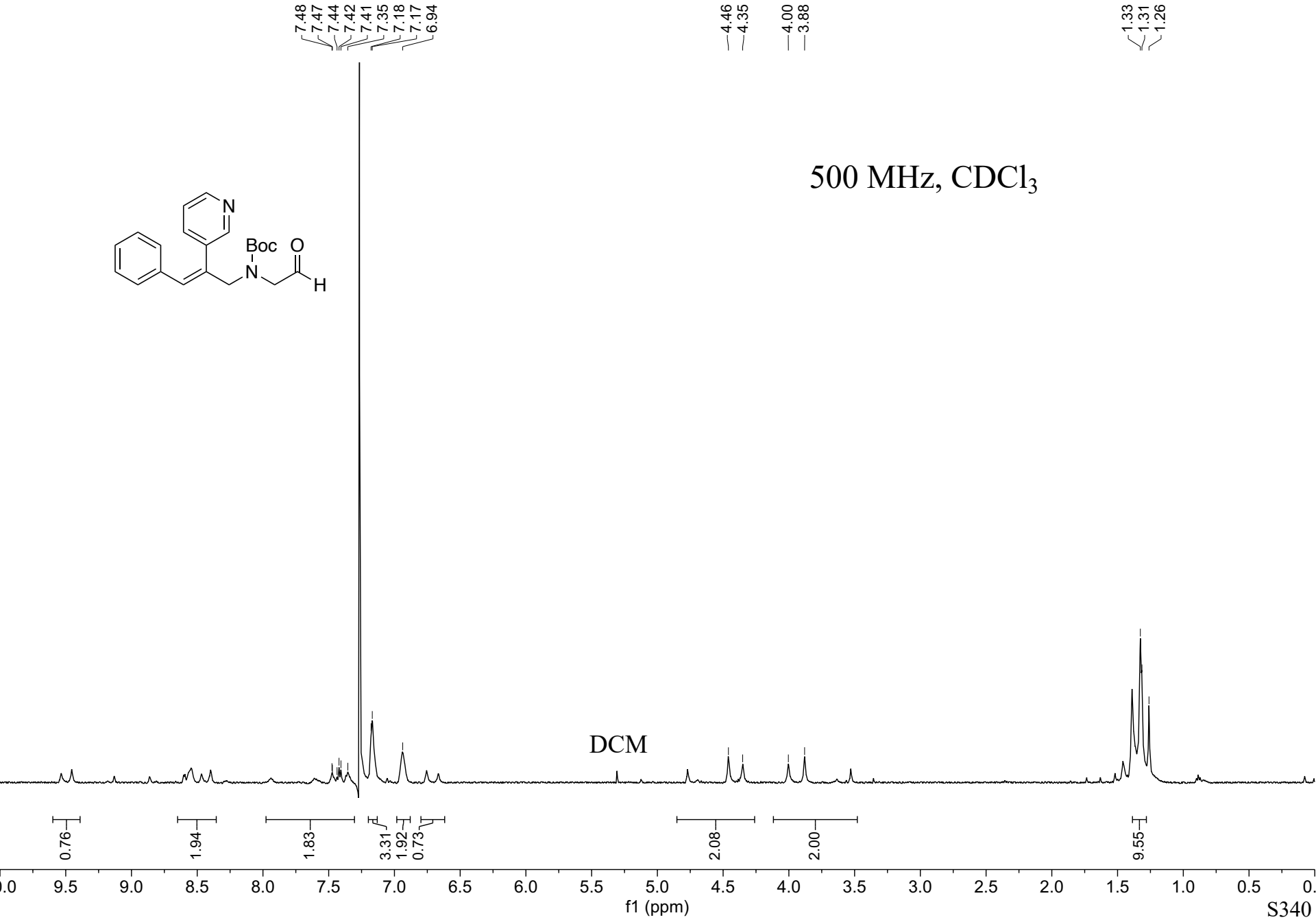
157.77
155.79
137.32
136.97
135.90
129.95
129.23
129.07
128.64
128.47
128.18
127.36
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80.57
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76.91 cdcl3
56.78
55.29
15.21



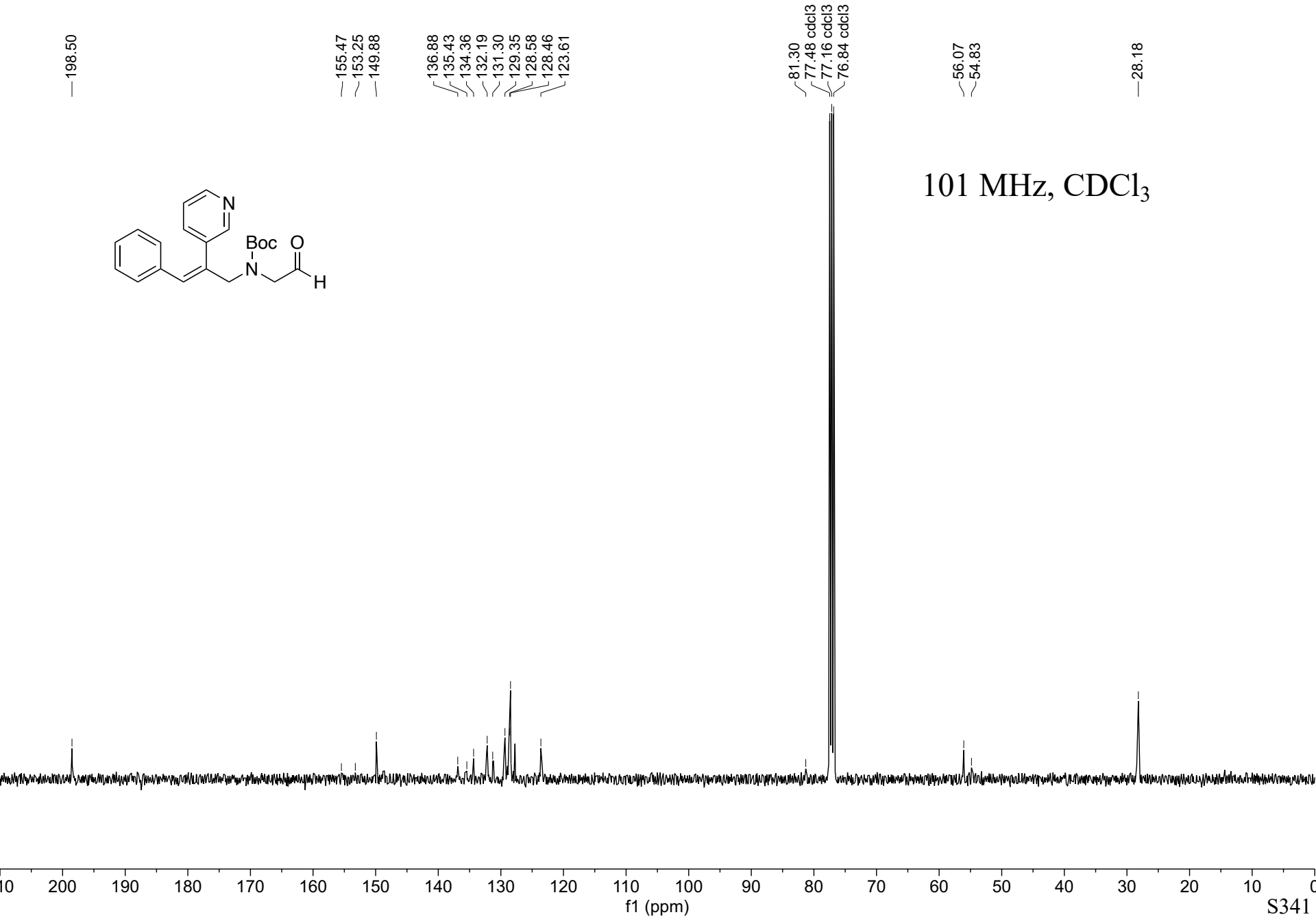
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

# $^1$H NMR *tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(pyridin-3-yl)allyl)carbamate (1k')



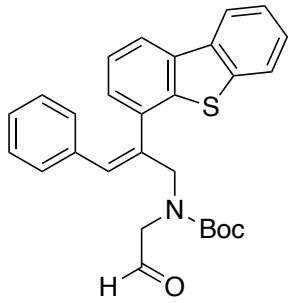
# $^{13}$C NMR *tert*-Butyl (*E*)-(2-oxoethyl)(3-phenyl-2-(pyridin-3-yl)allyl)carbamate (1k')

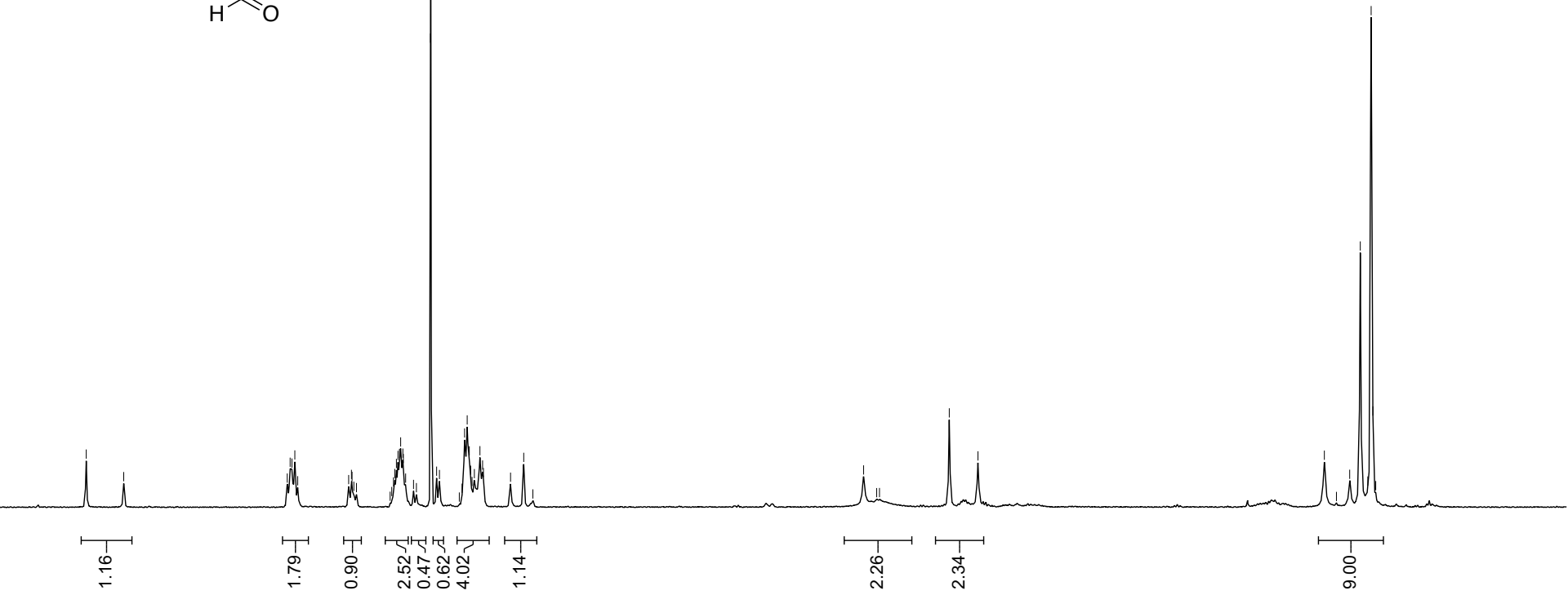


# $^{1}$H NMR *tert*-Butyl (*E*)-(2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1l')




400 MHz, $CDCl_3$

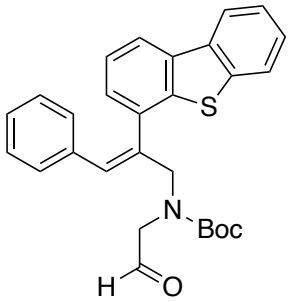


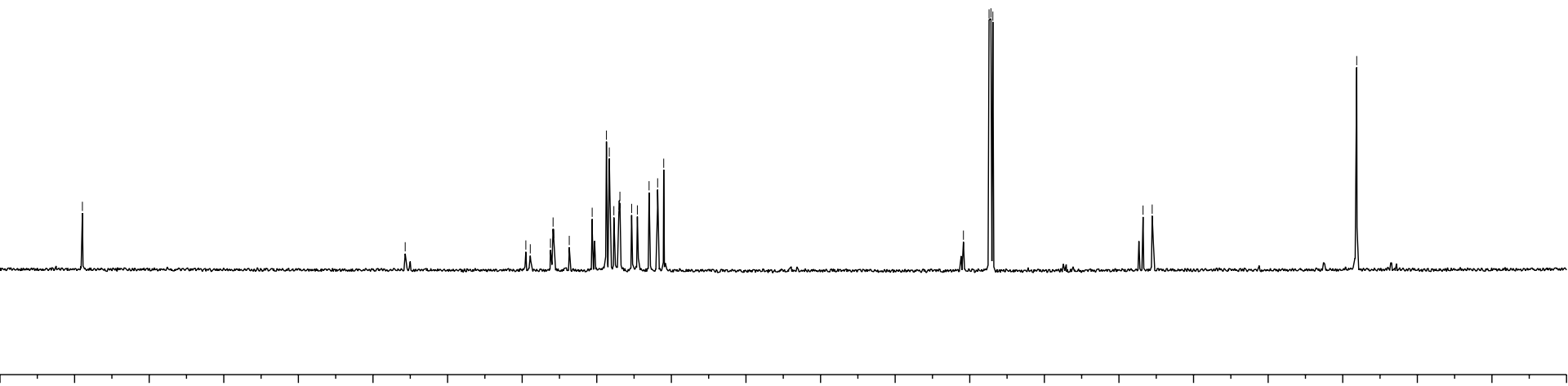



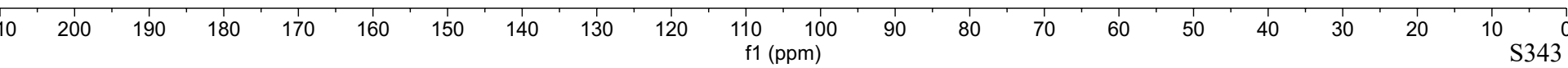
**$^{13}$C NMR *tert*-Butyl (*E*)-(2-(dibenzo[*b*,*d*]thiophen-4-yl)-3-phenylallyl)(2-oxoethyl)carbamate (1l')**

198.95
155.68
139.51
138.91
136.21
135.86
135.75
133.69
130.62
128.70
128.32
127.71
127.04
126.95
126.90
125.33
124.56
122.99
121.84
121.03
80.85
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
56.77
55.55
28.13

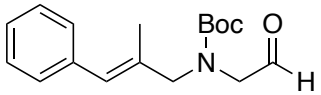
126 MHz, $CDCl_3$



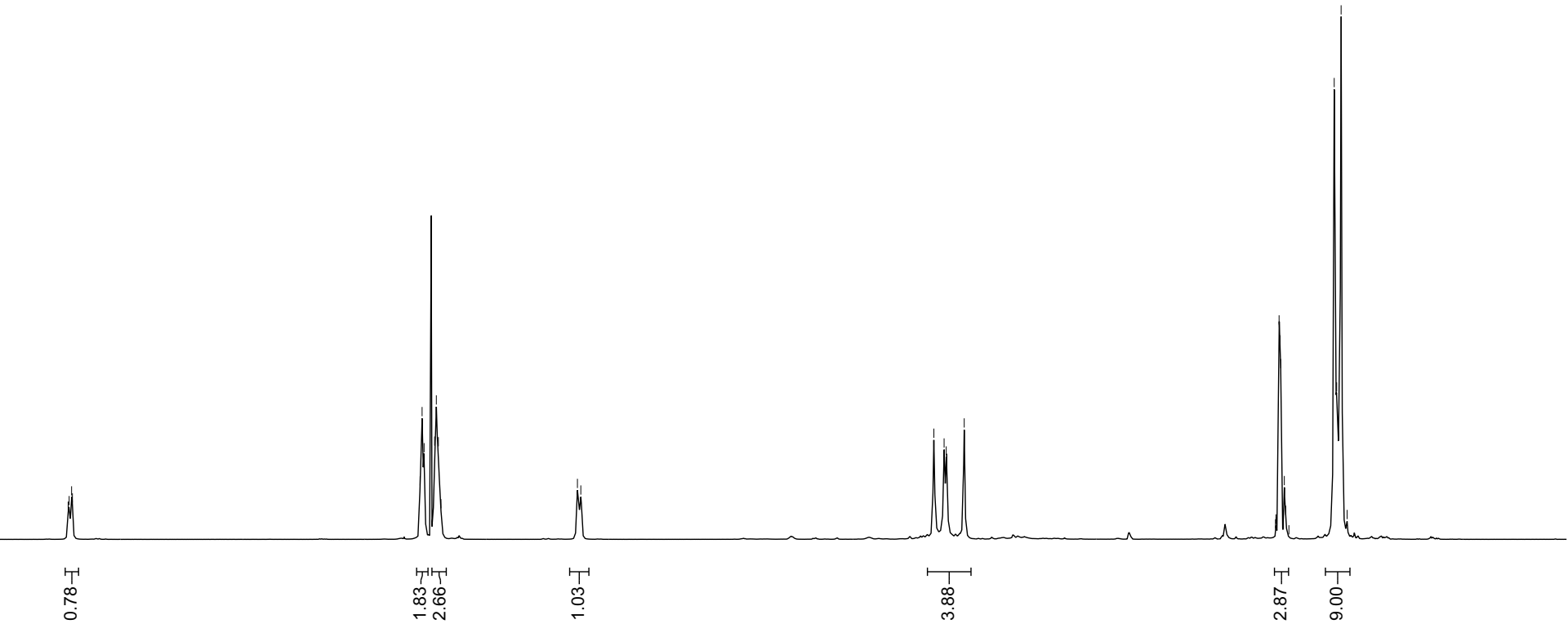





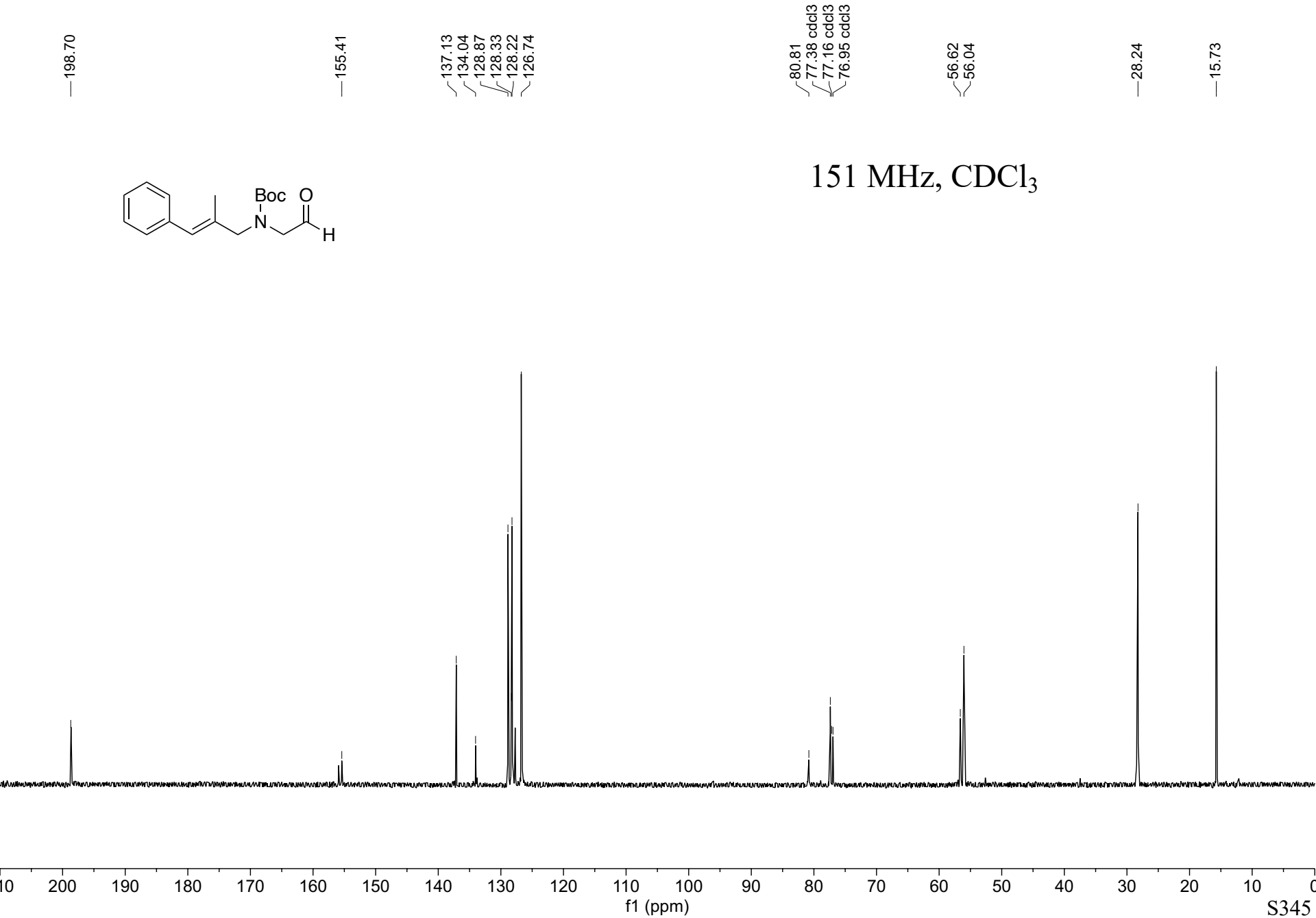
# $^1$H NMR *tert*-Butyl (*E*)-(2-methyl-3-phenylallyl)(2-oxoethyl)carbamate (1m')




600 MHz, $CDCl_3$

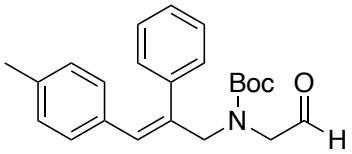


# $^{13}$C NMR *tert*-Butyl (*E*)-(2-methyl-3-phenylallyl)(2-oxoethyl)carbamate (1m')

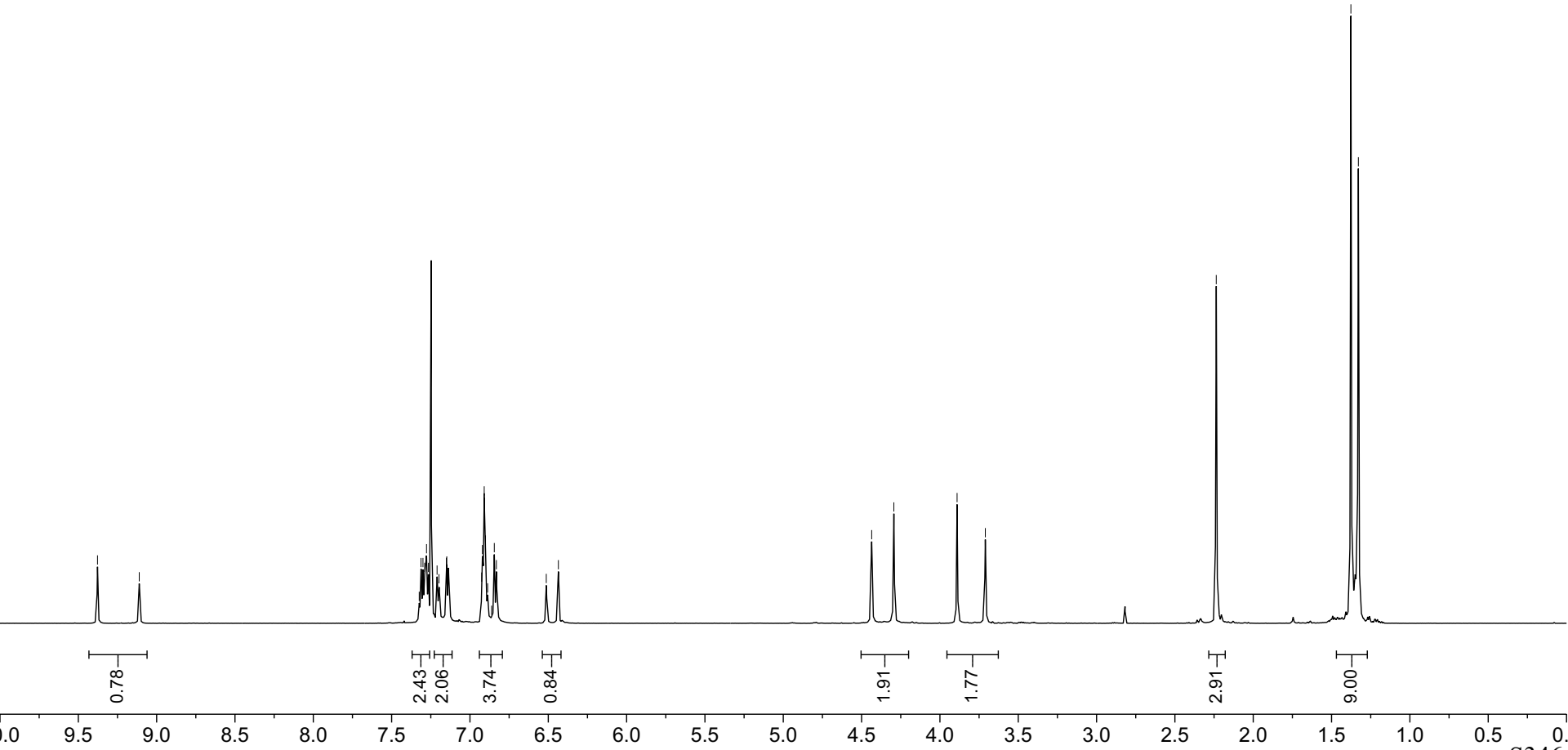


# $^{1}$H NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(*p*-tolyl)allyl)carbamate (1n')

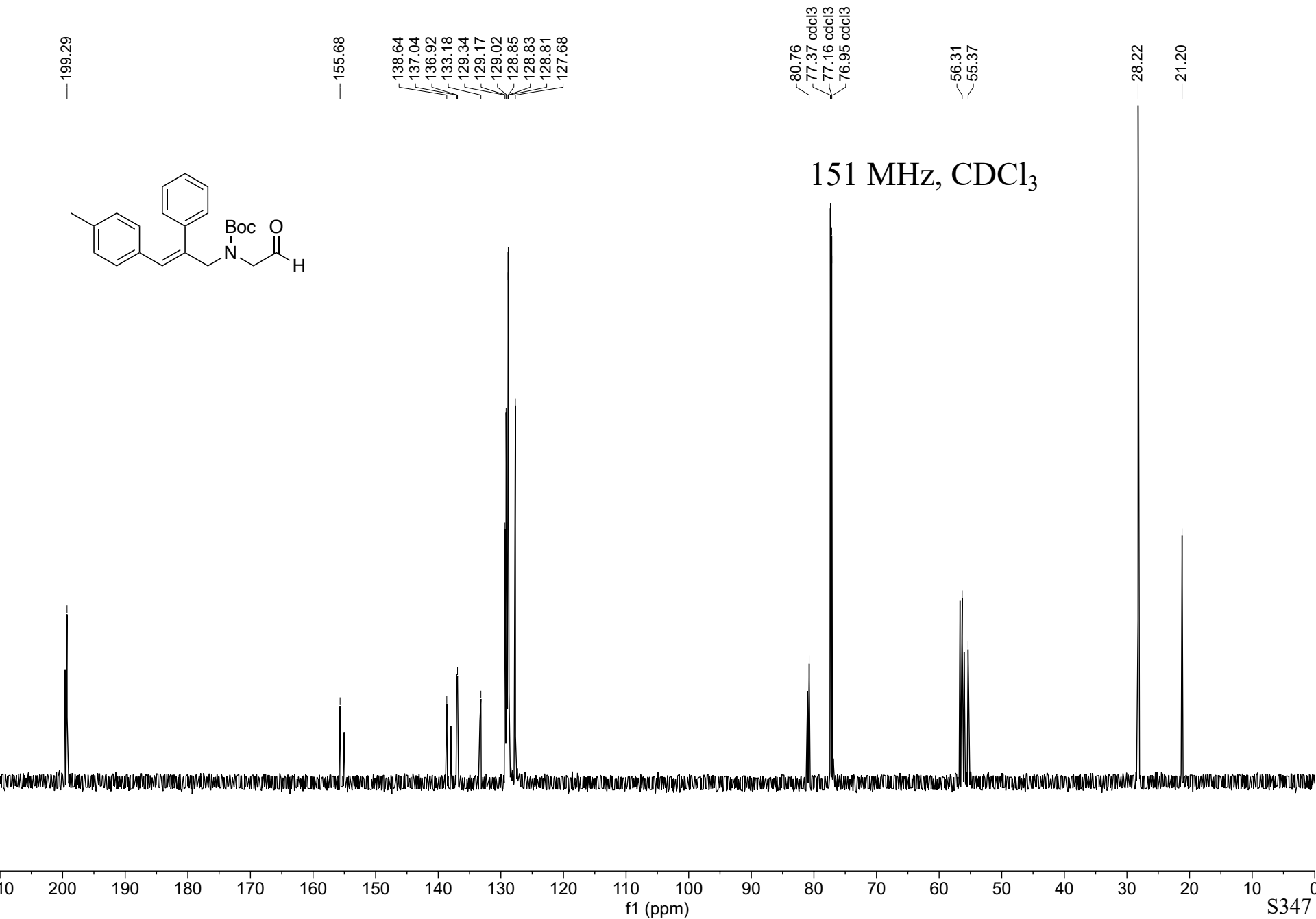



600 MHz, $CDCl_3$

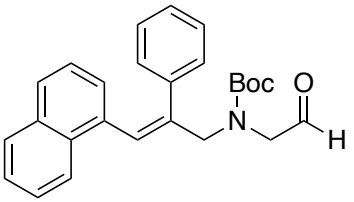


# $^{13}$C NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(*p*-tolyl)allyl)carbamate (1n')

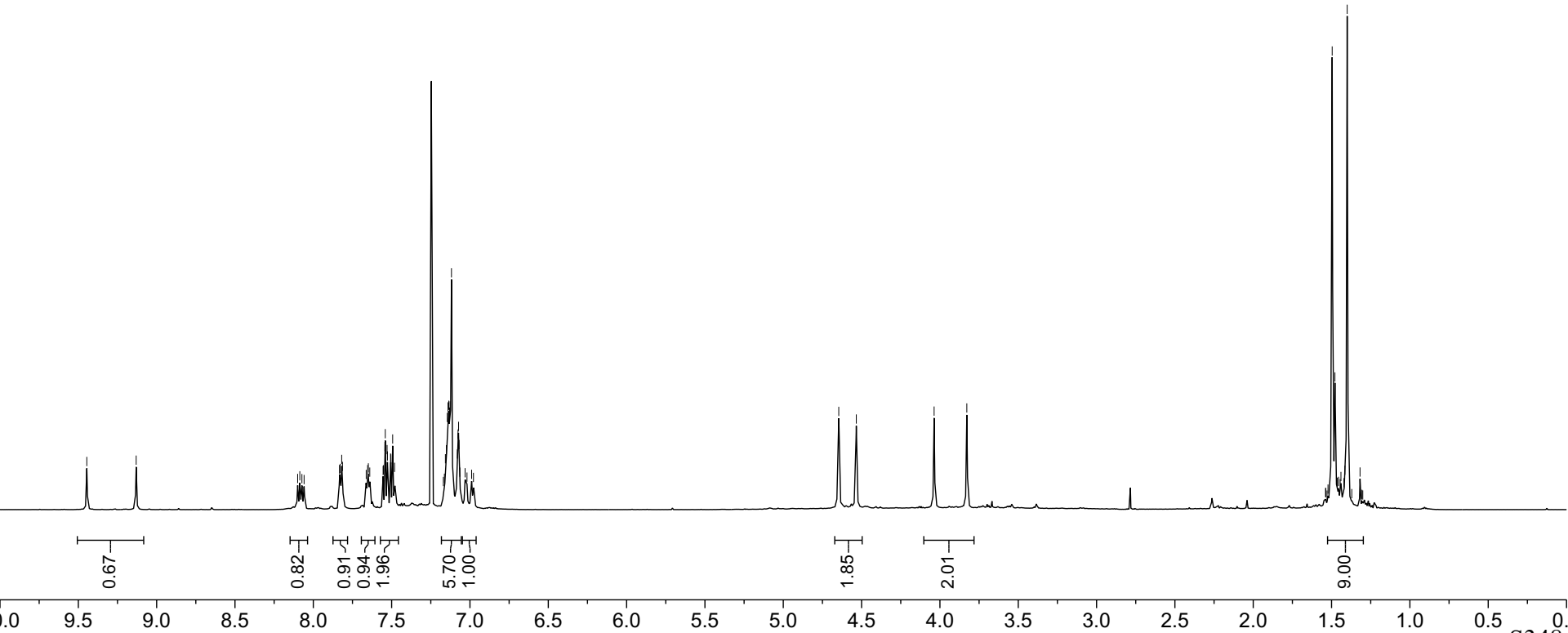


# $^{1}$H NMR *tert*-Butyl (*E*)-(3-(naphthalen-1-yl)-2-phenylallyl)(2-oxoethyl)carbamate (1o')

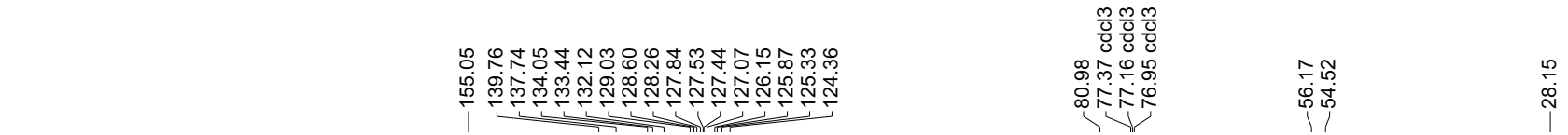


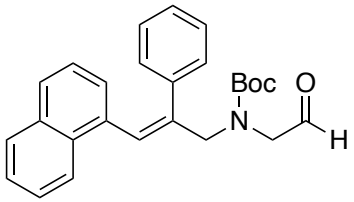




600 MHz, $CDCl_3$

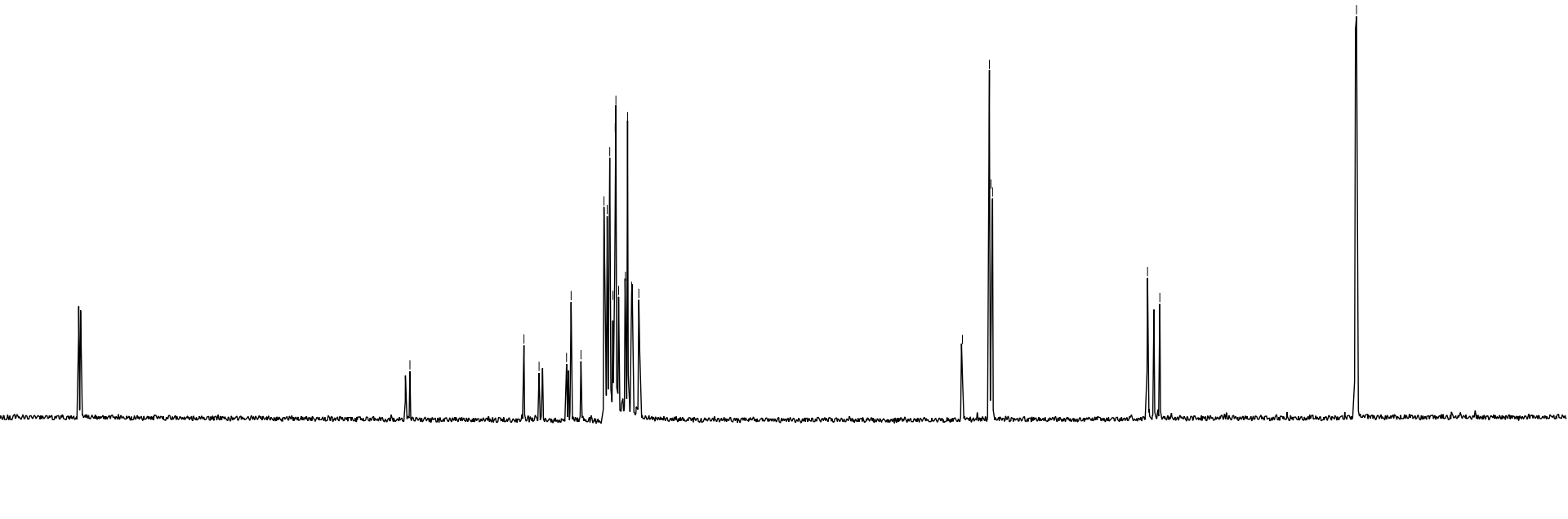


# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(naphthalen-1-yl)-2-phenylallyl)(2-oxoethyl)carbamate (1o')

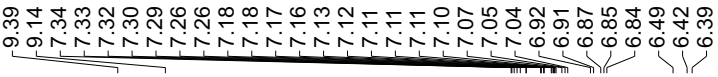


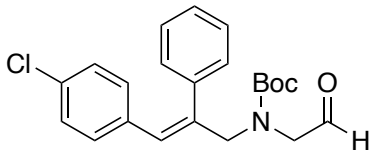




151 MHz, $CDCl_3$

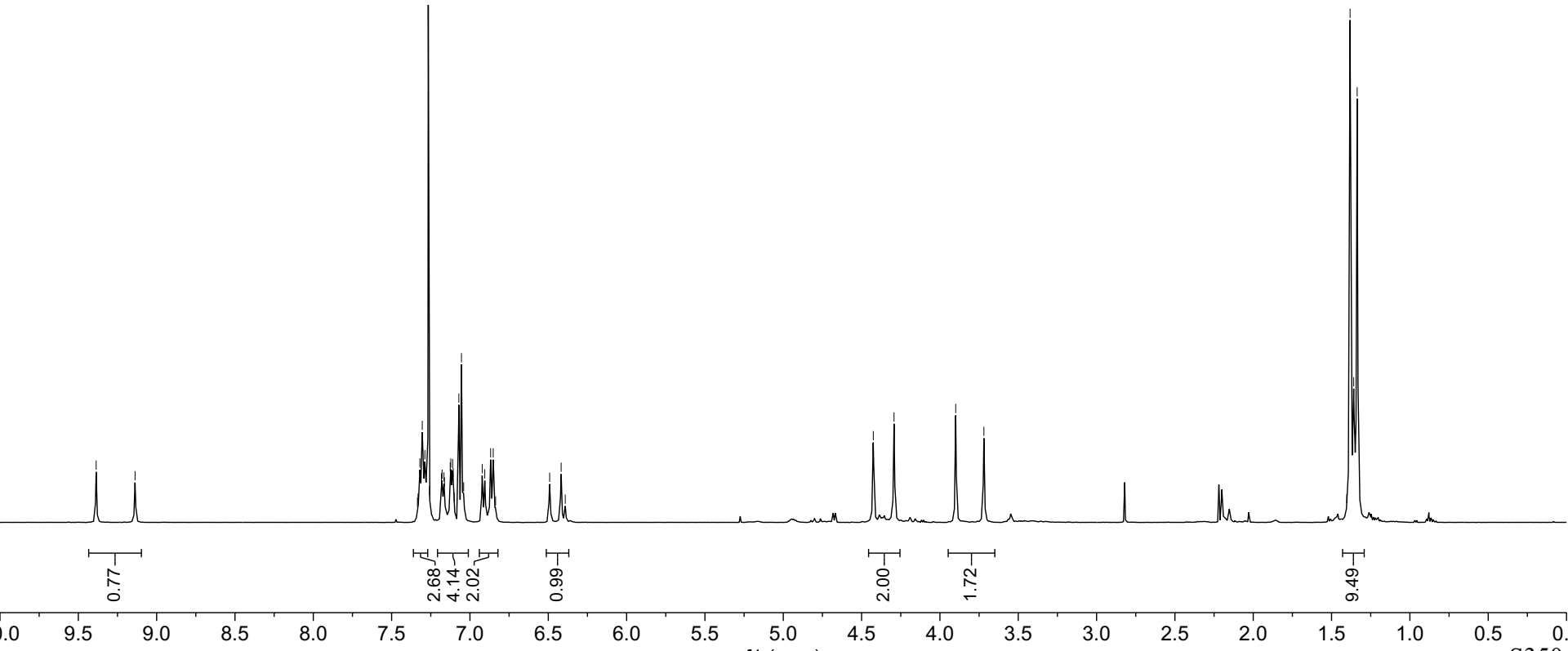


# $^1$H NMR *tert*-Butyl (*E*)-(3-(4-chlorophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1p')

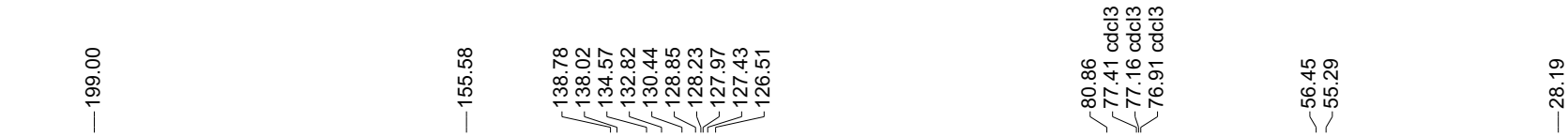


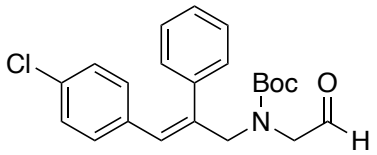




500 MHz, $CDCl_3$

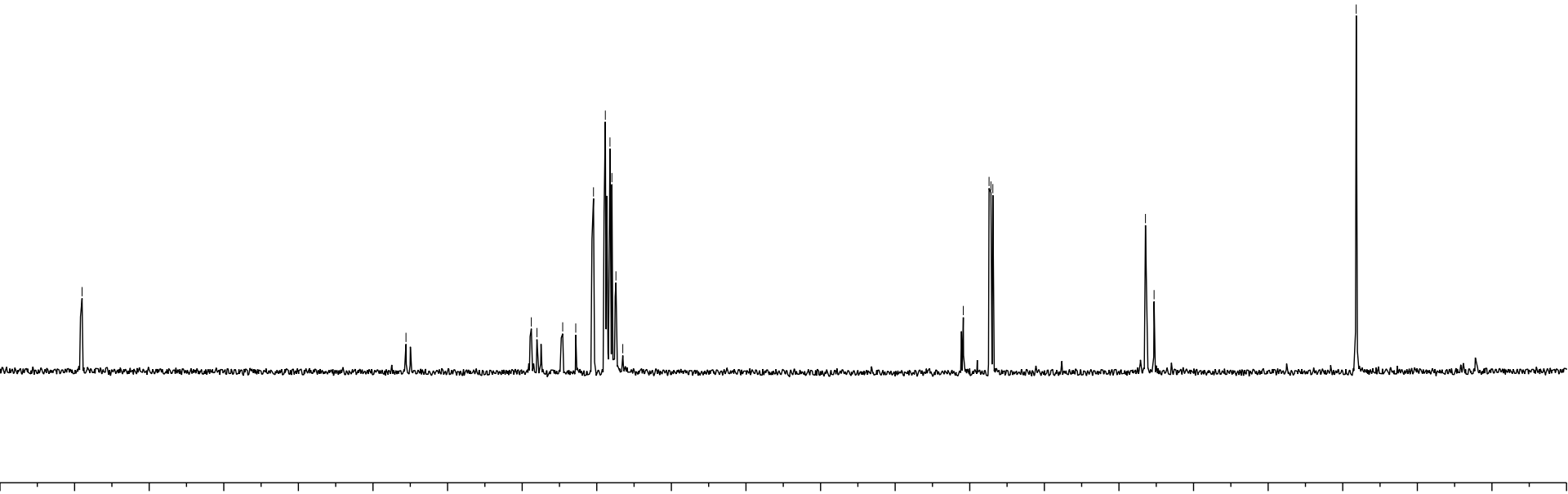


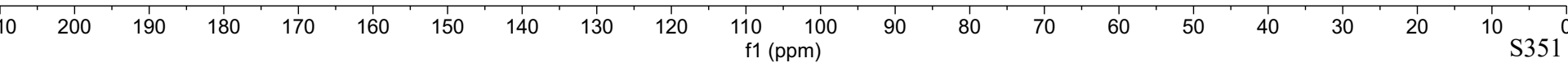
# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(4-chlorophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1p')



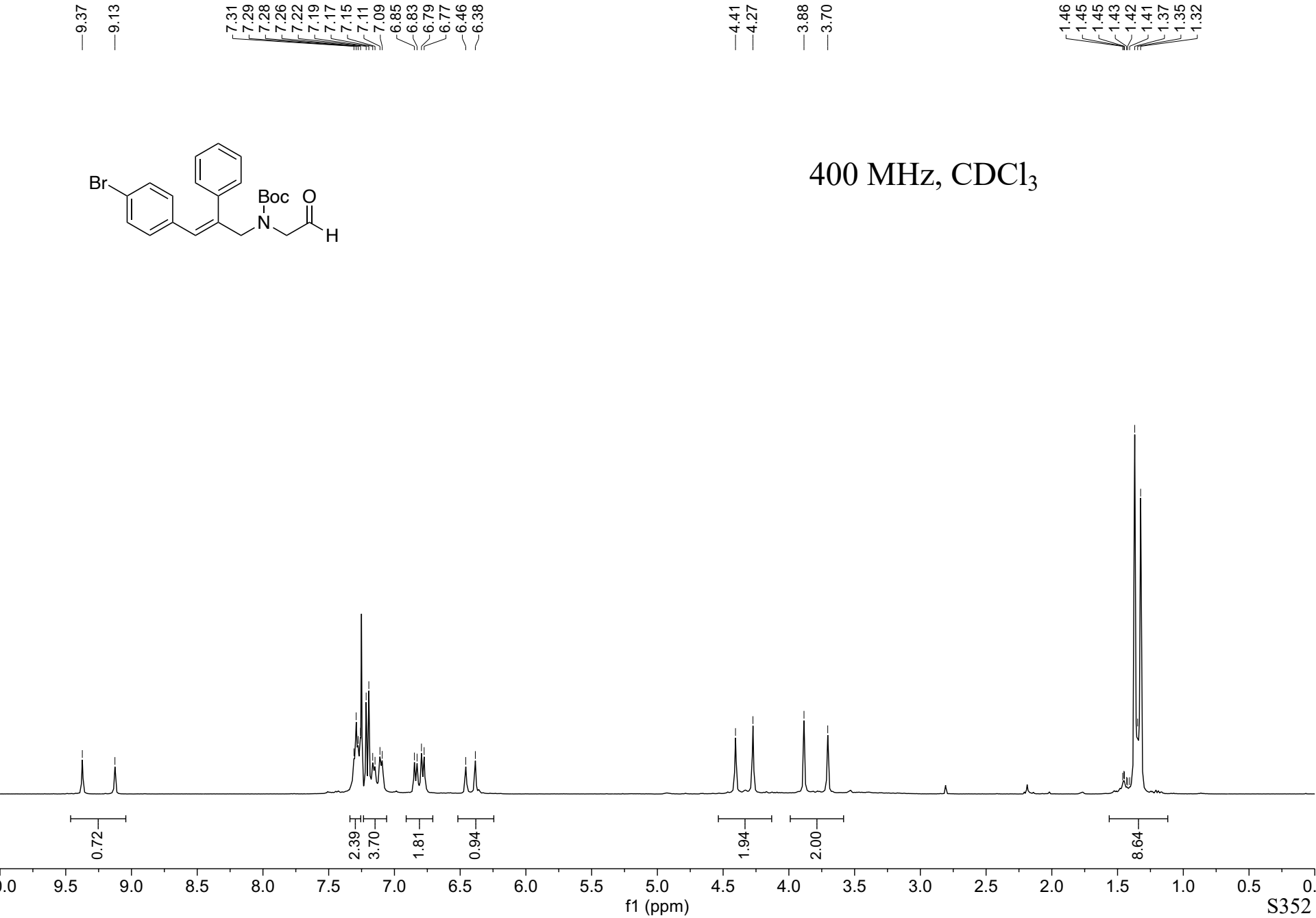




151 MHz, $CDCl_3$



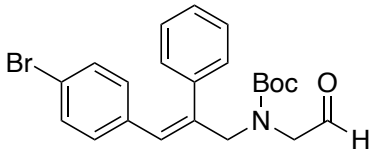


# $^1$H NMR *tert*-Butyl (*E*)-(3-(4-bromophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1q' )

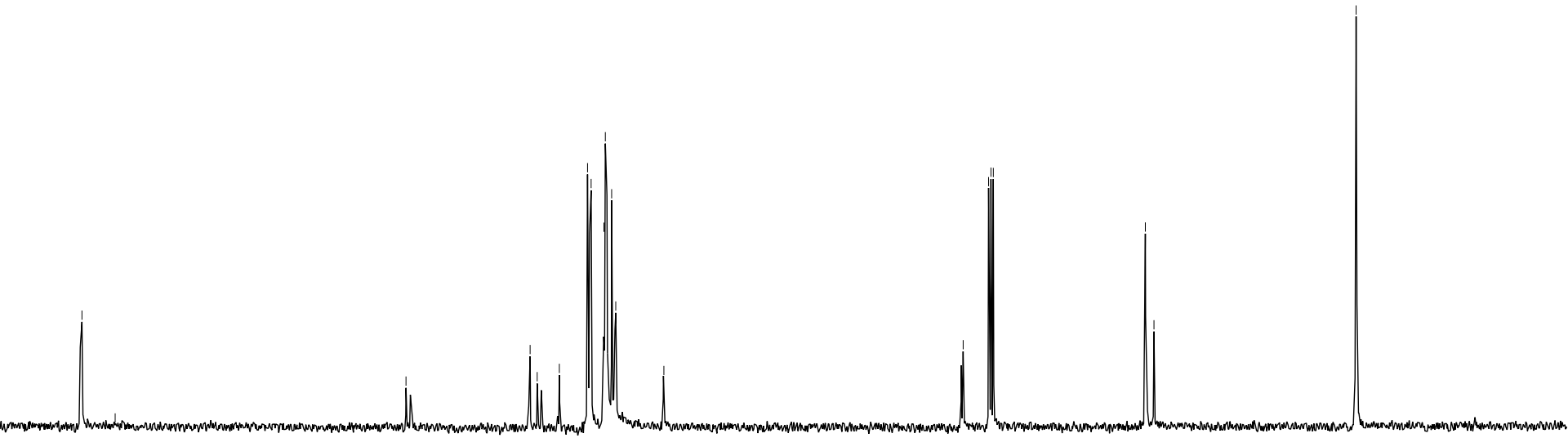


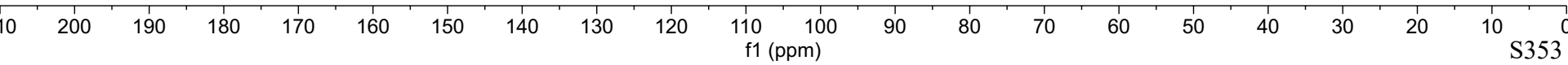
# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(4-bromophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1q' )

199.01
194.56
155.57
138.94
137.99
135.02
131.24
130.76
129.04
128.85
128.01
127.45
121.00
80.88
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
56.46
55.30
28.21

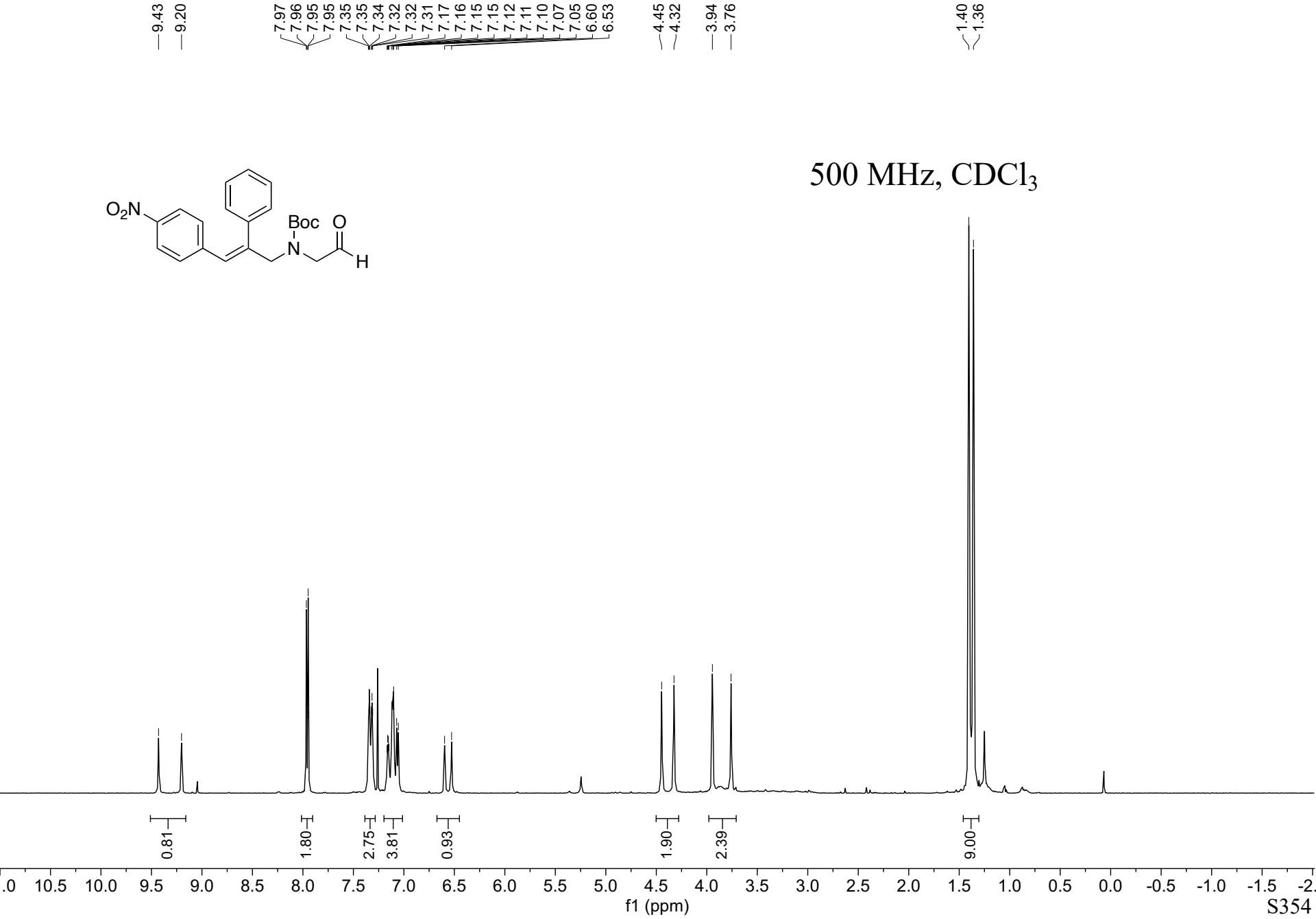



101 MHz, $CDCl_3$

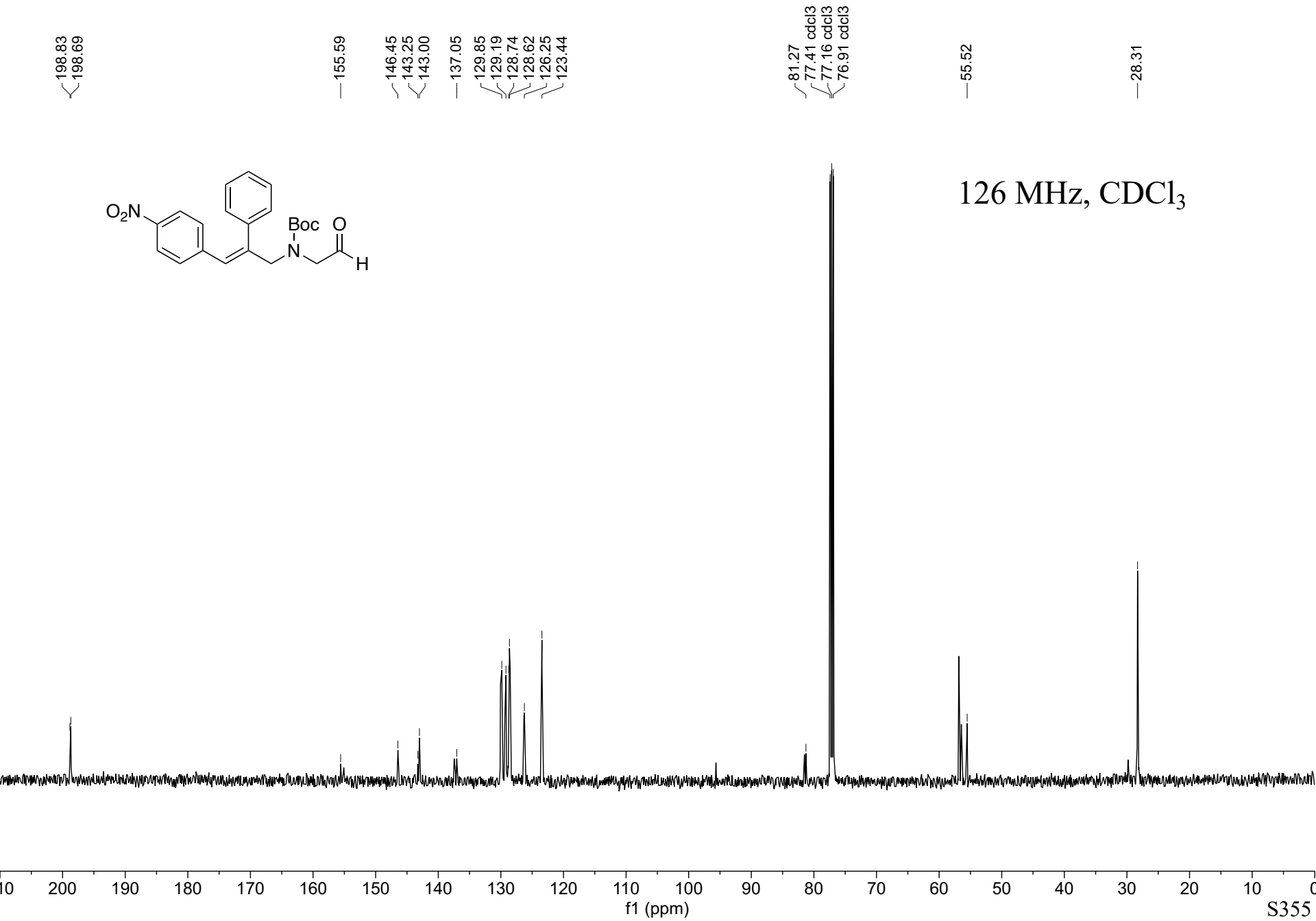




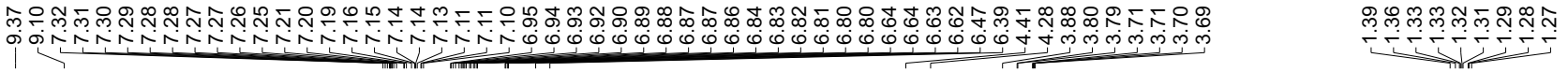
# $^1$H NMR *tert*-Butyl (*E*)-(3-(4-nitrophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1r')

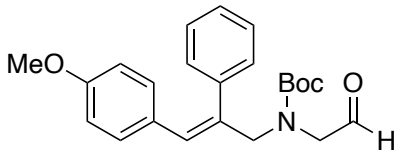


# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(4-nitrophenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1r')

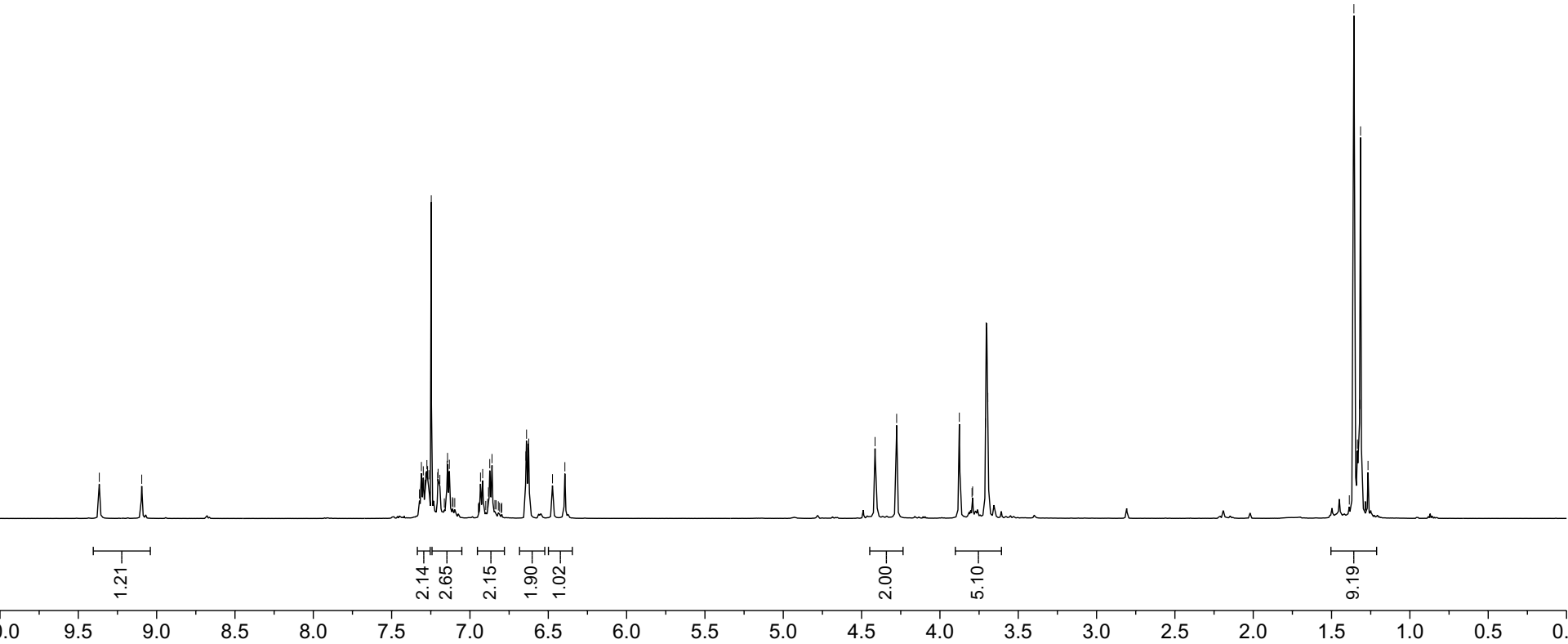


# $^1$H NMR *tert*-butyl (*E*)-(3-(4-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1s')

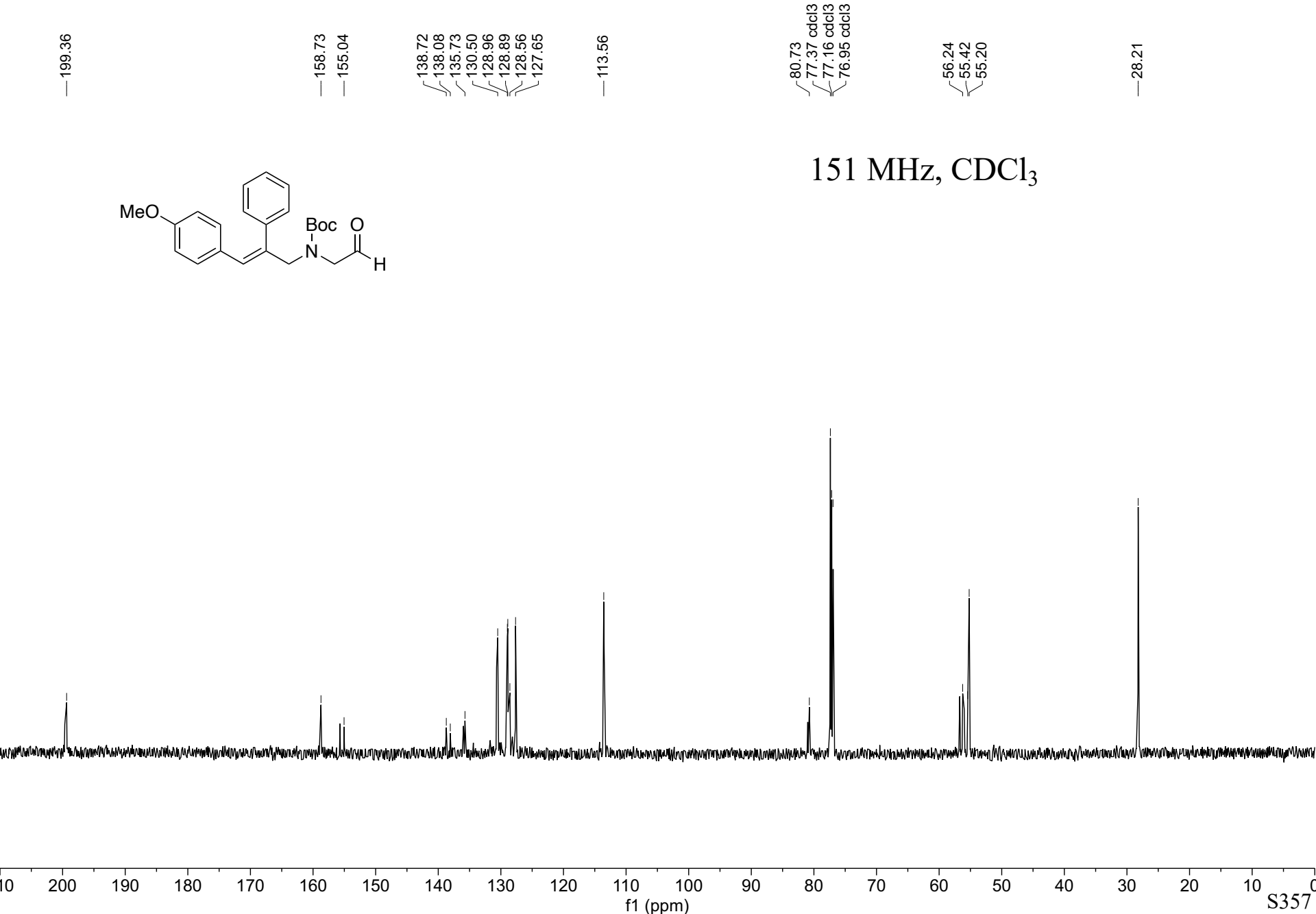



600 MHz, $CDCl_3$

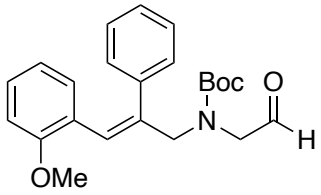


# $^{13}$C NMR *tert*-butyl (*E*)-(3-(4-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1s')

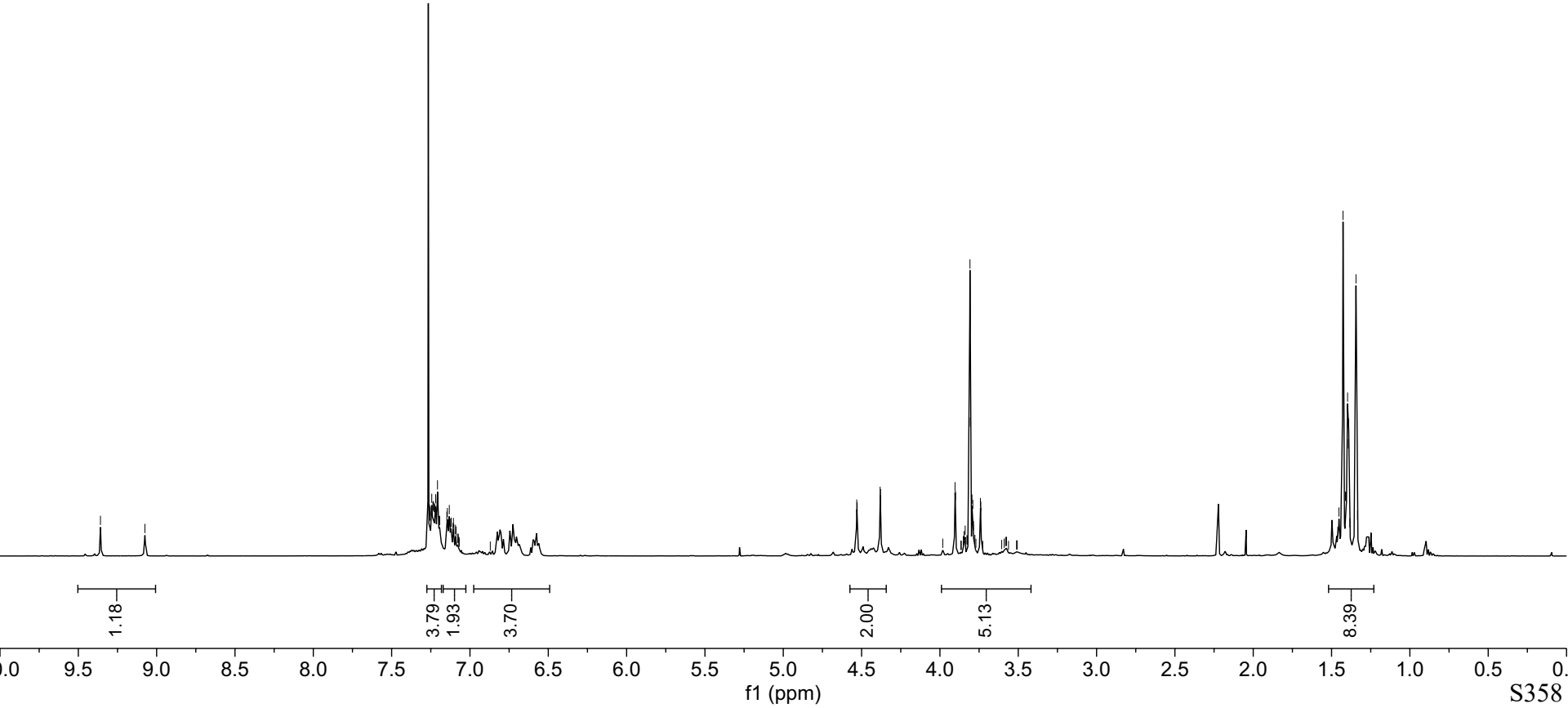


# $^1$H NMR *tert*-Butyl (*E*)-(3-(2-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1t')

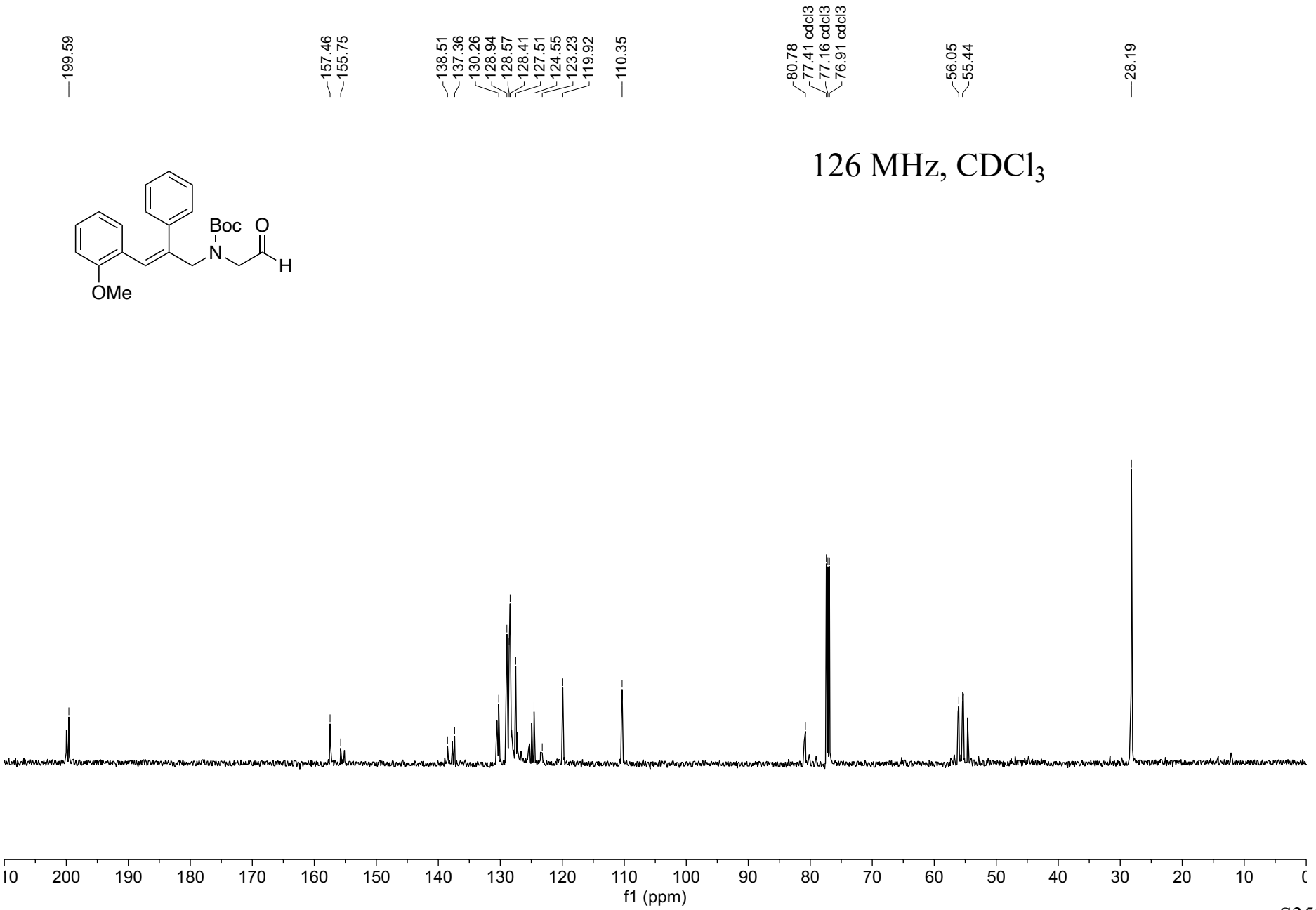


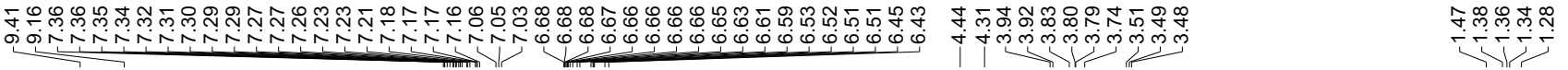

500 MHz, $CDCl_3$

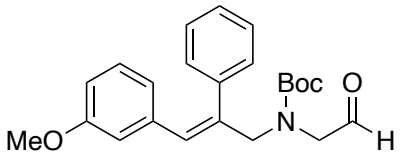


# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(2-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1t')

