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

by

Jing Ke

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Jing Ke

Advisor: Professor X. Peter Zhang

Chapter 1. Stereoselective Cyclopropanation of Alkenes with Alkynyl- and Vinyl-Substituted Diazo Compounds

Alkynyl- and vinyl-substituted cyclopropanes are ubiquitous structural motifs in drug molecules and bioactive compounds. In addition, alkynyl- and vinyl-substituted cyclopropanes may serve as useful intermediates for stereoselective organic synthesis. Metal-catalyzed cyclopropanation of alkenes with alkynyl- and vinyl-substituted diazo compounds offers a potentially general approach for stereoselective construction of these valuable three-membered ring structures. This chapter summarizes the development of stereoselective olefin cyclopropanation with alkynyl- and vinyl-substituted diazo compounds.

Chapter 2. Metalloradical Activation of In Situ-Generated α-Alkynyldiazomethanes for Asymmetric Radical Cyclopropanation of Alkenes

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

Chapter 3. Asymmetric Radical Process for Cyclopropanation of Alkenes with In Situ-Generated α-Vinyldiazomethanes

We have demonstrated the feasibility of using vinyl aldehyde-derived sulfonylhydrazones as new metalloradicophiles for the generation of allylic radicals. Through fine-tuning the cavity-like environments of D_2-symmetric chiral amidoporphyrins as supporting ligands, the key α-Co(III)-allylic radical intermediates are exclusively engaged in the highly asymmetric cyclopropanation with wide-ranging alkenes in the optimized Co(II)-based metalloradical system, as shown broadly applicable to activate different α-vinyldiazomethanes.

Chapter 4. Asymmetric Synthesis of Vinyl-Substituted Cyclopropanes by Radical C−H Alkylation from Alkynes and In Situ-Generated Alkyldiazomethanes via Co(II)-Based Metalloradical Catalysis

We have successfully expanded the application of Co(II)-based MRC by applying in-situ generated alkyldiazomethanes as new radical precursors for stereoselective synthesis of vinyl-substituted cyclopropanes by radical cascade C−H alkylation of alkynes. Through fine-tuning of D_2-symmetric chiral amidoporphyrins as the supporting ligands, the Co(II)-catalyzed radical cascade process, which proceeds in a single operation under mild conditions, enables asymmetric construction of vinyl-substituted cyclopropanes in high yields with excellent diastereoselectivities and good enantioselectivities.

DEDICATION

This thesis is lovingly dedicated to my grandparents – Chaoping Ke and Xiuzhen Zhou, my parents – Wenliang Ke and Xuan Zeng, and my love – Sheng Chen.

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CHAPTER 1

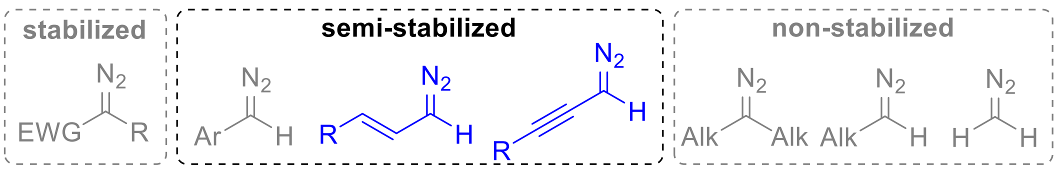
STEREOSELECTIVE CYCLOPROPANATION OF ALKENES WITH ALKYNYL- AND VINYL-SUBSTITUTED DIAZO COMPOUNDS

1.1. INTRODUCTION

Cyclopropane ring, as the smallest carbocycle, are among the most studied common structural motifs in organic synthesis and has continuously drawn the interest of chemists.[1] The three-membered ring units, carbon-carbon bonds of which remain kinetically stable even with the presence of ring strain, also widely exist in many biologically active molecules and help to improve the target selectivity and affinity in medicinal chemistry.[2] As important categories of cyclopropanes, alkynyl- and vinyl-substituted cyclopropanes, possessing the C≡C triple bonds and C═C double bonds respectively, can be employed as versatile synthetic motifs for the construction of other cycloalkanes and acyclic compounds by either ring-extension or ring-opening reactions.[3] As alkynyl- and vinyl-substituted cyclopropanes have found wide application in modern organic synthesis, the preparation of these important compounds has attracted considerable attention nowadays.[4] Among tremendous efforts made to access these valuable three-membered rings, transition-metal catalyzed cyclopropanation of alkenes with diazo compounds is considered to be a traditional, yet most reliable method to synthesize such species.[5]

Diazo compounds, serving as powerful and versatile reagents, have found broad implementation in modern synthetic organic chemistry, including olefin cyclopropanation processes.[6] The diazo compounds are classified as 1,3-dipole compounds, the electronic structure of which is characterized by π electron density delocalized over the α-carbon and two nitrogen atoms. Due to the delocalization of electrons, the most stable diazo compounds are α-diazoketones and α-diazoesters, whose electron density is further delocalized into the electron-withdrawing carbonyl group, while the diazo compounds bearing alkyl substituents are considered to be non-stabilized in which the electron-donating groups destabilized the partial negative charge positioned on the carbon atom (Scheme 1.1).[7] Apart from them, diazo compounds bearing additional conjugated π system involving aryl, vinyl, and alkynyl substituents are considered to be semi-stabilized diazo species.

Scheme 1.1. Relative Stability of Diazo Compounds



While cyclopropanation of alkenes with diazo compounds offers a potentially general approach for stereoselective construction of valuable chiral alkynyl- and vinylcyclopropanes, the application of these semi-stabilized diazo compounds has been rarely explored owing to their intrinsic nature of instability and inherent propensity towards the formation of stable aromatic pyrazoles.[8] To address the challenge, corresponding alkynyl and vinyl diazo precursors, including *N*-nitrosourea and *N*-sulfonylhydrazones, have been developed for the in situ generation of diazo compounds for the stereoselective synthesis of alkynyl- and vinyl-substituted cyclopropanes.

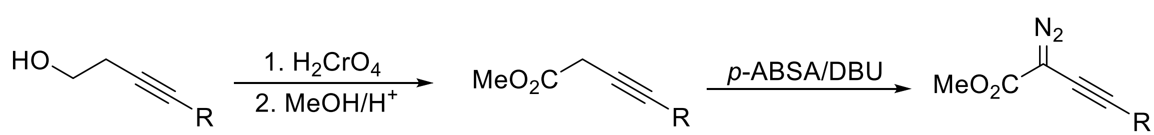
1.2. STEREOSELECTIVE CYCLOPROPANATION OF ALKENES WITH ALKYNYL-SUBSTITUTED DIAZO COMPOUNDS

1.2.1. Asymmetric Synthesis of Alkynylcyclopropanes from Alkynyldiazoacetates

Alkynyldiazoacetates, stabilized by the carbonyl substituent, have been successfully applied as effective diazo substrates in asymmetric olefin cyclopropanation for the construction of enantioenriched alkynyl-substituted cyclopropanes.[9] It has also been rationalized that this type of carbenoids containing both electron-withdrawing (EWG) and electron-donating (EDG) groups undergo highly diastereoselective cyclopropanation owing to the demanding trajectory of alkenes approaching these carbenoids, which occur side-on over the electron-withdrawing group.

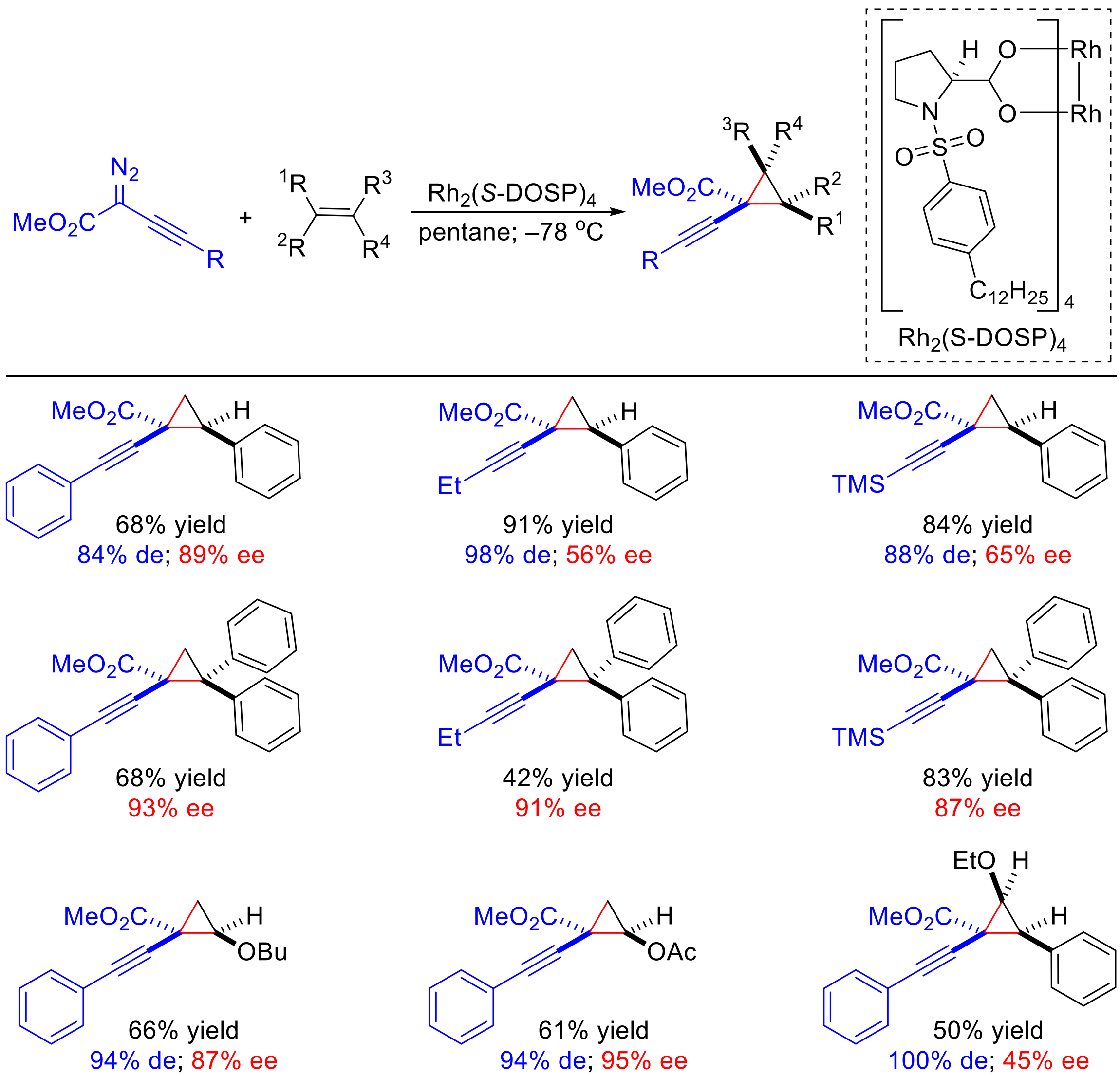
The alkynyldiazoacetates can be readily prepared and exhibit reasonable stability (Scheme 1.2). First, 3-alkyny-1-ols can be oxidized by chromic acid and then converted to 3-alkynoates. A diazo transfer reaction on 3-alkynoates with *p*-(acetamido)benzenesulfonyl azide (*p*-ABSA) and DBU as a base could furnish the alkynyldiazoacetates with various substituents to the alkynyl moieties.

Scheme 1.2. Synthesis of Alkynyldiazoacetate



With the application of the dirhodium tetraprolinates Rh_2(*S*-DOSP)$_4$ as the catalyst, which is sufficiently active even at –78 ºC, the highly enantioselective olefin cyclopropanation can be achieved (Scheme 1.3). Alkynyldiazoacetates bearing different substituents including phenyl, ethyl, and TMS groups could be effectively engaged in the cyclopropanation of styrene as well as 1,1-diphenylethene. Extension of the reaction to electron-rich alkenes resulted in desired cyclopropanes with similarly high stereoselectivities. One of the most distinctive features of this transformation is the exclusive reactivity towards the *cis*-alkenes as when the 1:1 mixture of *cis*- and *trans*-methyl-propenyl ethers were used as alkene substrates, the product was furnished as a single diastereomer while there is no observed reactivity towards the *trans*-alkene substrate.

Scheme 1.3. Substrate Scope of Asymmetric Cyclopropanation of Alkenes with Alkynyldiazoacetates

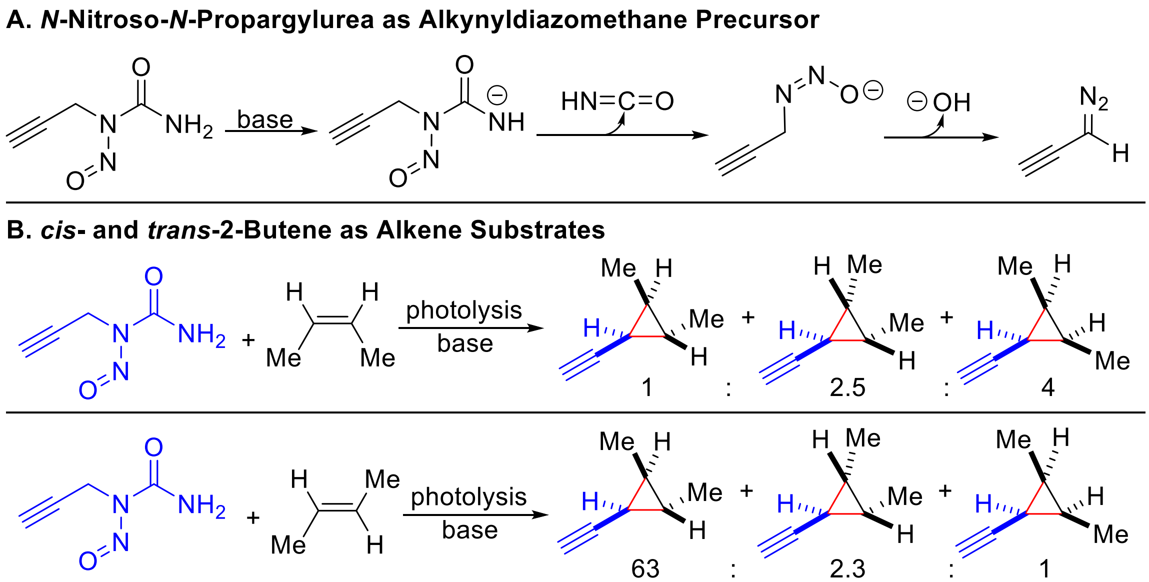


1.2.2. Diastereoselective Synthesis of Alkynylcyclopropanes from In Situ-Generated Alkynyldiazomethanes

Olefin cyclopropanation of alkenes with α-alkynyldiazomethanes offers a potentially general approach for stereoselective construction of valuable alkynyl cyclopropanes. However, α-alkynyldiazomethanes, considered to be semi-stabilized diazo compounds, can easily undergo self-cyclization towards the formation of stable aromatic pyrazoles. Rising to the challenges, *N*-nitroso-*N*-propargylureas, as well as alkynyl-*N*-sulfonylhydrazones, have emerged as potential diazo precursors that could generate the α-alkynyldiazomethanes in situ for stereoselective olefin cyclopropanation.

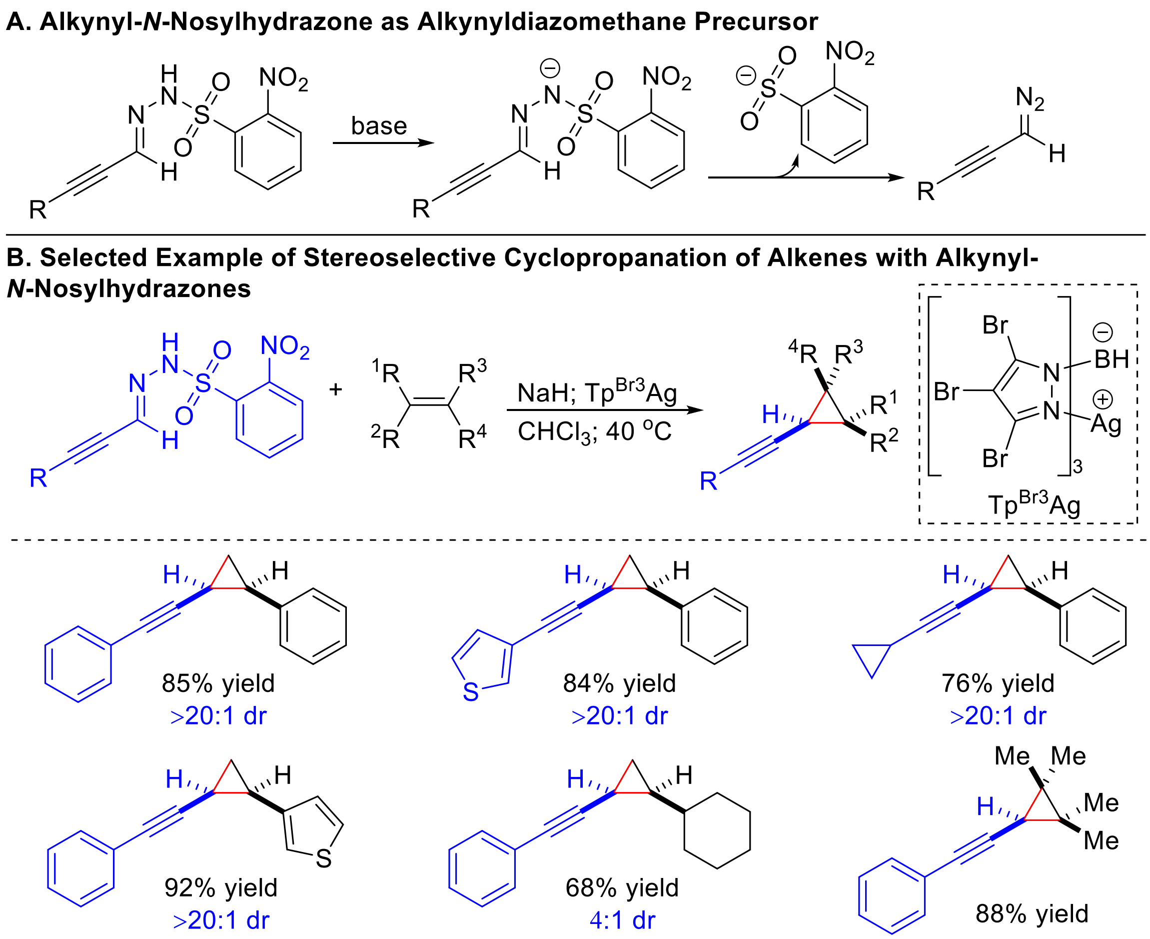
Skell and coworkers have first reported the use of *N*-nitroso-*N*-propargylurea as effective α-alkynyldiazomethane precursors for stereoselective cyclopropanation of 2-butene under photolytic conditions (Scheme 1.4).[10] In the presence of an aqueous base, alkynyldiazomethanes could be in situ-generated from the corresponding *N*-nitroso-*N*-propargylurea by releasing isocyanic acid as a byproduct (Scheme 1.4A). When *cis*-2-butene was used as an alkene substrate, three isomeric alkynylcyclopropanes could be generated in ratios = 1:2.5:4 favoring the *cis*-isomers (Scheme 1.4B). On the other hand, the isomeric alkynylcyclopropane products were generated in ratios = 63:2.3:1 in favor of the *trans*-isomers when *trans*-2-butene was applied (Scheme 1.4C). Inspired by this successful transformation, Meijere and coworkers have later reported the utilization of *N*-nitroso-*N*-propargylurea as an α-alkynyldiazomethane precursor for dirhodium(II) tetraacetate-catalyzed stereoselective cyclopropanation of different electron-rich alkenes, which is further highlighted by the first access to the important 2-(trimethylsiloxy)-1-ethynylcyclopropane.[11]

Scheme 1.4. Application of *N*-Nitroso-*N*-Propargylurea as Alkynyldiazomethane Precursor for Stereoselective Cyclopropanation of 2-Butene



Although *N*-nitroso-*N*-propargylurea was proved to be an efficient diazo precursor, it can only be generated in quantities of a few grams and requires to be handled with great care due to occasional explosions that have been reported. As a synthetic more practical approach, alkynyl-*N*-sulfonylhydrazones, which can be easily derived from the corresponding aldehyde, have been developed as alternative diazo precursors for the in situ generation of α-alkynyldiazomethanes through Bamford-Stevens reaction. Bi and coworkers have reported silver-catalyzed stereoselective cyclopropanation of alkenes with in situ-generated α-alkynyldiazomethanes from corresponding alkynyl-*N*-nosylhydrazones (Scheme 1.5).[12] A series of alkynyl-*N*-nosylhydrazones, which were derived from aryl-, heteroaryl-, and aliphatic-substituted propargyl aldehyde, were applied to the catalytic system and converted to the corresponding alkynylcyclopropanes in high yields with excellent diastereoselectivities. Apart from various styrene derivatives, heteroaryl-substituted alkene, as well as unactivated aliphatic alkene, were shown to be suitable olefin substrates. Moreover, this silver-based catalytic system was further highlighted by cyclopropanation of sterically bulky tetra-substituted alkene which can also react smoothly with in situ-generated alkynyldiazomethane under the optimized condition for the synthesis of penta-substituted alkynyl cyclopropane.

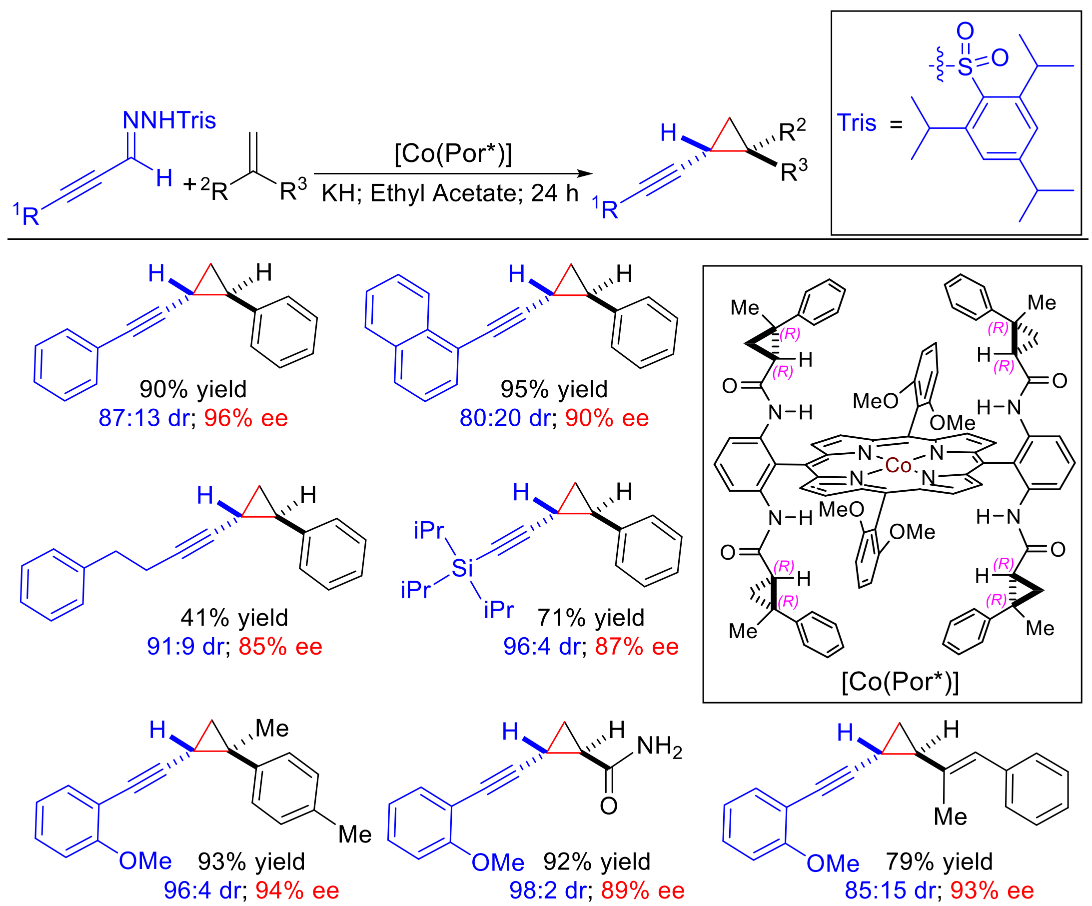
Scheme 1.5. Application of Alkynyl-*N*-Nosylhydrazones as Alkynyldiazomethane Precursors for Stereoselective Cyclopropanation of Alkenes



1.2.3. Asymmetric Synthesis of Alkynylcyclopropanes from In Situ-Generated Alkynyldiazomethanes

While tremendous effort has been made for the stereoselective cyclopropanation of alkenes with alkynyl-substituted diazo compounds, there has been no previous report on the catalytic system for asymmetric olefin cyclopropanation with α-alkynyldiazomethanes for stereoselective synthesis of alkynylcyclopropanes. As a new application of Co(II)-based metalloradical catalysis (MRC), we herein report the development of the first asymmetric catalytic system for olefin cyclopropanation that can effectively utilize α-alkynyldiazomethanes through in situ-generation from the corresponding sulfonyl-

Scheme 1.6. [Co(Por*)]-Catalyzed Asymmetric Radical Cyclopropanation of Alkenes with In Situ-Generated Alkynyl Diazomethanes



hydrazones in the presence of a base (Scheme 1.6).[13]

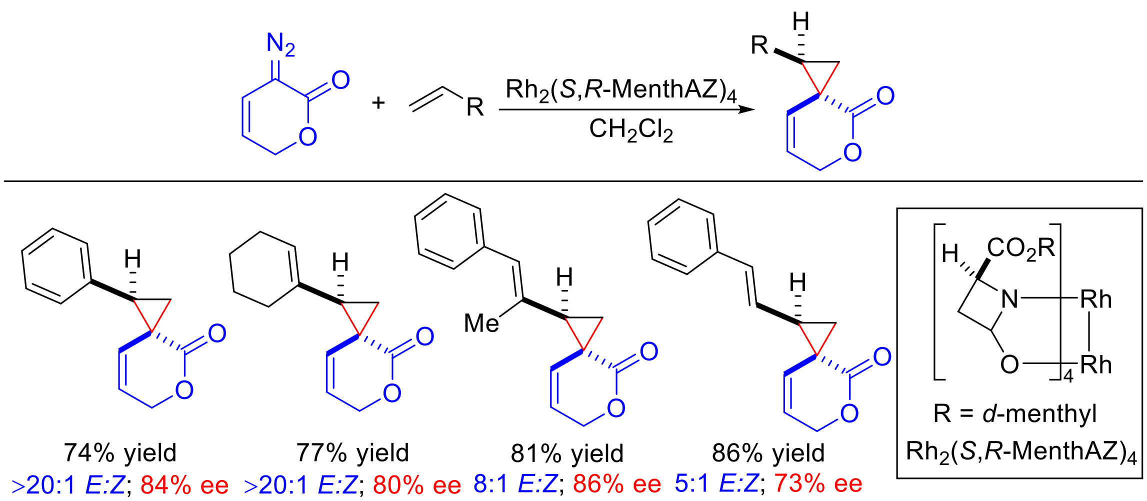
Through the identification of an optimal D_2-symmetric chiral amidoporphyrin (D_2-Por*) as the supporting ligand, the Co(II)-based catalytic system is capable of efficiently activating different alkynyldiazomethanes at room temperature to cyclopropanate a wide range of alkenes with varied electronic and steric properties, delivering alkynylcyclopropanes in high yields with excellent control of both diastereoselectivity and enantioselectivity. To further highlight the unique feature of Co(II)-based metalloradical catalysis, even electron-deficient olefins such as acrylamide and ethyl acrylate, which are challenging substrates for catalytic cyclopropanation systems involving electrophilic metallocarbene intermediates, could be effectively cyclopropanated to form the desired alkynylcyclopropanes in high yields with high stereoselectivities.

1.3. STEREOSELECTIVE CYCLOPROPANATION OF ALKENES WITH VINYL-SUBSTITUTED DIAZO COMPOUNDS

1.3.1. Asymmetric Synthesis of Vinylcyclopropanes from Vinyldiazolactones and Vinyldiazoacetates

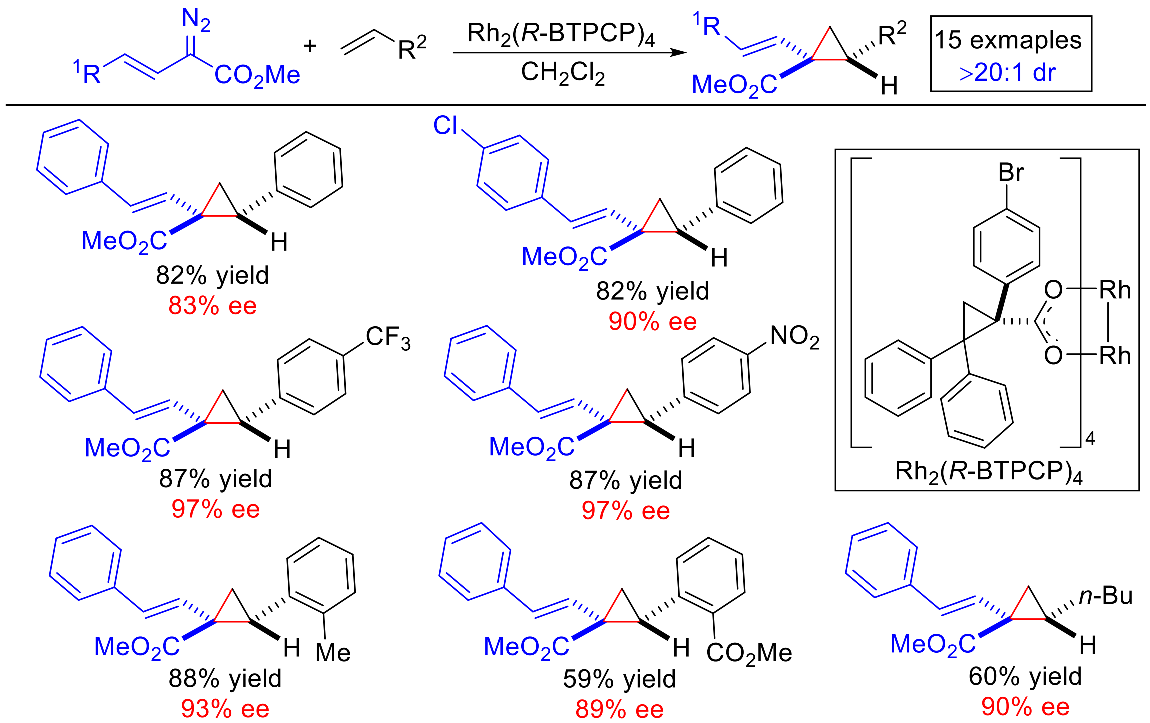
Doyle and coworkers have reported the first synthesis of α-vinyldiazolactone and its application in asymmetric cyclopropanation of terminal alkenes catalyzed by a chiral dirhodium carboxamidate (Scheme 1.7).[14] Reactions occurred cleanly as spiro-vinylcyclopropane products could be generated in high yields with notable diastereoselectivities as well as enantioselectivities. Throughout this study, vinyldiazolactone has been proved as not only an effective but also a stable vinylcarbene precursor which can be stored for a long period. Inspired by this work, Katzuki and coworkers also developed a powerful olefin cyclopropanation process by applying vinyldiazolactone substrates with the iridium-salen catalyst.[15] The cyclopropanation of aryl- and alkenyl-substituted olefins proceeded with high (*E*)-selectivity and excellent enantioselectivity. In particular, all the reactions of 1,3-dienes exhibited excellent enantio-, regio-, and *trans*-selectivity, regardless of the substitution pattern of the internal conjugated alkenyl group.

Scheme 1.7. Rh_2(*S,R*-MenthAZ)$_4$-Catalyzed Asymmetric Cyclopropanation of Terminal Alkenes with Vinyldiazolactones



Davies and coworkers have first developed dirhodium(II) tetrakis-triarylcyclopropanecarboxylates as a new class of chiral catalysts with a relatively rigid and easily tunable backbone for the highly stereoselective cyclopropanation of alkenes with vinyldiazoacetates (Scheme 1.8).[16] The generality of this catalyst in enantioselective cyclopropanation with donor/acceptor carbenoid intermediates was probed by evaluating various combinations of styryldiazoacetates with alkenes. Computational investigation on the cyclopropanation process indicated that as the carbenoid binds to the D_2-symmetric chiral catalyst, two of the *p*-bromophenyl groups on the ligand rotate outward, directing the alkene substrate to approach the carbenoid in a controlled manner.

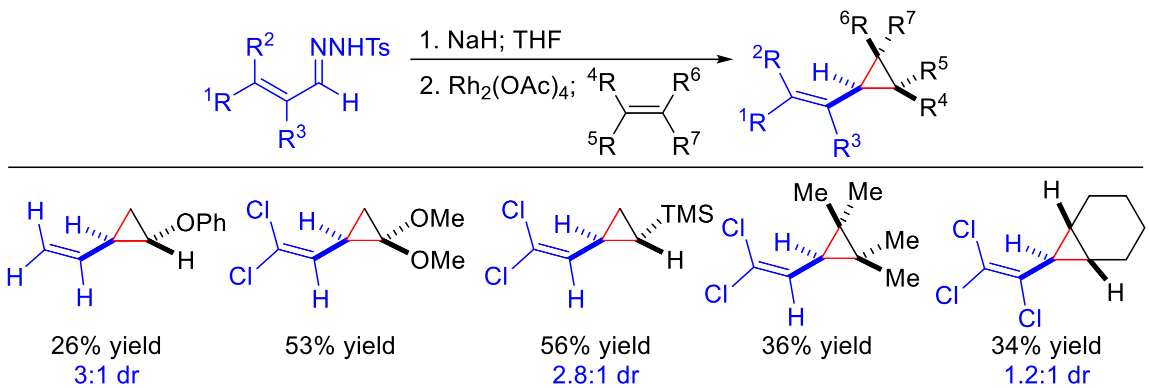
Scheme 1.8. Rh$_2$(*R*-BTPCP)$_4$-Catalyzed Asymmetric Olefin Cyclopropanation with Styryldiazoacetates



1.3.2. Diastereoselective Synthesis of Vinylcyclopropanes from In Situ-Generated Vinyldiazomethanes

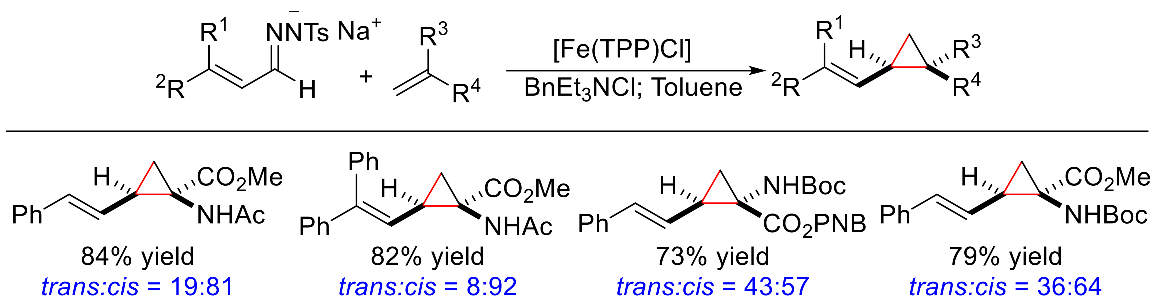
Similar to alkynyldiazomethanes, vinyldiazomethanes are semi-stabilized diazo compounds, which have an inherent propensity toward the formation of stable aromatic pyrazoles through self-cyclization reaction. To circumvent the problem, Meijere and coworkers first developed the rhodium-catalyzed diastereoselective cyclopropanation of alkenes with vinyldiazomethanes generated in situ from vinyl-*N*-tosylhydrazones (Scheme 1.9).[11] This transformation is applicable to a wide range of olefins especially the electron-rich alkenes, furnishing the corresponding vinylcyclopropane in moderate yields. It is worth noting that internal olefins, including tetra-substituted alkene and cyclic alkene, have exhibited notable reactivity in this catalytic transformation.

Scheme 1.9. $Rh_2(OAc)_4$-Catalyzed Stereoselective Olefin Cyclopropanation with Vinyl-*N*-Tosylhydrazones



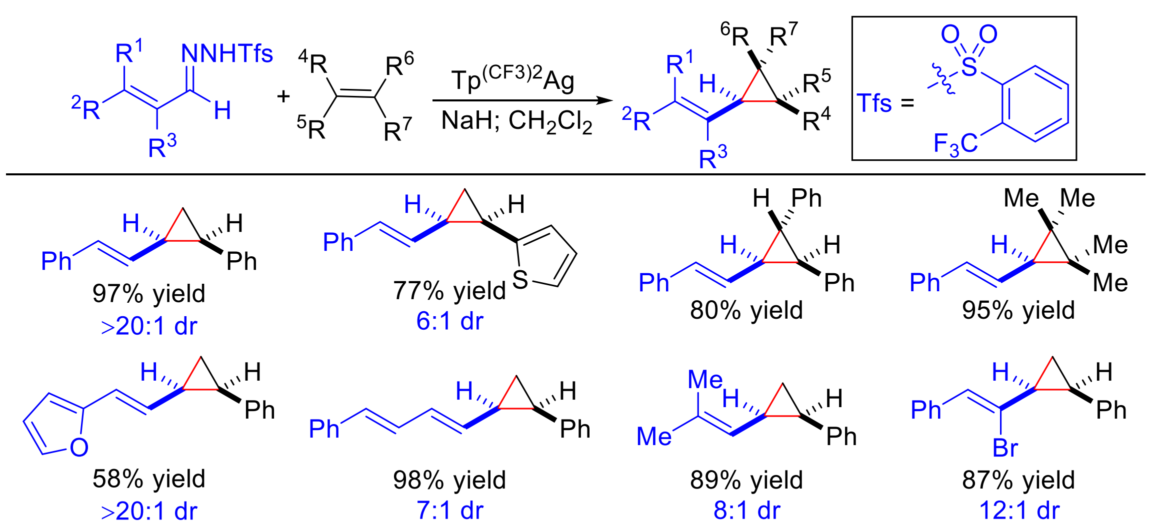
Inspired by the application of vinyl-*N*-tosylhydrazones as diazo precursors, Aggarwal and coworkers developed the [Fe(TPP)Cl]-catalyzed diastereoselective synthesis of cyclopropane amino acids using in situ-generated vinyldiazomethanes from corresponding vinyl-*N*-tosylhydrazone salts (Scheme 1.10).[17] The desired vinylcyclopropane products could be generated in high yields favoring the formation of (*Z*)-cyclopropanes. Even though the dehydroamino acids are not considered to be nucleophilic alkene substrates, [Fe(TPP)Cl] catalyst has exhibited high efficiency in catalyzing the desired cyclopropanation reaction, precluding the potential diazo dimerization process. Later, Charette and coworkers also reported two examples of [Fe(TPP)Cl]-catalyzed olefin cyclopropanation of in situ-generated vinyldiazomethanes from corresponding vinyl-*N*-nosylhydrazones, leading to the formation of vinylcyclopropanes in high yields with excellent diastereoselectivities.[18]

Scheme 1.10. [Fe(TPP)Cl]-Catalyzed Diastereoselective Cyclopropanation of Dehydroamino Acids with Vinyl-*N*-Tosylhydrazone Salts



Recently, Bi and coworkers have achieved a stereoselective vinylcyclopropanation of alkenes by the combination of easily decomposable vinyl-*N*-triftosylhydrazones and weakly coordinated silver catalysis, in which the inherent propensity of vinyl-*N*-sulfonylhydrazones to undergo intramolecular cyclization towards pyrazoles was suppressed (Scheme 1.11).[19] The practicality of this methodology has been demonstrated by its broad substrate scope, high product yields, and excellent *cis*-diastereoselectivity. It is worth noting that the highly electrophilic silver vinylcarbenoid species were engaged in

Scheme 1.11. Silver-Catalyzed Diastereoselective Cyclopropanation of Alkenes with Vinyl-*N*-Triftosylhydrazones

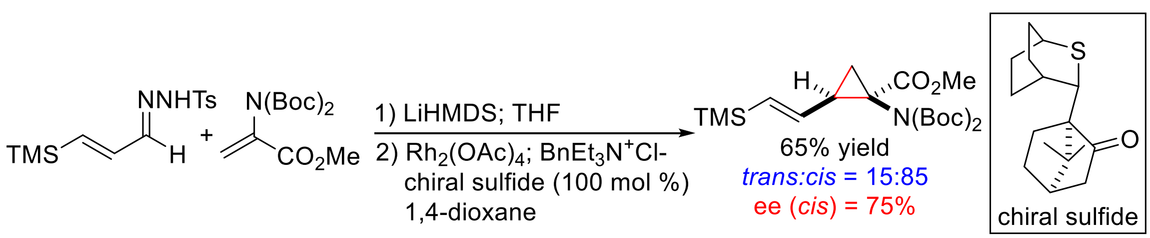


this transformation, restricted the alkene substrates to be electron-rich olefins.

1.3.3. Asymmetric Synthesis of Vinylcyclopropanes from In Situ-Generated Vinyldiazomethanes

While tremendous effort has been made for the stereoselective olefin cyclopropanation of in situ-generated α-vinyldiazomethanes, there are few reports on the asymmetric version of this transformation. Aggarwal and coworkers have reported one example using in situ-generated α-vinyldiazomethane from vinyl-*N*-tosylhydrazone for the Rh(II)-catalyzed asymmetric synthesis of vinylcyclopropyl amino acid (Scheme 1.12).[20] The vinylcyclopropane was generated in moderate yield favoring the *cis*-isomer with good enantioselectivity. This silane-containing product also provides a very useful handle for the incorporation of alternative functional groups onto the cyclopropane ring and will allow access to other conformationally locked amino acids.

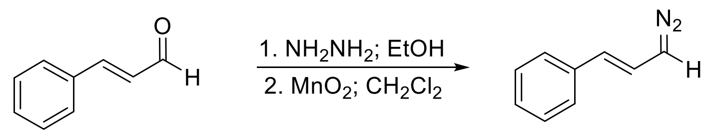
Scheme 1.12. Rhodium-Catalyzed Asymmetric Synthesis of Vinylcyclopropyl Amino Acids from In Situ-Generated α-Vinyldiazomethanes



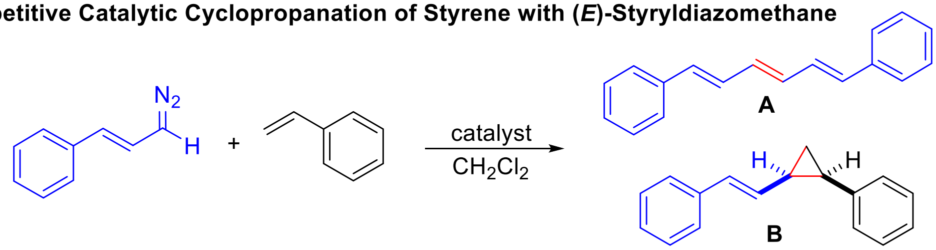
Doyle and coworkers have also observed reactivity associated with α-styryldiazomethane towards the formation of chiral cyclopropane in metal-catalyzed asymmetric cyclopropanation of styrene (Scheme 1.13).[21] In this case, the α-vinyldiazomethane was freshly prepared from cinnamaldehyde and then added to the reaction mixture containing styrene and catalyst. Regardless of the metal catalyst used, vinylcyclopropane could only be generated in trace amount favoring the *cis*-isomer with low enantioselectivity. On the other hand, trienes were observed as the other product of the carbene coupling process.

Scheme 1.13. Rhodium-Catalyzed Asymmetric Synthesis of Vinylcyclopropanes from Styryldiazomethanes

A. Synthesis of (*E*)-Styryldiazomethane



B. Competitive Catalytic Cyclopropanation of Styrene with (*E*)-Styryldiazomethane



catalyst	yield of A + B	A:B	B(*cis*):B(*trans*)	ee of B(*cis*)
$Rh_2(OAc)_4$	50%	92:8	7	N/A
$Cu(MeCN)_4PF_6$	57%	8:92	22	N/A
$CuPF_6$/bis(oxazoline)	17%	12:88	14	25%
Rh_2(*S*-DOSP)$_4$	15%	20:80	9	16%

1.4. SUMMARY AND OUTLOOK

Cyclopropanation of alkynyl- and vinyl-substituted diazo compounds provide a generally useful synthetic method for the stereoselective synthesis of valuable alkynyl- and vinylcyclopropanes which not only widely exist in drug molecules but also serve as important synthetic handles in organic synthesis. Chiral alkynylcyclopropanes have been successfully synthesized from olefin cyclopropanation of either alkynyldiazoacetates or in situ-generated alkynyldiazomethanes in high yields with excellent stereoselectivities. While donor/acceptor-substituted vinyl diazo compounds including vinyldiazolactones and vinyldiazoacetates have been employed as carbene precursors for asymmetric cyclopropanation, donor-substituted diazo compounds α-vinyldiazomethanes, on the other hand, have been scarcely explored. It would be highly desirable to develop a new catalytic system for asymmetric cyclopropanation of alkenes with α-vinyldiazomethanes for the stereoselective construction of valuable vinylcyclopropanes. Considering the ubiquity of chiral alkynyl- and vinylcyclopropanes, we believe the development of asymmetric olefin cyclopropanation processes involving alkynyl- and vinyldiazomethane will find useful applications in organic synthesis.

1.5. REFERENCES

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CHAPTER 2

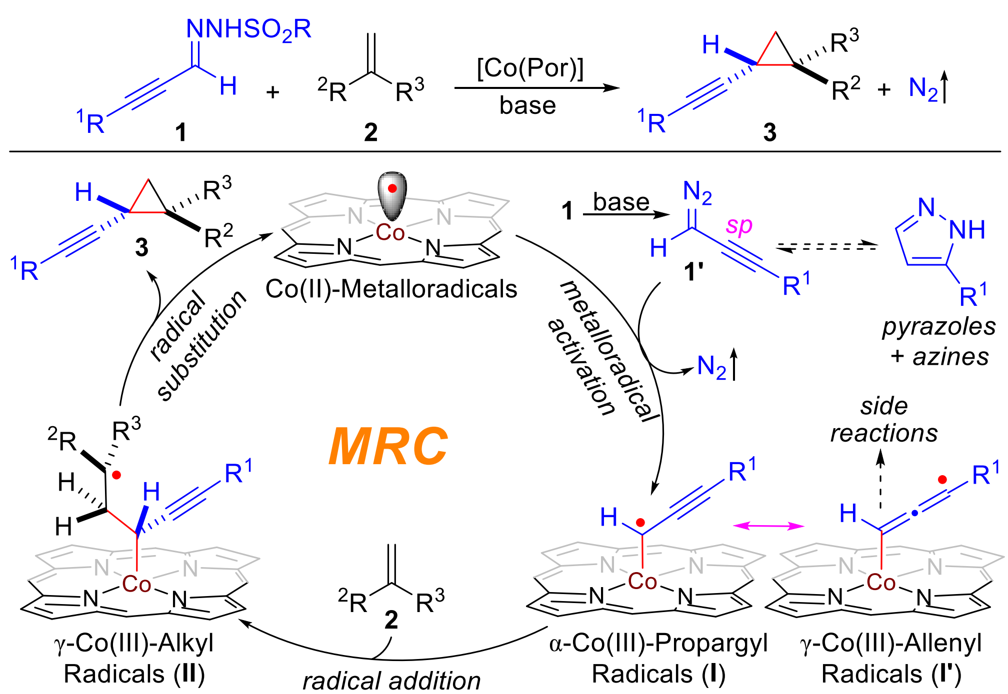
METALLORADICAL ACTIVATION OF IN SITU-GENERATED α-ALKYNYLDIAZOMETHANES FOR ASYMMETRIC RADICAL CYCLOPROPANATION OF ALKENES

(Portions of this chapter have appeared in the publication: Ke, J.; Lee, W.-C.; Wang, X.-X.; Wang, Y.; Wen, X.; Zhang, X. P. *J. Am. Chem. Soc.* **2022**, *144*, 2368–2378)

2.1. INTRODUCTION

Radical reactions have been increasingly exploited as complementary synthetic methods to ionic reactions in modern organic synthesis as they enjoy intrinsic attributes such as high reactivity and tolerance of functional groups.[1] Among significant challenges facing this endeavor is the control of reactivity as well as selectivities in the reactions of free organic radicals, especially enantioselectivity.[2] Rising to these challenges, metalloradical catalysis (MRC) has emerged as a conceptually new approach to the development of stereoselective radical reactions through the catalytic generation of metal-supported organic radicals as key catalytic intermediates.[3,4,5] As stable 15e-metalloradicals with well-defined low-spin d^7-configuration, Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have been recognized as a family of open-shell catalysts that are effective for asymmetric cyclopropanation of alkenes with diazo compounds.[6] During the Co(II)-catalyzed cyclopropanation, the initially-generated α-metalloalkyl radical intermediates from metalloradical activation of diazo compounds, which are centrally situated inside the pocket-like environment of the chiral porphyrin ligands,[7] can be precisely governed to perform a sequence of homolytic reactions such as radical addition and radical substitution with olefin substrates, leading to the productive formation of cyclopropanes with effective control of diastereoselectivity and enantioselectivity. Except for a few recent examples of using α-aryldiazomethanes,[8] Co(II)-based radical cyclopropanation has so far been mostly involved with the use of acceptor- and acceptor/acceptor-substituted diazo compounds as metalloradicophiles. In all the previous cases, the key α-Co(III)-supported C-centered radical intermediates are stabilized by C(sp^2)-based carbonyl or aryl substituents through potential H-bonding interactions with the amide units of the catalyst, facilitating the reactivity and stereoselectivity of the catalytic radical process. It was unclear if Co(II)-based metalloradical system could also apply to other types of diazo compounds with substituents beyond C(sp^2)-based carbonyl and aryl groups. Specifically, we were intrigued to learn whether α-alkynyldiazomethanes, a common type of diazo compounds containing C(sp)-based alkynyl substituents, could be employed as potential

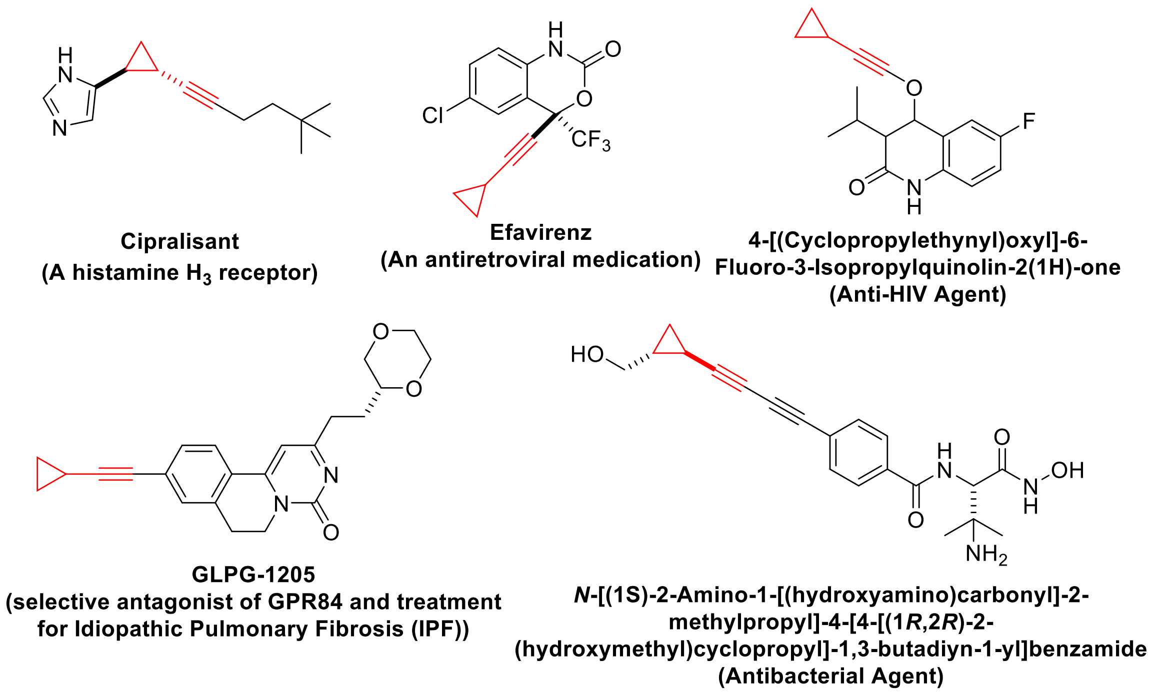
Scheme 2.1. Proposed Pathway for Radical Cyclopropanation of Alkenes with α-Alkynyldiazomethanes via Co(II)-MRC



metalloradicophiles by Co(II)-based metalloradical system for radical olefin cyclopropanation (Scheme 2.1).

As α-alkynyldiazomethanes **1'** are typically generated in situ from the corresponding hydrazones **1** under basic conditions,[9] it would be crucially important to match the rates between the diazomethane generation and the ensuing metalloradical activation to preclude their thermal decomposition to form pyrazole and azine side products. Apart from the concern with the effectiveness of metalloradical activation of α-alkynyldiazomethanes **1'**, an additional issue of regioselectivity could arise from two potential reactivity modes of the resulting α-metalloalkyl radical intermediates that are associated with the two resonance forms of α-Co(III)-propargyl radicals **I** and γ-Co(III)-allenyl radicals **I'**.[10] Furthermore, in the absence of the aforementioned H-bonding interactions, what elements could be utilized during the subsequent radical addition of the initially-generated α-Co(III)-propargyl radicals **I** to the olefin substrates to control the enantioselectivity for the first C–C bond formation? What also under question is the control of chemoselectivity as well as the diastereoselectivity during the final step of radical substitution of γ-Co(III)-alkyl radicals **II** for the second C–C bond formation. Considering the presence of the C≡C triple bond, could γ-Co(III)-alkyl radicals **II** undergo the desired *3-exo-tet* radical cyclization chemoselectively over the potentially competitive *4-exo-dig* and *5-endo-dig* cyclization, leading to diastereoselective construction of cyclopropanes? We hoped to address these and related issues through judicious development of Co(II)-based metalloradical catalyst by fine-tuning the environments of D_2-symmetric chiral amidoporphyrin ligand. If implemented successfully, it would lead to the development of a new catalytic radical process for asymmetric olefin cyclopropanation with in situ-generated α-alkynyl-

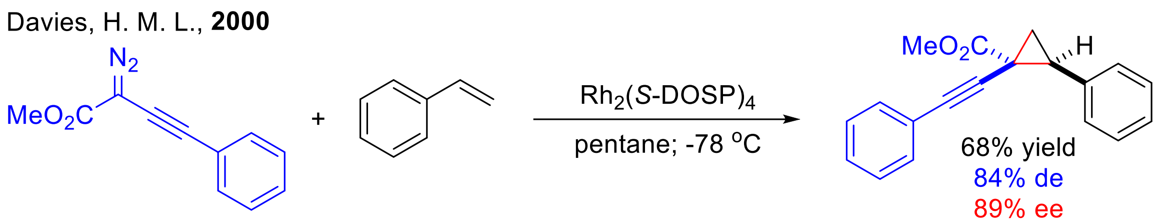
Figure 2.1. Selected Examples of Important Bioactive Compounds Containing Alkynyl Cyclopropane Motifs



diazomethanes to construct chiral alkynyl cyclopropanes. In addition to serving as useful intermediates for stereoselective organic synthesis, chiral alkynyl cyclopropanes occur as common substructures in many important natural products and drug molecules (Figure 2.1).[11]

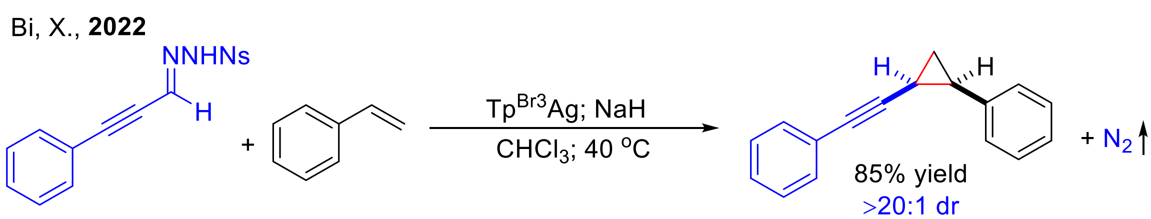
Metal-catalyzed asymmetric cyclopropanation of alkenes with α-alkynyldiazomethanes offers a potentially general approach for stereoselective construction of valuable chiral alkynyl cyclopropanes.[12,13,14] While donor/acceptor-substituted diazo compounds alkynyldiazoacetates were successfully employed by Davies and coworkers as carbene precursors for Rh_2-catalyzed asymmetric cyclopropanation (Scheme 2.2),[15] donor-substituted diazo compounds α-alkynyldiazomethanes, on the other hand, have been scarcely explored.[16]

Scheme 2.2. Enantioselective Cyclopropanation of Alkene with Alkynyldiazoacetate



The only examples of cyclopropanation with the use of α-alkynyldiazomethane were reported by Bi and coworkers who developed a Ag-based catalytic system for the diastereoselective synthesis of alkynyl cyclopropanes involving alkynyl *N*-nosylhydrazones as alkynyl carbene precursors (Scheme 2.3).[16c,16d] This underdevelopment is mainly attributed to the inherent propensity of α-alkynyldiazomethanes toward the formation of the stable aromatic pyrazoles.[17]

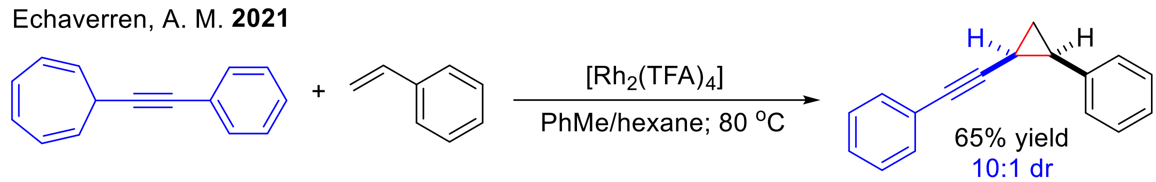
Scheme 2.3. Silver-Catalyzed Cyclopropanation of Alkenes with Alkynyl *N*-Nosylhydrazones



To circumvent the problem, Echavarren and coworkers recently reported an innovative two-step approach for the synthesis of alkynyl cyclopropanes from alkenes based on Rh_2-catalyzed decarbenation of 7-alkynyl cycloheptatrienes as alkynylcarbene precursors (Scheme 2.4).[18]

To the best of our knowledge, there has been no previous report on the catalytic system for asymmetric olefin cyclopropanation with α-alkynyldiazomethanes for stereoselective

Scheme 2.4. Rh(II)-Catalyzed Alkynylcyclopropanation of Alkenes by Decarbenation of Alkynylcycloheptatrienes



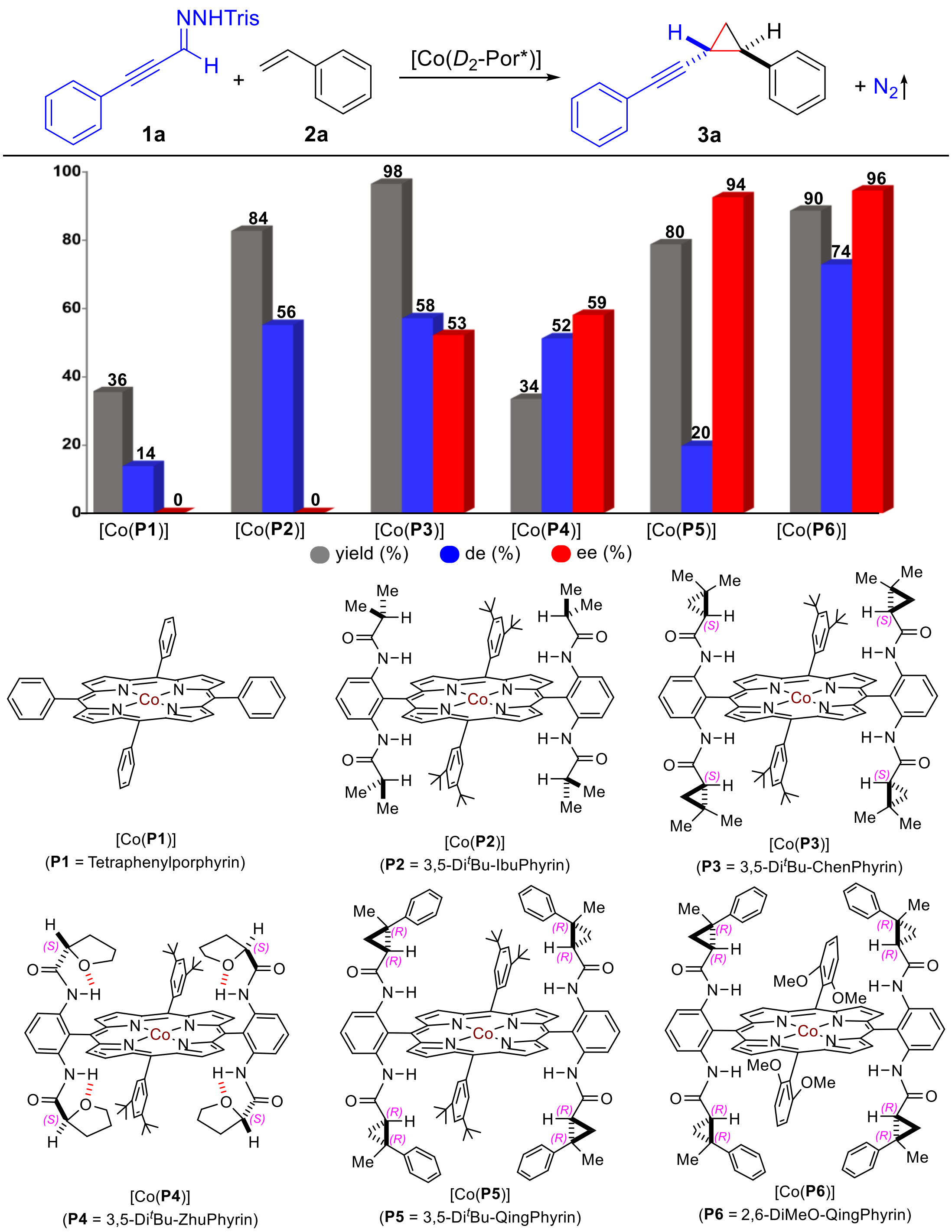
synthesis of chiral alkynyl cyclopropanes. As a new application of Co(II)-based metalloradical catalysis (MRC), we herein report the development of the first asymmetric catalytic system for olefin cyclopropanation that can effectively utilize α-alkynyldiazomethanes through in situ-generation from the corresponding sulfonyl hydrazones in the presence of a base. Through the identification of an optimal D_2-symmetric chiral amidoporphyrin (D_2-Por*) as the supporting ligand, the Co(II)-based catalytic system is capable of efficiently activating different alkynyldiazomethanes at room temperature to cyclopropanate a wide range of alkenes with varied electronic and steric properties, delivering alkynyl cyclopropanes in high yields with excellent control of both diastereoselectivity and enantioselectivity. We show the importance of catalyst development through fine-tuning of the ligand environment in achieving high reactivity as well as stereoselectivities. We present combined computational and experimental studies that shed light on the underlying stepwise radical mechanism of the Co(II)-catalyzed cyclopropanation. To demonstrate synthetic applications of the new catalytic system, we showcase several examples of stereoselective transformations of the resulting enantioenriched alkynyl cyclopropanes.

2.2. RESULTS AND DISCUSSION

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

At the outset of the project, α-(phenylethynyl)diazomethane (**1a'**), which was in situ generated from the corresponding trisylhydrazone **1a** in the presence of KH, was designated as the representative α-alkynyldiazomethane for asymmetric radical cyclopropanation of styrene (**2a**) using Co(II)-based metalloradical catalysts [Co(Por)] (Scheme 2.5). It was found that simple achiral metalloradical catalyst [Co(**P1**)] (**P1** = tetraphenylporphyrin) could activate the diazo compound to cyclopropanate styrene, giving the desired alkynyl cyclopropane **3a** in low yield (36%) with inferior control of diastereoselectivity (14% de). With the employment of the Co(II) complex of D_{2h}-symmetric achiral amidoporphyrin [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin) as the catalyst,[19] the catalytic cyclopropanation reaction was significantly enhanced, forming cyclopropane **3a** in higher yield (84%) with improved diastereoselectivity (56% de) in favor of the *trans*-isomer. To evaluate the feasibility of asymmetric induction during the catalytic process, Co(II) complexes of D_2-symmetric chiral amidoporphyrins were employed as the catalysts. When first-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)[6a] was used, the catalytic reaction produced cyclopropane **3a** in almost quantitative yield (98%) with the same level of diastereoselectivity (58% de) while exhibiting significant enantioselectivity (53% ee). To improve the stereoselectivities of the catalytic process, we then applied metalloradical catalyst [Co(**P4**)] (**P4** = 3,5-Di^{t}Bu-ZhuPhyrin),[20] which is devised to achieve conformational rigidity through unique intramolecular H-bonding interaction in (*S*)-(–)-2-tetrahydrofurancarboxamide units. As

Scheme 2.5. Ligand Effect on Co(II)-Based Catalytic System for Olefin Cyclopropanation with α-Alkynyldiazomethane



[a]Carried out with 1a (0.10 mmol) and 2a (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(Por)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric excess (de) determined by ^{1}H NMR; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC.

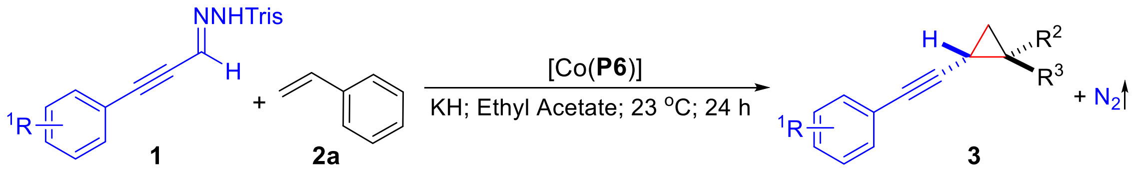
expected, the catalytic reaction by [Co(**P4**)] brought about improved enantioselectivity (59% ee) but reduced diastereoselectivity (52% de) and significantly decreased yield (34%) as a result of the more sterically-encumbered ligand environment. These results prompted us to explore second-generation chiral metalloradical catalysts bearing cyclopropanecarboxyamides with two contiguous stereogenic centers in the hope of further enhancing the asymmetric induction of the catalytic process. Gratifyingly, when [Co(**P5**)] (**P5** = 3,5-Di^{t}Bu-QingPhyrin) was used as the catalyst for the reaction,[6g] cyclopropane **3a** was produced in high yield (80%) with excellent enantioselectivity (94% ee) albeit with low diastereoselectivity (20% de). Inspired by this positive outcome, we then employed the analogous catalyst [Co(**P6**)] (**P6** = 2,6-DiMeO-QingPhyrin) bearing the same chiral amide units but with different achiral *meso*-aryl groups to further enhance the rigidity of the chiral environment. To our delight, the catalytic reaction by [Co(**P6**)] indeed improved both diastereoselectivity (74% de) and yield (90%) significantly while maintaining the excellent enantioselectivity (96% ee). The remarkable difference in performance among the metalloradical catalysts indicates that subtle alteration in the ligand environment can give rise to significant improvement in catalytic reactivity as well as stereoselectivities, manifesting the effectiveness of catalyst development in controlling the radical process.

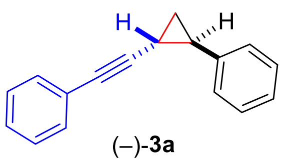
2.2.2. Asymmetric Radical Cyclopropanation of Styrene with Different α-Alkynyldiazomethanes

Under the optimized conditions, the scope and versatility of [Co(**P6**)]-catalyzed asymmetric cyclopropanation were evaluated using different α-alkynyldiazomethanes through in situ generation from the corresponding sulfonyl hydrazones **1** under the basic condition with various olefins (Table 2.1). Similar to α-alkynyldiazomethane **1a’** (entry 1), α-(arylethynyl)diazomethanes bearing substituents with varied electronic and steric properties on the phenyl group could be effectively employed as metalloradicophiles for the Co(II)-based catalytic system as shown for asymmetric cyclopropanation of styrene (**2a**) as the representative olefin substrate. For example, α-(arylethynyl)diazomethanes bearing alkyl substituents at different aryl positions such as *p*-Me and *o*-iPr could be efficiently activated by [Co(**P6**)] at room temperature to cyclopropanate styrene, producing the desired alkynyl cyclopropanes **3b** and **3c** in high yields with good diastereoselectivities and excellent enantioselectivities (entries 2 and 3). Furthermore, [Co(**P6**)] could activate α-(arylethynyl)diazomethanes containing electron-donating –OMe group at all the three different positions of the aryl group for the cyclopropanation reaction, allowing stereoselective construction of corresponding alkynyl cyclopropanes **3d**–**3f** in high yields with high diastereoselectivities and excellent enantioselectivities (entries 4–6). It is interesting to note that the observed diastereoselectivity increases when the position of MeO-substituent in cyclopropanes **3d**–**3f** moves from *para*- to *meta*- to *ortho*-position. Likewise, α-(arylethynyl)diazomethanes bearing electron-withdrawing groups could also be suitable metalloradicophiles as exemplified by the asymmetric synthesis of alkynyl cyclopropanes **3g** and **3h** in high yields with excellent control of stereoselectivities (entries 7 and 8). Moreover, naphthalene-containing α-alkynyldiazomethanes could also be effectively activated by [Co(**P6**)] under the same conditions for asymmetric cyclopropanation reaction, leading to the high-yielding formation of the corresponding alkynyl cyclopropane **3i** with both high diastereoselectivity and enantioselectivity (entry 9).

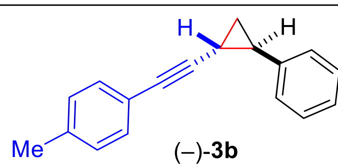
In addition to α-(arylethynyl)diazomethanes, the Co(II)-based metalloradical system was shown to apply to α-alkynyldiazomethanes containing certain non-aryl substituents

Table 2.1. Asymmetric Radical Cyclopropanation of Styrene with Different In Situ-Generated α-Alkynyldiazomethanes by [Co(P6)][a]

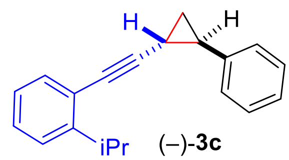




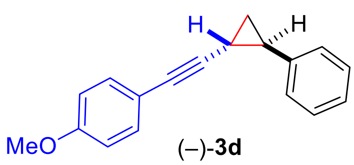
(–)-**3a**
entry 1: 90% yield
87:13 dr; 96% ee



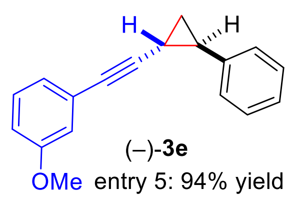
(–)-**3b**
entry 2: 90% yield
79:21 dr; 97% ee



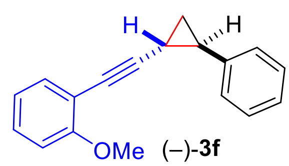
(–)-**3c**
entry 3: 90% yield
96:4 dr; 99% ee



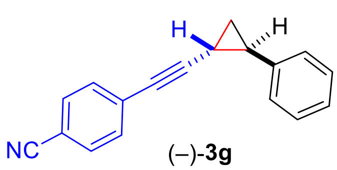
(–)-**3d**
entry 4: 90% yield
85:15 dr; 98% ee



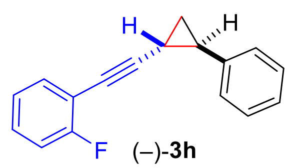
(–)-**3e**
entry 5: 94% yield
90:10 dr; 99% ee



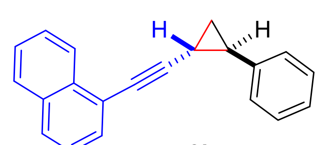
(–)-**3f**
entry 6: 99% yield
94:6 dr; 95% ee



(–)-**3g**
entry 7: 94% yield
90:10 dr; 90% ee



(–)-**3h**
entry 8: 90% yield
93:7 dr; 98% ee

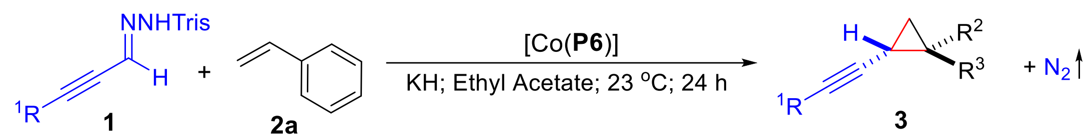


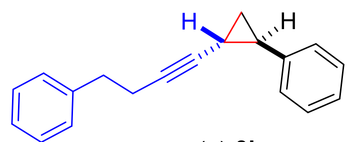
(–)-**3i**
entry 9: 95% yield
80:20 dr; 90% ee

[a]Carried out with **1** (0.10 mmol) and **2a** (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(**P6**)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC.

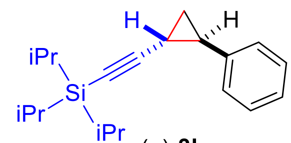
(Table 2.2). As demonstrated by catalytic asymmetric cyclopropanation of styrene with alkyl-substituted diazo derivative, desired cyclopropane **3j** can be generated with high stereoselectivities albeit in moderate yield (entry 1). Moreover, triisopropylsilyl (TIPS) substituted diazo derivative can also serve as a suitable substrate, furnishing the corresponding cyclopropane **3k** in good yield with high diastereoselectivity and enantioselectivity (entry 2).

Table 2.2. Asymmetric Radical Cyclopropanation of Styrene with In Situ-Generated α-Alkynyldiazomethanes containing non-aryl substituents by [Co(P6)][a]





(–)-**3j**
entry 1: 41% yield
91:9 dr; 85% ee



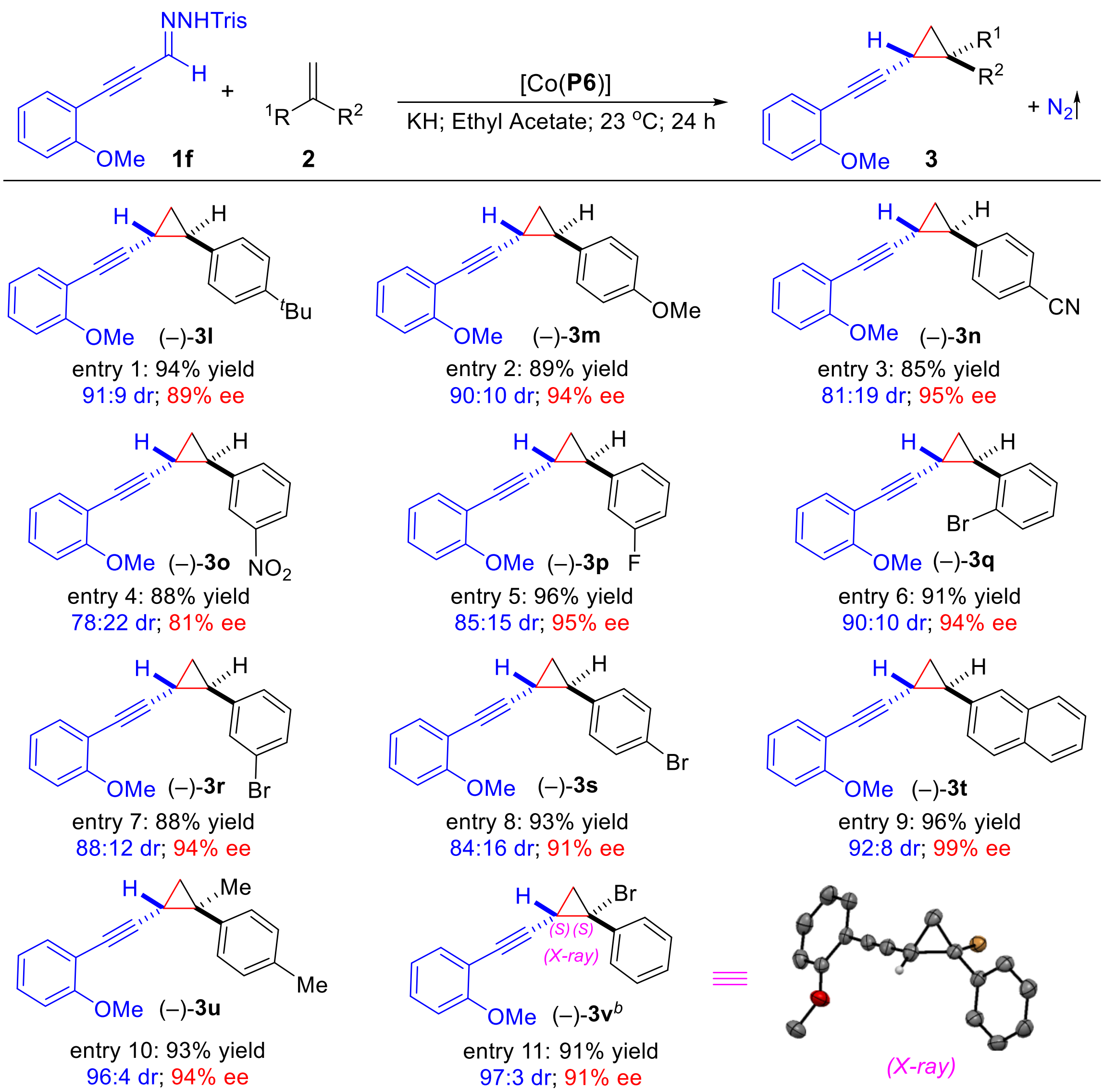
(–)-**3k**
entry 2: 71% yield
96:4 dr; 87% ee

[a]Carried out with **1** (0.10 mmol) and **2a** (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(**P6**)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC.

2.2.3. Asymmetric Radical Cyclopropanation of Different Alkenes with α-(Phenylethynyl)diazomethane

In addition to being capable of using different α-alkynyldiazomethanes, the Co(II)-based system for asymmetric cyclopropanation was found to be suitable for a wide range of alkenes under the optimized conditions (Table 2.3). Like styrene, its derivatives bearing various substituents such as –*tert*-Bu, –OMe, –CN, and –NO_2 groups at different positions could be reliably cyclopropanated by [Co(**P6**)] with α-alkynyldiazomethane **1f'**, generating the corresponding alkynyl cyclopropanes **3l**–**3o** in similarly high yields with effective control of diastereoselectivities and enantioselectivities (entries 1–4). Additionally, halogenated aromatic olefins could also serve as suitable substrates in [Co(**P6**)]-catalyzed asymmetric cyclopropanation as exemplified by the highly stereoselective generation of alkynyl cyclopropanes **3p**–**3s** with halogen atoms at various positions (entries 5–8). Furthermore, extended aromatic olefins like 2-vinylnaphthalene could be also effectively

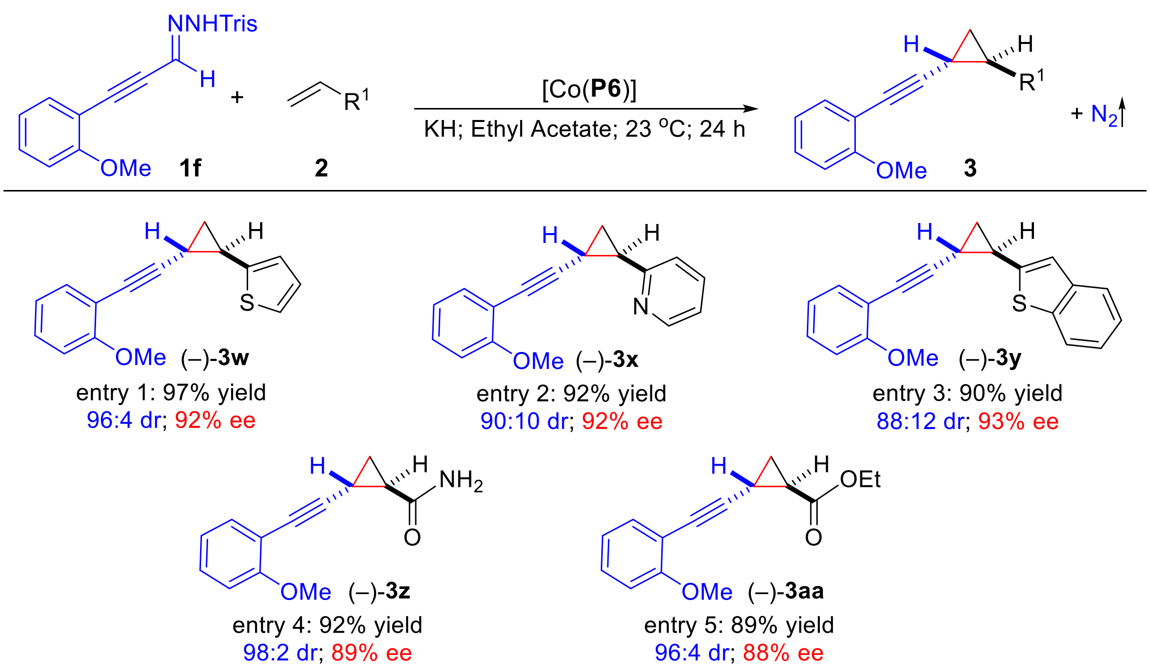
Table 2.3. Asymmetric Radical Cyclopropanation of Styrene Derivatives with In Situ-Generated α-Alkynyldiazomethane by [Co(P6)][a]



[a]Carried out with **1f** (0.10 mmol) and **2** (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(**P6**)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC. [b]Absolute configuration determined by X-ray crystallography.

applied to the catalytic system, affording alkynyl cyclopropane **3t** in excellent yield with high diastereoselectivity and outstanding enantioselectivity (entry 9). In addition to mono-substituted olefins, 1,1-disubstituted olefins like α-methylstyrene and α-bromostyrene could serve as suitable substrates as well, allowing for highly stereoselective construction of trisubstituted cyclopropanes **3u** and **3v** with excellent control of the newly-generated quaternary carbon stereogenic centers (entries 10 and 11). The absolute configuration of the major enantiomer of alkynyl cyclopropane **3v** was established as (*S*,*S*) by X-ray crystallography.

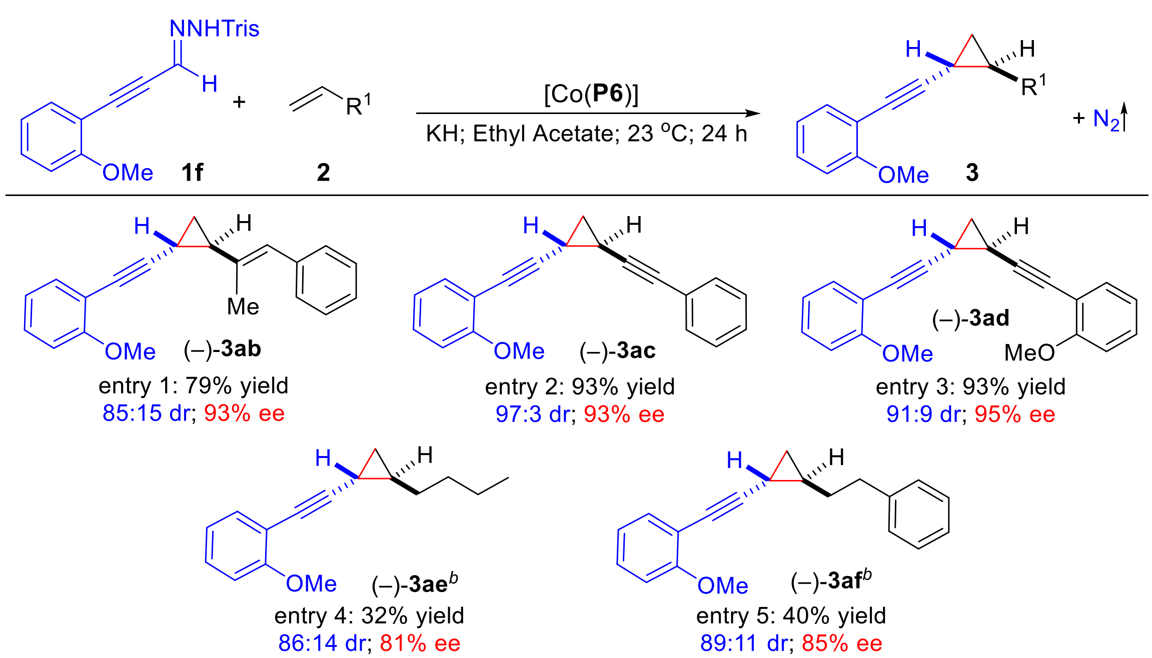
Table 2.4. Asymmetric Radical Cyclopropanation of Heteroaromatic Olefins and Electron Deficient Olefins with In Situ-Generated α-Alkynyldiazomethane by [Co(P6)][a]



[a]Carried out with **1f** (0.10 mmol) and **2** (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(**P6**)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC.

Moreover, the Co(II)-based cyclopropanation was shown to be compatible with heteroaryl alkenes such as those containing thiophene, pyridine, and benzothiophene, affording the corresponding heteroaryl cyclopropanes **3w**–**3y** in high yields with high stereoselectivities (Table 2.4; entries 1–3). To further highlight the unique feature of Co(II)-based metalloradical catalysis, even electron-deficient olefins such as acrylamide and ethyl acrylate, which are challenging substrates for catalytic cyclopropanation systems involving electrophilic metallocarbene intermediates, could be effectively cyclopropanated by [Co(**P6**)] to form the desired products **3z** and **3aa** in high yields with high stereoselectivities (entries 4 and 5).

Table 2.5. Asymmetric Radical Cyclopropanation of Aliphatic Olefins with In Situ-Generated α-Alkynyldiazomethane by [Co(P6)][a]



[a]Carried out with **1f** (0.10 mmol) and **2** (0.20 mmol) in the presence of KH (0.40 mmol) by [Co(**P6**)] (2 mol %) in ethyl acetate (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylbenzene sulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of *trans*-isomer determined by chiral HPLC. [b]Carried out with **2** (1.00 mmol) at 80 °C.

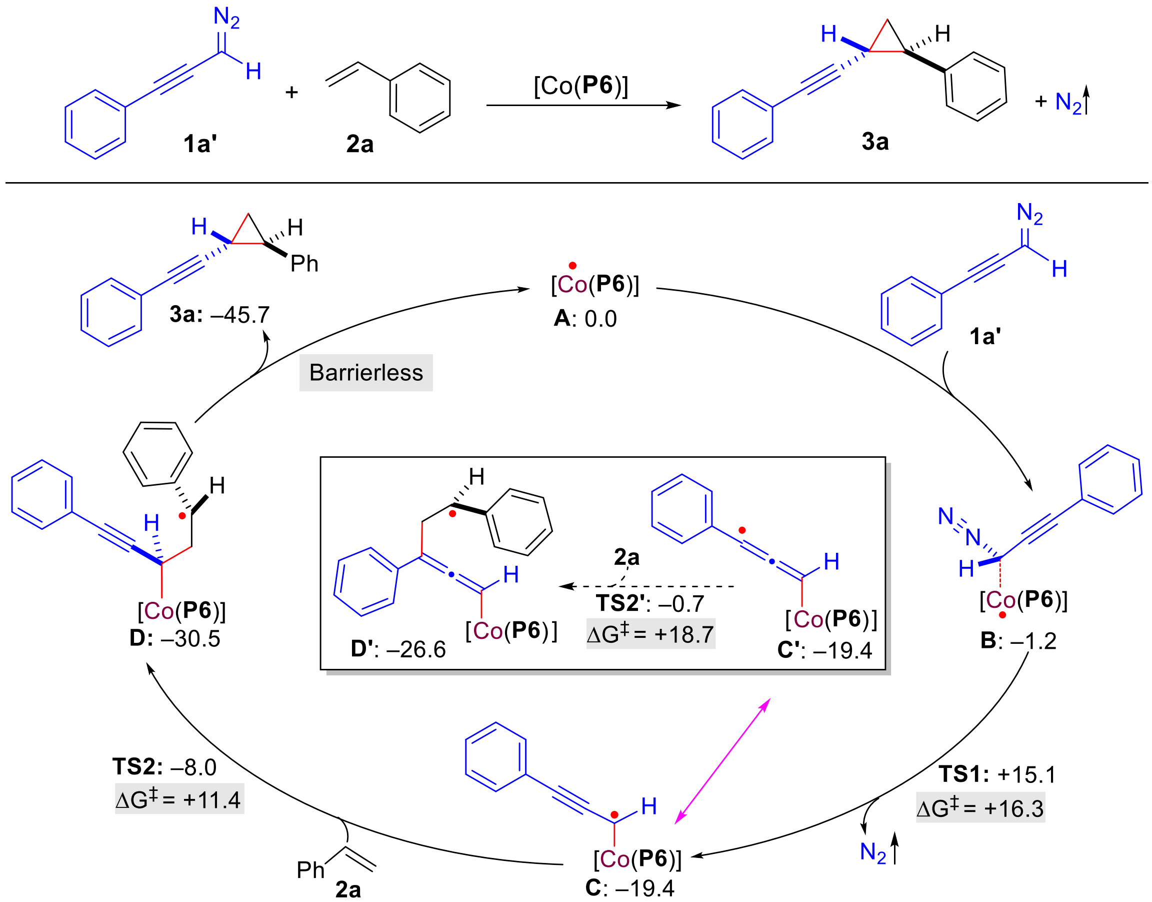
When conjugated dienes and enynes were used as the substrates, [Co(**P6**)] could regio- and chemo-selectively cyclopropanate the terminal double bonds, leading to the exclusive formation of cyclopropanes **3ab**–**3ad** in high yields with high stereoselectivities without affecting the internal alkene and alkyne units (Table 2.5; entries 1–3). It is interesting to note the C_2-symmetric structure of bisalkynyl cyclopropane **3ad**. Notably, [Co(**P6**)]-based catalytic system proved to be even more effective for asymmetric cyclopropanation of unactivated alkyl-substituted olefins, affording alkynylcyclopropanes **3ae** and **3af** in moderate yields with high stereoselectivities (entries 4 and 5).

2.2.4. Mechanistic Studies on Co(II)-Catalyzed Radical Olefin Cyclopropanation with α-Alkynyldiazomethanes

Combined computational and experimental studies were performed to shed light on the underlying stepwise radical mechanism of the Co(II)-based catalytic system for asymmetric cyclopropanation (Scheme 2.1). Firstly, density functional theory (DFT) calculations were conducted to examine the details of the catalytic pathway and associated energetics for asymmetric cyclopropanation of styrene (**2a**) with (phenylethynyl)diazomethane (**1a'**) by metalloradical catalyst [Co(**P6**)] (**A**) (Scheme 2.6; see Scheme S2 in Experimental Section for details). The geometry optimizations were performed with the Gaussian 16[21] at the BP86[22]/lanl2dz[23] level of the theory in the gas phase at room temperature. To further improve the accuracy of energies, single-point energies were carried out at B3LYP[24]/def2-tzvp[23] level of theory along with Grimme's dispersion correction[25] (D3BJ) and SMD[26] solvation model (in ethyl acetate).

The DFT calculations reveal the initial formation of intermediate **B** resulting from the binding of diazomethane **1a'** by catalyst [Co(**P6**)] through a network of noncovalent

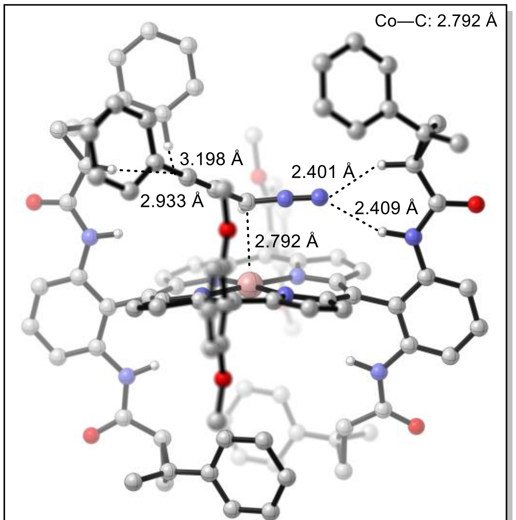
Scheme 2.6. DFT Calculations on Energetics of [Co(P6)]-Catalyzed Cyclopropanation[a]



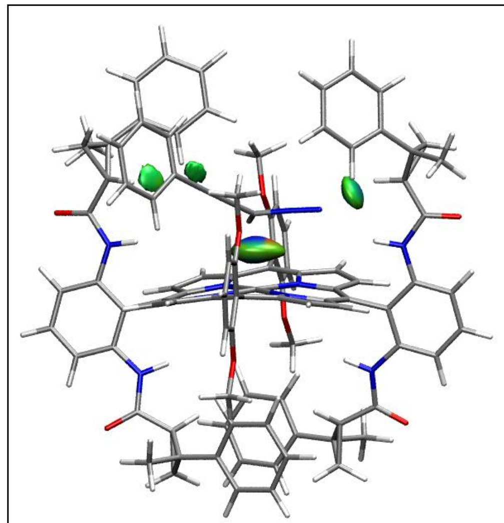
[a]Applied bp86/LANL2DZ for geometry optimization and B3LYP/def2-tzvp for calculations of single point energies (kcal/mol) along with Grimme's dispersion correction and SMD (ethyl acetate) solvation model.

attractive interactions, including H-bonding and π-stacking interactions, as illustrated in the DFT-optimized structure (Figure 2.2; see Scheme S3 in the Experimental Section for details). The binding event, which is slightly exergonic by 1.2 kcal/mol, positions the α-carbon atom of **1a'** in close proximity to the Co(II)-metalloradical center of [Co(**P6**)] (C···Co: ~2.792 Å) for the subsequent activation. The bound diazomethane **1a'** is then further activated by catalyst [Co(**P6**)] to generate α-Co(III)-propargyl radical intermediate **C** with the release of dinitrogen as a byproduct. The metalloradical activation, which is exergonic by 18.2 kcal/mol, is found to be the rate-determining step associated with a

Figure 2.2. DFT-Optimized Models Showing Noncovalent Attractive Interactions of Intermediate B



Intermediate B

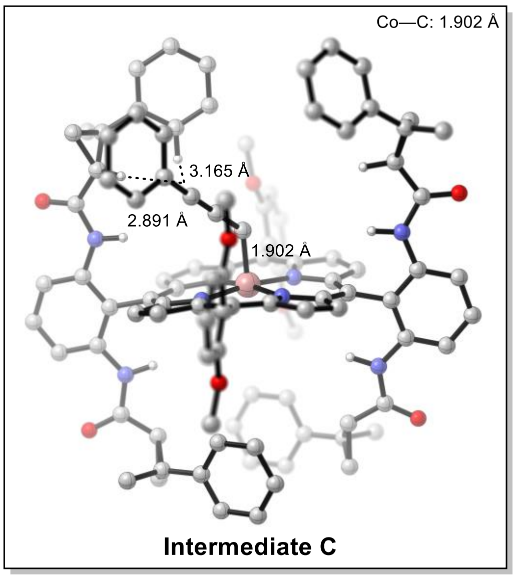

Intermediate B

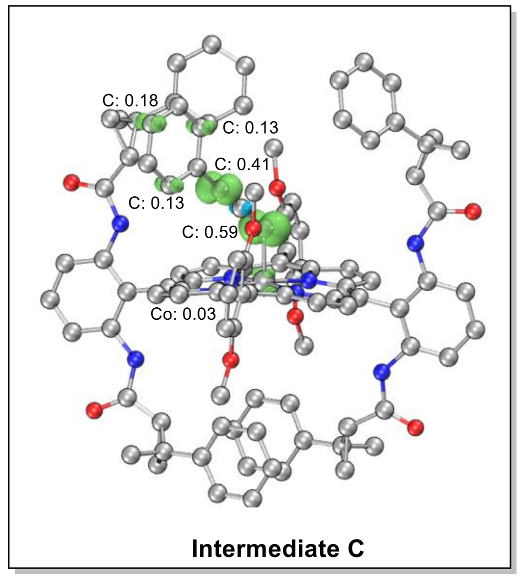
relatively high but accessible activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS1}}$ = 16.3 kcal/mol). As displayed by the spin plot of intermediate **C** (Figure 2.3), the spin density mainly distributes on α- and γ-carbon atoms in similar amounts (α-C: 0.59; γ-C: 0.41; shown as green region), which can be represented as two resonance forms of α-Co(III)-propargyl radical **C** and γ-Co(III)-allenyl radical **C'**.

To rationalize the observed regioselectivity of the catalytic reaction, we calculated the energetics associated with subsequent radical addition to alkene **2a** by both α-Co(III)-propargyl radical form **C** and γ-Co(III)-allenyl radical form **C'**, leading to the formation of γ-Co(III)-benzyl radical intermediate **D** and ε-Co(III)-benzyl radical intermediate **D'**, respectively. DFT calculations indicate radical addition of propargyl radical **C** is more favorable than allenyl radical **C'** both kinetically ($\Delta G^{\ddagger}_{\mathbf{TS2}}$ = 11.4 kcal/mol; $\Delta G^{\ddagger}_{\mathbf{TS2'}}$ = 18.7 kcal/mol) and thermodynamically ($\Delta G^{\circ}_{\mathbf{D}}$ = –11.1 kcal/mol; $\Delta G^{\circ}_{\mathbf{D'}}$ = –7.2 kcal/mol).

According to the DFT calculations, γ-Co(III)-alkyl radical **D** then undergoes radical substitution to produce alkynyl cyclopropane **3a** while regenerating metalloradical catalyst

Figure 2.3. DFT-Optimized Models Showing Spin Density Distribution of Intermediate C

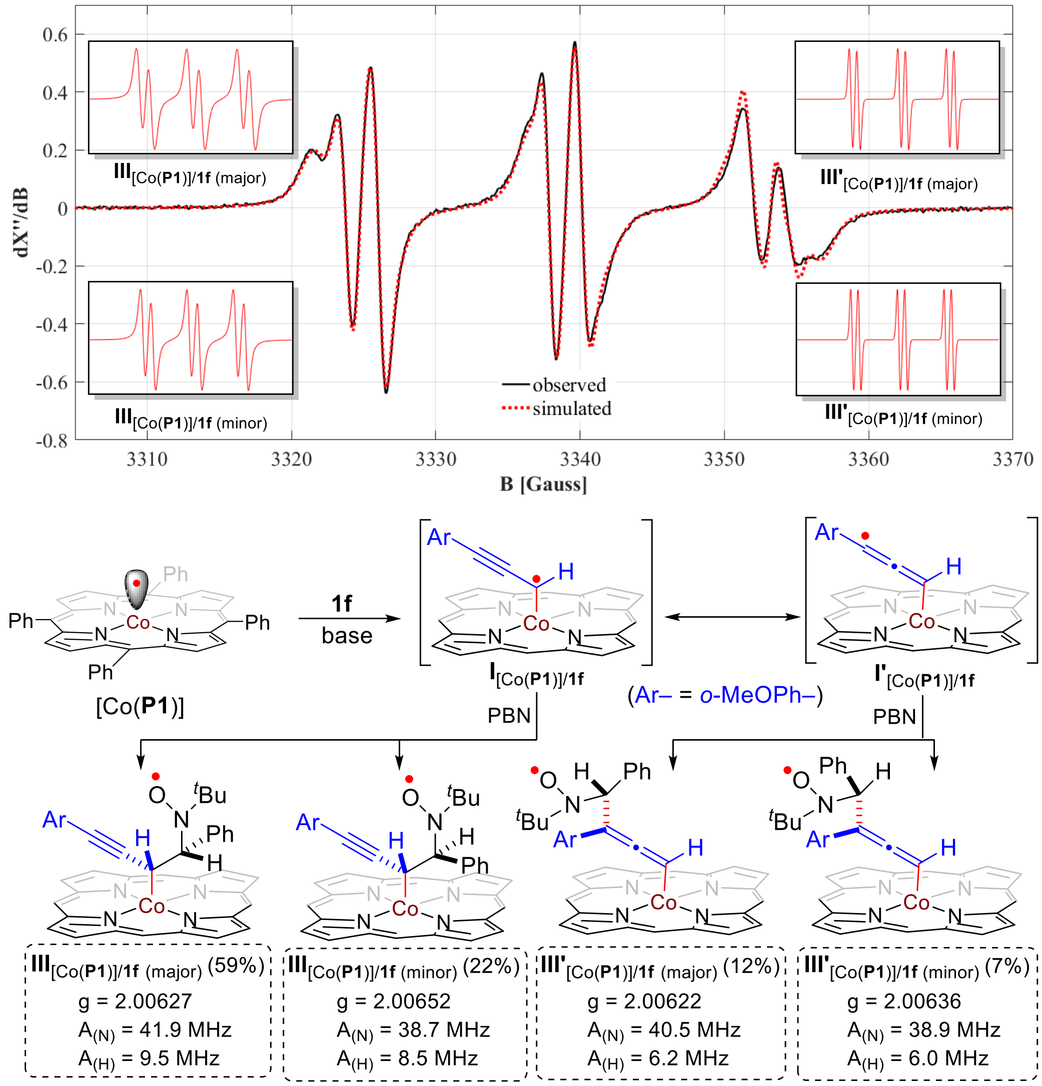




[Co(**P6**)]. This final step of *3-exo-tet* radical cyclization, which is exergonic by 15.2 kcal/mol, is found to be an almost barrierless process. The overall low activation barrier is in accordance with the experimental observation that the catalytic reaction could proceed effectively even at room temperature.

To provide direct evidence for the existence of the key α-Co(III)-propargyl radical intermediate, efforts were made to trap the Co-supported organic radicals for experimental detection and characterization. First, the spin trapping reagent *N*-*tert*-butyl-α-phenylnitrone (PBN) was added to the reaction mixture of alkynyldiazomethane **1f’** with metalloradical catalyst [Co(**P1**)] in the absence of olefin substrate and was then monitored by X- band electron paramagnetic resonance (EPR) spectroscopy at room temperature (Scheme 2.7; see Scheme S1 in Experimental Section for details). The observed isotropic

Scheme 2.7. Trapping of α-Co(III)-Propargyl Radical and γ-Co(III)-Allenyl Radical Intermediates by Spin Trap PBN[a]

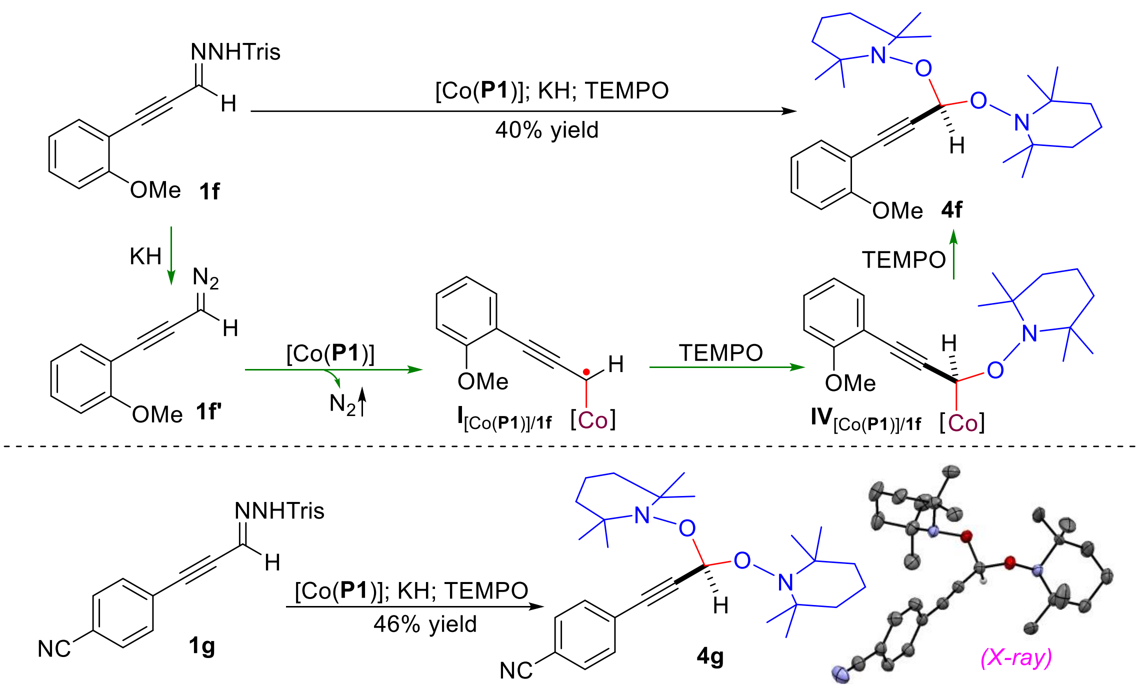


[a]Carried out with **1f** (0.10 mmol), [Co(**P1**)] (2 mol %) and PBN (0.12 mmol) in the presence of Et_3N (0.20 mmol) at 60 °C in benzene (1.0 mL) for 10 min; Ar = 2-methoxyphenyl; The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon.

EPR spectrum exhibits strong signals with the characteristic splitting pattern at a *g*-value of ~2.00, which was taken as the evidence for the formation of radical **III**$_{[Co(\mathbf{P1})]/\mathbf{1f}}$ resulting from PBN trapping of the initially-generated Co(III)-propargyl radical intermediate **I**$_{[Co(\mathbf{P1})]/\mathbf{1f}}$.[27] In accordance with the spin density distribution from DFT calculations (Scheme 2.6), the observed broad spectrum (in black) could be near perfectly simulated (in red) as four well-defined triplet of doublet signals (Scheme 1.7) by involving four isomeric PBN-trapped radical species that are originated from the two resonance forms of α-Co(III)-propargyl radical intermediate $\mathbf{I}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ and γ-Co(III)-allenyl radical intermediate $\mathbf{I'}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ on the basis of the hyperfine coupling by ^{14}N ($I = 1$) and ^{1}H ($I = 1/2$): 81% of O-centered radicals $\mathbf{III}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ from $\mathbf{I}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ as two diastereomers (59% of major diastereomer: g = 2.00627, $A_{(N)}$ = 41.9 MHz, $A_{(H)}$ = 9.5 MHz; 22% of minor diastereomer: g = 2.00652, $A_{(N)}$ = 38.7 MHz, $A_{(H)}$ = 8.5 MHz) and 19% of O-centered radicals $\mathbf{III'}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ from $\mathbf{I'}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ as two diastereomers (12% of major isomer: g = 2.00622, $A_{(N)}$ = 40.5 MHz, $A_{(H)}$ = 6.2 MHz; 7% of minor isomer: g = 2.00636, $A_{(N)}$ = 38.9 MHz, $A_{(H)}$ = 6.0 MHz).

Besides the spectroscopic observation of the key radical intermediate by EPR, significant efforts were devoted to directly trapping α-Co(III)-propargyl radical intermediate by stable TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical for structural characterization (Scheme 2.8). When the metalloradical activation of alkynyldiazomethane **1f'** by [Co(**P1**)] was conducted in the presence of TEMPO without alkene substrates, we were able to isolate product **4f** in 40% yield, which was shown to contain two geminal TEMPO units at the propargylic position. The formation of bis-TEMPO-trapped product **4f** evidently implies the initial generation of α-Co(III)-propargyl radical $\mathbf{I}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$, which was trapped by TEMPO through radical recombination to generate intermediate $\mathbf{IV}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$. Subsequent radical substitution reaction of $\mathbf{IV}_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1f}}$ with a second molecule of TEMPO was likely responsible for the final formation of bis-TEMPO-trapped product **4f** upon the homolytic cleavage of the weak Co(III)−C bond. An analogous TEMPO-trapping experiment was carried out with alkynyldiazomethane **1g**, resulting in the isolation of bis-TEMPO-trapped product **4g** in 46% yield, the structure of which was further confirmed by the X-ray

Scheme 2.8. Trapping of α-Co(III)-Propargyl Radical Intermediates by TEMPO and Characterizations of α,α-Bis-TEMPO-Trapped Products[a]



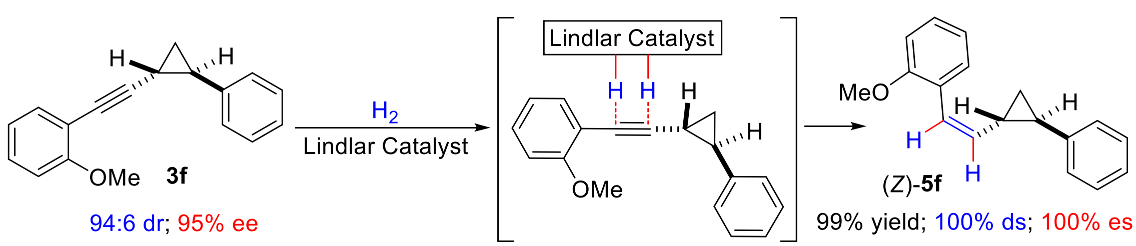
[a]Carried out with **1f** (0.10 mmol), [Co(**P1**)] (2 mol %) and PBN (0.12 mmol) in the presence of Et_3N (0.20 mmol) at 60 ^oC in benzene (1.0 mL) for 10 min; Ar = 2-methoxyphenyl; The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon.

crystallography (Scheme 2.8). In both reactions, α,α-bis-TEMPO-trapped products were exclusively generated from α-Co(III)-propargyl radical intermediate without the formation of α,γ-bis-TEMPO-trapped products from its γ-Co(III)-allenyl radical resonance form. The observed preference of reactivity at the α-propargyl position over the γ-allenyl position is in good accordance with the regioselectivity of the Co(II)-based catalytic system for asymmetric cyclopropanation, which is also supported by the DFT computational studies.

2.2.5. Synthetic Application of Co(II)-Catalyzed Radical Olefin Cyclopropanation with α-Alkynyldiazomethanes

Considering that the resulting enantioenriched alkynyl cyclopropanes contain both versatile C≡C triple bond as well as relatively acidic tertiary C–H bonds on the cyclopropane ring, they may serve as useful intermediates for stereoselective organic synthesis. To this end, we carried out several stereoselective transformations using enantioenriched alkynyl cyclopropanes **3f** (95% ee) and **3a** (96% ee) as the model compounds to demonstrate the synthetic utility of this methodology.[28] For example, it was shown that the enantioenriched alkynyl cyclopropane **3f** could undergo effective *cis*-hydrogenation with dihydrogen in the presence of Lindlar catalyst, generating vinyl cyclopropane **5f** with (*Z*)-configuration exclusively in almost quantitative yield (99% yield) without any erosion of the original diastereoselectivity (100% ds) and enantioselectivity (100% es) (Scheme 2.9).

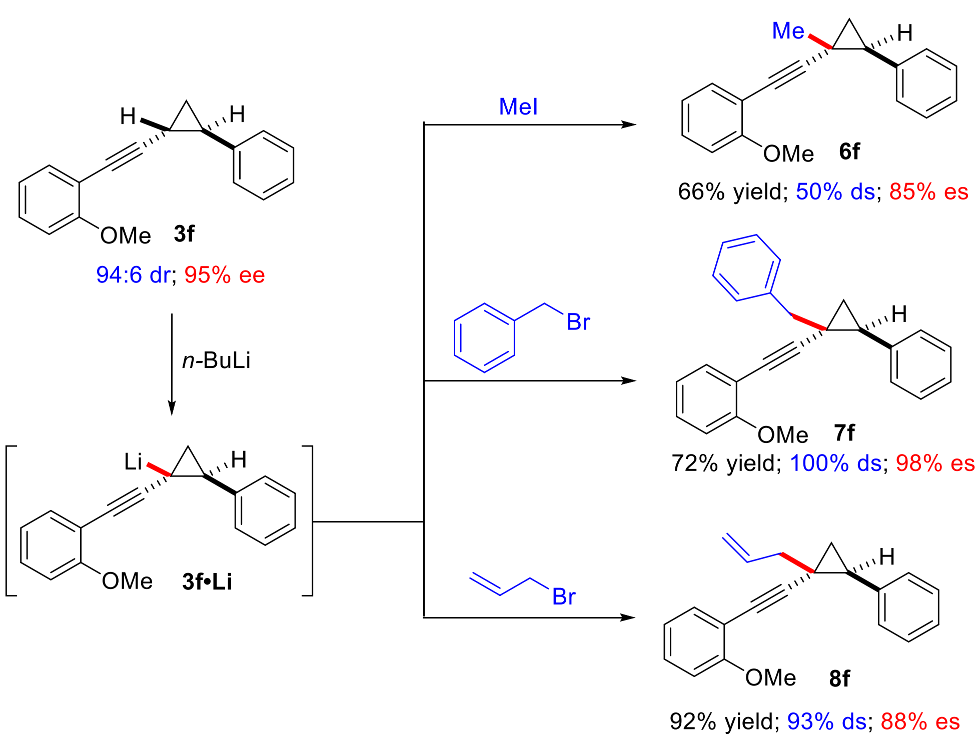
Scheme 2.9. Stereoselective Synthesis of (*Z*)-Vinyl Cyclopropane by Hydrogenation[a]



[a]Carried out with **3f** (0.10 mmol) and quinoline (2.0 equiv) by Lindlar catalyst (1.2 equiv) in mixed solvent (2.0 mL; hexane:ethyl acetate = 1:1) under H_2 atmosphere at 22 °C for 12 h.

Furthermore, by taking advantage of the difference in acidity between the two tertiary C–H bonds on the cyclopropane ring, we demonstrated that the C–H bond neighboring at the alkynyl substituent in cyclopropane **3f** could be preferentially cleaved with *n*-BuLi over the C–H bond neighboring at the aryl substituent, leading to site-selective generation of cyclopropyl lithium intermediate **3f·Li** (Scheme 2.10).[28a] By adding different alkyl halides as the electrophiles, the in situ-generated cyclopropyl lithium intermediate **3f·Li** could undergo subsequent nucleophilic substitution reactions, allowing for stereoselective synthesis of trisubstituted cyclopropanes with three different types of groups while creating an all-carbon quaternary stereogenic center without the formation of the potential allenylic products. For instance, the in situ reaction of **3f·Li** with methyl iodide furnished the corresponding 1-methyl-1-alkynyl-2-phenyl cyclopropane **6f** in moderate yield (66%) with a notable loss of stereopurities (50% ds and 85% es) presumably due to the small size of the electrophile. While the stereopurities were determined by crude NMR and HPLC, there is still uncertainty associate with the absolute configuration of the product.

Scheme 2.10. Stereoselective Synthesis of Trisubstituted Cyclopropane by Electrophilic Substitution*[a]*



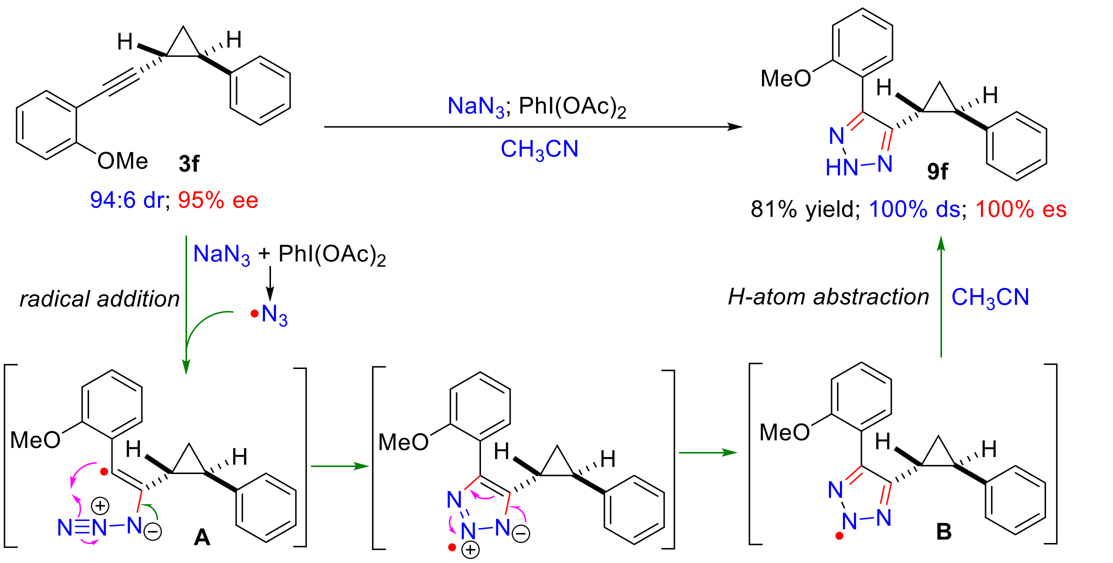
[a]Carried out with **3f** (0.10 mmol) and *n*-BuLi (1.6 equiv) in THF (2.0 mL) under N_2 atmosphere at –78 °C for 1 h, followed by addition of electrophile (1.6 equiv) and then stirred at 22 °C for 24 h.

When the larger benzyl bromide was added as the electrophile, the reaction could deliver the corresponding 1-benzyl-1-alkynyl-2-phenyl cyclopropane **7f** in higher yield (72%) with complete retention of the diastereopurity (100% ds) and without significant loss of the original enantiopurity (98% es). The reaction also worked similarly well with allylic bromide as the electrophilic partner, affording the desired 1-allyl-1-alkynyl-2-phenyl cyclopropane **8f** in high yield (92%) while maintaining the majority of the stereopurities (93% ds and 88% es).

Moreover, oxidative click reaction of cyclopropane **3f** with sodium azide could be successfully achieved in the presence of $PhI(OAc)_2$, producing 1,2,3-triazole-substituted cyclopropane **9f** in high yield (81%) without any erosion of the original diastereoselectivity (100% ds) and enantioselectivity (100% es) (Scheme 2.11).[28b] Presumably, the in situ-generated azidyl radical first underwent radical addition with the C≡C bond in cyclopropane **3f** to generate vinyl radical intermediate **A**. Ensuing homolytic addition of the terminal nitrogen of the azide functional group of vinyl radical intermediate **A** could lead to the formation of 5-membered aminyl radical intermediate **B**, which would give rise to final product **9f** after hydrogen atom abstraction from the solvent.

In addition to these demonstrated transformations for stereoselective synthesis of new cyclopropane derivatives, the three-membered cyclopropane ring in the resulting enantioenriched alkynyl cyclopropanes could be expanded to form a 5-membered cyclic structure as exemplified by the reaction of enantioenriched alkynyl cyclopropane **3a** with $Na_2S{\cdot}9H_2O$ in DMA at high temperature, affording 2-benzylidenetetrahydrothiophene **4a** in high yield (73%) with good configuration control of the trisubstituted olefin (*Z*/*E* = 85:15) but with only moderate enantioselectivity (36% ee) (Scheme 2.12). According to

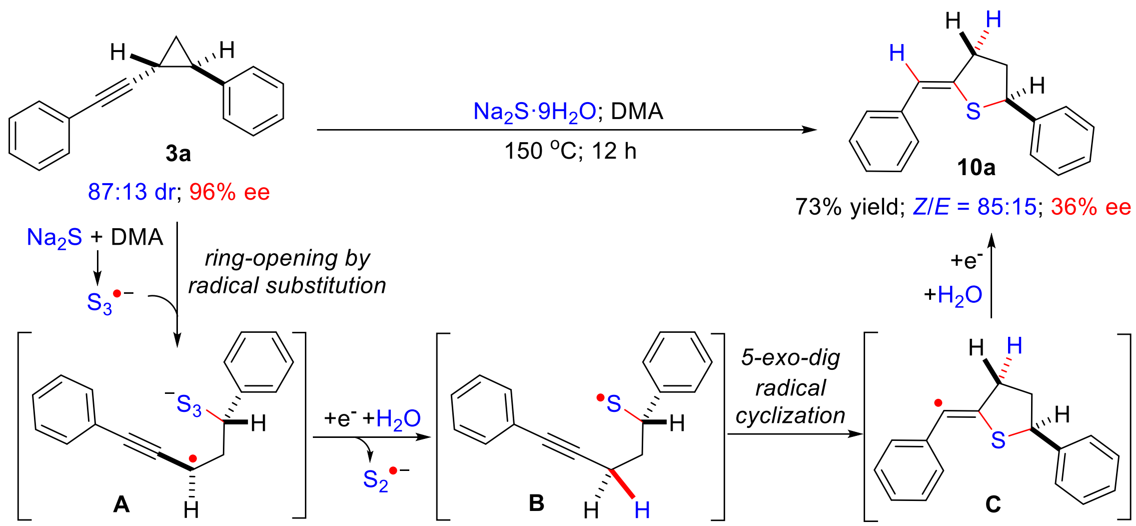
Scheme 2.11. Stereoselective Synthesis of 1,2,3-Triazole-Substituted Cyclopropane via Click Reaction[a]



[a]Carried out with **3f** (0.10 mmol), NaN_3 (1.5 equiv) and $PhI(OAc)_2$ (1.0 equiv) in MeCN (2.0 mL) under N_2 atmosphere at 22 °C for 12 h.

the proposed mechanism,[28c] the cyclopropane ring in **3a** was first opened by in situ-generated trisulfur radical anion $S_3^{\bullet-}$ via radical substitution to generate propargylic radical intermediate **C**, which was protonated by H_2O after one-electron reduction and followed by homolysis of the S−S bond to form thiyl radical intermediate **D** while releasing disulfur radical anion $S_2^{\bullet-}$. The following 5-*exo*-*dig* radical cyclization of intermediate **D** led to the formation of vinyl radical intermediate **E**, which went through another sequence of reduction and protonation to give the final product **4a**.

Scheme 2.12. Stereoselective Synthesis of 2-Benzylidenetetrahydrothiophene by Cycloaddition Involving Trisulfur Radical Anion[a]



[a]Carried out with **3a** (0.10 mmol) and $Na_2S\cdot9H_2O$ (6.0 equiv) in DMA (0.5 mL) at 150 °C for 12 h.

2.3. CONCLUSIONS AND OUTLOOK

In summary, we have developed the first asymmetric catalytic system that can use in situ-generated α-alkynyldiazomethanes for direct cyclopropanation of alkenes via Co(II)-based metalloradical catalysis (MRC). On the basis of a remarkable ligand effect on the Co(II)-based catalytic system, D_2-symmetric chiral amidoporphyrin 2,6-DiMeO-QingPhyrin has been identified as the optimal supporting ligand that offers suitable steric, electronic and chiral environments surrounding the Co(II)-metalloradical center for engaging a network of noncovalent attractive interactions to facilitate the cyclopropanation process. The Co(II)-based metalloradical system is capable of activating different alkynyldiazomethanes under mild conditions for highly asymmetric cyclopropanation of diverse alkenes with varied electronic and steric properties, affording chiral alkynyl cyclopropanes in high yields with high both diastereoselectivity and enantioselectivity. The combined computational and experimental studies have shed light on the underlying stepwise radical mechanism of the Co(II)-based cyclopropanation system involving a unique α-metalloradical intermediate that is associated with two resonance forms of α-Co(III)-propargyl radical and γ-Co(III)-allenyl radical. In addition to rationalizing the unique profile of reactivity and selectivity, the established mechanism offers a convincing explanation of the regioselectivity towards the formation of alkynyl cyclopropanes via α-Co(III)-propargylic radical form without any complication from potential reaction via γ-Co(III)-allenyl radical form. The resulting enantioenriched alkynyl cyclopropanes, as showcased in several stereospecific transformations, may serve as useful intermediates for stereospecific organic synthesis. Considering the ubiquity of chiral alkynyl cyclopropanes, we believe this Co(II)-catalyzed asymmetric radical cyclopropanation process will find useful applications in organic synthesis.

2.4. EXPERIMENTAL SECTION

2.4.1. General Considerations

All cyclopropanation reactions were performed in anhydrous solvents under N_2 atmosphere in oven-dried glassware following standard Schlenk techniques. Gas-tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. The solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin-layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR spectra were acquired using Varian INOVA 400 (400 MHz), Bruker 500 (500 MHz), or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to the residual solvent peak ($CHCl_3$ δ = 7.26 ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet), and coupling constants *J* (Hz). ^{13}C NMR spectra were acquired using Bruker 500 (126 MHz), or INOVA 600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ δ = 77.16 ppm) as the internal standard. ^{19}F NMR spectrum was acquired using Varian INOVA 600 (564 MHz) spectrometer. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, IA, IB, IC, ID, and IE columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals, or TCI and were used without further purification.

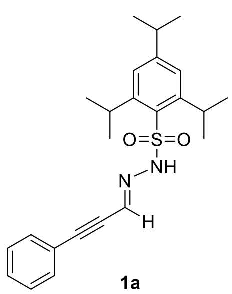
2.4.2. Synthesis and Characterization of *N*-Sulfonyl Hydrazones

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

To a stirred solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (1.0 mmol) in THF (10.0 mL) at room temperature, aldehyde (1.0 equiv) was added dropwise (or portionwise if solid).[1] After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by trituration.

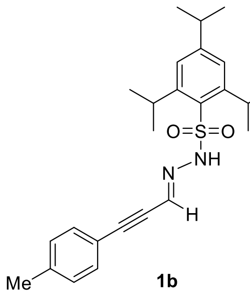
2.4.2.2. Characterization of *N*-2,4,6-Triisopropylbenzenesulfonyl Hydrazones

3-Phenylpropiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1a**) Yield: 87%. R_f = 0.30 (Hexane/Ethyl Acetate: 7/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.19 (s, 2H), 6.82 (s, 1H), 4.21 (hept, *J* = 6.7 Hz, 2H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.7 Hz, 12H), 1.26 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.71, 151.27, 132.19, 131.32, 130.48, 128.86, 124.39, 124.05, 120.41, 103.24, 77.75, 34.33, 30.15, 24.92, 23.66. IR (neat, cm^{-1}): 3208.36, 2959.66, 2929.18, 2869.34, 2198.09, 1599.13, 1560.44, 1488.75, 1462.75, 1425.72, 1335.96, 1167.42, 1036.71, 923.23, 757.24, 669.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{31}N_2O_2S^+$: 411.21008, found: 441.20865.



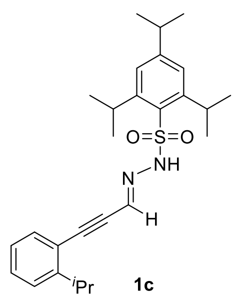
1a

3-(*p*-Tolyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1b) Yield:



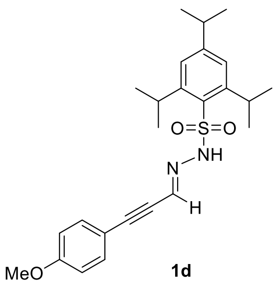
79%. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.18 (s, 2H), 6.80 (s, 1H), 4.27 – 4.14 (m, 2H), 2.91 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.40 (s, 3H), 1.27 (dd, *J* = 13.1, 6.8 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.67, 151.26, 141.11, 132.13, 131.37, 129.66, 124.71, 124.04, 117.33, 103.74, 77.40, 34.34, 30.16, 24.93, 23.67, 21.84. IR (neat, cm^{-1}): 3211.65, 2959.77, 2869.33, 2361.17, 2188.25, 1599.64, 1560.02, 1462.85, 1425.73, 1363.41, 1335.65, 1167.63, 1036.70, 924.00, 726.73. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{33}N_2O_2S^+$: 425.22573, found: 425.22601.

3-(2-Isopropylphenyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone



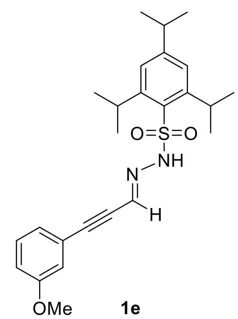
(**1c**) Yield: 90%. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.19 (s, 2H), 6.85 (s, 1H), 4.21 (hept, *J* = 6.7 Hz, 2H), 3.38 (hept, *J* = 6.9 Hz, 1H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 12H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.71, 151.32, 151.31, 133.14, 131.35, 130.97, 126.13, 125.46, 124.55, 124.05, 119.27, 102.41, 81.49, 34.34, 32.22, 30.18, 24.93, 23.67, 23.25. IR (neat, cm^{-1}): 3209.06, 2960.58, 2869.78, 2360.30, 2189.14, 1599.32, 1462.76, 1383.26, 1337.01, 1168.12, 1036.66, 758.10, 665.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{27}H_{37}N_2O_2S^+$: 453.25703, found: 453.25706.

3-(4-Methoxyphenyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone



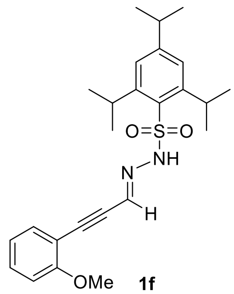
(**1d**) Yield: 85%. R_f = 0.3 (Hexane/Ethyl Acetate: 8/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.19 (s, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.80 (s, 1H), 4.22 (dt, J = 13.3, 6.7 Hz, 2H), 3.85 (s, 3H), 2.91 (dt, J = 13.8, 6.9 Hz, 1H), 1.27 (dd, J = 10.4, 7.0 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.32, 153.62, 151.21, 133.91, 131.36, 124.95, 124.00, 114.53, 112.27, 103.84, 77.14, 55.54, 34.30, 30.11, 24.90, 23.63. IR (neat, cm^{-1}): 3209.86, 2959.06, 2869.51, 2359.98, 2193.19, 1598.06, 1463.31, 1425.28, 1336.01, 1291.42, 1121.29, 1167.09, 1037.64, 943.18, 726.20, 666.89. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{33}N_2O_3S^+$: 441.22064, found: 441.22142.

3-(3-Methoxyphenyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone



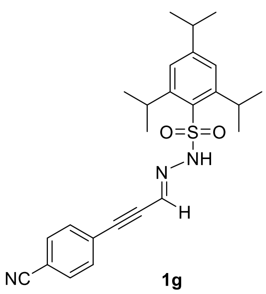
(**1e**) Yield: 85%. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.31 (td, J = 7.7, 0.9 Hz, 1H), 7.19 (s, 2H), 7.10 (dt, J = 7.6, 1.1 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.81 (s, 1H), 4.20 (hept, J = 6.7 Hz, 2H), 3.84 (s, 3H), 2.92 (dq, J = 13.8, 6.9 Hz, 1H), 1.36 – 1.24 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.63, 153.73, 151.27, 131.30, 129.99, 124.73, 124.33, 124.06, 121.33, 117.12, 116.83, 103.15, 77.46, 55.57, 34.34, 30.16, 24.93, 23.66. IR (neat, cm^{-1}): 3212.24, 2959.37, 2868.99, 2360.27, 2188.31, 1603.09, 1508.39, 1296.65, 1252.94, 1167.55, 1035.00, 833.52, 750.11. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{33}N_2O_3S^+$: 441.22064, found: 441.22163.

3-(2-Methoxyphenyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone



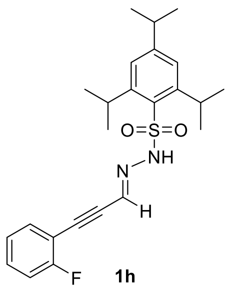
drazide (**1f**) Yield: 85%. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.46 – 7.43 (m, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.18 (s, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.74 (s, 1H), 4.31 – 4.24 (m, 2H), 4.10 (s, 3H), 2.94 – 2.87 (m, 1H), 1.26 (dd, J = 6.8, 3.7 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.72, 153.38, 151.03, 132.33, 132.21, 131.81, 124.00, 123.90, 120.90, 110.64, 109.74, 101.19, 83.83, 55.99, 34.24, 29.93, 24.87, 23.61. IR (neat, cm^{-1}): 3213.01, 2959.30, 2869.23, 2359.28, 2187.85, 1598.14, 1487.99, 1464.79, 1337.88, 1266.21, 1166.70, 1035.71, 1019.62, 753.08, 668.66. HRMS (DART) ($[M+H]^+$) Calcd. for Calcd. for $C_{25}H_{33}N_2O_3S^+$: 441.22064, found: 441.22216.

4-(3-Oxoprop-1-yn-1-yl)benzonitrile 2,4,6-triisopropylbenzenesulfonyl hydrazone



(**1g**) Yield: 90%. R_f = 0.3 (Hexane/Ethyl Acetate: 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.72 – 7.64 (m, 2H), 7.62 – 7.57 (m, 2H), 7.19 (s, 2H), 6.82 (s, 1H), 4.19 (hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.31 – 1.21 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.99, 151.36, 132.67, 132.44, 131.04, 125.17, 124.12, 122.99, 118.01, 113.82, 100.35, 80.98, 34.35, 30.14, 24.90, 23.66. IR (neat, cm^{-1}): 3207.45, 2962.26, 2229.10, 1598.26, 1380.52, 1332.57, 1219.45, 1166.34, 1037.44. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{30}N_3O_2S^+$: 436.20532, found: 436.20638.

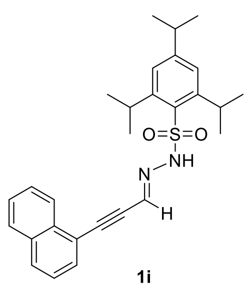
3-(2-Fluorophenyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1h)



1h

Yield: 91%. $R_f = 0.3$ (Hexane/Ethyl Acetate: 20/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.22 (s, 2H), 7.06 (dt, J = 17.7, 8.2 Hz, 2H), 4.29 – 4.21 (m, 2H), 2.96 – 2.88 (m, 1H), 1.33 (d, J = 6.8 Hz, 12H), 1.27 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89 (d, J = 253.6 Hz), 153.84, 151.69, 133.75, 131.30 (d, J = 8.0 Hz), 131.02, 128.89, 124.18 (d, J = 3.7 Hz), 124.15, 115.71 (d, J = 20.6 Hz), 110.47 (d, J = 15.5 Hz), 88.77 (d, J = 3.1 Hz), 87.26, 34.32, 30.20, 24.93, 23.62. ^{19}F NMR (564 MHz, $CDCl_3$): –113.83. IR (neat, cm^{-1}): 3202.62, 2960.19, 2870.09, 2197.93, 2078.94, 1599.11, 1489.80, 1459.77, 1426.07, 1363.70, 1336.84, 1260.07, 1167.91, 1058.83, 1036.83, 941.02, 821.70. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{30}FN_2O_2S^+$: 429.20065, found: 429.19980.

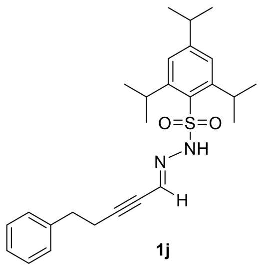
3-(Naphthalen-1-yl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1i)



1i

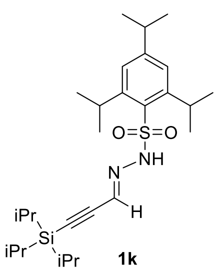
Yield: 93%. $R_f = 0.3$ (Hexane/Ethyl Acetate: 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.20 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.59 (dd, J = 11.0, 4.0 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.20 (s, 2H), 6.98 (s, 1H), 4.25 (dt, J = 13.5, 6.7 Hz, 2H), 2.92 (dt, J = 13.8, 6.9 Hz, 1H), 1.29 (d, J = 6.8 Hz, 12H), 1.27 (d, J = 6.9 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 153.75, 151.31, 133.25, 132.90, 132.11, 131.34, 131.21, 128.82, 127.84, 127.12, 125.51, 125.35, 124.45, 124.08, 117.99, 101.65, 82.29, 34.35, 30.21, 24.96, 23.67. IR (neat, cm^{-1}): 3210.51, 2959.06, 2868.68, 2184.79. 1599.00, 1461.98, 1425.64, 1334,26, 1166.76, 1105.60, 1035.93. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{28}H_{33}N_2O_2S^+$: 461.22573, found: 461.22563.

3-(Phenylethyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1j)



Yield: 82%. R_f =0.3 (Hexanes/Ethyl Acetate = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.16 (s, 2H), 6.53 (d, J = 1.7 Hz, 1H), 4.12 (hept, J = 6.7 Hz, 2H), 2.96 – 2.84 (m, 3H), 2.77 (t, J = 7.2 Hz, 2H), 1.26 (s, 6H), 1.24 (d, J = 7.0 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.55, 151.21, 139.57, 131.40, 128.96, 128.40, 127.03, 124.73, 123.97, 104.84, 71.29, 34.30, 34.26, 30.00, 24.85, 23.64, 21.94. IR (neat, cm^{-1}): 3215.93, 2958.77, 2209.25, 1599.51, 1425.21, 1334.27, 1167.71, 1035.85. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{35}N_2O_2S^+$: 439.2413, found: 439.2418.

3-(Triisopropylsilyl)propiolaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone hydrazide (1k)



Yield: 80%. R_f = 0.3 (Hexane/Ethyl Acetate: 25:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.18 (s, 2H), 6.60 (s, 1H), 4.25 – 4.12 (m, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 1.26 (dd, J = 6.8, 5.4 Hz, 18H), 1.15 – 1.10 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.68, 151.32, 131.41, 124.03, 123.94, 108.69, 94.38, 34.35, 30.19, 24.99, 23.67, 18.68, 11.13. IR (neat, cm^{-1}): 3209.88, 2960.97, 2866.10, 2361.47, 2341.66, 1599.80, 1550.36, 1462.13, 1425.85, 1380.21, 1363.82, 1335.33, 1172.34, 1103.99, 1070.21, 1037.47, 1019.85, 941.06, 922.35, 882.85, 757.41, 730.62. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{27}H_{47}N_2O_2SSi^+$: 491.31220, found: 491.31171.

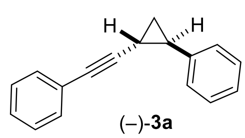
2.4.3. Synthesis and Characterization of Alkynylcyclopropanes

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

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol, 1.0 equiv), [Co(Por)] (2 mol %) and KH (0.40 mmol, 4.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, olefin (0.20 mmol, 2.0 equiv) and anhydrous ethyl acetate (0.6 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22°C for 24 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum, and purified by flash column chromatography.

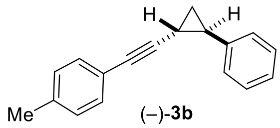
2.4.3.2. Characterization of Alkynylcyclopropane Products

((1*R*,2*R*)-(2-Phenylcyclopropyl)ethynyl)benzene ((–)-**3a**) Yield: 90%. dr: 87:13. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-192.98° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.33 – 7.27 (m, 5H), 7.21 – 7.18 (m, 1H), 7.15 – 7.12 (m, 2H), 2.37 (ddd, *J* = 8.8, 6.1, 4.6 Hz, 1H), 1.72 (ddd, *J* = 8.7, 5.6, 4.6 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.37 – 1.33 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.89, 131.76, 128.57, 128.35, 127.75, 126.38, 126.12, 123.86, 92.05, 77.19, 26.74, 18.18, 12.22. IR (neat, cm^{-1}): 3030.36, 2959.46, 2926.32, 2360.59, 2225.21, 1976.75, 1598.37, 1491.23, 1457.55, 1178.57, 1070.09, 911.31, 755.37, 691.47. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{15}^+$: 219.11683, found 219.11631. HPLC analysis: ee = 96%. IC (100% hexanes, 0.8 mL/min): t_{major} = 14.56 min, t_{minor} = 17.34 min.



(–)-**3a**

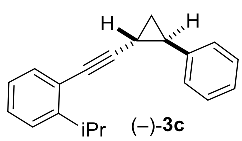
1-Methyl-4-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3b**) Yield: 90%. dr:



(–)-**3b**

79:21. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-187.98° (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H), 7.19 (t, J = 7.4 Hz, 1H), 7.14 – 7.09 (m, 4H), 2.41 – 2.35 (m, 1H), 2.34 (s, 3H), 1.70 (dt, J = 9.6, 5.0 Hz, 1H), 1.41 (dt, J = 9.9, 5.1 Hz, 1H), 1.33 (dt, J = 10.5, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.98, 137.75, 131.64, 129.11, 128.56, 126.34, 126.11, 120.75, 91.22, 77.24, 26.70, 21.56, 18.17, 12.27. IR (neat, cm^{-1}): 3027.56, 2921.15, 2225.19, 2157.79, 1604.05, 1509.97, 1457.26, 1030.99, 948.51, 816.04, 747.88, 696.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}^+$: 233.13248, found: 233.13261. HPLC analysis: ee = 97%. IC (100% hexanes, 0.8 mL/min): t_{major} = 20.35 min, t_{minor} = 26.07 min.

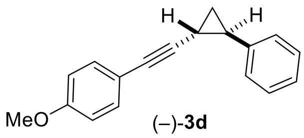
1-Isopropyl-2-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3c**) Yield: 90%. dr:



(–)-**3c**

96:4. R_f = 0.3 (Hexane/Ethyl Acetate: 30/1). $[\alpha]_D^{20}$ = (–)-417.51° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.3 Hz, 2H), 7.25 (d, J = 4.3 Hz, 2H), 7.21 (t, J = 7.1 Hz, 1H), 7.14 – 7.09 (m, 3H), 3.49 – 3.40 (m, 1H), 2.38 – 2.34 (m, 1H), 1.76 (dt, J = 9.4, 4.9 Hz, 1H), 1.45 – 1.42 (m, 1H), 1.39 – 1.35 (m, 1H), 1.27 (d, J = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.53, 141.00, 132.46, 128.59, 128.09, 126.37, 126.08, 125.54, 124.94, 122.55, 95.65, 75.79, 31.61, 26.87, 23.20, 23.18, 18.40, 12.50. IR (neat, cm^{-1}): 3025.41, 2958.77, 2221.27, 1603.66, 1483.61, 1027.89, 947.56, 757.37, 696.75. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}^+$: 261.16378, found: 261.16452. HPLC analysis: ee = 99%. IC (100% hexanes, 0.5 mL/min): t_{major} = 17.43 min, t_{minor} = 15.65 min.

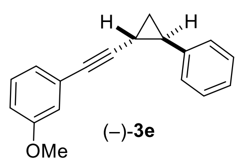
1-Methoxy-4-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3d**) Yield: 90%. dr:



(–)-**3d**

85:15. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-151.56° (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.19 (dd, *J* = 13.4, 7.0 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.37 (dd, *J* = 11.6, 7.3 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.47 – 1.40 (m, 1H), 1.35 (dd, *J* = 12.7, 6.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.32, 132.86, 131.74, 129.53, 128.33, 127.70, 127.35, 114.03, 92.30, 77.06, 55.46, 26.09, 17.73, 11.71. IR (neat, cm^{-1}): 3004.01, 2832.88, 2222.28, 1735.61, 1596.76, 1573.47, 1490.18, 1458.41, 1426.86, 1285.02, 1214.10, 1161.09, 1044.51, 900.13, 785.39, 697.99 HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O^+$: 249.12739, found: 249.12800. HPLC analysis: ee = 98%. ID (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 19.23 min, t_{minor} = 16.79 min.

1-Methoxy-3-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3e**) Yield: 94%. dr:

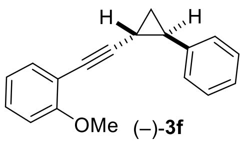


(–)-**3e**

90:10. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-90.93° (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.11 (m, 4H), 7.03 – 6.99 (m, 1H), 6.94 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.84 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 3.80 (s, 3H), 2.37 (ddd, *J* = 8.8, 6.1, 4.6 Hz, 1H), 1.71 (ddd, *J* = 8.7, 5.6, 4.6 Hz, 1H), 1.43 (ddd, *J* = 8.8, 5.6, 4.9 Hz, 1H), 1.35 (ddd, *J* = 8.7, 6.2, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.43, 140.85, 129.40, 128.58, 126.40, 126.13, 124.86, 124.33, 116.57, 114.47, 91.93, 77.13, 55.38, 26.75, 18.16, 12.19. IR (neat, cm^{-1}): 3029.78, 2931.66, 2835.34, 2225.55, 1605.33, 1510.25, 1457.81, 1288.71, 1248.50, 1173.27, 1029.39, 832.80, 749.26, 698.59. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O^+$:

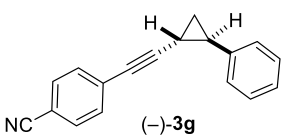
249.12739, found: 249.12807. HPLC analysis: ee = 99%. IE (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 19.52 min, t_{minor} = 16.54 min.

1-Methoxy-2-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3f**) Yield: 99%. dr: 94:6. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-120.65° (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.5, 1.5 Hz, 1H), 7.29 – 2.23 (m, 3H), 7.19 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 6.91 – 6.83 (m, 2H), 3.88 (s, 3H), 2.50 – 2.33 (m, 1H), 1.79 (dt, J = 8.8, 5.2 Hz, 1H), 1.46 (dt, J = 8.9, 5.3 Hz, 1H), 1.39 – 1.31 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.15, 141.04, 133.84, 129.15, 128.53, 126.31, 126.12, 120.55, 112.93, 110.67, 96.20, 73.24, 55.92, 26.89, 18.48, 12.60. IR (neat, cm^{-1}): 3026.46, 2933.30, 2224.21, 2144.80, 1595.45, 1574.20, 1494.20, 1461.81, 1434.12, 1262.24, 1025.21, 950.32, 752.69, 698.71. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O^+$: 249.12739, found: 249.12833. HPLC analysis: ee = 95%. IA (99% hexanes: 1% isopropanol, 0.8 mL/min): t_{major} = 7.84 min, t_{minor} = 7.35 min.



(–)-**3f**

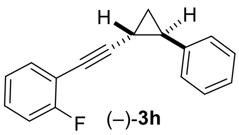
4-(((1*R*,2*R*)-2-Phenylcyclopropyl)ethynyl)benzonitrile ((–)-**3g**) Yield: 94%. dr: 90:10. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-96.44° (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.59 – 7.55 (m, 2H), 7.48 – 7.45 (m, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.14 – 7.11 (m, 2H), 2.40 (ddd, J = 8.9, 6.3, 4.6 Hz, 1H), 1.72 (ddd, J = 8.7, 5.6, 4.6 Hz, 1H), 1.48 – 1.43 (m, 1H), 1.41 (ddd, J = 8.7, 6.3, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.31, 132.22, 132.07, 128.96, 128.67, 126.64, 126.14, 118.76, 110.99, 97.27, 76.05, 27.04, 18.22, 12.11. IR (neat, cm^{-1}): 2960.52, 2916.60, 2224.00, 2171.15, 1602.59, 1500.30, 1458.90, 1344.91, 1219.35, 1178.01, 1105.49. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{14}N^+$: 244.11208, found:



(–)-**3g**

244.11371. HPLC analysis: ee = 90%. IA (99.2% hexanes: 0.8% isopropanol, 1.0 mL/min): t_{major} = 11.05 min, t_{minor} = 8.36 min.

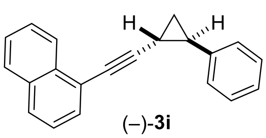
1-Fluoro-2-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene ((–)-**3h**) Yield: 90%. dr:



(–)-**3h**

93:7. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1); $[\alpha]_D^{20}$ = (–)-119.42° (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 7.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.05 (dd, J = 17.5, 8.5 Hz, 2H), 2.42 – 2.38 (m, 1H), 1.77 – 1.74 (m, 1H), 1.48 – 1.44 (m, 1H), 1.38 (dt, J = 9.5, 5.5 Hz, 1H). ^{13}C NMR (151MHz, $CDCl_3$) δ 163.05 (d, *J* = 250.3 Hz), 140.71, 133.71 (d, *J* = 1.2 Hz), 129.34 (d, *J* = 7.8 Hz), 128.59, 126.45, 126.13, 123.94 (d, *J* = 3.7 Hz), 115.50 (d, *J* = 21.0 Hz), 112.37 (d, *J* = 15.8 Hz), 97.43 (d, *J* = 3.1 Hz), 70.47, 26.88, 18.29, 12.29. ^{19}F NMR (564MHz, $CDCl_3$) δ –110.86 (s, 1F). IR (neat, cm^{-1}): 3053.04, 2925.74, 2853.66, 2157.23, 1604.00, 1494.46, 1264.14, 895.94, 731.81, 703.27. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{13}F^+$: 237.10741, found: 237.10823. HPLC analysis: ee = 98%. IC (100% hexanes, 0.8 mL/min): t_{major} = 17.56 min, t_{minor} = 15.84 min.

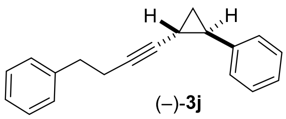
1-(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)naphthalene ((–)-**3i**) Yield: 95%. dr: 80:20.



(–)-**3i**

R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-94.31° (*c* = 0.5, $CHCl_3$) ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.59 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.42 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.27 – 7.22 (m, 1H), 7.19 (dd, *J* = 8.1, 1.0 Hz, 2H), 2.51 (ddd, *J* = 8.9, 6.1, 4.5 Hz, 1H), 1.90 (ddd, *J* = 8.7, 5.6, 4.6 Hz, 1H), 1.57 (ddd, *J* = 8.9, 5.7, 4.9 Hz, 1H), 1.46 (ddd, *J* = 8.7, 6.2, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.86, 133.69, 133.33, 130.29, 128.62, 128.37, 128.16, 126.67, 126.44, 126.40, 126.35, 126.14, 125.36, 121.53, 97.16, 75.25, 27.07, 18.52, 12.53. IR (neat, cm^{-1}): 3057.62, 2922.15, 2220.80, 1603.97, 1584.51, 1497.84, 1457.41, 1400.50, 1215.93, 1183.31, 1018.73. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{17}^+$: 269.13248, found: 269.13270. HPLC analysis: ee = 90%. IA (100% hexanes, 0.8 mL/min): t_{major} = 16.42 min, t_{minor} = 20.87 min.

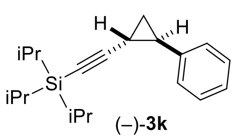
((1*R*,2*R*)-2-(4-phenylbut-1-yn-1-yl)cyclopropyl)benzene ((–)-**3j**) Yield: 41%. dr: 91:9.



(–)-**3j**

R_f =0.4 (Hexanes/Ethyl Acetate = 20/1).). $[\alpha]_D^{20}$ = (–)-253.30º (c=0.5, $CHCl_3$). ^1H NMR (500 MHz, $CHCl_3$) δ 7.29 (q, J = 6.6 Hz, 4H), 7.23 (t, J = 7.2 Hz, 3H), 7.17 (t, J = 7.4 Hz, 1H), 7.09 – 7.04 (m, 2H), 2.81 (t, J = 7.6 Hz, 2H), 2.45 (td, J = 7.6, 1.9 Hz, 2H), 2.14 (ddd, J = 8.7, 6.0, 4.5 Hz, 1H), 1.46 (dddt, J = 8.1, 6.3, 4.2, 1.9 Hz, 1H), 1.24 – 1.15 (m, 2H). ^{13}C NMR (151 MHz, $CHCl_3$) δ 141.29, 141.05, 128.63, 128.50, 128.45, 126.35, 126.20, 126.02, 82.88, 76.42, 35.64, 26.15, 21.25, 17.80, 11.75. IR (neat, cm^{-1}): 3026.43, 2924.37, 1603.83, 1495.48, 1453.88, 1275.36, 1260.61, 749.58. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{19}^+$: 247.1481, found: 247.1484. HPLC analysis: ee = 85%. IC (99.9% hexanes : 0.1% isopropanol, 0.8 mL/min): t_{major} = 6.50 min, t_{minor} = 7.19 min.

Triisopropyl(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)silane ((–)-**3k**) Yield: 71%. dr:

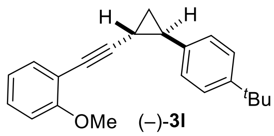


(–)-**3k**

96:4. R_f = 0.3 (Hexane/Ethyl Acetate: 30/1). $[\alpha]_D^{20}$ = (–)-62.18° (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.27 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.2 Hz, 2H), 2.25 (ddd, J = 8.8, 6.0, 4.6 Hz, 1H), 1.59 – 1.55 (m, 1H), 1.34 – 1.30(m, 1H), 1.24 (ddd, J = 8.7, 6.1, 4.7 Hz, 1H), 1.09 – 1.04 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.01, 128.54, 126.33, 126.02, 110.70, 76.90, 27.08, 18.79, 18.73, 12.56, 11.47. IR (neat, cm^{-1}): 3029.62, 2941.29, 2863.78, 2158.44, 1731.59, 1604.88, 1461.55, 1382.49, 1126.08, 1072.72, 995.91, 883.40, 747.93, 696.28,677.48.

HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{31}Si^+$: 299.21895, found: 299.21913. HPLC analysis: ee = 87%. IC (100% hexanes, 0.8 mL/min): t_{major} = 6.28 min, t_{minor} = 6.64 min.

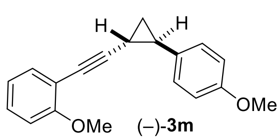
1-(((1*R*,2*R*)-2-(4-(*tert*-Butyl)phenyl)cyclopropyl)ethynyl)-2-methoxybenzene ((–)-**3l**)



(–)-**3l**

Yield: 94%. dr: 91:9. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-154.77° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.34 –7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.08 – 7.05 (m, 2H), 6.90 – 6.84 (m, 2H), 3.88 (s, 3H), 2.37 (ddd, *J* = 8.9, 6.1, 4.6 Hz, 1H), 1.76 (ddd, *J* = 8.7, 5.6, 4.6 Hz, 1H), 1.43 (ddd, *J* = 8.9, 5.5, 4.8 Hz, 1H), 1.36 – 1.31 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.14, 149.26, 137.99, 133.83, 129.09, 125.85, 125.44, 120.53, 113.01, 110.67, 96.40, 73.11, 55.91, 34.54, 31.50, 26.50, 18.30, 12.42. IR (neat, cm^{-1}): 3005.32, 2959.45, 2224.63, 1505.13, 1574.07, 1493.24, 1462.24, 1433.35, 1362.33, 1260.43, 1239.75, 1122.33, 1023.86, 913.75, 749.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{25}O^+$: 305.18999, found: 305.19136. HPLC analysis: ee = 89%. IC (99% hexanes: 1% isopropanol, 0.8 mL/min): t_{major} = 7.35 min, t_{minor} = 19.02 min.

1-Methoxy-2-(((1*R*,2*R*)-2-(4-methoxyphenyl)cyclopropyl)ethynyl)benzene ((–)-**3m**)

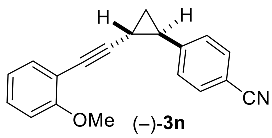


(–)-**3m**

Yield: 89%. dr: 90:10. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-268.89° (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.08 – 7.04 (m, 2H), 6.90 – 6.80 (m, 4H), 3.88 (s, 3H), 3.79 (s, 3H), 2.36 (ddd, *J* = 8.8, 6.1, 4.6 Hz, 1H), 1.70 (ddd, *J* = 8.7, 5.5, 4.6 Hz, 1H), 1.40 (ddd, *J* = 8.8, 5.5, 4.8 Hz, 1H), 1.28 (ddd, *J* = 8.7, 6.2, 4.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.12, 158.26, 133.81, 133.00, 129.08, 127.34, 120.52, 113.98, 112.99, 110.66, 96.45, 73.10, 55.90, 55.44, 26.22, 18.02, 12.07. IR (neat, cm^{-1}): 3004.06, 2834.59, 2221.30, 1712.67, 1595.27, 1514.93, 1493.71, 1246.07, 1032.57, 753.19.

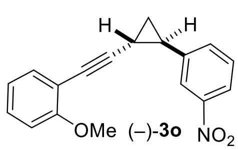
HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{19}O_2^+$: 279.13796, found: 279.13922. HPLC analysis: ee = 94%. IC (98% hexanes: 2% isopropanol, 0.8 mL/min): t_{major} = 12.62 min, t_{minor} = 26.52 min.

4-((1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropyl)benzonitrile ((–)-**3n**) Yield:


(–)-**3n**

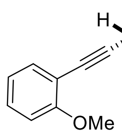
85%. dr: 81:19. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-166.32° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 7.6, 1.7 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 (d, J = 8.3 Hz, 2H), 6.89 – 6.85 (m, 2H), 3.88 (s, 3H), 2.42 (ddd, J = 8.8, 6.0, 4.5 Hz, 1H), 1.85 (ddd, J = 8.8, 5.9, 4.5 Hz, 1H), 1.57 (ddd, J = 8.8, 5.8, 5.1 Hz, 1H), 1.40 (ddd, J = 8.8, 6.0, 5.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.16, 146.93, 133.82, 132.35, 129.47, 126.61, 120.57, 119.08, 112.44, 110.67, 109.91, 94.82, 74.14, 55.90, 26.94, 19.31, 13.91. IR (neat, cm^{-1}): 2958.79, 2924.59, 2852.88, 2360.28, 2342.02, 2225.74, 2158.90, 1718.70, 1607.79, 1595.93, 1493.62, 1463.86, 1434.85, 1262.91, 1241.84, 1122.93, 1023.71, 837.06, 752.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{16}NO^+$: 274.12264, found: 274.12280. HPLC analysis: ee = 95%. IC (90% hexanes: 10% isopropanol, 1 mL/min): t_{major} = 26.22 min, t_{minor} = 45.85 min.

1-Methoxy-2-(((1*R*,2*R*)-2-(3-nitrophenyl)cyclopropyl)ethynyl)benzene ((–)-**3o**) Yield:


(–)-**3o**

88%. dr: 78:22. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-144.58° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (dd, J = 7.3, 2.1 Hz, 1H), 7.96 (s, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 (dd, J = 7.5, 1.3 Hz, 1H), 7.27 (d, J = 15.8 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H), 2.52 – 2.47 (m, 1H), 1.86 (dt, J = 10.1, 5.2 Hz, 1H), 1.58 (dt, J = 8.7, 5.4 Hz, 1H), 1.43 (dt, J = 8.8, 5.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.19, 143.34, 133.84, 132.49, 129.45, 129.41, 123.26, 121.37, 120.89, 120.57, 112.49, 110.68, 94.85, 74.07, 55.91, 26.43, 18.75, 13.38. IR (neat, cm^{-1}): 3074.86, 3008.02, 2933.88, 2835.38, 2223.53, 2155.68, 2045.47, 1698.41, 1595.06, 1528.15, 1493.62, 1463.66, 1348.20, 1263.54, 1241.89, 1024.19, 755.31. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}NO_3^+$, 294.11247, found: 294.11214. HPLC analysis: ee = 81%. IC (90% hexanes: 10% isopropanol, 1 mL/min): t_{major} =17.66 min, t_{minor} =18.52 min.

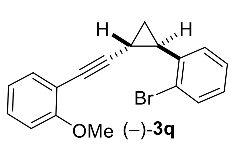
1-(((1*R*,2*R*)-2-(3-Fluorophenyl)cyclopropyl)ethynyl)-2-methoxybenzene ((–)-3p)



(–)-**3p**

Yield: 96%. dr: 85:15. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-96.21° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25 (ddd, *J* = 9.2, 6.4, 1.7 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.97 (ddd, *J* = 8.7, 7.8, 4.6 Hz, 2H), 6.88 (ddd, *J* = 10.8, 8.6, 4.6 Hz, 2H), 3.88 (s, 3H), 2.38 (ddd, *J* = 8.9, 6.0, 4.7 Hz, 1H), 1.73 (ddd, *J* = 8.7, 5.5, 4.7 Hz, 1H), 1.47 – 1.42 (m, 1H), 1.30 (ddd, *J* = 8.7, 6.2, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.59 (d, *J* = 244.2 Hz), 160.15, 136.62 (d, *J* = 3.3 Hz), 133.83, 130.06 (d, *J* = 7.8 Hz), 129.21, 127.70 (d, *J* = 8.0 Hz), 120.55, 115.41, 115.24, 112.84, 110.68, 95.94, 73.38, 55.91, 26.18, 18.27, 12.42. ^{19}F NMR (564MHz, $CDCl_3$) δ –108.26 (s, 1F). HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}FO^+$: 267.11797, found: 267.11835. HPLC analysis: ee = 95%. IA (99.7% hexanes: 0.3% isopropanol, 1 mL/min): t_{major} =12.10 min, t_{minor} =10.75 min.

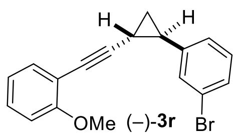
1-Bromo-2-((1*R*,2*R*)-2-((2-methoxyphenyl)ethynyl)cyclopropyl)benzene ((–)-3q)



(–)-**3q**

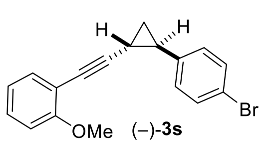
Yield: 91%. dr: 90:10. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-144.92° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.28 – 7.21 (m, 2H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H), 7.00 (dd, *J* = 11.6, 5.0 Hz, 1H), 6.88 (ddd, *J* = 12.0, 9.3, 4.7 Hz, 2H), 3.89 (s, 3H), 2.66 – 2.60 (m, 1H), 1.83 – 1.77 (m, 1H), 1.52 (ddd, J = 8.9, 5.5, 4.9 Hz, 1H), 1.33 – 1.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.23, 140.05, 133.92, 132.74, 131.55, 129.19, 127.95, 127.45, 127.22, 126.33, 120.54, 110.75, 95.87, 73.44, 55.96, 27.59, 17.77, 11.44. IR (neat, cm^{-1}): 2959.06, 1594.84, 1574.10, 1493.09, 1463.23, 1433.85, 1261.01, 1240.02, 1219.52, 1180.38, 1161.43, 1121.33, 1046.77, 1023,44. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}BrO^+$: 327.03790, found: 327.03886. HPLC analysis: ee = 94%. ODH (98% hexanes: 2% isopropanol, 1 mL/min): t_{major} = 36.73 min, t_{minor} = 50.38 min.

1-(((1*R*,2*R*)-2-(3-bBomophenyl)cyclopropyl)ethynyl)-2-methoxybenzene ((–)-3r)



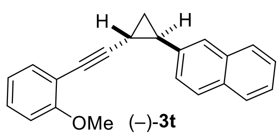
Yield: 88%. dr: 88:12. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-151.97° (c = 0.5, $CHCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (dd, J = 7.6, 1.5 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.14 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 7.7 Hz, 1H), 6.84 – 6.70 (m, 2H), 3.88 (s, 3H), 2.39 – 2.33 (m, 1H), 1.78 – 1.75 (m, 1H), 1.47 (dt, J = 8.8, 5.3 Hz, 1H), 1.34 (ddd, J = 8.7, 6.0, 5.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.18, 143.49, 133.85, 130.05, 129.42, 129.30, 129.29, 124.88, 122.69, 120.56, 112.73, 110.68, 95.55, 73.62, 55.92, 26.48, 18.47, 12.85. IR (neat, cm^{-1}): 3052.53, 2928.16, 2221.82, 2035.47, 1951.20, 1596.77, 1566.35, 1493.96, 1265.16, 1024.68, 895.64, 746.09. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}BrO^+$: 327.03790, found: 327.03788. HPLC analysis: ee = 94%. IC (99% hexanes : 1% isopropanol, 0.8 mL/min): t_{major} = 15.05 min, t_{minor} = 35.29 min.

1-(((1*R*,2*R*)-2-(4-Bromophenyl)cyclopropyl)ethynyl)-2-methoxybenzene ((–)-3s)



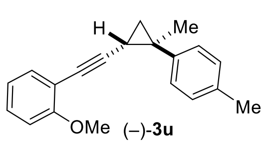
Yield: 93%. dr: 84:16. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-177.86° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, J = 14.3, 4.9 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.88 – 6.86 (m, 2H), 3.88 (s, 3H), 2.37 – 2.33 (m, 1H), 1.77 – 1.73 (m, 1H), 1.49 – 1.45 (m, 1H), 1.33 – 1.29 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.14, 140.11, 133.83, 131.56, 130.28, 129.27, 127.88, 120.56, 119.93, 110.67, 95.68, 73.55, 55.91, 26.38, 18.49, 12.74. IR (neat, cm^{-1}): 2915.93, 2848.44, 2361.23, 2181.48, 1596.50, 1565.70, 1493.74, 1463.52, 1434.28, 1261.97, 1240.71, 1179.48, 1024.49, 750.67. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{16}BrO^+$: 327.03790, found: 327.03750. HPLC analysis: ee = 91%. IA (99.7% hexanes: 0.3% isopropanol, 1 mL/min): t_{major} = 17.36 min, t_{minor} = 13.36 min.

2-((1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropyl)naphthalene ((–)-**3t**) Yield: 96%. dr: 92:8. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-186.99° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (dd, J = 17.6, 8.2 Hz, 3H), 7.58 (s, 1H), 7.47-7.40 (m, 3H), 7.27 – 7.24 (m, 2H), 6.91 – 6.86 (m, 2H), 3.89 (s, 3H), 2.57 (tt, J = 14.8, 7.2 Hz, 1H), 1.90 (dt, J = 8.9, 5.4 Hz, 1H), 1.54 – 1.52 (m, 1H), 1.50 – 1.46 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.17, 138.48, 133.86, 133.57, 132.33, 129.18, 128.19, 127.75, 127.53, 126.29, 125.43, 124.82, 124.51, 120.56, 112.91, 110.68, 96.18, 73.38, 55.93, 27.16, 18.41, 12.62. IR (neat, cm^{-1}): 3049.84, 2933.69, 2833.69, 2222.57, 1726.29, 1594.94, 1492.53, 1462.22, 1433.04, 1261.35, 1023.58, 974.27, 815.73, 750.18. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{19}O^+$: 299.14304, found: 299.14364. HPLC analysis: ee = 99%. IC (99% hexanes : 1% isopropanol, 0.8 mL/min): t_{major} = 19.71min, t_{minor} = 23.40 min.



(–)-**3t**

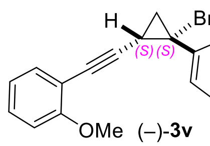
1-Methoxy-2-(((1*S*,2*R*)-2-Methyl-2-(p-tolyl)cyclopropyl)ethynyl)benzene ((–)-**3u**) Yield: 93%. dr: 96:4. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-240.41° (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 7.5 Hz, 1H), 7.25 (dd, J = 18.3, 7.9 Hz, 3H), 7.13 (d, J = 8.0 Hz, 2H), 6.89 (dd, J =



(–)-**3u**

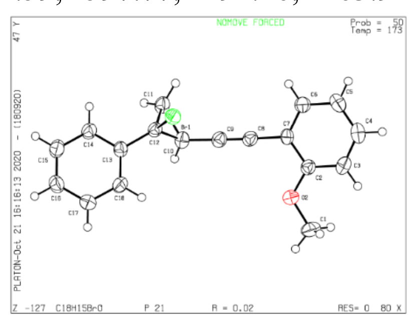
17.1, 8.1 Hz, 2H), 3.90 (s, 3H), 2.34 (s, 3H), 1.88 (dd, J = 8.9, 5.6 Hz, 1H), 1.65 (s, 3H), 1.48 (dd, J = 8.7, 4.2 Hz, 1H), 1.07 (t, J = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.19, 142.99, 135.91, 133.66, 129.17, 128.92, 127.35, 120.51, 113.36, 110.72, 94.98, 75.40, 55.91, 27.92, 23.64, 22.78, 21.11, 16.45. IR (neat, cm^{-1}): 2959.00, 2916.52, 2848.85, 2224.98, 1595.39, 1574,37, 1516,57, 1493.90, 1463.28, 1434,04, 1262.63, 1240.08, 1161.60, 1121.96, 1025.38. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{21}O^+$: 277.15869, found: 277.15930. HPLC analysis: ee = 94%. IC (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 14.22 min, t_{minor} = 16.97 min.

1-(((1*S*,2*S*)-2-Bromo-2-phenylcyclopropyl)ethynyl)-2-methoxybenzene ((–)-**3v**) Yield:

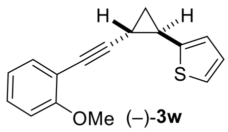


(–)-**3v**

91%. dr: 97:3. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-240.41° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.50 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 (dd, J = 11.1, 4.3 Hz, 2H), 6.93 – 6.87 (m, 2H), 3.91 (s, 3H), 2.13 (dd, J = 9.7, 6.8 Hz, 1H), 1.91 (dd, J = 9.7, 6.0 Hz, 1H), 1.75 (t, J = 6.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.30, 142.92, 134.16, 129.51, 128.79, 128.76, 128.49, 120.60, 112.67, 110.82, 93.10, 77.24, 56.03, 39.46, 25.96, 17.92. IR (neat, cm^{-1}): 259.61, 2925.60, 2359.96, 2341.91, 2158.64, 2006.36, 1724.59, 1597.77, 1494.16, 1463.91, 1258.03, 1180.03, 1121.41, 1025.10, 752.20, 697.42. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}OBr^+$: 327.03790, found: 327.03766. HPLC analysis: ee = 91%. IA (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 18.84 min, t_{minor} = 17.84 min.



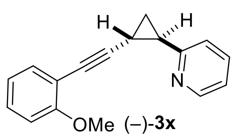
2-((1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropyl)thiophene ((–)-**3w**) Yield: 97%.



(–)-**3w**

dr: 96:4. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-212.02° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.91 – 6.82 (m, 4H), 3.88 (s, 3H), 2.59 – 2.55 (m, 1H), 1.83 (dt, *J* = 9.7, 5.0 Hz, 1H), 1.49 (ddd, *J* = 9.7, 5.5, 0.7 Hz, 1H), 1.37 – 1.33 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.12, 145.24, 133.82, 129.24, 126.93, 123.64, 122.92, 120.53, 112.73, 110.64, 95.45, 73.78, 55.88, 22.24, 19.35, 13.44. IR (neat, cm^{-1}): 3004.51, 2958.93, 2834.69, 2359.94, 2342.06, 1733.86, 1595.14, 1493.32, 1463.04, 1434.12, 1261.58, 1241.27, 1023.74, 752.03, 696.87. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{15}OS^+$: 255.08381, found: 255.08346. HPLC analysis: ee = 92%. IC (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 17.45 min, t_{minor} = 28.64 min.

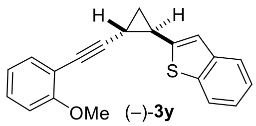
2-((1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropyl)pyridine ((–)-**3x**) Yield: 92%. dr:



(–)-**3x**

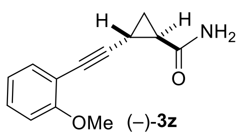
90:10. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-309.74° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.43 (d, *J* = 4.6 Hz, 1H), 7.54 (td, *J* = 7.6, 1.1 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.05 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.87 – 6.84 (m, 2H), 3.86 (s, 3H), 2.47 – 2.44 (m, 1H), 2.18 – 2.14 (m, 1H), 1.70 – 1.65 (m, 1H), 1.48 – 1.44 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.13, 159.60, 149.45, 135.94, 133.84, 129.13, 122.56, 121.07, 120.50, 112.87, 110.62, 96.10, 73.16, 55.86, 28.02, 19.06, 12.94. IR (neat, cm^{-1}): 2968.41, 2927.53, 2360.32, 1717.35, 1596.16, 1494.22, 1464.75, 1263.99, 1161.37, 1123.92, 1024.27, 950.53, 735.14, HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{16}NO^+$: 250.12264, found: 250.12161. HPLC analysis: ee = 92%. IC (99.5% hexanes: 0.5% isopropanol, 1.0 mL/min): t_{major} = 47.91 min, t_{minor} = 62.80 min.

2-((1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropyl)benzo[b]thiophene ((–)-3y)


(–)-**3y**

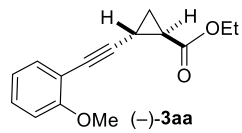
Yield: 90%. dr: 88:12. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-174.25° (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 7.43 (dd, J = 7.9, 7.2 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.28 – 7.26 (m, 1H), 7.02 (s, 1H), 6.92 – 6.86 (m, 2H), 3.90 (s, 3H), 2.56 – 2.52 (m, 1H), 1.81 – 1.77 (m, 1H), 1.50 (dt, J = 9.6, 5.0 Hz, 1H), 1.38 (ddd, J = 8.6, 6.2, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.22, 140.49, 139.61, 136.33, 133.85, 129.23, 124.71, 124.25, 122.92, 122.34, 120.91, 120.56, 112.91, 110.72, 96.10, 73.38, 55.94, 20.87, 16.42, 10.07. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{17}OS^+$: 305.09946, found: 305.09874. HPLC analysis: ee = 93%. IC (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} =17.74 min, t_{minor} = 29.07 min.

(1*R*,2*R*)-2-((2-Methoxyphenyl)ethynyl)cyclopropane-1-carboxamide ((–)-**3z**) Yield:


(–)-**3z**

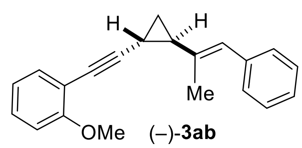
92%. dr: 98:2. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-96.32° (c = 0.5, $CHCl_3$) ^1H NMR (600 MHz, $CDCl_3$): δ 7.31 (dd, J = 7.6, 1.6 Hz, 1H), 7.22 (td, J = 8.4, 1.6 Hz, 1H), 6.84 (ddd, J = 11.1, 8.8, 4.6 Hz, 2H), 5.91 (s, 2H), 3.83 (s, 3H), 2.09 – 2.04 (m, 1H), 1.91 – 1.85 (m, 1H), 1.46 (ddd, J = 9.2, 5.3, 4.1 Hz, 1H), 1.22 (ddd, J = 8.4, 6.2, 4.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.20, 160.19, 133.89, 129.52, 120.58, 112.35, 110.68, 94.30, 73.74, 55.90, 24.57, 16.90, 10.95. IR (neat, cm^{-1}): 2964.37, 2934.13, 2361.03, 2342.20, 2158.68, 1724.96, 1596.50, 1494.77, 1334.80, 1261.55, 1192.09, 1180.94, 1124.56, 752.96. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{14}NO_2^+$: 216.10191, found: 216.10149. HPLC analysis: ee = 89%. IC (99% hexanes: 1% isopropanol, 0.8 mL/min): t_{major} = 30.75 min, t_{minor} = 36.84 min.

Ethyl-(1*R*,2*R*)-2-((2-methoxyphenyl)ethynyl)cyclopropane-1-carboxylate ((–)-3aa)



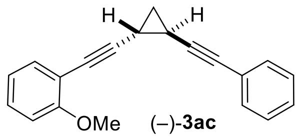
Yield: 89%. dr: 96:4. R$_f$ = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-116.67° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 (dd, J = 12.5, 5.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 4.16 (ddd, J = 14.3, 7.2, 3.0 Hz, 2H), 3.87 (s, 3H), 2.13 (ddd, J = 9.1, 6.2, 4.1 Hz, 1H), 2.08 – 2.03 (m, 1H), 1.47 (ddd, J = 9.4, 5.5, 4.2 Hz, 1H), 1.34 – 1.31 (m, 1H), 1.30 – 1.23 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.51, 160.26, 133.90, 129.54, 120.54, 112.32, 110.67, 93.74, 73.97, 61.05, 55.90, 23.46, 17.44, 14.39, 11.53. IR (neat, cm^{-1}): 2979.80, 1723.87, 1596.21, 1575.23, 1494.51, 1464.14, 1405.49, 1324.14, 1261.27, 1179.78, 1025.69. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{15}H_{17}O_3^+$: 245.11722, found: 245.11754. HPLC analysis: ee = 88%. IA (99.7% hexanes: 0.3% isopropanol, 1 mL/min): t_{major} = 9.47 min, t_{minor} = 10.72 min.

1-Methoxy-2-(((1*R*,2*R*)-2-((*E*)-1-phenylprop-1-en-2-yl)cyclopropyl)ethynyl)benzene



((–)-**3ab**) Yield: 79%. dr: 85:15. R$_f$ = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-62.99° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.5, 1.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 – 7.18 (m, 4H), 6.89 – 6.84 (m, 2H), 6.39 (s, 1H), 3.89 (s, 3H), 2.08 – 2.05 (m, 1H), 1.78 (s, 1H), 1.72 (dt, J = 8.8, 5.2 Hz, 1H), 1.23 – 1.19 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.13, 138.16, 136.81, 133.83, 129.08, 128.98, 128.22, 126.22, 125.30, 120.54, 113.00, 110.65, 96.66, 72.97, 55.94, 31.41, 15.73, 15.33, 8.52. IR (neat, cm^{-1}): 3444.24, 2925.13, 2360.20, 2341.42, 2204.65, 2158.56, 1717.77, 1596.20, 1493.40, 1456.63, 1260.50, 1023.79, 752.82. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{21}O^+$: 289.15869, found: 289.15712. HPLC analysis: ee = 93%. IB (99.5% hexanes: 0.5% isopropanol, 0.8 mL/min): t_{major} = 34.07 min, t_{minor} = 22.47 min.

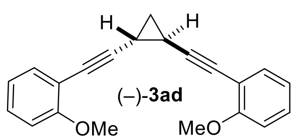
1-Methoxy-2-(((1*R*,2*R*)-2-(phenylethynyl)cyclopropyl)ethynyl)benzene ((–)-**3ac**)



(–)-**3ac**

Yield: 93%. dr: 97:3. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-108.98° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (ddd, *J* = 8.9, 7.4, 2.5 Hz, 3H), 7.28 – 7.24 (m, 4H), 6.87 (dd, *J* = 13.0, 5.4 Hz, 2H), 3.88 (s, 3H), 1.99 – 1.91 (m, 2H), 1.37 – 1.30 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.26, 133.90, 131.82, 129.42, 128.36, 127.95, 123.54, 120.55, 112.56, 110.69, 94.49, 90.55, 77.88, 74.06, 55.92, 18.62, 12.08, 11.88. IR (neat, cm^{-1}): 3009.91, 2922.50, 2834.60, 2229.39, 1722.14, 1595.33, 1573.80, 1492.27, 1463.11, 1433.89, 1264.86, 1024.60, 963.79, 756.20, 692.56. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{17}O^+$: 273.12739, found: 273.12716. HPLC analysis: ee = 93%. IC (99% hexanes: 1% isopropanol, 0.8 mL/min): t_{major} = 7.83 min, t_{minor} = 10.68 min.

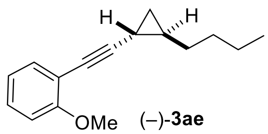
(1*R*,2*R*)-1,2-Bis((2-methoxyphenyl)ethynyl)cyclopropane ((–)-**3ad**) Yield: 93%. dr:



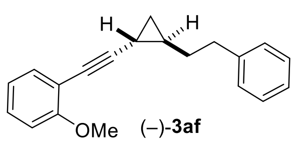
(–)-**3ad**

91:9. R_f = 0.3 (Hexane/Ethyl Acetate: 7/1). $[\alpha]_D^{20}$ = (–)-177.5° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.25 (ddd, *J* = 9.2, 5.7, 1.8 Hz, 2H), 6.89 – 6.83 (m, 4H), 3.87 (s, 6H), 2.02 – 1.97 (m, 2H), 1.37 – 1.33 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$): δ 160.26, 133.90, 129.36, 120.54, 112.63, 110.69, 94.66, 73.98, 55.91, 18.79, 12.25. IR (neat, cm^{-1}): 3006.54, 2959.73, 2835.23, 2232.65, 1731.22, 1595.29, 1574.14, 1493.23, 1463.39, 1434.14, 1361.97, 1278.67, 1260.77, 1241.06, 1181.03, 1161.99, 1119.91, 1047.91, 1024.30, 935.74, 907.42, 826.31, 751.48. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{19}O_2^+$: 303.13796, found: 303.13921. HPLC analysis: ee = 95%. IA (99.5% hexanes: 0.5% isopropanol, 1 mL/min): t_{major} = 12.22 min, t_{minor} = 17.06 min.

1-(((1*R*,2*R*)-2-Butylcyclopropyl)ethynyl)-2-methoxybenzene ((–)-**3ae**) Yield: 32%. dr: 86:14. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). $[\alpha]_D^{20}$ = (–)-82.6° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.21 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 6.85 (ddt, *J* = 13.1, 8.3, 2.6 Hz, 3H), 3.85 (s, 4H), 1.63 – 1.57 (m, 2H), 1.56 – 1.49 (m, 4H), 1.46 – 1.34 (m, 5H), 1.09 – 0.97 (m, 3H), 0.91 (dd, *J* = 13.5, 6.3 Hz, 4H), 0.49 (dt, *J* = 9.9, 5.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.21, 133.67, 128.74, 120.46, 113.56, 110.66, 95.62, 73.89, 55.87, 31.61, 30.04, 22.79, 19.25, 15.37, 14.31, 6.55. IR (neat, cm^{-1}): 2956.71, 2927.35, 2855.58, 2225.08, 1595.37, 1493.72, 1463.69, 1262.53, 1240.39, 1122.15, 1026.59. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{21}O_1^+$: 229.15869, found: 229.15926. HPLC analysis: ee = 81%. IF (99.7% hexanes: 0.3% isopropanol, 0.8 mL/min): t_{major} = 19.15 min, t_{minor} = 18.58 min.

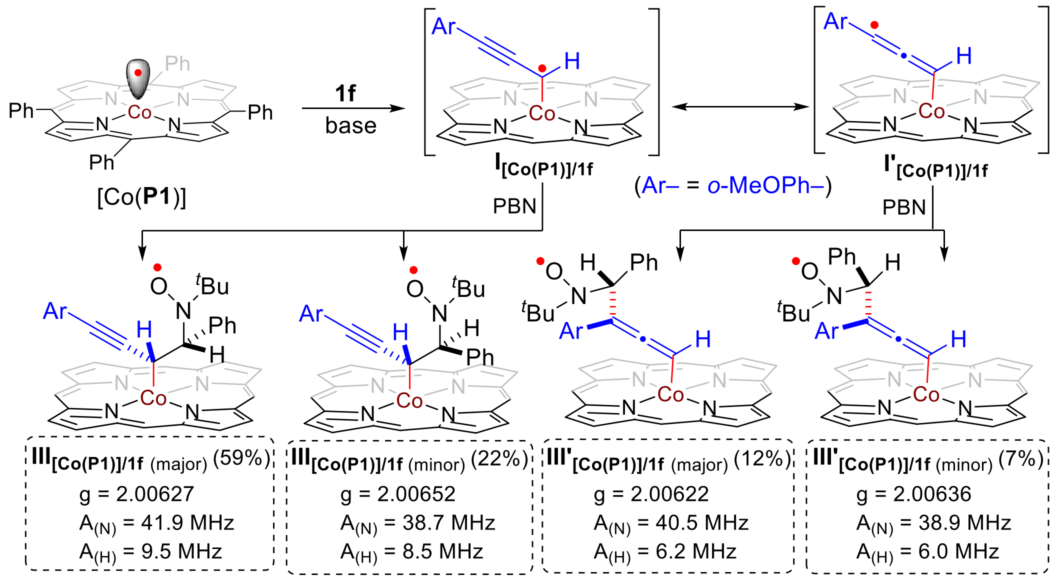


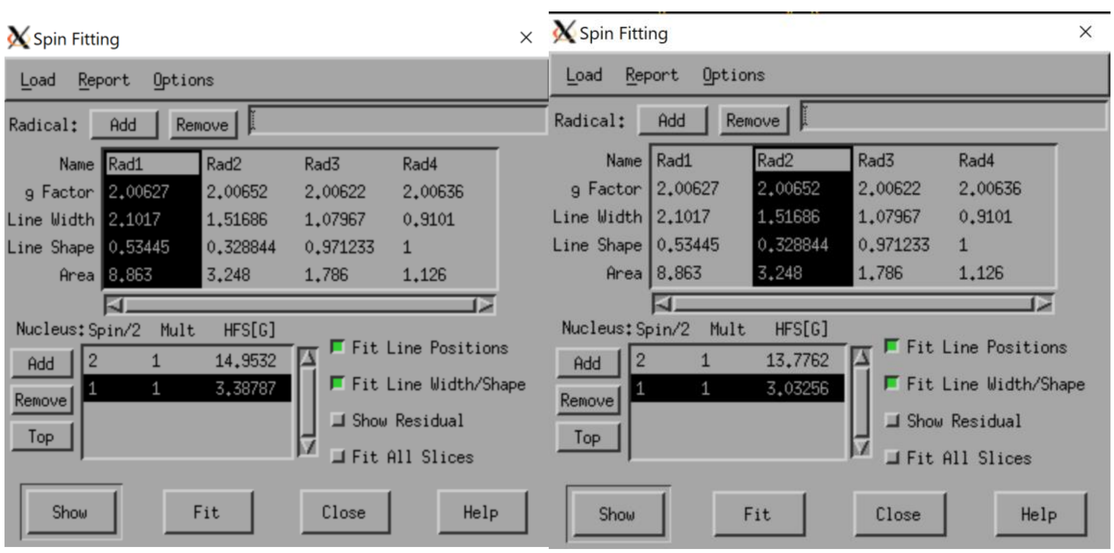
1-(((1*R*,2*R*)-2-Butylcyclopropyl)ethynyl)-2-methoxybenzene ((–)-**3af**) Yield: 40%. dr: 89:11. R_f = 0.3 (Hexane/Ethyl Acetate: 15:1). $[\alpha]_D^{20}$ = (–)-101.34° (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.30 – 7.14 (m, 6H), 6.85 (dd, *J* = 16.8, 8.1 Hz, 2H), 3.80 (s, 3H), 2.97 – 2.87 (m, 1H), 2.77 (ddd, *J* = 13.6, 9.3, 6.6 Hz, 1H), 1.98 – 1.82 (m, 2H), 1.69 – 1.61 (m, 1H), 1.11 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.04 (td, *J* = 8.3, 4.3 Hz, 1H), 0.55 (dd, *J* = 10.2, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.27, 142.74, 133.66, 128.84, 128.69, 128.56, 128.35, 125.75, 120.46, 110.62, 95.23, 74.12, 55.79, 35.62, 32.51, 18.83, 15.39, 6.59. IR (neat, cm^{-1}): 3025.09, 2923.97, 2333.48, 2032.88, 2005.85, 1595.32, 1493.34, 1453.99, 1241.32, 1116.57, 1026.87. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}O^+$: 277.15869, found: 277.15789. HPLC analysis: ee = 85%. IF (99.9% hexanes: 0.1% isopropanol, 1 mL/min): t_{major} = 14.51 min, t_{minor} = 15.37 min.

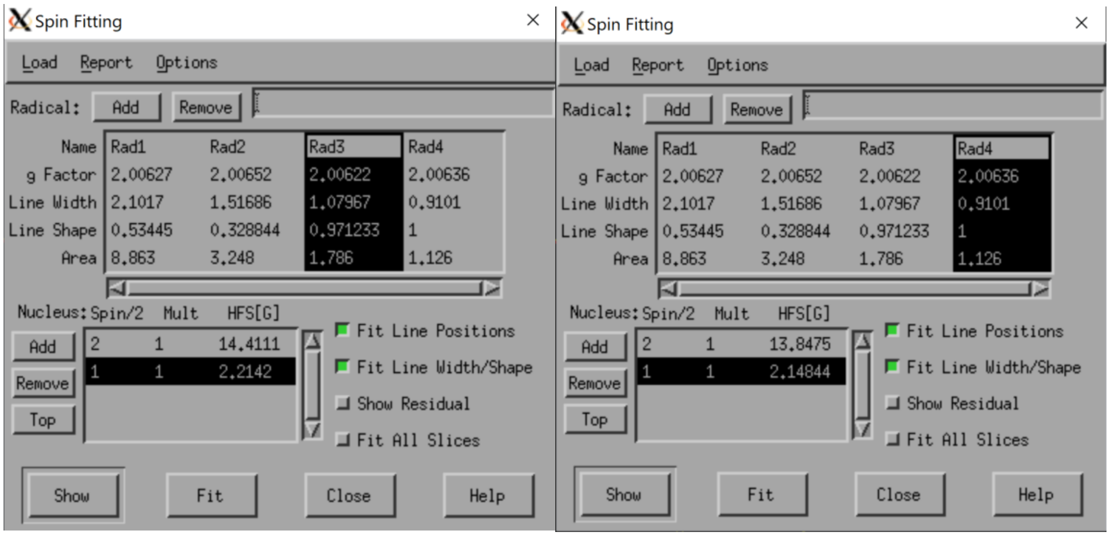


2.4.4. Mechanistic Studies of Stepwise Radical Mechanism

2.4.4.1. Characterization of α-Co(III)-Propargyl Radical and γ-Co(III)-Allenyl Radical Intermediates by EPR







The resulting notable EPR signal (in black) has been simulated (in red) for:

III$_{\mathbf{[Co(P1)]/1f\ (major)}}$ with g = 2.00627, $A_{(N)}$ = 41.9 MHz, $A_{(H)}$ = 9.5 MHz;

III$_{\mathbf{[Co(P1)]/1f\ (minor)}}$ with g = 2.00652, $A_{(N)}$ = 38.7 MHz, $A_{(H)}$ = 8.5 MHz;

III'$_{\mathbf{[Co(P1)]/1f\ (major)}}$ with g = 2.00622, $A_{(N)}$ = 40.5 MHz, $A_{(H)}$ = 6.2 MHz;

III'$_{\mathbf{[Co(P1)]/1f\ (minor)}}$ with g = 2.00636, $A_{(N)}$ = 38.9 MHz, $A_{(H)}$ = 6.0 MHz.

[The simulation of the EPR spectrum was performed by iteration of the isotopic g-values and line widths using the EPR simulation program SpinFit Xenon]

Experimental Procedure for EPR Experiment: A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone **1f** (0.10 mmol, 1.0 equiv), [Co(TPP)] (2 mol %) and PBN (0.12 mmol, 1.2 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, Et_3N (0.20 mmol, 2.0 equiv) and anhydrous benzene (1.0 mL) were added via a syringe. The reaction mixture was stirred at 60 °C for 10 min. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for the EPR experiment at room temperature.

EPR Simulation Details:

For **III**$_{\mathbf{[Co(P1)]/1f}}$:

Major diastereomer (59%)

g = 2.00627

$A_{(N)} = 14.9532 \times 2.00627 \times 1.399611451 = 41.9$ MHz

$A_{(H)} = 3.38787 \times 2.00627 \times 1.399611451 = 9.5$ MHz

Minor diastereomer: (22%)

g = 2.00652

$A_{(N)} = 13.7762 \times 2.00652 \times 1.399611451 = 38.7$ MHz

$A_{(H)} = 3.03256 \times 2.00652 \times 1.399611451 = 8.5$ MHz

For **III'**$_{\mathbf{[Co(TPP)]/1f}}$:

Major diastereomer: (12%)

g = 2.00622

$A_{(N)} = 14.4111 \times 2.00622 \times 1.399611451 = 40.5$ MHz

$A_{(H)} = 2.21420 \times 2.00622 \times 1.399611451 = 6.2$ MHz

Minor diastereomer: (7%)

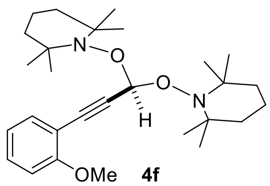
g = 2.00636

$A_{(N)} = 13.8475 \times 2.00636 \times 1.399611451 = 38.9$ MHz

$A_{(H)} = 2.14844 \times 2.00636 \times 1.399611451 = 6.0$ MHz

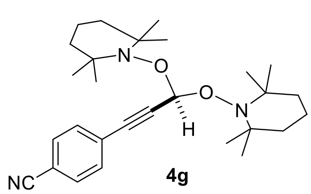
2.4.4.2. TEMPO Trapping Experiments

An oven-dried Schlenk tube was charged with sulfonyl hydrazone **1** (0.10 mmol, 1.0 equiv), [Co(**P1**)] (2 mol %) and KH (0.40 mmol, 4.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, TEMPO (0.60 mmol, 6.0 equiv) and anhydrous ethyl acetate (0.6 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22 °C for 24 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum, and purified by flash column chromatography.



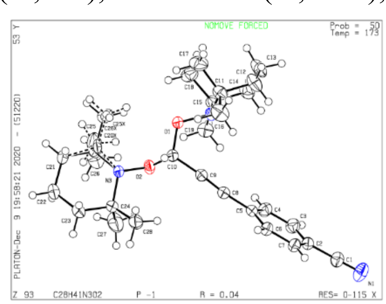
4f

1,1'-((3-(2-Methoxyphenyl)prop-2-yne-1,1-diyl)bis(oxy))bis(2,2,6,6-tetramethylpiperidine) (4f) Yield: 40%. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). ^{1}H NMR (600 MHz, $CDCl_3$):δ 7.40 (dd, J = 7.5, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.93 – 6.80 (m, 2H), 6.00 (s, 1H), 3.84 (s, 3H), 1.54 – 1.47 (m, 8H), 1.40 – 1.24 (m, 16H), 1.14 (d, J = 6.9 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.15, 131.98, 128.52, 118.70, 111.57, 106.14, 91.61, 87.42, 60.12, 40.35, 40.25, 33.41, 33.35, 20.91, 17.38. IR (neat, cm^{-1}): 2930.21, 2362.19, 1596.22, 1493.89, 1464.28, 1376.14, 1361.67, 1326.42, 1292.09, 1261.43, 1181.67, 1132.22, 1046.59, 1027.98, 946.38, 749.46. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{45}N_2O_3^+$: 457.34247, found: 457.34047.



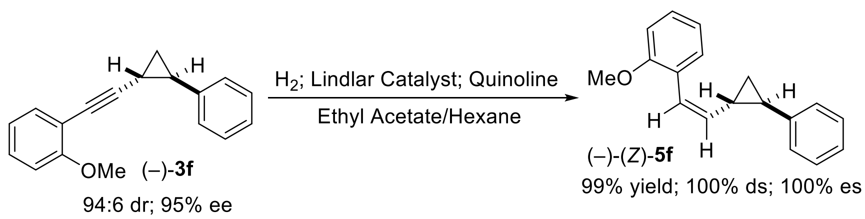
4g

1,1'-((3-(2-Methoxyphenyl)prop-2-yne-1,1-diyl)bis(oxy))bis(2,2,6,6-tetramethylpiperidine) (4g) Yield: 46%. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.54 – 7.49 (m, 2H), 5.98 (s, 1H), 1.50 – 1.44 (m, 6H), 1.34 – 1.25 (m, 18H), 1.14 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 132.16, 131.99, 128.53, 118.70, 111.59, 106.16, 91.64, 87.44, 60.12, 40.37, 40.28, 33.42, 33.36, 20.92, 17.40. IR (neat, cm^{-1}): 2928.93, 2871.34, 2228.55, 1977.59, 1603.99,



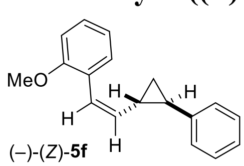
1500.27, 1464.91, 1376.67, 1362.39, 1326.60, 1219.31, 1180.12, 1132.51. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{42}N_3O_2^+$: 452.32715, found: 452.32842.

2.4.5. Further Transformations of Alkynylcyclopropanes



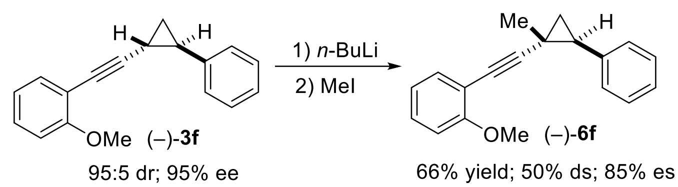
A round-bottomed flask was charged with alkynylcyclopropane **3f** (0.1 mmol, 1.0 equiv), Lindlar Catalyst (0.12 mmol, 1.2 equiv), quinoline (0.2 mmol, 2.0 equiv), anhydrous hexane (1.0 mL) and anhydrous ethyl acetate (1.0 mL). The flask then was bubbled with hydrogen for 2 h. The mixture was then stirred at room temperature in hydrogen atmosphere. After 10 h, the reaction mixture was concentrated and purified by flash chromatography. The fractions containing the product were collected and concentrated by rotary evaporation to afford the compound **5f**.

1-Methoxy-2-((*Z*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene ((–)-(*Z*)-**5f**) Yield:



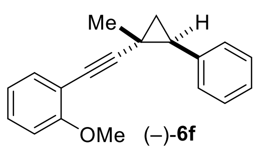
99%. dr: 94:6. R_f = 0.3 (Hexane/Ethyl Acetate: 15/1). $[\alpha]_D^{20}$ = (–)-92.33° (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.4, 1.6 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.23 – 7.19 (m, 1H), 7.18 – 7.14 (m, 1H), 7.07 (dd, J = 8.0, 1.0 Hz, 2H), 6.86 (t, J = 8.3 Hz, 2H), 6.55 (d, J = 11.4 Hz, 1H), 5.32 (dd, J = 11.4, 9.5 Hz, 1H), 3.80 (s, 3H), 2.11 – 2.03 (m, 2H), 1.28 (ddd, J = 8.5, 5.7, 5.0 Hz, 1H), 1.19 – 1.14 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.05, 142.18, 134.95, 130.19, 129.27, 128.43, 128.14, 125.88, 125.70, 123.43, 120.23, 110.49, 55.49, 26.14, 24.19, 18.17. IR (neat, cm^{-1}): 3025.74, 3000.38, 2956.38, 2833.56, 1597.39, 1488.04, 1461.62, 1435.77, 1289.31, 1240.61, 1174.08, 1107.72, 1028.08. HRMS (DART) ($[M+H]^+$) Calcd. for

$C_{18}H_{19}O^+$: 251.14304, found: 251.14301. HPLC analysis: ee = 95%. IB (100% hexanes, 1 mL/min): t_{major} = 22.58 min, t_{minor} = 16.67 min.

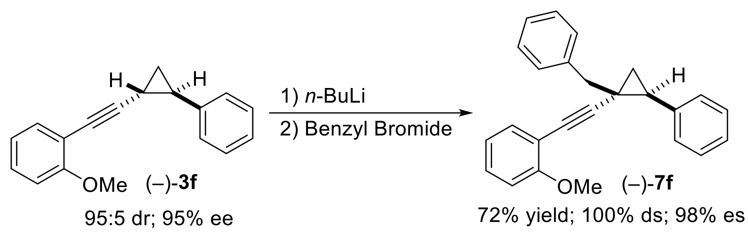


A 10 mL oven-dried Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, a solution of alkynylcyclopropane **3f** (0.10 mmol, 1.0 equiv) in anhydrous THF (2.0 mL) was added followed by the addition of *n*-BuLi (0.16 mmol, 1.6 M in hexanes, 1.6 equiv) at −78 °C. After being warmed up naturally and stirred at 22°C for 1 h, methyl iodide (0.16 mmol, 1.6 equiv) was added. The reaction mixture was stirred at 22°C for 24 h. Following completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, extracted with ether, dried over anhydrous $MgSO_4$, concentrated under vacuum, and purified by flash column chromatography to afford the compound **6f**.[2]

1-Methoxy-2-(((1S,2R)-1-methyl-2-phenylcyclopropyl)ethynyl)benzene ((–)-**6f**) Yield:

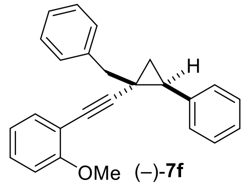


66%. dr: 72:28. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). $[\alpha]_D^{20}$ = (–)-133.98° (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 4H), 7.01 (dd, J = 7.7, 1.7 Hz, 1H), 6.89 (ddd, J = 12.6, 9.6, 4.6 Hz, 1H), 6.77 (ddd, J = 6.7, 3.3, 2.5 Hz, 2H), 3.78 (s, 3H), 2.18 (dd, J = 8.5, 6.7 Hz, 1H), 1.57 (s, 3H), 1.50 (dd, J = 6.6, 5.1 Hz, 1H), 1.28 (dd, J = 8.5, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.97, 138.97, 133.72, 129.39, 128.36, 127.81, 126.07, 120.35, 113.23, 110.69, 96.88, 76.42, 55.84, 32.79, 25.74, 23.29, 17.97. IR (neat, cm^{-1}): 2960.12, 2930.36, 2344.24, 2222.81, 1737.47, 1595.78, 1574.03, 1494.12, 1433.30, 1365.31, 1275.51, 1249.43, 1114,76, 1025.64 HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{19}O^+$: 263.14304, found: 263.14337. HPLC analysis: ee = 81%. ODH (99.7% hexanes : 0.3% isopropanol, 1 mL/min): t_{major} = 14.79 min, t_{minor} = 9.53 min.



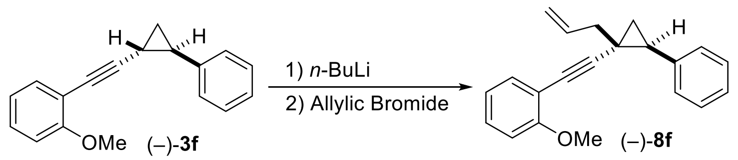
A 10 mL oven-dried Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, a solution of alkynylcyclopropane **3f** (0.10 mmol, 1.0 equiv) in anhydrous THF (2.0 mL) was added followed by the addition of *n*-BuLi (0.16 mmol, 1.6 M in hexanes, 1.6 equiv) at −78 °C. After being warmed up naturally and stirred at 22°C for 1 h, benzyl bromide (0.16 mmol, 1.6 equiv) was added. The reaction mixture was stirred at 22°C for 24 h. Following completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, extracted with ether, dried over anhydrous $MgSO_4$, concentrated under vacuum, and purified by flash column chromatography to afford the compound **7f**.[2]

1-(((1*R*,2*R*)-1-Benzyl-2-phenylcyclopropyl)ethynyl)-2-methoxybenzene ((–)-**7f**) Yield:



72%. dr: 94:6. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). $[\alpha]_D^{20}$ = (–)-121.93° (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, J = 7.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 10.9, 5.8 Hz, 4H), 7.28 – 7.21 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.78 (dd, *J* = 7.3, 6.5 Hz, 2H), 3.78 (s, 3H), 3.05 (s, 2H), 2.42 – 2.36 (m, 1H), 1.59 – 1.55 (m, 1H), 1.47 (dd,

J = 8.7, 5.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.62, 141.88, 141.11, 135.98, 132.16, 131.25, 131.04, 130.78, 130.35, 129.07, 128.71, 122.84, 115.86, 113.29, 98.25, 80.81, 58.32, 47.32, 34.09, 26.39, 24.27. IR (neat, cm^{-1}): 3060.24, 3026.95, 2932.32, 2224.94, 1715.68, 1595.77, 1493.83, 1453.91, 1433,20 1250.54, 1113.19, 1027.36. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{23}O^+$: 339.17434, found: 339.17432. HPLC analysis: ee = 93%. IA (99.5% hexanes: 0.5% isopropanol, 0.5 mL/min): t_{major} = 11.80 min, t_{minor} = 12.85 min.

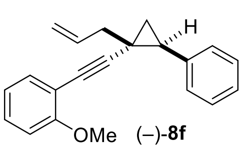


(–)-**3f** 94:6 dr; 95% ee

(–)-**8f** 91% yield; 93% ds; 88% es

A 10 mL oven-dried Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, a solution of alkynylcyclopropane **3f** (0.10 mmol, 1.0 equiv) in anhydrous THF (2.0 mL) was added followed by the addition of *n*-BuLi (0.16 mmol, 1.6 M in hexanes, 1.6 equiv) at −78 °C. After being warmed up naturally and stirred at 22°C for 1 h, allylic bromide (0.16 mmol, 1.6 equiv) was added. The reaction mixture was stirred at 22°C for 24 h. Following completion of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl, extracted with ether, dried over anhydrous $MgSO_4$, concentrated under vacuum, and purified by flash column chromatography to afford the compound **8f**.[2]

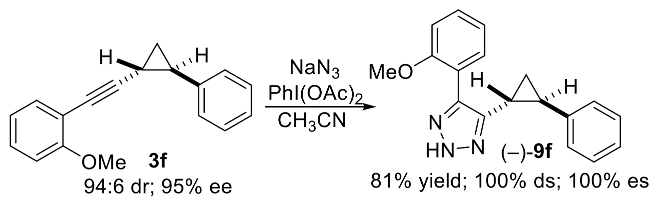
1-(((1*S*,2*R*)-1-Allyl-2-phenylcyclopropyl)ethynyl)-2-methoxybenzene ((–)-**8f**) Yield:



(–)-**8f**

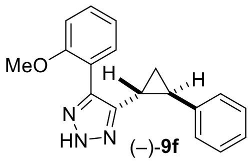
91%. dr: 91:9. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). $[\alpha]_D^{20}$ = (–)-83.28° (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (dt, J =

13.2, 7.5 Hz, 4H), 7.21 – 7.12 (m, 2H), 7.00 – 6.96 (m, 1H), 6.77 – 6.70 (m, 2H), 6.07 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.16 (ddd, *J* = 13.6, 11.0, 1.2 Hz, 2H), 3.75 (s, 3H), 2.42 (ddd, *J* = 81.5, 14.4, 6.8 Hz, 2H), 2.21 (dd, *J* = 8.5, 6.9 Hz, 1H), 1.49 (dd, *J* = 6.6, 5.3 Hz, 1H), 1.32 (dd, *J* = 8.7, 5.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.05, 138.70, 135.58, 133.62, 128.76, 128.47, 127.82, 126.14, 120.33, 116.85, 110.79, 107.50, 95.58, 77.68, 55.86, 43.42, 31.22, 22.61, 21.63. IR (neat, cm^{-1}): 3073.85, 3002.62, 2934.50, 2834.24, 2220.46, 1640.44, 1595.17, 1574.31, 1493.19, 1455.50, 1432.92, 1251.99, 1114.12, 1047.26, 1025.78. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{21}O^+$: 289.15869, found: 289.15874. HPLC analysis: ee = 84%. IB (99.8% hexanes: 0.2% isopropanol, 0.5 mL/min): t_{major} = 14.06 min, t_{minor} = 13.74 min.

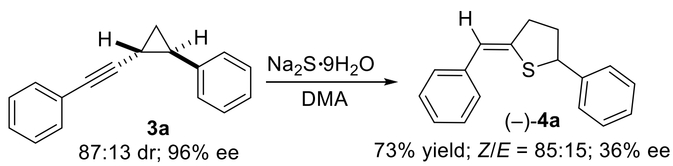


A 10 mL oven-dried Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, solution of alkynylcyclopropane **3f** (0.10 mmol, 1.0 equiv) in anhydrous acetonitrile (2.0 mL) was added followed by the addition of NaN_3 (0.15 mmol, 1.5 equiv) and $PhI(OAc)_2$ (0.1 mmol, 1.0 equiv). The reaction mixture was stirred at 22°C for 12 h. Following completion of the reaction, the reaction mixture was concentrated under vacuum and purified by flash column chromatography to afford the compound **9f**.[3]

4-(2-Methoxyphenyl)-5-((1*R*,2*R*)-2-phenylcyclopropyl)-2H-1,2,3-triazole ((–)-9f)

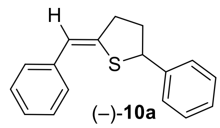


Yield: 81%. dr: 94:6. R_f = 0.3 (Hexane/Ethyl Acetate: 1/1). $[\alpha]_D^{20}$ = (–)-79.31° (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (dd, J = 7.6, 1.5 Hz, 1H), 7.36 (ddd, J = 8.5, 7.7, 1.7 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.18 (dd, J = 10.5, 4.2 Hz, 1H), 7.13 (d, J = 7.2 Hz, 2H), 6.97 (ddd, J = 8.4, 7.0, 3.1 Hz, 2H), 3.78 (s, 3H), 2.61 – 2.43 (m, 1H), 2.22 (ddd, J = 8.8, 5.8, 4.7 Hz, 1H), 1.81 (dt, J = 8.8, 5.4 Hz, 1H), 1.64 – 1.42 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 156.42, 144.67, 142.08, 130.32, 130.04, 129.97, 128.51, 125.99, 125.92, 121.25, 116.96, 111.39, 55.70, 26.33, 19.59, 17.50. IR (neat, cm^{-1}): 2933.53, 2836.57, 2103.14, 1604.31, 1489.90, 1462.88, 1434.70, 1117.48, 1024.70. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{18}N_3O^+$: 292.14444, found: 292.14493. HPLC analysis: ee = 95%. IB (85% hexanes: 15% isopropanol, 1 mL/min): t_{major} = 5.87 min, t_{minor} = 5.30 min.



A 10 mL oven-dried Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, solution of alkynylcyclopropane **3a** (0.10 mmol, 1.0 equiv) and $Na_2S\cdot9H_2O$ (0.60 mmol, 6.0 equiv) in DMA (0.5 mL) was added. The reaction mixture was stirred at 150 °C for 12 h. Following completion of the reaction, ethyl acetate (2.0 mL) was added. The solution was washed with water (3 × 3.0 mL) and extracted with ethyl acetate (3 × 3.0 mL). The organic layers were combined, dried over sodium sulfate, concentrated under vacuum, and purified by flash column chromatography to afford the compound **4a**.[4]

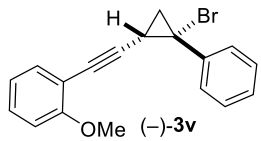
2-Benzylidene-5-phenyltetrahydrothiophene ((–)-**10a**) Yield: 73%. *Z*/*E*: 85:15. R_f =0.3



(Hexane/Ethyl Acetate = 20/1). $[\alpha]_D^{20}$ = (–)-17.49º (*c*=0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.9 Hz, 4H), 7.34 (ddd, *J* = 8.3, 6.2, 1.6 Hz, 5H), 7.17 (q, *J* = 6.8 Hz, 1H), 6.48 (s, 1H), 4.84 (dd, *J* = 10.0, 5.3 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.96 (dddd, *J* = 13.9, 11.7, 6.3, 2.2 Hz, 1H), 2.45 (dtd, *J* = 11.4, 5.7, 2.3 Hz, 1H), 2.10 (tddd, *J* = 11.4, 10.0, 6.3, 1.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.17, 140.70, 137.74, 128.73, 128.45, 127.90, 127.85, 127.24, 125.90, 116.89, 56.38, 46.87, 46.73, 40.44, 37.61. IR (neat, cm^{-1}): 3023.86, 2926.98, 1614.26, 1490.68, 1444.63, 1262.85, 1088.98, 750.35. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}S^+$: 253.1045, found: 253.1045. HPLC analysis: ee = 36%. ID (99.9% hexanes : 0.1% isopropanol, 0.8 mL/min): t_{major} = 13.41 min, t_{minor} = 12.17 min.

2.4.6. X-Ray Crystallography

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2*[29] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[30] Absorption correction was performed by the multi-scan method implemented in SADABS.[31] 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 v1.70.01[32] program.



(–)-3v

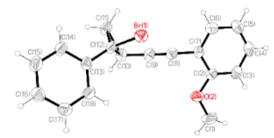
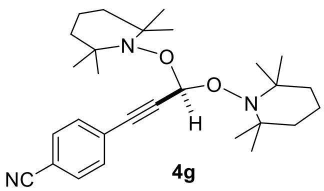


Table S1. Crystal data and structure refinement for (–)-3v

Identification code	C18H15BrO	
Empirical formula	C18 H15 Br O	
Formula weight	327.21	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.4438(8) Å	α= 90°.
	b = 5.8701(6) Å	β= 100.634(3)°.
	c = 15.4882(15) Å	γ = 90°.
Volume	754.50(13) $Å^3$	
Z	2	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	3.640 mm^{-1}	
F(000)	332	
Crystal size	0.380 x 0.080 x 0.060 mm^3	
Theta range for data collection	2.903 to 66.379°.	
Index ranges	-9<=h<=9, -6<=k<=6, -18<=l<=18	
Reflections collected	8320	
Independent reflections	2577 [R(int) = 0.0332]	
Completeness to theta = 66.380°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5569	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2577 / 1 / 181	
Goodness-of-fit on F2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0205, wR2 = 0.0546	
R indices (all data)	R1 = 0.0275, wR2 = 0.0553	
Absolute structure parameter	-0.038(14)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.215 and -0.219 e.Å-3	



4g

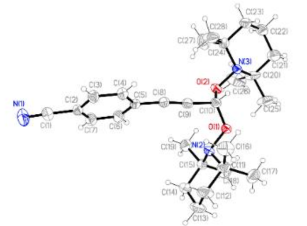


Table S2. Crystal data and structure refinement for 4g

identification code	C28H41N3O2	
Empirical formula	C28 H41 N3 O2	
Formula weight	451.64	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P_{-1}	
Unit cell dimensions	a = 7.6884(2) Å	α= 107.9050(10)°.
	b = 12.6896(3) Å	β= 90.1750(10)°.
	c = 14.6933(4) Å	γ = 99.4080(10)°.
Volume	1343.57(6) $Å^3$	
Z	2	
Density (calculated)	1.116 Mg/m^3	
Absorption coefficient	0.546 mm-1	
F(000)	492	
Crystal size	0.160 x 0.120 x 0.060 mm3	
Theta range for data collection	3.166 to 66.545°.	
Index ranges	-9<=h<=9, -15<=k<=15, -17<=l<=17	
Reflections collected	22818	
Independent reflections	4588 [R(int) = 0.0282]	
Completeness to theta = 66.545°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.7131	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4588 / 21 / 336	
Goodness-of-fit on F2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1093	
R indices (all data)	R1 = 0.0498, wR2 = 0.1195	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.184 and -0.180 e.$Å^{-3}$	

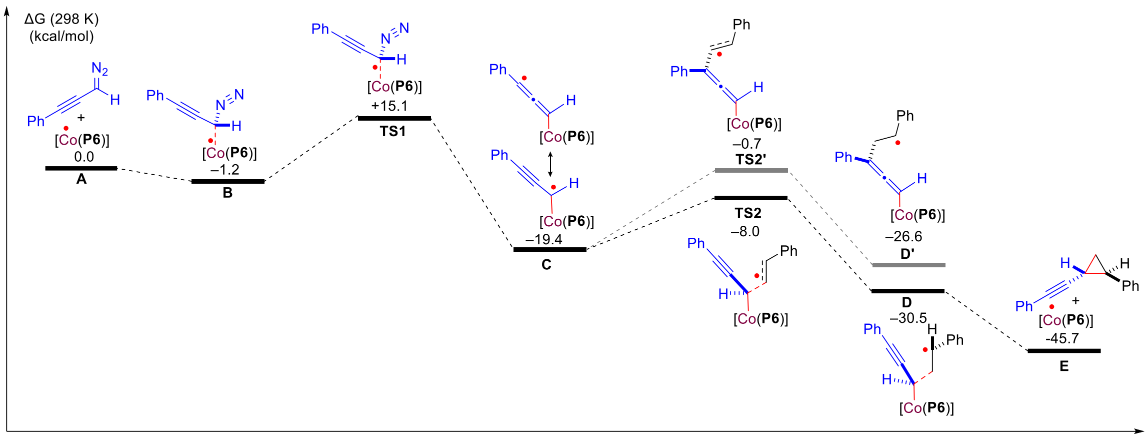
2.4.7. DFT Calculations

Considering the cost of time and computing resources for the large system with [Co(**P6**)], the geometry optimizations were performed with the Gaussian 16 at the BP86/lanl2dz level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

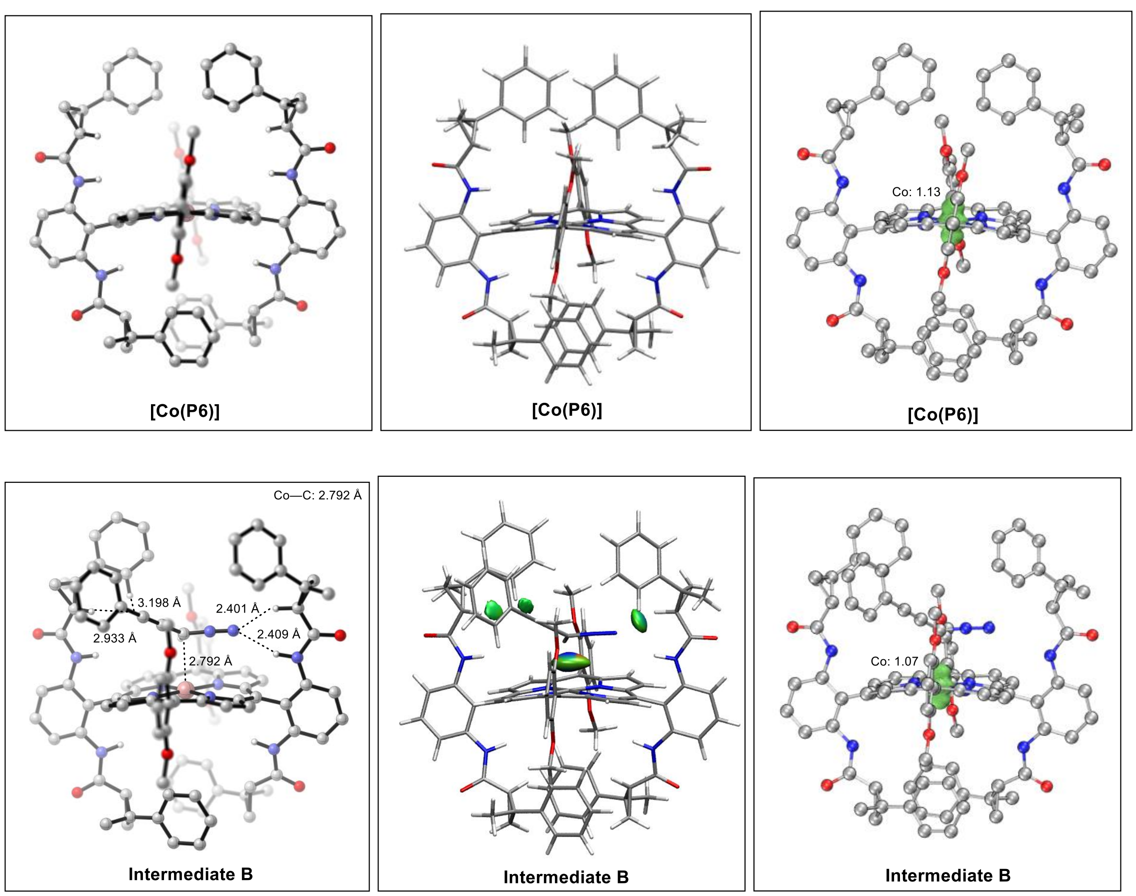
Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy, and thermal corrections (entropy and enthalpy, 298.15 K, 1 Atm) were obtained from these calculations. To further improve the accuracy of energies, single-point energies were carried out at the B3LYP/def2-tzvp level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

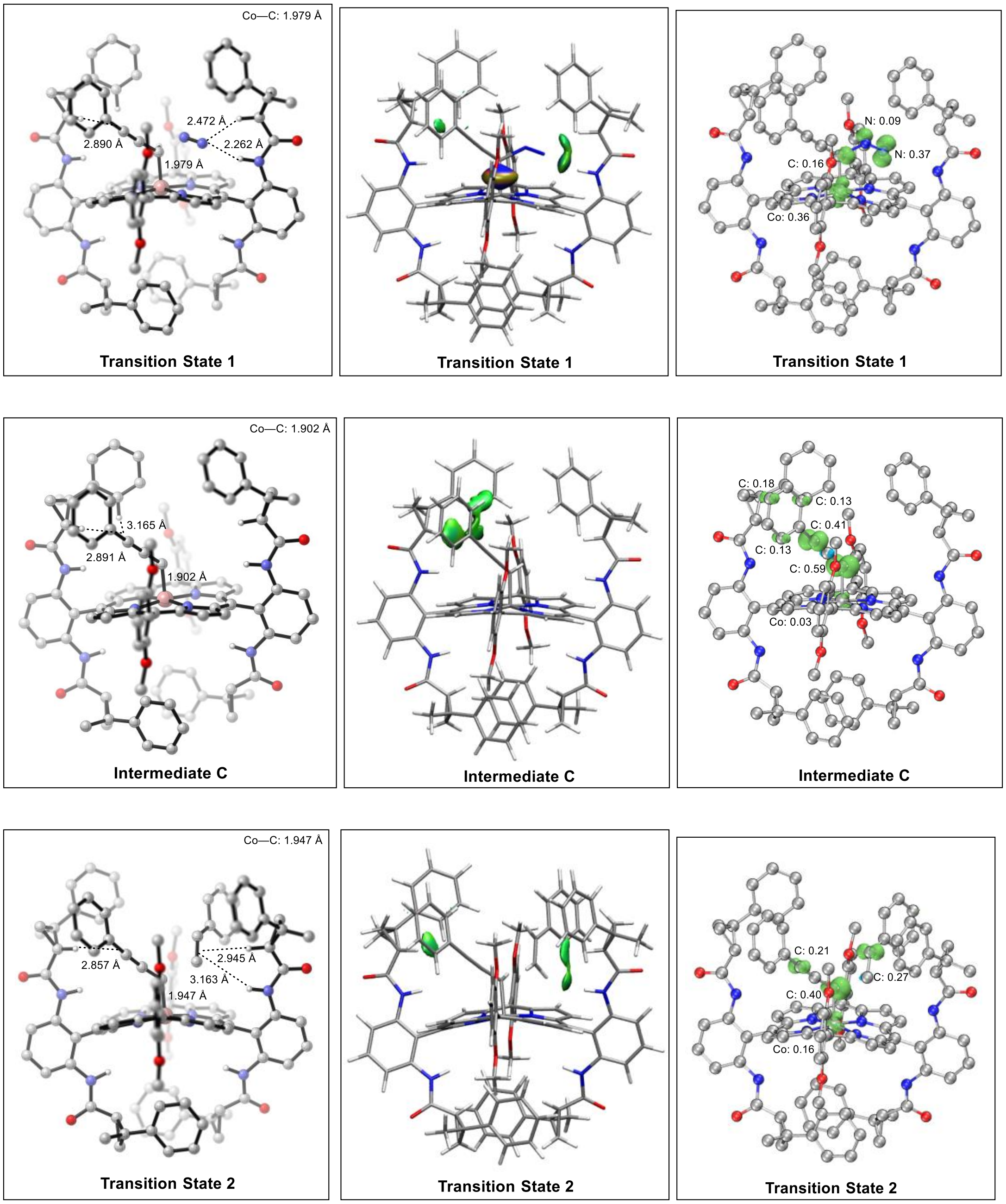
Independent Gradient Model (IGM)[33] analysis was performed with Multiwfn[34] software package using a high-quality grid option to generate files for further plotting. The visualization of IGM analysis results was presented with VMD[35] visualization software. As shown in Scheme S2, the 3D diagrams of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

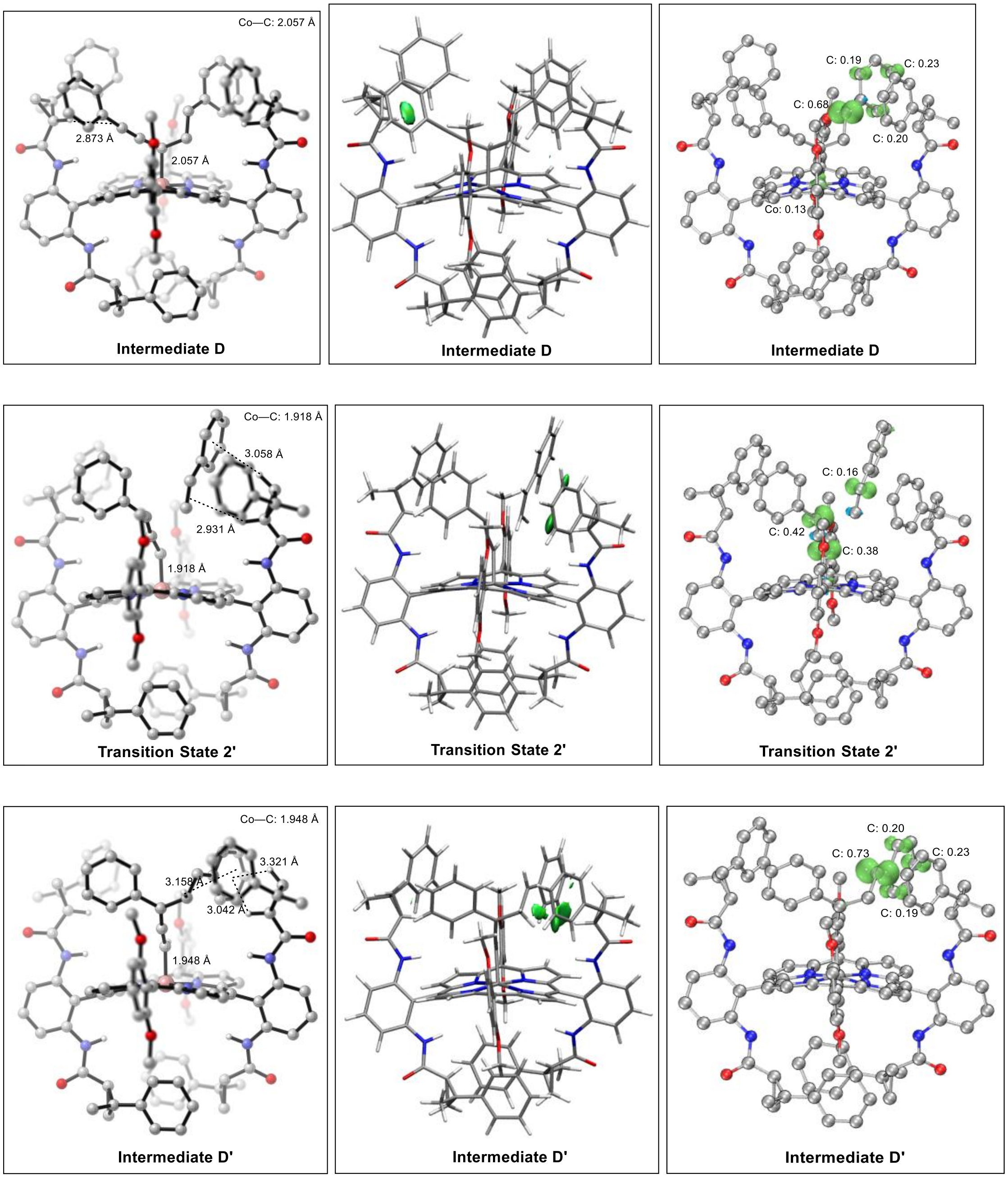
2.4.7.1. Scheme S2. Calculated Energy Diagram for [Co(P6)]-Catalyzed Radical Cyclopropanation of Styrene (2a) with Alkynyl Diazomethane (1a')



2.4.7.2. Scheme S3. Optimized Structure Models, NCI Plot, and Spin Density Representations of Intermediates and Transition States




Co—C: 1.979 Å
2.472 Å
2.890 Å
2.262 Å
1.979 Å
Transition State 1
Transition State 1
N: 0.09
N: 0.37
C: 0.16
Co: 0.36
Transition State 1
Co—C: 1.902 Å
3.165 Å
2.891 Å
1.902 Å
Intermediate C
Intermediate C
C: 0.18
C: 0.13
C: 0.41
C: 0.13
C: 0.59
Co: 0.03
Intermediate C
Co—C: 1.947 Å
2.857 Å
2.945 Å
3.163 Å
1.947 Å
Transition State 2
Transition State 2
C: 0.21
C: 0.27
C: 0.40
Co: 0.16
Transition State 2



2.4.7.3. Coordinates of Intermediates and Transition States

Intermediate A

A[Co(II)(P6)]

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.333865 Hartree

H_corr: 1.583795 Hartree

SCF: -4738.422006 Hartree

S: 526.023 Cal/Mol-Kelvin

H: -4736.838211 Hartree

G: -4737.088141 Hartree

Cartesian Coordinates:

Co	0.03934800	-0.00003300	0.00001000
O	3.08077300	7.33946200	0.26140600
O	-4.90023900	5.62002500	1.06249500
O	-1.78130800	-0.18595100	5.26643800
O	2.87722900	-0.86170600	4.48060600
N	0.05983900	1.24476900	1.53516800
N	0.01209800	-1.52989400	1.24959600
N	1.80702300	5.36918900	0.47554800
H	1.88057400	4.34710300	0.51694300
N	-2.95133500	4.36821100	0.62192900
H	-2.61075500	3.41062600	0.48572700
C	-0.29835800	3.43626100	0.35821500
C	-0.10254700	2.64686000	1.51000200
C	0.01093100	3.20182300	2.85253800
H	-0.08367500	4.26113300	3.08888000

C	0.26773900	2.14634300	3.70288600
H	0.41994300	2.16532200	4.78094400
C	0.26458100	0.93413100	2.89779400
C	0.34462300	-0.35788700	3.44409600
C	0.15853700	-1.50440100	2.65343200
C	0.02778800	-2.84446900	3.20543700
H	0.10321600	-3.07975500	4.26613500
C	-0.22242800	-3.69797100	2.15125300
H	-0.38252200	-4.77521800	2.16925200
C	-0.20362500	-2.89041200	0.93846000
C	-0.58298200	4.91134200	0.50847100
C	0.47456000	5.87233200	0.52250800
C	0.18725800	7.26155900	0.61306500
H	1.01024100	7.97775900	0.59745300
C	-1.15796200	7.67423200	0.71884400
H	-1.38022800	8.74510400	0.79364300
C	-2.22526300	6.75156000	0.73678200
H	-3.26416600	7.07108400	0.83412000
C	-1.93495600	5.36467500	0.62602500
C	3.01217200	6.07589000	0.40158400
C	4.23191000	5.19991800	0.51179200
H	4.07399900	4.22650200	0.99334800
C	5.58751000	5.88633800	0.78549700

H	6.25549000	5.40469300	1.50692700
H	5.54816300	6.98021800	0.82483300
C	5.36253100	5.22663500	-0.57706900
C	6.06524200	3.90716900	-0.84527700
C	7.48530200	3.86253800	-0.88261500
H	8.05460800	4.77809500	-0.67720700
C	8.16521200	2.65518100	-1.16671100
H	9.26158400	2.63731200	-1.18856300
C	7.43264700	1.46785400	-1.41263500
H	7.95535700	0.52601400	-1.61638600
C	6.01727800	1.50223500	-1.38162700
H	5.44321900	0.58382300	-1.55490800
C	5.34041900	2.71522500	-1.10812900
H	4.24346700	2.73443800	-1.09289600
C	5.19559300	6.11807800	-1.81578400
H	6.18833300	6.37704000	-2.23019500
H	4.66492900	7.05187700	-1.56257000
H	4.62625500	5.59078400	-2.60443900
C	-4.32833300	4.50521800	0.83688600
C	-5.06448900	3.19454400	0.79893700
H	-4.56995500	2.38644300	0.24515900
C	-6.60477700	3.20018200	0.74228800
H	-7.06809200	4.19248100	0.76748200

H	-7.07237800	2.46842900	0.07582200
C	-5.92641800	2.71772600	2.02541400
C	-5.89825800	1.22917200	2.32110200
C	-4.67466600	0.56547200	2.60389400
H	-3.73188600	1.12559000	2.56223000
C	-4.65476800	-0.81117500	2.93220600
H	-3.69803300	-1.30409400	3.14192200
C	-5.86628800	-1.54350000	2.99209900
H	-5.85356900	-2.61124700	3.24091600
C	-7.09315400	-0.88891200	2.72090200
H	-8.03476400	-1.44944800	2.76916200
C	-7.10708200	0.48664100	2.38824600
H	-8.05750700	0.99072700	2.17175200
C	-6.00510000	3.60240400	3.27825400
H	-6.93984800	3.38707100	3.82997300
H	-5.99131700	4.67272100	3.01013500
H	-5.15597500	3.39898000	3.95811500
C	0.55830100	-0.51798100	4.92373700
C	-0.52329300	-0.42191500	5.84550400
C	-0.31790500	-0.56588900	7.24392000
H	-1.15099700	-0.49072800	7.94782000
C	0.98655300	-0.81411600	7.72143700
H	1.15152900	-0.92601700	8.79931900

C	2.08233900	-0.92275900	6.83916600
H	3.08352100	-1.11474400	7.23414500
C	1.85922900	-0.77455400	5.44389400
C	-2.93434700	-0.04071500	6.17099300
C	4.23897400	-1.16179400	4.95137500
O	3.08104600	-7.33945400	-0.26115800
O	-4.90002400	-5.62015500	-1.06252300
O	-1.78143200	0.18583700	-5.26634000
O	2.87710100	0.86173400	-4.48066300
N	0.05990500	-1.24483600	-1.53514700
N	0.01199500	1.52982500	-1.24958000
N	1.80724200	-5.36923600	-0.47551300
H	1.88077000	-4.34715100	-0.51698300
N	-2.95111900	-4.36833300	-0.62197700
H	-2.61054700	-3.41074500	-0.48577700
C	-0.29817600	-3.43634700	-0.35819200
C	-0.10240900	-2.64693600	-1.50997900
C	0.01104900	-3.20189000	-2.85252100
H	-0.08351000	-4.26120400	-3.08886300
C	0.26776600	-2.14639300	-3.70287500
H	0.41992200	-2.16535400	-4.78094100
C	0.26457500	-0.93418500	-2.89777900
C	0.34454600	0.35783600	-3.44408200

C	0.15843000	1.50434400	-2.65341500
C	0.02763400	2.84440900	-3.20541500
H	0.10306900	3.07970300	-4.26611200
C	-0.22261400	3.69789700	-2.15122700
H	-0.38274500	4.77513900	-2.16922100
C	-0.20378300	2.89033300	-0.93843800
C	-0.58276900	-4.91143300	-0.50844600
C	0.47479100	-5.87240400	-0.52245100
C	0.18751100	-7.26163800	-0.61297100
H	1.01050400	-7.97782600	-0.59733500
C	-1.15770100	-7.67433700	-0.71876500
H	-1.37994300	-8.74521500	-0.79354700
C	-2.22501700	-6.75168200	-0.73674900
H	-3.26391300	-7.07122300	-0.83411000
C	-1.93473300	-5.36479000	-0.62601500
C	3.01241000	-6.07590300	-0.40151000
C	4.23212200	-5.19990100	-0.51176400
H	4.07420000	-4.22655900	-0.99346500
C	5.58776600	-5.88631400	-0.78529000
H	6.25576200	-5.40475100	-1.50676200
H	5.54845800	-6.98020000	-0.82446900
C	5.36268700	-5.22641700	0.57716000
C	6.06531800	-3.90687500	0.84520500

C	7.48537400	-3.86210100	0.88244500
H	8.05475500	-4.77762200	0.67708400
C	8.16518200	-2.65465000	1.16639600
H	9.26155300	-2.63666600	1.18817000
C	7.43251400	-1.46737700	1.41226900
H	7.95514300	-0.52546700	1.61590200
C	6.01714400	-1.50190100	1.38135500
H	5.44300600	-0.58352900	1.55458700
C	5.34039100	-2.71498100	1.10800300
H	4.24344000	-2.73430300	1.09281400
C	5.19569800	-6.11766600	1.81600600
H	6.18841800	-6.37650600	2.23053700
H	4.66509500	-7.05153000	1.56290200
H	4.62626800	-5.59027400	2.60453000
C	-4.32810500	-4.50533900	-0.83699200
C	-5.06426400	-3.19466200	-0.79901000
H	-4.56972400	-2.38658300	-0.24520500
C	-6.60455200	-3.20029900	-0.74235400
H	-7.06787000	-4.19259500	-0.76757500
H	-7.07214900	-2.46855400	-0.07587900
C	-5.92618300	-2.71781400	-2.02547100
C	-5.89802600	-1.22925000	-2.32111900
C	-4.67444200	-0.56550000	-2.60381200

H	-3.73164300	-1.12558200	-2.56210400
C	-4.65457700	0.81115700	-2.93209000
H	-3.69785100	1.30412000	-3.14174800
C	-5.86611800	1.54343900	-2.99204500
H	-5.85341900	2.61119400	-3.24082900
C	-7.09298100	0.88879900	-2.72094700
H	-8.03460800	1.44930200	-2.76925500
C	-7.10687700	-0.48676200	-2.38832900
H	-8.05729600	-0.99089200	-2.17191200
C	-6.00487300	-3.60246300	-3.27832900
H	-6.93962400	-3.38712100	-3.83003800
H	-5.99108900	-4.67278600	-3.01023100
H	-5.15575100	-3.39903000	-3.95819000
C	0.55817900	0.51794000	-4.92373000
C	-0.52345100	0.42185400	-5.84545300
C	-0.31811500	0.56583800	-7.24387600
H	-1.15122900	0.49066400	-7.94774800
C	0.98632300	0.81409500	-7.72143600
H	1.15125900	0.92600300	-8.79932400
C	2.08214000	0.92275700	-6.83920700
H	3.08330500	1.11476100	-7.23422100
C	1.85908100	0.77454200	-5.44392700
C	-2.93450200	0.04056600	-6.17084900

C	4.23882600	1.16185500	-4.95146300
H	4.84822200	-1.22351100	4.03848200
H	4.27196200	-2.13048600	5.48642700
H	4.61994500	-0.35558600	5.60810700
H	-3.79131200	0.14062400	5.50680200
H	-2.79575200	0.81735100	6.85675200
H	-3.10180900	-0.96675600	6.75447300
H	4.84808900	1.22361200	-4.03858100
H	4.27177800	2.13054400	-5.48652400
H	4.61980800	0.35565200	-5.60819200
H	-3.79143200	-0.14081600	-5.50662300
H	-2.79590300	-0.81748800	-6.85662400
H	-3.10202300	0.96660600	-6.75431400

$A_{1a'}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.084648 Hartree

H_corr: 0.131982 Hartree

SCF: -456.153645Hartree

S: 99.622 Cal/Mol-Kelvin

H: -455.757252 Hartree

G: -455.804586 Hartree

Cartesian Coordinates:

N	-4.85027900	1.00185300	0.00083100
N	-4.03063300	0.14431500	0.00015400
H	-3.51793700	-1.84750100	-0.00032800
C	-3.11657000	-0.82960100	-0.00020700
C	-1.73064700	-0.55419000	-0.00054500
C	-0.50204000	-0.35992600	-0.00065000
H	0.74035900	2.04581800	-0.00083600
C	0.91075500	-0.13281600	-0.00047000
C	1.43475200	1.19816300	-0.00048400
C	1.82602100	-1.23196800	0.00022600
H	1.43273300	-2.25473400	0.00043100
C	2.82854400	1.41628400	0.00001400
H	3.21576200	2.44188900	-0.00007400
C	3.21786700	-1.00166000	0.00045500
C	3.72769200	0.32074800	0.00037600
H	3.90752200	-1.85383800	0.00089600
H	4.80971100	0.49498500	0.00071900

Intermediate B

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.440962 Hartree

H_corr: 1.717747 Hartree

SCF: -5194.313943 Hartree

S: 582.542 Cal/Mol-Kelvin

H: -5192.596196 Hartree

G: -5192.872981 Hartree

Cartesian Coordinates:

N	2.30173200	1.68473800	0.71295300
N	2.21064600	2.86133900	0.66789400
Co	-0.36358800	0.05943400	0.13176100
O	3.30091400	-7.03292600	0.69027800
O	-4.49869500	-6.03228700	-1.48989300
O	-1.73735700	0.13111000	-5.31783200
O	2.79514800	0.88770900	-4.04922700
N	-0.10072000	-1.21552400	-1.35325600
N	-0.46938100	1.54833400	-1.16640700
N	1.97320500	-5.15598100	0.18414700
H	1.98569400	-4.13290700	0.11074000
N	-2.78646000	-4.59363800	-0.74169600
H	-2.57251400	-3.60765900	-0.55945400
C	-0.30083700	-3.40575800	-0.13314900
C	-0.11199200	-2.62517800	-1.29320200

C	0.14644500	-3.19672600	-2.60859500
H	0.17224600	-4.26557600	-2.81860200
C	0.34780200	-2.13972400	-3.47313300
H	0.55630100	-2.16679000	-4.54199500
C	0.17428000	-0.91581900	-2.70404400
C	0.19050300	0.36668400	-3.27882600
C	-0.17527900	1.50867600	-2.54578200
C	-0.39474800	2.81334600	-3.15359500
H	-0.23198600	3.03334300	-4.20782700
C	-0.86270300	3.65126900	-2.16266100
H	-1.15169600	4.69915900	-2.23473000
C	-0.88331700	2.87795300	-0.92758600
C	-0.41742600	-4.90543600	-0.26099000
C	0.70758300	-5.76676800	-0.06741300
C	0.55664700	-7.17834200	-0.15906000
H	1.42301700	-7.81725200	0.01560900
C	-0.71028400	-7.71477600	-0.46873100
H	-0.82164800	-8.80269500	-0.54506000
C	-1.83672500	-6.89439900	-0.68419400
H	-2.81473000	-7.30829600	-0.93478700
C	-1.68990700	-5.48565000	-0.57115100
C	3.18917400	-5.77874000	0.49502400
C	4.37188300	-4.84906700	0.54797200

H	4.22871600	-3.86445100	0.08729700
C	5.76492800	-5.49557100	0.35560500
H	6.47384500	-4.96190000	-0.28526300
H	5.75461200	-6.58699500	0.26467000
C	5.41162400	-4.90427500	1.72301800
C	6.09408900	-3.59973100	2.10003300
C	7.48017400	-3.61799200	2.42111700
H	8.03042700	-4.56576800	2.36161900
C	8.15562400	-2.43484900	2.79721400
H	9.22481900	-2.46901900	3.03902100
C	7.45562500	-1.20330200	2.85095500
H	7.97948600	-0.28088000	3.12864000
C	6.07704300	-1.17409200	2.53346800
H	5.53114400	-0.22240900	2.54606900
C	5.40071800	-2.36512100	2.17163700
H	4.33258900	-2.32985800	1.92851300
C	5.16850600	-5.85086700	2.90718500
H	6.13042700	-6.11015300	3.38882100
H	4.67828400	-6.78084800	2.57350200
H	4.52868500	-5.36670400	3.66901500
C	-4.09096100	-4.86889700	-1.17091100
C	-4.96360800	-3.64644600	-1.23796200
H	-4.65719300	-2.80673200	-0.60157400

C -6.48291100 -3.82749800 -1.42420900

H -6.81802000 -4.86483400 -1.53152400

H -7.12924700 -3.17265200 -0.83144100

C -5.67462600 -3.23519200 -2.57933800

C -5.77720800 -1.74547100 -2.85046300

C -4.61209100 -0.93782300 -2.93736300

H -3.62602400 -1.38653600 -2.76282400

C -4.70663500 0.44081700 -3.24388000

H -3.79388400 1.04493000 -3.30564900

C -5.97358400 1.03042000 -3.47809800

H -6.05026900 2.09973500 -3.70747200

C -7.14132500 0.23162900 -3.40355000

H -8.12471600 0.68203400 -3.58543300

C -7.04185500 -1.14543300 -3.09239300

H -7.94740200 -1.76225600 -3.02931100

C -5.45459700 -4.08608000 -3.83868100

H -6.31112700 -3.96213100 -4.52833600

H -5.35834400 -5.15536200 -3.58353500

H -4.53964900 -3.76786600 -4.37370400

C 0.54526300 0.51286700 -4.73310400

C -0.43053100 0.38903000 -5.76234100

C -0.07903600 0.52162400 -7.13303400

H -0.83174800 0.42663400 -7.92018800

C	1.26551600	0.78223200	-7.47330200
H	1.54151500	0.88655700	-8.52903500
C	2.26100100	0.91260000	-6.48155100
H	3.29611700	1.11559600	-6.76916700
C	1.89089300	0.77733200	-5.11690100
C	-2.78468500	-0.04429600	-6.33856100
C	4.21234300	1.10882900	-4.36984800
O	1.25540100	8.00568700	0.82088800
O	-6.15876100	4.68168900	0.63961400
O	-2.65977900	-0.33570000	5.22757200
O	2.09424000	-0.21665800	4.84704200
N	-0.69307100	1.33327600	1.61327200
N	-0.36654300	-1.43774000	1.42563700
N	0.50102900	5.79031500	0.52108100
H	0.81890600	4.81551300	0.44667300
N	-3.97790300	3.83558900	0.33307100
H	-3.45160300	2.96205900	0.22847300
C	-1.20238800	3.43261700	0.32836500
C	-1.03852600	2.69906900	1.52180200
C	-1.15091800	3.29034100	2.84828700
H	-1.41299400	4.33103900	3.03512500
C	-0.84256400	2.30039900	3.75844500
H	-0.81137300	2.36449600	4.84506900

C	-0.59196400	1.08349100	3.00085800
C	-0.38877300	-0.17413600	3.59554900
C	-0.35652700	-1.35747700	2.83621900
C	-0.37769400	-2.68855700	3.42365900
H	-0.37711600	-2.88615900	4.49469200
C	-0.42674100	-3.59294100	2.38277700
H	-0.46421600	-4.68066500	2.42679300
C	-0.38740000	-2.82144800	1.14710700
C	-1.75440800	4.83579800	0.40332900
C	-0.91279400	5.98962300	0.49216100
C	-1.48999400	7.28962100	0.56279400
H	-0.83167600	8.15597600	0.63239500
C	-2.89310100	7.42489600	0.55742400
H	-3.32908000	8.42911500	0.61525000
C	-3.75074000	6.30858400	0.48511900
H	-4.83706500	6.41006500	0.49600700
C	-3.17728100	5.01158700	0.40725500
C	1.49996800	6.76022500	0.69937000
C	2.89778800	6.21330800	0.75844400
H	2.98688900	5.12629200	0.84479500
C	3.95950200	7.04744600	1.51767200
H	4.64803000	6.49680700	2.16744300
H	3.60243500	8.00748700	1.90481100

C	4.08770900	6.91464500	0.00317000
C	5.16438900	5.99692800	-0.54762800
C	6.50938100	6.12301500	-0.10932900
H	6.74929400	6.85009500	0.67665600
C	7.53417900	5.32786700	-0.67503700
H	8.56794500	5.43825000	-0.32567800
C	7.22737500	4.39370100	-1.69370500
H	8.02002700	3.77736600	-2.13468000
C	5.88884600	4.26084300	-2.13749100
H	5.64302900	3.54022100	-2.92641600
C	4.86694300	5.05670900	-1.56981400
H	3.83133800	4.94895700	-1.91666200
C	3.82013200	8.14125900	-0.88179600
H	4.74154200	8.74892700	-0.96226000
H	3.01363800	8.76377900	-0.46032800
H	3.52986500	7.83205100	-1.90376600
C	-5.36615600	3.70145100	0.45914100
C	-5.83230400	2.27388300	0.38435300
H	-5.16003100	1.57881000	-0.13421500
C	-7.33892500	1.98696500	0.23423700
H	-7.98195000	2.87374900	0.22520200
H	-7.61726600	1.18535300	-0.45706600
C	-6.66144100	1.63522200	1.55920600

C	-6.36897900	0.17803100	1.86605700
C	-5.07017700	-0.23377900	2.26834700
H	-4.25670300	0.50140300	2.31298800
C	-4.81013600	-1.58253400	2.60983600
H	-3.80058400	-1.87665200	2.91989000
C	-5.85324500	-2.54033000	2.56050500
H	-5.65362800	-3.58709900	2.81832300
C	-7.15411000	-2.13855500	2.16880600
H	-7.96600600	-2.87518400	2.13203000
C	-7.40836000	-0.78921900	1.82543900
H	-8.41542800	-0.47939600	1.51854100
C	-6.98242300	2.48224100	2.79937700
H	-7.89048900	2.08977500	3.29543700
H	-7.15683700	3.53681400	2.52538200
H	-6.15206000	2.44162000	3.52986400
C	-0.28021900	-0.26648800	5.09146300
C	-1.43768100	-0.33971200	5.91785900
C	-1.33169000	-0.41719900	7.33235500
H	-2.22296800	-0.47096300	7.96325200
C	-0.04949700	-0.42666800	7.92176600
H	0.03957100	-0.48567300	9.01266700
C	1.12067300	-0.36318000	7.13532100
H	2.10178500	-0.37205600	7.61739900

C	0.99506000	-0.28454200	5.72266100
C	-3.89841800	-0.38960200	6.02228800
C	3.43904400	-0.27671500	5.44263600
H	4.71962400	1.12231900	-3.39475200
H	4.35711600	2.07522000	-4.89208400
H	4.61620600	0.28229800	-4.98518500
H	-3.70157100	-0.24519100	-5.76659500
H	-2.55371000	-0.90071000	-7.00115900
H	-2.91079500	0.87598500	-6.94120300
H	4.13140600	-0.26043900	4.58934800
H	3.58095900	-1.21419700	6.01353600
H	3.62357200	0.59683100	6.09743900
H	-4.70743000	-0.38442500	5.27812700
H	-3.98311100	0.49286600	6.68543600
H	-3.94639400	-1.31919300	6.62181800
C	3.16204600	-0.36999300	-0.16345700
C	5.05620800	-3.11154200	-3.85811300
C	4.74728800	-1.72241900	-1.84819100
C	4.20505500	-2.41246400	-2.97489700
C	6.45647400	-3.13023200	-3.63951300
C	3.88847100	-1.00288600	-0.94675000
C	7.00320900	-2.44843200	-2.52374500
C	2.34388300	0.34881800	0.74861100

C 6.15926800 -1.75314100 -1.63024500

H 6.57565900 -1.23725100 -0.75803400

H 8.08492200 -2.46406900 -2.34715400

H 7.11352400 -3.67467100 -4.32777400

H 3.12268400 -2.38971100 -3.14119700

H 4.62845100 -3.64383900 -4.71551000

H 1.88755200 -0.10440500 1.63636700

Transition State TS1

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -367.2223 cm-1

G_corr: 1.440841 Hartree

H_corr: 1.71512 Hartree

SCF: -5194.303944 Hartree

S: 577.269 Cal/Mol-Kelvin

H: -5192.588824 Hartree

G: -5192.863103 Hartree

Cartesian Coordinates:

N 2.62527600 1.31534700 0.68567000

N 2.44061600 2.42454100 0.31906800

Co -0.19089100 0.06699100 0.17177000

O	2.16242300	-7.41637700	0.76345900
O	-5.36407500	-5.31515400	-1.61969000
O	-1.55536000	0.37034900	-5.31742200
O	3.00809700	0.52437000	-3.95421500
N	-0.26262400	-1.19232900	-1.34845100
N	-0.12245600	1.56920500	-1.11131700
N	1.13507800	-5.38419200	0.16371600
H	1.30099500	-4.37584100	0.07170200
N	-3.47613500	-4.14242700	-0.83287100
H	-3.12516500	-3.19854700	-0.63992000
C	-0.85040100	-3.33345000	-0.16650500
C	-0.52826300	-2.57798600	-1.31201200
C	-0.38122400	-3.16429800	-2.63693400
H	-0.55939700	-4.21447600	-2.86597900
C	0.01721400	-2.14929200	-3.48293300
H	0.21281700	-2.19490200	-4.55348900
C	0.07844300	-0.93014200	-2.69175700
C	0.34909000	0.33409200	-3.24120600
C	0.17875200	1.50769800	-2.48880700
C	0.15533600	2.83653300	-3.08043800
H	0.35360600	3.04257200	-4.13139700
C	-0.20399400	3.71905400	-2.08304600
H	-0.34765900	4.79720300	-2.14399700

C	-0.34325700	2.94266800	-0.85926000
C	-1.18736300	-4.79651900	-0.31441500
C	-0.19938500	-5.80943100	-0.10772500
C	-0.54885100	-7.18437900	-0.20888100
H	0.21343500	-7.94163300	-0.02139800
C	-1.87436700	-7.53220300	-0.54270800
H	-2.13956400	-8.59258500	-0.62653700
C	-2.86812800	-6.55822500	-0.77382300
H	-3.89053300	-6.82780400	-1.04329800
C	-2.52363600	-5.18521300	-0.65028600
C	2.23841800	-6.16646400	0.53011100
C	3.53633200	-5.40782100	0.59953400
H	3.55148200	-4.44094200	0.08304200
C	4.83691600	-6.24077200	0.52551600
H	5.64274800	-5.84554400	-0.10111500
H	4.68614700	-7.32517000	0.49352200
C	4.49642700	-5.52569800	1.83584000
C	5.31735100	-4.29443200	2.18131900
C	6.68540700	-4.45402000	2.53711700
H	7.12695800	-5.45880600	2.52621300
C	7.48111700	-3.33843500	2.88490600
H	8.53501100	-3.48084700	3.15301700
C	6.92181600	-2.03591400	2.87602600

H	7.53986000	-1.16674800	3.13083200
C	5.56085500	-1.86572900	2.52549400
H	5.12297300	-0.86036100	2.49269700
C	4.76405400	-2.98852300	2.19087100
H	3.71182300	-2.84486700	1.91953700
C	4.06737700	-6.35977500	3.05113900
H	4.95945900	-6.71404100	3.60185900
H	3.47505500	-7.23612800	2.73773600
H	3.45893200	-5.75194100	3.74721100
C	-4.79919900	-4.22405800	-1.28555000
C	-5.48596200	-2.88848600	-1.35670000
H	-5.06899000	-2.10280700	-0.71418100
C	-7.01392100	-2.84988300	-1.55834100
H	-7.49250900	-3.82845400	-1.67338500
H	-7.56606300	-2.11097700	-0.96913900
C	-6.11772700	-2.37552100	-2.70288500
C	-6.00529300	-0.88524700	-2.96783700
C	-4.73729200	-0.24887600	-3.03468800
H	-3.82704000	-0.83206800	-2.84649900
C	-4.63321800	1.13030800	-3.33550200
H	-3.64446300	1.60222400	-3.37750500
C	-5.80127500	1.89265600	-3.58463200
H	-5.72375200	2.96272000	-3.81030800

C	-7.07045900	1.26547400	-3.52954900
H	-7.97837500	1.84969600	-3.72280900
C	-7.16955100	-0.11270200	-3.22340500
H	-8.15359100	-0.59613500	-3.17477000
C	-6.00874500	-3.24459700	-3.96428100
H	-6.83252400	-2.99811900	-4.66086100
H	-6.06726200	-4.31755300	-3.71321000
H	-5.05303900	-3.05721000	-4.48982000
C	0.74630800	0.43879600	-4.68720500
C	-0.21651600	0.44781700	-5.73568300
C	0.17768800	0.53235800	-7.09839300
H	-0.56442900	0.53994000	-7.90112700
C	1.55211900	0.60941100	-7.41016400
H	1.86122600	0.67343200	-8.45992500
C	2.53562200	0.60809600	-6.39812000
H	3.59449100	0.66849400	-6.66365500
C	2.12318900	0.52661300	-5.04132200
C	-2.59715300	0.34717700	-6.35842300
C	4.44987800	0.56711300	-4.23777500
O	2.61182800	7.53611100	1.17484600
O	-5.26323600	5.60254300	0.67830100
O	-2.71970300	0.04267200	5.17163300
O	1.98190800	-0.73027300	4.95006600

N	-0.42121900	1.35899200	1.65840400
N	-0.58798700	-1.41068400	1.42586800
N	1.49463000	5.54019100	0.59590800
H	1.64562500	4.54021300	0.40685500
N	-3.25403000	4.40062100	0.39031600
H	-2.88400500	3.45249300	0.26729700
C	-0.58754900	3.52514500	0.39912100
C	-0.54635900	2.76241400	1.58312000
C	-0.58004900	3.34778900	2.91645200
H	-0.67915600	4.41421500	3.11490500
C	-0.43974000	2.31107700	3.81514800
H	-0.41452700	2.35500600	4.90283900
C	-0.37600200	1.07995900	3.04196100
C	-0.40727600	-0.20114300	3.61893400
C	-0.58133000	-1.35667700	2.83745500
C	-0.85923400	-2.66894500	3.39950200
H	-0.91904100	-2.87776800	4.46666000
C	-1.05139600	-3.53361700	2.34187200
H	-1.28892600	-4.59634200	2.36471300
C	-0.84878800	-2.76425600	1.12181000
C	-0.89368100	4.99894700	0.49391200
C	0.13807000	5.98327600	0.60920600
C	-0.20403800	7.36009900	0.73227200

H	0.59455600	8.09492800	0.83793600
C	-1.56228400	7.73799100	0.73865000
H	-1.81655000	8.79996400	0.83587000
C	-2.60225700	6.79235200	0.62645600
H	-3.65409100	7.08226600	0.64066600
C	-2.26377500	5.41858000	0.50415700
C	2.64356800	6.29843600	0.86983700
C	3.92841800	5.52431000	0.79328600
H	3.82722200	4.43962100	0.67815600
C	5.11740400	6.01442600	1.65753900
H	5.69900900	5.24590700	2.17771100
H	4.93188600	6.93489300	2.22103000
C	5.22261800	6.13915100	0.14065500
C	6.12671300	5.17063800	-0.60071200
C	7.46777600	4.97022900	-0.17858800
H	7.82309500	5.47307100	0.72964600
C	8.34378700	4.13873900	-0.91608100
H	9.37685200	3.99527200	-0.57677500
C	7.89026200	3.49740900	-2.09389300
H	8.56850600	2.85588400	-2.66933900
C	6.55394200	3.69049100	-2.52232400
H	6.19579800	3.20057700	-3.43580500
C	5.68049400	4.52001300	-1.78175300

H	4.64484600	4.66253800	-2.11533500
C	5.17394900	7.53385200	-0.50175600
H	6.18777900	7.97765800	-0.49997100
H	4.48675000	8.19792900	0.04771200
H	4.83606200	7.46965000	-1.55340600
C	-4.64707600	4.50493100	0.48553200
C	-5.34929800	3.18144700	0.35737800
H	-4.78565400	2.38939900	-0.15178200
C	-6.87545000	3.16238800	0.13989900
H	-7.35548200	4.14697400	0.12904600
H	-7.25732600	2.43389100	-0.58229700
C	-6.32607700	2.67388700	1.48077300
C	-6.30306000	1.18244700	1.76094800
C	-5.10817200	0.53820300	2.17954600
H	-4.17770300	1.11512000	2.25458700
C	-5.10090400	-0.84109400	2.49738300
H	-4.16716700	-1.31703100	2.81911800
C	-6.29660600	-1.59599200	2.40809200
H	-6.29302900	-2.66569900	2.64843300
C	-7.49546200	-0.96140200	1.99910600
H	-8.42488400	-1.54001000	1.93158500
C	-7.49692400	0.41718600	1.67908000
H	-8.42502400	0.90689300	1.35789800

C	-6.55147900	3.53952300	2.72920800
H	-7.53397100	3.29925400	3.17825400
H	-6.53063100	4.61336800	2.47633900
H	-5.77297300	3.34276200	3.49076400
C	-0.36480400	-0.33217600	5.11546200
C	-1.54458400	-0.19671600	5.90175400
C	-1.50561800	-0.30741600	7.31732100
H	-2.41306700	-0.19972600	7.91748100
C	-0.26933900	-0.56257500	7.94837400
H	-0.23161400	-0.64788200	9.04053000
C	0.91896000	-0.71182100	7.20213600
H	1.86360900	-0.90920200	7.71559200
C	0.86156800	-0.59719000	5.78719900
C	-3.97360400	0.21244100	5.92505300
C	3.27388700	-1.03420500	5.58775100
H	4.93005200	0.55809500	-3.24940500
H	4.72092900	1.49227800	-4.78367900
H	4.76693600	-0.32152600	-4.81622600
H	-3.54450400	0.27624000	-5.80540400
H	-2.47700600	-0.53135500	-7.02143400
H	-2.58037400	1.27755700	-6.95847500
H	3.98490200	-1.13980400	4.75669900
H	3.22457300	-1.98379200	6.15443400

H	3.58948300	-0.21028000	6.25669900
H	-4.74186800	0.37512000	5.15590900
H	-3.91581800	1.08854500	6.59939600
H	-4.21405000	-0.69784300	6.50764600
C	2.51622400	-1.01902600	-0.24852000
C	4.58905800	-3.68110700	-3.91324100
C	4.16141900	-2.38991700	-1.85893500
C	3.69822000	-2.97282200	-3.07911900
C	5.95501400	-3.81327300	-3.55744200
C	3.26926100	-1.66072500	-1.00506500
C	6.42412100	-3.23614800	-2.35072300
C	1.73175300	-0.15649900	0.58371300
C	5.53939500	-2.53654400	-1.50229600
H	5.89795500	-2.10132500	-0.56314800
H	7.47814600	-3.33751700	-2.06731900
H	6.64339700	-4.36377700	-4.20922300
H	2.64346600	-2.86358900	-3.35124500
H	4.21890300	-4.13166200	-4.84151700
H	1.75721600	-0.41634600	1.65881500

Intermediate C

$C_{[Co(III)(P6)]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.434835 Hartree

H_corr: 1.705227 Hartree

SCF: -6325.50188201 Hartree

S: 569.087 Cal/Mol-Kelvin

H: -6323.796655 Hartree

G: -6324.067047 Hartree

Cartesian Coordinates:

Co	-0.21374200	0.10003500	0.14770900
O	2.68689800	-7.11820800	1.10494100
O	-5.13740600	-5.73513500	-0.84532600
O	-1.85809100	-0.14473700	-5.26259100
O	2.76036800	0.34977000	-4.19791200
N	-0.29462300	-1.28312900	-1.26404300
N	-0.21625000	1.49450000	-1.26147000
N	1.45134700	-5.20941600	0.49210300
H	1.52796900	-4.19784200	0.33891800
N	-3.28329300	-4.37929300	-0.31391900
H	-2.98512000	-3.40141800	-0.23576100
C	-0.69086000	-3.34236700	0.12129200
C	-0.46829800	-2.67344600	-1.09731600
C	-0.34516300	-3.36672500	-2.37217300

H	-0.46129400	-4.44251000	-2.49863200
C	-0.05586500	-2.40928300	-3.32164400
H	0.09925500	-2.53827000	-4.39185700
C	-0.03316800	-1.12371600	-2.64173400
C	0.15843000	0.09599800	-3.30950300
C	0.01807700	1.32280300	-2.64303800
C	-0.00379400	2.60328300	-3.33267200
H	0.14412600	2.72283500	-4.40499700
C	-0.27647600	3.56968700	-2.38782200
H	-0.39201300	4.64454400	-2.52263100
C	-0.37932900	2.88895400	-1.10376100
C	-0.92942000	-4.83187400	0.11319500
C	0.14260700	-5.75176400	0.33437100
C	-0.10879500	-7.15152500	0.36257500
H	0.71887500	-7.83542800	0.55543400
C	-1.42278200	-7.61628300	0.14468500
H	-1.61282800	-8.69583000	0.16139000
C	-2.49904800	-6.73636800	-0.09626700
H	-3.51297500	-7.09776400	-0.27525500
C	-2.25026400	-5.33752400	-0.10490100
C	2.63921600	-5.87788900	0.81890700
C	3.86266900	-5.00357100	0.78355900
H	3.76110000	-4.06304100	0.22898000

C	5.23258600	-5.71119800	0.67488800
H	5.96301100	-5.26742300	-0.00889400
H	5.18852900	-6.80550900	0.69380600
C	4.88676000	-4.97584300	1.97264300
C	5.59506600	-3.65730500	2.23398400
C	6.98531200	-3.66925800	2.53486400
H	7.52359500	-4.62581200	2.53625500
C	7.67973600	-2.46970400	2.81277000
H	8.75264400	-2.49861100	3.03869200
C	6.99333800	-1.22972500	2.78858800
H	7.53131900	-0.29554800	2.98955700
C	5.60956300	-1.20685700	2.49111900
H	5.07209600	-0.25159000	2.44802400
C	4.91491500	-2.41258600	2.22480300
H	3.84391000	-2.37913700	1.99348300
C	4.59958100	-5.79617600	3.23837400
H	5.54723900	-6.03583100	3.75721100
H	4.08558300	-6.73987300	2.98863800
H	3.96493900	-5.22278100	3.94039600
C	-4.62401400	-4.58458400	-0.66200700
C	-5.39834800	-3.30458300	-0.81951300
H	-4.99243300	-2.43243300	-0.29124500
C	-6.93541200	-3.37241600	-0.91913200

H	-7.35895800	-4.38246600	-0.90105100
H	-7.49565300	-2.60555400	-0.37492100
C	-6.14208000	-2.97277600	-2.16445000
C	-6.14089300	-1.51504600	-2.58782300
C	-4.92437900	-0.80352600	-2.76197100
H	-3.97008500	-1.29910100	-2.54355100
C	-4.92748400	0.53933000	-3.20940800
H	-3.97653300	1.07103600	-3.33293300
C	-6.15303900	1.18790700	-3.50069800
H	-6.15776900	2.22926300	-3.84398900
C	-7.37205800	0.48392900	-3.33910500
H	-8.32445100	0.97907400	-3.56462200
C	-7.36377100	-0.85648000	-2.88576100
H	-8.30908600	-1.39804800	-2.75348700
C	-6.05859000	-3.96308100	-3.33526900
H	-6.93724900	-3.83658300	-3.99596000
H	-6.03609300	-5.00511500	-2.97289500
H	-5.15045400	-3.78075000	-3.94075900
C	0.46908600	0.09104200	-4.78068500
C	-0.55016300	-0.04076800	-5.76552700
C	-0.23833400	-0.06031500	-7.15187900
H	-1.02387800	-0.16053900	-7.90553200
C	1.11023100	0.05467700	-7.55234800

H	1.35580400	0.03874500	-8.62057200
C	2.14766200	0.19202400	-6.60577600
H	3.18536600	0.27937300	-6.93884800
C	1.81768200	0.21276800	-5.22432900
C	-2.95049700	-0.32544100	-6.23397700
C	4.18256700	0.40805800	-4.56609100
O	2.72894900	7.50999700	0.69402100
O	-5.21082700	5.75121500	0.15960200
O	-2.65074400	0.47924300	5.16945200
O	2.05498800	-0.28480400	4.97749300
N	-0.41431800	1.50407000	1.53640700
N	-0.50573400	-1.27547000	1.53769200
N	1.53443200	5.53742000	0.21633900
H	1.63283100	4.52385800	0.09478600
N	-3.22107500	4.49330700	0.01538200
H	-2.86731200	3.53166900	-0.01663500
C	-0.56713600	3.57016700	0.11404100
C	-0.52076500	2.89992200	1.35166600
C	-0.53898000	3.59161500	2.63323200
H	-0.62760200	4.67131500	2.74633000
C	-0.40527100	2.62868200	3.61068500
H	-0.37183800	2.75821000	4.69127500
C	-0.35217900	1.33985200	2.93872700

C	-0.34827200	0.11359400	3.62233900
C	-0.47350800	-1.10614700	2.93949800
C	-0.65564500	-2.38117100	3.61495700
H	-0.68185500	-2.50191600	4.69689200
C	-0.80411200	-3.34202700	2.63801500
H	-0.96849900	-4.41252800	2.75241600
C	-0.68068900	-2.66409300	1.35457000
C	-0.85302600	5.05228000	0.10161100
C	0.19381200	6.02233900	0.16919300
C	-0.11260900	7.41103100	0.18892000
H	0.70129800	8.13378400	0.25744500
C	-1.46329200	7.81536900	0.14125700
H	-1.69731900	8.88619800	0.15753000
C	-2.52139200	6.88475900	0.07729600
H	-3.56664100	7.19731100	0.05192500
C	-2.21332200	5.49781800	0.06003500
C	2.70981200	6.25460700	0.47787100
C	3.95209300	5.40972000	0.50195000
H	3.79826300	4.32364400	0.46559700
C	5.13886100	5.89839700	1.37056400
H	5.65993300	5.14150200	1.96609700
H	4.98389100	6.86576300	1.85978000
C	5.30036800	5.90413200	-0.14601900

C	6.17348700	4.83666700	-0.78126900
C	7.48006200	4.58553200	-0.28503500
H	7.82827500	5.12630500	0.60393800
C	8.33247600	3.65597600	-0.92687800
H	9.33922500	3.47387100	-0.53184500
C	7.88948200	2.96538300	-2.08042900
H	8.54849100	2.24559200	-2.58029900
C	6.58773400	3.20925300	-2.58268200
H	6.23877800	2.67995100	-3.47721200
C	5.73795900	4.13774300	-1.93848100
H	4.72946900	4.32110700	-2.33079600
C	5.34478300	7.24749700	-0.88999500
H	6.38024100	7.63758200	-0.88436700
H	4.67759800	7.98584700	-0.41583700
H	5.03794700	7.12154800	-1.94539500
C	-4.61365300	4.62959000	0.08266100
C	-5.33560000	3.31077000	0.08124500
H	-4.78035100	2.46275600	-0.33961900
C	-6.86119100	3.28810500	-0.13946200
H	-7.32990200	4.27169300	-0.25275000
H	-7.25058300	2.49283300	-0.78315000
C	-6.32233400	2.93231100	1.24680200
C	-6.31720400	1.47702800	1.67811400

C	-5.12783100	0.86194200	2.15205900
H	-4.18917400	1.43034400	2.16109600
C	-5.13617400	-0.47772400	2.60860200
H	-4.20562800	-0.93226600	2.96855200
C	-6.34292200	-1.22032900	2.60602500
H	-6.35198600	-2.25946900	2.95584100
C	-7.53657700	-0.61330600	2.14329100
H	-8.47501800	-1.18127800	2.14340900
C	-7.52192700	0.72491100	1.68330800
H	-8.44575500	1.19149000	1.31859200
C	-6.54081200	3.92339000	2.39946300
H	-7.52794700	3.74217400	2.86559100
H	-6.50543700	4.96578700	2.03939700
H	-5.76817100	3.79487500	3.18121200
C	-0.29313300	0.10920400	5.12472700
C	-1.46792900	0.30340200	5.90635000
C	-1.41915500	0.30588200	7.32599400
H	-2.32329800	0.45629600	7.92183300
C	-0.17816000	0.10565600	7.96737100
H	-0.13347600	0.10665900	9.06260000
C	1.00583400	-0.09728700	7.22727500
H	1.95509200	-0.24917800	7.74776300
C	0.93940700	-0.09489900	5.80799500

C	-3.89671900	0.71194500	5.91942800
C	3.34779800	-0.56347100	5.62501100
H	4.71441500	0.47620600	-3.60689000
H	4.39580200	1.29886300	-5.18976200
H	4.49336300	-0.51210800	-5.09608500
H	-3.86078200	-0.40015500	-5.62233200
H	-2.81043700	-1.25329100	-6.82156400
H	-3.02473800	0.54439500	-6.91510900
H	4.04956200	-0.73667800	4.79716900
H	3.28892900	-1.47018600	6.25731400
H	3.68168300	0.29969300	6.23316500
H	-4.67238000	0.81838900	5.14786100
H	-3.82956400	1.63728700	6.52349700
H	-4.13427700	-0.14950700	6.57316700
C	2.53204200	-0.72055400	-0.36177200
C	4.77124900	-3.61515300	-3.75461400
C	4.27550900	-2.11944800	-1.84870900
C	3.83888900	-2.91007200	-2.96934600
C	6.15900800	-3.55742900	-3.45778400
C	3.34454200	-1.40371500	-1.05766300
C	6.60386600	-2.78393000	-2.35315300
C	1.67169400	0.02005500	0.38433100
C	5.68413400	-2.07638600	-1.55416200

H	6.02892000	-1.48949500	-0.69574800
H	7.67277400	-2.73862700	-2.11248200
H	6.87913800	-4.11104000	-4.07135800
H	2.76852000	-2.95293700	-3.19749300
H	4.41830400	-4.21787200	-4.60005300
H	1.97646400	0.61102900	1.25892100

$C_{[N2]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: -0.013594 Hartree

H_corr: 0.008229 Hartree

SCF: -109.490074 Hartree

S: 45.93 Cal/Mol-Kelvin

H: -109.481845 Hartree

G: -109.503668 Hartree

Cartesian Coordinates:

N	0.00000000	0.00000000	0.57307000
N	0.00000000	0.00000000	-0.57307000

$C_{[2a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.099513 Hartree

H_corr: 0.138461 Hartree

SCF: -309.600539 Hartree

S: 81.974 Cal/Mol-Kelvin

H: -309.462078 Hartree

G: -309.501026 Hartree

Cartesian Coordinates:

C	-1.80367300	-1.06029300	0.00000000
C	-0.41103500	-1.30025800	0.00000000
C	0.52368900	-0.22415100	0.00000000
C	-2.29347400	0.26752500	0.00000000
C	0.01393200	1.10796100	0.00000000
C	-1.37608400	1.34941800	0.00000000
H	-2.50370300	-1.90413500	0.00000000
H	-3.37285400	0.45913400	0.00000000
H	-0.03630000	-2.33249700	0.00000000
H	0.70708900	1.95750300	0.00000000
H	-1.74926300	2.38061400	0.00000000
C	1.97164800	-0.53998900	0.00000000
C	3.01280800	0.33989400	0.00000000
H	2.20893300	-1.61528500	0.00000000
H	2.86955800	1.42734700	-0.00000100

H 4.04967000 -0.01332600 0.00000000

Transition State TS2

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -315.3313 cm-1

G_corr: 1.557 Hartree

H_corr: 1.844644 Hartree

SCF: -6635.302918 Hartree

S: 605.398 Cal/Mol-Kelvin

H: -6633.458274 Hartree

G: -6633.745918 Hartree

Cartesian Coordinates:

Co 0.39503800 0.00765600 0.06756300

O -0.59689000 7.95663300 -0.53101300

O 6.27534600 3.96422600 -2.37493100

O 1.44993400 -1.21877400 -5.38664800

O -2.96377100 -0.34864900 -3.83527000

N 0.57616500 1.06462800 -1.57973500

N 0.19630100 -1.61769400 -1.04457100

N -0.00174700 5.67890100 -0.61930400

H -0.36864500 4.72819100 -0.49885200

N	4.22083600	3.35363700	-1.39017300
H	3.69324300	2.54452600	-1.04701500
C	1.50425100	3.21103600	-0.66366000
C	1.04430400	2.38729500	-1.71169000
C	0.92579900	2.83791300	-3.09241900
H	1.24648900	3.81658000	-3.44799600
C	0.33331300	1.81146400	-3.79995800
H	0.09024200	1.76974900	-4.86101700
C	0.14230600	0.70641800	-2.87188300
C	-0.27982400	-0.57284200	-3.26898600
C	-0.15471800	-1.67681000	-2.40788000
C	-0.24369200	-3.05811000	-2.85645700
H	-0.49076300	-3.35830100	-3.87380900
C	0.09271700	-3.85652700	-1.78084000
H	0.17069100	-4.94251700	-1.73538100
C	0.31923500	-2.96769100	-0.64809700
C	2.12857100	4.54360900	-0.99696700
C	1.38180100	5.76241300	-0.95372500
C	2.01087300	7.00052600	-1.26358100
H	1.42584400	7.91932700	-1.20883000
C	3.37143800	7.00646100	-1.63416800
H	3.85032700	7.96177600	-1.87880900
C	4.13317400	5.82169500	-1.70140100

H	5.18244700	5.82445700	-2.00069400
C	3.51014600	4.58755700	-1.37420600
C	-0.91978400	6.72636600	-0.45477000
C	-2.32991000	6.27547000	-0.20112400
H	-2.54428400	5.22222000	-0.41689600
C	-3.46021400	7.28033900	-0.53056700
H	-4.34341500	6.87653700	-1.03551100
H	-3.11638900	8.26412500	-0.86758100
C	-3.20717900	6.91727800	0.93255000
C	-4.21187000	6.00182900	1.60952000
C	-5.54884900	6.44926600	1.79186900
H	-5.84233300	7.42993400	1.39582600
C	-6.49807800	5.64511400	2.46385900
H	-7.52565700	6.00551300	2.59544000
C	-6.12334500	4.37320600	2.96377000
H	-6.85854500	3.74452100	3.48055000
C	-4.79419400	3.91910800	2.78681300
H	-4.49555200	2.93276200	3.15841300
C	-3.84497300	4.73033900	2.12021200
H	-2.81825000	4.36826500	1.98753700
C	-2.59383100	7.96711000	1.87032800
H	-3.39114800	8.61672000	2.27899200
H	-1.86248600	8.59533300	1.33455800

H	-2.08537300	7.47969600	2.72361100
C	5.51095600	3.08307800	-1.86469600
C	5.89749600	1.63652900	-1.73262300
H	5.36489600	1.07145100	-0.95758800
C	7.36425800	1.23154500	-1.97099800
H	8.03121100	2.05048000	-2.26124100
H	7.78600500	0.49417100	-1.28091800
C	6.31693700	0.79372100	-2.99490400
C	5.86281700	-0.65424500	-3.00549100
C	4.47933300	-0.97671900	-3.04654500
H	3.73306000	-0.17240000	-3.02555500
C	4.05026100	-2.32361200	-3.11021100
H	2.97792000	-2.54889400	-3.14413600
C	5.00433900	-3.37128800	-3.13880600
H	4.67492000	-4.41617600	-3.18046200
C	6.38583100	-3.06088300	-3.10575200
H	7.12840100	-3.86770700	-3.12723300
C	6.81011700	-1.71179400	-3.04142900
H	7.88079000	-1.47238900	-3.01688900
C	6.31364400	1.46246100	-4.37722500
H	7.01870600	0.93640900	-5.04863900
H	6.61632000	2.52133600	-4.30672700
H	5.30773100	1.41421000	-4.83602700

C	-0.78004300	-0.78565700	-4.66880700
C	0.09569100	-1.10846000	-5.74234700
C	-0.39490600	-1.29915900	-7.06203200
H	0.28084400	-1.54413900	-7.88597800
C	-1.78030300	-1.16713000	-7.30108200
H	-2.16481200	-1.31315500	-8.31724600
C	-2.68036900	-0.85230300	-6.25999900
H	-3.74920500	-0.75629200	-6.46972700
C	-2.17118600	-0.66380500	-4.94717000
C	2.41938100	-1.53305900	-6.44910800
C	-4.40581400	-0.14126400	-4.04624900
O	-3.06082400	-7.08189200	1.48078600
O	4.96871000	-5.70982700	1.76802400
O	2.81815700	0.87143700	5.10945200
O	-1.91786700	0.99467600	4.60890100
N	0.50318600	-1.12069200	1.67931300
N	0.94550800	1.55790700	1.14151000
N	-1.69631400	-5.29844400	0.76519900
H	-1.72636300	-4.35890500	0.35560000
N	3.10910400	-4.46529000	1.02232000
H	2.83460000	-3.53596300	0.68799800
C	0.51802400	-3.42432400	0.67068500
C	0.52405600	-2.53010100	1.76307500

C	0.50401000	-2.95865800	3.15563800
H	0.53269700	-3.99879700	3.47796400
C	0.42994100	-1.81717100	3.92815300
H	0.39879800	-1.73336500	5.01355500
C	0.45695500	-0.68179500	3.01897200
C	0.56482100	0.65394500	3.44665100
C	0.87422400	1.68690700	2.54518900
C	1.27944700	3.02321500	2.95375100
H	1.31101000	3.36532500	3.98690600
C	1.63947200	3.70758800	1.81059100
H	2.01292500	4.72646500	1.71564000
C	1.39151900	2.81602300	0.68470200
C	0.71077400	-4.89455300	0.95050400
C	-0.39268000	-5.79944700	1.05528900
C	-0.17552400	-7.15591500	1.42480200
H	-1.03445300	-7.81971000	1.53083900
C	1.14036400	-7.60143400	1.66659100
H	1.30251100	-8.64660200	1.95483700
C	2.25356400	-6.74446900	1.54305600
H	3.27239500	-7.08821300	1.72871700
C	2.03665900	-5.38800800	1.18070700
C	-2.93591900	-5.93622400	0.93848700
C	-4.10290900	-5.14594200	0.42401400

H	-3.89583800	-4.10690900	0.13868900
C	-5.49866000	-5.40133800	1.03954700
H	-6.10562200	-4.51491100	1.24967700
H	-5.53545800	-6.19231100	1.79593000
C	-5.25740800	-5.83502000	-0.40226600
C	-5.86152100	-5.01750800	-1.52961300
C	-7.22034800	-4.60840600	-1.48493100
H	-7.81603900	-4.82726500	-0.59006800
C	-7.81072000	-3.93480800	-2.58101500
H	-8.86303100	-3.62952600	-2.53215500
C	-7.04885900	-3.66392600	-3.74316800
H	-7.50949600	-3.15315700	-4.59758600
C	-5.69018700	-4.06400000	-3.79605000
H	-5.09179700	-3.86345200	-4.69354700
C	-5.10412500	-4.73424400	-2.69791000
H	-4.05126200	-5.04056600	-2.74304700
C	-5.17747900	-7.33569400	-0.72257900
H	-6.19772400	-7.73136600	-0.88762300
H	-4.70330700	-7.89221000	0.10242200
H	-4.59483300	-7.51198700	-1.64651700
C	4.47149000	-4.63435900	1.30204900
C	5.29002700	-3.40726500	1.01379100
H	4.85368700	-2.70291600	0.29449000

C	6.82670600	-3.52286000	0.99239400
H	7.22181700	-4.51630800	1.23051700
H	7.34702500	-2.97962400	0.19723200
C	6.17415100	-2.74334400	2.13408100
C	6.23948600	-1.22722100	2.11721800
C	5.06648800	-0.44983800	2.31395700
H	4.09719900	-0.94991200	2.43426100
C	5.13210600	0.96314000	2.35768500
H	4.21527700	1.54296800	2.51557500
C	6.37909300	1.62026100	2.21013100
H	6.43186000	2.71500900	2.23531000
C	7.55566100	0.85458200	2.02126400
H	8.52298800	1.35820400	1.90542600
C	7.48475900	-0.55850700	1.97680800
H	8.39690500	-1.15098800	1.83053100
C	6.18386000	-3.35333000	3.54337900
H	7.12797200	-3.09041000	4.05735100
H	6.09845800	-4.45266600	3.50099900
H	5.34621300	-2.95815700	4.14891500
C	0.44384000	0.96089800	4.91187000
C	1.58645400	1.07137500	5.75336400
C	1.45679300	1.35397400	7.13944300
H	2.33663100	1.43751200	7.78310000

C	0.16567200	1.52572500	7.68395500
H	0.05925700	1.74780400	8.75210300
C	-0.99058700	1.41678700	6.88212700
H	-1.97953700	1.55802900	7.32620600
C	-0.84188900	1.13124900	5.49871200
C	4.04086600	0.93378700	5.92741800
C	-3.27936100	1.04236000	5.16670400
H	-4.79007800	0.16477100	-3.06333300
H	-4.89749700	-1.07915500	-4.36765200
H	-4.58753800	0.66529300	-4.78158500
H	3.39082500	-1.57426100	-5.93595600
H	2.43017900	-0.74206700	-7.22369100
H	2.19759200	-2.51327500	-6.91381300
H	-3.93923600	0.79330100	4.32340400
H	-3.51143700	2.05213300	5.55749600
H	-3.40884600	0.28563300	5.96287400
H	4.85913300	0.73922400	5.21945300
H	4.02911600	0.15886500	6.71803400
H	4.16506800	1.93555200	6.38246500
C	-2.11712100	1.45420100	-0.32983100
C	-4.01043500	4.18940700	-4.04248700
C	-3.61893800	3.02810600	-1.89856900
C	-3.18700300	3.39850900	-3.21543400

C	-5.28288200	4.62410800	-3.58966300
C	-2.80137500	2.21372500	-1.06105500
C	-5.72056400	4.26690000	-2.28841900
C	-1.45943500	0.48334500	0.42473100
C	-4.90172600	3.48627100	-1.44634300
H	-5.23390100	3.22611900	-0.43520900
H	-6.69904800	4.60451100	-1.92704200
H	-5.91979700	5.23723500	-4.23782500
H	-2.20629100	3.05744700	-3.56358700
H	-3.66084400	4.47037200	-5.04309000
H	-1.61935500	0.46694100	1.51558600
C	-5.41950500	-2.16491600	4.69504000
C	-6.24849900	-1.45606700	3.78867300
C	-4.10218900	-2.51754300	4.30078400
C	-3.61848000	-2.17595500	3.02218600
C	-4.44508700	-1.47372900	2.08657800
C	-5.76765300	-1.11706600	2.50570100
H	-2.59620000	-2.45967100	2.74705200
H	-5.79442600	-2.44487000	5.68651100
H	-3.45434800	-3.06844200	4.99285300
H	-6.41862300	-0.57881700	1.80378200
H	-7.26896000	-1.17872400	4.07992400
C	-4.02110500	-1.14499800	0.72202200

C -2.77593800 -1.38202800   0.14559500

H -2.01202100 -1.96941500   0.66754100

H -2.64362400 -1.27126200 -0.93417500

H -4.77468400 -0.63189000   0.10625100

Intermediate D

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.560918 Hartree

H_corr: 1.847566 Hartree

SCF: -6635.34275100 Hartree

S: 603.302 Cal/Mol-Kelvin

H: -6633.455352 Hartree

G: -6633.742 Hartree

Cartesian Coordinates:

Co   0.34131200   0.00130900   0.04502300

O -0.59700200   7.99426400 -0.74827900

O   6.14440300   3.80548300 -2.62110400

O   1.47897800 -1.54803600 -5.31160000

O -2.94828100 -0.54166200 -3.88827500

N   0.50839400   0.98273400 -1.64953900

N   0.20644900 -1.67272300 -0.98322800

N	-0.08381800	5.69714900	-0.87348200
H	-0.47677000	4.75916400	-0.73698100
N	4.09827000	3.27008100	-1.57672800
H	3.57025500	2.48744900	-1.17760400
C	1.38094300	3.19420100	-0.83415500
C	0.96129400	2.30328100	-1.84491500
C	0.87039300	2.67418400	-3.25130300
H	1.18581400	3.63628900	-3.65376500
C	0.30815600	1.60163000	-3.91410300
H	0.09058700	1.49814200	-4.97655000
C	0.11180300	0.54720900	-2.93019300
C	-0.27851300	-0.76005900	-3.26377100
C	-0.13616600	-1.81360400	-2.34387400
C	-0.18539100	-3.21858000	-2.71857900
H	-0.41809400	-3.57877500	-3.71969000
C	0.17208400	-3.94939000	-1.60212000
H	0.28504600	-5.02863900	-1.50132100
C	0.37147800	-2.99619900	-0.51717000
C	2.01939400	4.50313100	-1.23101000
C	1.29560700	5.73662300	-1.23230500
C	1.93904900	6.94854000	-1.60814800
H	1.37088100	7.87909700	-1.58337400
C	3.29318600	6.91565000	-1.99900800

H	3.78323300	7.85025000	-2.29592300
C	4.03477800	5.71672200	-2.01889700
H	5.08009100	5.68849600	-2.33038400
C	3.39826000	4.50946000	-1.62416300
C	-0.95804100	6.77473700	-0.67141800
C	-2.37041200	6.36884100	-0.36270200
H	-2.63955400	5.33642600	-0.61431900
C	-3.47851300	7.42648300	-0.56970000
H	-4.40456800	7.08047300	-1.03963400
H	-3.12023300	8.41433700	-0.87848000
C	-3.15204900	6.98108700	0.85532800
C	-4.13502500	6.05650600	1.55048100
C	-5.47192900	6.48428400	1.77217300
H	-5.78890400	7.46452400	1.39368400
C	-6.39106400	5.66079600	2.46363700
H	-7.41966500	6.00528600	2.62623400
C	-5.98497900	4.39090300	2.94331000
H	-6.69777200	3.74832500	3.47428800
C	-4.65430200	3.95661000	2.72814900
H	-4.32897500	2.97298400	3.08395200
C	-3.73640200	4.78651200	2.04224500
H	-2.70820500	4.44105100	1.87895900
C	-2.44317100	7.96129100	1.80084900

H	-3.18917700	8.61670000	2.28935400
H	-1.72370800	8.59078300	1.25024600
H	-1.90110100	7.41582200	2.59635400
C	5.38394300	2.96429800	-2.04157600
C	5.77587700	1.53310900	-1.80307300
H	5.24292500	1.02377200	-0.99069400
C	7.24823000	1.12463000	-2.00145200
H	7.90913100	1.92625300	-2.34835000
H	7.67218400	0.44628000	-1.25453900
C	6.21185200	0.60080900	-2.99504400
C	5.77285000	-0.84855000	-2.89598200
C	4.39389400	-1.18999800	-2.93879900
H	3.63856300	-0.39646500	-3.00215400
C	3.98068800	-2.54272400	-2.89777400
H	2.91183200	-2.78321800	-2.93518500
C	4.94599500	-3.57750700	-2.81842900
H	4.62834600	-4.62612500	-2.77926800
C	6.32312700	-3.24876700	-2.78339000
H	7.07439900	-4.04531800	-2.72131200
C	6.73160100	-1.89390200	-2.82349800
H	7.79892200	-1.64015800	-2.79760400
C	6.21054400	1.16154100	-4.42444600
H	6.92591800	0.59372200	-5.04938600

H	6.50090300	2.22614100	-4.43323600
H	5.20821500	1.06691100	-4.88387700
C	-0.75759900	-1.05529000	-4.65605700
C	0.13118400	-1.45140200	-5.69377800
C	-0.34099600	-1.72030600	-7.00669600
H	0.34516900	-2.02133300	-7.80302700
C	-1.72109300	-1.59153500	-7.27581800
H	-2.09127600	-1.79774700	-8.28687500
C	-2.63379900	-1.20284000	-6.27117400
H	-3.69817100	-1.10942900	-6.50384800
C	-2.14253500	-0.93614200	-4.96506200
C	2.46168900	-1.93699600	-6.33629600
C	-4.38544000	-0.34029600	-4.13223100
O	-2.92251700	-7.05934500	1.75473100
O	5.07223500	-5.47081300	2.14846500
O	2.65105400	1.29513100	5.02106900
O	-2.08782100	1.05382900	4.55591800
N	0.48123200	-1.02868200	1.71300500
N	0.78889300	1.63542500	1.04139800
N	-1.57057600	-5.29287100	0.97702000
H	-1.60398600	-4.38117300	0.50947500
N	3.20466600	-4.33553300	1.26245900
H	2.91489600	-3.43919100	0.85792500

C	0.59137300	-3.37708500	0.82270600
C	0.56924800	-2.42957000	1.86939100
C	0.56558700	-2.78648000	3.28204600
H	0.64484200	-3.80555900	3.65856300
C	0.42936700	-1.61186400	3.99451400
H	0.38686200	-1.47504200	5.07412600
C	0.40007100	-0.52462400	3.02848600
C	0.41817200	0.83622900	3.38656400
C	0.68408700	1.83705800	2.43486400
C	1.03715900	3.20648500	2.78022200
H	1.03187700	3.60511900	3.79338900
C	1.41831700	3.83505700	1.61222300
H	1.77315500	4.85554600	1.47317400
C	1.22636300	2.87641900	0.53066700
C	0.81995400	-4.82510200	1.18074000
C	-0.26348300	-5.74906600	1.32024900
C	-0.02413600	-7.07585400	1.77255200
H	-0.86979600	-7.75242600	1.90312900
C	1.29753800	-7.47504900	2.06134500
H	1.47863300	-8.49722900	2.41364400
C	2.39302800	-6.60068500	1.90422100
H	3.41592300	-6.90887100	2.12661600
C	2.15211700	-5.27290700	1.45928300

C	-2.80093800	-5.94393300	1.15205400
C	-3.96612100	-5.20900200	0.55515400
H	-3.77194300	-4.17896700	0.23095600
C	-5.38065100	-5.47503300	1.11926000
H	-6.02184400	-4.59907900	1.26033000
H	-5.43011800	-6.23218800	1.90880900
C	-5.06229500	-5.96550700	-0.28975500
C	-5.63595100	-5.21616000	-1.47857200
C	-7.01615100	-4.88696600	-1.53072900
H	-7.65348600	-5.11353600	-0.66694900
C	-7.57302200	-4.28175200	-2.68258700
H	-8.64188500	-4.03736900	-2.70884000
C	-6.75521000	-4.00017900	-3.80363600
H	-7.18938300	-3.54312700	-4.70125600
C	-5.37519700	-4.31972200	-3.75953700
H	-4.73276600	-4.10836400	-4.62335700
C	-4.82282800	-4.92234700	-2.60587700
H	-3.75346900	-5.16744500	-2.57611000
C	-4.92708800	-7.47590600	-0.53762600
H	-5.92740400	-7.90824000	-0.73005100
H	-4.47688500	-7.98167200	0.33234800
H	-4.29792600	-7.67511500	-1.42566400
C	4.56151500	-4.44508800	1.59353000

C	5.35312900	-3.21509500	1.24784700
H	4.92946500	-2.58543600	0.45544500
C	6.89111700	-3.27159400	1.31095400
H	7.30907000	-4.22757500	1.64439200
H	7.43288200	-2.77012400	0.50278000
C	6.15363400	-2.43397800	2.35595100
C	6.16333900	-0.92200200	2.22692700
C	4.95554100	-0.18075300	2.33331000
H	4.00318000	-0.70975000	2.46459300
C	4.96498000	1.23301800	2.27398600
H	4.02231200	1.78509800	2.36469700
C	6.18954600	1.92795700	2.11124800
H	6.19890800	3.02282600	2.05613700
C	7.39987100	1.19925600	2.01127500
H	8.34989900	1.73201300	1.88341200
C	7.38529900	-0.21510300	2.07060900
H	8.32391300	-0.77868300	1.99457000
C	6.11197200	-2.93741400	3.80621300
H	7.01803400	-2.59994700	4.34455000
H	6.06900200	-4.03947300	3.84316100
H	5.23035800	-2.53258900	4.33844600
C	0.27504200	1.20566700	4.83571900
C	1.41068900	1.43609900	5.66357200

C	1.26808000	1.76984800	7.03684900
H	2.14294900	1.94606000	7.66845300
C	-0.02888200	1.86872400	7.58503800
H	-0.14590100	2.12847600	8.64353400
C	-1.17758100	1.63867800	6.79845800
H	-2.17168900	1.72400800	7.24520100
C	-1.01609100	1.30610800	5.42692100
C	3.86933400	1.47990700	5.82676900
C	-3.44105700	1.00708600	5.13409200
H	-4.78104600	0.02895600	-3.17573300
H	-4.87865400	-1.29402500	-4.40047600
H	-4.55320300	0.41814700	-4.92050800
H	3.42457900	-1.95294800	-5.80591300
H	2.49149300	-1.19706200	-7.15935500
H	2.23867100	-2.94313300	-6.74121200
H	-4.09220500	0.69139500	4.30634500
H	-3.74678300	2.00336300	5.50878700
H	-3.49856800	0.26081900	5.94872300
H	4.69633300	1.30766500	5.12317000
H	3.91394200	0.74441500	6.65311400
H	3.92599900	2.50834200	6.23325800
C	-2.21683900	1.33046700	-0.45072900
C	-3.87945000	4.13002300	-4.21991500

C	-3.55920800	3.01945500	-2.04209500
C	-3.12551100	3.28409500	-3.37777300
C	-5.08007000	4.72247400	-3.75522000
C	-2.81486600	2.13689000	-1.18491100
C	-5.51768800	4.46830900	-2.43168400
C	-1.66376200	0.29564200	0.39511100
C	-4.76591000	3.63114500	-1.57838800
H	-5.09955300	3.44444200	-0.55149100
H	-6.44375600	4.92423800	-2.06209800
H	-5.66279300	5.37777500	-4.41312100
H	-2.19857000	2.82234900	-3.73360300
H	-3.52902700	4.32989300	-5.23946000
H	-1.59334300	0.61924000	1.44946600
C	-5.53035500	-2.38135200	4.50200900
C	-6.30272200	-1.57287300	3.62233400
C	-4.17720700	-2.66884000	4.17544700
C	-3.59865800	-2.17024700	2.99457200
C	-4.36464800	-1.35946400	2.07759700
C	-5.73517300	-1.07065800	2.43830100
H	-2.54798800	-2.39455000	2.78030500
H	-5.97531800	-2.78205500	5.42006900
H	-3.57542500	-3.29034200	4.84888700
H	-6.33859300	-0.45475500	1.75841500

H -7.34771400 -1.34507300 3.86572200

C -3.84827400 -0.85886000 0.83727800

C -2.45891300 -1.05631900 0.29009700

H -1.90804100 -1.83093200 0.84739400

H -2.50421400 -1.35328600 -0.77385100

H -4.51858800 -0.23037500 0.23298400

Intermediate E

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

$E_{[3a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.203217 Hartree

H_corr: 0.263701 Hartree

SCF: -656.05379 Hartree

S: 127.3 Cal/Mol-Kelvin

H: -655.790089 Hartree

G: -655.850573 Hartree

Cartesian Coordinates:

H 7.08964000 -0.93150700 0.19645900

C 6.02993400 -0.66768500 0.10154900

H	5.91657500	0.27931200	2.06376100
H	5.81903100	-1.53397100	-1.88981500
C	5.36773400	0.01416700	1.15235800
C	5.31293500	-1.00617100	-1.07285200
C	4.00342700	0.35644500	1.03363900
C	3.94803700	-0.66916900	-1.19870300
C	3.27090200	0.01921900	-0.14563500
H	3.49168400	0.88545800	1.84566900
H	3.39258700	-0.93221400	-2.10596600
C	1.88178900	0.36412000	-0.27115900
C	0.68400900	0.66392100	-0.38460400
C	-0.71374200	1.00154100	-0.51681400
H	-0.69948900	2.62554500	1.06127200
C	-1.34991100	2.11424700	0.34608600
C	-1.72748600	0.65726300	0.64314500
H	-2.94648200	-1.42612500	1.88627100
C	-3.56202400	-1.01653100	1.07489200
C	-3.07437500	0.08641500	0.32021600
H	-2.09999800	2.75512800	-0.12851900
C	-4.82345000	-1.59013900	0.79482800
H	-5.18030300	-2.43851100	1.39092100
C	-3.88918500	0.59703100	-0.72944100
H	-3.54591200	1.45016800	-1.32916300

C -5.62415800 -1.07304600 -0.25172500

C -5.14945400 0.02345300 -1.01230900

H -6.60241800 -1.51625000 -0.47108400

H -5.76301600 0.43174500 -1.82438600

H -1.25006600 0.22122400 1.52779900

H -1.13171800 0.87950700 -1.52403900

<u>Transition State TS2'</u>

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -349.5155 cm-1

G_corr: 1.554791 Hartree

H_corr: 1.844453 Hartree

SCF: -6635.28914366 Hartree

S: 609.644 Cal/Mol-Kelvin

H: -6633.444691 Hartree

G: -6633.734353 Hartree

Cartesian Coordinates:

Co 0.56340200 -0.02682400 0.11565000

O -0.00147900 7.47241400 -2.32879000

O 6.55566600 2.77142400 -3.56674600

O 1.10013700 -2.13703100 -4.91024900

O	-3.29629200	-0.70550400	-3.71958300
N	0.62122000	0.74542600	-1.69513000
N	-0.07147900	-1.73250700	-0.66039300
N	0.72221500	5.41600000	-1.43717100
H	0.43117100	4.63070500	-0.84539900
N	4.58296500	2.56993200	-2.29072900
H	4.04647500	1.90737400	-1.72109900
C	1.96809800	2.82681700	-1.27717900
C	1.21433700	1.96147900	-2.09589100
C	0.93797500	2.23042200	-3.50119900
H	1.29638800	3.10623100	-4.04046200
C	0.15891100	1.19083200	-3.96372500
H	-0.23786800	1.03291500	-4.96567300
C	-0.01158900	0.25768000	-2.85947400
C	-0.59031400	-1.01323400	-3.00818600
C	-0.53853000	-1.96183300	-1.97218700
C	-0.86288900	-3.36698700	-2.16466500
H	-1.22847100	-3.78797900	-3.10012900
C	-0.57038300	-4.01816000	-0.98379500
H	-0.64937600	-5.08014300	-0.75246800
C	-0.11894300	-3.00335200	-0.03986200
C	2.65355000	4.00657700	-1.92160300
C	2.00144800	5.27194800	-2.04916600

C	2.63308600	6.33784500	-2.74757700
H	2.10552400	7.28593200	-2.86013800
C	3.91654100	6.13252000	-3.29600800
H	4.39981600	6.95422100	-3.83735300
C	4.59869200	4.90432800	-3.16628900
H	5.59070100	4.74548100	-3.59231800
C	3.96379300	3.83882500	-2.47318400
C	-0.18895700	6.47589200	-1.55755800
C	-1.40727900	6.32901400	-0.69331400
H	-1.52247400	5.36357900	-0.18497200
C	-2.72410700	7.00919300	-1.13691300
H	-3.63859100	6.41804100	-1.02524800
H	-2.65393500	7.60326600	-2.05412600
C	-2.01130900	7.55798300	0.09397300
C	-2.57671300	7.26441600	1.47193900
C	-3.97131500	7.34017300	1.72558300
H	-4.65707300	7.54839800	0.89530700
C	-4.48092900	7.16206100	3.03431500
H	-5.56103500	7.22647100	3.21285200
C	-3.59940800	6.91124300	4.11287000
H	-3.99285000	6.78669500	5.12910100
C	-2.20524100	6.82965800	3.86997000
H	-1.51205400	6.64383400	4.70004400

C	-1.70115400	7.00344500	2.56097800
H	-0.62085900	6.93803800	2.37887800
C	-1.33009500	8.93239300	0.00202600
H	-2.07405300	9.72446600	0.21110400
H	-0.89886000	9.09475400	-0.99919500
H	-0.52102300	9.02457200	0.75086400
C	5.79548100	2.09264500	-2.80363400
C	6.10363700	0.68487900	-2.37436400
H	5.60729300	0.34806200	-1.45545900
C	7.51873800	0.12308500	-2.61451600
H	8.20778300	0.80134600	-3.12926800
H	7.95042000	-0.47641900	-1.80681000
C	6.36189200	-0.44663000	-3.43619200
C	5.82457400	-1.82229500	-3.08646200
C	4.43317900	-2.02935500	-2.88685800
H	3.74455300	-1.17640800	-2.93842700
C	3.92388800	-3.32212500	-2.61714000
H	2.84628700	-3.45984200	-2.46840400
C	4.80281700	-4.43152300	-2.54978300
H	4.41190400	-5.43302000	-2.33510800
C	6.19102300	-4.23688200	-2.75394900
H	6.87606900	-5.09197700	-2.70447000
C	6.69598800	-2.94194100	-3.02143500

H	7.77197000	-2.79208800	-3.17660300
C	6.28265600	-0.10502600	-4.93128600
H	6.89250200	-0.82299300	-5.51196300
H	6.65647500	0.91487800	-5.12557400
H	5.23989700	-0.17184100	-5.29597500
C	-1.11289700	-1.43226100	-4.35617900
C	-0.23557300	-2.00477800	-5.32330400
C	-0.70289100	-2.40584100	-6.60325900
H	-0.02407300	-2.84115800	-7.34136100
C	-2.06824700	-2.23477600	-6.91602300
H	-2.43649900	-2.54286900	-7.90147000
C	-2.96782300	-1.67554900	-5.98471300
H	-4.02151400	-1.55448000	-6.24887000
C	-2.48329600	-1.27626600	-4.70924900
C	2.06155400	-2.70211300	-5.87205500
C	-4.70460700	-0.43783000	-4.06364900
O	-3.95610200	-6.04712600	2.85696100
O	4.19450500	-6.09988000	2.69019600
O	3.62529300	1.06114600	4.87215500
O	-0.95484200	2.24597700	4.33938600
N	0.70794700	-0.89429100	1.88153000
N	1.52733000	1.53670400	0.82733900
N	-2.35329100	-4.71417100	1.75739200

H	-2.24808600	-3.89234900	1.15394300
N	2.53614000	-4.68140600	1.79408300
H	2.40750800	-3.78865800	1.30725400
C	0.14142900	-3.27352800	1.31800100
C	0.44041000	-2.23471000	2.22436900
C	0.47143300	-2.41048800	3.67060000
H	0.30613200	-3.36036300	4.17708700
C	0.71556100	-1.16980900	4.22209300
H	0.80610100	-0.90002100	5.27329200
C	0.88905500	-0.23891100	3.11792300
C	1.29670700	1.09510300	3.28079500
C	1.68888400	1.88275700	2.18443600
C	2.37254300	3.16059500	2.30824100
H	2.62582400	3.63051300	3.25743100
C	2.64595800	3.60149700	1.02832100
H	3.15917800	4.50962100	0.71320900
C	2.07206200	2.62331500	0.11244800
C	0.09617800	-4.68437700	1.85142900
C	-1.13656100	-5.35326600	2.13896600
C	-1.13036300	-6.63071500	2.76510700
H	-2.08149900	-7.10294400	3.01390700
C	0.10183600	-7.24383400	3.06998500
H	0.10054600	-8.22706500	3.55473200

C	1.33509400	-6.63296500	2.76255200
H	2.28993300	-7.10905400	2.99094000
C	1.33079700	-5.35139900	2.15000800
C	-3.67129600	-5.10482600	2.04880700
C	-4.71717300	-4.32387600	1.30871300
H	-4.36852000	-3.43894500	0.76181300
C	-6.14025200	-4.21931400	1.90706200
H	-6.62297800	-3.23891300	1.84531400
H	-6.29309500	-4.76818700	2.84237000
C	-5.95133500	-5.05164200	0.64383200
C	-6.42862800	-4.49909000	-0.68694100
C	-7.72922500	-3.94617000	-0.81947100
H	-8.36150300	-3.84588600	0.07131100
C	-8.21513000	-3.53416900	-2.08341500
H	-9.22634300	-3.11812900	-2.17060100
C	-7.40476100	-3.67040700	-3.23666300
H	-7.78642000	-3.36407000	-4.21840600
C	-6.10210300	-4.21538800	-3.11369500
H	-5.46677800	-4.32800600	-4.00097300
C	-5.62189700	-4.62700400	-1.84917000
H	-4.61324900	-5.04992600	-1.75862800
C	-6.07976100	-6.58032600	0.73483200
H	-7.14431200	-6.86502700	0.63287100

H	-5.69614900	-6.95398200	1.69817800
H	-5.51999000	-7.07353900	-0.08229700
C	3.86362300	-5.05024100	2.04947900
C	4.86626100	-4.07681500	1.49644600
H	4.50429400	-3.42295900	0.69307100
C	6.34289700	-4.51094000	1.39208500
H	6.56052000	-5.51241600	1.77861300
H	6.87256300	-4.22457100	0.47796500
C	5.97388900	-3.43713900	2.41446400
C	6.32969200	-1.99272100	2.11288900
C	5.36388000	-0.96217300	2.26716300
H	4.33940100	-1.21683700	2.56643500
C	5.70542700	0.39151000	2.03646200
H	4.94383600	1.16962200	2.16396600
C	7.02583200	0.73494900	1.65299300
H	7.29175700	1.78236500	1.46743700
C	7.99877700	-0.28398200	1.50505700
H	9.02340300	-0.02385000	1.21246000
C	7.65170500	-1.63696000	1.73485700
H	8.40566500	-2.42573300	1.61826400
C	6.00997300	-3.79320400	3.90761800
H	7.03425300	-3.64902100	4.30100700
H	5.71107300	-4.84238900	4.07286400

H	5.32901700	-3.13883200	4.48436500
C	1.33563800	1.68340000	4.66151300
C	2.50682900	1.66644900	5.46748400
C	2.51020100	2.22868900	6.77239000
H	3.41086000	2.21233900	7.39209100
C	1.32465400	2.81433200	7.26717000
H	1.32160400	3.24983400	8.27312900
C	0.14271700	2.84947400	6.49549200
H	-0.76336200	3.30652600	6.90259300
C	0.15752300	2.27916700	5.19525200
C	4.86752600	0.98327600	5.65889100
C	-2.20605700	2.86522300	4.80462300
H	-5.10840600	0.10041100	-3.19536300
H	-5.25804700	-1.38362200	-4.21855600
H	-4.77692500	0.20661700	-4.95992400
H	3.02066300	-2.71443900	-5.33528400
H	2.13775200	-2.06765100	-6.77614600
H	1.77912100	-3.73392900	-6.15756000
H	-2.91660100	2.72031400	3.97837700
H	-2.06988000	3.94774300	4.98653500
H	-2.58085800	2.36642900	5.71941300
H	5.58517500	0.47950400	4.99571200
H	4.71698900	0.38846800	6.58038900

H	5.23897400	1.99364300	5.91809600
C	-2.13179900	1.08514600	-0.10147100
C	-4.03994800	3.53871600	-3.62661000
C	-3.99270300	2.13728700	-1.59432500
C	-3.34910000	2.66433300	-2.76155400
C	-5.38362800	3.90563900	-3.35652100
C	-3.26829200	1.24946000	-0.70923700
C	-6.03027000	3.38762200	-2.20593800
C	-1.07958300	0.79428700	0.66964800
C	-5.34804600	2.50997600	-1.33505000
H	-5.84562200	2.12208000	-0.44057600
H	-7.06593200	3.67225700	-1.98437200
H	-5.91580400	4.58769300	-4.03016900
H	-2.31436900	2.37461400	-2.97317800
H	-3.52897300	3.94088600	-4.50958900
H	-1.01399200	1.06323700	1.73455700
C	-8.06279300	0.23109000	3.42546300
C	-8.70444500	0.02541300	2.17803600
C	-6.64593300	0.18376500	3.49384300
C	-5.87875800	-0.06595000	2.33756400
C	-6.50897200	-0.28326100	1.06961700
C	-7.93909000	-0.22680700	1.02010700
H	-4.78519400	-0.09181900	2.41066400

H -8.65433200 0.42482200 4.32779700

H -6.14303700 0.34088900 4.45589100

H -8.44082900 -0.38884900 0.05681200

H -9.79861200 0.06152000 2.11243100

C -5.76236400 -0.56328900 -0.16077200

C -4.37950500 -0.70064700 -0.28222600

H -3.74920500 -0.81095200 0.60686400

H -3.94817400 -1.07384400 -1.21763400

H -6.37350300 -0.65244700 -1.07102700

<u>Intermediate D’</u>

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.559943 Hartree

H_corr: 1.846928 Hartree

SCF: -6635.33554801 Hartree

S: 604.009 Cal/Mol-Kelvin

H: -6633.48862 Hartree

G: -6633.775605 Hartree

Cartesian Coordinates:

Co -0.40814900 -0.06844200 0.01878600

O 0.06203100 7.46535500 2.38455500

O	-6.68120800	2.89800300	3.07615200
O	-1.67927700	-2.53791500	4.72620200
O	2.68004800	-0.59063500	4.55217000
N	-0.68593500	0.68816800	1.81329600
N	0.05612100	-1.80576800	0.84410000
N	-0.62482300	5.40571000	1.46987100
H	-0.31649400	4.62700400	0.87816200
N	-4.60310000	2.64269800	1.99238000
H	-4.03830900	1.97148800	1.46155400
C	-1.88903700	2.82513500	1.24929200
C	-1.28826400	1.92126400	2.14933400
C	-1.21539500	2.15501100	3.58605900
H	-1.61403100	3.03671300	4.08592300
C	-0.56244100	1.07361200	4.13666300
H	-0.32515100	0.88547100	5.18258100
C	-0.25997200	0.15366600	3.04968000
C	0.24231100	-1.14231700	3.25782200
C	0.32962500	-2.06933200	2.20412300
C	0.60715300	-3.48367900	2.40766400
H	0.84014800	-3.92868700	3.37383100
C	0.46674200	-4.10750600	1.18563300
H	0.56741500	-5.16515200	0.94384200
C	0.15774200	-3.06807600	0.21104300

C	-2.60729400	4.02490900	1.81685700
C	-1.94549600	5.27954900	1.99381800
C	-2.60738000	6.35658000	2.64504900
H	-2.07148200	7.29378400	2.80123500
C	-3.93420500	6.17716800	3.08937700
H	-4.44121700	7.00670400	3.59590300
C	-4.63119200	4.96639000	2.89374800
H	-5.65972300	4.82964000	3.23165500
C	-3.96538700	3.88909800	2.24926500
C	0.27813300	6.46731600	1.62253900
C	1.52472400	6.32880800	0.79666500
H	1.68480500	5.35105600	0.32495900
C	2.80349100	7.07485800	1.24312800
H	3.74407000	6.51980600	1.16730000
H	2.68981200	7.69928400	2.13578000
C	2.09759500	7.55108600	-0.02220200
C	2.70877100	7.23334700	-1.37486200
C	4.09104300	7.44764000	-1.61768900
H	4.73552900	7.77652600	-0.79310200
C	4.63835400	7.25134200	-2.90820500
H	5.70752800	7.42459100	-3.08013000
C	3.80705200	6.84086900	-3.97813100
H	4.22835000	6.70151400	-4.98118700

C	2.42668100	6.61839700	-3.74499200
H	1.77347500	6.30138600	-4.56727100
C	1.88489300	6.81364300	-2.45381000
H	0.81571200	6.63926300	-2.27820600
C	1.36044400	8.89915400	0.00321400
H	2.07634400	9.71288900	-0.21999600
H	0.90128200	9.08234500	0.98848400
H	0.56626800	8.92937400	-0.76638700
C	-5.87914500	2.20639300	2.36939000
C	-6.20829600	0.82985100	1.86134800
H	-5.63328700	0.49502400	0.98882700
C	-7.67186300	0.34752300	1.92553800
H	-8.37313900	1.05100500	2.38718700
H	-8.04535500	-0.20165800	1.05538800
C	-6.64527100	-0.31563700	2.84478100
C	-6.15969600	-1.71206100	2.50143600
C	-4.77364000	-1.99426900	2.37368200
H	-4.04254300	-1.18311000	2.48030000
C	-4.32358200	-3.31040400	2.11056000
H	-3.24893600	-3.50720900	2.01722900
C	-5.25735000	-4.36793000	1.97954100
H	-4.91118700	-5.38635200	1.76805400
C	-6.64174600	-4.09827200	2.11296400

H	-7.36965300	-4.91248200	2.01272700
C	-7.08726000	-2.78032400	2.37227500
H	-8.16024900	-2.57162900	2.47038600
C	-6.70959700	-0.02871000	4.35204400
H	-7.41947800	-0.72599300	4.83625400
H	-7.04275200	1.00546200	4.54479700
H	-5.71815100	-0.17232700	4.82208400
C	0.51877100	-1.59804300	4.66657200
C	-0.47211700	-2.30932800	5.40623100
C	-0.23825100	-2.73637600	6.74085400
H	-1.00230000	-3.28247500	7.30015600
C	1.00017100	-2.44006200	7.34751000
H	1.18693800	-2.76655100	8.37712200
C	2.00014100	-1.72757600	6.65415300
H	2.95086800	-1.50503300	7.14558500
C	1.75124000	-1.30941900	5.31849800
C	-2.75468800	-3.22659800	5.46041200
C	3.91170200	-0.14642700	5.22439000
O	4.11966300	-6.38722500	-2.21818000
O	-3.98350100	-5.94900000	-2.93111500
O	-2.71320900	1.25207600	-5.12591700
O	1.78377300	2.15681800	-3.86516100
N	-0.34198300	-0.90839000	-1.76713300

N	-1.20367200	1.54384400	-0.79234300
N	2.50944600	-4.83679400	-1.46799900
H	2.39838100	-3.93194500	-0.99932100
N	-2.35548200	-4.59705900	-1.88770600
H	-2.22808700	-3.69485900	-1.41823200
C	0.05147500	-3.31459300	-1.17264800
C	-0.09768100	-2.25667900	-2.09442900
C	0.03958400	-2.41882200	-3.53621500
H	0.21180800	-3.37303300	-4.03270300
C	-0.06926200	-1.16109200	-4.09461600
H	-0.02026000	-0.87713800	-5.14501900
C	-0.33287300	-0.23302600	-3.00590800
C	-0.65127500	1.12114200	-3.19779200
C	-1.16097100	1.91156200	-2.15273800
C	-1.77536100	3.21484100	-2.35133800
H	-1.87820500	3.70273500	-3.31948100
C	-2.21394300	3.64963200	-1.11566800
H	-2.74120000	4.56914800	-0.86249900
C	-1.80750900	2.64104200	-0.14466200
C	0.07678600	-4.72702600	-1.70656400
C	1.29487100	-5.45784700	-1.88286000
C	1.27747100	-6.76059100	-2.45412700
H	2.22157800	-7.28762100	-2.59701300

C	0.04505700	-7.32686000	-2.83854100
H	0.03620600	-8.32949200	-3.28169700
C	-1.17532400	-6.64174300	-2.66942400
H	-2.12940700	-7.07641100	-2.97145700
C	-1.15887600	-5.33979300	-2.10064900
C	3.82472300	-5.30395800	-1.61607900
C	4.86237000	-4.41151400	-1.00085200
H	4.51384700	-3.42629600	-0.66872900
C	6.30010900	-4.44686500	-1.56987500
H	6.79282000	-3.47808900	-1.70071600
H	6.46436200	-5.17710300	-2.36917600
C	6.06562200	-4.99837200	-0.16735300
C	6.51849800	-4.18073100	1.02847000
C	7.81284700	-3.59855000	1.06403500
H	8.46404800	-3.68821200	0.18578400
C	8.26905500	-2.91626900	2.21727700
H	9.27430900	-2.47757800	2.23055200
C	7.43485400	-2.80872100	3.35641600
H	7.79061500	-2.28788600	4.25367400
C	6.14034400	-3.38505200	3.33017400
H	5.48604500	-3.31017400	4.20722800
C	5.68899800	-4.06556500	2.17607800
H	4.68531400	-4.50915500	2.16162400

C	6.16704700	-6.51398000	0.06311500
H	7.22296500	-6.78833500	0.24861100
H	5.79673400	-7.07282200	-0.81196400
H	5.57930000	-6.81894800	0.94951400
C	-3.66563300	-4.89910100	-2.28410200
C	-4.66608300	-3.85493500	-1.87617900
H	-4.36366300	-3.20109700	-1.04884600
C	-6.16725400	-4.20297900	-1.94086600
H	-6.39476500	-5.20078500	-2.33122900
H	-6.78302900	-3.86520200	-1.10145200
C	-5.61864700	-3.17870900	-2.93272400
C	-5.92307300	-1.70959400	-2.70193200
C	-4.89040900	-0.73633700	-2.77403800
H	-3.85590500	-1.05259500	-2.95798700
C	-5.17764100	0.63888100	-2.60562900
H	-4.36410700	1.37121700	-2.66426900
C	-6.50940600	1.06196700	-2.36909200
H	-6.73394600	2.12643000	-2.23183300
C	-7.54796500	0.10087100	-2.30486500
H	-8.58120800	0.42262300	-2.12584600
C	-7.25509400	-1.27404100	-2.47130300
H	-8.05995300	-2.01810100	-2.41914200
C	-5.49841200	-3.57109600	-4.41219200

H	-6.45961700	-3.38312800	-4.92742000
H	-5.24141700	-4.63875100	-4.51989800
H	-4.71915000	-2.96909600	-4.91699100
C	-0.45258000	1.73431800	-4.55323800
C	-1.48444200	1.80196100	-5.52785900
C	-1.25520300	2.38743000	-6.80214600
H	-2.04866100	2.43564200	-7.55296100
C	0.02372400	2.91154700	-7.09255700
H	0.20602000	3.36483800	-8.07395800
C	1.07244000	2.86379100	-6.14808400
H	2.05449400	3.27557000	-6.39648400
C	0.82577600	2.27101000	-4.88129600
C	-3.82221100	1.25913100	-6.09390300
C	3.14418300	2.66129800	-4.12403200
H	4.43529400	0.46445500	4.47686200
H	4.53881500	-1.01083100	5.51941200
H	3.67796000	0.46984300	6.11371000
H	-3.59425500	-3.27068300	4.75265700
H	-3.04822500	-2.65486600	6.36191500
H	-2.44775200	-4.25128000	5.74673000
H	3.71432200	2.40273500	-3.22089300
H	3.13587200	3.75834900	-4.26595000
H	3.59354500	2.15660300	-5.00004300

H	-4.65946600	0.78636000	-5.56064800
H	-3.56525400	0.67212800	-6.99674000
H	-4.09436800	2.29326700	-6.38137400
C	2.41020100	0.68840100	0.46333200
C	3.47236800	3.80579900	3.31386600
C	4.01814700	1.77000000	2.02317000
C	3.07863900	2.75038200	2.46699900
C	4.81943200	3.91456200	3.74663400
C	3.59006000	0.66442200	1.12612600
C	5.76304600	2.94940600	3.32049800
C	1.35891400	0.68012100	-0.31441200
C	5.36730500	1.88893400	2.47275500
H	6.11748100	1.15905200	2.15139200
H	6.80816600	3.02328300	3.64499200
H	5.12443700	4.73619700	4.40518200
H	2.03297100	2.65779200	2.15164900
H	2.73016000	4.54110200	3.64559300
H	1.34102900	1.12387800	-1.32205800
C	5.38366500	-0.76488300	-4.40112300
C	6.60021000	-0.36219600	-3.78263800
C	4.23147100	-0.98007800	-3.59817700
C	4.28511700	-0.80991800	-2.20271900
C	5.51147100	-0.41802500	-1.54870200

C	6.66501800	-0.18887500	-2.38957600
H	3.37678600	-0.95367500	-1.60737600
H	5.33726100	-0.91135000	-5.48654300
H	3.28610600	-1.27905600	-4.06598300
H	7.60756600	0.11998600	-1.91812700
H	7.49339800	-0.19027400	-4.39576800
C	5.63219700	-0.26970600	-0.12892100
C	4.53798700	-0.54319200	0.88382100
H	3.91008400	-1.39032200	0.55300900
H	4.99451300	-0.84443700	1.84545900
H	6.60864800	0.05857300	0.25483600

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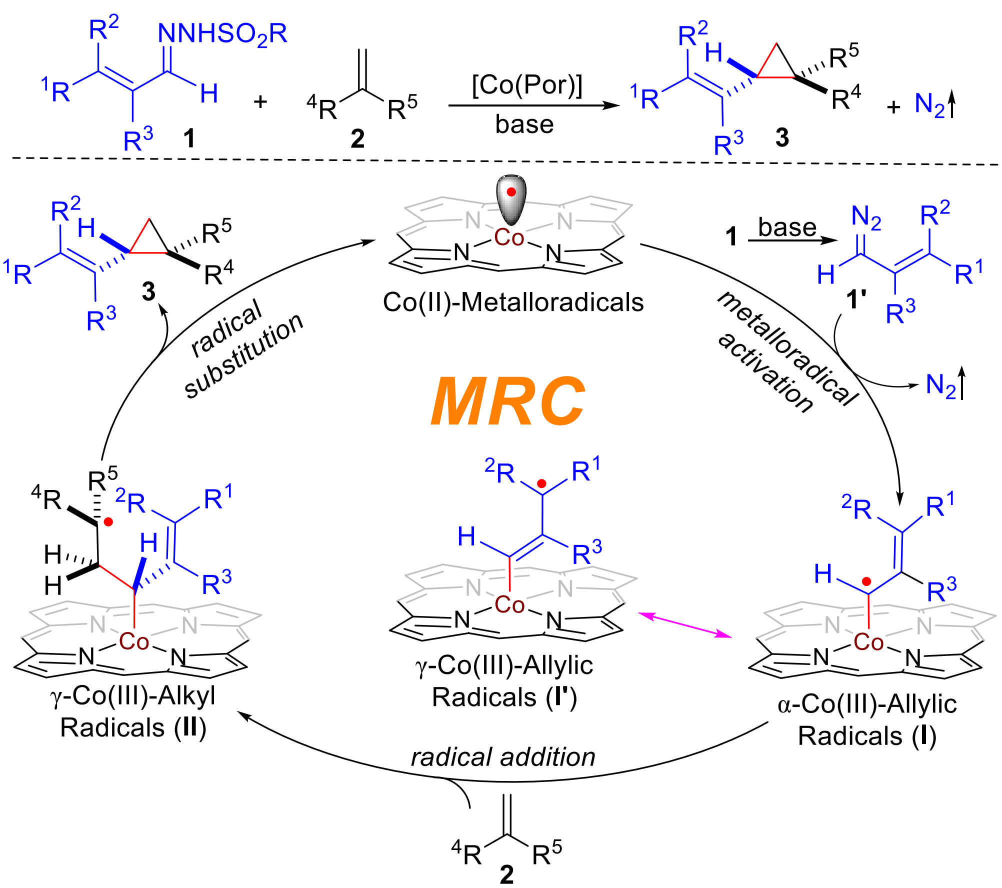
CHAPTER 3

ASYMMETRIC RADICAL PROCESS FOR CYCLOPROPANATION OF ALKENES WITH IN SITU-GENERATED α-VINYLDIAZOMETHANES

3.1. INTRODUCTION

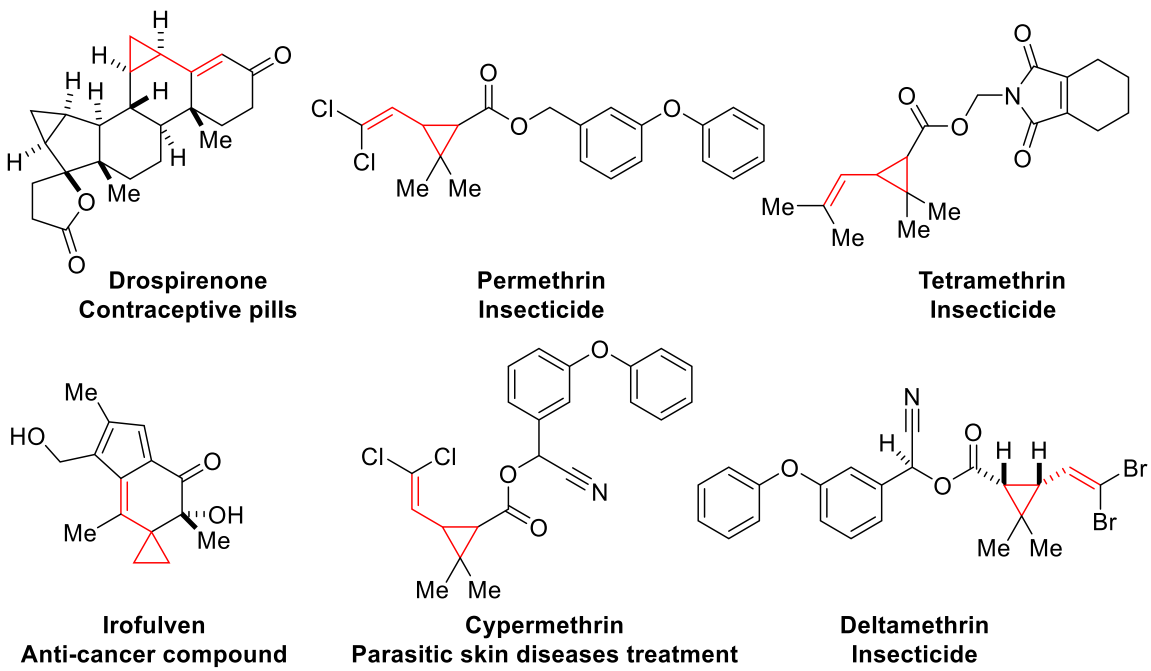
During the past several decades, radical chemistry has been increasingly explored for the development of new synthetic tools in the construction of organic molecules due to its unique reactivity and attractive characteristics.[1] Allylic radicals, being more stable radicals than other alkyl radicals due to the resonance effect, have long been recognized as key intermediates in a variety of radical transformations.[2] However, the development of reactions involving allylic radicals faces longstanding challenges that are associated with: 1) the generation of allylic radicals which is mainly restricted to direct activation of allylic C–H bonds, 1,3-dienes, and allenes;[3] 2) the control of formidable stereoselectivity, especially enantioselectivity.[4] Among recent advances,[5] metalloradical catalysis (MRC), which aims at the development of metalloradical-based systems for catalytic initiation and selective control of radical processes, has emerged as a conceptually new approach for the catalytic generation of metal-supported organic radicals.[6,7,8] As stable 15e-metalloradicals, Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] exhibit a high capability of homolytically activating different classes of diazo compounds as effective metalloradicophiles for the generation of α-Co(III)-alkyl radicals which can be precisely governed to undergo various radical transformations such as stereoselective cyclopropanation of alkenes inside the pocket-like environment of the chiral porphyrin ligands.[9] To broaden the synthetic applications of Co(II)-MRC, we were intrigued by the possibility of introducing vinyldiazomethanes as new allylic radical precursors for the generation of α-Co(III)-allylic radicals. Furthermore, although α-Co(III)-alkyl radicals with acceptor-, aryl-, and alkynyl-substituents have been successfully involved in Co(II)-based asymmetric radical cyclopropanation with alkenes,[10] none of the key α-Co(III)-alkyl radical intermediates in previous cases have two similar reacting sites like Co-supported allylic radicals due to the resonance effect. It was unclear if Co(II)-based metalloradical system could be applicable to Co(III)-allylic radicals for asymmetric site-selective transformations. Specifically, we sought to explore the feasibility of developing a catalytic process that would employ the α-Co(III)-allylic radicals for the synthesis of vinyl cyclopropane with effective control of stereoselectivities via Co(II)-MRC (Scheme 3.1).

