Stereoselective Radical Cascade Cyclizations via Co(II)-Based Metalloradical Catalysis

By

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Advisor: Professor X. Peter Zhang

This dissertation will present three projects focusing on the development of stereoselective radical cascade reactions via metalloradical catalysis (MRC) using Co(II) D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] as the catalyst. The first project demonstrated the feasibility of applying MRC for asymmetric radical cascade processes by achieving an enantioselective radical bicyclization of 1,6-enynes with diazo compounds, which constructed multi-substituted cyclopropane-fused tetrahydrofurans bearing three contiguous stereogenic centers and one trisubstituted alkene. Detailed mechanistic studies including EPR studies and DFT calculation unveiled a radical-based stepwise mechanism. The synthetic utility of this reaction was demonstrated by a series of diastereoselective transformations of the bicyclic products. In the second project, this strategy was expanded to the application of Co(II)-based MRC to catalyze radical cascade reactions involving hydrogen-atom abstraction (HAA) process. A broad array of homopropargyl ethers reacted with diazo compounds to generate enantiomerically enriched α,β-disubstituted tetrahydrofurans in good yields with high diastereoselectivities and enantioselectivities. The third project explored the utilization of the established strategy to accomplish more challenging bicyclization of 1,6,8-dienynes for the construction of cycloheptadiene-fused tetrahydrofurans in regio- and diastereoselective fashions. Such 5,7-fused ring system has been widely found in natural products and bioactive species.

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DEDICATED TO:

I dedicate this dissertation to my parents, my sister and my husband for unconditional love, care, guidance and lifelong sacrifice to make me who I am.

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TABLE OF ABBREVIATIONS

Å: angstrom

Ac: acetate

acac: acetylacetonate

aq: aqueous

Ar: aryl

Bn: benzyl

Boc: tert-butoxycarbonyl

Boc_2O: di-tert-butyldicarbonate

BOX: bis(oxazoline)

Bpin: pinacolatoboryl

COD: cyclooctadiene

DABCO: 1,4-diazabicyclo[2.2.2]octane

DART: direct analysis in real time

DCE: dichloroethane

DCM: dichloromethane

DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzo

de: diastereomeric excess

DFT: density functionaltheory

DMAP: 4-dimethylaminopyridine

DME: Dimethoxyethane

DMF: dimethylformamide

DMSO: dimethyl sulfoxide

dr: diastereomeric ratio

DTBP: 2,6-Di-*tert*-butyl-pyridine

dtbpy: 4.4'-Di-*tert*-butyl-2,2'-dipyridyl

ee: enantiomeric excess

EPR: electron paramagnetic resonance

hex_F: tetradecafluorohexane

HP: high-power

HPLC: high performance liquid chromatography

HRMS: high resolution mass

IMes: 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene

i-Pr: *iso*-propyl

IR: infrared spectroscopy

KIE: kinetic isotope effect

L: ligand

LED: light-emitting diode

LG: leaving group

M: molar or metal

M.S.: molecular sieves

Me: methyl

MeO: methoxy

Mes: mesityl

MRC: metalloradical catalysis

NMR: nuclear magnetic resonance

Ph: phenyl

Por: porphyrin

ppy: 2-pheynylpyridine

RA: radical addition

RT: room temperature

SET: single electron transfer

SiO_2: silica gel

SOMO: singly occupied molecular orbital

^{t}Bu: *tert*-butyl

eq: equation

equiv: equivalent(s)

er: enantiomeric ratio

es: enantiospecificity

ESI: electrospray ionization

Et: ethyl

EtOAc: ethyl acetate

HAA: hydrogen-atom abstraction

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

Tf: triflate

TFA: trifluoroacetic acid

THF: tetrahydrofuran

TMS: trimethylsilyl

TOF: time of flight

TPP: tetraphenyl porphyrin

VCP: vinylcyclopropane

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

CHAPTER 1

RECENT ADVANCES IN ENANTIOSELECTIVE RADICAL CASCADE REACTIONS

1.1. INTRODUCTION

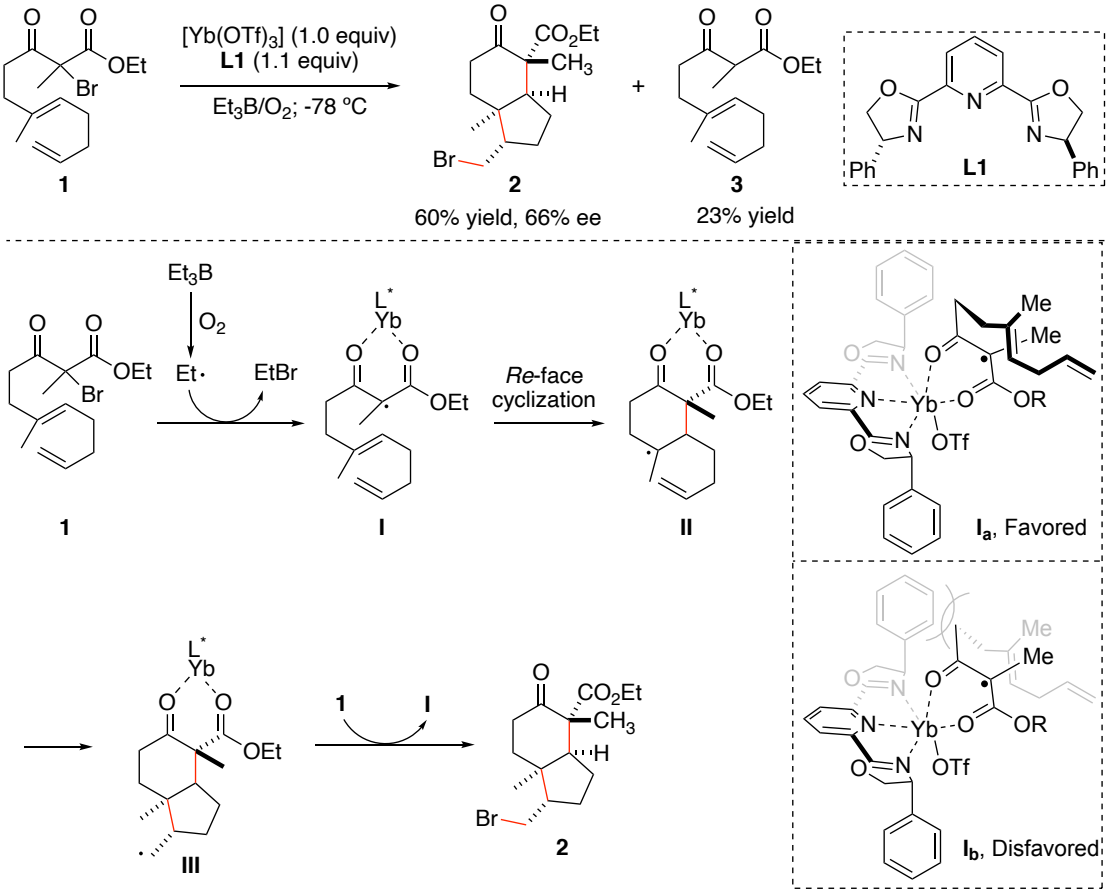
Over the past few decades, radical reactions elicited more and more attention from organic chemists. In comparison with polar reactions, radical reactions display several unique advantages including robust reactivity, excellent functional group tolerance and weakened influence from electronic properties.[1] Cascade reactions, also called domino reactions or tandem reactions, involve cleavage or formation of multiple bonds in a single operation.[2] As a result, this type of reaction can effectively reduce the time, cost and amount of waste produced during the synthesis of complex molecules. Combining the merits from both sides, radical cascade reactions exhibit high potency in modern synthetic organic chemistry.[3] However, the commonly high reactivity and low reaction barriers of radical species render the development of enantioselective radical cascade reactions challenging. Recently, advances in modern organic chemistry have led to key breakthroughs in the field of asymmetric radical cascade reactions. In this chapter, recent advances of enantioselective radical cascade reactions are summarized based on the chiral auxiliaries employed, which include chiral Lewis acids, small organic molecule catalysts and transition metal complexes. Radical/polar crossover type cascade reactions involving only one step of radical process will not be included in this review.[4]

1.2. CHIRAL LEWIS ACID

In 2002, Yang and coworkers reported the first example of enantioselective tandem radical cyclization by utilizing chiral Lewis acids as chiral auxiliaries (Scheme

1.1).[5] Optimal results were obtained by using $Yb(OTf)_3$/PyBox(**L1**) complex, where α-bromo β-keto ester **1** underwent enantioselective bicyclization successfully to furnish **2** in 60% yield and 66% ee. The Yb complex was proposed to chelate with the carbonyl groups of the ester and ketone. After the radical process initiated by Et_3B/O_2 through homolytic cleavage of C–Br bond in substrate **1**, intermediate **I** could undergo *6-endo-trig* cyclization to form a more stable tertiary radical intermediate **II** (comparing with the secondary radical intermediate generated from *5-exo-trig* cyclization). To minimize steric repulsion between the alkyl chain of the substrate and the phenyl groups of the ligand, the *Re*-face cyclization was favored over the *Si*-face cyclization (Scheme 1.1, $\mathbf{I_a}$ vs $\mathbf{I_b}$). After that, primary radical intermediate **III** was generated through a *5-exo-trig* cyclization,

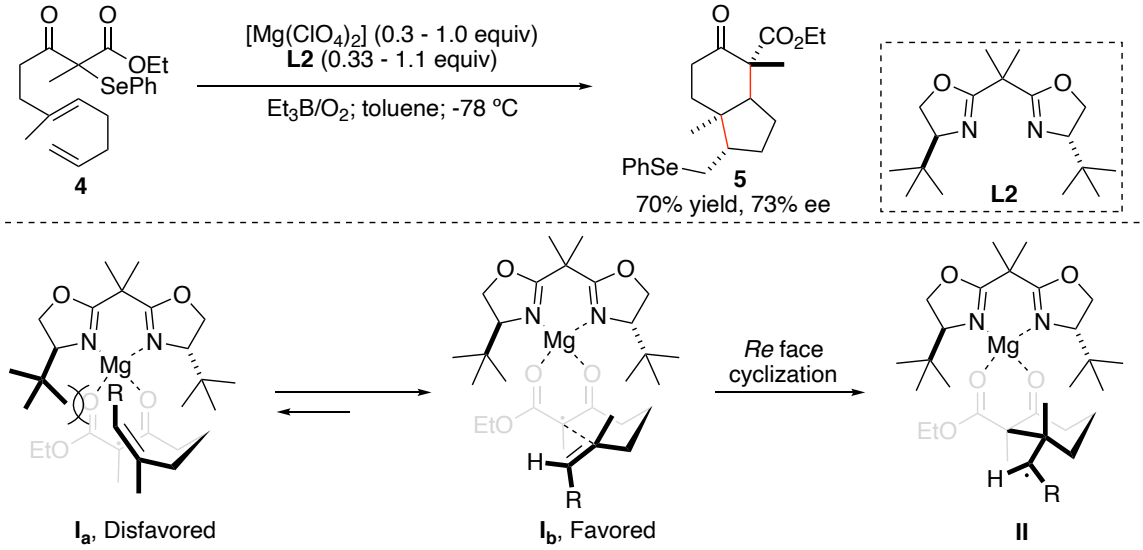
Scheme 1.1. Enantioselective Bromine Atom-Transfer Tandem Radical Cyclization



which could further abstract the bromine atom from substrate **1** to produce the desired bicyclization product **2**.

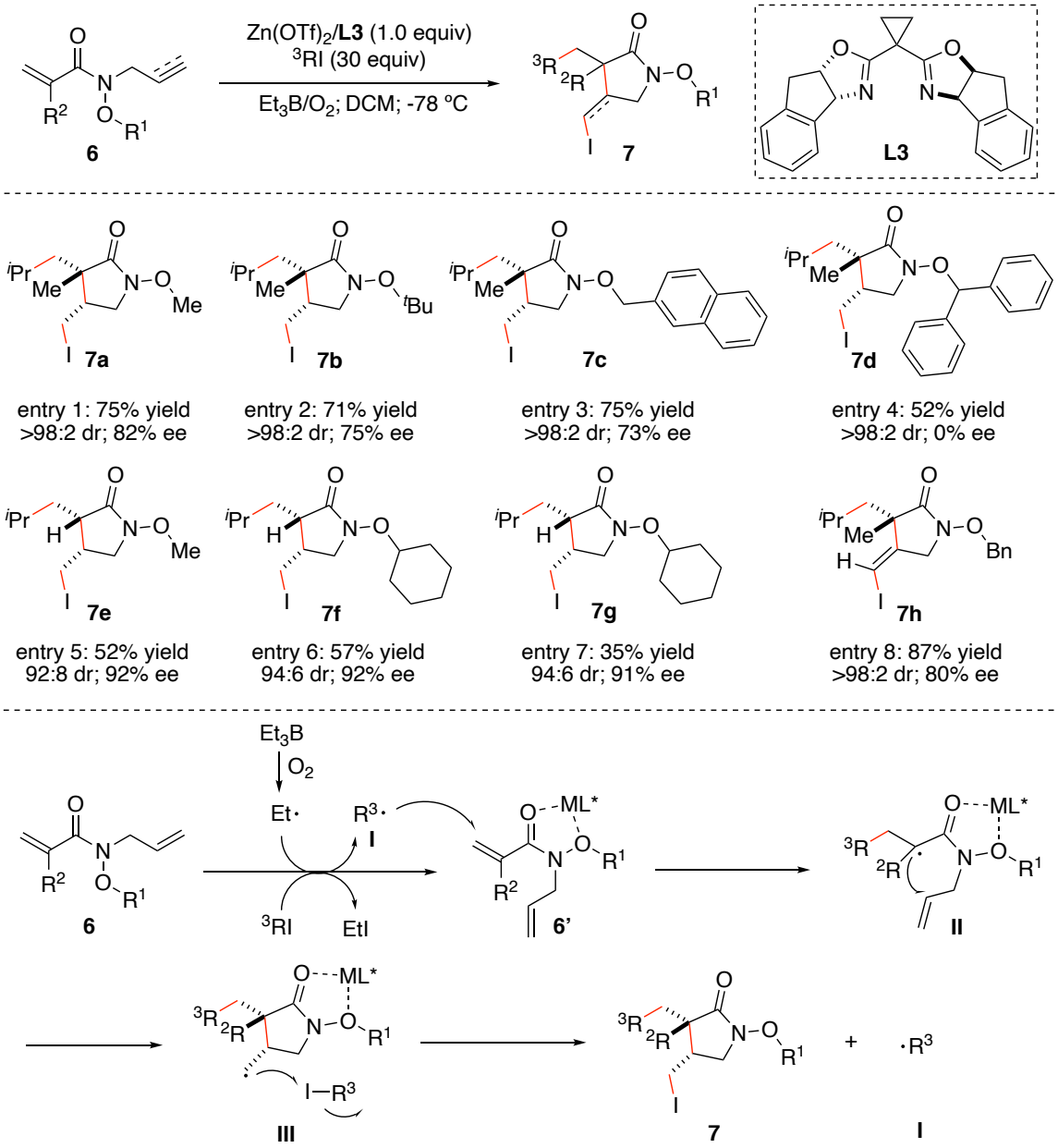
After their pioneering work, the same group also reported the first enantioselective group-transfer radical cyclization reaction of unsaturated α-phenylseleno-β-ketoesters **4** (Scheme 1.2).[6] In this case, Et_3B/O_2 serving as the radical initiator to cleave the C–Se bond, the newly generated radical intermediate **I** would go through two successive radical cyclization processes and abstract the PhSe group to give the bicyclic product **5** in high yield (up to 70%) and high levels of enantioselectivity (up to 91% ee). Different from the aforementioned bromine atom-transfer reaction, the most effective Lewis acid is chiral $Mg(ClO_4)_2$/**L2** complex. Due to the coordination of the dicarbonyl moiety of substrate **4** to the chiral catalyst, the olefin moiety would prefer to approach the radical center from the *Re* face (Scheme 1.2, $\mathbf{I_b}$) to avoid steric interactions with the α-*tert*-butyl group (Scheme 1.2, $\mathbf{I_a}$).

Scheme 1.2. Enantioselective PhSe-Group-Transfer Tandem Radical Cyclization



In 2006, Hideto and co-workers disclosed an enantioselective radical cascade addition-cyclization-trapping reaction of hydroxamate esters **6** (Scheme 1.3).[7] This process represents the first enantioselective radical cascade reaction involving both inter- and intramolecular C–C bond-forming processes, where three bonds and multiple stereogenic centers were constructed. After exploring a wide variety of Lewis acids and chiral ligands, $Zn(OTf)_2$ and **L3** were identified as the optimal combination for the generation of chiral γ-lactams **7**. A variety of R^1 groups were tested in the catalytic reaction. Interestingly, the size of the R^1 group plays an essential role in enantioselectivity (**7a–d**). The observed diminishment of enantioselectivity associated with sterically hindered R^1 could be due to the difficulty in generating a rigid 5-membered ring intermediate through the chelation of the substrate with the chiral Lewis acid. Moreover, reactions of acrylate substrates (R^2 = H, **7e–g**) gave excellent levels of enantioselectivity, while the lower yield is due to the polymerization through the acrylamide moiety. Enyne type substrate **6h** was also investigated and provided the corresponding product **7h** with high enantioselectivity. The high *Z*/*E* selectivity of compound **7h** indicated that the iodine atom-transfer process is extraordinarily efficient. It is proposed that the key to achieving high enantioselectivity in this process is the control of the rotamer population of the amide in **6** (**s-*cis*** vs **s-*trans***). After being initiated by Et_3B/O_2, the newly formed carbon-centered radical **I** could react with the stable five-membered chelation compound **6'**. The pre-rigidified radical intermediate **II** could further undergo *5-exo-trig* cyclization to deliver primary radical **III**. Finally, an iodine atom-transfer process from R^3I to primary radical intermediate **III** furnished the desired product **7**.

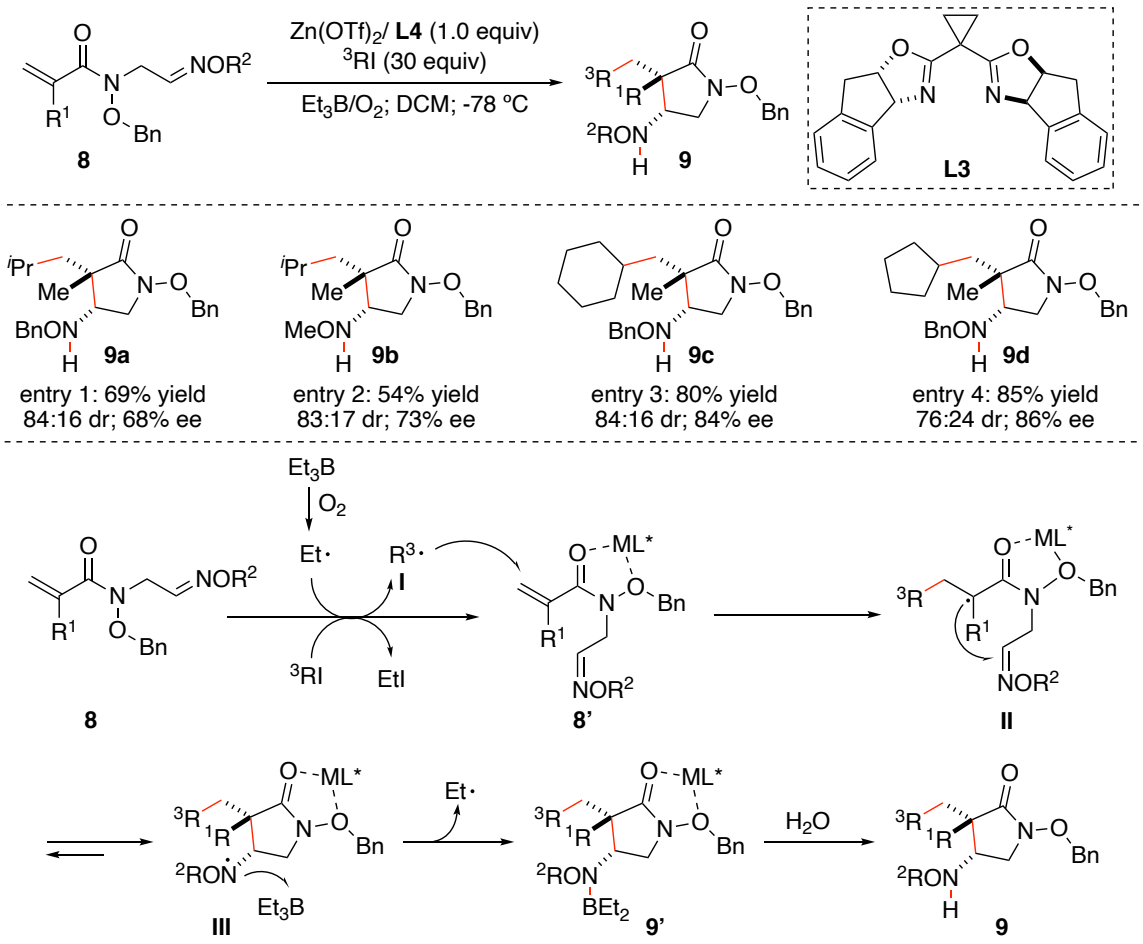
Scheme 1.3. Enantioselective Radical Cascade Addition-Cyclization-Trapping Reactions of Hydroxamate Esters



In 2007, the same group described an enantioselective radical cascade addition-cyclization of oxime ethers, which involved the utilization of C–N double bonds as radical acceptors (Scheme 1.4).[8] By utilizing hydroxamate ester as a coordinating site with a chiral Lewis acid complex, chiral γ-lactam products were obtained in up to 91%

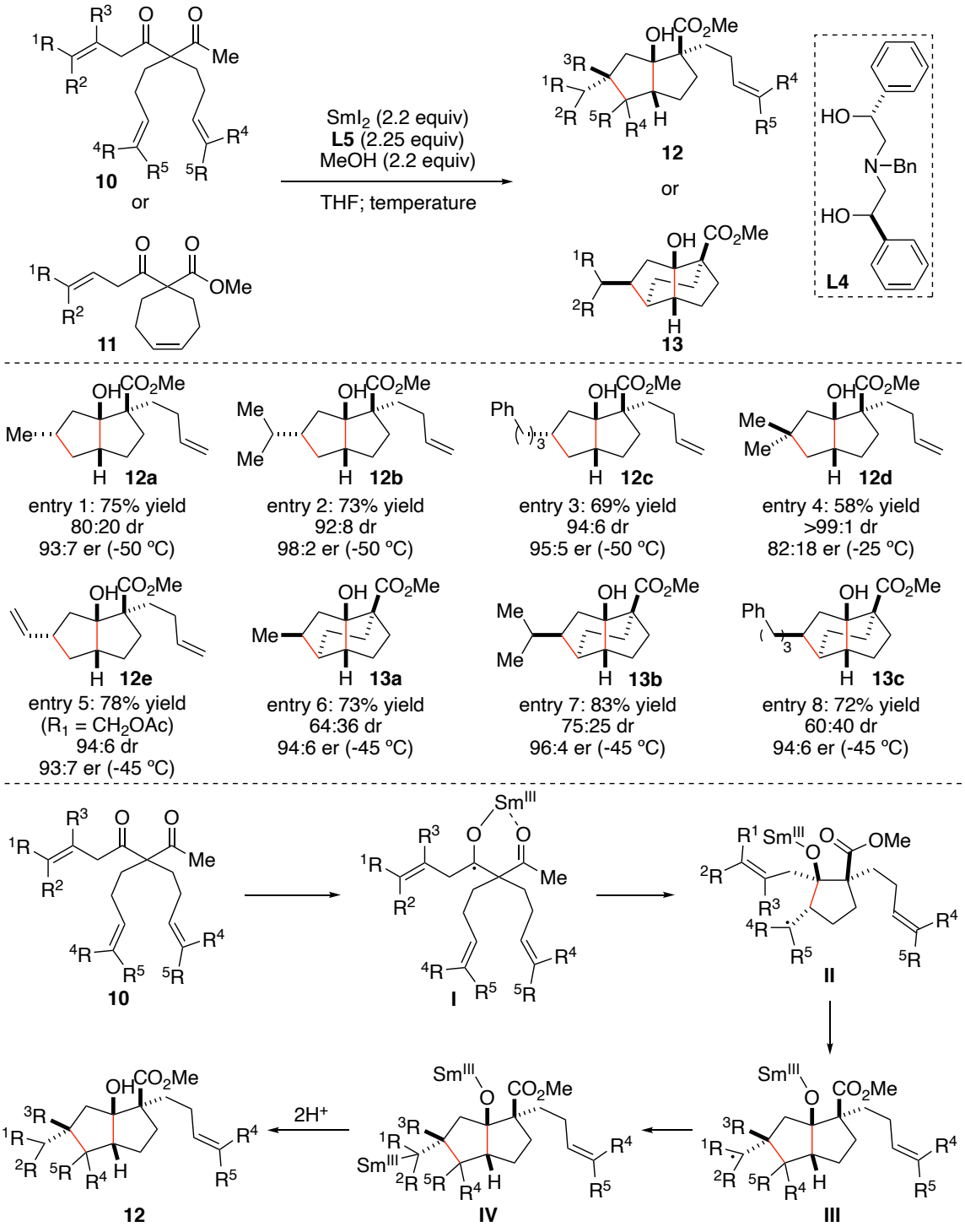
yield with up to 93:7 dr and up to 86% ee. In this reaction, Et_3B not only works as a radical initiator but also serves to propagate the radical chain reaction by generating ethyl radical after reacting with aminyl radical intermediate **III** to give compound **9'**. It is worth noting that diminished enantioselectivity was observed with elongated reaction time, which could be due to a reversible process between intermediates **II** and **III** caused by the slow trapping of aminyl radical by Et_3B.

Scheme 1.4. Enantioselective Radical Cascade Addition-Cyclization of Oxime Ethers



Instead of using chiral Lewis acids solely for chelation with the substrates, the Procter group introduced a novel strategy, where chiral Sm(II) complexes function as both radical initiators and chiral auxiliaries for an enantioselective radical cascade

Scheme 1.5. Enantioselective Desymmetrization of Dienyl β-Ketoesters



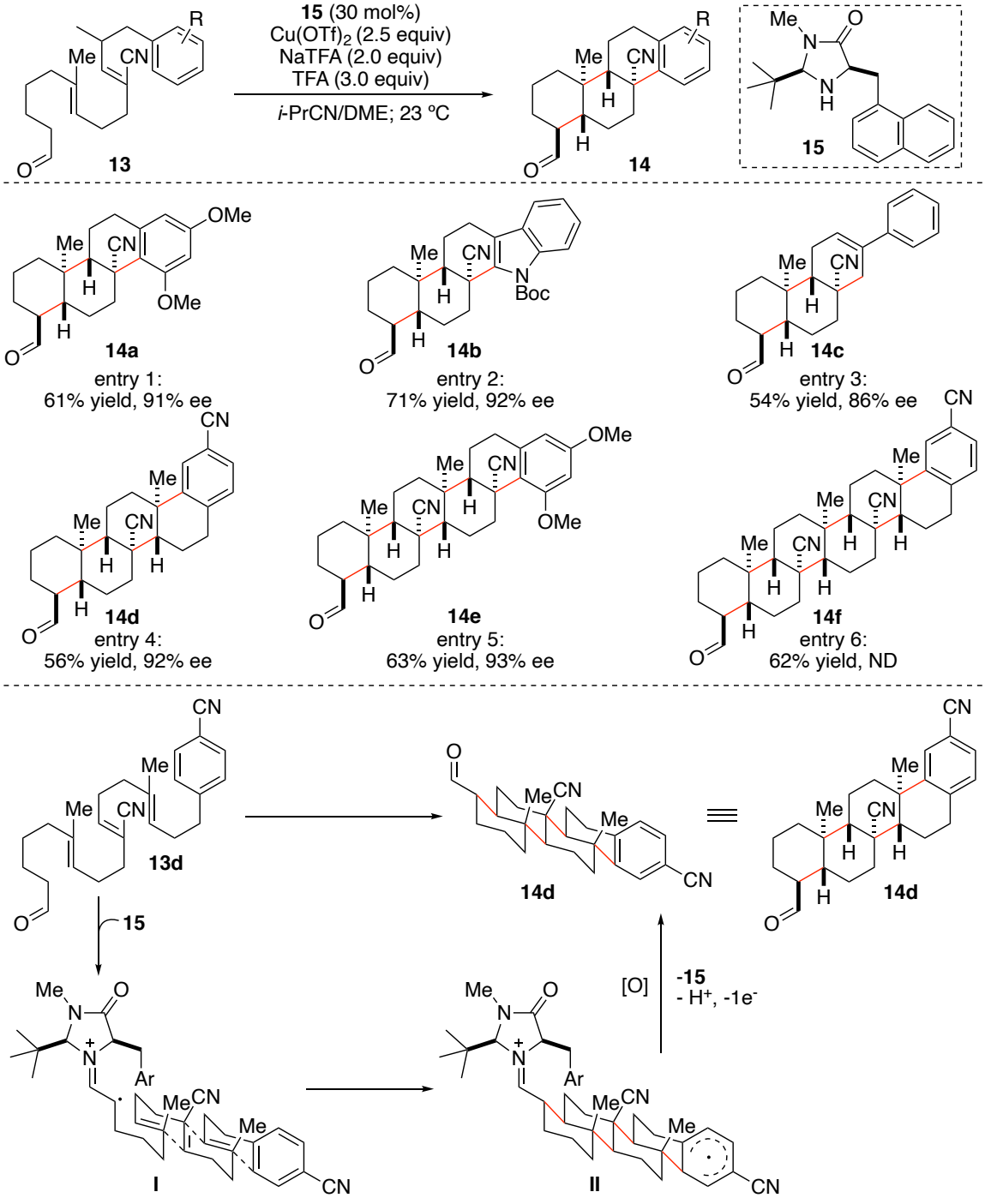
desymmetrization of dienyl β-ketoesters (Scheme 1.5).[9] Allyl ketones **10a**–**10e** were mediated by chiral Sm(II) reagent to provide the corresponding bicyclic all-carbon

scaffolds in good yield with good to excellent diastereo- and enantioselectivity. More complex cycloheptene substrates **13a**–**13c** were also competent in constructing the tricyclic products with high enantioselectivity while only moderate control of diastereoselectivity was obtained. In this reaction, chiral Sm(II) reagents could first reduce the starting material under single electron transfer (SET) to deliver chelated Sm(III) ketyl radical intermediate **I**, which could further undergo enantiotopic-group-selective *5-exo-trig* cyclization. The newly formed carbon-centered radical **II** could then go through a second *5-exo-trig* cyclization to afford intermediate **III**, which is further reduced by another equivalent of Sm(II) reagent to generate **IV**. Finally, the protonation of **IV** furnishes the desired product. The utilization of an achiral proton source, such as methanol, showed significant beneficial effects for enantioselectivity. It is proposed that the achiral proton source could act as a sacrificial proton donor during the protonation of intermediate **IV** so that the integrity of the tridentate chiral aminodiol ligand **L4** could be preserved. It could also serve as a spectator ligand for Sm(II) or Sm(III) center to affect the coordination chemistry and the chiral environment.

1.3. SMALL ORGANIC MOLECULE CATALYST

In recent years, organocatalysts have emerged as a new class of reagents that can promote enantioselective radical cascade reactions, which are challenging to realize in their absence. Pioneering work was reported by the MacMillan group, where they described a novel application of singly occupied molecular orbital (SOMO) catalysis to polyene cyclization for the enantioselective construction of steroidal and terpenoidal analogs (Scheme 1.6).[10] Imidazolidinone **15** was identified as the optimal chiral catalyst that could condense with the aldehydes to form enamine intermediates. Such species

Scheme 1.6. Enantioselective Polyene Cyclization via Organo-SOMO Catalysis

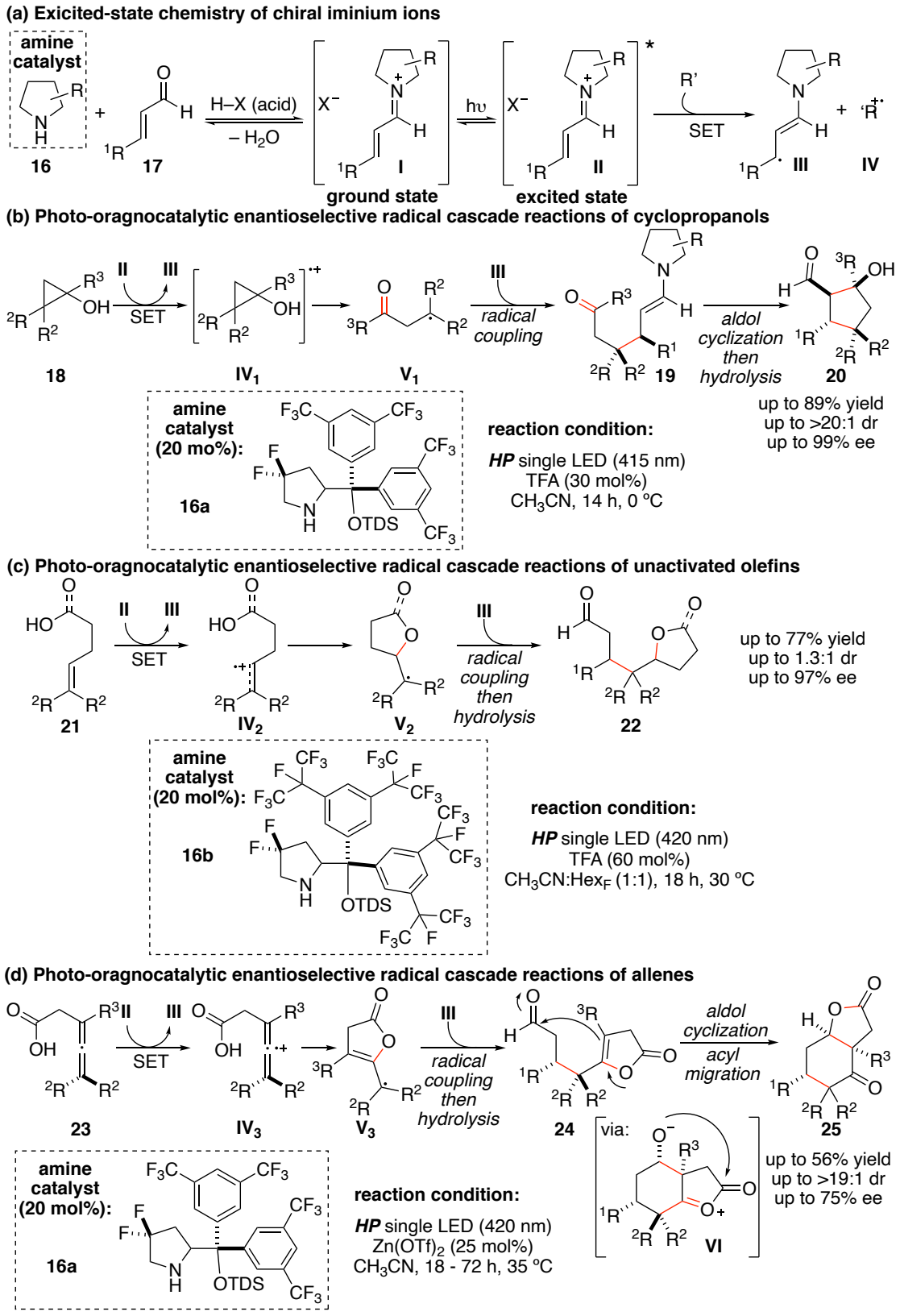


could be oxidized by $Cu(OTf)_2$ to generate α-imino radical intermediate **I**. The newly formed radical cation **I** would undergo a series of *6-endo-trig* radical cyclization, which will be terminated by arenes to furnish the cyclohexadienyl radical intermediate **II**.

Finally, a second oxidation step would occur to deliver the corresponding cyclohexadienyl cation, which could be deprotonated by NaTFA and rearomatize to give the desired multi-cyclized products. It was found that the slow addition of the oxidant significantly improved the yield of the desired products. A wide range of aryl substitutions were well tolerated under the optimized conditions (**14a**–**14b**). Moreover, a 1,1-disubstituted styrene type aldehyde is also suitable for the catalytic system to furnish **14c**. It is worth noting that the radical cyclization strategy via organo-SOMO catalysis could be extended to tetra-, penta- and hexacycles ring systems with high efficiency and excellent diastereo- and enantioselectivity (**14d**–**14f**). The stereochemistry of this reaction was proposed to be controlled in a way that the polyene chain is oriented away from the bulky *tert*-butyl substituent (as shown in intermediate **I**) and the aryl moiety on the catalyst framework could effectively shield the *Si* face of the carbon-centered radical, leaving the *Re* face exposed to the proximal trisubstituted alkene.

Later on, Melchiorre's group reported a series of enantioselective photo-organocatalytic cascade reactions (Scheme 1.7).[11] The cascade processes are initiated by the condensation of a chiral amine catalyst **16** with α,β-unsaturated aldehyde **17** to generate the iminium ions intermediate **I**. Then, selective excitation with high-power (HP) LED could bring the intermediate **I** into an electronically excited state **II**, which could later trigger the formation of $R^{\bullet+}$ with different radical precursors through single electron transfer (SET) (Scheme 1.7a). Specifically, the first radical precursor utilized was cyclopropanols **18**. Because of the high ring-strain energy of the cyclopropyl ring, intermediates $\mathbf{IV_1}$ could undergo rapid ring opening to afford β-keto radicals $\mathbf{V_1}$. Later stereocontrolled radical coupling between $\mathbf{V_1}$ and chiral allylic radical **III** would occur to

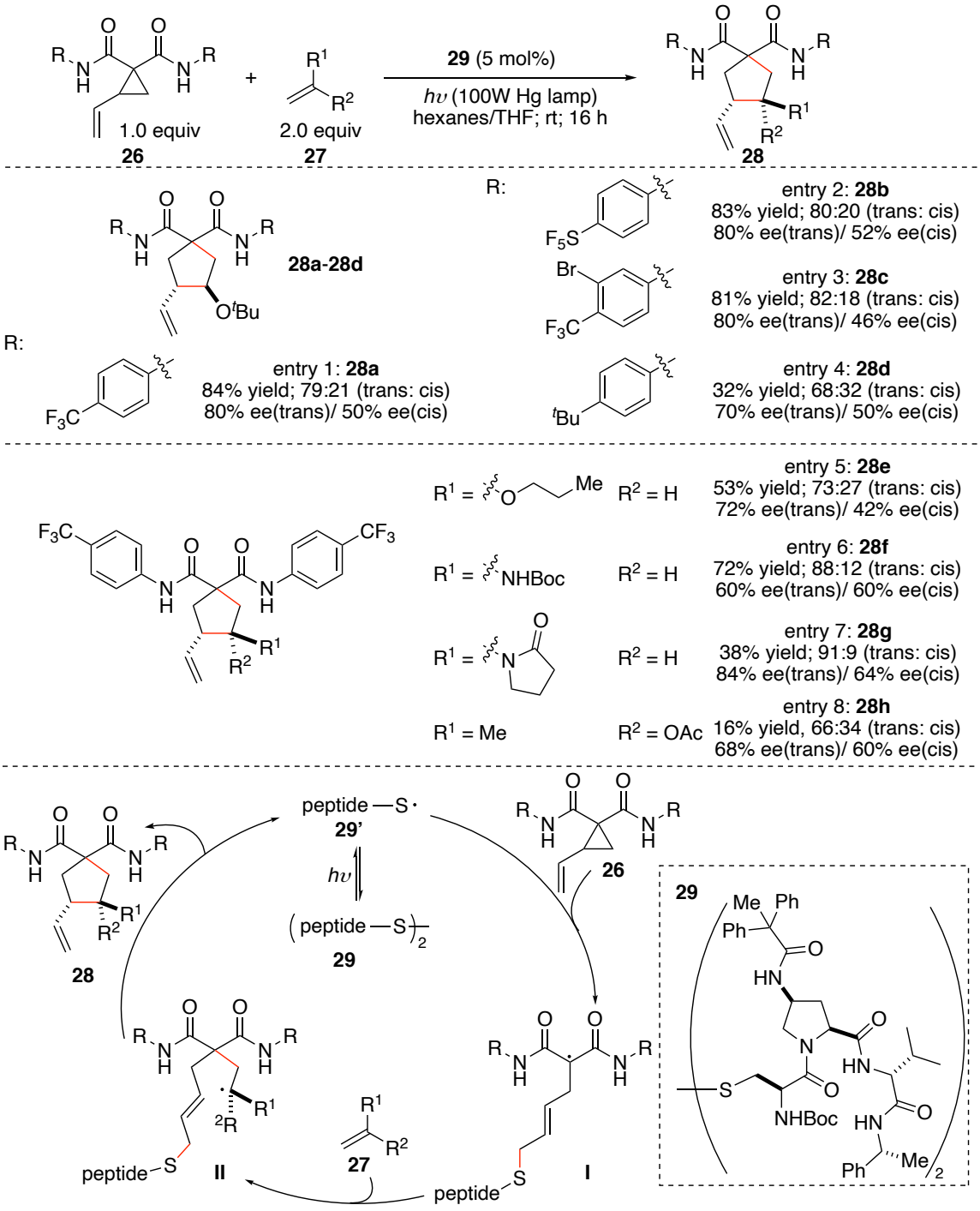
Scheme 1.7. Photo-Organocatalytic Enantioselective Radical Cascade Reactions



form the compound **19**, which would undergo an intramolecular aldol cyclization to give the product **20** in up to 89% yield, up to >20:1 dr and up to 99% ee (Scheme 1.7b). Following the initial discovery, they further applied the visible-light-mediated organocatalytic strategy to unactivated olefins **21**. The acid moiety within intermediate $\mathbf{IV_2}$ would proceed through an anti-Markovnikov addition to afford more stable radical intermediate $\mathbf{V_2}$, which will react with **III** followed by hydrolysis to deliver enantioenriched γ-lactone **22** (Scheme 1.7c). Very recently, they also demonstrated a visible light-driven enantioselective organocatalytic process between allenes **23** and **17**. After the generation of allene radical cation $\mathbf{IV_3}$, the nucleophilic carboxylic acid moiety of $\mathbf{IV_3}$ would add onto the *sp* hybridized carbon of allene to produce tertiary radical $\mathbf{V_3}$. A stereo-controlled radical coupling with **III** followed by an aldol cyclization/acyl migration sequence would furnish the bicyclic product **25** (Scheme 1.7d).

In 2018, the Miller group reported a new mode of peptide-based catalysis for vinylcyclopropane (VCP) ring-opening of **26** followed by enantioselective cycloaddition of **27** to furnish multi-substituted cyclopentanes **28** in high yield and moderate to high enantio- and diastereoselectivity (Scheme 1.8).[12] After extensive exploration, they found that substitutions at the C4-position of proline motif (Compound **29**) are crucial for stereoinduction. Nearly racemic products were obtained in the absence of C4-substitutions, hypothetically due to the long distance between the radical center and the chiral information, while the C4-substitutions could serve as an extension of chiral information to enhance stereochemical communication. They also speculated that the H-bond-donating ability of substrate **26** is vital for achieving high enantioselectivity. Although ester-functionalized VCP gave nearly racemic product, useful levels of

Scheme 1.8. Enantioselective VCP Ring-Opening/Cycloaddition Cascade with Peptide-Based Catalysis



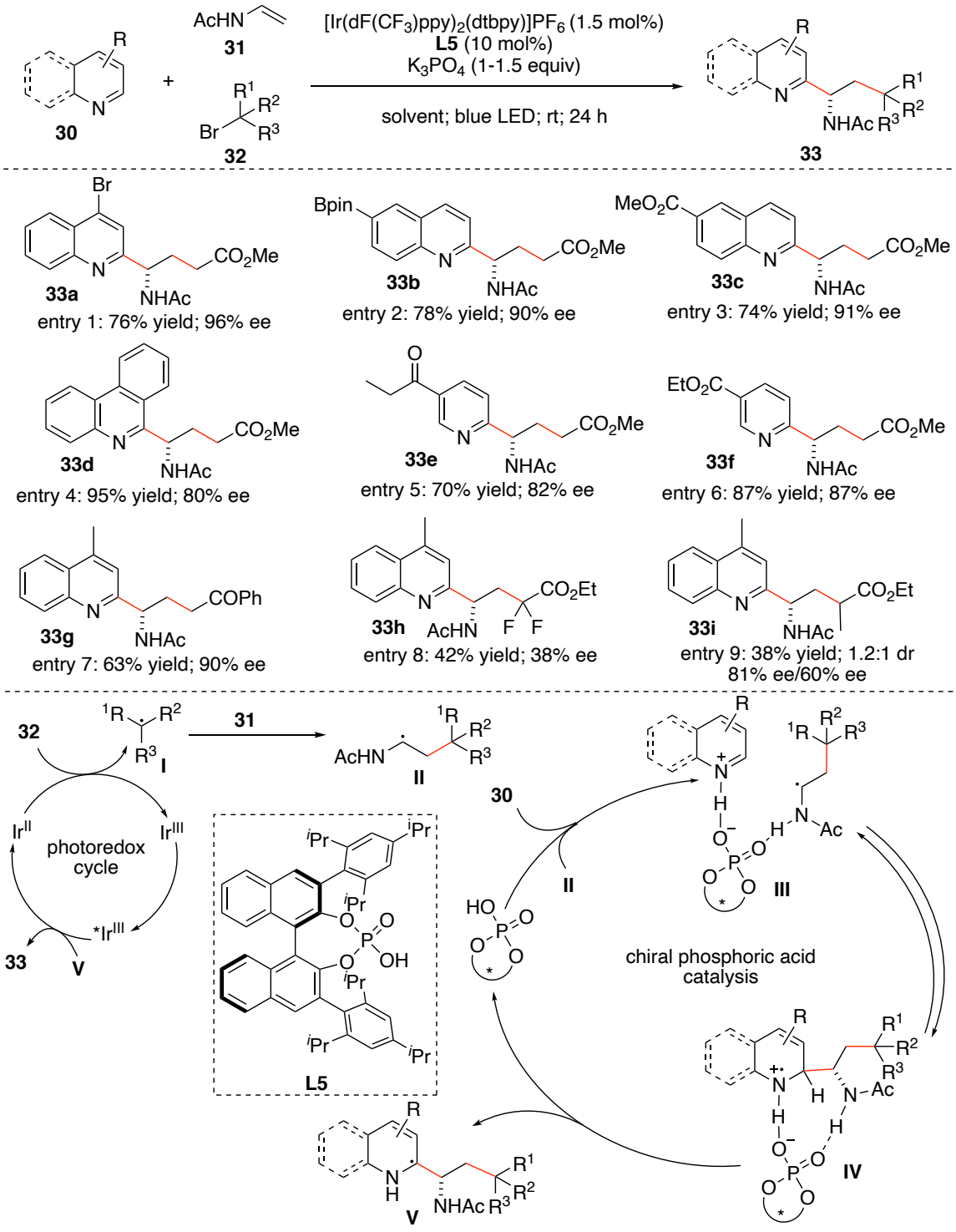
enantioselectivity were observed when amide-functionalized VCP substrates were used. A variety of amide-functionalized VCP substrates **26** containing electron-withdrawing

groups were examined in the catalytic system to furnish the desired multi-substituted cyclopentane derivatives in up to 72% yield with up to 99:1 dr and 84% ee (**28a**–**28c**). Consistent with the H-bonding hypothesis, diminished enantioselectivity was obtained when electron-rich amide substrate **26d** was utilized. Electron-rich enamide- or enol ether-type olefins **27** were required to achieve the good yield, which could be explained by a requirement for polarity-matching between electron-deficient α-dicarbonyl radical intermediate **I** and olefin. The mechanism was proposed that the homolysis of disulfide bond could be promoted by UV light to generate the corresponding thiyl radical intermediate **29'**. The thiyl radical would then undergo radical addition to the VCP followed by a cyclopropyl ring-opening process to deliver radical intermediate **I**. The newly formed tertiary radical would add to the olefin **27** and generate intermediate **II**, after which cyclization could occur to furnish the desired product and regenerate the thiyl radical catalyst.

In 2019, Studer's group reported an enantioselective three-component radical cascade for the preparation of γ-amino-acid derivatives by dual photoredox and chiral Bronsted acid catalysis (Scheme 1.9).[13] Various pyridines and quinoline-derivatives were evaluated in the reaction. Notably, a broad scope of functional groups, such as bromo-atom, boryl group, and carbonyl groups could be well tolerated on the heteroaromatic radical acceptor component (**33a**–**33f**). Moreover, a series of α-bromo carbonyl compounds were also examined in the reaction and successfully converted into the targeted products in good yields and good selectivities (**33g**–**33i**). The proposed mechanism is depicted in scheme 1.9. SET-reduction of the substrate **32** with Ir^{II} complex

could give the Ir^{III} complex and carbon-centered radical intermediate **I**, which would add to the electron-rich enamide to give the nucleophilic radical **II**. Due to polar effects,

Scheme 1.9. Enantioselective Three-Component Radical Cascade Reaction



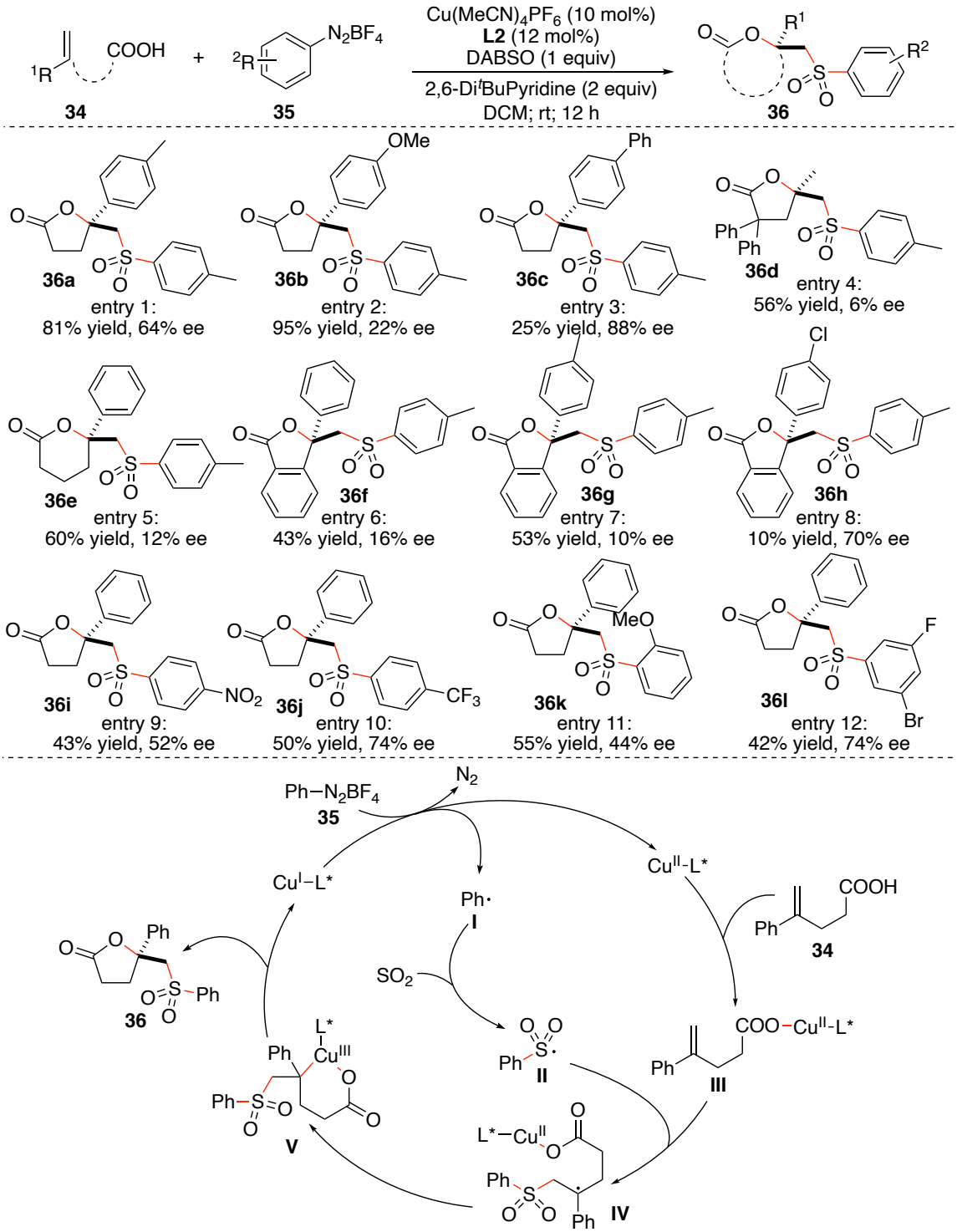
intermediate **II** would not add to the enamide but coordinate with chiral phosphoric acid. Assisted by the **L5**, the carbon-centered radical in intermediate **III** would add to the α-position of protonated quinoline to generate intermediate **IV** in a reversible fashion. After that, a dynamic-kinetic resolution, where one of the diastereomeric isomers of **IV** undergoes deprotonation process faster, could occur and furnish enantioenriched compound **V**, which would be oxidized by the excited Ir-complex $[Ir^{III}]^*$ to the corresponding cation and get deprotonated to provide **33**.

1.4. TRANSITION-METAL COMPLEX

In addition to small organic molecule catalysts, transition-metal complexes have also been utilized in catalyzing radical cascade reactions. In 2017, the Pan group reported a copper-catalyzed asymmetric radical multi-component reaction between unsaturated carboxylic acids, aryldiazonium tetrafluoroborates, and DABCO•$(SO_2)_2$ (DABSO), which was for the first time being utilized as a SO_2 surrogate in enantioselective synthesis (Scheme 1.10).[14] $[Cu(MeCN)_4]PF_6$ was demonstrated to be the optimal copper source with **L2** as the ligand and 2,6-Di^{t}Bupyridine (DTBP) as the base. 4-Arylpent-4-enoic acid substrates containing a variety of functional groups worked well in this reaction (**36a**–**36e**). Furthermore, benzo-fused lactones **36f**–**36h** were also successfully synthesized, which are important bioactive motifs. The mild conditions of this Cu-catalyzed asymmetric cyclization reaction also allowed for the utilization of a broad scope of aryl diazonium salts to furnish the corresponding products in up to 55% yield with up to 74% ee (**36i**–**36l**). Based on the mechanistic studies and previous reports,[15] the authors proposed that the aryldiazonium tetrafluoroborate could first be reduced by Cu(I) via single-electron-transfer to form phenyl radical intermediate **I** and a Cu(II) complex. The

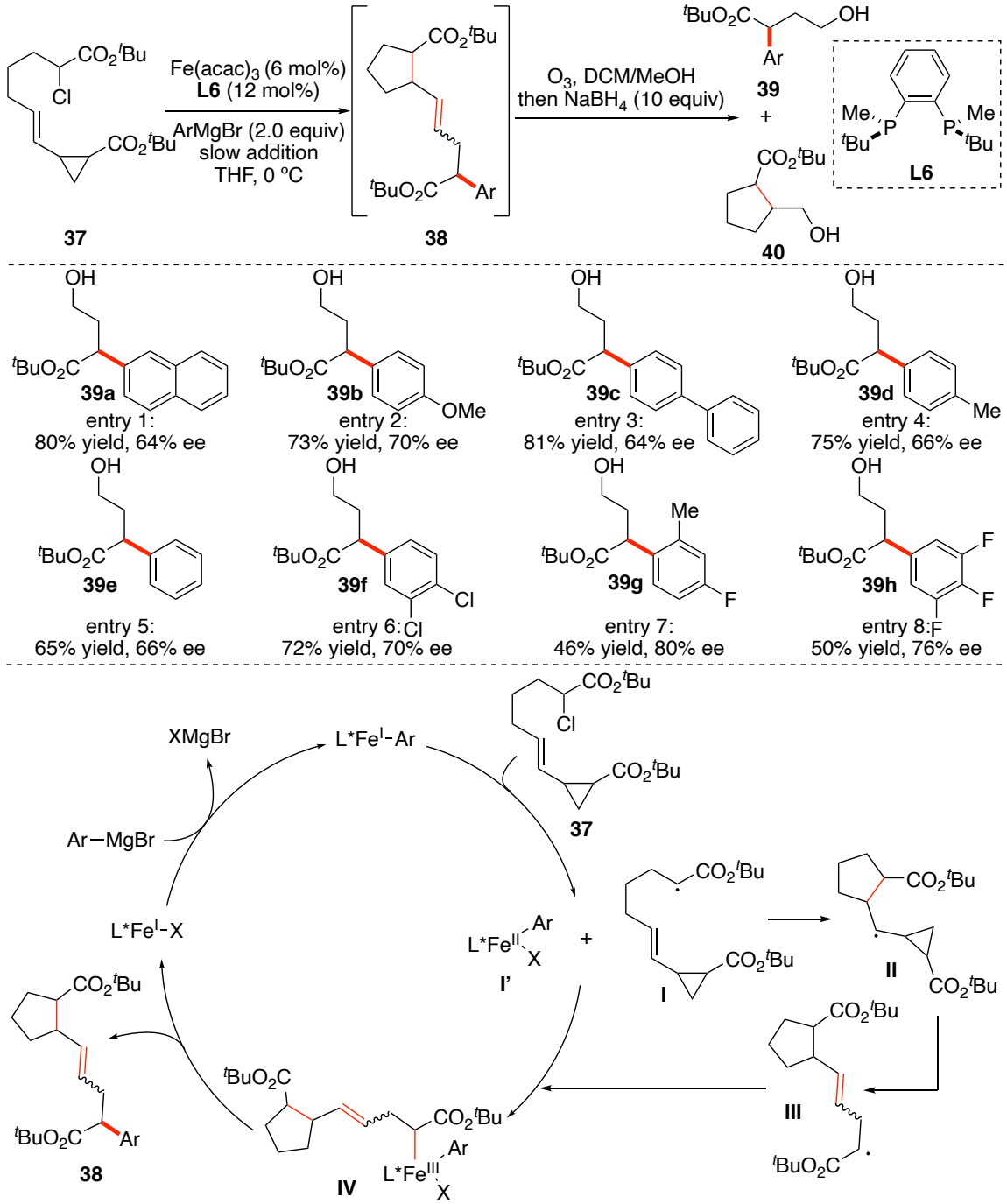
phenyl radical could be trapped by DABSO and generate the benzene sulfonyl radical **II**. In the meanwhile, the unsaturated carboxylic acid could react with Cu(II) complex in the

Scheme 1.10. Asymmetric Cu-Catalyzed Radical Multi-Component Reaction



presence of a base to provide the Cu(II)-carboxylic acid complex **III**. Then the benzene sulfonyl radical could undergo radical addition to the terminal alkene to form tertiary

Scheme 1.11. Enantioselective Fe-Catalyzed Intramolecular Radical Cascade/C(sp^2)-C(sp^3) Cross-Coupling Reactions



radical intermediate **IV**. Subsequently, a single electron oxidation process of intermediate **IV** could occur, which leads to the formation of Cu(III) complex **V** and gives the final product by reductive elimination.

Later, the Gutierrez group described an enantioselective Fe-catalyzed intramolecular radical cascade/C(sp^2)-C(sp^3) cross-coupling reactions of vinyl cyclopropanes (Scheme 1.11).[16] To explore the stereochemistry outcome of this process, they further conducted a one-pot ozonolysis to break the carbon-carbon double bond followed by a reduction by $NaBH_4$ to generate two pieces of products in good yields. The cyclopentane fragment **40** was obtained as a racemic mixture while the corresponding product **39** was formed with good enantioenrichment. These observations indicate that the chiral iron species could only control the stereochemistry of the C(sp^2)–C(sp^3) arylation step. $Fe(acac)_3$/**L6** complex was chosen as the chiral catalyst to promote the enantioselective cascade process with a broad scope of aryl Grignard reagents and construct the corresponding products in up to 98% yield with up to 80% ee. They proposed that a halogen atom abstraction of **37** by an Fe(I)-aryl complex led to an alkyl radical **I** and aryl Fe(II) halide species **I'**. The newly formed alkyl radical intermediate **I** would later undergo intramolecular *5-exo-trig* cyclization to furnish the intermediate **II** followed by a rapid cyclopropyl ring-opening process to deliver radical intermediate **IV.** Finally, alkyl radical **IV** could rebound with the Fe(II) complex and undergo reductive elimination to afford the desired product.

1.5. SUMMARY AND OUTLOOK

The development of enantioselective radical cascade reactions has attracted more and more attention in recent years. All of those intriguing strategies illustrated in this

chapter, which are mediated by chiral Lewis acids, catalyzed by small organic molecules and transition metal complexes, have been successfully utilized to promote otherwise challenging enantioselective reactions efficiently. The achievement of those methods clearly showcased the promising possibility in the construction of a wide array of bioactive compounds and key motifs that are of interest in pharmaceutical areas. Despite the enormous efforts in this field, one of the challenges remaining in this area is the requirement of using stoichiometric initiators or light to initiate most of the radical processes. Furthermore, even though chiral Lewis acids play an important role in enantioselective radical cascade reactions, the employment of substoichiometric or stoichiometric amounts of such reagents to obtain high enantioselectivity limited the application of these regents. More importantly, minimizing the background reactions to achieve higher levels of enantioselectivity is still challenging. Therefore, exploration of novel catalytic systems and catalyst structures for radical cascade reactions is needed to further broaden the scope and enhance the applications of such reactions in organic synthesis. In the past several decades, Co(II) porphyrin complex with D_2-symetric ligands has emerged as unique metalloradical catalysts for a variety of enantioselective radical reactions. Moreover, radical cascade cyclizations via Co(II)-based metalloradical catalysis have been successfully demonstrated to construct polyfunctionalized furans and 2*H*-chromenes.[17] Through fine-tuning of the chiral amidoporphyrins as the supporting ligands, the Co(II)-based metalloradical catalysis could be a promising strategy for enantioselective radical cascade reactions.

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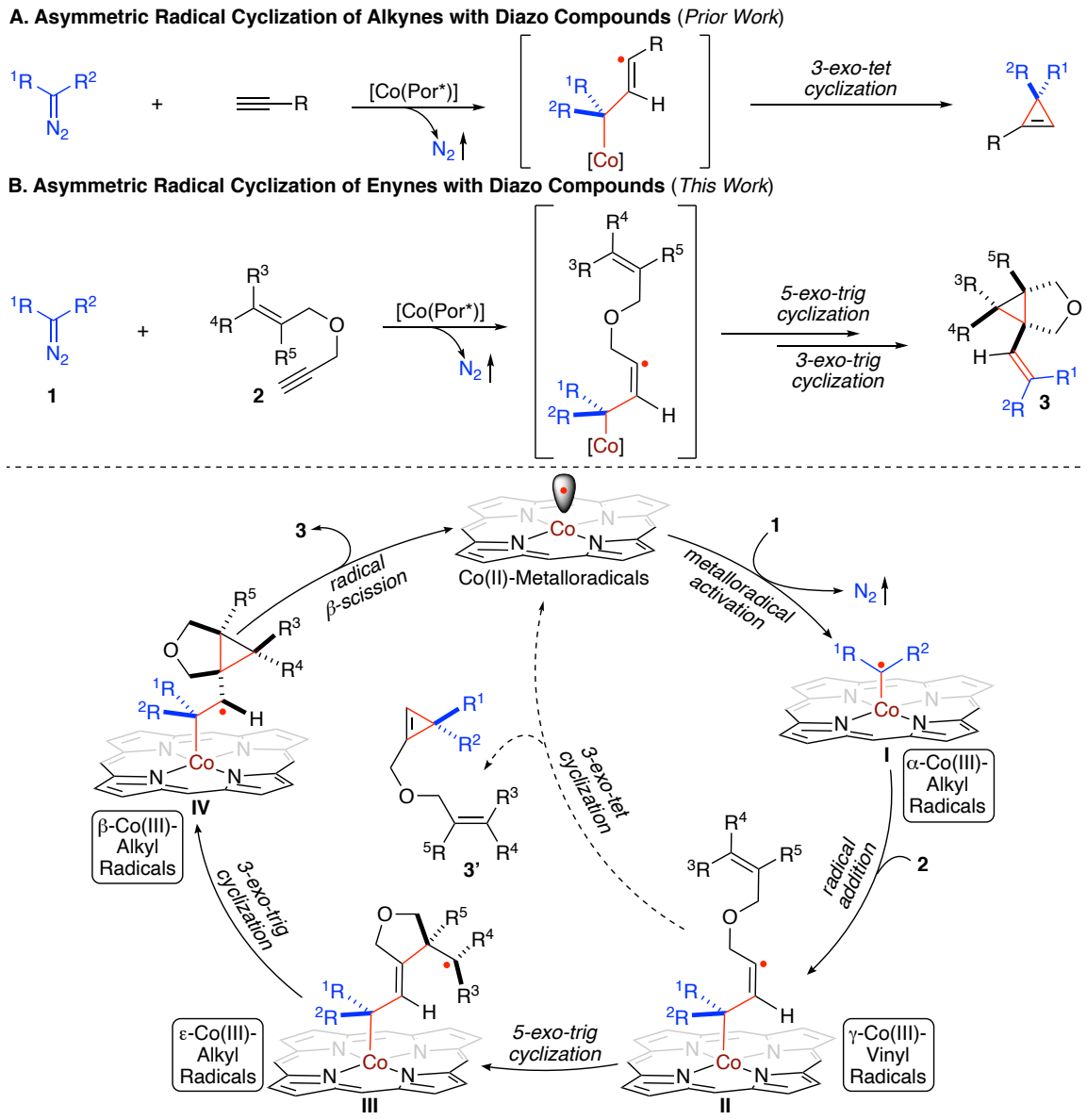
CHAPTER 2

CONTROLLING ENANTIOSELECTIVITY AND DIASTEREOSELECTIVITY IN RADICAL CASCADE CYCLIZATIONS FOR THE CONSTRUCTION OF BICYCLIC STRUCTURES

2.1. INTRODUCTION

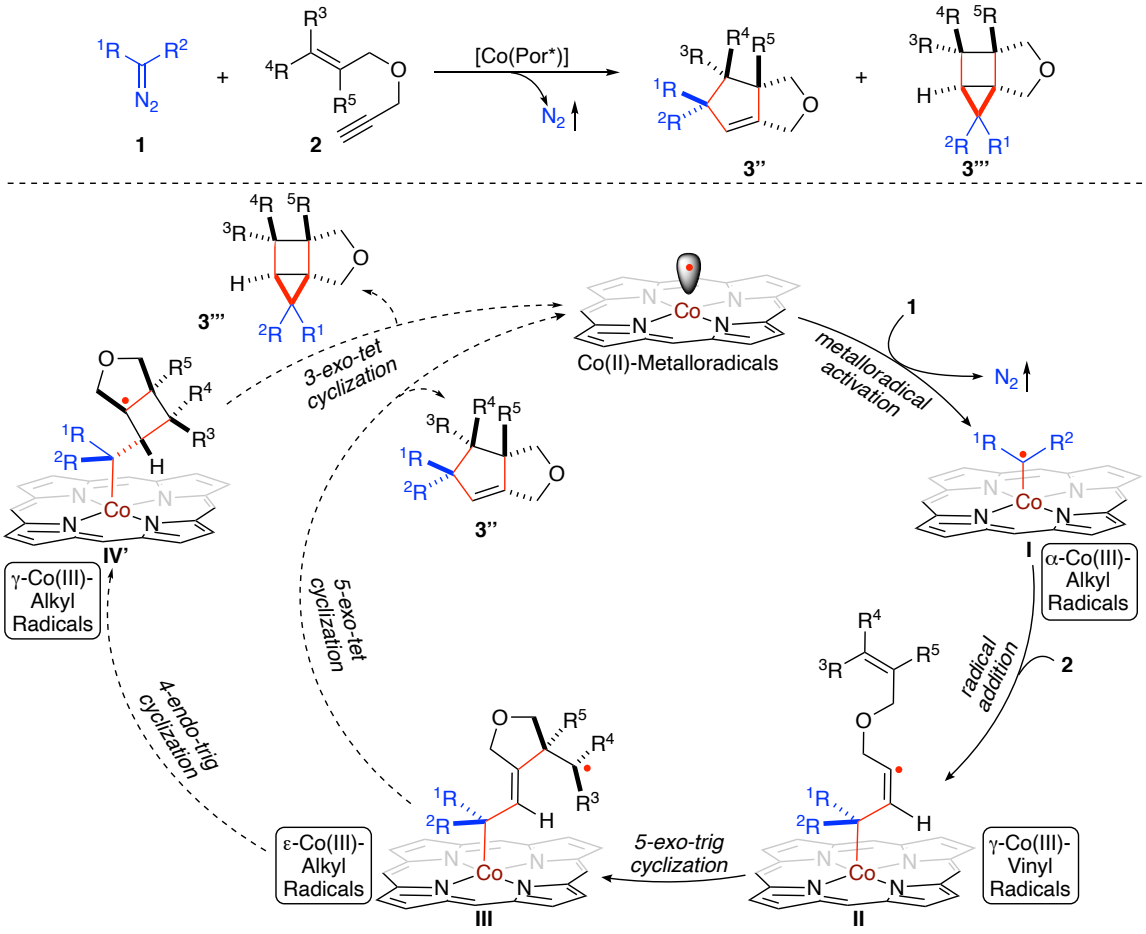
Radical cascade represents a powerful synthetic strategy to construct complex molecular structures bearing multiple stereogenic centers in a single operation.[1] Although they have often been employed for the diastereoselective total synthesis of natural products, control of enantioselectivity remains a formidable challenge in free radical cascade reactions.[2] Among recent advances,[3] metalloradical catalysis (MRC) offers a new catalytic approach to controlling reactivity as well as selectivity of radical reactions by generating metal-supported organic radicals as key catalytic intermediates.[1h, 4-6] As stable 15e-metalloradicals, Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] exhibit the unusual ability to homolytically activate diazo compounds for the generation of α-Co(III)-alkyl radicals, which can serve as kinetically competent intermediates in various asymmetric radical cyclization processes.[7] Among transformations, [Co(D_2-Por*)] was shown to catalyze enantioselective radical cyclopropenation of alkynes with diazo compounds by a stepwise radical mechanism that involves product-forming *3-exo-tet* radical cyclization of γ-Co(III)-vinyl radicals (Scheme 2.1A), which was formed by radical addition of initially-generated α-Co(III)-alkyl radicals to the C–C bonds.[8] To explore new reactivities of the Co-bonded vinyl radical intermediates beyond the demonstrated radical substitution for cyclopropene formation, we were attracted to the possibility of applying Co(II)-based MRC for the

Scheme 2.1. Working Proposal for Radical Cascade Cyclization of 1,6-Enynes with Diazo Compounds via Co(II)-MRC



development of radical cascade processes by engaging the intermediates for further radical addition to C=C bonds and subsequent radical reactions, with the potential to control enantioselectivity and other stereoselectivities. Specifically, we were interested in developing asymmetric radical bicyclization of 1,6-enynes **2** with diazo compounds **1** for

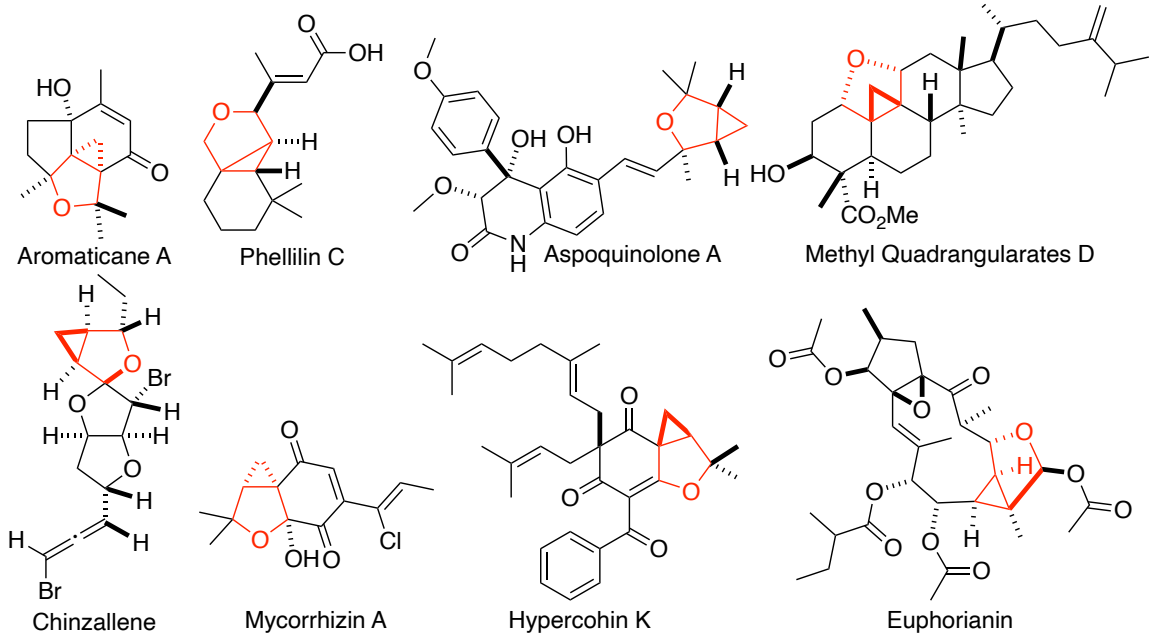
Scheme 2.2. Other Competitive Radical Cascade Pathways of 1,6-Enynes with Diazo Compounds



stereoselective construction of cyclopropane-fused tetrahydrofurans **3** (Scheme 2.1B). In addition to the prerequisite for generation of α-Co(III)-alkyl radicals **I** from metalloradical activation of diazo compounds **1**, it was unclear whether the intermediate **I** could undergo effective radical addition to aliphatic alkynes like **2** to form the corresponding γ-Co(III)-vinyl radicals **II** given that the previous report mainly involved the use of aryl and conjugated alkynes.[8] Furthermore, to avoid the production of the undesired cyclopropenes **3'** (Scheme 2.1B), the vinyl radical intermediate **II** would be required to undergo competitive *5-exo-trig* radical cyclization for formation of ε-Co(III)-

alkyl radicals **III** over the previously demonstrated *3-exo-tet* radical cyclization. Moreover, the subsequent *3-exo-trig* radical cyclization of the alkyl radical intermediate **III** for formation of β-Co(III)-alkyl radicals **IV** might also face competitive radical processes, such as potential *5-exo-tet* and *4-endo-trig* cyclization reactions (Scheme 2.2). Although radical β-scission is typically facile, it was an unsettled question how the α-substituents R^1 and R^2 in radical intermediate **IV** would influence the last step of the catalytic process for production of bicyclic compounds **3**. Along with the breaking and forming of the multiple bonds, the proposed radical cascade transformation would create five stereogenic centers (three sp^3-carbons plus a pair of sp^2-carbons) in the resulting 1-alkenylbicyclo[3.1.0]hexane structures **3**. Apart from the aforementioned reactivity issues, how to control stereoselectivities in this radical cascade reaction, including enantioselectivity and diastereoselectivity for the three chiral centers as well as (*E*)/(*Z*) -

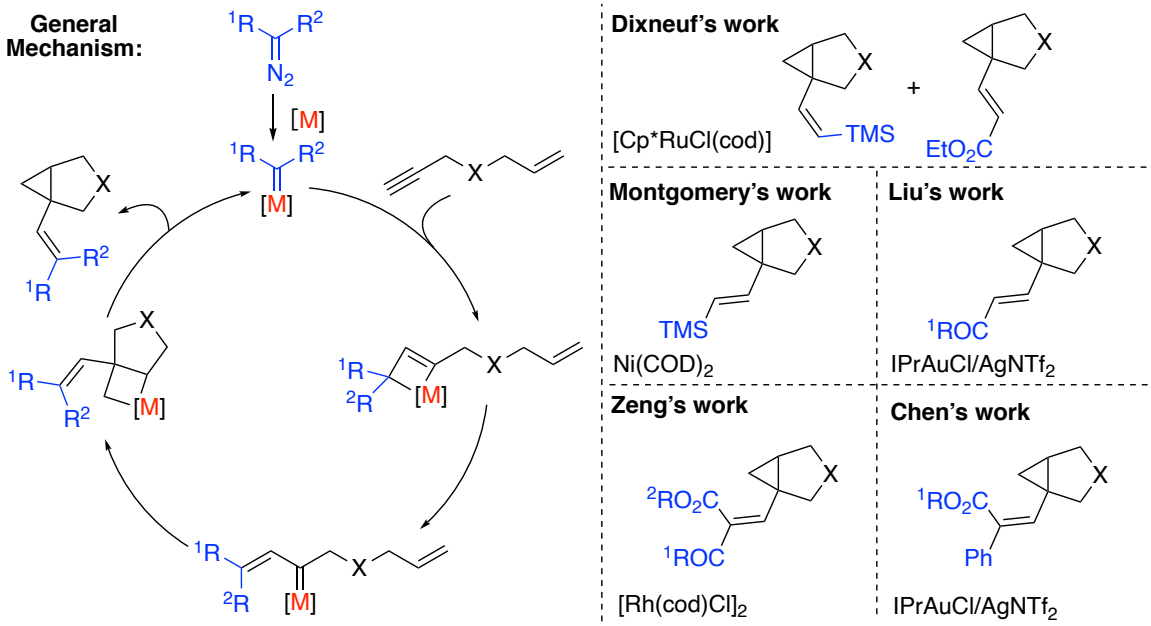
Figure 2.1. Selected Examples of Natural Products and Bioactive Compounds Containing Cyclopropane-Fused Tetrahydrofurans



selectivity for the C=C bond, is an equally important question. We hoped to address these and related issues by fine-tuning the D_2-Por* ligand platform to adopt proper steric, electronic and chiral environments to govern the course of the desired catalytic process. If achieved, it would lead to the development of a new catalytic process for asymmetric radical cascade cyclization to construct cyclopropane-fused tetrahydrofurans and other related 1-alkenylbicyclo[3.1.0]hexanes, which have found wide-ranging applications (Figure 2.1).[9]

Catalytic bicyclization of 1,6-enynes with diazo compounds represents an attractive method to construct 1-alkenylbicyclo[3.1.0]hexane structures such as cyclopropane-fused tetrahydrofurans with potential control of stereoselectivities (Scheme 2.3).[10] Among advances in the realm, Dixneuf and coworkers reported the first Ru-based catalytic system for diastereoselective synthesis of 1-alkenylbicyclo[3.1.0]hexane derivatives from bicyclization of 1,6-enynes with trimethylsilyldiazomethane and ethyl diazoacetate.[10a, 10b, 10d-f] Montgomery and coworkers also developed Ni-catalyzed system for diastereoselective synthesis of 1-alkenylbicyclo[3.1.0]hexanes, including cyclopropane-fused tetrahydrofurans, from cycloaddition of 1,6-enynes with trimethylsilyldiazomethane.[10c] Liu and coworkers subsequently developed Au-catalyzed system for diastereoselective synthesis of cyclopropane-fused tetrahydrofuran derivatives from reaction of 1,6-enynes with diazoketones.[10g] Zeng and coworkers later reported diastereoselective synthesis of cyclopropane-fused pyrrolidine derivatives through Rh-catalyzed cyclization of 1,6-enynes with α-diazocarbonyl compounds.[10h] More recently, Chen and coworkers employed Au-catalyzed diastereoselective bicyclization of 1,6-enynes with α-aryl-α-diazoacetates to generate 1-alkenylbicyclo[3.1.0]hexanes.[10i]

Scheme 2.3. Previous Strategies for Constructing 1-Alkenylbicyclo[3.1.0]hexane Structures of 1,6-Enynes with Diazo Compounds



Despite these advances in diastereoselective synthesis, asymmetric catalytic systems for stereoselective construction of 1-alkenylbicyclo[3.1.0]hexanes such as cyclopropane-fused tetrahydrofurans with control of enantioselectivity remain to be developed. As a new application of Co(II)-based MRC, we herein report the development of the first asymmetric catalytic system for radical cascade cyclization of 1,6-enynes with diazo compounds that enables stereoselective construction of multi-substituted cyclopropane-fused tetrahydrofurans bearing three contiguous stereogenic centers, including two all-carbon quaternary centers. In addition to practical attributes such as operational simplicity and mild conditions, we show that the Co(II)-catalyzed bicyclization proceeds through a fundamentally different mechanism from previous catalytic systems involving metallocarbene intermediates. Our combined experimental and computational studies unveil a stepwise radical mechanism that involves α-Co(III)-alkyl radicals as the key

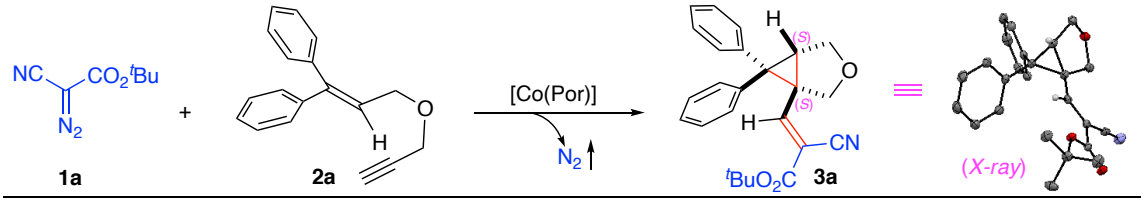
intermediate and its translocation among several different Co-supported C-centered radicals, including β-, γ- and ε-Co(III)-alkyl radicals. We further show that the resulting enantioenriched cyclopropane-fused tetrahydrofurans that contain a trisubstituted vinyl group at the bridgehead are useful intermediates for stereoselective organic synthesis.