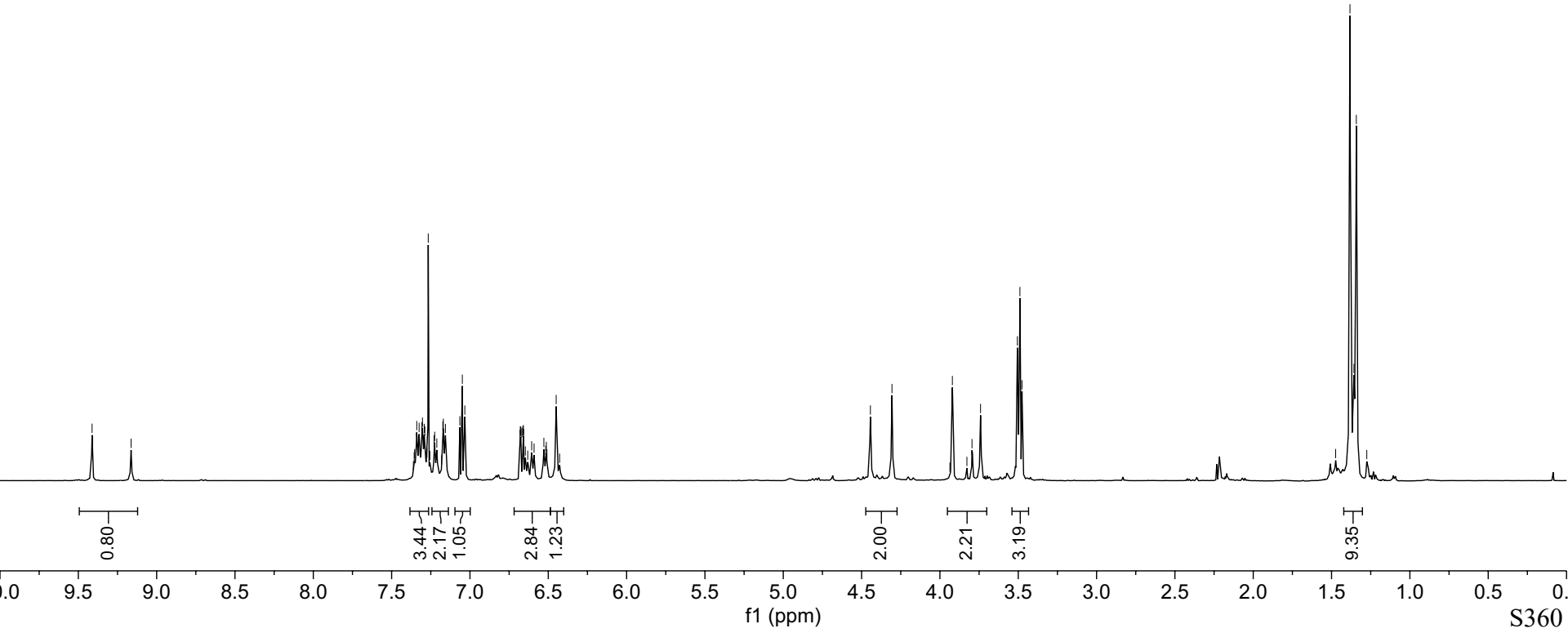


# $^1$H NMR *tert*-Butyl (*E*)-(3-(3-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1t')

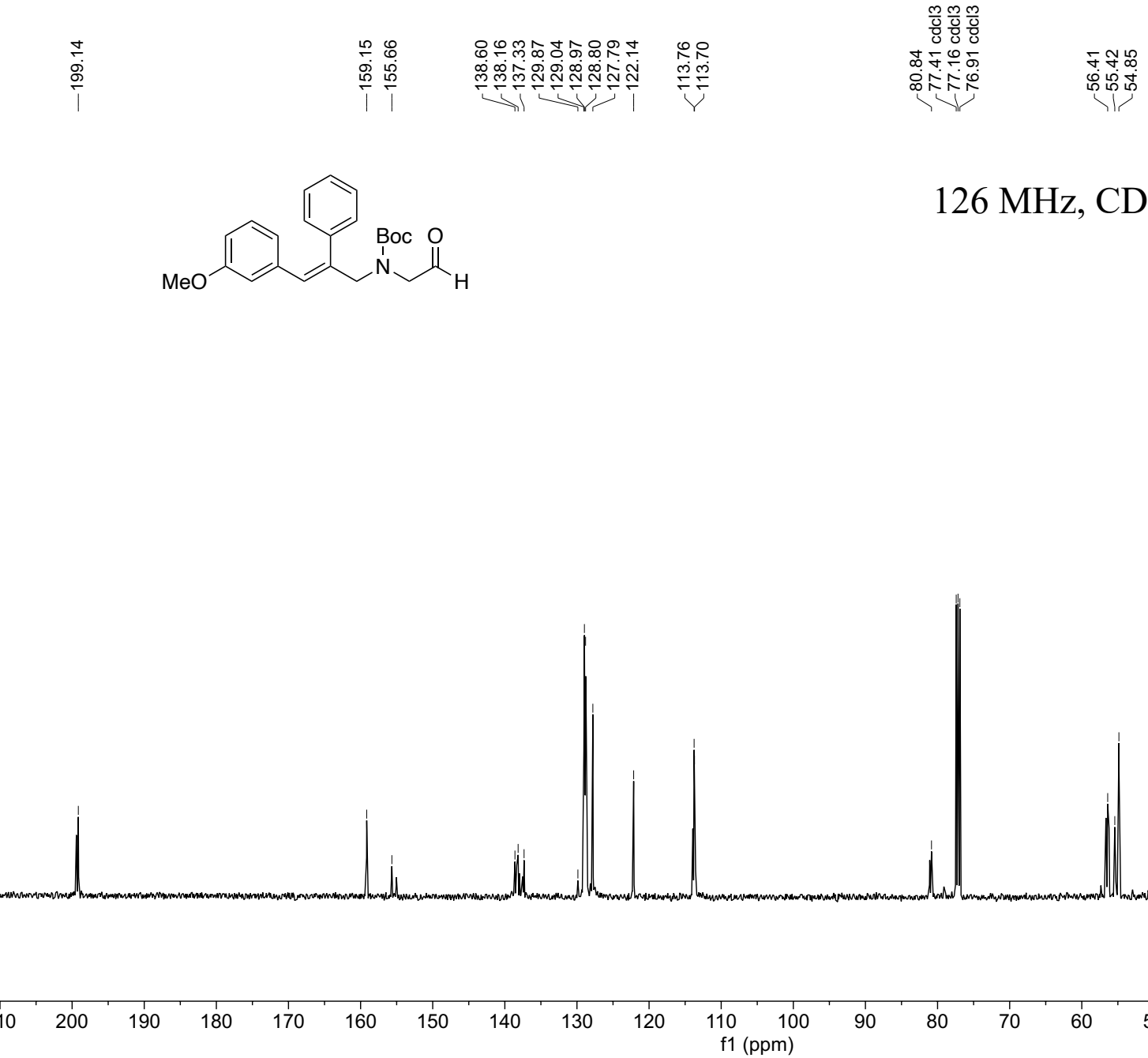


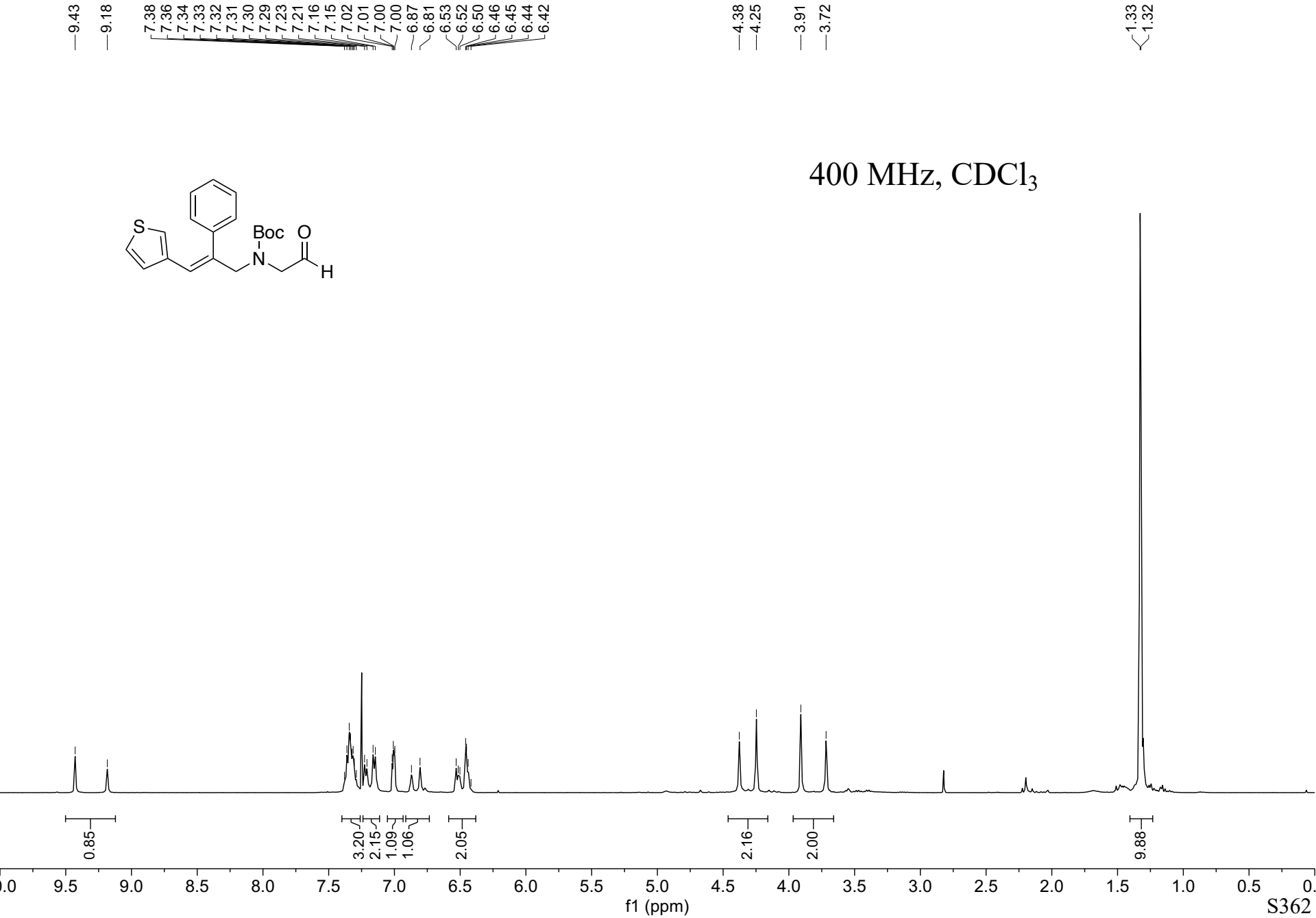

500 MHz, $CDCl_3$



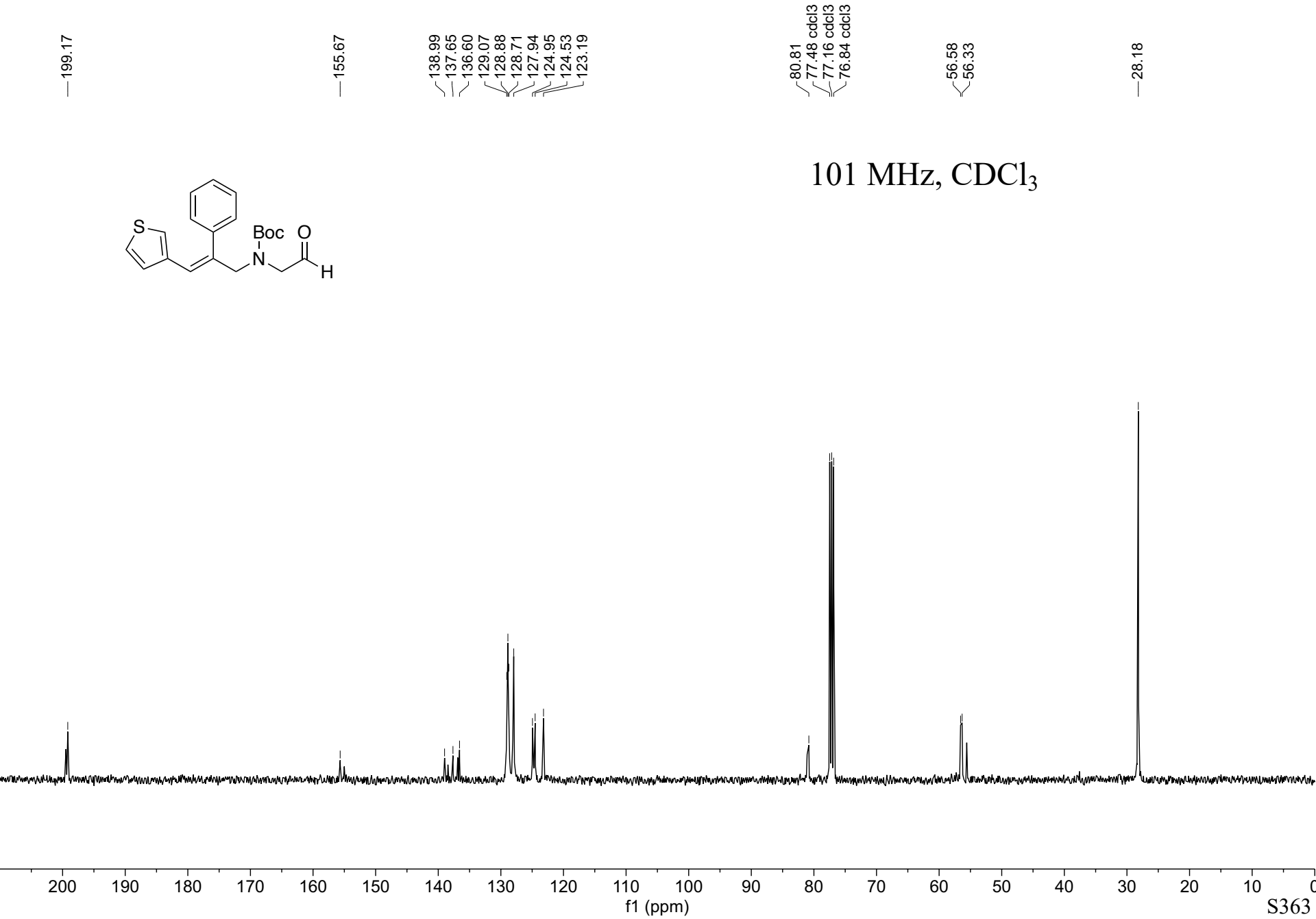
# $^{13}$C NMR *tert*-Butyl (*E*)-(3-(3-methoxyphenyl)-2-phenylallyl)(2-oxoethyl)carbamate (1t')



# $^{1}$H NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(thiophen-3-yl)allyl)carbamate (1v')

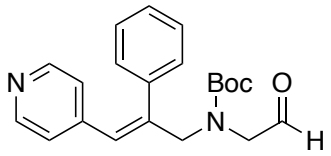


# $^{13}$C NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(thiophen-3-yl)allyl)carbamate (1v')

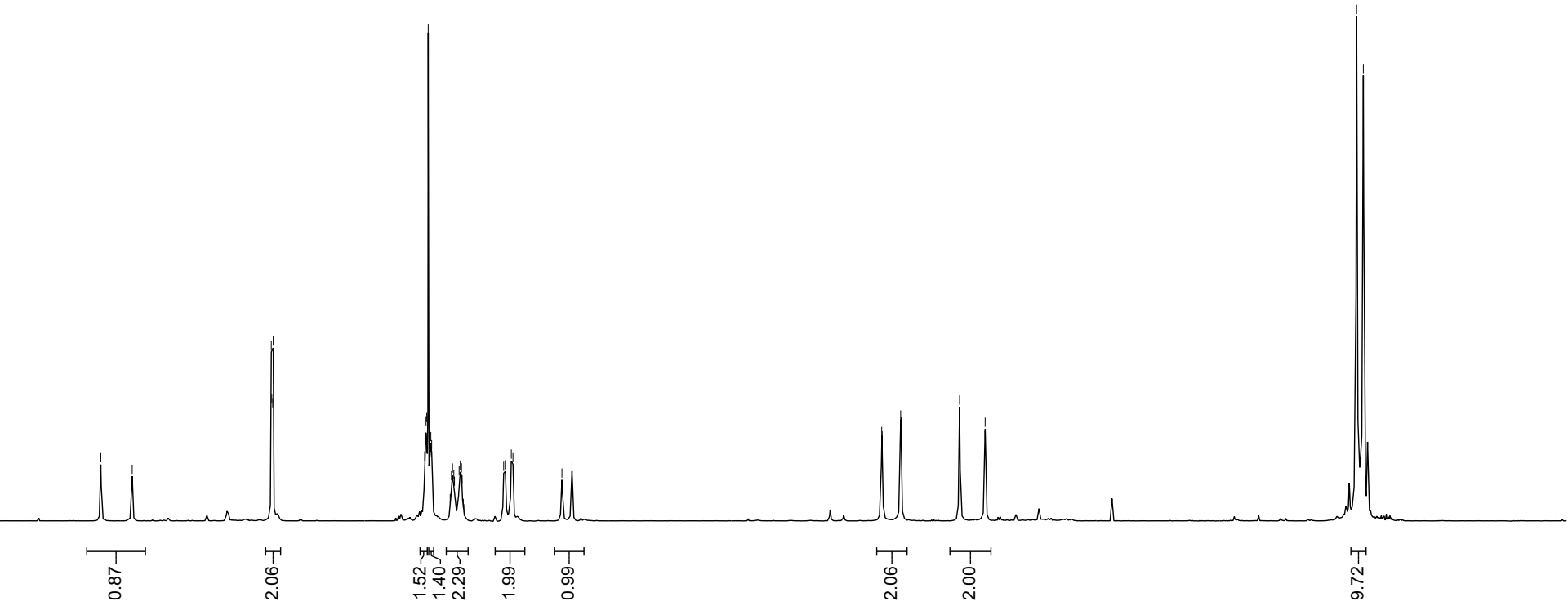


# $^1$H NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(pyridin-4-yl)allyl)carbamate (1w')



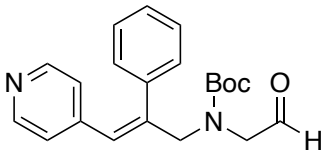

500 MHz, $CDCl_3$

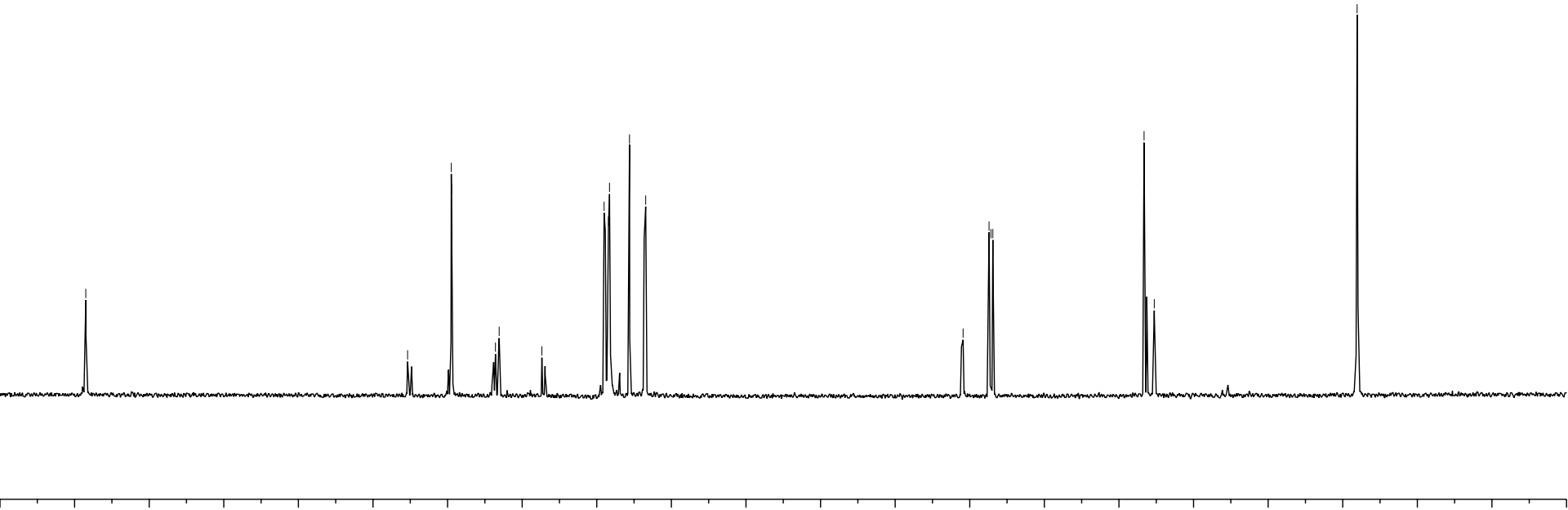


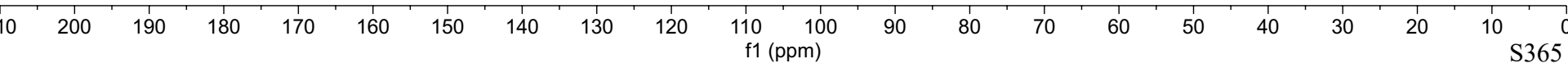
# $^{13}$C NMR *tert*-Butyl (*E*)-(2-oxoethyl)(2-phenyl-3-(pyridin-4-yl)allyl)carbamate (1w')

198.50
155.36
149.50
149.45
143.58
143.09
137.36
129.02
128.43
128.29
125.61
123.44
80.89
77.41 cdcl3
77.16 cdcl3
76.90 cdcl3
56.63
55.27
28.07

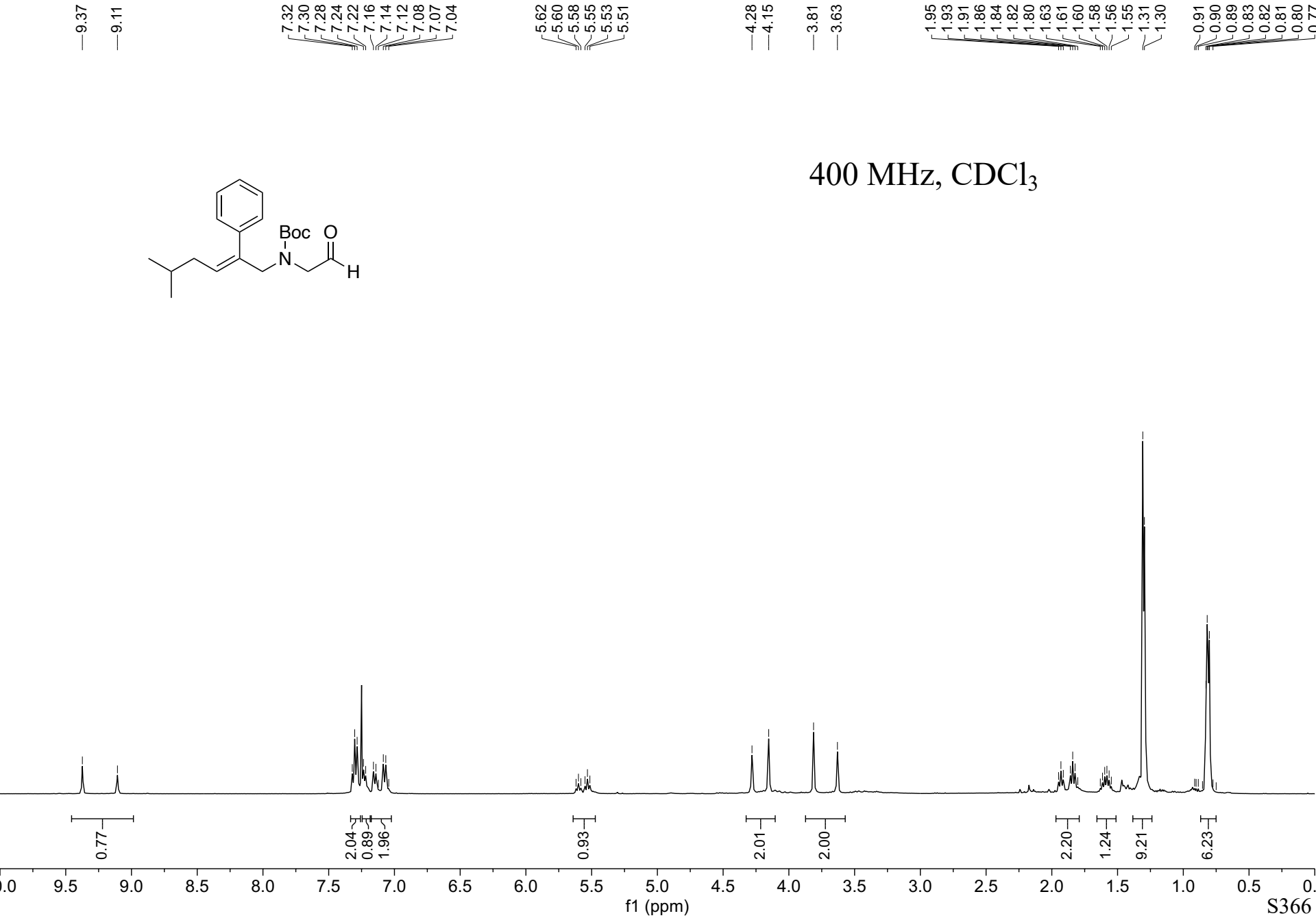
126 MHz, $CDCl_3$



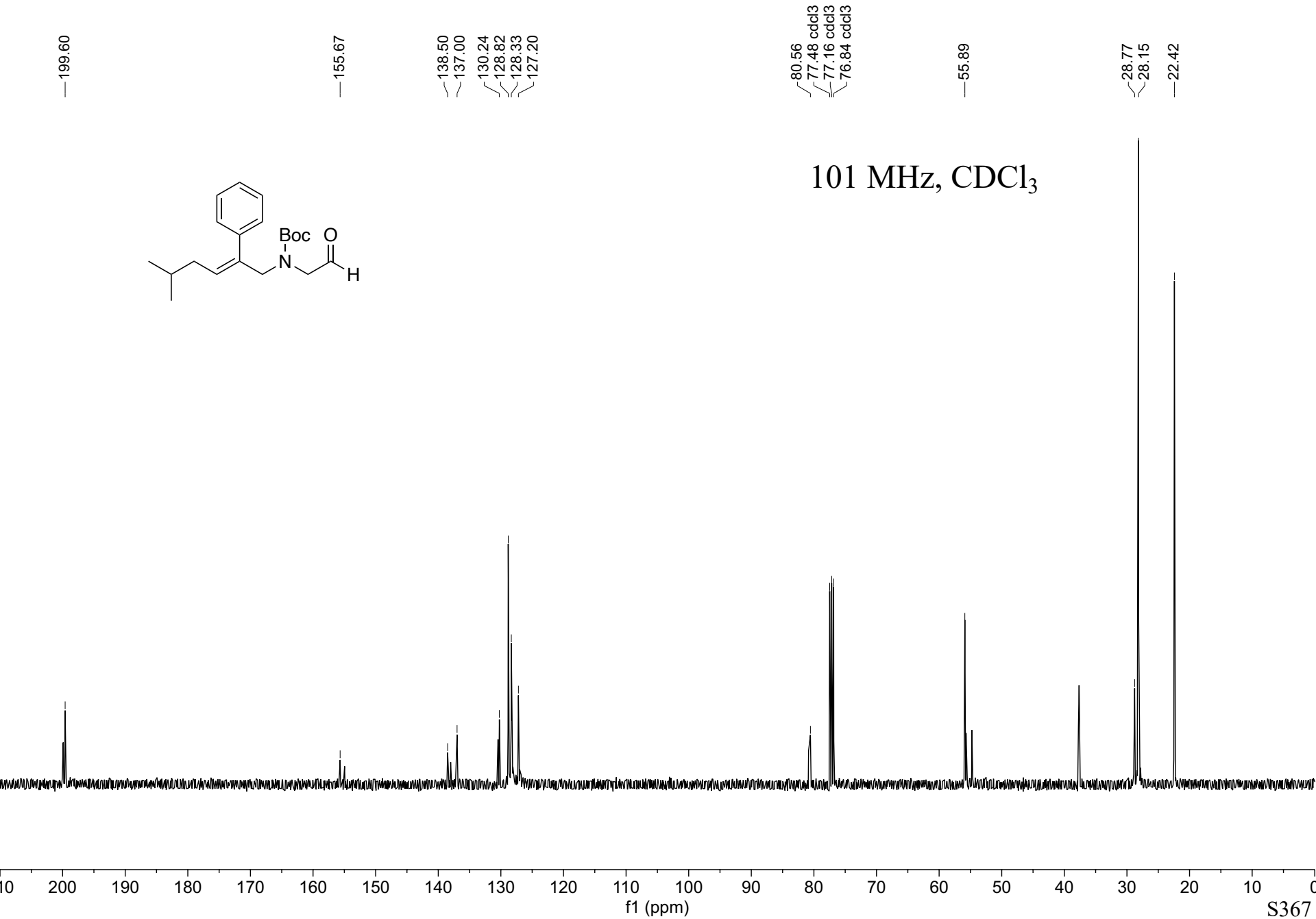





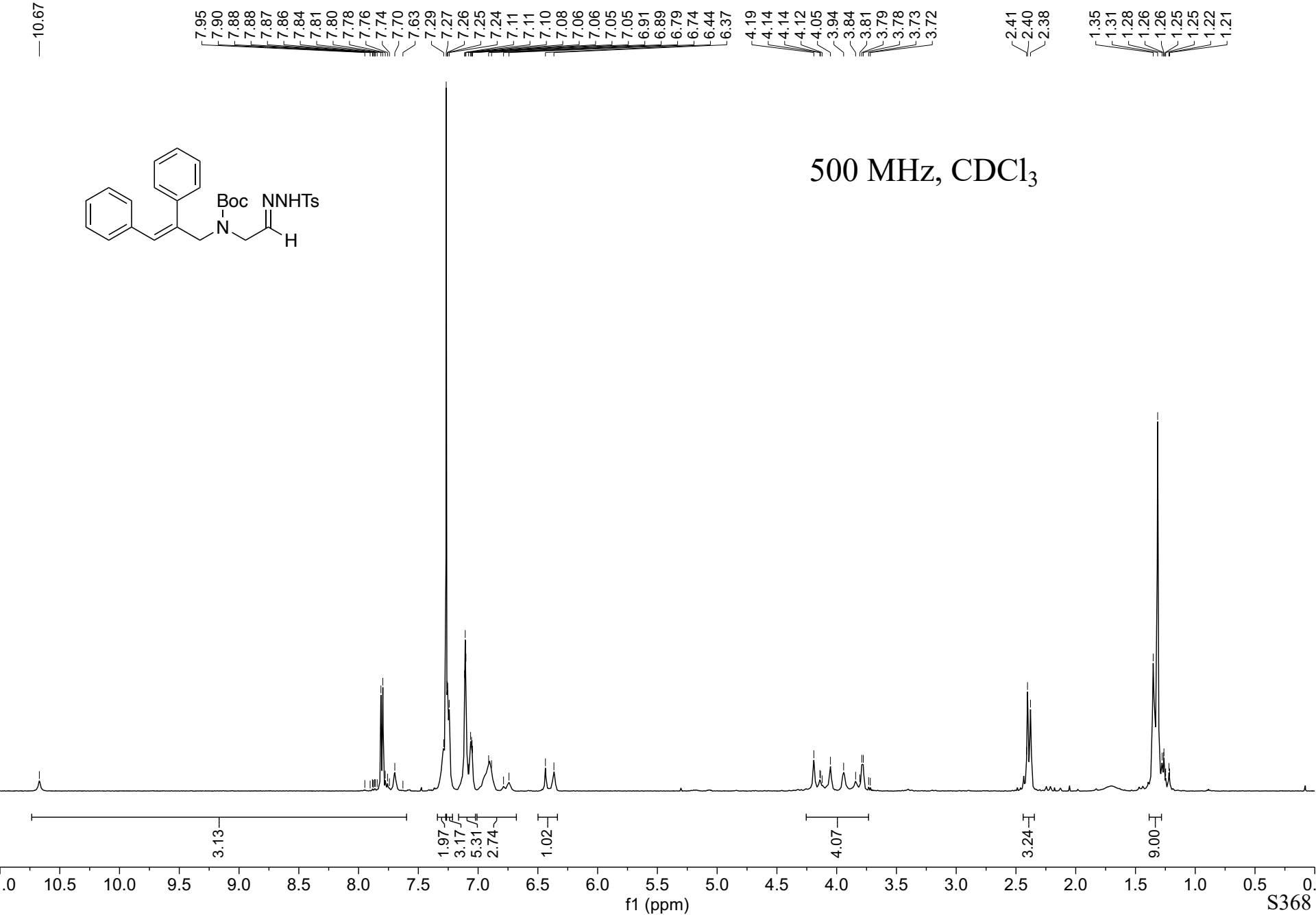
# $^1$H NMR *tert*-butyl (*E*)-(5-methyl-2-phenylhex-2-en-1-yl)(2-oxoethyl)carbamate (1x')



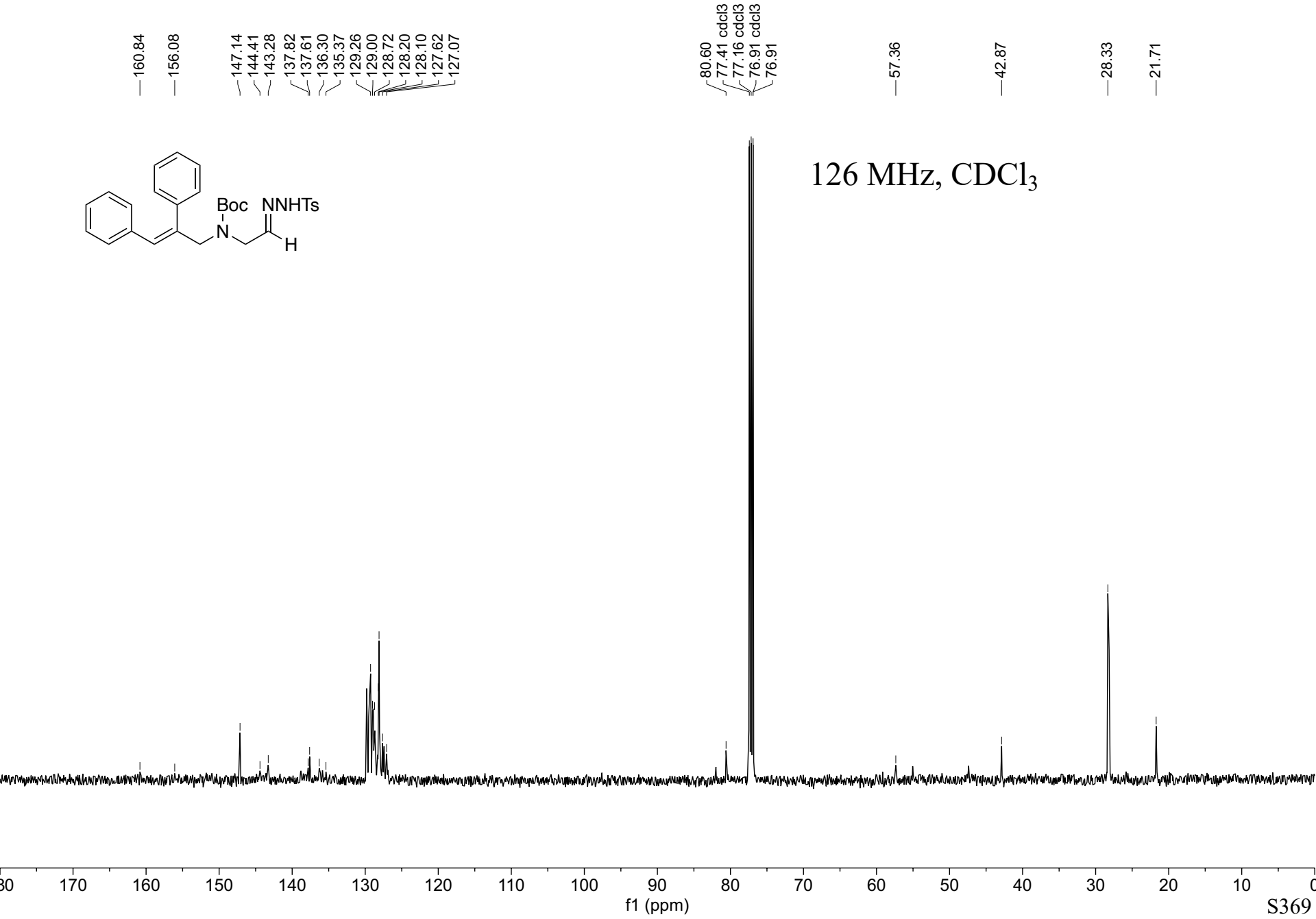
# $^{13}$C NMR *tert*-butyl (*E*)-(5-methyl-2-phenylhex-2-en-1-yl)(2-oxoethyl)carbamate (1x')



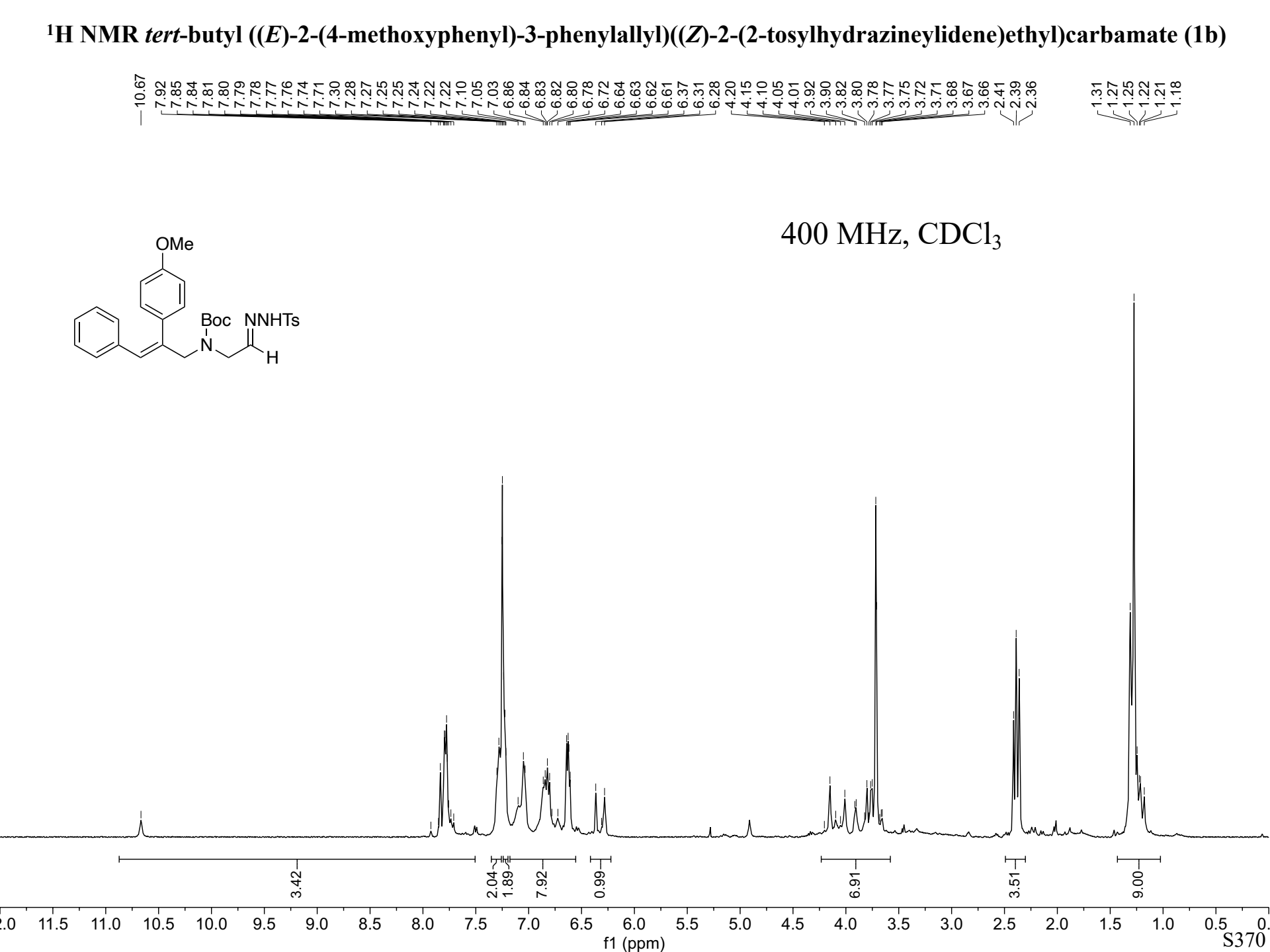
# $^1$H NMR *tert*-butyl ((*E*)-2,3-diphenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1a)



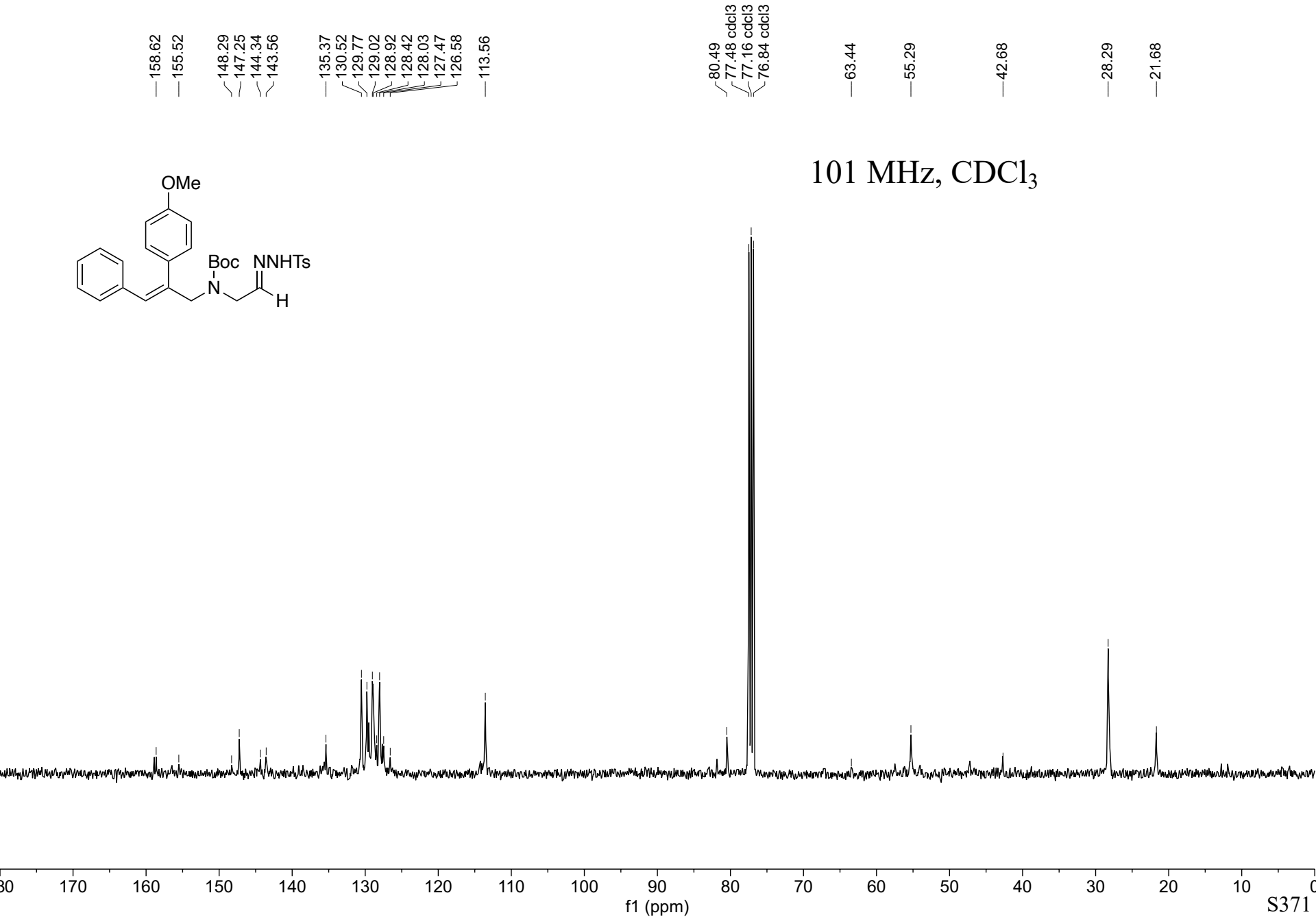
# $^{13}$C NMR *tert*-butyl ((*E*)-2,3-diphenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1a)



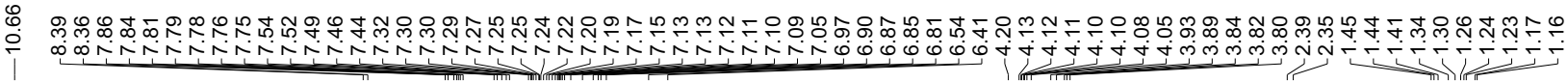
**$^1$H NMR *tert*-butyl ((*E*)-2-(4-methoxyphenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1b)**

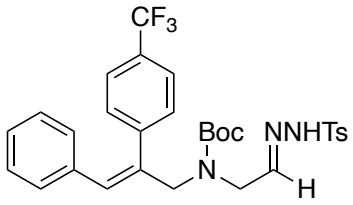


**$^{13}$C NMR *tert*-butyl ((*E*)-2-(4-methoxyphenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1b)**



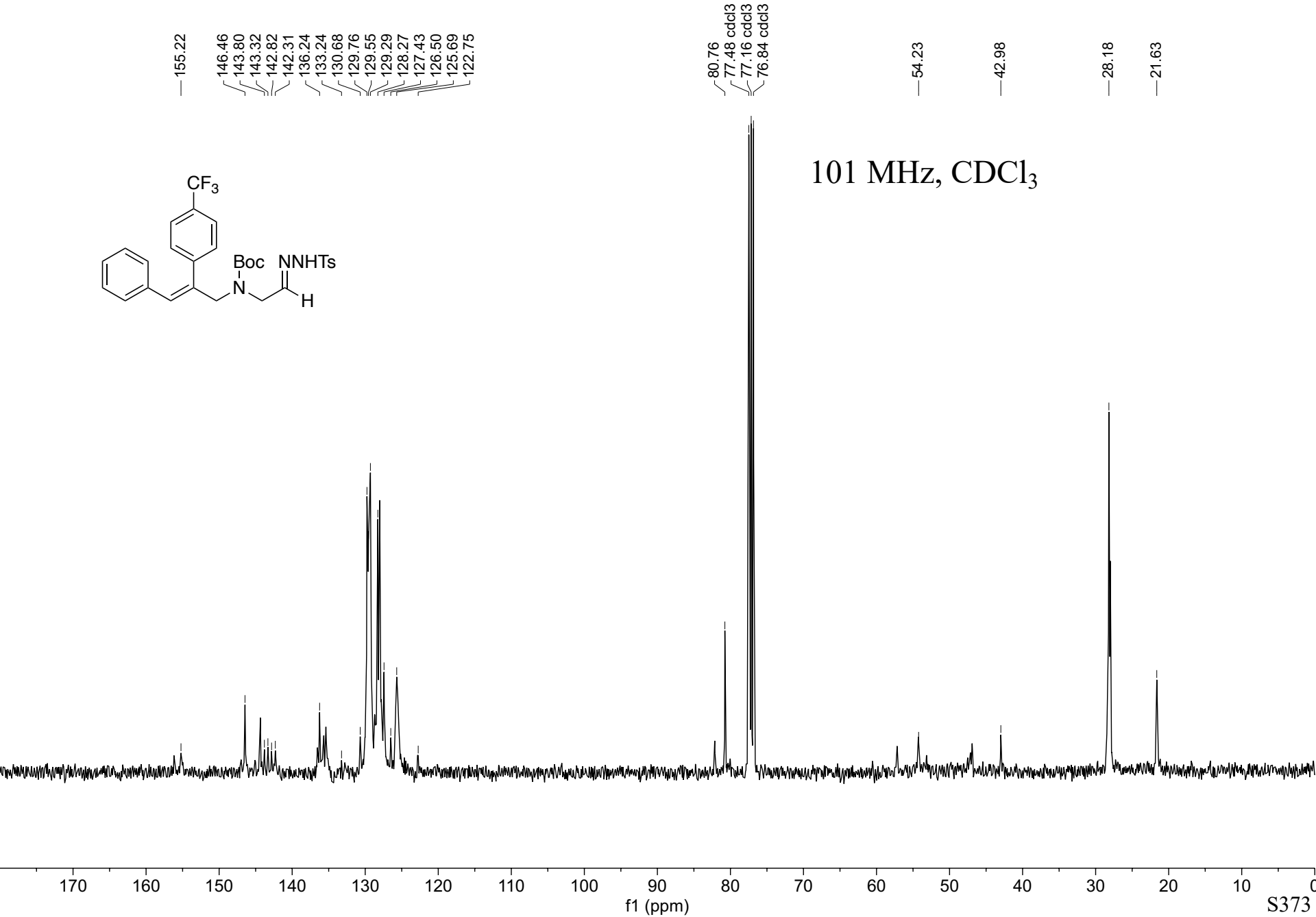
**$^1$H NMR *tert*-Butyl ((*E*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1c)**



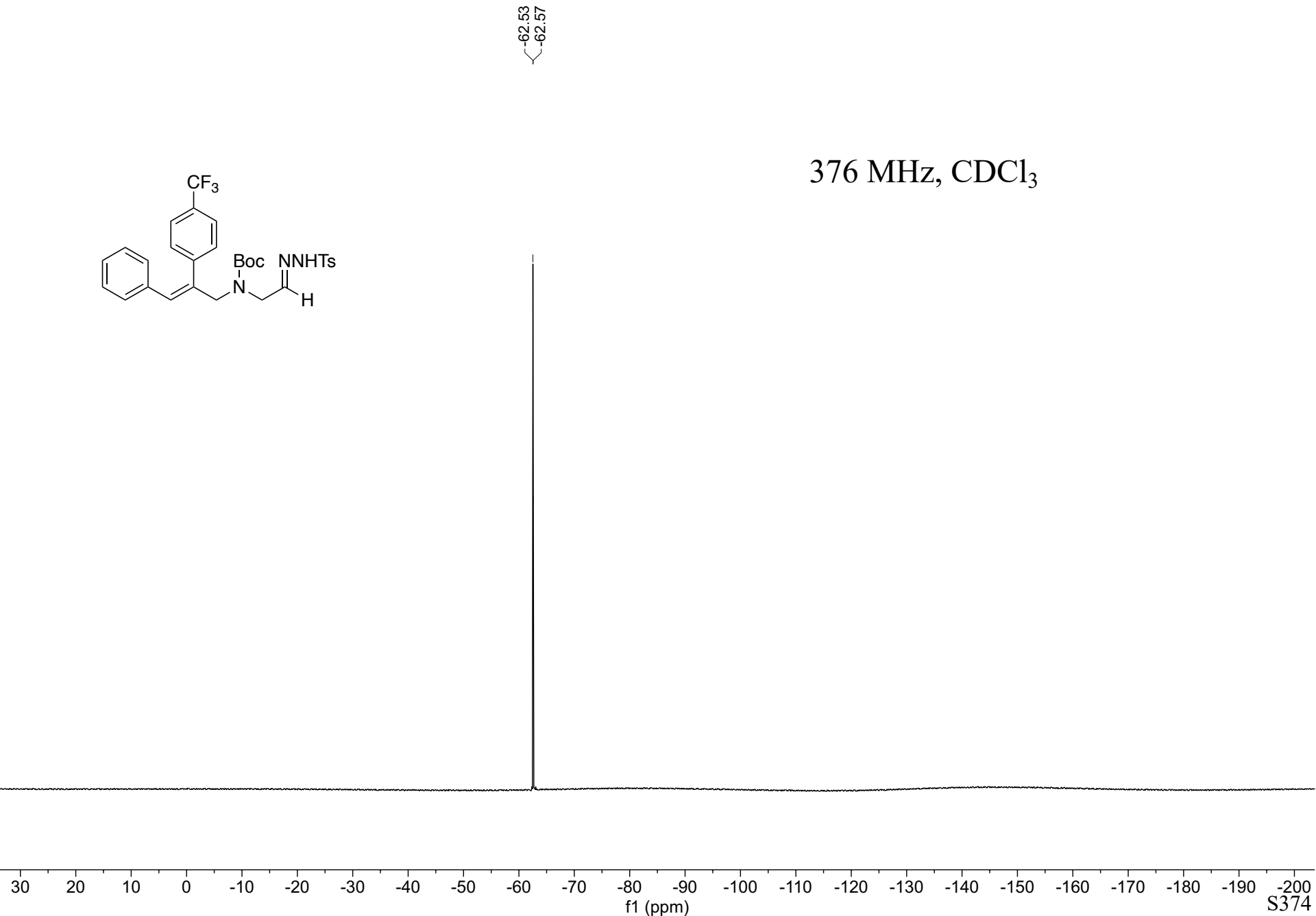




400 MHz, $CDCl_3$

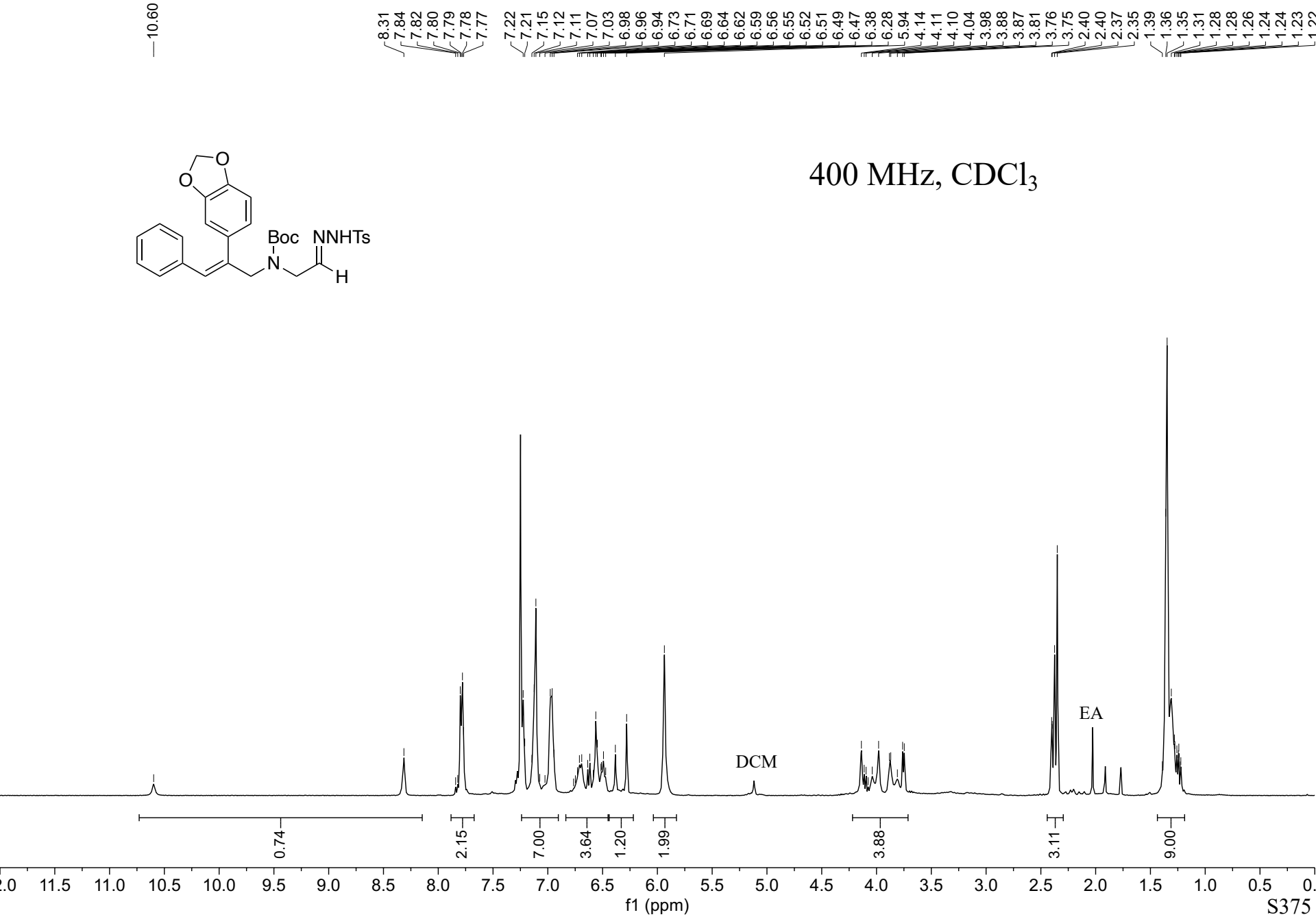
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1c)**



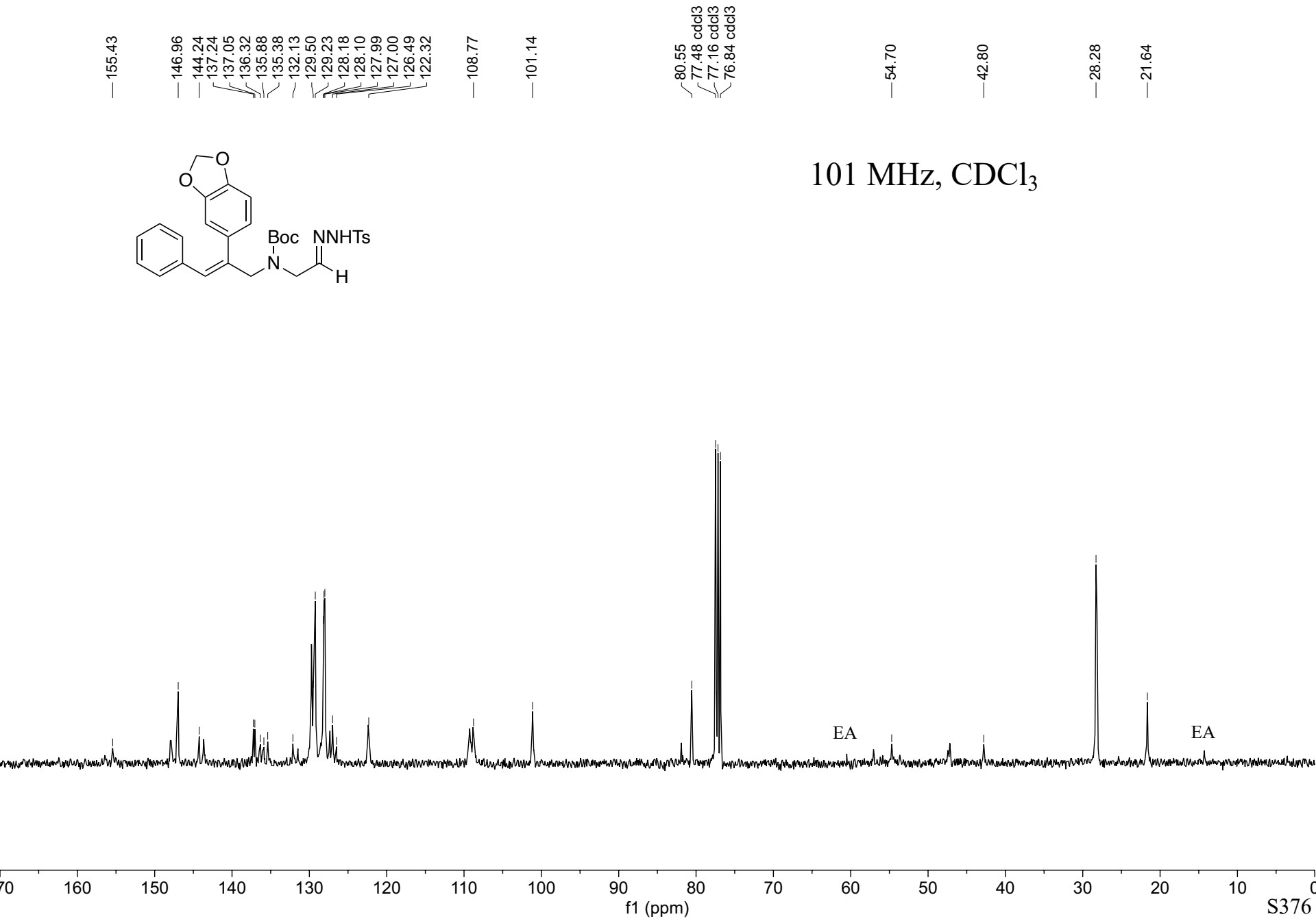
**$^{19}$F NMR *tert*-Butyl ((*E*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1c)**



**$^1$H NMR *tert*-butyl ((*E*)-2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1d)**

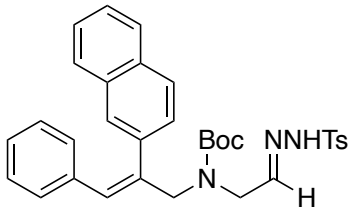


**$^{13}$C NMR *tert*-butyl ((*E*)-2-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1d)**



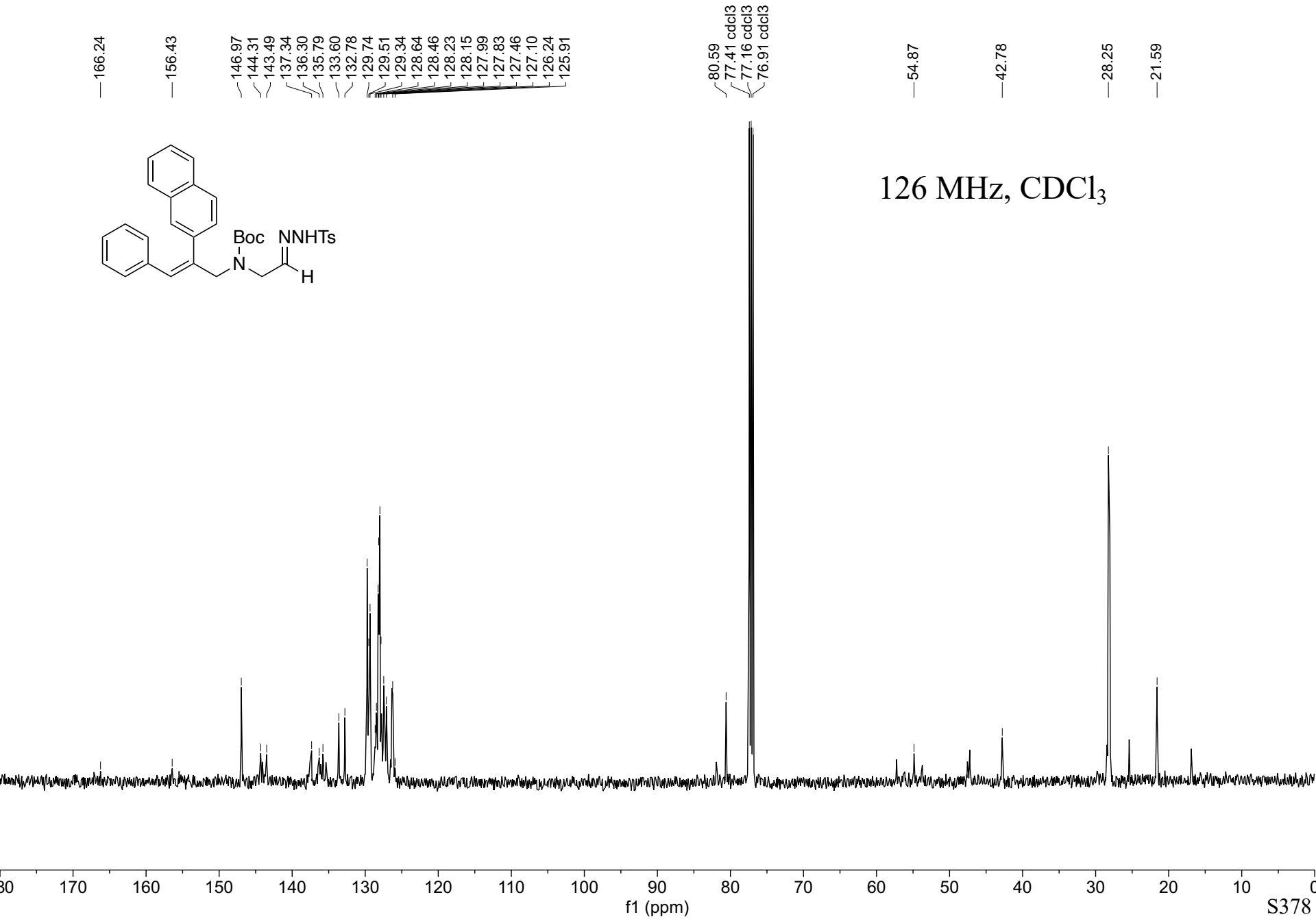
**$^1$H NMR *tert*-butyl ((*E*)-2-(naphthalen-2-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1e)**



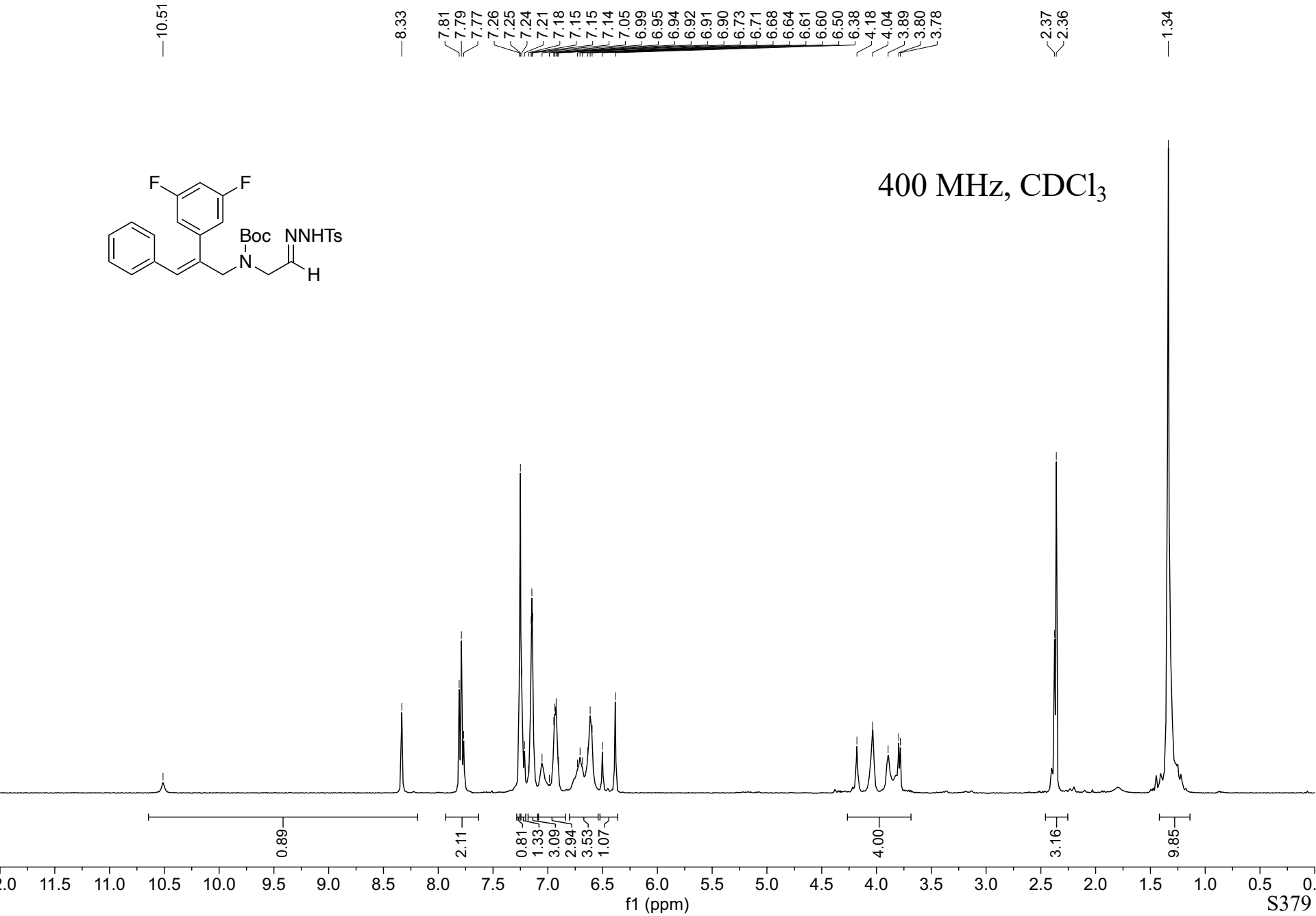




500 MHz, $CDCl_3$

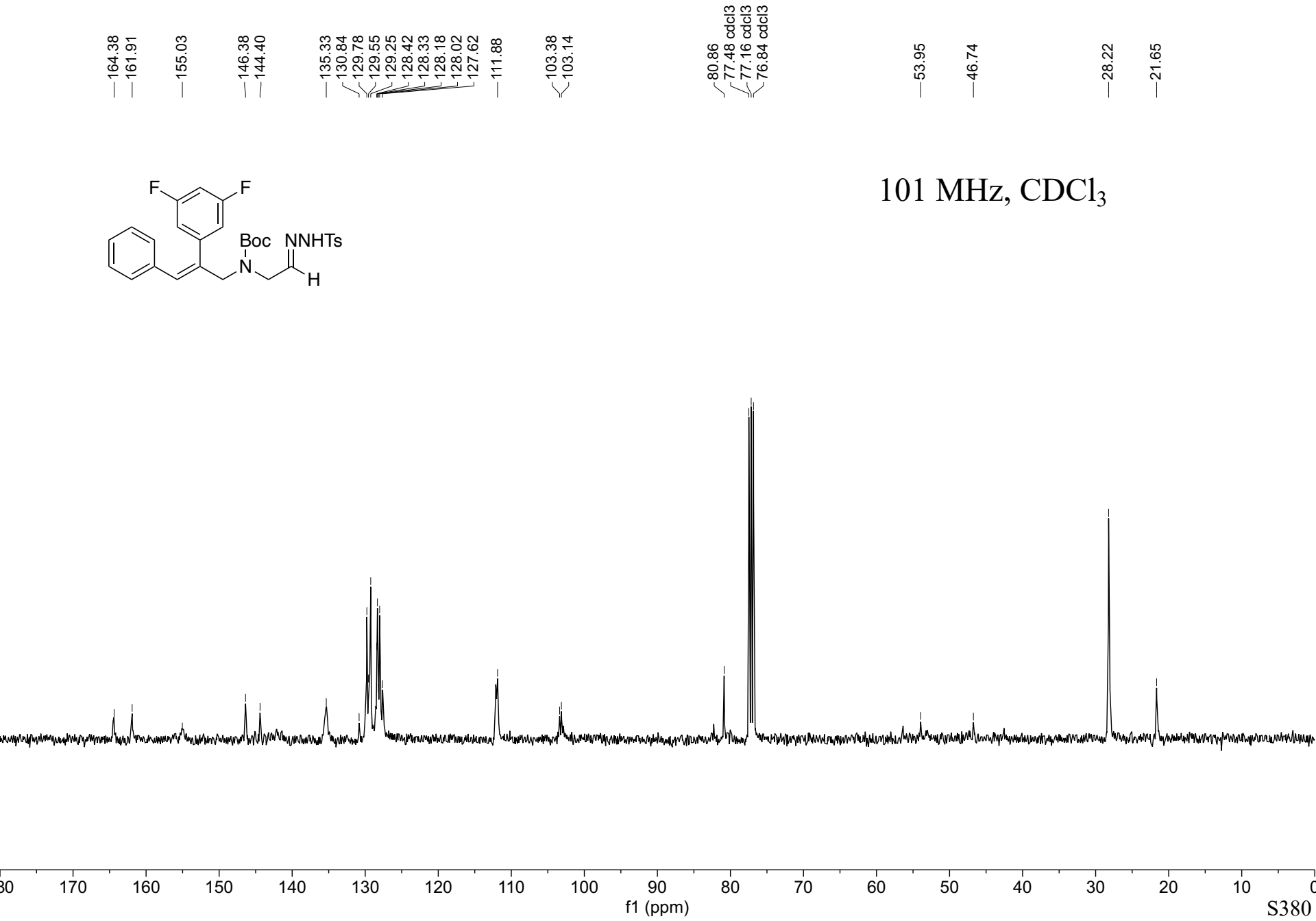
**$^{13}$C NMR *tert*-butyl ((*E*)-2-(naphthalen-2-yl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1e)**



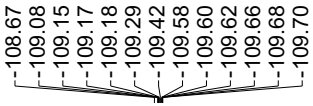
**$^1$H NMR *tert*-Butyl ((*E*)-2-(3,5-difluorophenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1f)**