Scheme 3.1. Proposed Pathway for Radical Cyclopropanation of Alkenes with α-Vinyldiazomethanes via Co(II)-MRC



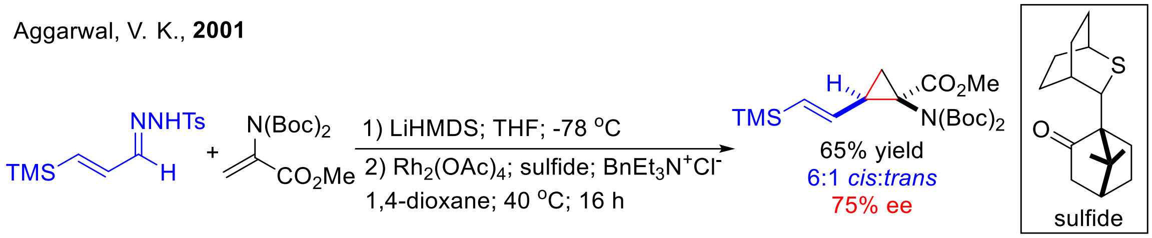
In view of the intrinsic properties of vinyl moieties, this proposed Co(II)-based catalytic process presented several potential challenges. Taking into account the well-known reactivity of vinyldiazomethane **1'** towards the formation of stable pyrazole compounds,[11] it would be critically important to match the rates between diazomethane generation from corresponding vinyl-substituted hydrazone **1** and the ensuing metalloradical activation.[12] Besides the concerns with the efficiency of metalloradical activation, a considerable challenge lies in the subsequent radical addition to alkene substrates **2**. Confronting the potential reactivity of resonance structure γ-Co(III)-allylic radicals **I'**, it is unclear whether α-Co(III)-allylic radicals **I** could be regioselectively and enantioselectively engaged. A significant challenge also lies in the issue of chemoselectivity as well as diastereoselectivity during the final step of radical substitution of the γ-Co(III)-alkyl radicals **II** for the second C–C bond formation. Considering the presence of the C═C double bond, it is still under question whether γ-Co(III)-alkyl radicals **II** could chemoselectively undergo the desired *3-exo-tet* radical cyclization over the potentially competitive *5-endo-trig* cyclization, leading to diastereoselective construction of cyclopropanes. If these and related issues could be resolved, it would not only provide an innovative approach to generating the allylic radical species from α-vinyldiazomethanes but also lead to the development of a new catalytic radical process for asymmetric olefin cyclopropanation to construct chiral vinyl cyclopropanes, which is considered to be highly desirable due to the wide existence of the vinylcyclopropane structures in many important natural products and drug molecules (Figure 3.1).[13]

Figure 3.1. Selected Examples of Important Bioactive Compounds Containing Vinylcyclopropane Motifs



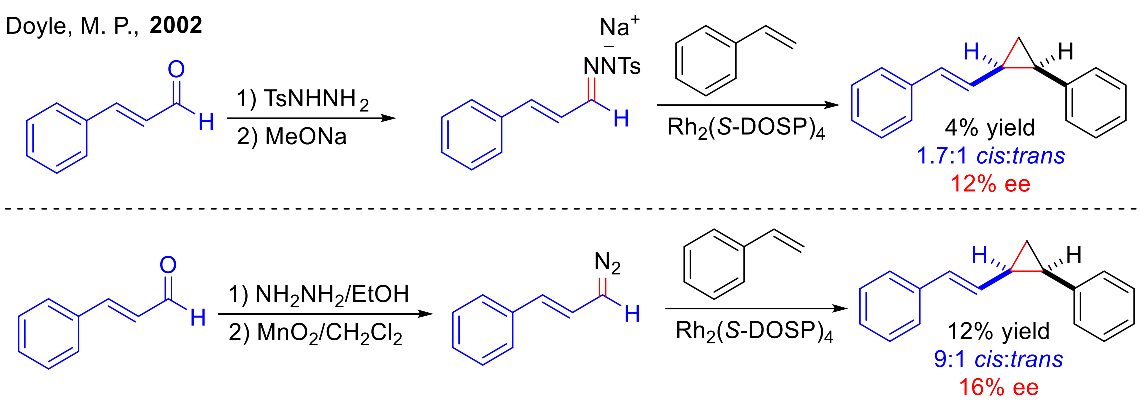
Transition-metal-catalyzed asymmetric cyclopropanation of alkenes with α-vinyldiazomethanes represents an appealing approach for the construction of vinylcyclopropanes with the potential to control both reactivity and enantioselectivity.[14] In contrast to the well-precedented asymmetric cyclopropanation with other common types of diazo compounds, α-vinyldiazomethanes involved olefin cyclopropanation, however, have rarely been demonstrated in an asymmetric manner with most of the reported methods restricted to the diazo esters.[15,16] The underdevelopment is largely attributed to their intrinsic instability as well as the high propensity for unwanted pyrazoles.[11] To circumvent the difficulties, Aggarwal and coworkers developed a catalytic system for stereoselective synthesis of vinylcyclopropyl amino acids based on Rh_2-catalyzed asymmetric cyclopropanation of in situ-generated (trimethylsilyl)ethenyldiazomethane (Scheme 3.2).[17]

Scheme 3.2. Catalytic Asymmetric Olefin Cyclopropanation with In Situ-Generated Vinyldiazomethane



Additionally, Doyle and coworkers reported an innovative solution that relied upon the use of tosylhydrazone sodium salt of cinnamaldehyde as well as (*E*)-styryldiazomethane for Rh_2-catalyzed asymmetric cyclopropanation of styrene (Scheme 3.3).[18]

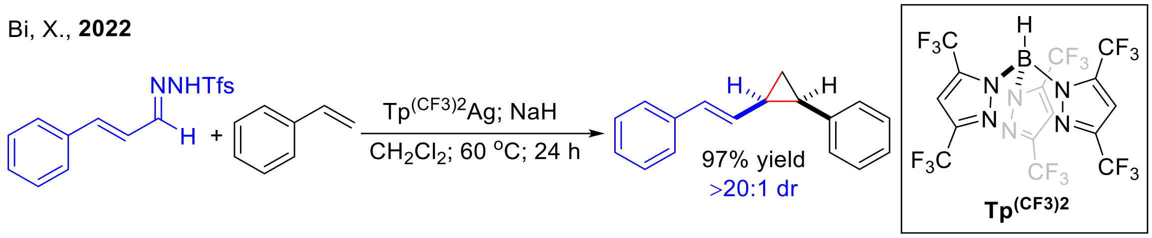
Scheme 3.3. Rh_2-Catalyzed Stereoselective Cyclopropanation of Styrene with In Situ-Generated Vinyldiazomethane



Recently, Bi and coworkers have developed Ag-catalyzed stereoselective cyclopropanation of alkenes with vinyl-*N*-triftosylhydrazones, which enables the synthesis of racemic vinyl cyclopropane in high yields with excellent diastereoselectivities (Scheme 3.4).[19]

While the reported in situ-protocols offer novel alternatives for catalytic synthesis of vinylcyclopropanes, the generalizability of asymmetric transformation to substrates with

Scheme 3.4. Ag-Catalyzed Stereoselective Cyclopropanation of Alkenes with Vinyl-*N*-triftosylhydrazones



varied steric or electronic properties remain elusive. Evidently, it would be highly desirable to develop new catalytic systems that are generally applicable for the direct stereoselective synthesis of valuable vinylcyclopropanes. As a new application of MRC, we herein report the development of a new Co(II)-based catalytic system that is highly efficient for the asymmetric cyclopropanation of alkenes with in situ-generated α-vinyldiazomethanes from the corresponding sulfonyl hydrazones in the presence of a base. Supported by the optimal D_2-symmetric chiral amidoporphyrin ligand, the Co(II)-based catalytic system is capable of efficiently activating a variety of vinyldiazomethanes at room temperature and further performing the cyclopropanation reaction with a wide range of alkenes, delivering the products in high yields with excellent control of enantioselectivities for both diastereomers. The importance of catalyst development is shown through fine-tuning of the ligand environment in achieving high reactivity as well as selectivities. Combined computational and experimental studies are presented to shed light on the underlying stepwise radical mechanism of the Co(II)-catalyzed cyclopropanation as well as the unique reactivity of the γ-Co(III)-allylic radicals which is the resonance structure of α-Co(III)-allylic radicals.

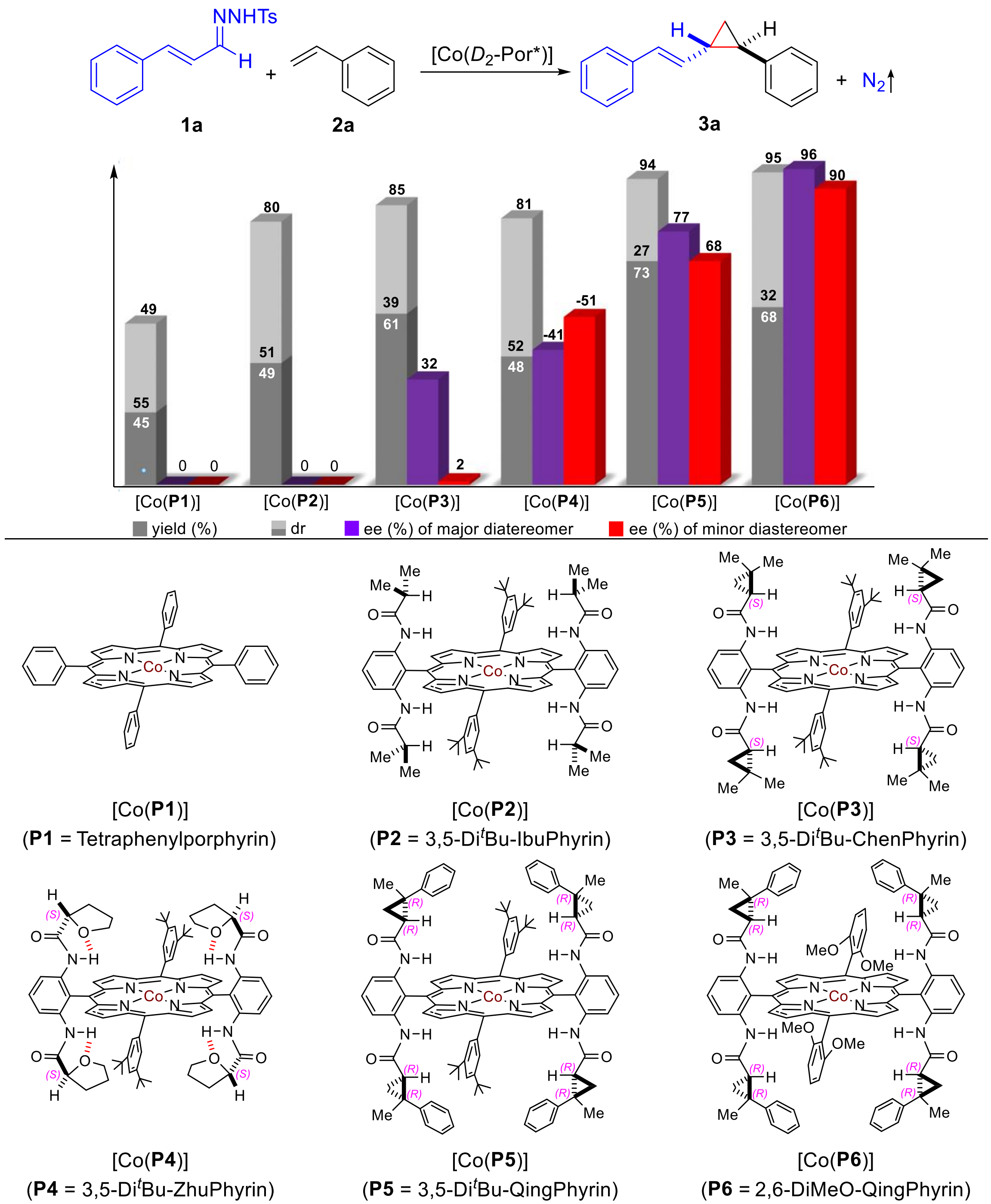
3.2. RESULTS AND DISCUSSION

3.2.1. Condition Optimization for Asymmetric Radical Cyclopropanation of Alkenes with α-Vinyldiazomethanes

At the outset, styryldiazomethane (**1a'**), which was in situ-generated from the corresponding tosylhydrazone **1a** in the presence of Cs_2CO_3, was chosen as the representative α-vinyldiazomethane for asymmetric radical cyclopropanation of styrene (**2a**) by Co(II)-based metalloradical catalysts [Co(Por)] (Scheme 3.5).

Simple achiral metalloradical catalyst [Co(**P1**)] (**P1** = tetraphenylporphyrin) was found to be capable of activating the diazo compound to cyclopropanate styrene, giving rise to the formation of desired vinyl cyclopropane **3a** in moderate yield (49%) consisting of a similar amount of the two diastereomers. The Co(II) complex of D_{2h}-symmetric amidoporphyrin [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin)[20] was identified as a more effective achiral metalloradical catalyst for the cyclopropanation reaction, delivering the desired vinyl cyclopropane **3a** in higher yield (80%). The high-yielding formation of the product implies that the in situ generation of the α-vinyldiazomethane from **1a** was facile and properly matched with the rate of metalloradical activation. To evaluate the feasibility of asymmetric induction during the proposed catalytic cycle, Co(II) complexes of a series of D_2-symmetric chiral amidoporphyrin ligands were employed as the catalysts. Metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)[10a] was first applied to the catalytic system, exhibiting promising capability of catalyzing the reaction in good yield (85%) albeit with inferior control of enantioselectivities for both diastereomers (32% and2% ee). On the hypothesis that the poor asymmetric induction may be attributed to the relative flexibility of the chiral arms in ChenPhyrin catalysts, metalloradical catalyst

Scheme 3.5. Ligand Effect on Co(II)-Based Catalytic System for Olefin Cyclopropanation with α-Vinyldiazomethane[a]



[a]Carried out with **1a** (0.10 mmol) and **2a** (0.12 mmol) in the presence of Cs_2CO_3 (0.15 mmol) by [Co(Por)] (2 mol %) in benzene (0.6 mL) at 60 °C for 24 h; Ts = 4-methylbenzene sulfonyl; Isolated yields of the mixture of two diastereomers; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

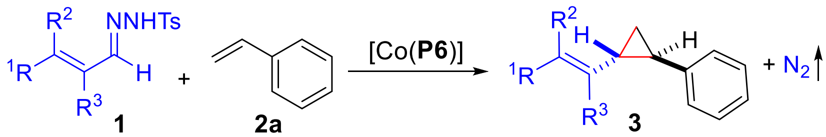
[Co(**P4**)] (**P4** = 3,5-Di^{t}Bu-ZhuPhyrin)[21] was further applied to the catalytic system, which is devised to achieve conformational rigidity benefiting from its unique intramolecular H-bonding interaction in the (*S*)-(–)-2-tetrahydrofurancarboxamide units. As shown, applying [Co(**P4**)] switched the asymmetric induction in favor of the opposite enantiomers with enhancement in the enantioselectivity of both diastereomers (–41% and –51% ee). These initial results prompted us to explore second-generation catalysts which bear cyclopropanecarboxyamides with two contiguous stereogenic centers for further improving the asymmetric induction of the catalytic process. Gratifyingly, by applying [Co(**P5**)] (**P5** = 3,5-Di^{t}Bu-QingPhyrin)[10g], the enantioselectivity was significantly improved from moderate to good level (77% and 68% ee) in conjunction with excellent reactivity (94% yield). This positive outcome inspired us to switch to analogous catalyst [Co(**P6**)] (**P6** = 2,6-DiMeO-QingPhyrin) bearing the same chiral amide units but with more sterically encumbered achiral meso-aryl groups to further enhanced the rigidity of the chiral environment. To our delight, alkynylcyclopropane **3a** was generated in dramatically improved enantioselectivities of both diastereomers (96% and 90% ee) without affecting the exceptional reactivity (95% yield). The difference in performance between [Co(**P6**)] and [Co(**P5**)] demonstrates that even a ligand modification as subtle as the substitution of functional groups in the same position can give rise to significant improvement in stereoselectivities, manifesting the effectiveness of catalyst development in controlling the radical process.

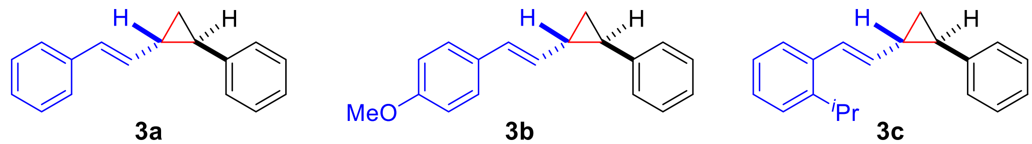
3.2.2. Asymmetric Radical Cyclopropanation of Styrene with Different α-Vinyldiazomethanes

Under the optimized conditions, the scope and versatility of [Co(**P6**)]-catalyzed asymmetric cyclopropanation were evaluated using different vinyl sulfonylhydrazone **1** as radical precursors with various olefin substrates **2**. Similar to hydrazone **1a**, its derivatives bearing substituents with varied electronic and steric properties on the phenyl group could be effectively employed in the Co(II)-based catalytic cycle under basic conditions as shown for asymmetric of styrene (**2a**) as representative olefin substrate (Table 3.1).

For example, the analogs α-(arylethenyl)diazomethane containing electron-donating –OMe group at *para*-positions of the aryl group could be effectively activated by [Co(**P6**)], allowing stereoselective construction of corresponding vinyl cyclopropanes **3b** in excellent yield and enantioselectivities (entry 2). When sterically bulky α-(arylethenyl)diazomethane bearing large alkyl substituent –iPr at the *ortho* position of the phenyl ring, the diastereoselectivity of the desired vinyl cyclopropane **3c** was dramatically increased (88:12 dr) while the enantioselectivity of the major diastereomer remains at excellent level (entry 3). Moreover, halogenated α-(arylethenyl)diazomethane derivatives could also serve as suitable metalloradicophiles as exemplified by the asymmetric synthesis of vinyl cyclopropanes **3d** and **3e** in high yields with remarkable control of enantioselectivities for both diastereomers (entries 4 and 5). Furthermore, the β,γ-disubstituted vinyldiazomethane could also be effectively activated by [Co(**P6**)] under the same conditions for asymmetric cyclopropanation reaction, giving rise to the high-yielding formation of vinyl cyclopropane **3f** with extraordinary enantioselectivities for both diastereomers (entry 6). Notably, sterically hindered γ,γ-disubstituted vinyldiazomethanes were also identified as competent

Table 3.1. Hydrazone Scope of Catalytic Asymmetric Cyclopropanation of Styrene[a]

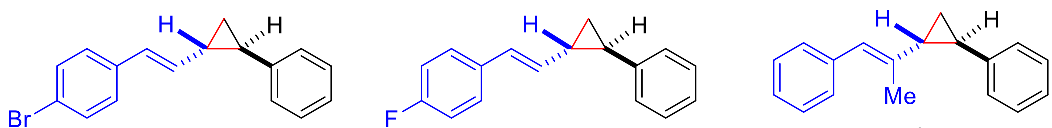




3a
entry 1: 95% yield; 68:32 dr
96% ee (major)/90% ee (minor)

3b
entry 2: 95% yield; 56:44 dr
96% ee (major)/89% ee (minor)

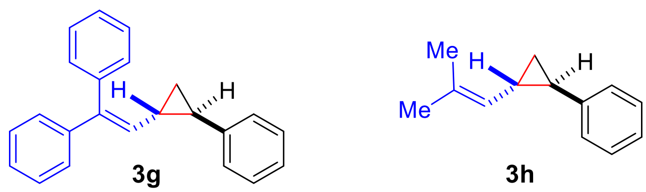
3c
entry 3: 91% yield; 88:12 dr
95% ee (major)/68% ee (minor)



3d
entry 4: 90% yield; 55:45 dr
86% ee (major)/80% ee (minor)

3e
entry 5: 92% yield; 62:38 dr
91% ee (major)/80% ee (minor)

3f
entry 6: 83% yield; 72:28 dr
90% ee (major)/97% ee (minor)



3g
entry 7: 81% yield; 55:45 dr
64% ee (major)/90% ee (minor)

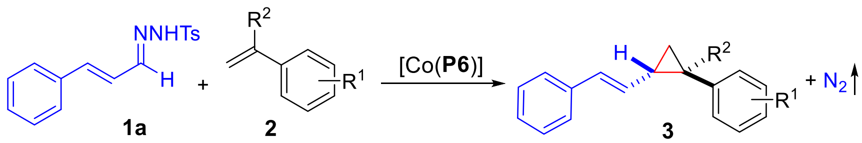
3h
entry 8: 93% yield; 56:44 dr
ee N.D.

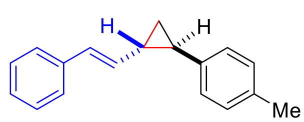
[a]Carried out with **1** (0.10 mmol) and **2a** (0.12 mmol) in the presence of Cs_2CO_3 (0.15 mmol) by [Co(**P6**)] (2 mol %) in benzene (0.6 mL) at 60 ^oC for 24 h; Ts = 4-methylbenzene sulfonyl; Isolated yields of the mixture of two diastereomers; Diastereomeric ratio (dr) determined by ^1H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

cyclopropanation reagents for the catalytic process, furnishing the corresponding product **3g** and **3h** in good yields (entries 7 and 8).

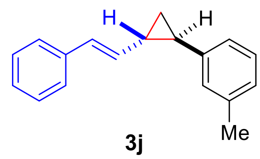
Apart from being able to activate different α-vinyldiazomethane derivatives, the Co(II)-based system also manifested an extraordinary capability of catalyzing the asymmetric cyclopropanation of a wide range of alkenes under the optimized conditions (Table 2.2). For instance, styrene derivatives bearing various substituents such as –Me, –*tert*-Bu, –OMe regardless of the positions could be reliably cyclopropanated by [Co(**P6**)] with α-

Table 3.2. Asymmetric Radical Cyclopropanation of Styrene Derivatives with In Situ-Generated α-Vinyldiazomethane[a]

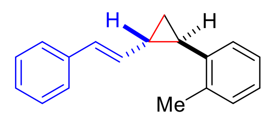




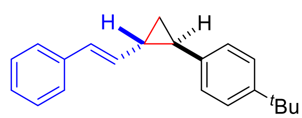
3i
entry 1: 90% yield; 58:42 dr
95% ee (major)/72% ee (minor)



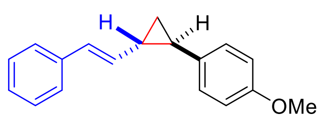
3j
entry 2: 89% yield; 69:31 dr
90% ee (major)/76% ee (minor)



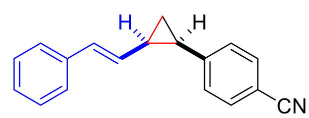
3k
entry 3: 93% yield; 76:24 dr
96% ee (major)/91% ee (minor)



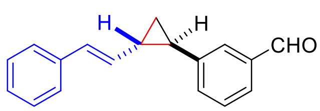
3l
entry 4: 95% yield; 57:43 dr
90% ee (major)/75% ee (minor)



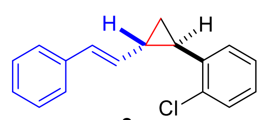
3m
entry 5: 94% yield; 66:34 dr
91% ee (major)/70% ee (minor)



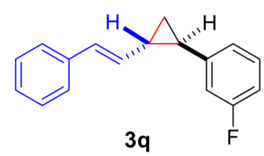
3n
entry 6: 83% yield; 55:45 dr
49% ee (major)/53% ee (minor)



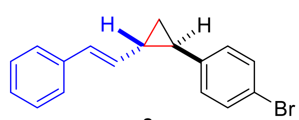
3o
entry 7: 93% yield; 76:24 dr
72% ee (major)/69% ee (minor)



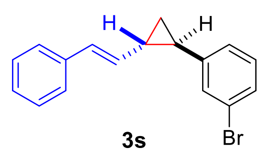
3p
entry 8: 91% yield; 61:39 dr
94% ee (major)/92% ee (minor)



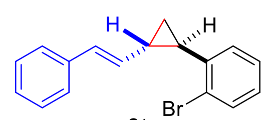
3q
entry 9: 93% yield; 71:29 dr
91% ee (major)/88% ee (minor)



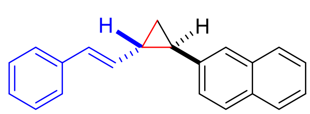
3r
entry 10: 90% yield; 57:43 dr
90% ee (major)/62% ee (minor)



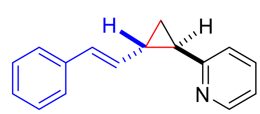
3s
entry 11: 83% yield; 59:41 dr
90% ee (major)/83% ee (minor)



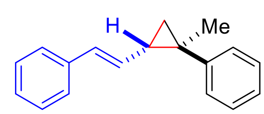
3t
entry 12: 88% yield; 62:38 dr
93% ee (major)/90% ee (minor)



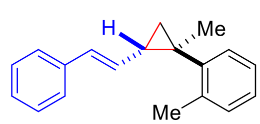
3u
entry 13: 87% yield; 68:32 dr
90% ee (major)/80% ee (minor)



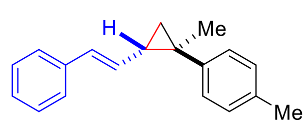
3v
entry 14: 91% yield; 66:34 dr
92% ee (major)/90% ee (minor)



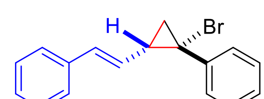
3w
entry 15: 96% yield; 71:29 dr
97% ee (major)/89% ee (minor)



3x
entry 16: 94% yield; 57:43 dr
93% ee (major)/73% ee (minor)



3y
entry 17: 94% yield; 54:46 dr
72% ee (major)/62% ee (minor)

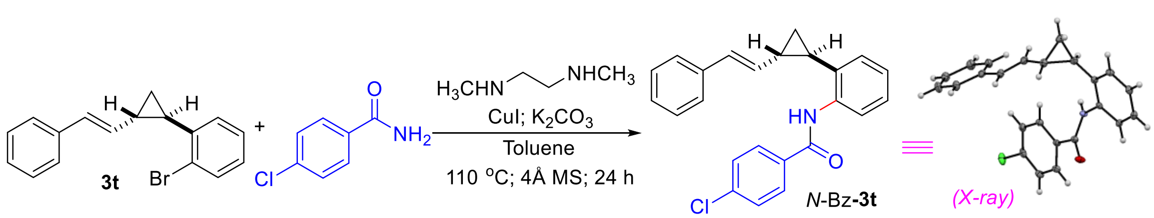


3z
entry 18: 93% yield; 71:29 dr
90% ee (major)/87% ee (minor)

[a]Carried out with **1a** (0.10 mmol) and **2** (0.12 mmol) in the presence of Cs_2CO_3 (0.15 mmol) by [Co(**P6**)] (2 mol %) in benzene (0.6 mL) at 60 °C for 24 h; Ts = 4-methylbenzene sulfonyl; Isolated yields of the mixture of two diastereomers; Diastereomeric ratio (dr) determined by ^1H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

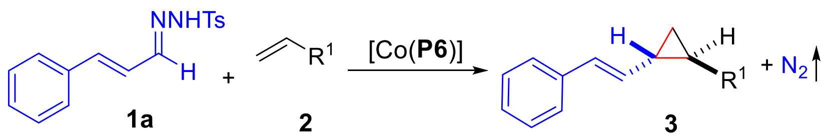
alkynyldiazomethane **1a'**, generating the corresponding vinylcyclopropanes **3i**–**3m** in good to excellent yields (entries 1–5). It is worth to noted that while the enantioselectivities of all these substrates remain at a similar level, *ortho*-substituted olefins seem to be extraordinary substrates for this catalytic system as the enantioselectivities of both diastereoselectivites were found to be excellent, which were also observed in the latter experiments. Functional groups like cyano and formyl moieties are also proved to be tolerated in the metalloradical catalysis, albeit delivering the products **3n** and **3o** respectively with moderate enantioselectivities (entries 6 and 7). Additionally, it was found that the halogen-containing olefins could also serve as suitable substrates in [Co(**P6**)]-based metalloradical system as exemplified by the stereoselective generation of corresponding cyclopropanes **3p**–**3t** in similarly high yields with good enantioselectivities (entries 8–12). The absolute configuration of the major enantiomer of vinyl cyclopropane **3t** was established as (*S*,*R*) by X-ray crystallography of its benzoyl derivative (Scheme 3.6).

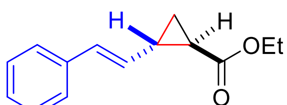
Scheme 3.6. Synthesis of Benzoyl Derivative of 3t for Absolute Configuration Determination



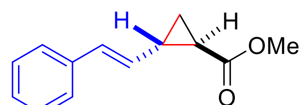
Furthermore, an extended ring system like 2-naphthalene could also be effectively applied to the catalytic system, affording vinyl cyclopropane **3u** in high yield with high ee for the two diastereomers (entry 13). In addition to the phenyl-derived olefins, heteroaryl-containing alkene such as 2-pyridine was successfully introduced to the catalytic processes for the exceedingly enantioselective synthesis of corresponding heteroaryl cyclopropane **3v** (entry 14). Apart from mono-substituted olefins, the Co(II)-based cyclopropanation was shown to be compatible with, 1,1-disubstituted olefins like *ortho*-α-dimethylstyrene, *para*-α-dimethylstyrene, and α-bromostyrene, allowing the highly stereoselective construction of trisubstituted cyclopropanes **3w**–**3z** with excellent control of the newly-generated quaternary stereogenic center (entries 15–18).

Table 3.3. Asymmetric Radical Cyclopropanation of Electron-deficient Olefins with In Situ-Generated α-Vinyldiazomethane[a]

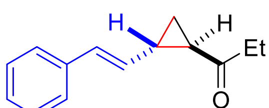




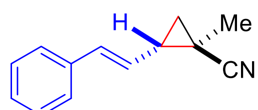
3aa
entry 27: 96% yield; 67:33 dr
91% ee (major)/82% ee (minor)



3ab
entry 28: 94% yield; 65:35 dr
65% ee (major)/55% ee (minor)



3ac
entry 29: 96% yield; 57:43 dr
71% ee (major)/84% ee (minor)



3ad
entry 30: 95% yield; 58:42 dr
91% ee (major)/80% ee (minor)

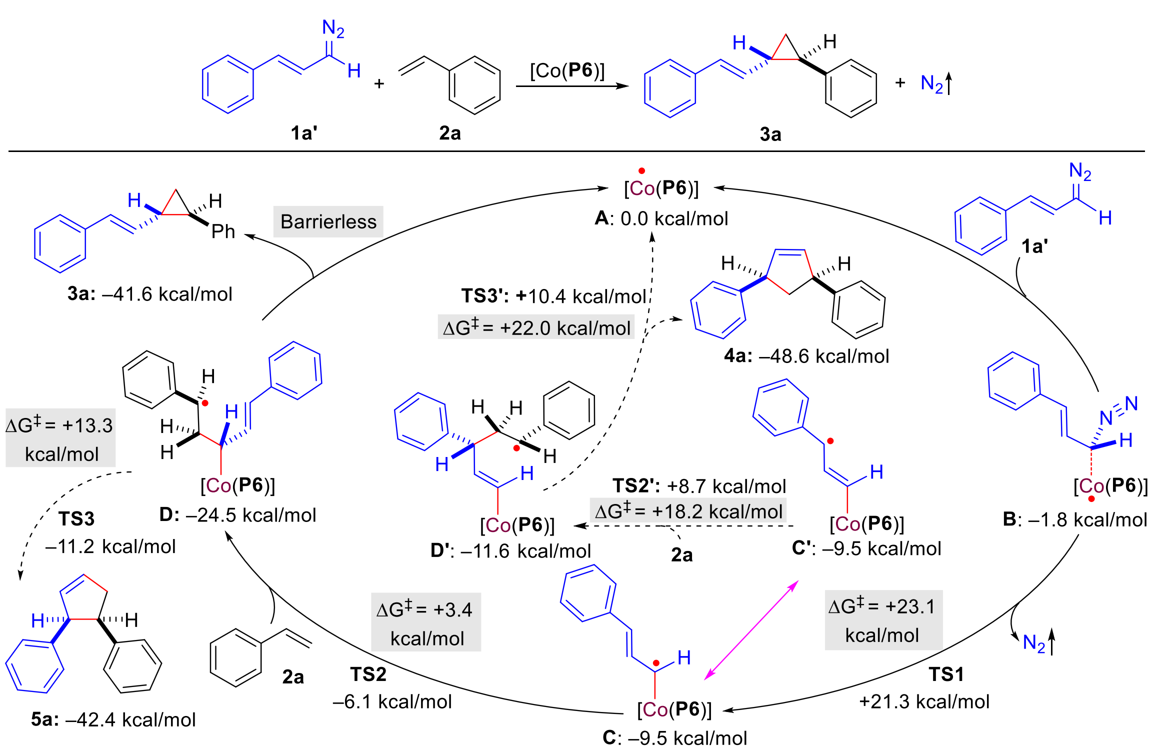
[a]Carried out with **1a** (0.10 mmol) and **2** (0.12 mmol) in the presence of Cs_2CO_3 (0.15 mmol) by [Co(**P6**)] (2 mol %) in benzene (0.6 mL) at 60 °C for 24 h; Ts = 4-methylbenzene sulfonyl; Isolated yields of the mixture of two diastereomers; Diastereomeric ratio (dr) determined by ^{1}H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

As a further highlight of the unique feature of Co(II)-based metalloradical catalysis, cyclopropanation of even the extremely electron-deficient acrylates and acrylonitrile could be efficiently performed to furnish the desired product **3aa**–**3ad** with excellent control of stereoselectivities (Table 3.3).

3.2.3. Mechanistic Studies on Co(II)-Catalyzed Radical Olefin Cyclopropanation with In Situ-Generated α-Vinyldiazomethane

To shed light on the underlying stepwise radical mechanism of Co(II)-based catalytic system for asymmetric cyclopropanation, combined computational and experimental studies were conducted. Firstly, associated energetics for asymmetric cyclopropanation of styrene (**2a**) with styryldiazomethane (**1a'**) by metalloradical catalyst [Co(**P6**)] (**A**) was calculated by conducting density functional theory (DFT) calculations to elucidate the details of the catalytic pathway (Scheme 3.6; see Scheme S2 in Experimental Section for details)

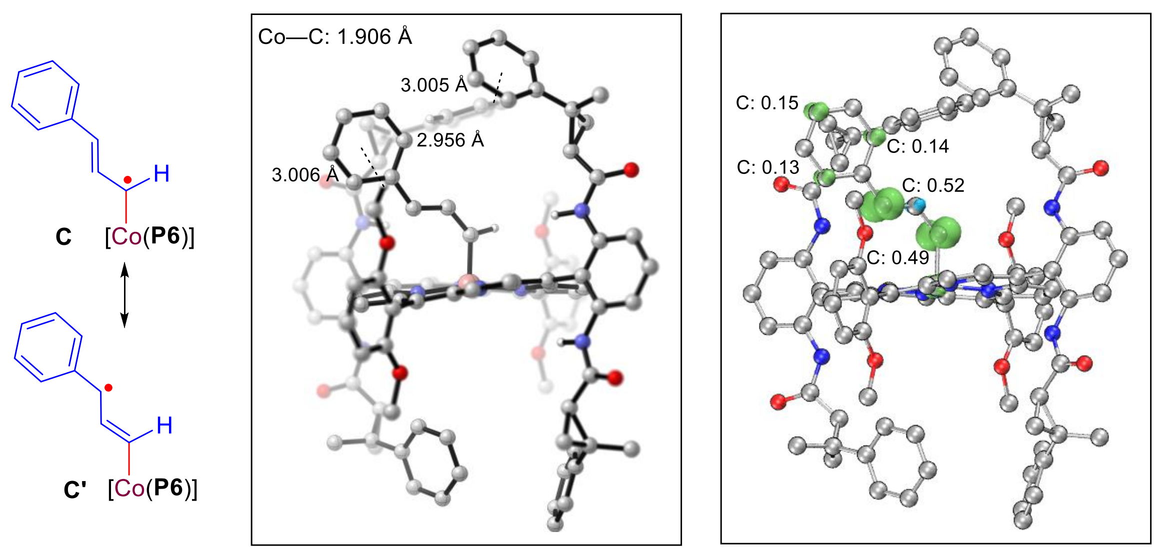
Scheme 3.6. Density Function Theory Calculation on Energetics of [Co(P6)] Catalyzed Cyclopropanation (kcal·mol^{-1})[a]



[a]Applied the method of bp86/LANL2DZ for geometry optimization and the B3LYP/def2-tzvp for single point energy calculation along with Grimme's dispersion correction and SMD (benzene) solvation model.

The DFT calculations indicate the initial formation of intermediate **B** upon a network of noncovalent attractive interactions between diazomethane **1a'** and catalyst [Co(**P6**)], including H-bonding and π-stacking interactions. This binding activity, which is slightly exergonic by 1.8 kcal/mol, positions the α-carbon atom of **1a'** in close proximity to the Co(II)-metalloradical center of [Co(**P6**)] (C···Co: ~3.402 Å) for the subsequent radical activation. The bound diazomethane **1a'** is further activated by catalyst [Co(**P6**)] to generate α-Co(III)-allylic radicals **C** with the elimination of dinitrogen as a byproduct. The metalloradical activation, which is exergonic by 7.7 kcal/mol, is found to be the rate-determining step associated with a relatively high but accessible activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS1}}$ = 23.1 kcal/mol). As displayed by the spin plot of intermediate C (Figure 3.2), the spin density mainly distributes on α- and γ-carbon atoms in similar amounts (α-C: 0.49; γ-C: 0.52), which can be represented as two resonance forms of α-Co(III)-allylic radicals **C** and γ- Co(III)-allylic radicals **C'**.

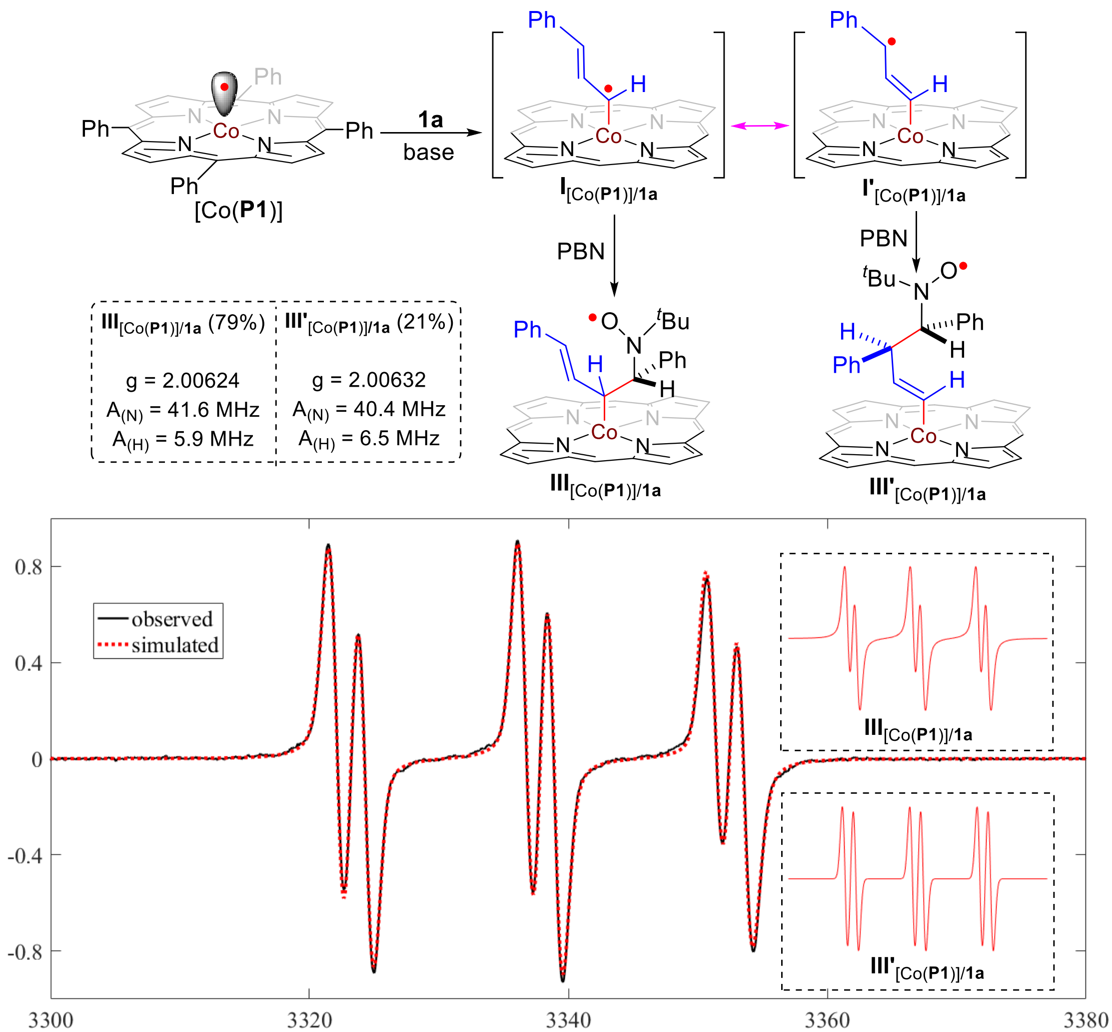
Figure 3.2. DFT-Optimized Models Showing Noncovalent Attractive Interactions and Spin Density Distribution of Intermediate C



To rationalize the observed regioselectivity of the catalytic reaction, we calculated the energetics associated with subsequent radical addition to alkene **2a** by both resonating structures (α-Co(III)-allylic radical **C** and γ-Co(III)-allylic radicals **C'**), leading to the formation of γ-Co(III)-benzyl radical intermediate **D** and ε-Co(III)-benzyl radical intermediate **D'**, respectively. DFT calculations indicate radical addition of allylic radicals **C** is more favorable than allylic radicals **C'** both kinetically ($\Delta G^{\ddagger}_{\mathbf{TS2}}$ = 3.4 kcal/mol; $\Delta G^{\ddagger}_{\mathbf{TS2'}}$ = 18.2 kcal/mol) and thermodynamically ($\Delta G^{\circ}_{\mathbf{D}}$ = –15.0 kcal/mol; $\Delta G^{\circ}_{\mathbf{D'}}$ = –2.1 kcal/mol). It is worth noting that the activation energy of ensuing *5-exo-trig* radical cyclization of ε-Co(III)-benzyl radical intermediate **D'** is also comparably high ($\Delta G^{\ddagger}_{\mathbf{TS3}}$ = 22.0 kcal/mol). According to the DFT calculations, γ-Co(III)-alkyl radicals **D** then undergo radical substitution to produce vinyl cyclopropane **3a** while regenerating metalloradical catalyst [Co(**P6**)]. This final step of *3-exo-tet* radical cyclization, which is exergonic by 17.1 kcal/mol, is found to be an almost barrierless process. Energetics associated with competitive 5-*endo-trig* cyclization of γ-Co(III)-alkyl radical **D**, which is exergonic by 17.9 kcal/mol, is associated with a much higher activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS3'}}$ = 13.3 kcal/mol).

To provide direct evidence for the existence of the key Co(III)-supported allylic radical intermediates, efforts were made to trap the Co-supported organic radicals for experimental detection and characterization. First, the spin trapping reagent *N*-*tert*-butyl-α-phenylnitrone (PBN) was added to the reaction mixture isotropic electron paramagnetic resonance (EPR) spectrum was recorded at room temperature for the reaction mixture containing vinyldiazomethane **1a'** with metalloradical catalyst [Co(**P1**)] in the absence of olefin substrate and was then monitored by X-band electron paramagnetic resonance (EPR) spectroscopy at room temperature (Scheme 3.7; see Figure S1 in Experimental Section for details). The observed isotropic EPR spectrum exhibits strong signals with the diagnostic splitting pattern at a g-value of ~2.00 that are consistent with the characteristic value of PBN- trapped Co(III)-supported alkyl radical species.[22] In accordance with the spin density distribution from DFT calculations (Figure 3.2), the observed broad spectrum (in black) could be near perfectly simulated (in red) as two well-defined triplets of doublet signals

Scheme 3.7. Trapping of α-Co(III)-Vinyl Radical and γ-Co(III)-Vinyl Radical Intermediates by Spin Trap PBN[a]

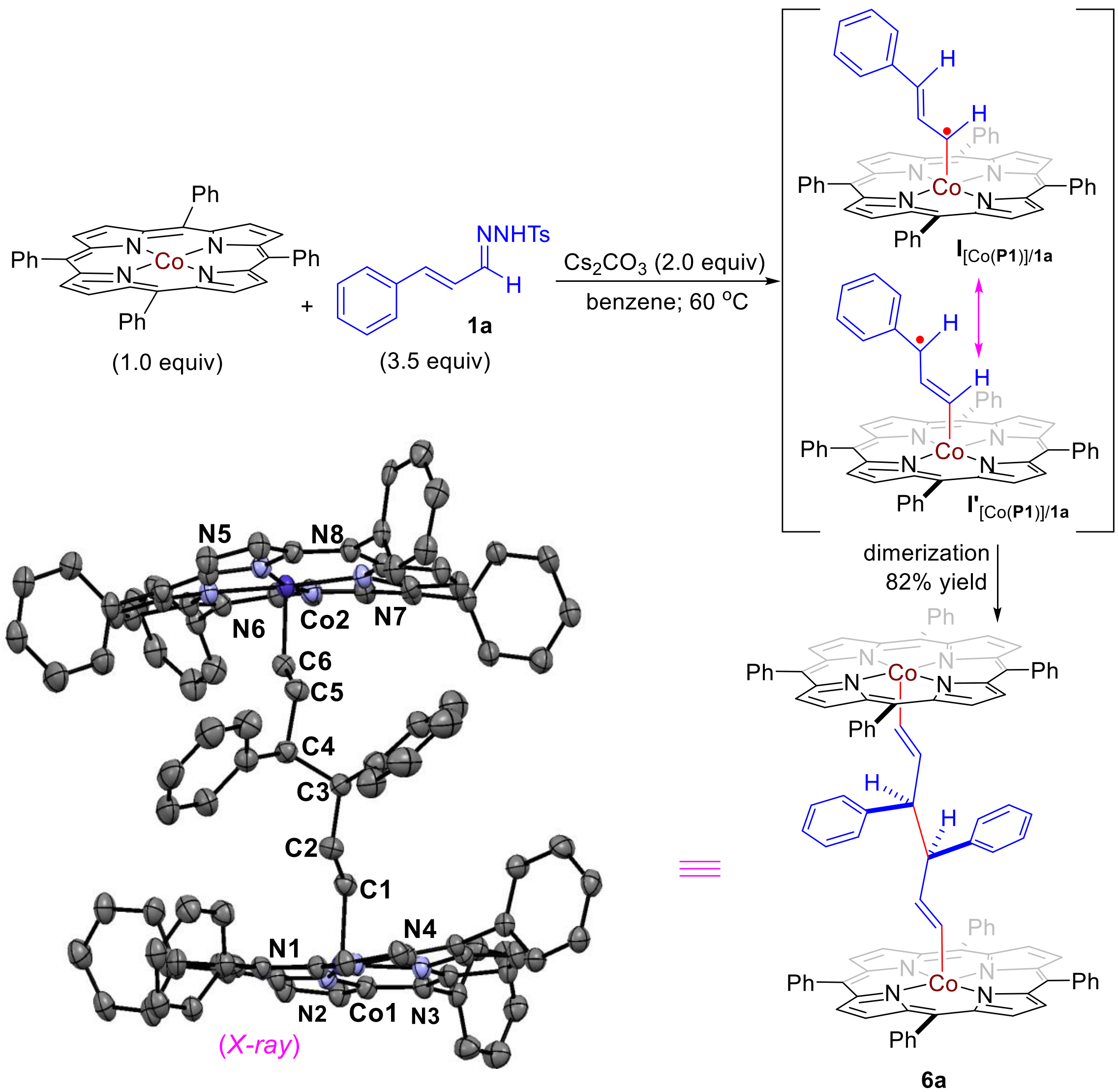


[a]Carried out with **1a'** (0.10 mmol), [Co(**P1**)] (4 mol %), and PBN (0.10 mmol) in benzene (0.6 mL) at RT for 5 min; The simulation of the EPR spectrum was per-formed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon.

(Scheme 3.7) by involving PBN-trapped radical species that are originated from the two resonance forms of α-Co(III)-allylic radical intermediate $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ and γ-Co(III)-allylic radical intermediate $\mathbf{I'}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ on the basis of the hyperfine coupling by ^{14}N (I = 1) and ^{1}H (I = 1/2): 79% of O-centered radicals $\mathbf{III}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ from $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ (g=2.00624, $A_{(N)}$ = 41.6 MHz, $A_{(H)}$ = 5.9 MHz) and 21% of O-centered radicals $\mathbf{III'}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ from $\mathbf{I'}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ (g=2.00632, $A_{(N)}$ = 40.4 MHz, $A_{(H)}$ = 6.5 MHz).

Besides observing the Co(III)-supported allylic radical intermediates spectroscopically, we were intrigued by the possibility of obtaining more definite experimental evidence for the existence of the radical intermediates (Scheme 3.8). The reaction of [Co(**P1**)] with 3.5 equiv of vinyldiazomethane **1a'** in the absence of the alkene substrates was found to proceed cleanly reaction and generate only one major product (**6a**), which could be isolated in high yield (82%). The data obtained from NMR and HRMS measurements show **6a** to be dimeric cobalt(III) porphyrin complex. Similar to the previously reported complex,[9c] proton resonances with unusual negative chemical shifts appeared in the high-field region of its ^{1}H NMR spectrum, indicating the presence of hydrogen-containing ligands in the axial position of **6a**. The detailed structure of **6a** was eventually unveiled by single-crystal X-ray diffraction, which is consistent with all the spectroscopic data. As shown, the two cobalt porphyrins in **6a** are arranged in a face-to-face fashion through a disubstituted 1,5-hexadiene C_6-bridge between the two Co(III) centers, the distance of which is 9.094 Å. The formation of the binuclear complex **6a** was proposed to be generated from the dimerization of the initially generated α-Co(III)-allylic radicals $\mathbf{I}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ via its γ-Co(III)-allylic radical resonance form $\mathbf{I'}_{[Co(\mathbf{P1})]/\mathbf{1a}}$. On the other hand, the absence of an alternative dimerization process through the α-Co(III)-allylic radicals is presumably steric in origin.

Scheme 3.8. Homodimerization of Allylic Radical from [Co(TPP)] and In Situ-Generated Vinyldiazomethanec[a]



[a]Carried out with **1a** (0.35 mmol) and [Co(**P1**)] (0.10 mmol) in the presence of Cs_2CO_3 (0.70 mmol) in benzene (3.0 mL) at 60 °C for 24 h; Ts = 4-methylbenzene sulfonyl; Isolated yield; Structure determined by X-ray crystallography; Selected bond distance (Å): Co1–C1: 1.893(7); C1–C2: 1.300(1); C2–C3: 1.511(9); C3–C4: 1.530(1); C4–C5: 1.509(9); C5–C6: 1.306(9); C6–Co2: 1.894(7); Co1–Co2: 9.094(1).

The clean self-dimerization of γ-Co(III)-allylic radicals **I'**$_{[Co(\mathbf{P1})]/\mathbf{1a}}$ via C–C coupling provide convincing evidence for the existence of Co(III)-supported allylic radicals as key intermediates in the radical-type mechanism of Co(II)-based metalloradical catalysis. Further DFT calculations using the broken-symmetry methodology (see Scheme S1 in

Experimental Section for details) indicate that the dimerization of γ-Co(III)-allylic radicals **I'**$_{[\mathrm{Co}(\mathbf{P1})]/\mathbf{1a}}$ via radical C–C coupling is a barrierless process, explaining the facile formation of **6a**.

3.3. CONCLUSIONS AND OUTLOOK

In summary, we have developed a highly effective catalytic system that can activate the in situ-generated vinyldiazomethane as a new type of metalloradicophiles for the generation of corresponding Co(III)-supported radicals that exist in α-carbon-based and γ-carbon-based allylic radical resonance forms. On the basis of a remarkable ligand effect on the Co(II)-based catalytic system, D_2-symmetric chiral amidoporphyrin 2,6-DiMeO-QingPhyrin has been identified as the optimal supporting ligand that offers suitable steric, electronic and chiral environments surrounding the Co(II)-metalloradical center for engaging a network of noncovalent attractive interactions to facilitate the cyclopropanation process involving α-Co(III)-allylic radicals. In addition to high reactivity, the [Co(**P6**)]-catalyzed cyclopropanation displays a distinct sense of enantioselectivity, thus permitting for the direct synthesis of chiral vinylcyclopropanes from a broad range of alkenes as well as vinyldiazomethanes. The combined computational and experimental studies have shed light on the underlying stepwise radical mechanism of the Co(II)-based cyclopropanation system involving a unique α-metalloradical intermediate that is associated with two resonance forms of α-Co(III)-allylic radical and γ-Co(III)-allylic radical. In addition to rationalizing the unique profile of reactivity and selectivity, the established mechanism offers a convincing explanation of the regioselectivity towards the formation of vinyl cyclopropanes via α-Co(III)-allylic radical form without any complication from potential reactions via γ-Co(III)-allylic radical form. On the other hand, γ-Co(III)-allylic radical form is found to be involved in the self-dimerization via radical C–C coupling, providing experimental evidence for the existence of Co(III)-supported allylic radicals. Considering the ubiquity of chiral vinyl cyclopropanes, we believe this Co(II)-catalyzed asymmetric radical cyclopropanation process will find useful applications in organic synthesis.

3.4. EXPERIMENTAL SECTION

3.4.1. General Considerations

All cyclopropanation reactions were performed in anhydrous solvents under N_2 atmosphere in oven-dried glassware following standard Schlenk techniques. Gas-tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. The solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin-layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR spectra were acquired using Varian INOVA 400 (400 MHz), Bruker 500 (500 MHz), or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to the residual solvent peak ($CHCl_3$ δ = 7.26 ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, br = broad, m = multiplet), and coupling constants J (Hz). ^{13}C NMR spectra were acquired using Bruker 500 (1265 MHz), or INOVA 600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ δ = 77.16 ppm or (DMSO-d_6 δ = 39.52 ppm) as the internal standard. ^{19}F NMR spectrum was acquired using Varian INOVA 600 (564 MHz) spectrometer. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, OJ-H, IA, IB, IC, ID, IE, and IF columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals, or TCI and were used without further purification.

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

3.4.2.1. Experimental Procedure for Preparation of *N*-Tosyl Hydrazone

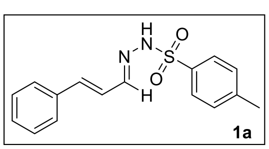
To a stirred solution of tosylhydrazide (1.0 mmol) in methanol (10.0 mL) at room temperature, aldehyde (1.0 equiv) was added dropwise (or portionwise if solid). After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified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

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

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

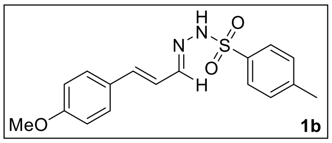
3.4.2.3. Characterization of *N*-Sulfonyl Hydrazones

(*E*)-Cinnamaldehyde 4-methylbenzenesulfonyl hydrazone (1a) Yield: 87%. R_f = 0.3



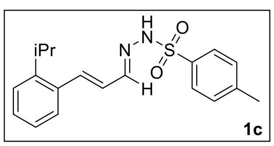
(Hexane/Ethyl Acetate: 7/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.31 (dt, J = 7.2, 4.6 Hz, 2H), 6.81 (dt, J = 25.4, 12.2 Hz, 1H), 2.41 (s, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 149.97, 144.46, 140.17, 135.69, 135.39, 129.90, 129.30, 128.96, 128.04, 127.20, 124.46, 21.76. IR (neat, cm^{-1}): 3205.94, 3059.33, 1625.80, 1596.88, 1493.62, 1450.91, 1359.92, 1335.08, 1303.25, 1163.21, 1045.27. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{17}N_2O_2S^+$: 301.10052, found 301.10097.

(*E*)-3-(4-methoxyphenyl)acrylaldehyde 4-methylbenzenesulfonyl hydrazone (**1b**)



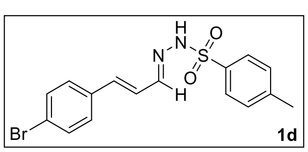
Yield: 90%. R_f = 0.3 (Hexane:Ethyl Acetate 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.33 (dd, J = 11.5, 8.5 Hz, 2H), 6.86 (dd, J = 9.0, 2.4 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 3.81 (s, 2H), 2.42 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.65, 150.65, 144.39, 140.03, 135.46, 129.87, 128.70, 128.50, 128.05, 122.24, 114.44, 55.50, 21.76. IR (neat, cm^{-1}): 3189.55,1627.72, 1603.90, 1510.42, 1441.85, 1359.80, 1329.27, 1304.21, 1255.03, 1165.36, 1091.78, 1032.48. HRMS (DART) ([M+H]$^+$) Calcd. for Calcd. for $C_{17}H_{19}N_2O_3S^+$: 331.11109, found 331.11168.

(*E*)-3-(2-isopropylphenyl)acrylaldehyde 4-methylbenzenesulfonyl hydrazone (**1c**)



Yield: 90%. R_f = 0.3 (Hexane:Ethyl Acetate 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 9.2 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.19 (d, J = 15.6 Hz, 2H), 6.74 (dd, J = 15.8, 9.2 Hz, 1H), 3.21 (hept, J = 6.9 Hz, 1H), 2.43 (s, 4H), 1.22 (dd, J = 6.8, 3.8 Hz, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.33, 146.78, 144.46, 137.83, 133.53, 129.89, 129.49, 128.08, 126.29, 126.23, 125.98, 125.45, 110.15, 29.20, 23.63, 21.77. IR (neat, cm^{-1}): 3198.77, 2963.52, 1622.16, 1597.52, 1482.11, 1447.44, 1361.46, 1325.31, 1163.97.1052.17. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{23}N_2O_2S^+$: 343.14748, found 343.14684.

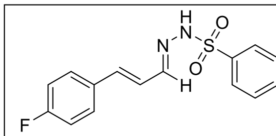
(*E*)-3-(4-bromophenyl)acrylaldehyde 4-methylbenzenesulfonyl hydrazone (**1d**) Yield:



93%. R_f = 0.3 (Hexane:Ethyl Acetate 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 9.0

Hz, 1H), 7.48 – 7.40 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 3H), 6.81 (dd, J = 16.1, 9.0 Hz, 1H), 6.70 (d, J = 16.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.32, 144.55, 138.64, 135.37, 134.63, 132.18, 129.92, 128.58, 128.06, 125.14, 123.34, 77.41, 77.16, 76.91, 21.78. IR (neat, cm^{-1}): 3188.94, 1626.20, 1596.80, 1486.36, 1443.76, 1400.51, 1358.30, 1326.58, 1304.99, 1163.12, 1070.15. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N_2O_2SBr^+$: 379.01104, found 379.01025.

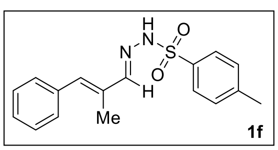
(*E*)-3-(4-Fluorophenyl)acrylaldehyde 4-methylbenzenesulfonyl hydrazone (**1e**) Yield:



1e

85%. R_f = 0.3 (Hexane/Ethyl Acetate: 8/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.58 (dd, J = 4.7, 3.8 Hz, 1H), 7.36 (ddd, J = 20.7, 12.0, 5.1 Hz, 2H), 7.03 (t, J = 8.6 Hz, 1H), 6.77–6.72 (m, 1H), 2.42 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.30 (d, J = 250.0 Hz), 149.71 (s), 144.48 (s), 138.78 (s), 135.41 (s), 131.96 (d, J = 3.4 Hz), 129.90 (s), 128.89 (d, J = 8.3 Hz), 128.04 (s), 124.26 (d, J = 2.4 Hz), 116.06 (d, J = 21.9 Hz), 21.76 (s). ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.36. IR (neat, cm^{-1}): 3189.82, 1626.04, 1600.32, 1507.56, 1442.93, 1358.69, 1327.41, 1232.63, 1158.46, 1051.14. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N_2O_2SF^+$: 319.09110, found 319.09055.

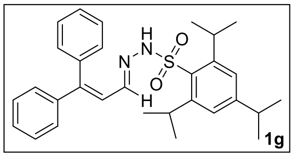
(*E*)-2-Methyl-3-phenylacrylaldehyde 4-methylbenzenesulfonyl hydrazone (**1f**) Yield:



1f

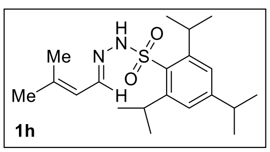
85%. R_f = 0.3 (Hexane/Ethyl Acetate: 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.87 (d, J = 8.3 Hz, 3H), 7.55 (s, 1H), 7.38 – 7.24 (m, 10H), 6.62 (s, 1H), 2.42 (s, 4H), 2.06 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.35, 144.30, 137.99, 136.35, 135.31, 134.03, 129.72, 129.45, 128.46, 128.09, 127.92, 21.73, 13.03. IR (neat, cm^{-1}): 3190.08, 1597.39, 1439.19, 1441.35, 1360.40, 1320.05, 1163.18, 1022.78. HRMS (DART) ($[M+H]^+$) Calcd. for Calcd. for $C_{17}H_{19}N_2O_2S^+$: 315.11617, found 315.11537.

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



80%. R_f = 0.3 (Hexane:Ethyl Acetate 25:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.41 – 7.38 (m, 3H), 7.35 (d, J = 9.5 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.24 (dd, J = 6.7, 3.1 Hz, 2H), 7.19 (s, 2H), 7.15 (dd, J = 6.5, 3.0 Hz, 2H), 6.72 (d, J = 9.5 Hz, 1H), 4.28 – 4.13 (m, 2H), 2.92 (dq, J = 13.8, 6.8 Hz, 1H), 1.27 (t, J = 7.2 Hz, 22H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.49, 151.43, 149.97, 147.04, 140.76, 138.32, 131.46, 130.38, 128.83, 128.54, 128.51, 128.46, 127.88, 124.00, 123.27, 34.32, 30.10, 24.98, 23.69. IR (neat, cm^{-1}): 3191.05, 2958.99, 2868.48, 1599.54, 1564.28, 1492.60, 1461.48, 1426.64, 1336.51, 1164.98, 1072.14, 1037.38 HRMS (DART) ($[M+H]^+$) Calcd. for $C_{30}H_{37}N_2O_2S^+$: 489.25703, found 489.25619.

3,3-Dimethylacrylaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1h**) Yield:



80%. R_f = 0.3 (Hexane:Ethyl Acetate 25:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 9.6 Hz, 1H), 7.42 (s, 1H), 7.26 (s, 1H), 7.17 (s, 1H), 5.92 – 5.83 (m, 1H), 4.27 – 4.15 (m, 1H), 1.81 (d, J = 11.8 Hz, 2H), 1.30 – 1.22 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.31, 151.47, 146.54, 145.15, 131.54, 123.94, 121.70, 34.29, 30.09, 26.53, 24.96, 23.67, 18.82. IR (neat, cm^{-1}): 3200.83, 2960.13, 2869.03, 2178.23, 2159.89, 1642.18, 1599.56, 1565.68, 1461.66, 1426.61, 1382.89, 1324.13, 1164.67, 1153.38, 1058.67, 1036.96. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{33}N_2O_2S^+$: 365.22573, found 365.22608.

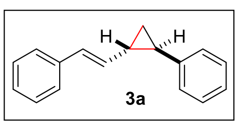
3.4.3. Synthesis and Characterization of Vinylcyclopropanes

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

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol, 1.0 equiv), [Co(Por)] (2 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, olefin (1.2 equiv) and anhydrous benzene (1.0 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 60°C for 24 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum, and purified by flash column chromatography.

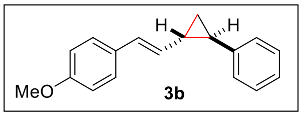
3.4.3.2. Characterization of Vinylcyclopropane Products

((*E*)-2-((1*S*,2*R*)-2-Phenylcyclopropyl)vinyl)benzene (**3a**) Yield: 95%. dr: 68:32. $R_f = 0.3$



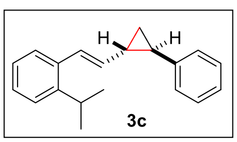
(Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 6H), 7.24 – 7.19 (m, 2H), 7.14 (dd, J = 14.3, 7.6 Hz, 2H), 6.51 (d, J = 15.5 Hz, 1H), 5.94 (dd, J = 15.8, 8.7 Hz, 1H), 2.10 – 2.05 (m, 1H), 1.90 – 1.83 (m, 1H), 1.35 (dt, J = 8.5, 5.5 Hz, 1H), 1.25 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.25, 133.92, 133.80, 128.83, 128.65, 128.64, 128.59, 128.50, 126.91, 125.83, 27.54, 25.87, 17.24. IR (neat, cm^{-1}): 3024.00, 1646,64, 1601.61, 1496.41, 1448.82, 1275.13, 1260.41, 1072.35, 1027.92. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}^+$: 221.13248, found 221.13280. HPLC analysis: IF (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 96%: t_{major} = 17.9 min, t_{minor} = 40.0 min; (minor) ee = 90%: t_{major} = 11.6 min, t_{minor} = 13.4 min.

1-Methoxy-4-((*E*)-2-((1*S*,2*R*)-2-phenylcyclopropyl)vinyl)benzene (**3b**) Yield: 95%. dr:



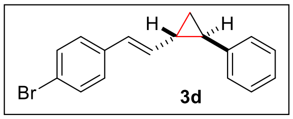
56:44. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 5H), 7.14 (d, J = 7.5 Hz, 2H), 6.88 (dd, J = 8.6, 1.7 Hz, 2H), 6.47 (d, J = 15.2 Hz, 1H), 5.83 (ddd, J = 15.7, 8.6, 1.7 Hz, 1H), 3.83 (s, 1H), 2.08 – 2.02 (m, 1H), 1.89 – 1.82 (m, 1H), 1.34 (ddd, J = 14.0, 6.8, 3.8 Hz, 1H), 1.27 – 1.21 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.76, 142.42, 130.72, 129.28, 128.47, 128.17, 127.82, 126.91, 125.79, 114.08, 55.38, 27.51, 25.75, 17.16. IR (neat, cm^{-1}): 3002.29, 2834.45, 1605,91, 1576.42, 1510.04, 1497.09, 1460.51, 1441.16, 1298.40, 1247.07, 1175.04, 1032.33. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14409. HPLC analysis: IA (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee =96%: t_{major} = 22.3 min, t_{minor} = 26.1 min. (minor) ee = 89%. t_{major} = 14.8 min, t_{minor} = 11.6 min.

1-Isopropyl-2-((*E*)-2-((1*S*,2*R*)-2-phenylcyclopropyl)vinyl)benzene (**3c**) Yield: 91%. dr:

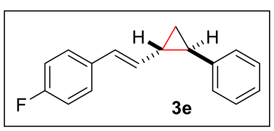


88:12. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 7.7 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 7.23 – 7.17 (m, 2H), 7.14 (ddd, J = 15.3, 6.0, 4.2 Hz, 2H), 6.83 (d, J = 15.5 Hz, 1H), 5.74 (dd, J = 15.5, 8.7 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.07 – 2.03 (m, 1H), 1.93 – 1.86 (m, 1H), 1.35 – 1.31 (m, 1H), 1.26 – 1.23 (m, 6H), 1.20 (dd, J = 11.5, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.37, 142.43, 135.83, 134.75, 128.53, 127.30, 126.44, 126.11, 126.06, 125.89, 125.82, 125.01, 77.41, 77.16, 76.91, 29.15, 27.89, 25.81, 23.52, 17.40. IR (neat, cm^{-1}): 3024.53, 2961.26, 1641.32, 1603.83, 1496.46, 1446.97, 1383.59, 1362.85, 125.38, 1260.60, 1078.00. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{23}^+$: 263.17943, found 263.17893. HPLC analysis: IA (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee =89%: t_{major} = 22.3 min, t_{minor} = 26.1 min; (minor) ee = 68%. t_{major} = 14.8 min, t_{minor} = 11.6 min.

1-Bromo-4-((*E*)-2-((1*S*,2*R*)-2-phenylcyclopropyl)vinyl)benzene (**3d**) Yield: 90%. dr: 55:45. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.46 (m, 2H), 7.40 – 7.34 (m, 4H), 7.27 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 2.16 – 2.10 (m, 1H), 1.95 – 1.86 (m, 1H), 1.44 – 1.39 (m, 1H), 1.30 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.02, 136.59, 133.91, 131.71, 128.53, 128.26, 127.34, 127.28, 125.84, 120.47, 25.93, 24.12, 17.25. IR (neat, cm^{-1}): 3022.58, 1645.47, 1602.44, 1496.49, 1486.96, 1457.80, 1404.56, 1275.39, 1260.55, 1178.54, 1071.66, 1007.23. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04392. HPLC analysis: IB (99.9% hexanes: 0.1% isopropanol, 1 mL/min): (major) ee =86%: t_{major} = 21.5 min, t_{minor} = 15.5 min; (minor) ee = 80%. t_{major} = 8.8 min, t_{minor} = 8.2 min.

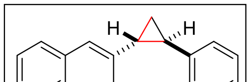


1-Fluoro-4-((*E*)-2-((1*S*,2*R*)-2-phenylcyclopropyl)vinyl)benzene (**3e**) Yield: 92%. dr: 62:38. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 6H), 7.12 – 7.05 (m, 3H), 7.01 – 6.95 (m, 2H), 6.44 (d, J = 15.8 Hz, 1H), 5.83 (dd, J = 15.7, 8.7 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.86 – 1.79 (m, 1H), 1.34 – 1.30 (m, 1H), 1.22 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.99 (d, J = 245.5 Hz), 142.19 (s), 138.80 (s), 132.73 (s), 129.31 (s), 128.53 (s), 128.25 (s), 127.24 (s), 125.84 (s), 115.52 (d, J = 21.5 Hz), 27.44 (s), 25.84 (s), 17.19 (s). ^{19}F NMR (564 MHz, $CDCl_3$): δ -115.73 (tt, J = 8.6, 5.4 Hz), -116.03 (tt, J = 8.6, 5.4 Hz). IR (neat, cm^{-1}): 3028.48, 1718.34, 1602.30, 1507.92, 1454.32, 1275.23, 1260.87, 1225.33, 1155.75, 1092.75. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}F^+$: 239.12306, found



239.12403. HPLC analysis: IB (99.9% hexanes : 0.1% isopropanol, 1 mL/min): (major) ee =91%: t_{major} = 10.0 min, t_{minor} = 8.5 min; (minor) ee = 80%. t_{major} = 5.6 min, t_{minor} = 5.4 min.

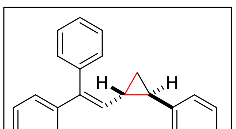
((*E*)-2-((1*R*,2*R*)-2-Phenylcyclopropyl)prop-1-en-1-yl)benzene (**3f**) Yield: 83%. dr:



3f

72:28. R_f = 0.3 (Hexanes/EtOAc = 20/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (ddd, J = 11.7, 9.4, 4.7 Hz, 5H), 7.25 (d, J = 7.5 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.16 – 7.12 (m, 4H), 6.38 (s, 1H), 2.09 (dt, J = 8.9, 5.2 Hz, 1H), 1.85 (s, 4H), 1.47 – 1.44 (m, 1H), 1.39 – 1.34 (m, 1H), 1.18 (dt, J = 8.7, 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.87, 142.50, 138.26, 138.15, 128.81, 128.70, 128.37, 128.34, 128.04, 127.93, 127.85, 127.57, 127.22, 125.89, 125.81, 125.75, 125.72, 125.58, 125.51, 124.08, 32.45, 29.51, 27.99, 23.75, 22.69, 18.74, 18.18, 15.93, 14.90, 9.97. IR (neat, cm^{-1}): 3025.18, 1731.27, 1602.89, 1496.19, 1451.31, 1275.31, 1260.66, 1182.41, 1072.99, 1029.70. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14875. HPLC analysis: IB (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 95%: t_{major} = 11.5 min, t_{minor} = 13.1 min; (minor) ee = 98%. t_{major} = 10.3 min, t_{minor} = 10.9 min.

(2-((1*S*,2*R*)-2-Phenylcyclopropyl)ethene-1,1-diyl)dibenzene ((–)-**3g**) Yield: 81%. dr:

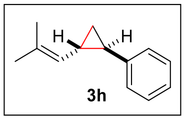


3g

55:45. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.39 (m, 1H), 7.34 – 7.30 (m, 3H), 7.23 (ddd, J = 5.4, 2.8, 1.6 Hz, 2H), 7.17 – 7.12 (m, 2H), 6.97 (dd, J = 8.0, 1.6 Hz, 1H), 5.34 (d, J = 10.1 Hz, 1H), 2.38 (dd, J = 15.2, 8.5 Hz, 1H), 1.95 (dtd, J = 10.0, 8.6, 5.6 Hz, 1H), 1.33 (dt, J = 8.3, 4.2 Hz, 1H), 1.16 (dd, J = 11.7, 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.88, 141.90, 140.62, 138.91, 132.75, 130.49, 129.33, 128.44, 128.29, 128.09, 127.43, 127.26, 126.71, 126.00, 24.85, 20.50, 13.76. IR (neat, cm^{-1}): 3005.16, 2172.18, 1992.27, 1495.52, 1275.35, 1260.63。 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{21}^+$: 297.16378, found

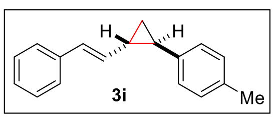
297.16397. HPLC analysis: IB (100% hexanes: 0% isopropanol, 1 mL/min): (major) ee = 64%: t_{major} = 9.6 min, t_{minor} = 8.6 min; (minor) ee = 90%: t_{major} = 7.0 min, t_{minor} = 7.3 min.

((1*R*,2*S*)-2-(2-Methylprop-1-en-1-yl)cyclopropyl)benzene (**3h**) Yield: 93%. dr: 56:44.



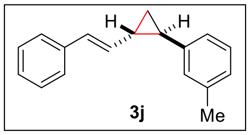
R_f = 0.3 (Hexanes/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.27 (m, 2H), 7.16 (ddd, J = 6.9, 3.5, 1.4 Hz, 1H), 7.11 – 7.08 (m, 2H), 4.78 – 4.75 (m, 1H), 1.85 (dt, J = 8.9, 3.6 Hz, 1H), 1.74 (s, 8H), 1.29 – 1.24 (m, 1H), 1.21 – 1.17 (m, 1H), 1.01 – 0.95 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.16, 129.10, 128.40, 125.78, 123.18, 77.41, 77.16, 76.91, 25.67, 25.05, 17.25, 12.52. IR (neat, cm^{-1}): 3027.70, 2969.84, 2924.23, 1717.57, 1684.44, 1603.53, 1497.25, 1449.57, 1375.49, 1275.25, 1260.95, 1139.51, 1094.93, 1069.94, 1028.31 HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{13}H_{17}^+$: 173.13248, found 173.13162.

1-Methyl-4-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3i**) Yield: 90%. dr: 58:42. R_f =

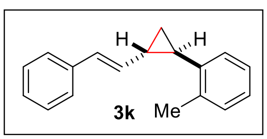


0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (dd, J = 16.3, 7.5 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.16 (d, J = 7.5 Hz, 4H), 6.52 (d, J = 15.8 Hz, 2H), 5.55 (dd, J = 15.7, 9.5 Hz, 1H), 2.42 (dd, J = 15.3, 8.5 Hz, 1H), 2.33 (s, 5H), 2.06 – 2.00 (m, 1H), 1.35 (td, J = 8.4, 5.2 Hz, 1H), 1.10 (dd, J = 11.7, 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.16, 137.93, 135.70, 133.20, 130.97, 129.17, 128.95, 128.48, 126.63, 125.79, 23.66, 22.77, 17.04, 12.77. IR (neat, cm^{-1}): 3022.51, 2920.78, 1646.63, 1598.75, 1516.00, 1495.62, 1448.26, 1275.31, 1260.57, 1072.02, 1030.47. HRMS (ESI) ([M+H]+) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14918. HPLC analysis: ODH (99.5% hexanes : 0.5% isopropanol, 0.8 mL/min): (major) ee = 95%: t_{major} = 9.9 min, t_{minor} = 13.4 min; (minor) ee = 72%. t_{major} = 6.5 min, t_{minor} = 7.2 min.

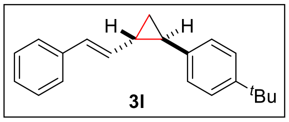
1-Methyl-3-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3j**) Yield: 89%. dr: 69:31. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, J = 7.5 Hz, 1H), 7.33 (dd, J = 15.3, 7.8 Hz, 2H), 7.18 (ddd, J = 31.5, 15.7, 7.6 Hz, 6H), 6.91 (dd, J = 14.2, 7.1 Hz, 1H), 2.42 (dd, J = 15.3, 8.4 Hz, 1H), 2.34 (s, 3H), 2.01 (ddd, J = 17.9, 8.9, 5.6 Hz, 2H), 1.38 – 1.33 (m, 1H), 1.13 (dd, J = 11.7, 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.21, 138.72, 137.93, 137.74, 130.88, 130.25, 129.55, 128.50, 128.09, 126.96, 125.79, 122.84, 25.82, 23.98, 22.87, 12.70. IR (neat, cm^{-1}): 3056.11, 3025.86, 2920.83, 2852.85, 1605.47, 1490.26, 1445.841071.73, 1029.43. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14835. HPLC analysis: IB (99.9% hexanes : 0.1% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 11.2 min, t_{minor} = 15.5 min; (minor) ee = 76%: t_{major} = 7.6 min, t_{minor} = 8.1 min.



1-Methyl-2-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3k**) Yield: 93%. dr: 76:24. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.8 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.25 – 7.13 (m, 5H), 6.55 (d, J = 15.7 Hz, 1H), 6.02 (dd, J = 15.7, 8.8 Hz, 1H), 2.42 (s, 3H), 2.11 – 2.06 (m, 1H), 1.76 – 1.69 (m, 1H), 1.41 – 1.34 (m, 1H), 1.19 (dt, J = 15.2, 5.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.92, 138.11, 137.74, 133.58, 129.81, 128.67, 128.25, 126.89, 126.16, 125.98, 125.83, 125.75, 25.43, 24.06, 20.01, 15.12. IR (neat, cm^{-1}): 3022.23, 1646.11, 1602.68, 1492.00, 1448.24, 1378.57, 1275.38, 1260.49, 1230.89, 1105.10, 1072.02. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14918. HPLC analysis: IB (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 96%: t_{major} = 15.9 min, t_{minor} = 24.4 min; (minor) ee = 91%: t_{major} = 12.0 min, t_{minor} = 13.7 min.

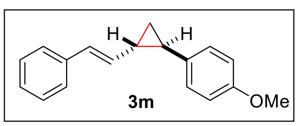


1-(tert-butyl)-4-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3l**) Yield: 95%. dr: 57:43.



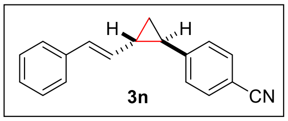
R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 7H), 7.22 – 7.14 (m, 7H), 6.52 (d, J = 15.8 Hz, 1H), 5.58 (dd, J = 15.7, 9.5 Hz, 1H), 2.41 (dd, J = 15.3, 8.4 Hz, 1H), 2.08 – 1.97 (m, 2H), 1.36 (dd, J = 8.4, 5.2 Hz, 1H), 1.32 (s, 15H), 1.11 (dd, J = 11.5, 5.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.96, 138.00, 135.76, 131.09, 128.92, 128.49, 126.63, 126.52, 125.83, 125.15, 31.54, 25.48, 23.61, 22.88, 12.90. IR (neat, cm^{-1}): 3023.51, 2960.89, 2866.17, 1646.90, 1599.70, 1515.27, 1494.44, 1448.64, 1362.42, 1267.59, 1201.97, 1071.94, 1016.69. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{25}^+$: 277.19508, found 277.19503. HPLC analysis: IB (100% hexanes: 0% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 16.4 min, t_{minor} = 17.2 min; (minor) ee = 75%: t_{major} = 9.9 min, t_{minor} = 12.5 min.

1-Methoxy-4-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3m**) Yield: 94%. dr: 66:34.

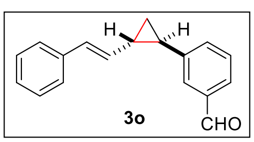


R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dt, J = 15.1, 7.7 Hz, 4H), 7.15 (d, J = 7.7 Hz, 1H), 7.05 (d, J = 8.5 Hz, 2H), 6.87 – 6.82 (m, 2H), 6.49 (d, J = 15.7 Hz, 1H), 5.92 (dd, J = 15.8, 8.7 Hz, 1H), 3.80 (s, 3H), 2.05 – 2.00 (m, 1H), 1.81 – 1.73 (m, 1H), 1.27 (dt, J = 8.5, 5.3 Hz, 1H), 1.21 – 1.15 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.97, 137.72, 133.25, 130.39, 128.65, 128.14, 127.00, 126.86, 125.79, 114.02, 55.48, 25.18, 23.19, 16.78. IR (neat, cm^{-1}): 3001.25, 2954.18, 1834.07, 1646.25, 1611.17, 1513.65, 1449.41, 1275.27, 1247.28, 1178.59, 1112.68, 1034.65 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14301. HPLC analysis: IB (100% hexanes: 0% isopropanol, 1 mL/min): (major) ee = 91%. t_{major} = 7.1 min, t_{minor} = 9.1 min. (minor) ee = 70%. t_{major} = 5.5 min, t_{minor} = 5.9 min.

4-((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)benzonitrile (**3n**) Yield: 83%. dr: 55:45. $R_f = 0.3$ (Hexanes/EtOAc = 20/1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 4H), 7.37 – 7.29 (m, 6H), 7.22 (t, J = 7.5 Hz, 3H), 7.18 – 7.06 (m, 6H), 6.51 (dd, J = 15.7, 7.7 Hz, 2H), 5.89 (dd, J = 15.8, 8.6 Hz, 1H), 5.45 (dd, J = 15.7, 9.1 Hz, 1H), 2.46 (dd, J = 15.3, 8.5 Hz, 1H), 2.13 (tt, J = 8.9, 4.4 Hz, 1H), 2.09 – 2.04 (m, 1H), 1.92 – 1.86 (m, 1H), 1.46 (td, J = 8.3, 5.5 Hz, 1H), 1.37 (ddt, J = 14.5, 8.7, 5.5 Hz, 2H), 1.20 (dd, J = 12.0, 5.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.18, 144.82, 137.20, 137.10, 132.18, 131.87, 131.47, 131.01, 129.69, 129.28, 128.60, 128.58, 128.48, 127.11, 127.01, 126.21, 125.76, 125.67, 119.06, 110.00, 109.76, 109.22, 28.64, 25.92, 24.01, 23.51, 17.98, 12.90. IR (neat, cm^{-1}): 3005.31, 2358.17, 2225.95, 1699.45, 1607.64, 1506.49, 1454.72, 1275.30, 1260.64. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{16}N^+$: 246.12773, found 246.12791. HPLC analysis: IE (98% hexanes : 2% isopropanol, 0.8 mL/min): (major) *ee* = 49%. t_{major} = 16.7 min, t_{minor} = 16.2 min. (minor) *ee* = 53%. t_{major} = 31.0 min, t_{minor} = 26.5 min.

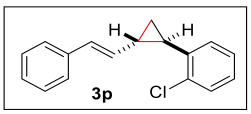


3-((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)benzaldehyde (**3o**) Yield: 93%. dr: 76:24. $R_f = 0.3$ (Hexanes/EtOAc = 20/1). ^1H NMR (600 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.78 (s, 1H), 7.69 (ddd, J = 8.8, 7.5, 4.5 Hz, 1H), 7.60 (t, J = 1.6 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.45 (dd, J = 7.5, 6.3 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.36 – 7.28 (m, 2H), 7.23 – 7.16 (m, 1H), 7.15 – 7.09 (m, 1H), 6.53 (d, J = 4.6 Hz, 1H), 6.50 (d, J = 4.6 Hz, 1H), 5.92 (dd, J = 15.8, 8.6 Hz, 1H), 5.46 (dd, J = 15.7, 9.3 Hz, 1H), 2.50 (dd, J = 15.2, 8.6 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.94 – 1.86 (m, 1H), 1.44 (td, J = 8.4, 5.4 Hz, 1H), 1.39 (dt, J = 8.5, 5.5 Hz, 1H), 1.30 (dt, J = 8.8, 5.5 Hz, 1H), 1.25 – 1.20 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 192.63, 192.55, 143.63, 140.24, 137.56, 137.45,



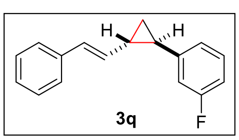
136.73, 135.56, 132.32, 132.25, 130.57, 130.17, 129.55, 129.15, 129.00, 128.92, 128.70, 128.56, 127.96, 127.75, 127.11, 126.94, 126.35, 125.88, 125.80, 77.41, 77.16, 76.91, 27.81, 25.51, 23.67, 22.99, 17.45, 12.71. IR (neat, cm^{-1}): 3025.80, 1695.54, 1603.03, 1584.53, 1491.03, 1449.99, 1391.12, 1292.36, 1244.38, 1192.29, 1074.10 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O^+$: 249.12739, found 249.12747. HPLC analysis: IB (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 72%: t_{major} = 8.5 min, t_{minor} = 9.9 min; (minor) ee = 69%: t_{major} = 17.4 min, t_{minor} = 15.2 min.

1-Chloro-2-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3p**) Yield: 91%. dr: 61:39. R_f = 0.3 (Hexanes/EtOAc = 20/1).



^1H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 5H), 7.25 – 7.18 (m, 4H), 7.12 (dd, J = 9.8, 1.5 Hz, 2H), 6.61 (d, J = 15.5 Hz, 1H), 5.40 (dd, J = 15.7, 9.2 Hz, 1H), 2.50 (dd, J = 15.4, 8.5 Hz, 1H), 2.17 (qd, J = 8.8, 5.6 Hz, 1H), 1.42 (td, J = 8.3, 5.4 Hz, 1H), 1.18 (dd, J = 12.1, 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.52, 133.72, 132.82, 130.07, 129.27, 128.79, 128.48, 127.68, 126.98, 126.72, 126.52, 125.81, 23.53, 23.00, 15.92. IR (neat, cm^{-1}): 3058.22, 3023.25, 2358.60, 1651.26, 1593.66, 1479.62, 1445.32, 1275.33, 1260.60, 1127.12, 1071.20, 1049.46, 1033.50. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Cl^+$: 255.09350, found 255.09248. HPLC analysis: IA (99.9% hexanes: 0.1% isopropanol, 1 mL/min): (major) ee = 94%: t_{major} = 6.8 min, t_{minor} = 7.4 min; (minor) ee = 92%: t_{major} = 5.4 min, t_{minor} = 5.2 min.

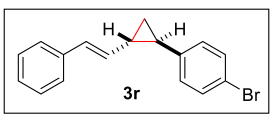
1-Fluoro-3-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3q**) Yield: 93%. dr: 71:29. R_f = 0.3 (Hexanes/EtOAc = 20/1).



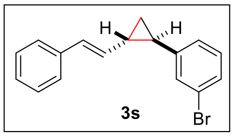
^1H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 3H), 7.16 – 7.13 (m, 1H), 6.90 (s, 1H), 6.89 – 6.83 (m, 1H), 6.80 – 6.75 (m, 1H), 6.50 (d, J = 15.8 Hz, 1H), 5.90 (dd, J = 15.8, 8.6 Hz, 1H), 2.07 – 2.02

(m, 1H), 1.89 – 1.81 (m, 1H), 1.34 – 1.30 (m, 1H), 1.26 (dt, J = 8.8, 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.12 (d, J = 7.5 Hz), 137.59 (d, J = 28.0 Hz), 132.42 (s), 130.07 (d, J = 43.1 Hz), 128.81 (s), 128.62 (d, J = 21.3 Hz), 126.96 (d, J = 29.8 Hz), 125.84 (d, J = 6.5 Hz), 121.67 (d, J = 2.7 Hz), 113.12 (d, J = 21.0 Hz), 112.67 (d, J = 15.8 Hz), 112.53 (d, J = 16.3 Hz), 27.78 (s), 23.06 (s), 17.45 (s). ^{19}F NMR (564 MHz, $CDCl_3$): δ -116.89. IR (neat, cm^{-1}): 3059.69, 3024.35, 1646.23, 1614.78, 1586.37, 1489.95, 1449.28, 1275.76, 1248.63, 1192.25, 1138.74, 1072.49, 1038.68. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{17}H_{16}F^+$: 239.12306, found 239.12383. HPLC analysis: IB (100% hexanes: 0% isopropanol, 1 mL/min): (major) ee = 91%: t_{major} = 21.0 min, t_{minor} = 40.3 min; (minor) ee = 88%: t_{major} = 13.6 min, t_{minor} = 15.5 min.

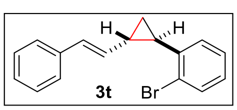
1-Bromo-4-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3r**) Yield: 90%. dr: 57:43. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 3H), 7.43 – 7.30 (m, 1H), 7.29 – 7.23 (m, 2H), 7.21 – 7.12 (m, 2H), 7.05 (d, J = 8.5 Hz, 1H), 6.49 (d, J = 15.7 Hz, 1H), 5.97 (dd, J = 15.7, 8.8 Hz, 1H), 2.17 – 2.11 (m, 1H), 1.95 – 1.87 (m, 1H), 1.48 – 1.38 (m, 1H), 1.30 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.02, 136.59, 131.71, 131.54, 128.53, 128.26, 127.34, 127.28, 125.84, 120.47, 25.93, 24.12, 17.25. IR (neat, cm^{-1}): 3057.74, 3012.34, 2924.90, 1690.77, 1593.40, 1492.00, 1474.26, 1446.25, 1264.44, 1178.89, 1022.83, 1000.62 HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04218. HPLC analysis: IB (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 16.1 min, t_{minor} = 12.7 min; (minor) ee = 62%: t_{major} = 6.2 min, t_{minor} = 6.6 min.



1-Bromo-3-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)benzene (**3s**) Yield: 83%. dr: 59:41. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 3H), 7.36 – 7.29 (m, 8H), 7.24 – 7.18 (m, 4H), 7.17 – 7.10 (m, 6H), 6.56 – 6.46 (m, 3H), 5.89 (dd, J = 15.8, 8.6 Hz, 1H), 5.49 (dd, J = 15.7, 9.4 Hz, 1H), 2.41 (dd, J = 15.3, 8.4 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.87 – 1.81 (m, 1H), 1.38 (td, J = 8.4, 5.4 Hz, 1H), 1.31 (dt, J = 8.6, 5.5 Hz, 1H), 1.28 – 1.22 (m, 2H), 1.12 (dd, J = 11.8, 5.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.79, 141.41, 137.66, 133.72, 132.82, 132.39, 132.35, 130.32, 130.00, 129.84, 129.73, 129.35, 129.27, 128.79, 128.69, 128.56, 127.93, 127.68, 127.07, 126.89, 126.52, 125.87, 125.84, 124.66, 27.71, 25.47, 23.66, 23.00, 17.32, 12.73. IR (neat, cm^{-1}): 3022.76, 2922.91, 2358.58, 1651.07, 1595.85, 1563.80, 1478.00, 1448.39, 1423.46, 1275.29, 1260.65, 1072.18. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04359. HPLC analysis: IF (99.9% hexanes : 0.1% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 10.6 min, t_{minor} = 11.6 min; (minor) ee = 83%: t_{major} = 6.7 min, t_{minor} = 6.2 min.

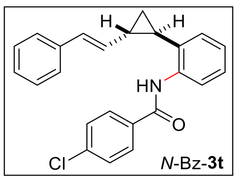


1-(((1*R*,2*R*)-2-(3-Bomophenyl)cyclopropyl)ethynyl)-2-methoxybenzene (**3t**) Yield: 90%. dr: 62:38. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (ddd, J = 15.6, 7.9, 1.0 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.25 – 7.17 (m, 3H), 7.14 – 7.00 (m, 3H), 6.64 – 6.48 (m, 1H), 6.02 (dd, J = 15.7, 8.5 Hz, 1H), 5.39 (dd, J = 15.7, 9.2 Hz, 1H), 2.48 (dd, J = 15.4, 8.4 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.18 (qd, J = 8.7, 5.6 Hz, 1H), 1.78 (ddd, J = 13.4, 8.6, 5.0 Hz, 1H), 1.43 (td, J = 8.3, 5.4 Hz, 1H), 1.35 – 1.30 (m, 1H), 1.25 (dt, J = 8.7, 5.3 Hz, 1H), 1.18 (q, J = 5.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.97, 138.31, 137.70, 137.49, 133.56, 132.55, 132.49, 130.01, 129.85, 129.51, 128.69, 128.63, 128.51, 128.32, 127.75, 127.35, 127.32, 127.18,

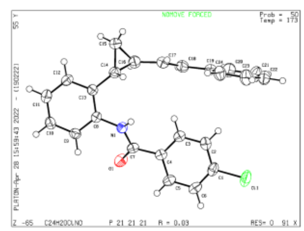


126.87, 126.82, 126.56, 126.35, 125.76, 125.66, 77.21, 77.00, 76.79, 26.19, 26.10, 25.40, 22.75, 15.86, 12.73. IR (neat, cm^{-1}): 3022.01, 1651.66, 1591.13, 1473.60, 1436.34, 1275.27, 1260.51, 1022.13. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04314. HPLC analysis: IA (99.9% hexanes: 0.1% isopropanol, 1 mL/min): (major) ee = 93%: t_{major} = 6.9 min, t_{minor} = 7.7 min; (minor) ee = 90%: t_{major} = 5.6 min, t_{minor} = 5.4 min.

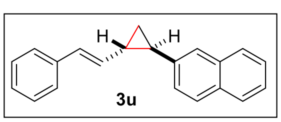
4-Chloro-*N*-(2-((1*R*,2*S*)-2-((*E*)-styryl)cyclopropyl)phenyl)benzamide (*N*-Bz-**3t**) Yield:



50%. dr: 99:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.2 Hz, 1H), 8.32 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 9.4 Hz, 1H), 2.00 (dd, *J* = 13.7, 5.5 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.57 (dd, *J* = 14.0, 5.4 Hz, 2H), 1.34 – 1.28 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.30, 138.03, 138.00, 136.66, 132.97, 131.91, 130.27, 129.75, 129.06, 128.92, 128.55, 128.36, 127.91, 127.73, 125.94, 124.43, 120.77, 24.82, 22.10, 14.28.

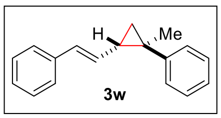


Ethyl-(1*R*,2*R*)-2-((2-methoxyphenyl)ethynyl)cyclopropane-1-carboxylate (3u) Yield:



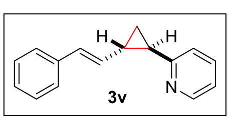
87%. dr: 68:32. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.25 (dd, *J* = 12.5, 5.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 4.16 (ddd, *J* = 14.3, 7.2, 3.0 Hz, 2H), 3.87 (s, 3H), 2.13 (ddd, *J* = 9.1, 6.2, 4.1 Hz, 1H), 2.08 – 2.03 (m, 1H), 1.47 (ddd, *J* = 9.4, 5.5, 4.2 Hz, 1H), 1.34 – 1.31 (m, 1H), 1.30 – 1.23 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.51, 160.26, 133.90, 129.54, 120.54, 112.32, 110.67, 93.74, 73.97, 61.05, 55.90, 23.46, 17.44, 14.39, 11.53. IR (neat, cm^{-1}): 2979.80, 1723.87, 1596.21, 1575.23, 1494.51, 1464.14, 1405.49, 1324.14, 1261.27, 1179.78, 1025.69. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{17}O_3^+$: 245.11722, found: 245.11754. HPLC analysis: IB (99% hexanes: 1% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 8.7 min, t_{minor} = 11.6 min; (minor) ee = 80%. t_{major} = 5.6 min, t_{minor} = 7.2 min.

2-((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)pyridine (**3v**) Yield: 91%. dr: 66:34. R_f = 0.3



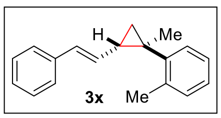
(Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 4.8 Hz, 1H), 7.55 (ddd, J = 15.3, 7.4, 1.8 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.17 (ddd, J = 13.1, 9.7, 6.0 Hz, 3H), 6.51 (d, J = 15.8 Hz, 1H), 5.92 (dd, J = 15.8, 8.6 Hz, 1H), 2.18 – 2.12 (m, 2H), 1.64 (ddd, J = 8.5, 5.5, 4.5 Hz, 1H), 1.25 (ddd, J = 8.5, 5.9, 4.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.02, 149.23, 137.60, 132.46, 128.99, 128.65, 128.50, 126.98, 125.86, 122.04, 120.77, 27.84, 27.23, 17.88. IR (neat, cm^{-1}): 3023.47, 1643.47, 1591.15, 1566.83, 1474.34, 1445.64, 1209.64, 1178.63, 1148.94, 1107.44, 1072.46, 1047.71 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N^+$: 222.12773, found 222.12785. HPLC analysis: OJH (99% hexanes: 1% isopropanol, 1 mL/min): (major) ee = 92%: t_{major} = 36.9 min, t_{minor} = 30.8 min; (minor) ee = 90%: t_{major} = 33.8 min, t_{minor} = 1.7 min.

((1*R*,2*S*)-1-Methyl-2-((*E*)-styryl)cyclopropyl)benzene (**3w**) Yield: 96%. dr: 71:29. R_f =

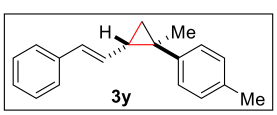


0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 7H), 7.22 (qd, J = 7.6, 4.1 Hz, 3H), 7.13 (d, J = 8.2 Hz, 1H), 6.58 (d, J = 15.7 Hz, 1H), 6.18 (dd, J = 15.7, 8.6 Hz, 1H), 1.93 (td, J = 8.7, 6.1 Hz, 1H), 1.53 – 1.48 (m, 4H), 0.98 (t, J = 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.59, 137.85, 130.76, 130.25, 129.72, 128.68, 128.46, 126.85, 125.89, 125.73, 30.50, 28.88, 22.39, 21.35. IR (neat, cm^{-1}): 3058.41, 3023.48, 2996.37, 2954.49, 1643.73, 1601.04, 1495.23, 1445.37, 1114.43, 1071.48, 1028.27. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14835. HPLC analysis: IB (100% hexanes: 0% isopropanol, 1.0 mL/min): (major) ee = 97%: t_{major} = 9.7 min, t_{minor} = 13.9 min; (minor) ee = 89%: t_{major} = 8.8 min, t_{minor} = 11.1 min.

1-Methyl-2-((1*R*,2*S*)-1-methyl-2-((*E*)-styryl)cyclopropyl)benzene (**3x**) Yield: 94%. dr: 57:43. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, J = 16.9, 7.4 Hz, 4H), 7.36 – 7.29 (m, 5H), 7.25 – 7.19 (m, 3H), 7.18 – 7.11 (m, 7H), 6.63 (d, J = 8.5 Hz, 2H), 6.20 (dd, J = 15.7, 9.0 Hz, 1H), 2.44 (s, 3H), 1.87 (td, J = 8.8, 5.7 Hz, 2H), 1.39 (s, 3H), 1.37 (dd, J = 8.8, 4.7 Hz, 1H), 0.95 (t, J = 5.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.76, 137.66, 133.72, 132.82, 130.64, 130.59, 128.79, 128.69, 128.51, 126.51, 125.89, 125.75, 28.65, 28.31, 22.11, 21.17, 19.54. IR (neat, cm^{-1}): 3059.57, 3023.82, 2962.23, 1597.65, 1492.20, 1461.18, 1449.89, 1381.29, 1259.46, 1084.65, 1017.21 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{21}^+$: 249.16378, found 249.16441. HPLC analysis: ID (100% hexanes: 0% isopropanol, 0.5 mL/min): (major) ee = 93%: t_{major} = 5.5 min, t_{minor} = 5.2 min; (minor) ee = 73%. t_{major} = 7.1 min, t_{minor} = 8.0 min.

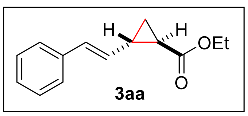


1-Methyl-4-((1*R*,2*S*)-1-methyl-2-((*E*)-styryl)cyclopropyl)benzene (**3y**) Yield: 94%. dr: 54:46. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dt, J = 15.4, 4.6 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.15 (dd, J = 10.8, 5.7 Hz, 3H), 6.49 (d, J = 15.8 Hz, 1H), 5.36 (dd, J = 15.7, 9.8 Hz, 1H), 2.36 (s, 2H), 1.82 (ddd, J = 9.7, 8.1, 5.4 Hz, 1H), 1.49 – 1.46 (m, 1H), 1.45 (s, 1H), 1.18 – 1.13 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.68, 138.07, 135.42, 132.97, 129.55, 129.11, 128.48, 126.80, 126.50, 125.76, 29.83, 29.02, 22.30, 21.49, 21.26. IR (neat, cm^{-1}): 3023.93,

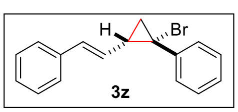


2996.94, 2922.96, 2860.55, 1597.70, 1515.23, 1492.55, 1450.42, 1378.49, 1244.38, 1110.96, 1019.84. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{19}H_{21}^+$: 249.16378, found 249.16388. HPLC analysis: IB (100% hexanes: 0% isopropanol, 0.8 mL/min): (major) ee = 72%. t_{major} = 10.8 min, t_{minor} = 15.5 min; (minor) ee = 62%. t_{major} = 10.1 min, t_{minor} = 12.2 min.

((1*S*,2*S*)-1-Bromo-2-((*E*)-styryl)cyclopropyl)benzene (**3z**) Yield: 93%. dr: 71:29. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.48 (m, 3H), 7.44 (d, J = 7.4 Hz, 2H), 7.35 (q, J = 7.3 Hz, 5H), 6.68 (d, J = 15.8 Hz, 1H), 6.28 (dd, J = 15.8, 8.5 Hz, 1H), 2.04 – 1.99 (m, 1H), 1.86 (dd, J = 9.7, 6.4 Hz, 1H), 1.56 (t, J = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.90, 137.17, 131.90, 130.03, 128.60, 128.58, 128.45, 128.06, 127.27, 126.06, 41.29, 29.19, 24.14. IR (neat, cm-^{1}): 3058.76, 3026.77, 1687.03, 1597.18, 1542.18, 1493.46, 1447.30, 1261.45, 1177.54, 1073.35, 1027.16 HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04144. HPLC analysis: IF (100% hexanes : 0% isopropanol, 1 mL/min): (major) ee = 90%: t_{major} = 12.7 min, t_{minor} = 14.4 min; (minor) ee = 87%. t_{major} = 8.1 min, t_{minor} = 8.7 min.

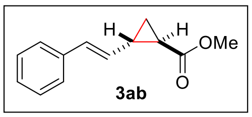


Ethyl (1*R*,2*S*)-2-((*E*)-styryl)cyclopropane-1-carboxylate ((–)-**3aa**) Yield: 96%. dr: 67:33. R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 6.54 (d, J = 15.8 Hz, 1H), 5.76 (dd, J = 15.8, 8.7 Hz, 1H), 4.16 (q, J = 7.1 Hz, 1H), 2.22 – 2.14 (m, 1H), 1.75 (ddd, J = 8.9, 5.2, 4.0 Hz, 1H), 1.51 – 1.45 (m, 1H), 1.28 (t, J = 7.1 Hz, 1H), 1.09 (ddd, J = 8.4, 6.2, 4.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.46, 137.13, 130.42, 128.69, 128.61, 127.34, 125.97, 60.81, 25.64, 22.44, 16.09, 14.41. IR (neat, cm^{-1}): 2981.40,



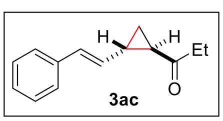
2160.07, 1722.19, 1601.66, 1492.31, 1450.45, 1406.63, 1341.80, 1262.85, 1179.06, 1092.84, 1037.13. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{17}O_2^+$: 217.12331, found 217.12228. HPLC analysis: ID (99% hexanes : 1% isopropanol, 1 mL/min): (major) ee = 91%: t_{major} = 8.7 min, t_{minor} = 8.1 min; (minor) ee = 82%: t_{major} = 6.2 min, t_{minor} = 5.9 min.

Methyl (1*R*,2*S*)-2-((*E*)-styryl)cyclopropane-1-carboxylate (3ab) Yield: 94%. dr: 65:35.



R_f = 0.3 (Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 7.5 Hz, 1H), 7.31 – 7.27 (m, 4H), 7.20 (ddd, J = 8.7, 6.6, 2.3 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 5.75 (dd, J = 15.8, 8.7 Hz, 1H), 3.71 (s, 2H), 2.23 – 2.15 (m, 1H), 1.76 (ddd, J = 9.0, 5.1, 4.0 Hz, 1H), 1.49 (dt, J = 9.6, 4.9 Hz, 1H), 1.10 (ddd, J = 8.4, 6.2, 4.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.92, 137.11, 130.56, 128.71, 128.63, 127.38, 126.00, 52.02, 25.74, 22.24, 16.14. IR (neat, cm^{-1}): 2952.49, 2159.32, 1958.62, 1725.87, 1492.30, 1439.99, 1383.44, 1347.03, 1200.17, 1172.84, 1091.41. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{15}O_2^+$: 203.10666, found 203.10645. HPLC analysis: IF (99% hexanes: 1% isopropanol, 1 mL/min): (major) ee = 65%: t_{major} = 14. min, t_{minor} = 11.0 min; (minor) ee = 55%: t_{major} = 6.4 min, t_{minor} = 5.9 min.

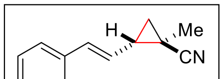
((1*R*,2*S*)-2-((*E*)-Styryl)cyclopropyl)propan-1-one (3ac) Yield: 96%. dr: 57:43. R_f = 0.3



(Hexanes/EtOAc = 7/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 1H), 7.17 – 7.13 (m, 1H), 6.48 (d, J = 15.8 Hz, 1H), 5.73 (dd, J = 15.8, 8.8 Hz, 1H), 2.57 (q, J = 7.2 Hz, 1H), 2.12 (ddd, J = 11.3, 7.6, 3.8 Hz, 1H), 2.03 (ddd, J = 8.6, 5.1, 3.9 Hz, 1H), 1.53 – 1.49 (m, 1H), 1.23 (td, J = 8.0, 4.6 Hz, 1H), 1.06 (t, J = 7.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 209.32, 208.42, 137.26, 136.93, 130.94, 130.43, 130.06, 128.53, 128.41, 127.31, 127.30, 127.16, 126.95, 125.90, 125.76, 77.21, 77.00, 76.79, 37.78, 37.01, 29.62, 28.33, 28.21, 27.28, 17.87, 15.36, 7.90, 7.83. IR (neat, cm-1):

2976.87, 2937.70, 1696.97, 1491.96, 1450.65, 1392.19, 1119.30, 1030.63. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{17}O^+$: 201.12739, found 201.12738. HPLC analysis: IE (99% hexanes : 1% isopropanol, 1 mL/min): (major) ee = 71%. t_{major} = 17.4 min, t_{minor} = 12.9 min; (minor) ee = 84%: t_{major} = 10.8 min, t_{minor} = 9.9 min.

((*E*)-2-((1*S*,2*R*)-2-Phenylcyclopropyl)vinyl)benzene (**3ad**) Yield: 95%. dr: 58:42. R_f =


3ad

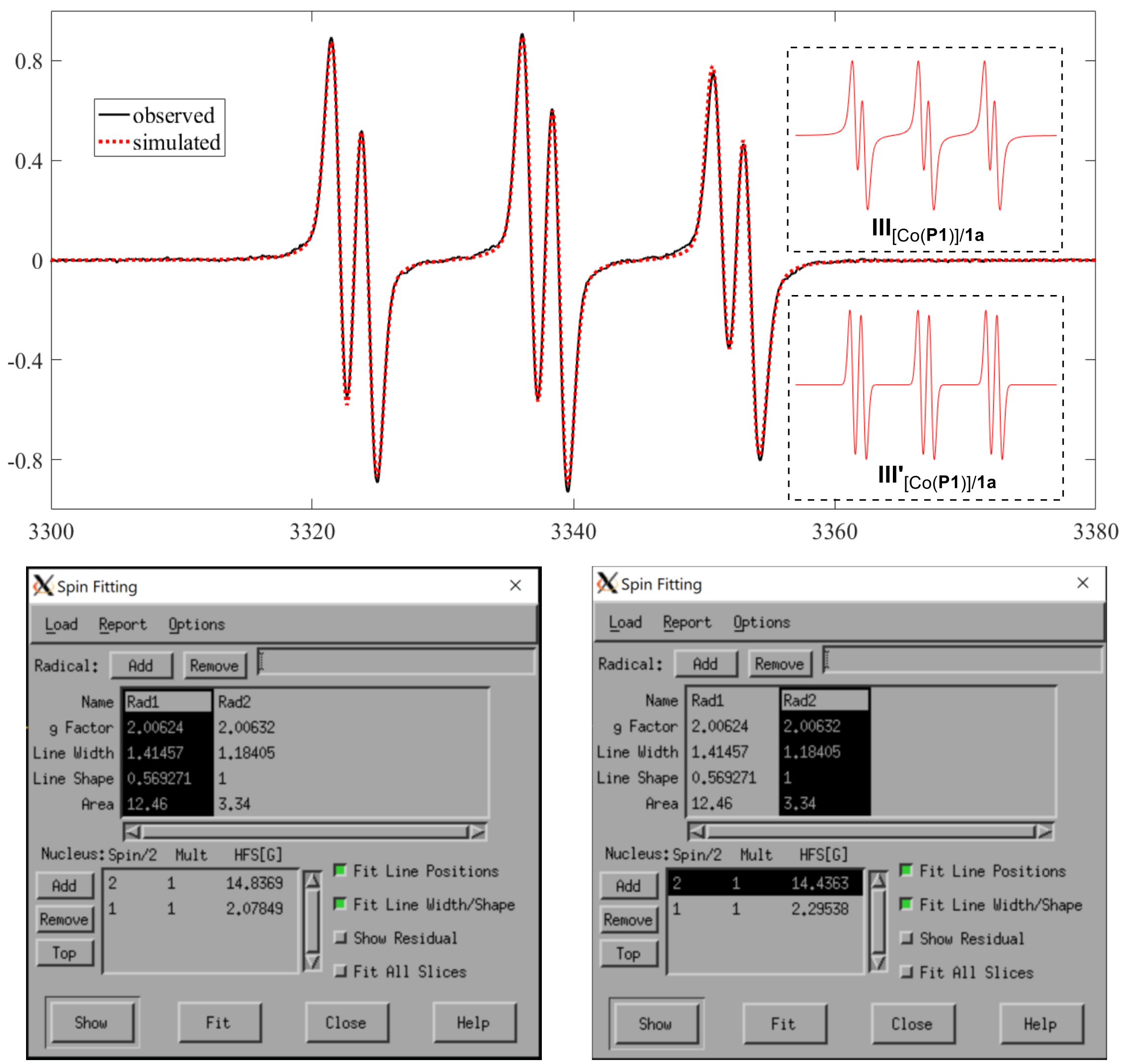
0.3 (Hexanes/EtOAc = 7/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, J = 9.3, 4.6 Hz, 1H), 7.31 (d, J = 7.7 Hz, 2H), 7.26 – 7.19 (m, 2H), 6.61 (d, J = 15.7 Hz, 1H), 5.87 (dd, J = 15.8, 7.7 Hz, 1H), 2.31 (dd, J = 16.4, 7.4 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.39 (s, 2H), 0.97 (dd, J = 6.7, 5.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.59, 134.76, 128.81, 128.72, 127.97, 126.24, 124.08, 28.28, 20.96, 16.28, 10.71. IR (neat, cm^{-1}): 3026.77, 2935.04, 2232.12, 1677.76, 1598.52, 1493.44, 1449.79, 1383.94, 1074.27, 1027.95. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{14}N^+$: 184.11208, found 184.11137. HPLC analysis: ID (99% hexanes: 1% isopropanol, 1 mL/min): (major) ee = 91%: t_{major} = 11.9 min, t_{minor} = 11.3 min; (minor) ee = 80%: t_{major} = 13.4 min, t_{minor} = 13.0 min.

3.4.4. Mechanistic Studies of Proposed Stepwise Radical Mechanism

3.4.4.1. Radical Trapping by EPR (Electron Paramagnetic Resonance Spectroscopy)

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone **1a** (0.10 mmol, 1.0 equiv), [Co(TPP)] (2 mol %) and PBN (0.12 mmol, 1.2 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, Et_3N (0.2 mmol, 2.0 equiv) and anhydrous benzene (1.0 mL) were added via a syringe. The reaction mixture was stirred at 60 °C for 10 min. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for the EPR experiment at room temperature.

Figure S1. EPR Spectrum and Simulation of α-Co(III)-Allylic Radicals III$_{[Co(TPP)]/1a}$ and III'$_{[Co(TPP)]/1a}$ with PBN in Benzene at RT



The resulting notable EPR signal (in black) has been simulated (in red) for:

III$_{[Co(P1)]/1a}$ with g = 2.00624, $A_{(N)}$ = 41.6 MHz, $A_{(H)}$ = 5.9 MHz;

III'$_{[Co(P1)]/1a}$ with g = 2.00632, $A_{(N)}$ = 40.4 MHz, $A_{(H)}$ = 6.5 MHz.

[The simulation of the EPR spectrum was performed by iteration of the isotopic g-values and line widths using the EPR simulation program SpinFit Xenon]

EPR Simulation Details:

For **III**$_{\mathbf{[Co(P1)]/1a}}$:

g = 2.00624

$A_{(N)}$ = 14.8 x 2.00624 x 1.399611451 = 41.6 MHz

$A_{(H)}$ = 2.1 x 2.00624 x 1.399611451 = 5.9 MHz

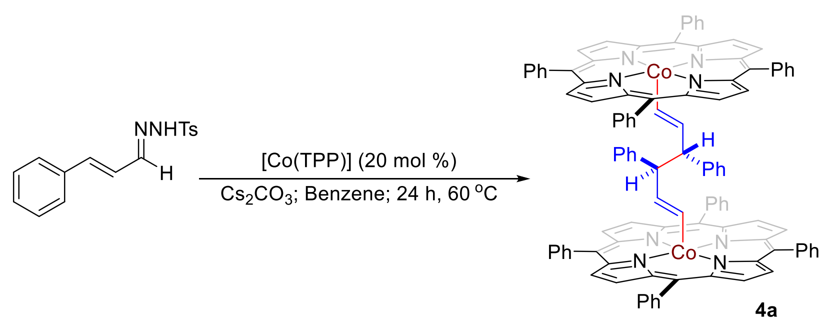
For **III'**$_{\mathbf{[Co(TPP)]/1a}}$:

g = 2.00632

$A_{(N)}$ = 14.4 x 2.00632 x 1.399611451 = 40.4 MHz

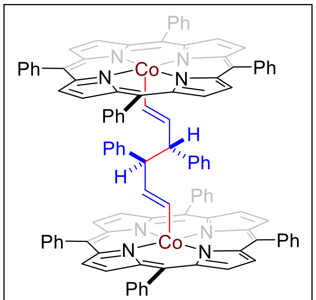
$A_{(H)}$ = 2.3 x 2.00632 x 1.399611451 = 6.5 MHz

3.4.4.2. General Procedure and Characterization for Homodimerization of Allylic Radical from [Co(TPP)] and In Situ-Generated Vinyldiazomethane



An oven-dried Schlenk tube was charged with sulfonyl hydrazone **1** (0.10 mmol, 1.0 equiv), [Co(**P1**)] (0.03 mmol, 30 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, anhydrous benzene (1.0 mL) was added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 60 °C for 24 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum, and purified by flash column chromatography.

(**4a**) Yield: 87%. $R_f = 0.3$ (Hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.55 (dd, J = 18.7, 4.8 Hz, 8H), 7.94 (s, 3H), 7.64 (t, J = 7.7 Hz, 6H), 7.52 (s, 8H), 6.74 (t, J = 7.4 Hz, 1H), 6.37 (t, J = 7.5 Hz, 2H), 3.57 (d, J = 7.2 Hz, 2H), -0.72 (d, J = 9.6 Hz, 1H), -1.73 (d, J = 10.6 Hz, 1H), -2.10 (t, J = 10.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.61, 144.48, 141.26, 138.22, 133.34, 132.47, 132.18, 127.39, 127.32, 126.51, 126.08, 124.14, 120.87, 77.21, 77.00, 76.79, 50.03. IR (neat, cm^{-1}): 3055.09, 3023.92, 2923.32, 2361.20, 1599.05, 1491.77, 1440.83, 1351.58, 1308.15, 1178.07, 1072.96, 1003.59. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{106}H_{72}Co_2N_8$: 1574.45439, found 1574.451416.



4a

3.4.5. X-Ray Crystallography

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2*[232] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[24] Absorption correction was performed by the multi-scan method implemented in SADABS.[25] 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 v1.70.01[26] program.

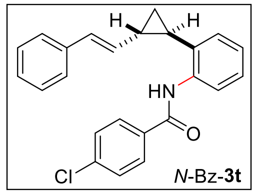
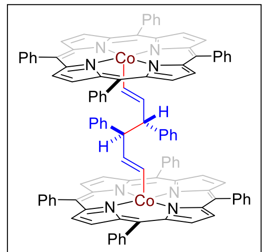


Table S1. Crystal data and structure refinement for *N*-Bz-3t

Identification code	C24H20ClNO	
Empirical formula	C24 H20 Cl N O	
Formula weight	373.86	
Temperature	173(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.0594(3) Å	α= 90°.
	b = 15.4472(8) Å	β= 90°.
	c = 24.4200(11) Å	γ = 90°.
Volume	1908.51(17) $Å^3$	
Z	4	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	1.863 mm^{-1}	
F(000)	784	
Crystal size	0.440 x 0.040 x 0.040 mm^3	
Theta range for data collection	3.385 to 66.472°.	
Index ranges	-5<=h<=6, -18<=k<=17, -28<=l<=28	
Reflections collected	33766	
Independent reflections	3310 [R(int) = 0.0548]	
Completeness to theta = 66.472°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6537	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3310 / 0 / 248	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0741	
R indices (all data)	R1 = 0.0381, wR2 = 0.0770	
Absolute structure parameter	0.009(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.205 and -0.144 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for 4a



4a

Identification code	C106H72Co2N8	
Empirical formula	C106 H72 Co2 N8	
Formula weight	1575.57	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.1605(5) Å	α= 80.846(2)°.
	b = 14.1985(6) Å	β= 75.808(2)°.
	c = 25.0354(9) Å	γ = 74.738(2)°.
Volume	4353.0(3) $Å^3$	
Z	2	
Density (calculated)	1.202 Mg/m^3	
Absorption coefficient	3.389 mm^{-1}	
F(000)	1636	
Crystal size	0.220 x 0.060 x 0.040 mm^3	
Theta range for data collection	1.829 to 66.660°.	
Index ranges	-15<=h<=15, -16<=k<=16, -29<=l<=29	
Reflections collected	73942	
Independent reflections	15060 [R(int) = 0.1780]	
Completeness to theta = 66.660°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5194	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15060 / 1551 / 1156	
Goodness-of-fit on F^2	0.928	
Final R indices [I>2sigma(I)]	R1 = 0.0764, wR2 = 0.1813	
R indices (all data)	R1 = 0.1771, wR2 = 0.2357	
Extinction coefficient	0.00030(8)	
Largest diff. peak and hole	0.297 and -0.345 e.$Å^{-3}$	

3.4.6. DFT Calculations

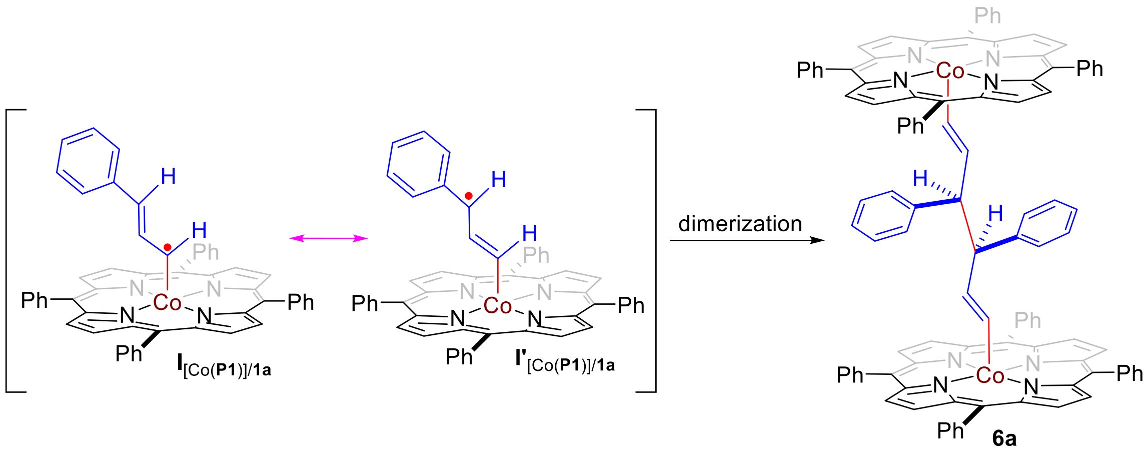
Considering the cost of time and computing resources for the large system with [Co(**P6**)], the geometry optimizations were performed with the Gaussian 16[27] at the BP86[28]/lanl2dz[29] level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

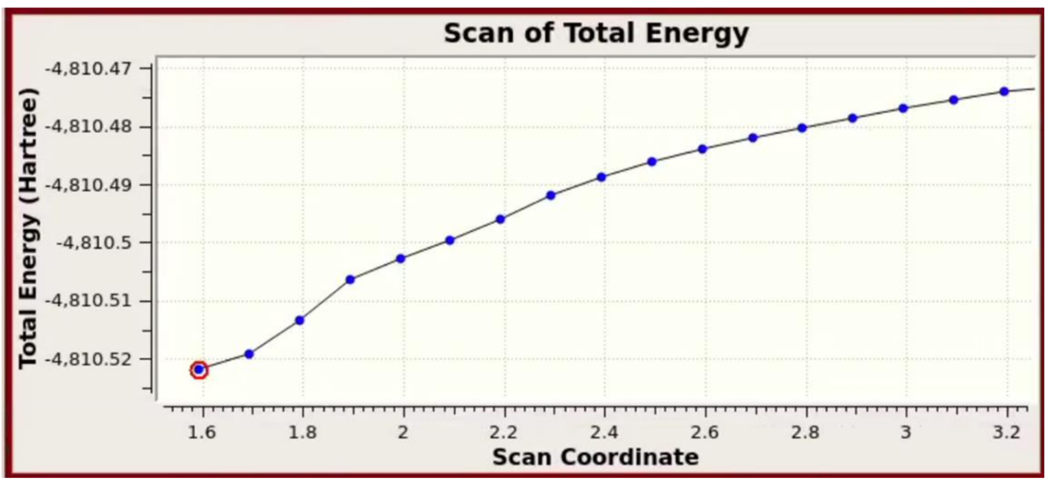
Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy, and thermal corrections (entropy and enthalpy, 298.15 K, 1 Atm) were obtained from these calculations. To further improve the accuracy of energies, single-point energies were carried out at the B3LYP[30]/def2-tzvp[29] level of theory along with Grimme's dispersion correction[31] (D3BJ) and SMD[32] solvation model (in benzene).

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

The process of homodimerization of allylic radical has been calculated at the SCF level with the broken symmetry formalism. The C–C coupling is essentially barrierless at the SCF/enthalpy surface according to these calculations. Elongating the C–C bond of species **6a** to 3 Å using the broken-symmetry DFT methodology led to a monotonic increase in the energy. It is indicated that the energetics associated with this process is consistent with the typical coupling of two carbon-centered radicals, which are frequently diffusion controlled.

Scheme S1: Calculated Energy Diagram for Homodimerization of Allylic Radical from [Co(TPP)] and In Situ-Generated Vinyldiazomethane





Scheme S2. Calculated Energy Diagram for [Co(P6)]-Catalyzed Radical Cyclopropanation of Styrene (2a) with Vinyl Diazomethane (1a')

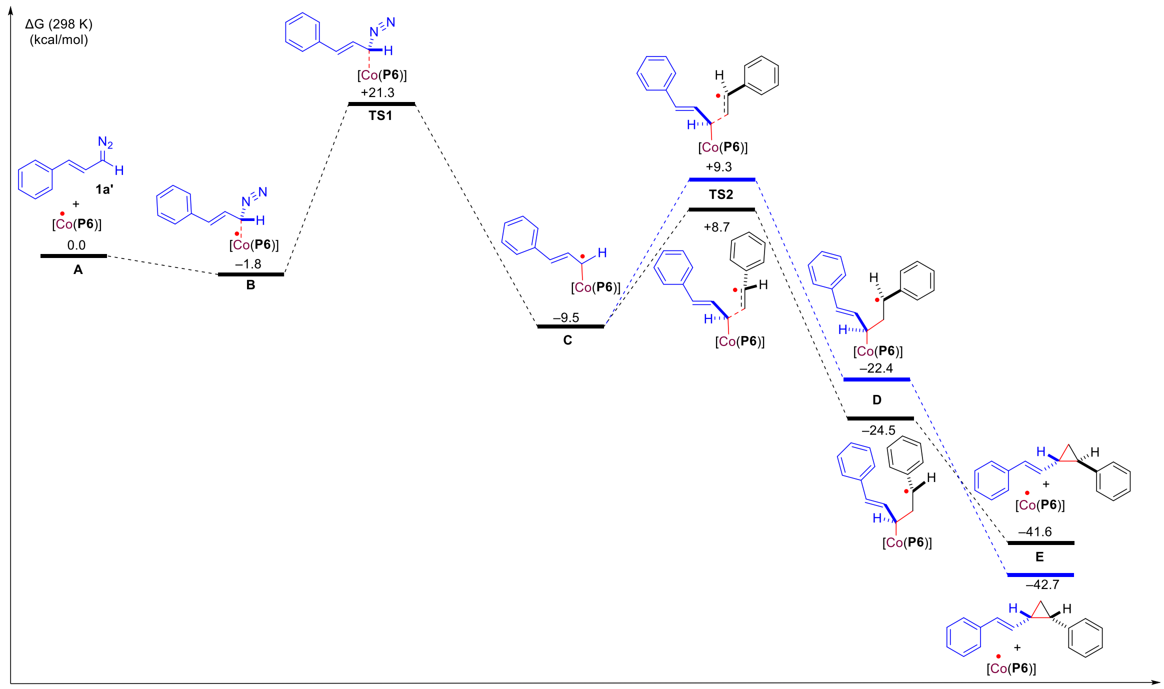
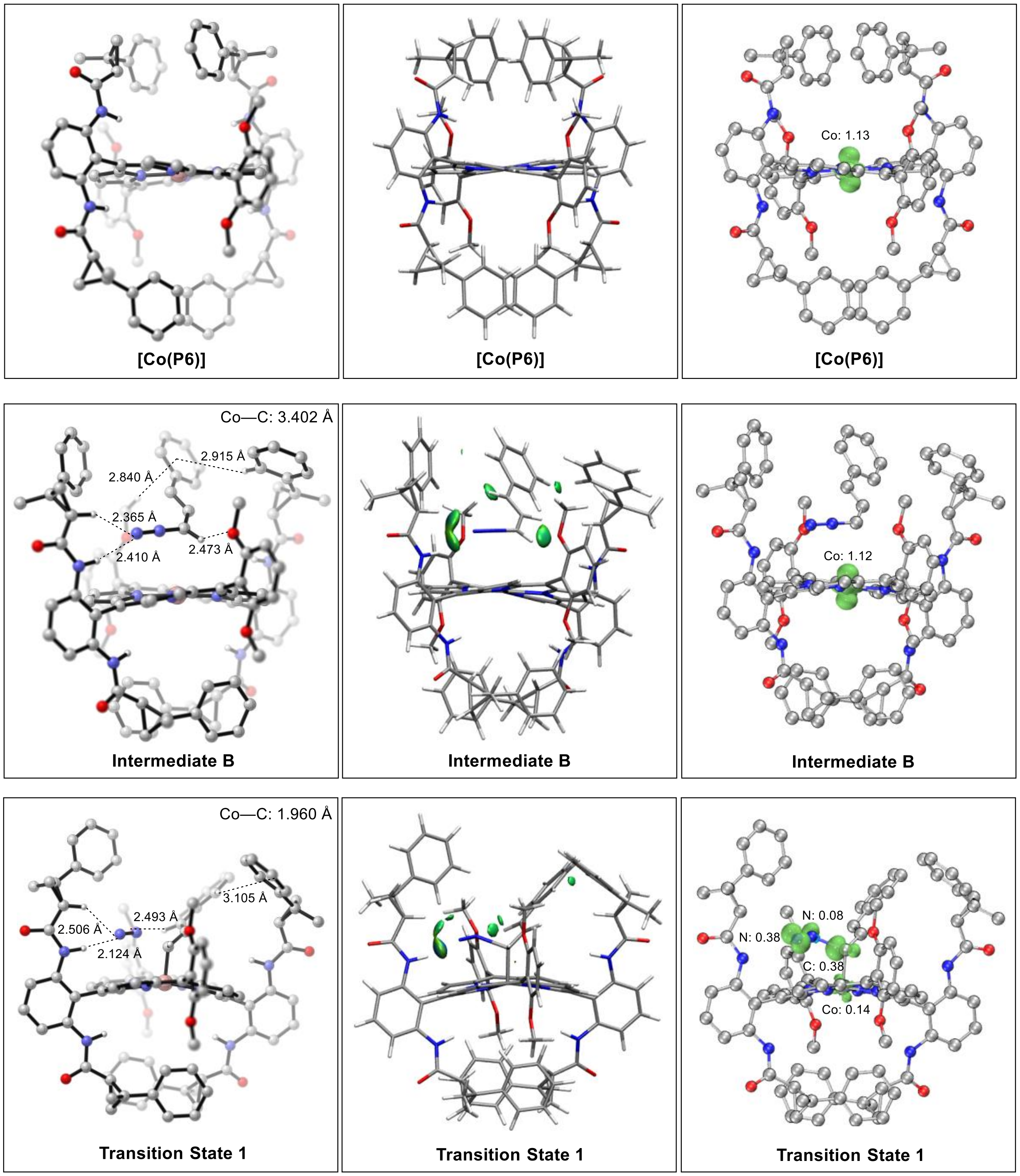
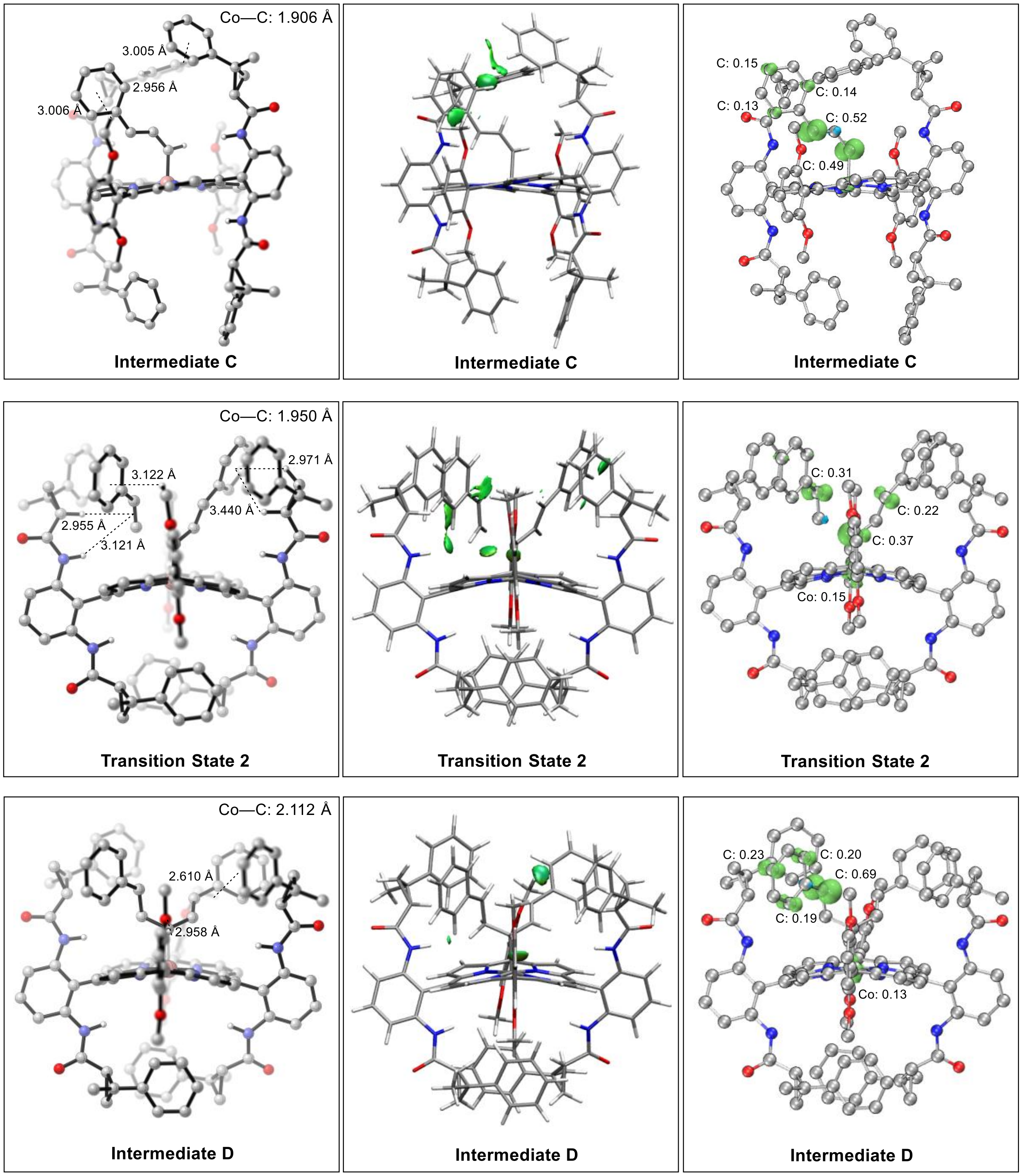
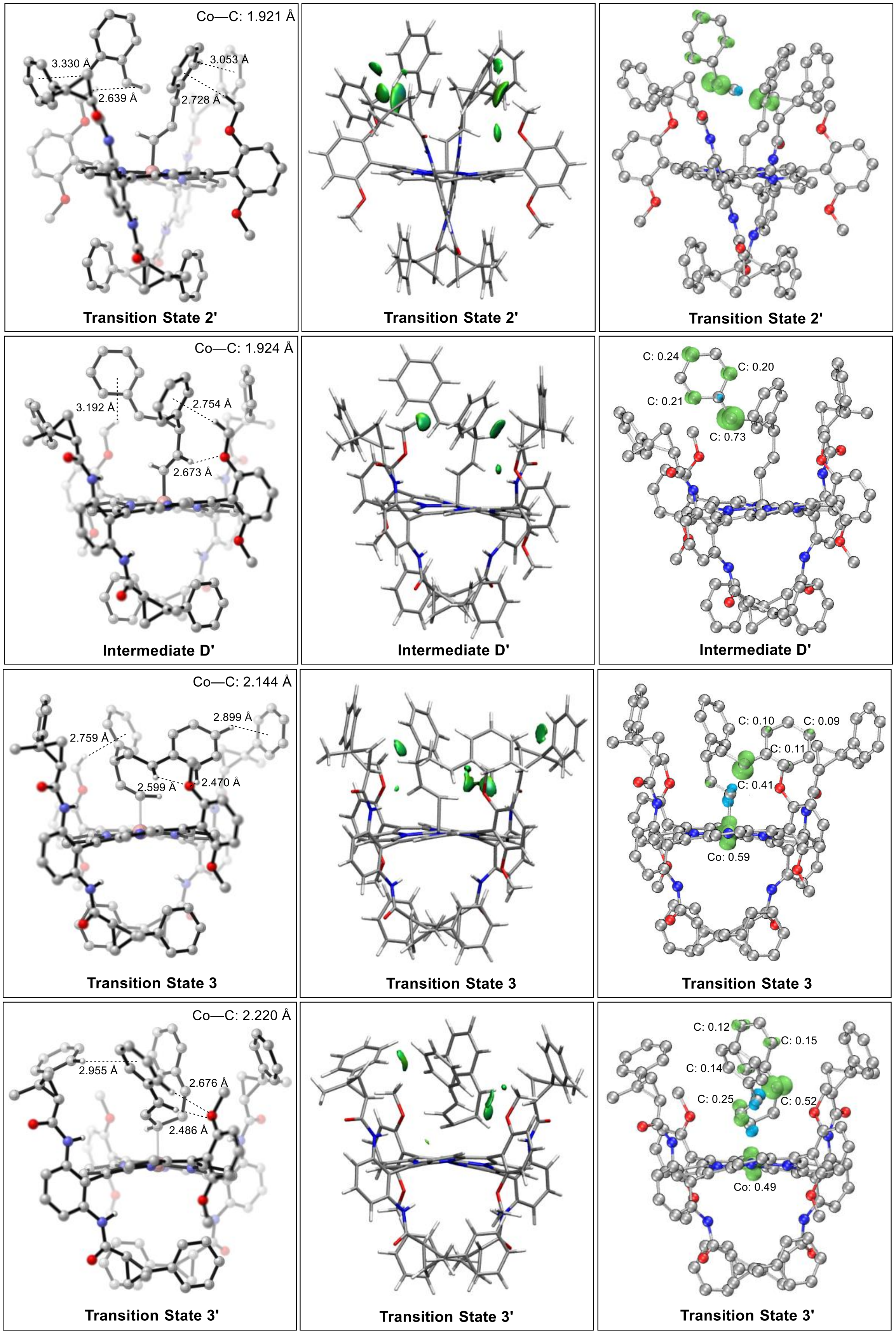


Figure S2. Optimized Structure Models and Spin Density Representation of Intermediates and Transition States




Co—C: 1.906 Å
3.005 Å
2.956 Å
3.006 Å
Intermediate C
Intermediate C
C: 0.15
C: 0.14
C: 0.13
C: 0.52
C: 0.49
Intermediate C
Co—C: 1.950 Å
3.122 Å
2.971 Å
3.440 Å
2.955 Å
3.121 Å
Transition State 2
Transition State 2
C: 0.31
C: 0.22
C: 0.37
Co: 0.15
Transition State 2
Co—C: 2.112 Å
2.610 Å
2.958 Å
Intermediate D
Intermediate D
C: 0.23
C: 0.20
C: 0.69
C: 0.19
Co: 0.13
Intermediate D


Co—C: 1.921 Å
3.330 Å
2.639 Å
3.053 Å
2.728 Å
Transition State 2'
Transition State 2'
Transition State 2'
Co—C: 1.924 Å
3.192 Å
2.754 Å
2.673 Å
Intermediate D'
Intermediate D'
C: 0.24
C: 0.20
C: 0.21
C: 0.73
Intermediate D'
Co—C: 2.144 Å
2.759 Å
2.899 Å
2.599 Å
2.470 Å
Transition State 3
Transition State 3
C: 0.10
C: 0.09
C: 0.11
C: 0.41
Co: 0.59
Transition State 3
Co—C: 2.220 Å
2.955 Å
2.676 Å
2.486 Å
Transition State 3'
Transition State 3'
C: 0.12
C: 0.15
C: 0.14
C: 0.25
C: 0.52
Co: 0.49
Transition State 3'

Coordinates of Intermediates and Transition States

Intermediate A

A[Co(II)(P6)]

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.333865 Hartree

H_corr: 1.583795 Hartree

SCF: -5978.86738 Hartree

S: 526.023 Cal/Mol-Kelvin

H: -5977.283585 Hartree

G: -5977.533515 Hartree

Cartesian Coordinates:

Co	0.03934800	-0.00003300	0.00001000
O	3.08077300	7.33946200	0.26140600
O	-4.90023900	5.62002500	1.06249500
O	-1.78130800	-0.18595100	5.26643800
O	2.87722900	-0.86170600	4.48060600
N	0.05983900	1.24476900	1.53516800
N	0.01209800	-1.52989400	1.24959600
N	1.80702300	5.36918900	0.47554800
H	1.88057400	4.34710300	0.51694300
N	-2.95133500	4.36821100	0.62192900

H	-2.61075500	3.41062600	0.48572700
C	-0.29835800	3.43626100	0.35821500
C	-0.10254700	2.64686000	1.51000200
C	0.01093100	3.20182300	2.85253800
H	-0.08367500	4.26113300	3.08888000
C	0.26773900	2.14634300	3.70288600
H	0.41994300	2.16532200	4.78094400
C	0.26458100	0.93413100	2.89779400
C	0.34462300	-0.35788700	3.44409600
C	0.15853700	-1.50440100	2.65343200
C	0.02778800	-2.84446900	3.20543700
H	0.10321600	-3.07975500	4.26613500
C	-0.22242800	-3.69797100	2.15125300
H	-0.38252200	-4.77521800	2.16925200
C	-0.20362500	-2.89041200	0.93846000
C	-0.58298200	4.91134200	0.50847100
C	0.47456000	5.87233200	0.52250800
C	0.18725800	7.26155900	0.61306500
H	1.01024100	7.97775900	0.59745300
C	-1.15796200	7.67423200	0.71884400
H	-1.38022800	8.74510400	0.79364300
C	-2.22526300	6.75156000	0.73678200
H	-3.26416600	7.07108400	0.83412000

C	-1.93495600	5.36467500	0.62602500
C	3.01217200	6.07589000	0.40158400
C	4.23191000	5.19991800	0.51179200
H	4.07399900	4.22650200	0.99334800
C	5.58751000	5.88633800	0.78549700
H	6.25549000	5.40469300	1.50692700
H	5.54816300	6.98021800	0.82483300
C	5.36253100	5.22663500	-0.57706900
C	6.06524200	3.90716900	-0.84527700
C	7.48530200	3.86253800	-0.88261500
H	8.05460800	4.77809500	-0.67720700
C	8.16521200	2.65518100	-1.16671100
H	9.26158400	2.63731200	-1.18856300
C	7.43264700	1.46785400	-1.41263500
H	7.95535700	0.52601400	-1.61638600
C	6.01727800	1.50223500	-1.38162700
H	5.44321900	0.58382300	-1.55490800
C	5.34041900	2.71522500	-1.10812900
H	4.24346700	2.73443800	-1.09289600
C	5.19559300	6.11807800	-1.81578400
H	6.18833300	6.37704000	-2.23019500
H	4.66492900	7.05187700	-1.56257000
H	4.62625500	5.59078400	-2.60443900

C	-4.32833300	4.50521800	0.83688600
C	-5.06448900	3.19454400	0.79893700
H	-4.56995500	2.38644300	0.24515900
C	-6.60477700	3.20018200	0.74228800
H	-7.06809200	4.19248100	0.76748200
H	-7.07237800	2.46842900	0.07582200
C	-5.92641800	2.71772600	2.02541400
C	-5.89825800	1.22917200	2.32110200
C	-4.67466600	0.56547200	2.60389400
H	-3.73188600	1.12559000	2.56223000
C	-4.65476800	-0.81117500	2.93220600
H	-3.69803300	-1.30409400	3.14192200
C	-5.86628800	-1.54350000	2.99209900
H	-5.85356900	-2.61124700	3.24091600
C	-7.09315400	-0.88891200	2.72090200
H	-8.03476400	-1.44944800	2.76916200
C	-7.10708200	0.48664100	2.38824600
H	-8.05750700	0.99072700	2.17175200
C	-6.00510000	3.60240400	3.27825400
H	-6.93984800	3.38707100	3.82997300
H	-5.99131700	4.67272100	3.01013500
H	-5.15597500	3.39898000	3.95811500
C	0.55830100	-0.51798100	4.92373700

C	-0.52329300	-0.42191500	5.84550400
C	-0.31790500	-0.56588900	7.24392000
H	-1.15099700	-0.49072800	7.94782000
C	0.98655300	-0.81411600	7.72143700
H	1.15152900	-0.92601700	8.79931900
C	2.08233900	-0.92275900	6.83916600
H	3.08352100	-1.11474400	7.23414500
C	1.85922900	-0.77455400	5.44389400
C	-2.93434700	-0.04071500	6.17099300
C	4.23897400	-1.16179400	4.95137500
O	3.08104600	-7.33945400	-0.26115800
O	-4.90002400	-5.62015500	-1.06252300
O	-1.78143200	0.18583700	-5.26634000
O	2.87710100	0.86173400	-4.48066300
N	0.05990500	-1.24483600	-1.53514700
N	0.01199500	1.52982500	-1.24958000
N	1.80724200	-5.36923600	-0.47551300
H	1.88077000	-4.34715100	-0.51698300
N	-2.95111900	-4.36833300	-0.62197700
H	-2.61054700	-3.41074500	-0.48577700
C	-0.29817600	-3.43634700	-0.35819200
C	-0.10240900	-2.64693600	-1.50997900
C	0.01104900	-3.20189000	-2.85252100

H -0.08351000 -4.26120400 -3.08886300

C 0.26776600 -2.14639300 -3.70287500

H 0.41992200 -2.16535400 -4.78094100

C 0.26457500 -0.93418500 -2.89777900

C 0.34454600 0.35783600 -3.44408200

C 0.15843000 1.50434400 -2.65341500

C 0.02763400 2.84440900 -3.20541500

H 0.10306900 3.07970300 -4.26611200

C -0.22261400 3.69789700 -2.15122700

H -0.38274500 4.77513900 -2.16922100

C -0.20378300 2.89033300 -0.93843800

C -0.58276900 -4.91143300 -0.50844600

C 0.47479100 -5.87240400 -0.52245100

C 0.18751100 -7.26163800 -0.61297100

H 1.01050400 -7.97782600 -0.59733500

C -1.15770100 -7.67433700 -0.71876500

H -1.37994300 -8.74521500 -0.79354700

C -2.22501700 -6.75168200 -0.73674900

H -3.26391300 -7.07122300 -0.83411000

C -1.93473300 -5.36479000 -0.62601500

C 3.01241000 -6.07590300 -0.40151000

C 4.23212200 -5.19990100 -0.51176400

H 4.07420000 -4.22655900 -0.99346500

C	5.58776600	-5.88631400	-0.78529000
H	6.25576200	-5.40475100	-1.50676200
H	5.54845800	-6.98020000	-0.82446900
C	5.36268700	-5.22641700	0.57716000
C	6.06531800	-3.90687500	0.84520500
C	7.48537400	-3.86210100	0.88244500
H	8.05475500	-4.77762200	0.67708400
C	8.16518200	-2.65465000	1.16639600
H	9.26155300	-2.63666600	1.18817000
C	7.43251400	-1.46737700	1.41226900
H	7.95514300	-0.52546700	1.61590200
C	6.01714400	-1.50190100	1.38135500
H	5.44300600	-0.58352900	1.55458700
C	5.34039100	-2.71498100	1.10800300
H	4.24344000	-2.73430300	1.09281400
C	5.19569800	-6.11766600	1.81600600
H	6.18841800	-6.37650600	2.23053700
H	4.66509500	-7.05153000	1.56290200
H	4.62626800	-5.59027400	2.60453000
C	-4.32810500	-4.50533900	-0.83699200
C	-5.06426400	-3.19466200	-0.79901000
H	-4.56972400	-2.38658300	-0.24520500
C	-6.60455200	-3.20029900	-0.74235400

H	-7.06787000	-4.19259500	-0.76757500
H	-7.07214900	-2.46855400	-0.07587900
C	-5.92618300	-2.71781400	-2.02547100
C	-5.89802600	-1.22925000	-2.32111900
C	-4.67444200	-0.56550000	-2.60381200
H	-3.73164300	-1.12558200	-2.56210400
C	-4.65457700	0.81115700	-2.93209000
H	-3.69785100	1.30412000	-3.14174800
C	-5.86611800	1.54343900	-2.99204500
H	-5.85341900	2.61119400	-3.24082900
C	-7.09298100	0.88879900	-2.72094700
H	-8.03460800	1.44930200	-2.76925500
C	-7.10687700	-0.48676200	-2.38832900
H	-8.05729600	-0.99089200	-2.17191200
C	-6.00487300	-3.60246300	-3.27832900
H	-6.93962400	-3.38712100	-3.83003800
H	-5.99108900	-4.67278600	-3.01023100
H	-5.15575100	-3.39903000	-3.95819000
C	0.55817900	0.51794000	-4.92373000
C	-0.52345100	0.42185400	-5.84545300
C	-0.31811500	0.56583800	-7.24387600
H	-1.15122900	0.49066400	-7.94774800
C	0.98632300	0.81409500	-7.72143600

H	1.15125900	0.92600300	-8.79932400
C	2.08214000	0.92275700	-6.83920700
H	3.08330500	1.11476100	-7.23422100
C	1.85908100	0.77454200	-5.44392700
C	-2.93450200	0.04056600	-6.17084900
C	4.23882600	1.16185500	-4.95146300
H	4.84822200	-1.22351100	4.03848200
H	4.27196200	-2.13048600	5.48642700
H	4.61994500	-0.35558600	5.60810700
H	-3.79131200	0.14062400	5.50680200
H	-2.79575200	0.81735100	6.85675200
H	-3.10180900	-0.96675600	6.75447300
H	4.84808900	1.22361200	-4.03858100
H	4.27177800	2.13054400	-5.48652400
H	4.61980800	0.35565200	-5.60819200
H	-3.79143200	-0.14081600	-5.50662300
H	-2.79590300	-0.81748800	-6.85662400
H	-3.10202300	0.96660600	-6.75431400

$A_{1a'}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.108377 Hartree

H_corr: 0.155175 Hartree

SCF: -457.4112548 Hartree

S: 98.493 Cal/Mol-Kelvin

H: -457.2560798 Hartree

G: -457.3028778 Hartree

Cartesian Coordinates:

N	-4.99436000	0.77784600	-0.00008300
N	-4.00915500	0.10978300	0.00026700
C	-2.91260800	-0.64131800	-0.00002500
H	-3.08249500	-1.72258700	0.00042400
H	-1.52512500	1.03017700	-0.00098300
C	-1.58278500	-0.06649400	-0.00029200
C	-0.43027700	-0.82321900	0.00003100
H	0.48956600	1.82906100	0.00040000
H	-0.53382300	-1.91925700	0.00017000
C	1.28399300	1.07302100	0.00010000
C	0.95026500	-0.31764900	-0.00008600
C	2.62917900	1.49532600	0.00004700
H	2.86112900	2.56724900	0.00012000
C	2.02556200	-1.25876300	0.00002100
H	1.79350500	-2.33212700	-0.00005800
C	3.68384400	0.54630000	-0.00001400

C 3.37223900 -0.83493100 -0.00001900

H 4.72795800 0.87969500 0.00002900

H 4.17742400 -1.57925200 0.00004000

Intermediate B

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.466123 Hartree

H_corr: 1.741222 Hartree

SCF: -6436.305433 Hartree

S: 578.994 Cal/Mol-Kelvin

H: -6434.564211 Hartree

G: -6434.83931 Hartree

Cartesian Coordinates:

N 2.40070100 1.68997700 1.43208400

N 2.11673100 2.84024500 1.49859800

H 4.69058700 1.76121600 -0.10012800

C 5.35534900 -5.56225700 0.66555300

Co -0.42183600 -0.00691500 0.04357500

O 3.46914500 -6.88396600 -1.52877800

O	-4.45005100	-5.53235600	-2.94156100
O	-1.96120100	1.53410100	-5.07143100
O	2.70818000	1.45251200	-4.08730200
N	-0.11639200	-0.91094300	-1.68097000
N	-0.59081800	1.72319300	-0.89192800
N	2.00014800	-5.11745600	-1.00905200
H	1.94770700	-4.18488900	-0.58587300
N	-2.74802600	-4.34604300	-1.82011600
H	-2.54506400	-3.45097500	-1.36316600
C	-0.26326700	-3.32130100	-0.97678300
C	-0.09828900	-2.29950700	-1.93622100
C	0.16481600	-2.55758800	-3.34597300
H	0.22328800	-3.55139700	-3.78804800
C	0.33323900	-1.33152700	-3.95454500
H	0.54848500	-1.11775600	-5.00044200
C	0.13349600	-0.31233900	-2.93451300
C	0.09154300	1.06475200	-3.21562800
C	-0.30690500	2.00259700	-2.24632400
C	-0.58191400	3.40058400	-2.54612600
H	-0.43233200	3.85836900	-3.52280000
C	-1.08232600	3.97477300	-1.39572400
H	-1.41546500	4.99924300	-1.23393300
C	-1.06098200	2.94642700	-0.36328200

C	-0.37330900	-4.74939300	-1.45447000
C	0.75827300	-5.62273900	-1.50036100
C	0.63111500	-6.94172700	-2.01666100
H	1.51203300	-7.58334000	-2.05727800
C	-0.62813200	-7.37918600	-2.47758200
H	-0.72261000	-8.39446100	-2.88002500
C	-1.76845000	-6.55124400	-2.43319900
H	-2.74217000	-6.88773800	-2.79288000
C	-1.64020900	-5.23412600	-1.91512800
C	3.25678800	-5.73270800	-1.02521100
C	4.35707200	-4.91746600	-0.39944200
H	4.12445100	-3.86265300	-0.20676600
C	5.80399800	-5.26811700	-0.77323600
H	6.51042800	-4.45258800	-0.95449400
H	5.90276300	-6.13377300	-1.43677600
C	5.84156700	-4.62793200	1.75941400
C	5.98274300	-5.08877700	3.09899400
H	5.71756800	-6.12015200	3.35130600
C	6.47902200	-4.24294300	4.11890500
H	6.58939100	-4.63324100	5.13811700
C	6.84454600	-2.90802100	3.82783500
H	7.24722300	-2.25691200	4.61312300
C	6.70031600	-2.42913500	2.50273500

C	6.20554600	-3.27605000	1.48676100
H	6.13069700	-2.87274100	0.46915300
C	5.14441800	-7.02666300	1.05437700
H	6.09328600	-7.46647900	1.41588600
H	4.80047500	-7.60881200	0.18463400
H	4.38539100	-7.13335300	1.85252900
C	-4.05355900	-4.50453800	-2.30343300
C	-4.93965700	-3.32690700	-2.00843800
H	-4.63499800	-2.70392300	-1.15819800
C	-6.45869500	-3.46247000	-2.23040700
H	-6.78607200	-4.42729100	-2.63257400
H	-7.10556900	-3.01672100	-1.46821300
C	-5.66661500	-2.55141300	-3.16863800
C	-5.77940100	-1.04806300	-2.99407500
C	-4.61574100	-0.23995000	-2.89058600
H	-3.62503100	-0.71164100	-2.89556400
C	-4.71740600	1.16758000	-2.78302500
H	-3.80562200	1.77158200	-2.70728800
C	-5.99106200	1.78906600	-2.78583900
H	-6.07340700	2.87840200	-2.69400200
C	-7.15753500	0.99321000	-2.89847900
H	-8.14566500	1.46907500	-2.90228400
C	-7.05062300	-0.41437000	-3.00237000

H	-7.95503100	-1.03033500	-3.08651000
C	-5.44976600	-2.99793800	-4.62184100
H	-6.31390600	-2.68956700	-5.24051300
H	-5.34079300	-4.09402600	-4.68863000
H	-4.54305500	-2.52722900	-5.04694600
C	0.38376300	1.52543600	-4.61760000
C	-0.66243300	1.75884900	-5.55616800
C	-0.38451400	2.17632700	-6.88546400
H	-1.19152900	2.35521500	-7.60086700
C	0.95825500	2.35500500	-7.28022100
H	1.17887700	2.67748500	-8.30438200
C	2.02204200	2.12449200	-6.38281100
H	3.05454600	2.26882800	-6.71176300
C	1.72613000	1.71003500	-5.05639900
C	-3.08127400	1.70623400	-6.01218700
C	4.11612200	1.51037200	-4.51200900
O	0.79608500	7.83096100	1.97720700
O	-6.35404500	3.95986000	1.97191500
O	-2.34979100	-1.75674500	5.08190100
O	2.29503900	-0.96671200	4.38473900
N	-0.73688500	0.89619100	1.76957800
N	-0.30911900	-1.74375100	0.97559400
N	0.17576300	5.60006200	1.51807900

H	0.55661300	4.66795500	1.30915200
N	-4.17745700	3.37333400	1.27474600
H	-3.61891400	2.58541800	0.93148000
C	-1.38836600	3.19279200	0.98580300
C	-1.15322200	2.22635800	1.98632200
C	-1.23919100	2.51085300	3.41237000
H	-1.54556100	3.46965100	3.82878900
C	-0.83729700	1.36971100	4.07625100
H	-0.76022100	1.20086100	5.14935000
C	-0.55839100	0.36130300	3.06503100
C	-0.26015300	-0.97890100	3.36389800
C	-0.22512600	-1.96931500	2.36628300
C	-0.18160100	-3.39562800	2.65084200
H	-0.11523000	-3.81988100	3.65169200
C	-0.27696000	-4.05542400	1.44164700
H	-0.29790300	-5.12790600	1.25055500
C	-0.31719900	-3.03394500	0.40282700
C	-2.01671600	4.50742200	1.38123500
C	-1.24471600	5.68627800	1.63314200
C	-1.89345800	6.89834500	2.00492800
H	-1.28721700	7.78649300	2.18517600
C	-3.29618700	6.92003400	2.13907200
H	-3.78679200	7.85607100	2.43058600

C	-4.08466500	5.77364800	1.91479000
H	-5.16913600	5.78395200	2.03375900
C	-3.44196900	4.56634800	1.53209600
C	1.11374800	6.62927500	1.69329900
C	2.54386200	6.20427700	1.51969000
H	2.72654700	5.12543500	1.52207200
C	3.64256500	7.08359400	2.16289200
H	4.46784000	6.56071400	2.65791800
H	3.27938500	7.98698600	2.66410700
C	3.53805100	7.04607700	0.63966300
C	4.57857600	6.25976800	-0.13610000
C	5.95850300	6.56309600	0.01141000
H	6.26335500	7.32304100	0.74197700
C	6.93350100	5.90080800	-0.77118900
H	7.99468400	6.14918900	-0.64843000
C	6.54012900	4.92094300	-1.71506500
H	7.29321500	4.41307400	-2.32995800
C	5.16681400	4.60679900	-1.86510600
H	4.85200100	3.84718800	-2.58977800
C	4.19477200	5.27429200	-1.08374700
H	3.13201600	5.03199900	-1.20914300
C	3.03839500	8.29317500	-0.10525900
H	3.88489500	8.98269200	-0.28622900

H	2.26605800	8.81967900	0.47976800
H	2.61145200	8.01803100	-1.08827400
C	-5.53538200	3.10863000	1.49539900
C	-5.93404600	1.70591600	1.13036900
H	-5.28625700	1.19978600	0.40393200
C	-7.43282400	1.35682300	1.05025400
H	-8.11388300	2.17466500	1.30925300
H	-7.74264400	0.72261200	0.21385100
C	-6.60912500	0.75417400	2.18796900
C	-6.21604400	-0.70954500	2.10773000
C	-4.87681200	-1.11357600	2.35769300
H	-4.11136200	-0.35672600	2.57101900
C	-4.51523500	-2.48150300	2.33200300
H	-3.47611100	-2.76927800	2.52974600
C	-5.49492000	-3.46933800	2.06189700
H	-5.21652900	-4.52946900	2.03465200
C	-6.83490900	-3.07830600	1.82135200
H	-7.59787000	-3.83875500	1.61487400
C	-7.19107300	-1.70843200	1.84555400
H	-8.22917300	-1.40632900	1.65773000
C	-6.84021600	1.26464900	3.61758100
H	-7.67526600	0.70717500	4.08304100
H	-7.08819800	2.33989900	3.61961200

H	-5.93939800	1.11066600	4.24164500
C	-0.01635100	-1.37461000	4.79179100
C	-1.07186300	-1.76482900	5.66208300
C	-0.81589700	-2.13337600	7.01020300
H	-1.62880200	-2.42990900	7.67861100
C	0.51405400	-2.11431300	7.48347100
H	0.71762700	-2.39900200	8.52222600
C	1.58745200	-1.73672100	6.64764200
H	2.60883800	-1.73176700	7.03748200
C	1.31017100	-1.36744400	5.30548100
C	-3.49385600	-2.13387800	5.92878400
C	3.69745400	-0.96378000	4.83343800
H	4.69294600	1.21425200	-3.62461700
H	4.39631300	2.53498400	-4.82713800
H	4.31146900	0.79981700	-5.33800600
H	-3.97755700	1.45298400	-5.42838100
H	-2.98372700	1.01899500	-6.87468300
H	-3.14455200	2.75272800	-6.36848900
H	4.27292000	-0.62871600	3.95856400
H	4.02436200	-1.98061300	5.12010200
H	3.84254700	-0.25987300	5.67555900
H	-4.36699700	-2.06150200	5.26476100
H	-3.60352200	-1.43624700	6.78137700

H	-3.38909900	-3.17155100	6.30050800
C	3.74322500	-0.08145700	0.43649900
C	7.81722200	0.45393600	-2.38366900
C	5.67381400	0.13754800	-1.18614000
C	6.81741200	0.93256700	-1.50824800
C	7.69688900	-0.82872400	-2.97410500
C	4.66618400	0.67173600	-0.25613800
C	6.55682000	-1.62128700	-2.68443500
C	2.70194900	0.40231300	1.32803500
C	5.55773800	-1.14546400	-1.80783700
H	4.65697900	-1.74856300	-1.64283100
H	6.43723000	-2.60204700	-3.16038500
H	8.47037000	-1.20060500	-3.65575600
H	6.92036400	1.92457800	-1.05025900
H	8.69133500	1.07834000	-2.60438900
H	2.16700900	-0.25867300	2.01869700
H	3.76824400	-1.17634100	0.36392700
H	6.98483000	-1.40003600	2.25332500

Transition State TS1

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -294.4334 cm-1

G_corr: 1.465316 Hartree

H_corr: 1.737845 Hartree

SCF: -6436.267744 Hartree

S: 573.586 Cal/Mol-Kelvin

H: -6434.529899 Hartree

G: -6434.802428 Hartree

Cartesian Coordinates:

N	-1.42633400	2.69675200	0.02397700
N	-0.91564000	3.41577300	-0.76444900
H	-2.27747600	1.42305900	2.33278800
C	-6.75152000	-4.01850400	-0.82957900
Co	0.16518100	0.03409100	-0.05746500
O	-5.20314100	-5.98193500	1.13835300
O	2.84224300	-6.47986500	2.28122800
O	2.23809600	-0.12002600	5.15407600
O	-1.39580200	2.82304500	4.19739200
N	-0.15040600	-0.90886900	1.64752200
N	1.09636100	1.46077900	0.94326200
N	-3.44306700	-4.43368000	0.90144400
H	-3.22234700	-3.47032800	0.62742100
N	1.40351900	-4.81640300	1.42839500
H	1.39507900	-3.86148000	1.05623200

C	-0.80484800	-3.19110700	0.81614200
C	-0.59335700	-2.23584800	1.83257500
C	-0.84318700	-2.50207100	3.24313700
H	-1.18640100	-3.45832100	3.63591100
C	-0.58474700	-1.33195900	3.92466900
H	-0.66026600	-1.14044800	4.99386100
C	-0.12017100	-0.35913900	2.94658700
C	0.40891400	0.89741800	3.29020900
C	1.04709200	1.70576900	2.33250200
C	1.84250600	2.87526200	2.67444400
H	1.96698600	3.25915800	3.68601800
C	2.40262800	3.34352000	1.50397100
H	3.06680100	4.19433600	1.35731000
C	1.91630800	2.49007000	0.42908400
C	-1.02175700	-4.63316400	1.20961600
C	-2.31862300	-5.23399600	1.26978400
C	-2.46679500	-6.58671600	1.68557000
H	-3.46602000	-7.02069100	1.72844900
C	-1.32067100	-7.32981000	2.03363600
H	-1.44076600	-8.36975300	2.35880500
C	-0.02628600	-6.77644100	1.97049800
H	0.86267400	-7.35057600	2.23627000
C	0.12347900	-5.42746400	1.55020000

C	-4.78798400	-4.81582200	0.83447700
C	-5.72906900	-3.73808100	0.36487900
H	-5.34616200	-2.71129500	0.40395000
C	-7.22355900	-3.94965500	0.63066900
H	-7.82392500	-3.09717900	0.96135700
H	-7.46771300	-4.90511100	1.10662500
C	-7.05634000	-2.83508800	-1.72960100
C	-7.17447900	-3.00159100	-3.13842600
H	-7.02411300	-3.98952900	-3.58437200
C	-7.50041200	-1.91413800	-3.98284300
H	-7.59786800	-2.08002400	-5.06276700
C	-7.71322300	-0.62466100	-3.44239900
H	-7.98303000	0.21548600	-4.09332200
C	-7.59171600	-0.43759500	-2.04378200
C	-7.26777700	-1.52611500	-1.20474100
H	-7.20312900	-1.35299500	-0.12369100
C	-6.71953100	-5.39587900	-1.49504000
H	-7.69823800	-5.61871900	-1.96090700
H	-6.50541900	-6.17745900	-0.74870400
H	-5.94018000	-5.45535800	-2.27848800
C	2.66334600	-5.33037400	1.76298200
C	3.79150700	-4.38572400	1.45859200
H	3.57133700	-3.60146200	0.72370100

C	5.23220200	-4.93749700	1.43919500
H	5.32623200	-5.99802500	1.69649400
H	5.88131600	-4.57969900	0.63397200
C	4.83375700	-3.98269400	2.56451200
C	5.33990200	-2.55241700	2.51712600
C	4.44281200	-1.45421800	2.60178900
H	3.36190100	-1.63573700	2.65481100
C	4.92665400	-0.12387300	2.61786800
H	4.21727300	0.70903200	2.68654900
C	6.31938600	0.12625400	2.55657200
H	6.69561500	1.15588200	2.56077200
C	7.22290900	-0.96219900	2.47977900
H	8.30221700	-0.77429300	2.42940800
C	6.73535100	-2.29041800	2.46143400
H	7.43576600	-3.13314600	2.39882600
C	4.67694100	-4.54408600	3.98523700
H	5.65607200	-4.53672600	4.50081300
H	4.29502800	-5.57896200	3.96290100
H	3.97478900	-3.92607700	4.57726100
C	0.40656900	1.34783300	4.72483200
C	1.34199400	0.82883300	5.66735500
C	1.35886200	1.27555400	7.01576100
H	2.07585500	0.86988200	7.73445500

C	0.43936300	2.26584700	7.42176100
H	0.45022100	2.61621200	8.46025100
C	-0.49170100	2.81562600	6.51494000
H	-1.19374000	3.58386300	6.85005500
C	-0.50004700	2.34968300	5.17393600
C	3.26314700	-0.66166900	6.06197800
C	-2.21494100	4.00213900	4.52896600
O	1.41215500	7.86407700	-1.50624400
O	7.10963300	2.09389900	-2.15323000
O	1.11906700	-1.97892400	-5.30360000
O	-2.87580000	0.35547100	-4.18280200
N	0.75405400	0.84630200	-1.75767200
N	-0.44032400	-1.55696500	-1.05466600
N	1.35006200	5.51172400	-1.32477500
H	0.70661700	4.71743300	-1.19373500
N	4.88302000	2.12137300	-1.37345100
H	4.13041700	1.50766400	-1.04542100
C	2.18150900	2.73774200	-0.93226700
C	1.56932600	1.98090400	-1.95006000
C	1.65090700	2.32212900	-3.36335200
H	2.23847300	3.14886300	-3.76059900
C	0.84261800	1.43227800	-4.03953200
H	0.64382000	1.37268800	-5.10857900

C	0.30866100	0.50553800	-3.05317500
C	-0.43766900	-0.63759400	-3.38542000
C	-0.69952100	-1.64350400	-2.43925900
C	-1.17814000	-2.97169800	-2.78682800
H	-1.43876700	-3.28453300	-3.79675000
C	-1.17957700	-3.72037800	-1.62644100
H	-1.44823400	-4.76748200	-1.49151600
C	-0.77028100	-2.83215600	-0.54676000
C	3.14643800	3.83511000	-1.30897400
C	2.73569800	5.19824500	-1.46459300
C	3.70103900	6.19582900	-1.78567300
H	3.37526200	7.23231200	-1.87800700
C	5.04690100	5.82448700	-1.97794100
H	5.77974300	6.59973900	-2.23066700
C	5.47668300	4.48698100	-1.86143100
H	6.51417200	4.19428000	-2.02981900
C	4.52224900	3.49211800	-1.52163400
C	0.75144200	6.77863900	-1.39601000
C	-0.75334500	6.76482000	-1.36664900
H	-1.22318800	5.78692900	-1.51346000
C	-1.47261700	7.98455100	-1.99429300
H	-2.35106800	7.77984500	-2.61526100
H	-0.80748900	8.77961700	-2.34777500

C	-1.56834000	7.77493700	-0.48193000
C	-2.89716400	7.28366800	0.06813600
C	-4.03506800	8.13334800	-0.00495200
H	-3.94245600	9.10984000	-0.49760600
C	-5.27801400	7.73065900	0.53536800
H	-6.14563700	8.39830000	0.46797400
C	-5.40619800	6.46260200	1.15470500
H	-6.37170400	6.14260200	1.56458300
C	-4.28038600	5.60817000	1.23042000
H	-4.37742600	4.61457100	1.68559600
C	-3.03386600	6.02018900	0.69913900
H	-2.16716200	5.35256000	0.75917200
C	-0.82821000	8.74017100	0.45558000
H	-1.45300100	9.63359200	0.64608500
H	0.12939200	9.06198700	0.01319700
H	-0.62359500	8.25705100	1.42987200
C	6.09123600	1.48700900	-1.68881500
C	6.05879700	0.00255100	-1.45103000
H	5.32910800	-0.34398400	-0.70856800
C	7.37415700	-0.79461300	-1.52410600
H	8.26073600	-0.20573600	-1.78304000
H	7.52050700	-1.56888700	-0.76453900
C	6.33623400	-1.00637700	-2.62712200

C	5.50875400	-2.27840100	-2.62175000
C	4.09532000	-2.22268300	-2.75732900
H	3.59443500	-1.24831700	-2.82100500
C	3.32406200	-3.40800400	-2.80871900
H	2.23482100	-3.34074400	-2.91353000
C	3.96061100	-4.67191000	-2.73119300
H	3.36524700	-5.59206500	-2.76190100
C	5.36969900	-4.73931200	-2.60454300
H	5.86744900	-5.71477700	-2.54394200
C	6.13653500	-3.55050700	-2.55148400
H	7.22827000	-3.60360100	-2.45306400
C	6.63234200	-0.45916000	-4.03117600
H	7.22206100	-1.19971100	-4.60431700
H	7.20461700	0.48287700	-3.97746600
H	5.69413900	-0.26973900	-4.58657100
C	-0.90187100	-0.82202800	-4.80107500
C	-0.11338900	-1.49727900	-5.77344400
C	-0.56899300	-1.65532600	-7.10975400
H	0.03954400	-2.17247100	-7.85659500
C	-1.83031400	-1.13139900	-7.46748600
H	-2.18784900	-1.25114200	-8.49679200
C	-2.64043700	-0.45596100	-6.52906100
H	-3.61356600	-0.05992800	-6.83160200

C	-2.16624600	-0.30416800	-5.19911400
C	2.00581400	-2.65733900	-6.26346800
C	-4.19558200	0.91379200	-4.51564600
H	-2.74485200	4.25074000	3.59895200
H	-1.57634700	4.85204300	4.83494300
H	-2.94693800	3.77090100	5.32667000
H	3.87104700	-1.32524600	5.43113200
H	2.79906500	-1.23446300	6.88799400
H	3.89939800	0.14676000	6.47026300
H	-4.54404900	1.38619300	-3.58598100
H	-4.90120900	0.11472800	-4.81163400
H	-4.11605000	1.67378400	-5.31698500
H	2.89368600	-2.93187200	-5.67601000
H	2.29103400	-1.97749600	-7.08933000
H	1.52760100	-3.56843700	-6.67249600
C	-2.77083500	0.42489600	0.51996700
C	-5.35946700	0.41255200	4.79369700
C	-4.24372500	0.50338100	2.58901100
C	-4.22586200	0.70014200	4.00360400
C	-6.54817600	-0.06292300	4.18770900
C	-3.03084700	0.81473700	1.81457800
C	-6.58902500	-0.24337200	2.78166500
C	-1.60984200	0.83549800	-0.27281100

C	-5.45398600	0.03540800	1.99205600
H	-5.51029600	-0.07245100	0.90199900
H	-7.51605700	-0.58917100	2.30754400
H	-7.43177600	-0.28266500	4.79795800
H	-3.30272500	1.06616500	4.46878700
H	-5.31909600	0.55719200	5.87984900
H	-1.78124300	0.83070800	-1.36676400
H	-3.50386200	-0.20281700	-0.01621600
H	-7.76119000	0.55365900	-1.60612100

<u>Intermediate C</u>

$C_{[Co(III)(P6)]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.45804 Hartree

H_corr: 1.728429 Hartree

SCF: -6326.735232 Hartree

S: 569.082 Cal/Mol-Kelvin

H: -6325.006803 Hartree

G: -6325.277192 Hartree

Cartesian Coordinates:

O	-2.91060300	-7.39822100	0.59286200
C	-2.81931100	-6.13951600	0.76065200
H	-5.33037400	-7.02622800	1.40776500
H	-4.68556100	-7.02826000	-1.05322100
C	-4.00954000	-5.26138600	1.03378800
C	-5.34667000	-5.93106000	1.41159300
C	-5.21518100	-6.07458900	-1.22051100
H	-4.71159400	-5.53096600	-2.04215300
C	-5.24164100	-5.22611500	0.05828900
H	-5.92863800	-5.46569900	2.21381600
H	-6.24967400	-6.29641200	-1.54465300
C	-5.91160800	-3.87265200	-0.09556200
H	-7.87341900	-4.59008300	0.51987400
C	-7.29815000	-3.72222000	0.17283100
C	-7.93295400	-2.46781700	0.01285700
H	-9.00166000	-2.36272700	0.23518000
C	-7.18905300	-1.34258100	-0.41852000
C	-5.80884300	-1.48669900	-0.70217900
H	-7.67523700	-0.36465000	-0.51113700
H	1.75963400	-1.26687200	-2.32117200
C	6.49315600	-3.17486000	1.38170500
Co	-0.24851100	-0.08717500	0.07753100

O	5.07362600	-5.76356800	0.19013900
O	-3.58911500	-1.08597900	-4.13148200
O	0.94785700	-0.19278900	-5.28015400
N	-0.32984500	-1.61613400	-1.16967900
N	-0.71454000	1.14006500	-1.40254400
N	3.13941500	-4.42017500	0.27796300
H	2.81475000	-3.44661600	0.29201800
N	-1.61317100	-5.43167100	0.70656000
H	-1.68586100	-4.41264200	0.79217500
C	0.41857900	-3.48986300	0.33173100
C	0.01623000	-2.96254000	-0.91102400
C	-0.15094800	-3.77759800	-2.10487900
H	0.04762100	-4.84740300	-2.15009300
C	-0.61283800	-2.94278100	-3.10083600
H	-0.86188900	-3.18779100	-4.13228500
C	-0.69499100	-1.60538600	-2.53756700
C	-0.99237000	-0.46929600	-3.30523900
C	-0.93220000	0.82257200	-2.76046000
C	-1.10879900	2.03096300	-3.55076600
H	-1.29646200	2.03911800	-4.62316200
C	-0.98977900	3.10117600	-2.69105100
H	-1.07072800	4.16485200	-2.91108700
C	-0.77990300	2.55168500	-1.35817200

C	0.76012400	-4.95813000	0.41820400
C	2.11539400	-5.40933700	0.34184900
C	2.40811300	-6.80230800	0.34587200
H	3.44770000	-7.12364200	0.27288400
C	1.34879400	-7.72804100	0.43815900
H	1.57879800	-8.79988100	0.43205200
C	0.00444600	-7.31656800	0.54715400
H	-0.81556700	-8.03232700	0.62339100
C	-0.28657400	-5.92626200	0.54928000
C	4.52678400	-4.61360800	0.24497600
C	5.32893900	-3.34406000	0.30078100
H	4.78118900	-2.42081000	0.07801900
C	6.80336400	-3.40472100	-0.10599000
H	7.20577700	-2.58480100	-0.70767700
H	7.16228500	-4.40351800	-0.37591100
C	6.66636000	-1.77668500	1.94326000
C	6.94484200	-1.57508100	3.32482900
H	7.02341800	-2.43621800	3.99578600
C	7.13815100	-0.27703500	3.85388700
H	7.36493600	-0.15649900	4.92070500
C	7.05755600	0.85817500	3.01421800
H	7.22475800	1.86334100	3.41980800
C	6.77716600	0.67699200	1.63734200

C	6.58198000	-0.61975900	1.11394300
H	6.37762700	-0.72733200	0.04172800
C	6.76019400	-4.33683600	2.34061100
H	7.80265800	-4.29572000	2.71027100
H	6.61187700	-5.29997700	1.82668400
H	6.08074500	-4.31371600	3.21407200
H	-3.78939300	-4.30530800	1.52557600
C	-5.17783300	-2.74350200	-0.54641500
H	-4.10727800	-2.84475100	-0.76541500
H	-5.21895000	-0.62125200	-1.02734300
C	-1.33237400	-0.63336300	-4.76071300
C	-2.65944500	-0.94052200	-5.17401300
C	-2.99007500	-1.08046500	-6.54897800
H	-4.01136400	-1.31153400	-6.86332600
C	-1.97737100	-0.91028500	-7.51713200
H	-2.22737100	-1.01450400	-8.57933300
C	-0.64934600	-0.60980500	-7.14551500
H	0.11917700	-0.48536700	-7.91321000
C	-0.33647800	-0.47642500	-5.76649500
C	-4.97335500	-1.43300900	-4.49326400
C	2.02521700	0.02900500	-6.25711900
O	2.72190300	6.88335800	0.84892700
O	-5.00638200	6.05230800	-1.36944700

O	-2.55859600	-0.25204800	5.10020500
O	2.07397600	0.81044700	4.86823900
N	-0.57287600	1.38462300	1.37055200
N	0.01624900	-1.34942000	1.58022900
N	1.49211200	5.07565400	-0.02220100
H	1.52949500	4.06979400	-0.21953700
N	-3.35064700	4.57893700	-0.57268500
H	-3.16953800	3.60102100	-0.32395300
C	-0.78886200	3.34067300	-0.19193500
C	-0.74870000	2.75705300	1.08993300
C	-0.90437800	3.52076500	2.32042600
H	-1.06776100	4.59703100	2.35856900
C	-0.80344200	2.62525300	3.36350400
H	-0.86433900	2.81846800	4.43344300
C	-0.56441900	1.31367300	2.78118800
C	-0.28082700	0.17399200	3.54901700
C	0.03151900	-1.06069600	2.96077500
C	0.41575000	-2.23527400	3.72871200
H	0.48741000	-2.25937600	4.81499300
C	0.65459200	-3.25056200	2.82778300
H	0.95434100	-4.28001400	3.02059600
C	0.39595000	-2.70780000	1.50092000
C	-0.93036200	4.83969800	-0.30801100

C	0.21363900	5.68956000	-0.18582100
C	0.07834100	7.10204700	-0.26968400
H	0.95948700	7.73145200	-0.14335800
C	-1.19594900	7.65773500	-0.49744500
H	-1.29802800	8.74648700	-0.57216600
C	-2.34391400	6.85084400	-0.62997700
H	-3.32813400	7.28087500	-0.81842700
C	-2.21374400	5.43979800	-0.52099000
C	2.67121100	5.67850600	0.43838300
C	3.88040600	4.78849700	0.40719900
H	3.69729500	3.73076900	0.17889900
C	5.02604800	5.08301300	1.40701200
H	5.49446400	4.21850800	1.88935300
H	4.86962600	5.95904500	2.04533500
C	5.27408200	5.34008500	-0.07670700
C	6.16194700	4.37841300	-0.84441400
C	7.48315900	4.11503600	-0.39370900
H	7.82122200	4.54795000	0.55641100
C	8.36359800	3.31534700	-1.16030300
H	9.38065500	3.12157700	-0.79936100
C	7.93295300	2.76817500	-2.39327100
H	8.61756400	2.15690100	-2.99342700
C	6.61481300	3.01891300	-2.84825000

H	6.27205000	2.59177500	-3.79777900
C	5.73834100	3.82009400	-2.07942900
H	4.72021800	4.01701300	-2.43855000
C	5.40147000	6.78833500	-0.57540700
H	6.44810000	7.12681000	-0.45529500
H	4.73574000	7.46260300	-0.01278700
H	5.14721000	6.85561700	-1.64998100
C	-4.66228600	4.90110600	-0.94587600
C	-5.64436900	3.77320100	-0.79853100
H	-5.21635100	2.78008600	-0.61134000
C	-6.92879500	3.81234800	-1.66185000
H	-7.03135300	4.69885100	-2.29667200
H	-7.25817900	2.86687900	-2.10554500
C	-7.05997700	4.01812500	-0.15455100
C	-7.63540800	2.89202600	0.68474900
C	-6.94515500	2.39450900	1.82124800
H	-5.94008100	2.77169200	2.04915600
C	-7.54060200	1.42241100	2.65879300
H	-6.99201500	1.04341400	3.52908800
C	-8.84106100	0.93877000	2.37699600
H	-9.30346300	0.18738100	3.02784500
C	-9.53800900	1.42788400	1.24525300
H	-10.54657800	1.06000800	1.02072100

C	-8.93754500	2.39610300	0.40622400
H	-9.48045200	2.77953900	-0.46716200
C	-7.43057300	5.41018500	0.38092400
H	-8.53124000	5.52374100	0.38090200
H	-6.98643400	6.20584300	-0.23922300
H	-7.07905200	5.53490100	1.42246400
C	-0.24189600	0.29511700	5.04632800
C	-1.40601300	0.07693400	5.83332900
C	-1.37134900	0.18814400	7.24925600
H	-2.26802300	0.02158200	7.85253200
C	-0.15129500	0.52088700	7.87725600
H	-0.11737100	0.61044600	8.96926000
C	1.02580600	0.74027200	7.12938600
H	1.95805900	0.99754200	7.63967900
C	0.97141300	0.62333400	5.71469800
C	-3.79153400	-0.53140500	5.84930000
C	3.37918900	1.09521300	5.48358800
H	2.92043200	0.21260000	-5.64700200
H	1.80604000	0.90650900	-6.89614500
H	2.18489500	-0.86738800	-6.88688400
H	-5.49987600	-1.53132400	-3.53313600
H	-5.01303800	-2.39423200	-5.04124100
H	-5.43735500	-0.63292400	-5.10229400

H	4.08420400	1.13978100	4.64106400
H	3.67813700	0.28462200	6.17604400
H	3.36347300	2.06411200	6.01967800
H	-4.53533900	-0.78622100	5.08015800
H	-4.12606600	0.35831100	6.41773500
H	-3.65644500	-1.38783100	6.53814400
C	2.66931200	-0.04086700	-0.79177400
C	4.89185300	-2.42206100	-4.62194000
C	3.87032700	-1.09011400	-2.79236700
C	3.78007500	-2.08577400	-3.82583500
C	6.13764300	-1.76817400	-4.42872000
C	2.69549900	-0.81322900	-1.98458700
C	6.24338600	-0.76550400	-3.42923400
C	1.62091900	0.28327300	0.06953400
C	5.13608600	-0.42906600	-2.62460700
H	5.23849100	0.37854600	-1.88982700
H	7.19505100	-0.24042900	-3.28109300
H	7.00532700	-2.03196900	-5.04447200
H	2.82128400	-2.59814000	-3.97543900
H	4.79573300	-3.19950000	-5.38969000
H	1.85035000	0.83476300	0.99496100
H	3.64185000	0.36314700	-0.45015800
H	6.72824800	1.54437500	0.96785500

$C_{[N2]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: -0.013594 Hartree
H_corr: 0.008229 Hartree
SCF: -109.5607783 Hartree
S: 45.93 Cal/Mol-Kelvin
H: -109.5525493 Hartree
G: -109.5743723 Hartree

Cartesian Coordinates:

N	0.00000000	0.00000000	0.57307000
N	0.00000000	0.00000000	-0.57307000

$C_{[2a]}$

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.099513 Hartree
H_corr: 0.138461 Hartree
SCF: -309.7966448 Hartree
S: 81.974 Cal/Mol-Kelvin
H: -309.6581838 Hartree
G: -309.6971318 Hartree

Cartesian Coordinates:

C	-1.80367300	-1.06029300	0.00000000
C	-0.41103500	-1.30025800	0.00000000
C	0.52368900	-0.22415100	0.00000000
C	-2.29347400	0.26752500	0.00000000
C	0.01393200	1.10796100	0.00000000
C	-1.37608400	1.34941800	0.00000000

H	-2.50370300	-1.90413500	0.00000000
H	-3.37285400	0.45913400	0.00000000
H	-0.03630000	-2.33249700	0.00000000
H	0.70708900	1.95750300	0.00000000
H	-1.74926300	2.38061400	0.00000000
C	1.97164800	-0.53998900	0.00000000
C	3.01280800	0.33989400	0.00000000
H	2.20893300	-1.61528500	0.00000000
H	2.86955800	1.42734700	-0.00000100
H	4.04967000	-0.01332600	0.00000000

Transition State TS2

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -357.3587 cm-1

G_corr: 1.581272 Hartree

H_corr: 1.867975 Hartree

SCF: -6636.550087 Hartree

S: 603.419 Cal/Mol-Kelvin

H: -6634.682112 Hartree

G: -6634.968815 Hartree

Cartesian Coordinates:

C	-1.49835700	0.48569100	-0.06481800
Co	0.33509700	-0.16949900	0.03557200
O	1.35714600	7.40668100	-2.35015300
O	6.91306900	1.48996900	-3.20617900

O	0.75079600	-2.78866500	-5.01359100
O	-2.99309100	-0.09994100	-3.82692000
N	0.75424400	0.48781200	-1.76639400
N	-0.27434800	-1.86094000	-0.74792100
N	1.54469400	5.21567000	-1.50121500
H	1.05325800	4.51292300	-0.93882800
N	4.86769900	1.68032800	-2.04653400
H	4.18802800	1.13754700	-1.50405800
C	2.27354700	2.42080600	-1.24544600
C	1.55596500	1.58969100	-2.13340300
C	1.50161600	1.80111900	-3.57460700
H	2.05185300	2.57968300	-4.10162000
C	0.63242400	0.85939800	-4.08834700
H	0.33799400	0.70203300	-5.12505300
C	0.19555200	0.02861100	-2.97636900
C	-0.55117400	-1.15272500	-3.13212300
C	-0.67184800	-2.08042500	-2.08221900
C	-1.12461500	-3.45187600	-2.25927000
H	-1.46903700	-3.86662600	-3.20526800
C	-0.97031900	-4.09161900	-1.04498400
H	-1.17478200	-5.13134300	-0.79107700
C	-0.49479800	-3.09268700	-0.09548800
C	3.20763500	3.45109400	-1.83052300

C	2.81678200	4.81652400	-2.00671300
C	3.68863300	5.73339500	-2.65739300
H	3.35792800	6.76191800	-2.80762300
C	4.94687100	5.28456700	-3.10920700
H	5.61339500	5.99378400	-3.61373400
C	5.37508300	3.95321200	-2.92717100
H	6.34867200	3.60507200	-3.27590700
C	4.50265300	3.03586100	-2.28255300
C	0.89658500	6.45403700	-1.64119200
C	-0.38735200	6.55649600	-0.87147900
H	-0.77566400	5.61994100	-0.45188600
C	-1.45751600	7.56797300	-1.34323400
H	-2.49462800	7.21782900	-1.33064700
H	-1.17276800	8.17876400	-2.20640500
C	-0.73226200	7.84636400	-0.03077200
C	-1.46326900	7.62398900	1.28069400
C	-2.77292200	8.13522100	1.47908600
H	-3.28588000	8.63073800	0.64548900
C	-3.41279400	8.02030200	2.73641600
H	-4.42295600	8.42461600	2.87434400
C	-2.74758900	7.39422100	3.81818400
H	-3.23771600	7.31825600	4.79660100
C	-1.44218000	6.87530000	3.62912800

H	-0.91572900	6.39151600	4.46138300
C	-0.80833900	6.98995800	2.37055300
H	0.20172200	6.58504400	2.22823600
C	0.26998400	9.00961300	0.02994900
H	-0.27002000	9.94945400	0.25312600
H	0.80679600	9.12030800	-0.92653200
H	1.01284900	8.84937800	0.83416700
C	5.99767700	0.97749800	-2.48471200
C	6.01212000	-0.45505200	-2.03123300
H	5.40243200	-0.67893800	-1.14697300
C	7.30883500	-1.27452400	-2.17672200
H	8.14347500	-0.74485100	-2.64844400
H	7.57173800	-1.92709900	-1.33815900
C	6.12208300	-1.63422500	-3.07003700
C	5.30924700	-2.87469800	-2.74786000
C	3.88885000	-2.82301200	-2.74609200
H	3.37966200	-1.86994100	-2.93783100
C	3.12132300	-3.98495400	-2.49605100
H	2.02679700	-3.92212000	-2.50000800
C	3.76749400	-5.22195100	-2.24803500
H	3.17569300	-6.12245500	-2.04583100
C	5.18216900	-5.28640100	-2.25550700
H	5.68722800	-6.24091300	-2.06417900

C	5.94589500	-4.12070200	-2.50547400
H	7.04200700	-4.17255300	-2.51296800
C	6.20343600	-1.30852800	-4.56842200
H	6.70871100	-2.13550000	-5.10267300
H	6.76876800	-0.37698300	-4.74236000
H	5.19211800	-1.19217000	-5.00212000
C	-1.15446000	-1.46594600	-4.47021000
C	-0.49844300	-2.29377300	-5.42272500
C	-1.08681900	-2.57304000	-6.68536600
H	-0.57963800	-3.20783600	-7.41706500
C	-2.34686900	-2.01311400	-6.98985300
H	-2.80676300	-2.22593000	-7.96192200
C	-3.02591000	-1.18366800	-6.07098400
H	-3.99929800	-0.75902600	-6.33147100
C	-2.42089200	-0.91248000	-4.81439600
C	1.50754700	-3.62394600	-5.96059300
C	-4.26053600	0.58343800	-4.13793700
O	-4.76562400	-5.89324600	2.42648000
O	3.36886900	-6.35897600	2.97363100
O	2.84826800	0.97320300	5.02349100
O	-1.59359000	2.38239200	4.04611000
N	0.17856900	-0.93374900	1.83463400
N	1.29900300	1.36665300	0.81505500

N	-2.99687700	-4.53198800	1.66840400
H	-2.79109500	-3.65301400	1.18167600
N	1.86430500	-4.86546900	1.93906000
H	1.82377700	-3.97936700	1.42530000
C	-0.39637400	-3.31790200	1.29236500
C	-0.16169200	-2.25477300	2.19012100
C	-0.30536400	-2.37518000	3.63525400
H	-0.55022800	-3.30186300	4.15276000
C	-0.09666800	-1.11866700	4.16698900
H	-0.11822600	-0.81201400	5.21194900
C	0.23565600	-0.23518800	3.05886000
C	0.69247200	1.08244200	3.22552600
C	1.28734200	1.78306400	2.16082500
C	2.08723400	2.98657600	2.33224800
H	2.23943400	3.49283200	3.28430900
C	2.62972300	3.29251100	1.09915300
H	3.30626100	4.10470700	0.83431300
C	2.10116200	2.32007200	0.15053300
C	-0.56688200	-4.70669500	1.85656500
C	-1.85757600	-5.28021800	2.08452400
C	-1.97665600	-6.55861300	2.69771300
H	-2.97163300	-6.96612200	2.88130200
C	-0.80767700	-7.25664900	3.06504500

H	-0.90419100	-8.23925900	3.54146700
C	0.48047300	-6.73091200	2.83488800
H	1.38543500	-7.27008600	3.11942100
C	0.59950300	-5.45347200	2.22464900
C	-4.35416500	-4.86243900	1.80090400
C	-5.28425400	-3.89851900	1.12464400
H	-4.84369000	-2.94679600	0.80241300
C	-6.75322900	-3.83049800	1.60101900
H	-7.18796400	-2.82984400	1.68772100
H	-7.01587000	-4.53712900	2.39545600
C	-6.46914500	-4.41770800	0.22212200
C	-6.79251400	-3.59685800	-1.01258500
C	-8.06575700	-2.98665500	-1.16366100
H	-8.78897500	-3.04856700	-0.34091600
C	-8.40943900	-2.31493900	-2.36114400
H	-9.39932000	-1.85392200	-2.46472800
C	-7.48240000	-2.24735500	-3.42951100
H	-7.75415200	-1.73911900	-4.36284400
C	-6.20656500	-2.84744900	-3.28632800
H	-5.48098300	-2.80438700	-4.10805300
C	-5.86697000	-3.51521600	-2.08714100
H	-4.87678300	-3.97621700	-1.98047500
C	-6.65838000	-5.92711500	0.00446400

H	-7.71650000	-6.13322600	-0.24578300
H	-6.38527600	-6.49530000	0.90890500
H	-6.03749200	-6.28540100	-0.83841900
C	3.14604800	-5.30559300	2.29395900
C	4.23796400	-4.39588900	1.80552400
H	3.97783700	-3.75742100	0.95205800
C	5.69823200	-4.88503400	1.85703500
H	5.84025600	-5.87968600	2.29313400
H	6.32309200	-4.65151300	0.98922500
C	5.27699000	-3.76481700	2.80741100
C	5.70745000	-2.34192600	2.50196600
C	4.77279800	-1.27438400	2.58615200
H	3.72483600	-1.48764400	2.83236400
C	5.17508900	0.06163200	2.35172700
H	4.43739400	0.86952600	2.42277600
C	6.52579100	0.35022900	2.03335300
H	6.83899300	1.38359400	1.84339400
C	7.46703300	-0.70492700	1.95480800
H	8.51340700	-0.48732100	1.70879200
C	7.05950500	-2.04041400	2.18937900
H	7.79045300	-2.85674000	2.13030500
C	5.15724000	-4.07668900	4.30615000
H	6.14419900	-3.95667100	4.79206700

H	4.80507000	-5.10951600	4.46989000
H	4.44970600	-3.38242300	4.79804000
C	0.62898600	1.71846800	4.58377400
C	1.72224300	1.66834100	5.49292800
C	1.64731700	2.28537600	6.77041200
H	2.48796000	2.24299300	7.46831700
C	0.46251200	2.96204400	7.13331300
H	0.39981200	3.44303900	8.11634100
C	-0.64398400	3.02997600	6.25887400
H	-1.55140400	3.55783000	6.56468000
C	-0.55366100	2.39957100	4.98930000
C	4.01184900	0.85714800	5.91818400
C	-2.83849400	3.09828600	4.37442200
H	-4.44412900	1.24261900	-3.27788500
H	-5.08453800	-0.14786600	-4.24298600
H	-4.16580100	1.19827800	-5.05216400
H	2.43459800	-3.87865500	-5.42708600
H	1.74271300	-3.06249000	-6.88531800
H	0.95066400	-4.54754400	-6.21142600
H	-3.50676700	2.90430800	3.52359500
H	-2.65416900	4.18483200	4.46990300
H	-3.29479700	2.70111400	5.30153000
H	4.75133200	0.28522900	5.33953800

H	3.74741500	0.31123400	6.84427800
H	4.42137700	1.85419500	6.17142900
C	-2.47523000	0.20073000	0.95661300
C	-7.36481700	0.10689700	2.11906800
C	-4.92729000	0.08080200	1.67231800
C	-6.28217500	0.15288200	1.21494300
C	-7.12738700	-0.02565100	3.51018300
C	-3.84141600	0.15297200	0.68829300
C	-5.79088800	-0.11154800	3.98103000
C	-4.70686100	-0.05435200	3.08182000
H	-3.68369200	-0.12314700	3.46925600
H	-5.59882900	-0.22868500	5.05453100
H	-7.96604900	-0.06662400	4.21488100
H	-6.47465700	0.24717900	0.13837700
H	-8.39225800	0.17440700	1.74164400
H	-4.15342500	0.21772400	-0.36592200
H	-2.13402500	0.14892800	1.99743800
C	-4.86799800	4.51352400	-3.27323300
C	-4.40219300	4.10466800	-2.00560000
C	-4.00680300	4.46216900	-4.39918300
C	-2.67867800	3.98777800	-4.23551200
C	-2.21228100	3.57505500	-2.97169700
C	-3.06239100	3.63003400	-1.81920400

H	-1.18260300	3.21222400	-2.87634200
H	-5.89585900	4.88000900	-3.38467400
H	-5.07040300	4.15710200	-1.13551500
H	-4.35938800	4.79388700	-5.38289100
H	-2.00337800	3.94869400	-5.09863500
C	-2.61922800	3.27007500	-0.47084500
C	-1.37934400	2.74910200	-0.09607700
H	-3.37373700	3.39778600	0.31969500
H	-1.84384200	0.43245500	-1.11443100
H	-0.55505300	2.68684700	-0.81485000
H	-1.09764100	2.73515300	0.96041500

Intermediate D

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.586685 Hartree

H_corr: 1.870851 Hartree

SCF: -6636.584927 Hartree

S: 598.077 Cal/Mol-Kelvin

H: -6634.714076 Hartree

G: -6634.998242 Hartree

Cartesian Coordinates:

C	-1.39383800	1.18865200	-0.23466700
Co	0.26885400	-0.07762900	0.06662200
O	2.91195600	7.28138900	-1.49643000
O	7.26700500	0.48524200	-2.82366600
O	0.66094600	-2.52479800	-5.12803200
O	-2.76691400	0.55901100	-3.95036600
N	0.97362200	0.48177500	-1.68745500
N	-0.67215300	-1.57259000	-0.82085100
N	2.51854900	4.97319500	-1.20590800
H	1.81150800	4.30192600	-0.88891800
N	5.23590800	0.95156700	-1.71838700
H	4.43304100	0.49996100	-1.26832300
C	2.75406600	2.11278800	-0.99250500
C	2.00483000	1.40610600	-1.95841500
C	2.14501200	1.61365600	-3.39446200
H	2.88923300	2.26510400	-3.85103100
C	1.16441600	0.85994100	-4.00752200
H	0.95072000	0.75868200	-5.07053800
C	0.45588000	0.14444500	-2.95781900
C	-0.52777000	-0.82665300	-3.20808300
C	-0.97341300	-1.69227100	-2.19403800
C	-1.71359100	-2.91642400	-2.45542500
H	-2.04317300	-3.23412900	-3.44360700

C	-1.83661100	-3.58054100	-1.25035700
H	-2.28969300	-4.55139100	-1.05016800
C	-1.23180300	-2.72827900	-0.23375600
C	3.89824100	2.97747900	-1.46549000
C	3.76792900	4.39907300	-1.57590300
C	4.84774700	5.18974900	-2.05577300
H	4.72096000	6.27114700	-2.12702500
C	6.04767300	4.55231000	-2.43369200
H	6.87800200	5.16177200	-2.80901700
C	6.21000900	3.15423300	-2.34538400
H	7.13361300	2.66010700	-2.65074700
C	5.13356900	2.36562200	-1.85599800
C	2.13908100	6.32276700	-1.17270100
C	0.73051100	6.53081400	-0.69652400
H	0.07351600	5.65397100	-0.74911000
C	0.04519700	7.89080900	-0.94322700
H	-1.00211700	7.86133100	-1.26059200
H	0.67034600	8.64530600	-1.43260900
C	0.41065100	7.51299100	0.49136200
C	-0.68747600	7.05917000	1.43475300
C	-1.85046800	7.84809500	1.63533700
H	-1.97530800	8.77500100	1.06152600
C	-2.84323800	7.44744400	2.56156500

H	-3.73597100	8.06790900	2.70749300
C	-2.68567500	6.24894400	3.29963700
H	-3.45590200	5.94147100	4.01793900
C	-1.52804800	5.45383900	3.10722900
H	-1.38942500	4.51965200	3.66433600
C	-0.53748700	5.86280300	2.18522800
H	0.36006400	5.24654100	2.04327400
C	1.55708700	8.26365500	1.18422200
H	1.16971100	9.19313000	1.64303700
H	2.35084300	8.52638700	0.46441700
H	2.00047200	7.64929700	1.99054100
C	6.24026200	0.09052200	-2.18205200
C	5.98135900	-1.35339400	-1.85634300
H	5.30360000	-1.53662800	-1.01377700
C	7.12807000	-2.36913400	-2.02783300
H	8.05966300	-1.95384400	-2.42719500
H	7.23843600	-3.11991000	-1.23902400
C	5.93935000	-2.45112300	-2.98470200
C	4.92128400	-3.55937600	-2.78572500
C	3.52971000	-3.27228000	-2.79917300
H	3.18940400	-2.23588200	-2.91719600
C	2.57466700	-4.30650700	-2.65683500
H	1.50642300	-4.06070000	-2.67173700

C	3.00052100	-5.64978500	-2.50489400
H	2.26285300	-6.45250700	-2.38762100
C	4.38518200	-5.94823900	-2.49939000
H	4.72091600	-6.98614300	-2.38497400
C	5.33685000	-4.90961400	-2.64021900
H	6.40927500	-5.14199100	-2.63397500
C	6.13816700	-2.03177700	-4.44808600
H	6.52111500	-2.88894500	-5.03404200
H	6.85795900	-1.19910400	-4.52768900
H	5.17980100	-1.71242400	-4.89986800
C	-1.07548900	-0.98099700	-4.59752900
C	-0.47729100	-1.82931000	-5.56893100
C	-1.01613700	-1.94311500	-6.87899800
H	-0.55323900	-2.59404000	-7.62568300
C	-2.16816800	-1.19706400	-7.21110500
H	-2.58668600	-1.27938100	-8.22102700
C	-2.79197600	-0.34795100	-6.27139100
H	-3.68141800	0.22256400	-6.55239300
C	-2.23914800	-0.24703500	-4.96668700
C	1.34550900	-3.40396500	-6.09033800
C	-3.93324200	1.40156200	-4.26567400
O	-6.20319900	-4.34821900	2.05510100
O	1.52702400	-6.90639100	2.89563200

O	3.13714100	0.24675800	4.72991500
O	-1.18813900	2.30004400	4.84356300
N	-0.18505900	-0.84210000	1.83341800
N	1.44737700	1.22149200	0.96870000
N	-4.12311400	-3.59693000	1.24162400
H	-3.68415800	-2.88292100	0.65109900
N	0.48050200	-5.08298700	1.82806100
H	0.67988600	-4.21384700	1.32221800
C	-1.28643100	-3.00148300	1.14773200
C	-0.84037400	-2.06536300	2.10473900
C	-1.02206100	-2.24509400	3.53997800
H	-1.49380000	-3.11405100	3.99671700
C	-0.49928700	-1.12782600	4.15374000
H	-0.44887500	-0.90131800	5.21756400
C	0.03631100	-0.27124600	3.10558400
C	0.78252900	0.89181000	3.36934300
C	1.47794200	1.55665300	2.34220600
C	2.45834800	2.60398400	2.59163500
H	2.66367700	3.03071400	3.57212600
C	3.07883000	2.87777600	1.39086900
H	3.88566800	3.58053800	1.18604800
C	2.43979000	2.04214000	0.38132500
C	-1.82439100	-4.32192500	1.64381900

C	-3.22625200	-4.57361600	1.77051300
C	-3.69133100	-5.77346600	2.37545000
H	-4.76463300	-5.92605100	2.49693800
C	-2.75159400	-6.72842600	2.81695400
H	-3.11211300	-7.65023300	3.28813400
C	-1.36304600	-6.53865800	2.65676400
H	-0.63528400	-7.28250400	2.98544400
C	-0.90049200	-5.33511600	2.06002000
C	-5.52210600	-3.55232000	1.33001000
C	-6.15188900	-2.49070200	0.47501300
H	-5.47359600	-1.72218300	0.08363000
C	-7.58364000	-2.01792400	0.80824300
H	-7.77263200	-0.94171600	0.74274900
H	-8.05782600	-2.53354600	1.65004700
C	-7.37170800	-2.82917500	-0.46697600
C	-7.40805800	-2.11680900	-1.80682600
C	-8.49440500	-1.26614500	-2.14252600
H	-9.27250900	-1.07052400	-1.39412700
C	-8.58341600	-0.67910700	-3.42712000
H	-9.43042300	-0.02702700	-3.67240100
C	-7.58519900	-0.93799600	-4.39757300
H	-7.65986200	-0.49241900	-5.39703000
C	-6.49381400	-1.78079400	-4.07059900

H	-5.71504700	-1.98700100	-4.81503400
C	-6.40888700	-2.36482300	-2.78548100
H	-5.56106700	-3.01561300	-2.53615000
C	-7.90951100	-4.26695900	-0.52936200
H	-8.96946600	-4.25046600	-0.84660900
H	-7.83728300	-4.76081000	0.45384100
H	-7.34637100	-4.86705100	-1.26884600
C	1.59708600	-5.84004600	2.20380700
C	2.89419400	-5.25860400	1.71280600
H	2.81826100	-4.60266200	0.83642800
C	4.17356300	-6.11420800	1.80119600
H	4.04401500	-7.09779400	2.26549200
H	4.84947800	-6.07533400	0.94102600
C	4.04984600	-4.89250100	2.71295100
C	4.85315600	-3.64939100	2.37712800
C	4.22126400	-2.38362400	2.25148200
H	3.13203700	-2.30657900	2.35664900
C	4.98109300	-1.21652800	1.99836300
H	4.47381500	-0.24809200	1.91581200
C	6.39028500	-1.29943900	1.87386300
H	6.98022100	-0.39781300	1.67162800
C	7.03106100	-2.55635500	2.00393000
H	8.12129700	-2.62666900	1.90784400

C	6.26682100	-3.72082500	2.25444100
H	6.76341400	-4.69471500	2.35143400
C	3.83709100	-5.11310100	4.21773800
H	4.81487200	-5.24133500	4.71986900
H	3.22424800	-6.01174600	4.40415600
H	3.33150800	-4.24129300	4.67466800
C	0.99439800	1.31063000	4.80166300
C	2.20288000	0.97260100	5.48460100
C	2.41827400	1.33463000	6.84094700
H	3.34823600	1.07296400	7.35219300
C	1.40790200	2.03261400	7.53393400
H	1.56846200	2.31613600	8.58042900
C	0.19342500	2.36815000	6.90233400
H	-0.57699400	2.91029100	7.45653100
C	-0.00480100	2.00313800	5.54361000
C	4.38122400	-0.16823100	5.40090800
C	-2.34066900	2.75903400	5.64081000
H	-4.12136200	1.97281200	-3.34623700
H	-4.81443500	0.77876800	-4.51115400
H	-3.70334000	2.09982900	-5.09242200
H	2.18893300	-3.82910000	-5.52770100
H	1.71852800	-2.82798700	-6.95920300
H	0.67534300	-4.21508700	-6.43542500

H	-3.18389200	2.76873000	4.93638000
H	-2.16694700	3.77407300	6.04899700
H	-2.55544400	2.05336400	6.46528200
H	4.93417800	-0.73340100	4.63793800
H	4.16416200	-0.81748200	6.27098300
H	4.97131000	0.71148400	5.72343900
C	-2.43617400	0.80332600	0.73399300
C	-6.07085800	1.96072000	3.91884100
C	-4.11367800	1.24006900	2.58560700
C	-4.96501900	2.26858400	3.09511400
C	-6.34506100	0.61464500	4.26673200
C	-2.99382500	1.60948800	1.70080400
C	-5.49937500	-0.41617400	3.78346400
C	-4.39768300	-0.10884100	2.95696000
H	-3.72874700	-0.91308800	2.63017700
H	-5.69595600	-1.45903400	4.05797800
H	-7.20033900	0.37142200	4.90786500
H	-4.76687100	3.31141700	2.81268400
H	-6.71905200	2.76583700	4.28598000
H	-2.63930200	2.64526700	1.80001600
H	-2.83342300	-0.21467200	0.60746900
C	-3.41969900	5.48545400	-3.81059500
C	-3.31177100	4.88336300	-2.54565100

C	-2.39489500	5.30538700	-4.78078700
C	-1.26416500	4.50684200	-4.45885900
C	-1.14532100	3.90015700	-3.19551800
C	-2.16617000	4.07484200	-2.19049900
H	-0.27278100	3.27181000	-2.98725600
H	-4.29548000	6.10127200	-4.04901000
H	-4.10126400	5.03285500	-1.79724500
H	-2.47440600	5.78075200	-5.76525300
H	-0.47253800	4.36028500	-5.20323100
C	-2.09495400	3.51070600	-0.87476200
C	-0.97100100	2.68023300	-0.29898700
H	-2.96335100	3.67588400	-0.22217900
H	-1.60264600	0.78807500	-1.24106500
H	-0.06320500	2.76391100	-0.91857800
H	-0.71598400	3.03755000	0.71743900

Intermediate E

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

$E_{[3a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.226804 Hartree

H_corr: 0.286779 Hartree

SCF: -657.7187376 Hartree

S: 126.229 Cal/Mol-Kelvin

H: -657.4319586 Hartree

G: -657.4919336 Hartree

Cartesian Coordinates:

H	6.76365600	1.13211600	-0.27473400
H	5.81342800	-0.77910500	-1.60761600
C	5.72748000	0.81094600	-0.11713200
C	5.19008000	-0.26453500	-0.86632100
C	4.91311700	1.46540200	0.83814200
H	5.31788200	2.29840800	1.42547900
C	3.85512600	-0.68117800	-0.66265900
H	3.46243100	-1.52039500	-1.25159300
C	3.57723000	1.04857800	1.03897600
C	3.02445000	-0.03120100	0.29436000
H	2.95307900	1.56298700	1.78136500
H	1.81777500	-2.61617800	-0.04593200
C	1.60305100	-0.43472400	0.53027000
C	1.09520300	-1.87249800	0.30598700
C	0.64367900	-0.79188900	-0.67631000
H	0.37345000	-2.26520400	1.02875700

C -0.74046500 -0.24229900 -0.72100600

H -1.68423900 -1.63154300 0.57474000

H -0.86075400 0.64013600 -1.36832400

C -1.82060200 -0.72458300 -0.03394500

C -3.19053700 -0.16823500 -0.02681300

H -3.96251800 -1.81504800 1.17863000

H -2.78354600 1.63028700 -1.21109700

C -4.21590700 -0.87697100 0.66688100

C -3.54770600 1.04995800 -0.68058100

C -5.54480500 -0.39850700 0.70185500

C -4.87447900 1.52800700 -0.64758900

H -6.31418400 -0.96383400 1.24112800

C -5.88274200 0.80767300 0.04271000

H -5.12654700 2.46644500 -1.15618400

H -6.91213500 1.18368300 0.06774000

H 1.10164900 0.11120000 1.33838300

H 1.16753400 -0.77761500 -1.64169700

<u>Transition State TS2’</u>

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -459.3972 cm-1

G_corr: 1.581749 Hartree

H_corr: 1.867403 Hartree

SCF: -6636.526995 Hartree

S: 601.209 Cal/Mol-Kelvin

H: -6634.659592 Hartree

G: -6634.945246 Hartree

Cartesian Coordinates:

C	-8.12767600	-1.09056000	-0.74921300
C	-1.23042300	0.78724700	0.02161000
Co	0.54876900	0.06406300	0.03078200
O	0.44834700	7.31173200	-3.30763800
O	6.77314700	2.19692100	-3.62868200
O	1.14449700	-2.96325700	-4.61714600
O	-2.96102100	-0.61400800	-3.96563100
N	0.78106500	0.58879300	-1.85919400
N	-0.03866500	-1.72336500	-0.57211900
N	0.94349900	5.27164600	-2.23855700
H	0.54499800	4.53381800	-1.64790000
N	4.76026800	2.24273300	-2.40031500
H	4.16423200	1.66865500	-1.79515000
C	2.09648900	2.71118600	-1.60529800
C	1.42402600	1.73549500	-2.36787600
C	1.26970100	1.81574000	-3.81473100
H	1.69280000	2.60510400	-4.43462500

C	0.49638500	0.73988300	-4.19587100
H	0.16664100	0.46147000	-5.19571500
C	0.21412100	-0.03193600	-2.99469100
C	-0.41360200	-1.28813700	-3.01464000
C	-0.44651000	-2.10407600	-1.86943400
C	-0.80277600	-3.51390000	-1.90149000
H	-1.12457600	-4.04459000	-2.79631100
C	-0.58561300	-4.01800100	-0.63425800
H	-0.70226700	-5.04133400	-0.27798000
C	-0.15993900	-2.90076600	0.19923100
C	2.87204000	3.78133800	-2.33486600
C	2.28319200	5.04005700	-2.66942100
C	3.01980400	6.00609500	-3.40876600
H	2.54441100	6.95338400	-3.66611000
C	4.33764400	5.70254500	-3.81006500
H	4.90215400	6.44642200	-4.38422700
C	4.94913300	4.47055300	-3.49816300
H	5.96287400	4.23008000	-3.82240000
C	4.21282500	3.50786500	-2.75637400
C	0.10054100	6.34476300	-2.55466100
C	-1.26431900	6.25646900	-1.93187700
H	-1.51933600	5.29628800	-1.46547100
C	-2.42782400	7.00555500	-2.62732600

H	-3.38590100	6.47962800	-2.69550100
H	-2.13945500	7.58755400	-3.50900800
C	-1.94421900	7.51265500	-1.27149300
C	-2.80859900	7.25072100	-0.05171200
C	-4.17066200	7.65339200	-0.04124000
H	-4.60739500	8.08713600	-0.94962700
C	-4.95990900	7.50677700	1.12405400
H	-6.00899400	7.82627700	1.11768900
C	-4.39514300	6.95393200	2.29924500
H	-5.00285900	6.84521000	3.20552200
C	-3.03916300	6.54365100	2.29655400
H	-2.59469300	6.11036900	3.20016600
C	-2.25271400	6.69374900	1.13065700
H	-1.20157100	6.37862000	1.13616900
C	-1.18383900	8.84577100	-1.19834800
H	-1.90733000	9.68030200	-1.13165200
H	-0.54916900	8.98954700	-2.08821700
H	-0.54288100	8.88239900	-0.29737600
C	5.95411900	1.64460700	-2.82587900
C	6.16186500	0.27064200	-2.25256300
H	5.64591400	0.06777100	-1.30592900
C	7.53002700	-0.41422300	-2.42980100
H	8.26379700	0.15534700	-3.01033500

H	7.92158400	-0.95500200	-1.56251400
C	6.33165400	-0.98123600	-3.19149500
C	5.69584600	-2.26845400	-2.69921400
C	4.28842000	-2.36101300	-2.52750900
H	3.65914200	-1.48143600	-2.71334100
C	3.68601500	-3.57452800	-2.11870300
H	2.59742600	-3.62467100	-1.99870300
C	4.48698900	-4.71937400	-1.88048600
H	4.02393500	-5.65938700	-1.55788700
C	5.89039000	-4.64010300	-2.05629700
H	6.51490200	-5.52356300	-1.87613900
C	6.48822600	-3.42345000	-2.46390700
H	7.57564800	-3.36252900	-2.59791100
C	6.26823000	-0.79039700	-4.71372000
H	6.82353900	-1.60484500	-5.21664900
H	6.71211100	0.17515800	-5.01143700
H	5.22157000	-0.82132000	-5.07162300
C	-0.93075000	-1.82255000	-4.32205800
C	-0.12757300	-2.67405400	-5.13534100
C	-0.59978900	-3.17259800	-6.37884500
H	0.02179200	-3.82475700	-6.99805900
C	-1.89161000	-2.80875700	-6.81413600
H	-2.26266100	-3.18887100	-7.77295400

C	-2.71345500	-1.96151800	-6.04112200
H	-3.70748900	-1.68720600	-6.40384800
C	-2.22558100	-1.46999500	-4.79949200
C	2.04480500	-3.79831300	-5.43052100
C	-4.28058600	-0.16283600	-4.44654700
O	-4.21543300	-5.65996200	3.05133200
O	3.94690000	-5.63995500	3.52929500
O	3.62089500	1.68529500	4.44357600
O	-1.03757500	2.73212100	4.35878700
N	0.53312200	-0.55094300	1.89687900
N	1.44362800	1.72159400	0.61267800
N	-2.51603800	-4.36637500	2.05302300
H	-2.35427100	-3.61397400	1.37578200
N	2.35537200	-4.34990800	2.36124800
H	2.26336300	-3.54338800	1.73532800
C	0.00224600	-2.99139500	1.59584600
C	0.24371800	-1.84544700	2.38106000
C	0.22276100	-1.85747700	3.83803200
H	0.02398400	-2.74137300	4.44215800
C	0.48278600	-0.57021400	4.25482700
H	0.55159500	-0.18703000	5.27170100
C	0.70292400	0.23105600	3.06057800
C	1.15359300	1.56186200	3.09856900

C	1.55850300	2.22502100	1.92706500
C	2.24273100	3.50915600	1.92772100
H	2.45421600	4.08936900	2.82456400
C	2.58020300	3.79169200	0.62034000
H	3.11556800	4.65394400	0.22393500
C	2.05465600	2.70522600	-0.19744900
C	-0.08356200	-4.32130000	2.30546100
C	-1.33641500	-4.94182800	2.61079200
C	-1.38230400	-6.11385000	3.41533800
H	-2.35168400	-6.54569600	3.66783100
C	-0.17560900	-6.67863100	3.87666300
H	-0.21472100	-7.57938500	4.50021500
C	1.07977800	-6.12535100	3.55040400
H	2.01486100	-6.56820100	3.89681800
C	1.12482100	-4.94691200	2.75797600
C	-3.84508000	-4.79284900	2.19598700
C	-4.79057100	-4.17336300	1.20620000
H	-4.43108000	-3.26948700	0.69801200
C	-6.31072500	-4.24259000	1.46206300
H	-6.89119300	-3.34854800	1.21187200
H	-6.60819600	-4.76815000	2.37604600
C	-5.72267500	-5.09658900	0.33618700
C	-5.94661300	-4.68613400	-1.10767800

C	-7.25886100	-4.72113000	-1.65303600
H	-8.10399300	-4.96843700	-0.99771100
C	-7.48108400	-4.44847700	-3.02266900
H	-8.49949200	-4.47971200	-3.42836800
C	-6.39034000	-4.13738300	-3.87178700
H	-6.56159600	-3.93349800	-4.93560000
C	-5.07936100	-4.09571400	-3.33855100
H	-4.22878700	-3.85774100	-3.98893400
C	-4.86158100	-4.37117400	-1.96699700
H	-3.84226300	-4.34364800	-1.56167300
C	-5.67382400	-6.62212100	0.51869500
H	-6.63666100	-7.06376700	0.19885200
H	-5.49080900	-6.89144300	1.57202500
H	-4.87591600	-7.06716000	-0.10540900
C	3.66449400	-4.70396000	2.71336500
C	4.71135200	-3.86810200	2.03123700
H	4.39030200	-3.35442500	1.11644300
C	6.17203200	-4.36646100	2.04212500
H	6.34162800	-5.29350500	2.60032500
H	6.73229400	-4.25853500	1.10795700
C	5.82265200	-3.11989700	2.85432200
C	6.24929400	-1.76508200	2.31930400
C	5.31310200	-0.70550200	2.18508700

H	4.25777400	-0.87781100	2.43014400
C	5.72623000	0.57439400	1.74346800
H	4.98801600	1.38019200	1.65579000
C	7.08843600	0.81445200	1.43583400
H	7.40962000	1.80326000	1.08797800
C	8.03146700	-0.23392200	1.57316900
H	9.08746500	-0.05393100	1.33786500
C	7.61328500	-1.51264100	2.01236300
H	8.34379400	-2.32510500	2.11572800
C	5.81445100	-3.21278900	4.38706100
H	6.83498700	-3.03868700	4.77807400
H	5.47157400	-4.20665400	4.72194100
H	5.14723800	-2.44524600	4.82317200
C	1.29695000	2.24280500	4.43246200
C	2.54824200	2.29715400	5.11201600
C	2.67394200	2.92034000	6.38261900
H	3.63672900	2.95884800	6.89874600
C	1.53089700	3.48829400	6.98347100
H	1.62160100	3.96860600	7.96457700
C	0.27310800	3.44649100	6.34660600
H	-0.59977700	3.89011900	6.83244600
C	0.16571700	2.82371000	5.07433400
C	4.92797400	1.67087500	5.12329000

C	-2.26531100	3.19990000	5.02586800
H	-4.65171600	0.50855900	-3.65895600
H	-4.97344300	-1.01824600	-4.55983400
H	-4.18527700	0.38387500	-5.40436100
H	2.96827000	-3.86956600	-4.83855900
H	2.25427100	-3.32028900	-6.40680800
H	1.61781500	-4.80774400	-5.58781800
H	-3.07431600	2.98602900	4.31445900
H	-2.21504500	4.28758500	5.23049100
H	-2.43585100	2.64746400	5.96936800
H	5.59448200	1.13279300	4.43495800
H	4.86569900	1.13478200	6.08990300
H	5.30299500	2.69995800	5.28567800
C	-1.79868200	1.52954800	1.00009300
C	-6.01633900	2.71191600	3.42163200
C	-4.12585500	1.96870000	2.01194000
C	-5.04899500	2.97823800	2.42895100
C	-6.08928200	1.42846500	4.02251200
C	-3.12497400	2.25553900	0.96109700
C	-5.18060700	0.41783400	3.61844000
C	-4.21198200	0.68251400	2.62601700
H	-3.50519500	-0.09739700	2.31886800
H	-5.23187000	-0.57726300	4.07651200

H	-6.84401600	1.21883400	4.78966400
H	-4.98998700	3.97691600	1.97534200
H	-6.71523000	3.50016300	3.72802700
H	-3.01347900	3.33420300	0.74574300
H	-1.25631800	1.70166900	1.94606200
H	-1.72238400	0.53384900	-0.92969300
H	-4.20590800	-0.18335000	-1.32459600
C	-4.79356100	0.69871600	-1.03086100
H	-6.11158900	-1.63742600	-1.34368100
H	-8.52644200	-2.09214000	-0.94762300
C	-6.76105900	-0.83315800	-0.97310800
C	-6.19883500	0.46864300	-0.74019500
C	-8.98482300	-0.06106200	-0.28144400
H	-10.04852800	-0.26111500	-0.10664700
C	-7.08423000	1.49588000	-0.26512300
C	-8.44830300	1.23133400	-0.04024800
H	-9.10182600	2.03117900	0.32912800
H	-6.69202600	2.49780300	-0.05997100
H	-4.70651500	2.86428900	-0.87153300
C	-4.10930400	1.94415000	-0.93765500
H	-3.17706700	2.05584700	-1.50697400

Intermediate D'

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.585572 Hartree

H_corr: 1.87052 Hartree

SCF: -6636.563203 Hartree

S: 599.725 Cal/Mol-Kelvin

H: -6634.692683 Hartree

G: -6634.977631 Hartree

Cartesian Coordinates:

C	-8.00779000	-0.92104800	-1.22234000
C	-1.23913400	0.76212500	0.01073500
Co	0.55327600	0.06276500	0.03449400
O	0.33495300	7.33004700	-3.22746400
O	6.73777000	2.31248600	-3.66254600
O	1.13747700	-2.91579900	-4.69813800
O	-2.97872500	-0.66877100	-3.83223900
N	0.78616500	0.58871300	-1.85437800
N	-0.01356400	-1.73135200	-0.56670800
N	0.86684000	5.27577900	-2.20370600
H	0.48326700	4.52205800	-1.62331600

N	4.72945700	2.31072200	-2.42571000
H	4.14499700	1.71963300	-1.82559400
C	2.06614400	2.73208100	-1.59990900
C	1.41239200	1.74429800	-2.36316000
C	1.25500100	1.82333500	-3.80987800
H	1.66686400	2.61850900	-4.42993100
C	0.49302500	0.73898600	-4.19010600
H	0.16332300	0.45769600	-5.18918300
C	0.22288800	-0.03666700	-2.98871300
C	-0.39812200	-1.29573000	-3.00614900
C	-0.42093000	-2.11395500	-1.86297300
C	-0.76798400	-3.52598000	-1.89630400
H	-1.08765200	-4.05752500	-2.79145400
C	-0.54638400	-4.02935600	-0.62933300
H	-0.65520400	-5.05373300	-0.27343200
C	-0.12676200	-2.90962600	0.20398900
C	2.81880700	3.81912900	-2.32824300
C	2.20705800	5.07138200	-2.64609100
C	2.92202900	6.05644300	-3.38148600
H	2.42955200	6.99873900	-3.62484600
C	4.24137400	5.77799100	-3.79601100
H	4.78948400	6.53655500	-4.36685400
C	4.87477200	4.55270700	-3.50174500

H	5.88967600	4.33178100	-3.83611200
C	4.15986200	3.57092000	-2.76397000
C	0.00648000	6.34237500	-2.49283100
C	-1.35291100	6.22002600	-1.86359500
H	-1.59168300	5.24503600	-1.41981600
C	-2.53139100	6.97068800	-2.53097900
H	-3.48283100	6.43371600	-2.60565200
H	-2.25766300	7.57908300	-3.39941200
C	-2.04426700	7.44947400	-1.16601400
C	-2.89483100	7.14339100	0.05315200
C	-4.26290400	7.52377500	0.08480300
H	-4.71357600	7.97491500	-0.80817700
C	-5.04052300	7.33290300	1.25156800
H	-6.09446800	7.63594000	1.26193100
C	-4.45788600	6.75737800	2.40695000
H	-5.05667600	6.61470000	3.31449100
C	-3.09545600	6.36958100	2.38313900
H	-2.63654500	5.91983100	3.27132100
C	-2.32077800	6.56393800	1.21588700
H	-1.26464800	6.26605900	1.20501600
C	-1.30098400	8.79029300	-1.06447600
H	-2.03460900	9.61338600	-0.97136200
H	-0.67509600	8.96489200	-1.95510000

H	-0.65354900	8.81262500	-0.16766600
C	5.93013800	1.73651300	-2.86473700
C	6.15984500	0.35732400	-2.31303300
H	5.64700000	0.13098400	-1.37001000
C	7.53798200	-0.30416800	-2.50149900
H	8.26302100	0.28532200	-3.07303800
H	7.93800400	-0.85228600	-1.64270000
C	6.34838900	-0.87726000	-3.27200500
C	5.73086100	-2.18081600	-2.79985700
C	4.32287900	-2.30061900	-2.65029400
H	3.68032600	-1.43123100	-2.83875100
C	3.73700800	-3.52751300	-2.25817800
H	2.64797800	-3.59764900	-2.15319200
C	4.55551800	-4.65881800	-2.01467800
H	4.10521100	-5.60927800	-1.70478300
C	5.95960000	-4.55256100	-2.16895800
H	6.59769300	-5.42559200	-1.98540900
C	6.54089000	-3.32241200	-2.55995200
H	7.62884800	-3.24083000	-2.67742100
C	6.28143700	-0.66297600	-4.79093900
H	6.84852600	-1.46109500	-5.30672700
H	6.71065200	0.31370900	-5.07336800
H	5.23523300	-0.70387800	-5.14915900

C	-0.94457500	-1.82084000	-4.30431200
C	-0.15818500	-2.64034100	-5.16350700
C	-0.67099300	-3.12411000	-6.39697200
H	-0.06284900	-3.75162900	-7.05396900
C	-1.98696800	-2.77843500	-6.77196500
H	-2.38848700	-3.14703000	-7.72302600
C	-2.79508400	-1.96514200	-5.94895900
H	-3.80890500	-1.70474700	-6.26445500
C	-2.26584500	-1.48859300	-4.71882400
C	2.02092600	-3.72113500	-5.55831000
C	-4.33454900	-0.24566500	-4.22870600
O	-4.16713600	-5.63854700	3.12060500
O	4.00750300	-5.65204700	3.47381500
O	3.62311800	1.73375400	4.41525300
O	-1.05718600	2.68336100	4.40091300
N	0.54320100	-0.55303900	1.90161300
N	1.42392400	1.73309400	0.61707500
N	-2.47277700	-4.37460600	2.07772400
H	-2.31452000	-3.63201200	1.38888600
N	2.39827000	-4.35610400	2.33719200
H	2.29653000	-3.54633200	1.71691200
C	0.03744700	-2.99895900	1.60025500
C	0.27117900	-1.85166600	2.38554800

C	0.25850500	-1.86628900	3.84264100
H	0.07360500	-2.75336700	4.44654500
C	0.50612100	-0.57679100	4.25988700
H	0.57661200	-0.19455200	5.27700500
C	0.70964200	0.22896000	3.06557000
C	1.14200200	1.56574200	3.10361500
C	1.53154600	2.23721800	1.93181700
C	2.19519200	3.53232700	1.93319300
H	2.39797400	4.11511000	2.83036200
C	2.52834800	3.82079400	0.62619600
H	3.05062300	4.69130500	0.23043900
C	2.02083100	2.72613600	-0.19217700
C	-0.03953900	-4.32978100	2.30882900
C	-1.28887100	-4.95018100	2.62656800
C	-1.32682700	-6.12220200	3.43131300
H	-2.29339000	-6.55374700	3.69503100
C	-0.11502700	-6.68753700	3.87899100
H	-0.14748900	-7.58856900	4.50252800
C	1.13710200	-6.13481600	3.53876700
H	2.07590800	-6.57860800	3.87389200
C	1.17356600	-4.95570700	2.74688100
C	-3.80248600	-4.78811400	2.24628600
C	-4.75718600	-4.17529800	1.26065200

H	-4.39335300	-3.28696700	0.72864100
C	-6.27379600	-4.21794900	1.54336200
H	-6.84804100	-3.32214500	1.28510600
H	-6.56305000	-4.72133500	2.47232400
C	-5.71682700	-5.10171200	0.42485600
C	-5.96048400	-4.71718800	-1.02303200
C	-7.28219400	-4.75096100	-1.54543400
H	-8.11867000	-4.97198600	-0.87007600
C	-7.52437000	-4.50977600	-2.91765800
H	-8.54930500	-4.54404100	-3.30663700
C	-6.44498000	-4.22972300	-3.79184200
H	-6.63154700	-4.05015100	-4.85743500
C	-5.12514800	-4.18742000	-3.28108900
H	-4.28335100	-3.97288700	-3.95075500
C	-4.88700300	-4.43302100	-1.90720300
H	-3.86056500	-4.40783300	-1.51996300
C	-5.68605600	-6.62403000	0.63649400
H	-6.66034100	-7.05789300	0.34171500
H	-5.48854800	-6.87536600	1.69161000
H	-4.90524600	-7.09229300	0.00784200
C	3.71242300	-4.71050800	2.66889600
C	4.74743500	-3.86565300	1.97967700
H	4.41256200	-3.34702700	1.07256000

C	6.21118200	-4.35435700	1.96994200
H	6.39373800	-5.28412300	2.51946400
H	6.75987400	-4.23602500	1.03016000
C	5.86326700	-3.11580800	2.79517700
C	6.27352600	-1.75390200	2.26539300
C	5.32733600	-0.70117000	2.14861700
H	4.27610500	-0.88411300	2.40350600
C	5.72495200	0.58486300	1.71074000
H	4.97894200	1.38468200	1.63495100
C	7.08173500	0.83811100	1.38979800
H	7.39096300	1.83169200	1.04468100
C	8.03478400	-0.20326400	1.51011600
H	9.08666300	-0.01298300	1.26464700
C	7.63192700	-1.48825300	1.94531200
H	8.37011200	-2.29538700	2.03500000
C	5.87380000	-3.22018200	4.32717400
H	6.89783200	-3.04259700	4.70730600
H	5.54114500	-4.21864500	4.65871800
H	5.20731400	-2.46000300	4.77702900
C	1.28816800	2.24363000	4.43870700
C	2.54748900	2.32013800	5.10150200
C	2.67773100	2.93818400	6.37412900
H	3.64662800	2.99396100	6.87710100

C	1.53137900	3.47774400	6.99458000
H	1.62561700	3.95393400	7.97736000
C	0.26593400	3.41271200	6.37505200
H	-0.60932300	3.83466800	6.87574700
C	0.15415400	2.79600800	5.10020700
C	4.93882500	1.73918500	5.07812900
C	-2.28706700	3.10063400	5.09662300
H	-4.68100300	0.39221900	-3.40300800
H	-5.00826600	-1.11768800	-4.32810900
H	-4.30781500	0.32958100	-5.17417700
H	2.96597100	-3.78850900	-5.00076000
H	2.18833800	-3.22225500	-6.53229100
H	1.60433500	-4.73430300	-5.71952900
H	-3.10160300	2.86729000	4.39765700
H	-2.27052700	4.18684800	5.31469000
H	-2.42069600	2.53144400	6.03609100
H	5.60570100	1.21546700	4.37906500
H	4.89840900	1.19772200	6.04290700
H	5.29800000	2.77392100	5.24055300
C	-1.82872500	1.48703400	0.98723500
C	-5.99233200	2.43572100	3.56625500
C	-4.13075300	1.82307400	2.06673400
C	-5.08110900	2.76979900	2.53624500

C	-5.96368700	1.14454800	4.14864100
C	-3.19206600	2.19551600	0.90768800
C	-5.01635600	0.19609300	3.69196200
C	-4.10998900	0.53374100	2.65909200
H	-3.36874100	-0.19724400	2.31499500
H	-4.98452900	-0.80520200	4.13801500
H	-6.66967800	0.88125900	4.94530600
H	-5.10132200	3.77635100	2.09669200
H	-6.72269500	3.17786300	3.91161900
H	-2.96351900	3.28031900	1.01570500
H	-1.30735400	1.67918500	1.93683200
H	-1.70480100	0.52030900	-0.95761100
H	-4.03485500	-0.12002600	-0.86996900
C	-4.66016400	0.77351000	-0.73082200
H	-5.93077900	-1.54244600	-1.29068900
H	-8.37955700	-1.92194100	-1.46958200
C	-6.62284500	-0.70684400	-1.12061900
C	-6.08154600	0.59641000	-0.80439800
C	-8.92064200	0.14882500	-1.01427000
H	-10.00092700	-0.01971500	-1.09391400
C	-7.03159900	1.66446000	-0.59359900
C	-8.41577200	1.43876100	-0.69770900
H	-9.11362700	2.26785300	-0.52693200

H -6.67242700 2.66580900 -0.33203200

H -4.65775800 2.91947200 -0.53461100

C -3.94536100 2.07629400 -0.47751200

H -3.18751400 2.24802000 -1.27192600

Transition State TS3

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -409.3551 cm-1

G_corr: 1.58548 Hartree

H_corr: 1.868887 Hartree

SCF: -6636.528657 Hartree

S: 596.48 Cal/Mol-Kelvin

H: -6634.65977 Hartree

G: -6634.942549 Hartree

Cartesian Coordinates:

C -1.70607400 0.26679000 -0.53053200

Co 0.43418000 -0.05165700 -0.03384200

O -1.03523300 7.01369000 -3.06339400

O 6.44095600 3.85840000 -2.64612900

O 2.53184600 -1.93581400 -4.94158800

O -2.17352800 -1.84192600 -4.17942700

N	0.85106500	0.66848100	-1.82137600
N	0.42200500	-1.87856600	-0.78588100
N	-0.08588200	5.30689500	-1.74814800
H	-0.31392100	4.53718600	-1.11043900
N	4.34166300	3.26213400	-1.75283400
H	3.84430400	2.50292300	-1.27537000
C	1.57179400	3.00377600	-1.25115700
C	1.25550000	1.97583100	-2.16359200
C	1.28087800	2.14390400	-3.61150900
H	1.56429200	3.06516100	-4.11886300
C	0.86938800	0.94836200	-4.16296700
H	0.76222800	0.68888700	-5.21510900
C	0.63828600	0.02501000	-3.06134900
C	0.37609100	-1.34540000	-3.23371700
C	0.38113700	-2.24018300	-2.14713900
C	0.42953400	-3.68785500	-2.29590700
H	0.41794700	-4.20772700	-3.25300400
C	0.52947500	-4.22389500	-1.02745500
H	0.60899800	-5.27015400	-0.73360400
C	0.47943800	-3.10693300	-0.09122800
C	2.13544600	4.29169900	-1.80106900
C	1.29114800	5.40307800	-2.10922000
C	1.82376300	6.56394900	-2.73278700

H	1.15402800	7.38389700	-2.99523300
C	3.20304100	6.61398200	-3.02340200
H	3.61304300	7.50867200	-3.50628400
C	4.07102000	5.54764900	-2.70781700
H	5.13801100	5.58471000	-2.93338300
C	3.53401100	4.38271600	-2.09577700
C	-1.15662100	6.09920500	-2.18530800
C	-2.46494200	5.76446100	-1.52688700
H	-2.45267000	4.90165600	-0.84908300
C	-3.78101200	5.96568600	-2.31653600
H	-4.52463600	5.16625900	-2.23567000
H	-3.66452300	6.40197000	-3.31403500
C	-3.50730600	6.88294200	-1.12992200
C	-4.26361000	6.66741600	0.16904100
C	-5.63219200	6.29026100	0.17848300
H	-6.14063800	6.08794400	-0.77172500
C	-6.34920600	6.19063700	1.39583700
H	-7.40891000	5.90830500	1.38262600
C	-5.70779700	6.47225500	2.62566200
H	-6.26703200	6.41161400	3.56719900
C	-4.33985300	6.84481800	2.62834600
H	-3.83611700	7.07788200	3.57486500
C	-3.62688400	6.93873800	1.41181600

H	-2.56893900	7.23023800	1.42103700
C	-3.18431200	8.36076600	-1.40124100
H	-4.12869800	8.93003400	-1.49382500
H	-2.59760600	8.47264500	-2.32714800
H	-2.60529000	8.80180600	-0.56831200
C	5.69600800	3.03256300	-2.02542500
C	6.18351100	1.70065500	-1.52861100
H	5.59524500	1.24977800	-0.71972900
C	7.70036500	1.43032800	-1.48747400
H	8.32817000	2.24367800	-1.86714500
H	8.07957600	0.90455900	-0.60553100
C	6.85549900	0.67038100	-2.51021100
C	6.54105100	-0.79261300	-2.25713100
C	5.20764200	-1.27469100	-2.35088100
H	4.38904600	-0.57431600	-2.55975600
C	4.91986500	-2.64882100	-2.17272200
H	3.88379200	-2.99859400	-2.24997800
C	5.96725900	-3.56444100	-1.90433000
H	5.74583700	-4.62821000	-1.75845900
C	7.30093300	-3.09541900	-1.81588600
H	8.11591800	-3.79957100	-1.60848200
C	7.58405700	-1.71971500	-1.99238800
H	8.61749000	-1.35701800	-1.92240100

C	6.99633000	1.03125900	-3.99622700
H	7.82954900	0.45616500	-4.44308400
H	7.19926100	2.10806400	-4.12591200
H	6.07262600	0.77957000	-4.55151400
C	0.16925800	-1.89347600	-4.61659300
C	1.26087900	-2.18925000	-5.48146400
C	1.04860400	-2.71776800	-6.78314500
H	1.88919600	-2.93982200	-7.44610500
C	-0.27279500	-2.96245100	-7.21497200
H	-0.44252000	-3.37153600	-8.21772700
C	-1.37949700	-2.69295200	-6.38154800
H	-2.39368200	-2.89201500	-6.73808700
C	-1.14802900	-2.15751700	-5.08670600
C	3.70584500	-2.23215400	-5.77890900
C	-3.54826500	-2.21996200	-4.54281800
O	-2.98354100	-7.14188800	2.15138600
O	4.77939400	-4.96117500	3.33972000
O	2.09276000	1.24941500	5.11565700
O	-2.30473300	2.56265700	3.78695100
N	0.22281200	-0.80067200	1.78211900
N	0.81464000	1.71374800	0.76972700
N	-1.71722400	-5.25751000	1.52453200
H	-1.76072000	-4.35720800	1.03529200

N	2.94603800	-3.98763800	2.21959600
H	2.66111500	-3.15346400	1.69619700
C	0.39327200	-3.26256800	1.30739800
C	0.17313800	-2.15859000	2.16000200
C	-0.14098500	-2.28821800	3.57783100
H	-0.23251700	-3.23856000	4.10250100
C	-0.30161900	-1.01092200	4.07201700
H	-0.53871700	-0.70320300	5.08958800
C	-0.03081600	-0.09085100	2.97518200
C	0.11940300	1.29630700	3.14417000
C	0.61149300	2.11271700	2.10856000
C	1.04056200	3.48935500	2.30467500
H	0.99684300	4.01688100	3.25676000
C	1.52125800	3.94347800	1.09158200
H	1.94642700	4.91685000	0.84736500
C	1.34581100	2.85934700	0.13346500
C	0.60878600	-4.62263400	1.92913400
C	-0.43751700	-5.58725300	2.06554100
C	-0.19283700	-6.83071200	2.71236500
H	-1.01163000	-7.54290900	2.81823100
C	1.09796100	-7.10540600	3.20827300
H	1.28121000	-8.06230200	3.71080700
C	2.15978100	-6.18865700	3.07136300

H	3.16093300	-6.40096000	3.44991900
C	1.91509200	-4.94781900	2.42377700
C	-2.89263400	-6.01540800	1.56153900
C	-4.06261600	-5.39639300	0.84446900
H	-3.96226200	-4.33471200	0.58817100
C	-5.46197000	-5.90492100	1.20892800
H	-6.27080900	-5.17500800	1.30761700
H	-5.47384600	-6.72181000	1.93813400
C	-4.92762700	-6.24820800	-0.19120100
C	-5.50074100	-5.48067200	-1.36840100
C	-5.59676700	-6.08264200	-2.65501200
H	-5.22781700	-7.10139500	-2.80841400
C	-6.17820400	-5.39515100	-3.74671500
H	-6.24967500	-5.89250700	-4.72182000
C	-6.67610700	-4.08151100	-3.58404900
H	-7.14010700	-3.55359900	-4.42576400
C	-6.57796100	-3.46129700	-2.31414100
H	-6.95868100	-2.44287300	-2.16958000
C	-5.99915500	-4.15215200	-1.22712100
H	-5.94790300	-3.65088500	-0.25339500
C	-4.51804400	-7.69862700	-0.45346000
H	-5.39334100	-8.29084700	-0.78207600
H	-4.11683100	-8.15518400	0.46528200

H	-3.73739000	-7.76836400	-1.23483000
C	4.28237900	-4.02258400	2.63638100
C	5.08087600	-2.83641100	2.17333000
H	4.66394700	-2.28499800	1.32146100
C	6.62108600	-2.91539300	2.23143400
H	7.02145100	-3.84042000	2.66021900
H	7.16412600	-2.51037600	1.37176300
C	5.90382000	-1.96111600	3.18631800
C	5.95278600	-0.47226000	2.89471000
C	4.76139500	0.29593000	2.80392900
H	3.78580000	-0.19719000	2.89886800
C	4.81595900	1.69390200	2.58752700
H	3.88416900	2.26777300	2.52243600
C	6.06791400	2.34529500	2.46640100
H	6.11259400	3.42679200	2.29222000
C	7.26239600	1.58946800	2.56320400
H	8.23450400	2.08863300	2.46927600
C	7.20335800	0.19190800	2.77670300
H	8.12867900	-0.39412800	2.84709000
C	5.86418600	-2.30610400	4.68211900
H	6.77184500	-1.91626200	5.18097200
H	5.81502600	-3.39762200	4.83565000
H	4.98276500	-1.84579400	5.16865900

C	-0.11357900	1.91015300	4.49723500
C	0.90128200	1.88147900	5.49861300
C	0.70042700	2.47190200	6.77497900
H	1.48096700	2.44058500	7.53986400
C	-0.52714300	3.11152700	7.04739500
H	-0.68792600	3.57132900	8.02931900
C	-1.55152800	3.17138800	6.07875600
H	-2.49346900	3.67418500	6.31305200
C	-1.33581500	2.56665300	4.81184100
C	3.19373800	1.20487000	6.09214200
C	-3.52697700	3.35475500	4.00710700
H	-4.15805300	-1.94990100	-3.66940200
H	-3.62852800	-3.30841500	-4.72247900
H	-3.89253300	-1.66185600	-5.43599300
H	4.56975100	-1.98833200	-5.14443100
H	3.71155400	-1.60546900	-6.69168600
H	3.73699800	-3.30367900	-6.05601300
H	-4.11230200	3.24433200	3.08332200
H	-3.28358100	4.42136400	4.16487800
H	-4.11072000	2.96583000	4.86367200
H	4.02004500	0.71557800	5.55757800
H	2.90913200	0.61404300	6.98415100
H	3.49972600	2.22507300	6.39384600

C	-2.52002500	-0.50410500	0.35341400
C	-5.74144000	-0.73397300	4.14549500
C	-4.37907700	-0.47004400	2.10142000
C	-4.62070200	-0.19219200	3.48205900
C	-6.66202100	-1.55036500	3.44095700
C	-3.21360200	0.11284600	1.42300200
C	-6.44806300	-1.81744400	2.06564100
C	-5.32122800	-1.28514000	1.40204200
H	-5.18043600	-1.45376900	0.32735500
H	-7.17625500	-2.42327800	1.51198200
H	-7.53700100	-1.96621100	3.95406000
H	-3.89572200	0.42450100	4.02734000
H	-5.89908300	-0.52733300	5.21089600
H	-2.71980000	0.94327400	1.94727500
H	-2.68054000	-1.56950200	0.13514600
C	-7.09582900	1.94144200	-1.38241600
C	-5.97419400	2.18046500	-0.56829800
C	-6.94344600	1.29968800	-2.64154900
C	-5.65045800	0.89766600	-3.06630100
C	-4.52143700	1.12640400	-2.25324000
C	-4.65431600	1.77938800	-0.97829900
H	-3.52932500	0.82184600	-2.60478300
H	-8.09141200	2.25563200	-1.04673800

H	-6.09709000	2.68074600	0.40108000
H	-7.81579900	1.12709000	-3.28285000
H	-5.52591800	0.42018100	-4.04581600
C	-3.52218400	2.02964500	-0.11565700
C	-2.06845500	1.77631900	-0.52626000
H	-3.69115600	2.71958500	0.72358000
H	-1.50596500	-0.18502900	-1.50970500
H	-1.85327400	2.19603500	-1.53127700
H	-1.42510600	2.31130200	0.19244200

Intermediate E'

E'$_{[Co(II)(P6)]}$=A$_{[Co(II)(P6)]}$

E'$_{[4a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -108.3397 cm-1

G_corr: 0.239478 Hartree

H_corr: 0.28782 Hartree

SCF: -657.7426414 Hartree

S: 101.744 Cal/Mol-Kelvin

H: -657.4548214 Hartree

G: -657.5031634 Hartree

Cartesian Coordinates:

H	-2.08233200	-1.98165600	2.35470800
H	-3.37603400	-2.97449400	0.49157600
C	-2.19928400	-1.43519600	1.42773700
C	-2.92853300	-1.99561500	0.37793300
C	-1.61931900	-0.17105700	1.28550700
H	-1.06051300	0.22731800	2.12100600
C	-3.08158700	-1.29261100	-0.81780000
H	-3.64841300	-1.72715400	-1.63100800
H	-0.80370500	2.76415500	1.96511800
C	-1.76111100	0.55098400	0.07886000
C	-2.50398700	-0.02877700	-0.96704100
C	-0.37499500	2.43877000	1.02631600
H	-2.63477200	0.50024800	-1.90298300
C	0.98220600	2.32077900	0.80890800
C	-1.15297800	1.92878700	-0.14498700
H	-1.96928300	2.63223400	-0.42167800
H	1.72614300	2.54805600	1.56108700
H	2.04972400	2.28735900	-1.08587100
C	1.26718300	1.72239200	-0.53262300
H	3.49849400	0.88187700	0.76169500

C	-0.07890700	1.94855900	-1.24408800
C	2.94090000	0.05333600	0.34269700
C	1.74647500	0.28603600	-0.36748800
C	3.42595300	-1.24523000	0.52129500
H	4.34342000	-1.40871100	1.07176800
C	1.05988400	-0.82322300	-0.90567900
H	-0.27619900	1.39841200	-2.18759000
C	2.72954000	-2.33143500	-0.00965400
H	0.14923800	-0.70713000	-1.46990100
C	1.54931500	-2.12001400	-0.72343100
H	-0.03857800	3.02015500	-1.55666700
H	3.10610800	-3.33662500	0.12898800
H	1.01217800	-2.96293400	-1.13900400

Transition State TS3’

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -736.7948 cm-1

G_corr: 1.586108 Hartree

H_corr: 1.868214 Hartree

SCF: -6636.562536 Hartree

S: 593.742 Cal/Mol-Kelvin

H: -6634.694322 Hartree

G: -6634.977056 Hartree

Cartesian Coordinates:

C	-5.27356800	-0.51731400	-2.47335300
C	-1.24368100	1.21271500	-0.14998100
Co	0.45448200	-0.08959000	-0.01491600
O	2.83750600	6.90954900	-2.88587600
O	7.57842800	0.34510200	-2.49953200
O	0.93563100	-3.28896000	-4.62267600
O	-1.95198800	0.51841300	-4.79508000
N	1.14008400	0.42155000	-1.79882100
N	-0.48619300	-1.63552000	-0.86222600
N	2.65570200	4.87157200	-1.71950700
H	2.00983100	4.28119500	-1.18413900
N	5.47295600	0.89140300	-1.58911200
H	4.65464900	0.48382500	-1.12462700
C	2.93438300	2.06211900	-1.15905000
C	2.15057800	1.35985600	-2.09717400
C	2.30743200	1.51098300	-3.53876700
H	3.03124100	2.17250800	-4.01298400
C	1.38815300	0.67404400	-4.13199000
H	1.21367900	0.50548200	-5.19344400
C	0.68470800	-0.02117000	-3.06168300

C	-0.21211000	-1.07965800	-3.29635400
C	-0.70105700	-1.87544000	-2.23965700
C	-1.42825900	-3.12150200	-2.43108200
H	-1.70893000	-3.52572400	-3.40236500
C	-1.62735100	-3.67640300	-1.18134600
H	-2.10285100	-4.62329200	-0.92498700
C	-1.07685600	-2.74091100	-0.20898700
C	4.08517900	2.89414900	-1.67386600
C	3.92495600	4.27798500	-1.99185700
C	5.00030800	5.02194800	-2.54976900
H	4.84558000	6.06965000	-2.80979600
C	6.23254400	4.37575700	-2.78023500
H	7.06058900	4.94860900	-3.21371700
C	6.42945700	3.01394200	-2.47182500
H	7.37802900	2.50992400	-2.66325400
C	5.35170500	2.27135900	-1.91746400
C	2.17489500	6.11649400	-2.14038900
C	0.79486900	6.44495800	-1.64203800
H	0.26332700	5.63330600	-1.12833600
C	-0.07864400	7.40187500	-2.49117700
H	-1.13535900	7.13872800	-2.60793000
H	0.41242100	7.80503900	-3.38304900
C	0.42998200	7.89116000	-1.13842500

C	-0.54940100	7.98199300	0.01726600
C	-1.78242900	8.66990000	-0.13642800
H	-2.05500400	9.06590400	-1.12275000
C	-2.64818700	8.86016900	0.96714600
H	-3.59287600	9.40098800	0.83347700
C	-2.29036700	8.36455200	2.24438200
H	-2.95615000	8.51631500	3.10216600
C	-1.06580500	7.67107000	2.40610900
H	-0.77975500	7.28623600	3.39216200
C	-0.20297200	7.48286300	1.30162100
H	0.74837400	6.95194600	1.43414900
C	1.50817700	8.98543000	-1.09444500
H	1.02575400	9.97958100	-1.15237300
H	2.21709700	8.87663000	-1.93121800
H	2.07430800	8.94018000	-0.14509400
C	6.51810600	0.00540300	-1.88151900
C	6.25746200	-1.39882700	-1.41223800
H	5.54955700	-1.49889400	-0.58019900
C	7.41623900	-2.41405500	-1.43577700
H	8.36120500	-2.03204800	-1.83706000
H	7.49667900	-3.08488200	-0.57471500
C	6.26565000	-2.60037300	-2.42650200
C	5.25370400	-3.70090500	-2.16647100

C	3.86290800	-3.41814000	-2.11562700
H	3.51481400	-2.38348800	-2.22429800
C	2.91872000	-4.45579100	-1.92929700
H	1.84969000	-4.21499900	-1.89925900
C	3.35498600	-5.79779300	-1.79972700
H	2.62636100	-6.60212400	-1.64406200
C	4.73963400	-6.09228200	-1.85929000
H	5.08340300	-7.12894300	-1.75866800
C	5.68003500	-5.05053300	-2.04173300
H	6.75293000	-5.27822300	-2.08223100
C	6.52168700	-2.32695200	-3.91581200
H	6.93081200	-3.23485400	-4.39864600
H	7.24181500	-1.50147300	-4.04930000
H	5.58080700	-2.06154300	-4.43416000
C	-0.55822100	-1.42278900	-4.72169300
C	0.02398500	-2.54368400	-5.38594900
C	-0.29705100	-2.85730500	-6.73428200
H	0.15104000	-3.72101900	-7.23240500
C	-1.19986700	-2.03228300	-7.43631200
H	-1.45096200	-2.27076000	-8.47626400
C	-1.77735600	-0.89983400	-6.82532700
H	-2.46651700	-0.26659900	-7.39004600
C	-1.44531700	-0.60087200	-5.47781700

C	1.62802200	-4.40797500	-5.28473600
C	-2.88261200	1.40260300	-5.51454400
O	-5.77749700	-3.92164600	3.05196500
O	1.71230800	-6.65081400	3.07792500
O	2.80738600	0.02151800	5.04669900
O	-0.68728400	3.13376200	4.11033900
N	-0.09184700	-0.72131200	1.76697400
N	1.68407400	1.20419900	0.84299500
N	-4.07634300	-3.56220200	1.46964400
H	-3.78461400	-2.96328400	0.69049600
N	0.62938200	-4.86764500	1.97748100
H	0.80607500	-3.99394900	1.47104200
C	-1.21472000	-2.89545400	1.18600800
C	-0.82710300	-1.88217600	2.08819600
C	-1.13360400	-1.91971500	3.51318100
H	-1.69702300	-2.71488500	3.99961300
C	-0.59609200	-0.77927800	4.07059900
H	-0.61843600	-0.45777200	5.11085000
C	0.08576100	-0.06051000	3.00298600
C	0.93367600	1.03765600	3.23011100
C	1.73944200	1.56775000	2.20595000
C	2.78440400	2.55492600	2.43276700
H	3.02397900	2.98074300	3.40634400

C	3.38727700	2.79640000	1.21411100
H	4.21743000	3.46365900	0.98316300
C	2.68377400	1.98642800	0.22615100
C	-1.71346300	-4.19784800	1.76719300
C	-3.09710000	-4.47784100	1.97060100
C	-3.50372200	-5.67262000	2.62506800
H	-4.56424300	-5.85295700	2.80335900
C	-2.52929200	-6.59087500	3.06063100
H	-2.84714600	-7.50908000	3.56791000
C	-1.15335900	-6.35992600	2.85516000
H	-0.39276600	-7.06551900	3.19273700
C	-0.74470700	-5.16370800	2.20786400
C	-5.38207600	-3.39501900	1.96219200
C	-6.28394800	-2.57068300	1.09097100
H	-5.81001300	-2.04697600	0.25107200
C	-7.48878300	-1.84963800	1.74025500
H	-7.69684700	-0.83433500	1.38658400
H	-7.60805400	-2.01495800	2.81641200
C	-7.76992900	-3.03702200	0.82433700
C	-8.32803400	-2.78332100	-0.56326100
C	-9.47173200	-1.96086700	-0.74129400
H	-9.90525300	-1.45186300	0.12864500
C	-10.05363600	-1.79655500	-2.02124000

H	-10.93712200	-1.15829400	-2.14250300
C	-9.49916300	-2.45771300	-3.14420200
H	-9.94781000	-2.33111400	-4.13650900
C	-8.36078500	-3.28490200	-2.97601300
H	-7.92821200	-3.80272400	-3.84057700
C	-7.78428600	-3.44789300	-1.69484700
H	-6.90494300	-4.09197300	-1.56691400
C	-8.29428900	-4.34493900	1.43840200
H	-9.39636100	-4.29174200	1.52399100
H	-7.86080900	-4.51736800	2.43663100
H	-8.04905300	-5.20913200	0.79234700
C	1.76384600	-5.57510800	2.39709100
C	3.05908000	-4.94237100	1.97272500
H	2.99804800	-4.24868300	1.12540200
C	4.34816900	-5.78625600	2.05871200
H	4.21625300	-6.79132500	2.47389600
H	5.04574400	-5.69985500	1.21998200
C	4.18213400	-4.61046400	3.02127300
C	4.98763200	-3.34962600	2.76526400
C	4.35541500	-2.08322800	2.64977900
H	3.26197900	-2.01265400	2.70050000
C	5.12108900	-0.90460000	2.47836700
H	4.61272800	0.06363800	2.40451800

C	6.53464900	-0.97726300	2.42577500
H	7.12903500	-0.06645700	2.28776200
C	7.17572000	-2.23530500	2.54524900
H	8.26997000	-2.29774300	2.50408100
C	6.40669300	-3.41080100	2.71459900
H	6.90310000	-4.38562700	2.80401900
C	3.93317600	-4.90119900	4.50842900
H	4.89955200	-5.03085100	5.03208000
H	3.33422100	-5.81877300	4.63765100
H	3.39456400	-4.06153800	4.98787600
C	1.05763600	1.58788100	4.62496300
C	2.00466100	1.05743900	5.54781200
C	2.10701600	1.55728700	6.87386800
H	2.83296900	1.14284800	7.57839400
C	1.24983400	2.60206000	7.27901300
H	1.32139400	2.99024000	8.30168400
C	0.30239400	3.15655000	6.39287700
H	-0.35118600	3.96534800	6.72989800
C	0.21598500	2.64596100	5.06971200
C	3.79525400	-0.58060700	5.95741800
C	-1.64652900	4.16317000	4.54373600
H	-3.15718200	2.17588300	-4.78264100
H	-3.79060200	0.85442600	-5.82976000

H	-2.39058200	1.86555500	-6.39146600
H	2.31409000	-4.80111500	-4.52145300
H	2.20194400	-4.05441900	-6.16285200
H	0.91105500	-5.19375100	-5.59304600
H	-2.26920100	4.36292800	3.66098800
H	-1.12185800	5.08691700	4.85798500
H	-2.27922300	3.78990000	5.37143500
H	4.30820900	-1.33884800	5.34939400
H	3.29701000	-1.05538900	6.82477600
H	4.52619100	0.17394400	6.30693300
C	-1.25236300	2.33025000	0.60998200
C	-5.15574800	5.04629000	2.18977500
C	-3.35972800	3.65301500	1.22814600
C	-4.00264000	4.91343200	1.38119700
C	-5.67745100	3.92008000	2.87461700
C	-2.12302600	3.55282300	0.31620900
C	-5.03435400	2.66580500	2.74137100
C	-3.88746100	2.53345200	1.92312800
H	-3.39198600	1.56141400	1.82694200
H	-5.42451300	1.78884600	3.27139100
H	-6.56835500	4.02119100	3.50600200
H	-3.59210400	5.79661100	0.87404200
H	-5.64025100	6.02505400	2.29113100

H	-1.52567700	4.47114700	0.50734100
H	-0.57473000	2.42734100	1.46887700
H	-1.76523700	0.39199700	-0.63396700
H	-1.89718700	1.76660400	-2.51599300
C	-2.60300000	2.09848300	-1.74143300
H	-3.13214700	-0.33494200	-2.79922300
H	-5.33936900	-1.50349300	-2.94822000
C	-4.02932100	0.13468900	-2.38056400
C	-3.91234800	1.42962700	-1.77288000
C	-6.44966100	0.10140400	-1.97357400
H	-7.41862000	-0.40027500	-2.06526500
C	-5.10606300	2.02783300	-1.25311500
C	-6.35243100	1.37621900	-1.36282100
H	-7.25332300	1.86496100	-0.97257000
H	-5.06137300	3.01264700	-0.77758400
H	-3.32103700	4.14444100	-1.44635200
C	-2.43457300	3.51675500	-1.22837600
H	-1.57160000	3.97421700	-1.74762000

Intermediate E’’

E’’$_{[Co(II)(P6)]}$=A$_{[Co(II)(P6)]}$

E’’$_{[5a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -106.4677 cm-1

G_corr: 0.238322 Hartree

H_corr: 0.287258 Hartree

SCF: -657.7315695 Hartree

S: 102.995 Cal/Mol-Kelvin

H: -657.4443115 Hartree

G: -657.4932475 Hartree

Cartesian Coordinates:

H	-4.39077000	-2.05755800	0.47936400
C	-3.80443700	-0.23211500	-0.49907500
C	-3.60461500	-1.32573300	0.34581800
C	-2.79103800	0.71553700	-0.67246800
C	-2.39240900	-1.47163900	1.02283200
H	-2.24024000	-2.31578900	1.68290100
C	-1.55920900	0.57531800	-0.00648900
C	-1.37635500	-0.52721400	0.85251200
H	-0.44919500	-0.65523100	1.39616800
C	0.84139700	-1.26869600	-1.01881200
C	1.44711100	-0.09204300	-0.53264100
H	0.87346300	-3.42018600	-1.07692000

C	1.35463100	-2.52784800	-0.69791000
C	2.48755400	-2.63640400	0.10778500
C	3.11164800	-1.48556200	0.58949800
H	2.88466000	-3.61228600	0.35555800
H	3.99365100	-1.57174900	1.21107300
H	-2.96889300	1.55597900	-1.33173100
C	-0.47598700	1.62316900	-0.19835400
H	-0.90641500	2.48056200	-0.76795400
H	-0.33719200	1.95610500	2.07200800
C	0.03865200	2.19590400	1.08542600
C	1.31053700	2.69771300	0.87632900
C	0.83904500	1.25746200	-0.94106400
H	1.33050500	3.36492700	-1.11326400
C	1.69514100	2.47637100	-0.54972500
H	2.01201800	2.85480300	1.68483400
C	2.60352900	-0.22218700	0.27153600
H	2.78224500	2.38025300	-0.75312100
H	3.12292800	0.63652500	0.66910800
H	-4.74630300	-0.11741000	-1.01987900
H	-0.03522200	-1.20962000	-1.65234500
H	0.72357700	1.21848800	-2.04697900

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(2) (a) Kochi, J. K.; Krusic, P. J., Isomerization and Electron Spin Resonance of Allylic Radicals. *J. Am. Chem. Soc.* **1968**, *90*, 7157–7159. (b) Huang, H.-M.; Bellotti, P.; Glorius, F., Transition Metal-Catalysed Allylic Functionalization Reactions Involving Radicals. *Chem. Soc. Rev.* **2020**, *49*, 6186–6197.

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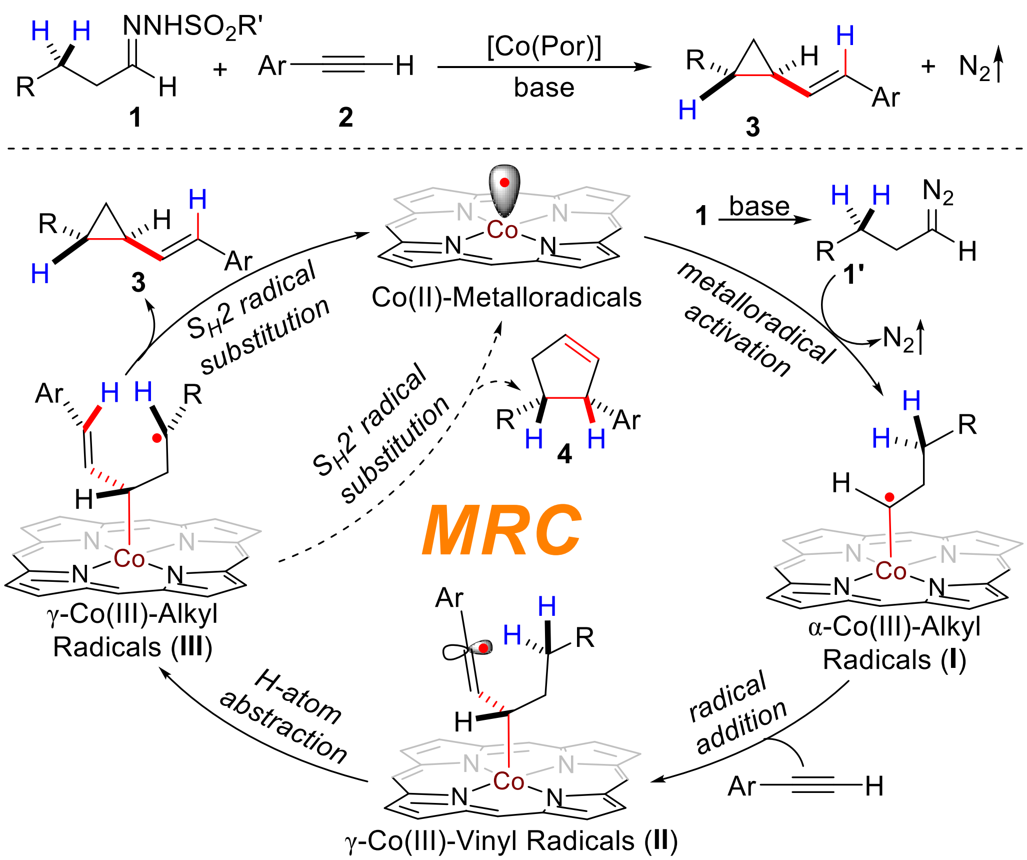
CHAPTER 4

ASYMMETRIC SYNTHESIS OF VINYLCYCLOPROPANES BY RADICAL C–H ALKYLATION FROM ALKYNES AND IN SITU-GENERATED ALKYLDIAZOMETHANES

4.1. INTRODUCTION

The potential of radical chemistry has drawn increasing attention nowadays, which offers new synthetic tools for the construction of organic molecules with unique properties of reactivity and selectivity.[1] Among many unique features, radical cascade reactions represent a powerful synthetic strategy for the rapid construction of molecular complexity from simple starting materials.[2] In addition to the prerequisite for the controlled generation of radicals, the development of radical cascade processes, however, faces formidable challenges in governing the chemo-, regio- and stereoselectivities of the successive reactions involving the radical species.[3] Among recent approaches to surmount the challenges in controlling the reactivity and selectivity of radical reactions,[4] metalloradical catalysis (MRC) has been introduced as a conceptually new approach to controlling reactivity as well as selectivity of radical reactions by generating metal-supported organic radicals as key catalytic intermediates.[5,6,7] As stable 15e-metalloradicals, Co(II) complexes of D_2-symmetric chiral amido porphyrins [Co(D_2-Por*)] have been demonstrated as efficient catalysts for asymmetric radical transformation through catalytic generation of metal-stabilized organic radicals, including the α-Co(III)-alkyl radicals from homolytic activation of the corresponding diazo compounds.[8] These metal-stabilized organic radicals can serve as key catalytic intermediates for asymmetric radical transformations. Vinyl radicals, which represent a unique type of highly reactive radical species, can be generated by the addition of radical species to the unsaturated triple bonds.[9] Serving as effective intermediates in a variety of radical transformations,[10] vinyl radicals are known to undergo 1,5-H-atom abstraction.[11] By applying the [Co(D_2-Por*)] metalloradical catalyst, we were intrigued if the alkyl diazo compounds, which could be generated from the corresponding sulfonyl hydrazone, could be employed in the radical cascade reaction with alkyne for the asymmetric construction of vinyl-substituted cyclopropane (Scheme 4.1).

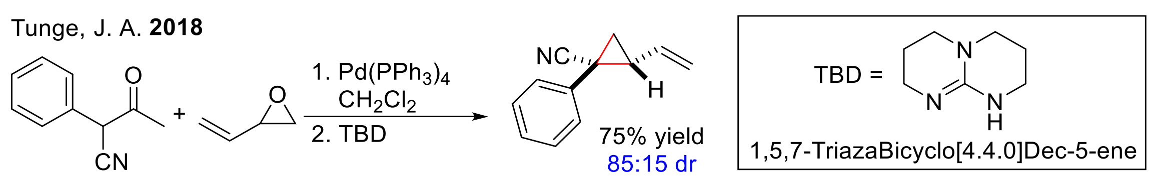
Scheme 4.1. Proposed Pathway for Asymmetric Radical Cascade C–H Alkylation of Alkynes and In Situ-Generated Alkyldiazomethanes



However, this proposed radical process presented several potential challenges. As for α-Co(III)-alkyl radical intermediate **I** possessing β hydrogens, could the competitive pathway of 1,2-H atom shift other than radical addition to the triple bond take place? Could the effective control of enantioselectivity of radical addition to the alkyne substrate be achieved with the relatively flexible nature of the linear C≡C triple bond? What also under question is whether the highly reactive γ-Co(III)-vinyl radical **II** could proceed with 1,5-H atom abstraction exclusively over the 1,4-H atom abstraction. An additional concern may arise for the potential tendency to undergo S_H2' radical substitution of γ-Co(III)-alkyl radical **III**, from which cyclopentene could be generated as a product via β-scission.[11] On the other hand, could the γ-Co(III)-alkyl radical **III** undergo effective and stereoselective 3-*exo*-*tet* cyclization without the conformational rigidity? If these questions could be answered positively, it would be both fundamentally appealing and synthetically useful for the asymmetric synthesis of vinylcyclopropane.

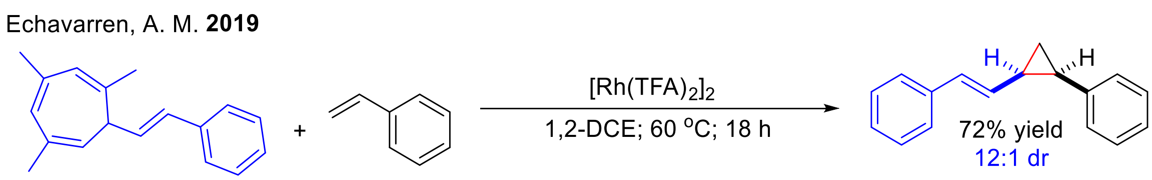
Vinylcyclopropanes are of great importance due to their wide existence in many natural products[12] and bioactive compounds.[13] Thus, various approaches (including carbenoids derived from diazo compounds,[14] Simmons-Smith-like reactions,[15] Michale-initiated ring closure (MIRC) of ylides[16] or functional group interconvergent of appropriately functionalized cyclopropane[17]) have been developed to prepare vinylcyclopropanes. Additionally, Tunge reported the non-asymmetric synthesis of vinyl cyclopropane converted from the readily available vinyl epoxides via anion relay cyclization with good reactivity and diastereoselectivity (Scheme 4.2).[18]

Scheme 4.2. Synthesis of Vinyl Cyclopropanes via Anion Relay Cyclization



Recently, Echavarren and co-workers have reported the non-asymmetric vinycyclopropane synthesis by rhodium(II)-catalyzed decarbenation of cycloheptatrienes via retro-Buchner reaction (Scheme 4.3).[19] While this protocol provides a novel alternative for the synthesis of alkynylcyclopropane in the racemic forms, it would be highly desirable to develop a fundamentally different catalytic system for the asymmetric synthesis of vinylcyclopropane moieties.

Scheme 4.3. Cyclopropanation of Donor Rhodium Carbenes by Retro-Buchner Reaction



As a new application of Co(II)-based metalloradical catalysis (MRC), we herein report the development of the first catalytic system that is highly effective for the asymmetric synthesis of vinyl-substituted cyclopropanes by radical C−H alkylation from alkynes and aliphatic diazo compounds via Co(II)-based metalloradical catalysis. Supported by an optimal D_2-symmetric chiral amidoporphyrin ligand (D_2-Por*), the Co(II)-based catalytic system is capable of efficiently activating various alkyldiazomethanes at room temperature to undergo cascade reactions with a wide range of alkenes with varied electronic and steric properties, delivering vinylcyclopropanes in high yields with excellent control of stereoselectivities. We show the importance of catalyst development through fine-tuning of the ligand environment in achieving high reactivity as well as stereoselectivity. Results from the combination of computational and experimental studies shed light on the underlying stepwise radical mechanism of the Co(II)-catalyzed cyclopropanation.

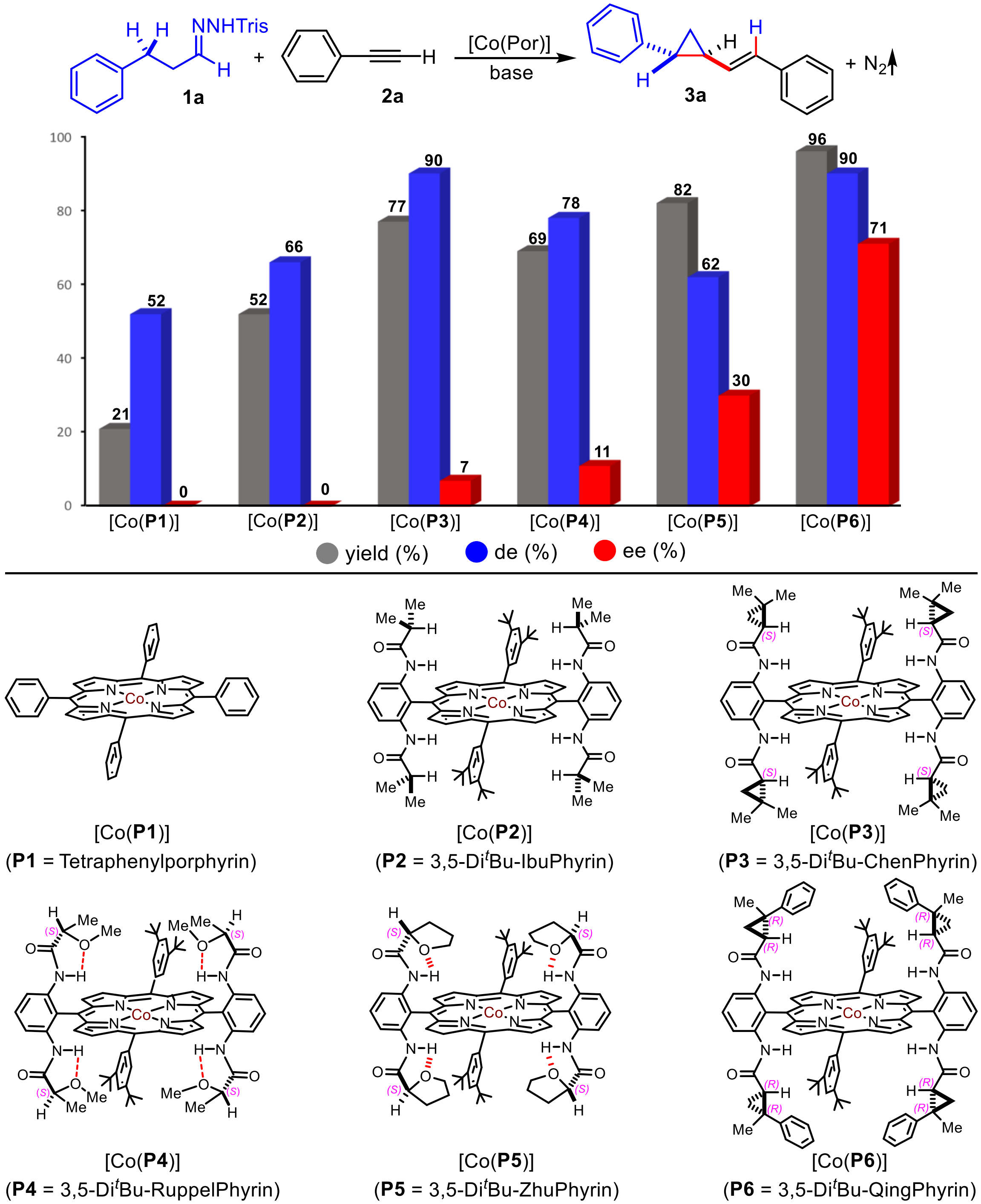
4.2. RESULTS AND DISCUSSION

4.2.1. Condition Optimization for Asymmetric Radical Cascade C–H Alkylation of Alkynes and Alkyl Diazo Compounds

At the outset of the project, α-(phenylethyl)diazomethane (**1a'**), which was in situ-generated from the corresponding trisylhydrazone **1a** in the presence of Cs_2CO_3, was used as the representative alkyldiazomethane for investigation of the proposed radical cascade process by Co(II)-based metalloradical catalysts [Co(Por)] with ethynylbenzene (**2a**) (Scheme 4.4).

It was found that simple achiral metalloradical catalyst [Co(**P1**)] (**P1** = 5,10,15,20-tetraphenylporphyrin) was able to catalyze the formation of desired vinylcyclopropane **3a** but in low reactivity (21% yield) with moderate control of diastereoselectivity (52% de) in favor of the *trans*-isomer. With the employment of the Co(II) complex of D_{2h}-symmetric achiral amidoporphyrin [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin)[20], which contains amide units in the supporting ligand for potential H-bonding stabilization of the corresponding α-Co(III)-alkyl radical intermediate, improvements in both reactivity (52% yield) and diastereoselectivity (66% de) for product **3a** were observed. Encouraged by these initial results, we decided to systematically investigate the ligand effect on the reactivity as well as the enantioselectivity of the Co(II)-catalyzed radical cascade cyclopropanation. When first-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin)[8a] was utilized, a further increase in the yield (77%) of **3a** was attained with excellent diastereoselectivity (90% de), while maintaining a low level of asymmetric induction (7% ee). To improve the stereoselectivities of the catalytic process, metalloradical catalyst [Co(**P4**)] (**P4** = 3,5-Di^{t}Bu-RuppelPhyrin)[21] was further applied, which is devised to achieve

Scheme 4.4. Ligand Effect on Co(II)-Based Catalytic System for Asymmetric Radical Cascade C–H Alkylation of Ethynylbenzene and α-(Phenylethyl)diazomethane[a]



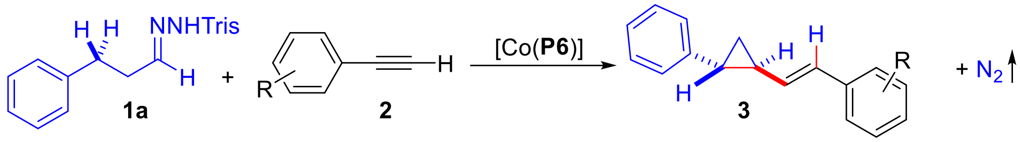
[a]Carried out with **1a** (0.10 mmol) and **2a** (0.20 mmol) in the presence of Cs_2CO_3 (0.20 mmol) by [Co(Por)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenyl sulfonyl; Isolated yields; Diastereomeric excess (de) determined by ^{1}H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

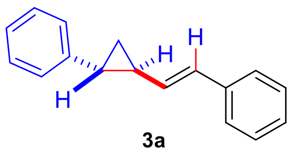
conformational rigidity benefiting from its unique intramolecular H-bonding interaction. As expected, improvement in the enantioselectivity of the product (11% ee) was observed although with relatively low reactivity (69% yield) as a result of the sterically-encumbered ligand environment. Further application of metalloradical catalyst [Co(**P5**)] (**P5** = 3,5-Di^{t}Bu-ZhuPhyrin) gave rise to the enhancement of both the reactivity (82% yield) as well as the enantioselectivity (30% ee). These initial results prompted us to explore second-generation catalysts bearing cyclopropanecarboxyamides with two contiguous stereogenic centers in the hope of further enhancing the asymmetric induction of the catalytic process. Gratifyingly, by applying [Co(**P6**)] (**P6** = 3,5-Di^{t}Bu-QingPhyrin),[8i] the diastereoselectivity and enantioselectivity were dramatically improved to a good level (90% de; 71% ee) without affecting the excellent reactivity (96% yield).

4.2.2. Asymmetric Radical Cascade C–H Alkylation of Different Alkynes with α-(Phenylethyl)diazomethane

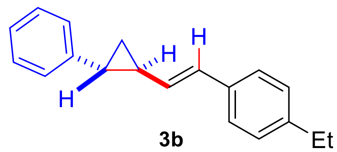
Under the optimized conditions, the scope and versatility of [Co(**P6**)]-catalyzed asymmetric radical cascade cyclopropanation with in situ-generated α-(phenylethyl)diazomethane (**1a'**) were explored by employing different types of alkynes as the substrates (Table 4.1). Similar to the formation of **3a** from ethynylbenzene (entry 1), its derivatives bearing alkyl substituents at different aryl positions could also be effectively engaged in the radical cascade reaction by [Co(**P6**)] with **1a'**, producing the desired cyclopropanes **3b**–**3e** in similarly high yields and stereoselectivities (entries 2–5). Additionally, derivatives bearing electron-donating as well as electron-withdrawing aryl substituents were also suitable alkyne substrates in the catalytic reaction, generating the desired vinylcyclopropanes **3f**–**3i** in excellent reactivity and a good level of

Table 4.1. Asymmetric Radical Cascade C–H Alkylation of Different Phenylacetylene Derivatives with In-Situ Generated α-(Phenylethyl)diazomethane[a]

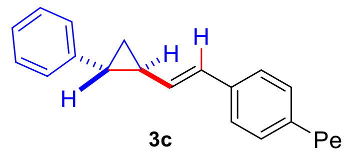




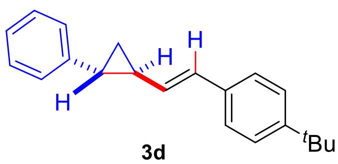
3a
entry 1: 96% yield
95:5 dr; 86:14 er



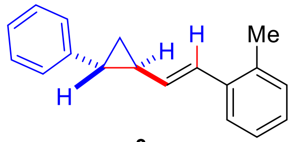
3b
entry 2: 90% yield
90:10 dr; 85:15 er



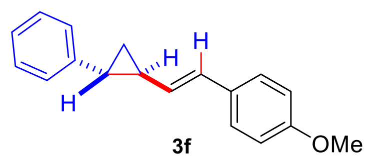
3c
entry 3: 96% yield
95:5 dr; 87:13 er



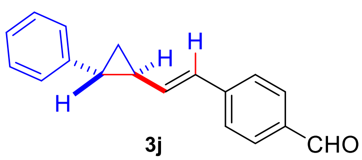
3d
entry 4: 96% yield
97:3 dr; 87:13 er



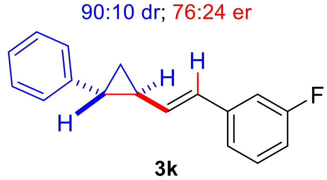
3e
entry 5: 95% yield
90:10 dr; 76:24 er



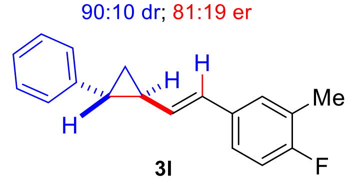
3f
entry 6: 94% yield
90:10 dr; 81:19 er



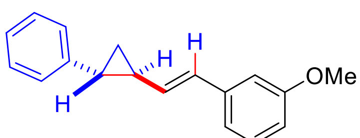
3j
entry 10: 92% yield
90:10 dr; 86:14 er



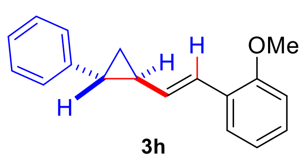
3k
entry 11: 92% yield
97:3 dr; 87:13 er



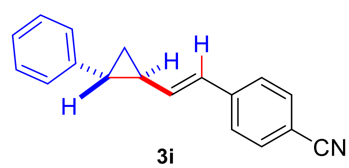
3l
entry 12: 90% yield
94:6 dr; 88:12 er



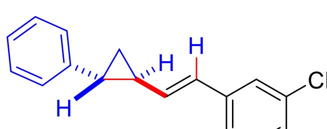
3g
entry 7: 91% yield
90:10 dr; 88:12 er



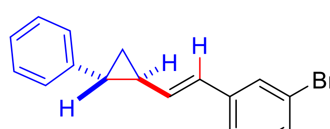
3h
entry 8: 95% yield
93:7 dr; 86:14 er



3i
entry 9: 88% yield
86:14 dr; 85:15 er



3m
entry 13: 99% yield
96:4 dr; 88:12 er



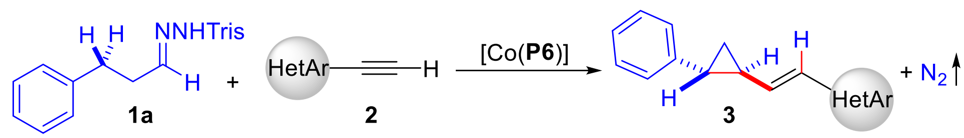
3n
entry 14: 90% yield
78:22 dr; 86:14 er

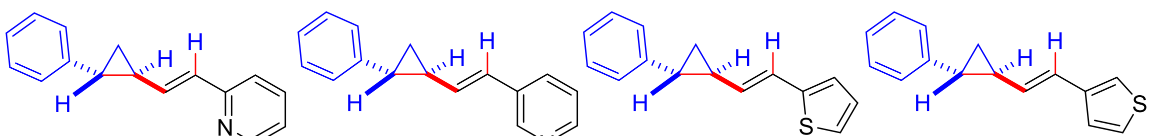
[a]Carried out with **1a** (0.10 mmol) and **2** (0.20 mmol) in the presence of Cs_2CO_3 (0.20 mmol) by [Co(**P6**)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^1H NMR analysis of reaction mixture; Enantiomeric excess (ee) of (*E*)-isomer determined by chiral HPLC.

stereoselectivities (entries 6–9). More interestingly, this [Co(**P6**)]-based metalloradical system was shown to be capable of tolerating various functional groups as exemplified by the stereoselective formation of **3j**–**3n** containing aryl substituents of formyl and halogen functionalities at different positions (entries 10–14).

Besides the phenyl-derived substituted alkynes, the Co(II)-based cascade cyclopropanation was further highlighted by its unique reactivity toward various heteroaromatic alkynes as shown with the highly stereoselective synthesis of vinyl-substituted cyclopropanes **3o**–**3r** containing pyridines and thiophenes (Table 4.2).

Table 4.2. Asymmetric Radical Cascade C–H Alkylation of Different Heteroaryl Containing Alkynes with In-Situ Generated α-(Phenylethyl)diazomethane[a]





3o	3p	3q	3r
entry 1: 96% yield	entry 2: 90% yield	entry 3: 82% yield	entry 4: 95% yield
96:4 dr; 87:13 er	90:10 dr; 86:14 er	85:15 dr; 80:20 er	88:12 dr; 85:15 er

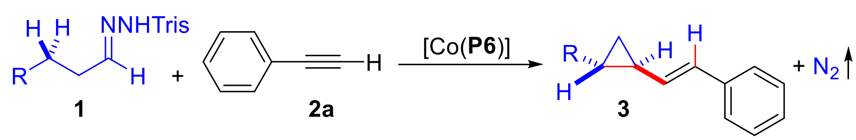
[a]Carried out with **1a** (0.10 mmol) and **2** (0.20 mmol) in the presence of Cs_2CO_3 (0.20 mmol) by [Co(**P6**)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of (*E*)-isomer determined by chiral HPLC.