2.2. RESULTS AND DISCUSSION

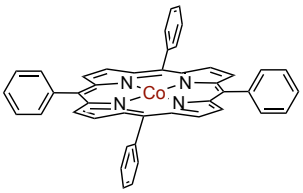
2.2.1. Condition Optimization for Enantioselective Radical Cascade Bicyclization of 1,6-Enynes with α-Cyano Diazoacetate

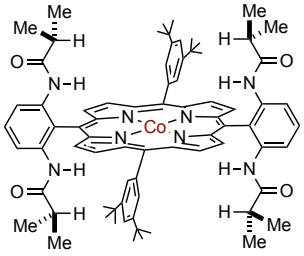
At the outset of this project, 1,1-diphenyl-1,6-enyne **2a** was chosen as the model substrate for investigation of the proposed radical cascade process by Co(II)-based metalloradical catalysts with *tert*-butyl α-cyanodiazoacetate (**1a**) as the radical precursor (Scheme 2.4). It was found that the simple achiral catalyst [Co(**P1**)] (**P1** = tetraphenylporphyrin) could catalyze the formation of the desired cyclopropane-fused tetrahydrofuran **3a** but in low reactivity (19% yield) with moderate control of the olefin configuration ((*E*):(*Z*) ratio of 80:20) as the allowed *cis*-ring junction. With the use of achiral catalyst [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin),[11] 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 yield (44%) and (*E*):(*Z*) selectivity (95:5) for product *cis*-**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 cyclization. When first-generation chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin) was utilized,[7a] further increase in the yield (53%) of *cis*-**3a** was attained while achieving a high level of asymmetric induction (85% ee) without affecting the high (*E*):(*Z*) selectivity

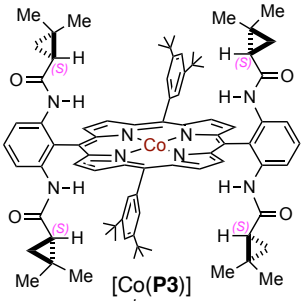
Scheme 2.4. Ligand Effect on Co(II)-Catalyzed Radical Cascade Cyclization of 1,6-Enyne with α-Cyanodiazoacetate[a]

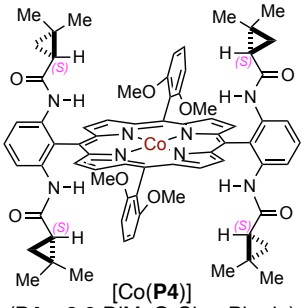


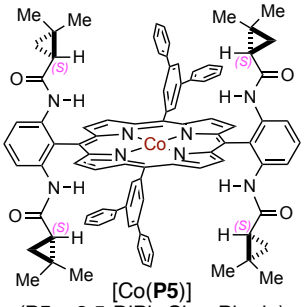
entry	catalyst	yield	(E):(Z)	ee
1	[Co(**P1**)]	19%	80:20	—
2	[Co(**P2**)]	44%	95:5	—
3	[Co(**P3**)]	53%	95:5	85%
4	[Co(**P4**)]	18%	96:4	4%
5	[Co(**P5**)]	58%	94:6	81%
6	[Co(**P6**)]	86%	98:2	91%

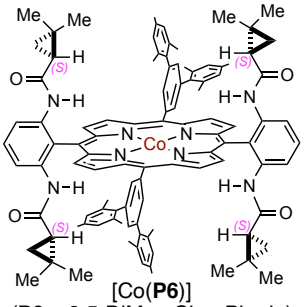

[Co(**P1**)]
(**P1** = Tetraphenylporphyrin)


[Co(**P2**)]
(**P2** = 3,5-Di*t*Bu-IbuPhyrin)


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


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


[Co(**P5**)]
(**P5** = 3,5-DiPh-ChenPhyrin)

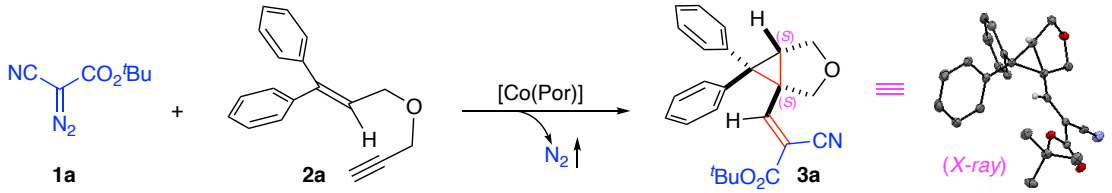

[Co(**P6**)]
(**P6** = 3,5-DiMes-ChenPhyrin)

[a]Carried out with **1a** (0.12 mmol) and **2a** (0.10 mmol) by [Co(Por)] (5 mol %) in CH_3CN (0.25 mL) at 40 °C for 16 h; Isolated yields; Only *cis*-ring junction product formed; (*E*):(*Z*) of olefin configuration determined by ^1H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

(95:5). During the process of investigating the ligand effect, it was discovered that the non-chiral substituents at the *meso*-phenyl rings of ChenPhyrin ligand has a significant influence on both reactivity and enantioselectivity of the catalytic reaction. While the use

of catalyst [Co(**P4**)] (**P4** = 2,6-DiMeO-ChenPhyrin) containing two methoxy groups at the proximal 2,6-positions of the *meso*-phenyl units resulted in dramatic diminishment in both yield (18%) and enantioselectivity (4% ee), [Co(**P5**)] (**P5** = 3,5-DiPh-ChenPhyrin) bearing two phenyl groups at the 3,5-positions further improved the yield (58%) without significantly affecting the enantioselectivity (81% ee). This positive outcome prompted

Scheme 2.5. Optimization of Reaction Conditions on Co(II)-Catalyzed Radical Cascade Cyclization of 1,6-Enyne with α-Cyanodiazoacetate[a]



entry	solvent	temp	amount of solvent	catalyst loading	yield	(E):(Z)	ee
1	Toluene	60 °C	0.5 mL	2 mol%	60%	95/5	84%
2	Toluene	40 °C	0.5 mL	2 mol%	49%	97/3	90%
3	Benzene	40 °C	0.5 mL	2 mol%	61%	97/3	88%
4	Diethyl ether	40 °C	0.5 mL	2 mol%	43%	97/3	86%
5	Dichloromethane	40 °C	0.5 mL	2 mol%	86%	97/3	84%
6	Hexanes	40 °C	0.5 mL	2 mol%	76%	97/3	86%
7	Methanol	40 °C	0.5 mL	2 mol%	22%	97/3	84%
8	Acetonitrile	40 °C	0.5 mL	2 mol%	43%	97/3	91%
9	Acetonitrile	40 °C	0.25 mL	2 mol%	60%	97/3	90%
10	Acetonitrile	40 °C	0.25 mL	5 mol%	86%	98/2	91%

[a]Carried out with **1a** (0.12 mmol) and **2a** (0.10 mmol) by [Co(**P6**)] for 16 h; Isolated yields; Only *cis*-ring junction product formed; (*E*):(*Z*) of olefin configuration determined by ^{1}H-NMR; Enantiomeric excess (ee) determined by chiral HPLC

us to fine-tune the substituents at 3,5-positions of ChenPhyrin ligand. Excitingly, when [Co(**P6**)] (**P6** = 3,5-DiMes-ChenPhyrin) bearing two mesityl groups at 3,5-positions was used as the catalyst, it afforded cyclopropane-fused tetrahydrofuran **3a** in high yield (86%) with excellent enantioselectivity (91% ee) as well as with near complete

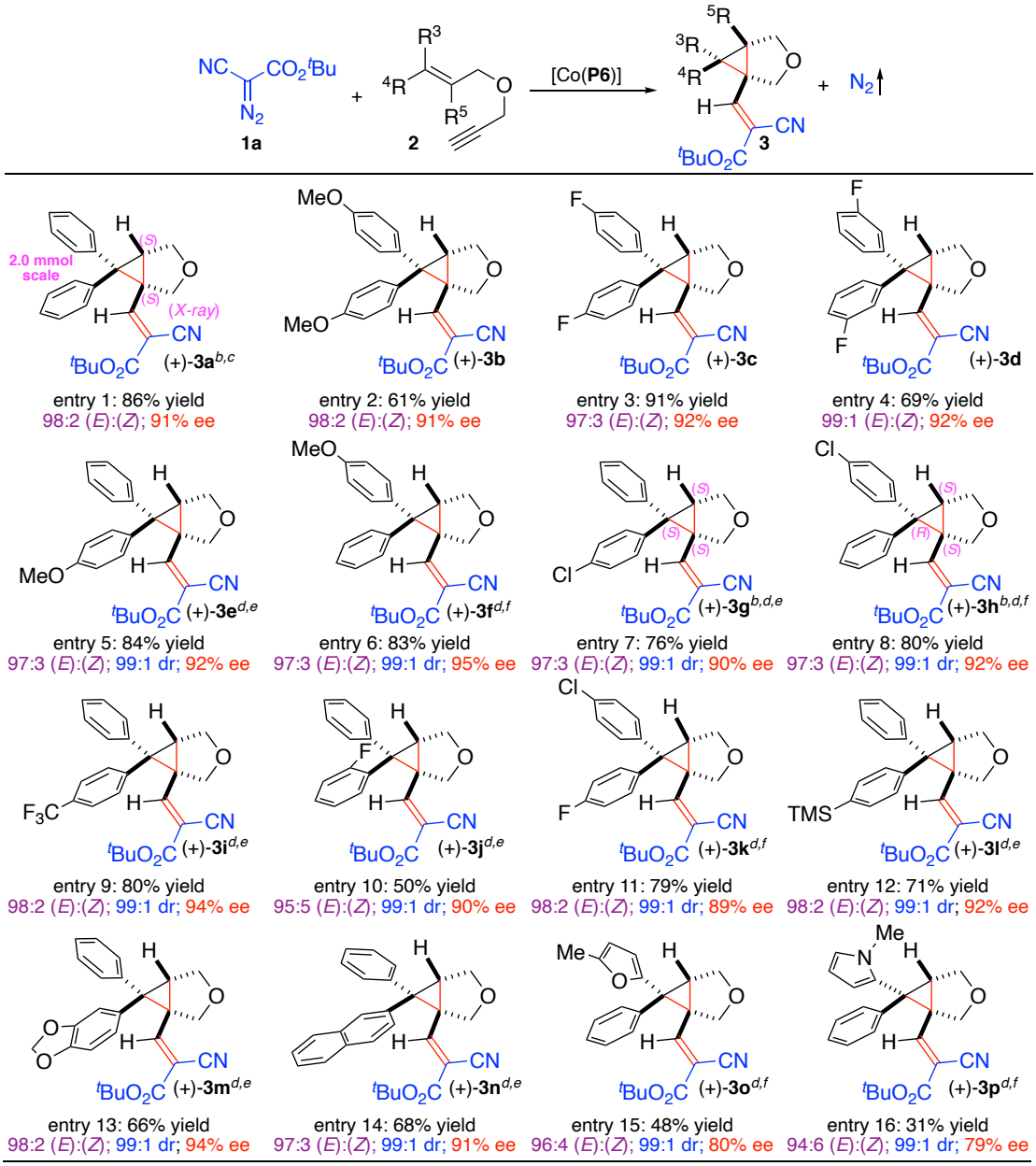
configurational control of the newly-formed trisubstituted alkene ((*E*):(*Z*) ratio of 98:2) at the bridgehead of the allowed *cis*-ring junction of the bicyclic structure. Considering that [Co(**P6**)] differs from [Co(**P5**)] only by the distal methyl groups at the 2',4',6' positions of the 3,5-positions of the phenyl group in the *meso*-phenyl units of the porphyrin core, these remarkable results signify the immense power of judicious tuning of ligand environment in controlling reactivity and stereoselectivity of Co(II)-based metalloradical system. It is worth mentioning that ChenPhyrin ligands **P3**–**P6** could be modularly synthesized in three steps from readily available starting materials by following the previously established prodedures.[7a] After extensive condition optimization, using 5 mol% of [Co(**P6**)] in CH_3CN (0.25 mL) at 40 ºC proved to be the optimal condition (Scheme 2.5). The absolute configurations of stereogenic centers in **3a** were confirmed by X-ray crystallography as (*S*,*S*) and (*E*), respectively. Among interesting structural features, the trisubstituted (*E*)-olefin unit is almost coplanar with the tetrahydrofuran ring, which is near perpendicular to the pentasubstituted cyclopropane plane.

2.2.2. Enantioselective Radical Cascade Reaction of Different 1,6-Enynes

Under the optimized conditions, the scope of the [Co(**P6**)]-catalyzed radical bicyclization with *tert*-butyl α-cyanodiazoacetate (**1a**) was then evaluated by employing different 1,6-enynes **2** (Table 2.1 and Table 2.2). Like 1,1-diphenyl-1,6-enyne **2a** (Table 2.1; entry 1), 1,1-diaryl-1,6-enynes containing various aryl groups with substituents at different positions, such as *p*-OMe (**2b**), *p*-F (**2c**), and *m*-F (**2d**), could be bicyclized with **1a** by [Co(**P6**)], affording the corresponding cyclopropane-fused tetrahydrofurans (+)-**3b**, (+)-**3c**, and (+)-**3d** as the allowed *cis*-ring junction in good to high yields with excellent (*E*):(*Z*)-selectivities and enantioselectivities (Table 2.1; entries 2–4). It is worth

mentioning that the catalytic radical cascade process could be readily scaled up as demonstrated with the bicyclization reaction of **2a** with **1a** on 2.0 mmol scale, delivering optically active compound (+)-*cis*-**3a** in 86% yield with 98:2 (*E*):(*Z*) and 91% ee (Table 2.1; entry 1). Both (*E*)- and (*Z*)-1,1-diaryl-1,6-enynes containing *p*-OMe substituted aryl group ((*E*)-**2e** and (*Z*)-**2f**) underwent radical cascade process stereospecifically to afford the corresponding (+)-**3e** and (+)-**3f** as *exo*- and *endo*-isomers, respectively (Table 2.1; entries 5 and 6). The same stereospecific transformations were observed for (*E*)- and (*Z*)-1,1-diaryl-1,6-enynes containing *p*-Cl substituted aryl group ((*E*)-**2g** and (*Z*)-**2h**), offering the relevant (+)-**3g** and (+)-**3h** as *exo*- and *endo*-isomers, respectively (Table 2.1; entries 7 and 8). The absolute configurations of (+)-**3g** and (+)-**3h** were established as (*S*,*S*,*S*) and (*R*,*S*,*S*), respectively, by X-ray crystallography, confirming the stereospecificity of the transformations. Likewise, 1,1-diaryl-1,6-enynes substituted with different aryl groups ((*E*)-**2i**, (*E*)-**2j**, (*Z*)-**2k,** (*E*)-**2l** and (*E*)-**2m**) could be stereospecifically bicyclized to generate the desired products ((+)-**3i**, (+)-**3j**, (+)-**3k,** (+)-**3l** and (+)-**3m**) in moderate to high yields with high levels of diastereoselectivities and enantioselectivities as well as (*E*):(*Z*)-selectivities (Table 2.1; entries 9–13). Furthermore, enyne substrates containing extended aromatic and heteroaromatic groups, including naphthalene ((*E*)-**2n**), furan ((*Z*)-**2o**) and pyrrole ((*Z*)-**2p**), were also compatible with the radical cascade cyclization, bringing about stereospecific production of the corresponding (+)-**3n**, (+)-**3o** and (+)-**3p** (Table 2.1; entries 14–16). Besides 1,1-diaryl-1,6-enynes, 1-aryl-1-alkyl-1,6-enynes such as (*E*)-**2q** and (*E*)-**2r** were also suitable substrates for the catalytic system, leading to stereospecific formation of cyclopropane-fused tetrahydrofurans (+)-**3q** and (+)-**3r** in good yields with excellent diastereoselectivities and good enantioselectivities (Table 2.2;

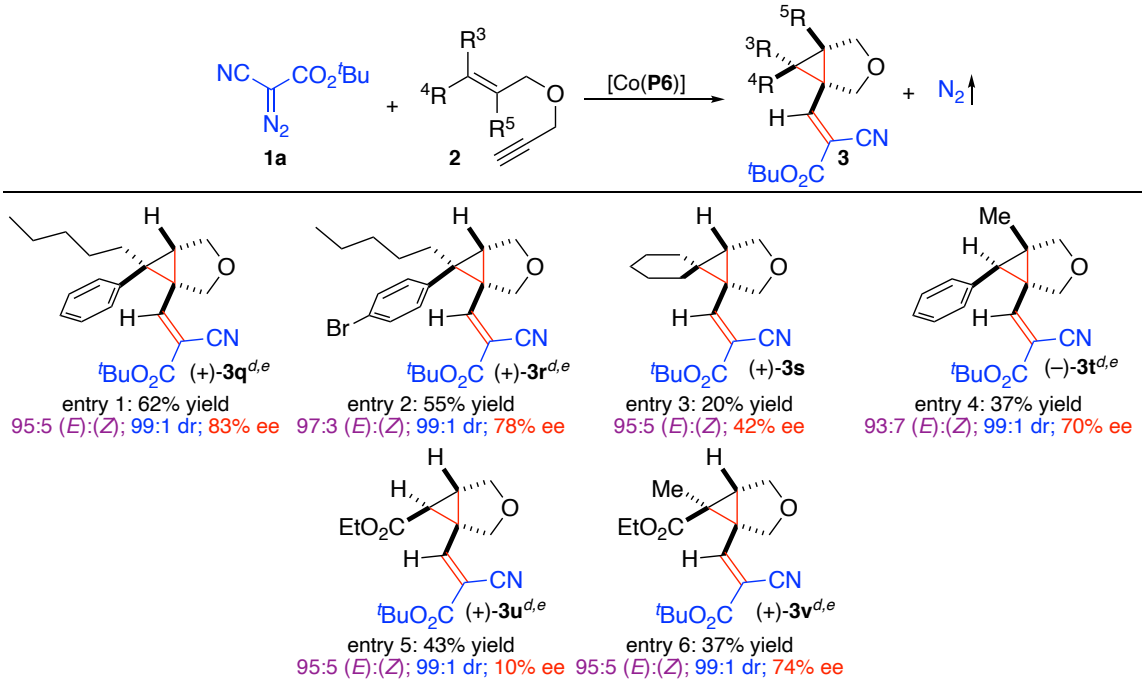
Table 2.1. Asymmetric Radical Bicyclization of 1,1-Diaryl-1,6-Enynes with *tert*-Butyl α-Cyanodiazoacetate Catalyzed by [Co(P6)][a]



[a]Carried out with **1a** (0.12 mmol) and **2** (0.10 mmol) by [Co(**P6**)] (5 mol %) in CH_3CN (0.25 mL) at 40 °C for 16 h; Isolated yields; Only *cis*-ring junction product formed; (*E*):(*Z*) of olefin configuration determined by ^1H NMR; Enantiomeric excess (ee) determined by chiral HPLC. [b]Absolute configurations determined by X-ray crystallography. [c]Performed on 2.0 mmol scale. [d]Diastereomeric ratio (dr) between *endo*- and *exo*-isomers determined by ^1H NMR. [e]From (*E*)-enyne. [f]From (*Z*)-enyne

entries 1 and 2). Tricyclic structure (+)-**3s** that contains both spiro and fused rings could be constructed by the catalytic system from 1,1-dialkyl-1,6-enyne **2s** containing exocyclic alkene unit (Table 2.2; entry 3). Notably, this cascade process was also applicable to 1,2-disubstituted 1,6-enynes such as 1-phenyl-2-methyl-1,6-enyne (*E*)-**2t**, resulting in stereospecific construction of cyclopropane-fused tetrahydrofuran (–)-**3t** bearing two all-carbon quaternary centers at both bridgeheads in moderate yield with good diastereoselectivity and enantioselectivity (Table 2.2; entry 4). Additionally, 1,6-enynes

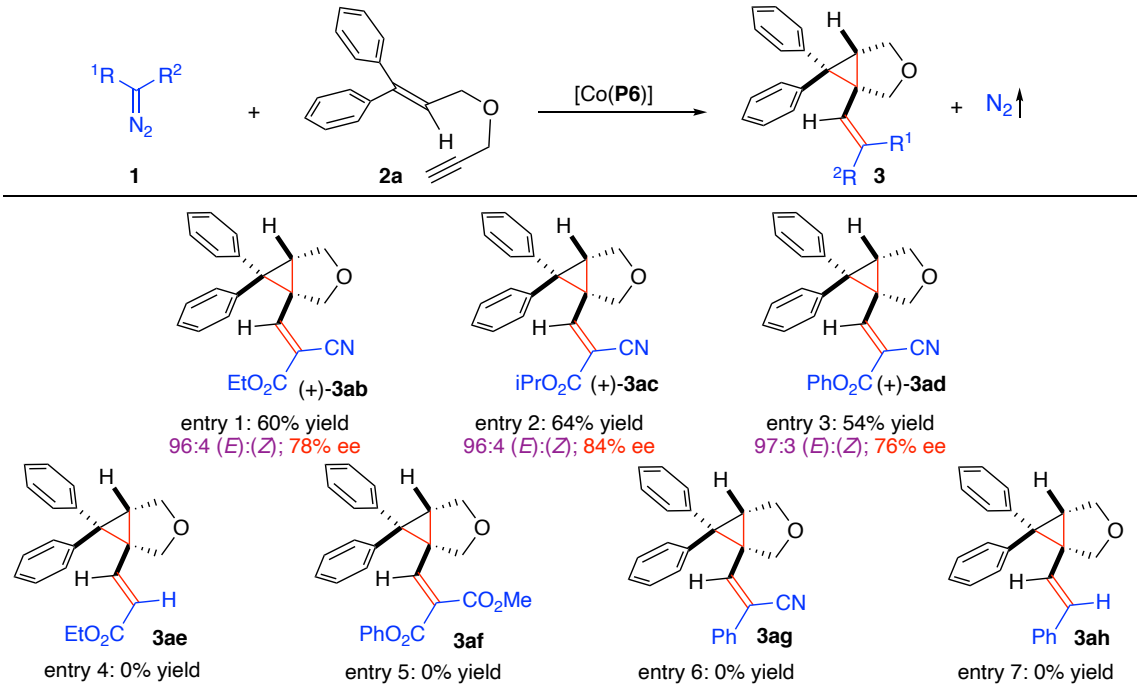
Table 2.2. Asymmetric Radical Bicyclization of Other 1,6-Enynes with *tert*-Butyl α-Cyanodiazoacetate Catalyzed by [Co(P6)][a]



[a]Carried out with **1a** (0.12 mmol) and **2** (0.10 mmol) by [Co(**P6**)] (5 mol %) in CH_3CN (0.25 mL) at 40 °C for 16 h; Isolated yields; Only *cis*-ring junction product formed; (*E*):(*Z*) of olefin configuration determined by ^{1}H NMR; Enantiomeric excess (ee) determined by chiral HPLC. [b]Absolute configurations determined by X-ray crystallography. [c]Performed on 2.0 mmol scale. [d]Diastereomeric ratio (dr) between *endo*- and *exo*-isomers determined by ^{1}H NMR. [e]From (*E*)-enyne. [f]From (*Z*)-enyne

bearing α,β-unsaturated esters as the alkene unit such as (*E*)-**2u** and (*E*)-**2v** could also be applied in the radical cascade process, affording the corresponding cyclopropane-fused tetrahydrofurans (+)-**3u** and (+)-**3v** in moderate yields with low to good enantioselectivities and high diastereoselectivities (Table 2.2; entries 5 and 6).

Table 2.3. Asymmetric Radical Bicyclization of 1,1-Diphenyl 1,6-enyne with different α-Cyanodiazoacetate Catalyzed by [Co(P6)][a]



[a]Carried out with **1** (0.12 mmol) and **2a** (0.10 mmol) by [Co(**P6**)] (5 mol %) in CH_3CN (0.25 mL) at 40 °C for 16 h; Isolated yields; Only *cis*-ring junction product formed; (*E*):(*Z*) of olefin configuration determined by ^1H NMR; Enantiomeric excess (ee) determined by chiral HPLC.

2.2.3. Enantioselective Radical Cascade Reaction of Different Diazo Compounds

In addition to *tert*-butyl α-cyanodiazoacetate, three other α-cyanodiazoacetate, including ethyl α-cyanodiazoacetate **1b**, isopropyl α-cyanodiazoacetate **1c** and phenyl α-cyanodiazoacetate **1d** were performed on the asymmetric radical bicyclization under the optimized reaction conditions (Table 2.3; entries 1–3). As the results indicated, the

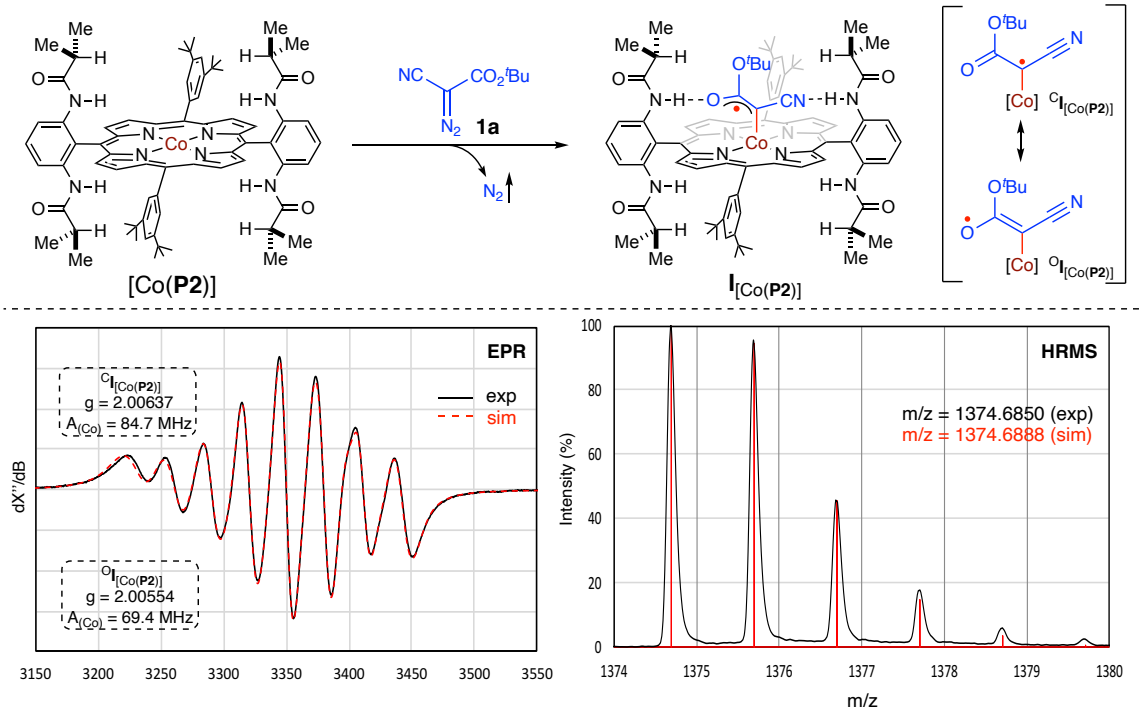
Co(II)-catalyzed asymmetric radical bicyclization are effective to generate the desired products in good yield with excellent (*E*):(*Z*) selectivity and good enantioselectivity. Further experiments on catalytic radical bicyclization of the 1,1-diphenyl-1,6-enyne **2a** with ethyl diazoacetate **1e** (acceptor diazo compound), 1-methyl 3-phenyl 2-diazomalonate **1f** (acceptor/acceptor diazo compounds), 2-diazo-2-phenylacetonitrile **1g** (donor/acceptor diazo compound) and (diazomethyl)benzene (donor diazo compound) **1h** were also carried out (Table 2.3; entries 4–7). However, none of them generated the corresponding cyclopropane-fused tetrahydrofurans. In the reaction of entry 4, dimer of the diazo compound was obtained as a side product. For entry 5, low conversion of diazo compound was observed. In entry 6 and 7, all the diazo species were consumed but produced a complex crude mixture. Although the reason for such results is unclear, one possibility is that radical addition of the α-Co(III)-alkyl radical is reversible. Due to high activation energy barrier of the *5-exo-trig* cyclization of the γ-Co(III)-vinyl radical generated from other diazo compounds, the vinyl radical would undergo more facile radical β-scission to regenerate the α-Co(III)-alkyl radical which could go through several side reactions. Further studies are in progress to broaden the scope of diazo compounds beyond the use of α-cyanodiazoacetate by developing new generation of Co(II)-based metalloradical catalysts to decrease the activation energy barrier of the *5-exo-trig* cyclization process.

2.2.4. Mechanistic Studies on Co(II)-Catalyzed System for Bicyclization of 1,6-Enynes with Diazo Compounds

Computational studies were carried out to comprehend the underlying mechanism of the Co(II)-based catalytic system for cascade cyclization. To detect the first α-Co(III)-

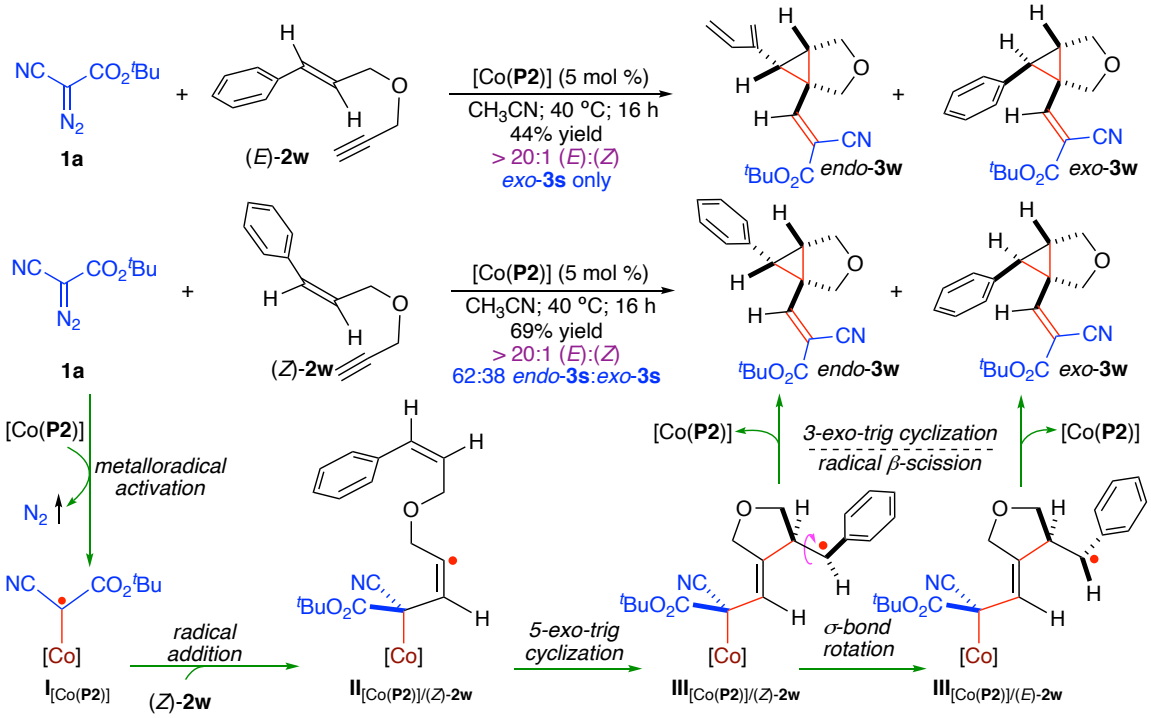
alkyl radical intermediate experimentally, the reaction solution of [Co(**P2**)] with α-cyanodiazoacetate **1a** in the absence of enyne substrate was monitored by electron paramagnetic resonance (EPR) spectroscopy at room temperature (Scheme 2.6). The isotropic EPR spectrum exhibits a strong signal at g-value of ~2.00 as well-resolved octet, which is diagnostic of the corresponding α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ generated from metalloradical activation of **1a** by [Co(**P2**)]. The observed spectrum (in black) could be near perfectly simulated (in red) by involving two resonance forms of radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ on the basis of hyperfine couplings by ^{59}Co (I = 7/2): 96% of C-centered radical at α-position $^{C}\mathbf{I}_{[Co(\mathbf{P2})]}$ (g = 2.00637; $A_{(Co)}$ = 84.7 MHz) and 4% of O-centered radical at γ-position $^{O}\mathbf{I}_{[Co(\mathbf{P2})]}$ (g = 2.00554; $A_{(Co)}$ = 69.4 MHz). The third resonance form of radical **I**, which is an unstable N-centered radical (iminyl radical), was not included in the

Scheme 2.6. Generation and Detection of α-Co(III)-Alkyl Radical Intermediate by EPR and HRMS



simulation. Moreover, α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ from the reaction solution could be detected by high-resolution mass spectrometry (HRMS) with electrospray ionization (ESI). The observed mass of 1374.6850 evidently resulted from α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ by the loss of one electron. Both the exact mass and the pattern of isotope distribution determined by ESI-HRMS match nicely with those calculated from the formula $[C_{83}H_{97}CoN_9O_6]^+$ (m/z = 1374.6888). The experimental detection of α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ by EPR and HRMS have provided strong evidence to support the first step of metalloradical activation in the proposed mechanism (Scheme 2.1).

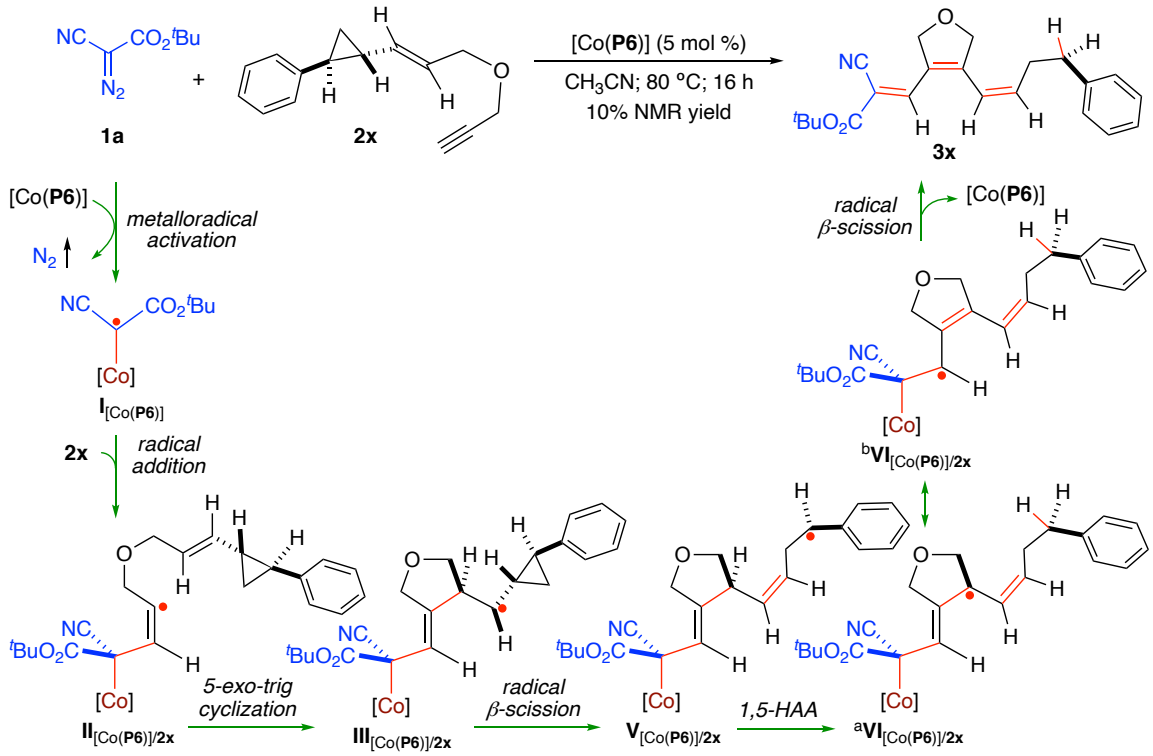
Scheme 2.7. Probing of ε-Co(III)-Alkyl Radical Intermediate by Reactions of (*E*)- and (*Z*)-1,6-Enynes



To experimentally probe the existence of γ-Co(III)-vinyl radical intermediate **II** and ε-Co(III)-benzyl radical intermediate **III**, both (*Z*)- and (*E*)-isomers of 1-phenyl-1,6-enyne **2w** were synthesized and subjected to the radical cascade cyclization by [Co(**P2**)]

(Scheme 2.7). While the reaction of (*E*)-**2w** afforded *exo*-**3w** as the only diastereomer, the radical cascade cyclization of (*Z*)-**2w** generated a diastereomeric mixture of *endo*-**3w** and *exo*-**3w** in a ratio of 62 to 38. The observation of both *endo*-**3w** and *exo*-**3w** from the reaction of (*Z*)-**2w** implies the existence of ε-Co(III)-benzyl radical $\mathbf{III}_{[\mathrm{Co}(\mathbf{P2})]/(Z)\text{-}\mathbf{2w}}$, which was generated from *5-exo-trig* cyclization of γ-Co(III)-alkyl radical intermediate $\mathbf{II}_{[\mathrm{Co}(\mathbf{P2})]/(Z)\text{-}\mathbf{2w}}$ and its conformational isomer $\mathbf{III}_{[\mathrm{Co}(\mathbf{P2})]/(E)\text{-}\mathbf{2w}}$ that resulted from σ-bond rotation (Scheme 2.7).

Scheme 2.8. Probing of ε-Co(III)-Alkyl Radical Intermediate through Cyclopropylcarbinyl radical Ring-Opening

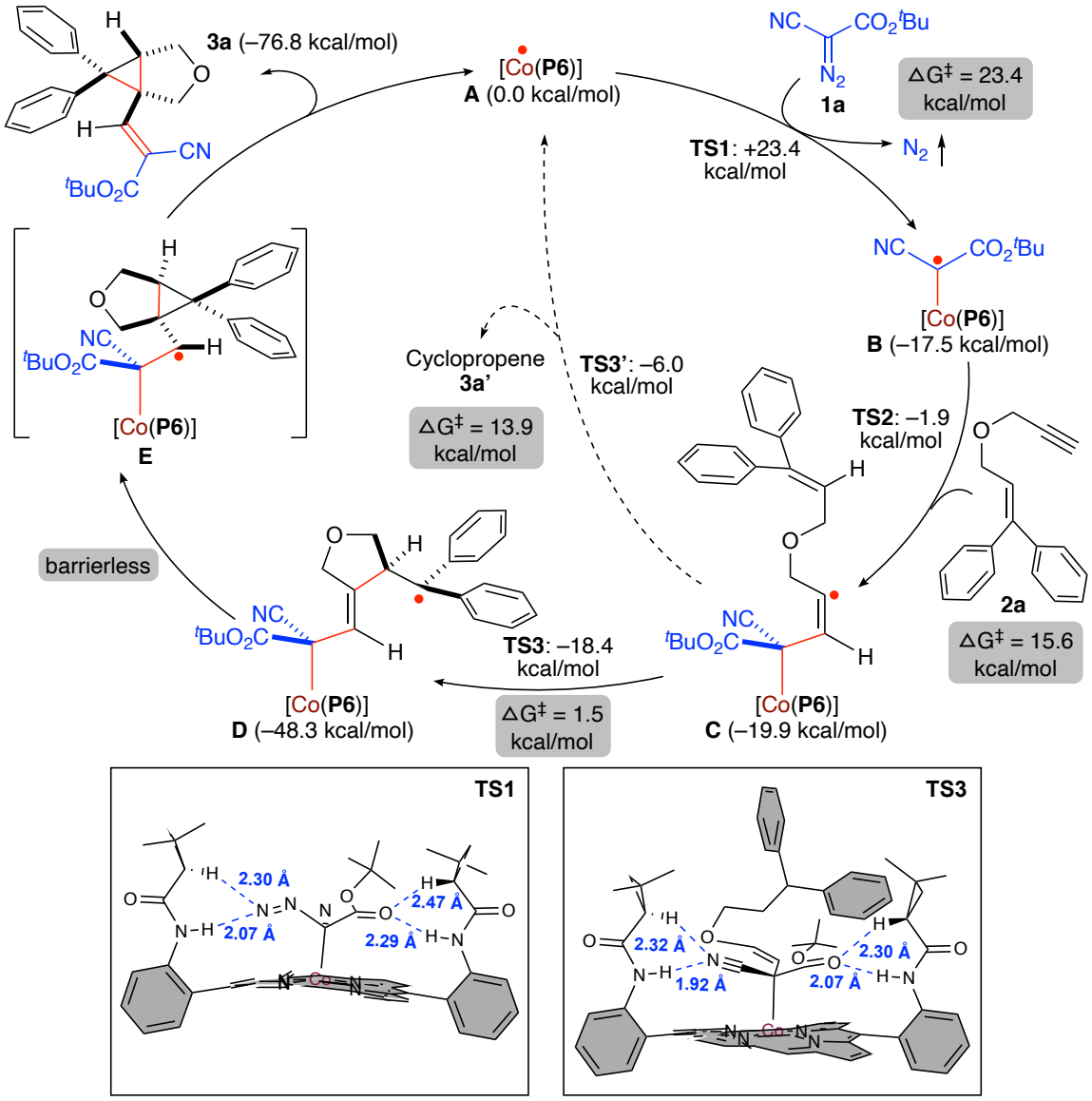


Furthermore, 1,6-enyne **2x** bearing a cyclopropyl ring was synthesized to probe the existence of ε-Co(III)-alkyl radical intermediate through cyclopropylcarbinyl radical ring-opening (Scheme 2.8). When the catalytic reaction of **2x** was conducted at elevated

temperature using [Co(**P6**)] as the catalyst, the formation of conjugated triene **3x** could be observed in 10% yield. Compound **3x** was likely originated from homoallylic alkyl radical $\mathbf{V}_{[\mathrm{Co}(\mathbf{P6})]/\mathbf{2x}}$ that was generated from the ring-opening of the corresponding ε-Co(III)-cyclopropylcarbinyl radical intermediate $\mathbf{III}_{[\mathrm{Co}(\mathbf{P6})]/\mathbf{2x}}$. Presumably, radical intermediate $\mathbf{V}_{[\mathrm{Co}(\mathbf{P6})]/\mathbf{2x}}$ first proceeded intramolecular 1,5-HAA (hydrogen atom abstraction) to deliver δ-Co(III)-allylic radical $^{\mathrm{a}}\mathbf{VI}_{[\mathrm{Co}(\mathbf{P6})]/\mathbf{2x}}$. And then its resonance form β-Co(III)-allylic radical intermediate $^{\mathrm{b}}\mathbf{VI}_{[\mathrm{Co}(\mathbf{P6})]/\mathbf{2x}}$ underwent radical β-scission to give the observed product **3x**. Collectively, these experimental results (Schemes 2.6–2.8) provided convincing evidence for the proposed stepwise radical mechanism of the Co(II)-based catalytic system for cascade cyclization.

DFT calculations (B3LYP-D3(BJ)/def2tzvp/SMD(Acetonitrile)//BP86/Lanl2dz level of theory) were also performed to examine the details of the catalytic pathway and associated energetics for the bicyclization reaction of 1,6-enyne **2a** with α-cyanodiazoacetate **1a** with the use of the actual catalyst [Co(**P6**)] (Scheme 2.9). The DFT calculations indicate the formation of α-Co(III)-alkyl radical intermediate **B** ($\mathbf{I}_{[\mathrm{Co}(\mathbf{P6})]}$) upon activation of diazo **1a** by [Co(**P6**)], with the generation of dinitrogen as the byproduct. The metalloradical activation, which is exergonic by 17.5 kcal/mol, has a relatively high but accessible activation barrier (**TS1**: $\Delta G^{\ddagger}$ = 23.4 kcal/mol) and is found to be the rate-determining step. As illustrated with the optimized structure of **TS1**, there exist multiple H-bonding interactions between the chiral amide units in [Co(**P6**)] and the cyano/ester groups of diazo **1a**. The subsequent radical addition of intermediate **B** to enyne **2a**, which is exergonic by 2.4 kcal/mol, has a lower activation barrier (**TS2**: $\Delta G^{\ddagger}$ = 15.6 kcal/mol), leading to the formation of γ-Co(III)-vinyl radical intermediate **C** as the

Scheme 2.9. DFT Studies on Catalytic Pathway and Energetics for Cascade Cyclization by [Co(P6)]



indicated (*Z*)-configuration. The presence of double hydrogen-bonding interactions between the two amide units of the catalyst and the α-cyano/ester groups was evident in both steps of metalloradical activation and radical addition (see Scheme 2.16 in Experimental Section for details), which rigidifies the conformations of the intermediates and lowers the activation barrier of the transition states. According to the DFT

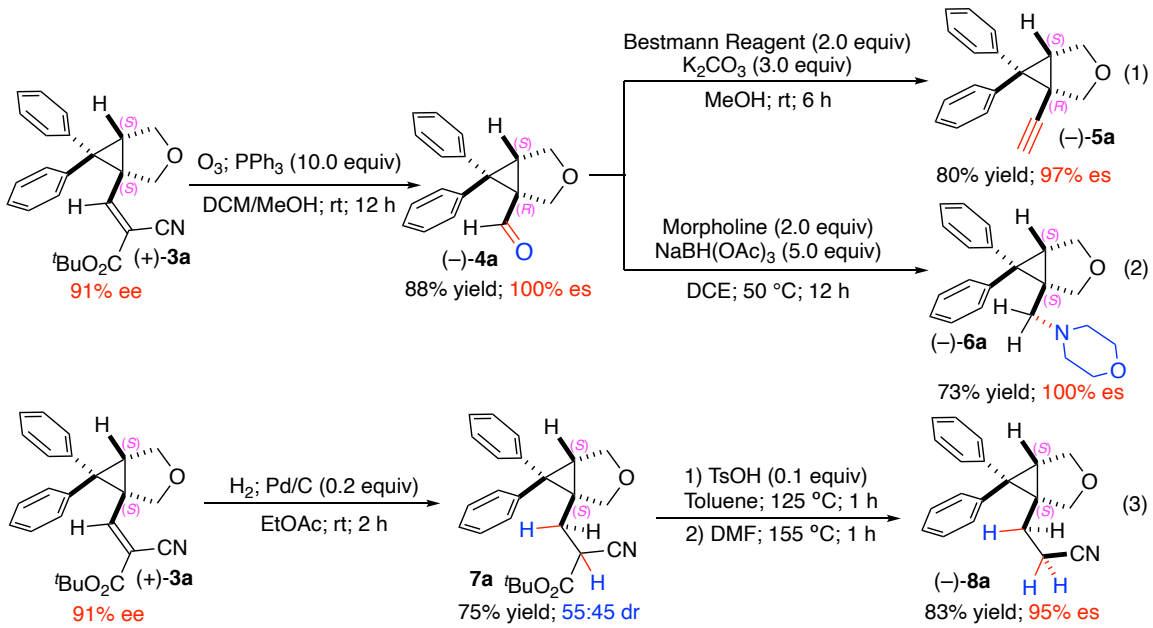
calculations, intermediate **C** undergoes facile *5-exo-trig* radical cyclization with an exceedingly low activation barrier (**TS3**: $\Delta G^{\ddagger}$ = 1.5 kcal/mol), which is also highly exergonic by 28.4 kcal/mol, delivering ε-Co(III)-alkyl radical intermediate **D**. The low barrier is attributed to the multiple H-bonding interactions between the cyclopropyl amide units in the catalyst and the cyano/ester functionalities as illustrated in the optimized structure of **TS3**. In contrast, the potential cyclopropenation of γ-Co(III)-vinyl radical **C** is found to have a significantly higher activation barrier (**TS3'**: $\Delta G^{\ddagger}$ = 13.9 kcal/mol). The large difference in activation barriers between the two competitive pathways of intermediate **C** explains the experimental absence of cyclopropenation product. As the initial stereogenic center generated from radical addition of intermediate **B** to enyne **2a** is nonconsequential, the subsequent *5-exo-trig* radical cyclization of intermediate **C** is considered as the enantio-determining step. To shed light on the asymmetric induction, the energy barrier for the transition state that leads to the formation of the minor enantiomer was also calculated and shown to be much higher than that for the major enantiomer (See Scheme 2.15 in Experimental Section, $\Delta\Delta G^{\ddagger}$ = 6.6 kcal/mol)), which is consistent with the observed high enantioselectivity. The DFT calculations indicate that intermediate **D**, once generated, proceeds with a near barrierless *3-exo-trig* cyclization, presumably through the potential β-Co(III)-alkyl radical intermediate **E**, to deliver the desired cyclopropane-fused tetrahydrofuran **3a** while regenerating catalyst [Co(**P6**)]. Despite considerable efforts, intermediate **E** could not be located by DFT computation, indicating that the last step of radical β-scission is exceedingly facile. The calculated catalytic pathway and associated energetics seem in

good agreement with the experimental observations for the Co(II)-based catalytic system for cascade cyclization.

2.2.5. Synthetic Applications of Resulting Bicyclo[3.1.0]hexanes from Co(II)-Based Asymmetric Radical Bicyclization

Given that the bicyclo[3.1.0]hexane structure represents a key motif in natural products and bioactive molecules, it would be synthetically useful if the dangling trisubstituted alkene unit at the bridgehead of the resulting enantioenriched cyclopropane-fused tetrahydrofurans **3** from the Co(II)-catalyzed radical cascade cyclization could be stereoselectively transformed to other functionalities. As an initial exploration of the synthetic applications, enantioenriched cyclopropane-fused tetrahydrofuran (+)-**3a** was chosen as the model substrate for various transformations (Scheme 2.10 and Scheme 2.11). Firstly, the alkene unit in (+)-**3a** could be converted to formyl functionality by

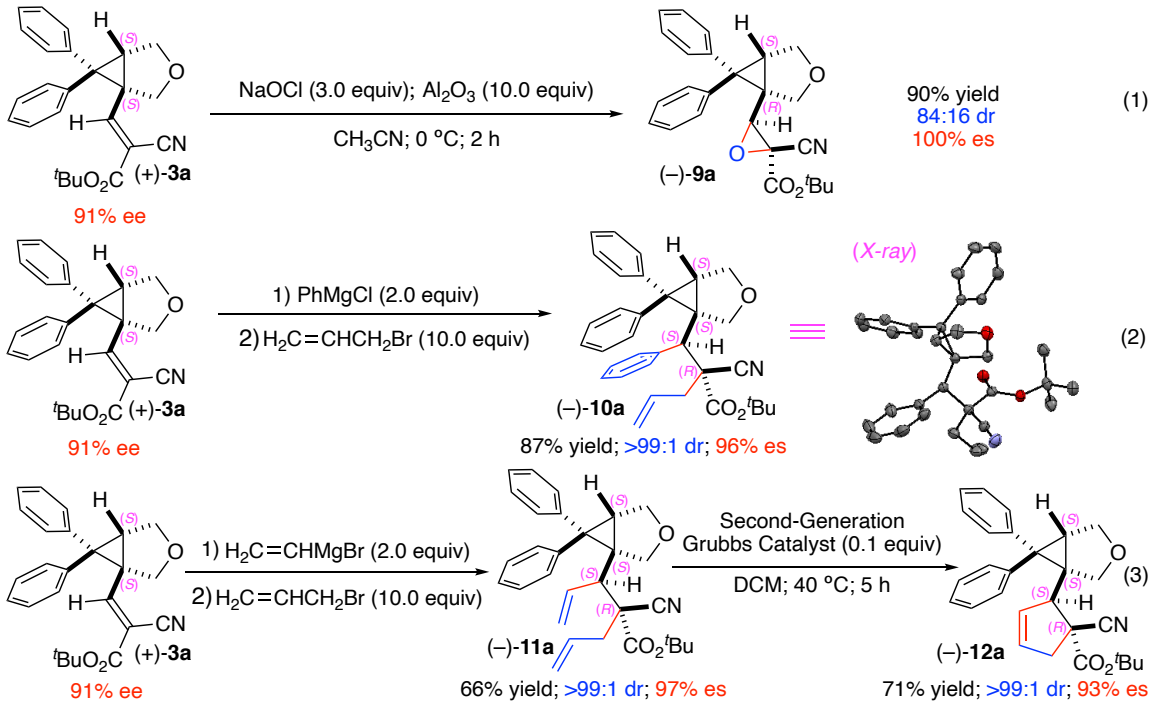
Scheme 2.10. Further Transformations of Resulting Bicyclo[3.1.0]hexanes without Forming New Stereogenic Center



ozonolysis, resulting in the formation of bicyclic aldehyde (–)-**4a** in high yield with complete retention of the stereochemistry. Considering the versatility of the formyl functionality, (–)-**4a** may serve as a valuable intermediate for further transformations. For instance, treatment of (–)-**4a** with Bestmann reagent under basic conditions led to high-yielding production of bicyclic compound (–)-**5a** bearing a terminal alkyne, which is a popular motif in click chemistry for bioconjugation applications (Scheme 2.10; eq.1).[12] As another example, the aldehyde functionality in (–)-**4a** could undergo reductive amination with different amines using sodium triacetoxyborohydride,[13] as shown by its productive reaction with secondary amine morpholine to generate bicyclic compound (–)-**6a** in good yield (Scheme 2.10; eq. 2).[12] Furthermore, the trisubstituted alkene in (+)-**3a** could be productively reduced with dihydrogen on Pd/C to give α-cyanoacetate-containing compound **7a**, which could undergo decarboxylation to afford bicyclic compound (–)-**8a** bearing propanenitrile in good yield with almost full preservation of the original optical purity (Scheme 2.10; eq. 3). In addition to the reduction, the electron-deficient olefin in (+)-**3a** could even undergo epoxidation with sodium hypochlorite in the presence of neutral alumina, furnishing tricyclic compound (–)-**9a** with the three-membered cyclic ether linked directly at the bridgehead in excellent yield with good diastereoselectivity and complete enantiospecificity (Scheme 2.11; eq. 1).[14] Moreover, the highly electron-deficient trisubstituted conjugated alkene in (+)-**3a** could serve as effective Michael acceptor for nucleophilic addition and subsequent alkylation, a sequential double C–C bond-forming process that would allow for the generation of two additional vicinal stereocenters. For example, the reaction of (+)-**3a** with Grignard reagent phenylmagnesium bromide, followed by addition of allyl bromide, resulted in

arylation and allylation of the C=C bond, affording compound (–)-**10a** in high yield with excellent diastereoselectivity and high retention of the original enantiopurity (Scheme 2.11; eq. 2). The configurations of the four contiguous stereogenic centers in (–)-**10a** were established by X-ray crystallography as (*S*,*S*,*S*,*R*), revealing remarkable *syn*-addition of the aryl and allyl groups to the C=C bond. This result demonstrates the effectiveness of the cyclopropane-fused tetrahydrofuran assembly as a chiral auxiliary for controlling the stereochemistry of the alkene vicinal difunctionalization process. To further showcase the synthetic application, (+)-**3a** was shown to proceed a sequential vinylation and allylation process by reacting first with vinylmagnesium bromide as the nucleophile and then with allyl bromide as the electrophile, giving rise to compound (–)-**11a** bearing four contiguous stereogenic centers in good yield with excellent diastereoselectivity and full

Scheme 2.11. Further Transformations of Resulting Bicyclo[3.1.0]hexanes with newly formed stereogenic center



preservation of the original enantiopurity (Scheme 2.11; eq. 3). Subsequent ring-closing metathesis of the two terminal olefin units in (–)-**11a** with second-generation Grubbs catalyst led to effective construction of tricyclic compound (–)-**12a** with the cyclopentene linked directly at the bridgehead in good yield with high retention of enantiopurity.

2.3. CONCLUSIONS

In summary, we have demonstrated the application of metalloradical catalysis (MRC) for controlling enantioselectivity as well as diastereoselectivity in radical cascade cyclization. Applying Co(II)-based metalloradical catalysis, the first asymmetric catalytic system has been successfully developed for radical bicyclization of 1,6-enynes with diazo compounds. With the D_2-symmetric chiral amidoporphyrin 3,5-DiMes-ChenPhyrin as the optimal supporting ligand, the Co(II)-catalyzed radical cascade process enables activation of *tert*-butyl α-cyanodiazoacetate under mild conditions to react with different 1,6-enynes for asymmetric construction of multisubstituted cyclopropane-fused tetrahydrofurans bearing three contiguous stereogenic centers, including two all-carbon quaternary centers, in high yields with excellent enantioselectivities and diastereoselectivities. Combined computational and experimental studies have shed light on the underlying stepwise radical mechanism involving several Co-supported C-centered radical intermediates for the Co(II)-based cascade bicyclization. The resulting enantioenriched cyclopropane-fused tetrahydrofurans that contain a trisubstituted vinyl group at the bridgehead, as showcased in several stereospecific transformations, may serve as useful intermediates for stereoselective organic synthesis. More broadly, we hope that the successful demonstration of this Co(II)-catalyzed asymmetric radical cascade cyclization will inspire further applications of metalloradical catalysis (MRC) as a potentially general

approach to controlling enantioselectivity as well as diastereoselectivity in synthetically attractive radical cascade reactions.

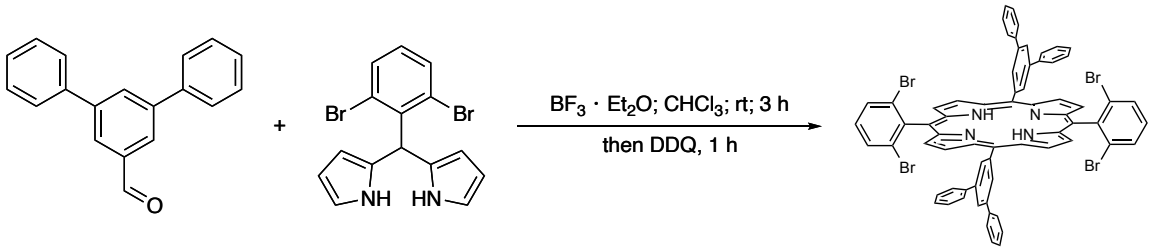
2.4. EXPERIMENTAL SECTION

2.4.1. General Considerations

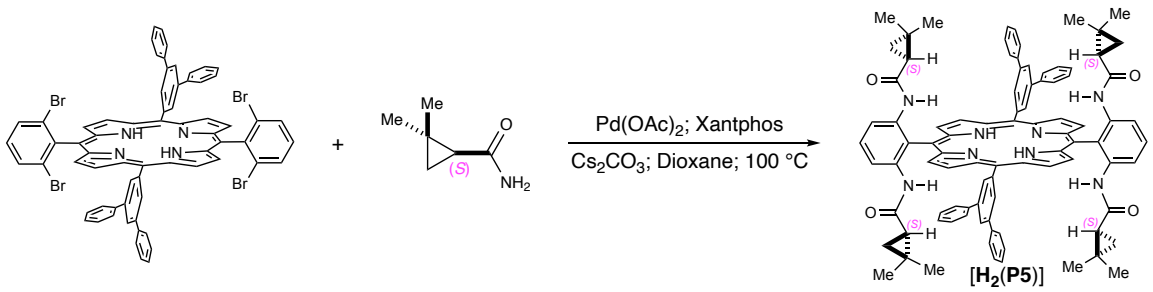
Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254), visualizing with UV-light 254 nm or ceriumammonium-molybdate (CAM) stain (ammonium pentamolybdate, cerium(IV) sulfate, sulfuric acid aqueous solution). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Inova600 (600 MHz), Inova500 (500 MHz), Inova400 (400 MHz) instrument with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel IA, IB, IC, ID, IE, IF and Whelk columns. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. High resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight (ESI-TOF) or direct analysis in real time (DART). The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents [Co(3,5-Di^{t}Bu-IbuPhyrin)], [Co(3,5-Di^{t}Bu-ChenPhyrin)], [Co(2,6-DiMeO-ChenPhyrin)], and [Co(3,5-DiMes-ChenPhyrin)] were prepared by following the literature.[15] *tert*-Butyl 2-cyano-2-diazoacetate, ethyl 2-cyano-2-diazoacetate, isopropyl 2-cyano-2-diazoacetate and phenyl 2-cyano-2-diazoacetate were synthesized according to

reported procedure.[15]

2.4.2. Synthesis of Catalysts

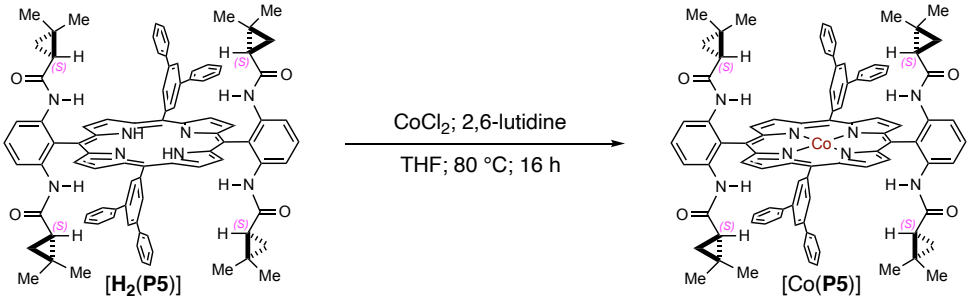


5,15-Di([1,1':3',1''-terphenyl]-5'-yl)-10,20-bis(2,6-dibromophenyl)porphyrin was synthesized according to our previous reported procedure in 65% yield.[15b] ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (d, *J* = 4.8 Hz, 4H), 8.68 (d, *J* = 4.8 Hz, 4H), 8.49 (d, *J* = 1.7 Hz, 4H), 8.26 (t, *J* = 1.8 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 4H), 7.91 (dt, *J* = 6.5, 1.3 Hz, 8H), 7.52 (dt, *J* = 13.4, 8.0 Hz, 10H), 7.41 (dd, *J* = 8.2, 6.4 Hz, 4H), -2.50 (s, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.58, 143.14, 141.37, 140.75, 133.00, 132.23, 131.98, 129.55, 128.80, 128.29, 128.14, 125.95, 120.73, 119.21. UV-vis ($CHCl_3$), λ_{max} nm (log ε): 423(5.64), 517(4.31), 550(3.74), 591(3.81), 646(3.40). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{68}H_{43}Br_4N_4^+$: 1231.0221; Found: 1231.0189.



[**H$_2$(P5)**] was synthesized according to our previous reported procedure in 78% yield.[15b] ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (d, *J* = 4.7 Hz, 4H), 8.94 (s, 4H), 8.49 (s, 8H), 8.30 (t, *J* = 1.7 Hz, 2H), 7.91 (d, *J* = 7.1 Hz, 8H), 7.85 (t, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 8H), 7.45 (t, *J* = 7.4 Hz, 4H), 6.50 (s, 4H), 0.90 (s, 12H), 0.66 (s, 4H), 0.29 – -0.10 (m, 20H), -

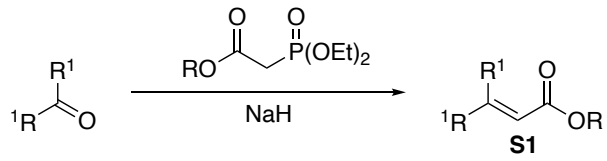
2.53 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.27, 144.42, 143.30, 143.19, 141.98, 135.20, 133.10, 131.77, 130.66, 130.27, 128.77, 123.90, 120.39, 111.80, 32.38, 31.70, 29.05, 25.11, 23.10, 20.98. UV-vis ($CHCl_3$), λ_{max} nm (log ε): 424(5.50), 517(4.24), 552(3.78), 590(3.75), 645(3.45). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{92}H_{83}N_8O_4^+$: 1363.6537; Found: 1363.6520



[Co(**P5**)] was synthesized according to our previously reported procedure in 90% yield.[15b] UV-vis ($CHCl_3$), λ_{max} nm (log ε): 415(5.20), 528(4.07). HRMS (ESI) ($[M]^+$) Calcd. for $C_{92}H_{80}CoN_8O_4^+$: 1419.5634; Found: 1419.5579.

2.4.3. Synthesis of Substrates

Procedure A and Characterization of 1,6-Enyne (2a-2d, 2s)



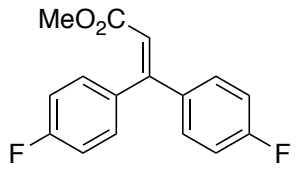
Step 1: To a cooled (0 °C) suspension of NaH (60 wt% in mineral oil, 1.5 equiv) in THF (0.1 M) is added methyl or ethyl diethylphosphonoacetate (1.5–3.0 equiv). The resulting mixture is stirred at 0 °C for 30 min and the corresponding ketone (1.0 equiv) is added (neat for liquids, in solution in THF for solids). The mixture is stirred at the indicated temperature until full conversion of the ketone is detected by TLC. The reaction is quenched by addition of H_2O and the aqueous phase is extracted with ethyl acetate (3 × 3

mL/mmol). The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure and purification by flash column chromatography (hexane/ethyl acetate) yields the pure products.[16]

Ethyl 3,3-diphenylacrylate S1a. Pale yellow oil; 96% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 3H), 7.39 – 7.30 (m, 5H), 7.30 – 7.19 (m, 2H), 6.41 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.18, 156.52, 140.92, 139.12, 129.47, 129.24, 128.47, 128.38, 128.19, 127.96, 117.63, 60.11, 14.10. IR (neat, cm^{-1}): 3056.40, 2947.52, 1721.18, 1615.51, 1445.25, 1263.16, 1150.42, 1033.35, 769.80, 727.44. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{17}O_2^+$: 253.1223; Found: 253.1222.

Ethyl 3,3-bis(4-methoxyphenyl)acrylate S1b. Pale yellow oil; 66% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.60, 160.90, 159.82, 156.52, 134.00, 131.45, 131.01, 130.14, 115.10, 113.85, 113.37, 60.01, 55.51, 55.39, 14.32. IR (neat, cm^{-1}): 2956.52, 2836.60, 1603.96, 1507.36, 1463.36, 1243.03, 1173.24, 1031.63, 831.30, 730.65. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}O_4^+$: 313.1434; Found: 313.1432.

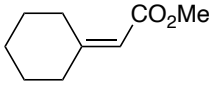
Methyl 3,3-bis(4-fluorophenyl)acrylate S1c. White solid; 92% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.07 (m, 2H), 7.03 (d, *J* = 6.6 Hz, 2H), 6.33 (s, 1H), 3.65 (s, 3H).



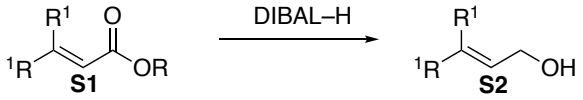
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.36, 163.81 (d, J_{CF} = 250.7 Hz), 162.99 (d, J_{CF} = 248.0 Hz), 155.14, 137.03 (d, J_{CF} = 3.4 Hz), 134.55 (d, J_{CF} = 3.6 Hz), 131.23 (d, J_{CF} = 8.1 Hz), 130.38 (d, J_{CF} = 8.3 Hz), 117.09, 115.69 (d, J_{CF} = 21.6 Hz), 115.26 (d, J_{CF} = 21.5 Hz), 51.50. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.24 (tt, J = 8.4, 5.3 Hz, 1F), -113.02 (tt, J = 8.6, 5.3 Hz, 1F). IR (neat, cm^{-1}): 2950.43, 1722.68, 1505.52, 1224.37, 1156.42, 836.17. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{13}O_2F_2^+$: 275.0878; Found: 275.0877.

Methyl 3,3-bis(3-fluorophenyl)acrylate S1d. Pale yellow oil; 89% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (td, J = 8.0, 5.9 Hz, 1H), 7.31 (td, J = 8.1, 5.9 Hz, 1H), 7.14 – 7.03(m, 3 H), 7.02– 6.95 (m, 2H), 6.92 (ddd, J = 9.4, 2.6, 1.5 Hz, 1H), 6.39(s, 1H), 3.63 (s, 3H)). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.98, 162.90 (d, J_{CF} = 246.8 Hz), 162.65 (d, J_{CF} = 246.5 Hz), 154.15, 142.46 (d, J = 7.2 Hz), 140.46 (d, J = 8.0 Hz), 130.20 (d, J = 8.1 Hz), 129.81 (d, J = 8.5 Hz), 124.96 (d, J = 2.9 Hz), 123.99 (d, J = 2.9 Hz), 118.59, 116.72 (d, J = 21.2 Hz), 116.28 (d, J = 22.2 Hz), 115.53 (d, J = 21.0 Hz), 115.27 (d, J = 22.8 Hz), 51.65. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.49 (ddd, J = 10.4, 8.4, 6.0 Hz, 1F), -113.17 (td, J = 9.0, 5.7 Hz, 1F). IR (neat, cm^{-1}): 2950.84, 1723.19, 1611.44, 1581.41, 1483.41, 1282.35, 1153.41, 868.68, 782.40. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{13}O_2F_2^+$: 275.0878; Found: 275.0878.

Methyl 2-cyclohexylideneacetate S1s. Colorless oil; 69% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.60 (s, 1H), 3.68 (s, 3H), 2.82 (t, J = 5.9 Hz, 2H), 2.22 – 2.17 (m, 2H), 1.70 – 1.56 (m,

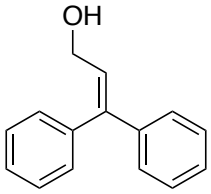


6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.47, 164.12, 112.76, 50.99, 38.19, 30.06, 28.82, 28.02, 26.44. This compound is known.[17]

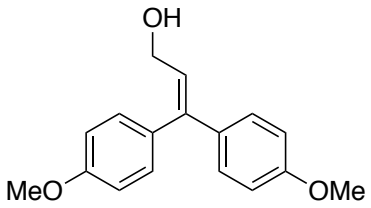


Step 2: To a solution of the corresponding α, β-unsaturated ester (1.0 equiv) in DCM (0.2 M) is added a solution of DIBAL-H (1 M in hexane, 3.0 equiv) at -78 °C. After complete addition, the cooling bath is removed and the resulting solution is stirred at r.t. until full conversion of the starting material is detected by TLC analysis. The reaction is quenched by slow addition of sat. aq. Na-, K-tartrate solution (Rochelle's salt) at 0 °C and is stirred until two distinct layers are obtained. The layers are separated and the aqueous phase is extracted with DCM (3 × 7 mL/mmol). The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude products, which are purified by flash column chromatography.[16]

3,3-Diphenylprop-2-en-1-ol S2a. White solid; 83% Yield; R_f = 0.2 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 3H), 7.32 – 7.22 (m, 5H), 7.19 – 7.14 (m, 2H), 6.25 (t, *J* = 6.9 Hz, 1H), 4.23 (d, *J* = 5.6 Hz, 2H), 1.36 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.42, 141.95, 139.23, 129.91, 128.40, 128.36, 127.79, 127.75, 127.63, 60.92. IR (neat, cm^{-1}): 3300.75, 3024.52, 1493.42, 1443.30, 1012.46, 757.68, 697.30. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{15}H_{13}^+$: 193.1012; Found: 193.1003.

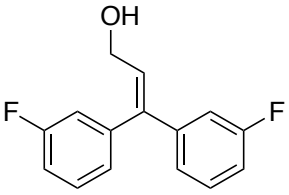


3,3-Bis(4-methoxyphenyl)prop-2-en-1-ol S2b. White solid; 72% Yield; R_f = 0.15 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.29 – 7.24 (m, 2H), 7.11 – 7.05 (m, 2H), 7.03 – 6.98 (m, 2H), 6.29 (t, *J* = 6.9 Hz, 1H), 4.39 (d,



J = 6.9 Hz, 2H), 4.02 (s, 3H), 3.98 (s, 3H), 1.98 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.33, 159.11, 143.58, 134.96, 131.71, 131.10, 129.01, 125.56, 113.67, 113.65, 60.90, 55.42, 55.40. IR (neat, cm^{-1}): 3435.33, 3001.27, 2835.87, 1603.51, 1508.58, 1245.55, 1173.89, 1030.83, 832.74. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{17}H_{17}O_2^+$: 253.1223; Found: 253.1224.

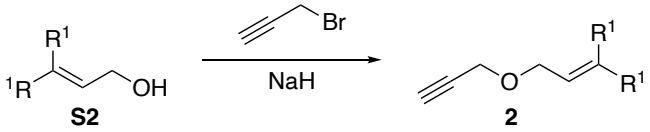
3,3-Bis(4-fluorophenyl)prop-2-en-1-ol S2c. White solid; 96% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 7.11 – 7.02 (m, 2H), 7.00 – 6.93 (m, 2H), 6.16 (t, J = 6.9 Hz, 1H), 4.18 (d, J = 6.8 Hz, 2H), 1.95 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.62 (d, J_{CF} = 247.4 Hz) 162.43 (d, J_{CF} = 247.2 Hz), 142.38, 137.94 (d, J_{CF} = 3.2 Hz), 134.89 (d, J_{CF} = 3.5 Hz), 131.50 (d, J_{CF} = 8.1 Hz), 129.35 (d, J_{CF} = 8.1 Hz), 127.74, 115.43 (d, J_{CF} = 21.4 Hz), 115.27 (d, J_{CF} = 21.5 Hz), 60.63. ^{19}F NMR (564 MHz, $CDCl_3$) δ -114.09(m, 1F), -114.55(m, 1F). IR (neat, cm^{-1}): 3414.10, 2918.49, 1726.06, 1485.32, 1441.87, 158.53, 839.71, 785.11. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{15}H_{11}F_2^+$: 229.0823; Found: 229.0827.



3,3-Bis(3-fluorophenyl)prop-2-en-1-ol S2d. White solid; 91% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 1H), 7.25 – 7.17 (m, 1H), 7.08 – 6.80 (m, 6H), 6.24 (t, J = 6.8 Hz, 1H), 4.17 (d, J = 6.8 Hz, 2H), 2.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.89 (d, J_{CF} = 245.6 Hz) 162.78 (d, J_{CF} = 247.0 Hz), 143.51 (d, J_{CF} = 7.3 Hz), 141.81, 140.73 (d, J_{CF} = 7.5 Hz), 130.05 (d, J_{CF} = 8.4 Hz), 129.84 (d, J_{CF} = 8.4 Hz), 129.31, 125.54 (d, J_{CF} = 3.0 Hz), 123.25 (d, J_{CF} = 2.7 Hz), 116.70 (d, J_{CF} =

21.4 Hz), 114.93 (d, J_{CF} = 21.0 Hz), 114.74 (d, J_{CF} = 21.2 Hz), 114.49 (d, J_{CF} = 22.2 Hz), 60.43. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.81 (td, J = 9.1, 5.9 Hz, 1F), -113.33 (ddd, J = 10.5, 8.5, 6.0 Hz, 1F). IR (neat, cm^{-1}): 3405.57, 2922.78, 1584.37, 1442.47, 1264.22, 1230.68, 878.97, 782.58, 699.86. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{15}H_{11}F_2^+$: 229.0823; Found: 229.0824.

2-Cyclohexylideneethan-1-ol S2s. White solid; 81% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (t, J = 7.2 Hz, 1H), 4.12 (d, J = 7.1 Hz, 2H), 2.17 (t, J = 5.7 Hz, 2H), 2.10 (d, J = 5.6 Hz, 2H), 1.54 (tt, J = 9.6, 4.2 Hz, 6H), 1.41 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.05, 122.93, 61.15, 39.67, 31.47, 31.03, 30.50, 29.32. IR (neat, cm^{-1}): 3318.48, 2924.34, 1668.88, 1446.28, 1078.18, 989.92, 846.92. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_8H_{13}^+$: 109.1012; Found: 109.1016.



Step 3: A solution of allylic alcohol (1 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture stirring for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

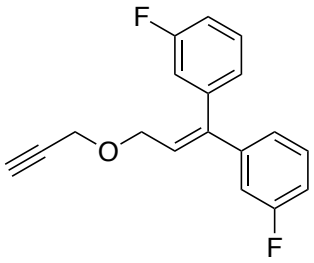
(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)dibenzene 2a. Pale yellow solid; 76% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.42 – 7.30 (m, 5H), 7.25 (d, *J* = 6.7 Hz, 2H), 6.28 (t, *J* = 6.8 Hz, 1H), 4.24 – 4.18 (m, 4H), 2.44 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.70, 141.93, 139.22, 129.96, 128.36, 128.34, 127.81, 127.74, 124.73, 79.94, 74.56, 67.86, 57.60. IR (neat, cm^{-1}): 3291.47, 3055.48, 2847.80, 1598.36, 1493.37, 1443.55, 1073.97, 760.00, 699.13, 631.17. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O^+$: 249.1274; Found: 249.1266.

4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(methoxybenzene) 2b. White solid; 48% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.07 (t, *J* = 6.9 Hz, 1H), 4.15 – 4.10 (m, 4H), 3.84 (s, 3H), 3.80 (s, 3H), 2.38 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.38, 159.14, 145.02, 134.90, 131.68, 131.14, 129.02, 122.46, 113.60, 80.03, 74.45, 67.93, 57.43, 55.35, 55.33. IR (neat, cm^{-1}): 3284.64, 2836.59, 1728.08, 1604.02, 1508.73, 1462.58, 1286.39, 1174.47, 1030.90, 833.36. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{21}O_3^+$: 309.1485; Found: 309.1473.

4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene) 2c. Yellow solid; 40% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.19 (m, 2H), 7.20 – 7.12 (m, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 6.15 (t, *J* = 6.9 Hz, 1H), 4.13 (d, *J* = 2.4 Hz, 2H),

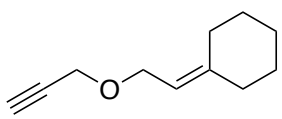
4.10 (d, J = 6.9 Hz, 2H), 2.39 (t, J = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.70 (d, J_{CF} = 247.4 Hz), 162.52 (d, J_{CF} = 247.1 Hz), 143.90, 137.83 (d, J_{CF} = 3.4 Hz), 134.29 (d, J_{CF} = 3.4 Hz), 131.61 (d, J_{CF} = 8.0 Hz), 129.42 (d, J_{CF} = 8.1 Hz), 124.63, 115.45 (d, J_{CF} = 18.1 Hz), 115.28 (d, J_{CF} = 18.1 Hz), 79.78, 74.71, 67.58, 57.68. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.24 (tt, J = 8.4, 5.3 Hz, 1F), -113.02 (tt, J = 8.6, 5.3 Hz, 1F). IR (neat, cm^{-1}): 3302.35, 2853.78, 2360.45, 1602.06, 1507.97, 1224.36, 1159.15, 1075.69, 840.64, 798.14. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{15}OF_2^+$: 285.1086; Found: 285.1081.

3,3'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene) 2d. Yellow oil;



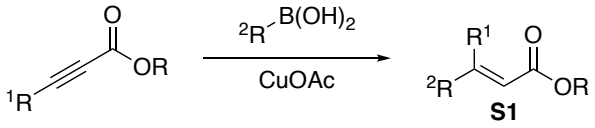
67% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 1H), 7.34 – 7.23 (m, 1H), 7.09 (dd, J = 14.5, 8.3 Hz, 2H), 6.99 (dd, J = 21.0, 10.6 Hz, 4H), 6.30 (t, J = 6.8 Hz, 1H), 4.27 – 4.04 (m, 4H), 2.44 (t, J = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.90 (d, J_{CF} = 245.6 Hz), 162.80 (d, J_{CF} = 246.9 Hz), 143.48 (d, J_{CF} = 7.4 Hz), 143.28, 140.71 (d, J_{CF} = 7.6 Hz), 130.05 (d, J_{CF} = 8.3 Hz), 129.85 (d, J_{CF} = 8.3 Hz), 126.49, 125.60 (d, J_{CF} = 2.9 Hz), 123.30 (d, J_{CF} = 2.8 Hz), 116.80 (d, J_{CF} = 21.4 Hz), 114.97 (d, J_{CF} = 21.0 Hz), 114.83 (d, J_{CF} = 21.3 Hz), 114.55 (d, J_{CF} = 22.3 Hz), 79.66, 74.82, 67.36, 57.68. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.85 (dd, J = 9.3, 5.7 Hz, 1F), -113.27 (m, 1F). IR (neat, cm^{-1}): 3301.72, 3069.78, 2851.91, 1609.59, 1581.06, 1483.73, 1441.90, 1228.24, 1073.20, 779.72. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{15}OF_2^+$: 285.1086; Found: 285.1085.

(2-(Prop-2-yn-1-yloxy)ethylidene)cyclohexane 2s. Light yellow oil; 38% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (d, J = 7.2 Hz, 1H),



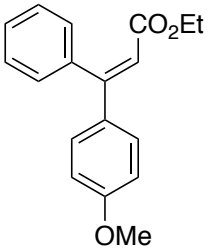
4.13 (d, *J* = 2.5 Hz, 2H), 4.08 (d, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 2.4 Hz, 1H), 2.20 (m, 2H), 2.13 (m, 2H), 1.56 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.53, 116.90, 80.29, 74.21, 65.27, 56.74, 37.30, 29.17, 28.62, 28.01, 26.86. IR (neat, cm^{-1}): 3294.38, 2853.29, 1738.98, 1667.59, 1446.94, 1245.61, 1082.04, 935.87, 667.62. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{11}H_{15}O^+$: 163.1117; Found: 163.1117.

Procedure B and Characterization of 1,6-enyne (2e-2n, 2q-2r)



Step 1: To a solution of propiolate (1.0 equiv) and arylboronic acid (3.0 equiv) in methanol (2.0 mL/mmol) was added CuOAc (0.01 equiv). The reaction mixture was stirred at room temperature under N_2 atmosphere and monitored by TLC. After filtrating through a pad of celite to remove insoluble materials, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give product.[19]

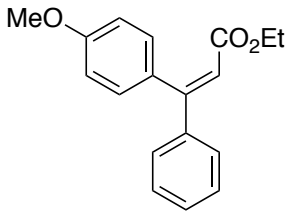
Ethyl (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate S1e. Colorless oil; 84% Yield; R_f =



0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.28 (d, *J* = 2.6 Hz, 2H), 7.25 – 7.20 (m, 2H), 6.89 – 6.82 (m, 2H), 6.33 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.46, 160.95, 156.42, 139.47, 133.34, 129.93, 129.26, 128.16, 128.01, 115.61, 113.95, 60.06, 55.53, 14.20. IR (neat, cm^{-1}): 2979.15, 2902.67, 1717.33, 1595.56, 1509.66, 1442.91, 1368.03,

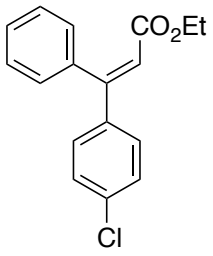
1248.43, 1145.60, 1074.42, 1032.77, 831.59. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{19}O_3^+$: 283.1329; Found: 283.1331.

Ethyl (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate S1f. Colorless oil; 84% Yield; R_f =



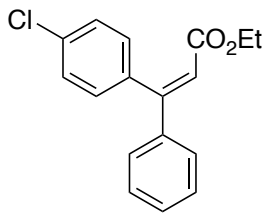
0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.20 – 7.13 (m, 2H), 6.94 – 6.87 (m, 2H), 6.28 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.47, 159.92, 156.72, 141.73, 131.23, 131.10, 129.48, 128.73, 128.47, 117.09, 113.41, 60.17, 55.40, 14.30. IR (neat, cm^{-1}): 2978.78, 2933.41, 2836.32, 1716.62, 1604.43, 1510.11, 1244.34, 1146.08, 1029.55, 831.41, 771.83. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{19}O_3^+$: 283.1329; Found: 283.1333.

Ethyl (*E*)-3-(4-chlorophenyl)-3-phenylacrylate S1g. Colorless oil; 83% Yield; R_f = 0.3



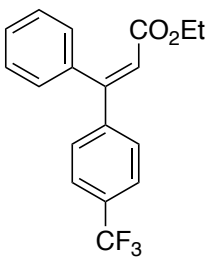
(hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 7.27 – 7.23 (m, 2H), 7.23 – 7.15 (m, 2H), 6.36 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.88, 155.13, 139.31, 138.56, 135.54, 129.60, 129.14, 128.66, 128.38, 128.04, 117.86, 60.19, 14.05. IR (neat, cm^{-1}): 2981.13, 2902.35, 1718.76, 1617.43, 1487.86, 1368.02, 1261.96, 1160.63, 1090.55, 1035.94, 828.80, 729.57. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{16}O_2Cl^+$: 287.0833; Found: 287.0835.

Ethyl (*Z*)-3-(4-chlorophenyl)-3-phenylacrylate S1h. Colorless oil; 58% Yield; R_f = 0. 2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 7.30 – 7.24 (m, 2H), 7.19 – 7.13 (m, 2H), 6.38 (s, 1H), 4.08 (q, *J* = 7.6 Hz,

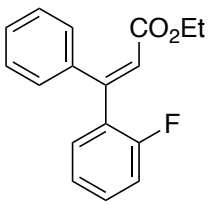


2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.01, 155.53, 140.56, 137.51, 134.33, 130.77, 129.77, 128.63, 128.40, 128.32, 118.00, 60.35, 14.21. IR (neat, cm^{-1}): 2980.19, 2901.88, 1717.49, 1616.62, 1488.52, 1368.11, 1269.96, 1151.43, 1088.89, 828.09. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{16}O_2Cl^+$: 287.0833; Found: 287.0836.

Ethyl (*E*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)acrylate S1i. Colorless oil; 100% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.45 – 7.37 (m, 5H), 7.22 (ddq, J = 4.8, 2.6, 1.2 Hz, 2H), 6.41 (s, 1H), 4.09 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.83, 154.78, 144.53, 138.36, 131.23 (q, J_{CF} = 32.1 Hz), 129.23, 128.71, 128.64, 128.22, 125.48 (q, J_{CF} = 3.7 Hz), 124.10 (q, J_{CF} = 272.1 Hz), 119.56, 60.44, 14.06. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.77(s, 3F). IR (neat, cm^{-1}): 3058.47, 2983.09. 1721.40, 1617.01, 1321.37, 1261.40, 1163.23, 1111.86, 1066.12, 1015.78, 840.89, 698.29. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{16}O_2F_3^+$: 321.1097; Found: 321.1114.

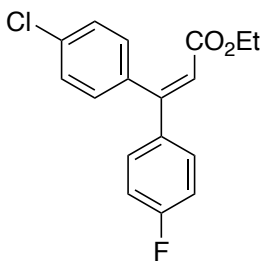


Ethyl (*E*)-3-(2-fluorophenyl)-3-phenylacrylate S1j. Colorless oil; 22% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 3H), 7.34 – 7.30 (m, 1H), 7.29 – 7.21 (m, 2H), 7.17 – 7.04 (m, 3H), 6.34 (s, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.20, 160.39 (d, J_{CF} = 251.4 Hz), 150.54, 139.08, 131.63 (d, J_{CF} = 2.5 Hz), 130.68 (d, J_{CF} = 8.6 Hz), 129.32 (d, J_{CF} = 11.9 Hz), 128.95, 128.44, 128.01, 124.17 (d, J_{CF} = 3.8 Hz), 121.79 (d, J_{CF} = 5.7 Hz), 116.40 (d, J_{CF} = 22.5 Hz), 60.40, 14.13. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.987 (m, 1F). IR (neat, cm^{-1}):

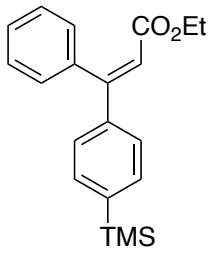


2981.46, 1721.95, 1610.58, 1485.52, 1449.60, 1368.91, 1251.64, 1165.57, 1035.54, 760.59, 698.18. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{16}O_2F^+$: 271.1129; Found: 271.1132.

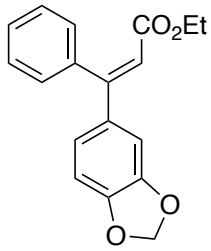
Ethyl (*Z*)-3-(4-chlorophenyl)-3-(4-fluorophenyl)acrylate S1k. Colorless oil; 51% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.11 (m, 2H), 7.02 (m, 2H), 6.32 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.61 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 165.85, 163.75 (d, *J* = 250.7 Hz), 154.36, 137.28, 136.68 (d, *J* = 3.3 Hz), 134.52, 130.70, 130.27 (d, *J* = 8.5 Hz), 128.41, 117.83, 115.69 (d, *J* = 21.6 Hz), 60.38, 14.18. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.20 (m, 1F). IR (neat, cm^{-1}): 2981.46, 1717.07, 1600.62, 1507.28, 1368.14, 1270.51, 1226.35, 1156.99, 1089.09, 830.10. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{15}O_2FCl^+$: 305.0739; Found: 305.0741.



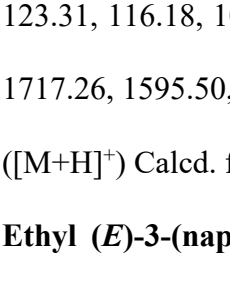
Ethyl (*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)acrylate S1l. Colorless oil; 66% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.40 – 7.36 (m, 3H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 4.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.38 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.28, 156.60, 142.46, 141.14, 139.13, 133.48, 129.23, 128.17, 127.98, 127.55, 117.60, 60.16, 14.12, -1.09. IR (neat, cm^{-1}): 2954.35, 1723.08, 1247.15, 1152.68, 1036.92, 837.08. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{25}O_2Si^+$: 325.1618; Found: 325.1615.



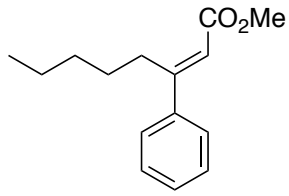
Ethyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylacrylate S1m. Colorless oil; 55% Yield; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 3H), 7.20 (ddd, *J* = 6.0, 3.9, 2.0 Hz, 2H), 6.82 (d, *J* = 1.8 Hz, 1H), 6.80 – 6.71 (m, 2H), 6.28 (s, 1H), 5.97 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.27, 156.25, 148.96, 148.01, 139.24, 135.14, 129.19, 128.21, 127.98, 123.31, 116.18, 108.34, 108.17, 101.58, 60.06, 14.11. IR (neat, cm^{-1}): 2980.60, 2901.17, 1717.26, 1595.50, 1486.29, 1442.85, 1227.84, 1155.34, 1036.58, 933.39. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O_4^+$: 297.1121; Found: 297.1125.



Ethyl (*E*)-3-(naphthalen-2-yl)-3-phenylacrylate S1n. Colorless oil; 90% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.71 – 7.65 (m, 1H), 7.53 – 7.44 (m, 3H), 7.44 – 7.38 (m, 3H), 7.31 – 7.26 (m, 2H), 6.51 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.31, 156.55, 139.17, 138.29, 133.83, 133.16, 129.42, 128.94, 128.84, 128.36, 128.24, 128.10, 127.75, 127.13, 126.66, 125.34, 118.05, 60.26, 14.20. IR (neat, cm^{-1}): 3055.41, 2979.07, 2901.04, 1718.29, 1611.84, 1443.28, 1368.64, 1147.13, 1035.87, 816.28. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{19}O_2^+$: 303.1380; Found: 303.1387.

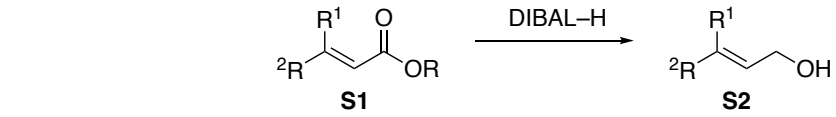


Methyl (*E*)-3-phenyloct-2-enoate S1q. Colorless oil; 100% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.41 – 7.33 (m, 3H), 6.03 (s, 1H), 3.75 (s, 3H), 3.12 – 3.07 (m, 2H), 1.47 – 1.39 (m, 2H), 1.36 – 1.26 (m,



4H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.07, 161.54, 141.59, 129.01, 128.67, 126.84, 116.91, 51.25, 32.07, 31.16, 28.88, 22.60, 14.17. IR (neat, cm^{-1}): 2928.69, 2859.28, 1715.32, 1622.77, 1431.94, 1160.83, 1045.93, 872.26, 769.69, 695.11. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{21}O_2^+$: 233.1536; Found: 233.1547.

Methyl (*E*)-3-(4-bromophenyl)oct-2-enoate S1r. Colorless oil; 98% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 5.99 (s, 1H), 3.74 (s, 3H), 3.15 – 2.92 (m, 2H), 1.45 – 1.37 (m, 2H), 1.37 – 1.15 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.80, 160.10, 140.42, 131.86, 128.44, 123.23, 117.32, 51.33, 31.97, 30.96, 28.77, 22.57, 14.14. IR (neat, cm^{-1}): 2952.23, 2928.16, 2858.85, 1716.05, 1621.93, 1488.55, 1281.88, 1161.37, 1073.57, 1006.71, 823.32. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{20}O_2Br^+$: 311.0641; Found: 311.0641.