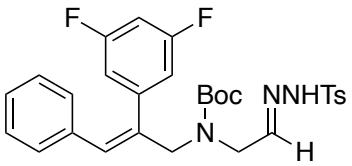


**$^{13}$C NMR *tert*-Butyl ((*E*)-2-(3,5-difluorophenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1f)**

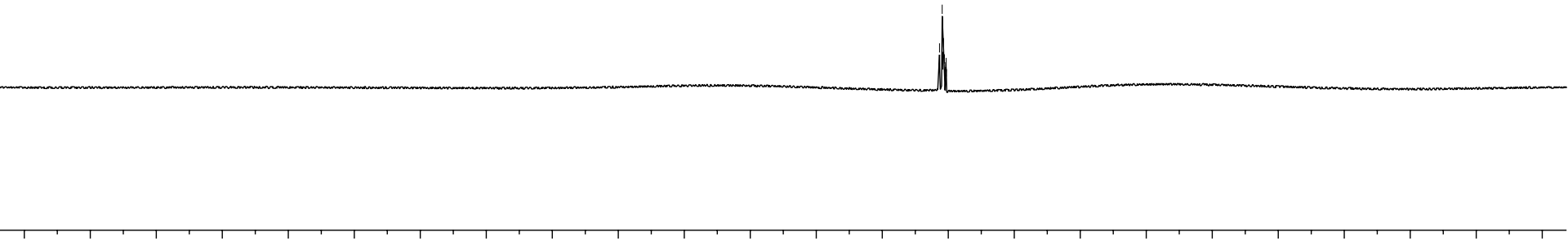


**$^{19}$F NMR *tert*-Butyl ((*E*)-2-(3,5-difluorophenyl)-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1f)**



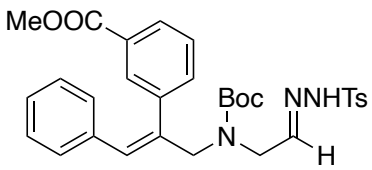




376 MHz, $CDCl_3$

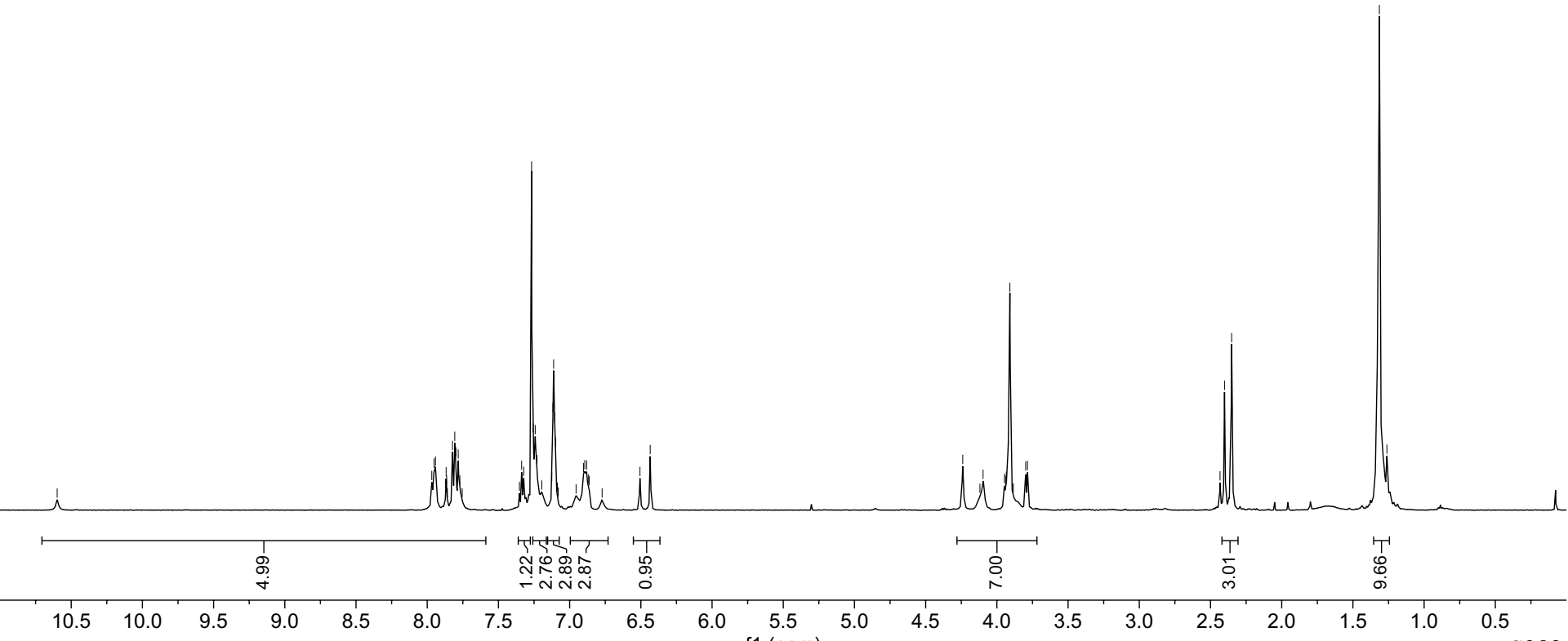


**$^1$H NMR Methyl 3-((*E*)-3-((*tert*-butoxycarbonyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g)**

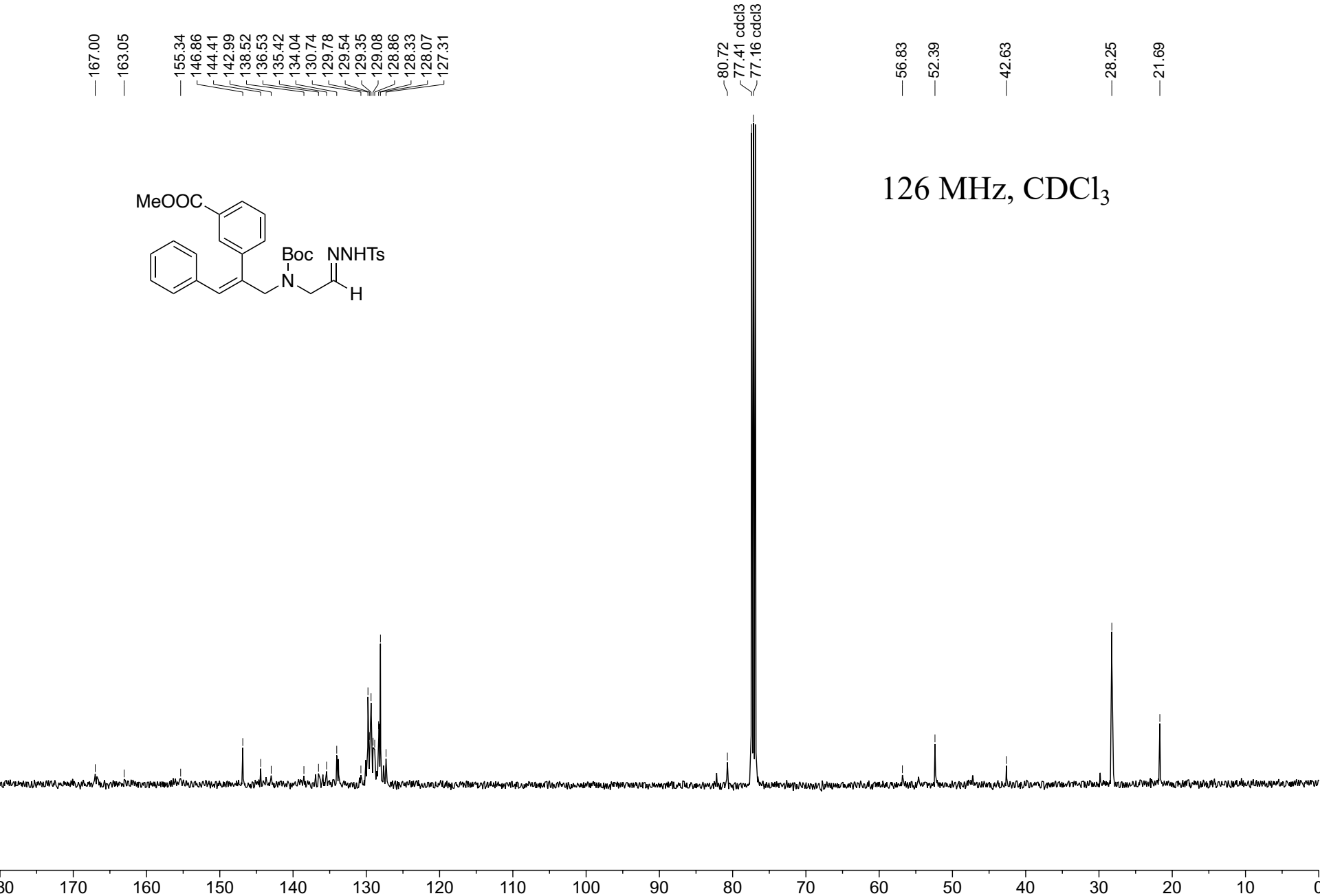


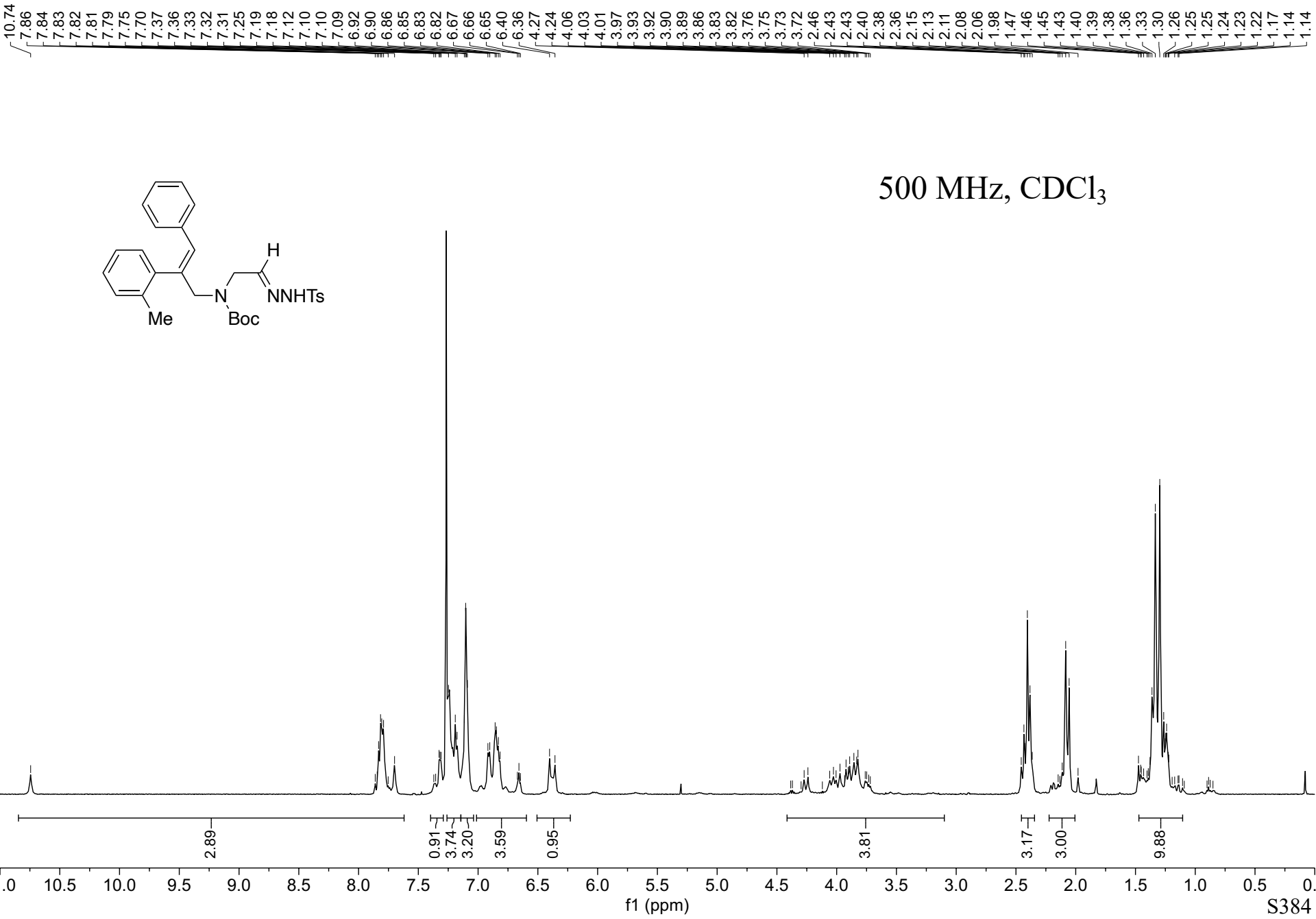

500 MHz, $CDCl_3$



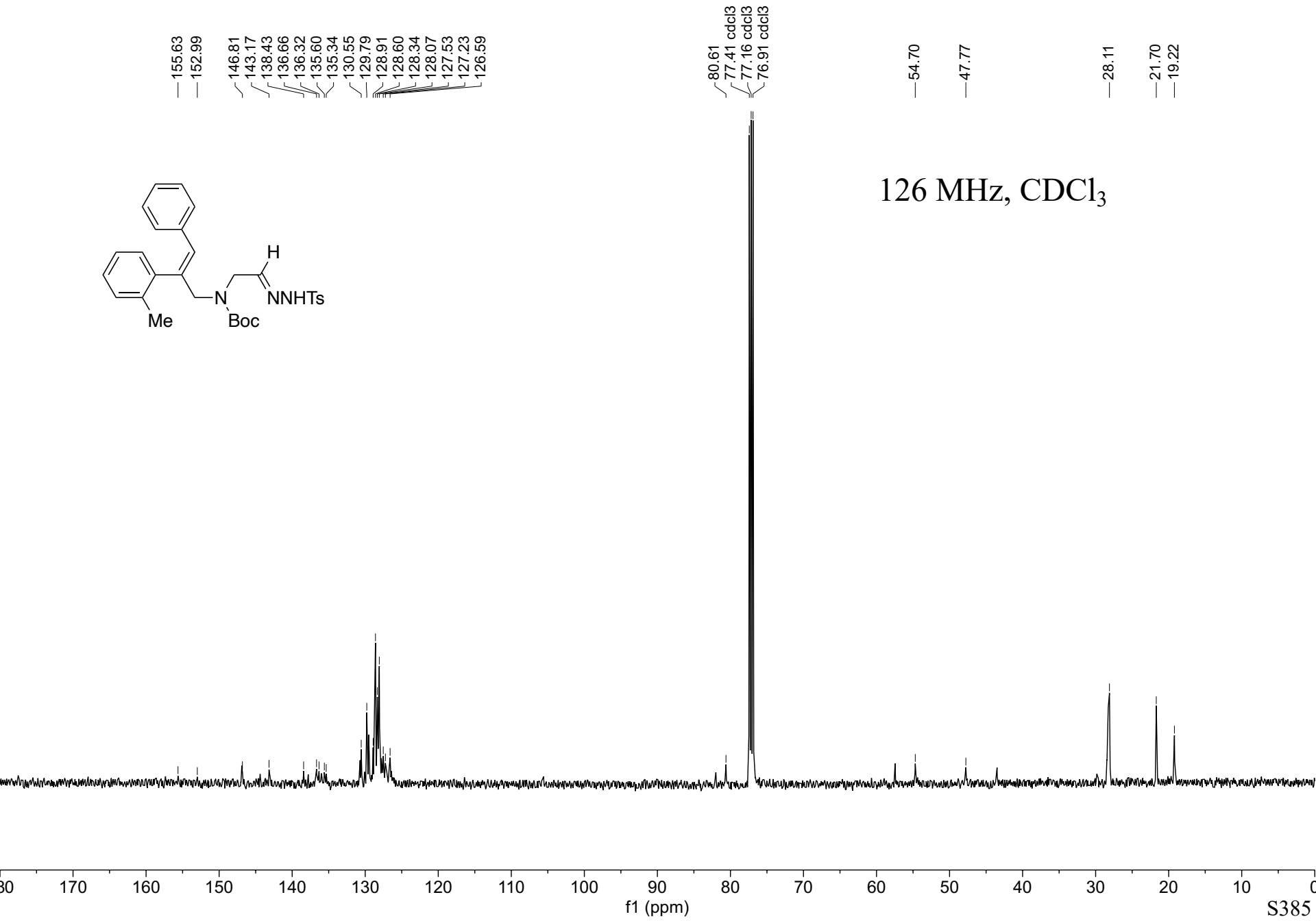
**$^{13}$C NMR Methyl 3-((*E*)-3-((*tert*-butoxycarbonyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)amino)-1-phenylprop-1-en-2-yl)benzoate (1g)**



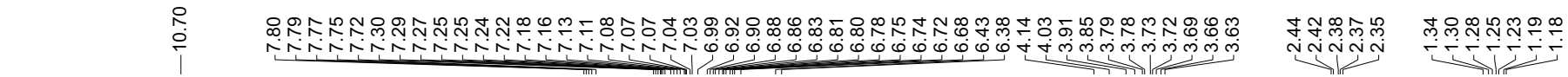
# $^1$H NMR *tert*-Butyl ((*E*)-3-phenyl-2-(*o*-tolyl)allyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1h)

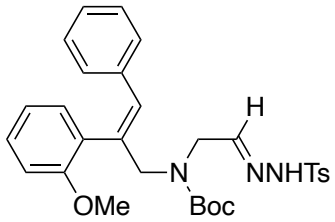


# $^{13}$C NMR *tert*-Butyl ((*E*)-3-phenyl-2-(*o*-tolyl)allyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1h)

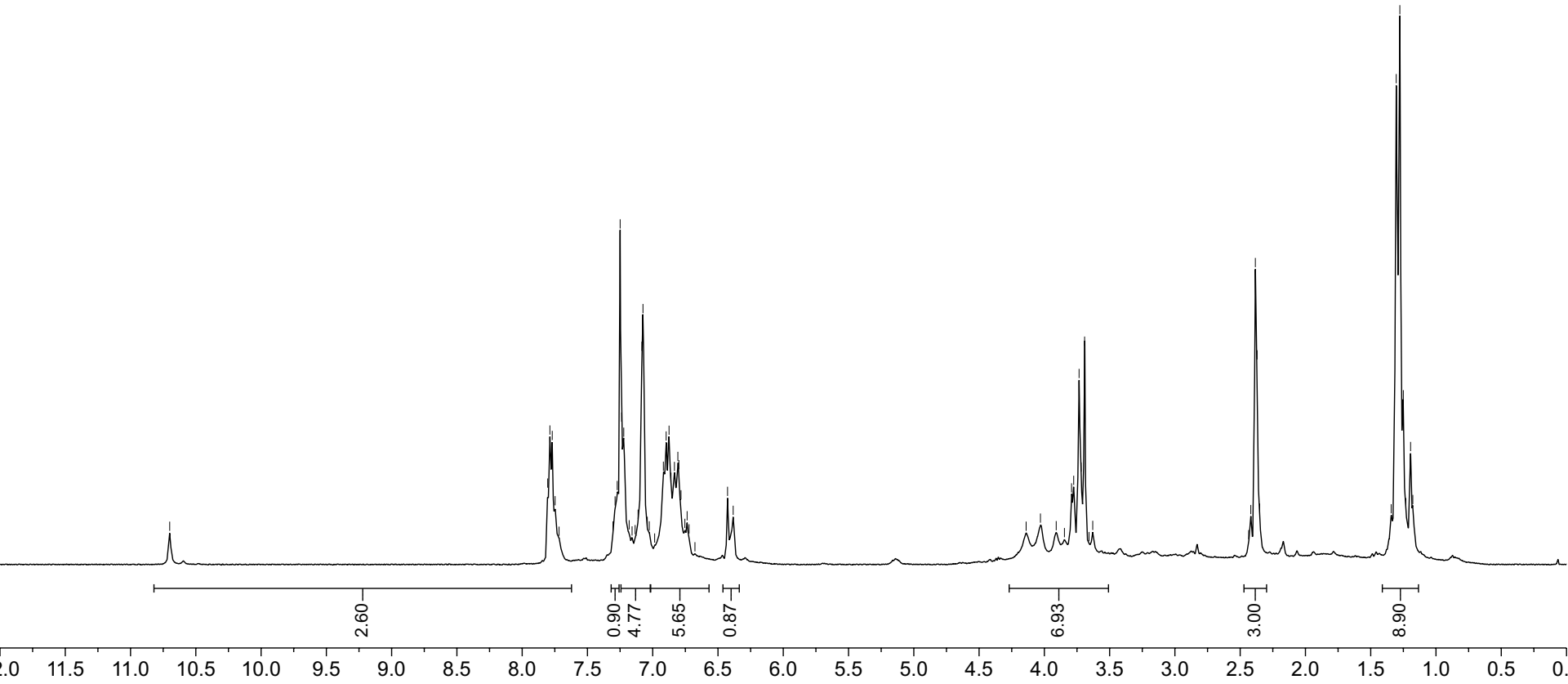


**$^1$H NMR *tert*-Butyl ((*E*)-2-(2-methoxyphenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1i)**

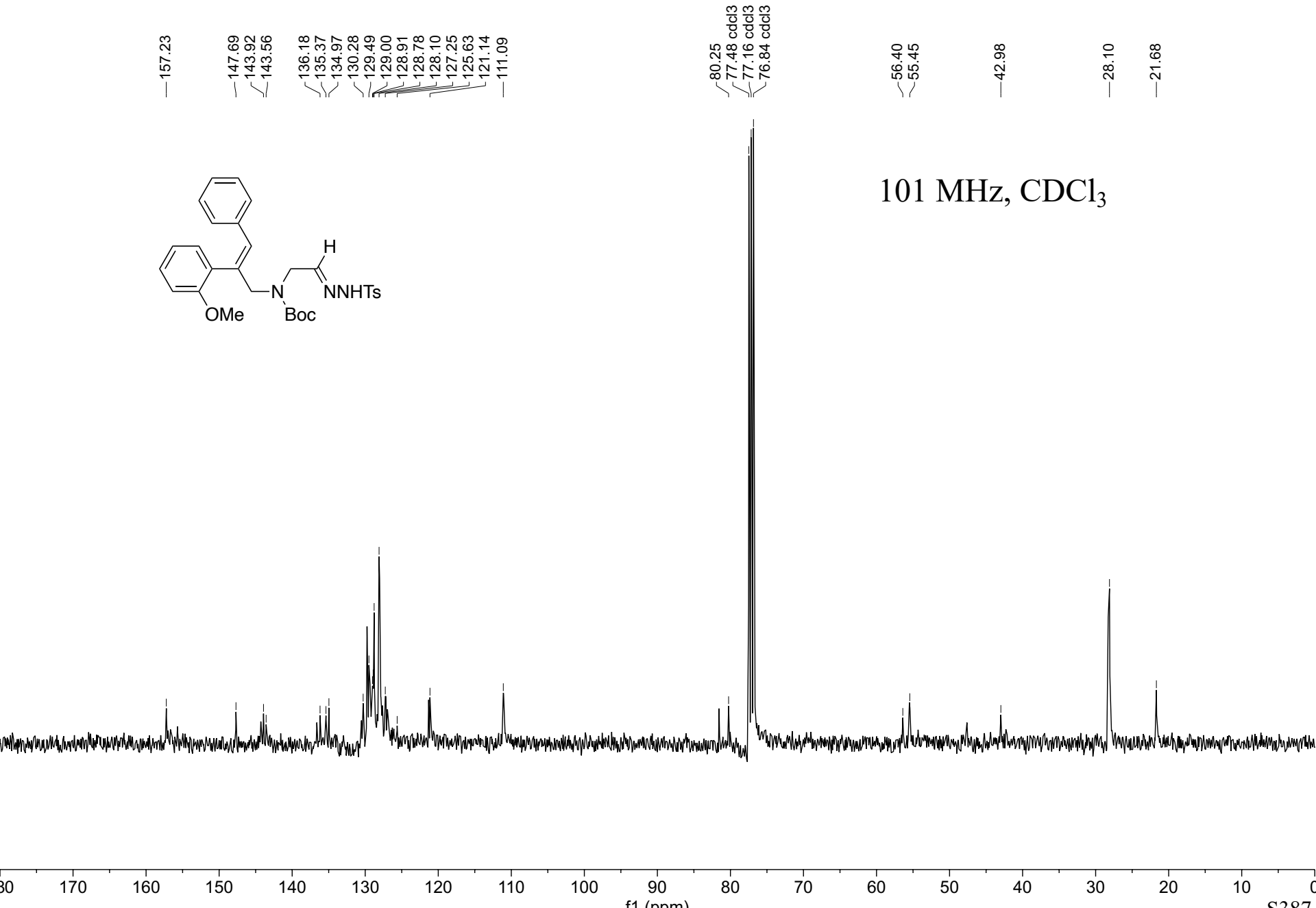


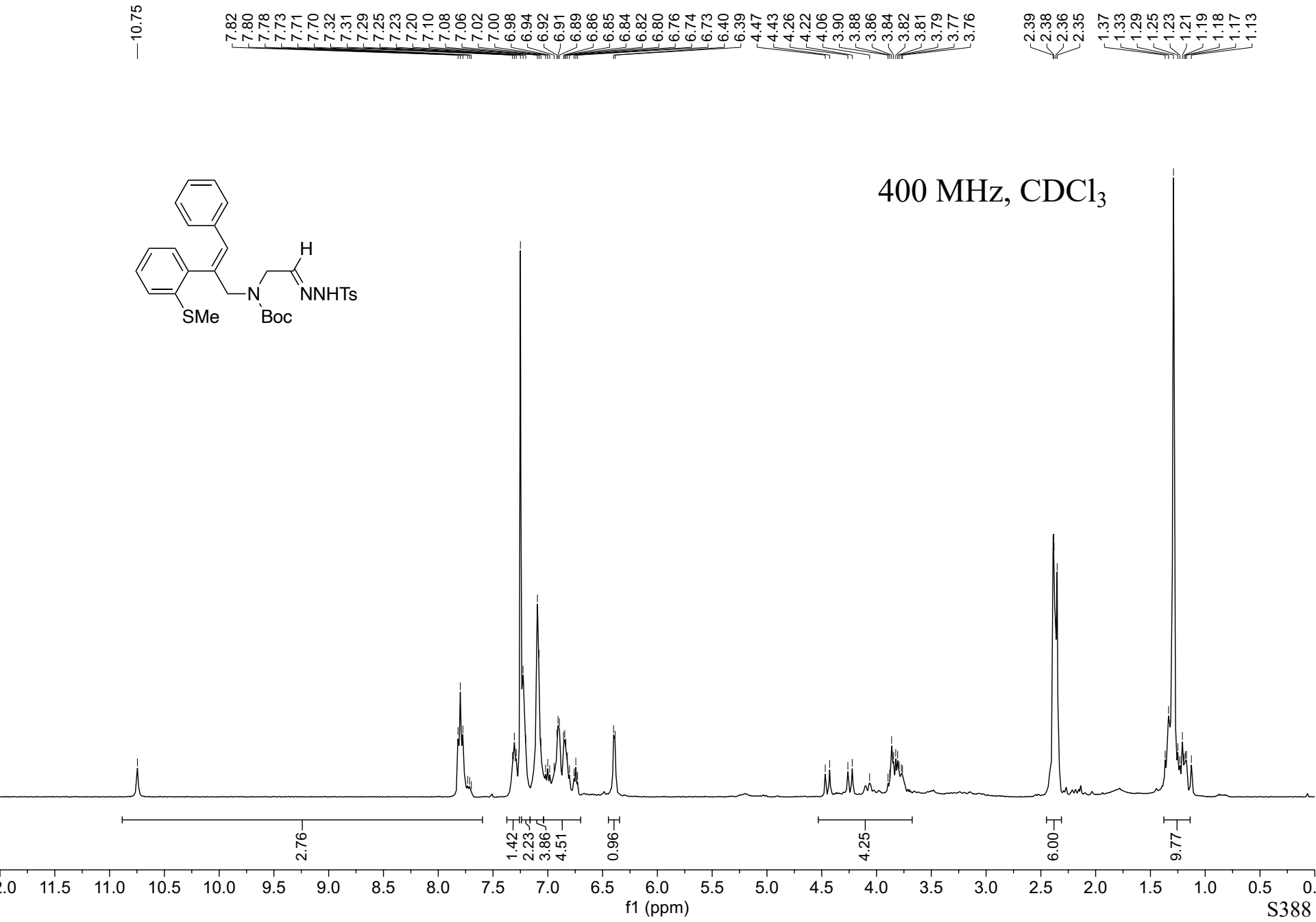

400 MHz, $CDCl_3$



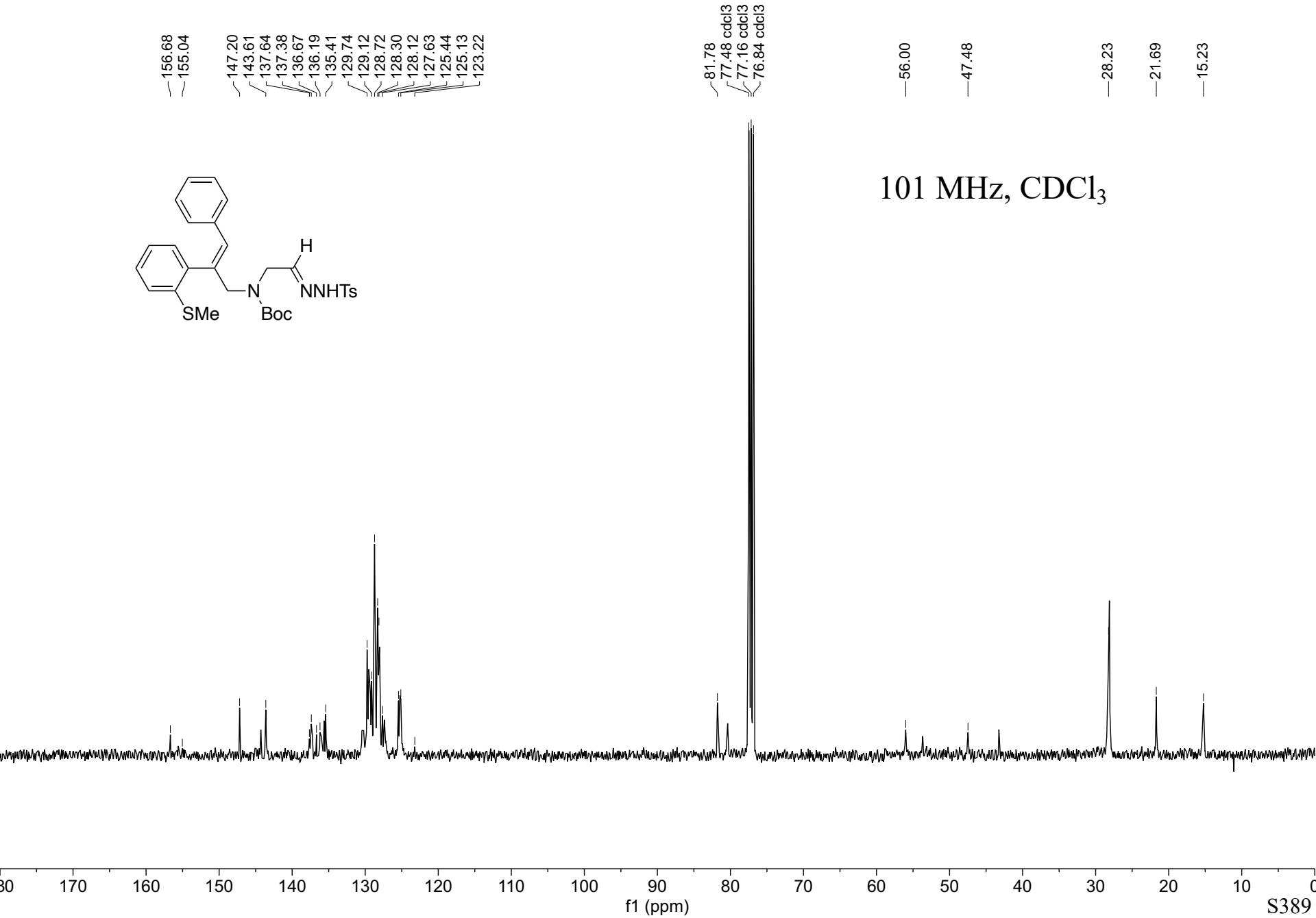
**$^{13}$C NMR *tert*-Butyl ((*E*)-2-(2-methoxyphenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1i)**



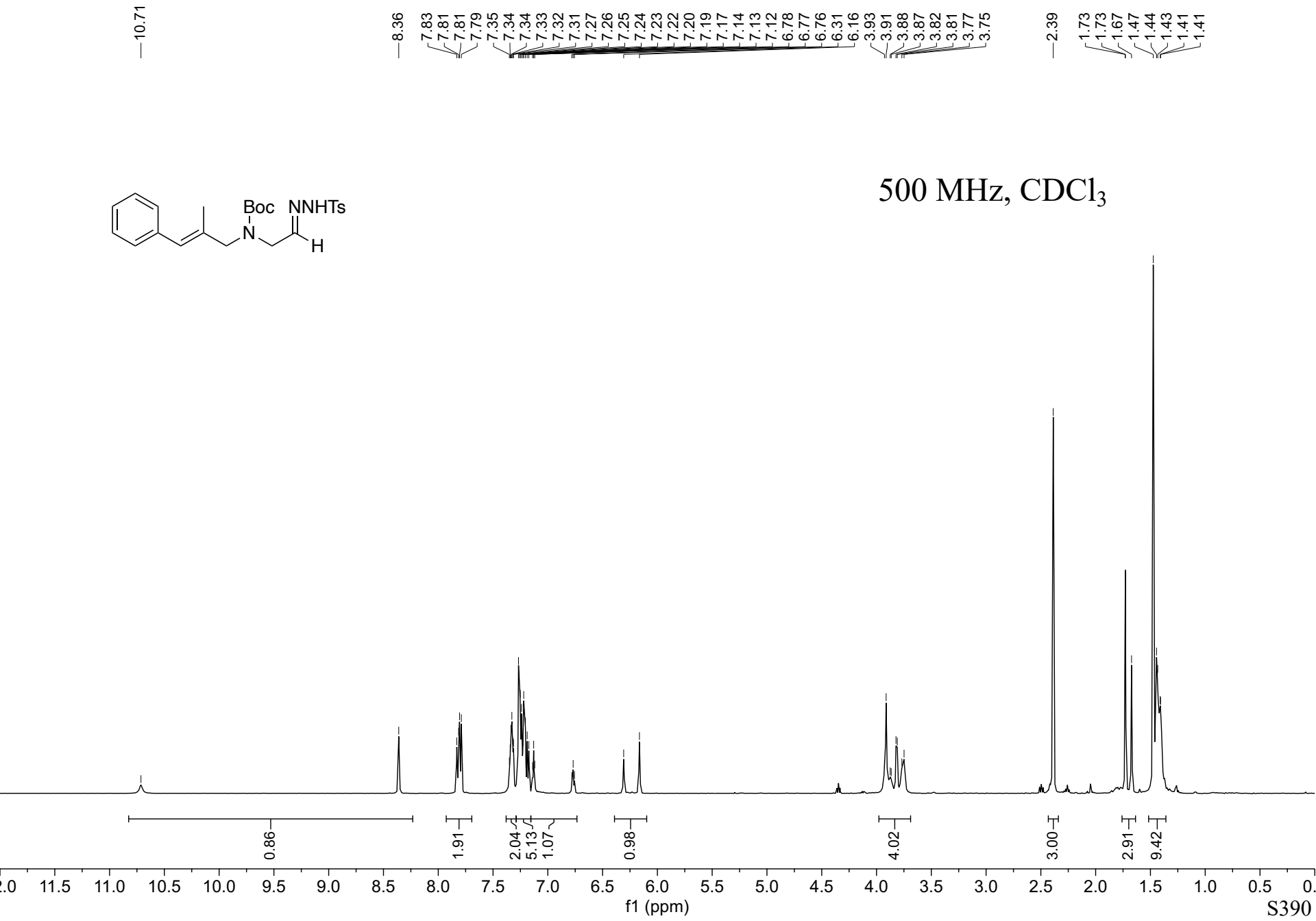
**$^1$H NMR *tert*-Butyl ((*E*)-2-(2-(methylthio)phenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1j)**



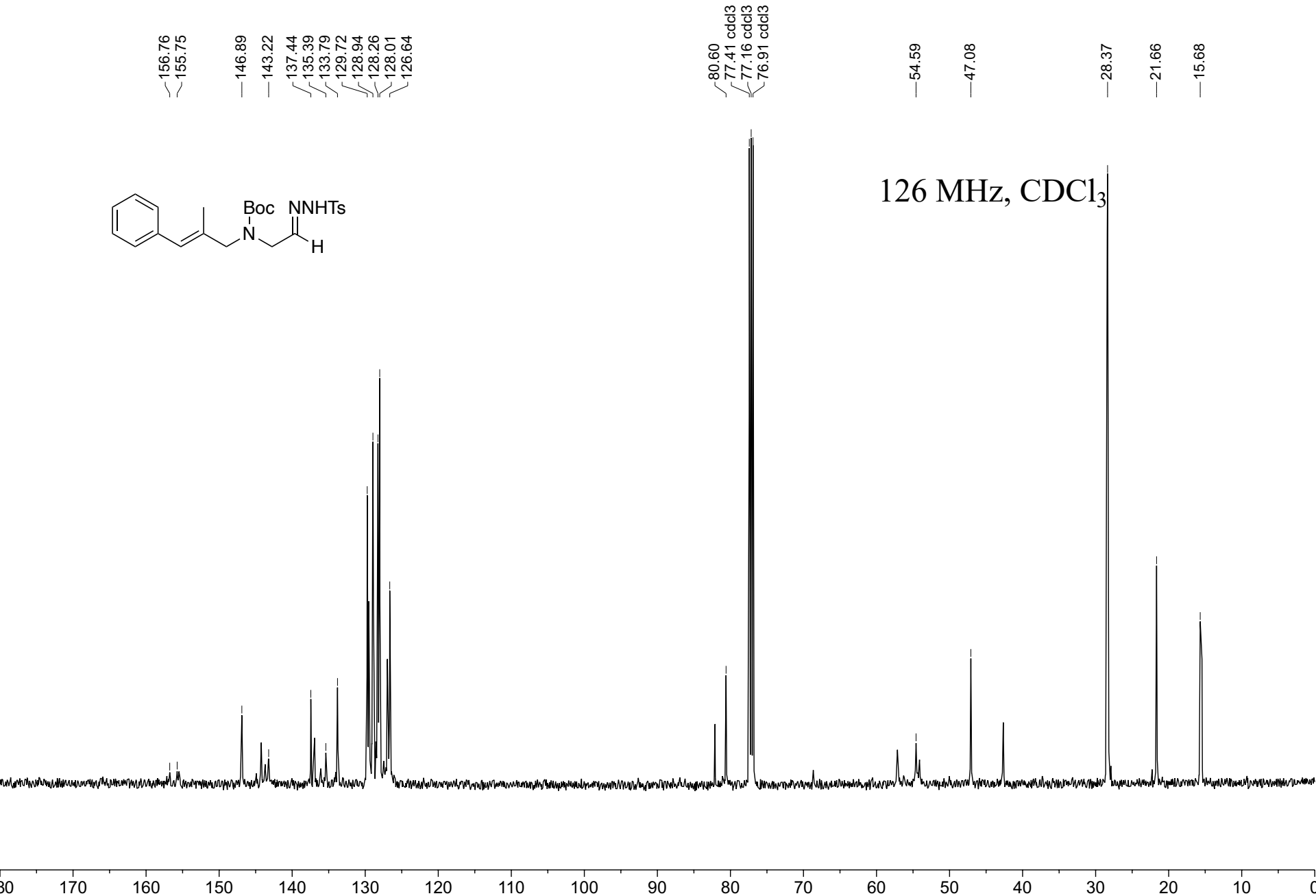
**$^{13}$C NMR *tert*-Butyl ((*E*)-2-(2-(methylthio)phenyl)-3-phenylallyl)((*E*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1j)**



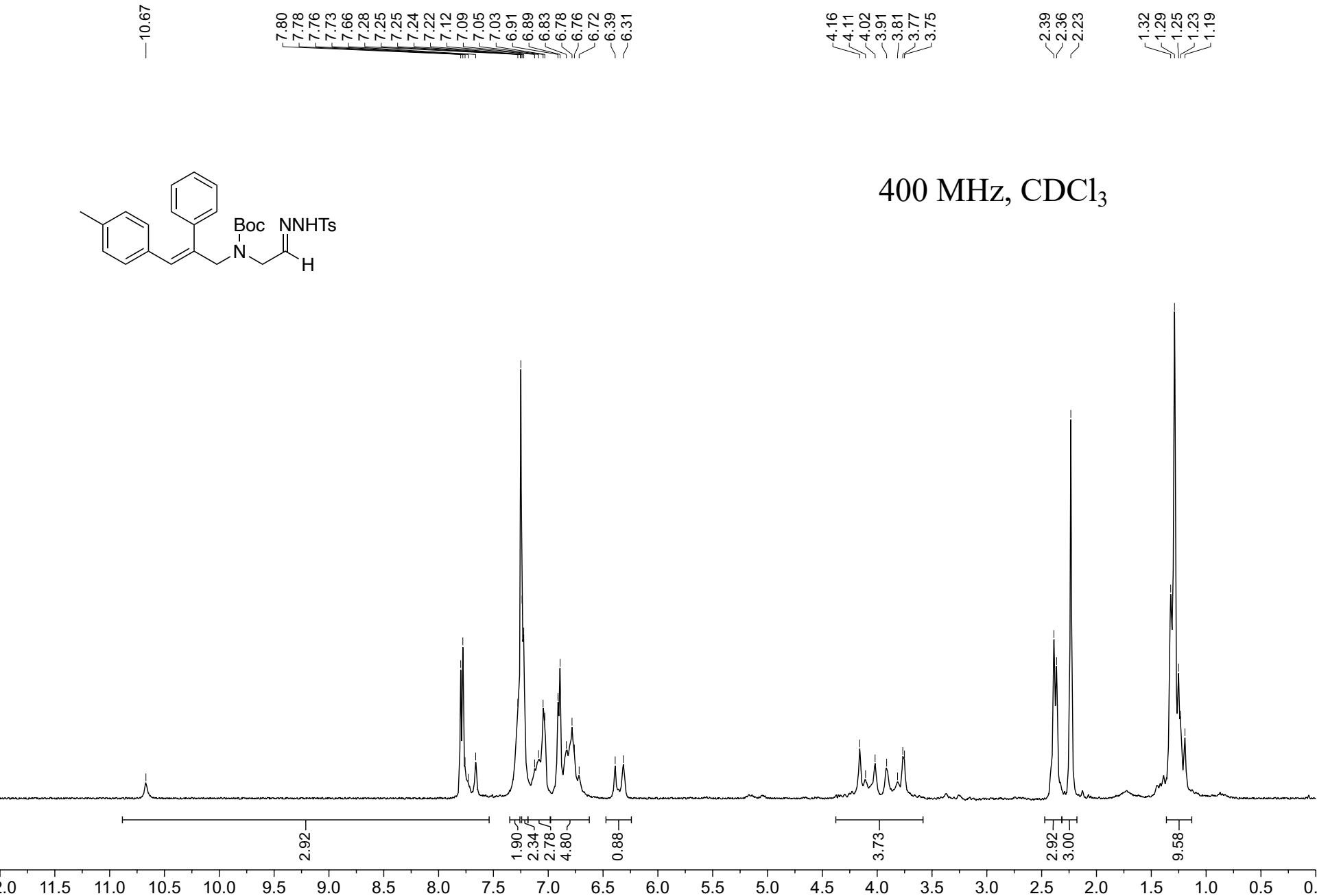
# $^1$H NMR *tert*-Butyl ((*E*)-2-methyl-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1m)



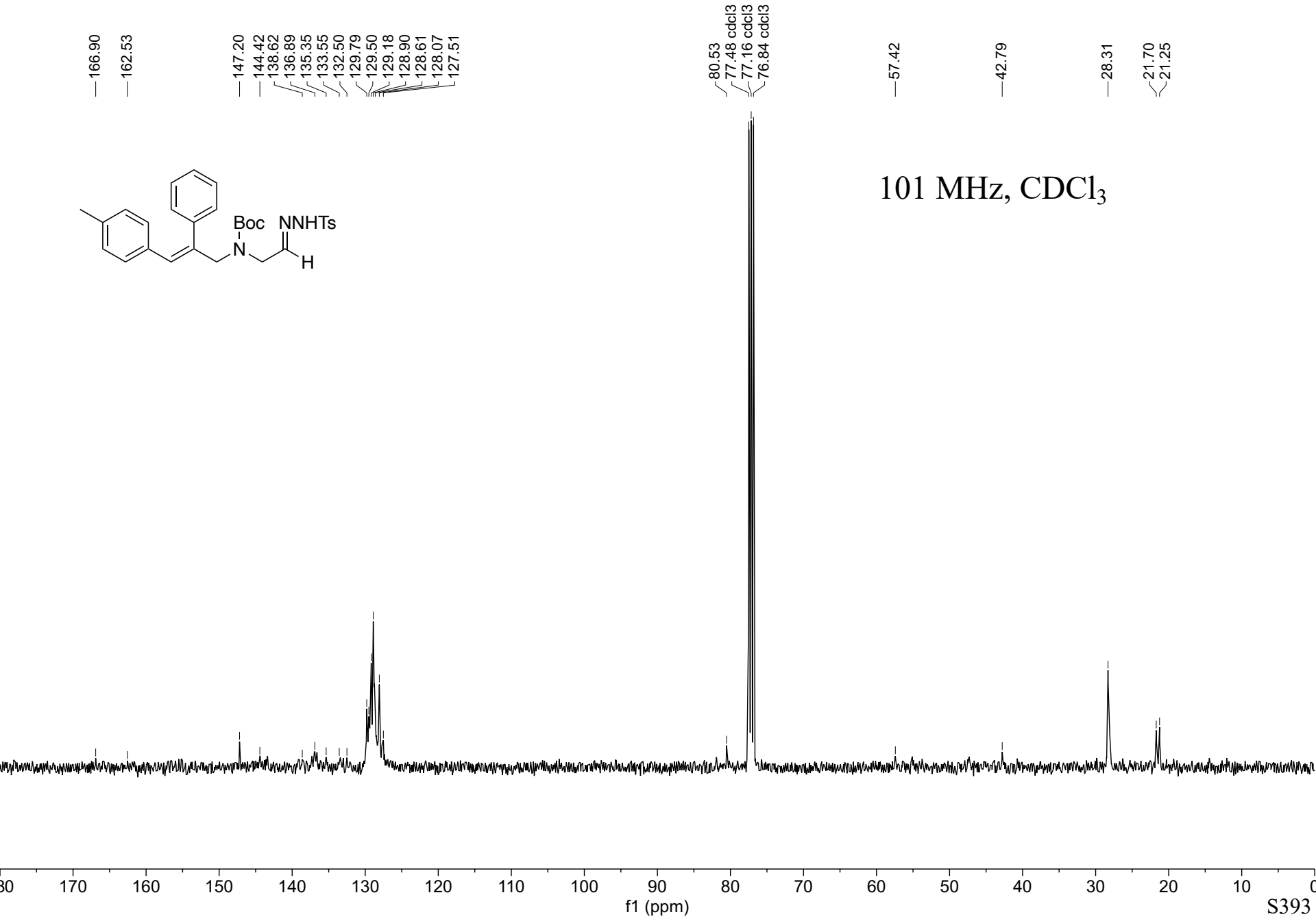
# $^{13}$C NMR *tert*-Butyl ((*E*)-2-methyl-3-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1m)



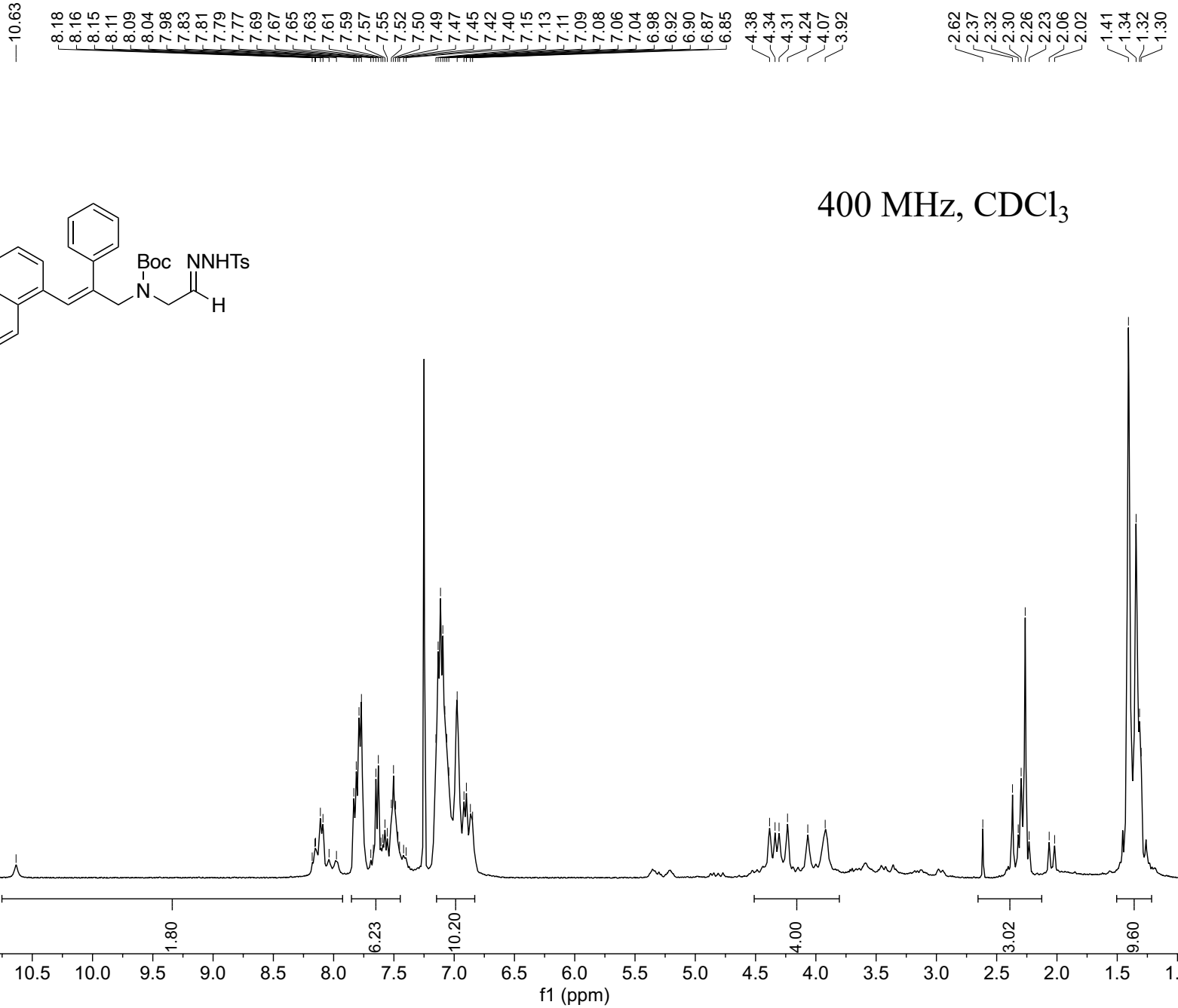
# $^1$H NMR *tert*-Butyl ((*E*)-2-phenyl-3-(*p*-tolyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1n)



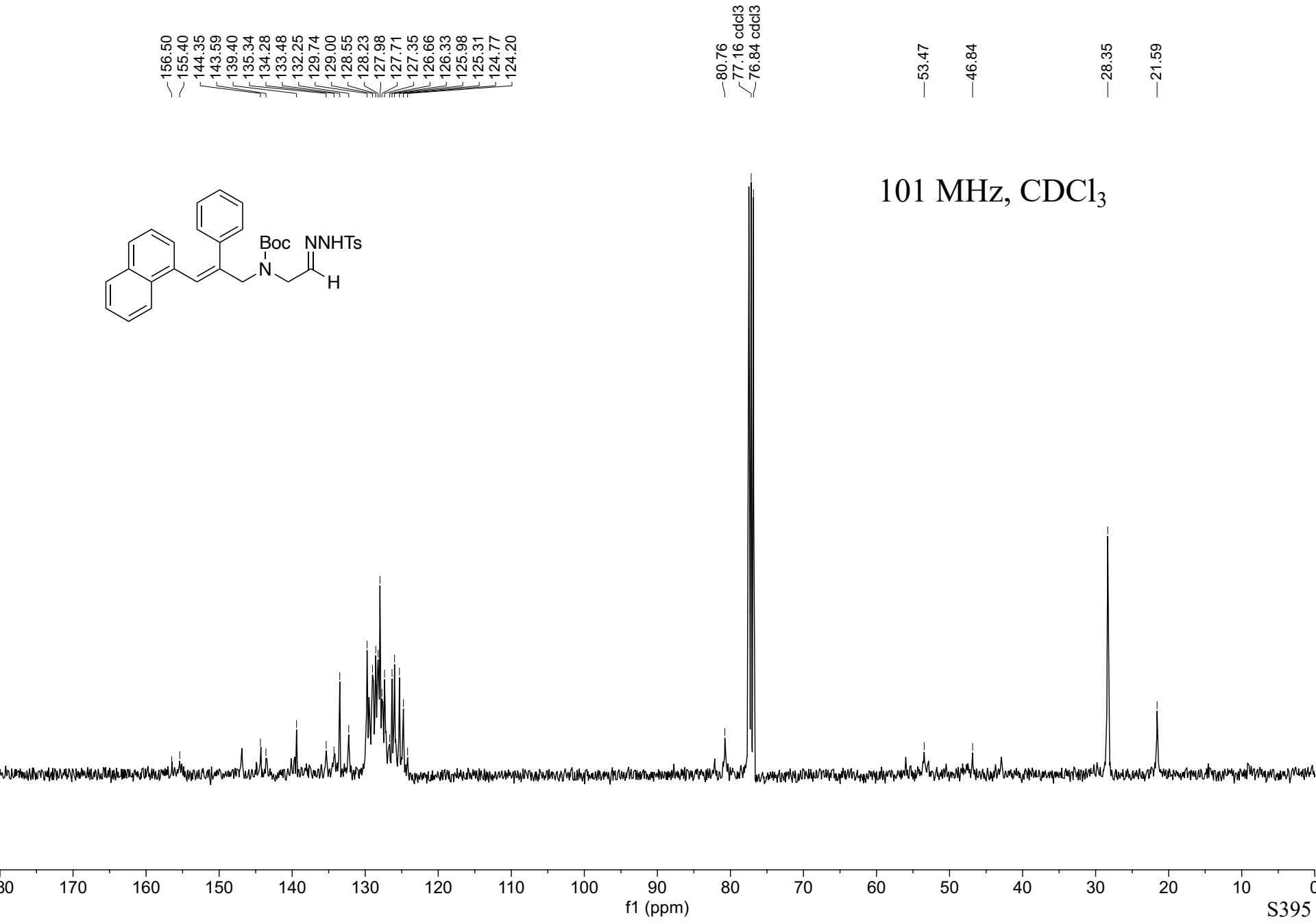
**$^{13}$C NMR *tert*-Butyl ((*E*)-2-phenyl-3-(*p*-tolyl)allyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1n)**



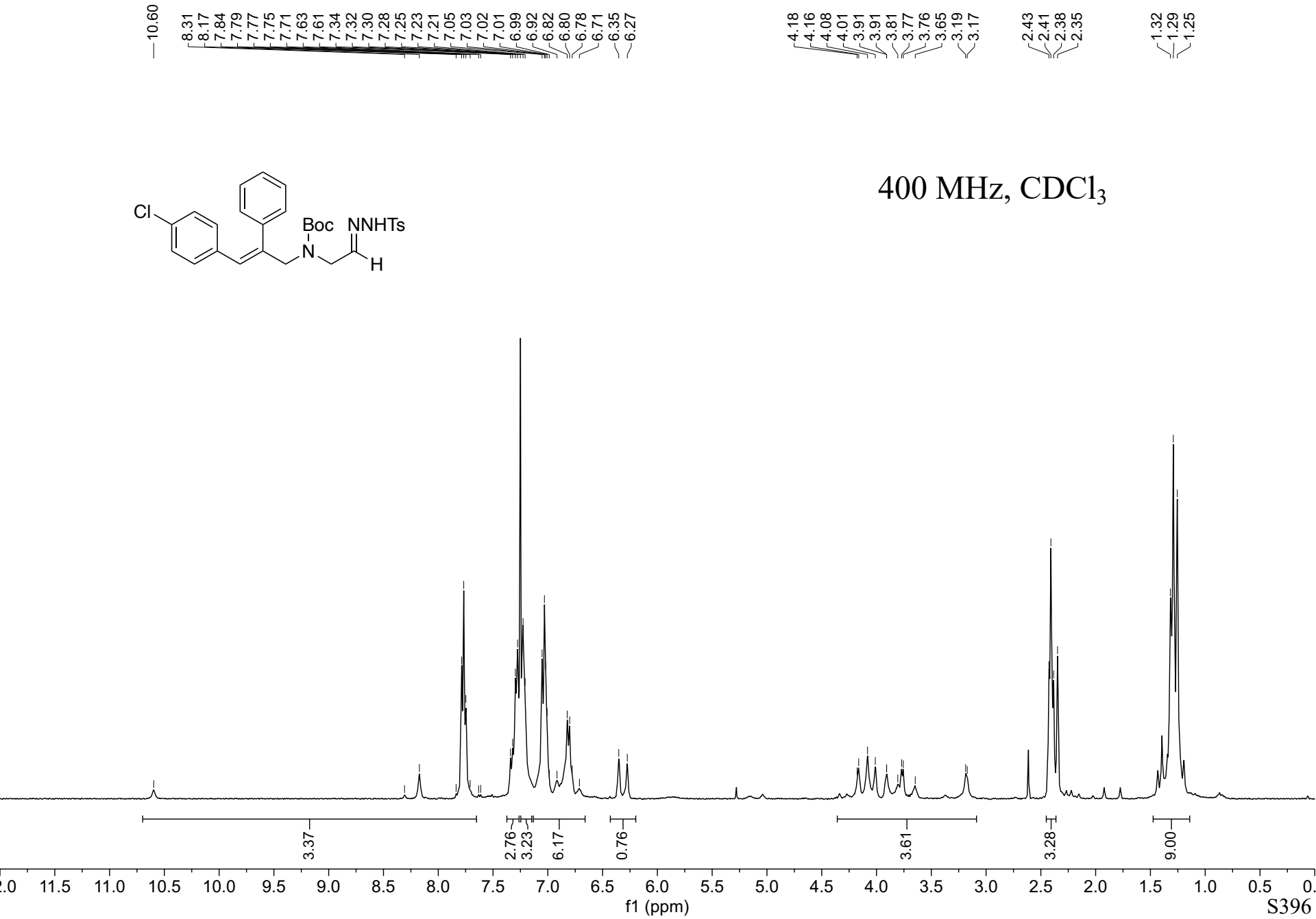
**$^1$H NMR *tert*-Butyl ((*E*)-3-(naphthalen-1-yl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1o)**



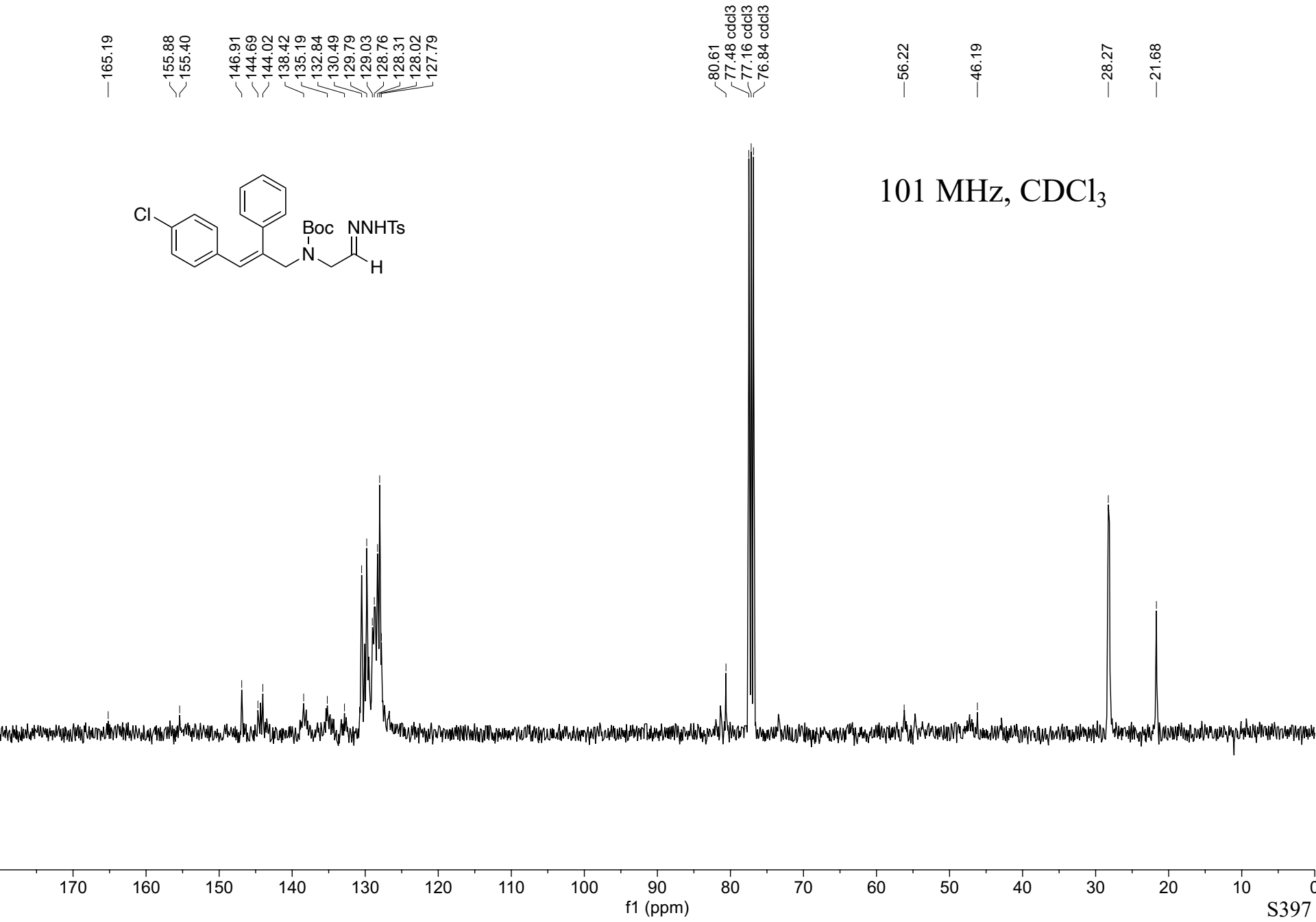
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(naphthalen-1-yl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1o)**



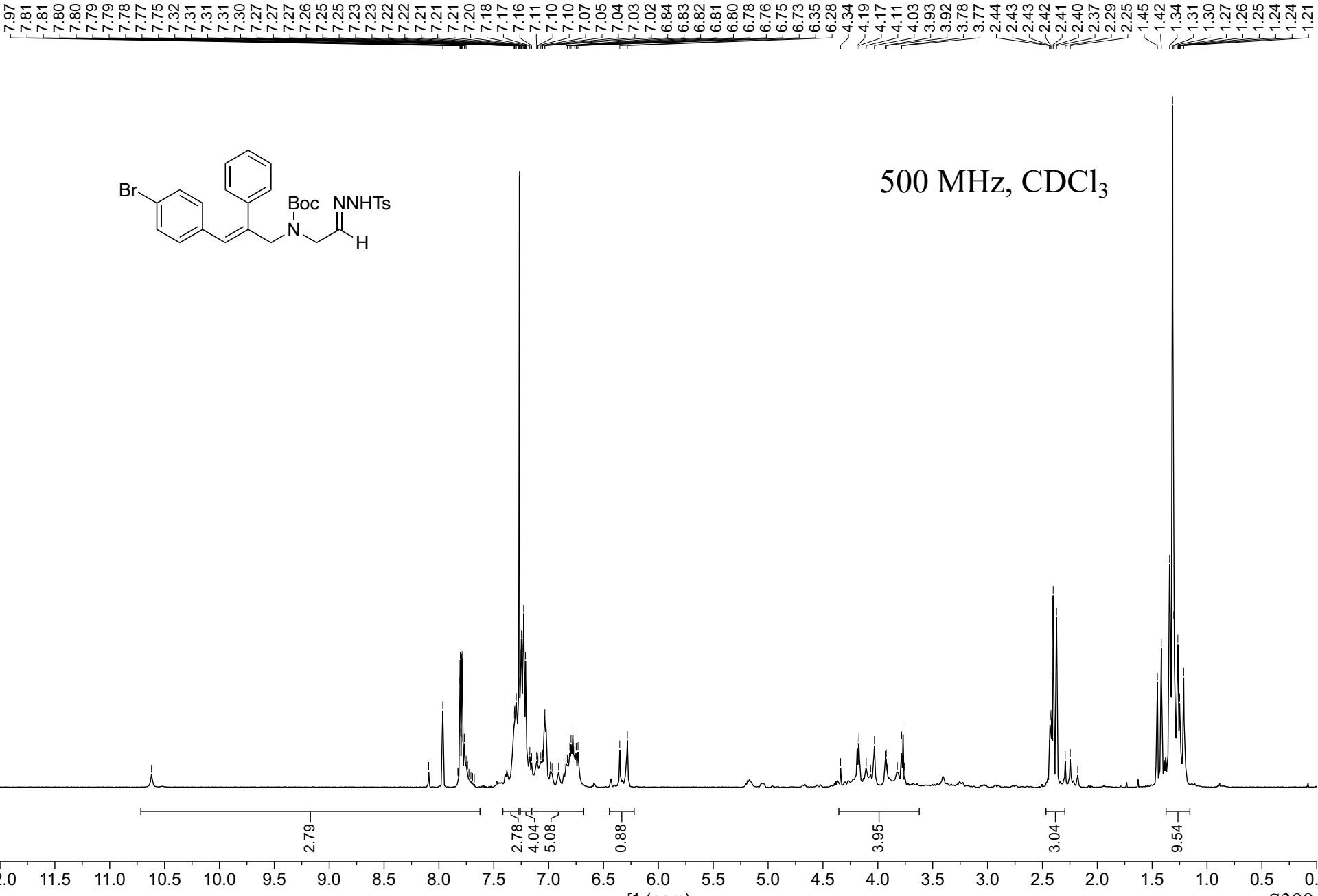
**$^1$H NMR *tert*-Butyl ((*E*)-3-(4-chlorophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1p)**



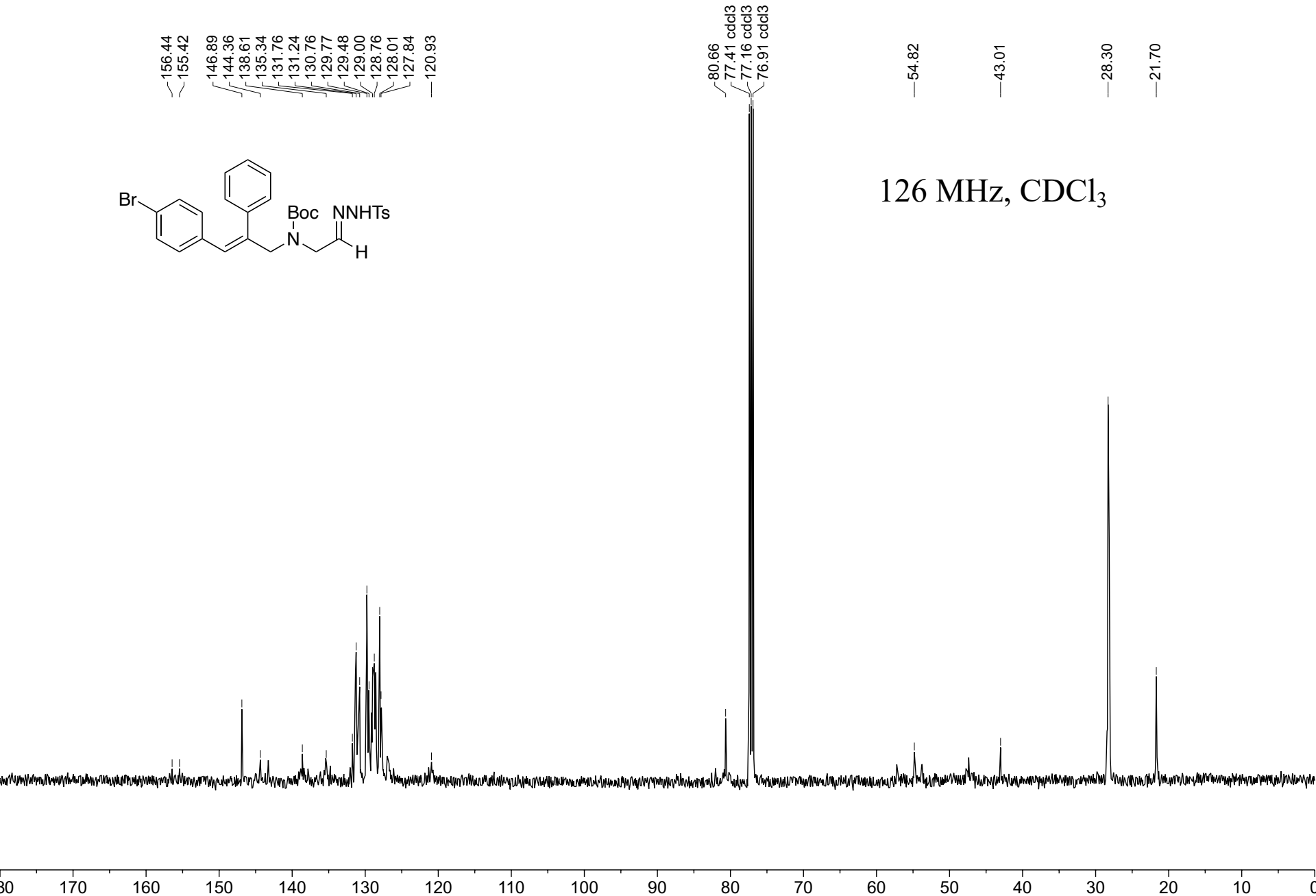
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(4-chlorophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1p)**



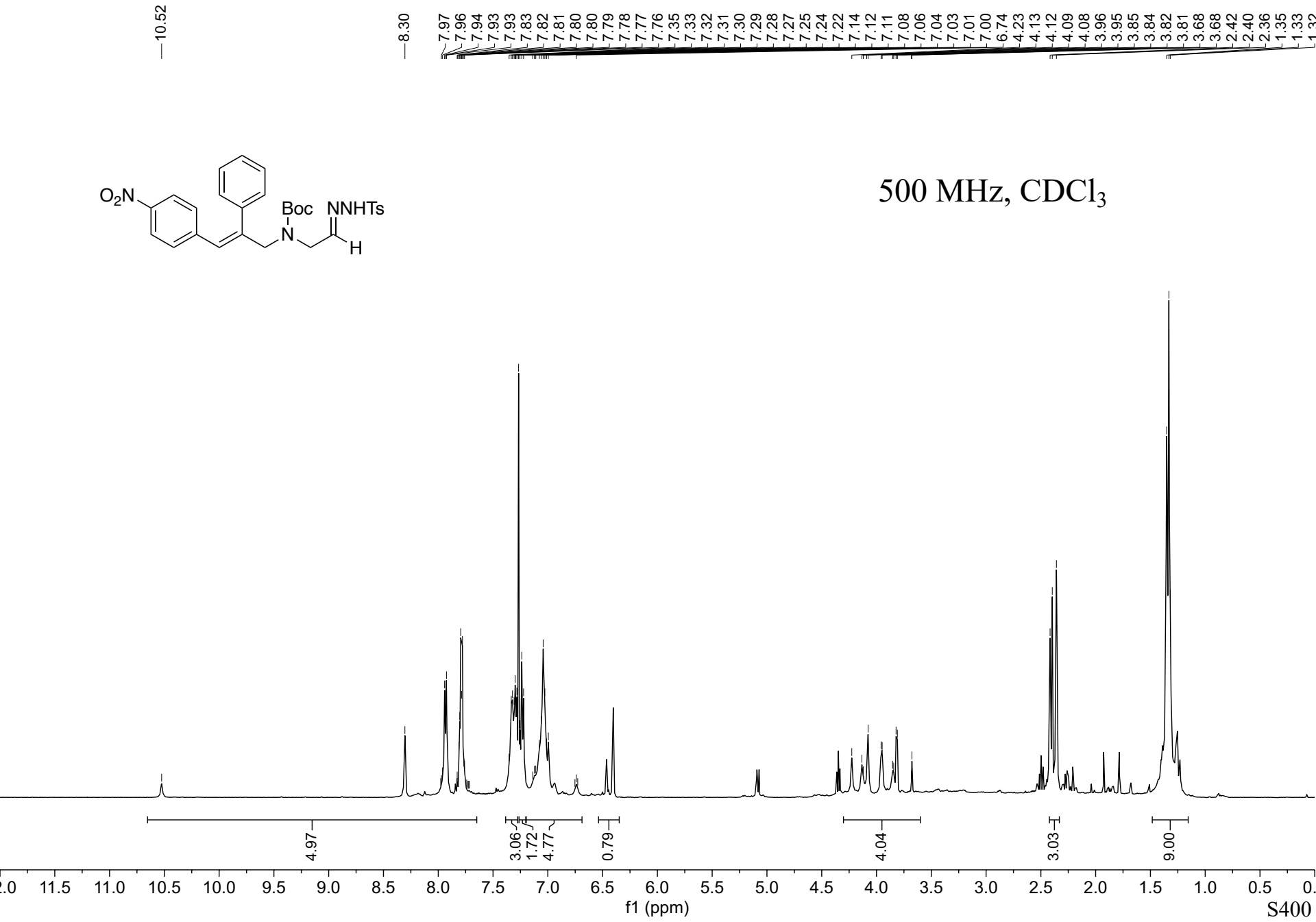
**$^1$H NMR *tert*-Butyl ((*E*)-3-(4-bromophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1q)**



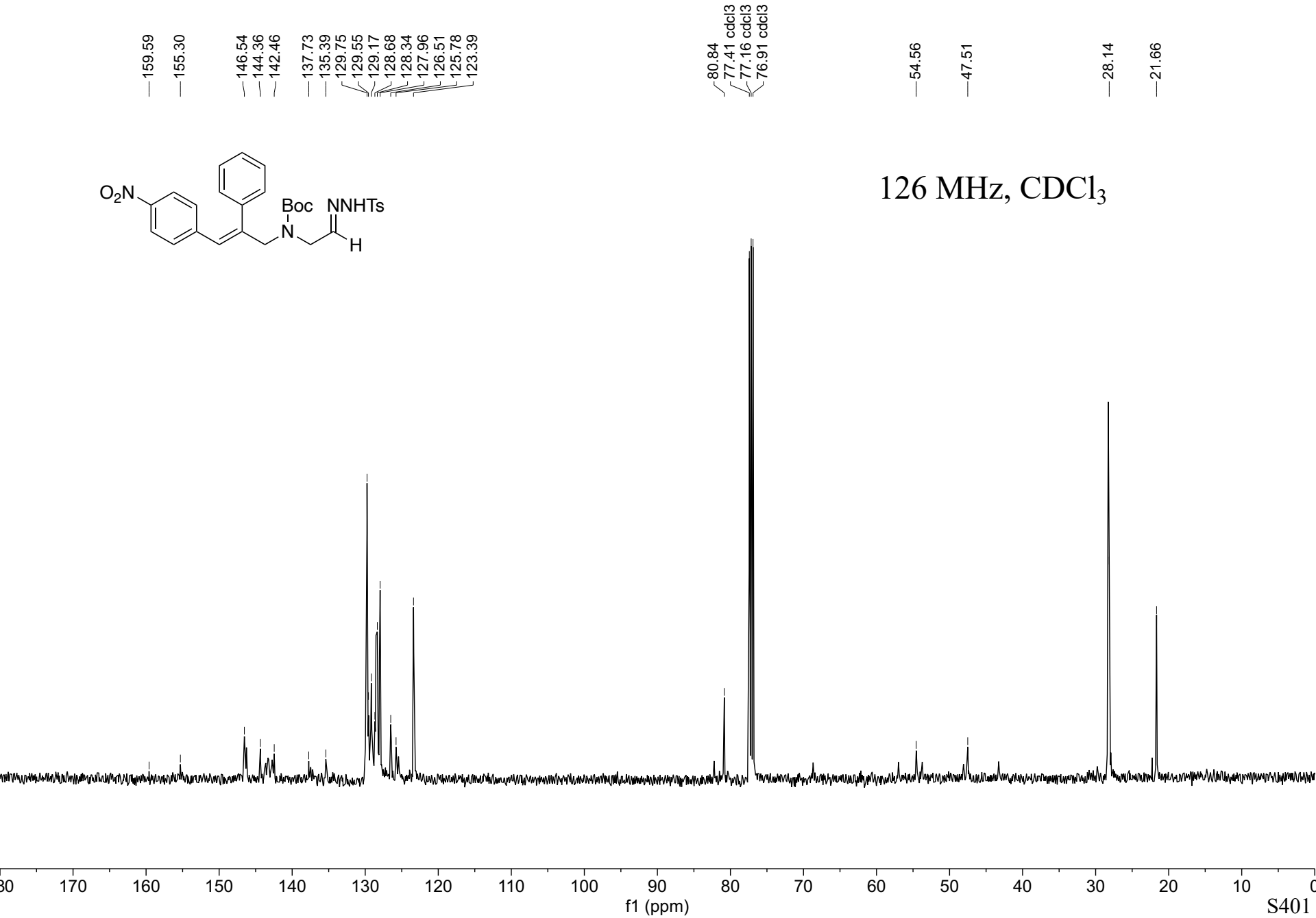
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(4-bromophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1q)**