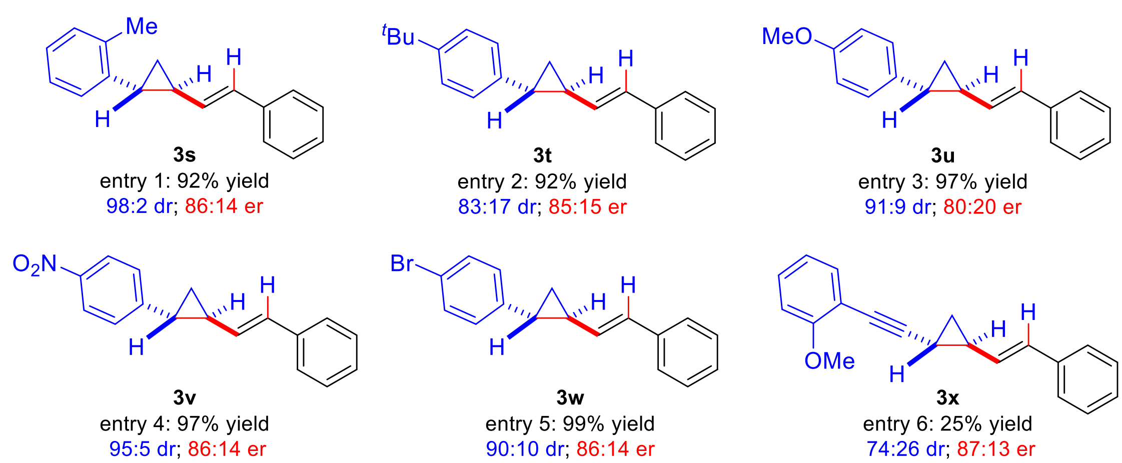
4.2.3. Asymmetric Radical Cascade C–H Alkylation of Phenylacetylene with Different In-Situ Generated Alkyldiazomethanes

In addition to the representative α-(phenylethyl)diazomethane (**1a'**), it was demonstrated that metalloradical catalyst [Co(**P6**)] could effectively activate different types of α-alkyldiazomethanes for asymmetric cascade cyclopropanation of ethynylbenzene (Table 4.3). For instance, the in situ-generated *o*-Me- and *p*-^{t}Bu-substituted α-alkyldiazomethanes could be effectively cyclopropanated, generating desired products **3s** and **3t** in similarly high yields with good stereoselectivities (entries 1 and 2). Apart from that, α-(4-

methoxyphenylethyl)diazomethane bearing the electron-donating group was also found to be a competent radical precursor, which could be effectively activated for the productive formation of the corresponding vinylcyclopropanes **3u** with exceptional control of stereoselectivities (entry 3). Likewise, α-(4-nitrophenylethyl)diazomethane bearing the electron-donating group was also shown to be effective radical precursors for [Co(**P6**)]-catalyzed asymmetric cascade cyclopropanation as exemplified with the room temperature reactions of ethynylbenzene as the model substrate, affording the corresponding vinylcyclopropane **3v** in similarly high yield with good stereoselectivities (entry 4). Additionally, by applying halogen-substituted hydrazone to the catalytic system, corresponding vinylcyclopropane product **3w** could be stereoselectively generated (entry 5). Propargylic C–H bond was shown to be could also be activated through the catalytic

Table 4.3. Asymmetric Radical Cascade C–H Alkylation of Phenylacetylene with Different In-Situ Generated Alkyldiazomethanes[a]





[a]Carried out with **1** (0.10 mmol) and **2a** (0.20 mmol) in the presence of Cs_2CO_3 (0.20 mmol) by [Co(**P6**)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl; Isolated yields; Diastereomeric ratio (dr) determined by ^{1}H NMR analysis of reaction mixture; Enantiomeric excess (ee) of (*E*)-isomer determined by chiral HPLC.

cycle, stereoselective generating the corresponding vinylcyclopropane **3x** with remarkable stereoselectivities albeit in moderate yield (entry 6).

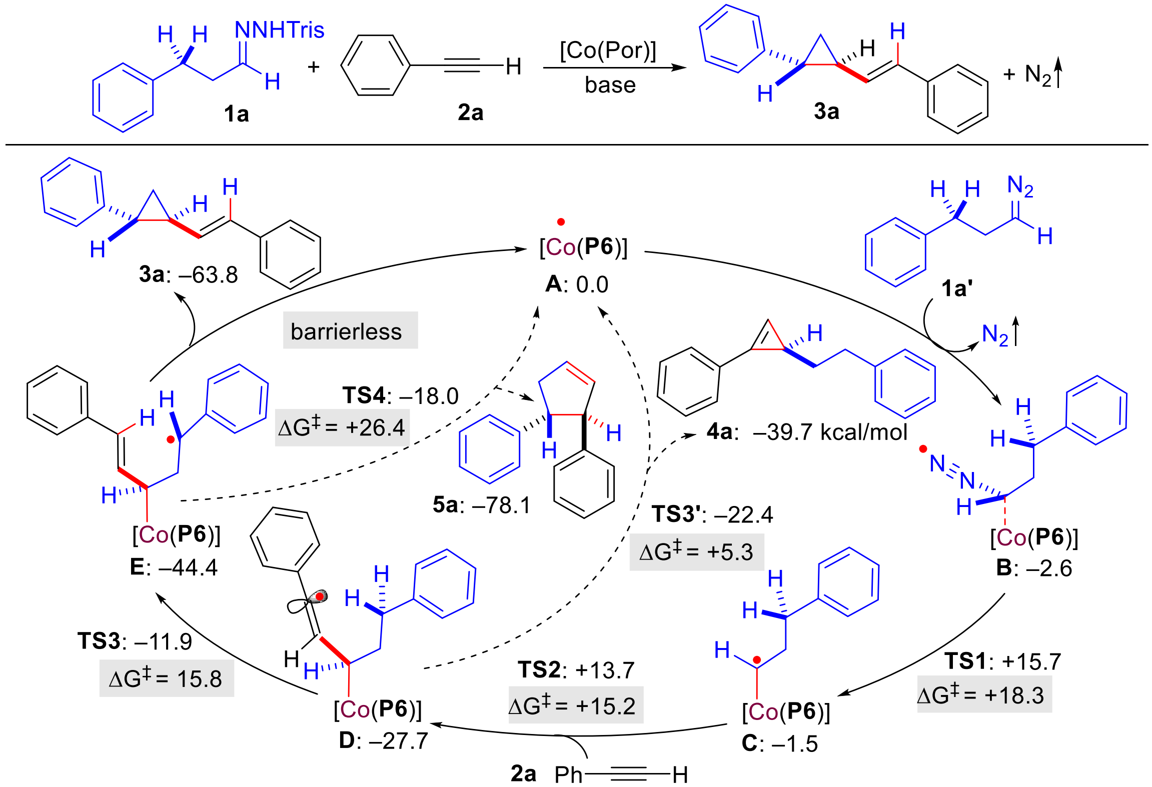
4.2.3. Mechanistic Study on Asymmetric Radical Cascade C–H Alkylation of Alkynes with In-Situ Generated Alkyldiazomethanes

To gain insight into the underlying stepwise radical mechanism (Scheme 4.1), combined computational and experimental studies were conducted. At first, Gibbs free energies associated with the Co(II)-catalyzed asymmetric cascade cyclopropanation of ethynylbenzene **2a** with α-(phenylethyl)diazomethane **1a'** was calculated by performing the density functional theory (DFT) to elucidate the details of the catalytic pathway (Scheme 4.5; see Scheme S1 in Experimental Section for details).

The DFT calculation indicated the initial formation of intermediate **B** upon the formation of non-covalent interaction between the catalyst and alkyldiazomethane **1a'** is slightly exergonic by 2.6 kcal/mol, the noncovalent complexation of which also positions the α-carbon atom of the diazo in close proximity to the Co(II)-metalloradical center of [Co(**P6**)] (C···Co: ~ 2.39 Å) for the subsequent metalloradical activation. As shown in the spin density distribution, a certain amount of spin is delocalized to the terminal nitrogen (Figure 4.1; see Figure S3 in Experimental Section for details).

Upon metalloradical activation, the coordinated diazomethane undergoes dinitrogen elimination to generate the α-Co(III)-alkyl radicals **C**, the activation energy of which is relatively high while reasonable ($\Delta G^{\ddagger}_{\mathbf{TS1}}$ = 18.3 kcal/mol). The subsequent radical addition of the resulting radical intermediate **C** to ethynylbenzene **2a** proceeds through an accessible activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS2}}$ = 15.2 kcal/mol), presumably due to the less steric hindered

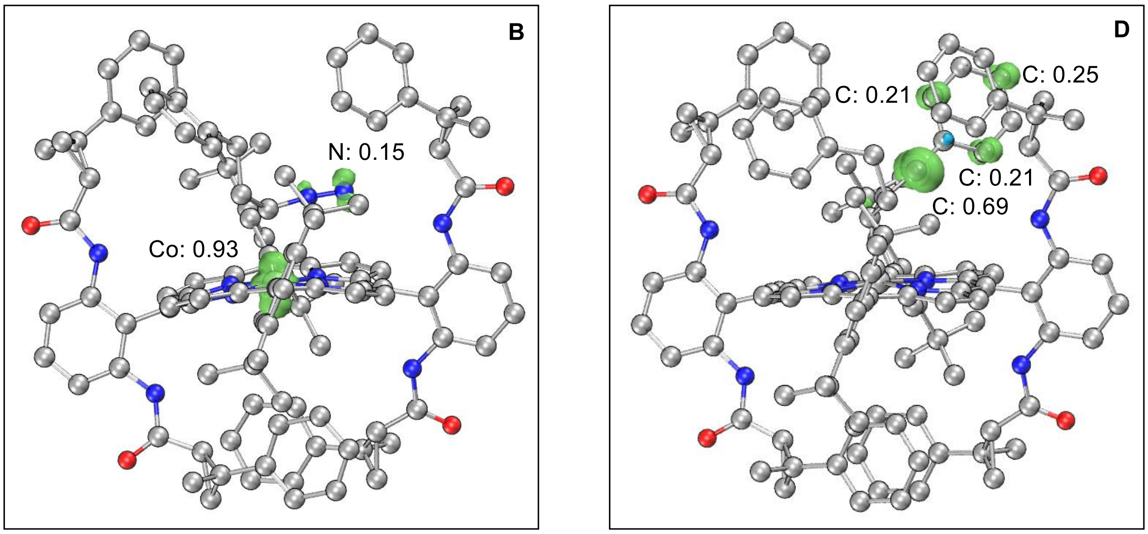
Scheme 4.5. DFT Calculations on Catalytic Pathways and Associated Energetics of Co(II)-Catalyzed C–H Alkylation Cyclopropanation (kcal·mol^{-1})^{a}



^{a}Applied the method of bp86/LANL2DZ for geometry optimization and the B3LYP/def2-tzvp for single point energy calculation along with Grimme's dispersion correction and SMD (chlorobenzene) solvation model.

environment of alkyl moiety. As shown, the resulting γ-Co(III)-vinyl radicals **D** possess a linear geometry in which the spin density was delocalized through the entire aromatic system (Figure 4.1). The ensuing step of 1,5-H-atom abstraction of γ-Co(III)-vinyl radicals **D**, which is exergonic by 16.7 kcal/mol, is found to be a process of a similar activation barrier ($\Delta G^{\ddagger}_{\mathbf{TS3}}$ = 15.8 kcal/mol) according to the DFT calculation, leading to the formation of the γ-Co(III)-alkyl radical **E**. The final *3-exo-tet* cyclization of the radical intermediate **E**, which is exergonic by 19.4 kcal/mol, undergoes an almost barrierless transition state, affording the corresponding vinylcyclopropane product **3a** while regenerating the

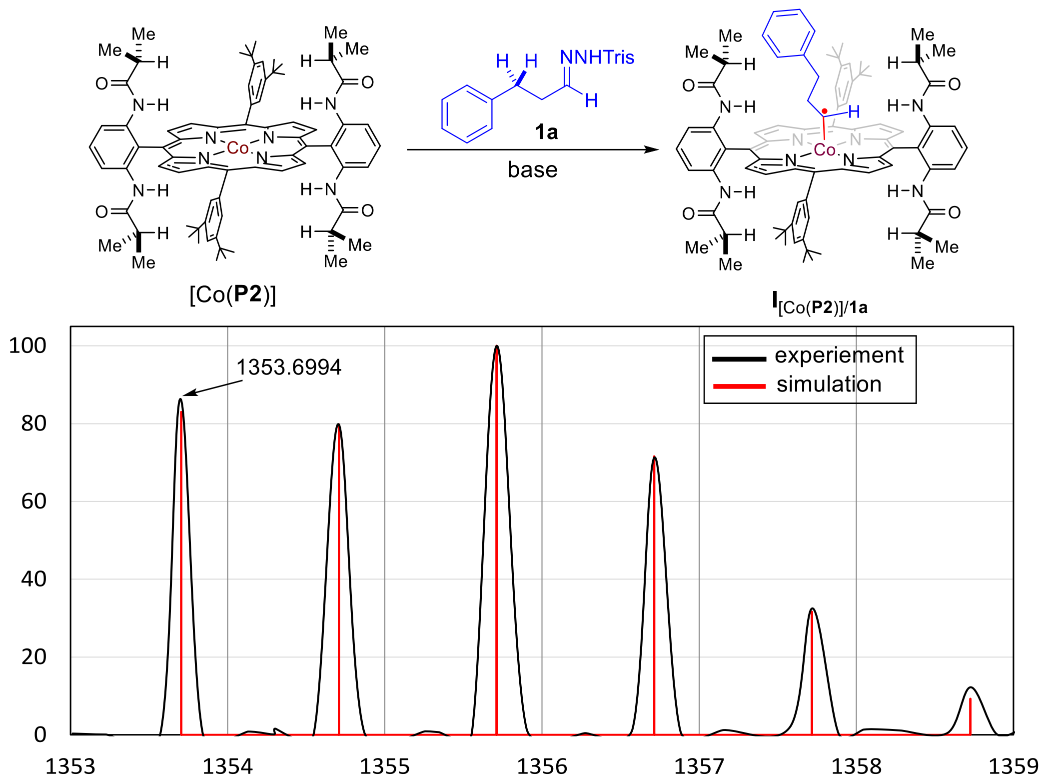
Figure 4.1. Optimized Geometry and Spin Density Distribution of Intermediate B and Intermediate D



metalloradical catalyst [Co(**P6**)]. The overall low activation barrier is in accordance with the highly effective catalytic pathway even at room temperature. To rationalize the chemoselectivity associated with γ-Co(III)-alkyl radical **E**, the energetics of competing S_H2' radical substitution has also been calculated. While the process is exergonic by 23.7 kcal/mol, the activation barrier was found to be much higher ($\Delta G^{\ddagger}_{\mathbf{TS4}}$ = 26.4 kcal/mol) compared to the desired pathway, indicating the favorable generation of cyclopropane product **3** to cyclopentene product **4**.

A set of mechanistic experiments were further performed to gain insight into the underlying mechanism of the Co(II)-catalyzed cyclopropanation (Scheme 4.6; see Figure S1 in Experimental Section for details). To experimentally detect the first α-Co(III)-alkyl radical intermediate, the mixture containing the in-situ generated α-(phenylethyl)diazomethane (**1a'**) and [Co(**P2**)] were used for the detection of high-resolution mass spectrometry (HRMS) with electrospray ionization (ESI). The observed mass of 1353.6994 evidently resulted from α-Co(III)-alkyl radical $\mathbf{I}_{[\mathrm{Co}(\mathbf{P2})]/\mathbf{1a}}$ by the loss of

Scheme 4.6. Detection of α-Co(III)-Alkyl Radical Intermediates by High-Resolution Mass Spectrometry (HRMS) Experiment[a]

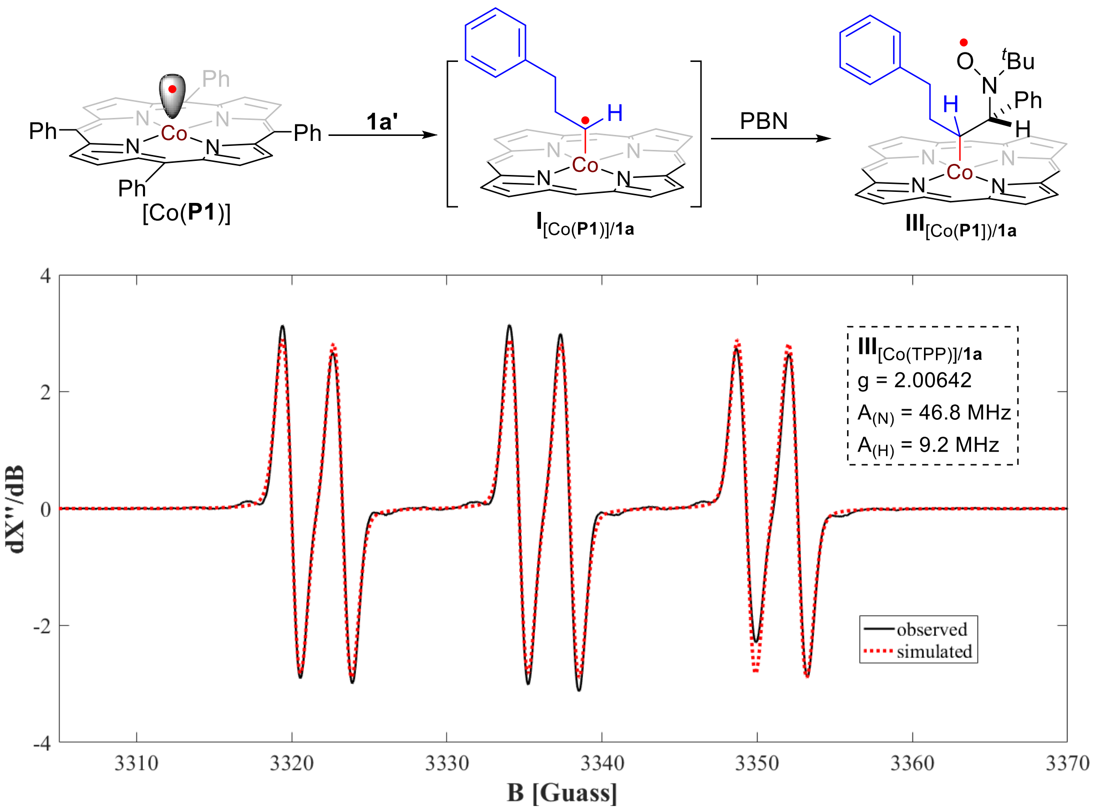


[a]Carried out with **1a** (0.10 mmol), [Co(**P2**)] (2 mol %), Cs_2CO_3 (0.20 mmol) in chlorobenzene (0.6 mL) at 23 °C for 30 min.

one electron. The exact mass determined by ESI-HRMS matches perfectly with the one calculated from the formula $[C_{85}H_{98}CoN_8O_4]^+$ (m/z= 1353.70375). The pattern of isotope distribution was nicely simulated as a mixture containing 57% of α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]/\mathbf{1a}}$ and 43% protonated species. On the other hand, detection of the γ-Co(III)-supported alkyl radicals was not successful, presumably due to the facile generation of the desired cyclopropane product through the low-energy barriers of the H-atom abstraction step as well as the radical cyclization.

The isotropic electron paramagnetic resonance (EPR) spectrum was further recorded at room temperature for the reaction mixture containing the alkyldiazomethane **1a'**, [Co(**P1**)],

Scheme 4.7. Trapping of α-Co(III)-Alkyl Radical Intermediate by Spin Trap PBN[a]

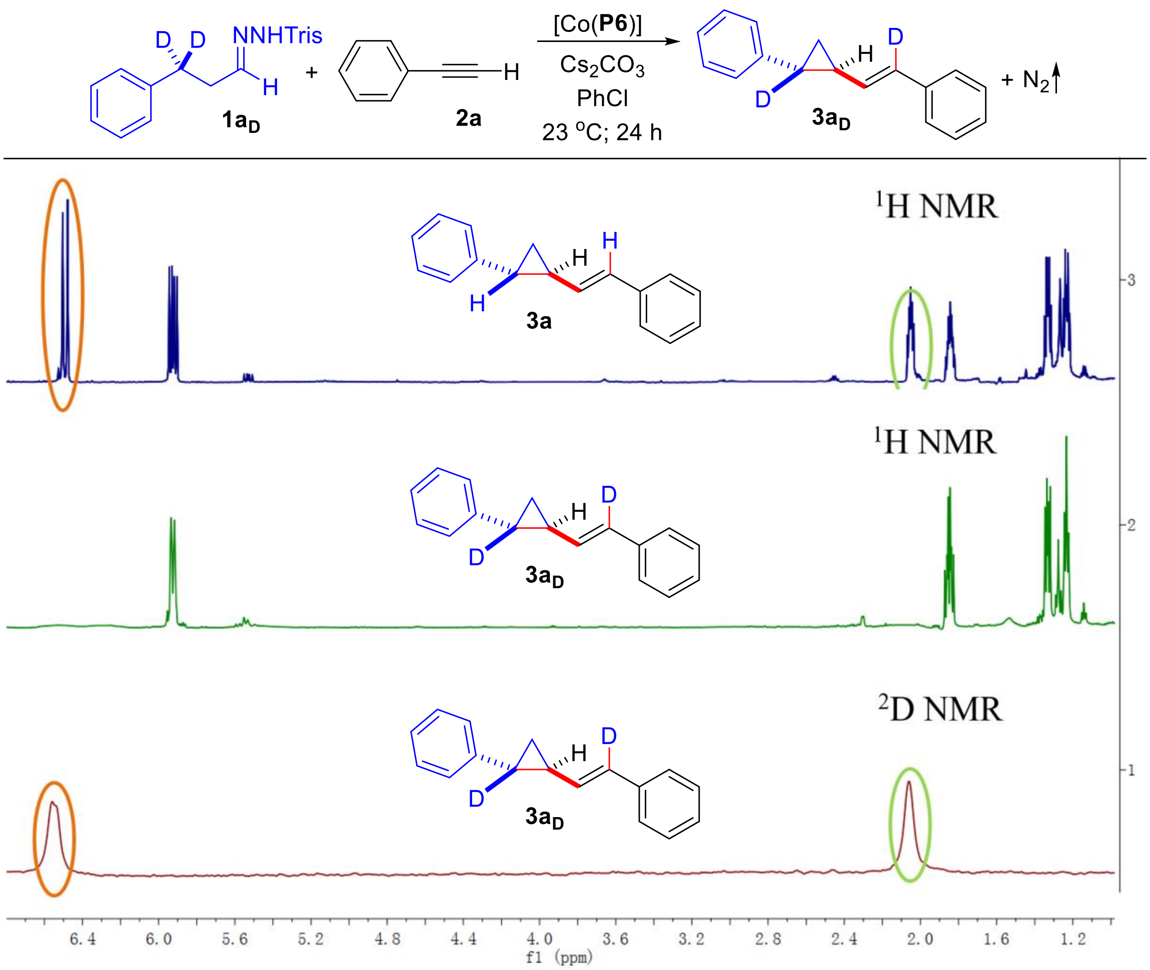


[a]Carried out with **1a'** (0.10 mmol), [Co(**P1**)] (4 mol %), and PBN (0.10 mmol) in benzene (0.6 mL) at RT for 5 min; The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon.

and the spin trapping reagent *N-tert*-butylnitrone (PBN) using benzene as the solvent in the absence of alkyne substrate (Scheme 4.7; see Figure S2 in Experimental Section for details). The observed strong EPR signals (in black) have been simulated (in red), displaying diagnostic signals at a g-value of ~2.00 that are consistent with the characteristic value of PBN-trapped Co(III)-supported alkyl radical species.[22] The observed signals could be well simulated on the basis of the hyperfine coupling by ^{14}N (I = 1) and ^{1}H (I = 1/2): O-centered radicals at δ-position $\mathbf{III}_{[Co(\mathbf{P1})]/\mathbf{1a}}$ (g = 2.00624, A(N) = 46.8 MHz; A(H) = 9.2 MHz).

Dideuterated alkylsulfonylhydrazone **1aD** has been synthesized to probe the mechanism of the radical atom abstraction step (Scheme 4.8). The resulting product **3aD** has been fully characterized, indicating the deuterium atom abstraction took place during the reaction process as proposed (Scheme 4.5).

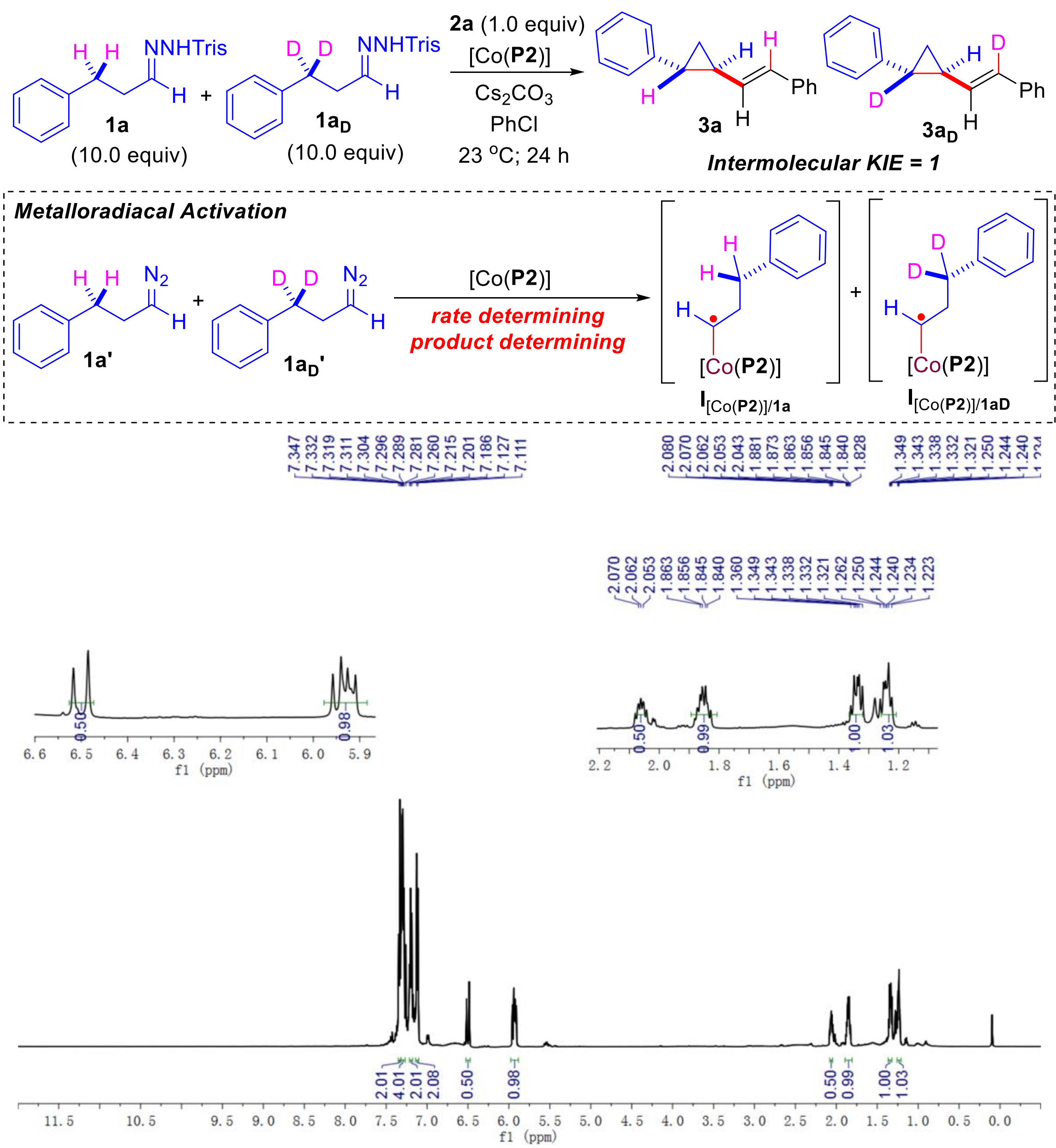
Scheme 4.8. Deuterium Labeling Experiment[a]



[a]Carried out with $1a_D$ (0.10 mmol) and **2a** (0.20 mmol) in the presence of Cs_2CO_3 (0.20 mmol) by [Co(**P6**)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl.

Furthermore, an excess amount of dideuterated substrate **1aD** and standard substrate **1a** has been applied to the reaction with phenylacetylene as the limiting reagent in order to determine the intermolecular kinetic isotope effect (KIE) value (Scheme 4.9). The intermolecular KIE value has been determined as 1 according to ^{1}H NMR. As proposed by

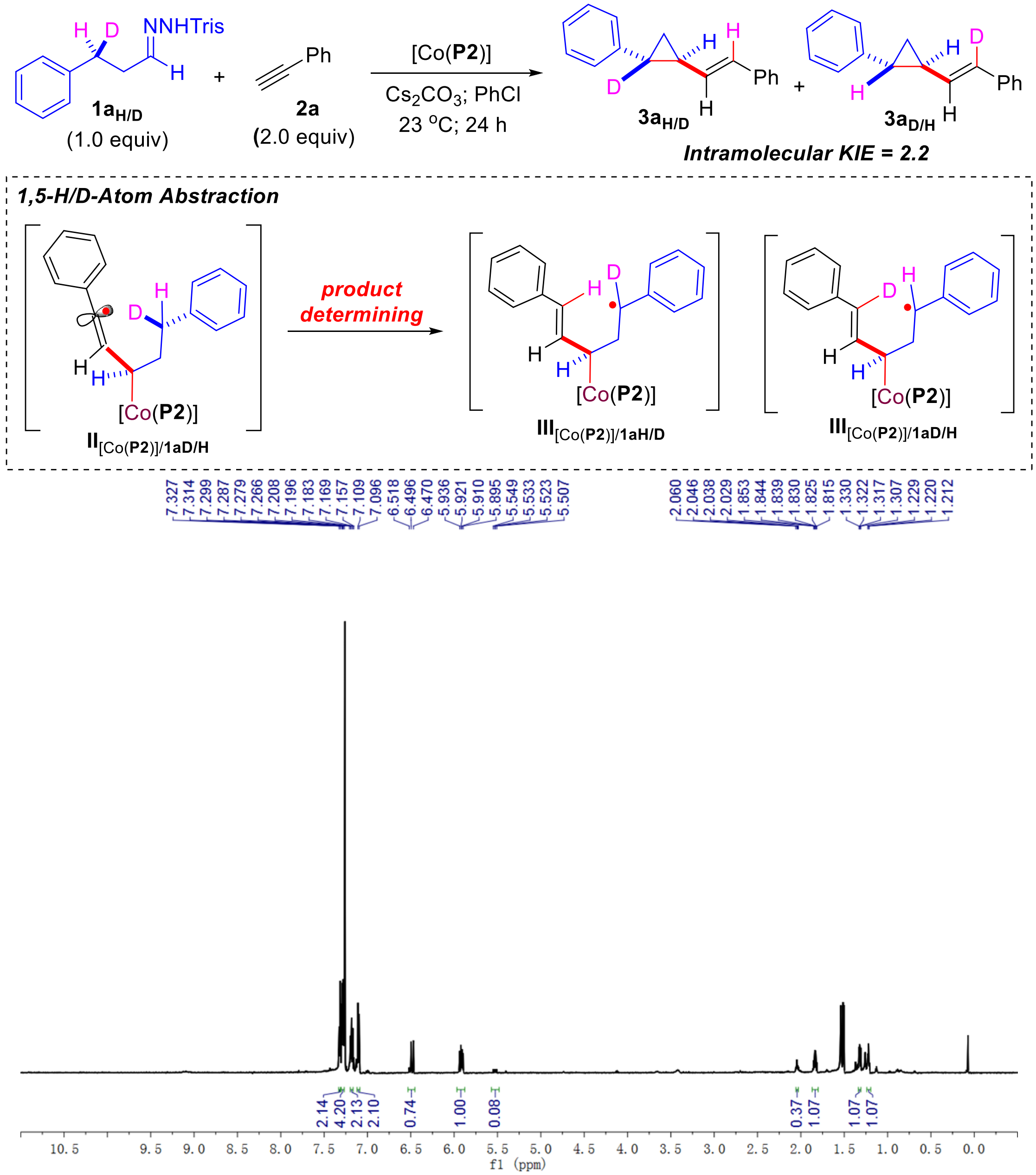
Scheme 4.9. Intermolecular Kinetic Isotope Effect Experiment[a]



[a]Carried out with **1a** (0.50 mmol), **1a$_D$** (0.50 mmol) and **2a** (0.05 mmol) in the presence of Cs_2CO_3 (2.00 mmol) by [Co(**P2**)] (2 mol %) in chlorobenzene (6.0 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl.

the computational study (Scheme 4.5), the metalloradical activation of the in-situ generated alkynyldiazomethane is the rate-determining step and can also be the product determining step based on the assumption that there is little difference between the activation rate of **1a'** and **1a$_D$'**, leading to the product distribution ratio as 1:1.

Scheme 4.10. Intramolecular Kinetic Isotope Effect Experiment[a]



[a]Carried out with $1a_{H/D}$ (0.10 mmol), and **2a** (0.20 mmol) in the presence of Cs_2CO_3 (2.00 mmol) by [Co(**P2**)] (2 mol %) in chlorobenzene (0.6 mL) at 22 °C for 24 h; Tris = 2,4,6-triisopropylphenylsulfonyl.

In order to measure the intramolecular KIE, mono-deuterated $\mathbf{1a_{H/D}}$ was synthesized (Scheme 4.10). According to ^{1}H NMR analysis, the intramolecular KIE value was determined as 2.2 according to the product distribution. As H-atom abstraction by γ-Co(III)-vinyl radicals **II** takes place after the rate-determining step as proposed by the computational study, the abstraction step is the product determining step which determines the distribution of **3a** and **3a$_D$** by the difference of abstraction rate of H-atom and D-atom respectively. The observed value is lower than the ones reported previously for the sp^3-based Co(III)-alkyl radical intermediate, which can be attributed to the less flexibility of the sp^2 orbitals leading to close proximity to orientated H/D atoms.

4.3. CONCLUSIONS AND OUTLOOK

In summary, we have developed the first asymmetric catalytic system for direct olefin cyclopropanation of in situ-generated α-alkyldiazomethanes via Co(II)-based metalloradical catalysis (MRC). With D_2-symmetric chiral amidoporphyrin 3,5-Di^{t}Bu-QingPhyrin as the optimal supporting ligand, the Co(II)-based metalloradical system enables stereoselective synthesis of vinylcyclopropanes in high yields with good stereoselectivities under mild conditions. A broad scope of substrates has been demonstrated as alkynes of varied electronic as well as steric properties have been effectively involved in the catalytic processes. Mechanistically, the detailed pathway of the underlying stepwise radical mechanism of Co(II)-based metalloradical cyclopropanation has been elucidated by the DFT study, revealing the feasibility of the reaction pathway. This Co(II)-based metalloradical catalysis may encourage further development of new catalytic systems for the wide use of this and other donor/H-substituted diazo reagents for various stereoselective radical processes.

4.4. EXPERIMENTAL SECTION

4.4.1. General Considerations

All cyclopropanation reactions were performed in anhydrous solvents under N_2 atmosphere in oven-dried glassware following standard Schlenk techniques. Gas-tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. The solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin-layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^1H NMR spectra were acquired using Varian INOVA 400 (400 MHz), Bruker 500 (500 MHz), or Varian INOVA 600 (600 MHz) spectrometer. Chemical shifts were internally referenced to the residual solvent peak ($CHCl_3$ $\delta = 7.26$ ppm). Data were reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, br = broad, m = multiplet), and coupling constants *J* (Hz). ^{13}C NMR spectra were acquired using Bruker 500 (1265 MHz), or INOVA 600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm with residual solvent peak ($CDCl_3$ $\delta = 77.16$ ppm) as the internal standard. ^{19}F NMR spectrum was acquired using Varian INOVA 600 (564 MHz) spectrometer. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, AD-H, OJ-H, IA, IB, ID, and IE columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS

SMART-APEXII CCD diffractometer. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals, or TCI and were used without further purification.

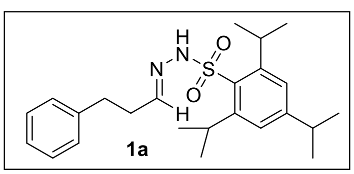
4.4.2. Synthesis and Characterization of *N*-2,4,6-Triisopropylbenzenesulfonyl Hydrazones

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

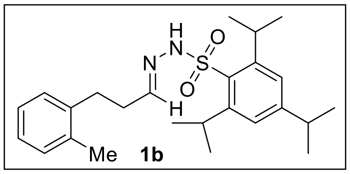
To a stirred solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (1.0 mmol) in THF (10.0 mL) at room temperature, aldehyde (1.0 equiv) was added dropwise (or portionwise if solid).[1] After the reaction was stirred overnight, the solvent was removed directly under reduced pressure, and the crude mixture was further purified by trituration.

4.4.2.2. Characterization of *N*-2,4,6-Triisopropylbenzenesulfonyl Hydrazones

3-Phenylpropanal 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1a**) Yield: 87%. R_f = 0.3 (Hexane/Ethyl Acetate: 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.28 – 7.16 (m, 4H), 7.08 (d, J = 6.9 Hz, 1H), 4.25 (dt, J = 13.4, 6.7 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.77 (t, J = 7.7 Hz, 1H), 2.51 (td, J = 7.8, 5.1 Hz, 1H), 1.34 – 1.24 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.30, 151.45, 149.77, 140.70, 131.42, 128.48, 128.38, 126.13, 123.87, 77.41, 77.16, 76.91, 34.27, 34.02, 32.19, 30.00, 24.93, 23.66.IR (neat, cm^{-1}): 3026.65, 2958.40, 2868.04, 1599.26, 1565.08, 1496.43, 1454.92, 1425.46, 1382.95, 1362.54, 1318.20, 1258.39, 1152.70, 1070.30, 1038.11, 1015.84. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{24}H_{35}N_2O_2S^+$: 415.24138, found 415.24126.

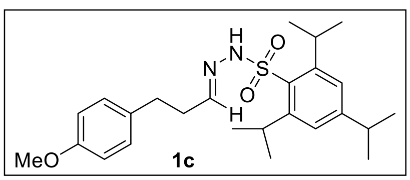


3-(2-Methylphenyl)propanal 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1b**) Yield:



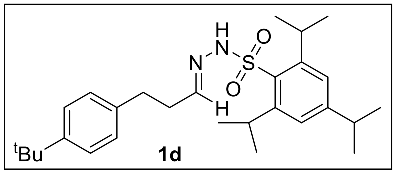
84%. R_f = 0.3 (Hexane:Ethyl Acetate 10/1). ^1H NMR (600 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.27 – 7.23 (m, 1H), 7.21 – 7.09 (m, 1H), 4.28 (dt, *J* = 13.5, 6.7 Hz, 1H), 3.10 – 3.05 (m, 1H), 3.02 – 2.93 (m, 1H), 2.78 – 2.72 (m, 1H), 2.37 (dd, *J* = 5.1, 2.0 Hz, 1H), 1.32 (td, *J* = 6.9, 3.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.29, 151.41, 149.95, 138.82, 137.51, 135.96, 130.51, 130.30, 128.70, 128.59, 123.85, 34.24, 32.76, 28.14, 24.92, 24.84, 23.64, 19.27.IR (neat, cm^{-1}): 3198.56, 2960.30, 2928.47, 2868.96, 1598.99, 1468.41, 1363.48, 1318.49, 1152.04, 1031.69. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{37}N_2O_2S^+$: 429.25703, found 429.25663.

3-(4-Methoxyphenyl)propanal 2,4,6-triisopropylbenzenesulfonyl hydrazone (**1c**)



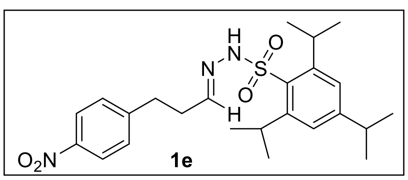
Yield: 82%. R_f = 0.3 (Hexane:Ethyl Acetate 10/1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, *J* = 5.9 Hz, 1H), 7.17 (dt, *J* = 27.4, 13.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.85 – 6.75 (m, 1H), 4.36 (dd, *J* = 13.2, 6.6 Hz, 1H), 3.77 (s, 1H), 3.09 – 2.92 (m, 1H), 2.79 – 2.70 (m, 1H), 2.51 (dd, *J* = 7.5, 5.0 Hz, 1H), 1.43 – 1.24 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$): δ 157.79, 153.06, 151.31, 149.77, 148.14, 132.70, 129.14, 123.65, 113.75, 55.01, 34.07, 31.14, 29.81, 24.79, 24.31, 23.49. IR (neat, cm^{-1}): 2960.39, 2869.65, 1697.17, 1599.92, 1460.81, 1383.05, 1363.15, 1154.86, 1053.86. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{37}N_2O_3S^+$: 445.25194, found 445.25359.

3-(4-*tert*-Butylphenyl)propanal 2,4,6-triisopropylbenzenesulfonyl hydrazone (1d)



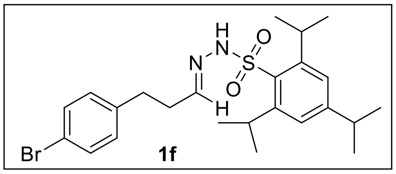
Yield: 82%. R_f = 0.3 (Hexane:Ethyl Acetate 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.31 (dd, J = 8.2, 3.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.06 (m, 2H), 7.00 (d, J = 8.2 Hz, 1H), 4.24 – 4.16 (m, 1H), 2.92 (dt, J = 14.0, 6.9 Hz, 1H), 2.77 – 2.70 (m, 1H), 2.55 – 2.49 (m, 1H), 1.32 – 1.24 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.48, 151.52, 150.31, 149.14, 137.61, 131.35, 128.13, 125.51, 123.97, 77.37, 77.16, 76.95, 34.34, 33.99, 31.78, 31.51, 30.11, 25.00, 24.51, 23.72. IR (neat, cm^{-1}): 2958.23, 2868.50, 1611.28, 1599.59, 1565.05, 1512.44, 1462.92, 1425.18, 1362.56, 1318.30, 1300.44, 1246.45, 1164.39, 1153.39, 1036.97. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{43}N_2O_2S^+$: 471.30398, found 471.30368.

3-(4-Nitrophenyl)propanal 2,4,6-triisopropylbenzenesulfonyl hydrazone hydrazone



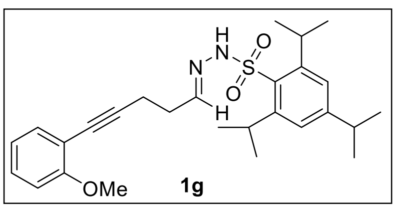
(**1e**) Yield: 85%. R_f = 0.3 (Hexane:Ethyl Acetate 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.7 Hz, 1H), 7.29 – 7.16 (m, 1H), 7.09 (s, 1H), 4.20 (tt, J = 13.5, 6.8 Hz, 1H), 4.08 (dt, J = 20.4, 6.7 Hz, 1H), 2.99 – 2.92 (m, 1H), 2.89 (t, J = 7.5 Hz, 1H), 2.55 (td, J = 7.4, 4.6 Hz, 1H), 1.31 – 1.22 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 153.73, 151.51, 148.61, 148.17, 129.38, 127.51, 124.01, 123.75, 122.88, 77.41, 77.16, 76.91, 34.28, 33.29, 31.60, 30.03, 24.93, 23.66. IR (neat, cm^{-1}): 2959.77, 2868.82, 1598.60, 1518.30, 1461.33, 1383.47, 1343.56, 1276.08, 1163.86, 1152.63, 1107.50, 1058.74, 1037.99. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{34}N_3O_4S^+$:460.22645, found 460.22506.

3-(4-Nitrophenyl)propanal 2,4,6-triisopropylbenzenesulfonyl hydrazone hydrazone



(**1f**) Yield: 90%. R_f = 0.3 (Hexane:Ethyl Acetate 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.13 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 4.23 – 4.14 (m, 1H), 2.97 – 2.90 (m, 1H), 2.72 (t, *J* = 7.6 Hz, 1H), 2.49 (td, *J* = 7.6, 4.9 Hz, 1H), 1.26 (dd, *J* = 13.5, 6.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.54, 151.50, 149.22, 139.60, 131.93, 131.59, 130.22, 123.98, 120.04, 77.41, 77.16, 76.91, 34.31, 33.70, 31.47, 30.07, 24.94, 23.71. IR (neat, cm^{-1}): 3201.55, 2958.89, 2928.52, 2868.02, 1598.97, 1564.63, 1488.04, 1460.92, 1425.49, 1362.61, 1315.72, 1163.87, 1152.58, 1071.68. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{34}N_2O_2SBr^+$: 493.15189, found 493.15354.

5-(2-Methoxyphenyl)pent-4-ynal 2,4,6-triisopropylbenzenesulfonyl hydrazone



hydrazone (**1g**) Yield: 83%. R_f = 0.3 (Hexane:Ethyl Acetate 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 1H), 7.24 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.17 (s, 1H), 6.88 – 6.82 (m, 1H), 4.27 – 4.13 (m, 1H), 3.85 (s, 2H), 2.90 (ddd, *J* = 10.3, 9.0, 5.1 Hz, 1H), 2.61 (t, *J* = 6.9 Hz, 1H), 2.57 – 2.48 (m, 1H), 1.34 – 1.19 (m, 11H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.83, 153.31, 151.36, 149.00, 133.64, 131.12, 129.23, 124.00, 123.80, 120.41, 110.54, 92.08, 77.81, 77.25, 77.00, 76.75, 55.75, 34.15, 31.59, 29.93, 24.81, 23.52, 16.99. IR (neat, cm^{-1}): 2958.91, 2868.48, 1597.29, 1566.05, 1492.50, 1462.26, 1433.76, 1382.93, 1362.46, 1318.91, 1260.89, 1162.60, 1104.70, 1049.83, 1065.62. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{27}H_{37}N_2O_3S^+$: 469.25194, found 469.25132.

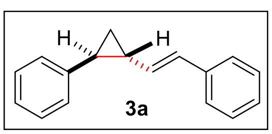
4.4.3. Synthesis and Characterization of Vinyl Cyclopropane

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

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone (0.10 mmol, 1.0 equiv), [Co(Por)] (2 mol %) and Cs_2CO_3 (0.20 mmol, 2.0 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under the nitrogen atmosphere, alkyne (2.0 equiv) and anhydrous chlorobenzene (1.0 mL) were added. The Schlenk tube was then purged with nitrogen for 1 min and sealed with the Teflon screw cap. The reaction mixture was stirred at 22°C for 24 h. Following completion of the reaction, the reaction mixture was filtered through a pad of silica gel, concentrated under vacuum, and purified by flash column chromatography.

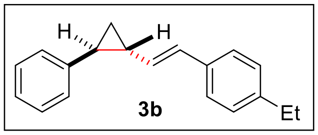
4.4.3.2. Characterization of Vinyl Cyclopropane

((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3a**) Yield: 96%. R_f = 0.3

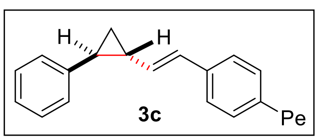


(Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 12.7, 7.4 Hz, 4H), 7.18 (dd, *J* = 15.9, 7.4 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.92 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.07 – 2.03 (m, 1H), 1.88 – 1.81 (m, 1H), 1.33 (dt, *J* = 8.5, 5.5 Hz, 1H), 1.23 (dt, *J* = 8.9, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.11, 137.50, 132.86, 128.50, 128.36, 128.23, 126.76, 125.69, 125.67, 125.66, 27.38, 25.72, 17.09. IR (neat, cm^{-1}): 3060.40, 3024.69, 1647.00, 1603.28, 1496.41, 144931, 1266.47, 1216.61, 1178.99, 1072.32, 1029.05. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{17}^+$: 221.13248, found 221.13142. HPLC analysis: *ee* = 71%. IA (100% hexanes : 0% isopropanol, 1 mL/min): t_{major} = 9.5 min, t_{minor} = 11.3 min.

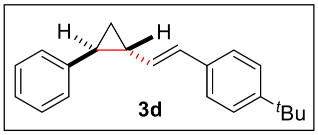
1-Ethyl-4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (3b) Yield: 90%. R_f = 0.3 (Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.25 (m, 1H), 7.19 (dt, J = 13.5, 4.4 Hz, 1H), 7.15 – 7.06 (m, 1H), 6.47 (d, J = 15.8 Hz, 1H), 5.88 (dd, J = 15.7, 8.6 Hz, 1H), 2.63 (q, J = 7.6 Hz, 1H), 2.07 – 2.02 (m, 1H), 1.84 (dt, J = 8.5, 4.7 Hz, 1H), 1.36 – 1.30 (m, 1H), 1.28 – 1.18 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.09, 142.39, 135.15, 132.01, 128.50, 128.28, 128.17, 125.83, 125.79, 125.78, 77.37, 77.16, 76.95, 28.70, 27.55, 25.83, 17.23, 15.72. IR (neat, cm^{-1}): 3022.10, 2962.90, 2929.43, 1647.13, 1603.90, 1511.54, 1496.88, 1454.57, 1181.88, 1030.52. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{21}^+$: 249.16378, found 221.16401. HPLC analysis: *ee* = 71%. ID (99.9% hexanes : 0.1% isopropanol, 1 mL/min): t_{major} = 6.8 min, t_{minor} = 7.9 min.



1-Pentyl-4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (3c) Yield: 96%. R_f = 0.3 (Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.47 (d, J = 15.7 Hz, 1H), 5.88 (dd, J = 15.7, 8.6 Hz, 1H), 2.62 – 2.55 (m, 1H), 2.06 – 2.01 (m, 1H), 1.87 – 1.80 (m, 1H), 1.61 (dt, J = 14.9, 7.6 Hz, 1H), 1.39 – 1.28 (m, 3H), 1.22 (dt, J = 8.8, 5.4 Hz, 1H), 0.90 (t, J = 7.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.39, 141.80, 135.08, 131.97, 128.73, 128.50, 128.29, 125.82, 125.77, 125.70, 77.37, 77.16, 76.95, 35.76, 31.63, 31.29, 27.58, 25.83, 22.70, 17.23, 14.19. IR (neat, cm^{-1}): 3028.04, 2956.10, 228.35, 2856.68, 1702.54, 1606.15, 1455.27, 1261.59, 1168.55, 1029.72, 1018.52. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{27}^+$: 291.21073, found 291.21076. HPLC analysis: ee = 73%. ID (99.9% hexanes : 0.1% isopropanol, 1 mL/min): t_{major} = 6.8 min, t_{minor} = 9.1 min.

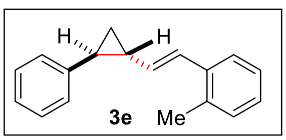


1-(*tert*-Butyl)-4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3d**) Yield: 96%.



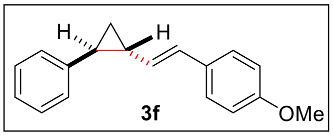
R_f = 0.3 (Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 5H), 7.21 – 7.16 (m, 1H), 7.14 – 7.10 (m, 2H), 6.49 (d, J = 15.8 Hz, 1H), 5.90 (dd, J = 15.7, 8.6 Hz, 1H), 2.07 – 2.02 (m, 1H), 1.89 – 1.80 (m, 1H), 1.36 – 1.30 (m, 9H), 1.26 – 1.21 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.96, 142.40, 134.91, 132.20, 128.50, 128.15, 125.83, 125.78, 125.57, 125.53, 34.64, 31.46, 27.53, 25.86, 17.24. IR (neat, cm^{-1}): 3024.50, 2961.61, 2902.76, 2866.35, 1604.21, 1512.87, 1496.09, 1459.75, 1363.14, 1269.19, 1109.08, 1029.95. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{25}^+$: 277.19508, found 277.19452. HPLC analysis: *ee* = 73%. OJH (99.2% hexanes: 0.8% isopropanol, 1 mL/min): t_{major} = 39.5 min, t_{minor} = 27.7 min.

1-Methyl-2-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3e**) Yield: 90%. R_f =

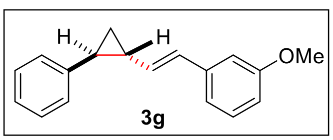


0.3 (Hexanes). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.20 – 7.10 (m, 6H), 6.69 (d, J = 15.6 Hz, 1H), 5.78 (dd, J = 15.6, 8.8 Hz, 1H), 2.34 (s, 3H), 2.09 – 2.02 (m, 1H), 1.88 (ddd, J = 13.2, 8.7, 4.8 Hz, 1H), 1.33 (dt, J = 8.5, 5.5 Hz, 1H), 1.23 (dt, J = 9.0, 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.36, 136.64, 134.89, 134.26, 130.38, 128.53, 128.52, 126.90, 126.16, 125.82, 125.80, 125.12, 77.37, 77.16, 76.95, 27.98, 25.89, 20.00, 17.44. IR (neat, cm^{-1}): 3024.66, 2961.99, 2159.33, 1642.14, 1602.14, 1496.29, 1458.25, 1260.01, 1089.59, 1029.18. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14824. HPLC analysis: *ee* = 52%. IE (99% hexanes: 1% isopropanol, 1 mL/min): t_{major} = 5.9 min, t_{minor} = 6.3 min.

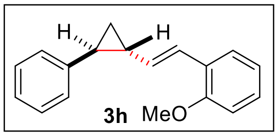
1-Methoxy-4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3f**) Yield: 94%. R_f = 0.3 (Hexane:Ethyl Acetate = 20/1). ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.25 (m, 1H), 7.18 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 5.80 (dd, J = 15.7, 8.6 Hz, 1H), 3.81 (s, 1H), 2.05 – 1.99 (m, 1H), 1.87 – 1.79 (m, 1H), 1.31 (dt, J = 8.5, 5.5 Hz, 1H), 1.22 (dt, J = 8.9, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.77, 142.43, 130.76, 130.53, 128.48, 127.82, 126.92, 125.81, 125.75, 114.10, 77.41, 77.16, 76.91, 55.42, 27.50, 25.76, 17.16. IR (neat, cm^{-1}): 3003.18, 2960.06, 2360.39, 2159.16, 1605.78, 1509.51, 1496.76, 1457.74, 1297.36, 1247.69, 1174.69, 1030.83 HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14381. HPLC analysis: *ee* = 61%. ODH (99% hexanes : 1% isopropanol, 1 mL/min): t_{major} = 19.7 min, t_{minor} = 17.9 min.



1-Methoxy-3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene ((–)-**3g**) Yield: 91%. R_f = 0.3 (Hexane:Ethyl Acetate = 20/1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, J = 7.7 Hz, 2H), 7.19 (dt, J = 14.8, 7.6 Hz, 2H), 7.11 (d, J = 7.3 Hz, 2H), 6.93 (d, J = 7.7 Hz, 1H), 6.86 (d, J = 1.9 Hz, 1H), 6.75 (dd, J = 8.2, 2.5 Hz, 1H), 6.46 (d, J = 15.7 Hz, 1H), 3.82 (s, 4H), 2.08 – 2.03 (m, 1H), 1.86 – 1.81 (m, 1H), 1.33 (dt, J = 8.5, 5.5 Hz, 1H), 1.23 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.94, 142.23, 139.12, 133.41, 129.63, 129.31, 128.52, 128.28, 125.84, 118.52, 112.57, 111.15, 55.34, 27.54, 25.90, 17.27. IR (neat, cm^{-1}): 3022.71, 2933.83, 2833.58, 2361.08, 2158.91, 1645.85, 1597.37, 1494.72, 1459.70, 1433.2, 1316.34, 1288.53, 1264.91, 1153.35, 1076.26. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14409. HPLC analysis: *ee* = 75%. ODH (99% hexanes : 1% isopropanol, 1 mL/min): t_{major} = 25.6 min, t_{minor} = 24.3 min.

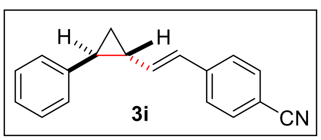


1-Methoxy-2-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3h**) Yield: 95%. R_f



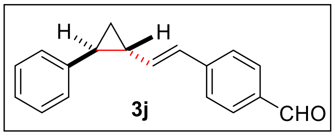
= 0.3 (Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.6, 1.4 Hz, 1H), 7.27 (dd, J = 9.9, 6.5 Hz, 3H), 7.21 – 7.15 (m, 2H), 7.10 (d, J = 7.3 Hz, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 5.93 (dd, J = 15.9, 8.7 Hz, 1H), 3.84 (s, 3H), 2.07 – 2.00 (m, 1H), 1.93 – 1.84 (m, 1H), 1.31 (dt, J = 8.4, 5.4 Hz, 1H), 1.23 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.32, 142.49, 133.78, 129.34, 128.47, 127.91, 126.37, 125.83, 125.73, 123.14, 120.79, 110.95, 55.58, 28.06, 25.95, 17.42. IR (neat, cm^{-1}): 3026.09, 2936.45, 2835.20, 1641.01, 1596.45, 1577.22, 1489.73, 1460.80, 1434.94, 1290.19, 1243.27, 1179.74, 1104.82, 1049.52, 1027.14. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14298. HPLC analysis: *ee* = 71%. ADH (99.8% hexanes : 0.2% isopropanol, 1 mL/min): t_{major} = 8.7 min, t_{minor} = 11.5 min.

4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzonitrile ((–)-**3i**) Yield: 88%. R_f = 0.3

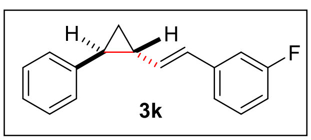


(Hexane:Ethyl Acetate = 8/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (dd, J = 8.1, 6.4 Hz, 2H), 7.38 (d, J = 8.3 Hz, 1H), 7.30 (dd, J = 10.5, 4.8 Hz, 2H), 7.19 (dd, J = 10.6, 4.2 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.48 (d, J = 15.7 Hz, 1H), 6.04 (dd, J = 15.7, 9.0 Hz, 1H), 2.18 – 2.06 (m, 1H), 1.92 – 1.82 (m, 1H), 1.40 (dt, J = 8.4, 5.6 Hz, 1H), 1.32 – 1.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.10, 137.53, 132.51, 128.58, 126.84, 126.18, 126.09, 125.85, 119.28, 109.91, 77.37, 77.16, 76.95, 27.74, 26.32, 17.51. IR (neat, cm^{-1}): 3002.44, 2357.97, 2210.53, 1658.82, 1536.62, 1454.16, 1275.30, 1266.10. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{16}N^+$: 246.12773, found 246.12791. HPLC analysis: *ee* = 69%. IE (99% hexanes : 1% isopropanol, 1 mL/min): t_{major} = 7.5 min, t_{minor} = 8.5 min.

4-((*E*)-2-((1*R*,2*S*)-2-Phenylcyclopropyl)vinyl)benzaldehyde (**3j**) Yield: 92%. R_f = 0.3 (Hexane:DCM = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.09 (dd, *J* = 15.7, 9.0 Hz, 1H), 2.16 – 2.09 (m, 1H), 1.93 – 1.84 (m, 1H), 1.40 (dt, *J* = 8.4, 5.6 Hz, 1H), 1.31 – 1.24 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.79, 143.79, 141.71, 137.38, 134.94, 130.36, 128.60, 127.43, 126.21, 126.08, 125.91, 77.41, 77.16, 76.91, 27.86, 26.36, 17.53. IR (neat, cm^{-1}): 3026.12, 2158.92, 1973.66, 1691.92, 1643.30, 1599.06, 1566.58, 1497.00, 1458.80, 1497.00, 1304.77, 1212.99, 1165.92. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{17}O^+$: 249.12739, found 249.12771. HPLC analysis: *ee* = 72%. ID (98% hexanes : 0.2% isopropanol, 1 mL/min): t_{major} = 8.3 min, t_{minor} = 9.4 min.

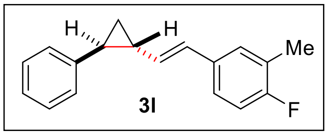


1-Fluoro-3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3k**) Yield: 92%. R_f = 0.3 (Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, J = 7.6 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.10 (dd, J = 16.3, 7.5 Hz, 3H), 7.02 (d, J = 1.8 Hz, 1H), 6.89 (td, J = 8.4, 2.3 Hz, 1H), 5.93 (dd, J = 15.7, 8.8 Hz, 1H), 2.11 – 2.05 (m, 1H), 1.91 – 1.80 (m, 1H), 1.36 (dt, J = 8.4, 5.5 Hz, 1H), 1.29 – 1.21 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.30 (d, J = 244.7 Hz), 142.02 (s), 140.06 (d, J = 7.7 Hz), 134.56 (s), 130.05 (d, J = 8.5 Hz), 128.55 (s), 127.35 (d, J = 2.6 Hz), 125.94 (s), 125.87 (s), 121.71 (d, J = 2.7 Hz), 113.66 (d, J = 21.4 Hz), 112.20 (d, J = 21.7 Hz), 27.43 (s), 25.99 (s), 17.28 (s).^{19}F NMR (470 MHz, $CDCl_3$): δ -115.73. IR (neat, cm^{-1}): 3024.34 2029.45, 2006.73, 1646.19, 1606.54, 1581.76, 1487.53, 1459.14, 1445.15, 1258.12, 1241.98, 1181.11, 1140.46, 1091.01, 1073.54, 1030.73. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{17}H_{16}F^+$: 239.12306, found 239.12401. HPLC analysis:



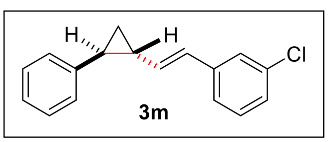
ee = 73%. IA (99% hexanes : 1% isopropanol, 1 mL/min): t_{major} = 9.7 min, t_{minor} = 11.5 min.

1-Fluoro-2-methyl-4-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (3l) Yield: 90%.



R_f = 0.3 (Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 3H), 7.20 – 7.07 (m, 5H), 6.91 (t, J = 9.0 Hz, 1H), 5.80 (dd, J = 15.7, 8.7 Hz, 1H), 2.25 (s, 3H), 2.07 – 2.00 (m, 1H), 1.85 – 1.77 (m, 1H), 1.31 (dt, J = 8.5, 5.5 Hz, 1H), 1.23 – 1.16 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.59 (d, J = 244.8 Hz), 142.26 (s), 133.49 (s), 132.38 (s), 129.32 (s), 128.71 (d, J = 5.0 Hz), 128.52 (s), 127.41 (s), 125.84 (s), 124.87 (d, J = 17.5 Hz), 124.60 (d, J = 7.9 Hz), 115.14 (d, J = 22.5 Hz), 27.47 (s), 25.81 (s), 17.18 (s), 14.73 (d, J = 3.5 Hz). ^{19}F NMR (465 MHz, $CDCl_3$): δ -120.042. IR (neat, cm^{-1}): 2963.04, 2360.43, 2344.37, 2159.99, 2151.31, 1683.71, 1558.58, 1497.721260.73, 1030.26. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{18}F^+$: 253.13871, found 253.13836. HPLC analysis: *ee* = 76%. ADH (99% hexanes : 10.5% isopropanol, 1 mL/min): t_{major} = 5.5 min, t_{minor} = 6.4 min.

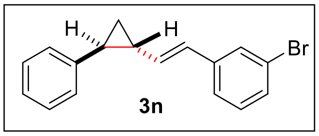
1-Chloro-3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (3m) Yield: 99%. R_f =



0.3 (Hexanes). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.56 – 8.49 (m, 1H), 7.60 (td, J = 7.7, 1.8 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.19 – 7.16 (m, 2H), 7.12 – 7.09 (m, 2H), 6.57 (d, J = 15.5 Hz, 1H), 6.48 (dd, J = 15.5, 9.1 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.91 – 1.86 (m, 1H), 1.39 (dt, J = 8.4, 5.6 Hz, 1H), 1.31 (dt, J = 8.8, 5.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 155.67, 149.45, 141.95, 138.29, 136.72, 129.32, 128.53, 128.30, 127.85, 125.93, 121.62, 121.32, 77.37, 77.16, 76.95, 27.62, 26.28, 17.48. IR (neat, cm-1): 3058.22, 3023.25, 2358.60, 1651.26, 1593.66, 1479.62, 1445.32, 1275.33, 1260.60, 1127.12, 1071.20, 1049.46, 1033.50. HRMS (ESI) ($[M+H]^+$) Calcd. for

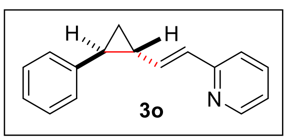
$C_{17}H_{16}Cl^+$: 255.09350, found 255.09248. HPLC analysis: *ee* = 75%. IA (99% hexanes : 10.5% isopropanol, 1 mL/min): t_{major}=9.8 min, t_{minor} = 11.7 min.

1-Bromo-3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)benzene (**3n**) Yield: 96%. R_f =



0.3 (Hexanes). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (t, *J* = 1.7 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.25 – 7.14 (m, 5H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.91 (dd, *J* = 15.7, 8.8 Hz, 1H), 2.09 – 2.04 (m, 1H), 1.86 – 1.80 (m, 1H), 1.37 – 1.32 (m, 1H), 1.23 (dt, *J* = 8.7, 5.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.98, 134.81, 130.16, 129.72, 129.30, 128.61, 128.56, 126.95, 125.95, 125.86, 124.53, 122.90, 27.54, 26.02, 17.32. IR (neat, cm^{-1}): 3023.87, 2922.65, 1645.10, 1602.13, 1560.78, 1496.11, 1473.31, 1090.68, 1071.14. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04097. HPLC analysis: *ee* = 72%. IB (99.7% hexanes : 0.3% isopropanol, 1 mL/min): t_{major} = 6.2 min, t_{minor} = 5.6 min.

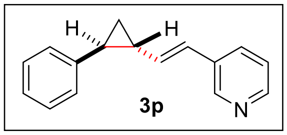
2-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)pyridine (**3o**) Yield: 96%. R_f = 0.3



(Hexanes). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.55 – 8.48 (m, 1H), 7.60 (td, J = 7.7, 1.8 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.20 – 7.15 (m, 2H), 7.12 – 7.07 (m, 3H), 6.57 (d, J = 15.5 Hz, 1H), 6.48 (dd, J = 15.5, 9.1 Hz, 1H), 6.01 (dd, J = 15.6, 9.9 Hz, 1H), 2.18 – 2.13 (m, 1H), 1.92 – 1.84 (m, 1H), 1.42 – 1.37 (m, 1H), 1.31 (dt, J = 8.8, 5.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 155.67, 149.45, 141.95, 138.29, 136.72, 129.32, 128.53, 127.85, 125.93, 121.62, 121.32, 77.37, 77.16, 76.95, 27.62, 26.28, 17.48. IR (neat, cm^{-1}): 3026.38, 3003.58, 2924.11, 2850.27, 1700.40, 1646.79, 1585.01, 1551.51, 1496.52, 1469.77, 1431.42, 1299.77, 1147.75, 1090.10, 1029.98. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N^+$: 222.12773, found 222.12763. HPLC analysis:

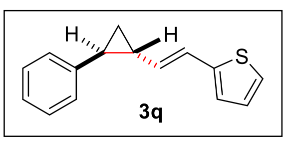
ee = 73%. ADH (95% hexanes : 5% isopropanol, 0.8 mL/min): t_{major} = 7.1 min, t_{minor} = 9.9 min.

3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)pyridine (**3p**) Yield: 42%. R_f = 0.3



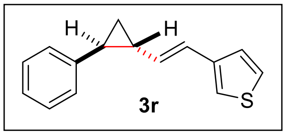
(Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$):δ 7.62 (d, J = 7.8 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.21 – 7.15 (m, 2H), 7.12 – 7.09 (m, 2H), 6.46 (d, J = 15.8 Hz, 1H), 5.98 (dd, J = 15.8, 8.8 Hz, 1H), 2.11 – 2.06 (m, 1H), 1.89 – 1.83 (m, 1H), 1.37 (dt, J = 8.5, 5.5 Hz, 1H), 1.28 – 1.23 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.83, 135.64, 133.55, 132.35, 129.27, 128.56, 128.31, 126.37, 126.01, 125.88, 124.78, 27.57, 26.07, 17.32. IR (neat, cm^{-1}): 3026.48, 3000.52, 2924.87, 2850.18, 1646.80, 1585.01, 1561.50, 1496.53, 1469.78, 1431.42, 1299.92, 1260.10, 1178.06, 1029.93. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{16}N^+$: 222.12773, found 222.12785. HPLC analysis: ee = 71%. IE (95% hexanes : 5% isopropanol, 1 mL/min): t_{major} = 24.1 min, t_{minor} = 23.2 min.

2-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)thiophene (**3q**) Yield: 52%. R_f = 0.3



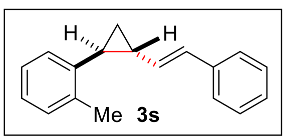
(Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.33 (m, 3H), 7.22 – 7.16 (m, 3H), 7.11 – 7.05 (m, 3H), 6.61 (dd, *J* = 15.6, 2.8 Hz, 1H), 5.78 (dd, *J* = 15.6, 8.6 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.83 – 1.74 (m, 1H), 1.34 – 1.30 (m, 1H), 1.21 (dt, *J* = 8.8, 5.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 142.90, 132.87, 128.52, 127.43, 125.86, 125.12, 124.22, 123.10, 122.15, 121.75, 77.41, 77.16, 76.91, 27.27, 25.90, 17.15. IR (neat, cm^{-1}): 2927.91, 2359.22, 1699.69, 1652.97, 1558.57, 1540.40, 1456/10, 1418.98, 1275.25, 1260.91, 1049.59. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{15}S^+$: 227.08890, found 227.08980. HPLC analysis: *ee* = 60%. ADH (99.9% hexanes : 0.1% isopropanol, 18 mL/min): t_{major}= 14.2 min, t_{minor} = 19.6 min.

3-((*E*)-2-((1*R*,2*S*)-2-phenylcyclopropyl)vinyl)thiophene (3r) Yield: 95%. R_f = 0.3



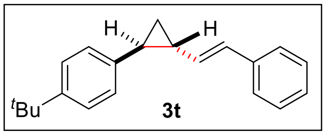
(Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 1H), 7.18 (d, J = 6.1 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 2.7 Hz, 1H), 6.51 (d, J = 15.7 Hz, 1H), 5.81 (dd, J = 15.7, 8.6 Hz, 1H), 2.06 – 2.01 (m, 1H), 1.84 – 1.77 (m, 1H), 1.32 (dt, J = 8.5, 5.4 Hz, 1H), 1.21 (dt, J = 8.8, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.29, 140.20, 132.85, 129.28, 128.50, 125.98, 125.84, 125.81, 124.88, 122.79, 120.32, 77.41, 77.16, 76.91, 27.24, 25.81, 17.10. IR (neat, cm^{-1}): 3023.83, 2360.01, 1683.73, 1652.84, 1604.03, 1558.73, 1496.16, 1456.84, 1418.16, 1275.25, 1260.57, 1090.1, 1029.87. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{15}H_{15}S^+$: 227.08890, found 227.08948. HPLC analysis: *ee* = 70%. IE (99.5% hexanes : 0.5% isopropanol, 0.8 mL/min): t_{major} = 6.1 min, t_{minor} = 6.4 min.

1-Methyl-2-((1*S*,2*R*)-2-((*E*)-styryl)cyclopropyl)benzene (3s) Yield: 98%. R_f = 0.3



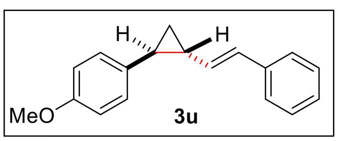
(Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 1H), 7.22 – 7.11 (m, 1H), 7.05 – 7.01 (m, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.00 (dd, *J* = 15.7, 8.8 Hz, 1H), 2.40 (s, 1H), 2.06 (dd, *J* = 8.5, 5.2 Hz, 1H), 1.70 (ddd, *J* = 13.5, 8.8, 5.0 Hz, 1H), 1.39 – 1.33 (m, 1H), 1.22 – 1.13 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.93, 138.12, 137.75, 133.59, 129.81, 128.68, 128.26, 126.90, 126.17, 125.99, 125.84, 125.75, 25.43, 24.07, 20.02, 15.13. IR (neat, cm^{-1}): 3022.06, 2925.14, 1492.26, 1459.53, 1448.26, 1071.68, 1031.92. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{19}^+$: 235.14813, found 235.14750. HPLC analysis: *ee* = 73%. IE (99.8% hexanes : 0.2% isopropanol, 1 mL/min): t_{major} = 12.9 min, t_{minor} = 15.7 min.

1-*tert*-Butyl-4-((1*S*,2*R*)-2-((*E*)-styryl)cyclopropyl)benzene (3t) Yield: 90%. R_f = 0.3



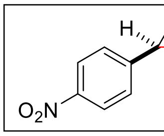
(Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 1H), 7.23 – 7.15 (m, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.03 (dt, *J* = 11.9, 4.1 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.32 (s, 2H), 1.30 – 1.27 (m, 1H), 1.24 – 1.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.78, 139.24, 137.74, 133.20, 128.66, 128.24, 126.88, 125.81, 125.54, 125.44, 31.54, 27.40, 25.49, 17.13, 12.90. IR (neat, cm^{-1}):3024.00, 2961.29, 2867.54, 1599.11, 1517.24, 1461.45, 1362.85, 1268.43, 1176.26, 1070.92. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{25}^+$: 277.19508, found 277.19522. HPLC analysis: *ee* = 70%. ADH (99.8% hexanes : 0.2% isopropanol, 1 mL/min): t_{major} = 6.1 min, t_{minor} = 7.4 min

1- Methoxy-4-((1*S*,2*R*)-2-((*E*)-styryl)cyclopropyl)benzene (3u) Yield: 90%. R_f = 0.3



(Hexanes/EtOAc = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 15.2, 7.6 Hz, 2H), 7.23 – 7.12 (m, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 5.93 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.80 (s, 2H), 2.09 – 1.96 (m, 1H), 1.82 – 1.71 (m, 1H), 1.27 (dt, *J* = 8.4, 5.4 Hz, 1H), 1.19 (dt, *J* = 9.0, 5.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.97, 137.72, 134.22, 133.25, 128.65, 128.14, 127.00, 126.86, 125.79, 114.01, 55.47, 26.98, 25.17, 16.78. IR (neat, cm^{-1}):3022.72, 2933.26, 2833.76, 1645.97, 1611.54, 1513.50, 1450.30 1297.62, 1246.67, 1178.44, 1035.15. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{19}O^+$: 251.14304, found 251.14370. HPLC analysis: *ee* = 60%. IA (100% hexanes : 0% isopropanol, 1 mL/min): t_{major} = 6.2 min, t_{minor} = 9.5 min

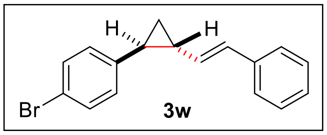
1-Nitro-4-((1*S*,2*R*)-2-((*E*)-styryl)cyclopropyl)benzene (**3v**) Yield: 97%. R_f = 0.3



3v

(Hexane:Ethyl Acetate = 20/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 – 8.11 (m, 1H), 7.35 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 6.53 (d, J = 15.8 Hz, 1H), 5.91 (dd, J = 15.8, 8.6 Hz, 1H), 2.16 – 2.10 (m, 1H), 1.98 – 1.91 (m, 1H), 1.42 (ddt, J = 16.7, 8.6, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.68, 146.12, 137.19, 131.44, 129.60, 128.74, 127.31, 126.18, 125.93, 123.88, 29.23, 26.04, 18.53. IR (neat, cm^{-1}): 3024.63, 2924.48, 2036.61, 1073.29, 1597.50, 1513.94, 1448.38, 1341.57, 1110.17. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}NO_2^+$: 266.11756, found 266.11828. HPLC analysis: *ee* = 71%. IA (100% hexanes : 0% isopropanol, 1 mL/min): t_{major} = 17.7 min, t_{minor} = 33.2 min.

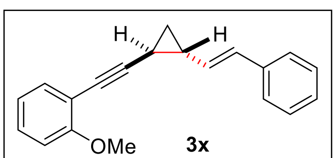
((1*S*,2*S*)-1-Bromo-2-((*E*)-styryl)cyclopropyl)benzene (**3w**) Yield: 99%. R_f = 0.3



3w

(Hexanes). ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.41 – 7.37 (m, 2H), 7.31 (dt, *J* = 15.1, 7.5 Hz, 4H), 7.17 (ddd, *J* = 17.2, 12.0, 7.5 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.85 – 1.73 (m, 1H), 1.29 (dt, *J* = 8.6, 5.6 Hz, 1H), 1.24 (dt, *J* = 8.7, 5.5 Hz, 1H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 141.36, 137.50, 132.49, 131.51, 128.69, 128.57, 127.61, 127.05, 125.85, 119.36, 27.62, 25.38, 17.26. IR (neat, cm^{-1}): 3022.86, 2924.00, 1647.17, 1594.14, 1488.75, 1447.85, 1386.87, 1214.61, 1178.59, 1073.07. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}Br^+$: 299.04299, found 299.04383. HPLC analysis: *ee* = 71%. IA (100% hexanes, 0.8 mL/min): t_{major} = 14.5 min, t_{minor} = 18.7min.

1-Methoxy-2-(((1*S*,2*R*)-2-((*E*)-styryl)cyclopropyl)ethynyl)benzene (**3x**) Yield: 30%. R_f

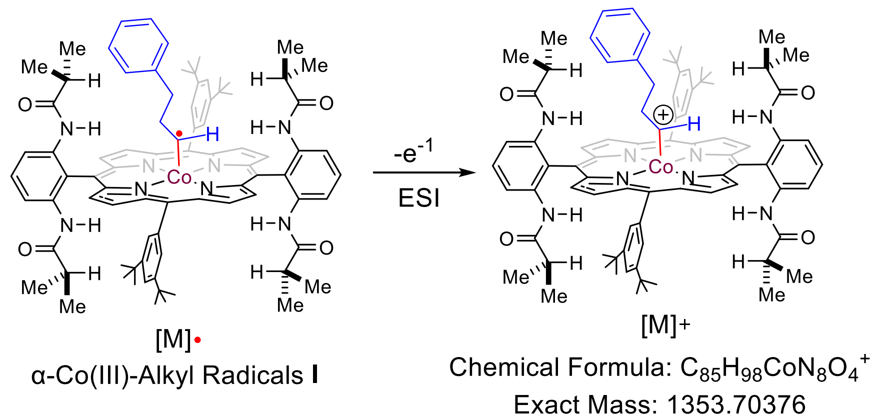


3x

= 0.3 (Hexane:Ethyl Acetate = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, J = 7.2 Hz, 2H), 7.36 (dd, J = 7.5, 1.7 Hz, 1H), 7.29 (d, J = 7.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.18 (t, J = 7.4 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 15.8 Hz, 1H), 6.29 – 6.17 (m, 1H), 3.80 (s, 3H), 1.97 (ddd, J = 7.2, 6.7, 3.2 Hz, 2H), 1.36 (td, J = 8.4, 4.8 Hz, 1H), 1.02 (dd, J = 10.7, 5.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.13, 137.74, 133.55, 130.44, 130.37, 128.90, 128.52, 128.42, 126.79, 125.90, 120.32, 110.46, 94.09, 75.13, 55.71, 22.48, 16.94, 9.40. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{19}O^+$: 275.14304, found 275.14334. IR (neat, cm^{-1}): 2961.42, 2835.26, 1595.37, 1493.43, 1463.53, 1260.68, 1240.63, 1181.31, 1024.41. HPLC analysis: *ee* = 75%. IA (99.5% hexanes : 0.5% isopropanol, 1 mL/min): t_{major} = 7.3 min, t_{minor} =6.2 min.

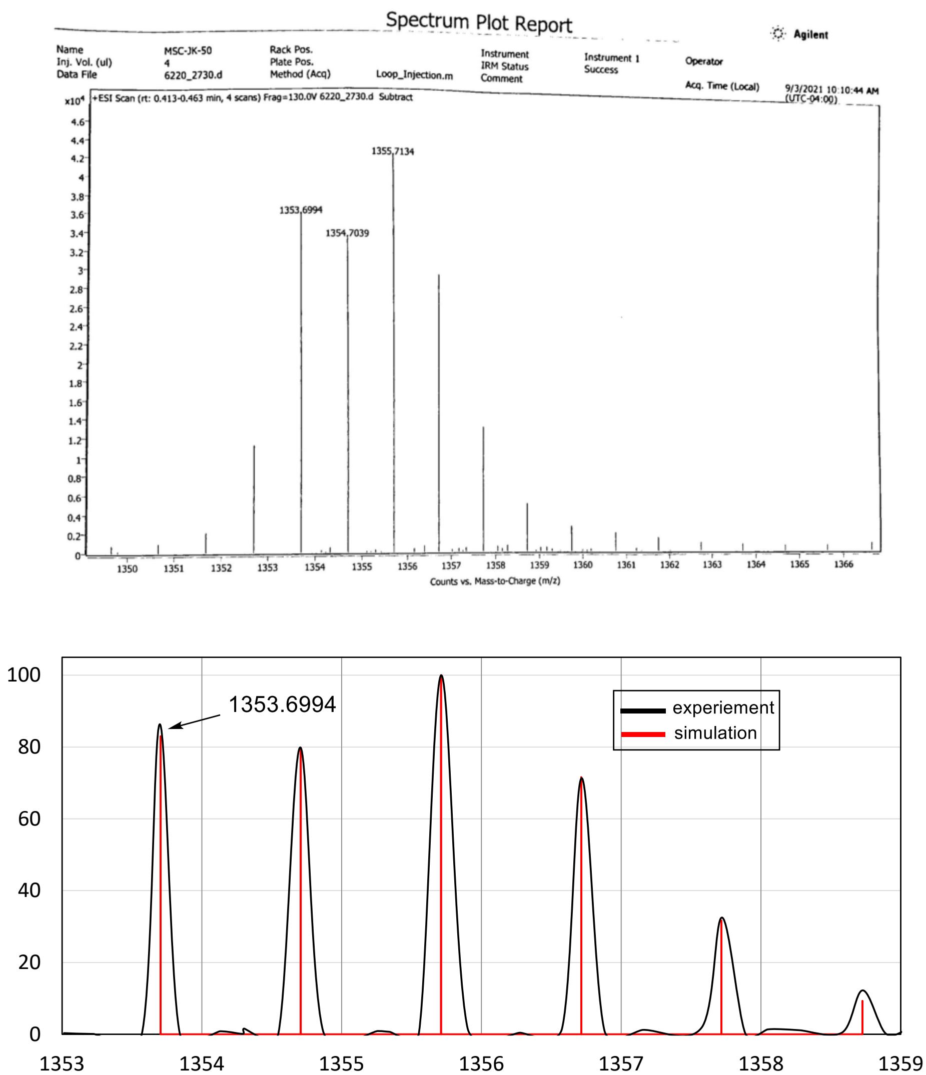
4.4.4. Mechanistic Studies of Stepwise Radical Mechanism

4.4.4.1. Characterization of α-Co(III)-Alkyl Radicals I by HRMS (High-Resolution Mass Spectrometry)



Procedure for HRMS Experiment: To an over-dried Schlenk tube, *N*-sulfonyl hydrazone **1a** (0.10 mmol, 1.0 equiv), [Co(**P2**)] (2 mol %), Cs_2CO_3 (0.20 mmol, 2 equiv.) were added. The Schlenk tube was then evacuated and backfilled with nitrogen 3 times. The Teflon screw cap was replaced with a rubber septum, and Chlorobenzene (0.6 mL) was added via a gas-tight syringe. The mixture was then stirred at room temperature for 30 min. The resulting solution was collected in an HPLC vial (degassed and backfilled with argon). The sample was further diluted with CH_3CN and immediately injected into the 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 the detection of the molecular ion signals corresponding to Co(III)-aminyl radical ($C_{85}H_{98}CoN_8O_4^+$) ($[M]^+$ m/z = 1353.6994 (observed)) by the loss of one electron

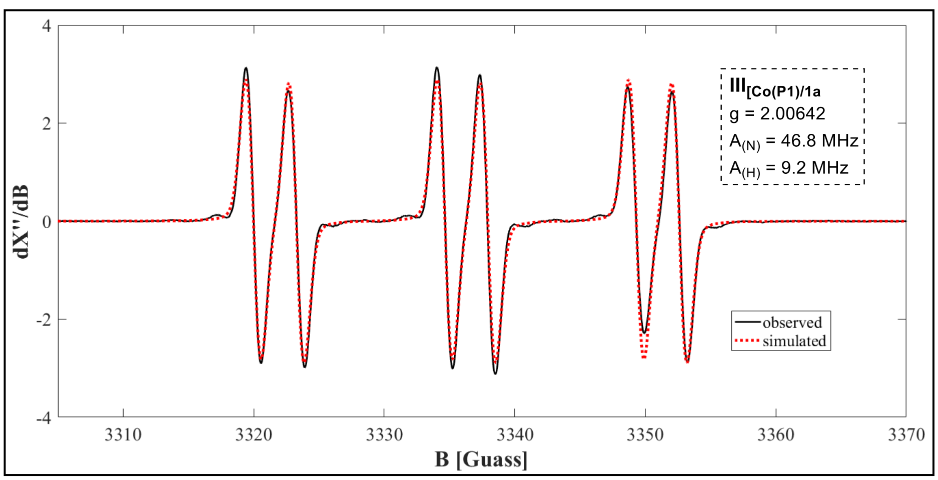
Figure S1. High-Resolution Mass Spectroscopy (HRMS) Spectrum for Co(III)-Supported Alkyl Radical Intermediate I.

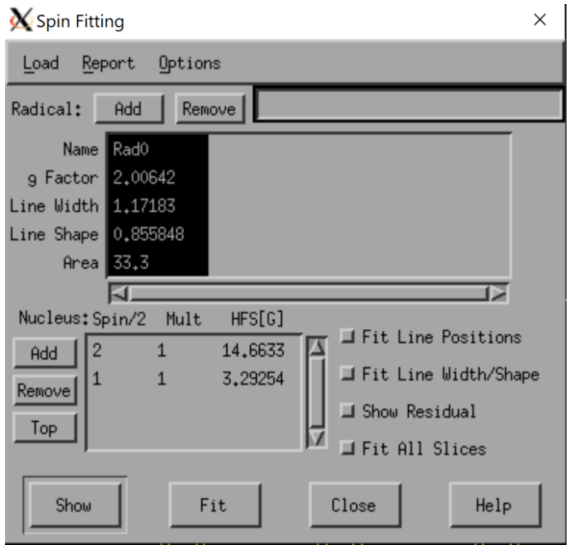


4.4.4.2. Radical Trapping by EPR (Electron Paramagnetic Resonance Spectroscopy)

A 10 mL oven-dried Schlenk tube was charged with *N*-sulfonyl hydrazone **1a** (0.10 mmol, 1.0 equiv), [Co(TPP)] (2 mol %) and PBN (0.12 mmol, 1.2 equiv). The Schlenk tube was capped with a Teflon screw cap, evacuated, and backfilled with nitrogen 3 times. Under nitrogen atmosphere, Et_3N (0.2 mmol, 2.0 equiv) and anhydrous benzene (1.0 mL) were added via a syringe. The reaction mixture was stirred at 60 °C for 10 min. The reaction mixture was then transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for the EPR experiment at room temperature.

Figure S2. EPR Spectrum and Simulation of α-Co(III)-Alkyl Radicals $\mathbf{III}_{\mathbf{[Co(TPP)]/1a}}$ with PBN in Benzene at RT





The resulting notable EPR signal (in black) has been simulated (in red) for:

III$_{\mathbf{[Co(P1)]/1a}}$ with g = 2.00642, $A_{(N)}$ = 46.8 MHz, $A_{(H)}$ = 9.2 MHz;

[The simulation of the EPR spectrum was performed by iteration of the isotopic g-values and line widths using the EPR simulation program SpinFit Xenon]

EPR Simulation Details:

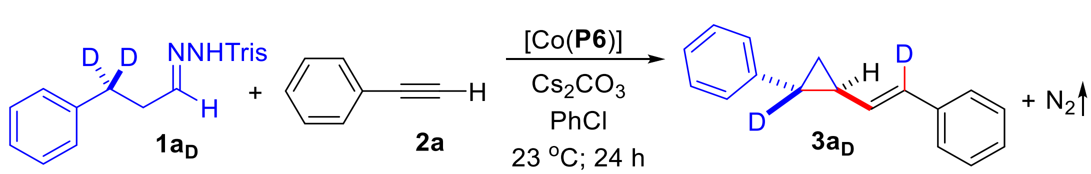
For **III**$_{\mathbf{[Co(P1)]/1a}}$:

g = 2.00642

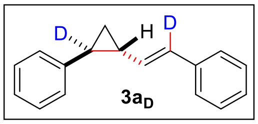
$A_{(N)}$ = 16.7 x 2.00624 x 1.399611451 = 46.8 MHz

$A_{(H)}$ = 3.3 x 2.00624 x 1.399611451 = 9.2 MHz

4.4.4.3. The Study of Radical C–D Alkylation with 1a$_{\mathrm{D}}$ for the Tracking of Deuterium Movement



((*E*)-2-((1*R*,2*S*)-2-Phenylcyclopropyl-2-d)vinyl-1-d)benzene (**3a$_D$**) Yield: 98%. R_f = 0.3



(Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (ddd, *J* = 11.6, 10.9, 5.4 Hz, 7H), 7.20 (dd, *J* = 9.9, 4.3 Hz, 2H), 7.12 (d, *J* = 7.3 Hz, 2H), 5.93 (d, *J* = 8.8 Hz, 1H), 1.85 (td, *J* = 8.6, 5.7 Hz, 1H), 1.33 (dd, *J* = 8.4, 5.1 Hz, 1H), 1.23 (t, *J* = 5.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.23, 137.61, 132.87, 128.67, 128.52, 128.23, 126.92, 125.83, 125.80, 77.41, 77.16, 76.91, 27.42, 17.16. ^{2}H NMR (77 MHz, $CDCl_3$) δ 6.56, 2.06. IR (neat, cm^{-1}): 3023.46, 222.98, 1634.24, 1602.66, 1495.72, 1447.03.

4.4.5. DFT Calculations

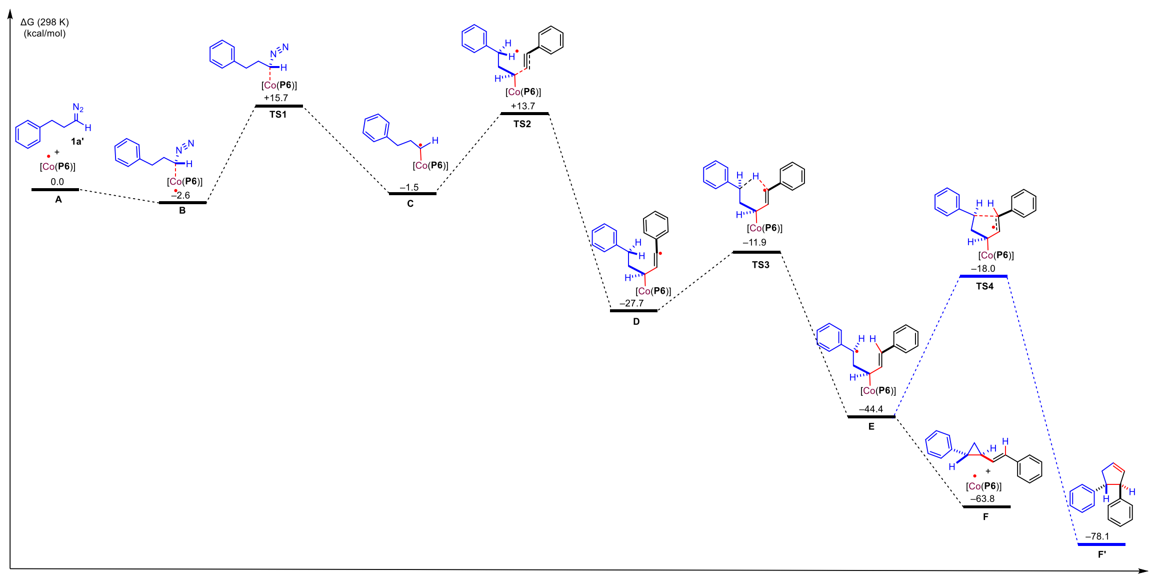
Considering the cost of time and computing resources for the large system with [Co(**P6**)], the geometry optimizations were performed with the Gaussian 16[23] at the BP86[24]/lanl2dz[25] level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy, and thermal corrections (entropy and enthalpy, 298.15 K, 1 Atm) were obtained from these calculations. To further improve the accuracy of energies, single-point energies were carried out at the B3LYP[26]/def2-tzvp[25] level of theory along with Grimme's dispersion correction[27] (D3BJ) and SMD[28] solvation model (in chlorobenzene).

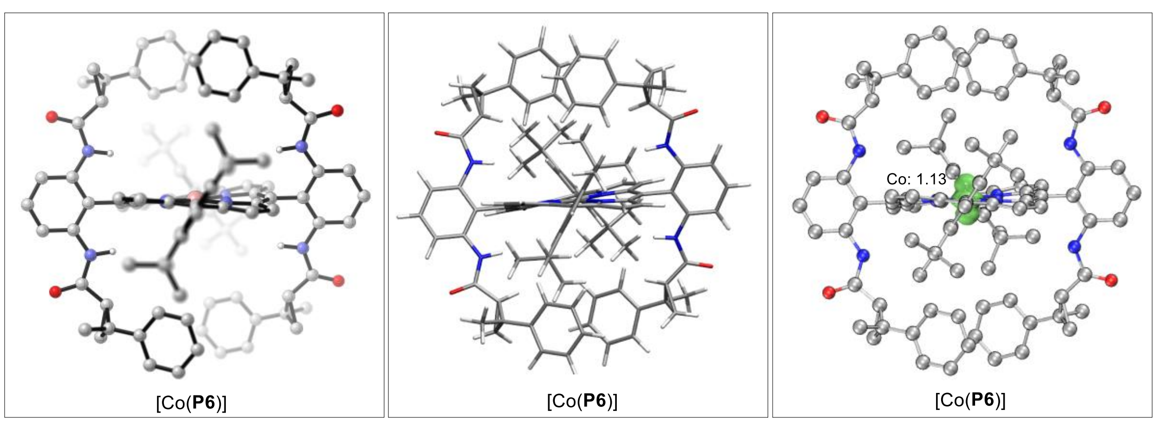
Independent Gradient Model (IGM)[29] analysis was performed with Multiwfn[30] software package using a high-quality grid option to generate files for further plotting. The visualization of IGM analysis results was presented with VMD[31] visualization software. As shown in Scheme S2, the 3D diagrams of optimized structures were generated with

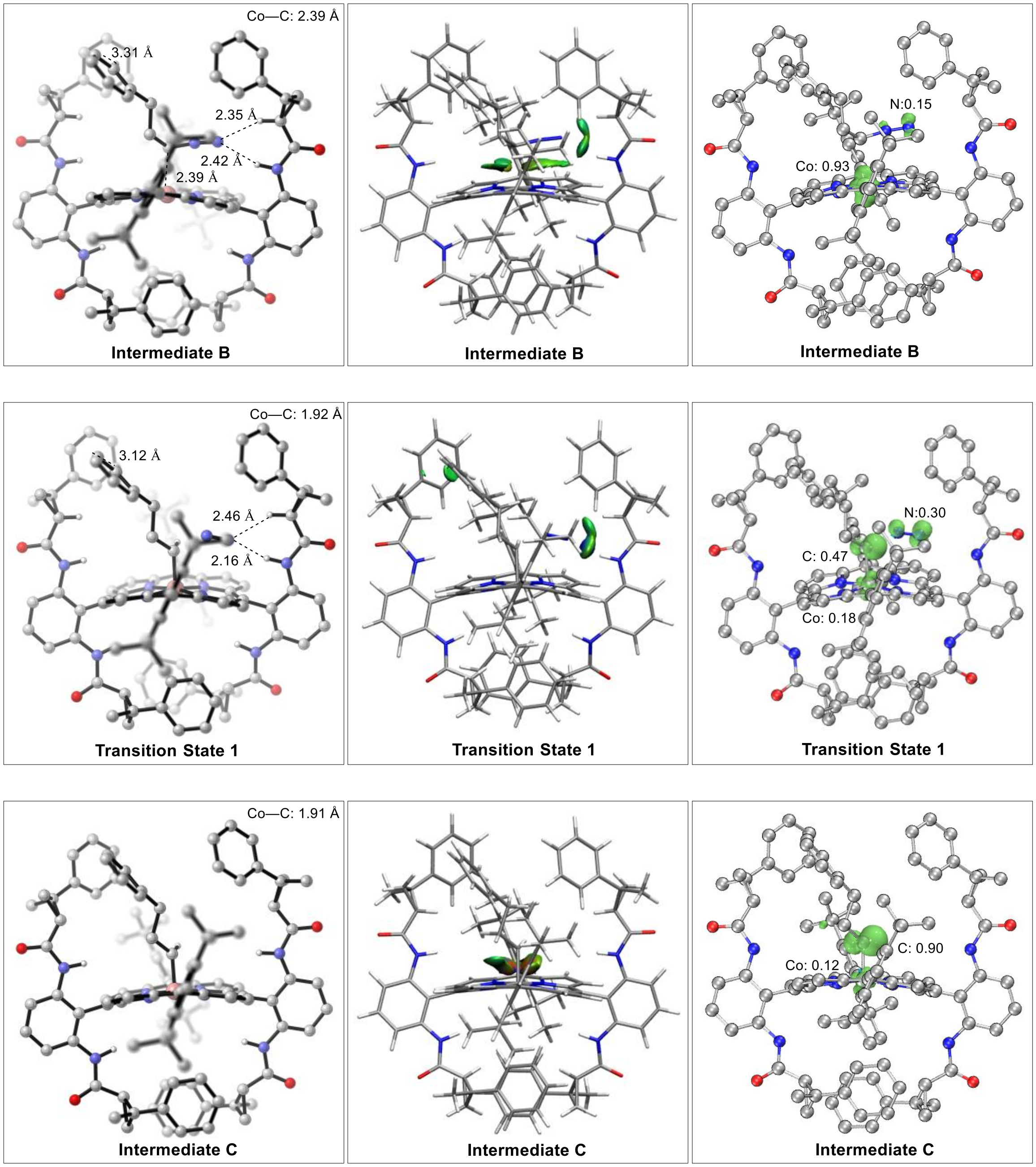
CYLview software.[32] The NCI (noncovalent interaction) visual representations of optimized structures were generated with VMD and rendered with Tachyon.[33]

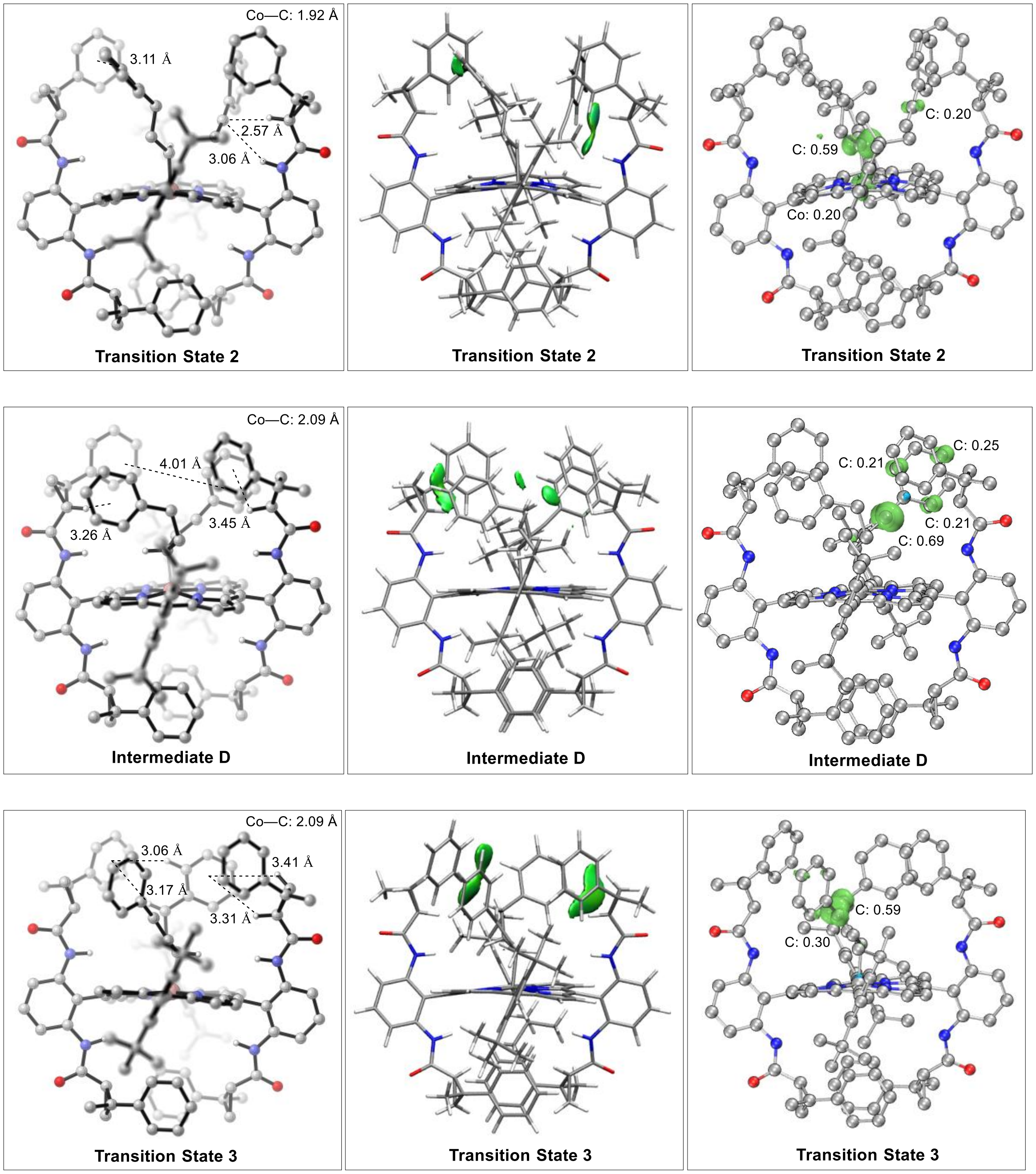
4.4.5.1. Scheme S1. Calculated Energy Diagram for [Co(P6)]-Catalyzed Radical Cyclopropanation of Phenylacetylene (2a) with Alkyl Diazomethane (1a')



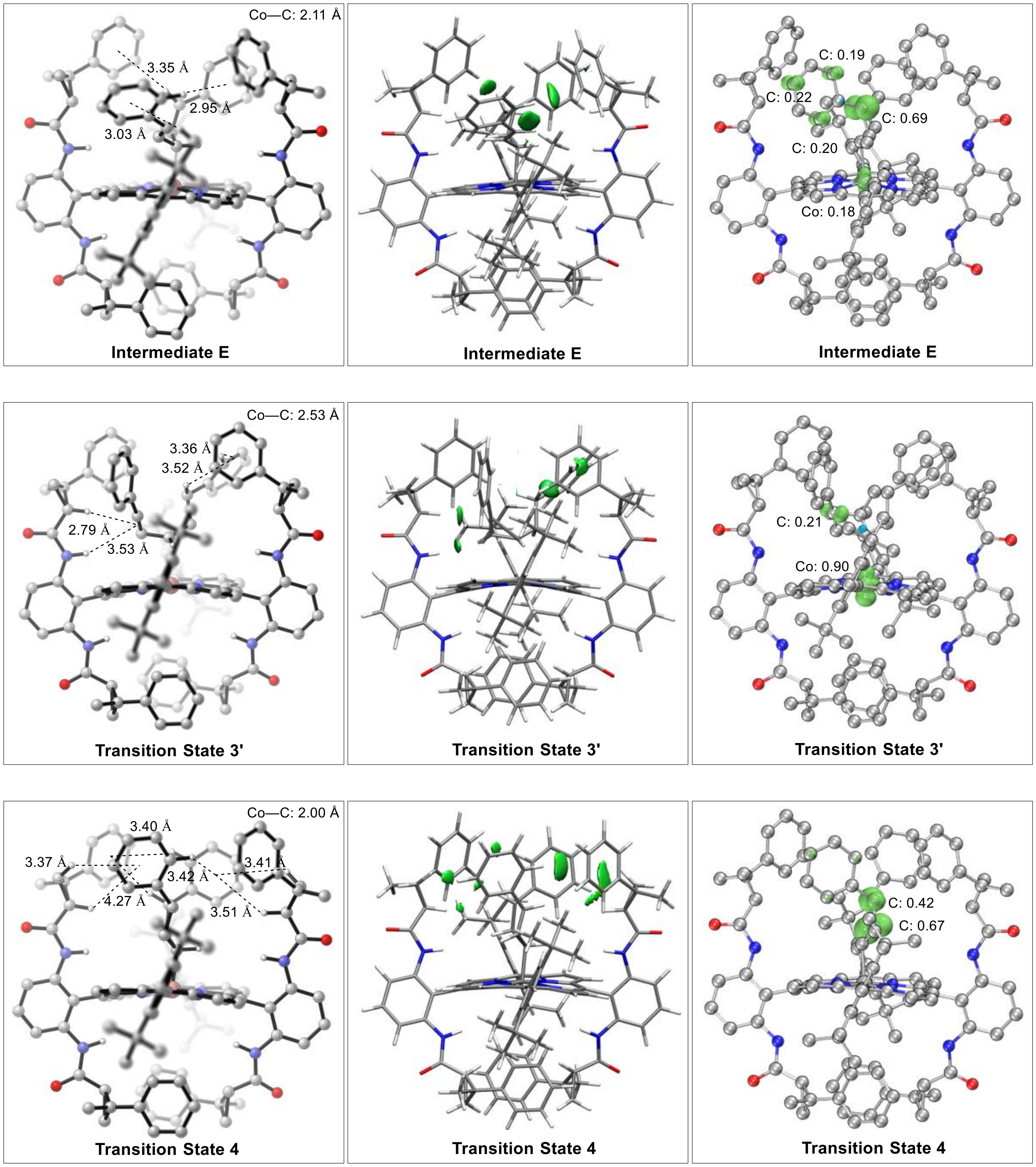
4.4.5.2. Figure S3. Optimized Structure Models, NCI Plot, and Spin Density Representations of Intermediates and Transition States




Co—C: 2.39 Å
3.31 Å
2.35 Å
2.42 Å
2.39 Å
Intermediate B
Intermediate B
N:0.15
Co: 0.93
Intermediate B
Co—C: 1.92 Å
3.12 Å
2.46 Å
2.16 Å
Transition State 1
Transition State 1
N:0.30
C: 0.47
Co: 0.18
Transition State 1
Co—C: 1.91 Å
Intermediate C
Intermediate C
Co: 0.12
C: 0.90
Intermediate C



Co—C: 1.92 Å
3.11 Å
2.57 Å
3.06 Å
Transition State 2
Transition State 2
C: 0.20
C: 0.59
Co: 0.20
Transition State 2
Co—C: 2.09 Å
4.01 Å
3.26 Å
3.45 Å
Intermediate D
Intermediate D
C: 0.21
C: 0.25
C: 0.21
C: 0.69
Intermediate D
Co—C: 2.09 Å
3.06 Å
3.41 Å
3.17 Å
3.31 Å
Transition State 3
Transition State 3
C: 0.59
C: 0.30
Transition State 3



4.4.5.2. Coordinates of Intermediates and Transition States

Intermediate A

A$_{[Co(II)(P6)]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.625551 Hartree

H_corr: 1.909997 Hartree

SCF: -6149.928751 Hartree

S: 598.668 Cal/Mol-Kelvin

H: -6148.018754 Hartree

G: -6148.3032 Hartree

Cartesian Coordinates:

Co	0.00159800	-0.00026800	0.00041300
O	0.77139700	3.92417700	-6.66778000
O	-0.73901800	-4.13925900	-6.53523600
N	-1.40548600	0.03933600	-1.39640700
N	-1.40820200	-0.04391600	1.39436000
N	0.38848100	2.32321200	-4.98081300
H	0.33347400	2.20578600	-3.96378300
N	-0.37642900	-2.48090500	-4.90026600
H	-0.32519700	-2.32933200	-3.88757300
C	0.00506500	-0.05358700	-3.47537500
C	-1.21815600	0.10652000	-2.79533300
C	-2.48765600	0.30446500	-3.47806900
H	-2.59495800	0.41096800	-4.55664600
C	-3.46641900	0.32696300	-2.50698600

H	-4.53824700	0.46736800	-2.63162200
C	-2.80645000	0.12849000	-1.22320100
C	-3.49963800	-0.00379700	-0.00312300
C	-2.80864900	-0.13536500	1.21828200
C	-3.47080900	-0.33650200	2.50052400
H	-4.54265300	-0.47880000	2.62286700
C	-2.49396800	-0.31390200	3.47353200
H	-2.60319300	-0.42212900	4.55174300
C	-1.22349100	-0.11268200	2.79356800
C	0.00543100	-0.07923900	-4.98466400
C	0.20707200	1.12510200	-5.72888100
C	0.21198100	1.10227400	-7.15008400
H	0.37389000	2.03295500	-7.69628300
C	0.00630000	-0.12676800	-7.81219000
H	0.00664700	-0.14530800	-8.90823800
C	-0.19967300	-1.33279800	-7.10912600
H	-0.36041400	-2.28143800	-7.62382500
C	-0.19559600	-1.30814300	-5.68784800
C	0.64493200	3.62235800	-5.43774600
C	0.76744300	4.63037600	-4.32868600
H	0.33240800	4.33427100	-3.36543600
C	0.67491800	6.13119800	-4.68003300
H	0.09761800	6.76558900	-3.99959800

H	0.56436100	6.35033100	-5.74748100
C	2.02162100	5.57334700	-4.21965800
C	2.49456800	5.89517000	-2.81311100
C	2.66389600	7.24635100	-2.40963400
H	2.39488100	8.05084400	-3.10584100
C	3.16596300	7.55981400	-1.12465100
H	3.28807300	8.60800600	-0.82634200
C	3.50709800	6.52325500	-0.22207200
H	3.89228600	6.76449700	0.77567700
C	3.34183900	5.17251400	-0.61429300
H	3.59465300	4.36481900	0.08335200
C	2.84312700	4.86344800	-1.90185000
H	2.71545500	3.81519300	-2.20172500
C	3.15763900	5.44242900	-5.24468500
H	3.70379300	6.40171500	-5.31992700
H	2.76507300	5.17853700	-6.24138700
H	3.88136400	4.66594300	-4.93268100
C	-0.62040500	-3.79664600	-5.31502900
C	-0.73605600	-4.77049300	-4.17521200
H	-0.31828000	-4.43540600	-3.21712400
C	-0.60638200	-6.27945200	-4.47926100
H	-0.47903900	-6.52804700	-5.53832500
H	-0.02196600	-6.87918100	-3.77390400

C -1.96974800 -5.73886000 -4.04982100

C -2.44928300 -6.02974200 -2.63868600

C -2.84868100 -4.98075300 -1.76895900

H -2.75691600 -3.93957800 -2.10437600

C -3.35366700 -5.26331200 -0.47781700

H -3.64664000 -4.44158500 0.18687100

C -3.47424700 -6.60483700 -0.04018200

H -3.86374100 -6.82571000 0.96066300

C -3.08245000 -7.65866400 -0.90127500

H -3.17007800 -8.69971900 -0.56787700

C -2.57425700 -7.37143900 -2.19001300

H -2.26646900 -8.18904200 -2.85411700

C -3.09847000 -5.66463600 -5.08839900

H -3.62081400 -6.63860200 -5.14068500

H -2.70262600 -5.41965600 -6.08857200

H -3.84342300 -4.89737100 -4.80477100

C -5.00283100 -0.00515800 -0.00456400

C -5.71814300 -1.01392500 -0.70247400

C -7.13619200 -1.03411800 -0.71389700

C -7.94893700 -2.12851200 -1.45627600

C -7.81831000 -0.00779000 -0.00714600

H -8.91544800 -0.00880600 -0.00816500

C -7.13940800 1.01978400 0.70089000

C	-5.72129900	1.00224100	0.69207200
O	-0.76916600	4.12448700	6.54471800
O	0.77570400	-3.93301300	6.65971500
N	1.40845200	0.08328400	1.39593700
N	1.41151400	-0.07977500	-1.39223500
N	-0.39512000	2.47195700	4.90645000
H	-0.34056500	2.32322500	3.89350900
N	0.38820200	-2.32926500	4.97641200
H	0.33459900	-2.20940700	3.95959400
C	-0.00200300	0.04935900	3.47625600
C	1.22143400	0.18971600	2.79250300
C	2.49180200	0.40171100	3.46978300
H	2.59958800	0.53559100	4.54526200
C	3.47081900	0.39383200	2.49869800
H	4.54370300	0.53040300	2.61968800
C	2.80948400	0.16594600	1.22048800
C	3.50187600	0.00647700	0.00389200
C	2.81251500	-0.15641400	-1.21398000
C	3.47728900	-0.38297100	-2.49064400
H	4.55098800	-0.51504600	-2.60939100
C	2.50017400	-0.39642300	-3.46357900
H	2.61059900	-0.53127100	-4.53866800
C	1.22763200	-0.18873700	-2.78903300

C	-0.00454900	0.07154200	4.98559900
C	-0.21172500	1.29786900	5.69145700
C	-0.21890200	1.31888600	7.11278300
H	-0.38444500	2.26556800	7.62956000
C	-0.00972000	0.11187400	7.81322600
H	-0.01178000	0.12763400	8.90931500
C	0.20222100	-1.11466400	7.14844800
H	0.36669300	-2.04608800	7.69262100
C	0.20038100	-1.13387300	5.72719100
C	-0.64551000	3.78560500	5.32397500
C	-0.76150400	4.76204100	4.18639200
H	-0.33906800	4.43129400	3.22883800
C	-0.63919800	6.27068500	4.49497500
H	-0.05503000	6.87484900	3.79320800
H	-0.51646300	6.51692500	5.55513500
C	-1.99883400	5.72548400	4.05947400
C	-2.47483300	6.01829000	2.64753600
C	-2.60603500	7.36080500	2.20306500
H	-2.30556500	8.17787400	2.87116800
C	-3.11099400	7.64954800	0.91340600
H	-3.20347700	8.69122900	0.58329300
C	-3.49324000	6.59645300	0.04713100
H	-3.88016200	6.81854400	-0.95444100

C	-3.36641200	5.25414500	0.48054500
H	-3.65195800	4.43303100	-0.18812100
C	-2.86470700	4.97003700	1.77263800
H	-2.76812700	3.92824600	2.10477000
C	-3.13066000	5.64369300	5.09409300
H	-3.65720600	6.61533700	5.14740800
H	-2.73708700	5.39754300	6.09487900
H	-3.87148300	4.87415200	4.80585600
C	0.65004300	-3.62840000	5.43029800
C	0.77974000	-4.63254400	4.31853900
H	0.34444000	-4.33600700	3.35554100
C	0.69540500	-6.13492800	4.66503100
H	0.58454900	-6.35811900	5.73160800
H	0.12284200	-6.77051100	3.98171500
C	2.03956200	-5.56779400	4.20848000
C	2.51665800	-5.88215600	2.80164800
C	2.86013800	-4.84530800	1.89427900
H	2.72536600	-3.79885200	2.19732500
C	3.36281300	-5.14701700	0.60651700
H	3.61164200	-4.33546000	-0.08807600
C	3.53717800	-6.49541700	0.21018500
H	3.92546600	-6.73098100	-0.78772000
C	3.20113900	-7.53702900	1.10885400

H	3.33030600	-8.58345800	0.80733500
C	2.69510400	-7.23092700	2.39405800
H	2.43004000	-8.03936300	3.08720700
C	3.17315100	-5.43354500	5.23576900
H	3.72481500	-6.38984300	5.30879200
H	2.77745300	-5.17522000	6.23269700
H	3.89279900	-4.65180100	4.92748000
C	5.00566800	0.00978700	0.00524000
C	5.72573600	-0.99965100	0.69455500
C	7.14528800	-1.01540500	0.70642300
C	7.82708000	0.01601500	0.00753200
H	8.91945100	0.01843600	0.00843300
C	7.14187700	1.04439400	-0.69250500
C	5.72239400	1.02235900	-0.68295400
H	5.15555100	1.80421500	-1.20262900
H	5.16153400	-1.78408000	1.21322800
C	7.88511400	2.17500100	-1.45330700
C	9.43037400	2.03471100	-1.36822000
C	7.48683500	3.55748800	-0.84403400
C	7.47590000	2.13957300	-2.96079300
C	7.89227700	-2.14280600	1.46831100
C	9.43703500	-1.99552200	1.38597000
C	7.50127600	-3.52693400	0.85804200

C	7.48026500	-2.10956200	2.97508300
H	9.80075600	-2.04918800	0.34223600
H	9.91502500	-2.81936600	1.94834700
H	9.78441000	-1.04288900	1.82923100
H	7.78424100	-3.58024200	-0.21023100
H	6.41538000	-3.71808700	0.93330800
H	8.02328900	-4.34140200	1.39606600
H	9.79200400	2.09017600	-0.32385300
H	9.90562400	2.86061900	-1.92989200
H	9.78283600	1.08359500	-1.81071400
H	7.76410500	1.17764500	-3.42541500
H	7.98146900	2.95544100	-3.51212400
H	6.38608600	2.26921300	-3.09239500
H	7.76330600	-1.14645400	3.44043500
H	7.98855200	-2.92326900	3.52710900
H	6.39082200	-2.24417500	3.10474300
H	7.76753400	3.61225600	0.22476100
H	6.40024100	3.74378600	-0.92140900
H	8.00621400	4.37417300	-1.38124400
H	-5.15750600	1.78064600	1.21547500
H	-5.15194000	-1.79130000	-1.22480500
C	-7.03817300	-3.14565400	-2.19762900
C	-8.88427700	-1.45563800	-2.51164600

C	-8.81907600	-2.91326600	-0.42247600
H	-8.29417300	-0.90105900	-3.26532500
H	-9.59004100	-0.74521500	-2.04344500
H	-9.47956200	-2.22661600	-3.03749000
H	-6.41036400	-2.65214900	-2.96379600
H	-7.66664300	-3.89521500	-2.71384400
H	-6.37409100	-3.69286200	-1.50249000
H	-8.18097600	-3.41254000	0.33059500
H	-9.41732400	-3.68872200	-0.93840400
H	-9.51844100	-2.24585200	0.11402000
C	-7.95555100	2.11262400	1.44182800
C	-7.04803400	3.13135200	2.18497400
C	-8.89164500	1.43796600	2.49539000
C	-8.82516900	2.89586900	0.40644300
H	-8.18655700	3.39630500	-0.34542100
H	-9.42574900	3.67023900	0.92129000
H	-9.52235300	2.22723600	-0.13137600
H	-6.42077700	2.63889600	2.95226800
H	-7.67883000	3.87971800	2.70008200
H	-6.38361400	3.67983900	1.49117500
H	-8.30194500	0.88440800	3.25013600
H	-9.59524300	0.72629900	2.02582300
H	-9.48930700	2.20782800	3.02017400

$A_{1a'}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.128796 Hartree

H_corr: 0.178619 Hartree

SCF: -458.6316798 Hartree

S: 104.861 Cal/Mol-Kelvin

H: -458.4530608 Hartree

G: -458.5028838 Hartree

Cartesian Coordinates:

C	2.90324300	-0.78325800	-0.15481100
C	1.44911800	-0.47290500	-0.47634900
C	0.52912300	-0.40000300	0.79441400
H	1.05910500	-1.25864100	-1.15242200
H	1.37850300	0.48242700	-1.03008000
C	-0.92513400	-0.13477600	0.42163900
C	-1.80930000	-1.20883900	0.13063900
C	-1.41610000	1.19421400	0.30761300
C	-2.75227100	1.44435800	-0.08524500
C	-3.62248900	0.36490800	-0.37349700

C	-3.14628000	-0.96409400	-0.26311100
H	-3.81569400	-1.80568900	-0.47826800
H	-1.44996300	-2.24269000	0.22210500
H	-4.65887300	0.55677700	-0.67534500
H	-3.11523600	2.47632500	-0.16214900
H	-0.74944300	2.03641500	0.53630100
H	0.91513100	0.39687300	1.45823000
N	3.82414600	0.15995900	-0.14113100
N	4.65067200	1.02017900	-0.14576700
H	3.23304300	-1.78503100	0.13539400
H	0.62023800	-1.35535600	1.34677100

Intermediate B

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.783802 Hartree

H_corr: 2.090361 Hartree

SCF: -6608.593998 Hartree

S: 645.207 Cal/Mol-Kelvin

H: -6606.503637 Hartree

G: -6606.810196 Hartree

Cartesian Coordinates:

Co	0.22044100	-0.26565400	0.02200700
O	-2.15517600	-1.02770700	7.70294800
O	2.21776400	-6.54106100	3.56979400
N	1.37728900	-0.45384200	1.62634200
N	1.73319700	0.57680800	-0.94395800
N	-1.25819900	-1.09384900	5.52103200
H	-1.14358600	-0.53677000	4.66448400
N	1.12623700	-4.52977000	2.99794200
H	0.99716600	-3.86827800	2.22566000
C	-0.03713200	-1.97583000	3.04172900
C	1.10683400	-1.18606500	2.80207400
C	2.15673400	-0.98104100	3.78986900
H	2.16720300	-1.43858600	4.77831000
C	3.06438200	-0.10117700	3.23680500
H	3.96908500	0.30578300	3.68439500
C	2.60715900	0.19491500	1.88426100
C	3.35448800	0.94072500	0.94912800
C	2.95190300	1.04466700	-0.39973600
C	3.81920100	1.55073300	-1.45692600
H	4.81817100	1.95113600	-1.29224500
C	3.15252100	1.37324000	-2.65258600
H	3.48856100	1.61118700	-3.66117000
C	1.85257300	0.79838200	-2.33335900

C	-0.08000300	-2.84202100	4.27671500
C	-0.69735600	-2.40559800	5.49137500
C	-0.71749300	-3.26233600	6.62826700
H	-1.20134000	-2.91578100	7.54217100
C	-0.10782400	-4.53132700	6.54711800
H	-0.12211300	-5.18323500	7.42837500
C	0.52093100	-4.98573500	5.36952600
H	1.00401600	-5.96238300	5.31006600
C	0.52903300	-4.13825500	4.22985200
C	-1.91547900	-0.46026600	6.58728100
C	-2.30717900	0.96310000	6.30919900
H	-1.84097800	1.42588000	5.43423100
C	-2.56324100	1.89290700	7.51811200
H	-2.15758200	2.90819400	7.45556800
H	-2.48740200	1.40923800	8.49762700
C	-3.74977300	1.50150800	6.64151500
C	-4.30496500	2.53649500	5.67919000
C	-4.61945900	3.84640900	6.12765900
H	-4.41251400	4.11864300	7.17017300
C	-5.19287800	4.79589700	5.24826200
H	-5.42892000	5.80377500	5.61044700
C	-5.46308100	4.44683600	3.90329900
H	-5.90357700	5.18050500	3.21819300

C	-5.15635400	3.14109500	3.44657600
H	-5.36840400	2.86685700	2.40571000
C	-4.58485500	2.19462500	4.32867500
H	-4.34898700	1.18292100	3.97352800
C	-4.80992400	0.54488100	7.20597800
H	-5.56016200	1.11876600	7.78245700
H	-4.34992400	-0.20828000	7.86749600
H	-5.34147300	0.01976100	6.38985800
C	1.92063700	-5.64821600	2.71299400
C	2.41412800	-5.66958800	1.29264500
H	1.79946400	-5.11912800	0.56922100
C	3.10741000	-6.93529500	0.75568800
H	3.22224500	-7.74807100	1.48099900
H	2.85268800	-7.23818100	-0.26482500
C	3.95524200	-5.68127300	0.97907400
C	4.40052900	-4.86899000	-0.22295600
C	4.14255700	-3.47376900	-0.29561400
H	3.56215200	-2.99060200	0.50120700
C	4.61897000	-2.70398600	-1.38325500
H	4.41040800	-1.62798400	-1.42524500
C	5.36681400	-3.32148500	-2.41595100
H	5.73248000	-2.72850400	-3.26233600
C	5.63155900	-4.71134800	-2.35234100

H	6.20723900	-5.19516200	-3.15057900
C	5.15286800	-5.47727300	-1.26276000
H	5.35834500	-6.55424900	-1.21455700
C	4.95889000	-5.67279300	2.14173100
H	5.91489000	-6.12309100	1.81365700
H	4.57503100	-6.24723700	3.00227600
H	5.16934200	-4.63833900	2.47343600
C	4.67702600	1.53170300	1.35709900
C	5.77096300	0.68438100	1.67270300
C	7.03154000	1.22122400	2.03945600
C	8.25313400	0.32464000	2.37558100
C	7.15966700	2.63522900	2.08843900
H	8.12789200	3.06561200	2.37317300
C	6.08735000	3.51508800	1.78300100
C	4.84579300	2.93888500	1.40842300
O	0.76246800	4.89601500	-6.16976200
O	2.01664700	-3.17627900	-6.59126300
N	-0.85982500	-0.25483600	-1.63829700
N	-1.21360800	-1.28894000	0.92690200
N	0.65120700	3.12145800	-4.62367800
H	0.41535600	2.89091000	-3.65297100
N	1.64618200	-1.64370800	-4.83744600
H	1.47997200	-1.59068900	-3.82736600

C	0.84611400	0.57020300	-3.29515000
C	-0.44912500	0.14555800	-2.92826800
C	-1.56739900	0.10516200	-3.86029500
H	-1.49977900	0.37453500	-4.91363500
C	-2.67522000	-0.29725200	-3.14330300
H	-3.69787600	-0.41770900	-3.49546000
C	-2.23288500	-0.56333500	-1.77941700
C	-3.05221600	-1.13721300	-0.78553000
C	-2.52437900	-1.53304800	0.46332300
C	-3.24888500	-2.37882500	1.40601000
H	-4.27272200	-2.72044800	1.26456900
C	-2.38154200	-2.67716000	2.43649800
H	-2.55602600	-3.29554600	3.31604500
C	-1.13225100	-1.98387300	2.15495900
C	1.17069900	0.74439500	-4.76012100
C	1.08497100	2.01434500	-5.41037600
C	1.40147400	2.14223700	-6.79070500
H	1.33504200	3.12375700	-7.26199900
C	1.78581700	0.99321700	-7.51327700
H	2.02414800	1.09146600	-8.57872300
C	1.87061300	-0.27747700	-6.90743300
H	2.15595600	-1.16825700	-7.46951300
C	1.56677300	-0.40041300	-5.52466400

C	0.48117300	4.45760100	-5.00759500
C	-0.07670900	5.33659900	-3.92361400
H	-0.53150400	4.81884200	-3.06927900
C	-0.75871600	6.65876800	-4.34463600
H	-1.69242300	6.91116500	-3.83208500
H	-0.72944700	6.87005000	-5.41875200
C	0.56321700	6.73472700	-3.58518600
C	0.53231700	7.14667500	-2.12482300
C	-0.14311500	8.32970800	-1.72375300
H	-0.68498200	8.91672000	-2.47583300
C	-0.12062300	8.75539900	-0.37397200
H	-0.64721100	9.67137400	-0.08052900
C	0.58265400	8.00207600	0.59709500
H	0.60081200	8.32938600	1.64318300
C	1.26452500	6.82318400	0.20645300
H	1.81683000	6.23957300	0.95272200
C	1.24080900	6.40218700	-1.14401500
H	1.77500700	5.49140300	-1.44465400
C	1.82652600	7.19114700	-4.32974800
H	1.88397500	8.29607200	-4.32208100
H	1.81677300	6.84117400	-5.37558400
H	2.73723600	6.80259400	-3.83596800
C	1.84588200	-2.93137200	-5.35435500

C	1.80639500	-3.99951900	-4.29744700
H	2.06279000	-3.67145200	-3.28223800
C	2.22569600	-5.43548300	-4.66260600
H	2.50488800	-5.58837800	-5.71072700
H	2.82965700	-5.97188900	-3.92405500
C	0.74894600	-5.16151400	-4.37075200
C	0.16278200	-5.61870200	-3.04767500
C	-0.51814400	-4.70760600	-2.19639000
H	-0.56948200	-3.64596700	-2.47170800
C	-1.12339700	-5.15095200	-0.99640400
H	-1.64505400	-4.43536500	-0.34941400
C	-1.05913900	-6.51842600	-0.63226700
H	-1.52305000	-6.86324000	0.29911000
C	-0.38487300	-7.43554000	-1.47488200
H	-0.32921700	-8.49470000	-1.19617200
C	0.21926300	-6.98776400	-2.67371500
H	0.74226300	-7.69905100	-3.32564000
C	-0.24745200	-5.19782700	-5.53904600
H	-0.59240900	-6.23615500	-5.70379000
H	0.21704000	-4.82857700	-6.46953300
H	-1.13688700	-4.57768200	-5.31849400
C	-4.49095200	-1.45268600	-1.09075900
C	-4.82391000	-2.40608200	-2.08653500

C	-6.17519200	-2.73513200	-2.37053700
C	-7.19040800	-2.07885000	-1.62507900
H	-8.23511700	-2.32179500	-1.83224600
C	-6.89699000	-1.12402800	-0.61562300
C	-5.53229000	-0.82519200	-0.36056500
H	-5.26183400	-0.09628500	0.41365100
H	-4.00988500	-2.90655900	-2.62411800
C	-8.00495400	-0.41183100	0.20607500
C	-9.43416700	-0.87386400	-0.19245900
C	-7.91149000	1.12993100	-0.02723700
C	-7.80205800	-0.71723600	1.72467300
C	-6.49008500	-3.79433400	-3.46048400
C	-8.01587500	-4.01522200	-3.65449200
C	-5.84696500	-5.15896000	-3.05252200
C	-5.88852500	-3.32851600	-4.82504200
H	-8.49879000	-4.38674400	-2.73076400
H	-8.18000000	-4.77262900	-4.44369400
H	-8.52989700	-3.08717600	-3.96967800
H	-6.26694000	-5.52162600	-2.09546400
H	-4.75146500	-5.07780800	-2.93228300
H	-6.04689000	-5.92153000	-3.82969300
H	-9.65778500	-0.65324500	-1.25348900
H	-10.17955900	-0.33779100	0.42441400

H	-9.57779000	-1.95774800	-0.02279500
H	-7.88132000	-1.80297200	1.92139500
H	-8.57389200	-0.19902200	2.32526500
H	-6.81299600	-0.37843200	2.08374600
H	-6.33826900	-2.37067300	-5.14843200
H	-6.08789800	-4.08570800	-5.60740200
H	-4.79381900	-3.18832500	-4.76388100
H	-8.07071700	1.37520500	-1.09435600
H	-6.92421700	1.52872600	0.27112100
H	-8.68189600	1.65503700	0.56925100
H	3.99096900	3.57727700	1.16308300
H	5.62880800	-0.39893900	1.61059500
C	7.91943500	-1.19033900	2.28915500
C	8.74075400	0.63404600	3.82739500
C	9.40790700	0.62887900	1.36774500
H	7.94622000	0.41549900	4.56544600
H	9.03253000	1.69370700	3.94655900
H	9.62183500	0.01067800	4.07317900
H	7.12325500	-1.47701000	3.00216500
H	8.82030000	-1.78090500	2.54030700
H	7.59971500	-1.48631400	1.27246200
H	9.09435900	0.40469400	0.33095900
H	10.29302400	0.00741900	1.60387200

H	9.71773600	1.68948700	1.40747200
C	6.30619500	5.04947900	1.86445600
C	5.01789700	5.85079600	1.53142700
C	7.41801000	5.46772100	0.84931700
C	6.75637300	5.43497900	3.31006500
H	5.98309400	5.15746100	4.05085600
H	6.92635200	6.52680300	3.37763000
H	7.69630600	4.92858300	3.59614900
H	4.66476700	5.65406100	0.50140400
H	5.22454200	6.93438300	1.60956900
H	4.19843200	5.61406100	2.23711000
H	7.11919500	5.22130700	-0.18689500
H	8.37466700	4.95428900	1.05715800
H	7.59804500	6.55843100	0.90793600
C	-0.51031200	1.88084800	0.77333500
C	-1.65330700	2.44998200	-0.07917800
C	-2.16466500	3.84151100	0.40836100
H	-2.48489800	1.72372800	-0.10437500
H	-1.27246900	2.52250800	-1.11278000
C	-3.23359800	4.45199500	-0.49757700
C	-4.38316900	3.71231100	-0.89056400
C	-3.11407600	5.79667300	-0.94030100
C	-4.11638200	6.38859400	-1.74643700

C	-5.25578200	5.64203600	-2.12985900
C	-5.38344200	4.29901200	-1.69955500
H	-6.26053000	3.70999300	-1.99263900
H	-4.50163200	2.66927300	-0.56935800
H	-6.03208300	6.09804000	-2.75534700
H	-4.00955400	7.43160600	-2.06853100
H	-2.23606500	6.38587000	-0.64607000
H	-1.30815200	4.53833200	0.48823800
N	-0.78140500	1.63501700	2.06568200
N	-1.03555500	1.26757800	3.15993400
H	0.50796600	2.26274500	0.61527900
H	-2.57335900	3.72337000	1.43410500

Transition State TS1

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -192.123 cm-1

G_corr: 1.78247 Hartree

H_corr: 2.087313 Hartree

SCF: -6608.563548 Hartree

S: 641.597 Cal/Mol-Kelvin

H: -6606.476235 Hartree

G: -6606.781078 Hartree

Cartesian Coordinates:

Co	-0.00642600	-0.28502900	0.02848800
O	-2.57195800	0.10277000	7.72355400
O	-1.61111700	-6.71772600	3.42129500
N	0.79597100	-0.95832400	1.70391900
N	1.77020000	-0.34854700	-0.81717800
N	-1.94900300	-0.30205600	5.48193500
H	-1.59378300	0.16313400	4.63493100
N	-1.55075600	-4.42377800	2.87391400
H	-1.30501600	-3.77823800	2.11701200
C	-1.25986400	-1.63996100	2.97968400
C	0.13043400	-1.46160500	2.84271000
C	1.07727500	-1.73442900	3.91341200
H	0.80030800	-2.12899800	4.89000700
C	2.32406200	-1.36532700	3.45374900
H	3.27589000	-1.40069500	3.98001100
C	2.16045000	-0.92795000	2.07297600
C	3.23658700	-0.65472500	1.20507700
C	3.02539500	-0.45255900	-0.17489200
C	4.09723100	-0.47966700	-1.16017700
H	5.15332000	-0.57552500	-0.91375200
C	3.50862100	-0.42148300	-2.40793500

H	3.98504700	-0.44482400	-3.38725200
C	2.07308900	-0.30657900	-2.19787800
C	-1.79012200	-2.37869100	4.18395200
C	-2.13362800	-1.71459100	5.40495900
C	-2.62662800	-2.47052900	6.50724600
H	-2.88488700	-1.94844000	7.42906700
C	-2.75317000	-3.86935200	6.38865900
H	-3.12904500	-4.44172800	7.24474200
C	-2.40594500	-4.55389300	5.20619800
H	-2.48401900	-5.63874100	5.11998700
C	-1.92480000	-3.80367900	4.10092100
C	-2.13842700	0.52522400	6.60158600
C	-1.76395300	1.96272300	6.38025100
H	-1.21810500	2.17759200	5.45609200
C	-1.37140700	2.80060300	7.62239800
H	-0.50684600	3.46463200	7.51775800
H	-1.45764000	2.27570800	8.57960400
C	-2.67012800	3.14188000	6.89743200
C	-2.69859800	4.38995000	6.03277500
C	-2.30072700	5.64303500	6.56989900
H	-1.91918100	5.68745700	7.59783400
C	-2.39023600	6.82428800	5.79595700
H	-2.07728500	7.78404900	6.22467100

C	-2.88230100	6.76887300	4.46947600
H	-2.94812800	7.68188900	3.86590600
C	-3.28263300	5.52402600	3.92499500
H	-3.65942500	5.47402000	2.89633800
C	-3.19361500	4.34581500	4.70247400
H	-3.50024700	3.38218900	4.27643400
C	-4.01157100	2.83605300	7.57979700
H	-4.28766200	3.67391000	8.24794100
H	-3.95154700	1.90817600	8.17254000
H	-4.81674000	2.72454800	6.82909400
C	-1.38695400	-5.78536900	2.58504600
C	-0.87850500	-6.03275600	1.19145100
H	-1.11724900	-5.25550800	0.45450000
C	-0.82868500	-7.47429900	0.65507200
H	-1.15544100	-8.24625000	1.36015600
H	-1.13140500	-7.62118600	-0.38636600
C	0.49326200	-6.76780800	0.96365200
C	1.34652200	-6.26139800	-0.18423100
C	1.78671000	-4.91092100	-0.22536200
H	1.45349300	-4.21105500	0.55222400
C	2.64689600	-4.45995600	-1.25462100
H	2.98084400	-3.41544500	-1.27109900
C	3.08311700	-5.35806900	-2.25967200

H	3.74587100	-5.00999800	-3.06038900
C	2.65133900	-6.70626100	-2.22757200
H	2.98148900	-7.40463500	-3.00582500
C	1.79132800	-7.15312300	-1.19633000
H	1.45915700	-8.19882200	-1.17125400
C	1.30662400	-7.23547300	2.17998600
H	1.95725600	-8.08259900	1.89128700
H	0.64390400	-7.56322500	2.99926000
H	1.95727600	-6.42309000	2.55572700
C	4.64758500	-0.74759200	1.71959800
C	5.16928000	-2.00511300	2.12184100
C	6.50017800	-2.12886600	2.59504700
C	7.10688100	-3.48948500	3.03017600
C	7.29000900	-0.95007500	2.66078700
H	8.32001000	-1.02782100	3.03059900
C	6.80346300	0.32460400	2.26649000
C	5.46993900	0.40544600	1.78619800
O	3.48309100	3.35629100	-6.34271100
O	0.32008000	-4.13901500	-6.31726400
N	-0.84499000	0.08682100	-1.72005400
N	-1.81288100	-0.53491800	0.79094300
N	2.42910300	2.04872700	-4.69010800
H	2.08136800	2.06637700	-3.72599700

N	0.74073400	-2.54139700	-4.63363000
H	0.58614300	-2.35176200	-3.63866800
C	1.14585300	-0.12169700	-3.24422200
C	-0.21358900	0.14897100	-2.98121400
C	-1.14615900	0.60365200	-4.00132300
H	-0.89201300	0.72968000	-5.05297600
C	-2.34275400	0.86521700	-3.36580700
H	-3.26431200	1.25103300	-3.79715000
C	-2.17335100	0.50623900	-1.96377000
C	-3.22229800	0.48519000	-1.02322200
C	-3.03785900	-0.08734900	0.25304400
C	-4.14060900	-0.43363800	1.14123500
H	-5.18651300	-0.20999000	0.93842600
C	-3.60163900	-1.11789400	2.21197300
H	-4.11139400	-1.55055400	3.07191200
C	-2.16008900	-1.14825600	2.01411200
C	1.59890100	-0.25294400	-4.67915300
C	2.23567800	0.81725200	-5.38410100
C	2.63740400	0.64880800	-6.73831900
H	3.12173100	1.47898600	-7.25340100
C	2.38931400	-0.58101000	-7.38108000
H	2.69559300	-0.70503100	-8.42622300
C	1.75789000	-1.65382000	-6.72046500

H	1.55459800	-2.60160700	-7.22107800
C	1.36526000	-1.49118100	-5.36454000
C	3.00177700	3.23679900	-5.16948600
C	2.98827500	4.37251600	-4.18735800
H	2.35492300	4.24381300	-3.30027900
C	3.05120700	5.80885500	-4.76239600
H	2.38417100	6.54504600	-4.30288900
H	3.15313900	5.86441900	-5.85128200
C	4.25151400	5.28974300	-3.97652800
C	4.46955700	5.82413500	-2.57286000
C	4.53519000	7.22471200	-2.34634300
H	4.37510200	7.90977900	-3.18841700
C	4.80287100	7.73894800	-1.05564400
H	4.84860300	8.82296900	-0.89688400
C	5.01009500	6.85547300	0.03145100
H	5.21220100	7.25088500	1.03373000
C	4.95241000	5.45688300	-0.18496400
H	5.11350300	4.76882800	0.65276800
C	4.68895100	4.94676100	-1.47822700
H	4.64691300	3.86224200	-1.64267300
C	5.55769000	4.97483300	-4.72082000
H	6.15914500	5.89827700	-4.82011900
H	5.35313400	4.57068900	-5.72604000

H 6.16234600 4.23777700 -4.15922000

C 0.24849300 -3.76892200 -5.10184400

C -0.40150300 -4.59614700 -4.02916100

H -0.07226200 -4.38920600 -3.00321500

C -0.76102200 -6.06212300 -4.33737000

H -0.53565200 -6.39217000 -5.35719300

H -0.56538500 -6.79139300 -3.54518000

C -1.89992800 -5.05554200 -4.16935600

C -2.71734300 -5.07958100 -2.89115700

C -2.88671100 -3.90581900 -2.10899300

H -2.36841500 -2.98307000 -2.40125900

C -3.71048900 -3.91493600 -0.95827900

H -3.83261000 -3.00123900 -0.36447500

C -4.38171600 -5.10193100 -0.57499200

H -5.01585700 -5.11231800 0.31901100

C -4.22136900 -6.27696100 -1.34873900

H -4.73433600 -7.20013600 -1.05380800

C -3.39652300 -6.26365500 -2.49845400

H -3.27344700 -7.17467800 -3.09795300

C -2.70214700 -4.63972400 -5.41131900

H -3.52196400 -5.36214000 -5.58526300

H -2.06015500 -4.61147600 -6.30834900

H -3.15680600 -3.64078300 -5.27076100

C	-4.59306500	0.96715100	-1.40698100
C	-5.34470500	0.30289500	-2.40929700
C	-6.64733100	0.74166600	-2.76405800
C	-7.17699700	1.87088400	-2.08453800
H	-8.17736900	2.22168500	-2.34830700
C	-6.45720300	2.55670200	-1.07038400
C	-5.15961000	2.08351500	-0.74088300
H	-4.56846000	2.58260900	0.03665800
H	-4.90847000	-0.57821400	-2.89474100
C	-7.03692600	3.78579300	-0.32032500
C	-8.46555300	4.16073600	-0.80310000
C	-6.10646000	5.01919300	-0.55232300
C	-7.10660300	3.47248800	1.20871500
C	-7.43911900	-0.02368700	-3.85789000
C	-8.83344000	0.60399600	-4.13411500
C	-7.65126600	-1.50259300	-3.39972500
C	-6.62642400	-0.00885000	-5.19220500
H	-9.47752700	0.58869100	-3.23446300
H	-9.34833000	0.02305500	-4.92203100
H	-8.75190400	1.64912800	-4.48878900
H	-8.23968000	-1.54422300	-2.46383900
H	-6.69112200	-2.01910000	-3.21924700
H	-8.19873100	-2.06762700	-4.17846800

H	-8.48075000	4.42748400	-1.87692900
H	-8.82706000	5.03868700	-0.23566700
H	-9.18525300	3.33685200	-0.63706200
H	-7.77649500	2.61418400	1.40466900
H	-7.49650500	4.34872000	1.76124200
H	-6.11146500	3.22735300	1.62298000
H	-6.47239000	1.02699000	-5.54937700
H	-7.17210400	-0.56740600	-5.97666900
H	-5.63372900	-0.48036500	-5.07307600
H	-6.04937300	5.27140300	-1.62798900
H	-5.07856400	4.82891900	-0.19222500
H	-6.49815200	5.90055400	-0.00909800
H	5.05011000	1.36663000	1.47281000
H	4.52677600	-2.88758200	2.04397200
C	6.09333200	-4.65996100	2.90064000
C	7.56179900	-3.40101100	4.52234400
C	8.34395400	-3.81295000	2.13196900
H	6.70247800	-3.18586300	5.18492600
H	8.31607600	-2.60750800	4.67613700
H	8.01127500	-4.36134700	4.84007000
H	5.20226000	-4.50493300	3.53815600
H	6.57471700	-5.60162700	3.22442200
H	5.75543600	-4.80022000	1.85669300

H	8.04826400	-3.89442600	1.06920800
H	8.79683500	-4.77485300	2.44006800
H	9.12236600	-3.03159600	2.20928900
C	7.72902200	1.56502900	2.38021300
C	7.03774900	2.86584300	1.88928200
C	9.01149600	1.34099200	1.51638200
C	8.14145500	1.76536200	3.87400000
H	7.25209000	1.93822300	4.50865600
H	8.81254800	2.64049500	3.97034500
H	8.67546900	0.88338400	4.27248100
H	6.74679300	2.79600300	0.82396300
H	7.73674500	3.71709900	1.98787200
H	6.13687000	3.09986700	2.48861100
H	8.75105200	1.21041600	0.44920800
H	9.57333400	0.44583000	1.84012700
H	9.68652500	2.21392800	1.60356700
C	0.28951200	1.55026200	0.51458300
C	0.00678500	2.68897300	-0.44657400
C	0.37371600	4.09393700	0.13181800
H	-1.05827000	2.67498800	-0.74041900
H	0.58639600	2.52225000	-1.38022600
C	-0.02481300	5.25333400	-0.78083100
C	-1.36620300	5.40280100	-1.23130900

C 0.92560700 6.23710200 -1.16251600

C 0.54807200 7.34038100 -1.96660100

C -0.78857000 7.47620900 -2.40947400

C -1.74540600 6.49955700 -2.03832700

H -2.78516300 6.59581700 -2.37346600

H -2.12328200 4.66212700 -0.94287900

H -1.08262000 8.33004500 -3.03133400

H 1.29805600 8.09423900 -2.23511500

H 1.96408700 6.14871600 -0.81946600

H 1.46131900 4.13731900 0.33666500

N -0.88303000 2.10340200 2.06894700

N -0.96097800 1.54323100 3.09472000

H 1.24650500 1.63269800 1.07514700

H -0.14167200 4.20061200 1.10573500

Intermediate C

$C_{[Co(III)(P6)]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.775515 Hartree

H_corr: 2.077763 Hartree

SCF: -6499.00986 Hartree

S: 636.134 Cal/Mol-Kelvin

H: -6496.932097 Hartree

G: -6497.234345 Hartree

Cartesian Coordinates:

Co	0.04249500	0.27201500	0.05664400
O	0.75739600	-1.14226400	7.83884900
O	3.09323700	5.83789400	4.30087800
N	-0.79814200	1.22326100	1.57992600
N	-1.48294600	0.79198200	-1.07711700
N	0.80707000	-0.36650000	5.61461200
H	0.53606800	-0.60654300	4.65508100
N	2.25826400	3.78140600	3.50563400
H	1.94022700	3.30559500	2.65517300
C	1.08851400	1.22270600	3.24327700
C	-0.23549200	1.49271400	2.84595800
C	-1.22742000	2.07307300	3.74073700
H	-1.02747400	2.36822600	4.76991400
C	-2.41323300	2.13471300	3.04047300
H	-3.38309000	2.49046900	3.38262200
C	-2.14335500	1.64080500	1.69596400
C	-3.08535500	1.67565200	0.65010500
C	-2.72754100	1.32145300	-0.66532100
C	-3.58093900	1.57394300	-1.81840400

H	-4.57954700	2.00316900	-1.75893100
C	-2.86584600	1.21654100	-2.94226900
H	-3.16218700	1.28122200	-3.98837800
C	-1.58208600	0.70505500	-2.48470800
C	1.56256000	1.71311300	4.59003800
C	1.42310700	0.91030300	5.76492100
C	1.87559400	1.39286300	7.02377700
H	1.75829700	0.76299700	7.90661100
C	2.45284800	2.67796000	7.09617700
H	2.79851400	3.05006400	8.06762700
C	2.59607700	3.50000400	5.95910700
H	3.03242000	4.49831800	6.01842400
C	2.14975600	3.01390900	4.70025600
C	0.47855900	-1.30121900	6.60627300
C	-0.25206000	-2.50787900	6.08909600
H	-0.63746600	-2.43429000	5.06410500
C	-1.12785600	-3.30059000	7.09040300
H	-2.10807800	-3.63472900	6.73491100
H	-1.09314900	-2.93326700	8.12150500
C	0.13264900	-3.96529400	6.54448000
C	-0.03216000	-5.05532200	5.50024700
C	-0.88611800	-6.16188700	5.75085900
H	-1.46429200	-6.19133300	6.68309200

C	-0.99744700	-7.21684300	4.81435300
H	-1.66314900	-8.06351200	5.02088900
C	-0.25387300	-7.17922800	3.61034200
H	-0.34596100	-7.98803900	2.87656500
C	0.60260000	-6.08113300	3.35245400
H	1.17534600	-6.04837500	2.41812100
C	0.71494200	-5.03032900	4.29272300
H	1.38044300	-4.18087400	4.09060500
C	1.33184400	-4.17962200	7.47948600
H	1.20229300	-5.12691000	8.03634700
H	1.42692300	-3.35032000	8.20013700
H	2.27173300	-4.25490500	6.90075400
C	2.69457700	5.10340500	3.34072400
C	2.62945200	5.57815500	1.91619200
H	2.61602200	4.79205300	1.15061000
C	3.37048700	6.87504300	1.53106800
H	3.87422200	7.38598100	2.35872100
H	3.90392800	6.86762700	0.57524100
C	1.84178600	6.88632100	1.53569400
C	1.10941800	6.86641500	0.20640000
C	0.12186700	5.88440400	-0.07130400
H	-0.07307100	5.09406400	0.66510800
C	-0.60534500	5.91134200	-1.28476900

H	-1.36074300	5.14242900	-1.48700500
C	-0.35952000	6.92977300	-2.23811500
H	-0.91894400	6.95012000	-3.18066200
C	0.62003100	7.91680700	-1.96886800
H	0.81474000	8.70851300	-2.70241400
C	1.34740300	7.88386300	-0.75556200
H	2.10847200	8.64715900	-0.54942800
C	1.11219400	7.67454400	2.63360800
H	1.00771800	8.73230300	2.32612400
H	1.66722700	7.63587000	3.58637500
H	0.09580200	7.26995300	2.79959900
C	-4.46540400	2.21535700	0.91129500
C	-4.64259900	3.58789000	1.22660300
C	-5.93404000	4.12575300	1.45936700
C	-6.16506700	5.62394100	1.79296500
C	-7.04296100	3.24185600	1.37591300
H	-8.04845500	3.64169100	1.55710000
C	-6.90489200	1.86223500	1.06776200
C	-5.59722600	1.36505600	0.82829700
O	-3.32051200	-2.95969000	-6.50821100
O	1.54397900	3.60601600	-6.47823500
N	1.00703200	-0.42768800	-1.52510400
N	1.70595900	0.02104500	1.12486300

N	-2.18363400	-1.76773700	-4.82390600
H	-1.97095900	-1.76448100	-3.82070800
N	0.57391400	2.25465700	-4.80603200
H	0.57348400	2.09159900	-3.79423600
C	-0.61561400	0.16167900	-3.35319300
C	0.56482000	-0.43377100	-2.86578400
C	1.48106600	-1.18372200	-3.71154000
H	1.34937100	-1.32799000	-4.78307800
C	2.47712500	-1.67017700	-2.89127900
H	3.32544900	-2.29709100	-3.15874900
C	2.20838000	-1.17501500	-1.54729000
C	3.08468900	-1.35680700	-0.46045000
C	2.85210900	-0.72332200	0.77663500
C	3.83995500	-0.67713300	1.84852300
H	4.81687800	-1.15542000	1.80536600
C	3.30851400	0.09859100	2.85731100
H	3.75305500	0.37374500	3.81288800
C	1.97852900	0.50380200	2.42231000
C	-0.82166600	0.25680400	-4.84598700
C	-1.60631900	-0.69648300	-5.56669600
C	-1.77674600	-0.57088700	-6.97334600
H	-2.38142700	-1.30908300	-7.50163600
C	-1.15195400	0.49930300	-7.64690400

H	-1.28218800	0.59151500	-8.73141600
C	-0.36287300	1.45158500	-6.96912400
H	0.12942500	2.27317200	-7.49200800
C	-0.19949700	1.32997900	-5.56309300
C	-2.97227600	-2.82943000	-5.29001000
C	-3.36679500	-3.81334300	-4.22592600
H	-2.82183500	-3.74456700	-3.27547400
C	-3.75040300	-5.24387400	-4.67443700
H	-3.35947400	-6.06512700	-4.06533300
H	-3.74874700	-5.40380100	-5.75785000
C	-4.84406800	-4.34349500	-4.10598900
C	-5.34528100	-4.62523500	-2.70144000
C	-5.83451800	-5.91519200	-2.36431200
H	-5.79411200	-6.71449800	-3.11500700
C	-6.36774600	-6.17538200	-1.07979900
H	-6.74141500	-7.17682700	-0.83470700
C	-6.41998700	-5.14419000	-0.11030300
H	-6.82982700	-5.34377200	0.88675700
C	-5.93847400	-3.85308500	-0.43813300
H	-5.97774900	-3.05021500	0.30744600
C	-5.40961900	-3.59643500	-1.72513400
H	-5.03899900	-2.59425000	-1.97602300
C	-5.92896700	-3.79797200	-5.04651400

H	-6.74231400	-4.54164800	-5.14572600
H	-5.51541100	-3.58451200	-6.04623500
H	-6.37019400	-2.86812600	-4.64031100
C	1.39411800	3.30024600	-5.25221500
C	2.10377600	4.00878000	-4.13220300
H	1.62949900	3.93350000	-3.14539500
C	2.83441800	5.33373400	-4.42358900
H	2.80939700	5.65967200	-5.46910700
H	2.73332300	6.12362000	-3.67262600
C	3.67383600	4.09546800	-4.10312900
C	4.32628900	3.98568300	-2.73713400
C	4.09407700	2.86062800	-1.90189200
H	3.38704000	2.08535200	-2.22484700
C	4.75542500	2.73296200	-0.65713000
H	4.56050400	1.86112500	-0.02086900
C	5.66795800	3.72971900	-0.23280000
H	6.17858700	3.63487900	0.73259300
C	5.91038300	4.85349700	-1.06036700
H	6.61626200	5.62824200	-0.73729600
C	5.24441900	4.97849500	-2.30254000
H	5.42946000	5.85178800	-2.94089000
C	4.48430100	3.44438000	-5.23373000
H	5.46756300	3.94373600	-5.32378800

H	3.95673400	3.52644900	-6.19944300
H	4.66753500	2.37398400	-5.02160500
C	4.34317600	-2.16080200	-0.63707700
C	5.36977500	-1.71645600	-1.50863100
C	6.57027200	-2.45696800	-1.66993700
C	6.71274200	-3.66195900	-0.93166500
H	7.63028700	-4.24363200	-1.04643900
C	5.70894700	-4.13600200	-0.04593200
C	4.52525100	-3.36377600	0.09093700
H	3.72434900	-3.69238400	0.76447300
H	5.22809500	-0.77158800	-2.04680000
C	5.86445500	-5.44914300	0.76714700
C	7.21997900	-6.16031900	0.49967200
C	4.71503600	-6.43494500	0.38282800
C	5.77777200	-5.12572400	2.29324200
C	7.67188500	-1.92648100	-2.62597100
C	8.90643900	-2.86759100	-2.69410300
C	8.15300200	-0.52487100	-2.13010500
C	7.08441500	-1.78954500	-4.06724700
H	9.39490100	-2.97791600	-1.70730700
H	9.65403400	-2.44316900	-3.39010600
H	8.63722100	-3.87451200	-3.06614500
H	8.58918200	-0.59469800	-1.11578400

H	7.32440100	0.20536200	-2.09317400
H	8.92678500	-0.12444000	-2.81303900
H	7.33168300	-6.44768600	-0.56306400
H	7.27555000	-7.08538200	1.10355000
H	8.08059400	-5.52495700	0.78251700
H	6.59481800	-4.44508800	2.59835500
H	5.86260500	-6.05630900	2.88651400
H	4.81833200	-4.64396700	2.55656500
H	6.74805100	-2.77117200	-4.45136100
H	7.85480500	-1.39394700	-4.75659800
H	6.22212500	-1.09849200	-4.09427400
H	4.76239600	-6.69394400	-0.69169300
H	3.71905800	-5.99920900	0.58429000
H	4.80049700	-7.36927800	0.97013400
H	-5.44058600	0.30869200	0.58817900
H	-3.75960900	4.23286200	1.27272500
C	-4.83857900	6.43100600	1.84949900
C	-6.86754400	5.74347400	3.18352400
C	-7.07819500	6.26196900	0.69724200
H	-6.23656900	5.31143400	3.98288300
H	-7.84073700	5.21928300	3.19886600
H	-7.05217600	6.80763800	3.42594200
H	-4.15466000	6.04500500	2.62906100

H	-5.05951700	7.48695400	2.09334500
H	-4.30531400	6.41803500	0.88031800
H	-6.59972300	6.20141200	-0.29822800
H	-7.26229600	7.32867800	0.92872200
H	-8.05856000	5.75483600	0.63421500
C	-8.16688500	0.96117400	1.00287000
C	-7.82160200	-0.51962000	0.68690300
C	-9.12284500	1.48942600	-0.11457200
C	-8.90746400	1.00373700	2.37792200
H	-8.25616700	0.62563000	3.18820800
H	-9.81655600	0.37319100	2.34030400
H	-9.21910200	2.03005900	2.64499700
H	-7.32670300	-0.62700600	-0.29678300
H	-8.75029500	-1.11925500	0.65748000
H	-7.16413900	-0.95747100	1.46244900
H	-8.62971600	1.45554200	-1.10421600
H	-9.43416300	2.53335300	0.07351600
H	-10.03626400	0.86583400	-0.16145100
C	-0.82008900	-1.36633700	0.51273300
C	-0.80847500	-2.60402900	-0.34725000
C	-1.26712300	-3.86196400	0.47288200
H	0.19744300	-2.79470200	-0.76157100
H	-1.49284300	-2.49587800	-1.22503400

C	-1.12638700	-5.15957800	-0.31870000
C	0.15749600	-5.62919000	-0.71356300
C	-2.26384900	-5.93302000	-0.67094700
C	-2.12323500	-7.14478000	-1.39139000
C	-0.84066100	-7.60172500	-1.77664400
C	0.30181000	-6.83576600	-1.43570800
H	1.30064600	-7.17976400	-1.73032600
H	1.05092700	-5.04530100	-0.45357600
H	-0.73070600	-8.53994100	-2.33346400
H	-3.01580000	-7.73043200	-1.64277500
H	-3.26398500	-5.59187100	-0.37515000
H	-2.31695800	-3.72644100	0.79564500
H	-1.73792400	-1.17773400	1.10762800
H	-0.65018200	-3.91418100	1.39209100

$C_{[N2]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: -0.013594 Hartree

H_corr: 0.008229 Hartree

SCF: -109.5605216 Hartree

S: 45.93 Cal/Mol-Kelvin

H: -109.5522926 Hartree

G: -109.5741156 Hartree

Cartesian Coordinates:

N	0.00000000	0.00000000	0.57307000
N	0.00000000	0.00000000	-0.57307000

$C_{[2a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.076494 Hartree

H_corr: 0.114617 Hartree

SCF: -308.5420493 Hartree

S: 80.236 Cal/Mol-Kelvin

H: -308.4274323 Hartree

G: -308.4655553 Hartree

Cartesian Coordinates:

C	-2.04360400	-0.00016800	-0.00000900
C	-0.60405700	-0.00017300	-0.00000600
C	0.12029700	-1.22969200	0.00000100
C	0.12009200	1.22957100	0.00000200
C	1.53197800	1.22537100	0.00000200
C	2.24357000	0.00013900	-0.00000100

C 1.53223000 -1.22519400 0.00000300

H 2.07804000 -2.17575100 0.00000600

H -0.43323500 -2.17518900 0.00000600

H 3.33965900 0.00026000 -0.00000500

H 2.07765600 2.17600600 0.00000500

H -0.43372800 2.17489600 0.00000700

C -3.27953200 0.00007500 -0.00000200

H -4.35423700 0.00020200 0.00005000

Transition State TS2

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -163.3686 cm-1

G_corr: 1.873731 Hartree

H_corr: 2.193064 Hartree

SCF: -6807.565056 Hartree

S: 672.092 Cal/Mol-Kelvin

H: -6805.371992 Hartree

G: -6805.691325 Hartree

Cartesian Coordinates:

Co 0.03678800 0.48905000 0.02053800

O -2.84173900 -2.19365400 -7.13077500

O	0.30035300	5.17632500	-5.72214800
N	1.07157100	0.33523500	-1.66307300
N	1.72518700	0.60333200	1.02112600
N	-1.73383700	-1.24696300	-5.27639300
H	-1.37500700	-1.45895900	-4.33684300
N	-0.23775300	3.32809600	-4.35856100
H	-0.18862500	2.99296200	-3.39156700
C	-0.72299000	0.74769200	-3.37894300
C	0.59200200	0.42346100	-2.98697300
C	1.64598500	0.10481100	-3.93935800
H	1.51798100	0.11421000	-5.02115300
C	2.76913700	-0.21538000	-3.20506500
H	3.75105600	-0.51577000	-3.56618500
C	2.42669300	-0.03535100	-1.79922100
C	3.36436400	-0.10835100	-0.75033300
C	3.01893700	0.26556600	0.56440400
C	4.00100400	0.47924500	1.61933000
H	5.07023300	0.30976500	1.50421400
C	3.32198700	0.96472300	2.71859100
H	3.71831500	1.25943000	3.68953100
C	1.91136500	1.00937600	2.36148500
C	-1.00301900	1.05644700	-4.83024300
C	-1.52393300	0.08635600	-5.74449600

C -1.79107700 0.45241100 -7.09458700

H -2.20808900 -0.29414300 -7.77082200

C -1.51587300 1.76592400 -7.52450900

H -1.71818000 2.03578900 -8.56753800

C -0.98734600 2.74048900 -6.65423300

H -0.76243800 3.75464700 -6.98791000

C -0.73835200 2.38564300 -5.30211100

C -2.32900700 -2.31559500 -5.97060100

C -2.28829900 -3.63098200 -5.24819400

H -1.64093000 -3.67534700 -4.36596500

C -2.35035300 -4.91377800 -6.11567800

H -1.66763000 -5.72498700 -5.84265400

H -2.48449200 -4.73831300 -7.18831200

C -3.53252600 -4.59342100 -5.20484900

C -3.69576700 -5.42482300 -3.94420600

C -3.80529100 -6.83823800 -4.03830600

H -3.71493600 -7.31659000 -5.02179500

C -4.02137800 -7.62749800 -2.88416200

H -4.10332200 -8.71750000 -2.97438500

C -4.13072500 -7.01213800 -1.61297600

H -4.29260000 -7.62044900 -0.71530800

C -4.02435300 -5.60360600 -1.50840500

H -4.10121000 -5.12366500 -0.52540800

C	-3.81342000	-4.81804900	-2.66636400
H	-3.72603200	-3.72799400	-2.58133900
C	-4.86435000	-4.15288400	-5.82972900
H	-5.45603000	-5.04425700	-6.11269900
H	-4.69450400	-3.53557000	-6.72761200
H	-5.46235900	-3.56762200	-5.10566500
C	0.24417400	4.62622100	-4.57584800
C	0.71422600	5.30034200	-3.31693100
H	0.27385500	4.92520200	-2.38454200
C	1.02563500	6.80880400	-3.35249100
H	0.90954400	7.28474300	-4.33218800
H	0.69363600	7.39834900	-2.49223900
C	2.18951700	5.82953900	-3.19029400
C	2.84046600	5.68471800	-1.82715700
C	2.96038900	4.41382700	-1.20388600
H	2.52245300	3.53145900	-1.68867000
C	3.63245300	4.27436000	0.03381200
H	3.71736200	3.28659600	0.50248300
C	4.19953000	5.40827600	0.66553100
H	4.71602200	5.30325200	1.62669100
C	4.08729100	6.67972500	0.05197400
H	4.52003500	7.56191100	0.53881900
C	3.41414100	6.81471000	-1.18535300

H	3.32745000	7.80041500	-1.66011400
C	3.16027000	5.64134100	-4.36554600
H	3.95154300	6.41368800	-4.32436300
H	2.63460600	5.72542200	-5.33215000
H	3.65198100	4.65128800	-4.31567600
C	4.79669200	-0.45585600	-1.05258500
C	5.60166000	0.43873400	-1.80506400
C	6.96089000	0.14378200	-2.08276600
C	7.87508900	1.10616500	-2.88725100
C	7.48596200	-1.08019100	-1.58851500
H	8.53536900	-1.32358900	-1.79643000
C	6.71079000	-2.00066500	-0.83397800
C	5.35773000	-1.66465700	-0.56800100
O	2.00459300	-1.19727000	7.66507200
O	0.93430300	6.29634600	4.62112200
N	-0.98593200	0.94604300	1.64775600
N	-1.64073600	0.69852600	-1.03827600
N	1.46896800	-0.36206200	5.52821400
H	1.20890800	-0.64377400	4.57734300
N	1.02416000	4.13410700	3.68301800
H	0.88746800	3.62538000	2.80398000
C	0.89180600	1.35412900	3.27091500
C	-0.47129900	1.23691900	2.93000700

C	-1.54649200	1.36099000	3.90285400
H	-1.39689900	1.58190000	4.95890700
C	-2.72593800	1.11342100	3.23246100
H	-3.73689100	1.08823300	3.63423100
C	-2.38837400	0.89917900	1.83057900
C	-3.34769500	0.77401000	0.80621400
C	-2.96514500	0.76280100	-0.55184000
C	-3.90440200	0.95731000	-1.64962400
H	-4.98167700	1.05490400	-1.52709400
C	-3.16279100	1.03914100	-2.81122800
H	-3.50997700	1.19888900	-3.83120300
C	-1.76883600	0.84682800	-2.44005000
C	1.26014500	1.89895700	4.63036400
C	1.54595100	1.04575600	5.74162800
C	1.87662300	1.60104700	7.00878100
H	2.09082600	0.92988700	7.84133500
C	1.90787400	3.00322900	7.15623000
H	2.15781100	3.42817800	8.13528800
C	1.62608700	3.87409800	6.08378600
H	1.63937200	4.95890900	6.20054200
C	1.30533300	3.31932400	4.81560400
C	1.67133700	-1.39752500	6.45219200
C	1.45016900	-2.77333300	5.89205600

H	0.93911800	-2.82643800	4.92210000
C	1.11382700	-3.90843600	6.88892200
H	0.32417700	-4.60344700	6.58607300
H	1.11574100	-3.61172400	7.94308600
C	2.46205100	-3.94595400	6.17424500
C	2.65133400	-4.95426600	5.05585000
C	2.41666200	-6.33468000	5.29406800
H	2.04782300	-6.65185300	6.27767900
C	2.65122200	-7.29490400	4.28157900
H	2.46301800	-8.35679500	4.48022600
C	3.12620100	-6.88617400	3.01155800
H	3.30240200	-7.62678800	2.22282200
C	3.36805000	-5.51246300	2.76536500
H	3.73428200	-5.19071900	1.78358200
C	3.13637600	-4.55602300	3.78209100
H	3.32626800	-3.49240600	3.58832300
C	3.74275000	-3.67215700	6.97668300
H	4.08985900	-4.60912100	7.45206600
H	3.56478800	-2.91749400	7.76075000
H	4.55189000	-3.31052800	6.31431400
C	0.84348000	5.52295200	3.61482900
C	0.49898300	6.00373300	2.23323300
H	0.83371000	5.36026400	1.40984900

C	0.49696900	7.51631000	1.94386800
H	0.72705600	8.15615500	2.80262200
H	0.92168100	7.83220900	0.98588100
C	-0.84336300	6.77941000	1.96683400
C	-1.54167200	6.47929000	0.65350200
C	-1.94779600	5.15711500	0.32879300
H	-1.69895600	4.33337300	1.01073400
C	-2.66342500	4.89090600	-0.86263700
H	-2.97084300	3.86519200	-1.09949100
C	-2.98756700	5.94878200	-1.74720100
H	-3.53756700	5.74423300	-2.67304500
C	-2.58922600	7.27068600	-1.43221300
H	-2.83373900	8.09274800	-2.11553900
C	-1.87333800	7.53247200	-0.23985200
H	-1.56566500	8.55739800	0.00378800
C	-1.80476300	7.04241200	3.13547300
H	-2.42815000	7.92926300	2.91380800
H	-1.25140600	7.22517300	4.07258000
H	-2.48390400	6.18238000	3.28860800
C	-4.81310100	0.77265800	1.14155700
C	-5.42363200	1.91037600	1.72810300
C	-6.81021400	1.92809100	2.03148300
C	-7.57178200	0.76765200	1.73039900

H	-8.63974600	0.76552900	1.96015100
C	-6.99755500	-0.38759900	1.13657600
C	-5.60822400	-0.36319700	0.84423100
H	-5.12452400	-1.23440400	0.38556700
H	-4.80447900	2.79336700	1.92608400
C	-7.82910900	-1.65447000	0.80048600
C	-9.32756400	-1.50382600	1.18346600
C	-7.24903500	-2.87644700	1.58221900
C	-7.74512800	-1.93660500	-0.73387400
C	-7.43708600	3.19956200	2.66369300
C	-8.95641200	3.03793000	2.94646800
C	-7.24730000	4.40642800	1.68933200
C	-6.72101800	3.51183100	4.01677700
H	-9.53035500	2.85163200	2.01890800
H	-9.34712000	3.96876900	3.39850100
H	-9.15808100	2.21210000	3.65503600
H	-7.75888400	4.21941300	0.72643700
H	-6.18032900	4.59756800	1.47428900
H	-7.67297100	5.32604700	2.13490100
H	-9.46029900	-1.33446100	2.26891300
H	-9.86918000	-2.43196700	0.92139800
H	-9.80984400	-0.67077300	0.63778000
H	-8.16766700	-1.09380300	-1.31271800

H	-8.31584900	-2.85070000	-0.98623700
H	-6.70215100	-2.08866600	-1.06697200
H	-6.85102000	2.67918700	4.73374400
H	-7.14588100	4.42794200	4.47001400
H	-5.63685400	3.67699800	3.87821600
H	-7.30796900	-2.70792200	2.67406700
H	-6.19056700	-3.06179600	1.32207200
H	-7.82174700	-3.79192600	1.33924500
H	4.71979900	-2.34349500	0.00669100
H	5.15734600	1.37625400	-2.15346000
C	7.12271700	2.37871500	-3.36529400
C	8.42934000	0.36582800	-4.14654900
C	9.06966700	1.55482400	-1.98522000
H	7.60478000	0.04730400	-4.81176200
H	9.01138800	-0.53332500	-3.87268000
H	9.09572300	1.03839100	-4.72001100
H	6.27583500	2.12906400	-4.03242100
H	7.81661500	3.02480100	-3.93489300
H	6.73487400	2.97297000	-2.51681900
H	8.70606500	2.09483400	-1.09100300
H	9.73994500	2.23135500	-2.54951100
H	9.66964700	0.69232900	-1.64084800
C	7.35835400	-3.31950900	-0.33386500

C	6.36068400	-4.20449200	0.46205300
C	8.56508100	-2.98353000	0.60010900
C	7.86859000	-4.14359800	-1.55932000
H	7.03088900	-4.40619200	-2.23242300
H	8.34506700	-5.08193500	-1.21583200
H	8.61501500	-3.58135800	-2.14980700
H	5.98760300	-3.68920000	1.36736000
H	6.86810700	-5.12984300	0.79263100
H	5.49357600	-4.50036700	-0.15899700
H	8.23067900	-2.41271600	1.48668200
H	9.33162700	-2.38146400	0.07862500
H	9.04695400	-3.91638300	0.95078300
C	0.03494900	-1.41335100	0.30784600
C	-0.71911200	-2.06703000	1.44504900
C	-0.69756500	-3.63148000	1.37271900
H	-1.76753400	-1.71544800	1.47268000
H	-0.27425700	-1.76016900	2.42189600
C	-1.48361700	-4.29434700	2.50190000
C	-2.86686000	-4.01856100	2.69027300
C	-0.86092700	-5.22866700	3.37195100
C	-1.59735700	-5.87055100	4.39767600
C	-2.97191300	-5.58570900	4.57494300
C	-3.60432400	-4.65386200	3.71530300

H	-4.66947300	-4.42570500	3.84270600
H	-3.37237600	-3.30155500	2.02960600
H	-3.54315400	-6.08191400	5.36849300
H	-1.09693400	-6.59761900	5.04892800
H	0.20269500	-5.46389000	3.24021600
H	0.35149200	-3.98449900	1.38721100
H	-1.11858000	-3.92952100	0.39355700
C	-0.87890800	-2.44553500	-1.83006200
C	-0.18775000	-3.38412600	-2.26972100
H	-1.58829900	-1.65820000	-1.64221500
C	0.65062700	-4.46723800	-2.69106500
C	1.91181600	-4.21318800	-3.31627200
C	2.72513900	-5.28520600	-3.73957400
C	2.30323800	-6.62541500	-3.54829200
C	1.05419600	-6.88613900	-2.93029700
C	0.22973900	-5.82228100	-2.50646300
H	-0.74094600	-6.02295300	-2.03920200
H	0.71997600	-7.91966900	-2.78338500
H	3.68769800	-5.07742100	-4.22131100
H	2.93756700	-7.45540800	-3.88059800
H	2.23340600	-3.17587900	-3.46253000
H	1.03195800	-1.84052000	0.07503000

Intermediate D

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.878775 Hartree

H_corr: 2.196797 Hartree

SCF: -6807.620452 Hartree

S: 669.334 Cal/Mol-Kelvin

H: -6805.423655 Hartree

G: -6805.741677 Hartree

Cartesian Coordinates:

Co -0.10023000 0.33947800 0.03152700

O -0.38698200 -3.43607900 -6.99649300

O -0.71438200 4.69594900 -6.12842300

N 1.12736500 0.62086400 -1.50902500

N 1.36981700 0.86693700 1.26361300

N -0.51762300 -1.98249800 -5.14685200

H -0.50686100 -1.95512300 -4.12175500

N -0.73204900 2.85818600 -4.65043800

H -0.70527300 2.61878600 -3.65427000

C -0.45626300 0.33592300 -3.44064600

C 0.82669400 0.49331600 -2.88204900

C 2.02833500 0.61431100 -3.69495400

H	2.04260800	0.55371100	-4.78242600
C	3.07800500	0.82661500	-2.82755700
H	4.13322800	0.95778000	-3.05930200
C	2.52259300	0.85420400	-1.48161600
C	3.29529000	1.12535500	-0.33790100
C	2.71884800	1.15843000	0.94637900
C	3.45471900	1.55557700	2.13932100
H	4.50116000	1.85484600	2.14308800
C	2.57512100	1.49855200	3.19872300
H	2.75307300	1.73544700	4.24676200
C	1.29402400	1.06213400	2.66291300
C	-0.60719800	0.44382700	-4.93915100
C	-0.61126600	-0.71015100	-5.78166100
C	-0.70950900	-0.56822700	-7.19376900
H	-0.69616900	-1.46220500	-7.81871800
C	-0.80879600	0.72580400	-7.74693700
H	-0.88173900	0.83279100	-8.83548900
C	-0.81915700	1.88562500	-6.94359800
H	-0.89309800	2.88652300	-7.37232400
C	-0.72044500	1.74206800	-5.53373400
C	-0.42750700	-3.25217700	-5.73663600
C	-0.38152600	-4.37878100	-4.74682900
H	-0.21960900	-4.09273200	-3.69989200

C	0.26098900	-5.71660800	-5.17857300
H	0.92115600	-6.19664700	-4.44944600
H	0.59902300	-5.75214100	-6.21950300
C	-1.24526100	-5.68702700	-4.94397600
C	-1.80473300	-6.31235800	-3.67905300
C	-1.32493500	-7.56042600	-3.20265800
H	-0.50081200	-8.05501000	-3.73121500
C	-1.90264500	-8.17226100	-2.06401700
H	-1.52087100	-9.13741600	-1.70983800
C	-2.97427600	-7.54448200	-1.38562200
H	-3.42205300	-8.01585000	-0.50294700
C	-3.46281400	-6.29946100	-1.85448600
H	-4.29608300	-5.80982300	-1.33623400
C	-2.88289200	-5.69138400	-2.99141500
H	-3.26577900	-4.72779500	-3.35207900
C	-2.18551100	-5.80034300	-6.15331400
H	-2.35113500	-6.86816900	-6.39147200
H	-1.75827500	-5.29656300	-7.03601600
H	-3.17089000	-5.34798700	-5.93356200
C	-0.72421800	4.22807600	-4.94506700
C	-0.70688300	5.09146300	-3.71388200
H	-1.07802300	4.61799500	-2.79591200
C	-0.98997600	6.60099100	-3.84863500

H	-1.15614500	6.95504800	-4.87183200
H	-1.62148800	7.05273000	-3.07687500
C	0.42857900	6.15604300	-3.48912000
C	0.90997600	6.32850300	-2.05980600
C	1.42303100	5.22788900	-1.32301300
H	1.41666900	4.22690600	-1.77385400
C	1.93042100	5.40538300	-0.01408500
H	2.31751700	4.54384000	0.54346900
C	1.93778600	6.69313100	0.57610700
H	2.32805200	6.83242700	1.59114500
C	1.43147700	7.79806300	-0.15139300
H	1.43380100	8.79770500	0.29981900
C	0.92284600	7.61534900	-1.45916500
H	0.52666300	8.47155000	-2.01975100
C	1.53583000	6.30961600	-4.54220400
H	1.96068600	7.32998200	-4.49095800
H	1.14332300	6.14045100	-5.55952800
H	2.35751600	5.59217900	-4.35662900
C	4.76000100	1.43321000	-0.48984500
C	5.17461800	2.62176700	-1.14507500
C	6.55024500	2.93844500	-1.28569200
C	7.03953500	4.23781500	-1.97944600
C	7.49779800	2.02233000	-0.75572900

H	8.56558700	2.25295200	-0.85773200
C	7.12121900	0.81945900	-0.10067100
C	5.73566500	0.54377800	0.02889700
O	1.86365900	-1.85967700	7.53856400
O	-1.36400900	5.35984700	5.45209000
N	-1.38576200	0.34206100	1.55106700
N	-1.63419300	0.16799200	-1.22531700
N	1.07408600	-0.94132600	5.51804200
H	0.94113300	-1.14196400	4.52132100
N	-0.60417300	3.46582800	4.26924100
H	-0.52156200	3.08216000	3.32268700
C	0.15182500	0.88627100	3.46725100
C	-1.09167200	0.50698300	2.92475300
C	-2.27821300	0.29840600	3.74079900
H	-2.29641300	0.37422100	4.82716300
C	-3.31373400	0.00896300	2.87807500
H	-4.35353400	-0.20844500	3.11517900
C	-2.77195300	0.05560300	1.52665500
C	-3.55970700	-0.10673900	0.37252100
C	-3.00349300	-0.00954100	-0.91613600
C	-3.80801000	-0.05568000	-2.12996100
H	-4.89140600	-0.16073400	-2.14385200
C	-2.94367100	0.07876100	-3.19472700

H	-3.17033800	0.10452100	-4.25987700
C	-1.60351200	0.20162500	-2.63813100
C	0.21786100	1.26762300	4.92737000
C	0.67578000	0.36276200	5.93424500
C	0.71539300	0.76787100	7.29787300
H	1.07395000	0.06309500	8.04904600
C	0.29262700	2.06885900	7.64105300
H	0.31994500	2.37480600	8.69334100
C	-0.16084900	2.98844300	6.67242900
H	-0.48951800	3.99474600	6.93767200
C	-0.19062600	2.58733200	5.31035900
C	1.63323600	-1.97003900	6.29056200
C	1.94617600	-3.21995700	5.51856500
H	1.44855100	-3.32801400	4.54679300
C	2.14964800	-4.52632100	6.31844700
H	1.69963900	-5.43093400	5.89777800
H	2.08630600	-4.41743700	7.40644600
C	3.36075900	-3.90512600	5.62698400
C	3.88941600	-4.56844200	4.36826300
C	4.26002000	-5.93945900	4.38771100
H	4.09956400	-6.52369300	5.30268900
C	4.82902400	-6.55186000	3.24624400
H	5.11193600	-7.61107100	3.27767400

C	5.03570900	-5.79847700	2.06510700
H	5.47861800	-6.26861500	1.17899700
C	4.66711200	-4.43124500	2.03471500
H	4.81983600	-3.84570300	1.12033300
C	4.10303000	-3.82220500	3.17978500
H	3.82019700	-2.76195600	3.15424200
C	4.45648900	-3.25559100	6.48527300
H	5.17630200	-4.02828600	6.81581200
H	4.02588000	-2.76626400	7.37501300
H	5.01727300	-2.50084600	5.90199500
C	-1.14782400	4.75429900	4.35400700
C	-1.47092300	5.34301500	3.00804900
H	-0.91796600	4.92052400	2.15935400
C	-1.80874500	6.84358600	2.90612100
H	-1.82255300	7.38413300	3.85876100
H	-1.38652000	7.38506600	2.05351300
C	-2.92710200	5.82712000	2.66709600
C	-3.39840000	5.58157900	1.24508900
C	-3.38867300	4.27709700	0.68349400
H	-2.98053300	3.44122500	1.26658200
C	-3.88522500	4.04586800	-0.62151300
H	-3.86390400	3.03358900	-1.04309600
C	-4.40734600	5.12005800	-1.38298200

H	-4.79053900	4.94352900	-2.39489600
C	-4.42554100	6.42437700	-0.83066900
H	-4.82800200	7.26056200	-1.41520700
C	-3.92538400	6.65115800	0.47331300
H	-3.93446400	7.66321400	0.89756200
C	-4.03227700	5.68848600	3.72434200
H	-4.82787200	6.43347100	3.53394900
H	-3.63257200	5.84972600	4.74016200
H	-4.49336600	4.68339800	3.68266300
C	-5.03744400	-0.35244500	0.51722300
C	-5.89554600	0.67672200	0.97938700
C	-7.29239500	0.46160000	1.11888700
C	-7.80402200	-0.82120300	0.78717000
H	-8.87600700	-1.00309300	0.89315600
C	-6.97419600	-1.87563500	0.32210400
C	-5.58426100	-1.61772400	0.18834600
H	-4.90616200	-2.40479600	-0.16346500
H	-5.46086300	1.65507500	1.21690100
C	-7.52872200	-3.28047700	-0.03586300
C	-9.06657800	-3.38387100	0.16115200
C	-6.84823600	-4.35102800	0.87634200
C	-7.20854400	-3.59696100	-1.53184400
C	-8.19822800	1.62011500	1.61487700

C	-9.69053100	1.20271800	1.73050100
C	-8.10055100	2.81450300	0.61201400
C	-7.71424800	2.09005900	3.02407300
H	-10.10889900	0.89472600	0.75341400
H	-10.28545000	2.06264400	2.09119800
H	-9.83209200	0.37320900	2.44932600
H	-8.45124700	2.51347500	-0.39327200
H	-7.06423500	3.18528700	0.51351400
H	-8.72944300	3.65632700	0.96047900
H	-9.35950200	-3.20296400	1.21270300
H	-9.40484400	-4.40181200	-0.10908000
H	-9.61302500	-2.66839200	-0.48222200
H	-7.69626800	-2.86479400	-2.20264200
H	-7.57593900	-4.60705900	-1.79657100
H	-6.12158200	-3.56734500	-1.73263600
H	-7.78455800	1.26735300	3.76062200
H	-8.34132400	2.92923200	3.38156000
H	-6.66588000	2.43947900	3.00120900
H	-7.07574000	-4.16210600	1.94219200
H	-5.74851900	-4.34794600	0.76293300
H	-7.21620200	-5.36269400	0.61759000
H	5.39920500	-0.37350600	0.52213000
H	4.40940400	3.30303000	-1.53009600

C	5.86707700	5.09073100	-2.53763900
C	7.98295200	3.87053400	-3.16943600
C	7.82728100	5.10499900	-0.94524300
H	7.44775500	3.26447200	-3.92447200
H	8.86460500	3.29390400	-2.83429000
H	8.34901900	4.79184100	-3.66189400
H	5.28161300	4.53609000	-3.29553000
H	6.27092400	5.99749000	-3.02570500
H	5.17717900	5.42172500	-1.73906500
H	7.17748600	5.39245300	-0.09755000
H	8.19785700	6.03023900	-1.42701400
H	8.69924800	4.56187200	-0.53630800
C	8.21682900	-0.13589500	0.44302300
C	7.62033100	-1.40857400	1.10432200
C	9.07309100	0.61551300	1.51256000
C	9.14104300	-0.58795200	-0.73290700
H	8.56118100	-1.13097700	-1.50261500
H	9.93396100	-1.26216700	-0.35581200
H	9.63313300	0.27223600	-1.22283000
H	6.97771600	-1.16237600	1.97070800
H	8.43999400	-2.05332500	1.47235700
H	7.02589400	-2.00310100	0.38497300
H	8.44671100	0.93312600	2.36730400

H	9.55502800	1.51711500	1.09173900
H	9.87136200	-0.04839400	1.89651900
C	0.28780500	-1.69009700	0.34562600
C	-0.83194300	-2.58765600	-0.19218100
C	-0.73370700	-4.07315300	0.28073900
H	-0.80414100	-2.58969800	-1.29925900
H	-1.81519400	-2.18248700	0.10037800
C	-0.92261200	-4.34719100	1.77449800
C	-1.67862600	-3.49710800	2.62558000
C	-0.38242900	-5.53918400	2.33195300
C	-0.60135500	-5.88130800	3.68634300
C	-1.36129500	-5.02633000	4.52201700
C	-1.89408800	-3.83071800	3.98483400
H	-2.48042600	-3.15603000	4.62001300
H	-2.11532800	-2.57171500	2.23368100
H	-1.53016400	-5.28407300	5.57408100
H	-0.18030900	-6.81139600	4.08756200
H	0.21041700	-6.20732600	1.69348900
H	0.23765300	-4.49228900	-0.04348900
H	-1.50849700	-4.64222600	-0.27658400
C	1.67066300	-2.00004900	-0.12501100
C	2.02064500	-2.80895800	-1.13174300
H	2.47662100	-1.51521200	0.45759800

C	2.75224500	-3.62398700	-2.00188700
C	3.14364800	-3.16558600	-3.32036800
C	3.85852000	-4.00726500	-4.18823700
C	4.20658700	-5.33001700	-3.79816400
C	3.82883500	-5.80134500	-2.51041100
C	3.11723600	-4.97650000	-1.62275400
H	2.83265200	-5.34075700	-0.62901300
H	4.09764000	-6.81912900	-2.20248300
H	4.14601100	-3.63828400	-5.17970700
H	4.76131100	-5.98010700	-4.48410100
H	2.88020000	-2.14588500	-3.62147900
H	0.26817300	-1.60034900	1.44582800

Transition State TS3

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -928.3504 cm-1

G_corr: 1.87628 Hartree

H_corr: 2.191859 Hartree

SCF: -6807.592801 Hartree

S: 664.192 Cal/Mol-Kelvin

H: -6805.400942 Hartree

G: -6805.716521 Hartree

Cartesian Coordinates:

Co	0.33454500	-0.28929500	0.02096400
O	-1.13686800	3.16197300	-7.05268100
O	3.19879800	-3.68151500	-6.05410400
N	-0.62204300	-0.99267500	-1.57260800
N	-0.78184000	-1.46733400	1.17336200
N	-0.26746700	2.04555000	-5.16980200
H	-0.28353800	2.02788700	-4.14462200
N	2.25793000	-2.08297000	-4.59690500
H	2.07048300	-1.90115200	-3.60593000
C	0.75907600	-0.01269400	-3.42940300
C	-0.36131800	-0.70362200	-2.93020500
C	-1.37579400	-1.28931600	-3.79448700
H	-1.38800200	-1.19436300	-4.87938300
C	-2.26019600	-1.95876000	-2.97671100
H	-3.14846700	-2.52241300	-3.25580100
C	-1.78094100	-1.80408000	-1.60957000
C	-2.37548000	-2.44814200	-0.50930100
C	-1.85850500	-2.30303100	0.79268700
C	-2.35826400	-3.05423300	1.93634600
H	-3.16517200	-3.78300600	1.88585700
C	-1.60777500	-2.67868100	3.02997900

H	-1.67518000	-3.03248900	4.05797300
C	-0.64797300	-1.68747300	2.56489500
C	1.00239900	-0.02054600	-4.92002100
C	0.46822600	0.98764400	-5.77940200
C	0.67938200	0.92004500	-7.18455700
H	0.24755300	1.69087000	-7.82402400
C	1.42460600	-0.15386300	-7.71478300
H	1.58425700	-0.20478700	-8.79809700
C	1.96791700	-1.16521600	-6.89496800
H	2.53572700	-2.00149700	-7.30637300
C	1.75431300	-1.09764500	-5.49217100
C	-1.01040500	3.06145300	-5.78932900
C	-1.64994000	4.02124000	-4.82883600
H	-1.61668000	3.73653600	-3.76941800
C	-2.92679100	4.77269200	-5.27668600
H	-3.73035300	4.85133400	-4.53746000
H	-3.24556000	4.57248600	-6.30496200
C	-1.64384800	5.57635000	-5.09500600
C	-1.50109400	6.46848500	-3.87571200
C	-2.55406500	7.33356700	-3.47832500
H	-3.50609700	7.30354600	-4.02238700
C	-2.38254800	8.23540100	-2.40041000
H	-3.20395700	8.90169600	-2.11028800

C	-1.15159900	8.28468500	-1.70295400
H	-1.01525400	8.98348600	-0.86933200
C	-0.09484500	7.42325400	-2.08970200
H	0.86054800	7.45550200	-1.55279300
C	-0.26950500	6.52560500	-3.16816500
H	0.55423400	5.86603800	-3.47080400
C	-0.93401500	6.13505200	-6.33803400
H	-1.38004900	7.11116900	-6.60754700
H	-1.02965300	5.44565600	-7.19277200
H	0.14150300	6.30013500	-6.13812200
C	2.91824900	-3.28701700	-4.87729500
C	3.23935600	-4.07966200	-3.64058200
H	3.29674500	-3.50367200	-2.70811000
C	4.19871500	-5.28162900	-3.74189000
H	4.56781100	-5.50116800	-4.74960700
H	4.92327600	-5.39923200	-2.92976800
C	2.71818700	-5.55396400	-3.47038300
C	2.28987700	-5.95463900	-2.07040200
C	1.27848000	-5.23355600	-1.38148700
H	0.84315300	-4.33901800	-1.84573900
C	0.83476500	-5.64846400	-0.10352800
H	0.05637800	-5.07728600	0.41701600
C	1.39476200	-6.79970900	0.50294500

H	1.05496200	-7.12160300	1.49434600
C	2.40135100	-7.52827500	-0.17714900
H	2.83849900	-8.42075800	0.28683000
C	2.84343300	-7.10813900	-1.45407700
H	3.62621400	-7.67122400	-1.97798500
C	1.87200200	-6.18685300	-4.58494000
H	1.96888200	-7.28843400	-4.54712900
H	2.19833900	-5.83713300	-5.57934000
H	0.80159300	-5.93777700	-4.45656500
C	-3.54565800	-3.36698800	-0.73411300
C	-3.36419300	-4.58684300	-1.43630900
C	-4.44688400	-5.47883000	-1.64642500
C	-4.28180000	-6.82837900	-2.39507000
C	-5.71952300	-5.10559300	-1.13735300
H	-6.56733600	-5.78442200	-1.29284000
C	-5.94095800	-3.89011700	-0.43650200
C	-4.83041100	-3.02946700	-0.23760700
O	-2.34824200	0.70605500	7.55952900
O	3.63079200	-4.39747000	5.36169800
N	1.44604900	0.21324900	1.59396500
N	1.67720900	0.57435300	-1.16171300
N	-1.45169200	0.05156600	5.48215700
H	-1.51027600	0.21505500	4.47175100

N	2.10737700	-3.02907900	4.19086500
H	1.87561800	-2.69581500	3.24997700
C	0.26911800	-1.05121100	3.42339900
C	1.20992700	-0.11456200	2.94922600
C	2.12162200	0.60582100	3.82545900
H	2.12665900	0.51929400	4.91111600
C	2.92962300	1.37768900	3.01781800
H	3.72626500	2.05921700	3.31000100
C	2.53471200	1.11644100	1.64036300
C	3.20615600	1.64987700	0.52480300
C	2.81064100	1.33480400	-0.78893400
C	3.55876700	1.75787600	-1.96522300
H	4.48293900	2.33207300	-1.93044600
C	2.88508100	1.28043800	-3.06920300
H	3.13999600	1.38424700	-4.12317500
C	1.71447700	0.56935300	-2.57511200
C	0.35062900	-1.48028500	4.86962100
C	-0.48413500	-0.91681700	5.88389200
C	-0.33919000	-1.32269600	7.23993600
H	-0.97625200	-0.86828900	7.99951300
C	0.63186800	-2.29144400	7.56750300
H	0.74218600	-2.59884500	8.61389400
C	1.46197900	-2.87858000	6.59033900

H	2.21411900	-3.62769800	6.84325400
C	1.31763100	-2.47320100	5.23669600
C	-2.32580600	0.79626700	6.28911700
C	-3.23486000	1.71998900	5.53047300
H	-2.98778900	1.89188900	4.47502600
C	-3.82353200	2.93279500	6.29308000
H	-3.85261600	3.88423400	5.75224500
H	-3.55318300	2.98636900	7.35313900
C	-4.77027300	1.81249000	5.87268200
C	-5.70803900	2.07241900	4.70725000
C	-6.60536700	3.17231000	4.75396800
H	-6.56326800	3.86138300	5.60703900
C	-7.54122600	3.38700000	3.71538800
H	-8.22631400	4.24201700	3.76481600
C	-7.59200400	2.50149300	2.61171600
H	-8.31166800	2.66778500	1.80152800
C	-6.70109500	1.40263000	2.55571800
H	-6.72951400	0.72092800	1.69803600
C	-5.77025700	1.18824100	3.59891400
H	-5.08183700	0.33454000	3.55241500
C	-5.37083600	0.89420300	6.94740200
H	-6.28400100	1.36077400	7.36309000
H	-4.65428700	0.71733400	7.76656200

H	-5.66004500	-0.08097200	6.51211500
C	3.18562000	-3.92102900	4.26891300
C	3.78030100	-4.24250500	2.92578900
H	3.11874300	-4.09151200	2.06321000
C	4.77690300	-5.41260800	2.80720700
H	5.01227500	-5.92201100	3.74796700
H	4.67621500	-6.05440900	1.92614900
C	5.30477300	-3.98678600	2.63807200
C	5.65033200	-3.49604000	1.24392000
C	5.06452600	-2.31488000	0.71584500
H	4.30493400	-1.78050400	1.30139100
C	5.43839000	-1.82818400	-0.55942700
H	4.97230600	-0.91768100	-0.95510300
C	6.41250000	-2.51570700	-1.32406200
H	6.70142200	-2.14191100	-2.31333600
C	7.00584500	-3.69258200	-0.80493200
H	7.76095500	-4.22934600	-1.39194000
C	6.62715600	-4.17675900	0.46950600
H	7.08382800	-5.09137800	0.86858000
C	6.19015500	-3.39447300	3.74437600
H	7.24532400	-3.67881300	3.57115000
H	5.88334500	-3.76199100	4.73852400
H	6.13370500	-2.28933100	3.74455200

C	4.39547100	2.54611100	0.73734400
C	5.59948700	2.02951900	1.27860000
C	6.73078000	2.86313400	1.48303900
C	6.61750400	4.23528700	1.13428100
H	7.47814400	4.88994600	1.28982300
C	5.42743900	4.78756500	0.59041500
C	4.32154000	3.91921000	0.39347300
H	3.38106100	4.30492700	-0.01828700
H	5.64828400	0.96214000	1.52547400
C	5.29794400	6.28781300	0.21394100
C	6.60227200	7.08684300	0.48740700
C	4.14743400	6.93217500	1.05218500
C	4.96168500	6.41247200	-1.30672100
C	8.03396700	2.25284300	2.06448200
C	9.15739000	3.31051200	2.24851000
C	8.55900300	1.14479700	1.09580000
C	7.73167700	1.61729500	3.45930400
H	9.44955900	3.77262400	1.28637800
H	10.05611000	2.82224600	2.66971700
H	8.85586000	4.11494700	2.94621800
H	8.79735600	1.57113000	0.10303600
H	7.81578900	0.34019100	0.94971000
H	9.47929600	0.68575500	1.50561000

H	6.87905400	7.06799200	1.55854600
H	6.45330900	8.14457000	0.19987900
H	7.45466200	6.69743500	-0.10103600
H	5.77113900	5.98183100	-1.92584800
H	4.84232500	7.47714600	-1.58568900
H	4.02326400	5.88688700	-1.56261600
H	7.37119800	2.38273000	4.17234100
H	8.64956900	1.16058300	3.87657700
H	6.96318700	0.82577100	3.39096700
H	4.36720800	6.87098100	2.13452300
H	3.17953400	6.42803500	0.87659300
H	4.03031200	7.99958600	0.78237600
H	-4.95413400	-2.07956900	0.29180500
H	-2.36390800	-4.83673400	-1.80360200
C	-2.83231500	-7.04880900	-2.90915000
C	-5.24452700	-6.86273500	-3.62516100
C	-4.64118900	-8.00045800	-1.42604900
H	-5.00471100	-6.05012500	-4.33650400
H	-6.30219800	-6.74921800	-3.32413600
H	-5.14619000	-7.82830600	-4.15745500
H	-2.52628100	-6.26048700	-3.62299700
H	-2.77219100	-8.01881600	-3.43730300
H	-2.09817100	-7.07391400	-2.08223300

H	-3.96396100	-8.00943000	-0.55156100
H	-4.54393700	-8.97109400	-1.94937700
H	-5.67843300	-7.91870100	-1.05194800
C	-7.36415300	-3.54913700	0.08008300
C	-7.41864400	-2.17446400	0.80113700
C	-7.82637100	-4.64941600	1.08859700
C	-8.35728400	-3.50429500	-1.12525600
H	-8.05992700	-2.72429000	-1.85102800
H	-9.37930700	-3.27392600	-0.76765700
H	-8.39619100	-4.47021900	-1.66138500
H	-6.76177900	-2.15049300	1.69133000
H	-8.45097500	-1.97723600	1.14524600
H	-7.12648200	-1.34876400	0.12463700
H	-7.14962900	-4.69276800	1.96262000
H	-7.84266000	-5.65163400	0.62227200
H	-8.84795600	-4.42771000	1.45275700
C	-0.89432500	1.35883300	0.40162200
C	-0.22492800	2.67874500	-0.04221900
C	-1.17498000	3.90548200	-0.04206800
H	0.12120300	2.55283100	-1.08300100
H	0.66897400	2.87511800	0.57837600
C	-1.50210100	4.59452700	1.24446100
C	-1.16848800	4.05442700	2.52144800

C	-2.17912800	5.85252300	1.20786400
C	-2.51043200	6.53833900	2.39526000
C	-2.16784200	5.98859700	3.65706600
C	-1.49242800	4.74519800	3.71176700
H	-1.20859600	4.31943900	4.68174900
H	-0.62429700	3.10514600	2.58494100
H	-2.41512800	6.52535900	4.58055000
H	-3.02858300	7.50353200	2.34085600
H	-2.43158200	6.29314300	0.23444600
H	-2.19323000	3.34755300	-0.51588600
H	-0.91772600	4.63167400	-0.83663400
C	-2.25975100	1.14244500	-0.14440300
C	-2.95191000	2.09983100	-0.81984200
H	-2.75907300	0.19423300	0.11521100
C	-4.22755900	2.21172100	-1.49281900
C	-4.59157800	1.28431600	-2.52707500
C	-5.81967900	1.41625100	-3.20910700
C	-6.71021800	2.47330000	-2.89089600
C	-6.35864300	3.40235800	-1.87704300
C	-5.13312300	3.28124400	-1.19062700
H	-4.86759500	3.99683100	-0.40362800
H	-7.04267900	4.22141200	-1.62452100
H	-6.08163400	0.69814400	-3.99542700

H -7.66034400 2.57524300 -3.42817900

H -3.89759100 0.47573700 -2.78479800

H -0.86044200 1.17164200 1.48858400

Intermediate E

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 1.881005 Hartree

H_corr: 2.197165 Hartree

SCF: -6807.649333 Hartree

S: 665.414 Cal/Mol-Kelvin

H: -6805.452168 Hartree

G: -6805.768328 Hartree

Cartesian Coordinates:

Co 0.25534400 0.24068700 0.00783000

O -0.07072900 -1.67704400 7.78227300

O 2.38288500 5.57520900 4.90986500

N -0.79340100 1.13314300 1.45072000

N -1.13457500 0.78956600 -1.30455500

N 0.30822000 -0.80613300 5.62663400

H 0.22038700 -1.01515200 4.62666900

N 1.79983500 3.50968500 3.93184000

H	1.62450700	3.06181500	3.02674900
C	0.79797000	0.93959900	3.38905200
C	-0.44399400	1.26872100	2.81358300
C	-1.53765600	1.84963300	3.57900300
H	-1.50274800	2.04562700	4.64985700
C	-2.56706900	2.07970800	2.69234300
H	-3.55577600	2.48688200	2.89390400
C	-2.10257100	1.66284800	1.37547700
C	-2.86552300	1.82417700	0.20434000
C	-2.37131500	1.42777700	-1.05469500
C	-3.06871300	1.70704300	-2.30437700
H	-4.02508700	2.22172300	-2.37174500
C	-2.27611000	1.23666000	-3.32856500
H	-2.45069900	1.28142000	-4.40293500
C	-1.08839300	0.66164200	-2.71357200
C	1.06952300	1.36066200	4.81431100
C	0.81847100	0.49272700	5.92069600
C	1.06612100	0.92998500	7.25110300
H	0.86026900	0.25177800	8.08024500
C	1.55881700	2.23518500	7.46129600
H	1.74693200	2.57223000	8.48728500
C	1.81499300	3.11987100	6.39284700
H	2.18706300	4.13272900	6.55640700

C	1.57001000	2.67937600	5.06441500
C	-0.11985300	-1.80142200	6.51573800
C	-0.66051700	-3.03068300	5.84220800
H	-0.85847900	-2.94326500	4.76605400
C	-1.64519100	-3.91994700	6.64039000
H	-2.51855300	-4.29860400	6.09948400
H	-1.82511100	-3.59565900	7.67081200
C	-0.26237900	-4.47854300	6.31937200
C	-0.14838200	-5.53166200	5.23161300
C	-0.97815400	-6.68375600	5.25596900
H	-1.74247800	-6.77706400	6.03759100
C	-0.82616000	-7.70525800	4.28835800
H	-1.47357600	-8.58983300	4.32160200
C	0.15995600	-7.58710600	3.27927200
H	0.28027200	-8.37589800	2.52741200
C	0.99261000	-6.44139700	3.24596300
H	1.75274000	-6.34113000	2.46263700
C	0.84108800	-5.42548500	4.21816600
H	1.49210300	-4.54189700	4.19262400
C	0.75739400	-4.65204500	7.45453600
H	0.59598700	-5.62807500	7.94999600
H	0.65880400	-3.84877500	8.20349500
H	1.79062100	-4.64179900	7.05929900

C	2.16537700	4.86169400	3.87887400
C	2.24828400	5.39107400	2.47401800
H	2.41518000	4.63980900	1.69152700
C	2.89134600	6.76899500	2.22343300
H	3.22687100	7.29849100	3.12177000
H	3.54055000	6.85341300	1.34609200
C	1.38118400	6.62454400	2.02651600
C	0.82558400	6.57607600	0.61485000
C	0.00701800	5.49676700	0.18779500
H	-0.17640400	4.65629400	0.86977700
C	-0.56463700	5.48844800	-1.10660700
H	-1.19022500	4.64465900	-1.42224700
C	-0.32954400	6.56775500	-1.99341000
H	-0.76899200	6.56217600	-2.99780400
C	0.48265600	7.65080200	-1.57622800
H	0.66816600	8.48973600	-2.25793000
C	1.05402500	7.65360300	-0.28166600
H	1.68641200	8.49131300	0.03876000
C	0.44175000	7.29243700	3.04154400
H	0.26764000	8.34603000	2.75179500
H	0.87366700	7.27187900	4.05677800
H	-0.53987100	6.78235000	3.06461900
C	-4.19528200	2.52324900	0.27851800

C	-4.25297800	3.88234500	0.68636600
C	-5.48577800	4.58063900	0.74159100
C	-5.58328400	6.06781100	1.17504800
C	-6.66173000	3.87527900	0.37189600
H	-7.62350600	4.40194700	0.40802200
C	-6.64418300	2.51721400	-0.04363400
C	-5.39162600	1.85189300	-0.08267200
O	-1.87190500	-3.38826400	-6.84237500
O	2.27393800	3.62149400	-6.35960700
N	1.42944800	-0.36922300	-1.48026900
N	1.77751800	-0.00208100	1.27037700
N	-1.41045600	-1.89214300	-5.08253500
H	-1.48912700	-1.76688400	-4.06816200
N	1.17964300	2.23013700	-4.80068800
H	1.04804500	2.08692500	-3.79447000
C	-0.04711100	0.08538500	-3.46500800
C	1.11212500	-0.43451000	-2.85631400
C	2.18594300	-1.06241500	-3.61148400
H	2.16498500	-1.22684800	-4.68782500
C	3.17827100	-1.38144300	-2.70911200
H	4.13540400	-1.86464800	-2.89649400
C	2.72621500	-0.93443000	-1.39859100
C	3.51504500	-1.02668000	-0.23684000

C	3.05549700	-0.55036600	1.00512100
C	3.88858300	-0.52630000	2.20008100
H	4.91848800	-0.87665100	2.23727400
C	3.13393400	0.02998300	3.21016200
H	3.41609800	0.22777000	4.24350100
C	1.83176000	0.34598900	2.64018800
C	-0.08711500	0.15513200	-4.97396700
C	-0.72221200	-0.84842000	-5.76773400
C	-0.67221700	-0.78148600	-7.18776700
H	-1.13881000	-1.57433700	-7.77359100
C	-0.00298900	0.29804900	-7.80069500
H	0.03483600	0.34678100	-8.89515100
C	0.61665800	1.31767800	-7.04824100
H	1.13592600	2.15265200	-7.52166900
C	0.57442200	1.24454800	-5.63021800
C	-1.97081200	-3.06283000	-5.61486500
C	-2.70403200	-3.90025500	-4.60864200
H	-2.58435300	-3.60673800	-3.55814700
C	-2.84285000	-5.41928000	-4.86329400
H	-2.68409000	-6.07286300	-3.99977000
H	-2.41850400	-5.77134000	-5.80939200
C	-4.09857800	-4.55914400	-4.95018300
C	-5.11187800	-4.61246300	-3.82152000

C -5.50080500 -5.84892800 -3.24295600

H -5.01149800 -6.77318100 -3.57389900

C -6.51647200 -5.90031300 -2.25823600

H -6.80710900 -6.86390400 -1.82288600

C -7.16285900 -4.71263700 -1.84074000

H -7.95605700 -4.75340600 -1.08473200

C -6.78042600 -3.47206600 -2.40961300

H -7.28103300 -2.54774700 -2.09696300

C -5.76375800 -3.42503600 -3.39077700

H -5.47368900 -2.46263800 -3.83194200

C -4.73893000 -4.32038000 -6.32642500

H -5.42464100 -5.15655400 -6.56105300

H -3.97141600 -4.24986500 -7.11430400

H -5.33290100 -3.38711100 -6.33063700

C 1.98196900 3.32223100 -5.15764100

C 2.48684000 4.09254600 -3.96913300

H 1.90002000 3.98595900 -3.04785100

C 3.14286400 5.47016600 -4.18709800

H 3.22456000 5.78866700 -5.23200700

H 2.88903900 6.25272700 -3.46490300

C 4.02873500 4.30336500 -3.74570500

C 4.51224500 4.25302500 -2.30784600

C 4.25506600 3.12367000 -1.48595300

H	3.64386700	2.29946500	-1.87622900
C	4.76687500	3.05475700	-0.16819500
H	4.55458700	2.17789400	0.45539200
C	5.55193300	4.11619800	0.34496800
H	5.94724400	4.06589600	1.36625800
C	5.81721200	5.24570200	-0.46781600
H	6.42486800	6.07064000	-0.07646800
C	5.30143700	5.31126400	-1.78370900
H	5.50354400	6.18892700	-2.41078600
C	5.02357600	3.71342800	-4.75633200
H	5.96878500	4.28800300	-4.72905700
H	4.61721500	3.74916700	-5.78156200
H	5.26040600	2.66150200	-4.50769300
C	4.89556000	-1.61905300	-0.32770900
C	5.93091100	-0.93115800	-1.00892000
C	7.23989200	-1.47478700	-1.09753900
C	7.47985500	-2.73453600	-0.48687500
H	8.48116100	-3.16700500	-0.54940700
C	6.46695700	-3.45227600	0.20294900
C	5.17329600	-2.87133900	0.27512100
H	4.36030100	-3.39370500	0.79390400
H	5.70594400	0.04343200	-1.45855000
C	6.72402500	-4.83099400	0.86799500

C	8.19315800	-5.30930500	0.70220900
C	5.78774100	-5.89969800	0.21796300
C	6.41419500	-4.73423800	2.39629700
C	8.34811800	-0.68084600	-1.83944700
C	9.70650100	-1.43500000	-1.86481000
C	8.56353900	0.69124500	-1.12328800
C	7.90544400	-0.42747200	-3.31609000
H	10.09905100	-1.61087400	-0.84522300
H	10.45377100	-0.82761700	-2.40908200
H	9.62680900	-2.41004400	-2.38229200
H	8.89269500	0.54129300	-0.07764400
H	7.63826900	1.29510600	-1.10475900
H	9.34047300	1.27800600	-1.65030100
H	8.46791000	-5.43288300	-0.36253300
H	8.31814400	-6.29163700	1.19521300
H	8.90989500	-4.60736500	1.16923300
H	7.07709200	-3.99662100	2.88676700
H	6.57147100	-5.71705700	2.88083400
H	5.36854600	-4.42847100	2.58375200
H	7.75847400	-1.38324200	-3.85388600
H	8.67983300	0.15512200	-3.85104000
H	6.95994800	0.14256300	-3.36793500
H	5.99927800	-6.00293800	-0.86289600

H	4.72106600	-5.63215600	0.32824800
H	5.94289800	-6.88538200	0.69759500
H	-5.33201100	0.79921300	-0.37513600
H	-3.31951900	4.39207100	0.94456900
C	-4.20449100	6.66115900	1.57567500
C	-6.54082800	6.18947400	2.40362700
C	-6.15408500	6.91257500	-0.00919100
H	-6.15528200	5.60917700	3.26294400
H	-7.55657900	5.81920500	2.17263000
H	-6.62912800	7.24866600	2.71304400
H	-3.75759800	6.11795800	2.43007900
H	-4.33207700	7.71670700	1.88086200
H	-3.48478700	6.64185900	0.73606700
H	-5.48604000	6.85723600	-0.88900600
H	-6.24614300	7.97457600	0.28958100
H	-7.15476100	6.55875900	-0.31917000
C	-7.97558600	1.81706800	-0.42600600
C	-7.75799500	0.35942100	-0.91744200
C	-8.67809000	2.61490000	-1.57072000
C	-8.91083500	1.77639500	0.82517500
H	-8.44226200	1.20128100	1.64538600
H	-9.87405100	1.29487200	0.56729300
H	-9.12916800	2.79210400	1.20331000

H	-7.11202300	0.32540800	-1.81603100
H	-8.73466000	-0.08589300	-1.18694200
H	-7.30211800	-0.27214200	-0.13248300
H	-8.04123300	2.65200700	-2.47461700
H	-8.90216600	3.65507600	-1.27148200
H	-9.63504100	2.12828100	-1.84107500
C	-0.59089800	-1.68289000	0.19169200
C	0.50023000	-2.70167000	0.63731400
C	-0.08106700	-4.08456200	0.47409500
H	0.76002700	-2.51740100	1.69724700
H	1.41563600	-2.57666400	0.04159800
C	0.12487900	-4.96373100	-0.63993900
C	0.97722200	-4.64210700	-1.75991000
C	-0.53151400	-6.25113800	-0.65343100
C	-0.33779500	-7.15784400	-1.70937700
C	0.51012900	-6.81994100	-2.80006400
C	1.15969800	-5.55602900	-2.81341900
H	1.80784200	-5.28761600	-3.65597800
H	1.48913700	-3.67378800	-1.79658000
H	0.65923500	-7.52568600	-3.62528300
H	-0.84265000	-8.13142400	-1.69198500
H	-1.18715700	-6.51427500	0.18665900
H	-3.29118200	-1.82692000	-0.34213800

H	-0.78445300	-4.41712000	1.25067000
C	-1.74758600	-1.61696400	1.10610100
C	-3.06680200	-1.70381700	0.72898300
H	-1.50390600	-1.57105000	2.17991800
C	-4.22435600	-1.75350800	1.64082500
C	-4.16496100	-1.30394200	2.99582600
C	-5.28534200	-1.41660400	3.84471400
C	-6.49808500	-1.97438300	3.36480800
C	-6.57743800	-2.41131200	2.02000000
C	-5.45676100	-2.29663600	1.16766900
H	-5.52018500	-2.65886100	0.13337000
H	-7.50949400	-2.84553200	1.63891700
H	-5.21927200	-1.06078300	4.87977000
H	-7.36688600	-2.06116600	4.02774300
H	-3.24837200	-0.83868500	3.37633500
H	-0.88241400	-1.83449700	-0.86360900

Transition State TS4

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -250.3406 cm-1

G_corr: 1.879911 Hartree

H_corr: 2.196148 Hartree

SCF: -6807.654093 Hartree

S: 665.576 Cal/Mol-Kelvin

H: -6805.457945 Hartree

G: -6805.774182 Hartree

Cartesian Coordinates:

Co	0.28099800	0.23726500	-0.00631100
O	-0.05538100	-1.47877000	7.79728100
O	2.39219900	5.71100800	4.74607900
N	-0.78877700	1.12769700	1.41245100
N	-1.13805500	0.68244600	-1.33195800
N	0.32544400	-0.65007700	5.62499700
H	0.23881000	-0.87807400	4.62892500
N	1.80496900	3.62200600	3.82254800
H	1.63219800	3.14806100	2.93015700
C	0.81592000	1.02948600	3.34771700
C	-0.43693500	1.31064000	2.76832000
C	-1.54036100	1.89382000	3.51920600
H	-1.50945300	2.11751800	4.58476100
C	-2.57306800	2.08509400	2.62749300
H	-3.56895200	2.47865500	2.82009200
C	-2.10217700	1.64155600	1.32086000
C	-2.86088800	1.77817300	0.14250900

C	-2.36899700	1.34042900	-1.10444200
C	-3.06209400	1.58377700	-2.36428800
H	-4.01430500	2.10310700	-2.45145900
C	-2.27170800	1.07350500	-3.37123400
H	-2.44539900	1.08419500	-4.44666200
C	-1.08807800	0.51144300	-2.73612300
C	1.08139400	1.49542600	4.76026600
C	0.83012600	0.65733200	5.88925500
C	1.07132500	1.12944600	7.20852200
H	0.86610400	0.47226400	8.05469900
C	1.55784200	2.44213600	7.38512600
H	1.74130800	2.80762200	8.40219900
C	1.81341400	3.29897200	6.29398400
H	2.18061600	4.31746300	6.43163500
C	1.57506000	2.82217500	4.97664300
C	-0.10186500	-1.62683900	6.53312300
C	-0.64027700	-2.86901600	5.88091300
H	-0.83184200	-2.80086500	4.80201900
C	-1.62900700	-3.74578300	6.68656100
H	-2.50108800	-4.12990100	6.14749300
H	-1.81406600	-3.40636700	7.71113500
C	-0.24476500	-4.30998500	6.38277100
C	-0.11966600	-5.37530600	5.30821000

C	-0.99588800	-6.49226100	5.28707000
H	-1.80259100	-6.55488700	6.02788000
C	-0.83462200	-7.52069500	4.32779400
H	-1.51823800	-8.37821400	4.32672500
C	0.20815100	-7.44555800	3.37330700
H	0.33646600	-8.24059400	2.62938200
C	1.08910000	-6.33566100	3.38671800
H	1.89680500	-6.27060900	2.64834400
C	0.92696600	-5.31244800	4.34917100
H	1.61570100	-4.45758000	4.36072500
C	0.76707200	-4.46406100	7.52770600
H	0.60183900	-5.43126500	8.03892200
H	0.66300300	-3.64755900	8.26145000
H	1.80351800	-4.46012200	7.14093700
C	2.17560100	4.97049300	3.73384700
C	2.26836000	5.46128000	2.31569400
H	2.42775700	4.68737700	1.55403300
C	2.93182800	6.82330700	2.03160400
H	3.27104400	7.37130300	2.91736300
H	3.58578300	6.87538400	1.15524800
C	1.42078300	6.69469300	1.83182100
C	0.87163200	6.61664100	0.41891500
C	0.03801500	5.53918600	0.01710500

H	-0.16289800	4.72159000	0.72155600
C	-0.52615900	5.50360600	-1.28003900
H	-1.16316300	4.66122200	-1.57586600
C	-0.26849000	6.55373600	-2.19516000
H	-0.70199200	6.52682500	-3.20179200
C	0.55844500	7.63506900	-1.80325600
H	0.76138000	8.45157400	-2.50689200
C	1.12249500	7.66492900	-0.50579400
H	1.76656700	8.50101900	-0.20500200
C	0.48614900	7.40243400	2.82394200
H	0.32990900	8.45084000	2.50642100
H	0.91204100	7.40097300	3.84191400
H	-0.50329900	6.90811800	2.85391700
C	-4.17835900	2.50243100	0.19405300
C	-4.21118500	3.86743500	0.58580300
C	-5.42764500	4.59484200	0.61762100
C	-5.49583600	6.08830700	1.03460800
C	-6.61479100	3.91315000	0.23981300
H	-7.56448700	4.46230500	0.25689000
C	-6.62310200	2.55022900	-0.15940100
C	-5.38604800	1.85568400	-0.17465500
O	-2.00329400	-3.58208200	-6.77132100
O	2.32150800	3.33630300	-6.45045500

N	1.43456700	-0.47471800	-1.46907900
N	1.80412400	0.02618600	1.26338900
N	-1.44617900	-2.08787700	-5.03722900
H	-1.50643600	-1.94348200	-4.02401000
N	1.21636400	1.99380800	-4.85681500
H	1.08096000	1.87776500	-3.84754100
C	-0.04679300	-0.09285200	-3.46664600
C	1.11193600	-0.59529000	-2.83979000
C	2.18043700	-1.26038800	-3.57053300
H	2.15477600	-1.47190500	-4.63862100
C	3.17650600	-1.54201500	-2.65902600
H	4.13101800	-2.03647100	-2.82984800
C	2.73339200	-1.03273900	-1.36785900
C	3.53401900	-1.05924000	-0.20946700
C	3.08437900	-0.52233400	1.01206800
C	3.92431800	-0.43838000	2.20022800
H	4.95730700	-0.77846600	2.24740400
C	3.16936800	0.15268400	3.19086800
H	3.45495200	0.39370100	4.21409100
C	1.86032300	0.43090500	2.61605000
C	-0.08134100	-0.06576200	-4.97746800
C	-0.73620100	-1.07536600	-5.74748800
C	-0.68370000	-1.04543700	-7.16878900

H	-1.16853500	-1.84175500	-7.73475800
C	0.00817500	0.00416400	-7.80796400
H	0.04814600	0.02420600	-8.90326900
C	0.64649000	1.03019800	-7.08057200
H	1.18116200	1.84364500	-7.57393600
C	0.60016300	0.99444700	-5.66119100
C	-2.06185000	-3.24040800	-5.54523900
C	-2.80587100	-4.04162300	-4.51702200
H	-2.63869900	-3.75909700	-3.47004800
C	-3.03085100	-5.54903400	-4.77519400
H	-2.88148000	-6.21624400	-3.92062400
H	-2.65461600	-5.91486300	-5.73637200
C	-4.24322700	-4.62551500	-4.81723700
C	-5.21885700	-4.63809200	-3.65461800
C	-5.64420200	-5.85860300	-3.06769600
H	-5.21376000	-6.80296300	-3.42289800
C	-6.62149000	-5.86851500	-2.04366500
H	-6.94062500	-6.82015200	-1.60196900
C	-7.19334800	-4.65436900	-1.59495400
H	-7.95505700	-4.66199000	-0.80630800
C	-6.77589600	-3.43006100	-2.17387900
H	-7.22205200	-2.48549300	-1.84015600
C	-5.79727300	-3.42428000	-3.19393600

H	-5.47968400	-2.47380200	-3.64186500
C	-4.91376300	-4.34312600	-6.17039000
H	-5.64872000	-5.14093200	-6.38894100
H	-4.16897100	-4.30609200	-6.98213500
H	-5.45860000	-3.38054900	-6.14946800
C	2.02324300	3.07264000	-5.24147800
C	2.52172600	3.87922900	-4.07453300
H	1.93590900	3.79242700	-3.15058500
C	3.16123900	5.25822900	-4.33284300
H	3.23889900	5.54628300	-5.38686500
H	2.89775700	6.05854300	-3.63391800
C	4.06051600	4.11549700	-3.85728800
C	4.54330800	4.11610000	-2.41821200
C	4.29046200	3.01536500	-1.55720100
H	3.68342800	2.17502500	-1.91855300
C	4.80051000	2.99573300	-0.23701700
H	4.59155700	2.14040800	0.41676100
C	5.57956700	4.07848500	0.23917600
H	5.97332700	4.06633200	1.26223700
C	5.84079700	5.17972500	-0.61282300
H	6.44389500	6.02100900	-0.25020100
C	5.32667200	5.19610700	-1.93082500
H	5.52499000	6.05227100	-2.58813200

C	5.06343100	3.50789600	-4.84919600
H	6.00112600	4.09524200	-4.83953400
H	4.65677400	3.50676000	-5.87491500
H	5.31374400	2.46726900	-4.56821200
C	4.91813500	-1.64617100	-0.28444600
C	5.93822800	-0.99283800	-1.02068200
C	7.25022400	-1.53086800	-1.09732600
C	7.51029300	-2.74992100	-0.41640500
H	8.51418200	-3.17773700	-0.46869400
C	6.51386600	-3.43223800	0.33087100
C	5.21660500	-2.85778600	0.38789200
H	4.41639300	-3.35423200	0.95034200
H	5.69833900	-0.04827000	-1.52336800
C	6.79280100	-4.76605100	1.07430000
C	8.26157100	-5.24582500	0.90975500
C	5.85172300	-5.87832700	0.50995100
C	6.51147100	-4.57676600	2.59946900
C	8.33994300	-0.77478800	-1.90339800
C	9.70464200	-1.51788500	-1.90384500
C	8.55371200	0.64044400	-1.27637500
C	7.87258700	-0.61627700	-3.38572500
H	10.11384400	-1.62788200	-0.88156700
H	10.43811100	-0.93864400	-2.49551400

H	9.62634500	-2.52334800	-2.35971600
H	8.90161500	0.55796700	-0.22931500
H	7.62309400	1.23622800	-1.27848700
H	9.31603700	1.20051400	-1.85159400
H	8.51700900	-5.43213000	-0.15063900
H	8.40250600	-6.19563100	1.45906800
H	8.98220200	-4.51278600	1.31936800
H	7.17974100	-3.80768000	3.03062400
H	6.68293000	-5.52711600	3.14075200
H	5.46811500	-4.26338500	2.78755200
H	7.72684600	-1.60444700	-3.86179800
H	8.63302200	-0.06065600	-3.96738300
H	6.92073400	-0.05909000	-3.45746500
H	6.04253200	-6.04630300	-0.56663400
H	4.78562900	-5.60995500	0.62521900
H	6.02301900	-6.83184500	1.04588500
H	-5.34761200	0.79866700	-0.45464600
H	-3.26960800	4.35825600	0.85076700
C	-4.10885000	6.65331400	1.44776300
C	-6.46611000	6.24480700	2.24920800
C	-6.03123800	6.93399300	-0.16536500
H	-6.10566600	5.66390300	3.11893400
H	-7.48732600	5.89646600	2.00829800

H	-6.53306200	7.30880300	2.54736000
H	-3.68609300	6.10786800	2.31296800
H	-4.21571700	7.71443600	1.74140800
H	-3.37906300	6.60937800	0.61781700
H	-5.35335300	6.85402500	-1.03568900
H	-6.10216100	8.00088900	0.12154400
H	-7.03588700	6.60045300	-0.48488800
C	-7.96587700	1.87781500	-0.55176600
C	-7.77869500	0.40497800	-1.00878700
C	-8.62567400	2.66977700	-1.72557100
C	-8.92467400	1.88720900	0.68203000
H	-8.48429700	1.32077600	1.52370700
H	-9.89436700	1.42280000	0.41691100
H	-9.12579000	2.91592100	1.03339500
H	-7.11921900	0.33420600	-1.89521500
H	-8.76156400	-0.02195000	-1.28491600
H	-7.35128100	-0.21723500	-0.20052600
H	-7.97221700	2.66999700	-2.61828900
H	-8.82468500	3.72194700	-1.45172600
H	-9.59126800	2.20469900	-2.00314900
C	-0.70875600	-2.03663400	0.38452300
C	0.54681800	-2.79898400	0.82971100
C	-0.10359900	-4.12447100	0.59931700

H	0.79515400	-2.60395100	1.88529900
H	1.42547800	-2.60564000	0.20449200
C	0.01328300	-4.94427200	-0.58481000
C	0.85217100	-4.60294200	-1.70158100
C	-0.70657300	-6.18875400	-0.64118100
C	-0.57587500	-7.05457000	-1.74296100
C	0.26162700	-6.70176200	-2.83395700
C	0.96781300	-5.47018700	-2.80421300
H	1.60861900	-5.18956900	-3.64797400
H	1.41079700	-3.66013600	-1.70199100
H	0.35890800	-7.37139300	-3.69610900
H	-1.12373800	-8.00435000	-1.75855100
H	-1.35675200	-6.46143500	0.19999300
H	-3.41383100	-1.89232900	-0.08403500
H	-0.77412400	-4.48320400	1.39103300
C	-1.80707400	-1.84963500	1.31569000
C	-3.14408000	-1.77088600	0.97652900
H	-1.53026400	-1.81487500	2.38223500
C	-4.26494300	-1.63796500	1.91615700
C	-4.10330200	-1.20396200	3.26930200
C	-5.20456500	-1.14672800	4.14738900
C	-6.50090300	-1.51223000	3.70168900
C	-6.68159300	-1.92989600	2.36007200

C -5.58009300 -1.98645100   1.47887700

H -5.72207300 -2.33663300   0.44808500

H -7.67924900 -2.21617900   2.00578800

H -5.05735900 -0.80603400   5.17916200

H -7.35480900 -1.46566400   4.38751400

H -3.11837800 -0.87960900   3.62394400

H -0.95049800 -2.07994100 -0.68672300

Intermediate F

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

$F_{[3a]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.226804 Hartree

H_corr: 0.286779 Hartree

SCF: -657.7227662 Hartree

S: 126.228 Cal/Mol-Kelvin

H: -657.4359872 Hartree

G: -657.4959622 Hartree

Cartesian Coordinates:

C   0.64371500 -0.79216200 -0.67690300

C	1.09517600	-1.87293700	0.30525100
C	1.60293200	-0.43516500	0.52980000
H	1.81783100	-2.61647800	-0.04679700
H	0.37340300	-2.26585600	1.02790200
C	3.02429500	-0.03133500	0.29421300
H	-1.68399000	-1.63139000	0.57473600
C	3.57684000	1.04807800	1.03956400
C	3.85516400	-0.68059800	-0.66308500
C	5.19009300	-0.26362400	-0.86635600
C	5.72725600	0.81146100	-0.11645700
C	4.91268600	1.46520700	0.83914900
H	5.31726500	2.29790200	1.42705400
H	2.95253200	1.56192500	1.78221100
H	6.76338900	1.13290600	-0.27377900
H	5.81357700	-0.77765500	-1.60791400
H	3.46268300	-1.51952600	-1.25257400
C	-0.74038800	-0.24246700	-0.72147400
C	-1.82044400	-0.72459700	-0.03418800
H	-0.86067000	0.63991100	-1.36888100
C	-3.19037500	-0.16823700	-0.02692200
C	-3.54800100	1.04908200	-0.68205900
C	-4.87474500	1.52718900	-0.64875800
C	-5.88253800	0.80776400	0.04317200

C -4.21529300 -0.87610600 0.66832800

C -5.54416300 -0.39758700 0.70360900

H -6.31317500 -0.96222800 1.24412100

H -3.96156200 -1.81352900 1.18110700

H -5.12716600 2.46494100 -1.15844200

H -6.91191100 1.18381000 0.06841300

H -2.78424900 1.62865700 -1.21398600

H 1.10130300 0.11062400 1.33788300

H 1.16747200 -0.77780800 -1.64235800

Transition State TS3’

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -455.6663 cm-1

G_corr: 1.871219 Hartree

H_corr: 2.195141 Hartree

SCF: -6807.608223 Hartree

S: 681.751 Cal/Mol-Kelvin

H: -6805.413082 Hartree

G: -6805.733205 Hartree

Cartesian Coordinates:

Co 0.40836600 0.40478300 -0.04399700

O	-0.40899200	-1.60446700	7.64470500
O	4.23492500	4.57501900	4.97050100
N	-0.32862000	1.50169000	1.43613300
N	-0.69185400	1.43824800	-1.33083500
N	0.09908500	-0.72236300	5.51916600
H	-0.13608600	-0.79425300	4.52336600
N	2.99926900	2.85620600	3.93128200
H	2.68066000	2.52509500	3.01498200
C	1.17127300	0.79901300	3.32632400
C	0.07941200	1.50963000	2.78670800
C	-0.79694300	2.35266400	3.58780700
H	-0.68075800	2.51801100	4.65821300
C	-1.76231200	2.85105300	2.73720500
H	-2.59403400	3.51319300	2.97166600
C	-1.45398800	2.35571400	1.40058500
C	-2.14073600	2.76500100	0.24001400
C	-1.71224000	2.37320900	-1.04457400
C	-2.21425200	2.97550200	-2.27376500
H	-2.99239600	3.73602400	-2.31133000
C	-1.49385700	2.43228900	-3.31747500
H	-1.57011600	2.64634700	-4.38284300
C	-0.57515500	1.46101100	-2.73872100
C	1.57875800	1.05998700	4.75694500

C	1.04655700	0.29378300	5.84022700
C	1.44863500	0.56214000	7.17782300
H	1.03131100	-0.03803300	7.98752000
C	2.36839600	1.60407400	7.42017200
H	2.67408500	1.81224700	8.45213100
C	2.90231500	2.38898100	6.37699100
H	3.60270900	3.20415700	6.56618100
C	2.50669500	2.11277300	5.04030100
C	-0.58458100	-1.58922900	6.38318900
C	-1.55908100	-2.49740900	5.68835400
H	-1.78857600	-2.25075100	4.64414200
C	-2.73709800	-3.06893500	6.51366400
H	-3.71822600	-3.07492100	6.02783100
H	-2.73036200	-2.79904100	7.57495800
C	-1.65462800	-4.03151200	6.03567800
C	-1.97403100	-4.95968800	4.87757400
C	-3.16520600	-5.73211500	4.87640400
H	-3.88341400	-5.60874800	5.69647400
C	-3.42971100	-6.65471600	3.83577300
H	-4.35271300	-7.24691300	3.85154300
C	-2.50258300	-6.81916300	2.77848900
H	-2.70472200	-7.53050100	1.96934500
C	-1.30937700	-6.05473100	2.77230000

H	-0.58624900	-6.18276100	1.95779700
C	-1.04784700	-5.13606400	3.81501100
H	-0.12115900	-4.54714900	3.80892100
C	-0.69057800	-4.64165700	7.06385900
H	-1.15169100	-5.54066700	7.51509500
H	-0.45455800	-3.91995200	7.86350000
H	0.25450300	-4.95435000	6.58097800
C	3.79522000	4.00933500	3.91883000
C	4.04906300	4.53125800	2.53135500
H	4.00740300	3.78429400	1.72873900
C	5.05898700	5.67592800	2.33195200
H	5.51791800	6.05945500	3.24970400
H	5.71953100	5.59997200	1.46240700
C	3.57284300	5.97346700	2.12103200
C	3.04809800	6.13158800	0.70573800
C	1.94068200	5.36898900	0.24736300
H	1.49574000	4.61248500	0.90683100
C	1.41099500	5.56743300	-1.04964500
H	0.55662500	4.96884800	-1.38828300
C	1.98193600	6.53811400	-1.90908000
H	1.57663800	6.69000000	-2.91625400
C	3.08527000	7.30515400	-1.46144900
H	3.53256800	8.05698800	-2.12284800

C	3.61163600	7.10343000	-0.16334000
H	4.46697700	7.69803600	0.18193800
C	2.84495800	6.84401100	3.15598200
H	2.97568700	7.91340200	2.90389600
H	3.24135400	6.67025600	4.17120700
H	1.75972500	6.62819800	3.15867900
C	-3.29368200	3.72454100	0.35914800
C	-3.07231900	5.06545800	0.76681100
C	-4.14690300	5.98544800	0.87115800
C	-3.94048000	7.46355800	1.29764000
C	-5.45249100	5.51622400	0.56389000
H	-6.29376100	6.21605900	0.64504300
C	-5.71259800	4.18193000	0.15233300
C	-4.60922700	3.29542500	0.04881100
O	-2.83179500	-1.09945100	-7.32289100
O	3.94949100	3.23833700	-5.91654200
N	1.24542600	-0.58407600	-1.53979600
N	1.66220400	-0.47152000	1.21124000
N	-1.58815100	-0.57251000	-5.39264300
H	-1.52909800	-0.73625500	-4.38215400
N	2.30703100	2.23795200	-4.55154500
H	2.07430100	2.04212000	-3.57277600
C	0.25489700	0.62448400	-3.51172600

C	1.04064600	-0.38857300	-2.92268100
C	1.74736500	-1.39778000	-3.69852200
H	1.73484000	-1.45630000	-4.78619800
C	2.37561200	-2.23138900	-2.79698600
H	2.97946600	-3.11352600	-3.00111700
C	2.10580800	-1.70453700	-1.46404400
C	2.71697600	-2.19157300	-0.29145900
C	2.54630500	-1.54105800	0.94874200
C	3.34052100	-1.84997600	2.13212200
H	4.10560800	-2.62334100	2.17457500
C	2.95440800	-0.97115800	3.12362800
H	3.32794100	-0.88766700	4.14351400
C	1.89784000	-0.13874200	2.56508900
C	0.35164900	0.85471200	-5.00139500
C	-0.57578700	0.27947800	-5.92437900
C	-0.45847700	0.53672300	-7.31844700
H	-1.18601700	0.09677700	-8.00161900
C	0.59662700	1.35164100	-7.77873800
H	0.68805100	1.54401300	-8.85406900
C	1.53831800	1.92345200	-6.89850100
H	2.36181900	2.54418800	-7.25528500
C	1.41085400	1.67779900	-5.50494300
C	-2.61760300	-1.23545900	-6.07449300

C -3.44302600 -2.14404700 -5.20827300

H -3.02064000 -2.39329000 -4.22642000

C -4.22319500 -3.28132000 -5.90941900

H -4.20022000 -4.26012900 -5.42037000

H -4.14404800 -3.28605600 -7.00158700

C -5.01533800 -2.14188700 -5.27382300

C -5.74036900 -2.41771400 -3.96928300

C -6.65258800 -3.50215800 -3.87546700

H -6.78527400 -4.16436900 -4.74028400

C -7.38260800 -3.73426400 -2.68558300

H -8.08312900 -4.57621800 -2.62905300

C -7.20983000 -2.88066000 -1.56874400

H -7.77000300 -3.05910300 -0.64350400

C -6.30591800 -1.79315000 -1.65325400

H -6.16795200 -1.13066800 -0.79064200

C -5.58099600 -1.56329000 -2.84637300

H -4.88294400 -0.71868500 -2.90950400

C -5.73765900 -1.13506100 -6.18120000

H -6.73532200 -1.52883800 -6.45324300

H -5.16264000 -0.95064400 -7.10408200

H -5.88599900 -0.17126400 -5.65844200

C 3.48877900 2.96024700 -4.76322200

C 4.17492000 3.35337100 -3.48430500

H	3.52724300	3.43377500	-2.60199600
C	5.35728400	4.33904000	-3.54292400
H	5.63786400	4.66999800	-4.54867300
H	5.39813000	5.10206400	-2.75926500
C	5.64498400	2.88013400	-3.18493600
C	5.95487600	2.52928400	-1.74129500
C	5.24301200	1.49847600	-1.07132400
H	4.41798800	0.98864600	-1.58599800
C	5.57656800	1.13134400	0.25392100
H	5.01442600	0.33696500	0.75937600
C	6.63586500	1.78809600	0.92734300
H	6.89321200	1.50767200	1.95540200
C	7.35415200	2.81502000	0.26736900
H	8.17398100	3.32809900	0.78447300
C	7.01521400	3.18074000	-1.05694900
H	7.57116900	3.97734500	-1.56751000
C	6.37267100	1.99888800	-4.21097200
H	7.46682300	2.11816100	-4.09743500
H	6.09294400	2.27499300	-5.24215500
H	6.13164400	0.93037900	-4.05422200
C	3.65003800	-3.36930400	-0.36601700
C	4.87433600	-3.28153100	-1.07608400
C	5.77116200	-4.38061600	-1.13908800

C	5.40457600	-5.57692100	-0.46683900
H	6.08359000	-6.43175200	-0.50501000
C	4.18938100	-5.70183200	0.25705800
C	3.32198800	-4.57830200	0.29810500
H	2.37337700	-4.63136800	0.84673100
H	5.12818700	-2.33289500	-1.56414800
C	3.78746400	-7.00590700	0.99695800
C	4.85056700	-8.12981200	0.84910000
C	2.43844000	-7.53669600	0.41534600
C	3.61031000	-6.70169700	2.51926000
C	7.10694700	-4.23329400	-1.91569400
C	7.94679500	-5.54067300	-1.91244500
C	7.95996100	-3.10170900	-1.25718900
C	6.80553200	-3.85408300	-3.40104300
H	8.24700000	-5.83442600	-0.88860400
H	8.87191700	-5.38457100	-2.49841300
H	7.39827300	-6.38464800	-2.37254500
H	8.19416700	-3.34682100	-0.20414000
H	7.43185800	-2.13109800	-1.26983000
H	8.91400000	-2.97604900	-1.80443100
H	5.00544000	-8.41277100	-0.20935500
H	4.50966900	-9.03245000	1.38997300
H	5.82614800	-7.83193300	1.27783400

H	4.55814100	-6.34058800	2.96092500
H	3.30260000	-7.61744500	3.05941700
H	2.83884700	-5.92977200	2.69573800
H	6.22570100	-4.65250100	-3.90178300
H	7.75179400	-3.71298500	-3.95766500
H	6.22763900	-2.91508100	-3.47664000
H	2.54876600	-7.80129200	-0.65315200
H	1.63336500	-6.78288500	0.49516500
H	2.11310100	-8.44047400	0.96537100
H	-4.76052000	2.25647500	-0.26101200
H	-2.04833300	5.38404800	0.98454700
C	-2.44968400	7.79775300	1.57934600
C	-4.75973600	7.74524700	2.59832400
C	-4.44537700	8.40608200	0.15793500
H	-4.43907900	7.07681200	3.41947700
H	-5.84358600	7.59435700	2.44029100
H	-4.60671700	8.79183500	2.92483500
H	-2.04154500	7.19046900	2.40949000
H	-2.35846700	8.86151900	1.86817700
H	-1.81501100	7.63879600	0.68744800
H	-3.85596800	8.25714400	-0.76614000
H	-4.34439700	9.46454800	0.46617700
H	-5.50854800	8.22369200	-0.08466000

C	-7.16580600	3.74391500	-0.17093300
C	-7.25808600	2.24619100	-0.57345900
C	-7.71300900	4.60199400	-1.35697800
C	-8.06905200	3.96665100	1.08402900
H	-7.71091200	3.36235100	1.93868900
H	-9.11174000	3.66881300	0.86102800
H	-8.08030900	5.02619000	1.39909100
H	-6.66142700	2.02535200	-1.47851800
H	-8.30935200	1.98727600	-0.79889600
H	-6.91598600	1.58158500	0.24291400
H	-7.10156500	4.45204100	-2.26655200
H	-7.70703800	5.68144000	-1.11831700
H	-8.75556600	4.31082100	-1.58863700
C	-1.45773300	-1.27609200	0.28392900
C	-1.45766100	-2.36122800	-0.79120400
C	-2.34422500	-3.60790400	-0.46450200
H	-0.41782200	-2.71110600	-0.94963500
H	-1.79631300	-1.92108400	-1.74854000
C	-2.26348900	-4.70367700	-1.52304500
C	-1.02889500	-5.34861400	-1.81422100
C	-3.42515700	-5.12649600	-2.22287700
C	-3.35827300	-6.16921700	-3.17951300
C	-2.12451100	-6.80341500	-3.45839700

C	-0.95753200	-6.38572500	-2.77206500
H	0.00414900	-6.86929700	-2.98166600
H	-0.11623400	-5.03989800	-1.28714200
H	-2.07129100	-7.61034200	-4.19879800
H	-4.27023200	-6.48921500	-3.69853000
H	-4.38766500	-4.64189500	-2.01440100
H	-3.39366400	-3.27861100	-0.34515000
H	-2.01789500	-4.01589300	0.51322900
C	-1.19444300	-1.61639000	1.72624000
C	-2.47626700	-1.60880100	2.01552800
H	-0.26159800	-1.88001500	2.23392100
C	-3.82205000	-1.57921400	2.47353800
C	-4.38964900	-0.34741300	2.95124400
C	-5.71384700	-0.31424100	3.43070500
C	-6.50948600	-1.48932200	3.43257200
C	-5.96063800	-2.70896800	2.95765200
C	-4.63403000	-2.76389800	2.48711700
H	-4.20552300	-3.71125800	2.14383100
H	-6.56620700	-3.62257200	2.96770200
H	-6.12896100	0.62867600	3.80467300
H	-7.54037300	-1.45580000	3.80317500
H	-3.77458200	0.55967900	2.94522200
H	-1.91639100	-0.30822600	0.05266900

Intermediate E’

E’$_{[Co(II)(P6)]}$=A$_{[Co(II)(P6)]}$

E’$_{[3a’]}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.22482 Hartree

H_corr: 0.28596 Hartree

SCF: -657.6823301 Hartree

S: 128.68 Cal/Mol-Kelvin

H: -657.3963701 Hartree

G: -657.4575101 Hartree

Cartesian Coordinates:

H	3.84644500	-2.54736300	1.59341300
H	5.46990200	-2.50660100	-0.32615800
C	3.80235800	-1.73766300	0.85569300
C	4.71785800	-1.71535200	-0.22533900
H	2.12275700	-0.72752000	1.82031000
C	2.83303600	-0.71851600	0.98490200
C	4.65833900	-0.66510900	-1.17767100
H	5.36604000	-0.64656100	-2.01486300

C	2.76486700	0.34135600	0.03434100
C	3.69183400	0.35430600	-1.05132000
C	1.76882800	1.38836900	0.18060200
H	3.64331400	1.16694100	-1.78601500
C	1.21929600	2.53725600	-0.23095400
H	1.20353300	3.36918300	-0.93041100
H	0.82655500	2.37095600	2.00502000
C	0.58477700	1.90547500	1.03257200
H	-1.16454800	1.38805600	-1.11956300
H	-0.45405100	-0.15616000	-0.60652000
C	-0.80990000	1.24989800	1.02438200
C	-1.20929700	0.60706200	-0.33441000
H	-1.56492000	2.01661300	1.29712700
H	-0.85562900	0.47664800	1.81969000
H	-1.88353500	-2.02552900	0.17124500
C	-2.59863500	-0.01823700	-0.28742000
C	-2.76968900	-1.39729700	0.00999900
C	-3.76034200	0.77223800	-0.50405700
H	-3.64797700	1.83807400	-0.74413900
C	-4.06123400	-1.97052000	0.09337500
H	-4.17175400	-3.03794600	0.32041600
C	-5.05378500	0.20467400	-0.42286200
C	-5.20958300	-1.17062800	-0.12193000

H -5.93749000 0.83051100 -0.59777200

H -6.21101400 -1.61317300 -0.06120000

Transition State TS4'

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -486.0045 cm-1

G_corr: 1.881175 Hartree

H_corr: 2.195321 Hartree

SCF: -6807.607376 Hartree

S: 661.176 Cal/Mol-Kelvin

H: -6805.412055 Hartree

G: -6805.726201 Hartree

Cartesian Coordinates:

Co 0.45519500 -0.27350100 0.02009700

O -0.66894900 2.32871700 -7.44862600

O 4.88503800 -3.25822100 -5.31847100

N -0.01850400 -1.31621100 -1.59649300

N -0.43958000 -1.64156600 1.13423600

N 0.11859700 1.51359400 -5.38342600

H -0.04716100 1.53991700 -4.37199900

N	3.43866100	-1.82527100	-4.12809300
H	3.07988900	-1.63447100	-3.18717300
C	1.33306300	-0.12672800	-3.35225400
C	0.38274100	-1.07610700	-2.92995400
C	-0.31316100	-1.96180800	-3.85141900
H	-0.16910400	-1.96067900	-4.93097800
C	-1.15566600	-2.74733700	-3.09368400
H	-1.84711000	-3.51789100	-3.42893000
C	-0.95342500	-2.37406900	-1.70069800
C	-1.57050200	-3.03694600	-0.62523000
C	-1.26574600	-2.70546500	0.70854900
C	-1.71004000	-3.49981700	1.84615000
H	-2.33681200	-4.38627400	1.76673200
C	-1.16137900	-2.93378100	2.97749900
H	-1.25129100	-3.25498600	4.01455500
C	-0.40210900	-1.76997600	2.54236400
C	1.79361100	-0.15577900	-4.78997600
C	1.17343300	0.64751500	-5.79611000
C	1.60426100	0.56622100	-7.14895000
H	1.10668500	1.17805000	-7.90248300
C	2.65141300	-0.31857600	-7.48193200
H	2.98053600	-0.38191500	-8.52561100
C	3.28627000	-1.12504400	-6.51433700

H	4.08895600	-1.81713000	-6.77433800
C	2.85466600	-1.04240400	-5.16312900
C	-0.73856800	2.28891900	-6.17767000
C	-1.75969100	3.06351000	-5.39522500
H	-1.84899500	2.80647100	-4.33177700
C	-3.07775100	3.46046100	-6.10514000
H	-4.00033300	3.34571600	-5.52678000
H	-3.13544900	3.17863100	-7.16185900
C	-2.09421900	4.56575600	-5.73481800
C	-2.42588200	5.45965500	-4.55354000
C	-3.69719900	6.08402200	-4.45648400
H	-4.46148600	5.86408900	-5.21220700
C	-3.98334800	6.98136600	-3.40016900
H	-4.97010000	7.45598700	-3.33906300
C	-2.99896000	7.26689700	-2.42366600
H	-3.21941000	7.95676700	-1.60079200
C	-1.72727600	6.64928600	-2.51213400
H	-0.96333200	6.86249600	-1.75528200
C	-1.44354900	5.75635700	-3.57117100
H	-0.45530400	5.28317100	-3.63949900
C	-1.32203100	5.28582800	-6.85024600
H	-1.93731400	6.11520100	-7.24749200
H	-1.07480200	4.59488300	-7.67306500

H	-0.38256800	5.72067100	-6.46010800
C	4.37114200	-2.86789000	-4.22194100
C	4.67815200	-3.49981500	-2.89291800
H	4.50808600	-2.86498300	-2.01399900
C	5.84888300	-4.49466500	-2.78284200
H	6.37765600	-4.70013600	-3.71991500
H	6.47393900	-4.41779500	-1.88752800
C	4.42282600	-5.03427500	-2.65798000
C	3.90036500	-5.42399000	-1.28746700
C	2.68256200	-4.88680900	-0.79120600
H	2.14395700	-4.13494500	-1.38270000
C	2.16194300	-5.30341700	0.45684400
H	1.22200400	-4.87639500	0.82727300
C	2.85255300	-6.27168500	1.22649500
H	2.45354900	-6.59296700	2.19568300
C	4.06616700	-6.81590900	0.73946600
H	4.60547800	-7.56549300	1.33113000
C	4.58390100	-6.39507400	-0.50858100
H	5.52531300	-6.81588200	-0.88410300
C	3.85763900	-5.88654800	-3.80393400
H	4.14767900	-6.94462700	-3.66045000
H	4.24086700	-5.54476400	-4.78069700
H	2.75229300	-5.83921400	-3.82202300

C	-2.51362800	-4.17628900	-0.89628100
C	-2.03026400	-5.39093800	-1.44810400
C	-2.90480000	-6.47948800	-1.69785200
C	-2.41047500	-7.82826300	-2.28570300
C	-4.27982500	-6.30826100	-1.38463300
H	-4.96949900	-7.13980400	-1.57607800
C	-4.79948300	-5.10640100	-0.83384600
C	-3.89170900	-4.04374000	-0.58879300
O	-2.94812300	0.45534900	7.31866700
O	4.13694300	-3.25362900	5.76425200
N	1.14054700	0.62704200	1.65177700
N	1.62733800	0.89804300	-1.07400500
N	-1.84101700	-0.14401000	5.32836400
H	-1.87464100	-0.05395100	4.30761700
N	2.42518600	-2.33652600	4.42491100
H	2.19621400	-2.09473700	3.45577800
C	0.23196800	-0.89053100	3.44030400
C	0.89252900	0.27276700	2.99774000
C	1.43681500	1.26961000	3.90731200
H	1.36706500	1.21330200	4.99277600
C	2.01561700	2.25021500	3.12953600
H	2.51311200	3.16344200	3.45056600
C	1.86740900	1.83900600	1.74015100

C	2.46099900	2.51965500	0.66154400
C	2.38108400	2.01803400	-0.65131600
C	3.13795900	2.58040500	-1.76157100
H	3.80944700	3.43295900	-1.67638500
C	2.85484900	1.81763300	-2.87477900
H	3.24053800	1.91919200	-3.88850100
C	1.90516200	0.79622800	-2.45699700
C	0.30032600	-1.24249700	4.90768700
C	-0.71122200	-0.85089100	5.83799200
C	-0.57791900	-1.16640100	7.21886300
H	-1.35320000	-0.84231900	7.91388100
C	0.56185800	-1.87280100	7.65545500
H	0.66192400	-2.11191600	8.72053300
C	1.57597800	-2.27980500	6.76419500
H	2.46194100	-2.81973800	7.10235600
C	1.44358800	-1.96332800	5.38570900
C	-2.88585900	0.45752400	6.04642700
C	-3.92910000	1.11467800	5.18933500
H	-3.67720000	1.24557500	4.12912800
C	-4.77586900	2.24570300	5.82409300
H	-4.96857400	3.12209000	5.19678300
H	-4.56452400	2.44404900	6.88030300
C	-5.46375700	0.92549400	5.48909500

C	-6.39197500	0.88398700	4.28883300
C	-7.49389200	1.77713000	4.21628200
H	-7.61708200	2.53917600	4.99619800
C	-8.42529700	1.69229900	3.15504900
H	-9.27196000	2.38816500	3.11368600
C	-8.26552200	0.71041800	2.14741200
H	-8.98528300	0.64091100	1.32321400
C	-7.16723900	-0.18151100	2.20796500
H	-7.03332000	-0.93572300	1.42448900
C	-6.24132900	-0.09721800	3.27403400
H	-5.39495500	-0.79448100	3.32100600
C	-5.91209800	0.00213500	6.63220700
H	-6.91547900	0.30997800	6.98262500
H	-5.20727200	0.04529700	7.47882600
H	-5.98423800	-1.04552600	6.28402500
C	3.68200800	-2.92577200	4.62198300
C	4.45163500	-3.10755200	3.34375400
H	3.84929800	-3.14948400	2.42739400
C	5.72256300	-3.97909800	3.34717700
H	6.00164400	-4.39378300	4.32187100
H	5.86352900	-4.64087600	2.48672500
C	5.87778500	-2.46828000	3.16590000
C	6.19895700	-1.92332500	1.78635100

C	5.38700300	-0.92223900	1.18955600
H	4.48152400	-0.58204100	1.70887600
C	5.72631400	-0.36759100	-0.06733800
H	5.08724500	0.40248900	-0.51616500
C	6.89122500	-0.80472900	-0.74455200
H	7.15484600	-0.37899000	-1.71974900
C	7.70965200	-1.80020900	-0.15678900
H	8.61256400	-2.14254200	-0.67673500
C	7.36538100	-2.35316400	1.09948200
H	7.99870400	-3.12622700	1.55293500
C	6.48384500	-1.64879000	4.31482300
H	7.58740200	-1.65315200	4.23476900
H	6.19871900	-2.06713900	5.29526900
H	6.14627800	-0.59604500	4.26904200
C	3.25804800	3.76929700	0.91804000
C	4.48925300	3.70817800	1.61813800
C	5.25848800	4.87769900	1.85619500
C	4.75285100	6.11519900	1.37611900
H	5.33202700	7.02424000	1.55424400
C	3.52352500	6.21449100	0.67200700
C	2.78822600	5.02071500	0.44713200
H	1.83166100	5.05172600	-0.08854600
H	4.84883600	2.73085100	1.96202300

C	2.96478500	7.56566400	0.15116600
C	3.90133800	8.76315700	0.47279900
C	1.57782000	7.84005600	0.81614900
C	2.78872400	7.48990400	-1.39932600
C	6.60725100	4.76360200	2.61570300
C	7.30591800	6.13921800	2.80041000
C	7.57176900	3.82959000	1.81621900
C	6.35417100	4.15281000	4.03135800
H	7.54811800	6.61158700	1.82945300
H	8.25623700	5.99794300	3.34851400
H	6.68357800	6.84218900	3.38628900
H	7.78217000	4.24673600	0.81335600
H	7.14688600	2.81853600	1.68048400
H	8.53266100	3.72327100	2.35557400
H	4.03981600	8.89590700	1.56254900
H	3.45602900	9.69525000	0.07718200
H	4.89726800	8.64403400	0.00542100
H	3.76085600	7.31709600	-1.89841400
H	2.36650900	8.43843200	-1.78311000
H	2.10642500	6.67150300	-1.69452100
H	5.68547200	4.80212300	4.62756000
H	7.31126100	4.04753700	4.57738000
H	5.89040200	3.15145800	3.96873500

H	1.67650900	7.91736000	1.91515600
H	0.85251800	7.03423300	0.60034400
H	1.15485100	8.79091200	0.43836500
H	-4.24407400	-3.09459800	-0.17325700
H	-0.96104700	-5.48016000	-1.66459900
C	-0.88663000	-7.82106700	-2.58846900
C	-3.17016000	-8.12451600	-3.61851500
C	-2.70008700	-8.97259000	-1.26178600
H	-2.97460600	-7.33463200	-4.36794300
H	-4.26338100	-8.18340700	-3.46505500
H	-2.83503200	-9.09172100	-4.03992300
H	-0.61956500	-7.04637200	-3.33217800
H	-0.58920600	-8.80111600	-3.00624400
H	-0.28407900	-7.65073700	-1.67667400
H	-2.16124500	-8.79611700	-0.31202500
H	-2.36785600	-9.94521400	-1.67303100
H	-3.77842000	-9.05205400	-1.03088500
C	-6.31727600	-4.99412100	-0.53054900
C	-6.69737000	-3.62063800	0.08774100
C	-6.73202600	-6.11304500	0.47786300
C	-7.12213100	-5.17140200	-1.85816800
H	-6.85765300	-4.38222500	-2.58663000
H	-8.20890500	-5.10792800	-1.65680700

H	-6.92118400	-6.15060600	-2.33045200
H	-6.17506600	-3.44839500	1.04823300
H	-7.78484100	-3.59546100	0.28855300
H	-6.46165900	-2.78373900	-0.59648200
H	-6.18658600	-6.00429100	1.43415300
H	-6.52181400	-7.12296200	0.08053200
H	-7.81690200	-6.05169000	0.68932500
C	-1.19444800	0.86493300	0.05908000
C	-0.99217200	2.35388200	-0.39261800
C	-2.37681900	3.03062500	-0.42279000
H	-0.56190200	2.37053900	-1.41010400
H	-0.28974800	2.88418900	0.27453000
C	-2.86257300	3.82848400	0.71096100
C	-2.31115900	3.71427700	2.02861300
C	-3.95293700	4.73937800	0.52186000
C	-4.45731600	5.50469100	1.59278200
C	-3.89337900	5.38434600	2.88927100
C	-2.81740600	4.48407500	3.09762400
H	-2.37020900	4.38904900	4.09464300
H	-1.46772400	3.03668500	2.20979200
H	-4.28022200	5.98592600	3.72023100
H	-5.28787600	6.19983200	1.41990700
H	-4.38669800	4.84695100	-0.48030100

H	-3.79133100	1.37392200	0.58827300
H	-2.71100900	3.38919500	-1.40730500
C	-2.39159000	0.41446300	-0.74331500
C	-3.54151600	1.21434600	-0.47263200
H	-2.25984100	-0.07896400	-1.71271800
C	-4.70436200	1.33952800	-1.39470100
C	-4.61828100	1.03368200	-2.78513800
C	-5.74042600	1.17736800	-3.63055700
C	-6.97382800	1.64551500	-3.11153800
C	-7.07030400	1.96459500	-1.73534600
C	-5.94974300	1.81255600	-0.88810100
H	-6.03860800	2.05070100	0.17924400
H	-8.01742800	2.33035800	-1.32088500
H	-5.65522600	0.92405700	-4.69442200
H	-7.84290300	1.75976500	-3.77023300
H	-3.67131900	0.67765700	-3.20926100
H	-1.41153400	0.83430800	1.14664600

Intermediate F'

$\mathbf{F_{[Co(II)(P6)]}=A_{[Co(II)(P6)]}}$

$\mathbf{F'_{[3a'']}}$

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.230142 Hartree

H_corr: 0.287639 Hartree

SCF: -657.7488833 Hartree

S: 121.012 Cal/Mol-Kelvin

H: -657.4612443 Hartree

G: -657.5187413 Hartree

Cartesian Coordinates:

H	4.30974300	-0.55369000	-1.82106500
H	4.62183600	-2.48987000	-0.24353200
C	3.62446000	-0.68777700	-0.97514800
C	3.80178900	-1.77880500	-0.08821500
C	2.56825900	0.22928600	-0.77269500
H	2.44473500	1.06924100	-1.46948100
C	2.91066300	-1.94241900	0.99841400
H	3.03659400	-2.78455300	1.68953100
C	1.66644000	0.07880500	0.31822200
H	1.90188000	2.76877900	0.13359500
C	1.85384600	-1.02110000	1.19592900
H	-0.30393700	4.41857000	0.06327500
C	0.94667300	2.57074000	0.66216000
C	0.51986000	1.06185800	0.53356500

C	-0.20178400	3.32857800	0.00715500
H	1.16286700	-1.15765100	2.03798900
H	1.11033500	2.85725700	1.71894800
H	-0.08343600	0.76980900	-1.58166900
H	-0.00715400	0.78358600	1.46695800
C	-0.57745700	1.03967000	-0.62322000
C	-1.02793600	2.49946800	-0.68332200
H	-0.87849900	-1.46161100	-1.75042200
C	-1.67983700	-1.23703100	-1.03440600
C	-1.68806800	0.01875200	-0.37213000
H	-1.89903100	2.81027600	-1.27183200
C	-2.68509500	-2.19989300	-0.77873300
H	-2.66173400	-3.16498100	-1.29911700
C	-2.73151300	0.28957500	0.55492900
H	-2.75286000	1.25974300	1.06861000
C	-3.72021200	-1.91859200	0.14509000
C	-3.73977300	-0.66812200	0.81096100
H	-4.50236700	-2.66157400	0.34171100
H	-4.54084500	-0.44128500	1.52516100

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Chapter 5

Spectral Data

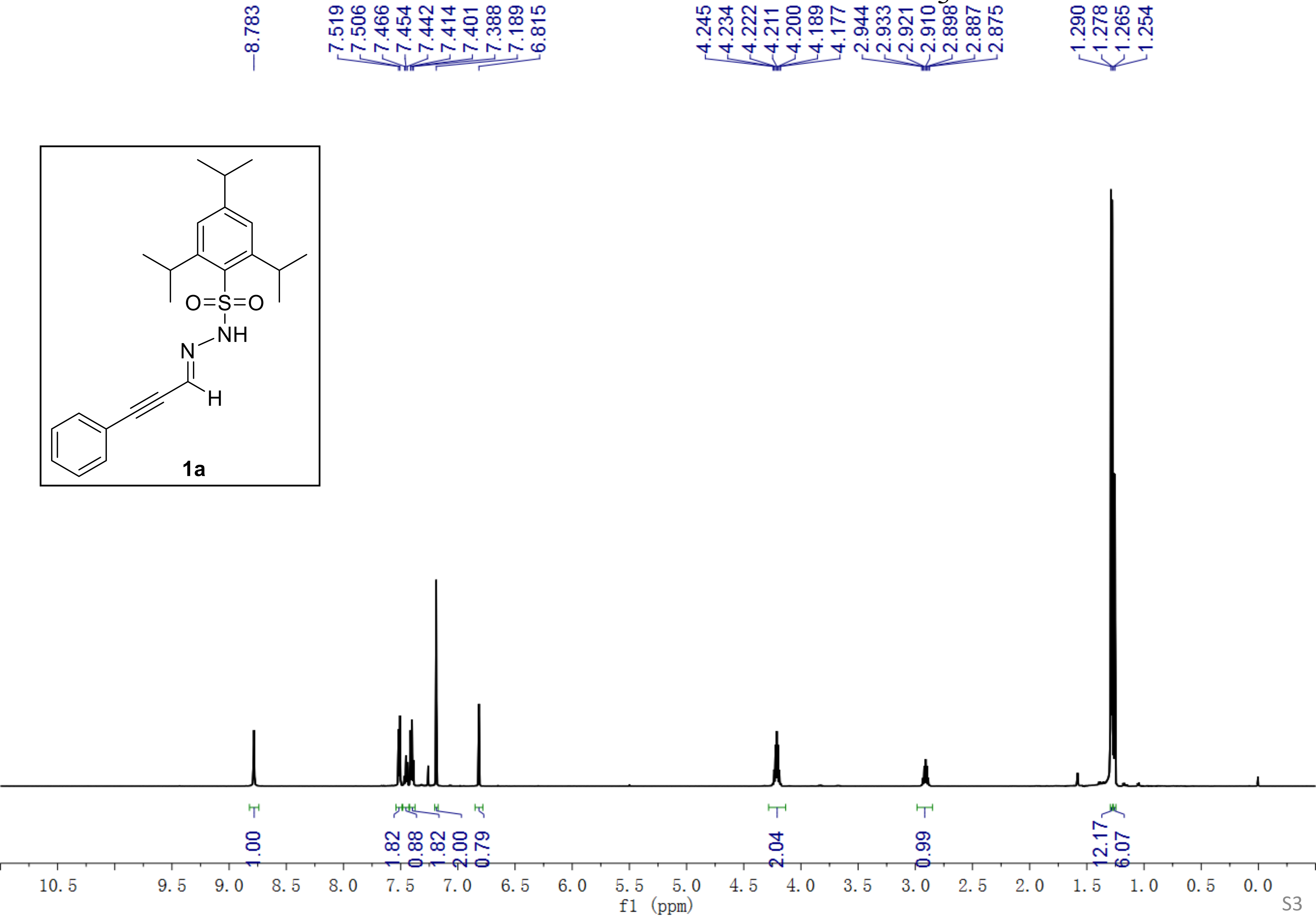
Spectral Data

for

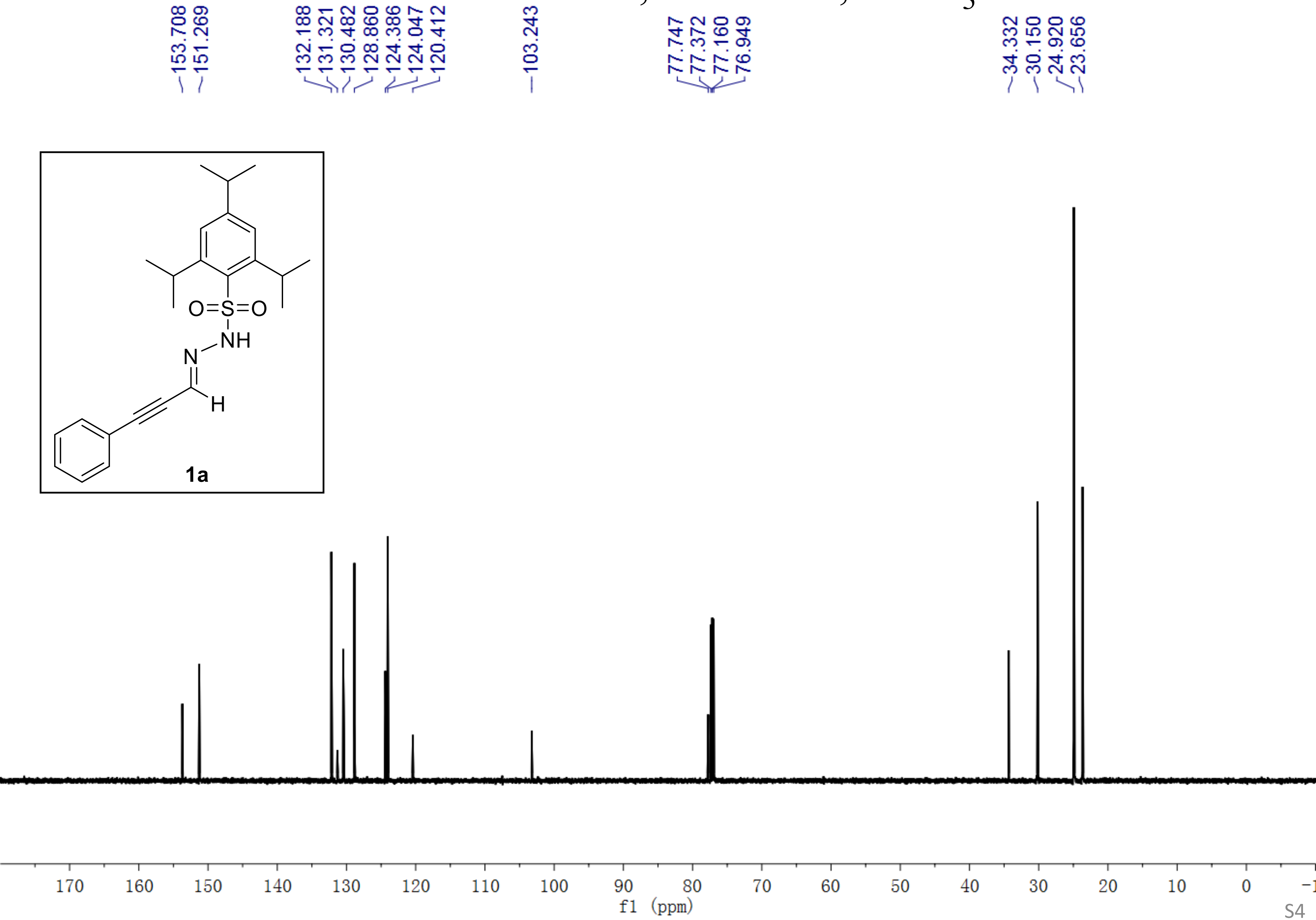
Chapter 2

Metalloradical Activation of In Situ-Generated α-Alkynyldiazomethanes for Asymmetric Radical Cyclopropanation of Alkenes