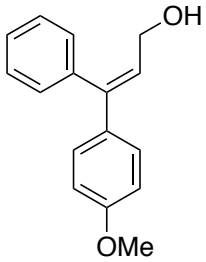


S1 **S2**

Step 2: To a solution of the corresponding α, β-unsaturated ester (1.0 equiv) in DCM (0.2 M) is added a solution of DIBAL-H (1 M in hexane, 3.0 equiv) at -78 °C. After complete addition, the cooling bath is removed and the resulting solution is stirred at r.t. until full conversion of the starting material is detected by TLC analysis. The reaction is quenched by slow addition of sat. aq. Na-, K-tartrate solution (Rochelle's salt) at 0 °C and is stirred until two distinct layers are obtained. The layers are separated and the aqueous phase is extracted with DCM (3 × 7 mL/mmol). The combined organic layers are dried over

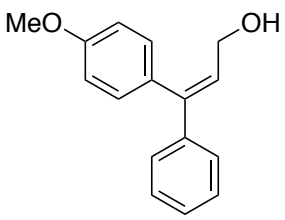
Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude products, which are purified by flash column chromatography.[16]

(*E*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol S2e. Colorless oil; 53% Yield; R_f =



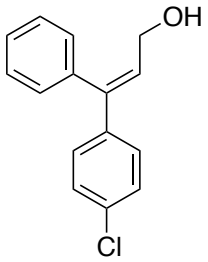
0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 3H), 7.23 – 7.14 (m, 4H), 6.87 – 6.78 (m, 2H), 6.18 (t, *J* = 6.9 Hz, 1H), 4.19 (d, *J* = 6.9 Hz, 2H), 3.80 (s, 3H), 1.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.46, 144.07, 139.48, 134.57, 129.90, 128.94, 128.38, 127.70, 125.85, 113.76, 60.97, 55.48. IR (neat, cm^{-1}): 3384.83, 2932.57, 2835.62, 1603.84, 1507.88, 1244.19, 1177.20, 1030.40, 826.92, 700.08. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{16}H_{15}O^+$: 223.1117; Found: 223.1123.

(*Z*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol S2f. Colorless oil; 86% Yield; R_f =



0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 7.15 – 7.04 (m, 2H), 6.95 – 6.87 (m, 2H), 6.19 (t, *J* = 6.8 Hz, 1H), 4.25 (d, *J* = 6.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.24, 144.16, 142.41, 131.54, 131.17, 128.32, 127.92, 127.73, 127.28, 113.76, 60.97, 55.45. IR (neat, cm^{-1}): 3385.01, 2930.71, 2836.05, 1604.99, 1509.39, 1243.92, 1174.98, 1029.74, 832.91, 698.72. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{16}H_{15}O^+$: 223.1117; Found: 233.1127.

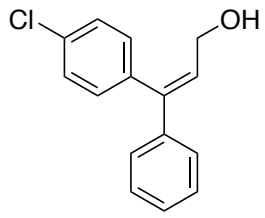
(*E*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol S2g. Colorless oil; 97% Yield; R_f =



0.15 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 3H), 7.35 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 6.29 (t, *J* = 6.8 Hz, 1H), 4.28 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.18, 140.42, 138.73, 133.64,

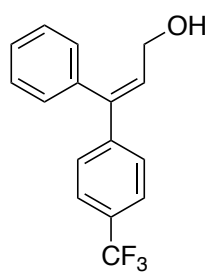
129.81, 129.03, 128.50, 128.09, 127.95, 60.75. IR (neat, cm^{-1}): 3393.03, 3026.99, 1659.15, 1487.34, 1400.54, 1273.31, 1089.79, 1012.46, 818.83, 700.04. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{15}H_{12}Cl^+$: 227.0622; Found: 227.0626.

(*Z*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol S2h. White solid; 81 % Yield; R_f = 0.2



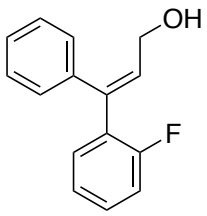
(hexanes/ethyl acetate, 4:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.17 (m, 3H), 7.17 – 7.10 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.16 (t, *J* = 6.9 Hz, 1H), 4.12 (dd, *J* = 6.8, 4.6 Hz, 2H), 1.39 – 1.28 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.37, 141.56, 137.65, 133.77, 131.30, 128.65, 128.47, 128.09, 128.01, 127.78, 60.77. IR (neat, cm^{-1}): 3439.30, 3057.59, 1658.53, 1488.34, 1272.87, 1089.53, 1013.63, 922.45, 828.58. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{15}H_{12}Cl^+$: 227.0622; Found: 227.0629.

(*E*)-3-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol S2i. Colorless oil; 60%



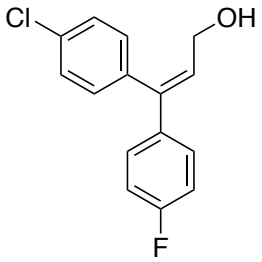
Yield; R_f = 0.15 (hexanes/ethyl acetate, 4:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.31 (m, 5H), 7.14 – 7.09 (m, 2H), 6.27 (t, *J* = 6.7 Hz, 1H), 4.22 (d, *J* = 6.7 Hz, 2H), 1.73 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.45, 143.07, 138.42, 130.32, 130.01, 129.86, 128.66, 128.07, 125.25, 123.44, 60.75. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.53 (s, 3F). IR (neat, cm^{-1}): 3057.55, 1712.02, 1522.98, 1445.16, 1265.12, 1152.45, 1023.20, 771.27. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{16}H_{12}F_3^+$: 261.0886; Found: 261.0887.

(*E*)-3-(2-Fluorophenyl)-3-phenylprop-2-en-1-ol S2j. Colorless oil; 70% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.27 – 7.22 (m, 1H), 7.17 (t, *J* = 7.0 Hz, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.02 (dd, *J* = 10.8, 8.1 Hz,



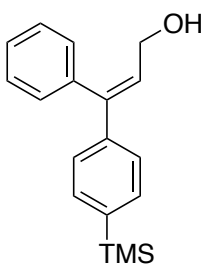
1H), 6.17 (t, J = 6.7 Hz, 1H), 4.30 (d, J = 6.7 Hz, 2H), 1.71 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.32 (d, J_{CF} = 249.0 Hz), 139.11, 138.83, 131.73 (d, J_{CF} = 3.7 Hz), 131.40 (d, J_{CF} = 3.4 Hz), 130.37 (d, J_{CF} = 12.7 Hz), 129.31, 129.23, 128.28, 127.74, 124.01 (d, J_{CF} = 3.6 Hz), 116.05 (d, J_{CF} = 22.5 Hz), 60.54. ^{19}F NMR (564 MHz, $CDCl_3$) δ -114.10 (ddd, J = 11.6, 7.8, 4.9 Hz, 1F). IR (neat, cm^{-1}): 3373.64, 3056.22, 1486.24, 1264.77, 1214.95, 1014.05, 733.17, 699.91. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{15}H_{12}F^+$: 211.0918; Found: 211.0914.

(*Z*)-3-(4-Chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-ol S2k. Colorless oil; 87%



Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 8.6, 5.5 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 6.18 (t, J = 6.9 Hz, 1H), 4.19 (dd, J = 7.1 Hz, 2H), 1.52 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.70 (d, J_{CF} = 247.6 Hz), 142.37, 137.71 (d, J_{CF} = 3.3 Hz), 137.45, 133.94, 129.41 (d, J_{CF} = 8.1 Hz), 128.75, 127.97, 115.36 (d, J_{CF} = 21.6 Hz), 60.68. ^{19}F NMR (564 MHz, $CDCl_3$) δ -114.40 (tt, J = 8.6, 5.3 Hz, 1F). IR (neat, cm^{-1}): 3436.12, 2922.67, 1599.09, 1507.18, 1226.94, 1158.45, 1090.23, 1013.48, 832.16, 763.02. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{15}H_{11}FCl^+$: 245.0528; Found: 245.0536.

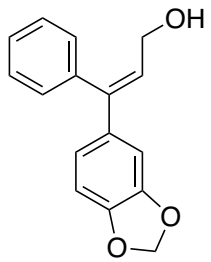
(*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)prop-2-en-1-ol S2l. Colorless oil; 82% Yield;



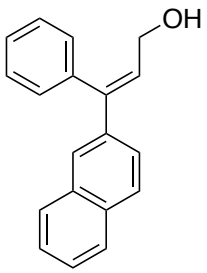
R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.2, 2.1 Hz, 2H), 7.36 (dd, J = 13.4, 6.4 Hz, 3H), 7.32 – 7.22 (m, 2H), 7.22 – 7.08 (m, 2H), 6.29 (t, J = 6.8 Hz, 1H), 4.23 (d, J = 6.8 Hz, 2H), 1.40 (s, 1H), 0.27 (s, 9H). ^{13}C NMR (150 MHz,

$CDCl_3$) δ 144.04, 142.16, 139.85, 139.10, 133.32, 129.83, 128.29, 127.79, 127.60, 126.94, 60.70, -1.02. IR (neat, cm^{-1}): 3299.85, 3060.29, 3017.03, 2953.72, 1247.86, 1110.03, 1014.39, 827.87, 702.41. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{23}OSi^+$: 283.1513; Found: 283.1511.

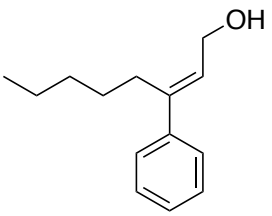
(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-ol S2m. Yellow solid; 65% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.23 – 7.09 (m, 2H), 6.78 (d, *J* = 1.8 Hz, 1H), 6.74 – 6.66 (m, 2H), 6.14 (t, *J* = 6.9 Hz, 1H), 5.94 (s, 2H), 4.17 (d, *J* = 7.0 Hz, 2H), 1.54 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.76, 147.35, 144.03, 139.27, 136.36, 129.82, 128.36, 127.74, 126.39, 121.78, 108.04, 108.03, 101.23, 60.84. IR (neat, cm^{-1}): 3335.08, 2886.19, 1485.77, 1441.83, 1234.84, 1038.83, 933.53, 702.15. HRMS (DART) ($[M]^+$) Calcd. for $C_{16}H_{14}O_3^+$: 254.0938; Found: 254.0948.



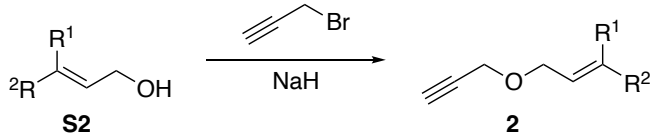
(*E*)-3-(Naphthalen-2-yl)-3-phenylprop-2-en-1-ol S2n. Colorless oil; 86% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.48 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.47 – 7.35 (m, 5H), 7.25 – 7.20 (m, 2H), 6.39 (t, *J* = 6.8 Hz, 1H), 4.28 (d, *J* = 6.8 Hz, 2H), 1.45 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.39, 139.30, 139.21, 133.42, 133.03, 130.02, 128.49, 128.42, 128.20, 127.93, 127.87, 127.70, 127.22, 126.35, 126.23, 125.60, 61.01. IR (neat, cm^{-1}): 3411.62, 3055.32, 1654.61, 1597.45, 1444.57, 1287.18, 1119.92, 1018.28, 816.84, 749.06, 700.63. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{19}H_{15}^+$: 243.1168; Found: 243.1172.



(*E*)-3-Phenyloct-2-en-1-ol S2q. Colorless oil; 50% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.80 (t, *J* = 6.7 Hz, 1H), 4.29 (d, *J* = 6.8 Hz, 2H), 2.48 – 2.43 (m, 2H), 2.02 (s, 1H), 1.29 (p, *J* = 6.9 Hz, 2H), 1.26 – 1.17 (m, 4H), 0.84 – 0.77 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.38, 142.40, 128.35, 127.23, 127.03, 126.51, 59.77, 31.81, 30.14, 28.72, 22.55, 14.12. IR (neat, cm^{-1}): 3319.45, 2954.31, 1493.20, 1377.44, 1103.38, 1013.82, 756.59, 695.54. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{14}H_{19}^+$: 187.1481; Found: 187.1486.



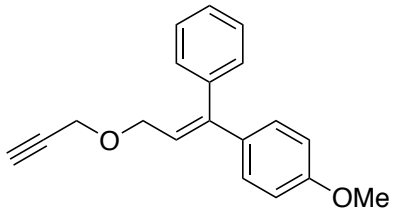
(*E*)-3-(4-Bromophenyl)oct-2-en-1-ol S2r. Colorless oil; 65% Yield; R_f = 0.25 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.83 (t, *J* = 6.7 Hz, 1H), 4.33 (d, *J* = 6.7 Hz, 2H), 2.50 – 2.44 (m, 2H), 1.50 (s, 1H), 1.37 – 1.19 (m, 6H), 0.84 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.53, 141.34, 131.54, 128.25, 127.58, 121.25, 59.85, 31.78, 30.07, 28.64, 22.59, 14.16. IR (neat, cm^{-1}): 3439.62, 2954.09, 1685.40, 1585.21, 1486.87, 1395.90, 1070.88, 1008.29, 821.95. HRMS (DART) ($[M+H-H_2O]^+$) Calcd. for $C_{14}H_{18}Br^+$: 281.0536; Found: 281.0522.



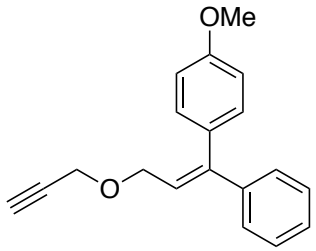
Step 3: A solution of allylic alcohol (1 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture stirring for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2 equiv).

The reaction mixture was stir at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

(*E*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2e. White solid; 56% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 3H), 7.20 – 7.17(m, 4H), 6.91 – 6.69 (m, 2H), 6.13 (d, *J* = 8.8 Hz, 1H), 4.19 – 4.05 (m, 4H), 3.80 (s, 3H), 2.37 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.48, 145.32, 139.46, 134.55, 129.95, 128.97, 128.32, 127.67, 122.90, 113.73, 80.02, 74.48, 67.93, 57.52, 55.47. IR (neat, cm^{-1}): 3296.37, 3055.62, 2849.03, 1660.76, 1590.79, 1487.36, 1403.54, 1073.15, 1012.68, 702.67. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{19}O_2^+$: 279.1380; Found: 279.1381.

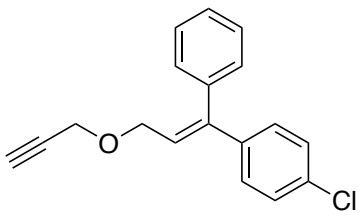


(*Z*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2f. White solid; 65% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 7.14 – 7.07 (m, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.16 (t, *J* = 6.8 Hz, 1H), 4.17 (d, *J* = 6.8 Hz, 2H), 4.14 (d, *J* = 2.3 Hz, 2H), 3.84 (s, 3H), 2.39 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.16, 145.37, 142.30, 131.44, 131.14, 128.22, 127.87, 127.68, 124.25, 113.63, 79.95, 74.53, 67.85, 57.50, 55.32. IR (neat, cm^{-1}): 3296.01, 3057.28, 2848.95, 1632.91, 1596.39,

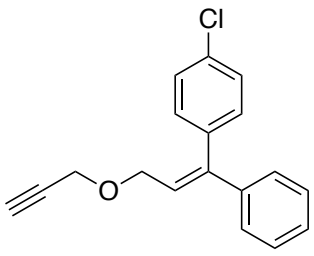


1488.86, 1445.41, 1357.88. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{19}O_2^+$: 279.1380; Found: 289.1387.

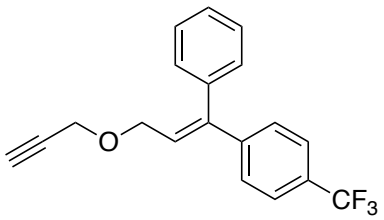
(*E*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2g. White solid; 75% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.34 – 7.31 (m, 2H), 7.25 – 7.20 (m, 4H), 6.26 (t, *J* = 6.8 Hz, 1H), 4.19 (dd, *J* = 4.6, 2.2 Hz, 4H), 2.45 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.55, 140.41, 138.73, 133.73, 129.87, 129.08, 128.51, 127.97, 125.19, 79.84, 74.64, 67.78, 57.72. IR (neat, cm^{-1}): 3296.37, 3055.62, 2849.03, 1660.76, 1590.79, 1487.36, 1403.54, 1073.15, 1012.68, 702.67. HRMS (DART) ([M–H]$^-$) Calcd. for $C_{18}H_{14}OCl^-$: 281.0728; Found: 281.07217.



(*Z*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2h. White solid; 70% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.16 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.18 (t, *J* = 6.8 Hz, 1H), 4.09 (d, *J* = 2.4 Hz, 2H), 4.07 (d, *J* = 6.9 Hz, 2H), 2.35 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.71, 141.50, 137.62, 133.75, 131.35, 128.62, 128.44, 128.04, 127.78, 125.20, 79.79, 74.73, 67.58, 57.66. IR (neat, cm^{-1}): 3296.01, 3057.28, 2848.95, 1632.91, 1596.39, 1488.86, 1445.41, 1357.88. HRMS (DART) ([M–H]$^-$) Calcd. for $C_{18}H_{14}OCl^-$: 281.0733; Found: 281.0713.

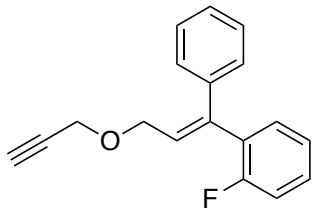


(*E*)-1-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene 2i. Light yellow solid; 78% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.09 (m, 5H), 7.09 – 7.02 (m, 2H), 6.17

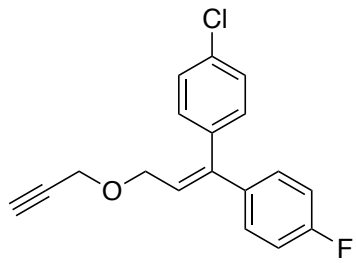


(t, J = 6.7 Hz, 1H), 4.04 (d, J = 6.6 Hz, 2H), 4.02 (d, J = 2.4 Hz, 2H), 2.27 (t, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.42, 144.31, 138.40, 129.84, 129.04 (q, J_{CF} = 45.8 Hz), 128.59, 128.12, 128.04, 126.90, 125.28 (q, J_{CF} = 3.8 Hz), 124.31 (q, J_{CF} = 272.0 Hz), 79.75, 74.75, 67.70, 57.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.548 (s, 3F). IR (neat, cm^{-1}): 3304.66, 3025.31, 2850.74, 1616.28, 1324.09, 1166.07, 1122.32, 1067.21, 1016.70, 833.19. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{16}OF_3^+$: 317.1148; Found: 317.1143.

(*E*)-1-Fluoro-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2j. Light yellow oil; 48% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 7H), 7.10 – 7.08 (m, 1H), 7.06 – 7.00 (m, 1H), 6.15 (t, J = 6.8 Hz, 1H), 4.23 (d, J = 6.7 Hz, 2H), 4.16 (d, J = 2.4 Hz, 2H), 2.38 (t, J = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.33 (d, J_{CF} = 249.0 Hz), 140.34, 139.10, 131.39 (d, J_{CF} = 3.4 Hz), 130.35 (d, J_{CF} = 12.7 Hz), 129.39, 129.28, 128.77 (d, J_{CF} = 3.6 Hz), 128.27, 127.77, 124.01 (d, J_{CF} = 3.7 Hz), 116.07 (d, J_{CF} = 22.6 Hz), 79.84, 74.64, 67.37, 57.59. ^{19}F NMR (470 MHz, $CDCl_3$) δ 114.00 (m, 1F). IR (neat, cm^{-1}): 3295.30, 3057.72, 2917.87, 2849.61, 1723.65, 1575.59, 1486.34, 1450.12, 1212.78, 757.80. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{18}H_{19}NOF^+$: 284.1445 Found 284.1450.

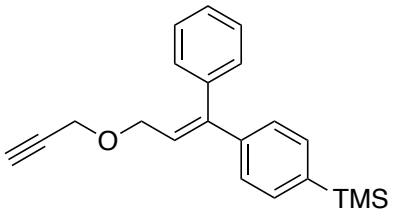


(*Z*)-1-Chloro-4-(1-(4-fluorophenyl)-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2k. Light yellow solid; 54% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 8.5 Hz, 2H), 7.20 (dd, J = 8.9, 5.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.97 (t, J = 8.7 Hz, 2H), 6.16 (t, J = 6.9 Hz, 1H), 4.13 (d, J = 2.1 Hz, 2H), 4.09



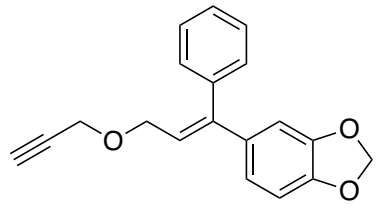
(d, J = 6.9 Hz, 2H), 2.40 (t, J = 2.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.73 (d, J_{CF} = 247.6 Hz), 143.74, 137.67 (d, J_{CF} = 3.0 Hz), 137.42, 133.94, 131.27, 129.44 (d, J_{CF} = 8.1 Hz), 128.72, 125.06, 115.35 (d, J_{CF} = 21.4 Hz), 79.74, 74.78, 67.56, 57.74. ^{19}F NMR (564 MHz, $CDCl_3$) δ 114.35 (m, 1F). IR (neat, cm^{-1}): 3290.86, 3055.06, 2847.98, 1597.15, 1504.33, 1442.19, 1357.16, 1273.81, 1074.55, 749.39. HRMS (DART) ([M–H]$^-$) Calcd. for $C_{18}H_{13}OFCl^-$: 299.0639; Found: 299.0598.

(*E*)-trimethyl(4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)phenyl)silane 2l.



Yellow oil; 77% Yield; R_f = 0.4 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.42 – 7.31 (m, 3H), 7.29 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 6.26 (t, J = 6.8 Hz, 1H), 4.16 (d, J = 6.7 Hz, 2H), 4.14 (d, J = 2.3 Hz, 2H), 2.39 (t, J = 2.4 Hz, 1H), 0.27 (d, J = 0.9 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.56, 142.11, 140.01, 139.13, 133.35, 129.90, 128.31, 127.67, 126.97, 124.80, 79.90, 74.52, 67.83, 57.54, -1.00. IR (neat, cm^{-1}): 3298.79, 3060.81, 2953.65, 1247.96, 1109.05, 1074.83, 837.93, 722.14. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{25}OSi^+$: 321.1669; Found: 321.1649.

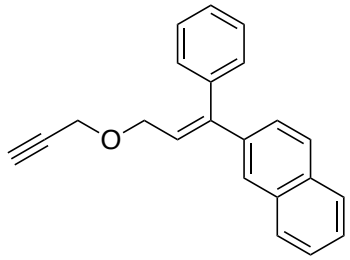
(*E*)-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzo[*d*][1,3]dioxole 2m.



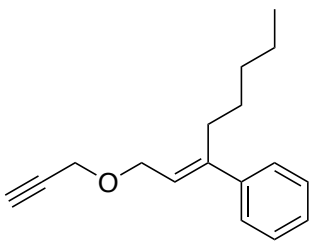
Yellow solid; 54% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.23 – 7.15 (m, 2H), 6.78 (dd, J = 1.6, 0.7 Hz, 1H), 6.74 – 6.68 (m, 2H), 6.11 (t, J = 6.8 Hz, 1H), 5.94

(s, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 4.09 (d, *J* = 6.8 Hz, 2H), 2.37 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.75, 147.38, 145.32, 139.25, 136.33, 129.87, 128.31, 127.73, 123.44, 121.83, 108.05, 108.02, 101.23, 79.91, 74.49, 67.82, 57.50. IR (neat, cm^{-1}): 3291.25, 3017.77, 2970.00, 2891.71, 1738.21, 1485.98, 1365.28, 1231.07, 1039.00, 933.34, 731.22. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{17}O_3^+$: 293.1172; Found: 293.1170.

(*E*)-2-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)naphthalene 2n. White solid; 27% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.83 – 7.69 (m, 3H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.34 (m, 6H), 7.25 – 7.20 (m, 2H), 6.36 (t, *J* = 6.8 Hz, 1H), 4.19 (d, *J* = 6.8 Hz, 2H), 4.16 (d, *J* = 2.4 Hz, 2H), 2.39 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.60, 139.26, 139.17, 133.39, 133.03, 130.04, 128.42, 127.89, 127.83, 127.68, 127.22, 126.32, 126.21, 125.61, 125.30, 79.94, 74.61, 67.93, 57.67. IR (neat, cm^{-1}): 3296.37, 3055.62, 2849.03, 1660.76, 1590.79, 1487.36, 1403.54, 1073.15, 1012.68, 702.67. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{19}O^+$: 299.1430; Found: 299.1424.

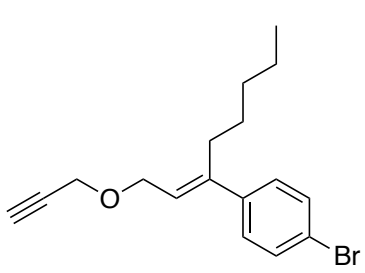


(*E*)-(1-(Prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene 2q. Light yellow oil; 80% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.24 (m, 1H), 5.82 (t, *J* = 6.7 Hz, 1H), 4.31 (d, *J* = 6.7 Hz, 2H), 4.22 (d, *J* = 2.3 Hz, 2H), 2.59 – 2.53 (m, 2H), 2.47 (t, *J* = 2.4 Hz, 1H), 1.45 – 1.24 (m, 6H), 0.89 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.22, 142.33, 128.34, 127.30, 126.53, 123.72, 80.03, 74.51, 66.36, 57.17,

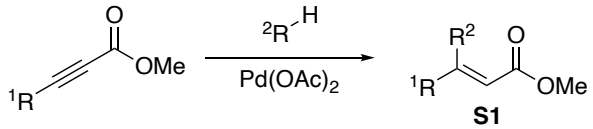


31.83, 30.27, 28.64, 22.55, 14.14. IR (neat, cm^{-1}): 3293.75, 3024.11, 2954.34, 2927.99, 2857.78, 1493.20, 1443.94, 1356.62, 1073.68, 758.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{23}O^+$: 243.1743; Found 243.1747.

(*E*)-1-Bromo-4-(1-(prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene 2r. Light yellow oil; 76% Yield; R_f = 0.5 (hexanes/ethyl acetate, 20:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.78 (t, *J* = 6.7 Hz, 1H), 4.26 (d, *J* = 6.7 Hz, 2H), 4.19 (d, *J* = 2.3 Hz, 2H), 2.50 – 2.46 (m, 3H), 1.34 – 1.33 (m, 2H), 1.31 – 1.25 (m, 4H), 0.86 – 0.84 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.00, 141.20, 131.46, 128.20, 124.38, 121.23, 79.92, 74.64, 66.32, 57.35, 31.74, 30.14, 28.51, 22.54, 14.13. IR (neat, cm^{-1}): 3299.34, 2954.16, 2927.54, 2857.39, 1487.23, 1355.89, 1071.88, 1008.04, 814.15, 630.81. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{17}H_{25}NOBr^+$: 338.1114; Found: 338.1098.

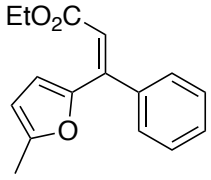


Procedure C and Characterization of 1,6-enyne 2o, 2p.



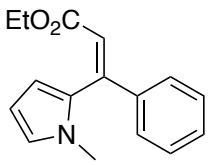
Step 1: To a solution of $Pd(OAc)_2$ (0.05 equiv) and pyrrole (3.0 equiv) in acetic acid (1.0 M) was added propiolate (1.0 equiv). The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC. After propiolate was completely consumed, the reaction mixture was poured into a saturated NaCl solution and extracted with ether. The organic layer was dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure and purification by flash column chromatography (hexane/ethyl acetate) yields the pure products product.[20]

Ethyl (*Z*)-3-(5-methylfuran-2-yl)-3-phenylacrylate S1o. Light yellow oil; 66% Yield;

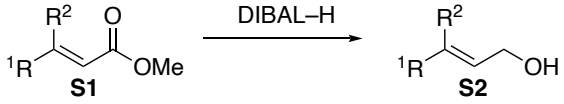


R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.31 (m, 5H), 6.56 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 3.3 Hz, 1H), 5.90 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.69, 153.97, 149.41, 142.11, 139.77, 129.01, 128.28, 116.39, 116.36, 116.04, 108.00, 60.40, 14.39, 14.14. This compound is known.[6]

Ethyl (*Z*)-3-(1-methyl-1*H*-pyrrol-2-yl)-3-phenylacrylate S1p. Light yellow oil; 99%



Yield; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 6.76 – 6.72 (m, 1H), 6.38 (s, 1H), 6.23 – 6.18 (m, 1H), 6.13 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.33 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.18, 147.26, 140.58, 130.07, 129.74, 128.64, 128.22, 123.91, 119.02, 111.84, 107.94, 60.27, 34.57, 14.37. This compound is known.[20]

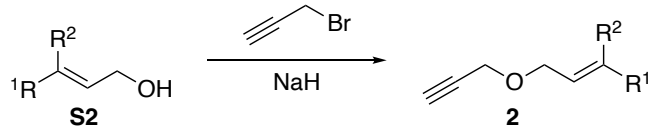


Step 2: To a solution of the corresponding α, β-unsaturated ester (1.0 equiv) in DCM (0.2 M) is added a solution of DIBAL-H (1 M in hexane, 3.0 equiv) at -78 °C. After complete addition, the cooling bath is removed and the resulting solution is stirred at r.t. until full conversion of the starting material is detected by TLC analysis. The reaction is quenched by slow addition of sat. aq. Na-, K-tartrate solution (Rochelle's salt) at 0 °C and is stirred until two distinct layers are obtained. The layers are separated and the aqueous phase is extracted with DCM (3 × 7 mL/mmol). The combined organic layers are dried over

Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude products, which are purified by flash column chromatography.[14]

(*Z*)-3-(5-Methylfuran-2-yl)-3-phenylprop-2-en-1-ol S2o. Colorless oil; 54% Yield; R_f = 0.15 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 6.08 (d, *J* = 3.2 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 5.82 (t, *J* = 6.5 Hz, 1H), 4.61 (d, *J* = 6.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.80, 151.50, 140.85, 133.06, 129.00, 128.68, 127.86, 127.47, 112.90, 107.32, 60.77, 13.97. IR (neat, cm^{-1}): 3426.25, 3057.14, 2922.78, 1715.28, 1597.24, 1446.66, 1022.22, 908.87, 730.18, 698.33. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{14}H_{12}O^+$: 197.0961; Found: 197.0965.

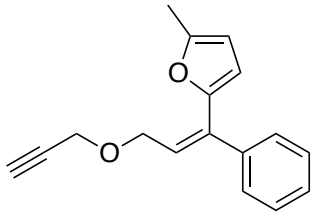
(*Z*)-3-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-en-1-ol S2p. Colorless oil; 60% Yield; R_f = 0.15 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.04 (m, 5H), 6.66 – 6.62 (m, 1H), 6.31 (t, *J* = 6.5 Hz, 1H), 6.19 – 6.14 (m, 1H), 6.10 (d, *J* = 3.5 Hz, 1H), 4.28 (d, *J* = 6.6 Hz, 2H), 3.14 (s, 3H), 1.75 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.95, 135.46, 131.13, 129.55, 128.62, 127.84, 126.86, 123.12, 111.21, 107.40, 61.08, 34.65. IR (neat, cm^{-1}): 3385.32, 3036.89, 1446.12, 1264.87, 1009.64, 906.91, 726.47. HRMS (DART) ([M+H-H_2O]$^+$) Calcd. for $C_{14}H_{14}N^+$: 196.1121; Found: 196.1121.



Step 3: A solution of allylic alcohol (1 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture stirrung for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2 equiv).

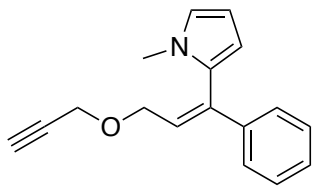
The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

(*Z*)-2-Methyl-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)furan 2o. Light yellow oil; 65% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 6.05 (d, *J* = 3.2 Hz, 1H), 5.96 (d, *J* = 3.2 Hz, 1H), 5.70 (t, *J* = 6.2 Hz, 1H), 4.54 (d, *J* = 6.2 Hz, 2H), 4.21 – 4.18 (m, 2H), 2.39 (t, *J* = 2.4 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.89, 151.42, 140.89, 133.77, 128.70, 128.26, 127.91, 125.78, 113.04, 107.34, 80.14, 74.50, 68.14, 57.77, 14.02. IR (neat, cm^{-1}): 3288.44, 3057.26, 2921.56, 2850.47, 2363.46, 1724.23, 1597.82, 1445.69, 1357.45, 1024.12, 700.29. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{17}O_2^+$: 253.1223 Found: 253.1235.

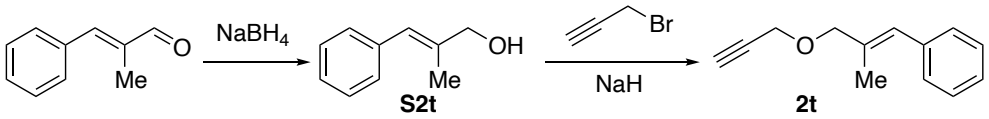
(*Z*)-1-Methyl-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-1*H*-pyrrole 2p. Light yellow solid; 68% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1).



^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $cdcl_3$) δ 7.21 – 7.10 (m, 5H), 6.55 (d, *J* = 2.6 Hz, 1H), 6.18 (t, *J* = 6.6 Hz, 1H), 6.07 (s, 1H), 6.03 (s, 1H), 4.14 (d, *J* = 6.5 Hz, 2H), 4.03 (s, 2H), 3.05 (s, 3H), 2.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.86, 136.68, 136.52, 129.40, 128.58, 128.24, 127.86, 126.88, 123.05, 111.51, 107.31, 79.91, 74.58, 68.14, 34.63. IR (neat, cm^-

[1]): 3288.90, 3057.21, 2941.73, 2848.98, 1701.98, 1482.58, 1357.14, 1290.09, 1076.20, 789.91, 698.69. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{18}NO^+$: 252.1383; Found: 252.1378.

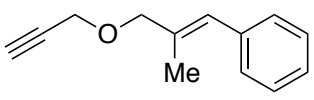
Procedure D and Characterization of 1,6-enyne 2t



Step 1: A solution of α-methyl cinnamaldehyde (1.0 equiv) in ethanol (0.5 M) was added to $NaBH_4$ (1.2 equiv) in an ice-bath over 20 min. After completion of the reaction (40 min), it was quenched with saturated NH_4Cl and water. The aqueous phase was extracted with diethyl ether (3 x 150 mL). The combined organics were washed with brine and dried over anhydrous sodium sulfate. The crude product was directly used for next step without purification.[21]

Step 2: A solution of allylic alcohol (1 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2 equiv). The reaction mixture was stir at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

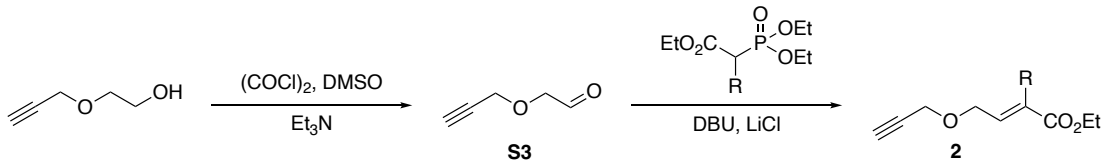
(*E*)-(2-Methyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene 2t. Light yellow oil; 55%



Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.28 (m, 2H),

7.25 (td, J = 7.1, 1.5 Hz, 1H), 6.56 (s, 1H), 4.21 (d, J = 2.3 Hz, 2H), 4.15 (d, J = 1.3 Hz, 2H), 2.48 (t, J = 2.4 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.53, 134.42, 129.09, 128.30, 128.11, 126.76, 80.00, 76.10, 74.56, 57.07, 15.74. IR (neat, cm^{-1}): 3291.11, 3023.86, 2852.19, 1599.45, 1490.80, 1442.64, 1353.75, 1074.43, 745.33, 697.91. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{13}H_{15}O^+$: 187.1117; Found: 187.1105.

Procedure E and Characterization of 1,6-enyne 2u, 2v.

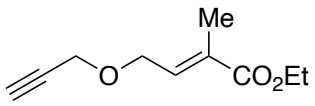


Step 1: Dimethyl sulfoxide (2.5 equiv) was added to a stirred solution of oxalyl chloride (1.4 equiv) in dichloromethane (0.2 M) at −78 °C. The mixture was stirred for 0.3 h before alcohol (1 equiv) in dichloromethane (0.8 M) was slowly added. The mixture was stirred for a further 0.3 h before triethylamine (5 equiv) was added. This reaction mixture was stirred for 0.5 h at −78 °C and then allowed to warm to room temperature and stirred for a further 3 h. The Swern solution was concentrated in vacuo and used in next step without further purification.

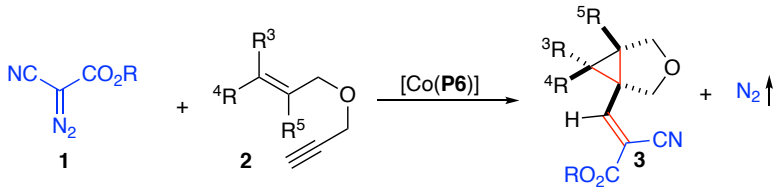
Step 2: A solution of lithium chloride (1.8 equiv), triethyl phosphonoacetate (1.8 equiv) and 1,8-diazabicyclo[5,4,0]undec-7-ene (1.8 equiv) in acetonitrile (0.3 M) was then prepared and stirred for 1 h. The Horner-Wadsworth-Emmons solution was added into the aldehyde **S3**, and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with a saturated solution of ammonium chloride and concentrated to give an orange residue, which was then extracted with diethyl ether. The organic layers were combined, dried ($MgSO_4$) and concentrated to give an orange oil. Purification by

flash column chromatography (diethyl ether/ petroleum ether, 1:9) to give **2**.[8] Spectroscopic data of compound **2u** is consistent with literature.[22]

Ethyl (*E*)-2-methyl-4-(prop-2-yn-1-yloxy)but-2-enoate 2v. Light yellow oil; 35% Yield; R_f = 0.4 (hexanes/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (t, *J* = 6.0 Hz, 1H), 4.27 (d, *J* = 6.1 Hz, 2H), 4.24 – 4.15 (m, 4H), 2.46 (s, 1H), 1.87 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.58, 136.89, 130.40, 79.41, 75.01, 66.37, 60.92, 57.91, 14.38, 12.99. IR (neat, cm^{-1}): 2927.49, 1714.19, 1261.01, 1080.63, 700.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{10}H_{15}O_3^+$: 183.1016; Found: 183.1011.

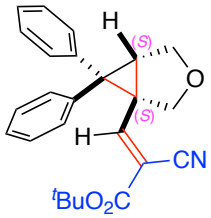


2.4.4 General Procedure for Enantioselective Radical Cascade Cyclization

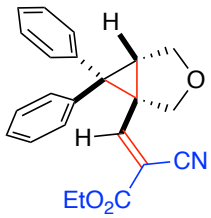


An oven dried Schlenk tube, that was previously charged with catalyst (5 mol %), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum, and 0.125 ml of anhydrous CH_3CN and enyne (0.10 mmol) were added followed by cyano diazoacetate (0.12 mmol, 1.2 equiv) and the remaining solvent (total 0.25 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. Following completion of the reaction (16 h), the reaction mixture was purified via flash column chromatography (DCM) to afford compound **3**.

<u>Characterization of Alkenyl Bicyclo[3.1.0]hexanes</u>

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (+)-3a.** 

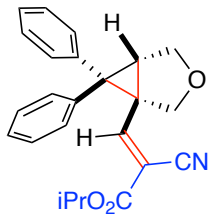
White solid; 86% Yield; 98:2 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 6H), 7.35 – 7.25 (m, 3H), 7.25 – 7.19 (m, 1H), 7.16 (s, 1H), 4.55 (d, *J* = 9.5 Hz, 1H), 4.33 (d, *J* = 9.4 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 4.09 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.08 (d, *J* = 3.2 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.44, 160.23, 140.79, 138.13, 129.07, 129.02, 128.99, 127.44, 127.32, 127.22, 115.43, 109.16, 83.68, 68.17, 66.75, 48.84, 42.33, 40.79, 27.94. $[\alpha]_D^{20}$ = +101.20° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 13.9 min., t_{minor} = 15.9 min. *ee* 91%. IR (neat, cm^{-1}): 2977.83, 2929.98, 2864.30, 2226.90, 1718.43, 1609.43, 1493.82, 1282.64, 1142.35, 1088.04. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{25}H_{26}NO_3^+$: 388.1907; Found: 388.1920.

Ethyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (+)-3ab. 

White solid; 60% Yield; 96:4 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 6H), 7.30 – 7.21 (m, 4H), 7.20 – 7.09 (m, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 4.34 – 4.20 (m, 3H), 4.13 (d, *J* = 9.3 Hz, 1H), 4.06 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.06 (d, *J* = 3.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.82, 161.43, 140.76, 138.09, 129.19, 129.06, 128.99, 127.55, 127.32, 127.30, 115.21, 107.67, 68.19, 66.76, 62.65, 49.26, 42.63, 41.09, 14.17. $[\alpha]_D^{20}$ = +77.27° (*c* = 1, $CHCl_3$). HPLC (Chiral IA, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 12.4 min., t_{minor} = 14.1 min. *ee* 78%. IR (neat, cm^{-1}): 3056.53, 2927.18, 2861.32, 2227.03, 1724.09,

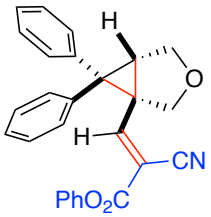
1608.08, 1261.66, 1144.67, 1087.31, 709.89. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{22}NO_3^+$: 360.1594; Found: 360.1598.

Isopropyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (+)-



3ac. White solid; 64% Yield; 96:4 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 6H), 7.30 – 7.22 (m, 3H), 7.21 (s, 1H), 7.20 – 7.14 (m, 1H), 5.05 (hept, *J* = 6.2 Hz, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 4.13 (d, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.06 (d, *J* = 3.4 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.42, 160.89, 140.75, 138.09, 129.14, 129.03, 129.00, 127.49, 127.31, 127.29, 115.22, 108.06, 70.68, 68.16, 66.75, 49.13, 42.54, 40.98, 21.74, 21.70. $[\alpha]_D^{20}$ = +91.03° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 15.1 min., t_{minor} = 17.6 min. *ee* 84%. IR (neat, cm^{-1}): 3023.95, 2982.02, 2862.05, 2227.23, 1719.55, 1607.76, 1265.62, 1085.57, 746.77, 707.93. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{24}H_{24}NO_3^+$: 374.1751; Found: 374.1760.

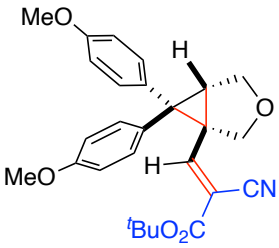
Phenyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (+)-**3ad.**



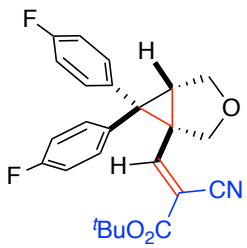
White solid; 54% Yield; 97:3 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 9H), 7.32 – 7.22 (m, 4H), 7.21 – 7.14 (m, 1H), 7.11 (dd, *J* = 7.5, 1.6 Hz, 2H), 4.58 (d, *J* = 9.7 Hz, 1H), 4.39 (d, *J* = 9.5 Hz, 1H), 4.16 (d, *J* = 9.4 Hz, 1H), 4.08 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.15 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.84, 160.10, 150.27, 140.59, 138.00, 129.64, 129.27, 129.09, 128.97, 127.66, 127.40, 127.24, 126.57, 121.23, 114.94, 106.76, 68.02, 66.72, 50.04, 43.20, 41.67. $[\alpha]_D^{20}$ = +46.21° (*c* = 1,

$CHCl_3$). HPLC (Chiral IA, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 19.0 min., t_{minor} = 23.5 min. *ee* 76%. IR (neat, cm^{-1}): 3057.86, 2926.71, 2866.15, 2228.30, 1735.21, 1599.75, 1246.78, 1191.17, 737.61, 710.25. HRMS (DART) ($[M+H]^+$) Calcd. for $C27H22NO3^+$: 408.1594; Found: 408.1601.

***tert*-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate** (+)-**3b.** White solid; 61% Yield; 98:2 *E*/*Z*. R_f = 0.1 (hexanes/ethyl acetate, 4:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 7.14 (s, 1H), 6.87 – 6.83 (m, 2H), 6.80 – 6.74 (m, 2H), 4.46 (d, *J* = 9.5 Hz, 1H), 4.28 (d, *J* = 9.5 Hz, 1H), 4.08 (d, *J* = 9.2 Hz, 1H), 4.04 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.98 (d, *J* = 3.6 Hz), 1.46 (s, 9H). ^{13}C NMR (150MHz, $CDCl_3$) δ 162.02, 160.39, 158.70, 158.63, 133.42, 130.73, 129.91, 128.28, 115.57, 114.59, 114.52, 108.98, 83.73, 68.32, 66.87, 55.40, 55.30, 47.88, 42.83, 41.26, 28.05. $[\alpha]_D^{20}$ = +98.00° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 25% isopropanol- 75% hexanes rate 0.8 mL/min): t_{major} = 18.5 min., t_{minor} = 20.4 min. *ee* 91%. IR (neat, cm^{-1}): 2932.10, 2861.95, 2227.15, 1718.34, 1607.60, 1511.51, 1284.57, 1246.10, 1143.91, 1173.63. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{27}H_{30}NO_5^+$: 448.2119; Found: 448.2118.



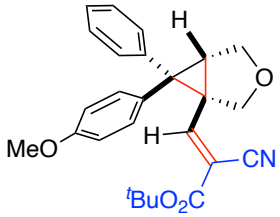
***tert*-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate** (+)-**3c.** White solid; 91% Yield; 97:3 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 4H), 7.06 (s, 1H), 7.00 – 6.97 (m, 2H), 6.94 – 6.91 (m, 2H), 4.42 (d, *J* = 9.6 Hz, 1H), 4.21 (d, *J* = 9.6 Hz, 1H), 4.04 – 4.00 (m, 2H), 2.93 (d, *J* = 2.7 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.04 (d, J_{CF}



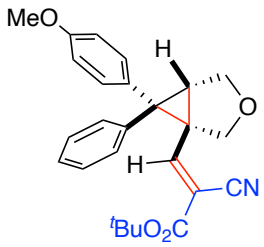
= 246.3 Hz), 161.95 (d, J_{CF} = 247.5 Hz), 160.51, 160.07, 136.61 (d, J_{CF} = 3.4 Hz), 133.93 (d, J_{CF} = 3.6 Hz), 130.69 (d, J_{CF} = 8.1 Hz), 128.78 (d, J_{CF} = 8.1 Hz), 116.27 (d, J_{CF} = 21.7 Hz), 116.22 (d, J_{CF} = 21.6 Hz), 115.31, 110.06, 84.09, 68.29, 66.79, 47.01, 42.31, 40.65, 28.01. ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.30 (m, 1F), -114.85 (m, 1F). $[\alpha]_D^{20}$ = +86.43° (*c* = 1, $CHCl_3$). HPLC (Chiral IB, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 12.2 min., t_{minor} = 10.0 min. *ee* 92%. IR (neat, cm^{-1}): 2980.22, 2933.46,2865.71, 2230.94, 1716.00, 1603.75, 1508.78, 1283.63, 1223.97, 1142.02. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{24}NO_3F_2^+$: 424.1719; Found: 424.1735.

***tert*-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate** (+)-**3d.** White solid; 69% Yield; 99:1 *E*/*Z*. R_f = 0.3 (hexnaes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 1H), 7.28 – 7.22 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.09 – 7.07 (m, 2H), 7.01 – 6.98 (m, 2H), 6.94 (td, *J* = 8.4, 2.2 Hz, 1H), 6.90 (td, *J* = 8.2, 2.3 Hz, 1H), 4.48 (d, *J* = 9.7 Hz, 1H), 4.25 (d, *J* = 9.7 Hz, 1H), 4.09 (d, *J* = 9.5 Hz, 1H), 4.05 (dd, *J* = 9.5, 3.3 Hz, 1H), 2.97 (d, *J* = 3.2 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.09 (d, J_{CF} = 247.2 Hz), 163.00 (d, J_{CF} = 248.0 Hz), 160.01, 159.73, 142.57 (d, J_{CF} = 7.2 Hz), 139.91 (d, J_{CF} = 7.2 Hz), 130.86 (d, J_{CF} = 10.0 Hz), 130.79 (d, J_{CF} = 10.1 Hz), 124.75 (d, J_{CF} = 2.8 Hz), 123.12 (d, J_{CF} = 2.9 Hz), 116.19 (d, J_{CF} = 22.3 Hz), 115.18, 114.89 (d, J_{CF} = 21.1 Hz), 114.62 (d, J_{CF} = 21.2 Hz), 114.43 (d, J_{CF} = 22.1 Hz), 110.41, 84.12, 68.32, 66.78, 47.20, 42.16, 40.32, 28.01. ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.45 (m, 1F), -111.71 (td, *J* = 9.1, 5.8 Hz, 1F). $[\alpha]_D^{20}$ = +60.81° (*c* = 1, $CHCl_3$). HPLC (Chiral IF, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 14.2 min., t_{minor} = 18.6 min. *ee* 92%. IR (neat, cm^{-1}): 2984.70, 2934.52, 2865.90, 2229.40,

1720.30, 1610.65, 1587.40, 1485.79, 1284.36, 1157.09. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{25}H_{24}NO_3F_2^+$: 424.1719; Found: 424.1723.



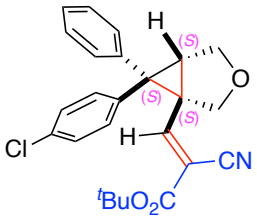
***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3e.** White solid; 84% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 4H), 7.24 – 7.20 (m, 3H), 7.16 (s, 1H), 6.82 – 6.74 (m, 2H), 4.48 (d, *J* = 9.5 Hz, 1H), 4.28 (d, *J* = 9.6 Hz, 1H), 4.10 (d, *J* = 9.3 Hz, 1H), 4.03 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.73 (s, 3H), 2.99 (d, *J* = 3.4 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.79, 160.35, 158.78, 138.53, 132.92, 130.06, 129.03, 127.22, 127.15, 115.51, 114.53, 109.07, 83.73, 68.27, 66.81, 55.37, 48.30, 42.61, 41.10, 28.03. $[\alpha]_D^{20}$ = +122.57° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 10% isopropanol- 90% hexanes rate 1.0 mL/min): t_{major} = 13.7 min., t_{minor} = 19.8 min. *ee* 92%. IR (neat, cm^{-1}): 2976.28, 2931.60, 2862.79, 2226.74, 1718.24, 1608.48, 1511.73, 1369.85, 1249.45, 1142.72. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{28}NO_4^+$: 418.2013; Found: 418.2028.



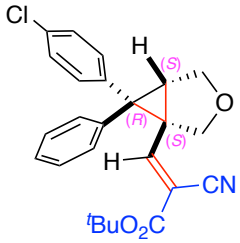
***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (+)-3f**. White solid; 83% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 6H), 7.20 – 7.13 (m, 1H), 7.10 (s, 1H), 6.99 – 6.69 (m, 2H), 4.49 (d, *J* = 9.5 Hz, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 4.10 (d, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.74 (s, 3H), 3.01 (d, *J* = 3.4 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.67, 160.31, 158.73, 141.29, 130.32, 129.11, 128.90, 128.43, 127.37, 115.52, 114.58, 109.12,

83.71, 68.28, 66.86, 55.28, 48.45, 42.59, 40.98, 28.00. $[\alpha]_D^{20}$= +77.82° (*c* = 1, $CHCl_3$). HPLC (Chiral IB, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 35.4 min., t_{minor} = 31.6 min. *ee* 95%. IR (neat, cm^{-1}): 2976.55, 2930.95, 2861.82, 2365.37, 1718.29, 1609.25, 1510.67, 1510.67, 1247.19, 1143.99. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{28}NO_4^+$: 418.2013; Found: 418.2032.

***tert*-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate (+)-3g.** White solid; 76% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.22 (m, 5H), 7.12 (s, 1H), 4.48 (d, *J* = 9.5 Hz, 1H), 4.26 (d, *J* = 9.7 Hz, 1H), 4.10 (d, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 9.4, 3.4 Hz, 1H), 2.98 (d, *J* = 3.4 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.68, 160.16, 139.47, 137.76, 133.48, 130.41, 129.37, 129.22, 127.53, 127.30, 115.32, 109.90, 84.05, 68.33, 66.80, 47.95, 42.34, 40.68, 28.03. $[\alpha]_D^{20}$= +110.03° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 19.7 min., t_{minor} = 24.7 min. *ee* 90%. IR (neat, cm^{-1}) 2975.65, 2930.29, 2864.82, 2232.61, 1713.91, 1614.61, 1486.96, 1308.41, 1164.99, 1090.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{25}NO_3Cl^+$: 422.1518; Found: 422.1522.



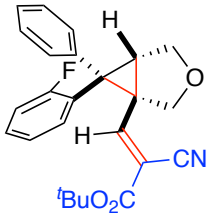
***tert*-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate (+)-3h.** White solid; 80% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 8H), 7.21 – 7.18 (m, 1H), 7.11 (s, 1H), 4.48 (d, *J* = 9.7 Hz, 1H), 4.28 (d, *J* = 9.7 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.02 (d, *J* = 2.7 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.79,



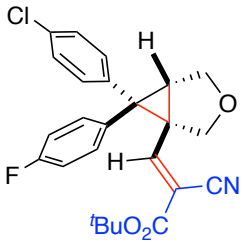
160.14, 140.32, 136.79, 133.21, 129.40, 129.27, 128.98, 128.65, 127.74, 115.39, 109.75, 83.89, 68.24, 66.80, 47.88, 42.16, 40.51, 28.00. $[\alpha]_D^{20}$ = +62.01° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 18.4 min., t_{minor} = 17.6 min. *ee* 92%. IR (neat, cm^{-1}): 2975.96, 2930.40, 2864.93, 2228.51, 1718.41, 1610.61, 1488.93, 1282.66, 1141.69, 1086.12. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{25}NO_3Cl^+$: 422.1518; Found: 422.1494.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3i**. White solid; 80% Yield; 98:2 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.34 (m, 3H), 7.29 – 7.24 (m, 2H), 7.06 (s, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 4.26 (d, *J* = 9.5 Hz, 1H), 4.12 (d, *J* = 9.3 Hz, 1H), 4.07 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.02 (d, *J* = 3.3 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.01, 144.93, 137.27, 129.53, 129.31, 127.74, 127.42, 126.17 (q, J_{CF} = 3.8 Hz), 115.20, 110.40, 84.14, 68.37, 66.83, 48.06, 42.22, 40.41, 27.99. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.73 (s, 3F). $[\alpha]_D^{20}$ = +34.59° (*c* = 0.25, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 18.5 min., t_{minor} = 17.0 min. *ee* 94%. IR (neat, cm^{-1}): 2929.20, 2861.16, 1714.31, 1614.33, 1366.97, 1306.49, 1147.31, 1086.54, 763.11, 704.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{25}NO_3F_3^+$: 456.1781; Found: 456.1768.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3j.** Colorless oil; 50% Yield; 95:5 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m,

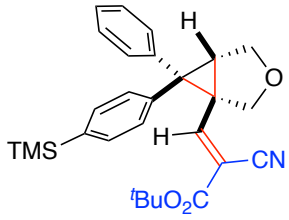


2H), 7.40 – 7.29 (m, 3H), 7.29 – 7.15 (m, 3H), 7.09 – 7.05 (m, 1H), 6.98 – 6.94 (m, 1H), 4.51 (d, J = 9.5 Hz, 1H), 4.29 (d, J = 9.6 Hz, 1H), 4.13 (d, J = 9.4 Hz, 1H), 4.05 (dd, J = 9.4, 3.4 Hz, 1H), 2.90 (d, J = 3.3 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.95 (d, J_{CF} = 248.2 Hz), 160.37, 160.32, 136.99, 131.00, 129.73 (d, J_{CF} = 8.5 Hz), 128.97, 128.50 (d, J_{CF} = 13.7 Hz), 127.54 (d, J_{CF} = 2.7 Hz), 127.47, 124.91 (d, J_{CF} = 3.5 Hz), 116.49 (d, J_{CF} = 22.2 Hz), 115.26, 109.85, 83.86, 68.44, 66.94, 43.77, 41.68, 41.19, 28.04. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.25 (m, 1F). $[\alpha]_D^{20}$ = +82.42° (c = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1 mL/min): t_{major} = 13.8 min., t_{minor} = 16.7 min. *ee* 90%. IR (neat, cm^{-1}): 2929.79, 2862.79, 2228.97, 1720.00, 1612.10, 1490.66, 1451.39, 1370.07, 1284.54, 1142.94. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{25}H_{25}NO_3F^+$: 406.1813; Found: 406.1799.

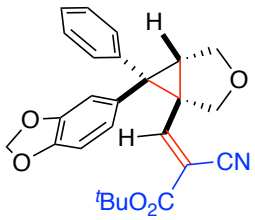


***tert*-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate (+)-3k.** White solid; 79% Yield; 98:2 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 6H), 7.09 (s, 1H), 6.98 – 6.94 (m, 2H), 4.46 (d, J = 9.7 Hz, 1H), 4.25 (d, J = 9.7 Hz, 1H), 4.08 – 4.03 (m, 2H), 2.97 (d, J = 2.4 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.21 (d, J_{CF} = 247.6 Hz), 160.25, 160.04, 136.63, 136.27 (d, J_{CF} = 3.3 Hz), 133.35, 130.63 (d, J_{CF} = 8.2 Hz), 129.51, 128.55, 116.27 (d, J_{CF} = 21.7 Hz), 115.27, 110.20, 84.11, 68.29, 66.78, 46.95, 42.19, 40.53, 28.02. ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.09 (ddd, J = 13.9, 8.7, 5.3 Hz, 1F). $[\alpha]_D^{20}$ = +62.01° (c = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 13.9 min., t_{minor} = 17.4 min. *ee*

89%. IR (neat, cm^{-1}): 2931.39, 2864.28, 2231.97, 1713.41, 1612.86, 1508.53, 1309.53, 1257.49, 1159.27, 1087.82. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{25}H_{24}NO_3FCl^+$: 440.1423; Found: 440.1408.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trimethylsilyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3l.** 

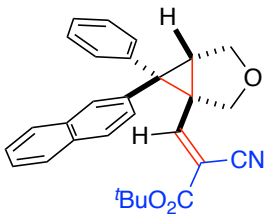
White solid; 71% Yield; 98:2 *E*/*Z*; 99:1 dr. R_f = 0.4 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.20 (m, 9H), 7.12 (s, 1H), 4.50 (d, *J* = 9.5 Hz, 1H), 4.28 (d, *J* = 9.5 Hz, 1H), 4.12 (d, *J* = 9.3 Hz, 1H), 4.05 (d, *J* = 9.3 Hz, 1H), 3.02 (s, 1H), 1.44 (s, 9H), 0.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.41, 160.27, 141.18, 139.61, 138.06, 134.06, 129.01, 128.32, 127.38, 127.26, 115.40, 109.32, 83.61, 68.21, 66.80, 48.79, 42.30, 40.71, 27.94, -1.10. $[\alpha]_D^{20}$ = +137.02° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 17.8 min., t_{minor} = 16.5 min. *ee* 92%. IR (neat, cm^{-1}): 2955.96, 2860.83, 2229.74, 1719.62, 1609.96, 1370.02, 1282.70, 1250.06, 1145.94, 840.13. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{34}NO_3Si^+$: 460.2303; Found: 460.2316.

***tert*-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate** (+)-**3m.** 

Yellow solid; 66% Yield; 98:2 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.23 (tt, *J* = 6.3, 1.8 Hz, 1H), 7.19 (s, 1H), 6.82 – 6.76 (m, 2H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.89 – 5.85 (m, 2H), 4.47 (d, *J* = 9.5 Hz, 1H), 4.27 (d, *J* = 9.5 Hz, 1H), 4.07 (d, *J* = 9.4 Hz, 1H), 4.01 (dd, *J* = 9.4, 3.5 Hz, 1H), 2.96 (d, *J* = 3.4 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.55, 160.31, 148.10, 146.89, 138.29,

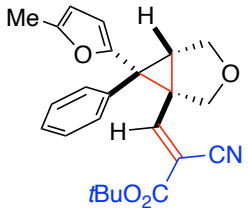
134.64, 129.02, 127.22, 127.16, 122.09, 115.43, 109.50, 109.10, 108.66, 101.32, 83.78, 68.17, 66.69, 48.54, 42.58, 41.25, 27.97. $[\alpha]_D^{20}$ = +108.25° (*c* = 1, $CHCl_3$). HPLC (Chiral IF, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 13.2 min., t_{minor} = 16.8 min. *ee* 94%. IR (neat, cm^{-1}): 3015.89, 2970.02, 2945.50, 1738.01, 1366.10, 1229.15, 1037.76, 705.75. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{26}H_{26}NO_5^+$: 432.1806; Found: 432.1814.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(naphthalen-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3n.**



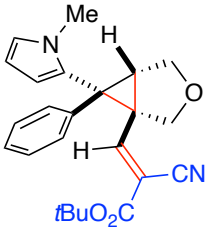
White solid; 68% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.65 (m, 4H), 7.48 – 7.40 (m, 5H), 7.35 – 7.32 (m, 2H), 7.25 – 7.19 (m, 1H), 7.15 (s, 1H), 4.57 (d, *J* = 9.5 Hz, 1H), 4.34 (d, *J* = 9.6 Hz, 1H), 4.17 (d, *J* = 9.2 Hz, 1H), 4.09 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.18 (d, *J* = 3.3 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.30, 160.21, 138.32, 137.91, 133.61, 132.57, 129.07, 129.02, 127.86, 127.82, 127.48, 127.36, 127.35, 127.18, 126.62, 126.40, 115.52, 109.35, 83.72, 68.27, 66.86, 49.09, 42.60, 41.06, 27.90. $[\alpha]_D^{20}$ = +143.42° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 19.0 min., t_{minor} = 25.4 min. *ee* 91%. IR (neat, cm^{-1}): 3055.93, 3022.36, 2928.71, 2860.10, 2228.18, 1717.48, 1609.15, 1369.66, 1282.36, 1140.98. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{29}H_{28}NO_3^+$: 438.2064; Found: 438.2080.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*R*,6*S*)-6-(5-methylfuran-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3o.** Light yellow oil; 48% Yield; 96:4 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.26 – 7.25 (m, 2H), 7.01 (s, 1H), 6.13 – 6.08 (m, 1H), 5.91 – 5.87 (m, 1H), 4.47 (d, *J* = 9.4 Hz, 1H), 4.31 (d, *J* = 9.2 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 4.12 – 4.05 (m,

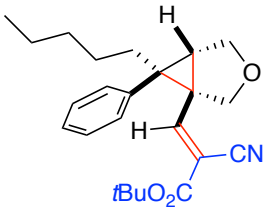


1H), 3.04 (d, J = 3.3 Hz, 1H), 2.24 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.19, 159.44, 151.42, 149.24, 138.78, 129.07, 127.70, 115.22, 109.97, 107.28, 106.93, 83.80, 69.10, 67.78, 43.22, 41.10, 40.30, 27.99, 13.85. $[\alpha]_D^{20}$ = +36.79° (c = 0.25, $CHCl_3$). HPLC (Chiral IA, 1% isopropanol-hexanes rate 1 ml/min): t_{major} = 9.7 min., t_{minor} =10.6 min. *ee* 80%. IR (neat, cm^{-1}): 2978.30, 2924.53, 2867.39, 2231.09, 1721.15, 1610.21, 1370.15, 1282.06, 1148.91, 703.25. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{26}NO_4^+$: 392.1856; Found: 392.1840.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(1-methyl-1*H*-pyrrol-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3p.** Light yellow oil; 31% Yield; 94:6 *E*/*Z*; 99:1 dr. R_f = 0.1 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 1H), 7.23 – 7.14 (m, 4H), 7.05 (s, 1H), 6.54 – 6.53 (m, 1H), 6.27 – 6.26 (m, 1H), 6.13 – 6.12 (m, 1H), 4.59 (d, J = 9.7 Hz, 1H), 4.29 (d, J = 9.4 Hz, 1H), 4.17 (d, J = 9.3 Hz, 1H), 4.06 – 4.04 (m, 1H), 3.53 (s, 3H), 3.20 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.08, 138.59, 129.06, 129.00, 128.16, 127.40, 122.40, 115.14, 110.49, 107.87, 107.74, 101.54, 83.86, 69.88, 68.20, 42.61, 40.28, 34.31, 29.90, 27.99. $[\alpha]_D^{20}$ = +35.19° (c = 0.25, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 52.6 min., t_{minor} = 49.1 min. *ee* 79%. IR (neat, cm^{-1}): 2976.26, 2928.34, 2856.24, 2231.51, 1719.97, 1610.30, 1370.04, 1141.81, 1089.89, 705.45. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{27}N_2O_3^+$: 391.2016; Found: 391.2010.

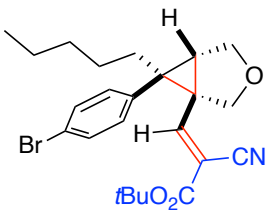


***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-pentyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (+)-**3q.** Cololess oil; 62% Yield; 95:5 *E*/*Z*; 99:1 dr. R_f = 0.4 (hexanes/ethyl



acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.13 (m, 2H), 6.84 (s, 1H), 4.50 – 4.41 (m, 2H), 4.15 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.12 (d, *J* = 9.0 Hz, 1H), 2.73 (d, *J* = 3.9 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.93 – 1.87 (m, 1H), 1.40 (s, 9H), 1.28 – 1.09 (m, 6H), 0.86 – 0.74 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.40, 160.48, 140.73, 129.79, 128.75, 127.44, 115.66, 107.82, 83.43, 68.54, 67.90, 47.57, 42.29, 40.90, 32.00, 29.54, 27.99, 26.91, 22.69, 14.13. $[\alpha]_D^{20}$ = +174.43° (*c* = 1, $CHCl_3$). HPLC (Chiral whelk, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 28.4 min., t_{minor} = 25.8 min. *ee* 83%. IR (neat, cm^{-1}): 3055.93, 3022.36, 2928.71, 2860.10, 2228.18, 1717.48, 1609.15, 1369.66, 1282.36, 1140.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{32}NO_3^+$: 382.2377; Found: 382.2375.

***tert*-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-bromophenyl)-6-pentyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate (+)-3r.** Colorless oil; 55% Yield; 97:3 *E*/*Z*; 99:1 dr. R_f = 0.2 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 2H), 7.14 – 6.99 (m, 2H), 6.84 (s, 1H), 4.43 (s, 2H), 4.15 (dd, *J* = 9.1, 4.1 Hz, 1H), 4.10 (d, *J* = 9.1 Hz, 1H), 2.67 (d, *J* = 4.0 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.89 – 1.83 (m, 1H), 1.43 (s, 9H), 1.32 – 1.05 (m, 6H), 0.82 – 0.80 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.52, 160.31, 139.87, 131.95, 131.48, 121.43, 115.47, 108.46, 83.72, 68.57, 67.83, 46.68, 42.08, 40.65, 31.94, 29.43, 28.01, 26.89, 22.68, 14.13. $[\alpha]_D^{20}$ = +169.81° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 3% isopropanol- 97% hexanes rate 1.0 mL/min): t_{major} = 18.2 min., t_{minor} = 17.4 min. *ee* 78%. IR (neat, cm^{-1}): 3028.22, 2956.16, 2927.95, 2868.19, 2228.14, 1719.65, 1607.50,



1369.21, 1282.22, 1159.51. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{24}H_{31}NO_3Br^+$: 460.1482; Found: 460.1501.

***tert*-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-3-oxaspiro[bicyclo[3.1.0]hexane-6,1'-cyclohexan]-1-yl)acrylate** (+)-**3s.** Colorless oil; 20% Yield; 95:5 *E*/*Z*. R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 4.23 (d, *J* = 9.1 Hz, 1H), 4.20 (d, *J* = 9.1 Hz, 1H), 4.02 (dd, *J* = 8.8, 4.1 Hz, 1H), 3.93 (d, *J* = 8.9 Hz, 1H), 2.09 (d, *J* = 4.0 Hz, 1H), 1.78 – 1.74 (m, 1H), 1.70 – 1.66 (m, 1H), 1.59 – 1.52 (m, 17H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.84, 160.84, 115.49, 109.95, 83.76, 68.96, 67.79, 42.46, 41.10, 34.19, 28.13, 26.40, 25.86, 25.34. $[\alpha]_D^{20}$ = +68.79° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 15.4 min., t_{minor} = 20.4 min. *ee* 42%. IR (neat, cm^{-1}): 2928.61, 2854.35, 2365.42, 1720.39, 1601.82, 1369.77, 1280.32, 1258.40, 1160.51, 1126.09. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{26}NO_3^+$: 304.1907; Found: 304.1922.

***tert*-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate** (–)-**3t.** Cololess oil; 37% Yield; 93:7 *E*/*Z*; 99:1 dr. R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 7.12 (d, *J* = 9.4 Hz, 2H), 4.49 (d, *J* = 8.9 Hz, 1H), 4.27 (d, *J* = 8.9 Hz, 1H), 4.06 (d, *J* = 8.5 Hz, 1H), 3.65 (d, *J* = 8.5 Hz, 1H), 3.01 (s, 1H), 1.49 (s, 9H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.62, 159.47, 134.13, 130.38, 128.85, 127.49, 115.82, 108.41, 83.72, 74.26, 70.43, 41.44, 39.24, 38.78, 28.09, 11.80. $[\alpha]_D^{20}$ = -85.38° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 10.8 min., t_{minor} = 10.2 min. *ee* 70%. IR (neat, cm^{-1}): 2979.06, 2931.24, 2857.27, 1720.28, 1608.62, 1369.90, 1278.77,

1161.45, 1124.65, 1069.89. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.1751; Found: 326.1760.

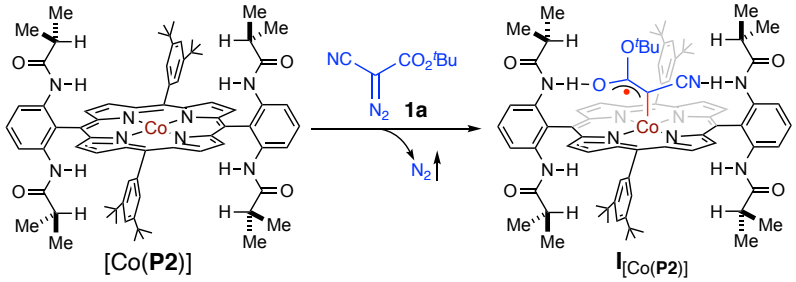
Ethyl (1*S*,5*S*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-6-carboxylate (+)-**3u.** Colorless oil; 43% Yield; 95:5 *E*/*Z*; 99:1 dr. R_f = 0.4 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 4.30 (d, *J* = 9.1 Hz, 1H), 4.18 (qq, *J* = 10.9, 7.2 Hz, 2H), 4.09 (d, *J* = 9.1 Hz, 1H), 3.99 (d, *J* = 9.0 Hz, 1H), 3.86 (dd, *J* = 9.0, 2.5 Hz, 1H), 2.65 (dd, *J* = 4.6, 2.5 Hz, 1H), 2.34 (d, *J* = 4.7 Hz, 1H), 1.52 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.60, 160.04, 155.92, 114.95, 111.71, 84.02, 70.17, 68.55, 61.61, 37.78, 36.07, 30.75, 28.03, 14.29. $[\alpha]_D^{20}$ = +18.03° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 19.3 min., t_{minor} = 17.8 min. *ee* 10%. IR (neat, cm^{-1}): 2980.94, 2933.84, 2869.43, 1723.84, 1617.11, 1283.19, 1156.88, 1074.49, 917.71, 840.00. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{22}NO_5^+$: 308.1493; Found: 308.1496.

Ethyl (1*S*,5*R*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-6-methyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate (+)-**3v.** Colorless oil; 37% Yield; 95:5 *E*/*Z*; 99:1 dr. R_f = 0.4 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 4.28 (d, *J* = 9.8 Hz, 1H), 4.22 – 4.10 (m, 4H), 3.98 (d, *J* = 9.3 Hz, 1H), 2.83 (d, *J* = 3.7 Hz, 1H), 1.51 (s, 9H), 1.49 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.02, 160.02, 158.17, 114.73, 112.52, 83.97, 69.46, 67.94, 61.84, 40.82, 38.74, 36.72, 28.02, 14.25, 8.46. $[\alpha]_D^{20}$ = +111.20° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 26.8 min., t_{minor} = 23.9 min. *ee* 74%. IR (neat, cm^{-1}): 2980.63, 2935.64,

2874.49, 1722.33, 1614.70, 1370.08, 1281.87, 1160.03, 1079.38, 840.19. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{17}H_{24}NO_5^+$: 322.1649; Found: 322.1647.

2.4.5 Mechanistic Studies of the Proposed Stepwise Radical Mechanism

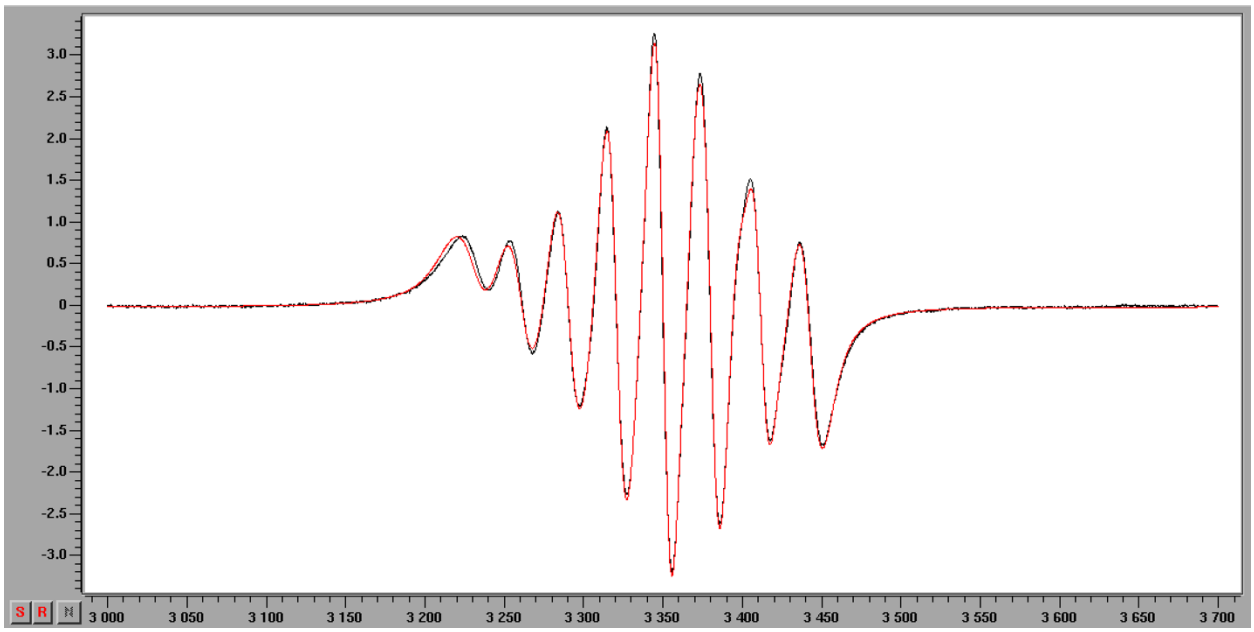
2.4.5.1 Characterization of α-Co(III)-Alkyl Radical I by EPR and HRMS



Procedure for EPR Experiment: To an over-dried Schlenk tube, [Co(**P2**)] (5 mol %) was added. The Schlenk tube was then evacuated and backfilled with nitrogen 3 times. The Teflon screw cap was replaced with a rubber septum, and cyano diazoacetate (0.12 mmol) and Benzene (5 mL) were added via a gas-tight syringe. The mixture was then stirred at rt for 5 min and transferred into a degassed EPR tube (filled with argon) through a gas tight syringe. The sample was then carried out for EPR experiment at room temperature (EPR settings: T = 298 K; microwave frequency: 9.37762 GHz; power: 20 mW; modulation amplitude: 1.0 G).

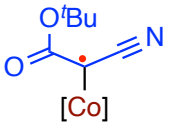
X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit in Xenon.

Figure 2.2. Experimental and simulated X-Band EPR spectra for α-Co(III)-alkyl radical $\mathbf{I}_{[Co(\mathbf{P2})]}$ in benzene at r.t.

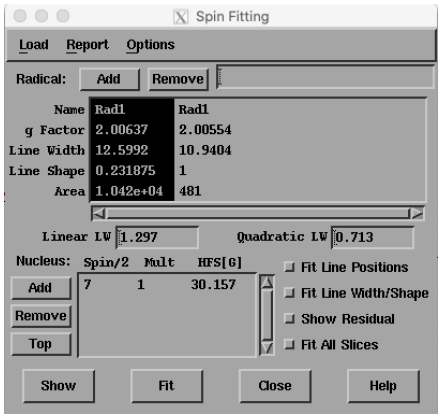


EPR Simulation Details：

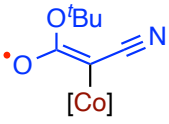
$^{C}\mathbf{I}_{[Co(\mathbf{P2})]}$: (8951/(8951+413)) x 100%= 96%



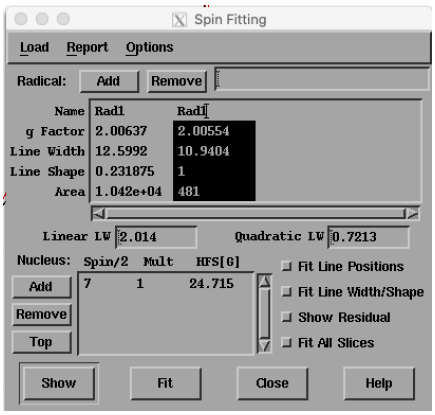
g = 2.00637
$A_{(Co)}$ = 30.157 x 2.00637 x 1.399611451 = 84.7 MHz

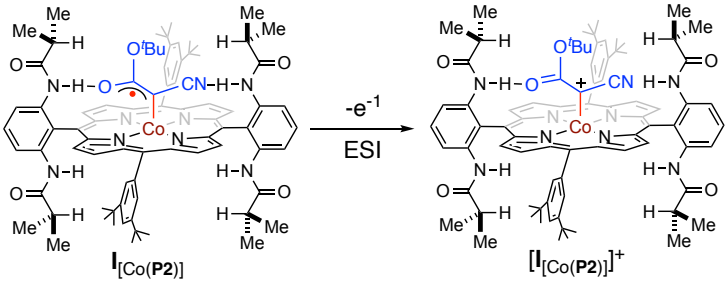


$^{O}\mathbf{I}_{[Co(\mathbf{P2})]}$: (413/(8951+413)) x 100%= 4%



g = 2.00554
$A_{(Co)}$ = 24.715 x 2.00554 x 1.399611451 = 69.4 MHz





Chemical Formula: $C_{83}H_{97}CoN_9O_6^+$
Calculated Exact Mass: 1374.6888

Procedure for HRMS Experiment: To an over-dried Schlenk tube, [Co(**P2**)] (5 mol %) was added. The Schlenk tube was then evacuated and backfilled with nitrogen 3 times. The Teflon screw cap was replaced with a rubber septum, and cyano diazoacetate (0.12 mmol) and CH_3CN (0.5 mL) were added via a gas-tight syringe. The mixture was then stirred at room temperature for 30 min. The resulting solution was collected in a HPLC vial (degassed and backfilled with argon). The sample was further diluted with CH_3CN and immediately injected into HRMS instrument. The HRMS experiment was carried out in the absence of any additives such as formic acid, which commonly act as electron carriers for ionization, allowing the detection of the molecular ion signals corresponding to α-Co(III)-alkyl radical ($C_{83}H_{97}CoN_9O_6^+$) ($[M]^+$ m/z = 1374.6850 (observed)) by the loss of one electron.

Figure 2.3. High Resolution Mass Spectroscopy (HRMS) Spectrum for Co(III)-Supported Alkyl Radical Intermediate I. (Observed in black and Simulated in green)

1/29/2020 10:30:51 AM

sCLIPS Report - G:\6220_1725.d\AcqData\MSProfile.bin

Self-Calibration Mass Range (Da)
Start: -0.45
End: 0.45

RT Windows
Average of Scans 20 thru 29 (0.3262 to 0.4753)

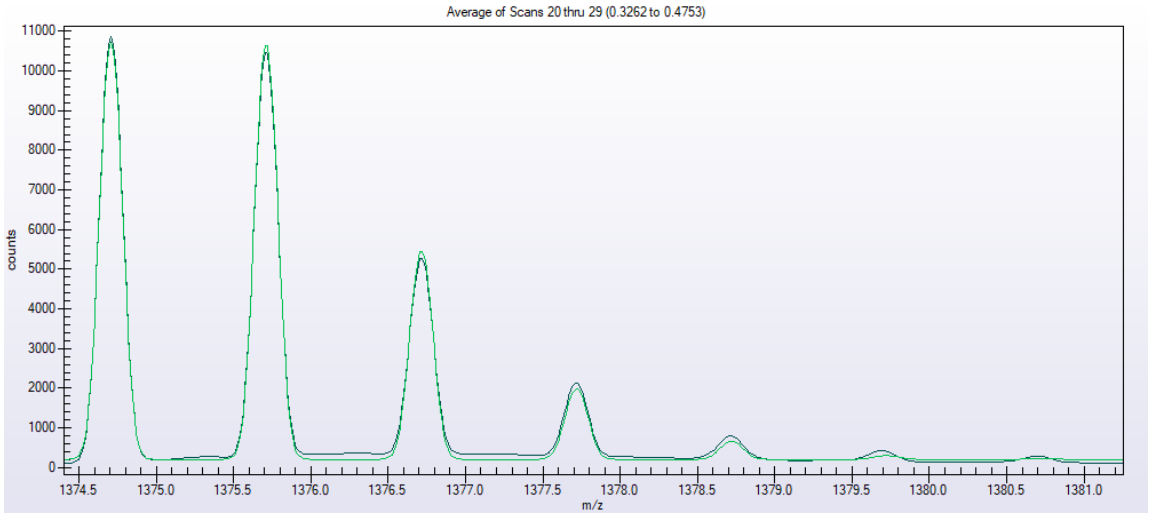
sCLIPS Parameters

Accurate Mass:	1374.6850
Charge:	1
Mass Tolerance (mDa):	10.00
Electron State:	Odd
Double Bond Equivalent Range	
Minimum:	-50.00
Maximum:	50.00
Profile Mass Range (Da)	
Start:	-0.50
End:	14.50
Empirical Rules:	Enabled
Empirical Elemental Limits:	Wiley
H/C Ratio:	Extended
Heteroatom Ratios:	Extended

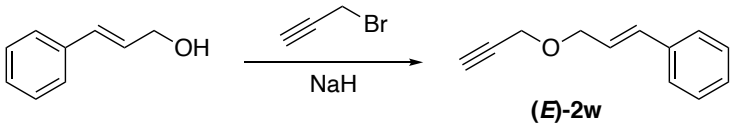
Element	Minimum	Maximum
C	1	85
H	0	101
Co	0	1
N	0	9
O	0	6

sCLIPS Search Results

	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C83H97CoN9O6	1,374.6888	-3.8335	-2.7886	90.4787	147	40.0

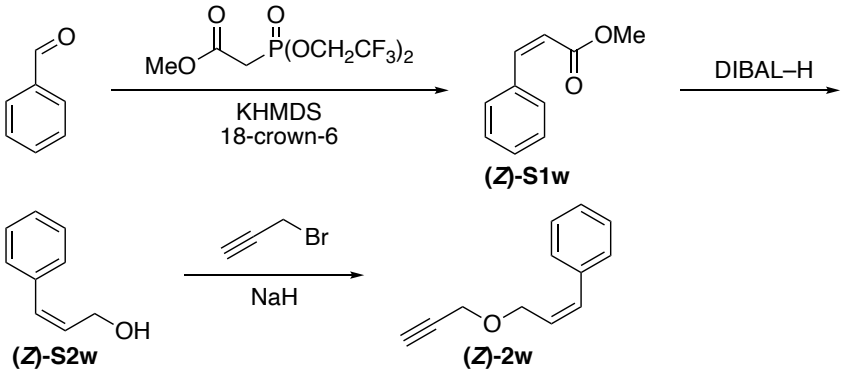


2.4.5.2 Probing of e-Co(III)-Alkyl Radical Intermediate by Reaction of (E)- and (Z)-1,6-Enynes



A solution of allylic alcohol (1.0 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2.0 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

(*E*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (*E*)-2w, colorless oil; 70% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.25 (dd, *J* = 6.2, 1.5 Hz, 2H), 4.21 (d, *J* = 2.4 Hz, 2H), 2.46 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.71, 133.60, 128.76, 128.01, 126.73, 125.22, 79.89, 74.68, 70.40, 57.22. This compound is known.[9]



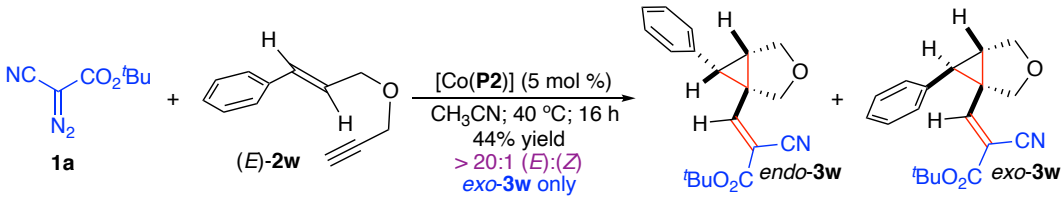
Step 1: A solution of methyl P,P-bis(2,2,2-trifluoroethyl)phosphonoacetate (1.4 equiv) and 18-crown-6 (2.5 equiv) in THF (0.05 M) under argon was treated with KHMDS (0.5 M in toluene, 1.4 equiv) at – 78 °C and was stirred for 30 min at this temperature. To this suspension, a solution of appropriate aldehyde (1.0 equiv.) in THF (2 mL) was added dropwise, and the reaction mixture was stirred at –78 °C until full consumption of starting material was indicated by TLC. The reaction was quenched with sat. NH_4Cl solution and the organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel.[24]

Step 2: To a solution of the corresponding α, β-unsaturated ester (1.0 equiv) in DCM (0.2 M) is added a solution of DIBAL-H (1 M in hexane, 3.0 equiv) at -78 °C. After complete addition, the cooling bath is removed and the resulting solution is stirred at r.t. until full conversion of the starting material is detected by TLC analysis. The reaction is quenched by slow addition of sat. aq. Na-, K-tartrate solution (Rochelle's salt) at 0 °C and is stirred until two distinct layers are obtained. The layers are separated and the aqueous phase is extracted with DCM (3 × 7 mL/mmol). The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude products, which are purified by flash column chromatography.[16]

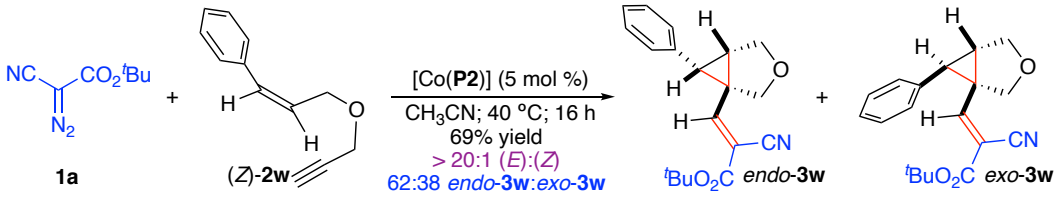
Step 3: A solution of allylic alcohol (1.0 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2.0 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers

were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

(*Z*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (*Z*)-2w, colorless oil; 65% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.28 – 7.16 (m, 3H), 6.61 (d, *J* = 11.8 Hz, 1H), 5.82 (dt, *J* = 11.8, 6.4 Hz, 1H), 4.31 (dd, *J* = 6.4, 1.7 Hz, 2H), 4.14 (d, *J* = 2.4 Hz, 2H) 2.38 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.65, 132.59, 128.98, 128.43, 128.14, 127.46, 79.81, 74.69, 66.75, 57.74. This Compound is known.[23]

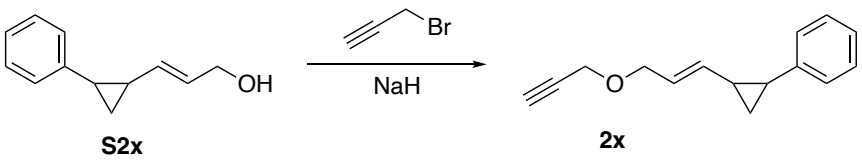


44% yield; >20:1 *E*/*Z*; *exo*-**3w** only; colorless oil; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.21 (s, 2H), 7.12 (s, 1H), 4.39 (d, *J* = 9.0 Hz, 1H), 4.32 (d, *J* = 9.0 Hz, 1H), 4.09 (d, *J* = 8.8 Hz, 1H), 3.93 (dd, *J* = 8.7, 3.0 Hz, 1H), 2.96 (d, *J* = 5.6 Hz, 1H), 2.73 (dd, *J* = 5.6, 2.9 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.39, 159.58, 134.80, 128.97, 128.76, 127.58, 115.49, 108.79, 83.60, 69.76, 68.77, 39.38, 35.76, 35.40, 28.00. IR (neat, cm^{-1}): 2978.22, 2931.81, 2866.31, 2226.79, 1717.60, 1608.38, 1369.59, 1281.51, 1153.59, 1021.63. HRMS (DART) ($[M+Na]^+$) Calcd. for $C_{19}H_{21}NO_3Na^+$: 334.1419; Found: 334.1428.