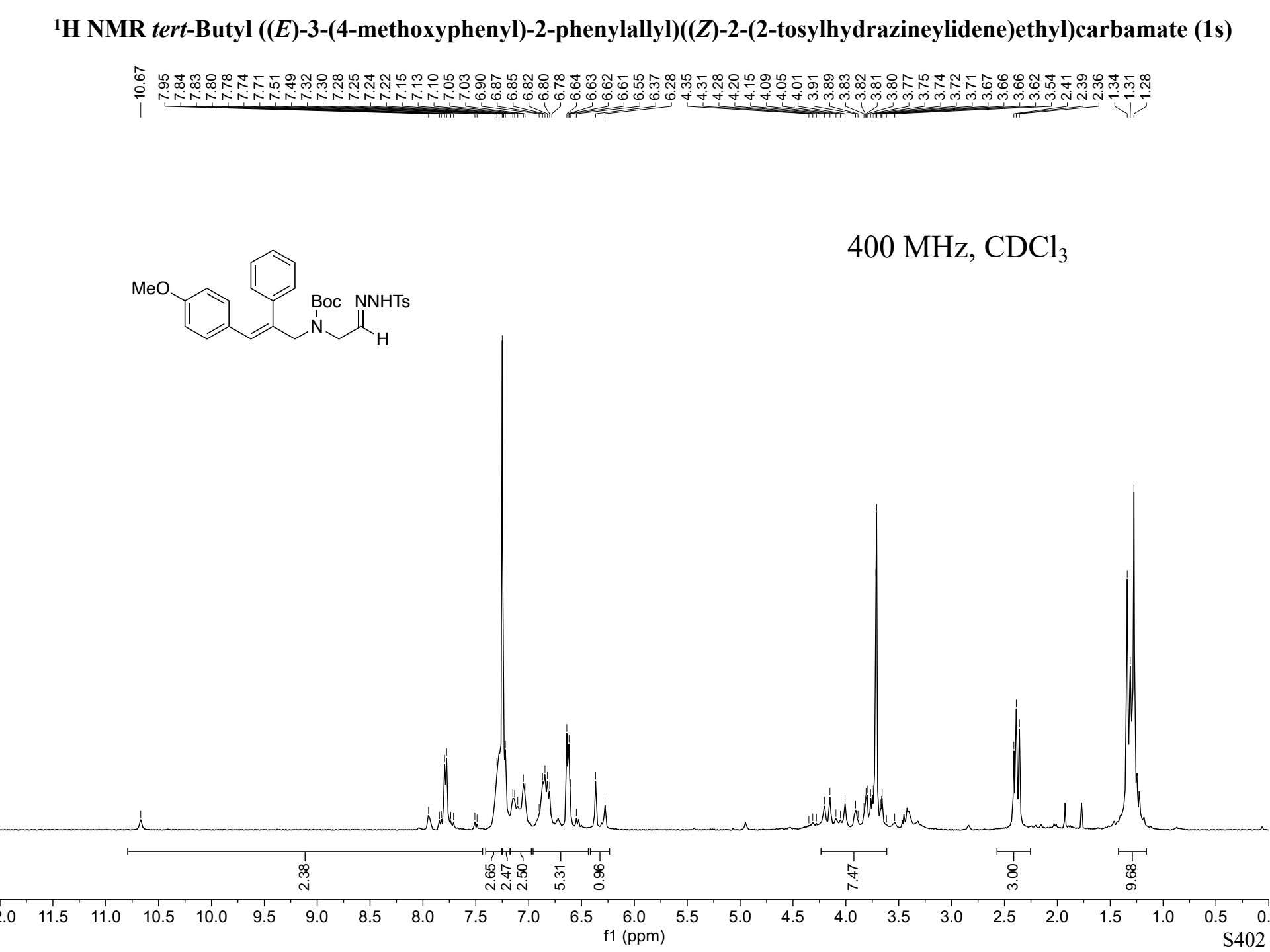
**$^1$H NMR *tert*-Butyl ((*E*)-3-(4-nitrophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylh ydrazineylidene)ethyl)carbamate (1r)**



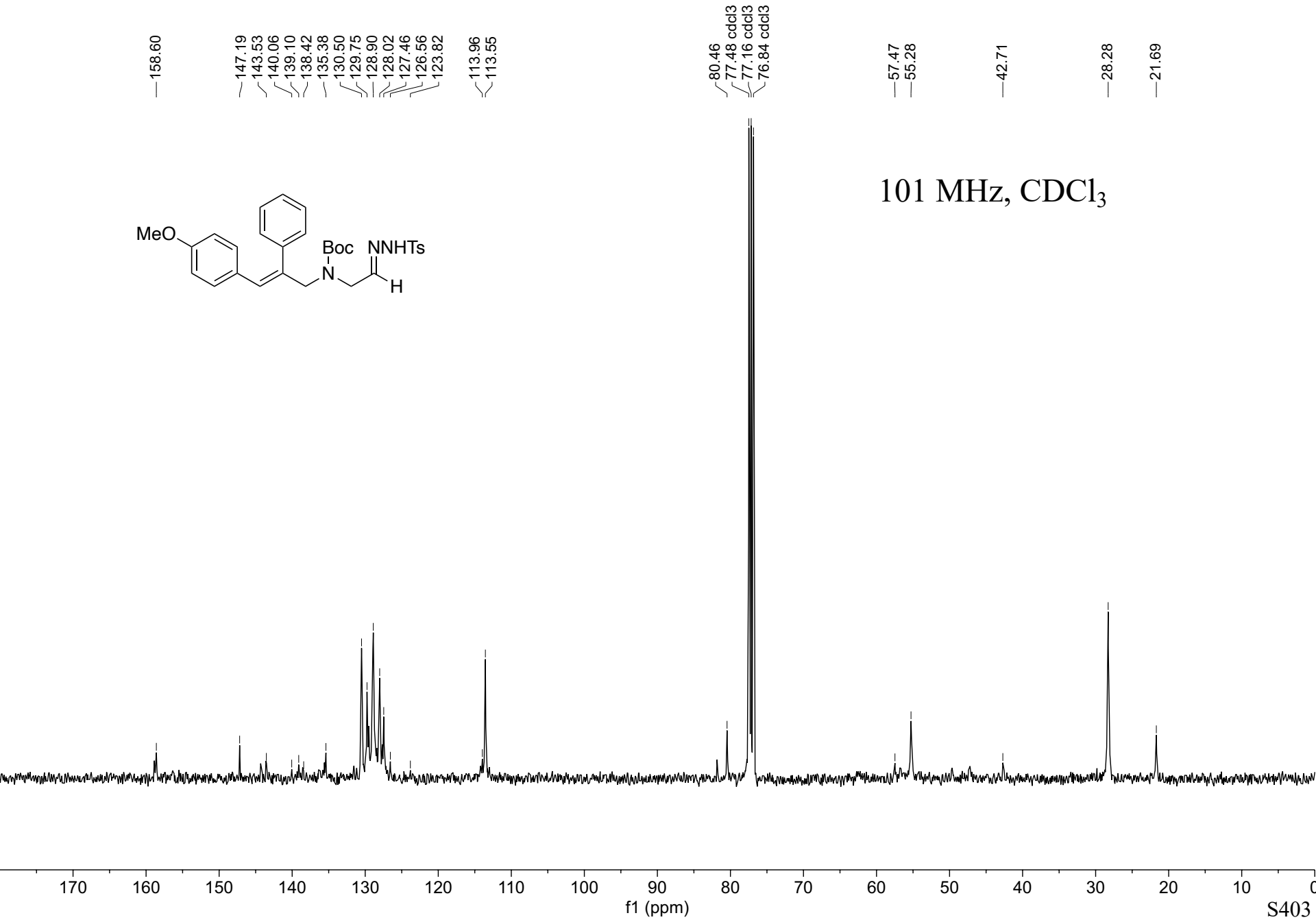
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(4-nitrophenyl)-2-phenylallyl)((*Z*)-2-(2-tosylh ydrazineylidene)ethyl)carbamate (1r)**



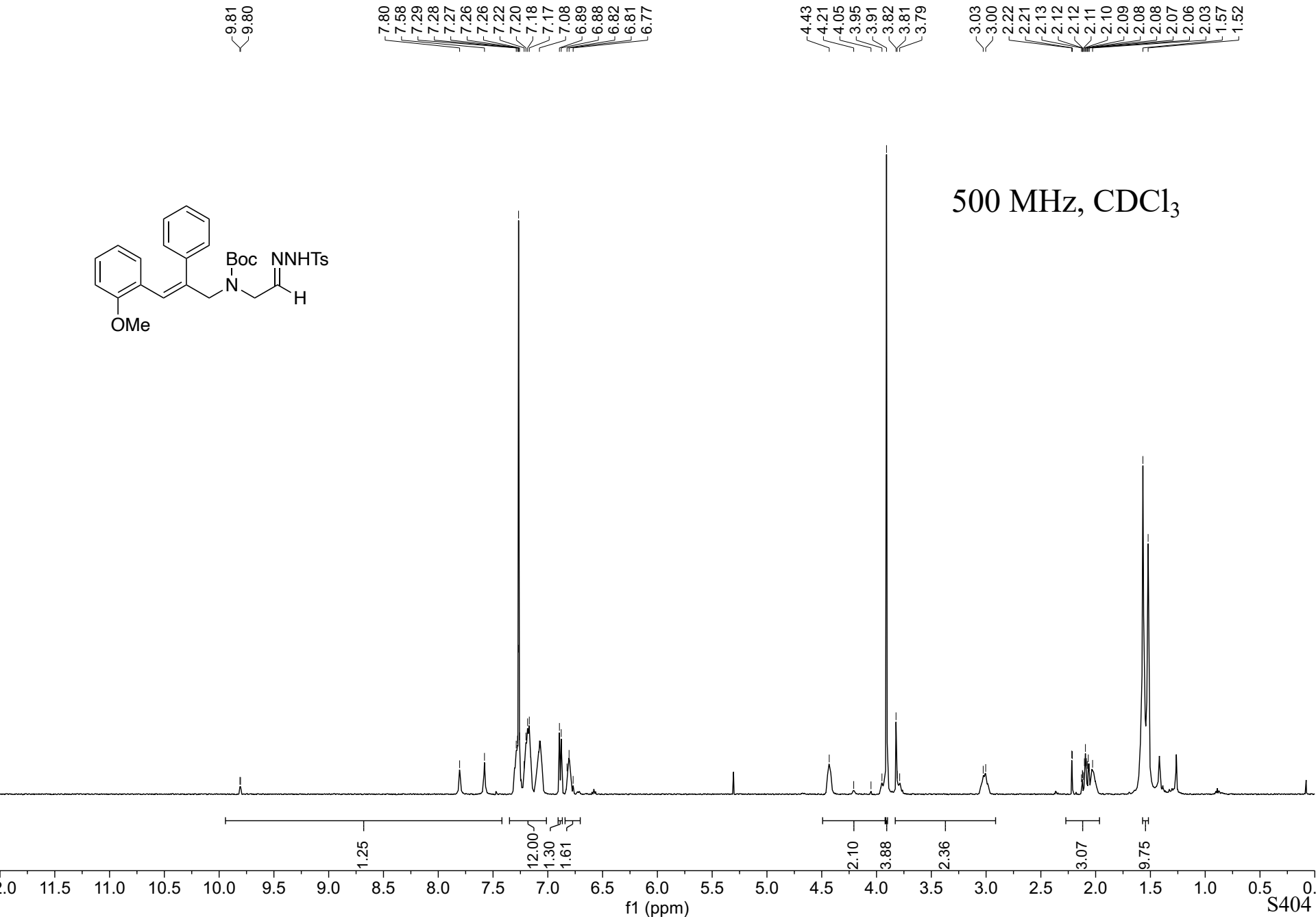
**$^1$H NMR *tert*-Butyl ((*E*)-3-(4-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1s)**



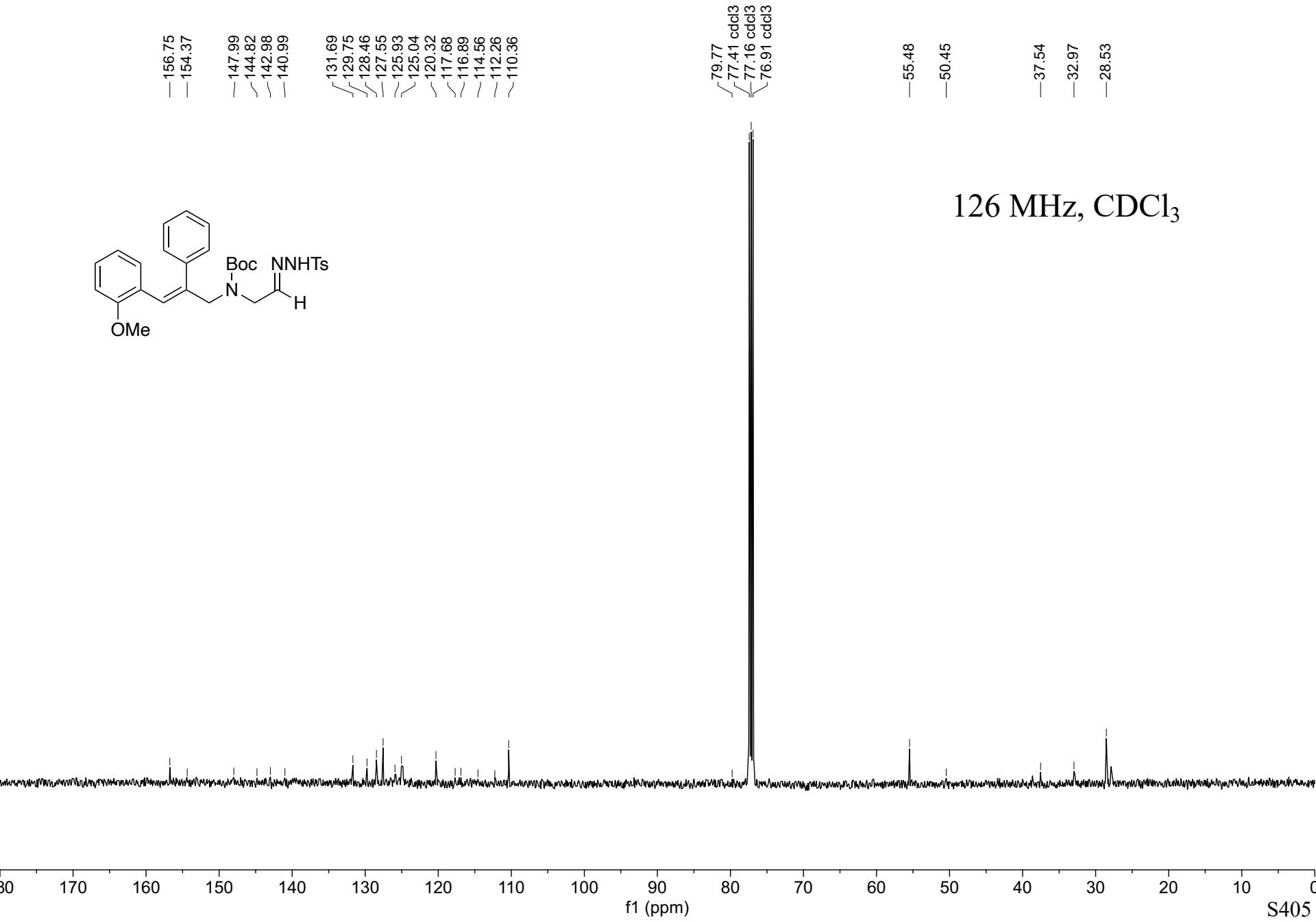
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(4-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1s)**



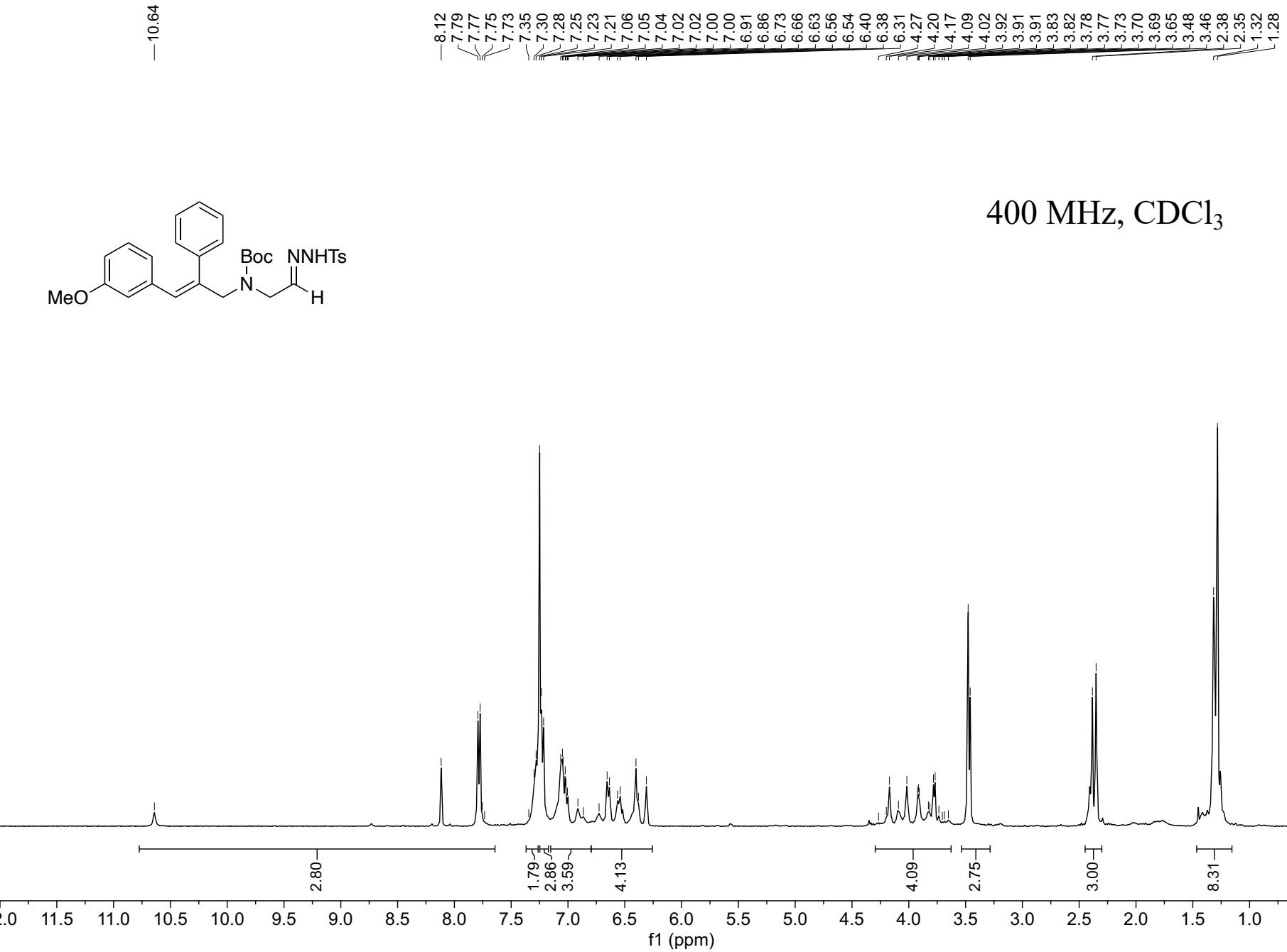
**$^1$H NMR *tert*-Butyl ((*E*)-3-(2-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1t)**



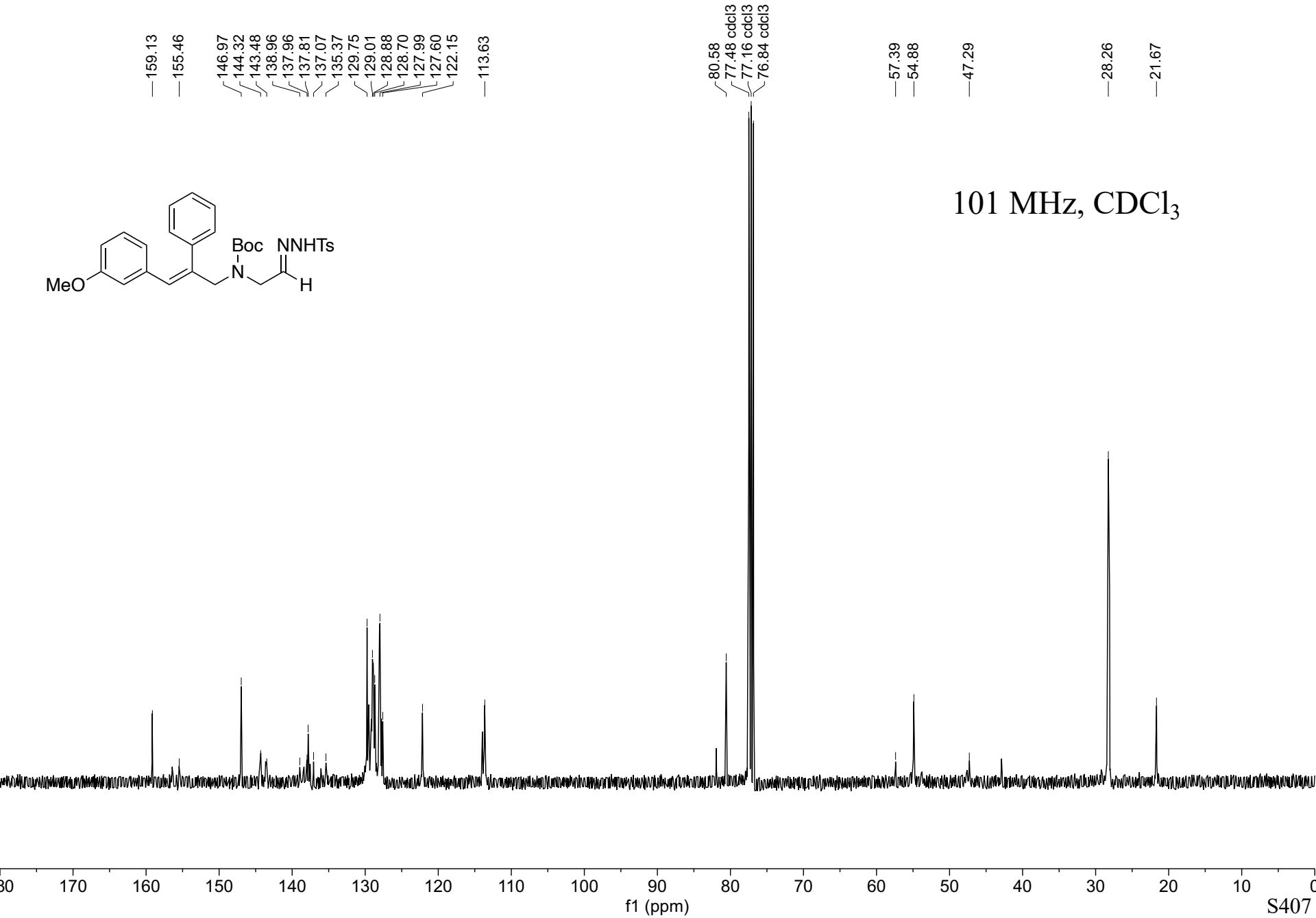
**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(2-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1t)**



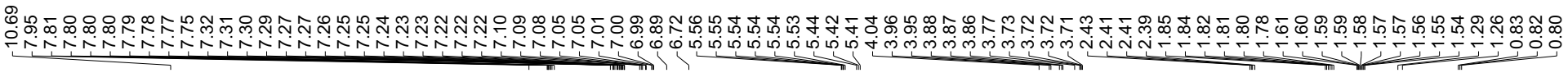
**$^1$H NMR *tert*-Butyl ((*E*)-3-(3-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1u)**

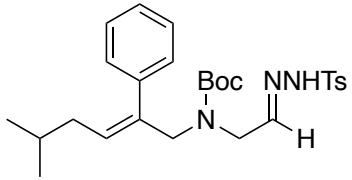


**$^{13}$C NMR *tert*-Butyl ((*E*)-3-(3-methoxyphenyl)-2-phenylallyl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1u)**



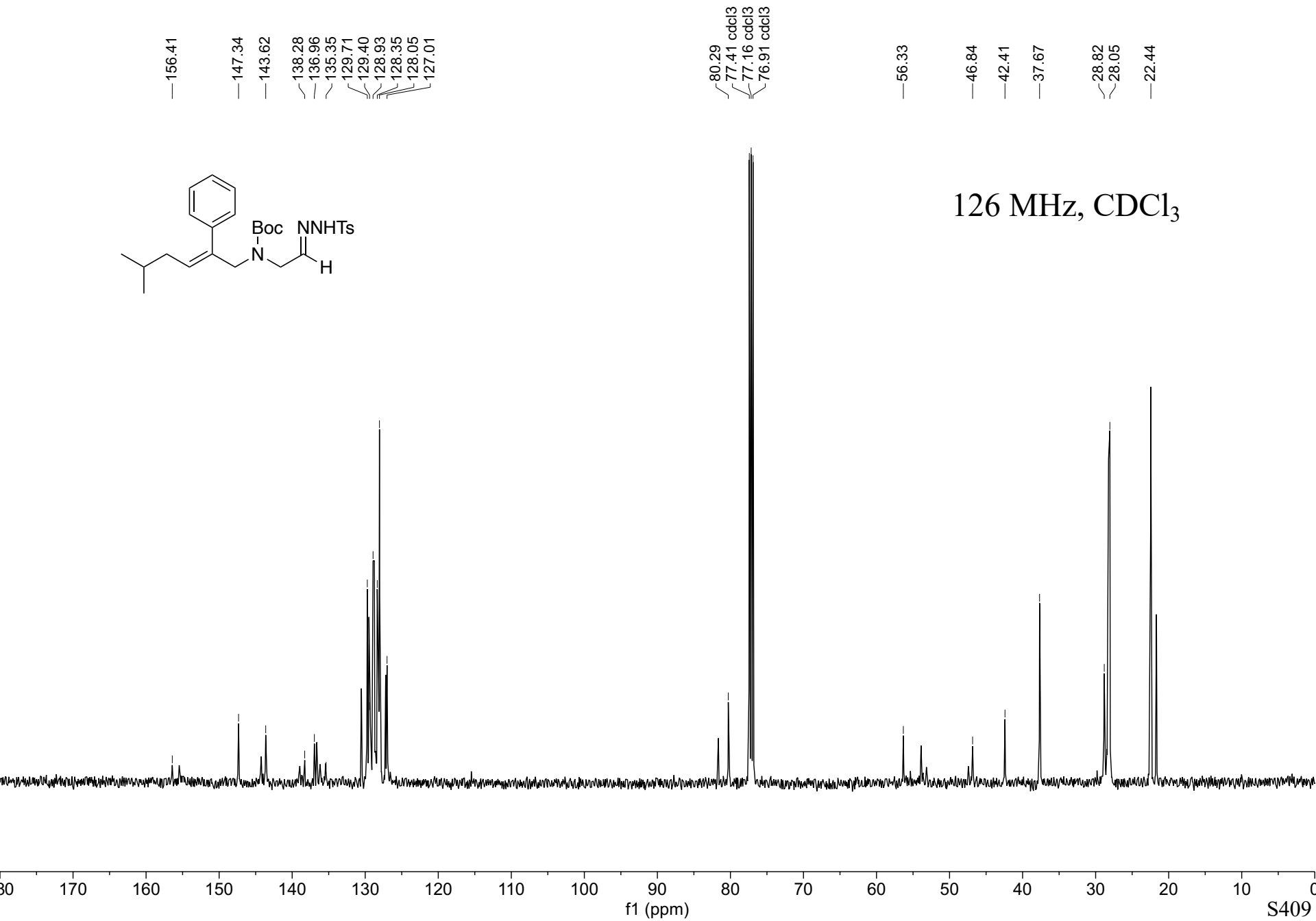
**$^1$H NMR *tert*-Butyl ((*E*)-5-methyl-2-phenylhex-2-en-1-yl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1x)**



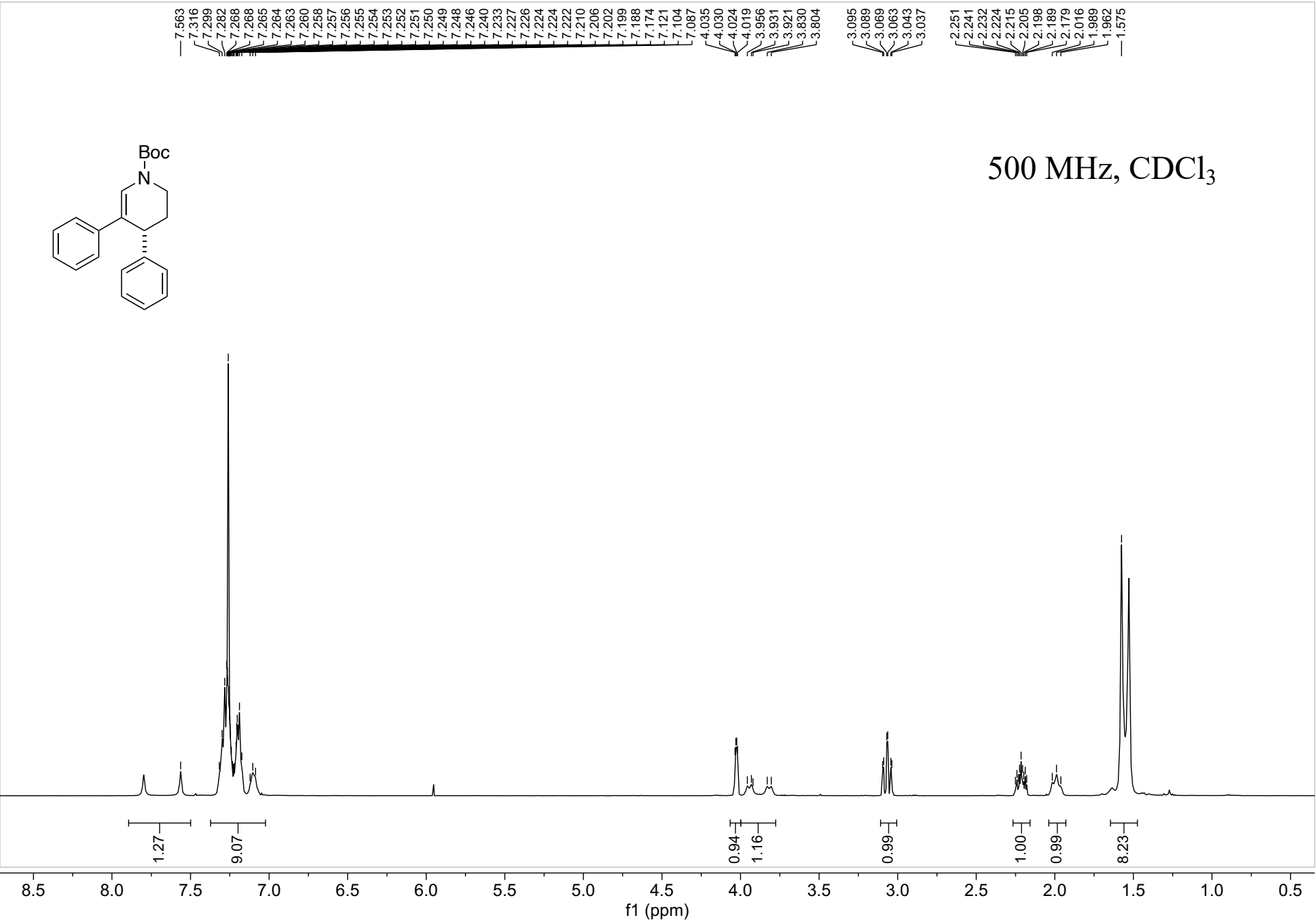




500 MHz, $CDCl_3$

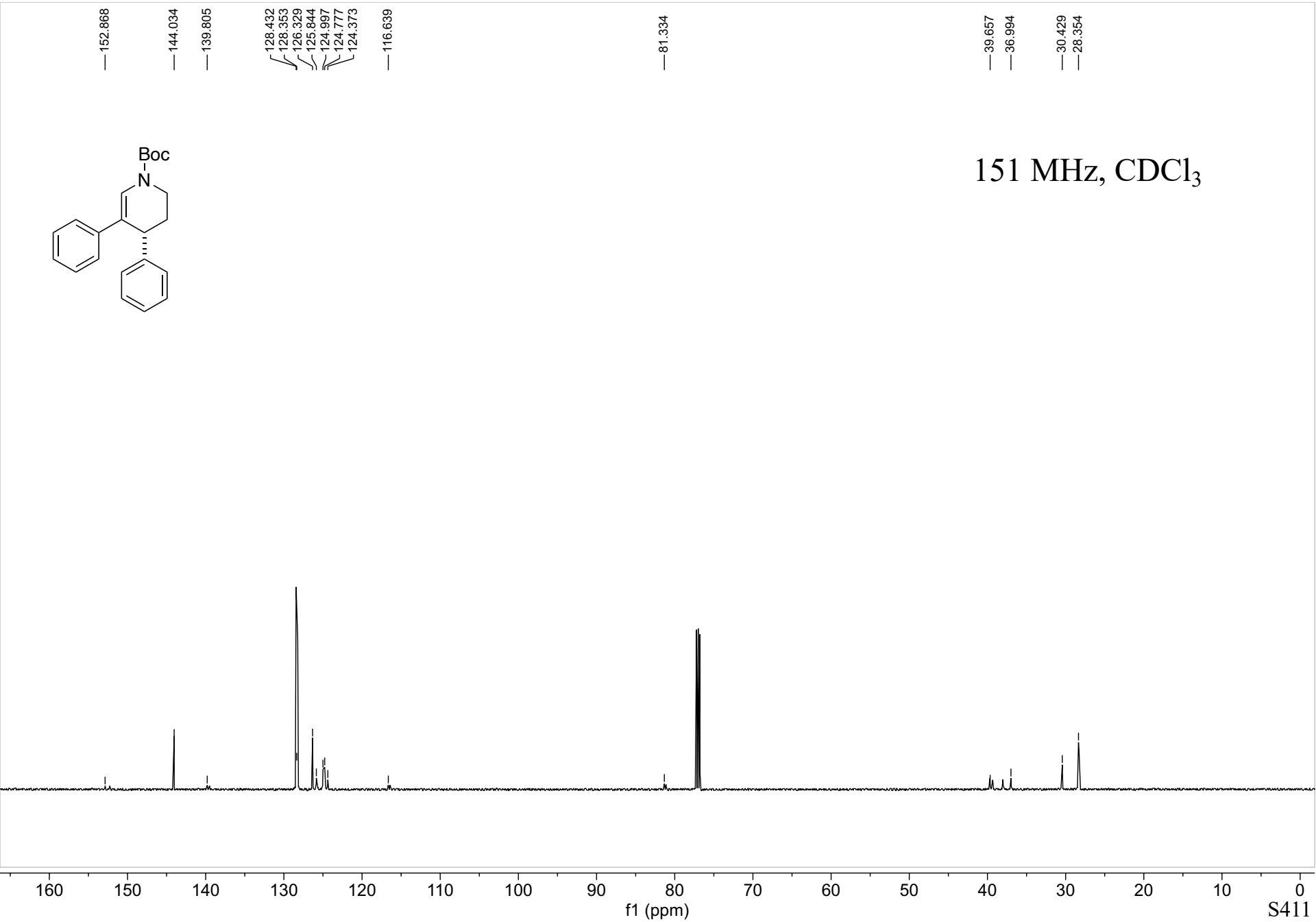
**$^{13}$C NMR *tert*-Butyl ((*E*)-5-methyl-2-phenylhex-2-en-1-yl)((*Z*)-2-(2-tosylhydrazineylidene)ethyl)carbamate (1x)**

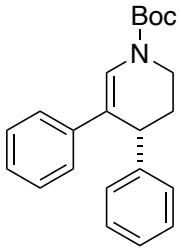


# $^{1}$H NMR *tert*-Butyl (*R*)-4,5-diphenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2a)



# $^{13}$C NMR *tert*-Butyl (*R*)-4,5-diphenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2a)

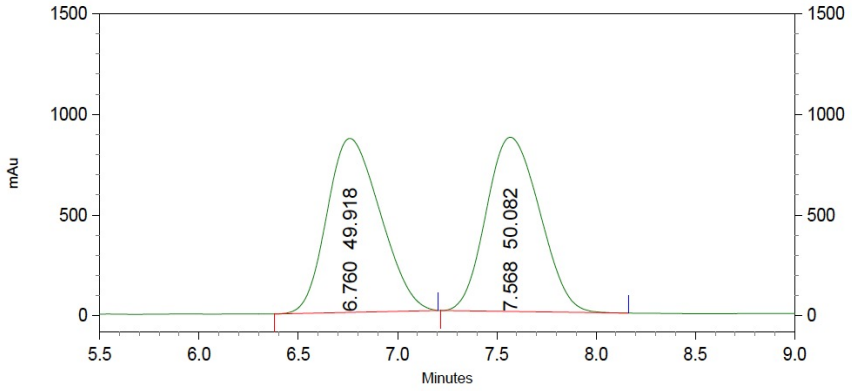


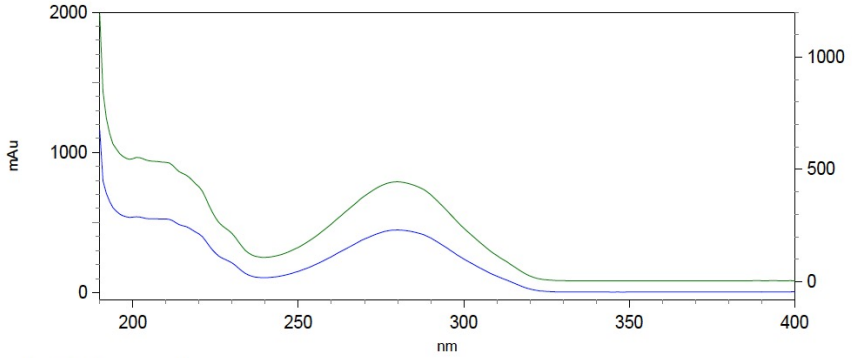



# HPLC

## *tert*-Butyl (*R*)-4,5-diphenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2a)

C:\EZStart\Projects\Default\Data\JJX-2416P-IA-2%-0.8ML
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



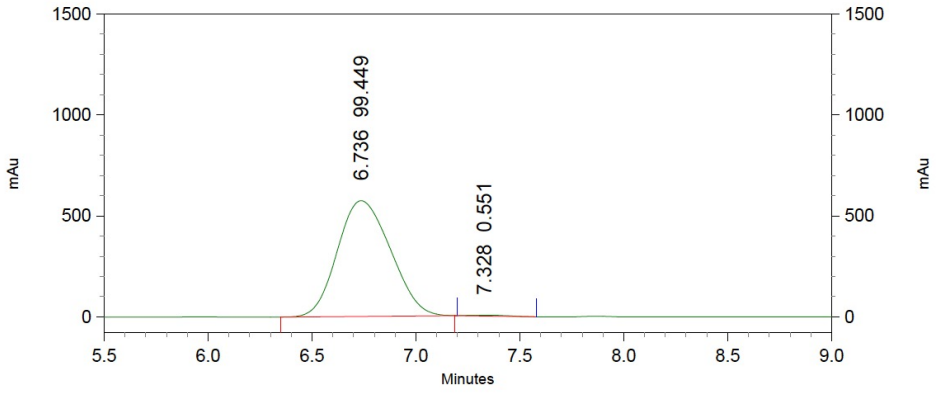



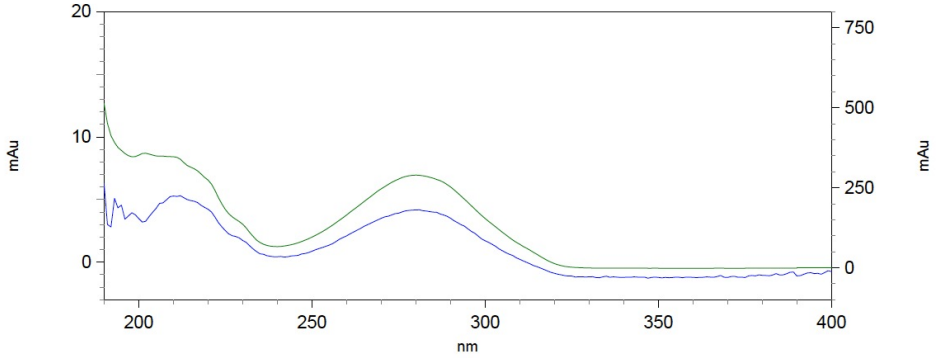

4: 282 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.760 | 49.918 |
| 2 | 7.568 | 50.082 |

| Totals | | 100.000 |
|---|---|---|

C:\EZStart\Projects\Default\Data\JJX-2414P-IA-2%-0.8ML-1
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



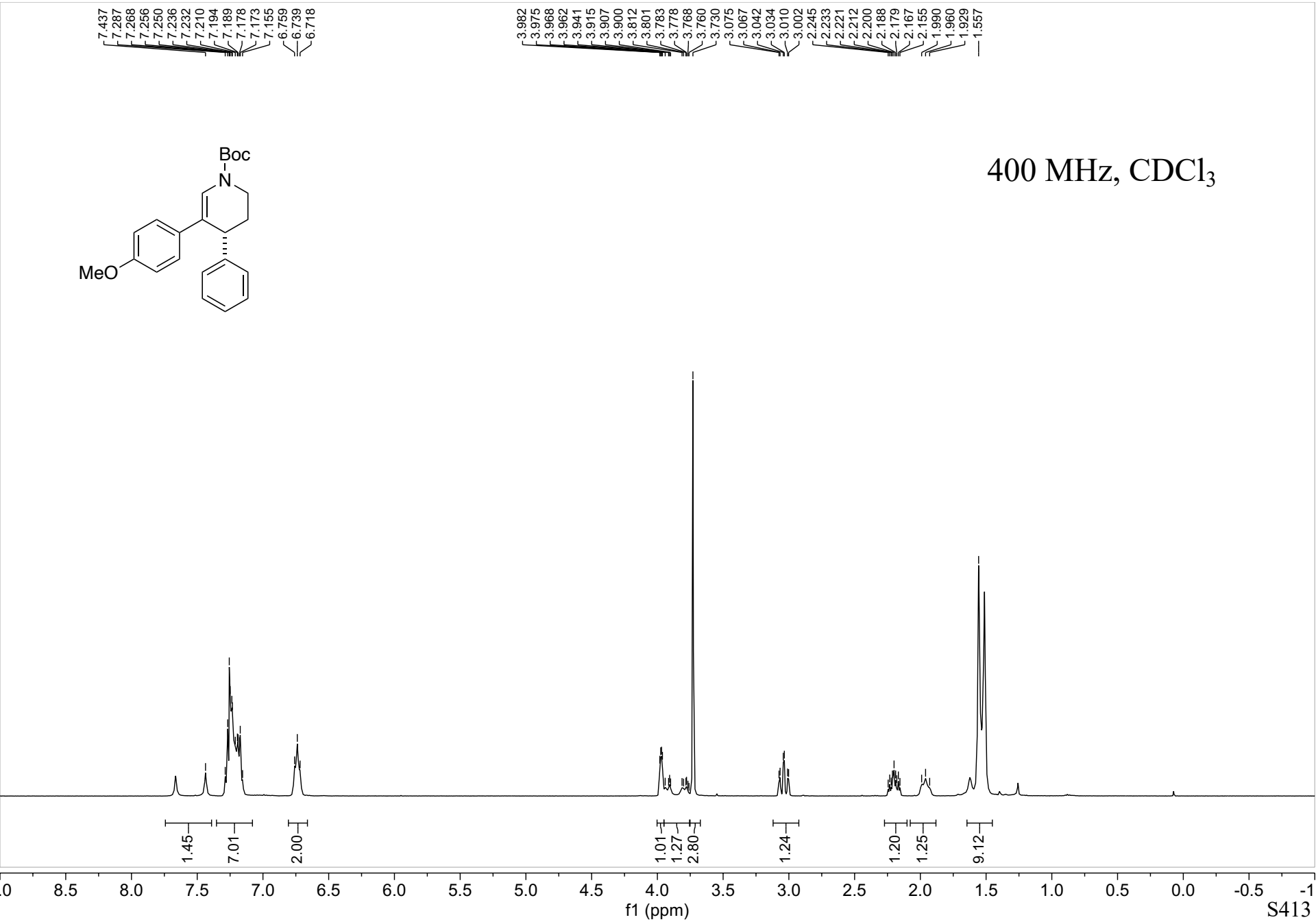




4: 282 nm, 4
nm Results

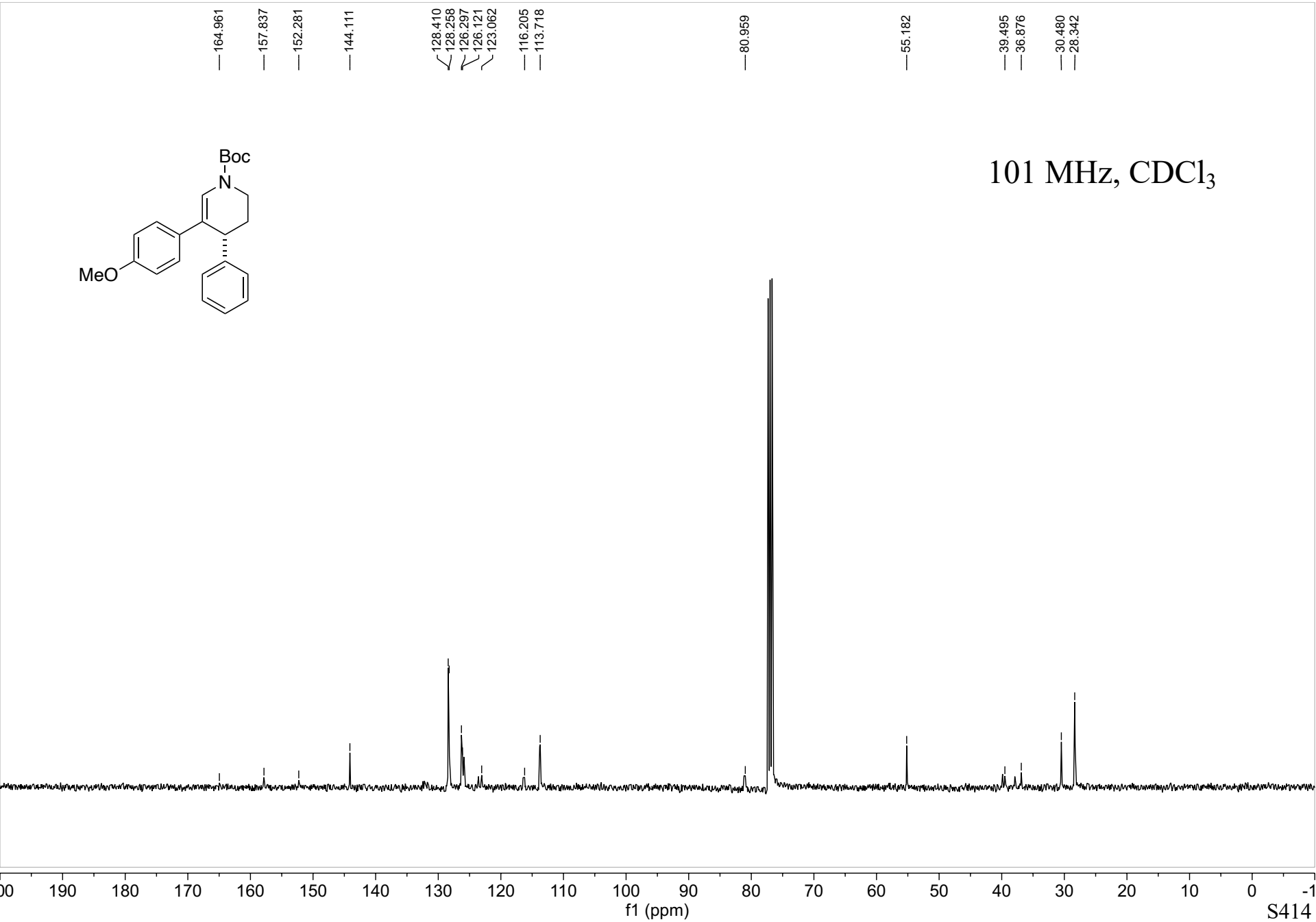
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.736 | 99.449 |
| 2 | 7.328 | 0.551 |

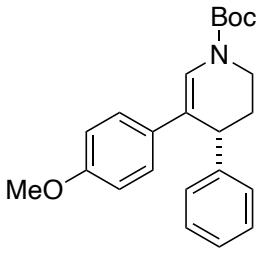
| Totals | | 100.000 |
|---|---|---|

# $^{1}$H NMR *tert*-Butyl (*R*)-5-(4-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2b)



# $^{13}$C NMR *tert*-Butyl (*R*)-5-(4-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2b)

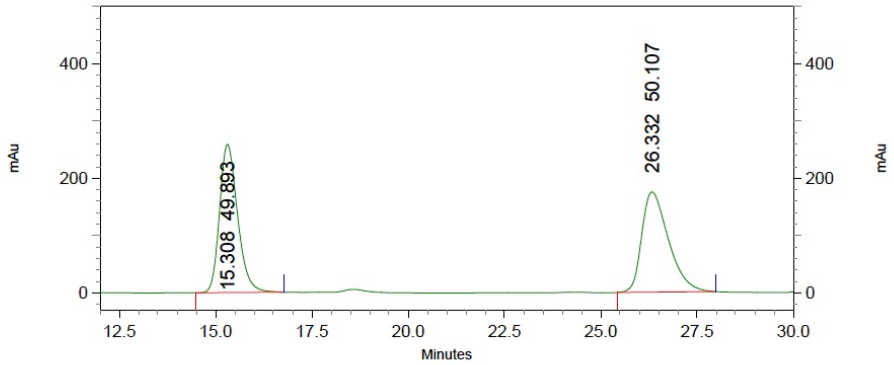


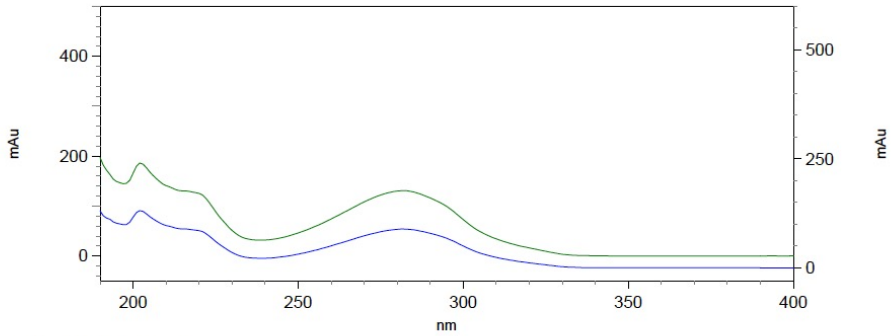



# HPLC

## *tert*-Butyl (*R*)-5-(4-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2b)

C:\EZStart\Projects\Default\Data\JJX-2437P-IA-2%-0.8ML-IBU-R1
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



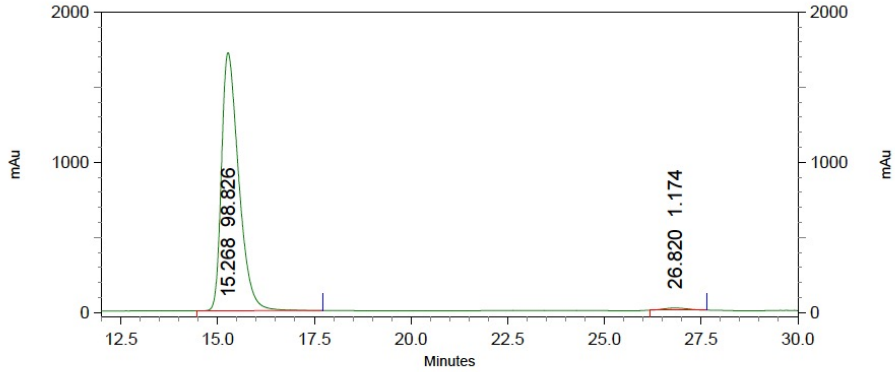



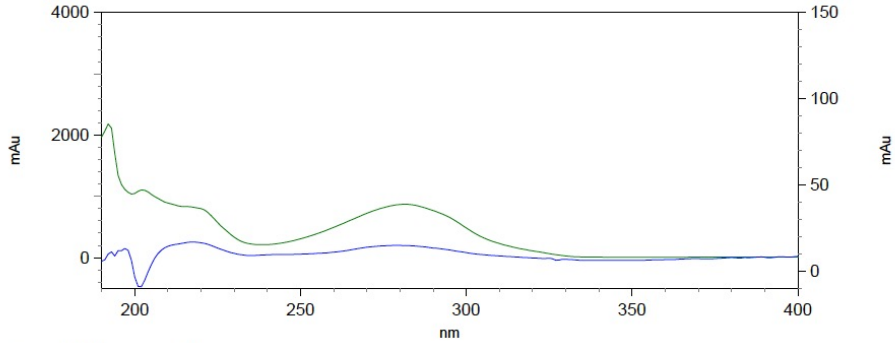

4: 280 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.308 | 49.893 |
| 2 | 26.332 | 50.107 |

| Totals | | 100.000 |
|---|---|---|

C:\EZStart\Projects\Default\Data\JJX-2438P-IA-2%-0.8ML-TAO
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



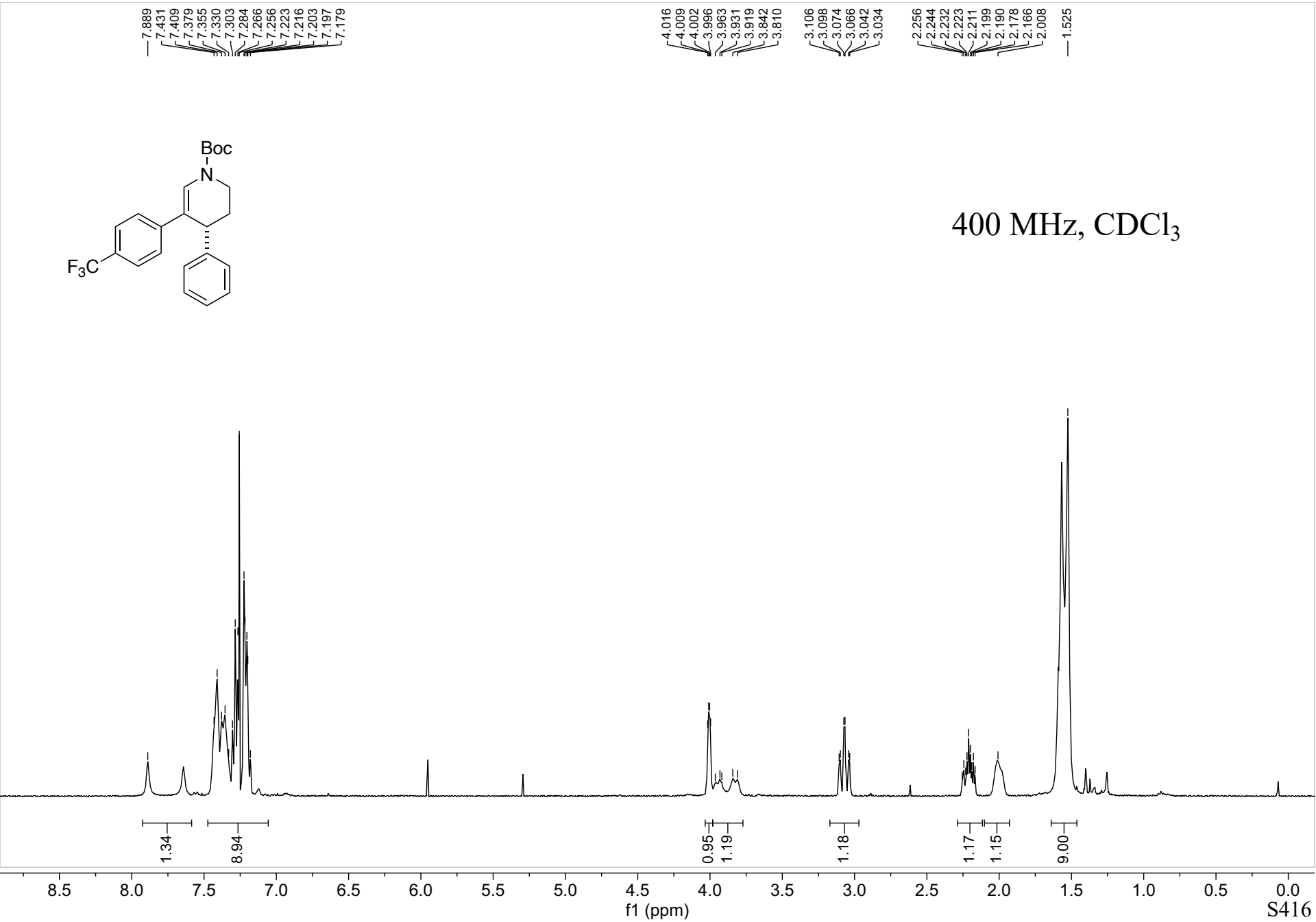




4: 280 nm, 4
nm Results

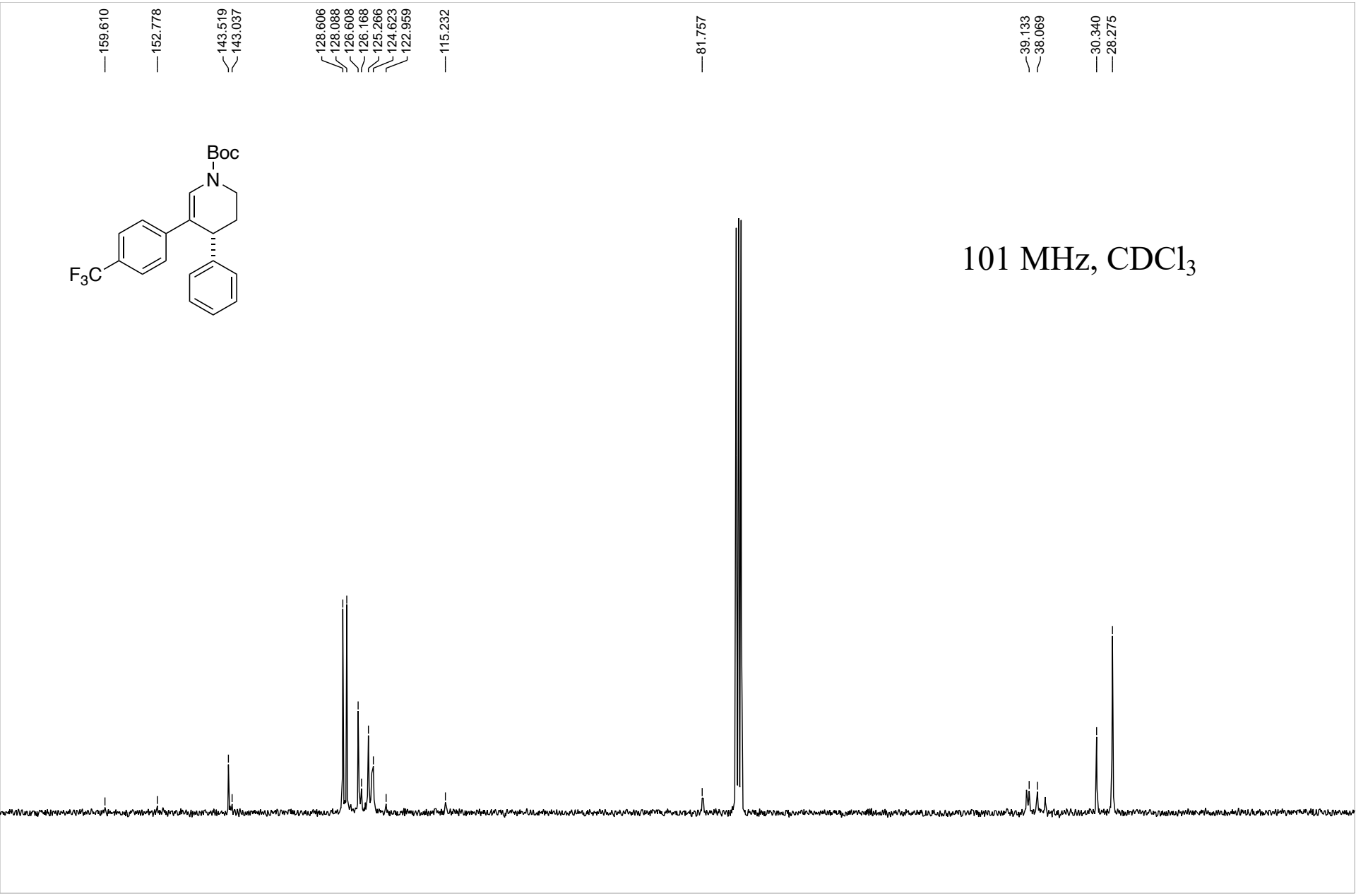
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 15.268 | 98.826 |
| 2 | 26.820 | 1.174 |

| Totals | | 100.000 |
|---|---|---|

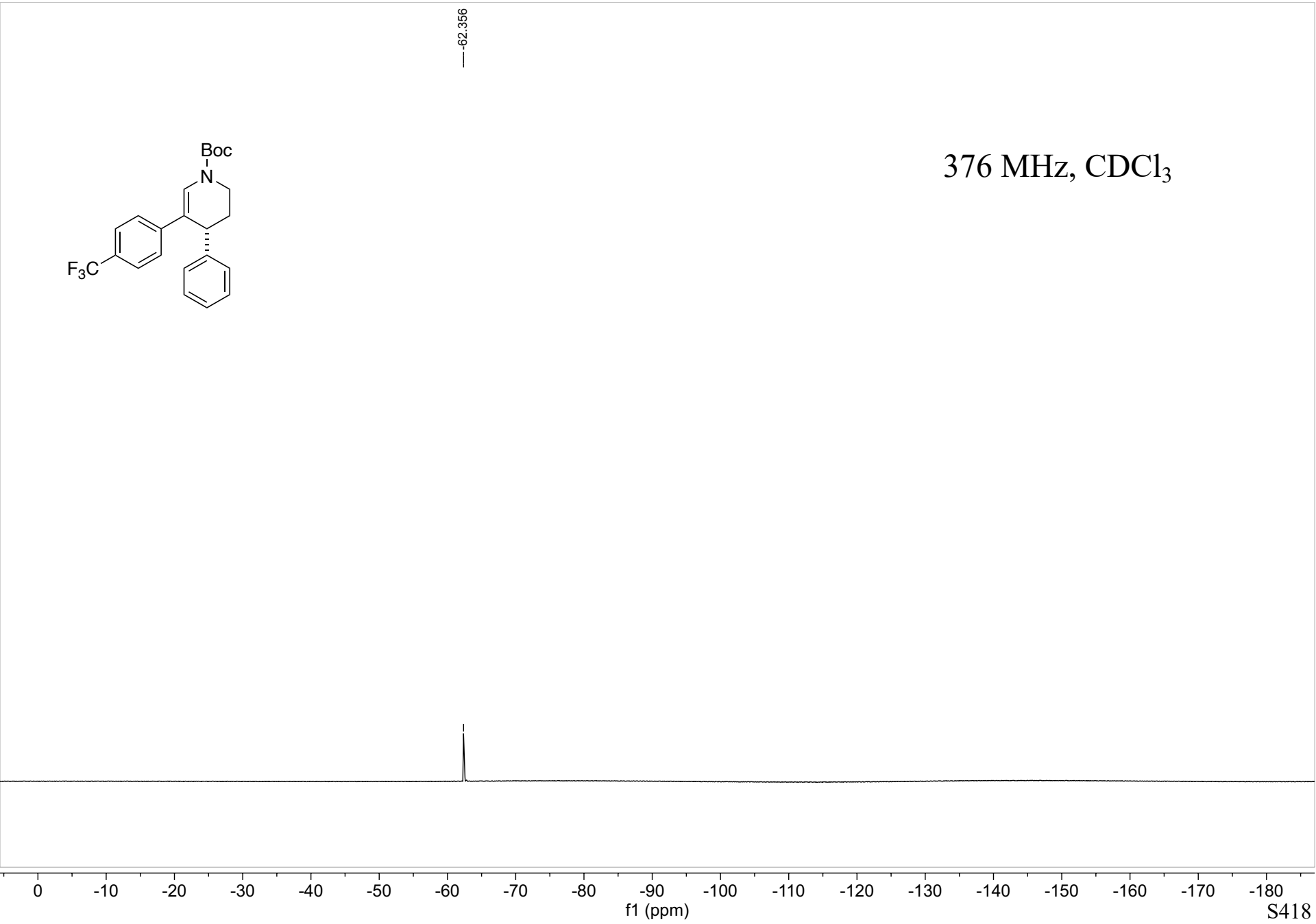
**$^1$H NMR *tert*-butyl (*R*)-4-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)**

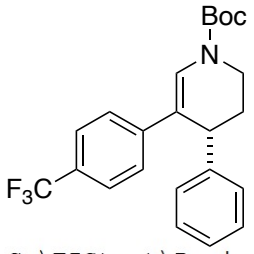


**$^{13}$C NMR *tert*-butyl (*R*)-4-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)**



**$^{19}$F NMR *tert*-butyl (*R*)-4-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)**

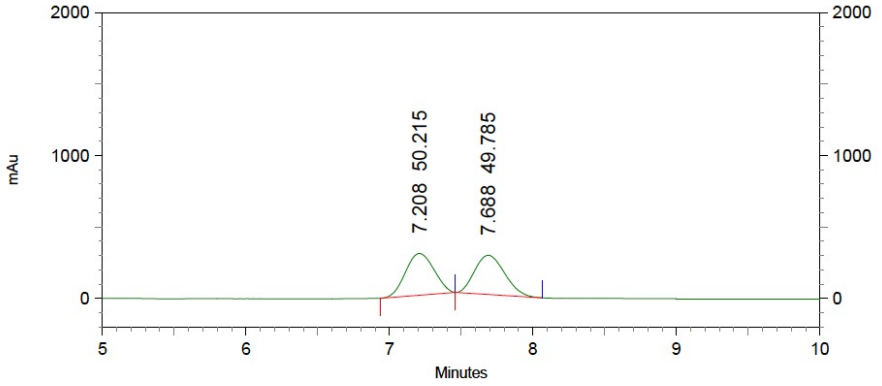


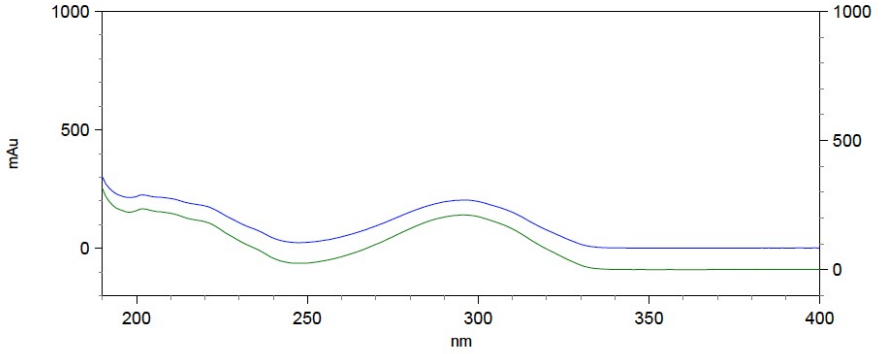



# HPLC

## *tert*-butyl (*R*)-4-phenyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2c)

C:\EZStart\Projects\Default\Data\JJX-2461p-2%-IC-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



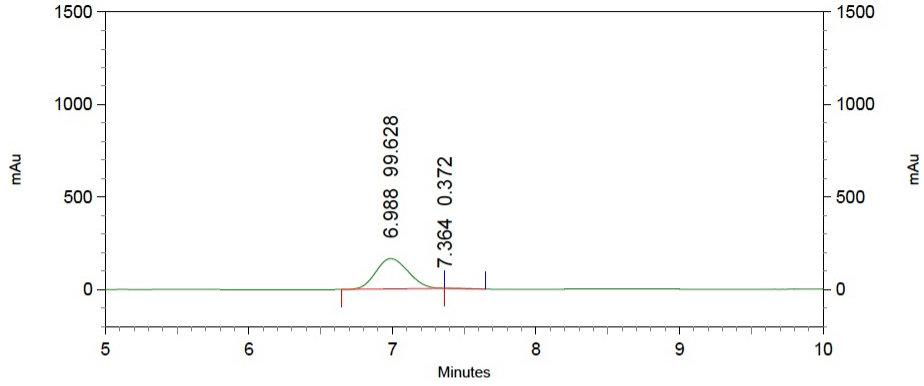



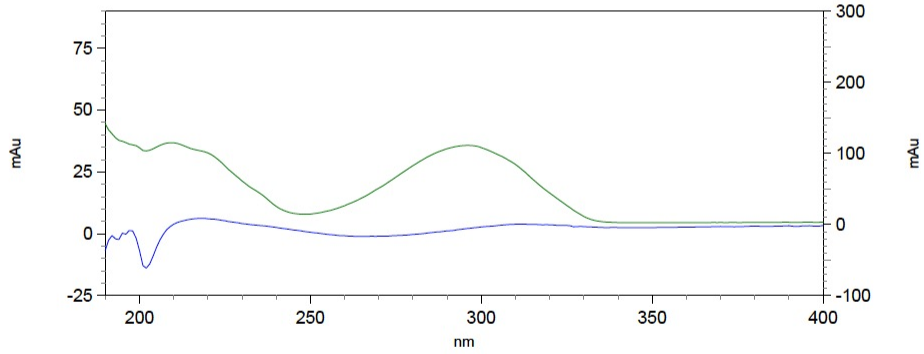

4: 310 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.208 | 50.215 |
| 2 | 7.688 | 49.785 |

| Totals | | 100.000 |
|---|---|---|

C:\EZStart\Projects\Default\Data\JJX-2462p-2%-IC-0.8ml
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



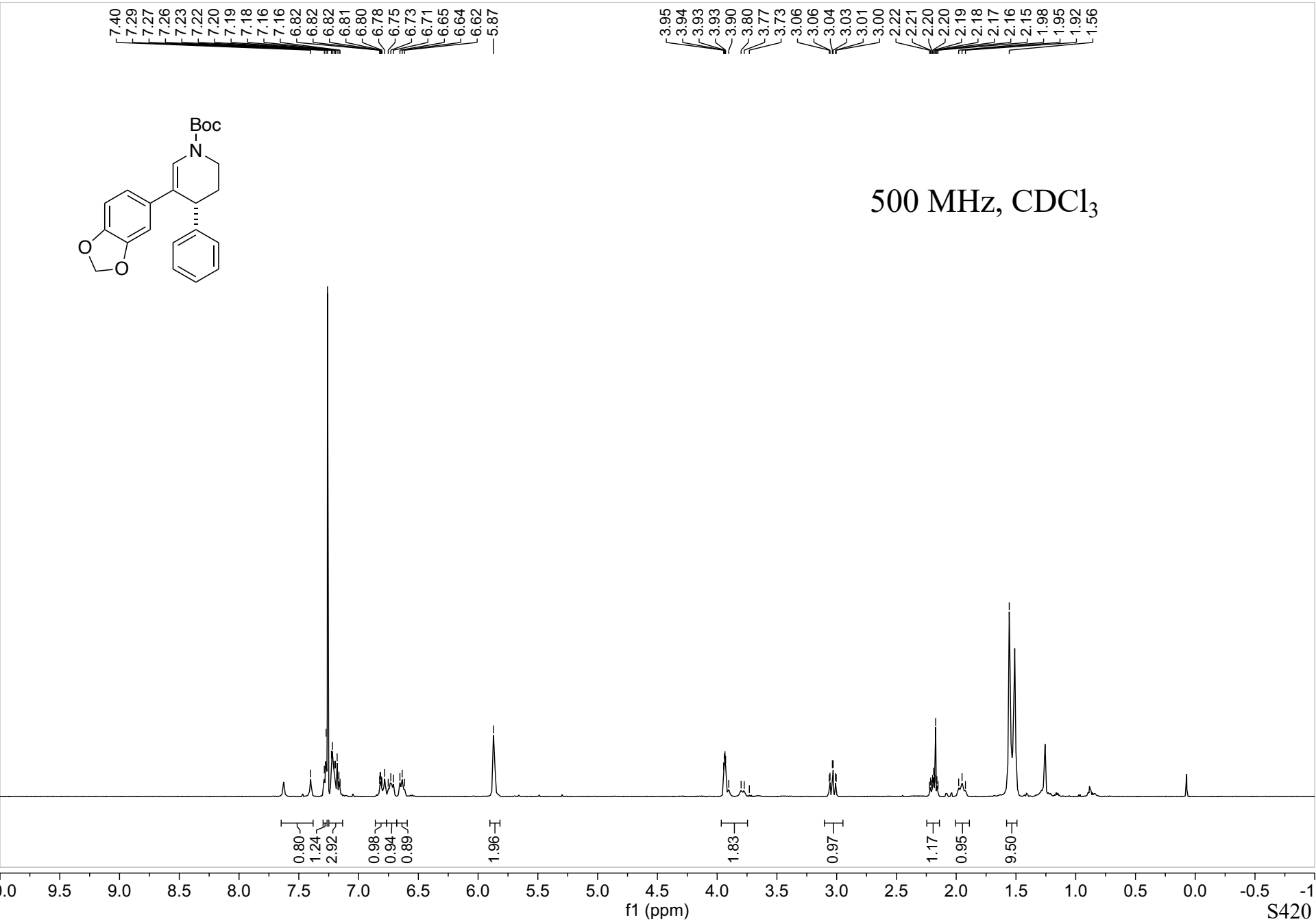




4: 310 nm, 4
nm Results

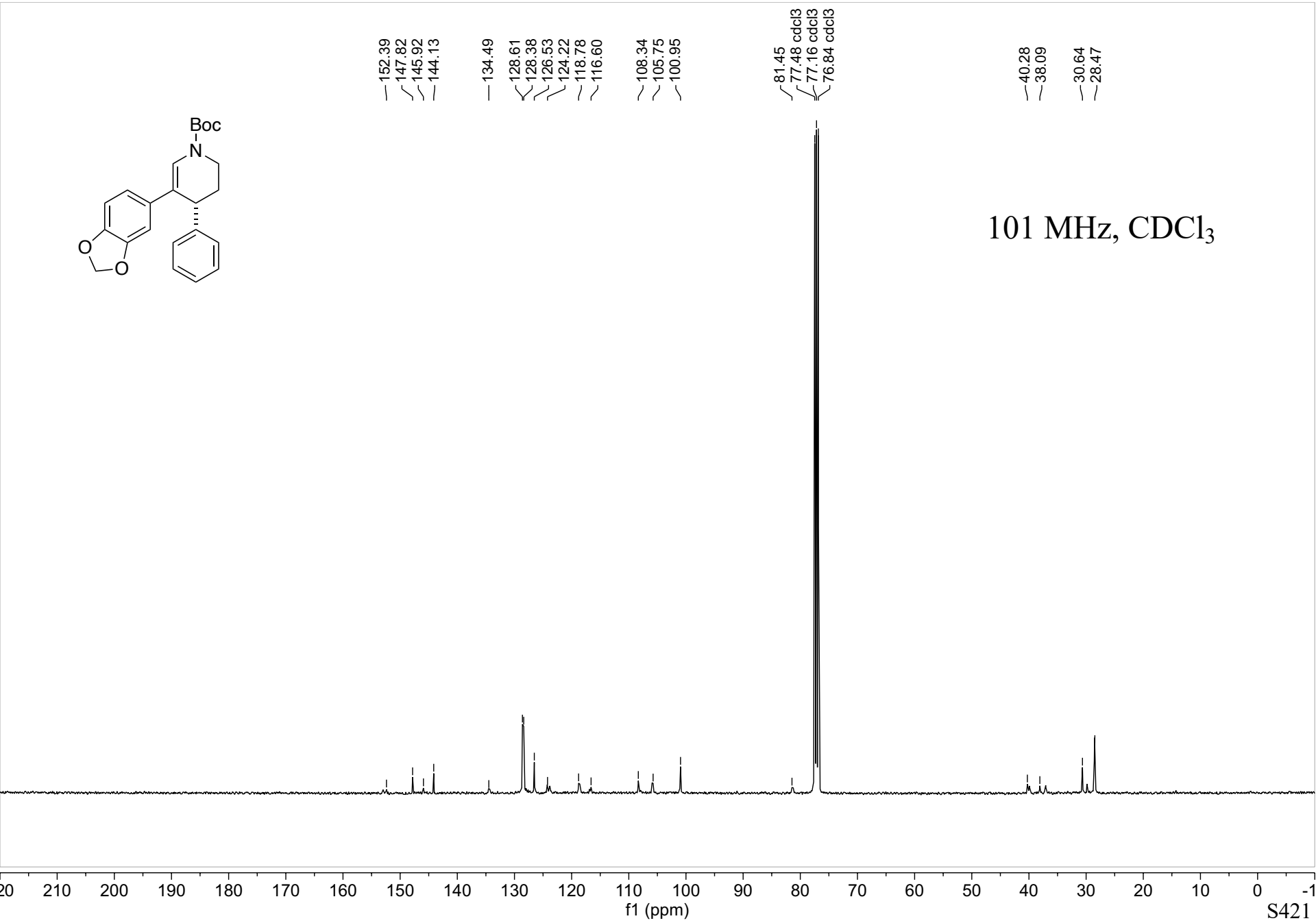
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.988 | 99.628 |
| 2 | 7.364 | 0.372 |