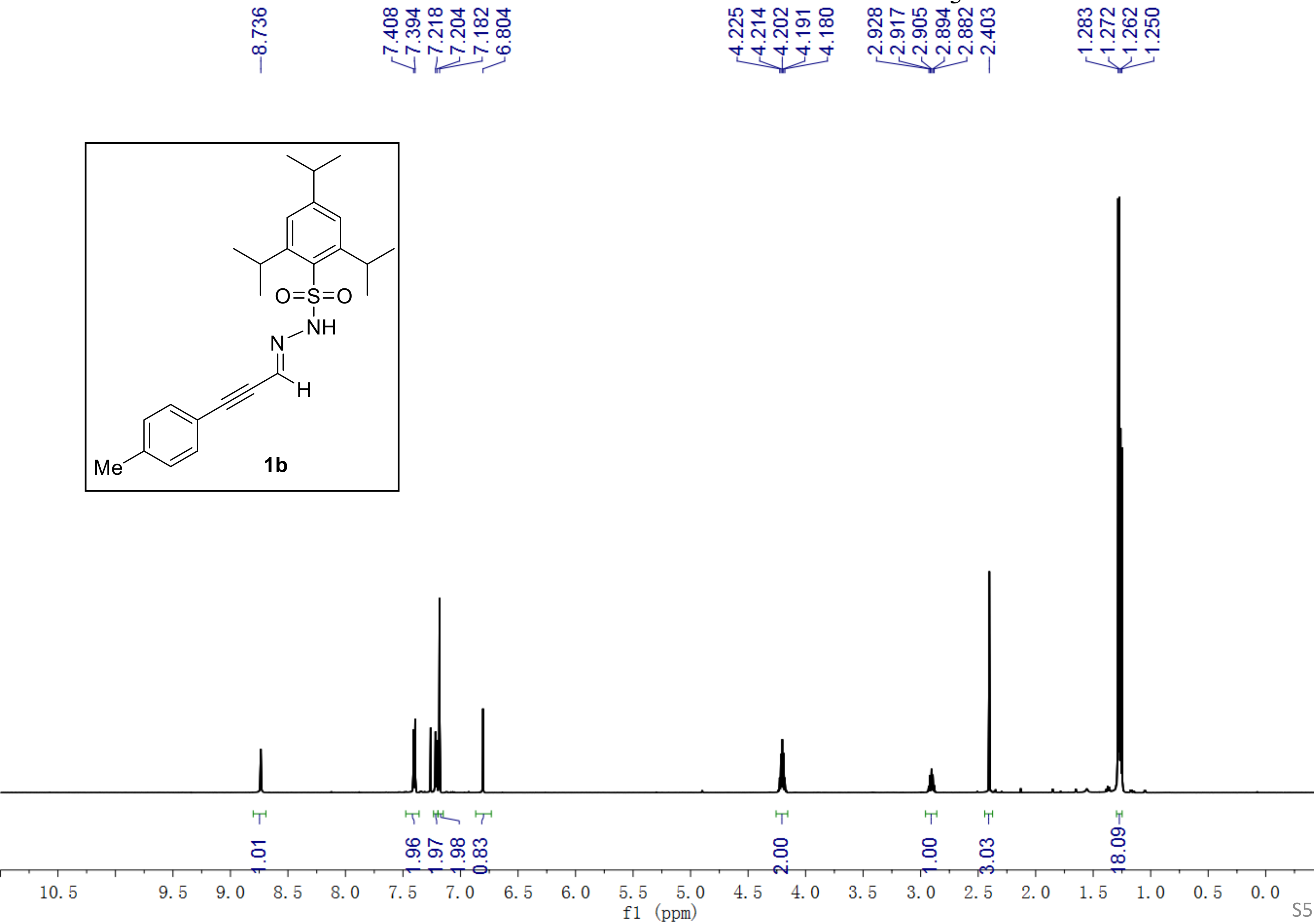
^{1}H NMR of **1a**, 600 MHz, $CDCl_3$



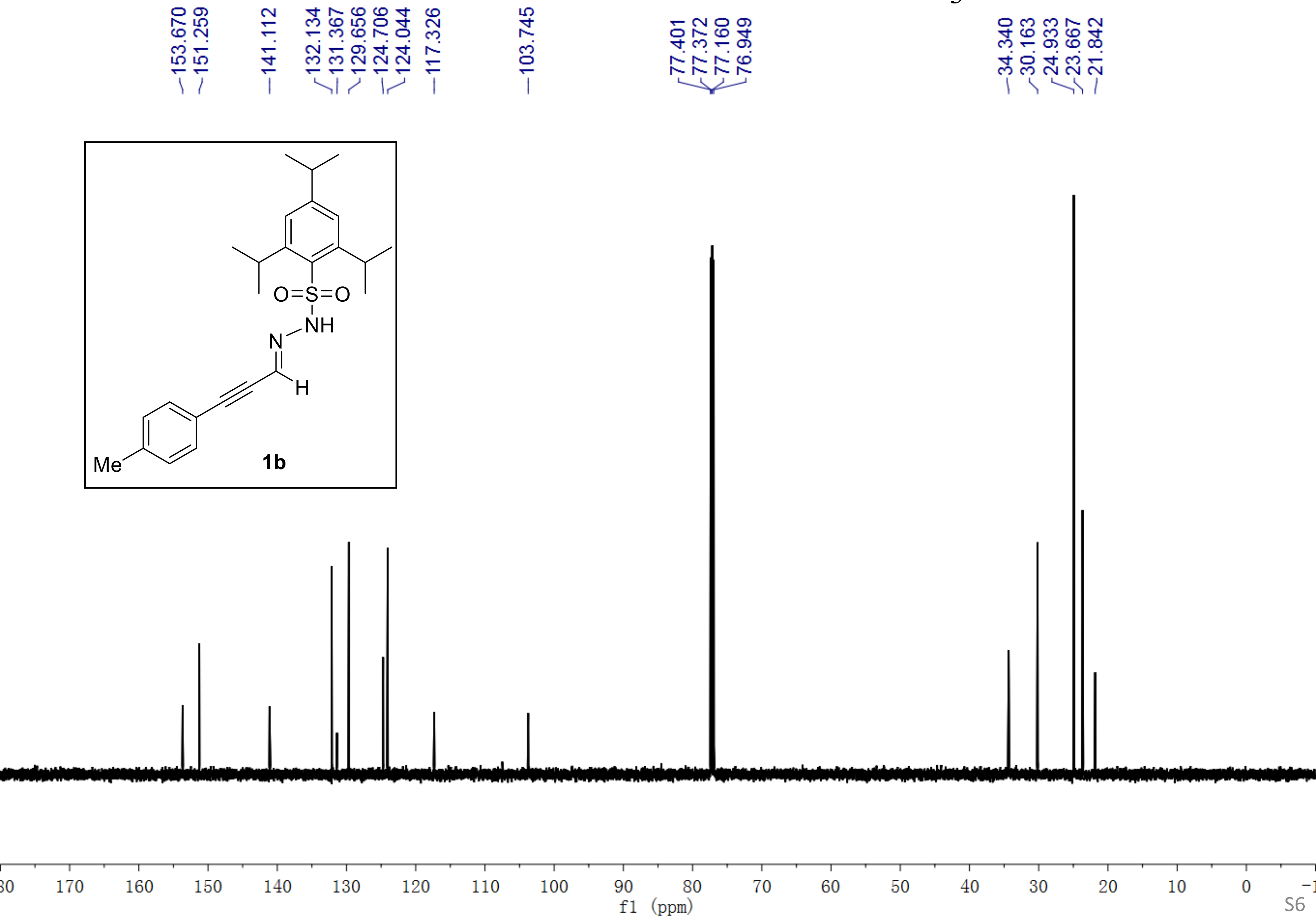
^{13}C NMR of **1a**, 151 MHz, $CDCl_3$



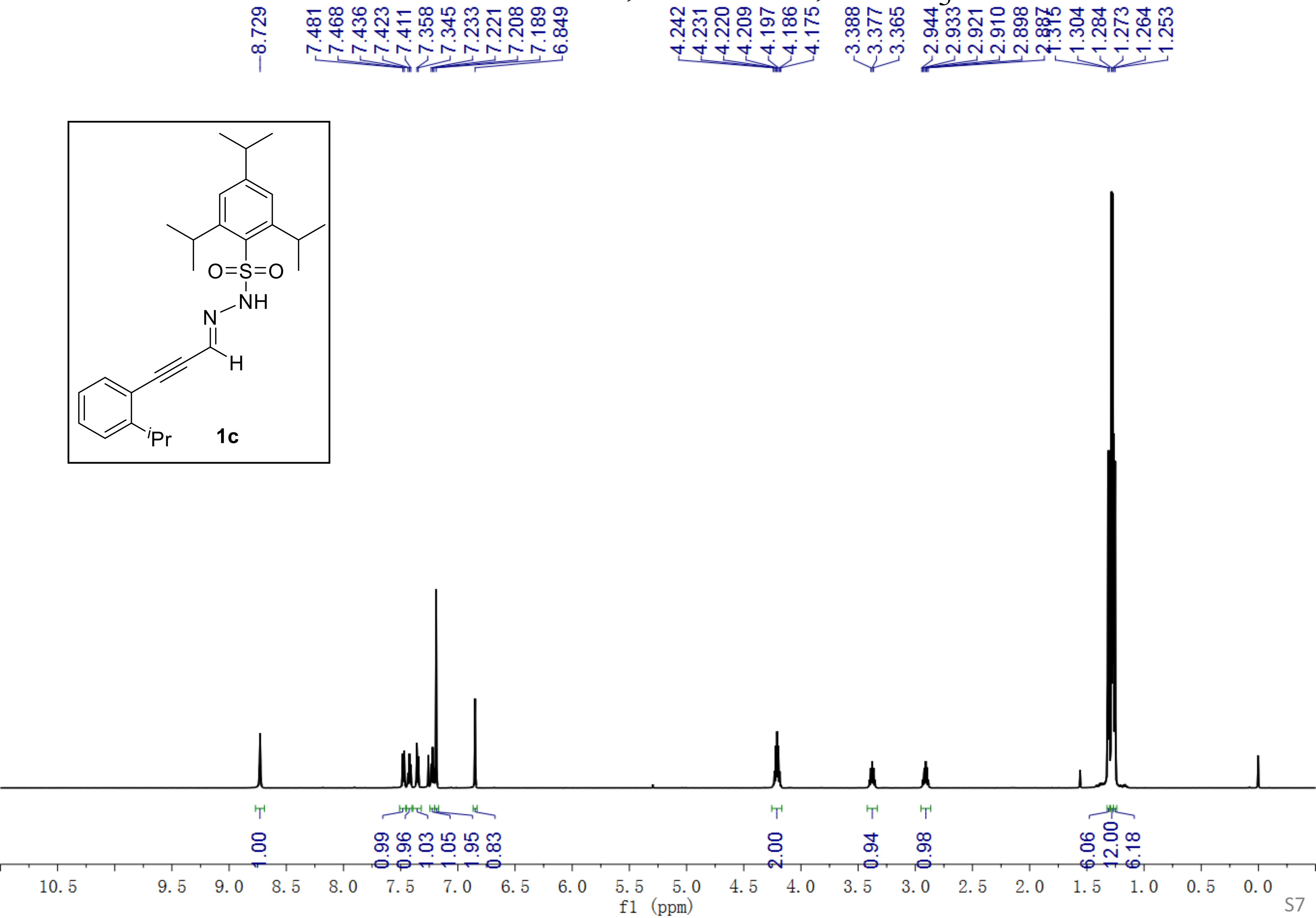
^{1}H NMR of **1b**, 600 MHz, $CDCl_3$



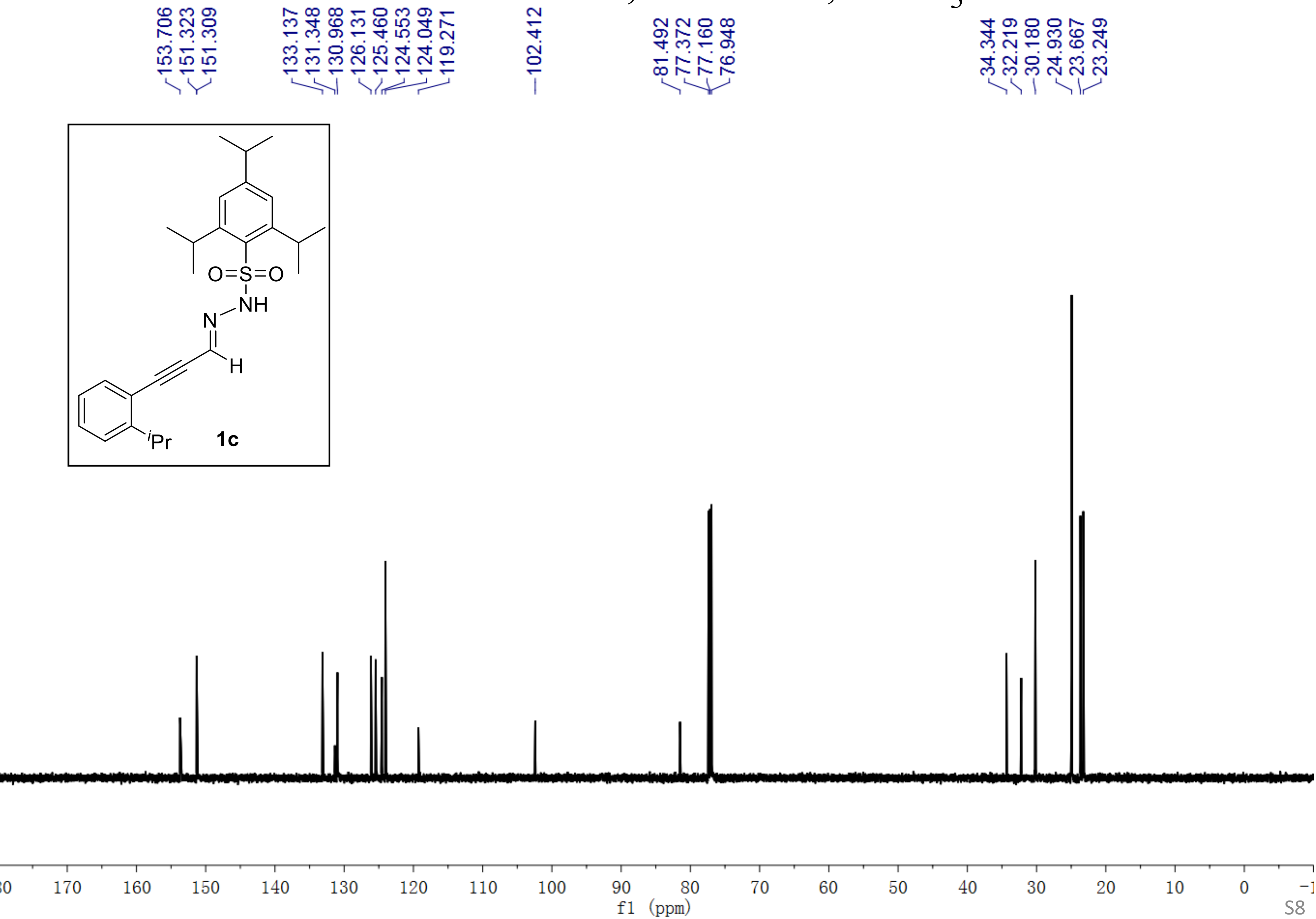
^{13}C NMR of **1b**, 151 MHz, $CDCl_3$



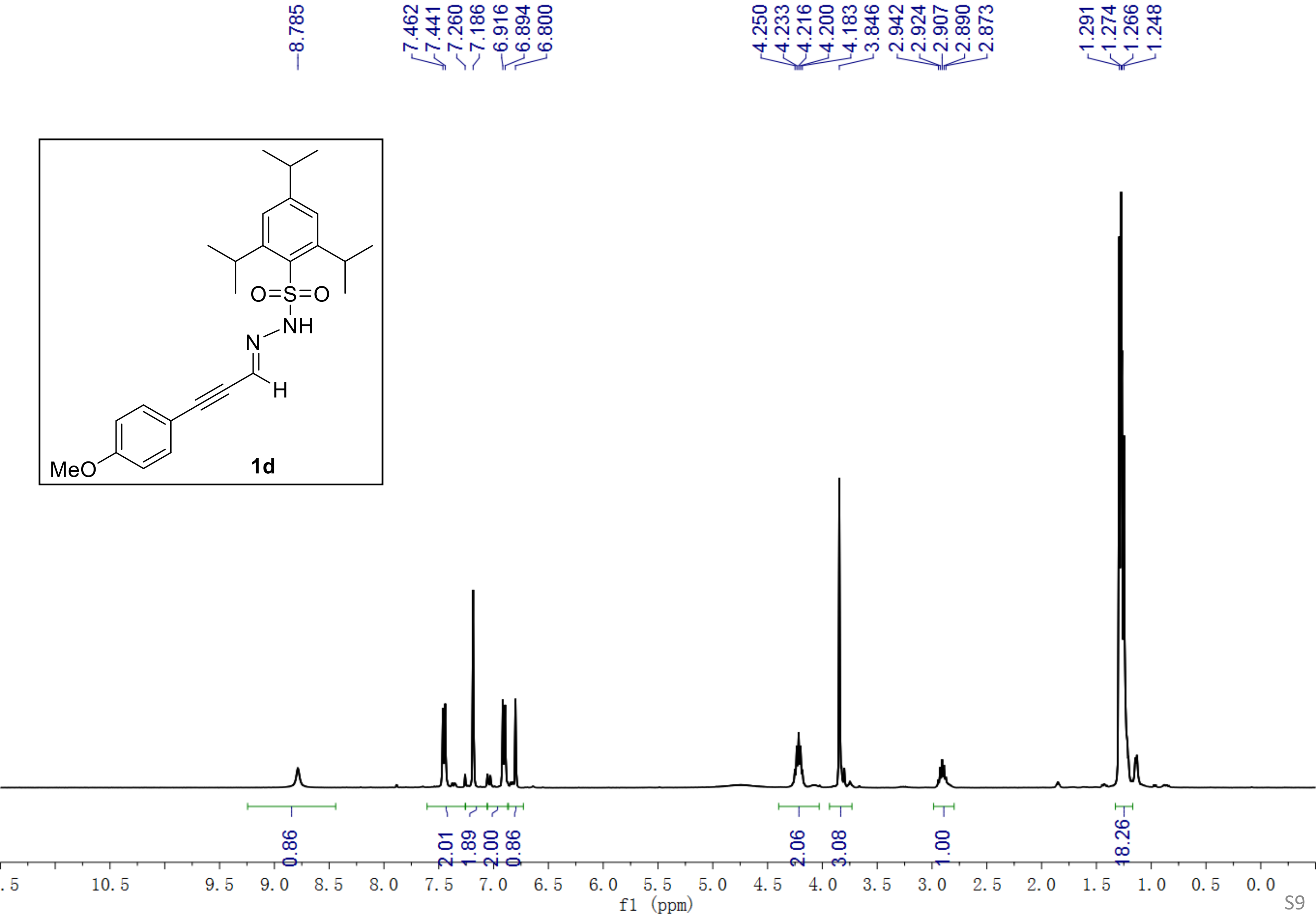
^{1}H NMR of **1c**, 600 MHz, $CDCl_3$



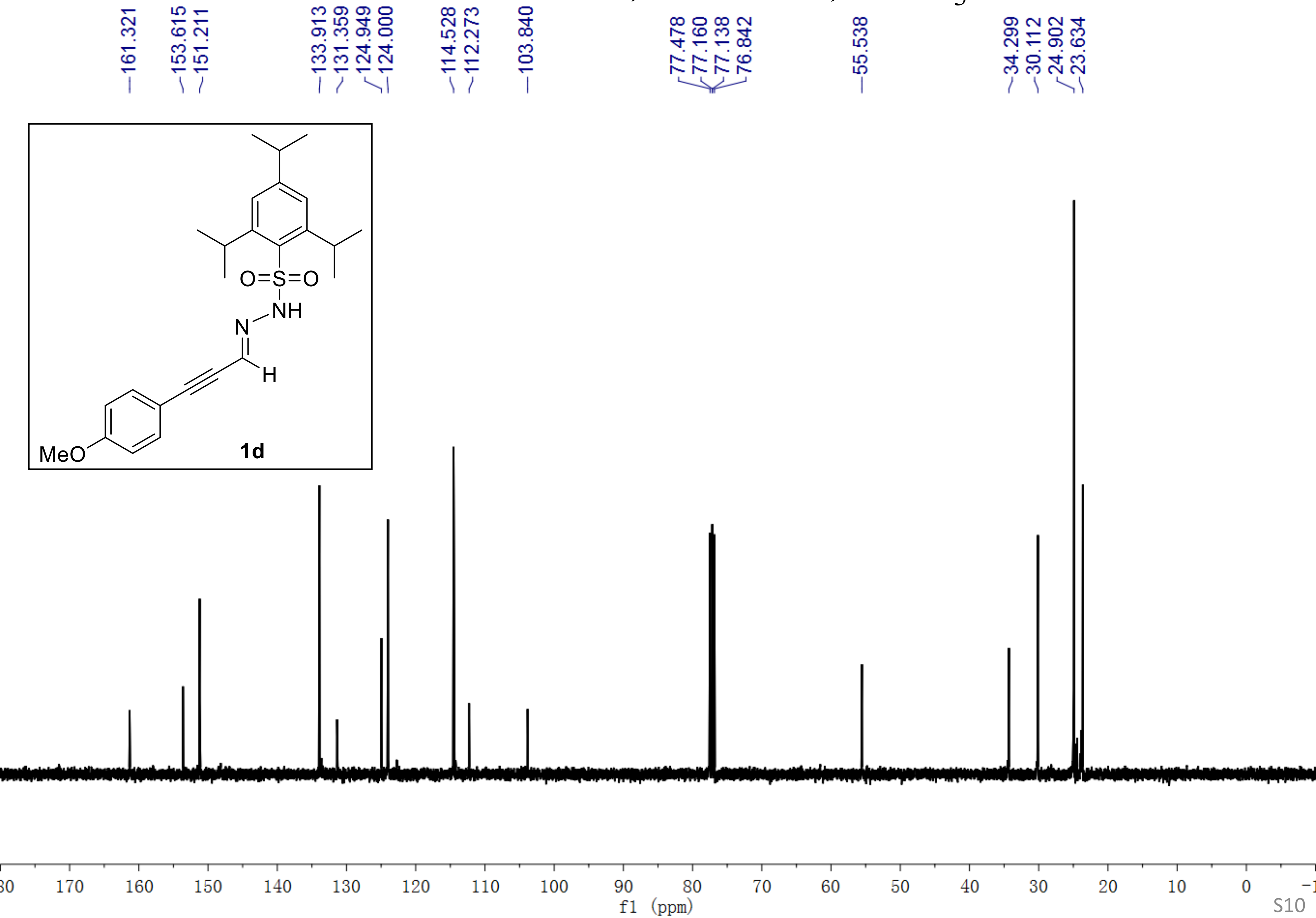
^{13}C NMR of **1c**, 151 MHz, $CDCl_3$



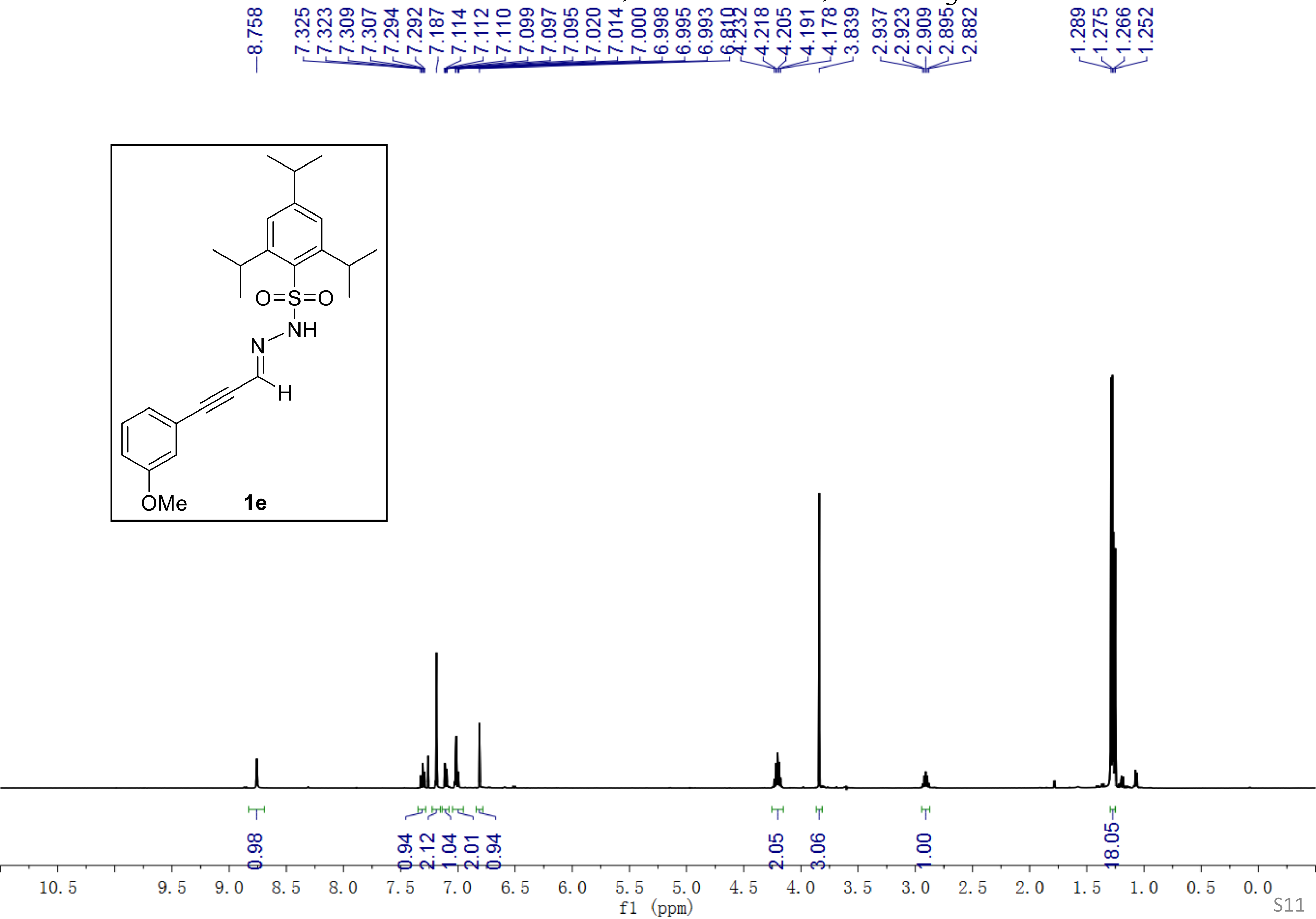
^{1}H NMR of **1d**, 400 MHz, $CDCl_3$



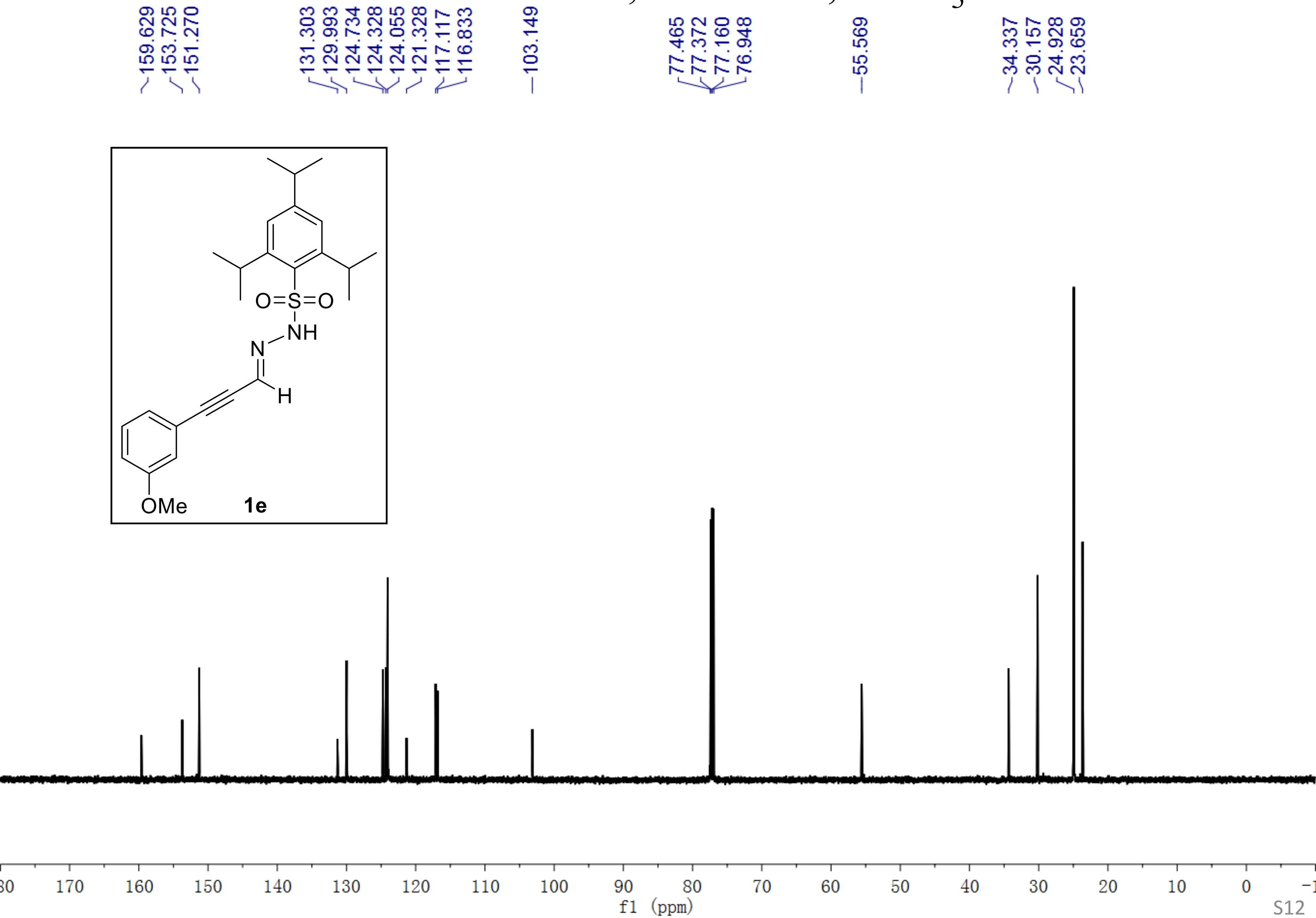
^{13}C NMR of **1d**, 101 MHz, $CDCl_3$



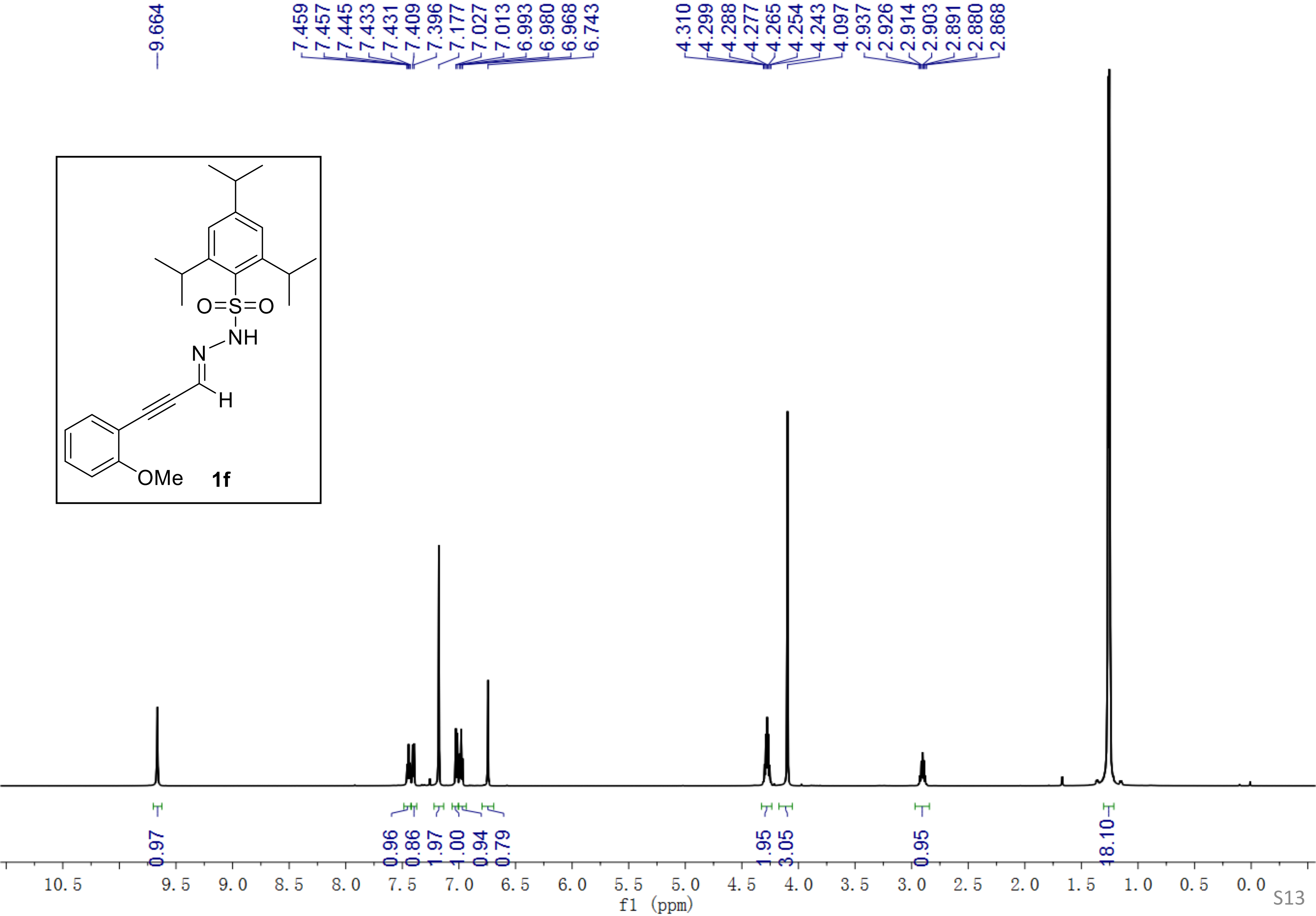
^{1}H NMR of **1e**, 600 MHz, $CDCl_3$



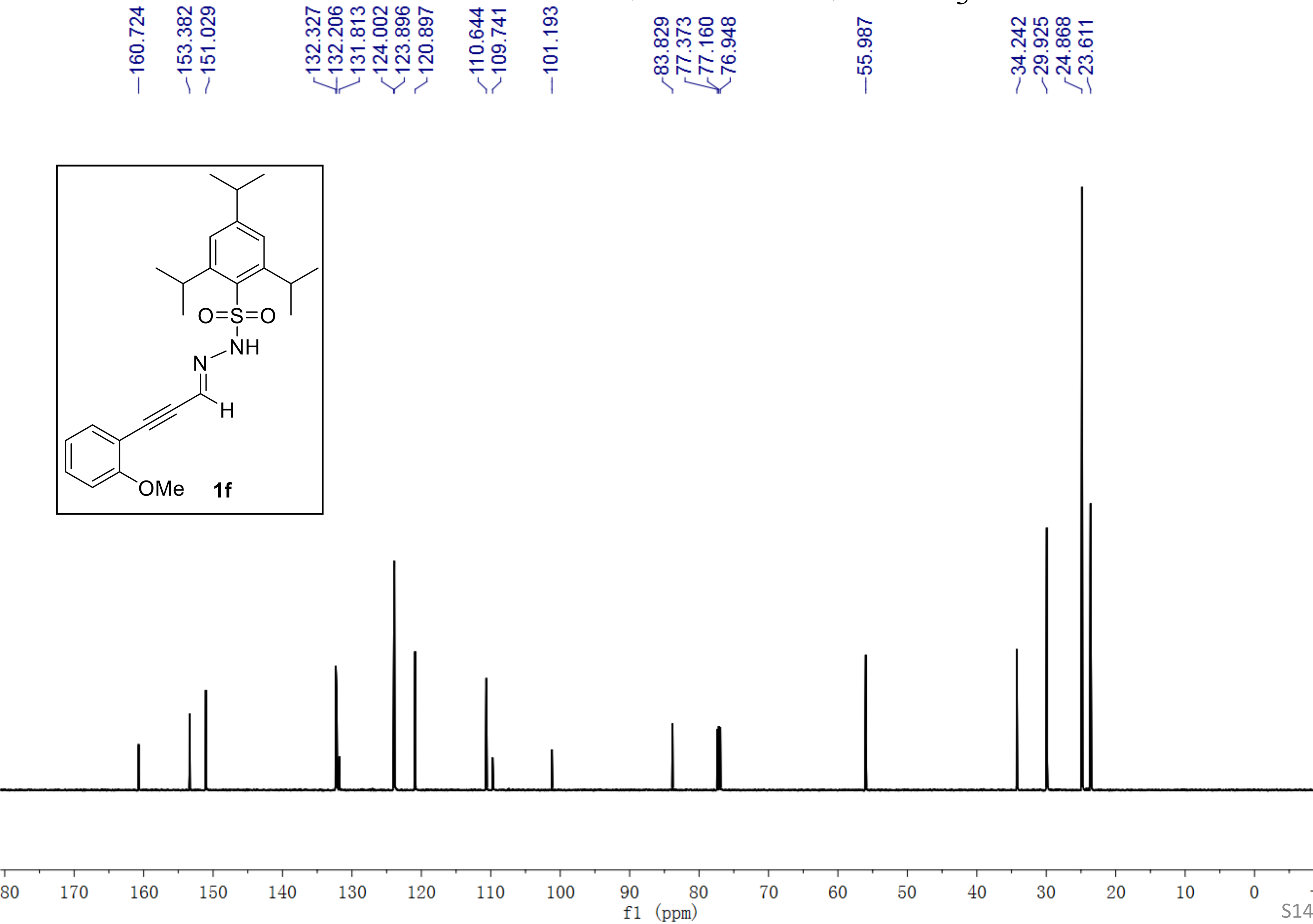
^{13}C NMR of **1e**, 151 MHz, $CDCl_3$



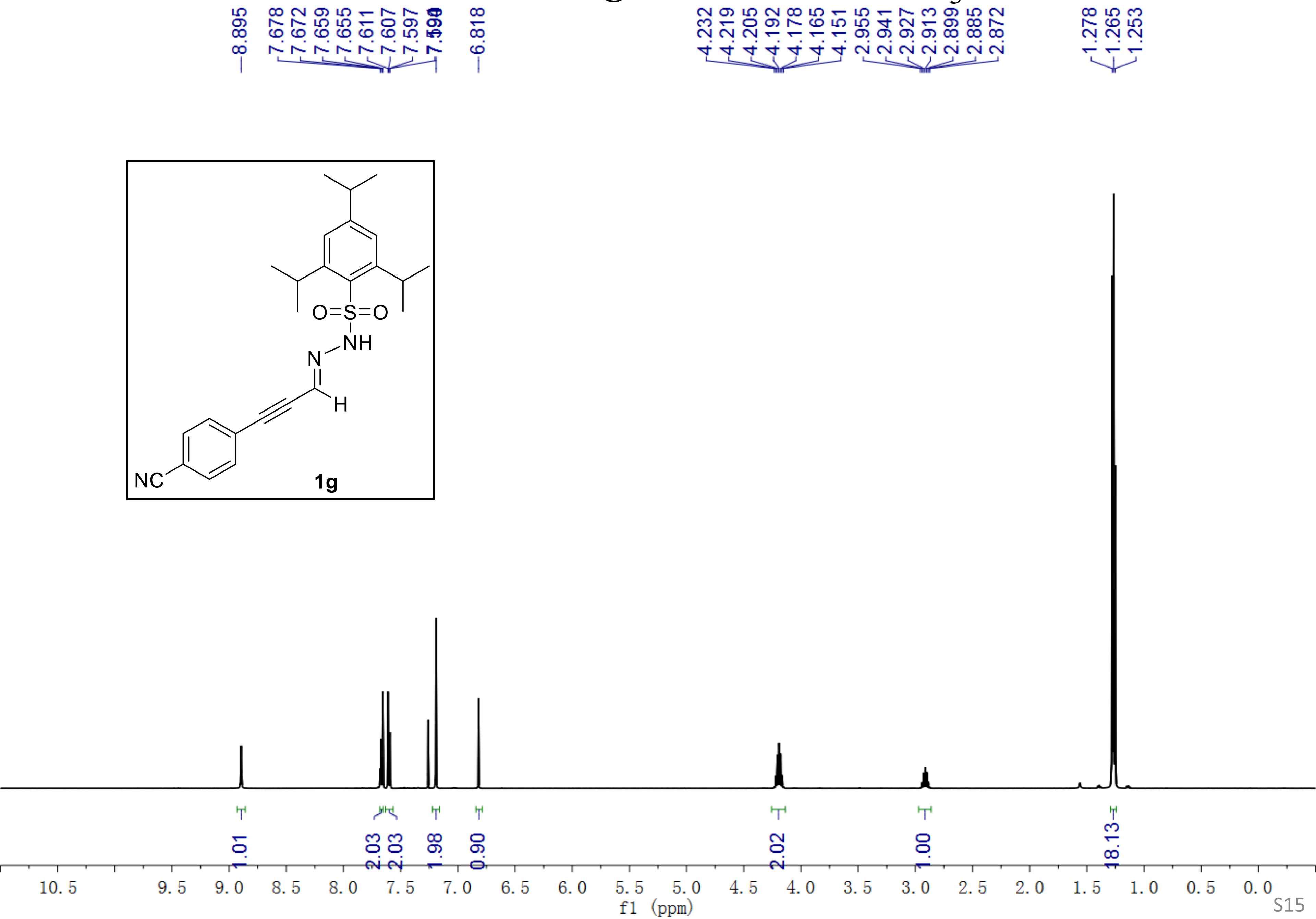
^{1}H NMR of **1f**, 600 MHz, $CDCl_3$



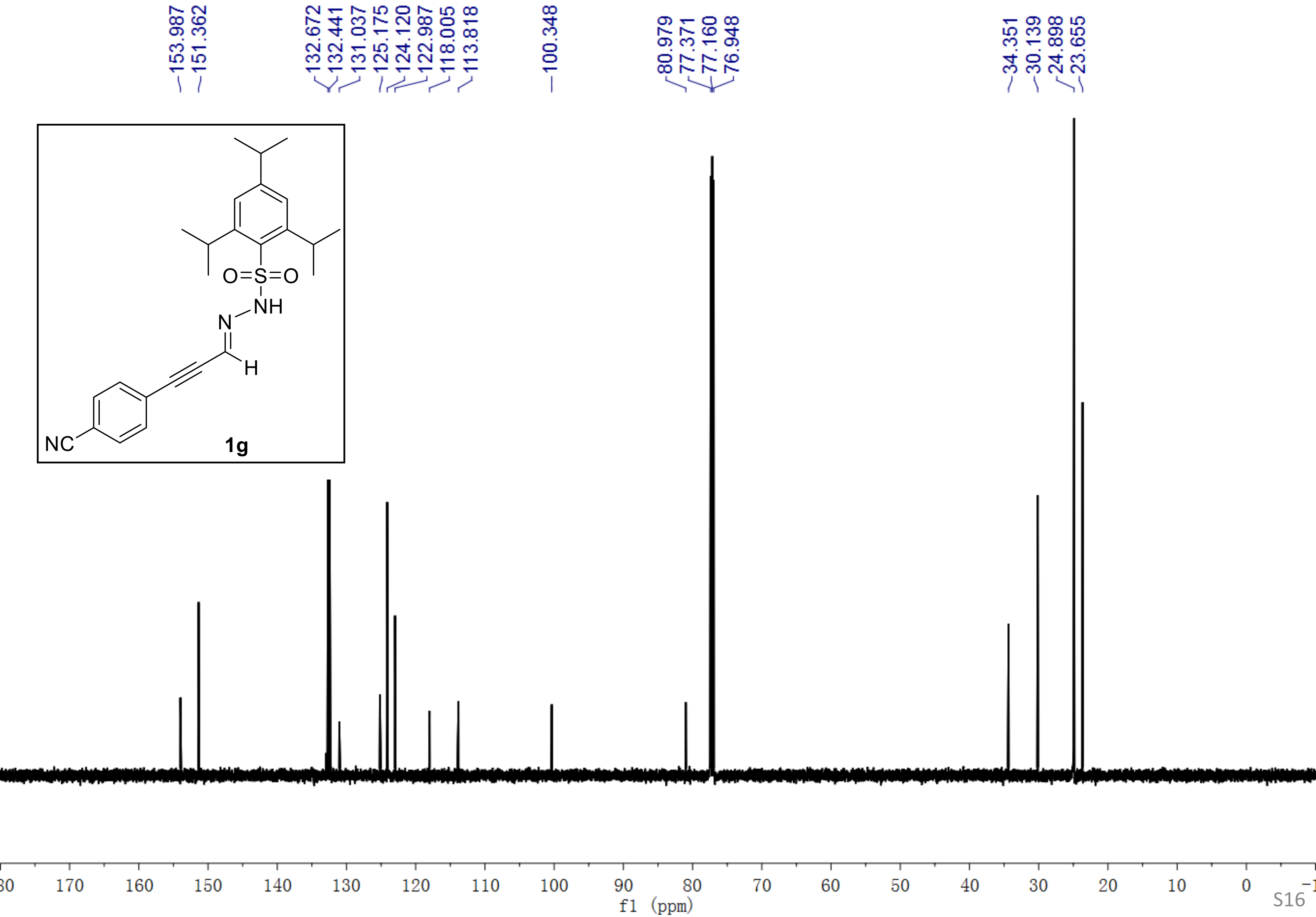
^{13}C NMR of **1f**, 151 MHz, $CDCl_3$



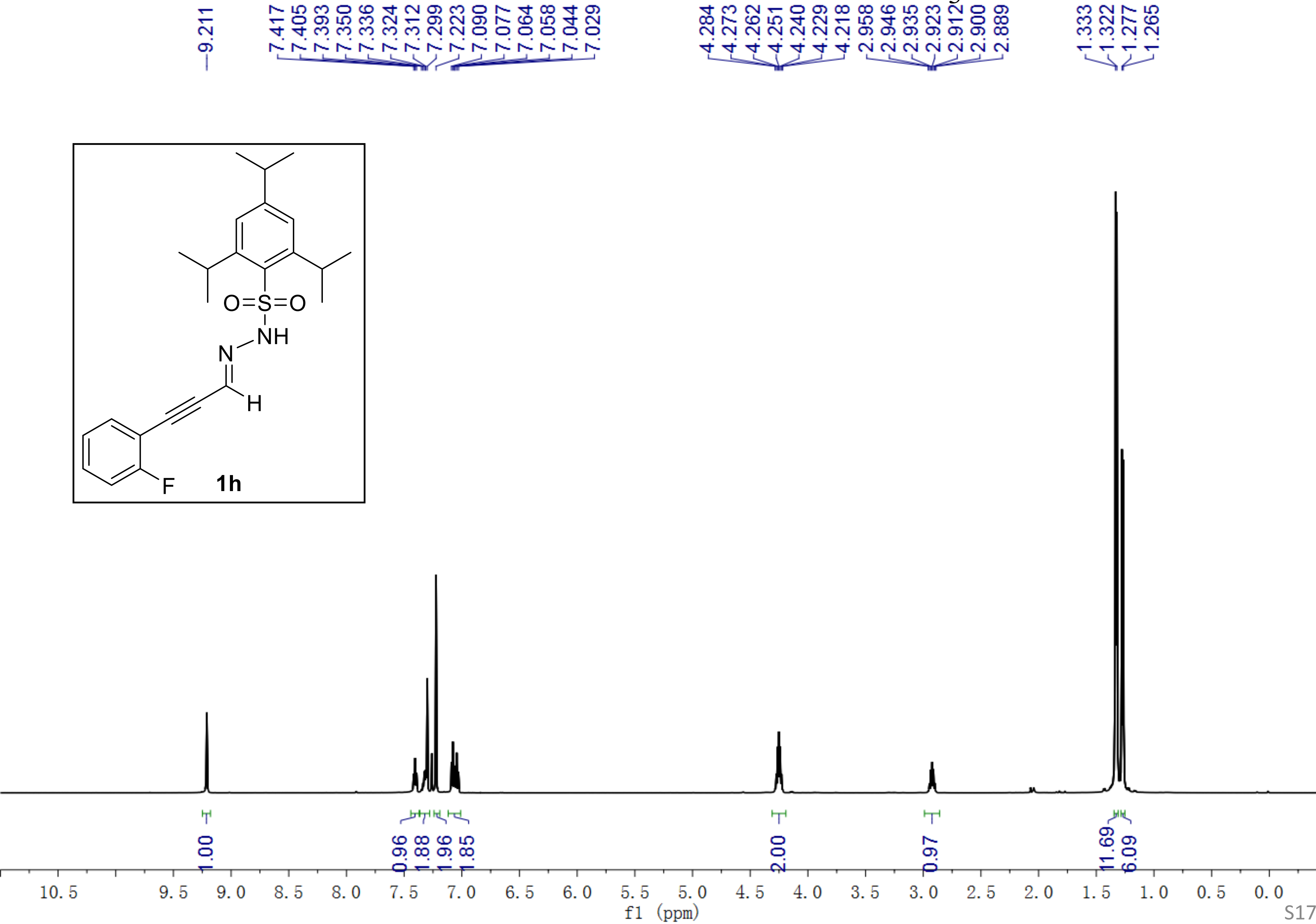
[1]H NMR of **1g**, 600 MHz, $CDCl_3$



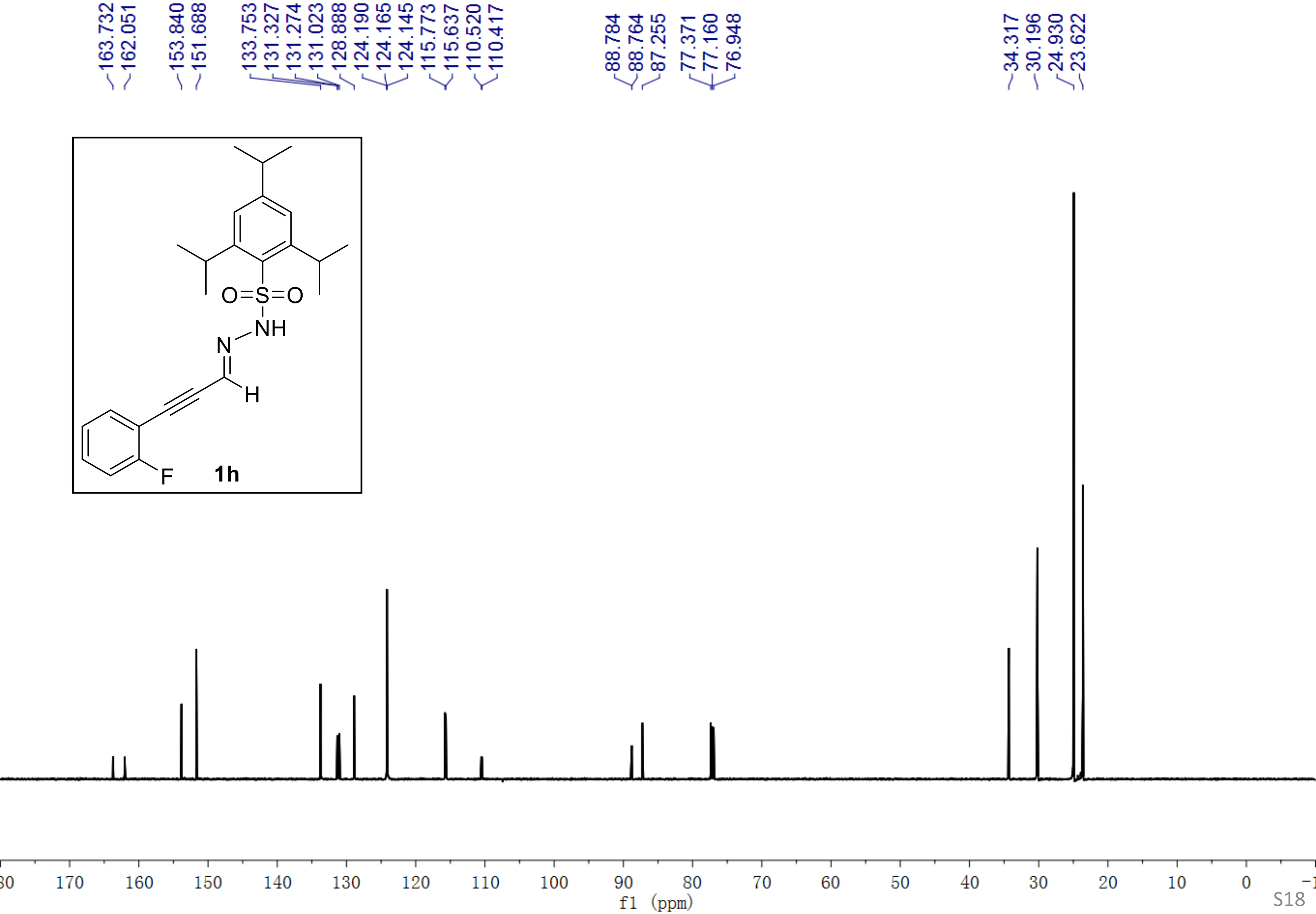
^{13}C NMR of **1g**, 151 MHz, $CDCl_3$



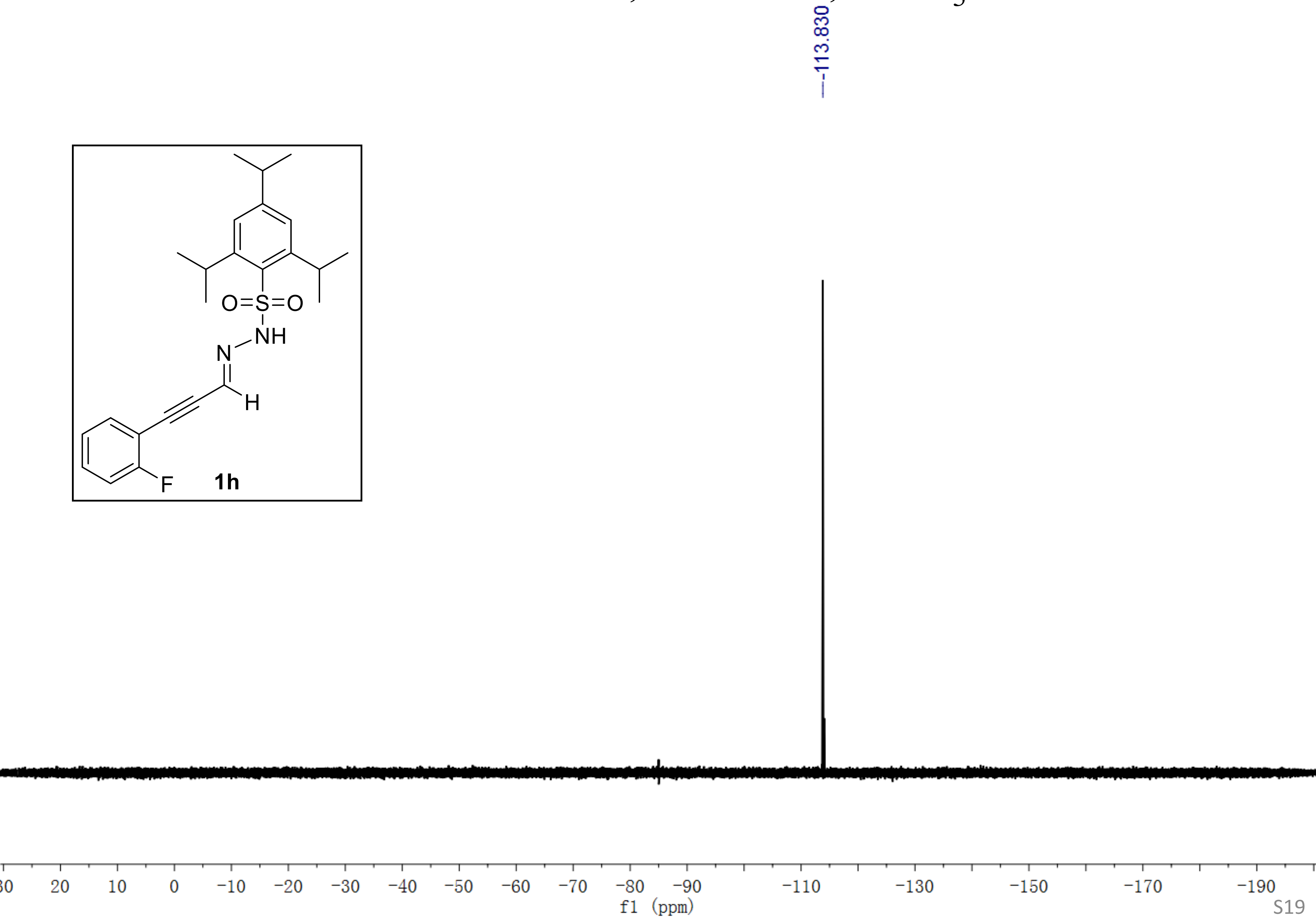
^{1}H NMR of **1h**, 600 MHz, $CDCl_3$



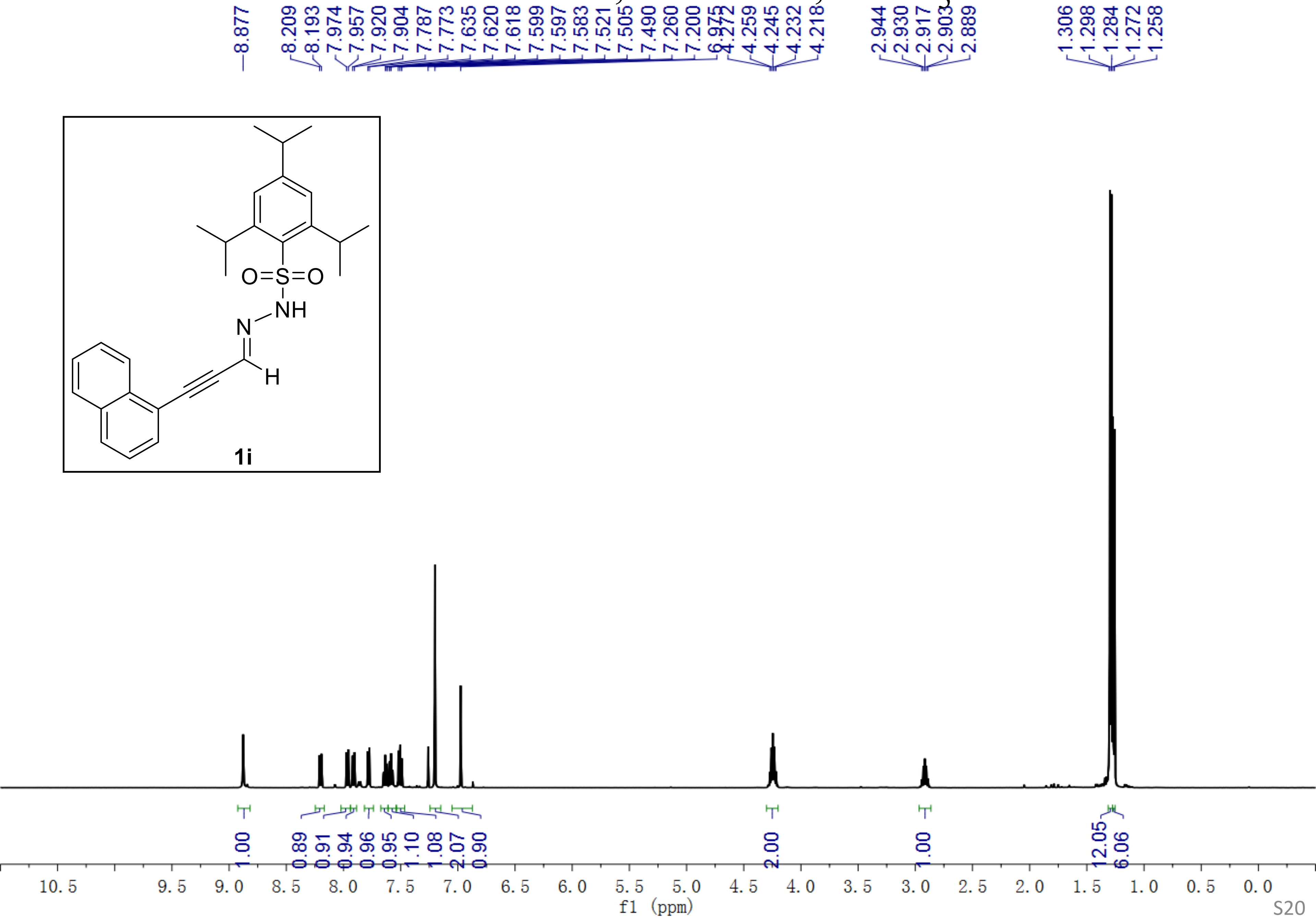
^{13}C NMR of **1h**, 151 MHz, $CDCl_3$



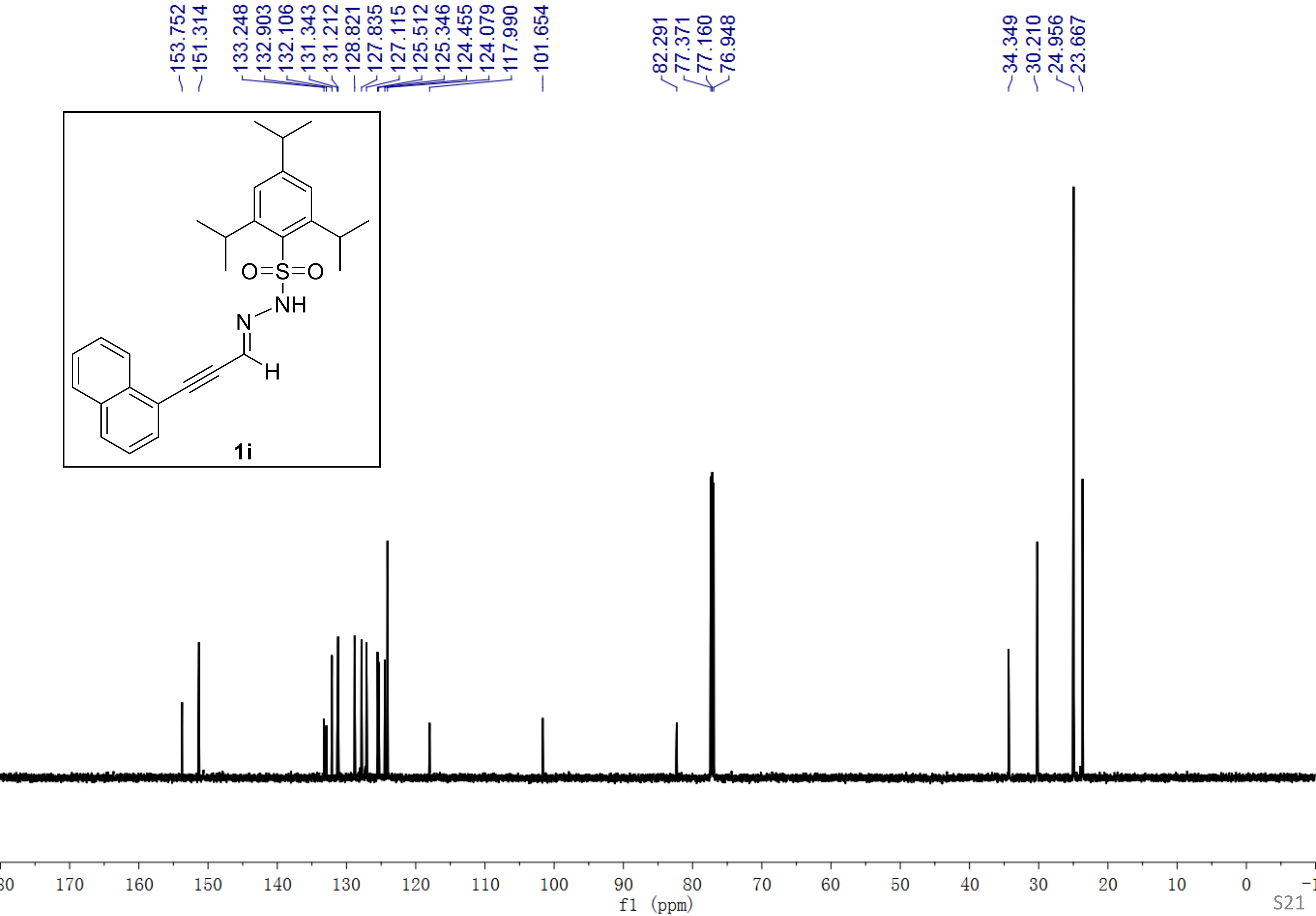
^{19}F NMR of **1h**, 564 MHz, $CDCl_3$



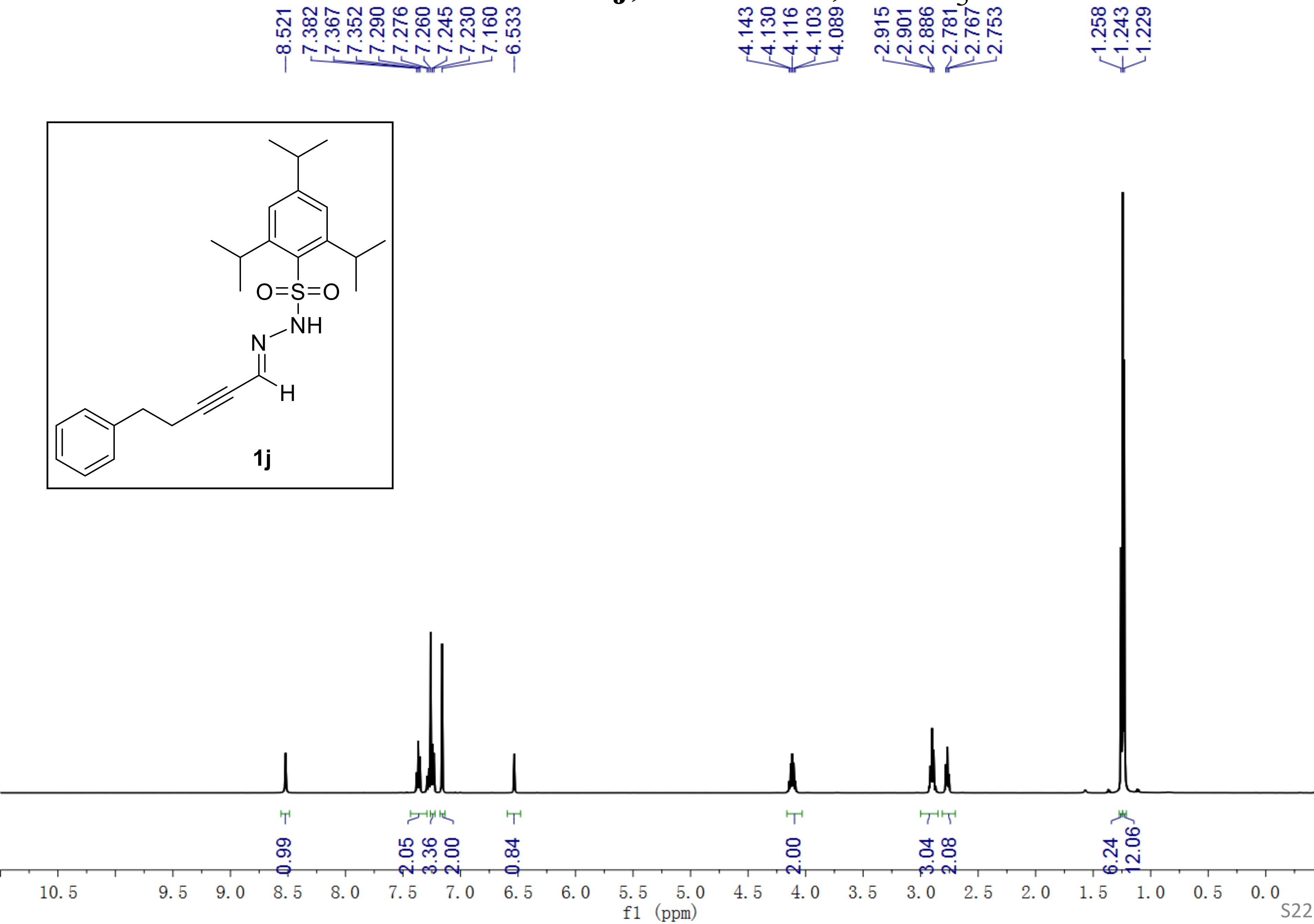
^1H NMR of **1i**, 600 MHz, $CDCl_3$



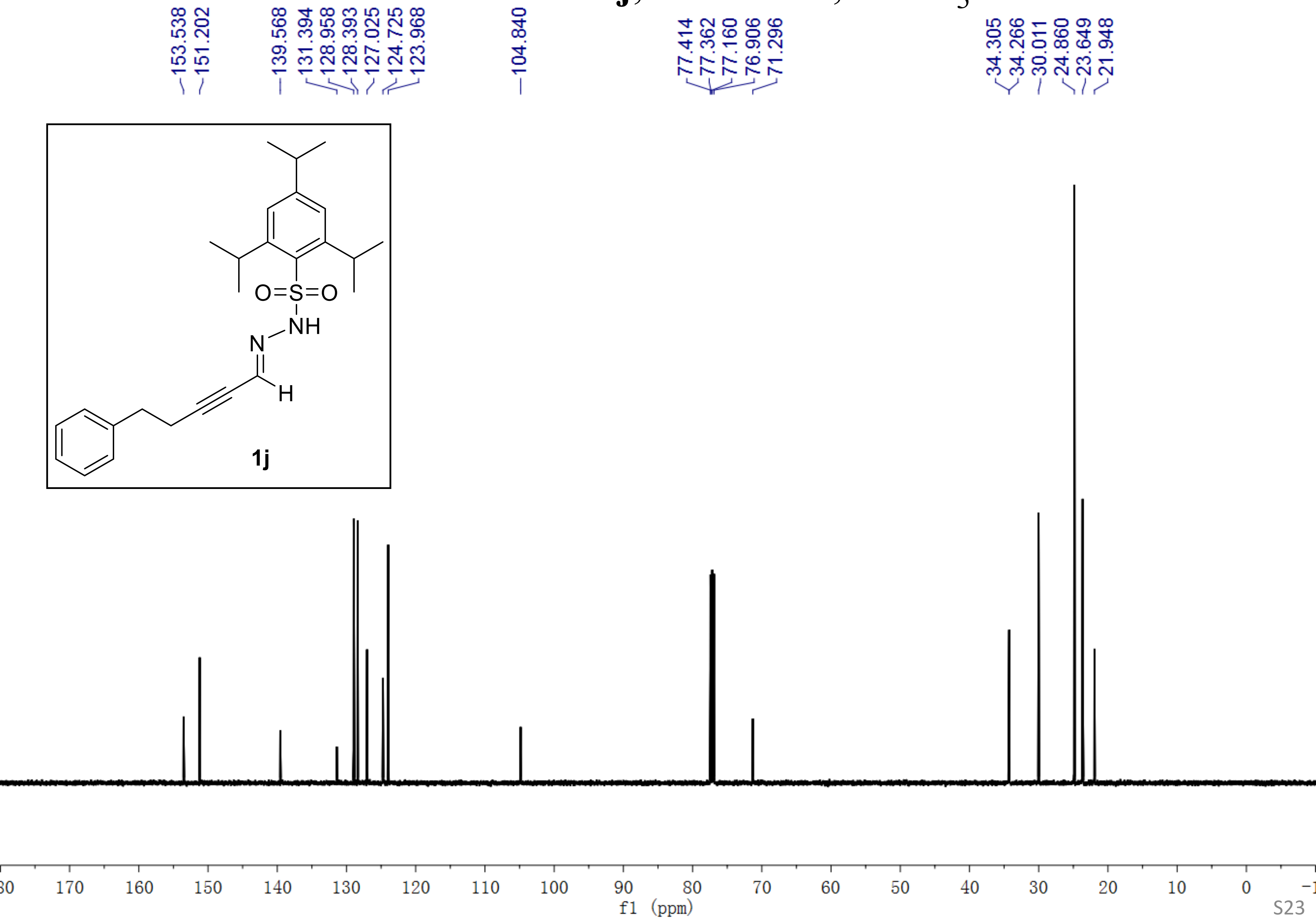
^{13}C NMR of **1i**, 151 MHz, $CDCl_3$



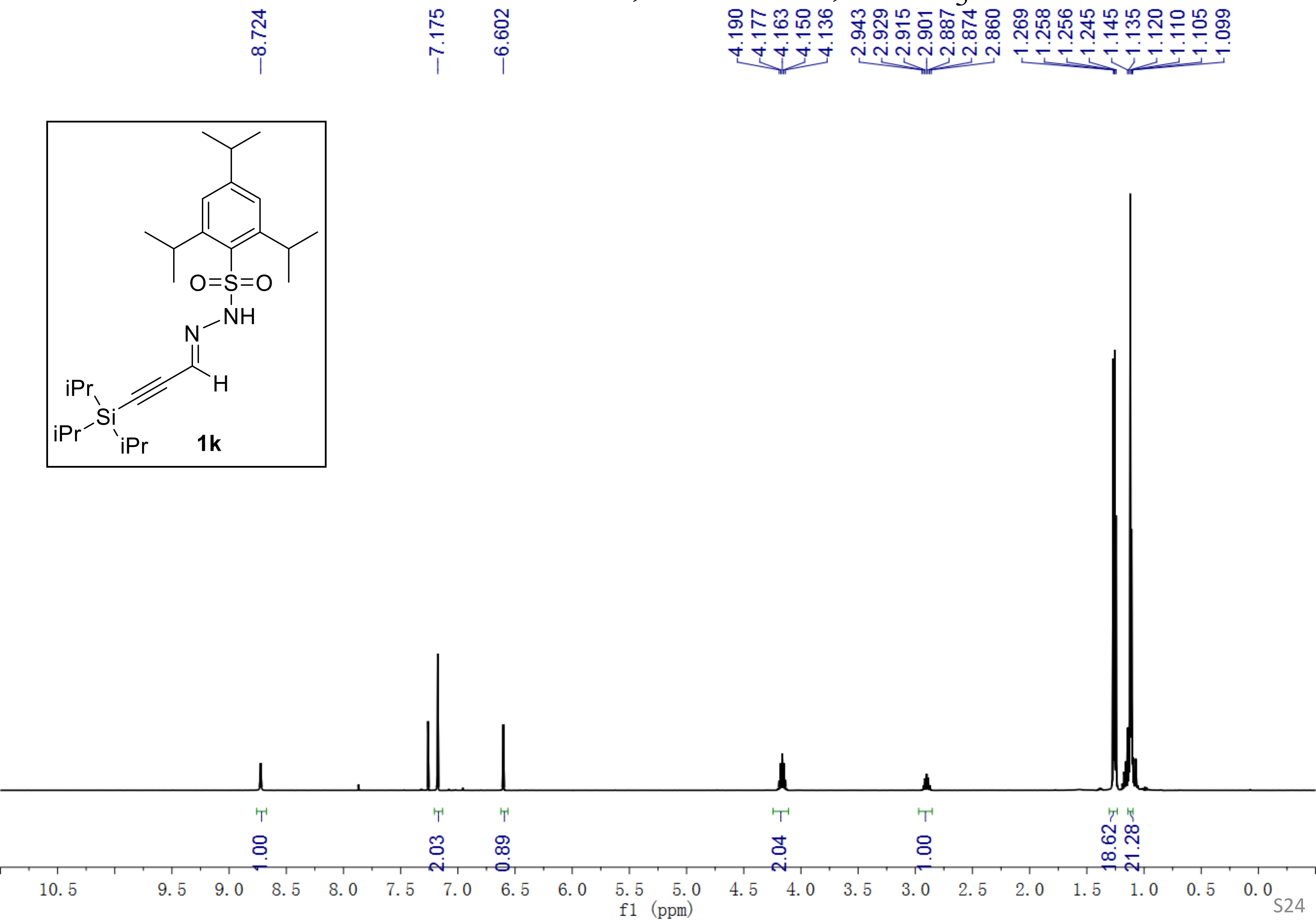
^{1}H NMR of **1j**, 500 MHz, $CDCl_3$



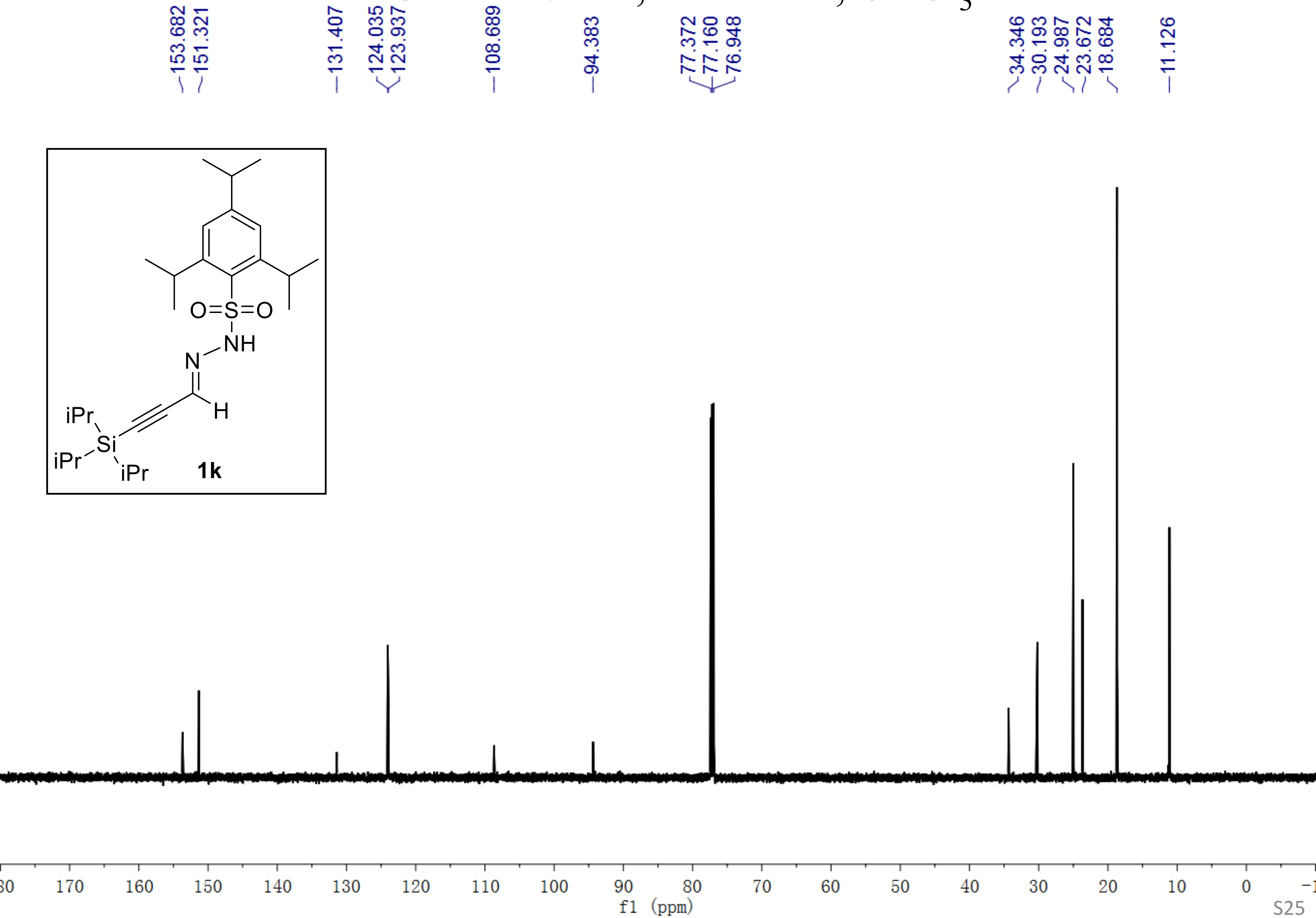
^{13}C NMR of **1j**, 126 MHz, $CDCl_3$



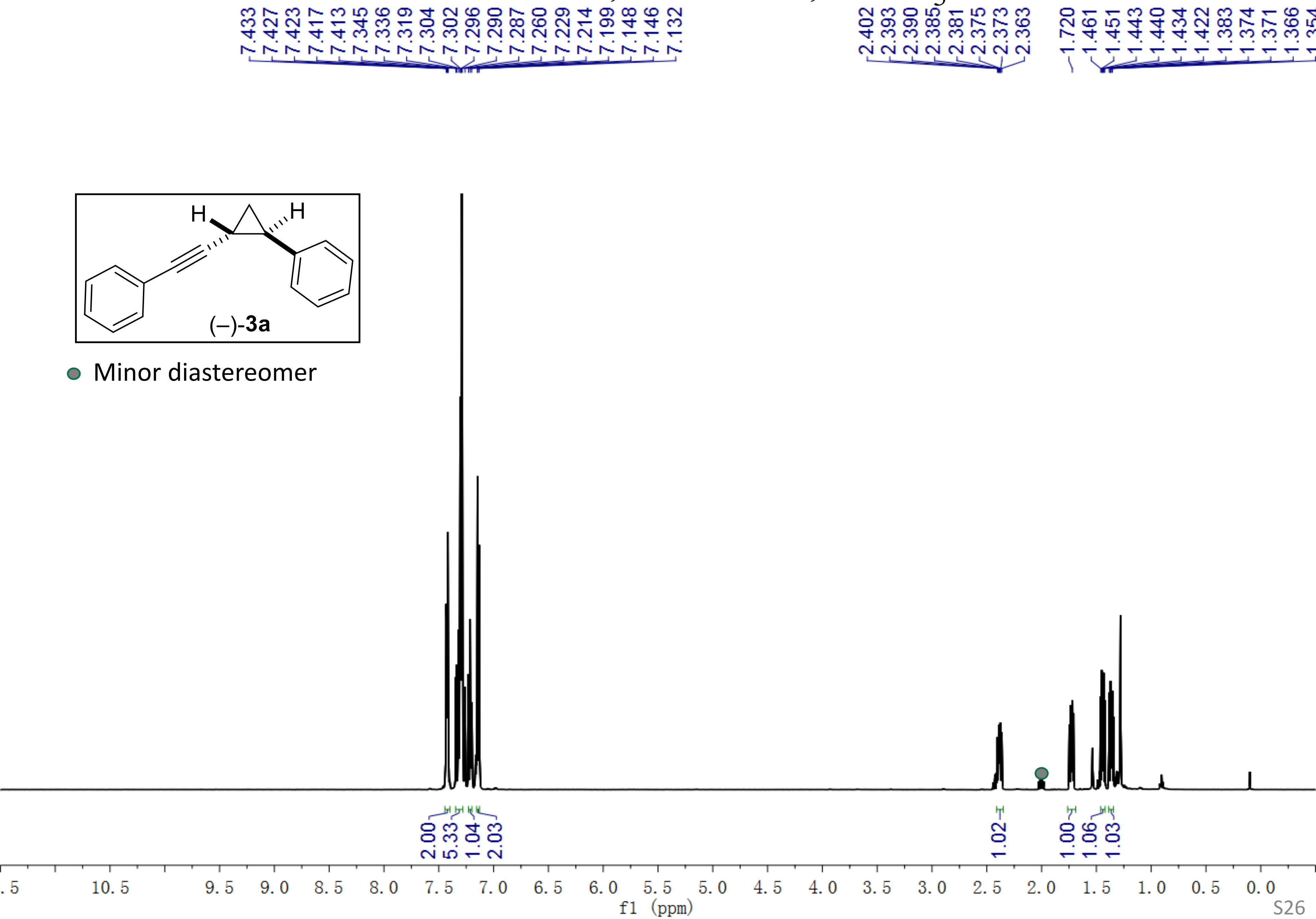
^{1}H NMR of **1k**, 600 MHz, $CDCl_3$



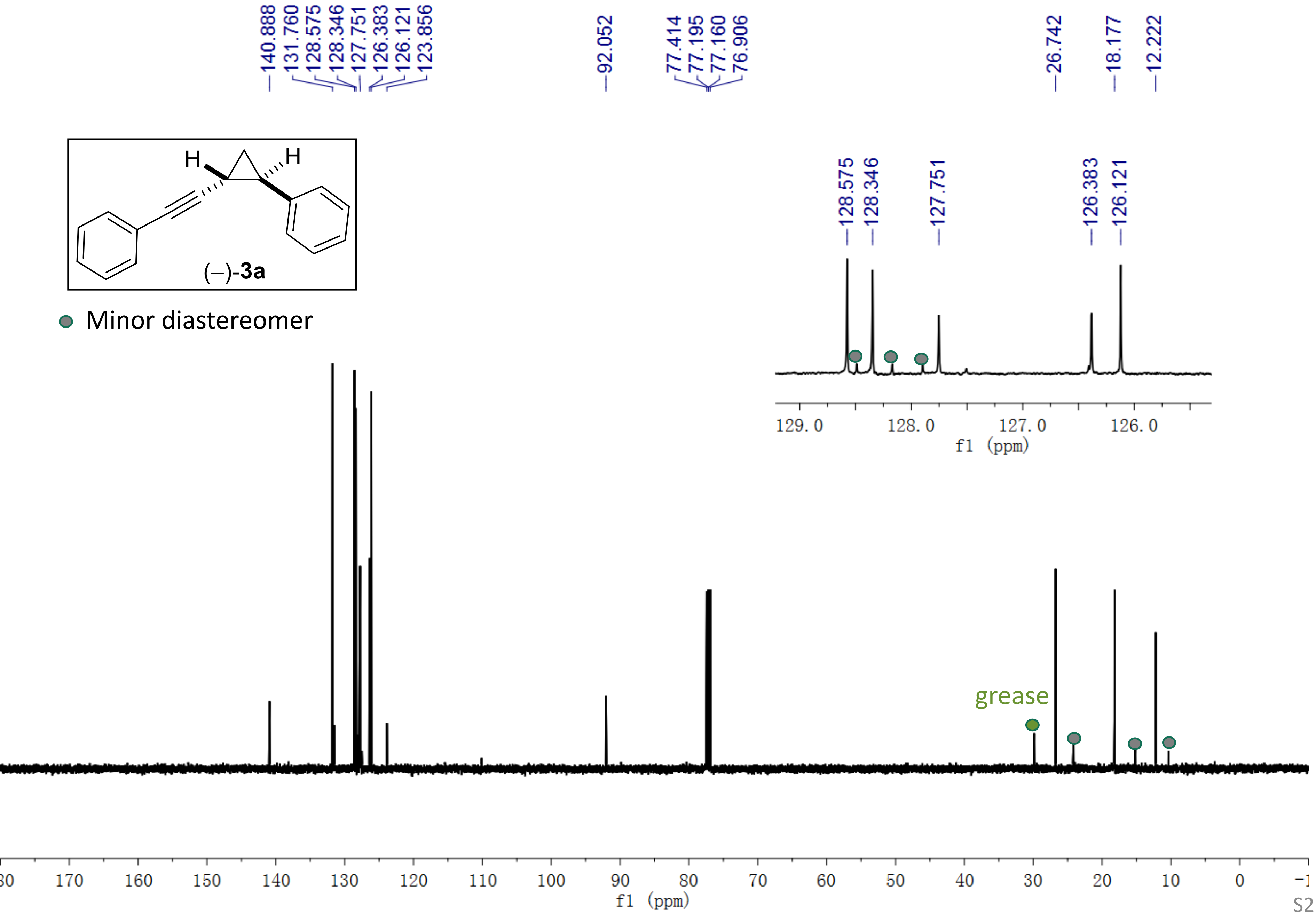
^{13}C NMR of **1k**, 151 MHz, $CDCl_3$



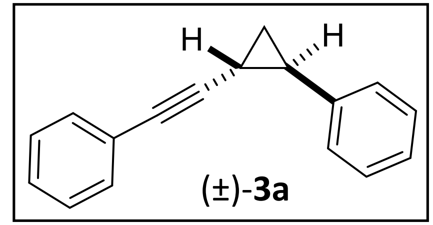
^{1}H NMR of **3a**, 500 MHz, $CDCl_3$



^{13}C NMR of **3a**, 126 MHz, $CDCl_3$

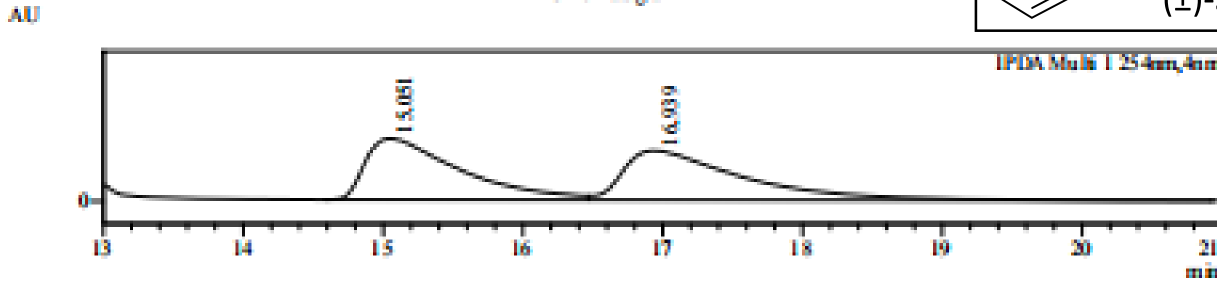


Data File	: J0K-0070-IC-0%-0.8ML-isopropanol-solvent004.lcd
Sample Name	: J0K-0070-IC-0%-0.8ML-isopropanol-solvent004
Sample ID	: J0K-0070-IC-0%-0.8ML-isopropano
Method File	: JK-0%-0.8ml.lcm

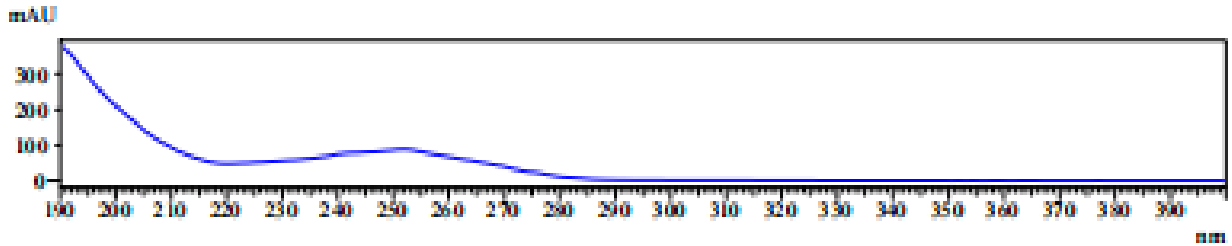


(±)-**3a**

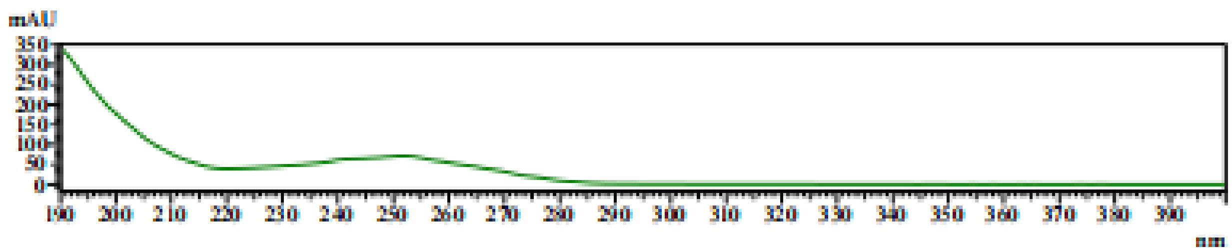
Chromatogram



UV Spectrum
Retention time = 15.051



UV Spectrum
Retention time = 16.939

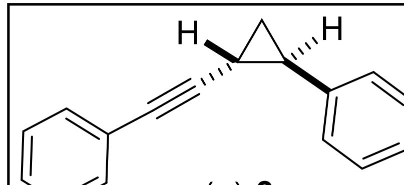


Peak Table

PDA Ch1 254nm

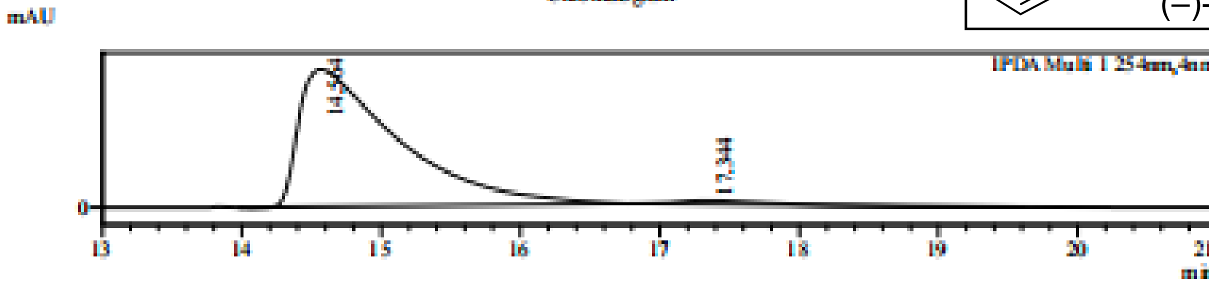
Peak#	Ret. Time	Area	Area%
1	15.051	3817557	49.333
2	16.939	3920860	50.667
Total		7738417	100.000

Data File : J0K-0068-IC-0%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0068-IC-0%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0068-IC-0%-0.8ML-isopropano
Method File : JK-0%-0.8ml.lcm

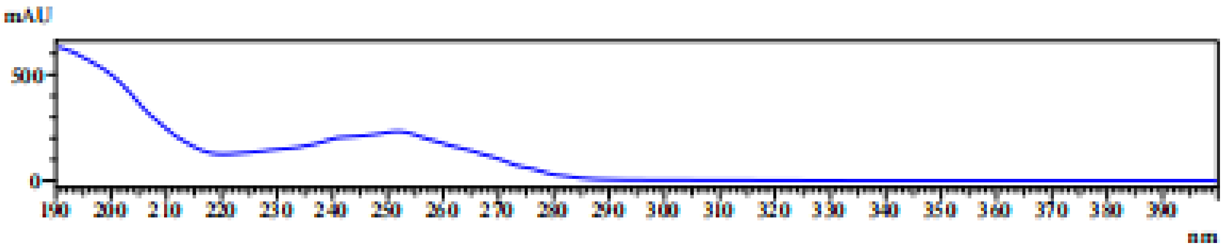


(–)-**3a**

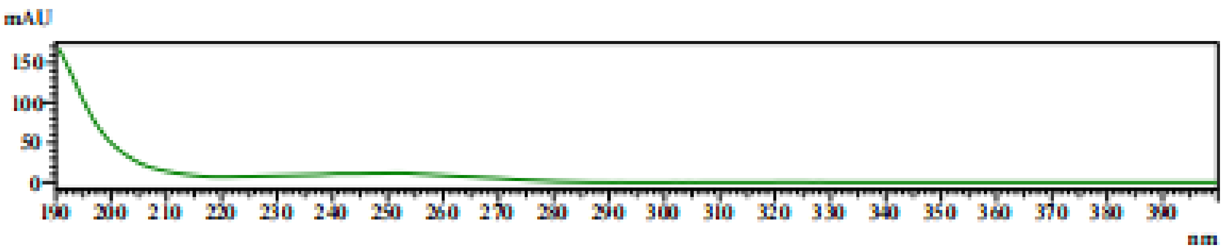
Chromatogram



UV Spectrum
Retention time= 14.564



UV Spectrum
Retention time= 17.344

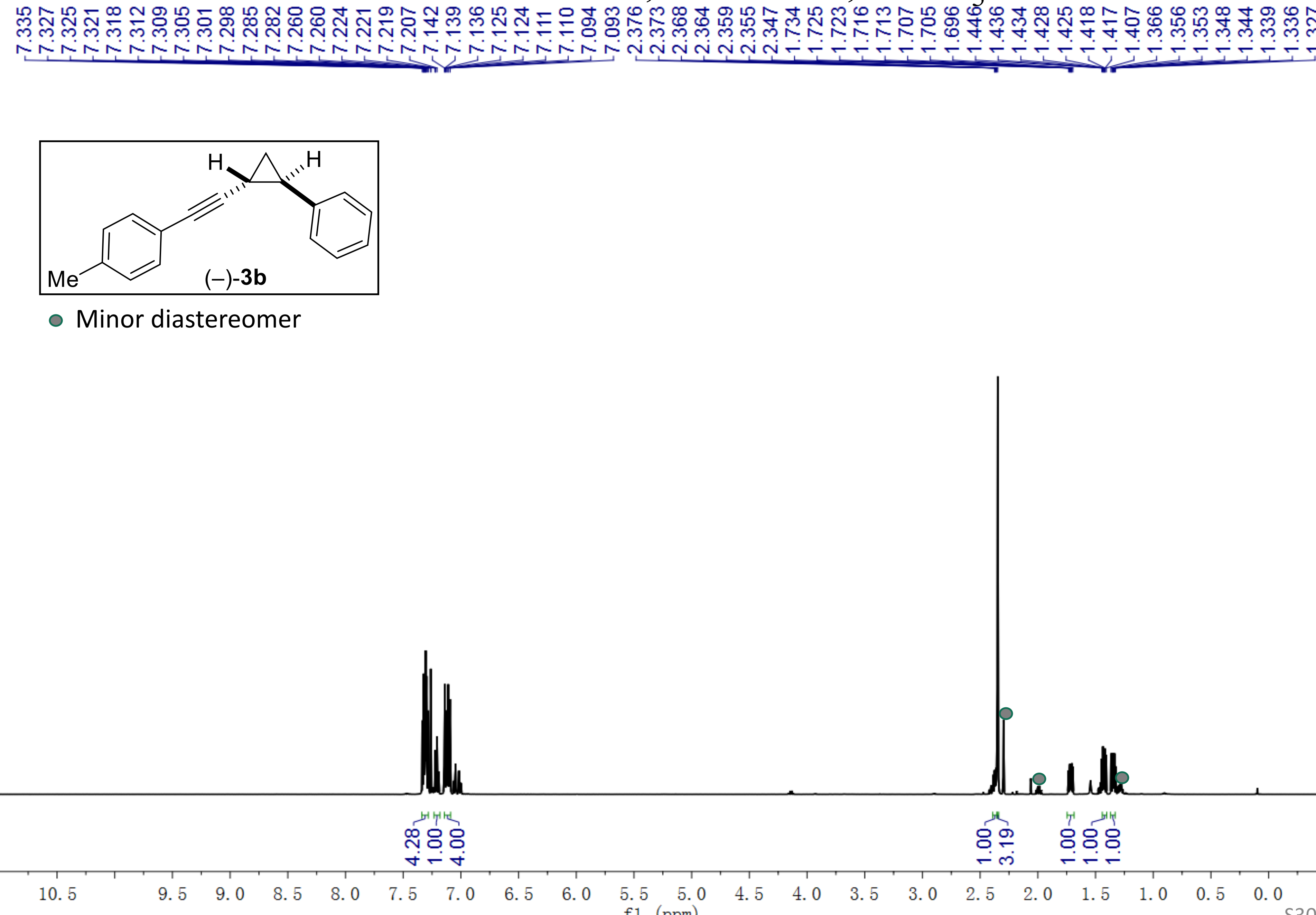


Peak Table

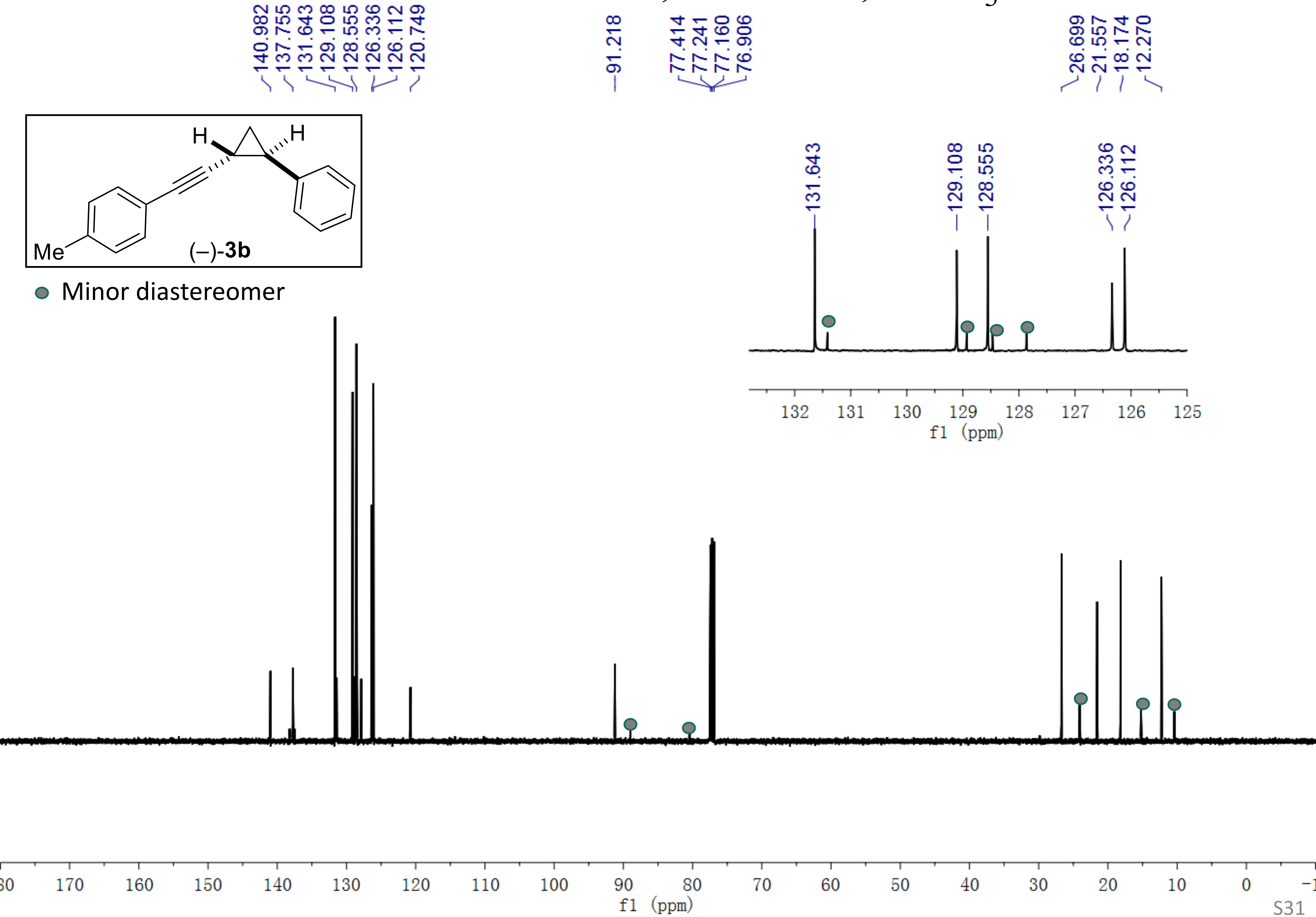
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.564	10795024	97.917
2	17.344	229635	2.083
Total		11024660	100.000

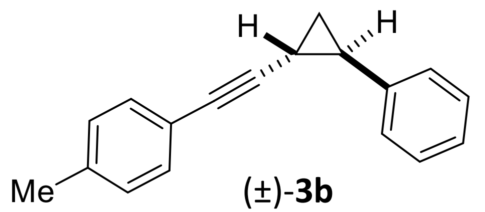
^{1}H NMR of **3b**, 500 MHz, $CDCl_3$



^{13}C NMR of **3b**, 126 MHz, $CDCl_3$

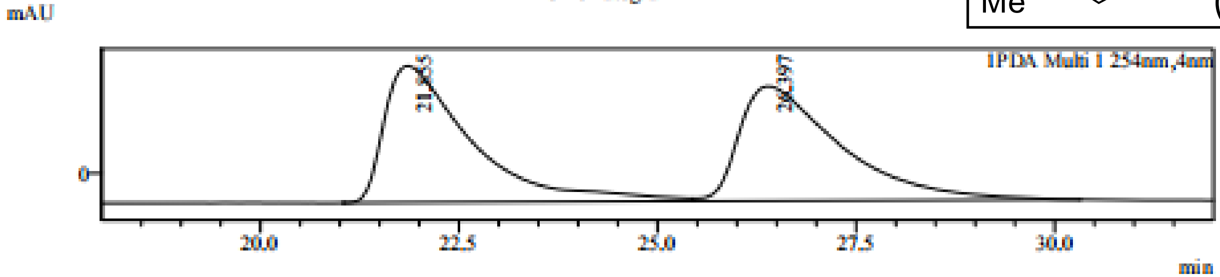


Data File : J0K-0097-IC-0%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0097-IC-0%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0097-IC-0%-0.8ML-isopropano
Method File : JK-0%-0.8ml.lcm

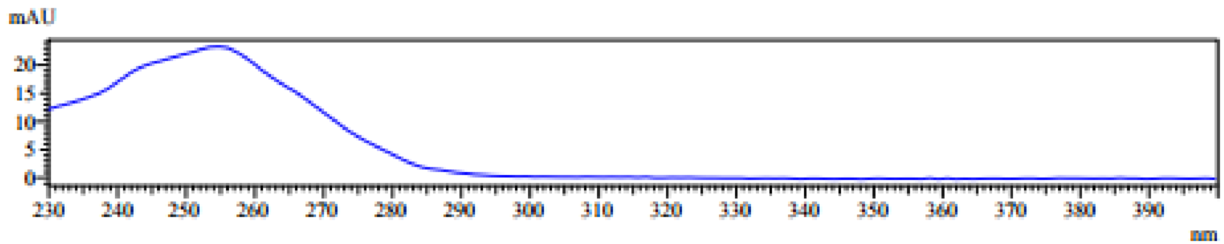


(±)-**3b**

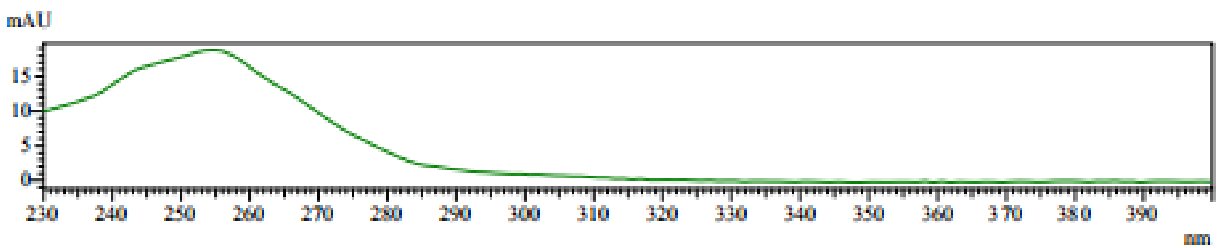
Chromatogram



UV Spectrum
Retention time = 21.855



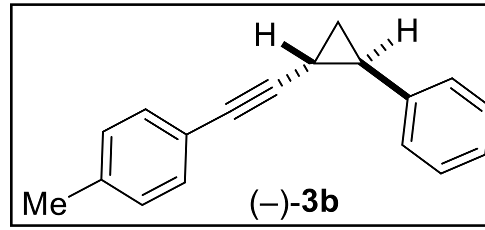
Retention time = 26.397



Peak Table

PDA Ch1 254nm

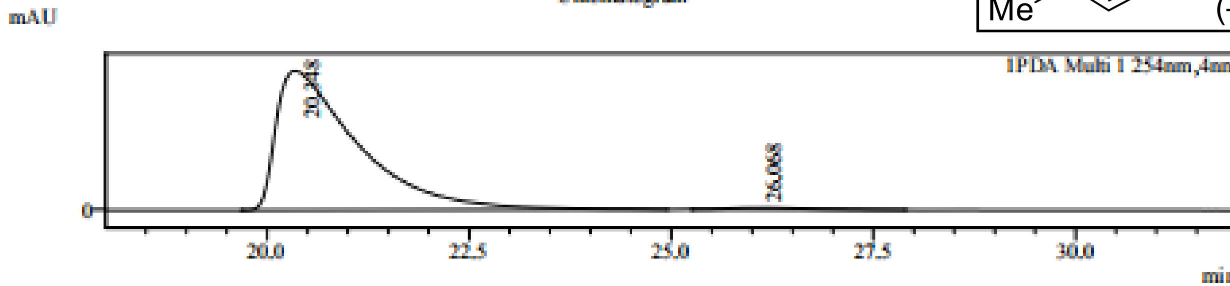
Peak#	Ret. Time	Area	Area%
1	21.855	2215993	50.737
2	26.397	2151617	49.263
Total		4367610	100.000



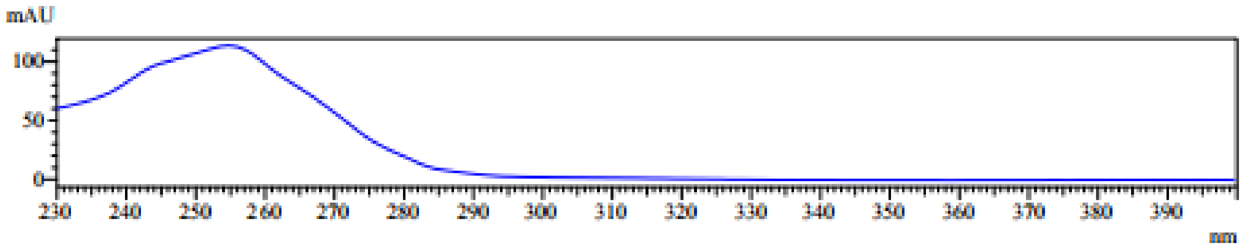
(–)-**3b**

Data File : J0K-0115-IC-0%-0.8ML-isopropanol-solvent004.lcd
Sample Name : J0K-0115-IC-0%-0.8ML-isopropanol-solvent004
Sample ID : J0K-0115-IC-0%-0.8ML-isopropano
Method File : JK-0%-0.8ml.lcm

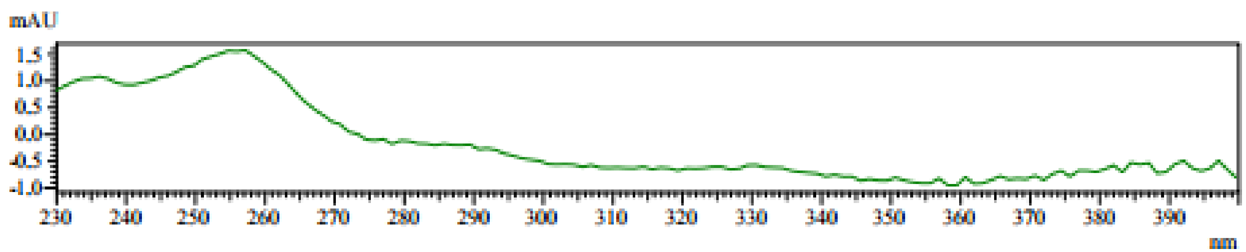
Chromatogram



UV Spectrum
Retention time = 20.348



I
Retention time = 26.068

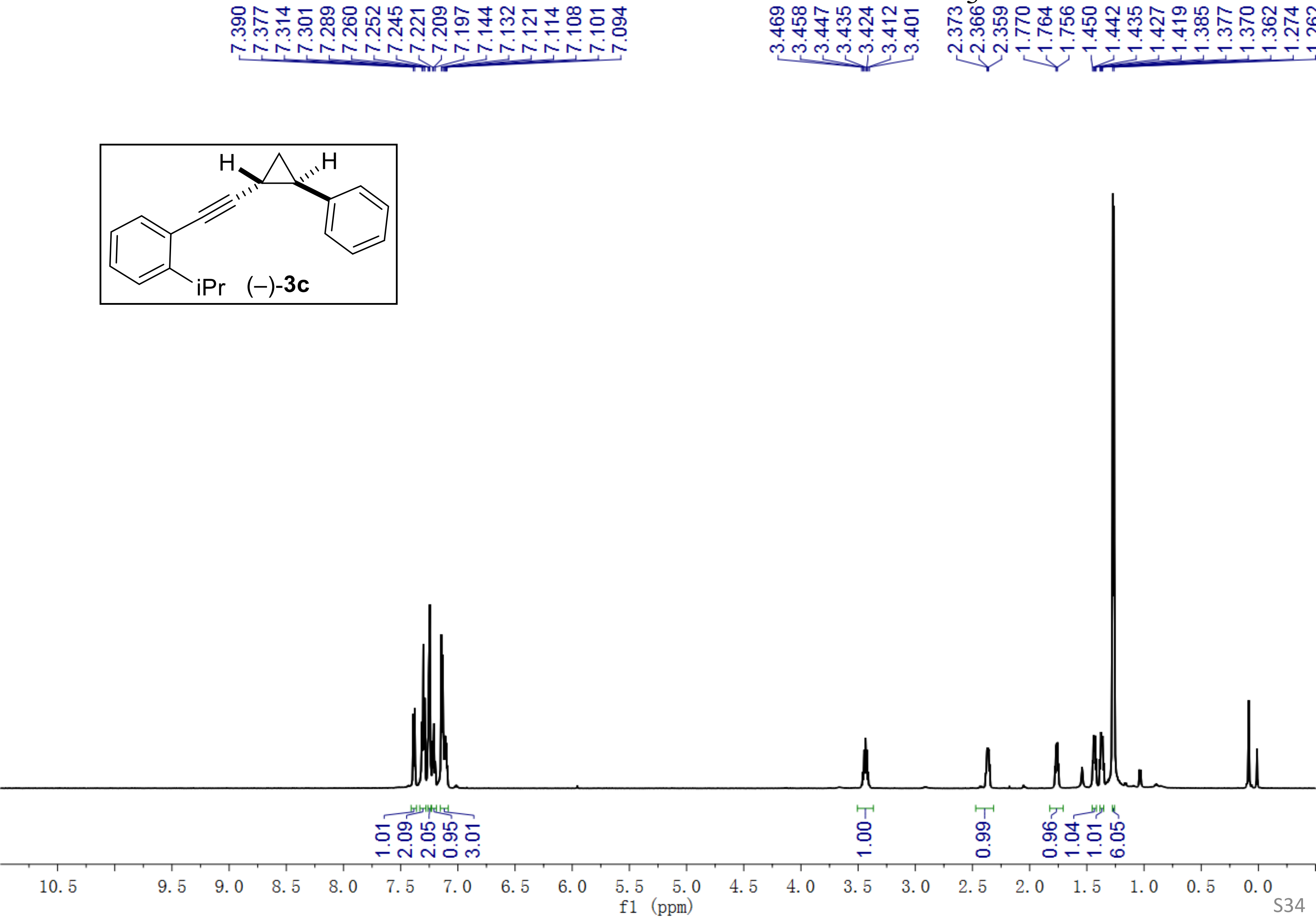


Peak Table

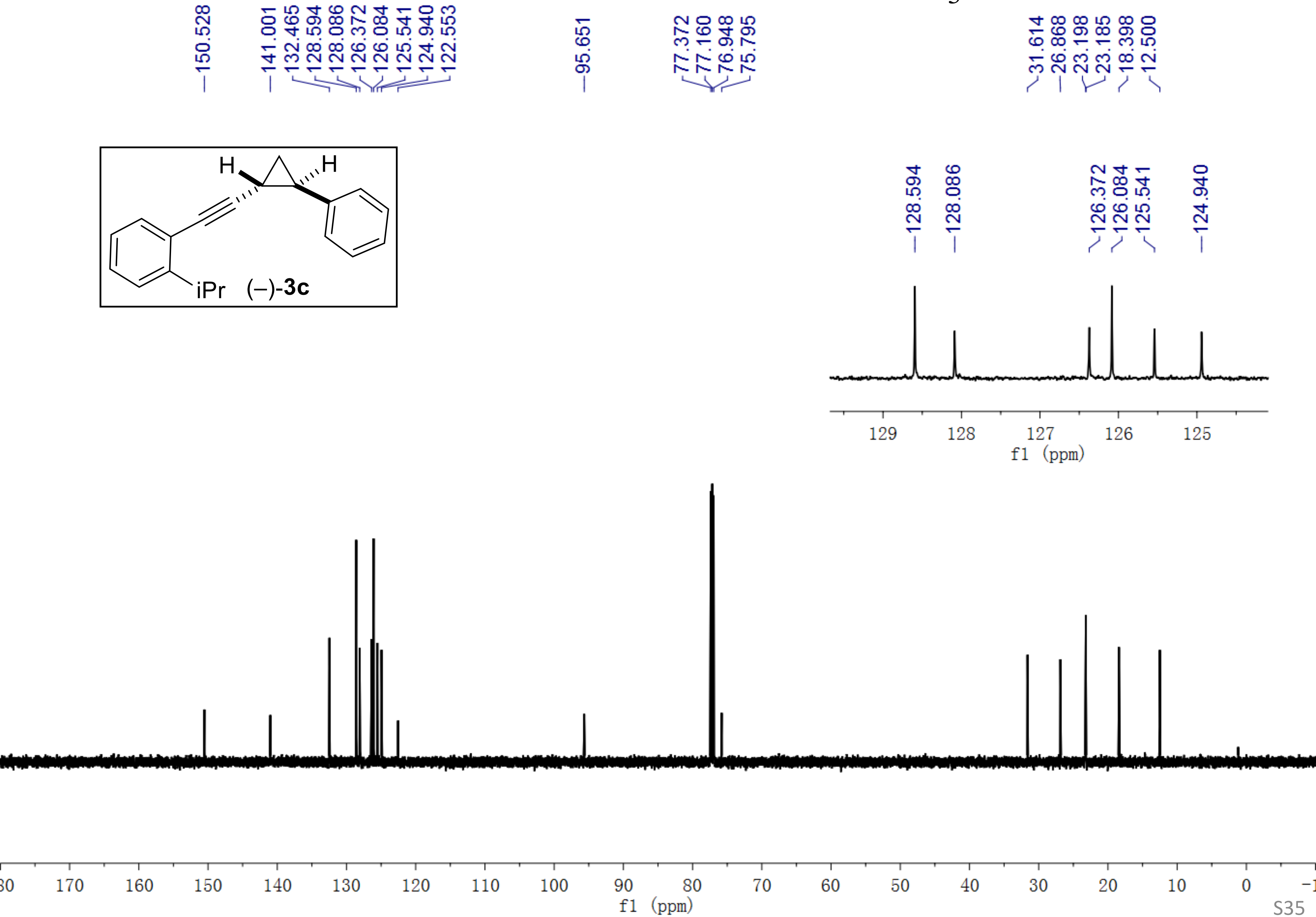
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.348	7849014	98.625
2	26.068	109463	1.375
Total		7958477	100.000

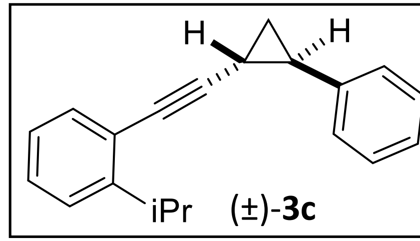
^{1}H NMR of **3c**, 600 MHz, $CDCl_3$


(–)-**3c**

^{13}C NMR of **3c**, 151 MHz, $CDCl_3$

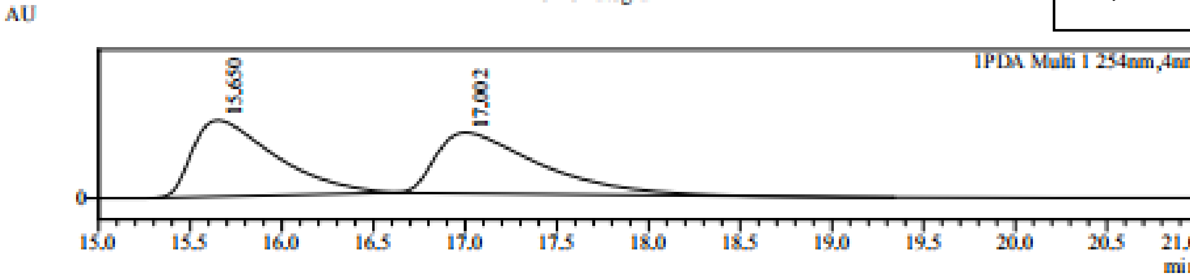


Data File : J0K-0241-12-IC-0%-0.5ML-isopropanol-solvent006-modified.lcd
Sample Name : J0K-0241-12-IC-0%-0.5ML-isopropanol-solvent006
Sample ID : J0K-0241-12-IC-0%-0.5ML-isoprop
Method File : J0K-0%-0.5ml.lcm

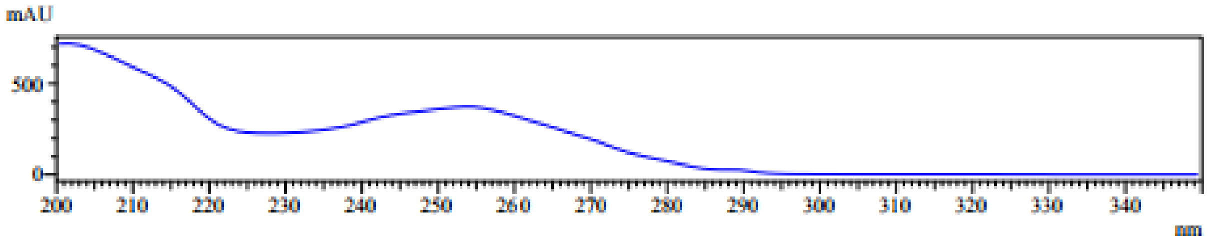


(±)-**3c**

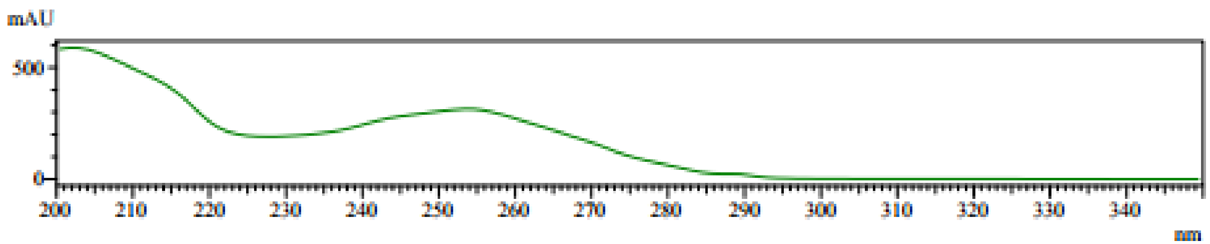
Chromatogram



UV Spectrum
Retention time = 15.650



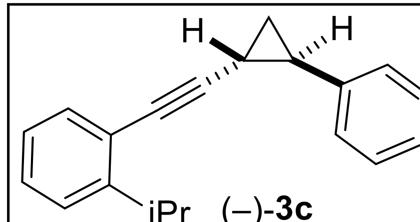
Retention time = 17.002



Peak Table

PDA Ch1 254nm

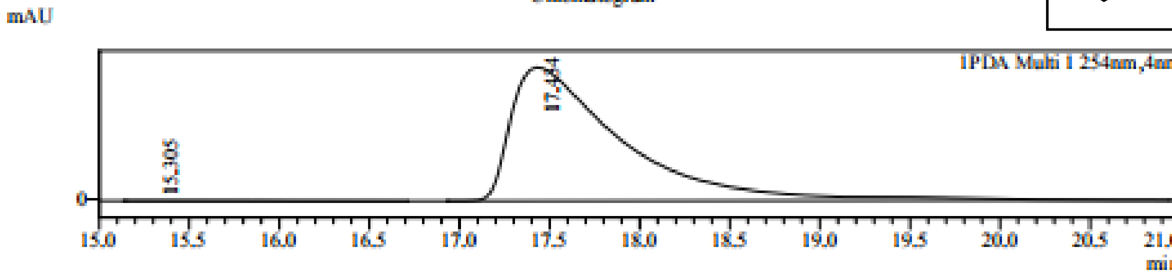
Peak#	Ret. Time	Area	Area%
1	15.650	11294352	50.388
2	17.002	11120560	49.612
Total		22414912	100.000



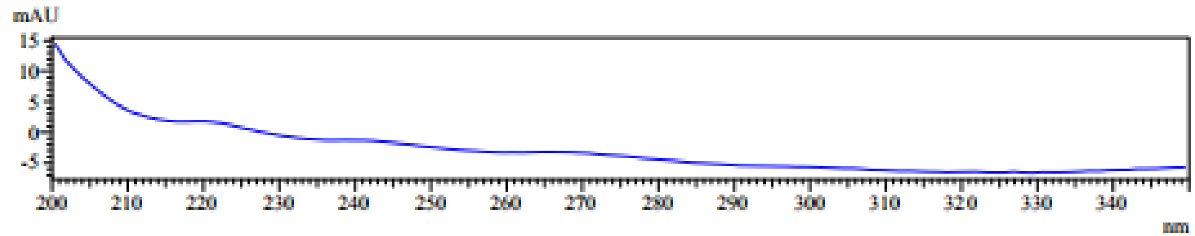
(–)-**3c**

Data File	:	J0K-0242-13-IC-0%-0.5ML-isopropanol-solvent005-modified.lcd
Sample Name	:	J0K-0242-13-IC-0%-0.5ML-isopropanol-solvent005
Sample ID	:	J0K-0242-13-IC-0%-0.5ML-isoprop
Method File	:	J0K-0%-0.5ml.lcm

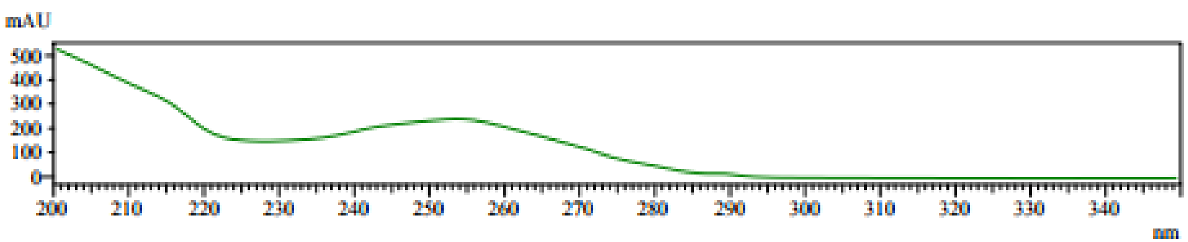
Chromatogram



UV Spectrum
Retention time = 15.305



Retention time = 17.434

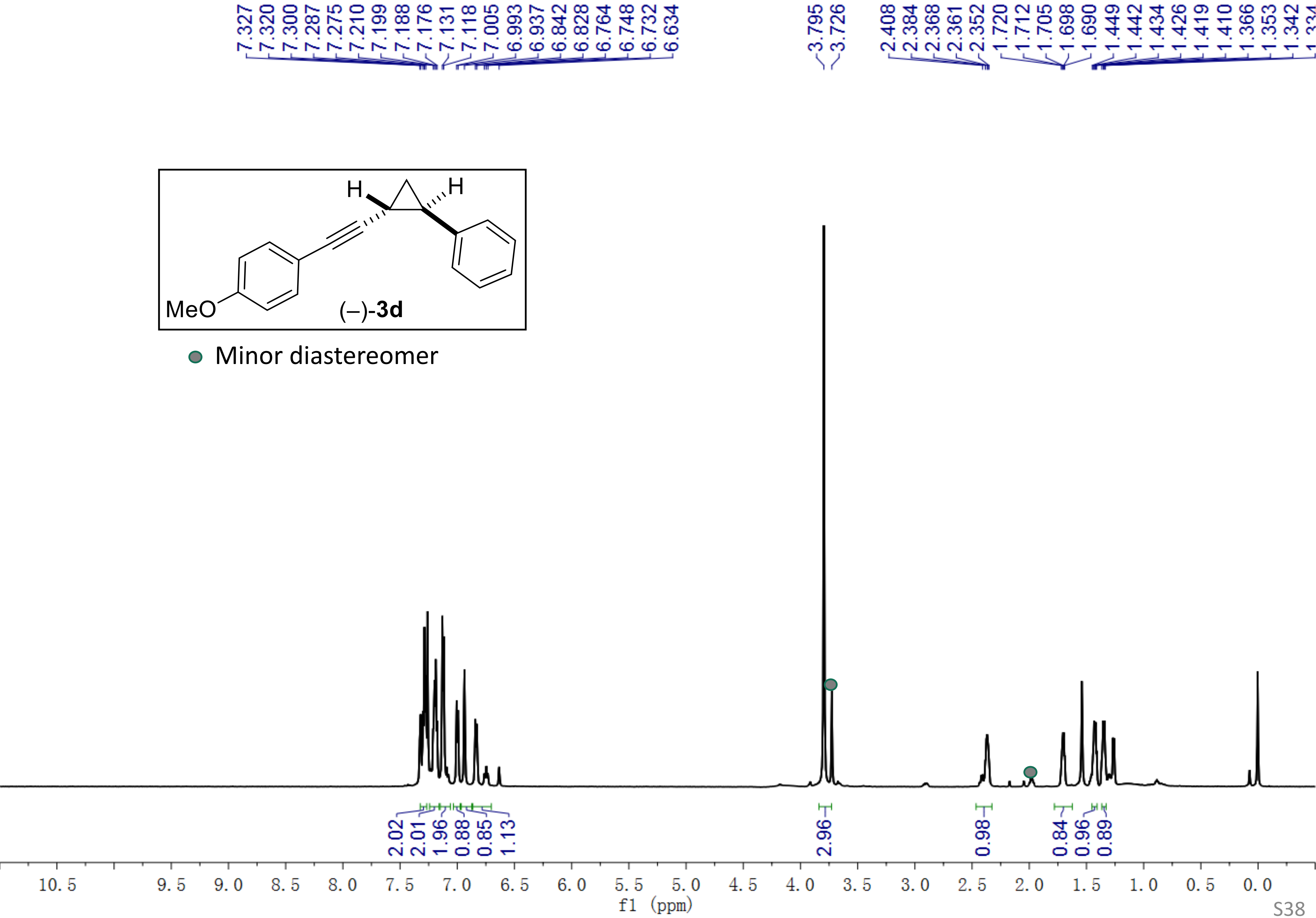


Peak Table

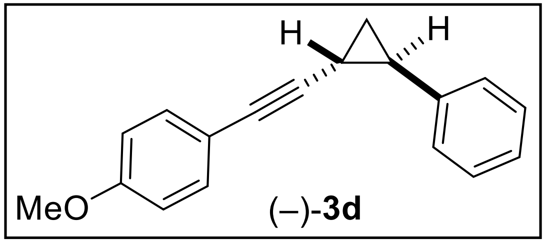
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.305	21830	0.213
2	17.434	10222096	99.787
Total		10243926	100.000

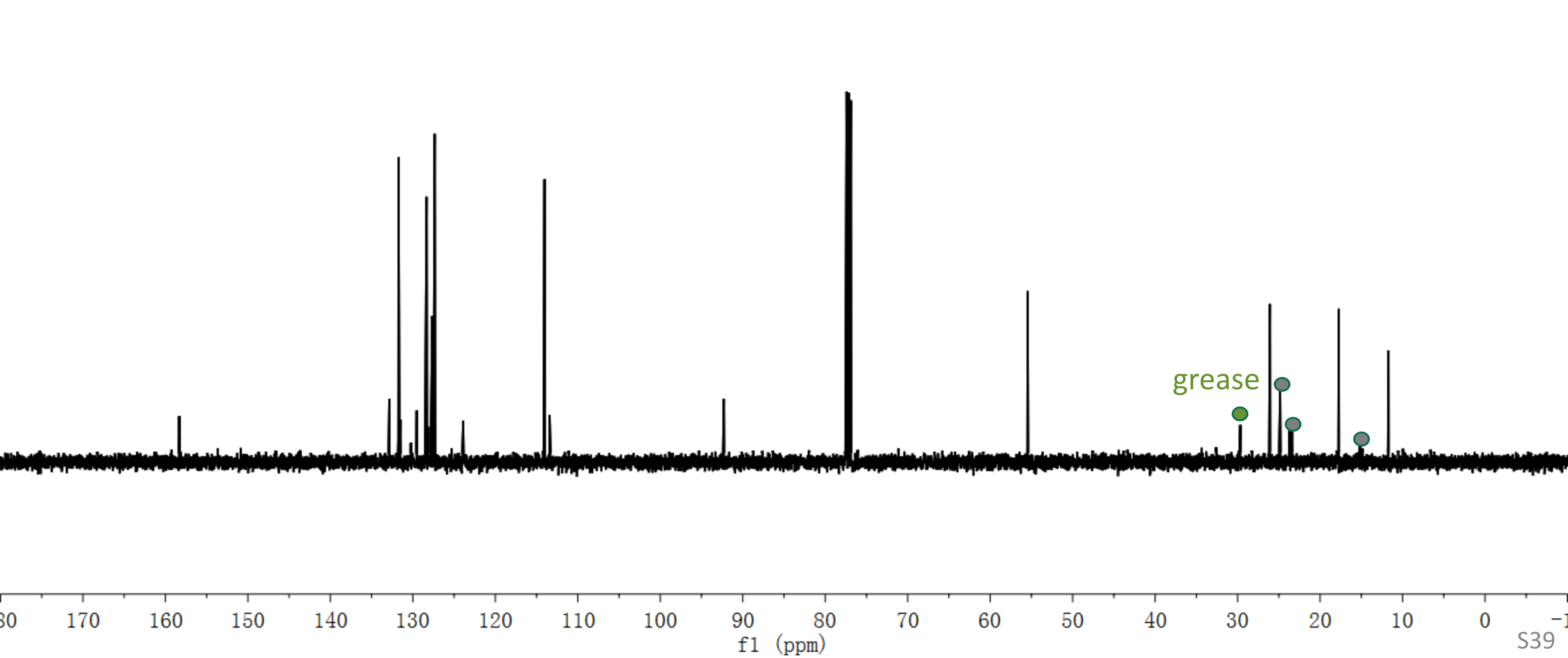
^{1}H NMR of **3d**, 500 MHz, $CDCl_3$

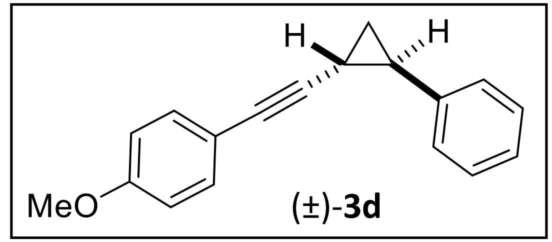


^{13}C NMR of **3d**, 126 MHz, $CDCl_3$



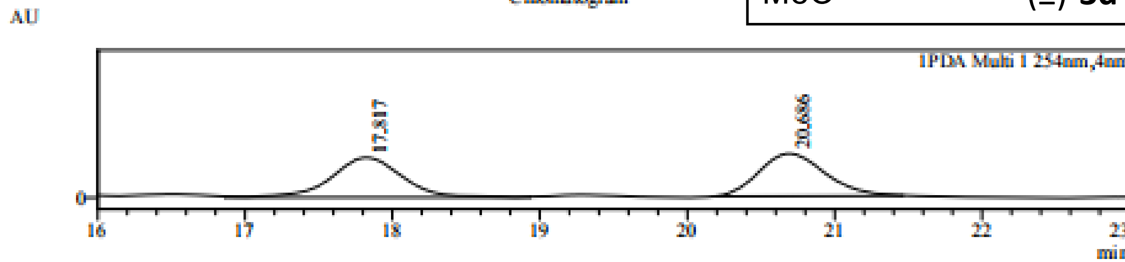
(–)-**3d**



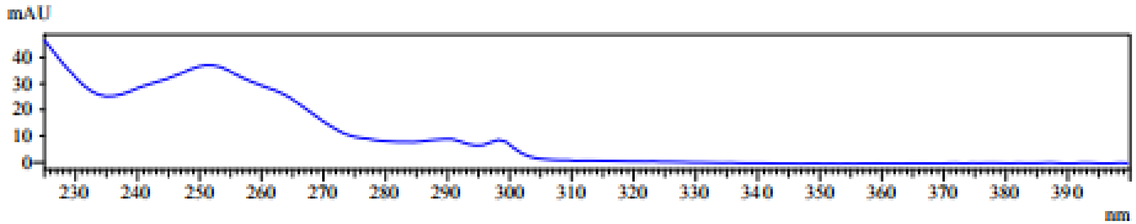


Data File : J0K-0608-ID-0.5%-0.8ML.lcd
Sample Name : J0K-0608-ID-0.5%-0.8ML
Sample ID : J0K-0608-ID-0.5%-0.8ML
Method File : J0K-0.5%--35min-0.8ml.lcm

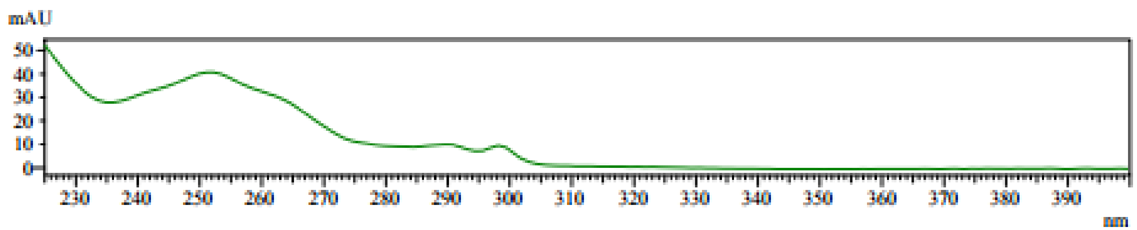
Chromatogram



UV Spectrum
Retention time = 17.817



Retention time = 20.686

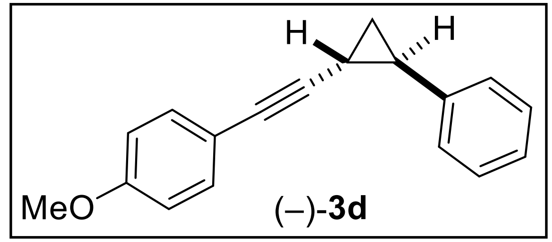


Peak Table

PDA Ch1 254nm

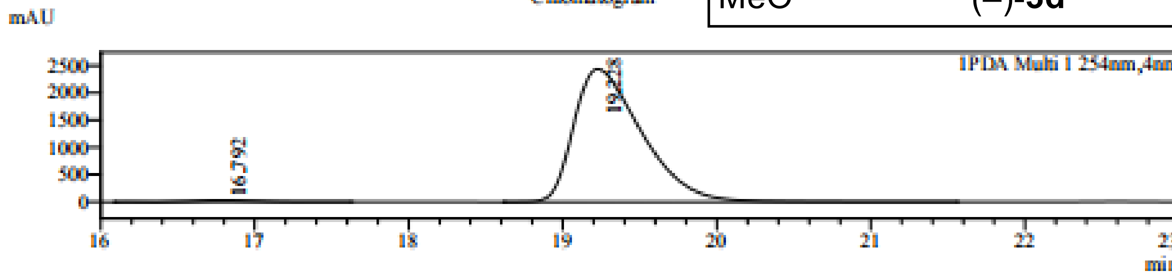
Peak#	Ret. Time	Area	Area%
1	17.817	1175582	50.070
2	20.686	1172308	49.930
Total		2347890	100.000

Data File : J0K-0607-ID-3-0.5%-0.8ML.lcd
Sample Name : J0K-0607-ID-3-0.5%-0.8ML
Sample ID : J0K-0607-ID-3-0.5%-0.8ML
Method File : J0K-0.5%--35min-0.8ml.lcm

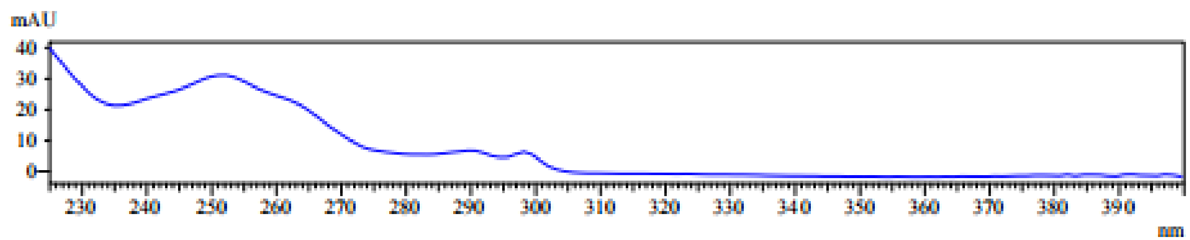


(–)-**3d**

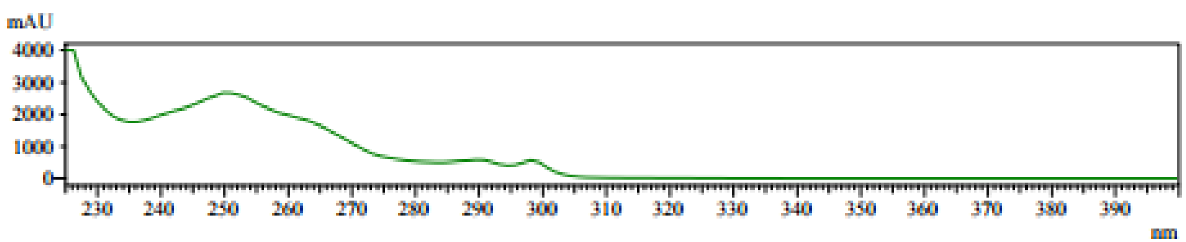
Chromatogram



UV Spectrum
Retention time = 16.792



Retention time = 19.228

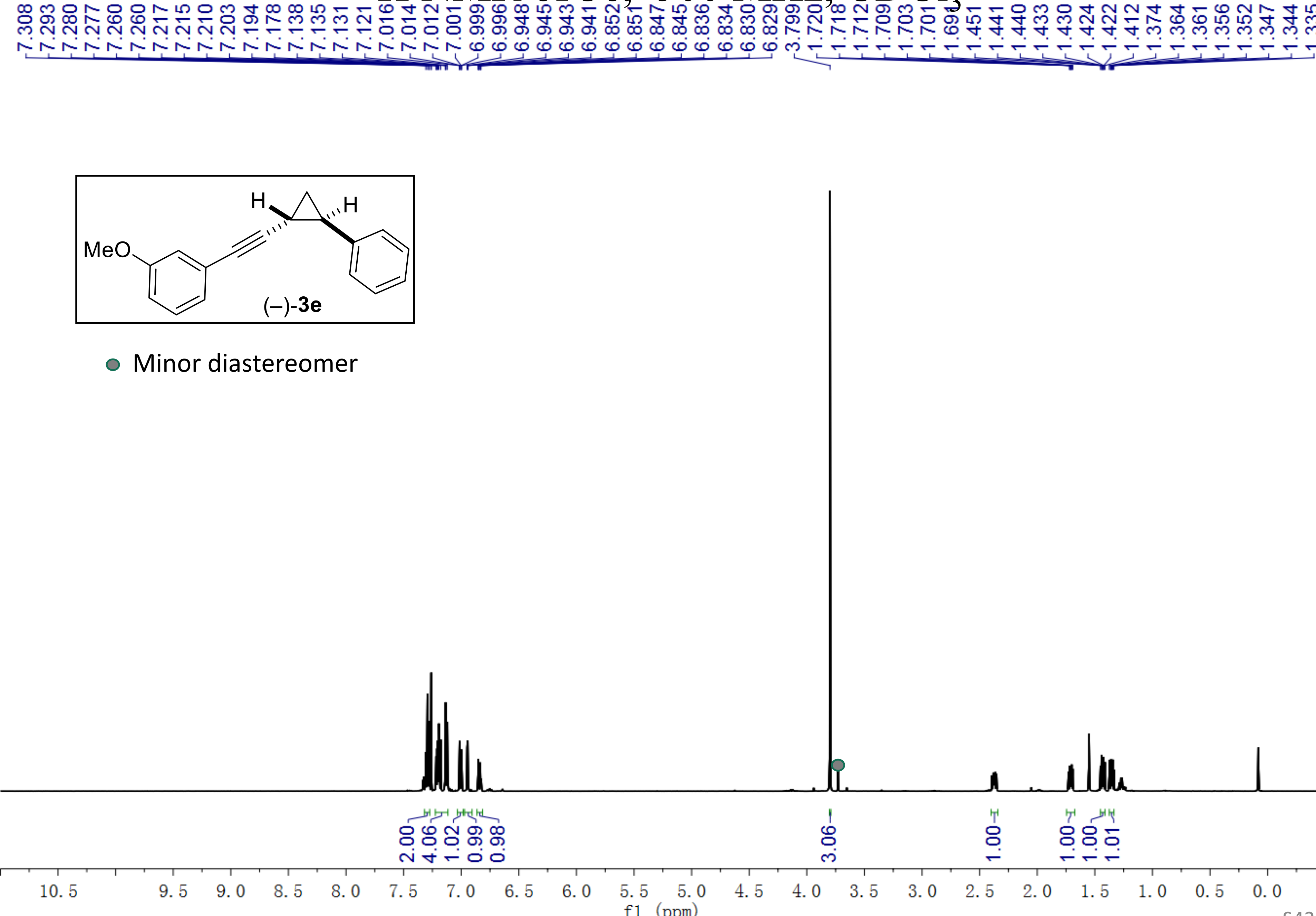


Peak Table

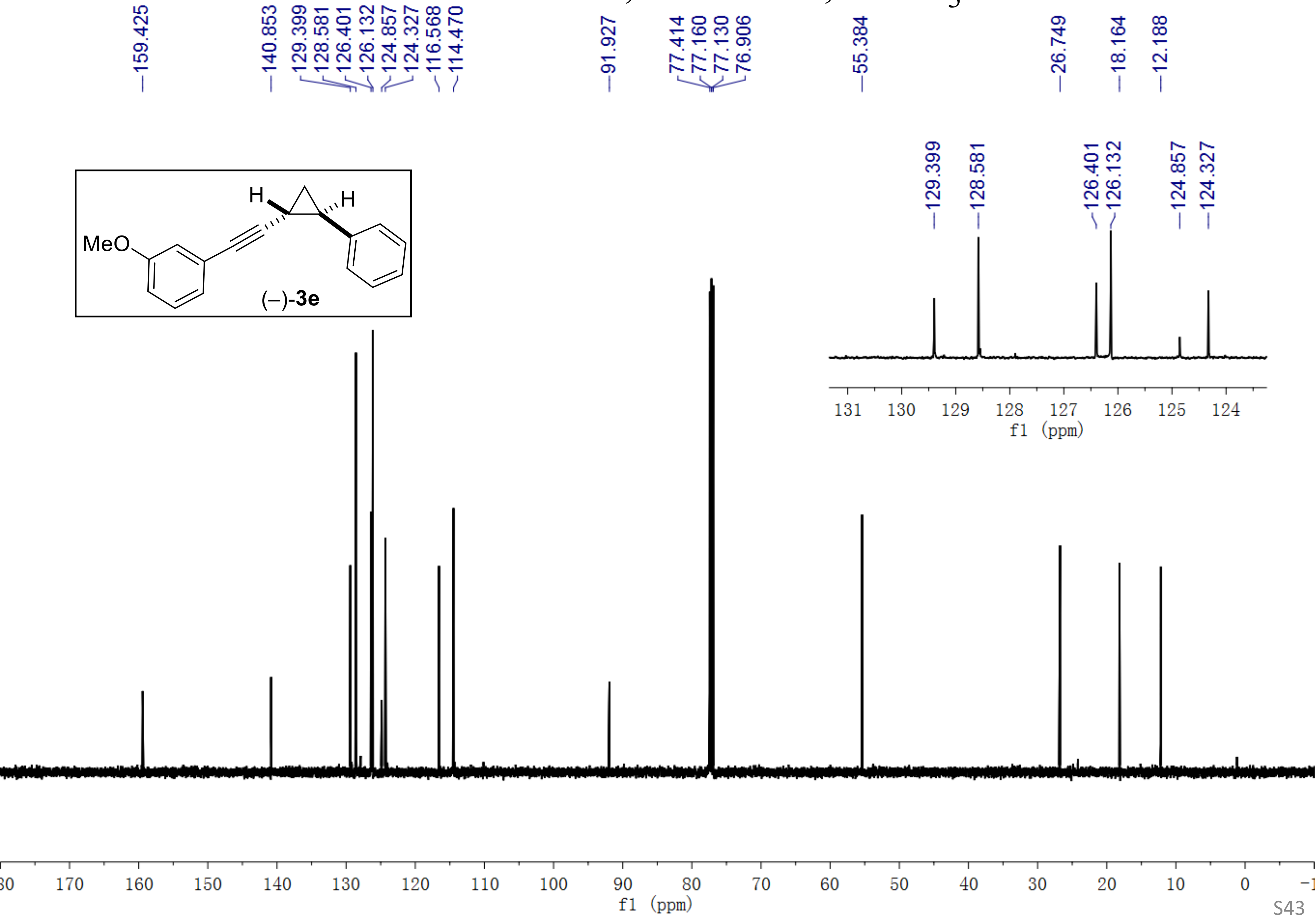
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.792	866540	1.151
2	19.228	74413811	98.849
Total		75280351	100.000

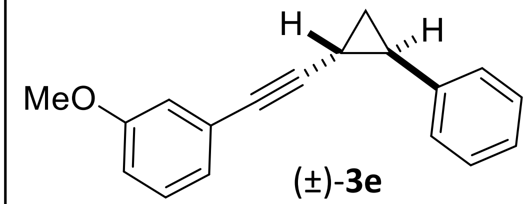
[1]H NMR of **3e**, 500 MHz, $CDCl_3$



^{13}C NMR of **3e**, 126 MHz, $CDCl_3$

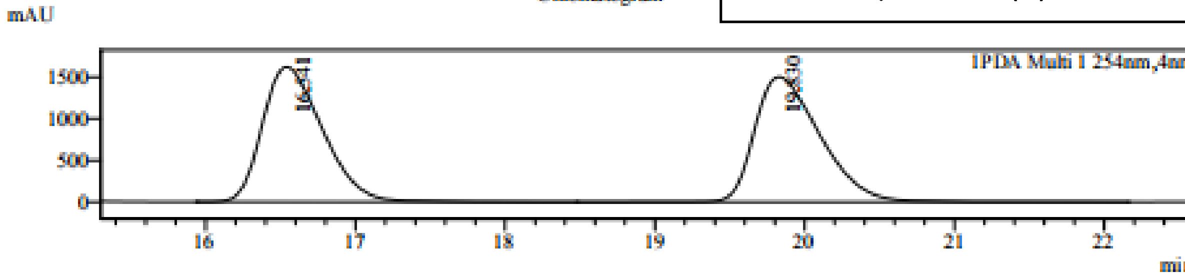


Data File : J0K-0606-IE-0.5%-0.8ML.lcd
Sample Name : J0K-0606-IE-0.5%-0.8ML
Sample ID : J0K-0606-IE-0.5%-0.8ML
Method File : J0K-0.5%--35min-0.8ml.lcm

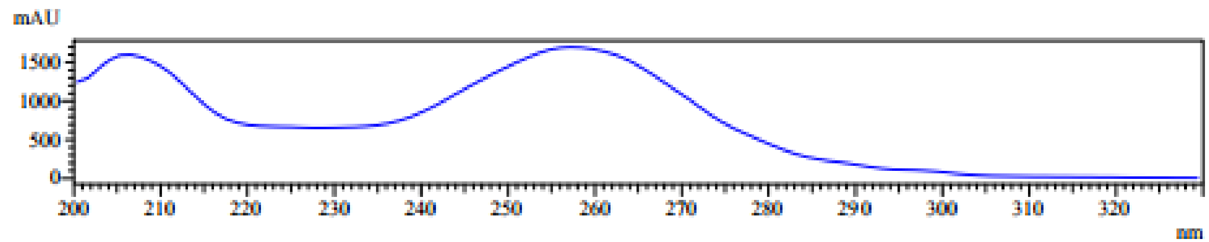


(±)-3e

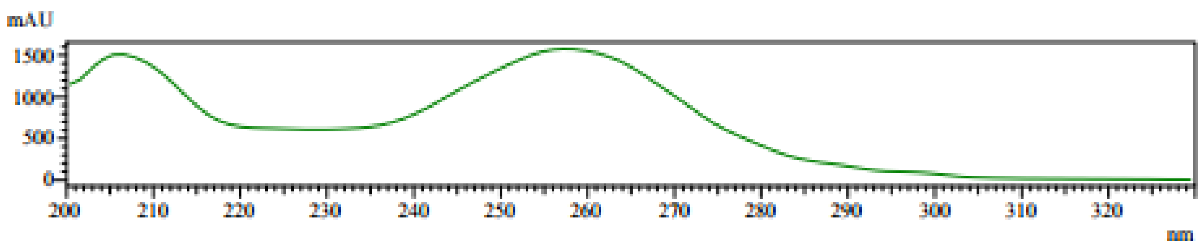
Chromatogram



UV Spectrum
Retention time = 16.541



L
Retention time = 19.830

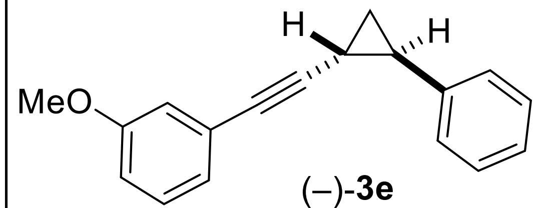


Peak Table

PDA Ch1 254nm

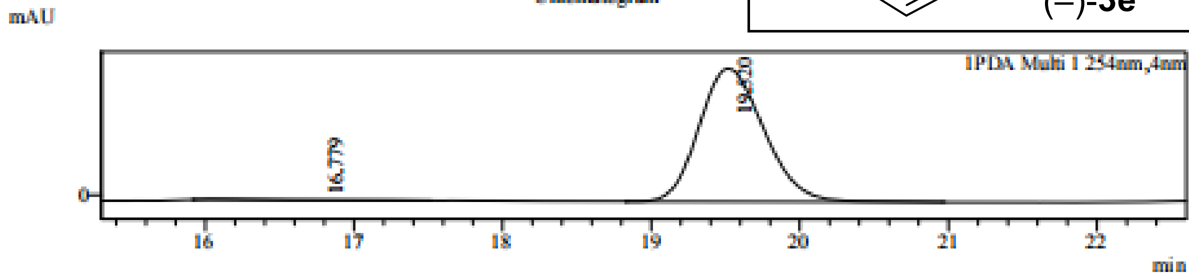
Peak#	Ret. Time	Area	Area%
1	16.541	45091963	49.821
2	19.830	45416294	50.179
Total		90508257	100.000

Data File : J0K-0605-IE-2-0.5%-0.8ML.lcd
Sample Name : J0K-0605-IE-2-0.5%-0.8ML
Sample ID : J0K-0605-IE-2-0.5%-0.8ML
Method File : J0K-0.5%--35min-0.8ml.lcm

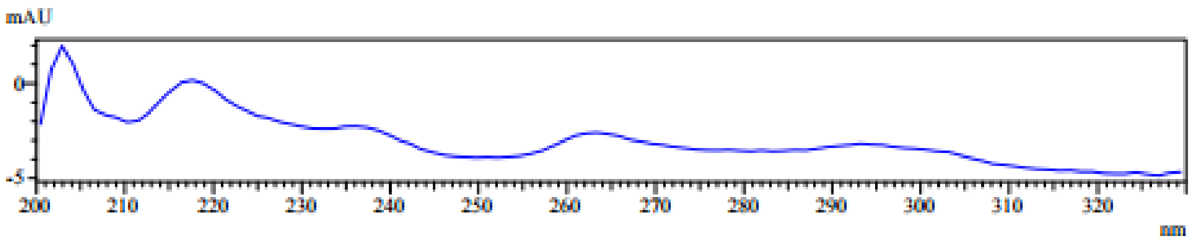


(–)-**3e**

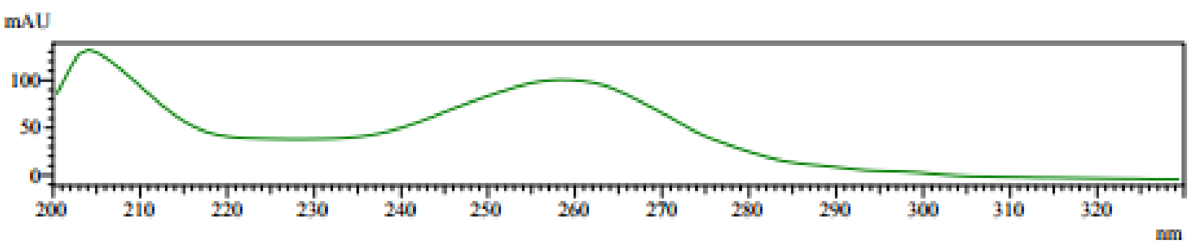
Chromatogram



UV Spectrum
Retention time = 16.779



I.
Retention time = 19.520

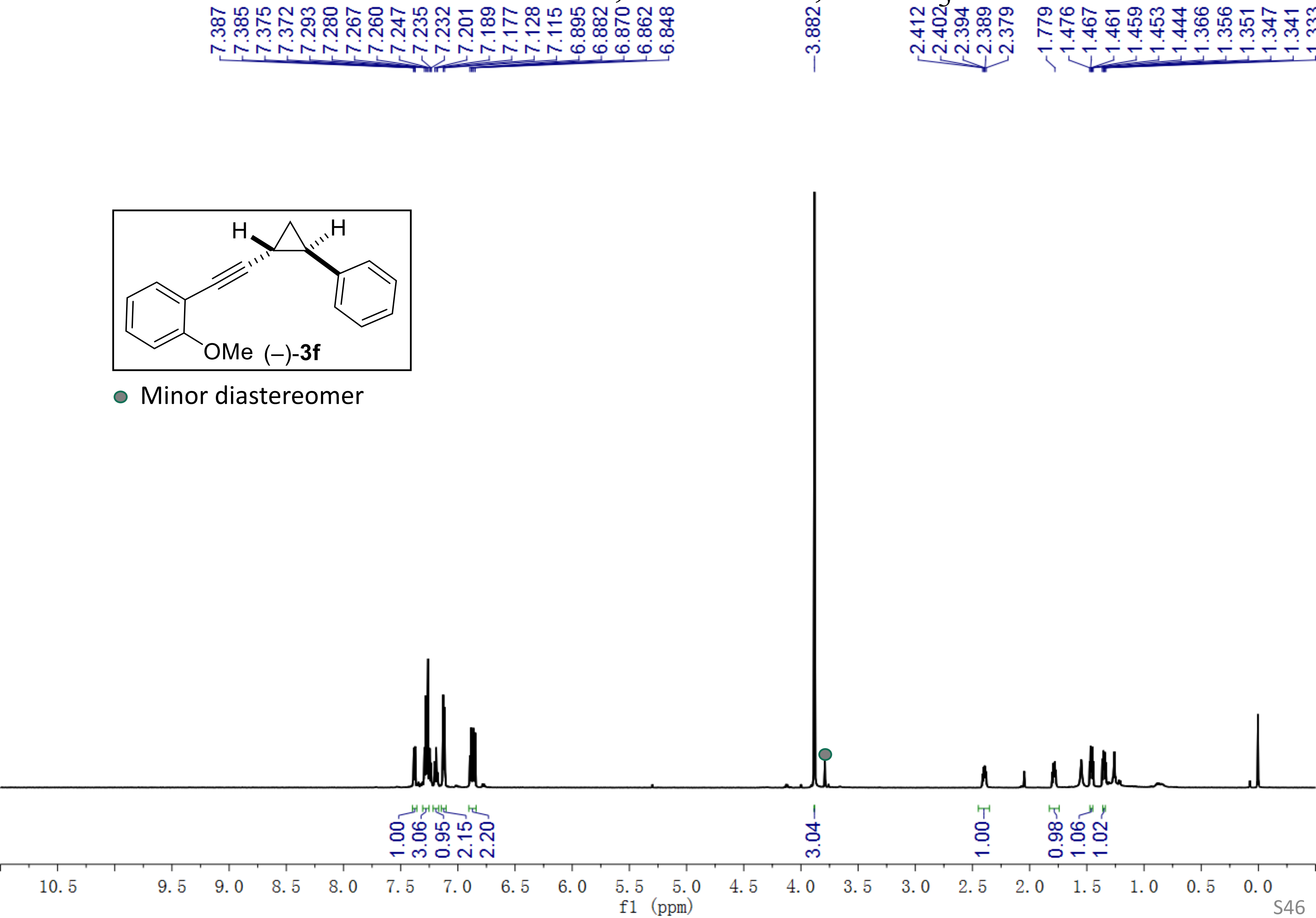


Peak Table

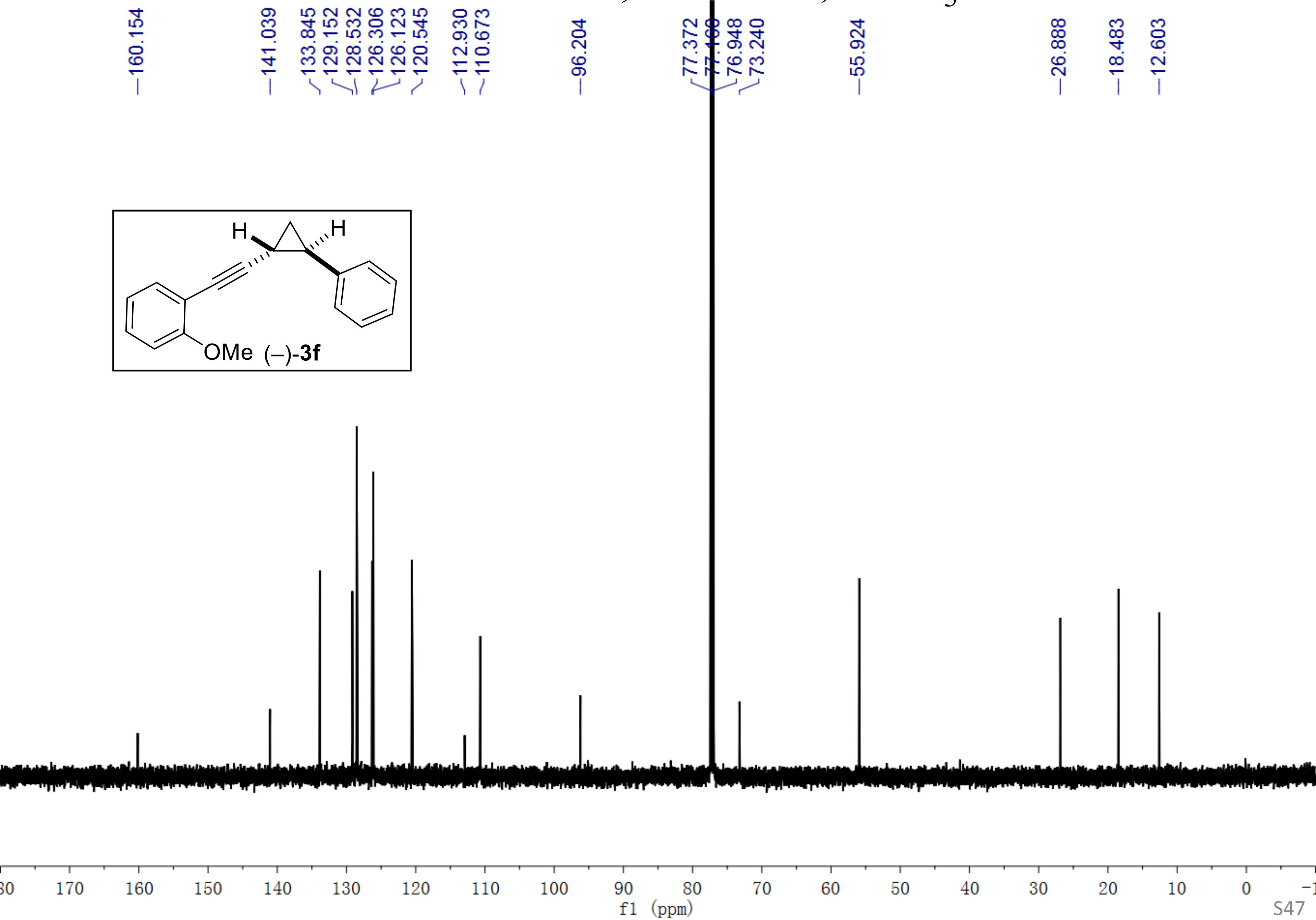
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.779	10536	0.348
2	19.520	3013872	99.652
Total		3024408	100.000

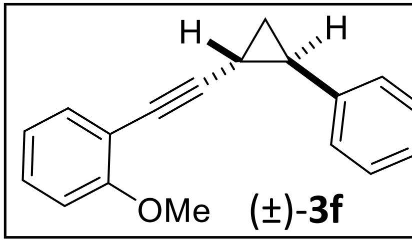
^{1}H NMR of **3f**, 600 MHz, $CDCl_3$



^{13}C NMR of **3f**, 151 MHz, $CDCl_3$

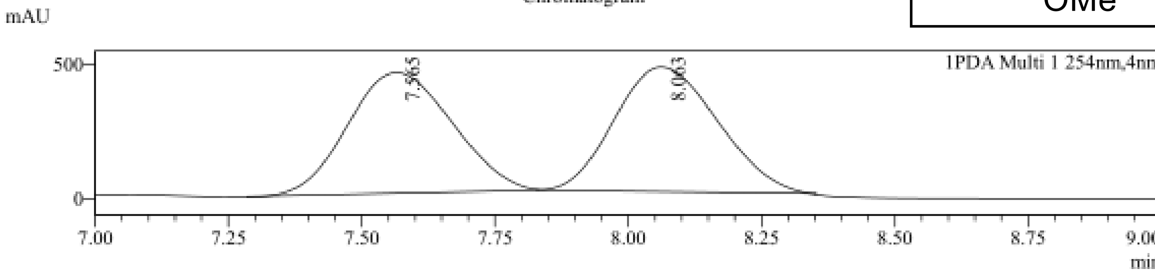


Data File : J0K-0143-IA-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0143-IA-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0143-IA-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml.lcm

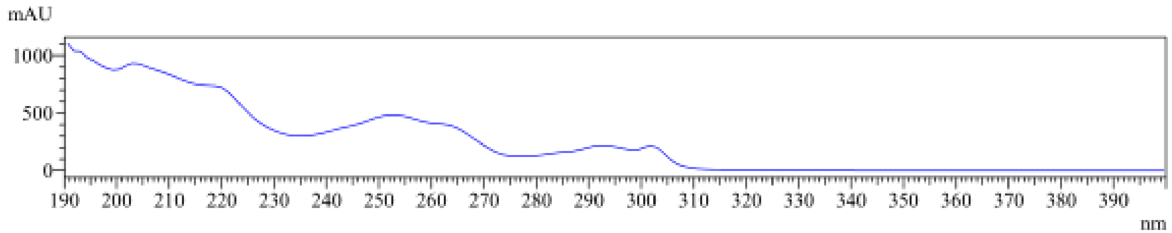


(±)-3f

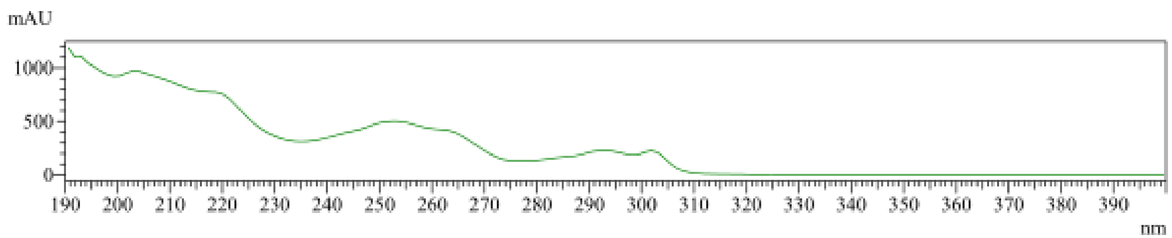
Chromatogram



UV Spectrum
Retention time = 7.565



UV Spectrum
Retention time = 8.063

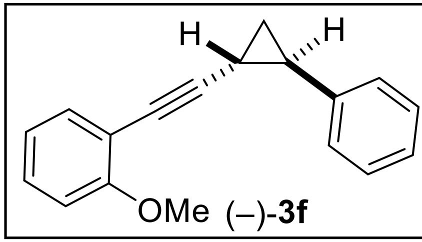


Peak Table

PDA Ch1 254nm

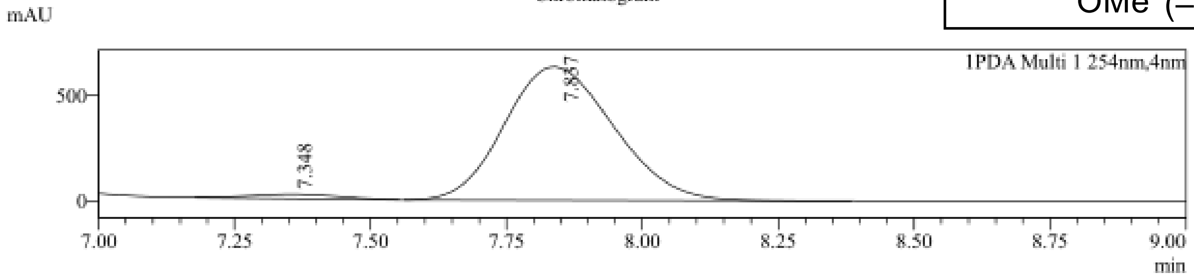
Peak#	Ret. Time	Area	Area%
1	7.565	6121948	49.586
2	8.063	6224168	50.414
Total		12346117	100.000

Data File : J0K-0153-IA-6-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0153-IA-6-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0153-IA-6-1%-0.8ML-isopropa
Method File : J0K-1%--15min-0.8ml.lcm

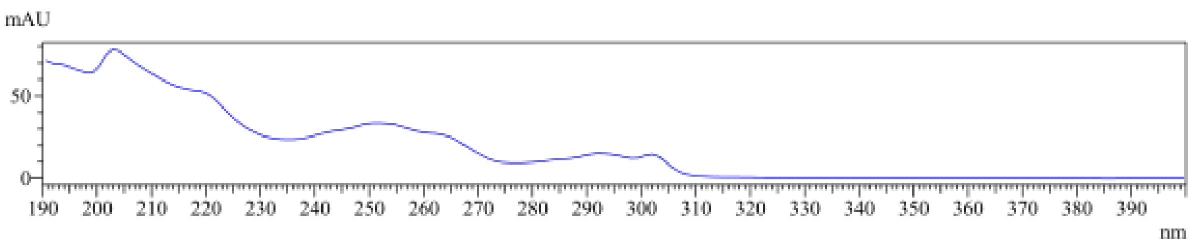


(–)-**3f**

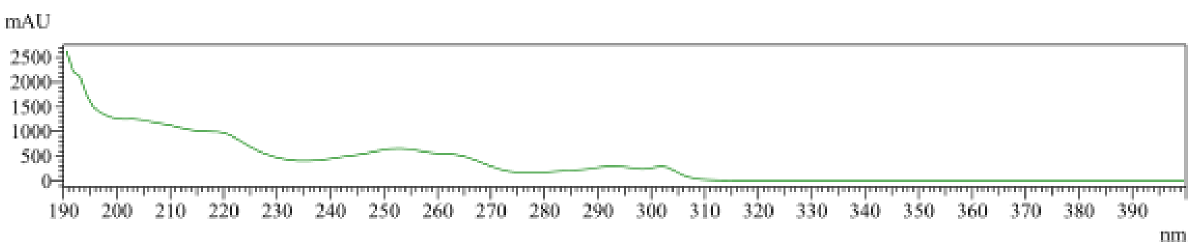
Chromatogram



UV Spectrum
Retention time = 7.348



UV Spectrum
Retention time = 7.837

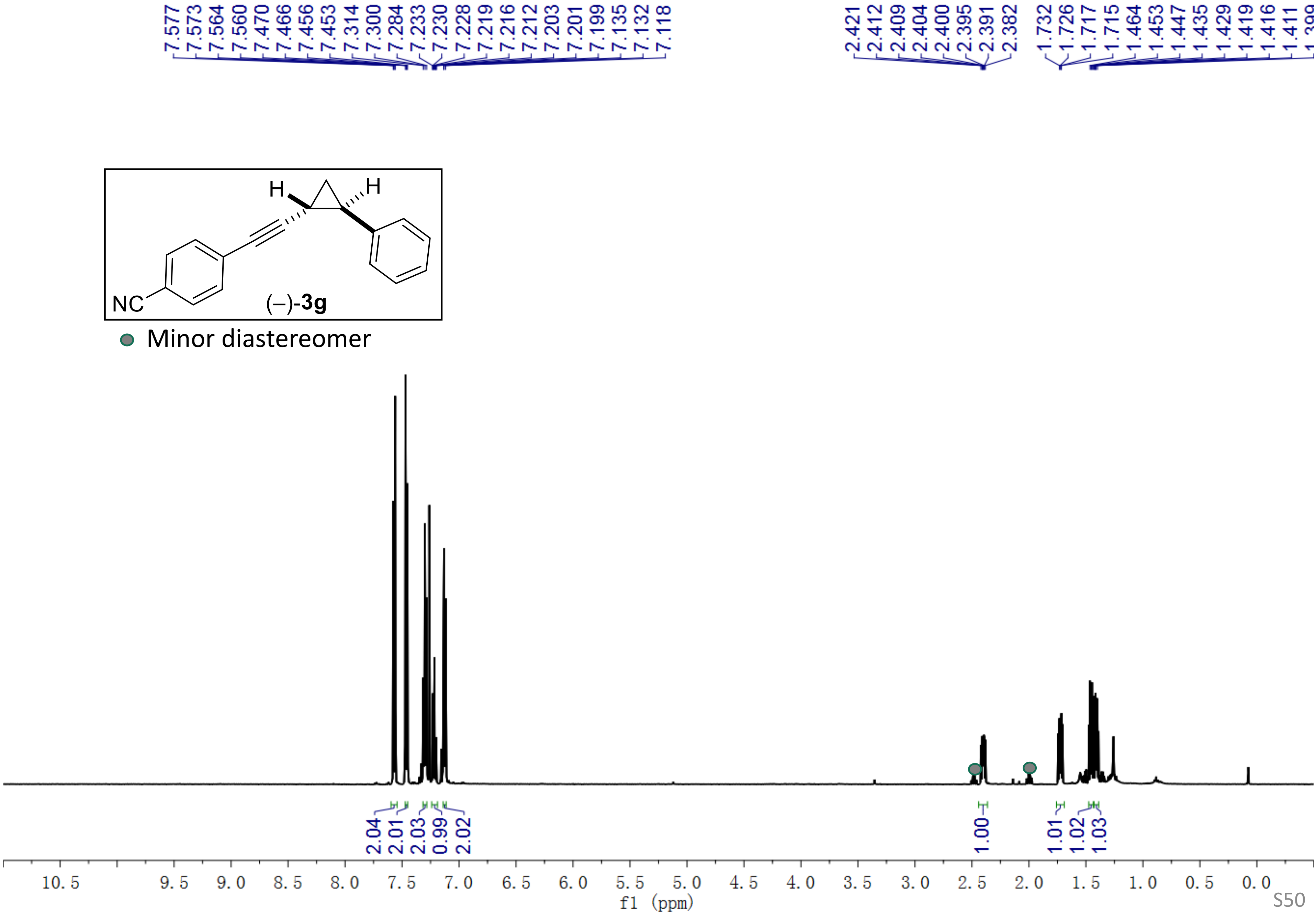


Peak Table

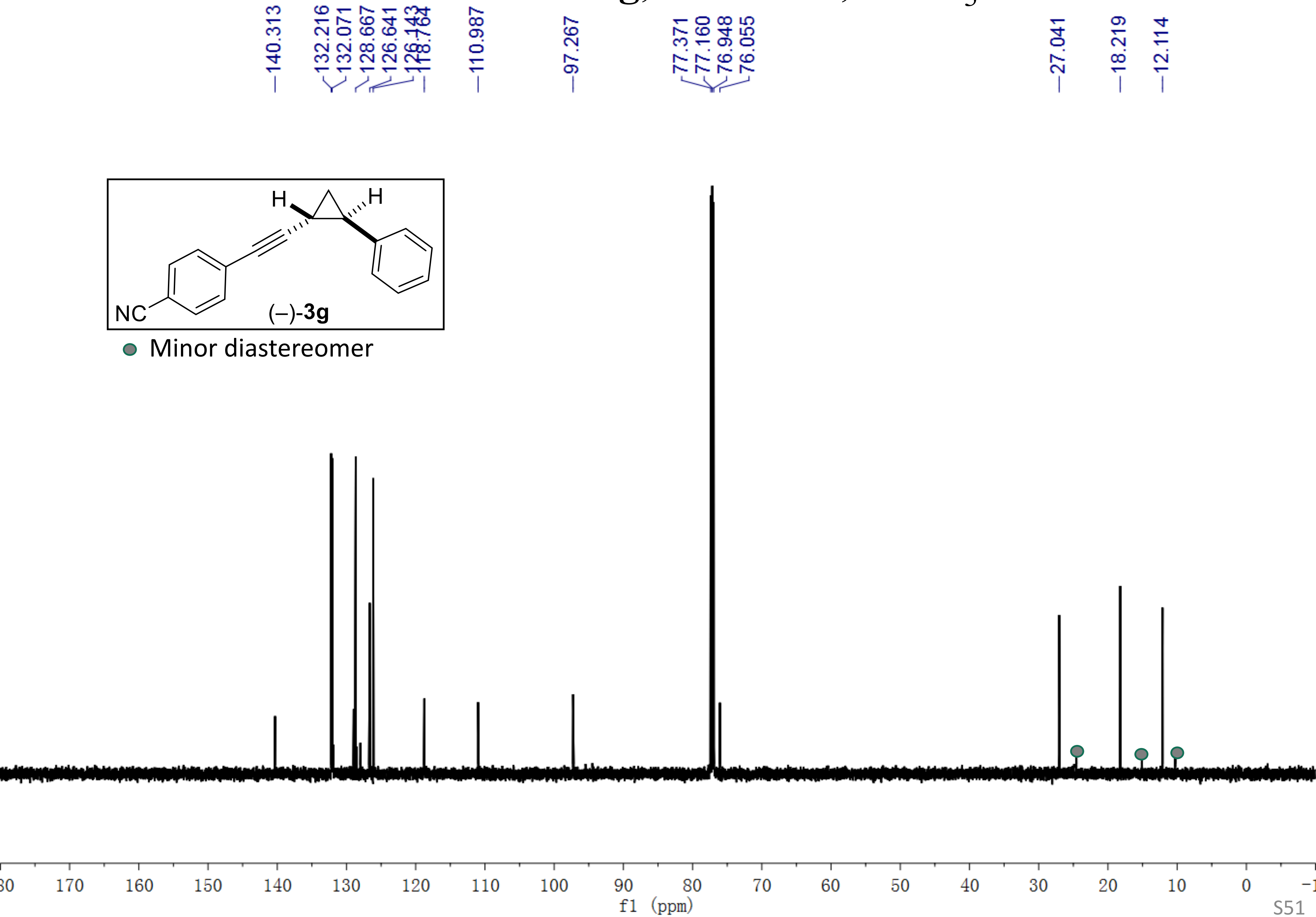
PDA Ch1 254nm

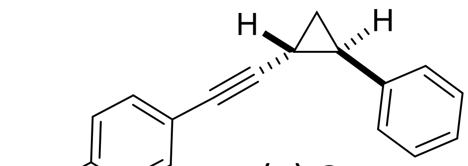
Peak#	Ret. Time	Area	Area%
1	7.348	224745	2.487
2	7.837	8812566	97.513
Total		9037311	100.000

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



^{13}C NMR of **3g**, 151 MHz, $CDCl_3$

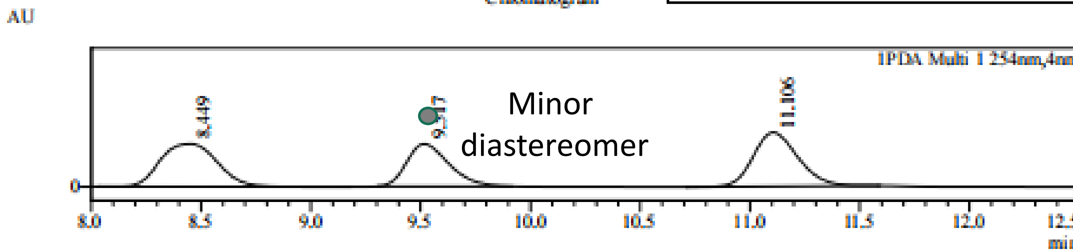




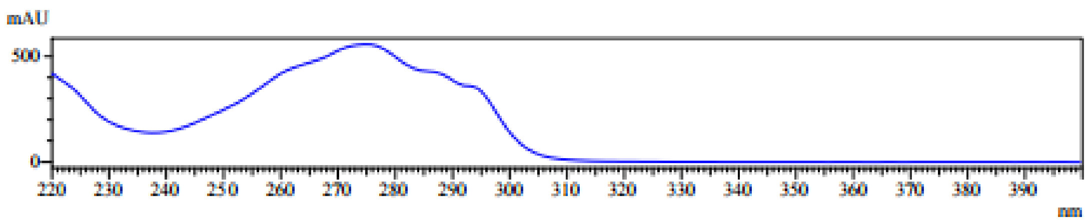
(±)-**3g**

Data File	: J0K-1474-IA--0.8%-1ML.lcd
Sample Name	: J0K-1474-IA--0.8%-1ML
Sample ID	: J0K-1474-IA--0.8%-1ML
Method File	: J0K-0.8%-50min-1ml.lcm

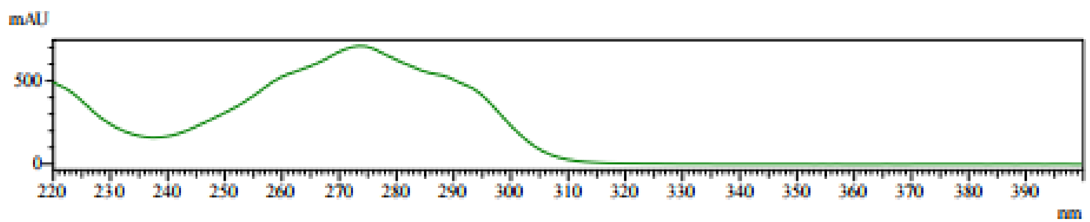
Chromatogram



UV Spectrum
Retention time = 8.449



UV Spectrum
Retention time = 11.106

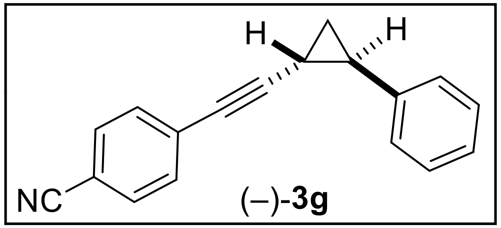


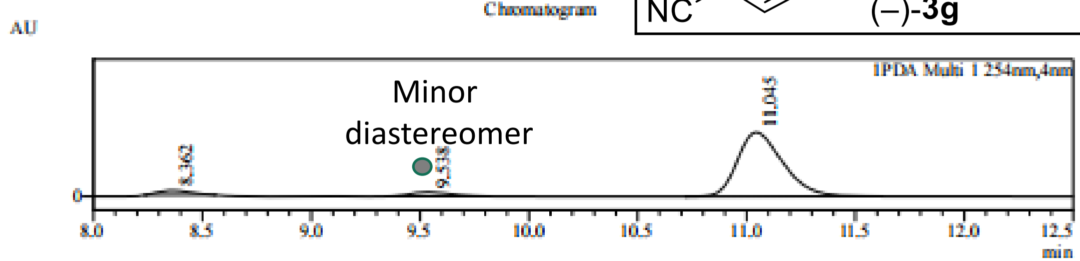
Peak Table

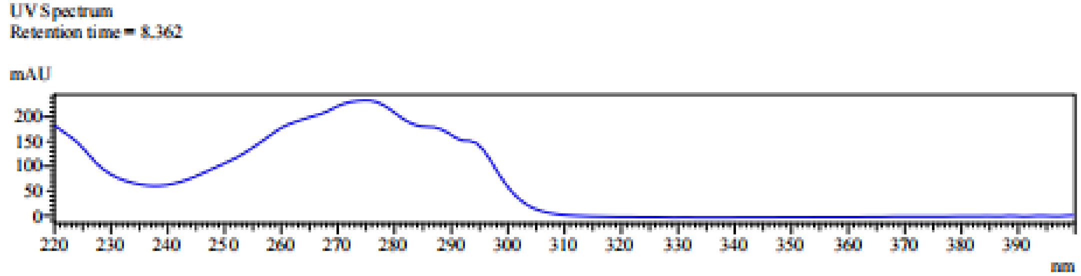
PDA Ch1 254nm

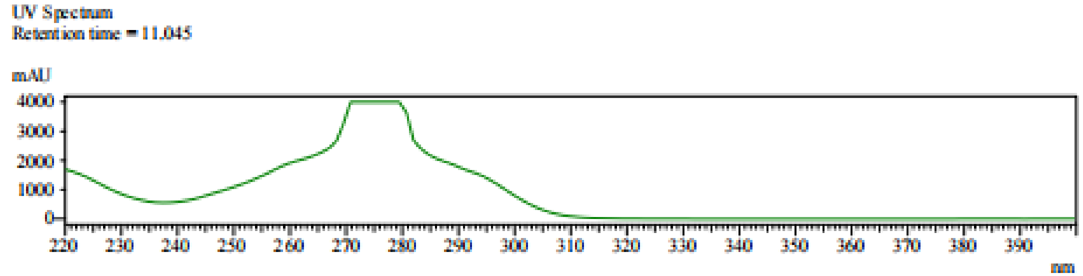
Peak#	Ret. Time	Area	Area%
1	8.449	5520988	36.621
2	9.517	4073960	27.023
3	11.106	5480991	36.356
Total		15075939	100.000

Data File : J0K-1473-IA--0.8%-1ML.lcd
Sample Name : J0K-1473-IA--0.8%-1ML
Sample ID : J0K-1473-IA--0.8%-1ML
Method File : J0K-0.8%-50min-1ml.lcm







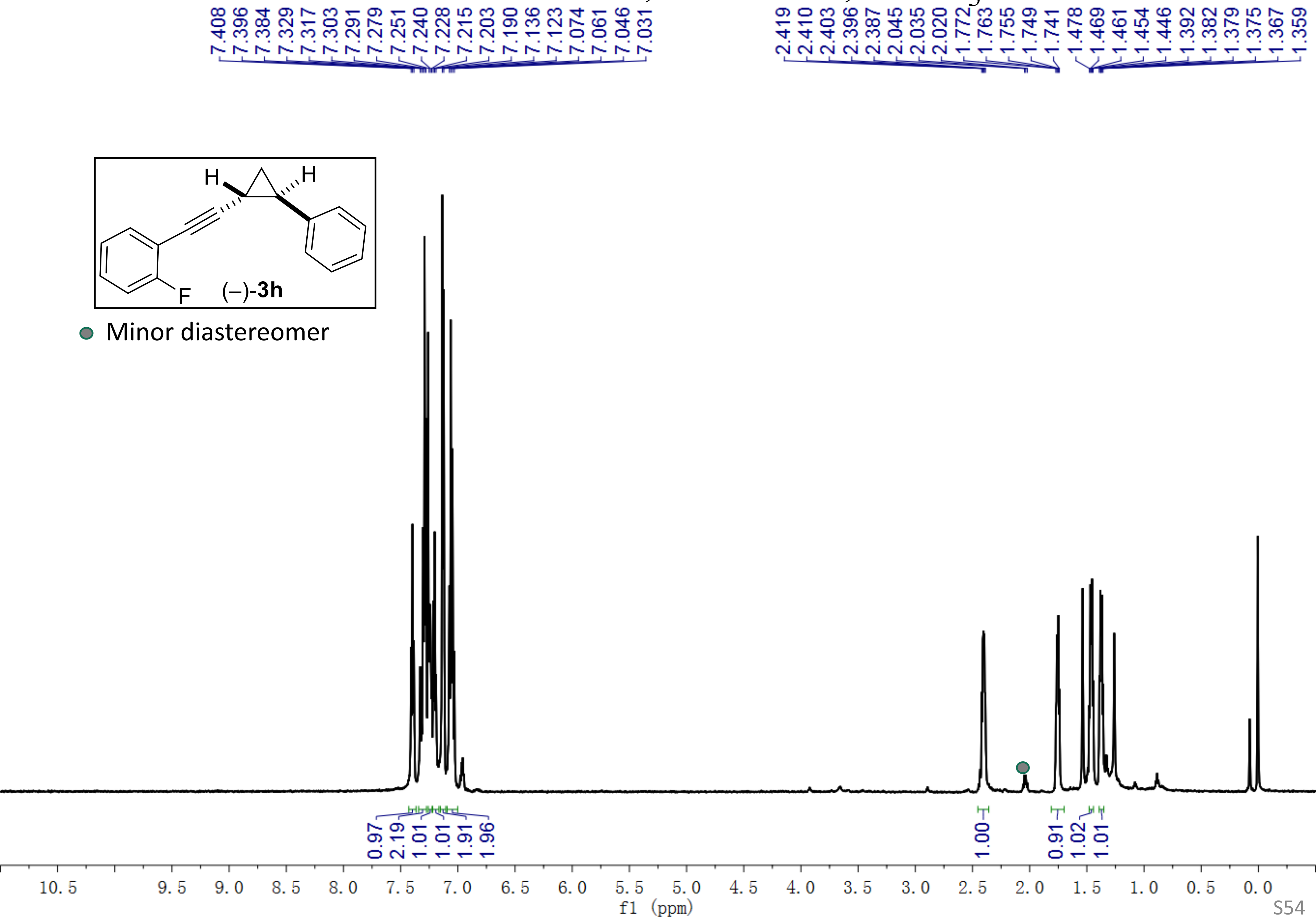


Peak Table

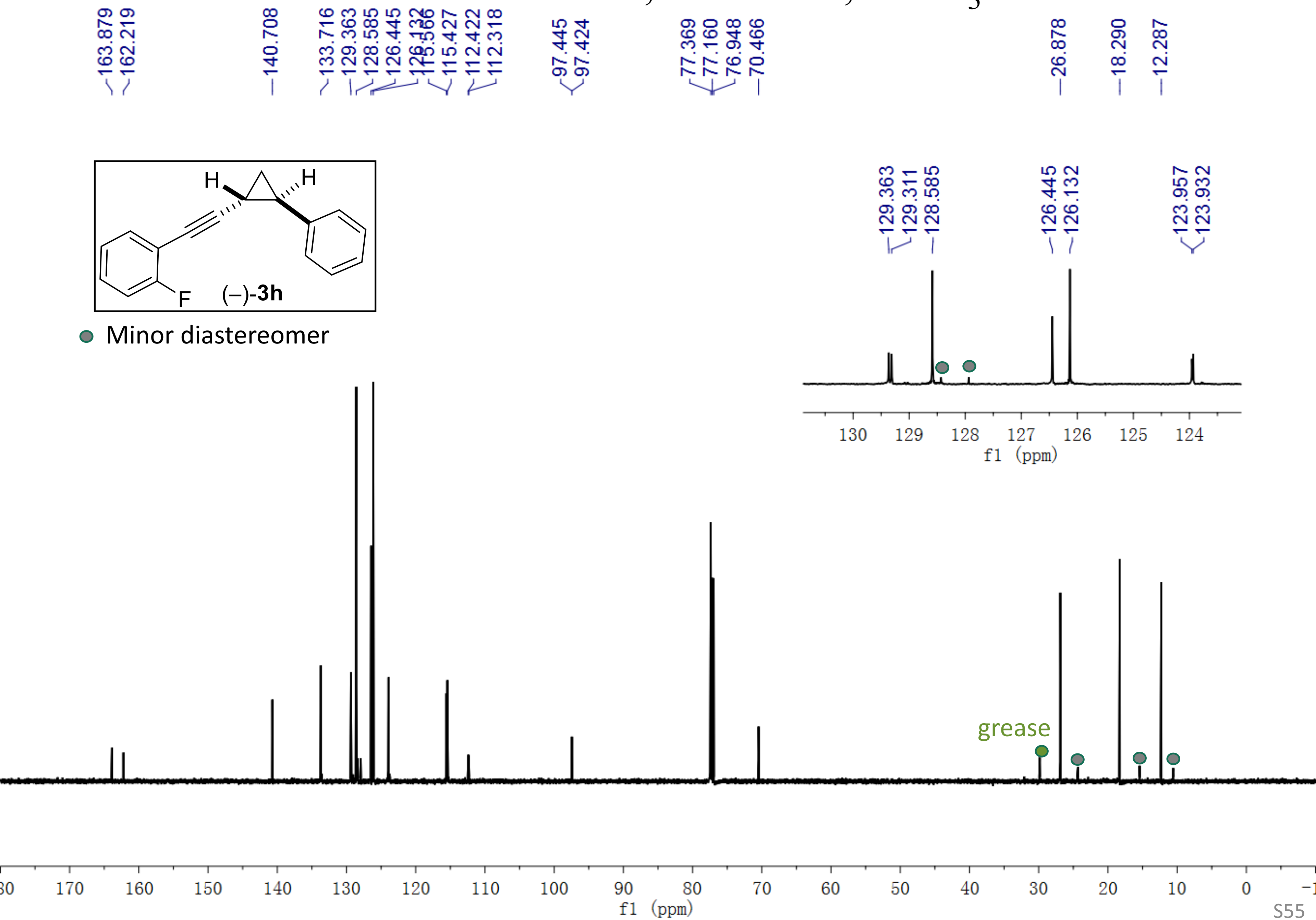
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.362	1045994	4.641
2	9.538	1171121	5.196
3	11.045	20321950	90.163
Total		22539065	100.000

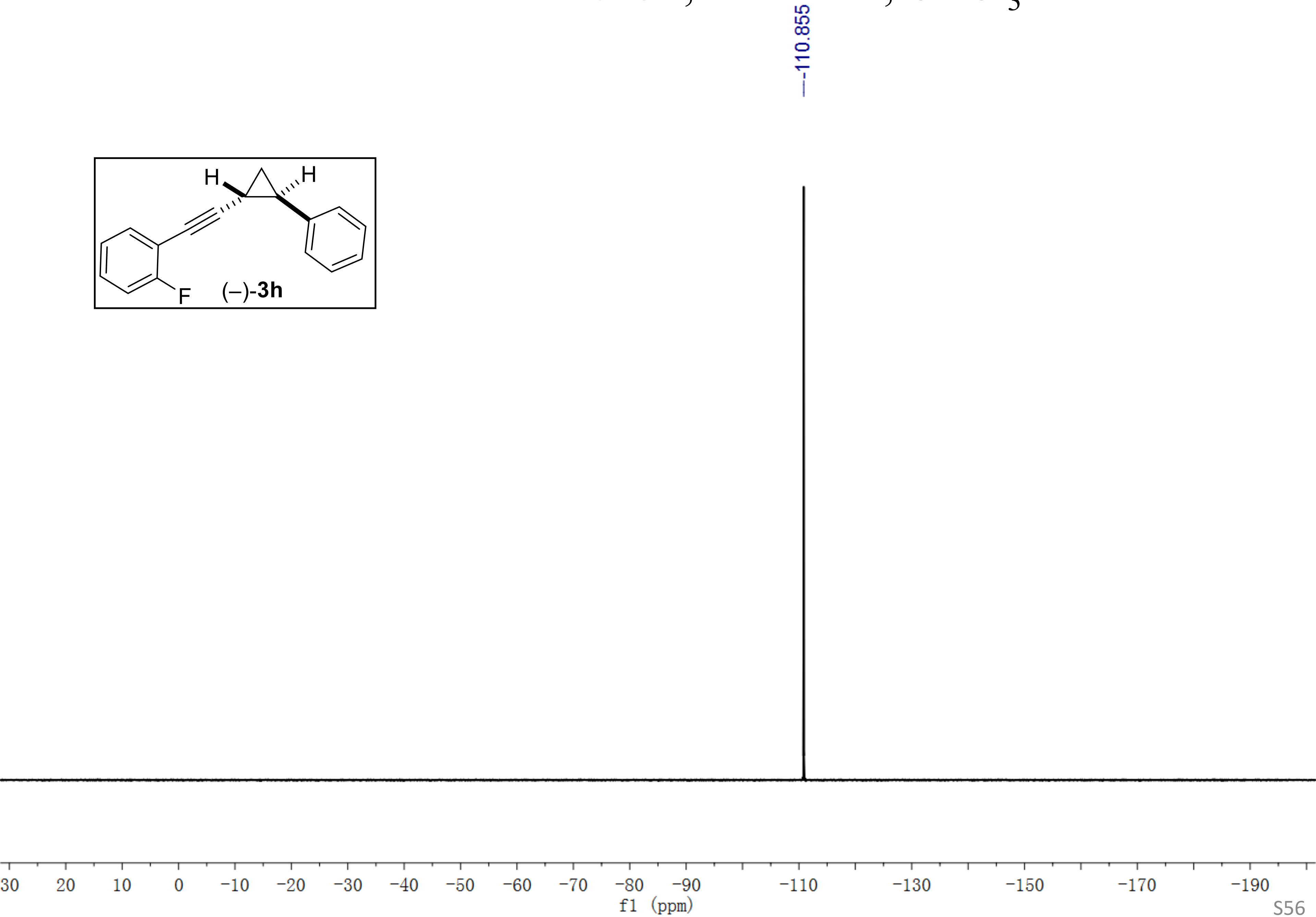
^{1}H NMR of **3h**, 400 MHz, $CDCl_3$



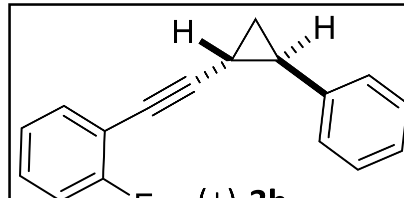
^{13}C NMR of **3h**, 151 MHz, $CDCl_3$



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

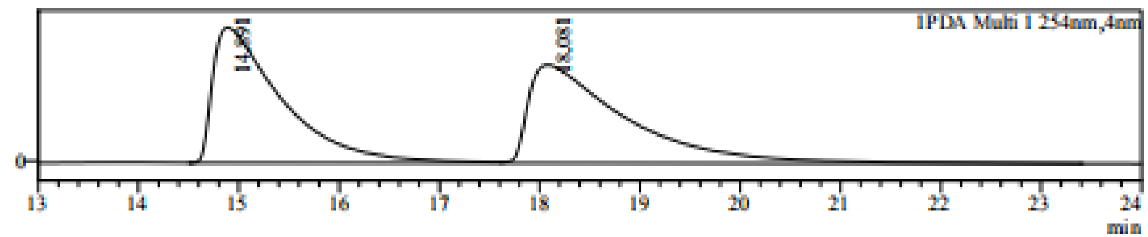


Data File : J0K-0222-4-IC-0%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0222-4-IC-0%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0222-4-IC-0%-0.8ML-isopropa
Method File : J0K-0%-0.8ml.lcm

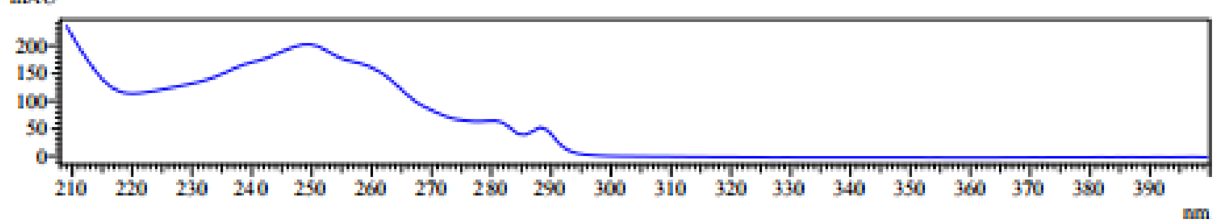


(±)-**3h**

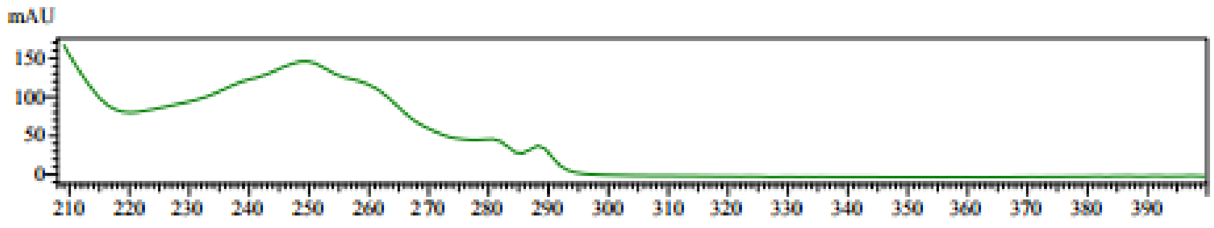
Chromatogram



UV Spectrum
Retention time = 14.891



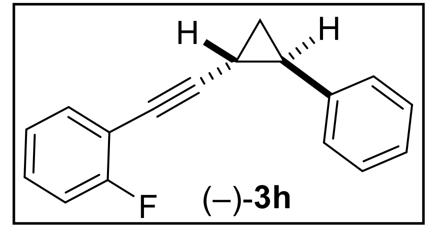
L
Retention time = 18.081



Peak Table

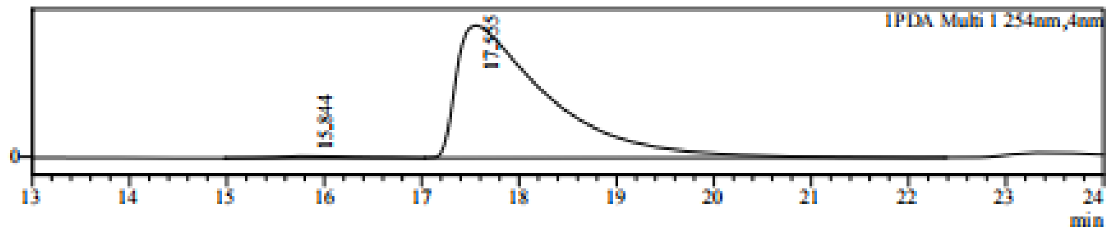
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.891	8882879	49.608
2	18.081	9023178	50.392
Total		17906056	100.000

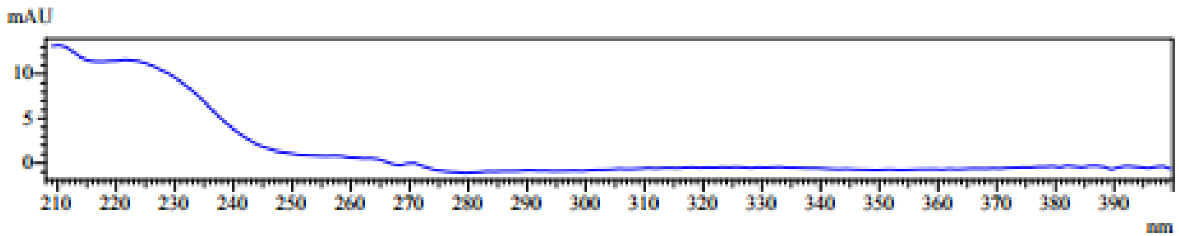


Data File	: J0K-0223-4-IC-0%-0.8ML-isopropanol-solvent004.lcd
Sample Name	: J0K-0223-4-IC-0%-0.8ML-isopropanol-solvent004
Sample ID	: J0K-0223-4-IC-0%-0.8ML-isopropa
Method File	: J0K-0%-0.8ml.lcm

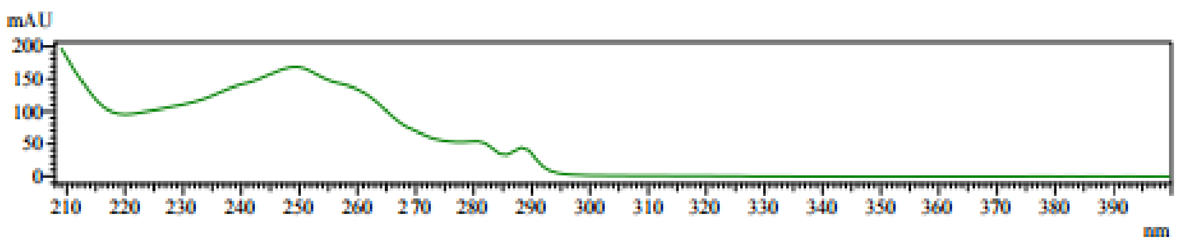
Chromatogram



UV Spectrum
Retention time = 15.844



L
Retention time = 17.555

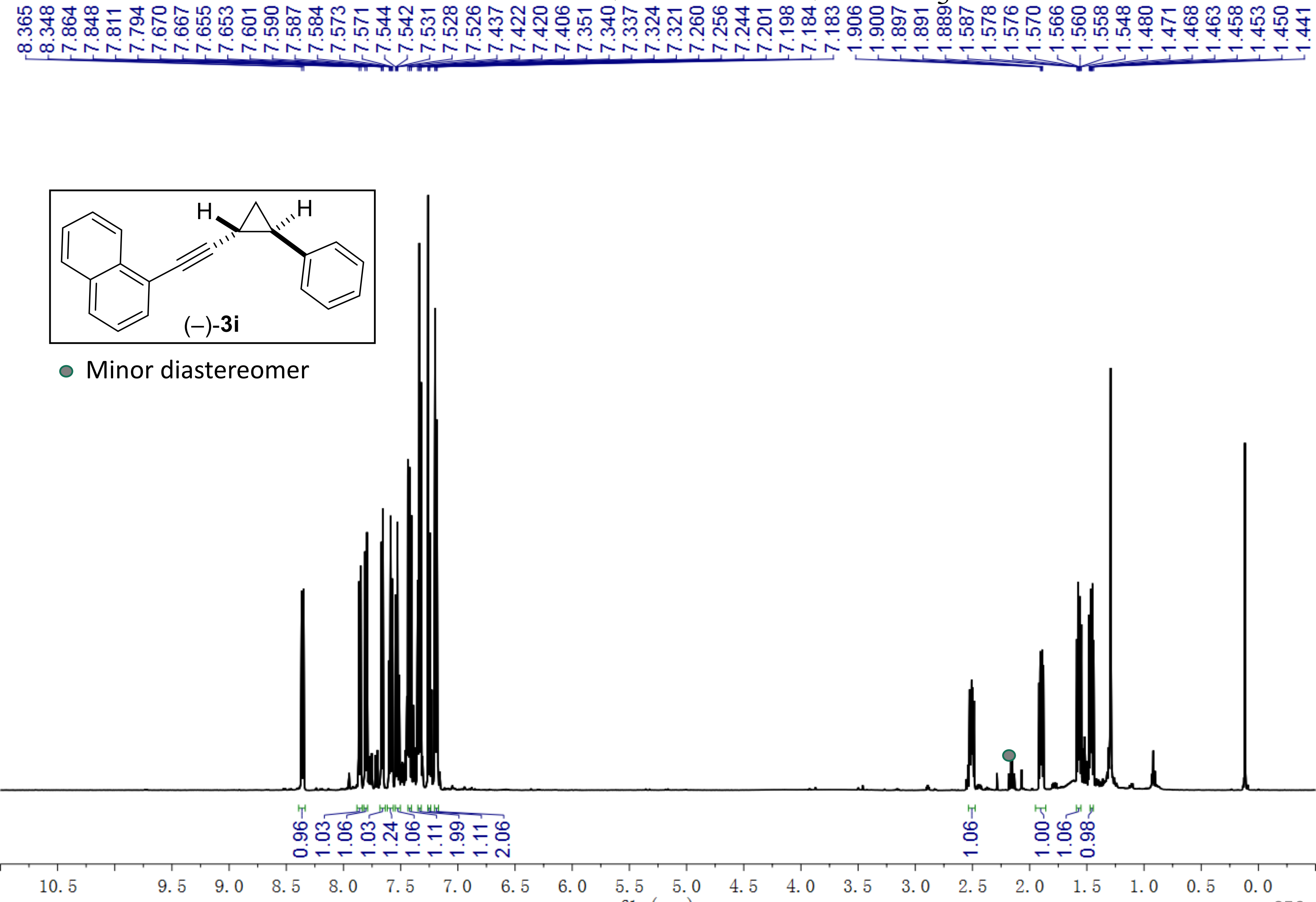


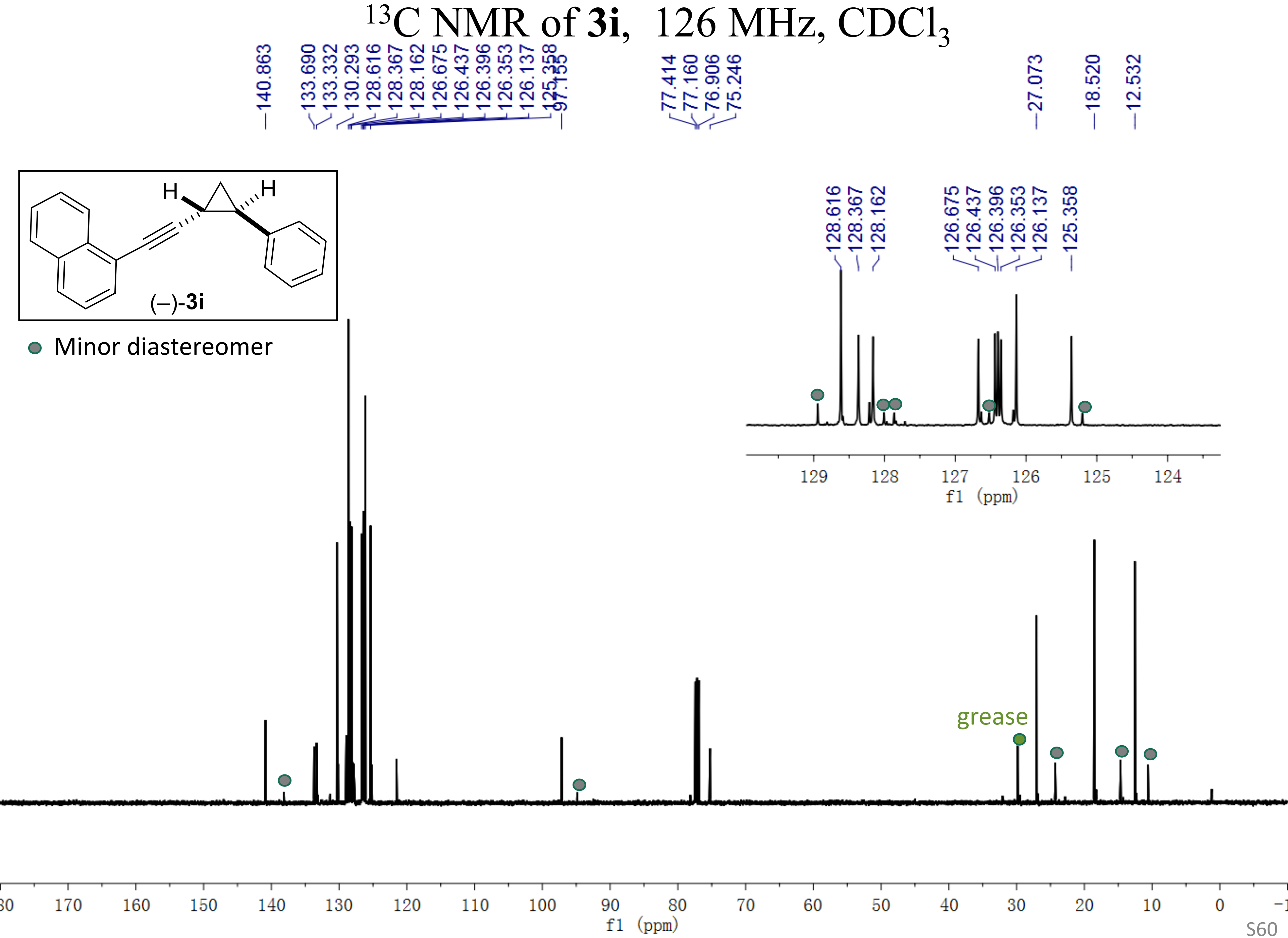
Peak Table

PDA Ch1 254nm

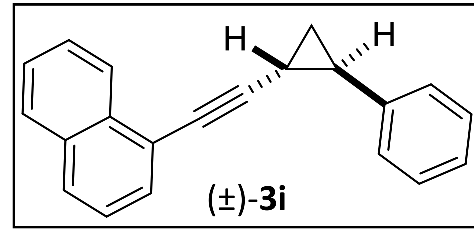
Peak#	Ret. Time	Area	Area%
1	15.844	125202	1.231
2	17.555	10045730	98.769
Total		10170931	100.000

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





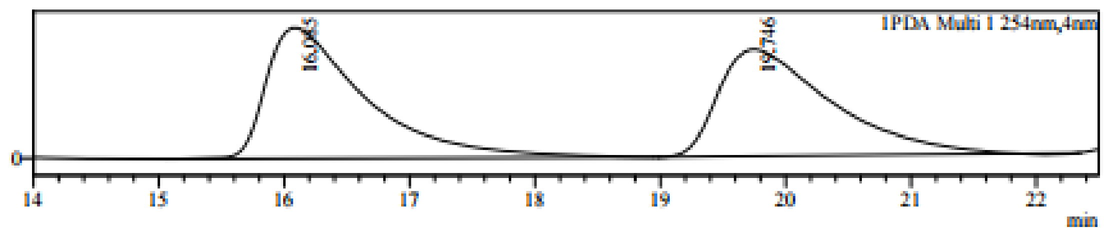
^{13}C NMR of **3i**, 126 MHz, CDCl$_3$
140.863
133.690
133.332
130.293
128.616
128.367
128.162
126.675
126.437
126.396
126.353
126.137
125.358
97.155
77.414
77.160
76.906
75.246
27.073
18.520
12.532
H
H
(–)-**3i**
Minor diastereomer
grease
f1 (ppm)


(±)-3i

Data File : J0K-0119-IC-0%-0.8ML-isopropanol-solvent004.lcd
Sample Name : J0K-0119-IC-0%-0.8ML-isopropanol-solvent004
Sample ID : J0K-0119-IC-0%-0.8ML-isopropano
Method File : JK-0%-0.8ml.lcm

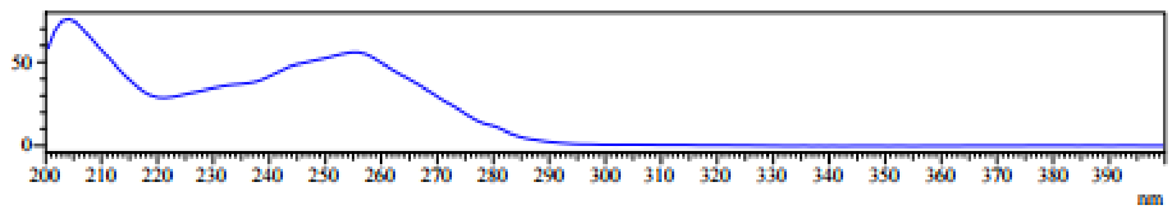
Chromatogram

mAU



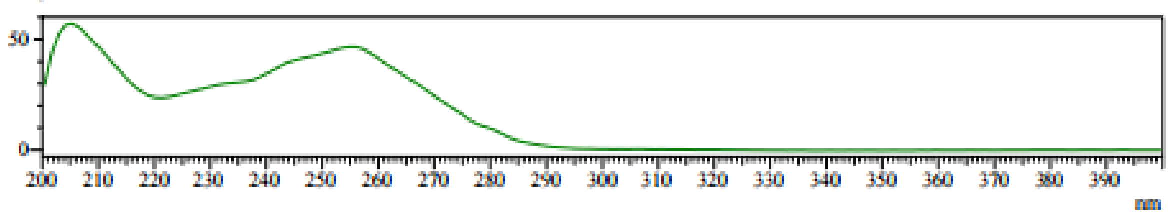
UV Spectrum
Retention time = 16.085

mAU



U
Retention time = 19.746

mAU

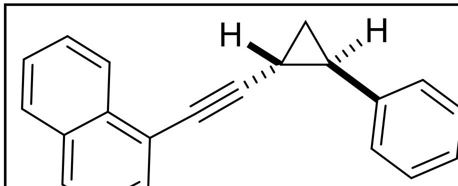


Peak Table

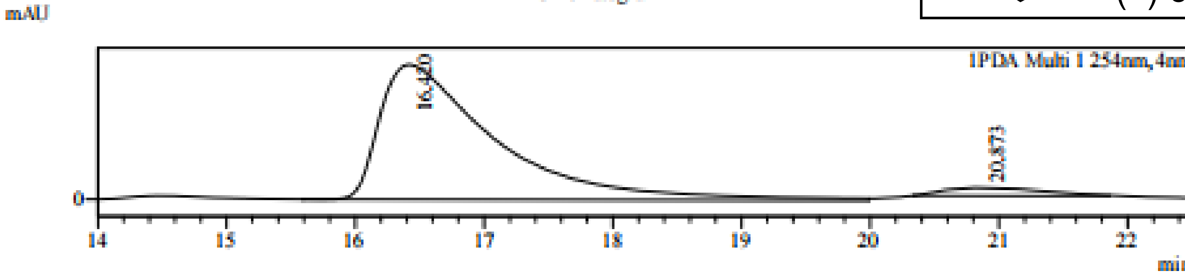
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.085	3026512	51.835
2	19.746	2812184	48.165
Total		5838697	100.000

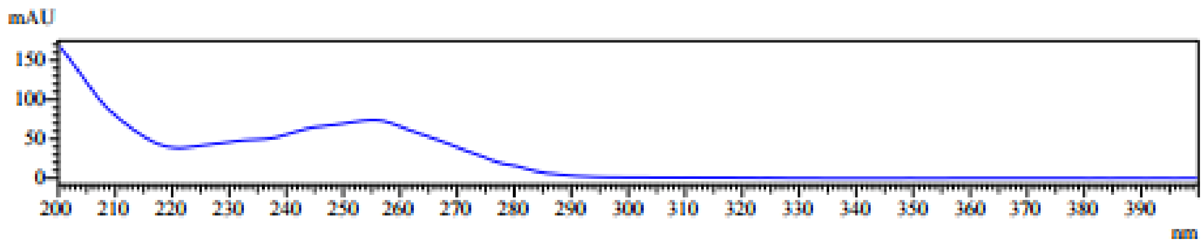
Data File : J0K-0120-IC-0%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0120-IC-0%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0120-IC-0%-0.8ML-isopropano
Method File : JK-0%-0.8ml.lcm


(–)-3i

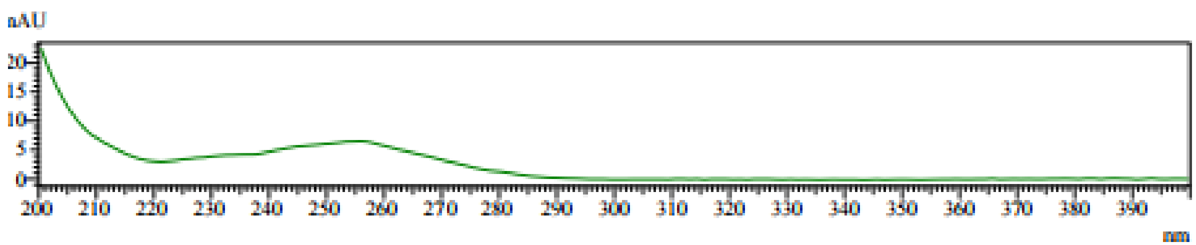
Chromatogram



UV Spectrum
Retention time = 16.420



Retention time = 20.873

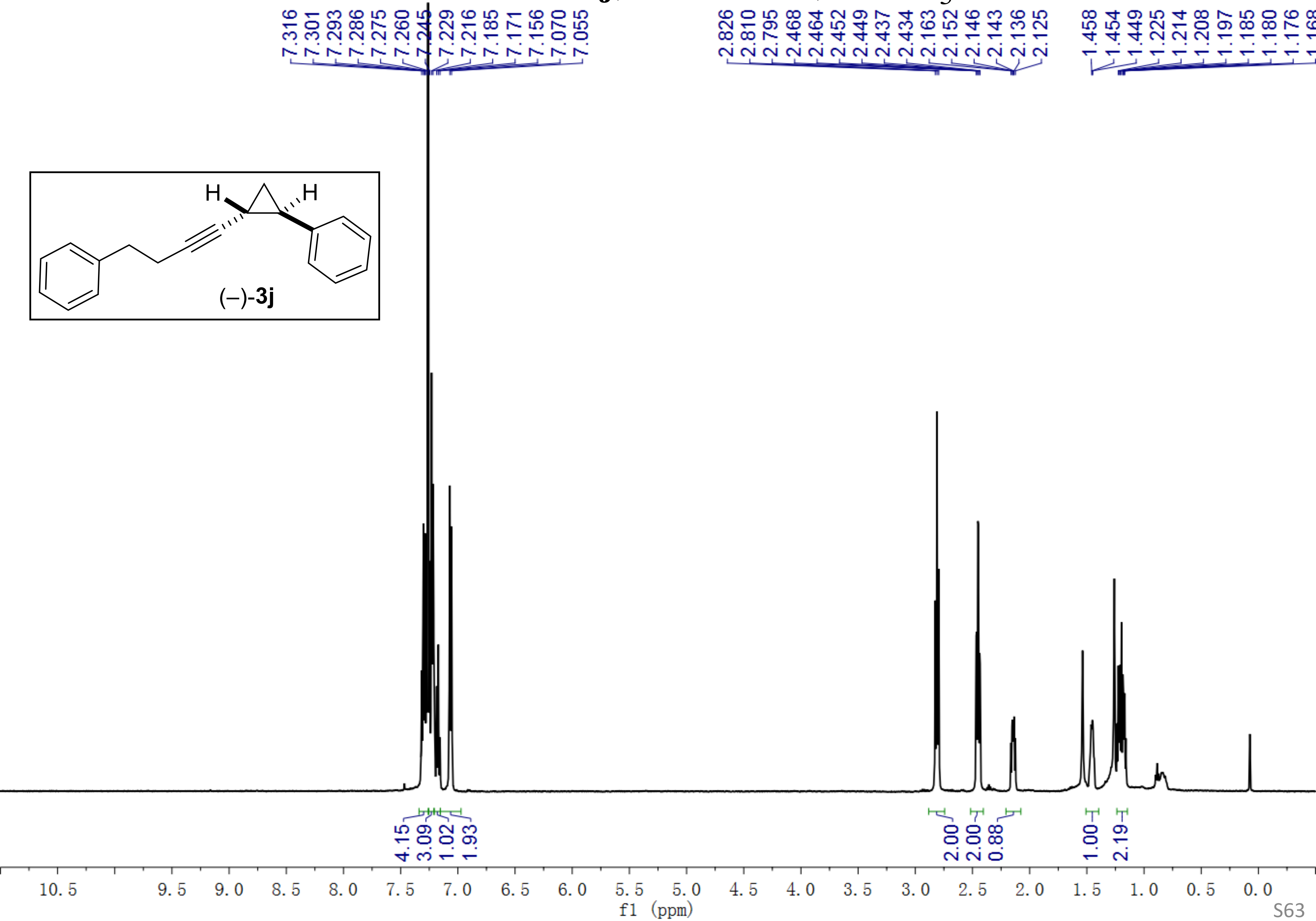


Peak Table

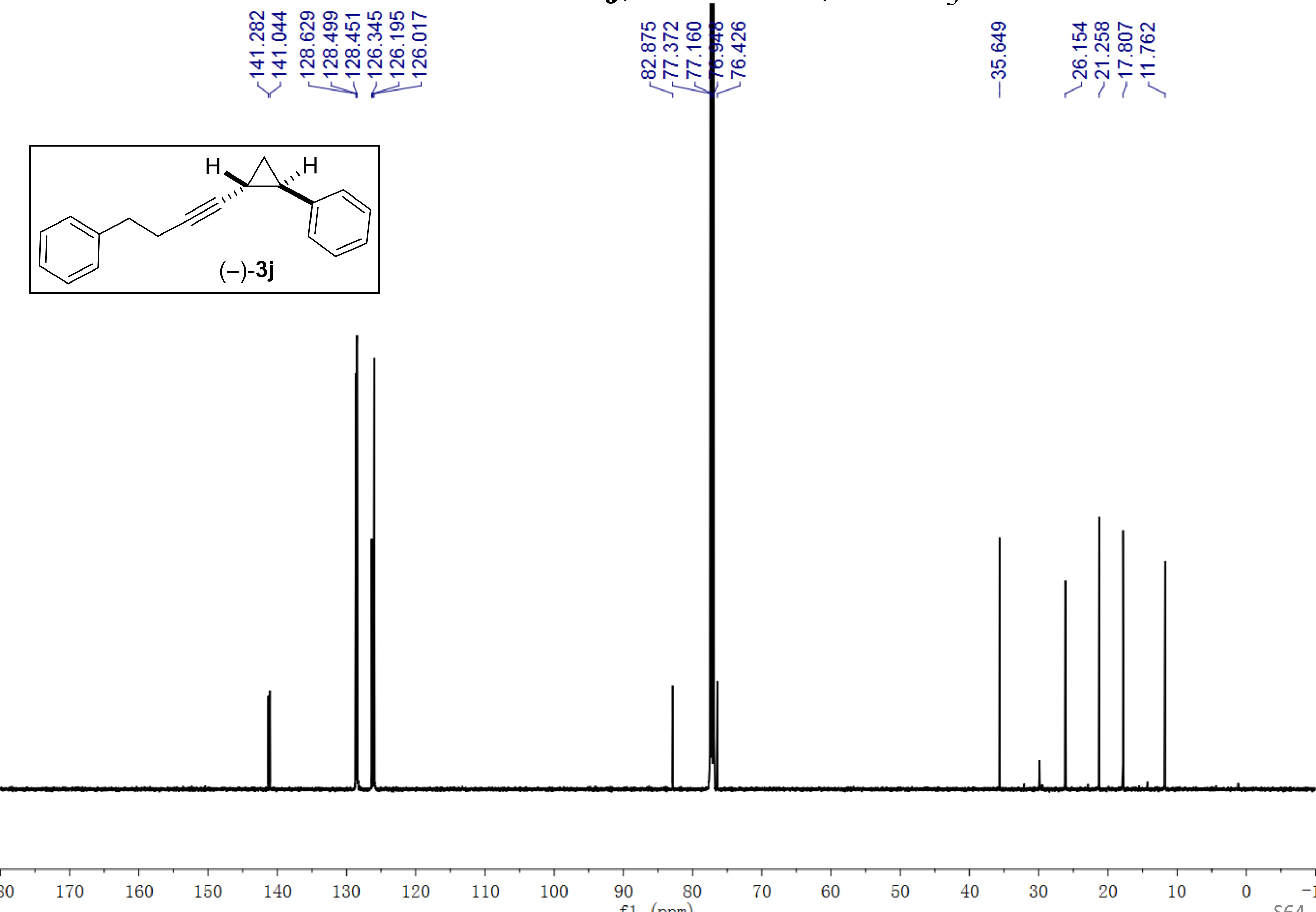
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.420	4527761	95.035
2	20.873	236566	4.965
Total		4764327	100.000

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

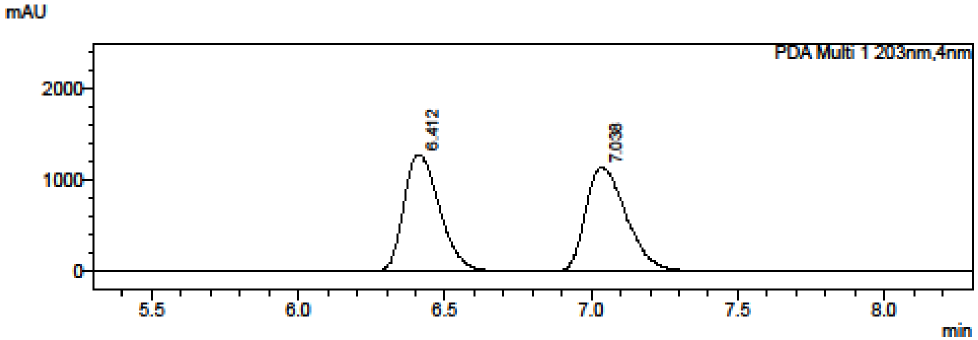


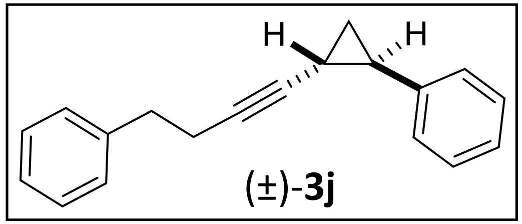
^{13}C NMR of **3j**, 151 MHz, $CDCl_3$



==== Shimadzu LabSolutions Analysis Report ====

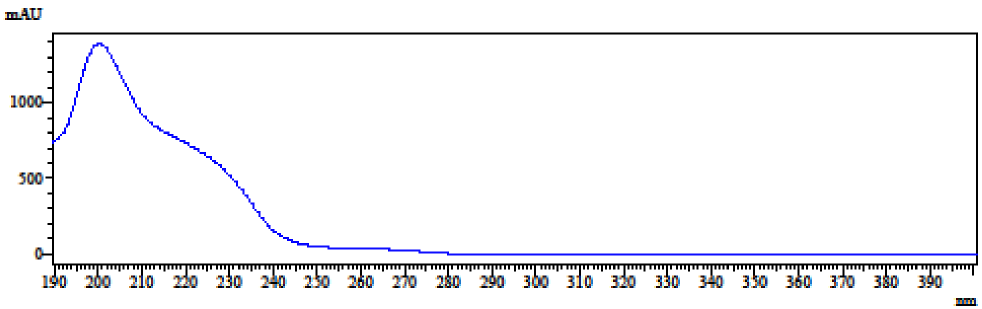
WCL-1844-2-IC-0.1%0.8mL
WCL-0.1%-20min0.8mL.lcm

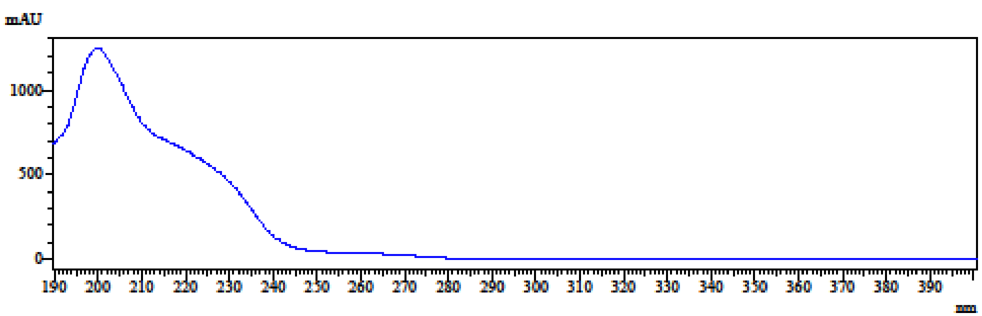




(±)-**3j**

UV Spectrum





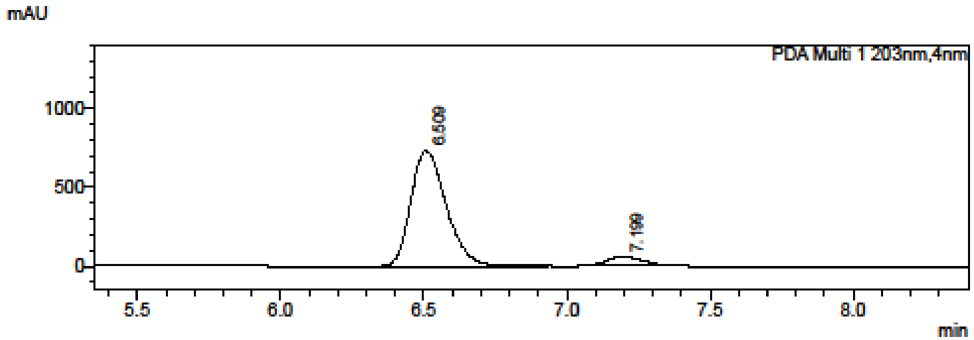
Peak Table

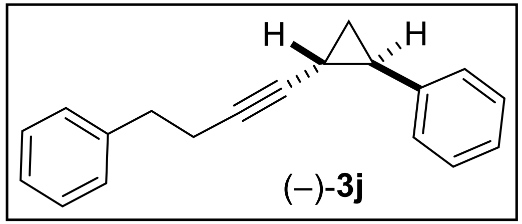
PDA Ch1 203nm

Peak#	Ret. Time	Area%
1	6.412	49.969
2	7.038	50.031
Total		100.000

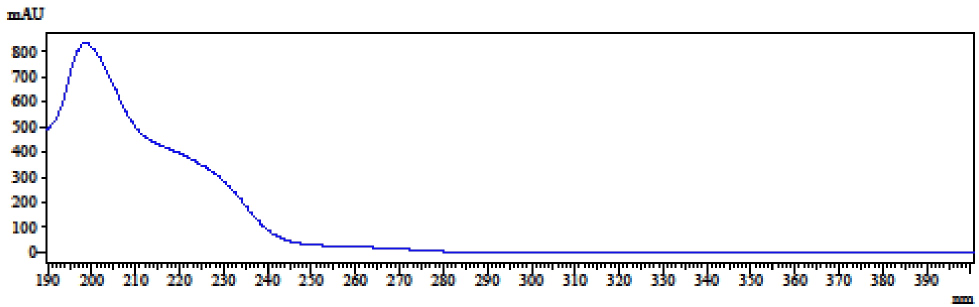
==== Shimadzu LabSolutions Analysis Report ====

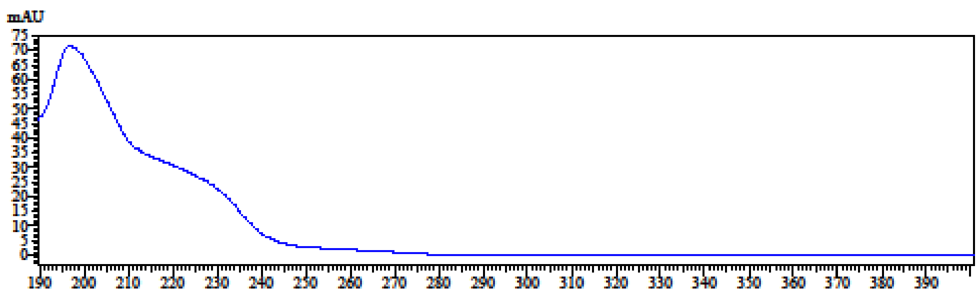
WCL-1845-1-IC-0.1%0.8mL
WCL-0.1%-20min0.8mL.lcm





UV Spectrum



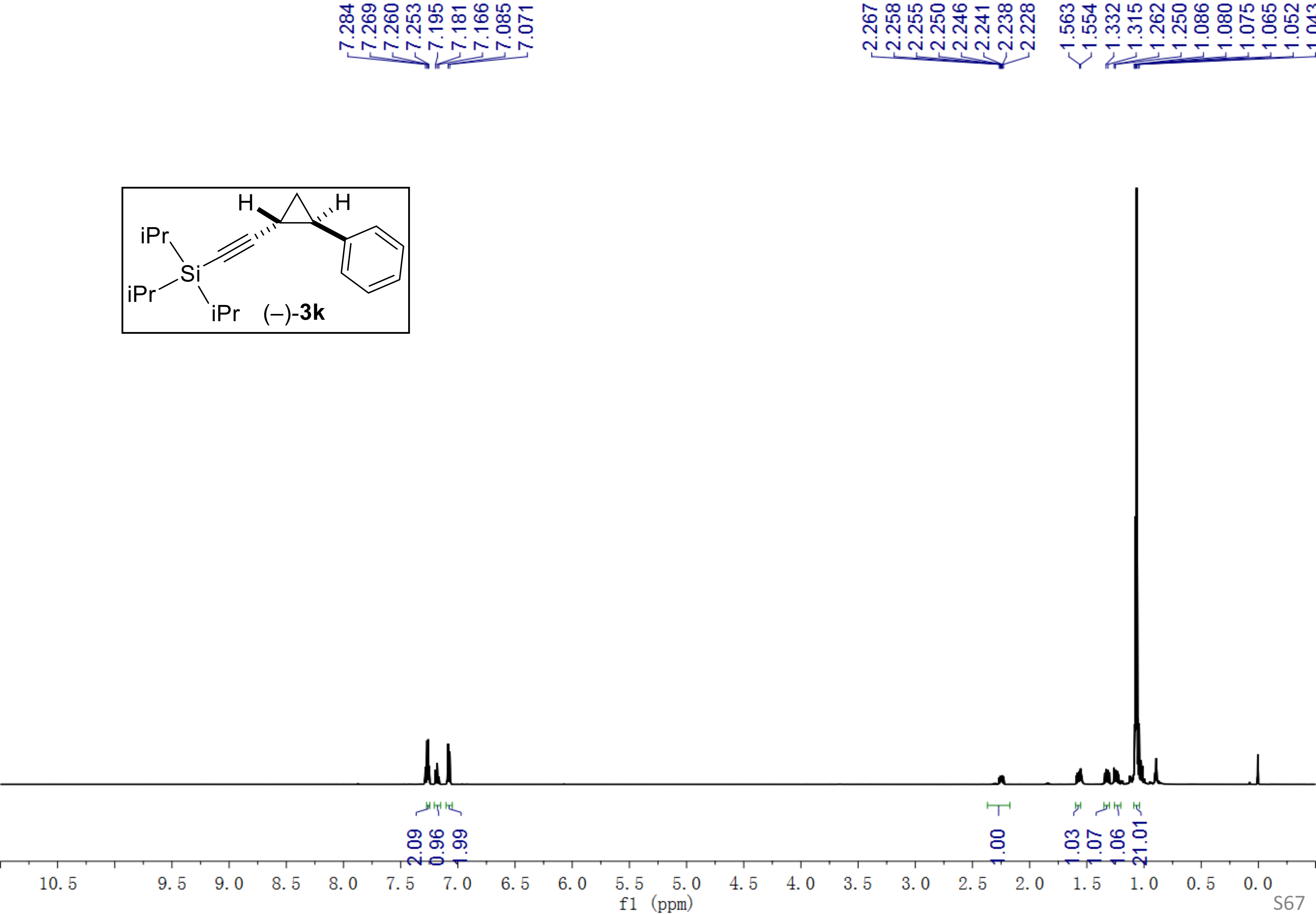


Peak Table

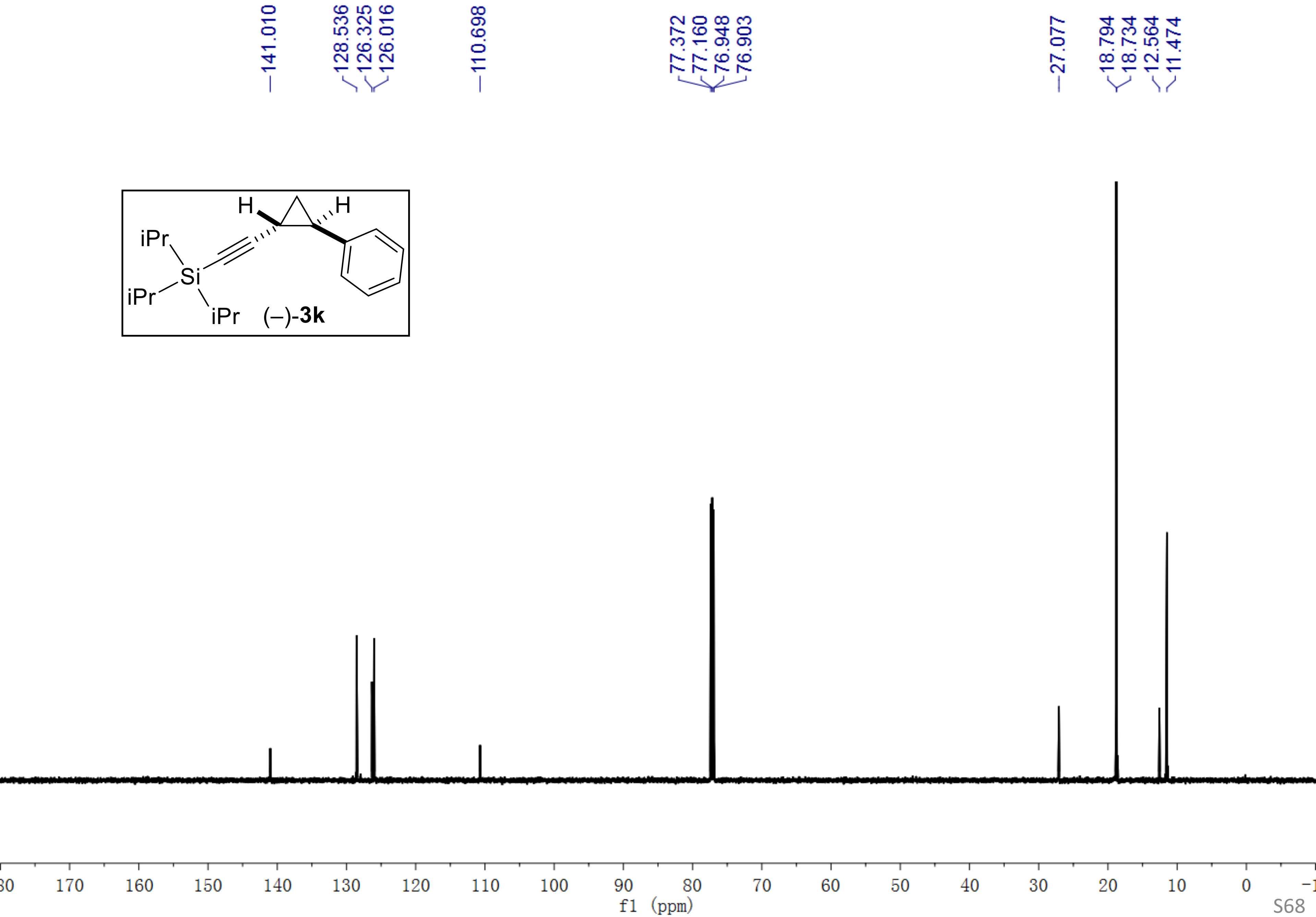
PDA Ch1 203nm

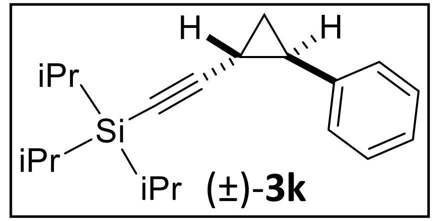
Peak#	Ret. Time	Area%
1	6.509	92.506
2	7.199	7.494
Total		100.000

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



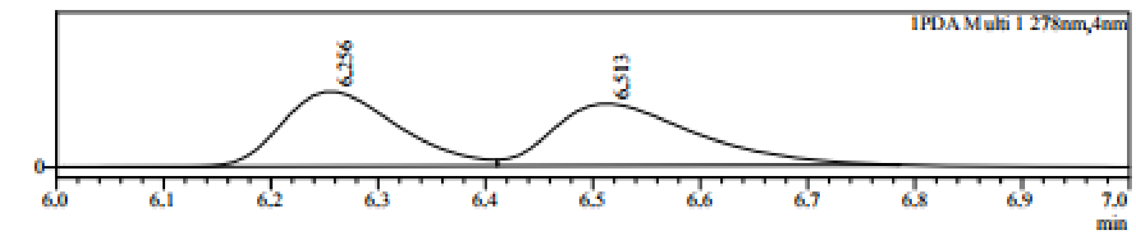
^{13}C NMR of **3j**, 151 MHz, $CDCl_3$



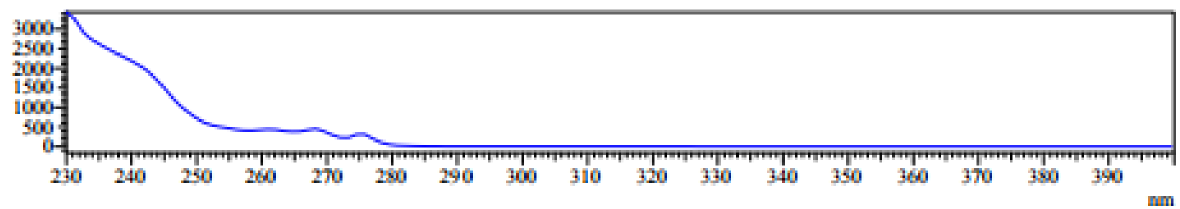


Data File : J0K-1401-IC-0%-0.8ML001.lcd
Sample Name : J0K-1401-IC-0%-0.8ML
Sample ID : J0K-1401-IC-0%-0.8ML
Method File : J0K-0%--25min-0.6ml.lcm

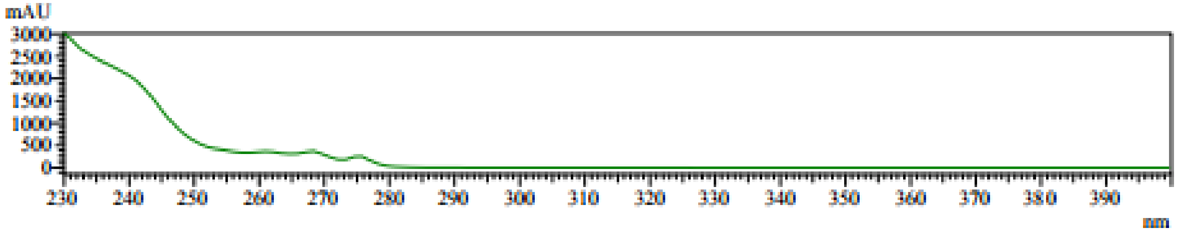
Chromatogram



UV Spectrum
Retention time = 6.256



l
Retention time = 6.51 3

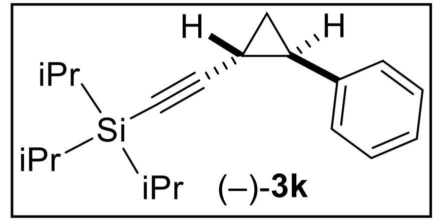


Peak Table

PDA Ch1 278nm

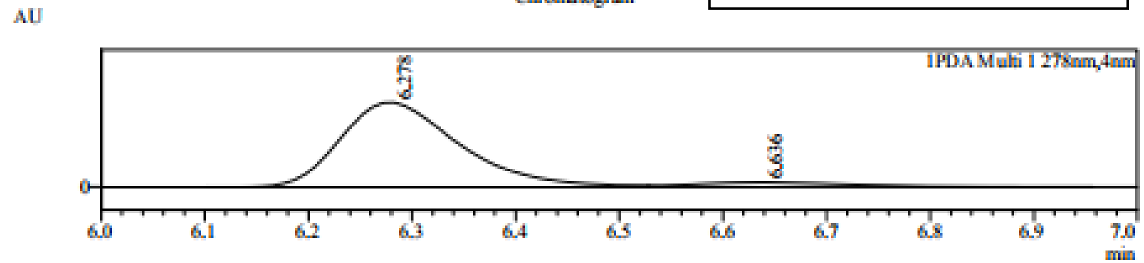
Peak#	Ret. Time	Area	Area%
1	6.256	1083124	49.482
2	6.513	1105802	50.518
Total		2188926	100.000

Data File : J0K-1402-IC-0%-0.8ML-3.lcd
Sample Name : J0K-1402-IC-0%-0.8ML-3
Sample ID : J0K-1402-IC-0%-0.8ML-3
Method File : J0K-0%--25min-0.6ml.lcm

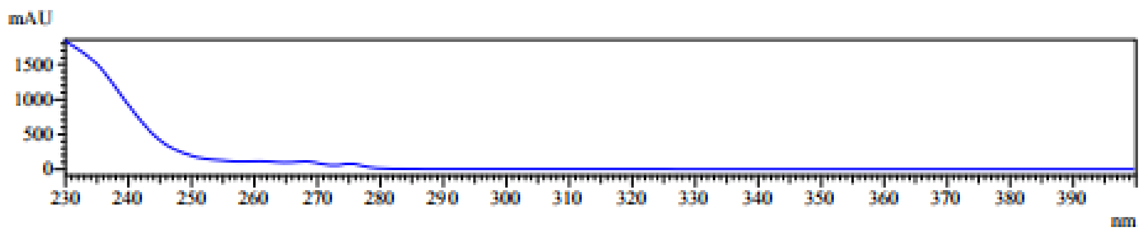


(–)-**3k**

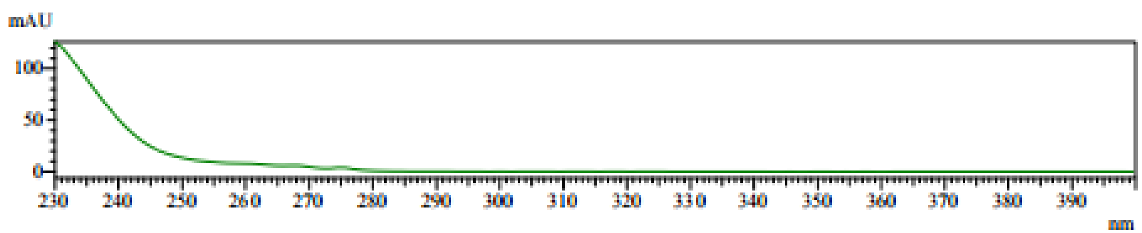
Chromatogram



UV Spectrum
Retention time = 6.278



L
Retention time = 6.636

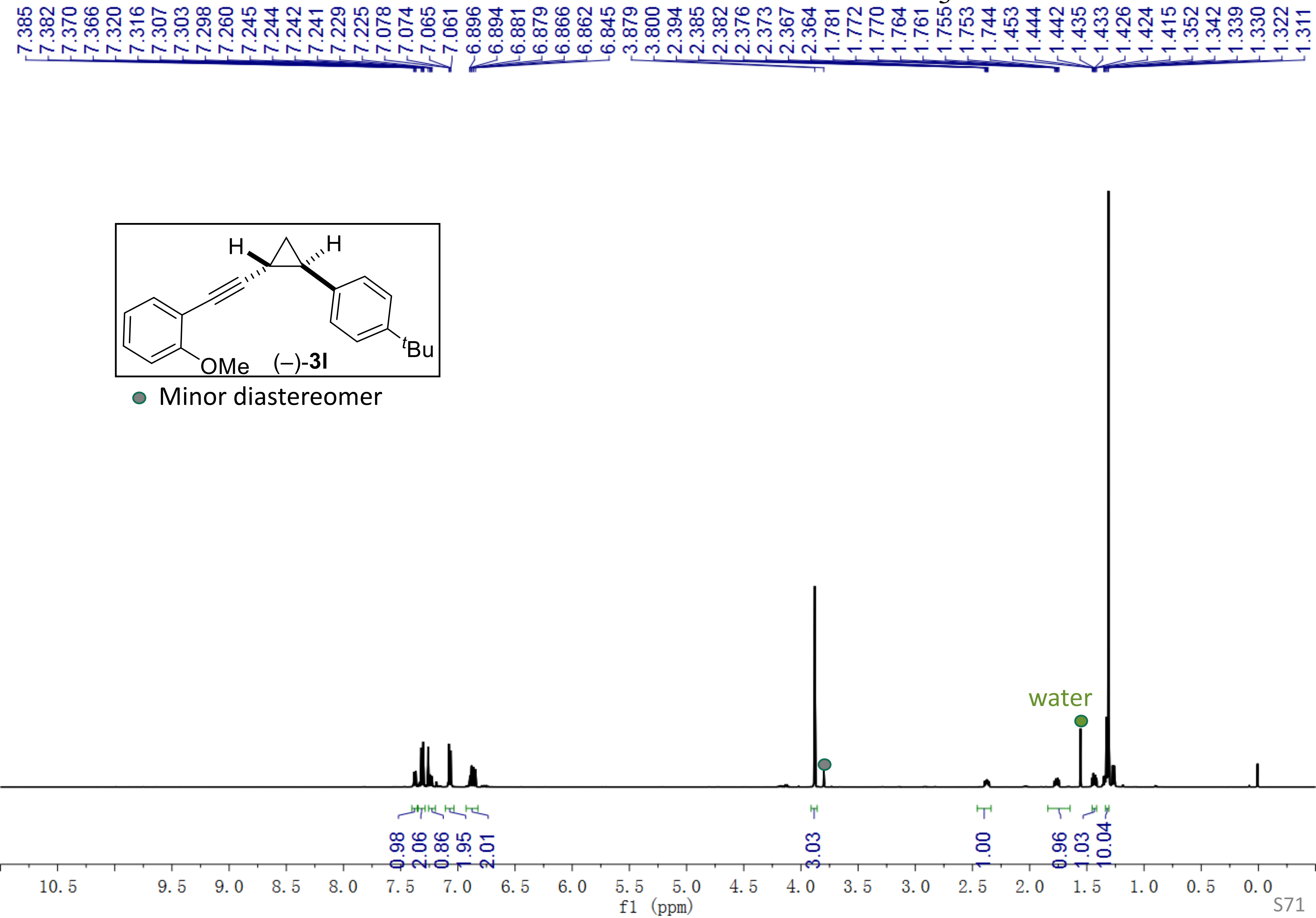


Peak Table

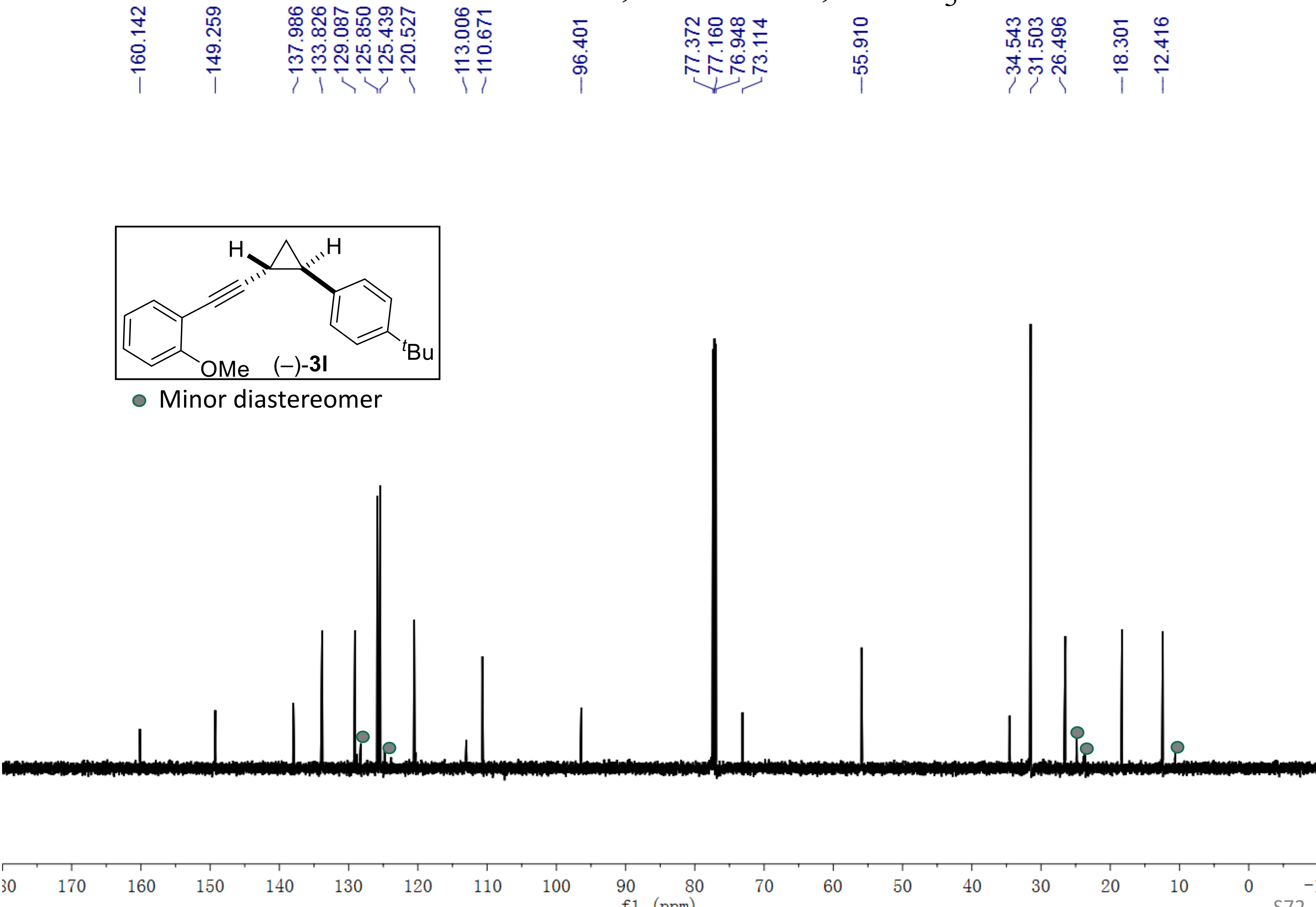
PDA Ch1 278nm

Peak#	Ret. Time	Area	Area%
1	6.278	296817	93.309
2	6.636	21284	6.691
Total		318101	100.000

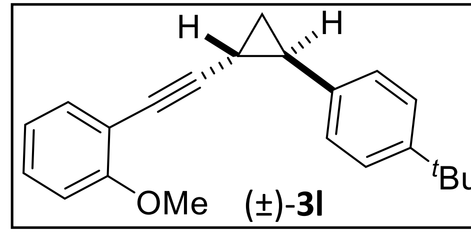
^{1}H NMR of **3l**, 600 MHz, $CDCl_3$



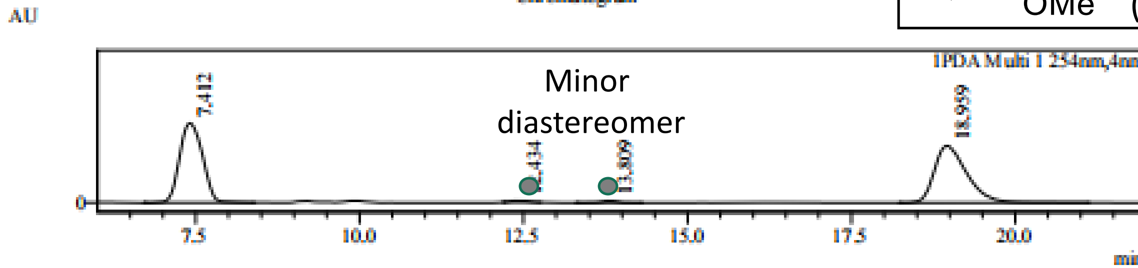
^{13}C NMR of **3l**, 151 MHz, $CDCl_3$



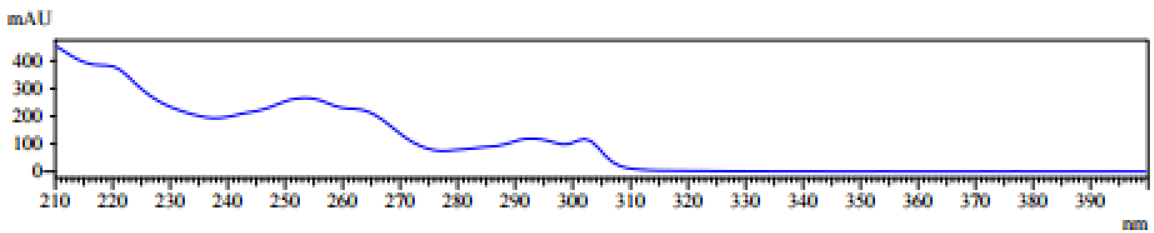
Data File : J0K-0169-2-IC-1%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0169-2-IC-1%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0169-2-IC-1%-0.8ML-isopropa
Method File : J0K-1%-0.8ml.lcm



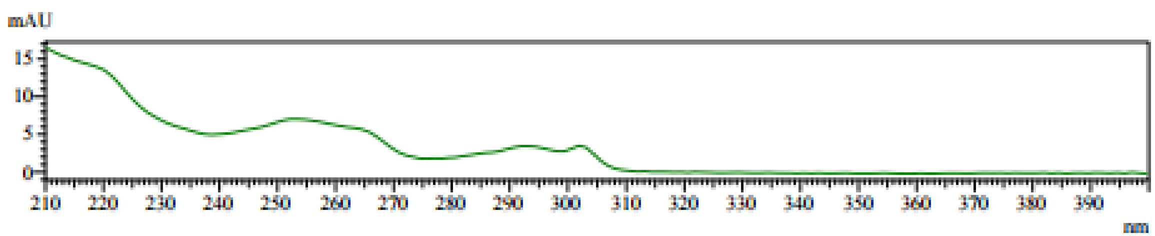
Chromatogram



UV Spectrum
Retention time = 7.412



U
Retention time = 12.434

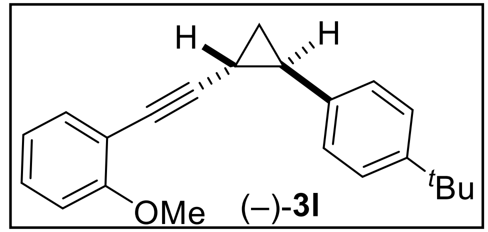


Peak Table

PDA Ch1 254nm

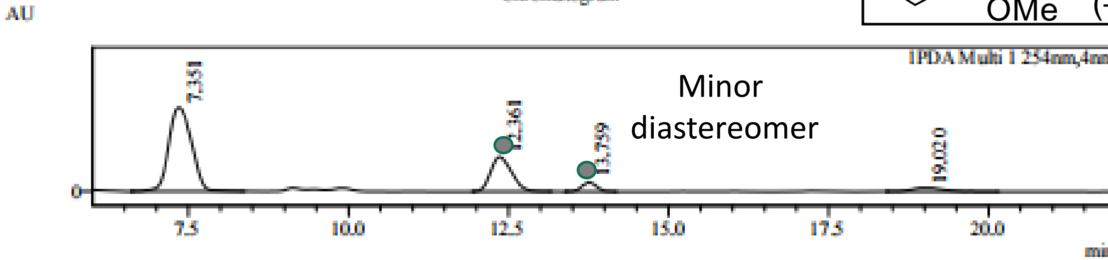
Peak#	Ret. Time	Area	Area%
1	7.412	6343268	49.007
2	12.434	99943	0.772
3	13.809	101856	0.787
4	18.959	6398503	49.434
Total		12943570	100.000

Data File : J0K-0170-IC-1%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0170-IC-1%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0170-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml.lcm

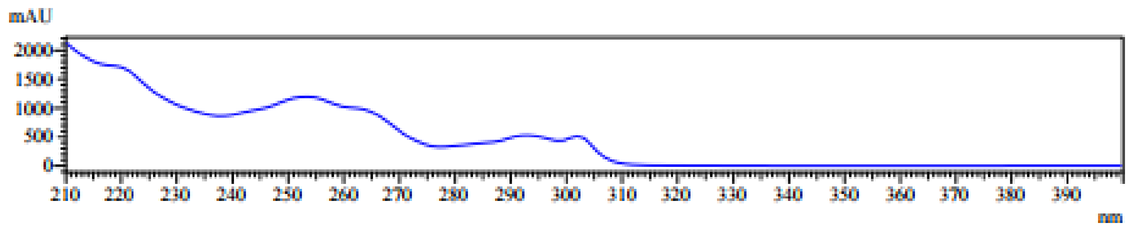


(–)-**3l**

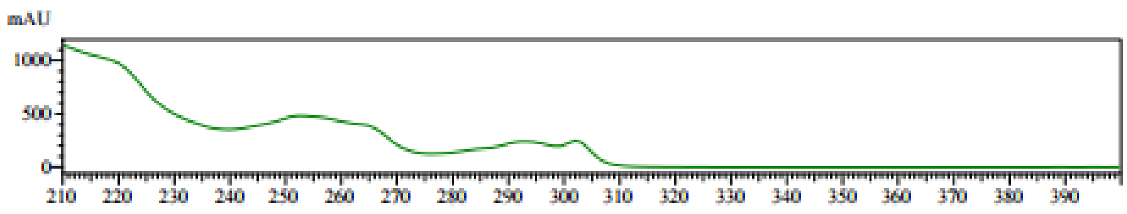
Chromatogram



UV Spectrum
Retention time = 7.351



U
Retention time = 12.361

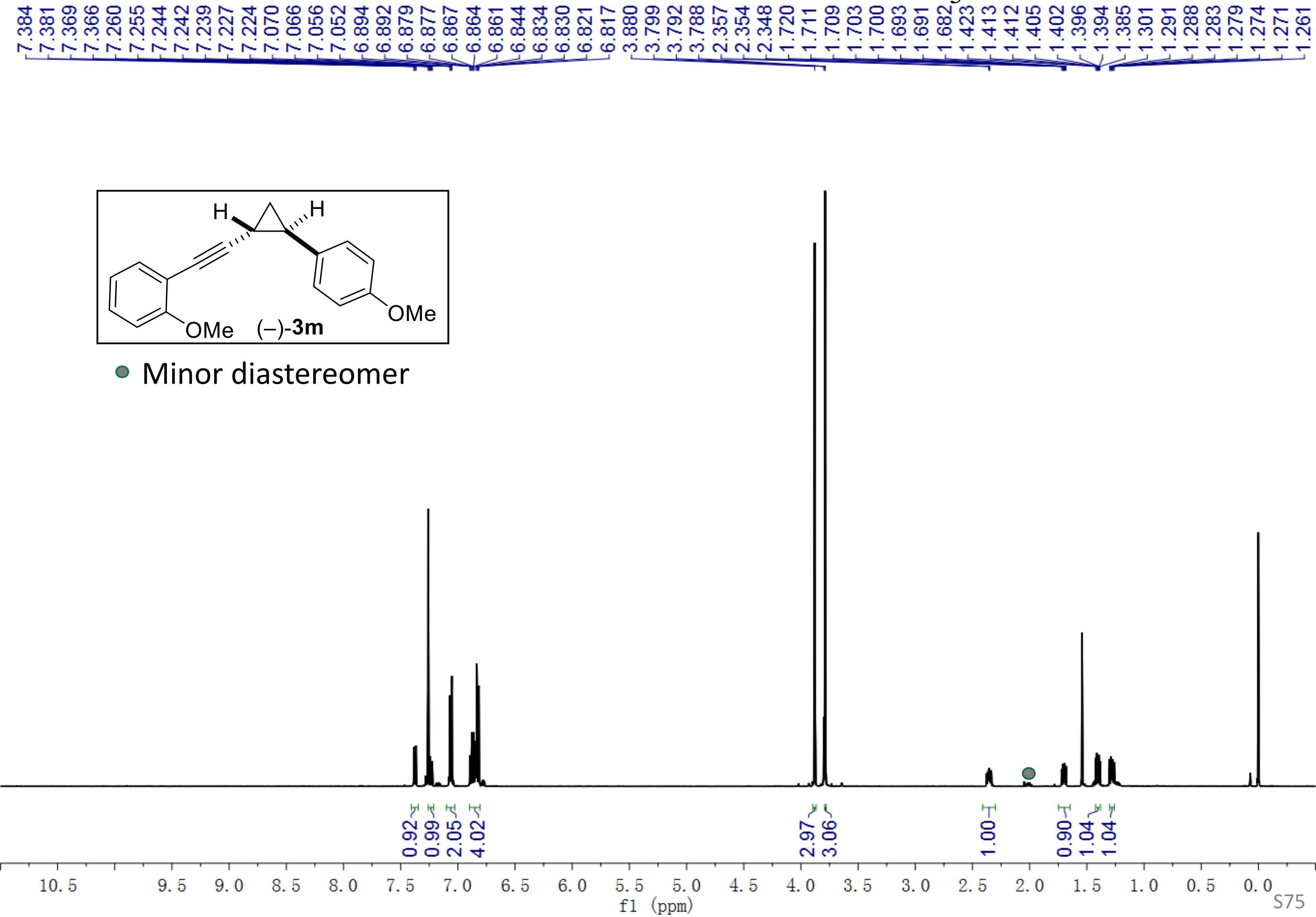


Peak Table

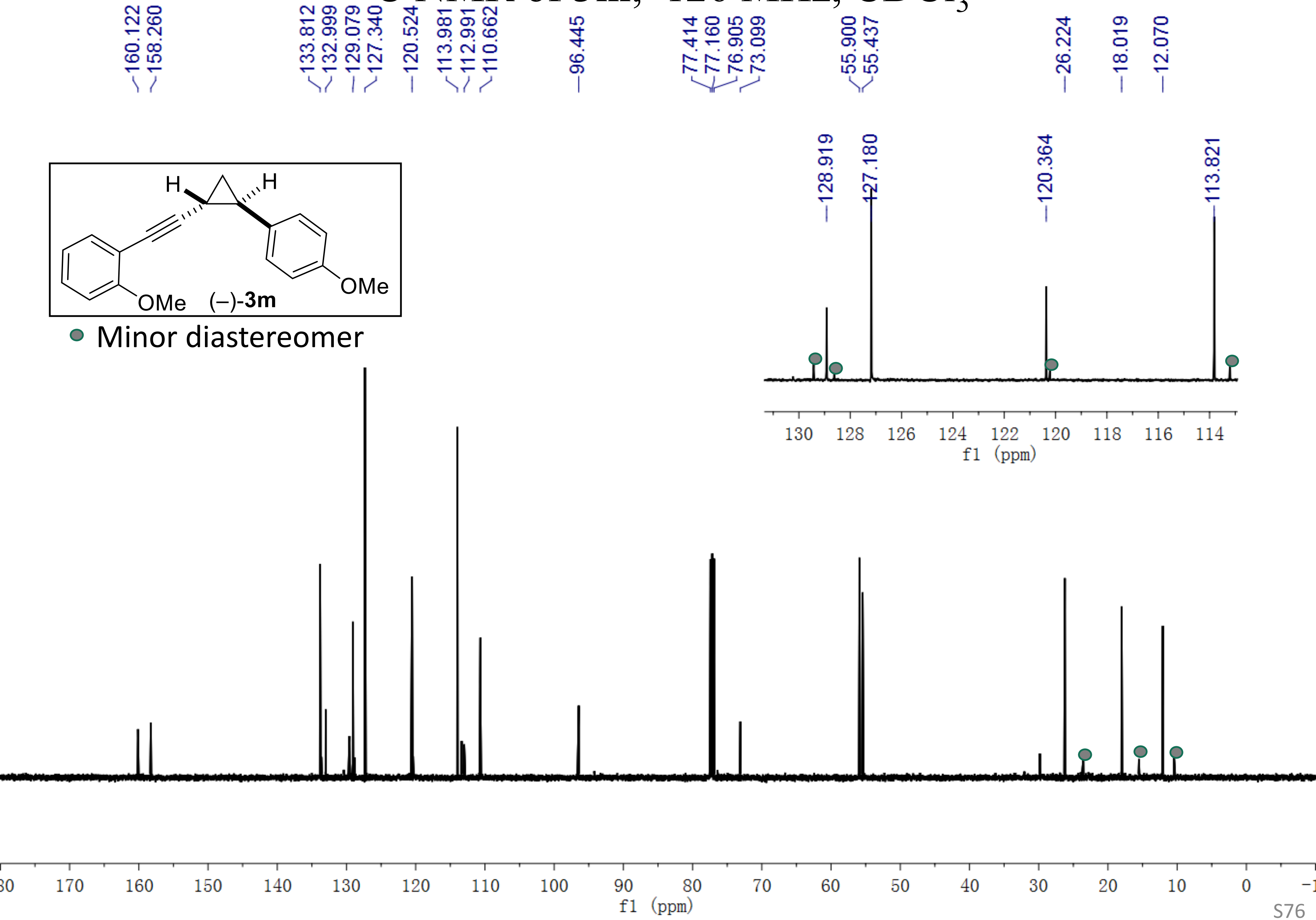
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.351	28725643	66.428
2	12.361	10836399	25.059
3	13.759	1966955	4.549
4	19.020	1714331	3.964
Total		43243327	100.000

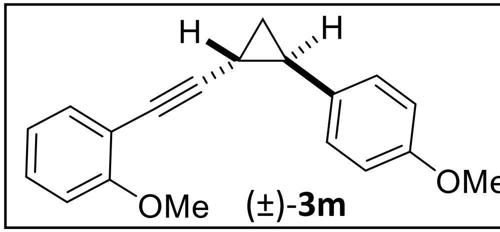
^{1}H NMR of **3m**, 500 MHz, $CDCl_3$



^{13}C NMR of **3m**, 126 MHz, $CDCl_3$

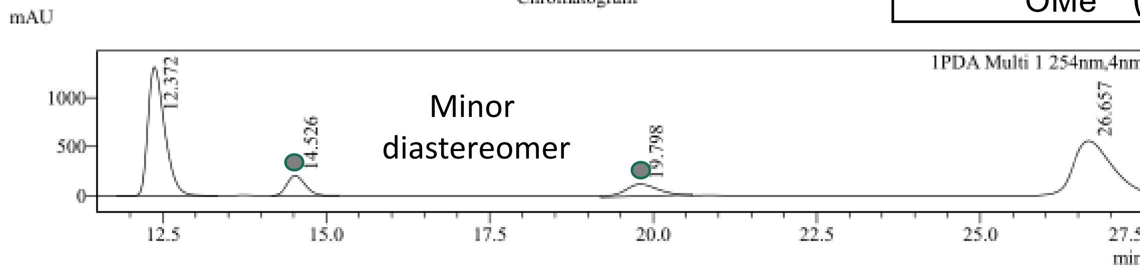


Data File : J0K-0171-IC-2%-0.8ML-isopropanol-solvent004.lcd
Sample Name : J0K-0171-IC-2%-0.8ML-isopropanol-solvent004
Sample ID : J0K-0171-IC-2%-0.8ML-isopropano
Method File : J0K-2%-0.8ml.lcm

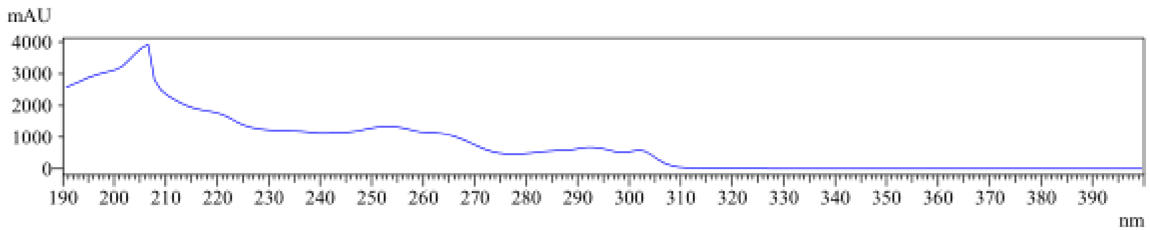


(±)-**3m**

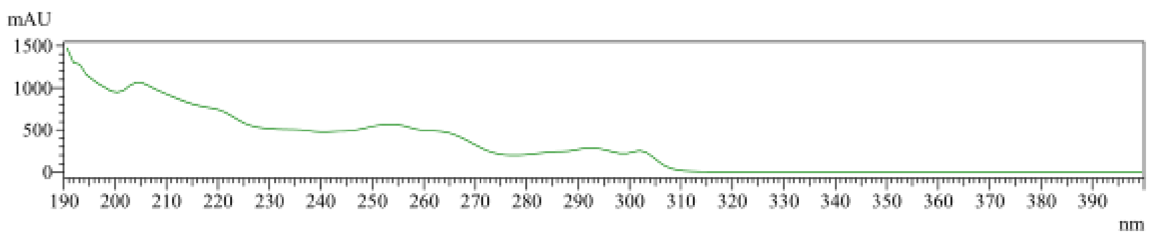
Chromatogram



UV Spectrum
Retention time = 12.372



UV Spectrum
Retention time = 26.657

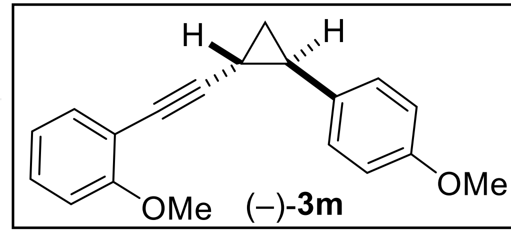


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.372	23278478	41.919
2	14.526	4205933	7.574
3	19.798	4184760	7.536
4	26.657	23862693	42.971
Total		55531864	100.000

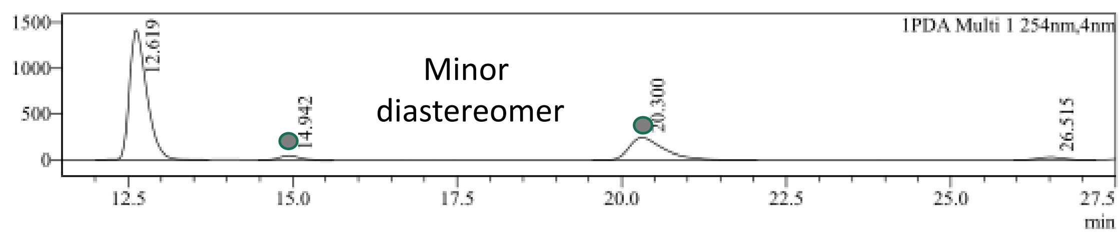
Data File : J0K-0172-IC-2%-0.8ML-isopropanol-solvent004.lcd
Sample Name : J0K-0172-IC-2%-0.8ML-isopropanol-solvent004
Sample ID : J0K-0172-IC-2%-0.8ML-isopropano
Method File : J0K-2%-0.8ml.lcm



(–)-**3m**

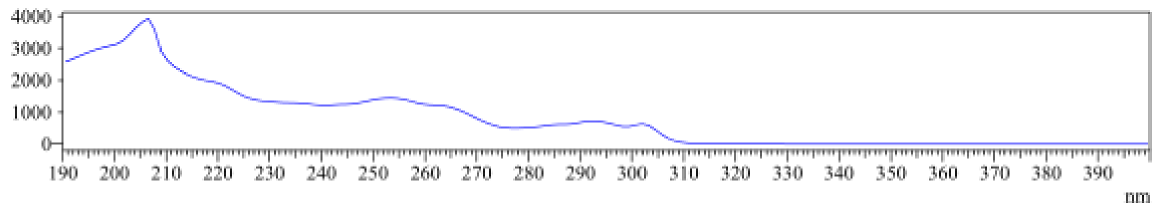
Chromatogram

mAU



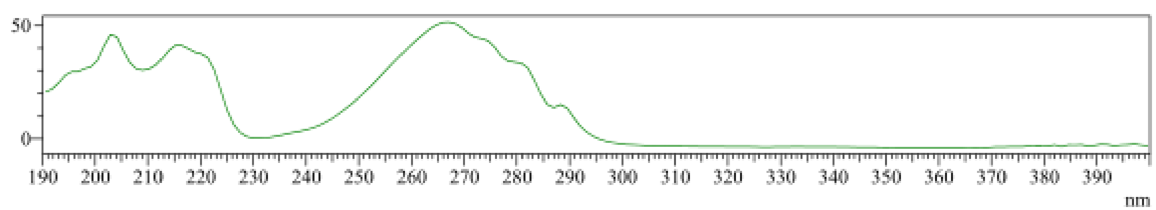
UV Spectrum
Retention time = 12.619

mAU



UV Spectrum
Retention time = 26.515

mAU

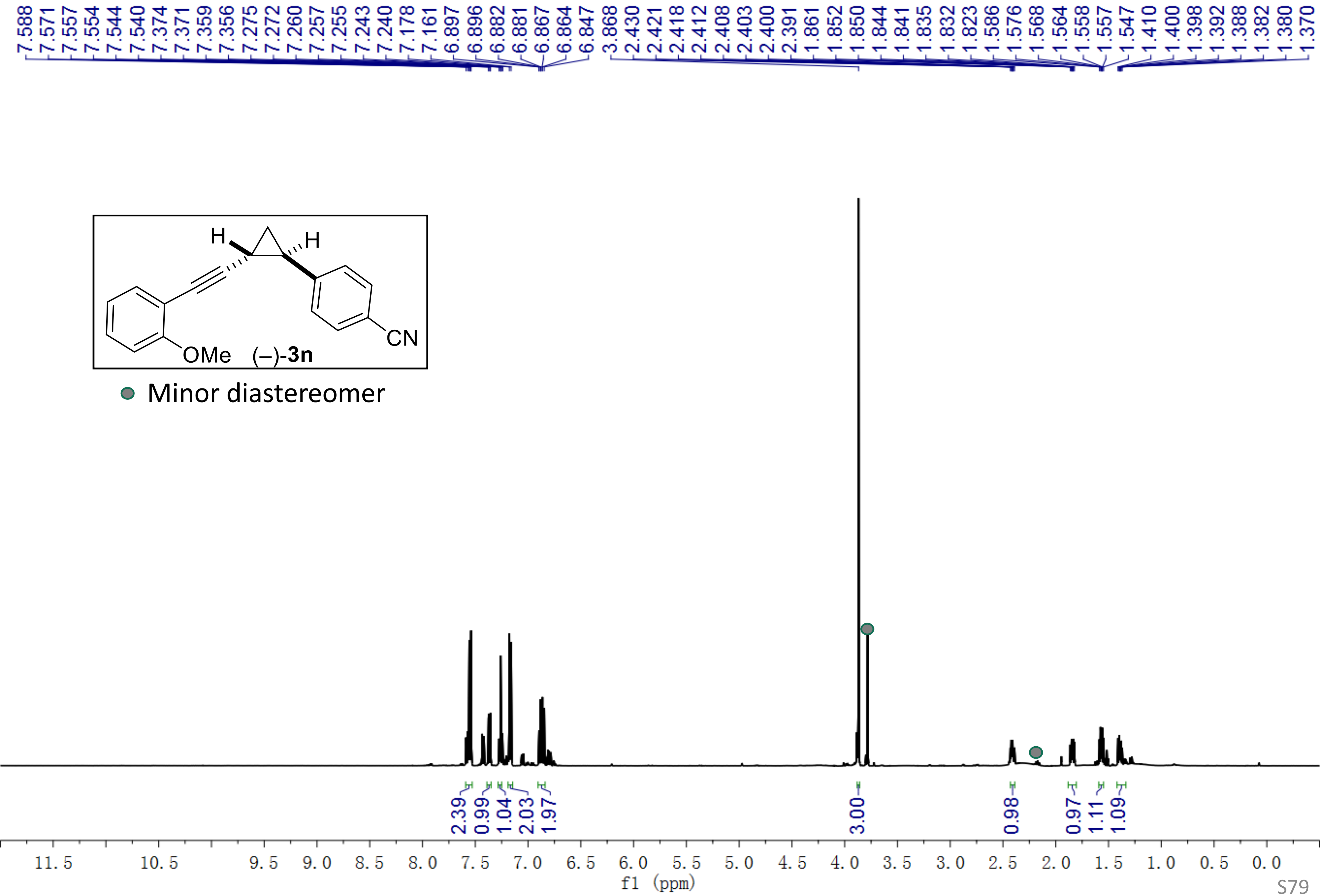


Peak Table

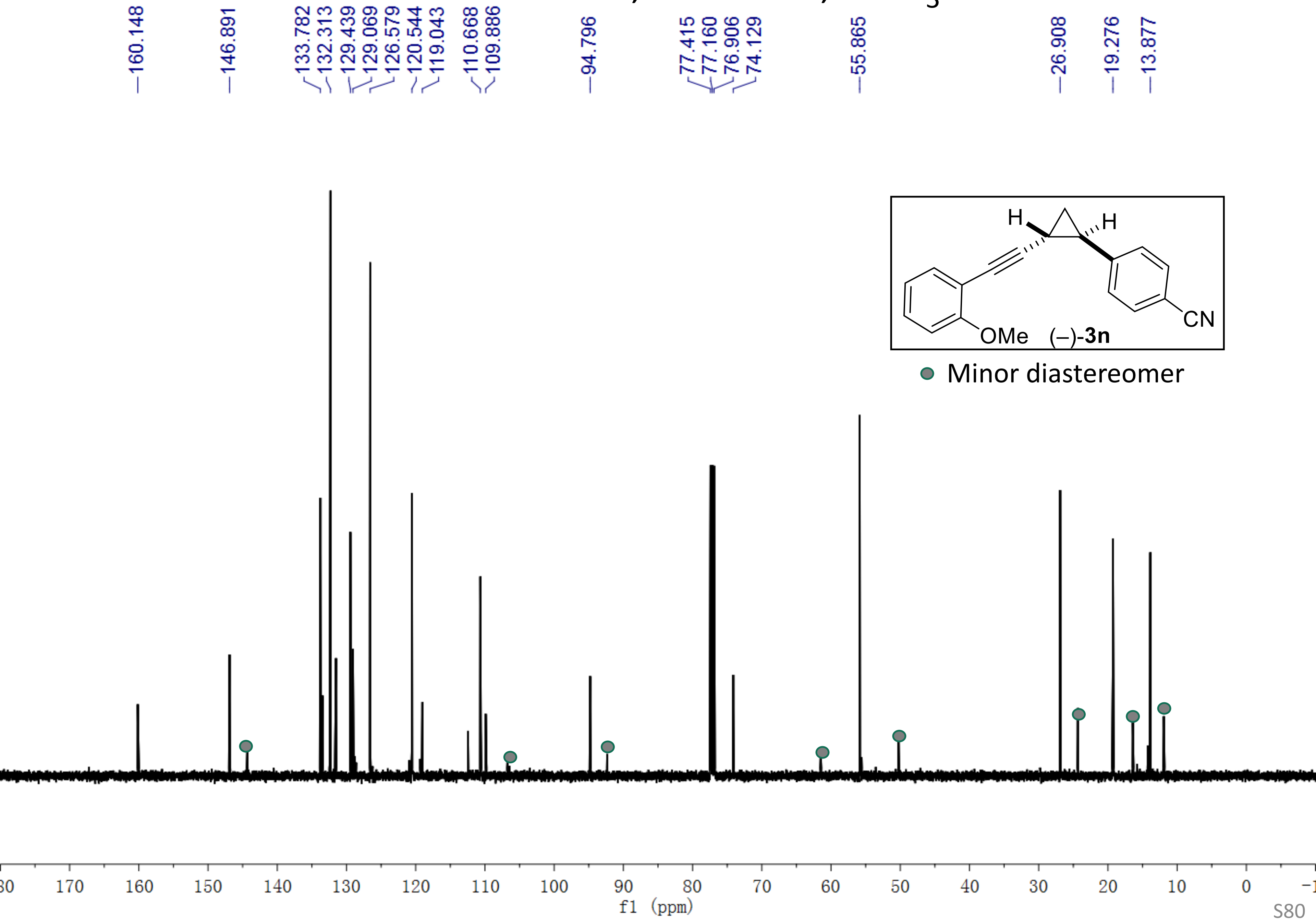
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.619	25840960	70.332
2	14.942	1295076	3.525
3	20.300	8808180	23.973
4	26.515	797214	2.170
Total		36741431	100.000

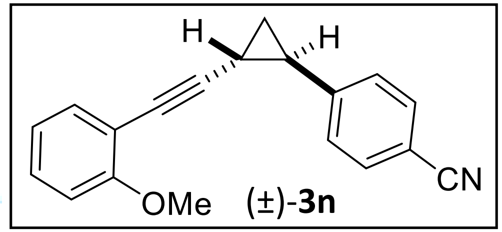
^{1}H NMR of **3n**, 600 MHz, $CDCl_3$



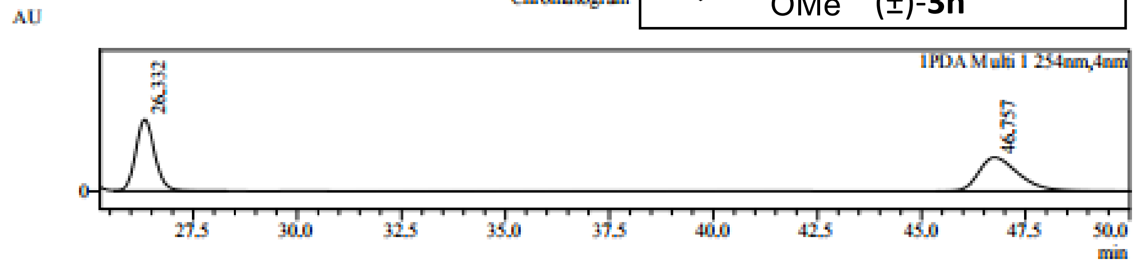
^{13}C NMR of **3n**, 151 MHz, $CDCl_3$



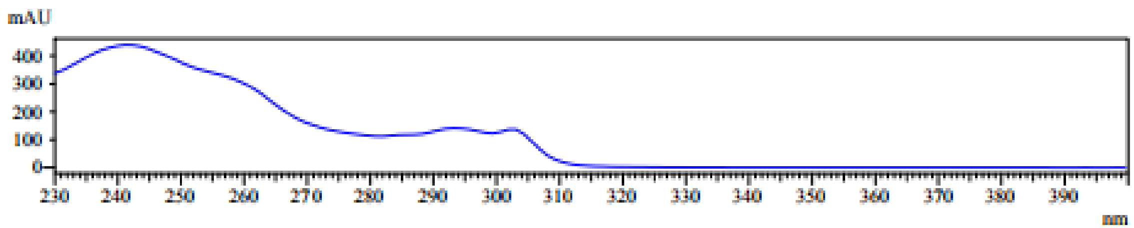
Data File : J0K-0631-IC--10%-1ML.lcd
Sample Name : J0K-0631-IC--10%-1ML
Sample ID : J0K-0631-IC--10%-1ML
Method File : J0K-10%--50min-1ml.lcm



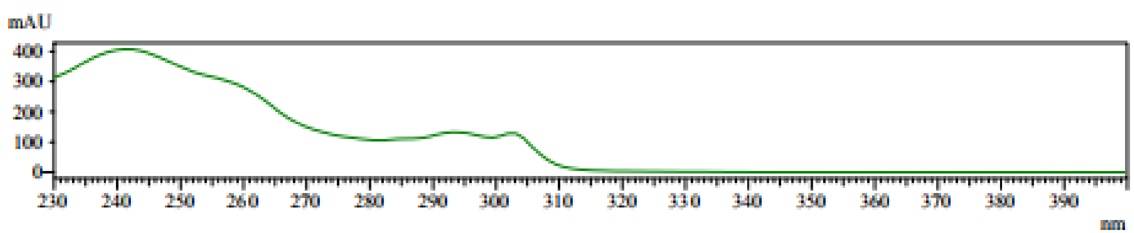
Chromatogram



UV Spectrum
Retention time = 23.718



L
Retention time = 24.752

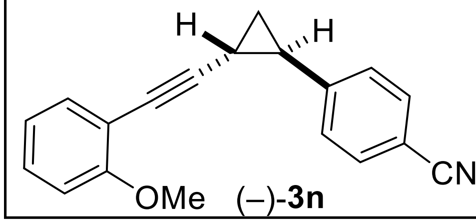


Peak Table

PDA Ch1 254nm

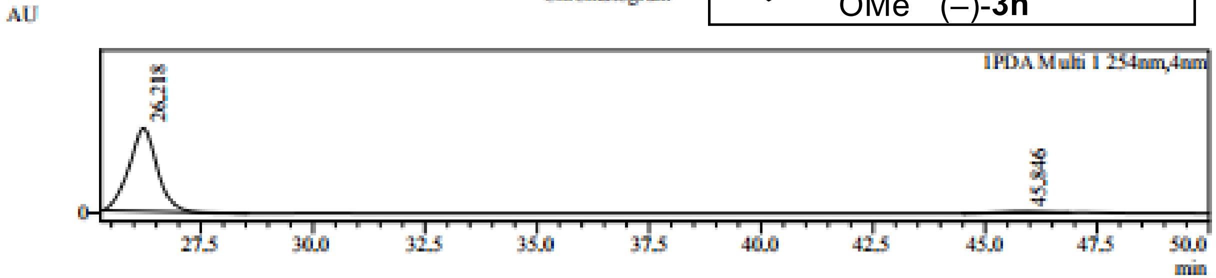
Peak#	Ret. Time	Area	Area%
1	23.718	9570289	21.223
2	24.752	9632285	21.361
3	26.332	12974775	28.773
4	46.757	12916100	28.643
Total		45093449	100.000

Data File : J0K-0630-IC--10%-1ML.lcd
Sample Name : J0K-0630-IC--10%-1ML
Sample ID : J0K-0630-IC--10%-1ML
Method File : J0K-10%--50min-1ml.lcm

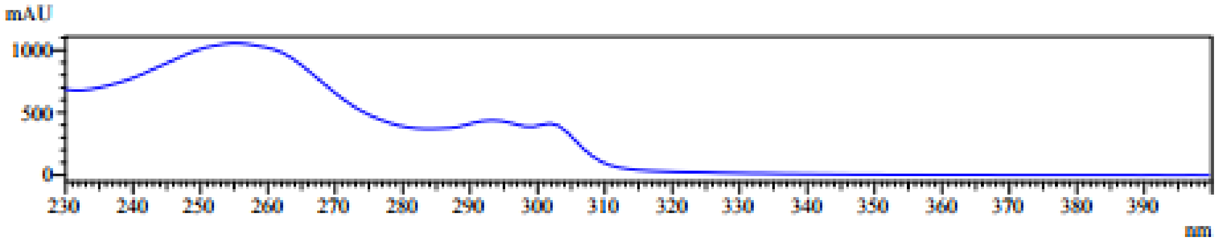


(–)-**3n**

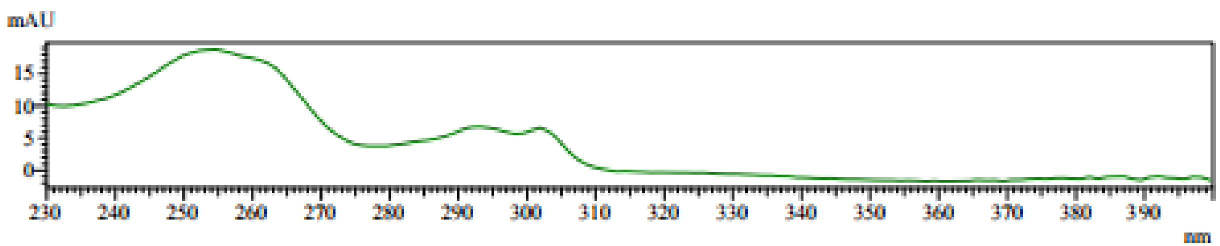
Chromatogram



UV Spectrum
Retention time = 26.218



Retention time = 45.846

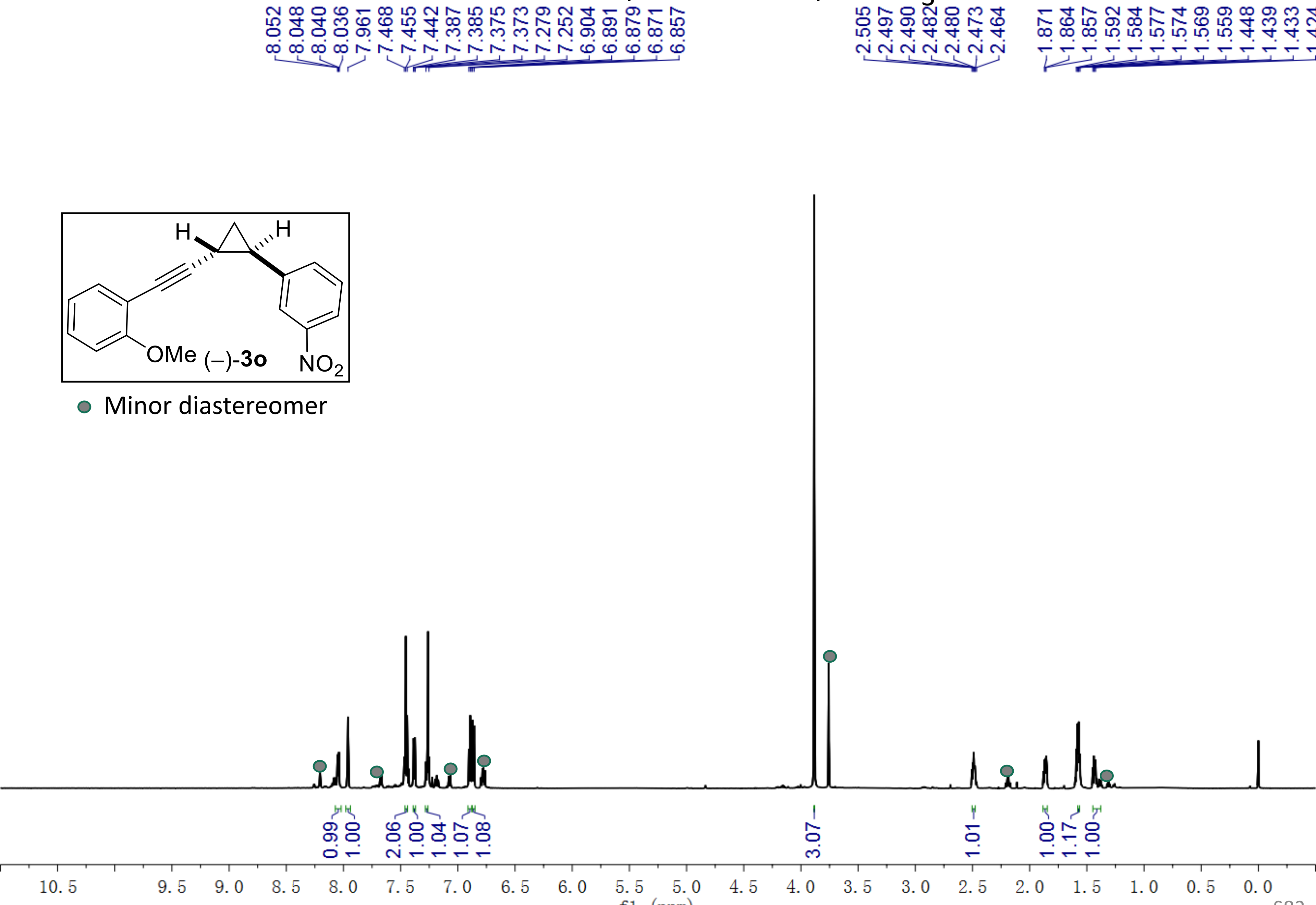


Peak Table

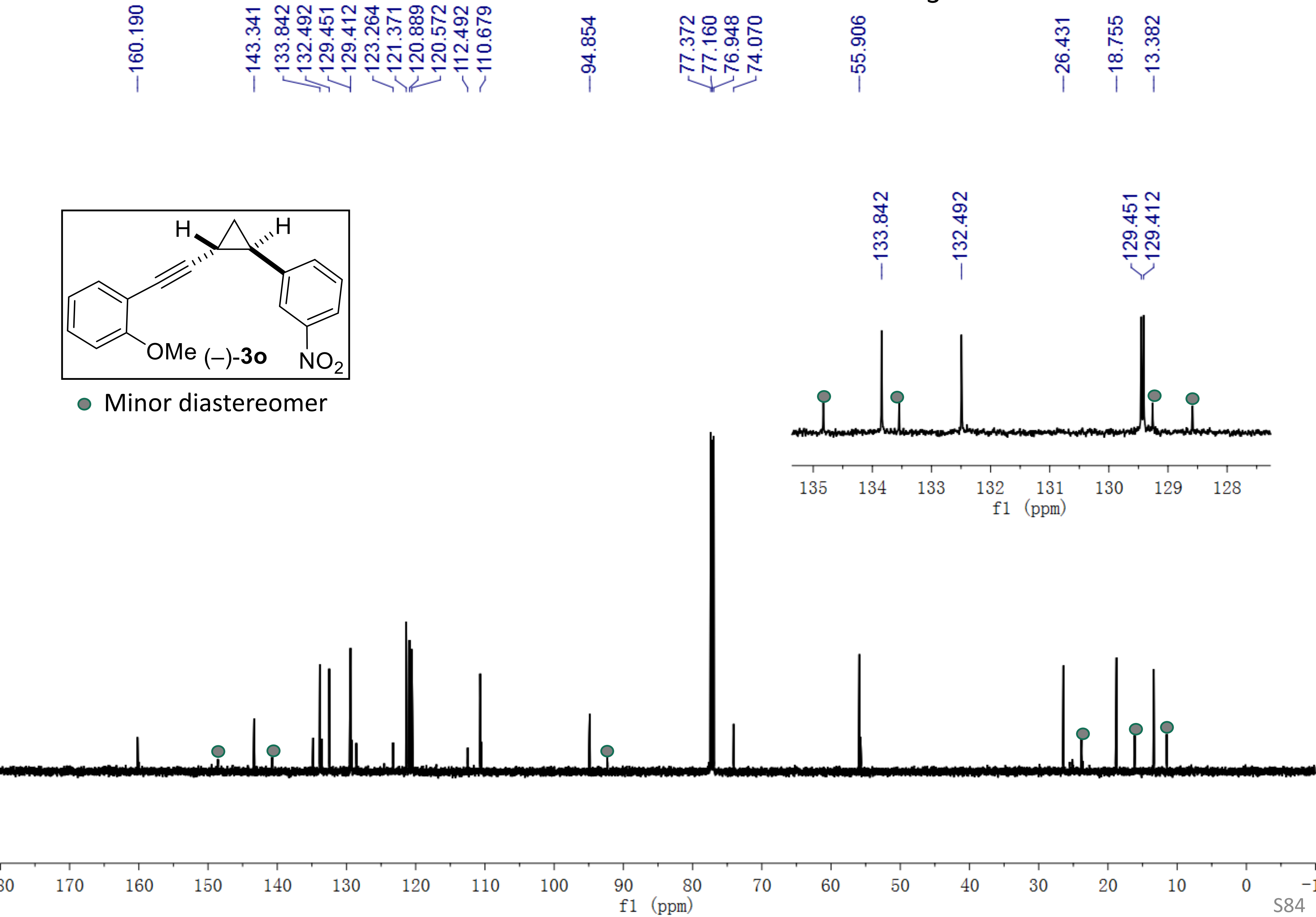
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.218	44689706	97.722
2	45.846	1041945	2.278
Total		45731651	100.000

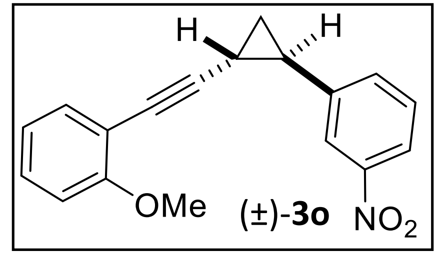
^{1}H NMR of **3o**, 600 MHz, $CDCl_3$



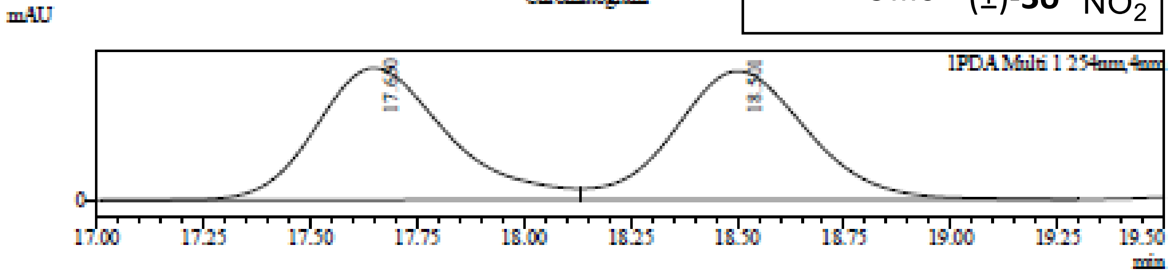
^{13}C NMR of **3o**, 151 MHz, $CDCl_3$



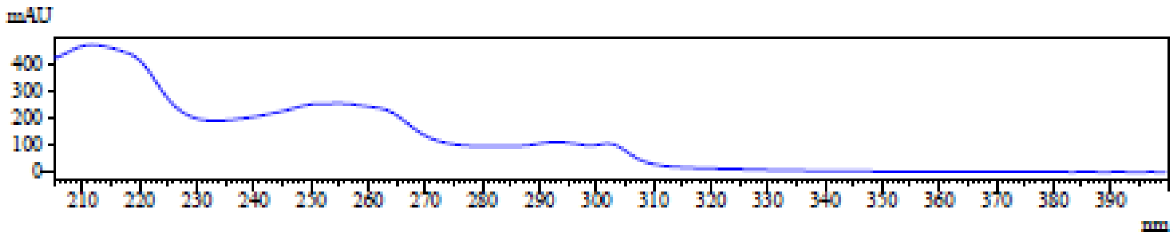
Data File	: J0K-0629-IC--10%-1ML.lcd
Sample Name	: J0K-0629-IC--10%-1ML
Sample ID	: J0K-0629-IC--10%-1ML
Method File	: J0K-10%--50min-1ml.lcm



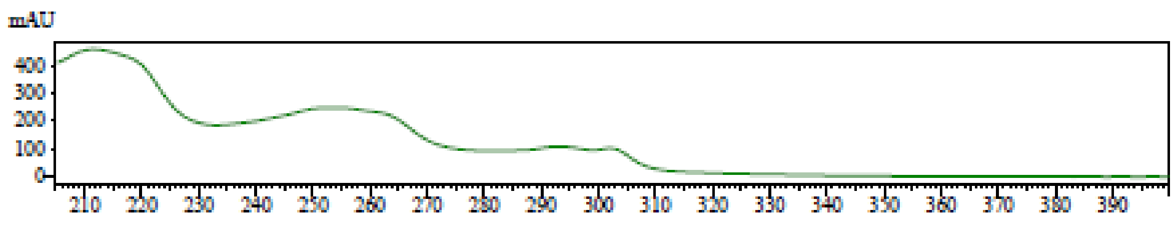
Chromatogram



UV Spectrum
Retention time = 17.650



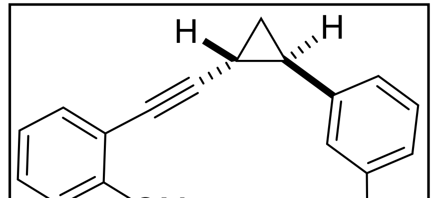
UV Spectrum
Retention time = 18.501



Peak Table

PDA Ch1 254nm

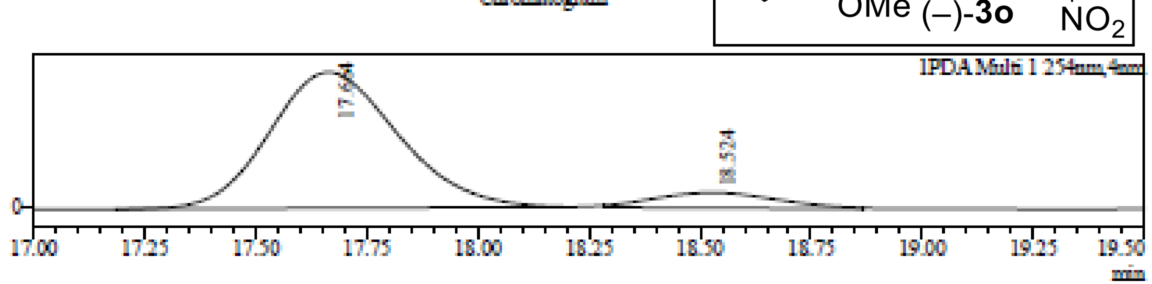
Peak#	Ret. Time	Area	Area%
1	17.650	5392862	50.364
2	18.501	5314868	49.636
Total		10707730	100.000



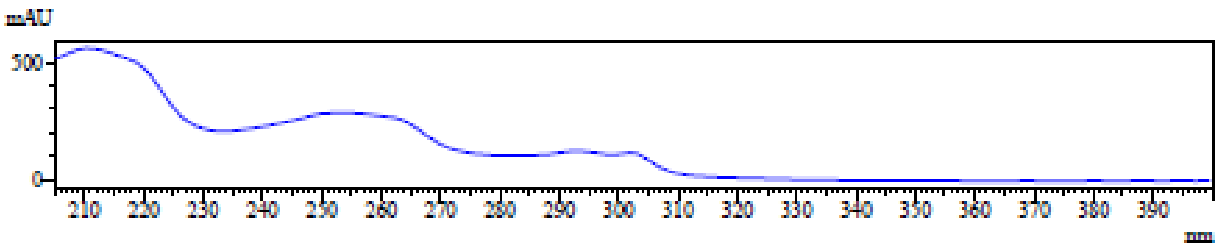
(–)-**3o**

Data File : J0K-0628-IC--10%-1ML.lcd
Sample Name : J0K-0628-IC--10%-1ML
Sample ID : J0K-0628-IC--10%-1ML
Method File : J0K-10%--50min-1ml.lcm

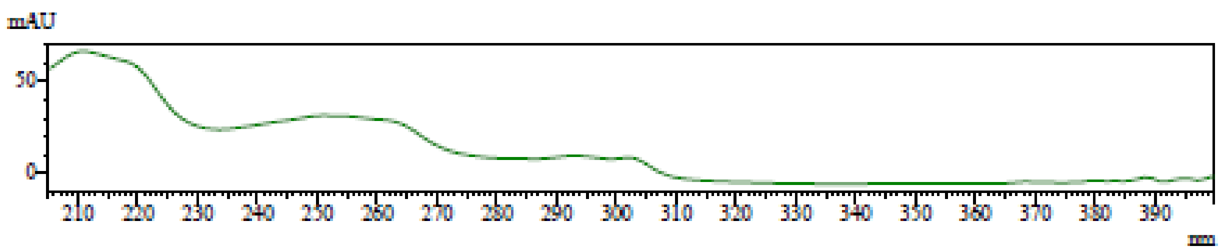
Chromatogram



UV Spectrum
Retention time = 17.664



UV Spectrum
Retention time = 18.524

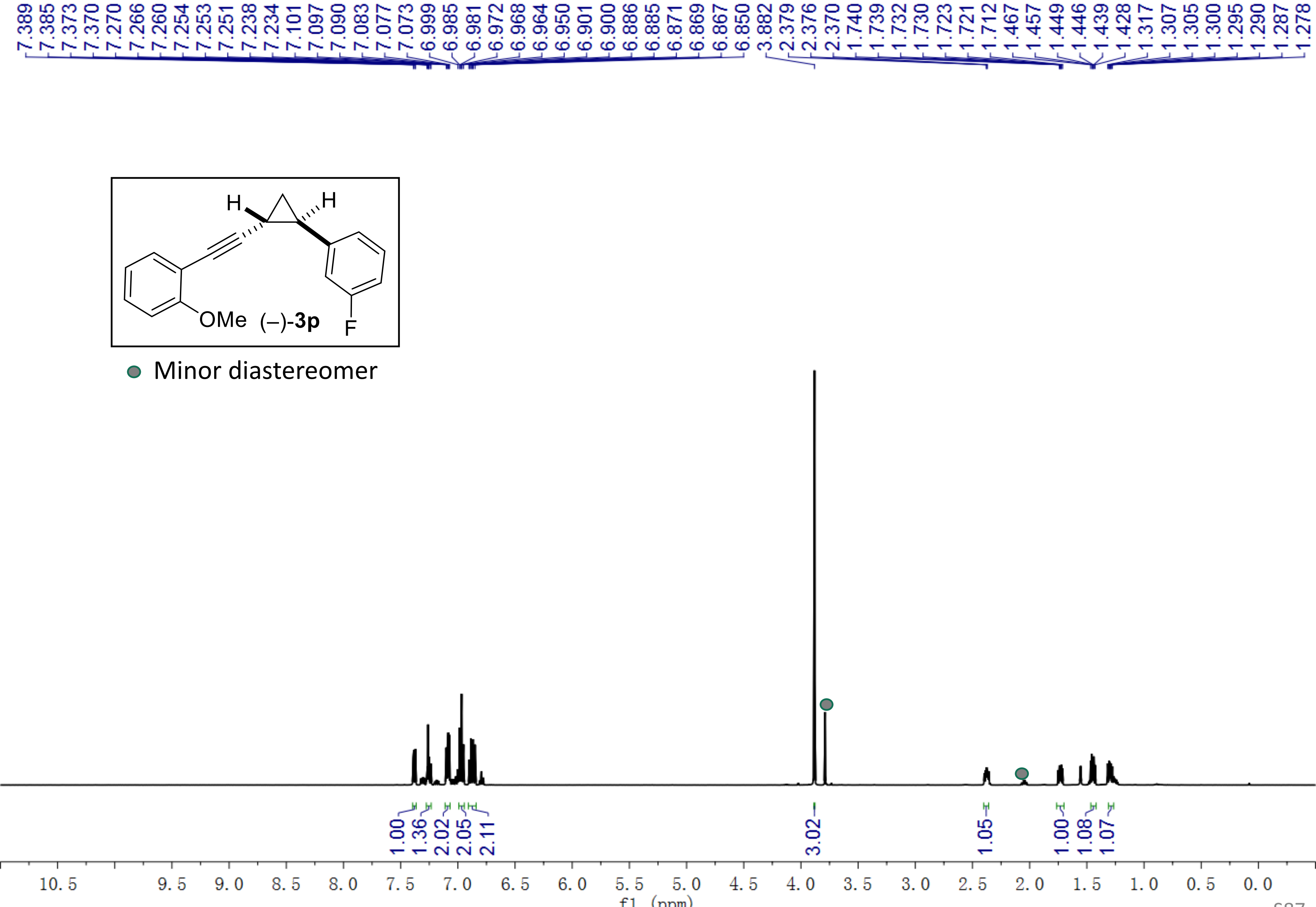


Peak Table

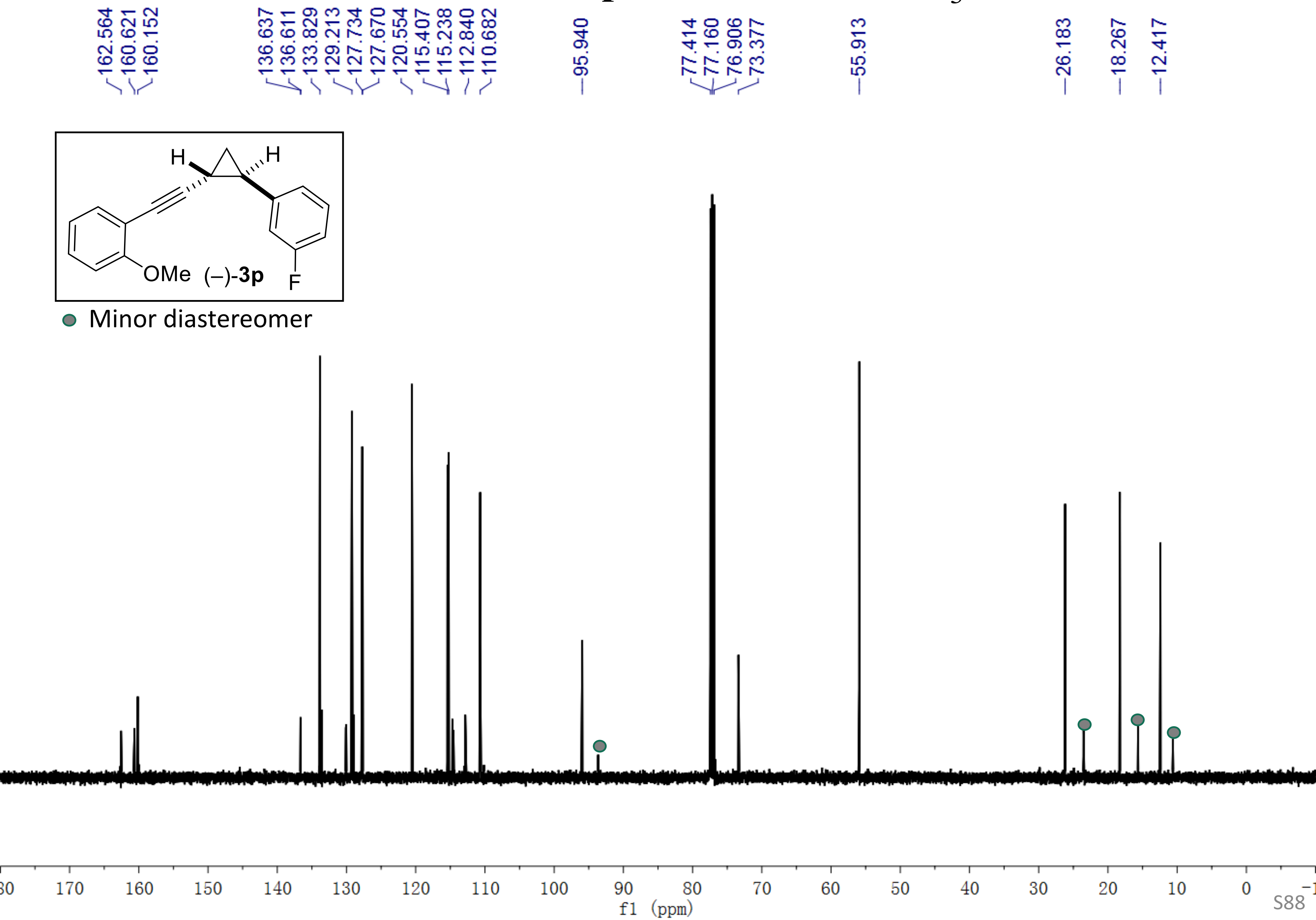
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.664	5722100	90.281
2	18.524	616010	9.719
Total		6338110	100.000

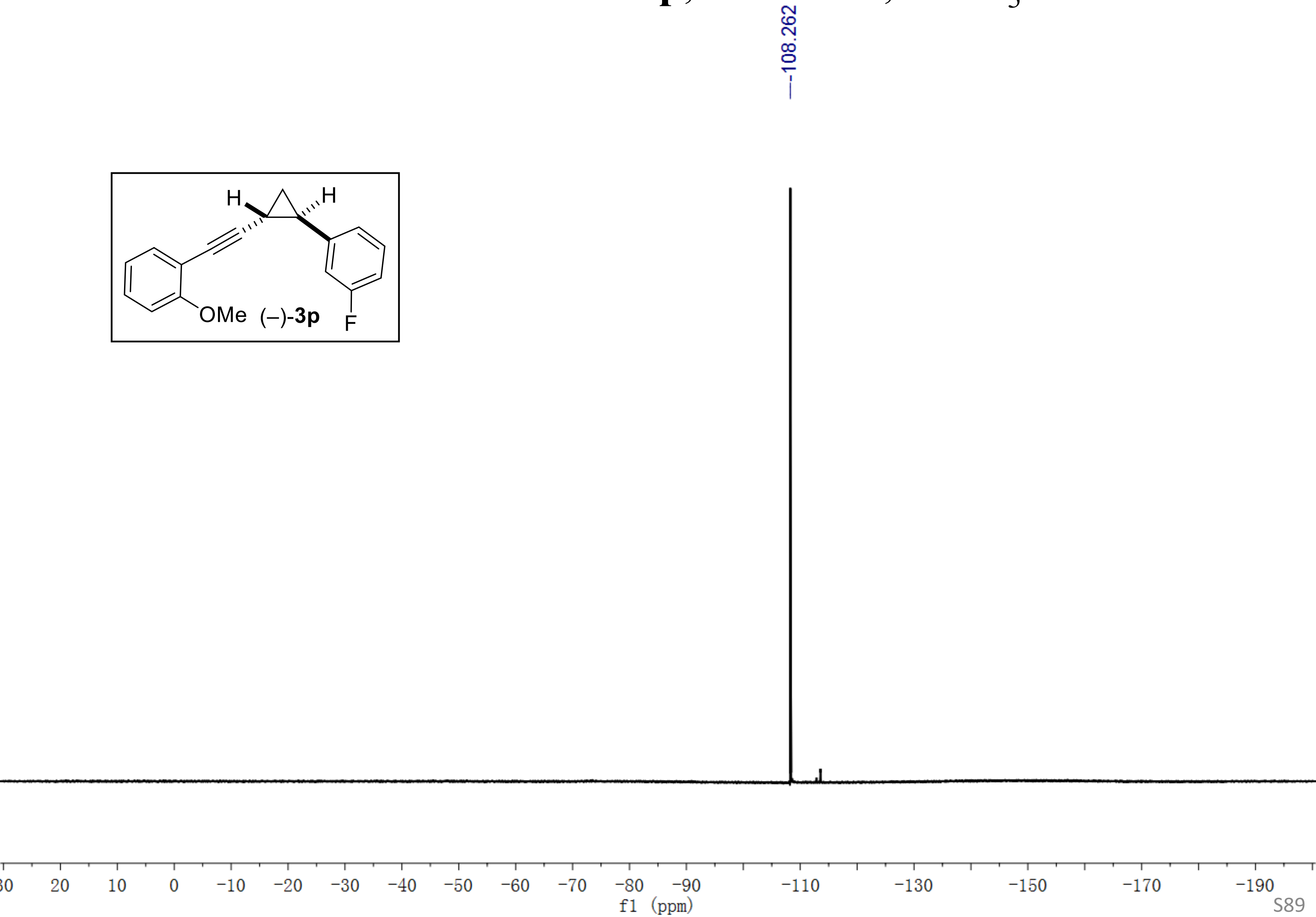
^{1}H NMR of **3p**, 500 MHz, $CDCl_3$



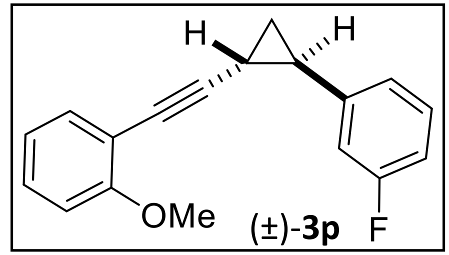
^{13}C NMR of **3p**, 126 MHz, $CDCl_3$



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

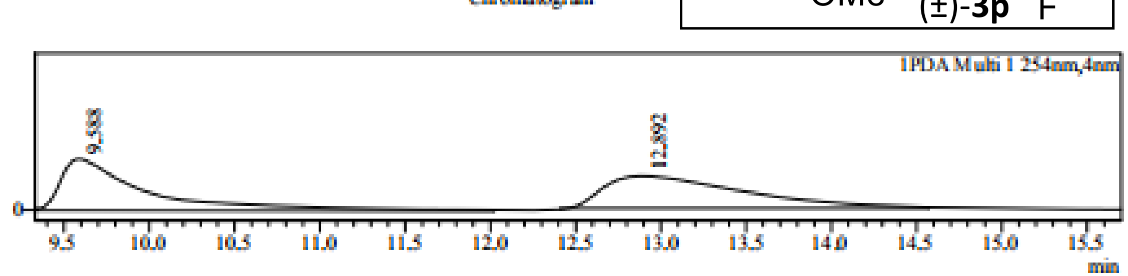


Data File : J0K-1512-new-IA--0.3%-1ML.lcd
Sample Name : J0K-1512-new-IA--0.3%-1ML
Sample ID : J0K-1512-new-IA--0.3%-1ML
Method File : J0K-0.3%--45min-1ml.lcm

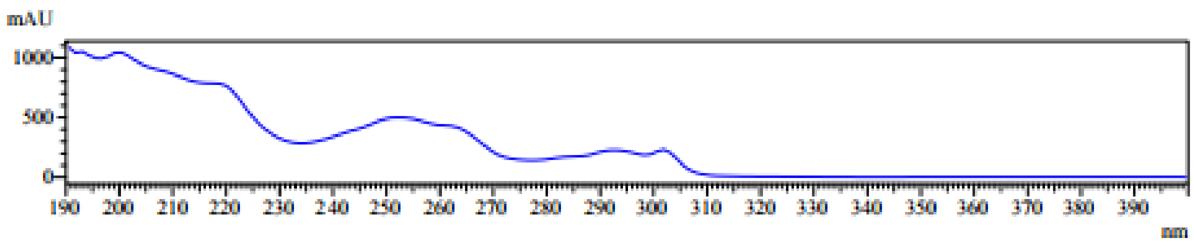


(±)-3p

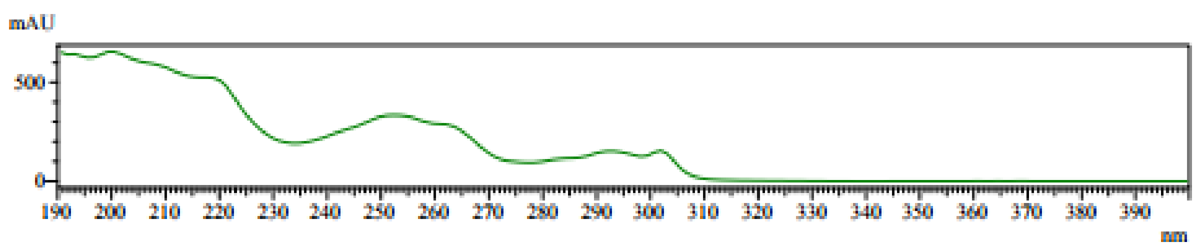
Chromatogram



UV Spectrum
Retention time = 9.588



L
Retention time = 12.892

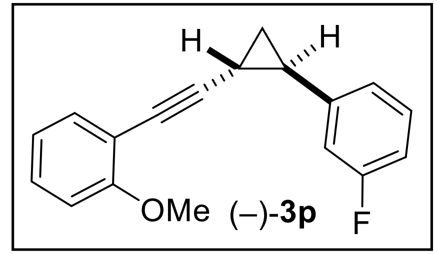


Peak Table

PDA Ch1 254nm

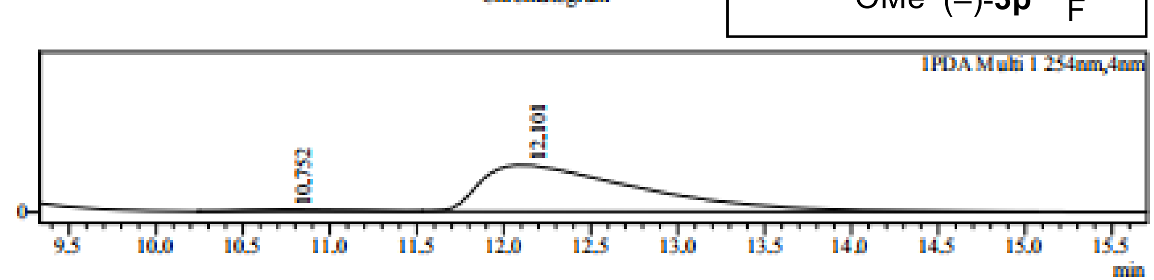
Peak#	Ret. Time	Area	Area%
1	9.588	17225820	49.482
2	12.892	17586782	50.518
Total		34812602	100.000

Data File : J0K-1511-IA--0.3%-1ML.lcd
Sample Name : J0K-1511-IA--0.3%-1ML
Sample ID : J0K-1511-IA--0.3%-1ML
Method File : J0K-0.3%--25min-1ml.lcm

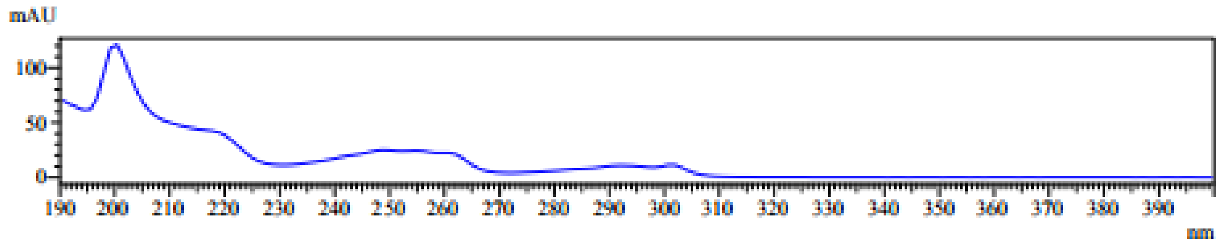


(–)-**3p**

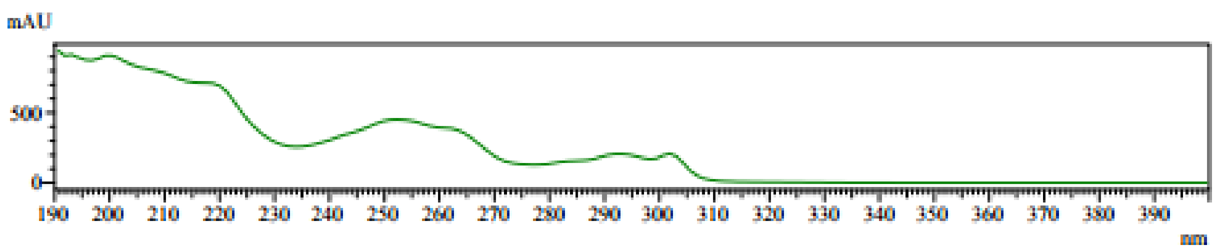
Chromatogram



UV Spectrum
Retention time = 10.752



Retention time = 12.101

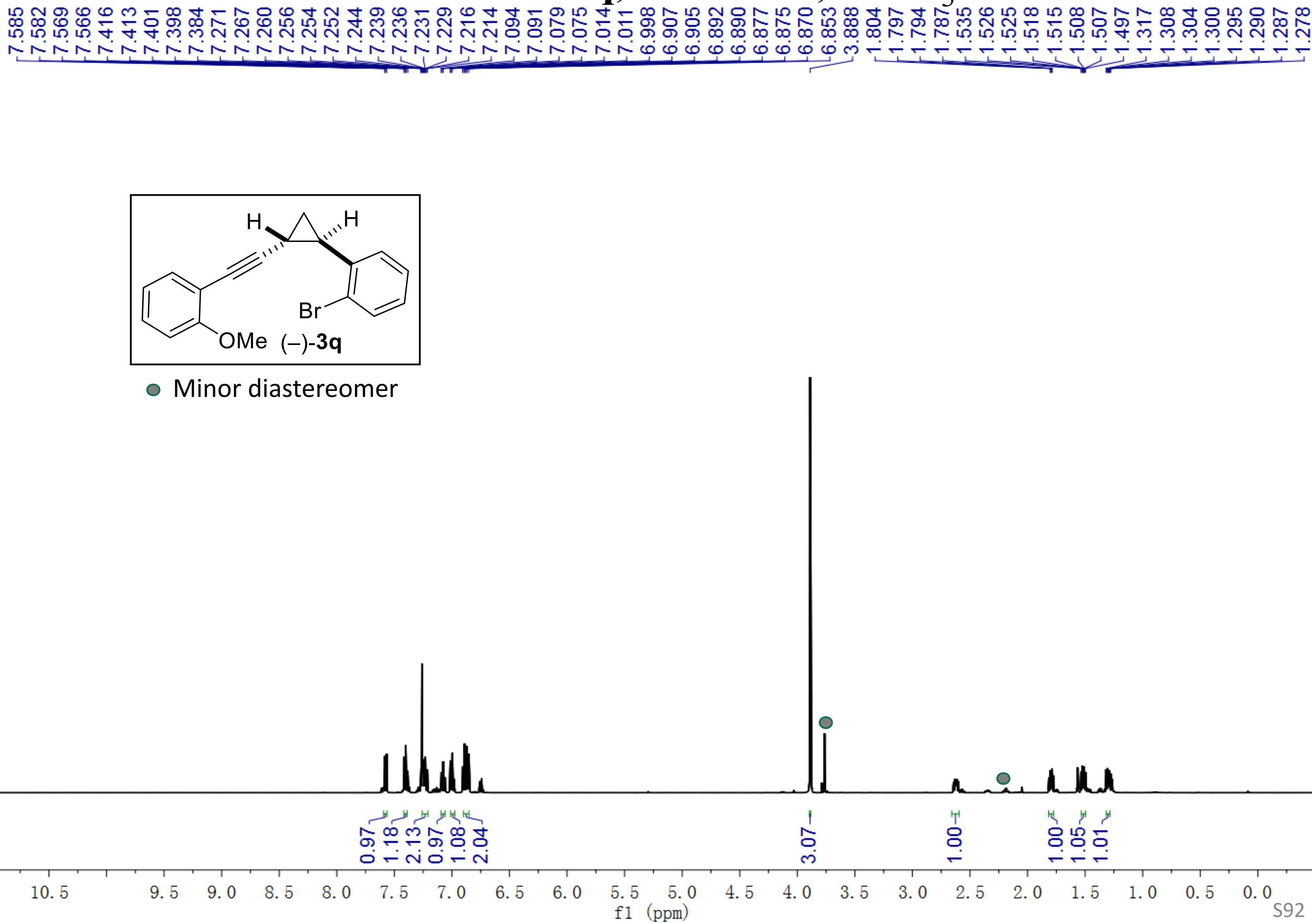


Peak Table

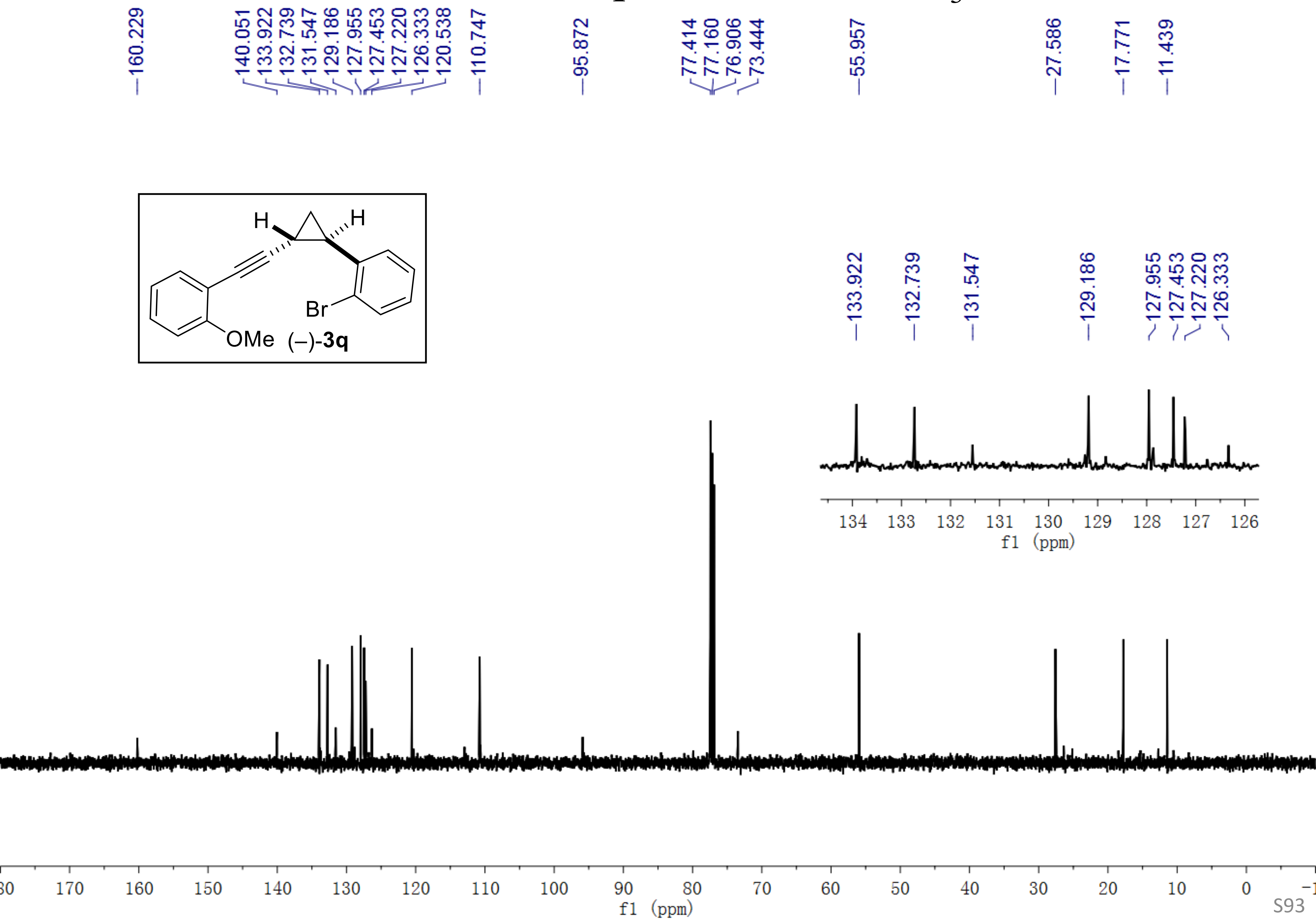
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.752	770306	2.706
2	12.101	27700720	97.294
Total		28471026	100.000

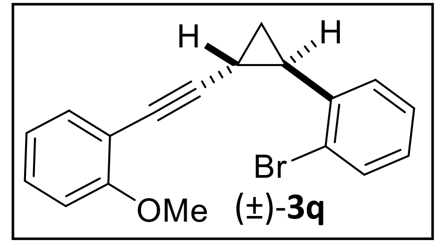
^{1}H NMR of **3q**, 500 MHz, $CDCl_3$



^{13}C NMR of **3q**, 151 MHz, $CDCl_3$

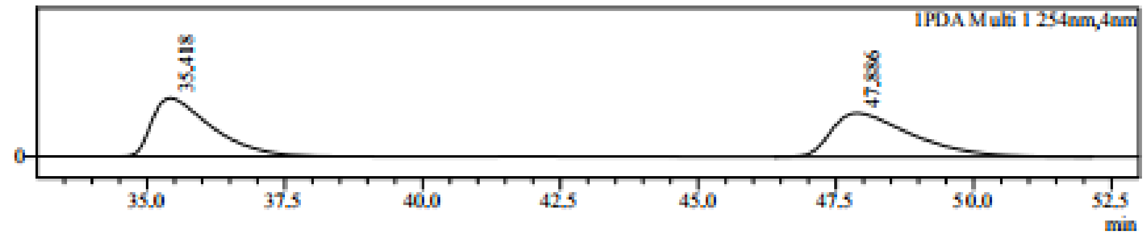


Data File : J0K-1451-ODH-2%-1ML-2.lcd
Sample Name : J0K-1451-ODH-2%-1ML-2
Sample ID : J0K-1451-ODH-2%-1ML-2
Method File : J0K-2%-40min-1mL1cm

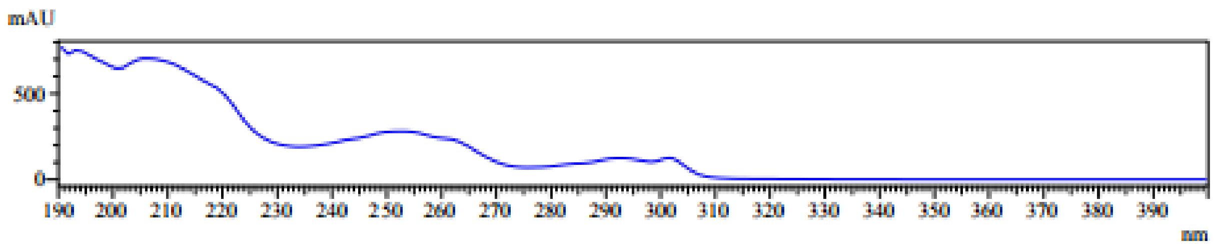


(±)-**3q**

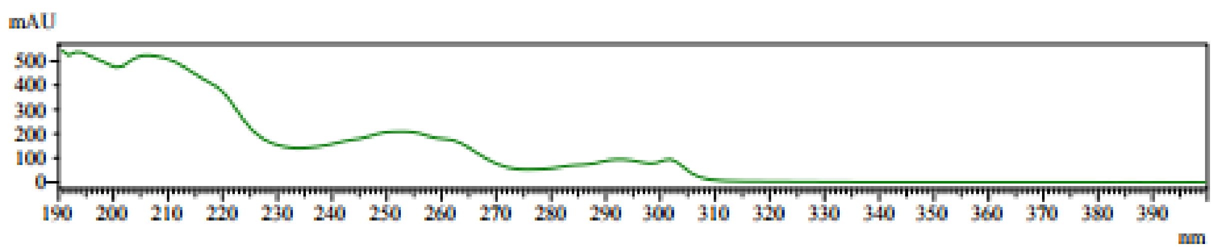
Chromatogram



UV Spectrum
Retention time = 35.418



Retention time = 47.886

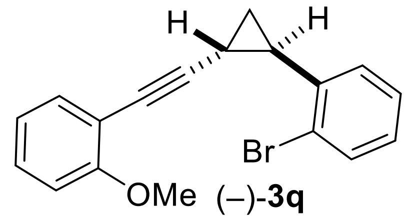


Peak Table

PDA Ch1 254nm

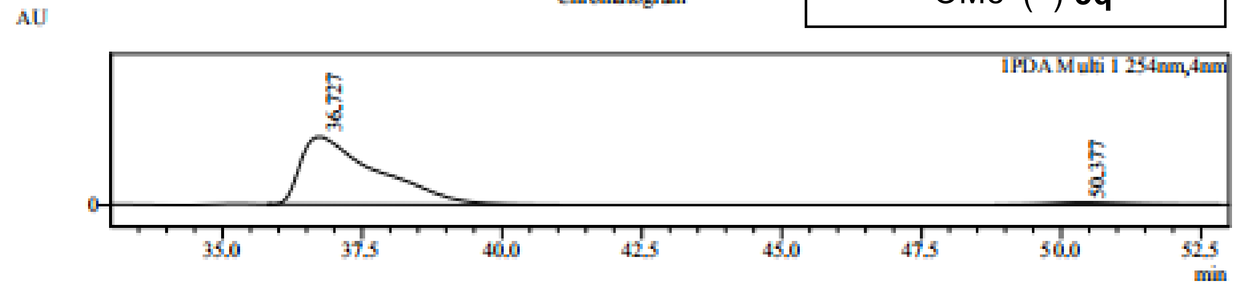
Peak#	Ret. Time	Area	Area%
1	35.418	20668199	50.095
2	47.886	20589932	49.905
Total		41258131	100.000

Data File : J0K-1449-ODH-2%-1ML-2.lcd
Sample Name : J0K-1449-ODH-2%-1ML-2
Sample ID : J0K-1449-ODH-2%-1ML-2
Method File : J0K-2%-40min-1ml.lcm

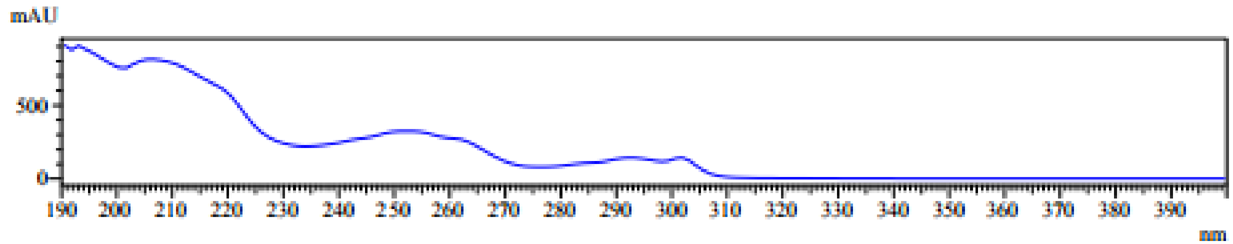


(–)-**3q**

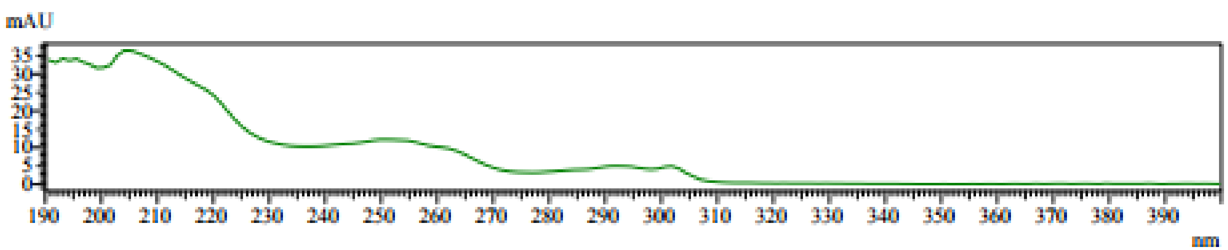
Chromatogram



UV Spectrum
Retention time = 36.727



Retention time = 50.377

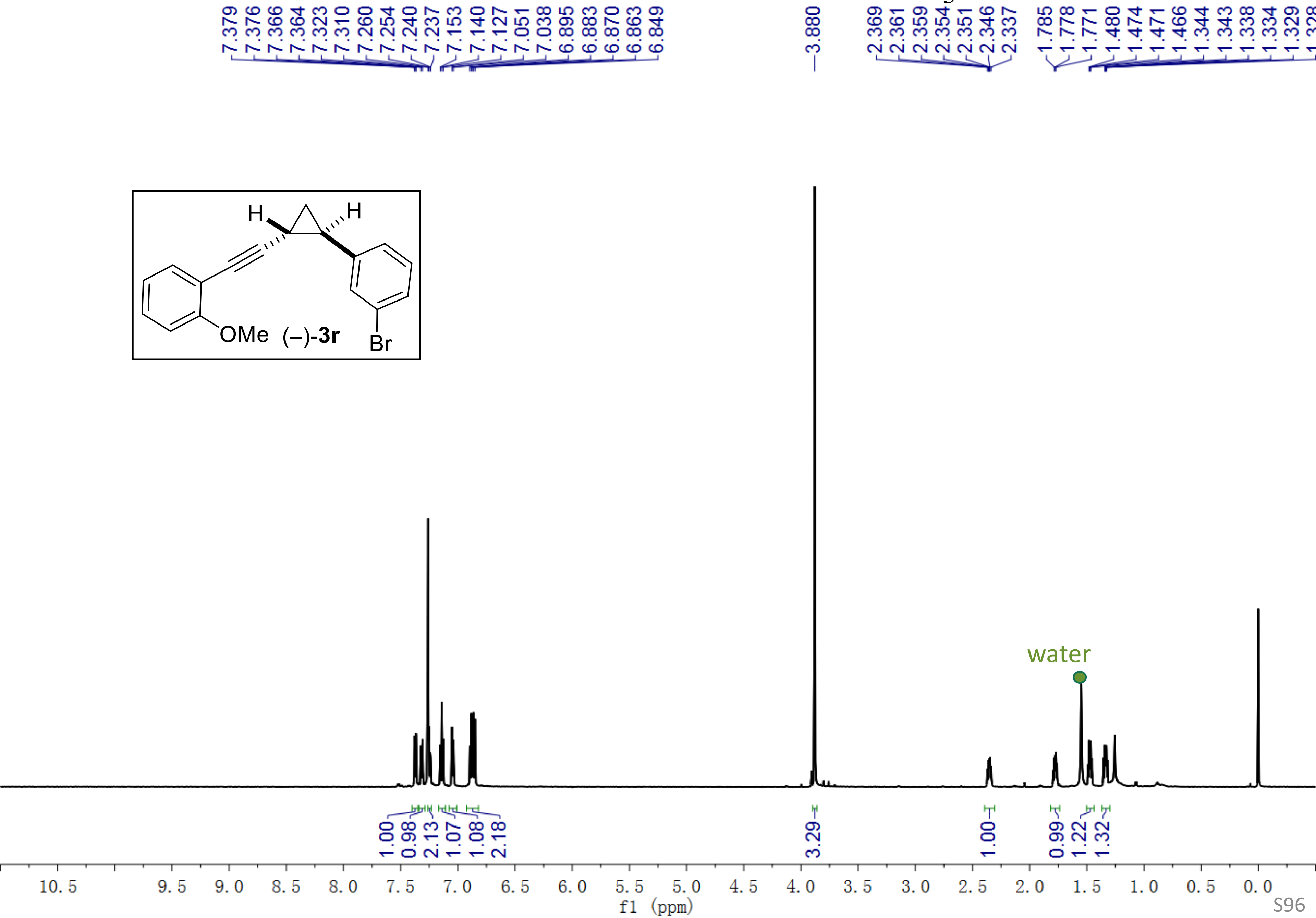


Peak Table

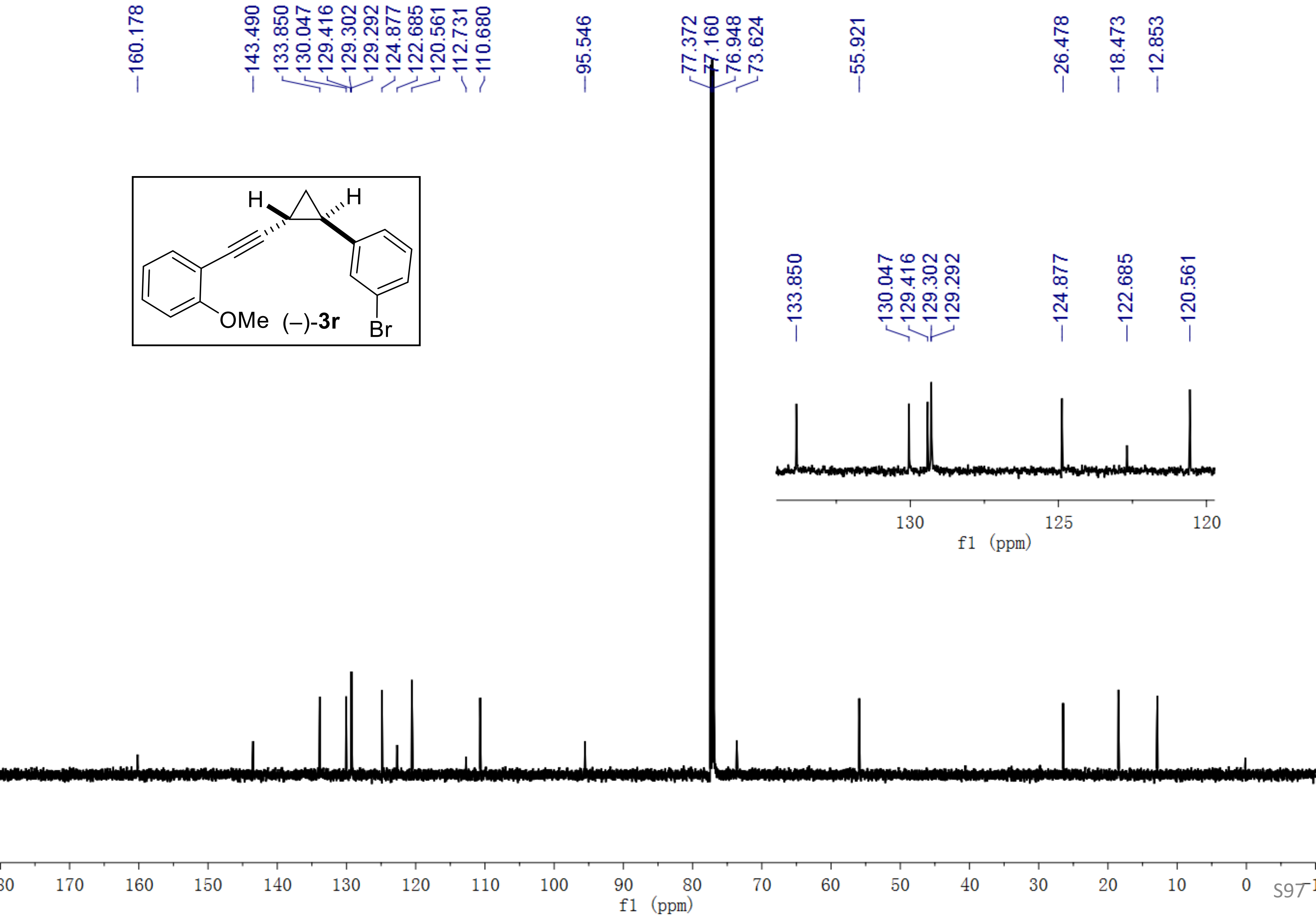
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	36.727	29767184	97.041
2	50.377	907689	2.959
Total		30674873	100.000