69% yield; >20:1 *E*/*Z*; 62:38 *endo*-**3w**: *exo*-**3w**; colorless oil; R_f = 0.3 (hexanes/ethyl acetate, 4:1). For *endo*-**3w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.37 – 7.30 (m, 2H), 7.31 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 4.23 (d, *J* = 9.3 Hz, 1H), 4.18 (d, *J* = 9.4 Hz, 1H), 4.04 (d, *J* = 9.3 Hz, 1H), 3.98 – 3.89 (m, 1H), 2.99 (d, *J* = 8.7 Hz, 1H), 2.56 (dd, *J* = 8.7, 3.2 Hz, 1H), 1.57 (s, 9H). For *exo*-**3w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.21 (s, 2H), 7.12 (s, 1H), 4.39 (d, *J* = 9.0 Hz, 1H), 4.32 (d, *J* = 9.0 Hz, 1H), 4.09 (d, *J* = 8.8 Hz, 1H), 3.93 (dd, *J* = 8.7, 3.0 Hz, 1H), 2.96 (d, *J* = 5.6 Hz, 1H), 2.73 (dd, *J* = 5.6, 2.9 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.66, 160.92, 160.39, 159.57, 134.82, 133.14, 128.98, 128.78, 128.77, 128.23, 127.59, 127.45, 115.50, 115.16, 108.82, 107.68, 84.01, 83.61, 69.78, 68.79, 67.30, 66.29, 39.39, 37.88, 36.60, 35.77, 35.40, 34.99, 28.11, 28.01. IR (neat, cm^{-1}): 2978.94, 2930.16, 2864.56, 2227.18, 1719.00, 1610.08, 1369.88, 1283.73, 1153.37, 1025.75. HRMS (DART) ($[M+Na]^+$) Calcd. for $C_{19}H_{21}NO_3Na^+$: 334.1419; Found: 334.1428.

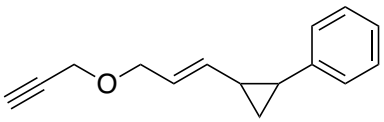
2.4.5.3. Probing of ε-Co(III)-Alkyl Radical Intermediate through Cyclopropylcarbinyl Radical Ring-Opening



Compound **S2x** was synthesized followed literature procedure and spectroscopic data of compound **S2x** is consistent with literature.[25] A solution of allylic alcohol (1.0 equiv) in

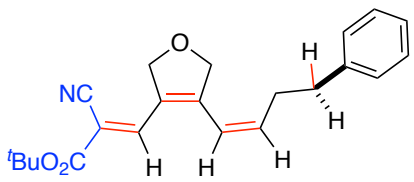
DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture for 20 minutes and dropwise addition of 3-bromoprop-1-yne (2.0 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[18]

(*E*)-(2-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)cyclopropyl)benzene 2x. Colorless oil;



79% Yield; R_f = 0.4 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.14 (m, 1H), 7.13 – 7.04 (m, 2H), 5.68 (dt, *J* = 15.4, 6.4 Hz, 1H), 5.50 (ddt, *J* = 15.3, 8.6, 1.2 Hz, 1H), 4.16 (d, *J* = 2.4 Hz, 2H), 4.05 (dd, *J* = 6.4, 1.3 Hz, 2H), 2.45 (td, *J* = 2.4, 0.8 Hz, 1H), 1.96 (ddd, *J* = 8.8, 5.8, 4.2 Hz, 1H), 1.72 (tdd, *J* = 8.4, 5.6, 4.2 Hz, 1H), 1.24 (dt, *J* = 8.6, 5.4 Hz, 1H), 1.13 (dt, *J* = 8.7, 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 142.19, 137.69, 128.46, 125.82, 125.80, 123.93, 79.95, 74.43, 70.18, 56.93, 26.21, 25.40, 16.87. IR (neat, cm^{-1}):3293.61, 3025.89, 2850.46, 1665.36, 1497.24, 1355.79, 1076.77, 964.14, 697.24. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{17}O^+$: 213.1274; Found: 213.1271.

***tert*-Butyl (*E*)-2-cyano-3-(4-((*Z*)-4-phenylbut-1-en-1-yl)-2,5-dihydrofuran-3-yl)acrylate 3x.**

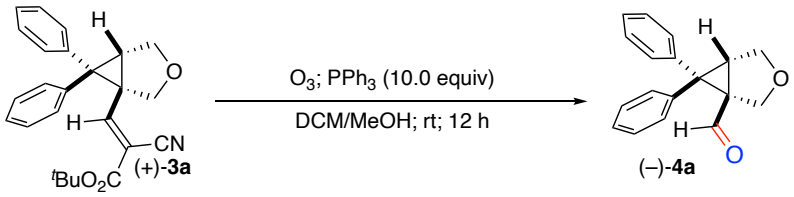


10% NMR yield; Light yellow oil; R_f = 0.4 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.34 – 7.25 (m, 2H),

7.22 – 7.20 (m, 1H), 7.18 – 7.15 (m,2H), 6.33 (d, J = 11.9 Hz, 1H), 5.93 (dt, J = 12.0, 7.7 Hz, 1H), 5.17 (t, J = 4.2 Hz, 2H), 4.87 (t, J = 4.2 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.51 – 2.41 (m, 2H), 1.55 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 161.58, 151.47, 142.98, 140.66, 139.68, 130.79, 128.70, 128.54, 126.49, 118.83, 115.88, 104.27, 83.92, 77.08, 73.89, 35.74, 32.25, 28.07. IR (neat, cm^{-1}): 2979.22, 2929.86, 2221.14, 1716.95, 1579.98, 1369.66, 1272.75, 1157.23, 1100.74, 700.85z. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{26}NO_3^+$: 352.1907; Found: 352.1904.

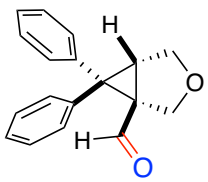
2.4.6. Further Transformations

2.4.6.1. Ozonolysis



A flow of O_3/O_2, generated from a regular ozone generator, was passed through a MeOH/DCM solution (1:1, 30 mL/mmol) of the (+)-**3a** at room temperature for several minutes until the solution turned blue. A flow of N_2 was passed through the solution for 2 minutes. PPh_3 (10 equiv) was added, and the reaction was stirred overnight. The reaction was then concentrated and purified by flash column chromatography over silica to give the product (–)-**4a**.

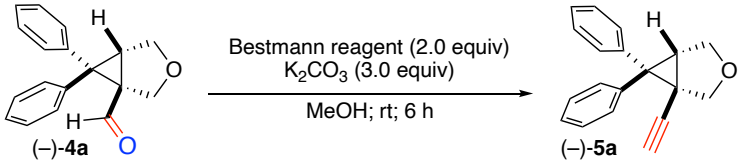
(1*R*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde (–)-**4a,** white solid;



88% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.45 – 7.38 (m, 2H), 7.37 – 7.13 (m, 8H), 4.33 (d, J = 9.7 Hz, 1H), 4.11 – 4.06 (m, 2H), 3.99 (dd, J = 9.4, 3.6 Hz, 1H), 3.25 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.90, 139.83, 137.91,

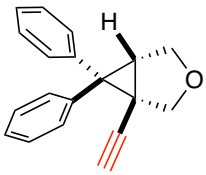
129.30, 129.07, 127.59, 127.50, 127.38, 67.09, 65.99, 50.82, 47.65, 37.38. $[\alpha]_D^{20}$ = -85.40° (*c* = 1, $CHCl_3$). HPLC (Chiral WHELK, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 31.6 min., t_{minor} = 28.6 min. *ee* 91%. IR (neat, cm^{-1}): 3057.19, 3025.51, 2865.12, 1692.57, 1493.75, 1447.30, 1087.71, 1055.33, 911.67, 709.57. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{17}O_2^+$: 265.1223; Found: 265.1227.

2.4.6.2. Seyferth-Gilbert Homologation



To a flame-dried flask equipped with a magnetic stir bar were added aldehyde (1.0 equiv), K_2CO_3 (3.0 equiv) and MeOH (2 mL/mmol). To the stirred solution, Bestmann reagent (dimethyl(acetyldiazomethyl)phosphonate, 2.0 equiv) was added and the resulting mixture was stirred at room temperature for 6 h. After completion, the mixture was treated with saturated $NaHCO_3$ solution, then extracted with ethyl acetate. The organic layer was then concentrated and purified by flash column chromatography over silica to give the product (–)-**5a**.[26]

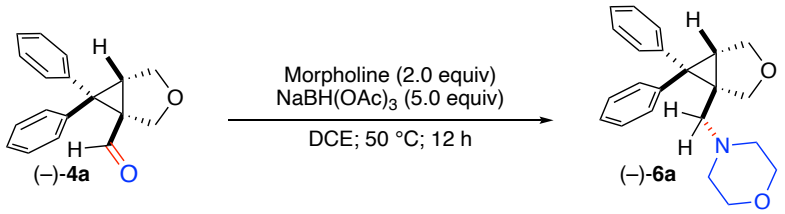
(1*R*,5*S*)-1-Ethynyl-6,6-diphenyl-3-oxabicyclo[3.1.0]hexane (–)-**5a,** white solid; 80%



Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.39 – 7.27 (m, 6H), 7.27 – 7.16 (m, 2H), 4.18 (d, *J* = 9.0 Hz, 1H), 4.12 (dd, *J* = 9.2, 2.6 Hz, 1H), 4.07 (d, *J* = 9.3, 1H), 4.04 (d, *J* = 9.0 Hz, 1H), 2.77 – 2.76 (m, 1H), 2.12 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.14, 138.04, 129.30, 128.80, 128.40, 127.95, 126.95, 126.84, 82.04, 72.44, 71.56, 67.97, 42.98, 38.11, 31.18. $[\alpha]_D^{20}$ = -166.41° (*c* = 1, $CHCl_3$).

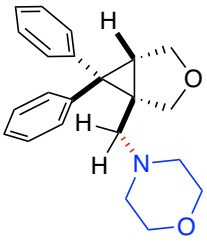
HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 9.4 min., t_{minor} = 10.7 min. *ee* 88%. IR (neat, cm^{-1}): 3282.00, 3057.12, 2859.60, 1657.64, 1598.60, 1493.35, 1446.98, 1086.21, 915.39, 766.60, 707.32. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{17}O^+$: 261.1274; Found: 261.1279.

2.4.6.3. Reductive Amination



To a flame-dried flask equipped with a magnetic stir bar were added aldehyde (1.0 equiv), morpholine (2.0 equiv), and DCE (30 mL/mmol). To the stirred solution, $NaBH(OAc)_3$ (5.0 equiv) was added and the resulting mixture was stirred at 50 °C overnight. After completion, the mixture was treated with saturated $NaHCO_3$ solution, then extracted with ethyl acetate. The organic layer was washed with brine, dried with $MgSO_4$, filtered and concentrated. Flash chromatography gave the product (–)-**6a**.[26]

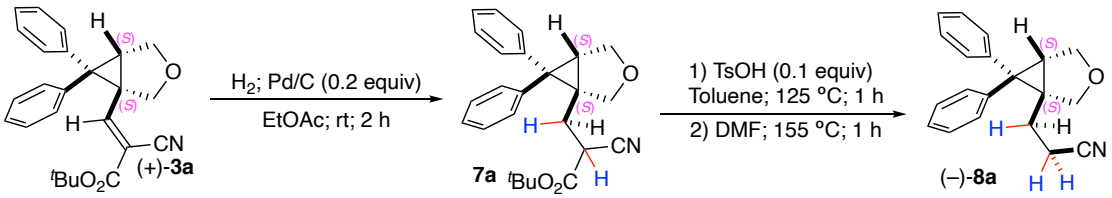
4-(((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)methyl)morpholine



(–)-**6a,** white solid; 73% Yield; R_f = 0.3 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 6H), 7.24 – 7.18 (m, 3H), 7.16 – 7.05 (m, 1H), 4.06 (s, 2H), 4.00 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.96 (d, *J* = 9.0 Hz, 1H), 3.70 (t, *J* = 5.0 Hz, 4H), 2.62 (d, *J* = 13.4 Hz, 1H), 2.45 – 2.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.93, 139.56, 129.47, 128.61, 128.46, 128.41, 126.56, 126.38, 70.90, 67.75, 67.11, 58.65, 53.99, 40.48, 38.41, 33.47. $[\alpha]_D^{20}$ = -119.62° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 15.3 min., t_{minor} = 13.3 min. *ee* 91%. IR (neat, cm^{-1}): 3055.34,

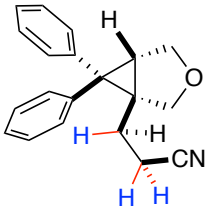
2955.64, 2849.54, 1599.07, 1493.32, 1446.02, 1116.88, 1054.16, 865.14, 708.43. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{22}H_{26}NO_2^+$: 336.1958; Found: 336.1969.

2.4.6.4. Hydrogenation



A solution of (+)-**3a** (1.0 equiv) and Pd/C (0.2 equiv, 10% w/w) in EtOAc (10 mL/mmol) was subjected to 1 atm H_2-pressure (balloon) at r.t. until full conversion of the (+)-**3a** was detected by TLC. Work-up by filtering through celite and evaporation yielded **7a**. To a solution of **7a** (1.0 equiv) in toluene was added *p*-toluenesulfonic acid. The resulting mixture was stirred at 125 °C for 1h. Removing all the volatiles under reduced pressure and adding DMF (10 mL/mmol). The reaction mixture was stirred at 155 °C for another 1h. Removal of all volatiles under reduced pressure yields the crude products (–)-**8a,** which are purified by flash column chromatography.

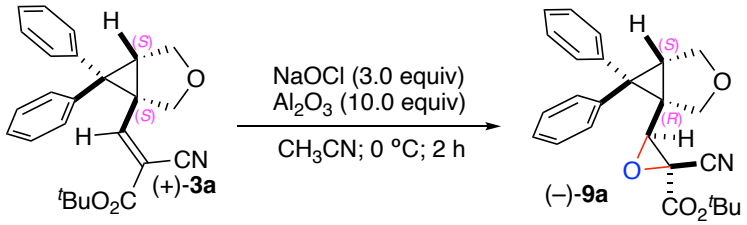
3-((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)propanenitrile (–)-8a,



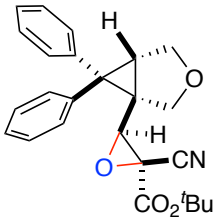
colorless oil; 83% Yield; R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 8H), 7.20 – 7.14 (m, 2H), 4.14 (d, *J* = 9.2 Hz, 1H), 4.03 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.94 (d, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 2.48 (d, *J* = 3.4 Hz, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.86 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.27, 138.86, 129.20, 128.97, 128.74, 128.45, 126.85, 126.77, 119.46, 70.70, 68.25, 41.83, 38.94, 32.71, 25.62, 15.63. $[\alpha]_D^{20}$ = -124.77° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 10% isopropanol- 90% hexanes rate 1.0 mL/min): t_{major} = 23.0 min., t_{minor} = 18.7 min. *ee* 86%. IR (neat, cm^{-1}): 3052.72,

2923.91, 2855.79, 2356.35, 1598.89, 1493.47, 1445.95, 1086.97, 918.41, 748.14. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{20}NO^+$: 290.1539; Found: 290.1543.

2.4.6.5. Epoxidation

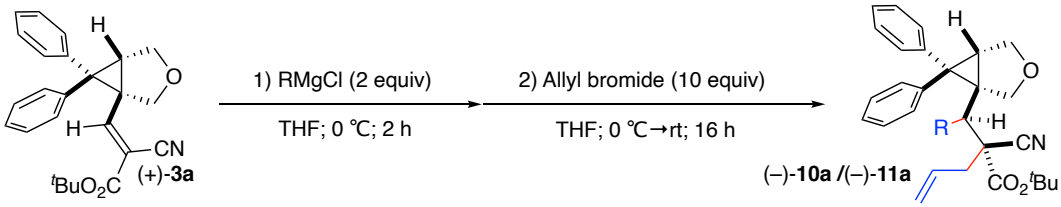


To a solution of (+)-**3a** (1.0 equiv) in CH_3CN (10 mL/mmol) was added neutral alumina (10.0 equiv). Then NaOCl (3.0 equiv) was added slowly at 0 °C and the mixture was stirred for 2h, The epoxide is extracted with DCM, the solvent was removed and the product (–)-**9a** was purified by flash column chromatography.[27]

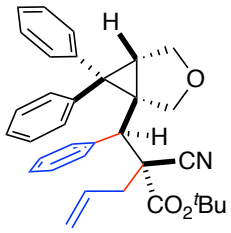


***tert*-Butyl (3*S*)-2-cyano-3-((1*R*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)oxirane-2-carboxylate** (–)-**9a,** colorless oil; 90% Yield; 84:16 dr; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 4H), 7.35 – 7.20 (m, 3H), 7.17 – 7.13 (m, 3H), 4.17 (d, J = 9.3 Hz, 1H), 4.14 – 4.05 (m, 1H), 4.01 – 3.98 (m, 2H), 3.18 (s, 1H), 2.74 (d, J = 3.5 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.31, 140.73, 137.57, 129.26, 129.01, 128.81, 128.01, 127.25, 127.14, 114.81, 86.24, 67.39, 66.78, 65.27, 50.06, 42.01, 37.04, 34.90, 27.88. $[\alpha]_D^{20}$ = -98.02° (c = 1, $CHCl_3$). HPLC (Chiral WHELK, 3% isopropanol- 97% hexanes rate 1.0 mL/min): t_{major} = 33.3 min., t_{minor} = 31.4 min. *ee* 91%. IR (neat, cm^{-1}): 2980.91, 2868.61, 1752.65, 1599.37, 1494.35, 1447.56, 1371.91, 1293.99, 1090.87, 749.34. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{25}H_{26}NO_4^+$: 404.4772; Found: 404.1859.

2.4.6.6. 1,4-Addition



To a solution of (+)-**3a** (1.0 equiv) in THF (10 mL/mmol) was added a solution of Grignard reagent (2.0 equiv) at 0 °C. After complete addition, the resulting solution is stirred at 0 °C for 2 h. Then allyl bromide (10 equiv) was added dropwise at 0 °C. The resulting solution was slowly warmed to r.t. and detected by TLC. The reaction is quenched by slow addition of water at 0 °C. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude products (–)-**10a** and (–)-**11a**, which are purified by flash column chromatography.

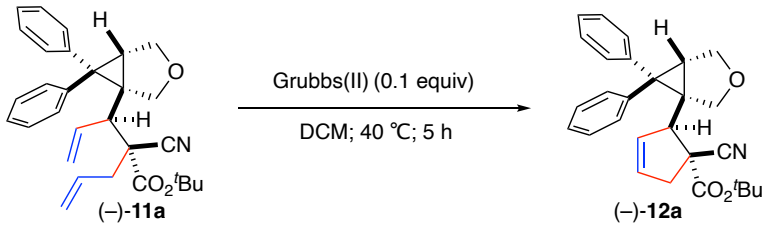


***tert*-Butyl (*R*)-2-cyano-2-((*S*)-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methyl)pent-4-enoate** (–)-**10a**, white solid; 87% Yield; >99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 3H), 7.45 – 7.08 (m, 10H), 6.81 (s, 2H), 5.81 – 5.60 (m, 1H), 5.19 – 5.02 (m, 2H), 4.85 (d, *J* = 9.2 Hz, 1H), 4.06 (d, *J* = 9.2 Hz, 1H), 3.94 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.87 (d, *J* = 8.9 Hz, 1H), 3.29 (s, 1H), 2.29 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.26 – 2.17 (m, 1H), 1.75 (d, *J* = 3.2 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.62, 140.89, 139.75, 139.32, 130.55, 129.93, 128.63, 128.43, 128.27, 127.74, 126.75, 126.44, 120.83, 119.36, 85.62, 69.23, 67.74, 53.05, 48.57, 44.73, 43.78, 42.04, 35.59, 28.34. $[\alpha]_D^{20}$ = -93.60° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 10% isopropanol- 90% hexanes rate 1.0 mL/min): t_{major} = 18.2 min., t_{minor} =

29.7 min. *ee* 87%. IR (neat, cm^{-1}): 3025.42, 2979.25, 2848.49, 2356.30, 1731.29, 1494.47, 1370.20, 1256.20, 1153.54, 1087.91. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{34}H_{36}NO_3^+$: 506.6531; Found: 506.2689.

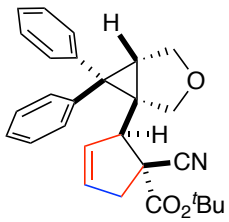
***tert*-Butyl (2*R*,3*S*)-2-allyl-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)pent-4-enoate** (–)-**11a,** colorless oil, 66% Yield; >99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 4H), 7.36 – 7.24 (m, 4H), 7.19 (dd, *J* = 11.4, 7.4 Hz, 2H), 5.93 (dt, *J* = 16.9, 10.1 Hz, 1H), 5.85 – 5.69 (m, 1H), 5.26 – 5.11 (m, 3H), 4.50 (d, *J* = 15.0 Hz, 1H), 4.33 (d, *J* = 9.2 Hz, 1H), 4.05 (d, *J* = 9.2 Hz, 1H), 3.96 – 3.87 (m, 2H), 2.60 – 2.45 (m, 3H), 2.36 (d, *J* = 3.2 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.83, 140.69, 139.46, 134.22, 130.74, 130.14, 128.51, 128.42, 126.64, 126.48, 120.94, 119.74, 119.02, 85.15, 68.13, 67.79, 51.93, 47.43, 43.41, 42.43, 41.19, 34.29, 28.19. $[\alpha]_D^{20}$ = -50.51° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 17.1 min., t_{minor} = 25.8 min. *ee* 89%. IR (neat, cm^{-1}): 3058.79, 2979.83, 2929.35, 2854.56, 1733.54, 1641.17, 1599.95, 1494.63, 1446.58, 1370.19, 1253.27, 1149.45, 1087.43, 923.96. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{30}H_{34}NO_3^+$: 456.2533; Found: 456.2536.

2.4.6.7. Olefin Metathesis



A solution of Grubbs 2nd generation catalyst (0.1 equiv) in anhydrous dichloromethane (10 mL/mmol) was added dropwise to the (–)-**11a** and the resulting mixture stirred at

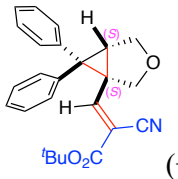
40 °C for 5 h. Removal of all volatiles under reduced pressure yields the crude products (–)-**12a**, which are purified by flash column chromatography.



***tert*-Butyl (1*R*)-1-cyano-2-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)cyclopent-3-ene-1-carboxylate** (–)-**12a,** white solid, 71% Yield; >99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 6.8 Hz, 1H), 7.12 (t, *J* = 6.8 Hz, 1H), 5.77 (dd, *J* = 5.9, 1.9 Hz, 1H), 5.67 – 5.61 (m, 1H), 4.37 (d, *J* = 8.8 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.79 (d, *J* = 9.5 Hz, 1H), 3.15 (d, *J* = 2.4 Hz, 1H), 3.12 – 2.96 (m, 2H), 2.42 (d, *J* = 3.3 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53, 141.90, 138.89, 131.77, 129.59, 129.18, 128.70, 128.08, 126.69, 126.61, 121.04, 83.99, 67.85, 67.22, 54.67, 48.39, 46.15, 44.51, 41.67, 34.26, 27.73. $[\alpha]_D^{20}$ = -206.10° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 31.8 min., t_{minor} = 28.6 min. *ee* 84%. IR (neat, cm^{-1}): 3059.07, 2978.73, 2928.56, 2857.04, 1735.42, 1494.45, 1369.97, 1251.49, 1150.60, 710.23 HRMS (DART) ($[M+H]^+$) Calcd. for $C_{28}H_{30}NO_3^+$: 428.2220; Found: 428.2219.

2.4.7. X-ray Crystallographic Information

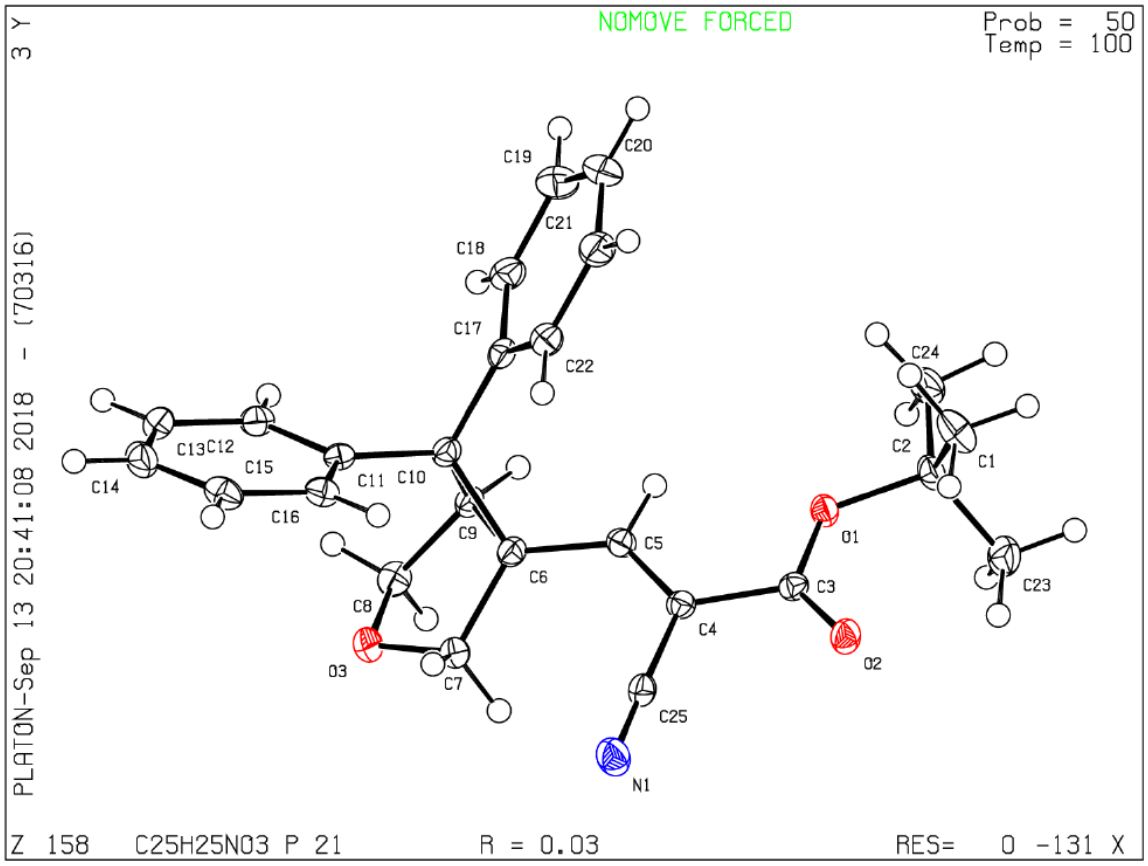
The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (Cu K_α, λ = 1.54178 Å). Indexing was performed using *APEX2*[28] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[29] Absorption correction was performed by multi-scan method implemented in SADABS.[30] Space group were determined using XPREP implemented in APEX2.[28] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[21-23]program.

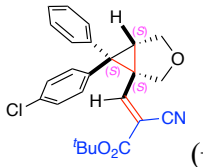


(+)-**3a**

Table 1. Crystal data and structure refinement for (+)-**3a**.

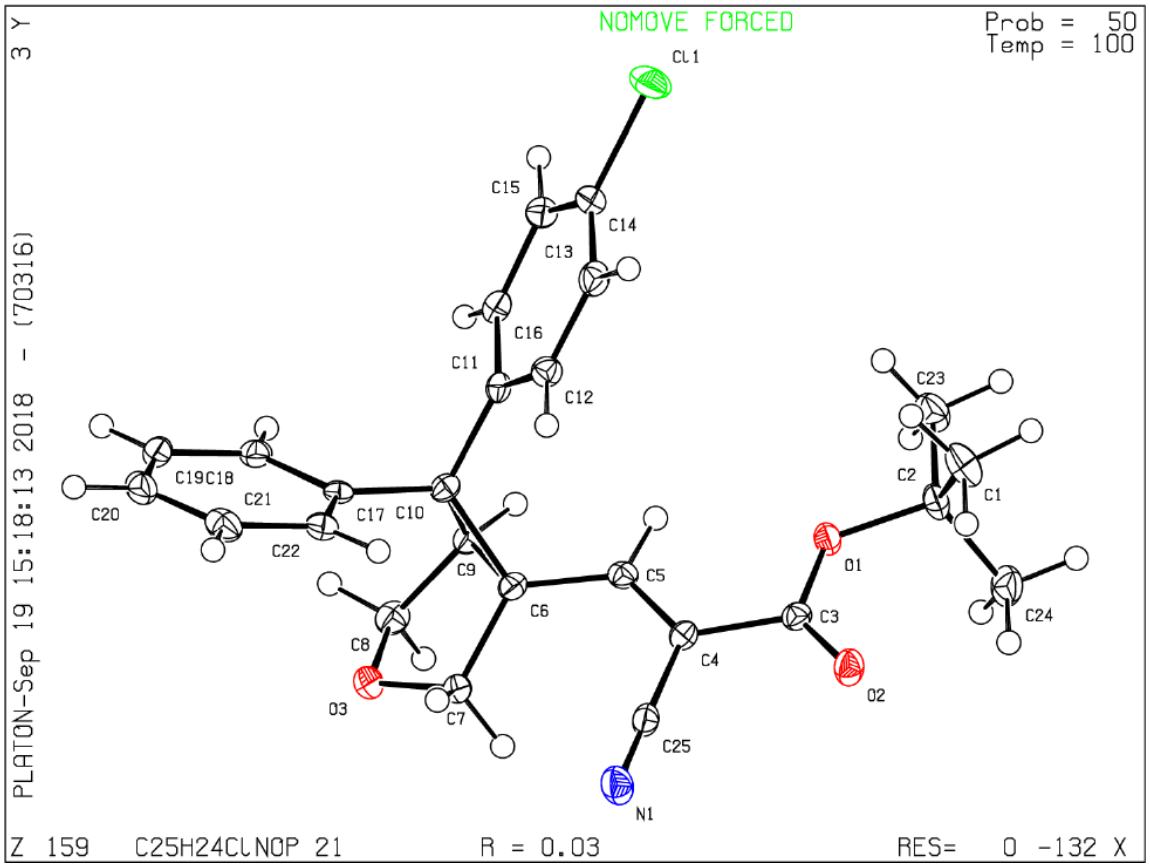
Identification code	(+)-**3a**	
Empirical formula	C25 H25 N O3	
Formula weight	387.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.4821(3) Å	α= 90°.
	b = 6.9014(2) Å	β= 112.5160(10) °.
	c = 14.4574(4) Å	γ = 90°.
Volume	1058.31(5) $Å^3$	
Z	2	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.633 mm^{-1}	
F(000)	412	
Crystal size	0.420 x 0.120 x 0.100 mm^3	
Theta range for data collection	3.309 to 70.046°.	
Index ranges	-13<=h<=13, -8<=k<=8, -17<=l<=17	
Reflections collected	13422	
Independent reflections	3960 [R(int) = 0.0213]	
Completeness to theta = 67.679°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6581	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3960 / 1 / 262	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R_1 = 0.0311, wR_2 = 0.0826	
R indices (all data)	R_1 = 0.0313, wR_2 = 0.0829	
Absolute structure parameter	0.06(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.208 and -0.202 $e.Å^{-3}$	

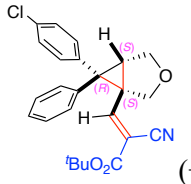

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C18
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C13
C12
C15
C14
C11
C10
C16
C9
C5
O1
C6
C3
C8
C4
C23
O3
C7
O2
C25
N1
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R = 0.03
RES= 0 -131 X



(+)-**3g**

Table 2. Crystal data and structure refinement for (+)-**3g**.		
Identification code	(+)-**3g**	
Empirical formula	C25 H24 Cl N O3	
Formula weight	421.90	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.6183(5) Å	α = 90°.
	b = 6.9280(3) Å	β = 112.661(2) °.
	c = 14.4610(7) Å	γ = 90°.
Volume	1074.13(8) $Å^3$	
Z	2	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	1.785 mm^{-1}	
F(000)	444	
Crystal size	0.320 x 0.140 x 0.080 mm^3	
Theta range for data collection	3.312 to 66.584°.	
Index ranges	-13<=h<=13, -8<=k<=8, -17<=l<=17	
Reflections collected	11867	
Independent reflections	3771 [R(int) = 0.0251]	
Completeness to theta = 66.584°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5533	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3771 / 1 / 274	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R_1 = 0.0276, wR_2 = 0.0741	
R indices (all data)	R_1 = 0.0278, wR_2 = 0.0743	
Absolute structure parameter	-0.001(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.293 and -0.164 $e.Å^{-3}$	

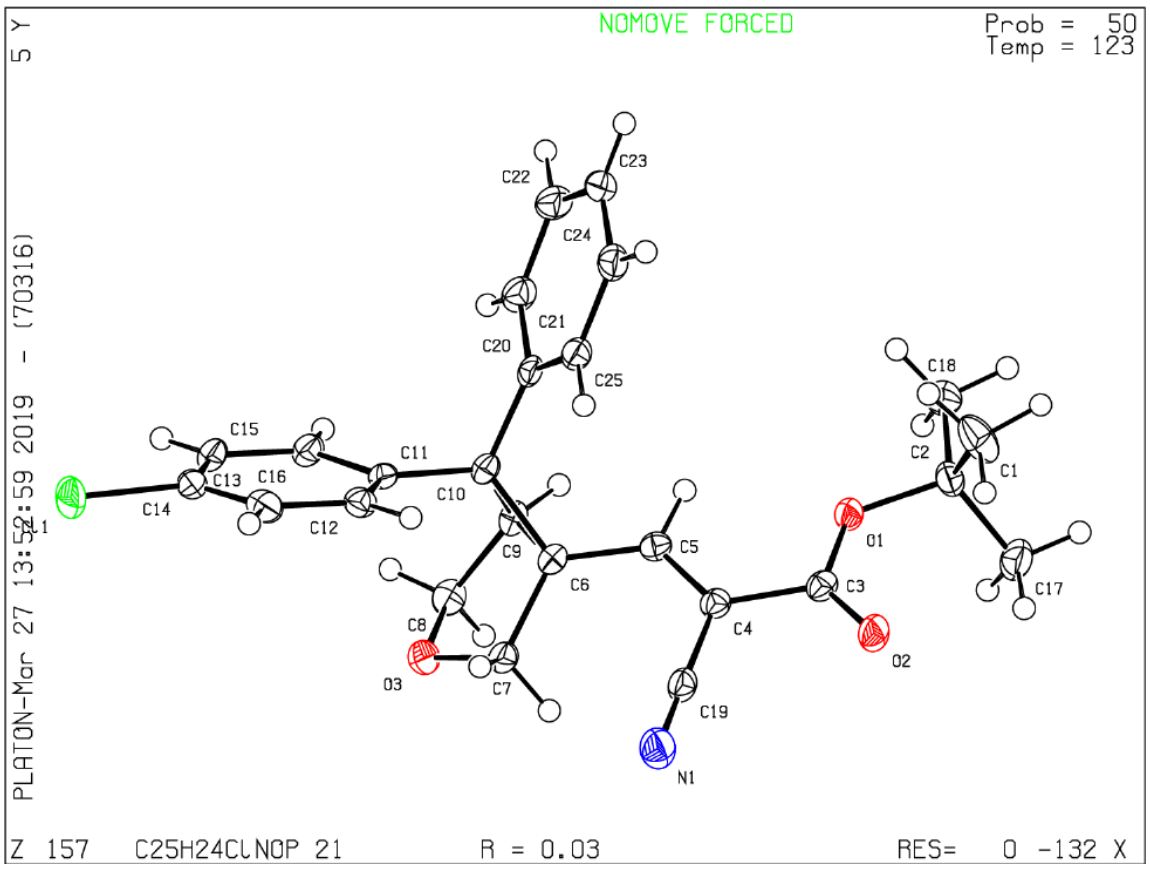

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C5
C8
O3
C7
C4
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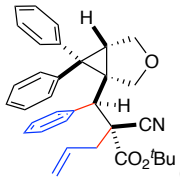


(+)-**3h**

Table 3. Crystal data and structure refinement for (+)-**3h**.

Identification code	(+)-**3h**	
Empirical formula	C25 H24 Cl N O3	
Formula weight	421.90	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.6185(6) Å	α = 90°.
	b = 6.9488(3) Å	β = 107.4210(10) °.
	c = 14.0532(7) Å	γ = 90°.
Volume	1082.54(9) $Å^3$	
Z	2	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	1.771 mm^{-1}	
F(000)	444	
Crystal size	0.540 x 0.320 x 0.140 mm^3	
Theta range for data collection	3.988 to 66.702°.	
Index ranges	-13<=h<=13, -8<=k<=8, -16<=l<=16	
Reflections collected	12960	
Independent reflections	3779 [R(int) = 0.0221]	
Completeness to theta = 66.702°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5352	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3779 / 1 / 274	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R_1 = 0.0260, wR_2 = 0.0680	
R indices (all data)	R_1 = 0.0260, wR_2 = 0.0680	
Absolute structure parameter	0.003(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.156 and -0.172 e. $Å^{-3}$	

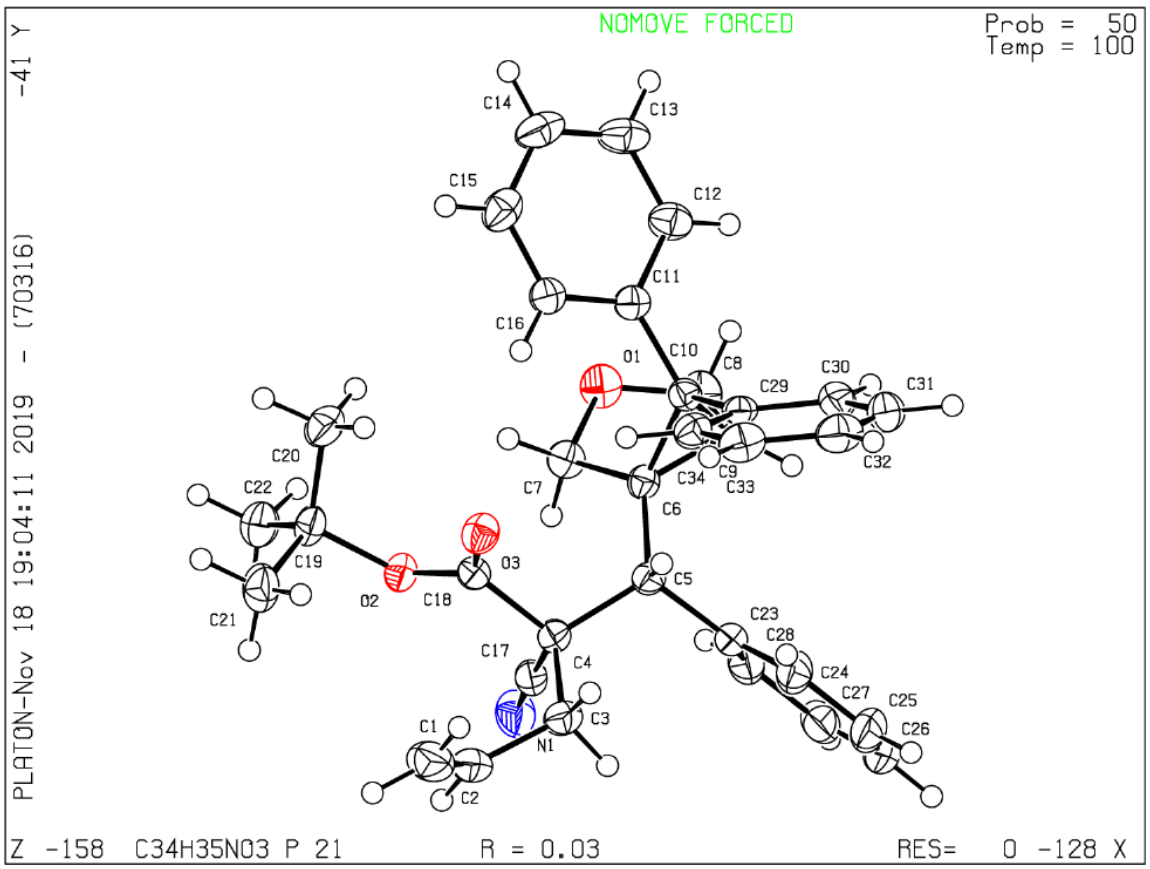

NOMOVE FORCED
Prob = 50
Temp = 123
5 Y
PLATON-Mar 27 13:52:59 2019 - (70316)
Z 157 C25H24ClNOP 21
R = 0.03
RES= 0 -132 X
C22
C23
C24
C21
C20
C25
C15
C11
C13
C16
C14
C12
C10
C9
C6
C5
C8
O3
C7
C4
C3
O1
C2
C1
C18
C17
O2
C19
N1



(–)-**10a**

Table 4. Crystal data and structure refinement for (–)-**10a**.

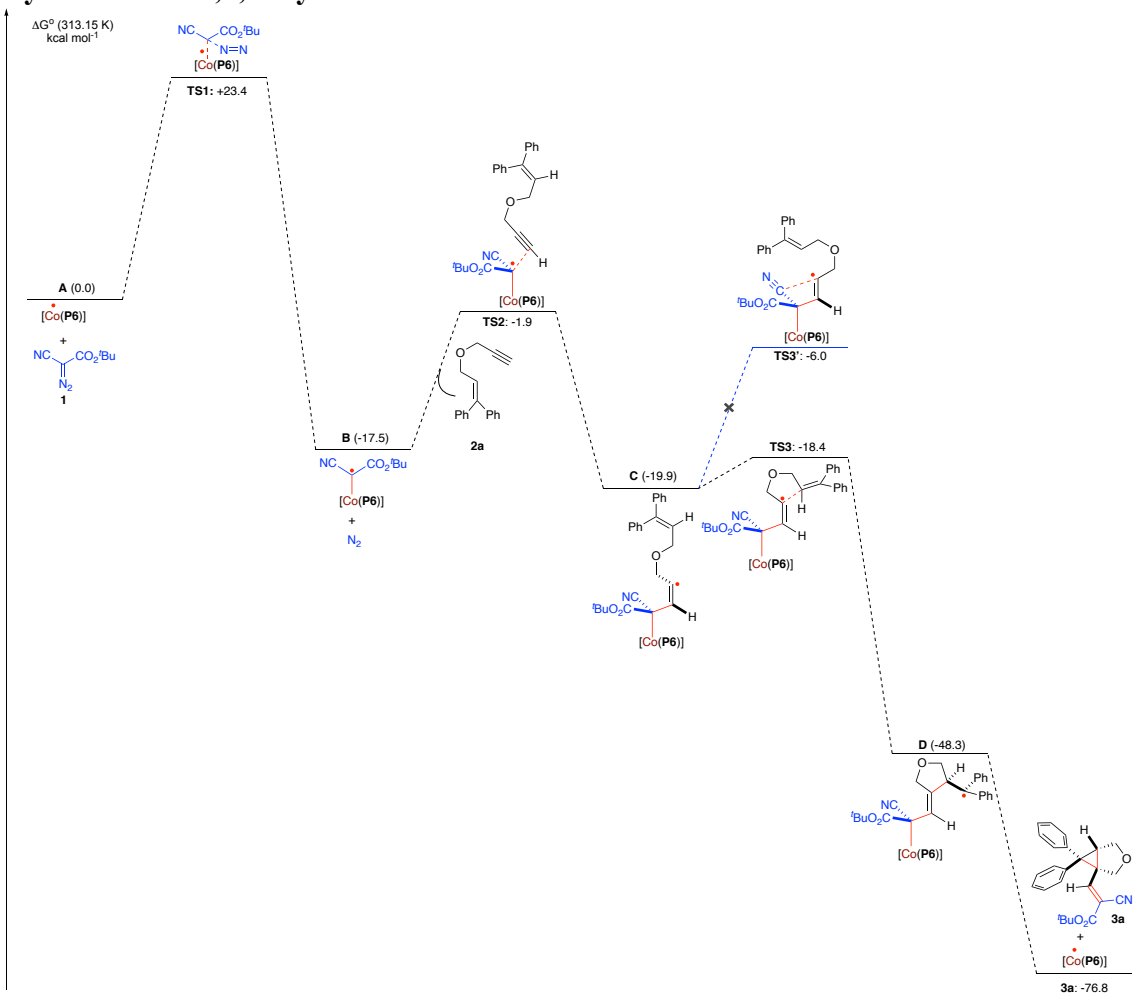
Identification code	(–)-**10a**	
Empirical formula	C34 H35 N O3	
Formula weight	505.63	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.1407(6) Å	α = 90°.
	b = 10.2131(6) Å	β = 93.648(2)°.
	c = 14.9900(9) Å	γ = 90°.
Volume	1396.55(15) $Å^3$	
Z	2	
Density (calculated)	1.202 Mg/m^3	
Absorption coefficient	0.596 mm^{-1}	
F(000)	540	
Crystal size	0.580 x 0.260 x 0.140 mm^3	
Theta range for data collection	2.954 to 66.480°.	
Index ranges	-10<=h<=10, -12<=k<=12, -17<=l<=17	
Reflections collected	26421	
Independent reflections	4863 [R(int) = 0.0227]	
Completeness to theta = 66.480°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.7001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4863 / 1 / 343	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R_1 = 0.0280, wR_2 = 0.0732	
R indices (all data)	R_1 = 0.0282, wR_2 = 0.0734	
Absolute structure parameter	-0.06(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.151 and -0.161 $e.Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 100
PLATON-Nov 18 19:04:11 2019 - (70316)
-41 Y
Z -158 C34H35NO3 P 21
R = 0.03
RES= 0 -128 X
C14
C13
C15
C12
C11
C16
O1
C10
C8
C30
C29
C31
C20
C22
C7
C34
C9
C33
C32
C6
C19
O3
C5
O2
C18
C21
C23
C28
C17
C4
C24
C27
C25
C1
C3
C26
N1
C2

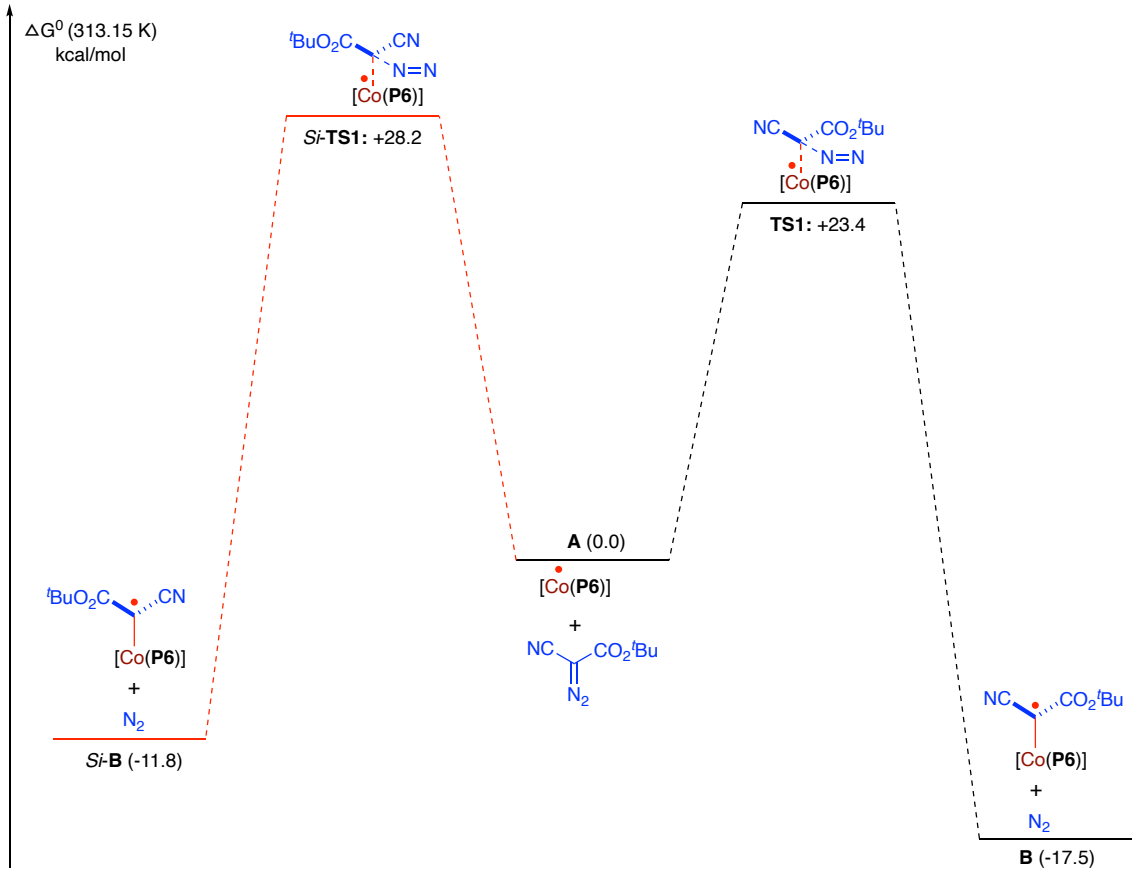
2.4.8 DFT Calculation

Considering the cost of time and computing resources for the large system with [Co(**P6**)], the geometry optimizations were performed with the Gaussian 16[34] at the BP86[35,36]/lanl2dz[37,38] 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 (room temperature), 1 atm) were obtained from these calculations. Thermal corrections (entropy and enthalpy) at 313.15 K (40 ^{o}C) were obtained by applying freqchk utility with the above obtained checkpoint file of frequency calculation. To further improve the accuracy of energies, single point energies were carried out at the b3lyp[39]/def2-tzvp[37,38] level of theory along with Grimme's dispersion correction[40] (D3BJ) and SMD[41] solvation model (in Acetonitrile).

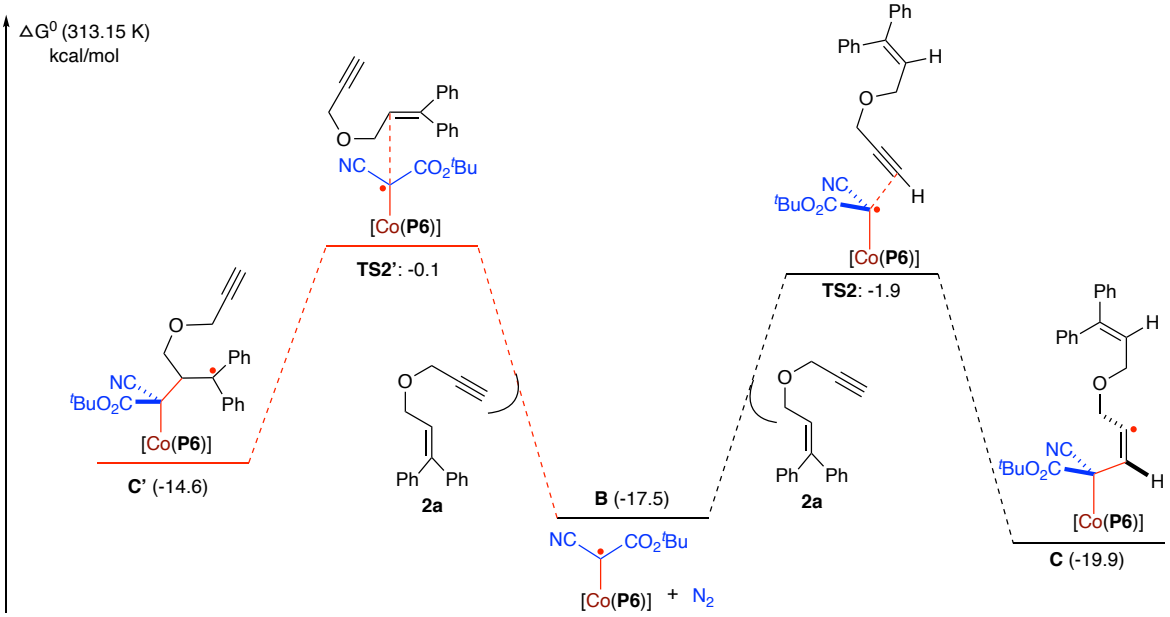
Scheme 2.12. Calculated Energy Diagram for [Co(P6)] Catalyzed Radical Cascade Cyclization of 1,6,-Enyne 2a with Diazo 1a



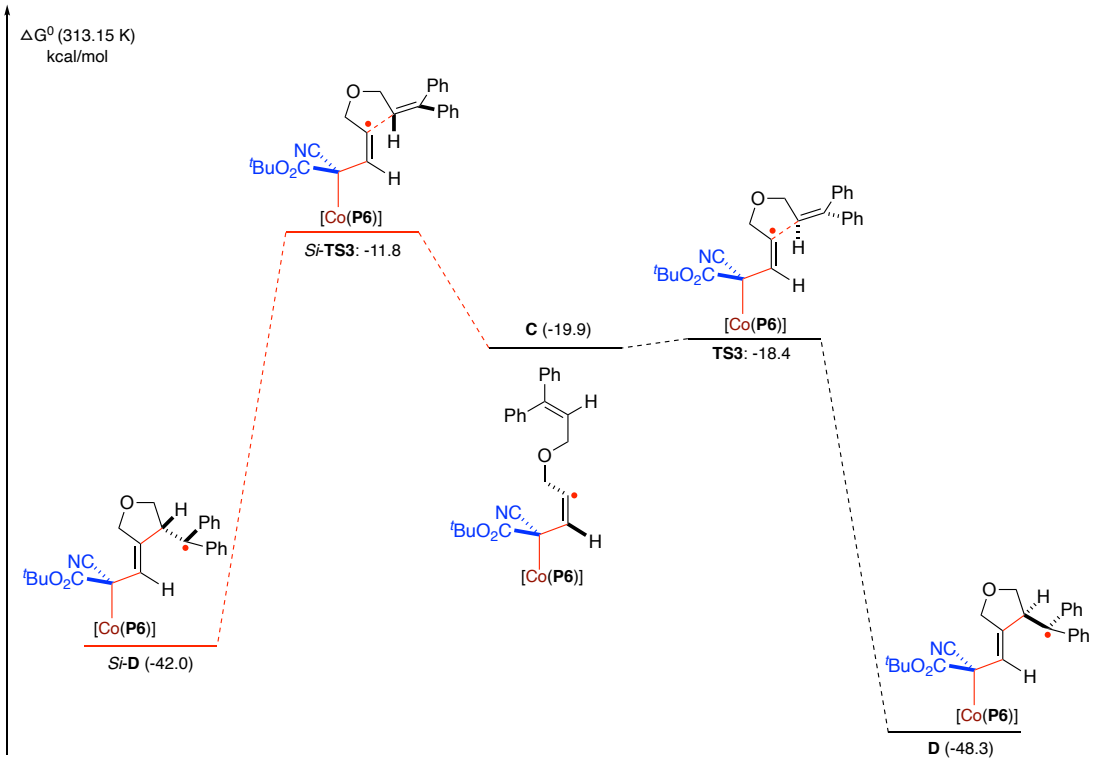
Scheme 2.13. Calculated Energy Diagram for Metalloradical Activation



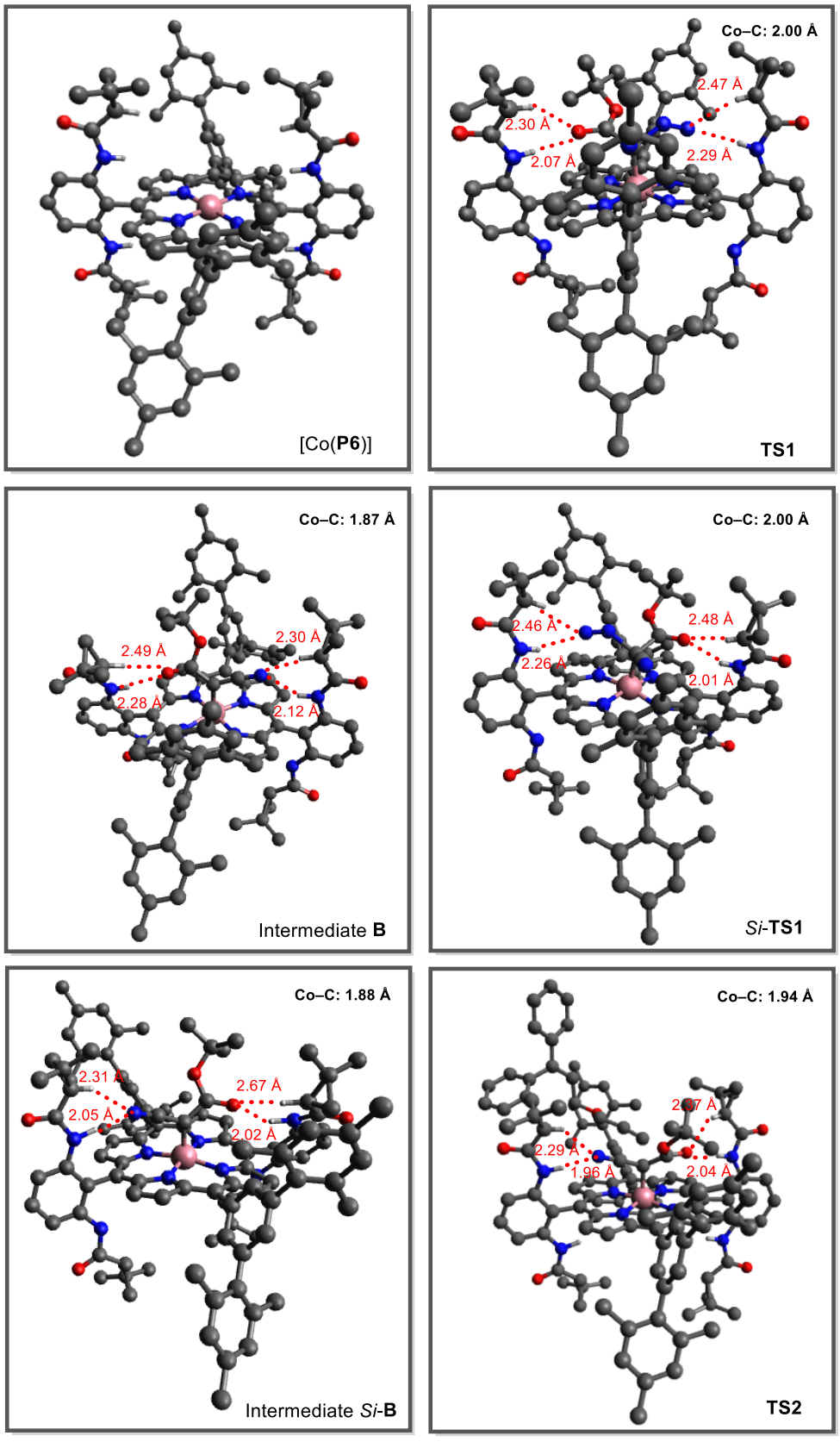
Scheme 2.14. Calculated Energy Diagram for Radical Addition to Alkyne vs Alkene

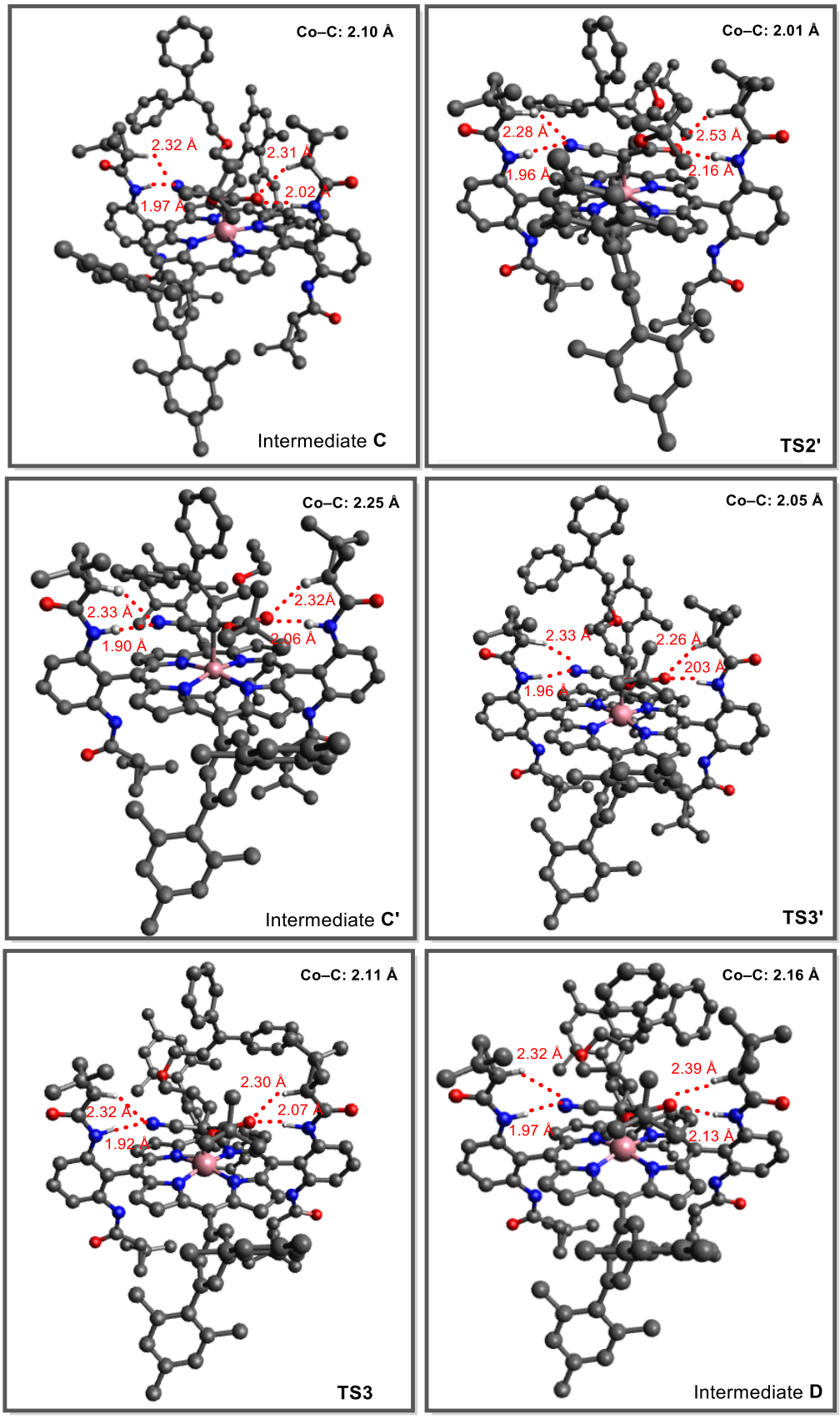


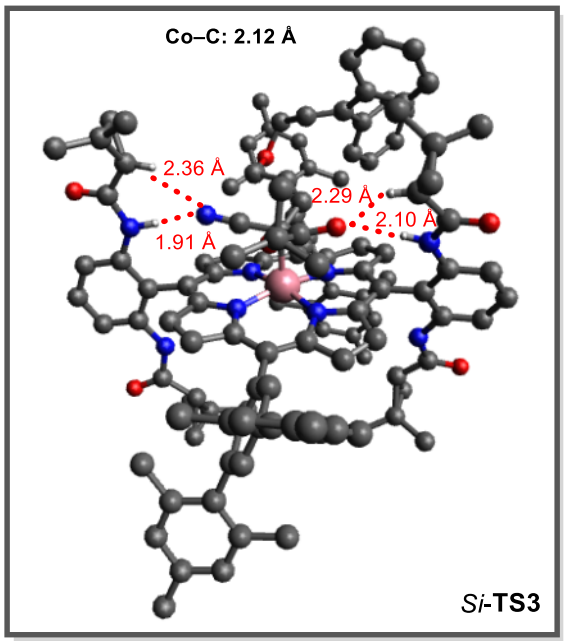
Scheme 2.15. Calculated Energy Diagram for *5-Exo-Trig* Cyclization.

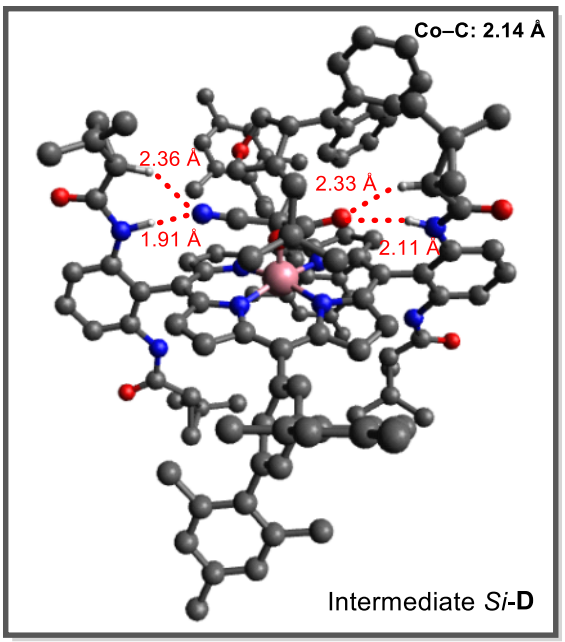


Scheme 2.16. Optimized Geometries for All Intermediates and Transition States




Co–C: 2.10 Å
2.32 Å
2.31 Å
2.02 Å
1.97 Å
Intermediate C
Co–C: 2.01 Å
2.28 Å
2.53 Å
1.96 Å
2.16 Å
TS2'
Co–C: 2.25 Å
2.33 Å
2.32Å
1.90 Å
2.06 Å
Intermediate C'
Co–C: 2.05 Å
2.33 Å
2.26 Å
203 Å
1.96 Å
TS3'
Co–C: 2.11 Å
2.30 Å
2.32 Å
2.07 Å
1.92 Å
TS3
Co–C: 2.16 Å
2.32 Å
2.39 Å
1.97 Å
2.13 Å
Intermediate D





Intermediate A

A-[Co(P6)]:

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.59535 Hartree
H_corr: 1.918018 Hartree
SCF: -6149.959874 Hartree
S: 646.582 Cal/Mol-Kelvin
H: -6148.041856 Hartree
G: -6148.364524 Hartree

Cartesian Coordinates:

N	-1.40912300	-1.40146800	-0.02342800
N	1.40912500	1.40149200	-0.02340700
N	1.40909400	-1.40149800	0.02322000
N	-1.40909800	1.40152700	0.02296000
C	-1.22916400	2.80280200	0.06850000
C	-2.81155300	1.22691600	0.06469900
C	-2.81157400	-1.22682500	-0.06510300
C	-1.22921600	-2.80274100	-0.06915600
C	1.22915700	-2.80277000	0.06886200
C	2.81154400	-1.22688400	0.06508600
C	2.81158000	1.22684600	-0.06492900
C	1.22922400	2.80276200	-0.06927600
C	2.50964200	3.48687400	-0.17146000
C	0.00003600	3.48652000	-0.00048800
C	-2.50955600	3.48696200	0.17068900
C	-3.49720800	0.00004900	-0.00015300

C 3.48539200 2.51357700 -0.17434700
C 3.49720600 -0.00002400 0.00019600
C 3.48530600 -2.51364100 0.17450200
C -3.48537400 -2.51356600 -0.17448300
C -0.00003500 -3.48649400 -0.00018800
C 2.50954000 -3.48692000 0.17123300
C -3.48532400 2.51368400 0.17394500
C -2.50962400 -3.48686200 -0.17141100
C -0.00005100 -4.99663000 -0.00021400
C -0.00006900 -7.82486700 -0.00025600
C 0.09887800 -5.72062700 -1.22996300
C -0.09899300 -5.72066300 1.22951400
C -0.09647900 -7.14235100 1.23082600
C 0.09634700 -7.14231500 -1.23131700
C -5.00152100 0.00004300 -0.00007100
C -7.83323600 -0.00005700 0.00006400
C -5.72042600 0.50688800 -1.11455100
C -5.72028600 -0.50684200 1.11448100
C -7.13988700 -0.50795200 1.13099900
C -7.14002900 0.50789900 -1.13093100
C 0.00004900 4.99665700 -0.00065100
C 0.00005900 7.82489400 -0.00094800
C -0.09864900 5.72054200 -1.23048500
C 0.09875700 5.72080200 1.22903100
C 0.09623700 7.14249000 1.23021500
C -0.09612100 7.14223000 -1.23196600
C 5.00151900 -0.00002100 0.00042100
C 7.83323400 0.00001700 0.00087900
C 5.72016900 0.50694700 1.11500900
C 5.72053900 -0.50697000 -1.11393800
C 7.14014400 -0.50801300 -1.13015400
C 7.13976900 0.50803000 1.13168900
C 0.29866400 -5.39432200 -3.75394000
N 0.19497300 -4.95450400 -2.42634700
C -0.29879800 -5.39442000 3.75350100
N -0.19508700 -4.95457200 2.42591900
C 0.29805800 5.39479500 3.75308700
N 0.19462000 4.95482300 2.42552400
C -0.29791300 5.39400400 -3.75447500
N -0.19450600 4.95430900 -2.42681800
C -0.37906600 4.27348400 -4.75069400
C -0.91907800 4.58396000 -6.16683200
C 0.55957200 4.23210800 -6.01688800
C 0.37921000 4.27447800 4.74953500
C 0.91925000 4.58522700 6.16560200
C -0.55940800 4.23336700 6.01575300

C	-0.38017800	-4.27401000	4.74982700
C	-0.92056100	-4.58463400	6.16578900
C	0.55813300	-4.23279100	6.01626700
C	0.38004400	-4.27389300	-4.75024400
C	0.92039800	-4.58449700	-6.16622200
C	-0.55829000	-4.23263700	-6.01666800
C	1.01134800	-2.83383000	6.44806000
C	1.60885600	-5.32657000	6.21576800
C	-1.01148700	-2.83366100	-6.44842700
C	-1.60903500	-5.32639300	-6.21617200
C	1.01286300	2.83308700	-6.44840600
C	1.61037800	5.32583400	-6.21623300
C	-1.01271900	2.83443900	6.44755000
C	-1.61018900	5.32715300	6.21489900
H	-1.60285300	-3.85583600	6.61641200
H	-4.56385800	-2.63784600	-0.25074900
H	-4.56380100	2.63799700	0.25023700
H	4.56377700	-2.63794600	0.25090700
H	-2.62369000	4.56820300	0.23327000
H	-2.62378100	-4.56809300	-0.23414000
H	4.56388400	2.63785000	-0.25051000
H	2.62366800	-4.56815600	0.23391300
H	2.62380700	4.56809900	-0.23426900
Co	-0.00000100	0.00001300	-0.00015700
H	-0.17047800	-7.67261900	2.18162600
H	0.17034000	-7.67255600	-2.18213300
H	-0.00007500	-8.92111800	-0.00027200
H	-8.93038100	-0.00010200	0.00011100
H	0.17005100	7.67284300	2.18098200
H	-0.16993100	7.67238600	-2.18284300
H	0.00006100	8.92114400	-0.00106400
H	8.93037900	0.00004200	0.00104600
O	0.31409000	-6.62303600	-4.08734200
O	-0.31423500	-6.62314200	4.08687800
O	0.31340900	6.62354700	4.08635100
O	-0.31326100	6.62268700	-4.08799700
H	-0.62753000	3.28813000	-4.33475300
H	0.62765200	3.28903700	4.33378700
H	1.17282200	5.63662800	6.33733000
H	-0.62851600	-3.28860700	4.33393100
H	-1.17417700	-5.63602000	6.33754600
H	0.62840300	-3.28850000	-4.33433400
H	1.60143400	3.85646900	6.61645200
H	-0.18152200	3.93873000	-2.28853300
H	1.90772900	-2.51595200	5.88118000
H	1.27297600	-2.83175600	7.52422600

H 0.21872200 -2.07767300 6.29194900
H 2.54740000 -5.07238500 5.68571600
H 1.25400400 -6.30235200 5.84420900
H 1.84450800 -5.42628400 7.29326400
H 1.17399700 -5.63588400 -6.33800100
H 1.60269100 -3.85570000 -6.61684400
H -1.27312900 -2.83156200 -7.52459000
H -0.21884600 -2.07752100 -6.29231200
H -1.90785600 -2.51577800 -5.88152900
H -1.84471100 -5.42607800 -7.29366500
H -2.54756300 -5.07220500 -5.68609400
H -1.25419200 -6.30219000 -5.84464400
H -1.60126400 3.85512100 -6.61755000
H -1.17263300 5.63533000 -6.33877000
H 0.22017800 2.07696800 -6.29241000
H 1.90909300 2.51524900 -5.88126200
H 1.27476500 2.83088500 -7.52450500
H 2.54877600 5.07167800 -5.68590900
H 1.25545800 6.30166600 -5.84487100
H 1.84631200 5.42542500 -7.29367900
H -0.22005000 2.07827400 6.29170100
H -1.90895700 2.51650700 5.88047100
H -1.27461700 2.83245400 7.52365100
H -1.84609100 5.42697400 7.29233100
H -2.54860600 5.07290200 5.68465500
H -1.25526200 6.30290100 5.84332300
H 0.18196100 -3.93891200 -2.28815700
H -0.18206400 -3.93897700 2.28775800
H 0.18162800 3.93921400 2.28745400
H -5.17022100 0.88445200 -1.98503200
H -5.16997200 -0.88438100 1.98490400
H 5.17042600 -0.88460600 -1.98444600
H 5.16976200 0.88456500 1.98534000
C -7.89643400 1.03125900 -2.32424600
C -7.99435100 2.43865100 -2.55204400
C -8.52003300 0.12004100 -3.23405200
C -8.71776500 2.90976300 -3.67771500
C -9.22820500 0.63196100 -4.34952500
C -9.34519500 2.02470100 -4.58815300
H -8.79220100 3.99282600 -3.84423900
H -9.69716300 -0.07362600 -5.04881200
C -7.89613600 -1.03136900 2.32438700
C -7.99372500 -2.43876400 2.55232300
C -8.51990300 -0.12020700 3.23413300
C -8.71698400 -2.90993100 3.67807000
C -9.22790800 -0.63218200 4.34968900

C -9.34457200 -2.02492500 4.58845400
H -8.79116600 -3.99299500 3.84470100
H -9.69698500 0.07336600 5.04893500
C -8.42033500 1.38773600 3.03558600
H -8.97914900 1.72050000 2.13998200
H -7.37158500 1.70996700 2.89380900
C -7.34286200 -3.44205200 1.60750200
H -6.23969300 -3.43504400 1.70409600
H -7.57496500 -3.21478500 0.55021300
H -8.83131600 1.92691600 3.90721500
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H -7.37123800 -1.70991000 -2.89417200
H -7.68936800 4.46815900 -1.82305800
H -8.83117400 -1.92709200 -3.90723000
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C 7.99458900 -2.43890700 -2.55099700
C 8.52040000 -0.12036900 -3.23315000
C 8.71812700 -2.91013500 -3.67654100
C 9.22869600 -0.63240300 -4.34849200
C 9.34568500 -2.02516600 -4.58698200
H 8.79255600 -3.99321400 -3.84296200
H 9.69775100 0.07311300 -5.04778700
C 7.89588900 1.03153900 2.32511700
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C 8.51954500 0.12044700 3.23501000
C 8.71661500 2.91020500 3.67873200
C 9.22743300 0.63250600 4.35060000
C 9.34408900 2.02526800 4.58926000
H 8.79080000 3.99328300 3.84527400
H 9.69642700 -0.07298800 5.04995600
C 8.42046700 1.38758800 -3.03489600
H 8.97881600 1.72060800 -2.13909900
H 7.37158900 1.70964000 -2.89363900
C 7.34377000 -3.44214700 -1.60609400
H 6.24060900 -3.43529200 -1.70279200
H 7.57574300 -3.21469600 -0.54881500
C 7.34274400 3.44217500 1.60796000
H 6.23956500 3.43521600 1.70443600
H 7.57495300 3.21480100 0.55071700
C 8.41998100 -1.38751300 3.03658400
H 8.97892900 -1.72037200 2.14109900

H	7.37124600	-1.70973800	2.89467300
H	8.83081500	-1.92662000	3.90832700
H	7.68826200	4.46839500	1.82388200
H	7.68942600	-4.46834600	-1.82189200
H	8.83172300	1.92670200	-3.90643600
C	10.13840600	2.55121700	5.77692900
H	9.96767600	1.93871600	6.68154500
H	9.86717700	3.59516900	6.01494200
C	-10.13981200	2.55049200	-5.77569000
H	-9.96904300	1.93807500	-6.68035600
H	-9.86889100	3.59452600	-6.01369500
C	-10.13901900	-2.55079100	5.77607100
H	-9.96878400	-1.93792900	6.68053400
H	-9.86745800	-3.59456200	6.01450000
C	10.14042900	-2.55108100	-5.77437900
H	9.96986300	-1.93867900	-6.67909300
H	9.86943800	-3.59509600	-6.01238700
H	-11.22723300	-2.53043700	5.56762100
H	-11.22804200	2.52934700	-5.56740800
H	11.22667000	2.53037000	5.56879500
H	11.22863000	-2.53004200	-5.56593100

A-Diazo 1:

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.111124 Hartree
H_corr: 0.169479 Hartree
SCF: -587.070504 Hartree
S: 116.935 Cal/Mol-Kelvin
H: -586.901025 Hartree
G: -586.95938 Hartree

Cartesian Coordinates:

C	-1.74594600	0.12223900	0.00001200
C	-0.41335100	-0.55395700	-0.00015600
O	-0.28180500	-1.80008500	-0.00000300
O	0.59171500	0.40174700	-0.00014400
C	2.08062300	-0.00847500	-0.00007300
C	2.78089400	1.36322800	-0.00018400
C	2.37380600	-0.80727600	-1.28743200
C	2.37375500	-0.80704100	1.28744600
C	-2.96573400	-0.61446900	0.00023200
N	-3.97763600	-1.25585400	0.00038900
N	-1.79991800	1.46260900	-0.00003100
N	-1.79811000	2.63904900	0.00000800
H	2.50429900	1.94531400	0.89627700

H 3.87670700 1.21909500 -0.00015700
H 2.50432300 1.94515100 -0.89675200
H 1.84416700 -1.77342300 -1.28924600
H 3.46056600 -1.00202100 -1.35131600
H 2.07574300 -0.22948700 -2.18073800
H 3.46051800 -1.00175300 1.35142000
H 2.07563600 -0.22909200 2.18063600
H 1.84413200 -1.77320000 1.28941600

Transition State TS1

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.726605 Hartree
H_corr: 2.086492 Hartree
SCF: -6737.013287 Hartree
S: 721.163 Cal/Mol-Kelvin
H: -6734.926795 Hartree
G: -6735.286682 Hartree

Cartesian Coordinates:
N 1.36358500 0.99743400 1.01618600
N -1.53025900 -1.22690900 -0.49919400
N -1.43927000 1.13133900 0.99977600
N 1.28242300 -1.29563800 -0.57661600
C 1.05478500 -2.50069600 -1.27945200
C 2.69228600 -1.16488500 -0.54703700
C 2.76134800 0.81892600 0.89736400
C 1.22580400 2.02590500 1.98281200
C -1.21922600 2.22007200 1.87794600
C -2.84296600 1.07980400 0.85611700
C -2.92600400 -1.02605900 -0.40015700
C -1.40154300 -2.46028100 -1.18007500
C -2.70860100 -3.03091000 -1.46455100
C -0.19830700 -3.07811900 -1.56199800
C 2.31117600 -3.10527500 -1.68597900
C 3.41242000 -0.15783300 0.11934000
C -3.64829400 -2.13819600 -0.99716800
C -3.56681200 0.07875100 0.18559400
C -3.47874200 2.15711700 1.59867400
C 3.47210500 1.71424100 1.79713700
C 0.02247900 2.61995900 2.40481900
C -2.47740100 2.85432900 2.23994300
C 3.32043200 -2.27345100 -1.24805100
C 2.52347700 2.44392100 2.48115700
C 0.05383800 3.67049900 3.48799100
C 0.04624000 5.58789300 5.56964200

C 0.31005500 5.04909600 3.19839000
C -0.19037100 3.27450300 4.84467500
C -0.19348600 4.23598400 5.89016000
C 0.29824400 6.01025500 4.24878600
C 4.91518400 -0.16536200 0.08468100
C 7.74769900 -0.13844000 0.05570700
C 5.61899800 0.90640500 -0.52499800
C 5.65109100 -1.22115200 0.68556900
C 7.07058400 -1.21795500 0.68330700
C 7.03838300 0.93000100 -0.55448700
C -0.24651800 -4.41362700 -2.26130200
C -0.32815800 -6.94620700 -3.51938300
C -0.51713400 -4.51018400 -3.66529900
C -0.03054700 -5.61181500 -1.50415700
C -0.06773400 -6.88375600 -2.13481000
C -0.55435400 -5.78917500 -4.29160800
C -5.06763800 0.17563400 0.13100300
C -7.88361100 0.38022600 0.03070400
C -5.86962000 -0.55794000 1.04245200
C -5.68523400 1.01136100 -0.83542800
C -7.10040200 1.11997300 -0.89552700
C -7.28596000 -0.46287200 1.00486100
C 0.74913400 6.70830100 1.31995800
N 0.57740600 5.41536000 1.84649000
C -0.66925700 1.23573900 6.30680200
N -0.42152500 1.89026400 5.09090700
C 0.43520000 -6.45900000 0.86065600
N 0.20079500 -5.46878000 -0.10456500
C -1.15221900 -3.17966800 -5.73478000
N -0.74746300 -3.30775100 -4.39318600
C -1.41491600 -1.76581500 -6.15808100
C -1.38360000 -1.43345700 -7.67049300
C -2.72621800 -1.37909000 -6.94503000
C 0.61247100 -5.91160000 2.24806100
C 0.40300800 -6.86910400 3.44627500
C 1.81459700 -6.35938800 3.16429100
C -0.86734800 -0.24532800 6.15830100
C -0.68997800 -1.13990500 7.40869900
C -2.09192200 -0.98224700 6.82409900
C 1.02032300 6.73838300 -0.15432100
C 0.70663700 8.04328700 -0.92756600
C 2.16767600 7.63153400 -0.76416100
C -2.66900000 -2.15017400 6.01688400
C -3.13539600 -0.17308900 7.59666700
C 2.88103500 7.03169000 -1.98094300
C 3.07509600 8.44623300 0.15930100

C	-3.30185900	-0.00002000	-6.60517700
C	-3.78130400	-2.44462500	-7.24721800
C	2.37910600	-5.26879600	4.08118600
C	2.86339600	-7.33060900	2.61921900
H	-0.15803500	-2.08875100	7.27984400
H	4.55401600	1.74003700	1.91044700
H	4.39483700	-2.39226400	-1.37382900
H	-4.55341100	2.32565200	1.63204800
H	2.38865100	-4.03897600	-2.24092900
H	2.66844300	3.19863900	3.25263300
H	-4.73342200	-2.20862100	-1.04102300
H	-2.55933700	3.71377900	2.90365700
H	-2.86281500	-3.98422600	-1.96744100
Co	-0.07752800	0.01369000	0.05551100
H	-0.38023000	3.90678500	6.91346400
H	0.47697600	7.05817300	4.00542300
H	0.03942900	6.33408400	6.37268500
H	8.84467100	-0.12676800	0.04896000
H	0.09915500	-7.77953700	-1.53478800
H	-0.76397100	-5.84352600	-5.36059300
H	-0.35858900	-7.92571500	-4.01083000
H	-8.97716800	0.46229500	-0.00699300
O	0.67988400	7.76753000	2.02491300
O	-0.72620200	1.83349500	7.42943300
O	0.49552800	-7.70251700	0.59380900
O	-1.29640800	-4.17053000	-6.52423100
H	-1.06126800	-0.99681300	-5.46399300
H	0.29445400	-4.87000200	2.38956000
H	0.17534400	-7.90379600	3.16896400
H	-0.54646100	-0.67151900	5.19839800
H	-0.46411900	-0.59520600	8.33153800
H	0.85256100	5.79539500	-0.68554900
H	-0.14460100	-6.48231200	4.31251000
H	-0.61570700	-2.42230800	-3.88356700
H	-3.40741500	-1.79150300	5.27420600
H	-3.18553900	-2.86222700	6.68959800
H	-1.88044300	-2.70751000	5.47637800
H	-3.91797600	0.21304800	6.91502800
H	-2.67789900	0.68276100	8.12031700
H	-3.62917000	-0.82089100	8.34695800
H	0.34299800	8.86845600	-0.30623300
H	0.22708700	7.94391300	-1.90750400
H	3.32337000	7.83711500	-2.59958100
H	2.18709100	6.45526500	-2.62124600
H	3.70031400	6.35650300	-1.66719500
H	3.48427100	9.31609000	-0.39102800