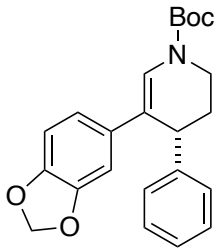
| Totals | | 100.000 |
|---|---|---|

**$^1$H NMR *tert*-Butyl (*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2d)**



**$^{13}$C NMR *tert*-Butyl (*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2d)**

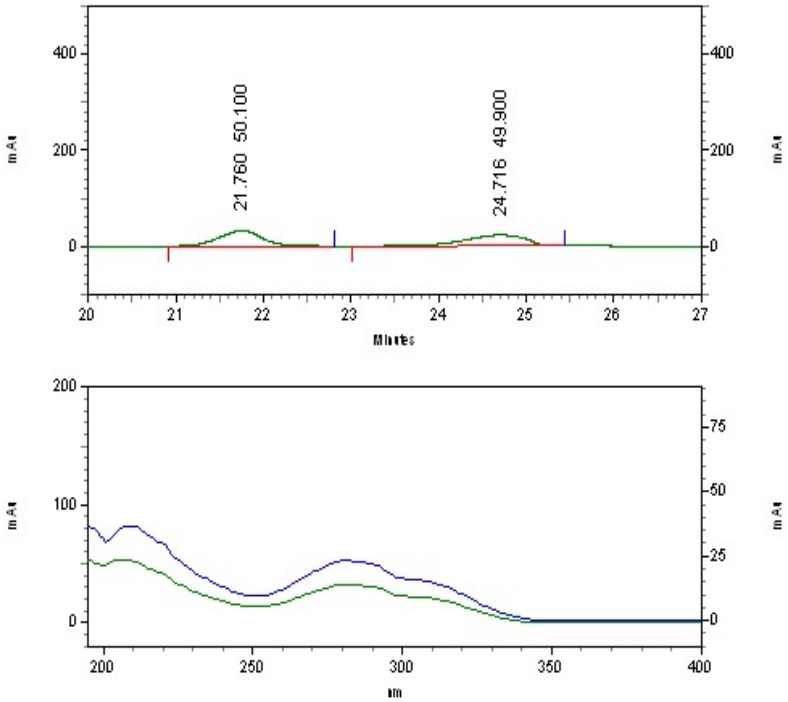





# HPLC

## *tert*-Butyl (*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2d)

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C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

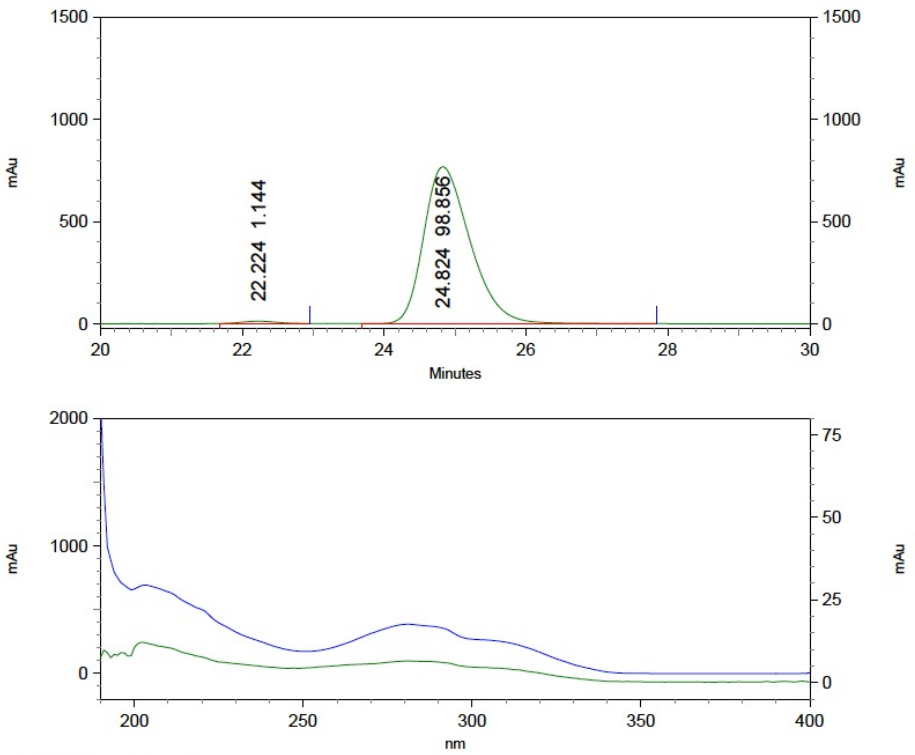



2: 280 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 21.760 | 50.100 |
| 2 | 24.716 | 49.900 |

| Totals | | 100.000 |
|---|---|---|

C:\EZStart\Projects\Default\Data\JJX-2468p-2%-IF-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\WCL\Method.met

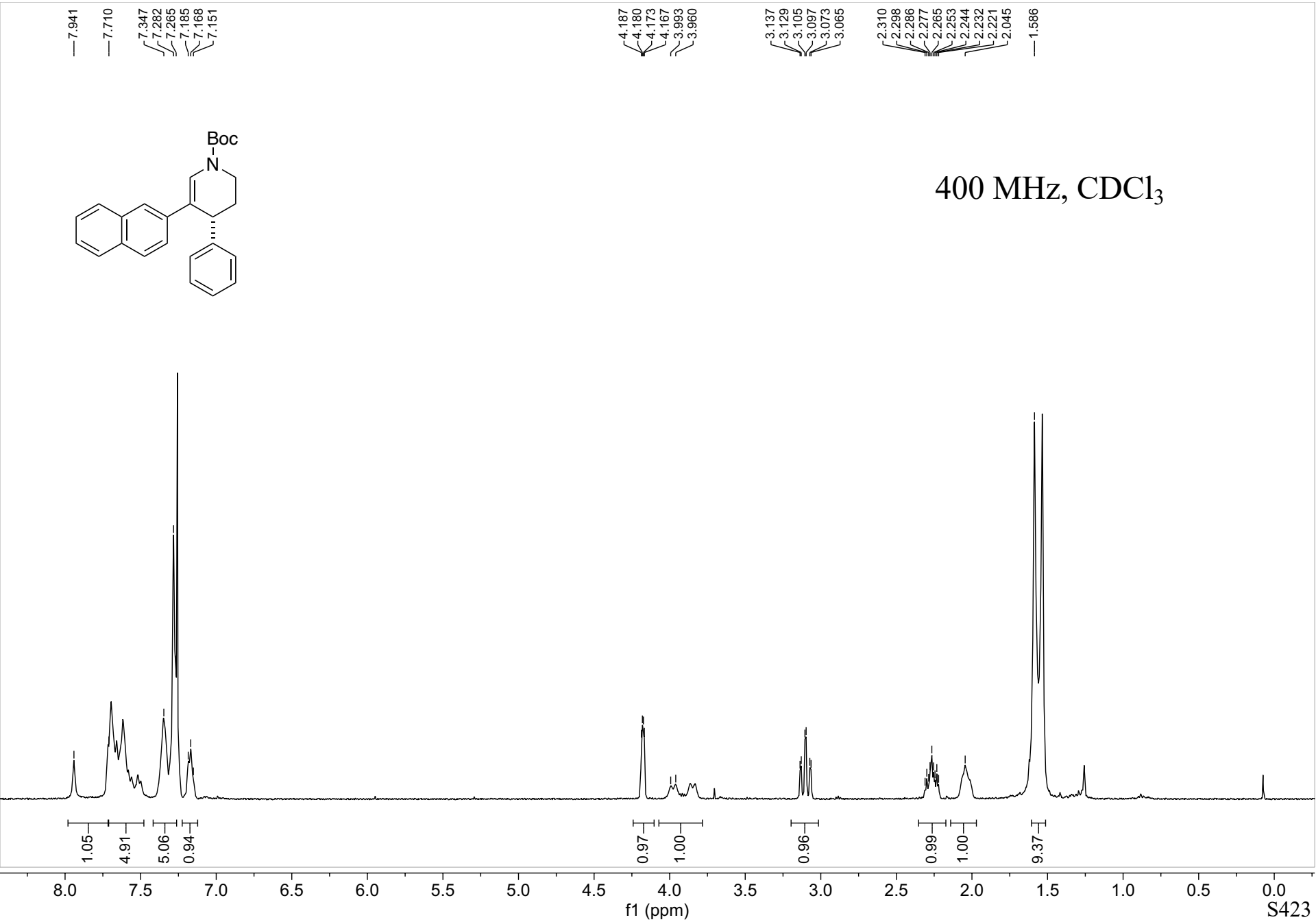



4: 280 nm, 4
nm Results

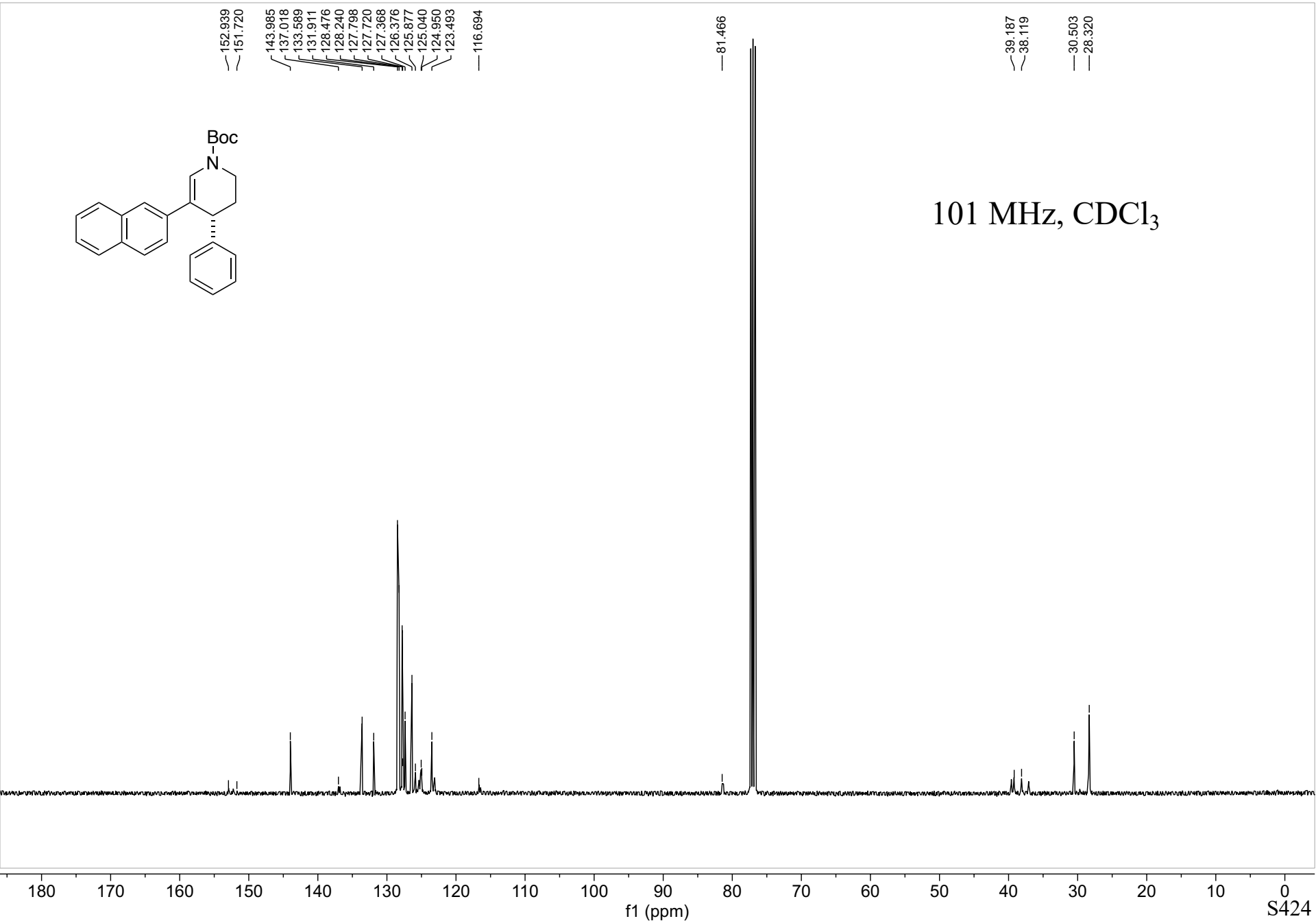
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 22.224 | 1.144 |
| 2 | 24.824 | 98.856 |

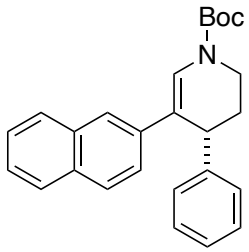
| Totals | 100.000 |
|---|---|

# $^1$H NMR *tert*-butyl (*R*)-5-(naphthalen-2-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2e)



# $^{13}$C NMR *tert*-butyl (*R*)-5-(naphthalen-2-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2e)

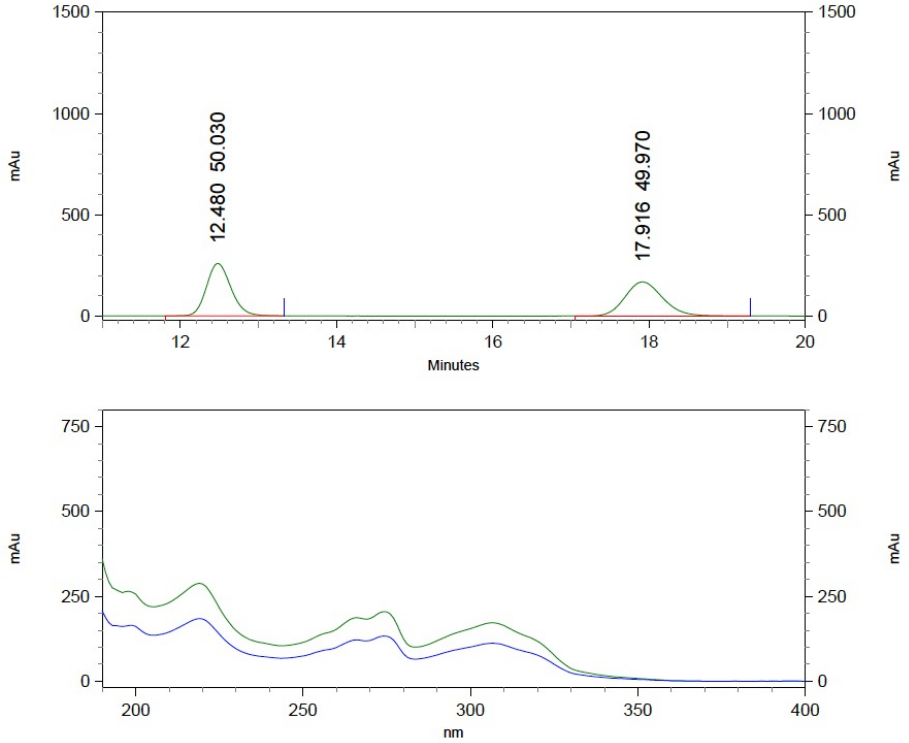





# HPLC

## *tert*-butyl (*R*)-5-(naphthalen-2-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2e)

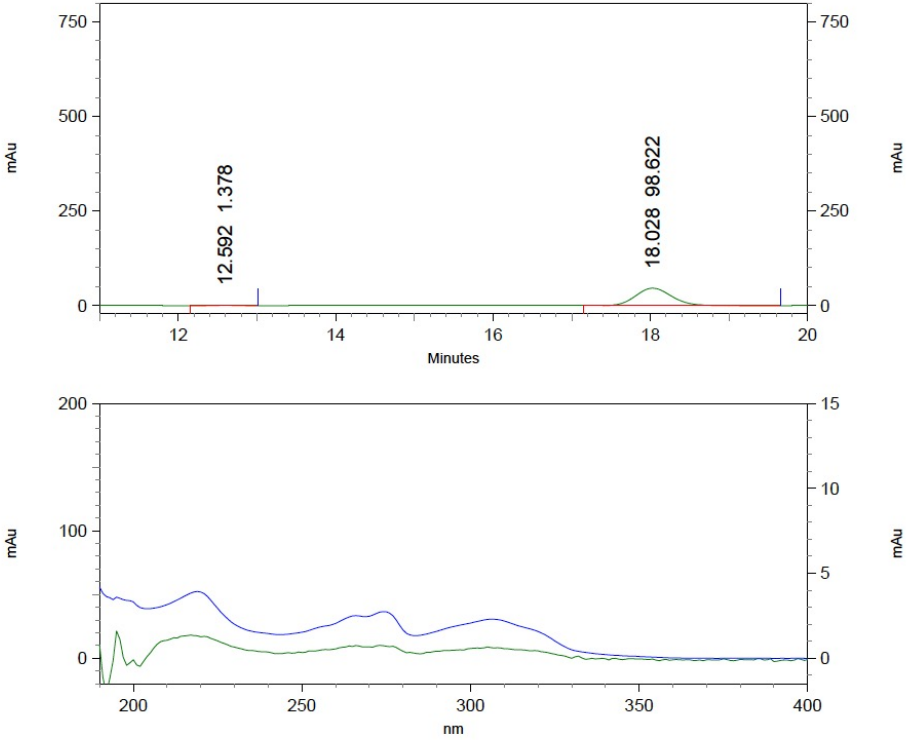
C:\EZStart\Projects\Default\Data\JJX-2463p-2%-IF-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\WCL\Method.met




4: 280 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.480 | 50.030 |
| 2 | 17.916 | 49.970 |
| Totals | | 100.000 |

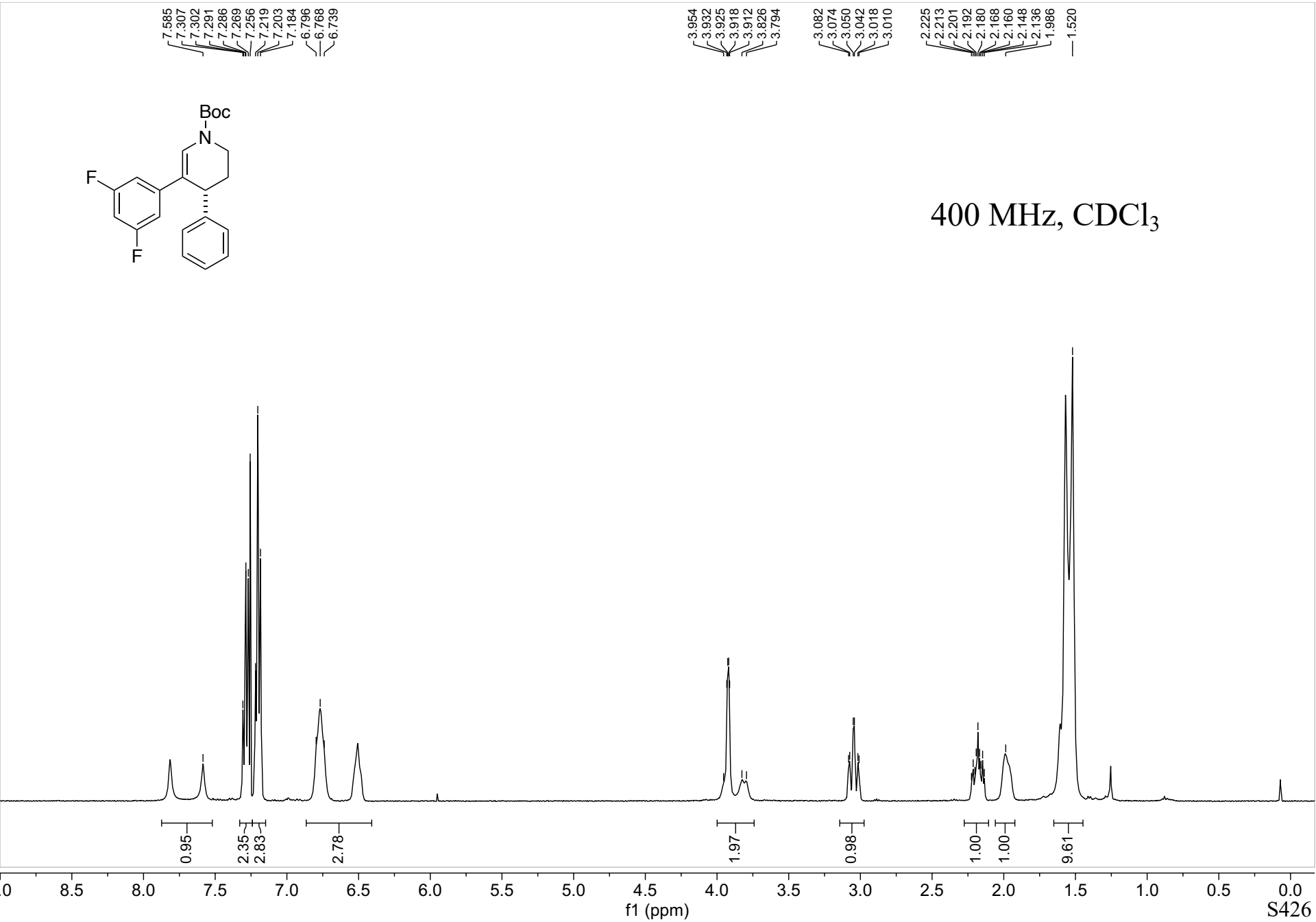
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C:\Documents and Settings\zhang\Desktop\WCL\Method.met



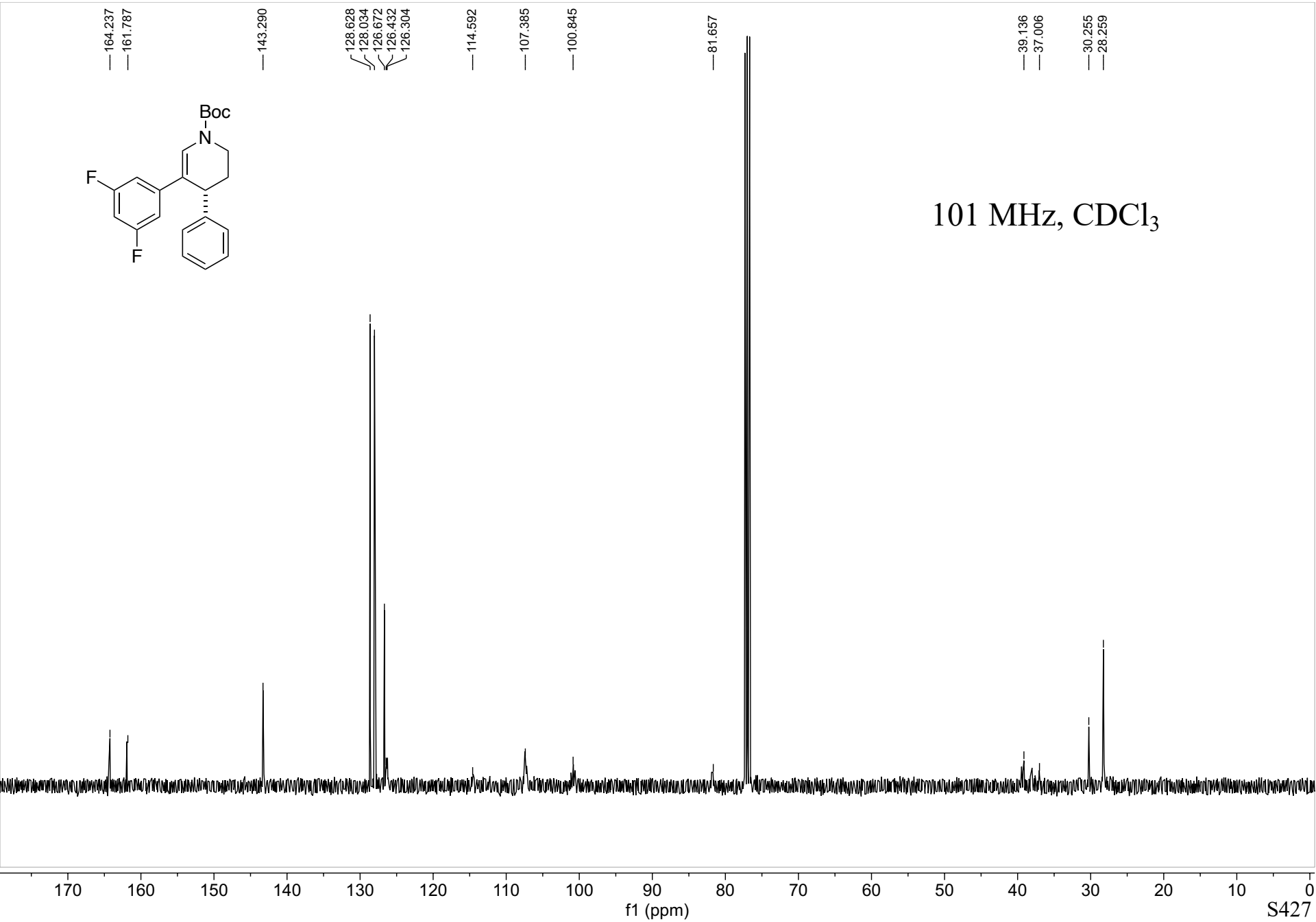

4: 280 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 12.592 | 1.378 |
| 2 | 18.028 | 98.622 |
| Totals | | 100.000 |

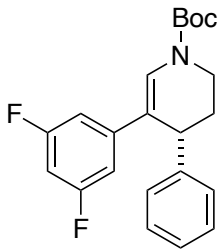
# $^1$H NMR *tert*-butyl (*R*)-5-(3,5-difluorophenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2f)



# $^{13}$C NMR *tert*-butyl (*R*)-5-(3,5-difluorophenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2f)



# $^{19}$F NMR *tert*-butyl (*R*)-5-(3,5-difluorophenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2f)

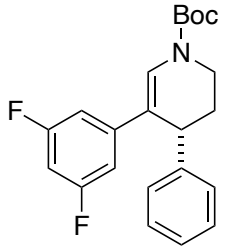



-110.771

376 MHz, $CDCl_3$

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

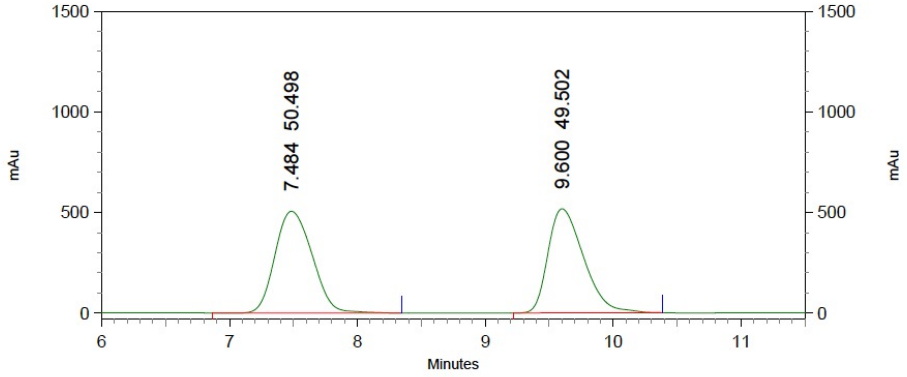
f1 (ppm)

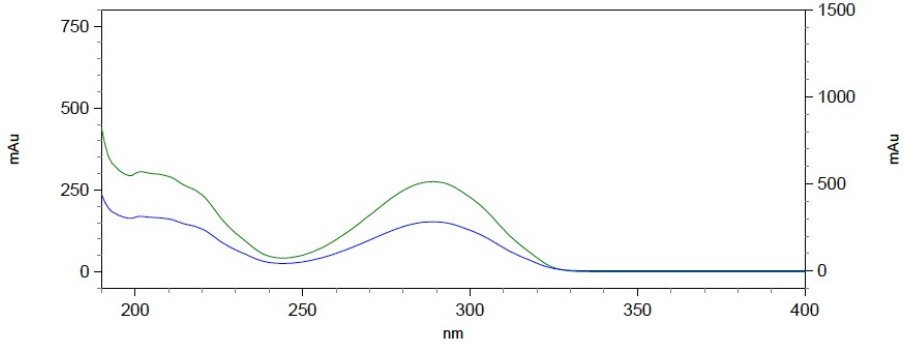



# HPLC

## *tert*-butyl (*R*)-5-(3,5-difluorophenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2f)

C:\EZStart\Projects\Default\Data\JJX-2439P-IF-2%-0.8ML-IBU
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



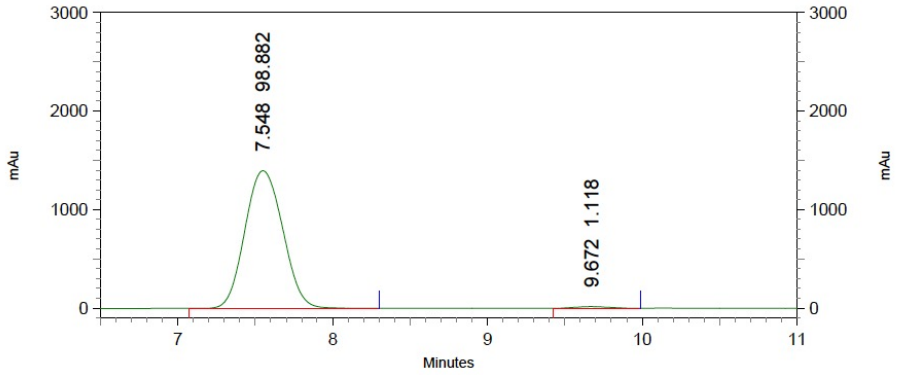



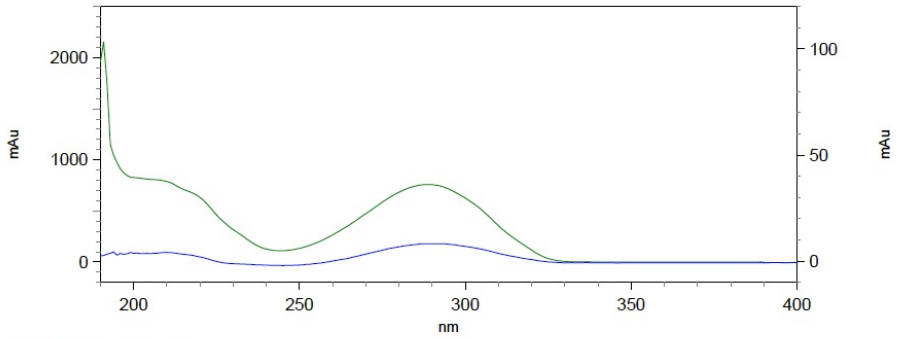

4: 281 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.484 | 50.498 |
| 2 | 9.600 | 49.502 |

| Totals | |
|---|---|
| | 100.000 |

C:\EZStart\Projects\Default\Data\JJX-2440P-IF-2%-0.8ML-TAO
C:\Documents and Settings\zhang\Desktop\WCL\Method.met



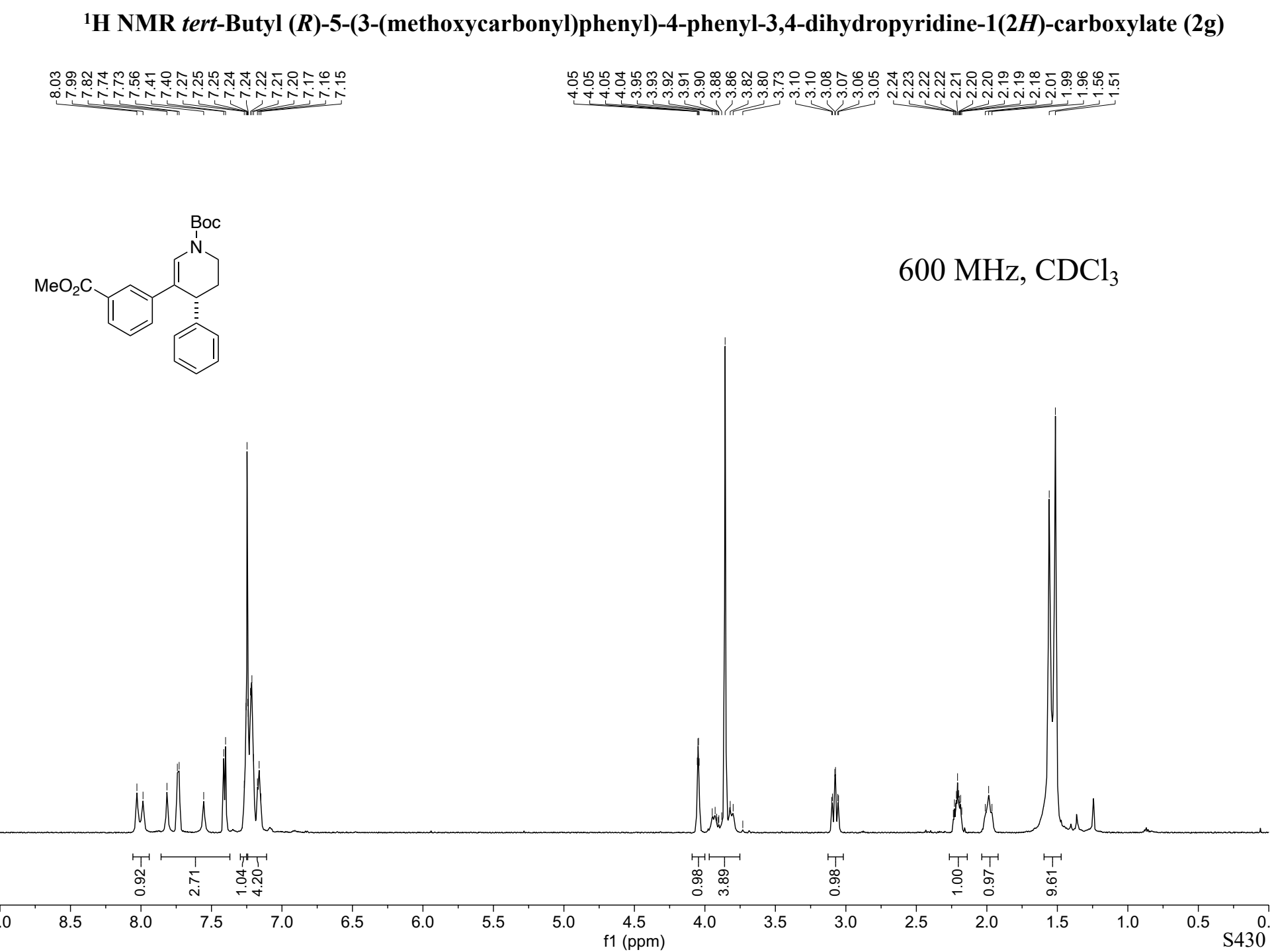




4: 281 nm, 4
nm Results

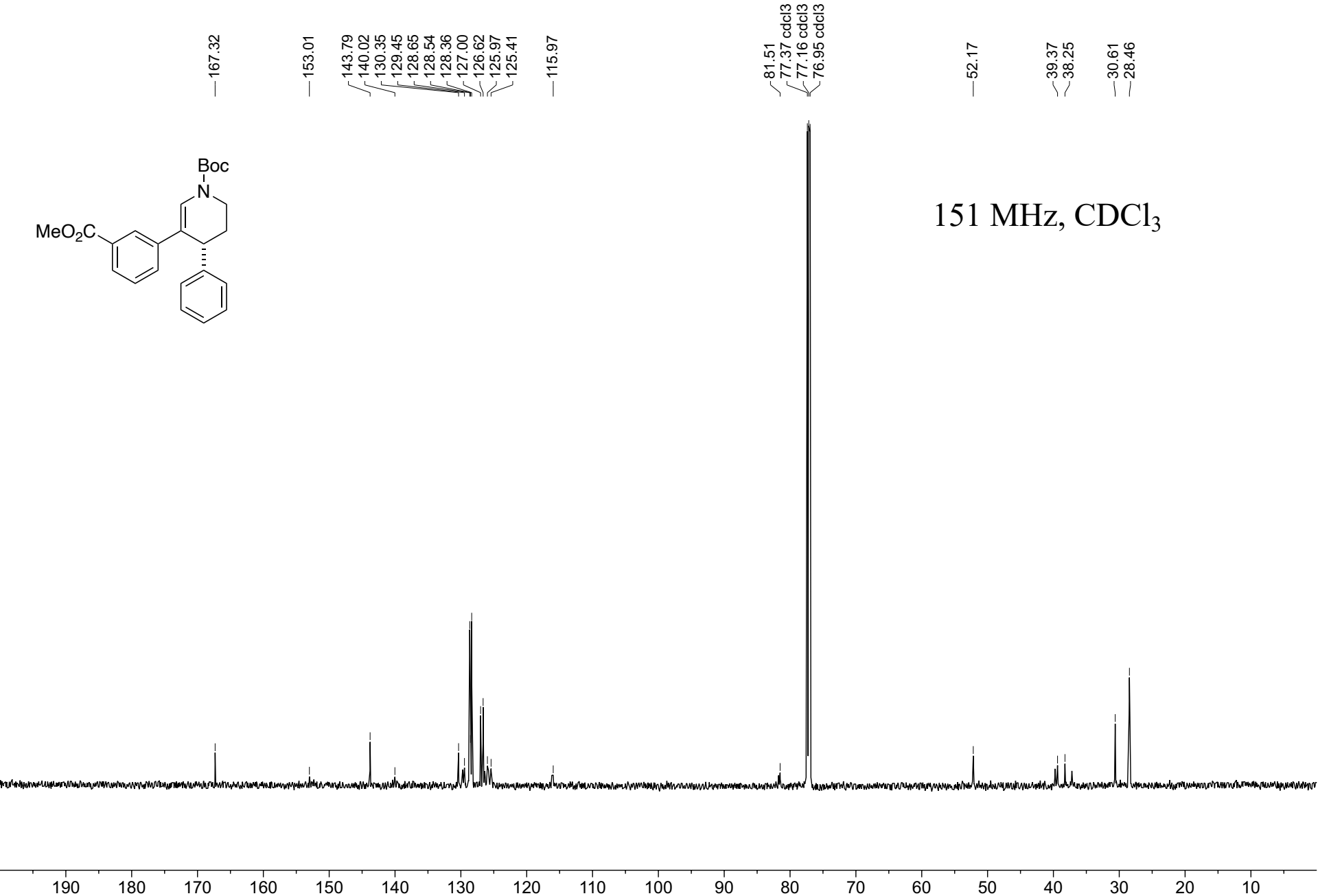
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.548 | 98.882 |
| 2 | 9.672 | 1.118 |

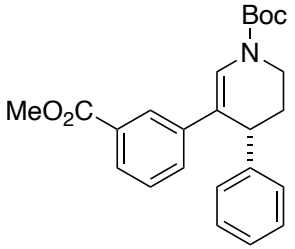
| Totals | |
|---|---|
| | 100.000 |

**$^1$H NMR *tert*-Butyl (*R*)-5-(3-(methoxycarbonyl)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2g)**



**$^{13}$C NMR *tert*-Butyl (*R*)-5-(3-(methoxycarbonyl)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2g)**



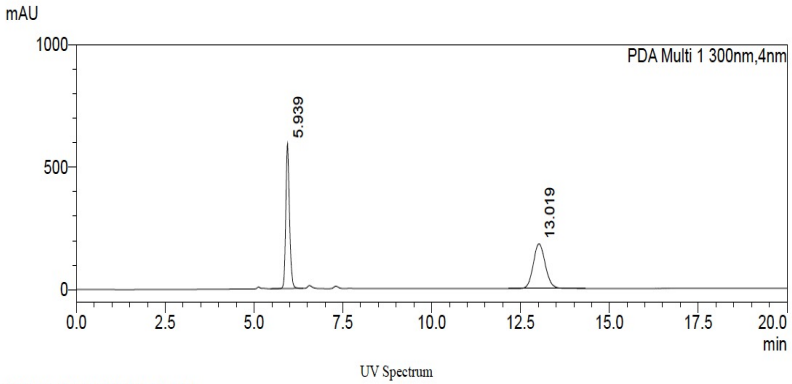



# HPLC

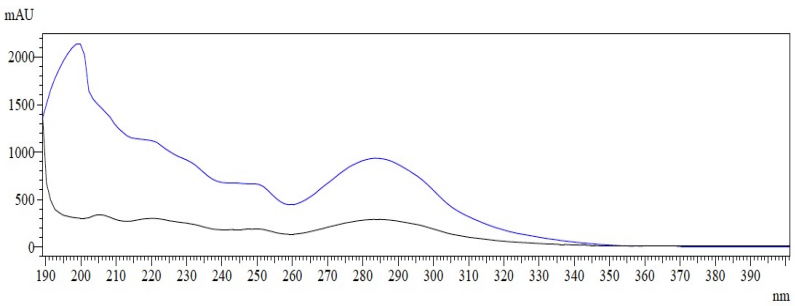
## *tert*-Butyl (*R*)-5-(3-(methoxycarbonyl)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2g)

**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3111-ibu-IB-2%0.8mL




JJX-3111-ibu-IB-2%0.8mL_001.lcd



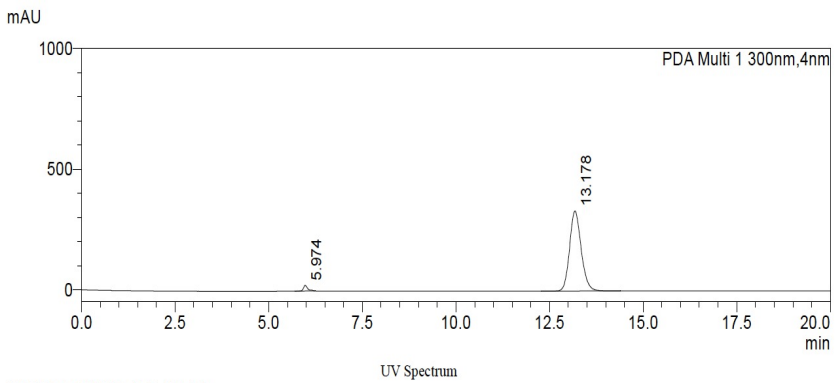

Peak Table

PDA Ch1 300nm

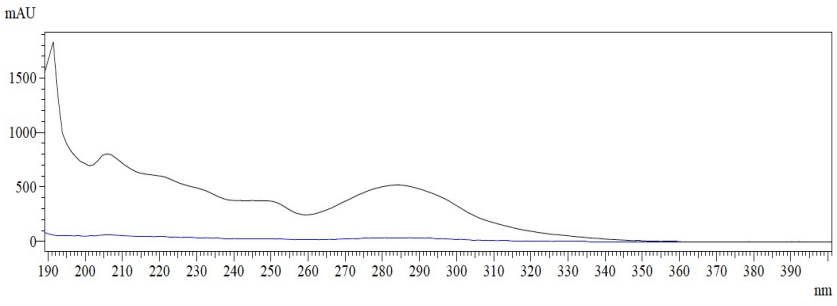
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.939 | 50.216 |
| 2 | 13.019 | 49.784 |
| Total | | 100.000 |

**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3112-tao-IB-2%0.8mL




JJX-3112-tao-IB-2%0.8mL_001.lcd

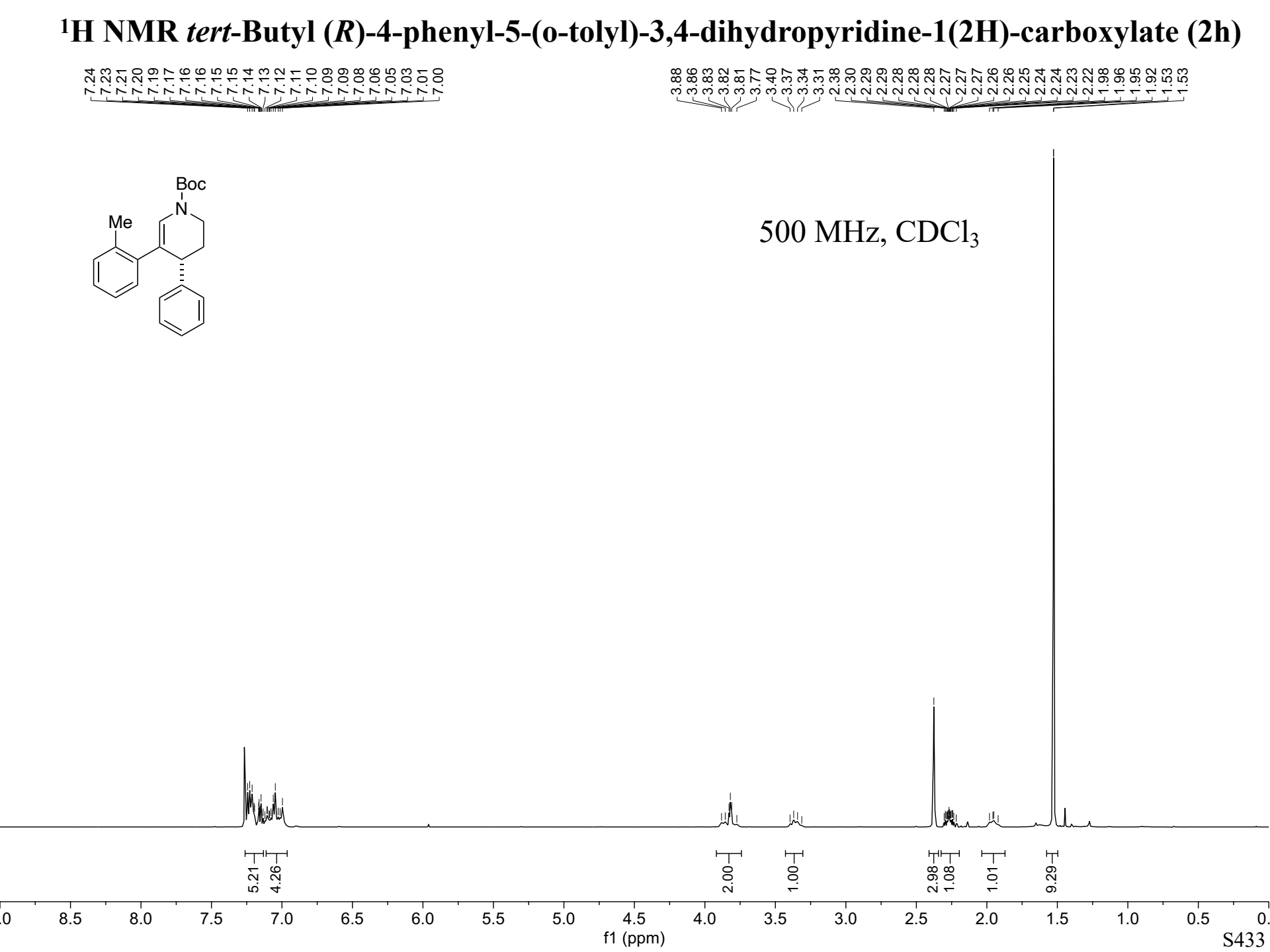



Peak Table

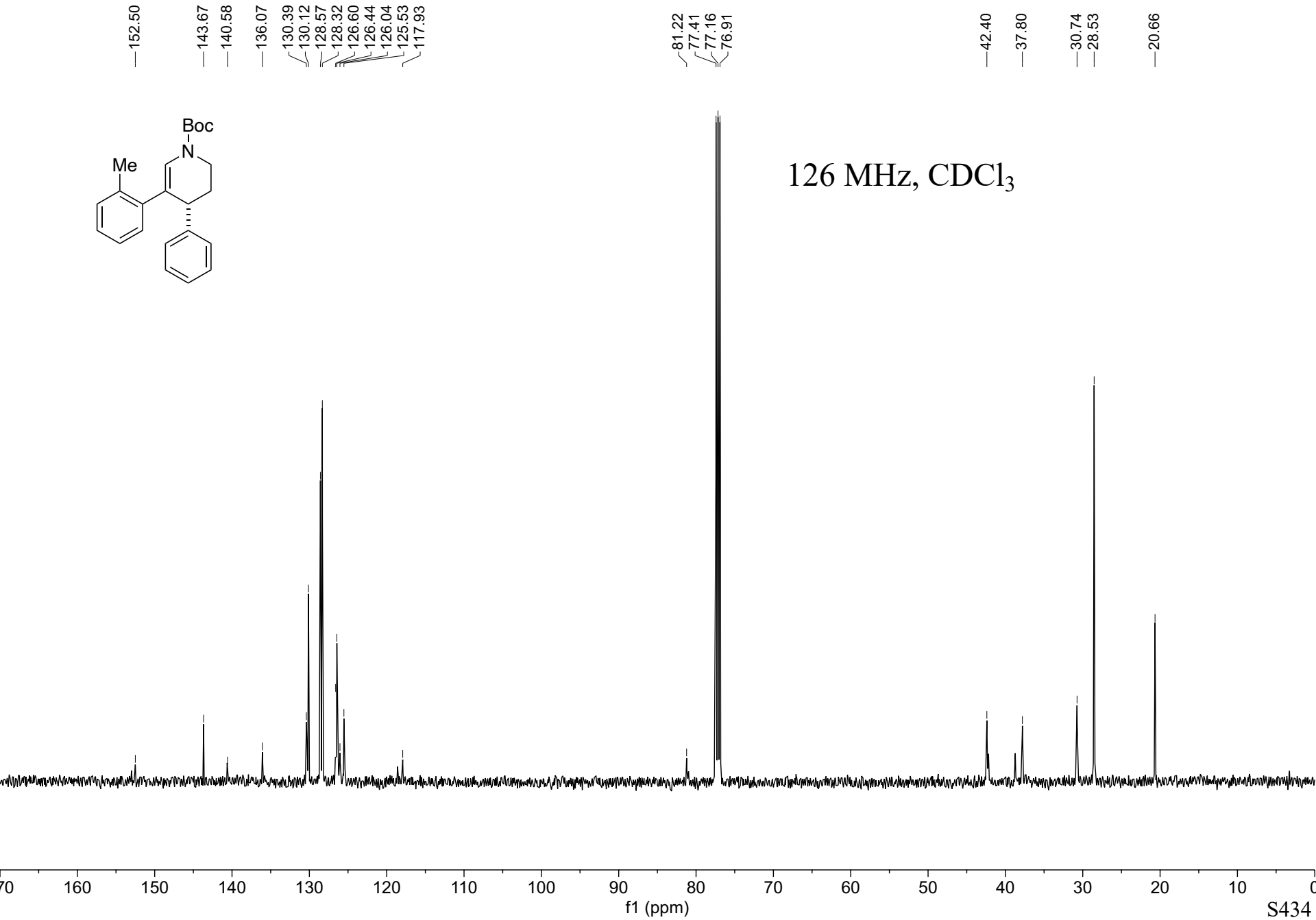
PDA Ch1 300nm

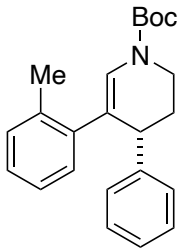
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.974 | 2.604 |
| 2 | 13.178 | 97.396 |
| Total | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*R*)-4-phenyl-5-(o-tolyl)-3,4-dihydropyridine-1(2H)-carboxylate (2h)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-phenyl-5-(o-tolyl)-3,4-dihydropyridine-1(2H)-carboxylate (2h)



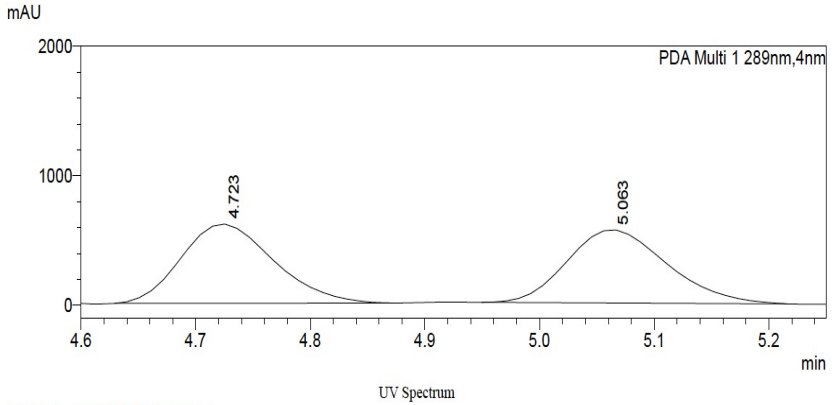



# HPLC

## *tert*-Butyl (*R*)-4-phenyl-5-(o-tolyl)-3,4-dihydropyridine-1(2H)-carboxylate (2h)

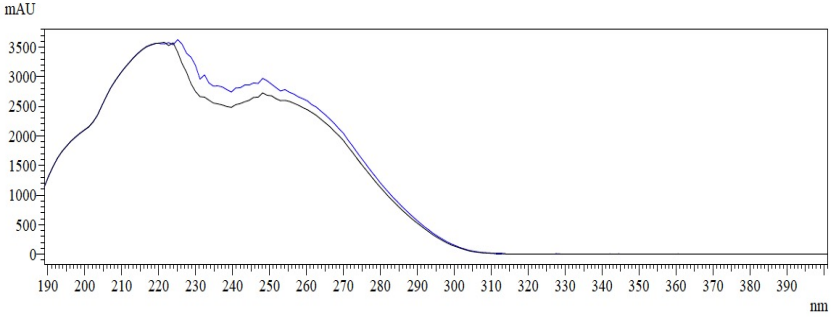
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3039p-Ibu-IB-2%0.8mL




UV Spectrum

JJX-3039p-Ibu-IB-2%0.8mL_001.lcd



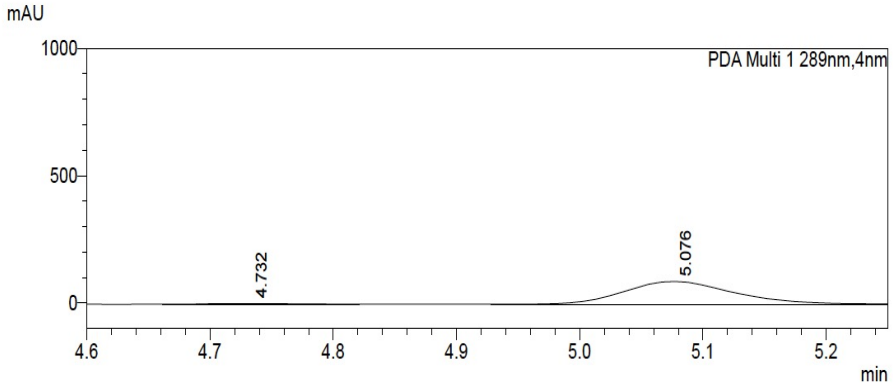

Peak Table

PDA Ch1 289nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 4.723 | 50.204 |
| 2 | 5.063 | 49.796 |
| Total | | 100.000 |

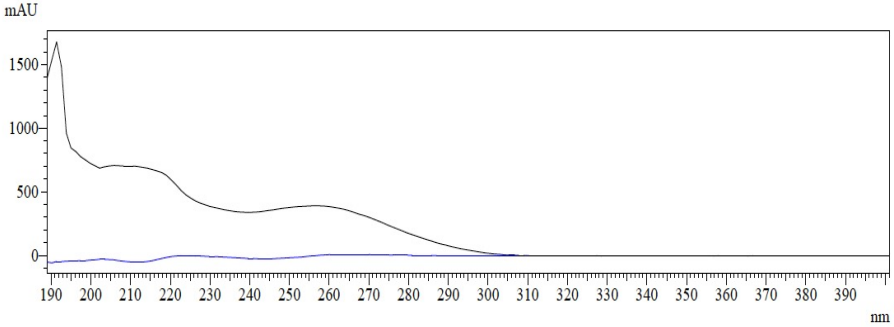
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3040p-Tao-IB-2%0.8mL




UV Spectrum

JJX-3040p-Tao-IB-2%0.8mL_001.lcd

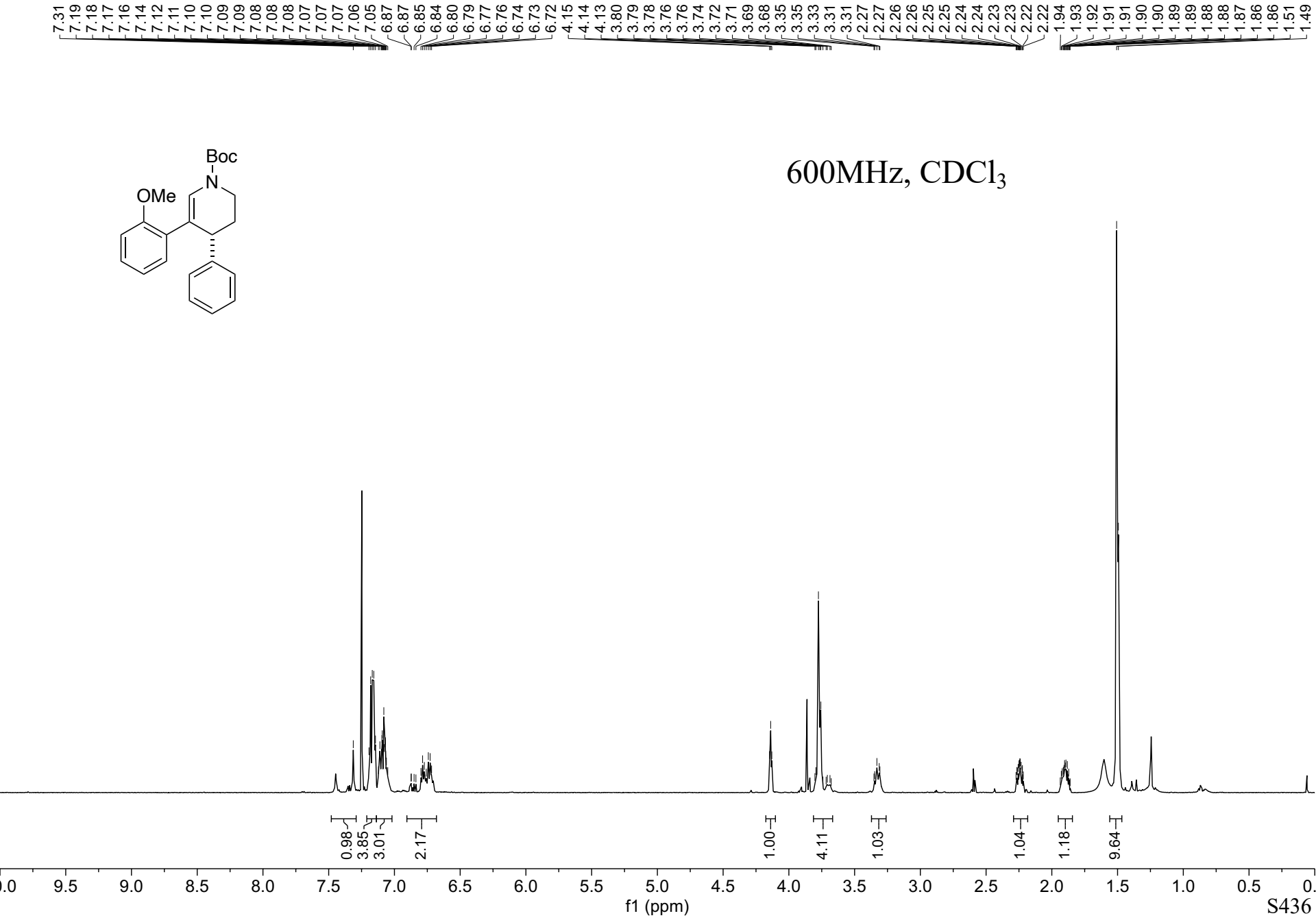



Peak Table

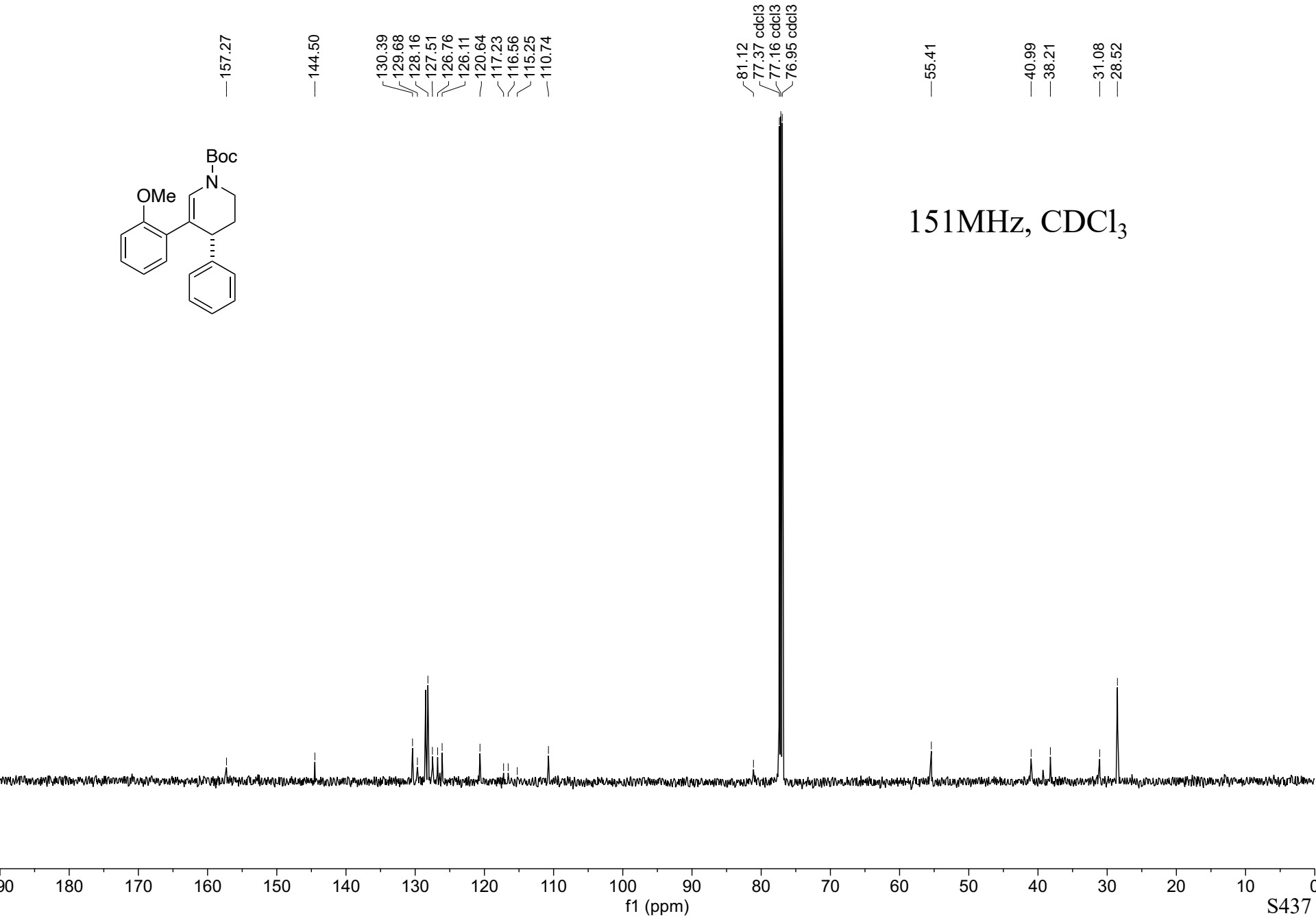
PDA Ch1 289nm

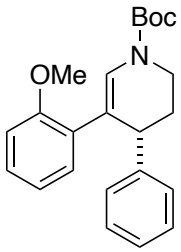
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 4.732 | 2.400 |
| 2 | 5.076 | 97.600 |
| Total | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*R*)-5-(2-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2i)



# $^{13}$C NMR *tert*-Butyl (*R*)-5-(2-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2i)



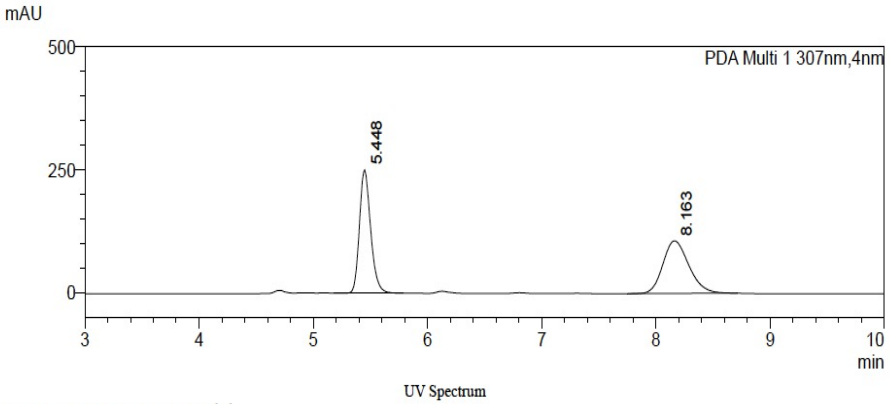



## *HPLC*

## *tert*-Butyl (*R*)-5-(2-methoxyphenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2i)

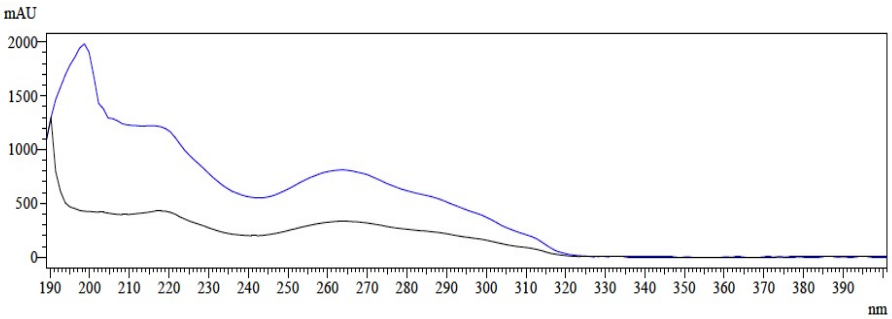
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3071p-IBU-IB-2%0.8mL




UV Spectrum

JJX-3071p-IBU-IB-2%0.8mL_001.lcd



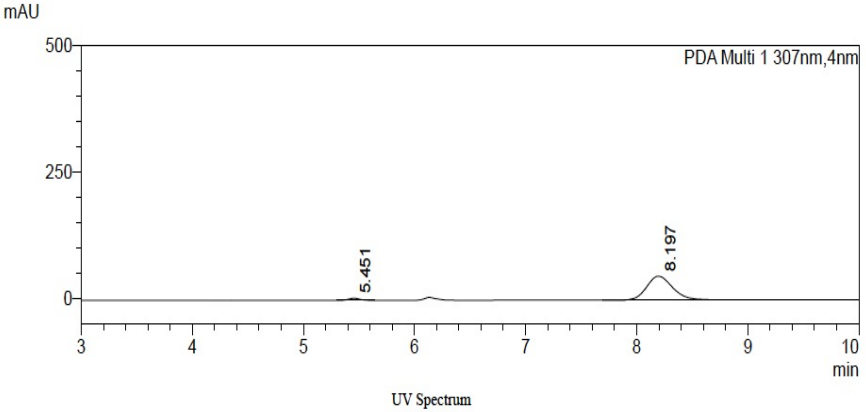

Peak Table

PDA Ch1 307nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.448 | 50.292 |
| 2 | 8.163 | 49.708 |
| Total | | 100.000 |

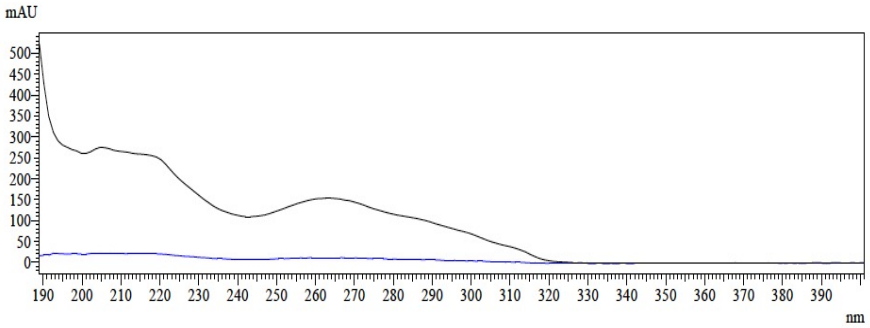
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3072p-TAO-IB-2%0.8mL




UV Spectrum

JJX-3072p-TAO-IB-2%0.8mL_002.lcd

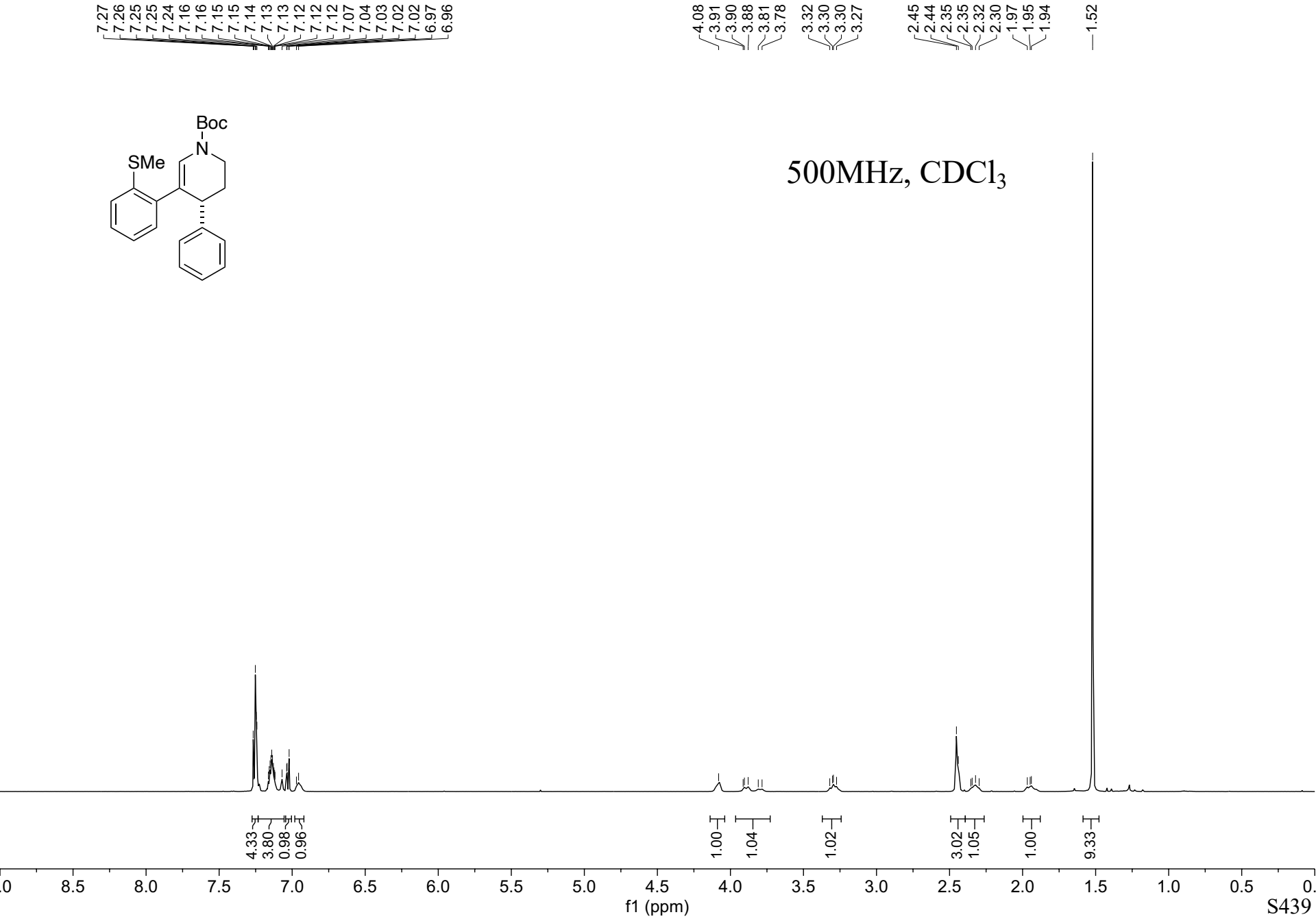



Peak Table

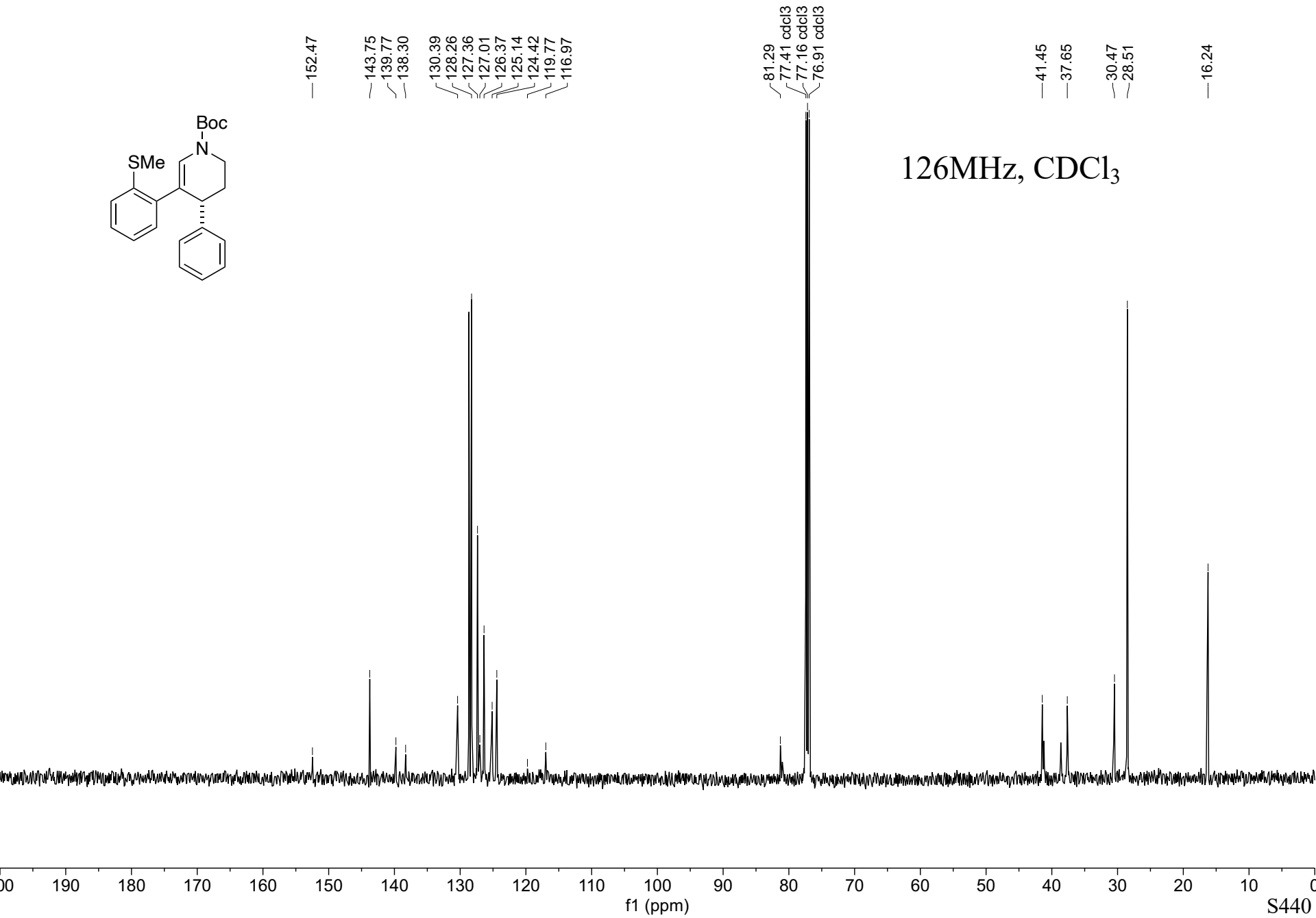
PDA Ch1 307nm

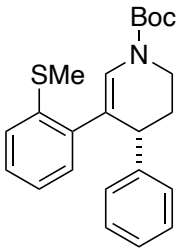
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.451 | 3.356 |
| 2 | 8.197 | 96.644 |
| Total | | 100.000 |