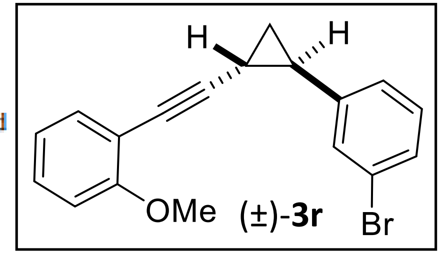
^{1}H NMR of **3r**, 600 MHz, $CDCl_3$



^{13}C NMR of **3r**, 151 MHz, $CDCl_3$

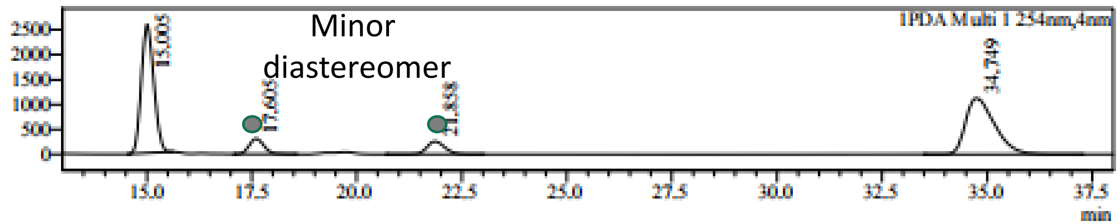


Data File : J0K-0341-IC-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0341-IC-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0341-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml-50min.lcm



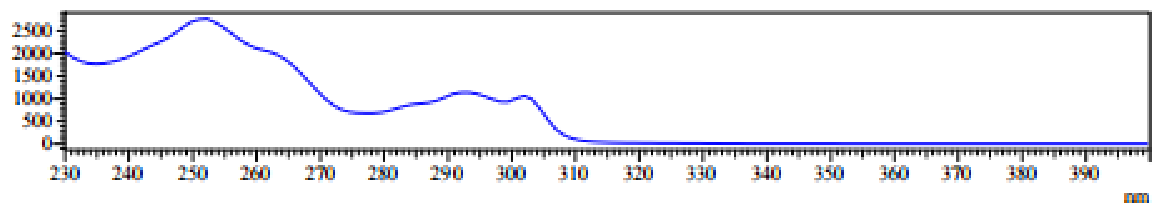
Chromatogram

mAU



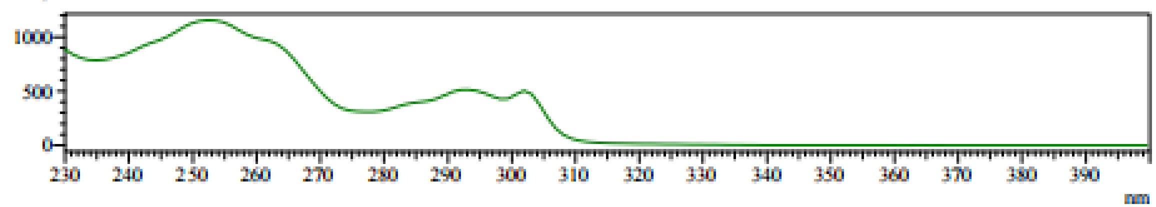
UV Spectrum
Retention time = 15.005

mAU



U
Retention time = 34.749

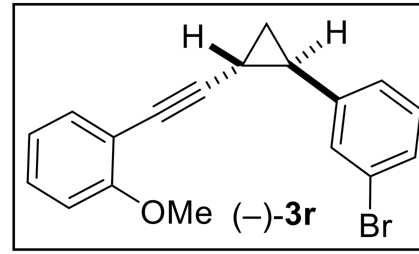
mAU



Peak Table

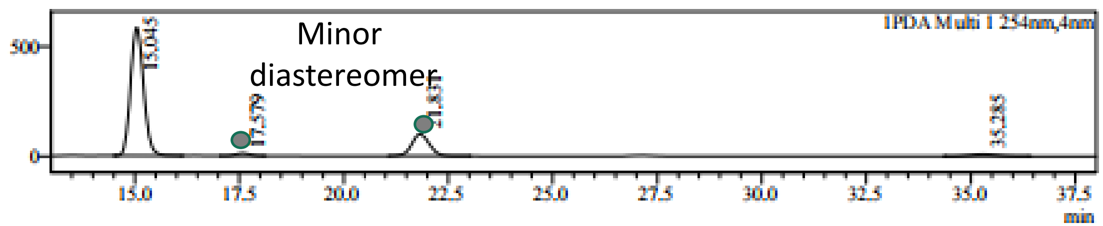
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.005	53369617	43.836
2	17.605	7481137	6.145
3	21.858	7551737	6.203
4	34.749	53346423	43.817
Total		121748915	100.000

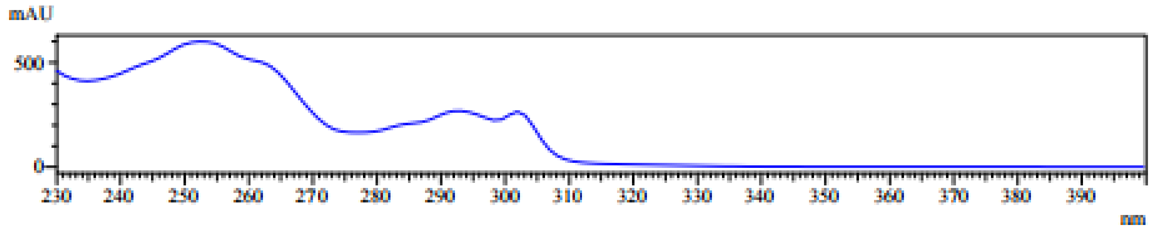


Data File : J0K-0297-IC-1%-0.8ML-isopropanol-solvent017.lcd
Sample Name : J0K-0297-IC-1%-0.8ML-isopropanol-solvent017
Sample ID : J0K-0297-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8m-50MINI.lcm

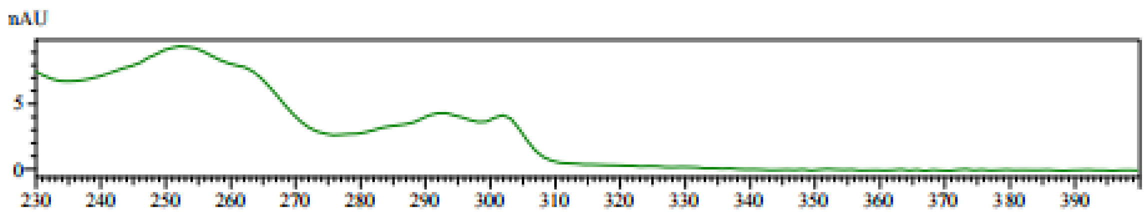
Chromatogram



UV Spectrum
Retention time = 15.045



Retention time = 35.285

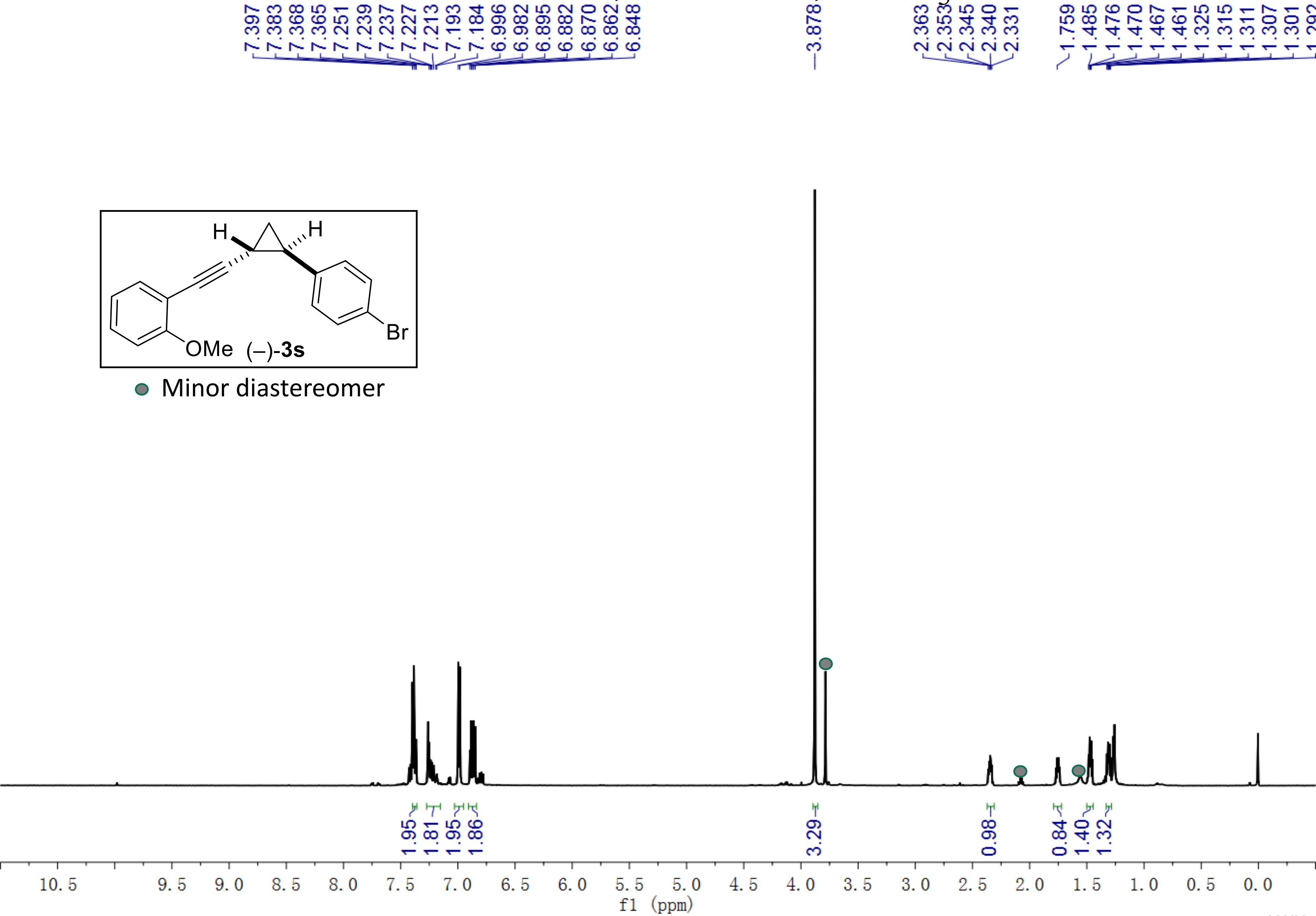


Peak Table

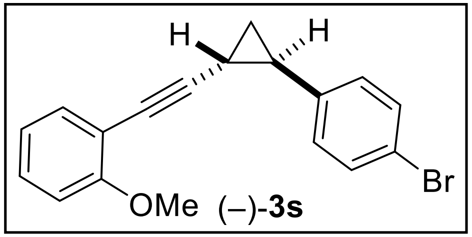
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.045	12643137	78.594
2	17.579	267298	1.662
3	21.831	2776700	17.261
4	35.285	399426	2.483
Total		16086561	100.000

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

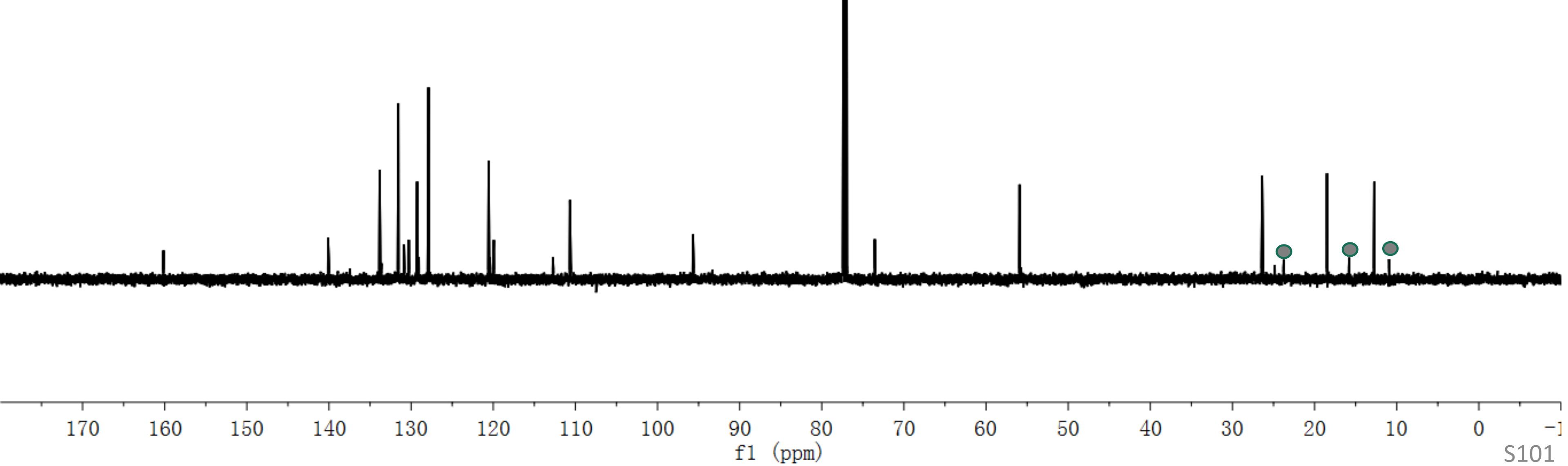


^{13}C NMR of **3s**, 151 MHz, $CDCl_3$

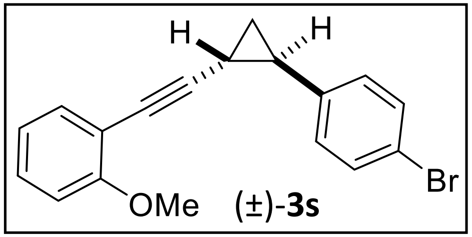


(–)-**3s**

Minor diastereomer

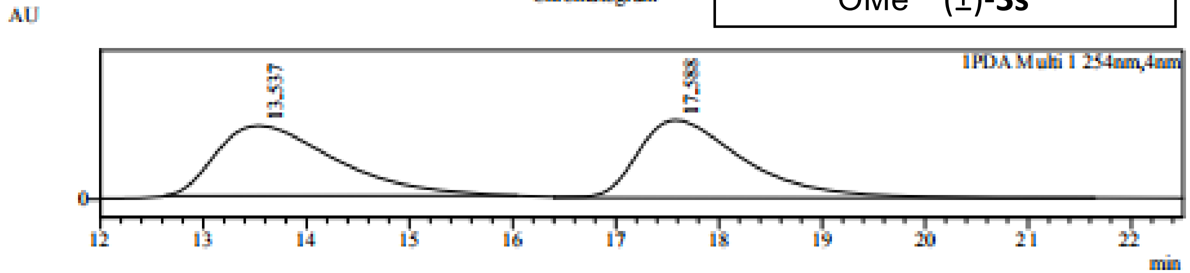


Data File : J0K-1452-IA--0.3%-1ML.lcd
Sample Name : J0K-1452-IA--0.3%-1ML
Sample ID : J0K-1452-IA--0.3%-1ML
Method File : J0K-0.3%--45min-1ml.lcm

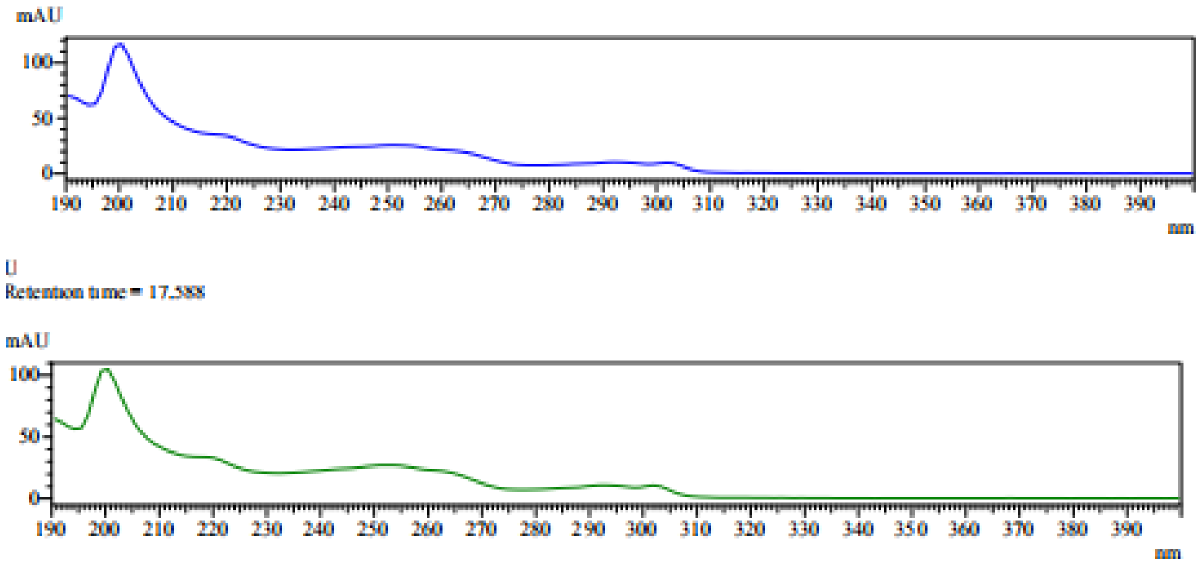


(±)-**3s**

Chromatogram



UV Spectrum
Retention time = 13.537

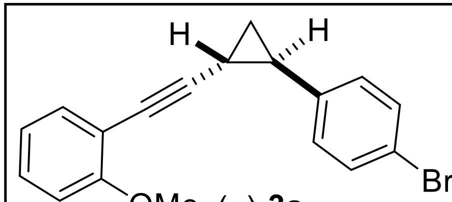


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.537	1903237	50.331
2	17.588	1878235	49.669
Total		3781472	100.000

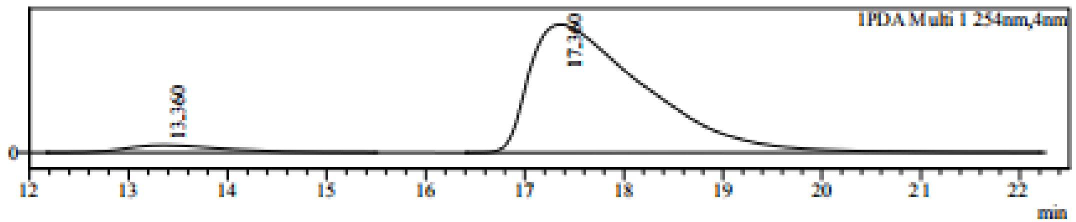
Data File	: J0K-1450-IA--0.3%-1ML.lcd
Sample Name	: J0K-1450-IA--0.3%-1ML
Sample ID	: J0K-1450-IA--0.3%-1ML
Method File	: J0K-0.3%--25min-1ml.lcm



(–)-**3s**

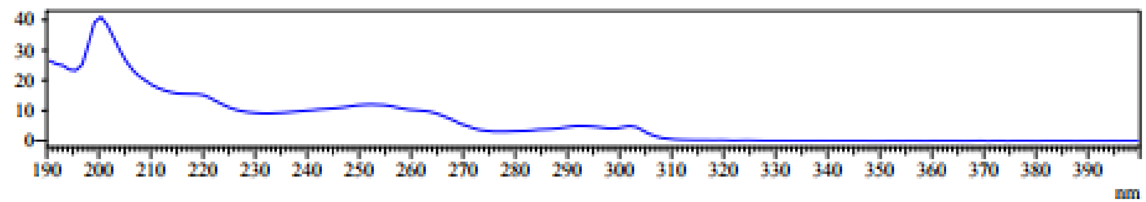
Chromatogram

mAU



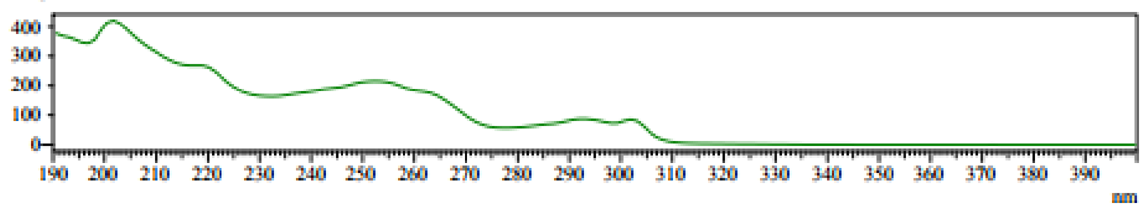
UV Spectrum
Retention time = 13.360

mAU



U
Retention time = 17.360

mAU

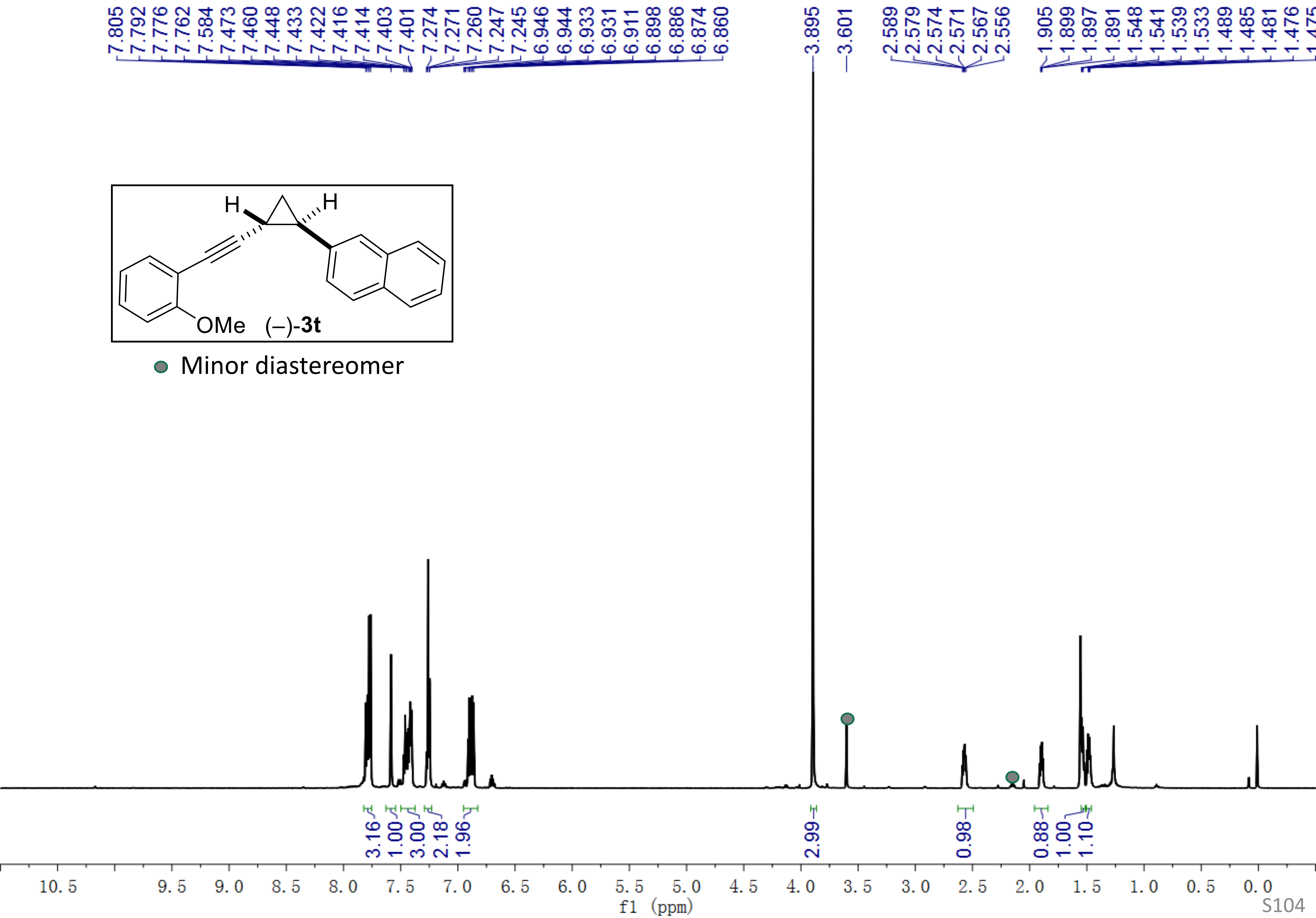


Peak Table

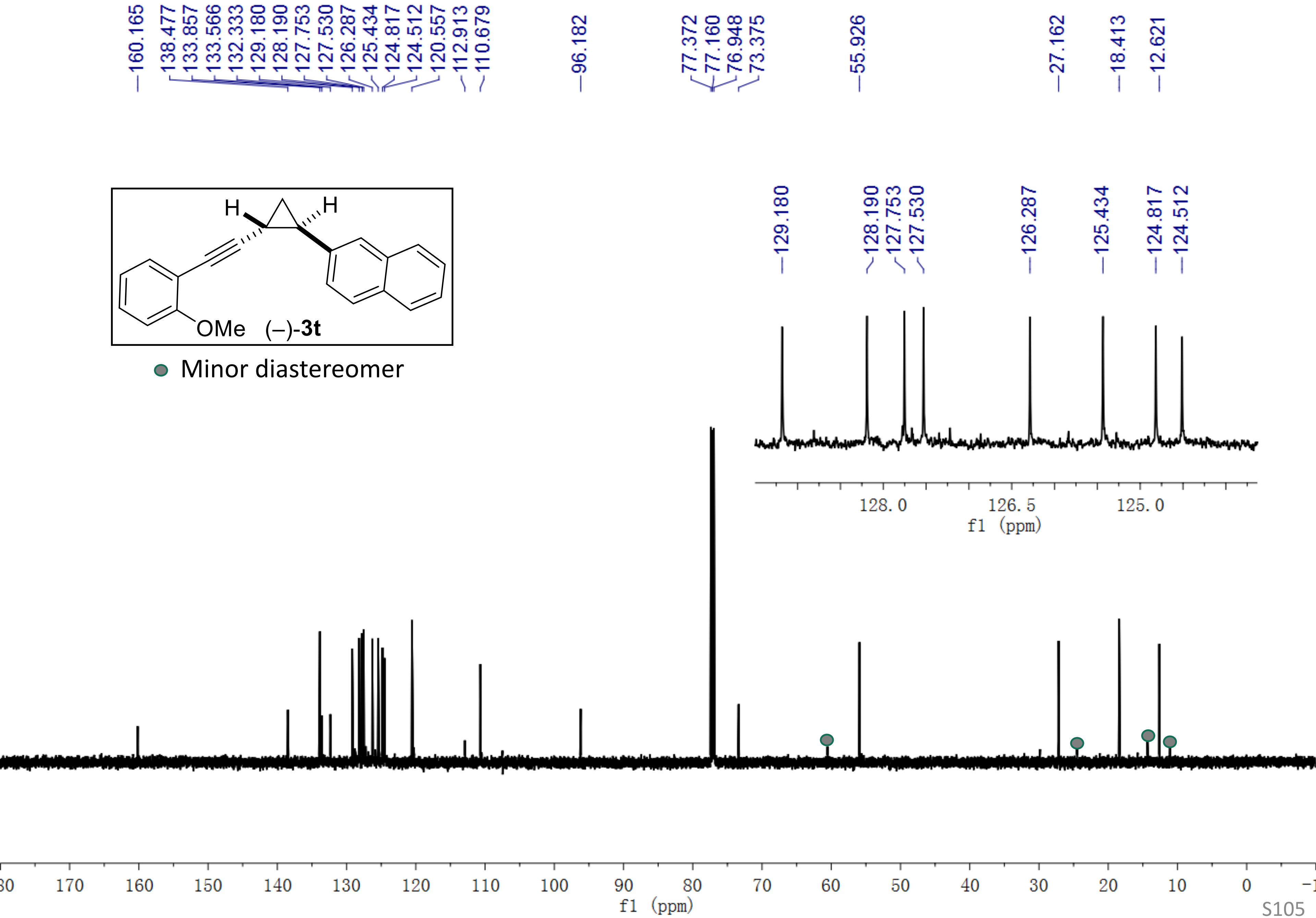
PDA Ch1 254nm

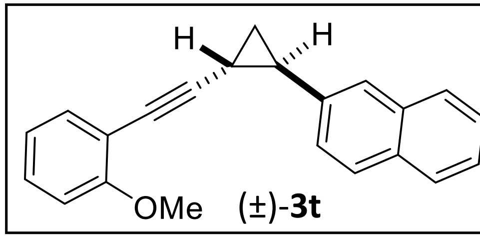
Peak#	Ret. Time	Area	Area%
1	13.360	804698	4.515
2	17.360	17019920	95.485
Total		17824619	100.000

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



^{13}C NMR of **3t**, 151 MHz, $CDCl_3$

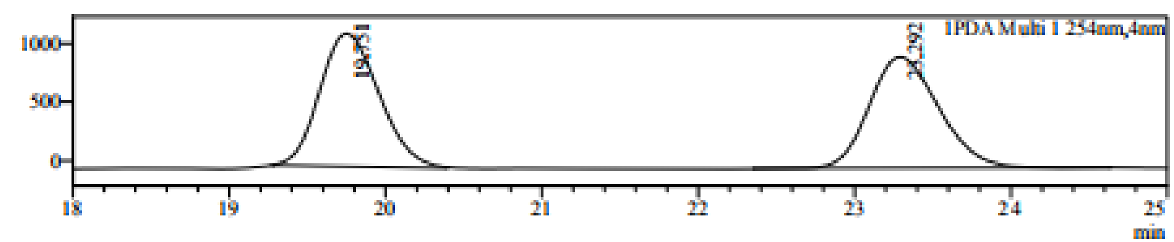




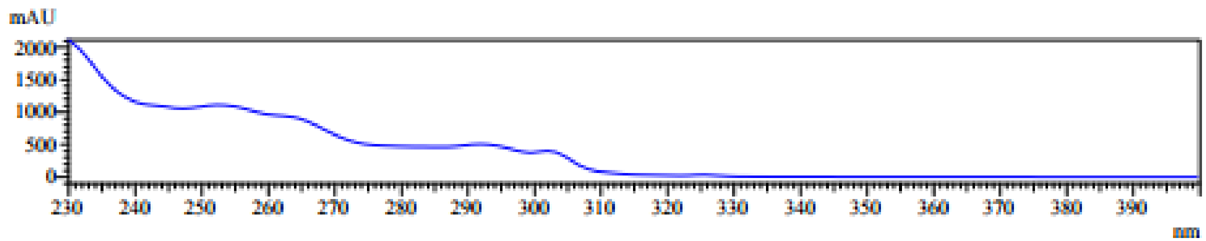
(±)-**3t**

Data File : J0K-0340-IC-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0340-IC-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0340-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml-50min.lcm

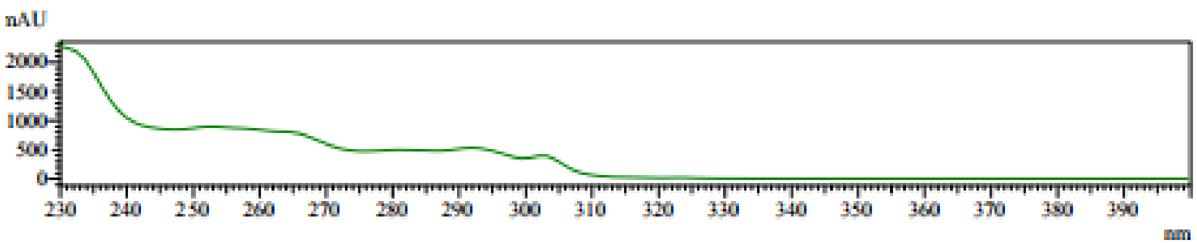
Chromatogram



UV Spectrum
Retention time = 19.751



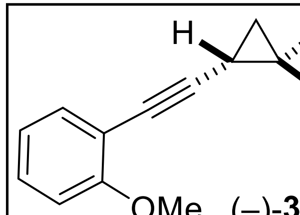
Retention time = 23.292



Peak Table

PDA Ch1 254nm

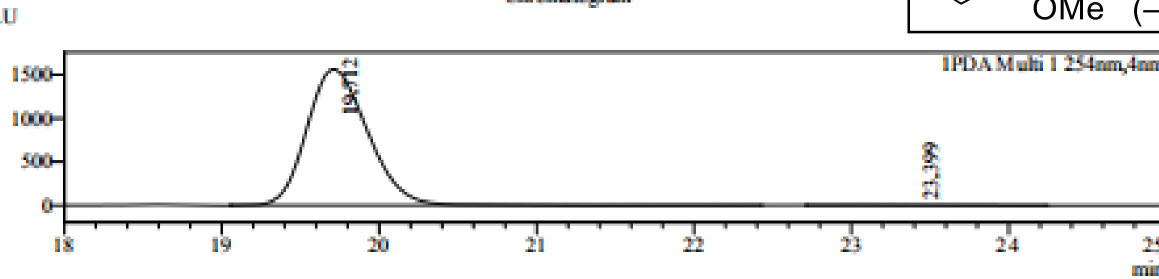
Peak#	Ret. Time	Area	Area%
1	19.751	29870447	50.717
2	23.292	29025910	49.283
Total		58896357	100.000



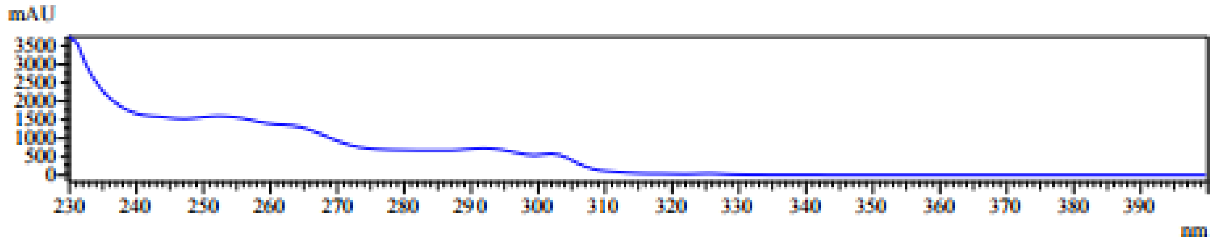
(–)-**3t**

Data File : J0K-0336-2-IC-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0336-2-IC-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0336-2-IC-1%-0.8ML-isopropa
Method File : J0K-1%-0.8ml-50min.lcm

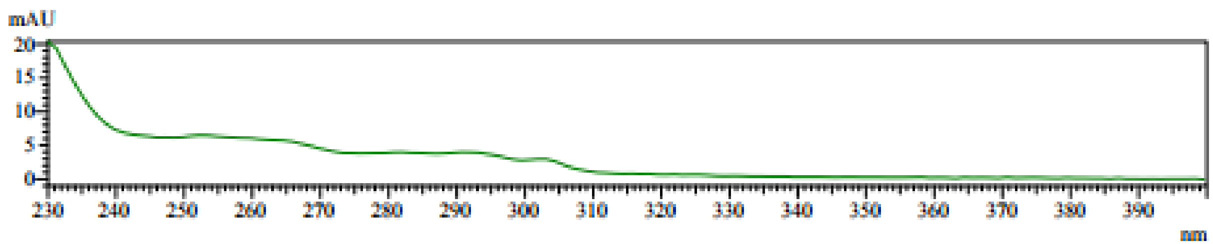
Chromatogram



UV Spectrum
Retention time = 19.712



U
Retention time = 23.399

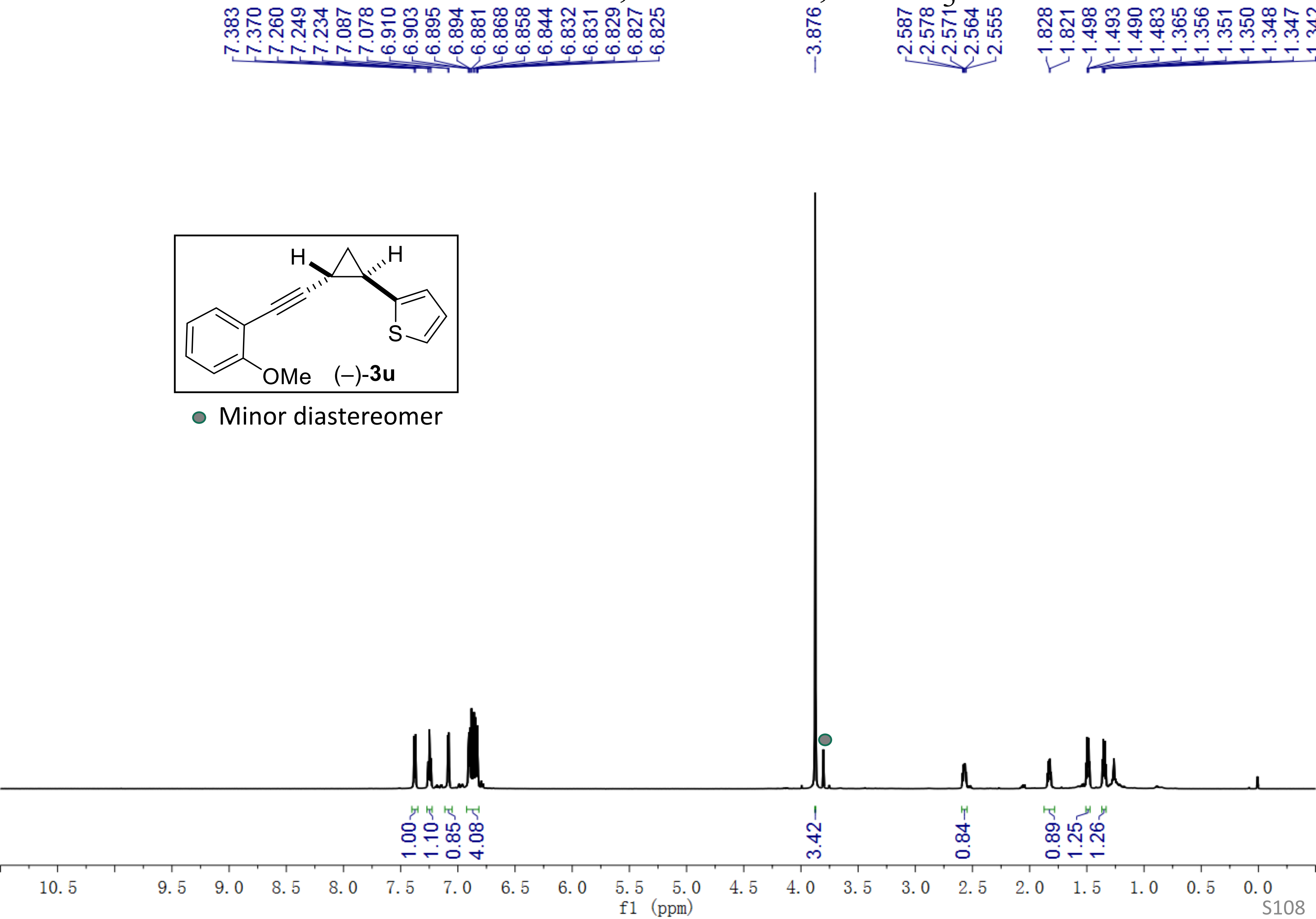


Peak Table

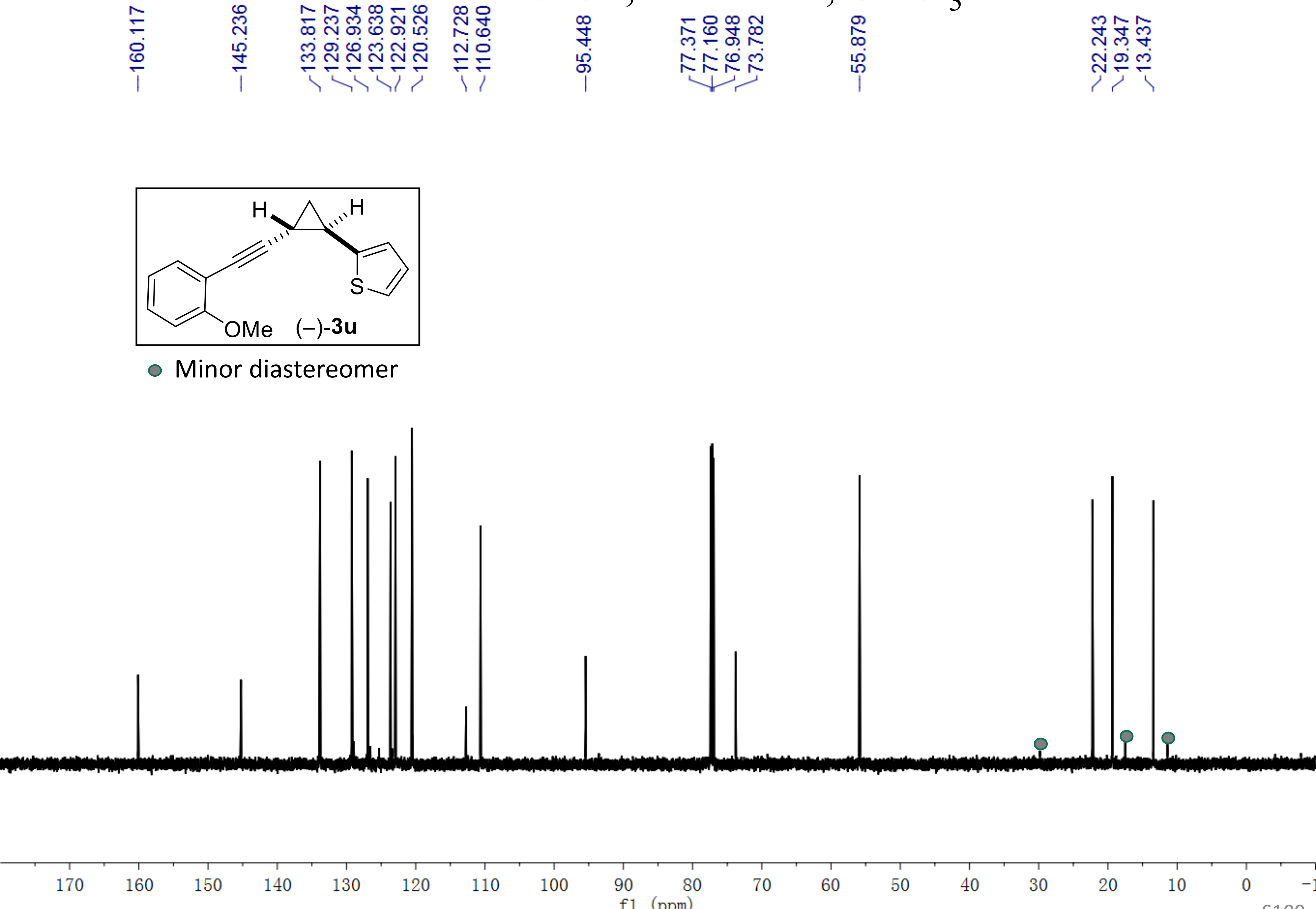
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.712	41874366	99.587
2	23.399	173574	0.413
Total		42047940	100.000

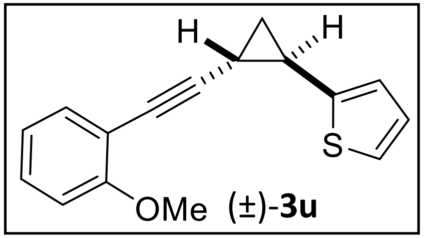
^{1}H NMR of **3u**, 600 MHz, $CDCl_3$



^{13}C NMR of **3u**, 151 MHz, $CDCl_3$

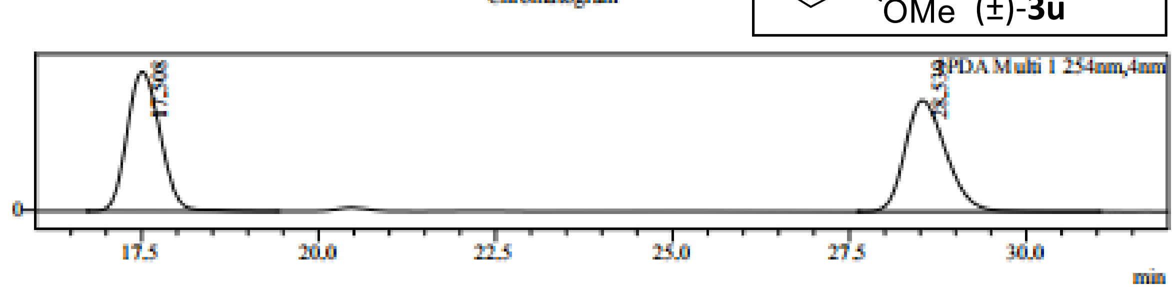


Data File : J0K-0589-4-IC-0.5%-0.8ML.lcd
Sample Name : J0K-0589-4-IC-0.5%-0.8ML
Sample ID : J0K-0589-4-IC-0.5%-0.8ML
Method File : J0K-0.5%--60min-0.8ml.lcm

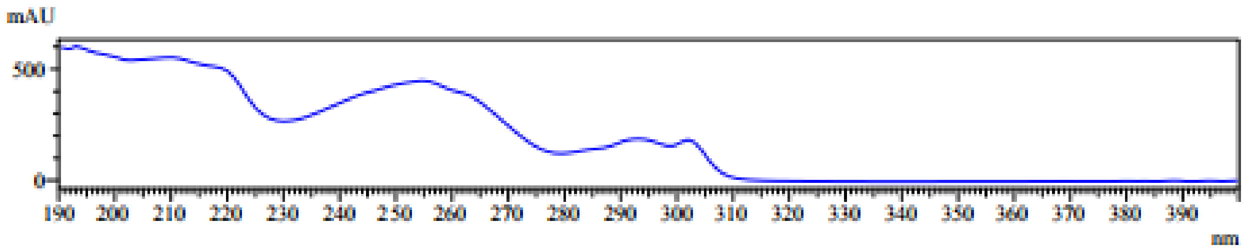


(±)-**3u**

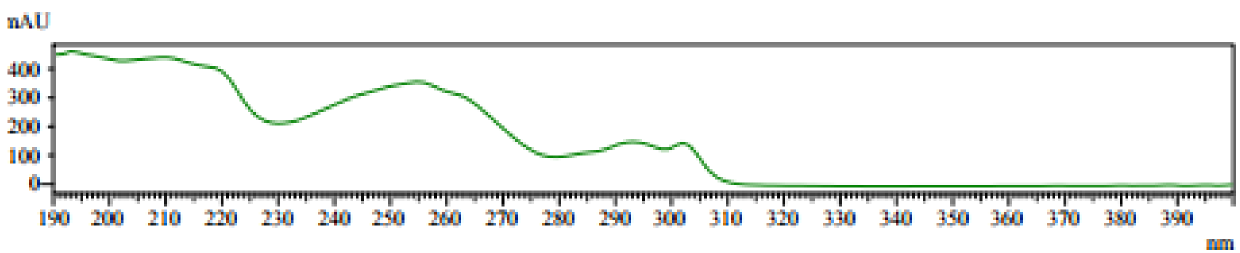
Chromatogram



UV Spectrum
Retention time = 17.508



Retention time = 28.539

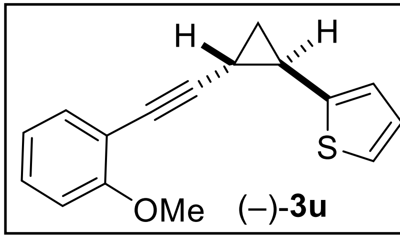


Peak Table

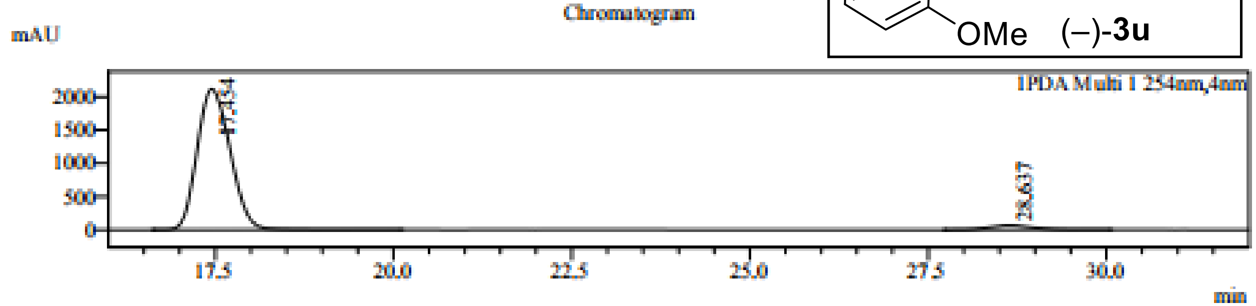
PDA Ch1 254nm

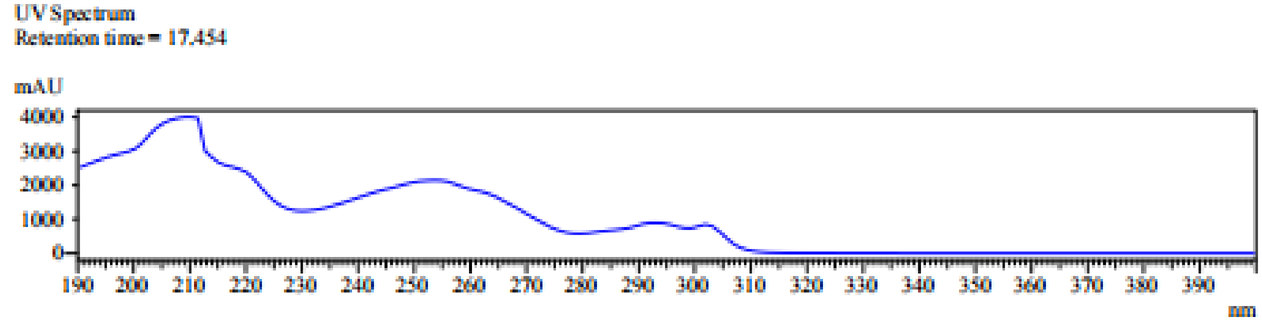
Peak#	Ret. Time	Area	Area%
1	17.508	14384167	50.400
2	28.539	14155965	49.600
Total		28540132	100.000

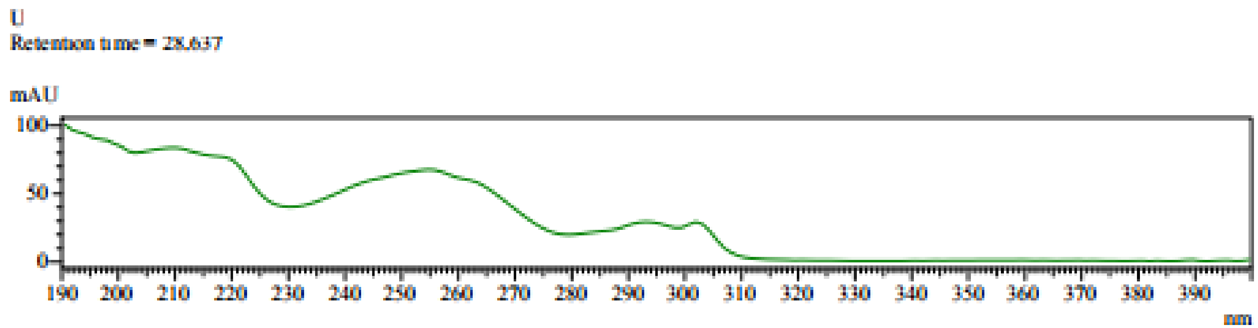
Data File : J0K-0588-4-IC-0.5%-0.8ML.lcd
Sample Name : J0K-0588-4-IC-0.5%-0.8ML
Sample ID : J0K-0588-4-IC-0.5%-0.8ML
Method File : J0K-0.5%--60min-0.8ml.lcm



(–)-**3u**





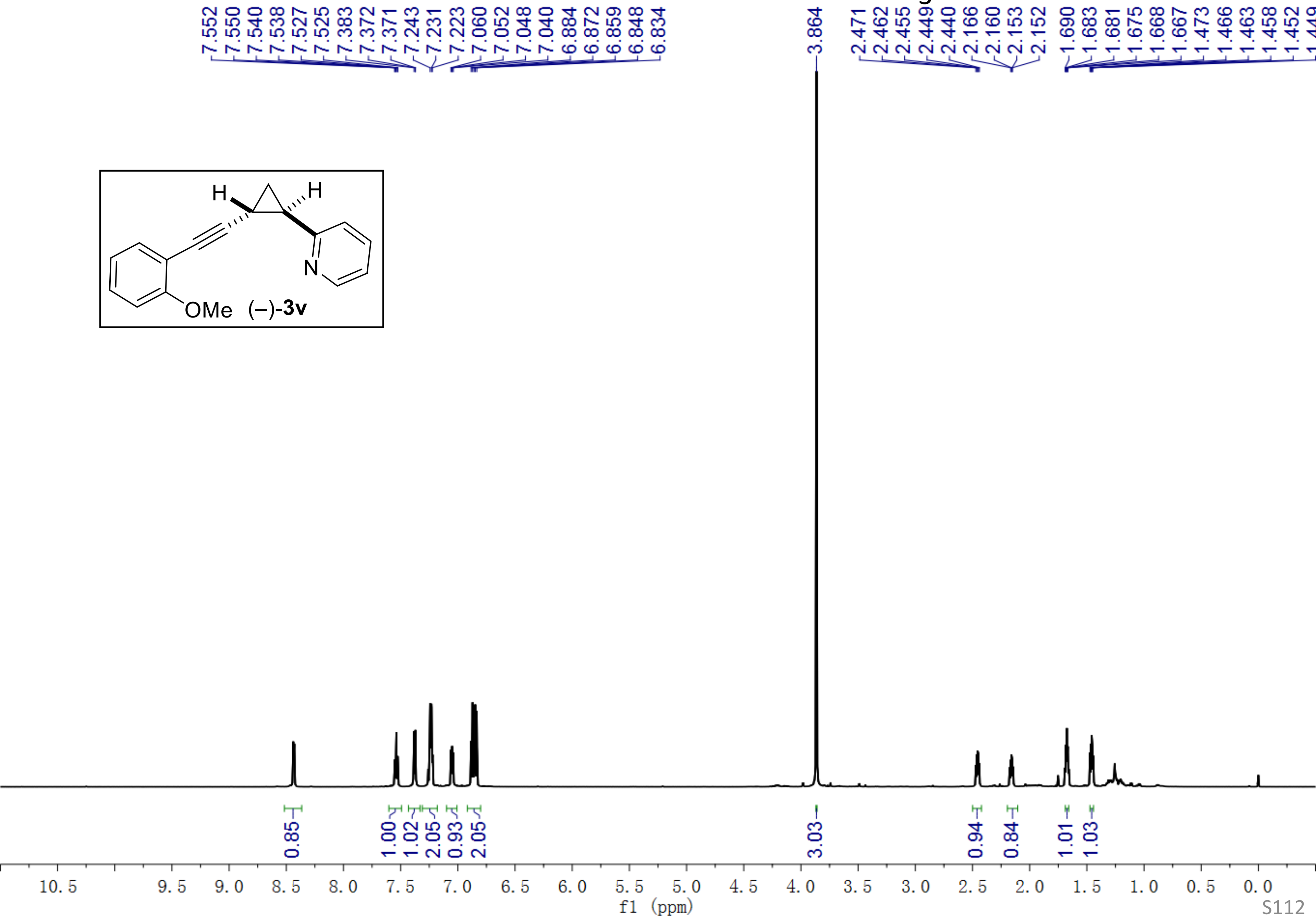


Peak Table

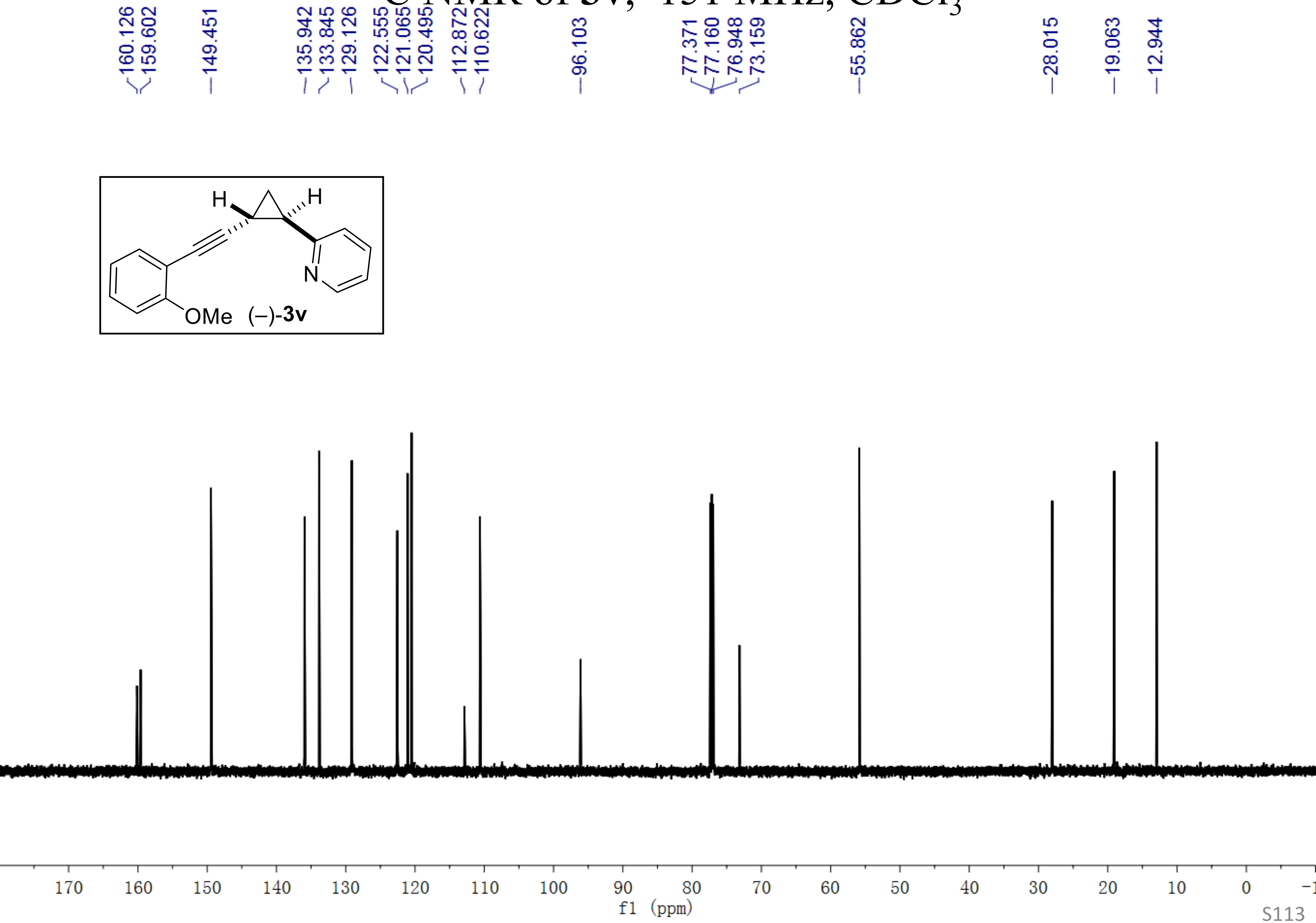
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.454	68120738	96.222
2	28.637	2674806	3.778
Total		70795544	100.000

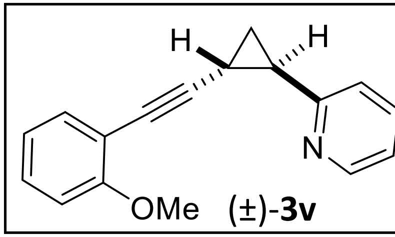
^{1}H NMR of **3v**, 600 MHz, $CDCl_3$



^{13}C NMR of **3v**, 151 MHz, $CDCl_3$

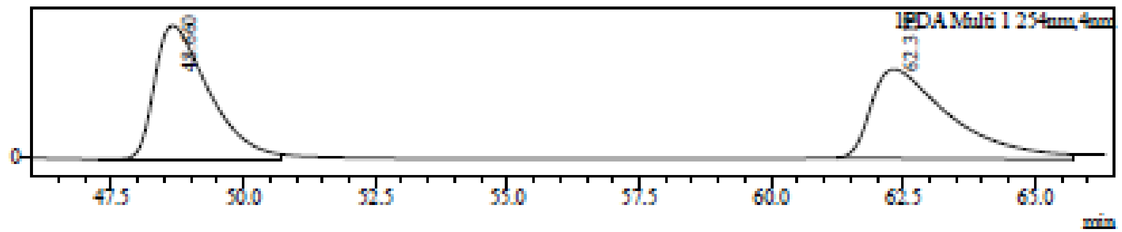


Data File : J0K-0600-2-IC--0.5%-1ML.lcd
Sample Name : J0K-0600-2-IC--0.5%-1ML
Sample ID : J0K-0600-2-IC--0.5%-1ML
Method File : J0K-0.5%--80min-1ml.lcm

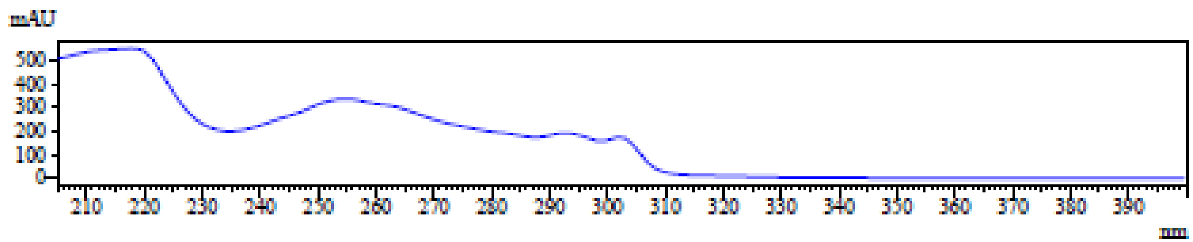


(±)-**3v**

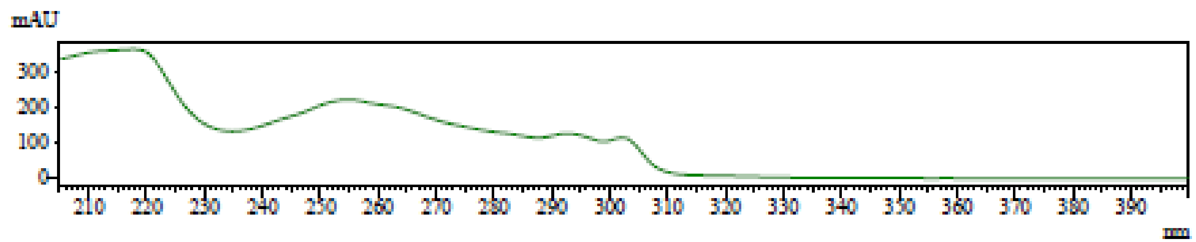
Chromatogram



UV Spectrum
Retention time = 48.660



UV Spectrum
Retention time = 62.317

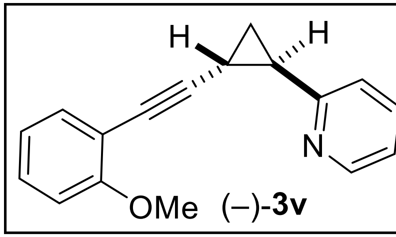


Peak Table

PDA Ch1 254nm

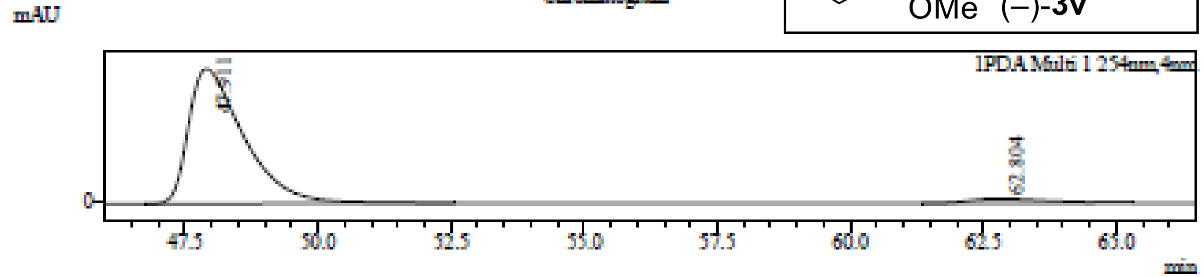
Peak#	Ret. Time	Area	Area%
1	48.660	24316400	50.828
2	62.317	23524334	49.172
Total		47840733	100.000

Data File : J0K-0599--2-IC--0.5%-1ML.lcd
Sample Name : J0K-0599--2-IC--0.5%-1ML
Sample ID : J0K-0599--2-IC--0.5%-1ML
Method File : J0K-0.5%--80min-1ml.lcm

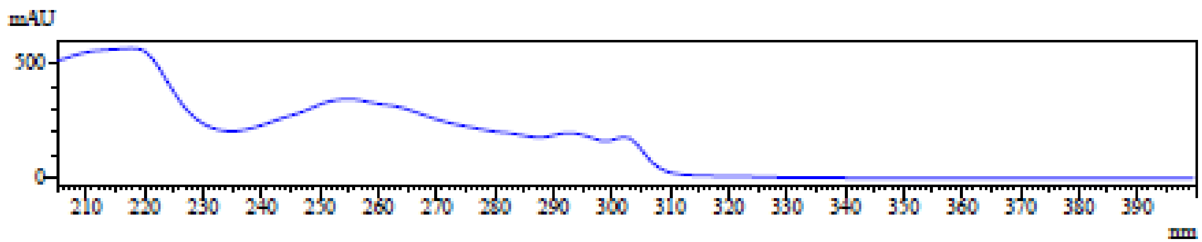


(–)-**3v**

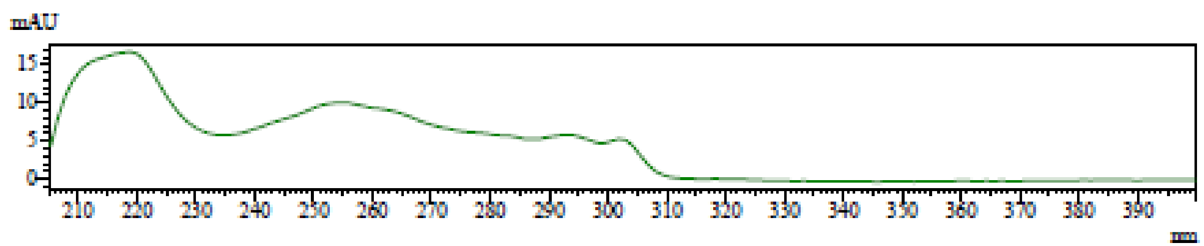
Chromatogram



UV Spectrum
Retention time = 47.911



UV Spectrum
Retention time = 62.804

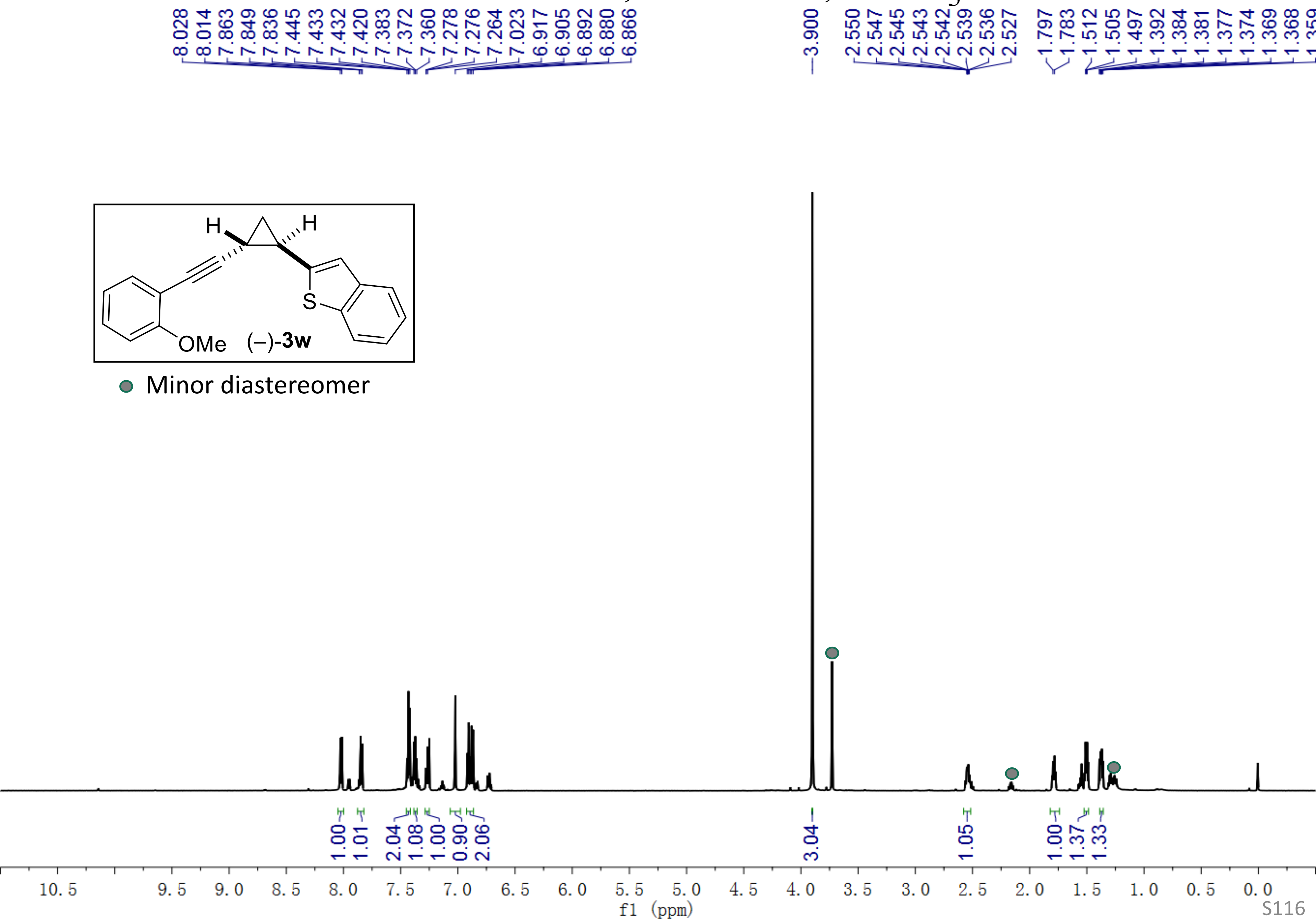


Peak Table

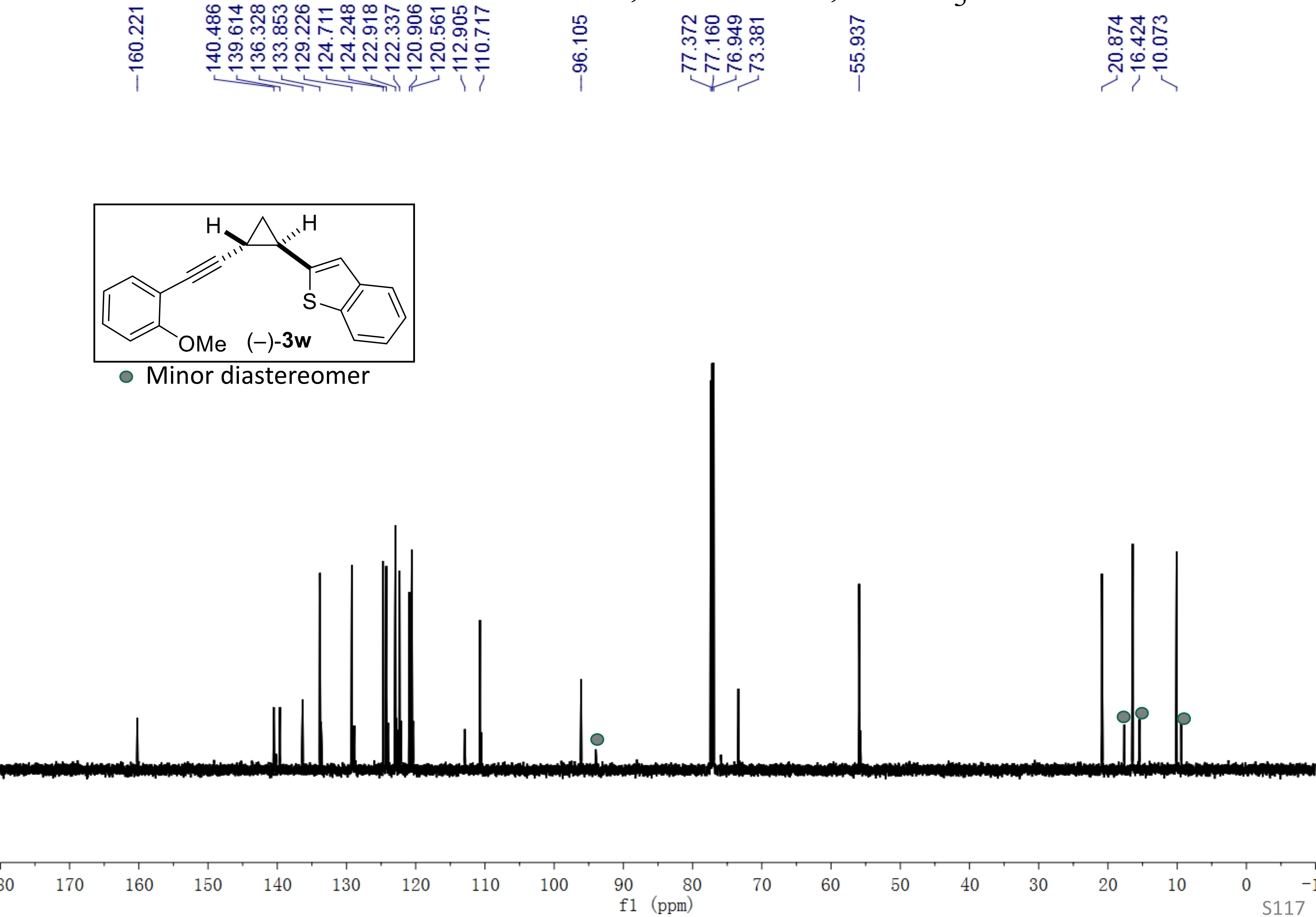
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	47.911	24636457	95.788
2	62.804	1083431	4.212
Total		25719888	100.000

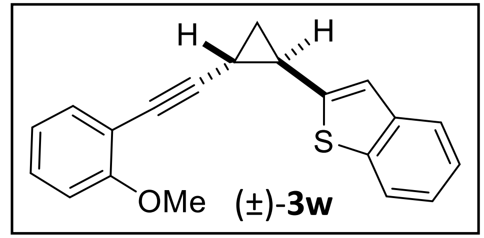
^{1}H NMR of **3w**, 600 MHz, $CDCl_3$



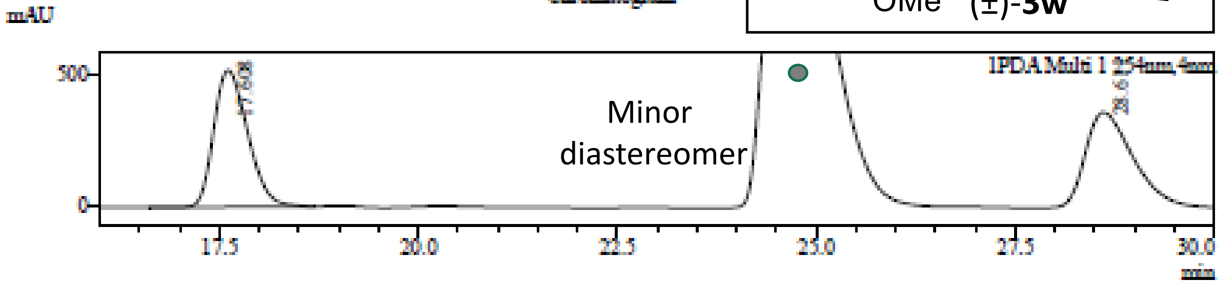
^{13}C NMR of **3w**, 151 MHz, $CDCl_3$



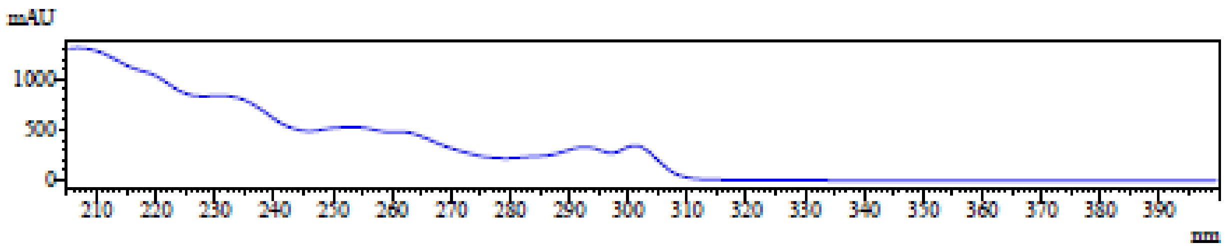
Data File : J0K-0587-3-IC-0.5%-0.8ML.lcd
Sample Name : J0K-0587-3-IC-0.5%-0.8ML
Sample ID : J0K-0587-3-IC-0.5%-0.8ML
Method File : J0K-0.5%--60min-0.8ml.lcm



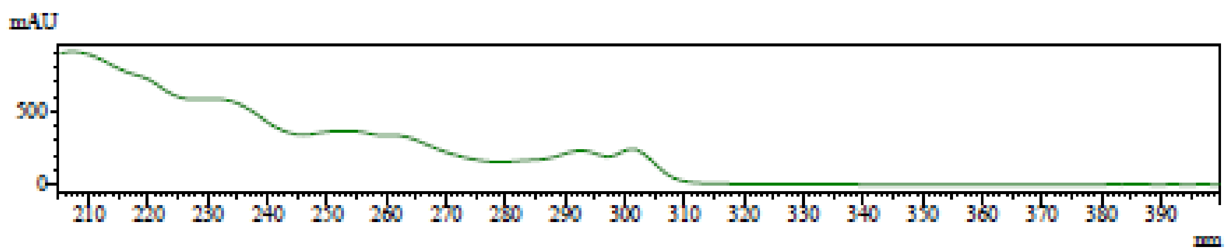
Chromatogram



UV Spectrum
Retention time = 17.608



UV Spectrum
Retention time = 28.611

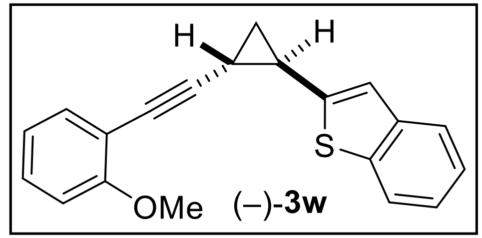


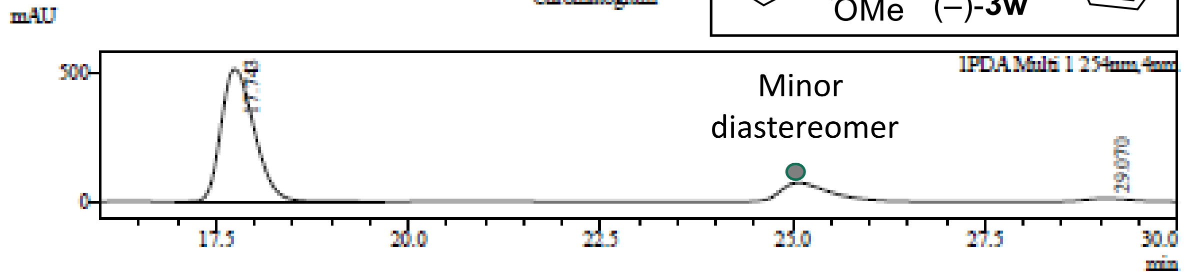
Peak Table

PDA Ch1 254nm

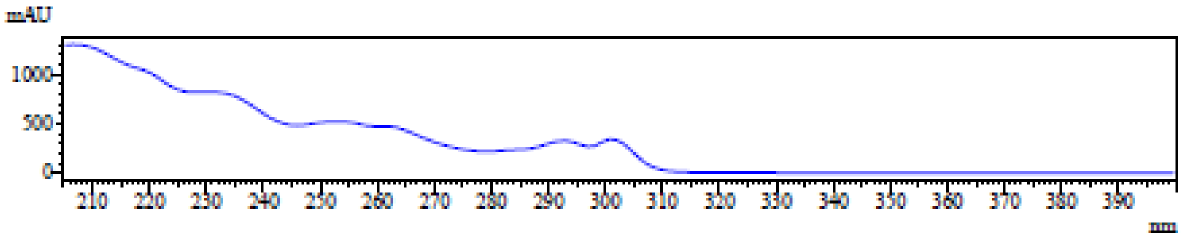
Peak#	Ret. Time	Area	Area%
1	17.608	15423522	50.194
2	28.611	15304308	49.806
Total		30727830	100.000

Data File : J0K-0586-IC-0.5%-0.8ML.lcd
Sample Name : J0K-0586-IC-0.5%-0.8ML
Sample ID : J0K-0586-IC-0.5%-0.8ML
Method File : J0K-0.5%--60min-0.8ml.lcm

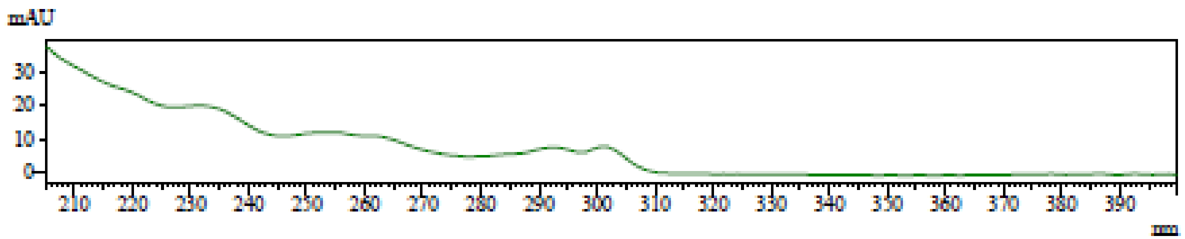




UV Spectrum
Retention time = 17.743



UV Spectrum
Retention time = 29.070

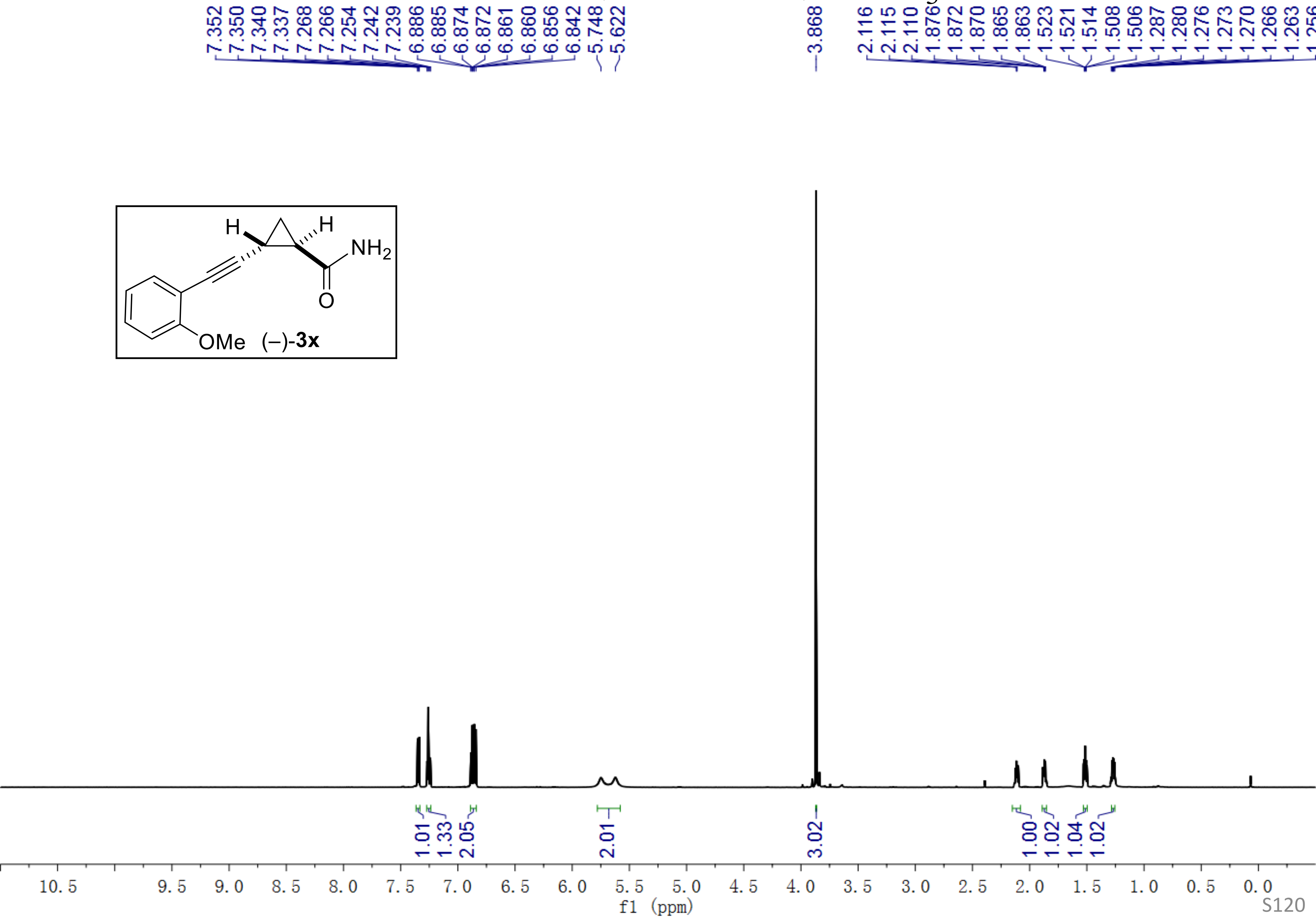


Peak Table

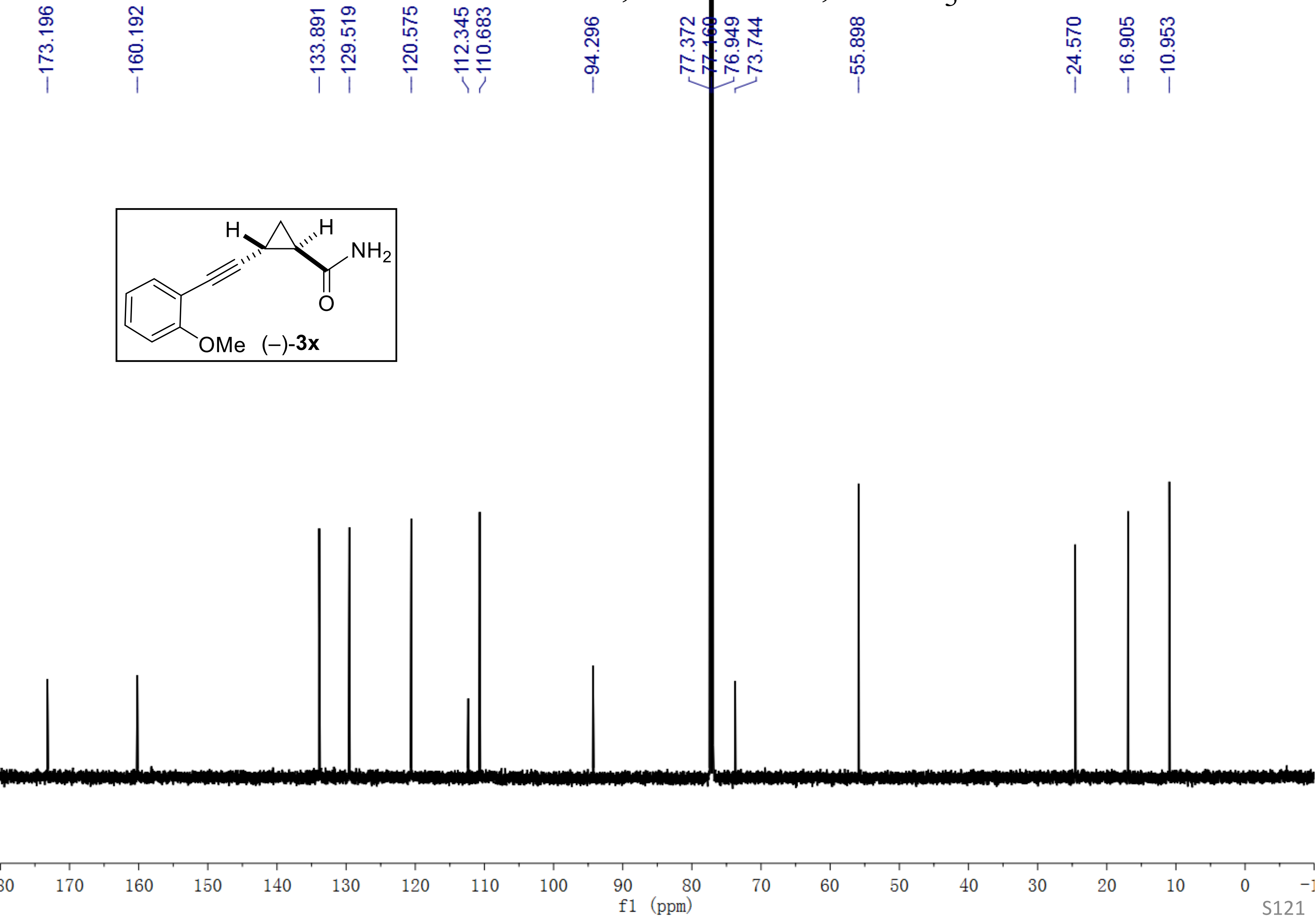
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.743	15440731	96.643
2	29.070	536357	3.357
Total		15977089	100.000

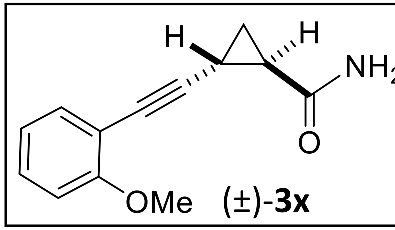
^{1}H NMR of **3x**, 600 MHz, $CDCl_3$



^{13}C NMR of **3x**, 151 MHz, $CDCl_3$

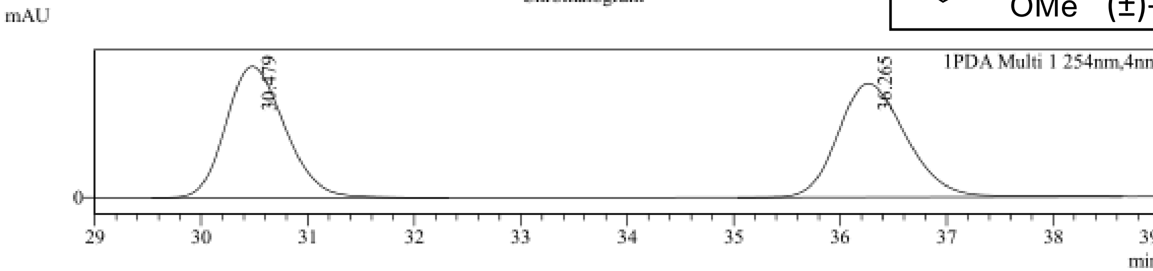


Data File : J0K-0342-IC-1%-0.8ML-isopropanol-solvent005.lcd
Sample Name : J0K-0342-IC-1%-0.8ML-isopropanol-solvent005
Sample ID : J0K-0342-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml-50min.lcm

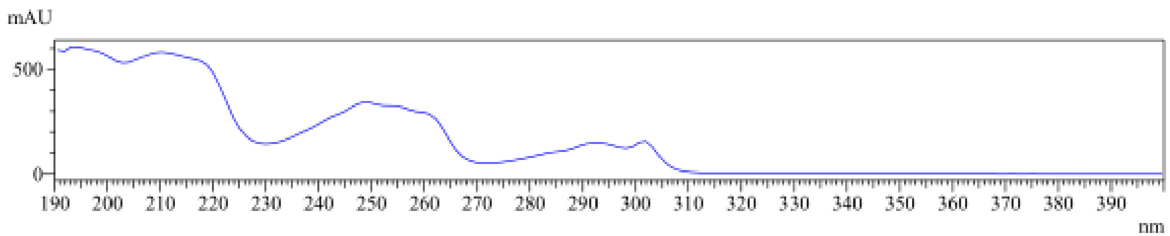


(±)-**3x**

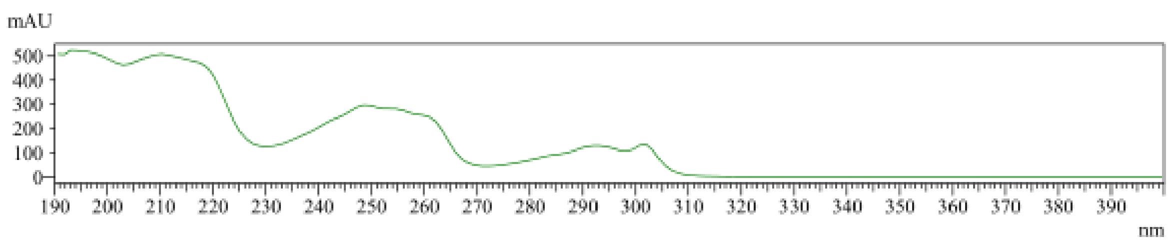
Chromatogram



UV Spectrum
Retention time = 30.479



UV Spectrum
Retention time = 36.265

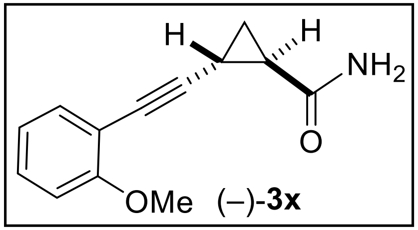


Peak Table

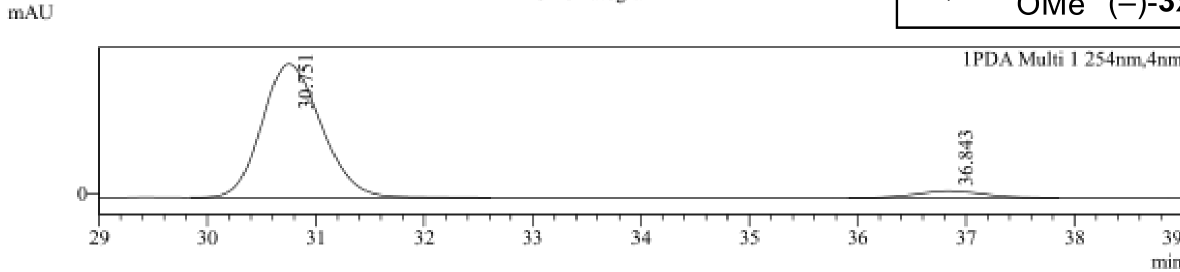
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.479	12463706	50.047
2	36.265	12440286	49.953
Total		24903992	100.000

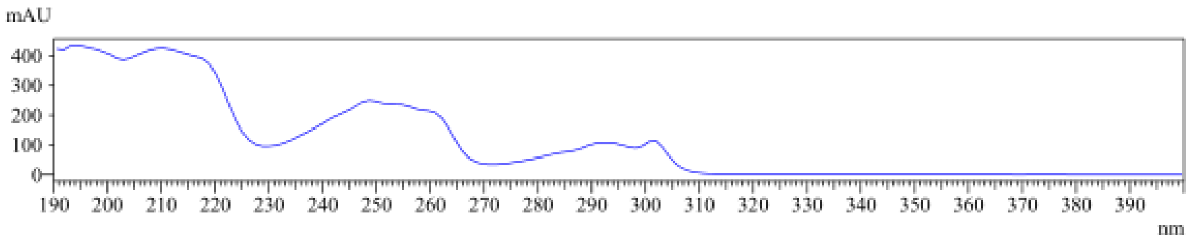
Data File : J0K-0310-IC-1%-0.8ML-isopropanol-solvent008.lcd
Sample Name : J0K-0310-IC-1%-0.8ML-isopropanol-solvent008
Sample ID : J0K-0310-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8m-50MINl.lcm



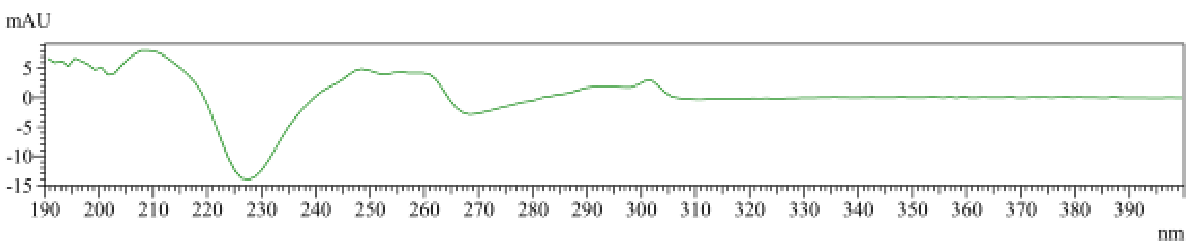
(–)-**3x**



UV Spectrum
Retention time = 30.751



UV Spectrum
Retention time = 36.843

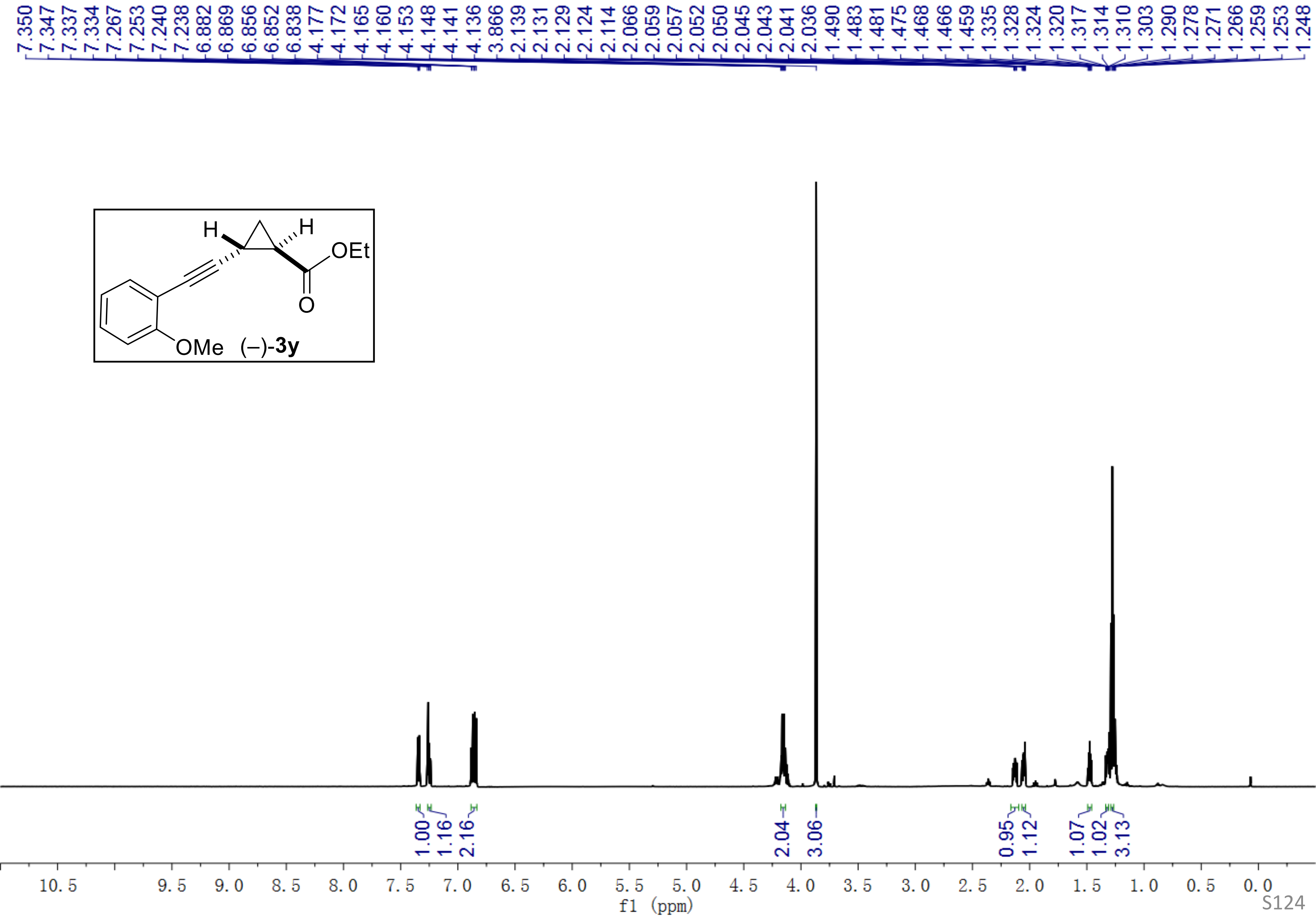


Peak Table

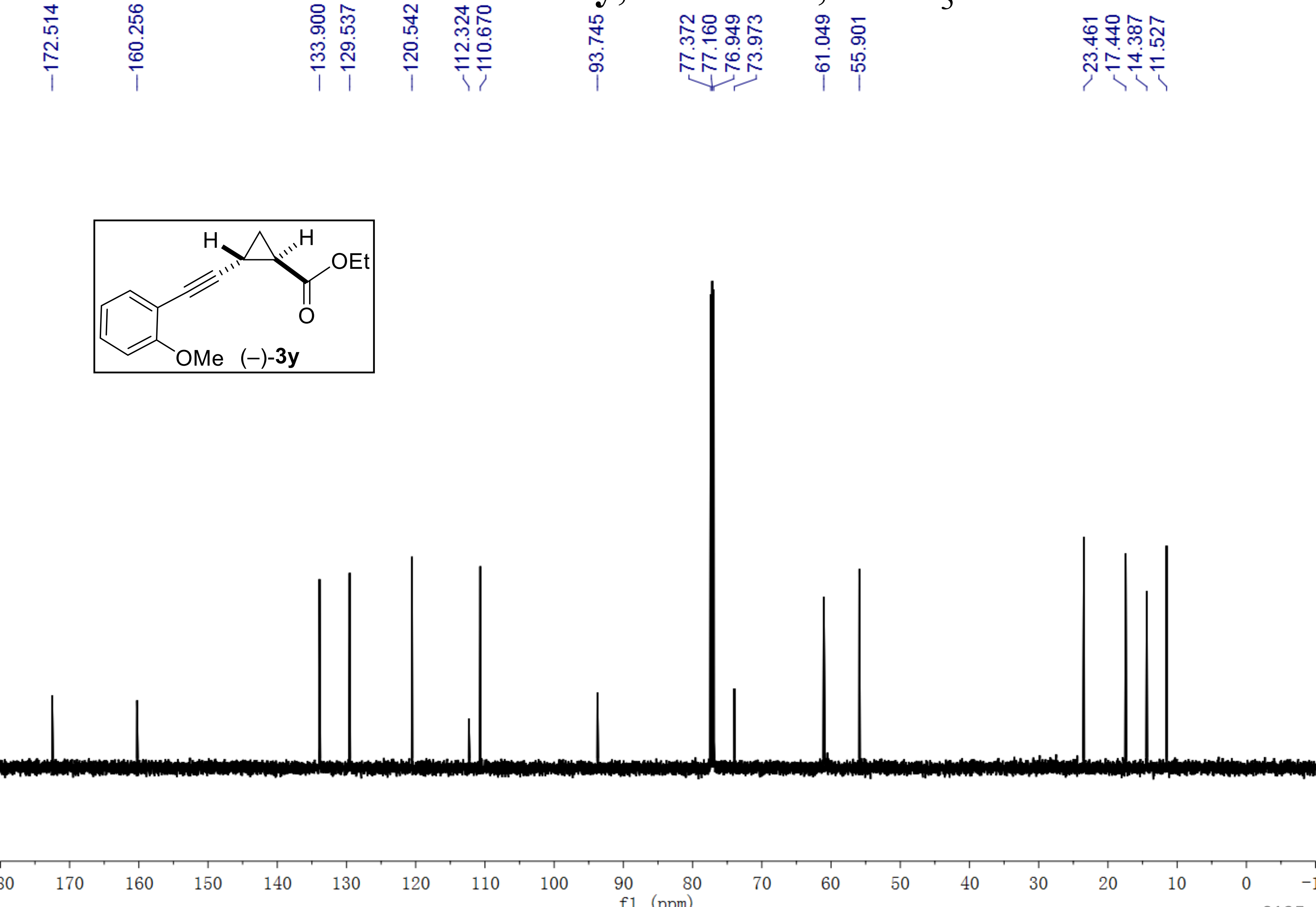
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.751	9217551	94.697
2	36.843	516187	5.303
Total		9733738	100.000

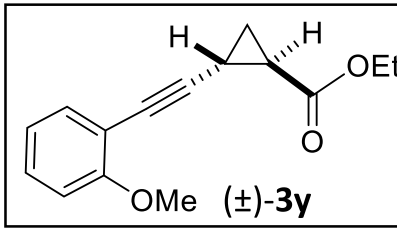
^{1}H NMR of **3y**, 600 MHz, $CDCl_3$



^{13}C NMR of **3y**, 151 MHz, $CDCl_3$

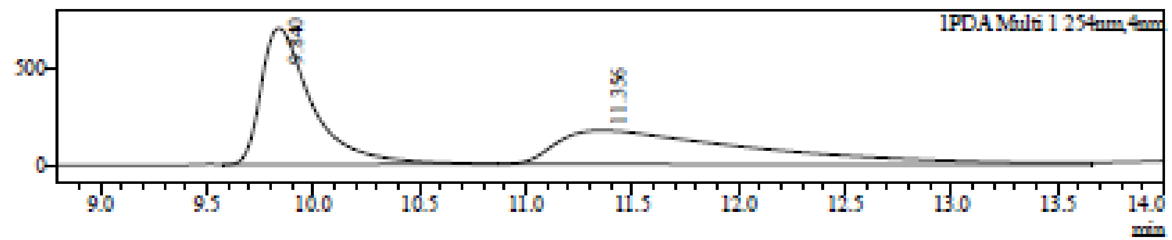


Data File : J0K-1514-new-IA--0.3%-1ML.lcd
Sample Name : J0K-1514-new-IA--0.3%-1ML
Sample ID : J0K-1514-new-IA--0.3%-1ML
Method File : J0K-0.3%--45min-1ml.lcm

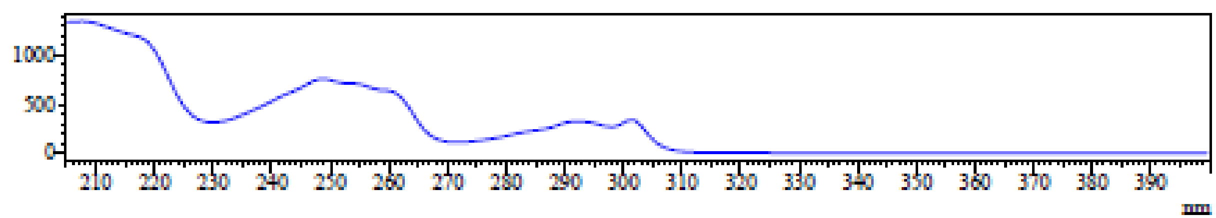


(±)-**3y**

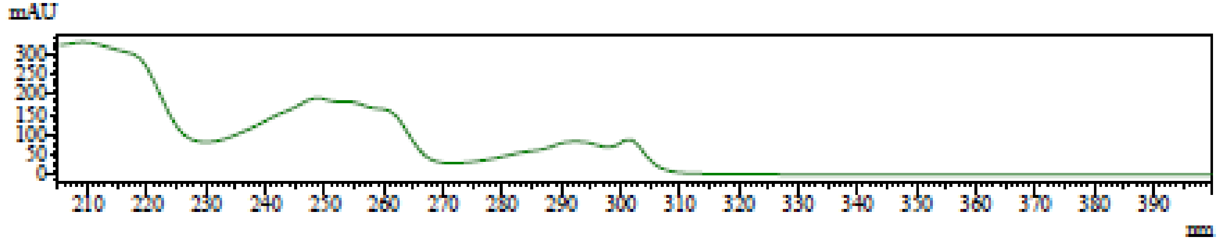
Chromatogram



UV Spectrum
Retention time = 9.840



UV Spectrum
Retention time = 11.356

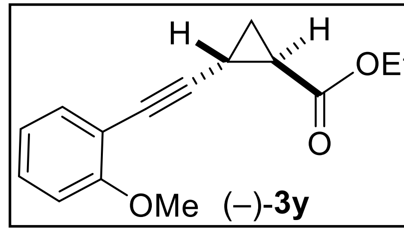


Peak Table

PDA Ch1 254nm

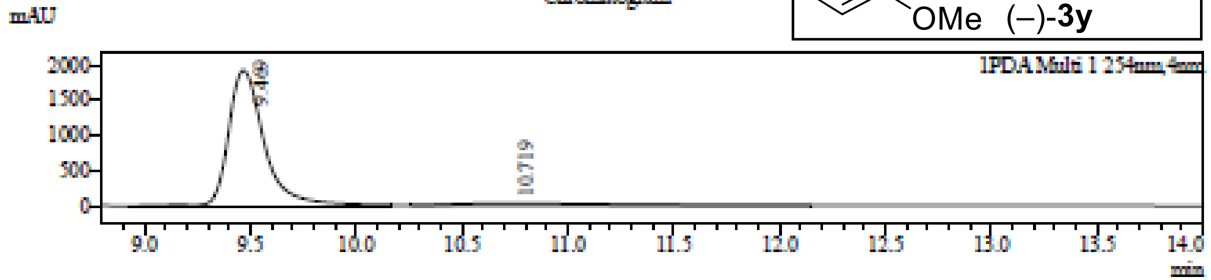
Peak#	Ret. Time	Area	Area%
1	9.840	11607489	50.875
2	11.356	11208328	49.125
Total		22815817	100.000

Data File : J0K-1513-IA--0.3%-1ML.lcd
Sample Name : J0K-1513-IA--0.3%-1ML
Sample ID : J0K-1513-IA--0.3%-1ML
Method File : J0K-0.3%--25min-1ml.lcm

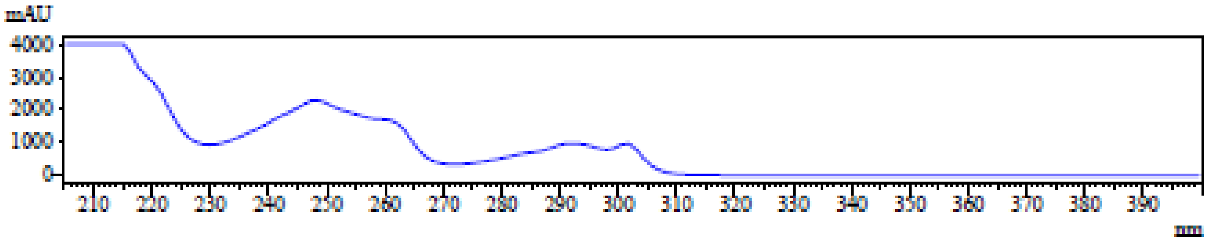


(–)-3y

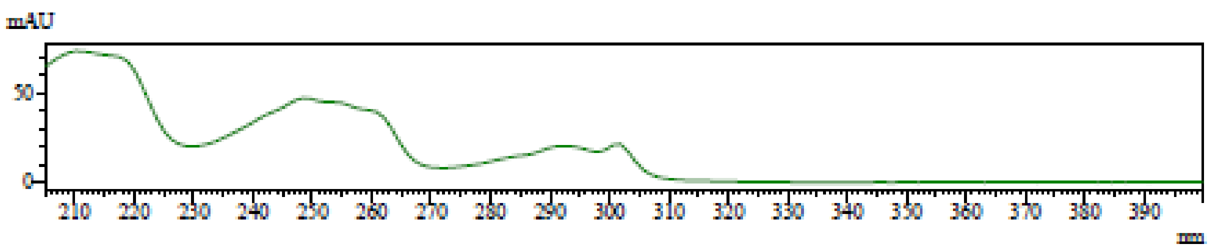
Chromatogram



UV Spectrum
Retention time = 9.469



UV Spectrum
Retention time = 10.719

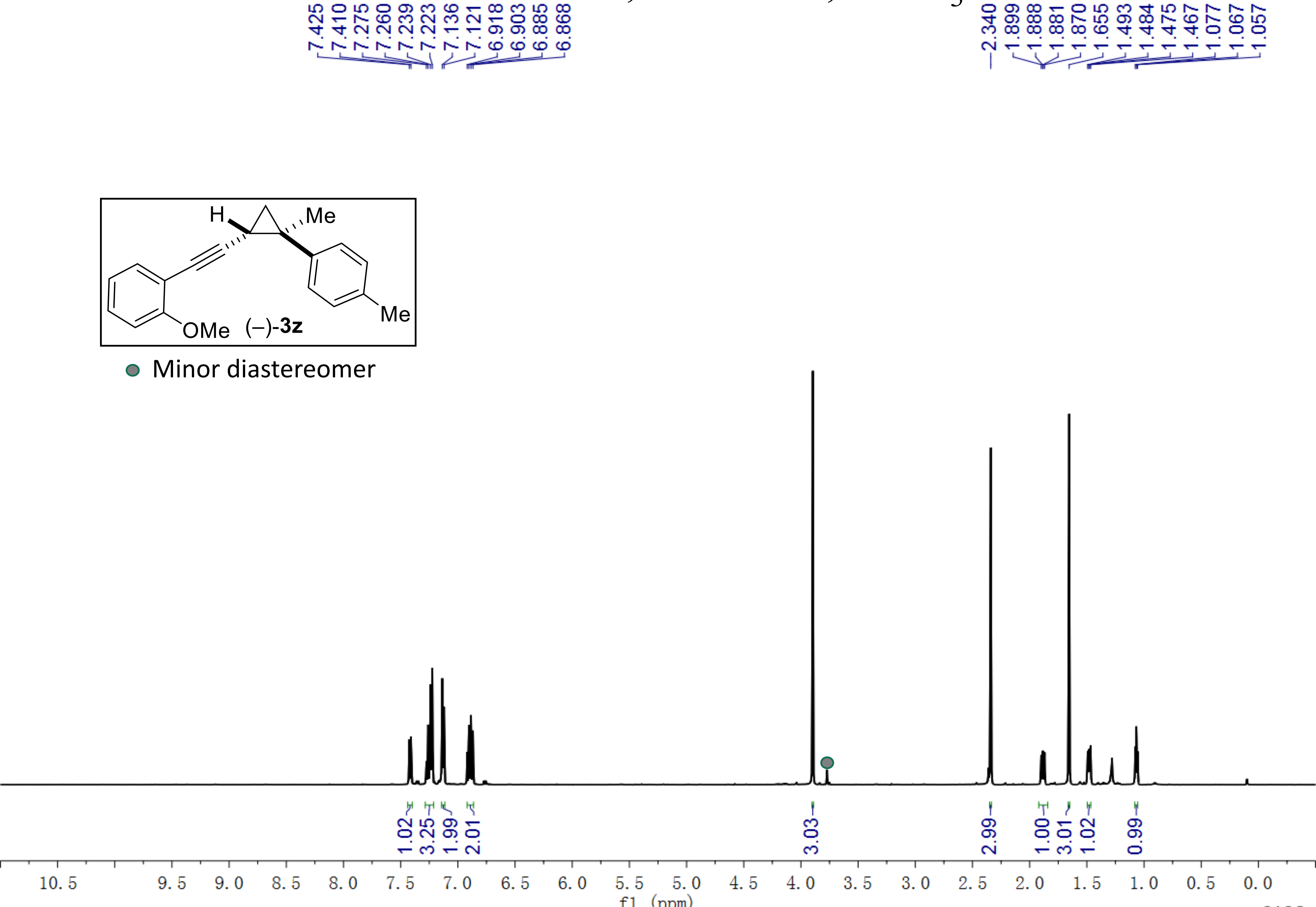


Peak Table

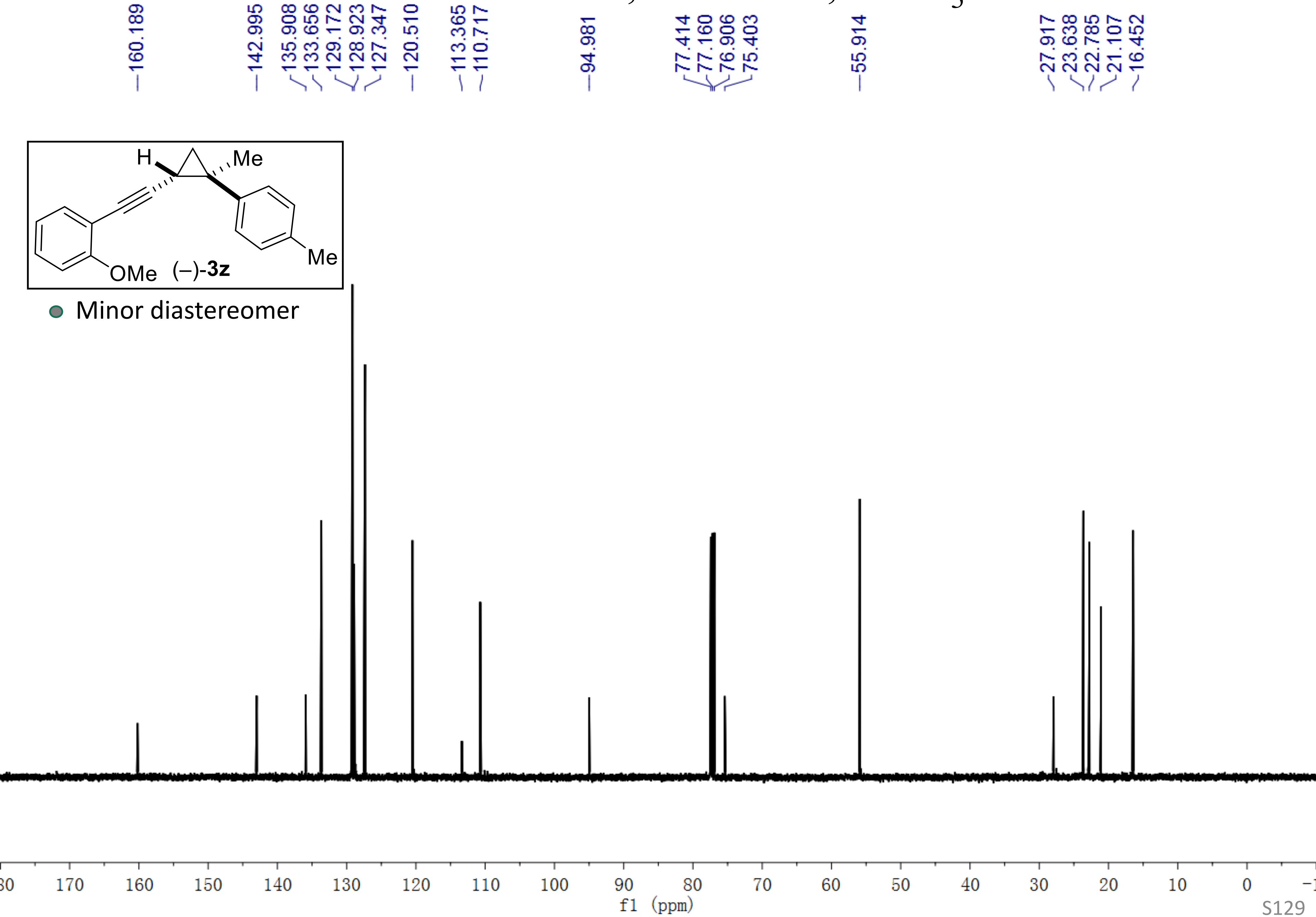
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.469	22666700	93.877
2	10.719	1478374	6.123
Total		24145074	100.000

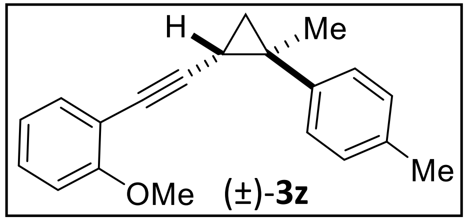
^{1}H NMR of **3z**, 500 MHz, $CDCl_3$



^{13}C NMR of **3z**, 126 MHz, $CDCl_3$

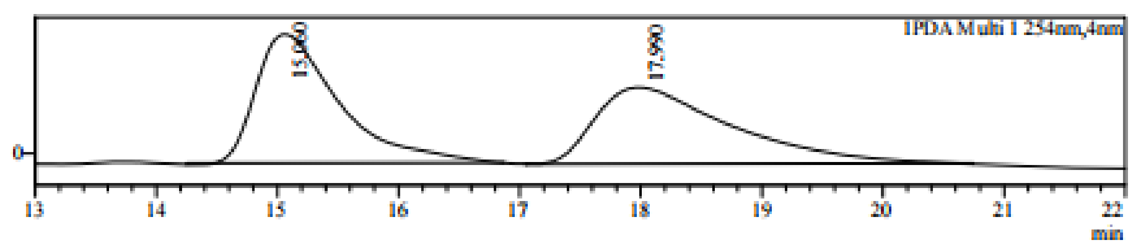


Data File : J0K-0106-IC-0.5%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0106-IC-0.5%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0106-IC-0.5%-0.8ML-isopropa
Method File : JK-0%-0.8ml.lcm

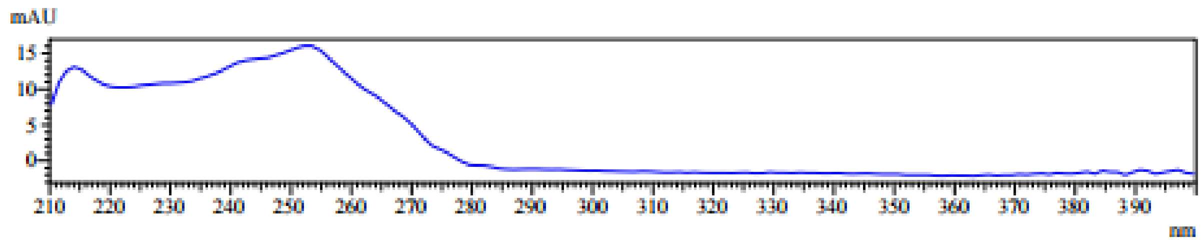


(±)-**3z**

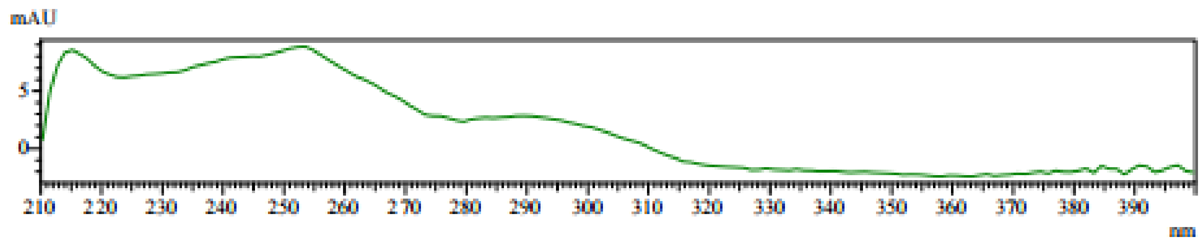
Chromatogram



UV Spectrum
Retention time = 15.060



U
Retention time = 17.990

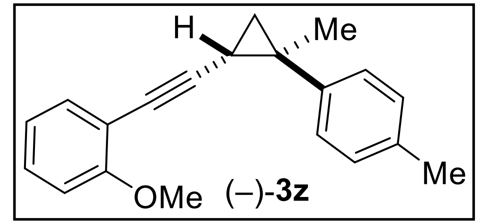


Peak Table

PDA Ch1 254nm

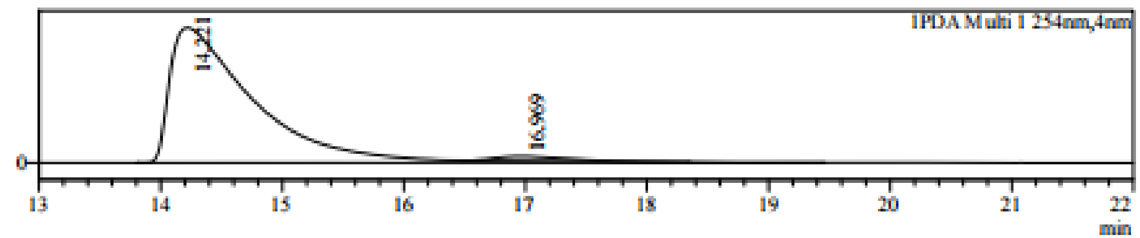
Peak#	Ret. Time	Area	Area%
1	15.060	780497	50.719
2	17.990	758360	49.281
Total		1538857	100.000

Data File : J0K-0108-IC-0.5%-0.8ML-isopropanol-solvent004.lcd
Sample Name : J0K-0108-IC-0.5%-0.8ML-isopropanol-solvent004
Sample ID : J0K-0108-IC-0.5%-0.8ML-isopropa
Method File : JK-0%-0.8ml.lcm

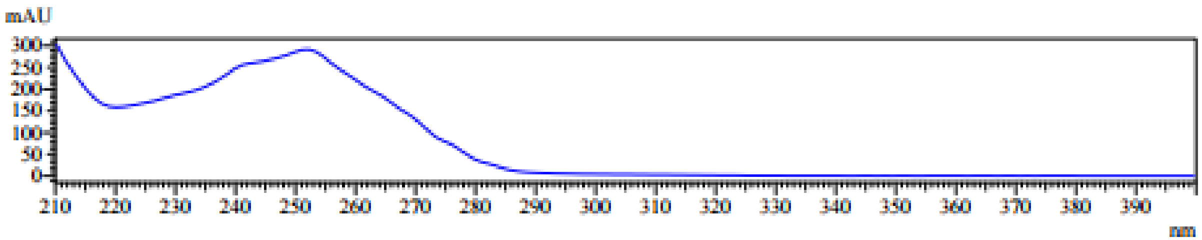


(–)-**3z**

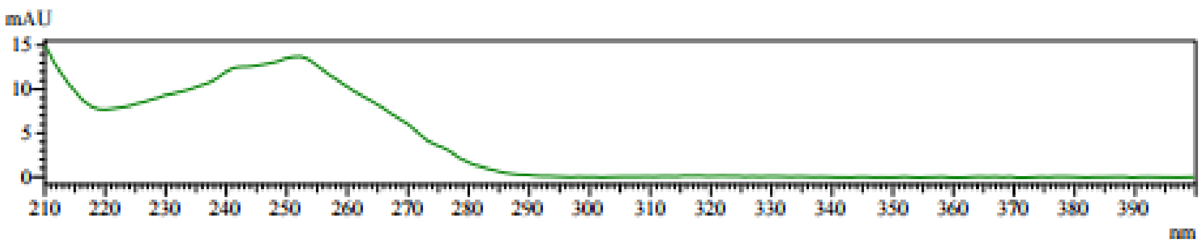
Chromatogram



UV Spectrum
Retention time = 14.221



U
Retention time = 16.969

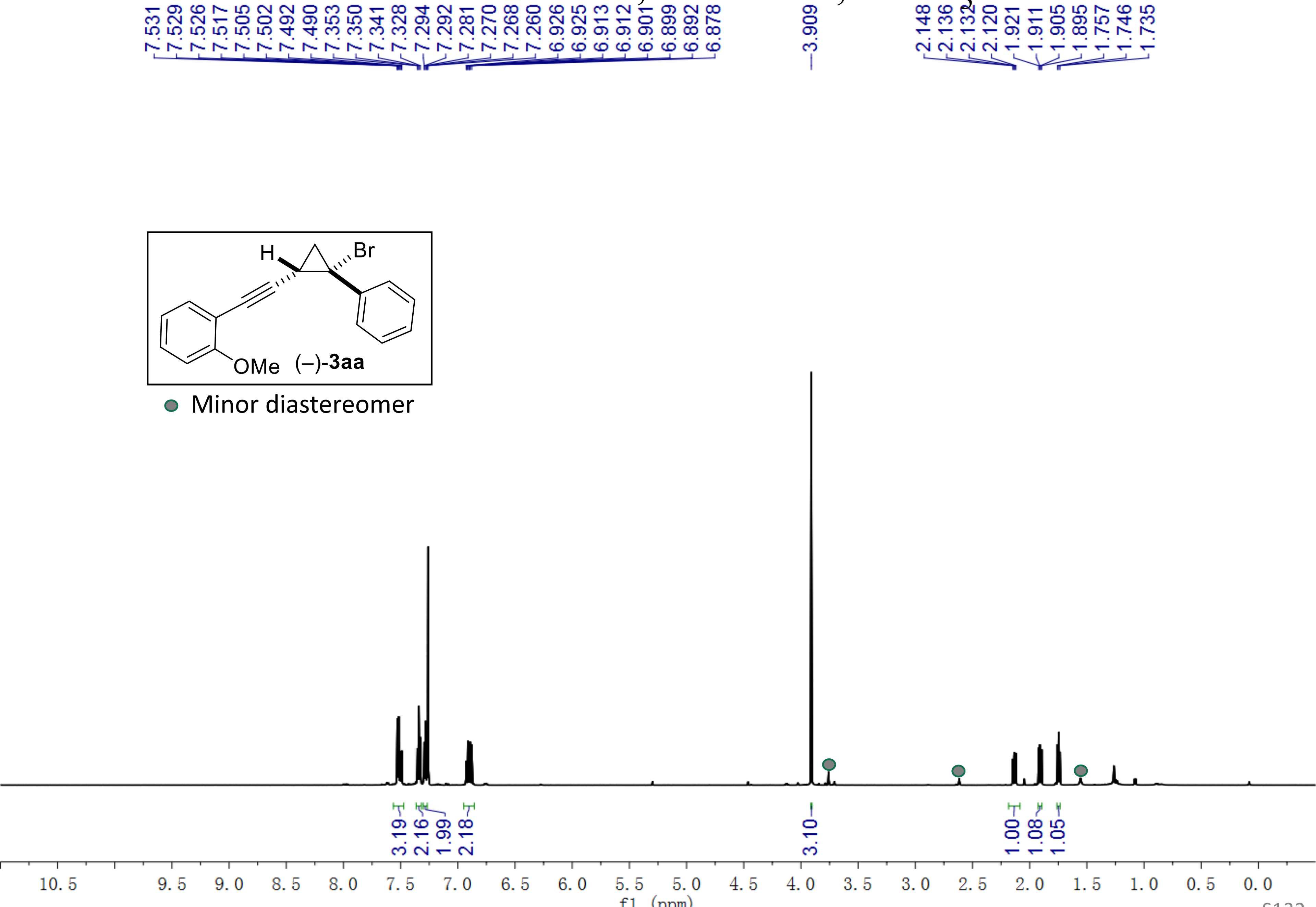


Peak Table

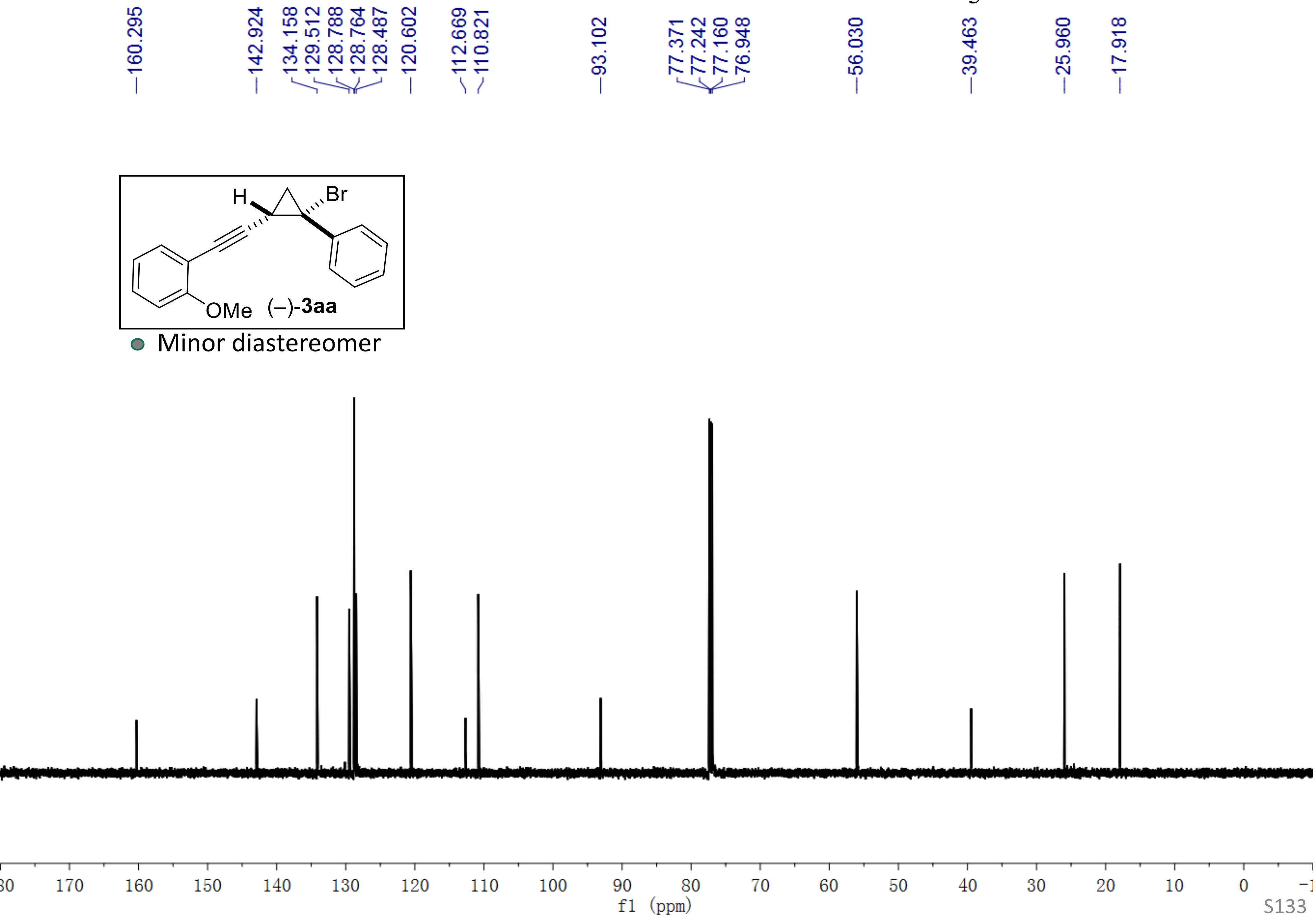
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.221	13283795	97.162
2	16.969	388070	2.838
Total		13671865	100.000

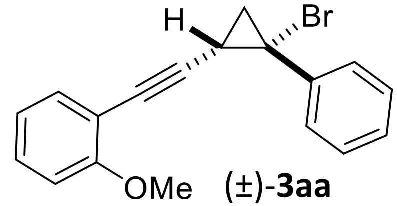
^{1}H NMR of **3aa**, 600 MHz, $CDCl_3$



^{13}C NMR of **3ab**, 151 MHz, $CDCl_3$

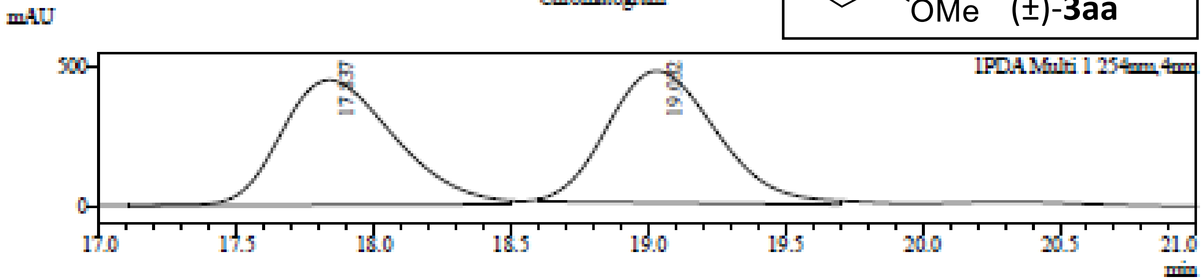


Data File : J0K-0620-IA-0.5%-0.8ML.lcd
Sample Name : J0K-0620-IA-0.5%-0.8ML
Sample ID : J0K-0620-IA-0.5%-0.8ML
Method File : J0K-0.5%--35min-0.8ml.lcm

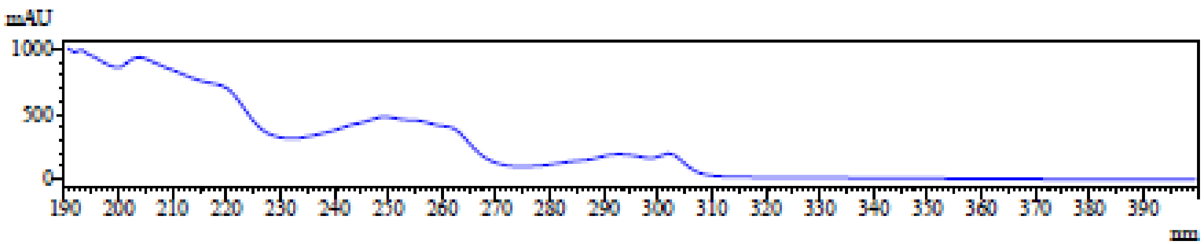


(±)-**3aa**

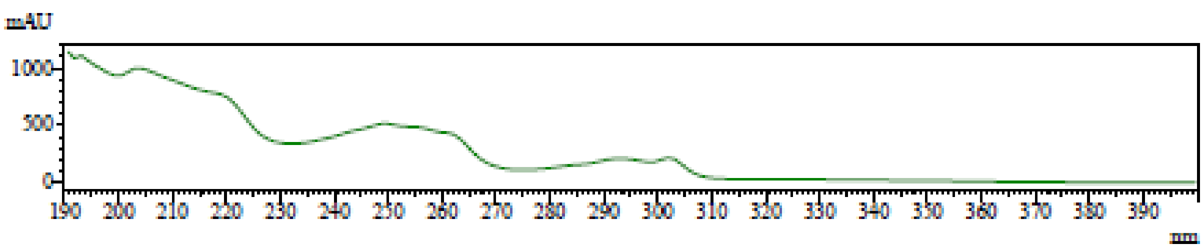
Chromatogram



UV Spectrum
Retention time = 17.837



UV Spectrum
Retention time = 19.032

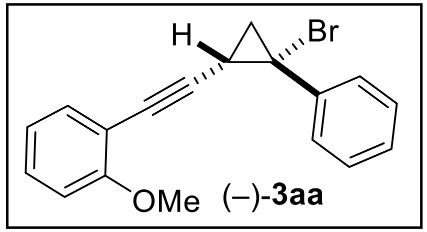


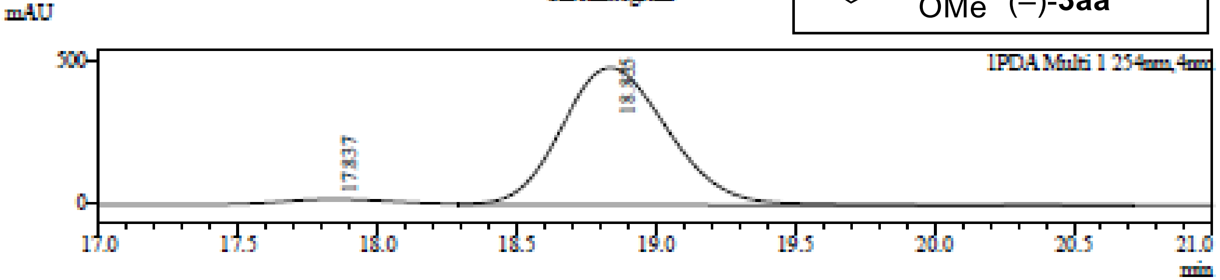
Peak Table

PDA Ch1 254nm

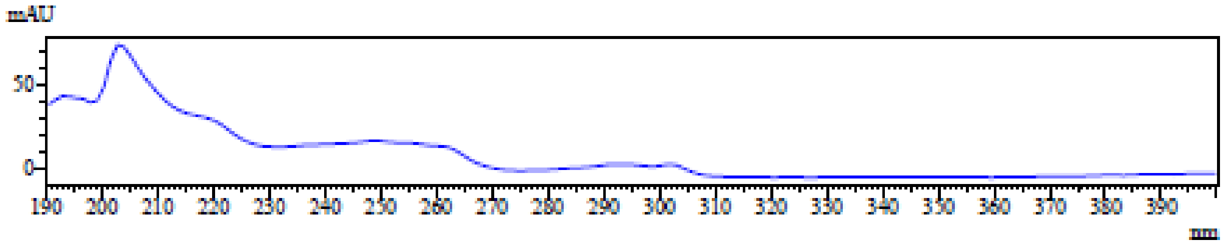
Peak#	Ret. Time	Area	Area%
1	17.837	12883307	49.717
2	19.032	13030156	50.283
Total		25913463	100.000

Data File	: J0K-0619-IA-0.5%-0.8ML.lcd
Sample Name	: J0K-0619-IA-0.5%-0.8ML
Sample ID	: J0K-0619-IA-0.5%-0.8ML
Method File	: J0K-0.5%--35min-0.8ml.lcm

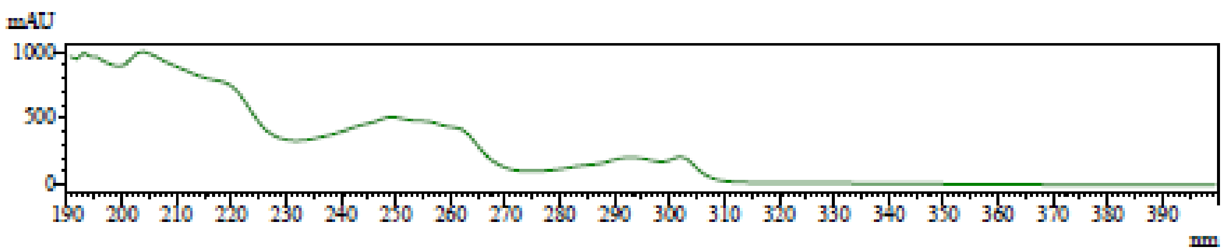




UV Spectrum
Retention time = 17.837



UV Spectrum
Retention time = 18.835

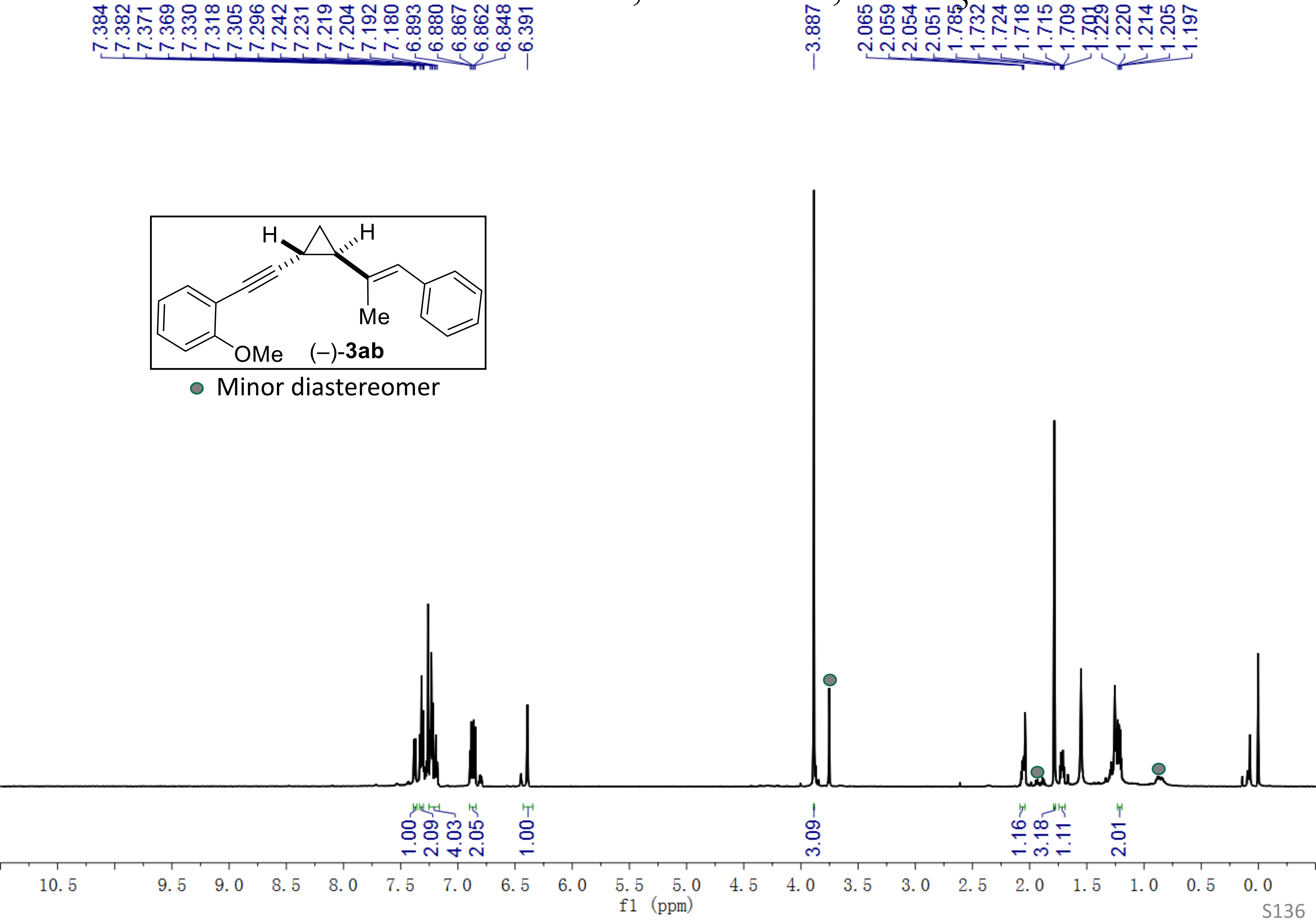


Peak Table

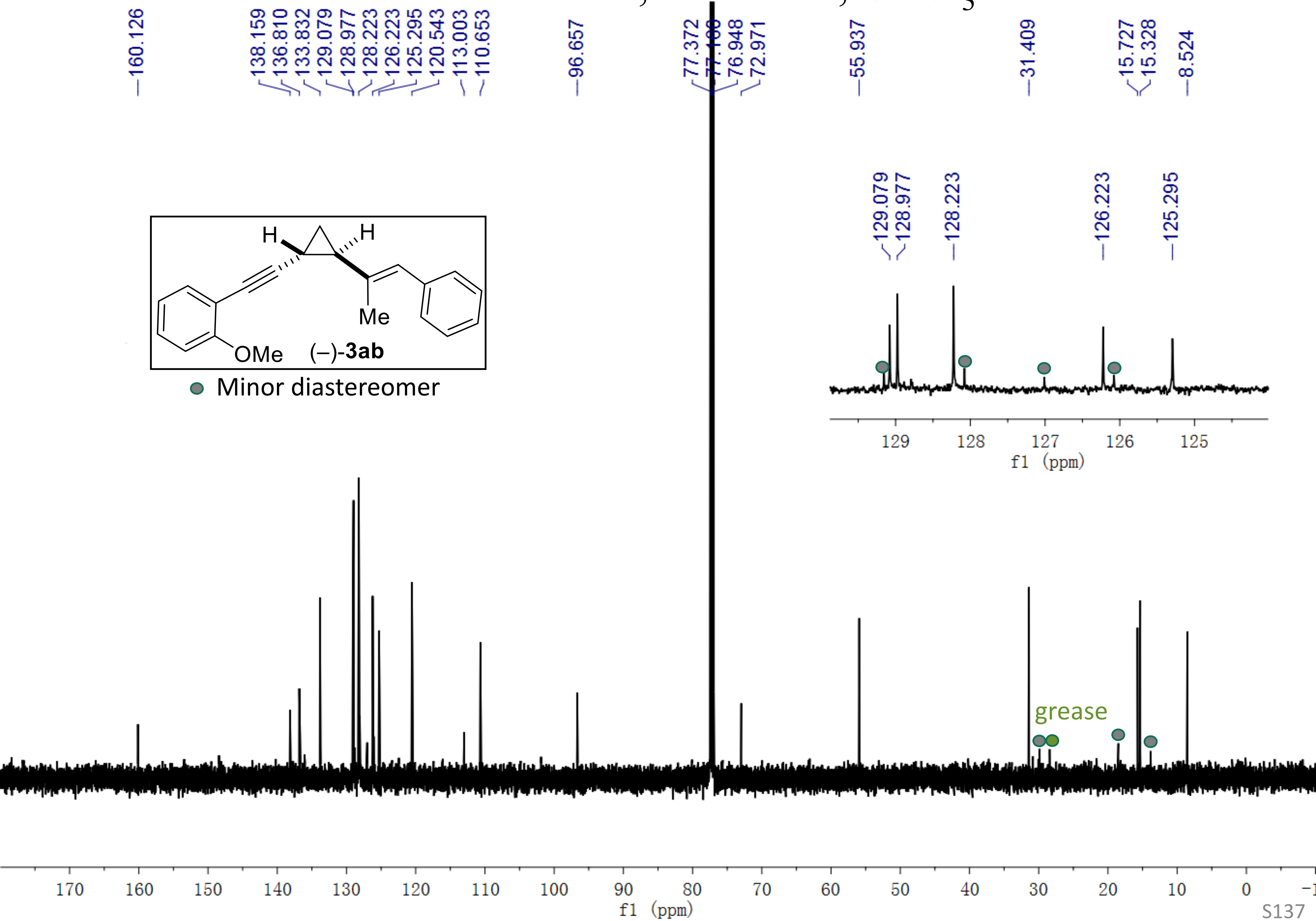
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.837	580094	4.292
2	18.835	12935914	95.708
Total		13516008	100.000

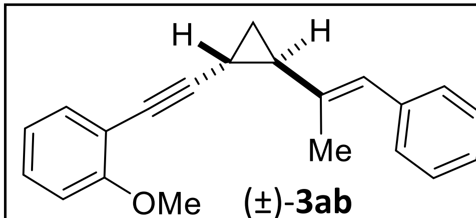
^{1}H NMR of **3ab**, 600 MHz, $CDCl_3$



^{13}C NMR of **3ab**, 151 MHz, CDCl$_3$

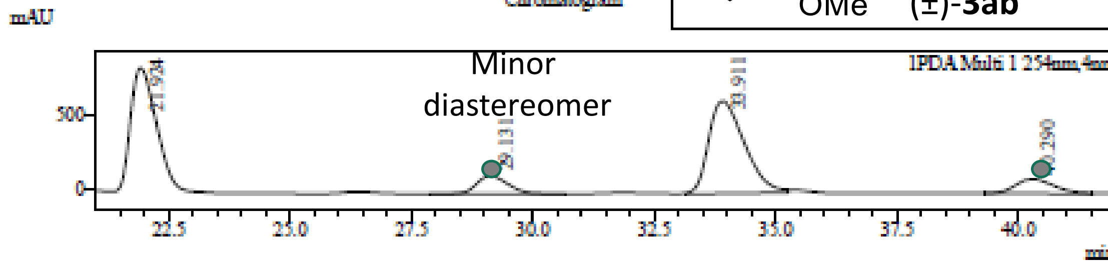


Data File : J0K-0572-IB-2-0.5%-0.8ML.lcd
Sample Name : J0K-0572-IB-2-0.5%-0.8ML
Sample ID : J0K-0572-IB-2-0.5%-0.8ML
Method File : J0K-0.5%--50min-0.8ml.lcm

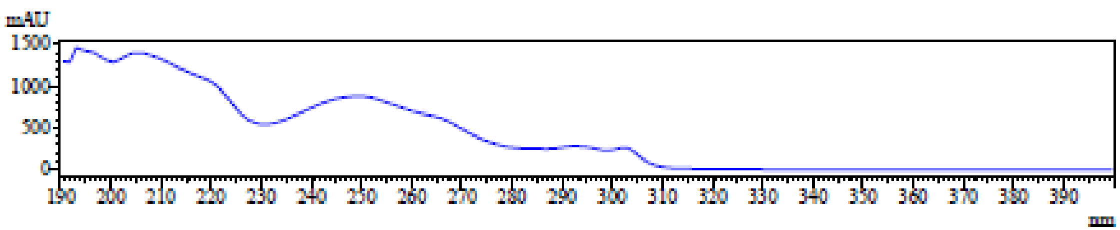


(±)-**3ab**

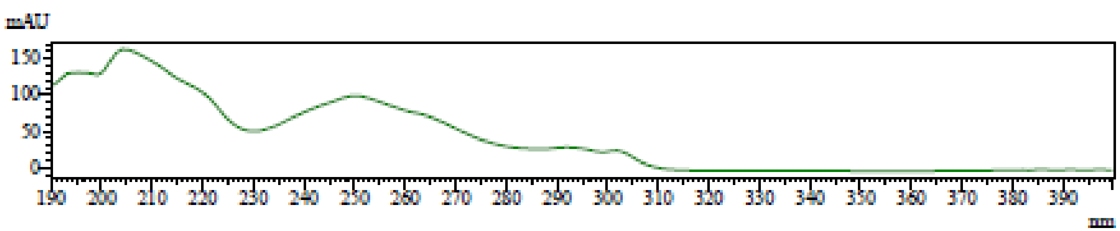
Chromatogram



UV Spectrum
Retention time = 21.924



UV Spectrum
Retention time = 29.131

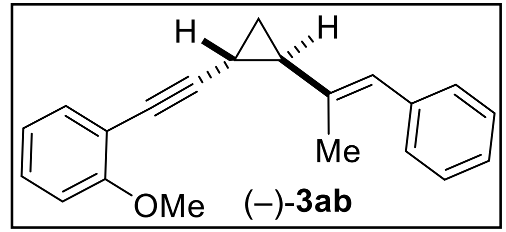


Peak Table

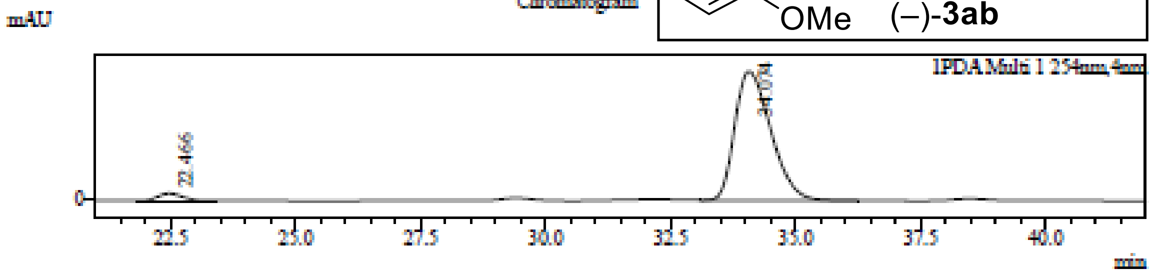
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.924	32295768	43.019
2	29.131	5296135	7.055
3	33.911	32148350	42.822
4	40.290	5333635	7.105
Total		75073888	100.000

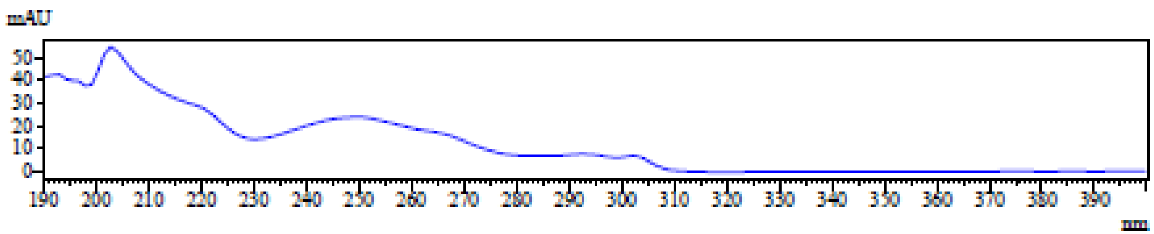
Data File : J0K-0571-IB-0.5%-0.8ML.lcd
Sample Name : J0K-0571-IB-0.5%-0.8ML
Sample ID : J0K-0571-IB-0.5%-0.8ML
Method File : J0K-0.5%--50min-0.8ml.lcm



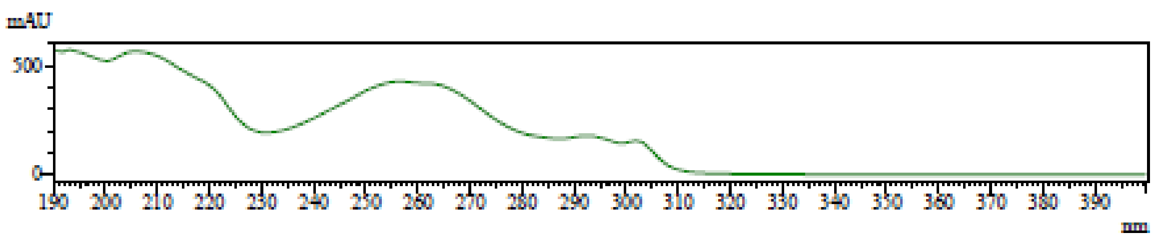
Chromatogram



UV Spectrum
Retention time = 22.466



UV Spectrum
Retention time = 34.074

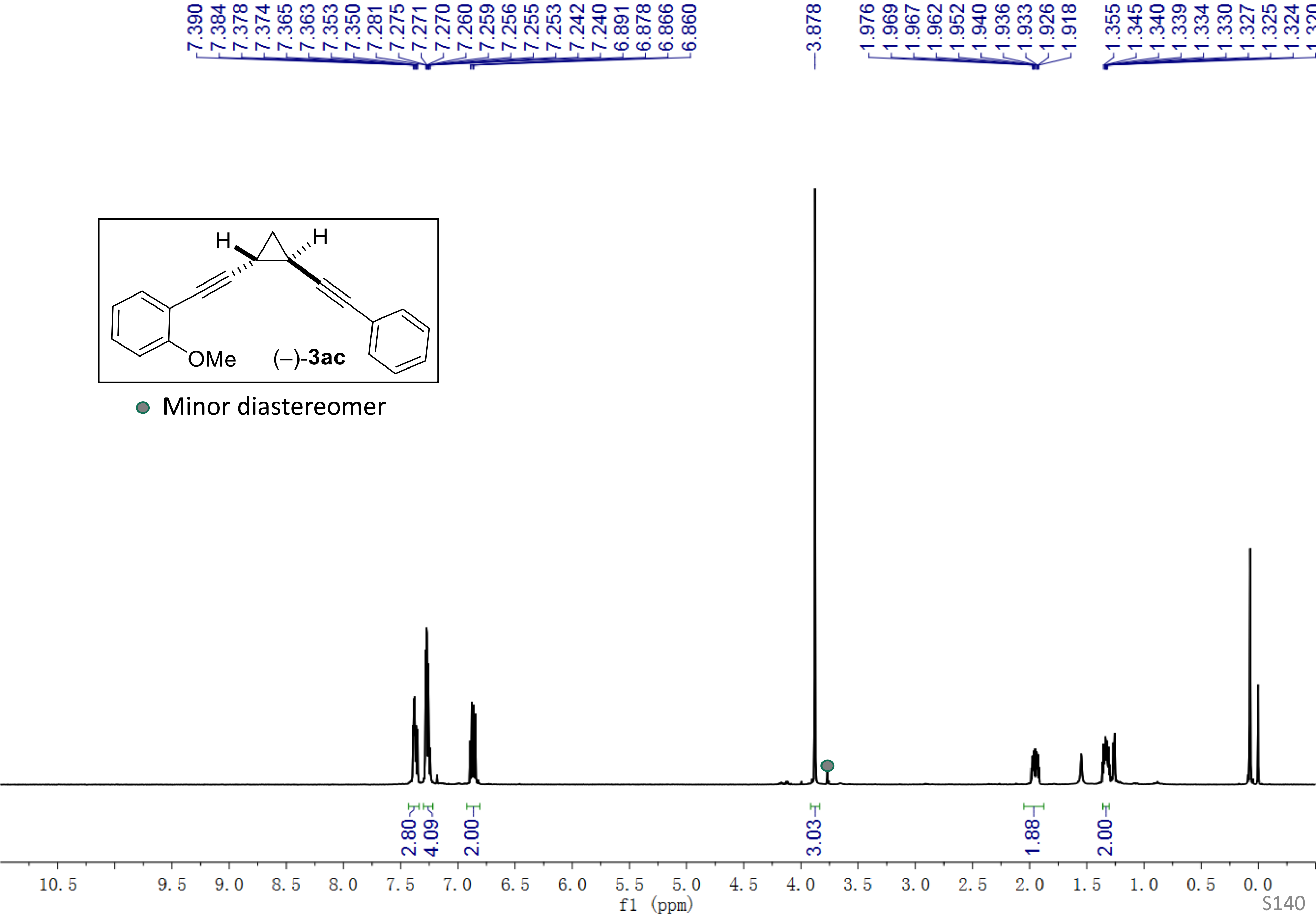


Peak Table

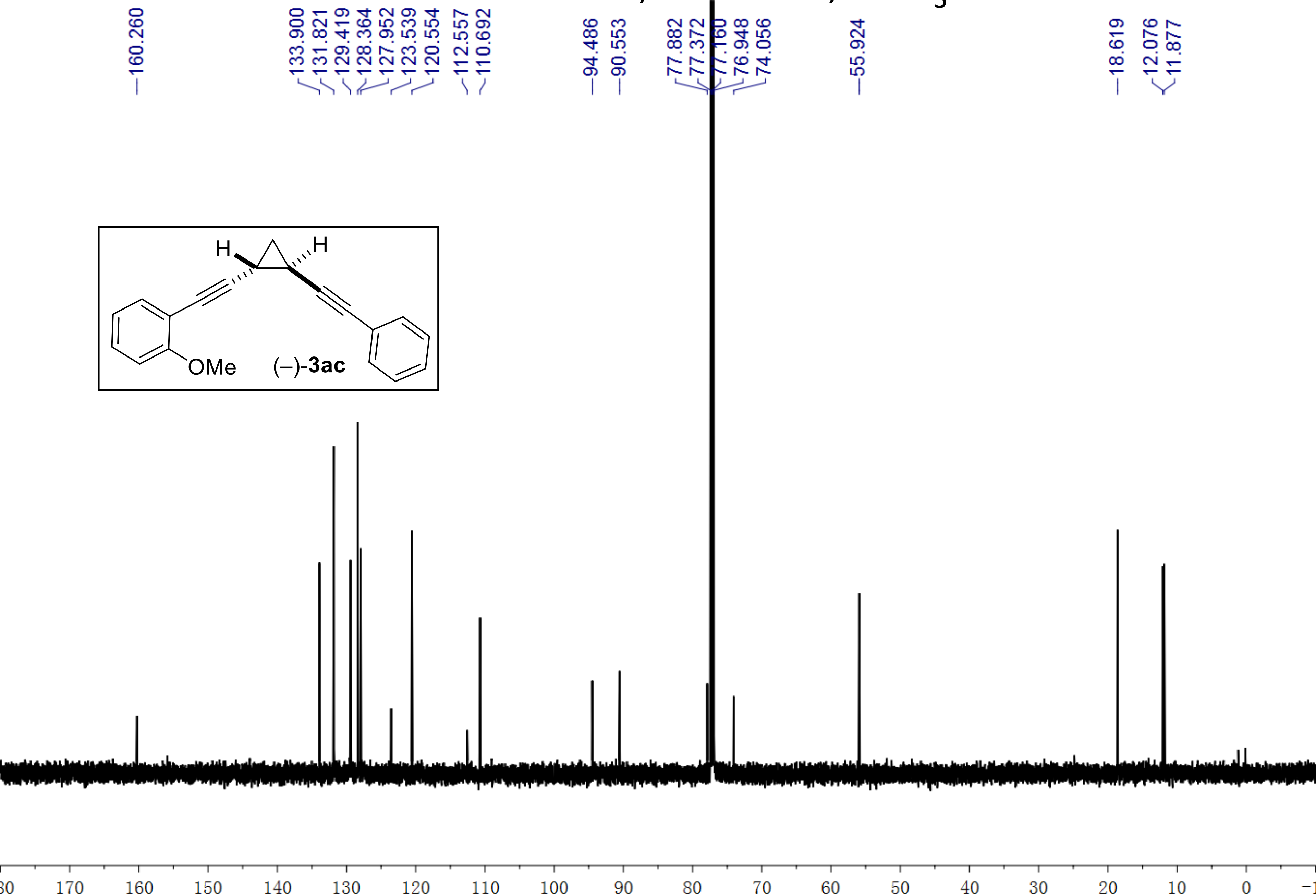
PDA Ch1 254nm

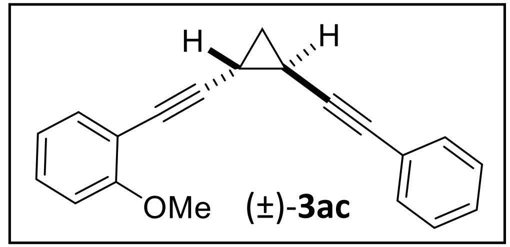
Peak#	Ret. Time	Area	Area%
1	22.466	796063	3.676
2	34.074	20857854	96.324
Total		21653917	100.000

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



^{13}C NMR of **3ac**, 151 MHz, $CDCl_3$

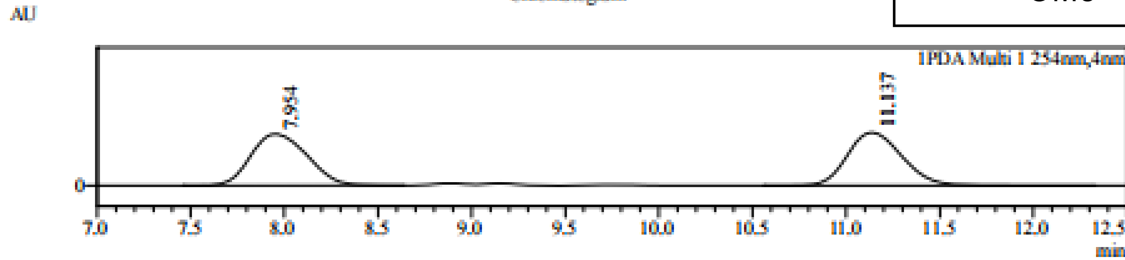




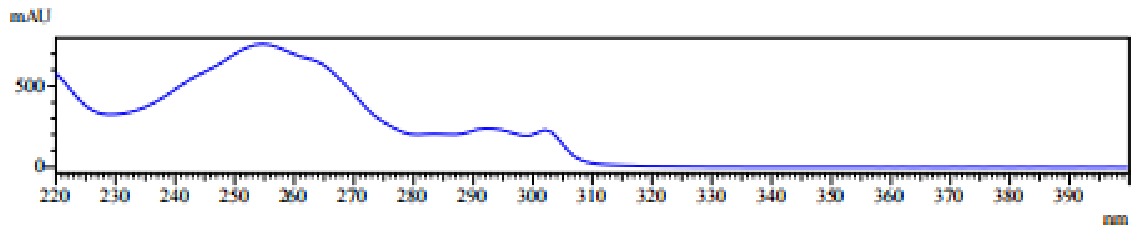
(±)-**3ac**

Data File : J0K-0168-IC-1%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0168-IC-1%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0168-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml.lcm

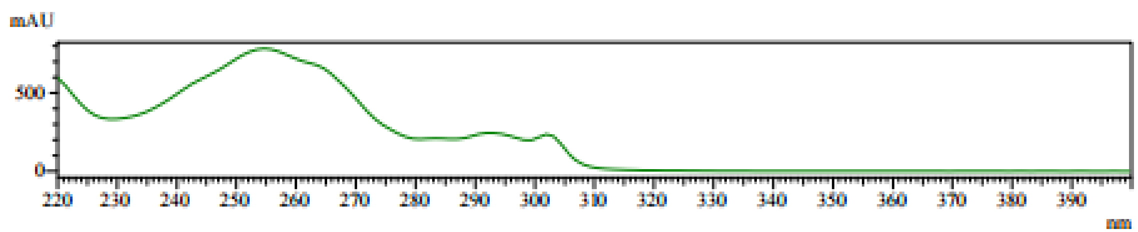
Chromatogram



UV Spectrum
Retention time = 7.954



UV Spectrum
Retention time = 11.137

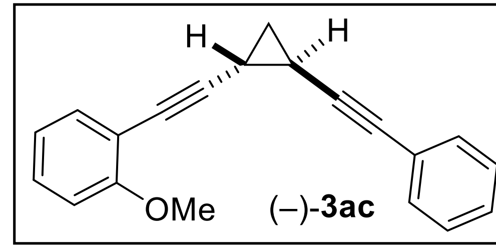


Peak Table

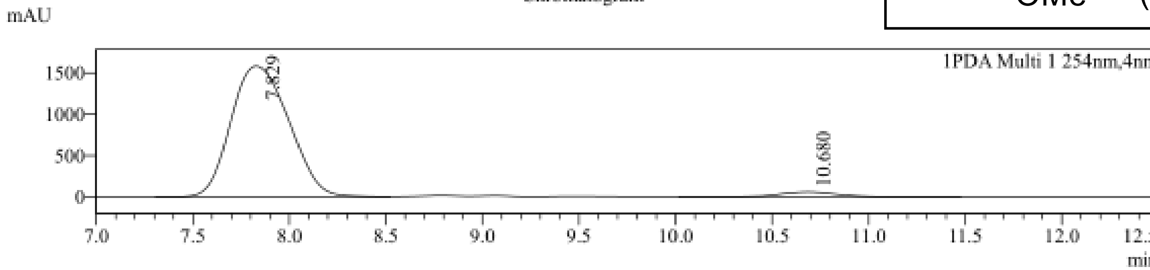
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.954	15546478	50.007
2	11.137	15542218	49.993
Total		31088696	100.000

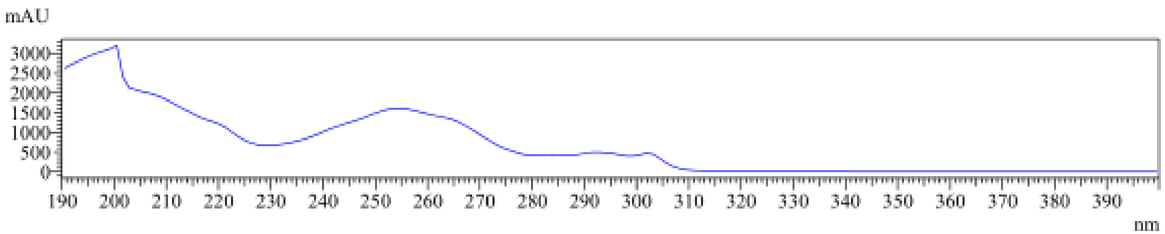
Data File : J0K-0167-IC-1%-0.8ML-isopropanol-solvent003.lcd
Sample Name : J0K-0167-IC-1%-0.8ML-isopropanol-solvent003
Sample ID : J0K-0167-IC-1%-0.8ML-isopropano
Method File : J0K-1%-0.8ml.lcm



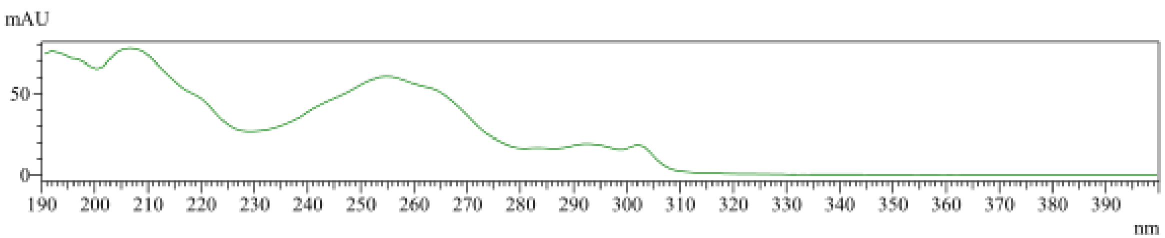
Chromatogram



UV Spectrum
Retention time = 7.829



UV Spectrum
Retention time = 10.680

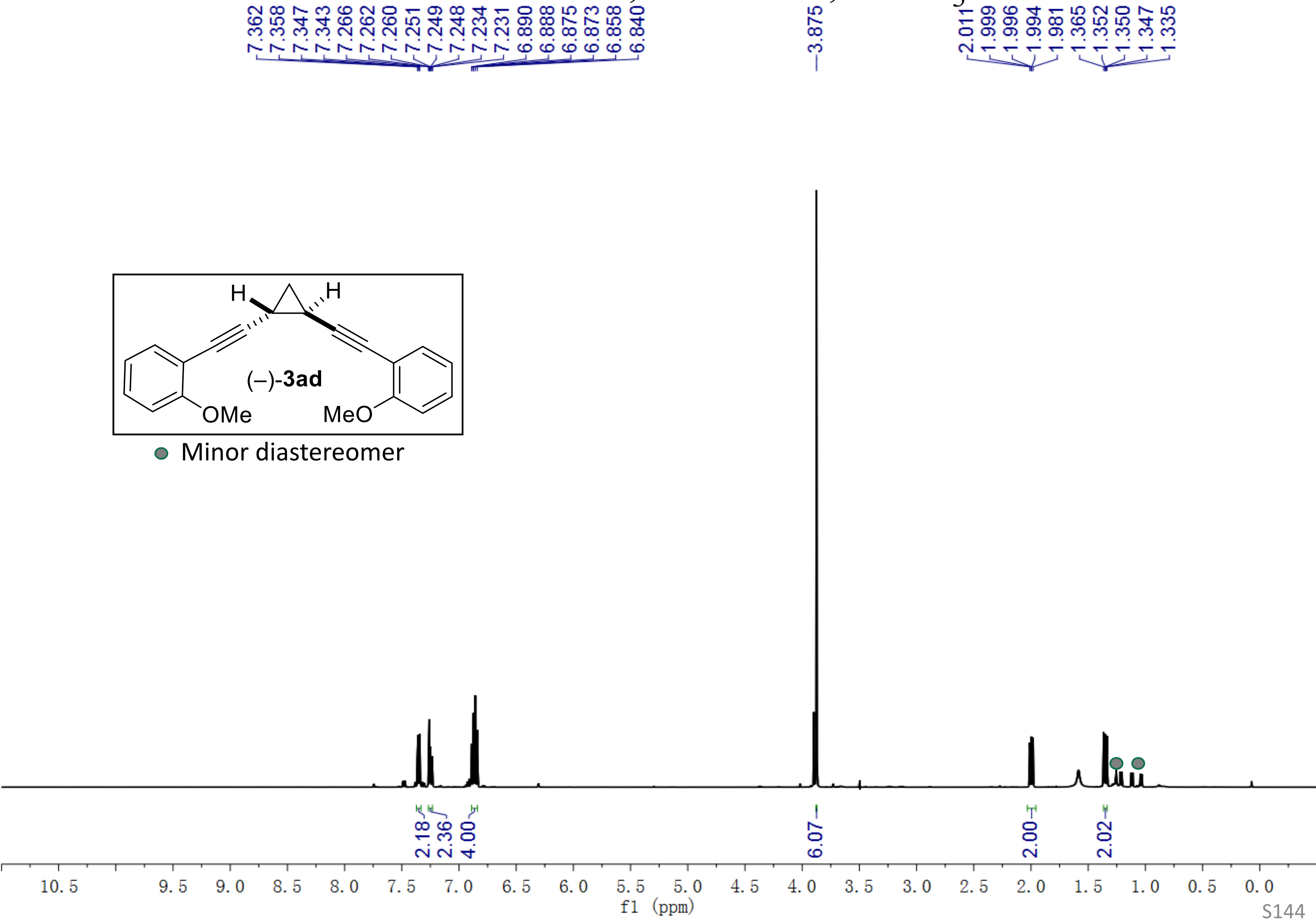


Peak Table

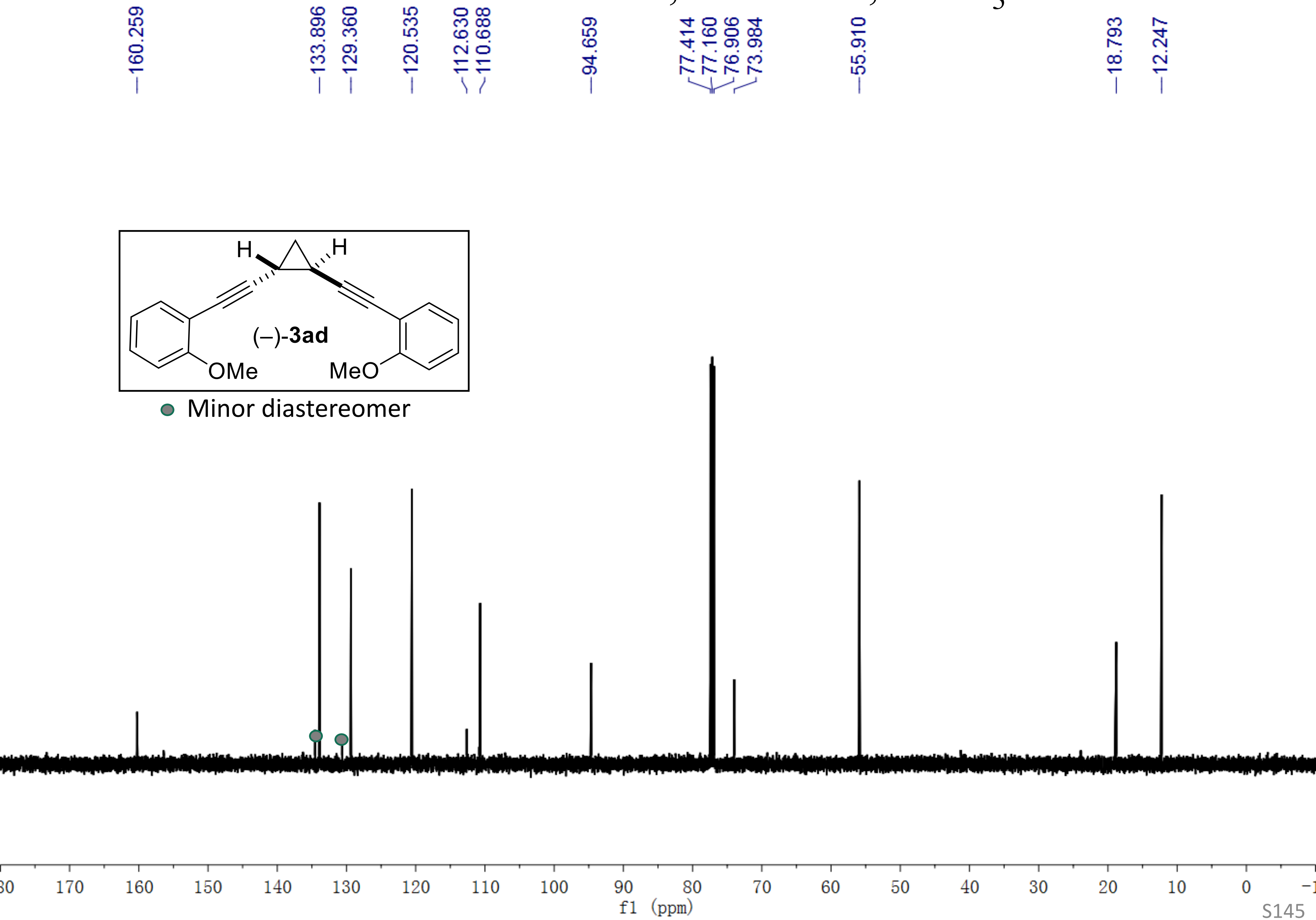
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.829	32959040	96.411
2	10.680	1227035	3.589
Total		34186075	100.000

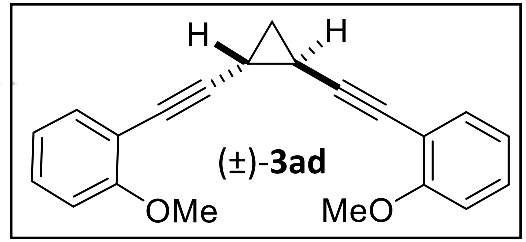
^{1}H NMR of **3ad**, 600 MHz, $CDCl_3$



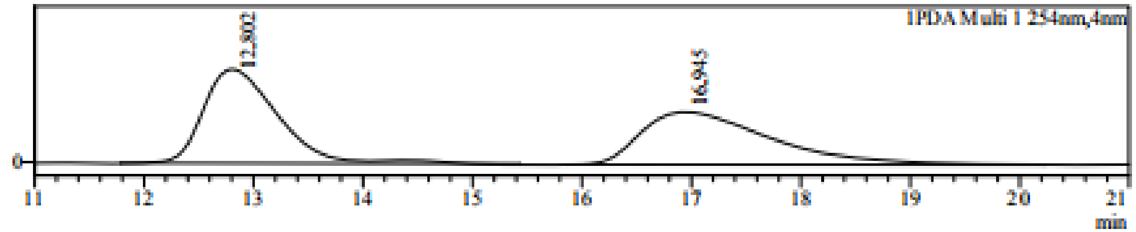
^{13}C NMR of **3ad**, 151 MHz, $CDCl_3$



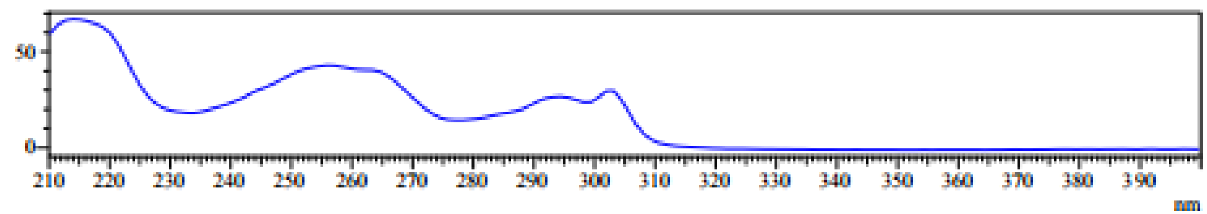
Data File : J0K-0831-IA--0.5%-1ML.lcd
Sample Name : J0K-0831-IA--0.5%-1ML
Sample ID : J0K-0831-IA--0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm



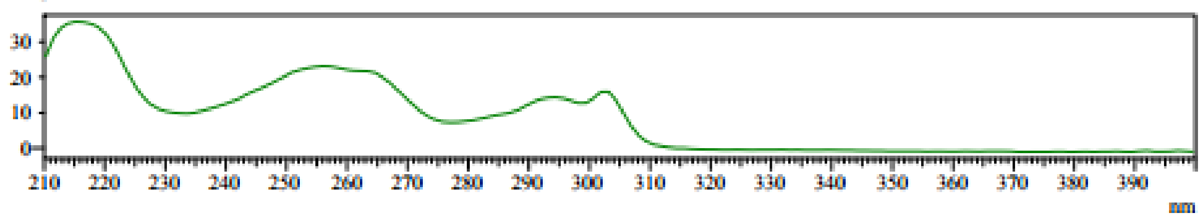
Chromatogram



UV Spectrum
Retention time = 12.802



U
Retention time = 16.945

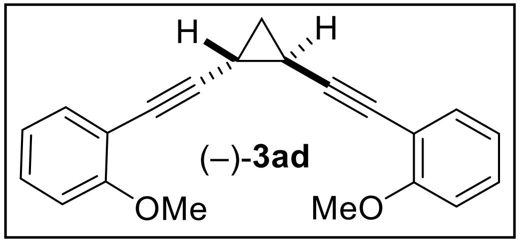


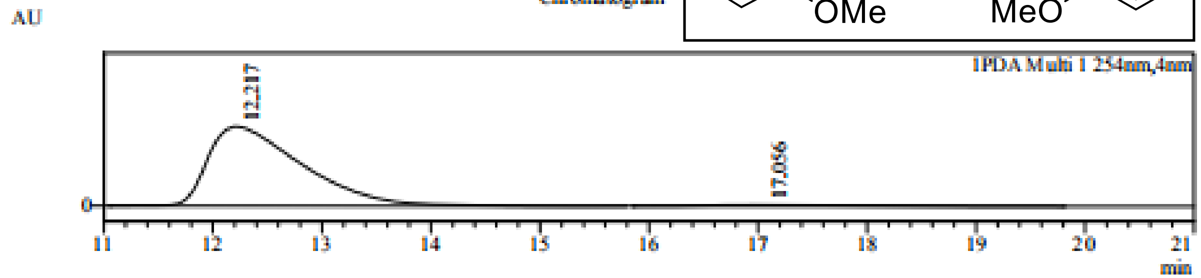
Peak Table

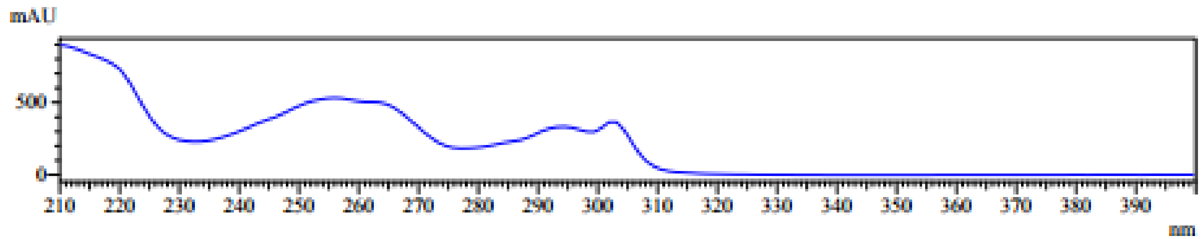
PDA Ch1 254nm

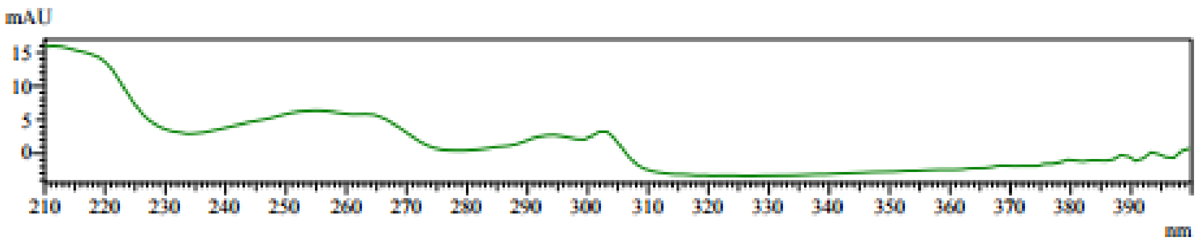
Peak#	Ret. Time	Area	Area%
1	12.802	1979132	50.313
2	16.945	1954522	49.687
Total		3933655	100.000

Data File : J0K-0830-2-IA--0.5%-1ML.lcd
Sample Name : J0K-0830-2-IA--0.5%-1ML
Sample ID : J0K-0830-2-IA--0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm







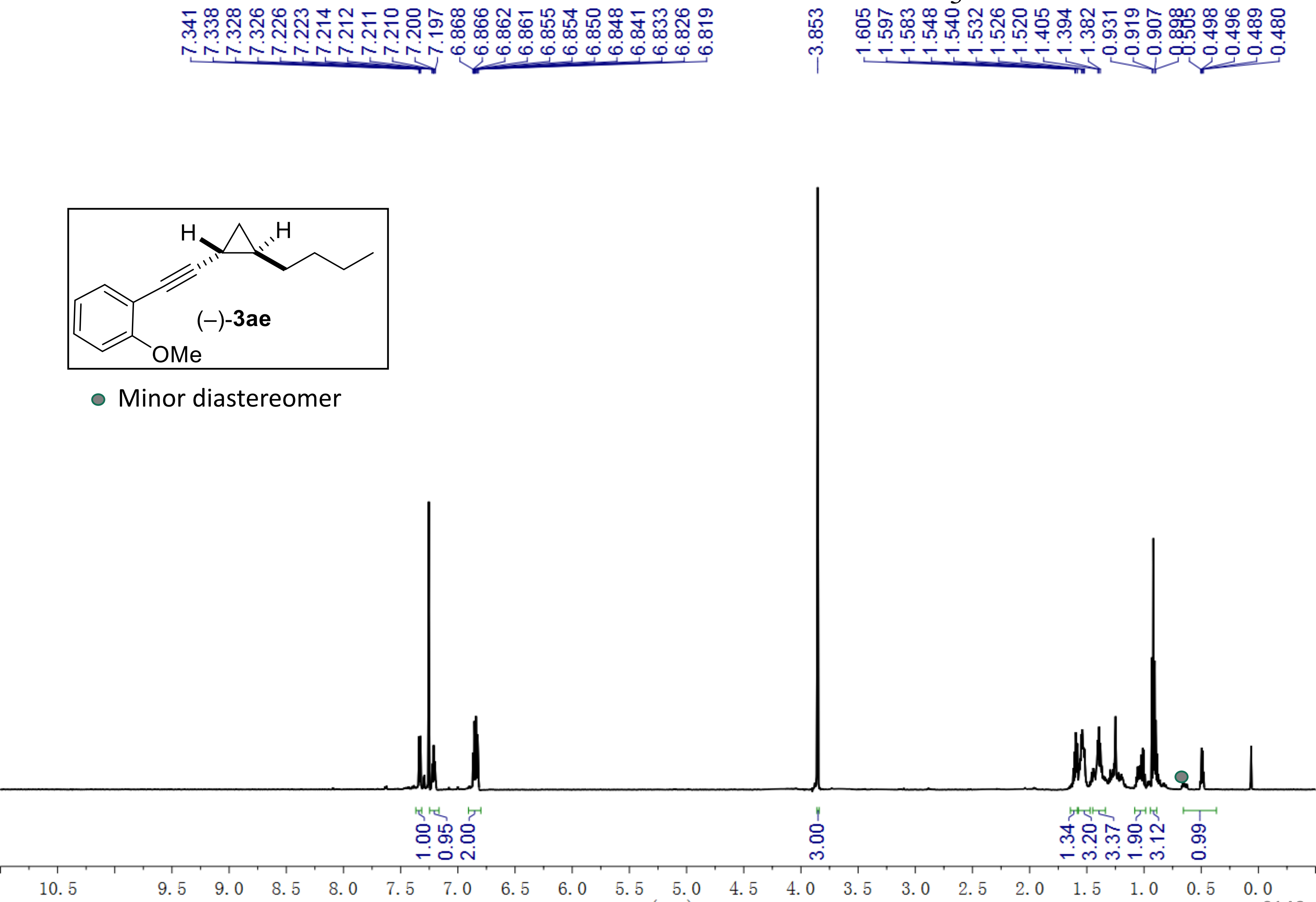


Peak Table

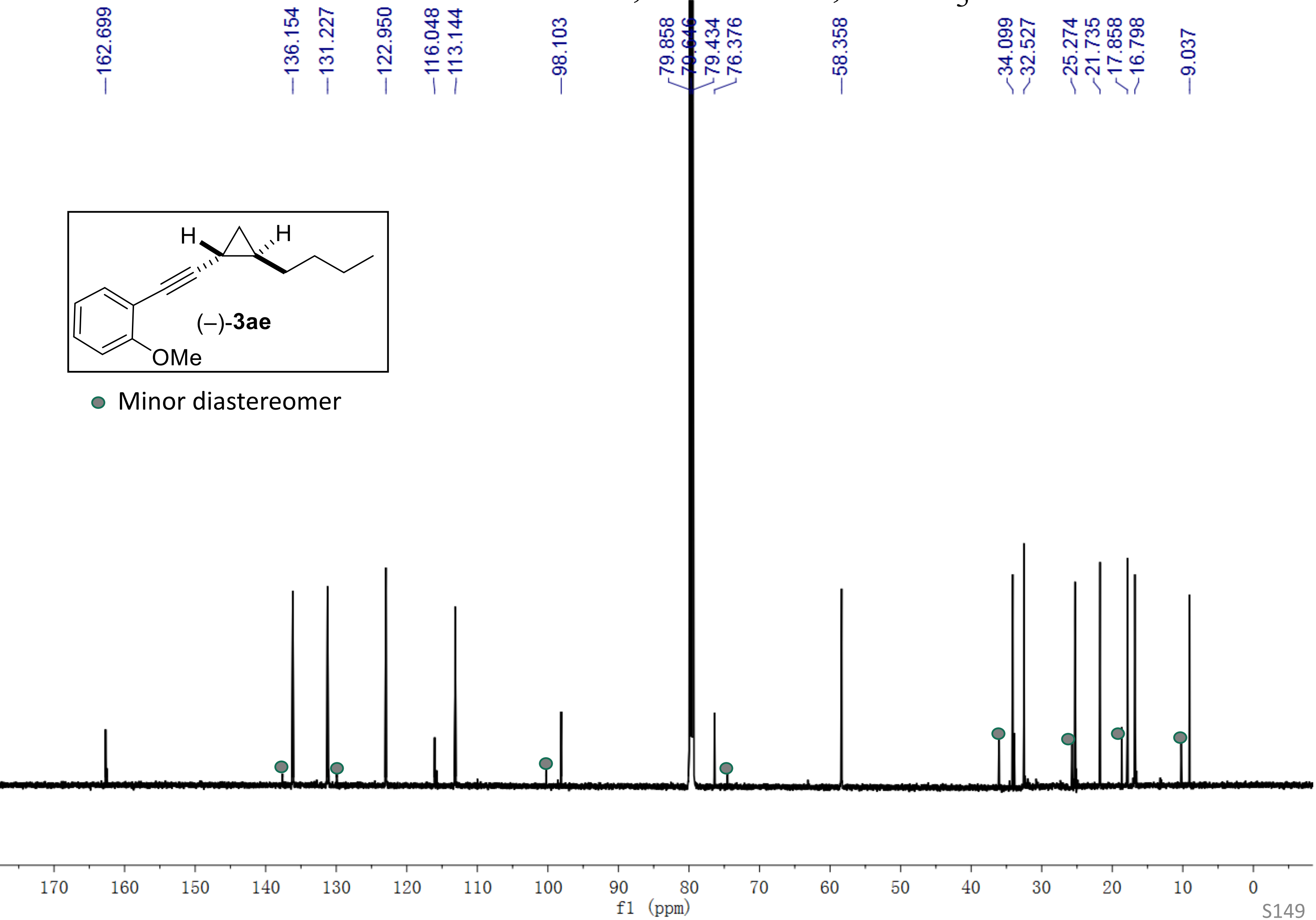
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.217	31115081	97.598
2	17.056	765709	2.402
Total		31880790	100.000

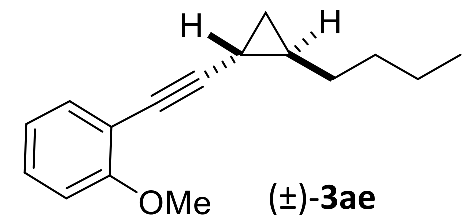
^{1}H NMR of **3ae**, 600 MHz, $CDCl_3$



^{13}C NMR of **3ae**, 151 MHz, $CDCl_3$

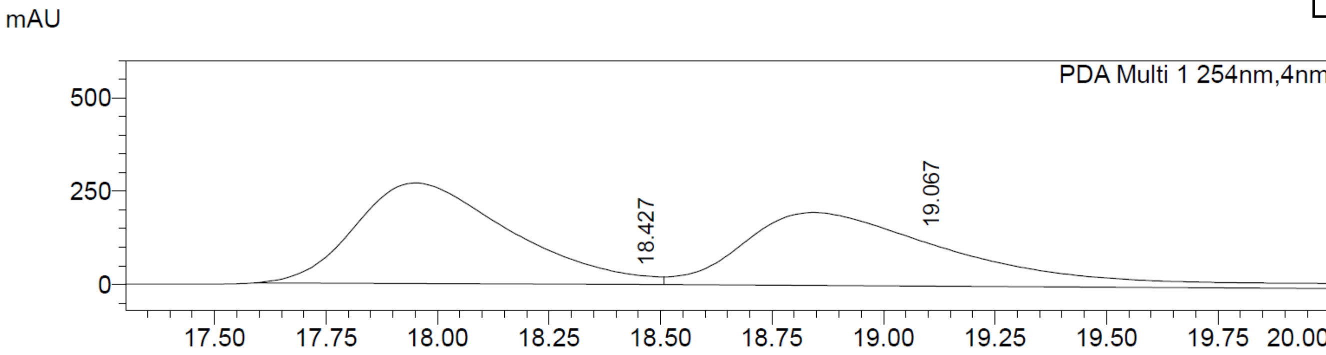


==== Shimadzu LabSolutions Analysis Report ====



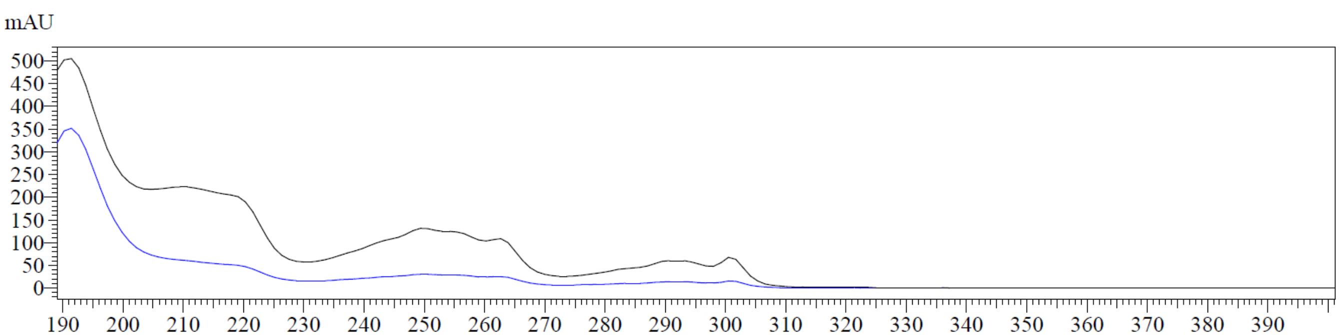
(±)-**3ae**

JK-1857-IF-0.3%-0.8mL
JK-0.3%-40min-0.8mL.lcm



UV Spectrum

JK-1857-IF-0.3%-0.8mL_002.lcd

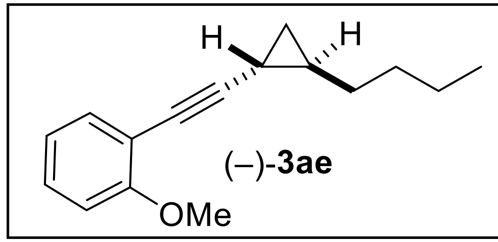


Peak Table

PDA Ch1 254nm

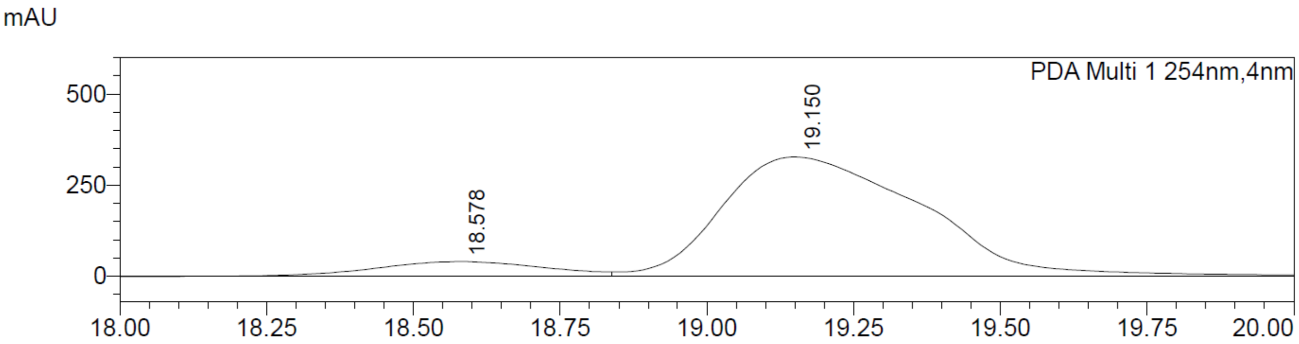
Peak#	Ret. Time	Area%
1	18.427	50.164
2	19.067	49.836
Total		100.000

==== Shimadzu LabSolutions Analysis Report ====



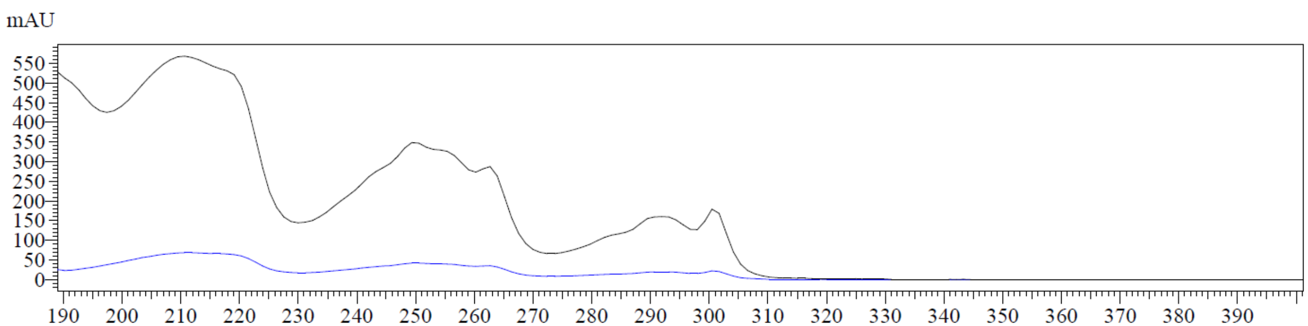
(–)-**3ae**

JK-1856-IF-0.3%-0.8mL
JK-0.3%-40min-0.8mL.lcm



UV Spectrum

JK-1856-IF-0.3%-0.8mL_001.lcd

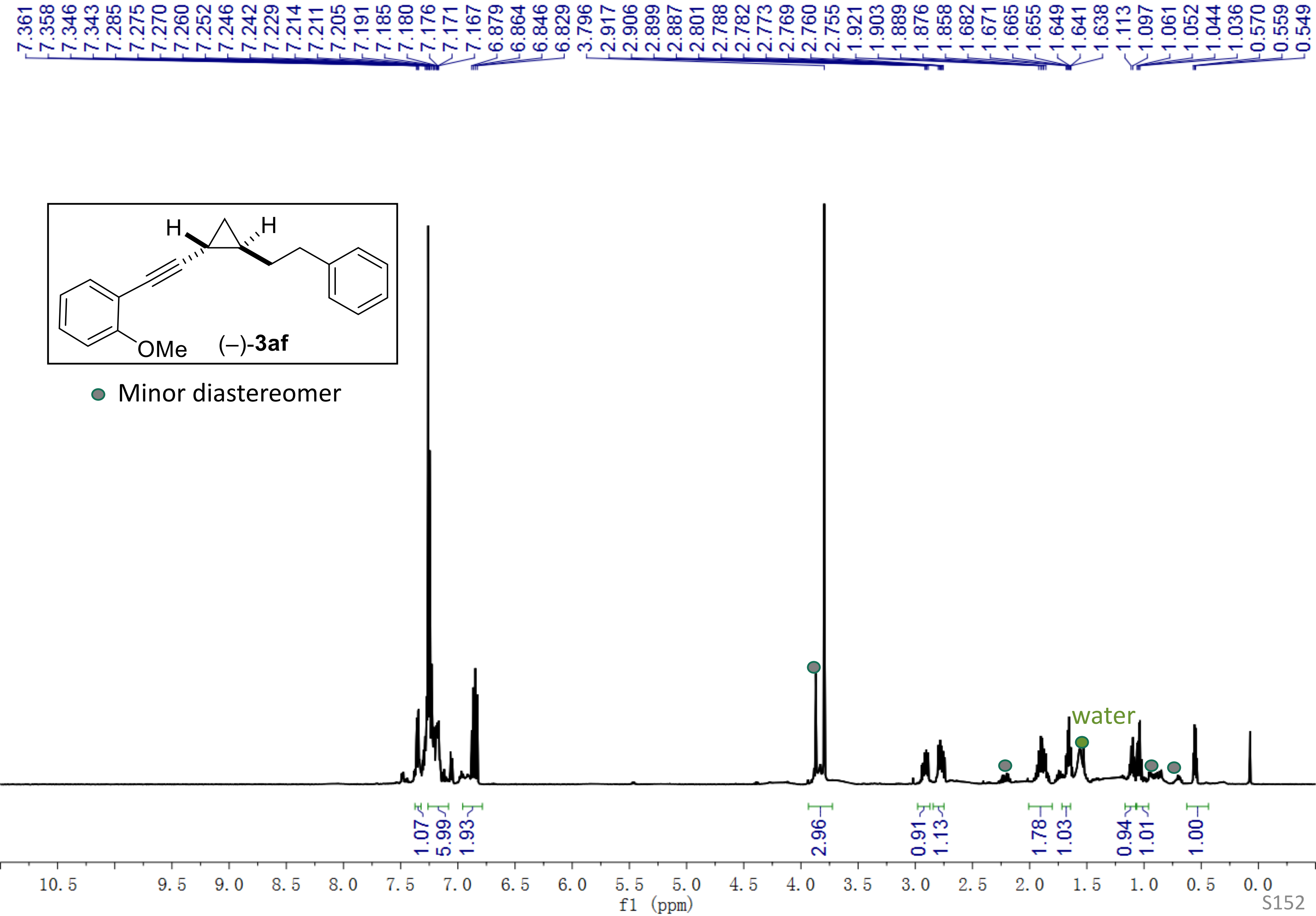


Peak Table

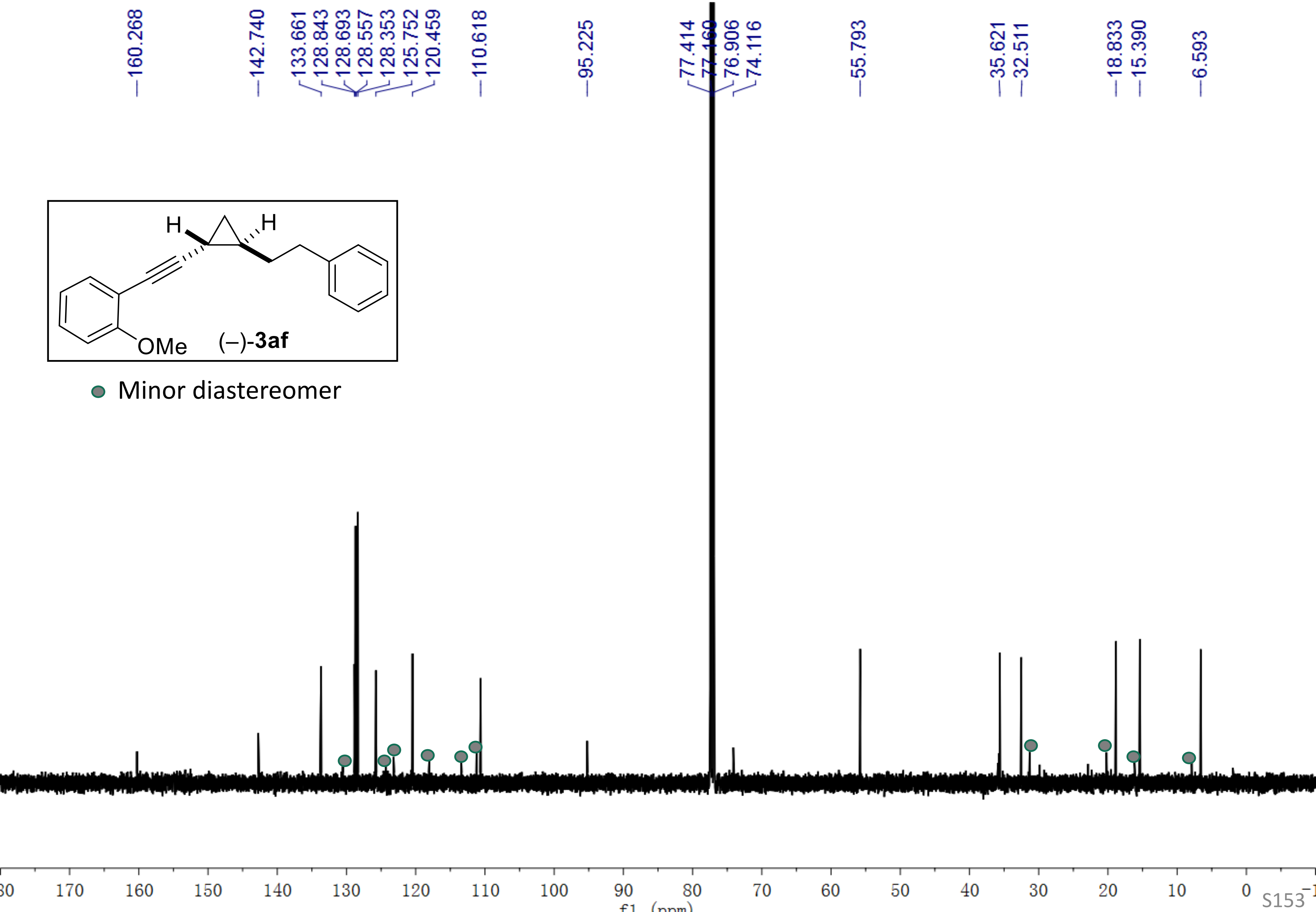
PDA Ch1 254nm

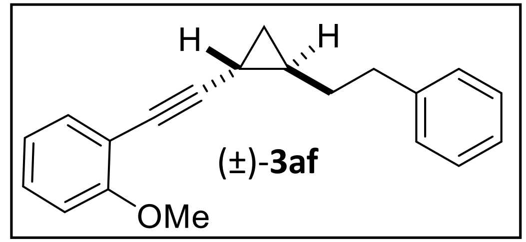
Peak#	Ret. Time	Area%
1	18.578	9.502
2	19.150	90.498
Total		100.000

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



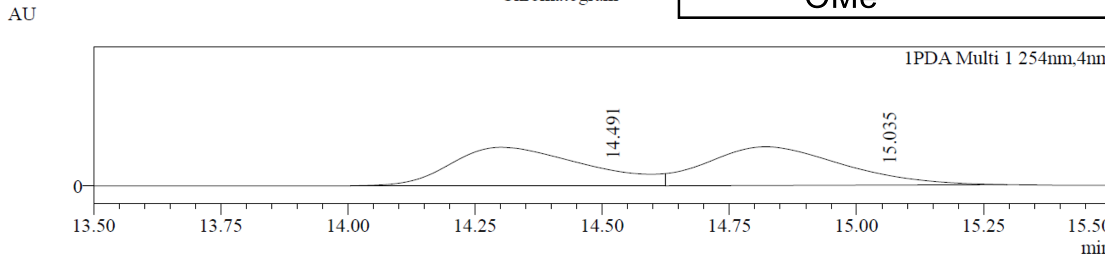
^{13}C NMR of **3af**, 126 MHz, $CDCl_3$



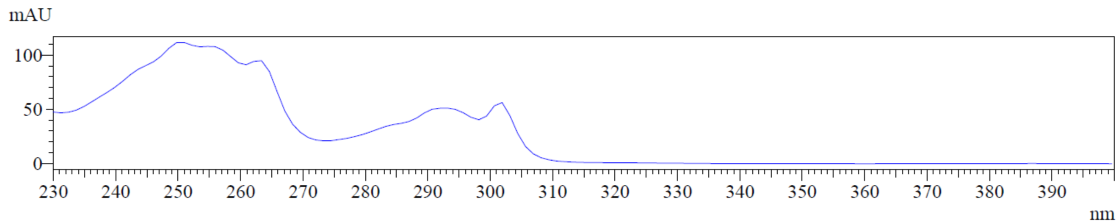


Data File : J0K-1843--IF-0.1%-1ML-3.lcd
Sample Name : J0K-1843--IF-0.1%-1ML-3
Sample ID : J0K-1843--IF-0.1%-1ML-3
Method File : J0K-0.1%--40min-1ml.lcm

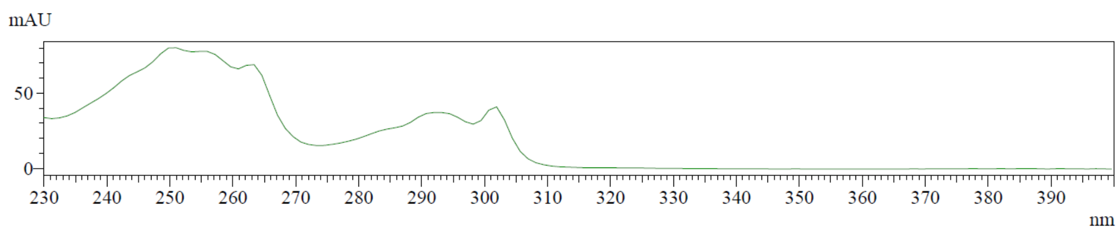
Chromatogram



UV Spectrum
Retention time = 14.491



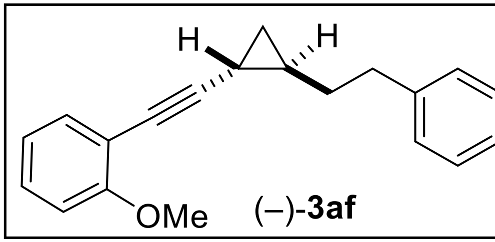
UV Spectrum
Retention time = 15.035



Peak Table

PDA Ch1 254nm

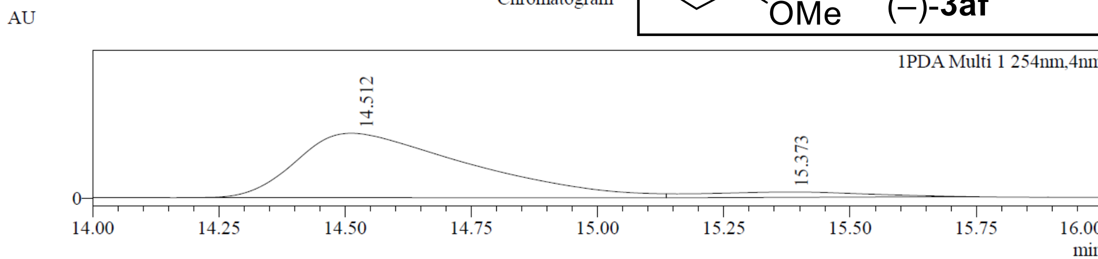
Peak#	Ret. Time	Area	Area%
1	14.491	4118530	49.946
2	15.035	4127418	50.054
Total		8245948	100.000



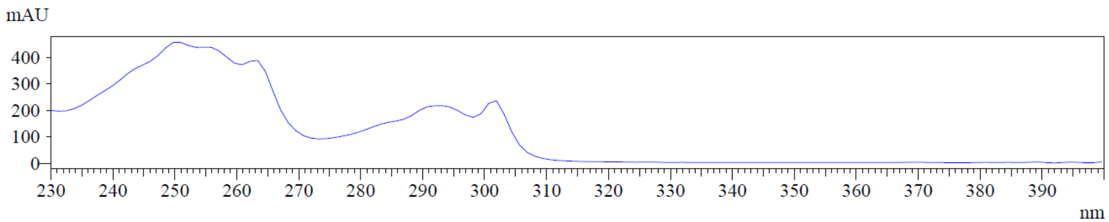
(–)-**3af**

Data File : J0K-1842--IF-0.1%-1ML-2.lcd
Sample Name : J0K-1842--IF-0.1%-1ML-2
Sample ID : J0K-1842--IF-0.1%-1ML-2
Method File : J0K-0.1%--40min-1ml.lcm

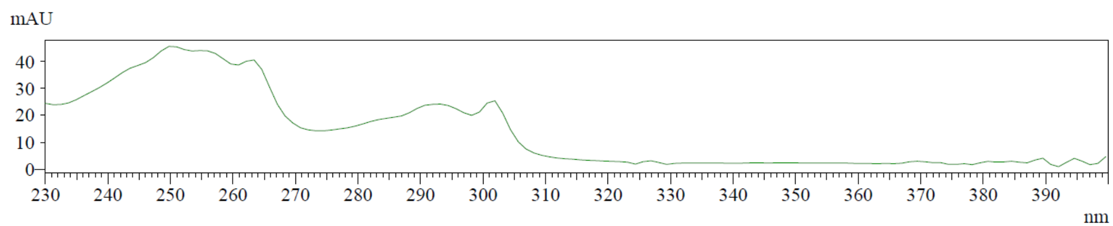
Chromatogram



UV Spectrum
Retention time = 14.512



UV Spectrum
Retention time = 15.373

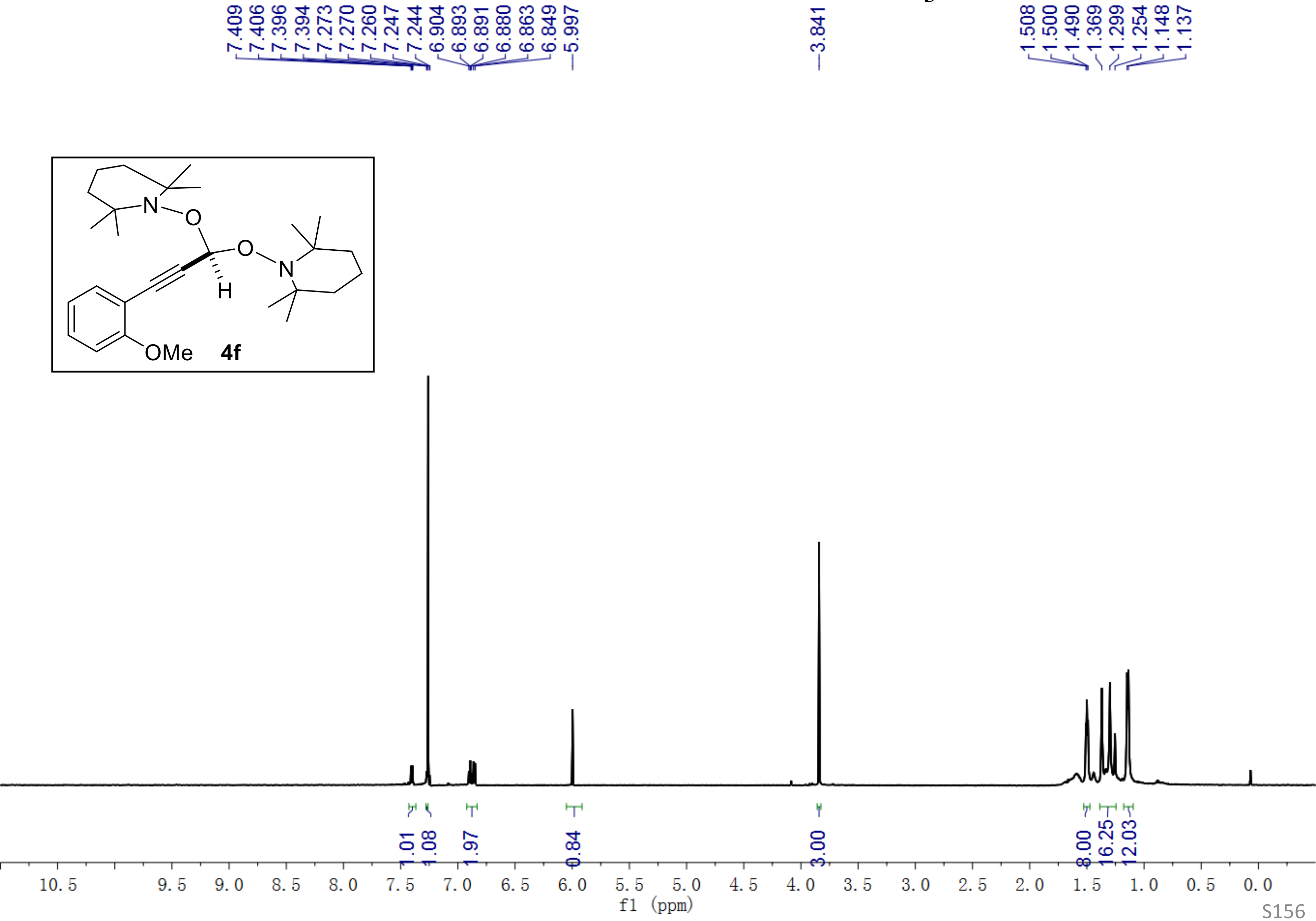


Peak Table

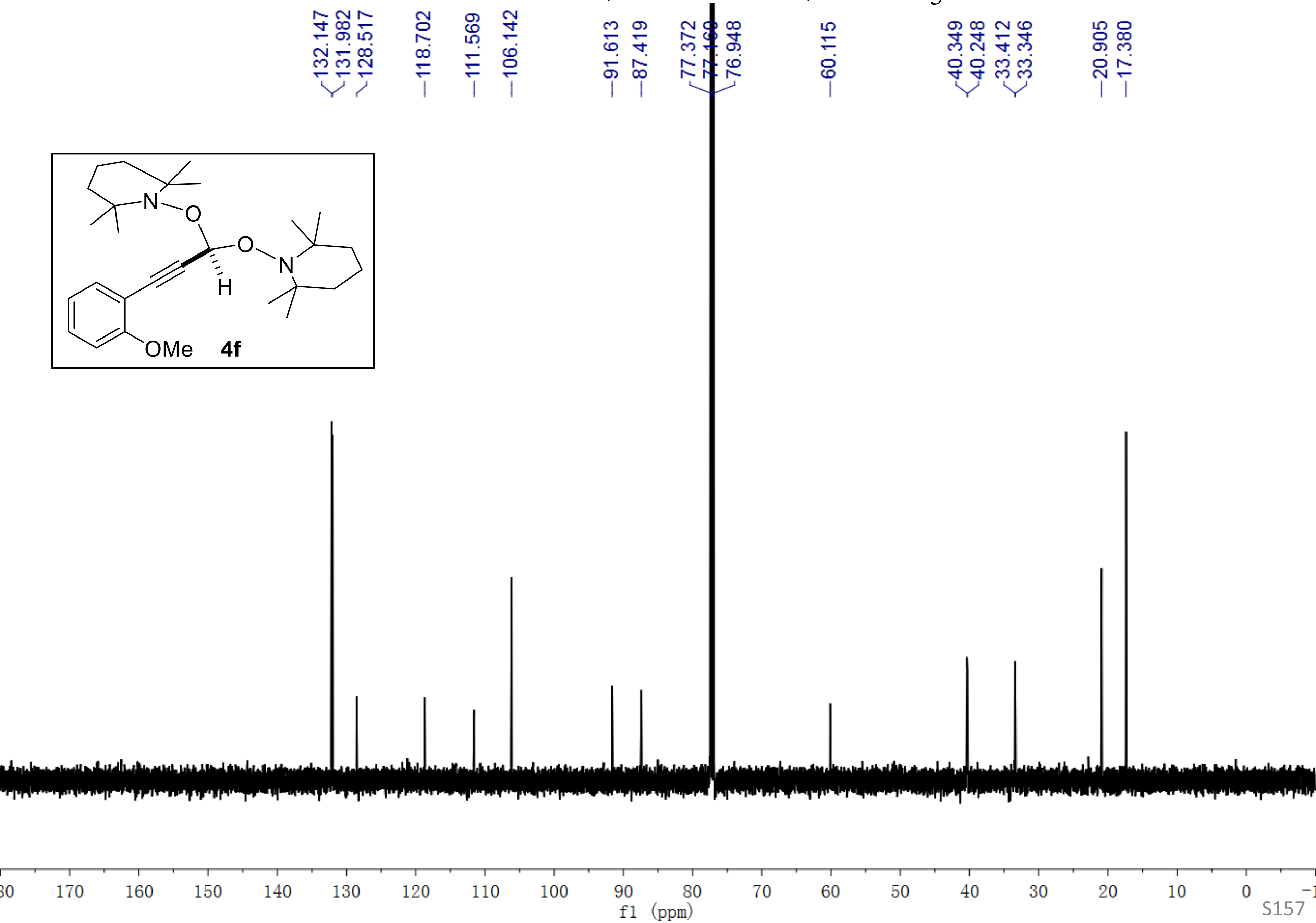
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.512	10300218	92.536
2	15.373	830833	7.464
Total		11131051	100.000

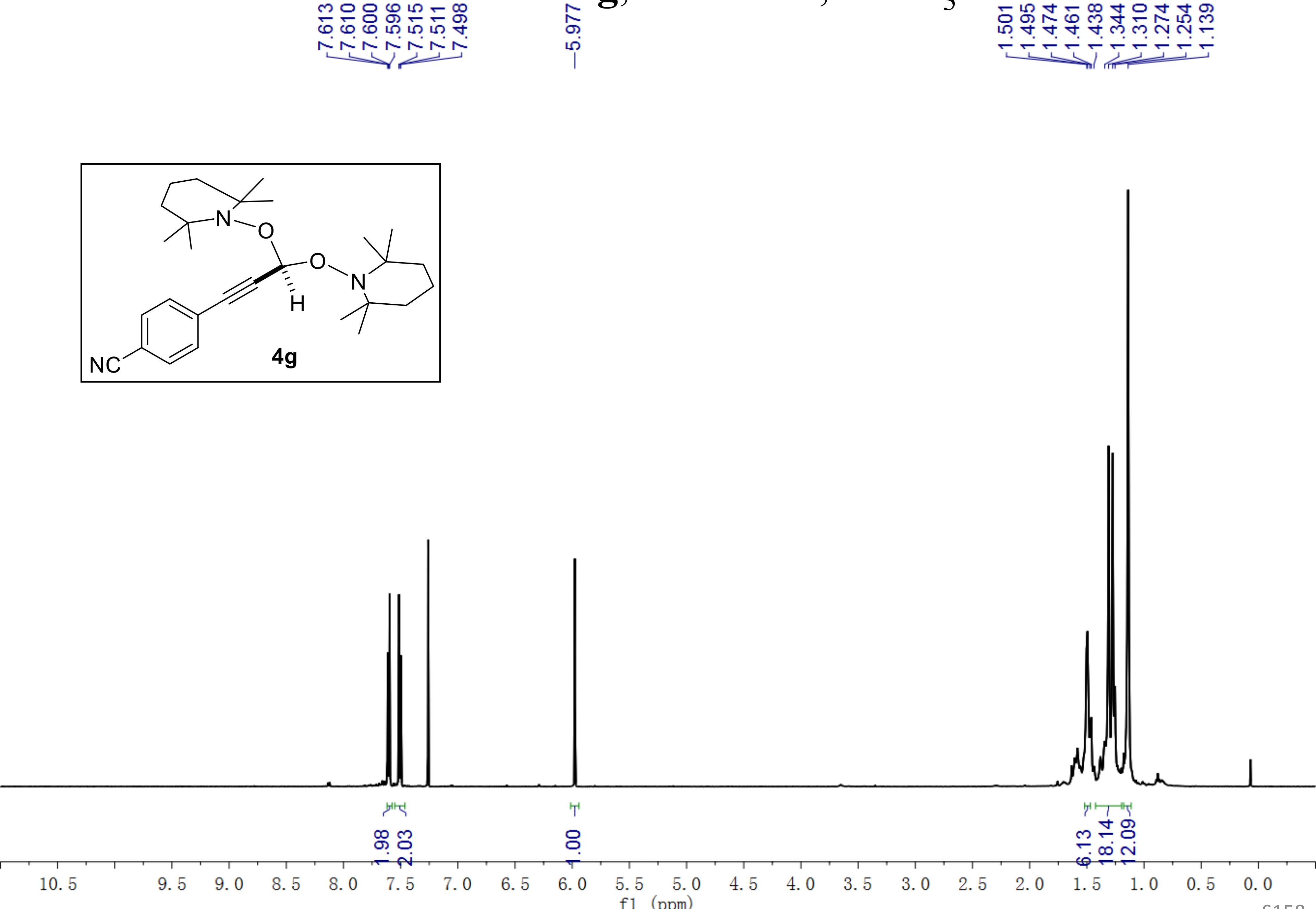
^{1}H NMR of **4f**, 600 MHz, $CDCl_3$



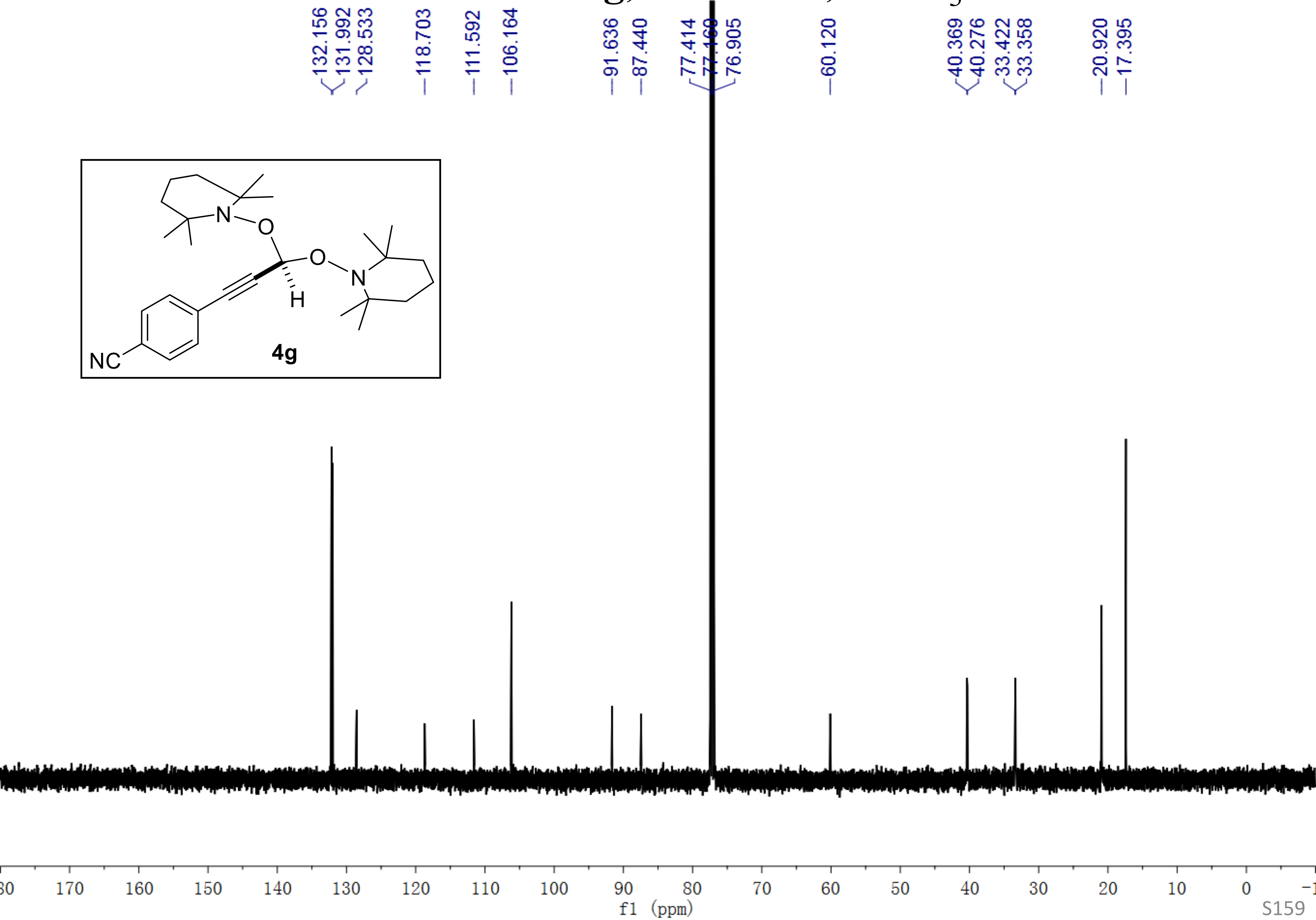
^{13}C NMR of **4f**, 151 MHz, $CDCl_3$



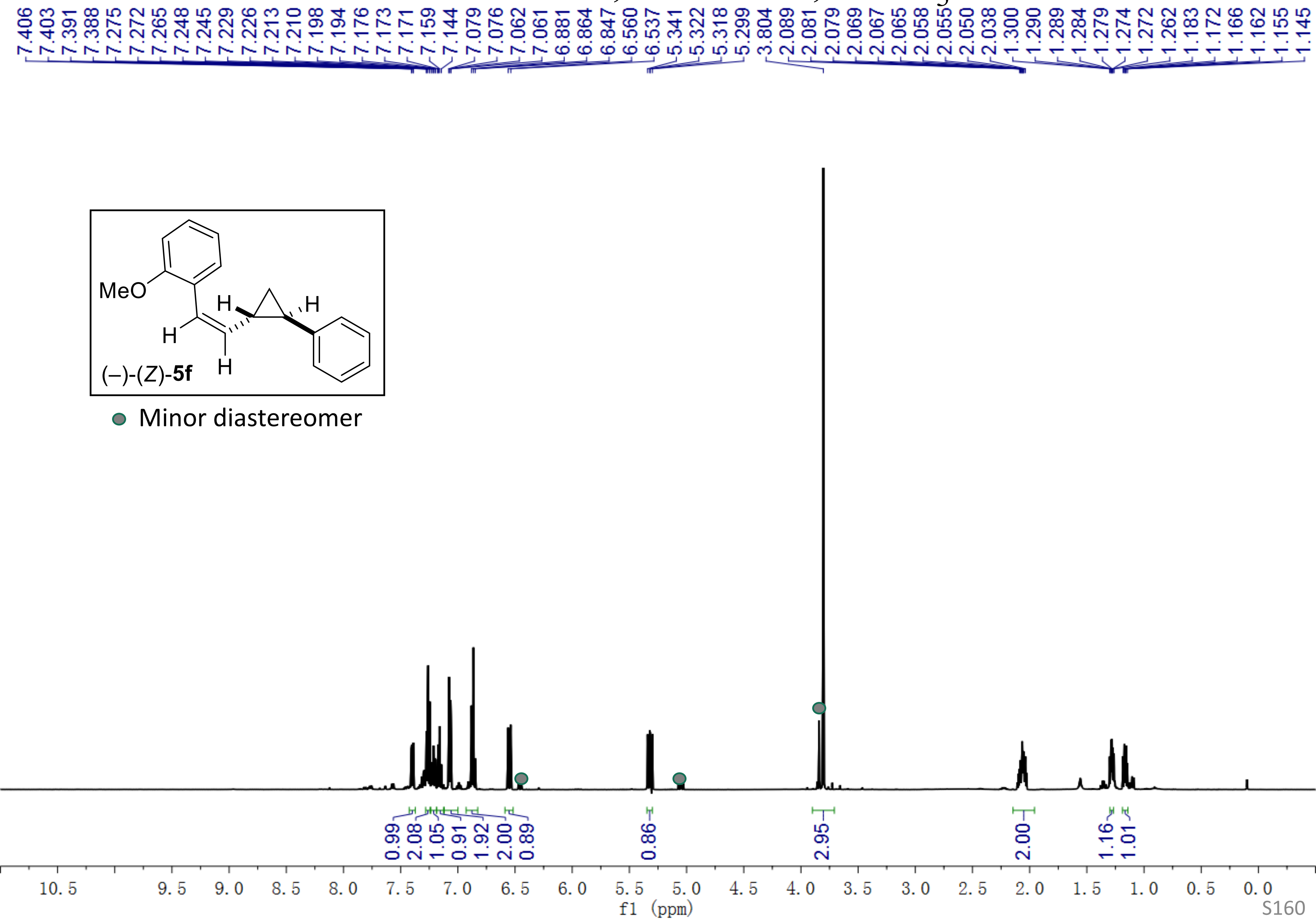
^{1}H NMR of **4g**, 500 MHz, $CDCl_3$



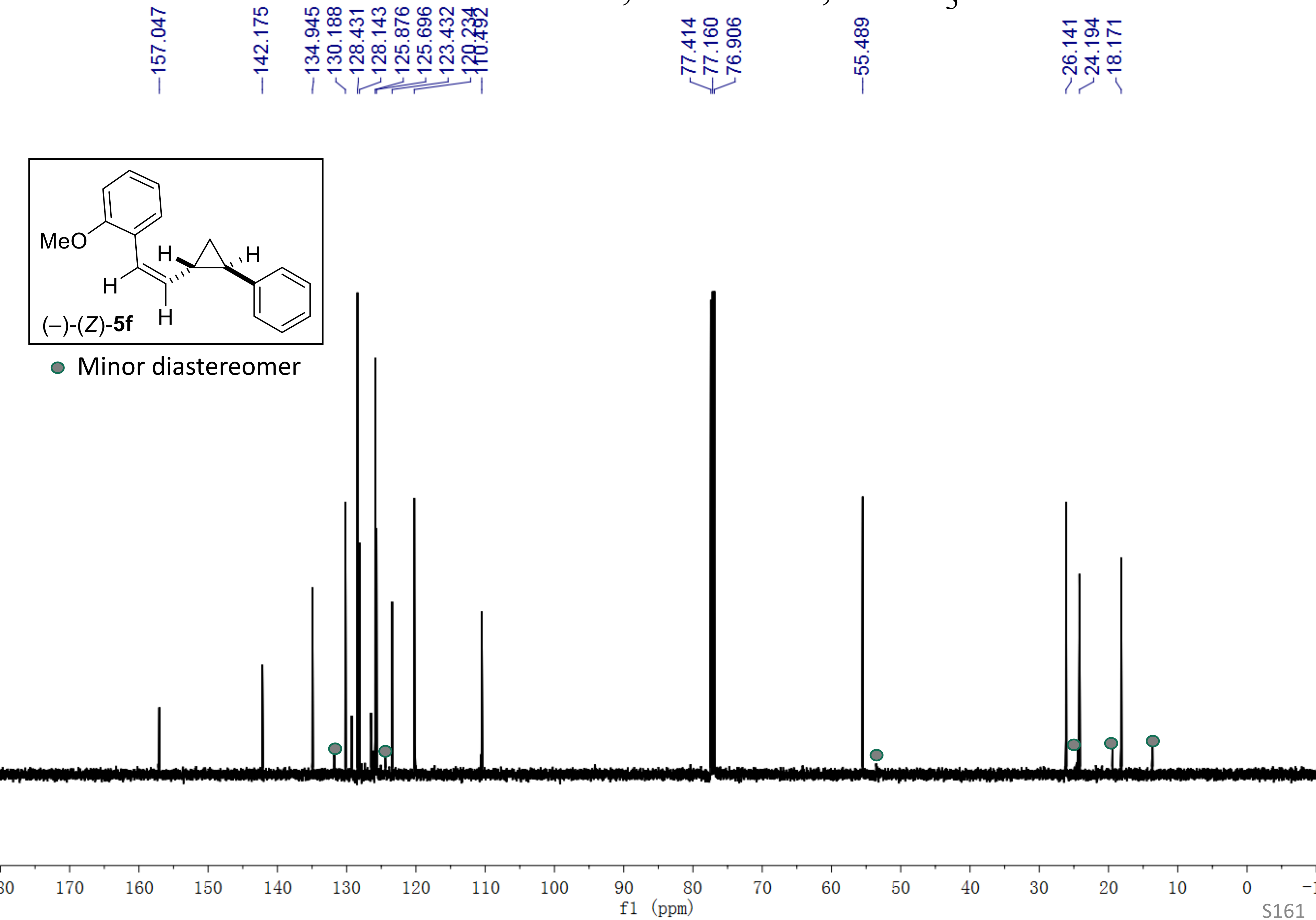
^{13}C NMR of **4g**, 126 MHz, $CDCl_3$



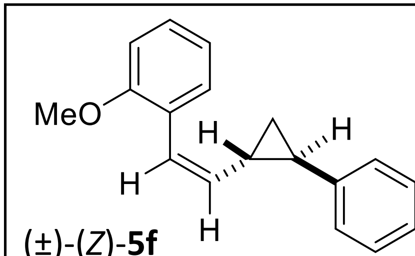
^{1}H NMR of **5f**, 500 MHz, $CDCl_3$



^{13}C NMR of **5f**, 126 MHz, $CDCl_3$

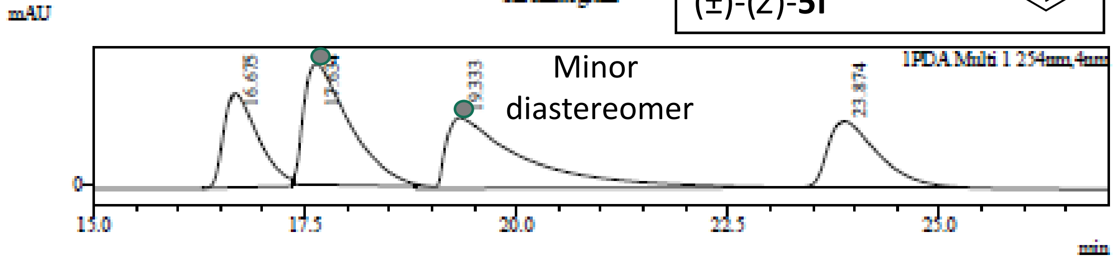


Data File : J0K-1000-IB-0%-1ML.lcd
Sample Name : J0K-1000-IB-0%-1ML
Sample ID : J0K-1000-IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm

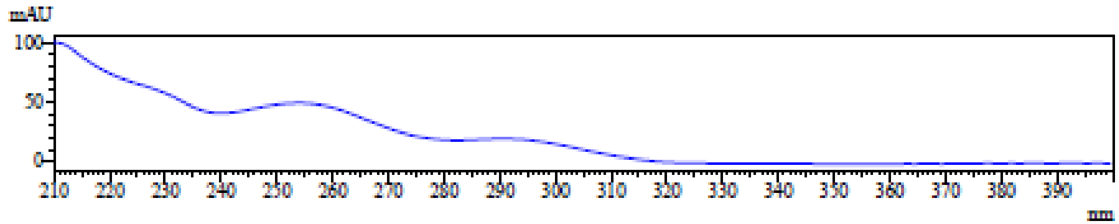


(±)-(*Z*)-**5f**

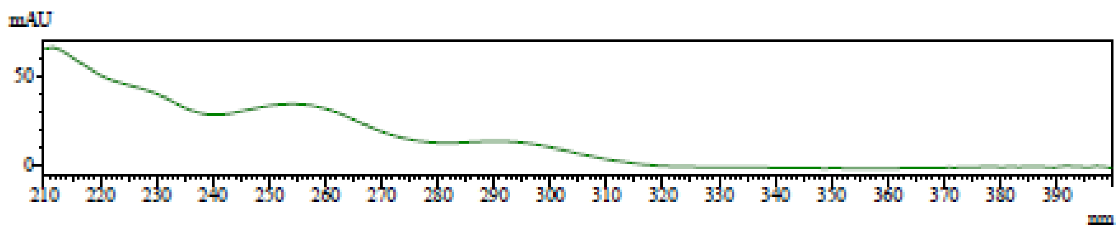
Chromatogram



UV Spectrum
Retention time = 16.675



UV Spectrum
Retention time = 23.874

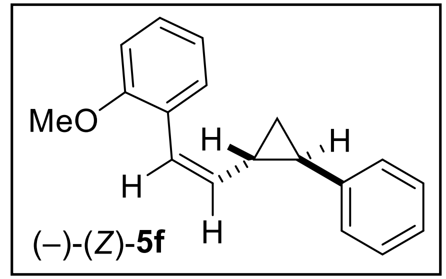


Peak Table

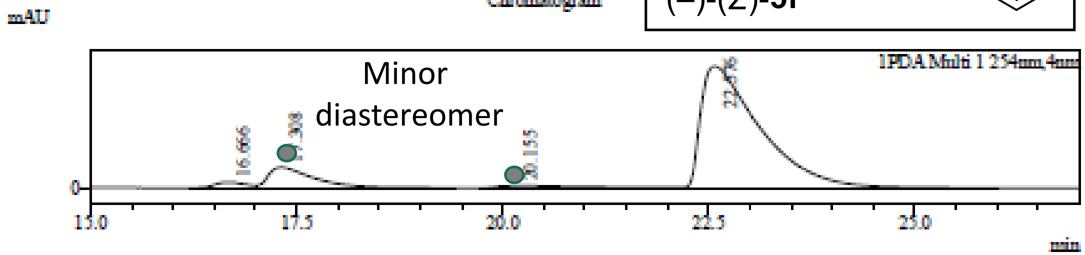
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.675	1401565	18.515
2	17.634	2380278	31.444
3	19.333	2366946	31.268
4	23.874	1421163	18.774
Total		7569951	100.000

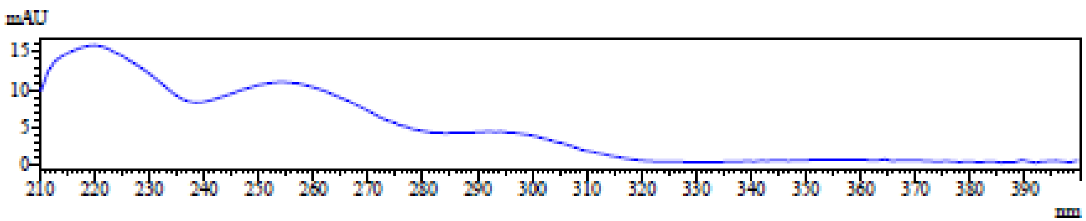
Data File	: J0K-1003-IB-0%-1ML-6.lcd
Sample Name	: J0K-1003-IB-0%-1ML-5
Sample ID	: J0K-1003-IB-0%-1ML-5
Method File	: J0K-0%--45min-1ml.lcm



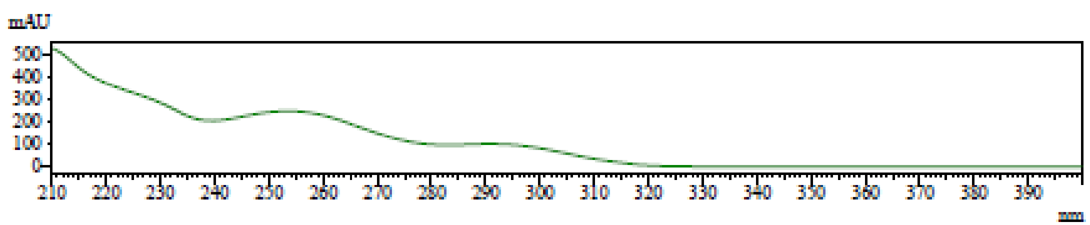
(–)-(Z)-**5f**



UV Spectrum
Retention time = 16.666



UV Spectrum
Retention time = 22.576

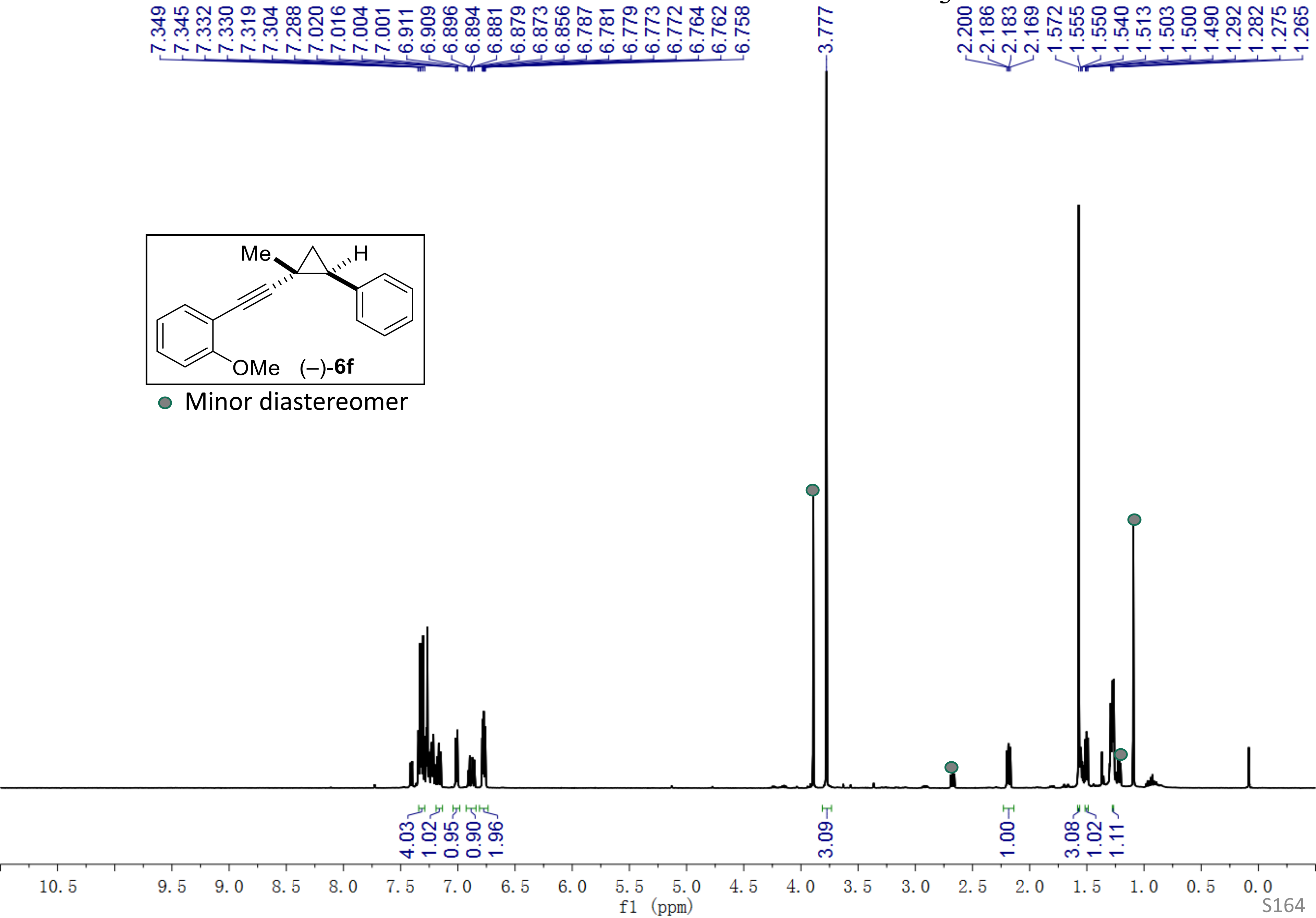


Peak Table

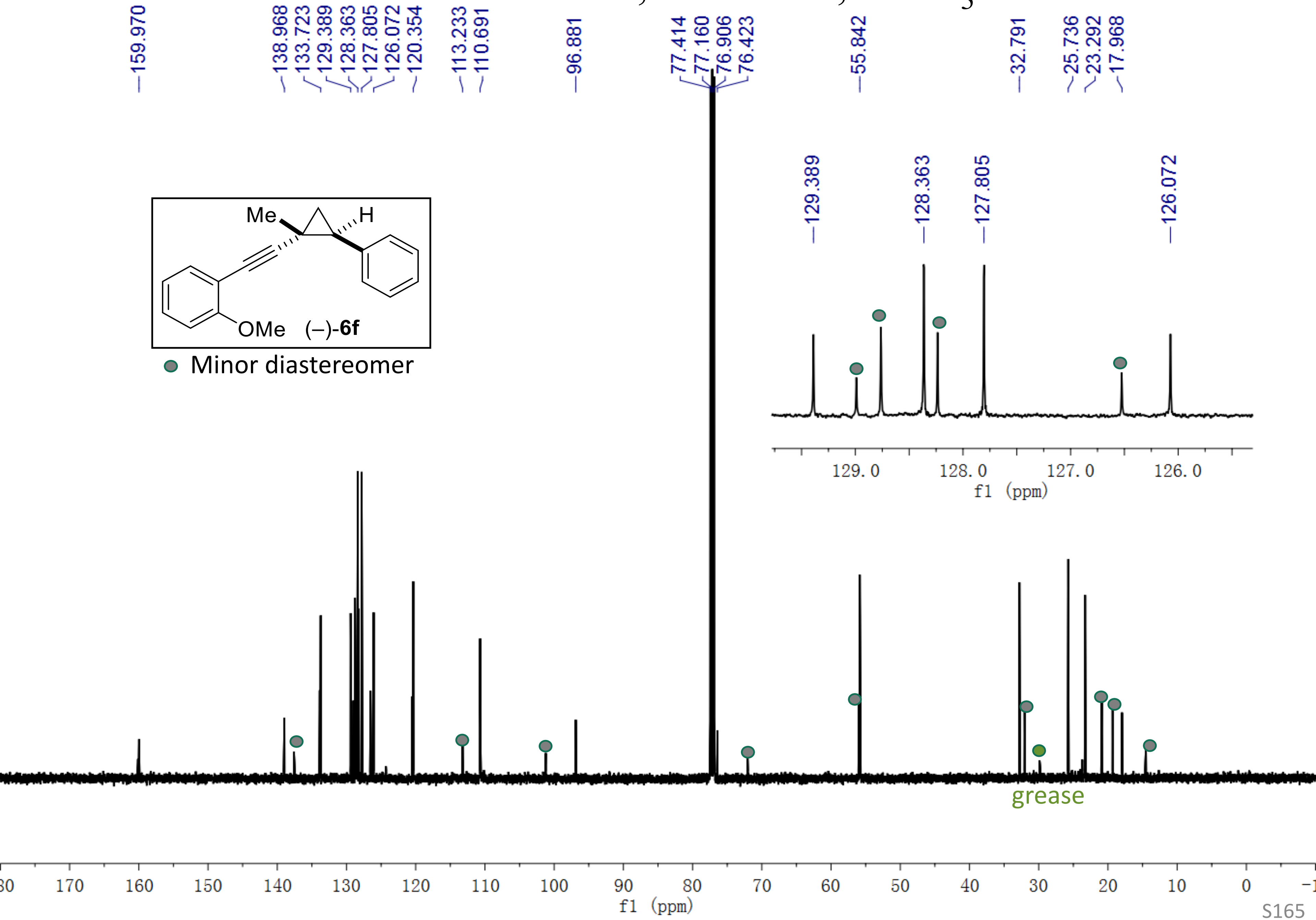
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.666	288690	1.983
2	17.308	1599163	10.982
3	20.155	311844	2.142
4	22.576	12362128	84.894
Total		14561825	100.000

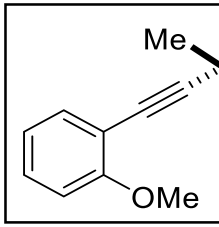
^{1}H NMR of **6f**, 500 MHz, $CDCl_3$



^{13}C NMR of **6f**, 126 MHz, $CDCl_3$

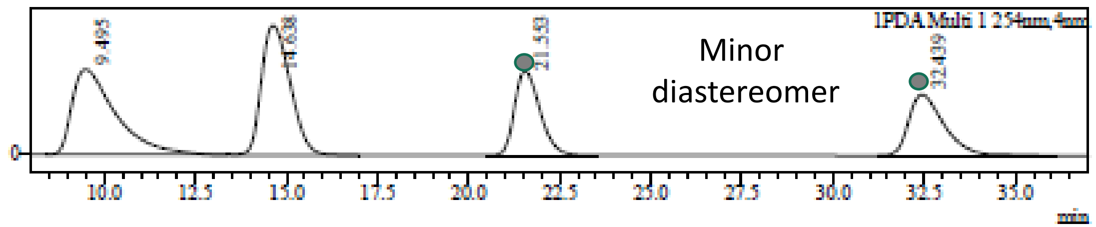


Data File : J0K-1538-ODH--0.3%-1ML.lcd
Sample Name : J0K-1538-ODH--0.3%-1ML
Sample ID : J0K-1538-ODH--0.3%-1ML
Method File : J0K-0.3%--45min-1ml.lcm

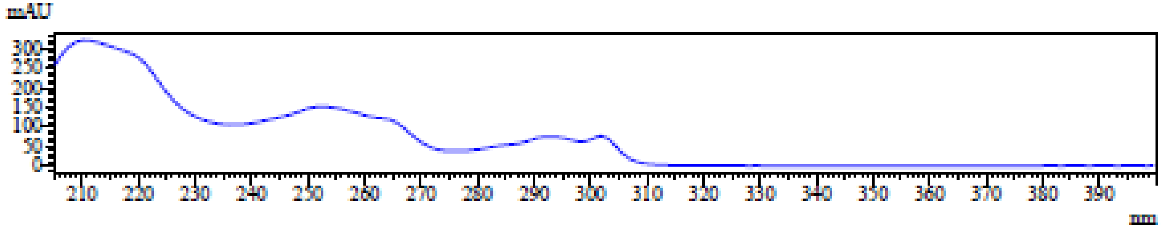


(±)-**6f**

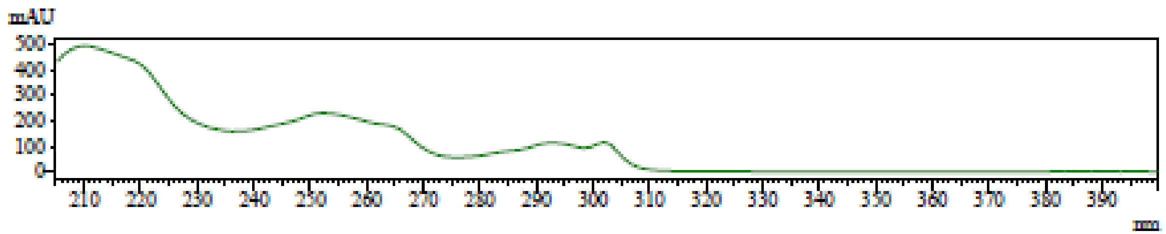
Chromatogram



UV Spectrum
Retention time = 9.495



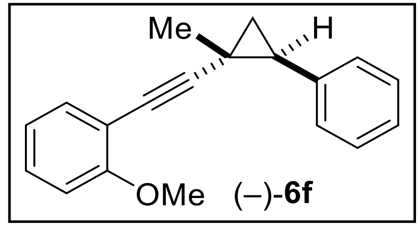
UV Spectrum
Retention time = 14.638



Peak Table

PDA Ch1 254nm

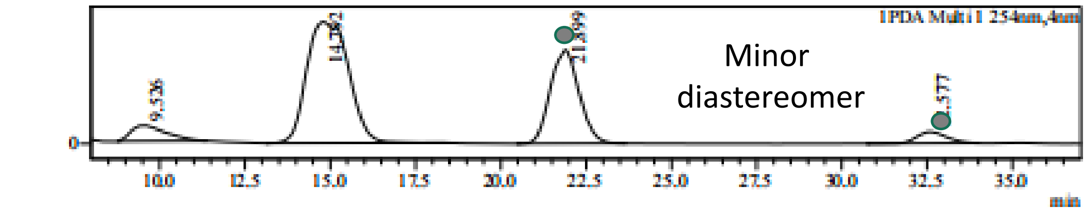
Peak#	Ret. Time	Area	Area%
1	9.495	12369764	31.724
2	14.638	12353166	31.682
3	21.553	7090460	18.185
4	32.439	7178261	18.410
Total		38991652	100.000



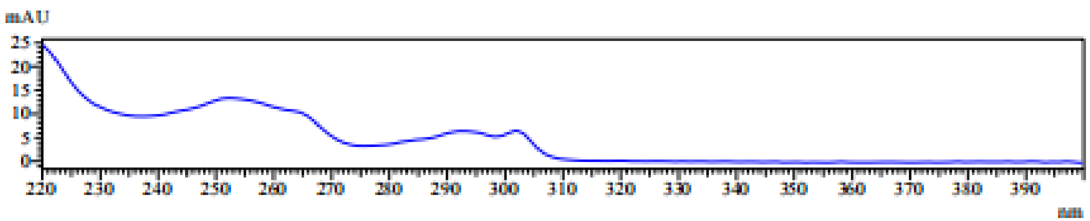
(–)-**6f**

Data File	: J0K-1539-ODH--0.3%-1ML.lcd
Sample Name	: J0K-1539-ODH--0.3%-1ML
Sample ID	: J0K-1539-ODH--0.3%-1ML
Method File	: J0K-0.3%--45min-1ml.lcm

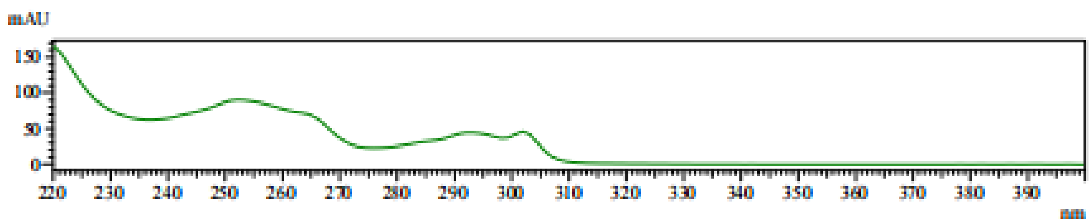
Chromatogram



UV Spectrum
Retention time = 9.526



UV Spectrum
Retention time = 14.792

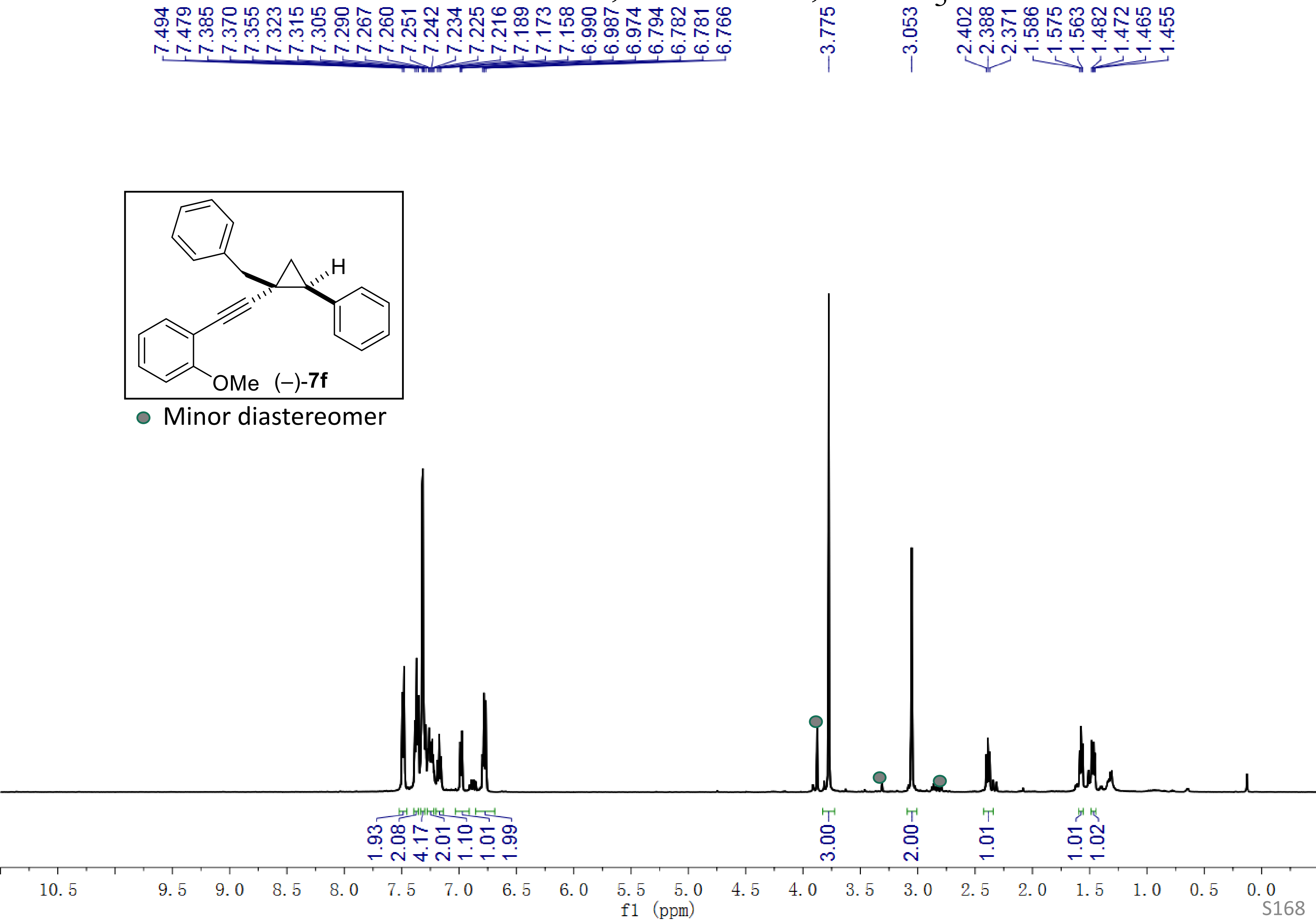


Peak Table

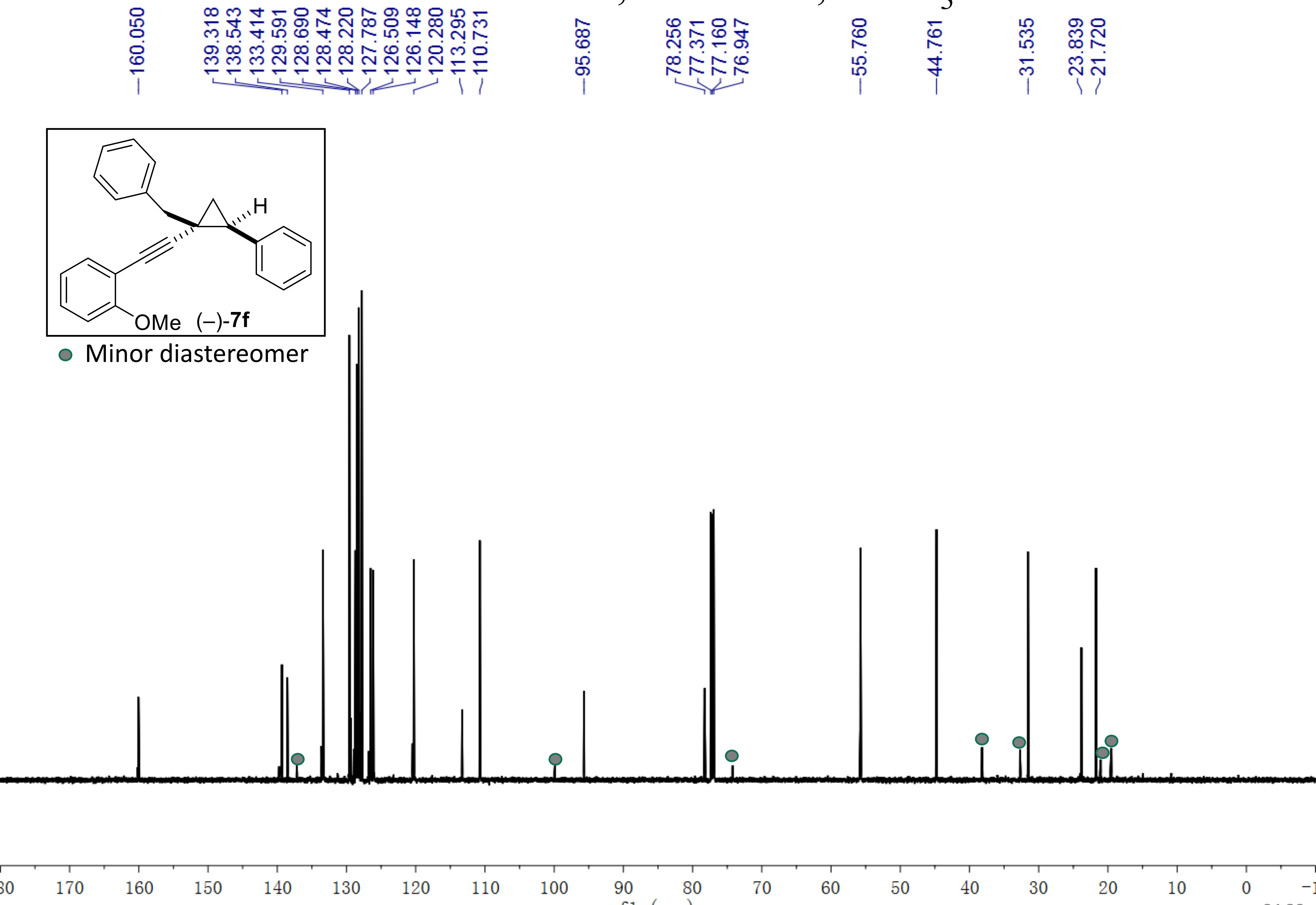
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.526	793506	6.221
2	14.792	7495637	58.764
3	21.899	3969097	31.117
4	32.577	497335	3.899
Total		12755575	100.000

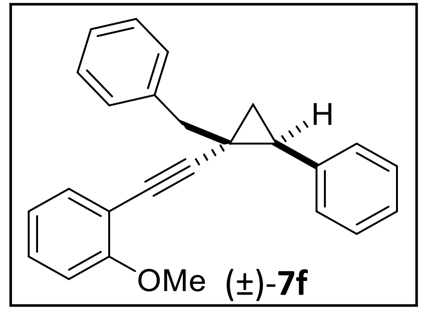
[1]H NMR of **7f**, 600 MHz, $CDCl_3$

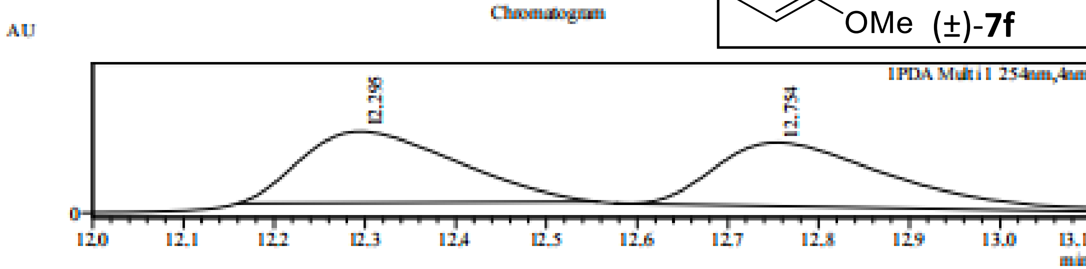


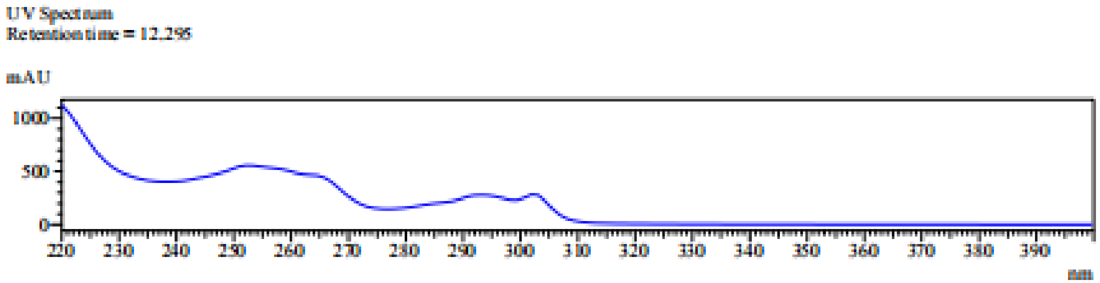
^{13}C NMR of **7f**, 151 MHz, $CDCl_3$

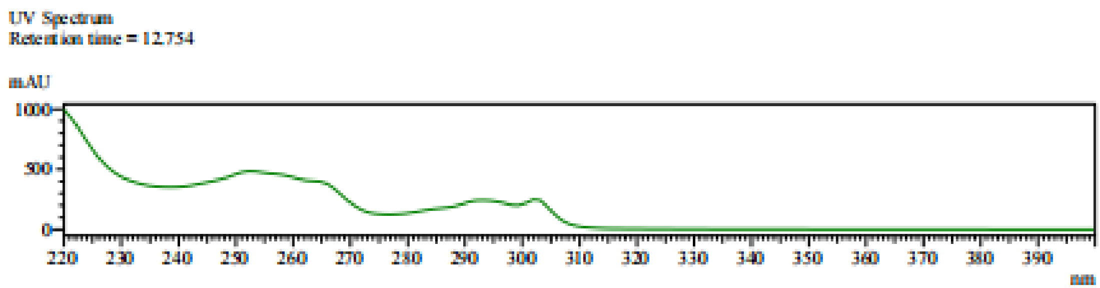


Data File : J0K-1476-IA-NEW--0.5%-0.5Ml.lcd
Sample Name : J0K-1476-IA-NEW--0.5%-0.5Ml
Sample ID : J0K-1476-IA-NEW--0.5%-0.5Ml
Method File : J0K-0.5%--35min-0.5ml.lcm





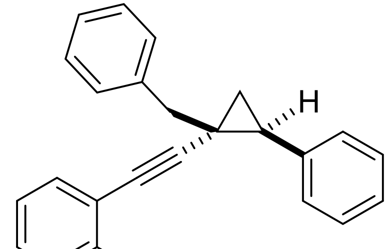




Peak Table

PDA Ch1 254nm

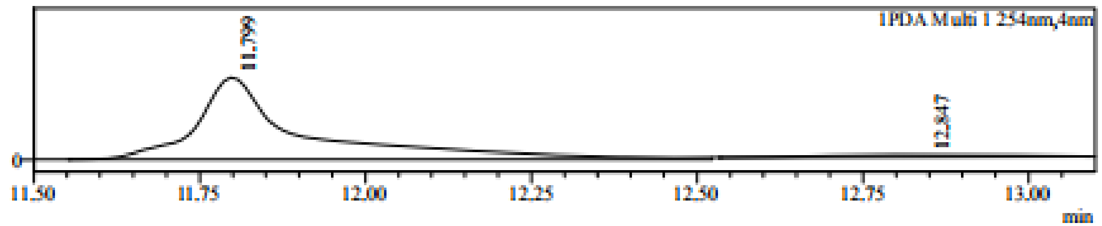
Peak#	Ret. Time	Area	Area%
1	12.295	5702969	50.172
2	12.754	5663776	49.828
Total		11366745	100.000



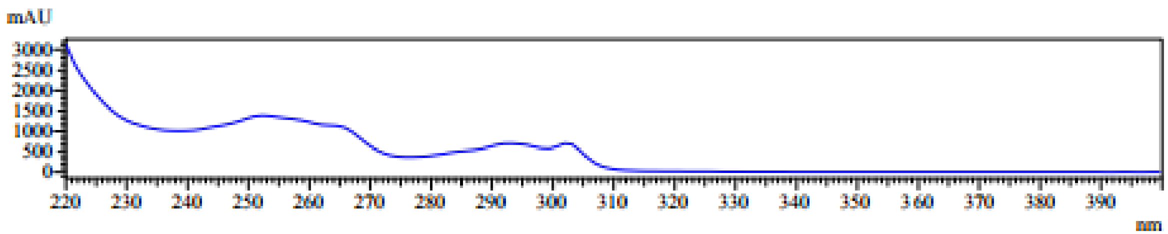
(–)-**7f**

Data File	: J0K-1462-IA-0.5%-0.5ML.lcd
Sample Name	: J0K-1462-IA-0.5%-0.5ML
Sample ID	: J0K-1462-IA-0.5%-0.5ML
Method File	: J0K-0.5%--35min-0.5ml.lcm

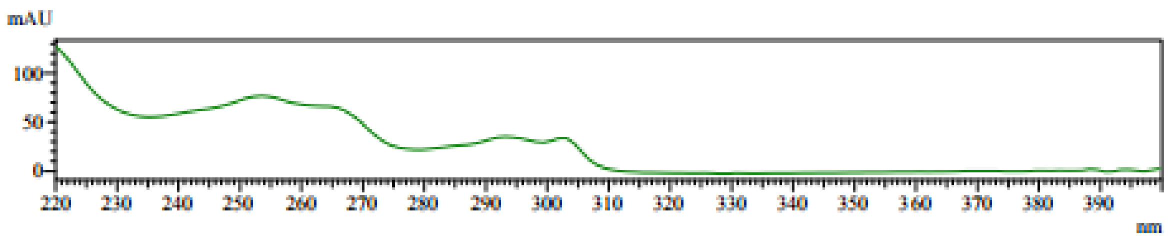
Chromatogram



UV Spectrum
Retention time = 11.799



U
Retention time = 12.847

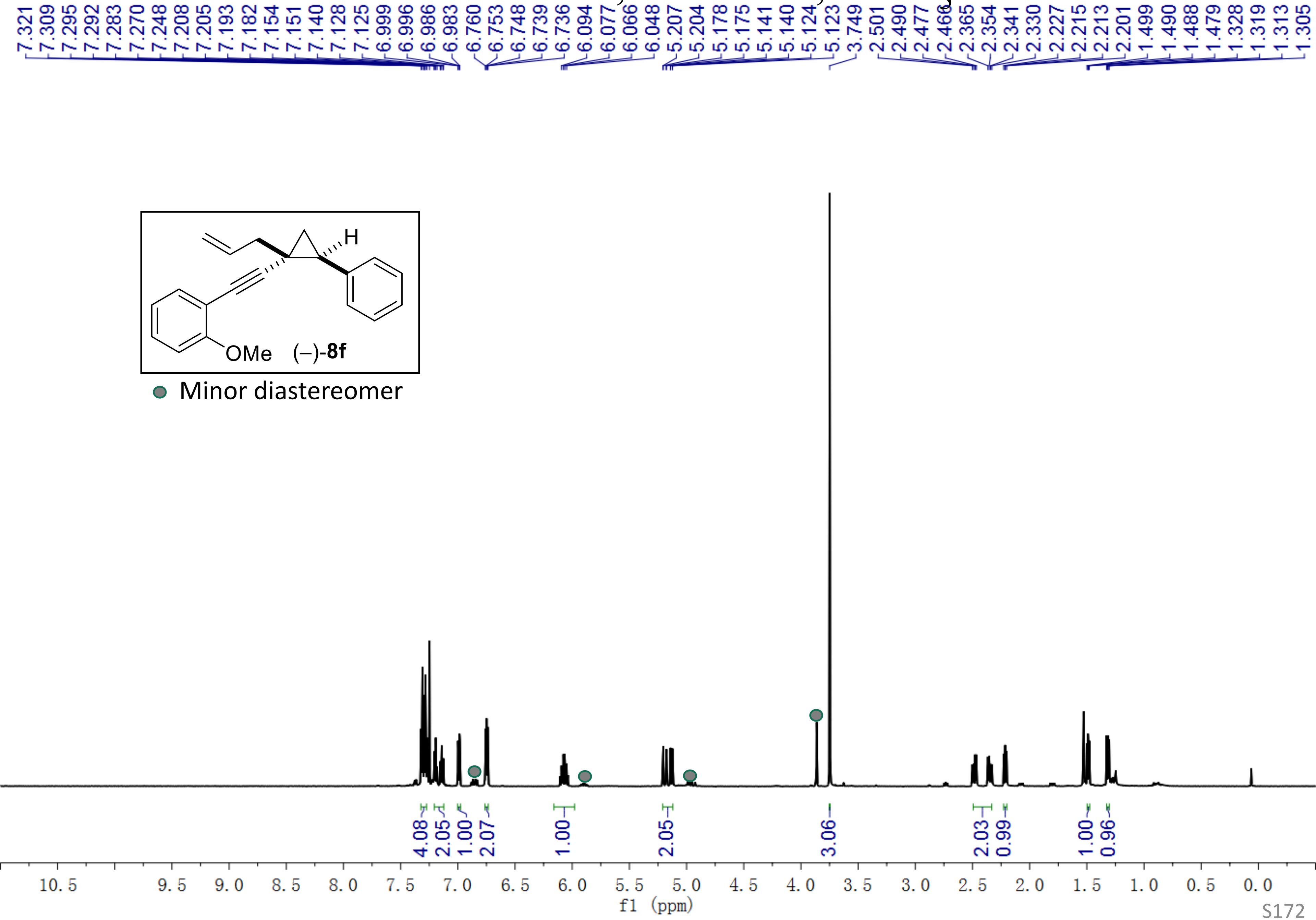


Peak Table

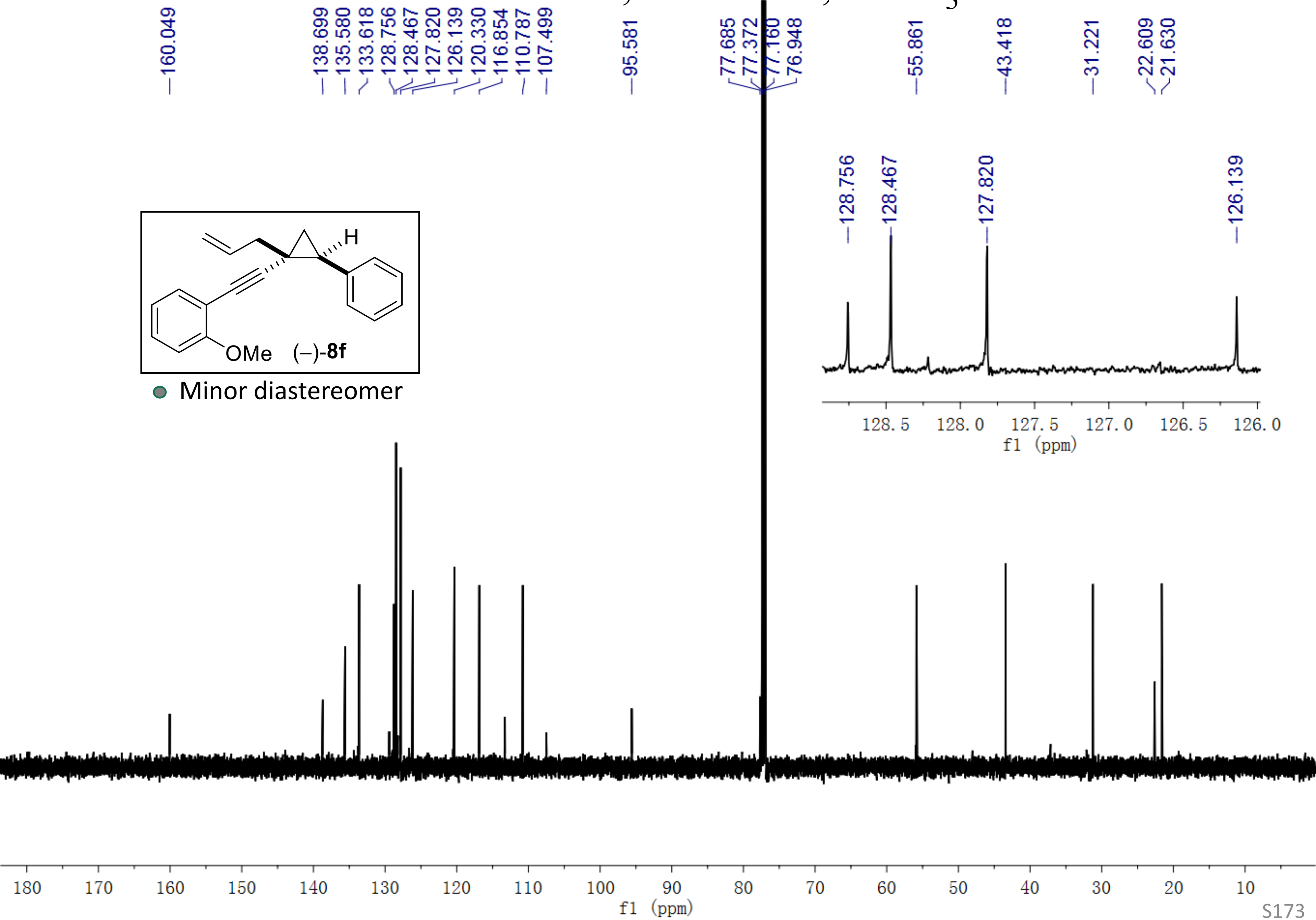
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.799	14758228	96.142
2	12.847	592161	3.858
Total		15350389	100.000

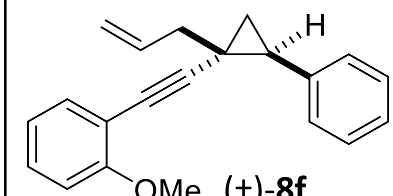
^{1}H NMR of **8f**, 500 MHz, $CDCl_3$



^{13}C NMR of **8f**, 126 MHz, $CDCl_3$

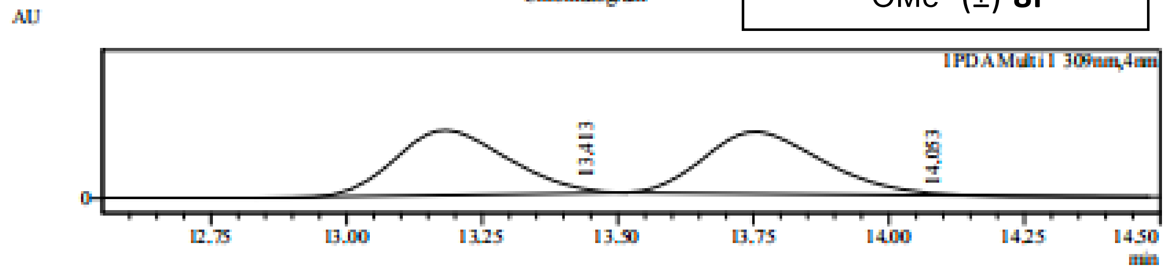


Data File	: J0K-1549-IB--0.2%-0.5ML-2.lcd
Sample Name	: J0K-1549-IB--0.2%-0.5ML-2
Sample ID	: J0K-1549-IB--0.2%-0.5ML-2
Method File	: J0K-0.2%--40min-0.5ml.lcm

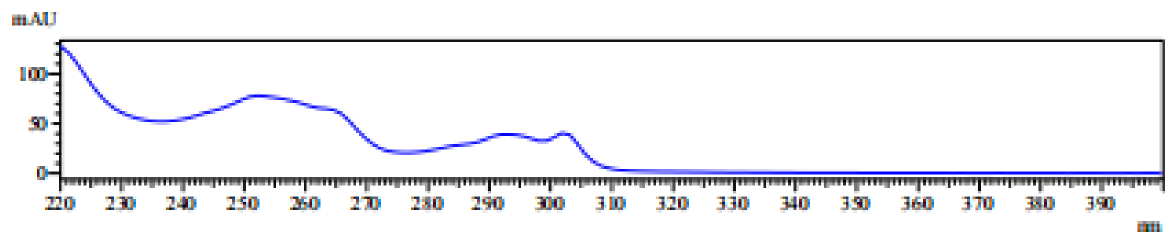


(±)-**8f**

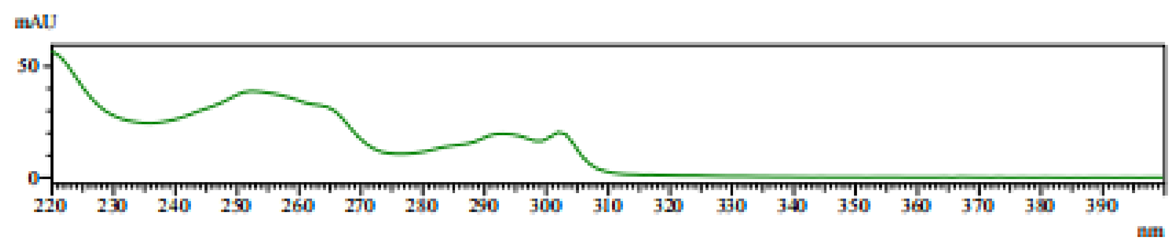
Chromatogram



UV Spectrum
Retention time = 13.413



UV Spectrum
Retention time = 14.053

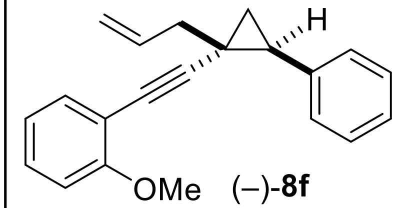


Peak Table

PDA Ch1 309nm

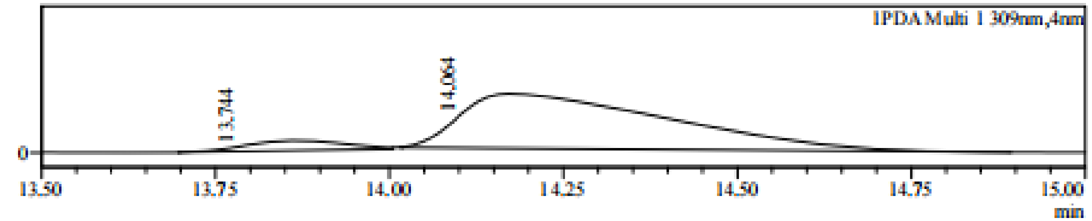
Peak#	Ret. Time	Area	Area%
1	13.413	631887	49.937
2	14.053	633470	50.063
Total		1265357	100.000

Data File	: J0K-1560-IB--0.2%-0.5ML-3.lcd
Sample Name	: J0K-1560-IB--0.2%-0.5ML-3
Sample ID	: J0K-1560-IB--0.2%-0.5ML-3
Method File	: J0K-0.2%--40min-0.5ml.lcm

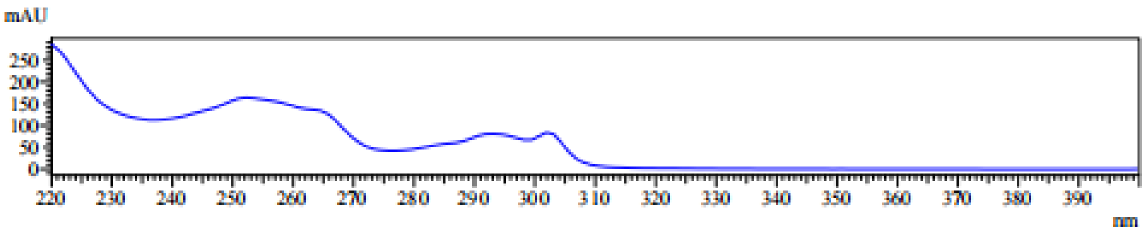


(–)-**8f**

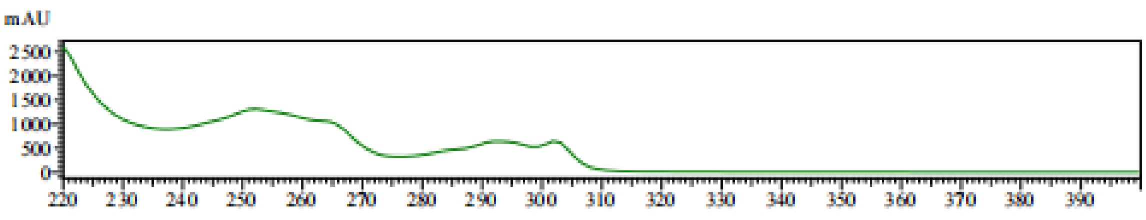
Chromatogram



UV Spectrum
Retention time = 13.744



UV Spectrum
Retention time = 14.064

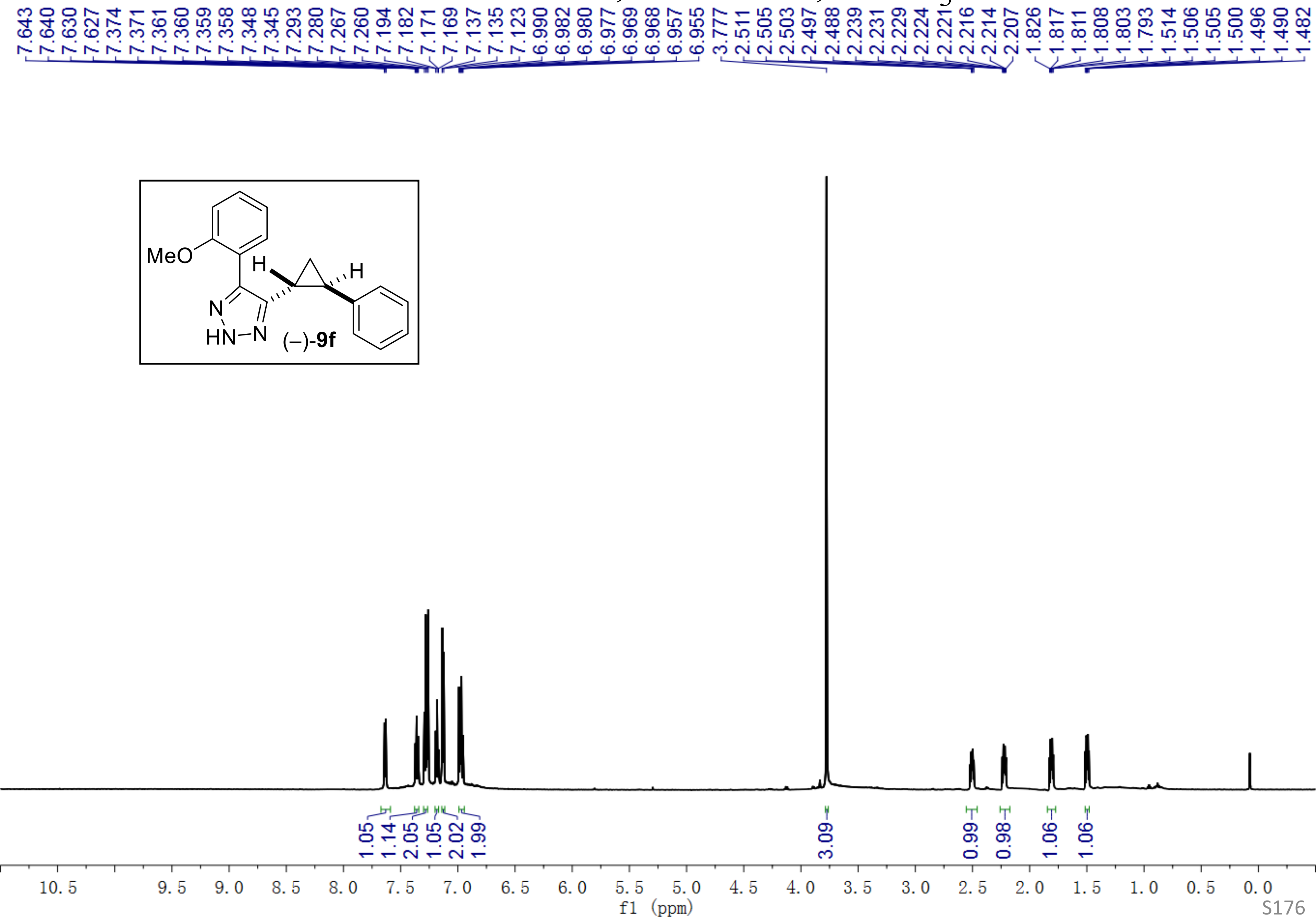


Peak Table

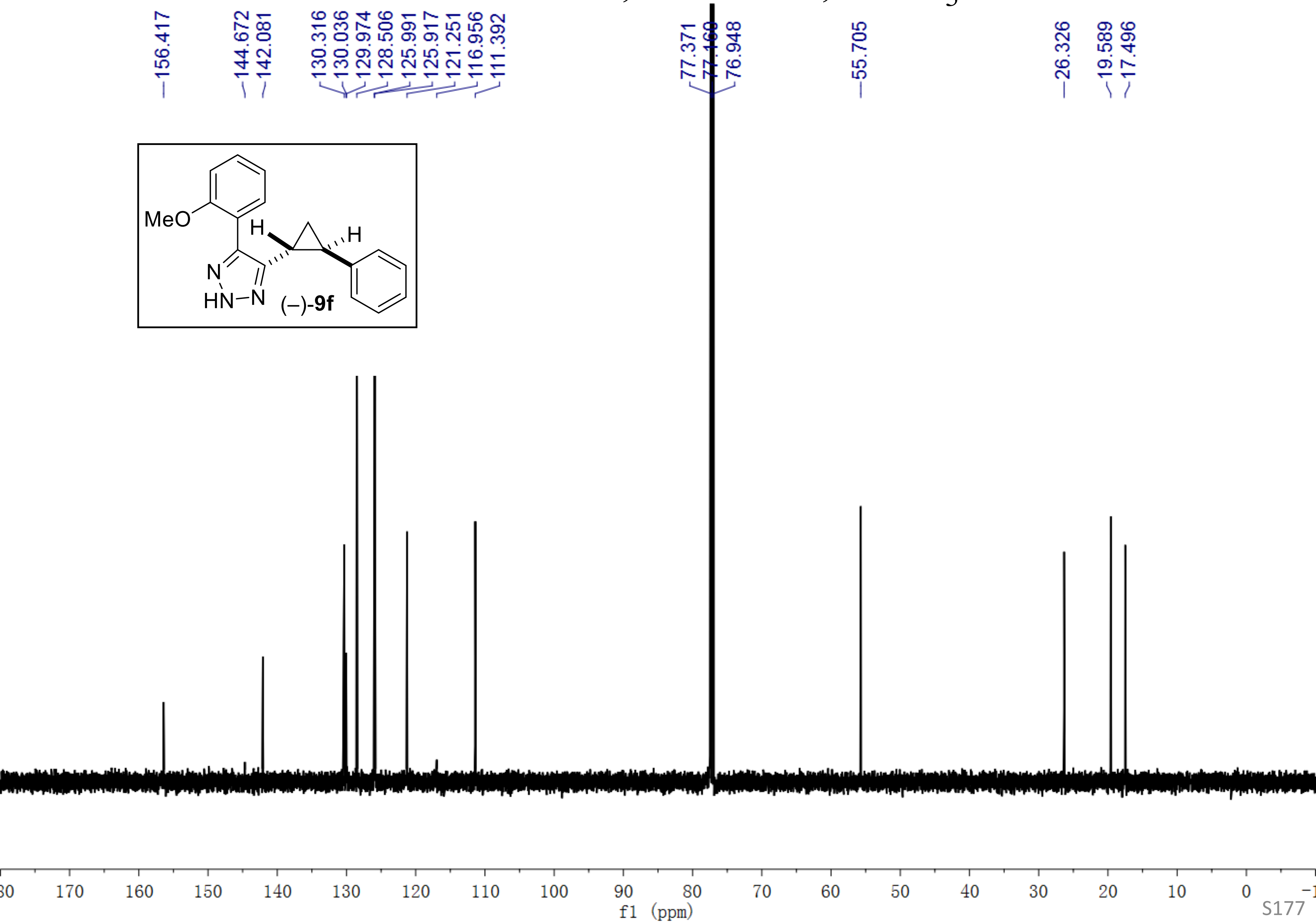
PDA Ch1 309nm

Peak#	Ret. Time	Area	Area%
1	13.744	673967	8.053
2	14.064	7695259	91.947
Total		8369226	100.000

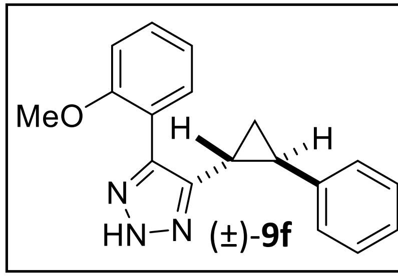
^{1}H NMR of **9f**, 600 MHz, $CDCl_3$



^{13}C NMR of **9f**, 151 MHz, $CDCl_3$

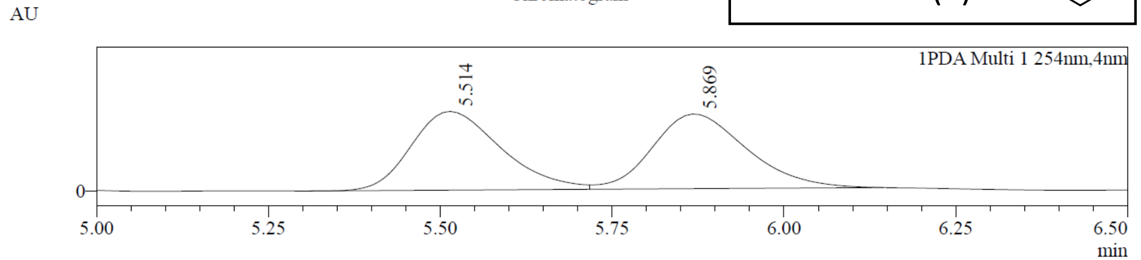


Data File : J0K-1852--IB-15%-1ML-3.lcd
Sample Name : J0K-1852--IB-15%-1ML-3
Sample ID : J0K-1852--IB-15%-1ML-3
Method File : J0K-15%--40min-1ml.lcm

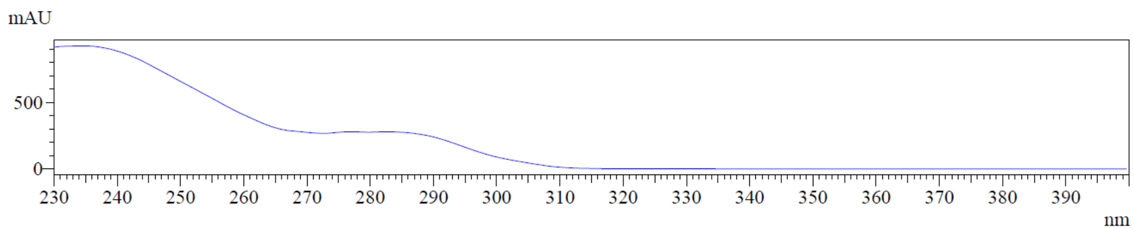


(±)-9f

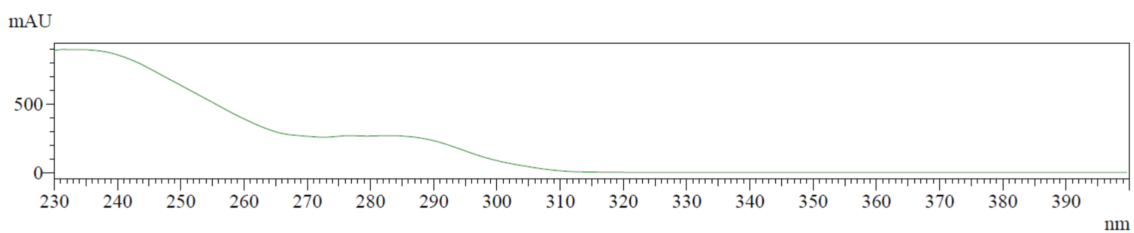
Chromatogram



UV Spectrum
Retention time = 5.514



UV Spectrum
Retention time = 5.869

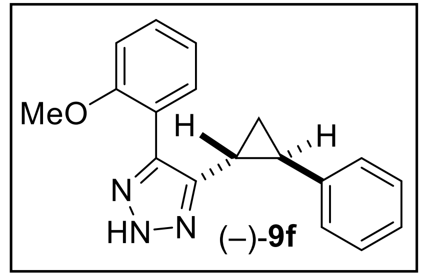


Peak Table

PDA Ch1 254nm

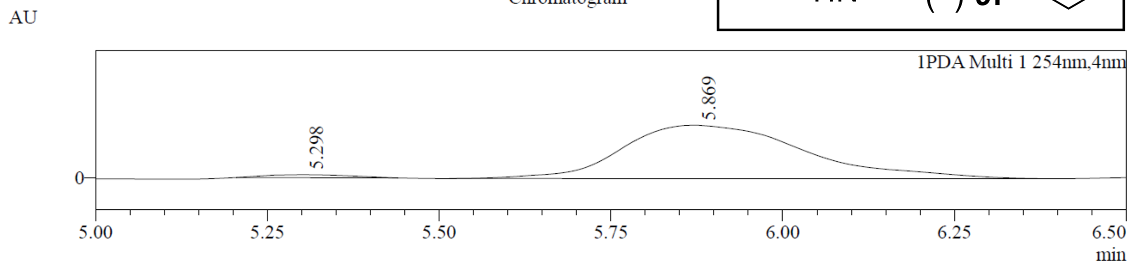
Peak#	Ret. Time	Area	Area%
1	5.514	4977612	50.153
2	5.869	4947185	49.847
Total		9924797	100.000

Data File	: J0K-1853--IB-15%-1ML.lcd
Sample Name	: J0K-1853--IB-15%-1ML
Sample ID	: J0K-1853--IB-15%-1ML
Method File	: J0K-15%--40min-1ml.lcm