H 3.92934500 7.83513700 0.51102300
H 2.52639600 8.81534700 1.04157500
H -0.90188700 -0.49699800 -7.97397300
H -1.20019200 -2.29163400 -8.32587300
H -2.50593500 0.74211600 -6.40700900
H -3.94799200 -0.04872200 -5.70848400
H -3.91547900 0.37629300 -7.44727700
H -4.49158000 -2.54384500 -6.40330100
H -3.32095100 -3.42949700 -7.43149000
H -4.36094900 -2.15213600 -8.14475100
H 1.58660600 -4.59202600 4.45316900
H 3.13388600 -4.65645600 3.55111100
H 2.87294000 -5.72613300 4.96060400
H 3.33427300 -7.88034900 3.45736500
H 3.66273100 -6.78550000 2.08045100
H 2.41554700 -8.06344900 1.92756700
H 0.66518300 4.64288600 1.17486500
H -0.41359600 1.29412900 4.25777700
H 0.19408600 -4.50392200 0.23973100
H 5.05473600 1.72597100 -0.98634900
H 5.11591700 -2.03748600 1.18529000
H -5.05758000 1.55754100 -1.54912200
H -5.39087000 -1.19592300 1.79570100
C -0.13575400 1.06416300 -1.64856600
N 0.52679100 2.66480000 -1.56928800
N 0.93643600 3.32628500 -0.68215000
C -1.50504600 1.36685100 -2.03172100
N -2.62919000 1.66405600 -2.31491100
C 0.59633900 0.41576700 -2.84079200
O 0.07062100 -0.50593500 -3.51789000
O 1.81794100 0.98857100 -3.07293000
C 2.58822300 0.77390100 -4.41164900
C 2.97688700 -0.70739900 -4.57112800
H 3.63528000 -0.80612600 -5.45495200
H 3.52910300 -1.06355200 -3.68563100
H 2.09336600 -1.34734400 -4.71898600
C 3.81813500 1.67376800 -4.20016900
H 3.51416200 2.71799200 -4.01221400
H 4.45256800 1.64981800 -5.10495700
C 1.68719600 1.28816400 -5.55381900
H 1.37146700 2.32971400 -5.36544200
H 0.79484900 0.65407000 -5.68186600
H 4.41830700 1.32033800 -3.34438500
H 2.26066700 1.26671300 -6.49893600
C 7.77574400 2.06460200 -1.21641700
C 7.82112000 3.35305400 -0.59430400

C 8.43677500 1.85846600 -2.46655300
C 8.52472100 4.40473000 -1.23068100
C 9.12452700 2.94135600 -3.07366600
C 9.18480800 4.22176400 -2.47259300
H 8.56096700 5.38879500 -0.74366600
H 9.62374600 2.77768200 -4.03810600
C 7.84345000 -2.32775700 1.34775500
C 7.98041800 -3.59593700 0.70431700
C 8.44171400 -2.11345000 2.62970600
C 8.71696200 -4.62358500 1.34792600
C 9.16341200 -3.16834400 3.24095600
C 9.31888200 -4.43136300 2.61530300
H 8.82177300 -5.59468200 0.84572600
H 9.61270300 -3.00018000 4.22912700
C -7.76039600 2.00240200 -1.92291400
C -8.41087600 1.42221000 -3.05589200
C -7.74371400 3.42355200 -1.76530000
C -9.03248800 2.27052100 -4.00713300
C -8.38242500 4.23543500 -2.73586200
C -9.02849100 3.68044000 -3.86859900
H -9.52782300 1.81807700 -4.87689500
H -8.37488600 5.32581200 -2.60263800
C -8.13343000 -1.23690800 1.98111200
C -8.72332900 -0.57310300 3.10336000
C -8.35074700 -2.63582600 1.79100600
C -9.51528300 -1.31850000 4.01060800
C -9.15551000 -3.34504900 2.72057100
C -9.74670500 -2.70729800 3.83765300
H -9.96075600 -0.80334300 4.87269500
H -9.32387100 -4.41902700 2.56445900
C 7.14245800 3.61107800 0.74604400
H 7.44075600 4.59226100 1.15509400
H 7.40375100 2.83485700 1.48962800
C -8.43518900 -0.08696000 -3.26788100
H -9.05047500 -0.59912100 -2.50363100
H -7.41934500 -0.51989500 -3.20200600
C -7.06624400 4.07863500 -0.56755700
H -5.96543300 3.97296000 -0.61645700
H -7.39073400 3.61899500 0.38504100
C -7.74428600 -3.37746900 0.60562700
H -6.64412800 -3.46286300 0.69866300
H -7.94521000 -2.85352400 -0.34757800
C -8.50166900 0.91522000 3.34504300
H -8.96333900 1.53164400 2.55040900
H -7.42441900 1.16763200 3.35692900
C 8.29959100 -0.78054300 3.35493100

H 7.23942000 -0.47541600 3.43910900
H 8.82387800 0.03422600 2.82000000
C 7.35309800 -3.86608300 -0.65823800
H 6.25208800 -3.96504700 -0.58437700
H 7.74064000 -4.80471300 -1.09167900
H 8.72116900 -0.83999500 4.37360800
H 7.55680800 -3.04617000 -1.37176800
C 8.40729400 0.50546800 -3.16852700
H 7.38197500 0.09371200 -3.21839300
H 9.02474900 -0.24400700 -2.63728000
H 8.79694900 0.58893300 -4.19840400
H 6.03915700 3.60984700 0.65374400
H -8.93792800 1.22690000 4.31032500
H -8.15306300 -4.40033200 0.52930000
H -7.29762000 5.15755600 -0.52559500
H -8.85237700 -0.33807800 -4.25896000
C -9.67174300 4.57502400 -4.91946700
H -8.93106400 4.88492300 -5.68384500
H -10.08332700 5.49723200 -4.47032300
C 9.94342400 5.36749500 -3.12812600
H 10.29548800 5.09329200 -4.13813100
H 10.83076400 5.65285300 -2.52982500
C -10.60768200 -3.48259100 4.82578500
H -11.63985500 -3.08330100 4.85931000
H -10.20019600 -3.41576700 5.85299000
C 10.12709100 -5.53772500 3.27901200
H 9.89402600 -6.52600400 2.84448800
H 9.92990500 -5.58668700 4.36587200
H 9.31111800 6.27079800 -3.22162200
H 11.21467300 -5.36715200 3.15187000
H -10.49120800 4.05514500 -5.44765300
H -10.66904100 -4.55166400 4.55623900

Intermediate B

B[Co(P6)]:
Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.721121 Hartree
H_corr: 2.078071 Hartree
SCF: -6627.497219 Hartree
S: 715.278 Cal/Mol-Kelvin
H: -6625.419148 Hartree
G: -6625.776098 Hartree

Cartesian Coordinates:
N 1.44120000 1.50643500 -0.05851600

N -1.43309600 -0.89685300 1.11540200
N -1.36292100 1.57734800 -0.09699200
N 1.35507900 -1.03885500 1.00760400
C 1.15412700 -2.20785000 1.76846100
C 2.73318500 -1.04530300 0.69361800
C 2.81922700 1.22768600 -0.21474000
C 1.30486000 2.85507900 -0.45620600
C -1.15010700 2.90926300 -0.51421700
C -2.75418100 1.37791600 -0.23632400
C -2.82446200 -0.79190900 0.89160500
C -1.28756000 -2.04182400 1.93066800
C -2.58843100 -2.60081200 2.26156900
C -0.07545200 -2.66018300 2.28339000
C 2.40467600 -2.92966600 1.93767200
C 3.44294300 0.00051100 0.07455800
C -3.53161200 -1.85917500 1.58204000
C -3.46588800 0.23872300 0.18073100
C -3.39542500 2.58888000 -0.72676200
C 3.52736900 2.41030000 -0.67839400
C 0.09532400 3.55152700 -0.63997700
C -2.40961000 3.54186200 -0.87202800
C 3.37394800 -2.22448800 1.25515800
C 2.59979500 3.42450900 -0.79087200
C 0.13349400 5.01618400 -0.99653100
C 0.20249300 7.78934600 -1.54640300
C 0.19399600 5.47358500 -2.35430200
C 0.10150200 5.97497500 0.06977100
C 0.13810700 7.36751400 -0.20266500
C 0.22891400 6.87505300 -2.61766800
C 4.90828400 -0.18160000 -0.20266400
C 7.66280300 -0.56399900 -0.73151200
C 5.32722000 -1.10282200 -1.19807500
C 5.88686600 0.54041700 0.53017900
C 7.27180300 0.35525600 0.27872700
C 6.70471000 -1.30006700 -1.47797600
C -0.08044500 -3.88794600 3.15580400
C -0.01693900 -6.17825100 4.81145900
C -0.41864600 -5.17176000 2.61828600
C 0.28532100 -3.77743100 4.53678500
C 0.31531000 -4.92699900 5.37044800
C -0.37968100 -6.32212300 3.45681400
C -4.94858600 0.18505300 -0.05950500
C -7.73445800 0.13144700 -0.55273900
C -5.86912500 0.34233400 1.00995800
C -5.44023000 0.00606200 -1.37885100
C -6.83538400 -0.02850200 -1.64051000

C	-7.26927700	0.32225800	0.77587800
C	0.24861000	4.77023000	-4.79487600
N	0.22007200	4.51560300	-3.40835300
C	-0.02392200	6.16581000	2.61508900
N	0.02497800	5.46719600	1.40051900
C	1.00353300	-2.08987200	6.31414000
N	0.60326800	-2.47734300	5.02656100
C	-1.28902700	-6.36979300	0.55752300
N	-0.80156300	-5.24578800	1.24758500
C	-1.82131300	-6.06114300	-0.80863800
C	-1.92938500	-7.21172700	-1.83786600
C	-3.22143000	-6.62677700	-1.27140200
C	1.26693300	-0.61700600	6.44023000
C	1.26483300	0.01355300	7.85341500
C	2.59114800	-0.07246900	7.10123100
C	-0.13155500	5.26787800	3.81494400
C	0.22255900	5.84662600	5.20455900
C	-1.23708700	5.50144600	4.91449300
C	0.28541600	3.53393800	-5.63987700
C	-0.19619200	3.63770400	-7.10766900
C	1.28975100	3.40071700	-6.84832300
C	-1.81451800	4.22811500	5.54182300
C	-2.25048400	6.63446200	4.74208800
C	1.84188000	1.98946200	-7.07703300
C	2.28622400	4.52211400	-7.14730800
C	-4.04250000	-5.69146300	-2.16541800
C	-4.06521200	-7.46966700	-0.31307700
C	3.14958900	1.21225400	6.47997000
C	3.65891300	-1.05552700	7.58447700
H	0.79904600	5.21143100	5.88582400
H	4.59447100	2.44502900	-0.88841300
H	4.43557500	-2.44713700	1.16587700
H	-4.46571400	2.69057800	-0.89576600
H	2.50546400	-3.85558100	2.50184400
H	2.74909100	4.45536200	-1.10807400
H	-4.61055500	-1.99850600	1.55614000
H	-2.50091800	4.57583400	-1.20117900
H	-2.73609300	-3.46927000	2.90151700
Co	-0.00751900	0.20560100	0.33317800
H	0.11440300	8.07361000	0.62865000
H	0.27023500	7.20941100	-3.65490400
H	0.23037900	8.86302800	-1.76633800
H	8.73028500	-0.71047600	-0.93810500
H	0.59418600	-4.81587100	6.41930600
H	-0.63158600	-7.29347300	3.02975200
H	0.00891700	-7.06896100	5.45006300

H -8.81464800 0.11341400 -0.74359400
O 0.24388900 5.94313000 -5.29593500
O 0.00790500 7.43563600 2.70131700
O 1.13884900 -2.90395500 7.28351800
O -1.30448000 -7.54523800 1.05045700
H -1.57872600 -5.06219800 -1.18856200
H 0.87760100 0.00450500 5.62279900
H 1.10160500 -0.69678500 8.67088200
H 0.12225400 4.21359400 3.64040300
H 0.50086400 6.90585300 5.20125000
H 0.08750300 2.59844500 -5.10973200
H 0.77709500 0.98716900 7.97163300
H -0.75428200 -4.37214800 0.70408500
H -2.63851100 3.82147700 4.92418200
H -2.22260700 4.44706600 6.54783300
H -1.04732000 3.43839100 5.65356200
H -3.12076500 6.29732200 4.14594900
H -1.80155100 7.50650500 4.23807300
H -2.62341100 6.95610800 5.73403100
H -0.49616300 4.64154900 -7.42684200
H -0.81199200 2.81677200 -7.49175700
H 2.15134400 1.86506500 -8.13380600
H 1.08872300 1.21296200 -6.84722300
H 2.72695800 1.80354000 -6.43855300
H 2.56716400 4.49840500 -8.21877100
H 3.21156300 4.39528600 -6.55163700
H 1.85905500 5.51239100 -6.91746500
H -1.65140200 -6.98927800 -2.87398100
H -1.61714400 -8.19339100 -1.46611900
H -3.40405200 -5.11200300 -2.85748300
H -4.62484200 -4.97378500 -1.55605000
H -4.75788000 -6.27717300 -2.77576200
H -4.69940900 -6.82372300 0.32521700
H -3.43367300 -8.09116200 0.34266300
H -4.73512900 -8.13444800 -0.89319000
H 2.34385300 1.89862200 6.15708800
H 3.78085300 0.98526400 5.59925100
H 3.77744700 1.75169000 7.21557400
H 4.26153700 -0.58620100 8.38631600
H 4.34585700 -1.32859700 6.75991300
H 3.20796800 -1.98015700 7.98152400
H 0.19968600 3.51446300 -3.15249600
H -0.01720300 4.44617800 1.47306300
H 0.54712200 -1.72671700 4.33157900
H 4.57391900 -1.65447900 -1.77321300
H 5.57128500 1.23214900 1.32067900

H -4.73201000 -0.12118100 -2.20664000
H -5.49542000 0.51070900 2.02734300
C 0.00186000 -0.51952100 -1.39568000
C 0.05481700 0.45789700 -2.39953300
N 0.07879000 1.39902200 -3.15221400
C 0.06482300 -1.95808600 -1.72685300
O -0.32485000 -2.92003900 -1.00303700
O 0.62822500 -2.09220900 -3.00420500
C 0.75984000 -3.43676000 -3.73485100
C 1.52351900 -3.02600300 -5.00896900
H 1.65007800 -3.90524600 -5.66715300
H 0.96880000 -2.24710800 -5.56015800
H 2.52217300 -2.62985500 -4.75544600
C -0.66091900 -3.94061500 -4.06343600
H -1.20592500 -3.19303300 -4.66690000
H -1.23138600 -4.14197100 -3.14250200
C 1.57725500 -4.42861100 -2.87971100
H 1.02650000 -4.74393400 -1.98049500
H 2.53490300 -3.97204100 -2.57130500
H 1.80682600 -5.32389100 -3.48766900
H -0.59543700 -4.87790900 -4.64685100
C -7.35018500 -0.22705800 -3.04228700
C -7.90869400 -1.48563600 -3.42956000
C -7.28030600 0.84034300 -3.99067400
C -8.38395600 -1.65345200 -4.75404000
C -7.77408000 0.63257800 -5.30391300
C -8.33216600 -0.60539400 -5.70716900
H -8.80223000 -2.62579100 -5.04786900
H -7.72107700 1.45804500 -6.02649900
C -8.24326000 0.51616400 1.90911200
C -8.91213300 1.77073700 2.07022100
C -8.50405000 -0.54913800 2.82497600
C -9.82618200 1.93472300 3.14022200
C -9.43196400 -0.34558900 3.87857600
C -10.10634700 0.88733000 4.05404700
H -10.32950000 2.90332700 3.26329100
H -9.63154600 -1.17025000 4.57589800
C 7.14083800 -2.27118400 -2.54441800
C 7.52424800 -1.79270500 -3.83649900
C 7.17321900 -3.67249700 -2.26713500
C 7.93147900 -2.72307500 -4.82495700
C 7.59236900 -4.56973300 -3.28278900
C 7.97875000 -4.11666700 -4.56817700
H 8.21807500 -2.35018700 -5.81768000
H 7.61838600 -5.64539800 -3.06243200
C 8.30662700 1.10516000 1.07681500

C 9.04493300 0.43095400 2.09981900
C 8.55519700 2.48872500 0.81766400
C 10.01443500 1.15095500 2.84187200
C 9.53935000 3.17007500 1.57813000
C 10.28303800 2.52039600 2.59388200
H 10.57093200 0.62985500 3.63258100
H 9.72787200 4.23200700 1.37042600
C -7.98183000 -2.65296700 -2.45229600
H -8.70342700 -2.45889400 -1.63577300
H -7.00304900 -2.84270100 -1.97305400
C -6.69433700 2.19686500 -3.61708200
H -5.59874500 2.14152100 -3.46718700
H -7.12877400 2.58234200 -2.67543500
C 7.48668700 -0.30608200 -4.16911900
H 8.21804000 0.26541800 -3.56630400
H 6.49216600 0.13133900 -3.96021100
C 6.77217500 -4.21672300 -0.90131700
H 5.68957700 -4.08257700 -0.71059500
H 7.30763400 -3.69711400 -0.08450300
H -6.88365100 2.93967200 -4.41162500
H -8.29832000 -3.57716900 -2.96699900
H 7.72055000 -0.13416200 -5.23437600
H 6.99365400 -5.29566600 -0.82513900
C 7.78677200 3.24556600 -0.25929200
H 6.74749100 3.45944700 0.05946000
H 7.72420400 2.66788200 -1.19993800
C 8.79447800 -1.03818300 2.41928200
H 9.12415800 -1.69818500 1.59410000
H 7.71880900 -1.24103300 2.57909200
C -8.64497400 2.93667200 1.12558800
H -9.00663300 2.72486600 0.10132500
H -7.56299800 3.15217000 1.04264300
C -7.80803800 -1.89839500 2.69058300
H -6.74198700 -1.83467200 2.98538100
H -7.83321900 -2.26935400 1.64914800
H -8.28544100 -2.65467800 3.33812600
H -9.15085000 3.85253800 1.47820400
H 8.26909400 4.21377700 -0.48078400
H 9.34061000 -1.34119400 3.32986000
C -8.88074700 -0.79945400 -7.11405300
H -8.69186400 -1.82369500 -7.48458600
H -8.42689400 -0.08835100 -7.82727900
C 11.35560700 3.26323300 3.37848000
H 11.44669300 2.87364700 4.40866300
H 11.13749100 4.34468700 3.43923400
C 8.45380000 -5.09260800 -5.63596000

H 8.09106500 -4.80341000 -6.63952000
H 8.10573400 -6.12046500 -5.42933500
C -11.11726500 1.07904700 5.17614300
H -11.02644900 2.08066000 5.63557200
H -10.98634300 0.32481200 5.97241800
H -9.97705300 -0.63896600 -7.13915300
H 12.34780300 3.15361400 2.89691800
H 9.56055600 -5.12138300 -5.68425800
H -12.15466000 0.98590000 4.79782700

Transition State *Si*-TS1

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.734023 Hartree
H_corr: 2.08691 Hartree
SCF: -6737.013019 Hartree
S: 707.136 Cal/Mol-Kelvin
H: -6734.926109 Hartree
G: -6735.278996 Hartree

Cartesian Coordinates:
N -1.33348000 -1.14975100 -0.77236200
N 1.41778900 0.99177500 1.13913800
N 1.47338600 -1.18016100 -0.63047200
N -1.38547000 0.92809400 1.10361400
C -1.23693400 1.84228900 2.17848100
C -2.78519600 0.77661100 0.97013200
C -2.74090000 -0.99646500 -0.72890800
C -1.12373700 -2.23519800 -1.65396300
C 1.32749000 -2.30075100 -1.48213200
C 2.87055800 -1.05538800 -0.45313600
C 2.82246300 0.90219800 1.02688200
C 1.21116100 1.99878900 2.11312700
C 2.47919800 2.55381200 2.56016400
C -0.02814200 2.37314800 2.66405900
C -2.52927900 2.21261500 2.72482700
C -3.44784400 -0.08526300 0.07533500
C 3.47368300 1.88130300 1.88337900
C 3.53006800 -0.05443000 0.27937100
C 3.57412400 -2.11170300 -1.16292400
C -3.38479000 -1.96819400 -1.59753800
C 0.11936200 -2.80299600 -1.99676600
C 2.62260600 -2.88693500 -1.78823800
C -3.48566000 1.56785200 1.97004000
C -2.38830700 -2.73662600 -2.16211800
C 0.15212100 -4.00041600 -2.91255400

C 0.21037900 -6.27743500 -4.59487300
C 0.57510900 -3.87794400 -4.27648200
C -0.21944000 -5.29138600 -2.40903800
C -0.20003600 -6.43212200 -3.25469200
C 0.60320100 -5.02807100 -5.11500100
C -4.95078400 -0.07223600 0.04401300
C -7.78319200 -0.00978100 0.03468000
C -5.64483600 1.08411600 -0.40067500
C -5.69679900 -1.19692600 0.48714800
C -7.11617500 -1.17682700 0.49375700
C -7.06376500 1.12819600 -0.41781900
C -0.04723200 3.31273300 3.84570200
C 0.01728900 5.02066700 6.10311300
C -0.27449400 4.71852200 3.69316900
C 0.19053000 2.78284100 5.15717500
C 0.22464300 3.63873100 6.29018500
C -0.23381500 5.57327900 4.83135300
C 5.03457100 -0.01727000 0.29004700
C 7.85892300 0.08083600 0.32239600
C 5.76920800 -0.87497000 1.14815800
C 5.72394500 0.88979200 -0.55578800
C 7.14346700 0.94621200 -0.54836900
C 7.18845700 -0.83415100 1.17675500
C 1.73443900 -2.31687700 -5.89877500
N 0.95256600 -2.59182700 -4.76225700
C -1.01411800 -6.49549600 -0.30161500
N -0.56327600 -5.38383300 -1.02849200
C 0.66612100 0.60827300 6.40838100
N 0.37270000 1.37395100 5.27045700
C -0.73526800 6.55935800 1.99743700
N -0.53466900 5.22213000 2.38535000
C -0.99913300 6.73795400 0.53210200
C -1.64958400 8.06049800 0.06103900
C -0.19464600 7.79523500 -0.31929600
C 0.77086700 -0.86348100 6.13010500
C 1.53992700 -1.74923600 7.14029400
C 0.02691500 -1.92346700 7.02948300
C -1.22841600 -6.21143200 1.15717100
C -2.11683300 -7.17969700 1.97406900
C -0.61846100 -7.14976400 2.26847600
C 2.06855500 -0.86575400 -6.07826200
C 3.39222700 -0.52765600 -6.81607100
C 2.07144200 -0.17981000 -7.49615900
C -0.14882600 -6.43709900 3.54105900
C 0.24573800 -8.34463000 1.86102800
C 1.65542900 1.29519500 -7.51441800

C	1.63599100	-0.96788100	-8.73309300
C	0.10652300	7.37781500	-1.76271600
C	0.91068800	8.62052100	0.34182100
C	-0.50078600	-3.15512800	6.28608000
C	-0.86347300	-1.45277300	8.18083900
H	-2.81444900	-6.73821400	2.69388000
H	-4.46039500	-2.04474800	-1.74355900
H	-4.56676500	1.58832300	2.09116900
H	4.65619400	-2.22691200	-1.17033500
H	-2.66557200	2.87987500	3.57457900
H	-2.48058800	-3.56729400	-2.86000200
H	4.55207700	2.00701400	1.95810000
H	2.76339300	-3.76843900	-2.41141800
H	2.57213000	3.34428900	3.30327600
Co	0.04631800	0.03006700	0.04546200
H	-0.49592600	-7.40015800	-2.84769600
H	0.94872000	-4.92173900	-6.14361200
H	0.23057000	-7.15610100	-5.25006200
H	-8.87991100	0.01519400	0.03826200
H	0.41500900	3.20946500	7.27497000
H	-0.39346000	6.64297300	4.69107300
H	0.04860800	5.68603800	6.97375800
H	8.95550500	0.11933200	0.33400600
O	2.15227200	-3.22087600	-6.69514400
O	-1.21301600	-7.64155900	-0.81974300
O	0.82226100	1.10557100	7.57007200
O	-0.69288600	7.54012700	2.80966600
H	-1.27366100	5.82799600	-0.01247600
H	0.85282000	-1.14133400	5.07088900
H	1.92209800	-1.21526400	8.01671000
H	-1.27572700	-5.14923100	1.43192800
H	-2.50202200	-8.03424200	1.40776400
H	1.78612000	-0.21033500	-5.24749900
H	2.20088400	-2.52176300	6.73284400
H	-0.60501700	4.52450200	1.63448800
H	0.88224900	-6.05195900	3.41997300
H	-0.14817000	-7.14195800	4.39531100
H	-0.80622200	-5.58731300	3.80575600
H	1.30310600	-8.04122300	1.73387300
H	-0.10304200	-8.79180600	0.91548800
H	0.20779100	-9.11926300	2.65147700
H	3.94007700	-1.39613500	-7.19639700
H	4.00727200	0.27495900	-6.39493800
H	2.11442900	1.80918100	-8.38184200
H	1.97626700	1.82611800	-6.59847500
H	0.55662400	1.39626000	-7.60844300

H 2.10129000 -0.52981400 -9.63801900
H 0.53664300 -0.92360700 -8.86210200
H 1.93302100 -2.02703900 -8.65986100
H -2.42590100 7.99280600 -0.70902200
H -1.83728500 8.78906500 0.85687200
H -0.72079500 6.78911100 -2.20192600
H 1.02821100 6.76702800 -1.81503700
H 0.25815500 8.27413600 -2.39575700
H 1.87457800 8.07566100 0.32171100
H 0.66702600 8.85683000 1.39105500
H 1.04757700 9.57151400 -0.20926400
H 0.17895200 -3.46735600 5.47061000
H -1.49790600 -2.95516100 5.84773600
H -0.60340300 -4.00816900 6.98498000
H -0.92276800 -2.24374200 8.95369100
H -1.89226900 -1.24737700 7.82621300
H -0.46760900 -0.53578000 8.64784700
H 0.67860400 -1.77523400 -4.19640600
H -0.45989200 -4.51472400 -0.49618800
H 0.28079600 0.85257700 4.39338800
H -5.07348300 1.95675400 -0.73994500
H -5.16977800 -2.08438500 0.85803600
H 5.14835000 1.54606700 -1.21906400
H 5.23668900 -1.57817400 1.80069700
C 0.17536300 1.27239200 -1.51817200
N -0.42855500 2.87648400 -1.25328800
N -0.88857100 3.41957900 -0.31209600
C 1.56298400 1.55543000 -1.84731500
N 2.70412500 1.83031000 -2.08132800
C -0.57003600 0.81305000 -2.78821100
O -0.06059600 0.00019400 -3.60419800
O -1.78896600 1.42296500 -2.91692400
C -2.56331300 1.44483400 -4.26911000
C -1.66156700 2.15522600 -5.29928500
H -2.22207900 2.27562200 -6.24485200
H -1.37099800 3.15847900 -4.94024600
H -0.75286000 1.56912800 -5.51171100
C -3.79542200 2.28903500 -3.90051900
H -4.39416800 1.78619700 -3.12207100
H -4.42944600 2.42583100 -4.79548600
C -2.94910100 0.01526200 -4.69284600
H -3.50329000 -0.49567700 -3.88808700
H -2.06313300 -0.58521100 -4.95039900
H -3.49401700 3.28345700 -3.52845300
H -3.60585700 0.07791600 -5.58121700
C -7.78969200 2.35818300 -0.89669200

C -8.46992900 2.34833900 -2.15427000
C -7.80250500 3.54224500 -0.09317500
C -9.14483000 3.51867900 -2.58605200
C -8.49446900 4.68789500 -0.55920900
C -9.17529500 4.69846200 -1.80235300
H -9.65827400 3.50604600 -3.55701400
H -8.50379400 5.59163000 0.06498400
C -7.90000300 -2.36246600 0.99410100
C -8.47738900 -2.33657600 2.30129100
C -8.06861700 -3.51583500 0.16581100
C -9.21030000 -3.46268700 2.75602400
C -8.81410000 -4.61694700 0.65542200
C -9.39561900 -4.61162400 1.94841900
H -9.64384000 -3.44066000 3.76483000
H -8.94213400 -5.49878700 0.01310600
C 7.87859200 1.90549800 -1.44831400
C 8.43902600 3.10517900 -0.91267000
C 8.01921800 1.61567100 -2.84226100
C 9.12998300 3.99303700 -1.77751400
C 8.72076700 2.52607900 -3.67021300
C 9.28335300 3.72343800 -3.15902200
H 9.55421900 4.91624800 -1.36049200
H 8.83104800 2.29396200 -4.73841500
C 7.96289100 -1.74157600 2.09739200
C 8.58045600 -2.92464600 1.58656400
C 8.07825900 -1.42250500 3.48681300
C 9.29913600 -3.76793300 2.47236600
C 8.80867500 -2.28945100 4.33730800
C 9.42993000 -3.46730900 3.85052900
H 9.76533800 -4.67989000 2.07575800
H 8.89590900 -2.03753300 5.40302800
C -8.47138100 1.11294400 -3.04766300
H -9.10214000 0.30585700 -2.62807300
H -7.45508200 0.69269800 -3.16497000
C 8.29516600 3.45536300 0.56362400
H 8.84790000 2.74605700 1.20888700
H 7.23706700 3.42096800 0.88511100
C 7.43752900 0.34278900 -3.44457700
H 6.33100000 0.35623900 -3.43360800
H 7.74968000 -0.55426400 -2.87723400
C 7.43835600 -0.16491700 4.06235500
H 6.33304600 -0.21573900 4.03052000
H 7.73056300 0.73540400 3.48964400
C 8.46726400 -3.29987800 0.11413600
H 9.00051500 -2.57738700 -0.53286800
H 7.41316600 -3.30787900 -0.22170800

C	-7.46290000	-3.58144100	-1.23116100
H	-6.36138900	-3.69176500	-1.18933200
H	-7.67372100	-2.66359000	-1.81104800
C	-8.30625700	-1.13141300	3.21846800
H	-8.83831800	-0.24246200	2.82882200
H	-7.24229700	-0.84601200	3.32046500
H	-7.86076800	-4.44418000	-1.79360400
H	-8.70282000	-1.34499900	4.22650700
C	-7.09851200	3.59195600	1.25775600
H	-5.99749800	3.61987000	1.14384100
H	-7.33698600	2.70368900	1.87224500
H	-7.39560600	4.49195000	1.82412800
H	-8.86381800	1.35496600	-4.05111700
H	8.89490700	-4.30049000	-0.07322900
H	7.73776400	-0.01545900	5.11455200
H	7.76324500	0.21719500	-4.49218700
H	8.68261700	4.46901800	0.76775100
C	10.02189100	4.69095900	-4.07410400
H	9.33660900	5.14081900	-4.81891400
H	10.82462600	4.17906900	-4.63847400
C	-10.20973300	-5.79898200	2.44377600
H	-10.32916000	-5.77784600	3.54162500
H	-9.73337500	-6.75861000	2.17022700
C	10.23164700	-4.36865900	4.77972700
H	10.35607300	-5.38038600	4.35406300
H	9.74317300	-4.47027600	5.76647700
C	-9.93568300	5.93250800	-2.26778700
H	-10.94760800	5.96892300	-1.81739500
H	-10.06299400	5.94011400	-3.36516200
H	10.48286500	5.51550400	-3.50209900
H	-11.22472600	-5.79970700	1.99917900
H	-9.41498500	6.86310400	-1.97671200
H	11.24497900	-3.95670900	4.95742700

Intermediate *Si*-B

***Si*-B**$_{[Co(P6)]:}$

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.731341 Hartree
H_corr: 2.078493 Hartree
SCF: -6627.498319 Hartree
S: 695.644 Cal/Mol-Kelvin
H: -6625.419826 Hartree
G: -6625.766978 Hartree

Cartesian Coordinates:

N -1.38354600 -1.40346700 0.14281700
N 1.32476500 1.43396900 0.68274800
N 1.39344100 -1.32601100 0.43681500
N -1.47503000 1.32767700 0.64165900
C -1.35276900 2.68162300 1.03256800
C -2.86357200 1.13689800 0.46319400
C -2.75784300 -1.23211200 -0.15556400
C -1.15377300 -2.78447500 -0.01711300
C 1.24507800 -2.73278200 0.48765900
C 2.78857800 -1.11541300 0.50856700
C 2.72658900 1.33195400 0.52052800
C 1.09398400 2.81121800 0.89272700
C 2.33951200 3.55743700 0.83693500
C -0.15459000 3.41163100 1.13765800
C -2.66341000 3.28681600 1.20033600
C -3.48498300 -0.04039600 0.00622900
C 3.34398800 2.64776400 0.58045100
C 3.44648800 0.12751000 0.44860700
C 3.48505600 -2.37844600 0.69615900
C -3.35106400 -2.49904100 -0.55027200
C 0.06387700 -3.44877500 0.22848200
C 2.53107400 -3.37326600 0.70590400
C -3.59488700 2.33846700 0.83367700
C -2.36548700 -3.45988800 -0.44915400
C 0.11017700 -4.94787200 0.11795300
C 0.16198300 -7.77167400 -0.09722100
C 0.78372000 -5.57575400 -0.98000900
C -0.52588400 -5.76818000 1.10949200
C -0.50148500 -7.18363400 0.99987100
C 0.80387300 -6.99362400 -1.08165000
C -4.96170500 -0.02164600 -0.26942300
C -7.74399500 0.05945200 -0.78134100
C -5.47154800 0.75061700 -1.34625500
C -5.86333600 -0.75375800 0.54759900
C -7.26190600 -0.71626700 0.30656600
C -6.86399200 0.79484600 -1.61965200
C -0.20670900 4.85971500 1.55632900
C -0.33133600 7.53527300 2.46784000
C -0.40529900 5.92602100 0.61792600
C -0.05978600 5.16710600 2.95060800
C -0.12217800 6.50822200 3.41082600
C -0.47199500 7.26973100 1.09184700
C 4.94632200 0.15840100 0.36649300
C 7.77078300 0.22215700 0.18429400
C 5.72511300 0.64473100 1.44969000
C 5.60108100 -0.30228200 -0.80596900

C	7.01561000	-0.26330200	-0.91643400
C	7.14251800	0.67316600	1.37575500
C	2.55771200	-5.11660000	-2.70491700
N	1.41643400	-4.75695400	-1.96561200
C	-1.90250400	-5.65647200	3.25732800
N	-1.13851400	-5.10941100	2.21513900
C	0.34180900	4.08550800	5.23110800
N	0.13858400	4.07279900	3.84376300
C	-0.80168900	6.51502800	-1.81954800
N	-0.51262500	5.62084400	-0.76915700
C	-0.79801400	5.88157300	-3.17737800
C	-1.57625800	6.58652400	-4.31496600
C	-0.05158700	6.55544500	-4.39196200
C	0.53405600	2.71578700	5.81747600
C	1.22066300	2.59595600	7.19915500
C	-0.26263000	2.24717200	7.09354700
C	-2.39736900	-4.63429400	4.23907900
C	-3.61428200	-4.99820700	5.12508800
C	-2.25070700	-4.84663000	5.79466900
C	3.12723600	-4.01825200	-3.55409700
C	4.66190400	-4.05871600	-3.80078200
C	3.73083100	-4.29891000	-4.98350200
C	-1.98935000	-3.57351700	6.60657900
C	-1.53881100	-6.09176200	6.32669300
C	3.59183900	-3.16109300	-6.00094600
C	3.63375700	-5.69668000	-5.59852800
C	0.59643700	5.57541200	-5.37625200
C	0.73344300	7.85247200	-4.18890500
C	-0.65342700	0.76556700	7.11009700
C	-1.29586800	3.18039600	7.72720700
H	-4.37623300	-4.22622700	5.27744900
H	-4.38889900	-2.62386700	-0.85323900
H	-4.67973300	2.42352700	0.82415400
H	4.56197200	-2.47164900	0.82225700
H	-2.82387600	4.31037200	1.53517600
H	-2.43247500	-4.52827200	-0.64849400
H	4.40915100	2.83374700	0.45859000
H	2.66776500	-4.44691800	0.82464800
H	2.41082300	4.63620600	0.96757100
Co	-0.02105000	0.02352700	0.29201700
H	-0.99458400	-7.78361700	1.76617700
H	1.33297800	-7.45867000	-1.91342300
H	0.18054900	-8.86411000	-0.18490500
H	-8.82296500	0.09353900	-0.97709600
H	-0.00877000	6.71095700	4.47676600
H	-0.63990300	8.06933800	0.36958700

H -0.38461100 8.57386500 2.81490700
H 8.86524200 0.24969900 0.11288300
O 3.09373600 -6.27122400 -2.63175300
O -2.15318800 -6.90020900 3.36622700
O 0.35847800 5.14782300 5.93293000
O -1.04537600 7.75488200 -1.64419000
H -0.77546900 4.78853000 -3.18371300
H 0.74694200 1.91773600 5.09350100
H 1.48330100 3.55222300 7.66372600
H -2.32365300 -3.58845400 3.91232600
H -3.99586700 -6.01468100 4.98179300
H 2.66755600 -3.03181200 -3.41993600
H 1.95277800 1.79180500 7.33004000
H -0.36341900 4.64047500 -1.06436900
H -0.90797500 -3.33789800 6.63652600
H -2.33484200 -3.70879700 7.65004000
H -2.52101100 -2.69904200 6.18608100
H -0.44582000 -5.92512800 6.38897900
H -1.72009600 -6.96734200 5.68150900
H -1.90506100 -6.32380400 7.34571000
H 5.16720300 -4.93063200 -3.37260800
H 5.21389700 -3.11466100 -3.73733900
H 4.41659600 -3.21332100 -6.73846900
H 3.63380000 -2.16696600 -5.51760200
H 2.63758800 -3.23560700 -6.55608300
H 4.44896500 -5.83746100 -6.33531100
H 2.67076800 -5.82538700 -6.13065800
H 3.71237200 -6.48161100 -4.82886300
H -2.16136700 5.95221700 -4.99017400
H -2.04504600 7.53574400 -4.03448700
H -0.00030000 4.65090200 -5.48710800
H 1.61003400 5.28752100 -5.03664700
H 0.69226100 6.04317300 -6.37626600
H 1.76744800 7.63736700 -3.85472200
H 0.25403600 8.50084200 -3.43678200
H 0.79567600 8.40778900 -5.14569000
H 0.12558200 0.12906800 6.64908300
H -1.60166200 0.60184600 6.56218300
H -0.80013100 0.41932100 8.15184000
H -1.41236600 2.93526700 8.80091100
H -2.28446400 3.06073900 7.24249500
H -0.99298200 4.23711600 7.63999500
H 1.09008300 -3.78252300 -2.05939500
H -1.01968300 -4.09215000 2.23575000
H 0.14365000 3.14802200 3.40327900
H -4.77704500 1.30759700 -1.98662300

H -5.47757400 -1.33477400 1.39418200
H 5.00325400 -0.68249100 -1.64308800
H 5.22627100 0.99468400 2.36164200
C 0.00633100 0.31172500 -1.56472300
C -0.10825500 1.66318800 -1.91285600
N -0.19208500 2.85551400 -2.06803500
C -0.03681800 -0.74723800 -2.59414800
O 0.42491500 -1.92033900 -2.48887800
O -0.68689300 -0.24936000 -3.72930800
C -1.00150200 -1.11556300 -4.96082100
C -1.76875200 -0.11865900 -5.85085700
H -2.06270000 -0.61186300 -6.79575900
H -2.68001300 0.23838700 -5.34043200
H -1.13765000 0.75508500 -6.08936100
C -1.89246100 -2.29987700 -4.52886300
H -2.78140400 -1.93479500 -3.98404600
H -1.34300800 -3.00464300 -3.88473400
C 0.32049800 -1.56424600 -5.61367800
H 0.86684500 -2.26735000 -4.96639900
H 0.96445200 -0.69205900 -5.82599500
H 0.09889300 -2.06992600 -6.57252800
H -2.23667900 -2.84147900 -5.42994500
C 7.70195200 -0.71198600 -2.18036800
C 7.72929600 0.15076300 -3.31964800
C 8.33300500 -1.99384900 -2.24357200
C 8.38868000 -0.28161400 -4.49911700
C 8.97727300 -2.38870300 -3.44234100
C 9.02200900 -1.54592300 -4.58182800
H 8.40965900 0.38715500 -5.37005900
H 9.45266500 -3.37799600 -3.48702600
C 7.96329000 1.17005500 2.53762500
C 8.18164600 0.32741300 3.67090000
C 8.52807200 2.48367800 2.50962000
C 8.96105800 0.81103000 4.75290400
C 9.29538700 2.93051400 3.61393900
C 9.52884000 2.10868100 4.74533700
H 9.12773200 0.15777700 5.61992300
H 9.71756900 3.94430800 3.59092500
C -7.39504700 1.60336000 -2.77416800
C -7.88285900 0.94352700 -3.94674700
C -7.41223300 3.03091900 -2.70526300
C -8.37365100 1.72062500 -5.02475100
C -7.91907100 3.77086600 -3.80466400
C -8.40564900 3.13736700 -4.97373900
H -8.73724700 1.20777300 -5.92571100
H -7.93280500 4.86724400 -3.74327400

C -8.21661200 -1.47365600 1.19263400
C -8.99240000 -0.77464700 2.17066700
C -8.35223700 -2.88995100 1.05988300
C -9.88606100 -1.50338500 2.99406800
C -9.26263600 -3.58084600 1.90023300
C -10.04178200 -2.90746100 2.87253400
H -10.47254200 -0.96188100 3.74873100
H -9.36386300 -4.66891400 1.79050100
C 7.07449500 1.52652500 -3.28449400
H 7.42766200 2.12170100 -2.42128900
H 5.97415700 1.45519400 -3.18921400
C 8.30902100 -2.94448800 -1.05296500
H 7.27548800 -3.13335400 -0.70597300
H 8.86541900 -2.53269700 -0.18953300
C -7.86669300 -0.57629700 -4.06578100
H -8.61224100 -1.04720500 -3.39662000
H -6.88143900 -0.99583100 -3.78879100
C -6.90857500 3.77511700 -1.47398000
H -5.80417500 3.74484800 -1.40150200
H -7.30583400 3.33330300 -0.54107200
H 8.76311900 -3.91605000 -1.31494100
H 7.29645300 2.09330400 -4.20573900
H -8.09849400 -0.89154200 -5.09843700
H -7.20789700 4.83732500 -1.50694100
C -7.54364300 -3.67036300 0.03022700
H -6.47261500 -3.71965000 0.30778500
H -7.59672100 -3.20099100 -0.96999900
C -8.86103300 0.73264600 2.35427400
H -9.24541700 1.28684100 1.47674600
H -7.80473400 1.03496200 2.48318600
C 8.30758800 3.41363400 1.32252700
H 7.23269000 3.51962800 1.08273600
H 8.80130200 3.03315200 0.40792700
C 7.60069500 -1.08033800 3.73461500
H 7.85048600 -1.66464200 2.82905000
H 6.49612100 -1.06455000 3.80718100
H 8.71238900 4.41959300 1.53006700
H 7.98739600 -1.62627800 4.61297200
H -9.42656600 1.07181300 3.23991500
H -7.91148700 -4.70780900 -0.05585900
C -8.96364300 3.94836800 -6.13523700
H -8.59917700 3.56639500 -7.10712000
H -8.67908600 5.01272800 -6.05894100
C 10.38151800 2.60119900 5.90659000
H 10.19533100 2.01371300 6.82327600
H 10.17912100 3.66393800 6.13465800

C	9.74708000	-1.98258600	-5.84738800
H	9.44455900	-1.37392200	-6.71804500
H	9.54383200	-3.04340000	-6.08435300
C	-11.03237400	-3.66258100	3.74805200
H	-11.02693500	-3.28192100	4.78613200
H	-10.80388700	-4.74279200	3.77899400
H	11.46129900	2.51687500	5.67193700
H	10.84437700	-1.87788800	-5.73397100
H	-10.07037000	3.90039100	-6.16008600
H	-12.06652500	-3.55283100	3.36525000

B[Co(P6)]-N2:
Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: -0.014698 Hartree
H_corr: 0.008394 Hartree
SCF: -109.5610963 Harree
S: 46.273 cal/mol-kelvin
H: -109.5527023 Hartree
G: -109.5757943 Hartree

Cartesian Coordinates:

N	0.00000	0.00000	0.57309
N	0.00000	0.00000	-0.57309

B[Co(P6)]-Enyne:
Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.226592 Hartree
H_corr: 0.297924 Hartree
SCF: -771.037213 Hartree
S: 142.939 Cal/Mol-Kelvin
H: -770.739289 Hartree
G: -770.810621 Hartree

Cartesian Coordinates:

C	0.59396100	3.67466500	0.67044700
C	0.32605300	2.30901900	0.92379000
C	0.79217000	1.29427200	0.03988900
C	1.55085800	1.69040400	-1.09991800
C	1.81138700	3.05437600	-1.35898600
C	1.33316200	4.05388900	-0.47533100
H	0.23468100	4.43881000	1.37003800
H	-0.21182500	2.02048900	1.83506800
H	1.92436600	0.92254300	-1.78732200
H	2.38645400	3.33848800	-2.24818500

H 1.54164200 5.11185700 -0.67336000
C 0.49733500 -0.15464700 0.29091900
C 1.62222600 -1.13921400 0.14768500
C 2.95122200 -0.78998700 0.52385900
C 1.38832500 -2.45237300 -0.35509100
C 4.00436100 -1.72739100 0.42409600
H 3.15384000 0.21605400 0.90924000
C 2.44078700 -3.38934100 -0.45542000
H 0.38205400 -2.72631400 -0.69378900
C 3.75451700 -3.03329100 -0.06289100
H 5.01770100 -1.44061500 0.72959300
H 2.23959700 -4.39192500 -0.85128400
H 4.57186300 -3.75952400 -0.14384000
C -0.75230900 -0.59951500 0.64460000
H -0.89184700 -1.66245900 0.88292100
C -2.02776900 0.19856000 0.72239200
H -1.95406900 1.15854500 0.16882400
H -2.30471300 0.42628200 1.78027800
O -3.08328800 -0.66405800 0.13128800
C -4.40931100 -0.01712700 0.23074400
H -4.40210800 0.95333900 -0.31501400
H -4.64970000 0.19419200 1.29805300
C -5.43356100 -0.90153600 -0.34295500
C -6.32371100 -1.61176900 -0.81464900
H -7.08986100 -2.24125700 -1.23060600

Transition State TS2

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.974585 Hartree
H_corr: 2.376876 Hartree
SCF: -7398.536398 Hartree
S: 806.135 Cal/Mol-Kelvin
H: -7396.159522 Hartree
G: -7396.561813 Hartree

Cartesian Coordinates:
N 1.84198700 -0.52335300 -1.28574000
N -0.16920900 2.11330300 0.88261600
N -0.80627600 0.43179900 -1.25695700
N 2.44466900 1.08002600 0.92365700
C 2.60610100 2.01109700 1.97384500
C 3.71467900 0.46453400 0.80450100
C 3.18691500 -0.93961100 -1.13640000
C 1.37895900 -1.25099600 -2.40615600
C -0.93844200 -0.43707400 -2.36600600

C -2.07653200 1.04430300 -1.14162100
C -1.51435400 2.52765000 0.72884100
C 0.32133900 2.90944900 1.94485600
C -0.71036700 3.80238100 2.44258700
C 1.62450900 2.88691900 2.46892400
C 3.96376700 1.98049600 2.49020700
C 4.08587500 -0.49642800 -0.15180900
C -1.84560300 3.55774500 1.70104700
C -2.43330000 2.04563900 -0.22121300
C -2.97772900 0.55403300 -2.17298500
C 3.54549800 -1.90177600 -2.16667200
C 0.07590400 -1.22987200 -2.93288300
C -2.27892500 -0.36574100 -2.92328000
C 4.64840700 1.02795300 1.76730800
C 2.43342100 -2.08272700 -2.95940800
C -0.21868900 -1.97813000 -4.21120300
C -0.80205100 -3.24527400 -6.67505600
C -0.67385500 -3.33702900 -4.22744900
C -0.04828300 -1.28037200 -5.45451600
C -0.33898200 -1.91395500 -6.69104100
C -0.97337900 -3.96099600 -5.47435900
C 5.49280400 -1.02812500 -0.14910200
C 8.14230700 -2.02964700 -0.15056500
C 5.94250900 -1.87299000 0.89850700
C 6.38940200 -0.68897200 -1.19657600
C 7.72075800 -1.18168700 -1.20959900
C 7.26628200 -2.38561400 0.90908400
C 1.99645200 3.85724600 3.56118700
C 2.71516400 5.70859800 5.57495100
C 1.65538300 3.60023400 4.92796500
C 2.69106700 5.06542500 3.22583200
C 3.05541700 5.99438400 4.23653800
C 2.02325500 4.53527900 5.93738600
C -3.80987900 2.64779100 -0.28123700
C -6.38849300 3.80836600 -0.41158900
C -3.96648700 4.01663800 -0.63140000
C -4.96029600 1.86389500 -0.00164400
C -6.25878400 2.43812000 -0.06011100
C -5.25314200 4.61011300 -0.70364700
C -1.30519100 -5.33796000 -2.80248000
N -0.79161800 -4.04471800 -2.99604400
C 0.68252100 0.96403600 -6.43474500
N 0.41706500 0.06583700 -5.39113000
C 3.62737800 6.38418200 1.24873600
N 2.98028200 5.29411100 1.84879300
C 0.35114900 2.04927800 6.45354700

N	0.94127800	2.40434900	5.22814700
C	-0.46558500	0.79355600	6.39234200
C	-0.73794000	0.02330200	7.70755100
C	-1.90924100	0.72624200	7.02493100
C	3.73811600	6.26535300	-0.24431000
C	3.98718500	7.55171800	-1.06811700
C	5.10437400	6.51320500	-0.99008400
C	1.16758400	2.30354800	-5.95823300
C	1.90728700	3.21828500	-6.96318100
C	0.52235800	3.64376700	-6.47933800
C	-1.14642600	-5.85532400	-1.40498900
C	-2.02436900	-7.04353000	-0.94437500
C	-0.52960500	-7.28411300	-1.13884200
C	0.43830000	4.77318400	-5.44696000
C	-0.65699000	3.58857700	-7.45212700
C	0.35102000	-7.38779300	0.11094000
C	-0.06236200	-8.14868200	-2.31097200
C	-2.91419200	-0.13988100	6.25761900
C	-2.51956400	1.96721500	7.67853600
C	5.34987300	5.62903300	-2.21756800
C	6.36278900	6.83235400	-0.18087900
H	2.79057300	3.75594000	-6.60175200
H	4.52175600	-2.37451100	-2.25177900
H	5.69480500	0.74020300	1.84839100
H	-4.00373200	0.89084700	-2.30193300
H	4.32669400	2.62177500	3.29188000
H	2.31102000	-2.72420100	-3.83075500
H	-2.82775600	4.01557800	1.79654200
H	-2.61250400	-0.93684900	-3.78814500
H	-0.56582600	4.50837200	3.25867200
Co	0.76689100	0.63417200	-0.04940000
H	-0.20033100	-1.35753900	-7.61926300
H	-1.33977500	-4.98797000	-5.46996400
H	-1.03448100	-3.73988400	-7.62546000
H	9.16685700	-2.42198900	-0.15352400
H	3.58314200	6.90656800	3.95407500
H	1.75274500	4.32469000	6.97269200
H	2.99540900	6.42235500	6.35844600
H	-7.38616400	4.26379100	-0.44235800
O	-1.85287300	-6.03000300	-3.72860600
O	0.52499700	0.68242000	-7.66645300
O	4.08339900	7.37839500	1.90056300
O	0.47826400	2.73252100	7.52259700
H	-0.33944700	0.20312400	5.47850600
H	3.09826700	5.50193700	-0.70672700
H	4.10165500	8.46225900	-0.47061600

H 1.51117100 2.33819000 -4.91566900
H 1.98501100 2.81300400 -7.97762500
H -0.88050300 -5.10227100 -0.65796600
H 3.42729800 7.66848200 -2.00229900
H 0.82872100 1.72340600 4.46161300
H -0.47545100 4.67841700 -4.82899600
H 0.40137500 5.75584500 -5.95638200
H 1.31293800 4.77643300 -4.76901000
H -1.61550700 3.50190400 -6.90429400
H -0.57368700 2.73223300 -8.14201900
H -0.69152200 4.51954100 -8.05099400
H -2.70023300 -7.44815600 -1.70504800
H -2.43140800 -7.00442100 0.07235100
H 0.37388700 -8.43313600 0.47768700
H -0.02390400 -6.74718900 0.93086400
H 1.39148200 -7.08256000 -0.11234700
H -0.10576100 -9.21892200 -2.02807400
H 0.98542000 -7.91224000 -2.58149500
H -0.69387700 -7.99565300 -3.20193800
H -0.67923400 -1.07053800 7.67573500
H -0.32604300 0.49136100 8.60793400
H -2.43194000 -1.02122100 5.79454000
H -3.40562700 0.44117900 5.45366700
H -3.70480400 -0.50669500 6.94156200
H -3.03392100 2.59516200 6.92506900
H -1.75029300 2.58138600 8.17488100
H -3.27020600 1.66077900 8.43339800
H 4.41517500 5.42834000 -2.77476000
H 5.79117000 4.65699600 -1.92384400
H 6.05641000 6.12515400 -2.91130600
H 7.07457400 7.40410400 -0.80780100
H 6.86877400 5.90248400 0.14437800
H 6.12682000 7.43028300 0.71518100
H -0.47516200 -3.57065000 -2.12914400
H 0.57253700 0.42765300 -4.44557000
H 2.67371400 4.55285400 1.21156300
H 5.24914800 -2.15201700 1.70095900
H 6.05362200 -0.02222900 -2.00015100
H -4.85279000 0.80513100 0.27085100
H -3.08202300 4.62089200 -0.86809700
C 0.25944300 -0.81162900 1.14213900
C 0.06239400 -2.00883100 0.40986600
N -0.22020200 -2.94112900 -0.28873100
C 0.88116500 -0.90347300 2.50068300
O 0.78065600 -0.01769200 3.39928400
O 1.52011300 -2.12640500 2.66315000

C 2.09289000 -2.60705800 4.01558500
C 3.15852300 -1.61184400 4.51838800
H 3.67606800 -2.05127200 5.39167700
H 3.91165500 -1.41872000 3.73344500
H 2.70911700 -0.65280200 4.81846900
C 2.71111700 -3.96136300 3.62027800
H 1.94421600 -4.62705000 3.18773700
H 3.14348500 -4.44936900 4.51287300
C 0.91914700 -2.78458300 5.00085700
H 0.14653300 -3.44502100 4.56844600
H 0.46532100 -1.81515000 5.26010000
H 3.51287200 -3.82432200 2.87403800
H 1.29323200 -3.25125800 5.93134500
C 7.72731600 -3.29587200 2.01800400
C 7.77794200 -4.70951800 1.80972500
C 8.11367900 -2.75024800 3.28125500
C 8.20983300 -5.54957500 2.86695800
C 8.54503000 -3.62486800 4.31081700
C 8.60356200 -5.02833200 4.12486200
H 8.23867900 -6.63528400 2.70301300
H 8.84371300 -3.19856000 5.27809000
C 8.66493600 -0.81284000 -2.32452000
C 9.68619400 0.16345500 -2.10695300
C 8.54092900 -1.43654800 -3.60556700
C 10.56084200 0.49920700 -3.17162500
C 9.43963300 -1.07702500 -4.64076500
C 10.45941500 -0.11211800 -4.44569300
H 11.33743200 1.25672200 -3.00022600
H 9.34012000 -1.56242000 -5.62112900
C -7.47763100 1.60804900 0.24981300
C -7.72331100 1.16037600 1.58554900
C -8.39928100 1.26453300 -0.79090300
C -8.88693700 0.39457100 1.85724000
C -9.54210500 0.48692300 -0.47837400
C -9.81186900 0.04812600 0.84263600
H -9.07332500 0.06459100 2.88814500
H -10.23756600 0.21857800 -1.28548100
C -5.41072700 6.06050100 -1.08248500
C -5.80207900 6.41516300 -2.41090900
C -5.16768700 7.08680700 -0.11726200
C -5.94515900 7.78484700 -2.74883400
C -5.32703100 8.44426900 -0.49409600
C -5.71843100 8.81652600 -1.80425000
H -6.23854000 8.05029700 -3.77355500
H -5.14119800 9.22736500 0.25346500
C 7.36602700 -5.32669000 0.47869800

H 7.35608400 -6.42897200 0.54178300
H 8.06123000 -5.04186700 -0.33413100
C -6.76441100 1.48509400 2.72376700
H -6.47374800 2.55187800 2.72243200
H -5.83291500 0.89449100 2.63732400
C -8.17098800 1.69834100 -2.23464400
H -7.12195100 1.54554700 -2.54801300
H -8.39245100 2.77385400 -2.37732600
C -4.73980800 6.74794700 1.30532300
H -3.70113900 6.36405700 1.33340900
H -5.38477200 5.96755700 1.75012100
C -6.04701900 5.34898700 -3.47181000
H -6.93521500 4.73229900 -3.23458500
H -5.19158600 4.65214500 -3.55139800
C 7.46483300 -2.48118500 -3.87713700
H 6.46013400 -2.02003100 -3.94682900
H 7.41818500 -3.23736500 -3.07152800
C 9.83993700 0.86176600 -0.76097700
H 8.88311400 1.29914900 -0.41883800
H 10.58675200 1.67274000 -0.82169400
H 7.65518300 -3.00478200 -4.83042400
H 10.16919500 0.15905600 0.02825300
C 8.07357400 -1.24872500 3.53908500
H 7.03337200 -0.87091300 3.58548800
H 8.58354800 -0.68424300 2.73622500
H 8.56131900 -0.99944300 4.49774600
H 6.35904800 -4.99064700 0.16721000
H -6.21091600 5.80830600 -4.46247200
H -4.78147200 7.64071300 1.95368300
H -8.82318900 1.13117300 -2.92208300
H -7.22252900 1.25308600 3.70167500
C -11.06454600 -0.75838400 1.15678300
H -11.02943000 -1.17959400 2.17714500
H -11.19479000 -1.59653600 0.44654900
C 9.09914600 -5.94676100 5.23347700
H 8.60552400 -6.93474300 5.19226600
H 8.91430400 -5.51259900 6.23262500
C -5.91089600 10.27982900 -2.17838300
H -5.75253700 10.44539700 -3.25930600
H -5.21250600 10.93417300 -1.62561500
C 11.42883800 0.23855900 -5.56598500
H 11.88986400 1.22984600 -5.40718400
H 10.92434500 0.24930000 -6.54953000
H 10.19019600 -6.12120900 5.14696100
H 12.25067600 -0.50238100 -5.62784700
H -11.97272800 -0.12785300 1.08700100

H	-6.93846900	10.61989100	-1.93974300
C	-1.78785800	-0.48238200	1.96335500
C	-2.72231200	-1.19105600	1.51028200
C	-3.65231600	-2.08339300	0.81011900
H	-3.76014900	-3.04595300	1.35464500
H	-3.27803000	-2.30260900	-0.21543700
O	-4.96699100	-1.39731200	0.72556500
C	-6.01961000	-2.23727000	0.08374200
H	-5.70692300	-2.53810800	-0.93517700
H	-6.86560600	-1.52824100	0.00278600
C	-6.40795400	-3.41971800	0.94095200
C	-6.74145000	-4.68009200	0.51078700
C	-7.27612700	-5.70131900	1.47146700
C	-7.98724300	-5.32366000	2.64928400
C	-7.07859900	-7.09153500	1.22582900
C	-8.45520000	-6.29655200	3.55953500
H	-8.20087100	-4.26443400	2.83556200
C	-7.54609100	-8.06505000	2.13710000
H	-6.54827700	-7.40521300	0.31960700
C	-8.23368200	-7.67381100	3.31119000
H	-9.00600700	-5.98333400	4.45461100
H	-7.37500300	-9.12821200	1.93048400
H	-8.60259200	-8.42915900	4.01496700
C	-6.61272800	-5.09528400	-0.93312600
C	-5.34260300	-5.18100100	-1.56691100
C	-7.77192200	-5.44004200	-1.68274300
C	-5.22862200	-5.58704200	-2.91885600
H	-4.43655200	-4.95541900	-0.99085600
C	-7.66380100	-5.83219900	-3.03712100
H	-8.75610700	-5.39505800	-1.20082400
C	-6.39267900	-5.90600800	-3.65869700
H	-4.23789300	-5.66763100	-3.38175000
H	-8.56807400	-6.08442800	-3.60410500
H	-6.30731700	-6.21929800	-4.70582200
H	-1.39960500	0.25392300	2.65868500
H	-6.48941500	-3.18096900	2.01212400

Intermediate C

C$_{[Co(P6)]}$:
Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.981064 Hartree
H_corr: 2.379422 Hartree
SCF: -7398.571576 Hartree
S: 798.254 Cal/Mol-Kelvin
H: -7396.192154 Hartree

G: -7396.590512 Hartree

Cartesian Coordinates:

N	1.70928300	-0.71642000	-1.15939800
N	-0.22772900	2.02385400	0.95606400
N	-0.89280700	0.34695200	-1.19440400
N	2.35623100	0.93916100	1.00576500
C	2.51801100	1.82892500	2.09400700
C	3.64161500	0.37160300	0.83009500
C	3.07308900	-1.08307300	-1.06480800
C	1.23670500	-1.44034100	-2.27907700
C	-1.04778600	-0.53603200	-2.29041600
C	-2.12005700	1.04901700	-1.13716200
C	-1.54095300	2.50610700	0.75627500
C	0.24060700	2.74588200	2.07937300
C	-0.77770100	3.65784200	2.57239700
C	1.52952500	2.66915300	2.63556900
C	3.88397600	1.80602700	2.58725600
C	4.00381600	-0.58085400	-0.13894800
C	-1.87706200	3.51018900	1.75494100
C	-2.44441200	2.08107700	-0.23603300
C	-3.01826300	0.59953600	-2.18990300
C	3.43225600	-2.01436600	-2.12438400
C	-0.06115200	-1.38988300	-2.81860500
C	-2.36290700	-0.38863300	-2.89222800
C	4.57828200	0.90910000	1.80505600
C	2.29692800	-2.23857900	-2.87075500
C	-0.35773400	-2.13301000	-4.10039300
C	-0.93820700	-3.39541800	-6.56887500
C	-0.83151300	-3.48510800	-4.12111400
C	-0.16312300	-1.44082800	-5.34365500
C	-0.45389000	-2.07162600	-6.58166600
C	-1.12977900	-4.10726700	-5.36896800
C	5.43559100	-1.03466900	-0.22157900
C	8.13417400	-1.87855300	-0.40725100
C	5.79389700	-2.37399200	0.08077600
C	6.44921300	-0.12383200	-0.62166000
C	7.80411200	-0.53401900	-0.72490600
C	7.14266400	-2.81027100	-0.00002600
C	1.88924500	3.59048400	3.77514100
C	2.55284900	5.37707700	5.86568000
C	1.58366700	3.25263900	5.13260900
C	2.52506800	4.84334500	3.48961200
C	2.86340600	5.73903800	4.53850600
C	1.92017000	4.15761800	6.18004100
C	-3.77422900	2.77204000	-0.35298700

C	-6.26359300	4.09592200	-0.58667300
C	-3.82615900	4.14459300	-0.71783300
C	-4.98230200	2.06810500	-0.10911100
C	-6.23810500	2.72373100	-0.21861200
C	-5.06840000	4.81844000	-0.84401200
C	-1.49794300	-5.47412500	-2.69501800
N	-0.96920700	-4.18755600	-2.88874200
C	0.62586600	0.78275000	-6.32537400
N	0.33230900	-0.10556200	-5.28072600
C	3.36666900	6.29686000	1.56468600
N	2.78185700	5.15013100	2.12122000
C	0.40251000	1.55791400	6.60649300
N	0.94040000	2.00742900	5.38824400
C	-0.28898200	0.23010700	6.51337700
C	-0.48184700	-0.59020700	7.81243200
C	-1.71759100	0.00608000	7.14158600
C	3.43540800	6.26501100	0.06461100
C	3.59561300	7.60691100	-0.69053200
C	4.76175200	6.62117800	-0.70887300
C	1.14552900	2.10979100	-5.85068700
C	1.92347200	2.99589200	-6.85274900
C	0.54750800	3.46634000	-6.38544400
C	-1.36368900	-5.98596600	-1.29242900
C	-2.28049900	-7.14498300	-0.83184000
C	-0.79089100	-7.42848600	-1.00634600
C	0.48784300	4.60304800	-5.35935100
C	-0.62270200	3.44278100	-7.37054000
C	0.07007600	-7.54471100	0.25613500
C	-0.33243000	-8.31636900	-2.16448300
C	-2.63174800	-0.94080700	6.35626300
C	-2.44796300	1.16690900	7.81919900
C	5.00405200	5.82166100	-1.99371300
C	6.03186200	6.95407700	0.07624300
H	2.81933400	3.50749700	-6.48453400
H	4.43243100	-2.41336500	-2.27977500
H	5.62479600	0.61918900	1.87614800
H	-4.01312100	1.00356700	-2.36266200
H	4.24298600	2.40690900	3.42141100
H	2.17133100	-2.86312700	-3.75386700
H	-2.83974200	4.01307500	1.81829100
H	-2.70841200	-0.95631000	-3.75470500
H	-0.64743300	4.31502200	3.43068500
Co	0.66711500	0.50364800	0.03884700
H	-0.29690000	-1.51882400	-7.50911900
H	-1.51148300	-5.12864900	-5.36645500
H	-1.17020900	-3.88707600	-7.52090200

H 9.17872300 -2.20547200 -0.48216200
H 3.34668400 6.68596300 4.29323400
H 1.67075500 3.88822100 7.20699900
H 2.80951900 6.06638400 6.67861000
H -7.22686300 4.61601500 -0.65879900
O -2.04268600 -6.16412100 -3.62366000
O 0.46677500 0.50187200 -7.55715000
O 3.80087500 7.27306600 2.25752100
O 0.47762300 2.21460100 7.69703800
H -0.10557600 -0.32625200 5.58844900
H 2.81538600 5.49965200 -0.42097200
H 3.68813900 8.48612000 -0.04420800
H 1.47994700 2.13993000 -4.80511000
H 1.99877000 2.58324500 -7.86438900
H -1.08722600 -5.23458400 -0.54736300
H 2.99862100 7.74965400 -1.59774400
H 0.86301000 1.35183400 4.59599300
H -0.43354600 4.53781300 -4.74896700
H 0.48411100 5.58382500 -5.87375500
H 1.35641200 4.58417800 -4.67389300
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H 5.01678100 -3.08127800 0.39371900
H 6.17752200 0.90725100 -0.87823400
H -4.94512200 1.00930700 0.18236800
H -2.89541700 4.68795000 -0.92252300
C -0.09708200 -0.93616400 1.36278000
C -0.22831900 -2.11209500 0.52519000
N -0.42546600 -3.04450100 -0.18942500
C 0.90252000 -1.11269900 2.51053800
O 0.92901200 -0.35930200 3.52012200
O 1.65716700 -2.25291700 2.34984100
C 2.48521300 -2.87167200 3.50807300
C 3.62468400 -1.91386300 3.90241300
H 4.25777300 -2.40674500 4.66432100
H 4.25539800 -1.67777400 3.02855600
H 3.23417100 -0.97443300 4.32394700
C 3.00938800 -4.16077500 2.85053900
H 2.17337800 -4.80599900 2.53004800
H 3.63370000 -4.71905100 3.57174300
C 1.52752200 -3.18194400 4.67829700
H 0.66787500 -3.78242800 4.33008700
H 1.16039900 -2.26058600 5.15739600
H 3.62535700 -3.92424200 1.96660400
H 2.07266900 -3.77249300 5.43789600
C 7.51411700 -4.22921200 0.34362900
C 7.18658100 -5.29653200 -0.55011600
C 8.19697000 -4.51430500 1.56772800
C 7.54965800 -6.62347900 -0.20708200
C 8.53521500 -5.85627900 1.87579300
C 8.22685200 -6.92683600 1.00001400
H 7.29924500 -7.43732400 -0.90095000
H 9.05116800 -6.06890400 2.82191300
C 8.86792200 0.43506500 -1.17150500
C 9.37286900 1.41696900 -0.26410200
C 9.37273600 0.37684900 -2.50842900
C 10.37586600 2.31720500 -0.70568400
C 10.37072200 1.29909800 -2.91135000
C 10.89158500 2.27465300 -2.02447300
H 10.76211100 3.06708900 -0.00221300
H 10.74789700 1.25507200 -3.94203900
C -7.51700800 1.97627400 0.05470500
C -7.79971700 1.48846200 1.37122900
C -8.45864100 1.74624400 -0.99904600
C -9.01564400 0.79768200 1.60790100
C -9.65647500 1.04015400 -0.72001000

C -9.96142800 0.56465900 0.57899300
H -9.22812600 0.43625600 2.62335000
H -10.36540900 0.85632200 -1.53877800
C -5.11698700 6.26993700 -1.24713900
C -5.36909100 6.62464600 -2.60829900
C -4.90815400 7.29546400 -0.27331600
C -5.41015700 7.99529400 -2.97081900
C -4.96133800 8.65355200 -0.67554500
C -5.21419500 9.02678100 -2.01952400
H -5.59838300 8.26116200 -4.01980000
H -4.80138300 9.43652800 0.07816400
C 6.46480400 -5.03653100 -1.86728100
H 6.49317600 -5.93065500 -2.51446500
H 6.92032900 -4.19522800 -2.42209300
C -6.82791200 1.69129800 2.52746300
H -6.41867400 2.71793200 2.54386000
H -5.96761400 0.99933400 2.44987400
C -8.19969800 2.21800300 -2.42617100
H -7.14997600 2.05328700 -2.72966300
H -8.40032400 3.30114900 -2.54077600
C -4.62799600 6.95177000 1.18438400
H -3.63308200 6.47991800 1.30413100
H -5.37238800 6.23846200 1.58470800
C -5.57750200 5.55591900 -3.67416200
H -6.48702300 4.95622100 -3.47869800
H -4.73141100 4.84343900 -3.70446400
C 8.84338100 -0.64379300 -3.50877400
H 7.74010300 -0.60585400 -3.58230000
H 9.10718700 -1.67797200 -3.21589000
C 8.85654200 1.51278400 1.16670900
H 7.82004400 1.90197200 1.19919200
H 9.48527200 2.19238800 1.76828600
H 9.26063400 -0.46215000 -4.51471400
H 8.84475900 0.52429900 1.66285900
C 8.55130000 -3.40794000 2.55478900
H 9.34844100 -2.74876100 2.16097300
H 8.90999000 -3.83265000 3.50891800
H 7.68116100 -2.75981300 2.76996900
H 5.40021200 -4.77791400 -1.70512500
H -5.68021700 6.01046300 -4.67518900
H -4.64529200 7.85803800 1.81483200
H -8.85378400 1.68435600 -3.13839300
H -7.32681400 1.50300200 3.49495200
C -11.27333000 -0.15315100 0.86472400
H -12.06505000 0.56660900 1.15393800
H -11.16820400 -0.87595200 1.69404400

C 8.63346500 -8.35560100 1.33341100
H 8.68329800 -8.51839600 2.42523900
H 9.63444400 -8.59057600 0.91970000
C -5.29423100 10.49316100 -2.42189100
H -5.12387900 10.62550600 -3.50538200
H -4.54729700 11.10290700 -1.88101200
C 11.98877700 3.23156900 -2.46999200
H 11.98217200 4.16156500 -1.87364000
H 11.87839500 3.50664000 -3.53482200
H 7.92339700 -9.08866300 0.90957800
H 12.98996300 2.77100100 -2.35244800
H -11.63687400 -0.70120300 -0.02343300
H -6.29201700 10.91589300 -2.18955300
C -1.42669800 -0.46860200 1.93355800
C -2.65530300 -0.88085300 1.59812000
C -3.55926100 -1.72407900 0.79316400
H -3.61674300 -2.75011800 1.22050800
H -3.21740000 -1.80538400 -0.26435800
O -4.91184000 -1.10189200 0.82036100
C -5.96751600 -1.98595600 0.24918100
H -5.70666800 -2.29124800 -0.78292800
H -6.84438000 -1.31147600 0.20757800
C -6.25491200 -3.16863600 1.14591300
C -6.60222000 -4.43730100 0.75473600
C -7.01895500 -5.46792000 1.76228300
C -7.59915000 -5.10361100 3.01396900
C -6.83876300 -6.85505700 1.48715200
C -7.95497800 -6.08575400 3.96387300
H -7.80045800 -4.04793700 3.23115400
C -7.19436200 -7.83794100 2.43812800
H -6.41045800 -7.15905100 0.52532700
C -7.75041200 -7.45961400 3.68378800
H -8.40578800 -5.78249600 4.91646700
H -7.03884100 -8.89833600 2.20650600
H -8.03255300 -8.22207100 4.41929600
C -6.60318300 -4.85446700 -0.69516200
C -5.38941600 -4.99648100 -1.42183300
C -7.82959700 -5.15264500 -1.35124200
C -5.39621900 -5.41821500 -2.77387400
H -4.43359000 -4.80287100 -0.91939000
C -7.84136700 -5.55877800 -2.70586600
H -8.77136000 -5.06207200 -0.79650400
C -6.62517500 -5.69349500 -3.42030900
H -4.44743200 -5.54816500 -3.30745200
H -8.79597300 -5.77504800 -3.20051000
H -6.63292100 -6.01950800 -4.46700900

H -1.30694100 0.25769900 2.75202700
H -6.23858300 -2.92252700 2.21840900

Transition State TS2'

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.98506 Hartree
H_corr: 2.37727 Hartree
SCF: -7398.544051 Hartree
S: 785.934 Cal/Mol-Kelvin
H: -7396.166781 Hartree
G: -7396.558991 Hartree

Cartesian Coordinates:

N 1.67463600 0.32348300 -1.35836200
N -1.21047900 0.80932400 1.32717100
N -1.13598100 0.28089300 -1.41775100
N 1.60557300 0.90969100 1.36778900
C 1.39281800 1.29172600 2.71107600
C 3.01486400 0.92234300 1.22600300
C 3.07438100 0.38624100 -1.16353600
C 1.53286100 0.10811400 -2.74720400
C -0.92060300 0.02912600 -2.79550900
C -2.54438600 0.36881300 -1.29662000
C -2.61107000 0.81251400 1.11976600
C -1.06053000 1.18004200 2.68420700
C -2.35441600 1.38672800 3.31201700
C 0.15000900 1.42882400 3.35123100
C 2.65273300 1.54930600 3.38726300
C 3.73154200 0.64647200 0.04973700
C -3.30985900 1.16545100 2.34602600
C -3.26458800 0.62121700 -0.11289500
C -3.18116200 0.16005600 -2.58710900
C 3.78021800 0.23887600 -2.42757600
C 0.32486500 -0.05376700 -3.44611900
C -2.18221900 -0.05450100 -3.50919600
C 3.65481500 1.30798100 2.47355300
C 2.82673500 0.07378400 -3.40706100
C 0.35328200 -0.17819300 -4.95109500
C 0.30830100 -0.29252500 -7.78147600
C 0.55006200 -1.43102600 -5.62145800
C 0.17457900 1.01317800 -5.73324100
C 0.14854600 0.95829100 -7.15120400
C 0.51042200 -1.47644400 -7.04684400
C 5.23487800 0.68544700 0.06776800
C 8.06580800 0.75272900 0.05986200

C 5.98192100 -0.50875700 -0.10507300
C 5.92474800 1.91506400 0.23447900
C 7.34345500 1.96435300 0.22700900
C 7.40180700 -0.49193800 -0.10474100
C 0.12123600 1.95003800 4.76627400
C 0.10451100 2.98901200 7.39601000
C 0.05012500 1.06377200 5.88670700
C 0.17317300 3.36459900 4.99133500
C 0.16527900 3.88817300 6.31141200
C 0.04720700 1.59315600 7.20933000
C -4.75555200 0.81061500 -0.18559900
C -7.53639800 1.31712100 -0.29231300
C -5.26294300 1.90471200 -0.93797800
C -5.66105100 -0.03426400 0.51399900
C -7.06053200 0.21177200 0.46435700
C -6.65346400 2.17421600 -0.99807200
C 0.95743500 -3.91629100 -5.32702700
N 0.81078700 -2.60059600 -4.85218000
C -0.10358700 3.54609000 -5.53702000
N 0.03877100 2.24696800 -5.02983700
C 0.27216000 5.60701700 3.77311300
N 0.22364800 4.20758500 3.84313100
C -0.18844300 -1.36528400 6.57231400
N -0.03298200 -0.33549000 5.62916900
C -0.41913700 -2.71870500 5.97181700
C -0.06875500 -3.96638700 6.82153400
C -1.53948100 -3.67559700 6.53344000
C 0.30247400 6.13429600 2.36698600
C -0.10373600 7.60810700 2.12648900
C 1.35710400 7.21543200 1.91619900
C -0.16920500 4.60114200 -4.46934700
C 0.18410700 6.05776900 -4.85872400
C -1.26266500 5.73511000 -4.49180800
C 1.37664800 -4.90013600 -4.27528300
C 1.06457200 -6.40091800 -4.50214200
C 2.52237100 -5.94742600 -4.54522300
C -1.76807900 6.18320000 -3.11613800
C -2.32955900 5.74093600 -5.58819400
C 3.40438200 -6.26478900 -3.33241300
C 3.26614700 -5.95187200 -5.88184600
C -2.24418700 -4.53268900 5.47668000
C -2.45357200 -3.21226500 7.66904800
C 1.86172300 7.07534100 0.47596200
C 2.41187400 7.70635400 2.90955100
H 0.80064800 6.63230500 -4.15889900
H 4.86174000 0.28770800 -2.53655100

H	4.73143600	1.37731000	2.61608500
H	-4.25666300	0.15677700	-2.74570500
H	2.73638000	1.86396800	4.42628700
H	2.96190600	-0.05155700	-4.48017000
H	-4.38971300	1.25299200	2.43570100
H	-2.26974900	-0.25853500	-4.57456600
H	-2.48958100	1.68621600	4.35006600
Co	0.22401100	0.35210500	0.03176100
H	0.00972200	1.88101300	-7.71646200
H	0.63212800	-2.44104400	-7.54075700
H	0.28189500	-0.34501600	-8.87628000
H	9.16251500	0.78045200	0.05212100
H	0.20469000	4.96903500	6.45485600
H	0.00167100	0.90281400	8.05219200
H	0.10125900	3.38742800	8.41735200
H	-8.61448200	1.51908300	-0.32111200
O	0.76231300	-4.26045200	-6.54148500
O	-0.16824300	3.81642800	-6.78002300
O	0.29302500	6.36360300	4.79721000
O	-0.15285400	-1.17657600	7.83302300
H	-0.26714900	-2.78176100	4.88858300
H	0.02507200	5.41402300	1.58582100
H	-0.34986400	8.16788300	3.03500600
H	0.13041600	4.27578500	-3.46413000
H	0.41492100	6.20313600	-5.91934300
H	1.34199500	-4.52564100	-3.24817500
H	-0.73262700	7.82279100	1.25571500
H	0.02664800	-0.62815900	4.64282500
H	-2.59142100	5.53216100	-2.76445300
H	-2.15661300	7.21888500	-3.16983000
H	-0.96351300	6.16280000	-2.35629700
H	-3.19569400	5.11517300	-5.29796700
H	-1.92935800	5.35995800	-6.54245400
H	-2.69624600	6.77382000	-5.74694800
H	0.58677900	-6.63510300	-5.45965200
H	0.70899000	-6.97851500	-3.64133300
H	3.85919800	-7.26936800	-3.44166400
H	2.82476300	-6.25264600	-2.39069800
H	4.22567800	-5.52839900	-3.23776700
H	3.67230500	-6.96322200	-6.08150700
H	4.11735000	-5.24326200	-5.86028900
H	2.60067800	-5.66789100	-6.71380100
H	0.41976900	-4.80551600	6.31333600
H	0.30050000	-3.74479500	7.82854500
H	-1.53611100	-4.89892500	4.70848500
H	-3.03801600	-3.95115900	4.97033000

H -2.71336900 -5.41622800 5.95211400
H -3.32875300 -2.66505800 7.26823200
H -1.92167500 -2.55062700 8.37212700
H -2.83022700 -4.09254800 8.22609300
H 1.06447900 6.72359700 -0.20635300
H 2.70454300 6.35962300 0.41868400
H 2.22191800 8.05263100 0.09957900
H 2.74671500 8.72340200 2.62679600
H 3.29882300 7.04327900 2.90225000
H 2.01358300 7.74210400 3.93722200
H 0.89719700 -2.50025200 -3.82302400
H 0.06517200 2.16989900 -4.00886300
H 0.22760200 3.71571400 2.94444700
H 5.45168500 -1.46048000 -0.23189800
H 5.35373200 2.84486100 0.34553000
H -5.27373600 -0.88192400 1.09458100
H -4.56331900 2.57157800 -1.45617500
C 0.26538200 -1.62138700 0.39052300
C 0.69876300 -2.25998600 -0.80685100
N 0.92009600 -2.75324800 -1.87544800
C 0.98557400 -1.98348500 1.66361300
O 0.65050900 -1.62982000 2.82967000
O 2.07322300 -2.82377400 1.39367400
C 3.03339100 -3.36239300 2.48052500
C 3.76863800 -2.17591900 3.13168000
H 4.51051300 -2.56537100 3.85432800
H 4.30399700 -1.58320500 2.37060500
H 3.07052300 -1.51680400 3.67162800
C 3.98222400 -4.23480400 1.63648500
H 3.42836800 -5.04845500 1.13601800
H 4.75772400 -4.68020000 2.28646100
C 2.26018400 -4.20313900 3.51789600
H 1.65300100 -4.98423700 3.02888400
H 1.60755400 -3.57342600 4.13997300
H 4.48112300 -3.62945200 0.86054000
H 2.99074000 -4.70565200 4.17972200
C 8.18596300 -1.76669700 -0.27580600
C 8.25223900 -2.40438700 -1.55561900
C 8.87111100 -2.34207800 0.83855900
C 9.00112100 -3.59848700 -1.69592200
C 9.60469300 -3.54317400 0.65594300
C 9.68426600 -4.18821500 -0.60191100
H 9.05464900 -4.07735400 -2.68318100
H 10.12477000 -3.98238600 1.51782100
C 8.06696000 3.27718000 0.38039700
C 8.20127400 3.87777900 1.66946200

C 8.62241900 3.92635400 -0.76742000
C 8.89214400 5.11135900 1.79053200
C 9.29959200 5.15976200 -0.60388800
C 9.44725100 5.77107100 0.66734100
H 8.99817300 5.56397300 2.78555600
H 9.72018700 5.65503400 -1.48966700
C -8.05972000 -0.64102700 1.20442600
C -8.17173400 -0.55344000 2.62785300
C -8.94785100 -1.49562300 0.47833000
C -9.17896600 -1.29877600 3.29226500
C -9.93393300 -2.23360700 1.18203800
C -10.07864600 -2.13901000 2.58938800
H -9.26286900 -1.21774500 4.38434100
H -10.60846700 -2.89023500 0.61614400
C -7.17790300 3.35535400 -1.77254700
C -7.27681000 3.29598400 -3.19656200
C -7.57647700 4.54292900 -1.08166200
C -7.77638400 4.41959600 -3.90400500
C -8.06439000 5.64528400 -1.82643000
C -8.17761100 5.60417100 -3.23926600
H -7.85315600 4.36584700 -4.99829500
H -8.36105000 6.55719700 -1.29050200
C 7.54849100 -1.81470300 -2.77237000
H 7.86390000 -2.32938500 -3.69686700
H 7.76895100 -0.73671300 -2.88623000
C -7.23228100 0.32085700 3.44771500
H -7.10179300 1.32034000 2.99286300
H -6.22876900 -0.14068200 3.52550900
C -8.84057900 -1.65032600 -1.03390400
H -7.79856500 -1.85549300 -1.34280300
H -9.15743900 -0.73264900 -1.56496300
C -7.46927900 4.64739100 0.43499500
H -6.45468700 4.38499000 0.78946200
H -8.17098700 3.95822400 0.94254500
C -6.85926400 2.04908400 -3.96686900
H -7.29044900 1.13275700 -3.52215800
H -5.75912000 1.92086500 -3.96531700
C 8.48569400 3.32159300 -2.15960000
H 7.42859000 3.10685900 -2.40591700
H 9.03348500 2.36385300 -2.24532100
C 7.62321400 3.21705200 2.91527200
H 6.51706100 3.27514900 2.92822000
H 7.99170400 3.71145200 3.83116300
H 8.88379900 4.00752500 -2.92777900
H 7.88980900 2.14513500 2.97016000
C 8.81948500 -1.70056100 2.22049300

H 7.78277800 -1.45240500 2.51545900
H 9.39413100 -0.75518700 2.25426100
H 9.24363300 -2.37670400 2.98363400
H 6.44827600 -1.91178400 -2.69579800
H -7.18527300 2.10806000 -5.02012900
H -7.69810400 5.67219300 0.77643200
H -9.47527400 -2.48083600 -1.38967400
H -7.61484700 0.45690700 4.47449900
C -11.18164300 -2.89297500 3.31947200
H -12.07837300 -2.25435400 3.44696700
H -10.85974300 -3.20876600 4.32855800
C 10.47347600 -5.47810500 -0.77964500
H 11.22273800 -5.38396300 -1.58873000
H 9.80831800 -6.32143300 -1.04928200
C -8.73110700 6.79269400 -4.01334200
H -9.83266200 6.85496800 -3.90983300
H -8.50296600 6.71502200 -5.09105500
C 10.17662600 7.09933900 0.81407200
H 10.35202700 7.35042600 1.87500100
H 9.59293300 7.92690500 0.36527200
H 11.00866800 -5.75503000 0.14575900
H 11.15781700 7.07953800 0.30284700
H -11.49728300 -3.79332900 2.76197500
H -8.31522700 7.74866200 -3.64396400
C -1.74312400 -2.65275600 0.51187500
C -1.83733500 -3.78799500 -0.37288100
H -2.21866900 -1.74858500 0.11632300
C -1.97983600 -2.79425900 2.01377000
H -1.62045200 -1.91309700 2.56083700
H -1.52381300 -3.71008200 2.43796400
O -3.45211000 -2.79593900 2.26636800
C -4.08036300 -4.12218300 2.02719500
H -3.66145600 -4.86260500 2.74225000
H -3.85149000 -4.47533000 1.00069500
C -5.53082700 -3.99159000 2.19737600
C -6.75269600 -3.87956000 2.31471700
H -7.81697100 -3.74106600 2.40645400
C -2.56518300 -3.64001800 -1.66655700
C -2.06579900 -4.22594200 -2.86984900
C -3.83437700 -2.98726500 -1.71038000
C -2.80065100 -4.15298800 -4.07145000
H -1.08941200 -4.72075500 -2.86030600
C -4.58652800 -2.95179700 -2.90505600
H -4.25391000 -2.55437200 -0.79427500
C -4.07268500 -3.52758800 -4.09209800
H -2.38287300 -4.58428300 -4.98804800

H	-5.57636900	-2.48000700	-2.90725400
H	-4.65378800	-3.49158700	-5.02103000
C	-1.32571400	-5.13879600	-0.04051800
C	-0.15717000	-5.34640800	0.75518600
C	-2.02493800	-6.30217700	-0.50568800
C	0.28337700	-6.64865800	1.07408700
H	0.44166200	-4.48671000	1.06678000
C	-1.58728900	-7.60084300	-0.17729700
H	-2.92812400	-6.17616400	-1.11271100
C	-0.42840500	-7.78476200	0.61771100
H	1.19518200	-6.78441800	1.66839000
H	-2.15019300	-8.46996700	-0.53701300
H	-0.08279200	-8.79401600	0.86954800

Intermediate C'

C'$_{[Co(P6)]}$

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.985255 Hartree
H_corr: 2.37929 Hartree
SCF: -7398.567277 Hartree
S: 789.591 Cal/Mol-Kelvin
H: -7396.187987 Hartree
G: -7396.582022 Hartree

Cartesian Coordinates:

N	-1.57467000	0.06641000	1.43484000
N	1.14724000	0.33626000	-1.43173000
N	1.21985000	0.16845100	1.37202000
N	-1.64523000	0.31696000	-1.35903000
C	-1.50318000	0.44887000	-2.75938000
C	-3.01481000	0.58341900	-1.12179000
C	-2.97590000	0.20054900	1.30408000
C	-1.37335000	-0.10260000	2.82270000
C	1.07796000	0.04749000	2.77572000
C	2.58547000	0.49545100	1.18389000
C	2.53483000	0.54807100	-1.27786000
C	0.94683000	0.31611000	-2.83325000
C	2.21426000	0.44075100	-3.53620000
C	-0.29948000	0.36445000	-3.48541000
C	-2.76569000	0.81707900	-3.37826000
C	-3.67039000	0.51647900	0.12226000
C	3.19223000	0.60028100	-2.57519000
C	3.22096000	0.70756100	-0.05557000
C	3.26923000	0.58666100	2.46577000

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C -0.13017000 -0.12364000 3.48283000
C 2.35023000 0.27657100 3.44274000
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C -2.64065000 -0.14301100 3.53392000
C -0.09853000 -0.08731000 4.99461000
C 0.07296000 0.12039000 7.81749000
C -0.12731000 -1.26900000 5.80592000
C -0.03268000 1.19646000 5.63741000
C 0.05709900 1.30280000 7.04986000
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C -0.43464000 1.09186000 -7.76238000
C -0.47146000 -0.50335000 -5.90373000
C -0.25168100 1.92273000 -5.48214000
C -0.29781100 2.18054000 -6.87751000
C -0.52411000 -0.23686000 -7.30312000
C 4.64497000 1.19059100 -0.09240000
C 7.29584900 2.19575200 -0.14970000
C 4.91808900 2.48300200 -0.61780000
C 5.72203000 0.41000200 0.40045000
C 7.05412000 0.89906200 0.37619000
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C -1.19834900 -5.56613000 -5.87256000
C 0.32642100 -5.49347000 -5.85047000
C 0.10888800 5.14543000 -3.46794000
C 0.70069800 6.57354000 -3.53968000
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C -0.61486200 6.09004000 4.23422000
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C	-0.63815900	-4.92872000	4.87909000
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C	-1.63143800	-6.05686000	5.35025000
C	1.22164800	6.18886100	2.36740000
C	1.95309800	6.08297100	4.83281000
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C	-1.82516200	6.83826000	-4.24777000
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H	4.31628000	0.85402100	2.58813000
H	-2.89721000	0.99644900	-4.44418000
H	-2.73499000	-0.28370100	4.60958000
H	4.26414000	0.72760100	-2.71420000
H	2.49126000	0.23373100	4.52124000
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Co	-0.19771000	-0.00933000	-0.01766000
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H	0.15242000	0.19370000	8.90854000
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H	-0.64087000	-1.07278000	-7.99306000
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H	8.32205900	2.58335300	-0.17018000
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O	-0.86868900	-3.04736000	-7.38920000
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H	0.96027800	6.90977000	-4.54911000
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H -2.13198200 6.04112000 -1.52899000
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C 8.41244000 -0.05465700 2.30510000
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H 2.16921000 -1.85334900 -0.05857000
C 1.96280100 -2.90554900 -1.89560000
H 1.68313000 -2.04771900 -2.52973000
H 1.52687100 -3.82819900 -2.32573000
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C 3.99436100 -3.26403900 -3.19153000
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H 7.73443100 -3.76588800 -3.04889000
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C 2.58973100 -4.17432900 2.88255000
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C 3.50023100 -3.98472900 3.94261000
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C 5.02902100 -2.82702800 2.41717000
H 4.33905100 -2.62177900 0.35185000
C 4.73163100 -3.32358800 3.71084000
H 3.24932100 -4.35261900 4.94371000
H 5.99827100 -2.34932800 2.22868000
H 5.45162100 -3.19795800 4.52790000
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C 0.39688100 -5.61594000 -0.65822000
C 2.25691200 -6.38148900 0.74137000
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H -0.21681900 -4.82544000 -1.09200000
C 1.90615200 -7.71753900 0.47780000
H 3.14256200 -6.17139900 1.34772000
C 0.79609200 -8.01927000 -0.35106000
H -0.81289800 -7.17660000 -1.55520000
H 2.50606200 -8.52796900 0.90756000
H 0.52040200 -9.06003000 -0.55555000

Transition State TS3'

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.977954 Hartree
H_corr: 2.377845 Hartree
SCF: -7398.546346 Hartree
S: 801.326 Cal/Mol-Kelvin
H: -7396.168501 Hartree
G: -7396.568392 Hartree

Cartesian Coordinates:
N 1.89833400 -0.27505400 -1.31609300
N -0.31735400 1.56370700 1.40580800
N -0.66052100 0.85464300 -1.29449900
N 2.25610600 0.46548900 1.36356700
C 2.27376000 0.90561000 2.70862100
C 3.57699900 0.01163300 1.13012200
C 3.23939000 -0.70769500 -1.19199000
C 1.56711300 -0.57065500 -2.66023600

C -0.66723700 0.44262600 -2.64754600
C -1.90428400 1.50475000 -1.12319200
C -1.60911200 2.11410200 1.23896200
C -0.01131200 1.79975600 2.76549100
C -1.10191500 2.49629100 3.42946100
C 1.20285100 1.49303600 3.40556700
C 3.59389200 0.73956300 3.29233600
C 4.06386000 -0.54520000 -0.06554600
C -2.08567700 2.69592400 2.48439900
C -2.36991600 2.10391200 0.05822200
C -2.66625600 1.49748400 -2.36240800
C 3.70708400 -1.30784400 -2.43354100
C 0.36960500 -0.23498900 -3.31650500
C -1.90273900 0.84080700 -3.30407400
C 4.40369300 0.20974400 2.31086100
C 2.67584300 -1.21850800 -3.34143900
C 0.25326300 -0.45698900 -4.80646300
C 0.02571400 -0.71960000 -7.61847200
C -0.18558300 -1.69621900 -5.37850800
C 0.59905100 0.63139600 -5.67791800
C 0.48374200 0.50301200 -7.08680400
C -0.30558600 -1.81290700 -6.79511700
C 5.52207100 -0.90519500 -0.17295300
C 8.27872100 -1.52772600 -0.39927800
C 6.07563000 -1.99620400 0.54511100
C 6.37185900 -0.12815900 -1.00473900
C 7.75503900 -0.42363700 -1.12356900
C 7.45294100 -2.32460600 0.43673400
C 1.39843600 1.91516800 4.84082900
C 1.76765200 2.77782900 7.50968100
C 0.95920700 1.09281800 5.92781100
C 2.01462400 3.17911700 5.12111100
C 2.20534000 3.61179500 6.46008500
C 1.14914200 1.53465700 7.26920200
C -3.72747000 2.75715100 0.06678200
C -6.26822500 3.99644300 0.11897800
C -3.84619200 4.15402700 -0.14936600
C -4.89117700 1.98214600 0.30679700
C -6.17212900 2.59674100 0.34050100
C -5.11636200 4.78888900 -0.13065600
C -0.96831000 -4.05773700 -4.88227700
N -0.47415900 -2.79286100 -4.51624000
C 1.49220800 3.02621800 -5.67454100
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C 3.01727900 5.23844000 3.98910600
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C	-1.19355500	-3.47947700	6.73693700
C	-2.38980700	-2.67475900	6.23226000
C	3.25744500	5.76669500	2.60352400
C	3.47785100	7.28818400	2.42550000
C	4.65730400	6.35048900	2.17571600
C	1.94248900	4.06606900	-4.68772300
C	2.85902100	5.20737500	-5.19069900
C	1.43293400	5.55471700	-4.76797800
C	-1.06964800	-5.02600000	-3.74084800
C	-2.03141400	-6.23111400	-3.88131200
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C	1.23533100	6.25109900	-3.41716800
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C	0.08753500	-7.08053400	-2.59391500
C	0.15624200	-6.95758600	-5.16151400
C	-3.19982200	-3.25273000	5.06662600
C	-3.21683100	-1.86251900	7.23049000
C	5.06225800	6.07832900	0.72291700
C	5.82057000	6.33512900	3.16919100
H	3.69640700	5.50256600	-4.54918100
H	4.69714300	-1.73744300	-2.57304300
H	5.46611300	-0.02069100	2.36253400
H	-3.65040900	1.94806800	-2.47833500
H	3.85182900	1.02227800	4.31182100
H	2.64727600	-1.54693000	-4.37919900
H	-3.04967600	3.18765900	2.60092300
H	-2.12915300	0.64044000	-4.35025600
H	-1.08894700	2.79492200	4.47656700
Co	0.71285800	0.48506200	0.10059000
H	0.75307200	1.34873600	-7.72131800
H	-0.66114500	-2.75578900	-7.21206700
H	-0.07115200	-0.82521800	-8.70544900
H	9.34504500	-1.77009900	-0.48784000
H	2.67828200	4.57761900	6.64432100
H	0.80201600	0.89934700	8.08480100
H	1.91055700	3.10728400	8.54553100
H	-7.25336200	4.47892400	0.14706900
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O	1.49863600	3.21904100	-6.93347700
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H 1.99751100 5.93833400 -2.67832800
H -0.61936700 5.76380200 -5.48629400
H 0.56961100 5.38698900 -6.77257900
H 0.50604000 7.03230700 -6.05973400
H -2.54654500 -6.30182300 -4.84525900
H -2.62988800 -6.50548700 -3.00521100
H 0.03480800 -8.18717100 -2.61079100
H -0.44078900 -6.72829700 -1.68811500
H 1.15276600 -6.79239100 -2.50347800
H 0.05715100 -8.05577600 -5.26948300
H 1.23693100 -6.71520800 -5.14092600
H -0.28989200 -6.47495000 -6.04683000
H -0.98093500 -4.45852000 6.29275800
H -0.92647600 -3.37347300 7.79376800
H -2.56483700 -3.83643300 4.37373900
H -3.68818500 -2.44768900 4.48453000
H -3.99282800 -3.92585300 5.44845000
H -3.75220600 -1.03843700 6.71932800
H -2.58183900 -1.42620300 8.01931400
H -3.97477100 -2.51480200 7.70742500
H 4.19150000 6.10874500 0.04076300
H 5.54209500 5.08539600 0.62446000
H 5.78803500 6.84061500 0.37830200
H 6.53662300 7.14208500 2.91890300
H 6.36522300 5.37192400 3.12311600
H 5.47037000 6.48641400 4.20387600
H -0.30704000 -2.66647000 -3.50054600
H 1.10006500 1.81953400 -4.04785500
H 2.21767700 3.56105900 3.08890000
H 5.42917800 -2.61052000 1.18215200
H 5.95538000 0.72731900 -1.55033700
H -4.80136700 0.89908600 0.46951300
H -2.94545300 4.75386200 -0.32906800
C -0.21478500 -1.23493300 0.70851600
C -0.51079500 -2.06201100 -0.51817500
N -0.32967700 -2.68736800 -1.54277000
C 0.63329300 -1.91152700 1.78020100
O 0.48836200 -1.64694200 3.00666500

O 1.45525300 -2.88411600 1.26675300
C 2.14844700 -3.93809300 2.16733400
C 3.07560300 -3.25087500 3.18939800
H 3.70026000 -4.02164100 3.67901300
H 3.74378800 -2.52891500 2.69026100
H 2.50163800 -2.71463600 3.96040800
C 2.93127900 -4.75702600 1.12497100
H 2.24491700 -5.19362100 0.37917500
H 3.48002600 -5.57447500 1.62747000
C 1.04152200 -4.77732100 2.84055400
H 0.36001700 -5.20326900 2.08284600
H 0.45994800 -4.17318800 3.55632900
H 3.65751300 -4.11935500 0.59223100
H 1.50820400 -5.61259900 3.39504800
C 8.02375600 -3.49897500 1.18865200
C 8.31217100 -4.71853100 0.49955500
C 8.27859600 -3.40001300 2.59187300
C 8.84590500 -5.81366700 1.22460800
C 8.81865500 -4.51703500 3.27855700
C 9.11285800 -5.73352200 2.61425500
H 9.05737600 -6.75006500 0.69076600
H 9.01619100 -4.43231300 4.35575100
C 8.64842200 0.42146600 -1.99371100
C 9.55446100 1.35245100 -1.39825500
C 8.59380500 0.29547700 -3.41787500
C 10.38696100 2.13997800 -2.23489000
C 9.44676400 1.09638600 -4.21656900
C 10.34974300 2.02913900 -3.64616500
H 11.07782400 2.85676600 -1.77109300
H 9.40522500 0.98845000 -5.30898900
C -7.40568600 1.77733300 0.61743100
C -7.67340800 1.31344500 1.94347400
C -8.31361800 1.45937100 -0.44088000
C -8.84173800 0.54582400 2.18659200
C -9.46647400 0.68466700 -0.15670100
C -9.75476200 0.22260600 1.15205200
H -9.04462300 0.19961700 3.20909800
H -10.15309800 0.43571000 -0.97711400
C -5.23657900 6.27210100 -0.36884800
C -5.24227000 6.78368700 -1.70289600
C -5.34153900 7.17148400 0.73765900
C -5.35606100 8.18277400 -1.90747100
C -5.45078500 8.56270100 0.49055000
C -5.46467800 9.09050100 -0.82528700
H -5.36078900 8.56980700 -2.93536600
H -5.52444100 9.24897500 1.34511600

C 8.04086800 -4.86656000 -0.99289100
H 8.19413400 -5.91017900 -1.31930800
H 8.71071800 -4.22350700 -1.59508900
C -6.73427300 1.63636700 3.09907100
H -6.51690400 2.71968700 3.15245500
H -5.76146700 1.12078200 2.98901100
C -8.05561100 1.92221400 -1.86984900
H -7.02682500 1.68003400 -2.19573100
H -8.17086900 3.01847500 -1.96999400
C -5.32220900 6.65891000 2.17241300
H -4.40629000 6.07341200 2.38032100
H -6.18023700 5.99123300 2.37860600
C -5.13210500 5.85227500 -2.90390500
H -5.91374600 5.06929600 -2.88242400
H -4.15836600 5.32636700 -2.92449600
C 7.64682000 -0.69210000 -4.08937200
H 6.59105400 -0.37129600 -3.99704000
H 7.71808500 -1.69796200 -3.63457000
C 9.63336500 1.52550600 0.11414000
H 8.63273000 1.68899200 0.55662400
H 10.27139500 2.38703100 0.37851800
H 7.87284100 -0.78427600 -5.16614900
H 10.05684600 0.62968500 0.60731500
C 7.98791100 -2.11658800 3.36094400
H 6.89917200 -1.94609500 3.47232700
H 8.40048900 -1.23012700 2.84409600
H 8.42278800 -2.15733600 4.37500500
H 7.00534300 -4.57371300 -1.24919900
H -5.23397200 6.41273200 -3.84973500
H -5.36260900 7.49565100 2.89159000
H -8.76110300 1.44456200 -2.57216400
H -7.17414800 1.32619900 4.06325500
C -11.01992400 -0.57389900 1.44008700
H -10.91622900 -1.18292100 2.35602300
H -11.27082700 -1.25200600 0.60391200
C 9.72214000 -6.90985700 3.36469800
H 9.42486700 -6.90984900 4.42896700
H 10.82930200 -6.87117300 3.33229800
C -5.61353700 10.58669900 -1.06565000
H -6.67414000 10.89887900 -0.98902900
H -5.25681100 10.87270000 -2.07127100
C 11.24032500 2.89260600 -4.52909900
H 10.64749700 3.65751500 -5.06822000
H 11.76021900 2.28581000 -5.29418500
H 9.41514300 -7.87523400 2.92293800
H 12.00711600 3.42165800 -3.93600700

H	-11.88780500	0.09932700	1.58763000
H	-5.04573100	11.17471900	-0.32117500
C	-1.64997000	-1.03669600	1.15843900
C	-2.38373900	-1.67444600	0.22595200
C	-3.71617900	-2.08399900	-0.26135200
H	-3.79953400	-3.19407100	-0.24217300
H	-3.85284500	-1.74730200	-1.31369200
O	-4.76202900	-1.48263900	0.60178700
C	-6.13186200	-1.99511000	0.26363100
H	-6.35452400	-1.80908200	-0.80435600
H	-6.78317300	-1.34699600	0.87925100
C	-6.31084500	-3.44301200	0.64885400
C	-6.85349600	-4.45070600	-0.11304600
C	-7.11476300	-5.79941700	0.49130700
C	-7.42785900	-5.94784300	1.87495400
C	-7.04701800	-6.97554400	-0.31127700
C	-7.63631200	-7.22540700	2.43957600
H	-7.53905200	-5.05556400	2.50238700
C	-7.25358200	-8.25389500	0.25417300
H	-6.81994500	-6.88449900	-1.37958900
C	-7.54571400	-8.38665500	1.63320100
H	-7.88350000	-7.31574800	3.50401800
H	-7.18630900	-9.14542900	-0.38038500
H	-7.71220300	-9.37788400	2.07080400
C	-7.22583900	-4.26537200	-1.56094300
C	-6.25285400	-3.91030700	-2.53584500
C	-8.56614400	-4.48041700	-1.98864400
C	-6.60958300	-3.75640400	-3.89620800
H	-5.20655800	-3.78835700	-2.23303200
C	-8.92723900	-4.31643700	-3.34555200
H	-9.32362500	-4.77226000	-1.25152800
C	-7.95044500	-3.95237000	-4.30512800
H	-5.84099900	-3.49697400	-4.63336100
H	-9.96671800	-4.47742600	-3.65499100
H	-8.22817600	-3.83418200	-5.35892000
H	-1.97008800	-0.52278000	2.06727900
H	-6.01007700	-3.66967800	1.68251100

Intermediate D'

$\mathbf{D'}_{[Co(P6)]} = \mathbf{A}_{[Co(P6)]}$

$\mathbf{D'}_{[Co(P6)]\text{-}3a'}$

Temperature: 313.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.358317 Hartree

H_corr: 0.459731 Hartree
SCF: -1248.618488 Hartree
S: 203.220 Cal/Mol-Kelvin
H: -1248.158757 Hartree
G: -1248.260171 Hartree

Cartesian Coordinates:

C	3.16750300	0.26943500	1.53409400
C	3.18246000	1.72835100	1.59276100
N	3.15862500	2.92023700	1.68095400
C	4.16202600	-0.41114500	0.60013300
O	4.29333700	-1.65785500	0.53699900
O	4.86566300	0.52938500	-0.12382800
C	5.92369900	0.11863000	-1.16522700
C	7.05468800	-0.65325100	-0.45213300
H	7.87555700	-0.83868100	-1.17017900
H	7.45913100	-0.05831500	0.38655800
H	6.69526900	-1.62128800	-0.06806900
C	6.39969300	1.48931500	-1.68185600
H	5.55739100	2.05299200	-2.11905900
H	7.17465700	1.34900900	-2.45787600
C	5.23340100	-0.70805000	-2.27123300
H	4.37851100	-0.14980000	-2.69287300
H	4.87334100	-1.67336600	-1.88082000
H	6.82636800	2.08835500	-0.85860700
H	5.95721100	-0.90119200	-3.08528900
C	2.70382500	-0.53664100	2.78369100
C	1.82581900	-0.48387400	1.80088300
C	0.52226800	-0.77538400	1.14825200
H	-0.26629700	-0.11045600	1.56893900
H	0.23220700	-1.83019900	1.35293600
O	0.67921800	-0.54379400	-0.29106200
C	-0.59380100	-0.71642600	-1.04440100
H	-0.98539700	-1.74390900	-0.91240100
H	-0.26223300	-0.59694500	-2.09281800
C	-1.62003400	0.33961300	-0.69988200
C	-2.95651800	0.15154300	-0.44039000
C	-3.87354300	1.33006200	-0.28937300
C	-3.63227800	2.55317900	-0.98187200
C	-5.01121000	1.25555800	0.56590300
C	-4.48030900	3.66800800	-0.80275600
H	-2.79297900	2.62063300	-1.68405700
C	-5.85882300	2.37160500	0.74624200
H	-5.22137200	0.32209200	1.10050000
C	-5.59635700	3.58508000	0.06565700
H	-4.27884400	4.59714700	-1.34878900

H -6.72199800 2.29520000 1.41790900
H -6.25625500 4.44981700 0.20138200
C -3.57142500 -1.21772700 -0.31151600
C -3.12623200 -2.13788900 0.67787400
C -4.63911900 -1.60885500 -1.16724700
C -3.71547300 -3.41835200 0.79713700
H -2.33617300 -1.83481400 1.37517600
C -5.22336000 -2.89142600 -1.05589300
H -5.00474100 -0.90434500 -1.92359600
C -4.76270400 -3.80292800 -0.07406700
H -3.36326300 -4.10998300 1.57157800
H -6.03766100 -3.17834200 -1.73154300
H -5.21929100 -4.79546000 0.01566700
H 3.04173400 -0.84883100 3.76500000
H -1.22617400 1.36654200 -0.72191900

Transition State TS3

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.98527 Hartree
H_corr: 2.378648 Hartree
SCF: -7398.573441 Hartree
S: 788.275 Cal/Mol-Kelvin
H: -7396.194793 Hartree
G: -7396.588171 Hartree

Cartesian Coordinates:
N -1.93839300 0.76217700 1.32012500
N 1.02926500 0.07955400 -1.21116100
N 0.80320700 1.29818700 1.31098300
N -1.71867600 -0.39892600 -1.22251900
C -1.43345500 -0.96990500 -2.48494200
C -3.13336500 -0.34376900 -1.17699800
C -3.31944000 0.54549000 1.10453300
C -1.87768100 1.33227700 2.61392800
C 0.51653000 1.87272200 2.57298600
C 2.15811600 1.63357500 1.07349700
C 2.37332200 0.48848800 -1.09168300
C 1.00300700 -0.69645300 -2.39589800
C 2.33121900 -0.79452600 -2.97848600
C -0.15286000 -1.19283700 -3.02561500
C -2.65585400 -1.23564000 -3.22278400
C -3.91117600 0.09416100 -0.08933000
C 3.17329100 -0.04736800 -2.18276200
C 2.91506000 1.27312900 -0.05571000
C 2.69042400 2.42417400 2.17299700

C -4.08972600 0.91912200 2.28215200
C -0.73178200 1.87234900 3.22686600
C 1.68394800 2.55654000 3.10567500
C -3.70382700 -0.82468400 -2.42625800
C -3.19837900 1.40272400 3.21529800
C -0.88837000 2.66588900 4.50439800
C -1.17009800 4.28657100 6.81218100
C -0.76903200 2.08438400 5.80939300
C -1.16711400 4.07092300 4.38858300
C -1.30784100 4.88433500 5.54302000
C -0.90656100 2.91186000 6.96318400
C -5.40969600 0.14618700 -0.21995100
C -8.22892200 0.31205400 -0.47684500
C -6.19187800 -1.03005400 -0.35775000
C -6.06307200 1.40808700 -0.21640800
C -7.47216800 1.50771800 -0.35228600
C -7.60504900 -0.96332800 -0.47838100
C -0.03056000 -1.78996800 -4.40673200
C 0.20705700 -2.79923000 -7.04130300
C 0.03847700 -3.20311100 -4.62961500
C 0.01504600 -0.89996000 -5.53267800
C 0.13418700 -1.40420300 -6.85432400
C 0.16050500 -3.70086900 -5.96015800
C 4.33369200 1.75761900 -0.17781100
C 6.97943800 2.72317200 -0.42534700
C 4.65419800 2.72532300 -1.16647300
C 5.35353000 1.27219600 0.68122900
C 6.69130900 1.73708700 0.55646400
C 5.97492500 3.22921200 -1.29176300
C -0.31856300 -0.04909500 7.10565500
N -0.52966300 0.68562900 5.92530100
C -1.58183800 5.92417500 2.67733600
N -1.29392200 4.61088300 3.07437100
C -0.02796800 1.57506700 -6.16631800
N -0.07746100 0.49804100 -5.26949700
C -0.00224500 -5.48489500 -3.52375700
N -0.01085600 -4.07899400 -3.50438200
C -0.10313300 -6.12759900 -2.17192800
C -0.80604900 -7.51119700 -2.09332000
C 0.69045700 -7.43812800 -1.80511300
C -0.14823400 2.91435800 -5.49715800
C 0.33642300 4.16665000 -6.26641400
C -1.16140800 4.00468400 -6.01594200
C -1.64144700 6.09590500 1.18577400
C -2.37908000 7.33145600 0.61690500
C -0.86147400 7.25678800 0.46011600

C	-0.13878900	-1.52199100	6.88146100
C	0.61569200	-2.33886600	7.95915300
C	-0.88082900	-2.58439900	7.77736700
C	-0.29961400	6.90222000	-0.92085300
C	0.02028000	8.20381800	1.27622400
C	-1.31200200	-3.86122600	7.04724700
C	-1.85048700	-2.12917800	8.86939800
C	1.13052800	-7.54711400	-0.34090900
C	1.67407200	-8.05877300	-2.79891800
C	-1.80432200	4.86969400	-4.92649900
C	-2.08400700	3.68305400	-7.19312300
H	-3.01777600	7.17905400	-0.25983500
H	-5.16964300	0.81535600	2.36840200
H	-4.76780700	-0.82982800	-2.65465500
H	3.70305400	2.81944100	2.21172500
H	-2.68504300	-1.65238200	-4.22850000
H	-3.39523200	1.78793600	4.21455500
H	4.24327600	0.11373800	-2.29736100
H	1.70183700	3.08148000	4.05949500
H	2.56733600	-1.35692100	-3.88024000
Co	-0.41278100	0.24941600	0.13742500
H	-1.51841200	5.94786200	5.42083800
H	-0.79621200	2.45481700	7.94719700
H	-1.27305100	4.90906400	7.70876000
H	-9.31974800	0.37558300	-0.57497400
H	0.16613600	-0.70283800	-7.68947100
H	0.20914200	-4.77917300	-6.11310800
H	0.29933000	-3.19627500	-8.05906300
H	8.00323500	3.10642800	-0.51601200
O	-0.27956700	0.47027100	8.27053200
O	-1.77153400	6.88463800	3.49178300
O	0.10031300	1.43954500	-7.42607500
O	0.06175200	-6.17460100	-4.59619700
H	-0.26197700	-5.43720400	-1.33798100
H	0.00551500	2.91541600	-4.40986200
H	0.70281400	3.96710600	-7.27897700
H	-1.71890500	5.16675900	0.60547800
H	-2.77448900	8.01591300	1.37486800
H	-0.00709300	-1.82183400	5.83790400
H	0.89705800	4.91969800	-5.70221200
H	-0.10149000	-3.64247300	-2.57408200
H	0.68706700	6.40766200	-0.83164000
H	-0.16509200	7.81949800	-1.52679300
H	-0.97588100	6.22552300	-1.47734100
H	1.03826100	7.78571900	1.40006100
H	-0.40307700	8.38758200	2.27774400

H 0.11358100 9.17413000 0.75050300
H 0.92675100 -1.76503500 8.83849800
H 1.33026900 -3.09402600 7.61267800
H -1.40204500 -4.70139300 7.76399400
H -0.58274100 -4.15459000 6.26863000
H -2.29676200 -3.72347100 6.56014100
H -1.91642100 -2.90323200 9.65934600
H -2.86709500 -1.97942300 8.45557600
H -1.52158800 -1.18277400 9.32954200
H -1.50367300 -7.67841500 -1.26480100
H -1.11333800 -7.92461700 -3.05973000
H 0.38428100 -7.10802200 0.34791500
H 2.09506800 -7.03325300 -0.16654600
H 1.26310900 -8.61078500 -0.06160900
H 2.68586900 -7.62530700 -2.67451800
H 1.34872300 -7.89856600 -3.83985800
H 1.75359700 -9.14795800 -2.61349200
H -1.09744800 5.08530100 -4.10280900
H -2.69343700 4.36906100 -4.49639300
H -2.13334500 5.83819400 -5.35118000
H -2.37165500 4.61970700 -7.70931700
H -3.01185400 3.18982800 -6.84332500
H -1.59182300 3.01846700 -7.92260700
H -0.50347400 0.12711500 5.05261700
H -1.15285400 3.94070900 2.31299700
H -0.18836800 0.74840000 -4.28255600
H -5.70395800 -2.01124100 -0.35318000
H -5.46515300 2.32330100 -0.12890500
H 5.10538100 0.52278600 1.44481300
H 3.86512800 3.10960300 -1.82445500
C 0.08823100 -1.59000000 1.03192200
C -0.17396100 -1.35749500 2.43744800
N -0.29281700 -1.14757300 3.60396900
C -0.84648600 -2.63413200 0.41640700
O -0.54580900 -3.31475700 -0.60014500
O -1.98523500 -2.78819100 1.17451300
C -2.94119700 -3.99565000 1.02268700
C -3.46027300 -4.11599100 -0.42454300
H -4.32629800 -4.80456700 -0.43515900
H -3.79252300 -3.13571800 -0.80582200
H -2.68918300 -4.50582400 -1.10581000
C -4.05920500 -3.62237400 2.01339500
H -3.64517300 -3.46777500 3.02458300
H -4.80754500 -4.43495700 2.05423200
C -2.16322800 -5.24631000 1.48259900
H -1.79864800 -5.12042500 2.51739100

H -1.30529800 -5.44708700 0.81895700
H -4.56394500 -2.69229300 1.70110800
H -2.83409300 -6.12491500 1.45452000
C -8.42561200 -2.22156100 -0.59723100
C -9.16244200 -2.70410100 0.52971800
C -8.47120400 -2.93786200 -1.83354100
C -9.92621800 -3.89140700 0.40046100
C -9.25312900 -4.11761300 -1.92247900
C -9.99115200 -4.61168600 -0.81854800
H -10.48310500 -4.26086600 1.27220600
H -9.28718100 -4.66014700 -2.87693200
C -8.14816800 2.85378000 -0.37371800
C -8.63079400 3.39134200 -1.60660600
C -8.30685200 3.59961900 0.83698700
C -9.26167700 4.66240100 -1.60753400
C -8.94821100 4.86177400 0.79293700
C -9.43369000 5.41386200 -0.41977900
H -9.62379500 5.07327000 -2.55946000
H -9.07062800 5.42674400 1.72704500
C 7.78417800 1.18629900 1.43424300
C 8.88221000 0.47403900 0.85153200
C 7.73659400 1.36239800 2.85554900
C 9.90294900 -0.04048400 1.69141300
C 8.78483100 0.84157500 3.65500400
C 9.88085200 0.13927800 3.09575600
H 10.73297100 -0.59689400 1.23506300
H 8.74115100 0.98898600 4.74265900
C 6.29954000 4.28450200 -2.31673200
C 6.47468300 5.64483200 -1.91212500
C 6.42612000 3.93276900 -3.69658500
C 6.77241300 6.62532400 -2.89203100
C 6.73006900 4.94294600 -4.64400300
C 6.91040300 6.29600200 -4.26355800
H 6.89701900 7.66985000 -2.57574300
H 6.82813000 4.66513200 -5.70217800
C -9.12783200 -1.97560700 1.86804800
H -9.63767000 -2.56493700 2.65032800
H -9.62816900 -0.99016600 1.80949500
C 8.97916300 0.22190300 -0.65038300
H 9.37092000 1.10512500 -1.19107400
H 7.99304300 -0.00901400 -1.09308100
C 6.58917500 2.09562700 3.53994600
H 5.70164600 1.44091800 3.63449100
H 6.28202100 2.99483400 2.97497100
C 6.24751900 2.49348700 -4.16510100
H 5.19551600 2.16116600 -4.07255500

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C 6.32775800 6.06008800 -0.45308500
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H 5.37043800 5.70731200 -0.02521600
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H -6.70145800 3.06079700 2.22359500
H -8.13541800 2.01471100 2.33585900
C -8.46481800 2.63614800 -2.92027800
H -7.41777000 2.31371100 -3.07389600
H -8.75931000 3.26793300 -3.77662500
H -8.18033700 3.67253400 3.00968800
H -9.08702700 1.72116000 -2.94810400
C -7.70147000 -2.45587800 -3.05754300
H -6.61112300 -2.61133900 -2.93915200
H -7.85515900 -1.37547300 -3.23644100
H -8.01726700 -3.00341600 -3.96283000
H -8.09018900 -1.78505800 2.20098800
H 6.36675400 7.15881500 -0.35041100
H 6.53960900 2.38482900 -5.22437100
H 6.87949800 2.41147900 4.55768600
H 9.66187200 -0.62108400 -0.85930500
C 11.00649800 -0.38675000 3.97542300
H 11.54975300 -1.21498700 3.48596700
H 10.62483000 -0.75323400 4.94600900
C -10.84902000 -5.86314800 -0.94495200
H -10.91085100 -6.41059700 0.01310200
H -10.44888100 -6.55365300 -1.70917200
C 7.26551200 7.35962000 -5.29359400
H 6.88164000 8.35308100 -4.99868500
H 6.85224900 7.11412400 -6.28864200
C -10.12268100 6.77151400 -0.43700400
H -10.36376400 7.08964600 -1.46661500
H -9.48494900 7.55258800 0.01903300
H -11.88490000 -5.60609600 -1.24361200
H -11.06888600 6.74800000 0.13791100
H 11.74538600 0.40986000 4.19400800
H 8.36415800 7.45215900 -5.40723800
C 1.53771100 -1.94787800 0.75935400
C 2.58407500 -1.80511700 1.58826600
C 3.06368200 -1.34880200 2.91383000
H 2.80415600 -2.09216100 3.70073100
H 2.64233600 -0.36926200 3.20968700
O 4.53344400 -1.11764800 2.93060900
C 5.30201600 -2.29156500 2.43876700
H 5.12109700 -3.17041200 3.08608200
H 6.34984200 -1.96127900 2.57197300

C	5.04003400	-2.57773700	0.97501600
C	4.96062800	-3.81373300	0.34573000
C	4.79127900	-5.10120900	1.09207800
C	5.60293500	-6.22897000	0.77296300
C	3.82046600	-5.24175700	2.12592000
C	5.47234400	-7.44212700	1.48562200
H	6.34595900	-6.14344100	-0.02859500
C	3.68474800	-6.45677700	2.83421500
H	3.14738200	-4.40303600	2.33865900
C	4.51581100	-7.56093300	2.52378300
H	6.11547600	-8.29309900	1.23222100
H	2.92572000	-6.54599600	3.62058800
H	4.41300400	-8.50275400	3.07534000
C	5.04329600	-3.87177200	-1.14694100
C	5.90061700	-2.99068800	-1.87189900
C	4.25337700	-4.79890800	-1.88921300
C	5.95195300	-3.02386400	-3.28293900
H	6.55489400	-2.30488500	-1.32011400
C	4.29468000	-4.82359400	-3.30064700
H	3.58732200	-5.48514800	-1.35368200
C	5.14405100	-3.93597000	-4.00571100
H	6.63077900	-2.34972700	-3.81906400
H	3.66028700	-5.52723300	-3.85152300
H	5.18053800	-3.96113300	-5.10093200
H	1.68892800	-2.41622500	-0.22503200
H	5.12420500	-1.68943600	0.33314500

Intermediate D

D$_{[Co(P6)]:}$

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.999184 Hartree
H_corr: 2.382282 Hartree
SCF: -7398.634908 Hartree
S: 767.675 Cal/Mol-Kelvin
H: -7396.252626 Hartree
G: -7396.635724 Hartree

Cartesian Coordinates:

N	-1.82690500	0.83607000	1.26940000
N	1.09482100	0.05531800	-1.30041300
N	0.94218200	1.23811800	1.24116100
N	-1.69321200	-0.21927300	-1.32188700
C	-1.45201500	-0.68970400	-2.63453000
C	-3.10198000	-0.10036700	-1.25122700
C	-3.21848000	0.67736500	1.07307500

C -1.72613300 1.37866600 2.57155800
C 0.68728000 1.82248200 2.50705700
C 2.31315800 1.50438800 1.00279300
C 2.46927700 0.34053900 -1.15824600
C 1.00108000 -0.62071100 -2.53864900
C 2.31648600 -0.80038300 -3.12966300
C -0.19400000 -0.94839900 -3.20701200
C -2.69436400 -0.82557500 -3.37596100
C -3.84652600 0.29979700 -0.12674700
C 3.22336800 -0.19938700 -2.27983800
C 3.05943000 1.07138900 -0.10864600
C 2.88054000 2.28265200 2.09297400
C -3.95637900 1.05213200 2.27150100
C -0.55238100 1.86188000 3.17710700
C 1.88498300 2.46096100 3.02933600
C -3.71140900 -0.44595000 -2.52724200
C -3.03378100 1.48786300 3.19672300
C -0.65496400 2.61588200 4.48333700
C -0.81213800 4.15138900 6.86139200
C -0.64910000 1.96494900 5.76152700
C -0.76966500 4.04732200 4.43077400
C -0.84865600 4.81786200 5.62010600
C -0.71597100 2.74987000 6.95072100
C -5.34319300 0.41769300 -0.23245900
C -8.15492900 0.70869000 -0.44689900
C -6.17347300 -0.71902200 -0.41308800
C -5.94414600 1.70381900 -0.16586700
C -7.34893900 1.86656200 -0.28185300
C -7.58411900 -0.59004900 -0.50987800
C -0.12830900 -1.40449400 -4.64357100
C -0.03188700 -2.16011500 -7.36966300
C -0.26791600 -2.77974100 -5.01198500
C 0.04496300 -0.41733200 -5.67211800
C 0.10044800 -0.79593600 -7.03917800
C -0.22050700 -3.15124000 -6.38688500
C 4.51897000 1.42238200 -0.19626500
C 7.25806000 2.10828300 -0.36261100
C 4.97768200 2.30146700 -1.21342600
C 5.44831500 0.89037700 0.73572100
C 6.82972800 1.21139500 0.65240700
C 6.34649700 2.66682900 -1.29747900
C -0.53548200 -0.26395500 6.96865400
N -0.59421100 0.54257800 5.81714800
C -0.92566000 6.01536500 2.80741700
N -0.80175800 4.65965200 3.14256900
C 0.30673100 2.09469500 -6.05277900

N	0.12848800	0.94670300	-5.26718900
C	-0.76282300	-5.10603400	-4.14622400
N	-0.41940000	-3.75202100	-3.97986900
C	-0.71788800	-5.91761200	-2.88759600
C	-1.63289000	-7.16759900	-2.79502500
C	-0.12418300	-7.37821900	-2.88259500
C	0.31233300	3.36823000	-5.25687000
C	0.90813800	4.63953300	-5.90636900
C	-0.59905500	4.58873600	-5.66436800
C	-0.90219300	6.26968700	1.32711900
C	-1.48805200	7.60157100	0.80006800
C	0.02063800	7.38352400	0.70181200
C	-0.58011300	-1.73661300	6.68543100
C	-0.01110300	-2.70556500	7.75018600
C	-1.51941400	-2.69762900	7.50880800
C	0.60854800	7.04766700	-0.67288200
C	0.95355800	8.19330100	1.60436200
C	-2.12398500	-3.85577800	6.70744200
C	-2.44493800	-2.13412400	8.58844700
C	0.61557000	-7.77322300	-1.60137200
C	0.47827000	-7.97683100	-4.15505600
C	-1.16640000	5.39851300	-4.49402500
C	-1.54326800	4.46283200	-6.86135600
H	-2.09650300	7.55960500	-0.10984600
H	-5.03789900	0.98610400	2.37306800
H	-4.77768200	-0.38447800	-2.73592800
H	3.90914000	2.63400200	2.12859200
H	-2.75543900	-1.14926700	-4.41383700
H	-3.20068700	1.86358700	4.20493500
H	4.30274800	-0.11203300	-2.39131400
H	1.93117500	2.98693900	3.98140200
H	2.49598500	-1.29963700	-4.08084900
Co	-0.33288600	0.27847000	0.05577100
H	-0.93577900	5.90276600	5.54530600
H	-0.68541400	2.23937900	7.91389800
H	-0.86437800	4.74007200	7.78477300
H	-9.24324600	0.82057800	-0.52965500
H	0.23530400	-0.02507500	-7.79942300
H	-0.35070700	-4.19944100	-6.65570400
H	0.00595900	-2.45880400	-8.42380400
H	8.31791100	2.38488200	-0.42202400
O	-0.45682800	0.19537800	8.15632100
O	-1.04131100	6.94885300	3.66600500
O	0.43975300	2.06970000	-7.31897900
O	-1.08526700	-5.61383900	-5.27078000
H	-0.54984700	-5.34734800	-1.96764200

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H 1.53169500 5.28339500 -5.27680400
H -0.31330100 -3.42590100 -3.00738200
H 1.53388300 6.44815700 -0.57130000
H 0.86462600 7.97742900 -1.21749400
H -0.10622200 6.47702000 -1.29597400
H 1.92140700 7.67189900 1.73825400
H 0.50924700 8.36038000 2.59963700
H 1.15977200 9.17798900 1.14124200
H 0.35246700 -2.22454800 8.66440500
H 0.58558600 -3.55348600 7.39503000
H -2.37454200 -4.69943700 7.38071900
H -1.42547900 -4.23098000 5.93573100
H -3.05515200 -3.53828500 6.19949700
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C 7.43576400 4.15870200 -4.66570800
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H 9.59741800 -1.54178100 -0.47185300
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H 10.35557400 -1.21003500 5.40779700
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H -11.14712200 -5.88810300 -0.19301300
H -10.74293900 -5.96355600 -1.93398600
C 8.23022800 6.48648500 -5.37262000
H 7.91201300 7.52035100 -5.14625900
H 7.86386300 6.22874600 -6.38272800
C -9.81874300 7.21620700 -0.14959100
H -9.75308200 7.72366800 -1.12875800
H -9.34850400 7.87015100 0.60733400
H -12.11096700 -4.96692400 -1.37503800

H	-10.89333200	7.13492500	0.10919800
H	11.65555100	-0.45990600	4.44634600
H	9.33783300	6.48505600	-5.41352500
C	1.49208100	-2.11993600	0.69008800
C	2.56269400	-2.04305000	1.53988600
C	2.69727300	-1.32480200	2.87889500
H	2.27714500	-1.91559300	3.72192500
H	2.24924600	-0.32241200	2.91056400
O	4.15984700	-1.15169000	3.07001000
C	4.78903500	-2.35816400	2.49239400
H	4.75744300	-3.19520500	3.21677500
H	5.83636600	-2.10443000	2.26737300
C	3.93703600	-2.66783800	1.20381200
C	4.01279700	-4.13243000	0.77599000
C	3.32493900	-5.19579300	1.50340600
C	3.20832400	-6.52100800	0.94727000
C	2.70077900	-4.98703800	2.78517400
C	2.56748000	-7.56341600	1.64195400
H	3.60298100	-6.71388300	-0.05522800
C	2.06386100	-6.03345100	3.47716500
H	2.72078100	-3.99963000	3.25143400
C	1.99831600	-7.33668600	2.92091900
H	2.49851700	-8.55537800	1.17992700
H	1.61772600	-5.83561200	4.45899400
H	1.50425200	-8.15037100	3.46383800
C	4.93555400	-4.43668800	-0.34106300
C	5.84341100	-5.54557200	-0.28304800
C	4.99450600	-3.59998200	-1.50255600
C	6.75286100	-5.80300200	-1.32959600
H	5.85939700	-6.17660800	0.61263500
C	5.89432600	-3.86998900	-2.55509900
H	4.29394800	-2.76201800	-1.60457300
C	6.78231900	-4.97138700	-2.47714700
H	7.44758700	-6.64721000	-1.24635500
H	5.89677500	-3.22722900	-3.44332100
H	7.48431000	-5.17667100	-3.29337600
H	1.62846600	-2.65677000	-0.25861900
H	4.38232900	-2.05640600	0.39494500

Transition State *Si*-TS3

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.991324 Hartree
H_corr: 2.378968 Hartree
SCF: -7398.568944 Hartree

S: 776.785 Cal/Mol-Kelvin
H: -7396.189976 Hartree
G: -7396.57762 Hartree

Cartesian Coordinates:

N	1.85688900	-0.78802900	1.33298000
N	-1.03732200	0.26142600	-1.15017400
N	-0.90524500	-1.13226900	1.28183600
N	1.73543000	0.49636000	-1.15459100
C	1.49876700	1.15918800	-2.38052200
C	3.13602500	0.28364700	-1.13593000
C	3.24974700	-0.69657700	1.11233700
C	1.74888900	-1.38662800	2.61121500
C	-0.66913200	-1.78753700	2.51462600
C	-2.26201900	-1.41732300	0.98662200
C	-2.40165100	-0.08448900	-1.07221400
C	-0.95295800	1.11925300	-2.27389400
C	-2.27145700	1.34550100	-2.84569200
C	0.24204300	1.54267000	-2.88893800
C	2.73434500	1.32466900	-3.12677200
C	3.87362300	-0.27814900	-0.07779700
C	-3.16059100	0.58068300	-2.11980000
C	-2.98658400	-0.94415600	-0.12220500
C	-2.84143000	-2.26251700	2.01945700
C	3.98795300	-1.16564200	2.27628100
C	0.56423500	-1.87527800	3.19304300
C	-1.86810200	-2.46908500	2.97366300
C	3.74008800	0.75968200	-2.37123400
C	3.05990900	-1.58287800	3.20632200
C	0.65597100	-2.73101600	4.43694800
C	0.81196400	-4.46464800	6.67483900
C	0.51503700	-2.20659600	5.76404100
C	0.88919900	-4.13890400	4.26452900
C	0.96811900	-5.00812400	5.38364500
C	0.58898000	-3.09016200	6.88154300
C	5.35385000	-0.50308100	-0.23430000
C	8.12712800	-1.00730600	-0.54487600
C	6.27496400	0.57164000	-0.33749400
C	5.84524300	-1.83544000	-0.28922500
C	7.22901500	-2.10387500	-0.45279200
C	7.66730200	0.33464000	-0.48471200
C	0.17147600	2.21517200	-4.23789900
C	-0.00045000	3.37721500	-6.81650600
C	0.40861100	3.61735000	-4.41156300
C	-0.11347700	1.40725200	-5.39242000
C	-0.20781400	1.98967700	-6.68327100

C	0.31238000	4.19294900	-5.71205700
C	-4.39221500	-1.44647800	-0.33020700
C	-6.93945600	-2.62652400	-0.64762900
C	-4.61457300	-2.40847900	-1.35160600
C	-5.46917800	-1.05288400	0.50635800
C	-6.76057100	-1.63671200	0.35831700
C	-5.88675000	-3.01396600	-1.51661800
C	0.08658000	-0.12248800	7.14409400
N	0.32089600	-0.80738900	5.93915000
C	1.29292900	-5.92808100	2.48352300
N	1.03054200	-4.62556600	2.93104300
C	-0.57457400	-0.99609600	-6.12897700
N	-0.26031100	0.00297000	-5.19602400
C	1.19893600	5.73838500	-3.27498400
N	0.72383900	4.41323300	-3.26954900
C	1.47149600	6.30985900	-1.91596000
C	2.60717500	7.36612300	-1.80492700
C	1.16834900	7.81559100	-1.57116800
C	-0.62079500	-2.37415100	-5.53364300
C	-1.36917600	-3.48605500	-6.30686900
C	0.15100000	-3.57967000	-6.19457900
C	1.37711400	-6.03856100	0.98749100
C	2.10057500	-7.26441800	0.38026100
C	0.58808200	-7.15194200	0.19948600
C	-0.02464600	1.36598800	6.98527800
C	-0.78549900	2.16354900	8.07263400
C	0.72608600	2.35185100	7.95822300
C	0.05944800	-6.72847000	-1.17517600
C	-0.32745000	-8.11406400	0.95874900
C	1.23827300	3.64168200	7.30758200
C	1.63257400	1.80359000	9.06166800
C	0.73646300	8.07536700	-0.12378100
C	0.48768300	8.72547000	-2.59506300
C	0.73725600	-4.59785900	-5.21077400
C	1.00693500	-3.34022500	-7.43977700
H	2.75891600	-7.08862500	-0.47732800
H	5.07348500	-1.16644200	2.35589800
H	4.79516900	0.65952200	-2.61838400
H	-3.86294100	-2.63459100	2.00645200
H	2.79792800	1.78617300	-4.11112200
H	3.22509600	-2.00715300	4.19547900
H	-4.23551200	0.47883400	-2.25763100
H	-1.92754500	-3.04703900	3.89453300
H	-2.46586600	1.98146800	-3.70783100
Co	0.38255800	-0.09944300	0.17683400
H	1.14669000	-6.07163700	5.21812100

H 0.46229000 -2.67496400 7.88202500
H 0.86695900 -5.13057000 7.54402000
H 9.20021200 -1.20162100 -0.66458100
H -0.43214500 1.35066300 -7.53868400
H 0.50460200 5.25918800 -5.82982900
H -0.07382900 3.83451200 -7.81012300
H -7.91814100 -3.10898100 -0.75492400
O -0.02403000 -0.69378800 8.27987700
O 1.44262400 -6.92663900 3.25967200
O -0.79175500 -0.76760800 -7.36283600
O 1.40821300 6.40471000 -4.34270200
H 1.34783600 5.61286000 -1.08133000
H -0.67547900 -2.41434600 -4.43760400
H -1.78437900 -3.17141300 -7.27022700
H 1.48389100 -5.08792600 0.44811100
H 2.46787200 -7.98802200 1.11568100
H -0.10188000 1.72010300 5.95324700
H -1.99451900 -4.17218900 -5.72574500
H 0.67341800 3.95575000 -2.34676400
H -0.91968700 -6.21971600 -1.08278100
H -0.08043800 -7.61665900 -1.82186400
H 0.75809900 -6.04210900 -1.69043800
H -1.33925000 -7.68085600 1.08137900
H 0.07293700 -8.34804400 1.95921400
H -0.42960100 -9.05937800 0.39079300
H -1.15417200 1.56337500 8.91121600
H -1.45297000 2.96565300 7.73770400
H 1.33537500 4.44243800 8.06722600
H 0.55322100 4.00329200 6.51764200
H 2.23478900 3.48420900 6.85132600
H 1.70068800 2.53612300 9.89007000
H 2.65715800 1.62872100 8.67852700
H 1.24646000 0.85207100 9.46307700
H 3.28921400 7.28820200 -0.95055600
H 3.07297200 7.63888700 -2.75775800
H 1.27777200 7.42692100 0.59045100
H -0.34734300 7.89746900 0.00476000
H 0.94640900 9.12792700 0.15218500
H -0.61365800 8.63431300 -2.52379700
H 0.79046400 8.47170400 -3.62385600
H 0.75560300 9.78132900 -2.39280700
H 0.08033700 -4.74737900 -4.33302200
H 1.73058500 -4.27010100 -4.84730900
H 0.86540200 -5.57949900 -5.70733400
H 1.09113400 -4.27898100 -8.02133200
H 2.03006100 -3.02186900 -7.15980400

H 0.56801100 -2.56462200 -8.08928300
H 0.35285800 -0.20670500 5.09424800
H 0.92611500 -3.91971900 2.19656300
H -0.11572700 -0.32030100 -4.23516200
H 5.91491400 1.60486500 -0.28260400
H 5.13901200 -2.67207100 -0.22541800
H -5.29826400 -0.28470000 1.27110800
H -3.78203600 -2.71621100 -1.99614500
C 0.04972600 1.74663100 1.15780100
C 0.22479200 1.39409600 2.55126700
N 0.27253400 1.11120400 3.70723900
C 1.14501400 2.68792200 0.64538800
O 0.97922500 3.47950000 -0.32064100
O 2.26792900 2.61204200 1.43828000
C 3.38765500 3.67858200 1.42276800
C 3.96780000 3.85891800 0.00517800
H 4.93847500 4.38463300 0.08249200
H 4.14096500 2.88045300 -0.47305600
H 3.30013500 4.44306800 -0.64466100
C 4.41090900 3.05896500 2.39218100
H 3.93982800 2.84319700 3.36646500
H 5.24856400 3.76328900 2.54838800
C 2.77297700 4.97543100 1.98916100
H 2.38030100 4.80827300 3.00763200
H 1.95552100 5.34125100 1.34484700
H 4.81320300 2.11547400 1.98544000
H 3.55111100 5.75954700 2.03995400
C 8.63771500 1.48450800 -0.56432900
C 9.45613000 1.80855400 0.56310800
C 8.74536900 2.25584000 -1.76332900
C 10.36166900 2.89557200 0.47171900
C 9.66872800 3.33078700 -1.81521100
C 10.48931600 3.66719300 -0.71020700
H 10.98097600 3.14414400 1.34419200
H 9.74909900 3.91599300 -2.74126700
C 7.73114300 -3.52177800 -0.53393900
C 8.13225600 -4.06753100 -1.79245400
C 7.80307900 -4.32831900 0.64553700
C 8.59690000 -5.40682400 -1.84934300
C 8.27872900 -5.65908300 0.54558500
C 8.68281700 -6.21946400 -0.69260400
H 8.89547400 -5.82313000 -2.82082200
H 8.33382800 -6.27169000 1.45568700
C -7.90956200 -1.23244300 1.24414500
C -9.15318800 -0.79782100 0.67679000
C -7.78349900 -1.29254700 2.67496000

C -10.21824200 -0.41727600 1.53456800
C -8.87887600 -0.91447300 3.48868700
C -10.10612600 -0.46366800 2.94263700
H -11.15902900 -0.07327800 1.08340200
H -8.77017000 -0.97968400 4.57996000
C -6.10712400 -4.06282400 -2.57523800
C -6.17833200 -5.44385200 -2.21141200
C -6.23905900 -3.68263700 -3.94728200
C -6.37967700 -6.41664900 -3.22337100
C -6.44340300 -4.68644600 -4.92755700
C -6.52046100 -6.06020900 -4.58769000
H -6.42514900 -7.47642500 -2.93804000
H -6.54617400 -4.38688500 -5.97934000
C 9.36002700 1.02002600 1.86400900
H 9.95364700 1.50170000 2.66078000
H 9.73527400 -0.01413500 1.74363300
C -9.40457400 -0.71073800 -0.82672000
H -9.86318200 -1.64167900 -1.21519300
H -8.47817500 -0.54488000 -1.40114100
C -6.51748200 -1.78497200 3.36817700
H -5.74545200 -0.99360000 3.41739200
H -6.07478000 -2.65091000 2.84301300
C -6.17586200 -2.22023200 -4.37167100
H -5.16889300 -1.78951400 -4.21266200
H -6.88375700 -1.60010100 -3.78959700
C -6.02267400 -5.88876100 -0.76195900
H -6.87276100 -5.55434600 -0.13730000
H -5.10886900 -5.46618600 -0.30338500
C 7.38580300 -3.78143300 2.00559100
H 6.28984300 -3.63720000 2.06835700
H 7.85184500 -2.79899300 2.20932000
C 8.05093300 -3.24718600 -3.07465500
H 7.05055400 -2.79270800 -3.20345000
H 8.25903800 -3.87664300 -3.95765700
H 7.67610300 -4.47452200 2.81444400
H 8.78086500 -2.41517500 -3.07556400
C 7.89266100 1.94290300 -2.98735000
H 6.83679800 2.24087800 -2.83423600
H 7.89240600 0.86157300 -3.21861800
H 8.26313200 2.48524200 -3.87487400
H 8.31382400 0.93883800 2.21431500
H -5.96634700 -6.98929400 -0.69168600
H -6.42180600 -2.10915300 -5.44222200
H -6.74206700 -2.09399000 4.40462100
H -10.10432200 0.11473800 -1.05048800
C -11.25496100 -0.03478600 3.84440100

H -11.04896400 0.94783200 4.31313900
H -11.41614500 -0.75896300 4.66486300
C 11.49616200 4.80578900 -0.79876300
H 12.47462300 4.44262300 -1.17168600
H 11.67302000 5.26808100 0.18926100
C -6.77106800 -7.11847300 -5.65338300
H -7.85696700 -7.27994400 -5.80578900
H -6.33145100 -8.09167600 -5.36912700
C 9.20651800 -7.64706800 -0.76898900
H 10.22770700 -7.72062100 -0.34554100
H 9.25277300 -8.00580600 -1.81252700
H 11.15443500 5.59642400 -1.49103900
H 8.56600100 -8.34370900 -0.19653200
H -12.19991100 0.05723500 3.28003600
H -6.34402000 -6.82103100 -6.62832200
C -1.32280700 2.33899400 0.88832400
C -2.42548600 2.20933400 1.64842200
C -3.00922900 1.48870400 2.80668600
H -2.73756900 1.97460000 3.77075600
H -2.69631200 0.43006800 2.85135400
O -4.48441400 1.43492600 2.66637000
C -5.07324700 2.80650700 2.75699100
H -5.12024600 3.06833800 3.83666700
H -6.09572300 2.68687700 2.36584700
C -4.31329000 3.90505200 2.03296500
H -3.52028600 4.39409100 2.61565700
C -4.74312100 4.57516700 0.88722800
C -4.17006900 5.91770900 0.56189800
C -3.93732700 6.31265500 -0.78932500
C -3.87202000 6.85572500 1.59521700
C -3.42845000 7.59357300 -1.09452000
H -4.14930900 5.60513000 -1.59878600
C -3.36662100 8.13871500 1.29008900
H -4.08410300 6.59133400 2.63810200
C -3.14475500 8.51598000 -0.05713200
H -3.25309000 7.87224200 -2.14010000
H -3.16291500 8.84997600 2.09925200
H -2.76392100 9.51586000 -0.29534000
C -5.77782200 4.01474400 -0.02784400
C -6.74517100 4.86310000 -0.64727200
C -5.82319700 2.61904100 -0.31147100
C -7.72618800 4.33223100 -1.51228000
H -6.73225800 5.93821100 -0.43490600
C -6.80237700 2.09166300 -1.18018000
H -5.07104700 1.95903600 0.13476300
C -7.75800100 2.94218300 -1.78572100

H	-8.46546600	4.99938100	-1.97090900
H	-6.81525400	1.01456100	-1.38098100
H	-8.51578500	2.52997200	-2.46234000
H	-1.34489200	2.99135300	0.00220600

Intermediate *Si*-D

***Si*-D**[Co(P6)]:

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.99489 Hartree
H_corr: 2.381781 Hartree
SCF: -7398.620689 Hartree
S: 775.276 Cal/Mol-Kelvin
H: -7396.238908 Hartree
G: -7396.625799 Hartree

Cartesian Coordinates:

N	1.72659600	-0.92825600	1.30683300
N	-1.11559500	0.43411600	-1.07227800
N	-1.04796700	-1.11464700	1.26268200
N	1.66275100	0.50513200	-1.09942300
C	1.45995200	1.26259700	-2.27463500
C	3.04387900	0.18886400	-1.12116400
C	3.11817400	-0.92855900	1.06263900
C	1.59666300	-1.58755900	2.55226700
C	-0.83933400	-1.84918500	2.45624000
C	-2.41582700	-1.32580900	0.95461400
C	-2.49230300	0.12917700	-1.02553700
C	-0.98905200	1.34845800	-2.14700500
C	-2.29222900	1.64500500	-2.72041000
C	0.22424600	1.75143900	-2.74192800
C	2.69446300	1.38979400	-3.03007000
C	3.75285700	-0.49252700	-0.11530300
C	-3.21206300	0.86693900	-2.05212600
C	-3.11827100	-0.75381700	-0.12211600
C	-3.02701400	-2.20970100	1.93469000
C	3.83954100	-1.51306000	2.18435100
C	0.39042200	-2.03621600	3.12125600
C	-2.06446800	-2.50794900	2.87525100
C	3.66492800	0.70105100	-2.33338200
C	2.89913500	-1.90838000	3.11133800
C	0.44309800	-2.96179400	4.31660300
C	0.52055300	-4.81780600	6.45858300
C	0.35648300	-2.50054600	5.67144600
C	0.58378500	-4.37047800	4.06734000
C	0.62308800	-5.30091900	5.13828900

C 0.38958800 -3.44480500 6.74019700
C 5.20638400 -0.82921800 -0.31738700
C 7.92098700 -1.54822600 -0.71485800
C 6.21518800 0.16724200 -0.37567100
C 5.58043800 -2.19275900 -0.46172300
C 6.93309700 -2.56785400 -0.66935000
C 7.57942800 -0.17825500 -0.56600100
C 0.18050100 2.51010500 -4.04570800
C 0.01055200 3.84940900 -6.53915400
C 0.53716000 3.89459300 -4.14460100
C -0.20307600 1.80388900 -5.23884300
C -0.29807900 2.47571300 -6.48523800
C 0.43440800 4.56089300 -5.40039400
C -4.55510200 -1.15126600 -0.33378500
C -7.19275400 -2.10474300 -0.69169200
C -4.88351900 -1.94893000 -1.46243600
C -5.57185200 -0.81173300 0.59883900
C -6.90601800 -1.28060700 0.43159200
C -6.20114900 -2.44024400 -1.65008000
C 0.08157200 -0.46926000 7.16390300
N 0.25636400 -1.10307600 5.92181800
C 0.84943400 -6.08444800 2.18900700
N 0.67588600 -4.79378300 2.70813800
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C	-6.26138100	2.35566400	-1.03520500
H	-4.70901800	1.98876300	0.42702900
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H	-7.03659200	5.41207300	-2.41035000
H	-6.56309600	1.30231200	-1.05394100
H	-7.74037300	2.99123800	-2.51730200
H	-1.13851700	3.34093500	0.36766800

Intermediate E

$\mathbf{E}_{[Co(P6)]} = \mathbf{A}_{[Co(P6)]}$

$\mathbf{E}_{[Co(P6)]\text{-}(+)\text{-}3a}$

Temperature: 313.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.366029 Hartree
H_corr: 0.461822 Hartree
SCF: -1248.682707 Hartree
S: 191.956 Cal/Mol-Kelvin
H: -1248.220885 Hartree
G: -1248.316678 Hartree

Cartesian Coordinates:

C	2.43186400	-1.57959700	2.46961800
O	2.25212600	-2.61470300	1.42583900
C	0.98823200	-2.33601900	0.70657500
C	0.73208800	-0.82187300	0.83418300
H	1.97631500	-1.89926800	3.43074300
H	3.52270500	-1.46890400	2.59859700
H	1.13859200	-2.70747100	-0.31954300
H	0.14762700	-2.88965100	1.17186800
C	1.72464500	-0.32983400	1.95248800
C	1.97013400	0.14723600	0.52614500
H	1.36372700	0.39694100	2.68783100
C	1.66900200	1.61245000	0.22787800
C	2.09318700	2.62999800	1.12135700
C	1.03700800	1.99024300	-0.98652400

C 1.88629200 3.99557100 0.81268000
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C 0.82545400 3.35218000 -1.29534100
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H -6.24358200 -2.08729600 -0.58190300

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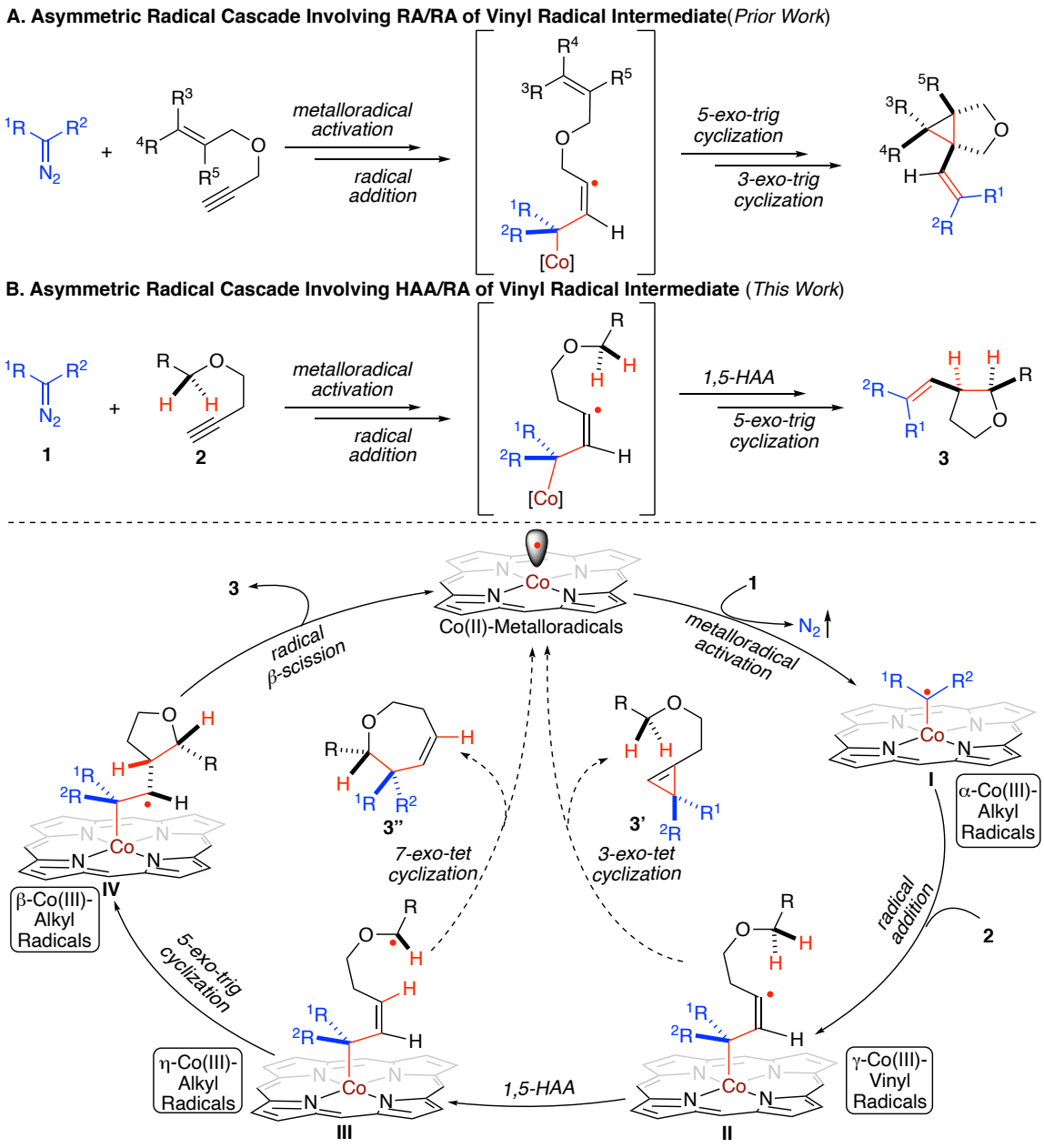
CHAPTER 3

ASYMMETRIC RADICAL CASCADE INVOLVING HYDROGEN-ATOM ABSTRACTION FOR STEREOSELECTIVE SYNTHESIS OF A,B-DISUBSTITUTED TETRAHYDROFURANS

3.1. INTRODUCTION

Radical cascade reactions have found wide use in the field of synthetic chemistry due to their notable compatibility with polar functional groups and ability to reduce time and cost associated with complex molecule synthesis.[1] Among all the radical cascade reactions, the tandem hydrogen-atom abstraction/radical addition (HAA/RA) processes have attracted considerable attention over the past few years as a highly regioselective and efficient approach toward functionalization of remote C(sp^3)–H bonds and construction of ring structures with different sizes and substitutions.[2] However, such processes triggered by vinyl radicals are rare due to limited strategies for the generation of vinyl radicals. At the same time, control of selectivities especially enantioselectivity of such processes also remains challenging.[3] Among recent advances,[4] metalloradical catalysis (MRC) provides a novel approach for generating radical intermediates and controlling selectivity of radical processes by utilizing metal-centered radicals as the catalyst.[1g, 5,6,7] As stable 15e metalloradicals, Co(II) complexes of porphyrins have been demonstrated to be effective catalysts for forming γ-Co(III)-vinyl radical intermediates through radical addition of α-Co(III)-alkyl radicals.[8] The supporting environment provided by the chiral porphyrin ligands could serve to control the stereochemistry of radical reactions. Recently, [Co(D_2-Por*)] has been demonstrated to catalyze enantioselective radical cascade bicyclization of 1,6-enynes with diazo compounds

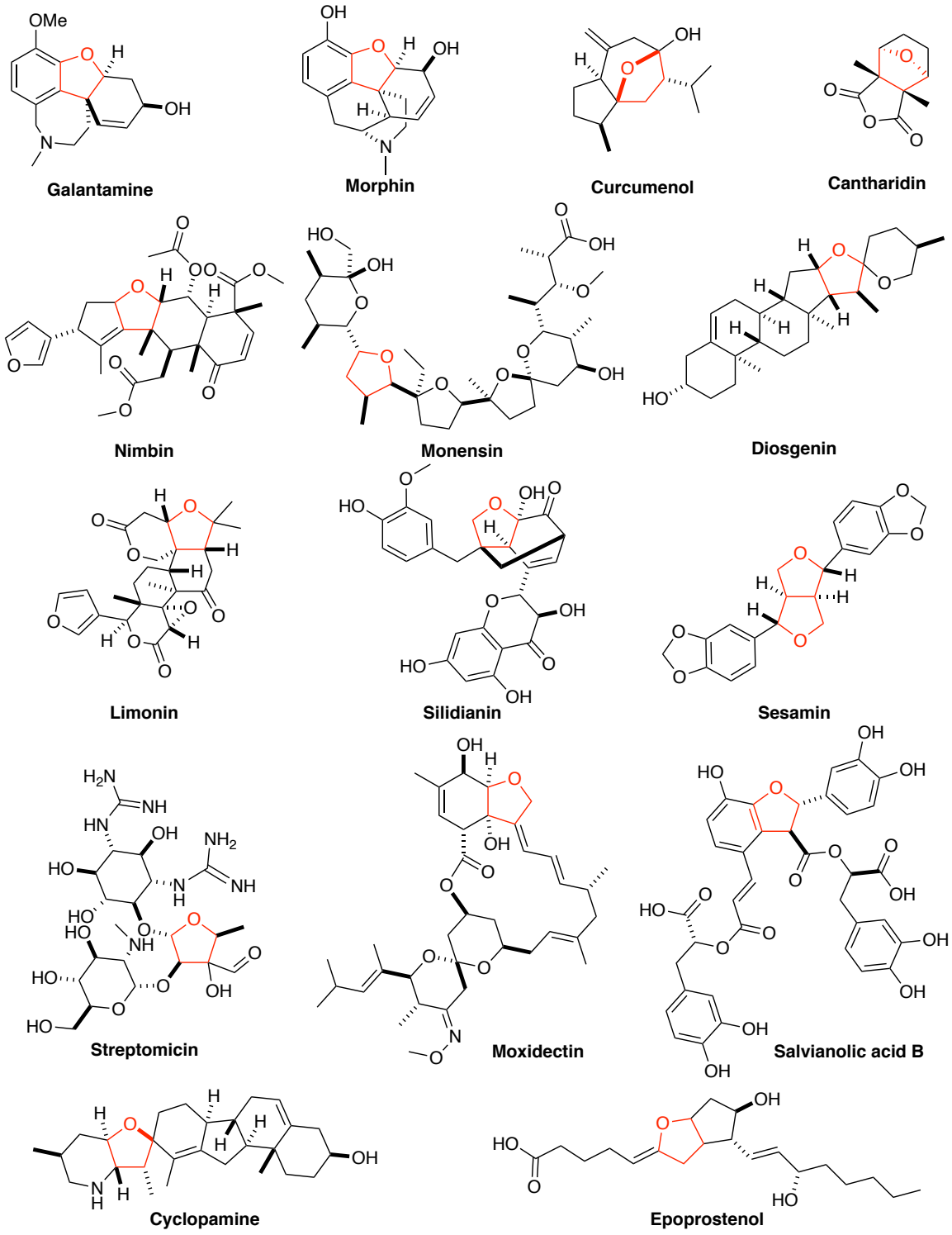
Scheme 3.1. Working Proposal for Radical Cascade Process Involving H-Atom Abstraction via Co(II)-Based MRC



(Scheme 3.1A).[8a] Instead of furnishing cyclopropenes through radical substitution, the γ-Co(III)-vinyl radicals generated from radical addition by Co-stabilized C-centered radicals to the carbon-carbon triple bonds could further go through radical cyclizations twice to realize cascade processes and produce enantioenriched bicyclo[3.1.0]hexane

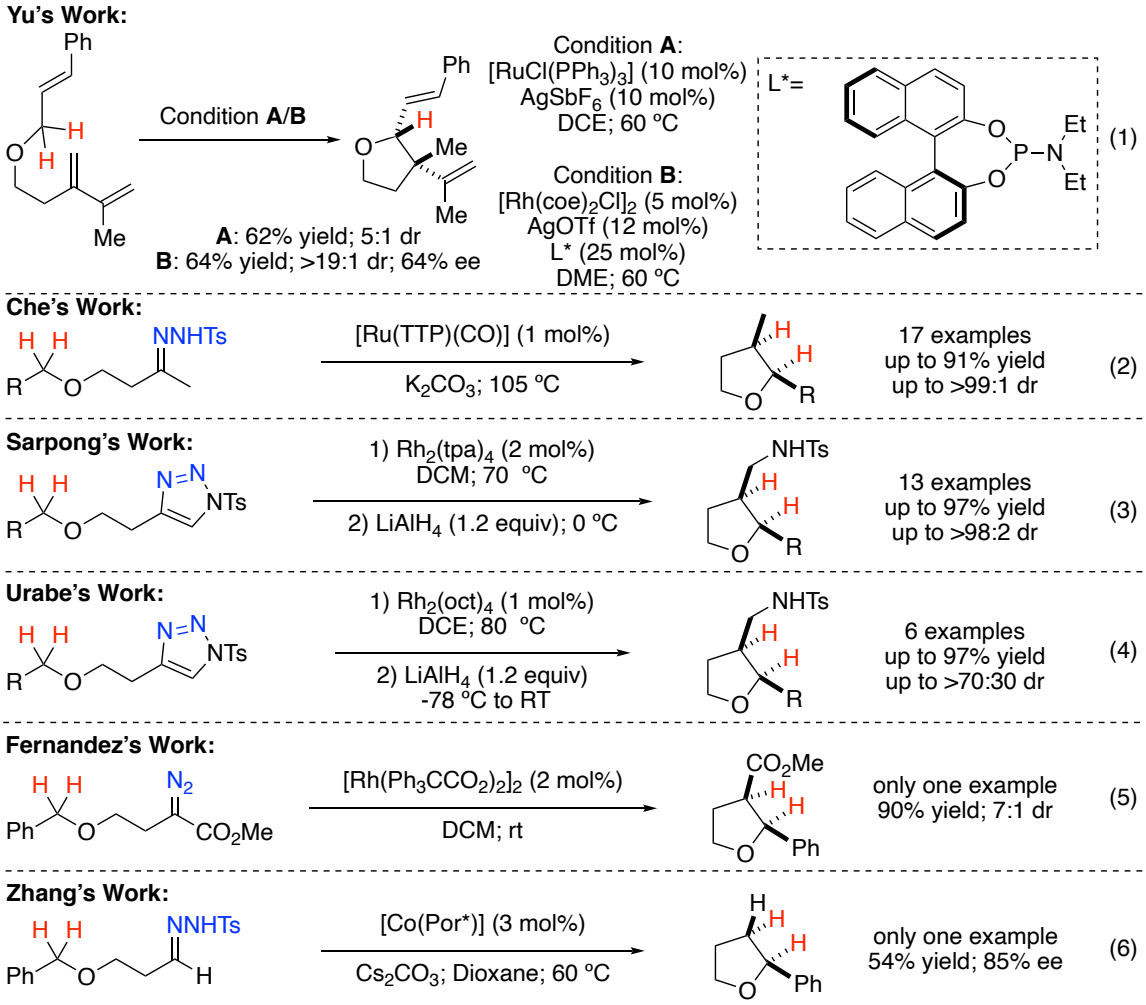
structures that are otherwise difficult to synthesis based on literature methods. Inspired by this work, we sought to develop a cascade reaction involving both hydrogen-atom abstraction and radical addition processes triggered by γ-Co(III)-vinyl radical **II**. To realize this idea, we were interested in developing asymmetric radical cascade process of homopropargylic ethers **2** with diazo compounds **1** for stereoselective construction of α, β-disubstituted tetrahydrofurans **3** (Scheme 3.1B). However, to avoid the production of undesired cyclopropenes **3'**, the vinyl radical intermediate **II** would be required to undergo competitive 1,5-HAA for the formation of ε-Co(III)-alkyl radicals **III** over the previously demonstrated *3-exo-tet* radical cyclization. Moreover, the subsequent *5-exo-trig* radical cyclization of the alkyl radical intermediate **III** followed by β-scission of the resulting β-Co(III)-alkyl radicals **IV** to release the product and generation of Co(II) might also face competitive *7-exo-tet* radical cyclization. Along with the breaking and formation of multiple bonds, the proposed radical cascade process, which involves both HAA and RA as the key steps, would create two stereogenic centers and one tri-substituted alkene in the resulting α, β-disubstituted tetrahydrofurans. Besides the aforementioned reactivity issues, how to control stereoselectivities in this cascade process, including enantioselectivity and diastereoselectivity for the two chiral centers as well as (*E*)/(*Z*)-selectivity for the C=C bond, is an equally important question. We hoped that these and related challenges could be addressed by fine-tuning the D_2-Por* ligand platform to adopt proper steric and electronic properties and chiral environments to govern the stereochemical course of the desired catalytic process. If realized, it would provide a novel strategy in enantioselective radical cascade process for stereoselective synthesis of substituted tetrahydrofurans, which have shown broad utilities (Figure 3.1).[9]

Figure 3.1. Selected Examples of Natural Products and Bioactive Compounds Containing Tetrahydrofurans



Catalytic cyclization of acyclic aliphatic ethers through intramolecular C–H bond alkylation, where the cyclization and the generation of stereocenters occur in the same step, represents an attractive approach to construct substituted tetrahydrofurans (Scheme 3.2). In 2010, Yu and Li developed a Rh-catalyzed allylic C–H activation/cyclization sequence for the construction of 5-membered heterocycles (Scheme 3.2; eq 1).[10] Such reaction was utilized in the formation of 2,3-disubstituted tetrahydrofuran with one example. Later, the same group reported an enantioselective version of this type of reactions by utilizing chiral phosphoramidites as ligands.[11] However, this strategy was applied to only one example of substituted tetrahydrofuran in good yield with excellent diastereoselectivity but moderate enantioselectivity. Transition-metal-catalyzed intramolecular carbene insertion into *a*-C–H bonds of ethers has been established by the Che, Sarpong, Urabe, and Fernandez groups using hydrazone, triazole or diazo as carbene precursors (Scheme 3.2; eq 2–5).[12] Despite the broad substrate scope and/or excellent diastereoselectivity, none of these reactions were rendered enantioselective. More recently, our group showcased one example of constructing tetrahydrofuran structure by metalloradical induced C–H alkylation in moderate yield with good enantioselectivity (Scheme 3.2; eq 6).[13] Although these intramolecular cyclizations exhibit high efficiency, tedious preparation of substrates is needed in most cases due to the requirement for preinstallation of diazo equivalents. Our proposed reaction, on the other hand, employs readily available start materials (one step from commercially available homopropargyl alcohol in most cases) because of the intermolecular nature. Furthermore, in comparison with most of the previous synthesis, the dangling trisubstituted alkene unit at 3-position generated in our proposed reaction can provide additional opportunities for further

Scheme 3.2. Previous Strategies for Constructing Substituted Tetrahydrofurans through Intramolecular C–H Alkylation of Acyclic Aliphatic Ethers



elaboration of the products. More importantly, enantioselective synthesis of tetrahydrofuran derivatives through intramolecular C–H alkylation has not been fully studied yet. As a novel application of Co(II)-based MRC, we herein describe the development of asymmetric radical cascade process of homopropargylic ether with diazo compounds that enables stereoselective construction of α, β-disubstituted tetrahydrofurans bearing two contiguous stereogenic centers. In addition to practical attributes such as operational simplicity and mild conditions, we show that the Co(II)-

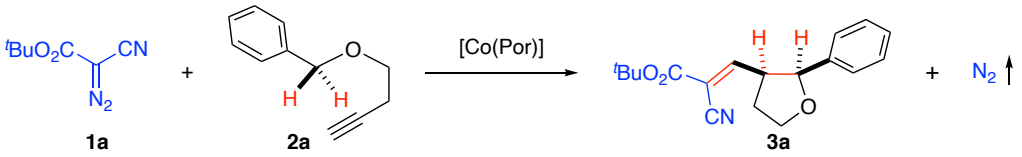
catalyzed cascade proceeds through a fundamentally different mechanism from previous catalytic systems. Our combined experimental and computational studies indicate a stepwise radical mechanism that involves several different Co-supported C-centered radicals, including α-, β-, γ- and η-Co(III)-alkyl radicals. A series of further transformations of the enantioenriched α,β-disubstituted tetrahydrofurans are shown to demonstrate the synthetic utilities.

3.2. RESULTS AND DISCUSSION

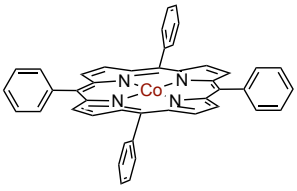
3.2.1. Condition Optimization for Enantioselective Radical Cascade Involving HAA of Homopropargyl Ethers with α-Cyano Diazoacetate

At the outset of this project, homopropargyl ether **2a** was chosen as the model substrate to explore the proposed radical cascade process with *tert*-butyl α-cyanodiazoacetate (**1a**) as the radical precursor (Scheme 3.3). Simple achiral catalyst [Co(**P1**)] (**P1** = tetraphenylporphyrin) was shown to produce low yield of the desired product (22%) with no diastereoselectivity (50:50 dr). Excitingly, when achiral amidoporphyrins catalyst [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin) was used,[14] it could catalyze the radical cascade process to construct disubstituted tetrahydrofuran **3a** in 37% yield with improved diastereoselectivity (34:66 dr). The difference in reactivity and diastereoselectivity between [Co(**P1**)] and [Co(**P2**)] might be due to the potential hydrogen bonding interaction between amide units of the porphyrin and the diazo compounds, which could stabilize the Co(III)-alkyl radicals. Encouraged by these initial results, we further investigated the enantioselectivity of the Co(II)-catalyzed intermolecular radical cascade cyclization. When chiral metalloradical catalyst [Co(**P3**)] (**P3** = 3,5-Di^{t}Bu-ChenPhyrin) was utilized,[15] yield was further increased and more

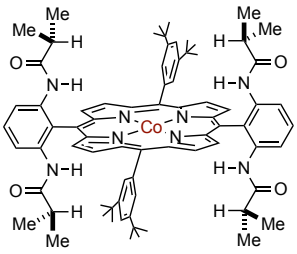
Scheme 3.3. Ligand Effect on Co(II)-Catalyzed Radical Cascade Process Involving H-Atom Abstraction of Homopropargylic Ether with *tert*-Butyl α-Cyanodiazoacetate[a]



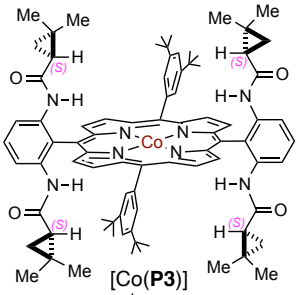
entry	catalyst	yield	dr	ee
1	[Co(**P1**)]	28%	50:50	—
2	[Co(**P2**)]	37%	34:66	—
3	[Co(**P3**)]	44%	55:45	77%
4	[Co(**P4**)]	47%	55:45	-43%
5	[Co(**P5**)]	0%	—:—	—
6	[Co(**P6**)]	38%	50:50	-38%



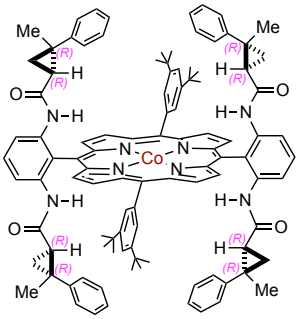
[Co(**P1**)]
(**P1** = Tetraphenylporphyrin)



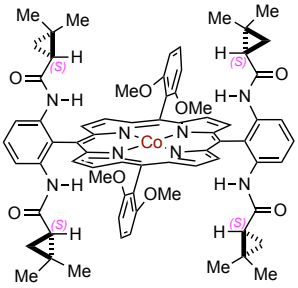
[Co(**P2**)]
(**P2** = 3,5-Di*t*Bu-IbuPhyrin)



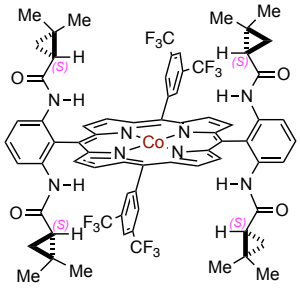
[Co(**P3**)]
(**P3** = 3,5-Di*t*Bu-ChenPhyrin)



[Co(**P4**)]
(**P4** = 3,5-Di*t*Bu-QingPhyrin)



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



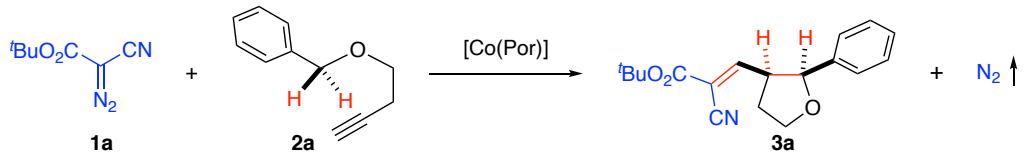
[Co(**P6**)]
(**P6** = 3,5-CF_3-ChenPhyrin)

[a]Carried out with **1a** (0.12 mmol) and **2a** (0.10 mmol) by [Co(Por)] (5 mol %) in MeOH (0.5 mL) at 20 °C for 24 h; isolated yields; configuration of all alkenes determined to be > 95:5 of (*E*):(*Z*); diastereomeric ratio determined by ^{1}H NMR. enantiomeric excess (ee) determined by chiral HPLC.

importantly, 77% ee was observed for the desired product. It is worth mentioning that both IbuPhyrin and ChenPhyrin ligands **P2**–**P3** could be synthesized in three

straightforward steps from readily available starting materials. However, the optimization of enantioselectivity of this reaction was challenging. A variety of ligand structures with different steric bulkiness and electronic properties of both chiral and non-chiral substituents on the porphyrin ligands were tested ([Co(**P4**)] – [Co(**P6**)]). None of those catalysts provided better results comparing with [Co(**P3**)]. After extensive exploration of solvents, a significant improvement of diastereoselectivity was observed when methanol was used (Scheme 3.4). The yield could be further improved by increasing the catalyst loading to 5 mol% while maintaining the high level of diastereo- and enantioselectivity.