# $^1$H NMR *tert*-Butyl (*R*)-5-(2-(methylthio)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2j)



# $^{13}$C NMR *tert*-Butyl (*R*)-5-(2-(methylthio)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2j)



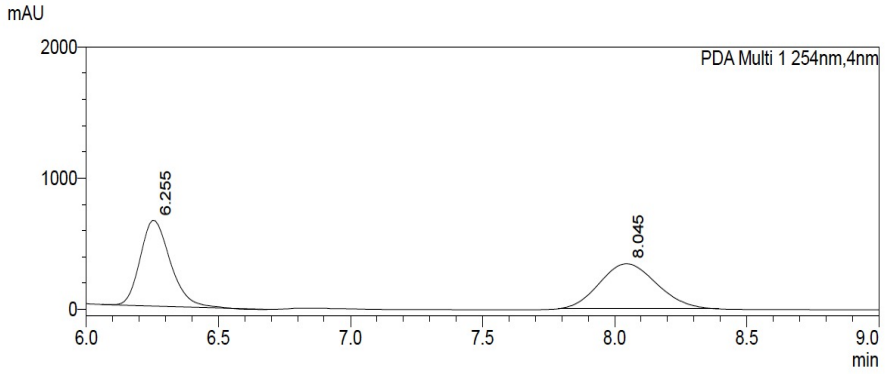



# HPLC

## *tert*-Butyl (*R*)-5-(2-(methylthio)phenyl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2j)

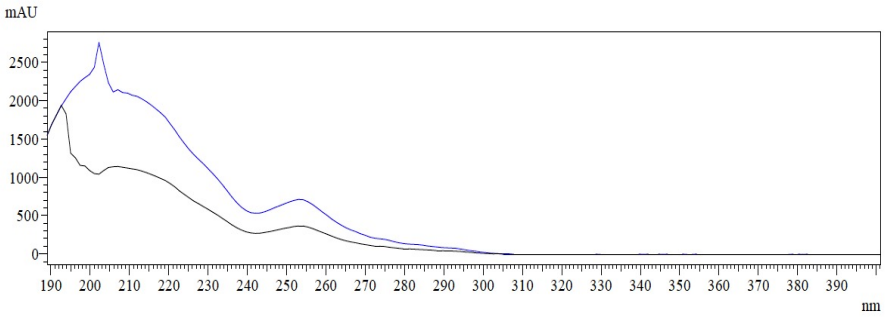
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : PLQ-0027p-ibu-IB-2%0.8mL001




UV Spectrum

PLQ-0027p-ibu-IB-2%0.8mL001_001.lcd



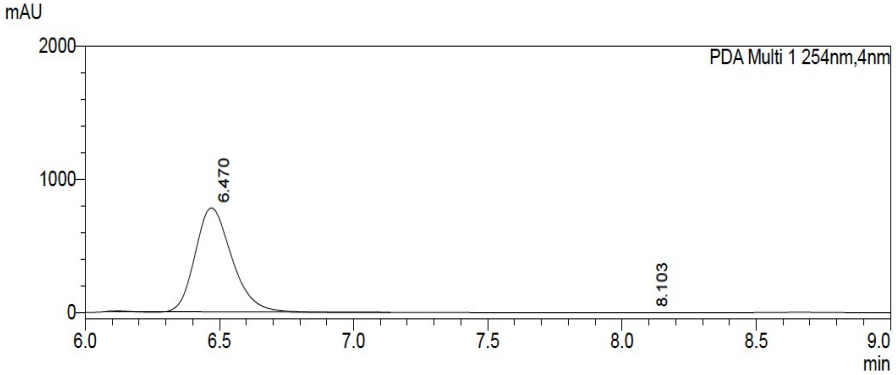

Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.255 | 49.999 |
| 2 | 8.045 | 50.001 |
| Total | | 100.000 |

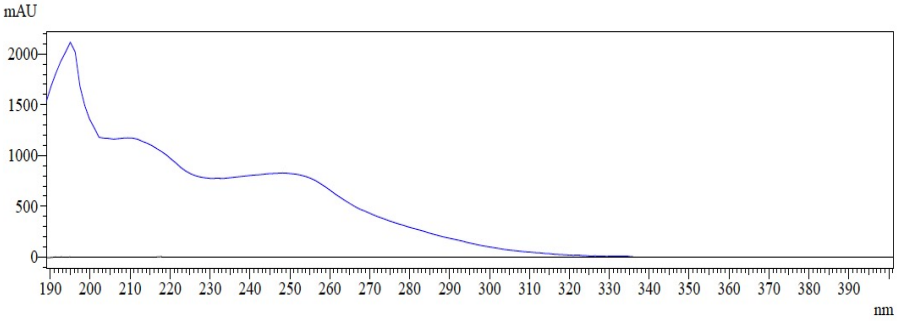
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3088p-tao-IB-2%0.8mL001




UV Spectrum

JJX-3088p-tao-IB-2%0.8mL001_002.lcd

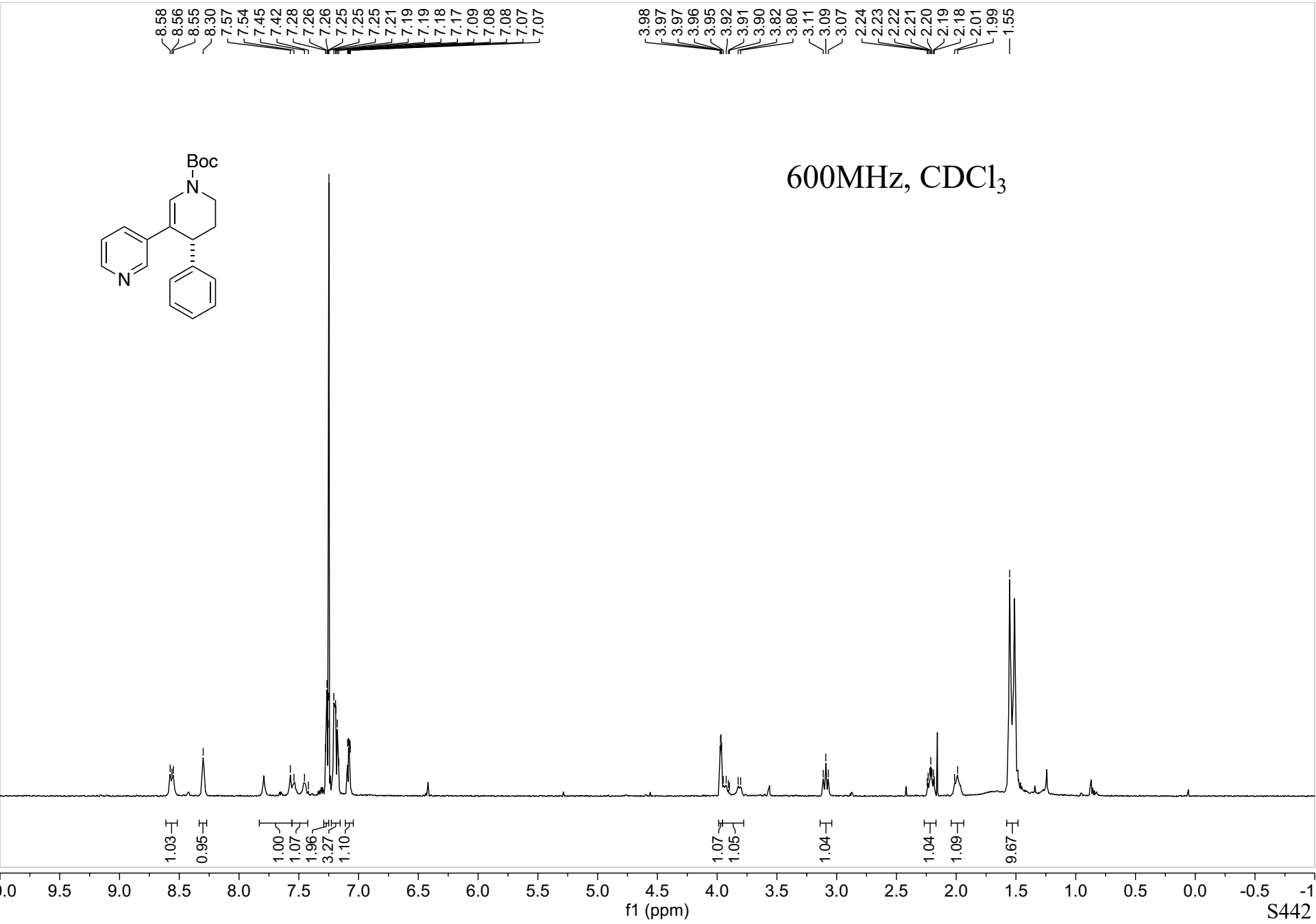


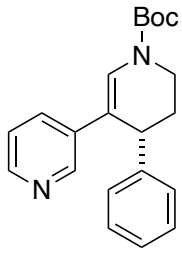

Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.470 | 99.964 |
| 2 | 8.103 | 0.036 |
| Total | | 100.000 |

# $^1$H NMR *tert*-butyl (*R*)-4-phenyl-5,6-dihydro-[3,3'-bipyridine]-1(4*H*)-carboxylate (2k)

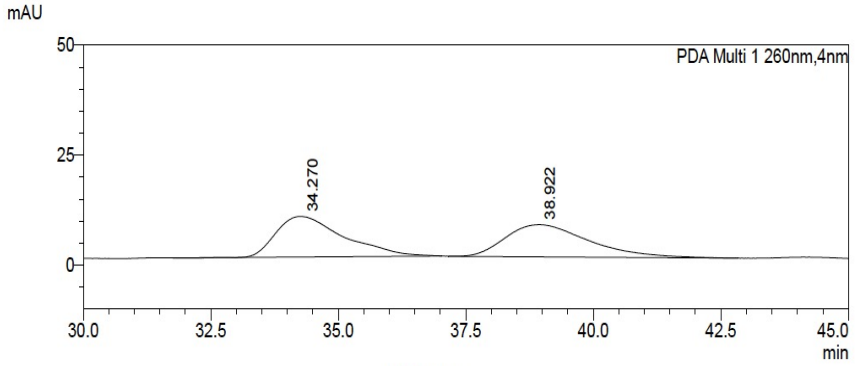





# HPLC

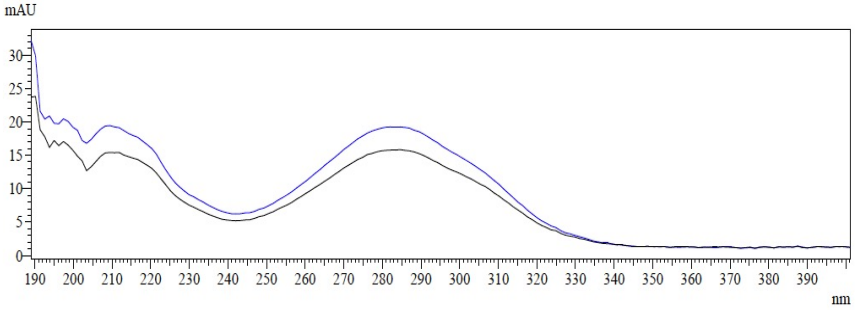
## *tert*-butyl (*R*)-4-phenyl-5,6-dihydro-[3,3'-bipyridine]-1(4*H*)-carboxylate (2k)

Sample Name : JJX-3-pyridine-rac-ID-10%0.8mL001




UV Spectrum

JJX-3-pyridine-rac-ID-10%0.8mL001_001.lcd

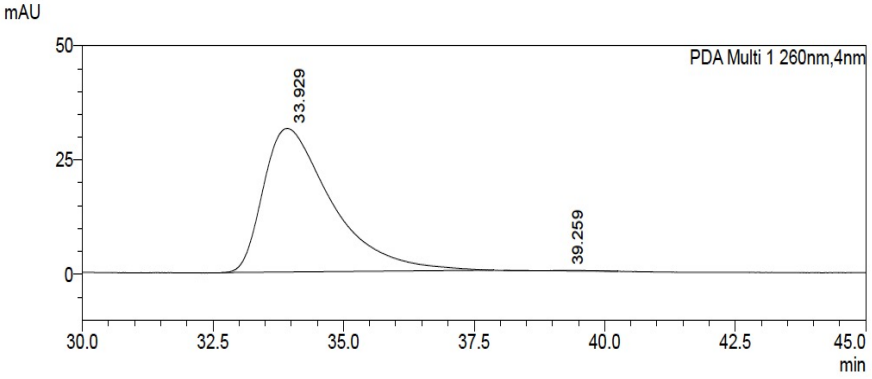



Peak Table

PDA Ch1 260nm

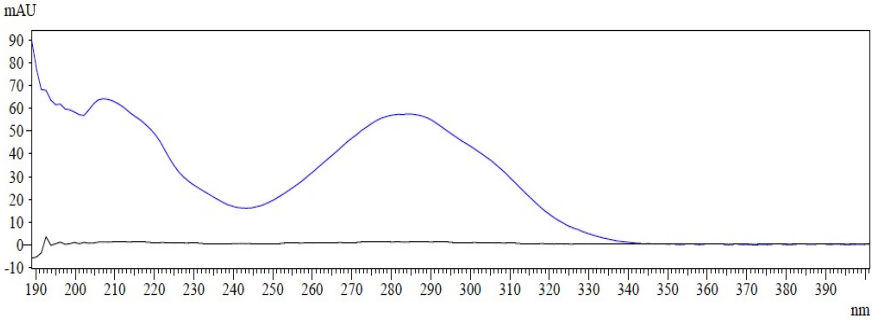
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 34.270 | 50.374 |
| 2 | 38.922 | 49.626 |
| Total | | 100.000 |

Sample Name : JJX-3-pyridine-chiral-ID-10%0.8mL002




UV Spectrum

JJX-3-pyridine-chiral-ID-10%0.8mL002_002.lcd

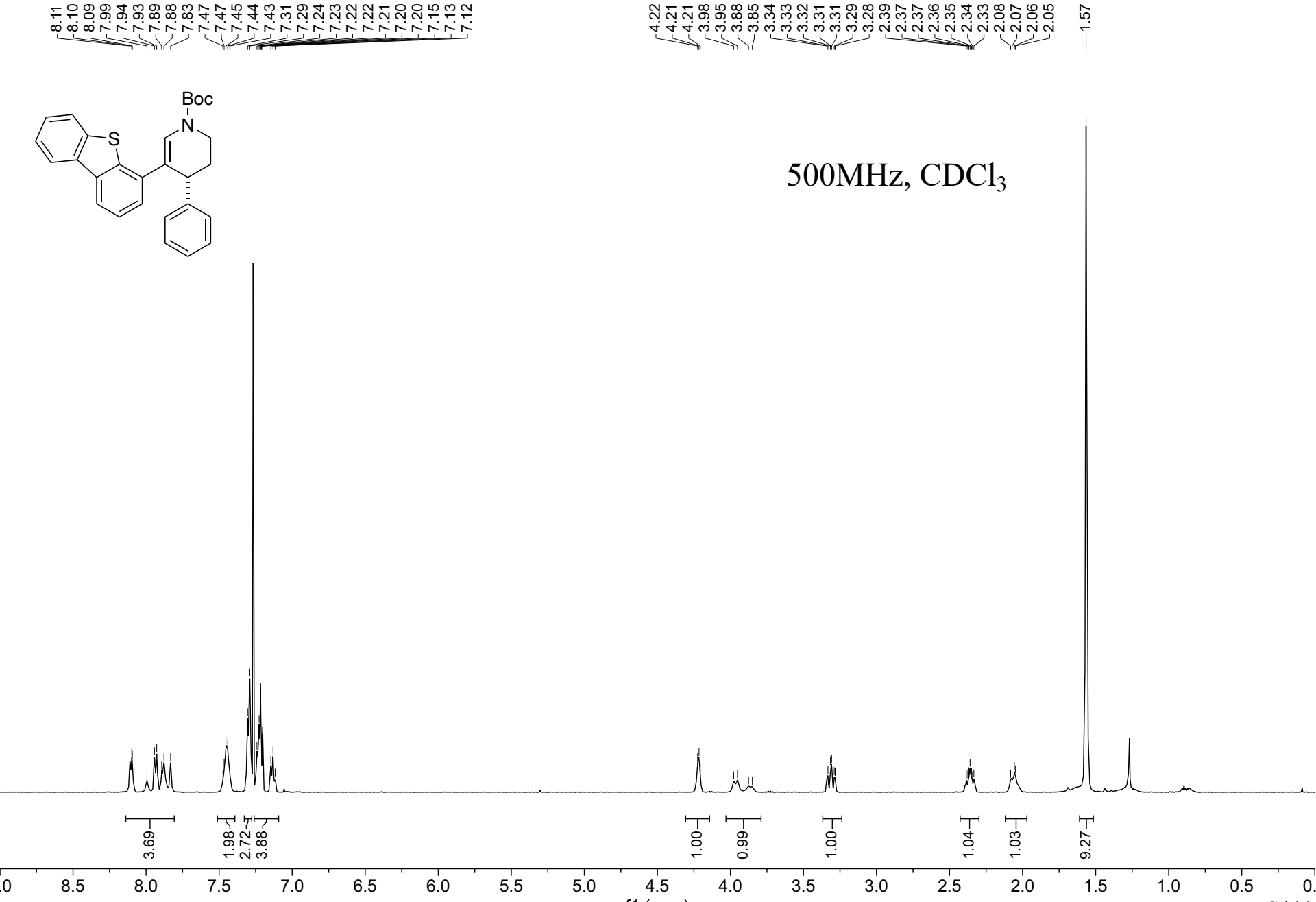



Peak Table

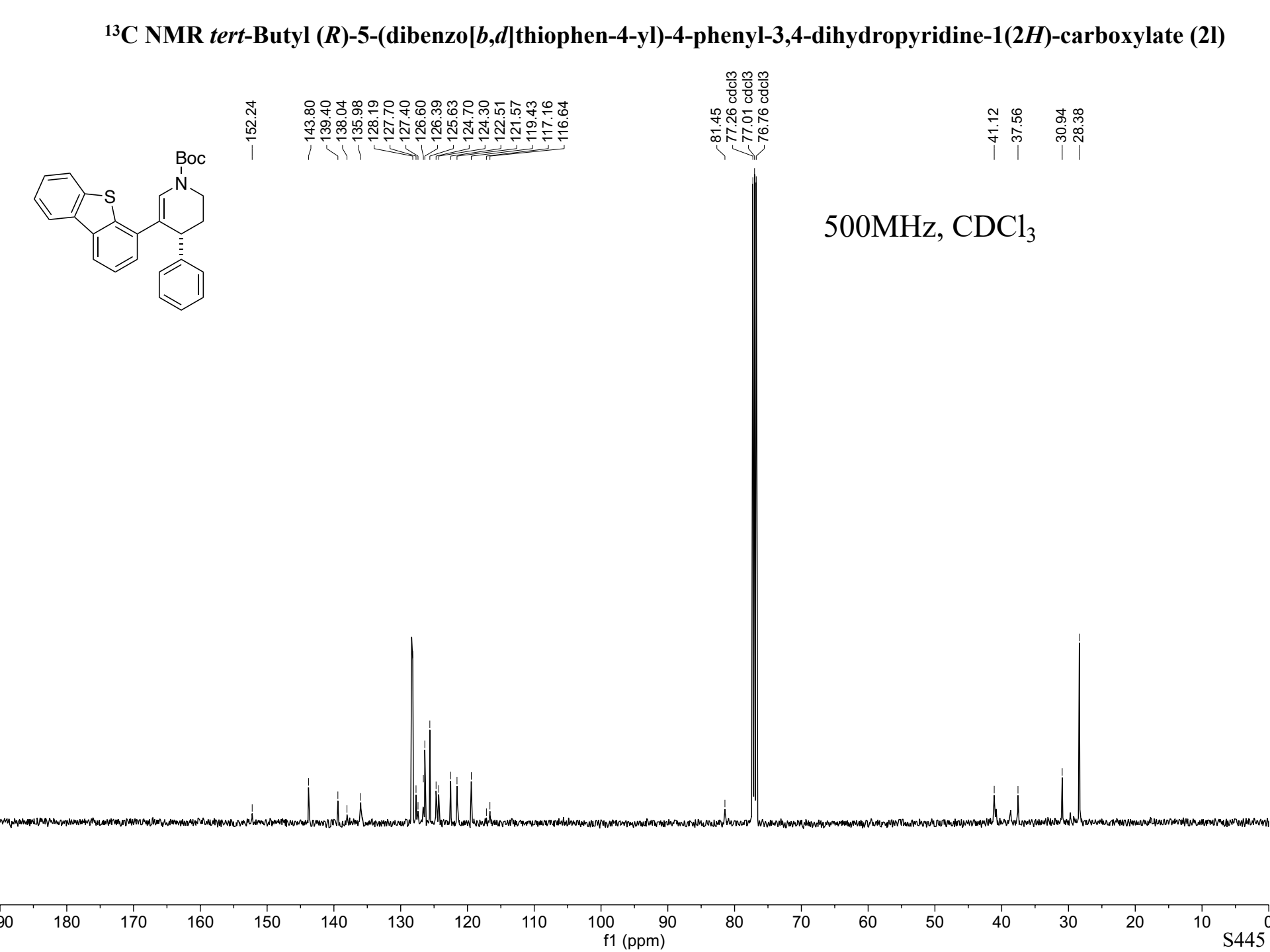
PDA Ch1 260nm

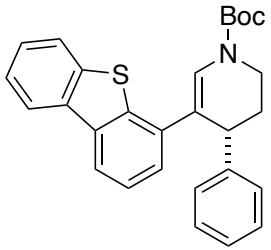
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 33.929 | 99.791 |
| 2 | 39.259 | 0.209 |
| Total | | 100.000 |

**$^1$H NMR *tert*-Butyl (*R*)-5-(dibenzo[*b*,*d*]thiophen-4-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2l)**



**$^{13}$C NMR *tert*-Butyl (*R*)-5-(dibenzo[*b*,*d*]thiophen-4-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2l)**



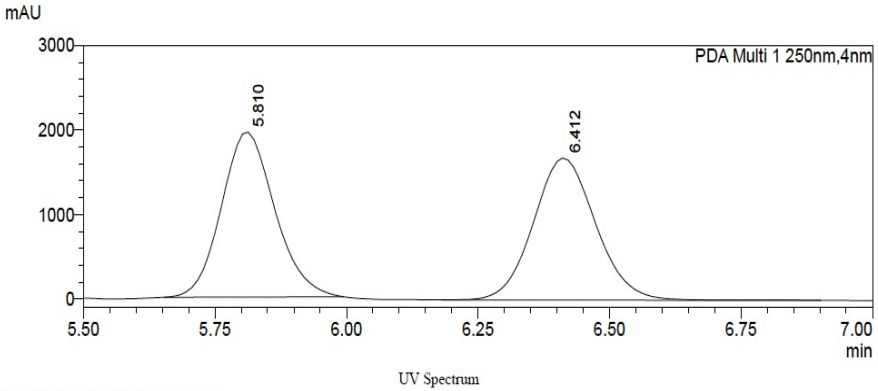



## *HPLC*

**tert-Butyl (*R*)-5-(dibenzo[*b*,*d*]thiophen-4-yl)-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2l)**

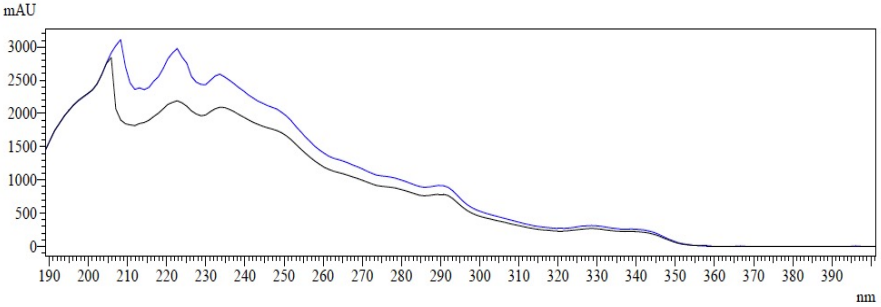
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3017-Ibu-IA-2%0.8mL




UV Spectrum

JJX-3017-Ibu-IA-2%0.8mL_001.lcd



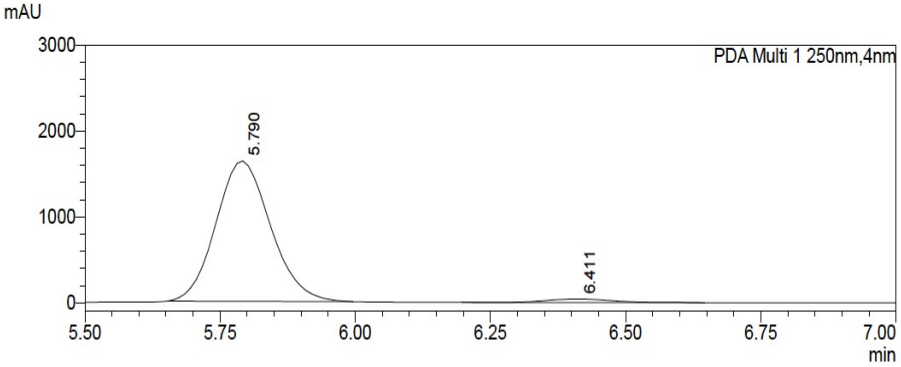

Peak Table

PDA Ch1 250nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.810 | 49.975 |
| 2 | 6.412 | 50.025 |
| Total | | 100.000 |

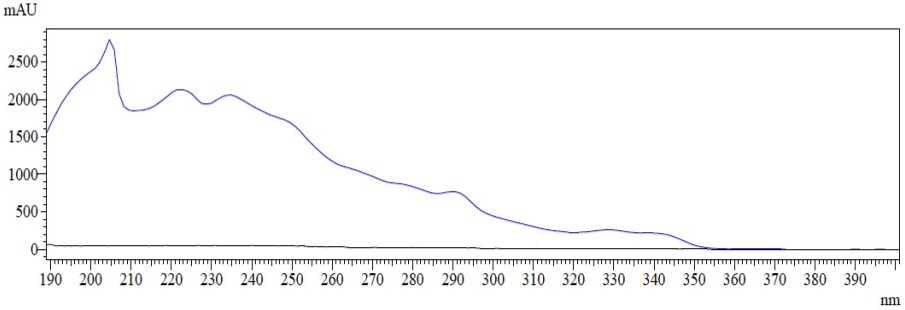
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3018-Tao-IA-2%0.8mL




UV Spectrum

JJX-3018-Tao-IA-2%0.8mL_001.lcd

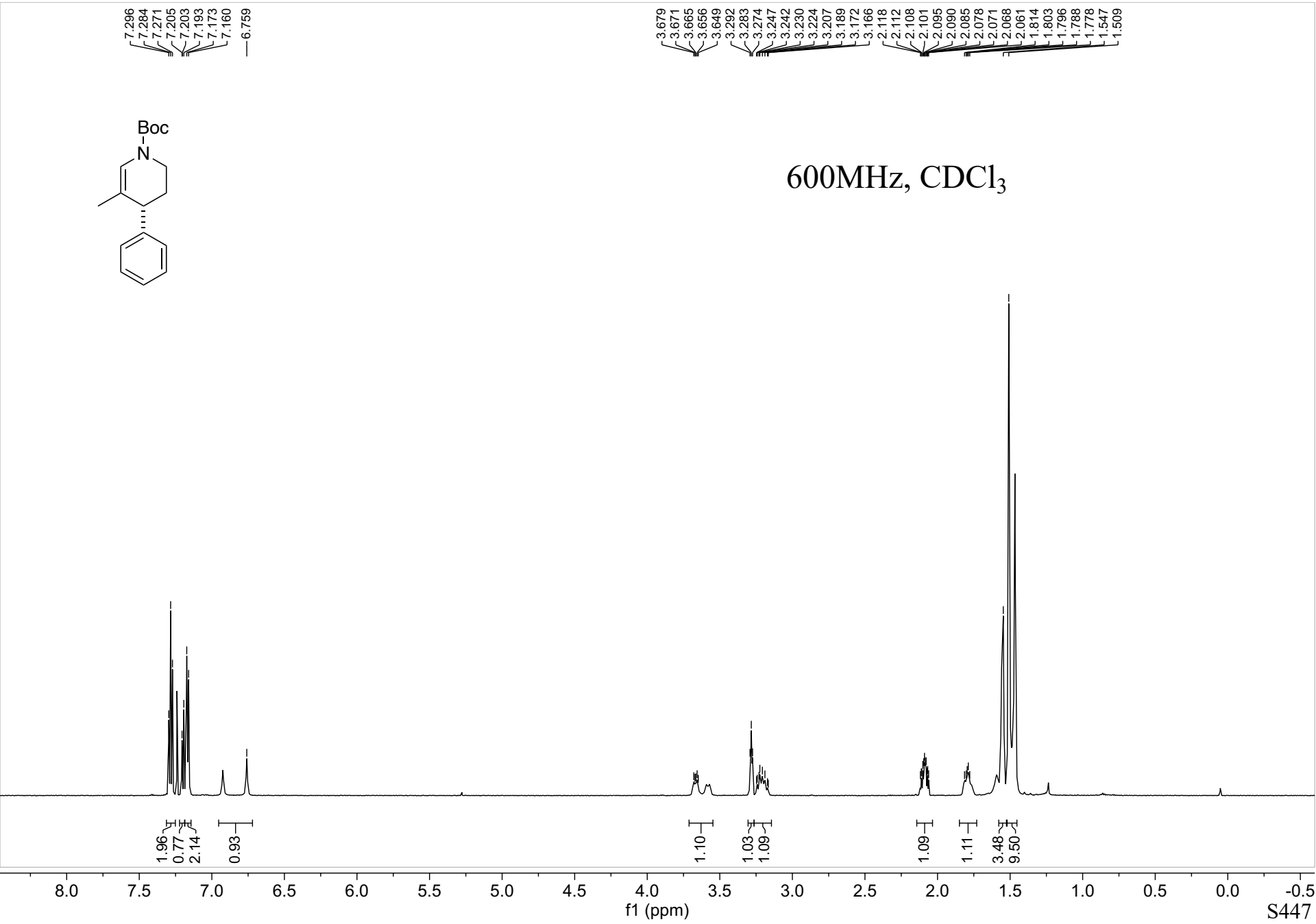



Peak Table

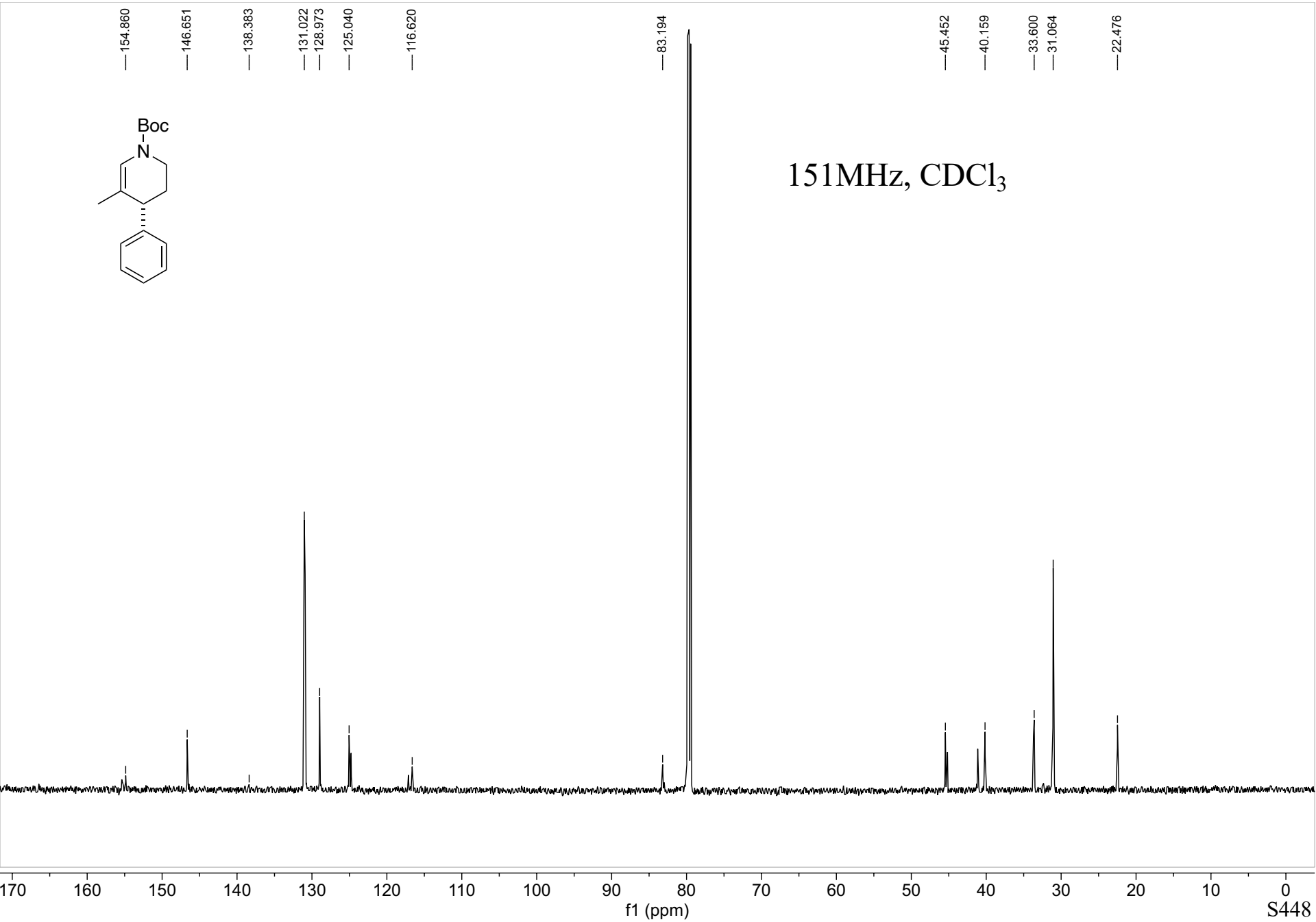
PDA Ch1 250nm

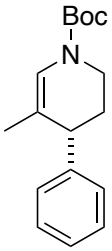
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 5.790 | 97.105 |
| 2 | 6.411 | 2.895 |
| Total | | 100.000 |

# $^1$H NMR *tert*-butyl (*R*)-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2m)



# $^{13}$C NMR *tert*-butyl (*R*)-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2m)

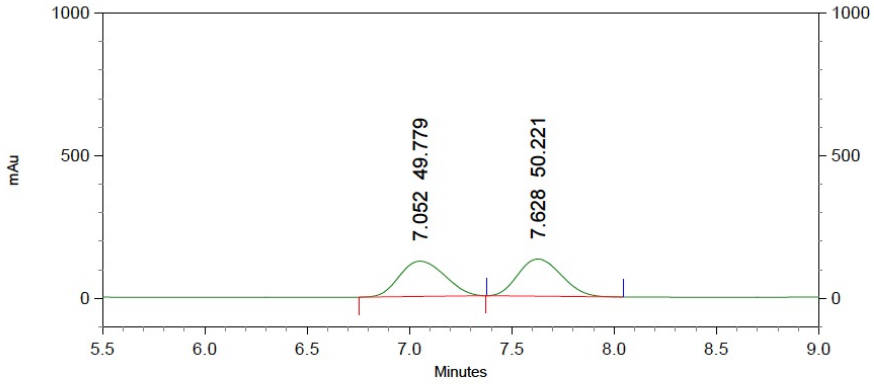


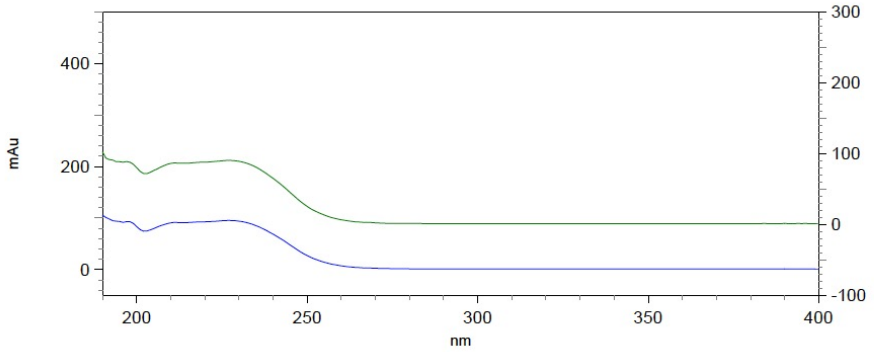



# HPLC

## *tert*-butyl (*R*)-5-methyl-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2m)

C:\EZStart\Projects\Default\Data\JJX-2415p-2%-IF-0.8ml
C:\Documents and Settings\zhang\Desktop\WCL\Method.met

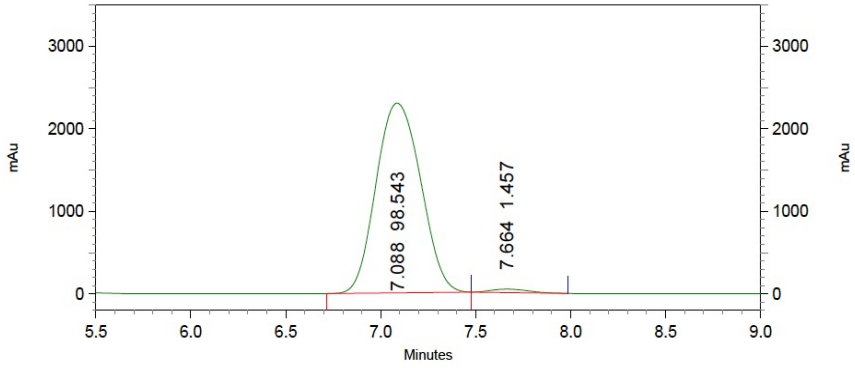


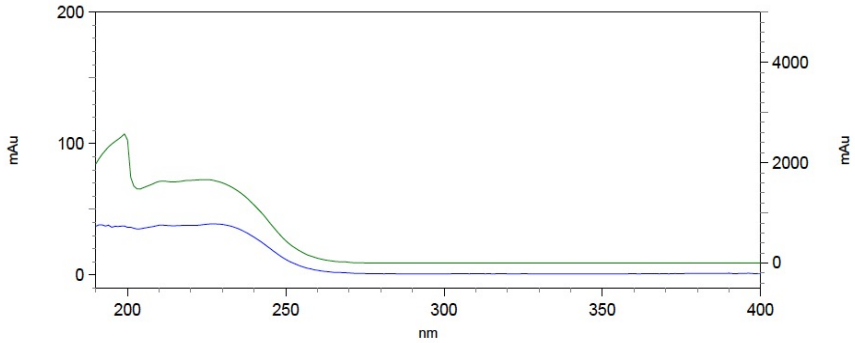




4: 240 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.052 | 49.779 |
| 2 | 7.628 | 50.221 |
| Totals | | 100.000 |

C:\EZStart\Projects\Default\Data\JJX-2386P-IF-2%-0.8ML-35MesitylTao
C:\Documents and Settings\zhang\Desktop\WCL\Method.met

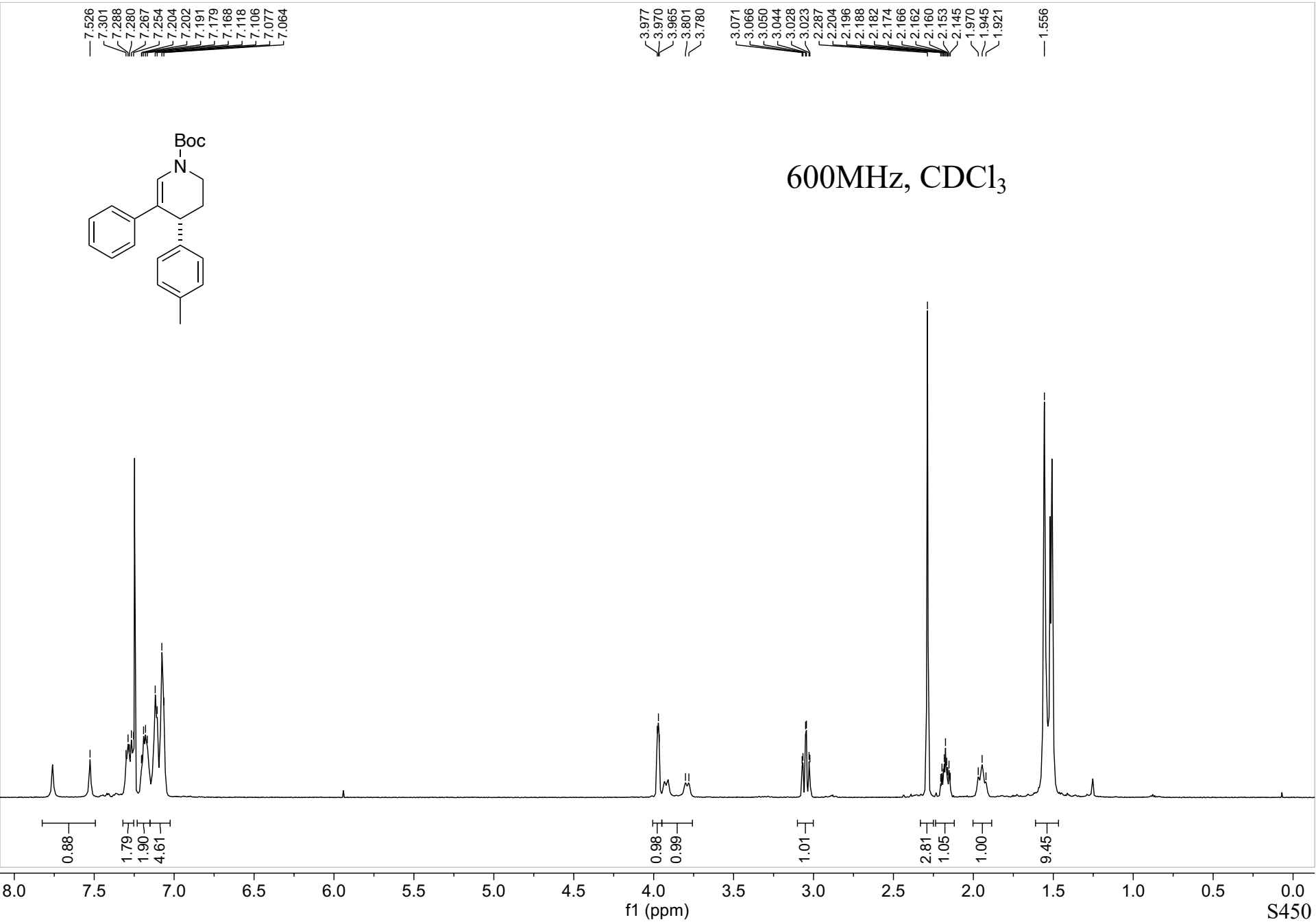


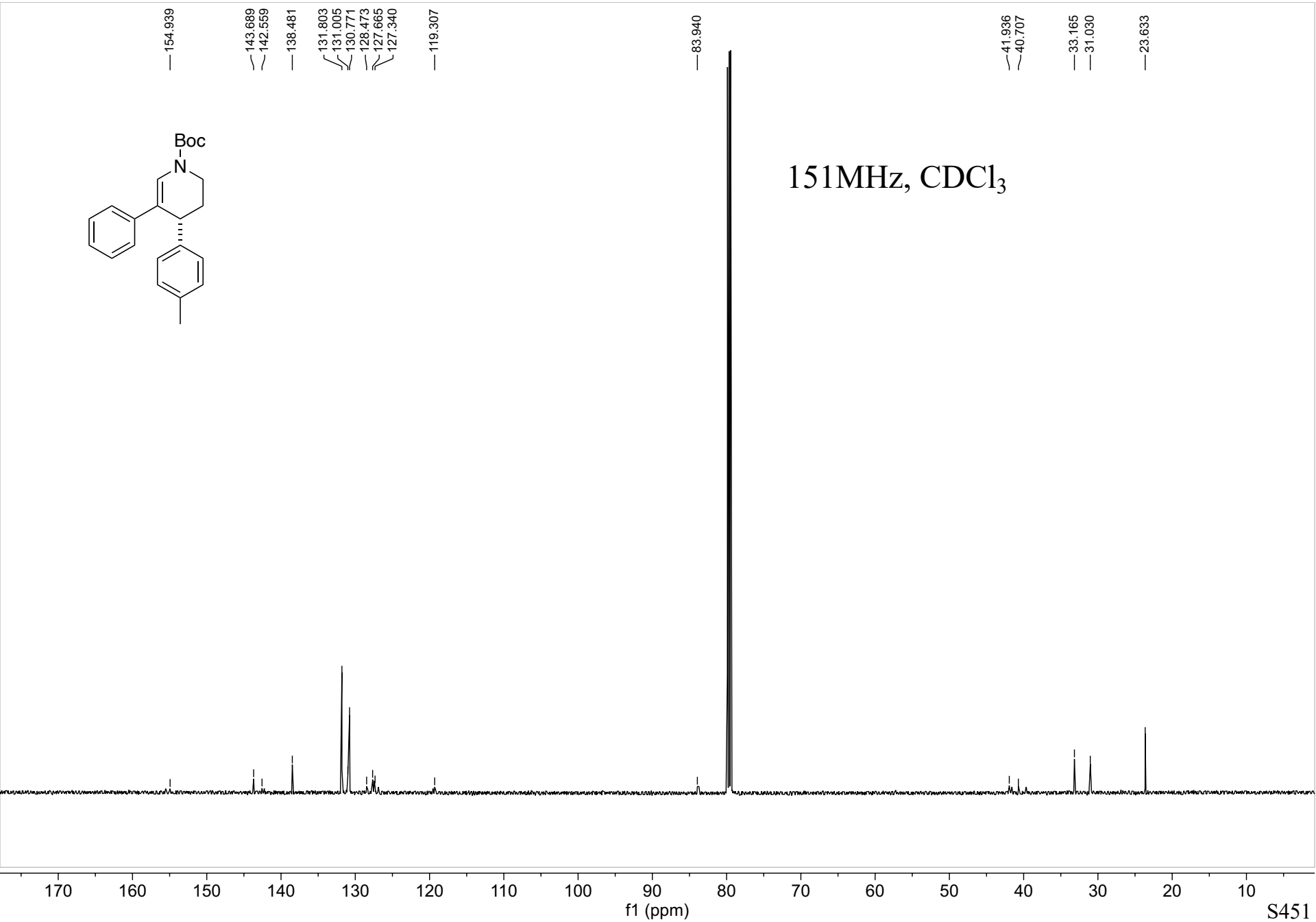

4: 240 nm, 4
nm Results

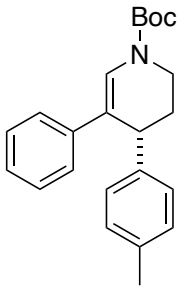
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.088 | 98.543 |
| 2 | 7.664 | 1.457 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-butyl (*R*)-5-phenyl-4-(*p*-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2n)



# $^{13}$C NMR *tert*-butyl (*R*)-5-phenyl-4-(*p*-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2n)

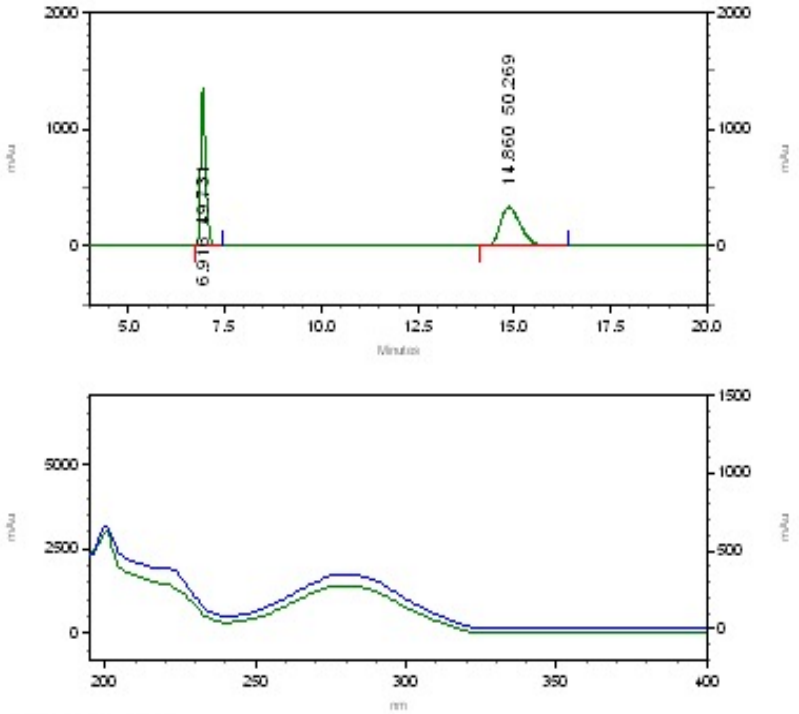





# HPLC

## *tert*-butyl (*R*)-5-phenyl-4-(*p*-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2n)

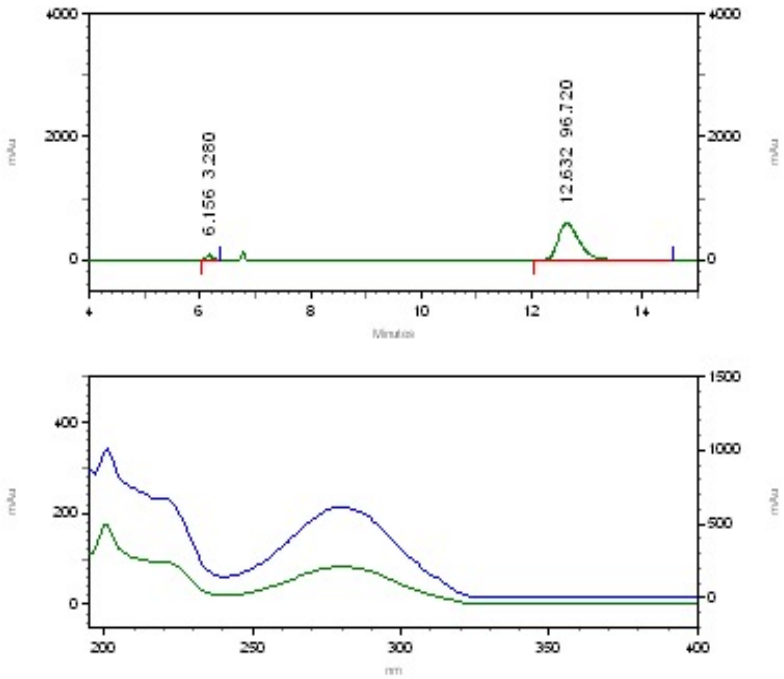
D:\HPLC\JJX-2607-2%-IB-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 285 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.916 | 49.731 |
| 2 | 14.860 | 50.269 |
| Totals | | 100.000 |

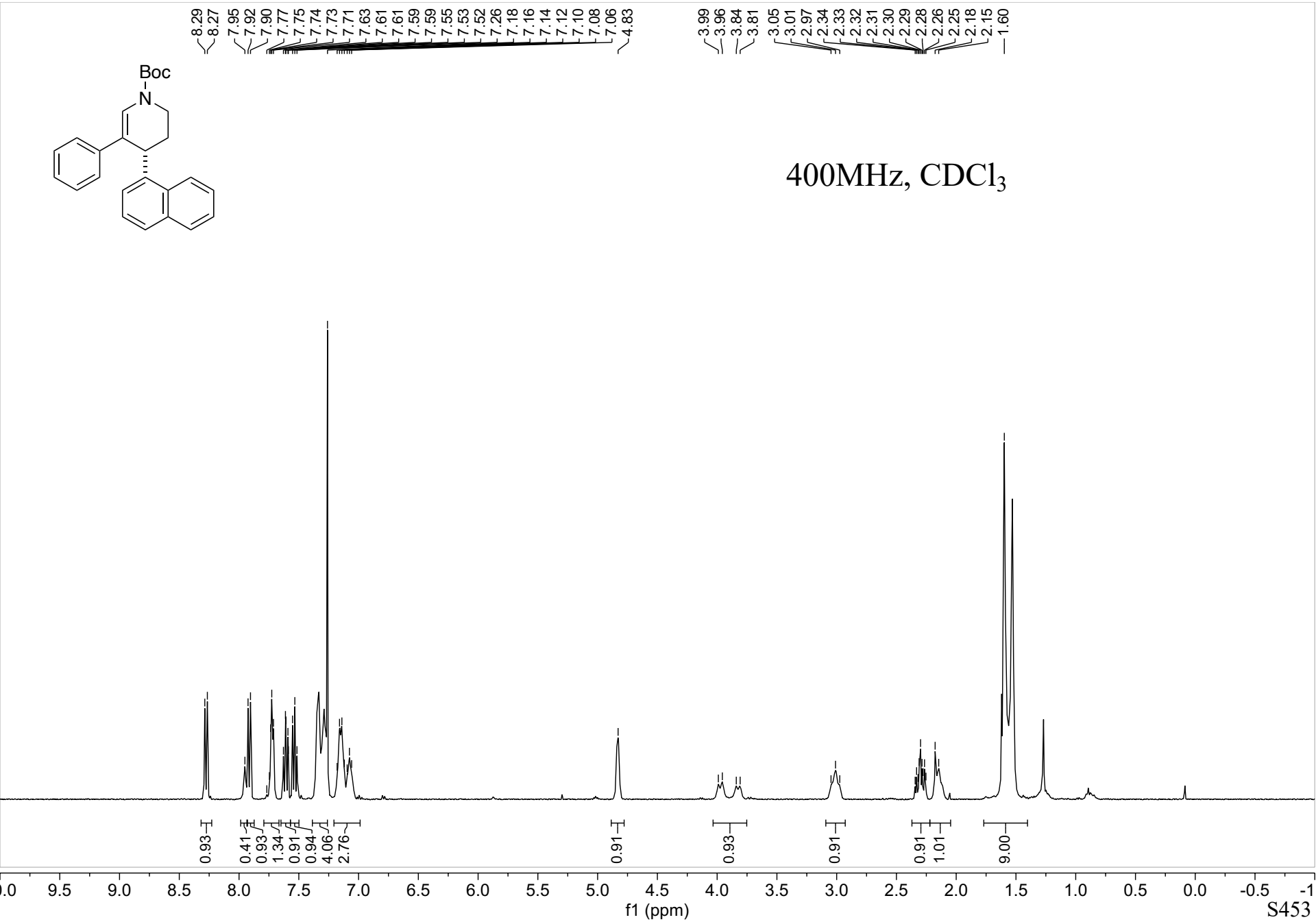
D:\HPLC\JJX-2608-2%-IB-0.8ml-TAO
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



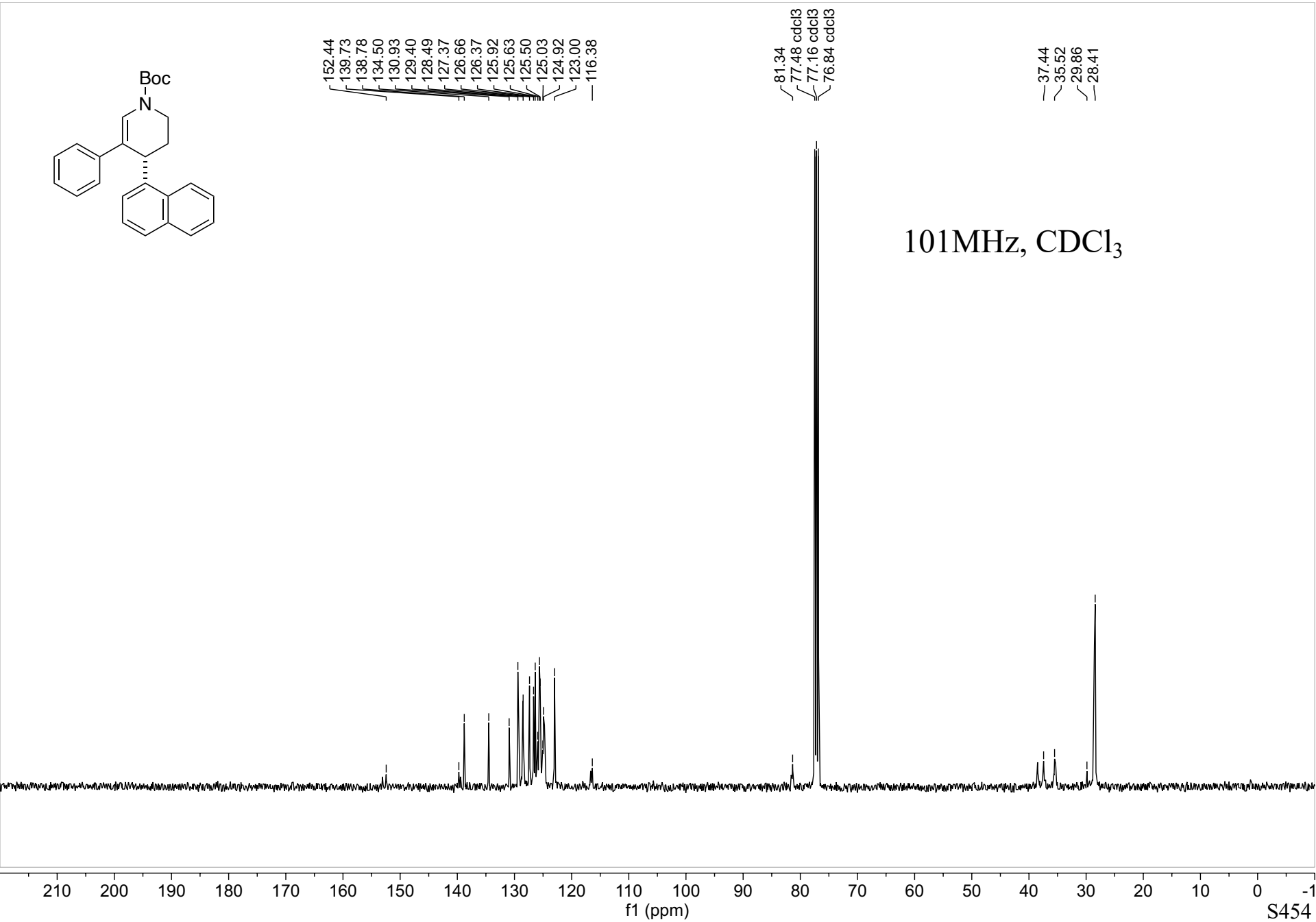

2: 285 nm, 4
nm Results

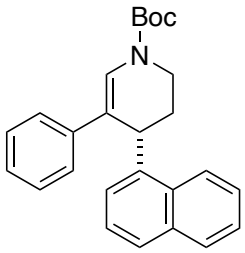
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.156 | 3.280 |
| 2 | 12.632 | 96.720 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-butyl (*R*)-4-(naphthalen-1-yl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2o)



# $^{13}$C NMR *tert*-butyl (*R*)-4-(naphthalen-1-yl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2o)

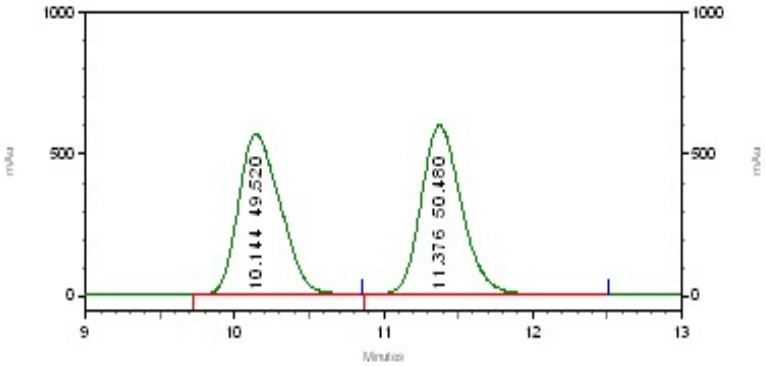


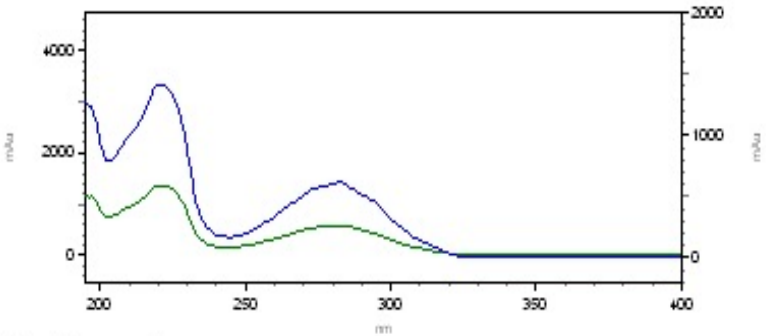



# HPLC

## *tert*-butyl (*R*)-4-(naphthalen-1-yl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2o)

D:\HPLC\JJX-2685-2*-IF-0.8ml-ibu-2
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

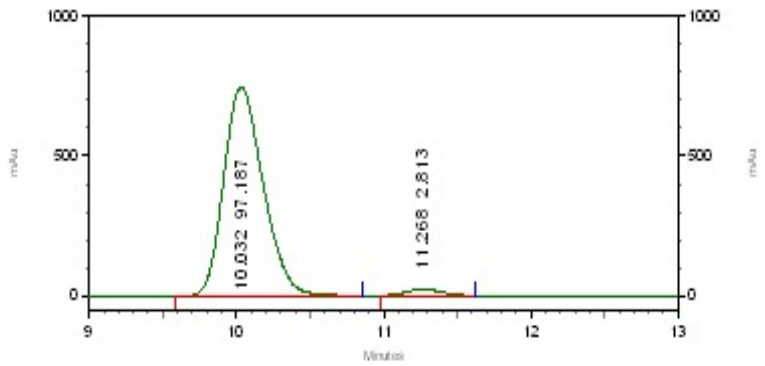


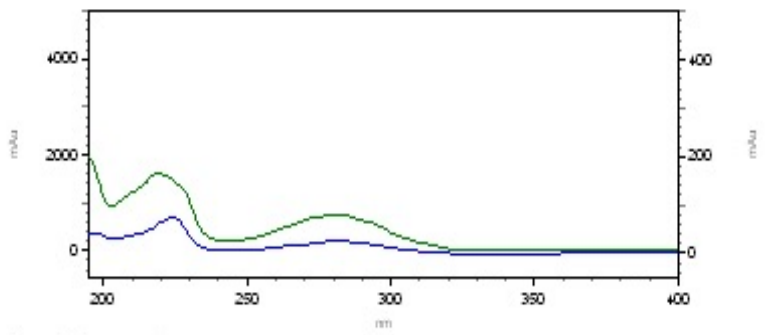




2: 280 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.144 | 49.520 |
| 2 | 11.376 | 50.480 |
| Totals | | 100.000 |

D:\HPLC\JJX-2685-2*-IF-0.8ml-tao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

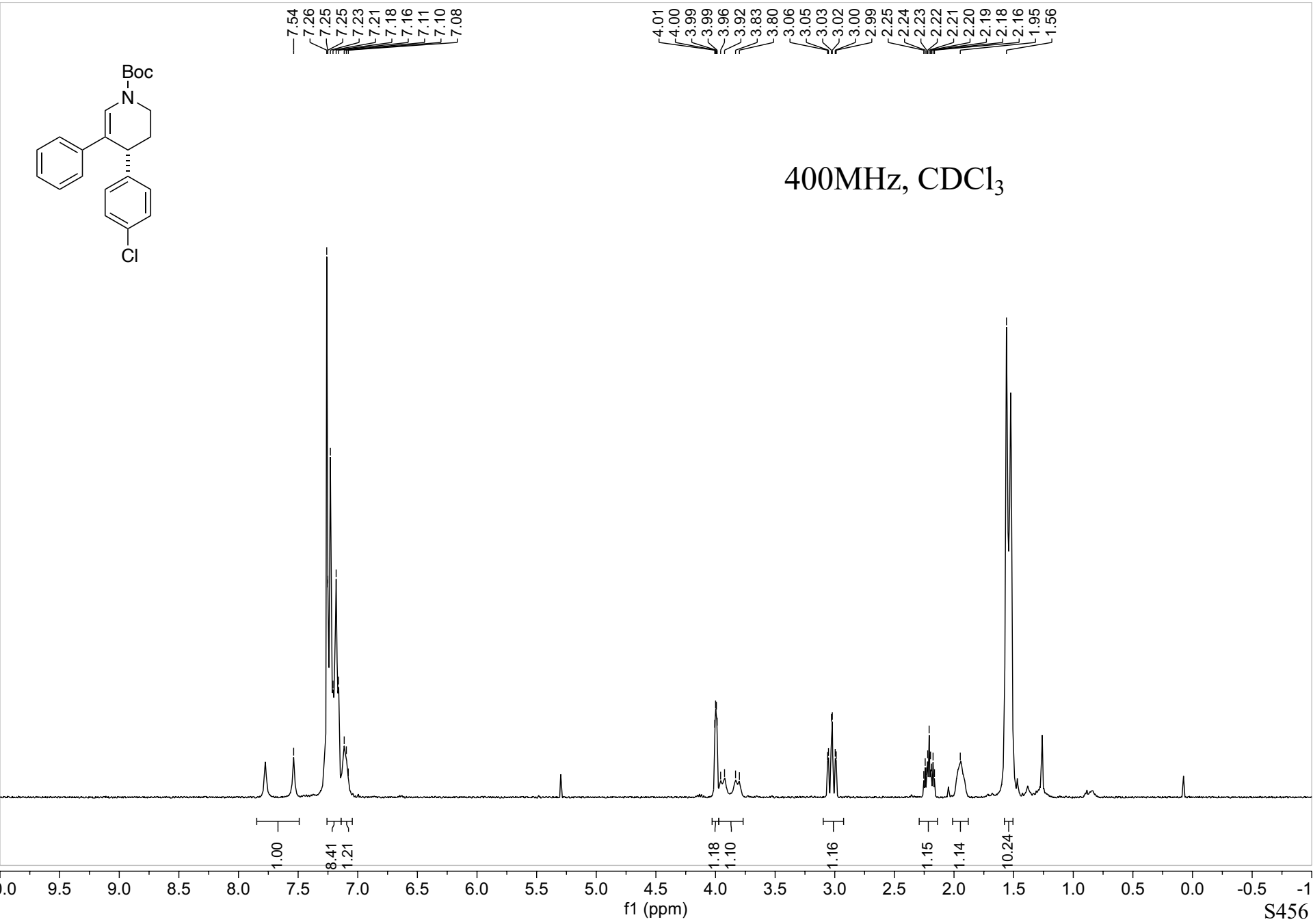


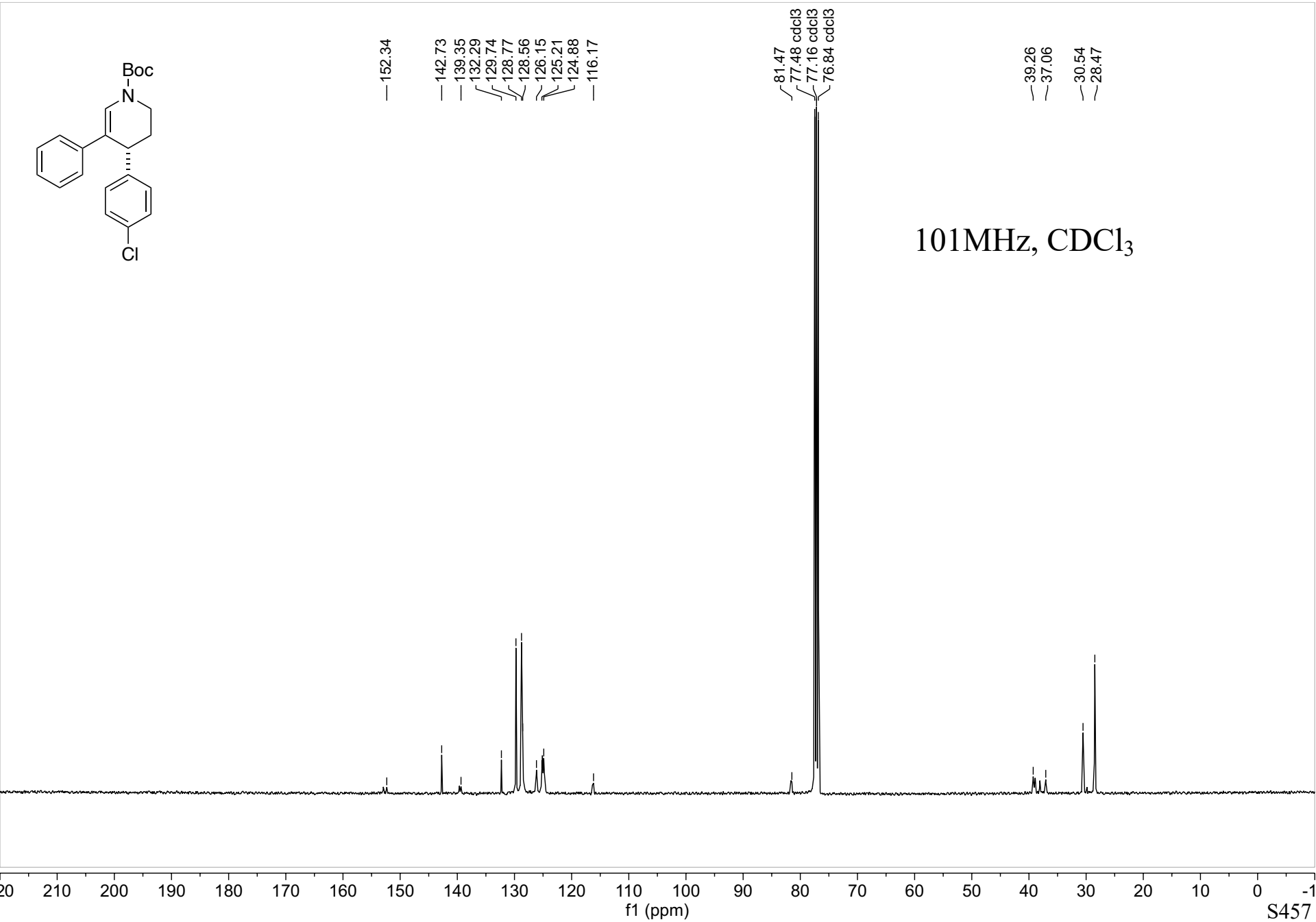

2: 280 nm, 4
nm Results

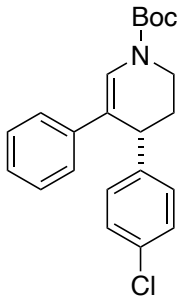
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.032 | 97.187 |
| 2 | 11.268 | 2.813 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-Butyl (*R*)-4-(4-chlorophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2p)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-(4-chlorophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2p)

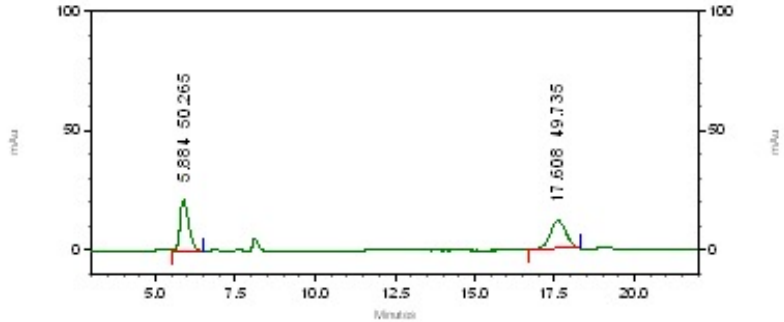


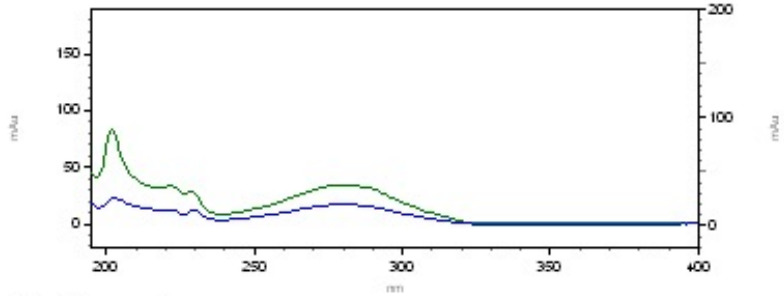



# HPLC

## *tert*-Butyl (*R*)-4-(4-chlorophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2p)

D:\HPLC\JJX-2576-2*-IB-0.8ml-ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

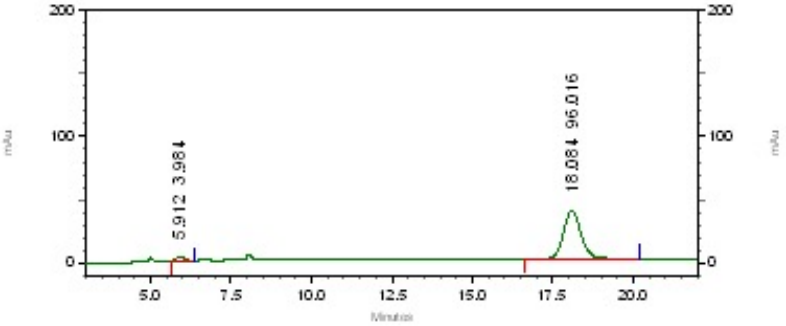


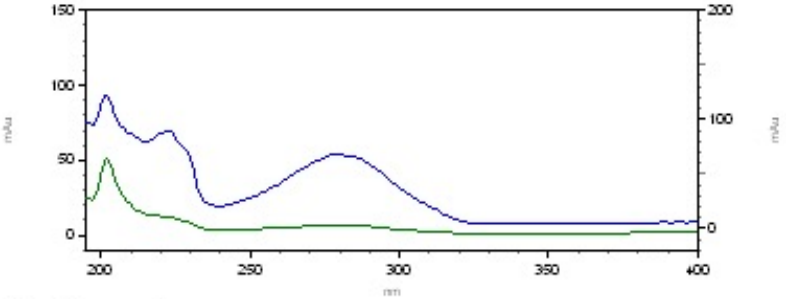




2: 260 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.884 | 50.265 |
| 2 | 17.608 | 49.735 |
| Totals | | 100.000 |

D:\HPLC\JJX-2577-2*-IB-0.8ml-tao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