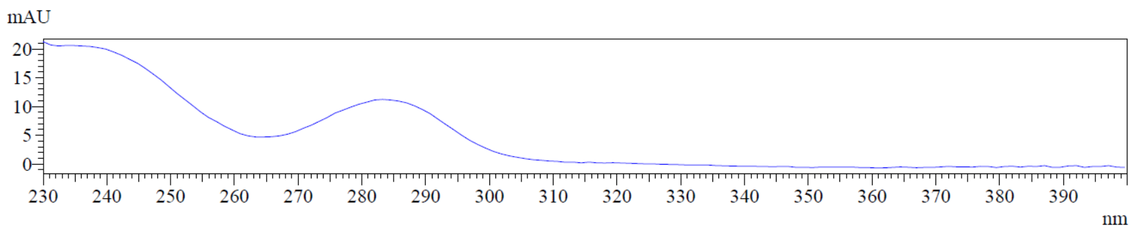


(–)-9f

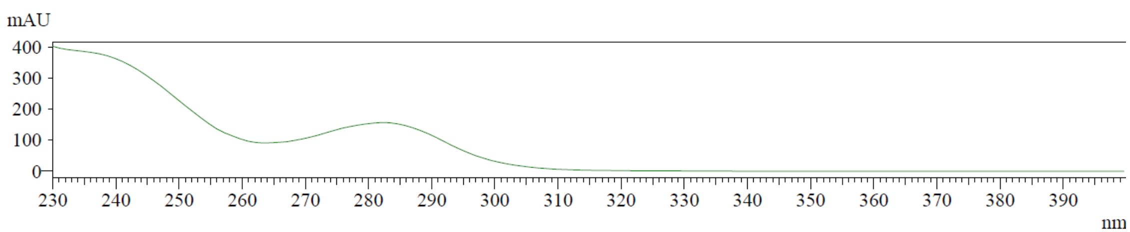
Chromatogram



UV Spectrum
Retention time = 5.298



UV Spectrum
Retention time = 5.869

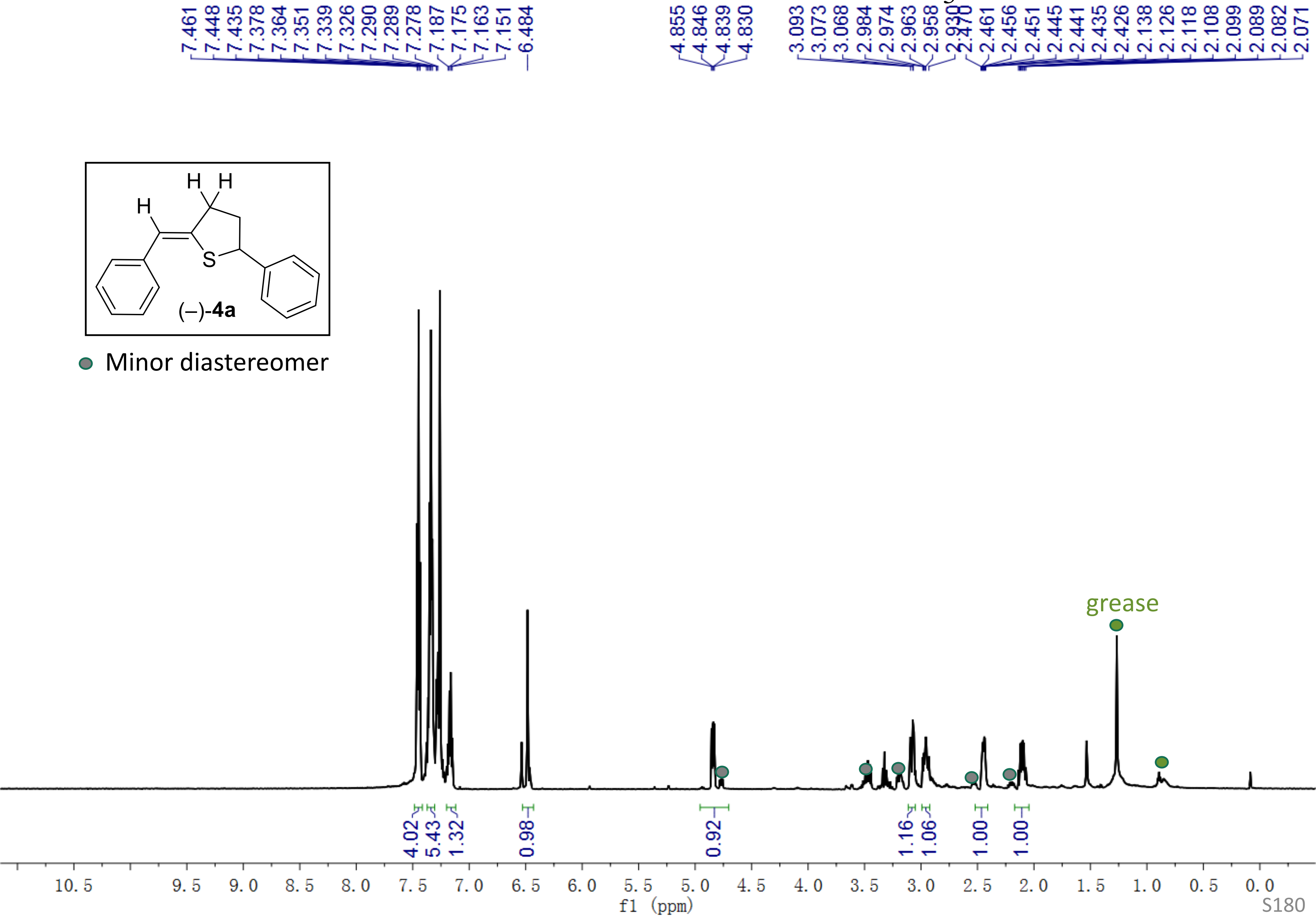


Peak Table

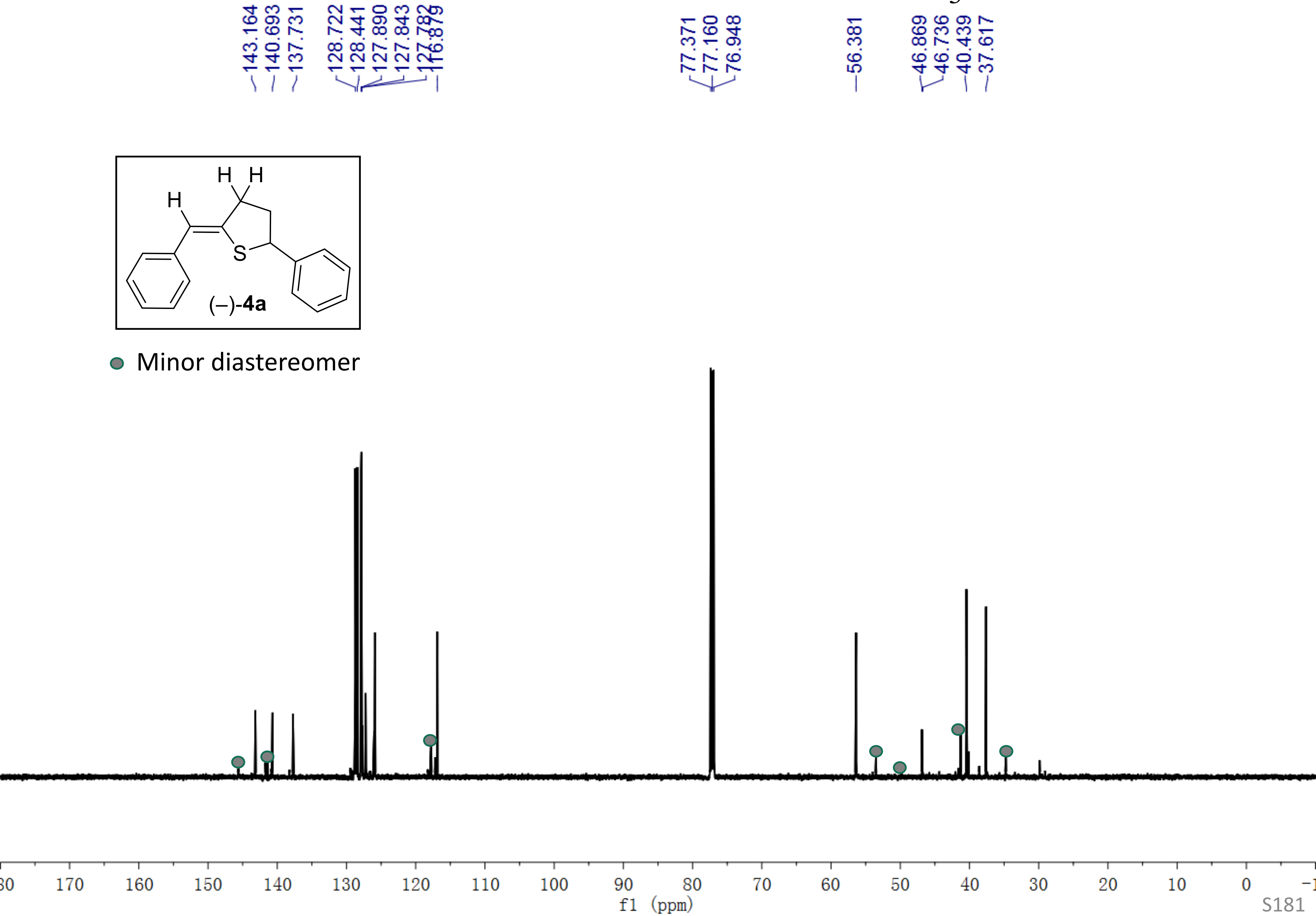
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.298	80413	2.527
2	5.869	3101211	97.473
Total		3181624	100.000

^{1}H NMR of **4a**, 600 MHz, $CDCl_3$

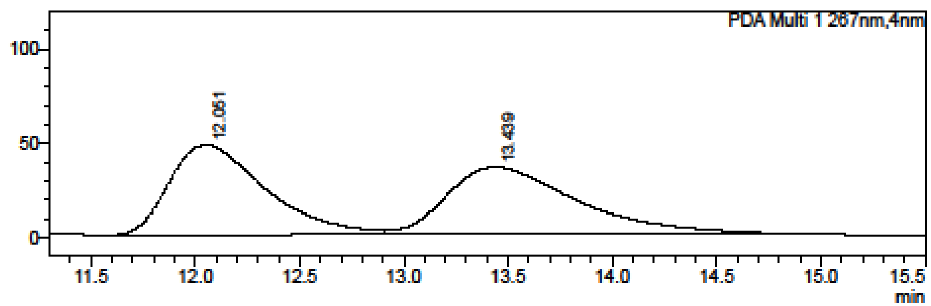


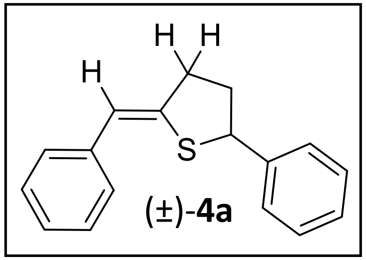
^{13}C NMR of **4a**, 151 MHz, $CDCl_3$



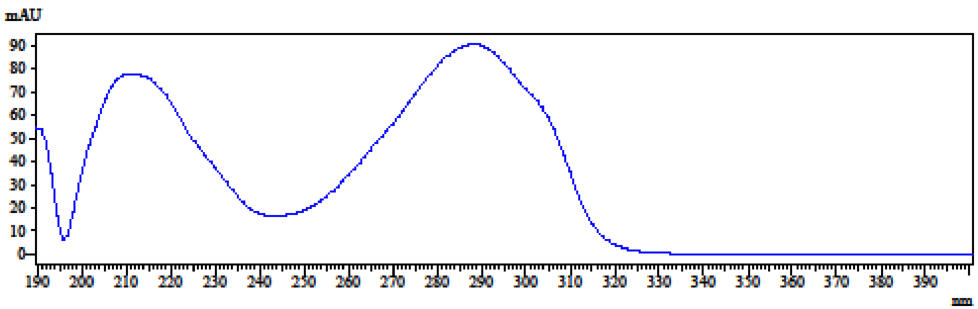
==== Shimadzu LabSolutions Analysis Report ====

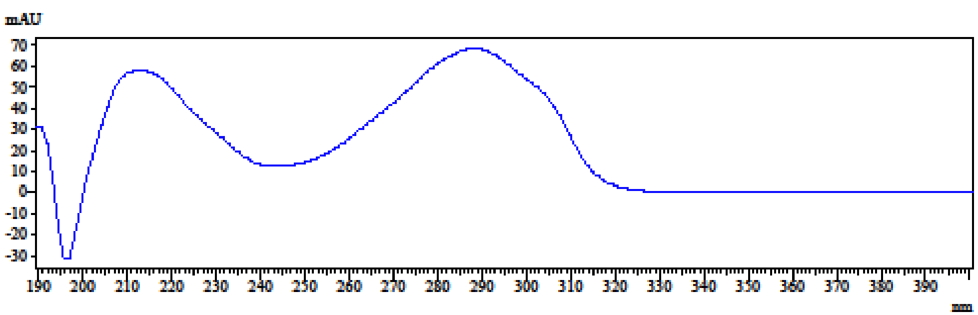
WCL1848-ID-0.1%0.8mL
WCL-0.1%-30min0.8mL.lcm





UV Spectrum





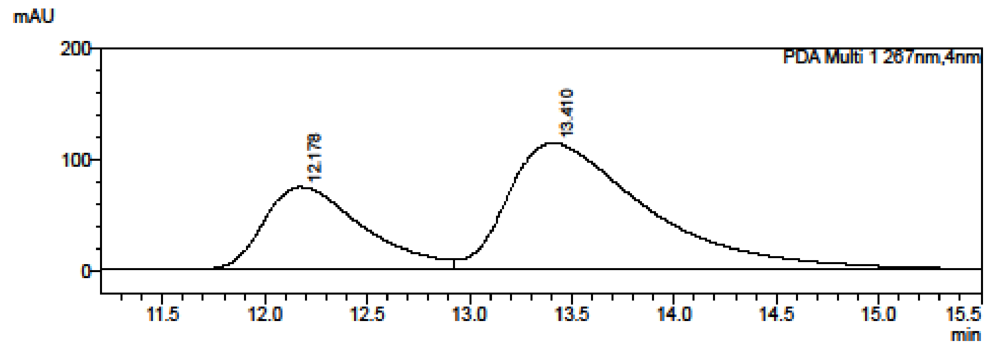
Peak Table

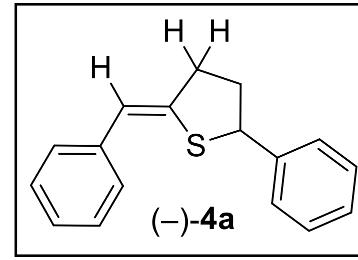
PDA Ch1 267nm

Peak#	Ret. Time	Area%
1	12.051	49.191
2	13.439	50.809
Total		100.000

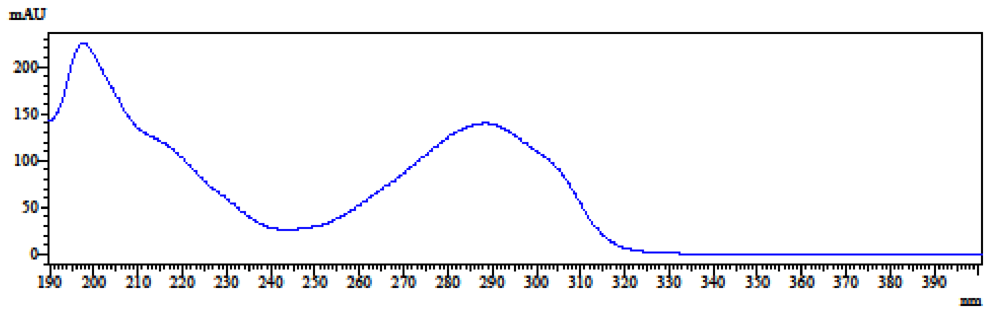
==== Shimadzu LabSolutions Analysis Report ====

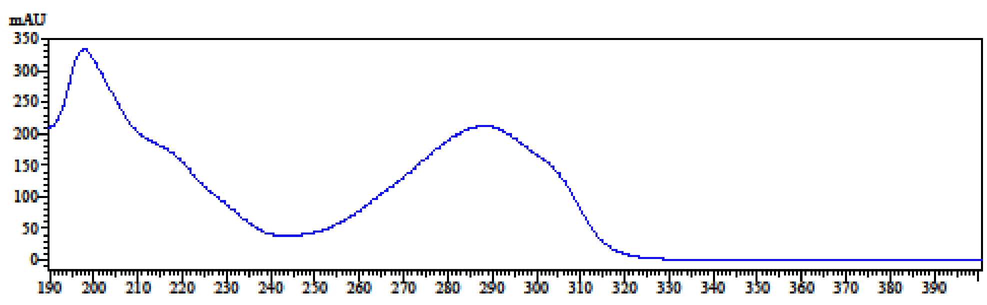
WCL1851-ID-0.1%0.8mL
WCL-0.1%-30min0.8mL.lcm





UV Spectrum





Peak Table

PDA Ch1 267nm

Peak#	Ret. Time	Area%
1	12.178	31.810
2	13.410	68.190
Total		100.000

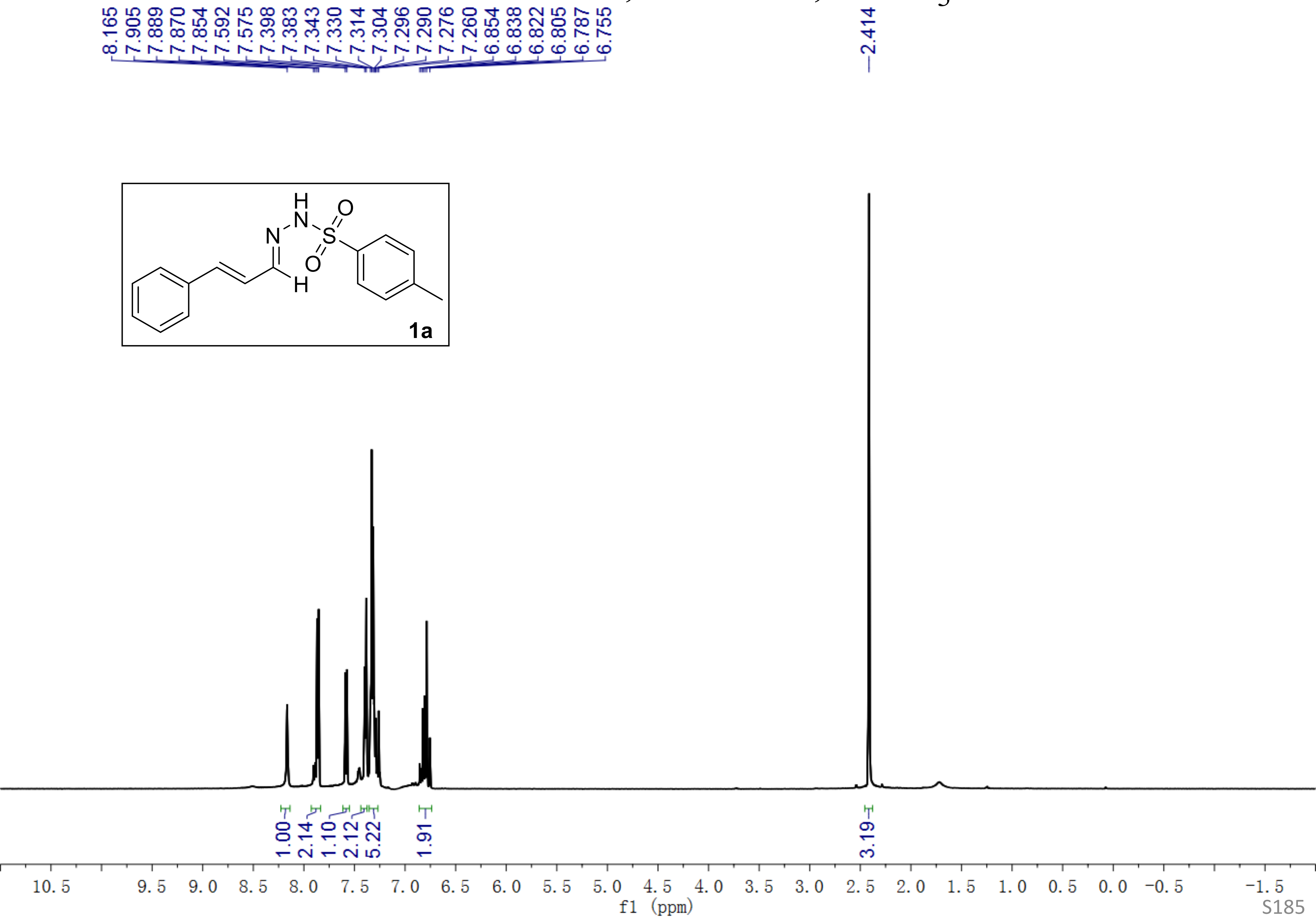
Spectral Data

for

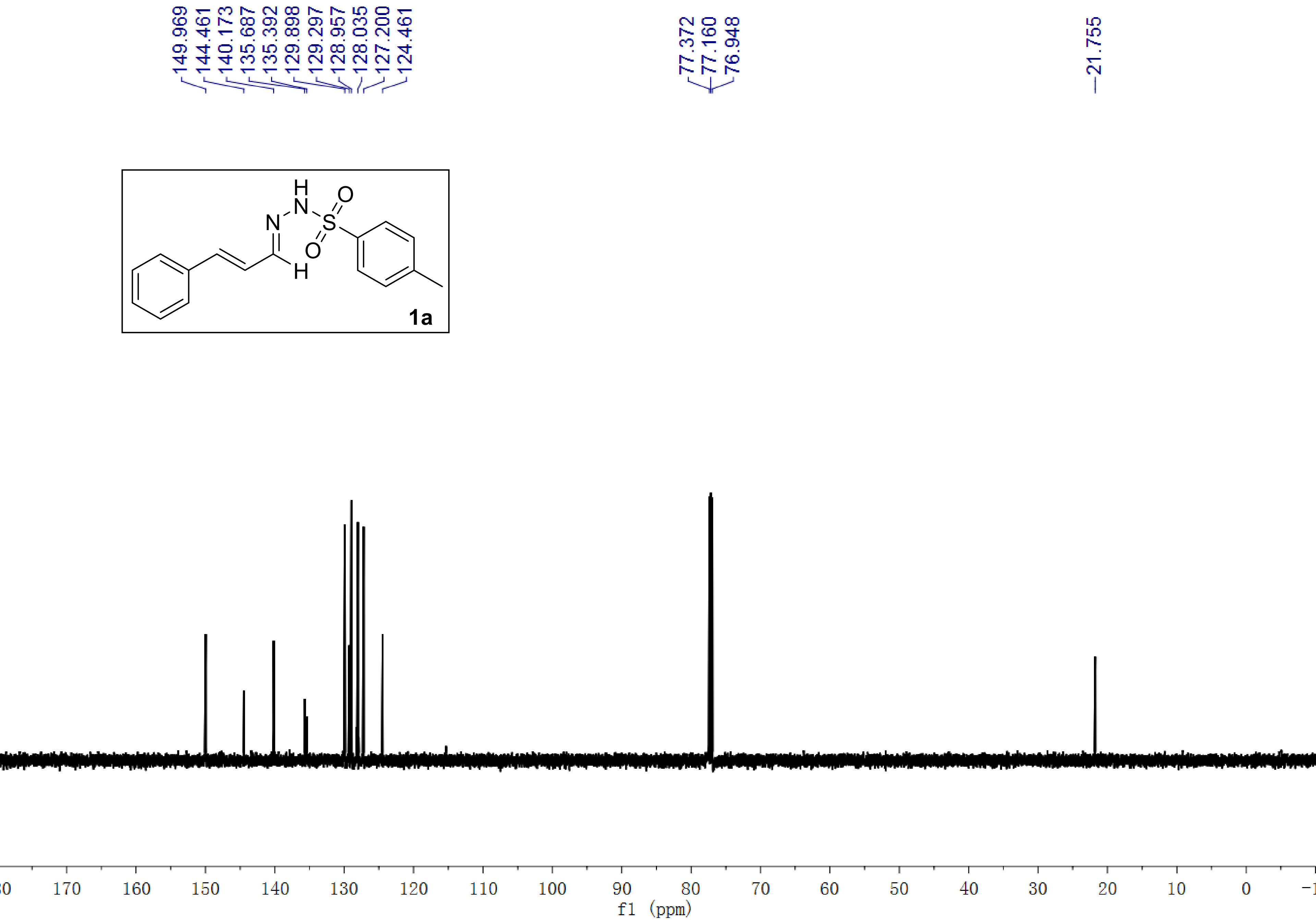
Chapter 3

Asymmetric Radical Process for Cyclopropanation of Alkenes with In Situ-Generated α-Vinyldiazomethanes

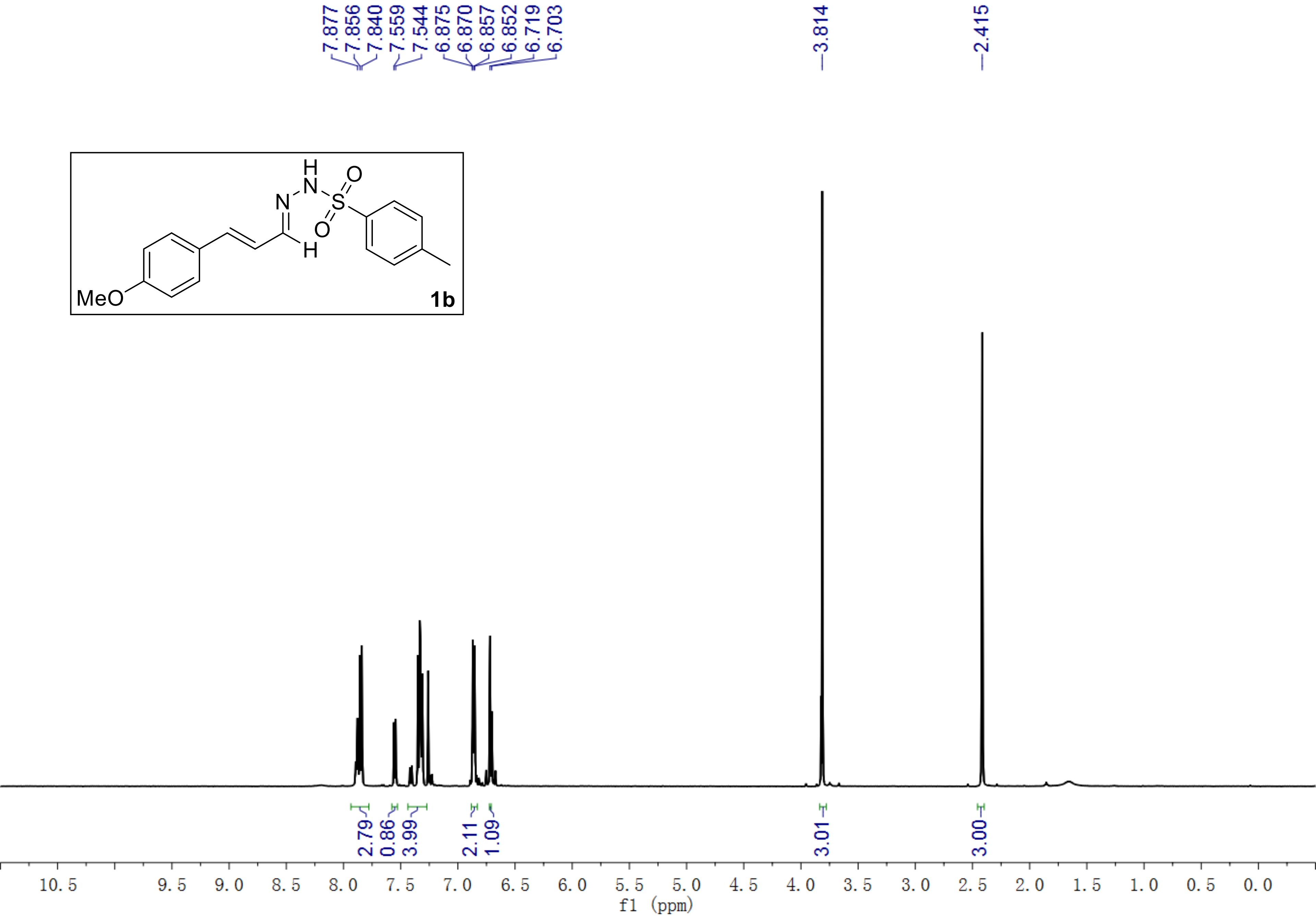
^{1}H NMR of **1a**, 500 MHz, $CDCl_3$



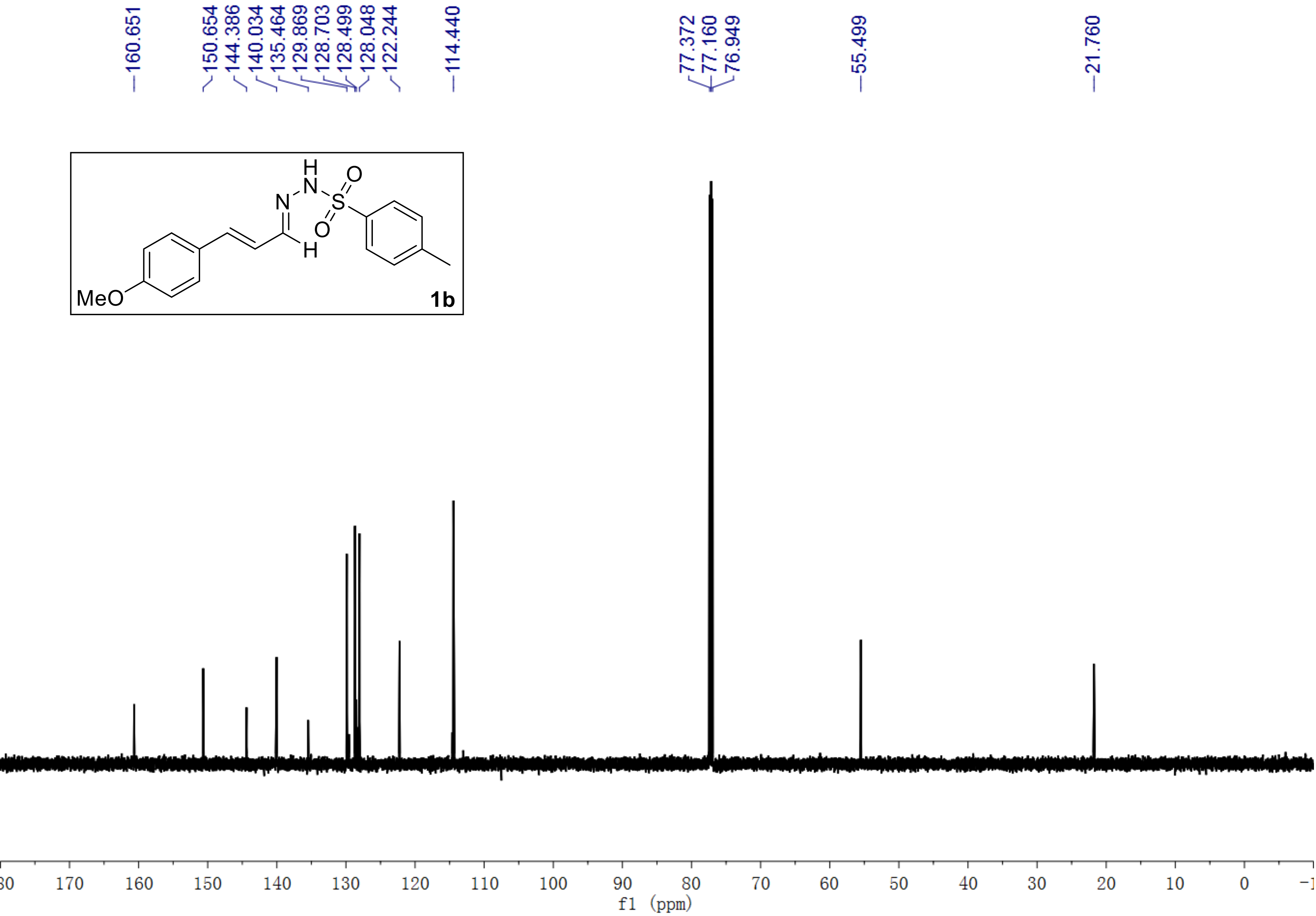
^{13}C NMR of **1a**, 151 MHz, $CDCl_3$



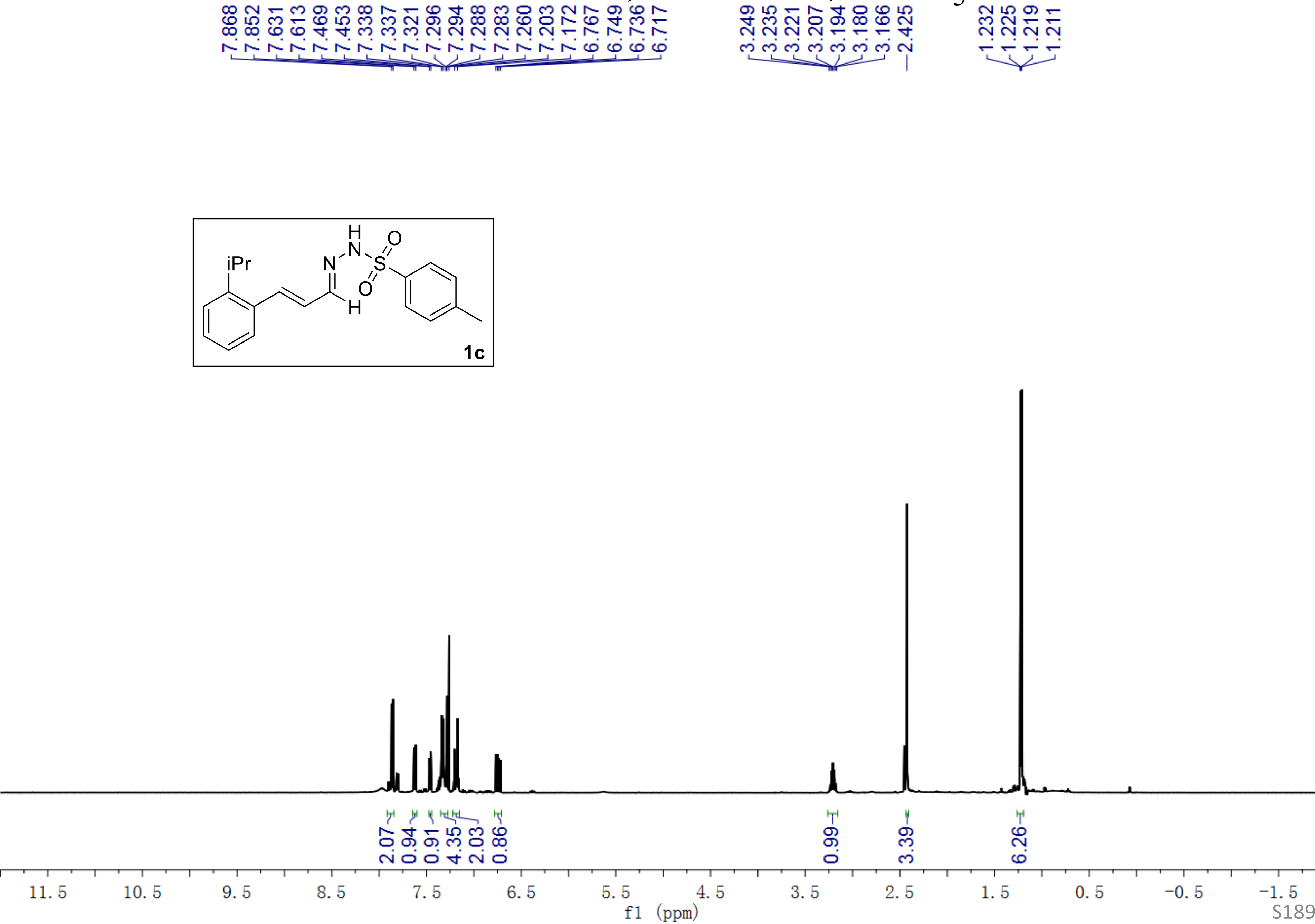
^{1}H NMR of **1b**, 600 MHz, $CDCl_3$



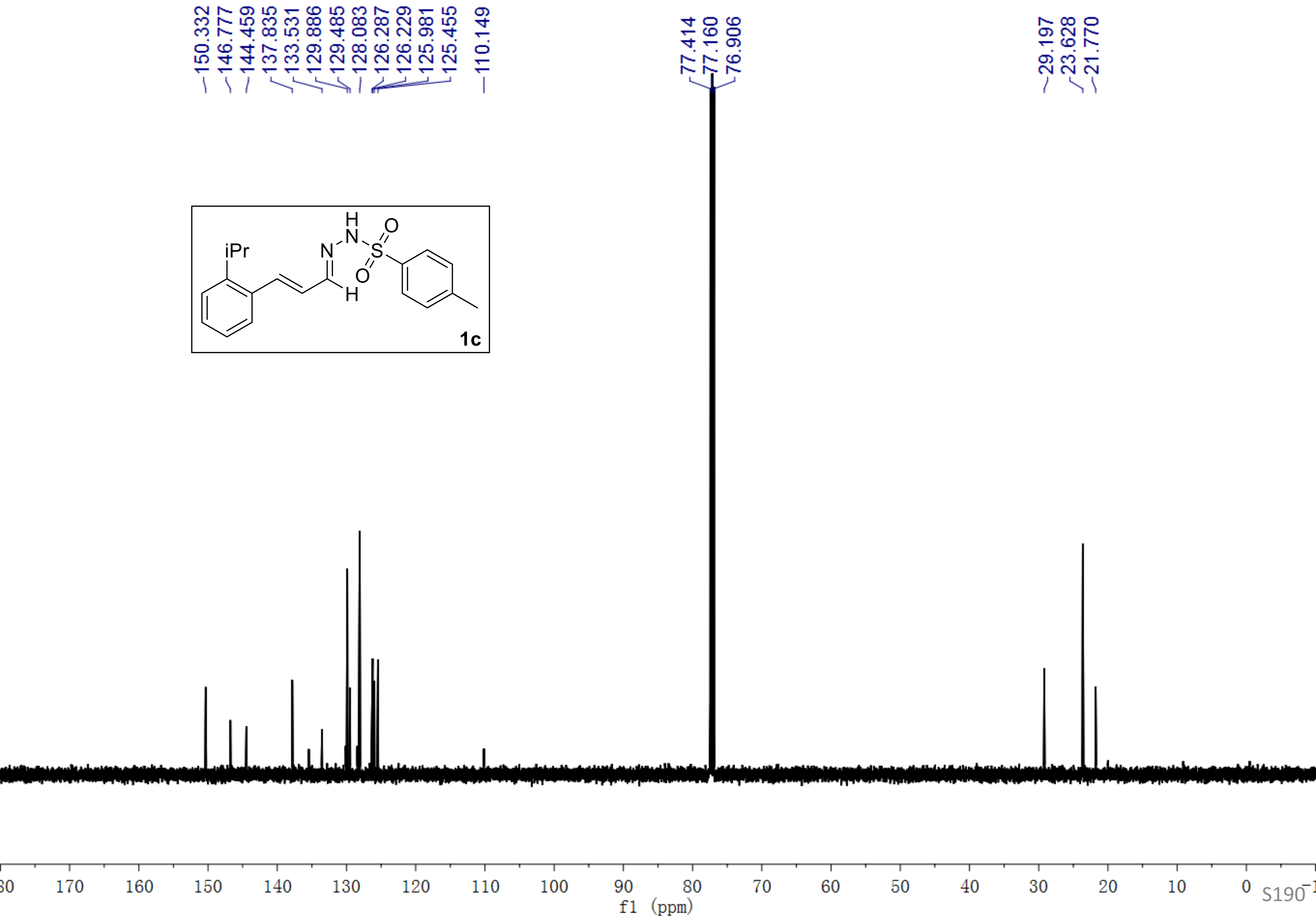
^{13}C NMR of **1b**, 151 MHz, $CDCl_3$



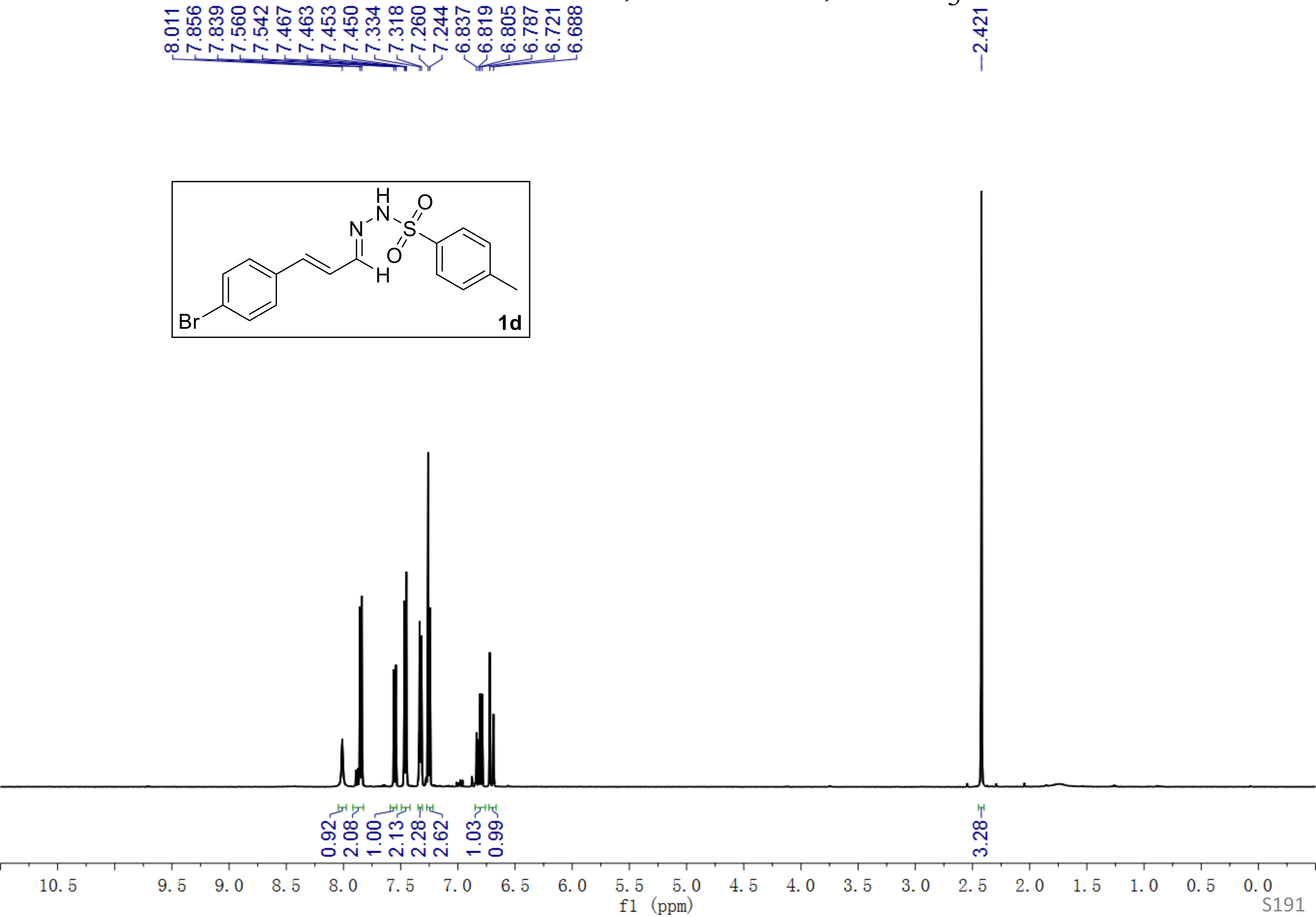
^{1}H NMR of **1c**, 600 MHz, $CDCl_3$



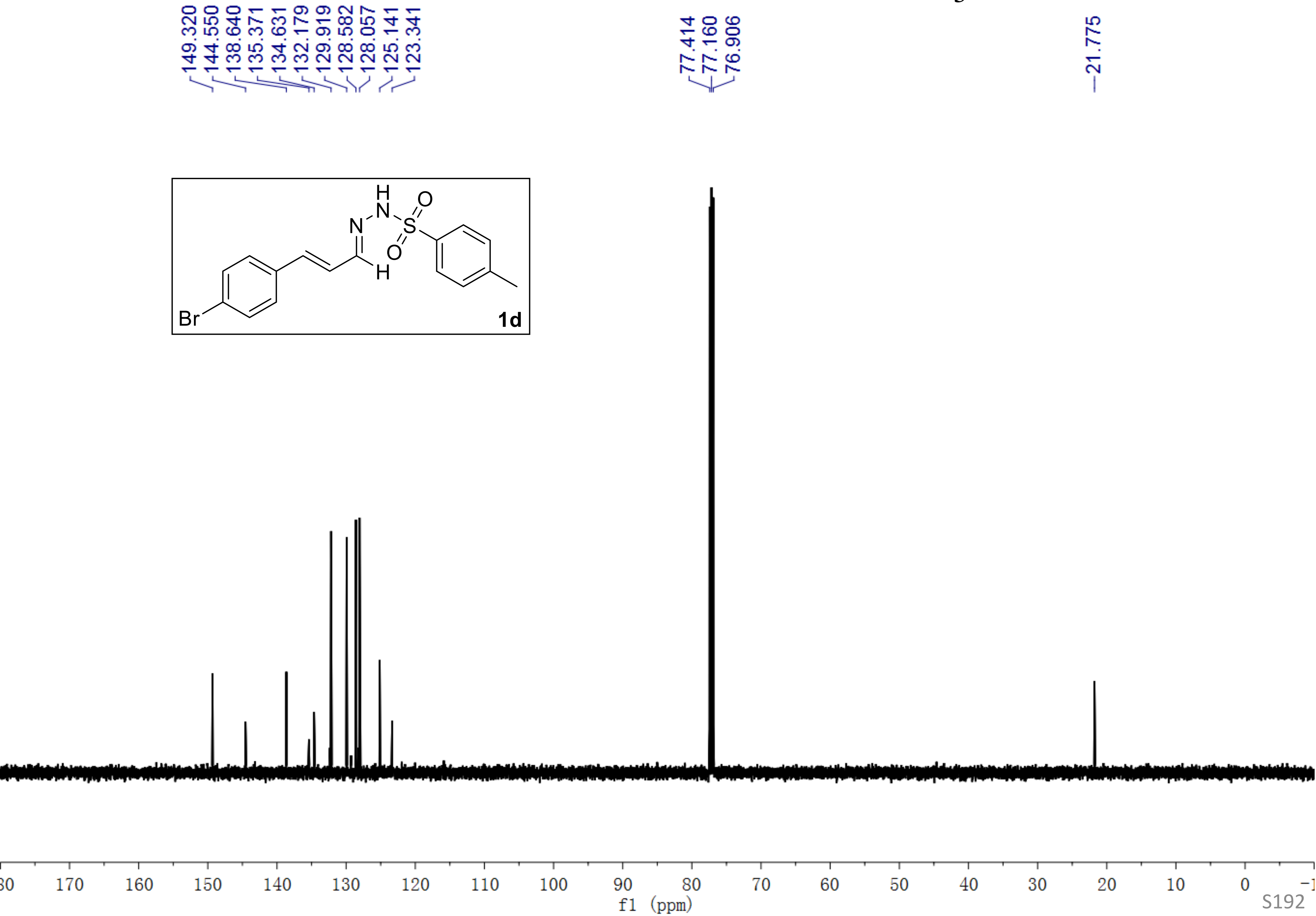
^{13}C NMR of **1c**, 151 MHz, $CDCl_3$



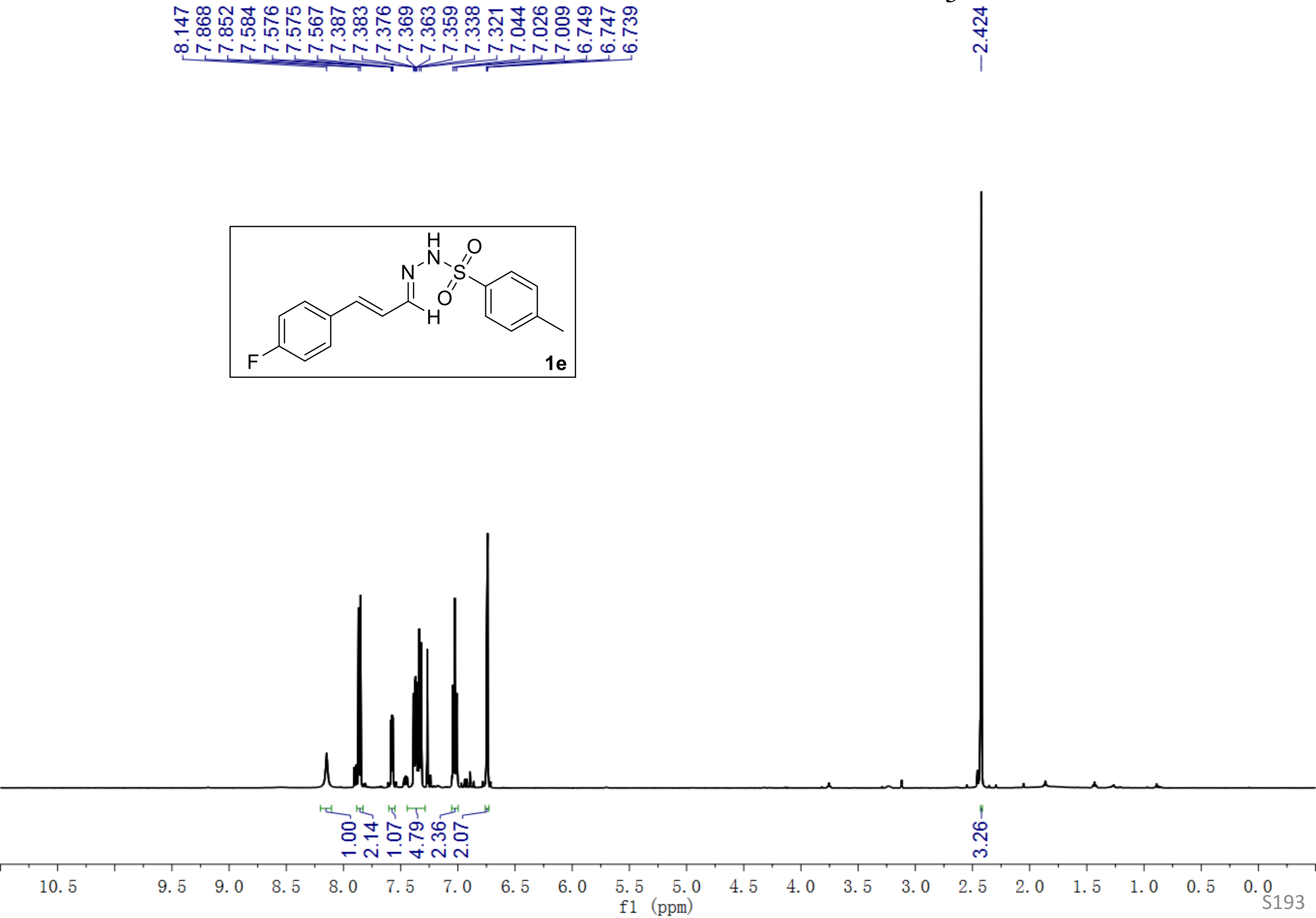
^{1}H NMR of **1d**, 600 MHz, $CDCl_3$



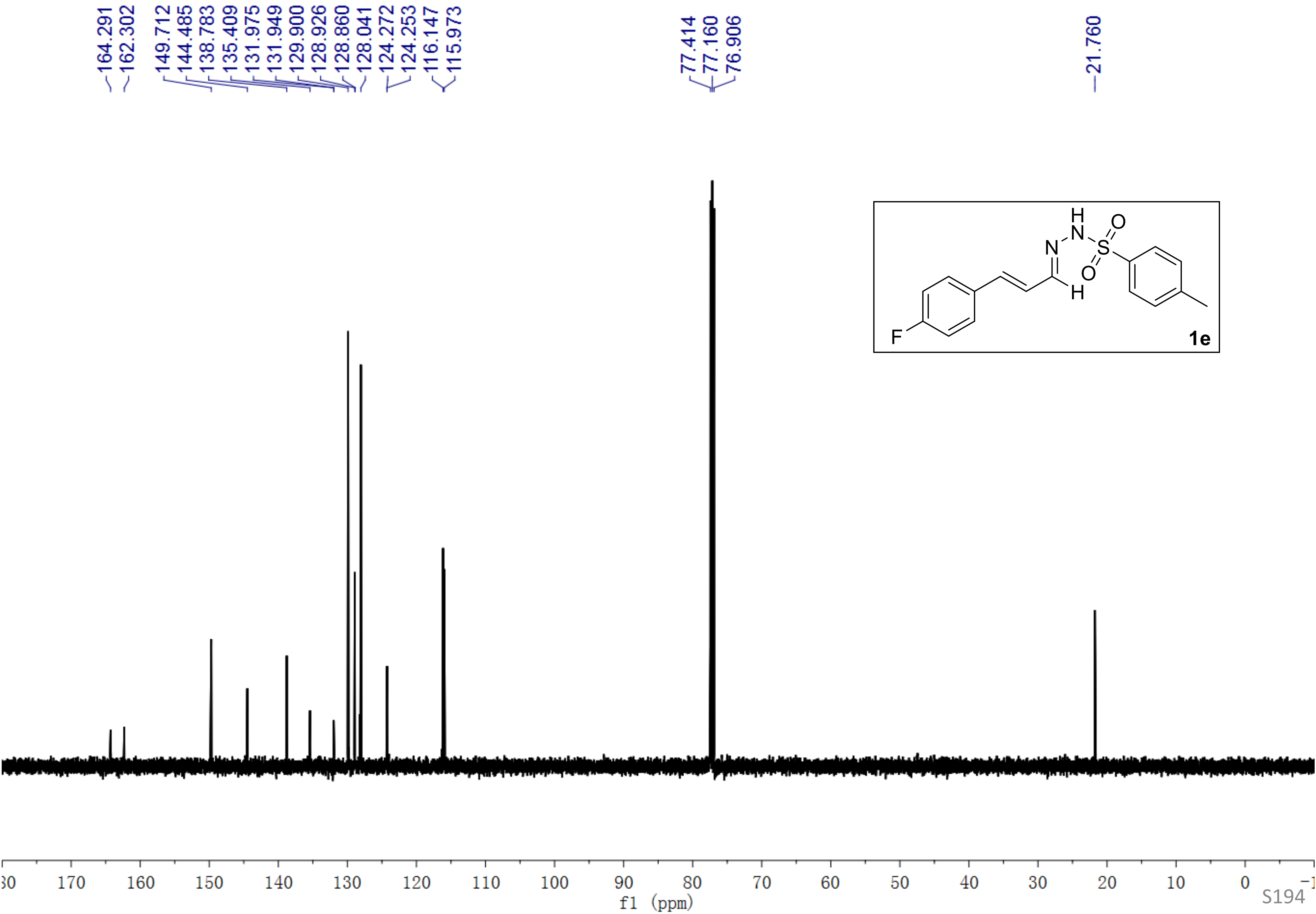
^{13}C NMR of **1d**, 151 MHz, $CDCl_3$



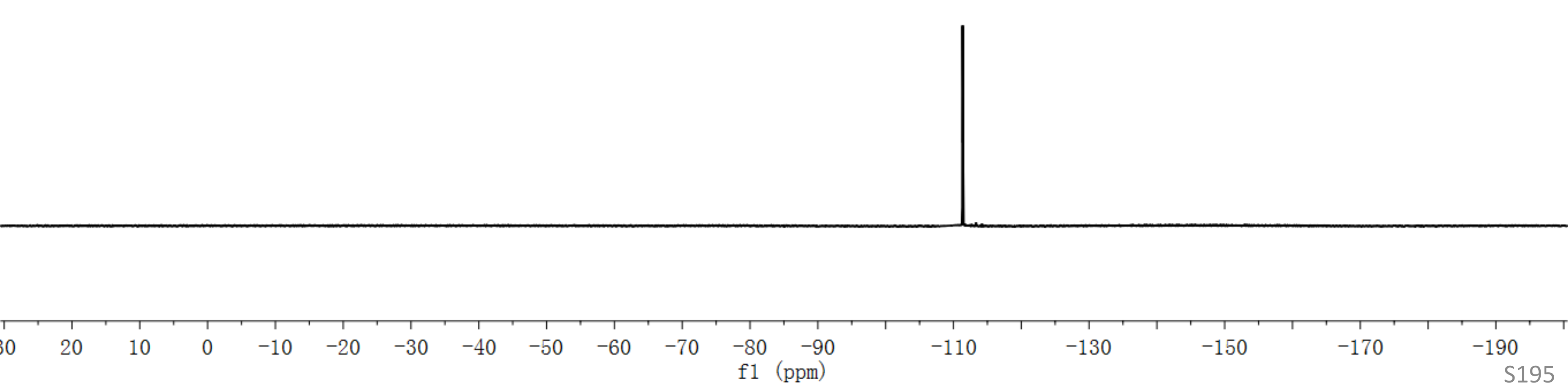
^1H NMR of **1e**, 600 MHz, $CDCl_3$

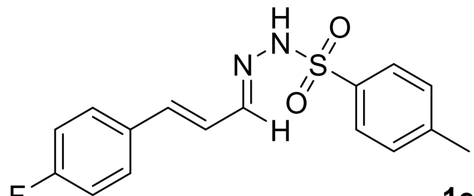


^{13}C NMR of **1e**, 151 MHz, $CDCl_3$



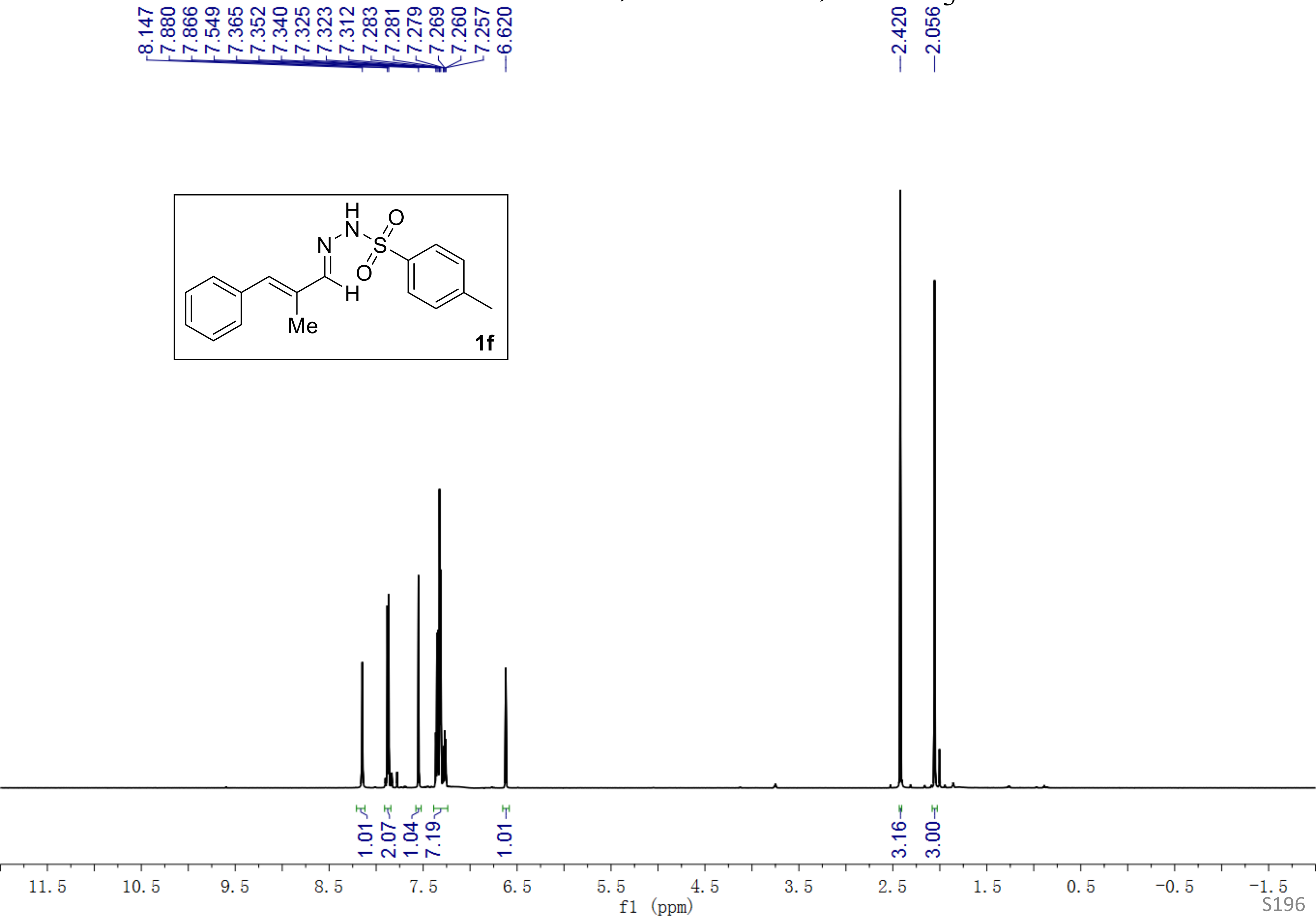
^{19}F NMR of **1e**, 470 MHz, $CDCl_3$





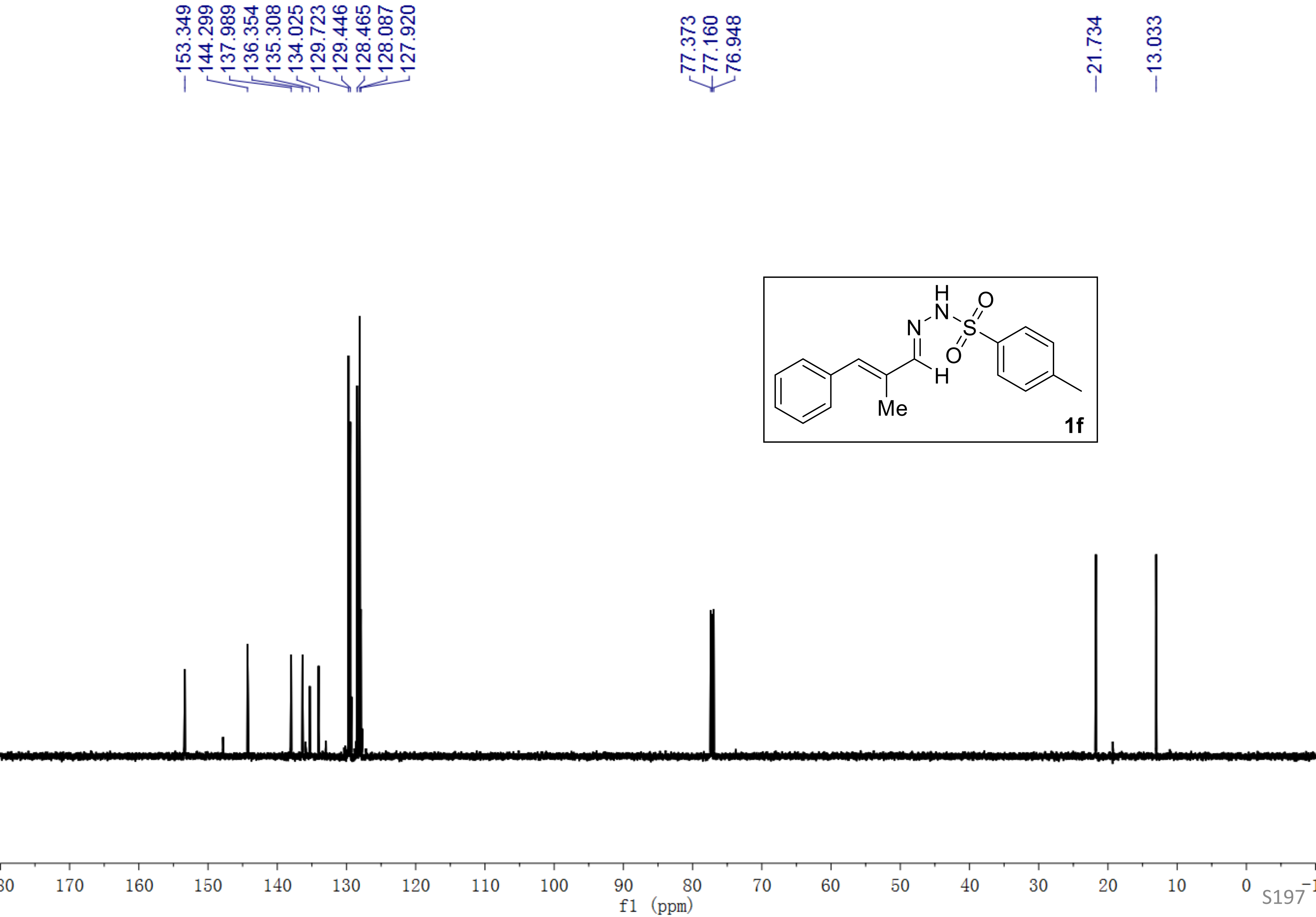
1e

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

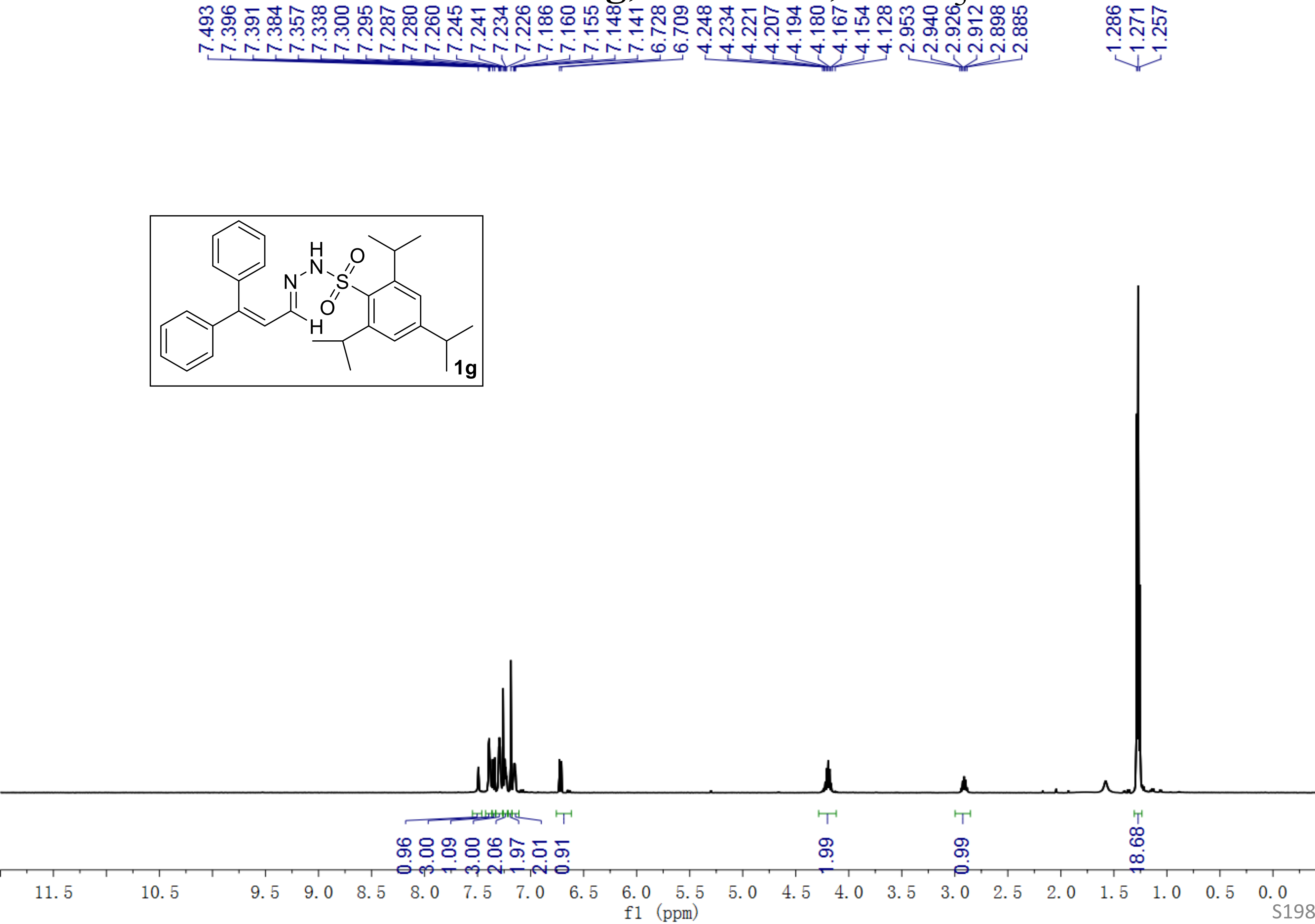


1f

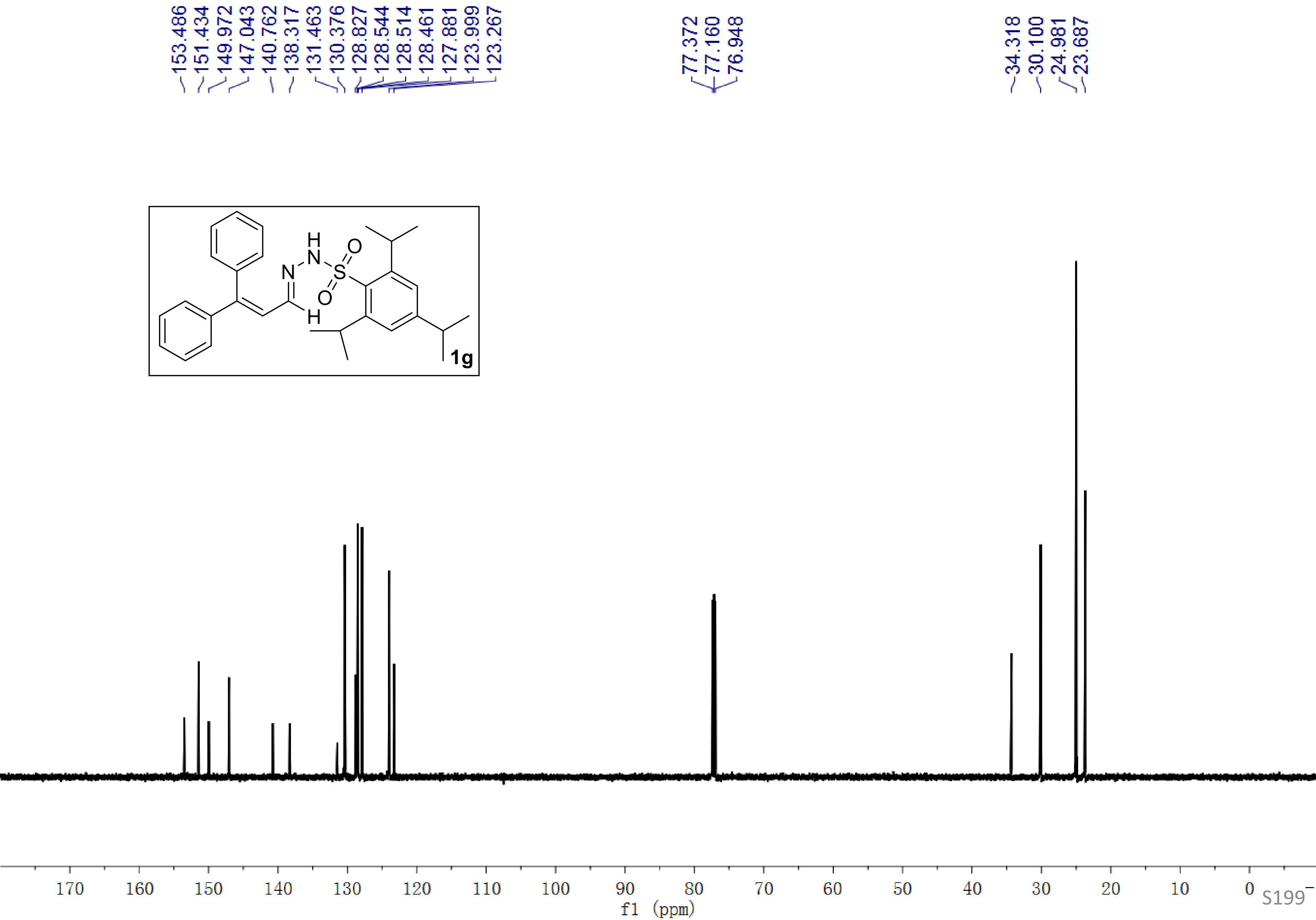
^{13}C NMR of **1f**, 151 MHz, $CDCl_3$



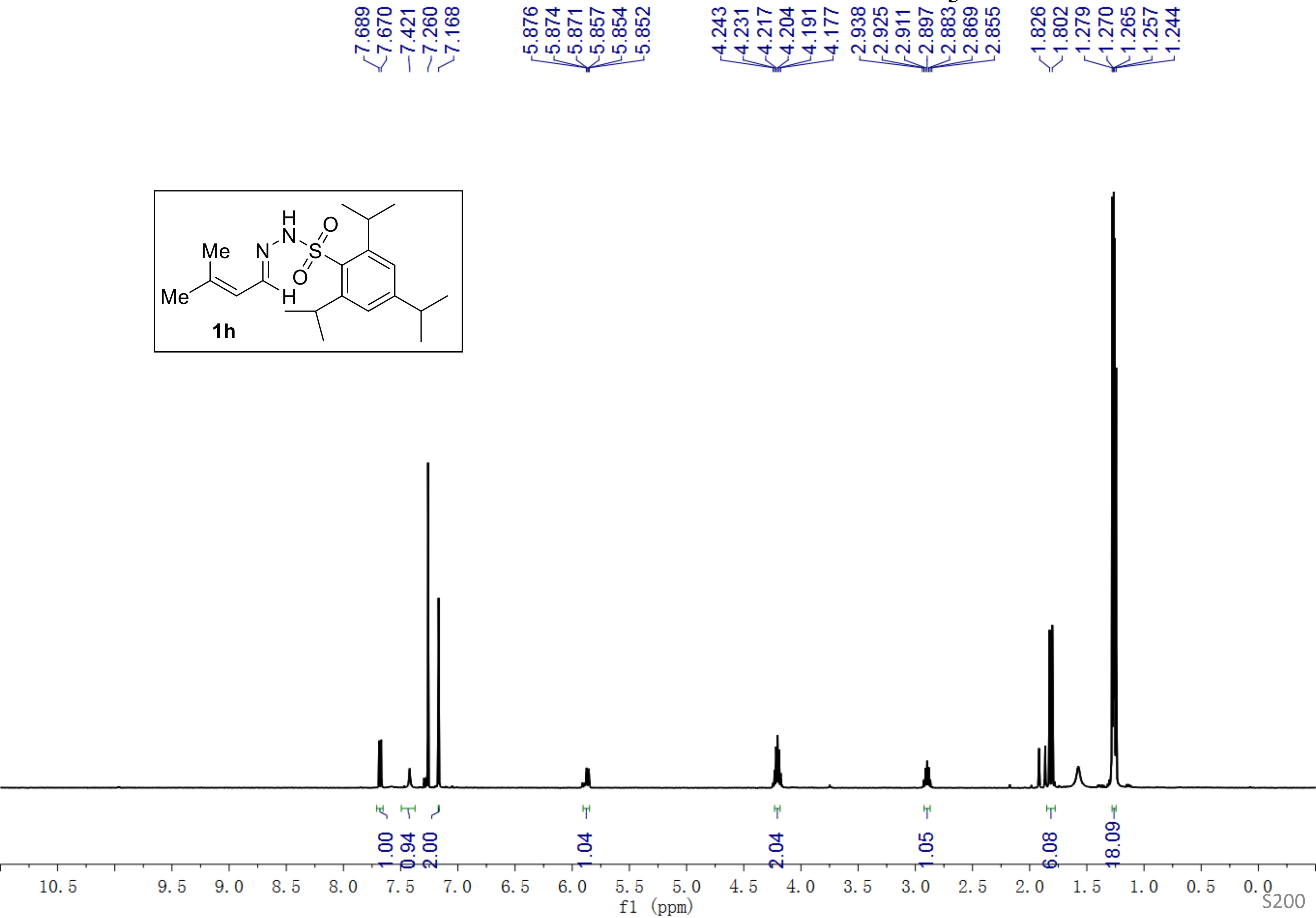
^{1}H NMR of **1g**, 500 MHz, $CDCl_3$



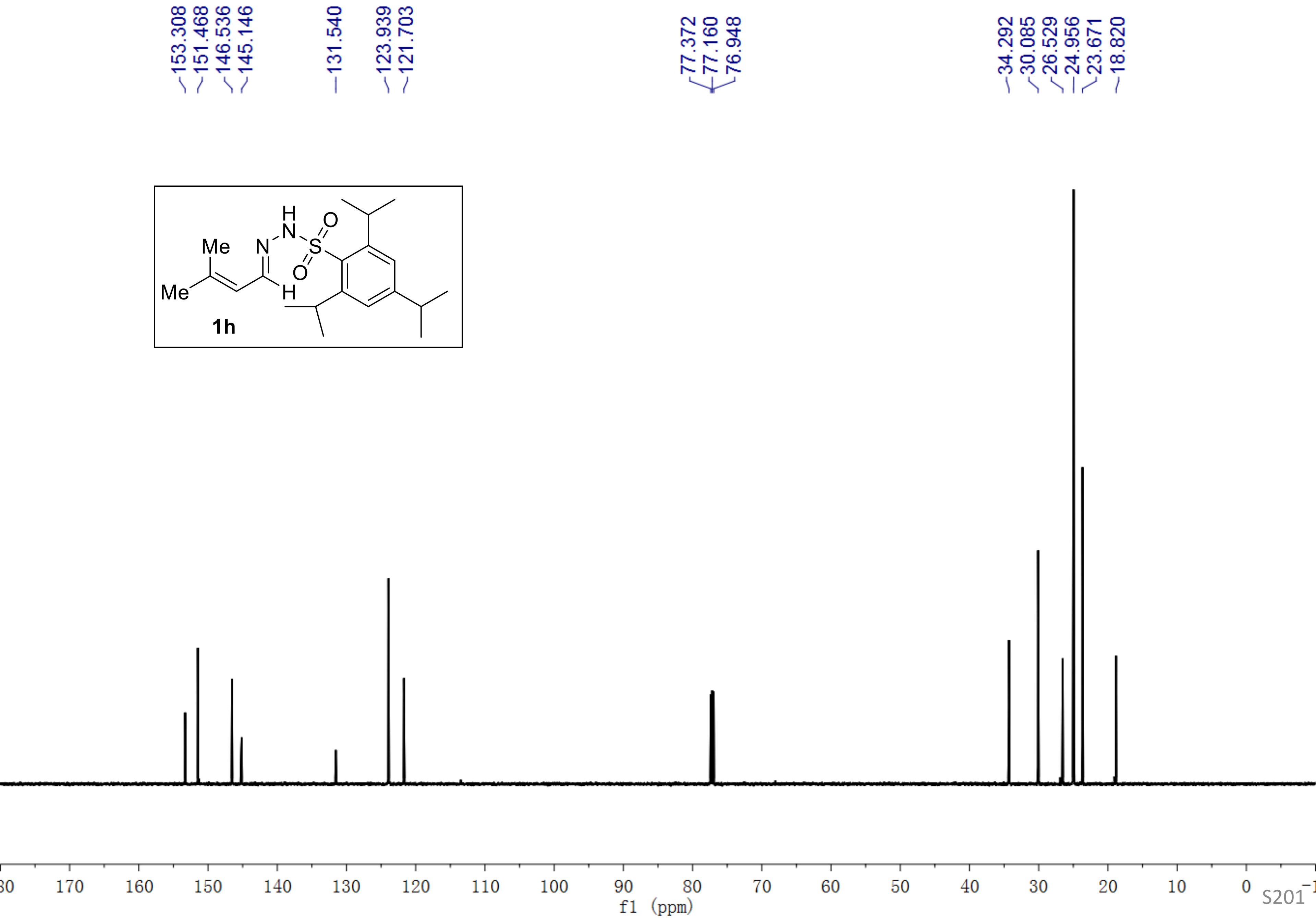
^{13}C NMR of **1g**, 151 MHz, $CDCl_3$



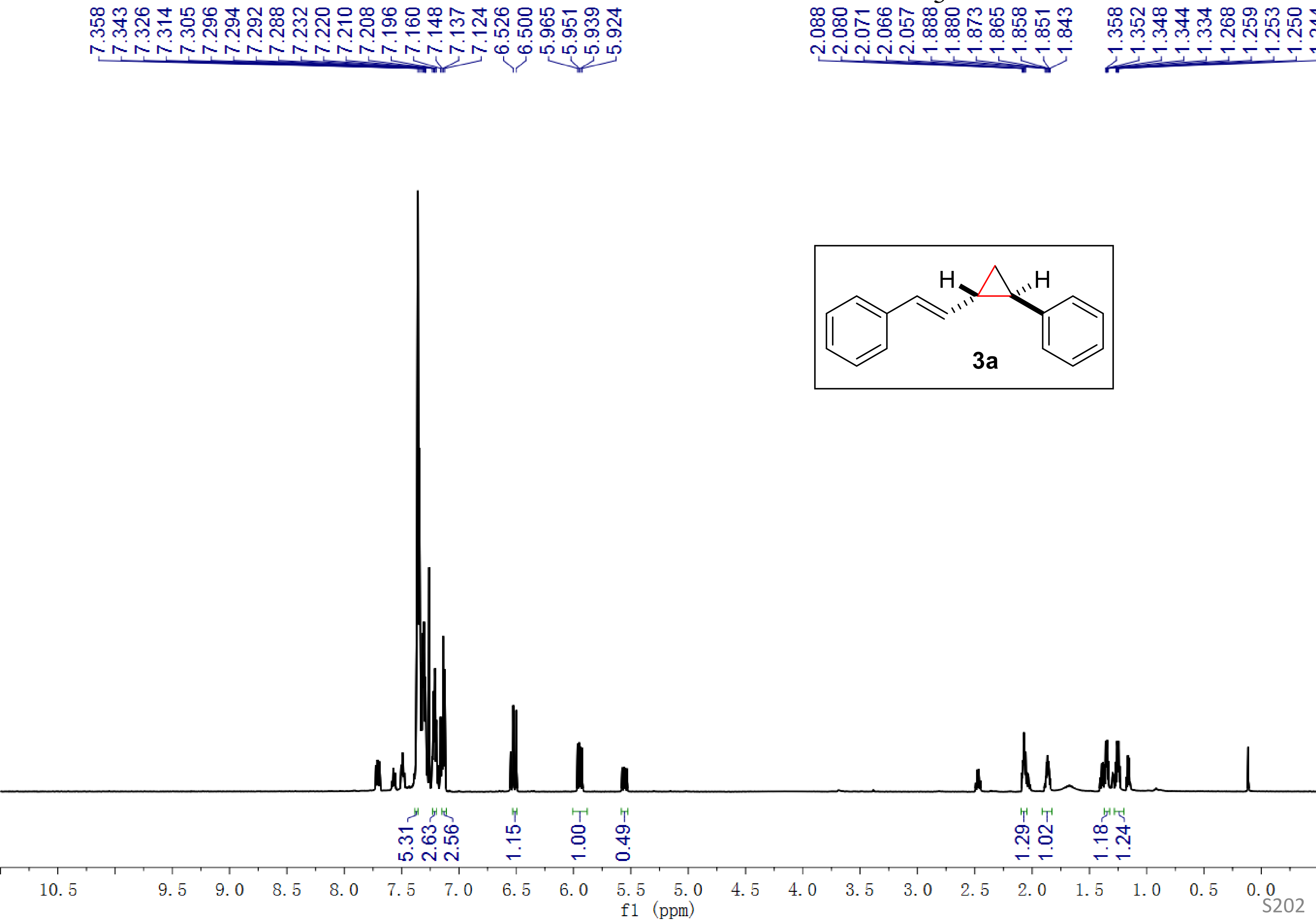
^{1}H NMR of **1h**, 500 MHz, $CDCl_3$



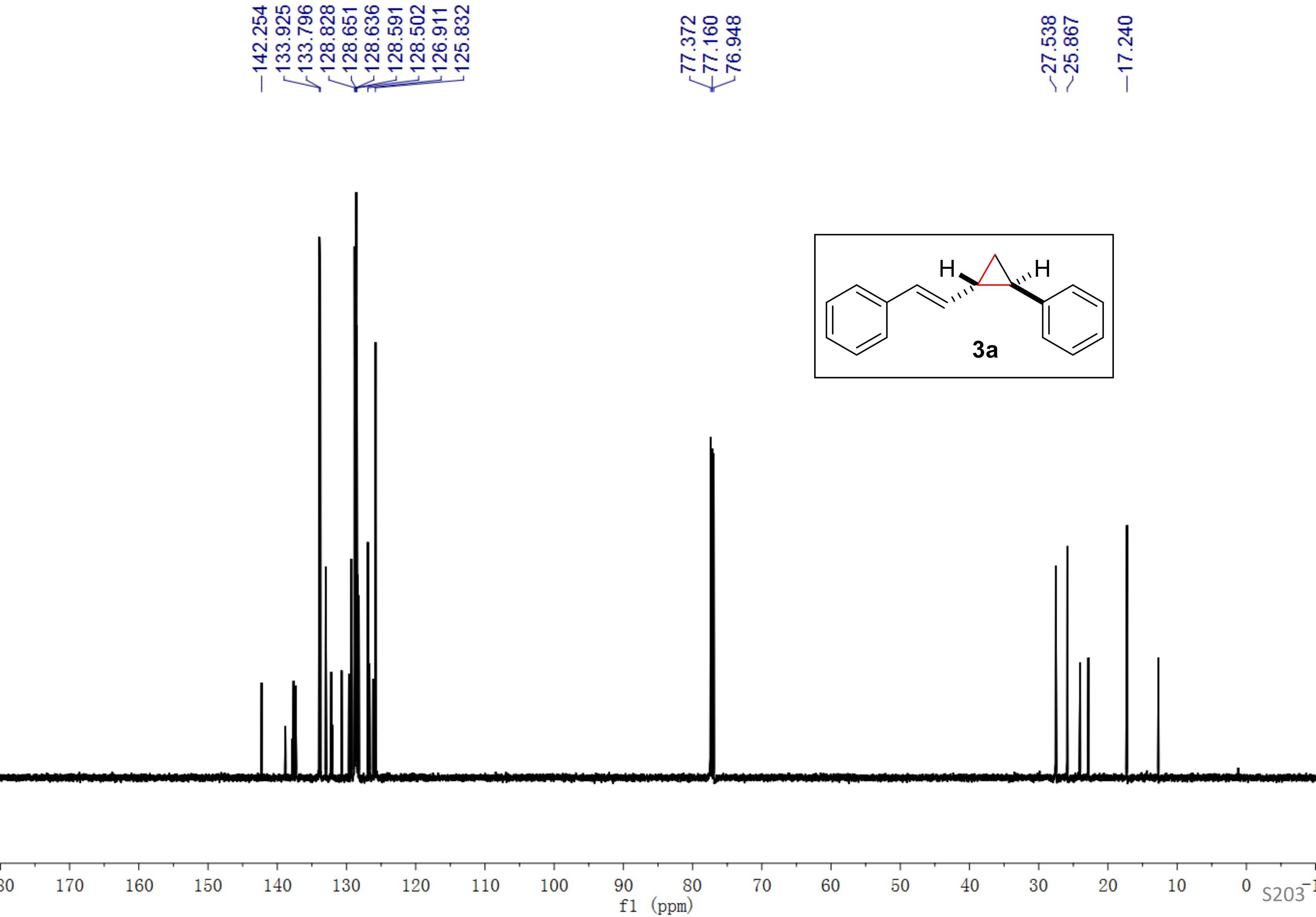
^{13}C NMR of **1h**, 151 MHz, $CDCl_3$



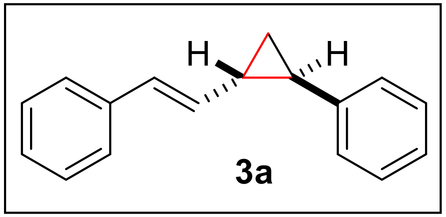
^{1}H NMR of **3a**, 500 MHz, $CDCl_3$

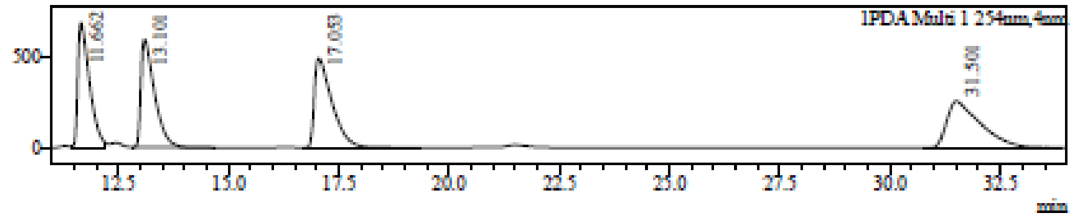


^{13}C NMR of **3a**, 126 MHz, $CDCl_3$

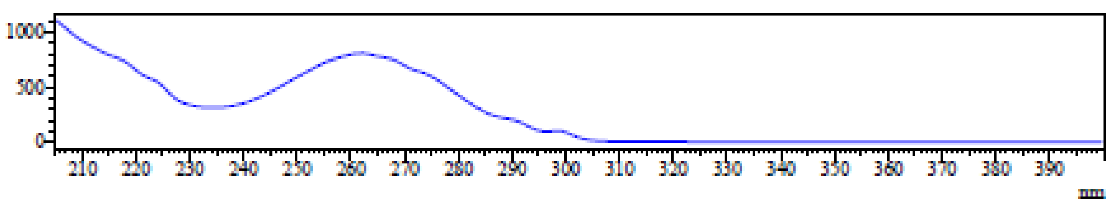


Data File : J0K-1220--IB-0%-1Ml001.lcd
Sample Name : J0K-1220--IB-0%-1Ml
Sample ID : J0K-1220--IB-0%-1Ml
Method File : J0K-0%--45min-1ml.lcm

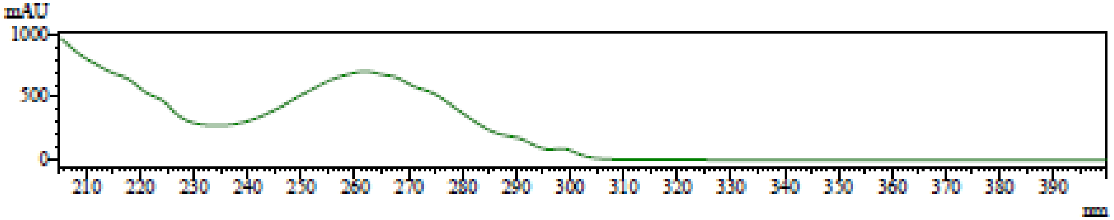




UV Spectrum
Retention time = 11.662



UV Spectrum
Retention time = 13.101

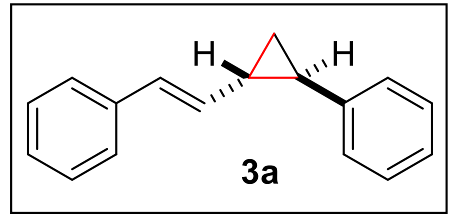


Peak Table

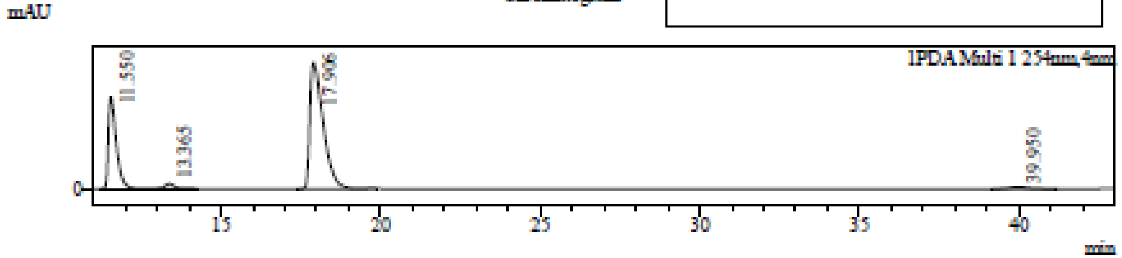
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.662	12925911	24.235
2	13.101	12848868	24.091
3	17.053	13812009	25.896
4	31.501	13748877	25.778
Total		53335665	100.000

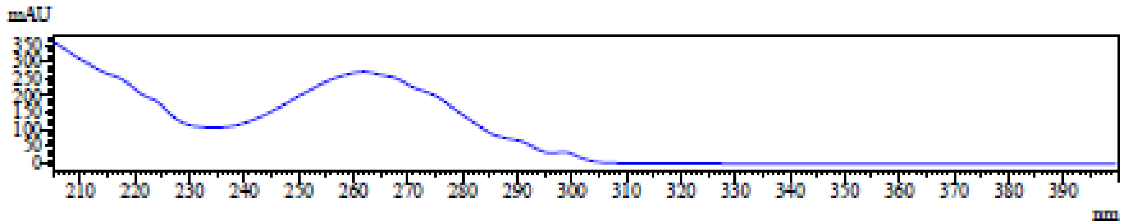
Data File : J0K-1243--IB-0%-1ML.lcd
Sample Name : J0K-1243--IB-0%-1ML
Sample ID : J0K-1243--IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm



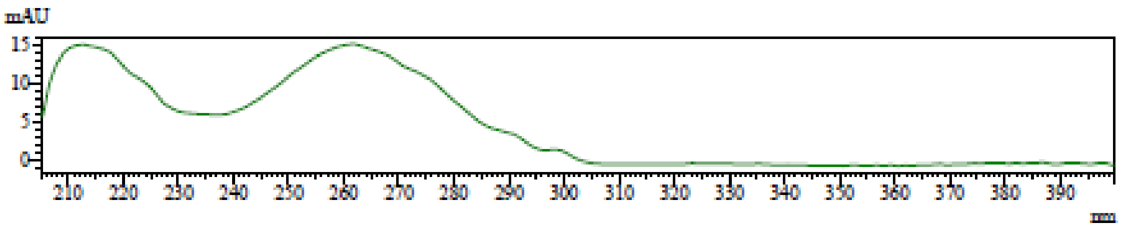
Chromatogram



UV Spectrum
Retention time = 11.550



UV Spectrum
Retention time = 13.365

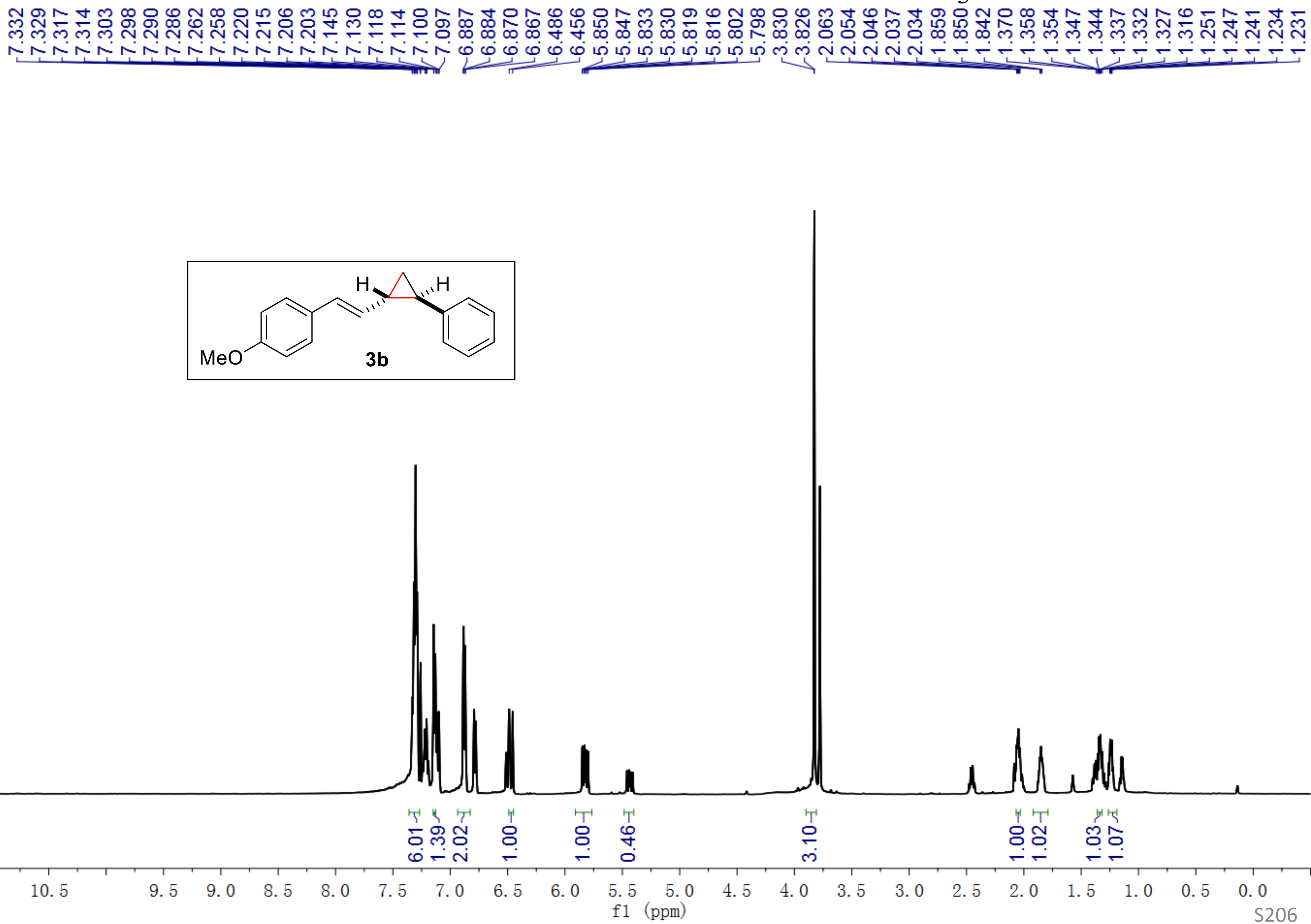


Peak Table

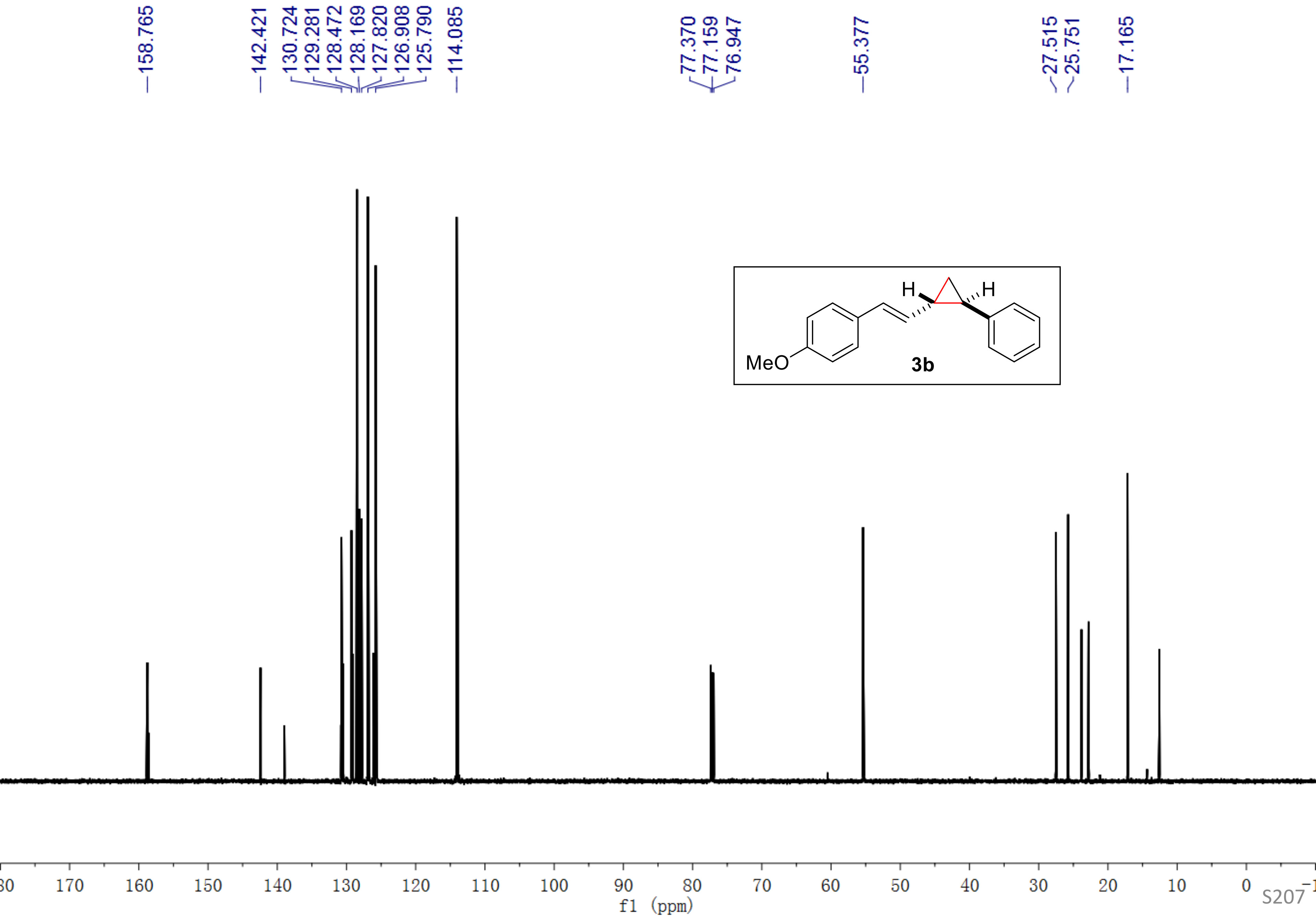
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.550	4157469	29.839
2	13.365	253605	1.820
3	17.906	9311768	66.832
4	39.950	210340	1.510
Total		13933182	100.000

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

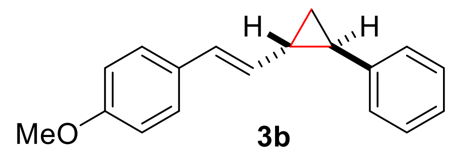


^{13}C NMR of **3b**, 126 MHz, $CDCl_3$



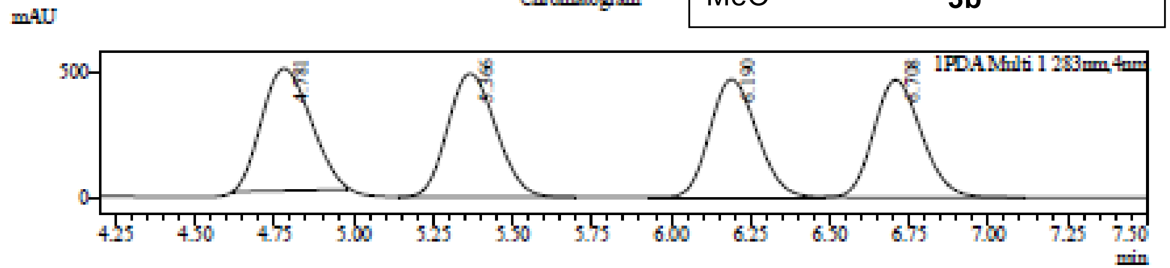
Sample Information

Data File : J0K-1370-IC-1%-1ML.lcd
Sample Name : J0K-1370-IC-1%-1ML
Sample ID : J0K-1370-IC-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

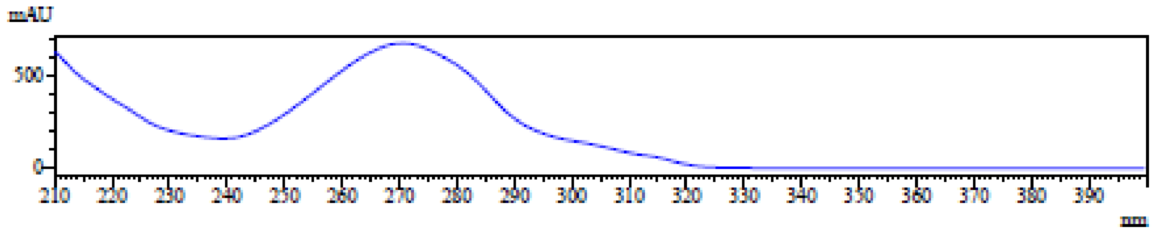


3b

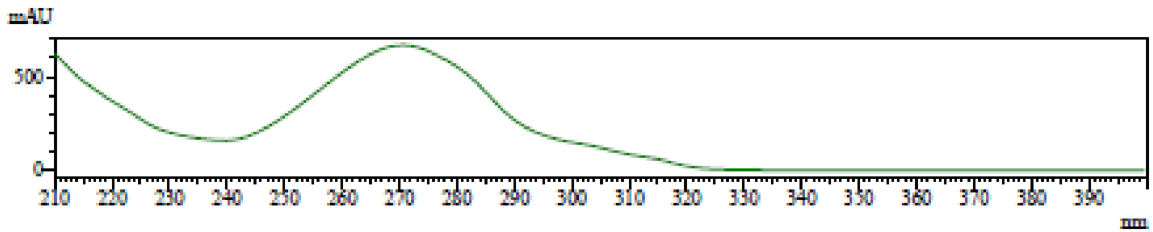
Chromatogram



UV Spectrum
Retention time = 6.190



UV Spectrum
Retention time = 6.708



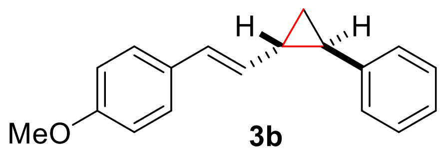
Peak Table

PDA Ch1 283nm

Peak#	Ret. Time	Area	Area%
1	4.781	5219115	25.960
2	5.366	5198116	25.856
3	6.190	4813778	23.944
4	6.708	4873169	24.240
Total		20104178	100.000

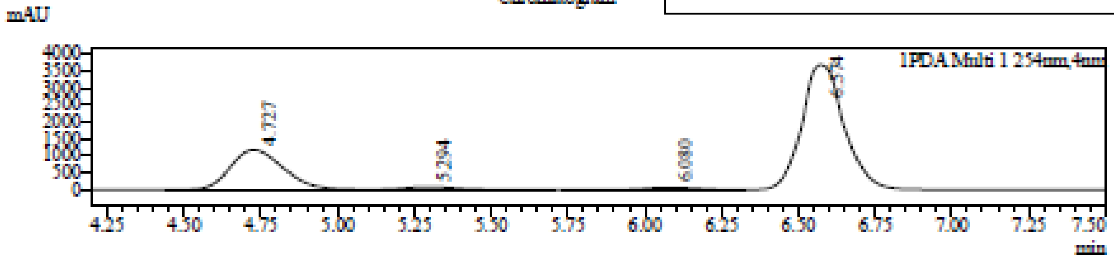
Sample Information

Data File	: J0K-1369-IC-1%-1ML.lcd
Sample Name	: J0K-1369-IC-1%-1ML
Sample ID	: J0K-1369-IC-1%-1ML
Method File	: J0K-1%-40min-1ml.lcm

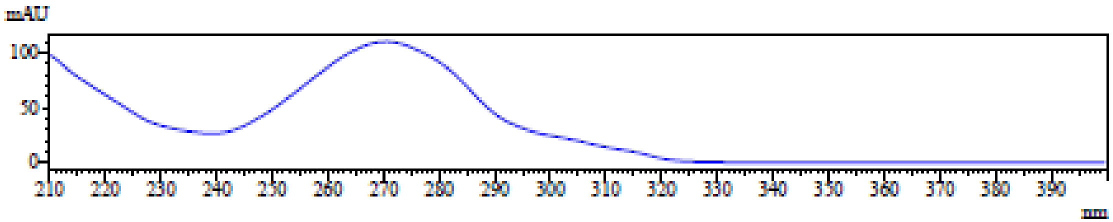


3b

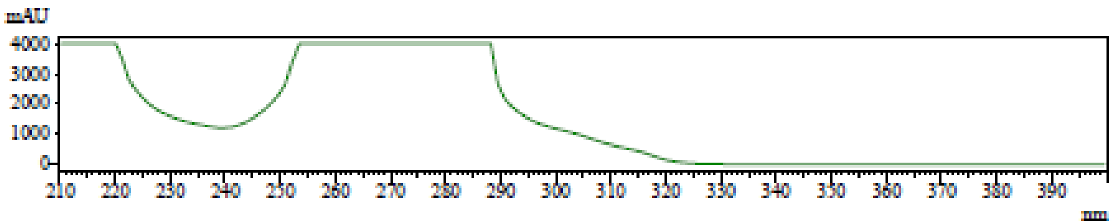
Chromatogram



UV Spectrum
Retention time = 6.080



UV Spectrum
Retention time = 6.574

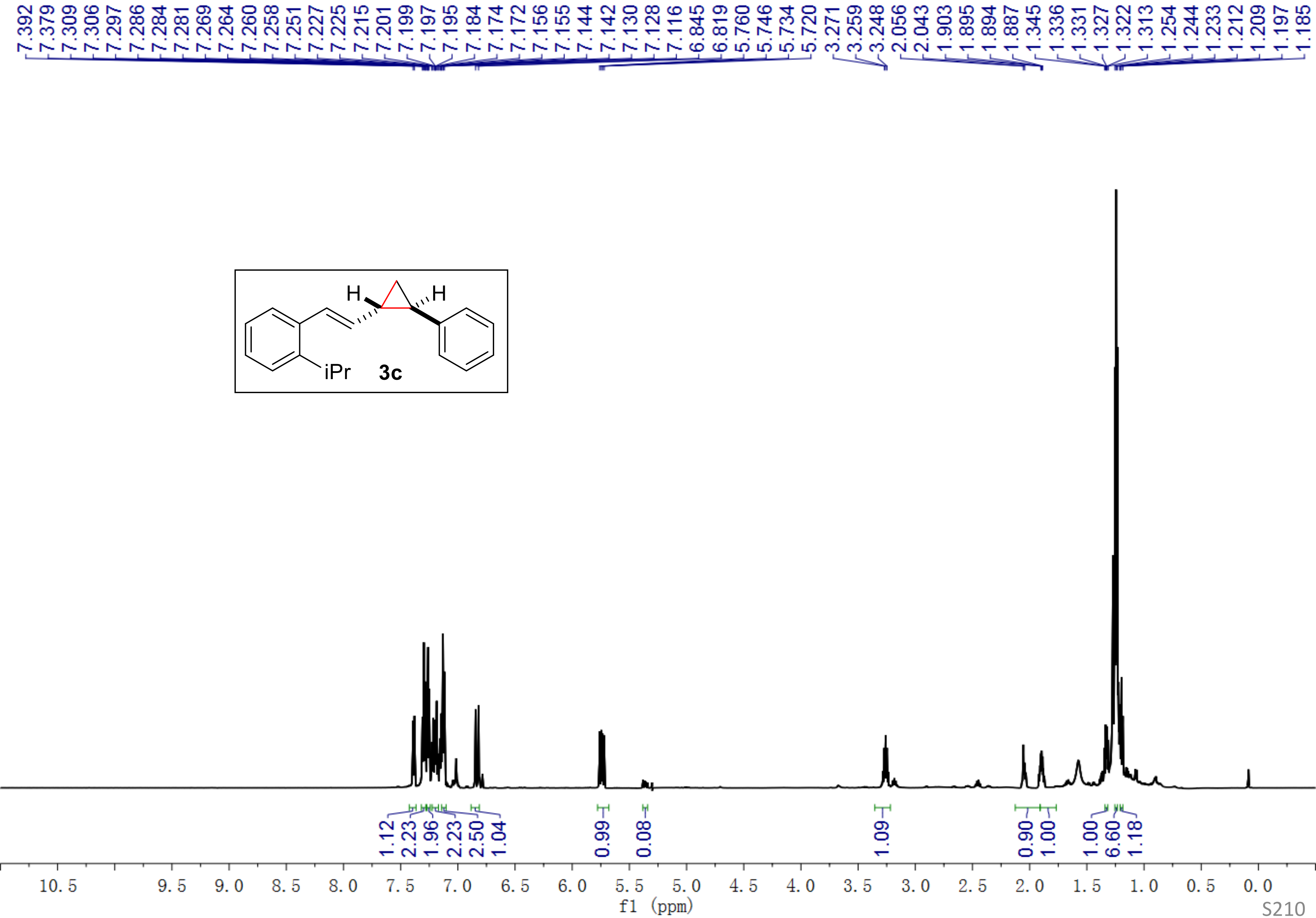


Peak Table

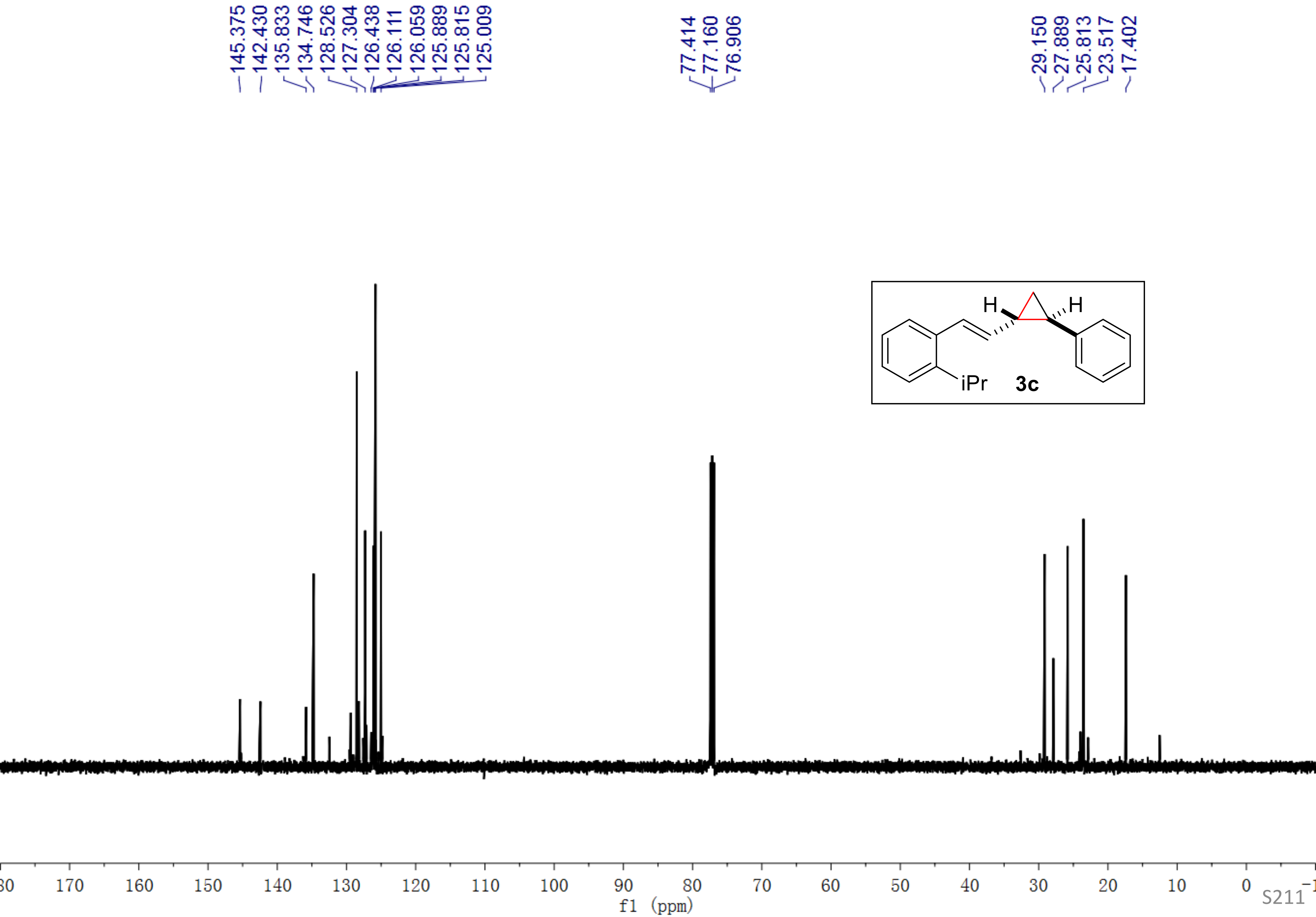
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.727	14037482	27.551
2	5.294	861303	1.690
3	6.080	653209	1.282
4	6.574	35398016	69.476
Total		50950009	100.000

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

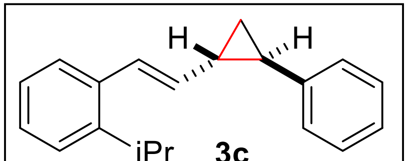


^{13}C NMR of **3c**, 126 MHz, $CDCl_3$



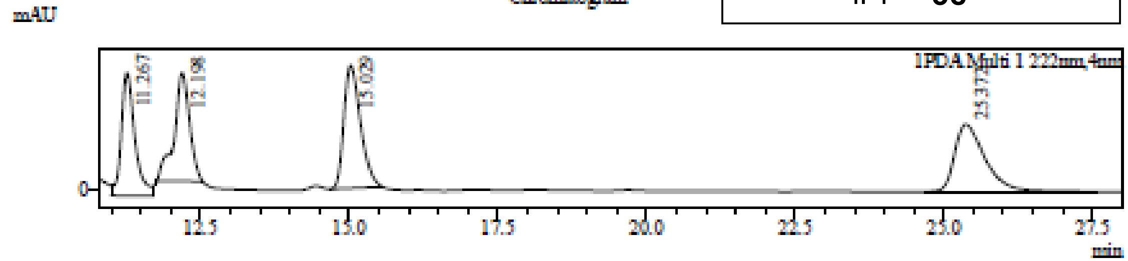
Sample Information

Data File : J0K-1306-2--IB--0%-0.8ML.lcd
Sample Name : J0K-1306-2--IB--0%-0.8ML
Sample ID : J0K-1306-2--IB--0%-0.8ML
Method File : J0K-0%--40min-0.8ml.lcm

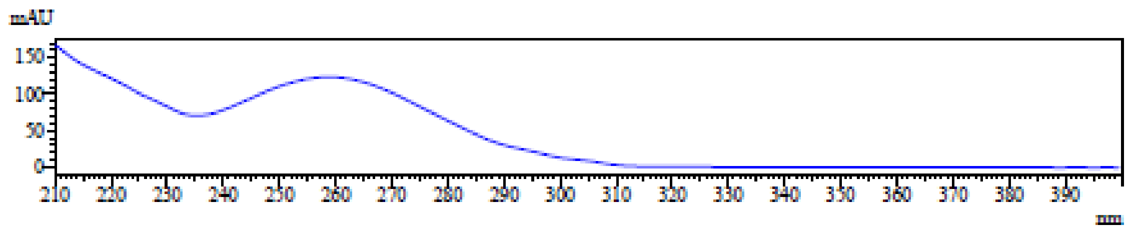


3c

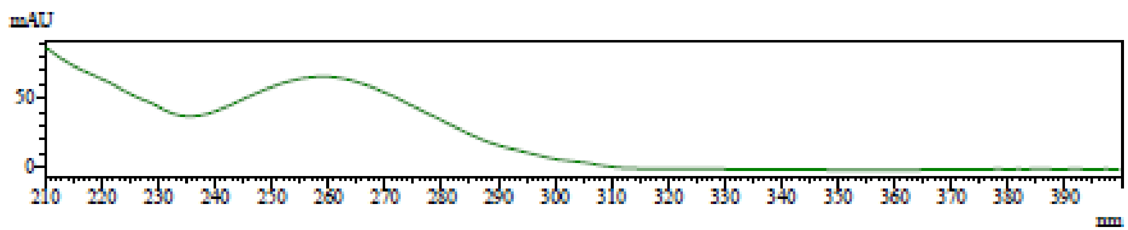
Chromatogram



UV Spectrum
Retention time = 15.029



UV Spectrum
Retention time = 25.372



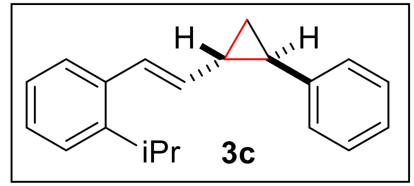
Peak Table

PDA Ch1 222nm

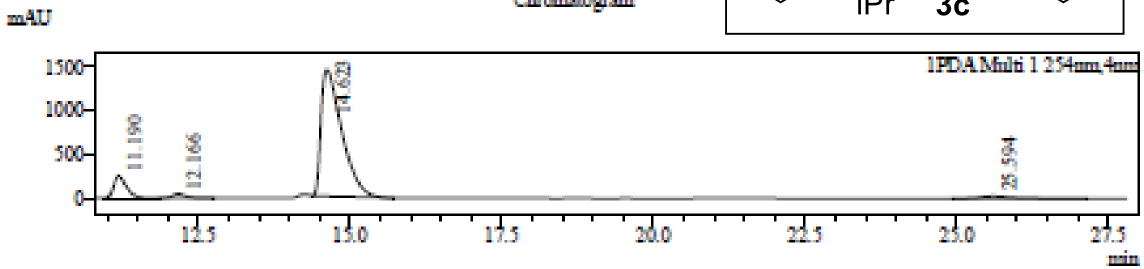
Peak#	Ret. Time	Area	Area%
1	11.267	1785911	22.402
2	12.198	1795712	22.525
3	15.029	2195432	27.539
4	25.372	2195081	27.534
Total		7972135	100.000

Sample Information

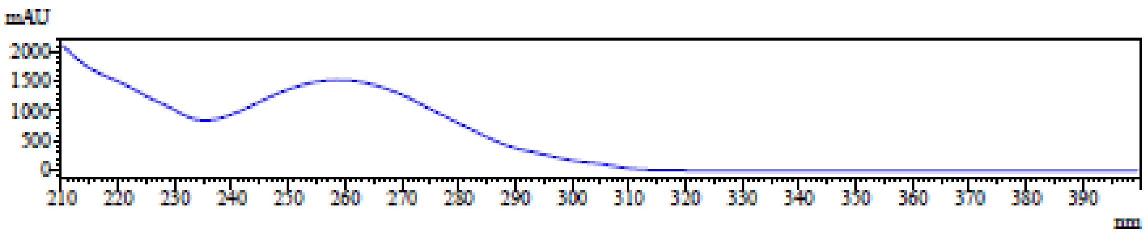
Data File	: J0K-1305--IB--0%-0.8ML.lcd
Sample Name	: J0K-1305--IB--0%-0.8ML
Sample ID	: J0K-1305--IB--0%-0.8ML
Method File	: J0K-0%--40min-0.8ml.lcm



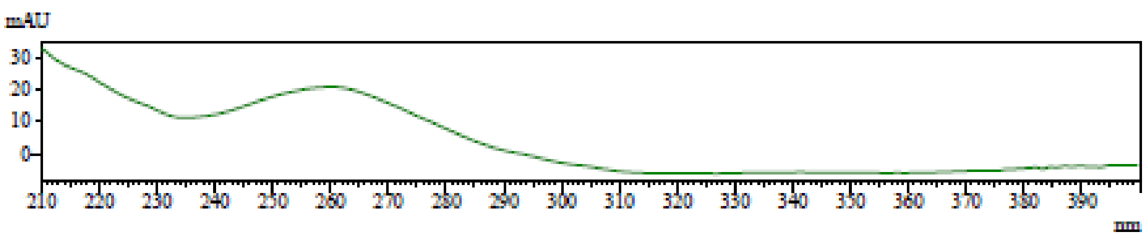
Chromatogram



UV Spectrum
Retention time = 14.623



UV Spectrum
Retention time = 25.594

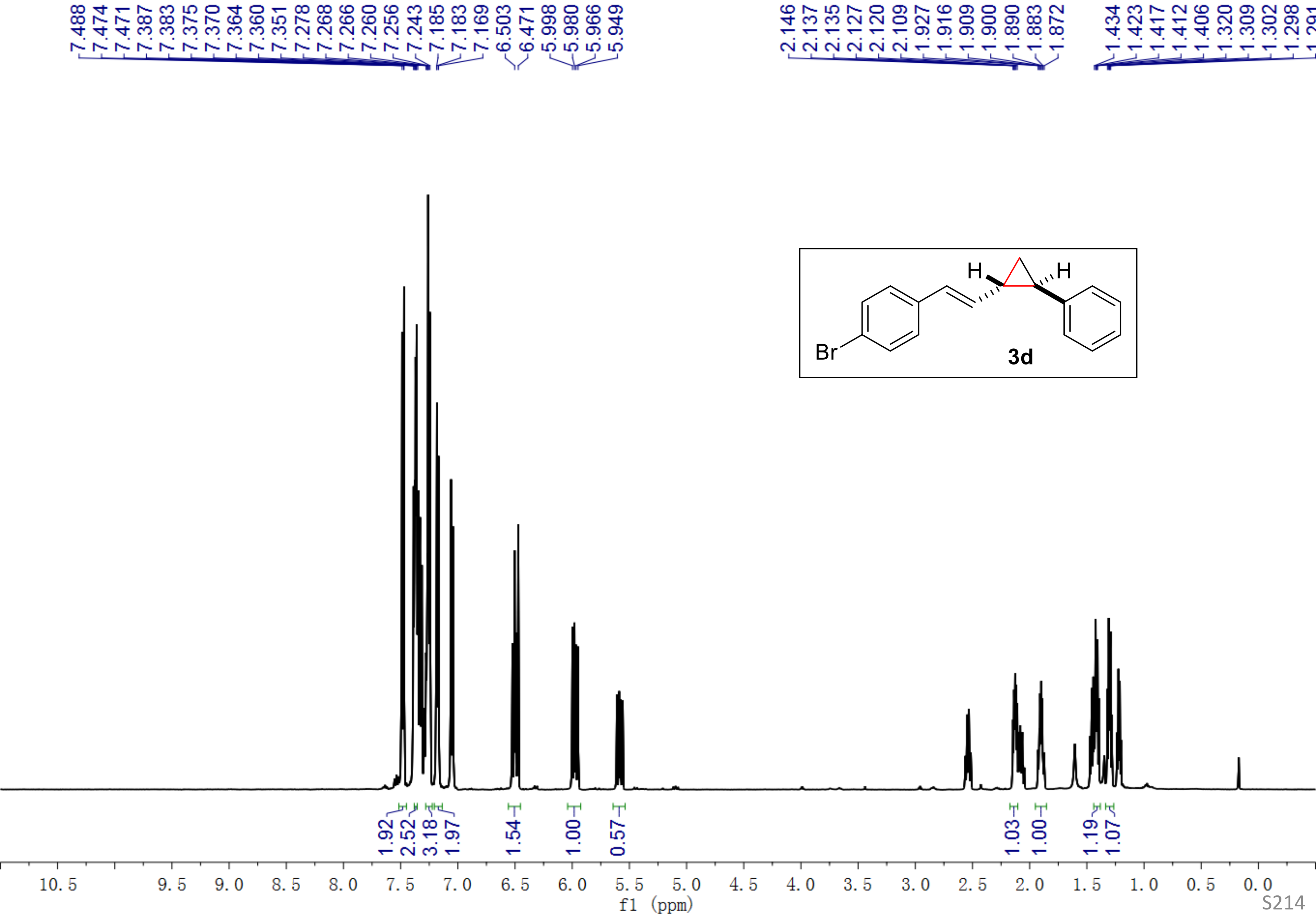


Peak Table

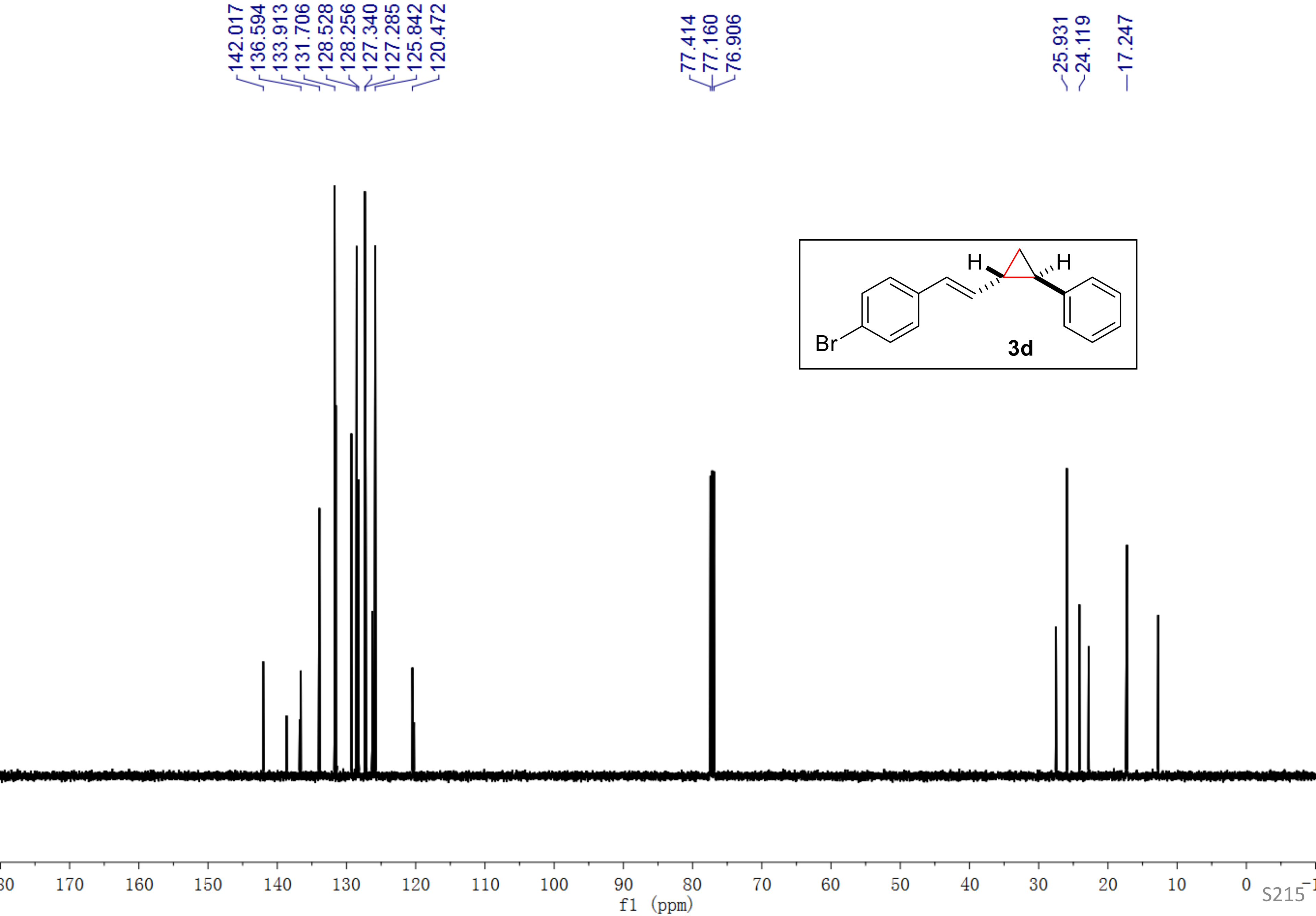
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.190	3657369	9.172
2	12.166	744577	1.867
3	14.623	34561627	86.678
4	25.594	910074	2.282
Total		39873648	100.000

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

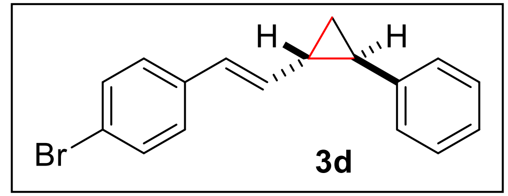


^{13}C of **3d**, 126 MHz, $CDCl_3$

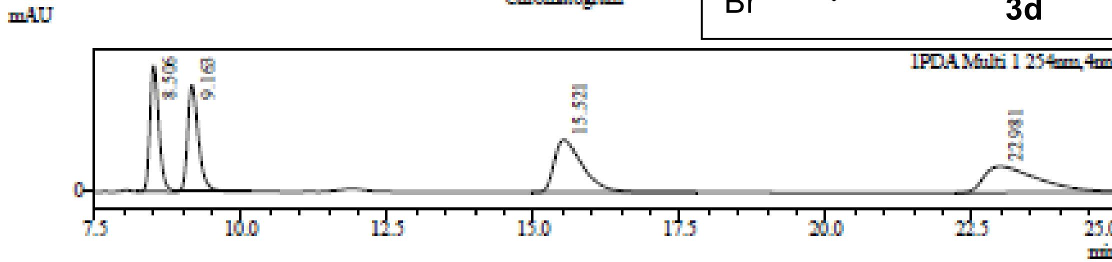


Sample Information

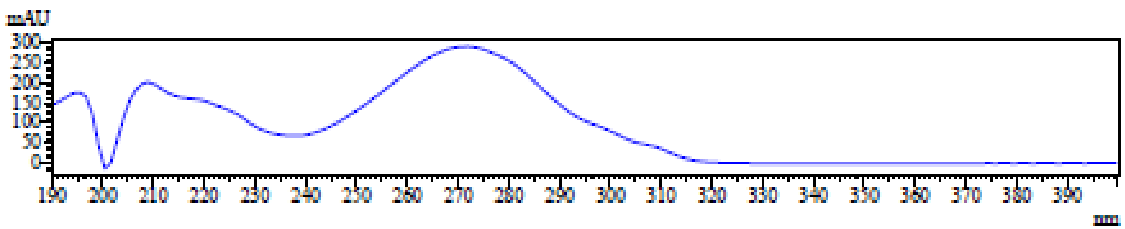
Data File : J0K-1631-IA-0.1%-1ML.lcd
Sample Name : J0K-1631-IA-0.1%-1ML
Sample ID : J0K-1631-IA-0.1%-1ML
Method File : J0K-0.1%--25min-1ml.lcm



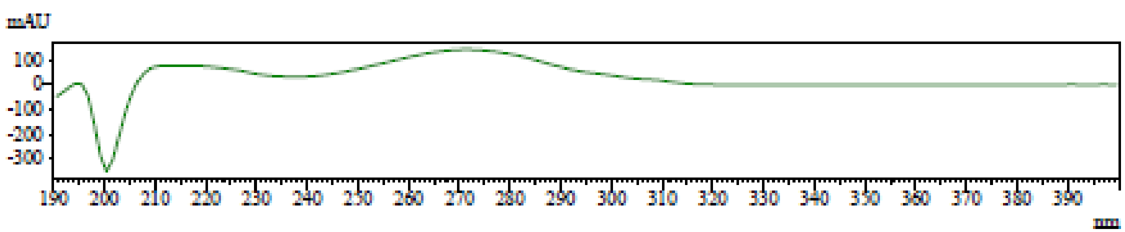
Chromatogram



UV Spectrum
Retention time = 15.521



UV Spectrum
Retention time = 22.981



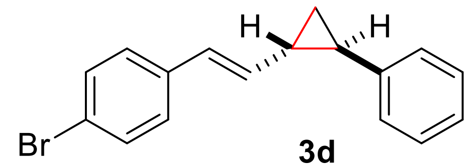
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.506	4310748	21.644
2	9.163	4497130	22.580
3	15.521	5726356	28.752
4	22.981	5382004	27.023
Total		19916239	100.000

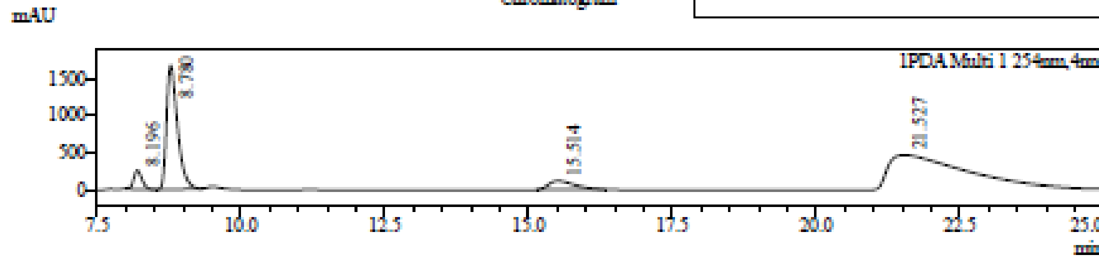
Sample Information

Data File : J0K-1630-IA-0.1%-1ML.lcd
Sample Name : J0K-1630-IA-0.1%-1ML
Sample ID : J0K-1630-IA-0.1%-1ML
Method File : J0K-0.1%--35min-1ml.lcm

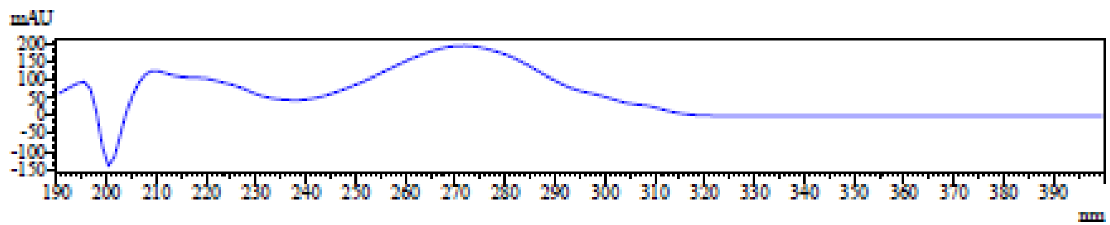


3d

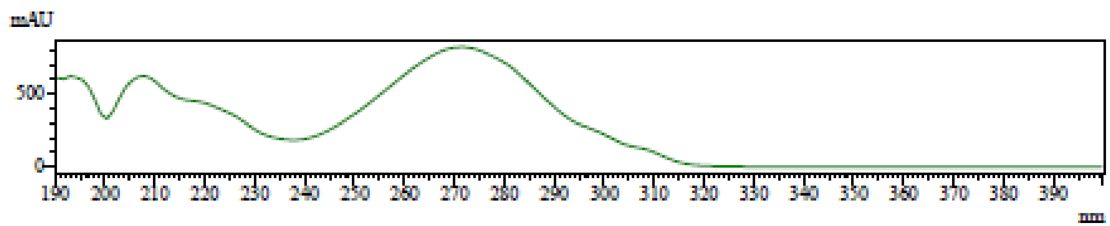
Chromatogram



UV Spectrum
Retention time = 15.514



UV Spectrum
Retention time = 21.527

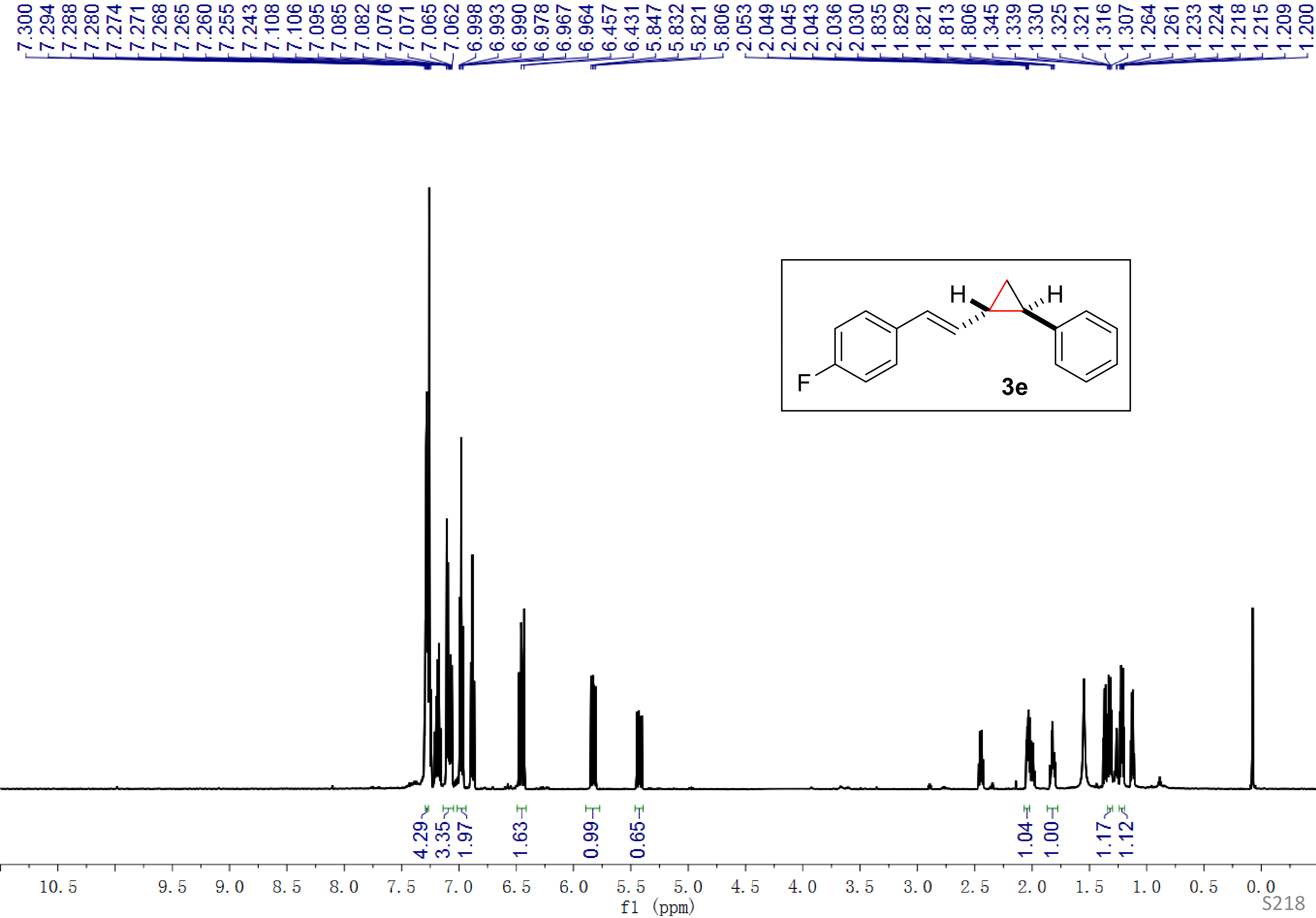


Peak Table

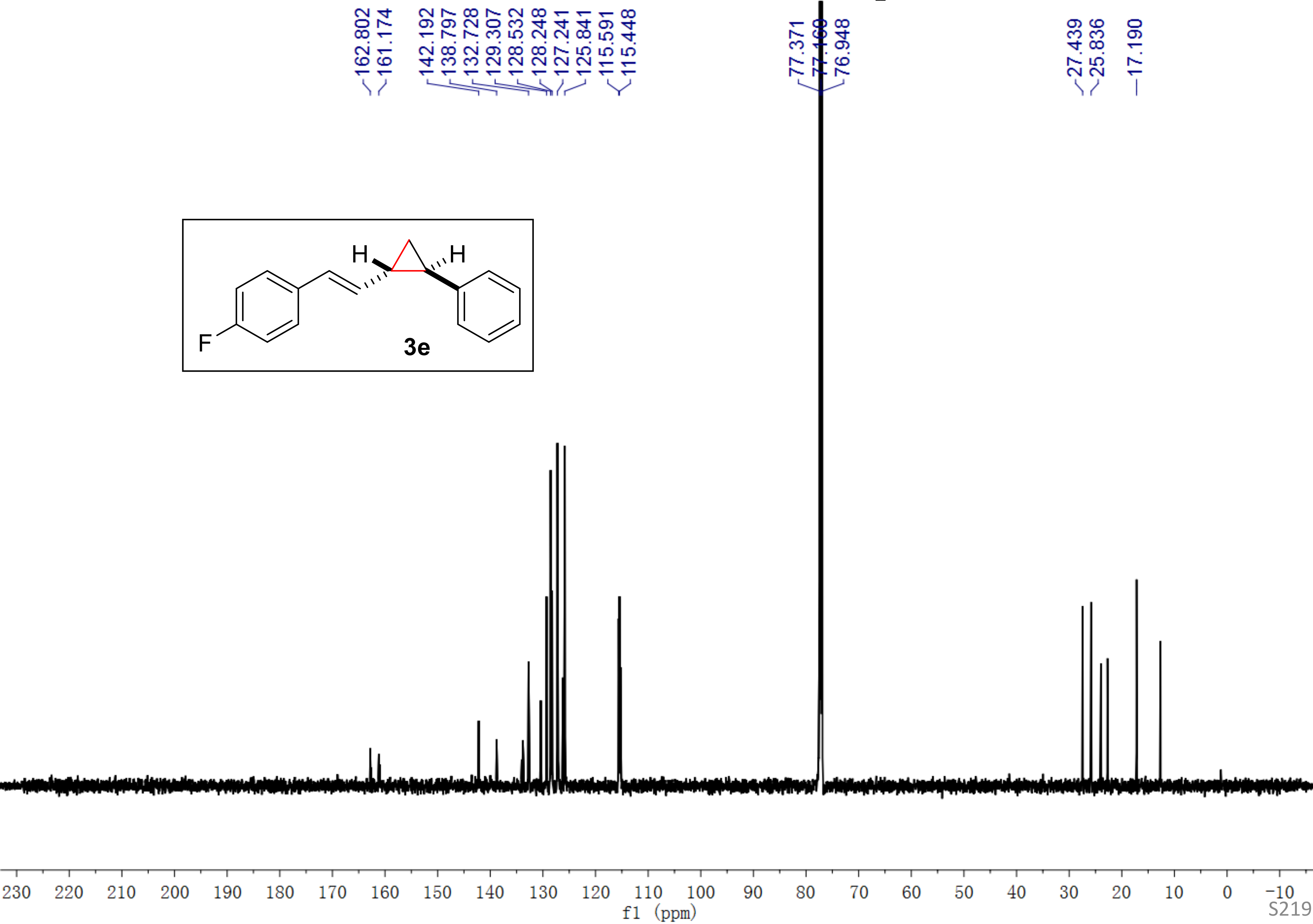
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.196	2468722	3.312
2	8.780	22167886	29.738
3	15.514	3479578	4.668
4	21.527	46427861	62.282
Total		74544046	100.000

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

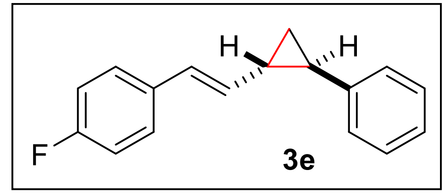


^{13}C of **3e**, 151 MHz, $CDCl_3$



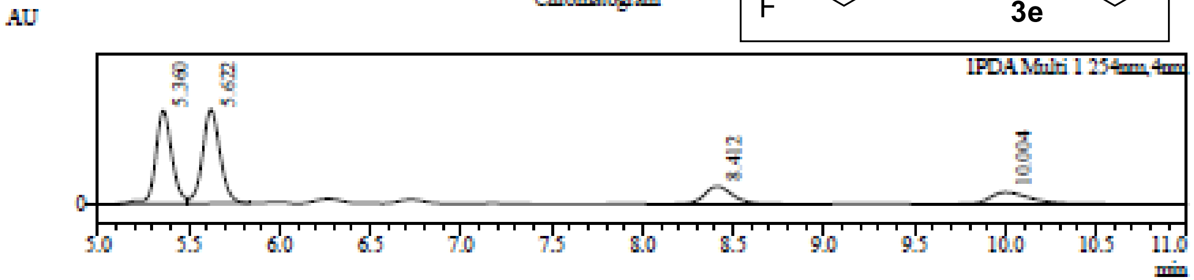
Sample Information

Data File	: J0K-1377-IA-0.1%-1ML.lcd
Sample Name	: J0K-1377-IA-0.1%-1ML
Sample ID	: J0K-1377-IA-0.1%-1ML
Method File	: J0K-0.1%--25min-1ml.lcm

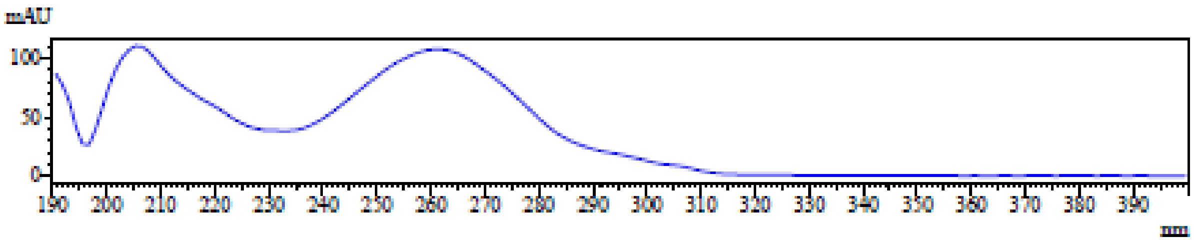


3e

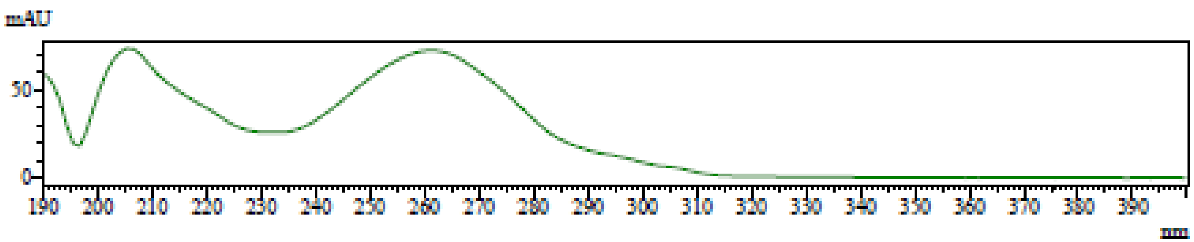
Chromatogram



UV Spectrum
Retention time = 8.412



UV Spectrum
Retention time = 10.004



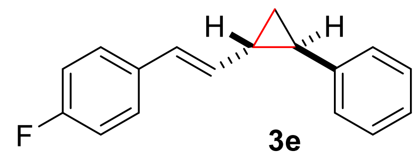
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.360	3120297	36.831
2	5.622	3345439	39.489
3	8.412	1028510	12.140
4	10.004	977585	11.539
Total		8471830	100.000

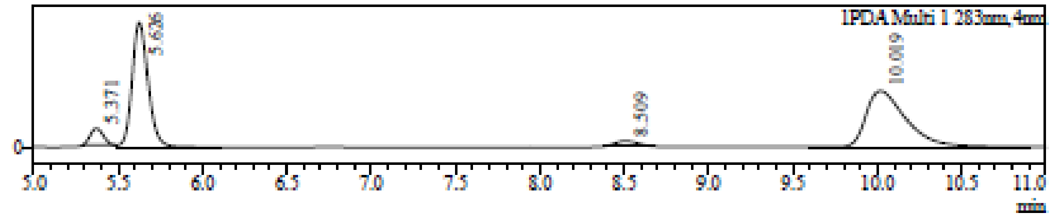
Sample Information

Data File : J0K-1376-IA-0.1%-1ML.lcd
Sample Name : J0K-1376-IA-0.1%-1ML
Sample ID : J0K-1376-IA-0.1%-1ML
Method File : J0K-0.1%--25min-1ml.lcm

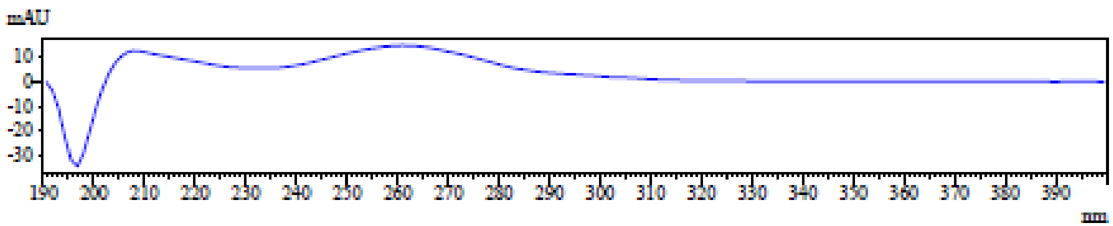


3e

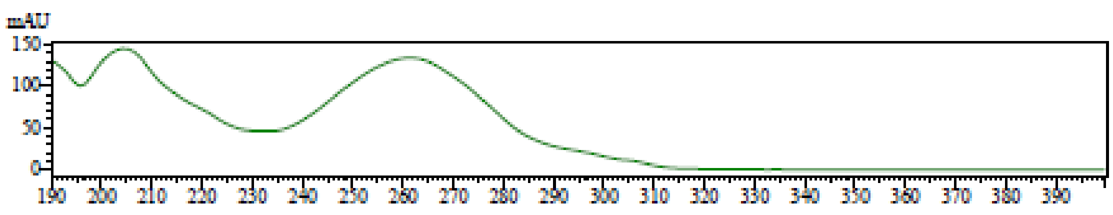
Chromatogram



UV Spectrum
Retention time = 8.509



UV Spectrum
Retention time = 10.019

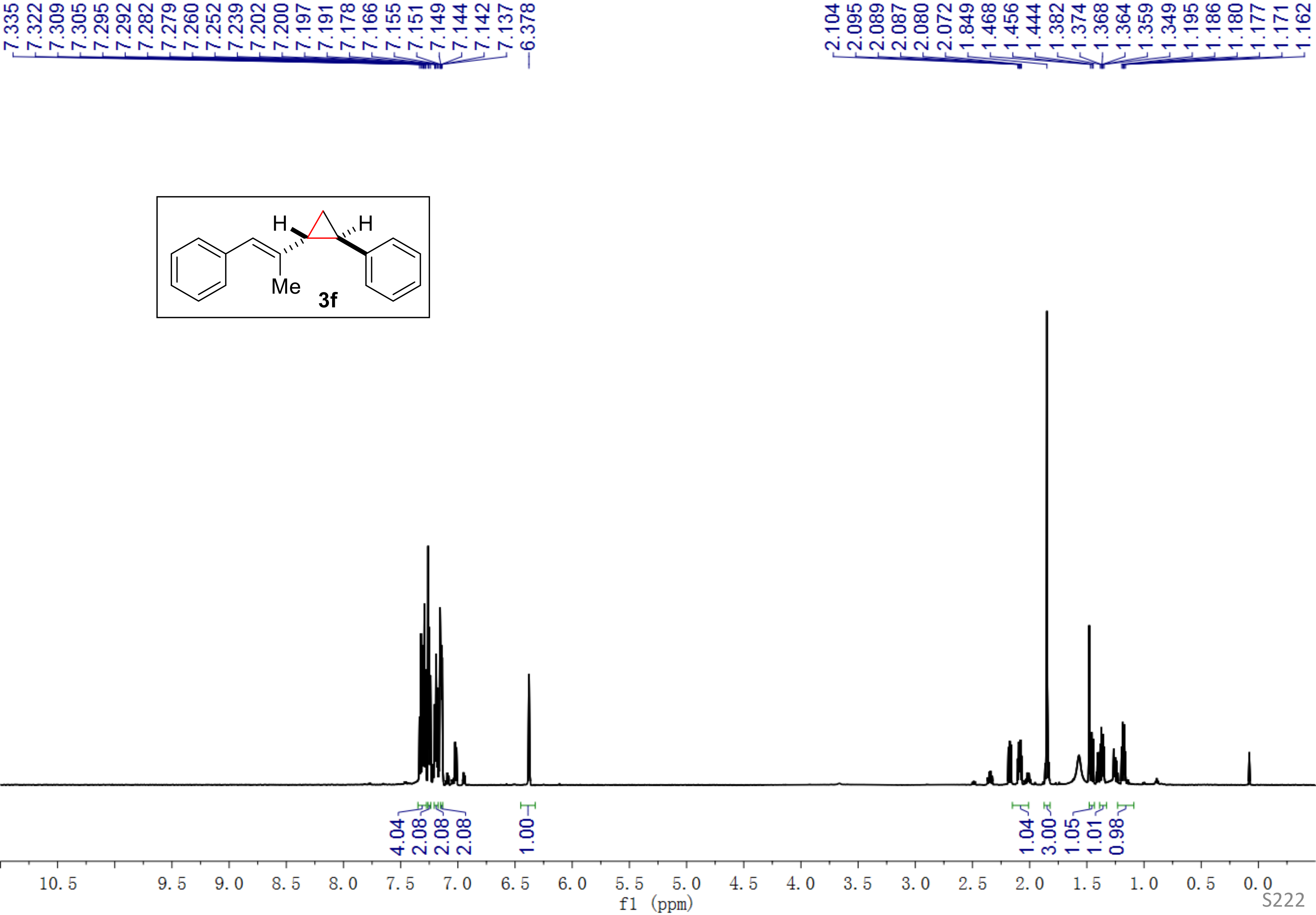


Peak Table

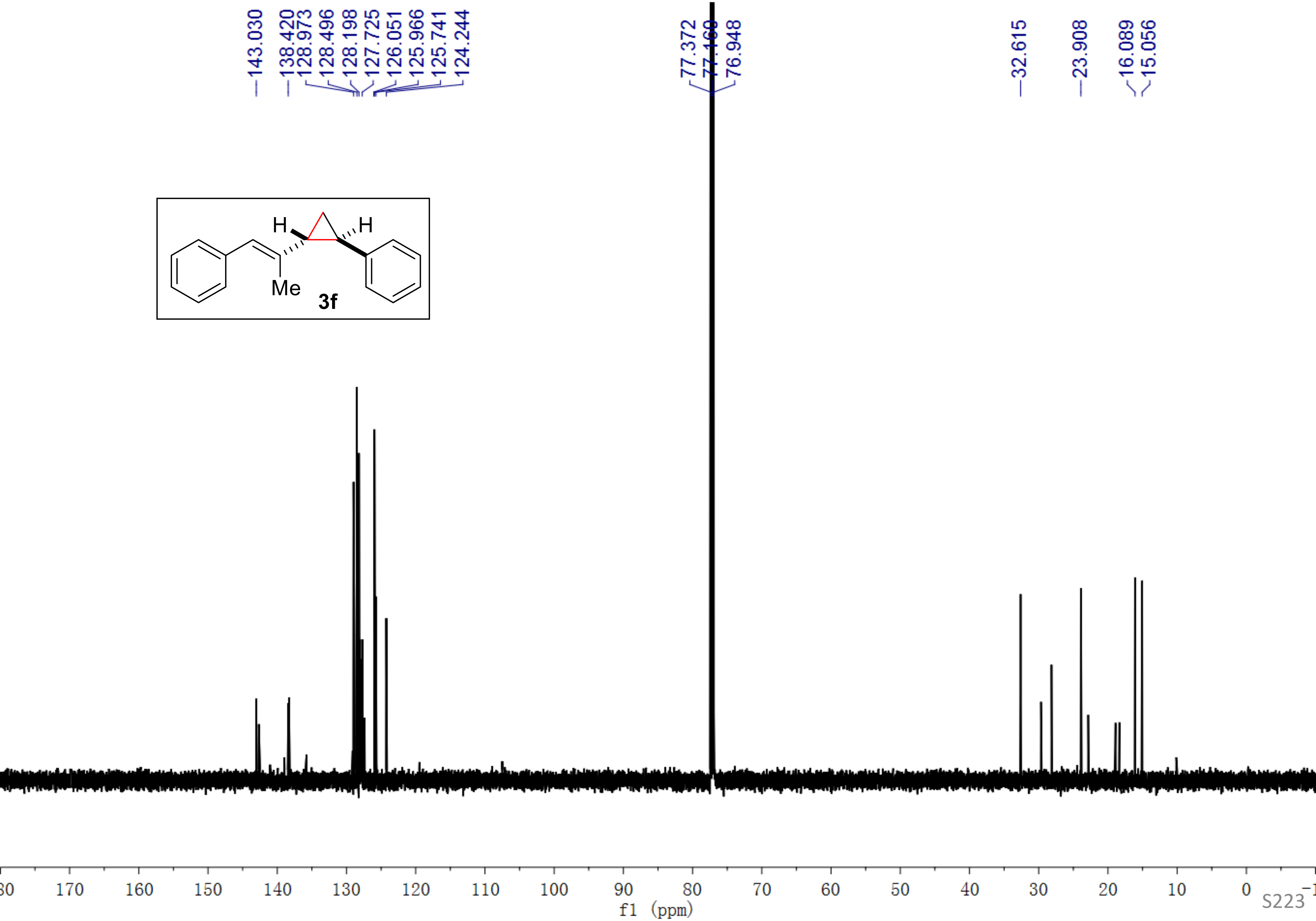
PDA Ch1 283nm

Peak#	Ret. Time	Area	Area%
1	5.371	76062	4.699
2	5.626	701652	43.349
3	8.509	38905	2.404
4	10.019	801991	49.548
Total		1618609	100.000

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

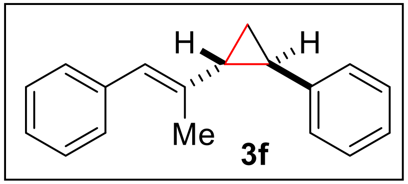


^{13}C of **3f**, 151 MHz, $CDCl_3$

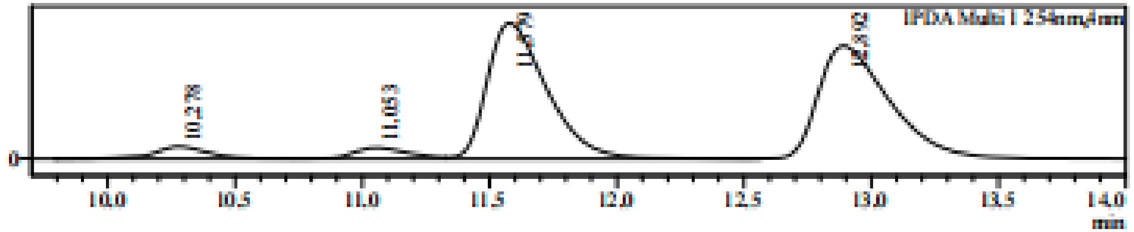


Sample Information

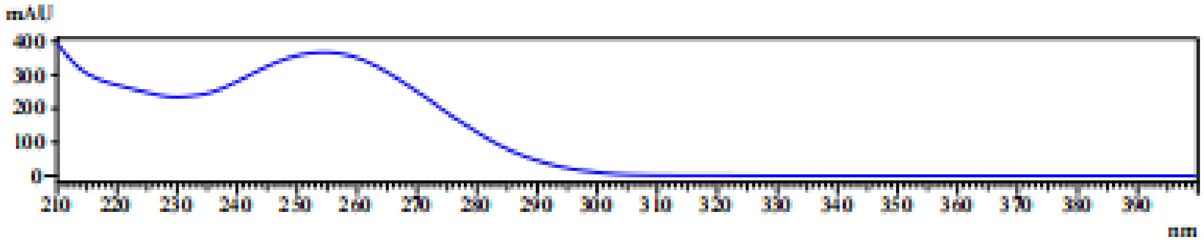
Data File : J0K-1285-IF-0%-0.8ML.lcd
Sample Name : J0K-1285-IF-0%-0.8ML
Sample ID : J0K-1285-IF-0%-0.8ML
Method File : J0K-0%--25min-0.8ml.lcm



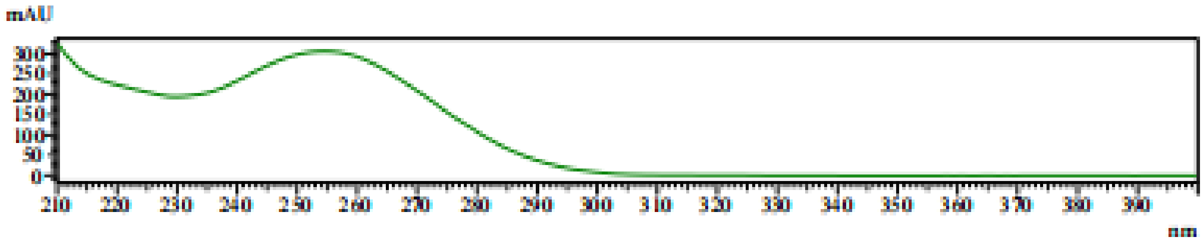
Chromatogram



UV Spectrum
Retention time= 11.579



UV Spectrum
Retention time= 12.892



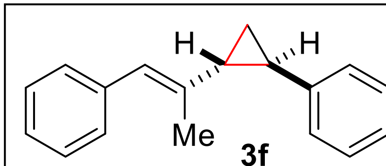
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.278	481395	3.765
2	11.053	433439	3.390
3	11.579	5945107	46.496
4	12.892	5926451	46.350
Total		12786392	100.000

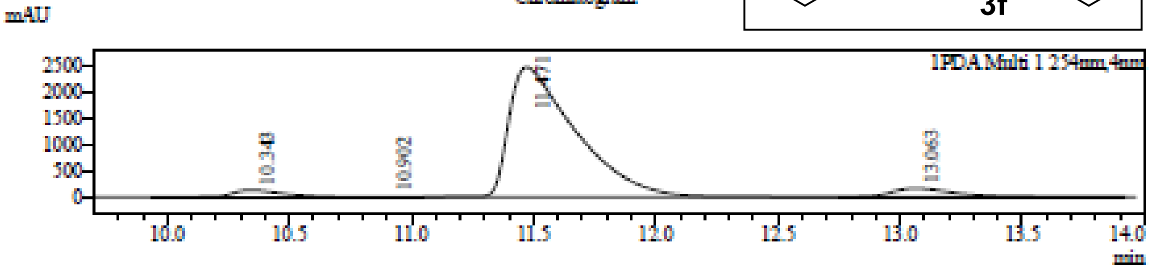
Sample Information

Data File : J0K-1284--IF-0%-0.8ML.lcd
Sample Name : J0K-1284--IF-0%-0.8ML
Sample ID : J0K-1284--IF-0%-0.8ML
Method File : J0K-0%--25min-0.8ml.lcm

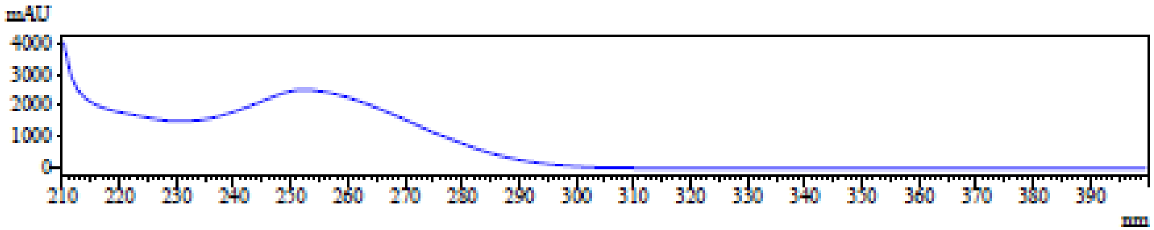


3f

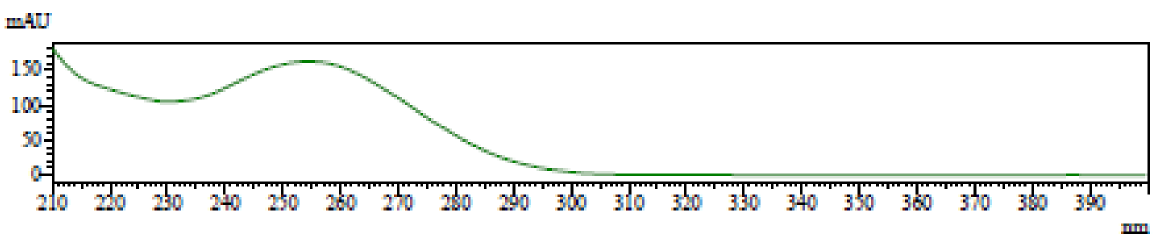
Chromatogram



UV Spectrum
Retention time = 11.471



UV Spectrum
Retention time = 13.063

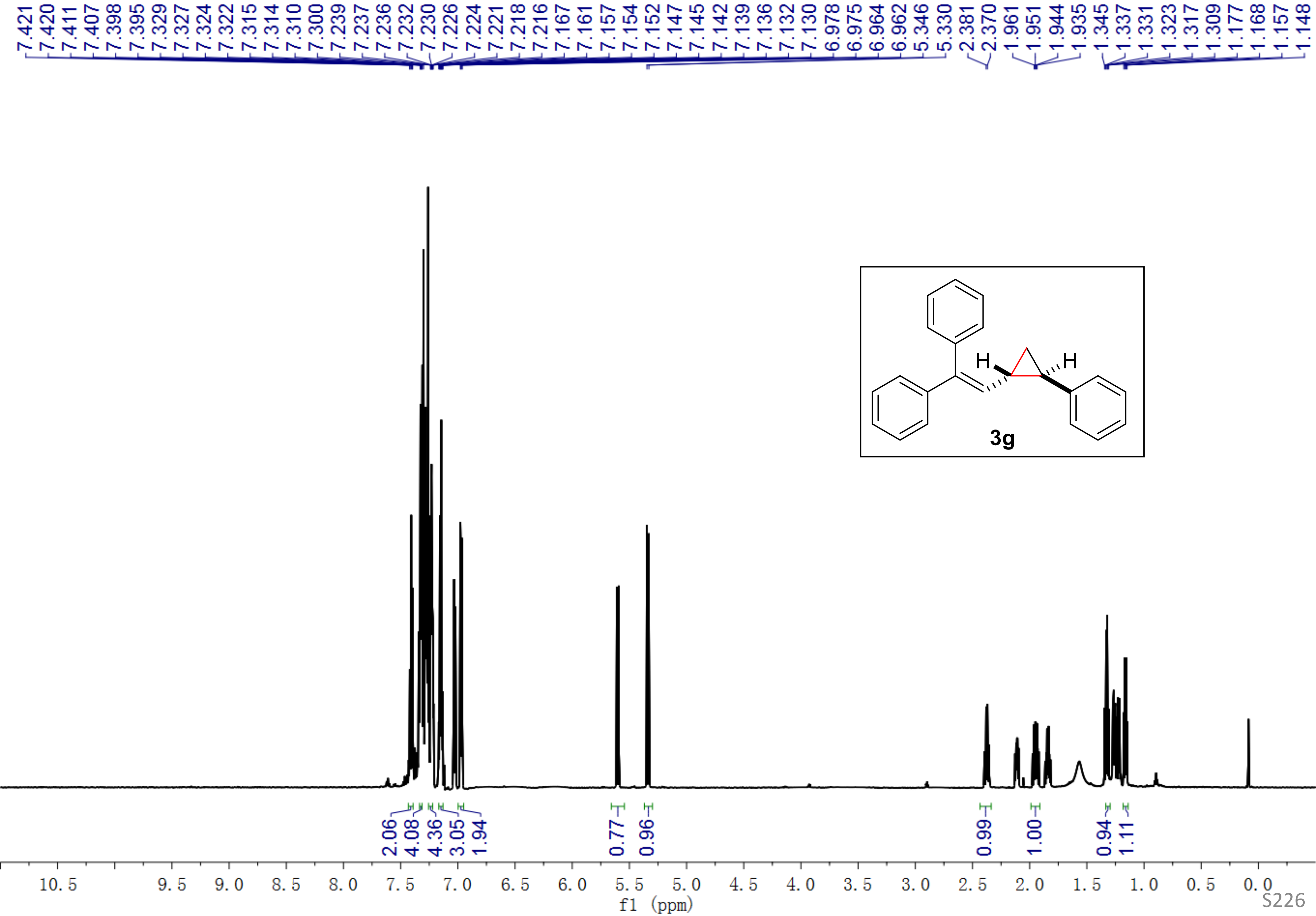


Peak Table

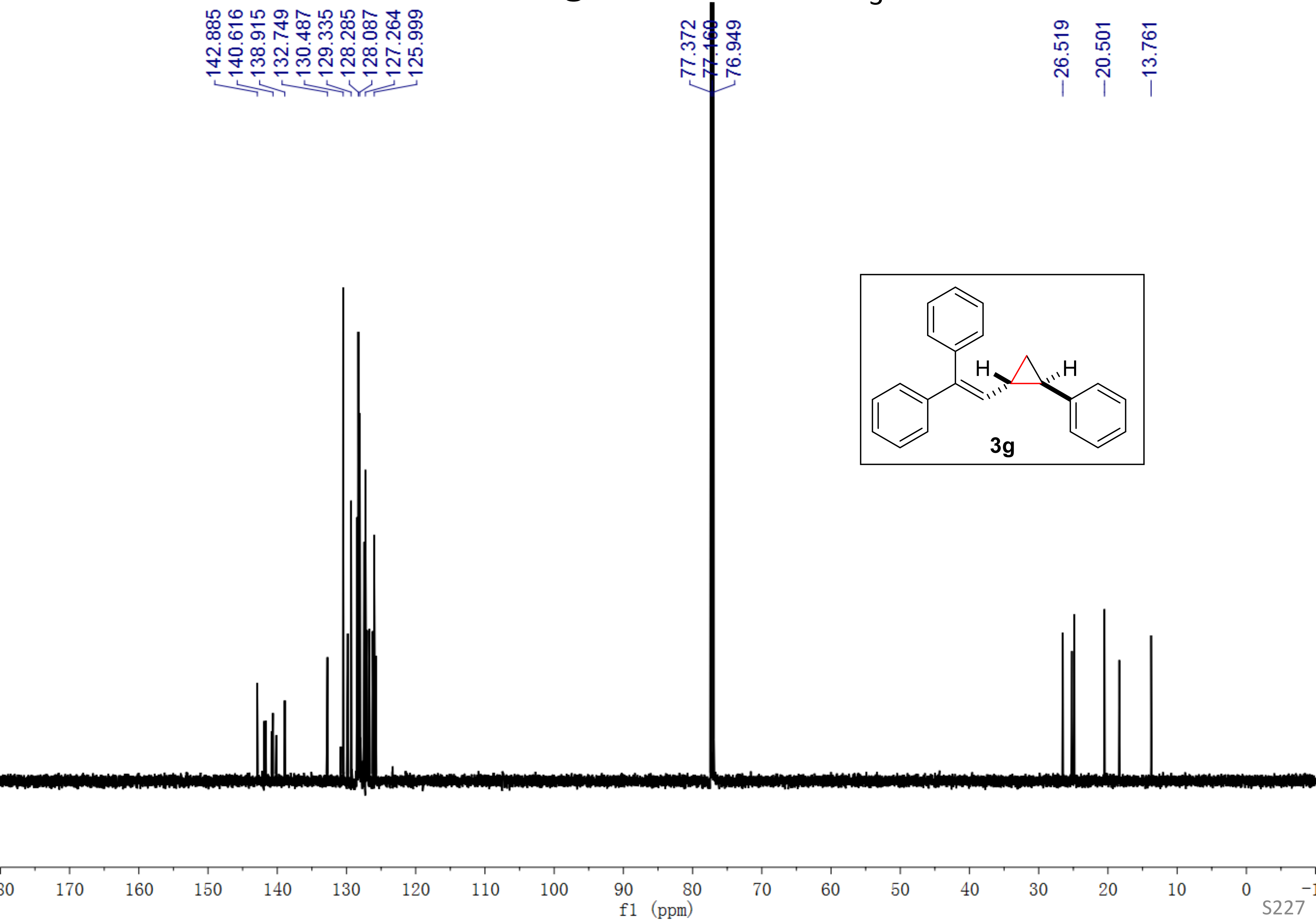
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.343	1827279	3.553
2	10.902	2749	0.005
3	11.471	46837166	91.076
4	13.063	2759252	5.365
Total		51426446	100.000

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

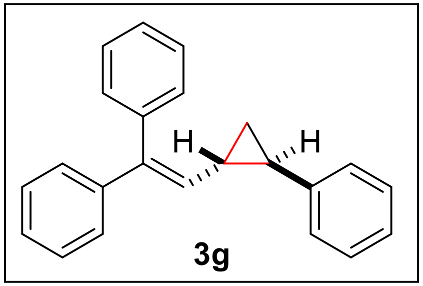


^{13}C of **3g**, 151 MHz, $CDCl_3$

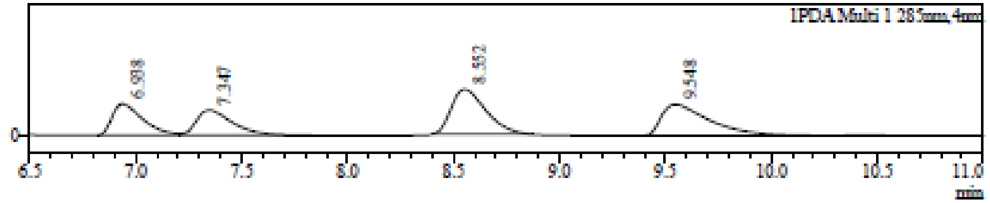


Sample Information

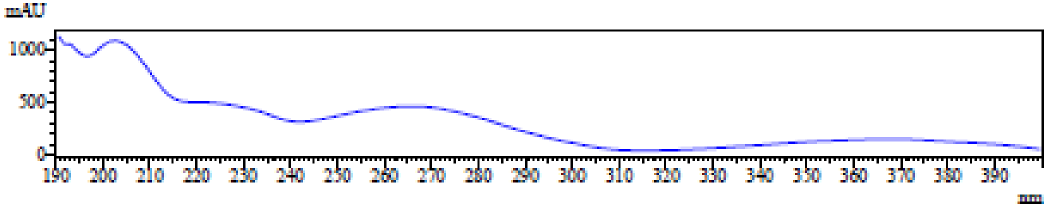
Data File : J0K-1283-IB-0.1%-1ML.lcd
Sample Name : J0K-1283-IB-0.1%-1ML
Sample ID : J0K-1283-IB-0.1%-1ML
Method File : J0K-0.1%--25min-1ml.lcm



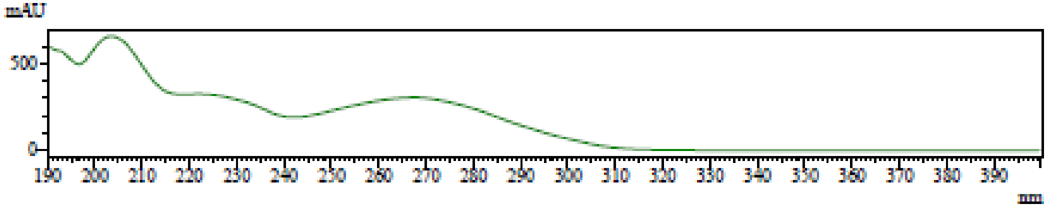
3g



UV Spectrum
Retention time = 8.552



UV Spectrum
Retention time = 9.548



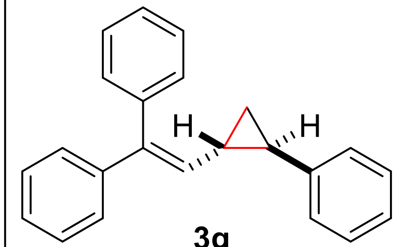
Peak Table

PDA Ch1 285nm

Peak#	Ret. Time	Area	Area%
1	6.938	1920411	19.304
2	7.347	1854083	18.637
3	8.552	3112729	31.289
4	9.548	3061035	30.770
Total		9948257	100.000

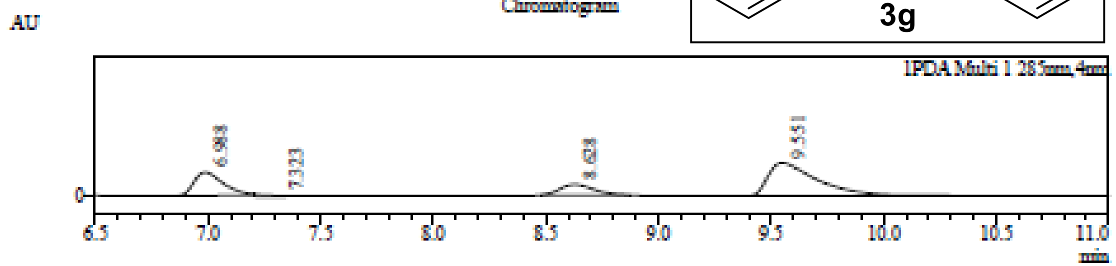
Sample Information

Data File	: J0K-1282-IB-0.1%-1ML.lcd
Sample Name	: J0K-1282-IB-0.1%-1ML
Sample ID	: J0K-1282-IB-0.1%-1ML
Method File	: J0K-0.1%--25min-1ml.lcm

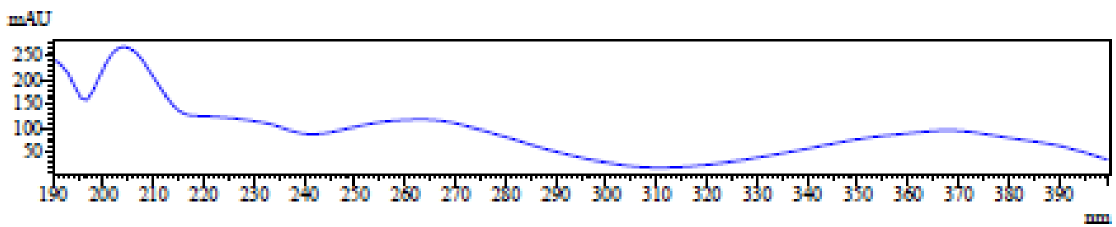


3g

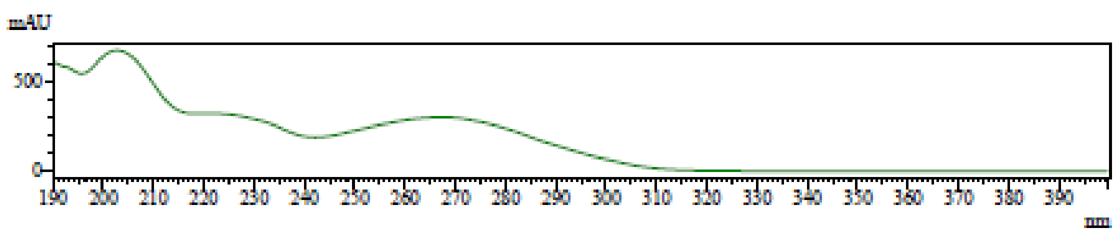
Chromatogram



UV Spectrum
Retention time = 8.628



UV Spectrum
Retention time = 9.551

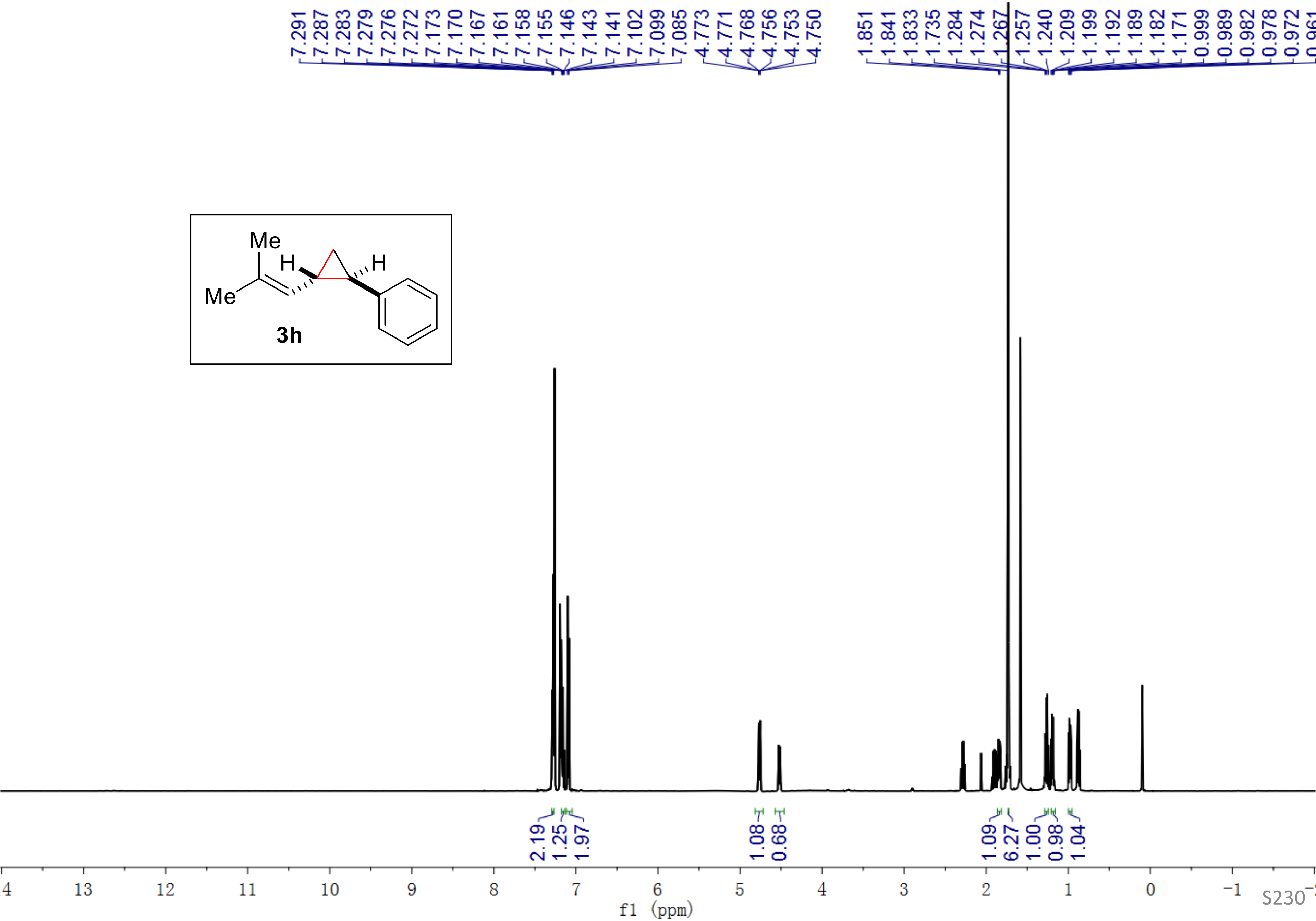


Peak Table

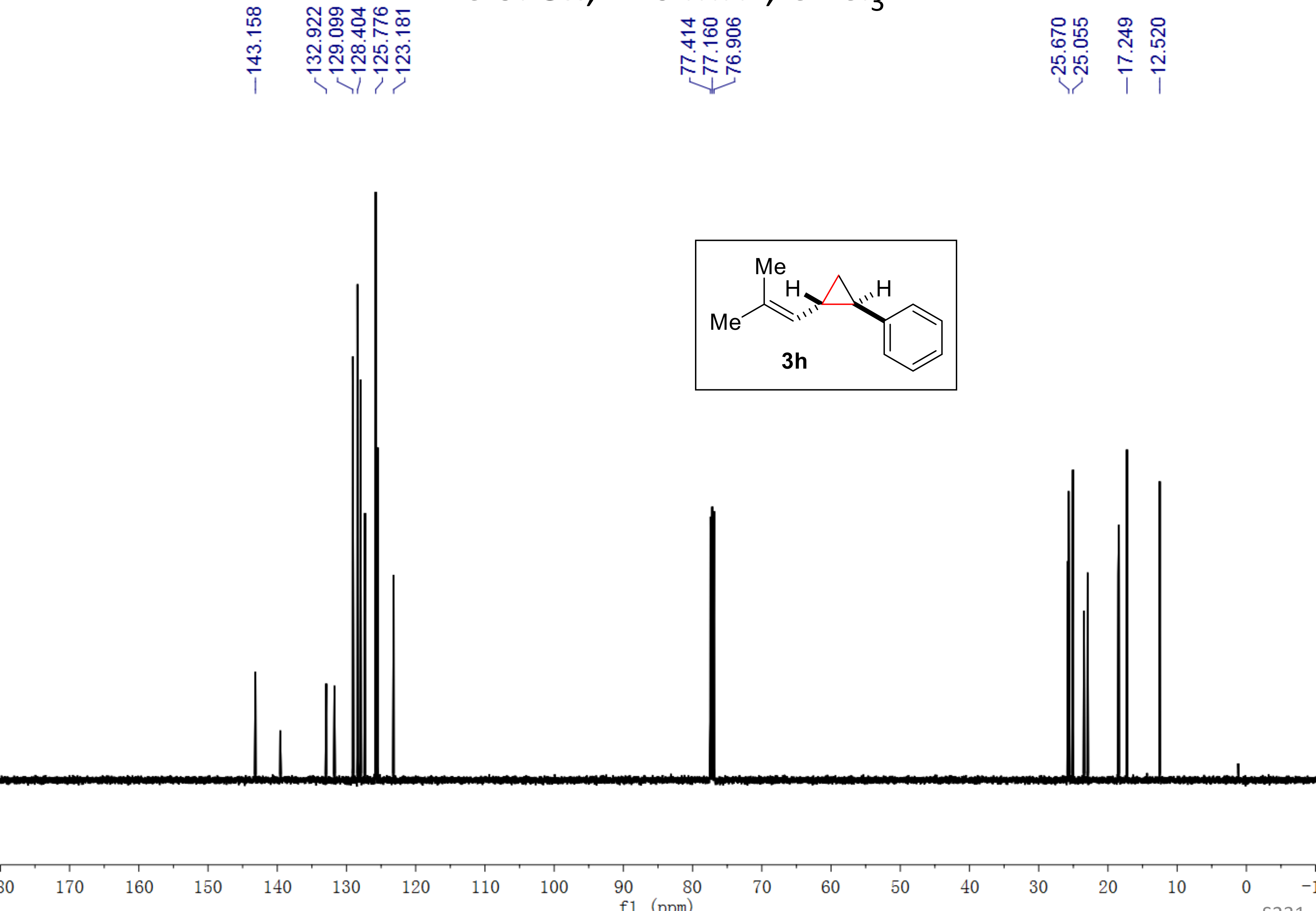
PDA Ch1 285nm

Peak#	Ret. Time	Area	Area%
1	6.988	1226785	25.052
2	7.323	61485	1.256
3	8.628	645434	13.181
4	9.551	2963179	60.512
Total		4896883	100.000

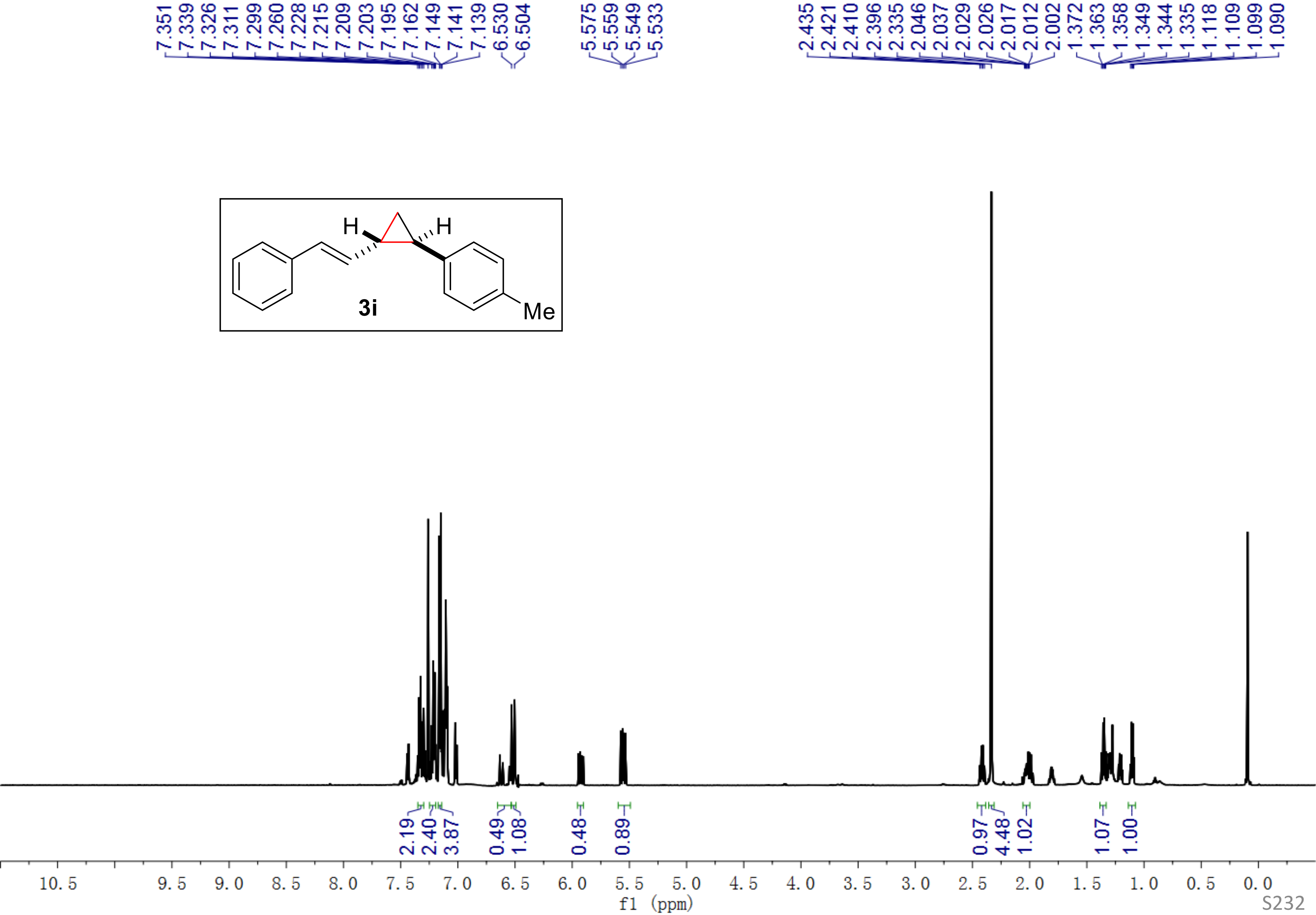
^{1}H of **3h**, 600 MHz, $CDCl_3$



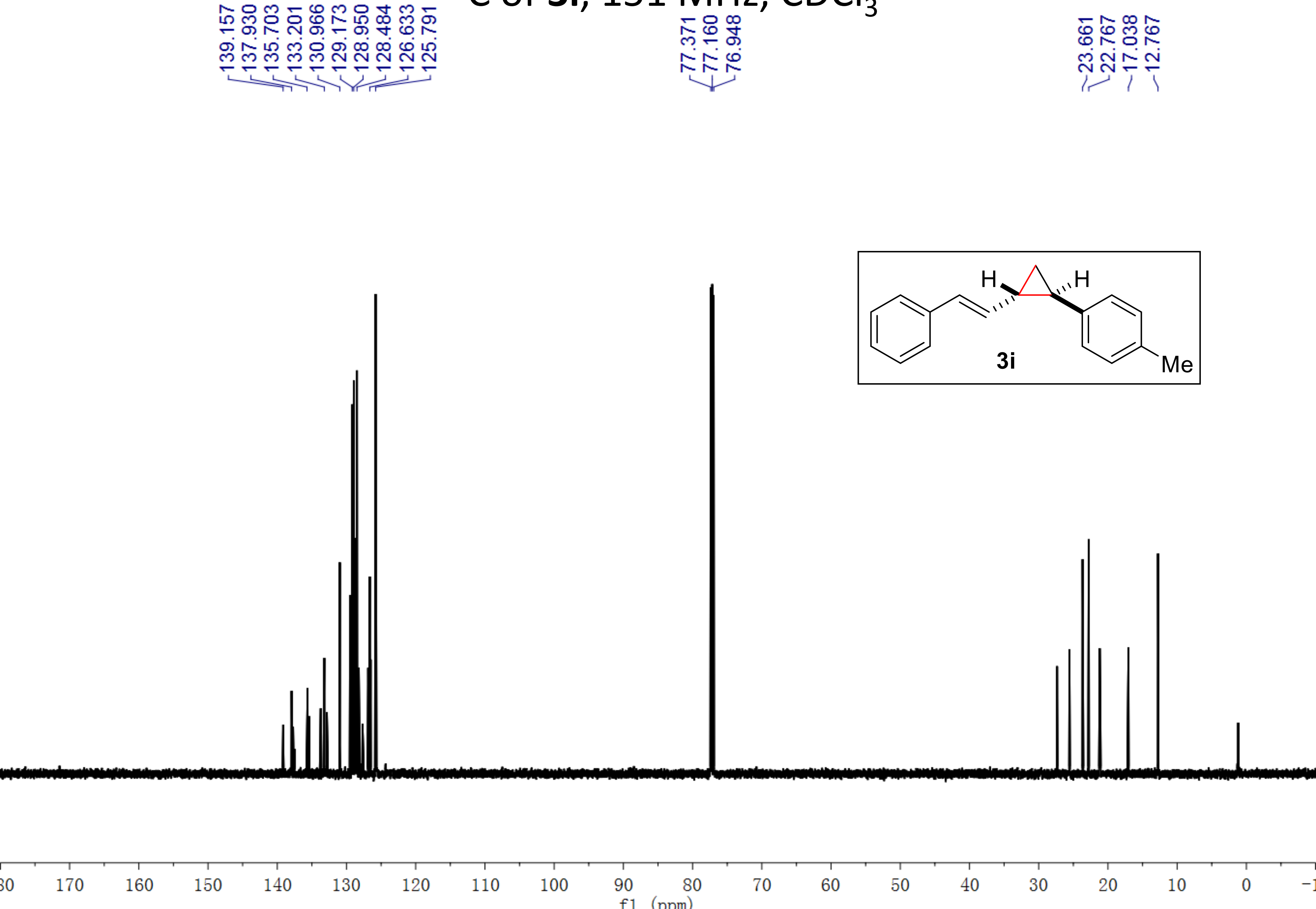
^{13}C of **3h**, 126 MHz, $CDCl_3$



^1H of **3i**, 600 MHz, $CDCl_3$

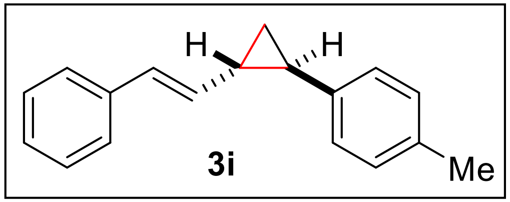


^{13}C of **3i**, 151 MHz, $CDCl_3$

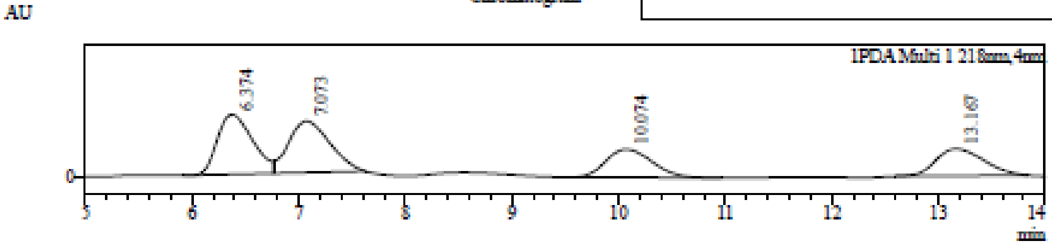


Sample Information

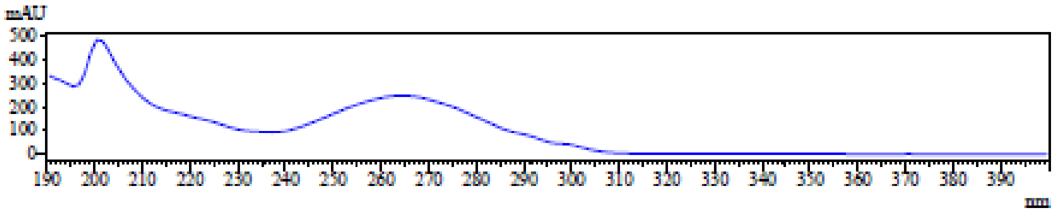
Data File	: J0K-1590-ODH-0.5%-0.8ML-2.lcd
Sample Name	: J0K-1590-ODH-0.5%-0.8ML-2
Sample ID	: J0K-1590-ODH-0.5%-0.8ML-2
Method File	: J0K-0.5%--60min-0.8ml.lcm



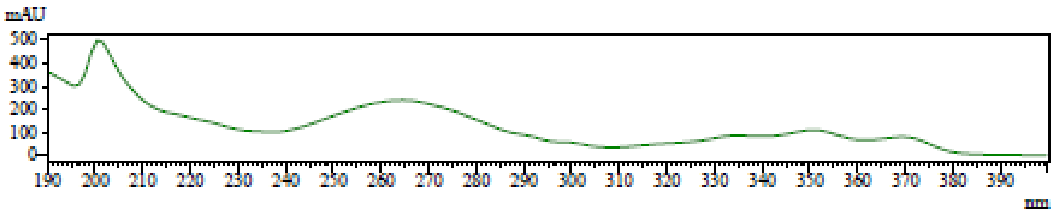
Chromatogram



UV Spectrum
Retention time = 10.074



UV Spectrum
Retention time = 13.167



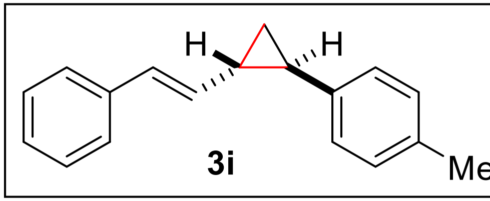
Peak Table

PDA Ch1 218nm

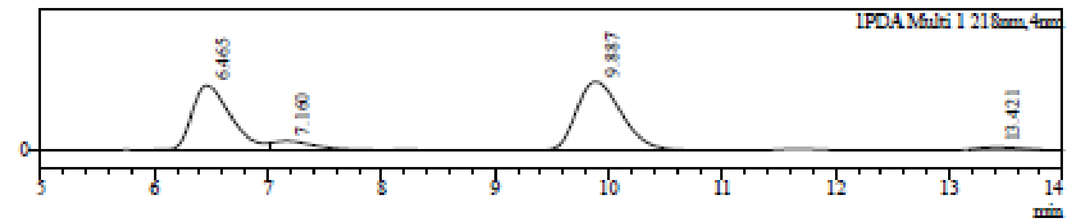
Peak#	Ret. Time	Area	Area%
1	6.374	8329828	30.842
2	7.073	8435615	31.234
3	10.074	5120959	18.961
4	13.167	5121816	18.964
Total		27008219	100.000

Sample Information

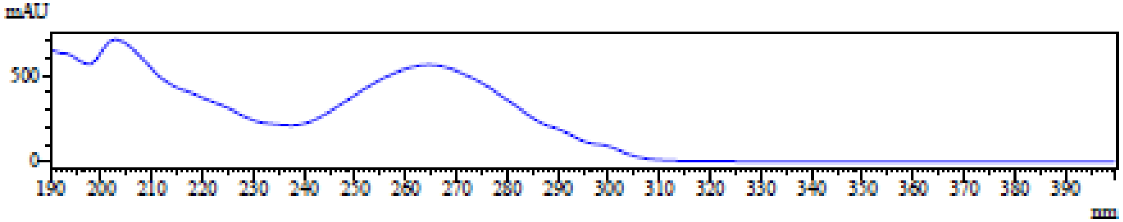
Data File	: J0K-1589-ODH-0.5%-0.8ML-2.lcd
Sample Name	: J0K-1589-ODH-0.5%-0.8ML-2
Sample ID	: J0K-1589-ODH-0.5%-0.8ML-2
Method File	: J0K-0.5%--60min-0.8ml.lcm



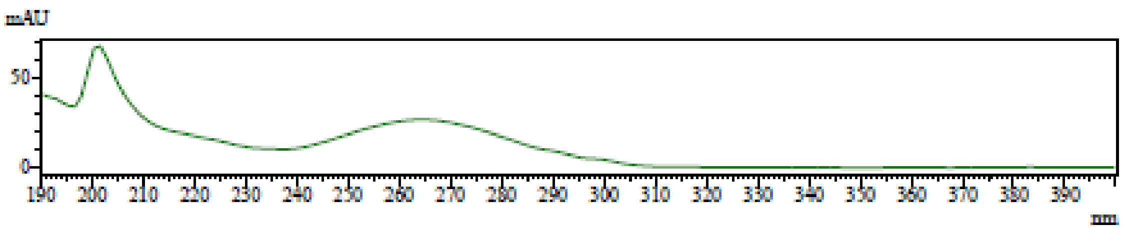
Chromatogram



UV Spectrum
Retention time = 9.887



UV Spectrum
Retention time = 13.421

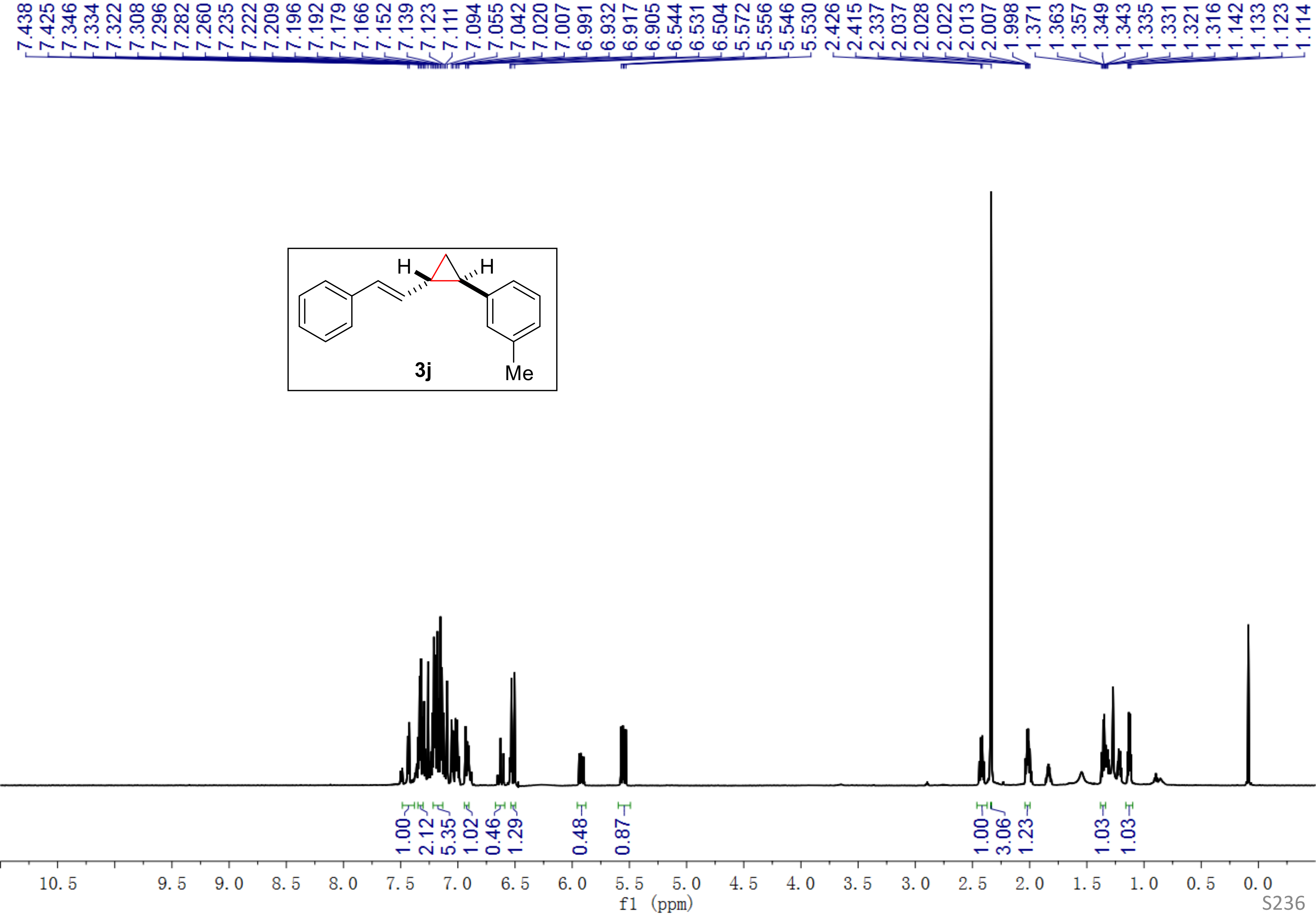


Peak Table

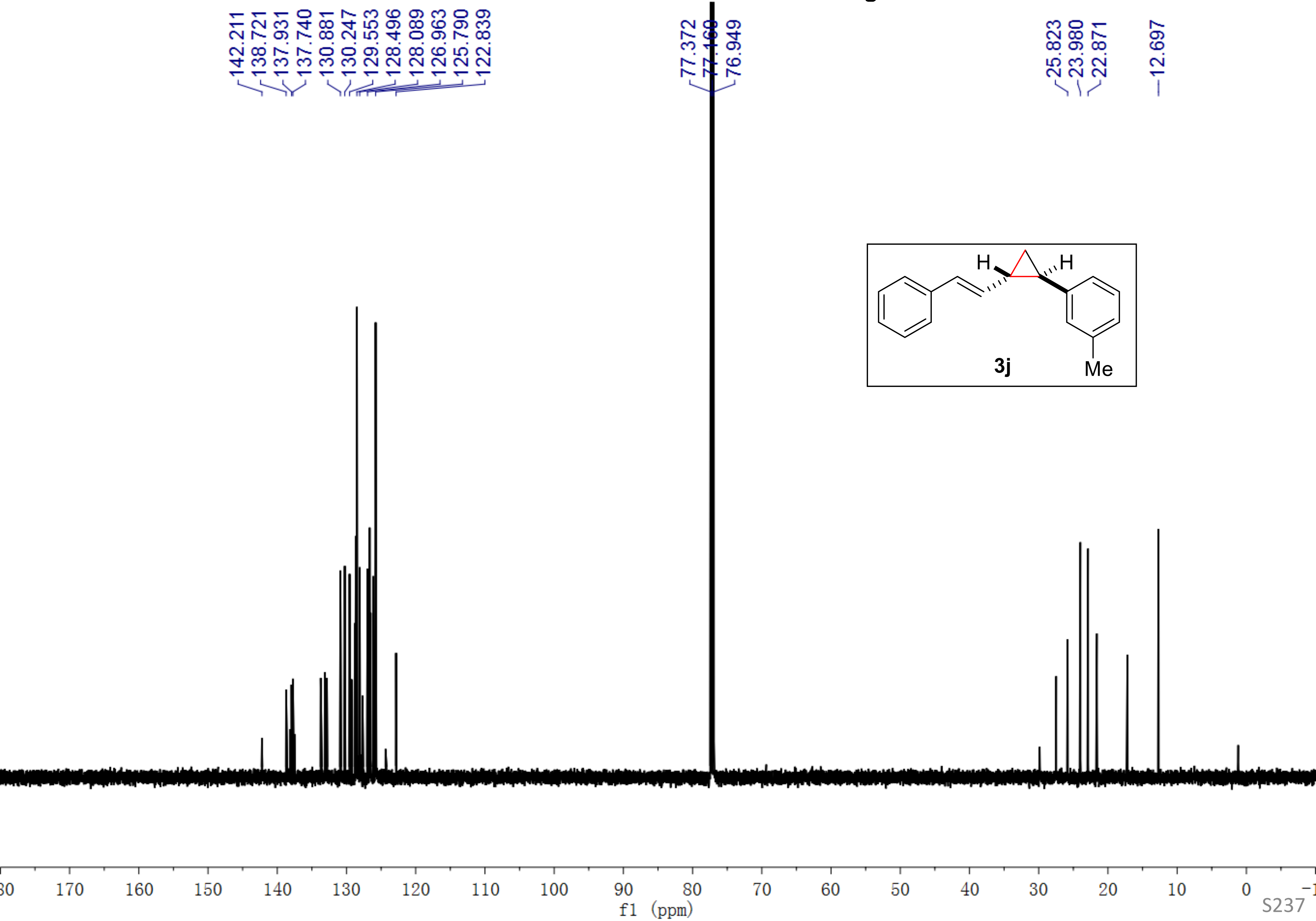
PDA Ch1 218nm

Peak#	Ret. Time	Area	Area%
1	6.465	8879375	41.433
2	7.160	1473465	6.876
3	9.887	10782091	50.312
4	13.421	295681	1.380
Total		21430612	100.000

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

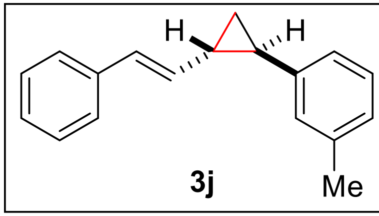


^{13}C of **3j**, 151 MHz, $CDCl_3$



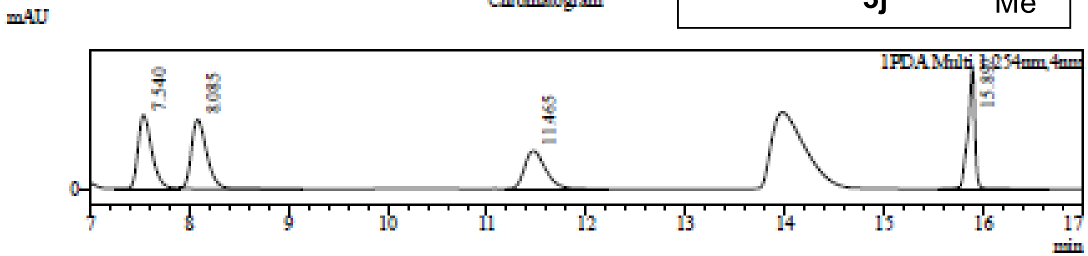
Sample Information

Data File	: J0K-1582-IB-0.1%-1ML.lcd
Sample Name	: J0K-1582-IB-0.1%-1ML
Sample ID	: J0K-1582-IB-0.1%-1ML
Method File	: J0K-0.1%--40min-1ml.lcm

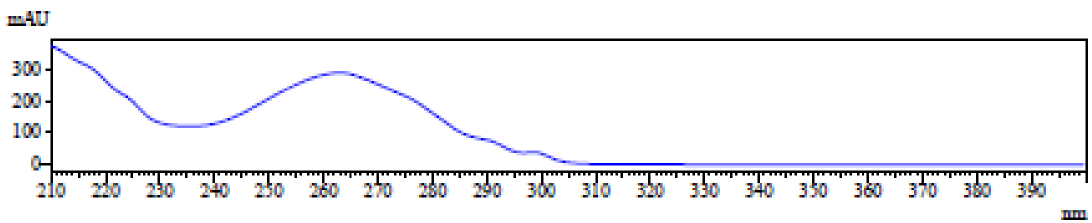


3j

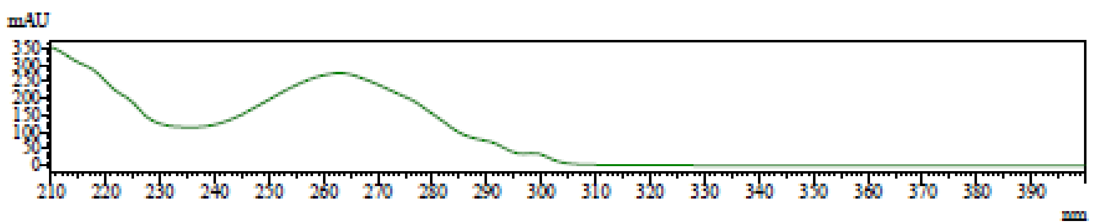
Chromatogram



UV Spectrum
Retention time = 7.540



UV Spectrum
Retention time = 8.085



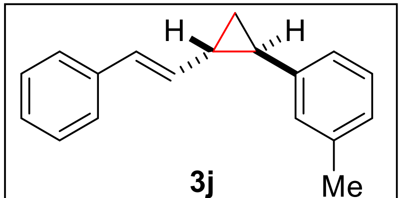
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.540	2448537	27.956
2	8.085	2476116	28.271
3	11.465	1858744	21.222
4	15.892	1975002	22.550
Total		8758399	100.000

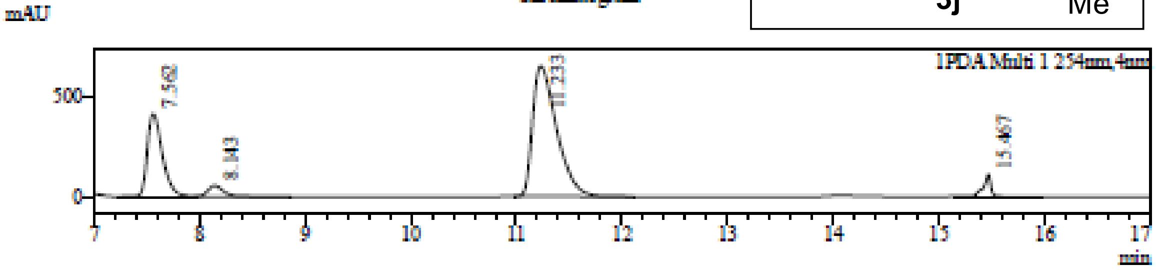
Sample Information

Data File : J0K-1581-IB-0.1%-1ML.lcd
Sample Name : J0K-1581-IB-0.1%-1ML
Sample ID : J0K-1581-IB-0.1%-1ML
Method File : J0K-0.1%--40min-1ml.lcm

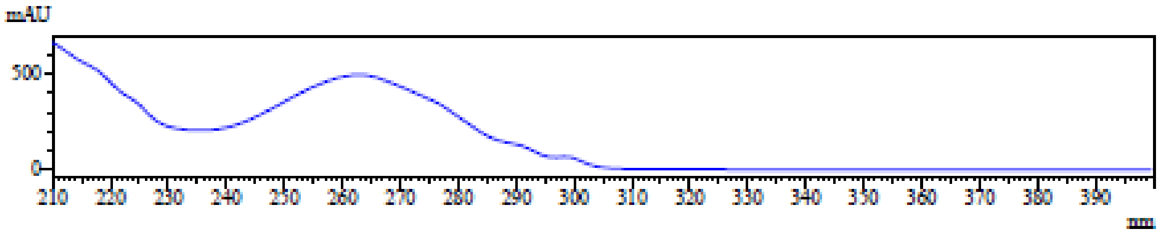


3j

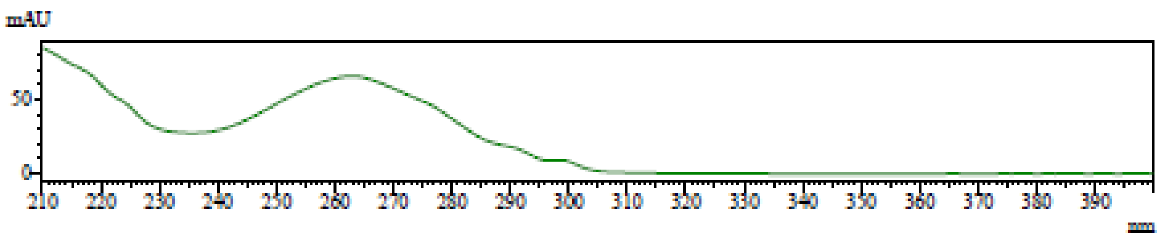
Chromatogram



UV Spectrum
Retention time = 7.562



UV Spectrum
Retention time = 8.143

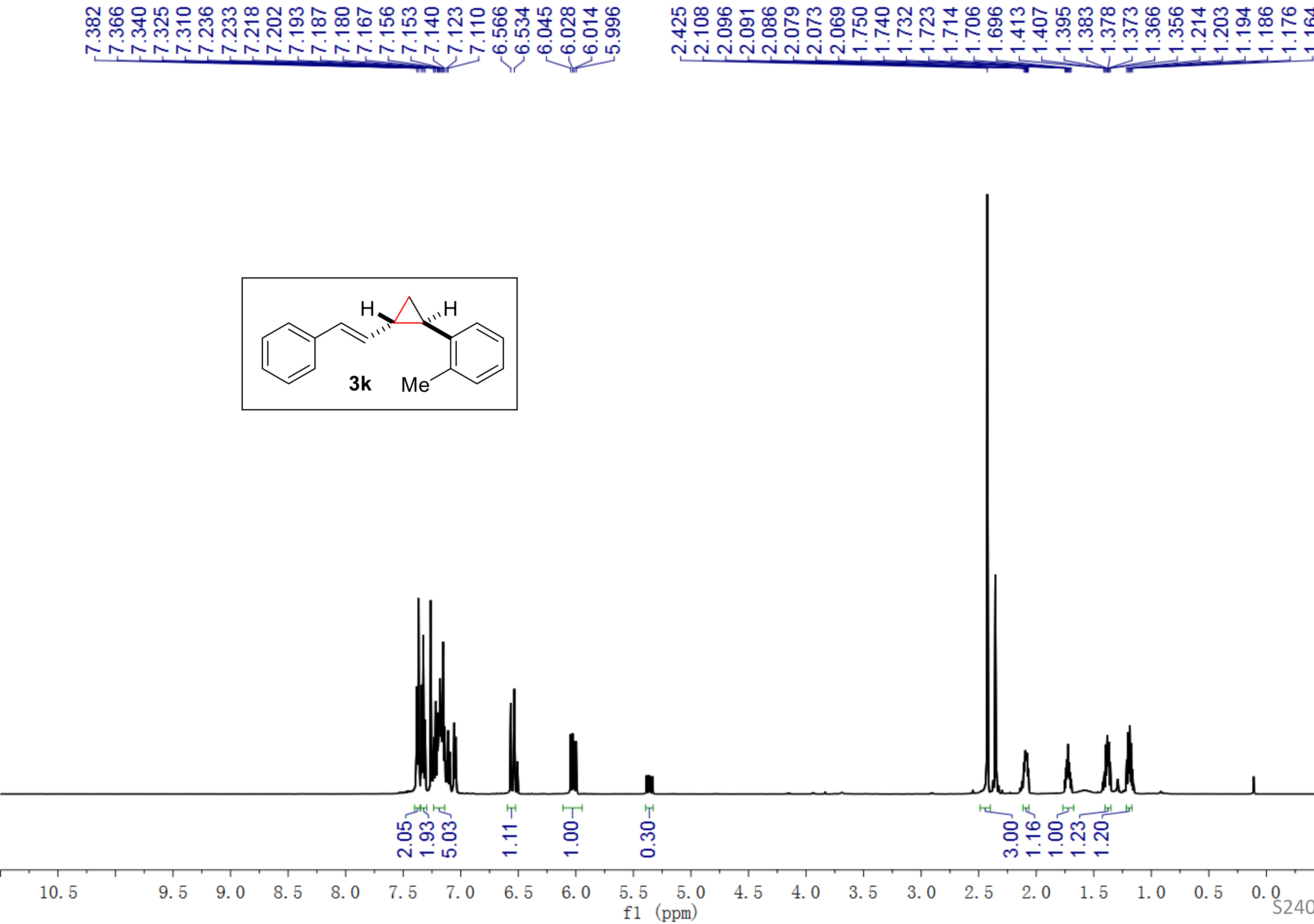


Peak Table

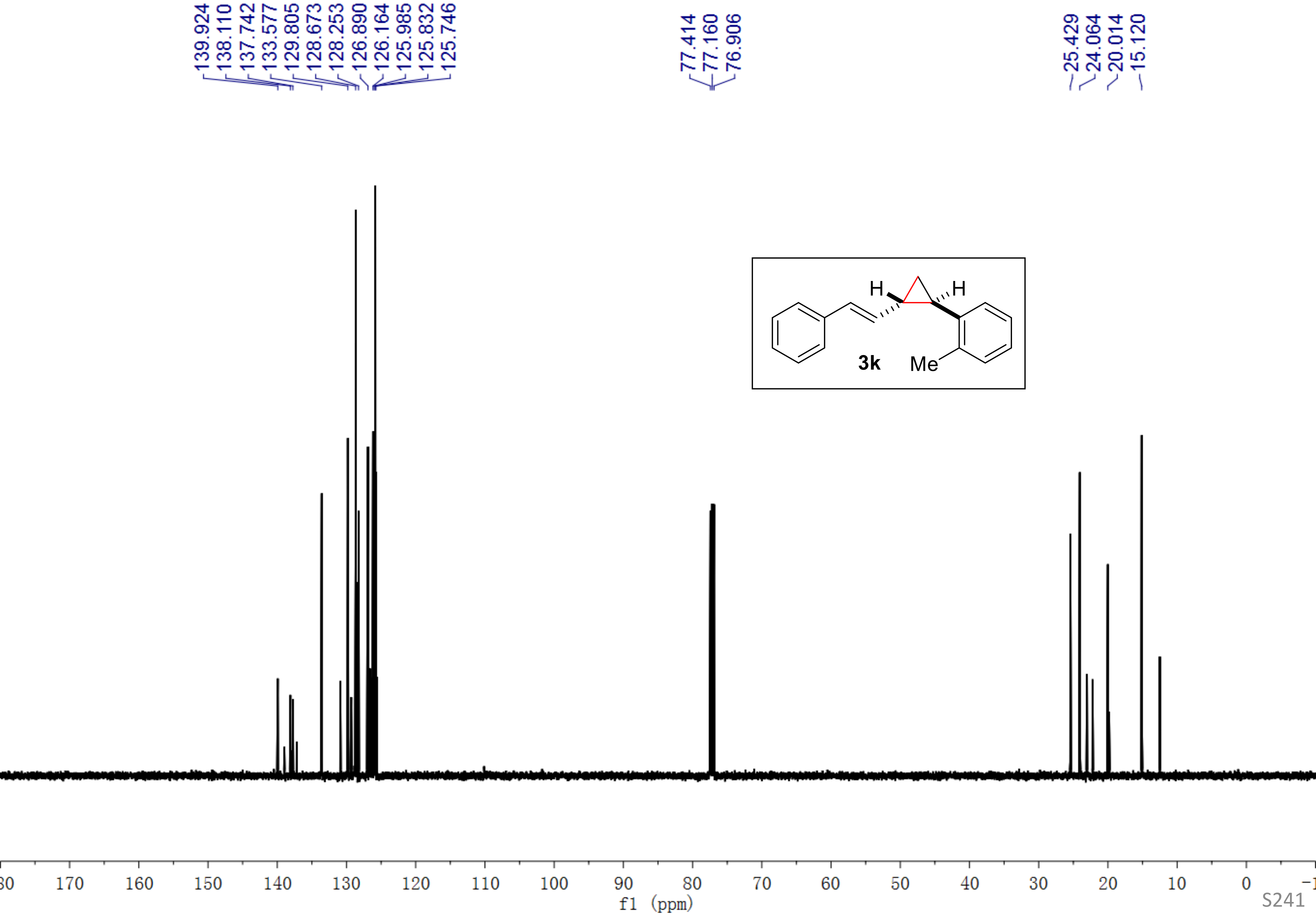
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.562	4144019	26.559
2	8.143	569834	3.652
3	11.233	10356217	66.372
4	15.467	533184	3.417
Total		15603255	100.000

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

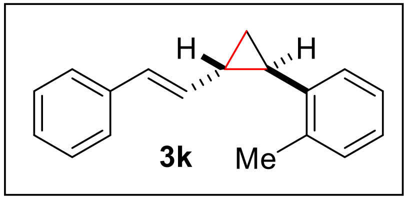


^{13}C of **3k**, 151 MHz, $CDCl_3$

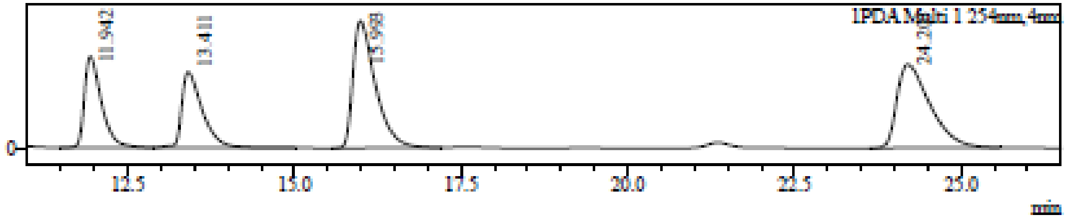


Sample Information

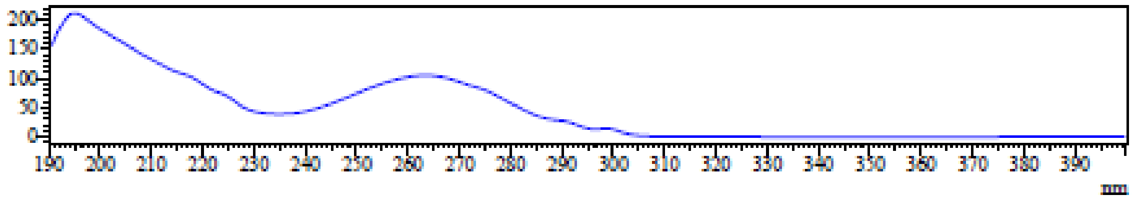
Data File : J0K-1256--IB-0%-1ML.lcd
Sample Name : J0K-1256--IB-0%-1ML
Sample ID : J0K-1256--IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm



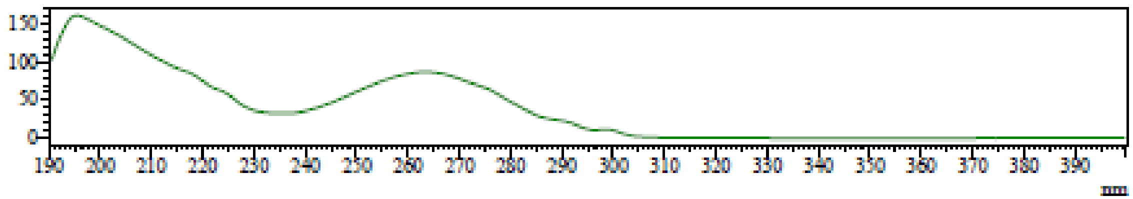
Chromatogram



UV Spectrum
Retention time = 11.942



UV Spectrum
Retention time = 13.411



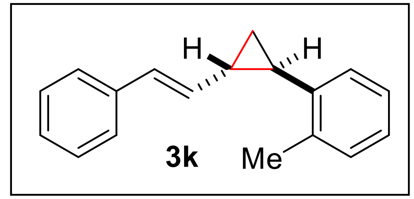
Peak Table

PDA Ch1 254nm

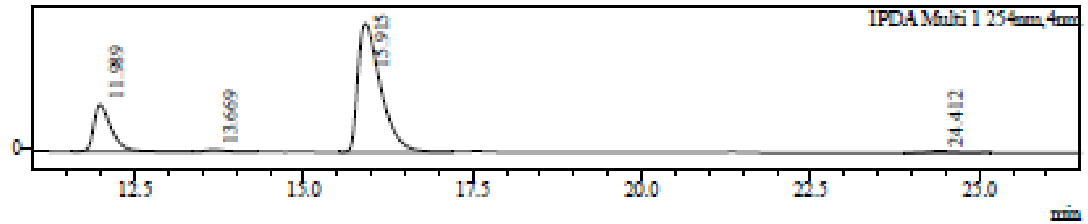
Peak#	Ret. Time	Area	Area%
1	11.942	1569267	17.980
2	13.411	1572804	18.021
3	15.993	2839738	32.537
4	24.203	2745845	31.461
Total		8727654	100.000

Sample Information

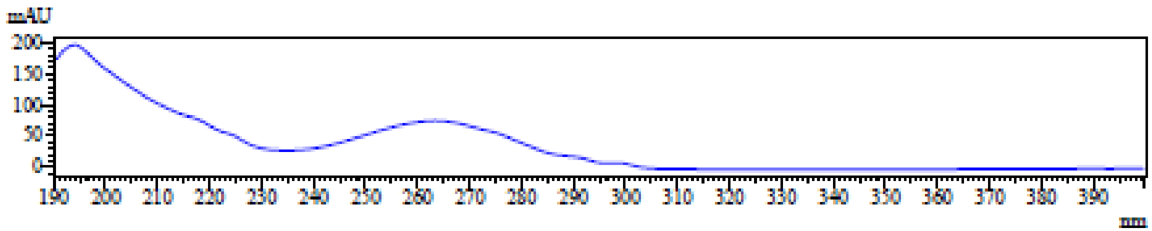
Data File : J0K-1255--IB-0%-1ML.lcd
Sample Name : J0K-1255--IB-0%-1ML
Sample ID : J0K-1255--IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm



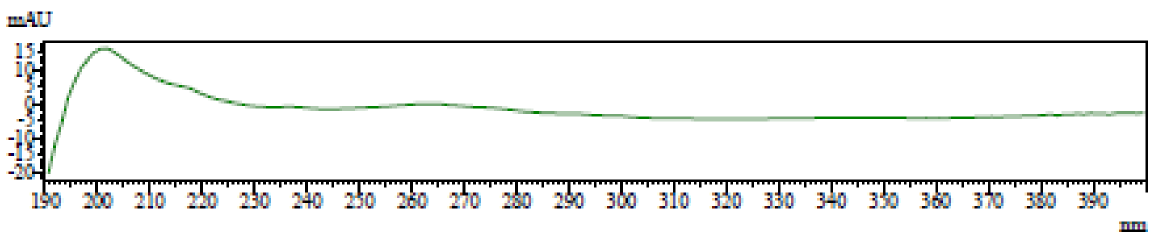
Chromatogram



UV Spectrum
Retention time = 11.989



UV Spectrum
Retention time = 13.669

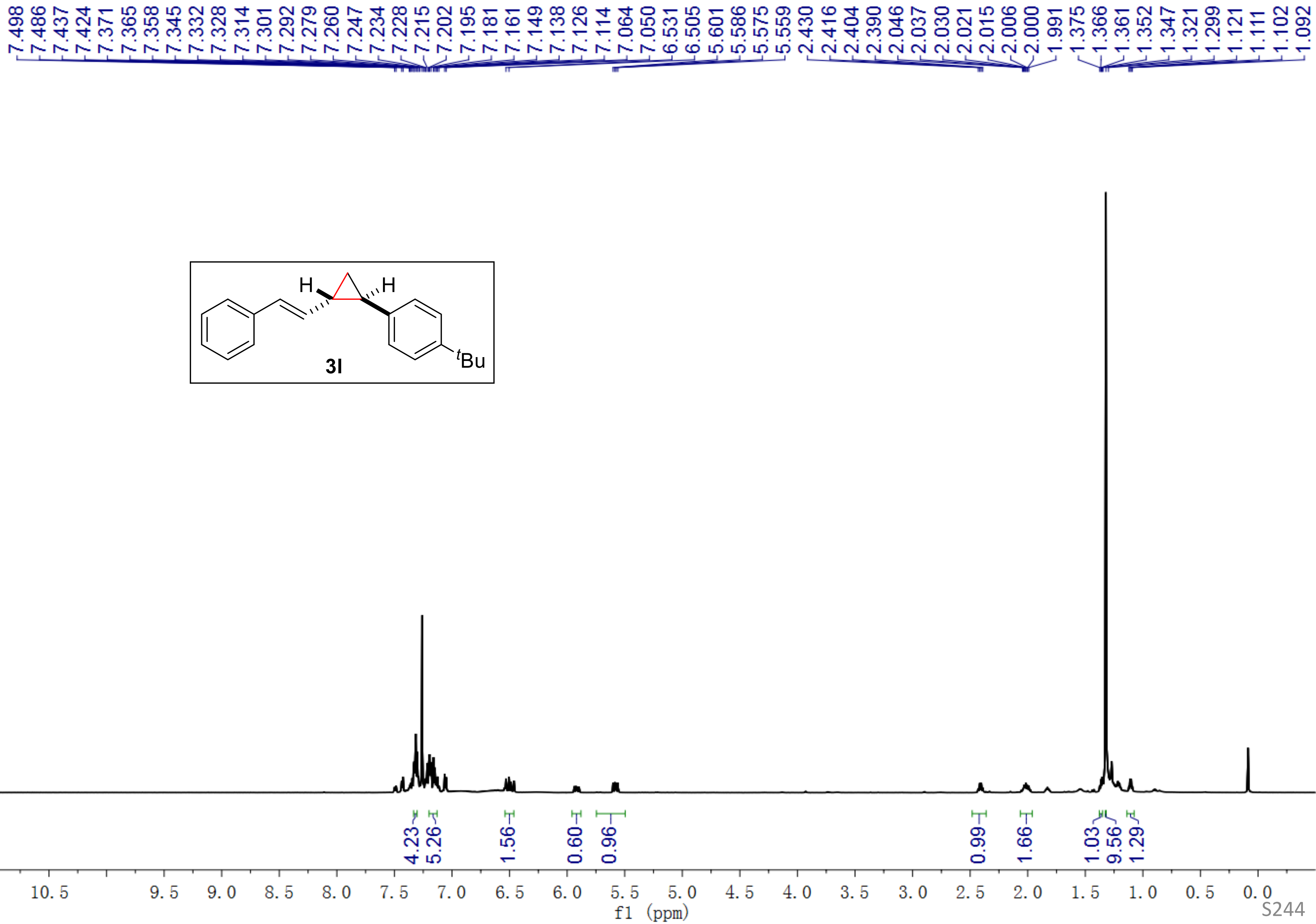


Peak Table

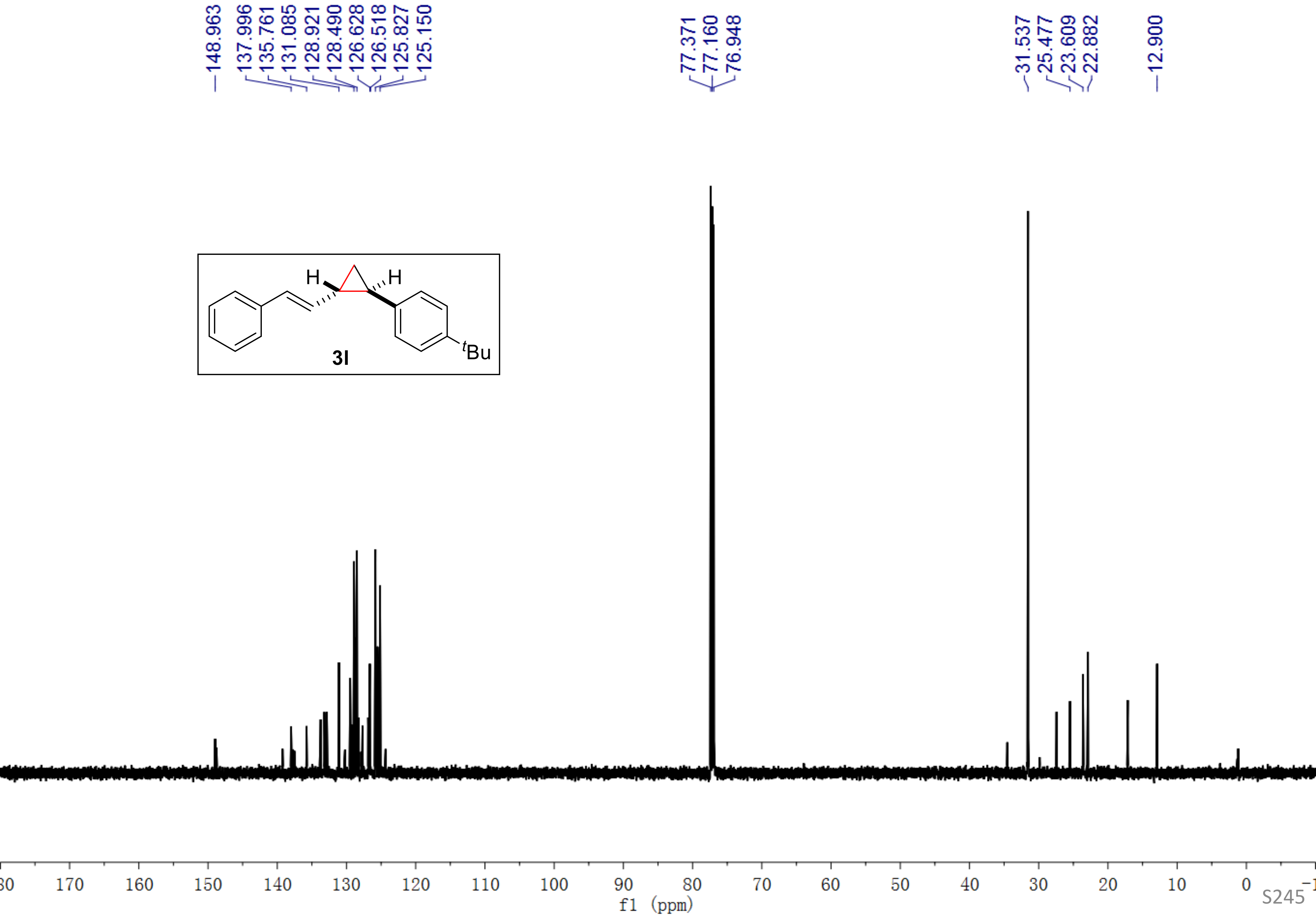
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.989	1161509	21.360
2	13.669	54806	1.008
3	15.915	4150955	76.334
4	24.412	70618	1.299
Total		5437888	100.000

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

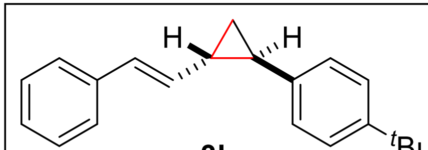


^{13}C of **3l**, 151 MHz, $CDCl_3$



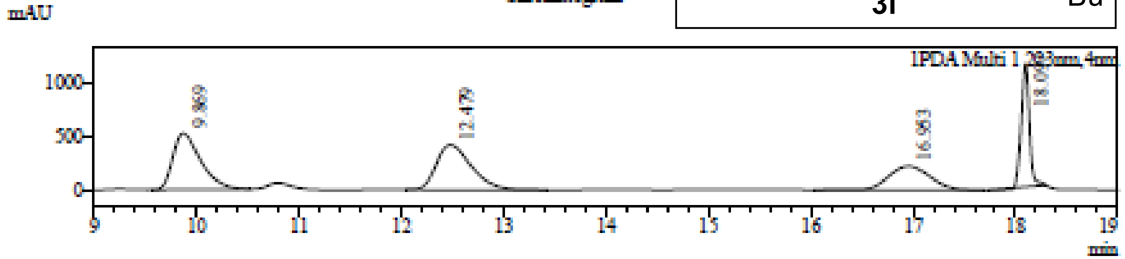
Sample Information

Data File	: J0K-1586-ODH-0.1%-1ML.lcd
Sample Name	: J0K-1586-ODH-0.1%-1ML
Sample ID	: J0K-1586-ODH-0.1%-1ML
Method File	: J0K-0.1%--40min-1ml.lcm

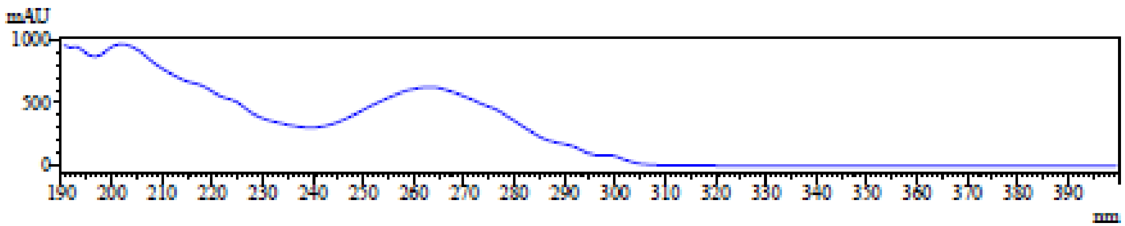


3l

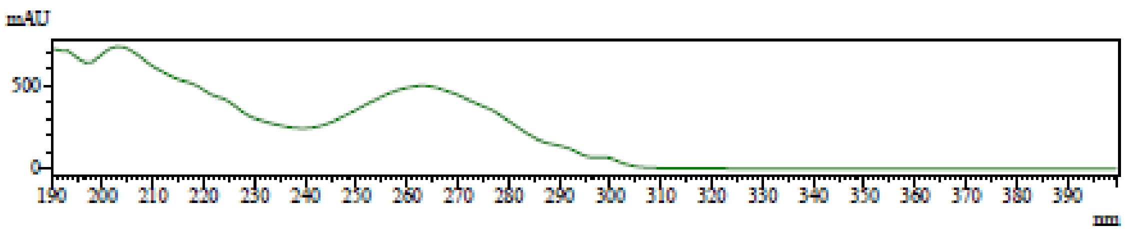
Chromatogram



UV Spectrum
Retention time = 9.869



UV Spectrum
Retention time = 12.479



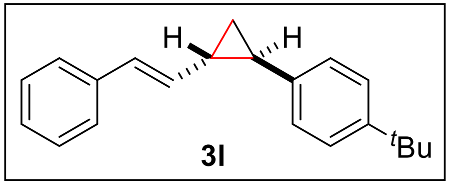
Peak Table

PDA Ch1 223nm

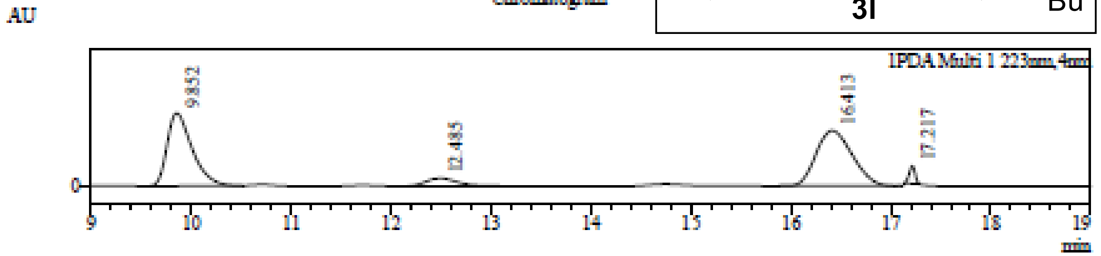
Peak#	Ret. Time	Area	Area%
1	9.869	9930275	30.719
2	12.479	9966540	30.831
3	16.953	6154164	19.038
4	18.097	6275158	19.412
Total		32326136	100.000

Sample Information

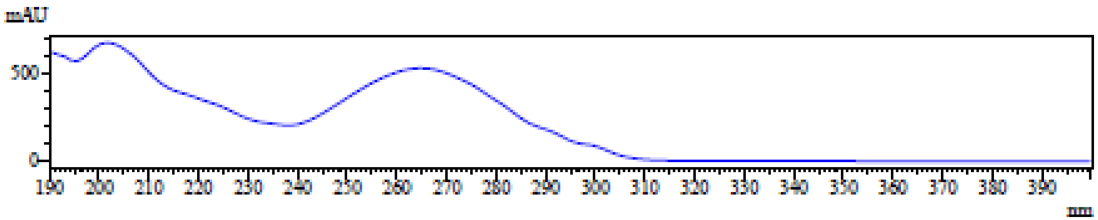
Data File	: J0K-1585-ODH-0.1%-1ML.lcd
Sample Name	: J0K-1585-ODH-0.1%-1ML
Sample ID	: J0K-1585-ODH-0.1%-1ML
Method File	: J0K-0.1%--40min-1ml.lcm



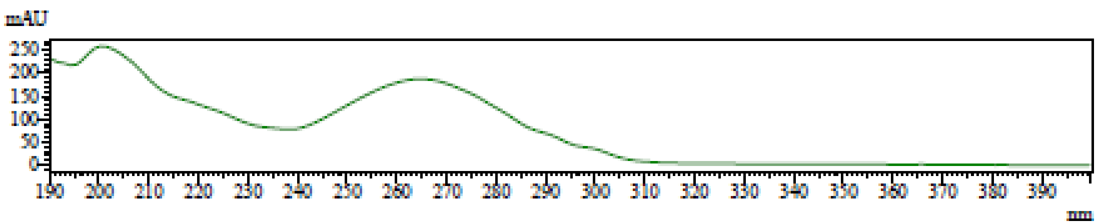
Chromatogram



UV Spectrum
Retention time = 16.413



UV Spectrum
Retention time = 17.217

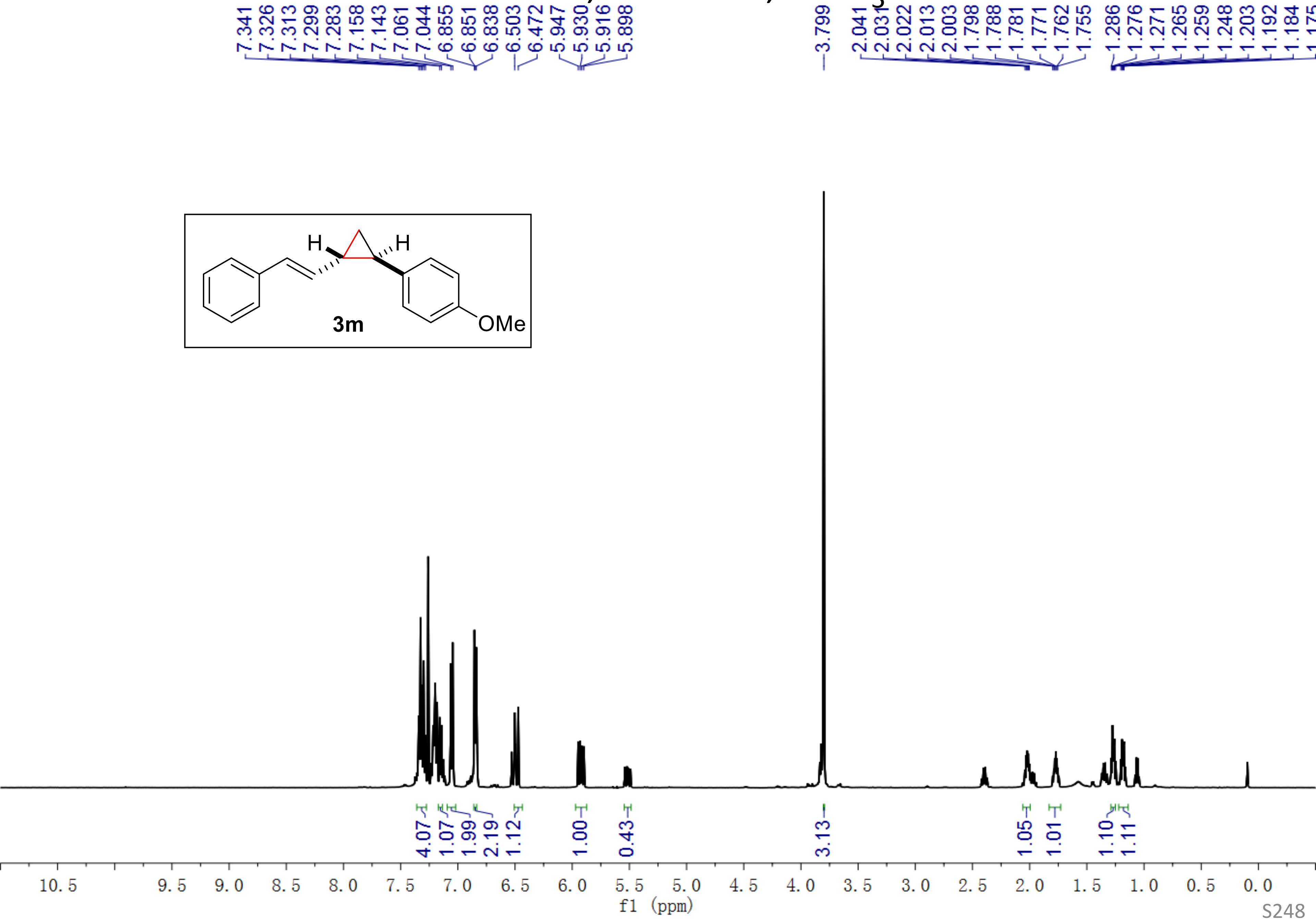


Peak Table

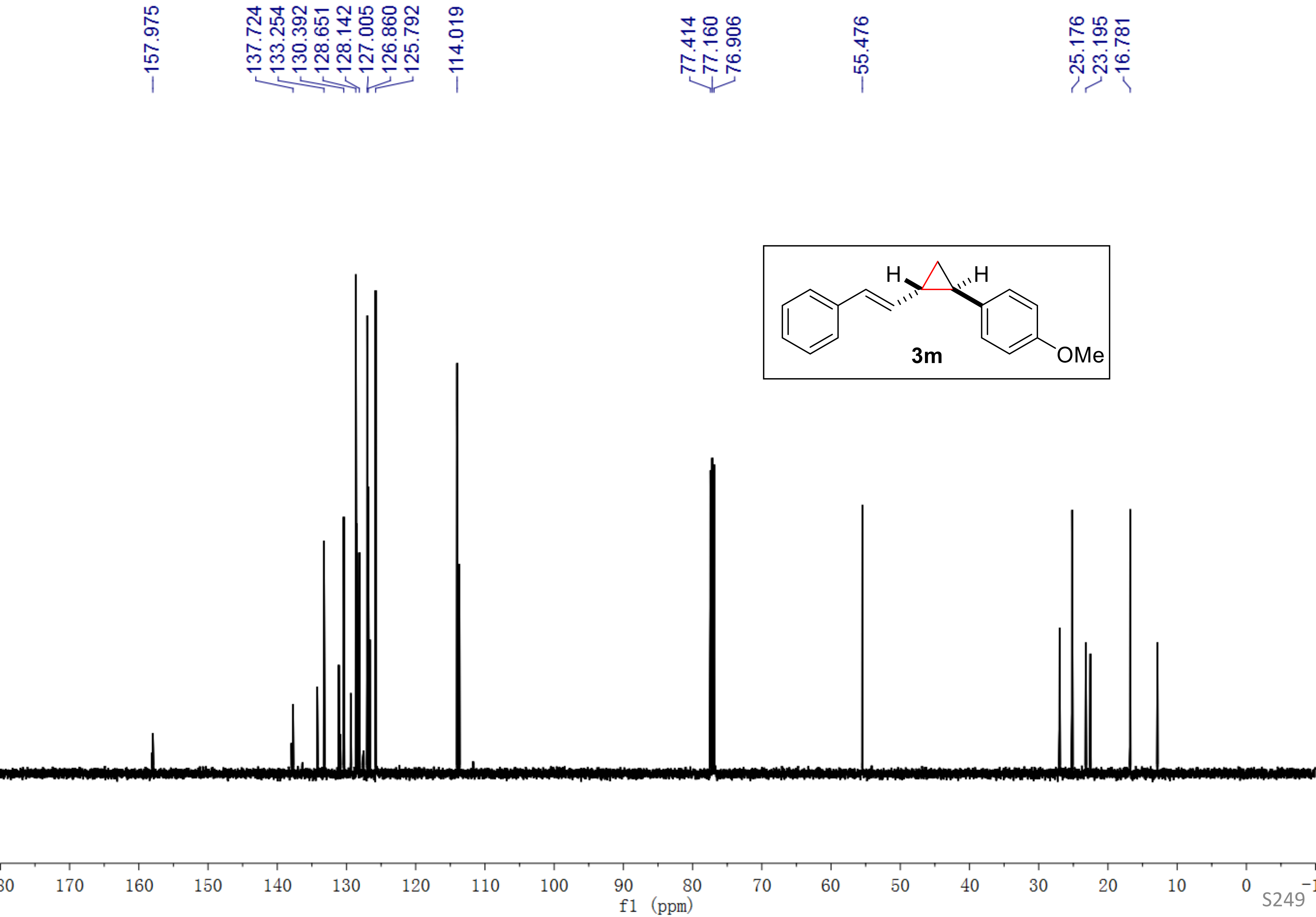
PDA Ch1 223nm

Peak#	Ret. Time	Area	Area%
1	9.852	7458076	43.594
2	12.485	1056115	6.173
3	16.413	8168763	47.749
4	17.217	424886	2.484
Total		17107839	100.000

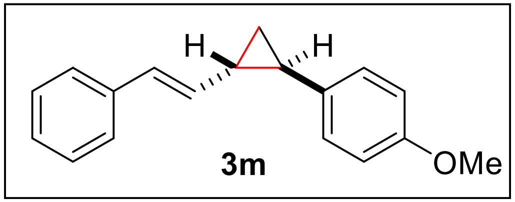
^{1}H of **3m**, 500 MHz, $CDCl_3$

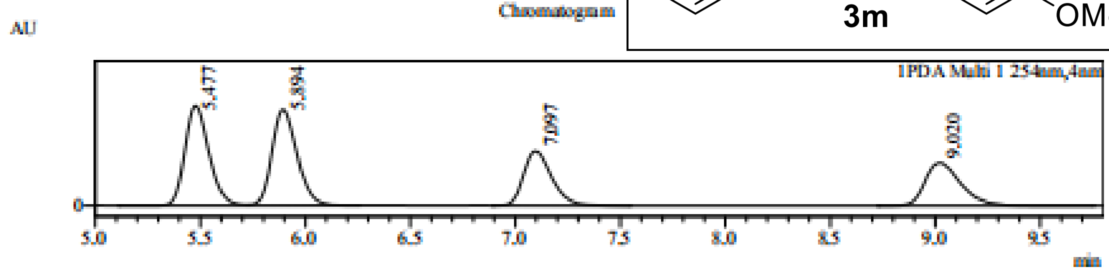


^{13}C of **3m**, 126 MHz, $CDCl_3$

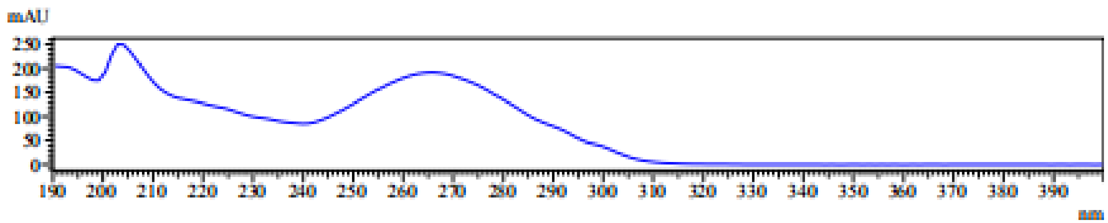


Data File : J0K-MeO-IB-1%-1ML.lcd
Sample Name : J0K-MeO-IB-1%-1ML
Sample ID : J0K-MeO-IB-1%-1ML
Method File : J0K-1%-80min-1ml.lcm

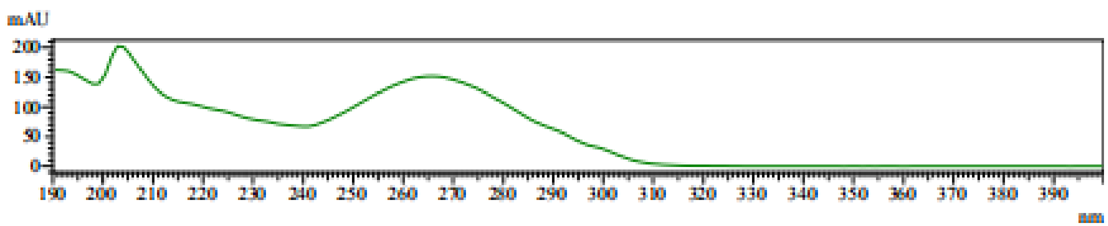




UV Spectrum
Retention time = 7.097



UV Spectrum
Retention time = 9.020

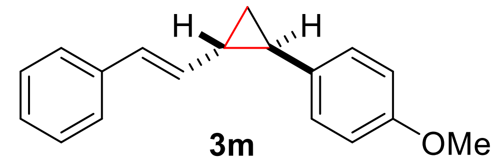


Peak Table

PDA Ch1 254nm

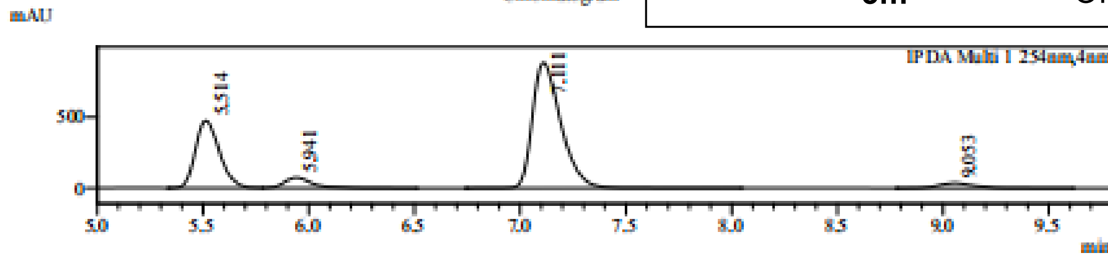
Peak#	Ret. Time	Area	Area%
1	5.477	2210715	30.712
2	5.894	2206546	30.654
3	7.097	1386377	19.260
4	9.020	1394658	19.375
Total		7198295	100.000

Data File : J0K-1257-IB-1%-1ML.lcd
Sample Name : J0K-1257-IB-1%-1ML
Sample ID : J0K-1257-IB-1%-1ML
Method File : J0K-1%-80min-1ml.lcm

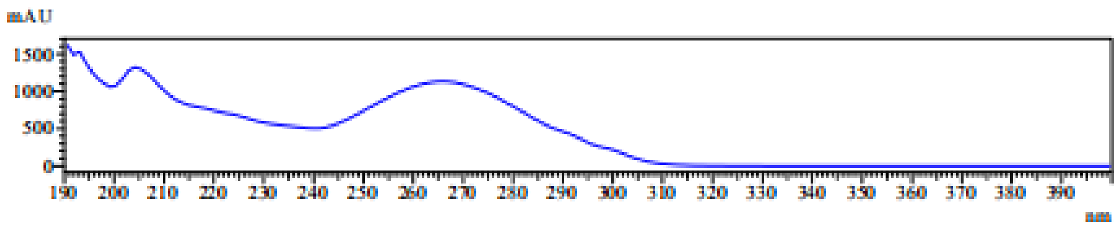


3m

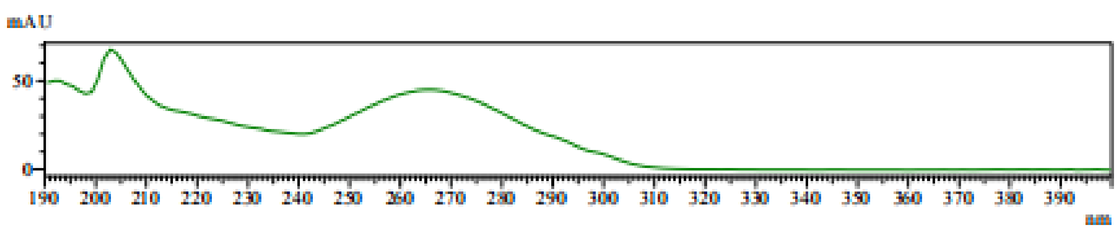
Chromatogram



UV Spectrum
Retention time = 7.111



UV Spectrum
Retention time = 9.053

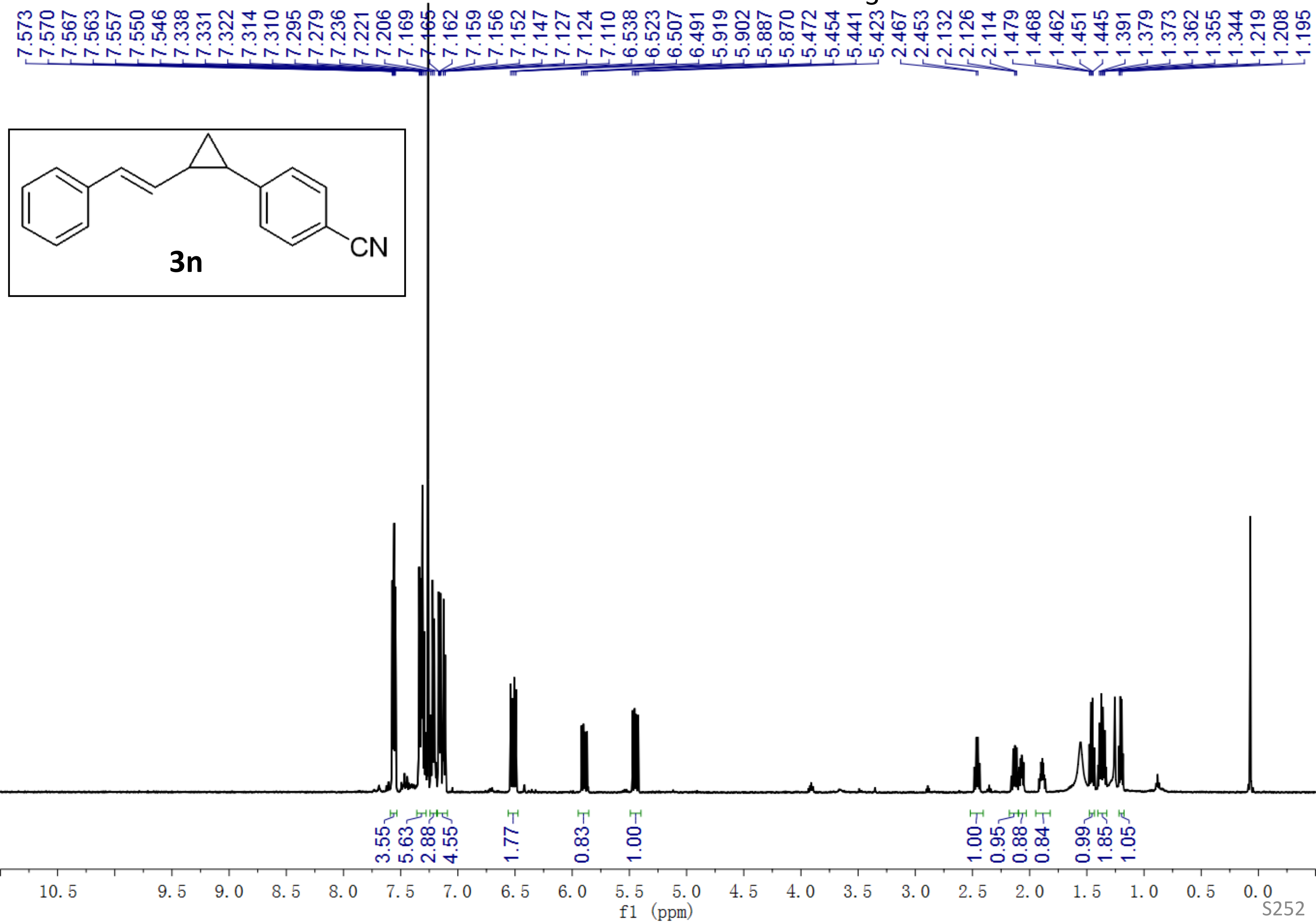


Peak Table

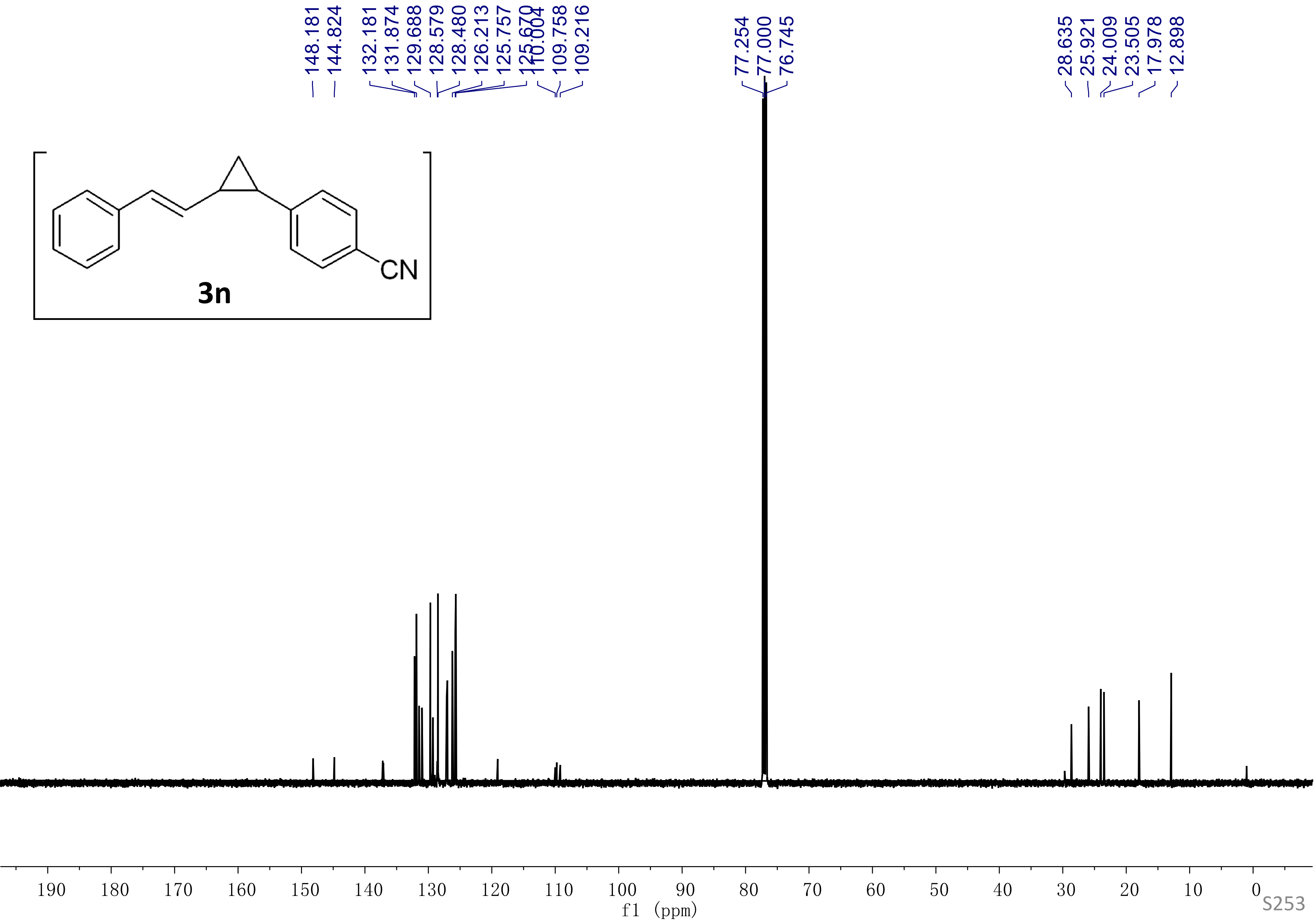
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.514	3757927	28.695
2	5.941	658983	5.032
3	7.111	8273351	63.174
4	9.053	405955	3.100
Total		13096216	100.000

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

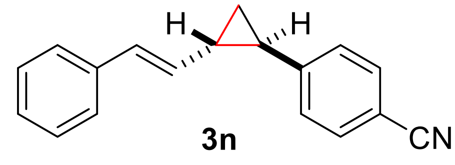


^{13}C of **3n**, 151 MHz, $CDCl_3$

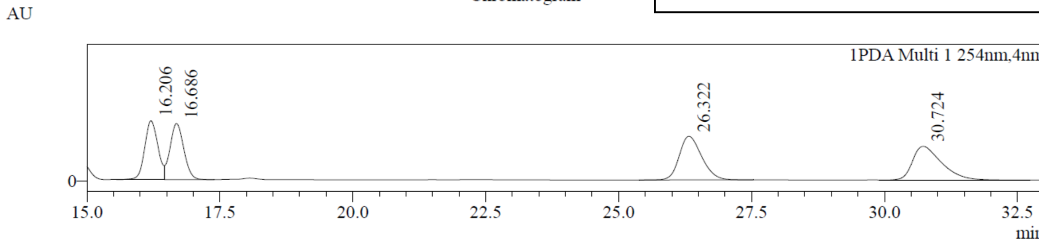


Sample Information

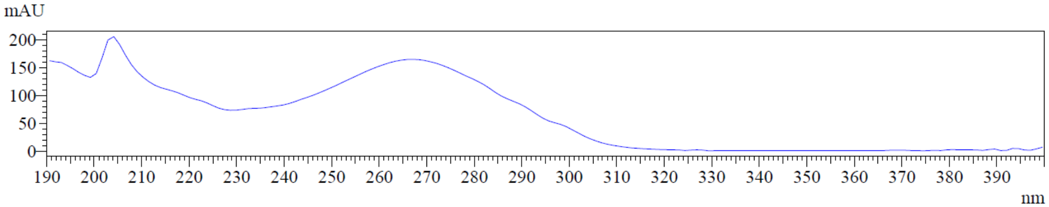
Data File	: J0K-CN-IE-2%-0.8ML.lcd
Sample Name	: J0K-CN-IE-2%-0.8ML
Sample ID	: J0K-CN-IE-2%-0.8ML
Method File	: J0K-2%-40min-0.8ml.lcm



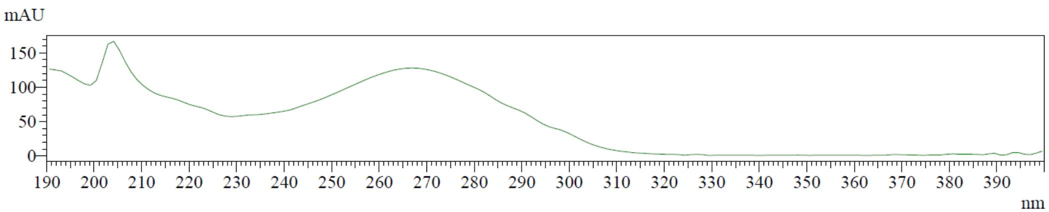
Chromatogram



UV Spectrum
Retention time = 26.322



UV Spectrum
Retention time = 30.724



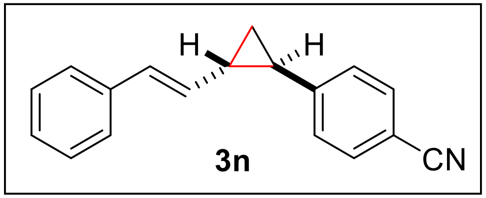
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.206	2987479	22.209
2	16.686	2958033	21.990
3	26.322	3749878	27.877
4	30.724	3756178	27.924
Total		13451567	100.000

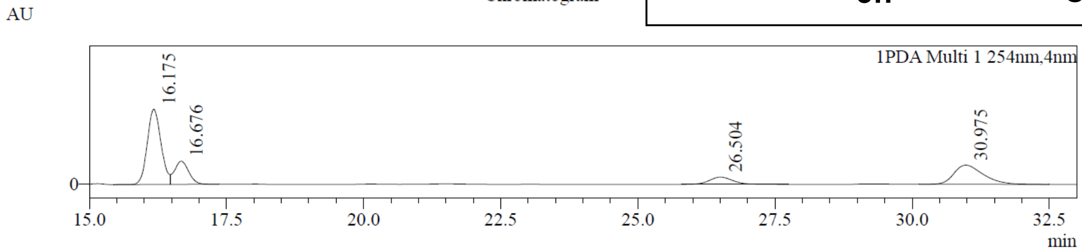
Sample Information

Data File	: J0K-1349-IE-2%-0.8ML.lcd
Sample Name	: J0K-1349-IE-2%-0.8ML
Sample ID	: J0K-1349-IE-2%-0.8ML
Method File	: J0K-2%-40min-0.8ml.lcm

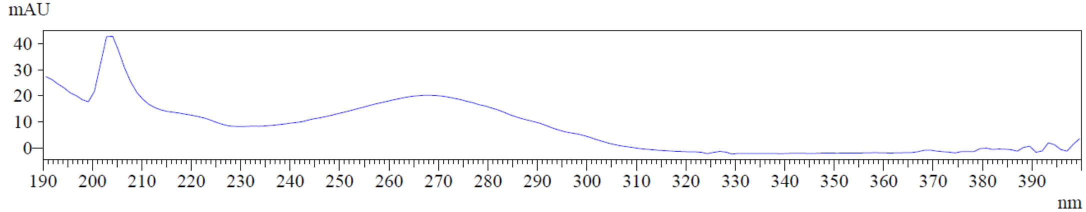


3n

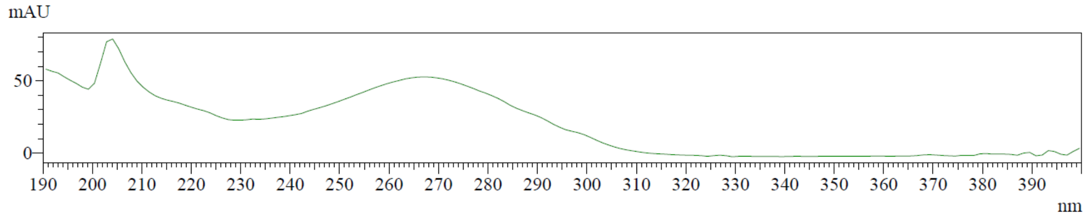
Chromatogram



UV Spectrum
Retention time = 26.504



UV Spectrum
Retention time = 30.975

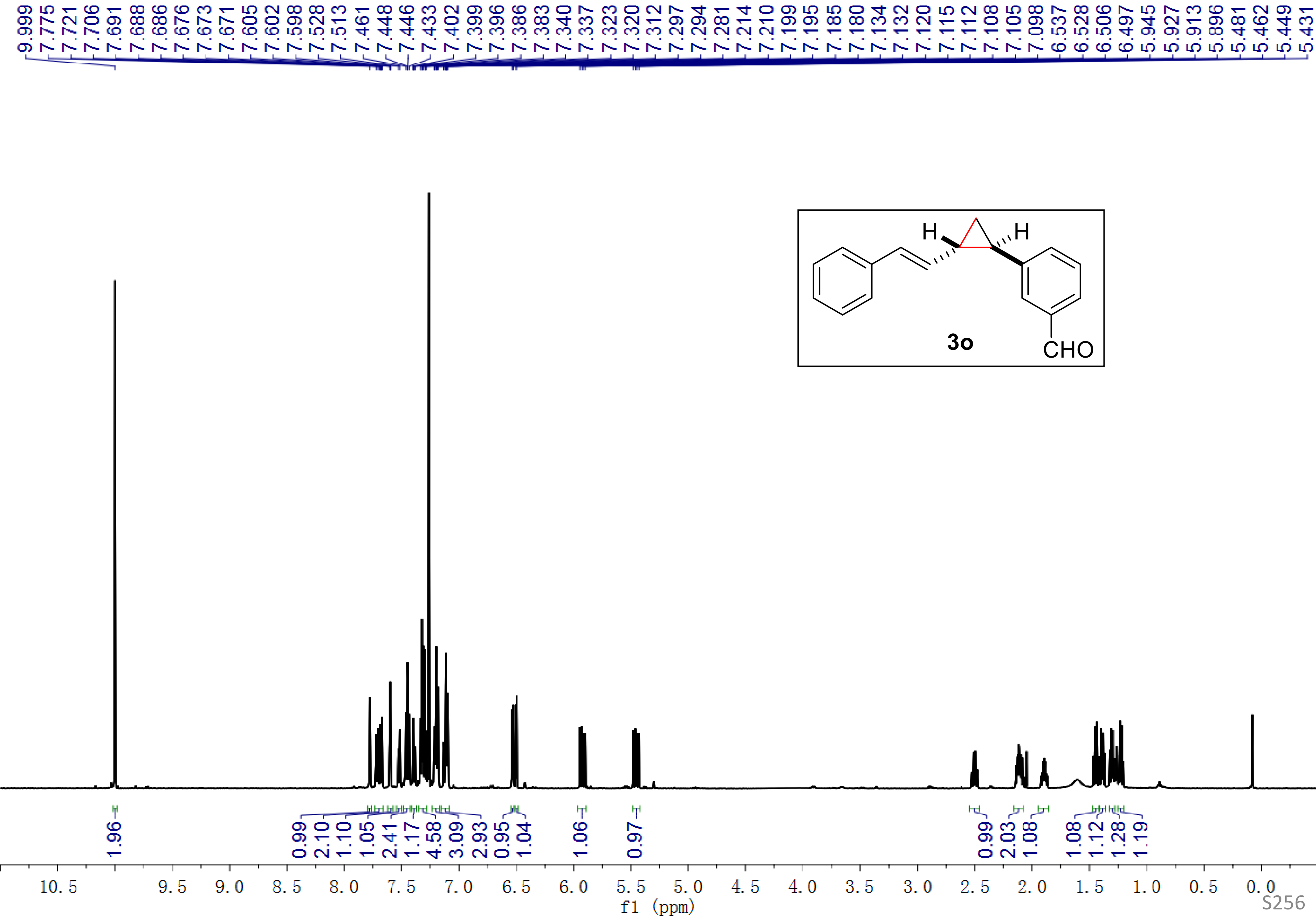


Peak Table

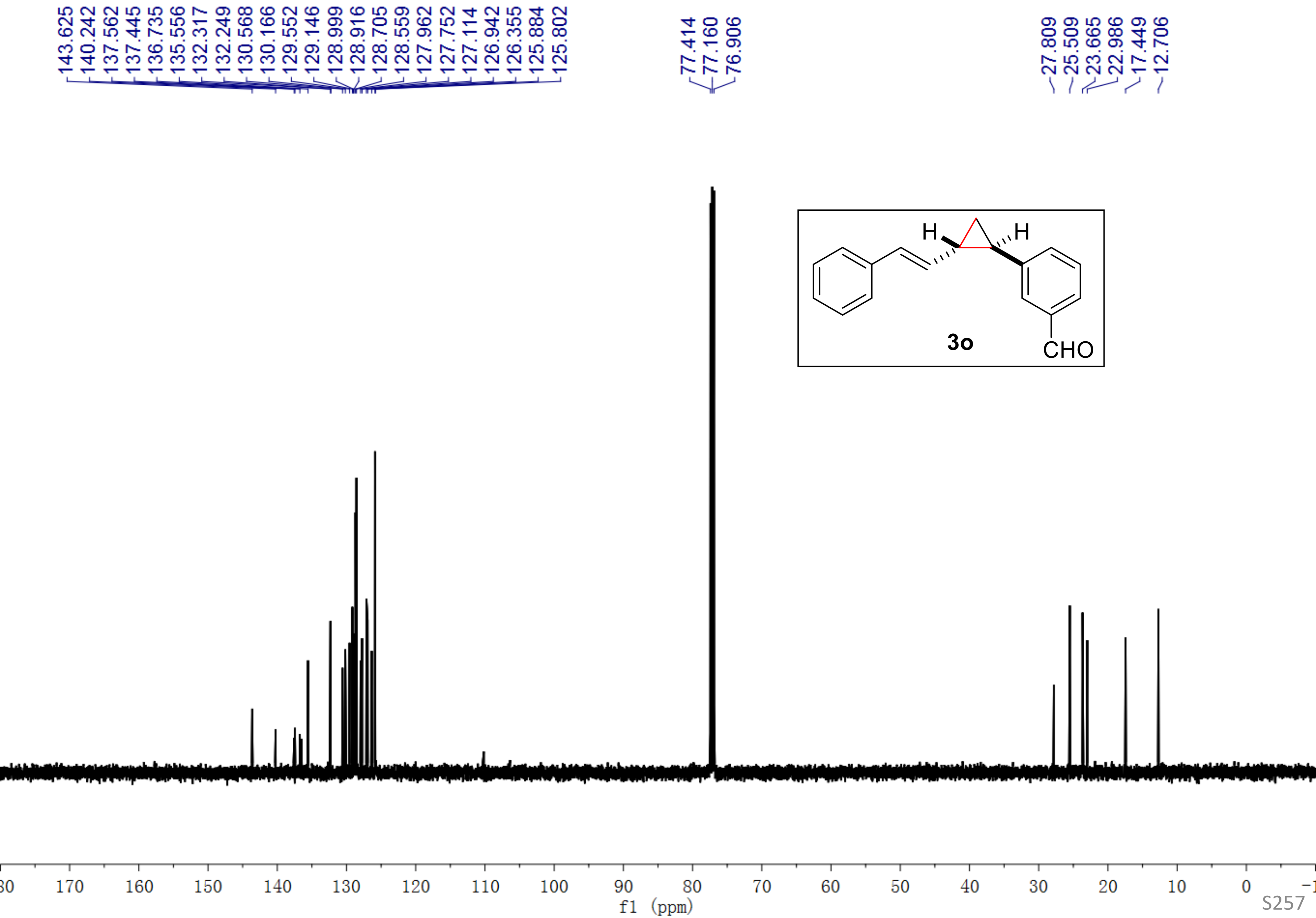
PDA Ch1 254nm

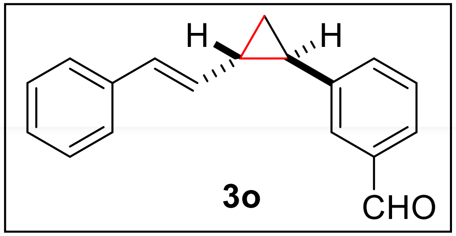
Peak#	Ret. Time	Area	Area%
1	16.175	2859353	49.497
2	16.676	906171	15.686
3	26.504	463485	8.023
4	30.975	1547867	26.794
Total		5776876	100.000

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



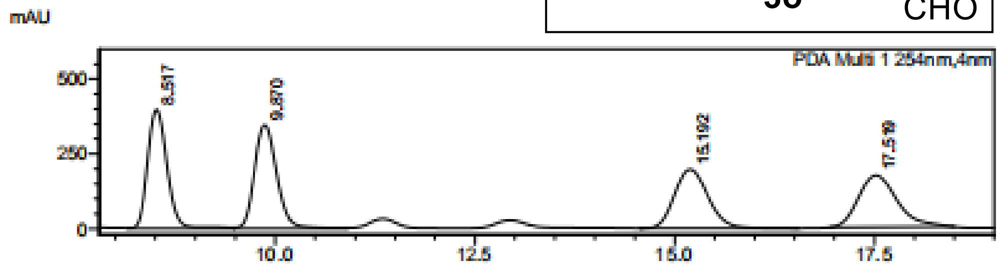
^{13}C of **3o**, 151 MHz, $CDCl_3$



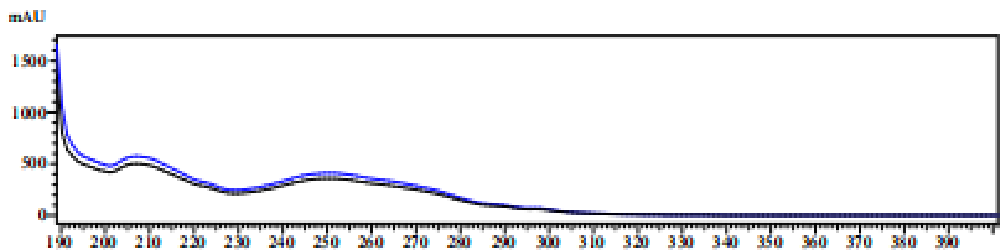


3o

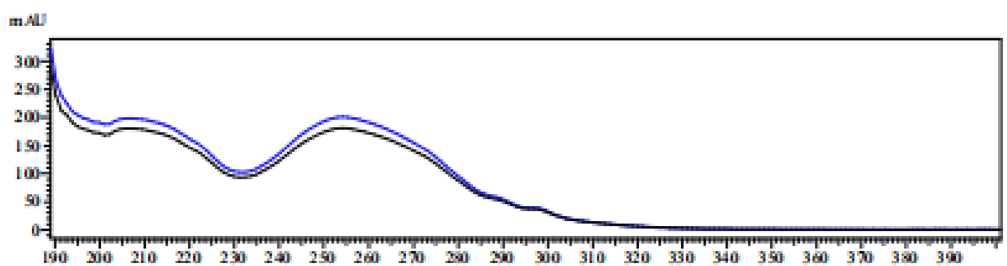
JK-CHO-ODH-5%-1mL-2
JK-5%-30min-1mL.lcm



UV Spectrum
JK-CHO-ODH-5%-1mL-2_001.lcd

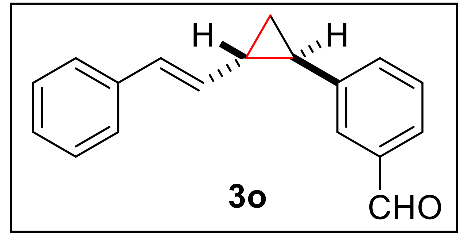


UV Spectrum
JK-CHO-ODH-5%-1mL-2_001.lcd



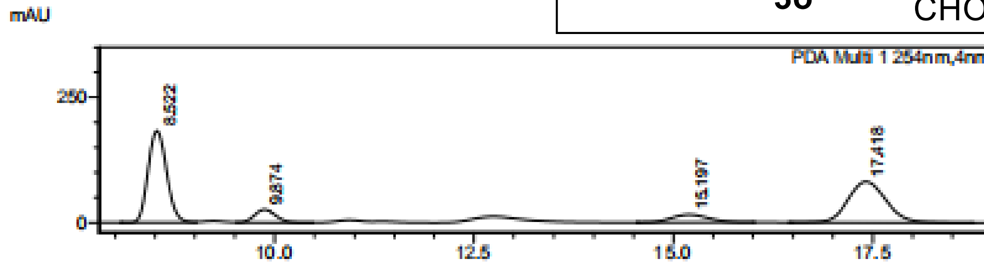
Peak Table
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.517	26.943
2	9.870	26.885
3	15.192	23.024
4	17.519	23.148
Total		100.000



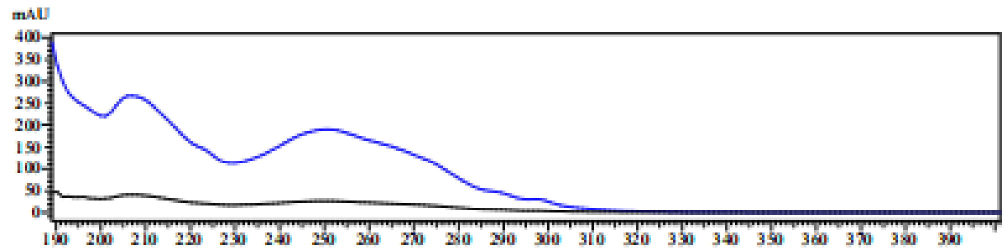
3o

JK-1351-ODH-5%-1mL
JK-5%-30min-1mL.lcm



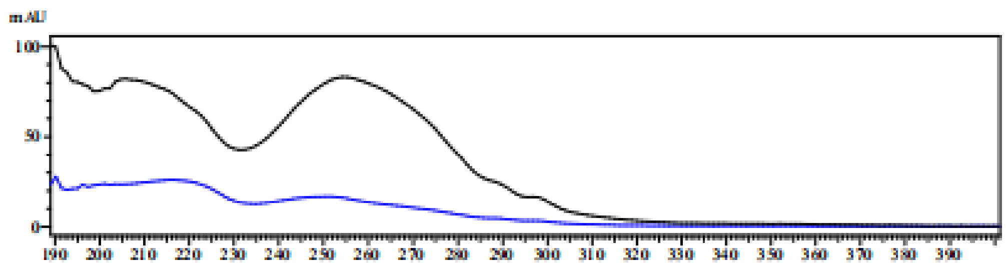
UV Spectrum

JK-1351-ODH-5%-1mL_001.lcd



UV Spectrum

JK-1351-ODH-5%-1mL_001.lcd

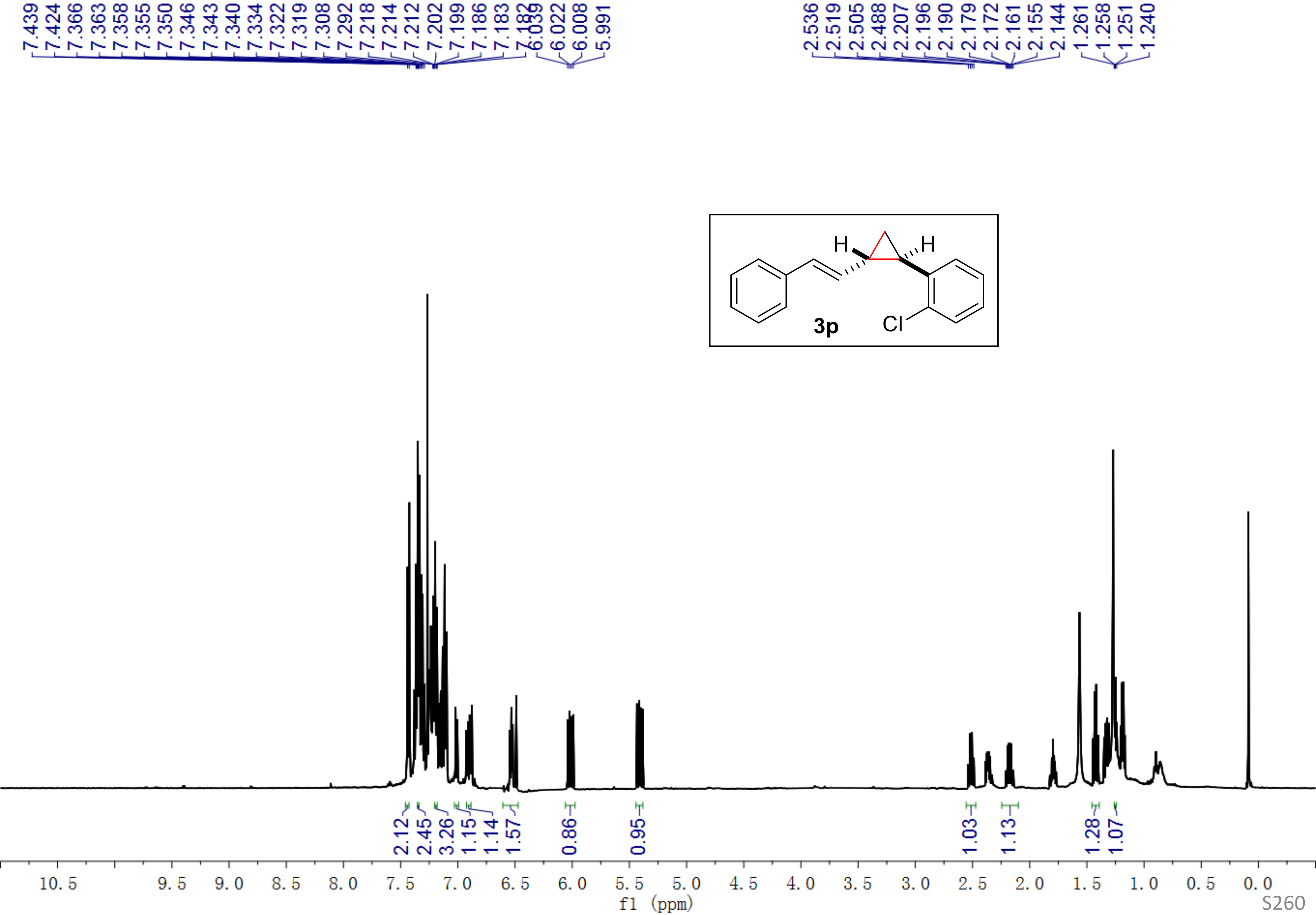


Peak Table

PDA Ch1 254nm

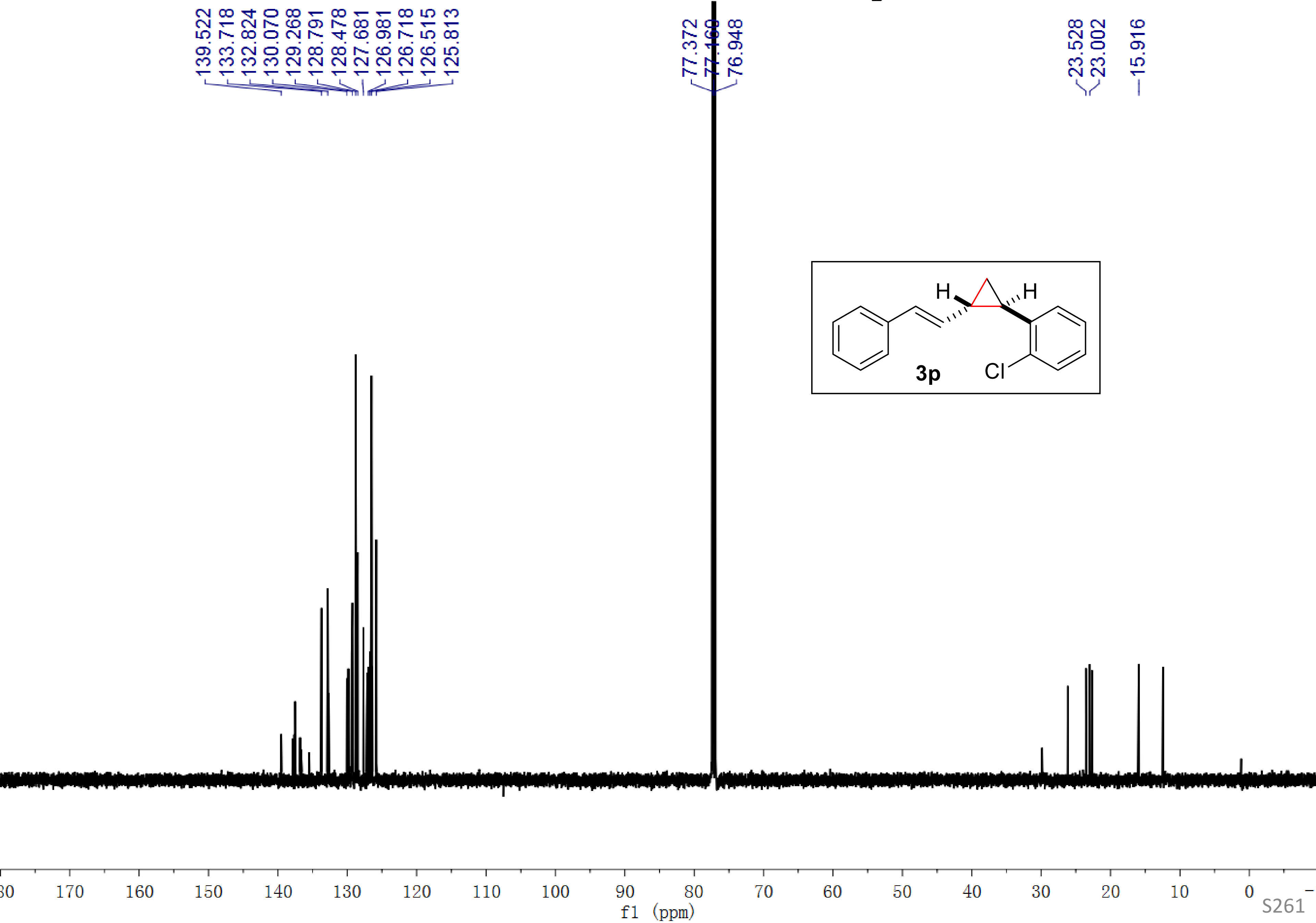
Peak#	Ret. Time	Area%
1	8.522	44.717
2	9.874	7.301
3	15.197	7.355
4	17.418	40.628
Total		100.000

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



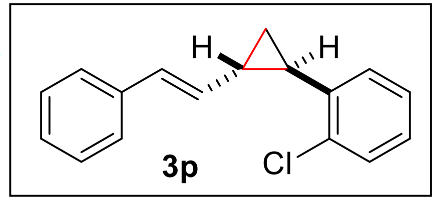
3p

^{13}C of **3p**, 151 MHz, $CDCl_3$



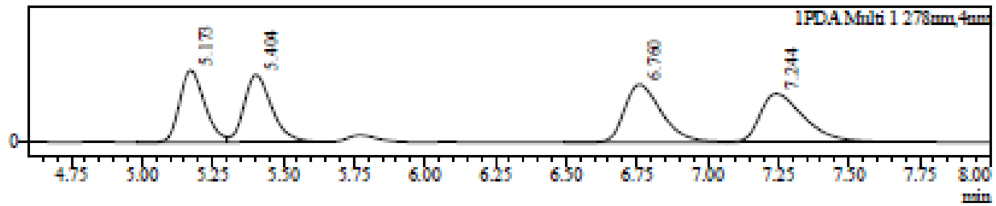
Sample Information

Data File : J0K-1588-IA-0.1%-1ML.lcd
Sample Name : J0K-1588-IA-0.1%-1ML
Sample ID : J0K-1588-IA-0.1%-1ML
Method File : J0K-0.1%-40min-1ml.lcm



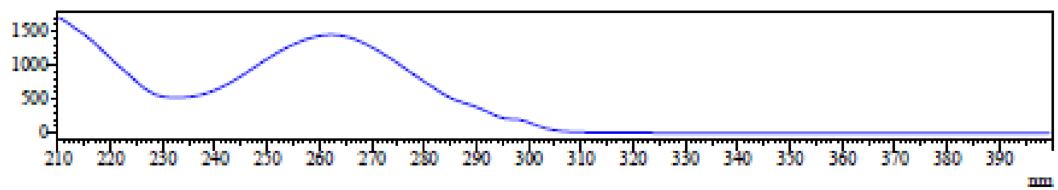
Chromatogram

AU



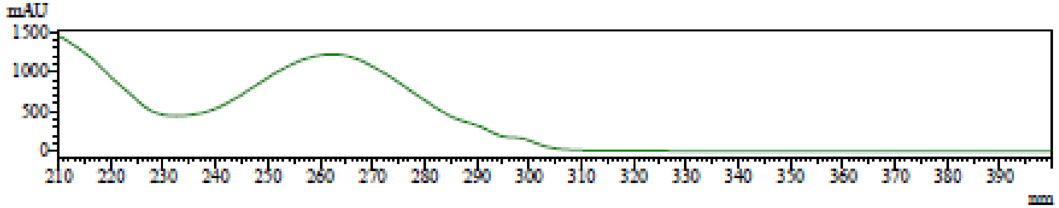
UV Spectrum
Retention time = 6.760

mAU



UV Spectrum
Retention time = 7.244

mAU



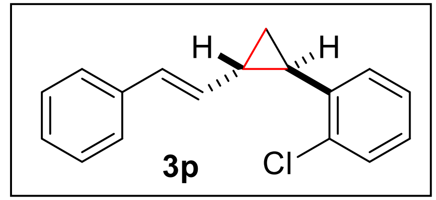
Peak Table

PDA Ch1 278nm

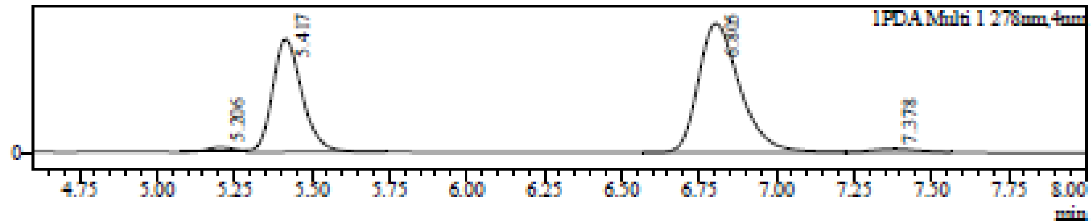
Peak#	Ret. Time	Area	Area%
1	5.173	6561813	22.830
2	5.404	6760359	23.520
3	6.760	7758333	26.993
4	7.244	7661946	26.657
Total		28742452	100.000

Sample Information

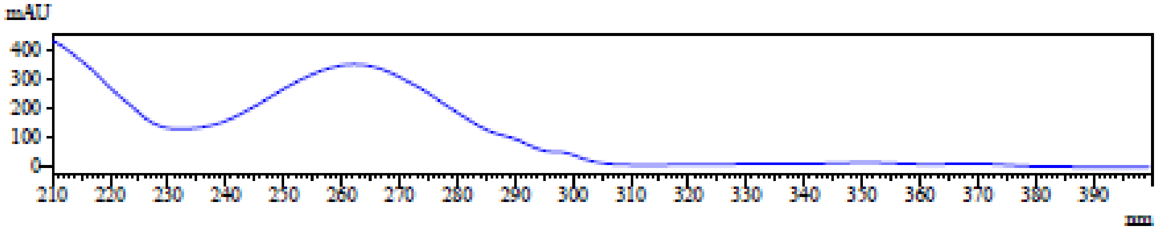
Data File	: J0K-1587-IA-0.1%-1ML-2.lcd
Sample Name	: J0K-1587-IA-0.1%-1ML-2
Sample ID	: J0K-1587-IA-0.1%-1ML-2
Method File	: J0K-0.1%--40min-1ml.lcm



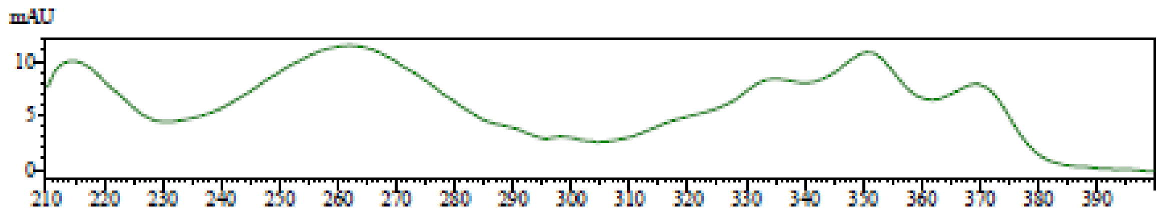
Chromatogram



UV Spectrum
Retention time = 6.805



UV Spectrum
Retention time = 7.378

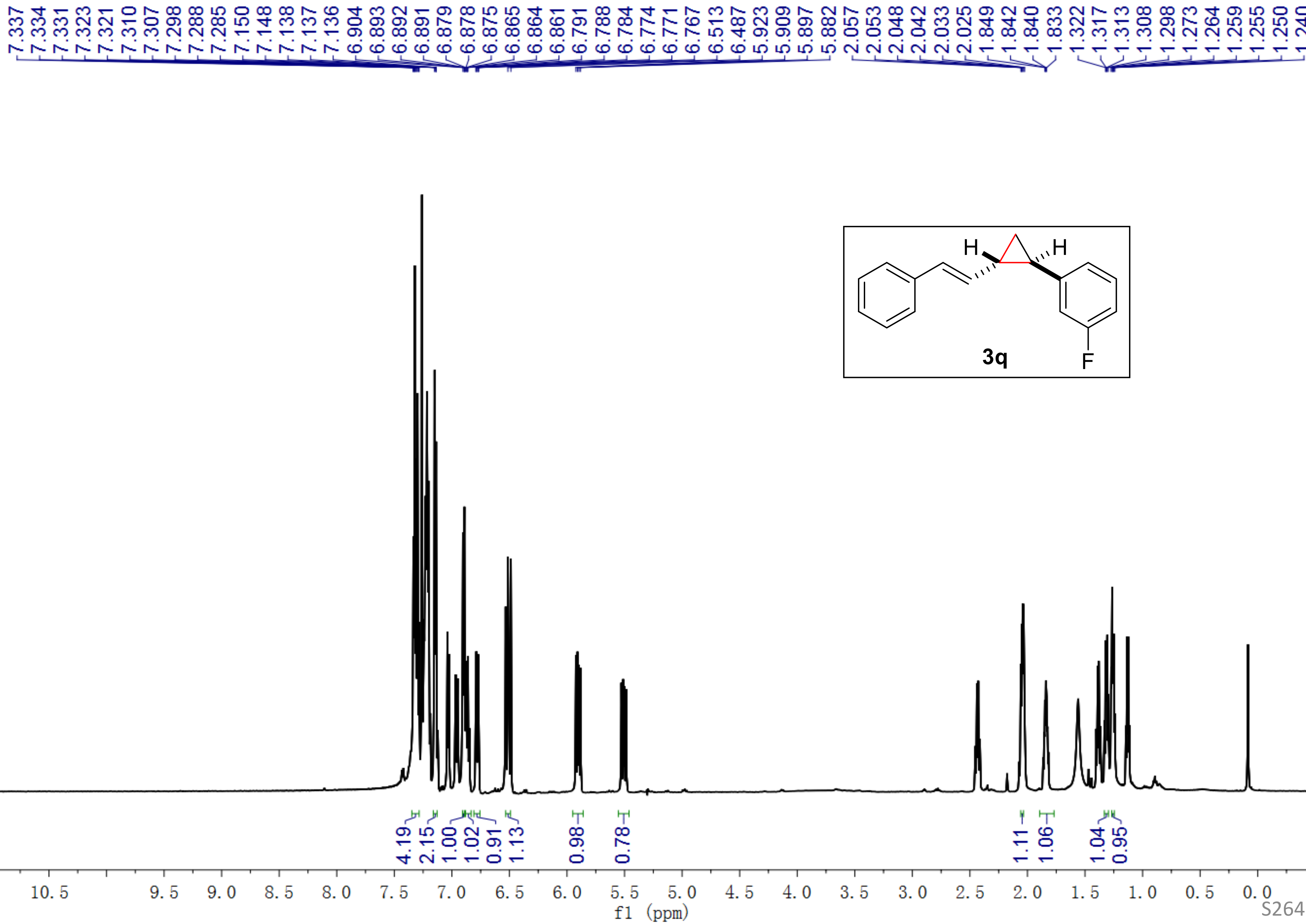


Peak Table

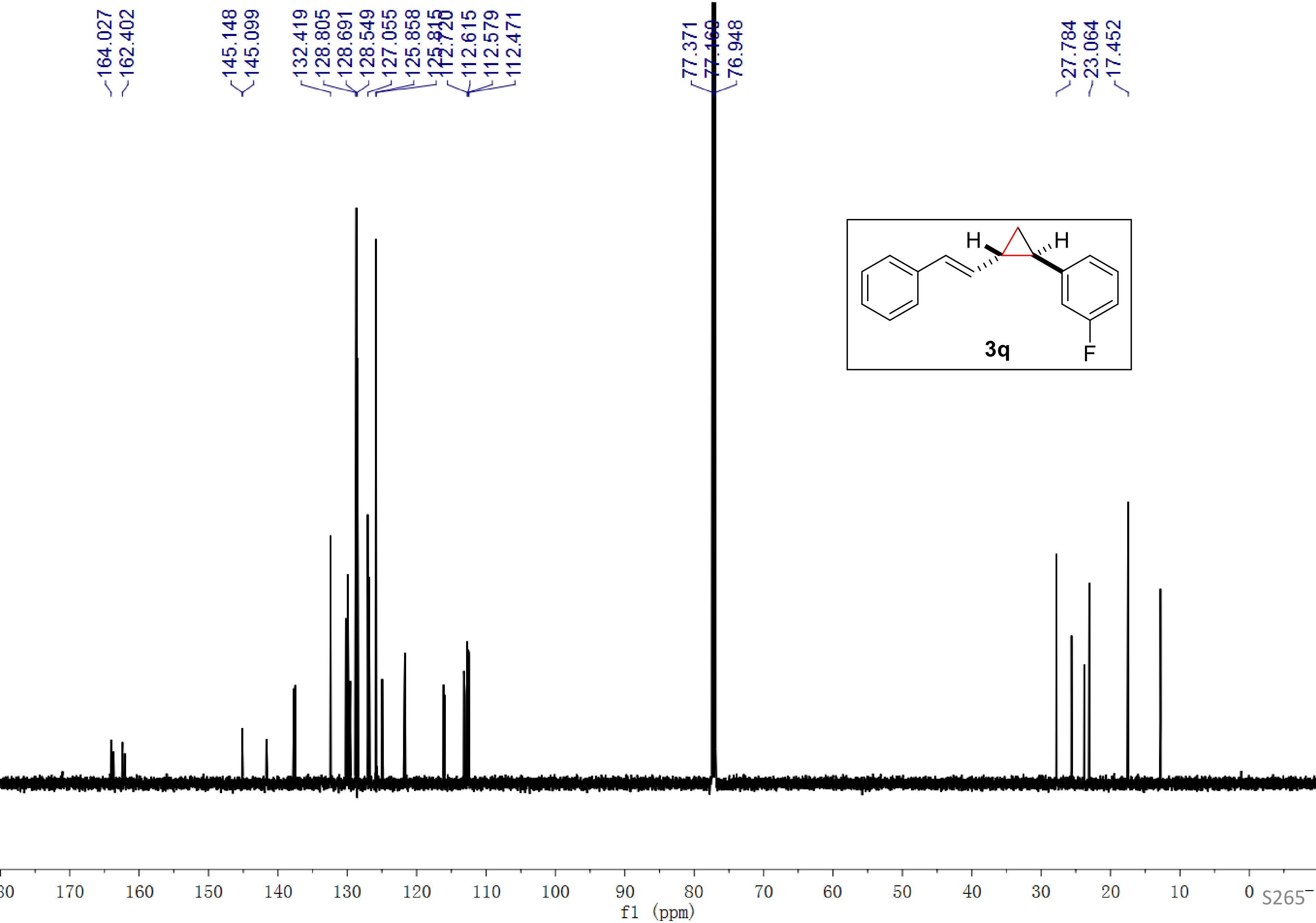
PDA Ch1 278nm

Peak#	Ret. Time	Area	Area%
1	5.206	48035	1.474
2	5.417	1206525	37.019
3	6.805	1946653	59.728
4	7.378	57978	1.779
Total		3259191	100.000