Scheme 3.4. Optimization of Reaction Conditions on Co(II)-Catalyzed Radical Cascade Cyclization of Homopropargylic Ether with *tert*-Butyl α-Cyanodiazoacetate[a]



entry	solvent	catalyst loading	yield	dr	ee
1	Toluene	2 mol %	44	55:45	77
2	Benzene	2 mol %	36	56:44	71
3	Chlorobenzene	2 mol %	40	50:50	78
4	Diethyl ether	2 mol %	28	57:43	79
5	Dichloromethane	2 mol %	43	56:44	77
6	*n*-Hexane	2 mol %	62	73:27	84
7	Acetonitrile	2 mol %	28	57:43	83
8	Methanol	2 mol %	29	90:10	86
9	Methanol	5 mol %	53	91:9	86

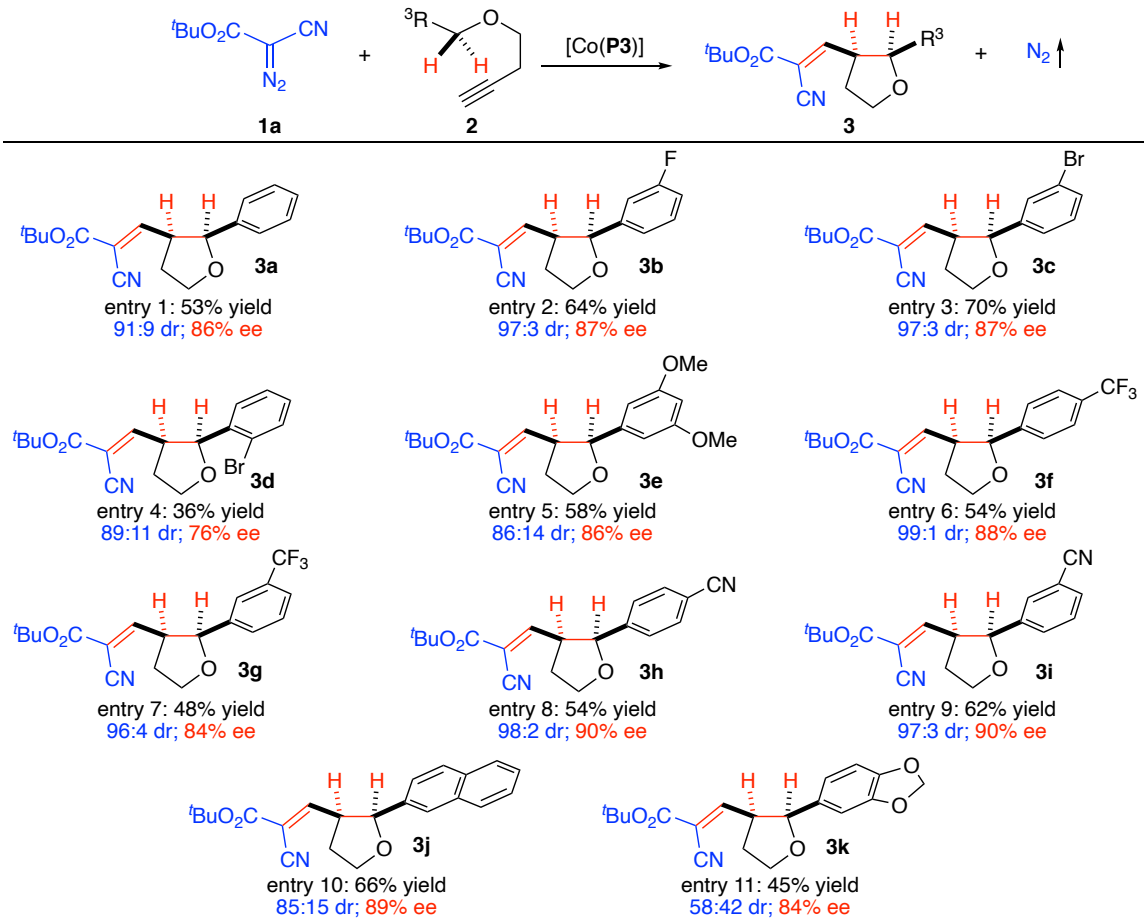
[a]Carried out with **1a** (0.12 mmol) and **2a** (0.10 mmol) by [Co(**P3**)] in solvent (0.5 mL) at 20 °C for 24 h; isolated yields; configuration of all alkenes determined to be > 95:5 of (*E*):(Z); diastereomeric ratio determined by ^{1}H NMR. enantiomeric excess (ee) determined by chiral HPLC

3.2.2. Enantioselective Radical Cascade Reaction of Different Substrates

Under the optimized conditions, the scope of the [Co(**P3**)]/**1a**-based catalytic system was then evaluated by employing different alkynes (Table 3.1). In addition to homopropargyl ether **2a**, the Co(II)-catalyzed cascade process was suitable for aryl derivative bearing fluro-atom at *meta*- position, affording desired product **3b** in good yields with high diastereoselectivities and enantioselectivities (Table 3.1; entry 2). Additionally, this [Co(**P3**)]-based metalloradical system was shown to tolerate bromo-atom at different positions of the aryl group as exemplified by the stereoselective formation of **3c** and **3d** (Table 3.1; entries 3 and 4), which can be readily further functionalized by coupling reactions. Besides, substrates containing benzylic C–H bond with electron-donating substituents on the aryl group deliver optically active compounds **3e** in good yields with high levels of diastereoselectivities as well as enantioselectivities (Table 3.1; entry 5). In addition to the electron-donating group, electron-withdrawing aryl substituents could be regio- and chemoselectively cyclized to form tetrahydrofurans **3f**–**3i** in good yields with excellent stereoselectivities (Table 3.1; entries 6–9). Furthermore, homopropargyl ether substrates containing extended aromatic group were also compatible with the radical cascade process, bringing corresponding **3j** in high yield with high stereoselectivities (Table 3.1; entry 10). Notably, substrates containing heterocycle could also be catalyzed to form the tetrahydrofuran **3k** in high enantiopurity (Table 3.1; entry 11). In addition to benzylic C–H bonds, allylic C–H bonds in 1,7-enynes could also be functionalized under optimized conditions. Of note, to demonstrate the robustness of this reaction, a radical cascade process of **2l** was carried out on a 3.0 mmol scale, which

furnished the desired bisvinyl tetrahydrofuran with equally good results (Table 3.2; entry 1). Furthermore, 1,7-enynes containing aryl groups (**2m**–**2t**) that are substituted by

Table 3.1. Asymmetric Synthesis of α,β-Disubstituted Tetrahydrofurans by [Co(P3)]-Catalyzed Radical Cascade Involving H-Atom Abstraction of Benzylic C–H bonds[a]

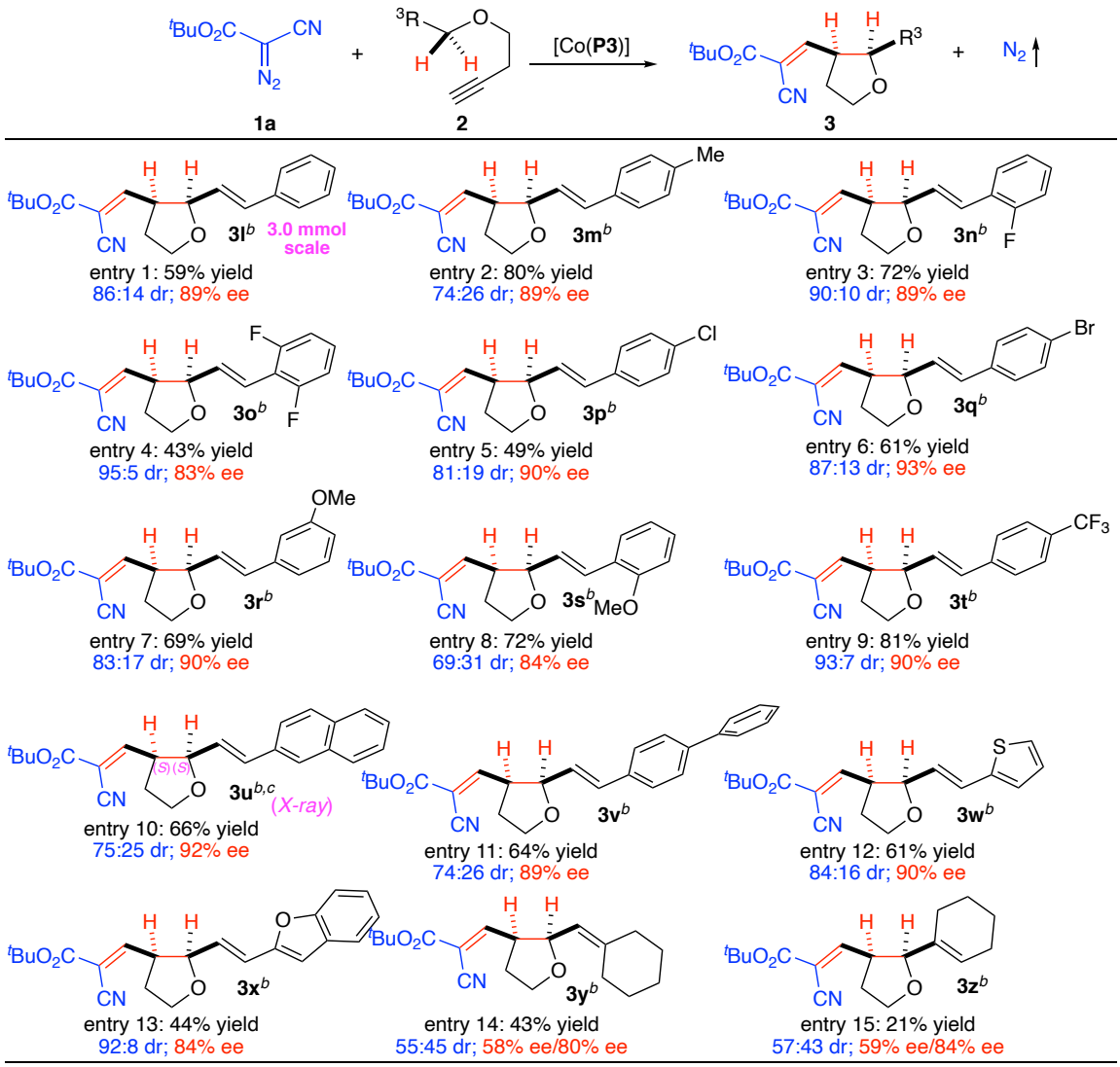


[a]Carried out with **1a** (0.12 mmol) and **2** (0.10 mmol) by [Co(**P3**)] (5 mol %) in MeOH (0.5 mL) at 20 °C for 24 h; isolated yields; configuration of all alkenes determined to be > 95:5 of (*E*):(Z); diastereomeric ratio (dr) determined by ^{1}H NMR; enantiomeric excess (ee) determined by chiral HPLC. [b]In *n*-hexane; [c]Absolute configuration determined by X-ray crystallography

methyl group, heteroatoms, electron-donating group, and electron-withdrawing group are found to be effective substrates, leading to the formation of desired products (**3m**–**3t**) in

moderate to good yields with high levels of diastereoselectivities and enantioselectivities (Table 3.2; entries 2–9). Likewise, 1,7-enynes containing extended aromatic group (**2u**)

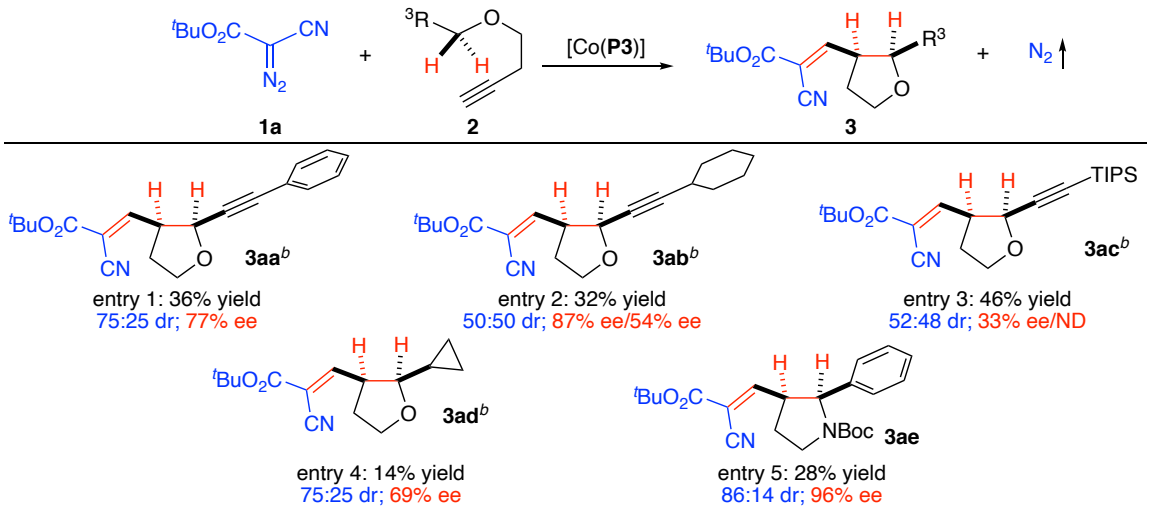
Table 3.2. Asymmetric Synthesis of α,β-Disubstituted Tetrahydrofurans by [Co(P3)]-Catalyzed Radical Cascade Involving H-Atom Abstraction of Allylic C–H bonds[a]



[a]Carried out with **1a** (0.12 mmol) and **2** (0.10 mmol) by [Co(**P3**)] (5 mol %) in MeOH (0.5 mL) at 20 °C for 24 h; isolated yields; configuration of all alkenes determined to be > 95:5 of (*E*):(Z); diastereomeric ratio (dr) determined by ^{1}H NMR; enantiomeric excess (ee) determined by chiral HPLC. [b]In *n*-Hexane; [c]Absolute configuration determined by X-ray crystallography

and heterocycles (**2w** and **2x**) could also participate in this process to generate the corresponding tetrahydrofurans with good to excellent enantiopurity (Table 3.2; entries 10–13). The absolute configurations of the newly-generated stereogenic centers in **3u** were established as (*S*,*S*) by X-ray crystallography. The Co(II)-based cascade process was further highlighted by its reactivity of alkyl-substituted 1,7-enynes (**2y** and **2z**), which gave synthetically useful yields and moderate to good selectivities (Table 3.2; entries 14 and 15). The generality of this reaction was further demonstrated by its successful application to the functionalization of propargylic C–H bonds in aryl, alkyl and silyl substituted 1,7-diynes (**2aa**–**2ac**) with moderate to good enantioselectivities

Table 3.3. Asymmetric Synthesis of α,β-Disubstituted Tetrahydrofurans by [Co(P3)]-Catalyzed Radical Cascade Involving H-Atom Abstraction of Other C–H bonds[a]



[a]Carried out with **1a** (0.12 mmol) and **2** (0.10 mmol) by [Co(**P3**)] (5 mol %) in MeOH (0.5 mL) at 20 °C for 24 h; isolated yields; configuration of all alkenes determined to be > 95:5 of (*E*):(Z); diastereomeric ratio (dr) determined by ^{1}H NMR; enantiomeric excess (ee) determined by chiral HPLC. [b]In *n*-Hexane; [c]Absolute configuration determined by X-ray crystallography

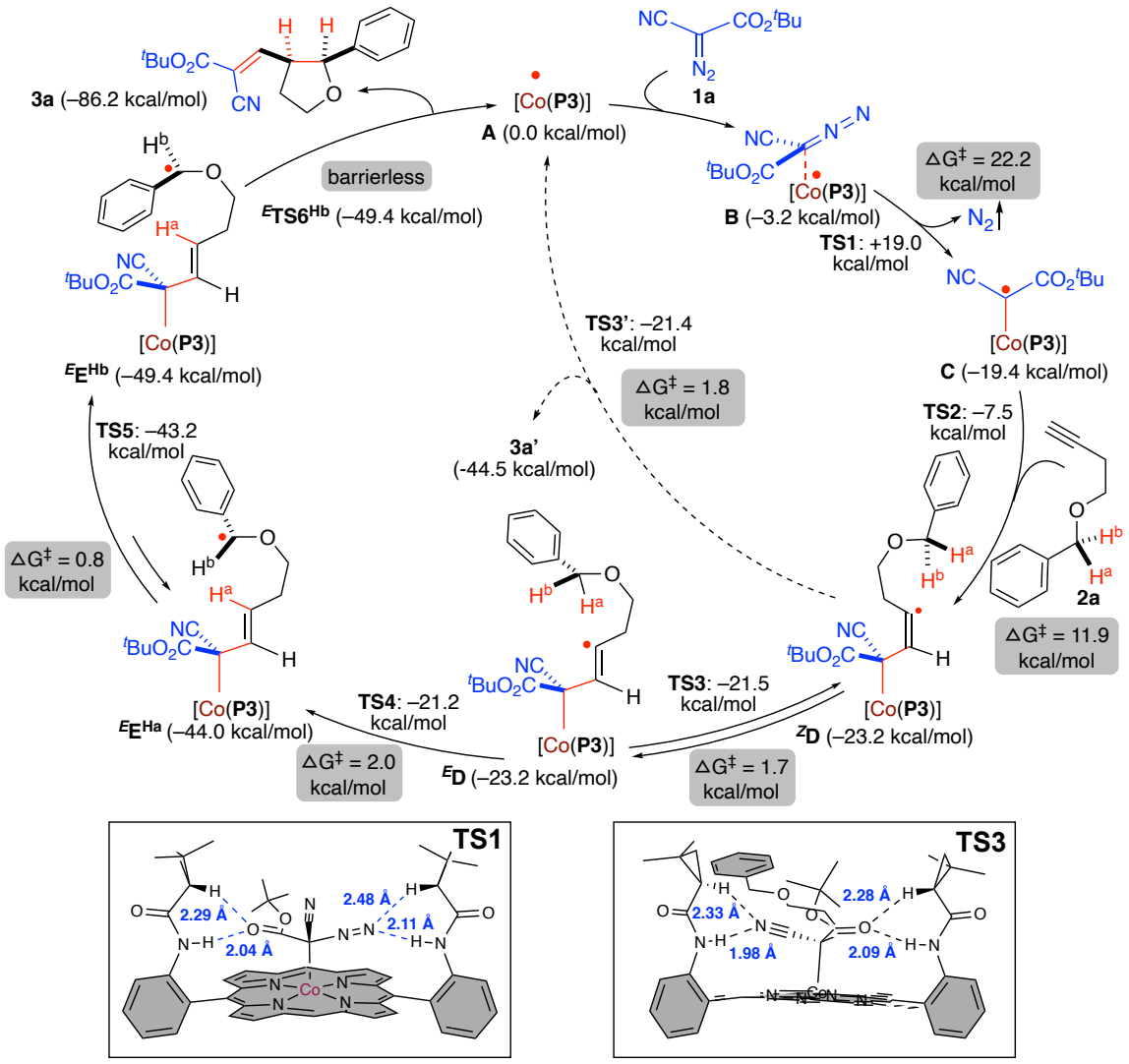
(Table 3.3; entries 1–3). More excitingly, the capability of this reaction is not limited to the functionalization of C–H bonds that are activated by an adjacent carbon-carbon unsaturated bond. The unactivated C–H bond next to a cyclopropyl ring in **2ad** was also selectively functionalized to furnish **3ad** in synthetic useful yield with good diastereoselectivity and moderate enantioselectivity (Table 3.3; entry 4). Interestingly, preliminary results showed this radical cascade process could also be applied for construction of pyrrolidine derivatives. Moderate yield with high diastereoselectivity and enantioselectivity was obtained when Boc-protected homopropargyl amine was utilized in the cascade process (Table 3.3; entry 5).

3.2.3. Mechanistic Studies on Co(II)-Catalyzed System for Radical Cascade Involving HAA

To gain direct evidence for the proposed stepwise radical mechanism, combined computational and experimental mechanistic studies were carried out (Scheme 3.5 – 3.6). First, density functional theory (DFT) calculations were performed to elucidate the details of the catalytic pathway and associated energetics for the cascade process involving hydrogen-atom abstraction of homopropargyl ether **2a** with *tert*-butyl α-cyanodiazoacetate (**1a**) by [Co(**P3**)] (Scheme 3.5). The DFT calculation reveals the initial formation of intermediate **B** between catalyst [Co(**P3**)] and *tert*-butyl α-cyanodiazoacetate (**1a**) through multiple noncovalent attractive interactions. The noncovalent complexation, which is exergonic by 3.2 kcal/mol, positions the diazo **1a** in a close proximity to the Co center of [Co(**P3**)] for further interaction. Upon metalloradical activation (MRA) by [Co(**P3**)], α-Co(III)-alkyl radical intermediate **C** was formed with the generation of dinitrogen as the byproduct. The metalloradical activation,

which is exergonic by 19.4 kcal/mol, has a comparatively high but accessible activation barrier (**TS1**: $\Delta G^{\ddagger}_{TS1}$ = 22.2 kcal/mol) and is found to be the rate-determining step. As

Scheme 3.5. DFT Study on Catalytic Pathways and Energetics for Cascade Cyclization by [Co(P3)]



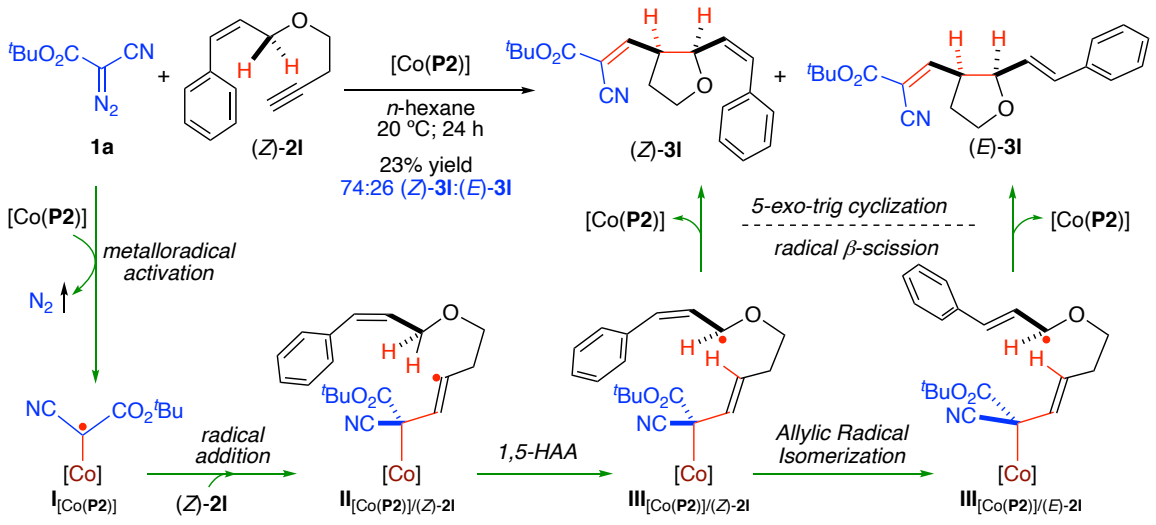
indicated in Scheme 3, the optimized structure of **TS1** shows multiple H-bonding interactions between the chiral amide units in [Co(**P3**)] and the cyano/ester groups of diazo **1a**. The subsequent radical addition of intermediate **C** to homopropargyl ether **2a**, which is exergonic by 3.8 kcal/mol, has a lower activation barrier (**TS2**: $\Delta G^{\ddagger}_{TS2}$ = 11.9

kcal/mol), delivering γ-Co(III)-vinyl radical intermediate ^{Z}**D** with (*Z*)-configuration. The presence of double hydrogen-bonding interactions between the two amide units of the catalyst and the α-cyano/ester groups was evident in both steps of metalloradical activation and radical addition (see Scheme 3.14 in Experimental Section for details), which rigidifies the conformations of the intermediates and lowers the activation barrier of the transition states. According to the DFT calculations, intermediate ^{Z}**D** and the corresponding intermediate ^{E}**D** (with (*E*)-configuration) are with the same thermal stability (-23.2 kcal/mol). They would be able to interconvert with an exceedingly low activation barrier (**TS3**: $\Delta G^{\ddagger}_{TS3}$ = 1.7 kcal/mol). The following 1,5-HAA is very facile through intermediate ^{E}**D** with a relatively low activation barrier (**TS4**: $\Delta G^{\ddagger}_{TS3}$ = 2.0 kcal/mol). This step is also highly exergonic by 20.8 kcal/mol, delivering ε-Co(III)-alkyl radical intermediate ^{E}**E** (See Scheme 3.12 in Experimental Section for details). The computed activation energy barrier for the competitive cyclopropenation of γ-Co(III)-vinyl radical ^{Z}**D** is found to be quite low (**TS3'**: $\Delta G^{\ddagger}_{TS3'}$ = 1.8 kcal/mol), which seems to be somewhat underestimated with the current level of theory as only trace amount of cyclopropene product was observed based on experiment results. To rationalize the observed stereoselectivity of the catalytic reaction, we calculated the energetics associated with 1,5-HAA and the subsequent simultaneous *5-exo-trig* cyclization/β-scission steps, respectively. Accordingly, the DFT calculations indicate that intermediate ^{E}**D** would first abstract Ha from the benzylic position to generate intermediate ^{E}**E**^{Ha} (-44.0 kcal/mol), which can further undergo σ-bond rotation with almost no energy barrier (**TS5**: $\Delta G^{\ddagger}_{TS5}$ = 0.8 kcal/mol) to give the thermodynamically more stable conformational isomer ^{E}**E**^{Hb} (-49.4 kcal/mol). The final radical substitution, which includes simultaneous

5-exo-trig cyclization and radical β-scission, is found to be an almost barrierless process and highly exergonic by 37.8 kcal/mol with intermediate $^{E}\mathbf{E}^{\mathbf{Hb}}$. Overall the calculated catalytic pathway and associated energetics seem in good agreement with the experimental observations for the Co(II)-based catalytic system for cascade cyclization.

The existence of η-Co(III)-allylic radical intermediates **III** could be probed during the catalytic reaction of 1,7-enyne (*Z*)-**2l** with diazo **1a** (Scheme 3.6). Unlike the reaction of (*E*)-**2l**, the radical cascade process of (*Z*)-**2l** resulted in a mixture of (*Z*)-**3l** and (*E*)-**3l** in 23% yield, indicating isomerization of the allylic radical during the cascade process. The generation of product (*E*)-**3l** implies the involvement of intermediate **III'**$_{[Co(\mathbf{P2})]/(E)\text{-}\mathbf{2l}}$, which could be formed by allylic radical isomerization from intermediate **III**$_{[Co(\mathbf{P2})]/(Z)\text{-}\mathbf{2l}}$. Collectively, these experimental results provided convincing evidence for the proposed stepwise radical mechanism of the Co(II)-catalyzed radical cascade process.

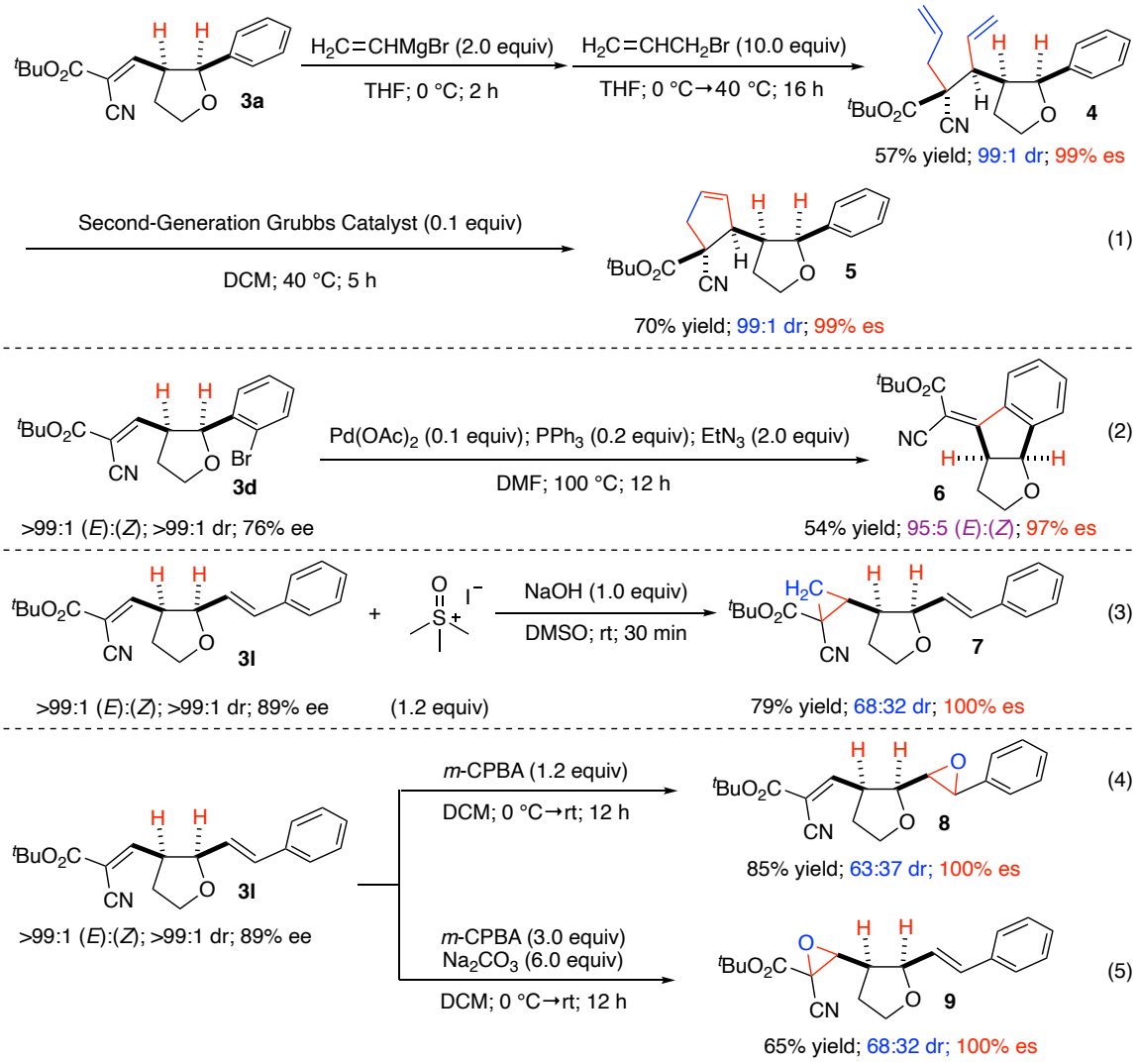
Scheme 3.6. Probing of η-Co(III)-Allylic Radical Intermediates via Olefin Isomerization



3.2.4. Synthetic Applications of Resulting Enantioenriched α,β-Disubstituted Tetrahydrofurans

Given that the tetrahydrofuran structures are widely found in natural products and bioactive compounds, exploring the further transformation of the enantioenriched α,β-substituted tetrahydrofurans are of our interest, especially those with diastereoselectivity (Scheme 3.7). First of all, the electron-deficient alkene in **3a** could serve as an effective Michael acceptor for nucleophilic addition and subsequent alkylation, which would generate two additional vicinal stereocenters (Scheme 3.7; eq 1). The reaction of **3a** with vinylmagnesium bromide, followed by addition of allyl bromide resulted in overall dicarbonfunctionalization of the C=C bond, producing compound **4** with excellent control of the stereochemistry for all four contiguous stereogenic centers. These results demonstrate the effectiveness of the tetrahydrofuran assembly as a chiral auxiliary for controlling the stereochemistry of the alkene vicinal difunctionalization process. Subsequent ring-closing metathesis of the two terminal olefin units in **4** with the second-generation Grubbs catalyst led to the effective construction of bicyclic compound **5** in good yield with high retention of enantiopurity. Taking advantage of the *cis*-relationship between the substituents of the tetrahydrofuran products, compound **3d** that contains an *ortho*-bromo substituent was subjected to an intramolecular Heck reaction, where tricyclic compound **6** bearing a tetrasubstituted olefin was obtained in good yield with high *E*/*Z* selectivity and high enantiopurity (Scheme 3.7; eq 2). In addition, chemoselective transformations of **3l** were explored, where the two C=C bonds could be distinguished based on their different electronic properties. Corey-Chaykoysky cyclopropanation occurred exclusively with the electron-deficient alkene and furnished **7**

Scheme 3.7. Further Transformations of Resulting Enantioenriched α,β-Disubstituted Tetrahydrofurans



in high yield with 100% enantiospecificity (Scheme 3.7; eq 3). In addition to cyclopropanation, epoxidation reaction represents another attractive way for the diversification of alkenes. Conditions that can chemoselectively epoxidize electron-rich or electron-poor alkenes have been established based on the electrophilic or nucleophilic nature of the reagents, respectively. As shown in Scheme 3.7, *m*-CPBA as an electrophilic epoxidation reagent reacted with the more electron-rich styrene-type double bond to

deliver compound **8** in high yield (Scheme 3.7; eq 4). On the other hand, upon utilizing sodium carbonate as a base, the weakly nucleophilic conjugate base of *m*-CPBA generated by deprotonation targeted at the highly electrophilic Michael accepter under otherwise identical conditions (Scheme 3.7; eq 5).

3.3. CONCLUSIONS

In summary, the feasibility of asymmetric radical cascade process involving H-atom abstraction via Co(II)-based metalloradical catalysis (MRC) has been successfully demonstrated. The Co(II)-catalyzed radical process provides, for the first time, an effective approach for stereoselective construction of chiral α,β-disubstituted tetrahydrofuran structures with homopropargyl ethers in good yields with high enantioselectivities and diastereoselectivities and broad substrate scope. Evidence for radical mechanism and radical intermediate has been obtained via combined computational and experimental studies. Synthetic utility of the enantioenriched α,β-disubstituted tetrahydrofurans has been showcased through several stereoselective transformations of the substituted vinyl group. More broadly, we hope that the successful demonstration of this Co(II)-catalyzed asymmetric radical cascade process involving H-atom abstraction will inspire further exploration of metalloradical catalysis (MRC) as a potentially general tools to control enantioselectivity as well as diastereoselectivity in synthetically useful radical cascade reactions.

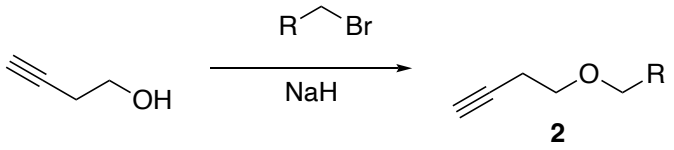
3.4. EXPERIMENT SECTION

3.4.1. General Considerations

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254), visualizing with UV-light 254 nm or ceriumammonium-molybdate (CAM) stain (ammonium pentamolybdate, cerium(IV) sulfate, sulfuric acid aqueous solution). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Inova600 (600 MHz), Inova500 (500 MHz), Inova400 (400 MHz) instrument with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel IA, IB, IC, ID, IE, IF and Whelk columns. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. High resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight (ESI-TOF) or direct analysis in real time (DART). The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. All reagents [Co(3,5-Di^{t}Bu-IbuPhyrin)], [Co(3,5-Di^{t}Bu-ChenPhyrin)], [Co(3,5-Di^{t}Bu-QingPhyrin)], [Co(2,6-DiMeO-ChePhyrin)] and [Co(3,5-DiCF$_3$-ChenPhyrin)] were prepared by following the literature.[16] *tert*-Butyl 2-cyano-2-diazoacetate were synthesized according to reported procedure.[16]

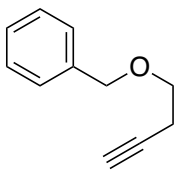
3.4.2. Synthesis of Substrates

Procedure A and Characterization of Alkyne

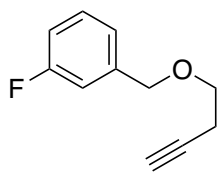


A solution of alcohol (1.2 equiv) in THF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.2 equiv) in DMF (0.5 M). Keep reaction mixture stirring for 20 minutes and dropwise addition of alkyl bromide (1 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[17]

((But-3-yn-1-yloxy)methyl)benzene 2a. 71% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 4.58 (s, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.52 (td, *J* = 6.9, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.13, 128.51, 127.79, 81.39, 73.08, 69.44, 68.25, 19.99. IR (neat, cm^{-1}): 3293.60, 2862.69, 1495.64, 1453.63, 1362.33, 1099.09, 736.45, 697.16. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{11}H_{13}O^+$: 161.0961; Found: 161.0957.

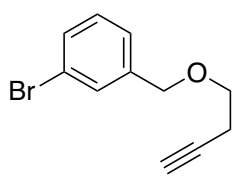


1-((But-3-yn-1-yloxy)methyl)-3-fluorobenzene 2b. 75% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 7.14 – 7.05 (m, 2H), 7.01 – 6.94 (m, 1H), 4.56 (s, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.52 (td, *J* = 6.8, 2.6 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.10 (d, J_{CF} = 245.6 Hz),

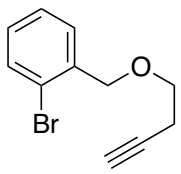


140.90 (d, J_{CF} = 7.2 Hz), 130.02 (d, J_{CF} = 8.1 Hz), 123.03 (d, J_{CF} = 2.9 Hz), 114.61 (d, J_{CF} = 21.0 Hz), 114.45 (d, J_{CF} = 21.0 Hz), 81.29, 72.31 (d, J_{CF} = 1.9 Hz), 69.56, 68.49, 20.00. ^{19}F NMR (470 MHz, $CDCl_3$) δ -113.25 (td, J = 9.5, 9.1, 5.4 Hz). IR (neat, cm^{-1}): 3303.74, 2866.72, 1591.43, 1450.43, 1253.70, 1105.17, 783.78, 641.17. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{11}H_{12}OF^+$: 179.0867; Found: 179.0865.

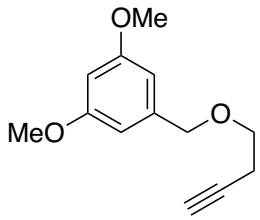
1-Bromo-3-((but-3-yn-1-yloxy)methyl)benzene 2c. 69% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, J = 1.9 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.29 – 7.26 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 4.53 (s, 2H), 3.61 (t, J = 6.8 Hz, 2H), 2.52 (td, J = 6.8, 2.7 Hz, 2H), 2.02 (t, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.58, 130.84, 130.64, 130.10, 126.13, 122.69, 81.28, 72.21, 69.60, 68.51, 20.00. IR (neat, cm^{-1}): 3299.15, 2865.55, 1571.15, 1473.79, 1108.24, 845.77. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{11}H_{12}OBr^+$: 239.0066; Found: 239.0068.



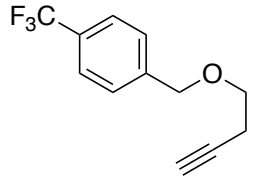
1-Bromo-2-((but-3-yn-1-yloxy)methyl)benzene 2d. 61% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.32 (td, J = 7.5, 1.3 Hz, 1H), 7.15 (td, J = 7.5, 1.8 Hz, 1H), 4.63 (s, 2H), 3.69 (t, J = 6.9 Hz, 2H), 2.56 (td, J = 6.9, 2.6 Hz, 2H), 2.01 (td, J = 2.7, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.55, 132.66, 129.15, 129.09, 127.56, 122.77, 81.33, 72.34, 69.57, 68.92, 20.04. IR (neat, cm^{-1}): 3298.56, 2866.56, 1569.11, 1439.25, 1357.46, 1102.69, 1026.61, 749.15, 637.76. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{11}H_{12}OBr^+$: 239.0066; Found: 239.0087.



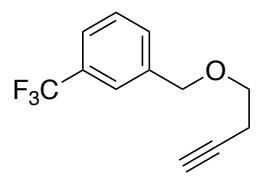
1-((But-3-yn-1-yloxy)methyl)-3,5-dimethoxybenzene 2e. 66% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (d, J = 2.3 Hz, 2H), 6.38 (t, J = 2.4 Hz, 1H), 4.50 (s, 2H), 3.79 (s, 6H), 3.59 (t, J = 6.9 Hz, 2H), 2.51 (td, J = 7.0, 2.7 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.03, 140.63, 105.43, 99.86, 81.44, 73.02, 69.44, 68.23, 55.43, 20.02. IR (neat, cm^{-1}): 3292.34, 2868.45, 2229.70, 1359.19, 1108.54, 794.53, 687.56. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{17}O_3^+$: 221.1172; Found: 221.1181.



1-((But-3-yn-1-yloxy)methyl)-4-(trifluoromethyl)benzene 2f. 79% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 4.63 (s, 2H), 3.64 (t, J = 6.8 Hz, 2H), 2.53 (td, J = 6.8, 2.7 Hz, 2H), 2.02 (t, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. 142.35, 130.01 (q, J_{CF} = 31.3 Hz), 127.67, 126.69 (q, J_{CF} = 286.3 Hz), 125.35 (q, J_{CF} = 3.8 Hz), 81.24, 72.30, 69.60, 68.69, 20.04. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.54. IR (neat, cm^{-1}): 3307.06, 2868.13, 1621.65, 1323.87, 1162.62, 1119.47, 1065.43, 1018.41. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{12}OF_3^+$: 229.0835; Found: 229.0820.

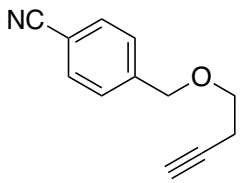


1-((But-3-yn-1-yloxy)methyl)-3-(trifluoromethyl)benzene 2g. 74% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 77.66 – 7.61 (m, 1H), 7.57 – 7.51 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 4.61 (s, 2H), 3.64 (t, J = 6.8 Hz, 2H), 2.53 (td, J = 6.8, 2.7 Hz, 2H), 2.02 (t, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.31, 130.94 (q, J_{CF} = 32.5 Hz), 130.84, 128.99, 124.60 (q, J_{CF} = 3.8 Hz), 124.32 (q, J_{CF} = 3.6 Hz). 124.27 (q, J_{CF} = 270.0

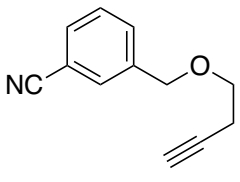


Hz) 81.24, 72.32, 69.61, 68.69, 20.02. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.65. IR (neat, cm^{-1}): 3311.14, 2868.99, 1328.27, 1163.10, 1120.03, 1072.57, 797.37. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{12}OF_3^+$: 229.0835; Found: 229.0846.

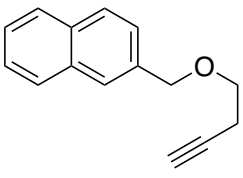
4-((But-3-yn-1-yloxy)methyl)benzonitrile 2h. 76% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.48 – 7.46 (m, 2H), 4.62 (s, 2H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.53 (td, *J* = 6.7, 2.7 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.81, 132.38, 127.82, 118.94, 111.53, 81.14, 72.11, 69.68, 68.89, 20.00. IR (neat, cm^{-1}): 3257.53, 2869.30, 2229.98, 1610.84, 1365.39, 1096.87, 825.15, 693.46. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{12}NO^+$: 186.0913; Found: 186.0913.



3-((But-3-yn-1-yloxy)methyl)benzonitrile 2i. 65% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.47 (dt, *J* = 7.9, 0.7 Hz, 2H), 4.62 (s, 2H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.53 (td, *J* = 6.7, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.88, 131.74, 131.40, 130.97, 129.31, 118.86, 112.68, 81.15, 71.82, 69.70, 68.80, 20.01. IR (neat, cm^{-1}): 3290.92, 2868.93, 2229.68, 1483.35, 1358.88, 1107.33, 1091.56, 793.56, 686.87, 642.36. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{12}NO^+$: 186.0913; Found: 186.0912.

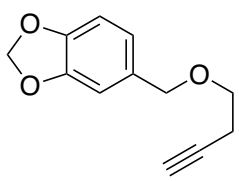


2-((But-3-yn-1-yloxy)methyl)naphthalene 2j. 66% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H), 7.55 – 7.45 (m, 3H), 4.74 (s, 2H), 3.66 (t, *J* = 6.9 Hz, 2H), 2.55 (td, *J* = 6.9, 2.7 Hz, 2H), 2.03 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.65, 133.40, 133.15, 128.35, 127.99, 127.82, 126.56, 126.24, 126.01, 125.81,

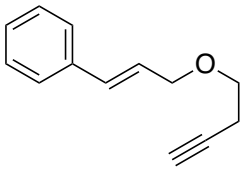


81.44, 73.21, 69.50, 68.30, 20.06. IR (neat, cm^{-1}): 3293.09, 3053.77, 2861.32, 1508.84, 1367.95, 1096.39, 814.54, 750.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{15}O^+$: 211.1117; Found: 211.1117.

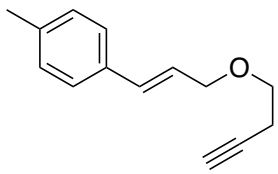
5-((But-3-yn-1-yloxy)methyl)benzo[*d*][1,3]dioxole 2k. 59% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.84 – 6.67 (m, 2H), 5.94 (s, 2H), 4.45 (s, 2H), 3.57 (t, *J* = 6.9 Hz, 2H), 2.48 (td, *J* = 6.9, 2.6 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.89, 147.28, 131.99, 121.40, 108.54, 108.15, 101.08, 81.40, 72.94, 69.45, 67.96, 19.98. IR (neat, cm^{-1}): 3292.77, 2865.14, 1489.25, 1442.77, 1239.48, 1098.90, 1037.68, 929.21, 807.47, 643.37. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{11}O_3^+$: 203.0703; Found: 203.0704.



(*E*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene 2l. 70% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.38 – 7.29 (m, 2H), 7.29 – 7.21 (m, 1H), 6.64 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.30 (dtd, *J* = 15.9, 6.1, 0.9 Hz, 1H), 4.20 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.64 (td, *J* = 7.0, 0.7 Hz, 2H), 2.53 (tdd, *J* = 7.0, 2.7, 0.9 Hz, 2H), 2.06 – 1.95 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.70, 132.67, 128.63, 127.80, 126.58, 125.89, 81.40, 71.63, 69.46, 68.23, 19.99. IR (neat, cm^{-1}): 3295.77, 3026.07, 2859.17, 1495.21, 1361.46, 1101.20, 966.13, 735.93, 691.99, 640.14. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{13}H_{18}NO^+$: 204.1383; Found: 204.1384.

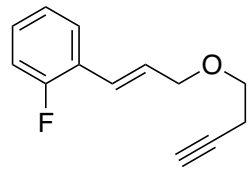


(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-methylbenzene 2m. 65% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.67 – 6.55 (m, 1H), 6.26 (dtd, *J* = 15.9, 6.2, 1.2 Hz, 1H), 4.19 (dd, *J* =



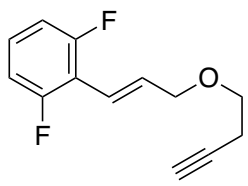
6.1, 1.6 Hz, 2H), 3.64 (td, *J* = 6.9, 0.7 Hz, 2H), 2.53 (tdd, *J* = 7.0, 2.7, 1.0 Hz, 2H), 2.36 (s, 3H), 2.03 (td, *J* = 2.7, 1.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.60, 133.90, 132.69, 129.32, 126.49, 124.78, 81.41, 71.73, 69.43, 68.14, 21.25, 19.97. IR (neat, cm^{-1}): 3295.28, 3023.08, 2919.23, 2859.64, 1512.97, 1361.39, 1104.77, 968.53, 790.15, 640.34. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{14}H_{20}NO^+$: 218.1539; Found: 218.1548.

(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-2-fluorobenzene 2n. 55% Yield; R_f = 0.2



(hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (tdd, *J* = 7.0, 5.2, 1.7 Hz, 1H), 7.09 (td, *J* = 7.5, 1.5 Hz, 1H), 7.03 (ddd, *J* = 11.0, 8.3, 1.5 Hz, 1H), 6.78 (dd, *J* = 16.1, 1.7 Hz, 1H), 6.37 (dt, *J* = 16.1, 6.0 Hz, 1H), 4.21 (dd, *J* = 5.9, 1.7 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 2.52 (td, *J* = 6.9, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.41 (d, J_{CF} = 249.1 Hz), 129.12 (d, J_{CF} = 8.1 Hz), 128.60 (d, J_{CF} = 4.6 Hz), 127.64 (d, J_{CF} = 4.0 Hz), 125.03 (d, J_{CF} = 3.5 Hz), 124.54 (d, J_{CF} = 12.1 Hz), 124.22 (d, J_{CF} = 4.0 Hz), 115.85 (d, J_{CF} = 22.0 Hz), 81.41, 71.81, 69.50, 68.39, 20.05. ^{19}F NMR (564 MHz, $CDCl_3$) δ -118.12 (ddd, *J* = 10.5, 7.5, 5.0 Hz). IR (neat, cm^{-1}): 3302.66, 2860.04, 1578.53, 1486.81, 1228.27, 1094.14, 968.64, 753.83, 641.47. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{13}H_{17}NOF^+$: 222.1289; Found: 222.1290.

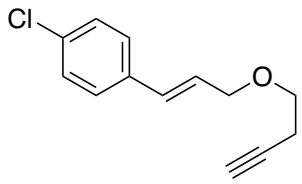
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-1,3-difluorobenzene 2o. 50% Yield; R_f =



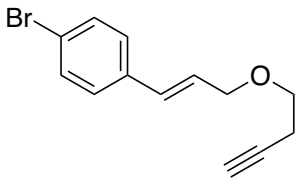
0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (tt, *J* = 8.3, 6.2 Hz, 1H), 6.92 – 6.81 (m, 2H), 6.67 (dt, *J* = 16.4, 1.2 Hz, 1H), 6.60 (dt, *J* = 16.4, 5.3 Hz, 1H), 4.22 (dt, *J* = 5.1, 0.9 Hz, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.52 (td, *J* = 6.9, 2.7 Hz, 2H), 2.01 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.11 (dd, J_{CF} = 251.5, 7.9 Hz), 133.21 (t, J_{CF} = 7.6 Hz), 128.31 (t, J_{CF} = 10.7 Hz), 118.63 (t, J_{CF} = 2.1 Hz), 114.14, 112.02 – 110.86 (m), 81.39, 72.19, 69.50, 68.51, 20.07. ^{19}F NMR (470 MHz, $CDCl_3$) δ -113.27 – -113.39 (m). IR (neat, cm^{-1}): 3304.40, 2869.86, 1621.12, 1464.17, 1233.92, 1199.93, 1113.33, 988.94, 778.47, 639.37. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{13}H_{16}NOF_2^+$: 240.1195; Found: 240.1203.

(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-chlorobenzene 2p. 60% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 6.56 (dt, *J* = 16.0, 1.4 Hz, 1H), 6.29 – 6.20 (m, 1H), 4.16 (dt, *J* = 6.0, 1.3 Hz, 2H), 3.61 (td, *J* = 6.8, 1.0 Hz, 2H), 2.51 (td, *J* = 6.9, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.20, 133.36, 131.18, 128.77, 127.75, 126.60, 81.34, 71.39, 69.51, 68.36, 19.96. IR (neat, cm^{-1}): 3300.08, 2859.92, 1490.99, 1361.38, 1090.99, 1012.35, 968.09, 843.95, 640.68. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{13}H_{17}NOCl^+$: 238.0993; Found: 238.0994.

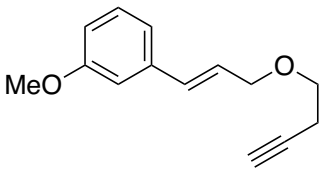


(*E*)-1-Bromo-4-(3-(but-3-yn-1-yloxy)prop-1-en-1-yl)benzene 2q. 58% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.23 (dd, *J* = 8.6, 2.3 Hz, 2H), 6.61 – 6.48 (m, 1H), 6.26 (dddd, *J* = 16.0, 7.6, 4.2, 1.2 Hz, 1H), 4.16 (dt, *J* = 6.0, 1.6 Hz, 2H), 3.61 (td, *J* = 6.9, 1.6 Hz, 2H), 2.50 (tdd, *J* = 6.8, 2.7, 1.0 Hz, 2H), 2.01 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.63, 131.70, 131.17, 128.06, 126.74, 121.51, 81.33, 71.37, 69.52, 68.37, 19.96. IR (neat, cm^{-1}): 3298.21,

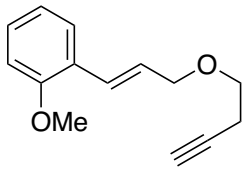


2860.50, 1587.81, 1487.16, 1400.19, 1361.01, 1072.04, 1008.53, 968.16, 842.39. HRMS (DART) ([M+NH_4]$^+$) Calcd. for $C_{13}H_{17}NOBr^+$: 282.0488; Found: 282.0483.

(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-3-methoxybenzene 2r. 66% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 1H), 6.99 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.94 (dd, *J* = 2.7, 1.6 Hz, 1H), 6.81 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.60 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.20 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.82 (s, 3H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.52 (td, *J* = 6.9, 2.7 Hz, 2H), 2.02 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.95, 138.23, 132.61, 129.67, 126.30, 119.34, 113.57, 111.92, 81.45, 71.65, 69.47, 68.33, 55.35, 20.06. IR (neat, cm^{-1}): 3292.07, 2860.91, 1579.16, 1488.73, 1433.56, 1361.17, 1262.48, 1155.24 1046.57, 969.19, 772.77, 688.26. HRMS (DART) ([M+NH_4]$^+$) Calcd. for $C_{14}H_{20}NO_2^+$: 234.1489; Found: 234.1498.



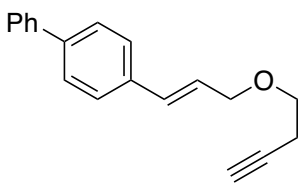
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-2-methoxybenzene 2s. 65% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.00 – 6.91 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.32 (dt, *J* = 16.1, 6.3 Hz, 1H), 4.21 (dd, *J* = 6.2, 1.6 Hz, 2H), 3.86 (s, 3H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.52 (td, *J* = 7.0, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.93, 128.93, 127.88, 127.18, 126.57, 125.78, 120.78, 111.00, 81.53, 72.27, 69.40, 68.15, 55.58, 20.06. IR (neat, cm^{-1}): 3292.44, 2837.08, 1597.33, 1488.61, 1240.99, 1116.44, 1101.39, 1027.18, 974.49, 750.65, 640.97. HRMS (DART) ([M+NH_4]$^+$) Calcd. for $C_{14}H_{20}NO_2^+$: 234.1489; Found: 234.1496.



(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene 2t. 70% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.54 – 7.45 (m, 2H), 6.68 (dt, *J* = 16.0, 1.8 Hz, 1H), 6.39 (dt, *J* = 16.0, 5.7 Hz, 1H), 4.23 (dd, *J* = 5.7, 1.6 Hz, 2H), 3.65 (t, *J* = 6.9 Hz, 2H), 2.54 (td, *J* = 6.9, 2.7 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.15, 130.73, 129.49 (d, J_{CF} = 32.2 Hz), 128.65, 126.60, 125.52 (q, J_{CF} = 3.9 Hz), 124.16 (q, J_{CF} = 271.8 Hz), 81.20, 71.17, 69.40, 68.48, 19.92. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.54 (s, 1F). IR (neat, cm^{-1}): 3308.56, 2864.91, 1615.40, 1322.13, 1105.39, 1065.34, 1016.29, 969.34, 854.01, 635.87. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{14}H_{12}OF_3^+$: 253.0835; Found: 253.0842.

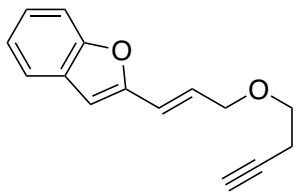
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)naphthalene 2u. 60% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 3H), 7.74 (t, *J* = 1.0 Hz, 1H), 7.61 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.45 (pd, *J* = 6.9, 1.5 Hz, 2H), 6.79 (dt, *J* = 16.0, 1.8 Hz, 1H), 6.42 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.25 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.66 (t, *J* = 6.9 Hz, 2H), 2.54 (td, *J* = 6.9, 2.6 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.23, 133.70, 133.21, 132.85, 128.35, 128.14, 127.81, 126.68, 126.41, 126.33, 126.07, 123.73, 81.47, 71.81, 69.51, 68.38, 20.09. IR (neat, cm^{-1}): 3286.64, 3055.19, 2865.91, 1507.86, 1370.86, 1118.99, 1091.31, 965.16, 864.46, 811.69, 739.16, 637.96. HRMS (DART) ([M+NH_4]$^+$) Calcd. for $C_{17}H_{20}NO^+$: 254.1539; Found: 254.1543.

(*E*)-4-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-1,1'-biphenyl 2v. 52% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.51 – 7.40 (m, 4H), 7.38 – 7.31 (m, 1H), 6.66 (dt, *J* = 16.0, 1.6 Hz, 1H),



6.34 (dt, *J* = 15.8, 6.0 Hz, 1H), 4.22 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.65 (t, *J* = 6.9 Hz, 2H), 2.53 (td, *J* = 6.9, 2.6 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.80, 140.64, 135.79, 132.31, 128.93, 127.47, 127.40, 127.08, 126.04, 81.46, 71.76, 69.49, 68.32, 20.07. IR (neat, cm^{-1}): 3303.16, 3030.84, 2861.66, 1487.35, 1361.73, 1265.36, 1106.99, 971.32, 850.60, 758.14, 736.38, 696.16. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{19}H_{22}NO^+$: 280.1696; Found: 280.1696.

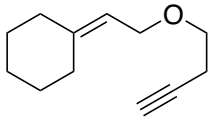
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)thiophene 2w. 45% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 1H), 6.96 (d, *J* = 4.4 Hz, 2H), 6.75 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.1 Hz, 1H), 4.15 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.51 (td, *J* = 7.0, 2.7 Hz, 2H), 2.01 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.86, 127.46, 125.98, 125.82, 125.53, 124.58, 81.42, 71.32, 69.49, 68.31, 20.04. IR (neat, cm^{-1}): 3292.52, 2865.54, 1673.10, 1433.18, 1363.85, 1107.69, 957.63, 853.91, 701.33, 642.74. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{11}H_{16}NOS^+$: 210.0947; Found: 210.0949.



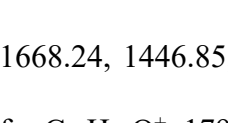
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzofuran 2x. 48% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 7.6, 1.6, 0.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.30 – 7.24 (m, 1H), 7.20 (tt, *J* = 7.4, 1.4 Hz, 1H), 6.64 – 6.57 (m, 2H), 6.51 (dt, *J* = 15.7, 4.9 Hz, 1H), 4.23 (dd, *J* = 5.1, 1.4 Hz, 2H), 3.65 (td, *J* = 6.8, 1.2 Hz, 2H), 2.54 (td, *J* = 6.8, 2.6 Hz, 2H), 2.03 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.90, 154.29, 128.99, 128.22, 124.65, 122.92, 121.01, 120.29, 111.04, 104.75, 81.38,

70.89, 69.54, 68.55, 20.05. IR (neat, cm^{-1}): 3296.32, 2858.19, 1556.11, 1451.02, 1361.03, 1253.61, 1107.14, 958.65, 747.89, 639.04. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{13}O_2^+$: 225.0910; Found: 225.0912.

(2-(But-3-yn-1-yloxy)ethylidene)cyclohexane 2y. 55% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (600 MHz, $CDCl_3$) δ 5.28 (t, *J* = 7.0 Hz, 1H), 4.02 (d, *J* = 7.0 Hz, 2H), 3.55 (t, *J* = 7.0 Hz, 2H), 2.47 (td, *J* = 7.1, 2.7 Hz, 2H), 2.17 (t, *J* = 5.9 Hz, 2H), 2.12 (d, *J* = 5.9 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.58 – 1.46 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.32, 117.57, 81.57, 69.32, 67.95, 66.63, 37.21, 29.14, 28.53, 27.89, 26.82, 20.04. IR (neat, cm^{-1}): 3309.17, 2925.84, 2853.52, 1668.24, 1446.85, 1097.51, 1004.85, 853.88, 632.05. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{12}H_{19}O^+$: 179.1430; Found: 179.1431.



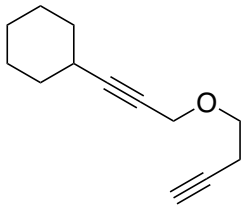
1-((But-3-yn-1-yloxy)methyl)cyclohex-1-ene 2z. 51% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 5.69 (qd, *J* = 3.3, 1.3 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.51 (t, *J* = 7.0 Hz, 2H), 2.47 (td, *J* = 7.0, 2.7 Hz, 2H), 2.14 – 1.92 (m, 5H), 1.72 – 1.62 (m, 2H), 1.62 – 1.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.91, 125.40, 81.63, 75.90, 69.29, 67.74, 25.99, 25.16, 22.65, 22.54, 20.00. IR (neat, cm^{-1}): 3308.53, 2924.07, 2856.70, 1436.83, 1357.09, 1137.47, 1097.79, 1007.75, 801.68, 634.81. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{11}H_{17}O^+$: 165.1274; Found: 165.1280.



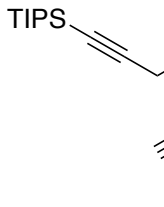
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)benzene 2aa. 59% Yield; R_f = 0.2 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.36 – 7.28 (m, 3H), 4.42 (s, 2H), 3.73 (t, *J* = 6.9 Hz, 2H), 2.54 (td, *J* = 6.9, 2.7 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 131.85, 128.58, 128.37, 122.63, 86.54, 84.85, 81.16, 69.55, 67.99, 59.02, 19.83. IR (neat, cm^{-1}): 3295.67, 2868.71, 1598.51, 1489.71, 1356.07, 1096.63, 756.61, 691.01, 641.10. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{13}H_{13}O^+$: 185.0961; Found: 185.0961.

(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)cyclohexane 2ab. 68% Yield; R_f = 0.4 (hexanes/ethyl acetate, 20:1). ^1H NMR (600 MHz, $CDCl_3$) δ 4.19 (t, *J* = 1.8 Hz, 2H), 3.64 (td, *J* = 7.0, 1.6 Hz, 2H), 2.50 (tdd, *J* = 6.9, 2.8, 1.5 Hz, 2H), 2.44 – 2.34 (m, 1H), 1.99 (td, *J* = 2.9, 1.4 Hz, 1H), 1.79 (d, *J* = 13.6 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.44 (dd, *J* = 13.2, 9.5 Hz, 2H), 1.35 – 1.21 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.59, 81.35, 75.52, 69.43, 67.68, 58.91, 32.74, 29.26, 25.99, 25.02, 19.85. IR (neat, cm^{-1}): 2930.50, 2406.08, 1771.69, 1717.03, 749.20. HRMS (DART) ($[M+H]^+$) Calcd. for C13H19O$^+$: 191.1430; Found: 191.1427.



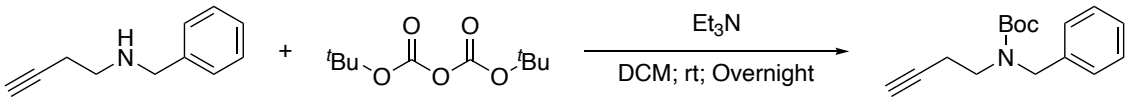
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)triisopropylsilane 2ac. 77% Yield; R_f = 0.4 (hexanes/ethyl acetate, 20:1). ^1H NMR (600 MHz, $CDCl_3$) 4.23 (s, 2H), 3.68 (t, *J* = 6.8 Hz, 2H), 2.49 (td, *J* = 6.8, 2.7 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.06 – 1.07 (m, 21H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 103.07, 88.06, 81.28, 69.42, 67.59, 59.06, 18.96, 18.71, 11.29. IR (neat, cm^{-1}): 3313.48, 2942.58, 2865.03, 1462.97, 1100.23, 882.22. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{16}H_{29}OSi^+$: 265.1982; Found: 265.1985.



((But-3-yn-1-yloxy)methyl)cyclopropane 2ad. 21% Yield; R_f = 0.3 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, $CDCl_3$) δ 3.60 (td, *J* = 7.1, 1.6 Hz, 2H), 3.32 (dd, *J* = 6.8, 1.6 Hz, 2H), 2.49 (tdd, *J* = 7.1, 2.8, 1.5 Hz, 2H), 1.98 (td, *J* = 2.8, 1.5 Hz, 1H), 1.13 – 1.02 (m, 1H), 0.54 (dq, *J* = 8.6, 2.7, 2.1 Hz,

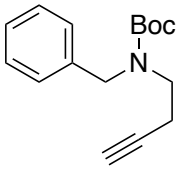
2H), 0.28 – 0.13 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.51, 75.88, 69.36, 68.66, 20.03, 10.67, 3.13. IR (neat, cm^{-1}): 2922.73, 2852.87, 1646.70, 1457.62, 1107.98, 1019.84. HRMS (DART) ([M+H]$^+$) Calcd. for $C_8H_{13}O^+$: 125.0961; Found: 125.0972.

Procedure A and Characterization of Alkyne



To a solution of amine in DCM (5 mL/mmol) were added Et_3N (1.5 equiv) and Boc_2O (1.2 equiv) at 0 °C under argon atmosphere. After stirring for 5 h at room temperature, the reaction mixture was extracted three times with DCM and water. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford the desired product.[18]

***tert*-Butyl benzyl(but-3-yn-1-yl)carbamate 2ae.** 81% Yield; R_f = 0.4 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.30 – 7.19 (m, 3H), 4.65 – 4.31 (m, 2H), 3.36 (d, *J* = 47.6 Hz, 2H), 2.39 (d, *J* = 35.5 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.55 – 1.37 (m, 9H).



^{13}C NMR (125 MHz, $CDCl_3$) 155.45, 138.23, 128.60, 127.82, 127.31, 82.09, 80.07, 69.72, 51.49, 45.89, 28.48, 18.40. IR (neat, cm^{-1}): 3294.16, 2975.87, 1690.12, 1411.81, 1365.93, 1246.43, 1163.00, 1120.02, 699.66. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{16}H_{22}ON^+$: 260.1645; Found: 260.1647.

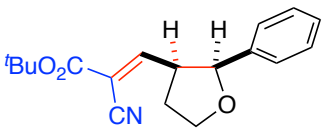
3.4.3. General Procedure for Enantioselective Radical Cascade Involving HAA

An oven dried Schlenk tube, that was previously charged with catalyst (5 mol %), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum, and 0.25 ml of solvent and alkyne (0.10 mmol) were added followed by

cyano diazoacetate (0.12 mmol, 1.2 equiv) and the remaining solvent (total 0.50 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. Following completion of the reaction (24 h), the reaction mixture was purified via flash column chromatography to afford compound **3**.

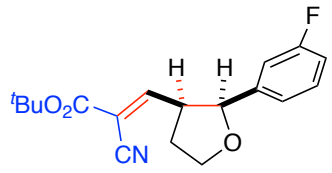
Characterization of Disubstituted Tetrahydrofurans

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)acrylate 3a.** 53%



Yield; >95:5 *E*/*Z* ; 91:9 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 2H), 7.28 – 7.17 (m, 3H), 7.00 (dd, *J* = 11.3, 0.8 Hz, 1H), 5.12 (d, *J* = 6.6 Hz, 1H), 4.33 (td, *J* = 8.2, 4.5 Hz, 1H), 4.01 (dtd, *J* = 8.6, 7.6, 0.9 Hz, 1H), 3.71 (ddt, *J* = 11.2, 6.8, 5.5 Hz, 1H), 2.54 – 2.34 (m, 1H), 2.06 – 1.97 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.52, 159.64, 137.88, 128.60, 127.93, 125.84, 114.04, 110.91, 83.64, 83.52, 68.04, 46.30, 32.44, 27.91. $[\alpha]_D^{20}$ = -20.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 11.5 min., t_{minor} = 8.5 min. *ee* 86%. IR (neat, cm^{-1}): 2981.07, 1720.05, 1450.77, 1370.62, 1273.55, 1150.85, 836.33. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{22}NO_3^+$: 300.1594; Found: 300.1586.

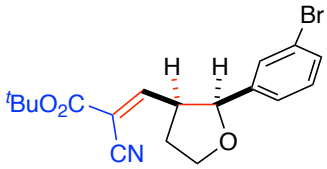
***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-fluorophenyl)tetrahydrofuran-3-yl)acrylate**



3b. 64% Yield; >95:5 *E*/*Z* ; 97:3 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 2H), 7.06 – 6.82 (m, 3H), 5.12 (dd, *J* = 6.5, 1.9 Hz, 1H), 4.34 (tdd, *J* = 8.6, 4.6, 2.0 Hz, 1H), 4.09 – 3.94 (m, 1H), 3.83 – 3.63 (m, 1H), 2.49 – 2.40 (m, 1H), 2.09 – 1.94 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.09 (d, J_{CF} = 246.5 Hz), 160.71, 159.54, 140.70 (d, J_{CF} = 7.2 Hz), 130.26 (d, J_{CF} = 8.6 Hz), 121.58 (d,

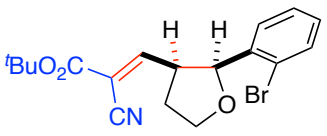
J_{CF} = 2.9 Hz), 114.83 (d, J_{CF} = 21.0 Hz), 113.92, 112.93 (d, J_{CF} = 22.4 Hz), 111.29, 83.85, 82.81 (d, J_{CF} = 2.4 Hz), 68.09, 46.22, 32.42, 27.91. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.42 (td, J = 9.5, 9.1, 5.4 Hz). $[\alpha]_D^{20}$ = -5.0° (c = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 5% hexanes rate 0.8 mL/min): t_{major} = 10.0 min., t_{minor} = 11.3 min. *ee* 87%. IR (neat, cm^{-1}): 2981.45, 1723.87, 1591.71, 1371.09, 1270.74, 1153.59, 758.43. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}NO_3F^+$: 318.1500; Found: 318.1495.

***tert*-Butyl (*E*)-3-((2*S*,3*S*)-2-(3-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate**



3c. 70% Yield; >95:5 *E*/*Z* ; 97:3 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 1H), 7.39 (dt, J = 7.8, 1.7 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.14 (ddt, J = 7.7, 1.8, 1.0 Hz, 1H), 6.97 (d, J = 11.2 Hz, 1H), 5.09 (d, J = 6.5 Hz, 1H), 4.34 (td, J = 8.3, 4.7 Hz, 1H), 4.02 (dt, J = 8.8, 7.6 Hz, 1H), 3.71 (dddd, J = 11.5, 7.6, 6.5, 5.3 Hz, 1H), 2.45 (dtd, J = 12.3, 7.6, 4.7 Hz, 1H), 2.00 (dtd, J = 13.1, 7.8, 5.3 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.57, 159.51, 140.35, 131.08, 130.20, 128.97, 124.64, 122.90, 113.89, 111.46, 83.91, 82.75, 68.13, 46.23, 32.40, 27.93. $[\alpha]_D^{20}$ = -10.0° (c = 1, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 12.0 min., t_{minor} = 11.1 min. *ee* 87%. IR (neat, cm^{-1}): 2980.77, 1722.89, 1569.87, 1370.65, 1256.71, 1152.55, 837.06. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{21}NO_3Br^+$: 378.0699; Found: 378.0602.

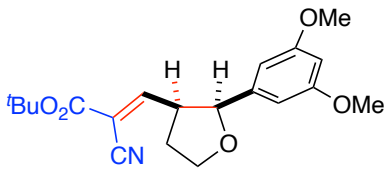
***tert*-Butyl (*E*)-3-((2*S*,3*S*)-2-(2-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate**



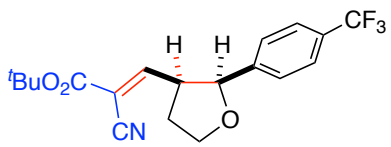
3d. 36% Yield; >95:5 *E*/*Z* ; 89:11 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (ddd, J = 12.8, 7.9, 1.7 Hz, 2H), 7.32 (td, J = 7.5, 1.3 Hz, 1H), 7.14 (td, J = 7.6, 1.8 Hz, 1H), 6.96

(d, J = 11.4 Hz, 1H), 5.32 (d, J = 6.5 Hz, 1H), 4.35 (td, J = 8.3, 4.3 Hz, 1H), 4.11 – 3.95 (m, 2H), 2.49 (dtd, J = 12.2, 7.6, 4.2 Hz, 1H), 1.96 (dtd, J = 13.4, 7.9, 5.5 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.44, 159.72, 137.30, 132.84, 129.43, 127.68, 127.55, 121.66, 113.78, 110.90, 83.65, 82.57, 67.93, 44.03, 32.80, 27.91. $[\alpha]_D^{20}$ = -5.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 15.0 min., t_{minor} = 14.0 min. *ee* 76%. IR (neat, cm^{-1}): 2978.90, 1723.13, 1625.76, 1369.60, 1256.02, 1158.04, 1089.67, 756.14. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{21}NO_3Br^+$: 378.0699; Found: 378.0698.

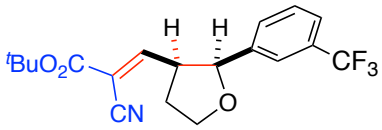
***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3,5-dimethoxyphenyl)tetrahydrofuran-3-yl)acrylate 3e.** 58% Yield; >95:5 *E*/*Z* ; 86:14 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) 7.05 (d, J = 11.3 Hz, 1H), 6.39 (d, J = 2.3 Hz, 2H), 6.33 (t, J = 2.3 Hz, 1H), 5.06 (d, J = 6.5 Hz, 1H), 4.32 (td, J = 8.4, 4.6 Hz, 1H), 4.01 (dt, J = 8.8, 7.6 Hz, 1H), 3.76 (s, 6H), 3.73 – 3.64 (m, 1H), 2.41 (dtd, J = 12.3, 7.6, 4.6 Hz, 1H), 1.99 (dtd, J = 13.1, 7.8, 5.3 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.43, 161.07, 159.73, 140.36, 114.12, 110.85, 103.62, 100.28, 83.68, 83.45, 68.09, 55.49, 46.29, 32.29, 27.91. $[\alpha]_D^{20}$ = -11.5° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 25% isopropanol- 75% hexanes rate 0.8 mL/min): t_{major} = 14.4 min., t_{minor} = 20.6 min. *ee* 86%. IR (neat, cm^{-1}): 2976.08, 1721.67, 1596.74, 1459.56, 1152.73, 1051.80, 837.65. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{26}NO_5^+$: 360.1806; Found: 360.1805.



***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate 3f.** 54% Yield; >95:5 *E*/*Z* ; 99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.46 – 7.36 (m, 2H), 6.95 (d, J =

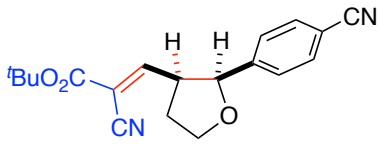


11.5 Hz, 1H), 5.17 (d, J = 6.4 Hz, 1H), 4.36 (td, J = 8.4, 5.0 Hz, 1H), 4.06 (dt, J = 8.8, 7.6 Hz, 1H), 3.76 (dddd, J = 11.4, 7.8, 6.4, 4.8 Hz, 1H), 2.49 (dtd, J = 12.7, 7.8, 5.0 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.45, 159.43, 142.05, 130.21, 126.24, 125.58 (q, J = 3.8 Hz), 113.87, 111.45, 83.98, 82.99, 68.12, 46.20, 32.43, 27.85. ^{19}F NMR (470 MHz, cdcl$_3$) δ -62.83. $[\alpha]_D^{20}$ = -20.0° (c = 1, $CHCl_3$). HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 9.4 min., t_{minor} = 10.9 min. *ee* 88%. IR (neat, cm^{-1}): 2983.14, 1724.14, 1324.38, 1124.52, 1066.98, 1016.72, 838.12. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}NO_3F_3^+$: 368.1468; Found: 368.1457.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate 3g.** 

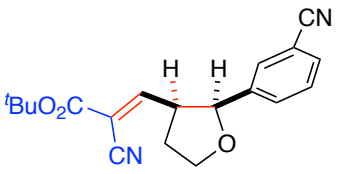
48% Yield; >95:5 E/Z ; 96:4 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.36 (m, 2H), 7.50 – 7.40 (m, 2H), 6.94 (dd, J = 11.4, 0.7 Hz, 1H), 5.18 (d, J = 6.5 Hz, 1H), 4.37 (td, J = 8.4, 4.9 Hz, 1H), 4.06 (dtd, J = 8.7, 7.8, 0.8 Hz, 1H), 3.76 (dtd, J = 11.7, 7.0, 4.7 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.03 (dtd, J = 12.2, 7.6, 7.2, 5.0 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.13, 159.24, 138.95, 129.27 (d, J = 1.9 Hz), 129.01, 124.64 (q, J = 3.8 Hz), 122.55 (q, J = 3.8 Hz), 113.65, 111.47, 83.79, 82.81, 67.98, 46.09, 32.21, 27.68. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.74. $[\alpha]_D^{20}$ = -5.0° (c = 1, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 7.8 min., t_{minor} = 7.2 min. *ee* 84%. IR (neat, cm^{-1}): 2982.98, 1724.65, 1334.58, 1256.55, 1124.85, 1072.95, 837.39. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{19}H_{21}NO_3F_3^+$: 368.1468; Found: 368.1471.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-cyanophenyl)tetrahydrofuran-3-yl)acrylate 3h.**



54% Yield; >95:5 *E*/*Z* ; 98:2 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 11.4 Hz, 1H), 5.15 (d, *J* = 6.3 Hz, 1H), 4.35 (td, *J* = 8.5, 5.2 Hz, 1H), 4.06 (q, *J* = 8.0 Hz, 1H), 3.86 – 3.67 (m, 1H), 2.50 (dtd, *J* = 13.0, 7.9, 5.2 Hz, 1H), 2.02 (dtd, *J* = 12.0, 7.2, 4.4 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.95, 159.32, 143.38, 132.46, 126.65, 118.67, 113.78, 111.85, 111.61, 84.19, 82.80, 68.06, 46.16, 32.46, 27.92. $[\alpha]_D^{20}$ = 33.2° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IE, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 18.2 min., t_{minor} = 20.0 min. *ee* 90%. IR (neat, cm^{-1}): 2981.58, 1722.89, 1370.52, 1273.71, 1153.12, 836.60. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}N_2O_3^+$: 325.1547; Found: 325.1563.

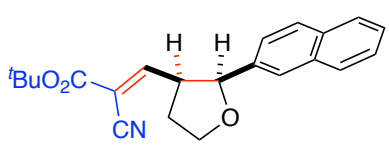
***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-cyanophenyl)tetrahydrofuran-3-yl)acrylate 3i.**



62% Yield; >95:5 *E*/*Z* ; 97:3 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56 (dtd, *J* = 6.5, 4.5, 3.9, 2.2 Hz, 1H), 7.48 – 7.44 (m, 2H), 6.93 (dd, *J* = 11.3, 1.7 Hz, 1H), 5.13 (d, *J* = 6.4 Hz, 1H), 4.39 – 4.28 (m, 1H), 4.13 – 3.94 (m, 1H), 3.76 (dq, *J* = 11.4, 6.2 Hz, 1H), 2.49 (dtdd, *J* = 12.8, 7.7, 5.0, 1.7 Hz, 1H), 2.02 (dtd, *J* = 14.7, 8.3, 7.8, 3.2 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.87, 159.32, 139.72, 131.69, 130.45, 129.46, 129.43, 118.61, 113.75, 112.90, 111.80, 84.16, 82.47, 68.10, 46.11, 32.46, 27.92. $[\alpha]_D^{20}$ = 15.3° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 27.0 min., t_{minor} = 24.1 min. *ee* 90%.

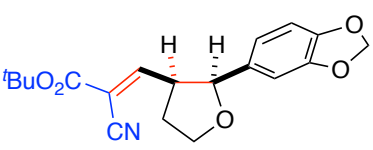
IR (neat, cm^{-1}): 2978.38, 2230.66, 1722.82, 1369.83, 1155.49, 754.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{21}N_2O_3^+$: 325.1547; Found: 325.1547.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(naphthalen-2-yl)tetrahydrofuran-3-yl)acrylate**



3j. 66% Yield; >95:5 *E*/*Z* ; 85:15 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.73 (m, 4H), 7.53 – 7.42 (m, 2H), 7.30 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.05 (d, *J* = 11.3 Hz, 1H), 5.30 (d, *J* = 6.6 Hz, 1H), 4.42 (td, *J* = 8.4, 4.7 Hz, 1H), 4.09 (dt, *J* = 8.8, 7.6 Hz, 1H), 3.82 (dddd, *J* = 11.4, 7.8, 6.5, 5.2 Hz, 1H), 2.50 (dtd, *J* = 12.5, 7.8, 4.7 Hz, 1H), 2.06 (dtd, *J* = 12.9, 7.8, 5.1 Hz, 1H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.32, 159.52, 135.35, 133.31, 133.10, 128.43, 128.15, 127.81, 126.40, 126.11, 124.71, 123.85, 114.04, 111.00, 85.67, 83.62, 68.11, 46.35, 32.59, 27.76. $[\alpha]_D^{20}$ = 90.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IF, 3% isopropanol- 97% hexanes rate 0.8 mL/min): t_{major} = 16.5 min., t_{minor} = 17.5 min. *ee* 89%. IR (neat, cm^{-1}): 2979.26, 1720.08, 1369.38, 1255.50, 1154.66, 820.44. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{24}NO_3^+$: 350.1751; Found: 350.1766.

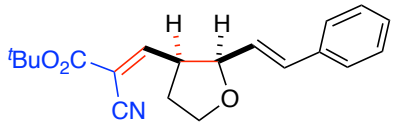
***tert*-Butyl (*E*)-3-((2*S*,3*S*)-2-(benzo[d][1,3]dioxol-5-yl)tetrahydrofuran-3-yl)-2-cyanoacrylate**



3k. 45% Yield; >95:5 *E*/*Z* ; 58:42 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 11.3 Hz, 1H), 6.78 – 6.74 (m, 2H), 6.72 – 6.66 (m, 1H), 5.94 (dd, *J* = 8.7, 1.5 Hz, 2H), 5.05 (d, *J* = 6.5 Hz, 1H), 4.31 (td, *J* = 8.3, 4.4 Hz, 1H), 3.99 (dt, *J* = 8.8, 7.6 Hz, 1H), 3.80 – 3.56 (m, 1H), 2.42 (dtd, *J* = 12.0, 7.6, 4.4 Hz, 1H), 1.99 (dtd, *J* = 13.4, 7.8, 5.6 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.49, 159.72, 147.99, 147.21, 131.89, 119.31, 114.07, 111.01, 108.41, 106.52,

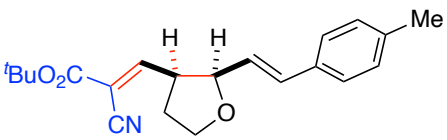
101.20, 83.75, 83.30, 68.03, 46.43, 32.48, 27.97. $[\alpha]_D^{20}$ = 91.6° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IA, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 18.0 min., t_{minor} = 15.6 min. *ee* 84%. IR (neat, cm^{-1}): 2979.57, 1722.49, 1488.90, 1249.27, 1036.72, 933.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{22}NO_5^+$: 344.1493; Found: 344.1494.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)acrylate 3l.** 59%



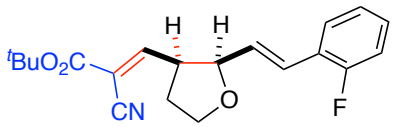
Yield; >95:5 *E*/*Z* ; 86:14 dr. R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 11.1 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.31 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.71 – 6.65 (m, 1H), 6.04 (ddd, *J* = 15.9, 6.4, 0.6 Hz, 1H), 4.68 (td, *J* = 6.4, 1.4 Hz, 1H), 4.21 (td, *J* = 8.4, 4.7 Hz, 1H), 3.95 (dt, *J* = 8.7, 7.6 Hz, 1H), 3.60 (ddt, *J* = 11.7, 7.7, 6.0 Hz, 1H), 1.99 (dtd, *J* = 13.3, 7.8, 5.7 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.02, 159.85, 136.32, 133.18, 128.71, 128.13, 126.80, 124.93, 114.05, 111.64, 84.01, 82.38, 67.63, 45.93, 32.50, 27.99. $[\alpha]_D^{20}$ = 79.8° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 22.5 min., t_{minor} = 19.9 min. *ee* 89 %. IR (neat, cm^{-1}): 2981.43, 1724.32, 1627.05, 1370.85, 1257.88, 1156.22, 752.64. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.1751; Found: 326.1748.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-4-methylstyryl)tetrahydrofuran-3-yl)acryla**

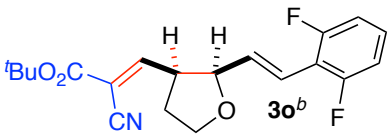


3m. 80% Yield; >95:5 *E*/*Z* ; 74:26 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 11.2, 1.4 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 2H), 6.64 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 6.7 Hz, 1H), 4.70 – 4.64 (m, 1H), 4.20 (tdd, *J* = 8.5, 4.8, 1.5 Hz, 1H), 3.94 (td, *J* = 8.9, 8.2, 6.9 Hz, 1H), 3.62 – 3.53 (m, 1H), 2.39 (dtdd, *J* = 12.6, 6.3, 4.7, 2.3 Hz, 1H), 2.33 (s, 3H), 2.05 – 1.91 (m, 1H), 1.49 (s, 9H). ^{13}C

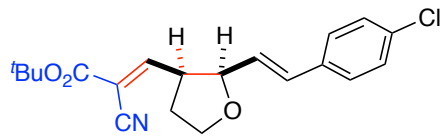
NMR (150 MHz, $CDCl_3$) δ 161.11, 159.87, 138.05, 133.54, 133.21, 129.40, 126.72, 123.80, 114.06, 111.58, 83.98, 82.53, 67.58, 45.96, 32.51, 28.00, 21.34. $[\alpha]_D^{20}$ = 61.8° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 23.1 min., t_{minor} = 20.7 min. *ee* 89 %. IR (neat, cm^{-1}): 2979.87, 2933.51, 1724.68, 1370.40, 1257.43, 1156.06, 838.26, 731.80. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{26}NO_3^+$: 340.1907; Found: 340.1910.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-fluorostyryl)tetrahydrofuran-3-yl)acrylate 3n.** 

72% Yield; >95:5 *E*/*Z* ; 90:10 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 11.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.8 Hz, 1H), 7.22 (tdd, *J* = 8.1, 5.2, 1.8 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (ddd, *J* = 10.7, 8.1, 1.2 Hz, 1H), 6.80 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.14 (dd, *J* = 16.1, 6.4 Hz, 1H), 4.70 (td, *J* = 6.5, 1.5 Hz, 1H), 4.22 (td, *J* = 8.4, 4.6 Hz, 1H), 3.95 (dt, *J* = 8.7, 7.6 Hz, 1H), 3.61 (ddt, *J* = 10.9, 7.5, 6.0 Hz, 1H), 2.40 (dtd, *J* = 12.5, 7.6, 4.7 Hz, 1H), 1.99 (dtd, *J* = 13.8, 7.8, 5.9 Hz, 1H), 1.49 (d, *J* = 1.0 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.85, 159.84, 160.51 (d, *J* = 250.3 Hz), 129.41 (d, *J* = 8.1 Hz), 128.11 (d, *J* = 4.0 Hz), 127.94 (d, *J* = 5.2 Hz), 125.72 (d, *J* = 2.9 Hz), 124.24 (d, *J* = 3.5 Hz), 124.17 (d, *J* = 12.1 Hz), 115.93 (d, *J* = 22.0 Hz), 114.01, 111.72, 84.01, 82.40, 67.73, 45.87, 32.44, 27.97. ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.26 – -117.41 (m). $[\alpha]_D^{20}$ = 52.8° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 15.3 min., t_{minor} = 14.2 min. *ee* 89%. IR (neat, cm^{-1}): 2981.43, 2934.83, 1724.98, 1371.01, 1257.65, 1155.64, 759.97. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{23}NO_3F^+$: 344.1657; Found: 344.1664.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2,6-difluorostyryl)tetrahydrofuran-3-yl)acrylate 3o.** 

43% Yield; >95:5 *E*/*Z* ; 95:5 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 11.2, 1.2 Hz, 1H), 7.16 (tt, *J* = 8.4, 6.2 Hz, 1H), 6.86 (t, *J* = 8.5 Hz, 2H), 6.69 (dt, *J* = 16.3, 1.4 Hz, 1H), 6.34 (dd, *J* = 16.3, 6.2 Hz, 1H), 4.70 (t, *J* = 5.9 Hz, 1H), 4.27 – 4.18 (m, 1H), 3.96 (dtd, *J* = 8.8, 7.7, 1.2 Hz, 1H), 3.63 (ddd, *J* = 10.3, 7.2, 5.7 Hz, 1H), 2.45 – 2.31 (m, 1H), 2.08 – 1.92 (m, 1H), 1.50 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.07 (dd, *J* = 251.4, 7.5 Hz), 160.74, 159.84, 132.34 (t, *J* = 7.2 Hz), 128.71 (t, *J* = 11.0 Hz), 118.98, 114.04, 113.83, 111.83, 111.63 (dd, *J* = 21.4, 5.2 Hz), 83.95, 82.67, 67.89, 45.85, 32.36, 27.99. $[\alpha]_D^{20}$ = 20.1° (*c* = 1, $CHCl_3$). HPLC (Chiral IA, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 6.3 min., t_{minor} = 5.9 min. *ee* 83%. IR (neat, cm^{-1}): 2981.16, 2029.31, 1726.81, 1622.35, 1466.23, 1157.90, 990.38, 733.23. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{22}NO_3F_2^+$: 362.1562; Found: 362.1556.