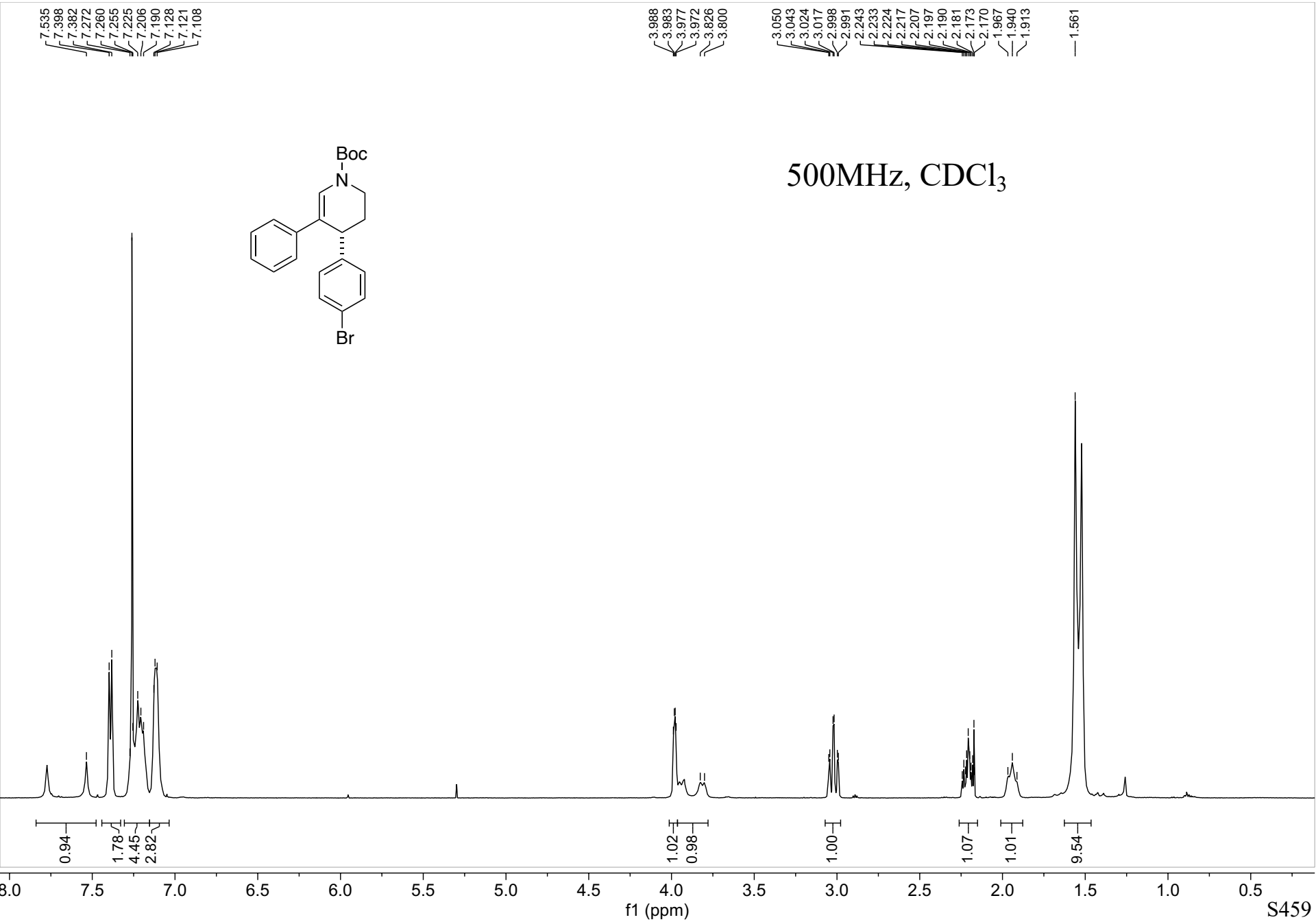


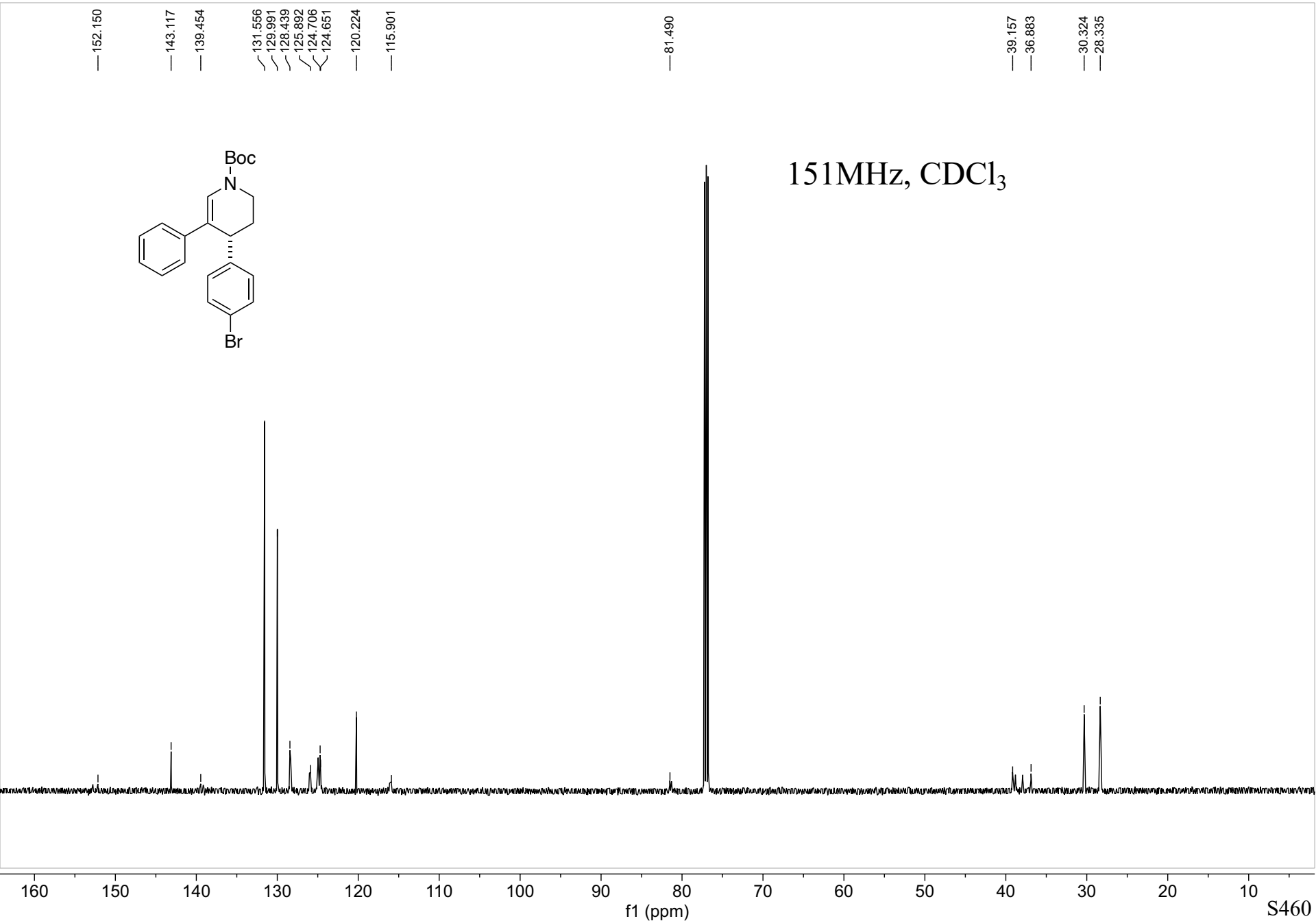

2: 260 nm, 4
nm Results

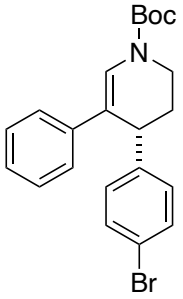
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.912 | 3.984 |
| 2 | 18.084 | 96.016 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-butyl (*R*)-4-(4-bromophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2q)



# $^{13}$C NMR *tert*-butyl (*R*)-4-(4-bromophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2q)

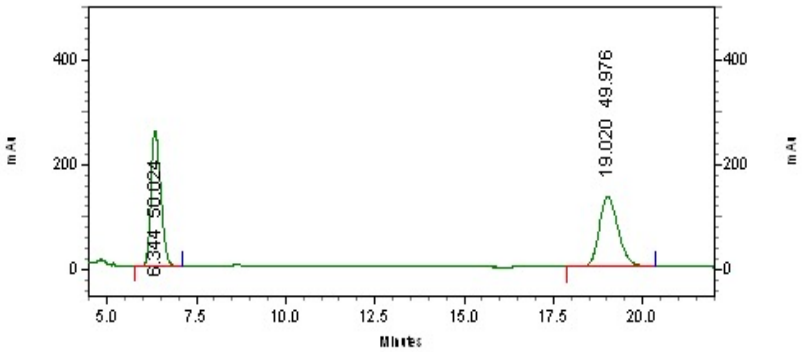


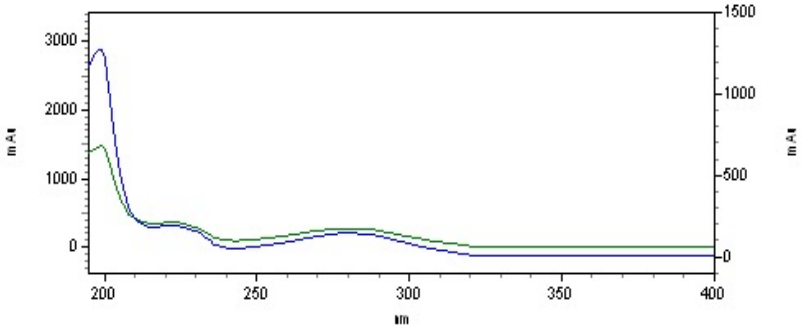



# HPLC

## *tert*-butyl (*R*)-4-(4-bromophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2q)

C:\Documents and Settings\zhang\Desktop\JJX\Jingjing HPLC\JJX-2598-2%-IB-0.8ml-IBU
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

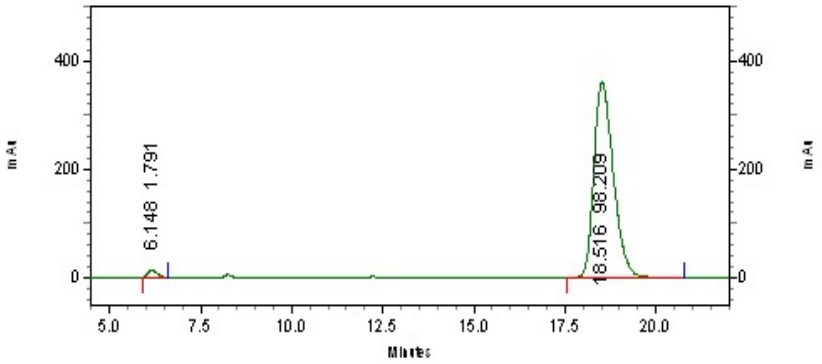


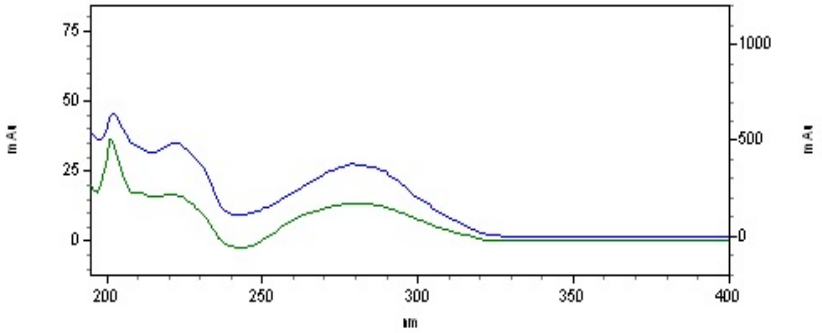




2: 285 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.344 | 50.024 |
| 2 | 19.020 | 49.976 |
| Totals | | 100.000 |

C:\Documents and Settings\zhang\Desktop\JJX\Jingjing HPLC\JJX-2598-2%-IB-0.8ml-TAO
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

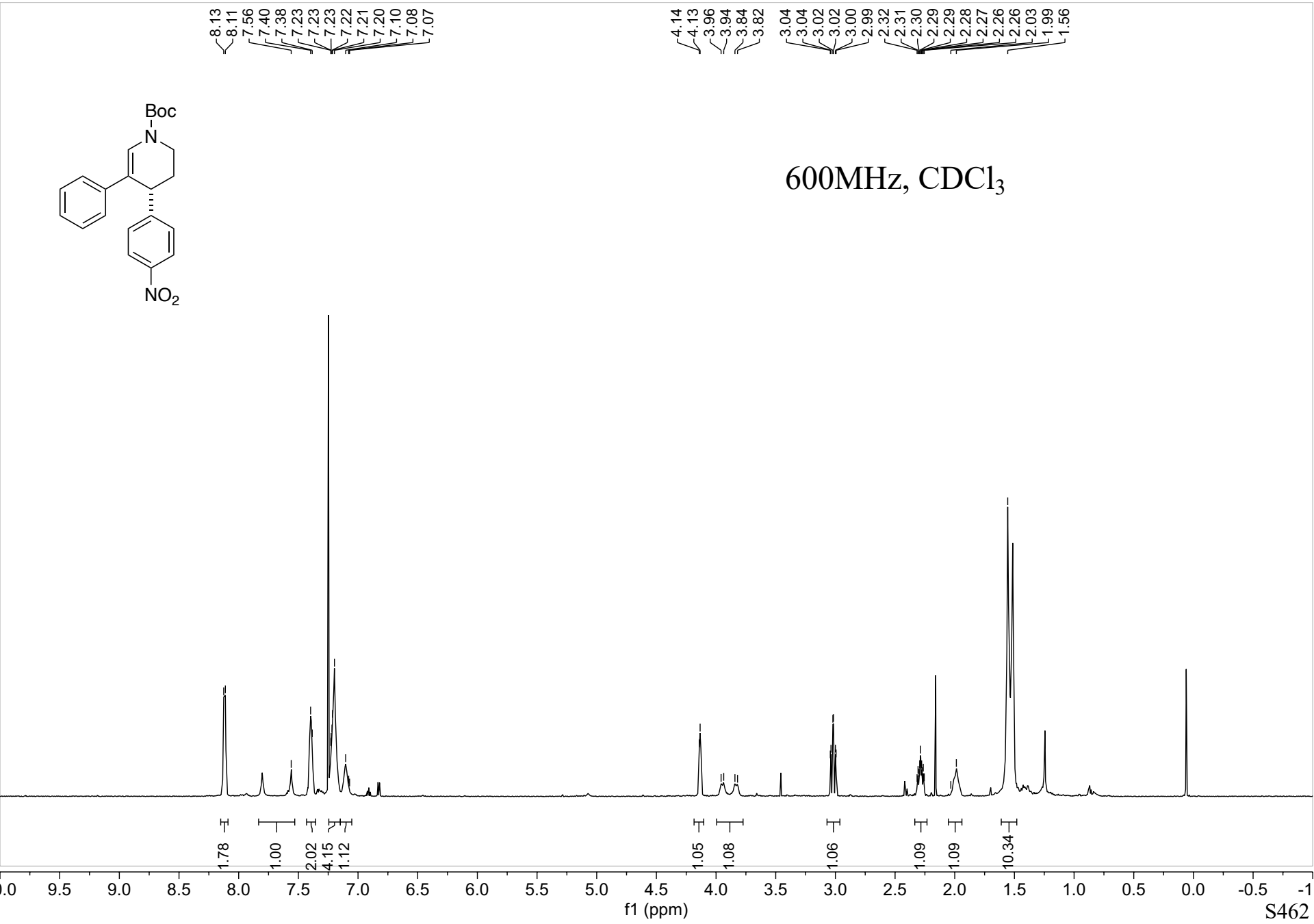


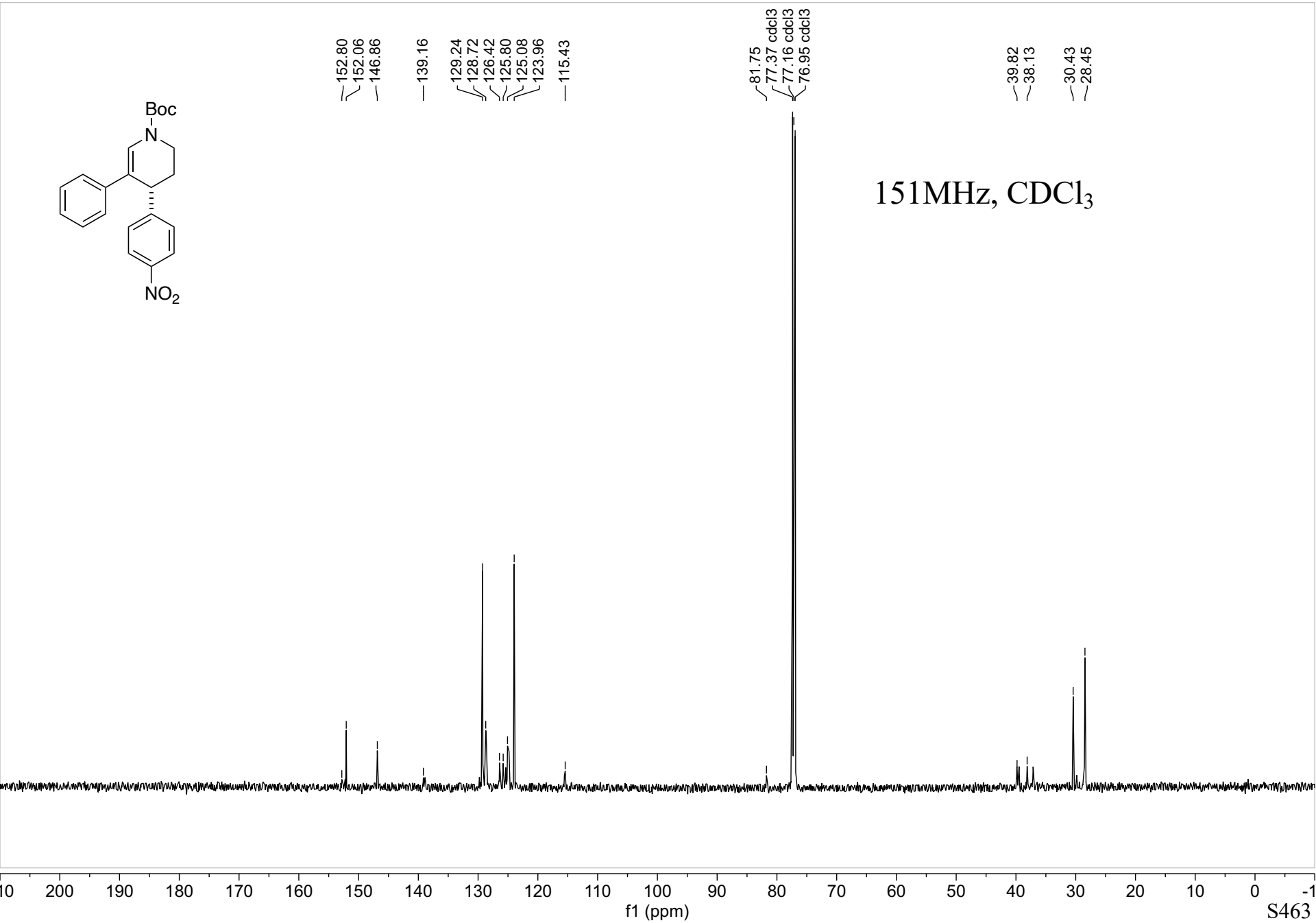

2: 285 nm, 4
nm Results

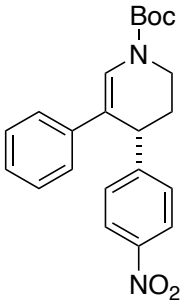
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.148 | 1.791 |
| 2 | 18.516 | 98.209 |
| Totals | | 100.000 |

# $^1$H NMR *tert*-Butyl (*R*)-4-(4-nitrophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2r)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-(4-nitrophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2r)

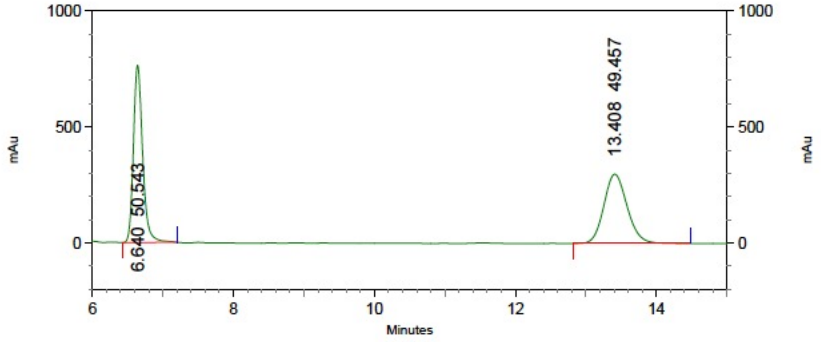


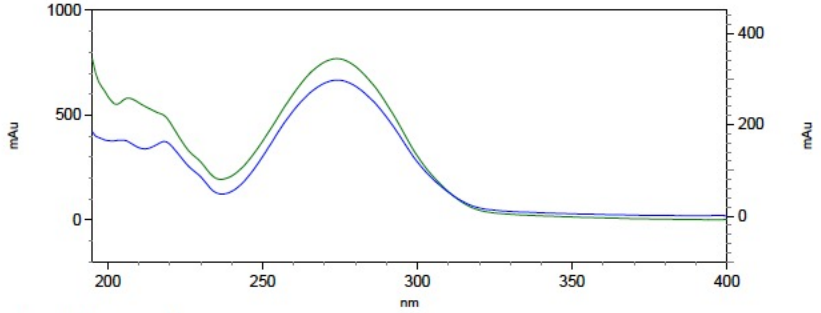



# HPLC

## $^{13}$C NMR *tert*-Butyl (*R*)-4-(4-nitrophenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2r)

C:\EZStart\Projects\Default\Data\JJX-2664-20%-IB-0.8ml-ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard0311.met



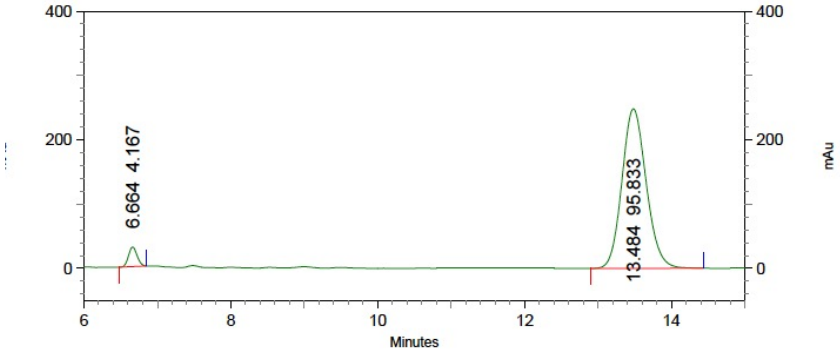



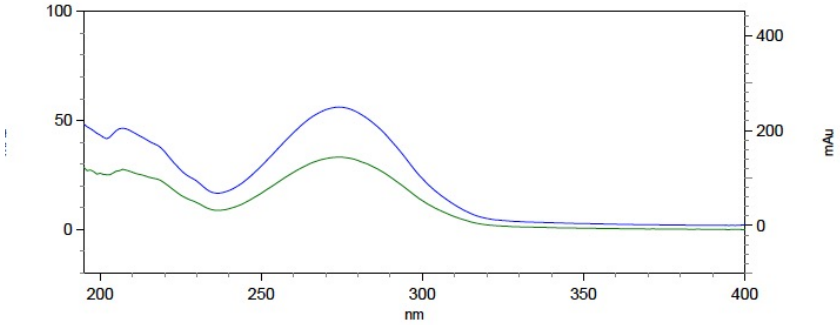

5: 275 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.640 | 50.543 |
| 2 | 13.408 | 49.457 |

| Totals | | |
|---|---|---|
| | | 100.000 |

C:\EZStart\Projects\Default\Data\JJX-2665-20%-IB-0.8ml-mesityltao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard0311.met



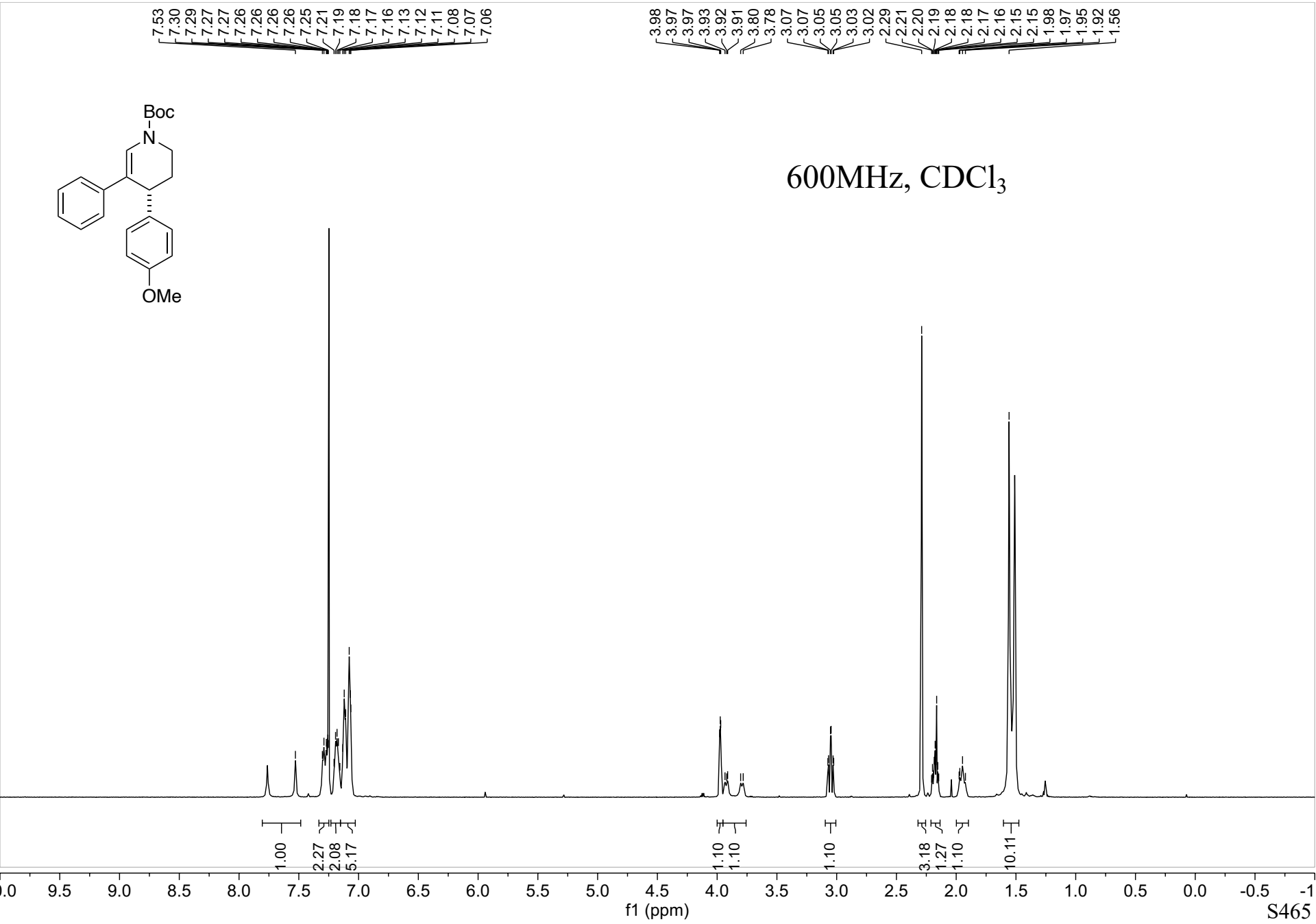




5: 275 nm, 4
nm Results

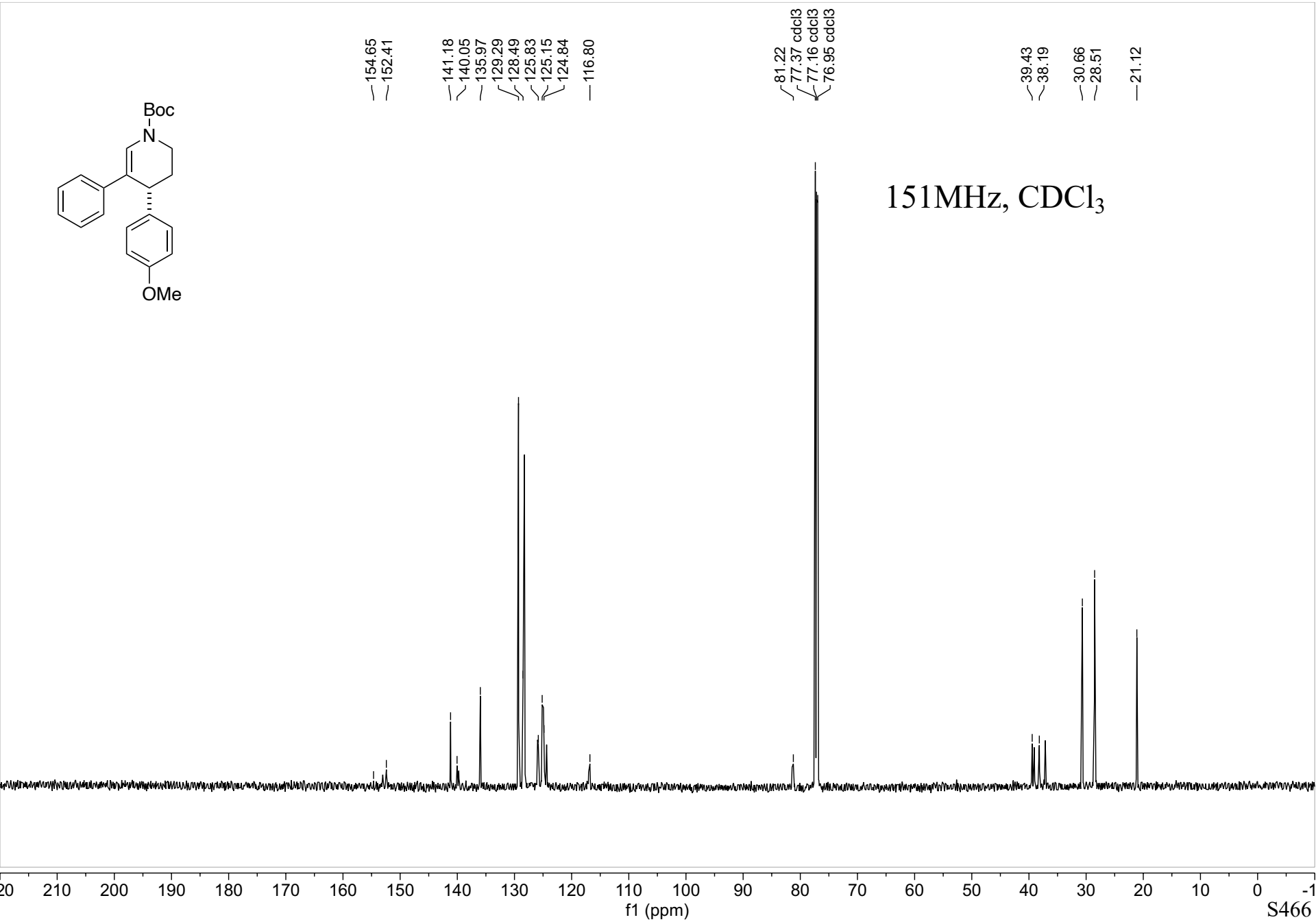
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 6.664 | 4.167 |
| 2 | 13.484 | 95.833 |

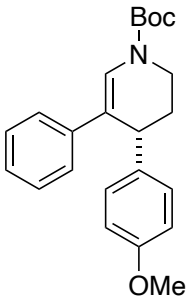
| Totals | | |
|---|---|---|
| | | 100.000 |

# $^1$H NMR *tert*-Butyl (*R*)-4-(4-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2s)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-(4-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2s)

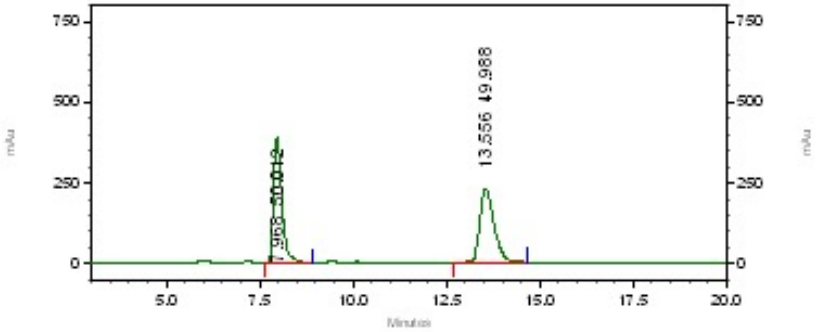


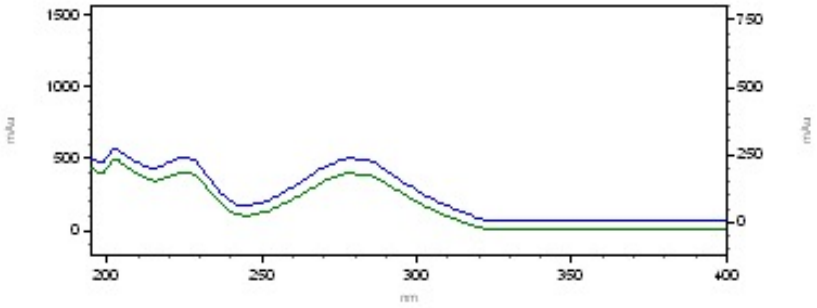



# HPLC

## *tert*-Butyl (*R*)-4-(4-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2s)

D:\HPLC\JJX-2691-2%-IB-0.8ml-ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

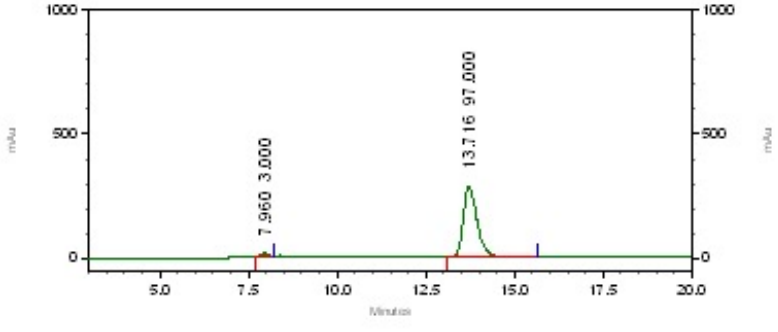


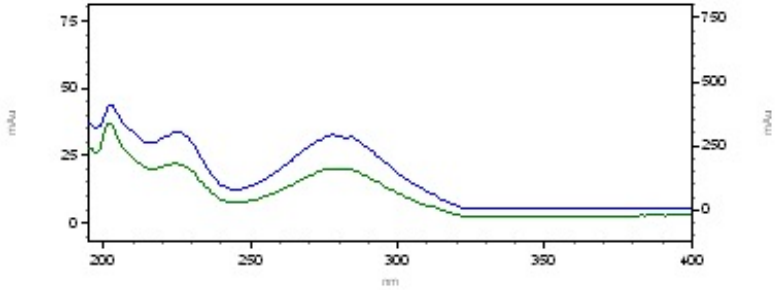




2: 280 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.968 | 50.012 |
| 2 | 13.556 | 49.988 |
| Totals | | 100.000 |

D:\HPLC\JJX-2692-2%-IB-0.8ml-tao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

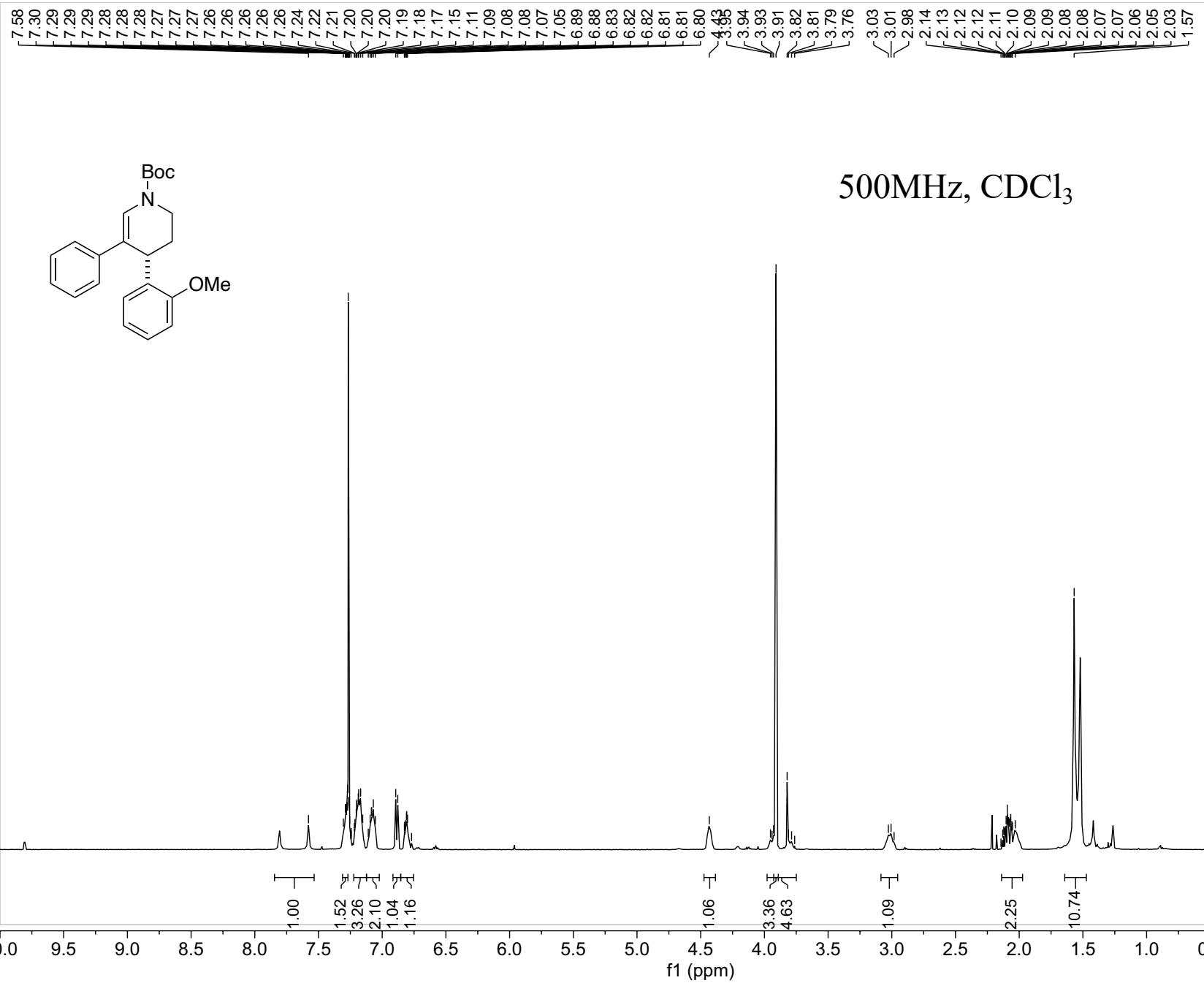


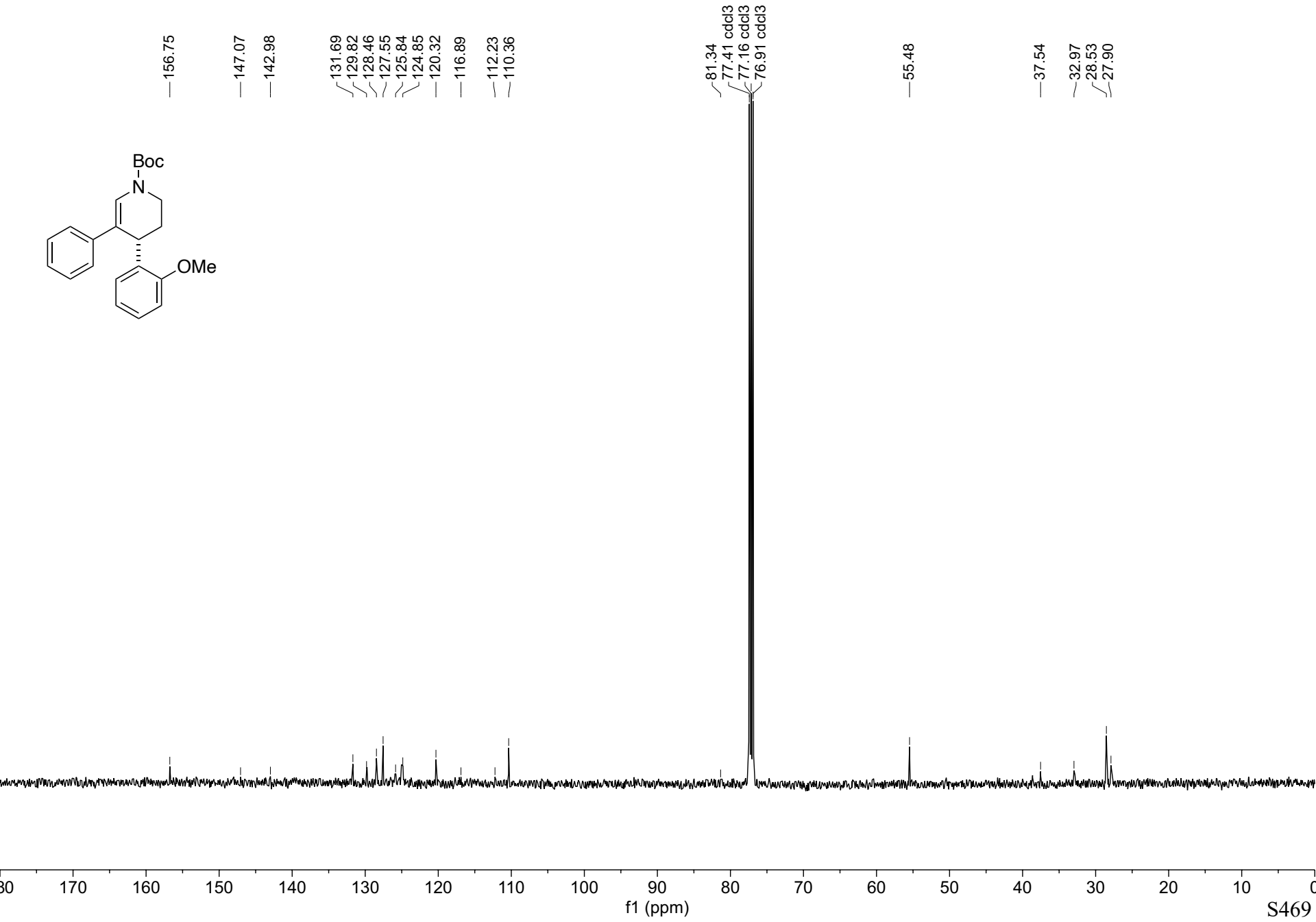

2: 280 nm, 4 nm Results

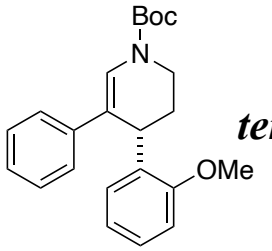
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.960 | 3.000 |
| 2 | 13.716 | 97.000 |
| Totals | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*R*)-4-(2-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2t)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-(2-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2t)

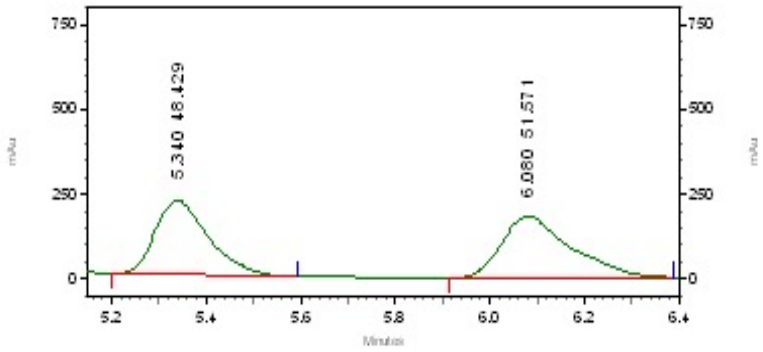


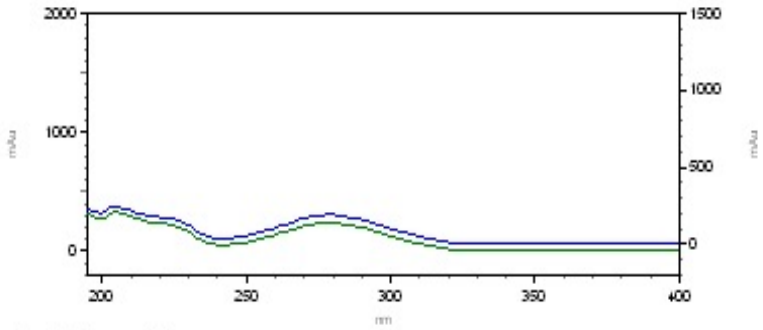



# HPLC

## *tert*-Butyl (*R*)-4-(2-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2t)

D:\HPLC\JJX-2662-5%-IB-0.8ml-ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

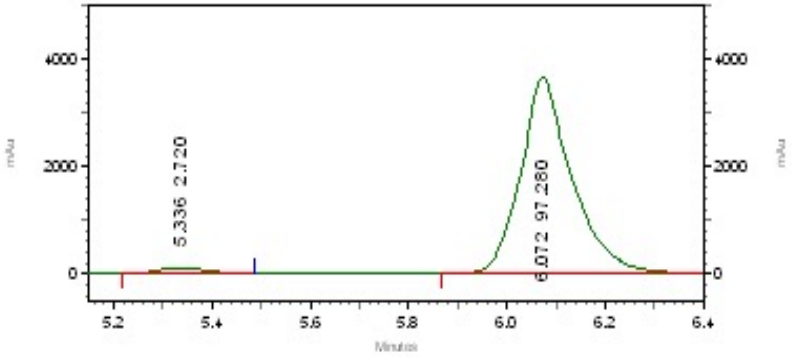


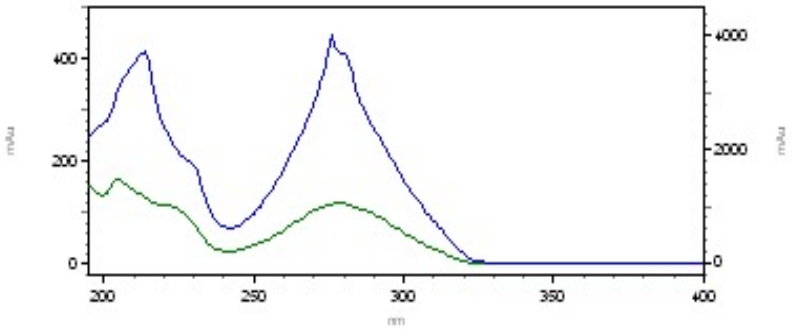




2: 275 nm, 4
nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.340 | 48.429 |
| 2 | 6.080 | 51.571 |
| Totals | | 100.000 |

D:\HPLC\JJX-2661-5%-IB-0.8ml-mesityltao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

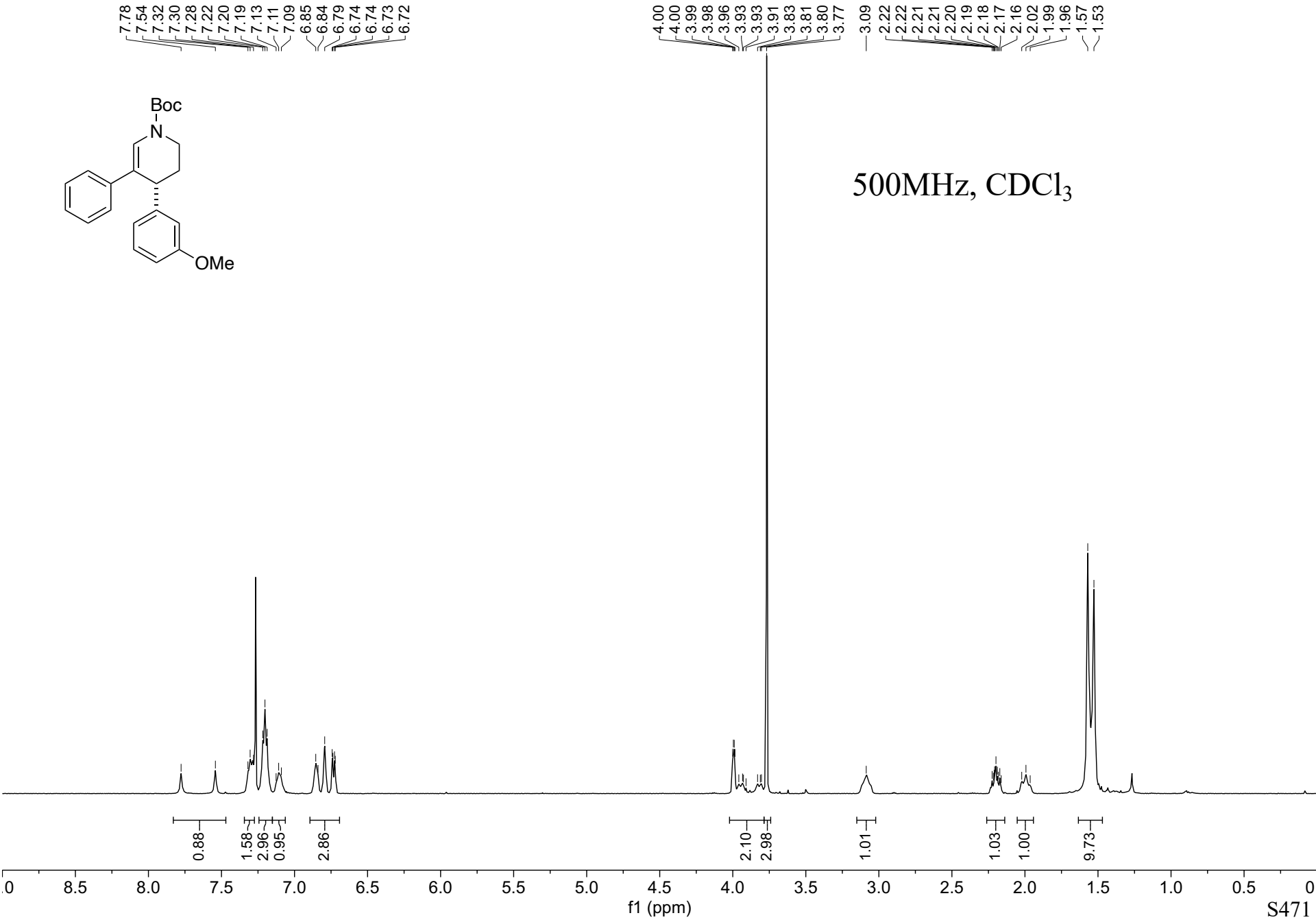


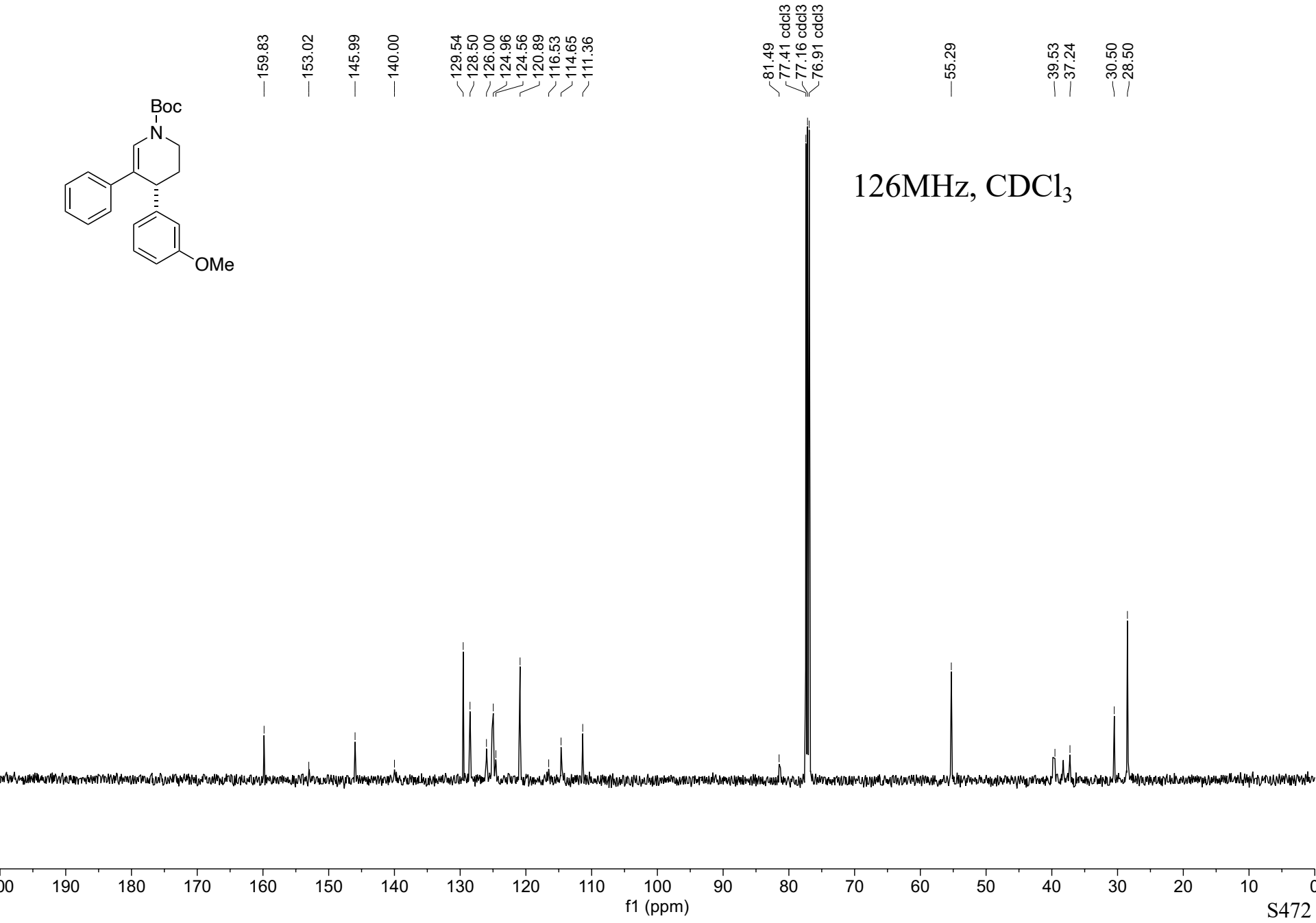

2: 275 nm, 4
nm Results

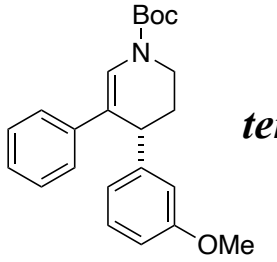
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 5.336 | 2.720 |
| 2 | 6.072 | 97.280 |
| Totals | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*R*)-4-(3-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2u)



# $^{13}$C NMR *tert*-Butyl (*R*)-4-(3-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2u)



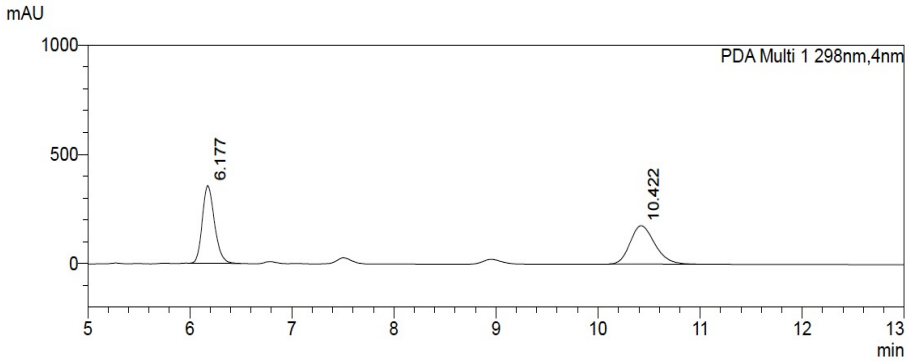



# HPLC

## *tert*-Butyl (*R*)-4-(3-methoxyphenyl)-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2u)

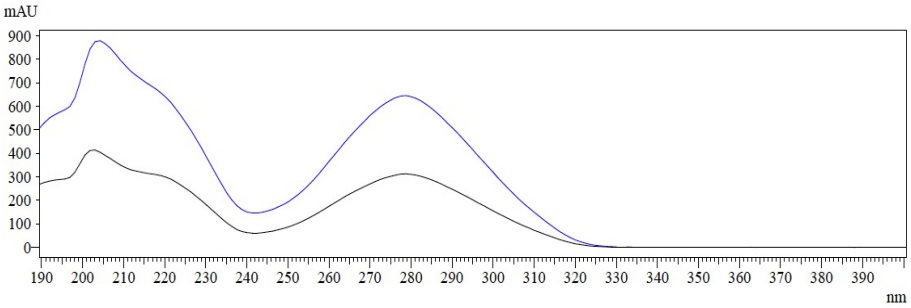
**==== Shimadzu LabSolutions Analysis Report ====**

JJX-3086IBU-IB-2%-0.8mL
JJX-2%-60min0.8mL.lcm




UV Spectrum

JJX-3086IBU-IB-2%-0.8mL_001.lcd



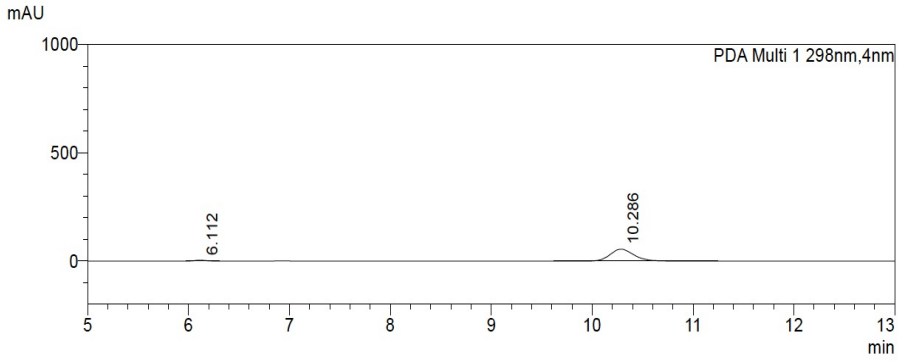

Peak Table

PDA Ch1 298nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.177 | 49.796 |
| 2 | 10.422 | 50.204 |
| Total | | 100.000 |

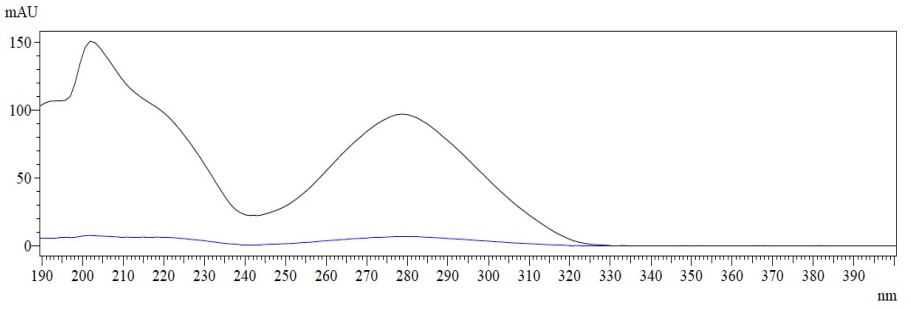
**==== Shimadzu LabSolutions Analysis Report ====**

JJX-3087-IBU-IB-2%-0.8mL
JJX-2%-60min0.8mL.lcm




UV Spectrum

JJX-3087-IBU-IB-2%-0.8mL_001.lcd

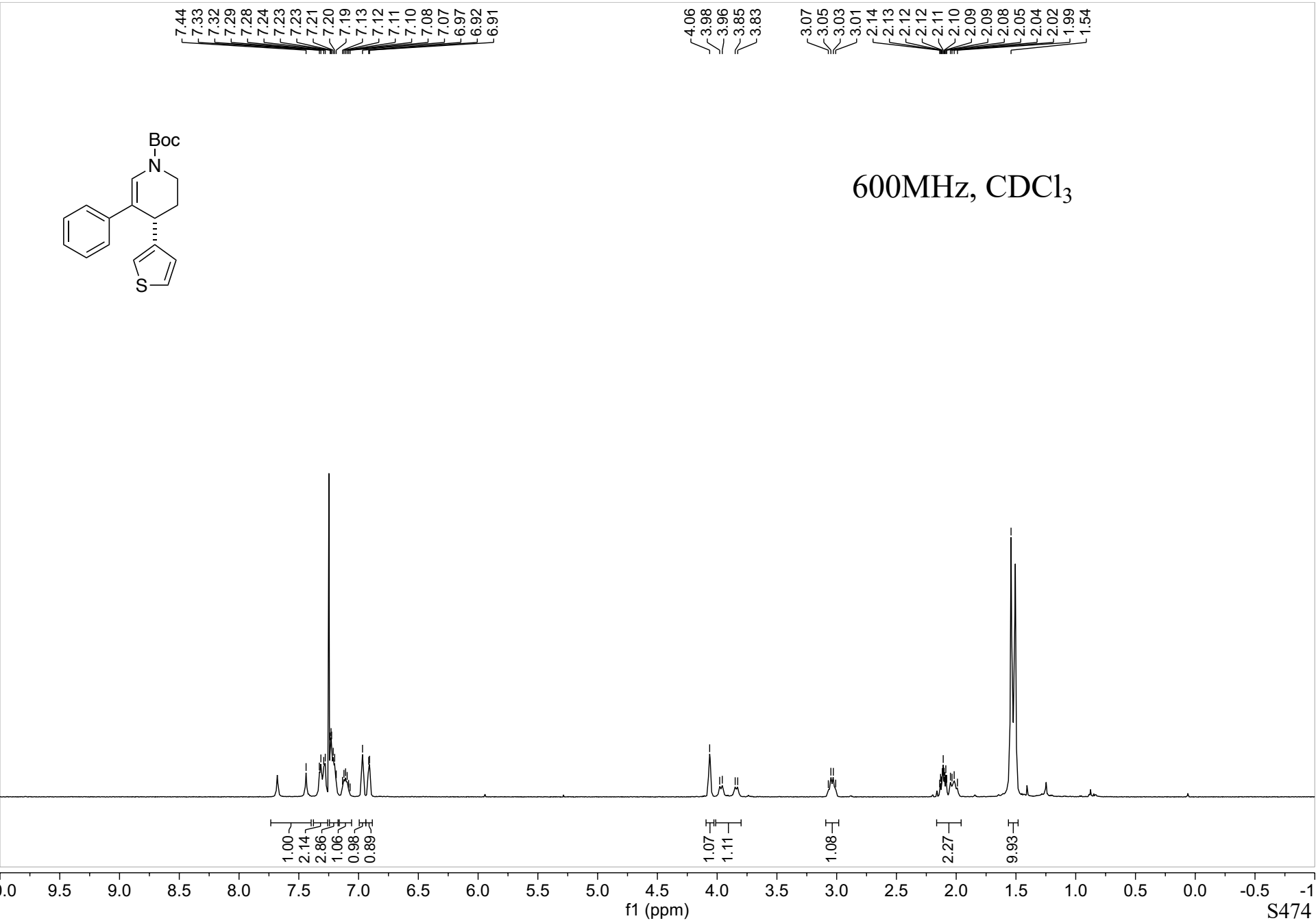



Peak Table

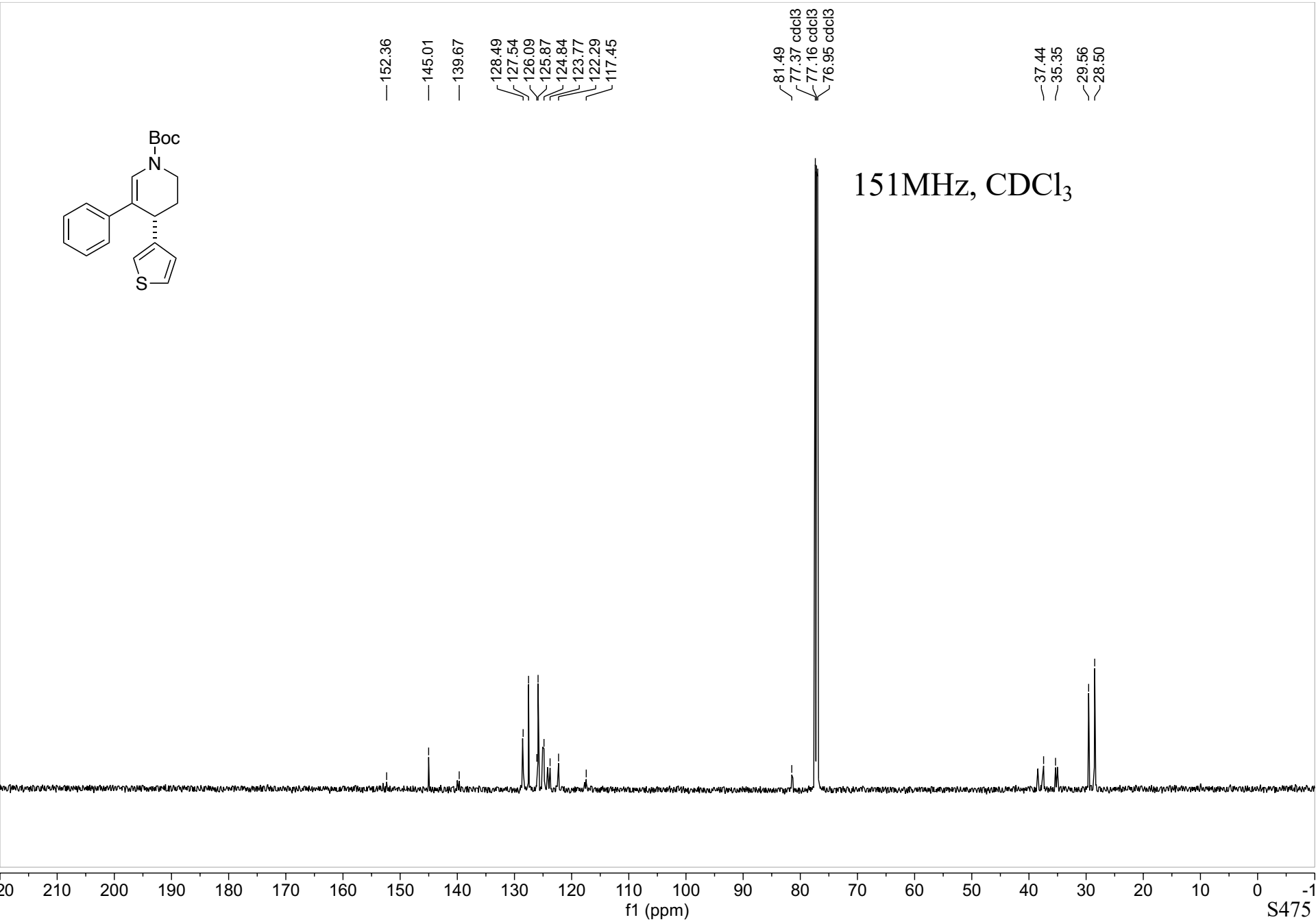
PDA Ch1 298nm

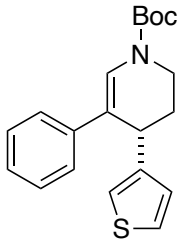
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.112 | 3.412 |
| 2 | 10.286 | 96.588 |
| Total | | 100.000 |

# $^1$H NMR *tert*-Butyl (*S*)-5-phenyl-4-(thiophen-3-yl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2v)



# $^{13}$C NMR *tert*-Butyl (*S*)-5-phenyl-4-(thiophen-3-yl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2v)



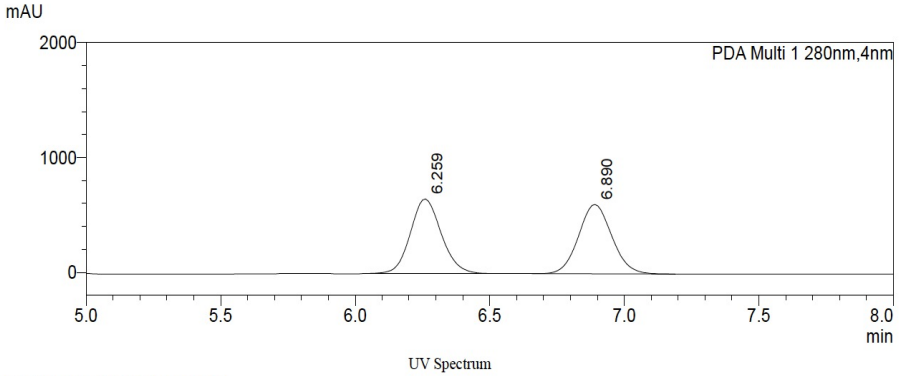



# HPLC

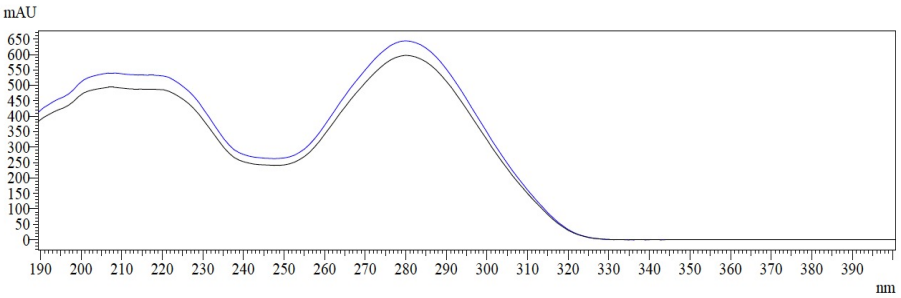
## *tert*-Butyl (*S*)-5-phenyl-4-(thiophen-3-yl)-3,4-dihydropyridine-1(2*H*)-carboxylate (2v)

**==== Shimadzu LabSolutions Analysis Report ====**

JJX-2897-IBU-IA-2%0.8mL
JJX-2%-60min0.8mL.lcm




UV Spectrum
JJX-2897-IBU-IA-2%0.8mL_001.lcd

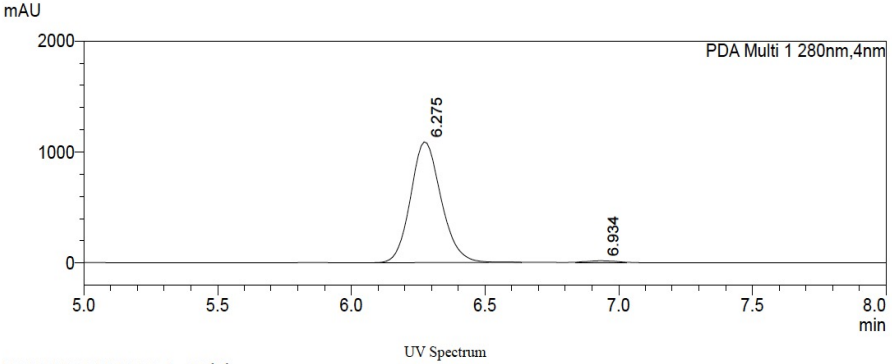



Peak Table
PDA Ch1 280nm

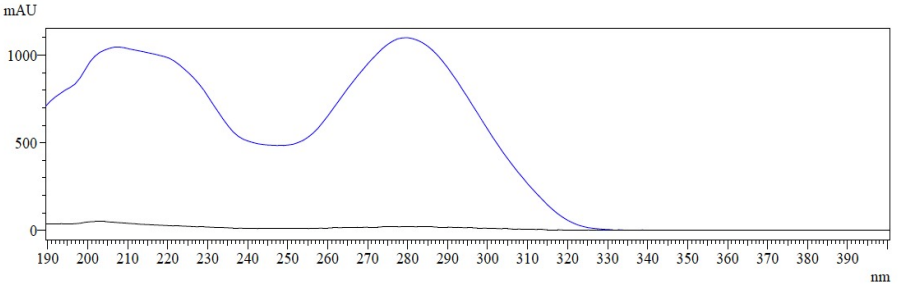
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.259 | 50.010 |
| 2 | 6.890 | 49.990 |
| Total | | 100.000 |

**==== Shimadzu LabSolutions Analysis Report ====**

JJX-2898-TAO-IA-2%0.8mL
JJX-2%-60min0.8mL.lcm



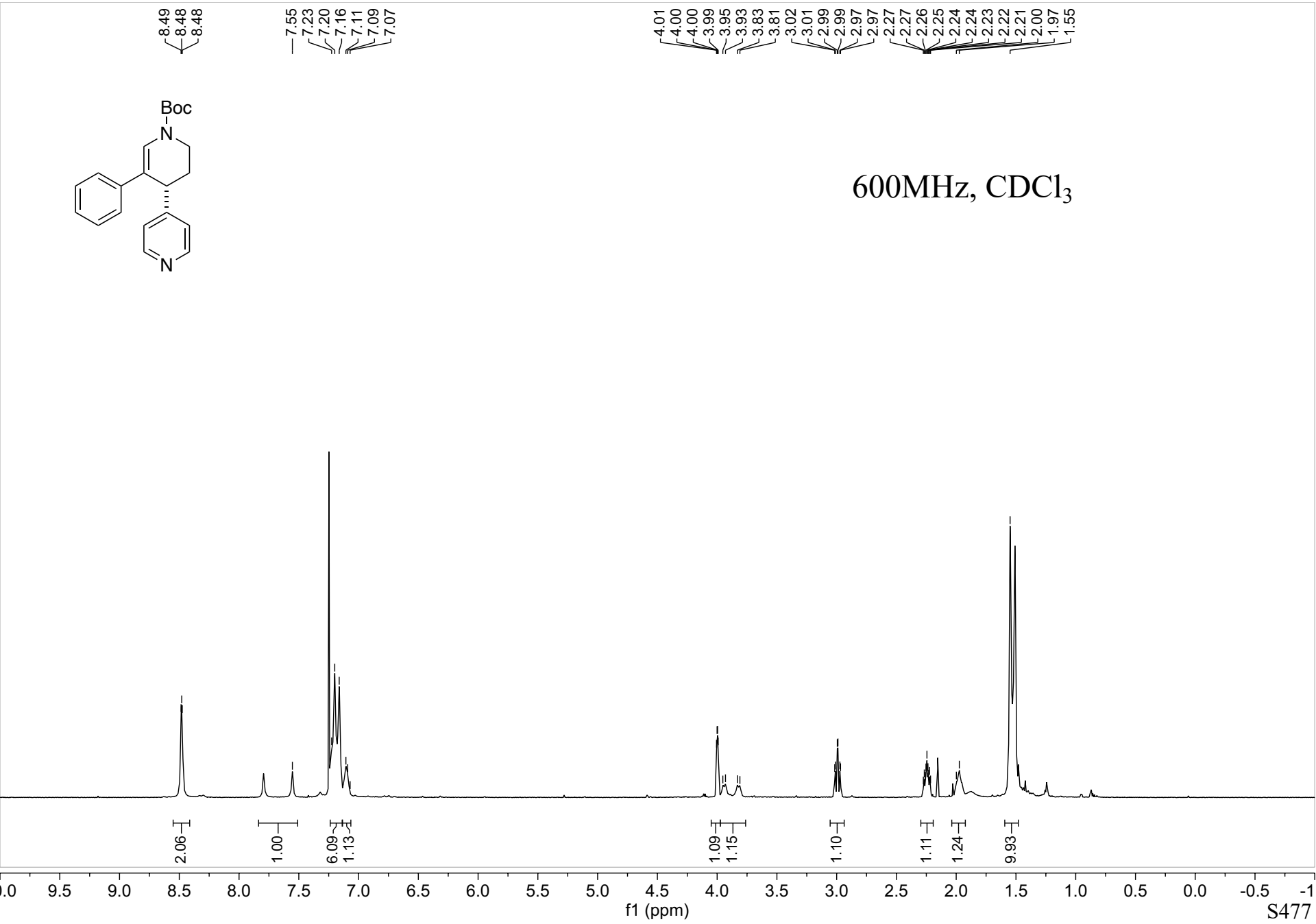

UV Spectrum
JJX-2898-TAO-IA-2%0.8mL_001.lcd



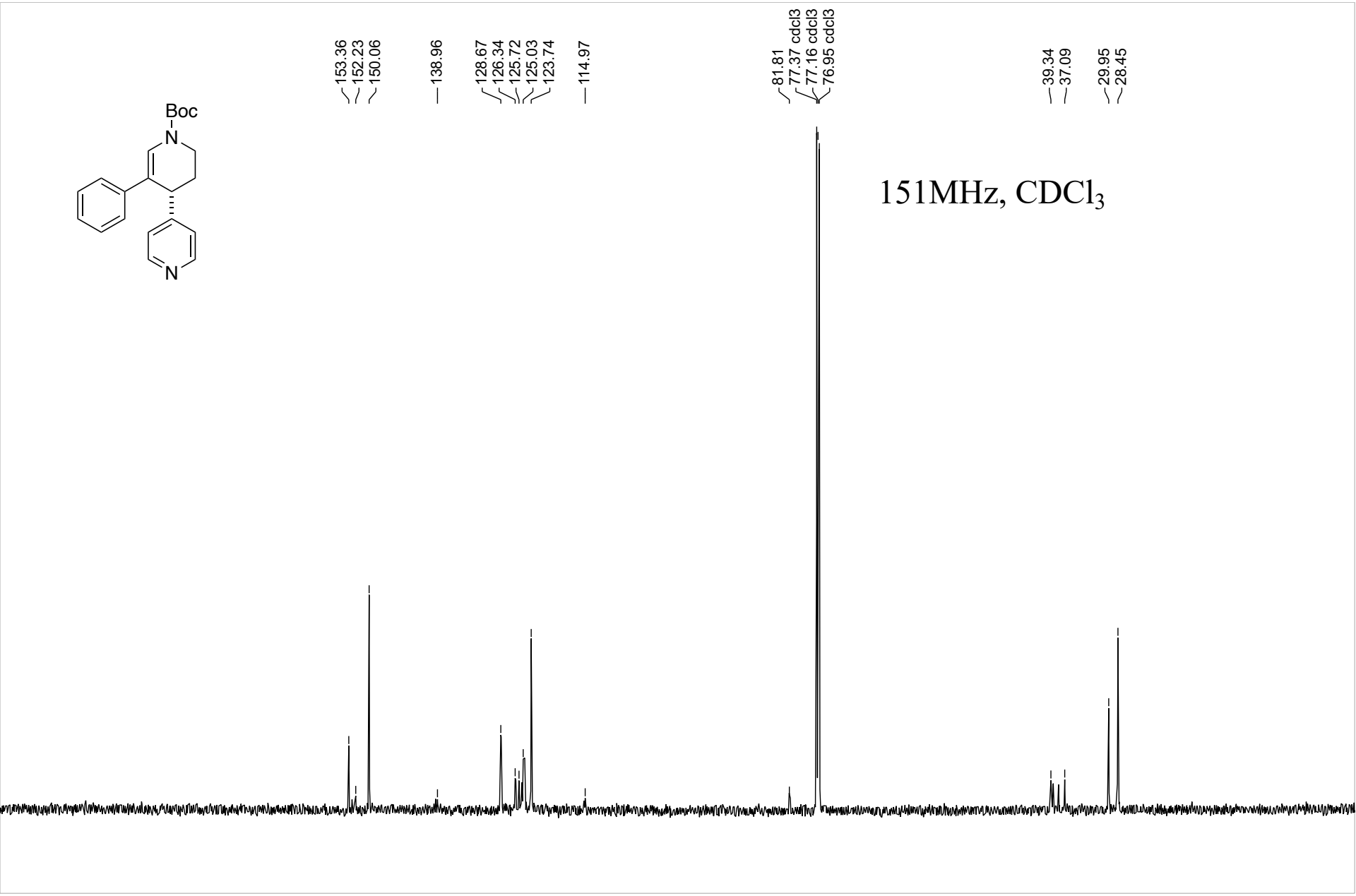

Peak Table
PDA Ch1 280nm

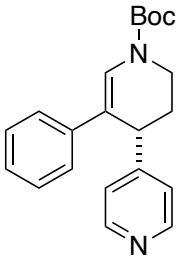
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 6.275 | 99.001 |
| 2 | 6.934 | 0.999 |
| Total | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*R*)-5-phenyl-3,4-dihydro-[4,4'-bipyridine]-1(2H)-carboxylate (2w)