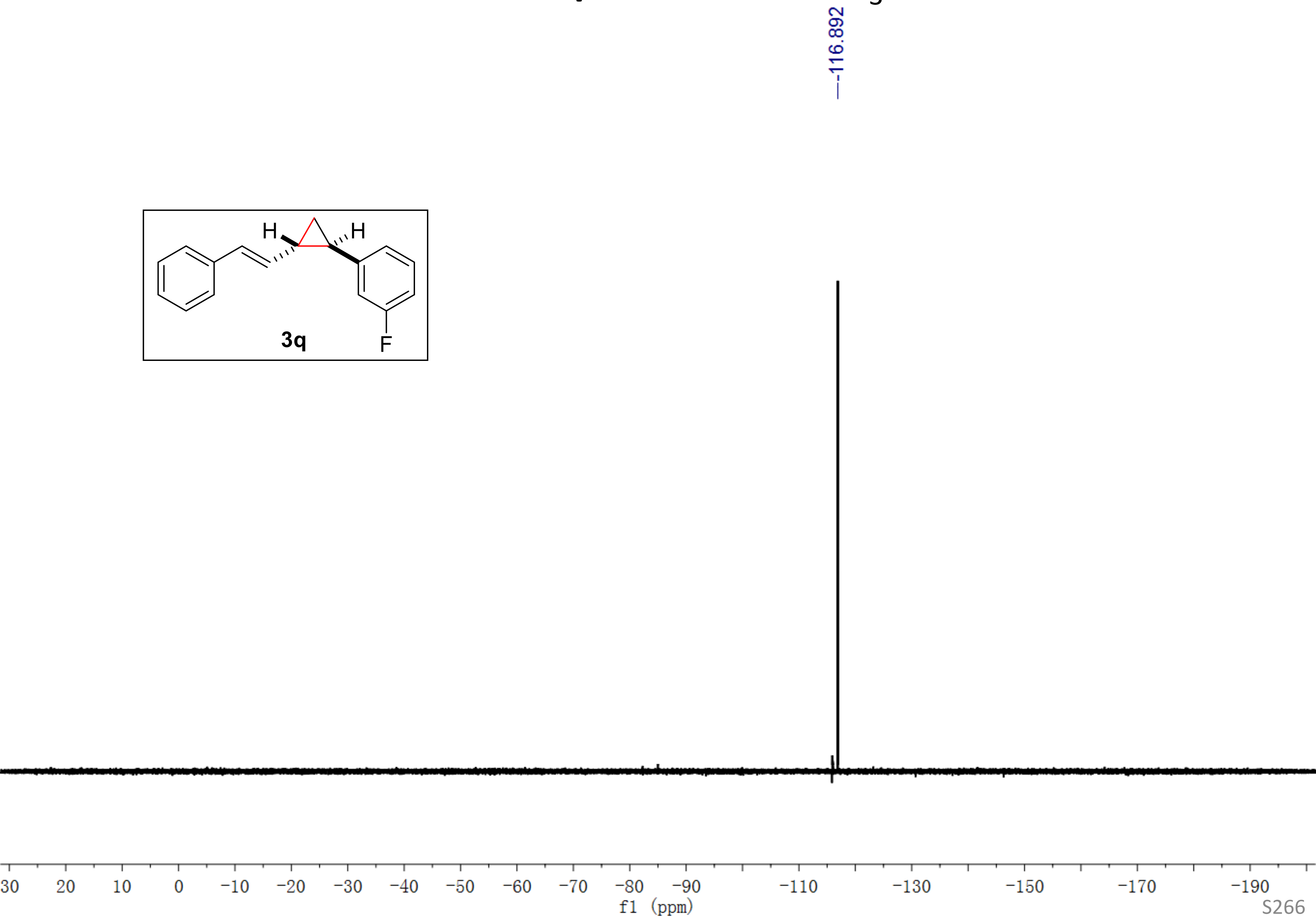
^1H of **3q**, 600 MHz, $CDCl_3$



^{13}C of **3q**, 151 MHz, $CDCl_3$

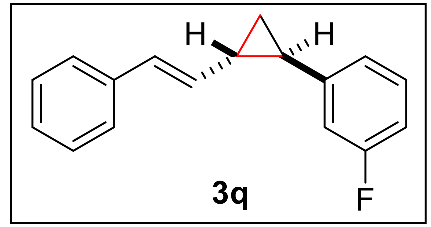


^{19}F of **3q**, 564 MHz, $CDCl_3$



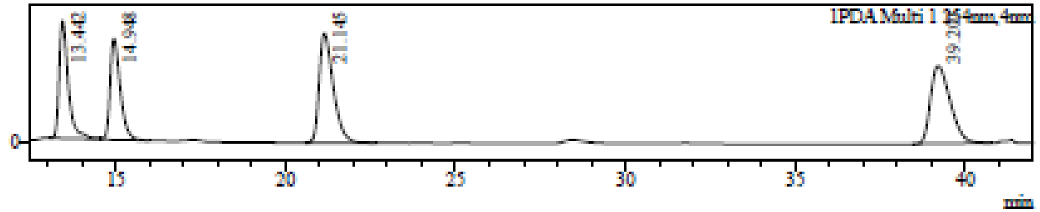
Sample Information

Data File	: J0K-1262-3--IB-0%-1ML.lcd
Sample Name	: J0K-1262-3--IB-0%-1ML
Sample ID	: J0K-1262-3--IB-0%-1ML
Method File	: J0K-0%--45min-1ml.lcm

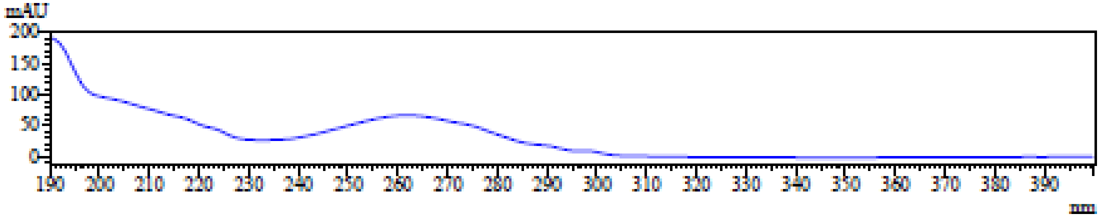


3q

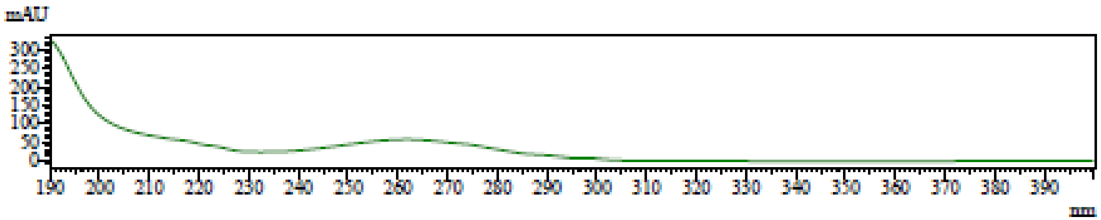
Chromatogram



UV Spectrum
Retention time = 13.442



UV Spectrum
Retention time = 14.948



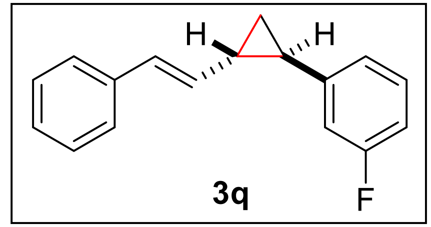
Peak Table

PDA Ch1 254nm

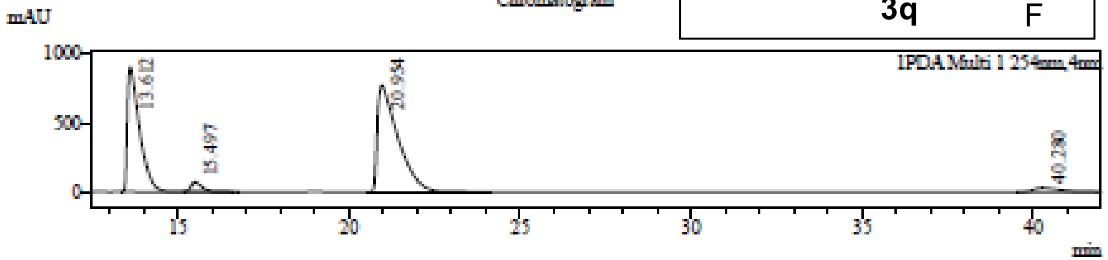
Peak#	Ret. Time	Area	Area%
1	13.442	1070285	20.758
2	14.948	1017042	19.726
3	21.145	1539941	29.867
4	39.207	1528696	29.649
Total		5155964	100.000

Sample Information

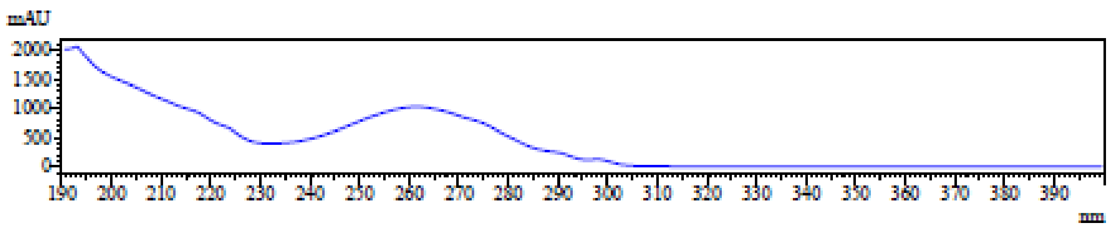
Data File	: J0K-1261-3--IB-0%-1ML.lcd
Sample Name	: J0K-1261-3--IB-0%-1ML
Sample ID	: J0K-1261-3--IB-0%-1ML
Method File	: J0K-0%--45min-1ml.lcm



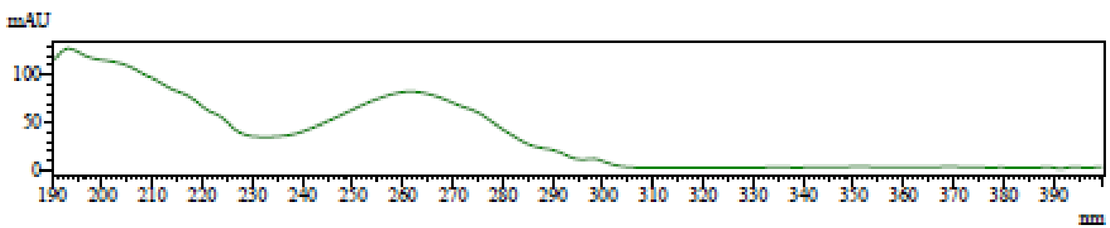
Chromatogram



UV Spectrum
Retention time = 13.612



UV Spectrum
Retention time = 15.497

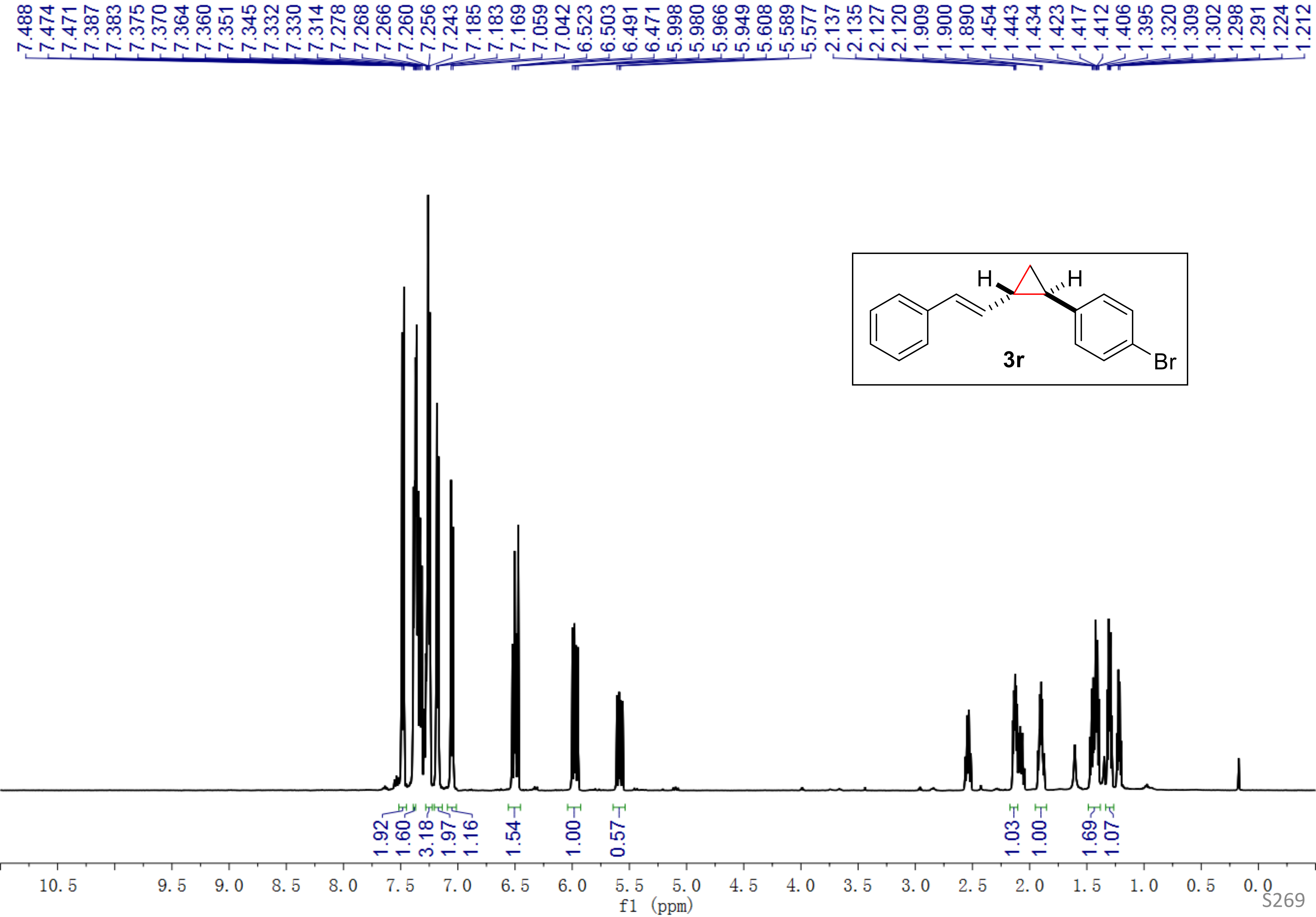


Peak Table

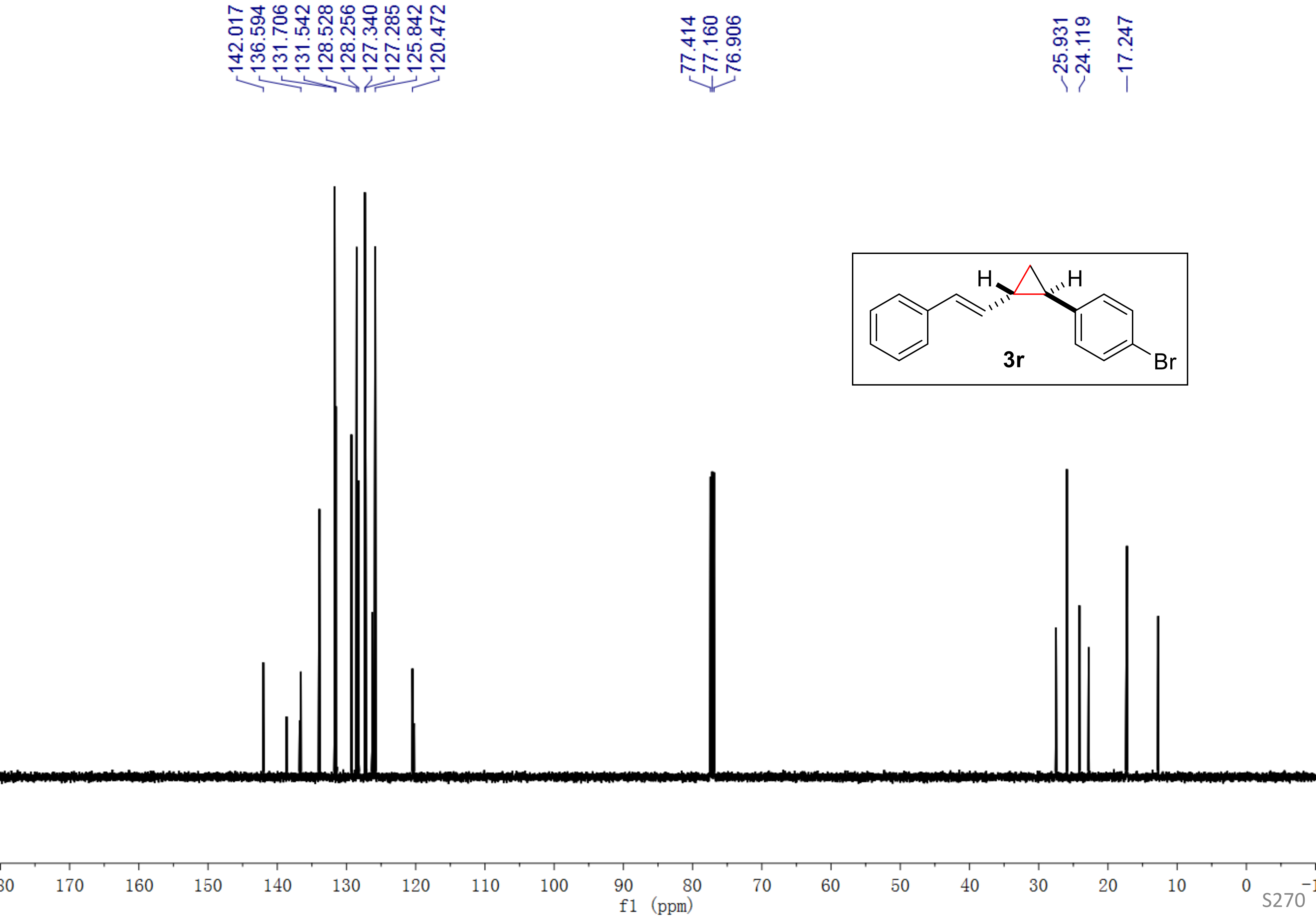
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.612	22366914	38.969
2	15.497	1466415	2.555
3	20.954	32104254	55.933
4	40.280	1459657	2.543
Total		57397240	100.000

^1H of **3r**, 500 MHz, $CDCl_3$

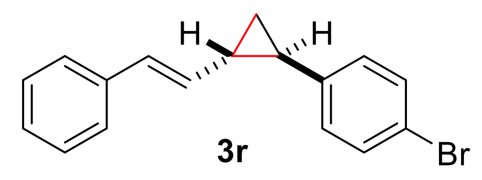


^{13}C of **3r**, 126 MHz, $CDCl_3$



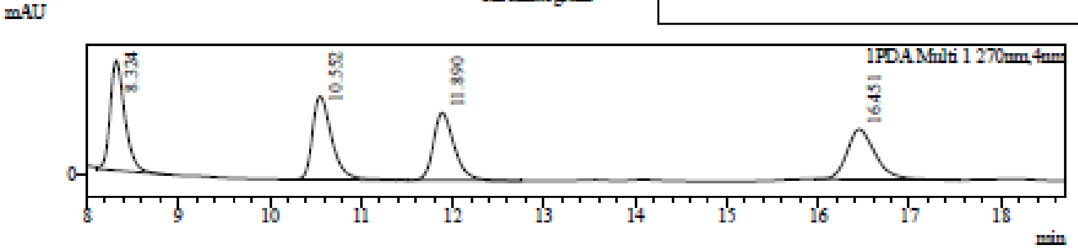
Sample Information

Data File : J0K-1281-2--IB-0%-1ML.lcd
Sample Name : J0K-1281-2--IB-0%-1ML
Sample ID : J0K-1281-2--IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm

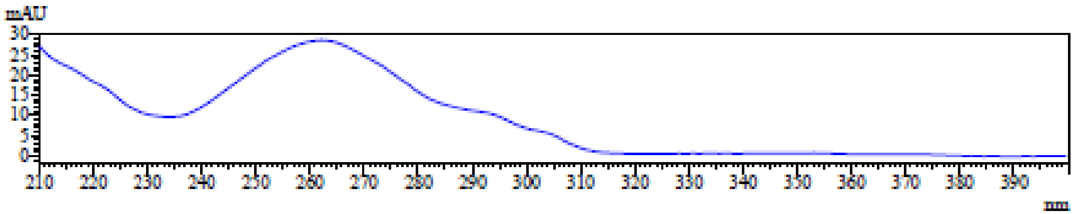


3r

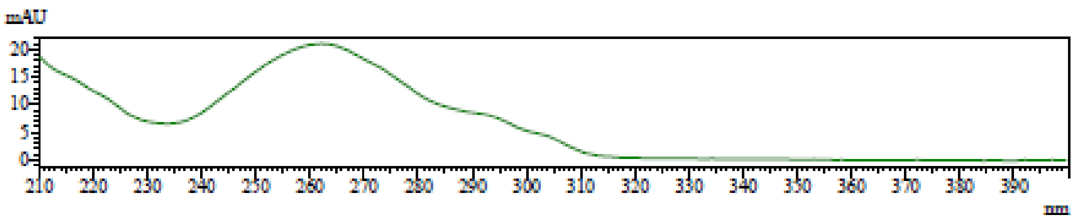
Chromatogram



UV Spectrum
Retention time = 11.890



UV Spectrum
Retention time = 16.451



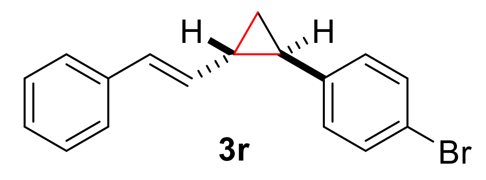
Peak Table

PDA Ch1 270nm

Peak#	Ret. Time	Area	Area%
1	8.324	477952	26.518
2	10.552	480199	26.643
3	11.890	419935	23.299
4	16.451	424261	23.539
Total		1802346	100.000

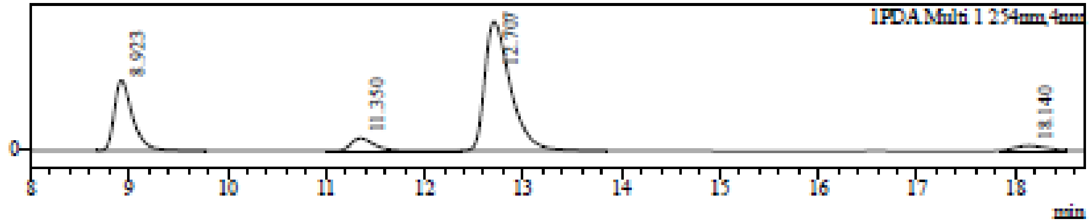
Sample Information

Data File : J0K-1280--IB-0%-1ML.lcd
Sample Name : J0K-1280--IB-0%-1ML
Sample ID : J0K-1280--IB-0%-1ML
Method File : J0K-0%--45min-1ml.lcm

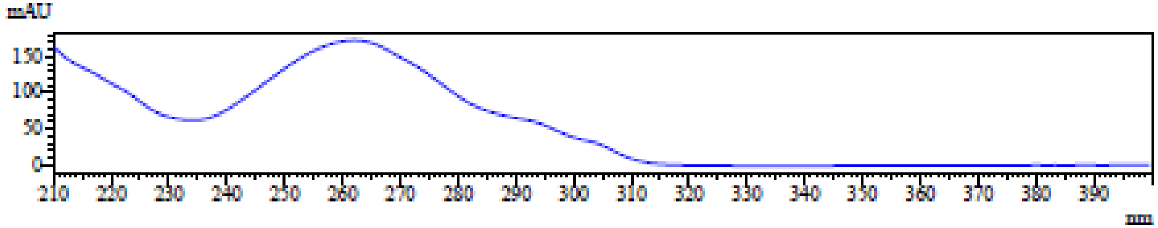


3r

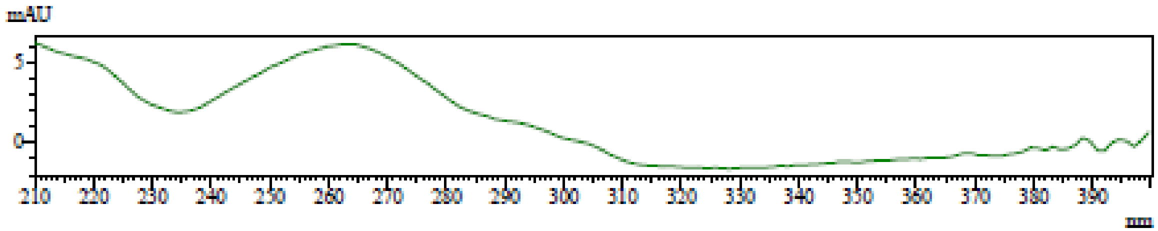
Chromatogram



UV Spectrum
Retention time = 12.707



UV Spectrum
Retention time = 18.140

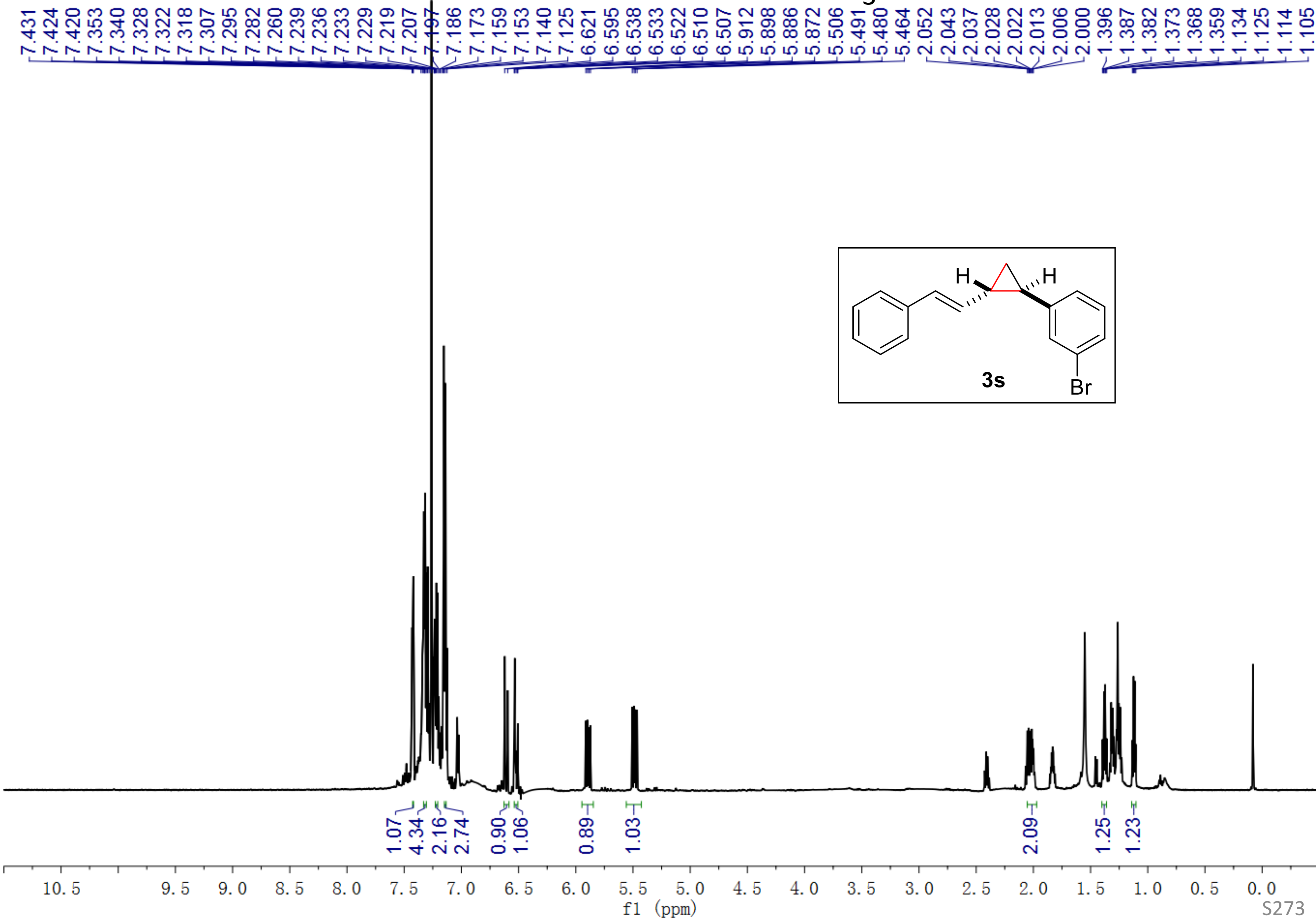


Peak Table

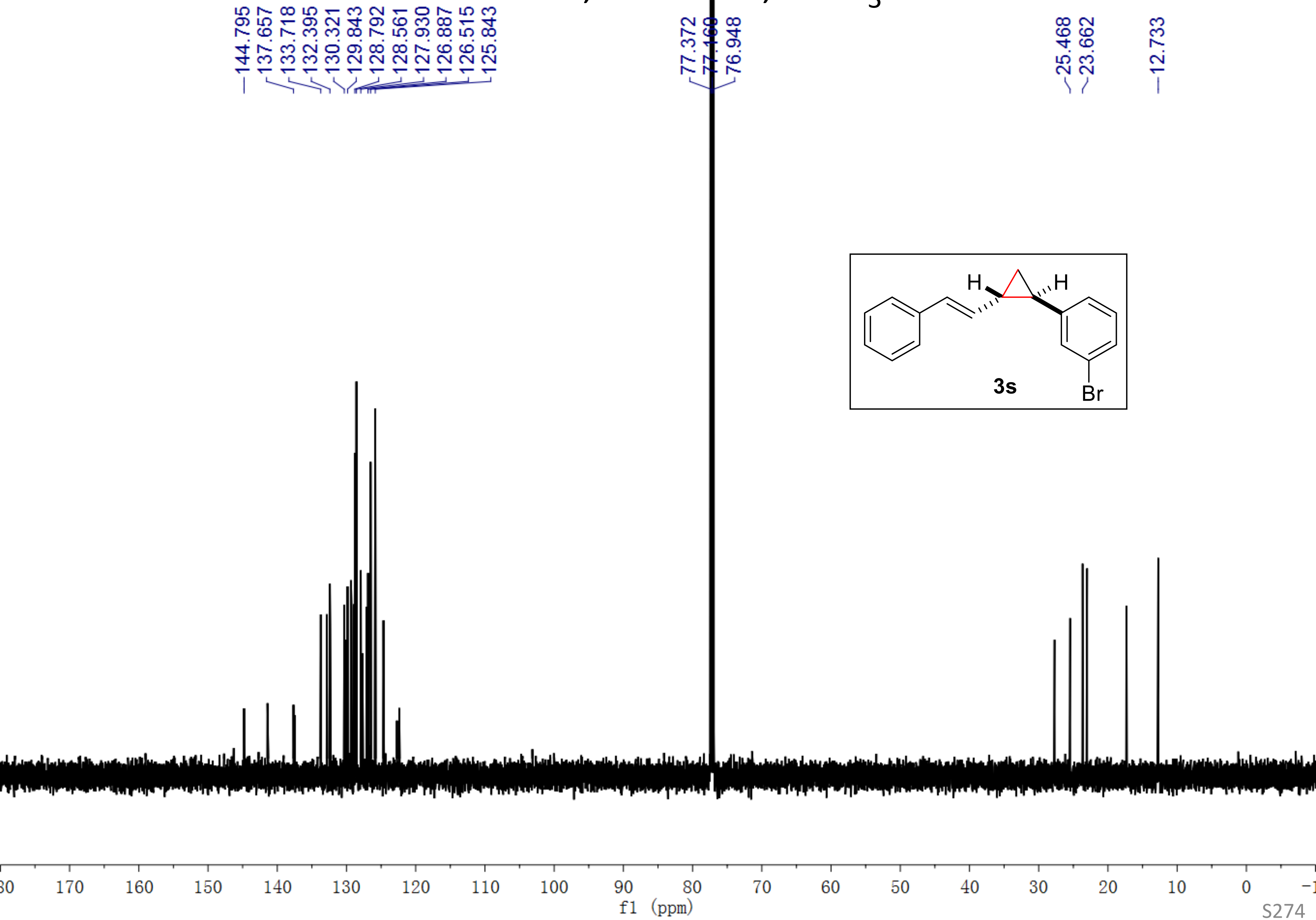
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.923	1066569	25.159
2	11.350	253777	5.986
3	12.707	2780018	65.577
4	18.140	138929	3.277
Total		4239293	100.000

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

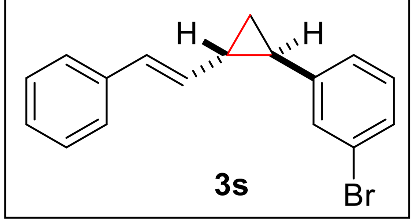


^{13}C of **3s**, 151 MHz, $CDCl_3$

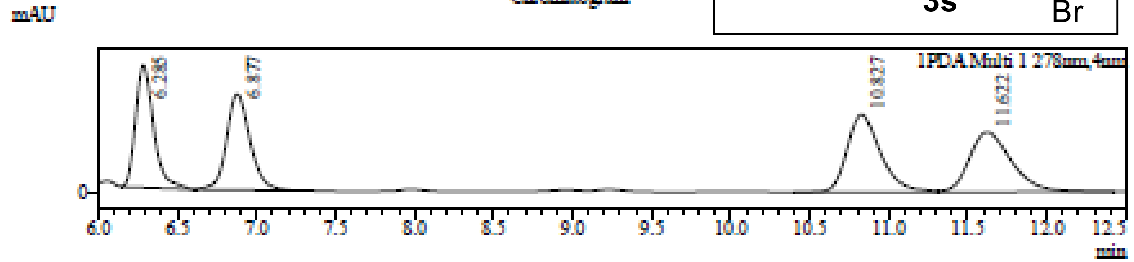


Sample Information

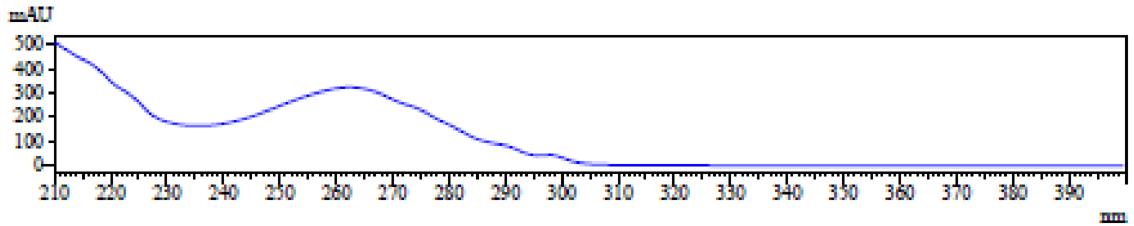
Data File : J0K-1568-IF-0.1%-1ML.lcd
Sample Name : J0K-1568-IF-0.1%-1ML
Sample ID : J0K-1568-IF-0.1%-1ML
Method File : J0K-0.1%--40min-1ml.lcm


3s

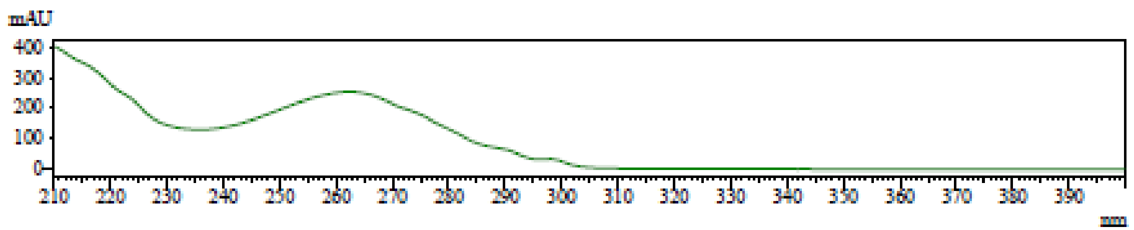
Chromatogram



UV Spectrum
Retention time = 6.285



UV Spectrum
Retention time = 6.877



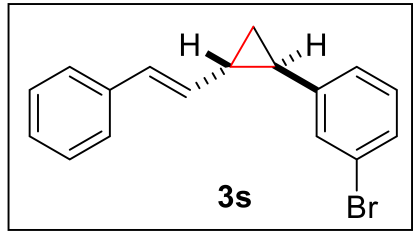
Peak Table

PDA Ch1 278nm

Peak#	Ret. Time	Area	Area%
1	6.285	1456543	23.043
2	6.877	1484560	23.486
3	10.827	1718017	27.179
4	11.622	1661994	26.293
Total		6321115	100.000

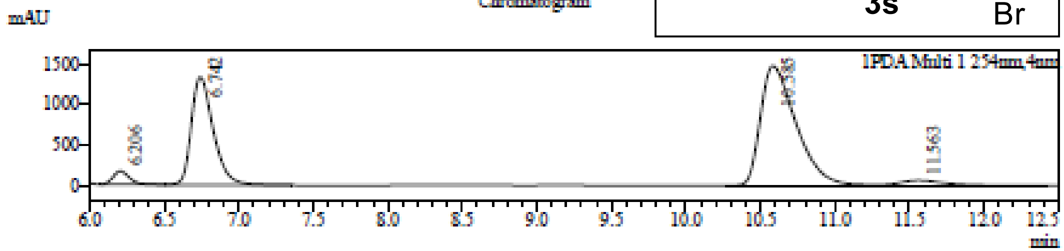
Sample Information

Data File	: J0K-1569-IF-0.1%-1ML.lcd
Sample Name	: J0K-1569-IF-0.1%-1ML
Sample ID	: J0K-1569-IF-0.1%-1ML
Method File	: J0K-0.1%--40min-1ml.lcm

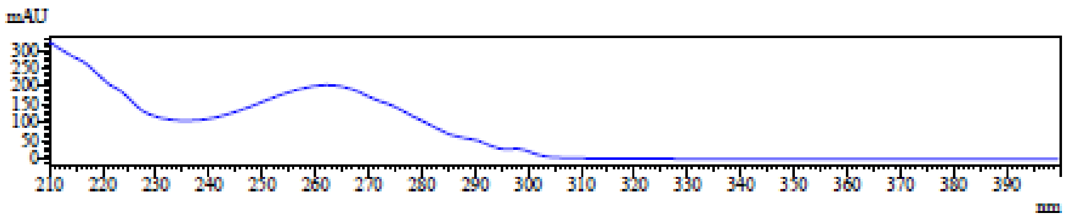


3s

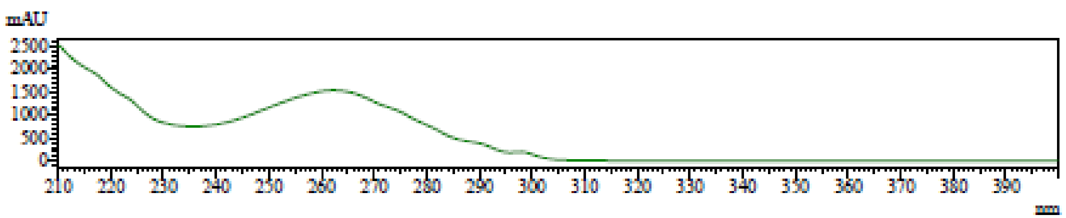
Chromatogram



UV Spectrum
Retention time = 6.206



UV Spectrum
Retention time = 6.742

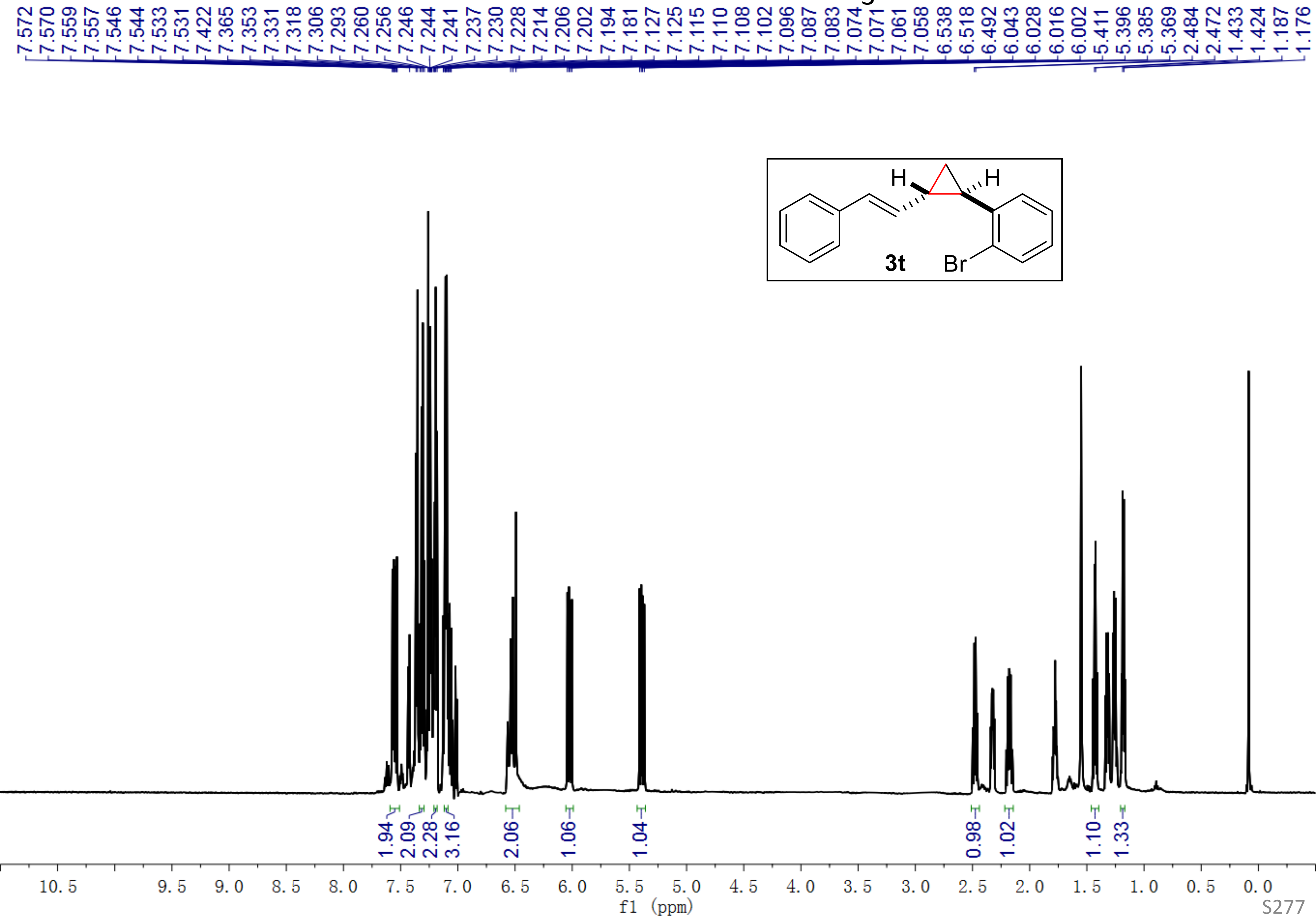


Peak Table

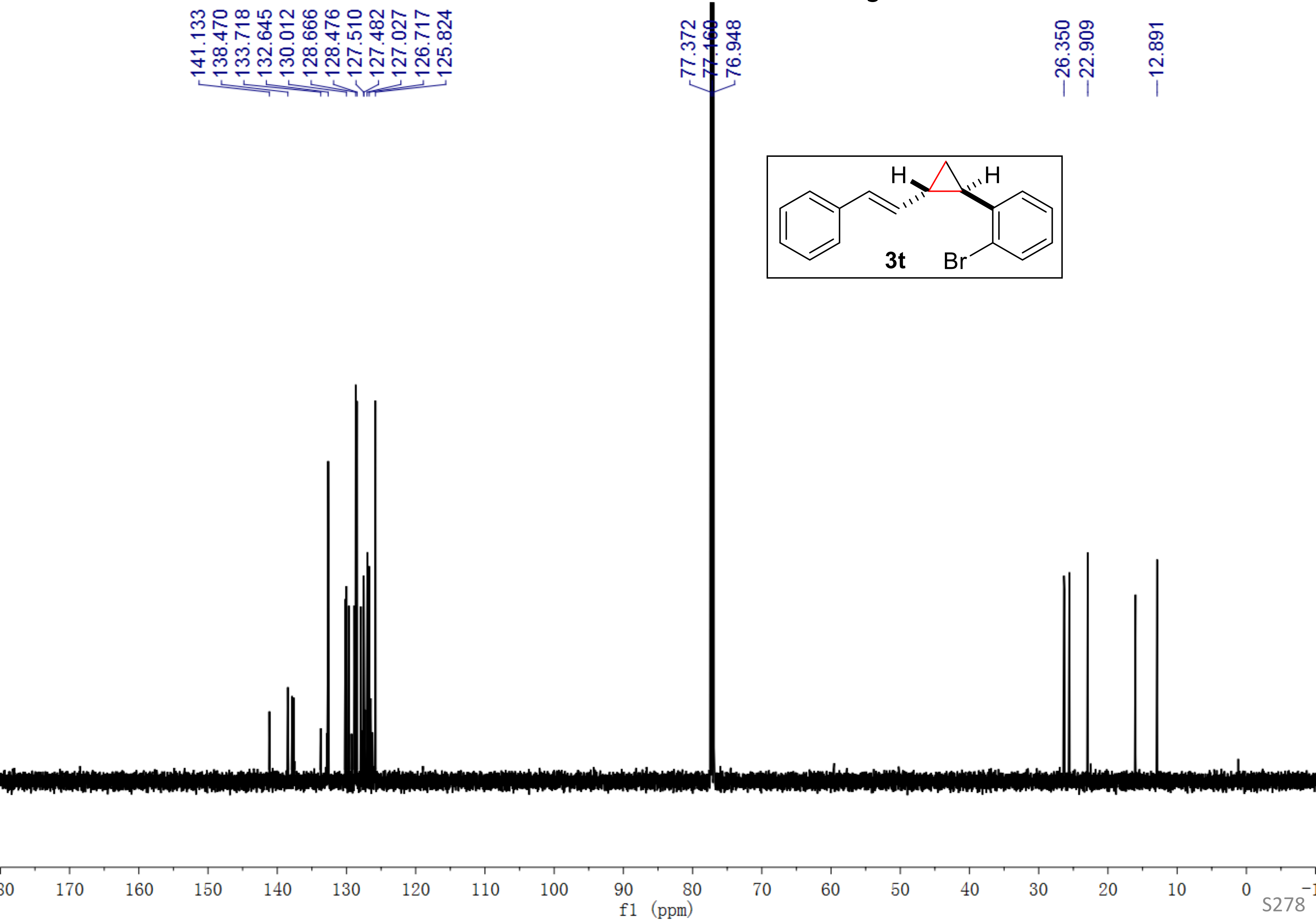
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.206	1271214	3.129
2	6.742	13609442	33.495
3	10.585	24497142	60.291
4	11.563	1253560	3.085
Total		40631357	100.000

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

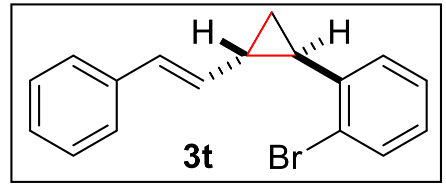


^{13}C of **3t**, 151 MHz, $CDCl_3$



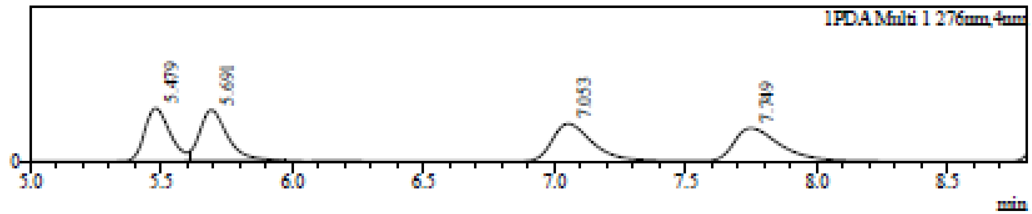
Sample Information

Data File : J0K-1576-IA-0.1%-1ML-2.lcd
Sample Name : J0K-1576-IA-0.1%-1ML-2
Sample ID : J0K-1576-IA-0.1%-1ML-2
Method File : J0K-0.1%--40min-1ml.lcm



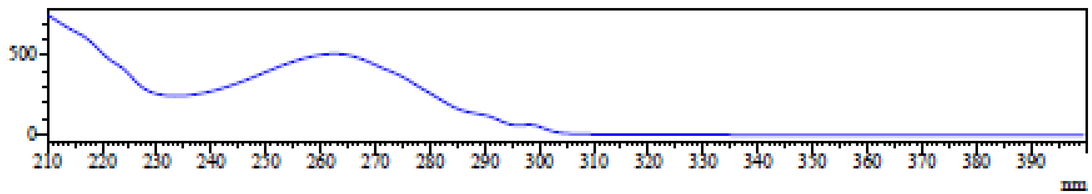
Chromatogram

AU



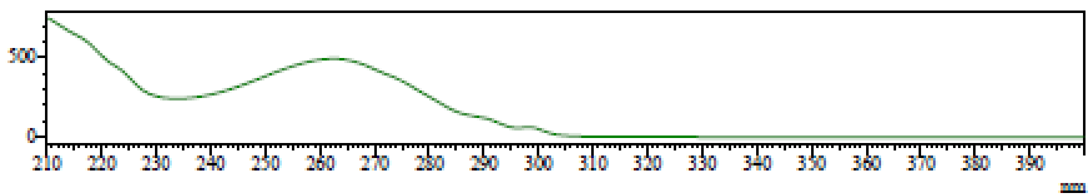
UV Spectrum
Retention time = 5.479

mAU



UV Spectrum
Retention time = 5.691

mAU



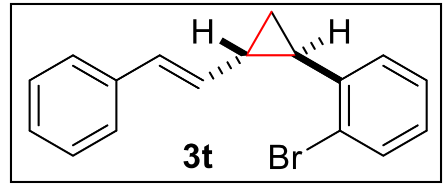
Peak Table

PDA Ch1 276nm

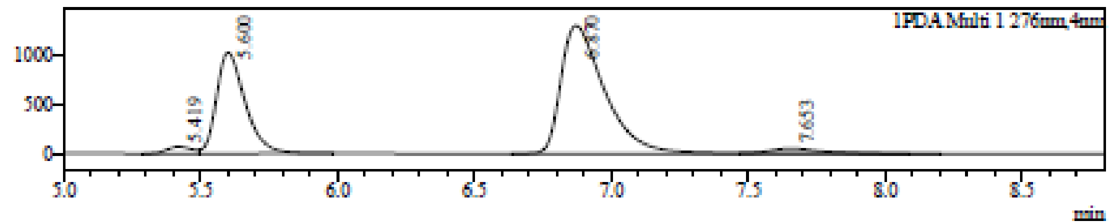
Peak#	Ret. Time	Area	Area%
1	5.479	2366826	23.188
2	5.691	2426294	23.771
3	7.053	2700266	26.455
4	7.749	2713736	26.587
Total		10207122	100.000

Sample Information

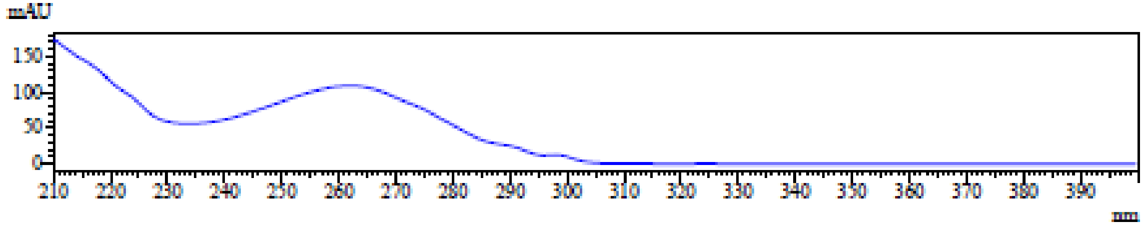
Data File : J0K-1570-IA-0.1%-1ML-2.lcd
Sample Name : J0K-1570-IA-0.1%-1ML-2
Sample ID : J0K-1570-IA-0.1%-1ML-2
Method File : J0K-0.1%--40min-1ml.lcm



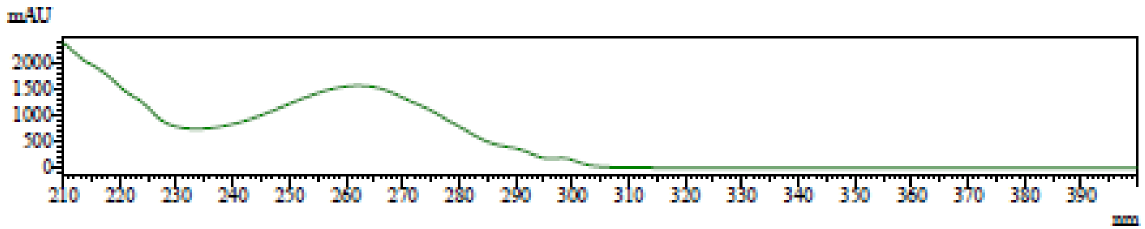
Chromatogram



UV Spectrum
Retention time = 5.419



UV Spectrum
Retention time = 5.600

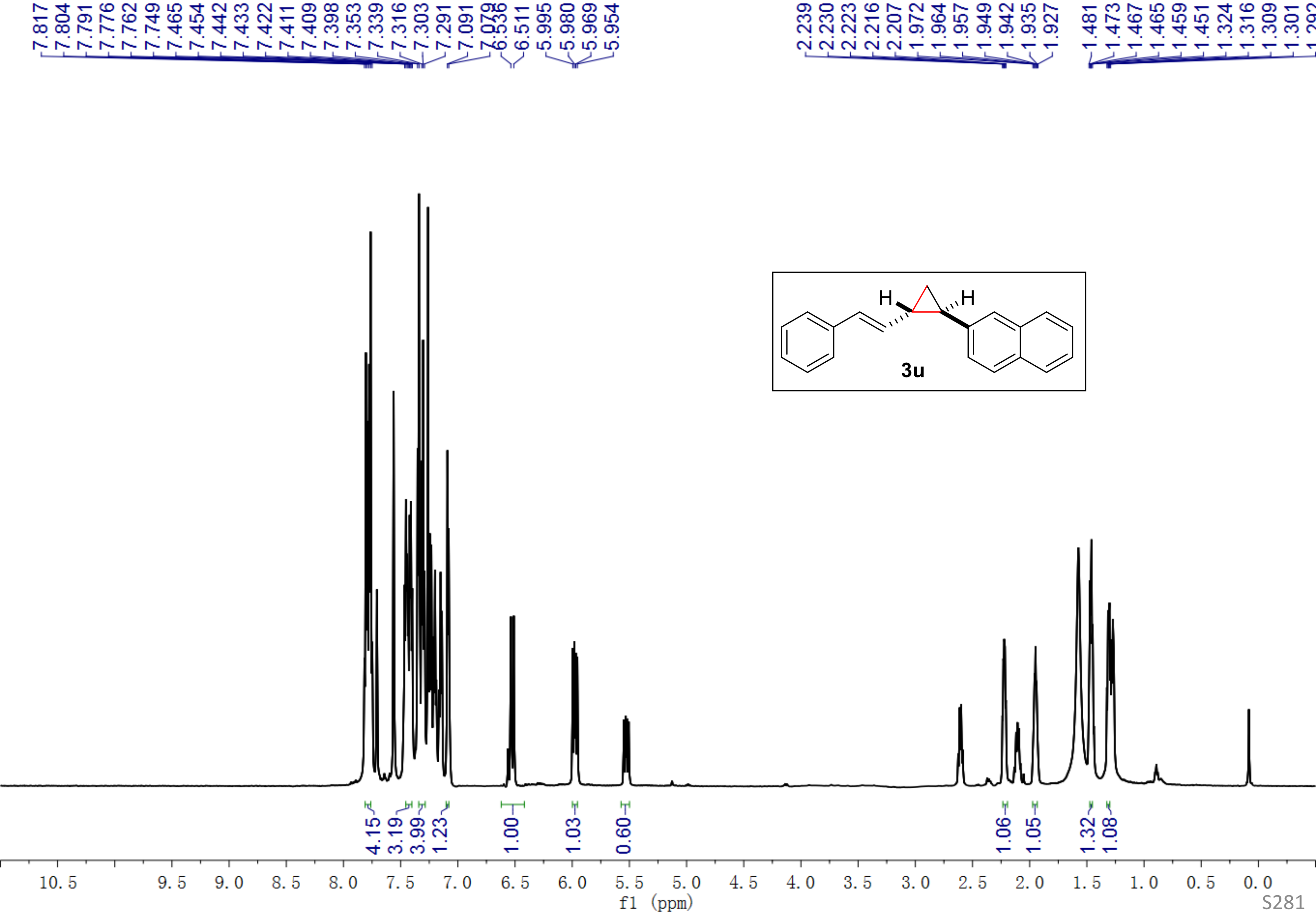


Peak Table

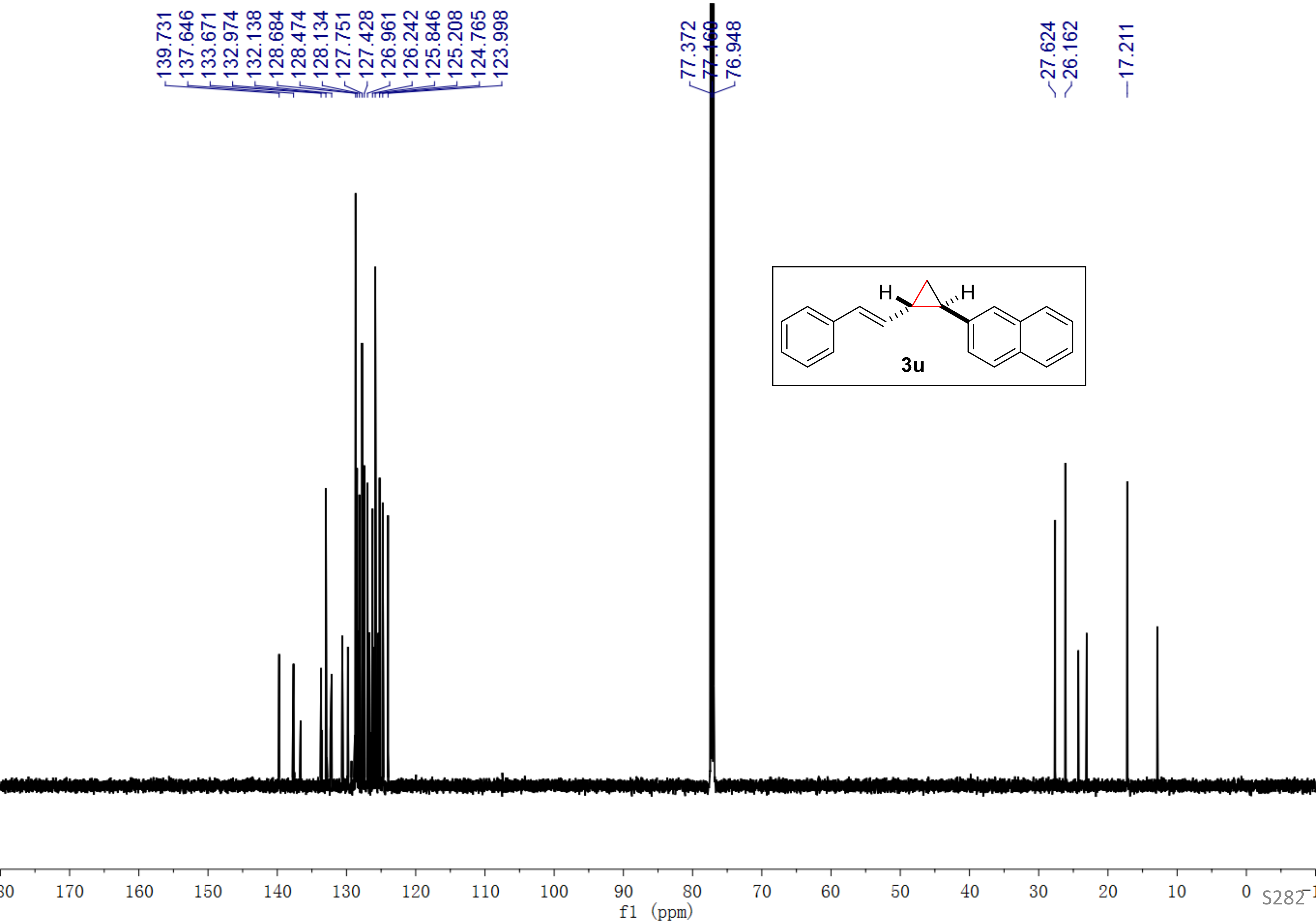
PDA Ch1 276nm

Peak#	Ret. Time	Area	Area%
1	5.419	451263	1.951
2	5.600	7492450	32.401
3	6.870	14621134	63.229
4	7.653	559246	2.418
Total		23124093	100.000

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

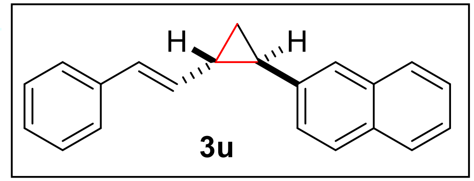


^{13}C of **3u**, 151 MHz, $CDCl_3$



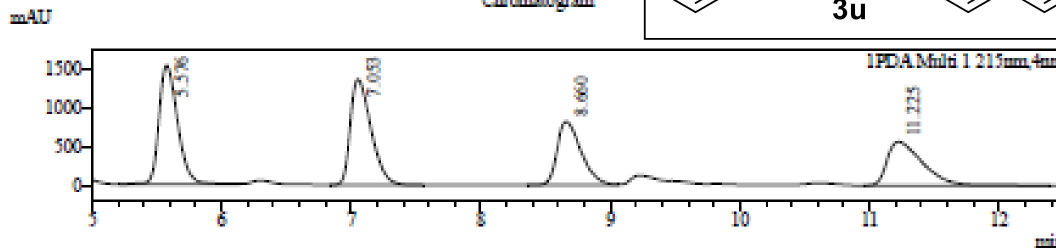
Sample Information

Data File	: J0K-1316--IB-1%-1ML.lcd
Sample Name	: J0K-1316--IB-1%-1ML
Sample ID	: J0K-1316--IB-1%-1ML
Method File	: J0K-1%-40min-1ml.lcm

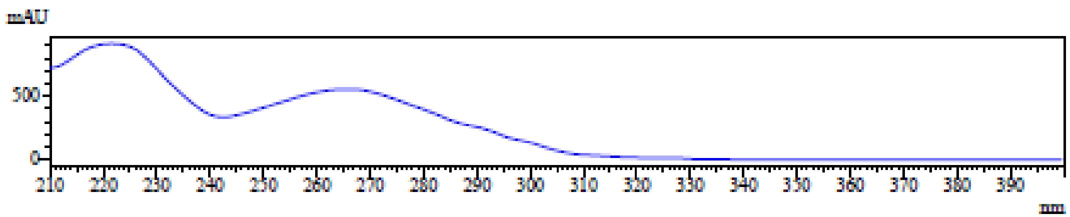


3u

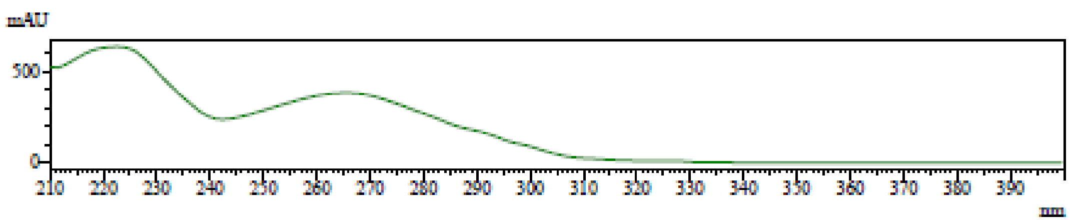
Chromatogram



UV Spectrum
Retention time = 8.660



UV Spectrum
Retention time = 11.225



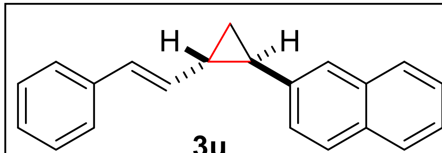
Peak Table

PDA Ch1 215nm

Peak#	Ret. Time	Area	Area%
1	5.576	15056194	29.893
2	7.053	14810899	29.406
3	8.660	10189274	20.230
4	11.225	10310804	20.471
Total		50367170	100.000

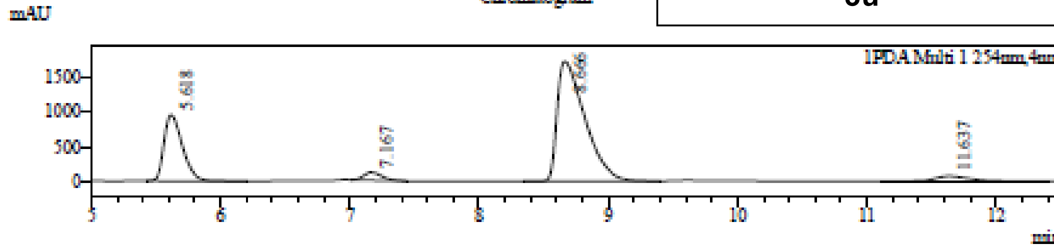
Sample Information

Data File : J0K-1315--IB-1%-1ML.lcd
Sample Name : J0K-1315--IB-1%-1ML
Sample ID : J0K-1315--IB-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

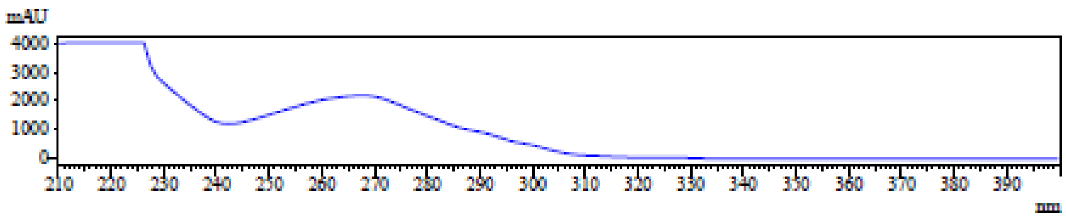


3u

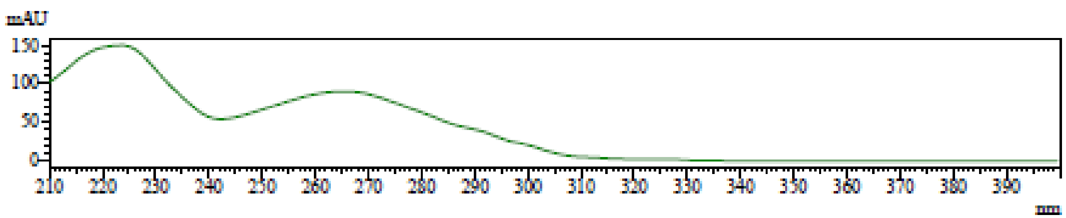
Chromatogram



UV Spectrum
Retention time = 8.666



UV Spectrum
Retention time = 11.637

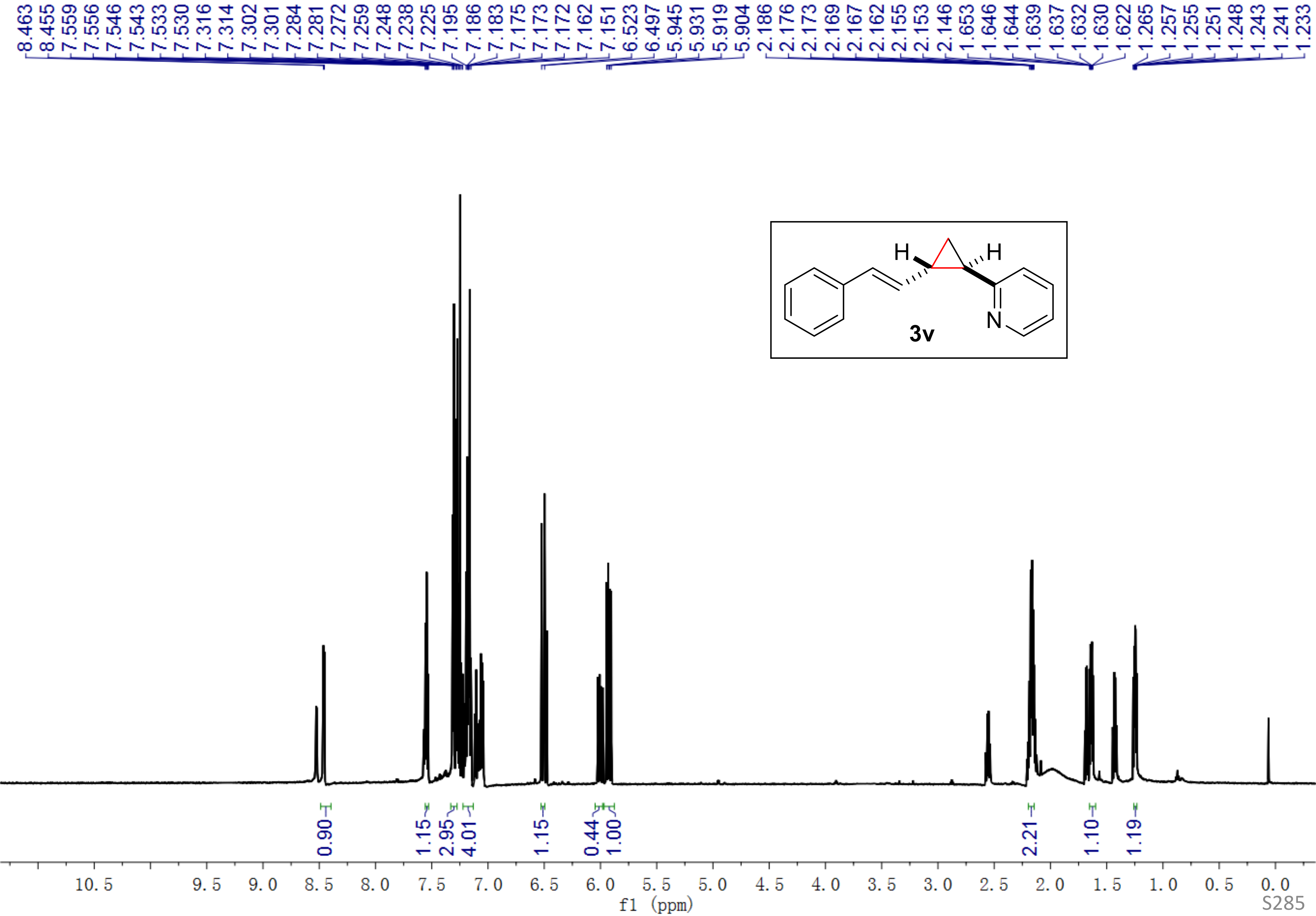


Peak Table

PDA Ch1 254nm

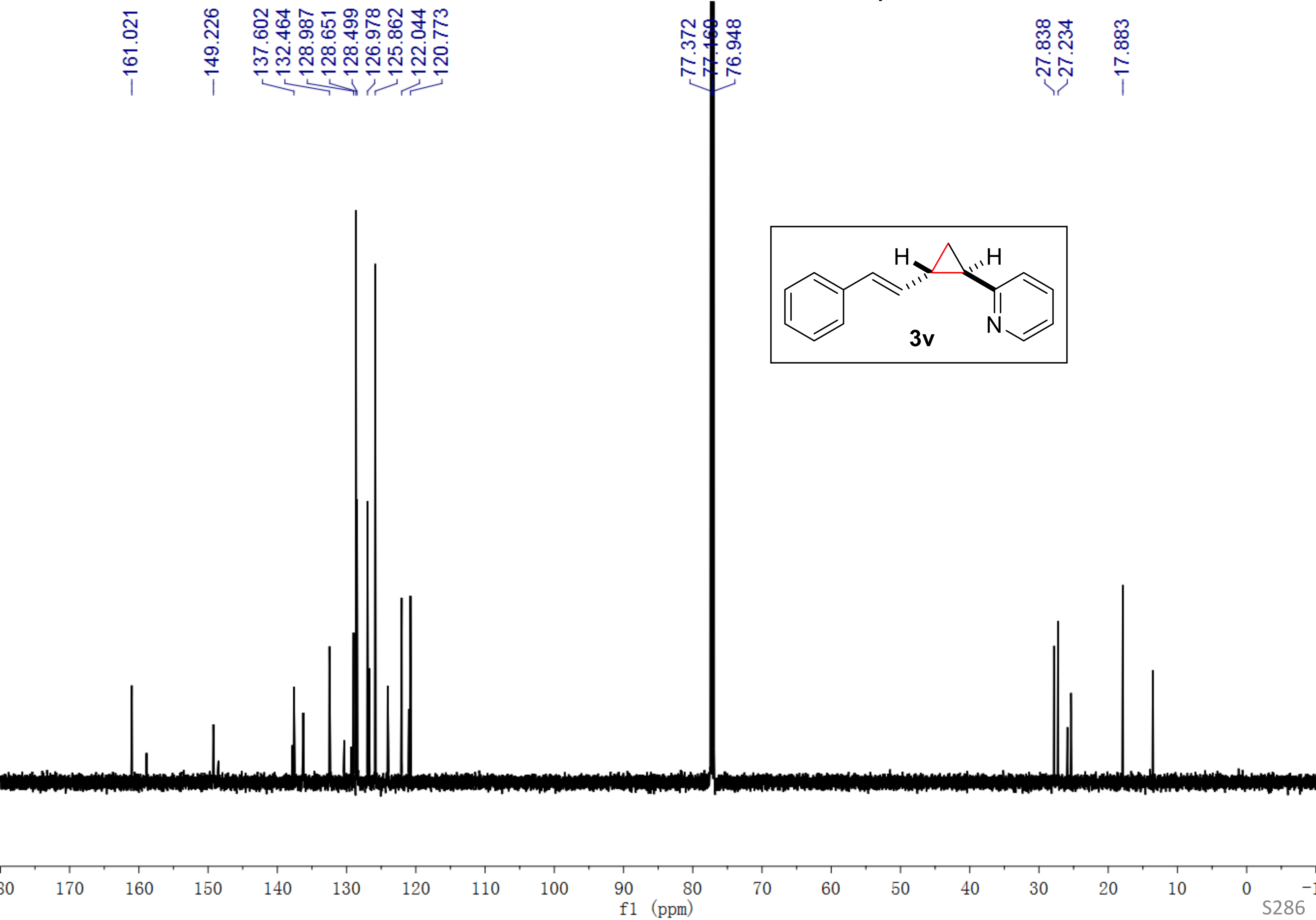
Peak#	Ret. Time	Area	Area%
1	5.618	9516485	24.990
2	7.167	1134749	2.980
3	8.666	26083123	68.495
4	11.637	1346087	3.535
Total		38080444	100.000

^1H of **3v**, 600 MHz, $CDCl_3$



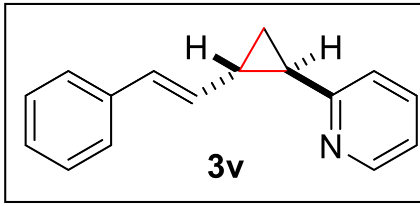
3v

^{13}C of **3v**, 151 MHz, $CDCl_3$



Sample Information

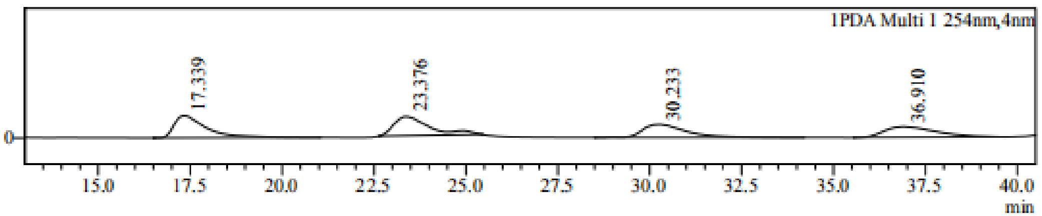
Data File : J0K-1645-OJH-1%-1ML.lcd
Sample Name : J0K-1645-OJH-1%-1ML
Sample ID : J0K-1645-OJH-1%-1ML
Method File : J0K-1%-80min-1ml.lcm



3v

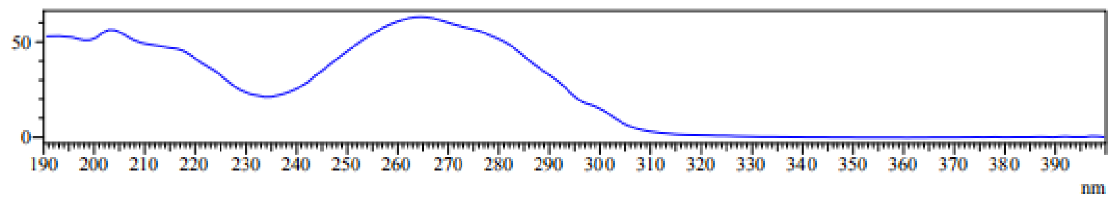
Chromatogram

AU



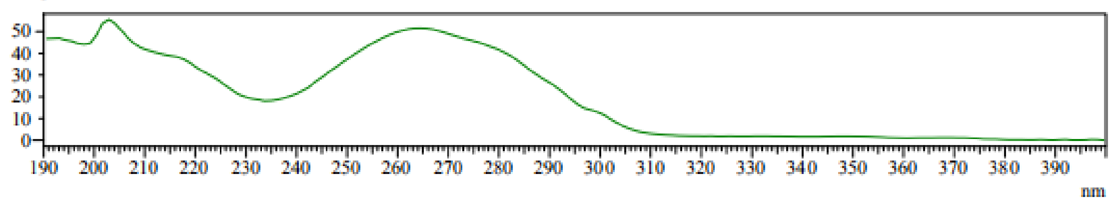
UV Spectrum
Retention time = 30.233

mAU



UV Spectrum
Retention time = 36.910

mAU



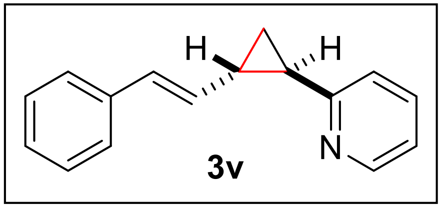
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.339	5190004	28.399
2	23.376	4964194	27.163
3	30.233	4084549	22.350
4	36.910	4036598	22.088
Total		18275345	100.000

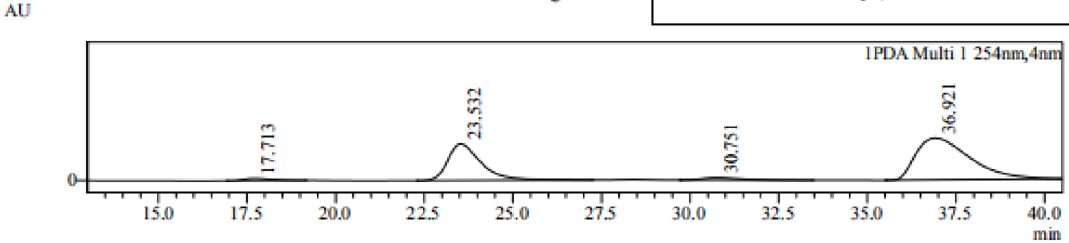
Sample Information

Data File	: J0K-1294-OJH-1%-1ML.lcd
Sample Name	: J0K-1294-OJH-1%-1ML
Sample ID	: J0K-1294-OJH-1%-1ML
Method File	: J0K-1%-80min-1ml.lcm

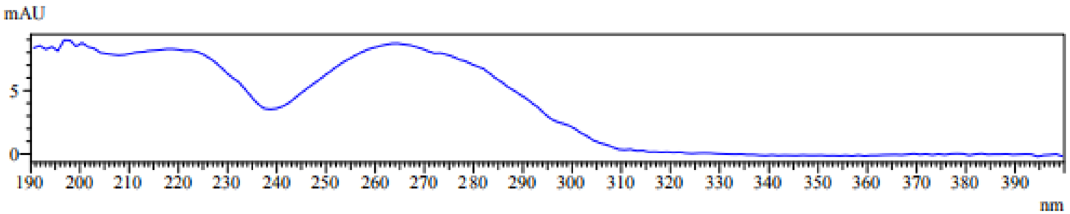


3v

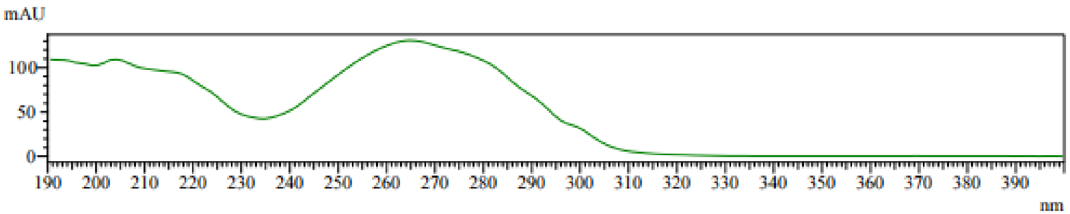
Chromatogram



UV Spectrum
Retention time = 30.751



UV Spectrum
Retention time = 36.921

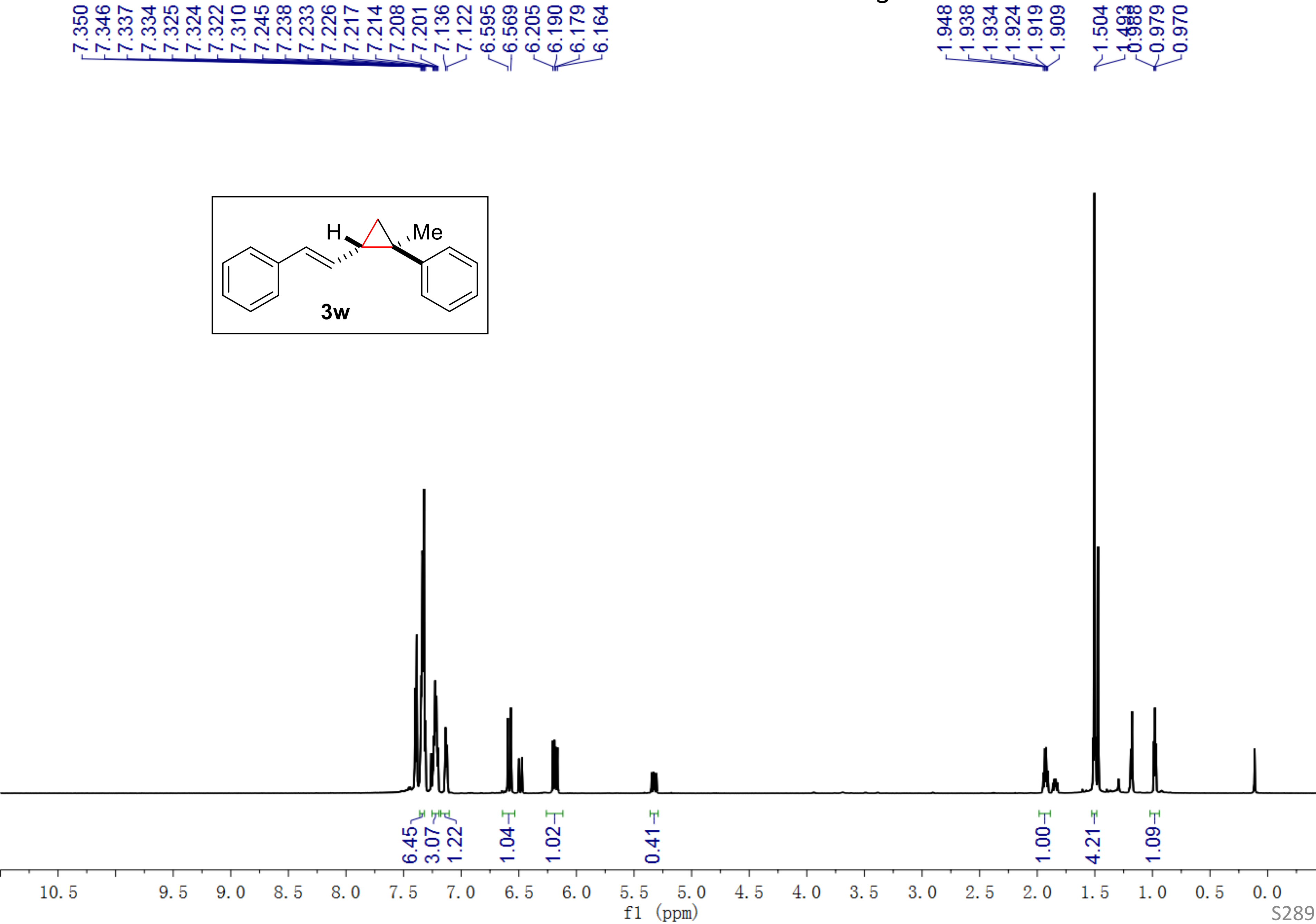


Peak Table

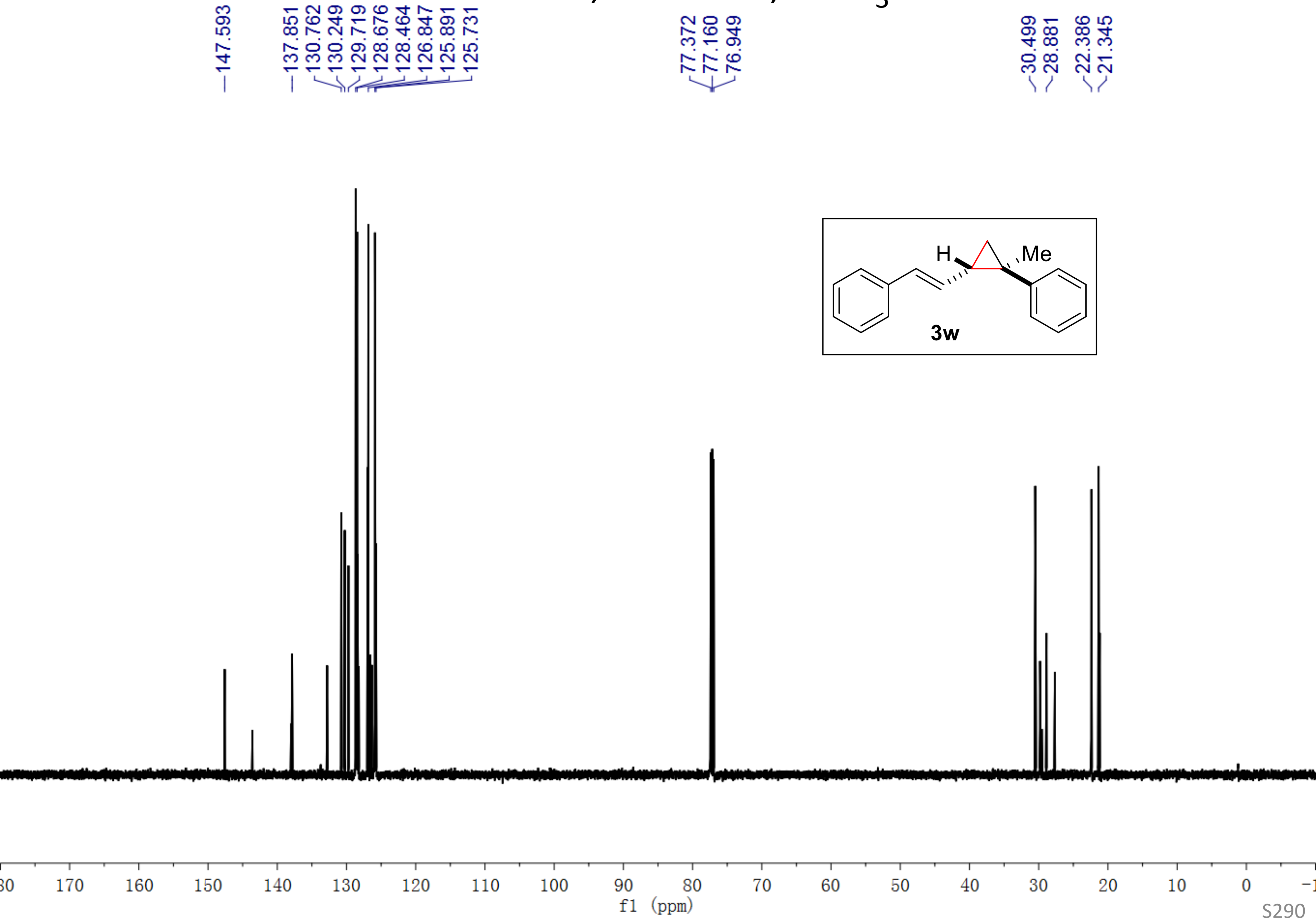
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.713	299091	1.660
2	23.532	6084439	33.770
3	30.751	461794	2.563
4	36.921	11172216	62.007
Total		18017541	100.000

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

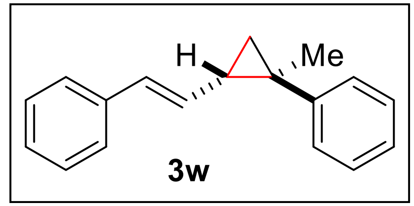


^{13}C of **3w**, 151 MHz, $CDCl_3$



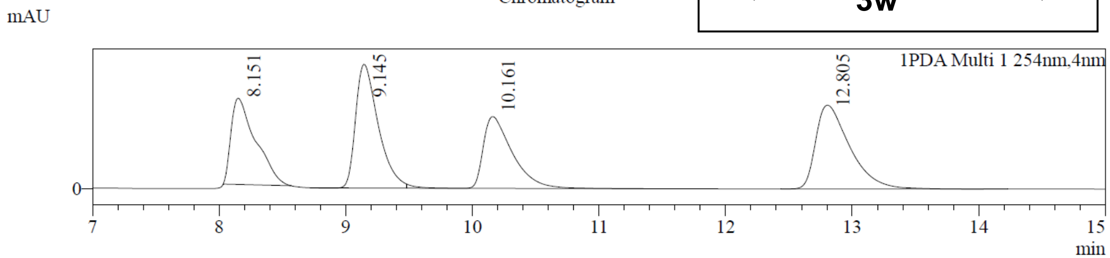
Sample Information

Data File : J0K-1882--IB--0%-1ML.lcd
Sample Name : J0K-1882--IB--0%-1ML
Sample ID : J0K-1882--IB--0%-1ML
Method File : J0K-0%--45min-1ml.lcm

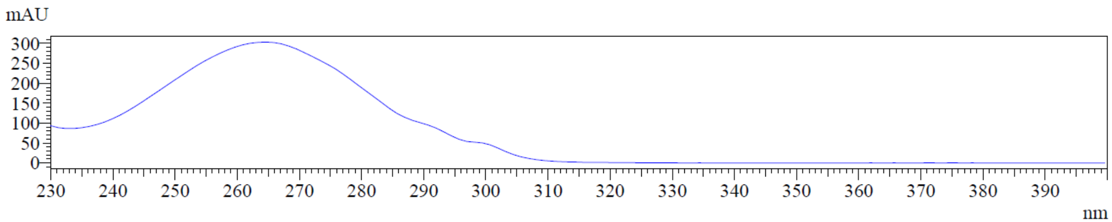


3w

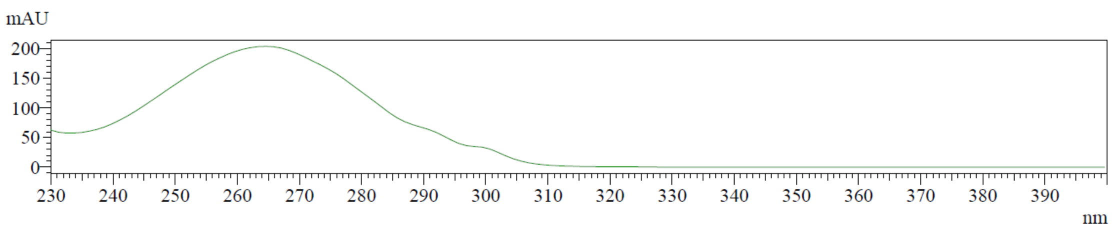
Chromatogram



UV Spectrum
Retention time = 9.145



UV Spectrum
Retention time = 12.805



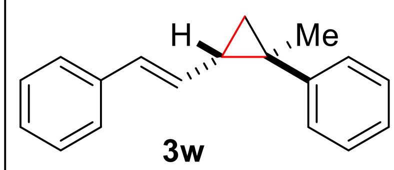
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.151	2331476	21.438
2	9.145	3076422	28.288
3	10.161	2322158	21.352
4	12.805	3145420	28.922
Total		10875476	100.000

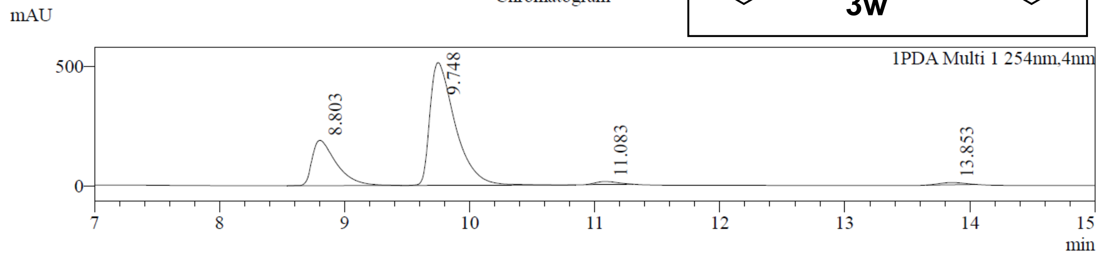
Sample Information

Data File	: J0K-1881--IB--0%-1ML-2.lcd
Sample Name	: J0K-1881--IB--0%-1ML-2
Sample ID	: J0K-1881--IB--0%-1ML-2
Method File	: J0K-0%--45min-1ml.lcm

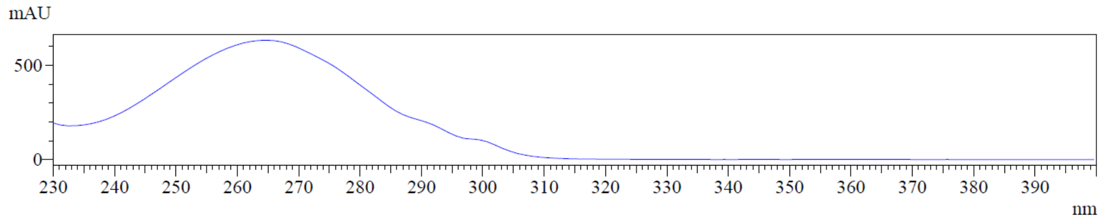


3w

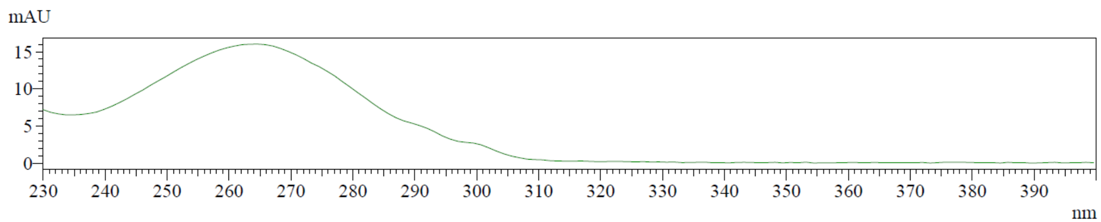
Chromatogram



UV Spectrum
Retention time = 9.748



UV Spectrum
Retention time = 13.853

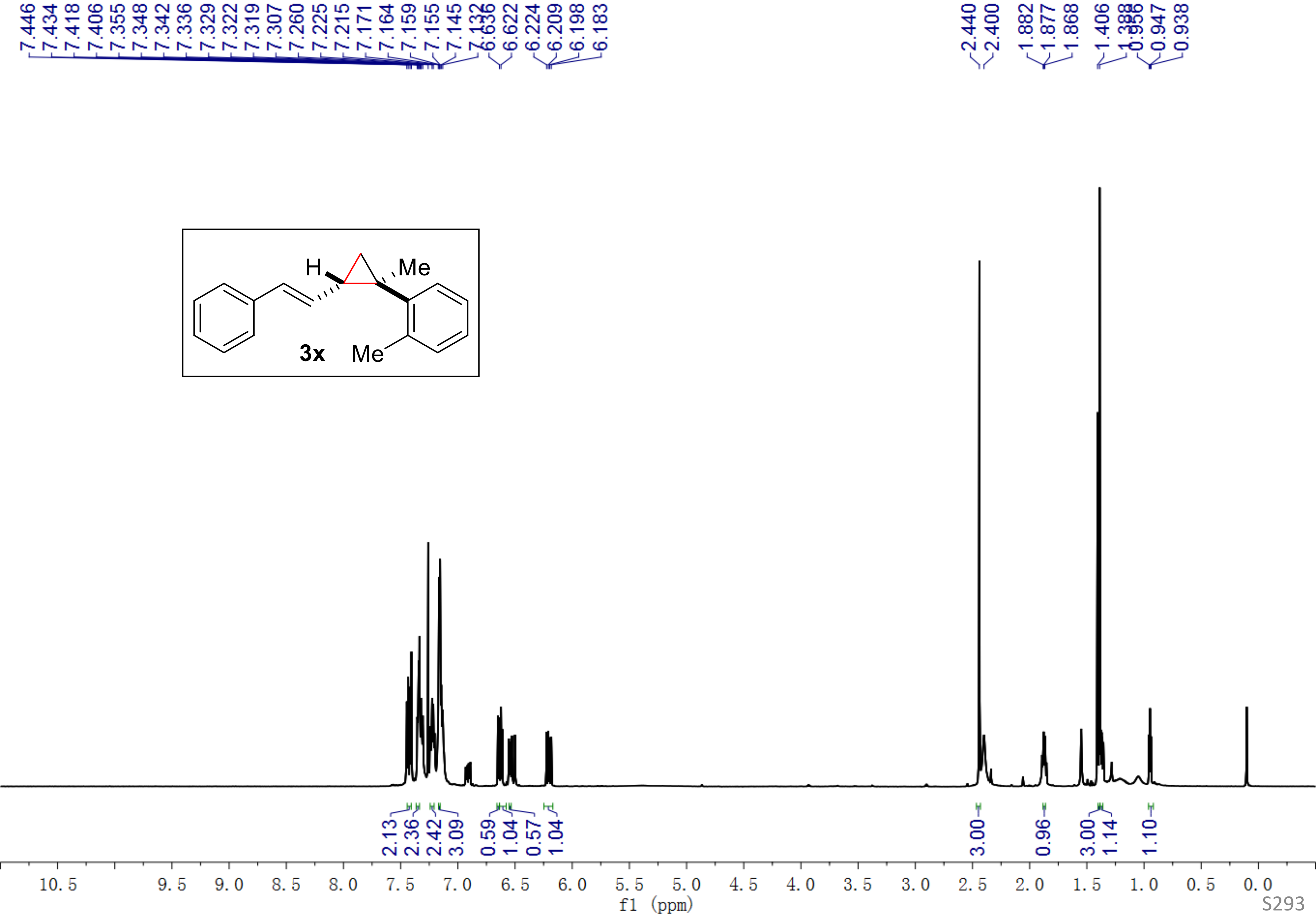


Peak Table

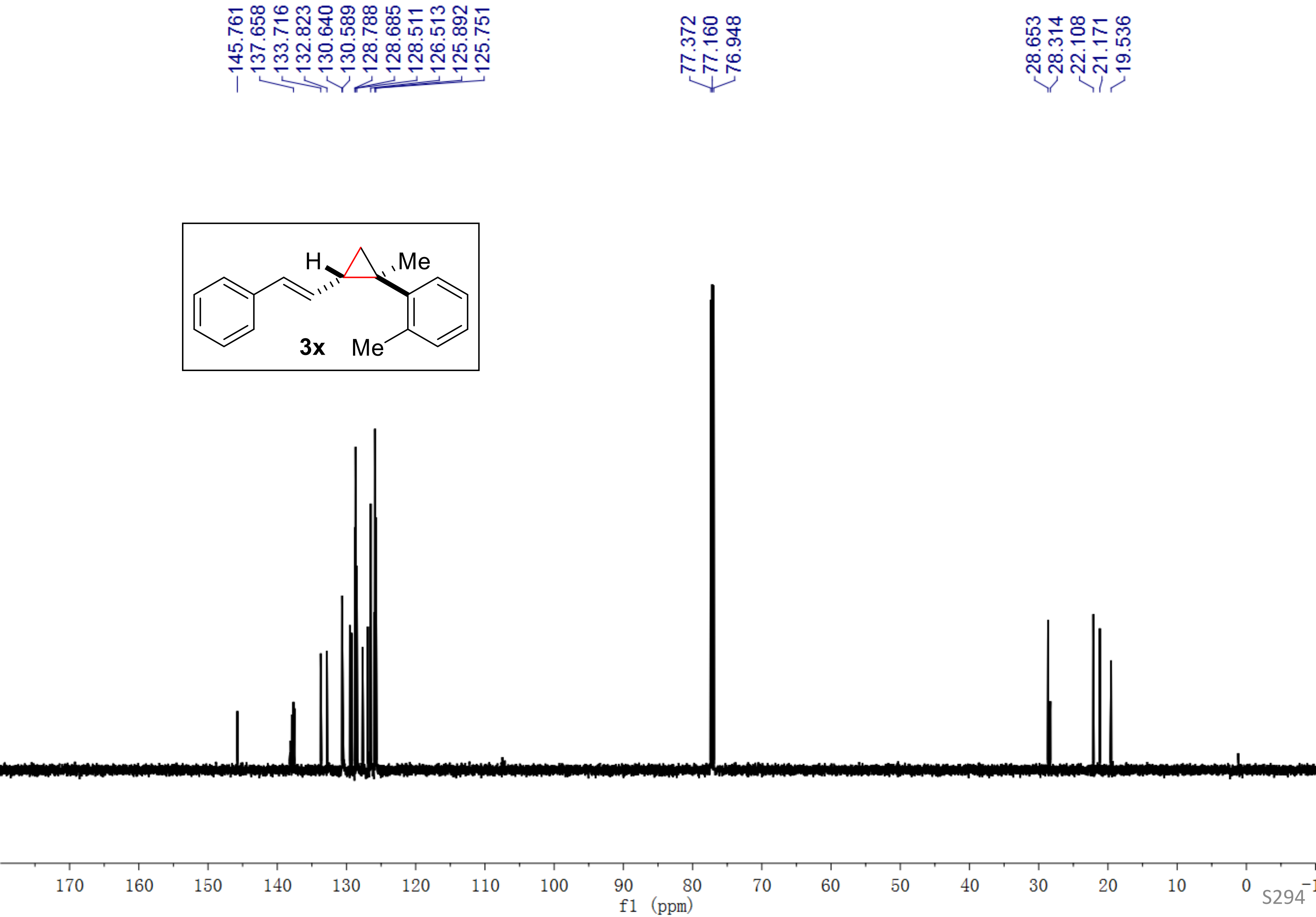
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.803	2560314	25.378
2	9.748	7248467	71.848
3	11.083	148712	1.474
4	13.853	131112	1.300
Total		10088605	100.000

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

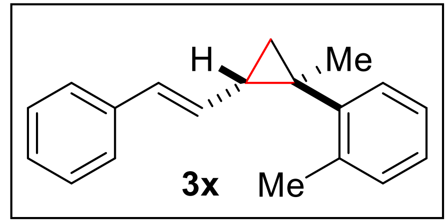


^{13}C of **3x**, 151 MHz, $CDCl_3$

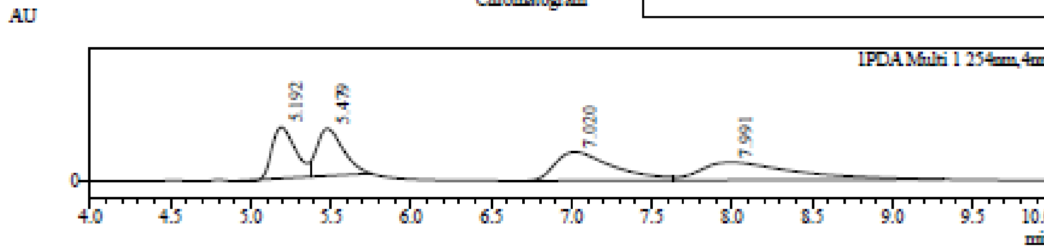


Sample Information

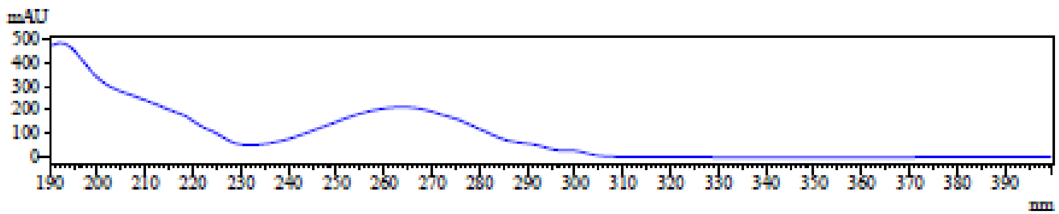
Data File : J0K-1625-ID-0%-0.5ML4.lcd
Sample Name : J0K-1625-ID-0%-0.5ML4
Sample ID : J0K-1625-ID-0%-0.5ML4
Method File : J0K-0%--45min-1ml.lcm



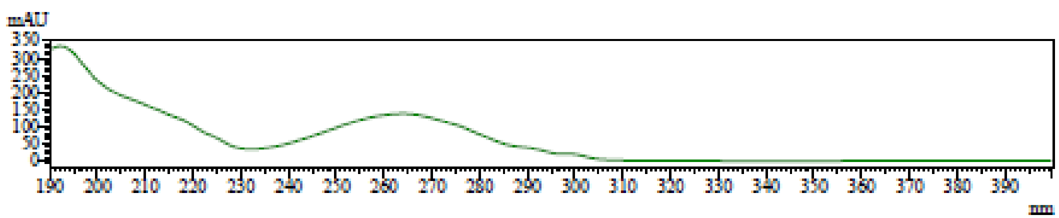
Chromatogram



UV Spectrum
Retention time = 7.020



UV Spectrum
Retention time = 7.991



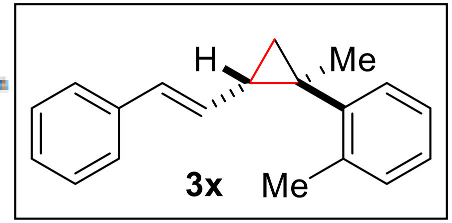
Peak Table

PDA Ch1 254nm

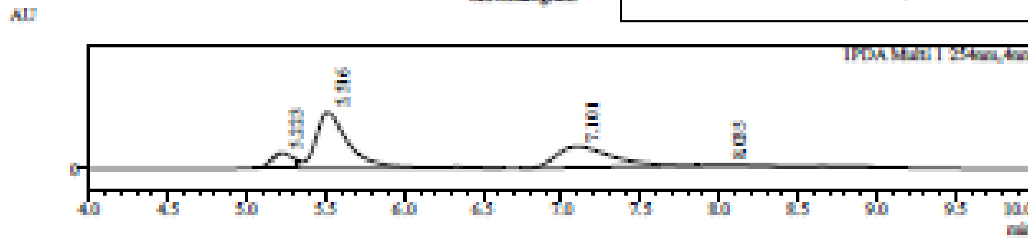
Peak#	Ret. Time	Area	Area%
1	5.192	3219416	21.207
2	5.479	3236796	21.321
3	7.020	4354822	28.686
4	7.991	4370184	28.787
Total		15181218	100.000

Sample Information

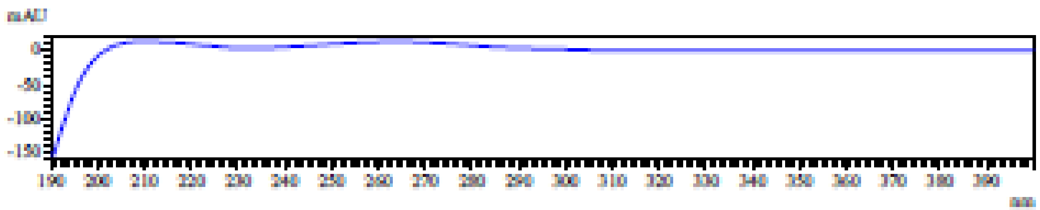
Data File	: J0K-1624-ID-0%-0.5ML4.lcd
Sample Name	: J0K-1624-ID-0%-0.5ML4
Sample ID	: J0K-1624-ID-0%-0.5ML4
Method File	: J0K-0%--45min-1ml.lcm



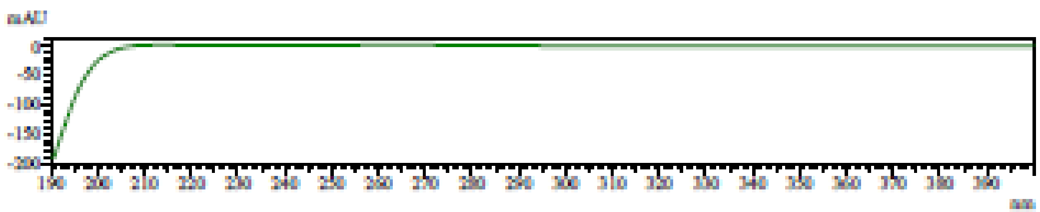
Chromatogram



UV Spectrum
Retention time = 7.101



UV Spectrum
Retention time = 8.035

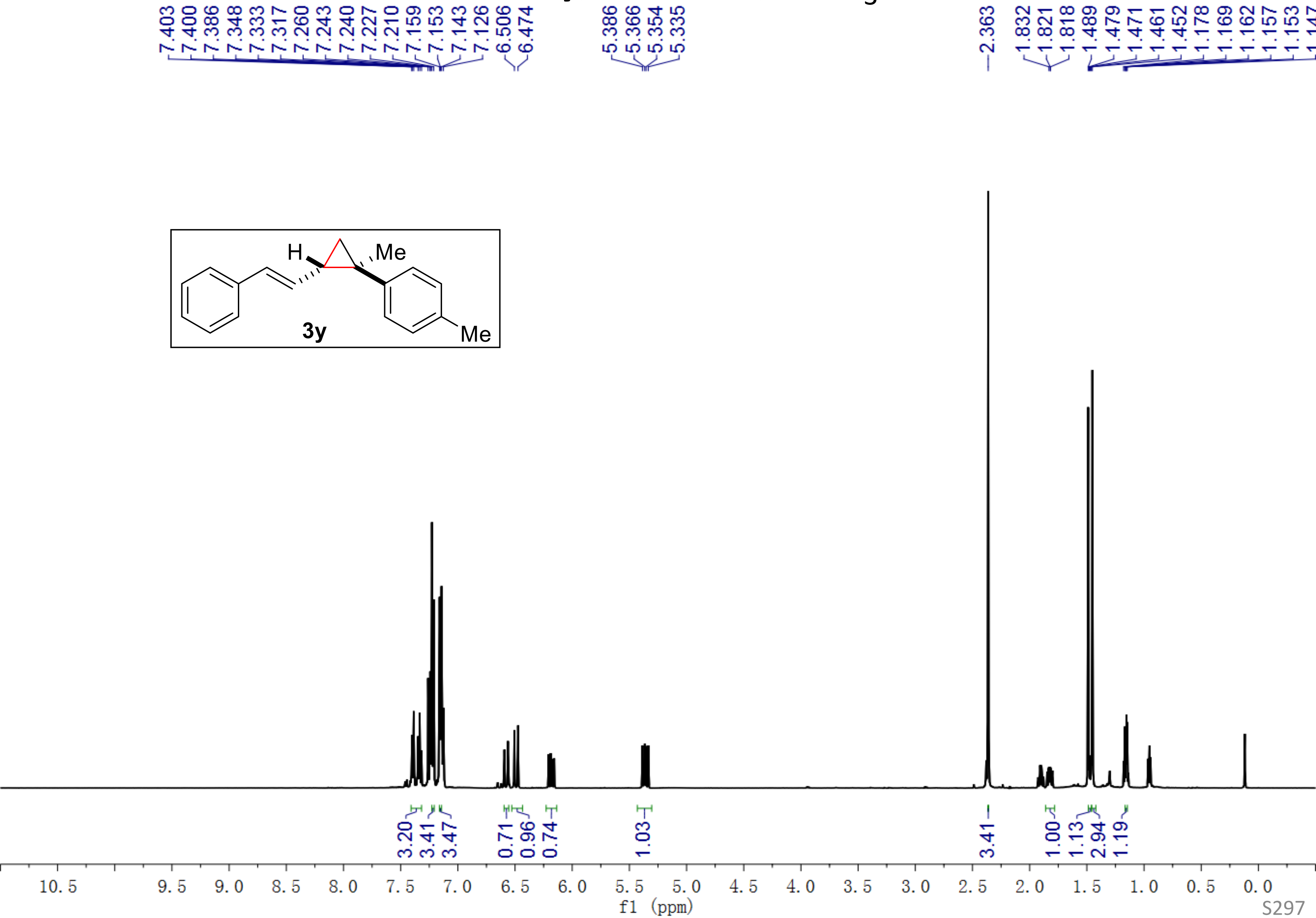


Peak Table

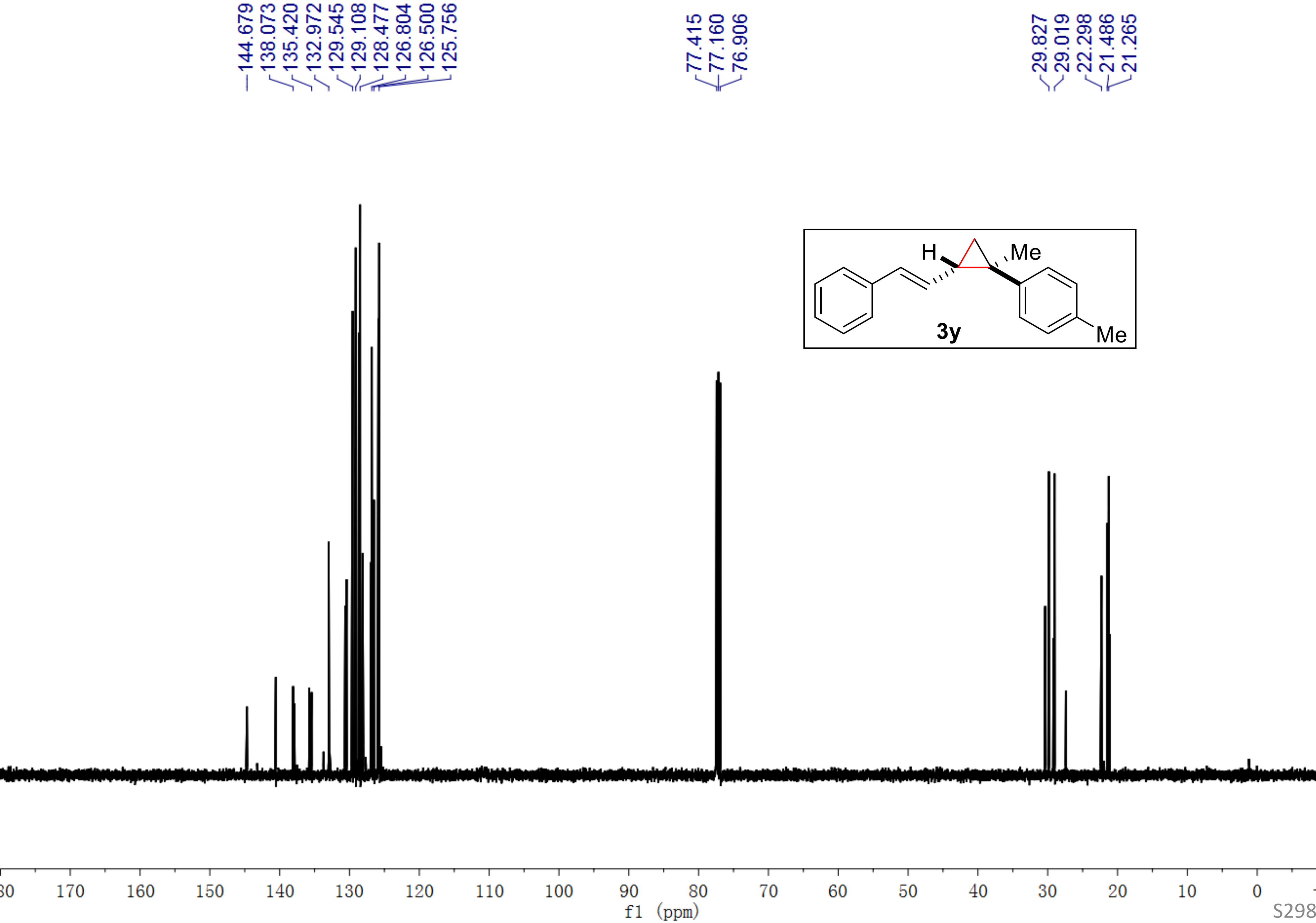
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.223	69699	9.585
2	5.516	400845	55.122
3	7.101	246749	33.932
4	8.035	9897	1.361
Total		727189	100.000

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

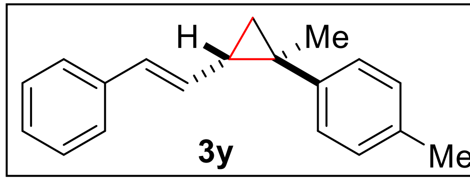


^{13}C of **3y**, 151 MHz, $CDCl_3$



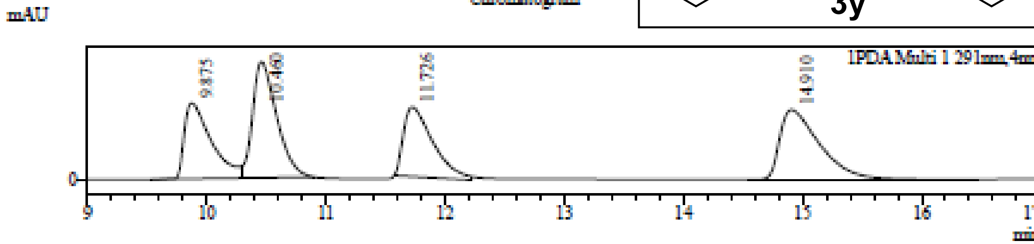
Sample Information

Data File : J0K-1359--IB-0%-0.8ML.lcd
Sample Name : J0K-1359--IB-0%-0.8ML
Sample ID : J0K-1359--IB-0%-0.8ML
Method File : J0K-0%--40min-0.8ml.lcm

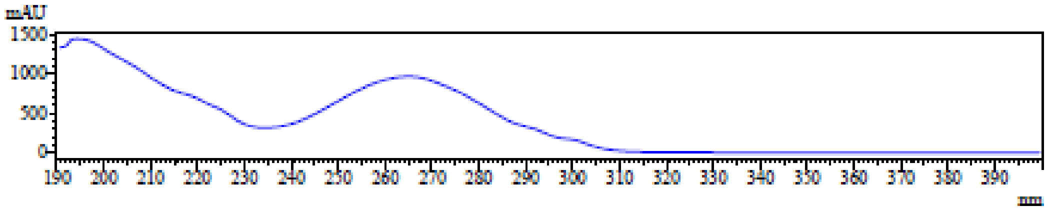


3y

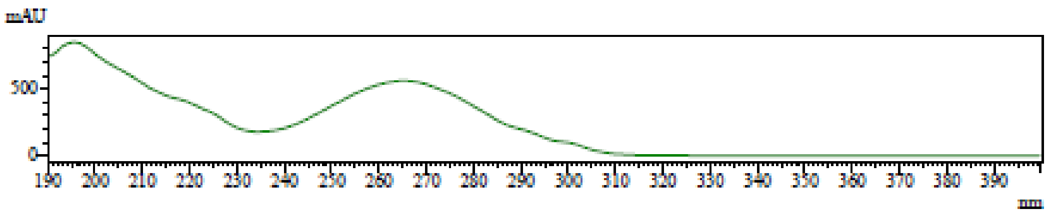
Chromatogram



UV Spectrum
Retention time = 10.460



UV Spectrum
Retention time = 14.910



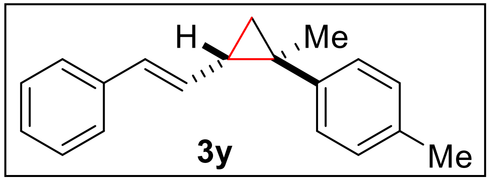
Peak Table

PDA Ch1 291nm

Peak#	Ret. Time	Area	Area%
1	9.875	3129130	21.225
2	10.460	4265956	28.937
3	11.726	3126757	21.209
4	14.910	4220518	28.629
Total		14742361	100.000

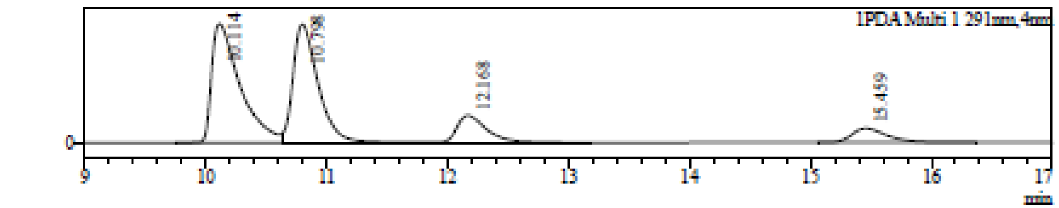
Sample Information

Data File : J0K-1358--IB-0%-0.8ML.lcd
Sample Name : J0K-1358--IB-0%-0.8ML
Sample ID : J0K-1358--IB-0%-0.8ML
Method File : J0K-0%--40min-0.8ml.lcm

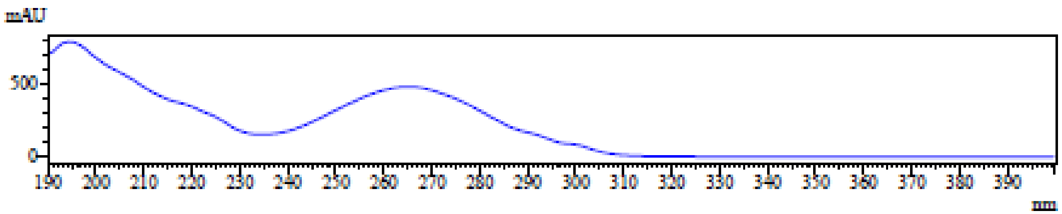


3y

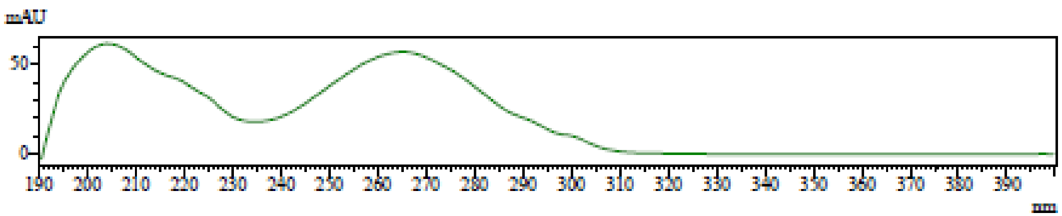
Chromatogram



UV Spectrum
Retention time = 10.798



UV Spectrum
Retention time = 15.459

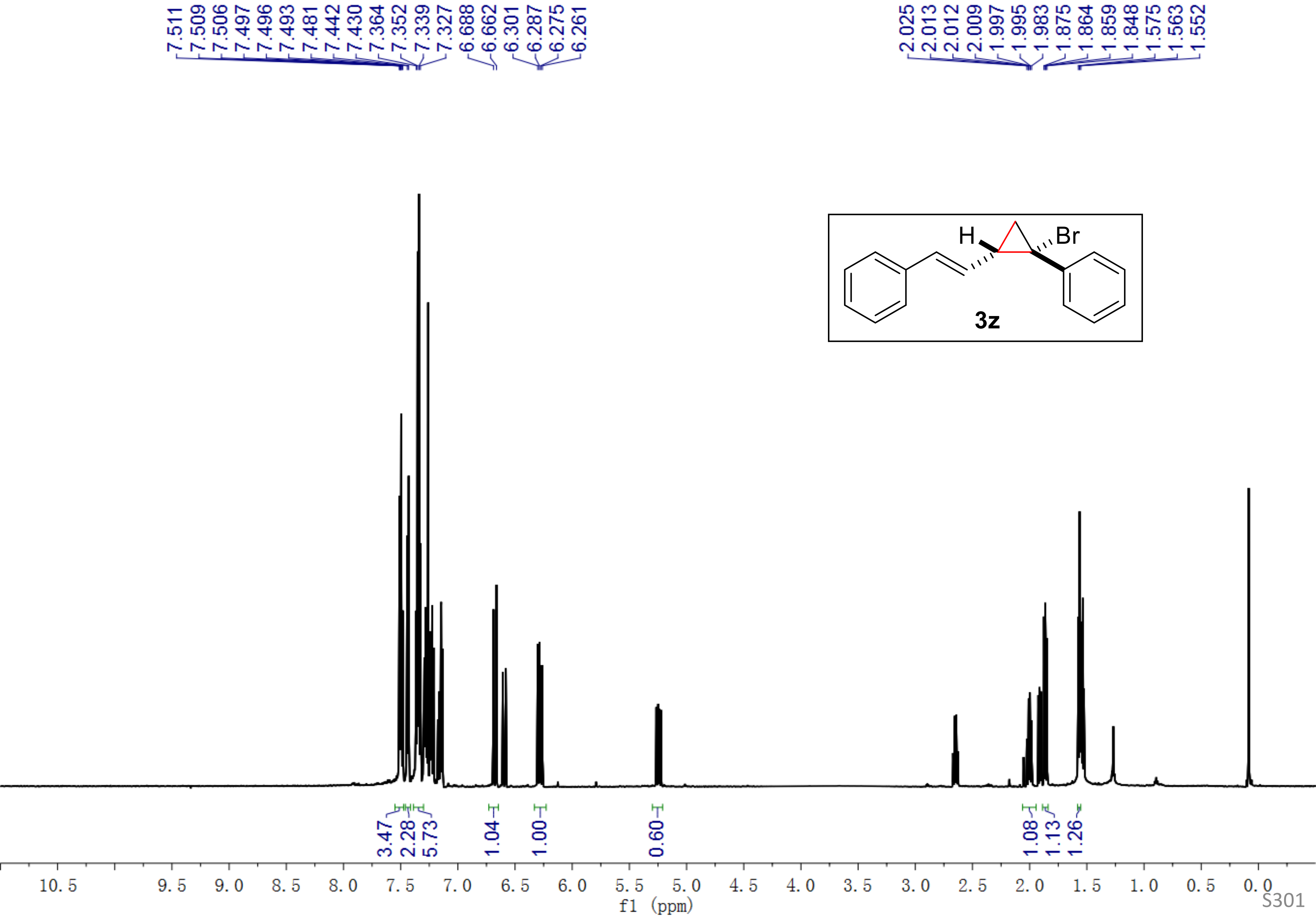


Peak Table

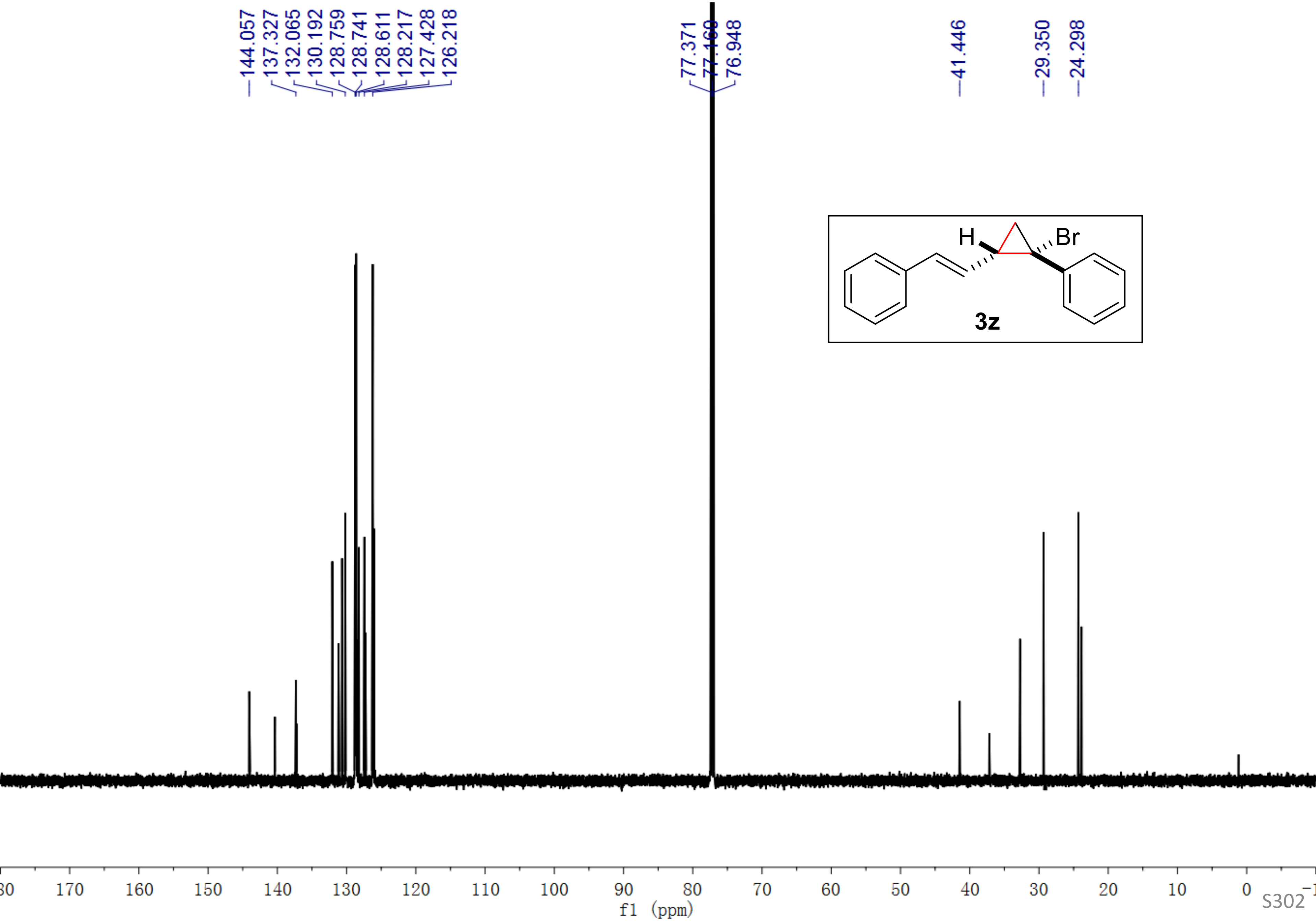
PDA Ch1 291nm

Peak#	Ret. Time	Area	Area%
1	10.114	2578359	44.347
2	10.798	2256637	38.813
3	12.168	608904	10.473
4	15.459	370187	6.367
Total		5814087	100.000

^1H of **3z**, 600 MHz, $CDCl_3$

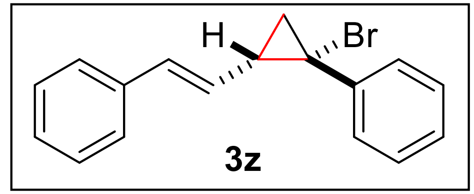


^{13}C of **3z**, 151 MHz, $CDCl_3$



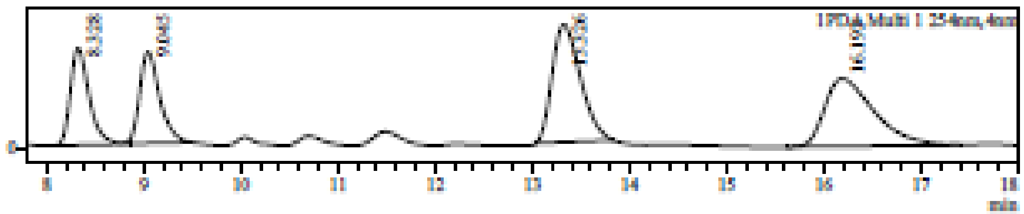
Sample Information

Data File	: J0K-1266--IF-0%-1ML.lcd
Sample Name	: J0K-1266--IF-0%-1ML
Sample ID	: J0K-1266--IF-0%-1ML
Method File	: J0K-0%--45min-1ml.lcm

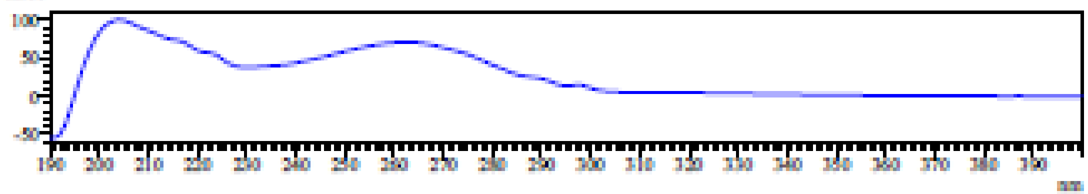


3z

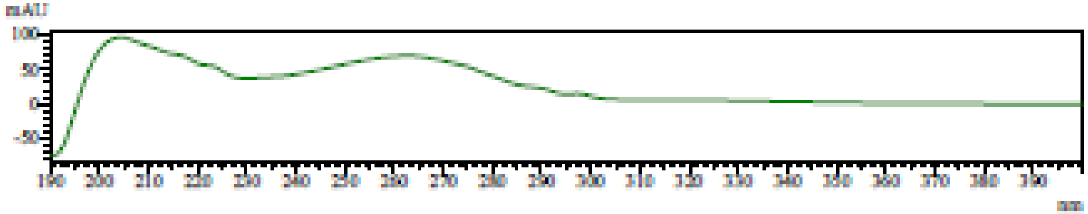
Chromatogram



UV Spectrum
Retention time = 8.328



UV Spectrum
Retention time = 9.045



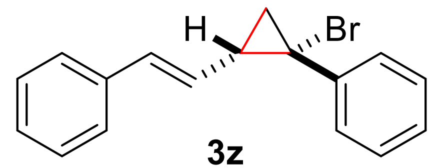
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.328	851015	17.595
2	9.045	857339	17.726
3	13.326	1568290	32.425
4	16.193	1560047	32.254
Total		4836691	100.000

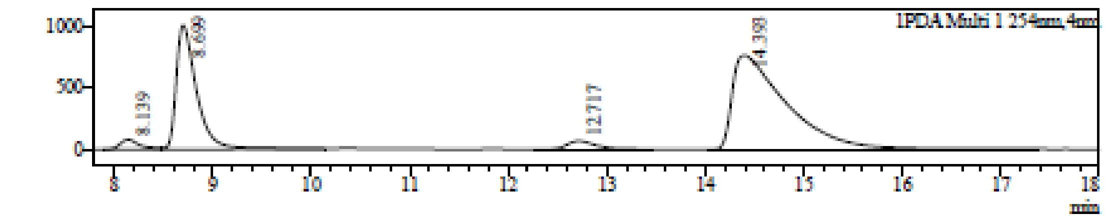
Sample Information

Data File	: J0K-1265--IF-0%-1ML.lcd
Sample Name	: J0K-1265--IF-0%-1ML
Sample ID	: J0K-1265--IF-0%-1ML
Method File	: J0K-0%--45min-1ml.lcm

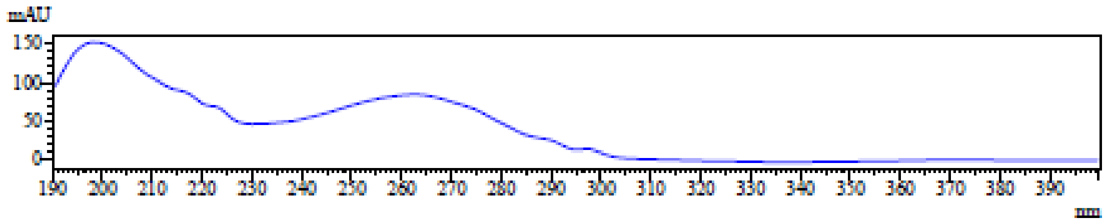


3z

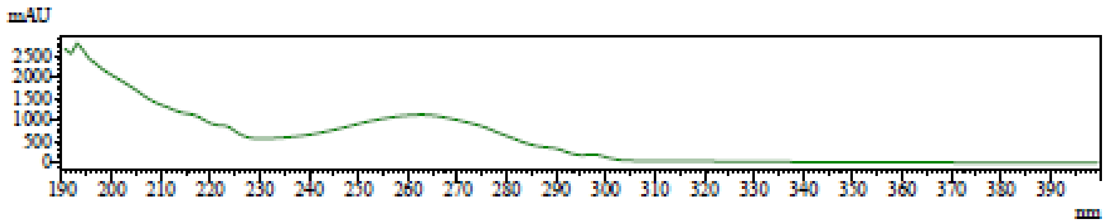
Chromatogram



UV Spectrum
Retention time = 8.139



UV Spectrum
Retention time = 8.699

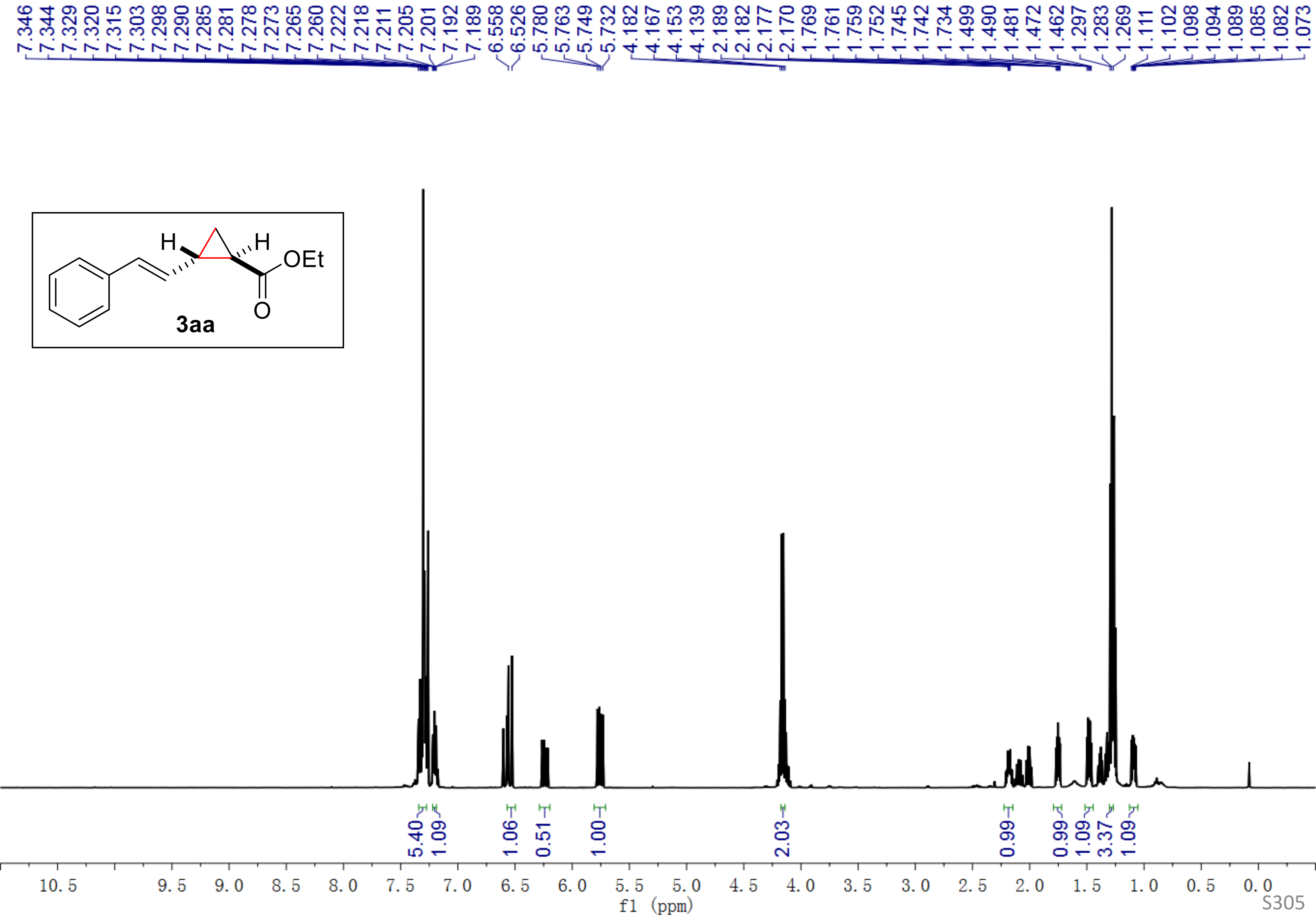


Peak Table

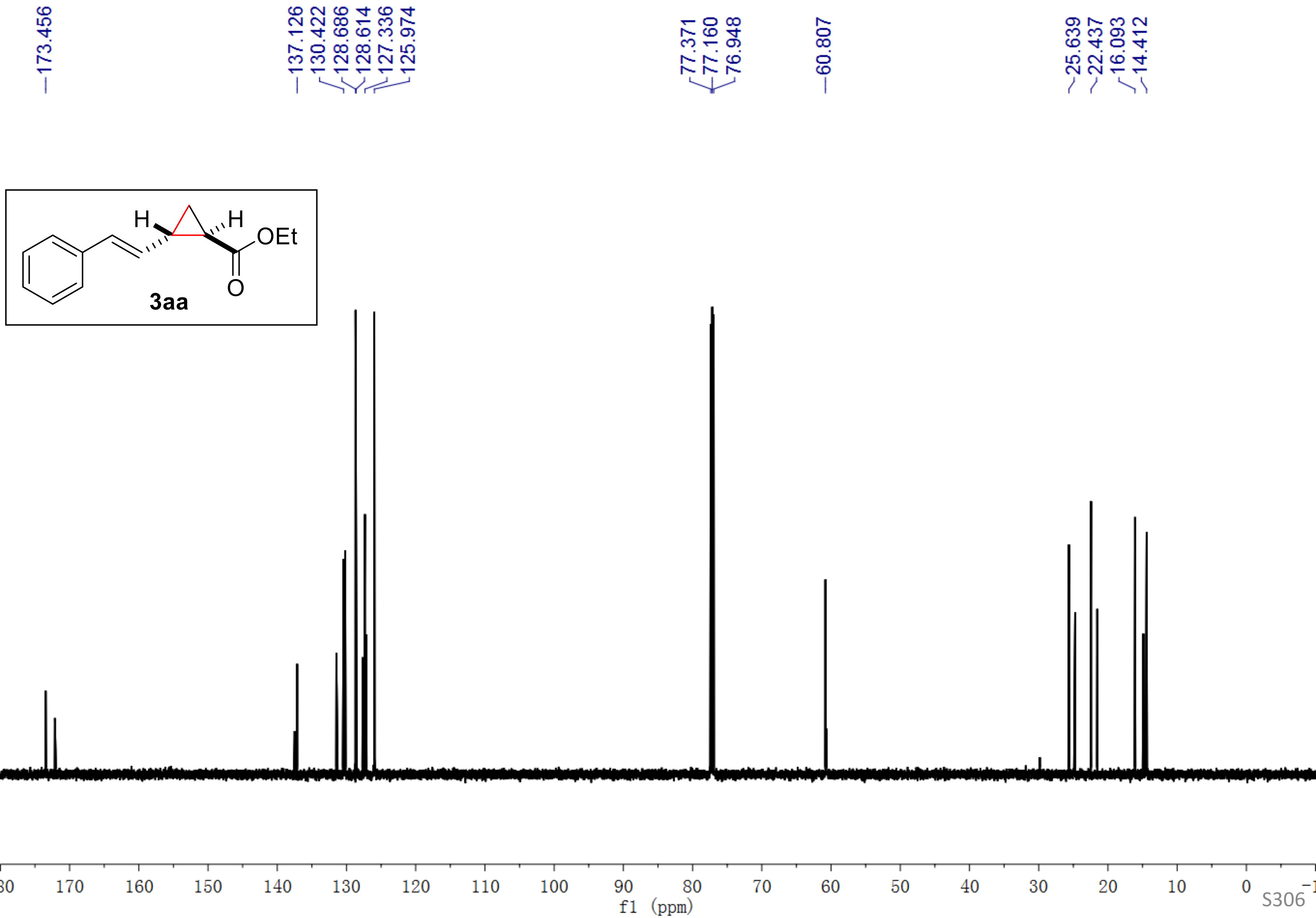
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.139	1021561	2.228
2	8.699	14476756	31.579
3	12.717	1251075	2.729
4	14.393	29093032	63.463
Total		45842424	100.000

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

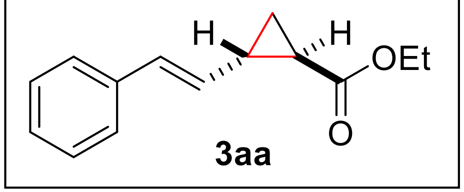


^{13}C of **3aa**, 151 MHz, $CDCl_3$



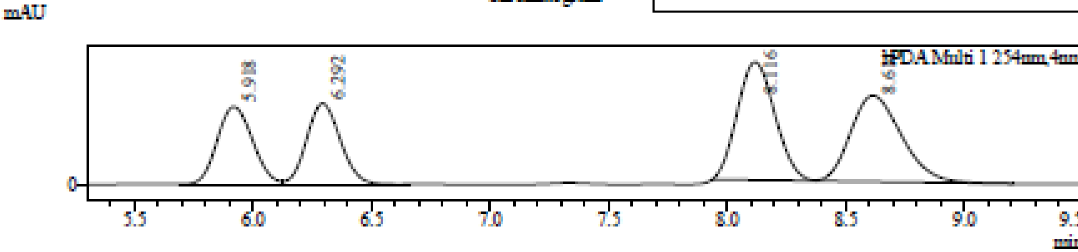
Sample Information

Data File	: J0K-1595-ID-1%-1ML.lcd
Sample Name	: J0K-1595-ID-1%-1ML
Sample ID	: J0K-1595-ID-1%-1ML
Method File	: J0K-1%-40min-1ml.lcm

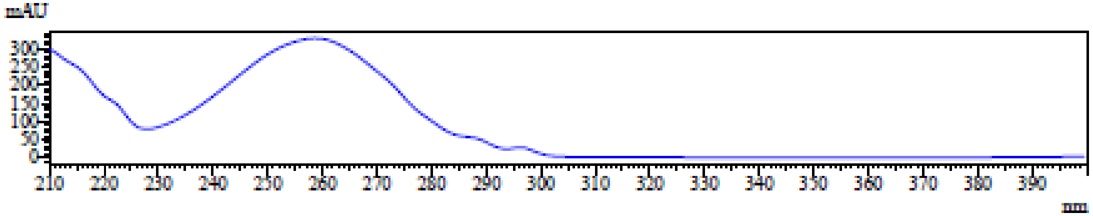


3aa

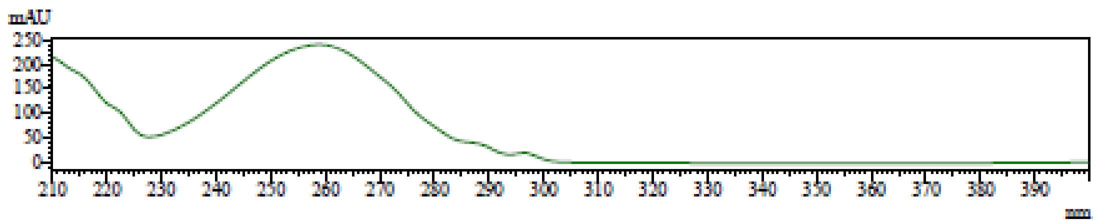
Chromatogram



UV Spectrum
Retention time = 8.116



UV Spectrum
Retention time = 8.614



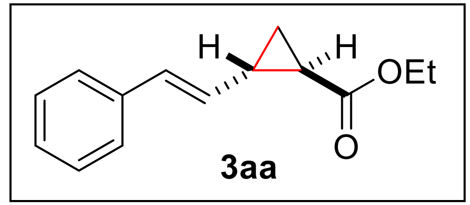
Peak Table

PDA Ch1 254nm

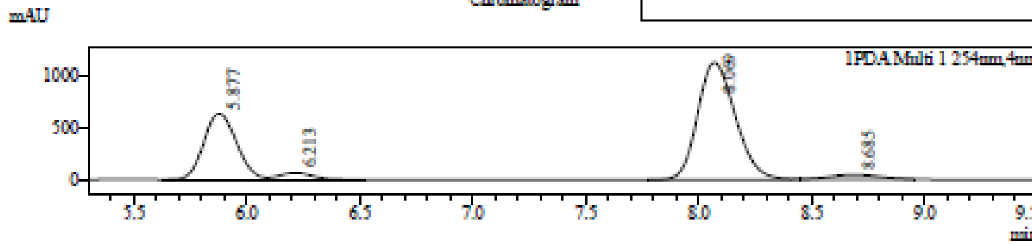
Peak#	Ret. Time	Area	Area%
1	5.918	2051168	19.077
2	6.292	2059421	19.154
3	8.116	3360887	31.258
4	8.614	3280597	30.511
Total		10752074	100.000

Sample Information

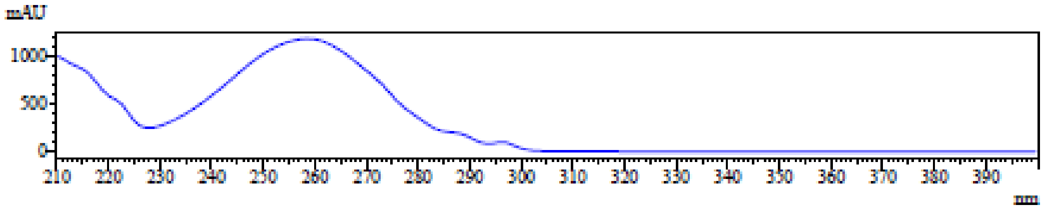
Data File	: J0K-1592-ID-1%-1ML.lcd
Sample Name	: J0K-1592-ID-1%-1ML
Sample ID	: J0K-1592-ID-1%-1ML
Method File	: J0K-1%-40min-1ml.lcm



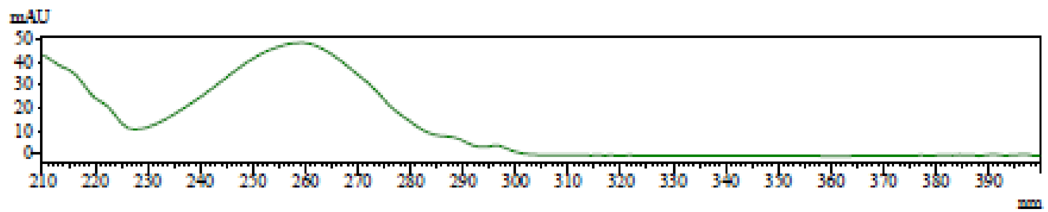
Chromatogram



UV Spectrum
Retention time = 8.069



UV Spectrum
Retention time = 8.685

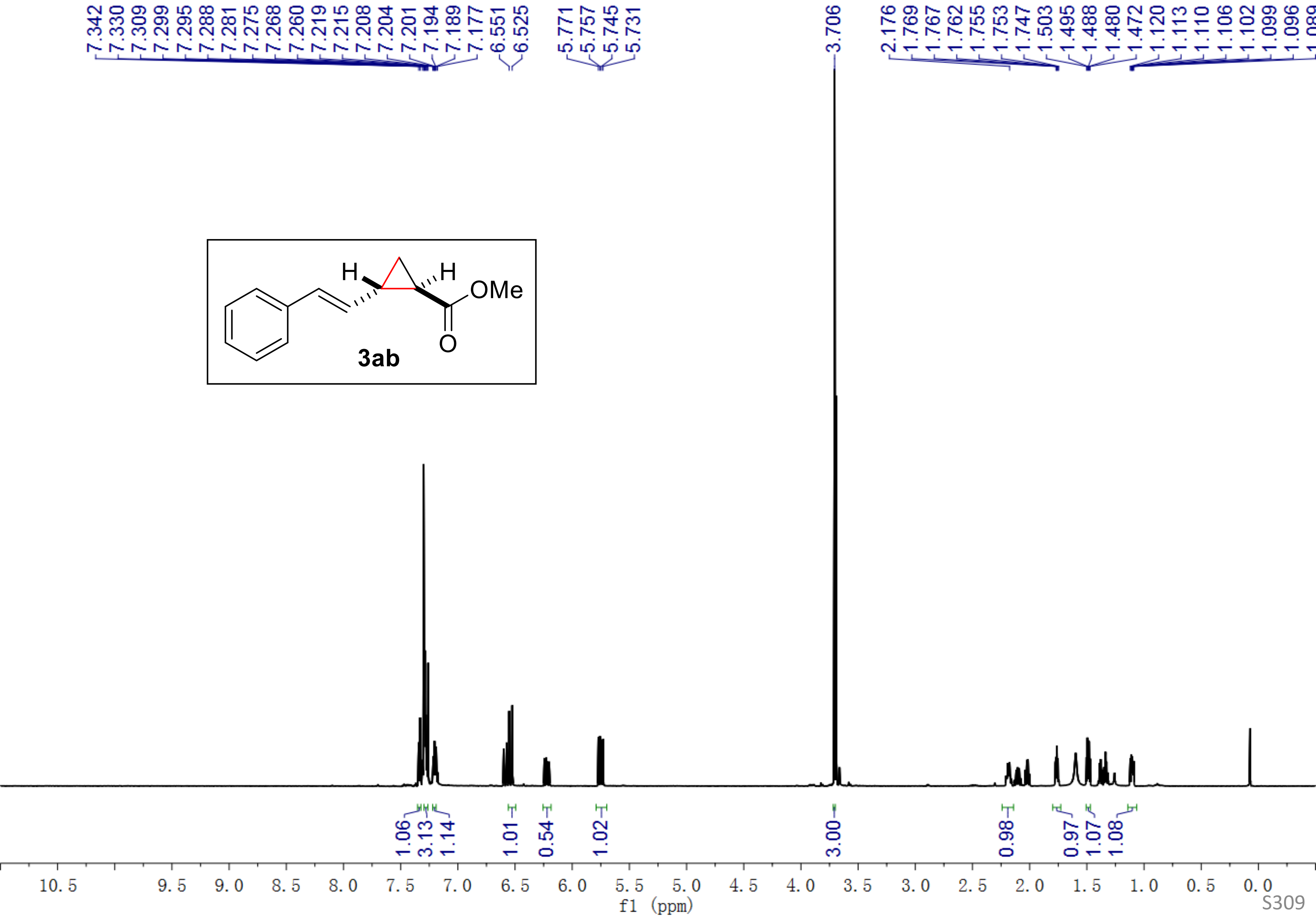


Peak Table

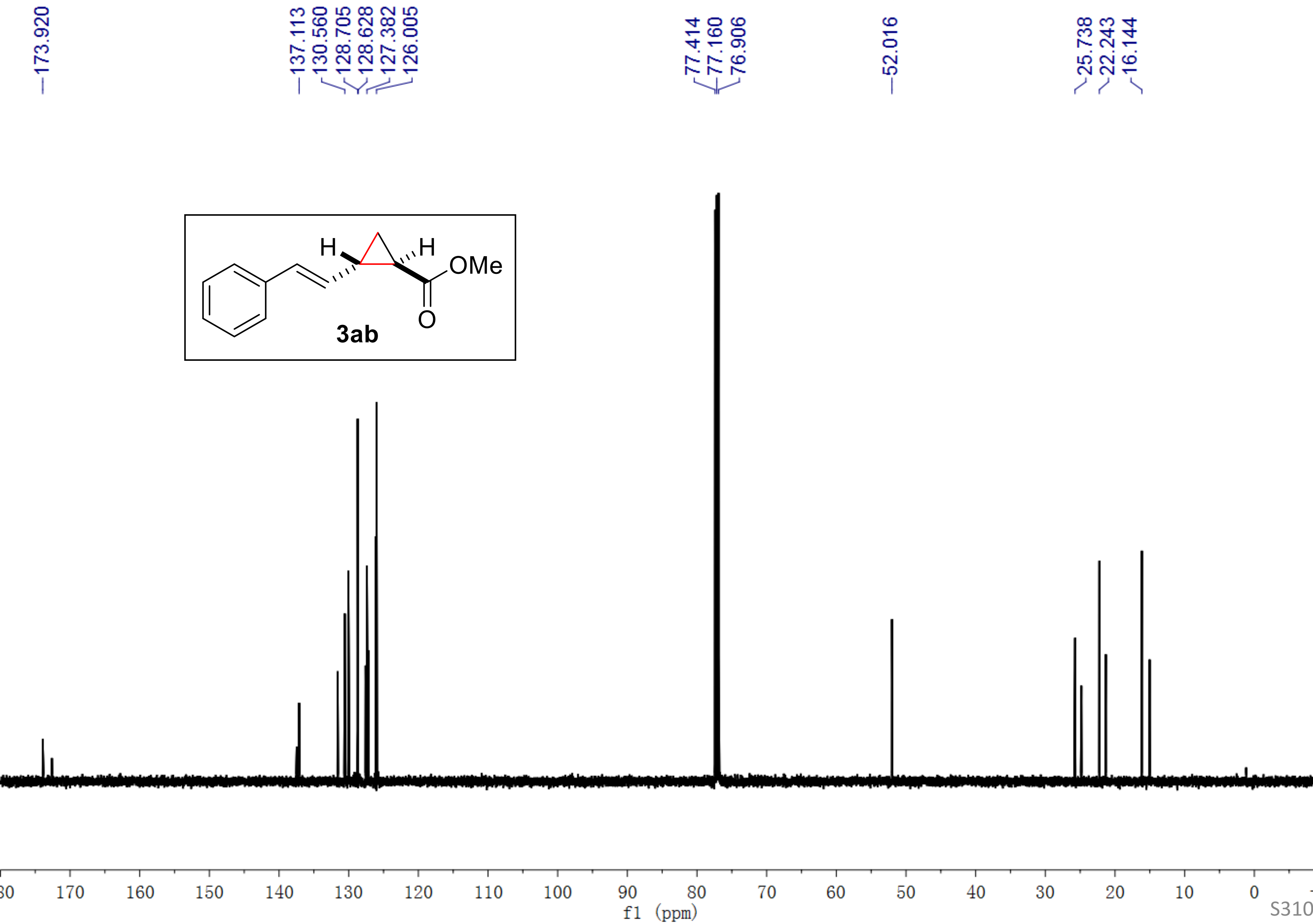
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.877	6334017	30.865
2	6.213	619428	3.018
3	8.069	12959585	63.151
4	8.685	608454	2.965
Total		20521484	100.000

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

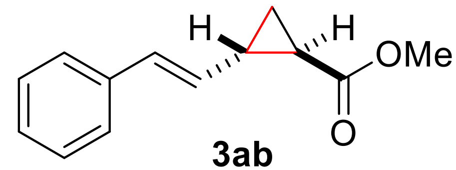


^{13}C of **3ab**, 151 MHz, $CDCl_3$



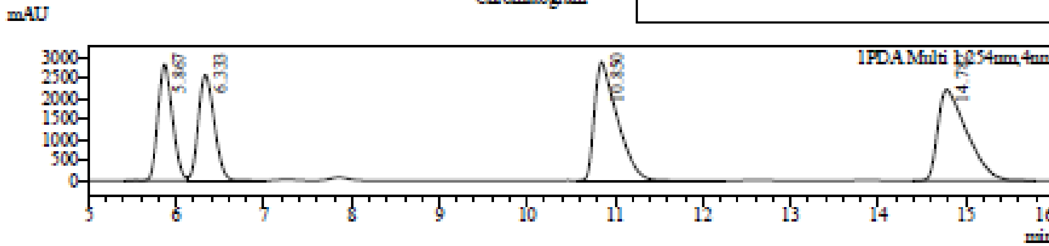
Sample Information

Data File : J0K-1393-IF-1%-1ML.lcd
Sample Name : J0K-1393-IF-1%-1ML
Sample ID : J0K-1393-IF-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

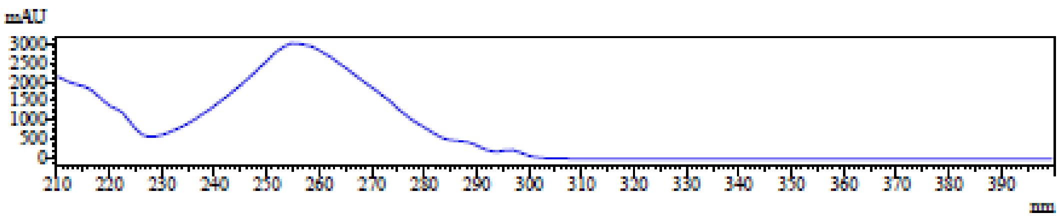


3ab

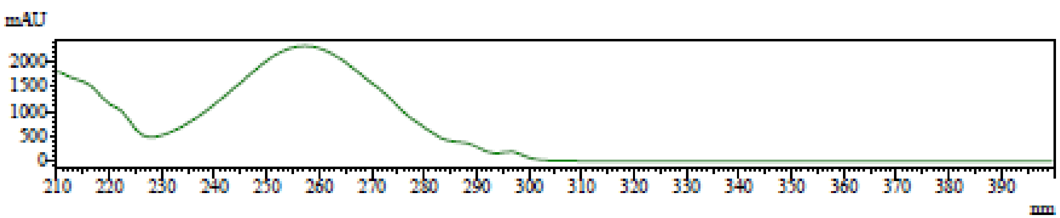
Chromatogram



UV Spectrum
Retention time = 10.850



UV Spectrum
Retention time = 14.782



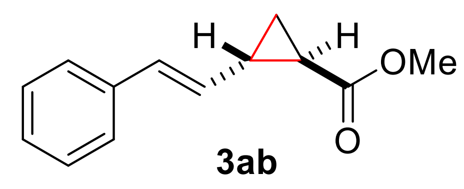
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.867	32746530	19.358
2	6.333	32535404	19.233
3	10.850	52587659	31.086
4	14.782	51297267	30.323
Total		169166860	100.000

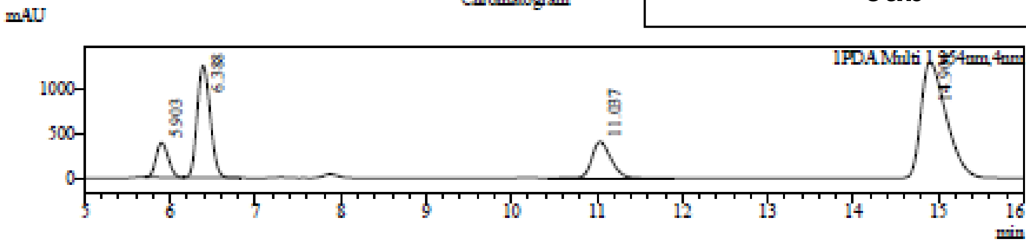
Sample Information

Data File	: J0K-1385-IF-1%-1ML.lcd
Sample Name	: J0K-1385-IF-1%-1ML
Sample ID	: J0K-1385-IF-1%-1ML
Method File	: J0K-1%-40min-1ml.lcm

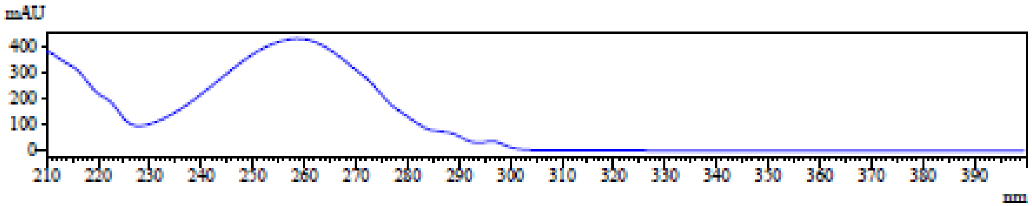


3ab

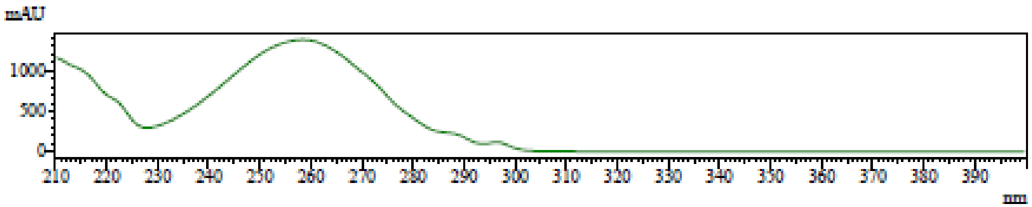
Chromatogram



UV Spectrum
Retention time = 11.037



UV Spectrum
Retention time = 14.904

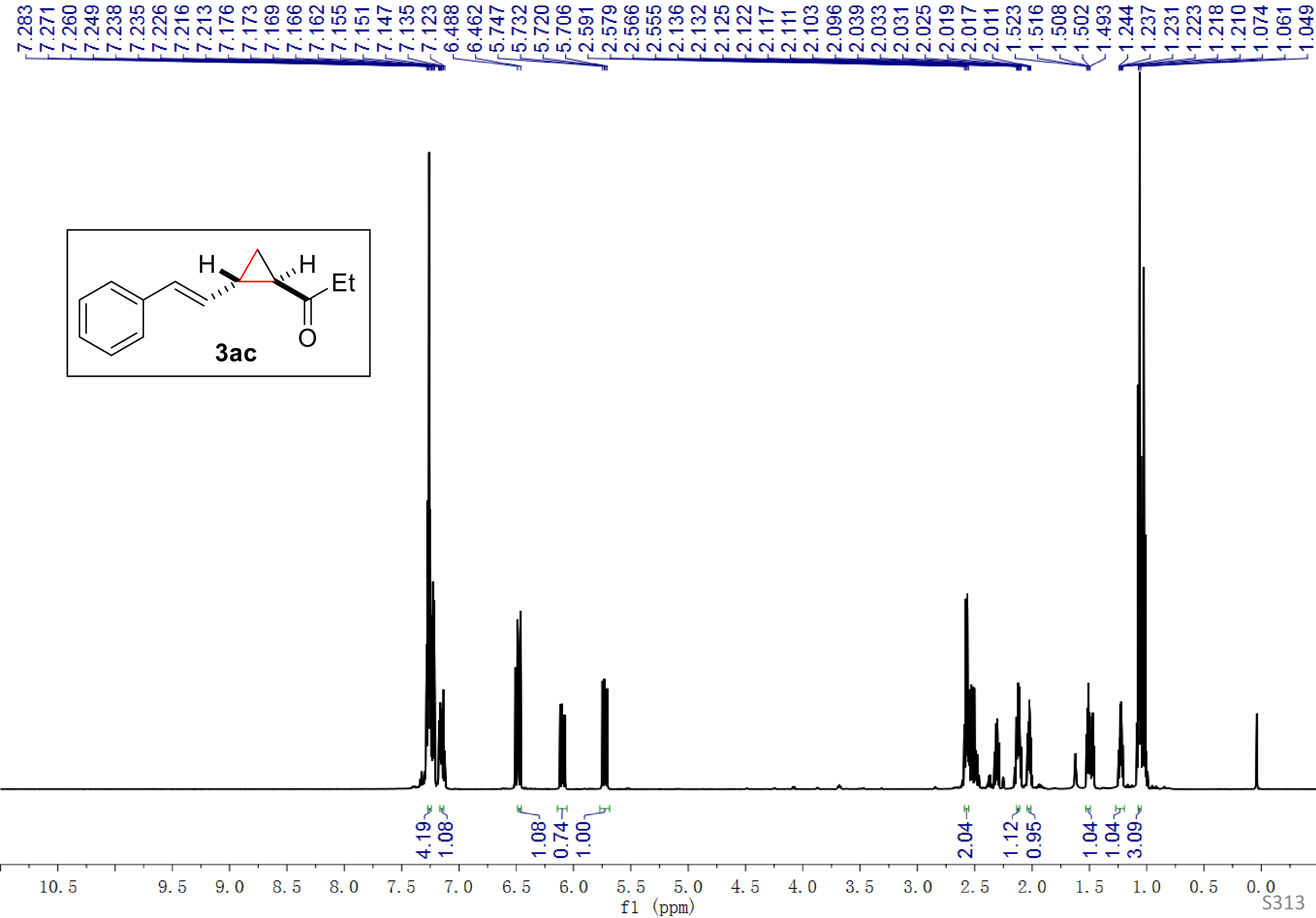


Peak Table

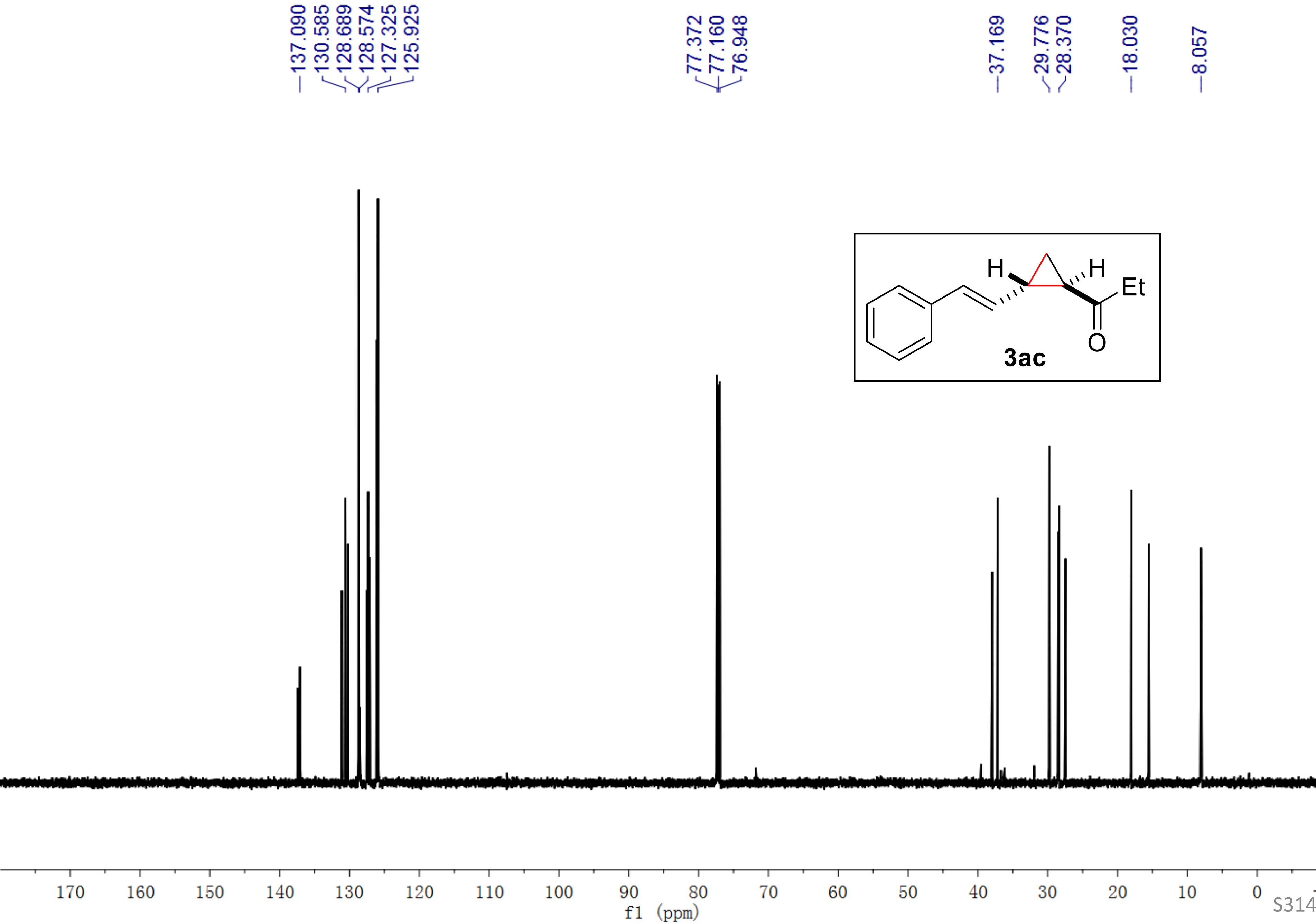
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.903	3950408	7.717
2	6.388	13610329	26.588
3	11.037	6433299	12.568
4	14.904	27194844	53.126
Total		51188880	100.000

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

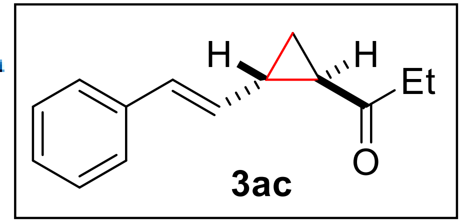


^{13}C of **3ac**, 151 MHz, $CDCl_3$



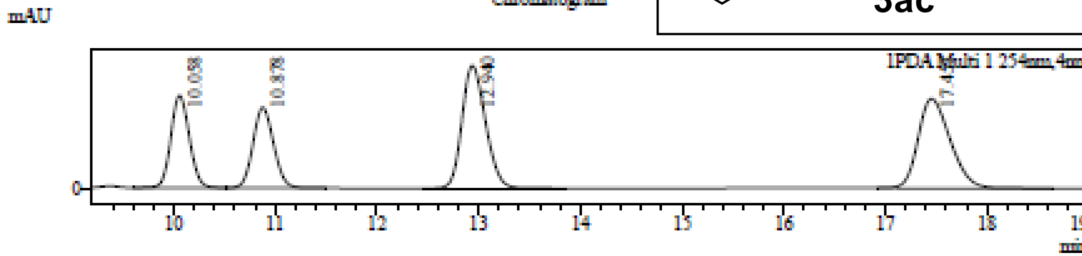
Sample information

Data File : J0K-1600-IE-1%-1ML.lcd
Sample Name : J0K-1600-IE-1%-1ML
Sample ID : J0K-1600-IE-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

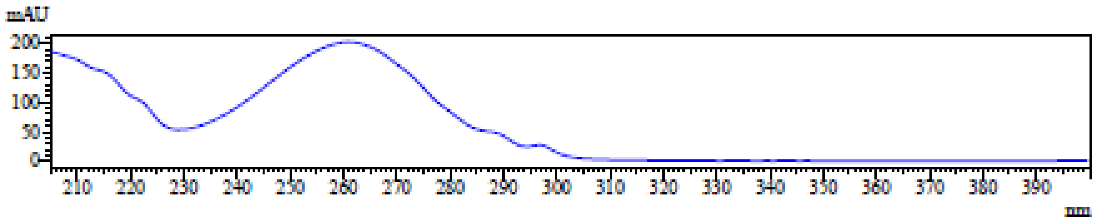


3ac

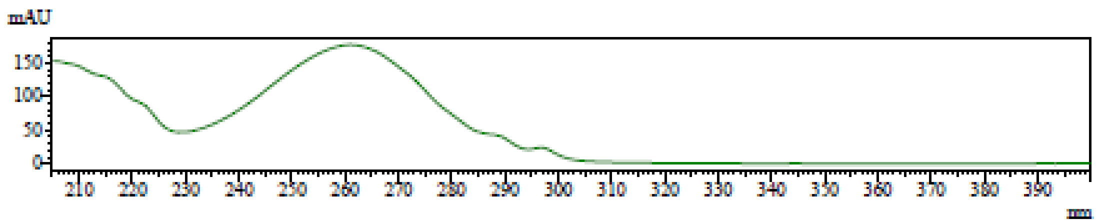
Chromatogram



UV Spectrum
Retention time = 10.058



UV Spectrum
Retention time = 10.878



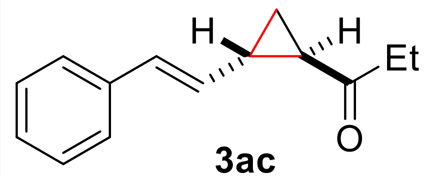
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.058	2317699	18.718
2	10.878	2297625	18.556
3	12.940	3890089	31.417
4	17.457	3876611	31.308
Total		12382024	100.000

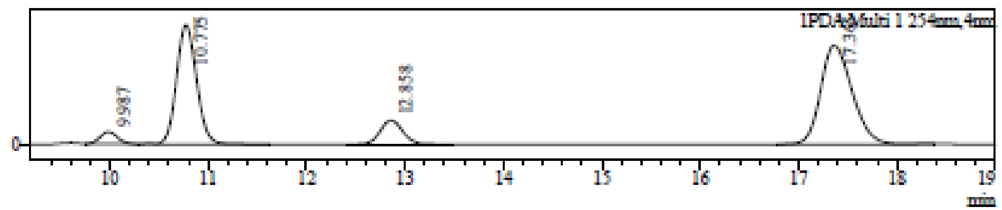
Sample information

Data File : J0K-1599-IE-1%-1ML.lcd
Sample Name : J0K-1599-IE-1%-1ML
Sample ID : J0K-1599-IE-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

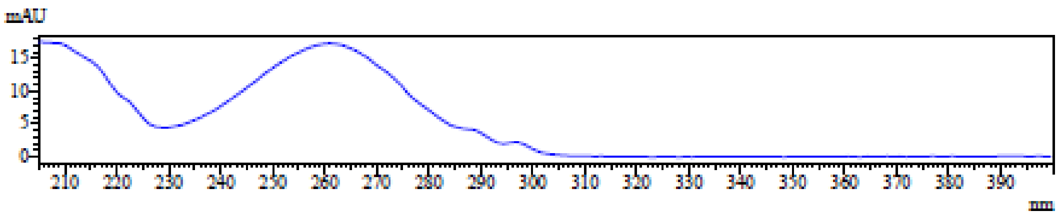


3ac

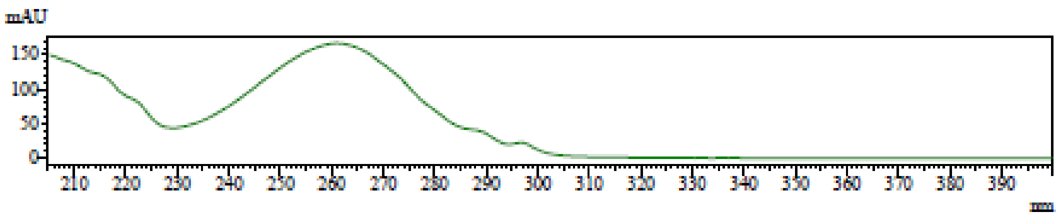
Chromatogram



UV Spectrum
Retention time = 9.987



UV Spectrum
Retention time = 10.775

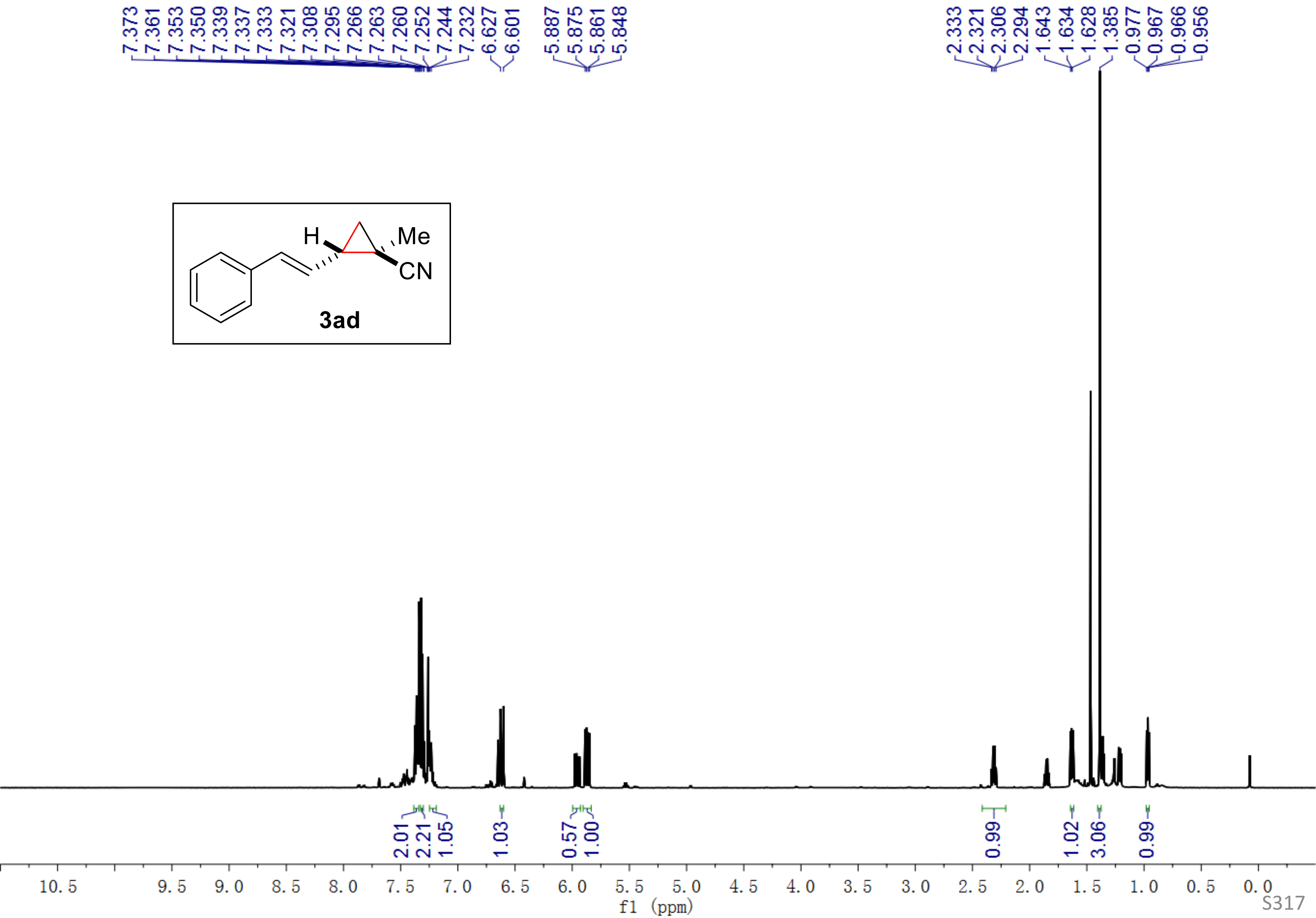


Peak Table

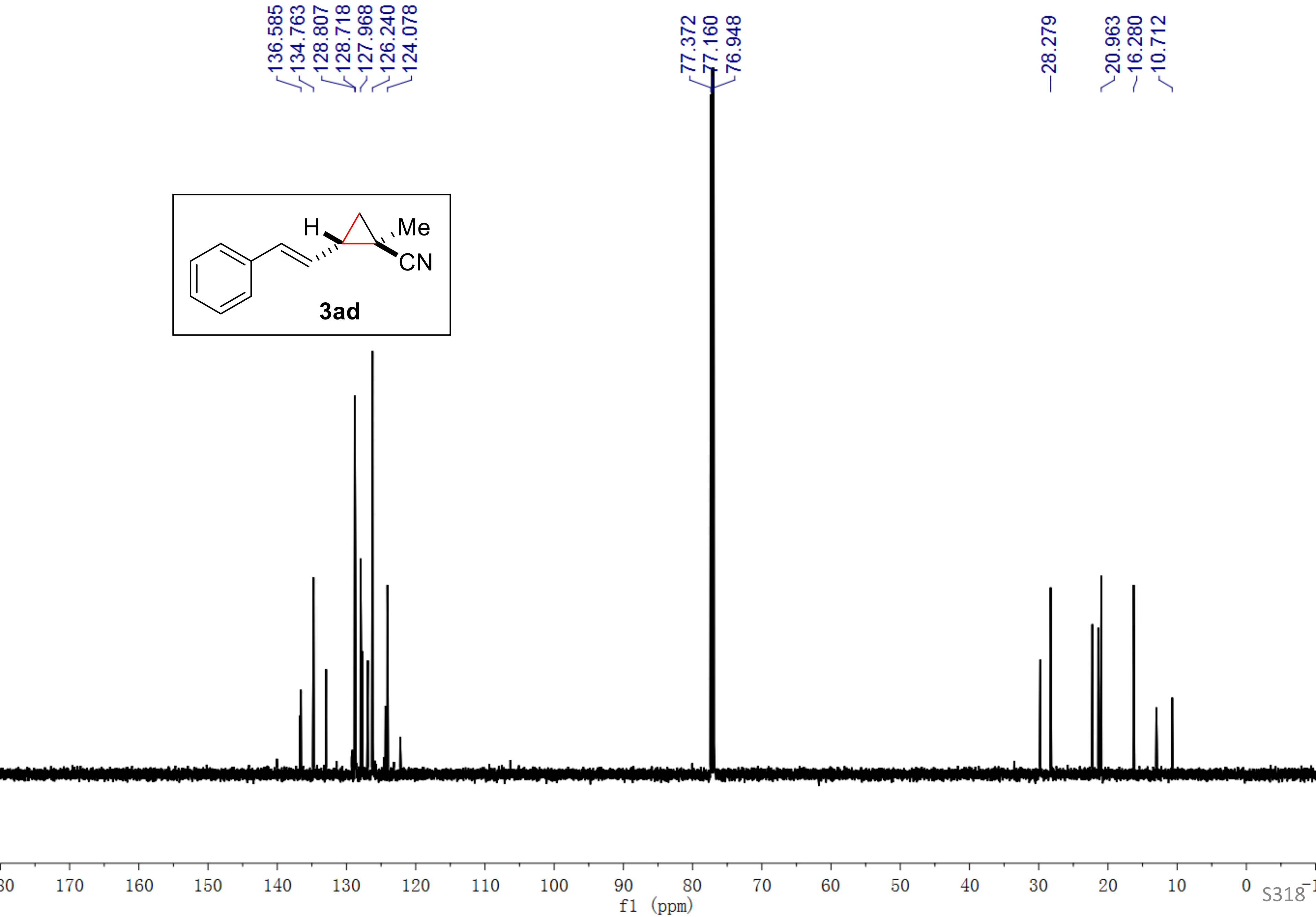
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.987	184413	3.345
2	10.775	2114154	38.343
3	12.858	472586	8.571
4	17.365	2742593	49.741
Total		5513746	100.000

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

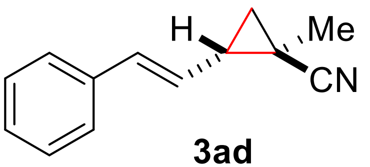


^{13}C of **3ad**, 151 MHz, $CDCl_3$



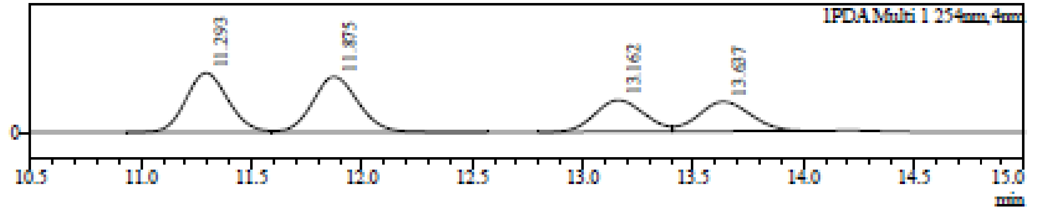
Sample Information

Data File : J0K-1598-ID-1%-1ML.lcd
Sample Name : J0K-1598-ID-1%-1ML
Sample ID : J0K-1598-ID-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

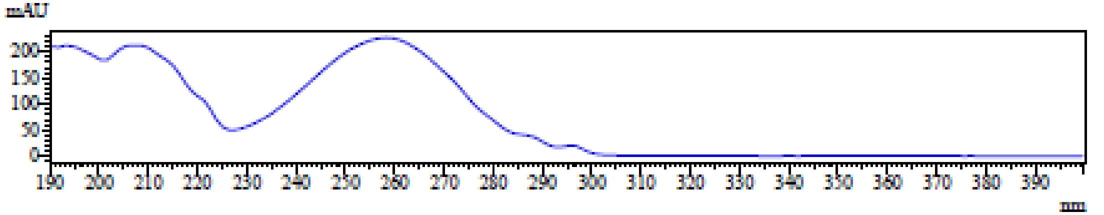


3ad

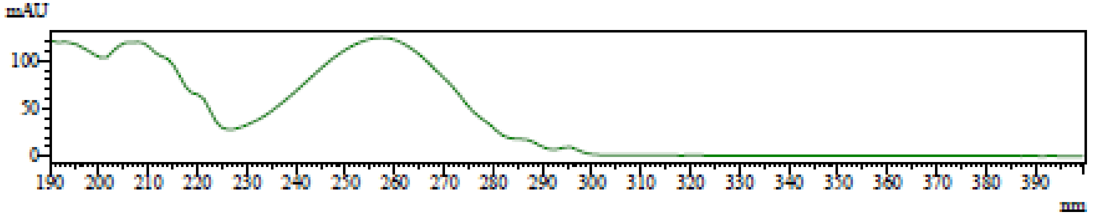
Chromatogram



UV Spectrum
Retention time = 11.875



UV Spectrum
Retention time = 13.637



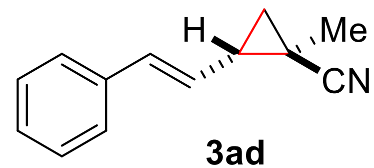
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.293	3100580	30.910
2	11.875	3114055	31.044
3	13.162	1926464	19.205
4	13.637	1889915	18.841
Total		10031013	100.000

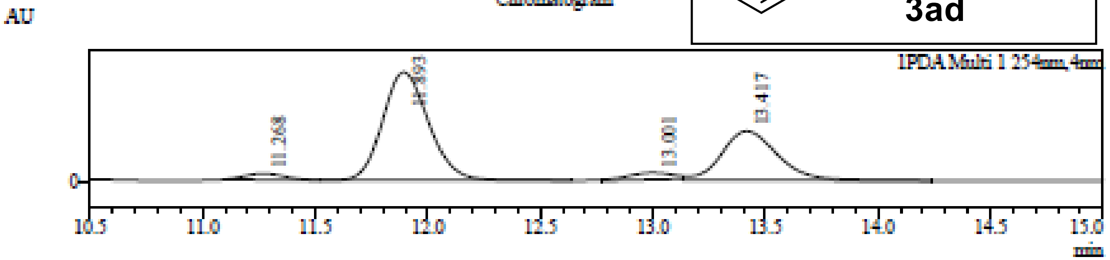
Sample Information

Data File : J0K-1597-ID-1%-1ML.lcd
Sample Name : J0K-1597-ID-1%-1ML
Sample ID : J0K-1597-ID-1%-1ML
Method File : J0K-1%-40min-1ml.lcm

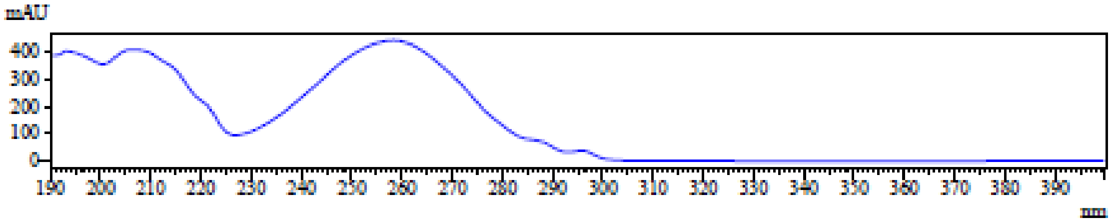


3ad

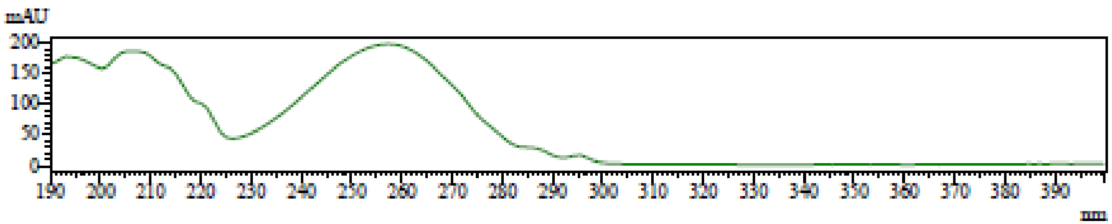
Chromatogram



UV Spectrum
Retention time = 11.893



UV Spectrum
Retention time = 13.417

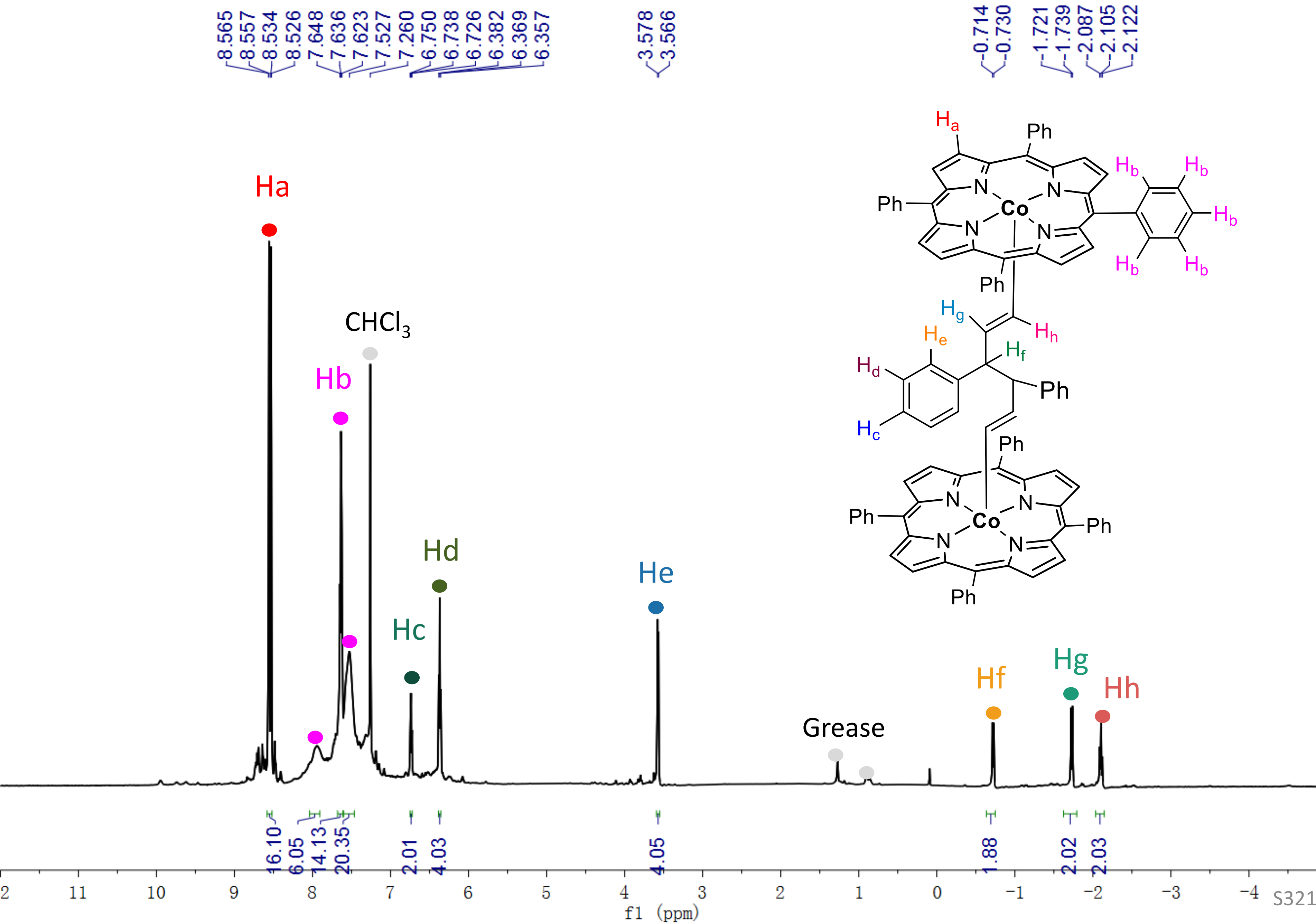


Peak Table

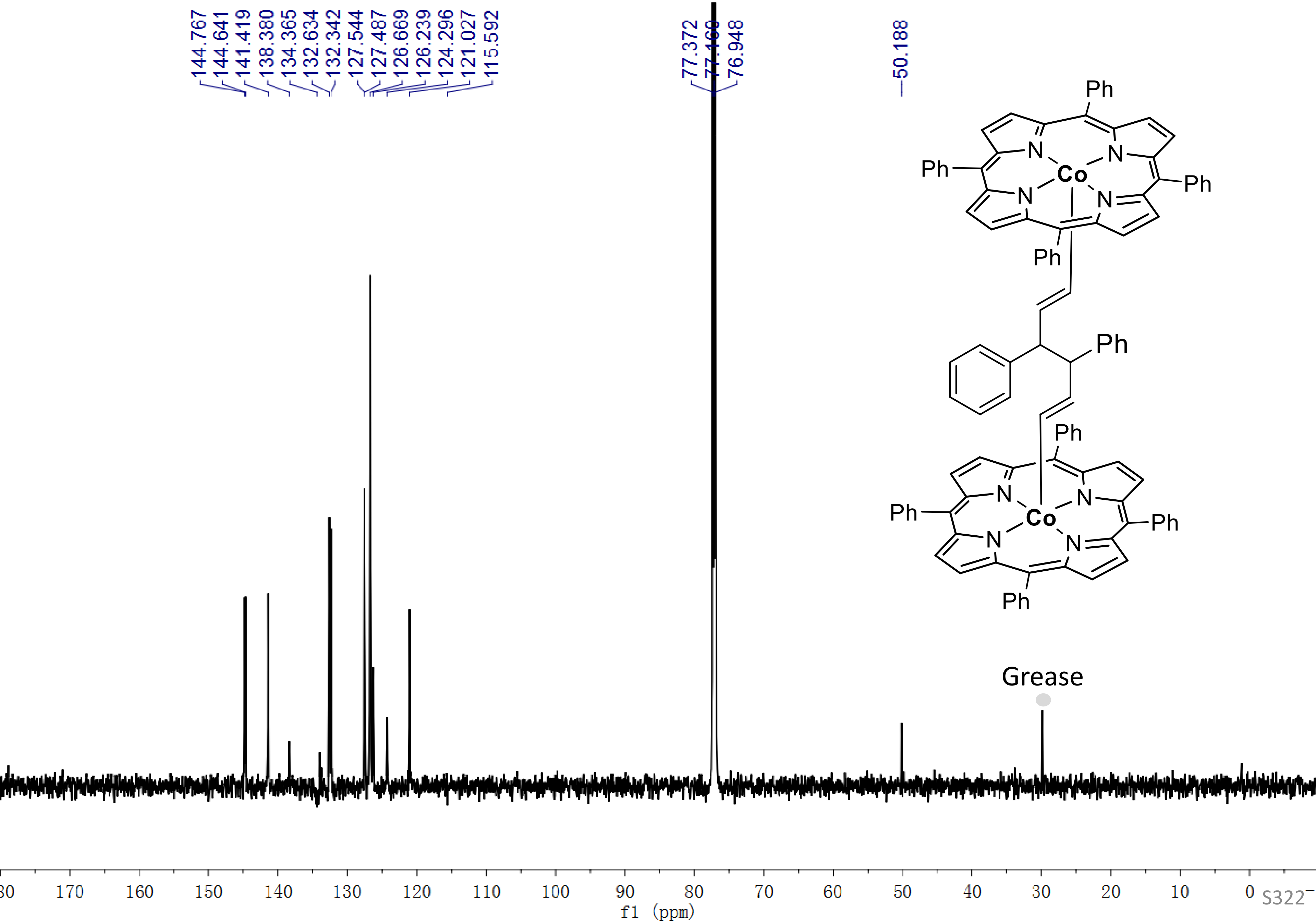
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.268	289671	2.947
2	11.893	5917266	60.194
3	13.001	365803	3.721
4	13.417	3257636	33.138
Total		9830376	100.000

^{1}H of **4a**, 600 MHz, $CDCl_3$



^{13}C of **4a**, 151 MHz, $CDCl_3$



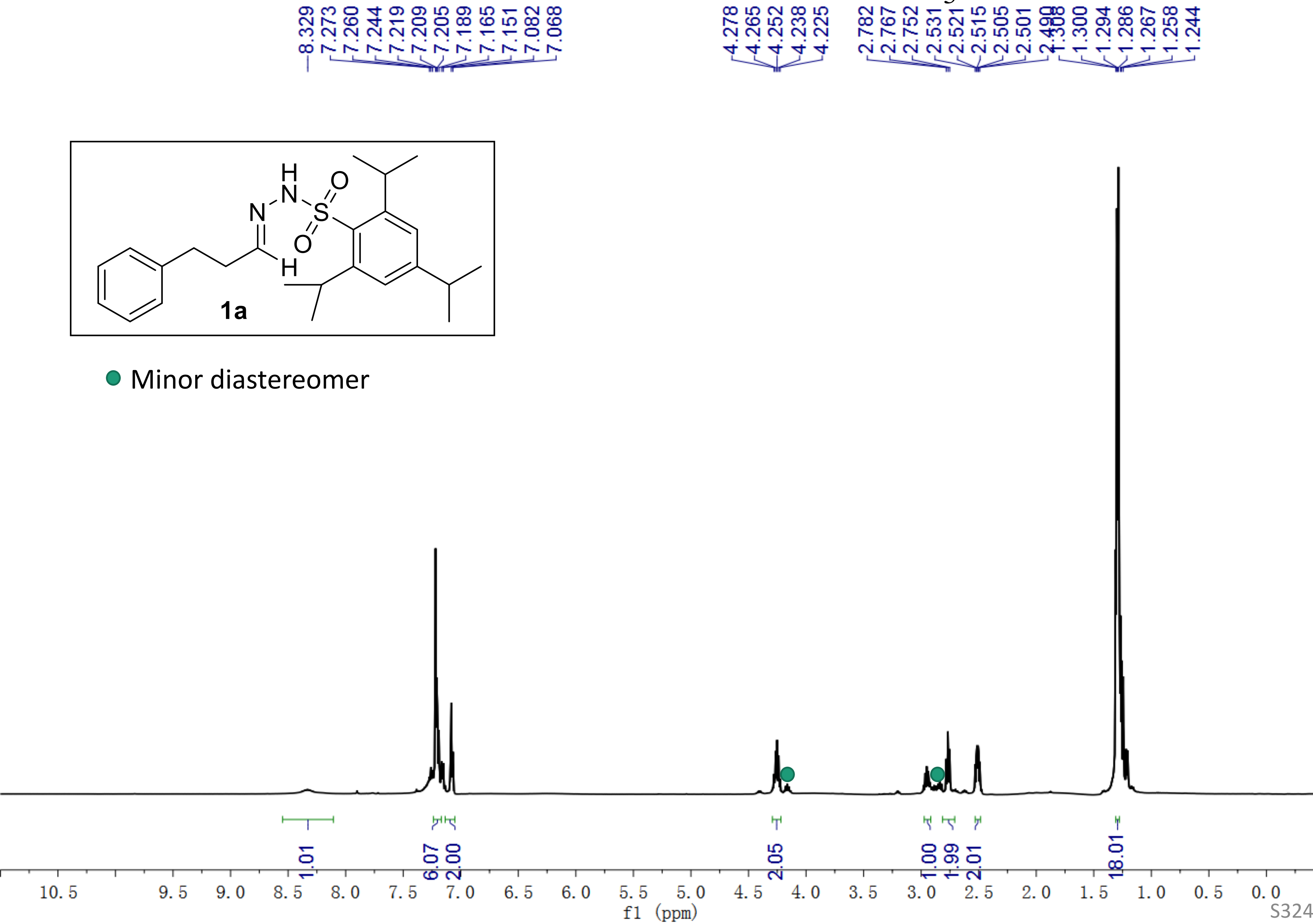
Spectral Data

for

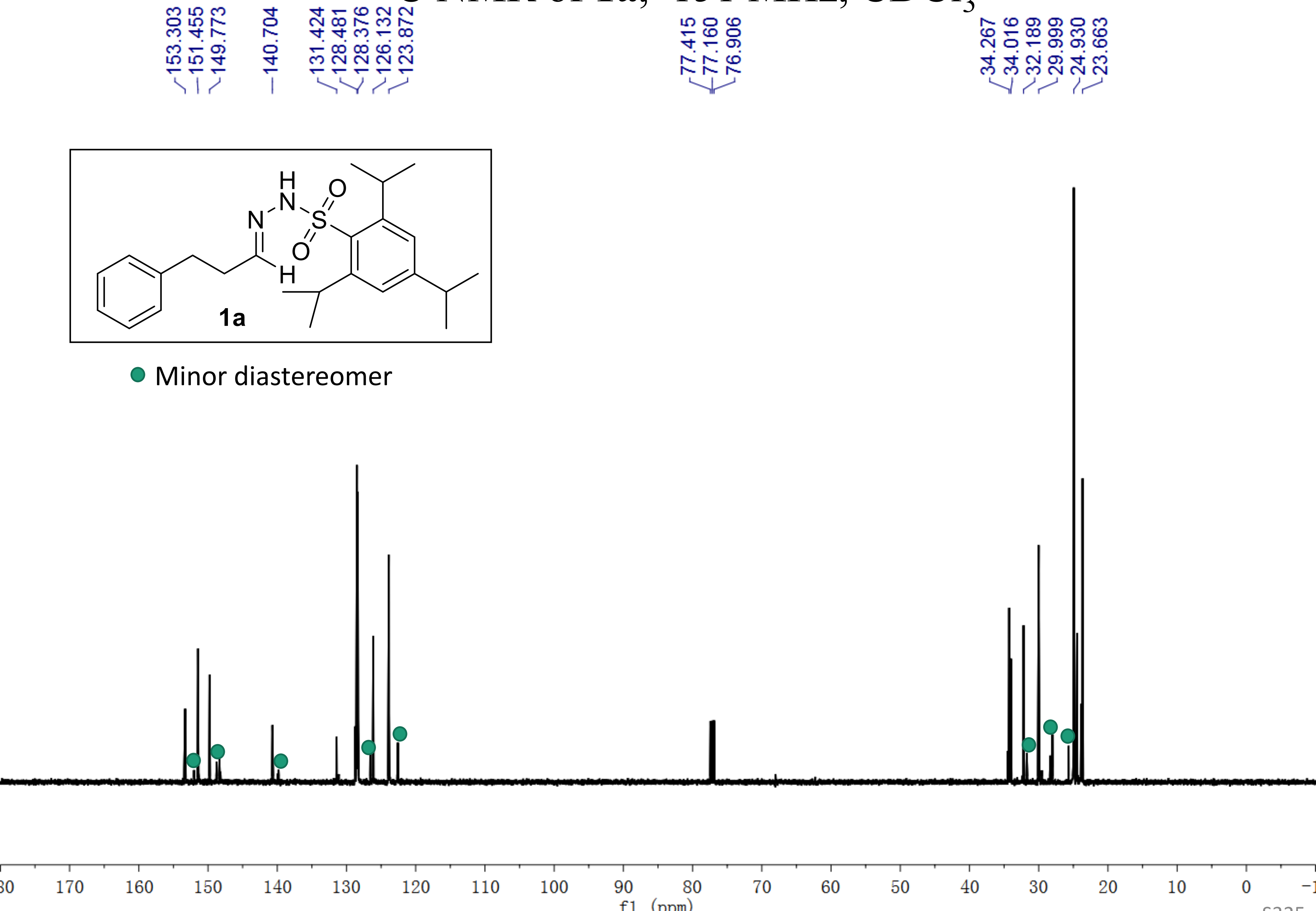
Chapter 4

Asymmetric Synthesis of Vinyl-Substituted Cyclopropanes by Radical C–H Alkylation from Alkynes and Alkyl Diazo Compounds via Co(II)-Based Metalloradical Catalysis

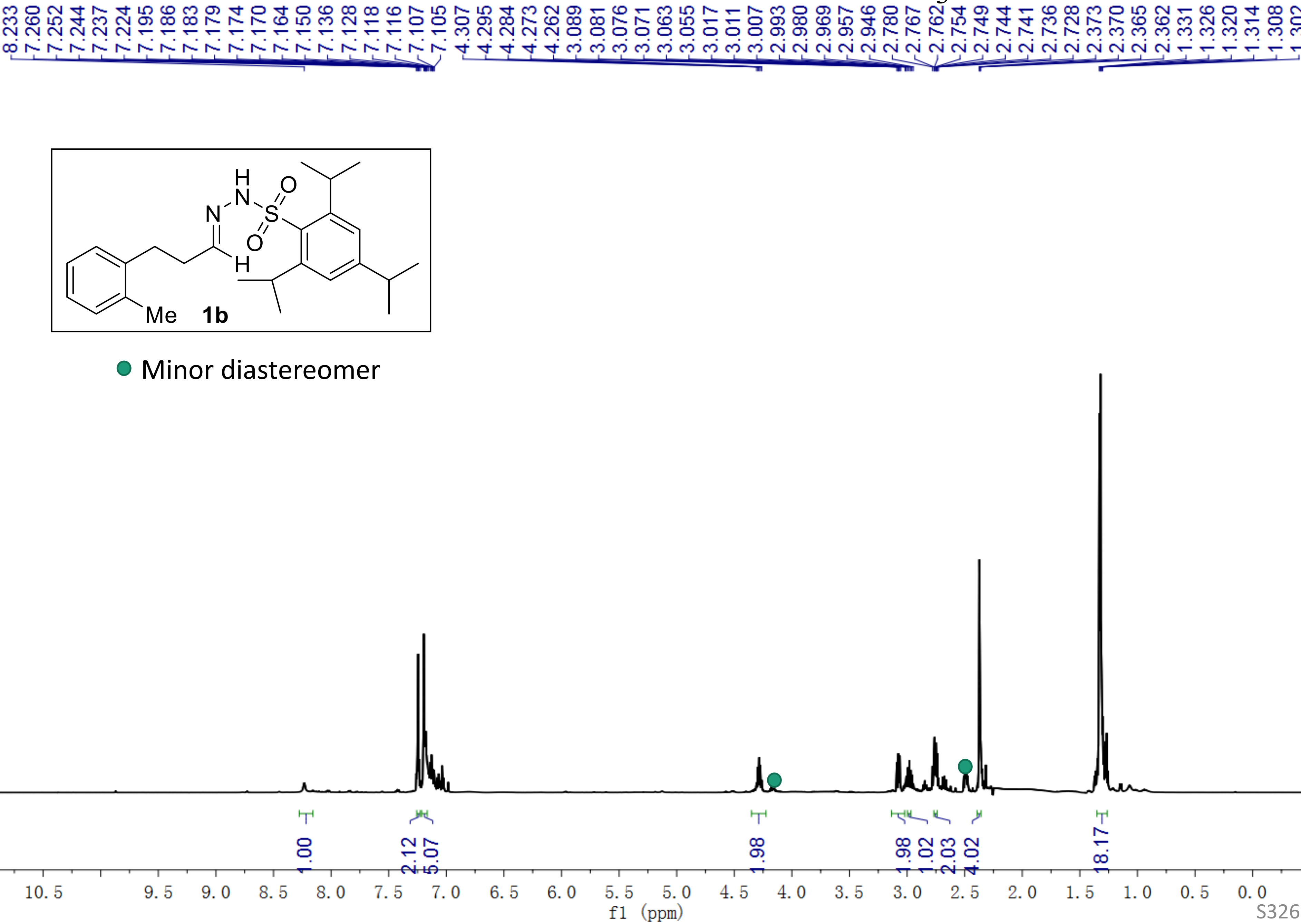
^{1}H NMR of **1a**, 500 MHz, $CDCl_3$



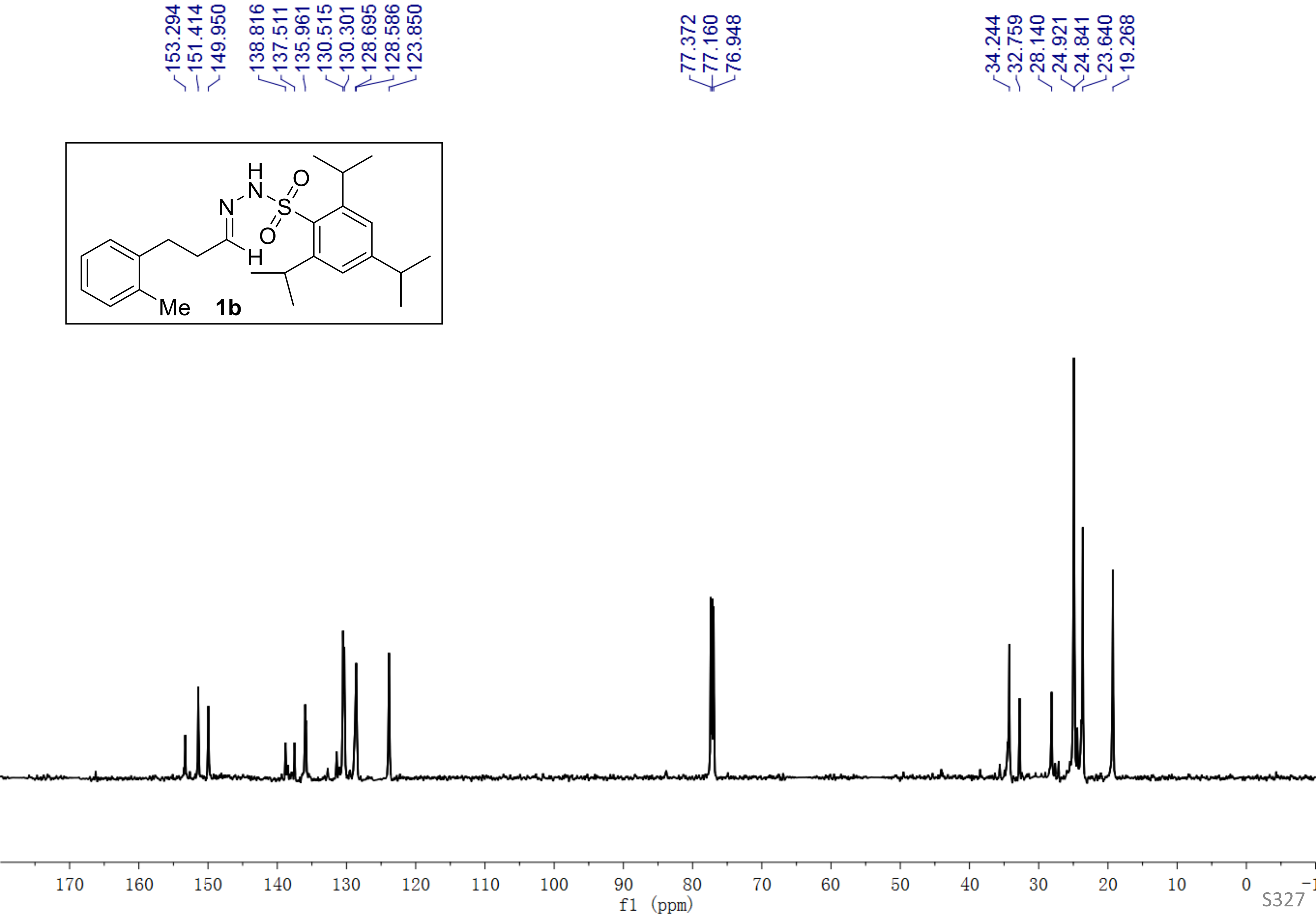
^{13}C NMR of **1a**, 151 MHz, $CDCl_3$



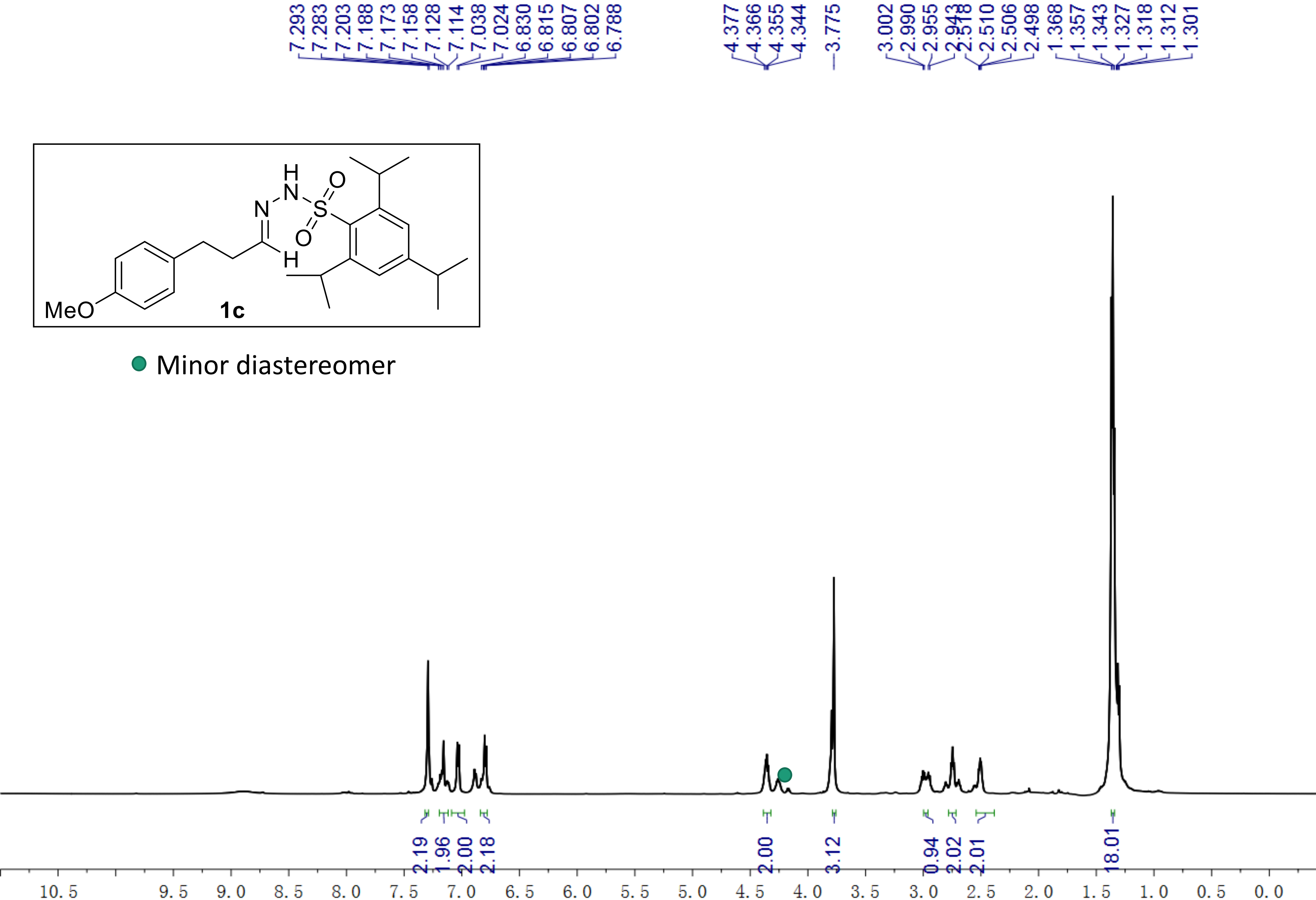
^{1}H NMR of **1b**, 600 MHz, $CDCl_3$



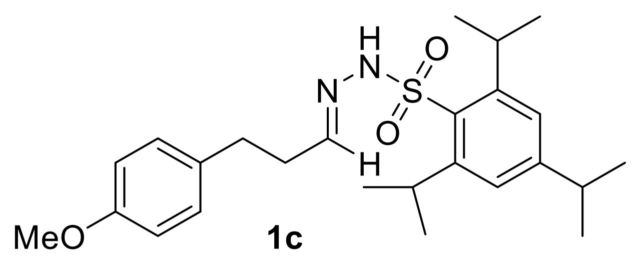
^{13}C NMR of **1b**, 151 MHz, $CDCl_3$



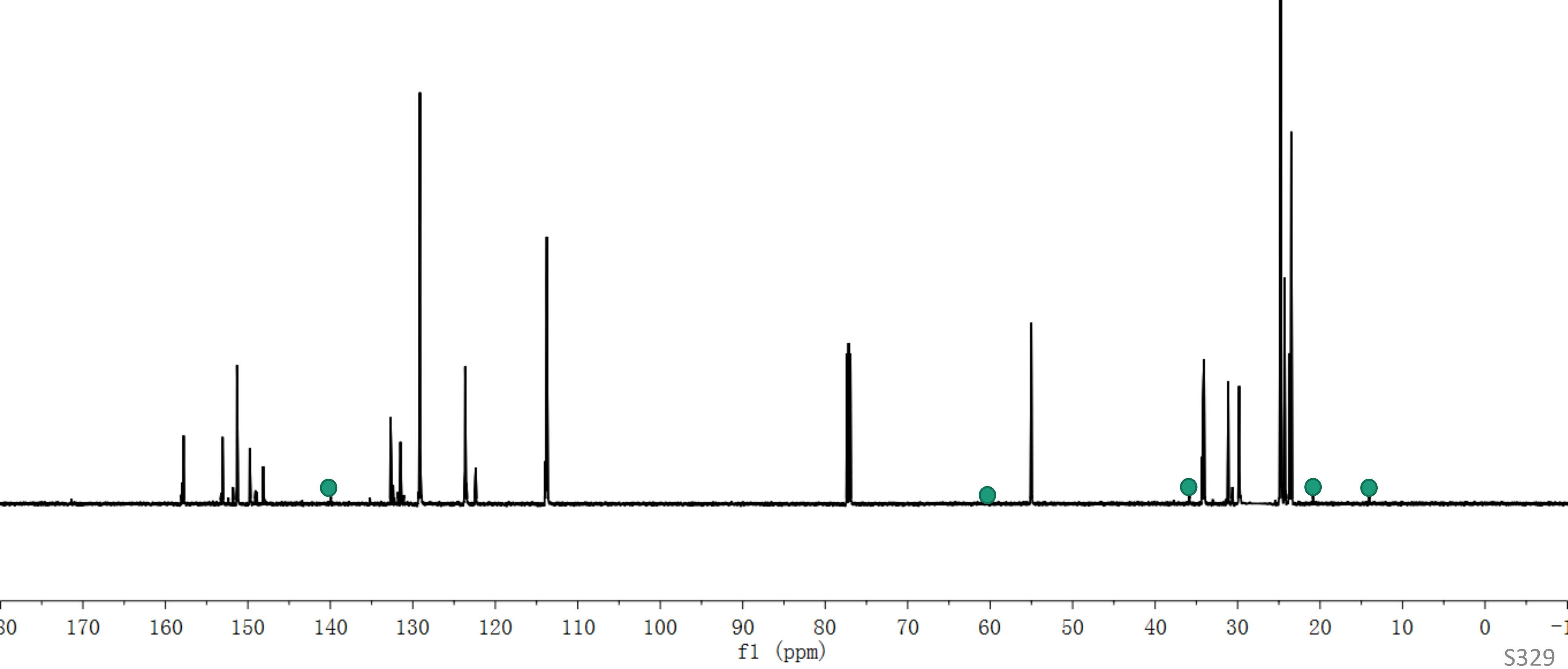
^{1}H NMR of **1c**, 500 MHz, $CDCl_3$



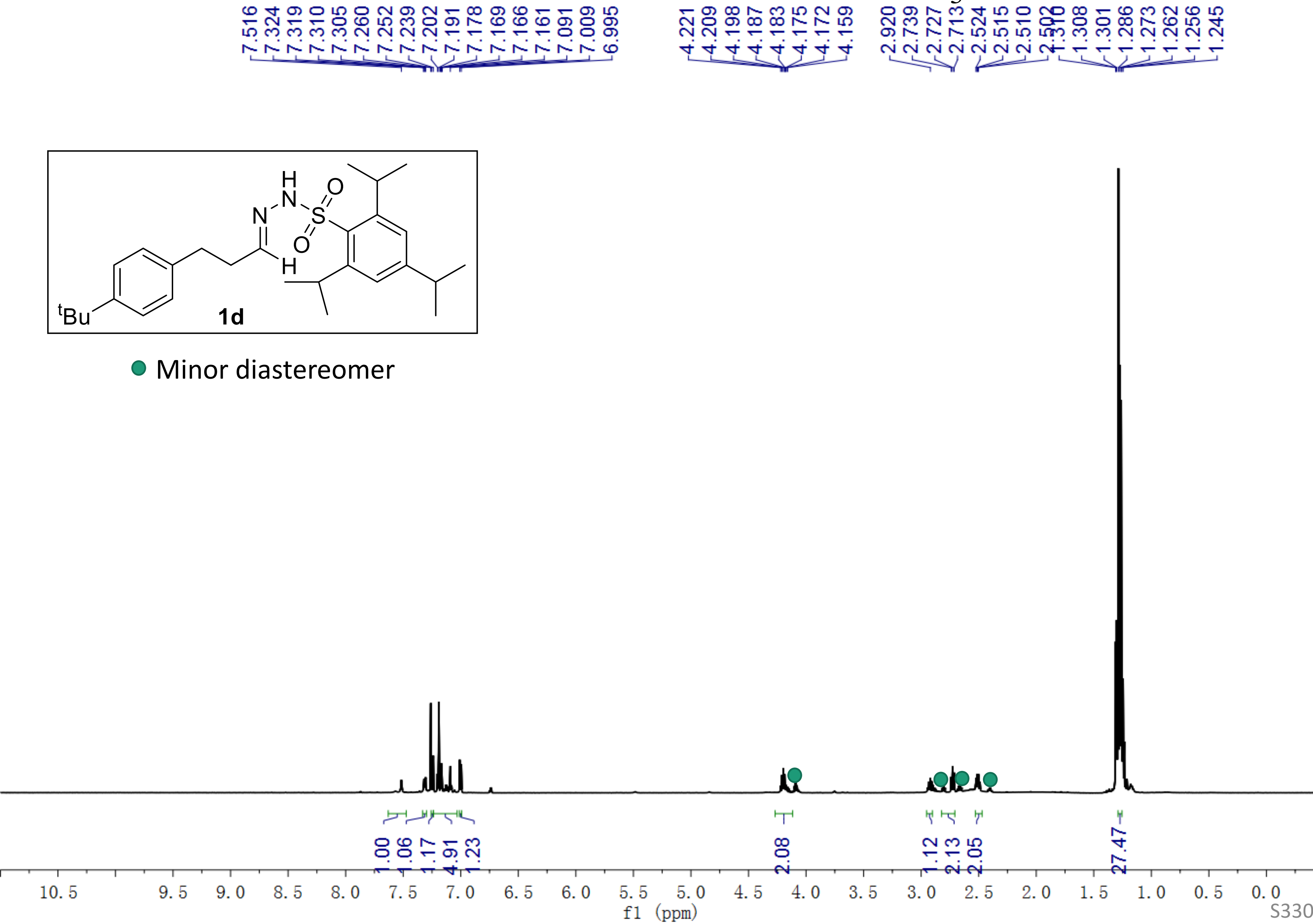
^{13}C NMR of **1c**, 126 MHz, $CDCl_3$



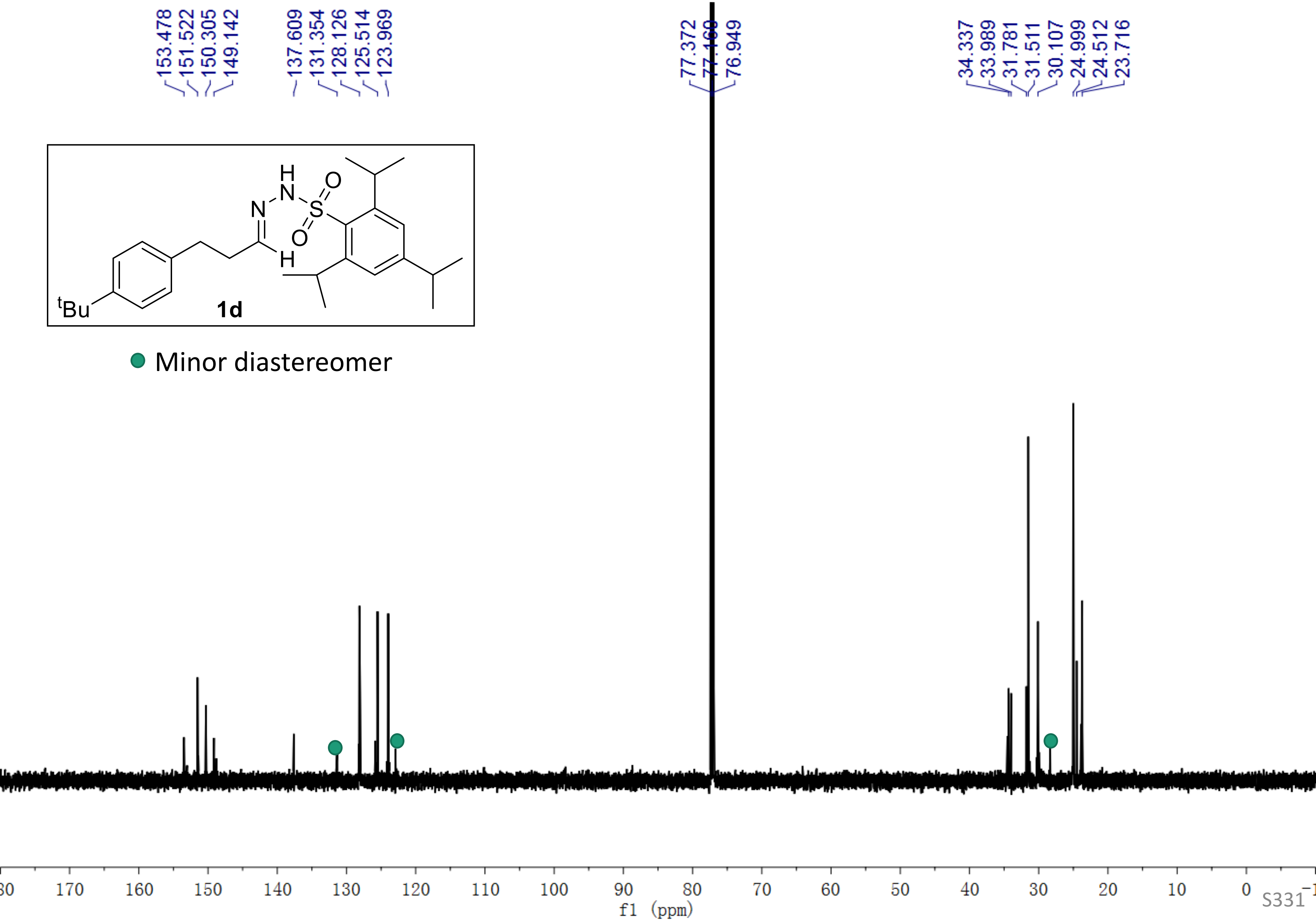
1c



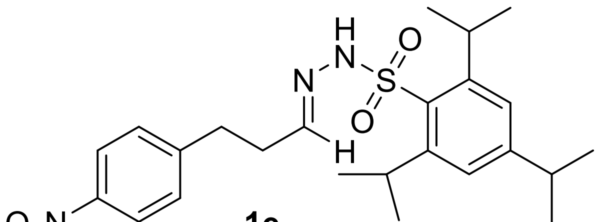
^{1}H NMR of **1d**, 600 MHz, $CDCl_3$



^{13}C NMR of **1d**, 151 MHz, $CDCl_3$

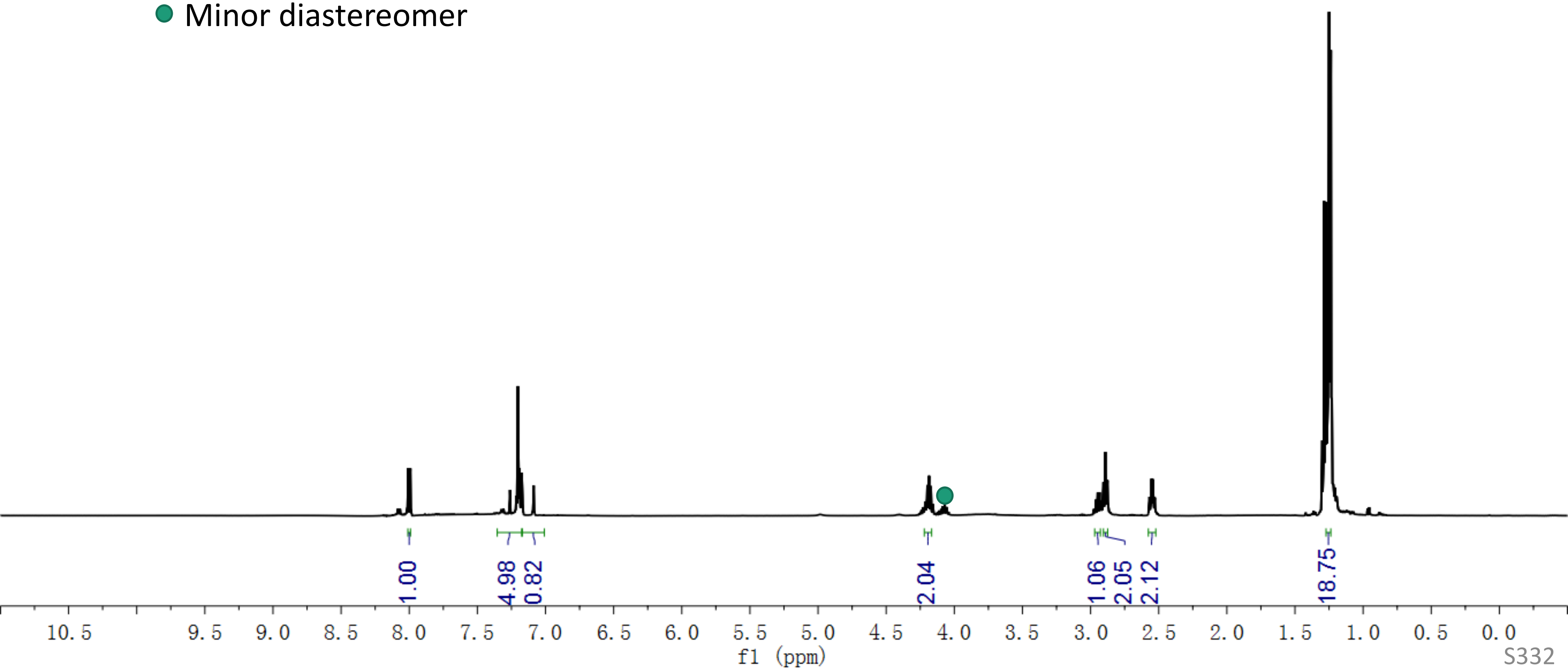


^1H NMR of **1e**, 400 MHz, $CDCl_3$

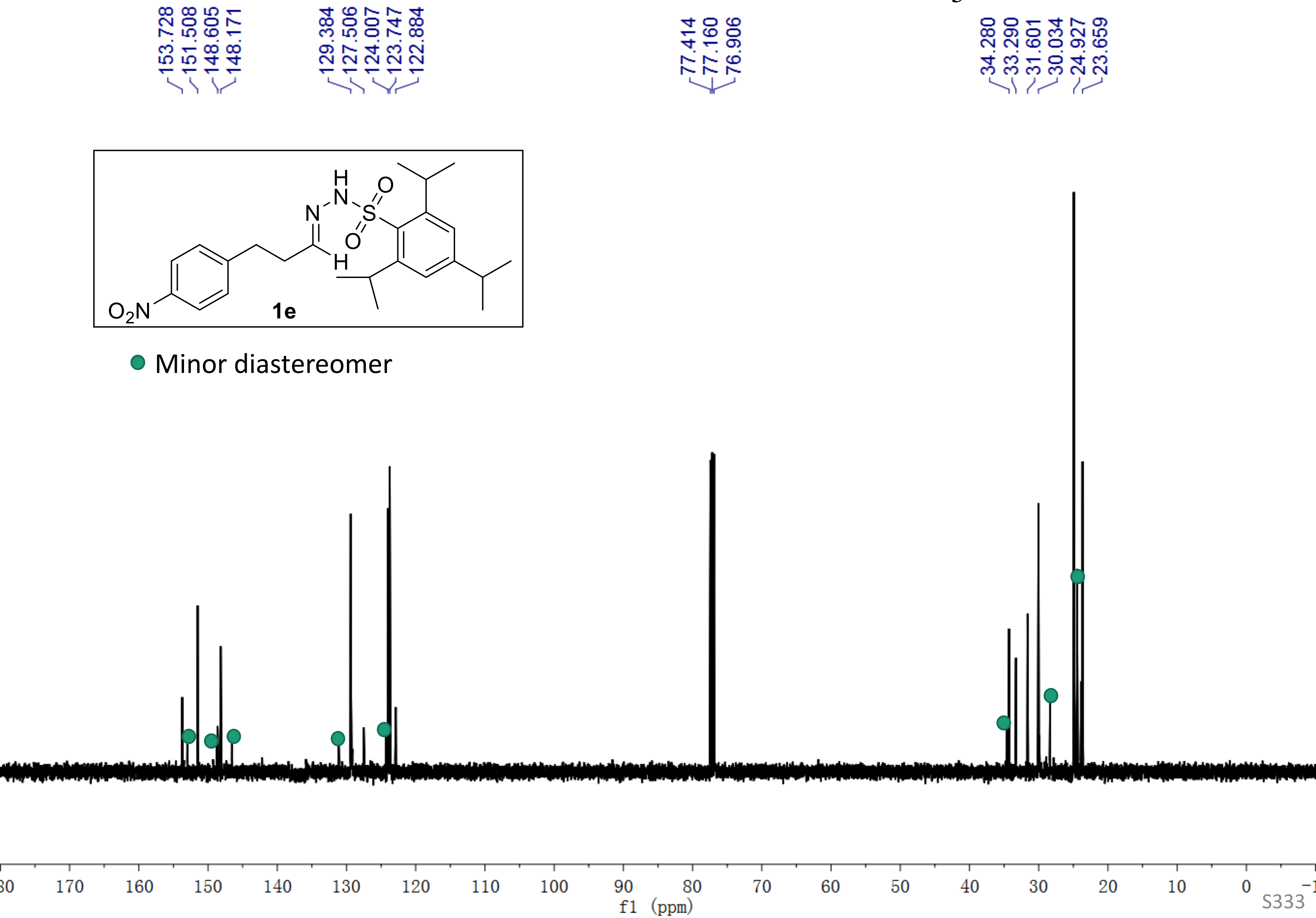


1e

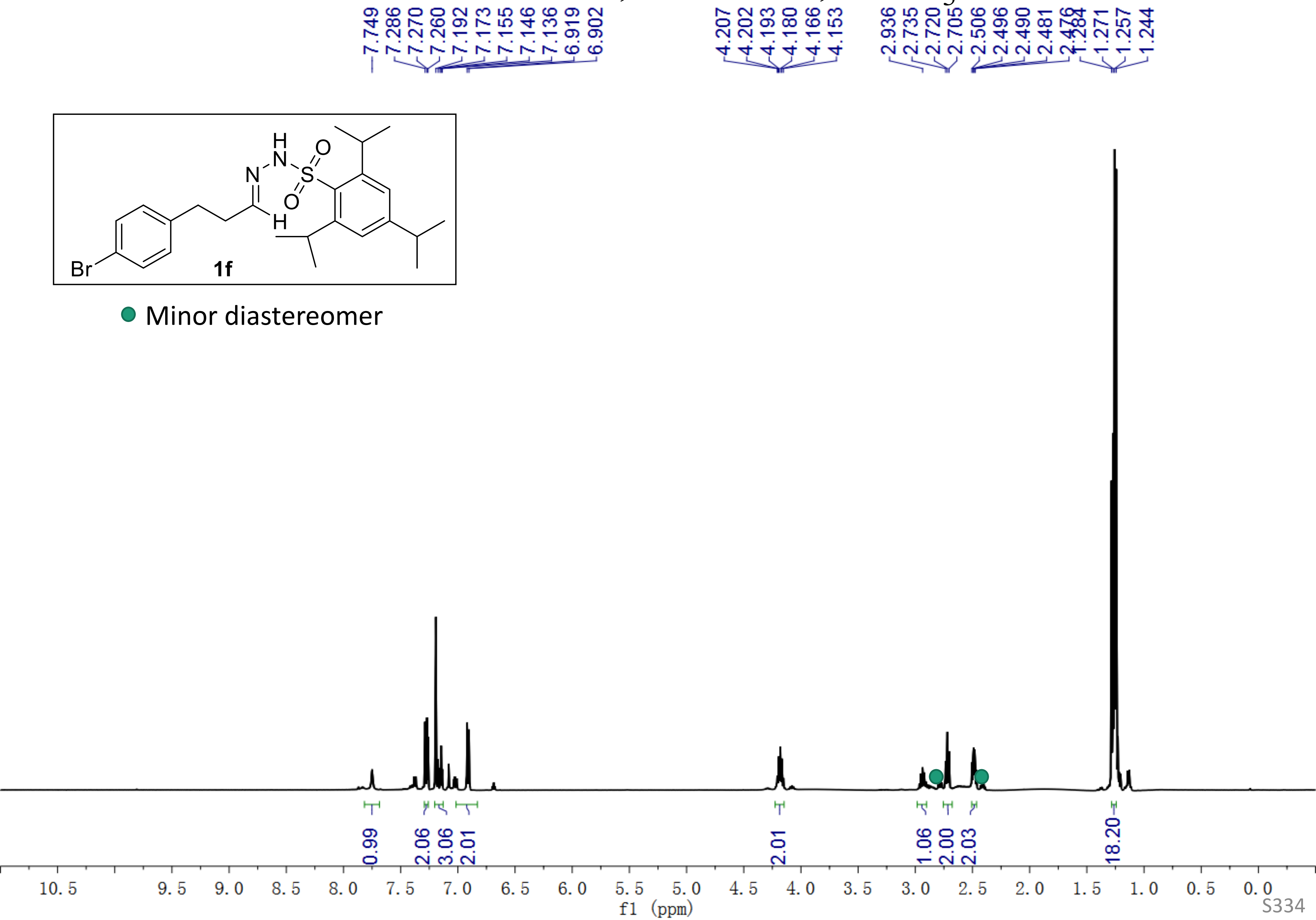
● Minor diastereomer



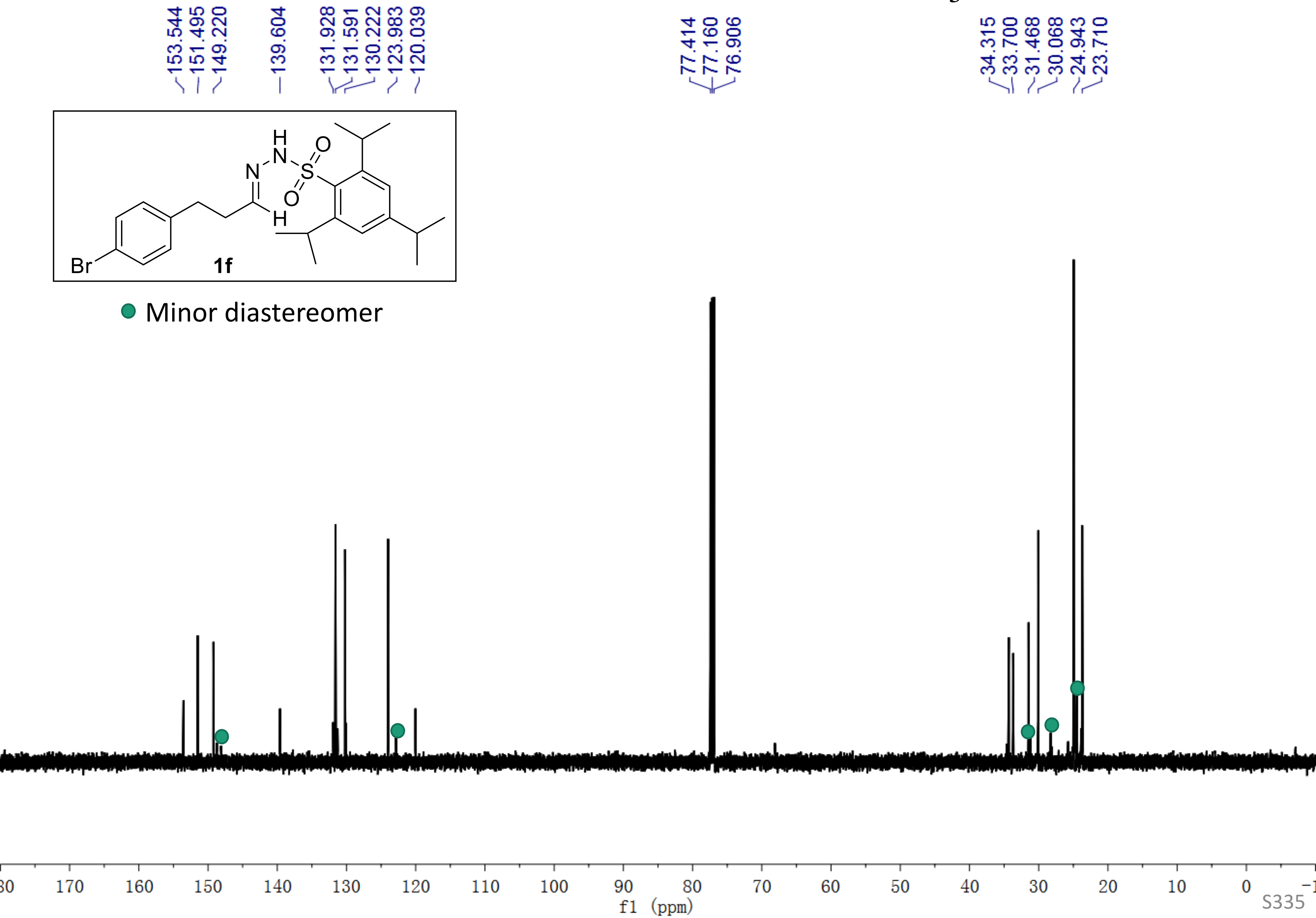
^{13}C NMR of **1e**, 101 MHz, $CDCl_3$



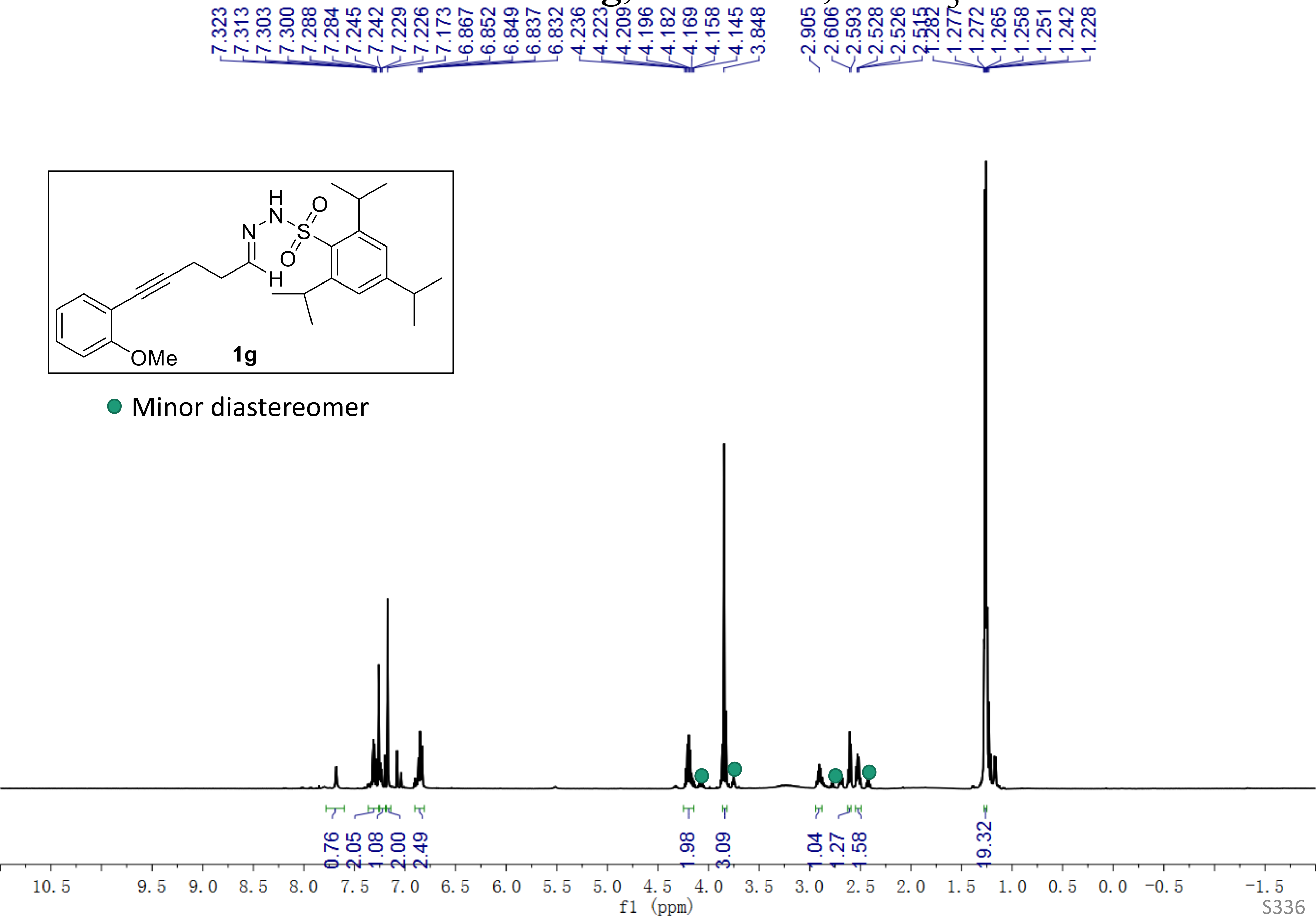
^{1}H NMR of **1f**, 600 MHz, $CDCl_3$



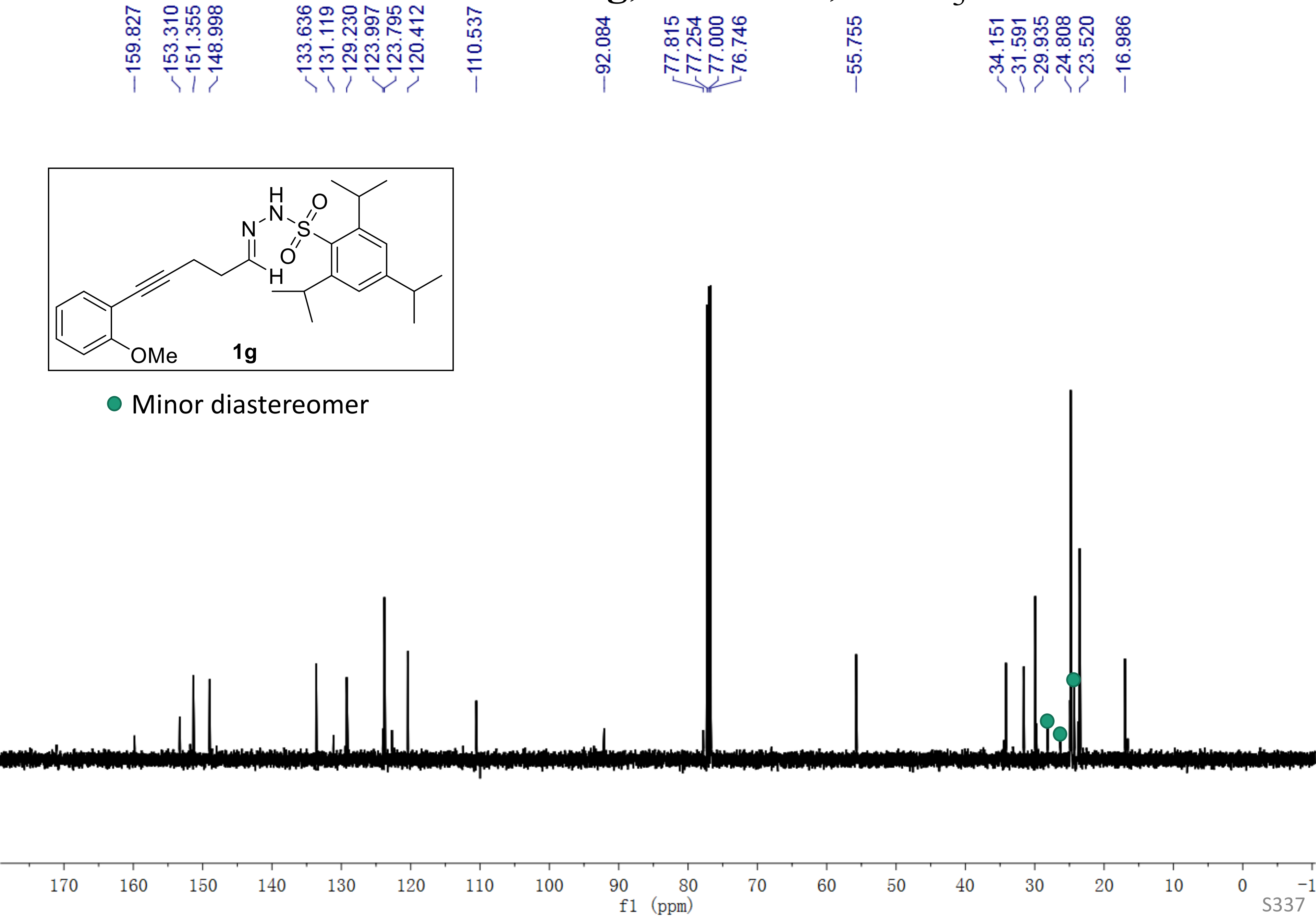
^{13}C NMR of **1f**, 151 MHz, $CDCl_3$



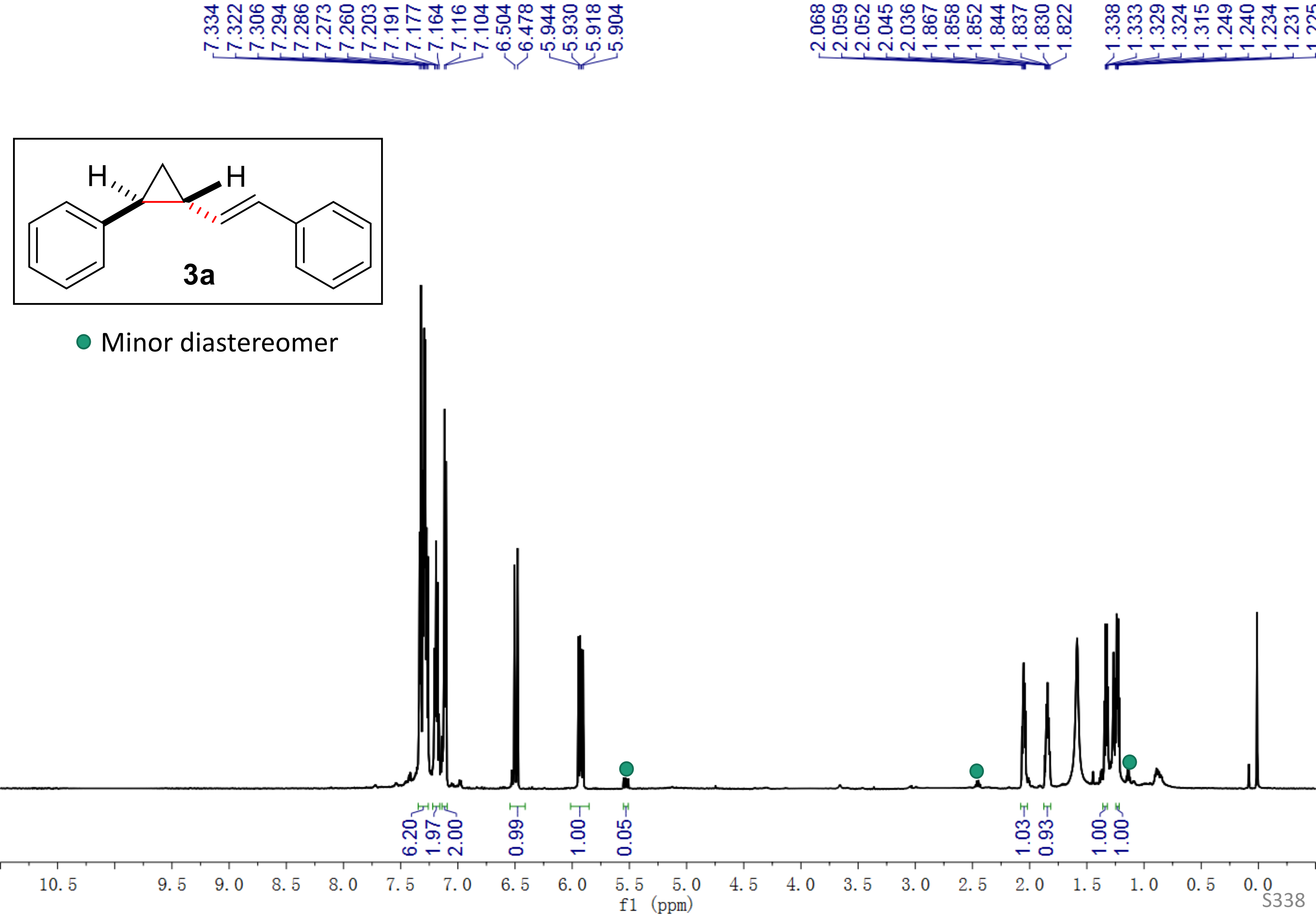
^{1}H NMR of **1g**, 600 MHz, $CDCl_3$



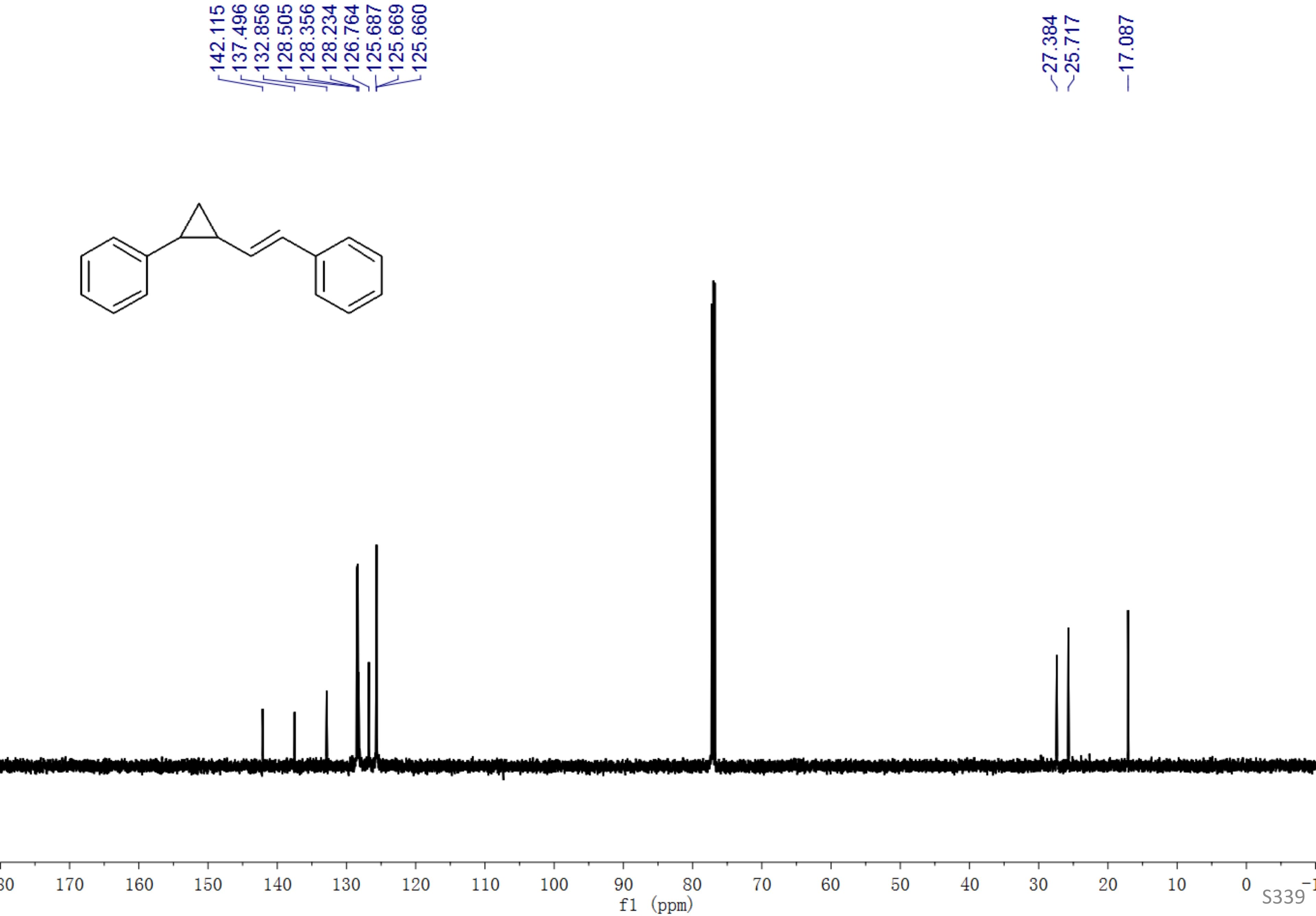
^{13}C NMR of **1g**, 151 MHz, $CDCl_3$



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



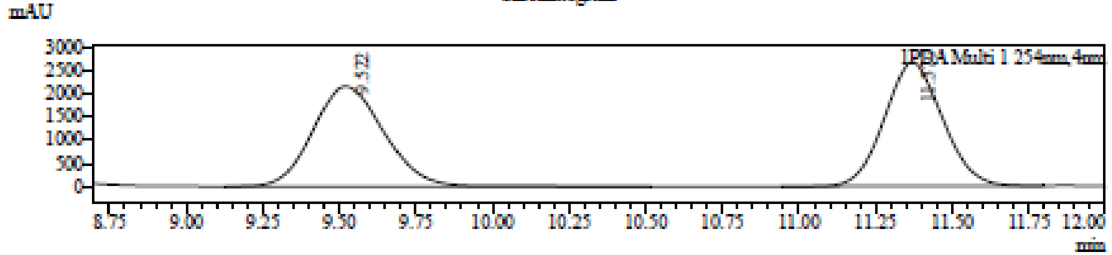
^{13}C NMR of **3a**, 126 MHz, $CDCl_3$



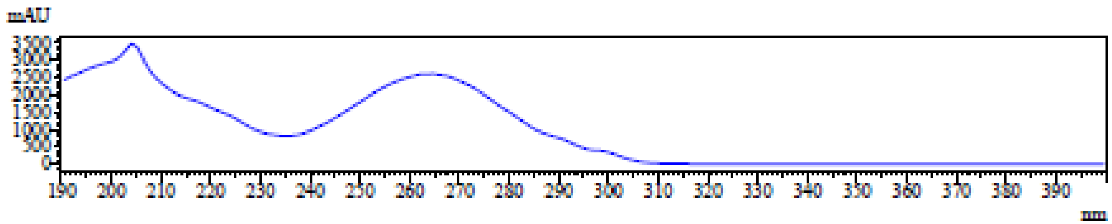
Sample Information

Data File	: J0K-0640-IA--0.8%-1ML001.lcd
Sample Name	: J0K-0640-IA--0.8%-1ML
Sample ID	: J0K-0640-IA--0.8%-1ML
Method File	: J0K-0.8%--15min-1ml.lcm

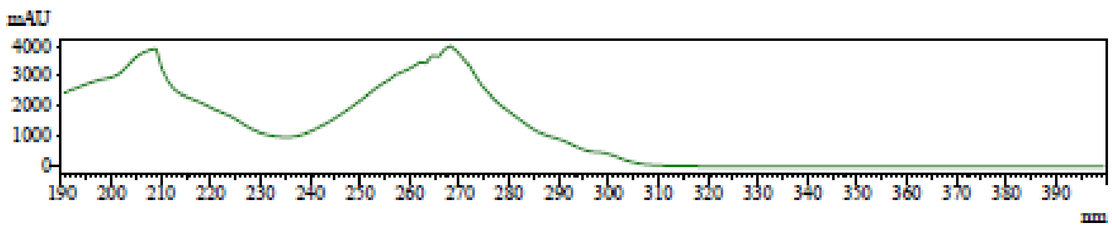
Chromatogram



UV Spectrum
Retention time = 9.522



UV Spectrum
Retention time = 11.370



Peak Table

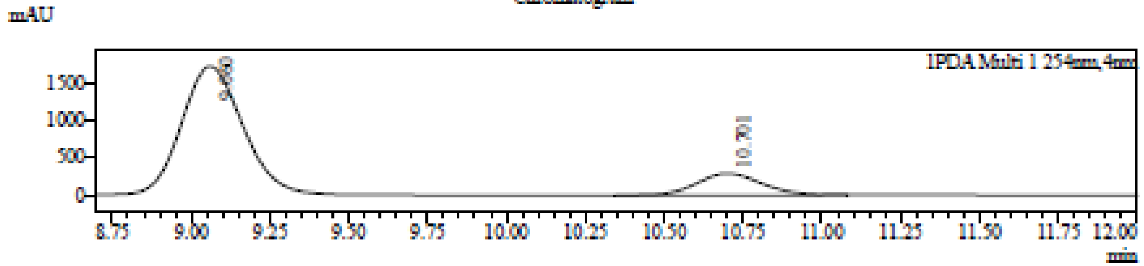
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.522	34645444	49.611
2	11.370	35189394	50.389
Total		69834837	100.000

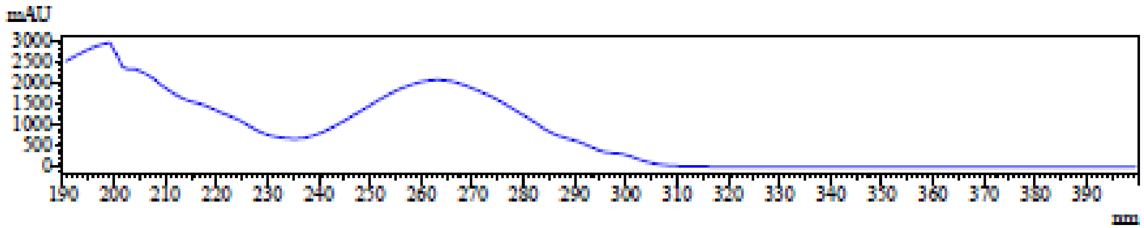
Sample Information

Data File	: J0K-0656-IA--0.8%-1ML.lcd
Sample Name	: J0K-0656-IA--0.8%-1ML
Sample ID	: J0K-0656-IA--0.8%-1ML
Method File	: J0K-0.8%--15min-1ml.lcm

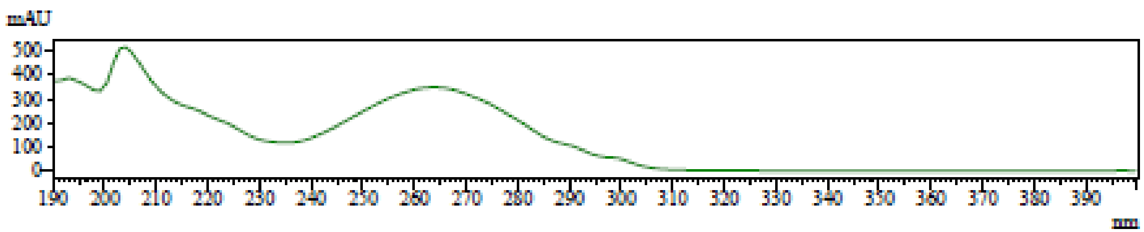
Chromatogram



UV Spectrum
Retention time = 9.060



UV Spectrum
Retention time = 10.701

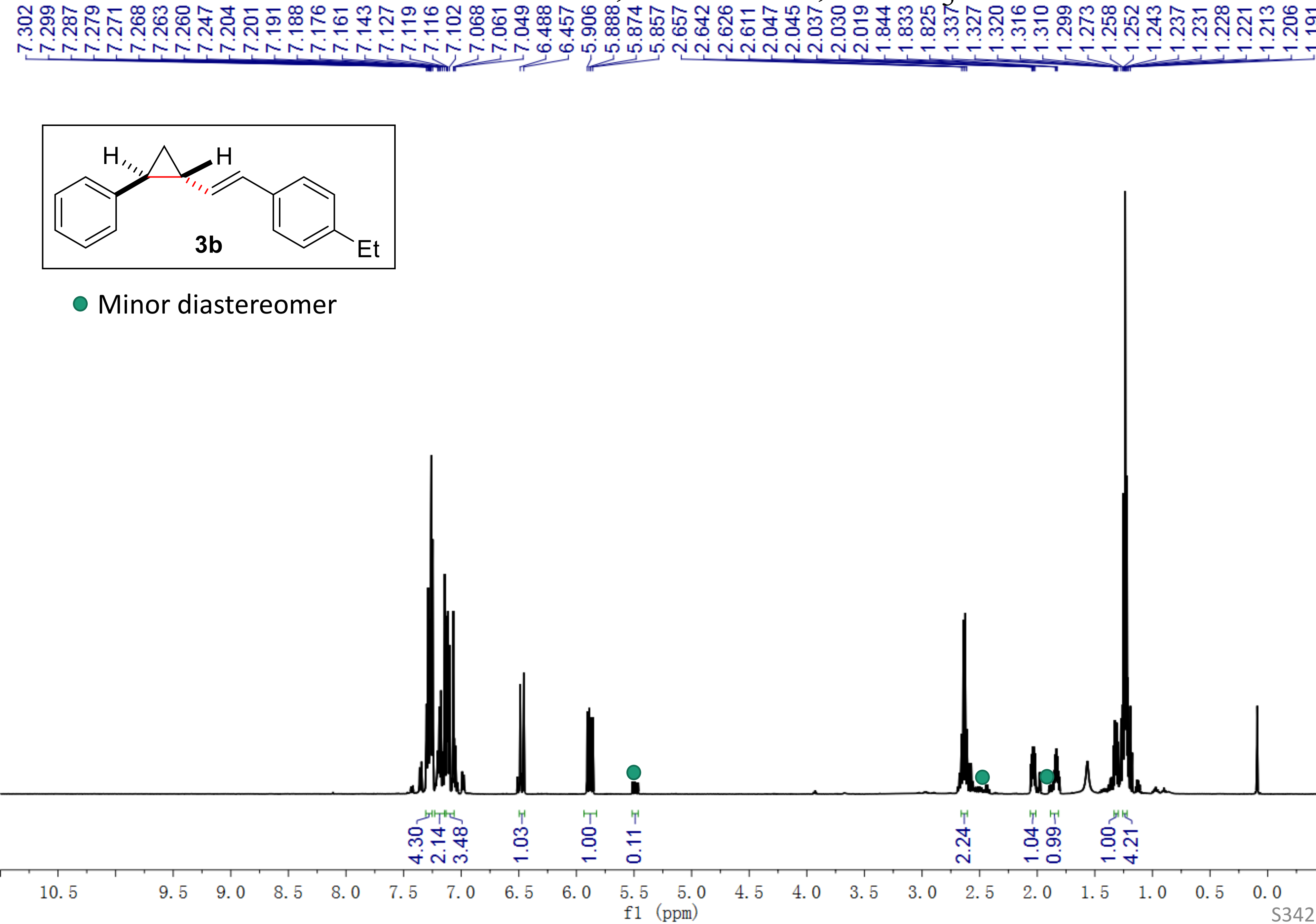


Peak Table

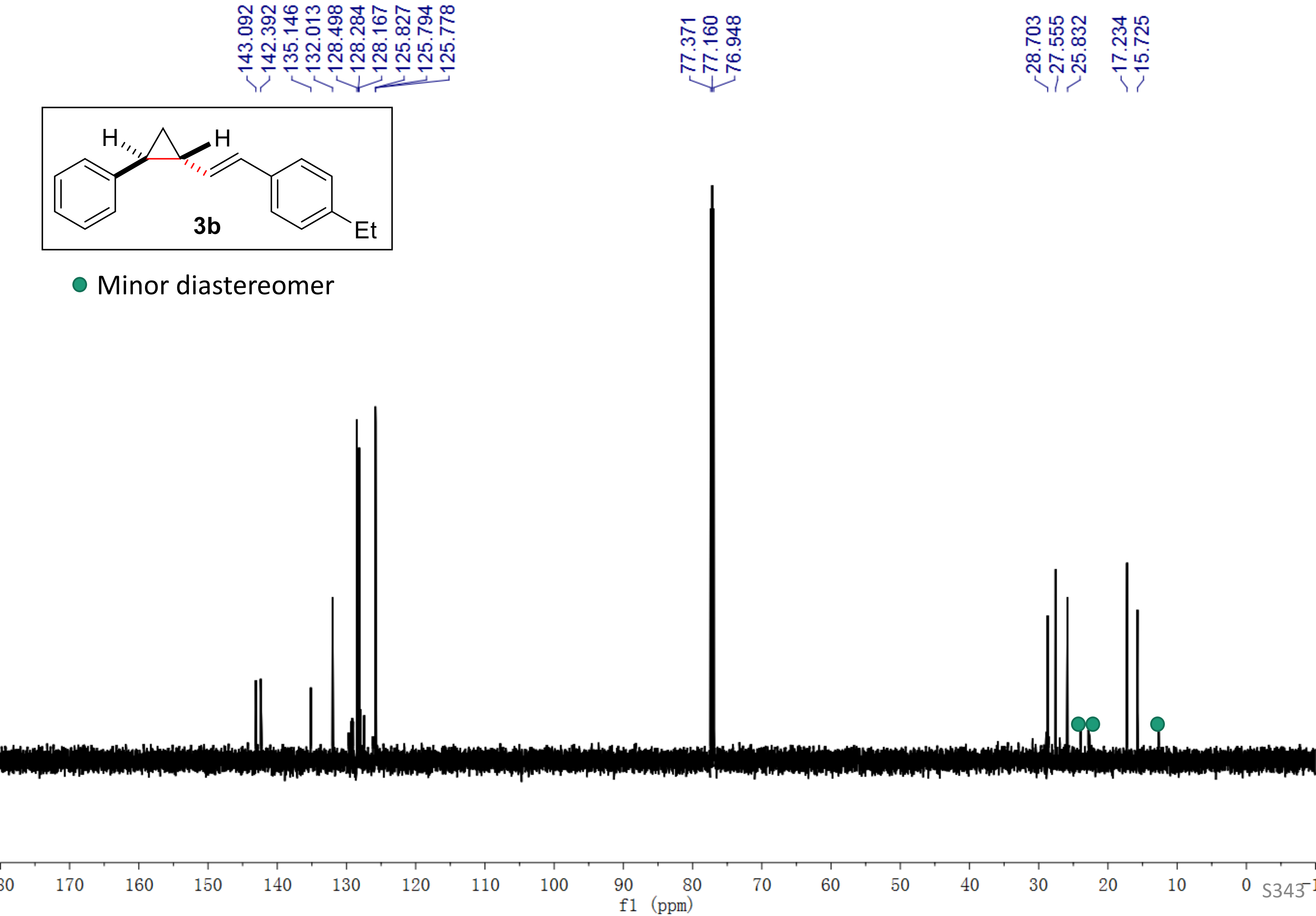
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.060	23545821	85.143
2	10.701	4108486	14.857
Total		27654307	100.000

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



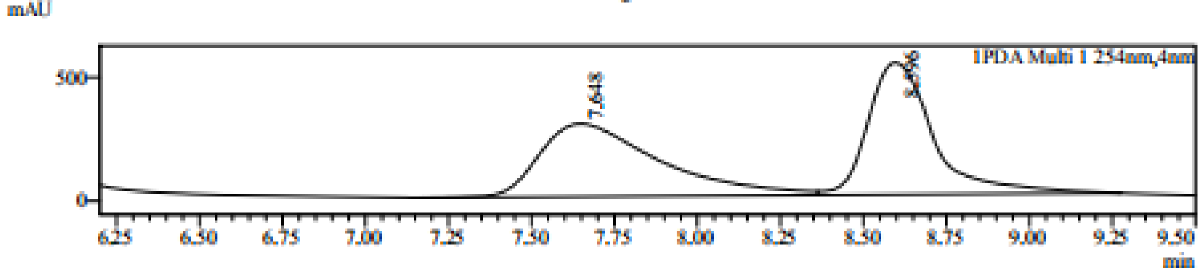
^{13}C NMR of **3b**, 126 MHz, $CDCl_3$



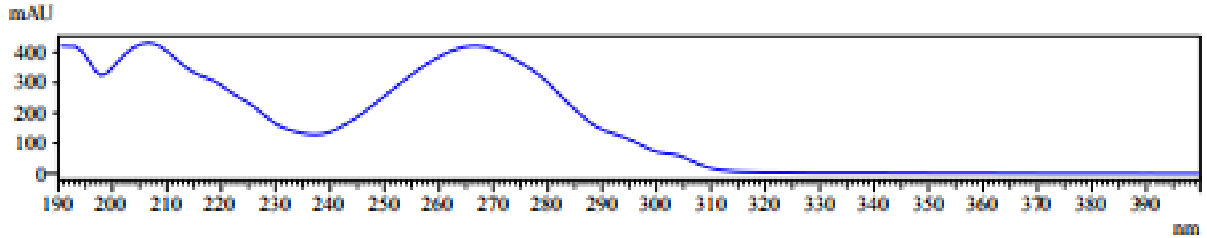
Sample Information

Data File : J0K-1728--ID-0.1%-1ML.lcd
Sample Name : J0K-1728--ID-0.1%-1ML
Sample ID : J0K-1728--ID-0.1%-1ML
Method File : J0K-0.1%--40min-1ml.lcm

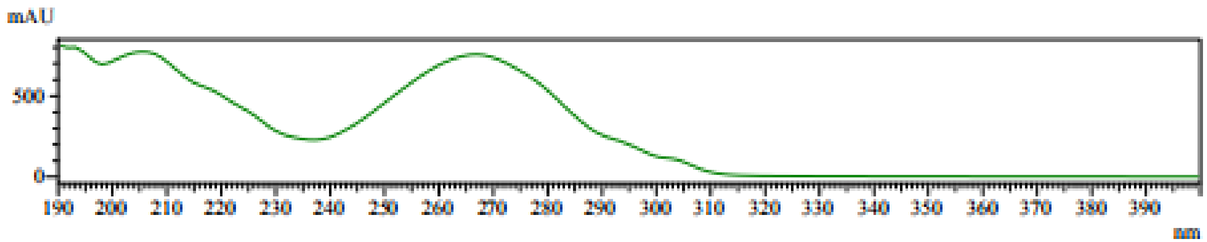
Chromatogram



UV Spectrum
Retention time = 7.648



L
Retention time = 8.596



Peak Table

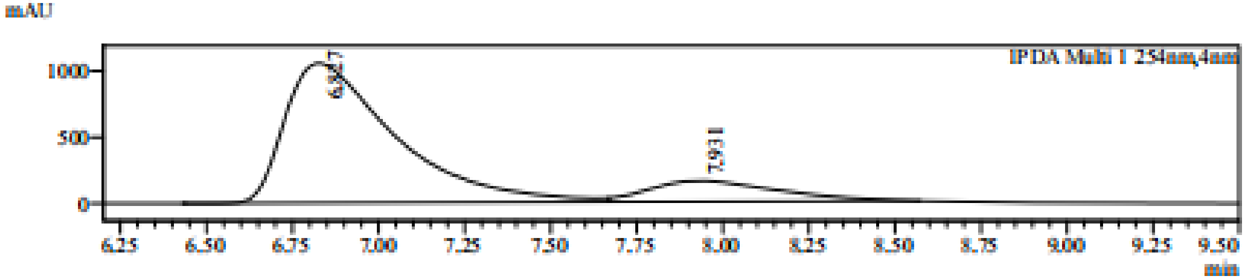
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.648	7362025	50.258
2	8.596	7286329	49.742
Total		14648354	100.000

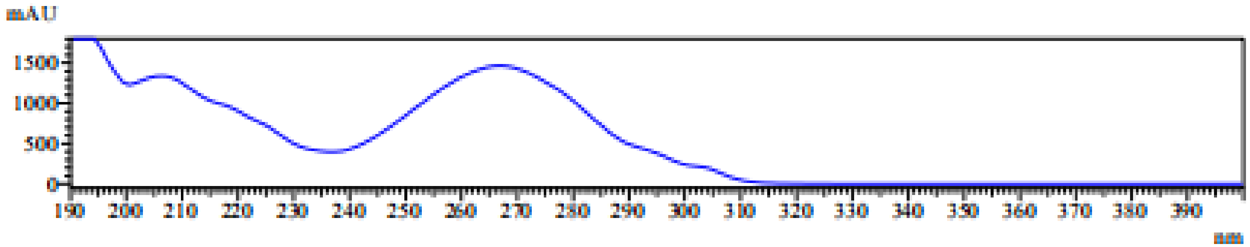
Sample Information

Data File : J0K-1727--ID-0.1%-1ML-2.lcd
Sample Name : J0K-1727--ID-0.1%-1ML-2
Sample ID : J0K-1727--ID-0.1%-1ML-2
Method File : J0K-0.1%--40min-1ml.lcm

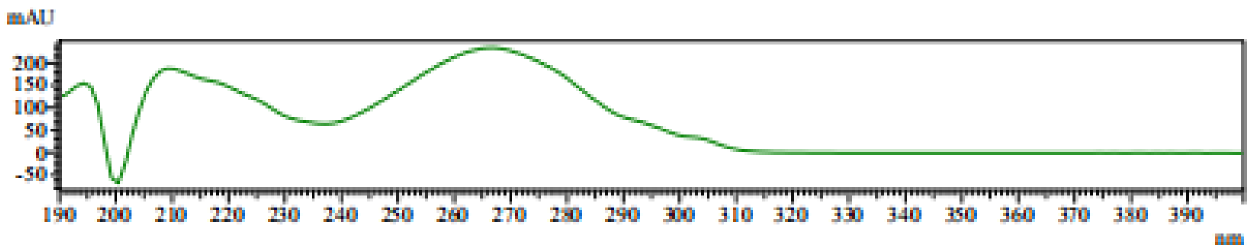
Chromatogram



UV Spectrum
Retention time = 6.827



U
Retention time = 7.931

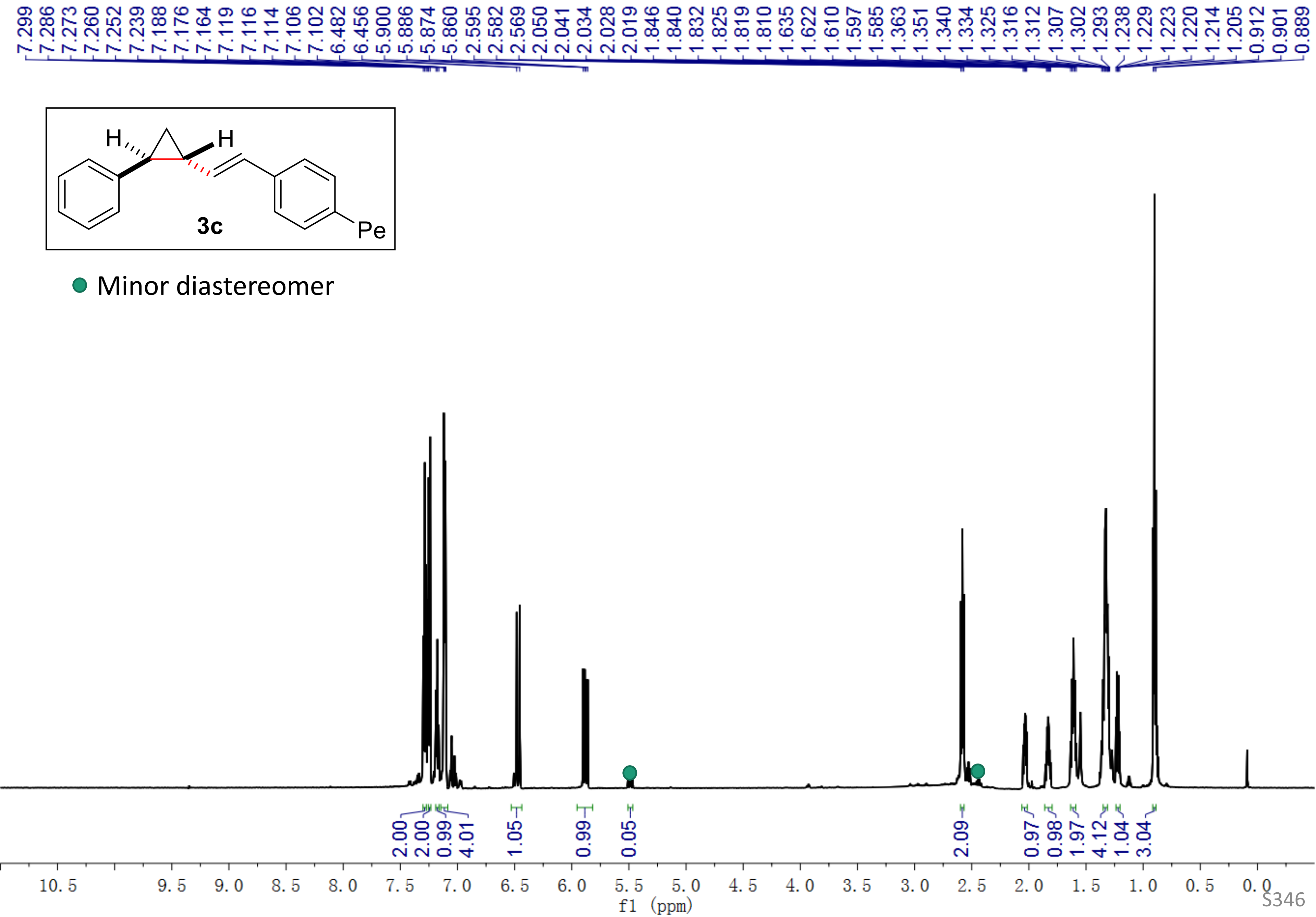


Peak Table

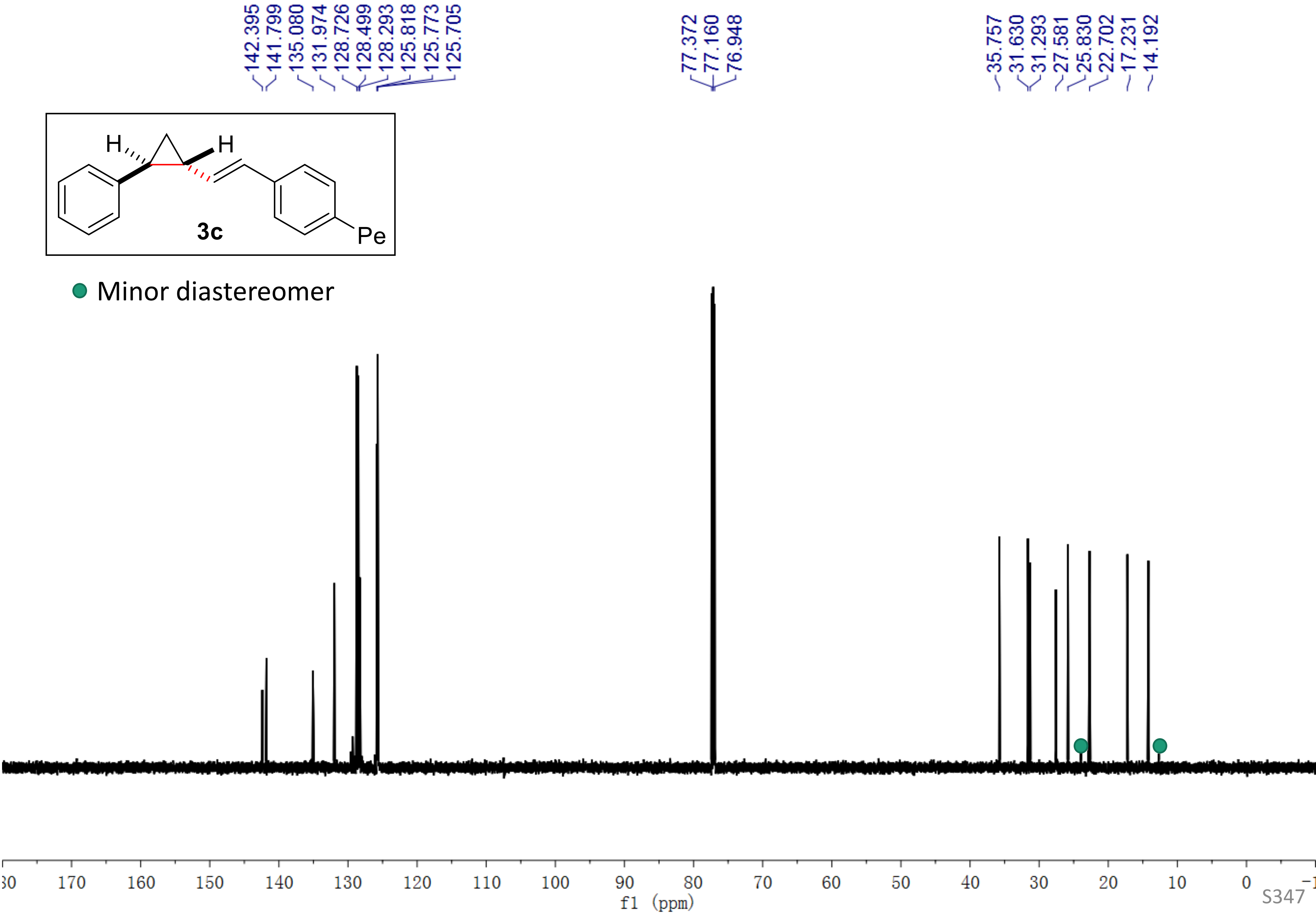
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.827	23494553	85.236
2	7.931	4069635	14.764
Total		27564188	100.000

^{1}H NMR of **3c**, 500 MHz, CDCl$_3$



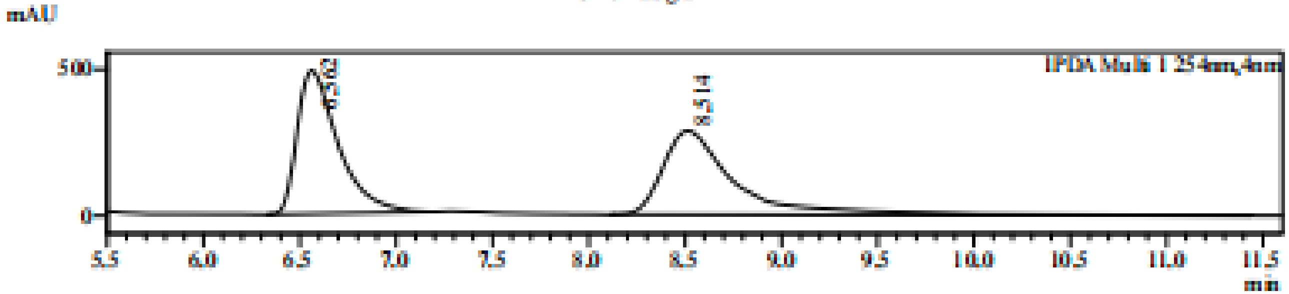
^{13}C NMR of **3c**, 126 MHz, $CDCl_3$



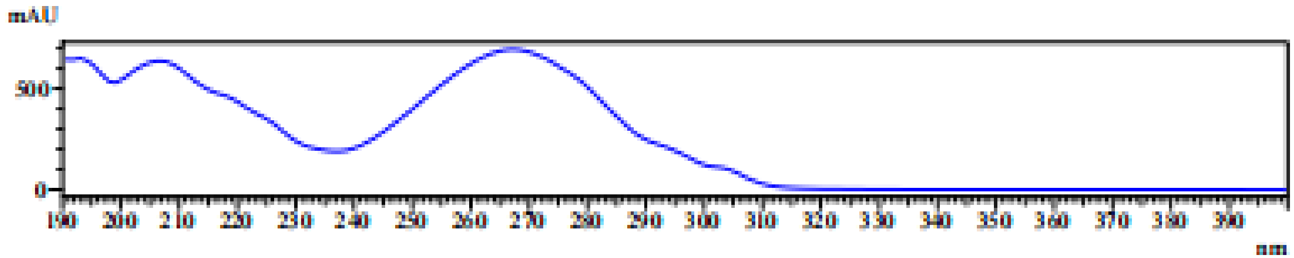
Sample Information

Data File : J0K-1722-ID-0.1%-1ML.lcd
Sample Name : J0K-1722-ID-0.1%-1ML
Sample ID : J0K-1722-ID-0.1%-1ML
Method File : J0K-0.1%-35min-1ml.lcm

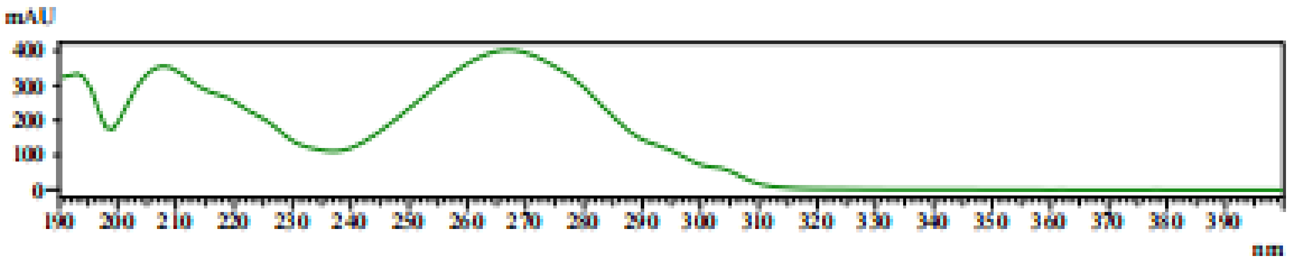
Chromatogram



UV Spectrum
Retention time = 6.562



l
Retention time = 8.514



Peak Table

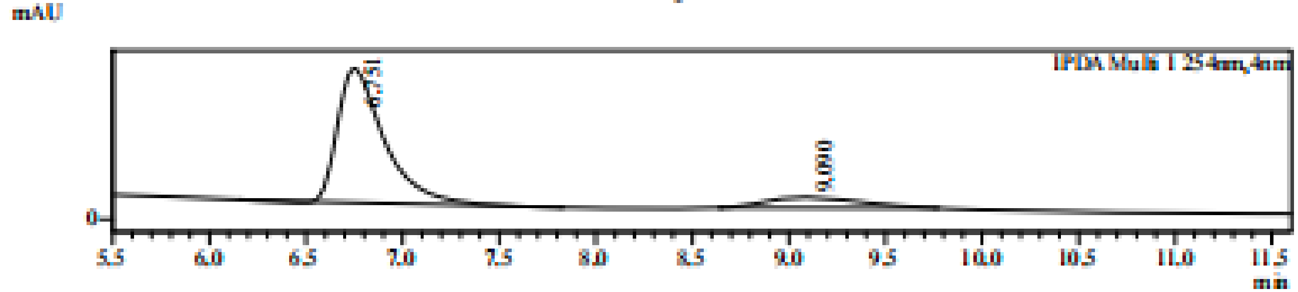
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.562	7204833	49.390
2	8.514	7382719	50.610
Total		14587553	100.000

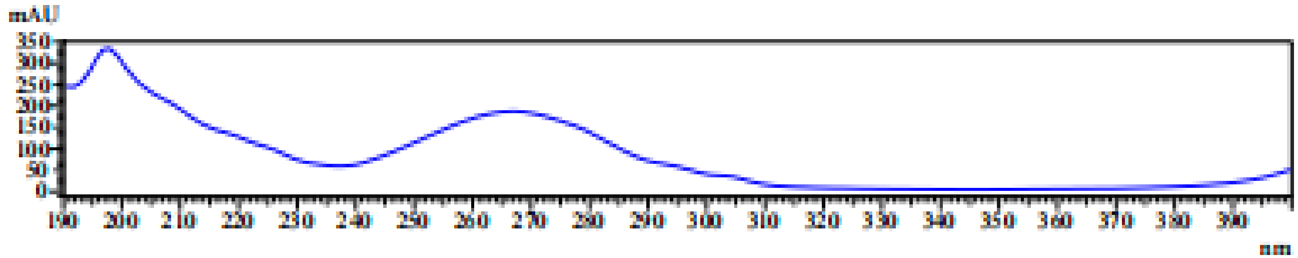
Sample Information

Data File	: J0K-1721-ID-0.1%-1ML-2.lcd
Sample Name	: J0K-1721-ID-0.1%-1ML-2
Sample ID	: J0K-1721-ID-0.1%-1ML-2
Method File	: J0K-0.1%--35min-1ml.lcm

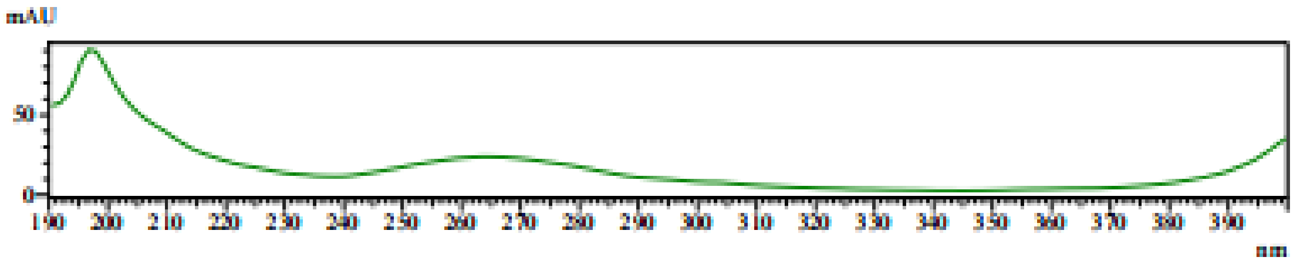
Chromatogram



UV Spectrum
Retention time = 6.751



I
Retention time = 9.090

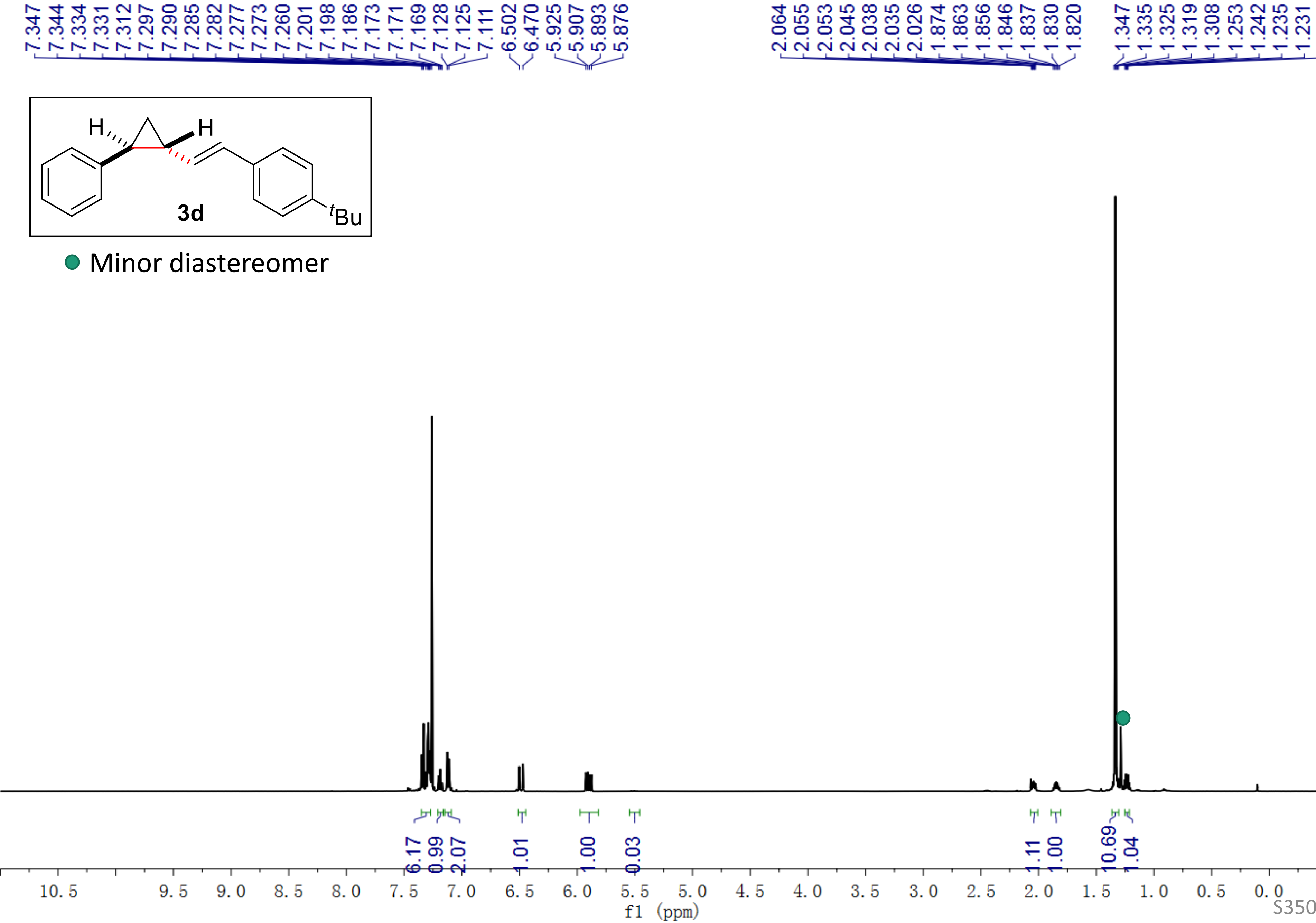


Peak Table

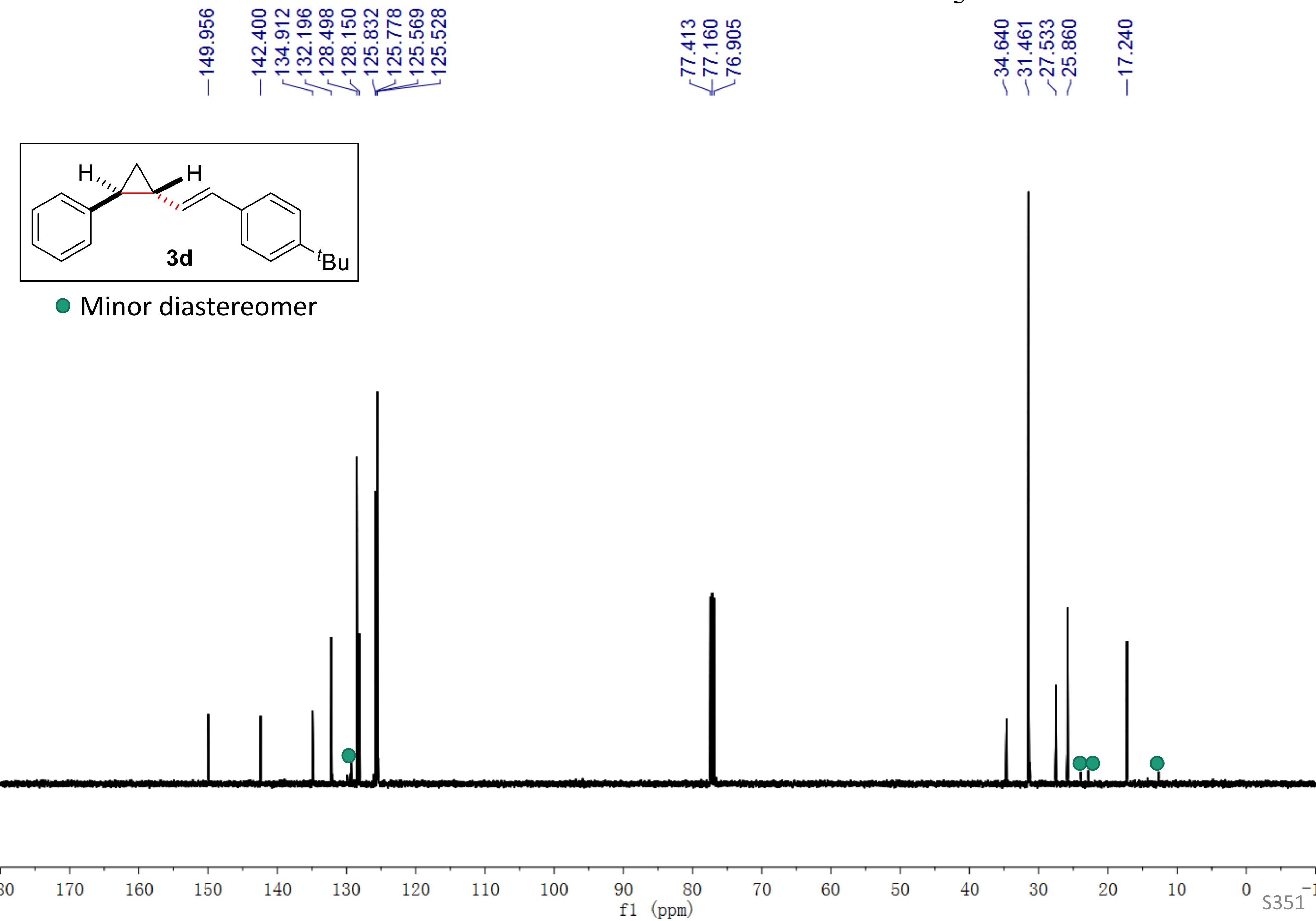
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.751	2064299	86.386
2	9.090	325319	13.614
Total		2389618	100.000

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

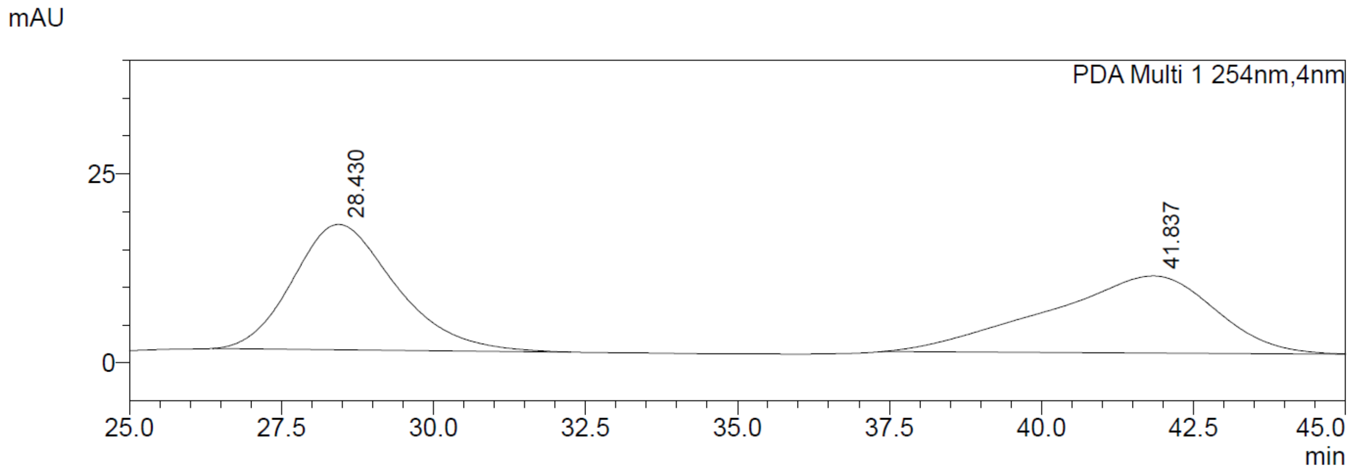


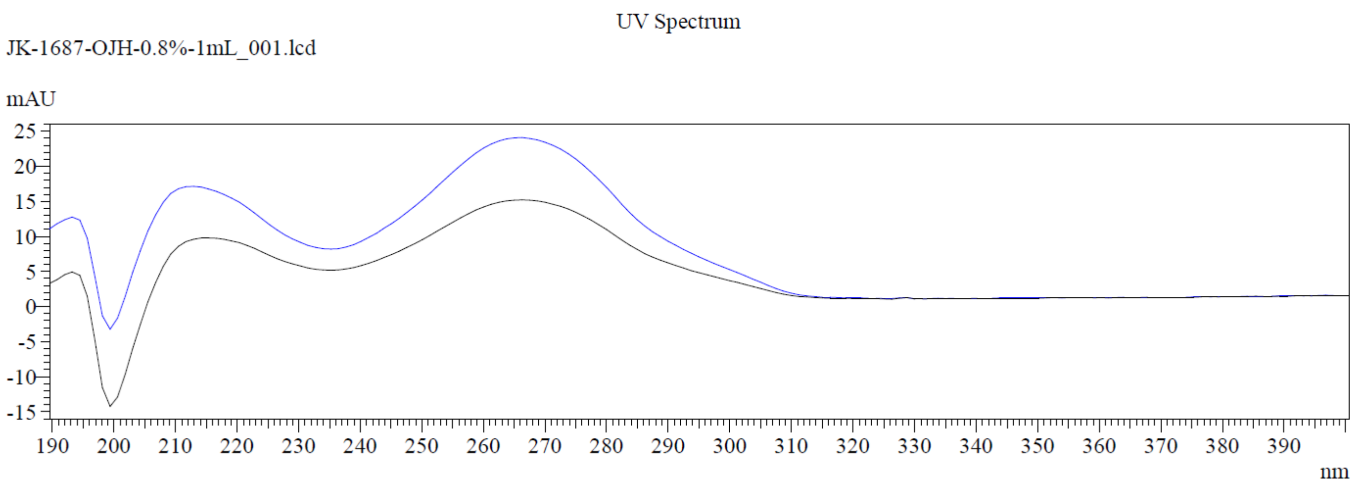
^{13}C NMR of **3d**, 126 MHz, $CDCl_3$



==== Shimadzu LabSolutions Analysis Report ====

JK-1687-OJH-0.8%-1mL
JK-0.8%-30min-1mL.lcm





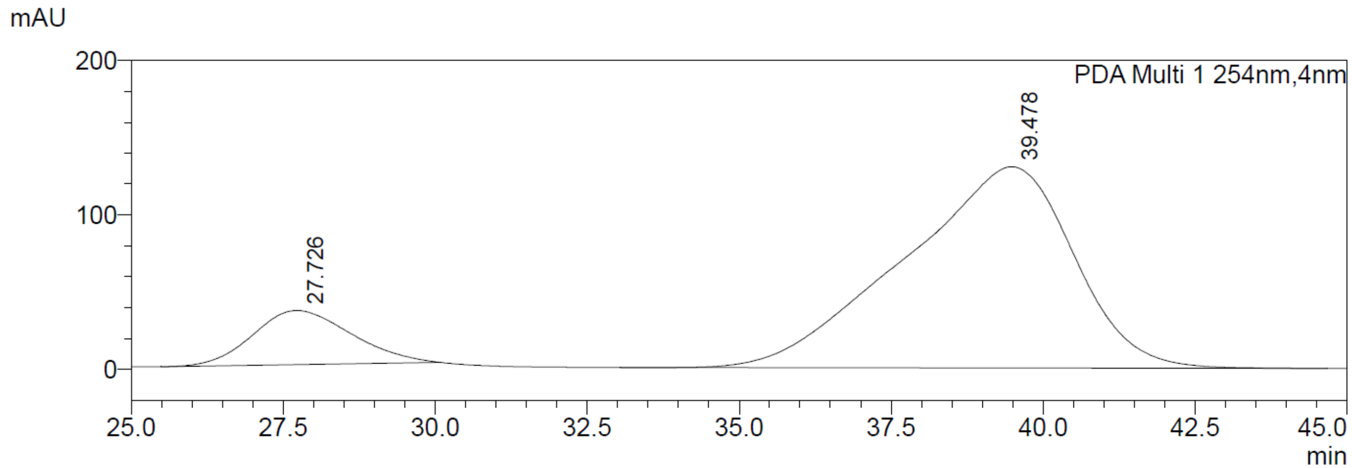
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	28.430	49.905
2	41.837	50.095
Total		100.000

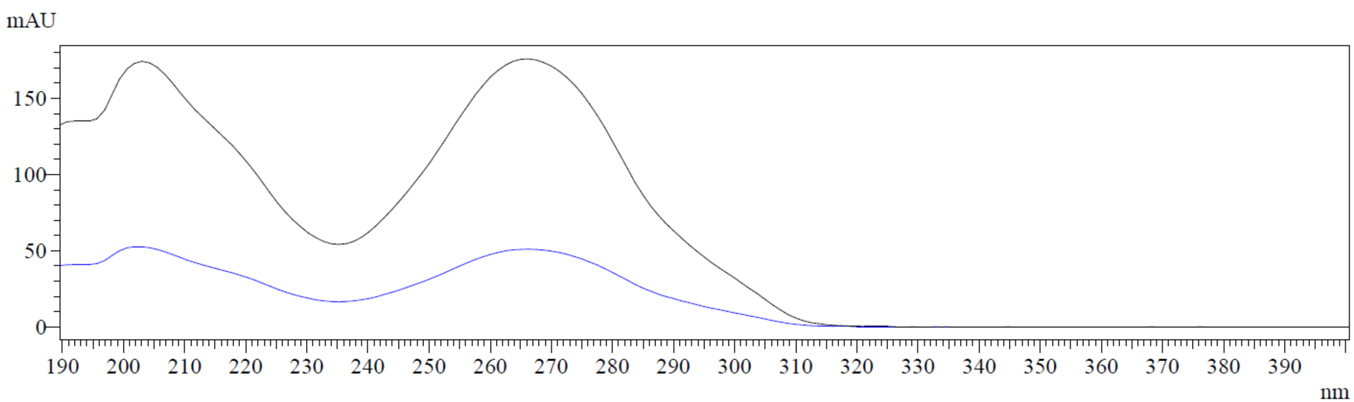
==== Shimadzu LabSolutions Analysis Report ====

JK-1710-OJH-0.8%-1mL
JK-0.8%-30min-1mL.lcm



UV Spectrum

JK-1710-OJH-0.8%-1mL_001.lcd

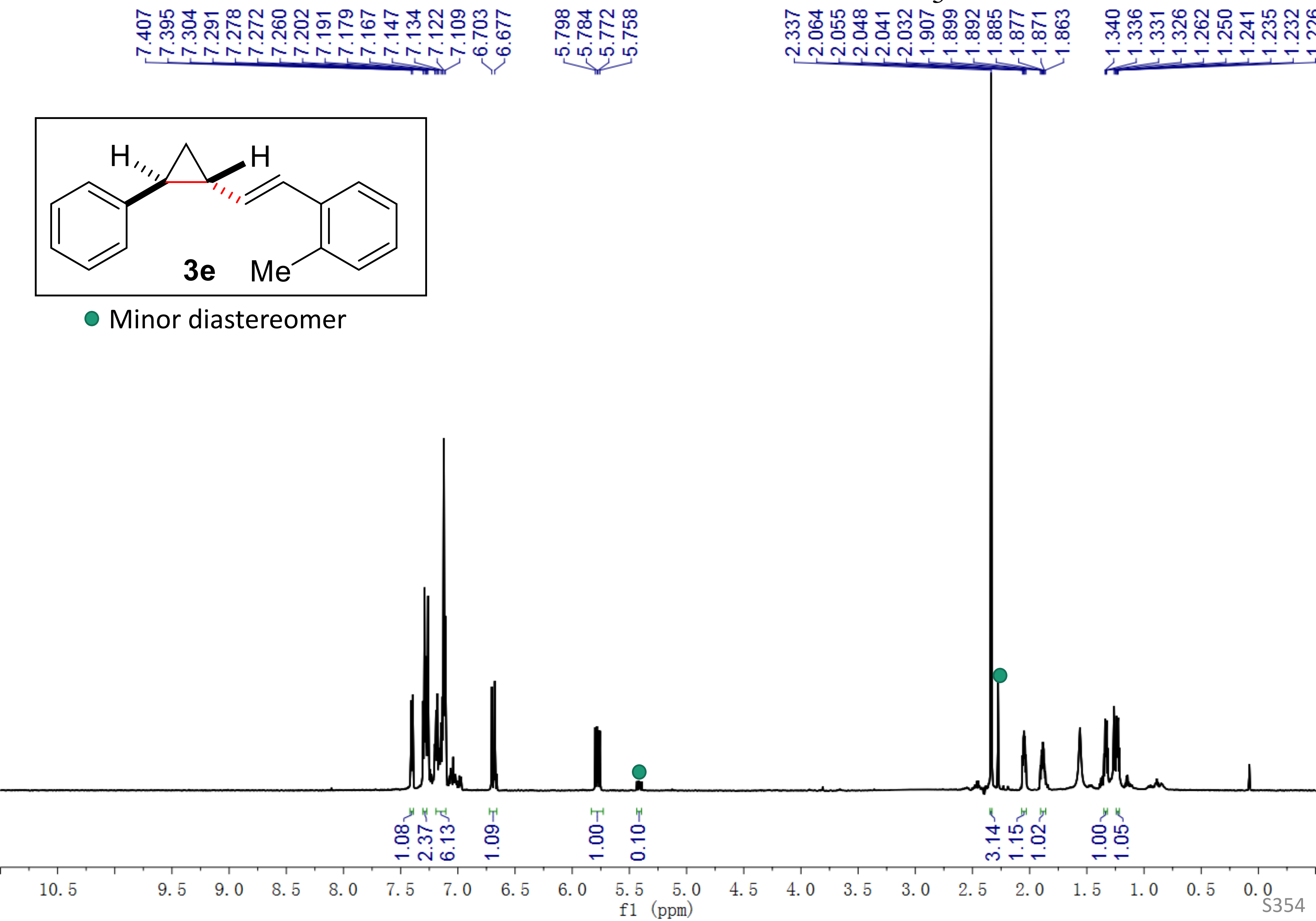


Peak Table

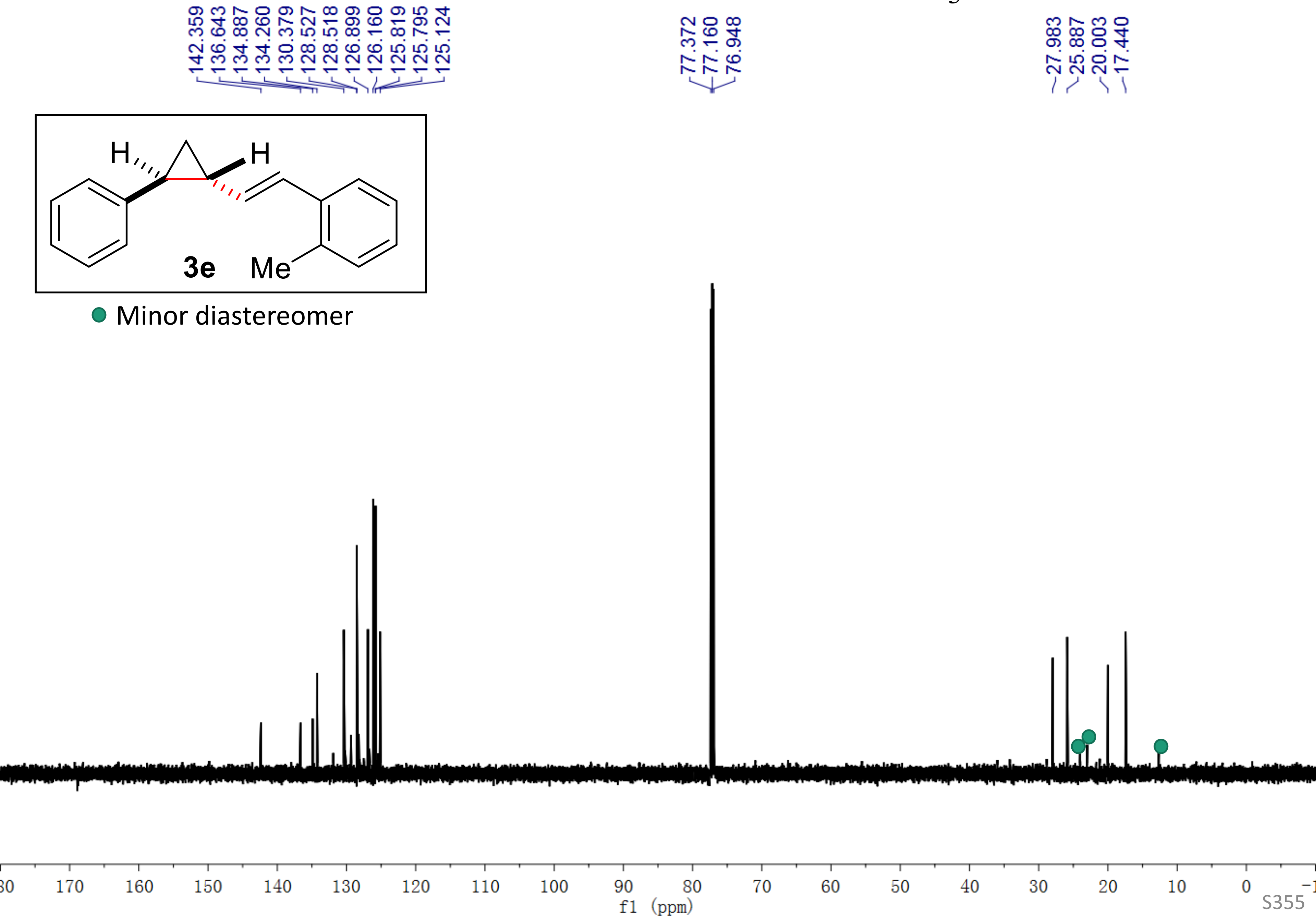
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	27.726	13.491
2	39.478	86.509
Total		100.000

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



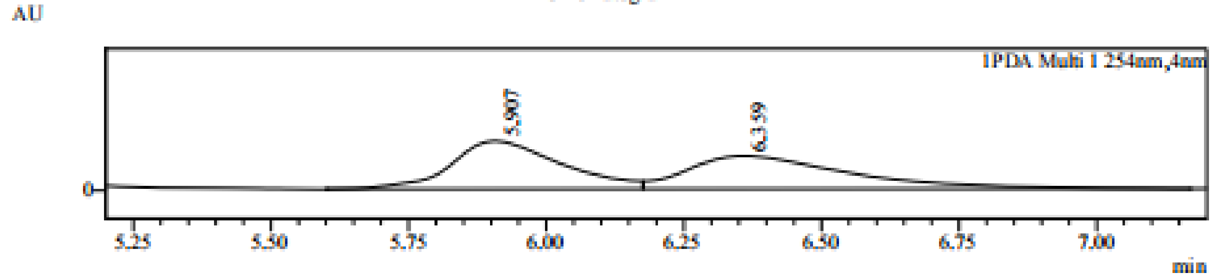
^{13}C NMR of **3e**, 126 MHz, $CDCl_3$



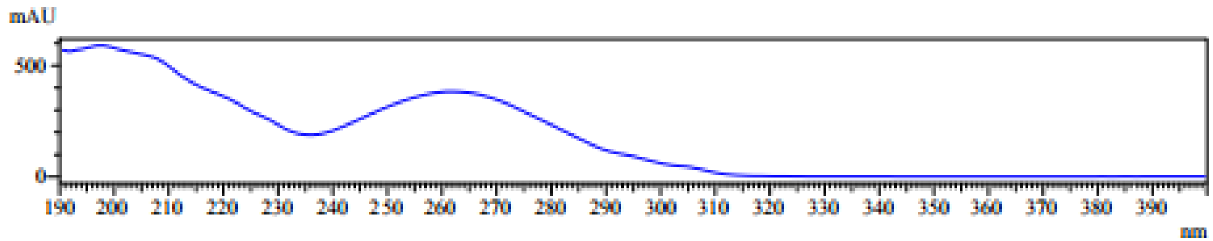
Sample Information

Data File	: J0K-1685--IE-1%-1ML-5.lcd
Sample Name	: J0K-1685--IE-1%-1ML-5
Sample ID	: J0K-1685--IE-1%-1ML-5
Method File	: J0K-0.1%--35min-1ml.lcm

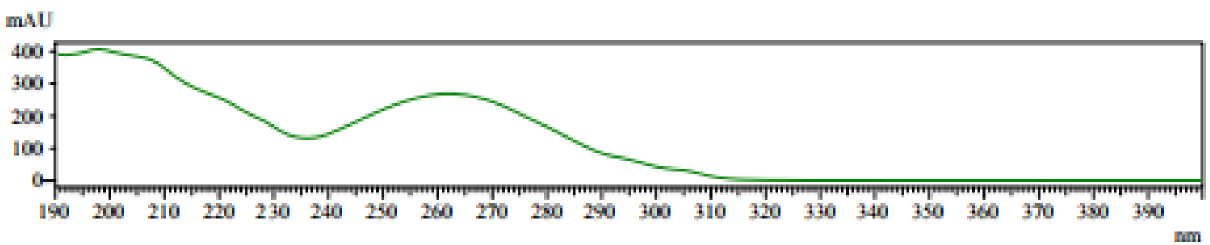
Chromatogram



UV Spectrum
Retention time = 5.907



I
Retention time = 6.359



Peak Table

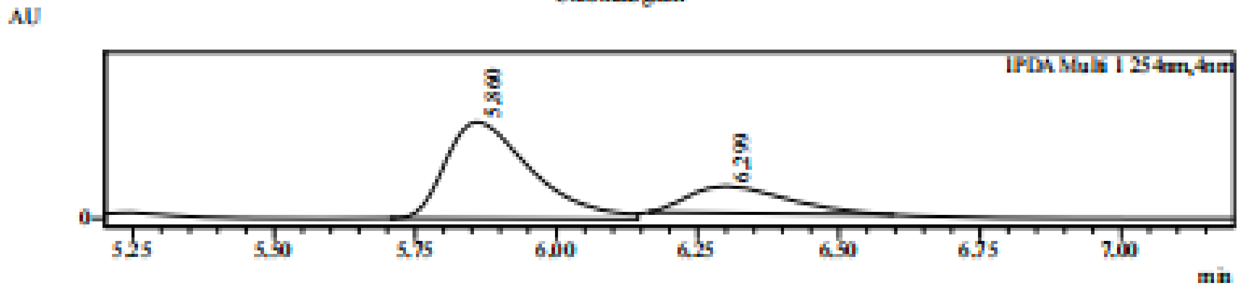
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.907	4743354	50.084
2	6.359	4727485	49.916
Total		9470840	100.000

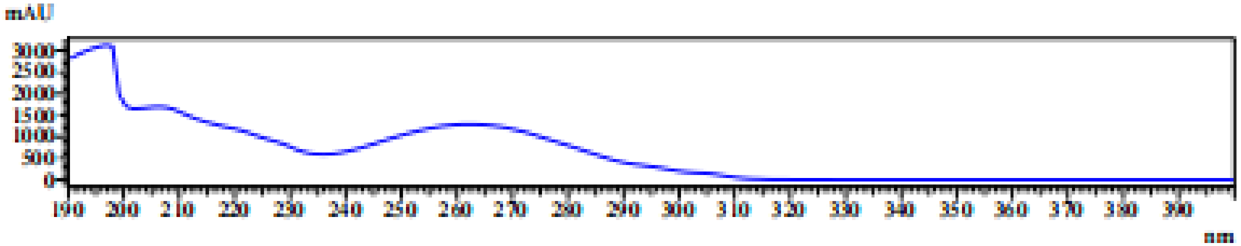
Sample Information

Data File	: J0K-1734-IE-1%-1ML-4.lcd
Sample Name	: J0K-1734-IE-1%-1ML-4
Sample ID	: J0K-1734-IE-1%-1ML-4
Method File	: J0K-0.1%--35min-1ml.lcm

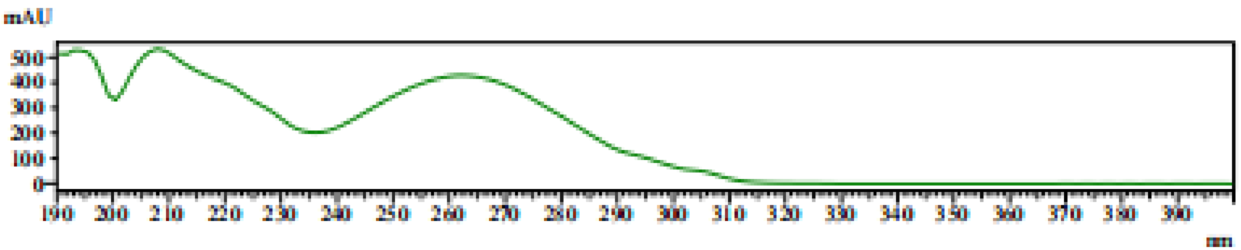
Chromatogram



UV Spectrum
Retention time = 5.860



U
Retention time = 6.299

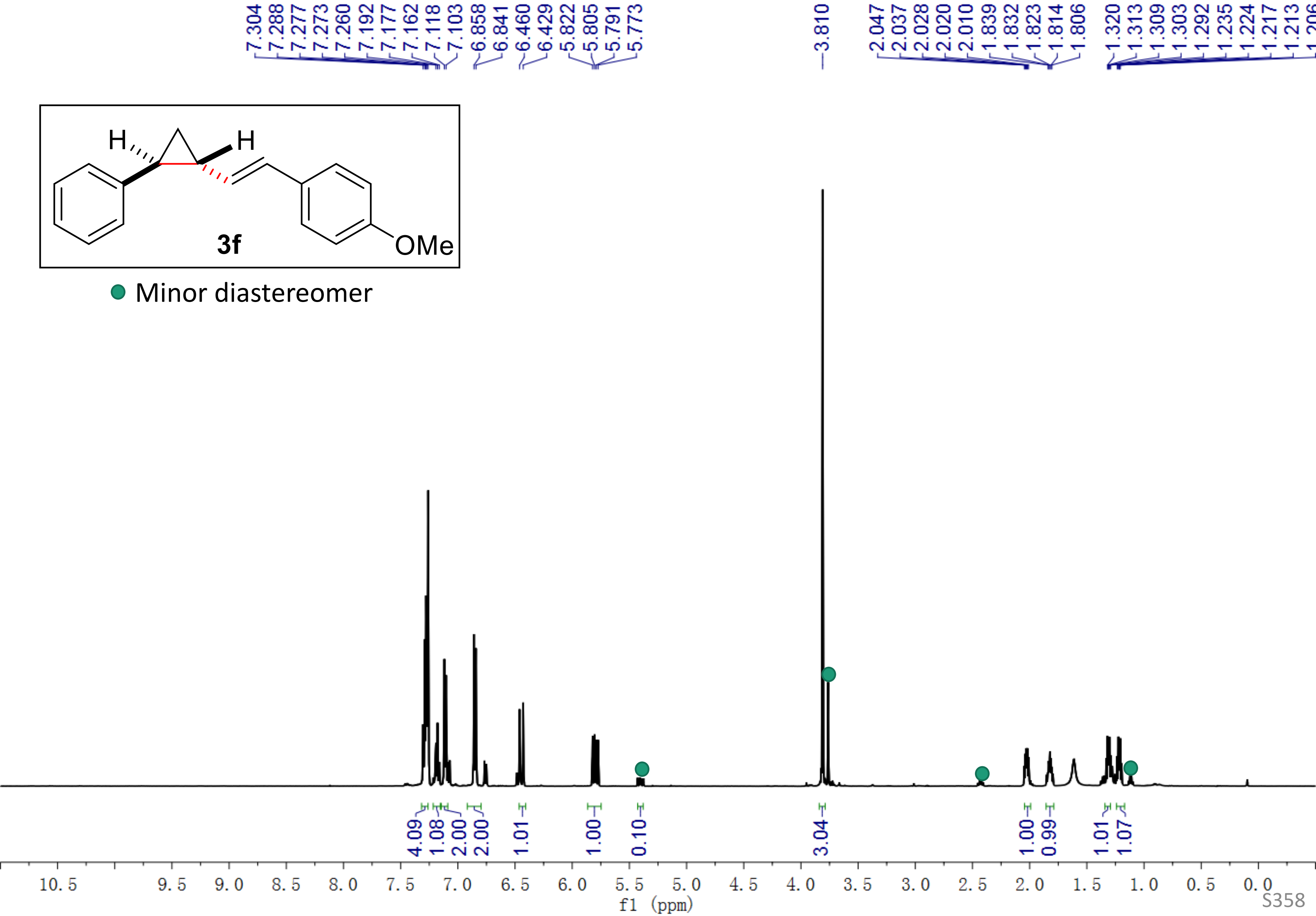


Peak Table

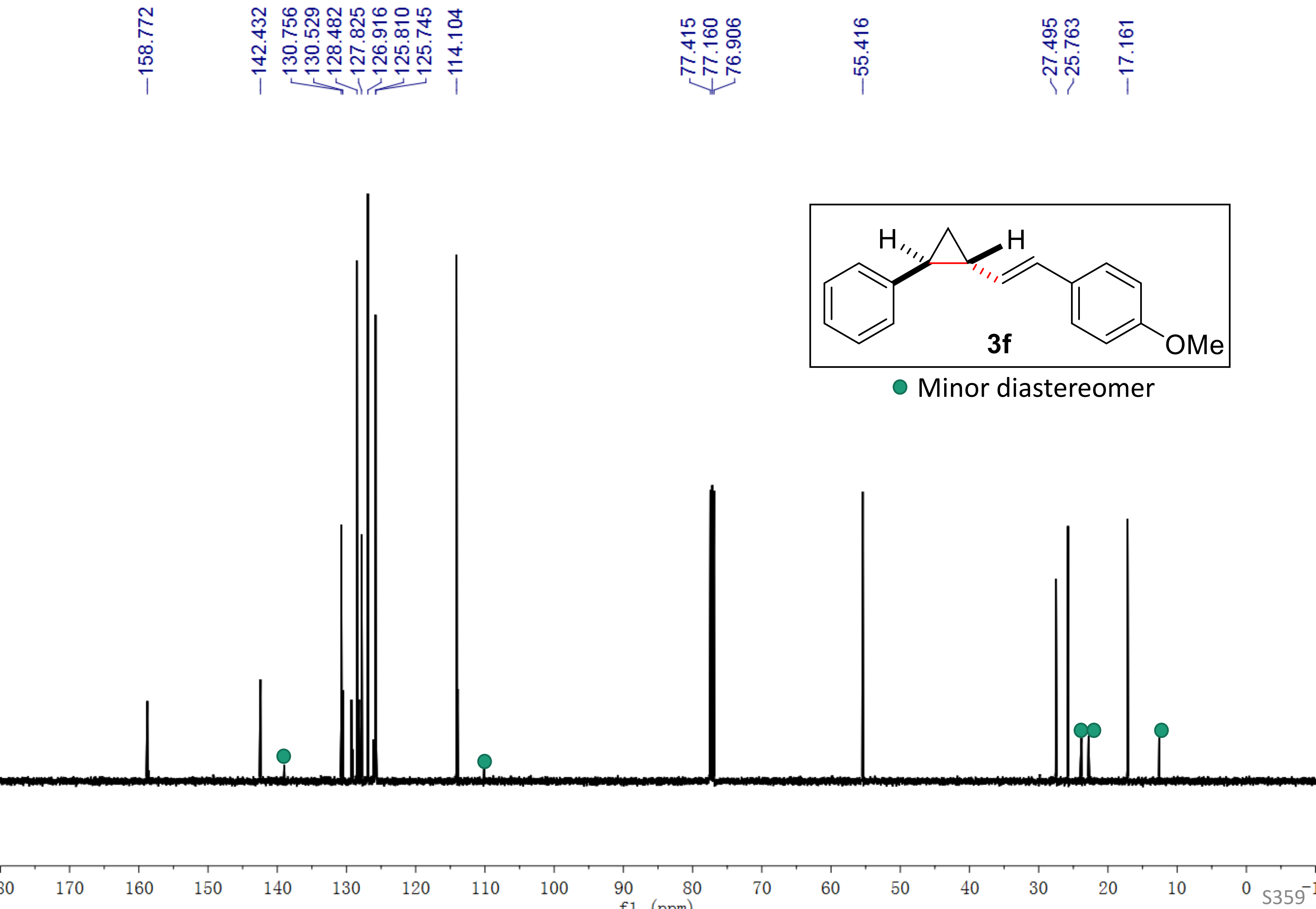
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.860	12289535	75.953
2	6.299	3890920	24.047
Total		16180455	100.000

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



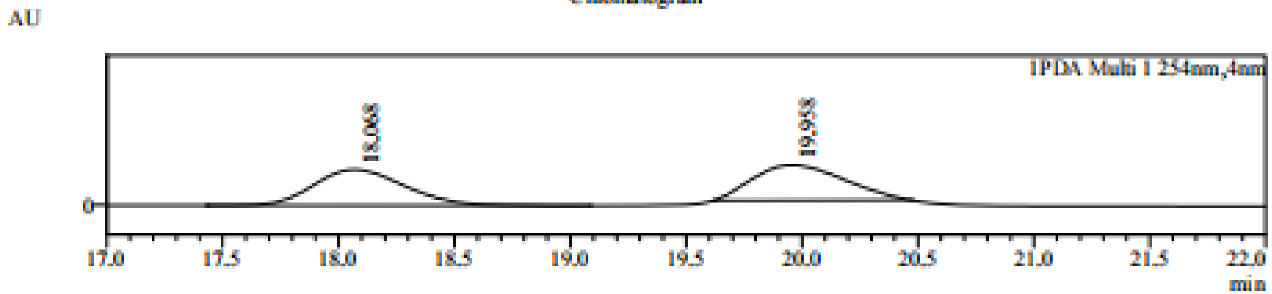
^{13}C NMR of **3f**, 126 MHz, $CDCl_3$



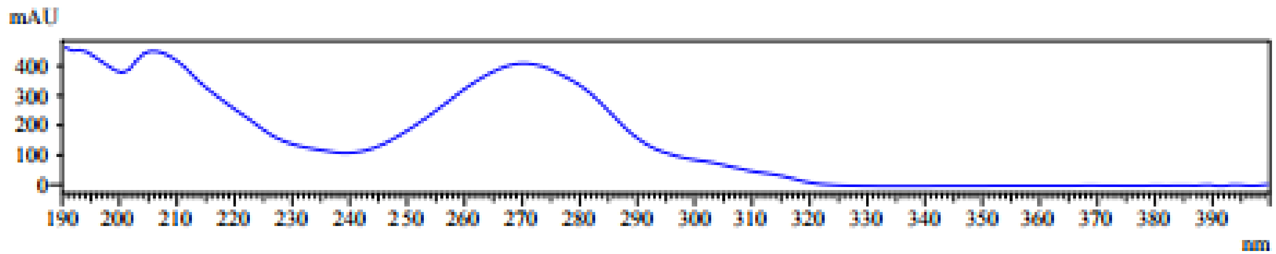
Sample Information

Data File	:	J0K-1744--ODH-1%-1ML-6.lcd
Sample Name	:	J0K-1744--ODH-1%-1ML-6
Sample ID	:	J0K-1744--ODH-1%-1ML-6
Method File	:	J0K-1%-80min-1ml.lcm

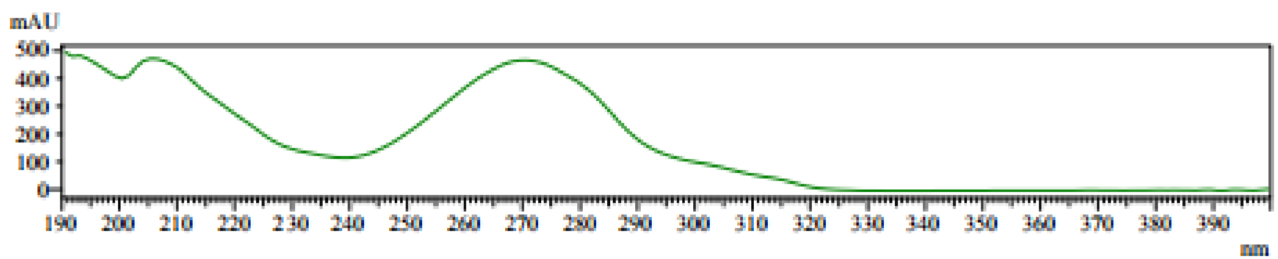
Chromatogram



UV Spectrum
Retention time = 18.068



Retention time = 19.958



Peak Table

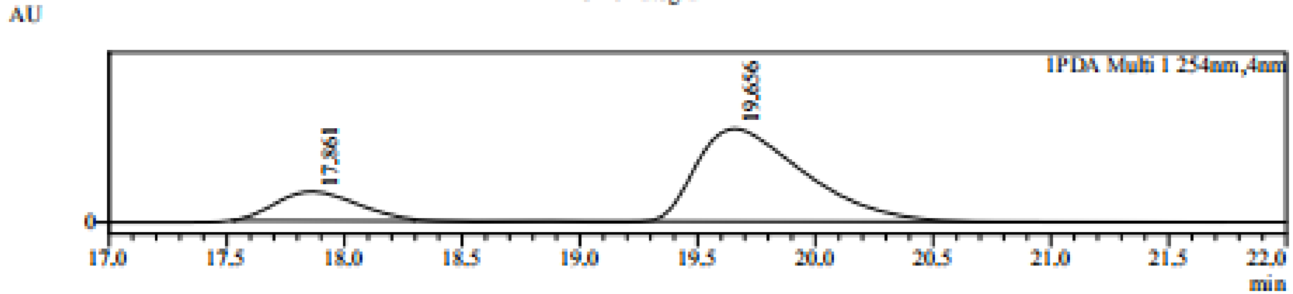
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.068	6523672	50.069
2	19.958	6505606	49.931
Total		13029278	100.000

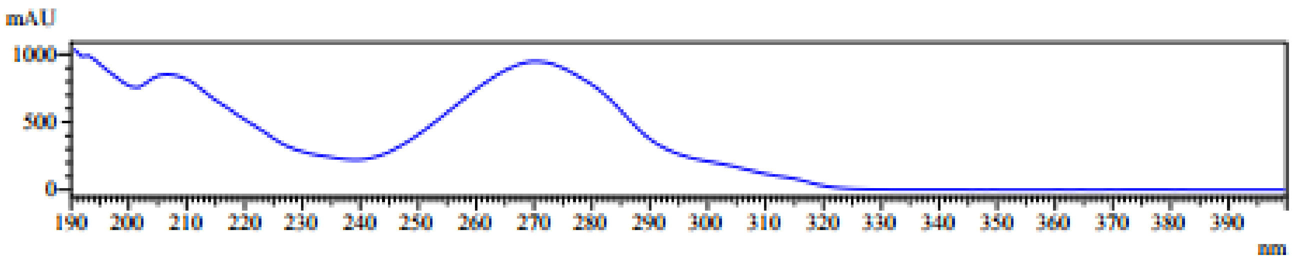
Sample Information

Data File : J0K-1743--ODH-1%-1ML-6.lcd
Sample Name : J0K-1743--ODH-1%-1ML-6
Sample ID : J0K-1743--ODH-1%-1ML-6
Method File : J0K-1%-80min-1mL.lcm

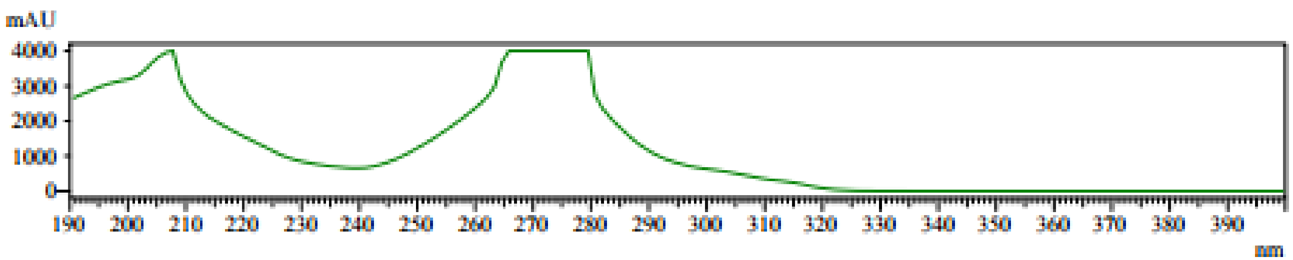
Chromatogram



UV Spectrum
Retention time = 17.861



Retention time = 19.656

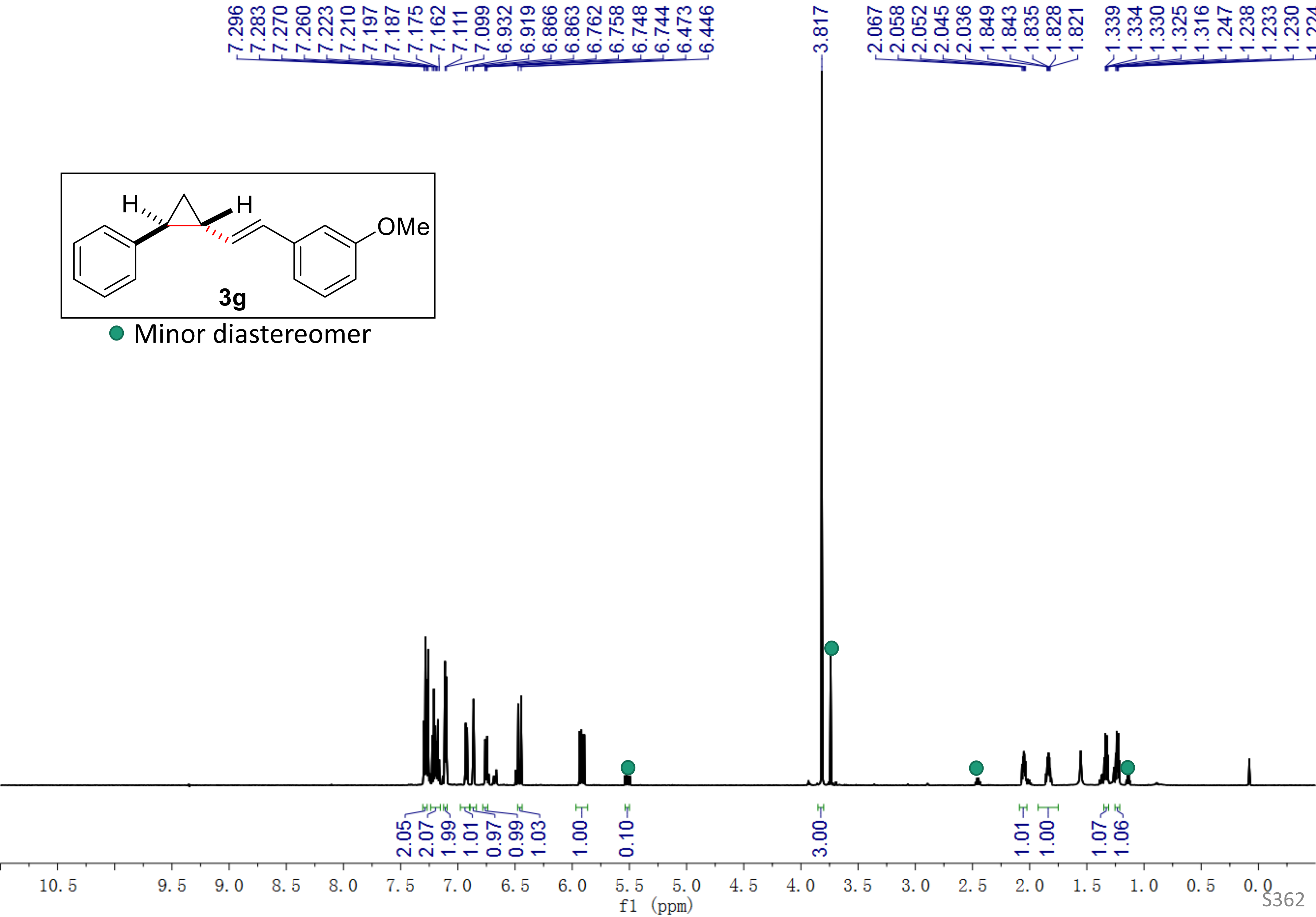


Peak Table

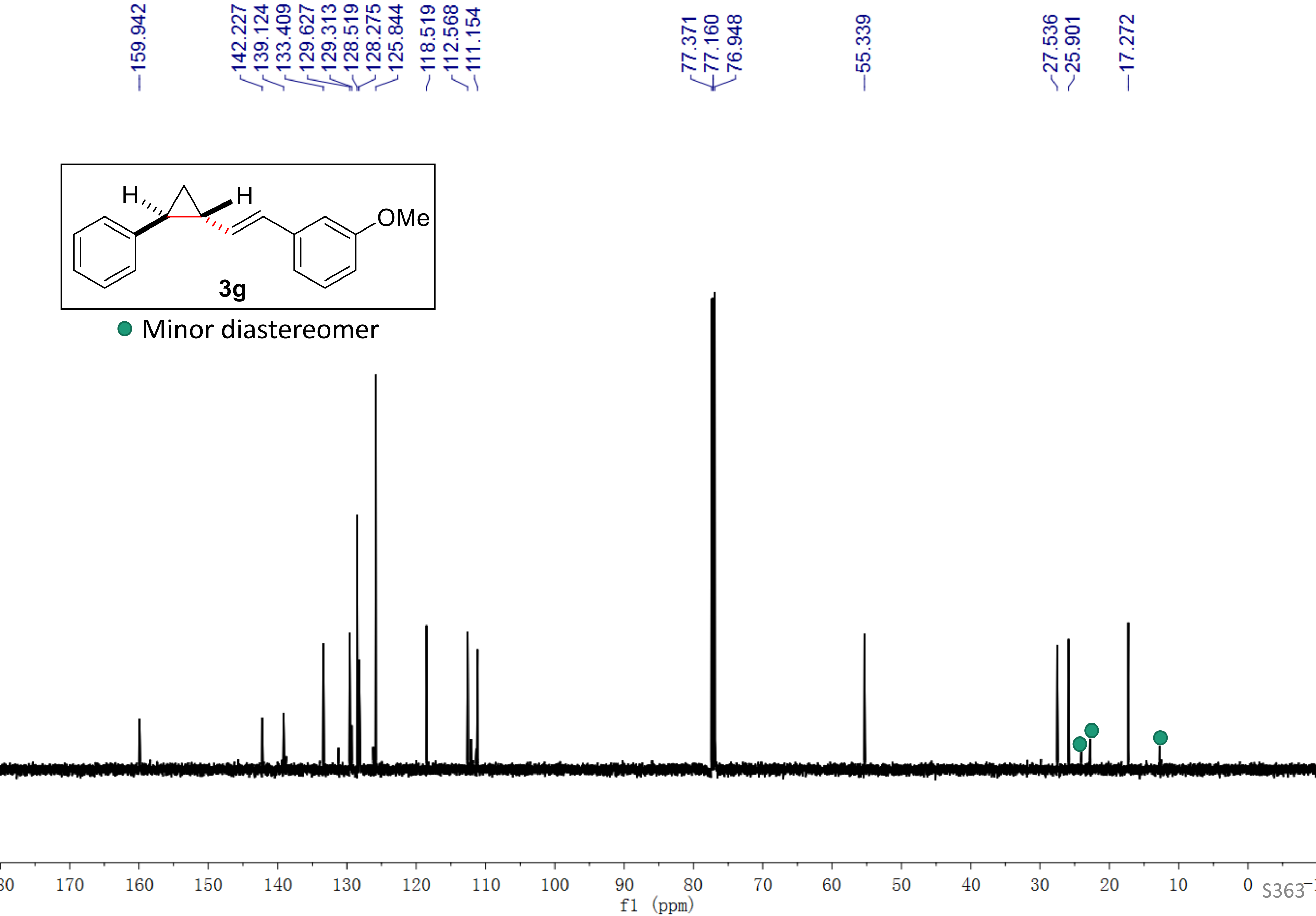
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.861	12306988	19.448
2	19.656	50973076	80.552
Total		63280064	100.000

[1]H NMR of **3g**, 500 MHz, $CDCl_3$



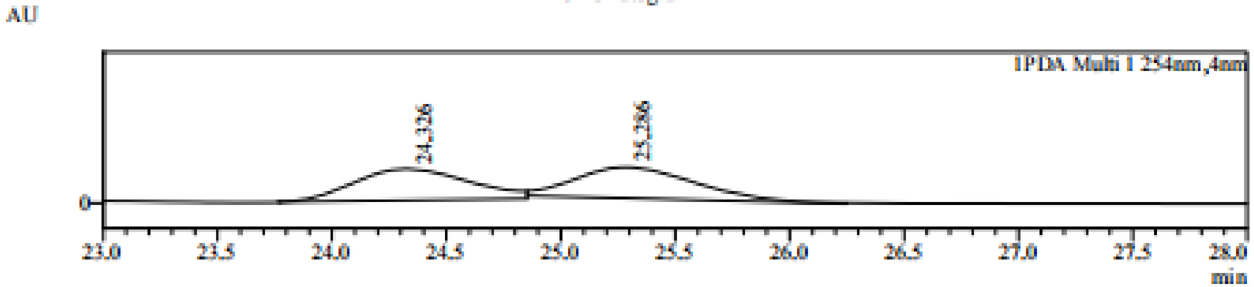
^{13}C NMR of **3g**, 126 MHz, $CDCl_3$



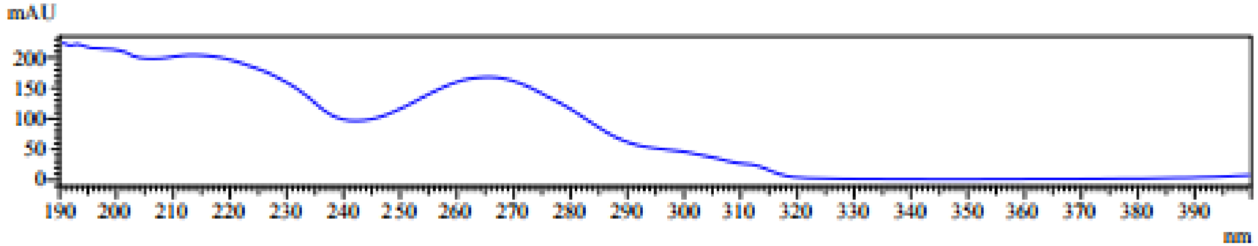
Sample Information

Data File	: J0K-1730--ODH-1%-1ML-2.lcd
Sample Name	: J0K-1730--ODH-1%-1ML-2
Sample ID	: J0K-1730--ODH-1%-1ML-2
Method File	: J0K-1%-80min-1ml.lcm

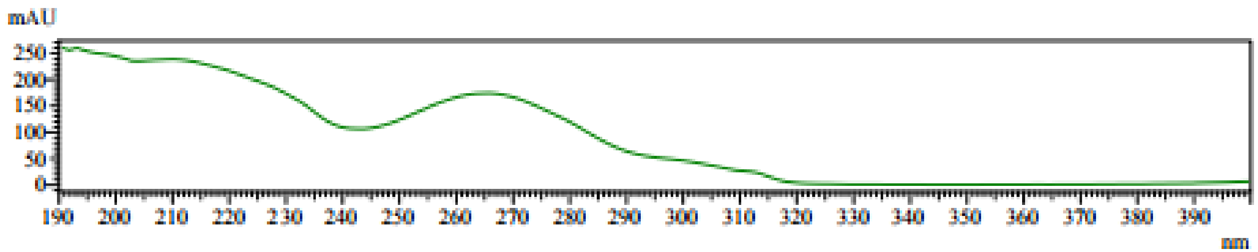
Chromatogram



UV Spectrum
Retention time = 24.326



l
Retention time = 25.286



Peak Table

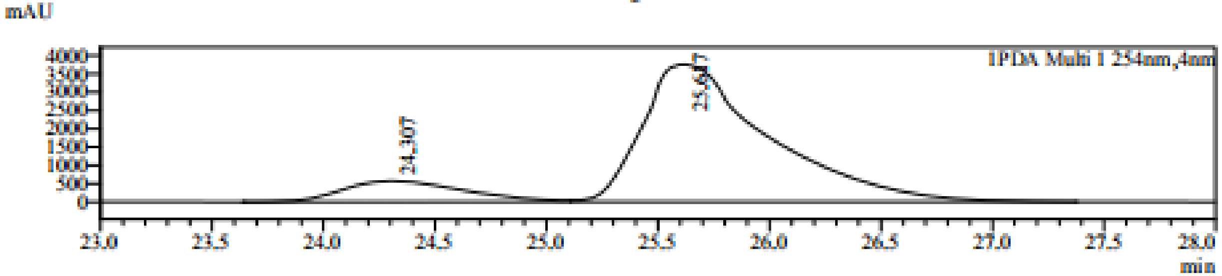
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.326	4385036	49.279
2	25.286	4513420	50.721
Total		8898456	100.000

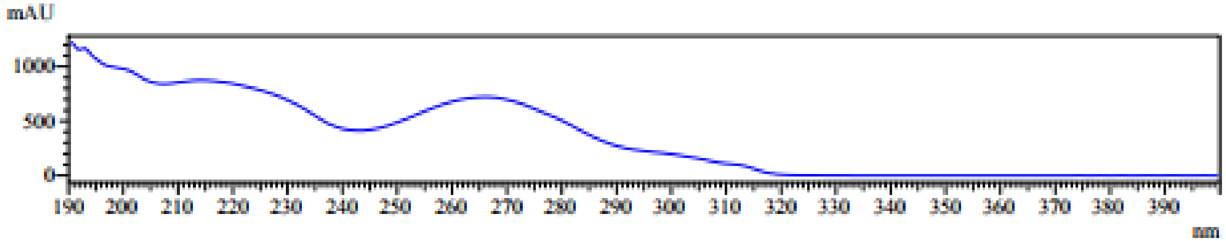
Sample Information

Data File : J0K-1729--ODH-1%-1ML-2.lcd
Sample Name : J0K-1729--ODH-1%-1ML-2
Sample ID : J0K-1729--ODH-1%-1ML-2
Method File : J0K-1%-80min-1ml.lcm

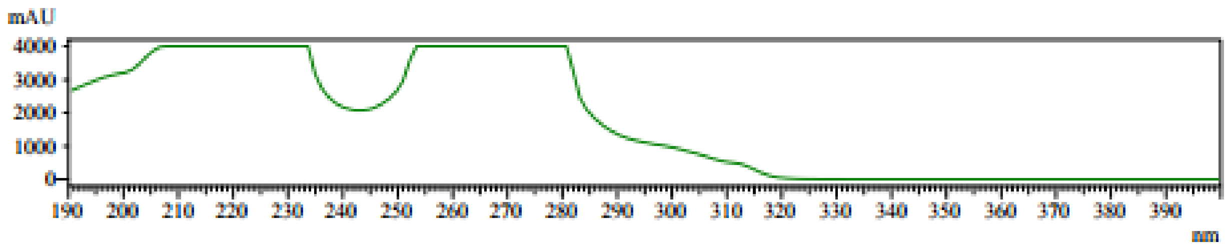
Chromatogram



UV Spectrum
Retention time = 24.307



Retention time = 25.617

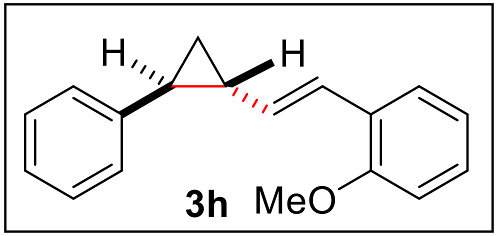


Peak Table

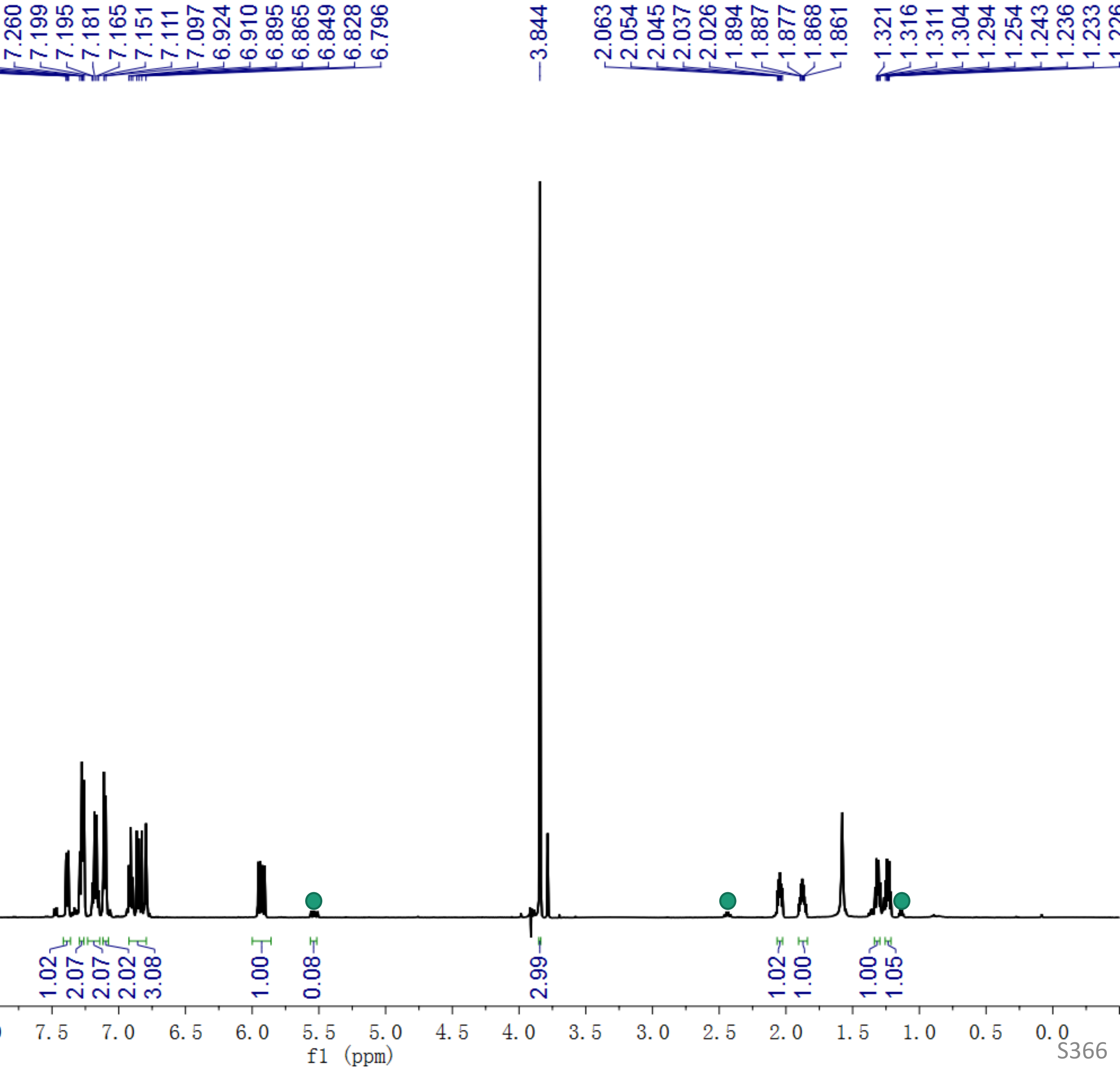
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	24.307	21404545	12.669
2	25.617	147551060	87.331
Total		168955604	100.000

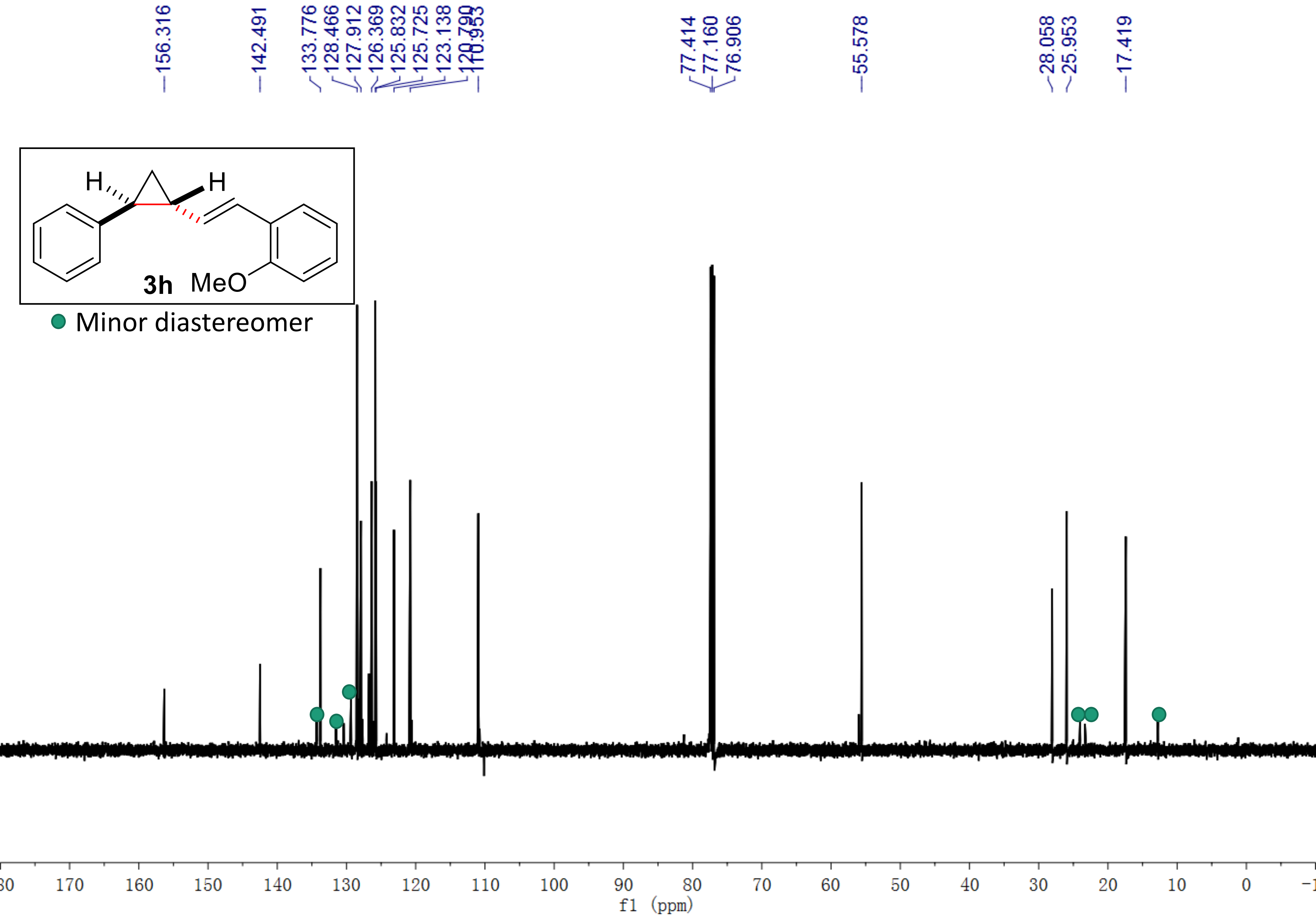
[1]H NMR of **3h**, 500 MHz, $CDCl_3$



● Minor diastereomer



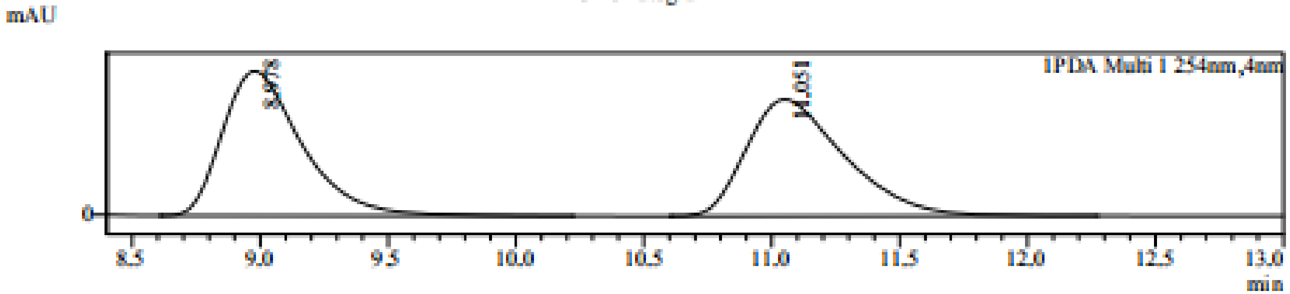
^{13}C NMR of **3h**, 126 MHz, $CDCl_3$



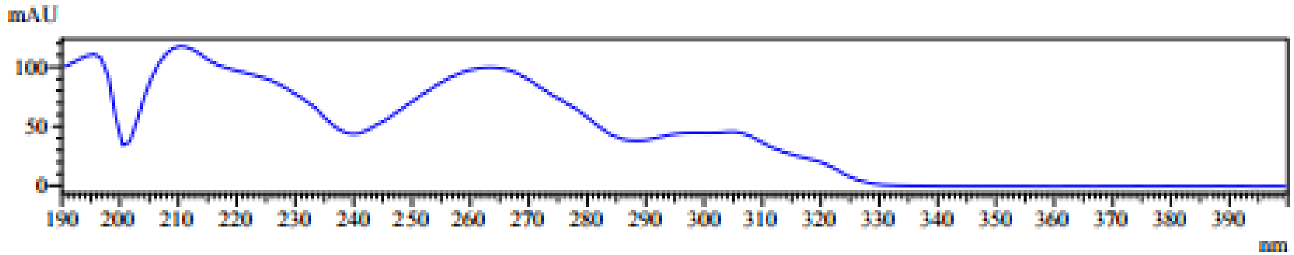
Sample Information

Data File : J0K-1691--ADH-0.2%-1ML.lcd
Sample Name : J0K-1691--ADH-0.2%-1ML
Sample ID : J0K-1691--ADH-0.2%-1ML
Method File : J0K-0.2%--40min-1ml.lcm

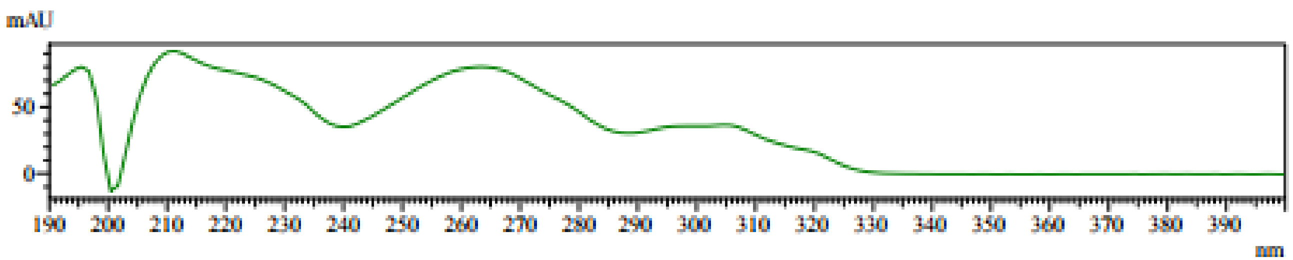
Chromatogram



UV Spectrum
Retention time = 8.978



Retention time = 11.051



Peak Table

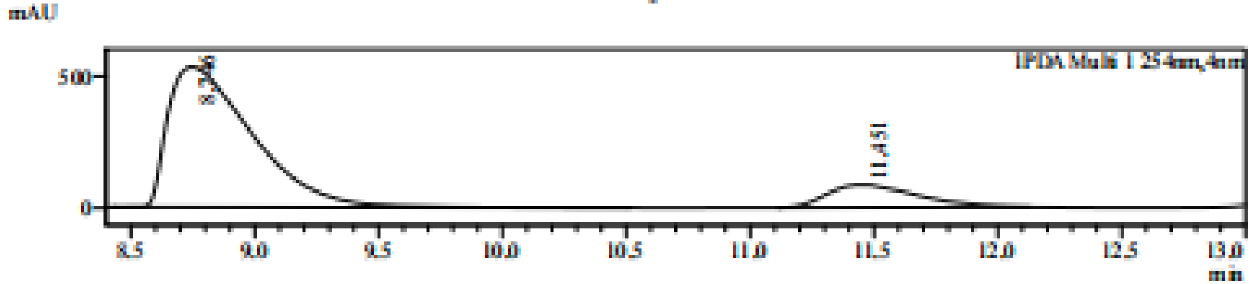
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.978	1810702	50.163
2	11.051	1798900	49.837
Total		3609601	100.000

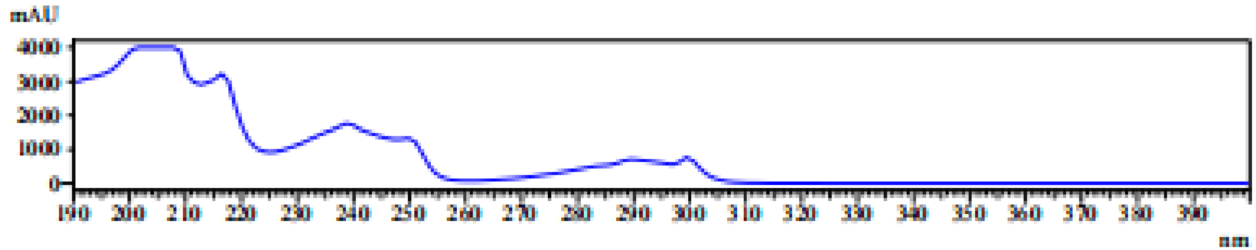
Sample Information

Data File	: J0K-1709-ADH-0.2%-1ML.lcd
Sample Name	: J0K-1709-ADH-0.2%-1 ML
Sample ID	: J0K-1709-ADH-0.2%-1 ML
Method File	: J0K-0.2%--40min-1ml.lcm

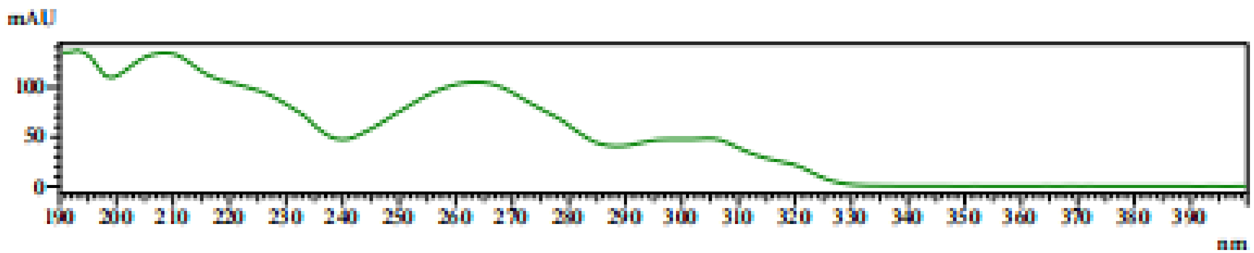
Chromatogram



UV Spectrum
Retention time = 8.746



I
Retention time = 11.451

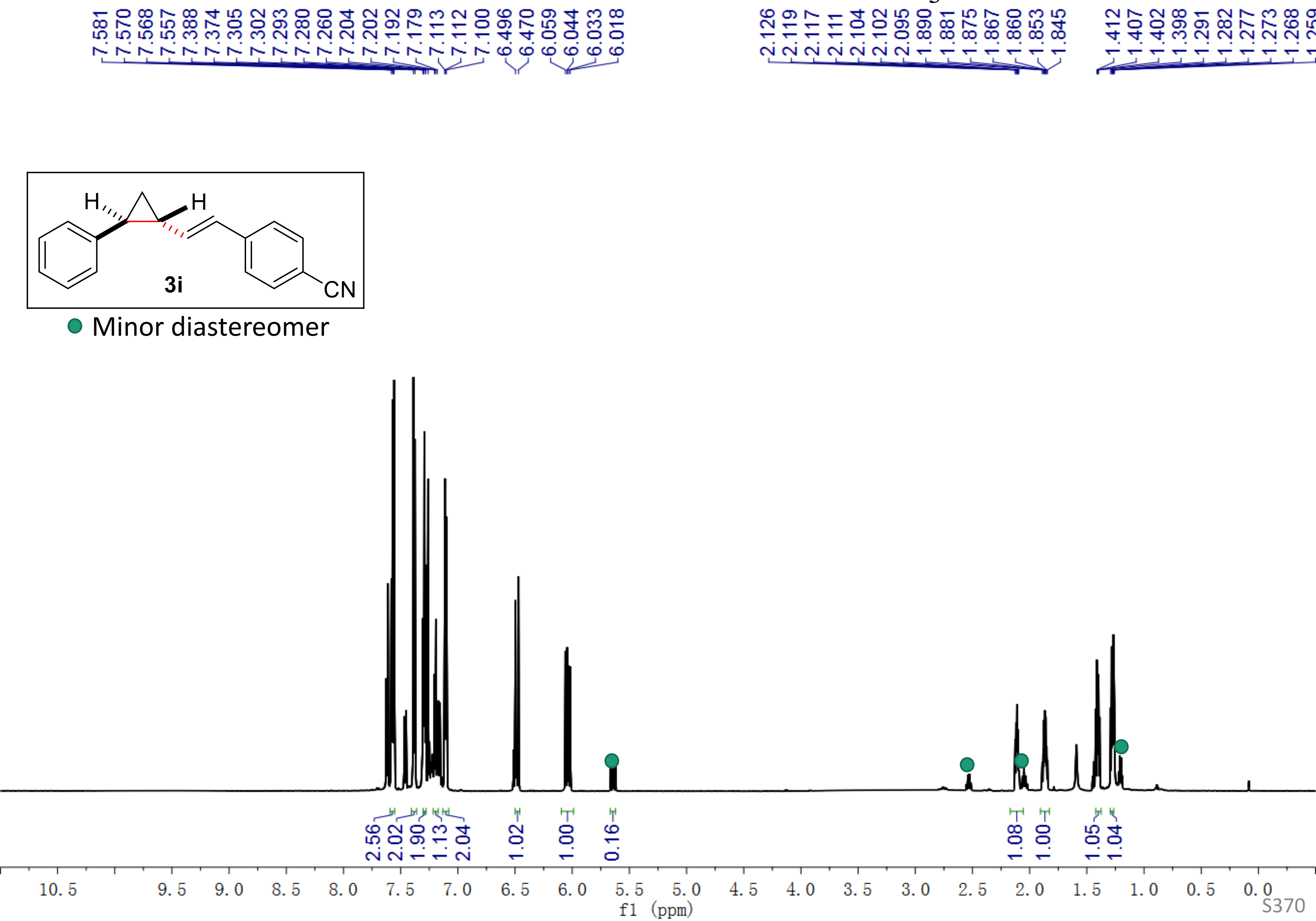


Peak Table

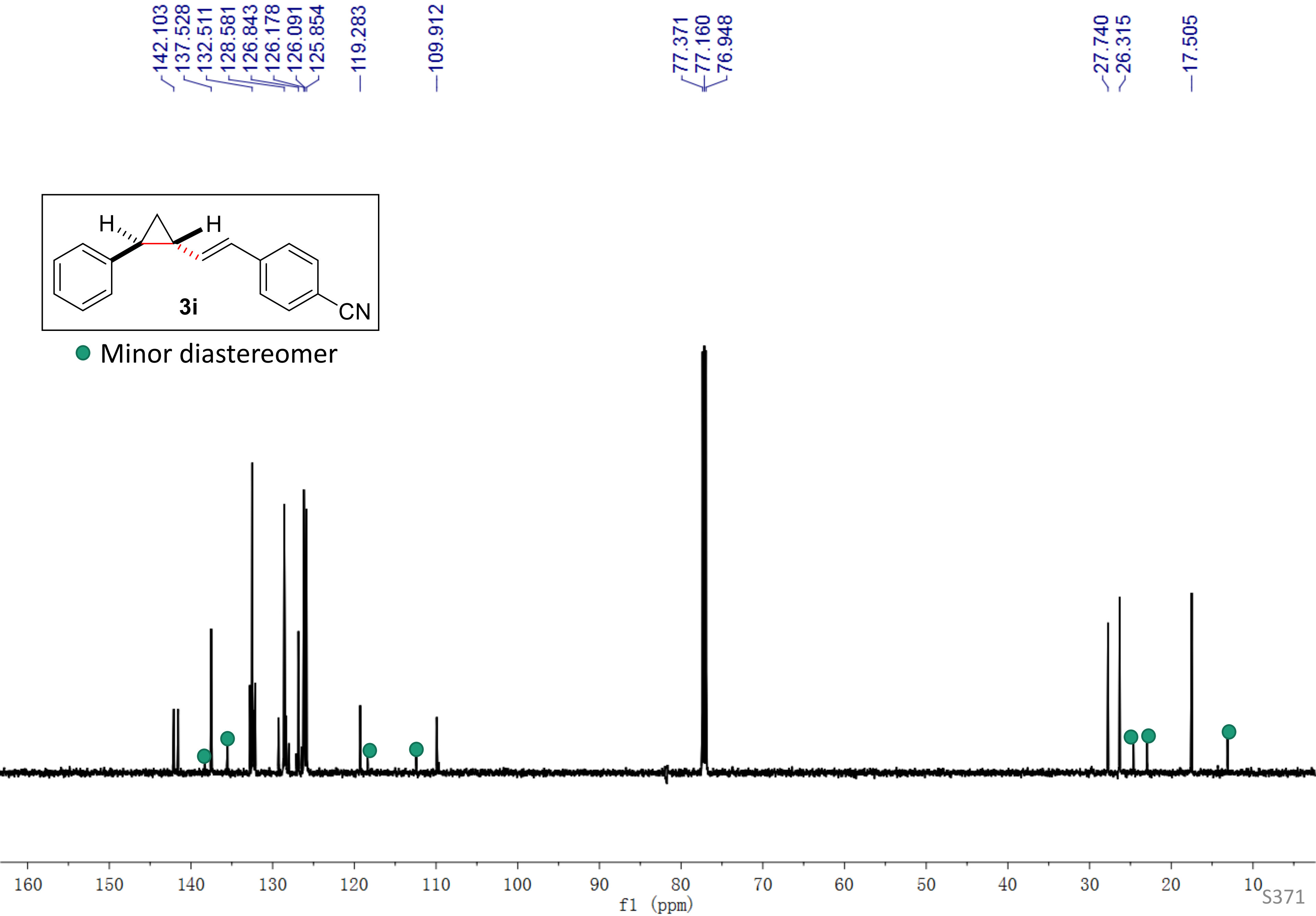
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.746	12544347	85.436
2	11.451	2138396	14.564
Total		14682744	100.000

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



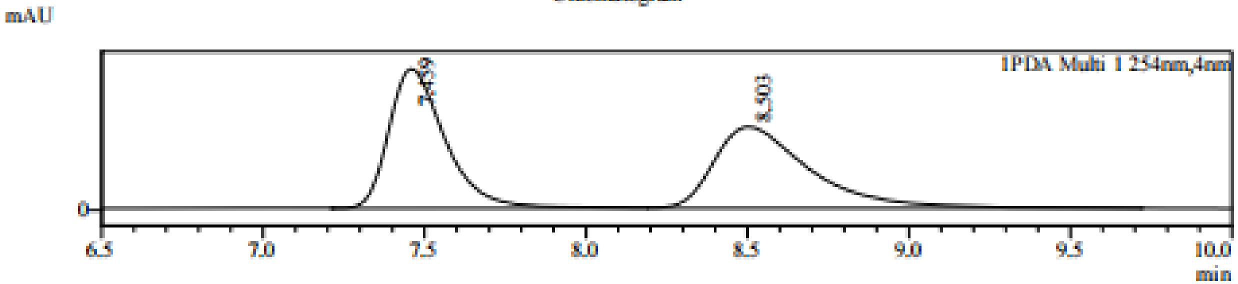
^{13}C NMR of **3i**, 126 MHz, $CDCl_3$



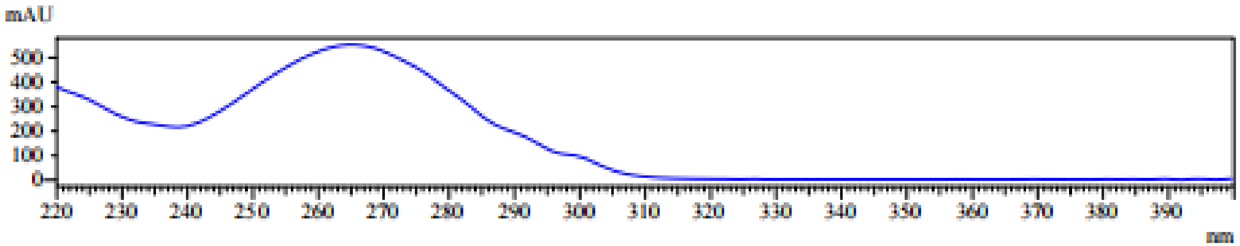
Sample Information

Data File : J0K-1854--IE-1%-1ML-3.lcd
Sample Name : J0K-1854--IE-1%-1ML-3
Sample ID : J0K-1854--IE-1%-1ML-3
Method File : J0K--1%--35min-1ml.lcm

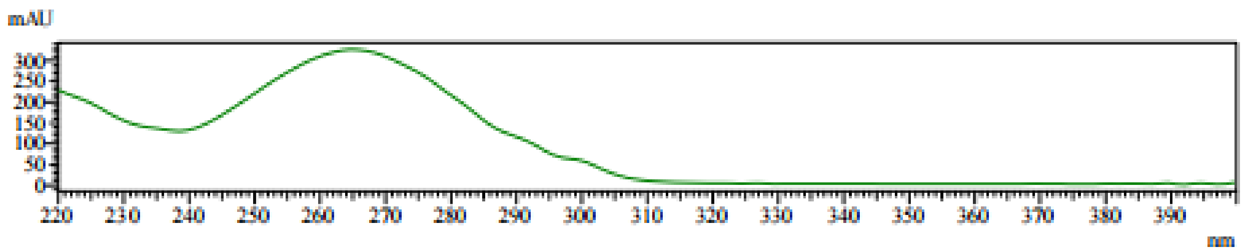
Chromatogram



UV Spectrum
Retention time = 7.459



UV Spectrum
Retention time = 8.503



Peak Table

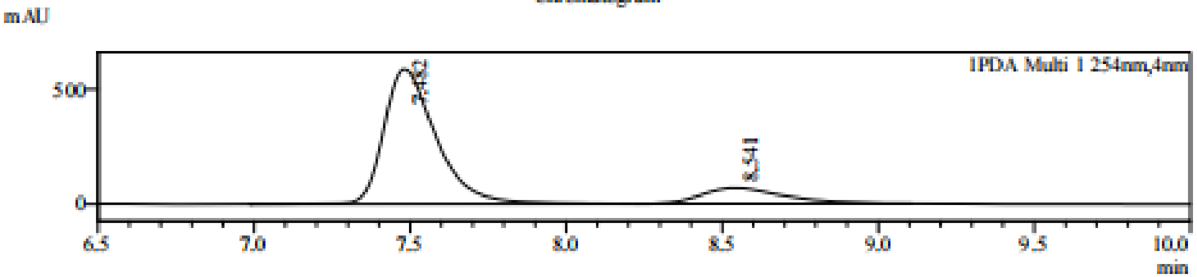
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.459	5326348	50.222
2	8.503	5279257	49.778
Total		10605605	100.000

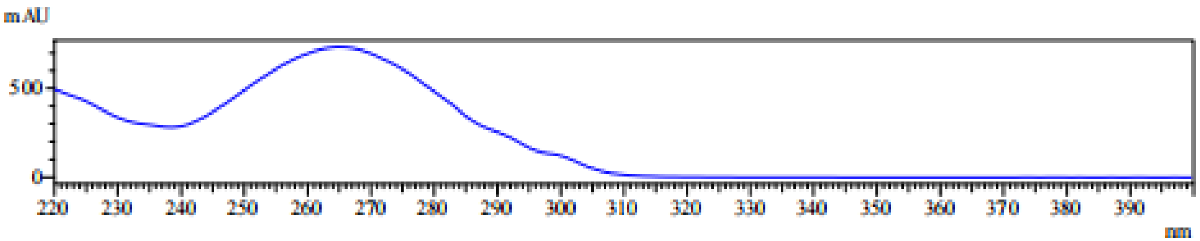
Sample Information

Data File : J0K-1831--IE-1%-1ML-3.lcd
Sample Name : J0K-1831--IE-1%-1ML-3
Sample ID : J0K-1831--IE-1%-1ML-3
Method File : J0K--1%--35min-1ml.lcm

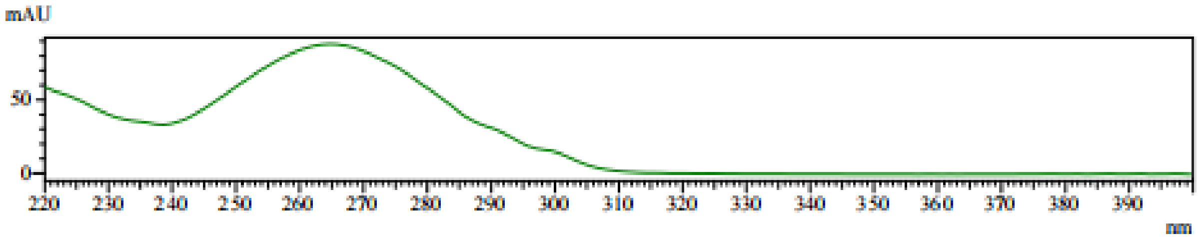
Chromatogram



UV Spectrum
Retention time = 7.482



UV Spectrum
Retention time = 8.541

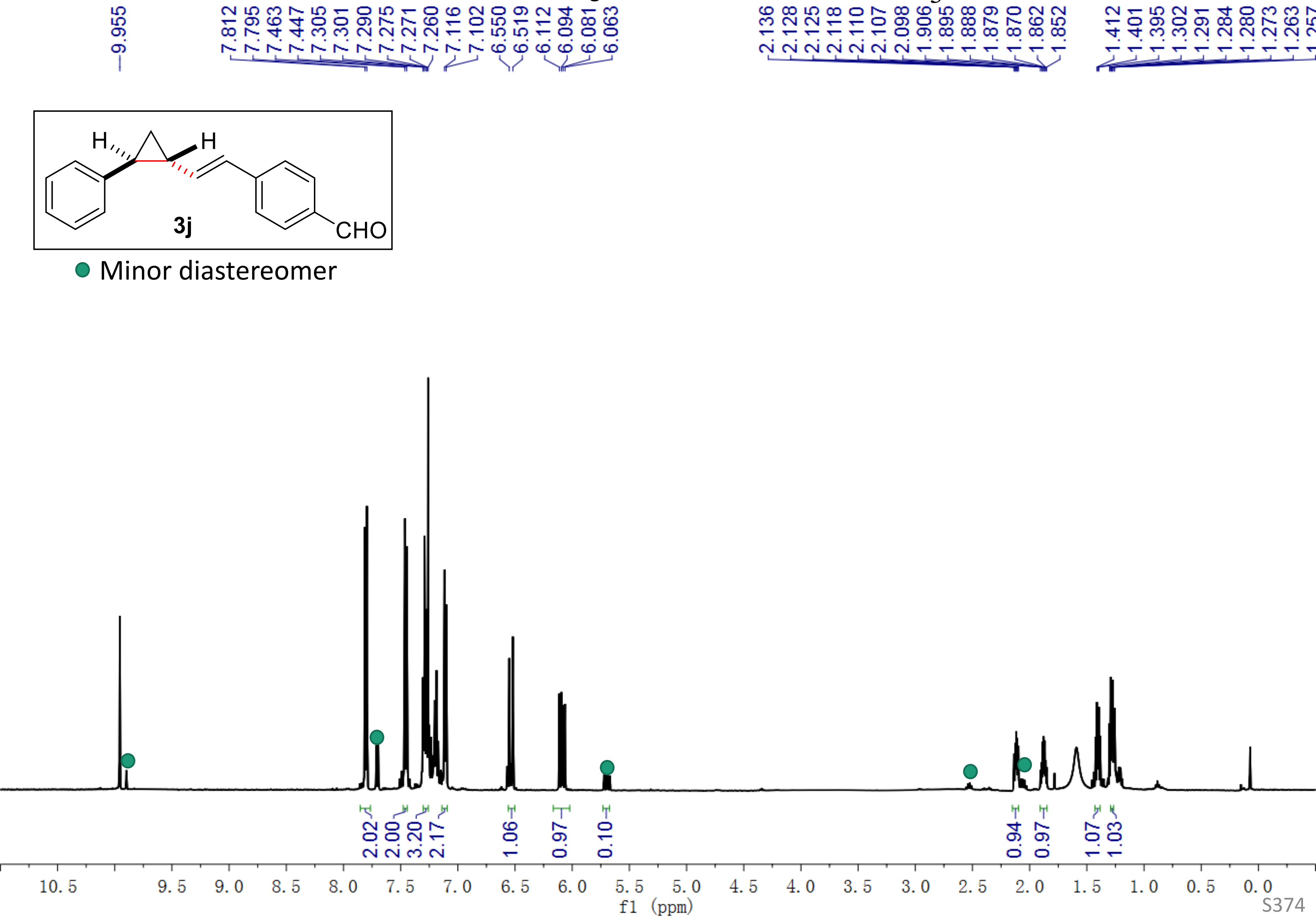


Peak Table

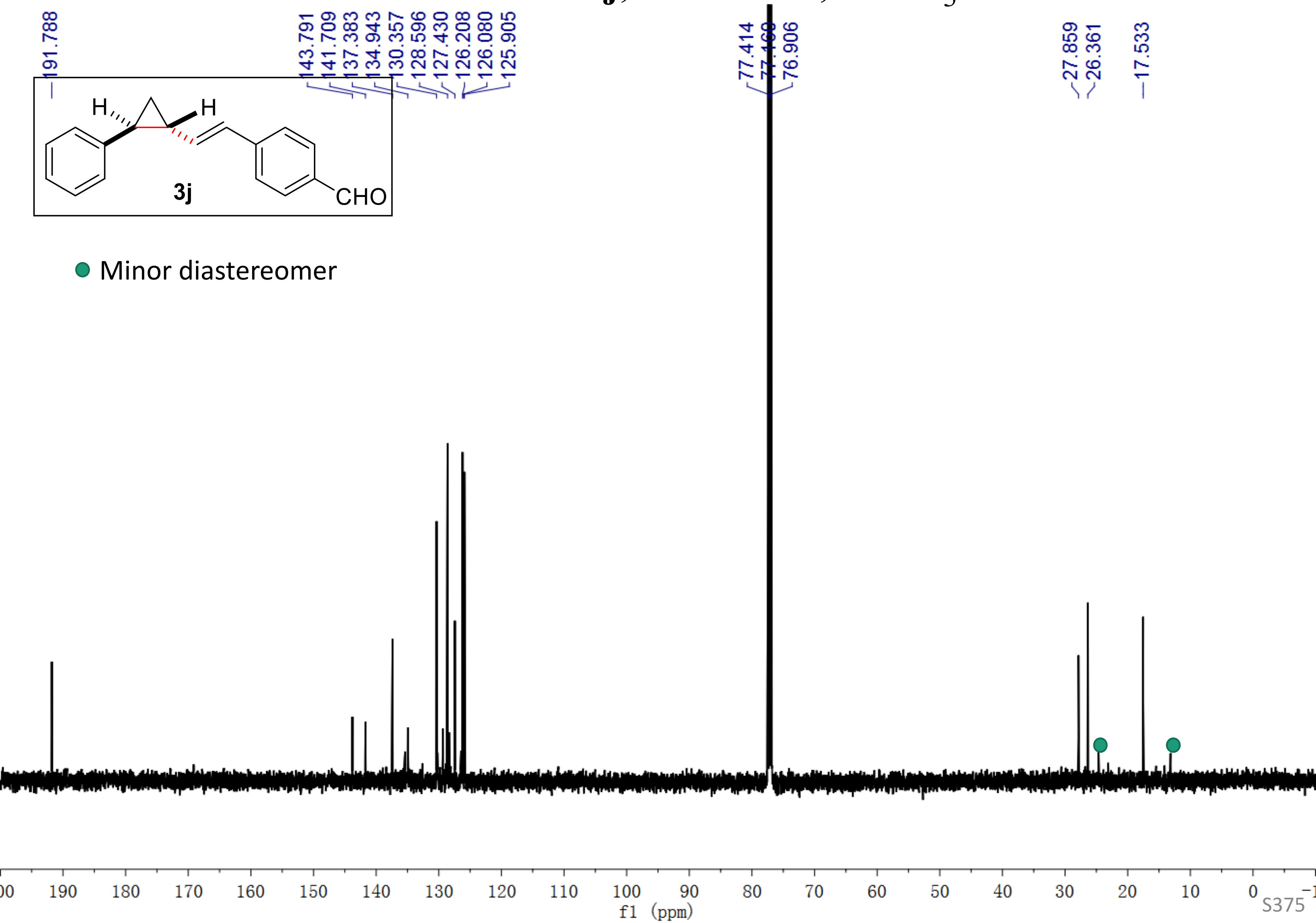
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.482	6829141	84.434
2	8.541	1259004	15.566
Total		8088146	100.000

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

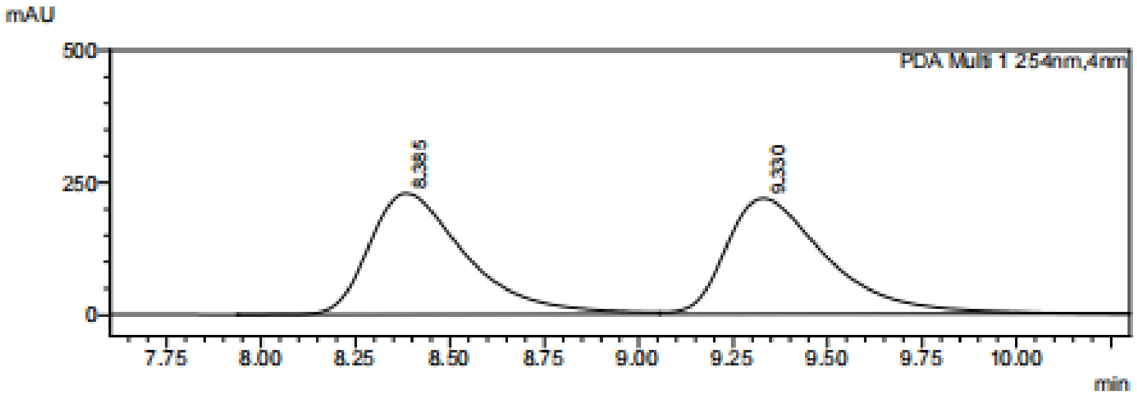


^{13}C NMR of **3j**, 126 MHz, $CDCl_3$



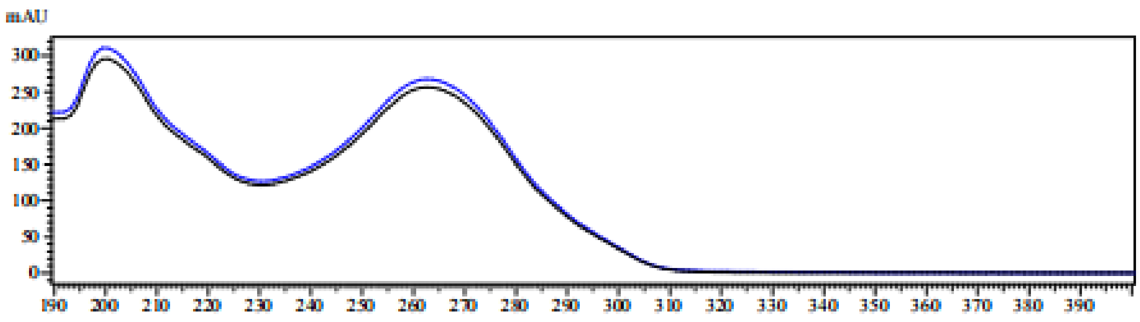
==== Shimadzu LabSolutions Analysis Report ====

JK-1787-ID-2%-0.8mL
JK-0.2%-30min0.8mL.lcm



UV Spectrum

JK-1787-ID-2%-0.8mL_001.lcd



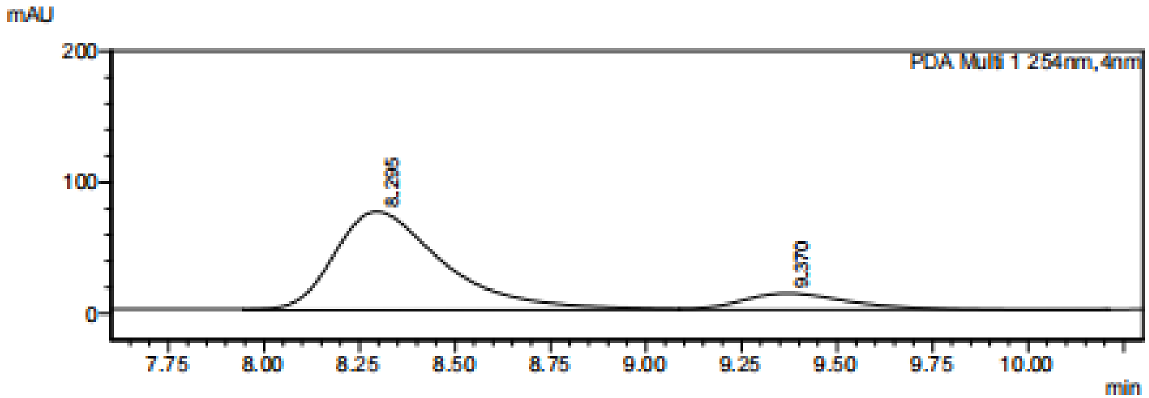
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.385	50.066
2	9.330	49.934
Total		100.000

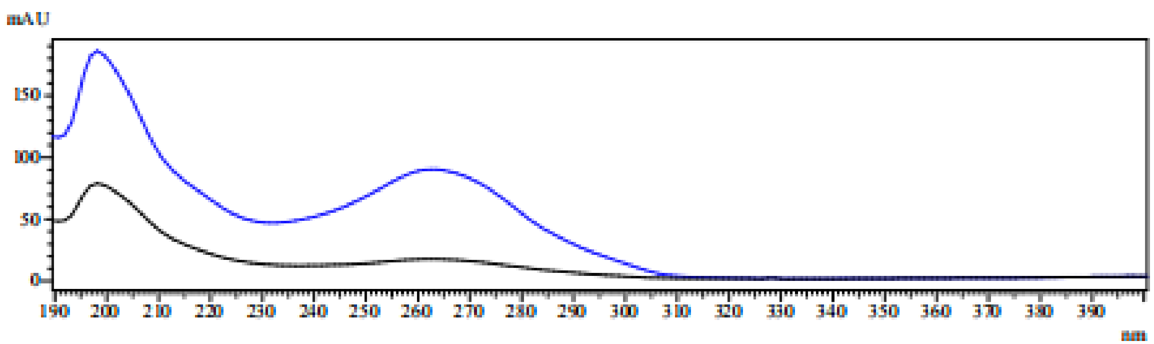
==== Shimadzu LabSolutions Analysis Report ====

JK-1786-ID-2%-0.8mL
JK-0.2%-30min0.8mL.lcm



UV Spectrum

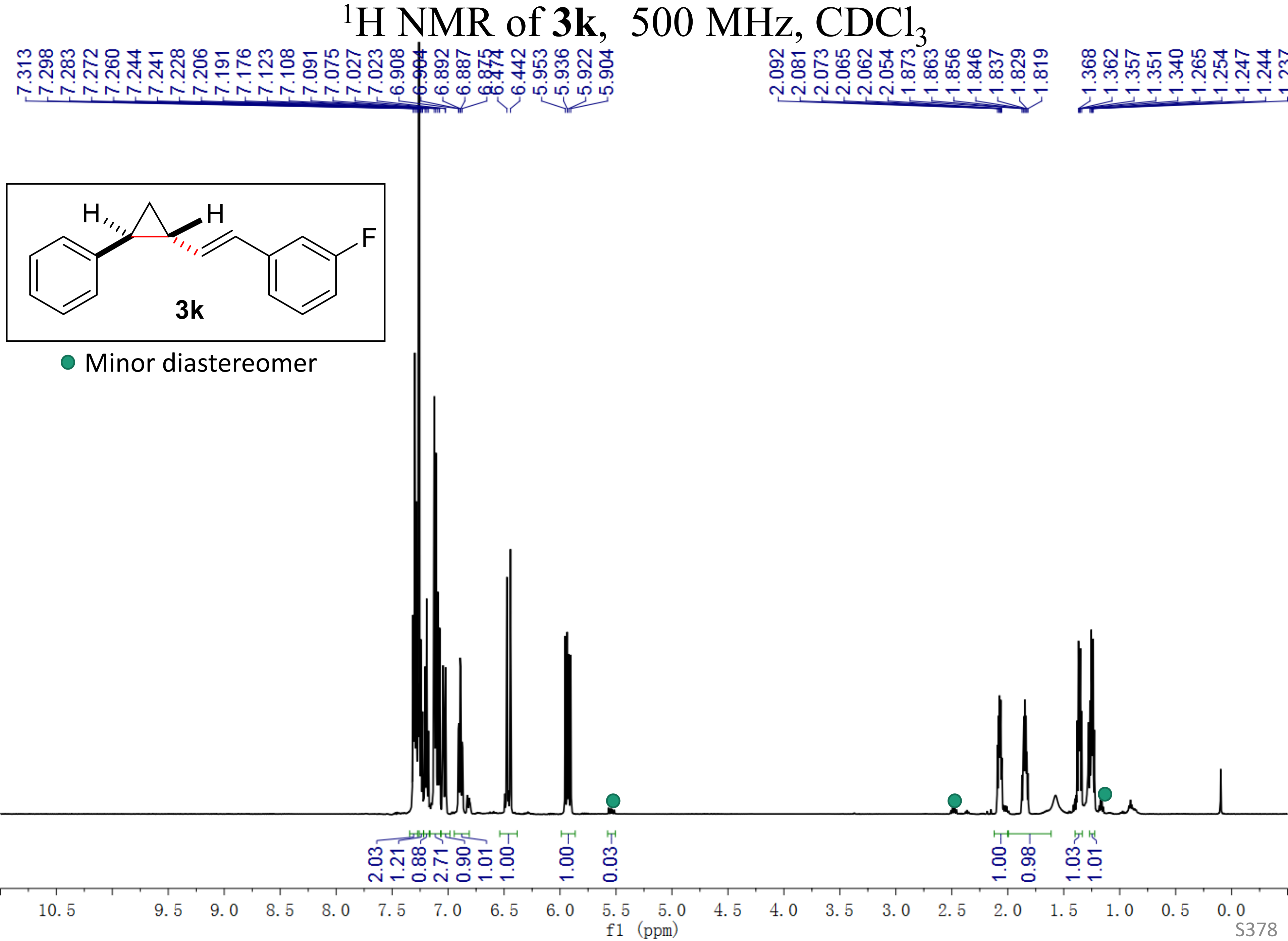
JK-1786-ID-2%-0.8mL_001.lcd



Peak Table

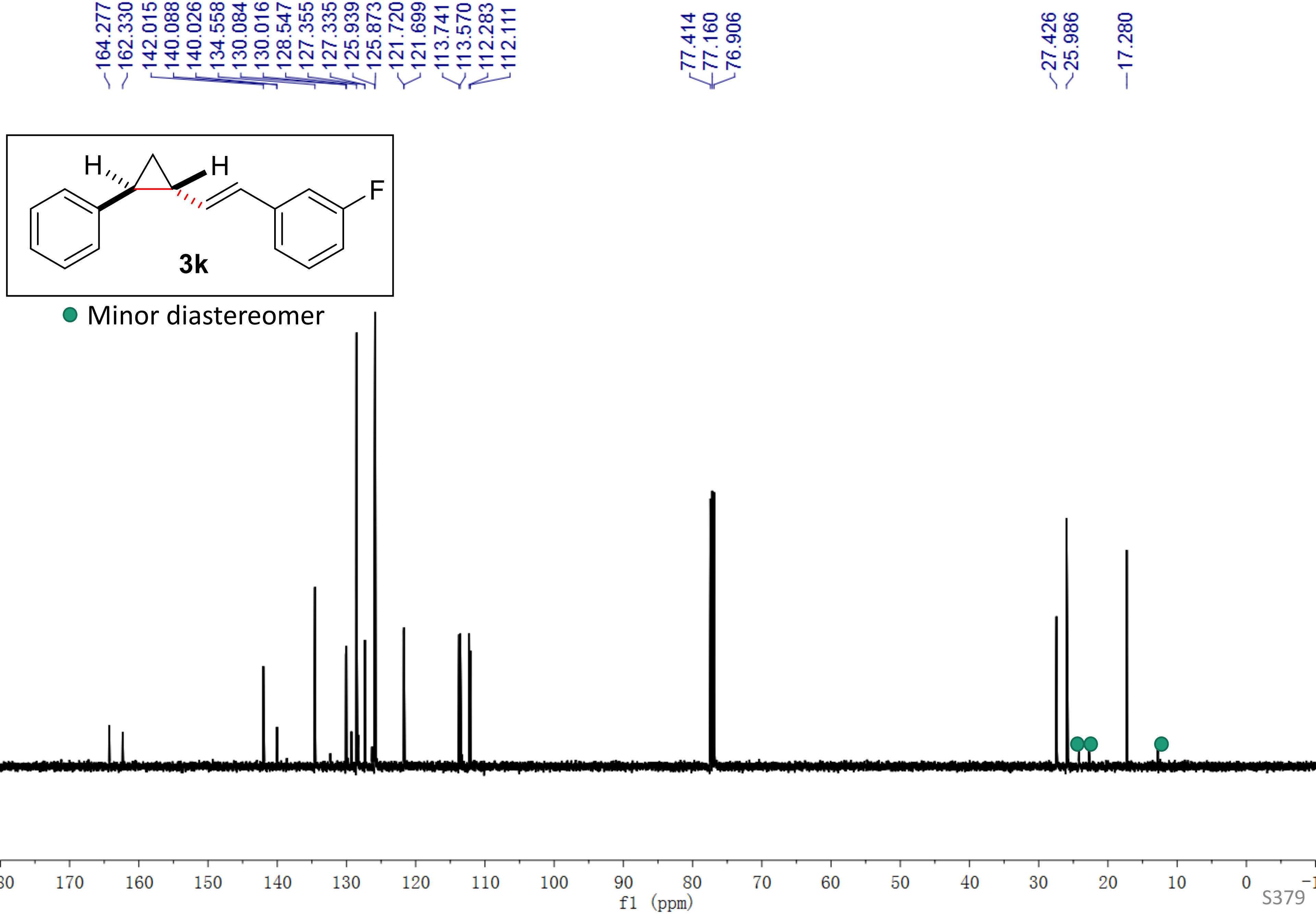
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.295	85.965
2	9.370	14.035
Total		100.000

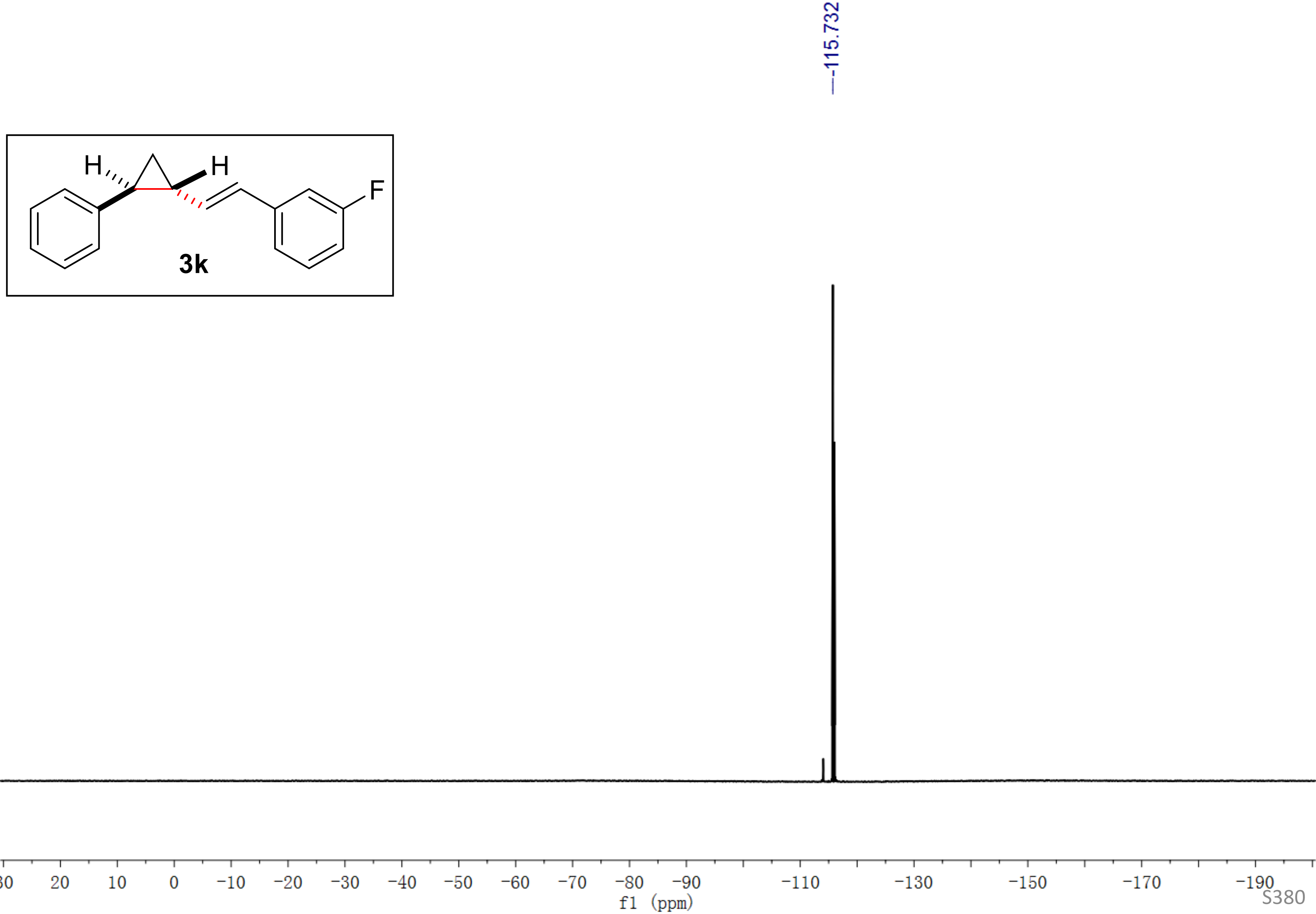


[1]H NMR of 3k, 500 MHz, CDCl3
3k
F
H
H
Minor diastereomer
f1 (ppm)

^{13}C NMR of **3k**, 126 MHz, $CDCl_3$



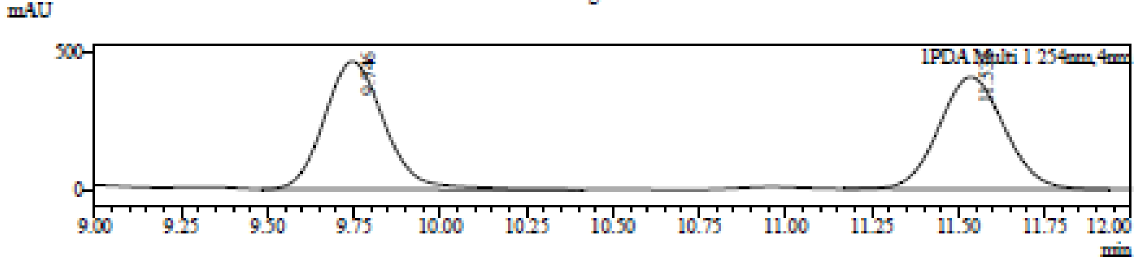
^{19}F NMR of **3k**, 564 MHz, $CDCl_3$



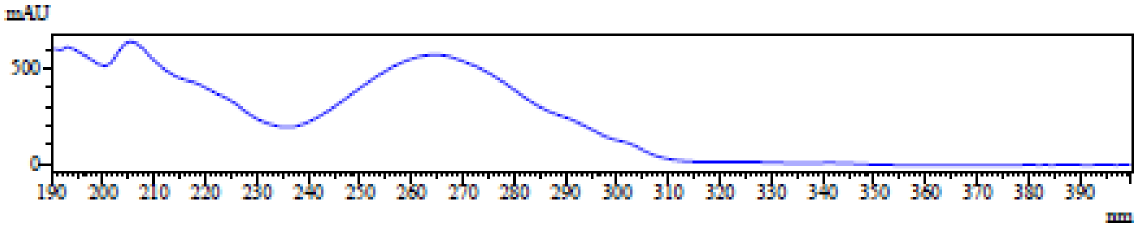
Sample Information

Data File : J0K-0717-3--IA--1%-1ML.lcd
Sample Name : J0K-0717-3--IA--1%-1ML
Sample ID : J0K-0717-3--IA--1%-1ML
Method File : J0K-1%--35min-1ml.lcm

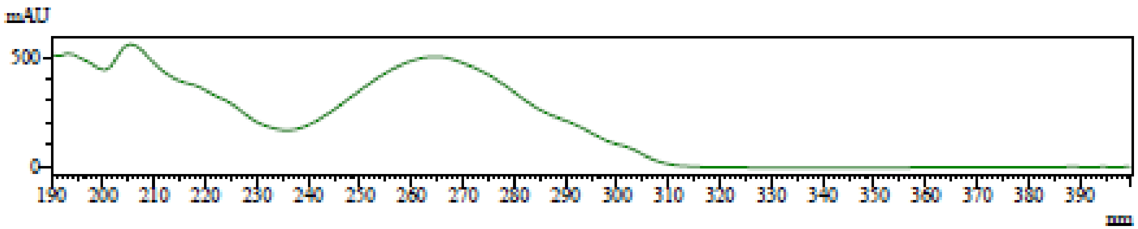
Chromatogram



UV Spectrum
Retention time = 9.746



UV Spectrum
Retention time = 11.536



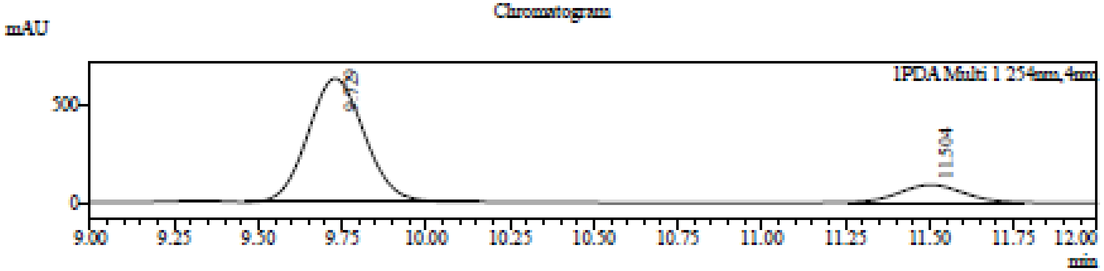
Peak Table

PDA Ch1 254nm

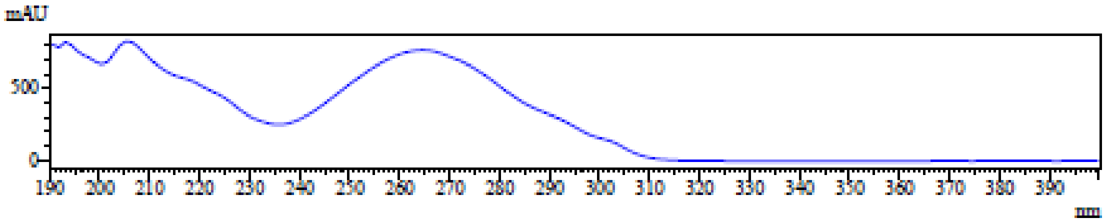
Peak#	Ret. Time	Area	Area%
1	9.746	5668129	51.150
2	11.536	5413242	48.850
Total		11081370	100.000

Sample Information

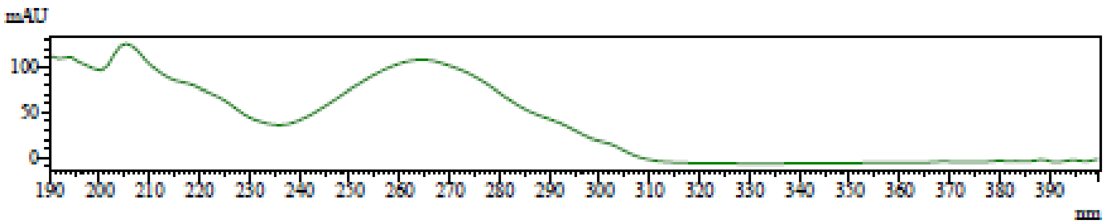
Data File : J0K-0716-3--IA--1%-1ML.lcd
Sample Name : J0K-0716-3--IA--1%-1ML
Sample ID : J0K-0716-3--IA--1%-1ML
Method File : J0K-1%--35min-1ml.lcm



UV Spectrum
Retention time = 9.729



UV Spectrum
Retention time = 11.504

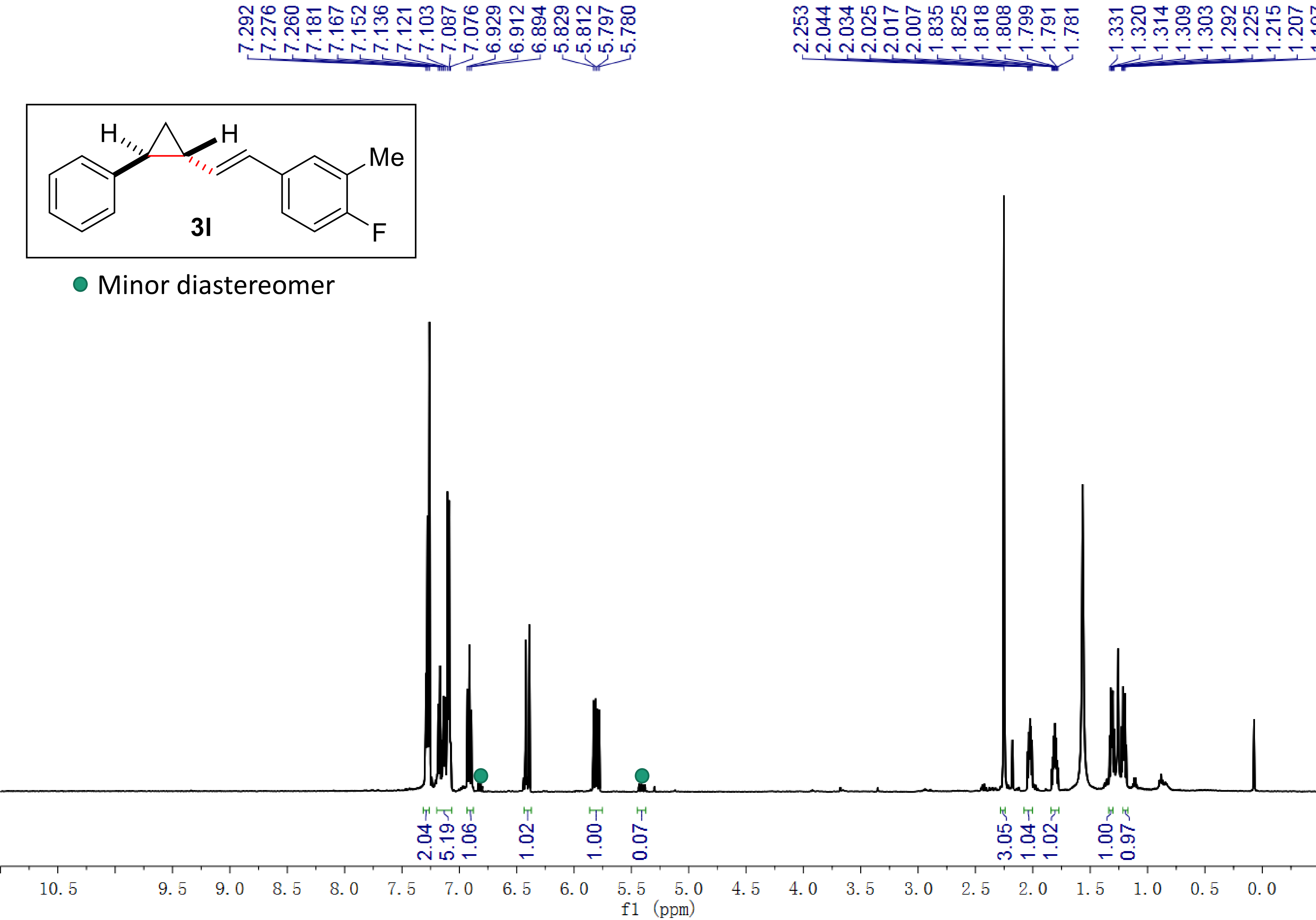


Peak Table

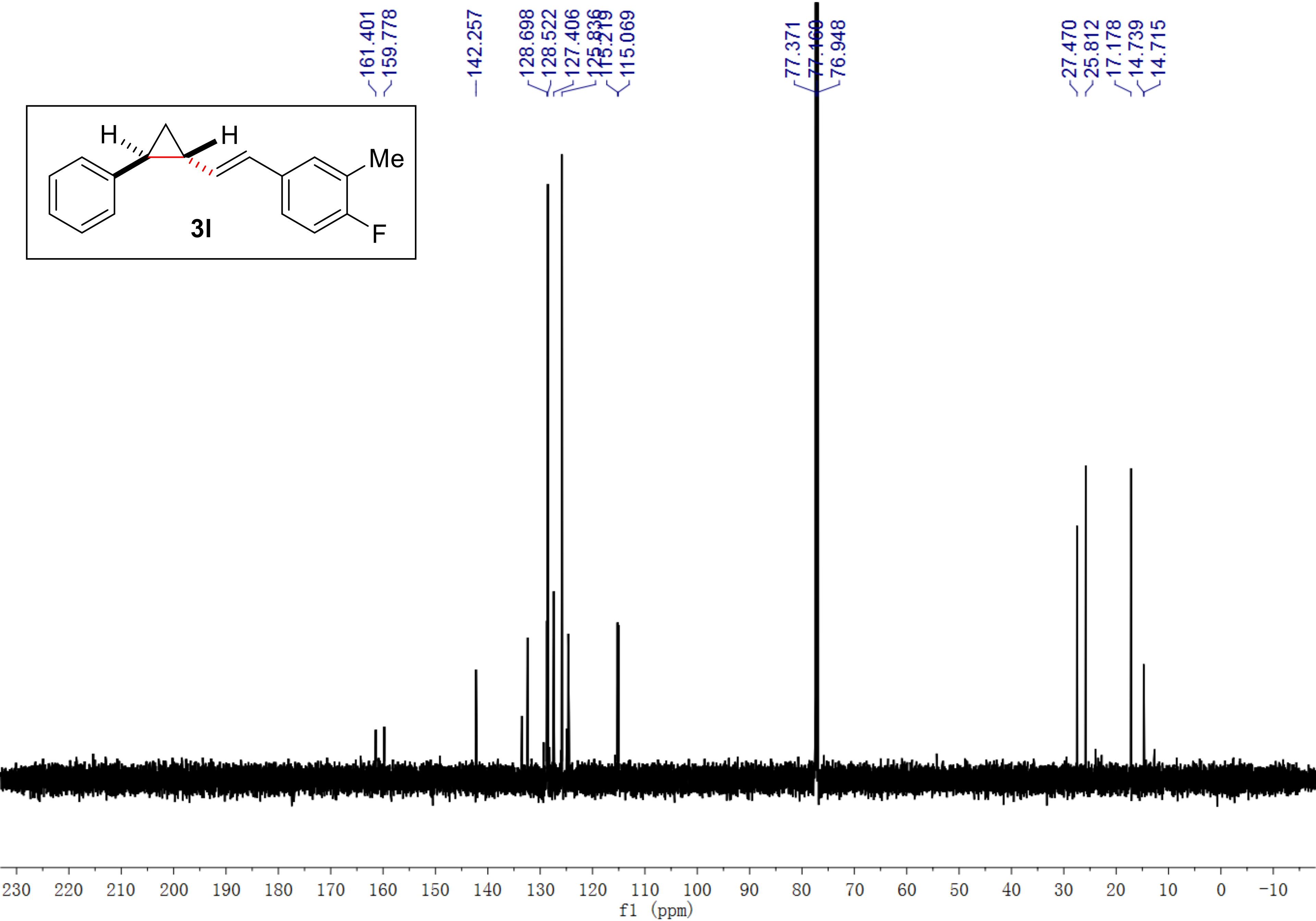
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.729	7329097	86.648
2	11.504	1129411	13.352
Total		8458508	100.000

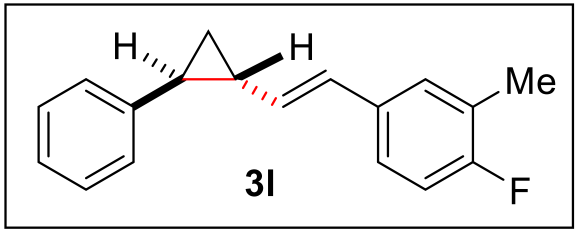
^{1}H NMR of **3l**, 500 MHz, $CDCl_3$

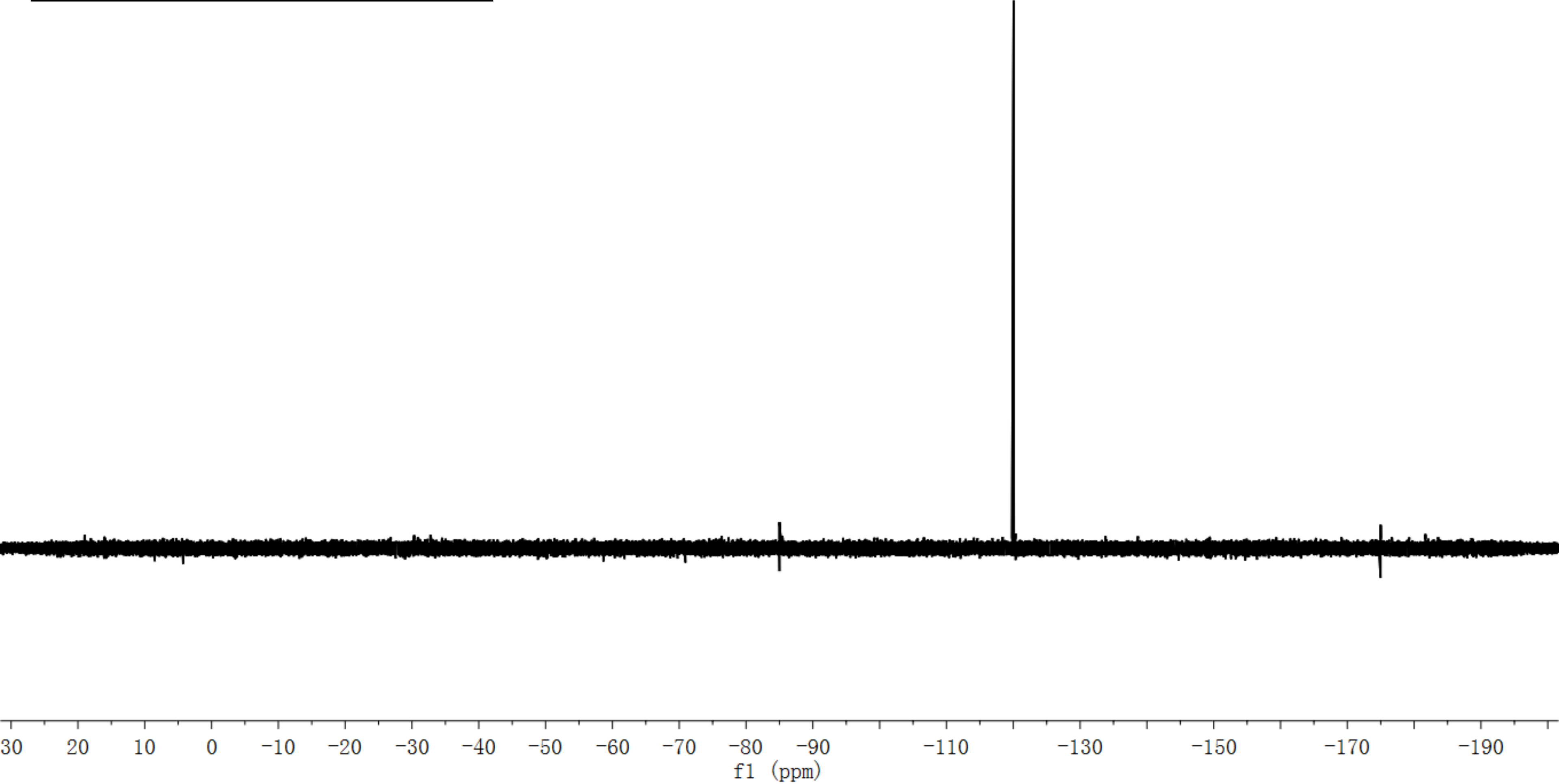


^{13}C NMR of **3l**, 126 MHz, $CDCl_3$



^{19}F NMR of **3l**, 465 MHz, $CDCl_3$

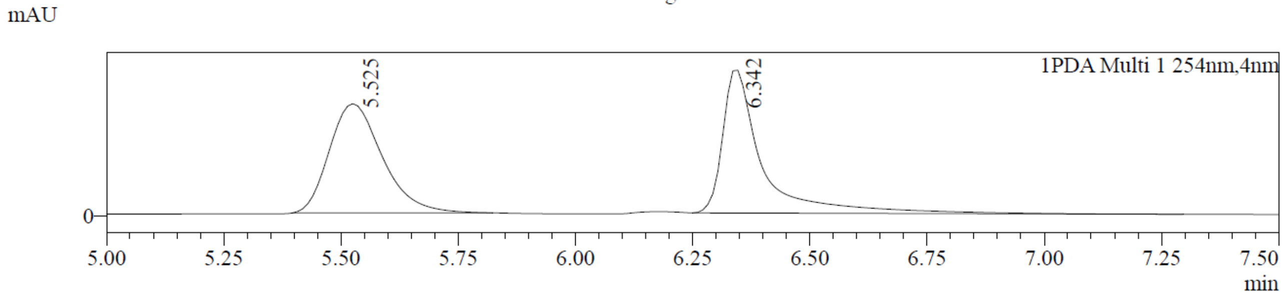




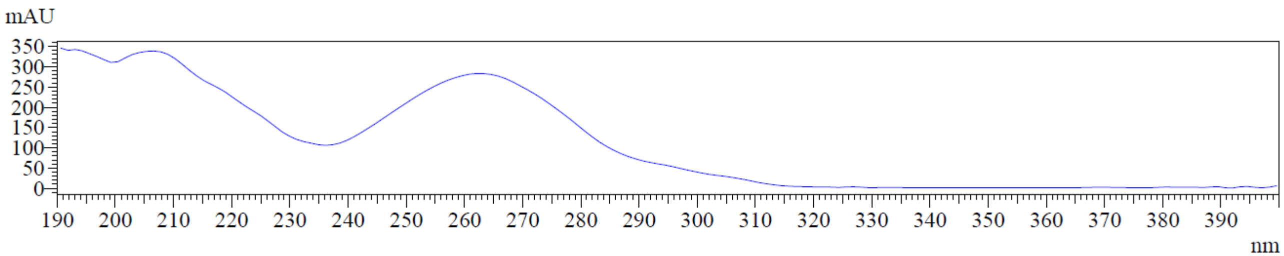
Sample Information

Data File : J0K-1683--ADH-0.5%-1ML.lcd
Sample Name : J0K-1683--ADH-0.5%-1ML
Sample ID : J0K-1683--ADH-0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm

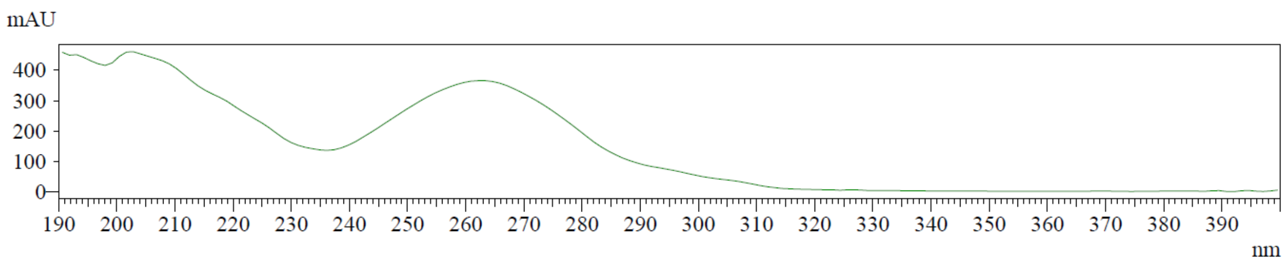
Chromatogram



UV Spectrum
Retention time = 5.525



l
Retention time = 6.342



Peak Table

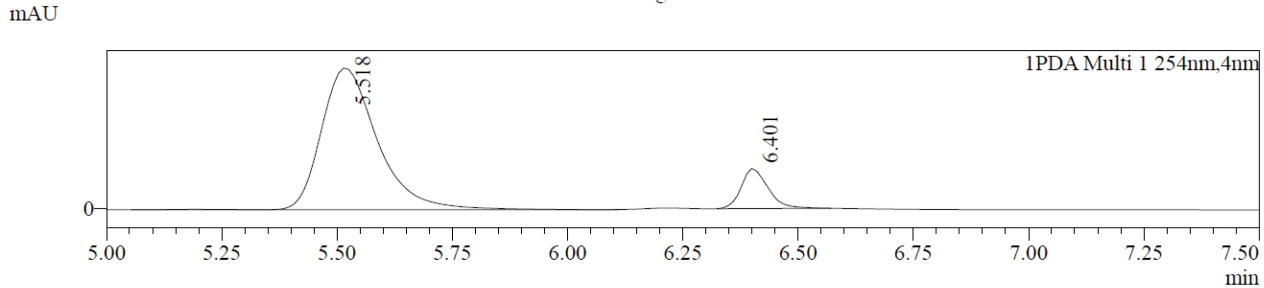
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.525	1863758	50.285
2	6.342	1842657	49.715
Total		3706416	100.000

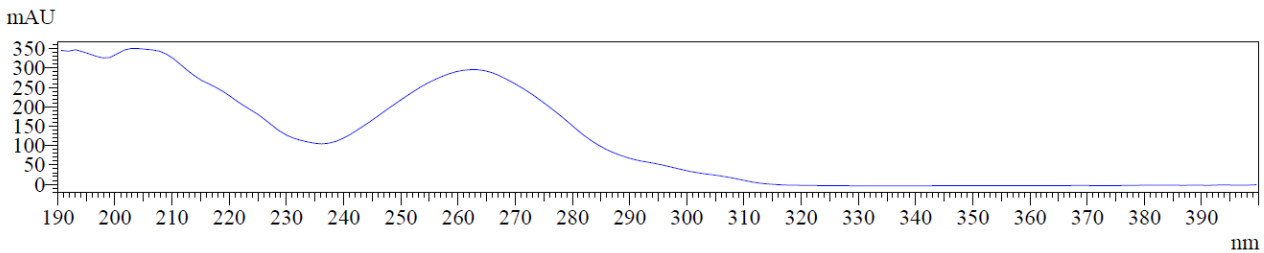
Sample Information

Data File : J0K-1711--ADH-0.5%-1ML.lcd
Sample Name : J0K-1711--ADH-0.5%-1ML
Sample ID : J0K-1711--ADH-0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm

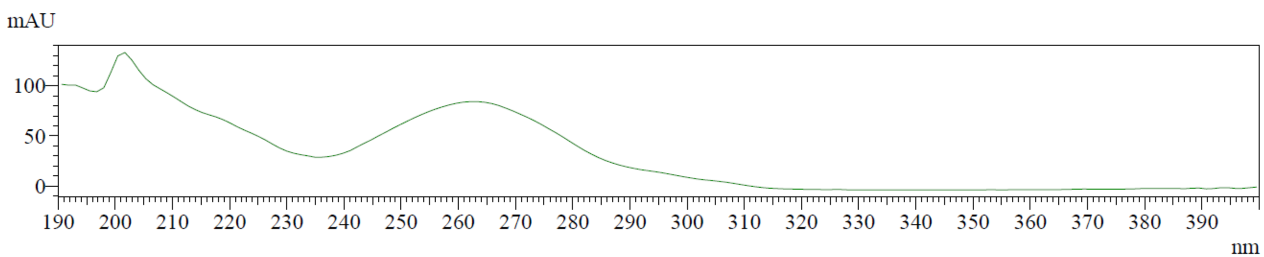
Chromatogram



UV Spectrum
Retention time = 5.518



Retention time = 6.401

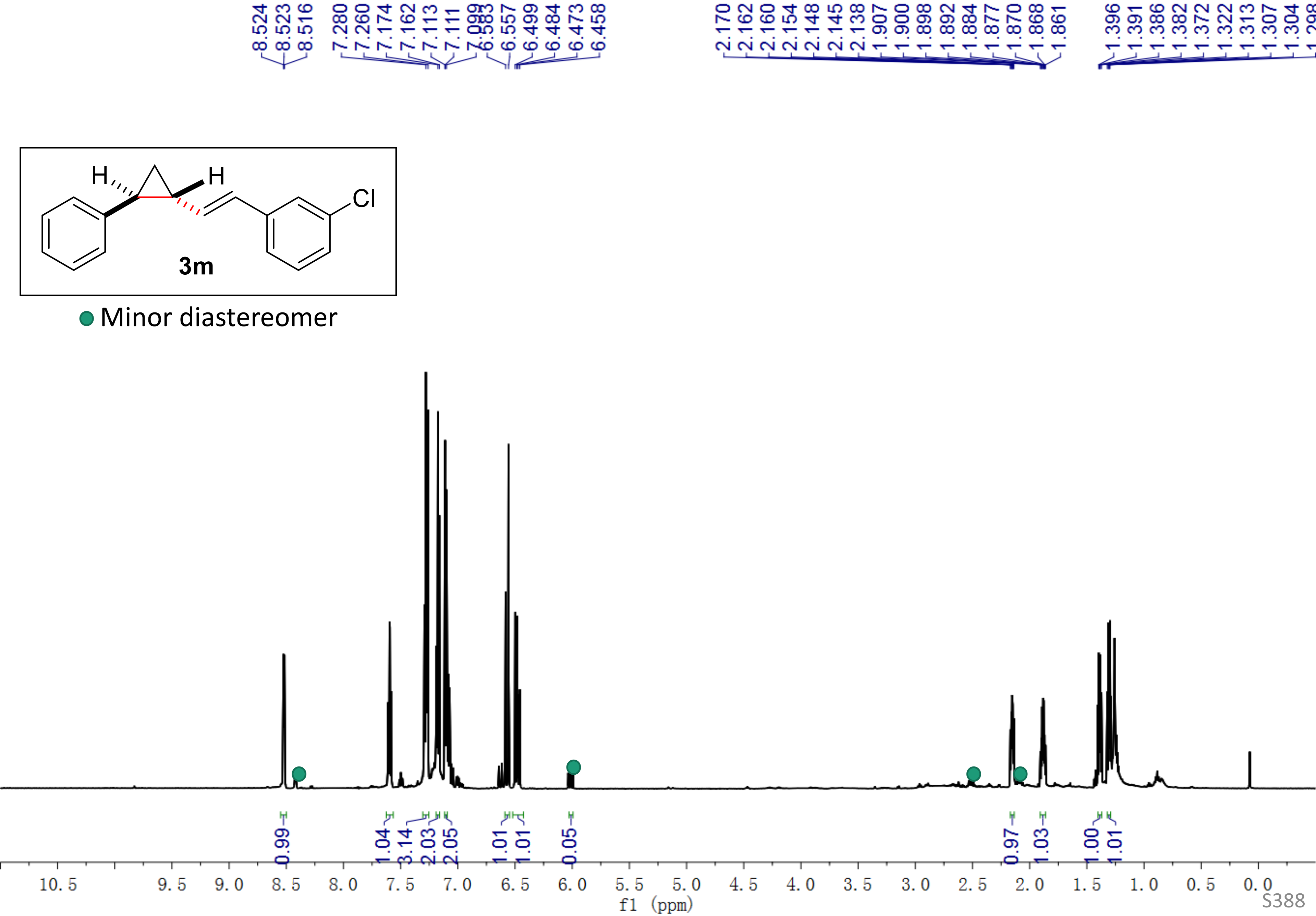


Peak Table

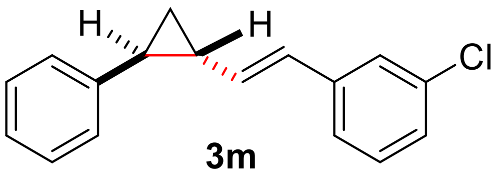
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.518	2189713	88.070
2	6.401	296629	11.930
Total		2486342	100.000

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

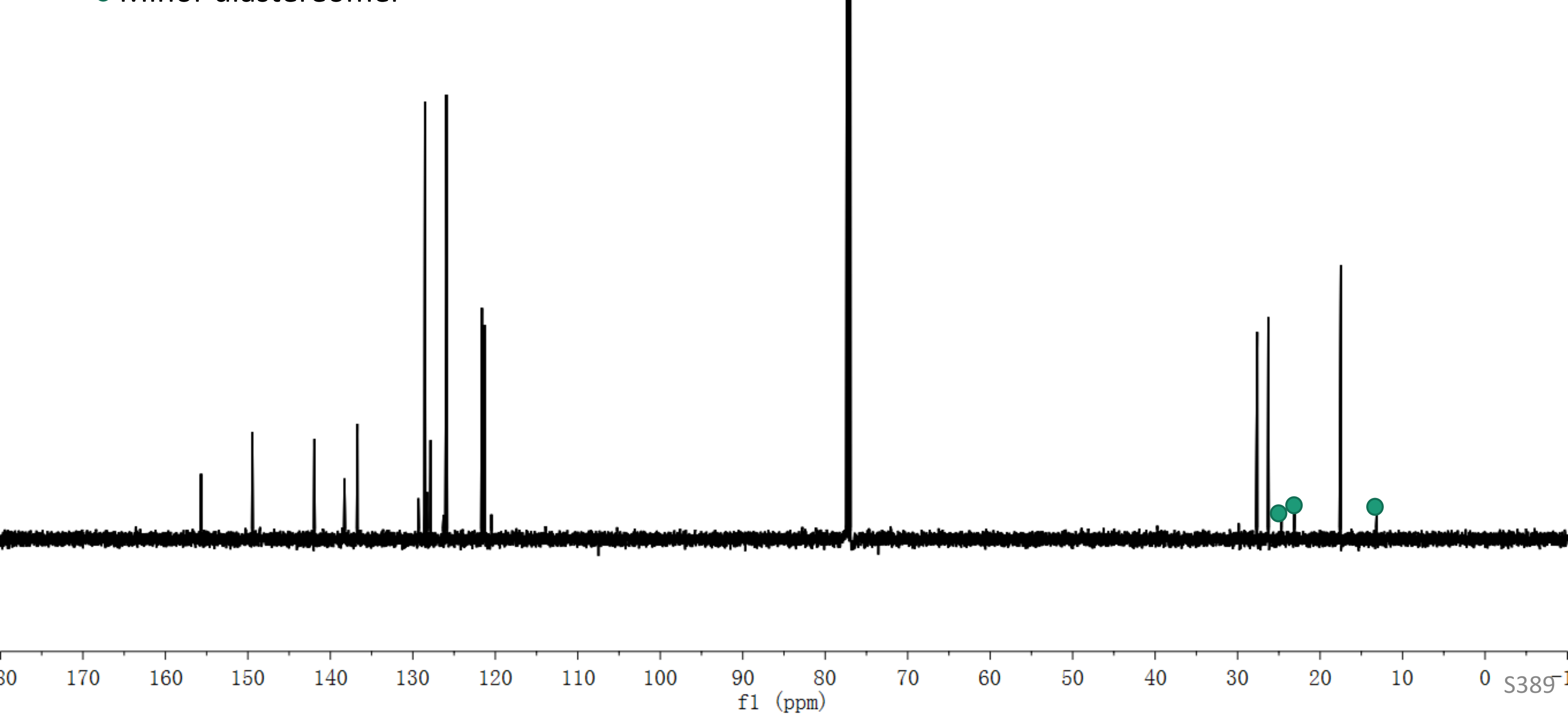


^{13}C NMR of **3m**, 126 MHz, $CDCl_3$



3m

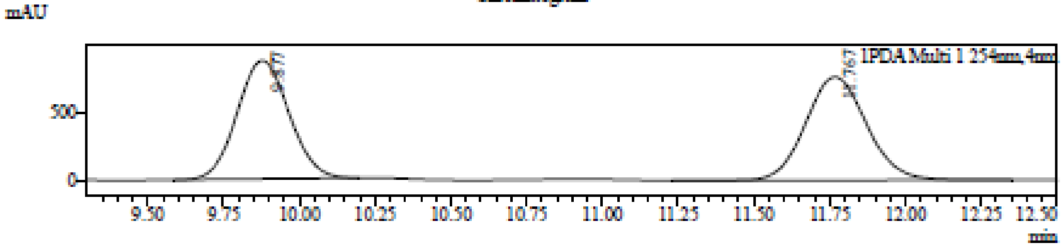
● Minor diastereomer



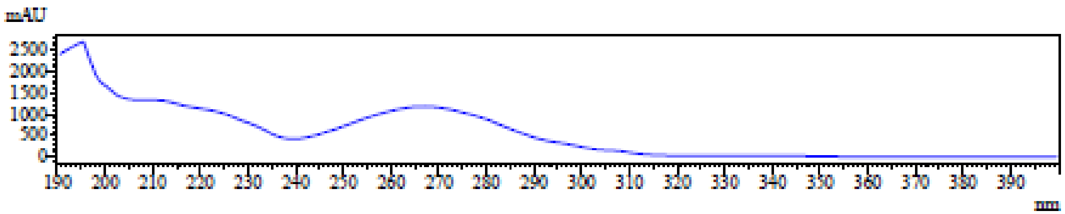
Sample Information

Data File : J0K-0721-3--IA--1%-1ML.lcd
Sample Name : J0K-0721-3--IA--1%-1ML
Sample ID : J0K-0721-3--IA--1%-1ML
Method File : J0K-1%--35min-1ml.lcm

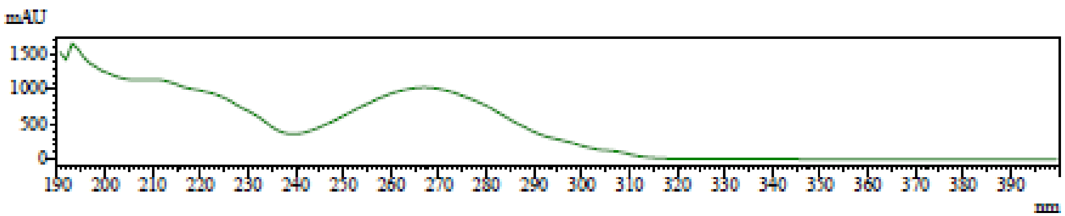
Chromatogram



UV Spectrum
Retention time = 9.877



UV Spectrum
Retention time = 11.767



Peak Table

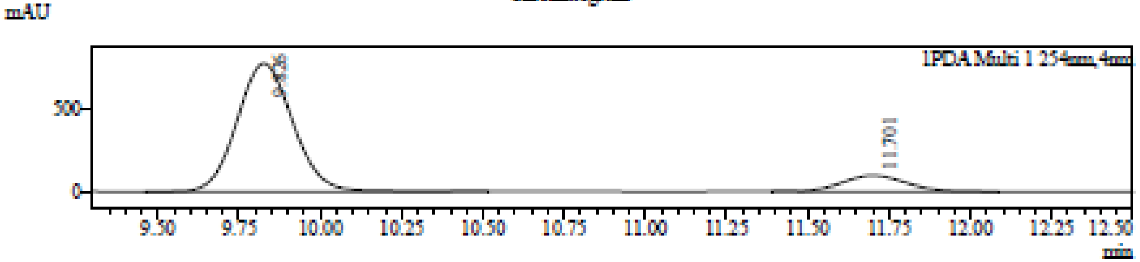
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.877	10293310	49.527
2	11.767	10490017	50.473
Total		20783327	100.000

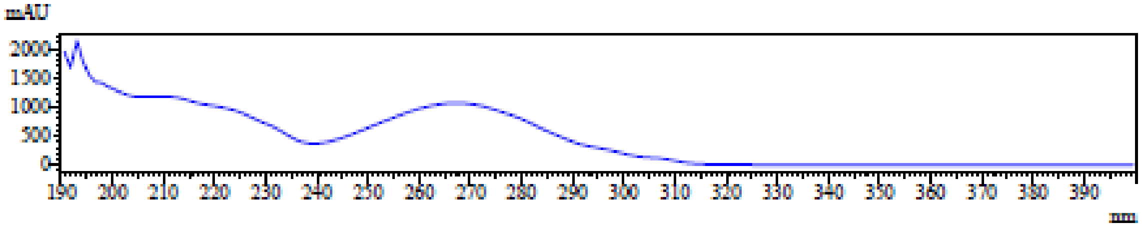
Sample Information

Data File	: J0K-0720-3--IA--1%-1ML.lcd
Sample Name	: J0K-0720-3--IA--1%-1ML
Sample ID	: J0K-0720-3--IA--1%-1ML
Method File	: J0K-1%--35min-1ml.lcm

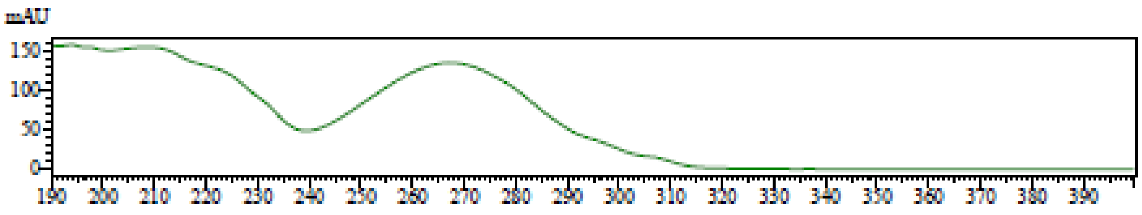
Chromatogram



UV Spectrum
Retention time = 9.826



UV Spectrum
Retention time = 11.701

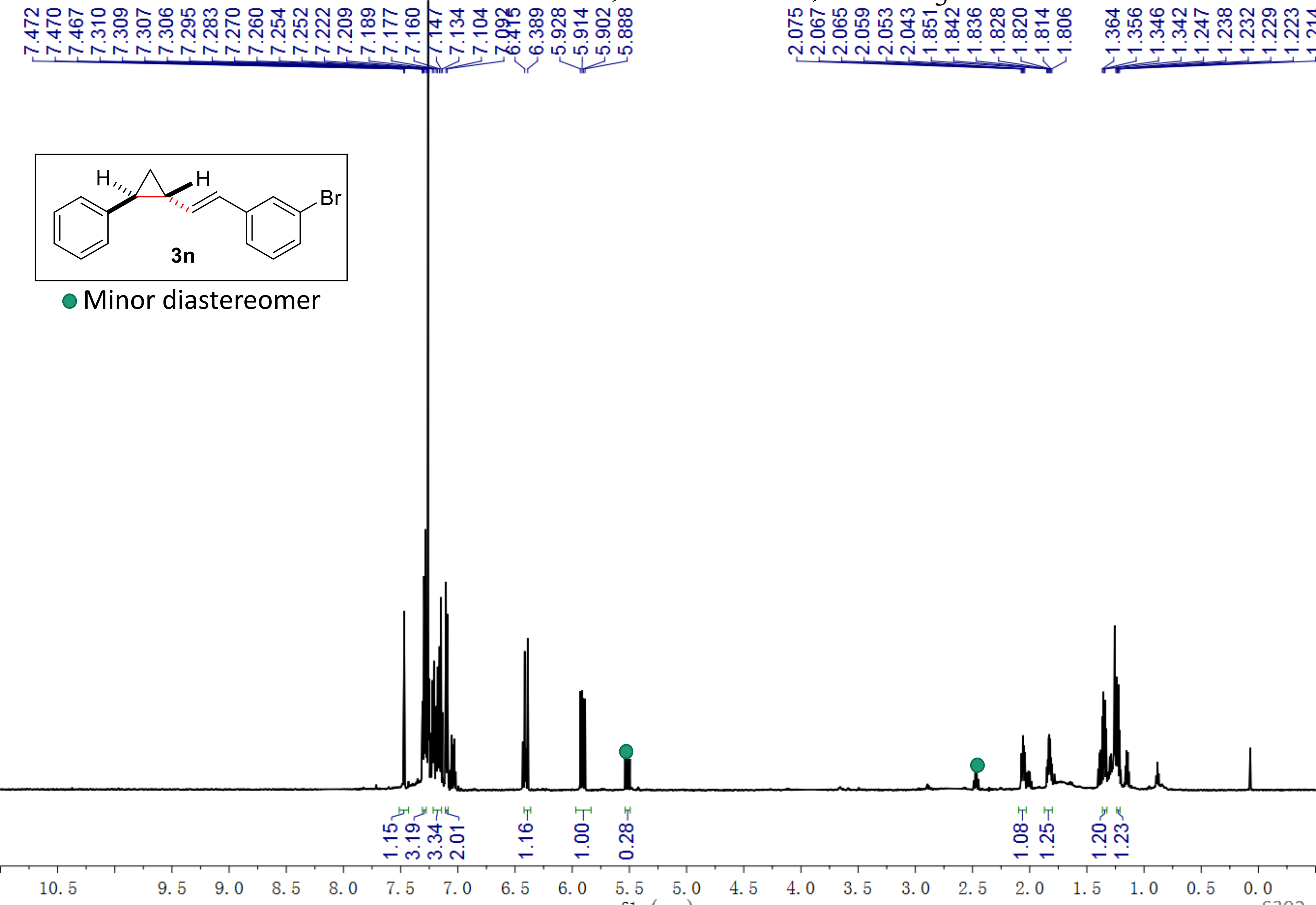


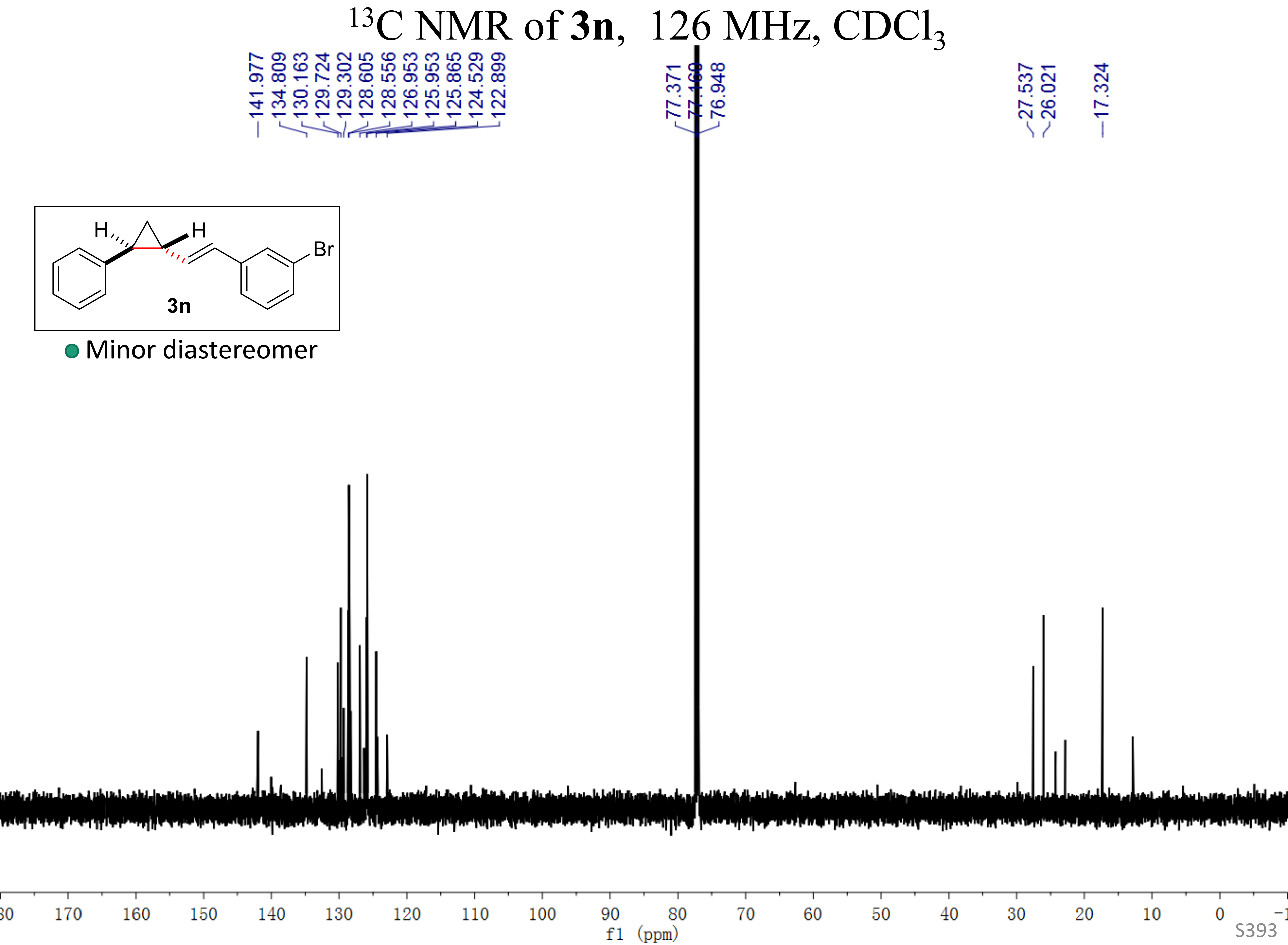
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.826	9405249	87.591
2	11.701	1332469	12.409
Total		10737717	100.000

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



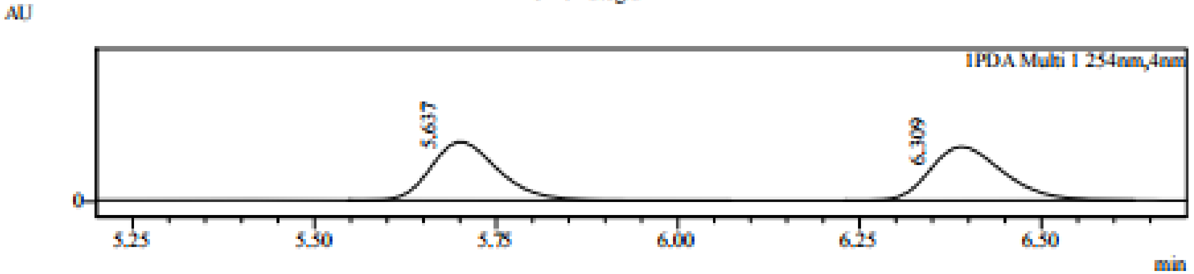


^{13}C NMR of **3n**, 126 MHz, CDCl$_3$
141.977
134.809
130.163
129.724
129.302
128.605
128.556
126.953
125.953
125.865
124.529
122.899
77.371
77.160
76.948
27.537
26.021
17.324
H
H
Br
3n
Minor diastereomer
f1 (ppm)

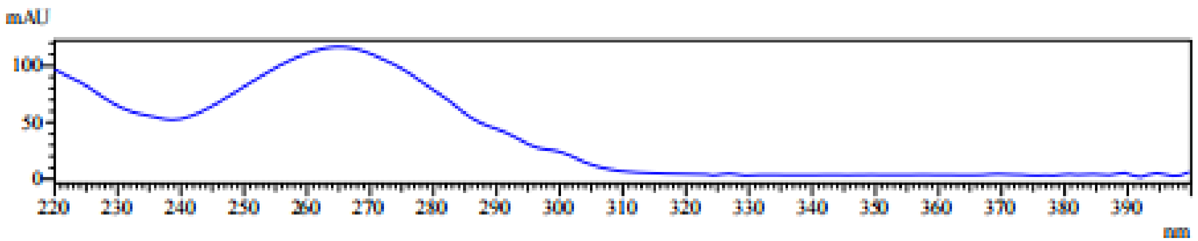
Sample Information

Data File : J0K-1821--IB-0.3%-1ML-2.lcd
Sample Name : J0K-1821--IB-0.3%-1ML-2
Sample ID : J0K-1821--IB-0.3%-1ML-2
Method File : J0K-0.3%--15min-1ml.lcm

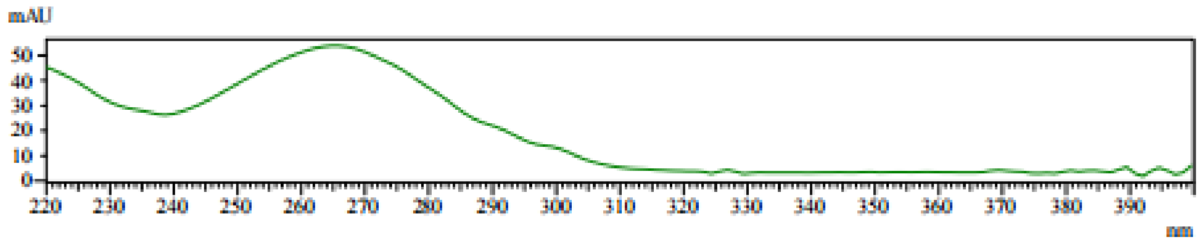
Chromatogram



UV Spectrum
Retention time = 5.637



UV Spectrum
Retention time = 6.309



Peak Table

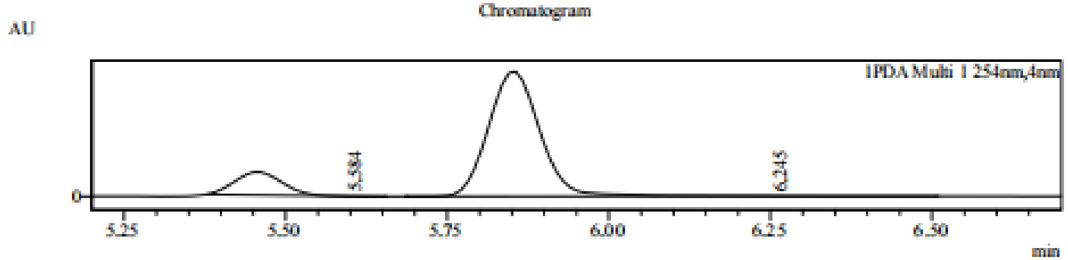
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.637	2459292	50.108
2	6.309	2448642	49.892
Total		4907935	100.000

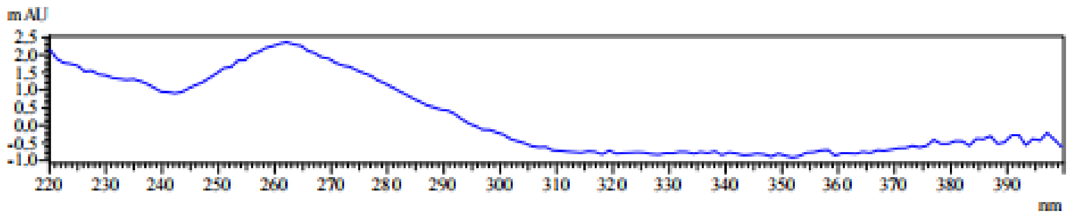
Sample Information

Data File : J0K-1820-IB-0.3%-1ML-2.lcd
Sample Name : J0K-1820-IB-0.3%-1ML-2
Sample ID : J0K-1820-IB-0.3%-1ML-2
Method File : J0K-0.3%--15min-1ml.lcm

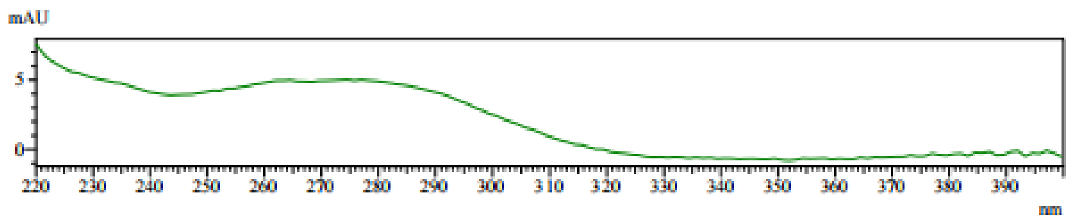
Chromatogram



UV Spectrum
Retention time = 5.584



UV Spectrum
Retention time = 6.245

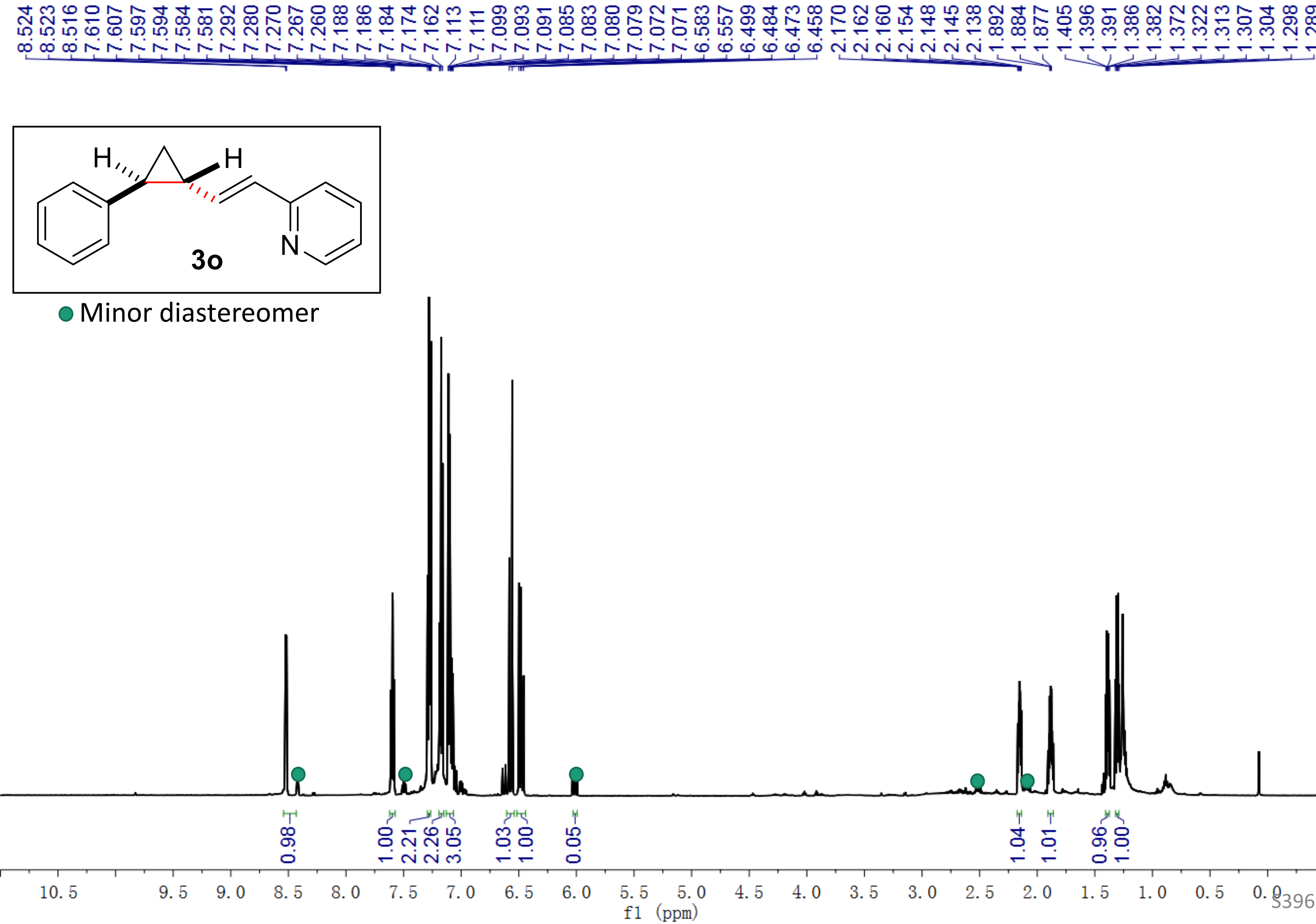


Peak Table

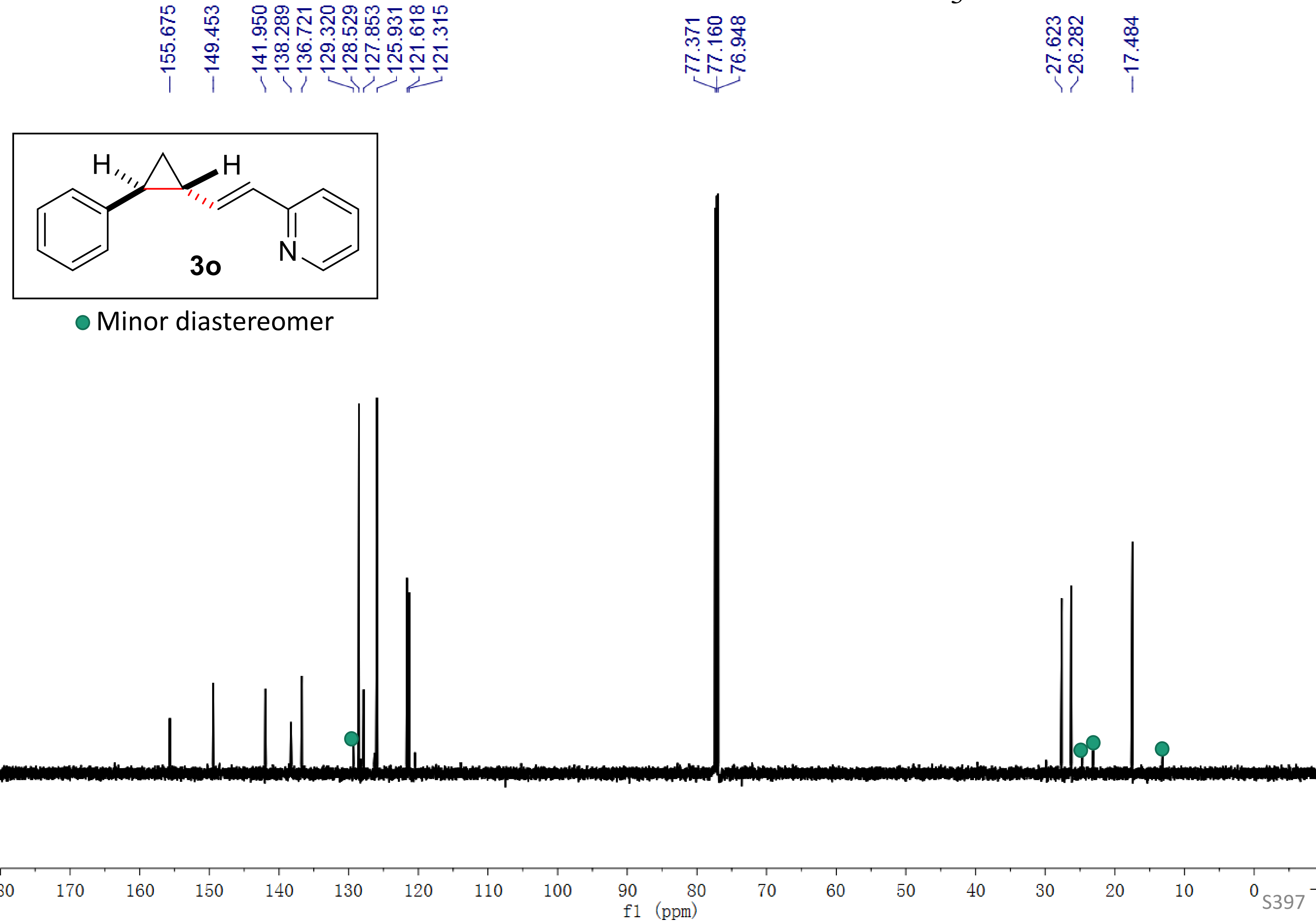
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.584	846861	14.191
2	6.245	5120744	85.809
Total		5967605	100.000

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

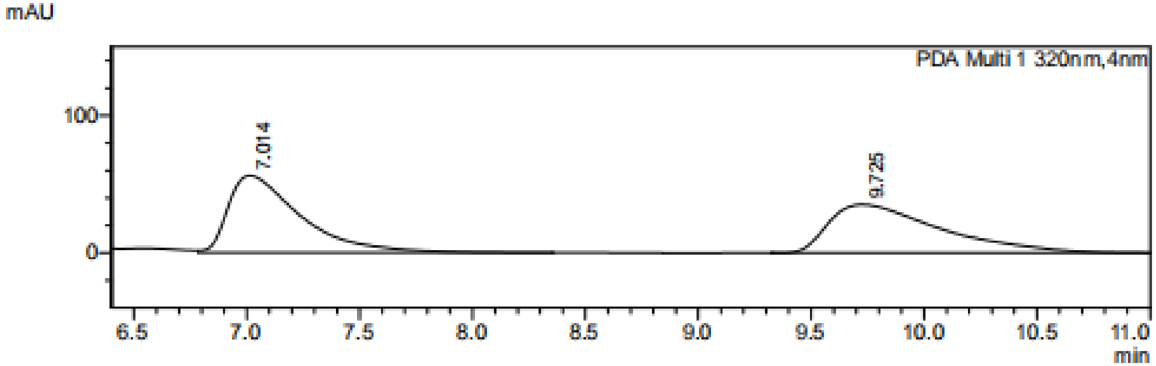


^{13}C NMR of **3o**, 126 MHz, $CDCl_3$



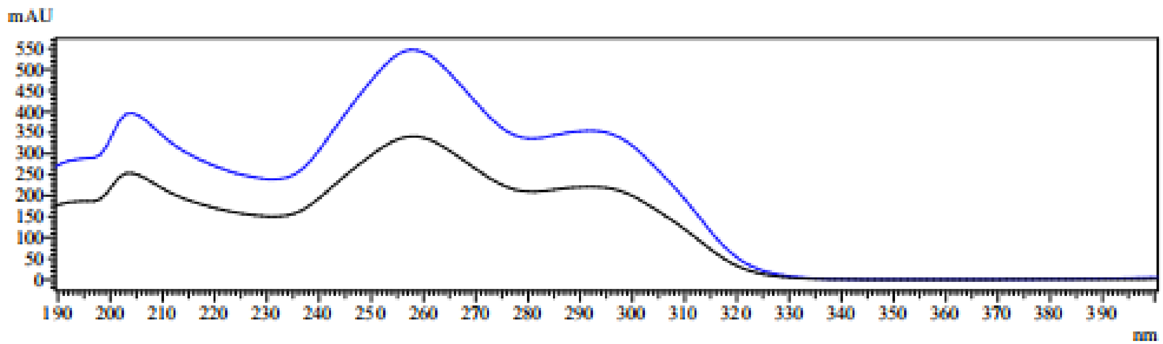
==== Shimadzu LabSolutions Analysis Report ====

JK-1753-ADH-5%-1mL
JK-5%-60min-1mL.lcm



UV Spectrum

JK-1753-ADH-5%-1mL_001.lcd



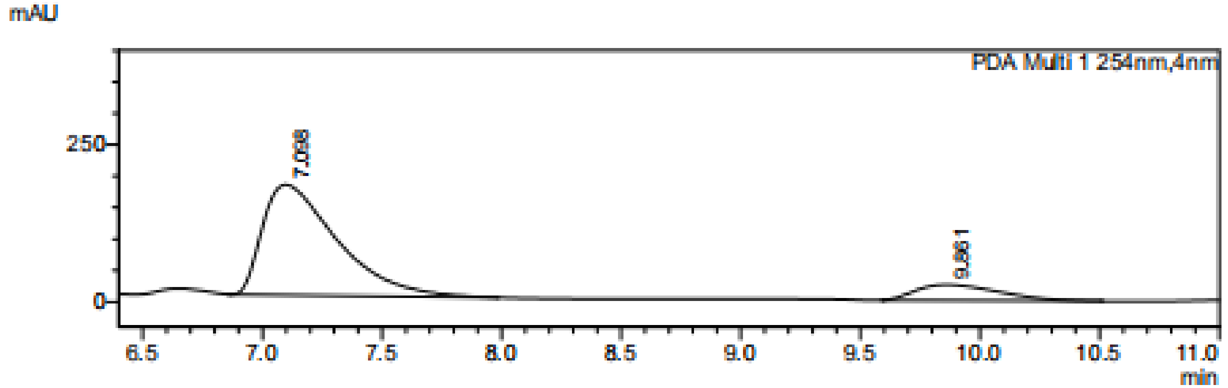
Peak Table

PDA Ch1 320nm

Peak#	Ret. Time	Area%
1	7.014	50.564
2	9.725	49.436
Total		100.000

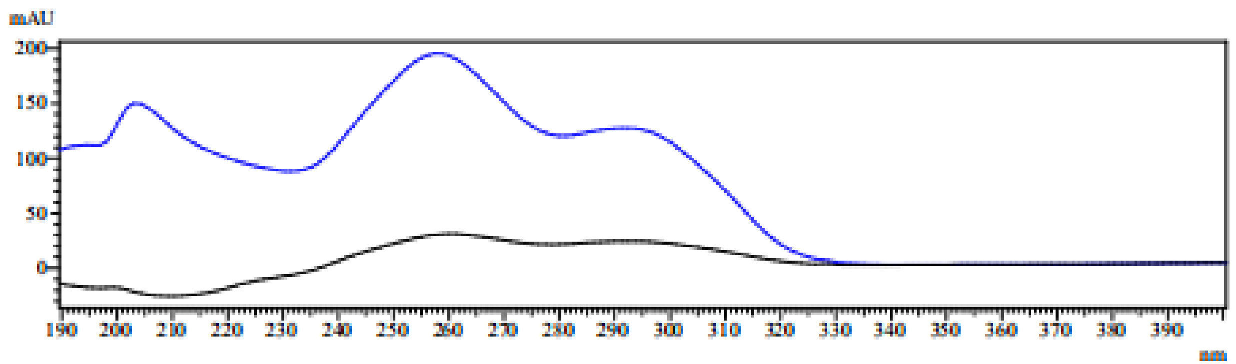
==== Shimadzu LabSolutions Analysis Report ====

JK-1752-ADH-5%-1mL
JK-5%-60min-1mL.lcm



UV Spectrum

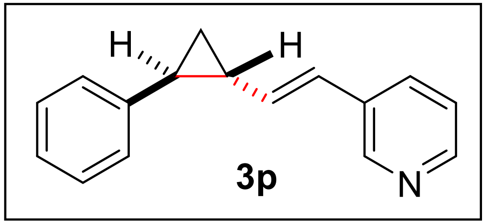
JK-1752-ADH-5%-1mL_001.lcd

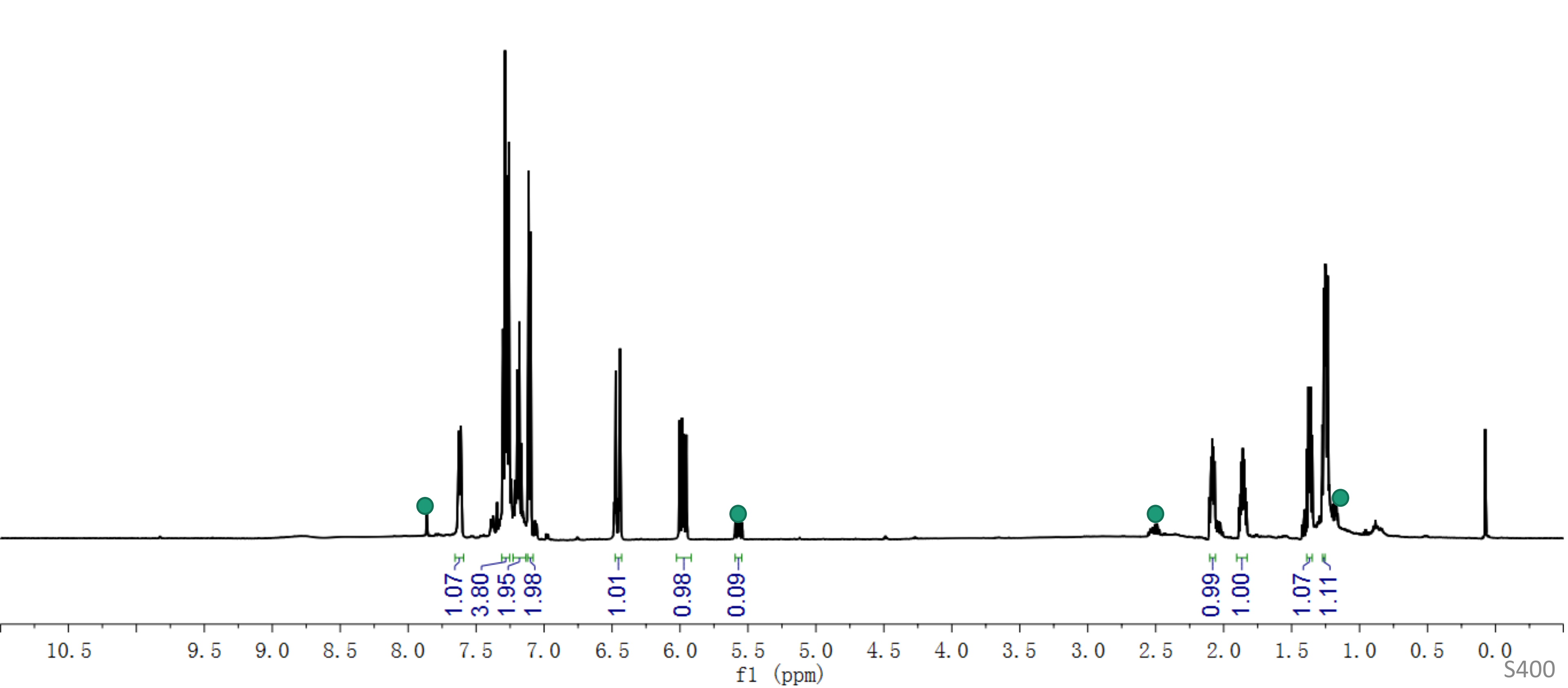


PDA Ch1 254nm

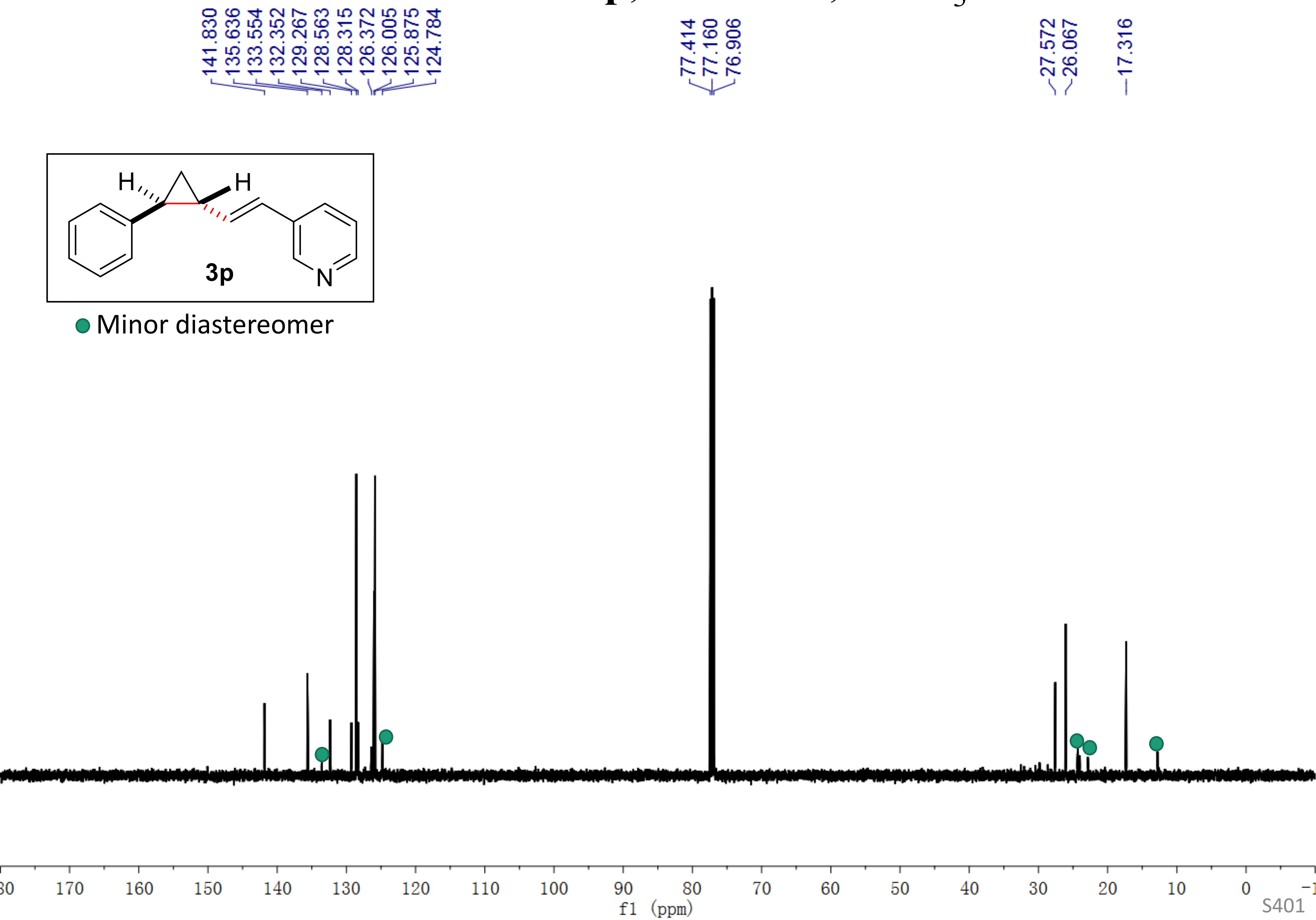
Peak#	Ret. Time	Area%
1	7.098	86.305
2	9.861	13.695
Total		100.000

[1]H NMR of **3p**, 500 MHz, $CDCl_3$



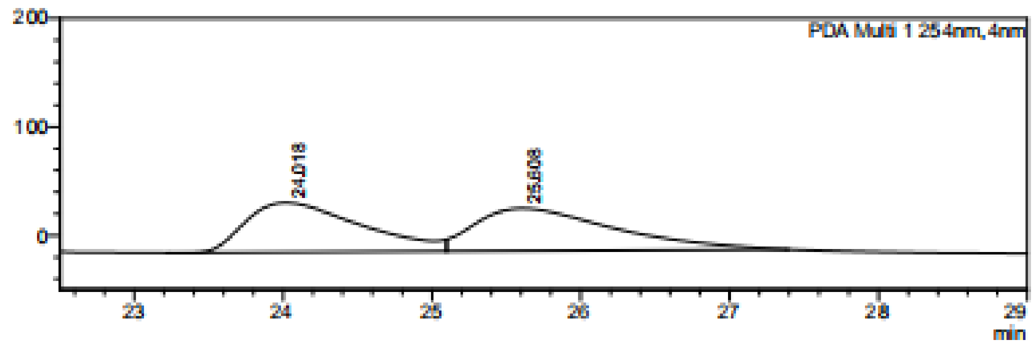


^{13}C NMR of **3p**, 126 MHz, $CDCl_3$



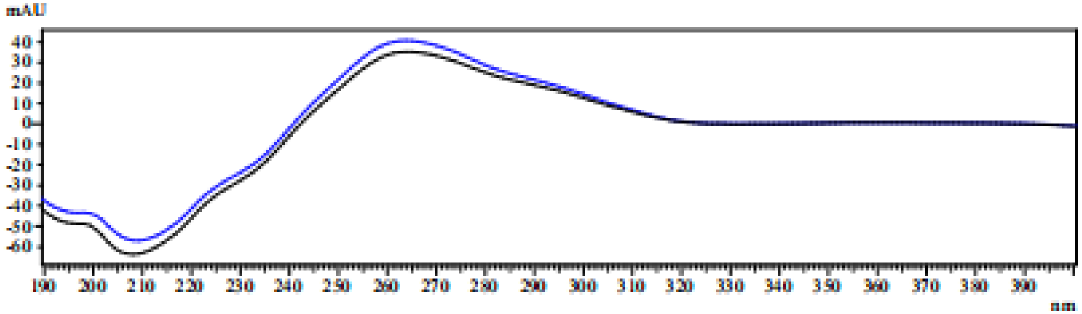
==== Shimadzu LabSolutions Analysis Report ====

JK-1751-IE-5%-1mL
JK-5%-60min-1mL.lcm



UV Spectrum

JK-1751-IE-5%-1mL_001.lcd



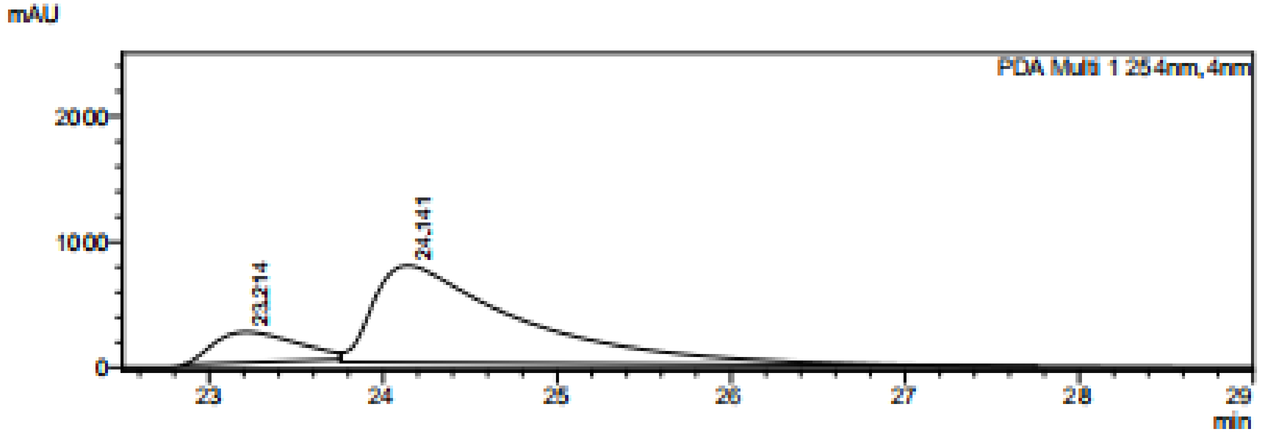
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	24.018	49.301
2	25.608	50.699
Total		100.000

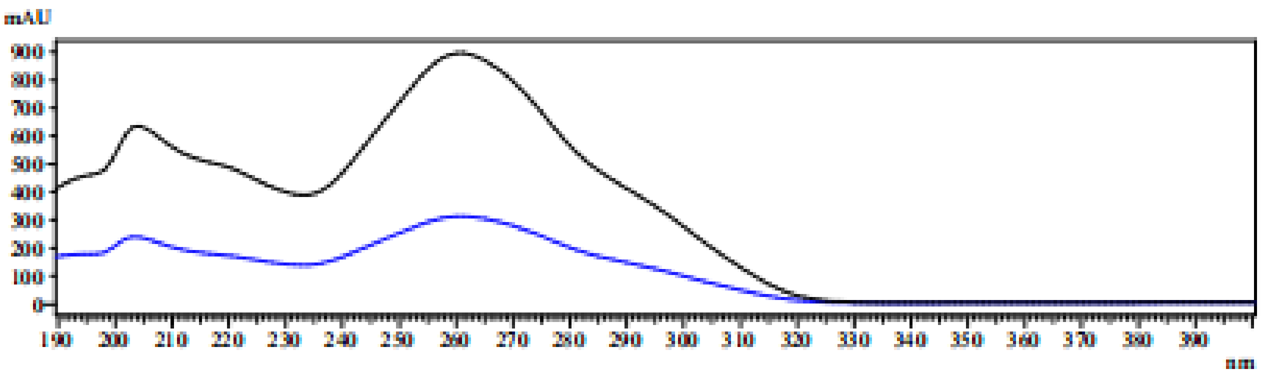
==== Shimadzu LabSolutions Analysis Report ====

JK-1750-IE-5%-1mL
JK-5%-60min-1mL.lcm



UV Spectrum

JK-1750-IE-5%-1mL_001.lcd

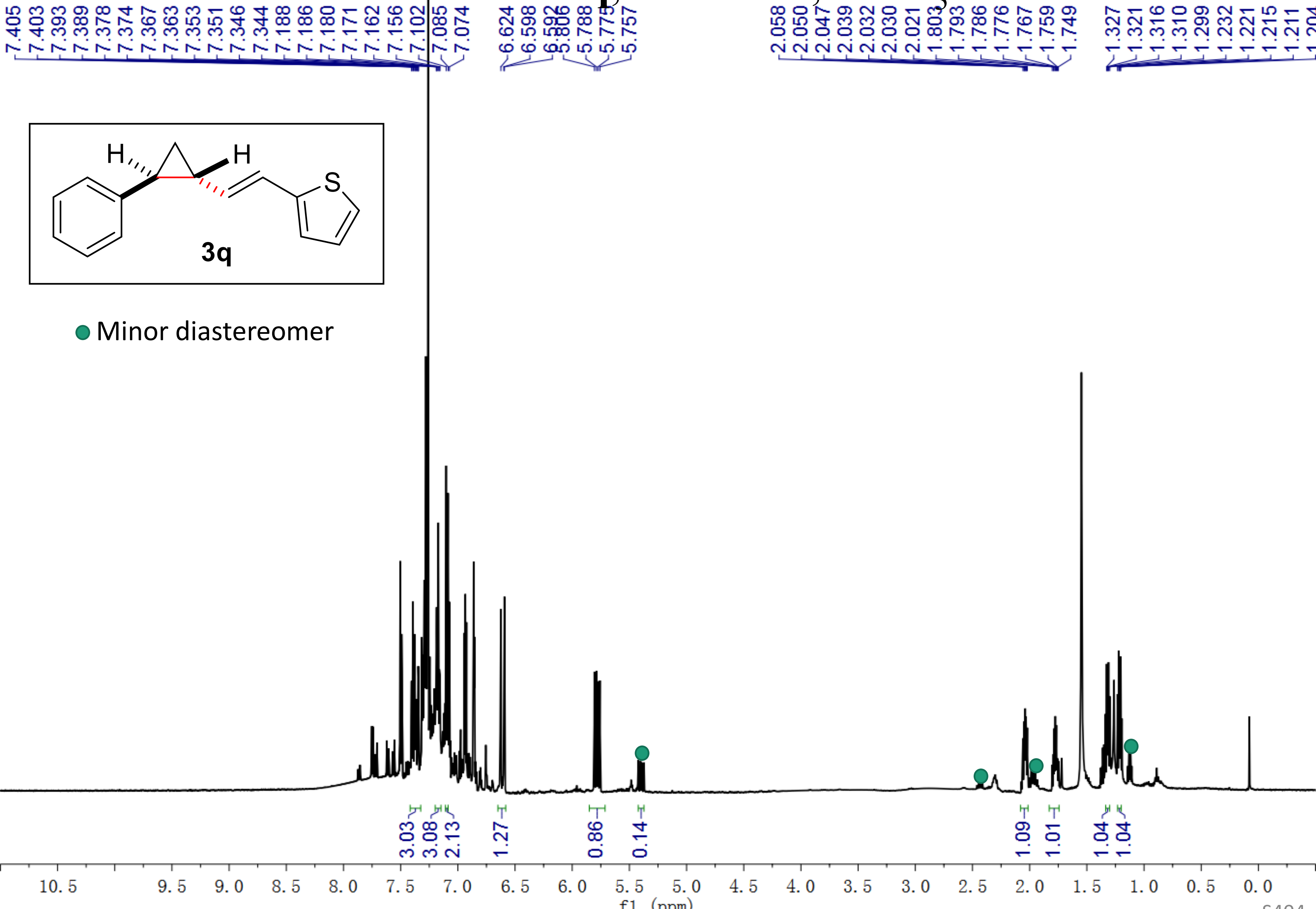


Peak Table

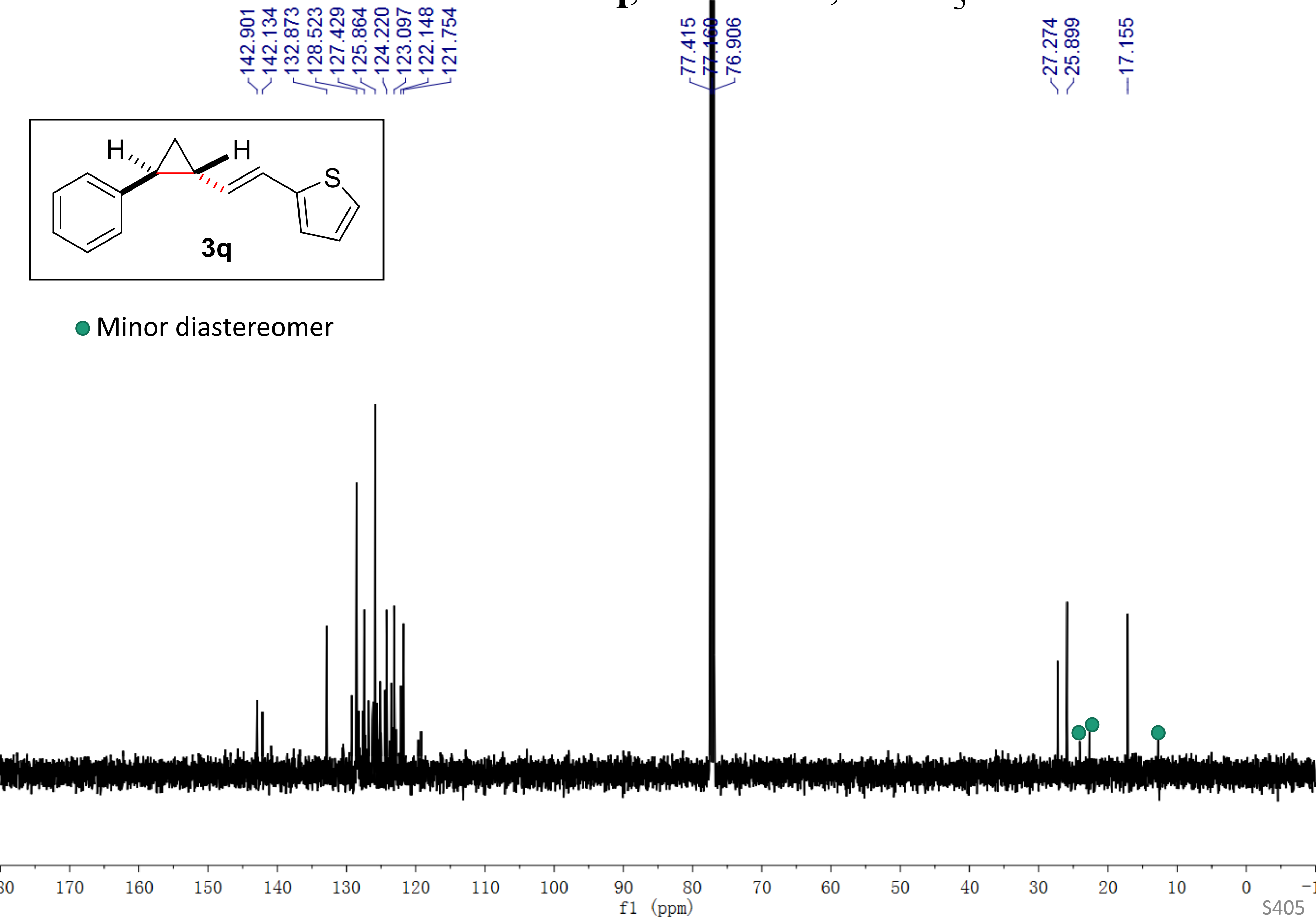
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	23.214	15.216
2	24.141	84.784
Total		100.000

[1]H NMR of **3q**, 500 MHz, $CDCl_3$



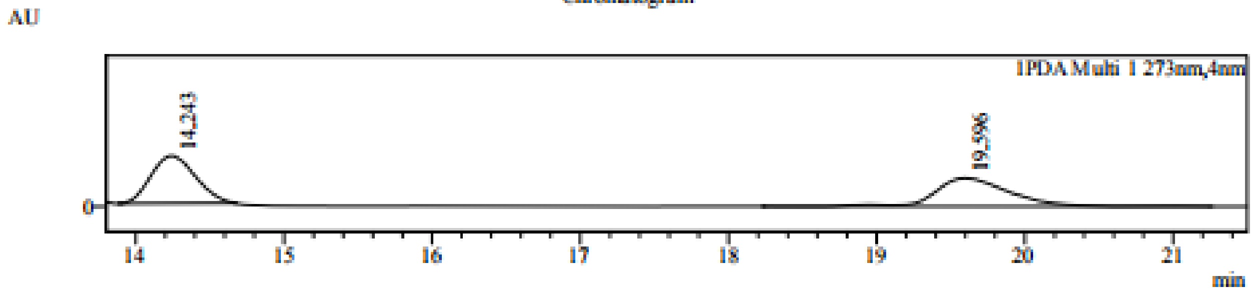
^{13}C NMR of **3q**, 126 MHz, $CDCl_3$



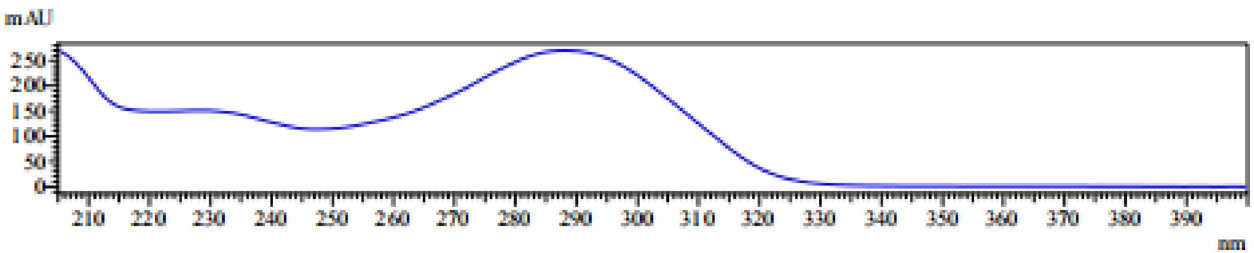
Sample information

Data File : J0K-1761--ADH-0.1%-1ML-2.lcd
Sample Name : J0K-1761--ADH-0.1%-1ML-2
Sample ID : J0K-1761--ADH-0.1%-1ML-2
Method File : J0K-0.1%--40min-1ml.lcm

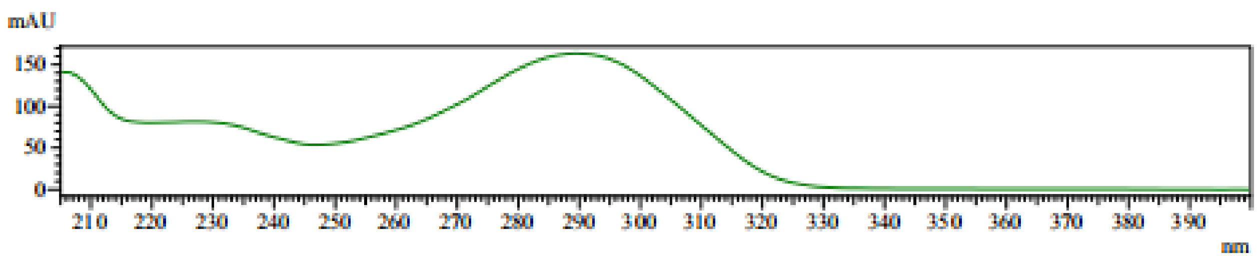
Chromatogram



UV Spectrum
Retention time = 14.243



UV Spectrum
Retention time = 19.596



Peak Table

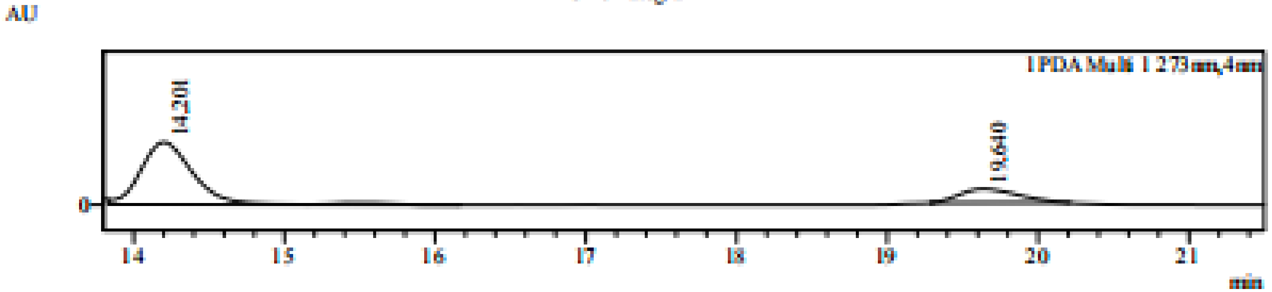
PDA Ch1 273nm

Peak#	Ret. Time	Area	Area%
1	14.243	3949803	50.503
2	19.596	3871115	49.497
Total		7820918	100.000

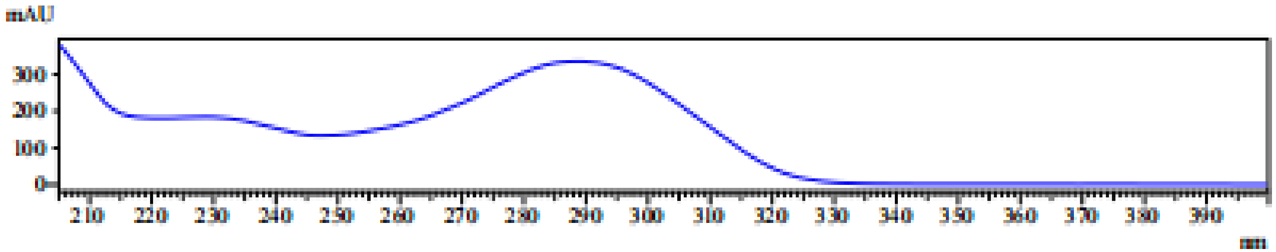
Sample information

Data File	: J0K-1760--ADH-0.1%-1ML-2.lcd
Sample Name	: J0K-1760--ADH-0.1%-1ML-2
Sample ID	: J0K-1760--ADH-0.1%-1ML-2
Method File	: J0K-0.1%--40min-1ml.lcm

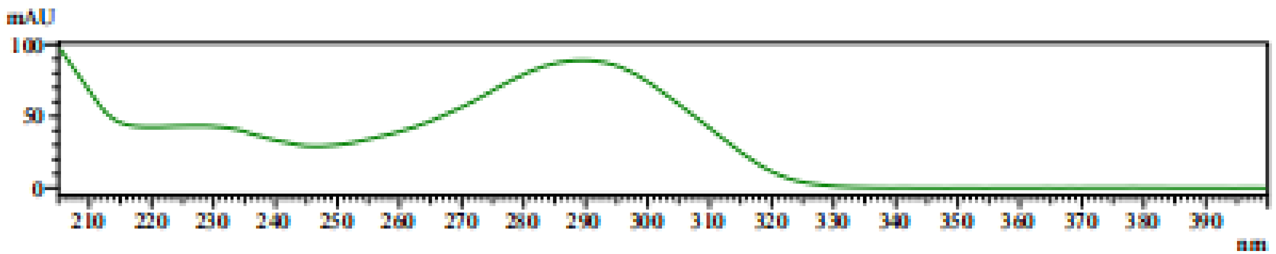
Chromatogram



UV Spectrum
Retention time = 14.201



UV Spectrum
Retention time = 19.640

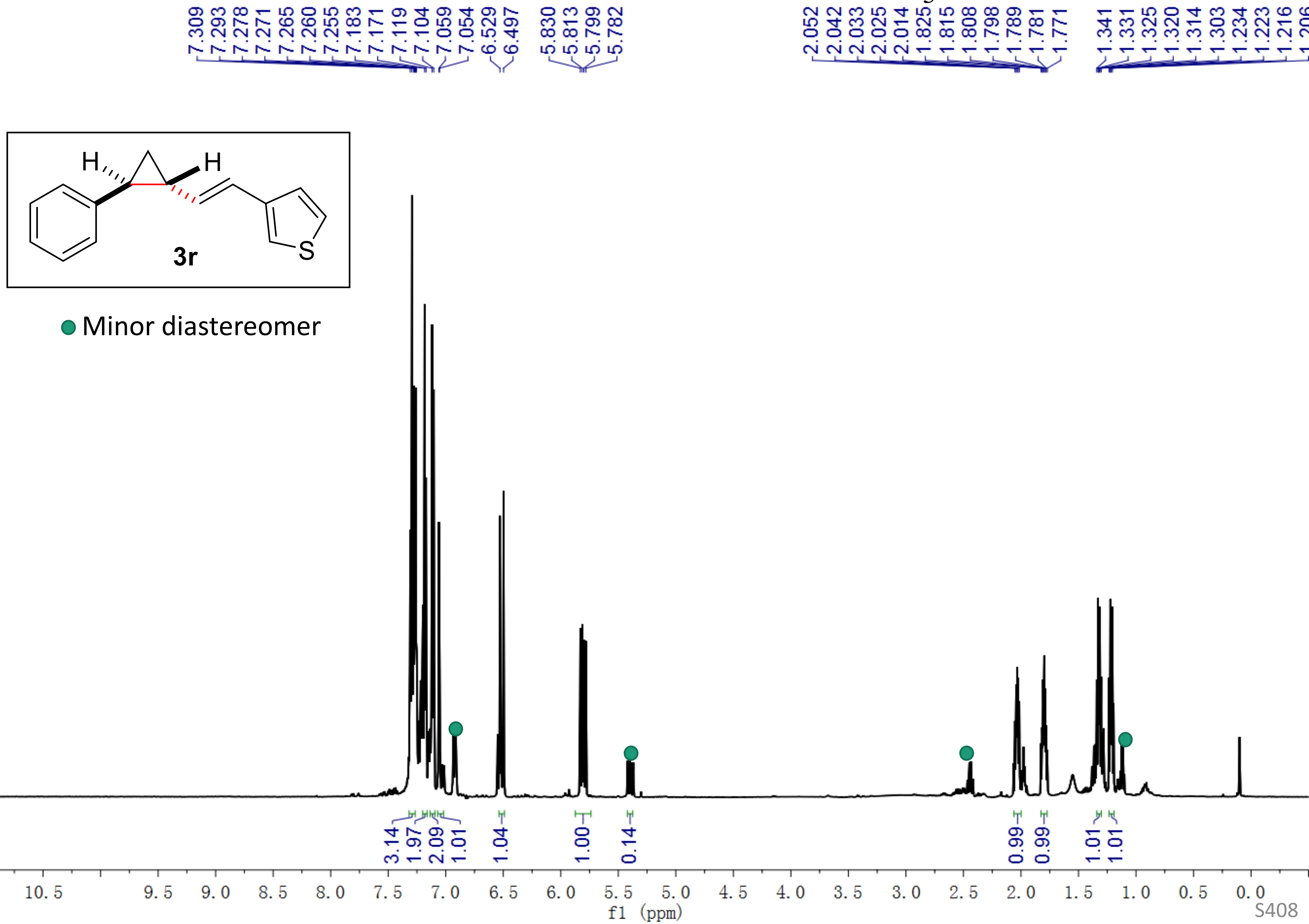


Peak Table

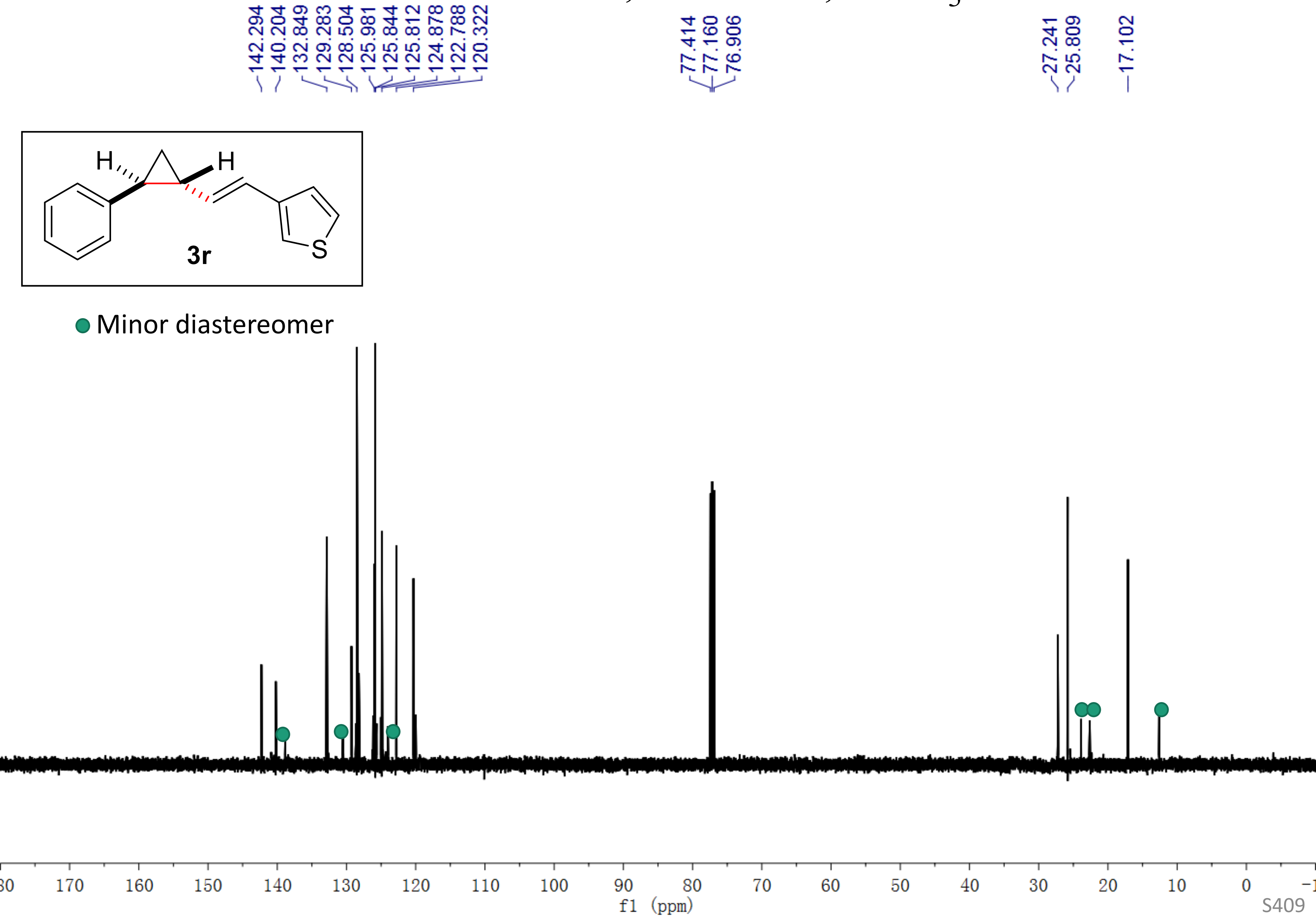
PDA Ch1 273nm

Peak#	Ret. Time	Area	Area%
1	14.201	5932715	80.113
2	19.640	1472703	19.887
Total		7405418	100.000

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

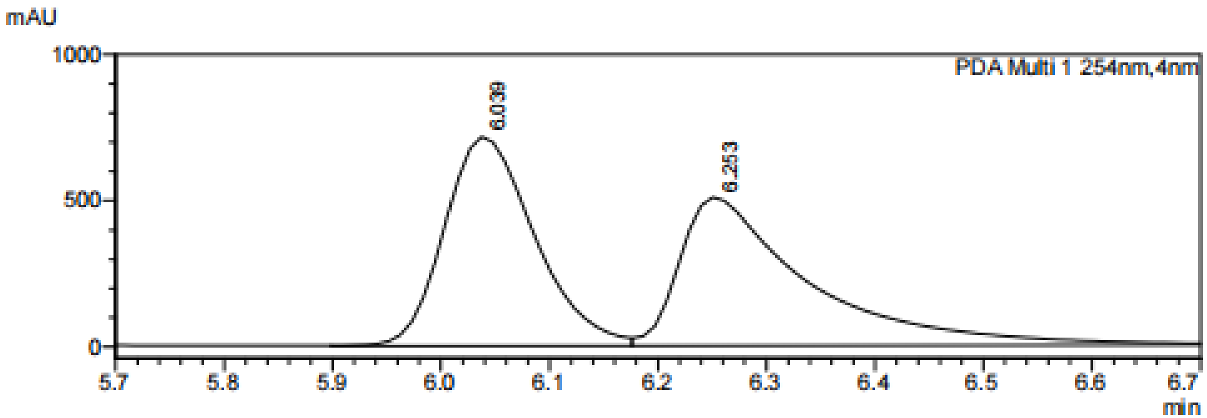


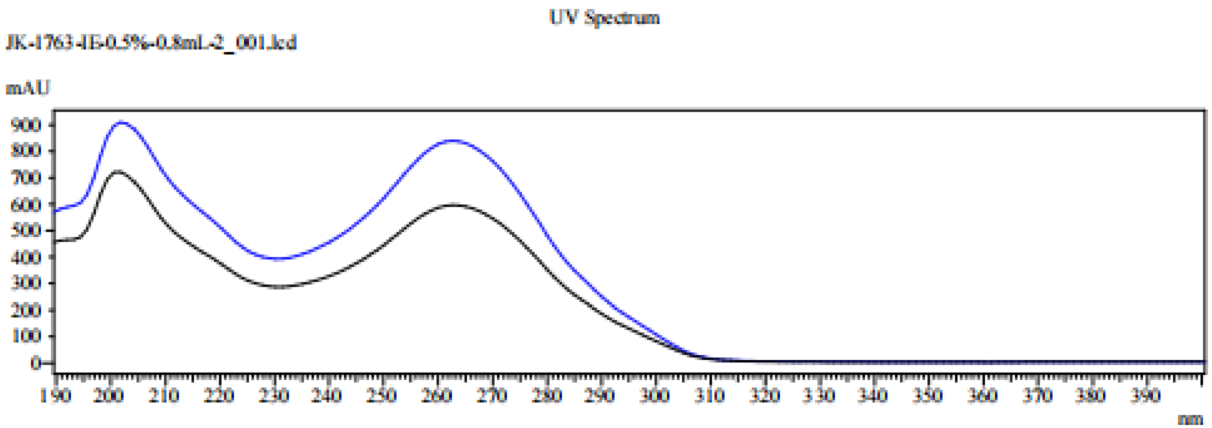
^{13}C NMR of **3r**, 126 MHz, $CDCl_3$



==== Shimadzu LabSolutions Analysis Report ====

JK-1763-IE-0.5%-0.8mL-2
JK-0.5%-30min0.8mL.lcm





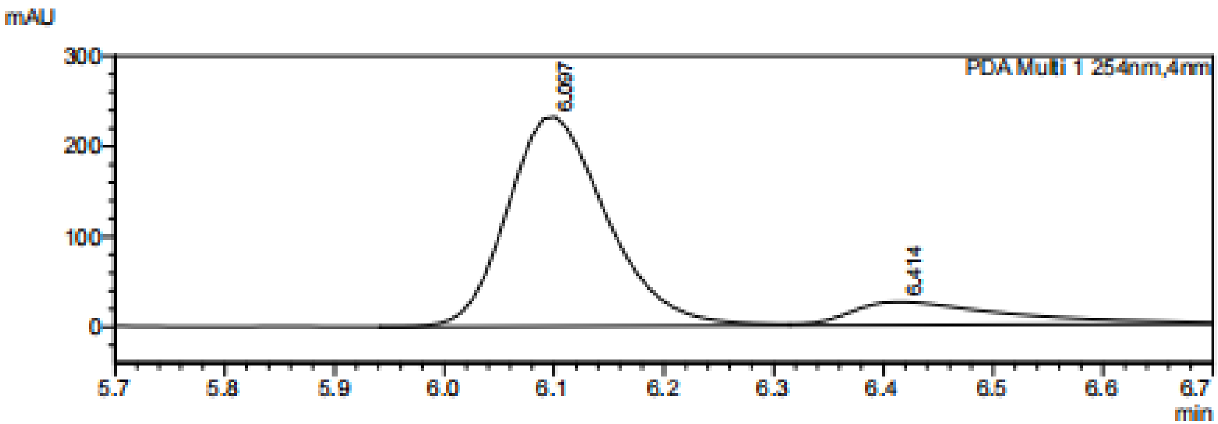
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.039	49.742
2	6.253	50.258
Total		100.000

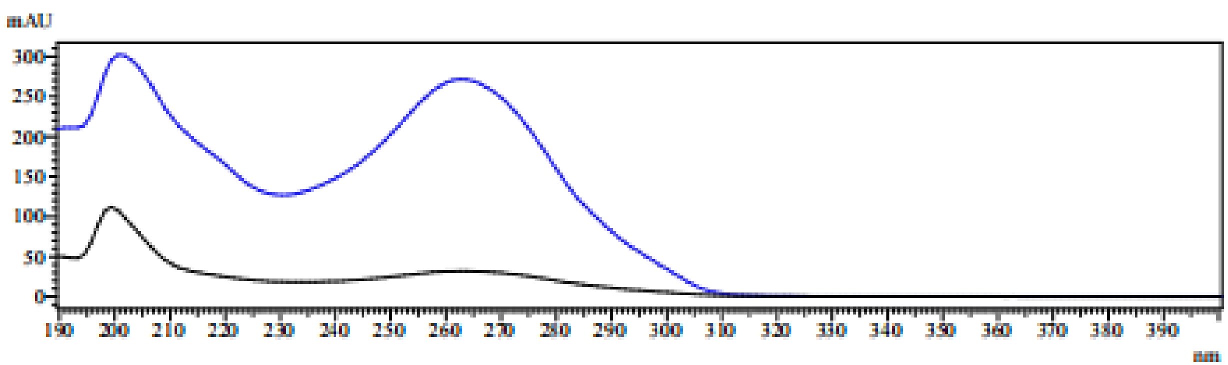
==== Shimadzu LabSolutions Analysis Report ====

JK-1762-IE-0.5%-0.8mL-3
JK-0.5%-30min0.8mL.lcm



UV Spectrum

JK-1762-IE-0.5%-0.8mL-3_001.lcd

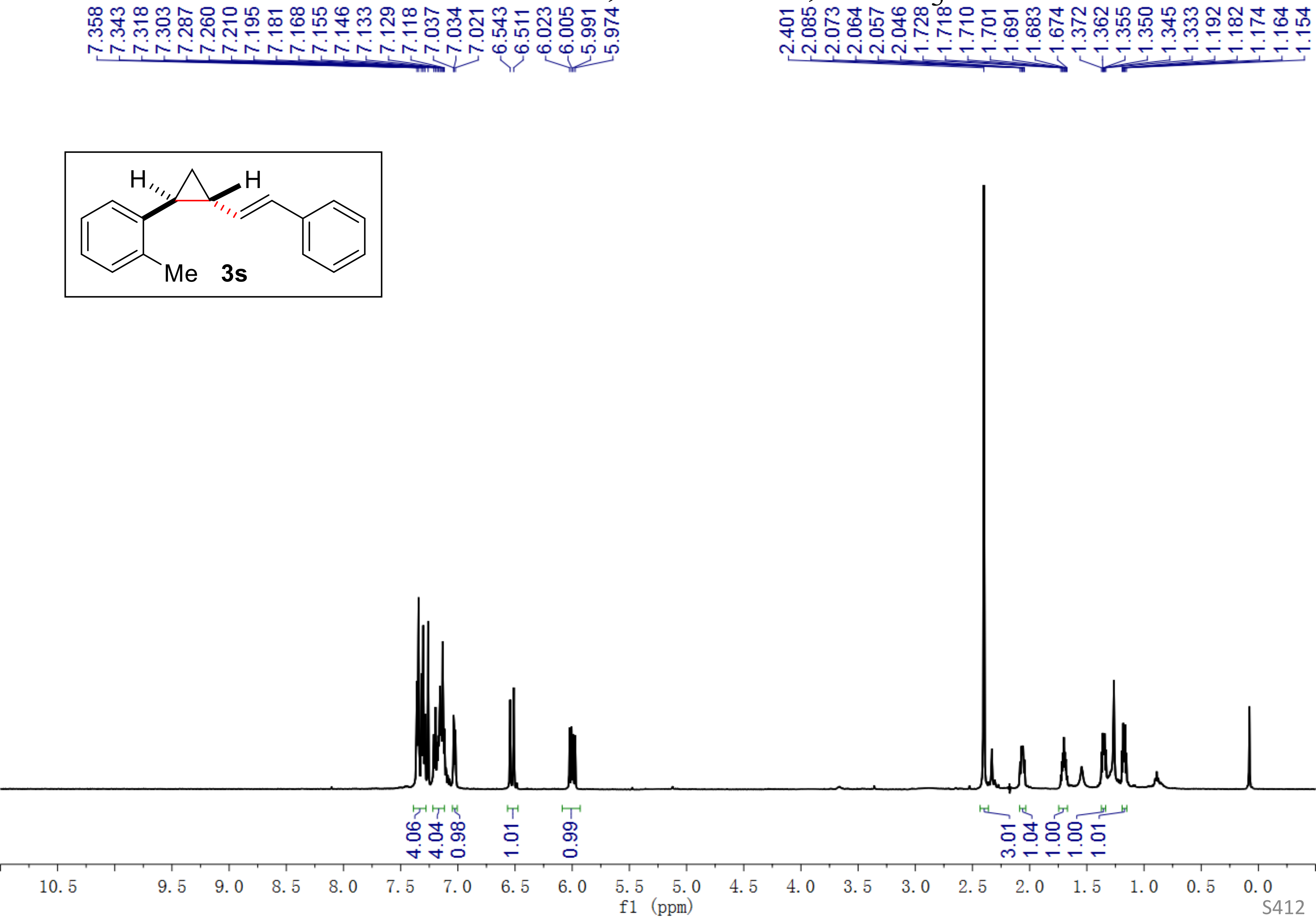


Peak Table

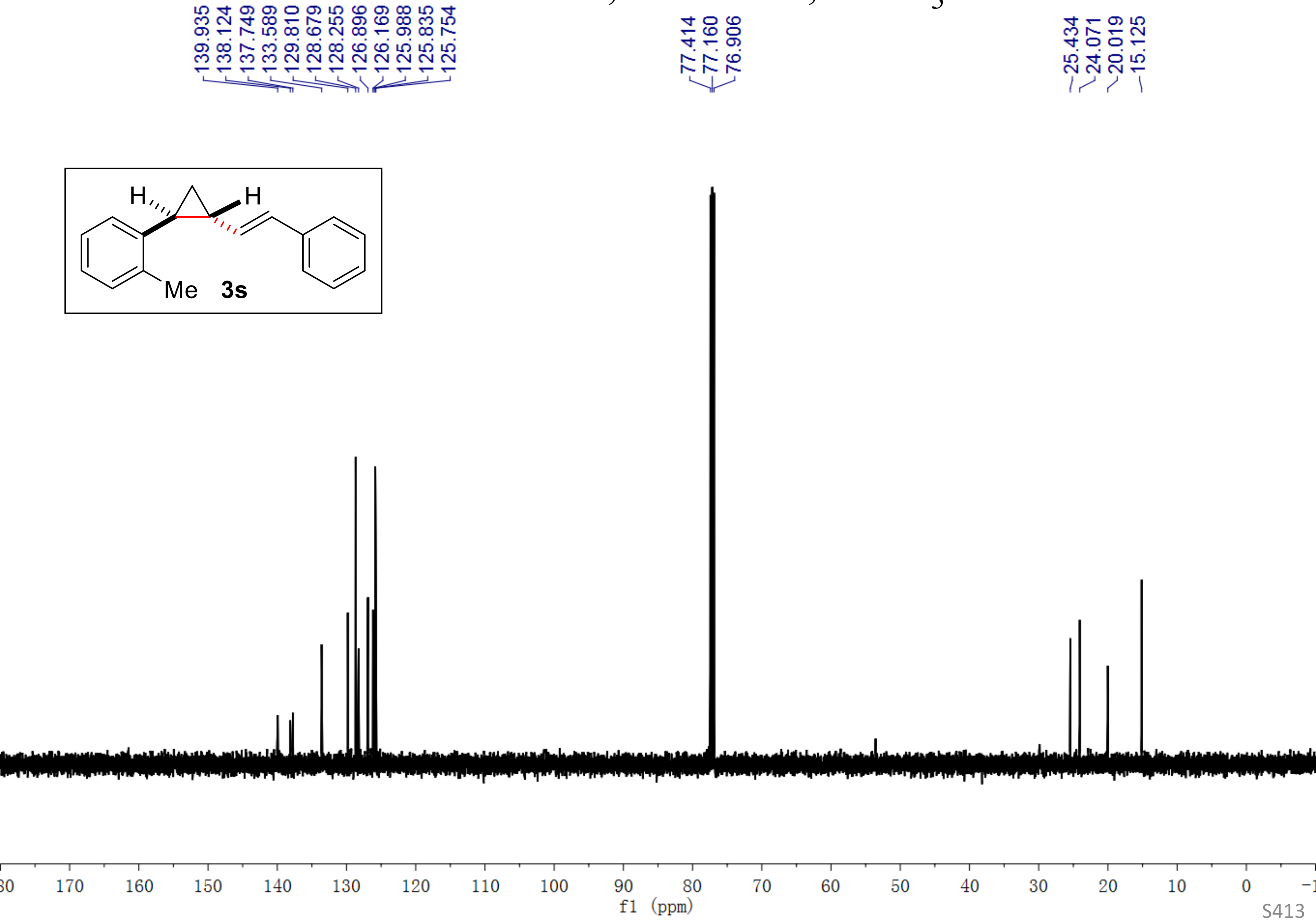
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.097	85.057
2	6.414	14.943
Total		100.000

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



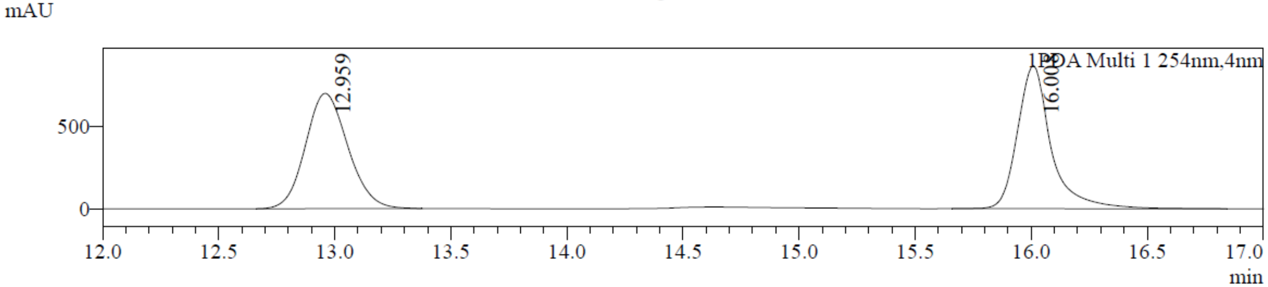
^{1}H NMR of **3s**, 500 MHz, $CDCl_3$



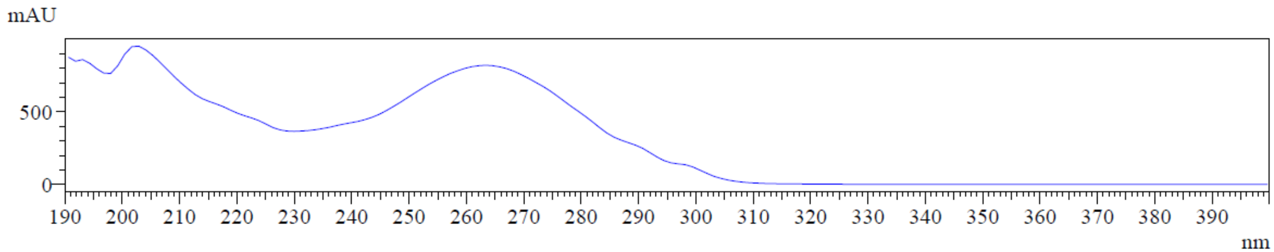
Sample Information

Data File	: J0K-1833-2--IE--0.2%-1ML.lcd
Sample Name	: J0K-1833-2--IE--0.2%-1ML
Sample ID	: J0K-1833-2--IE--0.2%-1ML
Method File	: J0K-0.2%--40min-1ml.lcm

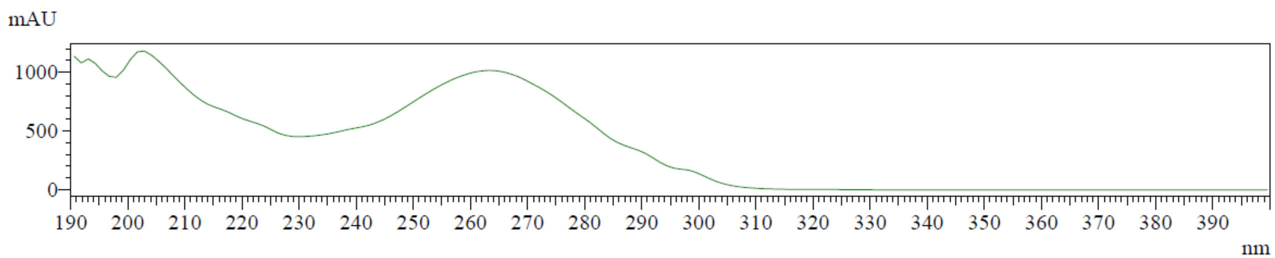
Chromatogram



UV Spectrum
Retention time = 12.959



UV Spectrum
Retention time = 16.008



Peak Table

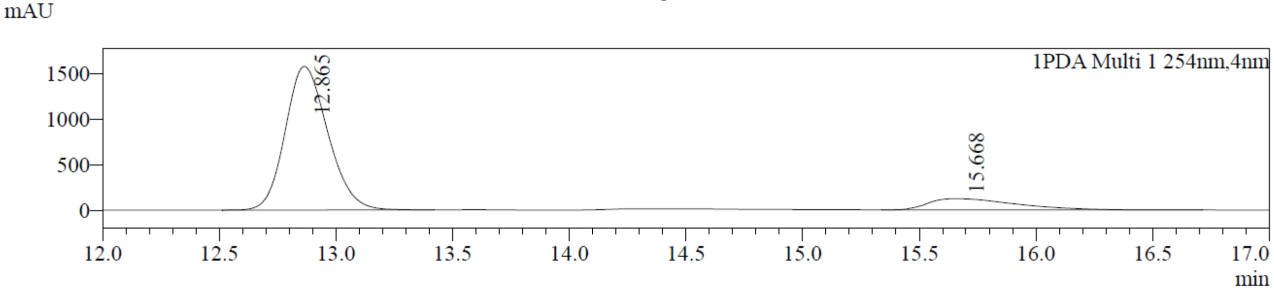
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.959	8880666	50.377
2	16.008	8747578	49.623
Total		17628244	100.000

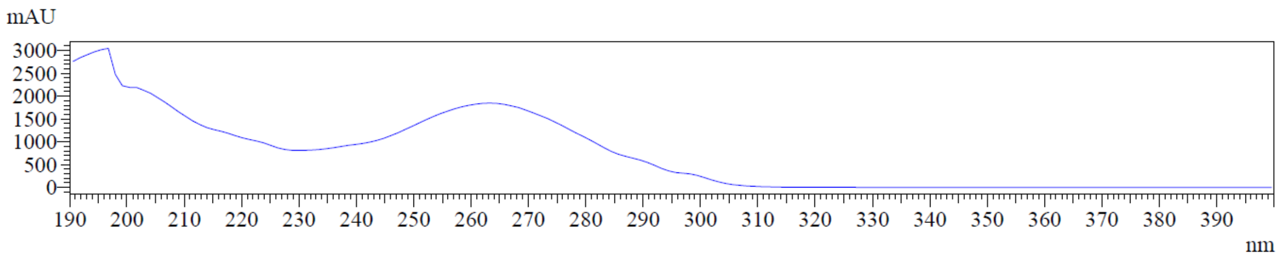
Sample Information

Data File	: J0K-1832-2--IE--0.2%-1ML.lcd
Sample Name	: J0K-1832-2--IE--0.2%-1ML
Sample ID	: J0K-1832-2--IE--0.2%-1ML
Method File	: J0K-0.2%--40min-1ml.lcm

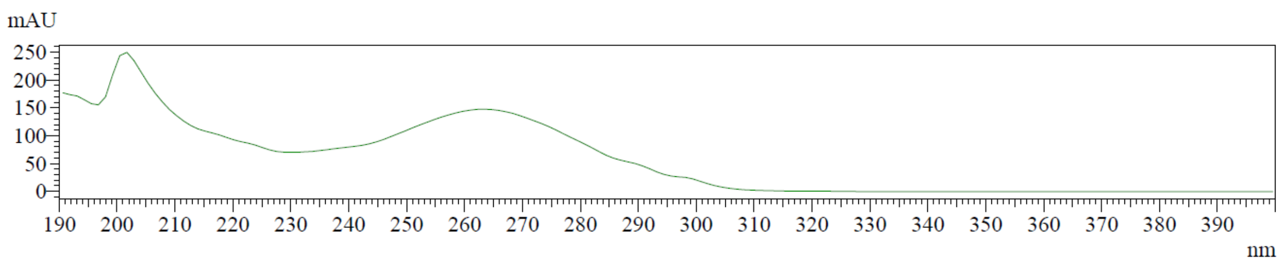
Chromatogram



UV Spectrum
Retention time = 12.865



UV Spectrum
Retention time = 15.668

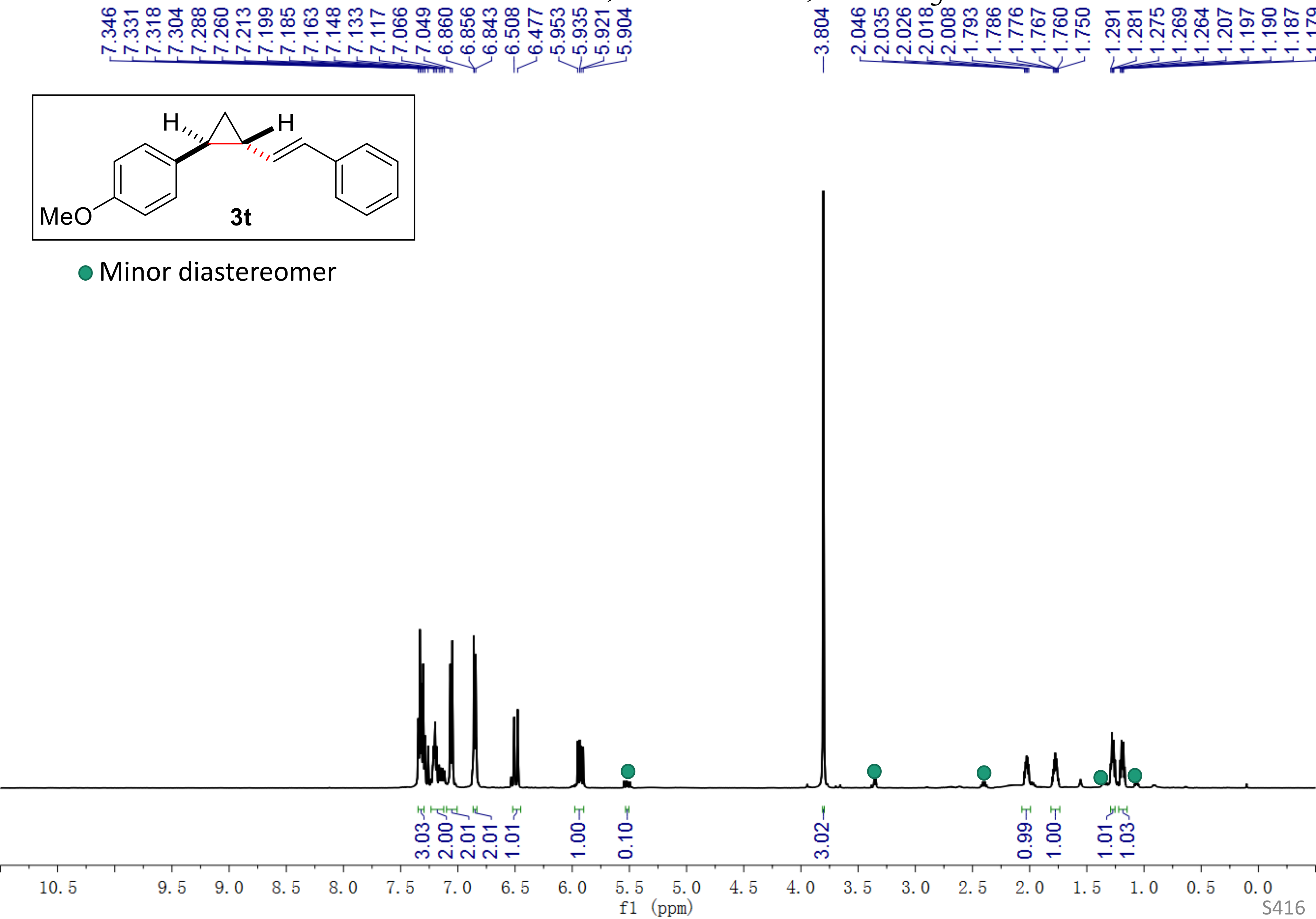


Peak Table

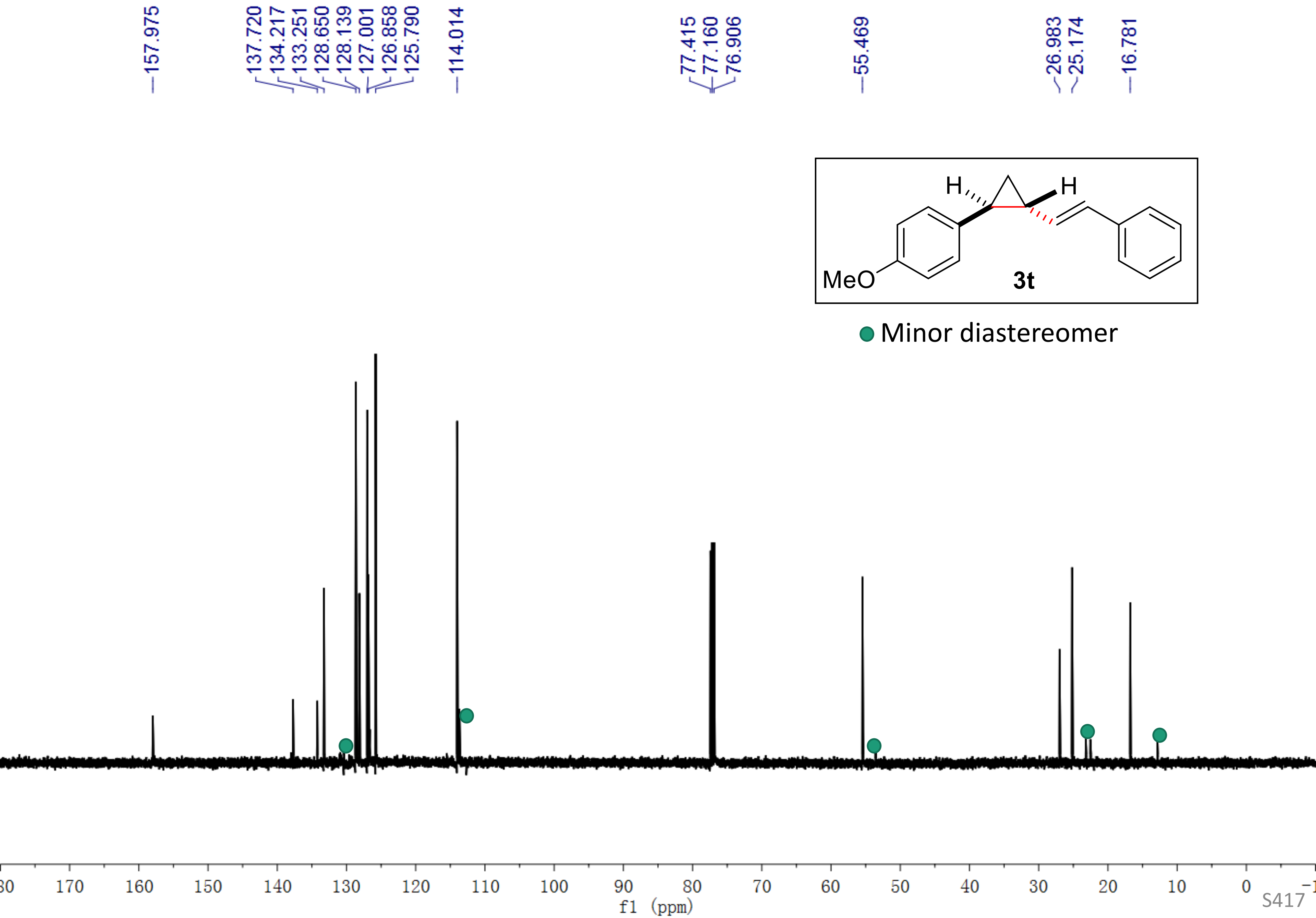
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.865	20057881	86.265
2	15.668	3193545	13.735
Total		23251426	100.000

[1]H NMR of **3t**, 500 MHz, $CDCl_3$



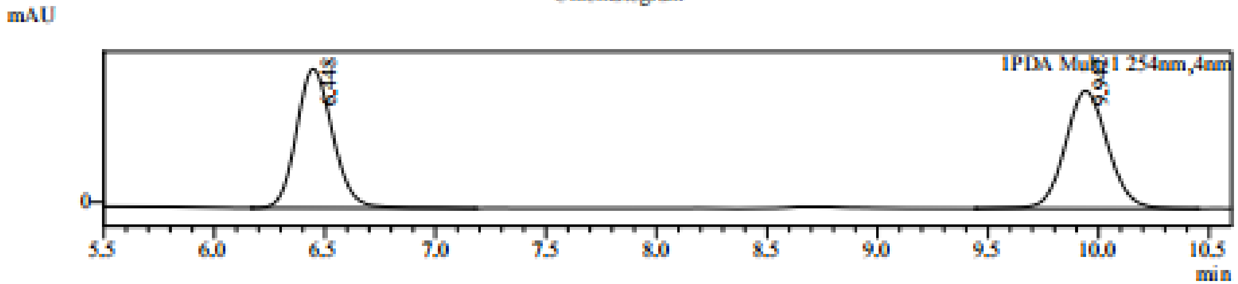
^{1}H NMR of **3t**, 500 MHz, $CDCl_3$



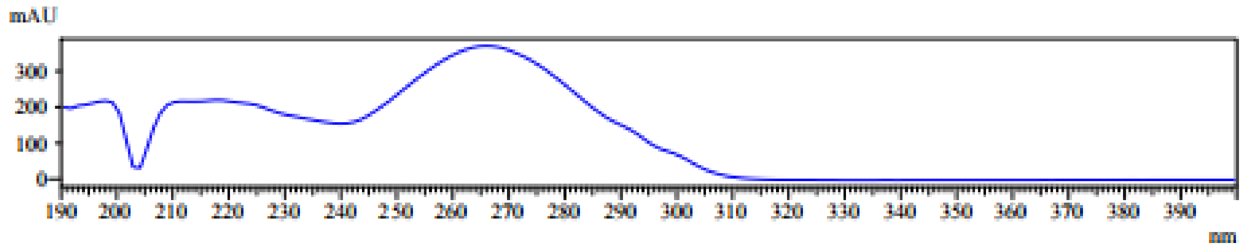
Sample Information

Data File	: J0K-0960-IA-0.8%-1ML.lcd
Sample Name	: J0K-0960-IA-0.8%-1ML
Sample ID	: J0K-0960-IA-0.8%-1ML
Method File	: J0K-0.8%-50min-1ml.lcm

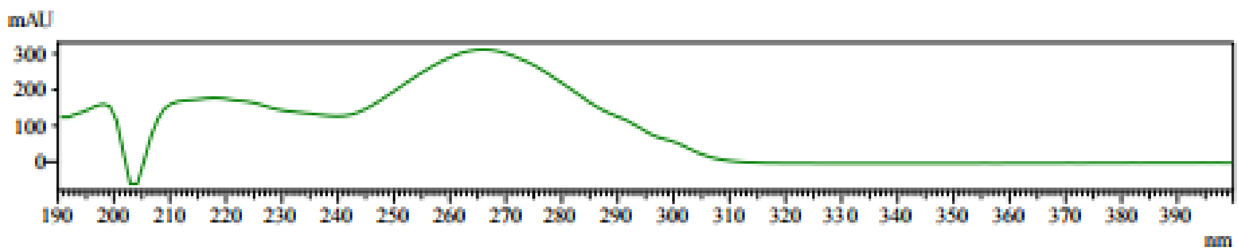
Chromatogram



UV Spectrum
Retention time = 6.448



I
Retention time = 9.942



Peak Table

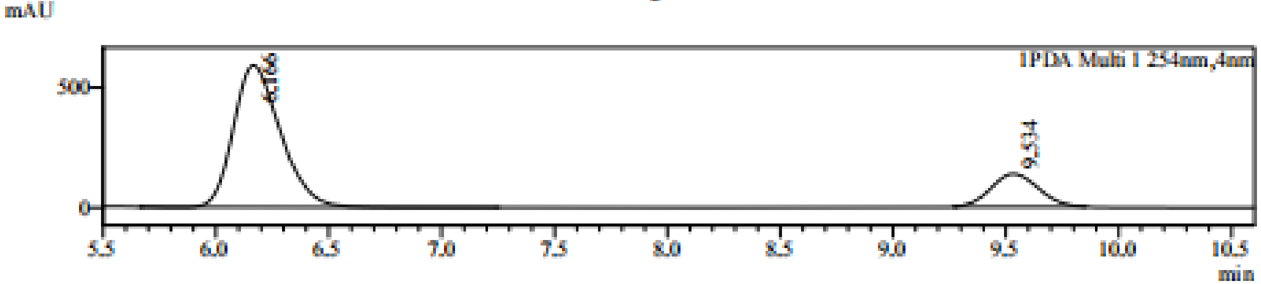
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.448	3390177	50.279
2	9.942	3352501	49.721
Total		6742677	100.000

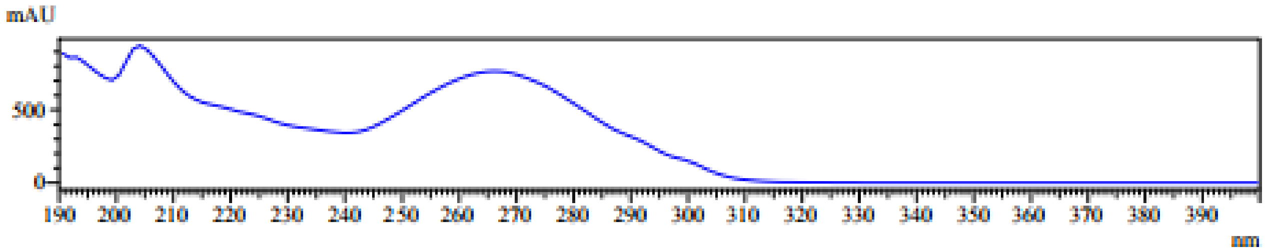
Sample Information

Data File : J0K-0959-IA-0.8%-1ML.lcd
Sample Name : J0K-0959-IA-0.8%-1ML
Sample ID : J0K-0959-IA-0.8%-1ML
Method File : J0K-0.8%-50min-1ml.lcm

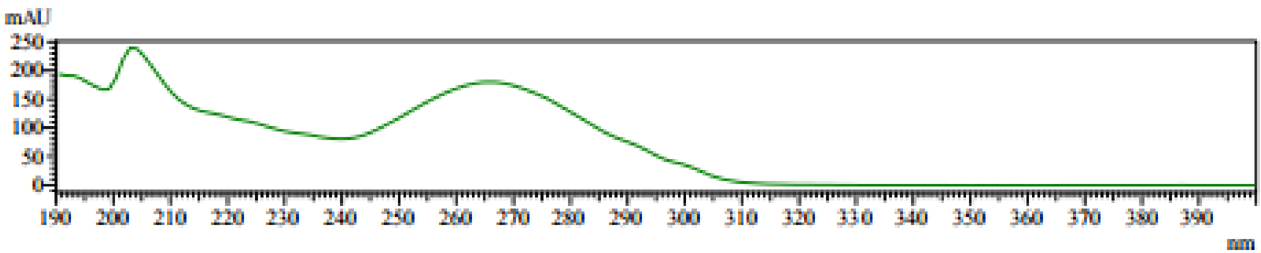
Chromatogram



UV Spectrum
Retention time = 6.166



Retention time = 9.534

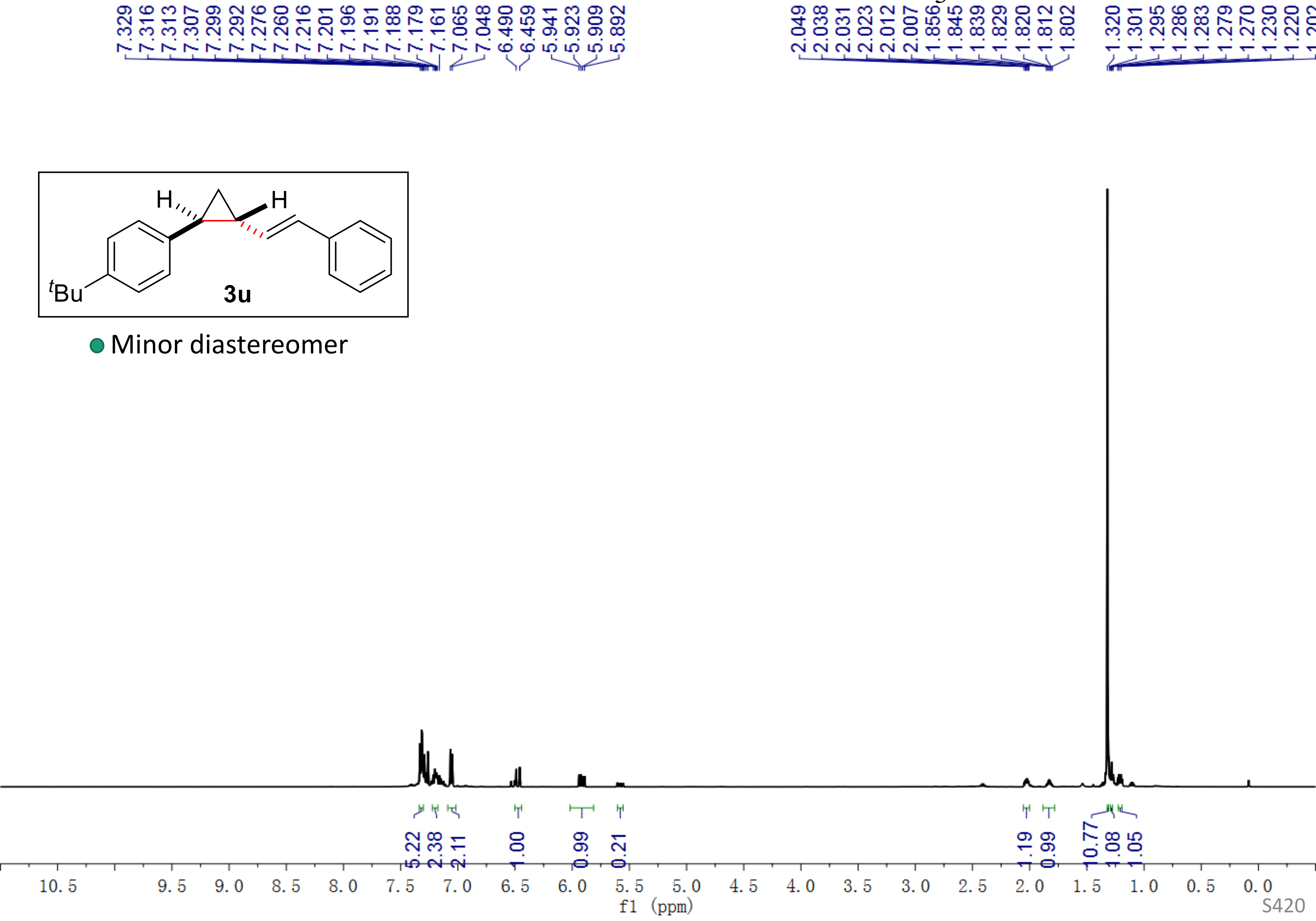


Peak Table

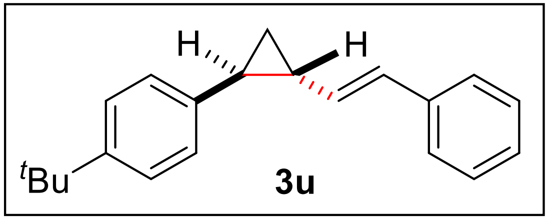
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.166	8498524	80.936
2	9.534	2001735	19.064
Total		10500259	100.000

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

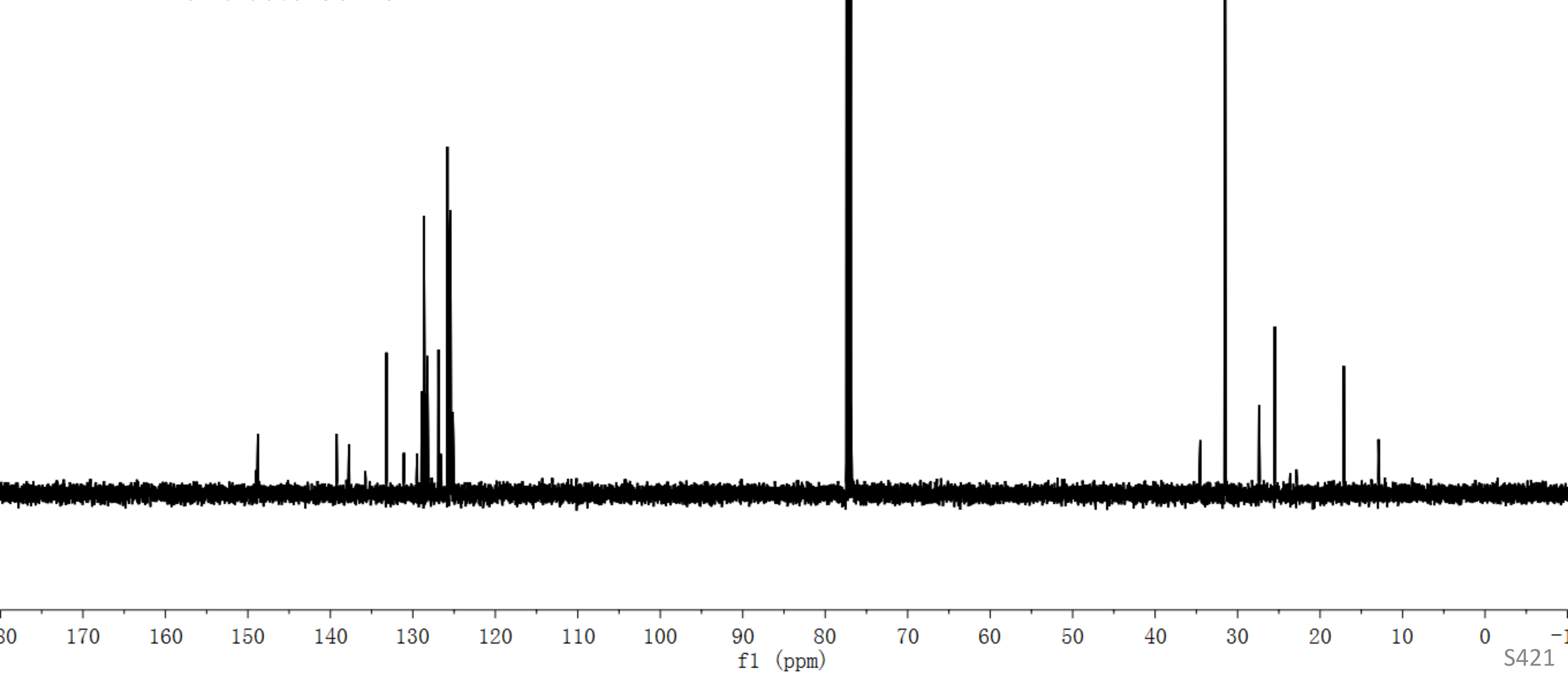


^{13}C NMR of **3u**, 126 MHz, $CDCl_3$



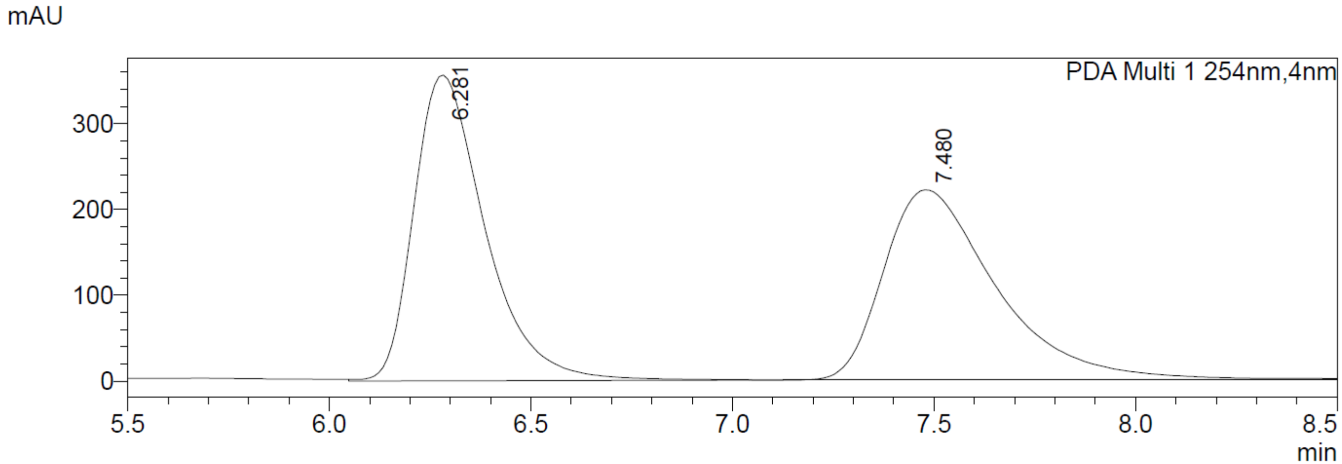
3u

● Minor diastereomer



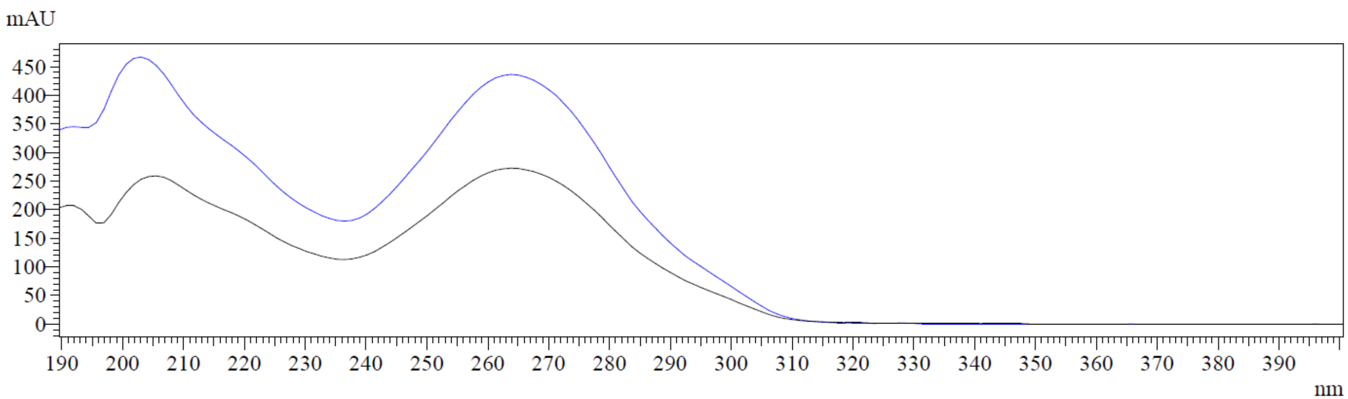
==== Shimadzu LabSolutions Analysis Report ====

JK-1821-ADH-0.2%-0.8mL
JK-0.2%-30min0.8mL.lcm



UV Spectrum

JK-1821-ADH-0.2%-0.8mL_001.lcd



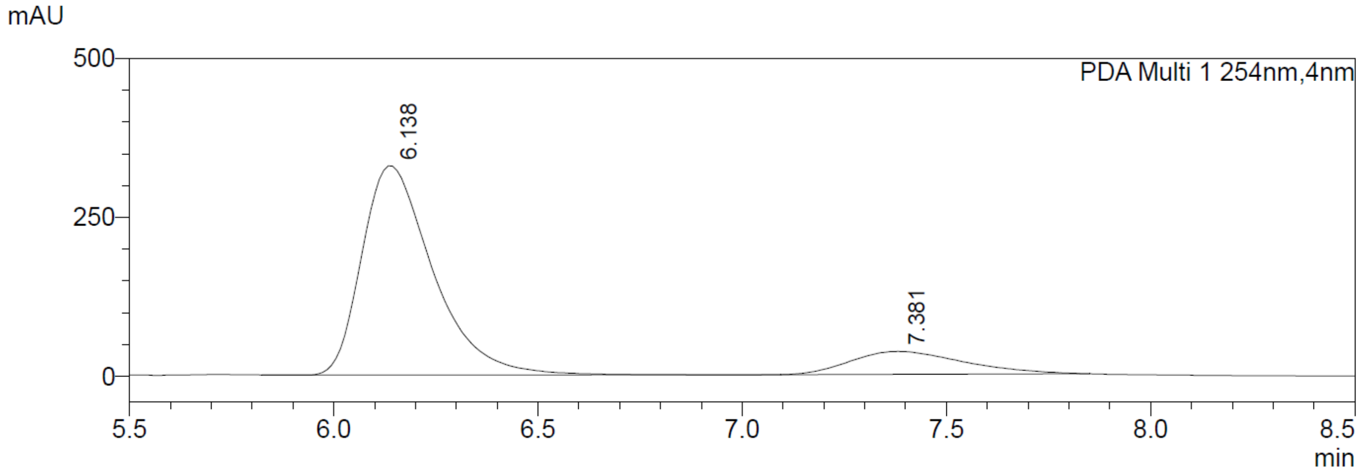
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.281	50.089
2	7.480	49.911
Total		100.000

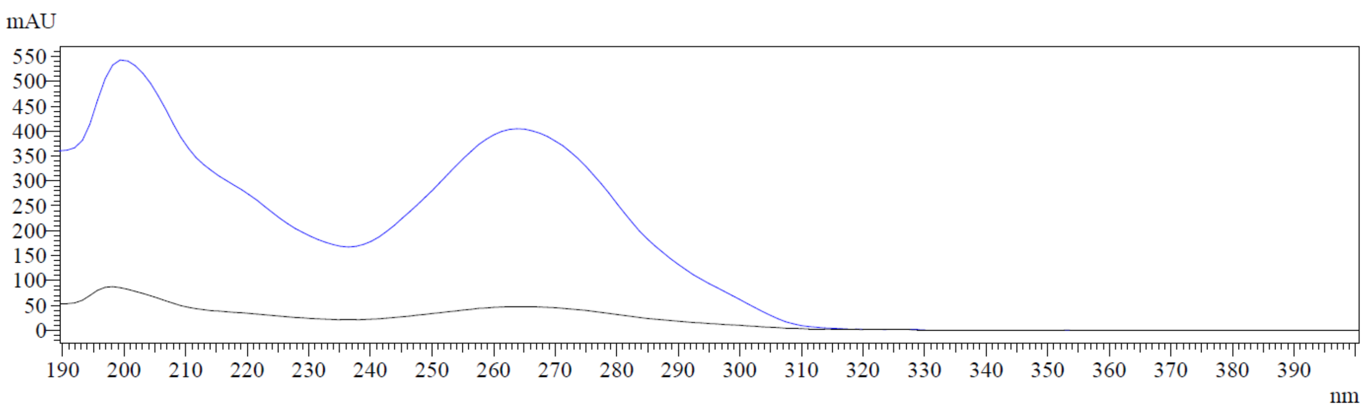
==== Shimadzu LabSolutions Analysis Report ====

JK-1820-ADH-0.2%-0.8mL-2
JK-0.2%-30min0.8mL.lcm



UV Spectrum

JK-1820-ADH-0.2%-0.8mL-2_001.lcd

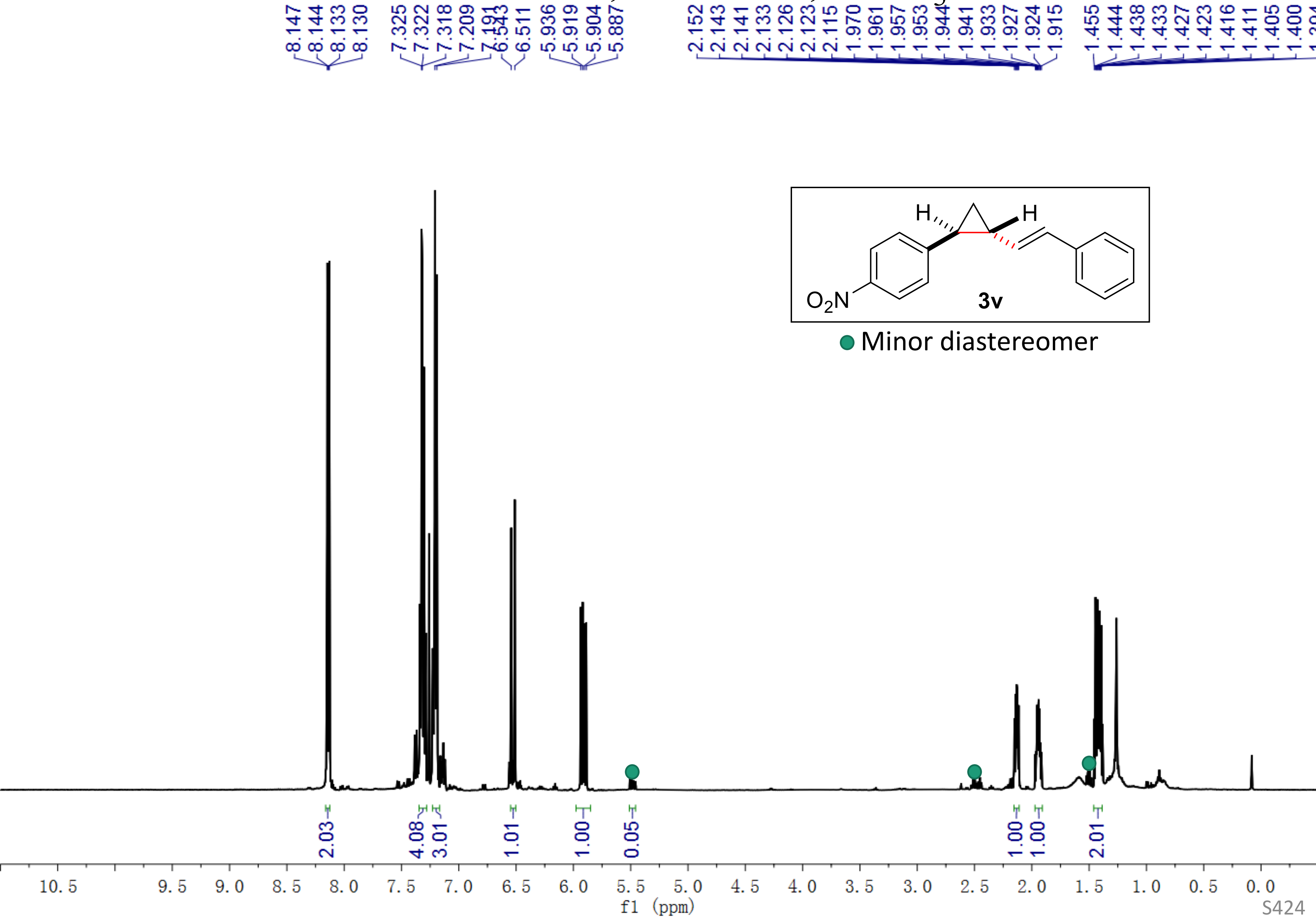


Peak Table

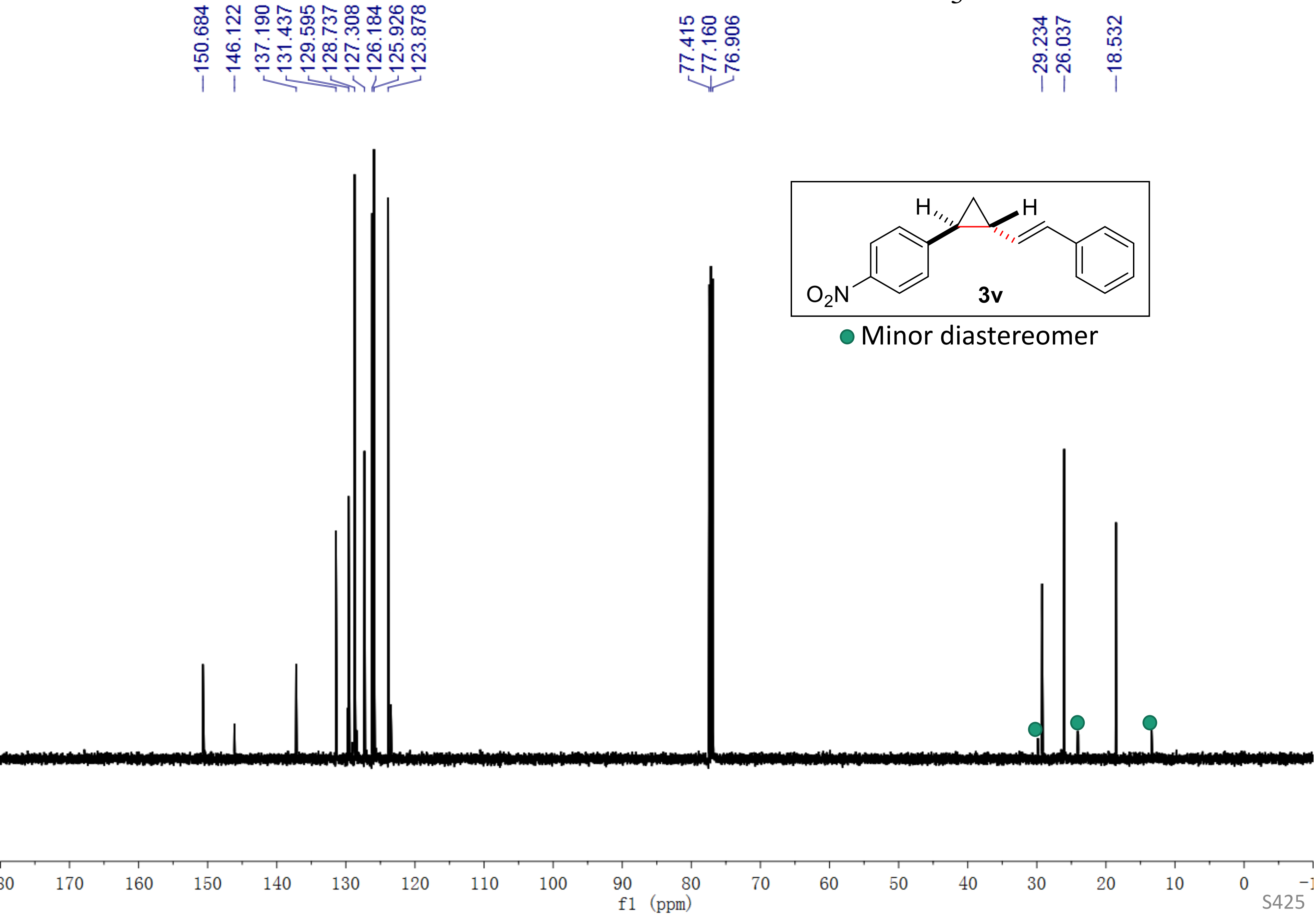
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.138	85.068
2	7.381	14.932
Total		100.000

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

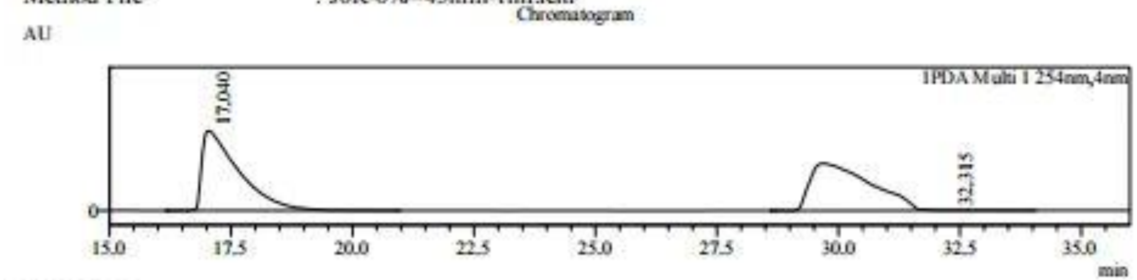


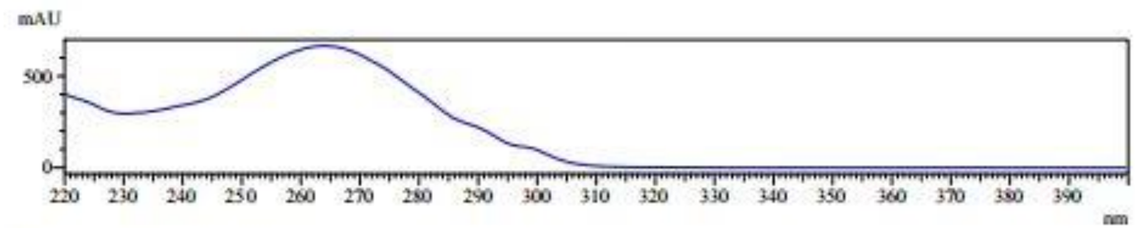
^{13}C NMR of **3v**, 126 MHz, $CDCl_3$

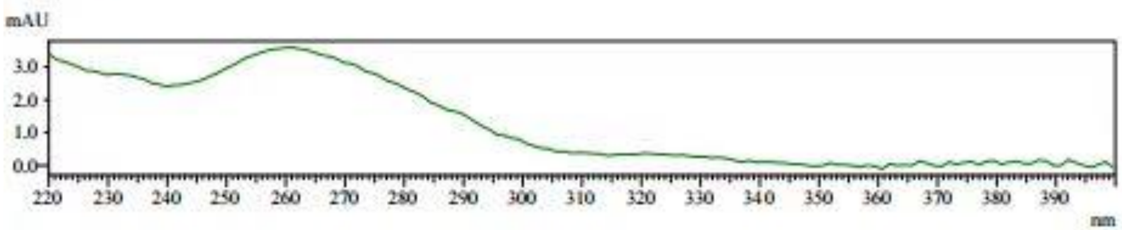


Sample Information

Data File : J0K-1758-2--IA-0%-1ML.lcd
Sample Name : J0K-1758-2--IA-0%-1ML
Sample ID : J0K-1758-2--IA-0%-1ML
Method File : J0K-0%--45min-1ml.lcm







Peak Table

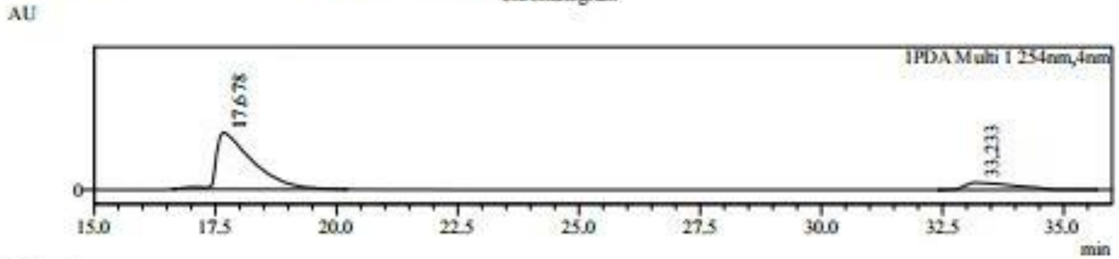
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.040	29454236	50.625
2	32.315	28727119	49.375
Total		58181355	100.000

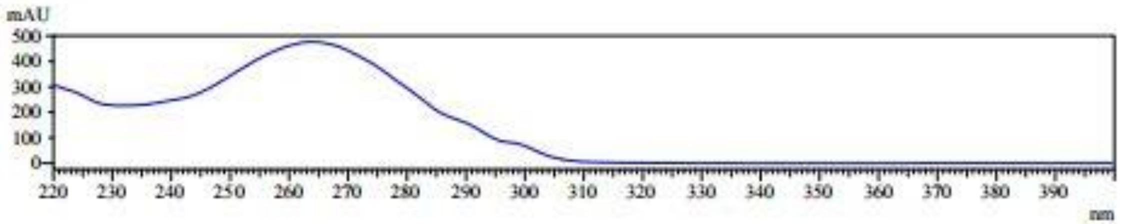
Sample Information

Data File	: J0K-1757--IA-0%-1ML.lcd
Sample Name	: J0K-1757--IA-0%-1ML
Sample ID	: J0K-1757--IA-0%-1ML
Method File	: J0K-0%--45min-1ml.lcm

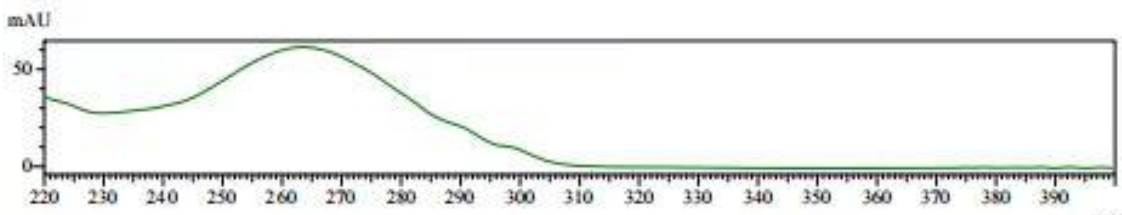
Chromatogram



UV Spectrum
Retention time = 17.678



U
Retention time = 33.233

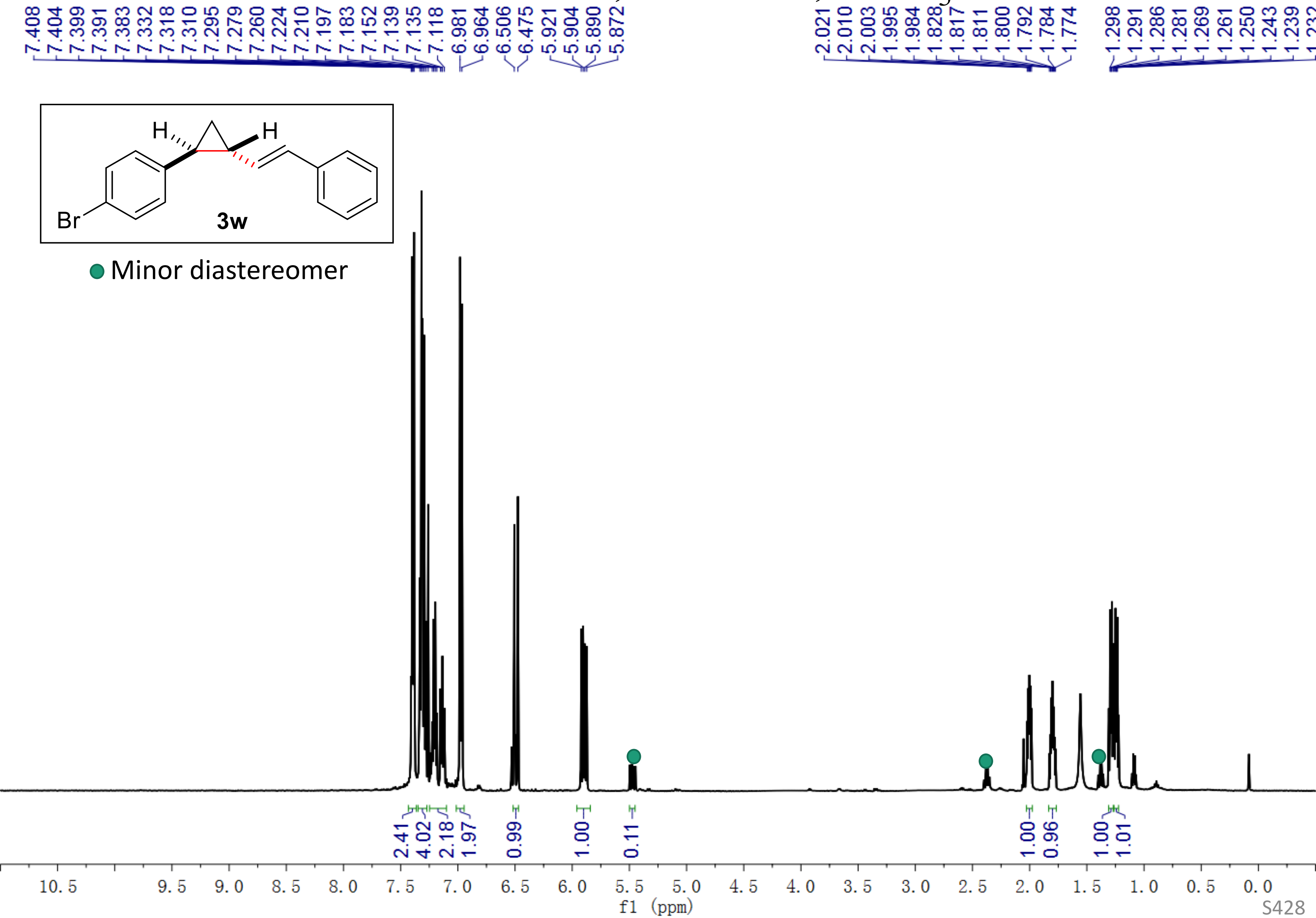


Peak Table

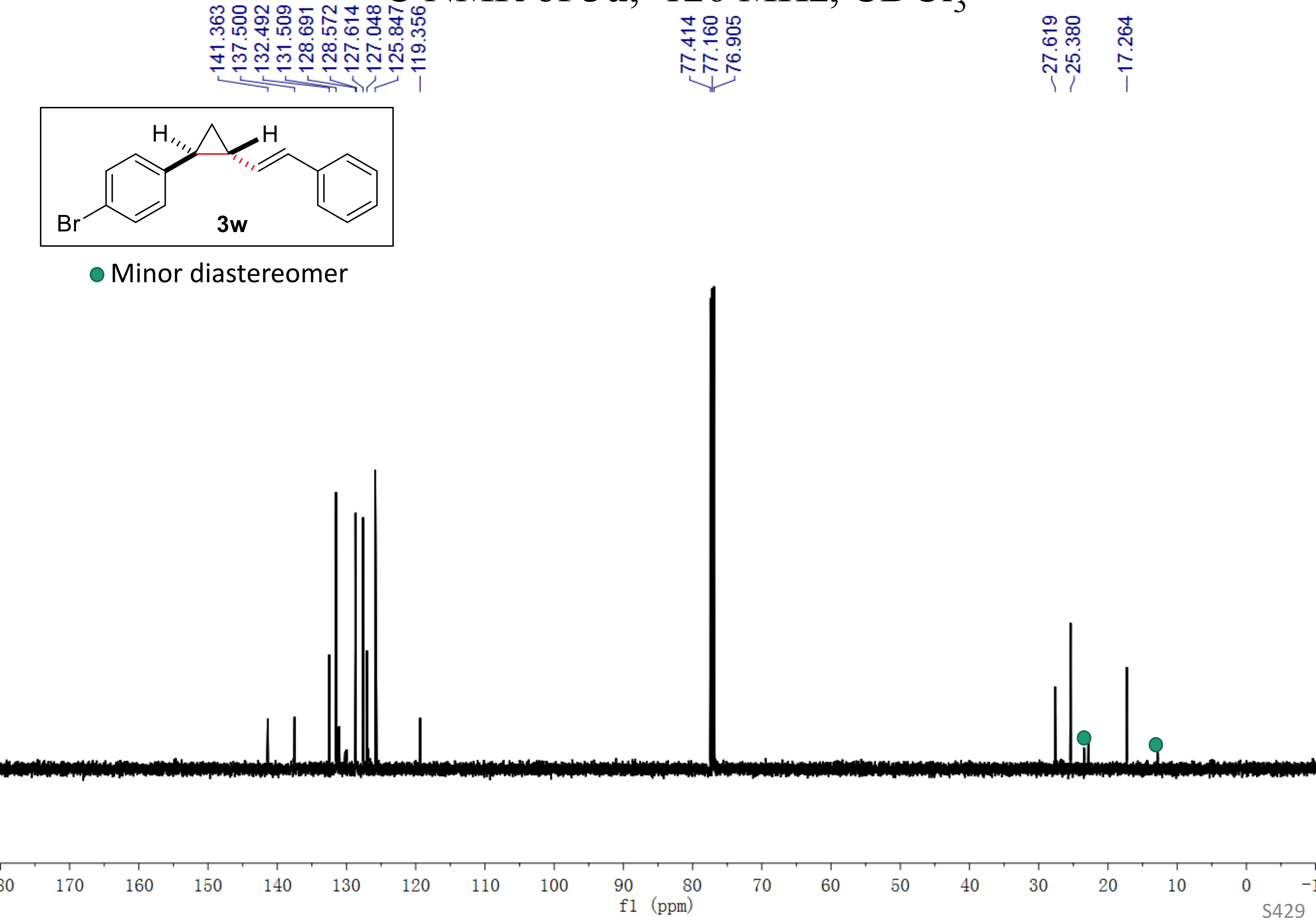
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.678	20742406	85.387
2	33.233	3549702	14.613
Total		24292107	100.000

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



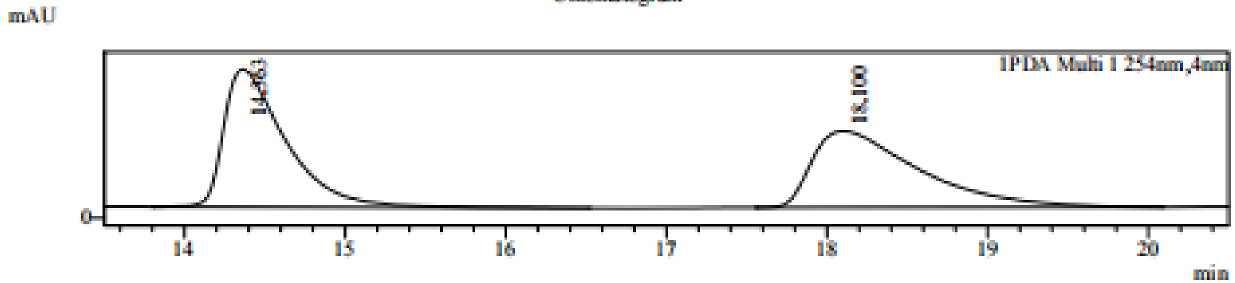
^{13}C NMR of **3u**, 126 MHz, $CDCl_3$



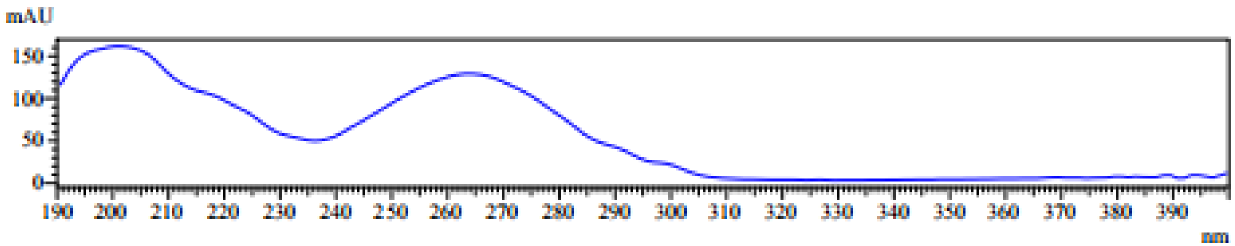
Sample Information

Data File	: J0K-0962-2--IA-0%-0.8ML.lcd
Sample Name	: J0K-0962-2--IA-0%-0.8ML
Sample ID	: J0K-0962-2--IA-0%-0.8ML
Method File	: JK1-0%-0.8ml.lcm

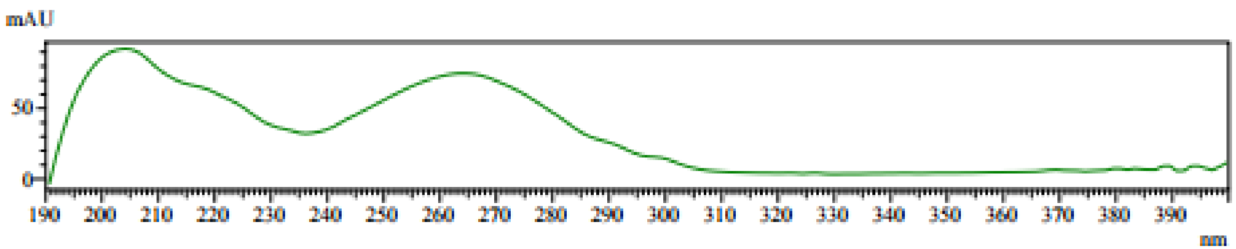
Chromatogram



UV Spectrum
Retention time = 14.363



Retention time = 18.100



Peak Table

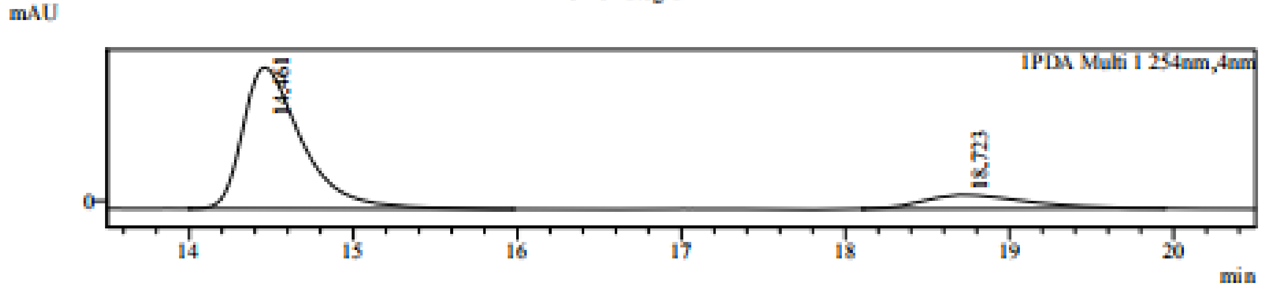
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.363	2705078	51.110
2	18.100	2587546	48.890
Total		5292624	100.000

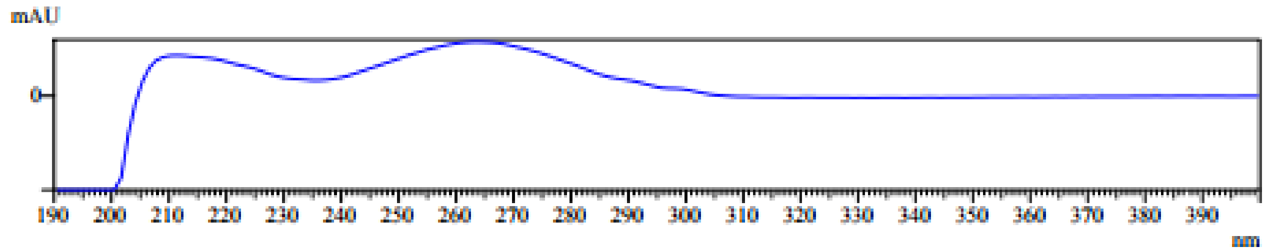
Sample Information

Data File	: J0K-0961-IA-0%-0.8ML.lcd
Sample Name	: J0K-0961-IA-0%-0.8ML
Sample ID	: J0K-0961-IA-0%-0.8ML
Method File	: JK1-0%-0.8ml.lcm

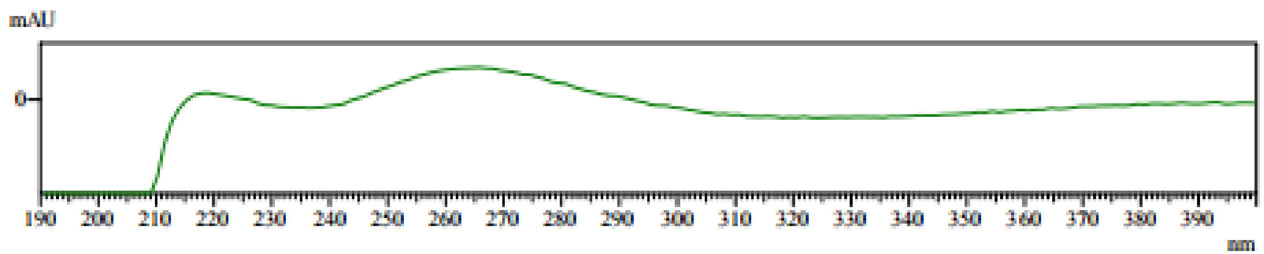
Chromatogram



UV Spectrum
Retention time = 14.461



Retention time = 18.723

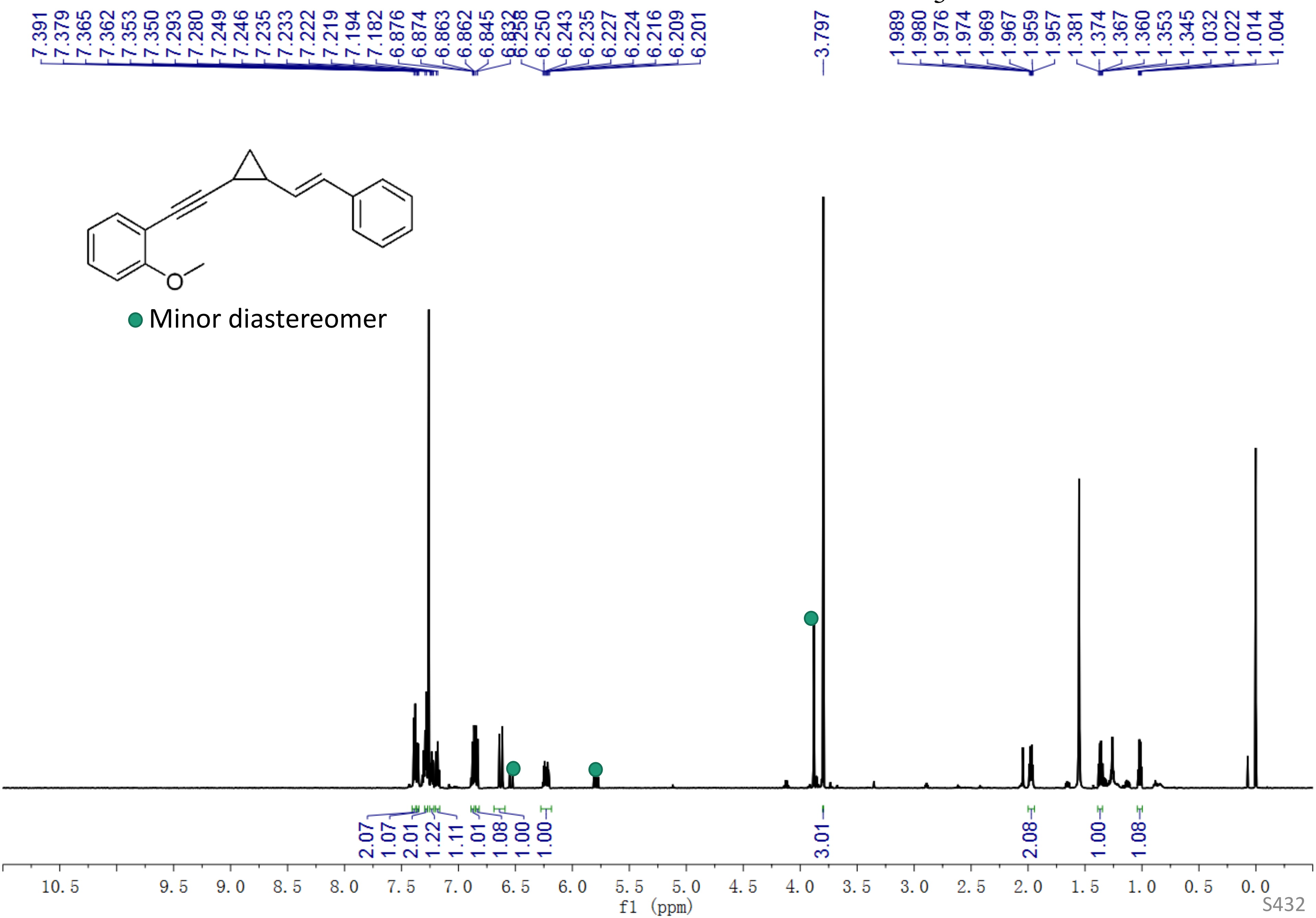


Peak Table

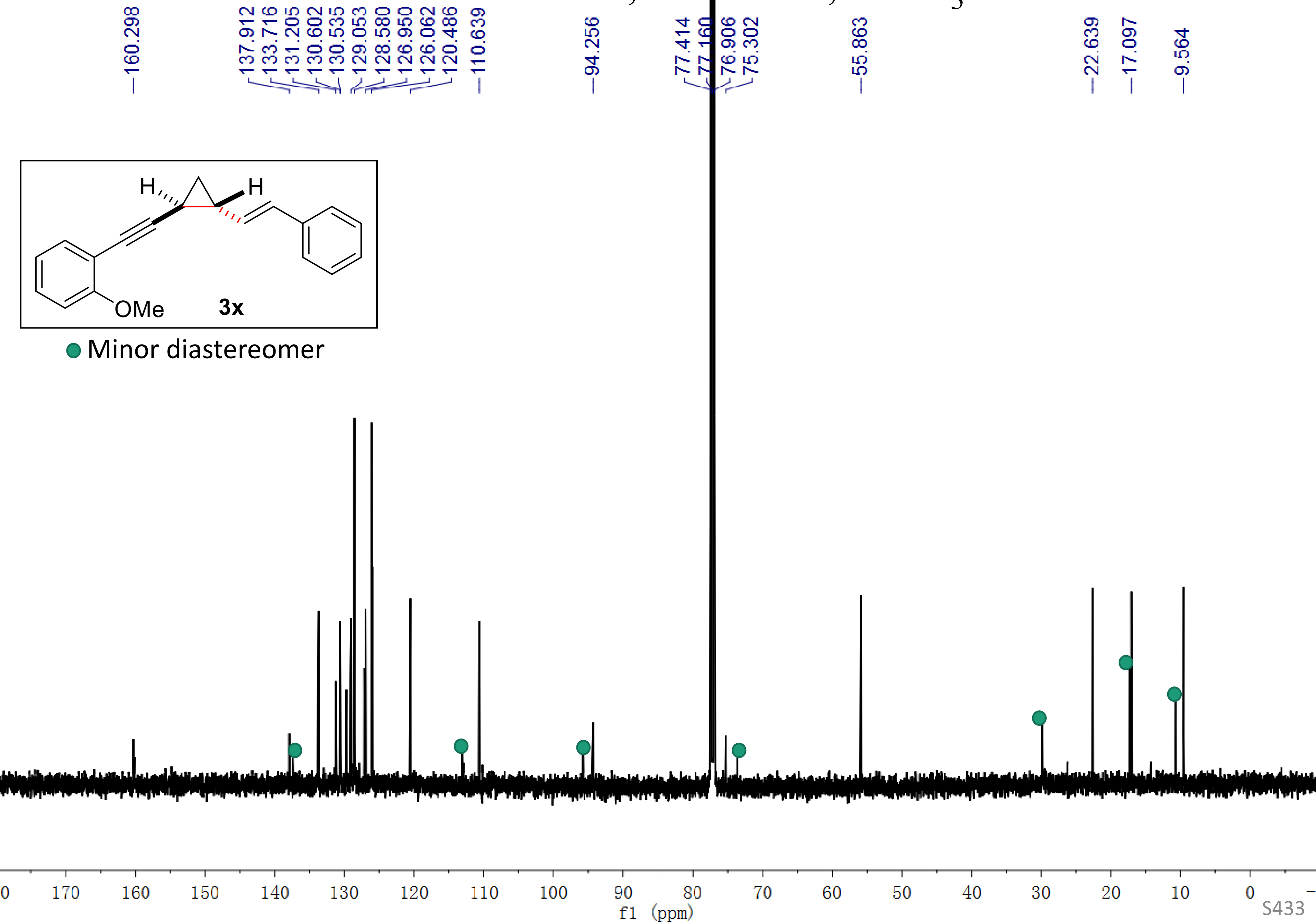
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.461	626571	85.417
2	18.723	106977	14.583
Total		733548	100.000

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



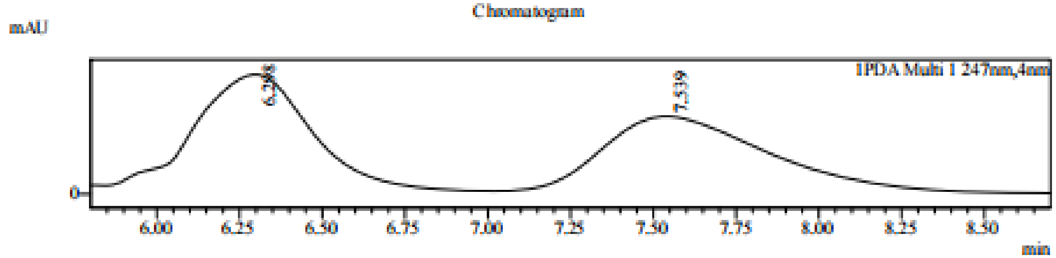
^{13}C NMR of **3x**, 126 MHz, $CDCl_3$



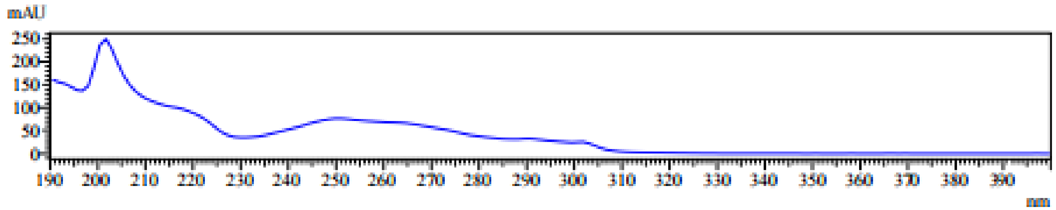
Sample Information

Data File : J0K-0815-2-IA--0.5%-1ML.lcd
Sample Name : J0K-0815-2-IA--0.5%-1ML
Sample ID : J0K-0815-2-IA--0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm

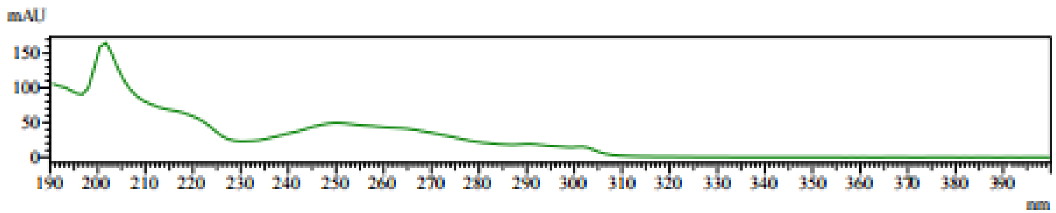
Chromatogram



UV Spectrum
Retention time = 6.298



UV Spectrum
Retention time = 7.539



Peak Table

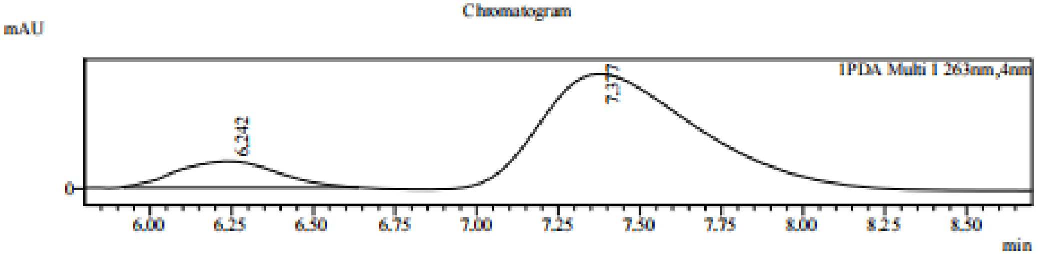
PDA Ch1 247nm

Peak#	Ret. Time	Area	Area%
1	6.298	1605529	50.998
2	7.539	1542705	49.002
Total		3148235	100.000

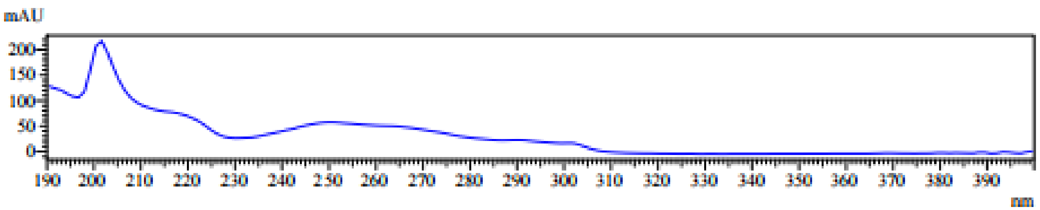
Sample Information

Data File : J0K-0814-2-IA--0.5%-1ML.lcd
Sample Name : J0K-0814-2-IA--0.5%-1ML
Sample ID : J0K-0814-2-IA--0.5%-1ML
Method File : J0K-0.5%--35min-1ml.lcm

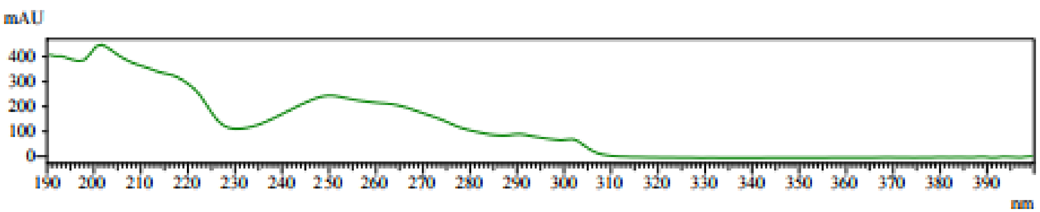
Chromatogram



UV Spectrum
Retention time = 6.242



UV Spectrum
Retention time = 7.377

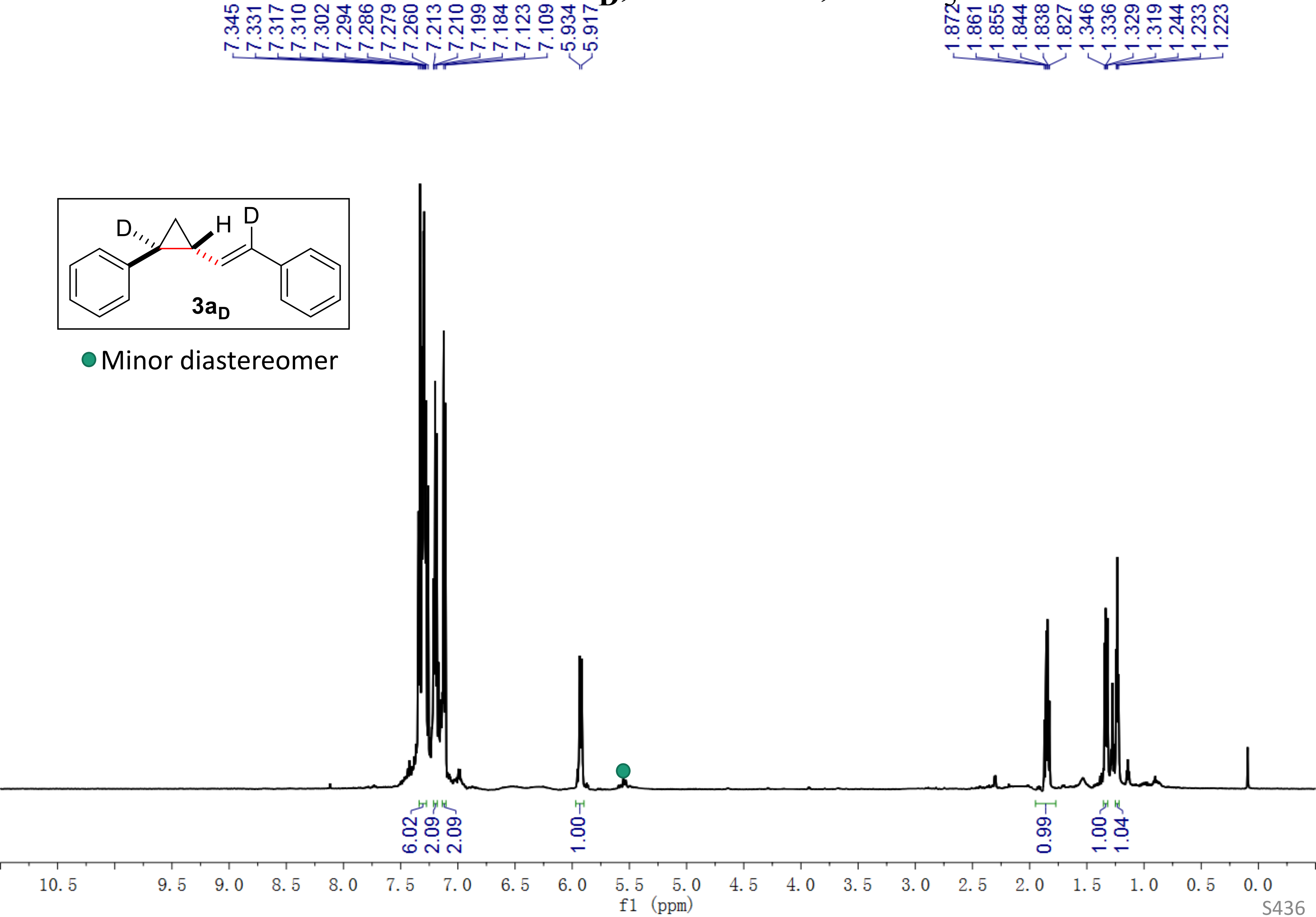


Peak Table

PDA Ch1 263nm

Peak#	Ret. Time	Area	Area%
1	6.242	1035543	12.840
2	7.377	7029629	87.160
Total		8065173	100.000

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



^{13}C NMR of **$3a_D$**, 126 MHz, $CDCl_3$