# $^{13}$C NMR *tert*-Butyl (*R*)-5-phenyl-3,4-dihydro-[4,4'-bipyridine]-1(2H)-carboxylate (2w)



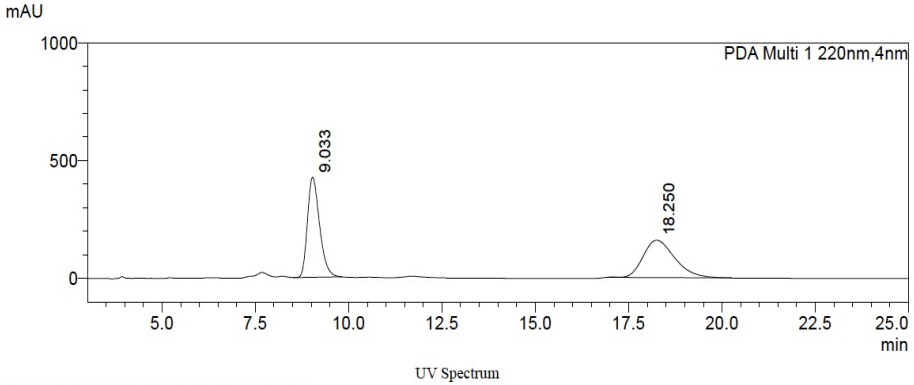



# HPLC

## *tert*-Butyl (*R*)-5-phenyl-3,4-dihydro-[4,4'-bipyridine]-1(2H)-carboxylate (2w)

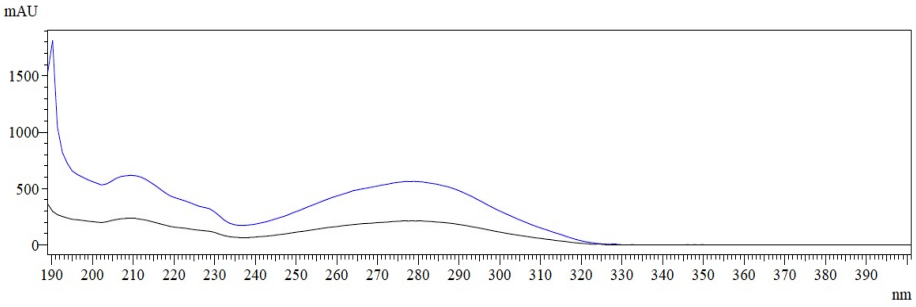
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-4-pyridine-rac-ODH-20%0.8mL001




UV Spectrum

JJX-4-pyridine-rac-ODH-20%0.8mL001_001.lcd



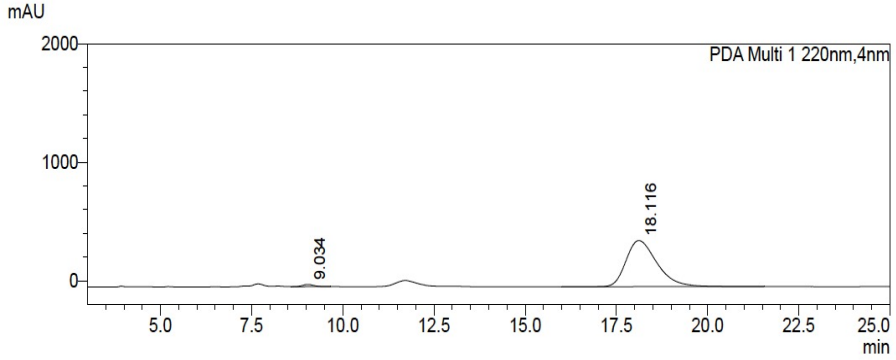

Peak Table

PDA Ch1 220nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.033 | 50.439 |
| 2 | 18.250 | 49.561 |
| Total | | 100.000 |

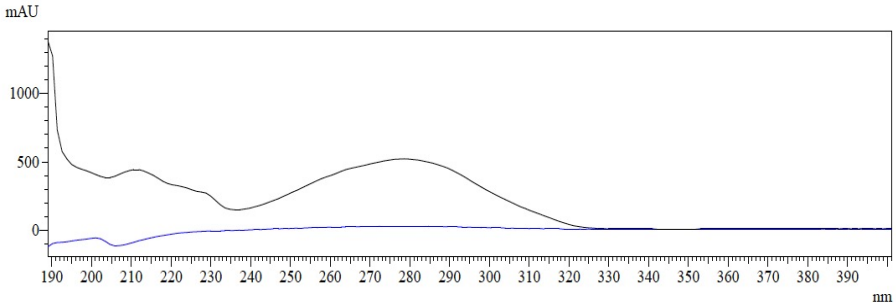
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-4-pyridine-chiral-ODH-20%0.8mL001




UV Spectrum

JJX-4-pyridine-chiral-ODH-20%0.8mL001_001.lcd

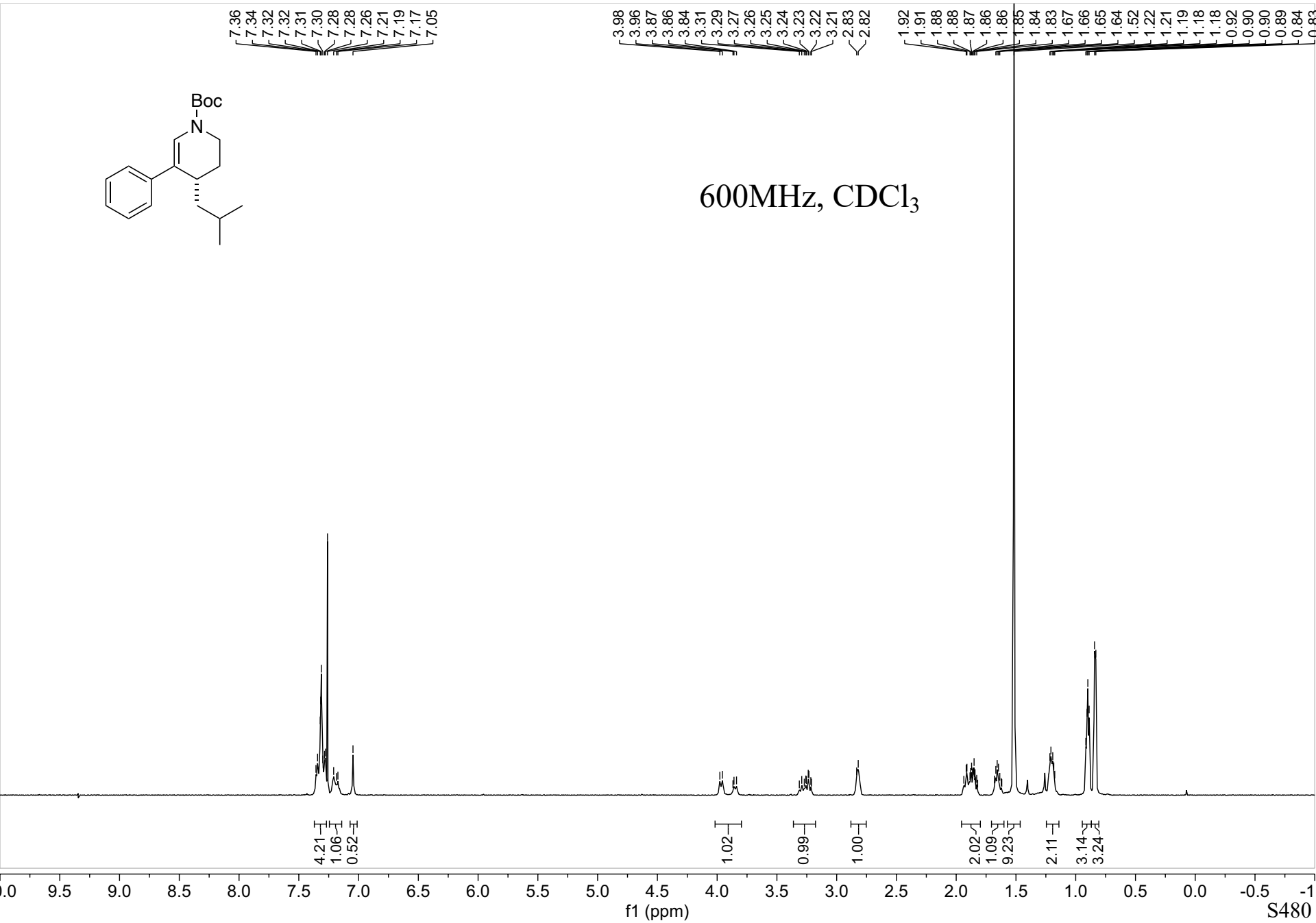



Peak Table

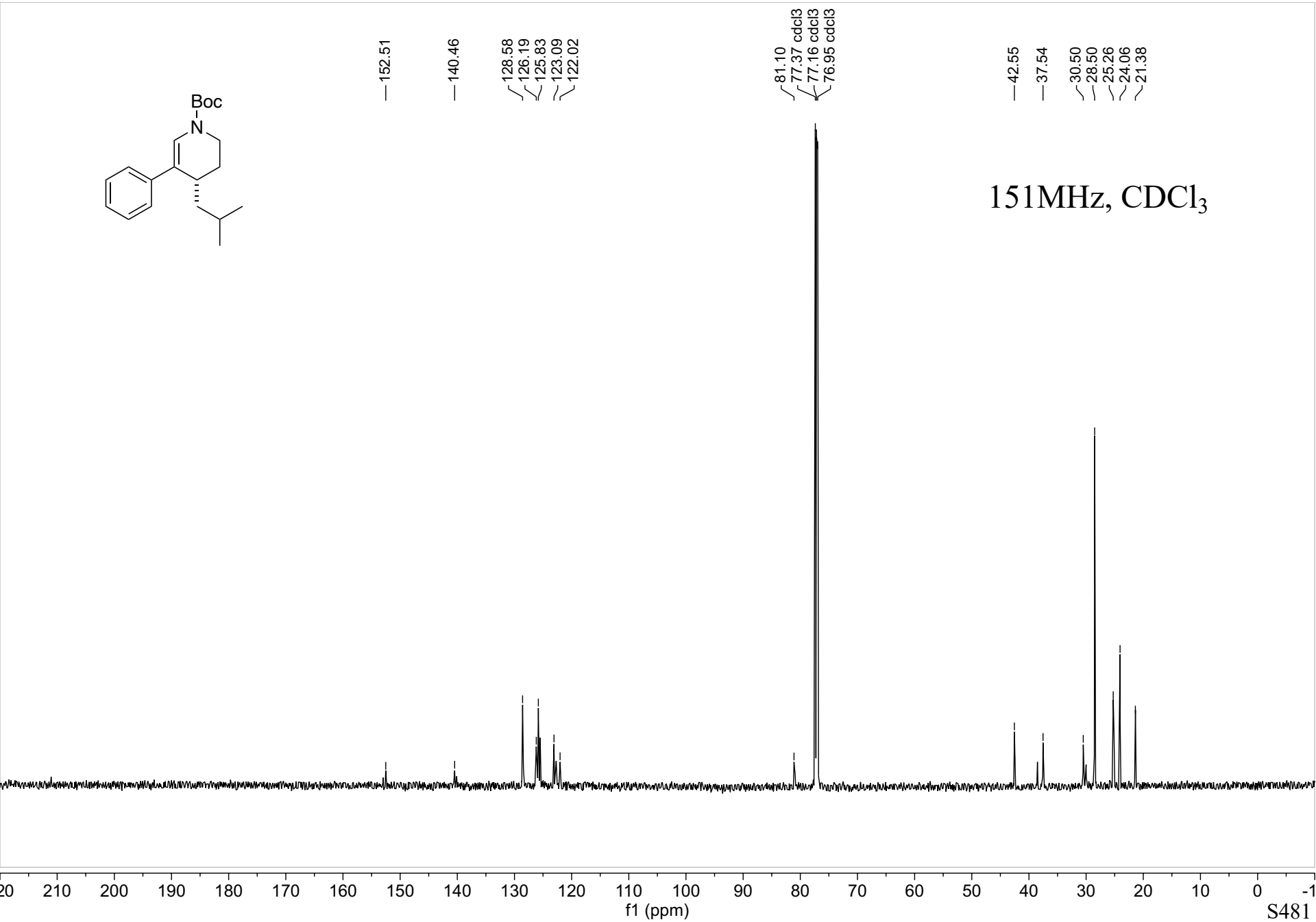
PDA Ch1 220nm

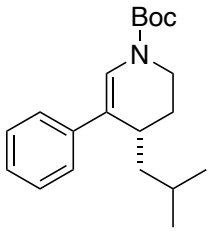
| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 9.034 | 1.592 |
| 2 | 18.116 | 98.408 |
| Total | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (*S*)-4-isobutyl-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2x)



# $^{13}$C NMR *tert*-Butyl (*S*)-4-isobutyl-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2x)

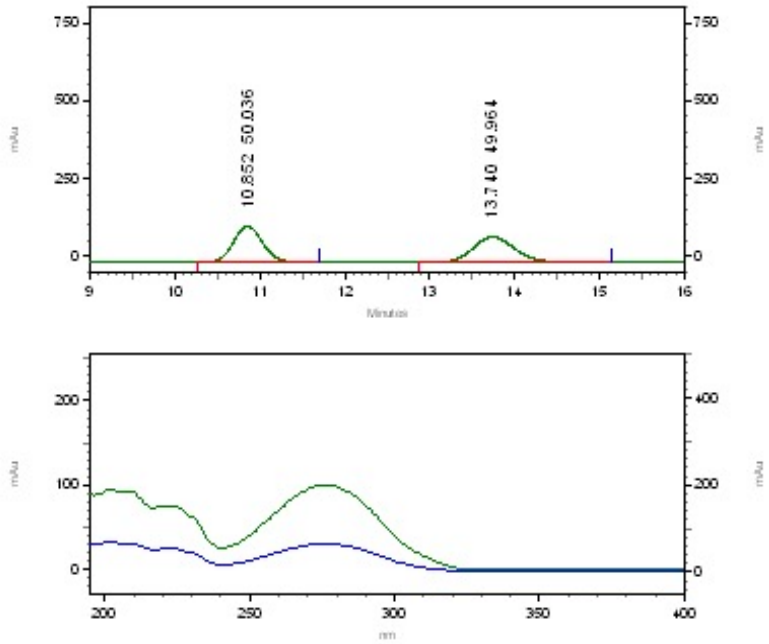





# HPLC

## *tert*-Butyl (*S*)-4-isobutyl-5-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (2x)

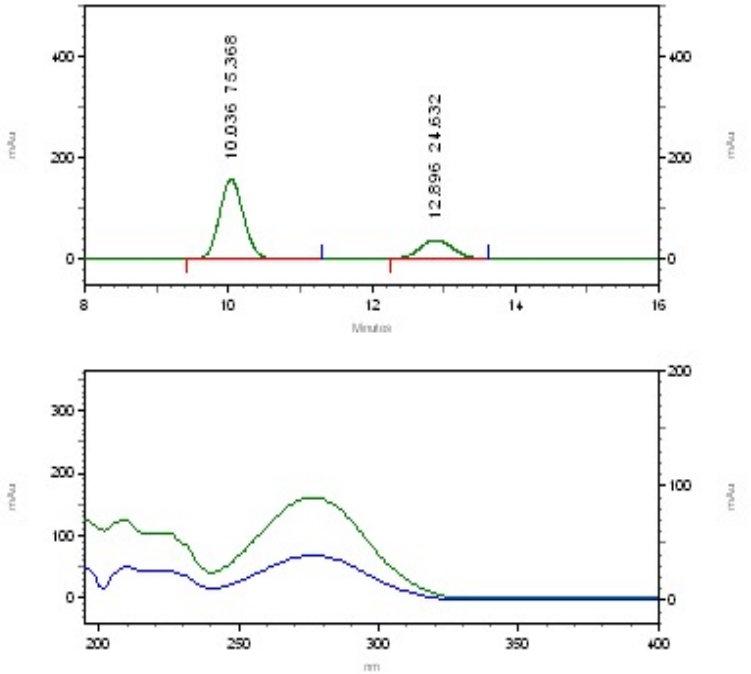
D:\HPLC\JJX-2681-2%-IC-0.8ml-ibu
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met




2: 280 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.852 | 50.036 |
| 2 | 13.740 | 49.964 |
| Totals | | 100.000 |

D:\HPLC\JJX-2682-2%-IC-0.8ml-tao
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

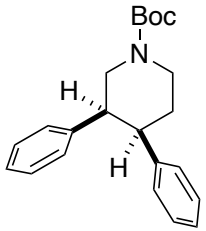



2: 280 nm, 4 nm Results

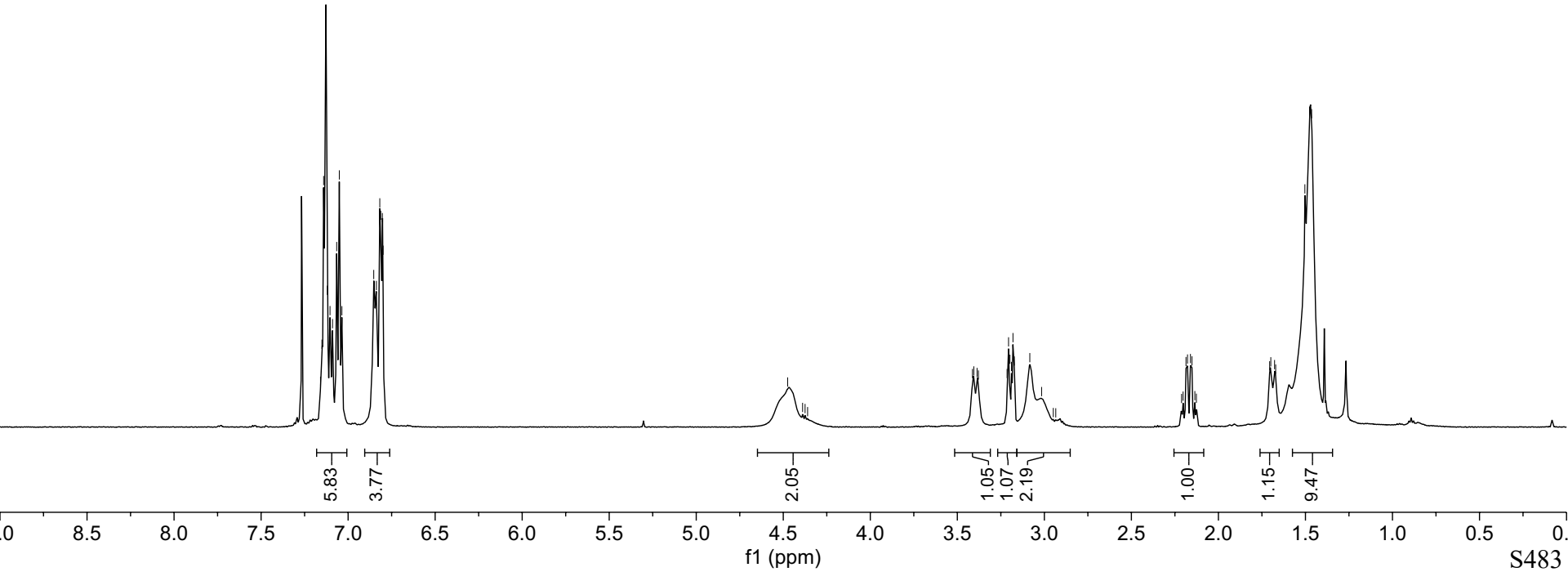
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 10.036 | 75.368 |
| 2 | 12.896 | 24.632 |
| Totals | | 100.000 |

# $^{1}$H NMR *tert*-Butyl (3*S*,4*R*)-3,4-diphenylpiperidine-1-carboxylate (3a)

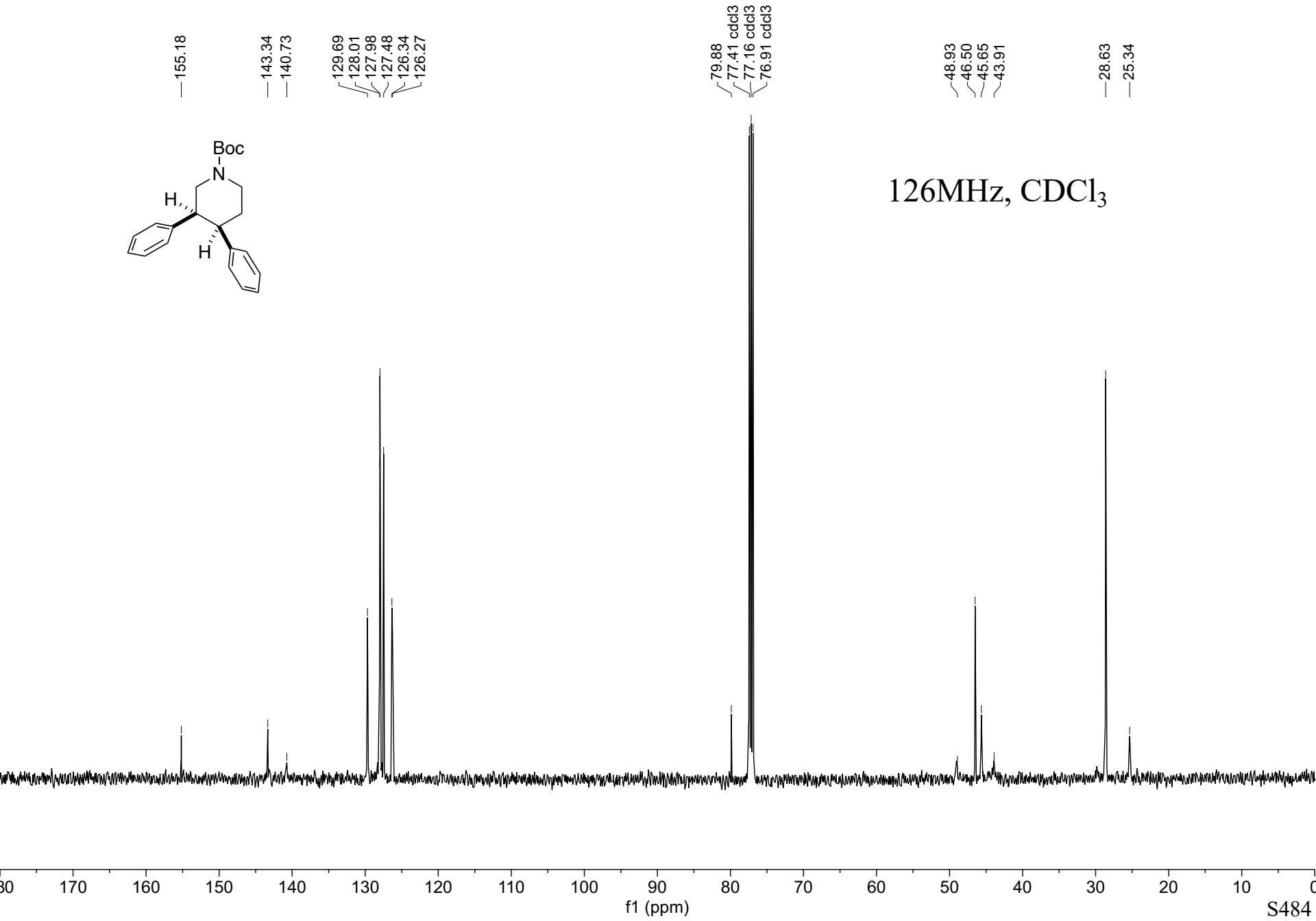


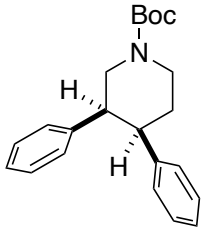




500MHz, $CDCl_3$



# $^{13}$C NMR *tert*-Butyl (3*S*,4*R*)-3,4-diphenylpiperidine-1-carboxylate (3a)

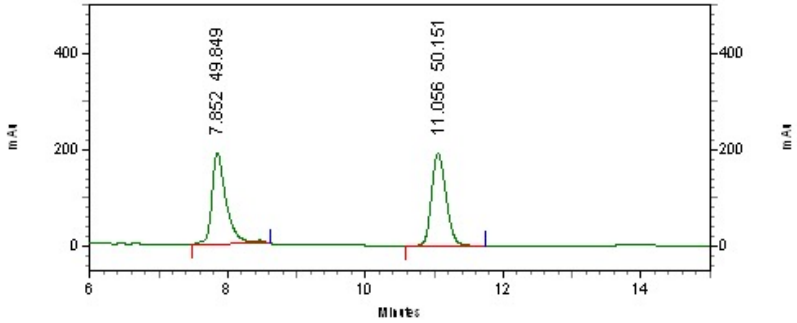


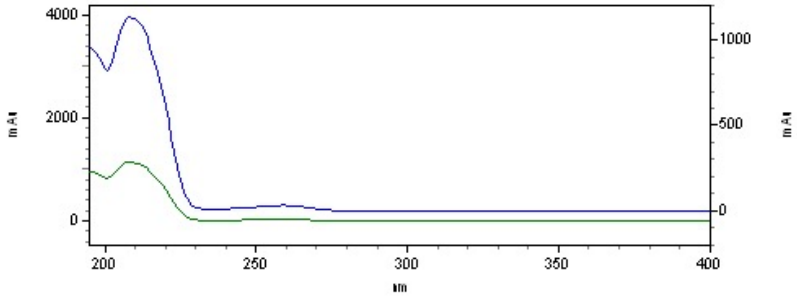



# HPLC

## *tert*-Butyl (3*S*,4*R*)-3,4-diphenylpiperidine-1-carboxylate (3a)

C:\Documents and Settings\zhang\Desktop\JJX\Jingjing HPLC\JJX-2500-5%-IF-0.8ml-RAC
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met



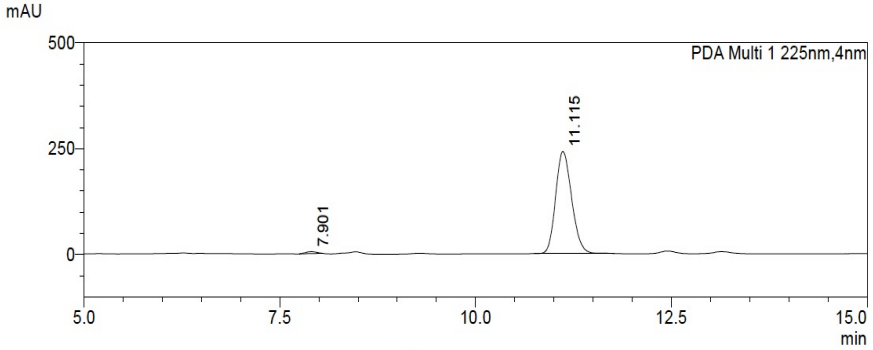

4: 225 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 7.852 | 49.849 |
| 2 | 11.056 | 50.151 |

| Totals | | 100.000 |
|---|---|---|

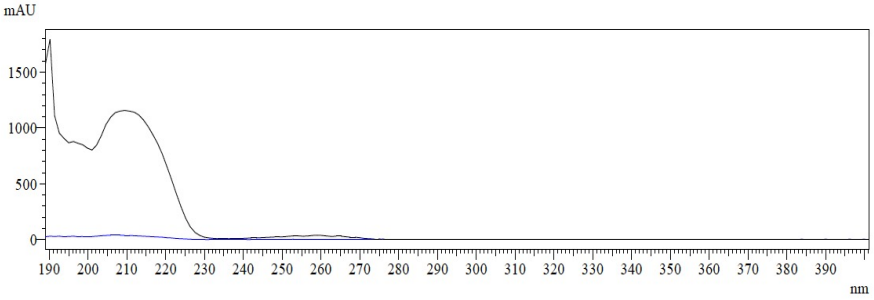
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-hydrogenation-tao-IF-5%0.8mL




UV Spectrum

JJX-hydrogenation-tao-IF-5%0.8mL_002.lcd

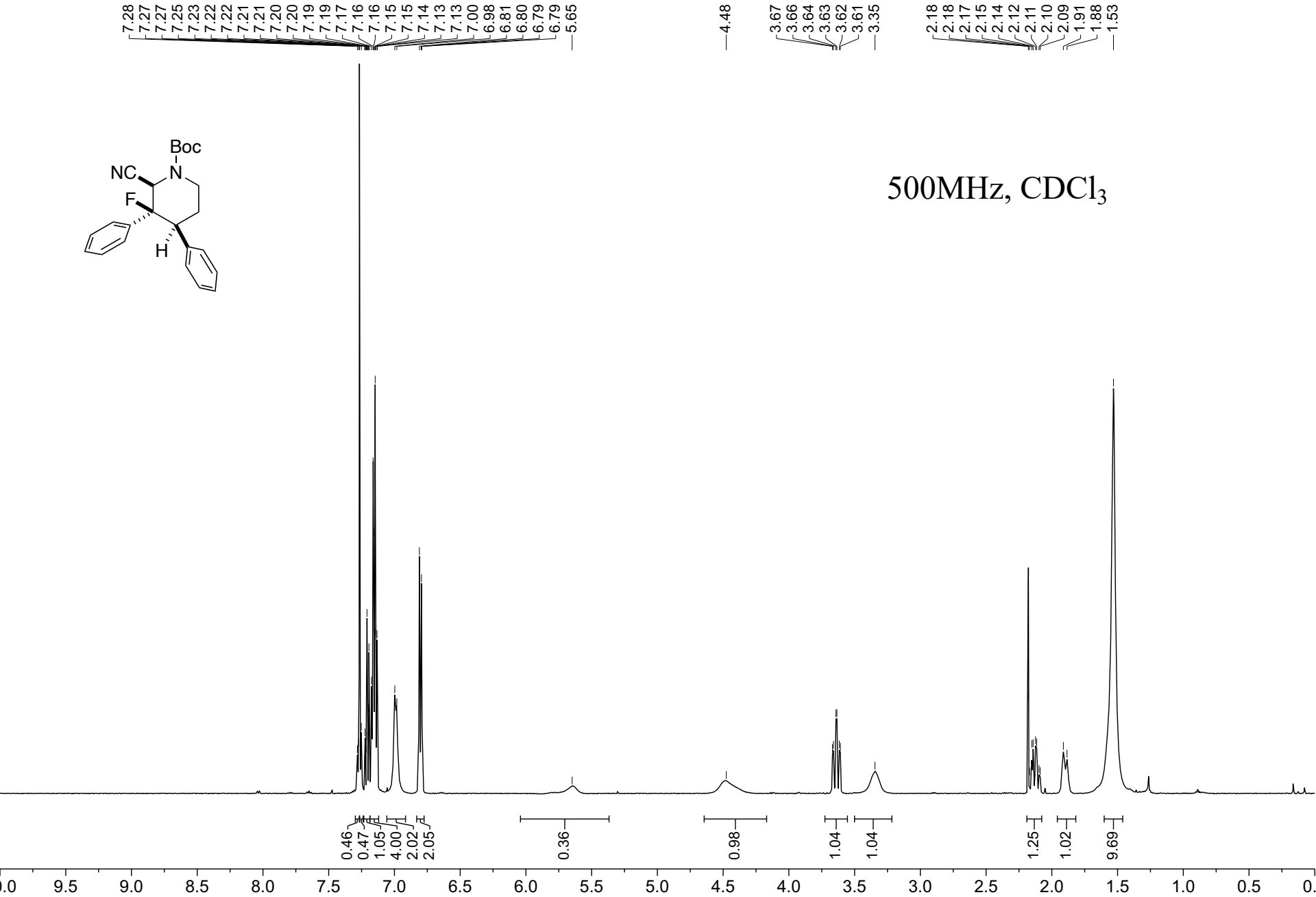



Peak Table

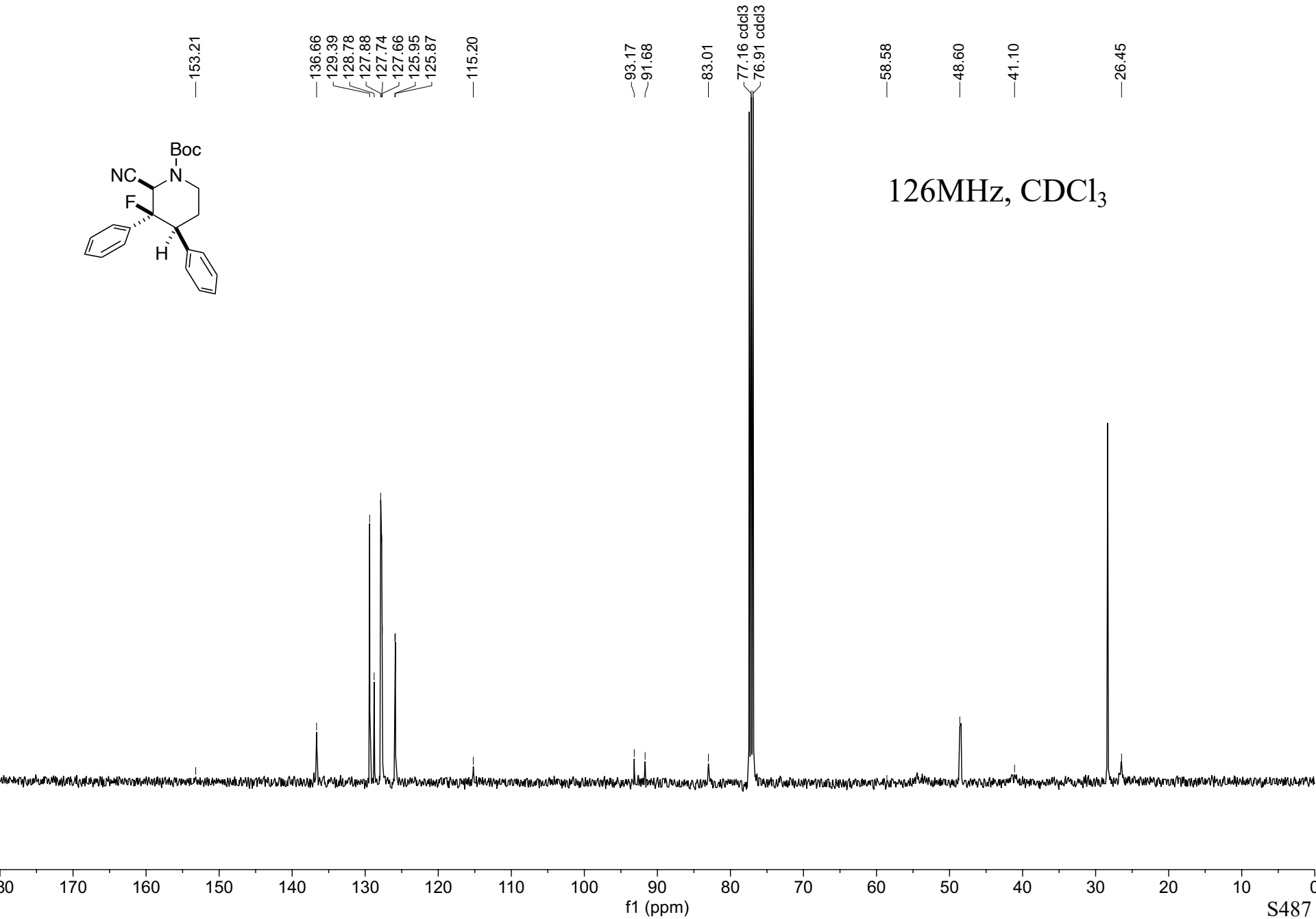
PDA Ch1 225nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 7.901 | 1.262 |
| 2 | 11.115 | 98.738 |
| Total | | 100.000 |

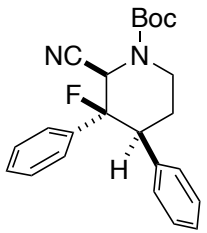
# $^{1}$H NMR *tert*-Butyl (2*R*,3*S*,4*S*)-2-cyano-3-fluoro-3,4-diphenylpiperidine-1-carboxylate (4a)



# $^{13}$C NMR *tert*-Butyl (2*R*,3*S*,4*S*)-2-cyano-3-fluoro-3,4-diphenylpiperidine-1-carboxylate (4a)

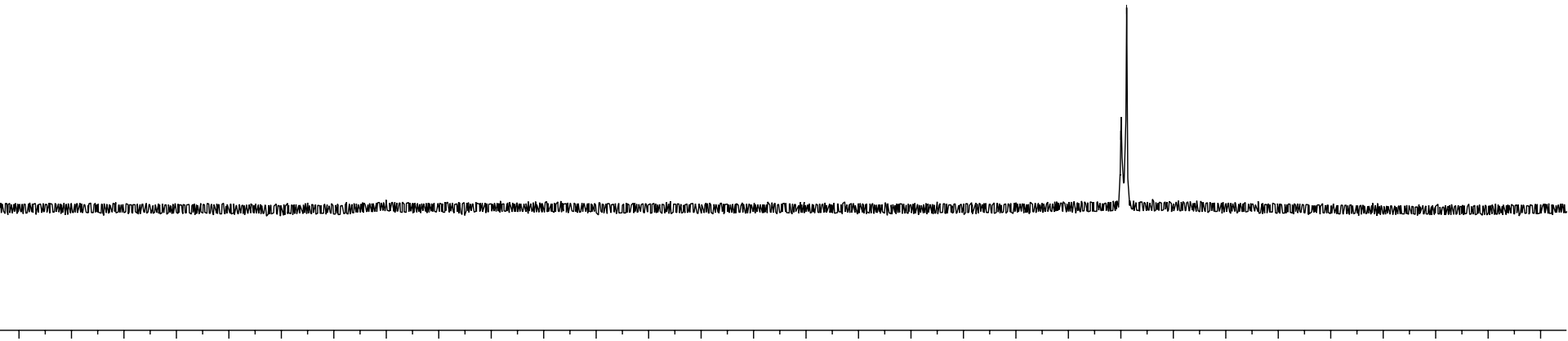


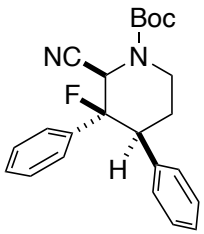
# $^{19}$F NMR *tert*-Butyl (2*R*,3*S*,4*S*)-2-cyano-3-fluoro-3,4-diphenylpiperidine-1-carboxylate (4a)




-139.98
-140.54

470MHz, $CDCl_3$



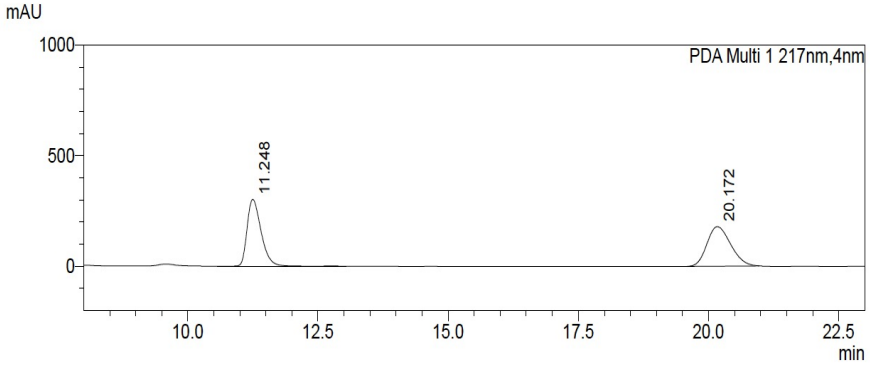



# HPLC

## *tert*-Butyl (2*R*,3*S*,4*S*)-2-cyano-3-fluoro-3,4-diphenylpiperidine-1-carboxylate (4a)

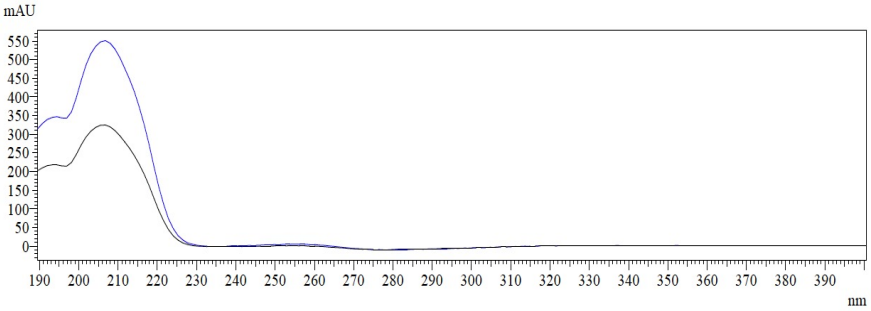
**==== Shimadzu LabSolutions Analysis Report ====**

JJX-CN-FT-RAC-IC-2%0.8mL
JJX-2%-60min0.8mL.lcm




UV Spectrum

JJX-CN-FT-RAC-IC-2%0.8mL_001.lcd

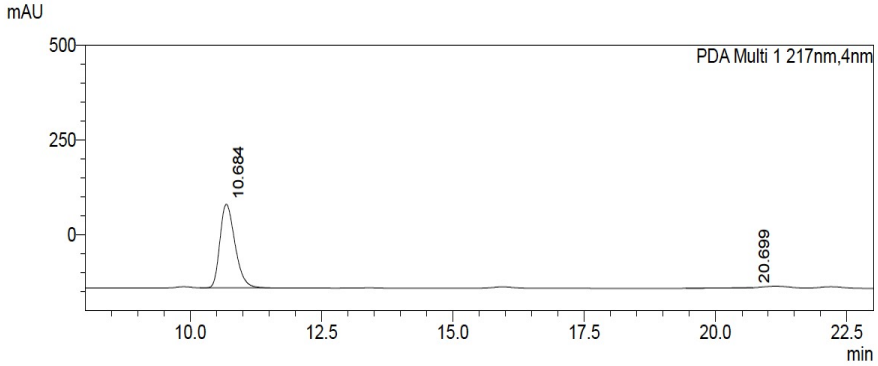



Peak Table
PDA Ch1 217nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 11.248 | 49.965 |
| 2 | 20.172 | 50.035 |
| Total | | 100.000 |

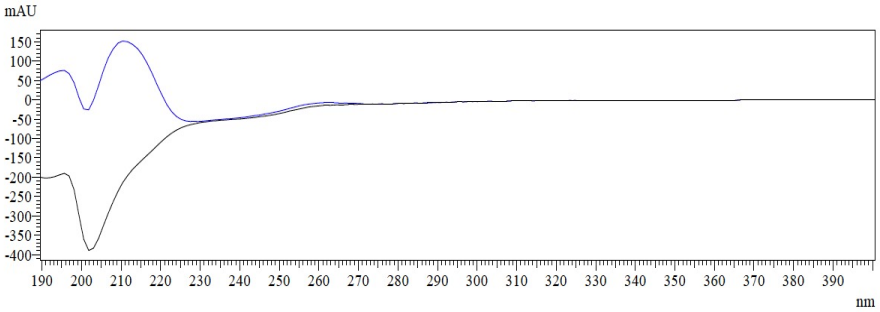
**==== Shimadzu LabSolutions Analysis Report ====**

JJX-CN-FT-CHIRAL-IC-2%0.8mL
JJX-2%-60min0.8mL.lcm




UV Spectrum

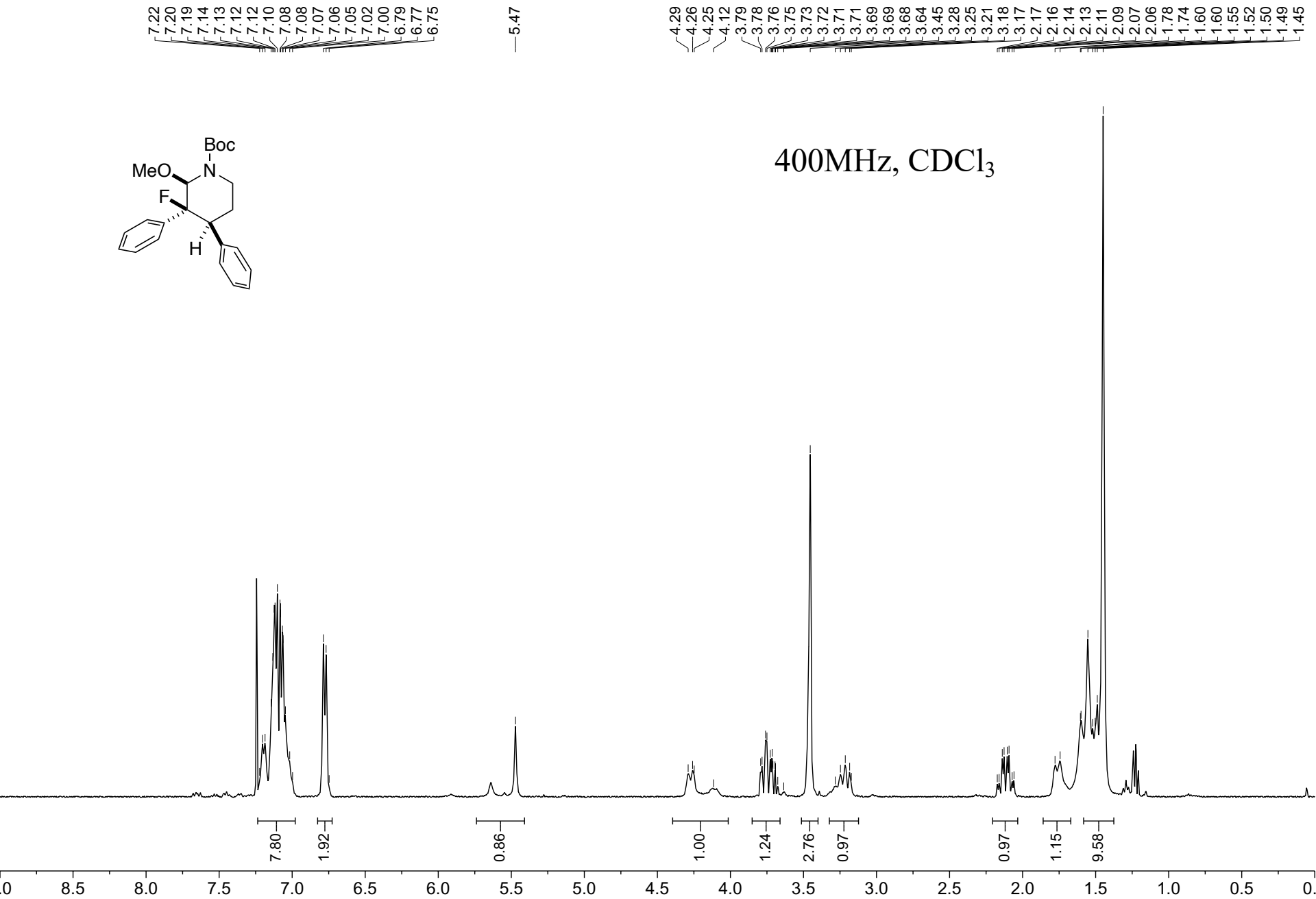
JJX-CN-FT-CHIRAL-IC-2%0.8mL_001.lcd



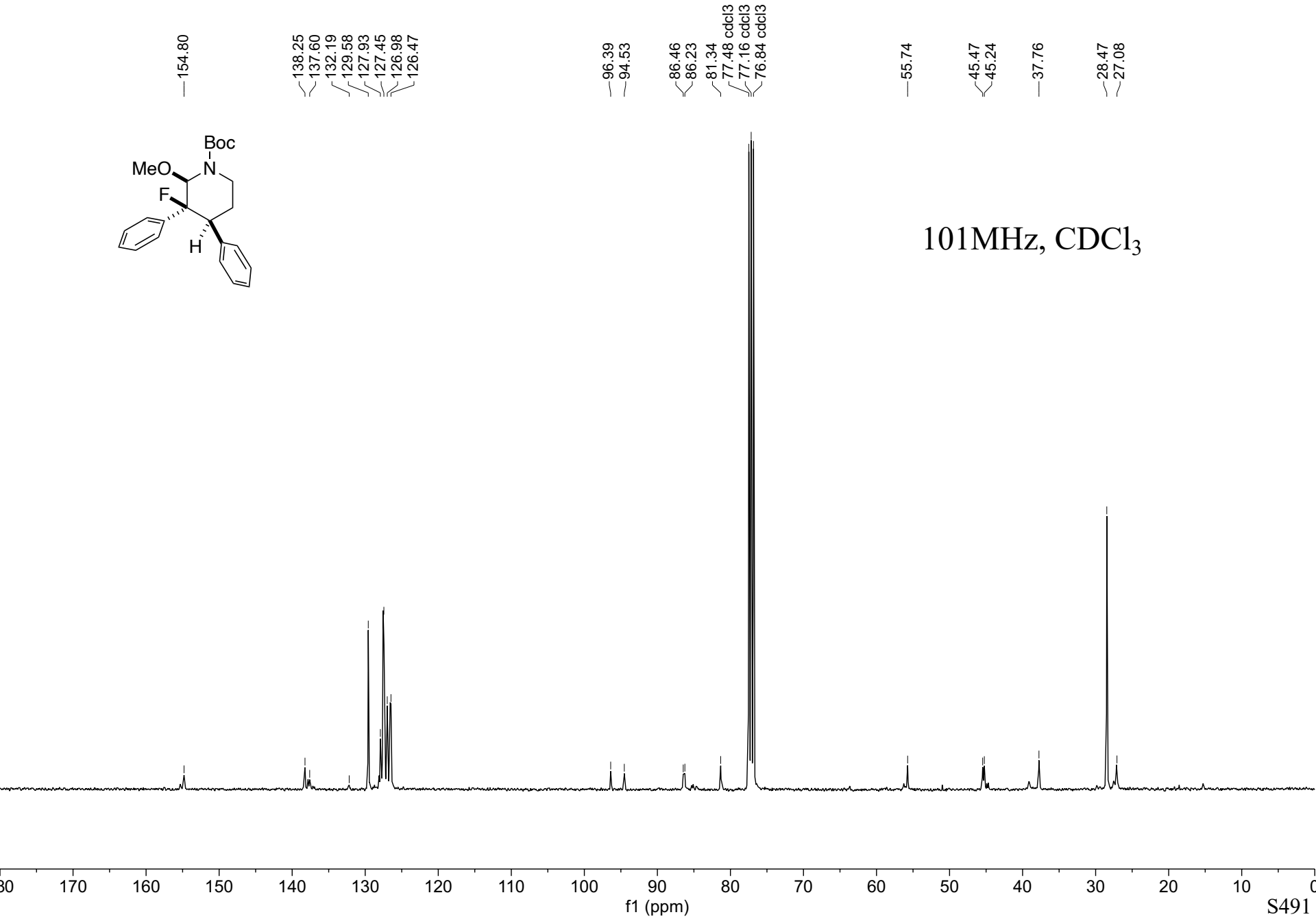

Peak Table
PDA Ch1 217nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 10.684 | 99.949 |
| 2 | 20.699 | 0.051 |
| Total | | 100.000 |

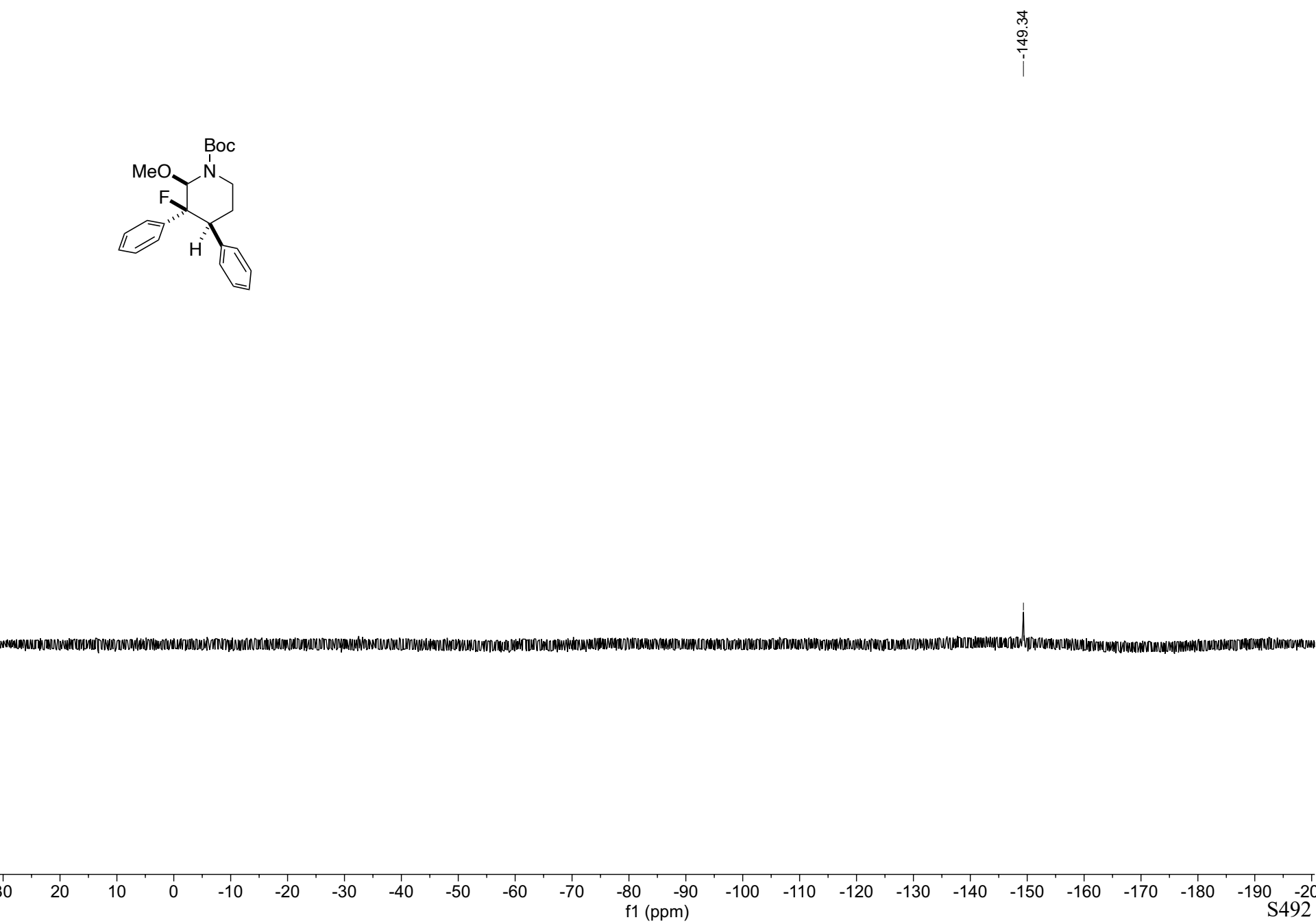
# $^{1}$H NMR *tert*-Butyl (2*R*,3*S*,4*S*)-3-fluoro-2-methoxy-3,4-diphenylpiperidine-1-carboxylate (5a)

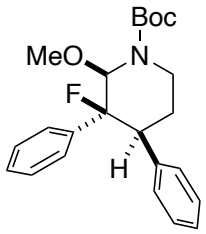


# $^{13}$C NMR *tert*-Butyl (2*R*,3*S*,4*S*)-3-fluoro-2-methoxy-3,4-diphenylpiperidine-1-carboxylate (5a)



# $^{19}$F NMR *tert*-Butyl (2*R*,3*S*,4*S*)-3-fluoro-2-methoxy-3,4-diphenylpiperidine-1-carboxylate (5a)

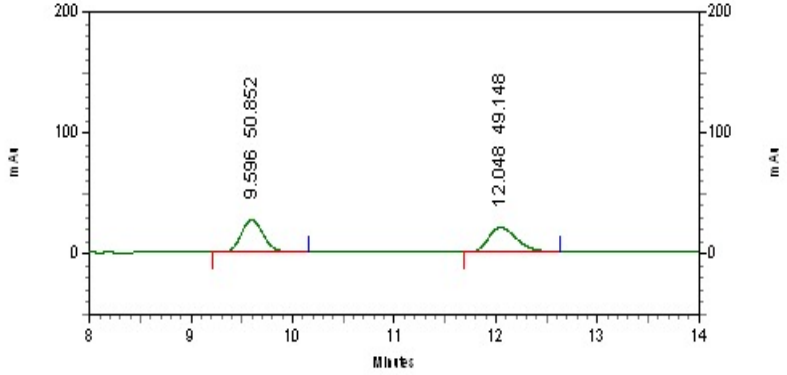


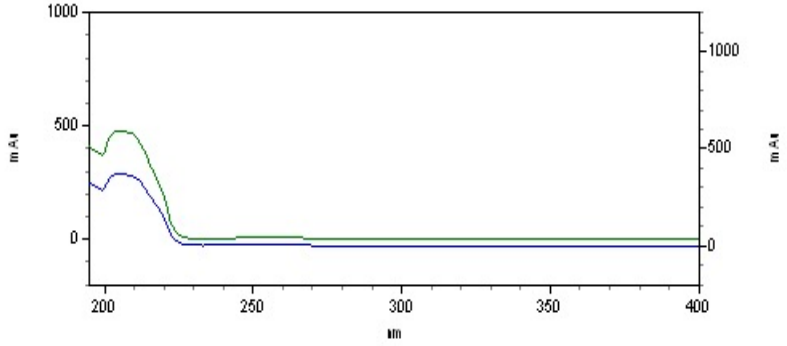



# *HPLC*

## *tert*-Butyl (2*R*,3*S*,4*S*)-3-fluoro-2-methoxy-3,4-diphenylpiperidine-1-carboxylate (5a)

C:\Documents and Settings\zhang\Desktop\JJX\Jingjing HPLC\JJX-2518-2%-IF-0.8ml-rac
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

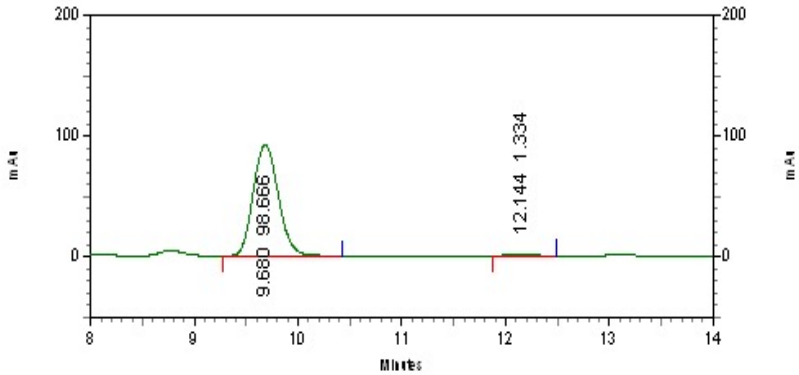


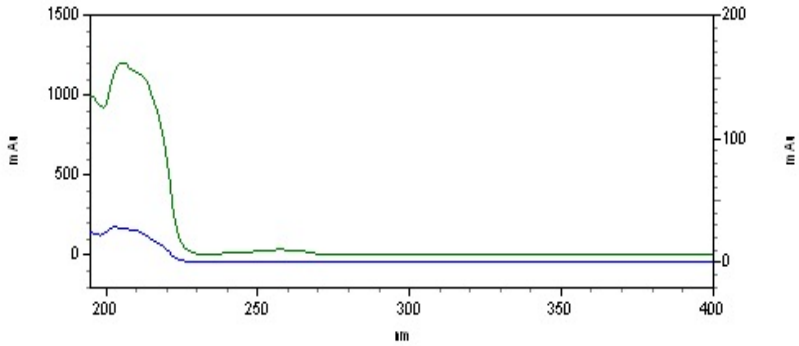




4: 225 nm, 4 nm Results

| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 9.596 | 50.852 |
| 2 | 12.048 | 49.148 |
| Totals | | 100.000 |

C:\Documents and Settings\zhang\Desktop\JJX\Jingjing HPLC\JJX-2518-2%-IF-0.8ml-chiral
C:\Documents and Settings\zhang\Desktop\DSW\Report-standard1228.met

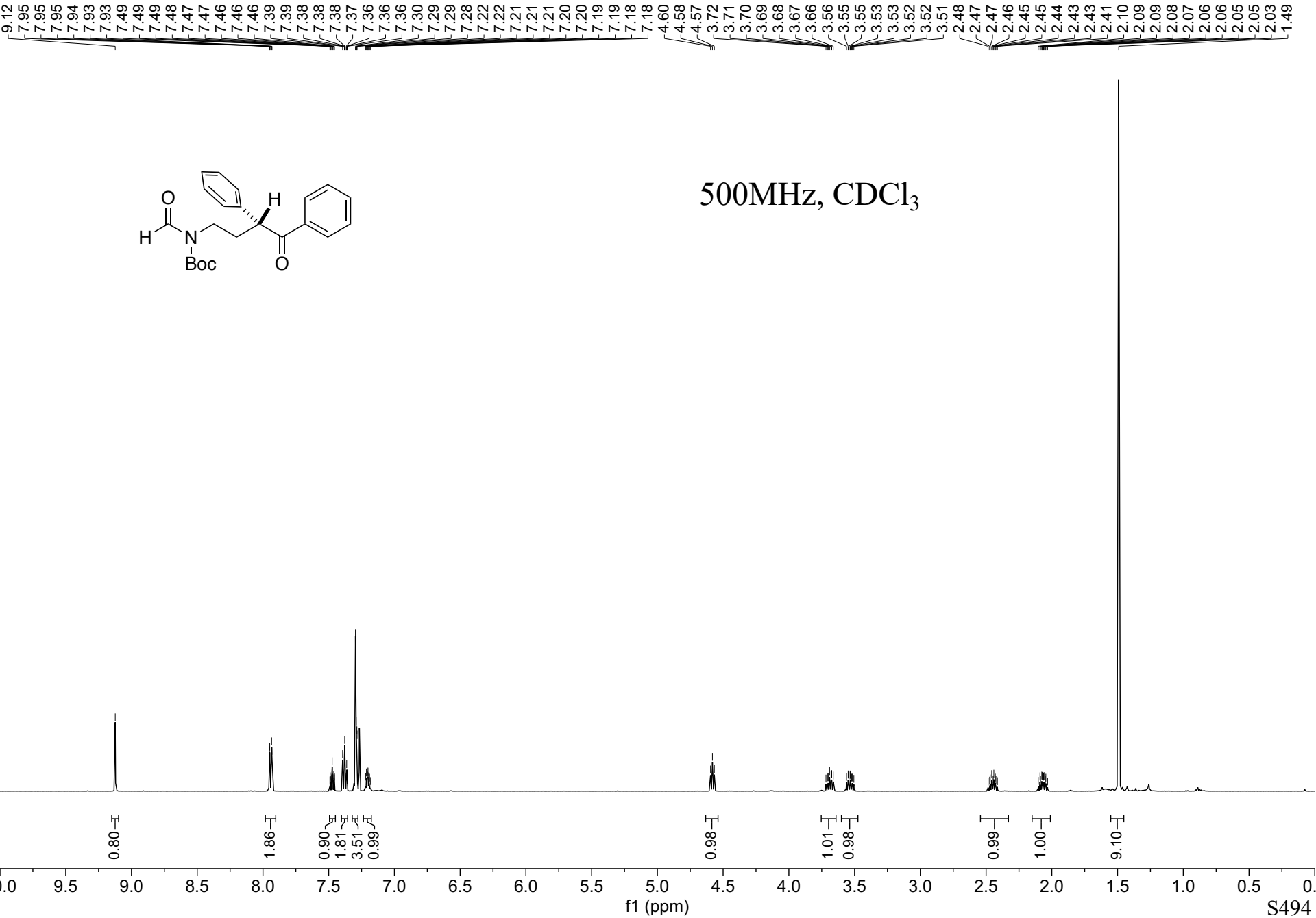


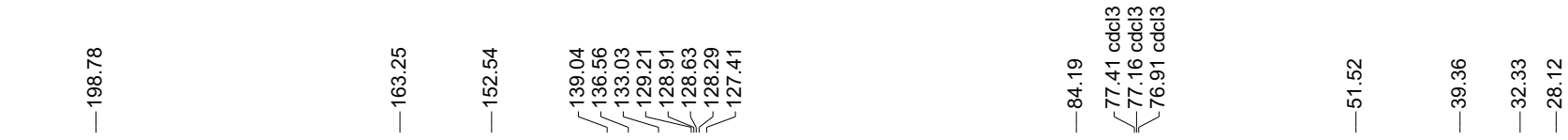

4: 225 nm, 4 nm Results

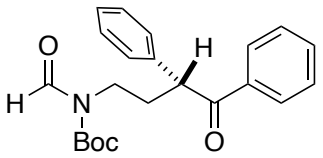
| Pk # | Retention Time | Area Percent |
|---|---|---|
| 1 | 9.680 | 98.666 |
| 2 | 12.144 | 1.334 |
| Totals | | 100.000 |

# $^{13}$C NMR *tert*-Butyl formyl(4-oxo-3,4-diphenylbutyl)carbamate (6a)

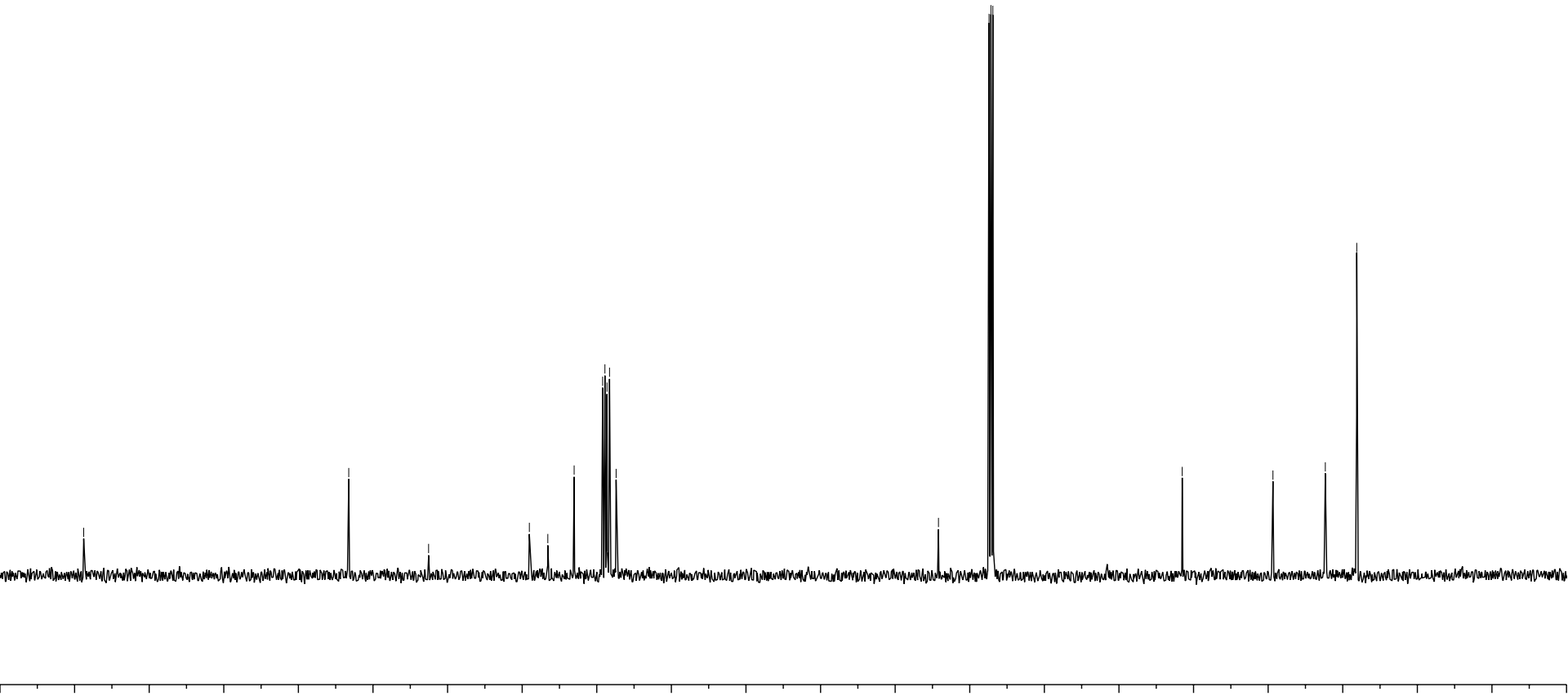


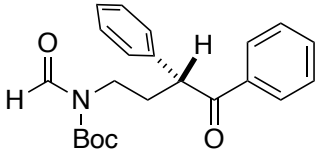
# $^{13}$C NMR *tert*-Butyl formyl(4-oxo-3,4-diphenylbutyl)carbamate (6a)




126MHz, $CDCl_3$

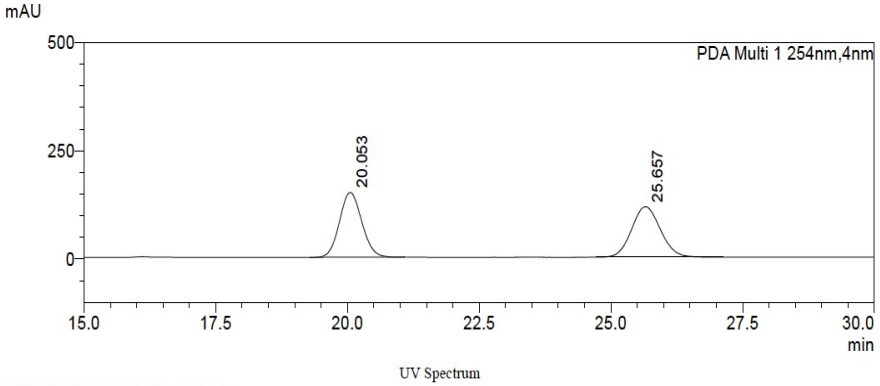





# HPLC
## *tert*-Butyl formyl(4-oxo-3,4-diphenylbutyl)carbamate (6a)

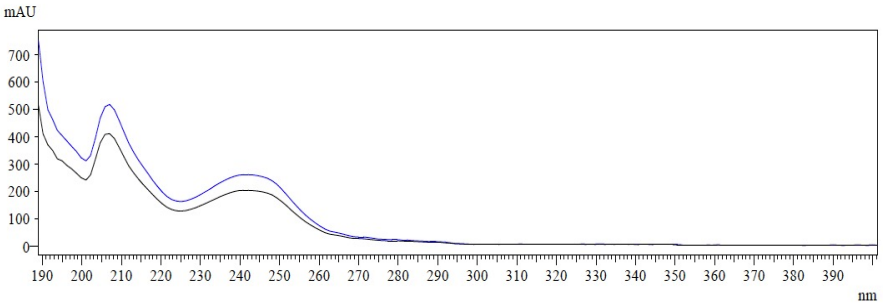
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3036p-Ibu-IC-2%0.8mL




UV Spectrum

JJX-3036p-Ibu-IC-2%0.8mL_001.lcd



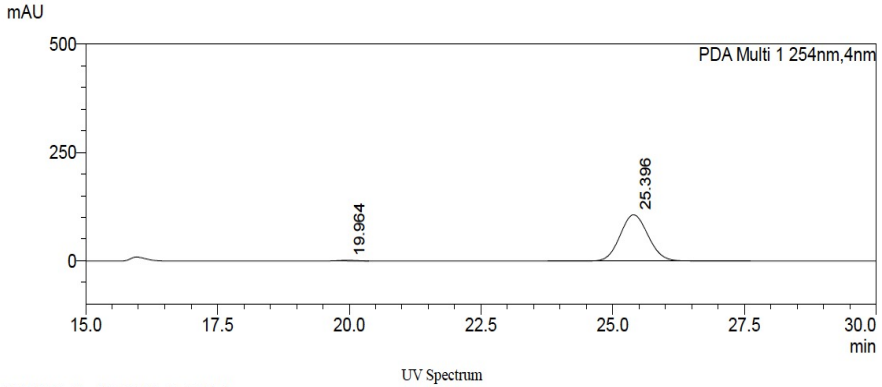

Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 20.053 | 49.881 |
| 2 | 25.657 | 50.119 |
| Total | | 100.000 |

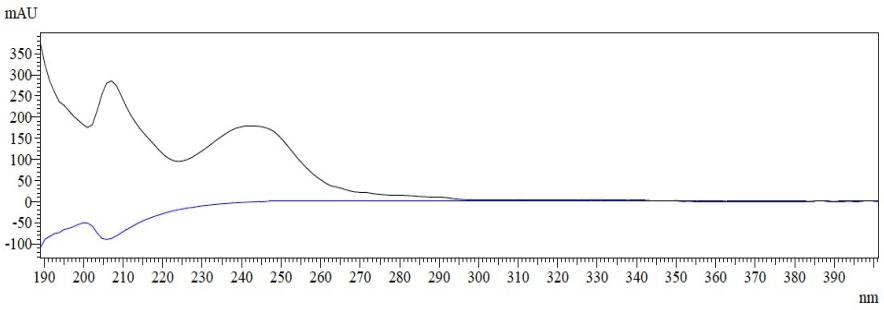
**==== Shimadzu LabSolutions Analysis Report ====**

Sample Name : JJX-3031p-Tao-IC-2%0.8mL




UV Spectrum

JJX-3031p-Tao-IC-2%0.8mL_001.lcd




Peak Table

PDA Ch1 254nm

| Peak# | Ret. Time | Area% |
|---|---|---|
| 1 | 19.964 | 0.788 |
| 2 | 25.396 | 99.212 |
| Total | | 100.000 |