***tert*-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-chlorostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate 3p.** 

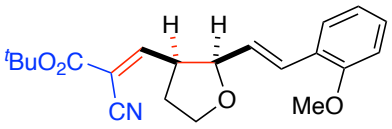
49% Yield; >95:5 *E*/*Z* ; 81:19 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 11.1, 1.2 Hz, 1H), 7.32 – 7.24 (m, 4H), 6.62 (dt, *J* = 15.9, 1.3 Hz, 1H), 6.01 (ddd, *J* = 15.9, 6.3, 1.2 Hz, 1H), 4.66 (tt, *J* = 6.3, 1.4 Hz, 1H), 4.20 (td, *J* = 8.4, 4.9 Hz, 1H), 3.94 (dtd, *J* = 8.7, 7.6, 1.2 Hz, 1H), 3.58 (dq, *J* = 12.1, 7.5, 6.9 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.07 – 1.86 (m, 1H), 1.48 (d, *J* = 1.2 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.85, 159.82, 134.81, 133.84, 131.87, 128.91, 127.99, 125.66, 114.01, 111.72, 84.11, 82.19, 67.68, 45.86, 32.50, 28.00. $[\alpha]_D^{20}$ = 118.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IA, 5% isopropanol- 95% hexanes rate 1.0

mL/min): t_{major} = 8.9 min., t_{minor} = 7.8 min. *ee* 90%. IR (neat, cm^{-1}): 2980.97, 1725.52, 1491.81, 1370.51, 1258.01, 1158.33, 1090.51, 764.10. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{23}NO_3Cl^+$: 360.1361; Found: 360.1378.

***tert*-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-bromostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate 3q.** 61% Yield; >95:5 *E*/*Z* ; 87:13 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 3H), 7.23 – 7.17 (m, 2H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.03 (ddd, *J* = 15.8, 6.3, 1.3 Hz, 1H), 4.66 (td, *J* = 6.3, 3.2 Hz, 1H), 4.21 (td, *J* = 8.4, 4.7 Hz, 1H), 3.95 (dtd, *J* = 8.9, 7.6, 1.2 Hz, 1H), 3.65 – 3.55 (m, 1H), 2.43 – 2.34 (m, 1H), 2.11 – 1.88 (m, 1H), 1.49 (d, *J* = 1.3 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.82, 159.81, 135.24, 131.91, 131.86, 128.30, 125.80, 122.00, 114.01, 111.73, 84.12, 82.18, 67.68, 45.83, 32.50, 28.01. $[\alpha]_D^{20}$ = 58.8° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 14.0 min., t_{minor} = 15.1 min. *ee* 93%. IR (neat, cm^{-1}): 2980.84, 1724.23, 1488.54, 1370.68, 1258.22, 1157.10, 838.13, 755.66. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{23}NO_3Br^+$: 404.0856; Found: 404.0861.

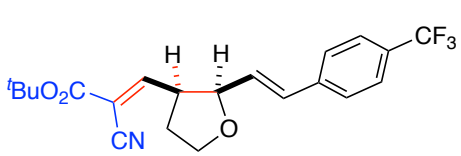
***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-3-methoxystyryl)tetrahydrofuran-3-yl)acrylate 3r.** 69% Yield; >95:5 *E*/*Z* ; 83:17 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 11.1 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (q, *J* = 2.3, 1.8 Hz, 1H), 6.81 (dd, *J* = 8.2, 3.5 Hz, 1H), 6.65 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.5 Hz, 1H), 4.68 (td, *J* = 6.4, 1.3 Hz, 1H), 4.21 (td, *J* = 8.4, 4.9 Hz, 1H), 3.95 (q, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.60 (ddt, *J* =

11.4, 7.8, 5.9 Hz, 1H), 2.40 (dtd, *J* = 12.6, 7.7, 4.8 Hz, 1H), 1.99 (dtd, *J* = 13.1, 8.1, 5.7 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.97, 159.94, 159.84, 137.79, 133.08, 129.69, 125.30, 119.83, 119.43, 113.82, 112.16, 111.69, 84.02, 82.33, 67.64, 55.36, 45.93, 32.52, 28.00. $[\alpha]_D^{20}$ = 79.8° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 1.0 mL/min): t_{major} = 35.8 min., t_{minor} = 19.5 min. *ee* 90%. IR (neat, cm^{-1}): 2980.39, 1724.07, 1599.83, 1370.69, 1258.31, 1157.18, 1043.32, 762.98. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{26}NO_4^+$: 356.1856; Found: 356.1851.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-methoxystyryl)tetrahydrofuran-3-yl)acrylate 3s.** 

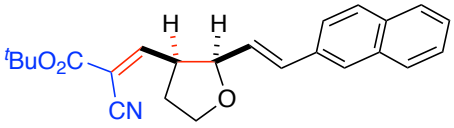
72% Yield; >95:5 *E*/*Z* ; 69:31 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 11.2 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.23 (tt, *J* = 7.6, 1.7 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.92 – 6.88 (m, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.09 (dd, *J* = 16.0, 6.7 Hz, 1H), 4.68 (td, *J* = 6.5, 1.5 Hz, 1H), 4.21 (td, *J* = 8.4, 4.7 Hz, 1H), 3.98 – 3.89 (m, 1H), 3.83 (s, 3H), 3.59 (ddt, *J* = 11.6, 7.8, 6.0 Hz, 1H), 2.39 (dtd, *J* = 12.6, 7.8, 4.7 Hz, 1H), 1.99 (tdd, *J* = 12.9, 10.1, 7.0 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.41, 159.93, 157.15, 129.17, 128.48, 127.56, 125.66, 125.44, 120.68, 114.11, 111.46, 111.01, 83.87, 82.95, 67.60, 55.55, 46.02, 32.50, 28.00. $[\alpha]_D^{20}$ = 55.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 14.4 min., t_{minor} = 18.2 min. *ee* 84%. IR (neat, cm^{-1}): 2980.67, 1724.27, 1490.17, 1370.69, 1247.39, 1158.13, 1027.86, 753.66. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{26}NO_4^+$: 356.1856; Found: 356.1852.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-4-(trifluoromethyl)styryl)tetrahydrofuran-3-yl)acrylate 3t.** 81% Yield; >95:5 *E*/*Z* ; 93:7 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H



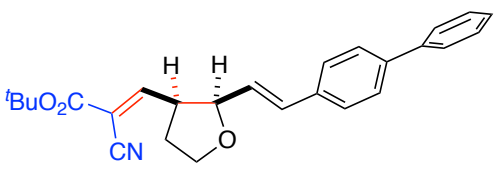
NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.39 (m, 3H), 6.72 (dd, *J* = 16.0, 1.5 Hz, 1H), 6.14 (dd, *J* = 15.8, 6.2 Hz, 1H), 4.70 (td, *J* = 6.2, 1.6 Hz, 1H), 4.22 (td, *J* = 8.4, 4.8 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.62 (ddt, *J* = 11.4, 7.6, 5.7 Hz, 1H), 2.42 (dtd, *J* = 12.6, 7.6, 4.8 Hz, 1H), 2.00 (dtd, *J* = 12.9, 7.8, 5.6 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.64, 159.77, 139.76, 131.51, 129.93 (q, *J* = 32.9 Hz), 127.81, 126.92, 125.71 (q, *J* = 3.5 Hz), 113.97, 111.81, 84.15, 81.97, 67.73, 45.81, 32.48, 27.97. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.61. $[\alpha]_D^{20}$ = 8.1° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 11.6 min., t_{minor} = 13.2 min. *ee* 90%. IR (neat, cm^{-1}): 2982.25, 1732.93, 1325.36, 1164.10, 1126.70, 1067.61, 758.65. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{23}NO_3F_3^+$: 394.1625; Found: 394.1613.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-(naphthalen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate 3u.** 66% Yield; >95:5 *E*/*Z* ; 75:25 dr;

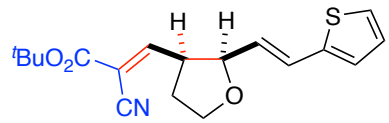


R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.68 (m, 4H), 7.53 (t, *J* = 10.5 Hz, 2H), 7.45 (ddt, *J* = 9.7, 7.3, 3.7 Hz, 2H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 6.5 Hz, 1H), 4.74 (t, *J* = 6.4 Hz, 1H), 4.25 (td, *J* = 8.5, 4.8 Hz, 1H), 3.97 (q, *J* = 7.9 Hz, 1H), 3.64 (ddd, *J* = 13.6, 11.5, 6.1 Hz, 1H), 2.42 (ddt, *J* = 15.4, 7.8, 3.9 Hz, 1H), 2.02 (ddd, *J* = 13.2, 10.5, 6.6 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.01, 159.84, 133.75, 133.62, 133.29, 133.26, 128.37, 128.18, 127.79, 126.95, 126.47, 126.21, 125.28, 123.71, 114.06, 111.69, 84.00, 82.46, 67.66, 45.97, 32.55, 27.98. $[\alpha]_D^{20}$ = 83.9° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 10% isopropanol- 90% hexanes rate mL/min): t_{major} = 13.6 min., t_{minor} = 15.2 min. *ee* 92%. IR

(neat, cm^{-1}): 2979.59, 2231.29, 1723.76, 1369.82, 1256.89, 1158.91, 968.76, 764.46. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{24}H_{26}NO_3^+$: 376.1907; Found: 376.1895.

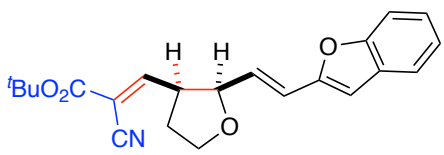
***tert*-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate 3v.** 

64% Yield; >95:5 *E*/*Z* ; 74:26 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.50 (dd, *J* = 11.2, 1.4 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.35 (tt, *J* = 6.7, 1.3 Hz, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.10 (ddd, *J* = 15.9, 6.5, 1.4 Hz, 1H), 4.71 (tt, *J* = 6.5, 1.5 Hz, 1H), 4.23 (tdd, *J* = 8.4, 4.8, 1.4 Hz, 1H), 3.96 (td, *J* = 8.9, 8.2, 6.8 Hz, 1H), 3.69 – 3.57 (m, 1H), 2.47 – 2.37 (m, 1H), 2.07 – 1.95 (m, 1H), 1.50 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.01, 159.85, 140.95, 140.74, 135.34, 132.71, 128.93, 127.53, 127.41, 127.24, 127.09, 125.02, 114.05, 111.68, 84.02, 82.42, 67.65, 45.96, 32.53, 28.01. $[\alpha]_D^{20}$ = 152.4° (*c* = 1, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 24.2 min., t_{minor} = 21.3 min. *ee* 89%. IR (neat, cm^{-1}): 2981.62, 1724.20, 1486.83, 1370.50, 1258.44, 1157.65, 760.45. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{26}H_{28}NO_3^+$: 402.2064; Found: 402.2065.

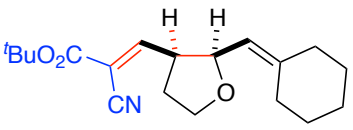
***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-(thiophen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate 3w.** 

61% Yield; >95:5 *E*/*Z* ; 84:16 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 10.9, 5.3 Hz, 1H), 7.17 (dd, *J* = 12.6, 4.3 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 5.87 (dd, *J* = 15.6, 6.5 Hz, 1H), 4.64 (td, *J* = 6.5, 1.5 Hz, 1H), 4.19 (td, *J* = 8.4, 4.6 Hz, 1H), 3.93 (q, *J* = 7.6 Hz, 1H), 3.57 (ddd, *J* = 13.8, 11.0, 6.2 Hz, 1H), 2.38 (dtd, *J* = 12.5, 7.6, 4.5 Hz, 1H), 1.98 (tdd, *J* = 15.7, 8.0, 5.0 Hz, 1H), 1.49

(s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.78, 159.80, 141.30, 127.55, 126.55, 126.10, 124.95, 124.43, 114.02, 111.78, 84.22, 81.99, 67.68, 45.89, 32.46, 28.00. $[\alpha]_D^{20}$ = 78.0° (*c* = 0.2, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 19.1 min., t_{minor} = 17.8 min. *ee* 90%. IR (neat, cm^{-1}): 2979.08, 2923.84, 1724.72, 1370.45, 1258.20, 1158.68, 764.96. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{22}NO_3S^+$: 332.1315; Found: 332.1304.

***tert*-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-2-(benzofuran-2-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate 3x.** 

44% Yield; >95:5 *E*/*Z* ; 92:8 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.36 (m, 3H), 7.30 – 7.23 (m, 1H), 7.22 – 7.14 (m, 1H), 6.67 – 6.54 (m, 2H), 6.29 (dd, *J* = 15.6, 5.9 Hz, 1H), 4.72 (t, *J* = 6.1 Hz, 1H), 4.22 (td, *J* = 8.4, 4.5 Hz, 1H), 3.96 (q, *J* = 7.7 Hz, 1H), 3.62 (dq, *J* = 13.5, 6.4 Hz, 1H), 2.48 – 2.31 (m, 1H), 2.01 (dt, *J* = 12.6, 7.0 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.64, 159.15, 153.71, 128.92, 126.85, 124.93, 123.00, 121.16, 120.96, 113.81, 111.84, 111.12, 105.69, 84.08, 81.57, 67.70, 45.81, 32.51, 28.00. $[\alpha]_D^{20}$ = 50.8° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 14.4 min., t_{minor} = 18.2 min. *ee* 84%. IR (neat, cm^{-1}): 2981.43, 1727.18, 1452.47, 1370.89, 1255.88, 1156.27, 752.75. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{24}NO_4^+$: 366.1700; Found: 366.1700.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylidenemethyl)tetrahydrofuran-3-yl)acrylate 3y.** 

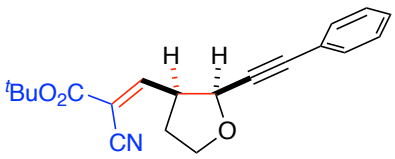
43% Yield; >95:5 *E*/*Z* ; 55:45 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 11.2 Hz, 1H), 7.26 (s, 1H), 5.04 (dt, *J* = 8.7, 1.2 Hz, 1H), 4.77 (dd, *J* = 8.7,

6.5 Hz, 1H), 4.13 (td, *J* = 8.4, 4.5 Hz, 1H), 3.83 (dt, *J* = 8.8, 7.7 Hz, 1H), 3.46 (ddt, *J* = 11.2, 7.9, 6.1 Hz, 1H), 2.34 (dtd, *J* = 12.3, 7.7, 4.4 Hz, 1H), 2.20 – 2.11 (m, 2H), 2.08 (td, *J* = 7.0, 3.5 Hz, 2H), 1.92 (dtd, *J* = 13.8, 7.9, 5.7 Hz, 1H), 1.64 – 1.54 (m, 4H), 1.53 (s, 9H), 1.50 – 1.39 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.15, 160.07, 146.06, 117.31, 114.13, 111.09, 83.84, 78.51, 67.24, 45.76, 37.17, 32.57, 29.64, 28.55, 28.05, 27.69, 26.63. $[\alpha]_D^{20}$ = 27.2° HPLC (Chiral IE, 2% isopropanol- 98% hexanes rate mL/min): t_{major} = 19.1 min., t_{minor} = 21.4 min. *ee* 80 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 10.7 Hz, 1H), 5.23 – 5.10 (m, 1H), 4.41 (t, *J* = 8.4 Hz, 1H), 4.05 (dt, *J* = 8.8, 7.3 Hz, 1H), 3.97 (td, *J* = 8.7, 4.8 Hz, 1H), 3.10 (dq, *J* = 10.7, 8.3 Hz, 1H), 2.34 (dtd, *J* = 12.5, 7.6, 4.8 Hz, 1H), 2.21 – 2.11 (m, 1H), 2.11 – 2.02 (m, 3H), 1.96 (dtd, *J* = 12.6, 8.8, 7.3 Hz, 1H), 1.71 – 1.56 (m, 5H), 1.53 (s, 9H), 1.39 – 1.27 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.61, 160.06, 146.48, 119.43, 114.04, 112.18, 84.00, 79.89, 67.78, 49.24, 37.23, 33.18, 29.66, 28.34, 28.22, 28.02, 26.69. $[\alpha]_D^{20}$ = 80.8° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IE, 2% isopropanol- 98% hexanes rate mL/min): t_{major} = 22.5 min., t_{minor} = 24.6 min. *ee* 58 %. IR (neat, cm^{-1}): 2931.33, 2854.49, 1725.43, 1256.68, 1160.12. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{28}NO_3^+$: 318.2064; Found: 318.2065.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohex-1-en-1-yl)tetrahydrofuran-3-yl)acrylate 3z.** 21% Yield; >95:5 *E*/*Z* ; 57:43 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 10.7 Hz, 1H), 7.36 (d, *J* = 11.3 Hz, 1H), 5.82 (tt, *J* = 3.8, 1.7 Hz, 1H), 5.73 – 5.56 (m, 1H), 4.34 – 4.23 (m, 1H), 4.15 (td, *J* = 8.3, 4.7 Hz, 1H), 4.03 – 3.95 (m, 3H), 3.85 (dt, *J* = 8.7, 7.6 Hz, 1H), 3.50 (dddd, *J* = 11.2, 7.9, 6.3, 4.7 Hz, 1H), 3.29 (dq, *J* = 10.6, 8.1 Hz, 1H), 2.42 – 2.23 (m, 2H), 2.09 – 1.93 (m, 7H), 1.88 (dtd, *J* = 12.8, 7.8, 4.8

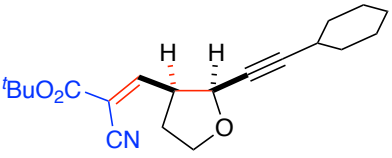
Hz, 1H), 1.83 – 1.68 (m, 3H), 1.65 – 1.57 (m, 3H), 1.54 (s, 9H), 1.52 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.40, 161.42, 160.08, 135.09, 133.65, 126.03, 123.65, 114.13, 113.98, 111.93, 110.18, 88.02, 84.81, 84.06, 83.72, 68.30, 67.48, 45.85, 44.30, 33.44, 32.54, 28.04, 26.51, 25.19, 24.86, 23.51, 22.60, 22.54, 22.48, 22.45. $[\alpha]_D^{20}$ = 37.4° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 10.8 min., t_{minor} = 8.4 min. *ee* 59%; t_{major} = 9.0 min., t_{minor} = 9.5 min. *ee* 84%. IR (neat, cm^{-1}): 2932.08, 1725.36, 1369.85, 1256.14, 1159.23, 1091.74, 838.89. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{18}H_{26}NO_3^+$: 304.1907; Found: 304.1909.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(phenylethynyl)tetrahydrofuran-3-yl)acrylate**



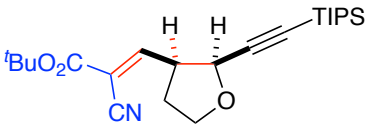
3aa. 36% Yield; >95:5 *E*/*Z*; 75:25 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 10.6 Hz, 1H), 7.51 – 7.37 (m, 2H), 7.37 – 7.28 (m, 3H), 5.00 (d, *J* = 6.8 Hz, 1H), 4.22 (td, *J* = 8.6, 4.5 Hz, 1H), 3.98 (dt, *J* = 8.7, 7.6 Hz, 1H), 3.61 (dtd, *J* = 10.6, 8.1, 6.7 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.16 – 2.05 (m, 1H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.36, 159.83, 131.95, 129.02, 128.47, 121.98, 114.01, 112.23, 89.21, 84.21, 84.04, 72.04, 67.84, 45.54, 31.89, 28.02. $[\alpha]_D^{20}$ = 112.8° (*c* = 1, $CHCl_3$). HPLC (Chiral IB, 5% isopropanol- 95% hexanes rate 1.0 mL/min): t_{major} = 7.0 min., t_{minor} = 7.7 min. *ee* 77%. IR (neat, cm^{-1}): 2980.90, 1724.61, 1370.84, 1257.58, 1156.01, 759.63, 691.81. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{22}NO^+$: 324.1594; Found: 324.1607.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylethynyl)tetrahydrofuran-3-yl)acrylate**



3ab. 32% Yield; >95:5 *E*/*Z*; 50:50 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz,

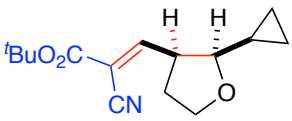
$CDCl_3$) δ 7.63 (d, *J* = 10.6 Hz, 1H), 7.38 (d, *J* = 10.8 Hz, 1H), 4.74 (dd, *J* = 6.7, 1.9 Hz, 1H), 4.40 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.14 (td, *J* = 8.6, 4.6 Hz, 1H), 4.07 (dt, *J* = 8.8, 7.5 Hz, 1H), 4.00 (td, *J* = 8.5, 4.8 Hz, 1H), 3.89 (dt, *J* = 8.7, 7.5 Hz, 1H), 3.53 – 3.43 (m, 2H), 2.44 – 2.36 (m, 3H), 2.30 (dtd, *J* = 12.6, 7.8, 4.6 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.88 (ddt, *J* = 12.6, 8.4, 7.3 Hz, 1H), 1.78 (qt, *J* = 12.0, 6.2 Hz, 4H), 1.72 – 1.62 (m, 4H), 1.54 (d, *J* = 2.9 Hz, 18H), 1.52 – 1.36 (m, 4H), 1.28 (ddt, *J* = 18.6, 8.3, 2.8 Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.09, 159.97, 159.94, 159.88, 114.06, 113.76, 112.25, 111.74, 94.30, 92.03, 84.14, 83.82, 76.75, 75.29, 72.92, 71.85, 67.52, 67.43, 49.72, 45.44, 32.54, 32.49, 32.43, 32.41, 31.77, 29.13, 29.08, 28.01, 25.92, 25.89, 24.93, 24.84. $[\alpha]_D^{20}$ = 11.0° (*c* = 1, $CHCl_3$). HPLC (Chiral IB, 2% isopropanol- 98% hexanes rate mL/min): t_{major} = 7.6 min., t_{minor} = 6.8 min. *ee* 87%; t_{major} = 8.1 min., t_{minor} = 14.4 min. *ee* 54%. IR (neat, cm^{-1}): 2931.65, 2855.32, 1726.33, 1370.35, 1157.01, 838.59. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{22}NO_3^+$: 324.1594; Found: 324.1607.

***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((triisopropylsilyl)ethynyl)tetrahydrofuran-3-yl)acrylate 3ac.** 

46% Yield; >95:5 *E*/*Z* ; 52:48 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 10.6 Hz, 1H), 7.37 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 6.5 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 1H), 4.21 – 3.99 (m, 3H), 3.93 (q, *J* = 8.4, 7.9 Hz, 1H), 3.58 – 3.44 (m, 2H), 2.45 (dtd, *J* = 12.6, 7.8, 4.6 Hz, 1H), 2.32 (dtd, *J* = 12.8, 8.0, 4.8 Hz, 1H), 2.01 (ddt, *J* = 12.6, 8.8, 7.2 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.52 (s, 18H), 1.06 (s, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.18, 159.85, 159.63, 159.60, 113.99, 113.56, 112.30, 112.17, 107.84, 103.84, 102.21, 90.52, 88.64, 85.68, 84.12, 83.81, 72.91, 71.88, 67.51, 67.40, 49.66, 45.44, 32.25, 31.69, 28.20, 27.97, 27.95, 18.66, 18.64, 11.15, 11.13. $[\alpha]_D^{20}$ =

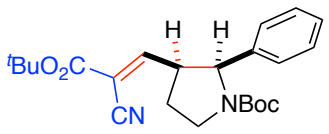
34.4° (c = 1, $CHCl_3$). HPLC (Chiral IC, 1% isopropanol- 99% hexanes rate mL/min): t_{major} = 20.3 min., t_{minor} = 9.5 min. *ee* 33%. IR (neat, cm^{-1}): 2943.17, 2865.92, 1725.22, 1461.88, 1370.26, 1257.10, 1159.07, 678.79. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{23}H_{38}NO_3Si^+$: 404.2616; Found: 404.2612.

***tert*-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-cyclopropyltetrahydrofuran-3-yl)acrylate 3ad.**



14% Yield; >95:5 *E*/*Z* ; 75:25 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). Major ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 10.8 Hz, 1H), 4.02 (dt, J = 8.6, 7.3 Hz, 1H), 3.94 (td, J = 8.5, 5.0 Hz, 1H), 3.36 – 3.26 (m, 1H), 3.08 (t, J = 7.8 Hz, 1H), 2.34 – 2.28 (m, 1H), 2.01 – 1.84 (m, 1H), 1.54 (s, 9H), 1.00 (qt, J = 8.1, 4.9 Hz, 1H), 0.66 – 0.48 (m, 2H), 0.46 – 0.31 (m, 1H), 0.26 – 0.13 (m, 1H). Minor ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 11.2 Hz, 1H), 4.12 (td, J = 8.4, 4.8 Hz, 1H), 3.82 (dt, J = 8.7, 7.5 Hz, 1H), 3.47 (ddt, J = 11.4, 7.8, 5.3 Hz, 1H), 3.36 – 3.26 (m, 1H), 2.34 – 2.28 (m, 1H), 2.01 – 1.84 (m, 1H), 1.54 (s, 9H), 0.93 – 0.70 (m, 2H), 0.66 – 0.48 (m, 1H), 0.46 – 0.31 (m, 1H), 0.26 – 0.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.95, 161.41, 160.13, 160.09, 114.15, 114.09, 111.86, 111.17, 88.08, 87.08, 84.12, 83.96, 67.81, 67.37, 48.41, 45.06, 33.29, 32.30, 28.07, 28.05, 14.32, 11.61, 4.27, 3.07, 2.00, 1.87. $[\alpha]_D^{20}$ = 29.1° (c = 0.2, $CHCl_3$). HPLC (Chiral IF, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 8.2 min., t_{minor} = 13.8 min. *ee* 66%; t_{major} = 9.25 min., t_{minor} = 12.48 min. *ee* 69%. IR (neat, cm^{-1}): 2930.65, 1725.84, 1370.12, 1257.48, 1159.55, 1053.98, 764.71. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{22}NO_3^+$: 264.1594; Found: 264.1609.

***tert*-Butyl (2*S*,3*S*)-3-((*E*)-3-(tert-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-2-phenylpyrrolidine-1-carboxylate 3ae.** 28% Yield; >95:5 *E*/*Z*; 86:14 dr; R_f = 0.3

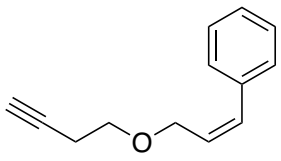


(hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.32 (dd, J = 8.1, 6.4 Hz, 3H), 7.05 (d, J = 7.5 Hz, 2H), 6.69 (d, J = 10.6 Hz, 1H), 5.24 – 4.92 (m, 1H), 3.89 (d, J = 47.2 Hz, 1H), 3.64 (t, J = 8.7 Hz, 2H), 2.20 – 1.98 (m, 2H), 1.44 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98, 159.52, 154.02, 139.53, 128.67, 127.88, 126.45, 113.93, 111.84, 84.30, 83.91, 80.01, 64.26, 46.42, 46.03, 28.18, 27.92. $[\alpha]_D^{20}$ = 73.4° (c = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 24.6 min., t_{minor} = 26.9 min. *ee* 96%. IR (neat, cm^{-1}): 2976.90, 1725.69, 1697.86, 1392.59, 1253.61, 1162.20, 764.55. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{31}N_2O_4^+$: 399.2278; Found: 399.2279.

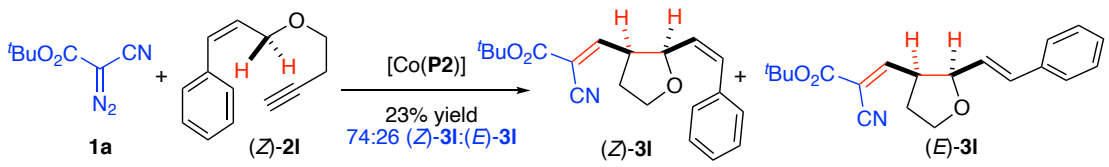
3.4.4. Mechanistic Studies of the Proposed Stepwise Radical Mechanism

3.4.4.1. Probing of ε-Co(III)-Alkyl Radical Intermediate by Reaction of (Z)-1,7-enynes

(*Z*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene (*Z*)-2l. 60% Yield; R_f = 0.3



(hexanes/ethyl acetate, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (q, J = 7.4 Hz, 2H), 7.32 – 7.19 (m, 3H), 6.63 (tt, J = 11.5, 2.0 Hz, 1H), 5.89 (dq, J = 12.5, 6.1 Hz, 1H), 4.31 (ddd, J = 7.6, 6.2, 1.9 Hz, 2H), 3.60 (t, J = 6.9 Hz, 2H), 2.50 (td, J = 6.9, 2.7 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.70, 132.05, 129.07, 128.91, 128.36, 127.35, 81.43, 69.42, 68.53, 67.73, 20.02.



An oven dried Schlenk tube, that was previously charged with catalyst (5 mol %), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum, and 0.25 ml of solvent and alkyne (*Z*)-**2l** (0.10 mmol) were added followed by cyano diazoacetate **1a** (0.12 mmol, 1.2 equiv) and the remaining solvent (total 0.50 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. Following completion of the reaction (24 h), the reaction mixture was purified via flash column chromatography to afford compound (*Z*)-**3l** and (*E*)-**3l**. 23% Yield; 74:26 (*Z*)-**3l**:(*E*)-**3l**; R_f = 0.2 (hexanes/ethyl acetate, 4:1).

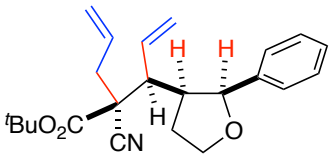
For (*Z*)-**3l** *cis*: ^{1}H NMR (600 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) 7.56 (dd, *J* = 11.4, 1.7 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.23 (dd, *J* = 7.8, 6.0 Hz, 2H), 6.73 (d, *J* = 11.7 Hz, 1H), 5.62 (ddd, *J* = 11.5, 9.3, 1.6 Hz, 1H), 4.89 – 4.72 (m, 1H), 4.22 – 4.14 (m, 1H), 3.89 – 3.77 (m, 1H), 3.58 (dq, *J* = 11.4, 5.7, 4.9 Hz, 1H), 2.39 (dddd, *J* = 12.7, 7.8, 4.9, 1.7 Hz, 1H), 1.97 (dddd, *J* = 12.8, 9.2, 6.1, 3.4 Hz, 1H), 1.54 (s, 9H).

For (*Z*)-**3l** *trans* : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 6H), 6.77 (d, *J* = 11.2 Hz, 1H), 5.74 (ddd, *J* = 11.4, 9.0, 1.7 Hz, 1H), 4.50 (t, *J* = 8.4 Hz, 1H), 4.13 – 4.06 (m, 1H), 4.03 (ddd, *J* = 9.9, 5.1, 2.5 Hz, 1H), 3.33 – 3.19 (m, 1H), 2.46 – 2.32 (m, 1H), 1.97 (dddd, *J* = 12.8, 9.2, 6.1, 3.4 Hz, 1H), 1.52 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.82, 160.14, 159.96, 136.09, 135.27, 134.50, 129.25, 128.86, 128.72, 128.57, 128.49, 127.83, 127.73, 127.05, 113.96, 111.51, 84.05, 79.48, 78.37, 67.95, 67.38, 49.19, 46.01, 33.50, 32.96, 28.06, 28.02. IR (neat, cm^{-1}): 2979.78, 2932.47, 2876.32, 1724.91, 1624.68, 1369.94, 1257.20, 1159.14, 1087.31, 766.08. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_3^+$: 326.1751; Found: 326.1759

3.4.5. Further Transformations

3.4.5.1. 1,4-Addition

To a solution of (+)-**3a** (1.0 equiv) in THF (10 mL/mmol) was added a solution of Grignard reagent (2.0 equiv) at 0 °C. After complete addition, the resulting solution is stirred at 0 °C for 2 h. Then allyl bromide (10 equiv) was added dropwise at 0 °C. The resulting solution was slowly warmed to 40 °C and detected by TLC. The reaction is quenched by slow addition of water at r.t. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude product, which is purified by flash column chromatography.

***tert*-Butyl (2*S*,3*S*)-2-allyl-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)pent-4-enoate 4** 

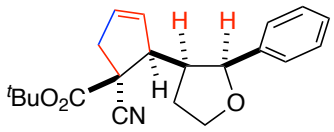
57 % Yield; 99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.19 (m, 2H), 5.72 (dddd, *J* = 16.6, 10.3, 8.3, 6.4 Hz, 1H), 5.50 (dt, *J* = 17.0, 10.3 Hz, 1H), 5.19 – 5.10 (m, 2H), 4.94 (d, *J* = 7.9 Hz, 1H), 4.87 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.27 (td, *J* = 8.2, 2.9 Hz, 1H), 3.98 (dd, *J* = 17.0, 1.7 Hz, 1H), 3.91 (ddd, *J* = 9.4, 8.3, 6.8 Hz, 1H), 2.53 (dd, *J* = 10.4, 1.8 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.30 – 2.12 (m, 3H), 1.56 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.54, 139.97, 131.87, 130.87, 127.94, 127.62, 127.58, 121.27, 120.49, 118.74, 84.77, 83.54, 68.49, 54.29, 47.29, 45.09, 41.16, 28.17, 27.29. $[\alpha]_D^{20}$ = 122.78° (*c* = 1.5, $CHCl_3$). HPLC (Chiral IC, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 8.7 min., t_{minor} = 10.6 min. *ee* 85%. IR (neat, cm^{-1}): 2980.12, 1733.54, 1253.22, 1150.04, 1060.01,

928.79, 701.90. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{23}H_{30}NO_3^+$: 368.2220; Found: 368.2216.

3.4.5.2. Olefin Metathesis

A solution of Grubbs 2nd generation catalyst (0.1 equiv) in anhydrous dichloromethane (10 mL/mmol) was added dropwise to the **4a** and the resulting mixture stirred at 40 °C for 5 h. Removal of all volatiles under reduced pressure yields the crude products **5a**, which are purified by flash column chromatography.

***tert*-Butyl (1*S*,2*S*)-1-cyano-2-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)cyclopent-3-ene-**



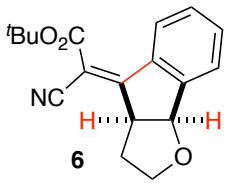
1-carboxylate 5 70% Yield; 99:1 dr; R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 4H), 7.28 – 7.17 (m, 1H), 5.63 (dq, *J* = 4.6, 2.4 Hz, 1H), 5.34 (dq, *J* = 4.6, 2.3 Hz, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 4.09 (td, *J* = 8.6, 5.0 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.11 – 3.03 (m, 1H), 2.99 (tt, *J* = 7.0, 3.5 Hz, 1H), 2.91 – 2.79 (m, 2H), 2.40 – 2.27 (m, 1H), 2.03 – 1.89 (m, 1H), 1.44 – 1.28 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.54, 139.26, 130.19, 128.56, 128.35, 127.45, 126.14, 120.20, 83.82, 67.59, 54.50, 50.98, 45.35, 42.68, 27.72, 18.63, 11.26. $[\alpha]_D^{20}$ = -32.4° (*c* = 1, $CHCl_3$). HPLC (Chiral IE, 5% isopropanol-95% hexanes rate 0.8 mL/min): t_{major} = 10.6 min., t_{minor} = 11.4 min. *ee* 84%. IR (neat, cm^{-1}): 2978.91, 2874.59, 1738.23, 1370.05, 1251.53, 1153.36, 1062.49, 840.70, 701.87. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{26}NO_3^+$: 340.1907; Found: 340.1904.

3.4.5.3. Intramolecular Heck Reaction

An oven dried Schlenk tube, that was previously charged with $Pd(OAc)_2$ (10 mol %), PPh_3 (0.2 equiv) and compound **3d** (0.1 mmol, 1.0 equiv), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum,

and 0.5 ml of DMF and Et3N (2.0 equiv) were added followed by the remaining DMF (total 1.0 mL). The resulting solution was heated at 100 °C and detected by TLC. The reaction is quenched by addition of water at r.t. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude product, which is purified by flash column chromatography.

***tert*-Butyl (*Z*)-2-cyano-2-((3a*S*,8b*S*)-2,3,3a,8b-tetrahydro-4*H*-indeno[1,2-*b*]furan-4-ylidene)acetate 6** 54% Yield; 95:5 *E*/*Z* ; R_f = 0.4 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.54 – 7.45 (m, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 4.54 – 4.46 (m, 1H), 3.88 (tdd, *J* = 8.9, 4.0, 1.5 Hz, 1H), 3.43 – 3.34 (m, 1H), 2.61 (tddd, *J* = 10.8, 8.8, 7.2, 1.6 Hz, 1H), 1.71 (dddd, *J* = 12.0, 5.9, 4.0, 1.7 Hz, 1H), 1.58 (d, *J* = 1.6 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.27, 161.76, 149.89, 136.50, 134.36, 129.89, 126.42, 126.09, 116.80, 98.47, 83.31, 82.81, 67.11, 49.24, 34.61, 28.15. $[\alpha]_D^{20}$ = -113° (*c* = 1, $CHCl_3$). HPLC (Chiral IC, 5% isopropanol- 95% hexanes rate 0.8 mL/min): t_{major} = 16.2 min., t_{minor} = 15.0 min. *ee* 74%. IR (neat, cm^{-1}): 2979.59, 2216.80, 1716.85, 1579.25, 1255.42, 1125.19, 772.32. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{18}H_{20}NO_3^+$: 298.1438; Found: 298.1439.



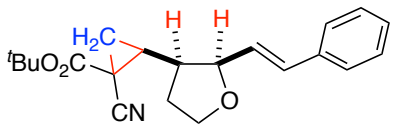
6

3.4.5.4. Cyclopropanation

To a solution of (+)-**3l** (1.0 equiv) and trimethylsulfoxonium iodide (1.2 equiv) in DMSO (10 mL/mmol) was added NaOH (1.0 equiv) at rt. the resulting solution is stirred at r.t. for 30 min. The reaction is quenched by slow addition of water at r.t. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are

dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude product, which is purified by flash column chromatography.

***tert*-Butyl (2*S*)-1-cyano-2-((2*R*,3*S*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)cyclopropane-**

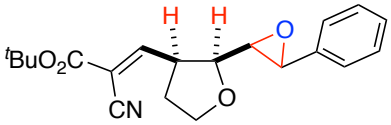


1-carboxylate 7 Colorless liquid; 79% Yield; 68:32 dr. R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.30 (dd, *J* = 15.9, 6.2 Hz, 1H), 4.66 (td, *J* = 6.2, 1.4 Hz, 1H), 4.14 (td, *J* = 8.2, 5.5 Hz, 1H), 3.87 (td, *J* = 8.3, 6.9 Hz, 1H), 2.32 (dtd, *J* = 13.1, 7.8, 5.5 Hz, 1H), 2.20 (ddt, *J* = 10.6, 8.8, 4.6 Hz, 1H), 1.99 (dtd, *J* = 12.5, 7.3, 5.0 Hz, 1H), 1.85 (dt, *J* = 10.9, 8.4 Hz, 1H), 1.74 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.34 – 1.28 (m, 1H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.04, 136.80, 132.11, 128.68, 127.79, 126.81, 125.86, 118.14, 83.96, 80.98, 66.81, 44.97, 32.40, 31.56, 27.53, 23.64, 21.44. $[\alpha]_D^{20}$ = 94.4° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IB, 5% isopropanol- 95% hexanes rate 0.8 ml/min): t_{major} = 10.6 min., t_{minor} = 12.3 min. *ee* 89%. IR (neat, cm^{-1}): 2980.61, 1725.62, 1370.36, 1257.25, 1159.81, 1086.95, 892.42, 763.00. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{26}NO_3^+$: 340.1907, found 340.1898.

3.4.5.5. Chemoselective Epoxidation

To a solution of (+)-**3l** (1.0 equiv) in DCM (10 mL/mmol) was added *m*-CPBA (1.0 equiv) at 0 °C. The resulting solution was slowly warmed to r.t. and detected by TLC. The reaction is quenched by slow addition of water at r.t. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude product, which is purified by flash column chromatography.

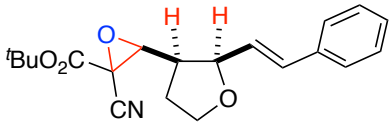
***tert*-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((2*S*)-3-phenyloxiran-2-yl)tetrahydrofuran-3-yl)acrylate 8**



85% Yield; 63:37 dr; R_f = 0.3 (hexanes/ethyl acetate, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 11.3 Hz, 1H), 7.30 (dq, *J* = 8.7, 6.7 Hz, 3H), 7.26 – 7.21 (m, 2H), 4.15 (td, *J* = 8.3, 5.0 Hz, 1H), 4.06 (t, *J* = 5.7 Hz, 1H), 3.93 (dt, *J* = 8.5, 7.5 Hz, 1H), 3.88 (d, *J* = 2.2 Hz, 1H), 3.65 (ddt, *J* = 11.4, 7.5, 5.7 Hz, 1H), 2.97 (dd, *J* = 5.3, 2.1 Hz, 1H), 2.39 (dtd, *J* = 12.8, 7.6, 5.0 Hz, 1H), 1.99 (dtd, *J* = 13.2, 7.6, 5.5 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.69, 159.19, 136.23, 128.65, 128.52, 125.79, 113.83, 111.91, 84.15, 80.86, 68.01, 60.36, 57.02, 44.13, 32.18, 27.98. $[\alpha]_D^{20}$ = 15.0° (*c* = 0.5, $CHCl_3$). HPLC (Chiral IF, 10% isopropanol- 90% hexanes rate 0.8 mL/min): t_{major} = 22.1 min., t_{minor} = 14.5 min. *ee* 89%. IR (neat, cm^{-1}): 2923.35, 2850.68, 1727.00, 1369.98, 1318.51, 1260.67, 1152.90, 840.35, 751.02. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{20}H_{24}NO_4^+$: 342.1700; Found: 342.1691.

To a solution of (+)-**3l** (1.0 equiv) in DCM (10 mL/mmol) was added Na_2CO_3 (2.0 equiv), then *m*-CPBA (2.0 equiv) was added at 0 °C. The resulting solution was slowly warmed to r.t. and detected by TLC. The reaction is quenched by slow addition of water at r.t. The layers are separated and the aqueous phase is extracted with Et_2O. The combined organic layers are dried over Na_2SO_4 and filtered. Removal of all volatiles under reduced pressure yields the crude product, which is purified by flash column chromatograph

***tert*-Butyl (3*S*)-2-cyano-3-((2*R*,3*R*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)oxirane-2-carboxylate 9**



65% Yield; 68:32 dr; R_f = 0.3 (hexanes/ethyl acetate,

6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.20 (m, 1H), 6.79 – 6.73 (m, 1H), 6.26 (ddd, *J* = 16.0, 5.9, 1.6 Hz, 1H), 4.67 (td, *J* = 6.0, 3.0 Hz, 1H), 4.26 – 4.14 (m, 1H), 3.92 (tdd, *J* = 8.4, 6.7, 1.7 Hz, 1H), 3.32 (dd, *J* = 9.7, 1.6 Hz, 1H), 2.47 (dtt, *J* = 7.6, 3.8, 1.8 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.30 – 2.15 (m, 1H), 1.19 (d, *J* = 1.6 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.40, 136.19, 132.36, 128.83, 128.19, 126.71, 124.35, 114.21, 86.18, 80.18, 67.14, 65.14, 51.87, 43.78, 30.51, 27.39. $[\alpha]_D^{20}$ = 24.8° (*c* = 0.5, $CHCl_3$). HPLC (Chiral ID, 5% isopropanol- 95% hexanes rate mL/min): t_{major} = 17.7 min., t_{minor} = 12.4 min. *ee* 89%. IR (neat, cm^{-1}): 2981.34, 2934.80, 1751.59, 1371.48, 1301.45, 1153.84, 1069.25, 973.44, 834.56, 757.23. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{24}NO_4^+$: 342.1700; Found: 342.1709.

3.4.6. X-ray Crystallographic Information

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (Cu K_α, λ = 1.54178 Å). Indexing was performed using *APEX2*[19] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[20] Absorption correction was performed by multi-scan method implemented in SADABS.[21] Space group were determined using XPREP implemented in APEX2.[19] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[22-24]program.

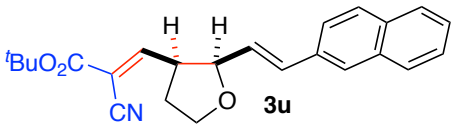
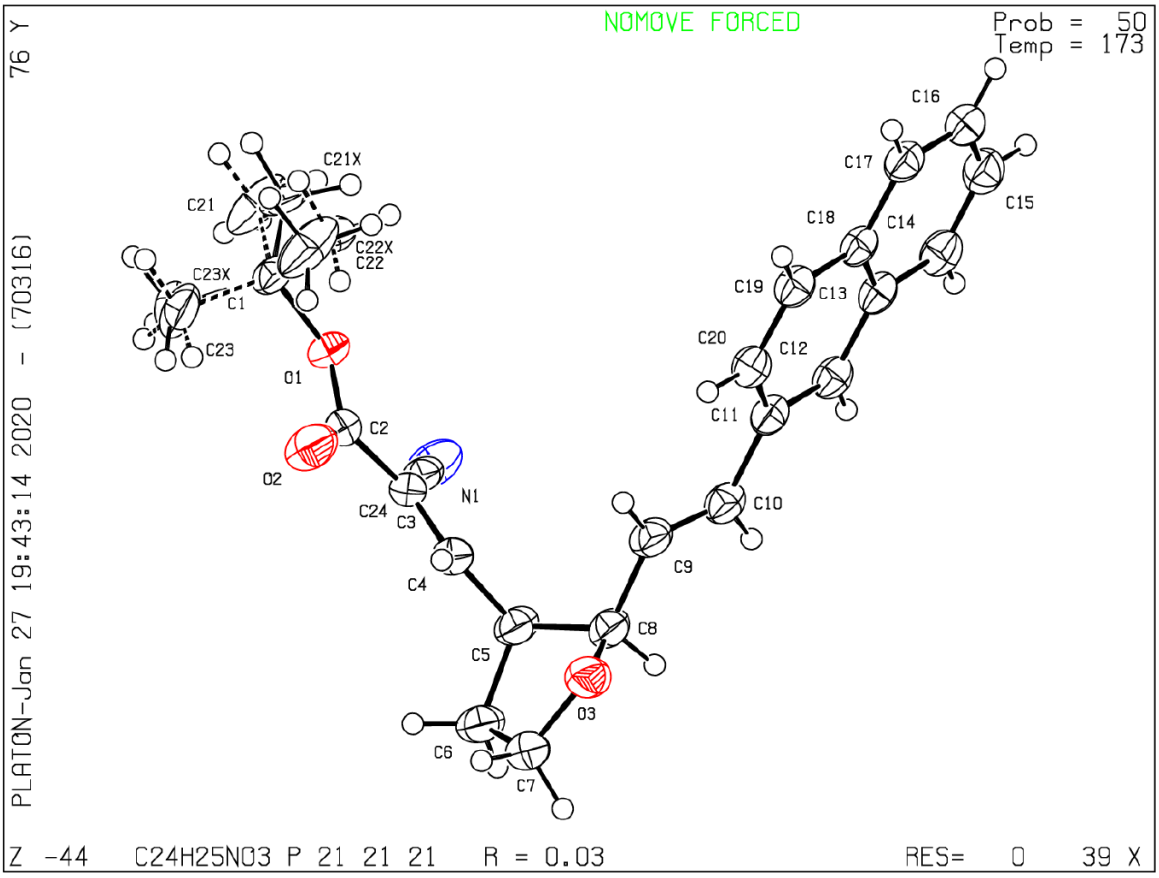


Table 1. Crystal data and structure refinement for (+)-**3u**.

Identification code	(+)-**3u**	
Empirical formula	C24 H25 N O3	
Formula weight	375.45	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8166(3) Å	α= 90°.
	b = 10.8885(6) Å	β= 90°.
	c = 32.2640(18) Å	γ = 90°.
Volume	2043.41(19) Å^3	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.638 mm^{-1}	
F(000)	800	
Crystal size	0.420 x 0.160 x 0.120 mm^3	
Theta range for data collection	2.739 to 66.289°.	
Index ranges	-6<=h<=6, -12<=k<=12, -38<=l<=37	
Reflections collected	41216	
Independent reflections	3559 [R(int) = 0.0288]	
Completeness to theta = 66.289°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6927	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3559 / 18 / 282	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R_1 = 0.0258, wR_2 = 0.0664	
R indices (all data)	R_1 = 0.0270, wR_2 = 0.0682	
Absolute structure parameter	0.01(4)	
Extinction coefficient	0.0045(5)	
Largest diff. peak and hole	0.120 and -0.123 e. Å^{-3}	


NOMOVE FORCED
Prob = 50
Temp = 173
PLATON-Jan 27 19:43:14 2020 - (70316)
76 Y
C16
C17
C15
C18
C14
C19
C13
C20
C12
C11
C10
C9
C8
C21X
C21
C22X
C22
C23X
C1
C23
O1
C2
O2
C24
C3
N1
C4
C5
O3
C6
C7
Z -44 C24H25NO3 P 21 21 21 R = 0.03
RES= 0 39 X

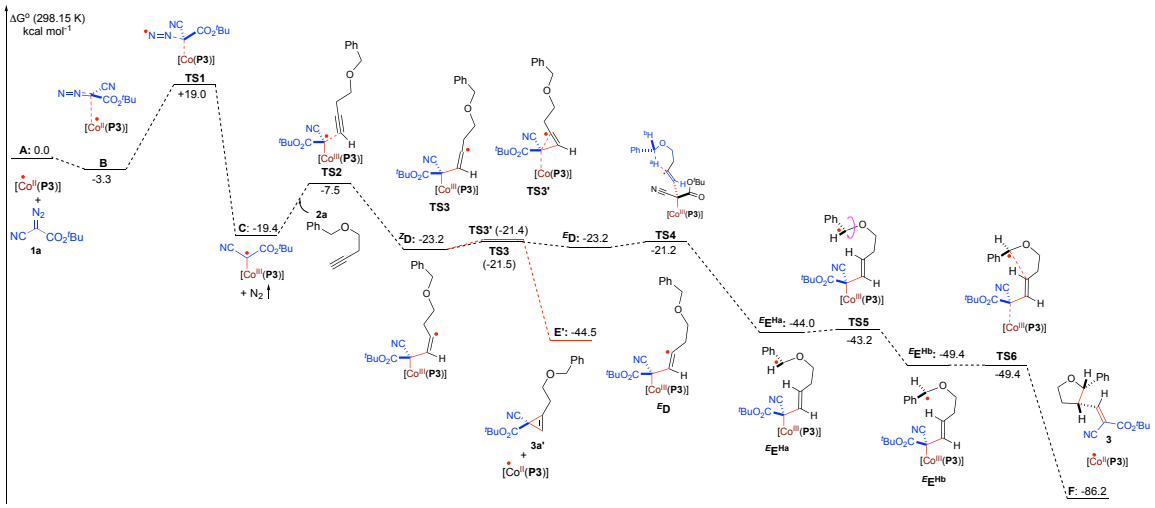
3.4.7. DFT Calculations

Considering the cost of time and computing resources for the large system with [Co(**P3**)], the geometry optimizations were performed with the Gaussian 16[25] at the BP86[26,27]/lanl2dz[28,29] 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).

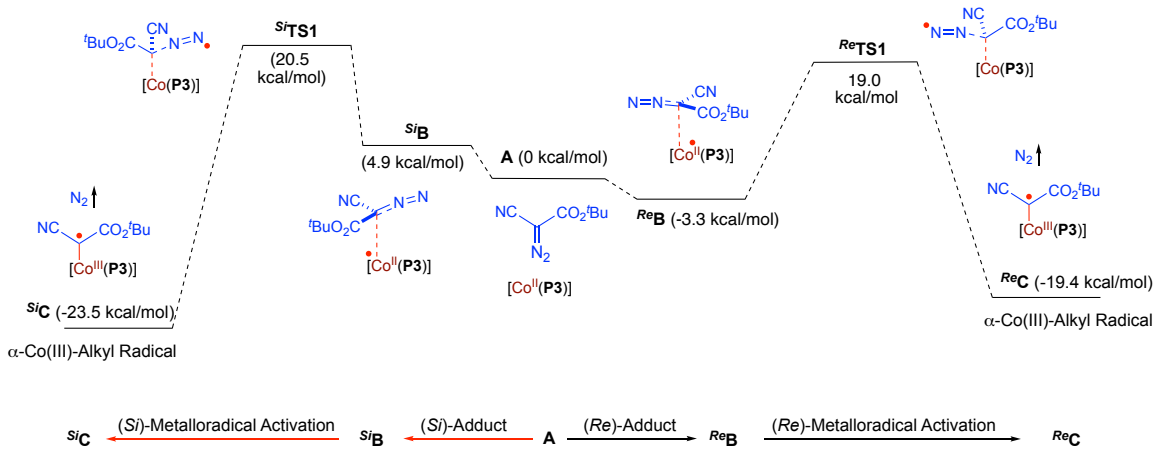
Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy and thermal corrections (entropy and enthalpy, 298.15 K (room temperature), 1 atm) were obtained from these calculations. Intrinsic reaction coordinate (IRC) calculations were performed with local quadratic approximation (LQA)[30,31] method to ensure the transition states found connected the reactant and the product. To further improve the accuracy of energies, single point energies were carried out at the b3lyp[32]/def2-tzvp[28,29] level of theory along with Grimme's dispersion correction[33] (D3BJ) and SMD[34] solvation model (in MeOH).

Independent Gradient Model (IGM)[35]analysis was performed with Multiwfn[36] software package using high quality grid option to generate files for further plotting. The visualization of IGM analysis results were presented with VMD[37] visualization software. As shown in Scheme S5, the 3D diagrams of optimized structures were generated with CYLview software,[38] and the NCI (noncovalent interaction) visual representations and spin density isosurface map of optimized structures were generated with VMD.

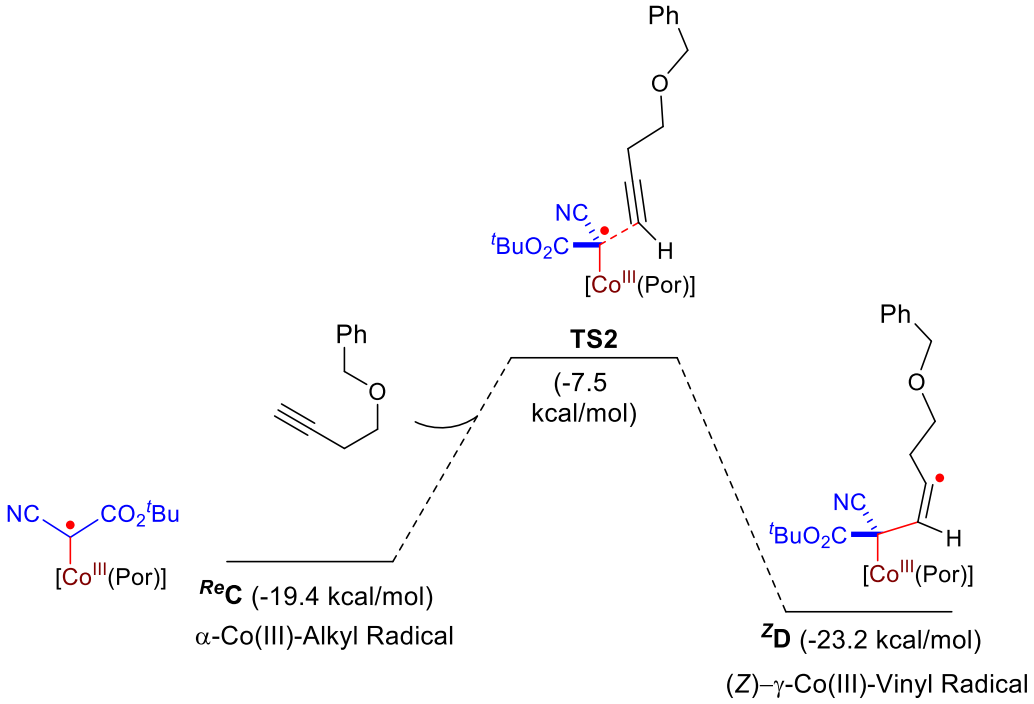
Scheme 3.8. Calculated Energy Diagram for [Co(P3)]-Catalyzed Radical Cascade Involving HAA Process of Homopropargylic Ether 2a with *tert*-Butyl α-Cyanodiazoacetate 1a



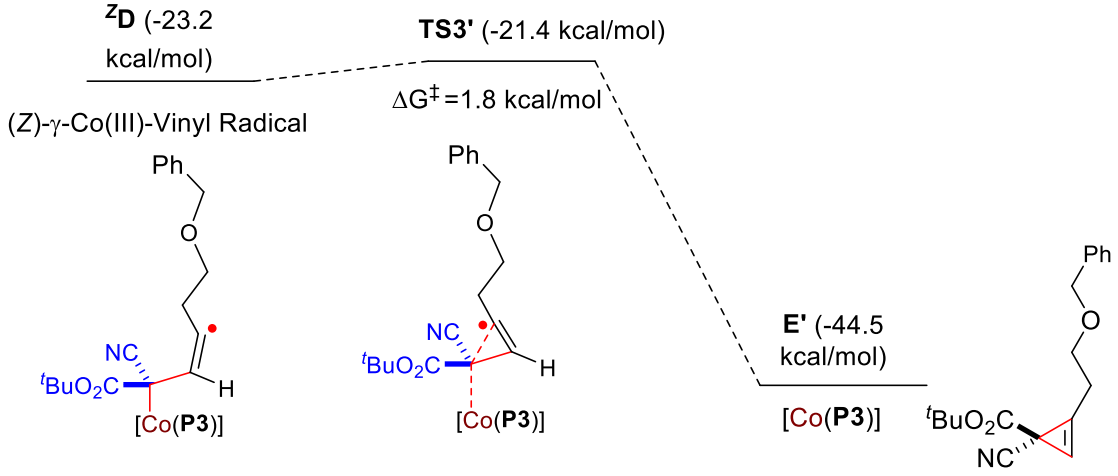
Scheme 3.9. Calculated Energy Diagram for Metalloradical Activation



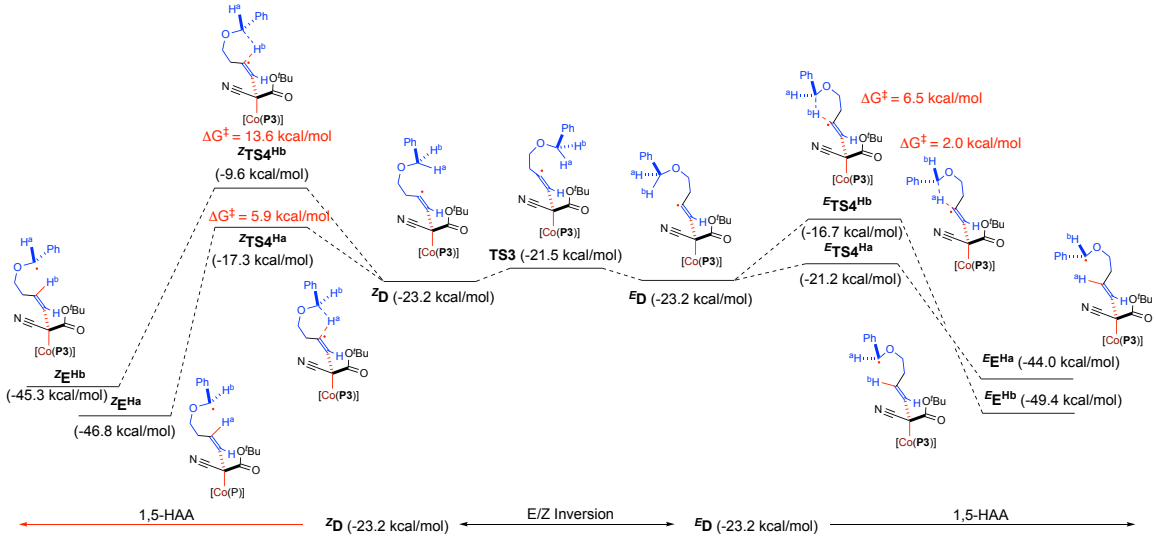
Scheme 3.10. Calculated Energy Diagram for Radical Addition



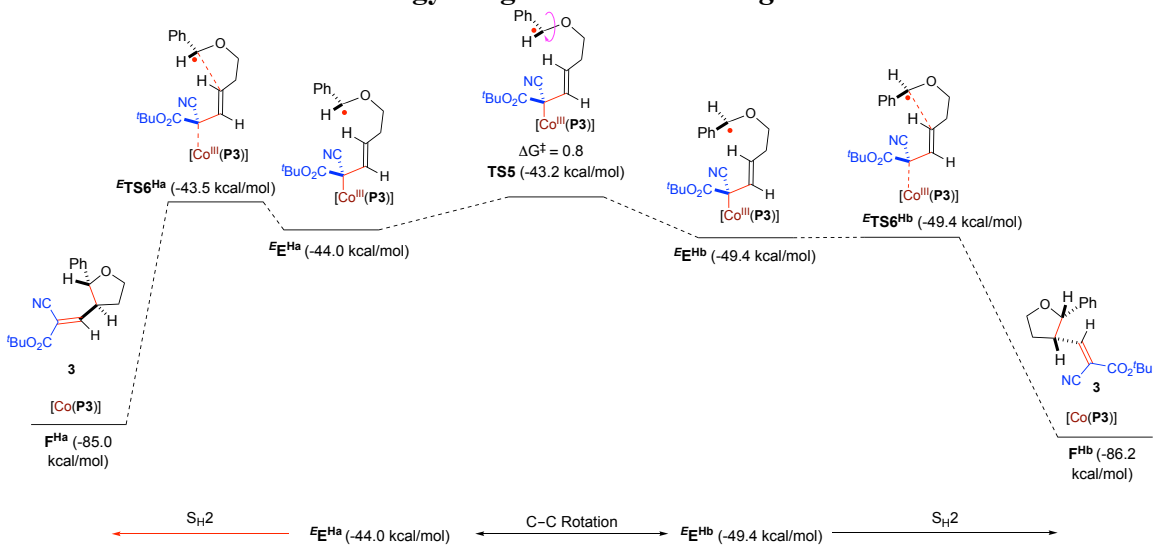
Scheme 3.11. Calculated Energy Diagram for *3-Exo-Tet* Radical Substitution



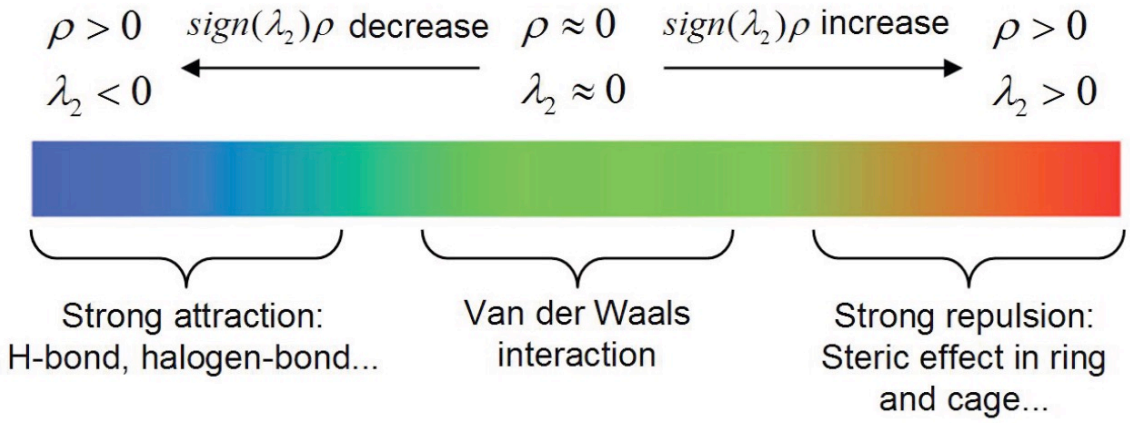
Scheme 3.12. Calculated Energy Diagram for Selective 1,5-HAA

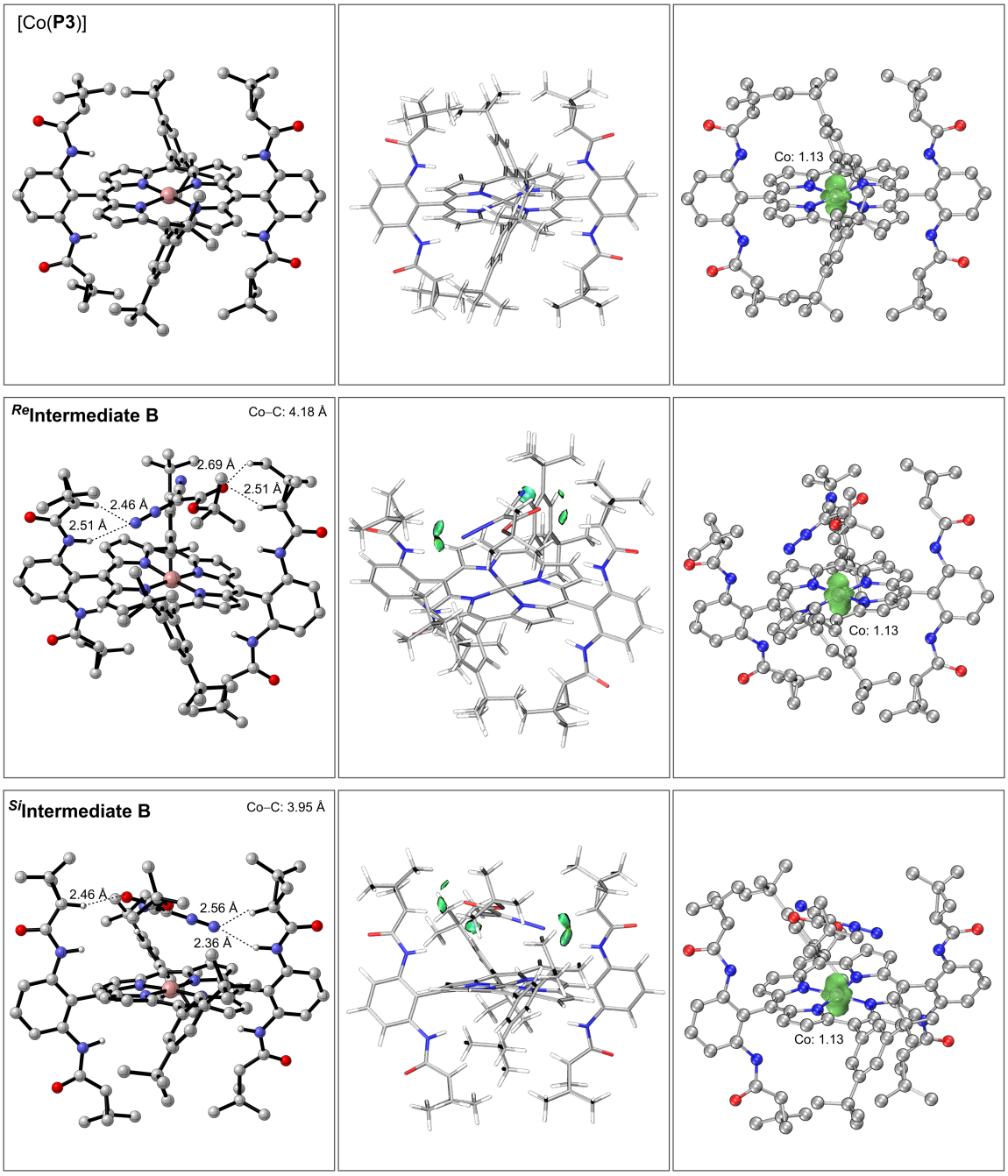


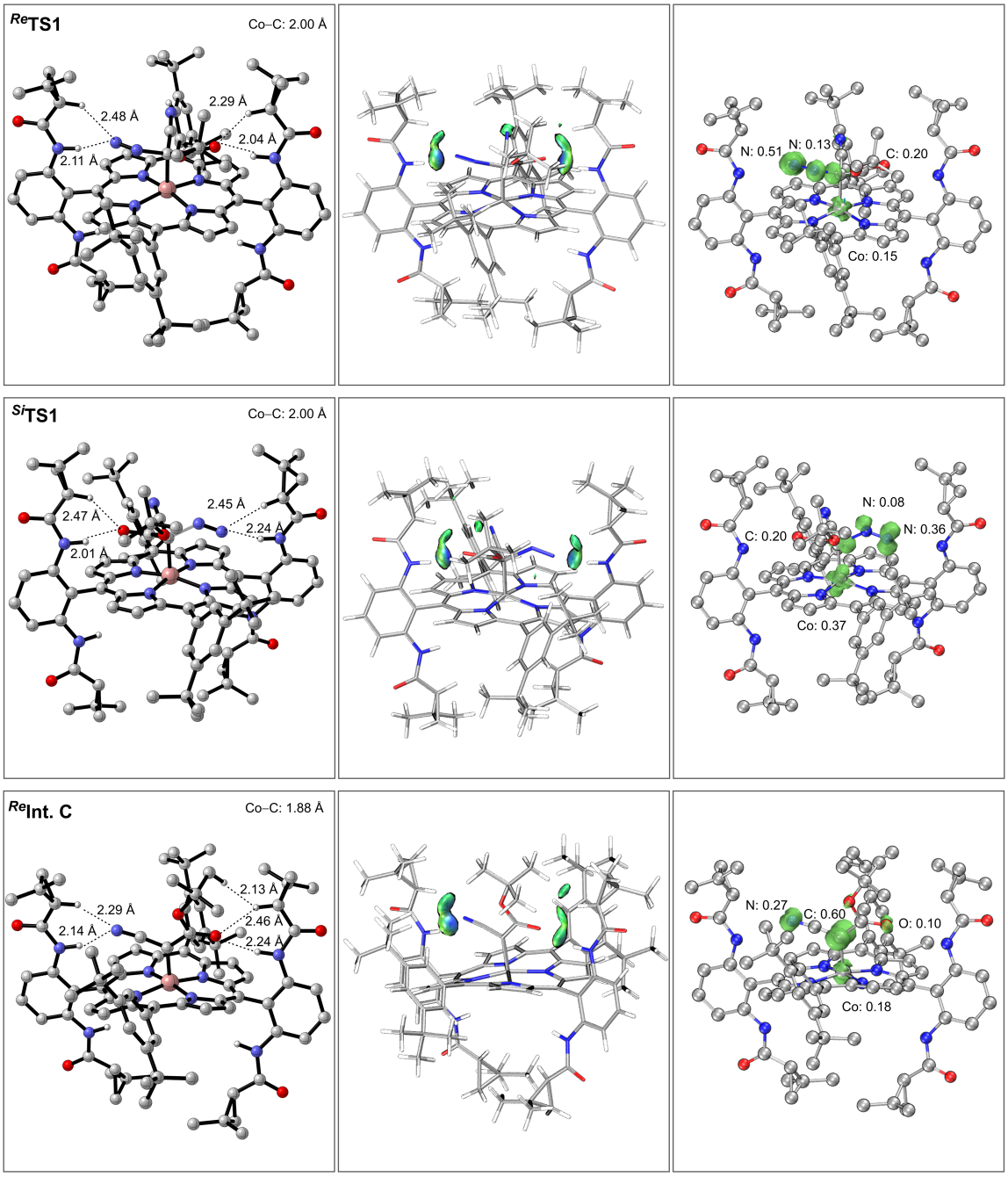
Scheme 3.13. Calculated Energy Diagram for *5-Exo-Trig* Radical Substitution

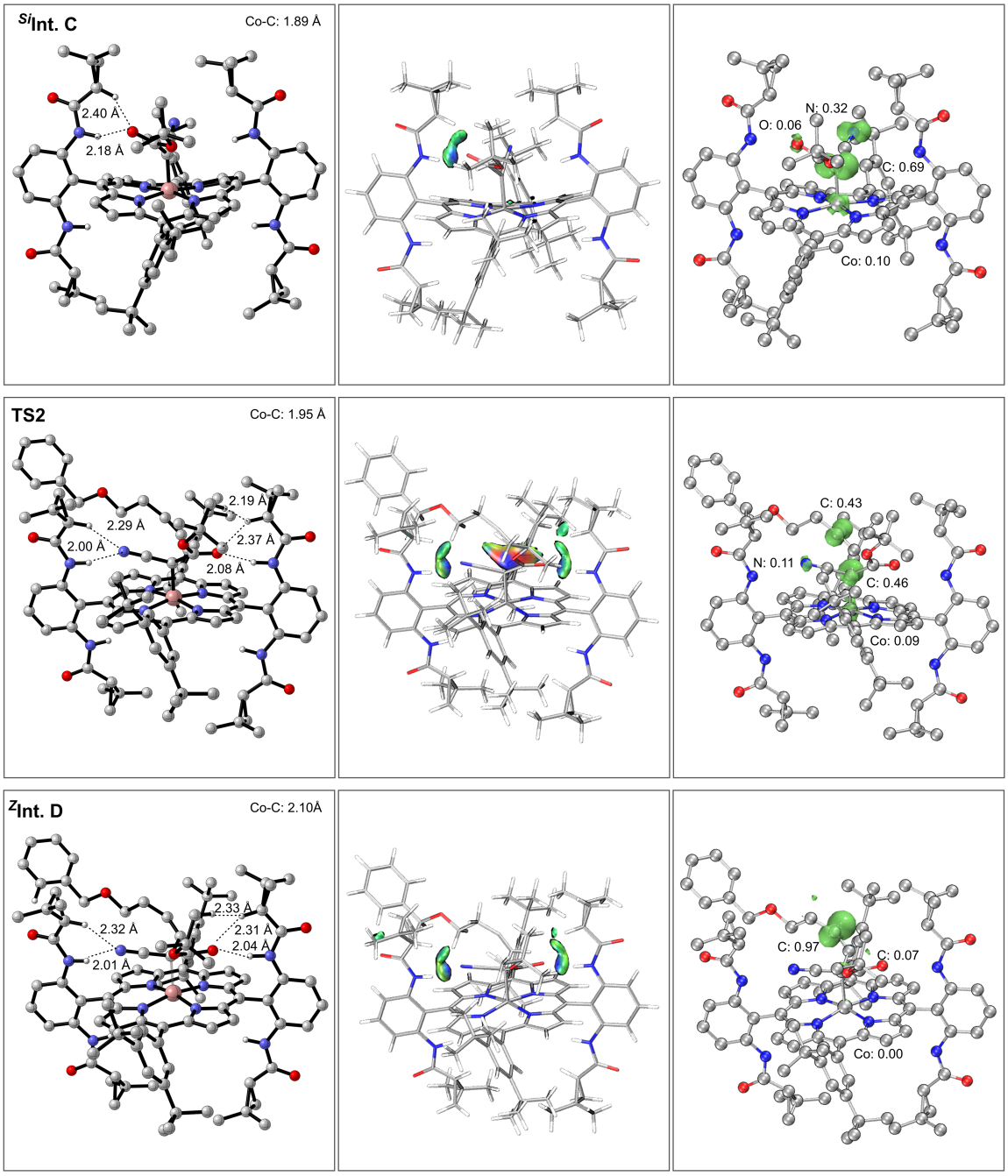


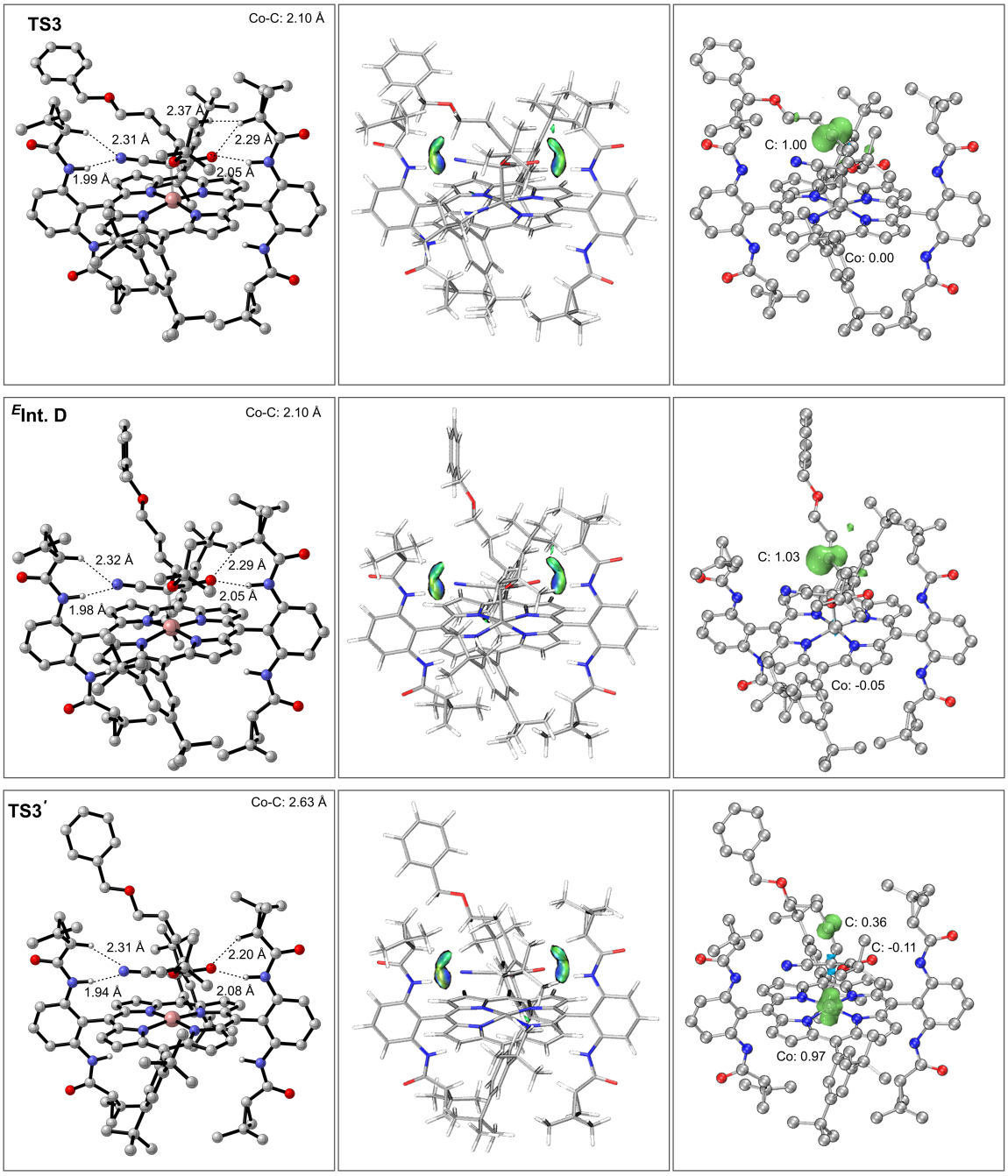
Scheme 3.14. Optimized Geometries with Spin Plot and NCI Visual Representation for Intermediates and Transition States.

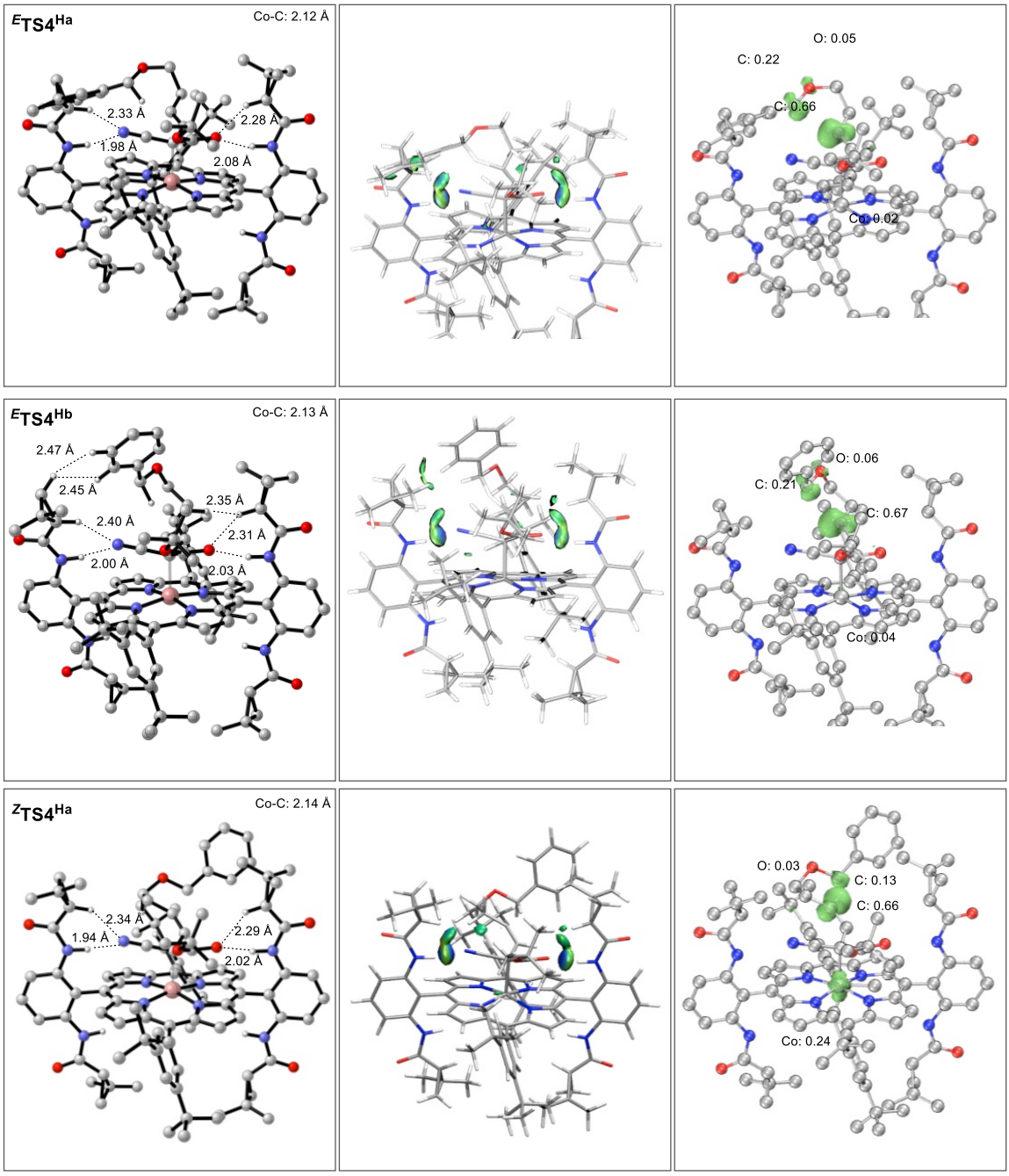


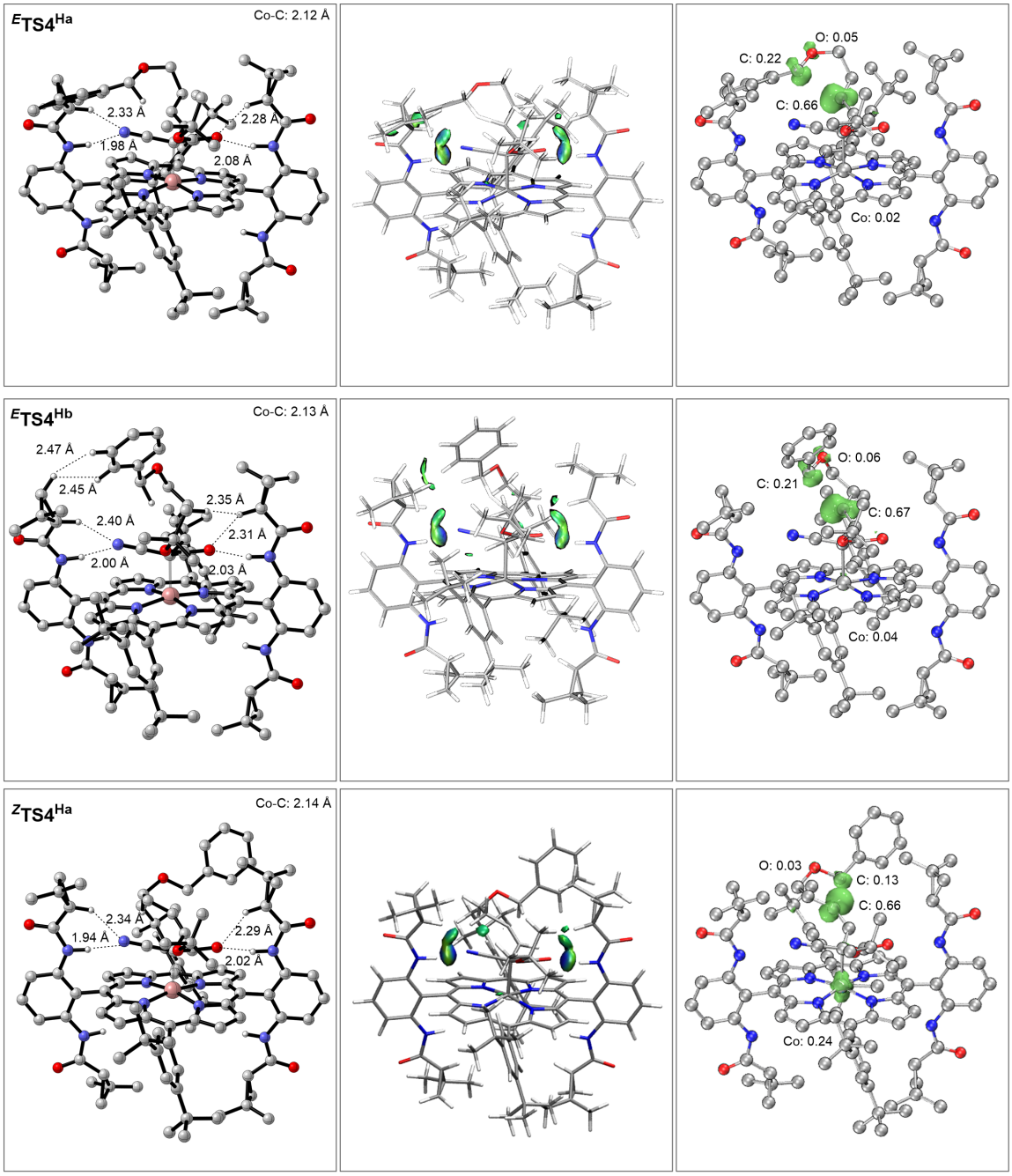

[Co(P3)]
Co: 1.13
ReIntermediate B
Co–C: 4.18 Å
2.69 Å
2.51 Å
2.46 Å
2.51 Å
Co: 1.13
SiIntermediate B
Co–C: 3.95 Å
2.46 Å
2.56 Å
2.36 Å
Co: 1.13

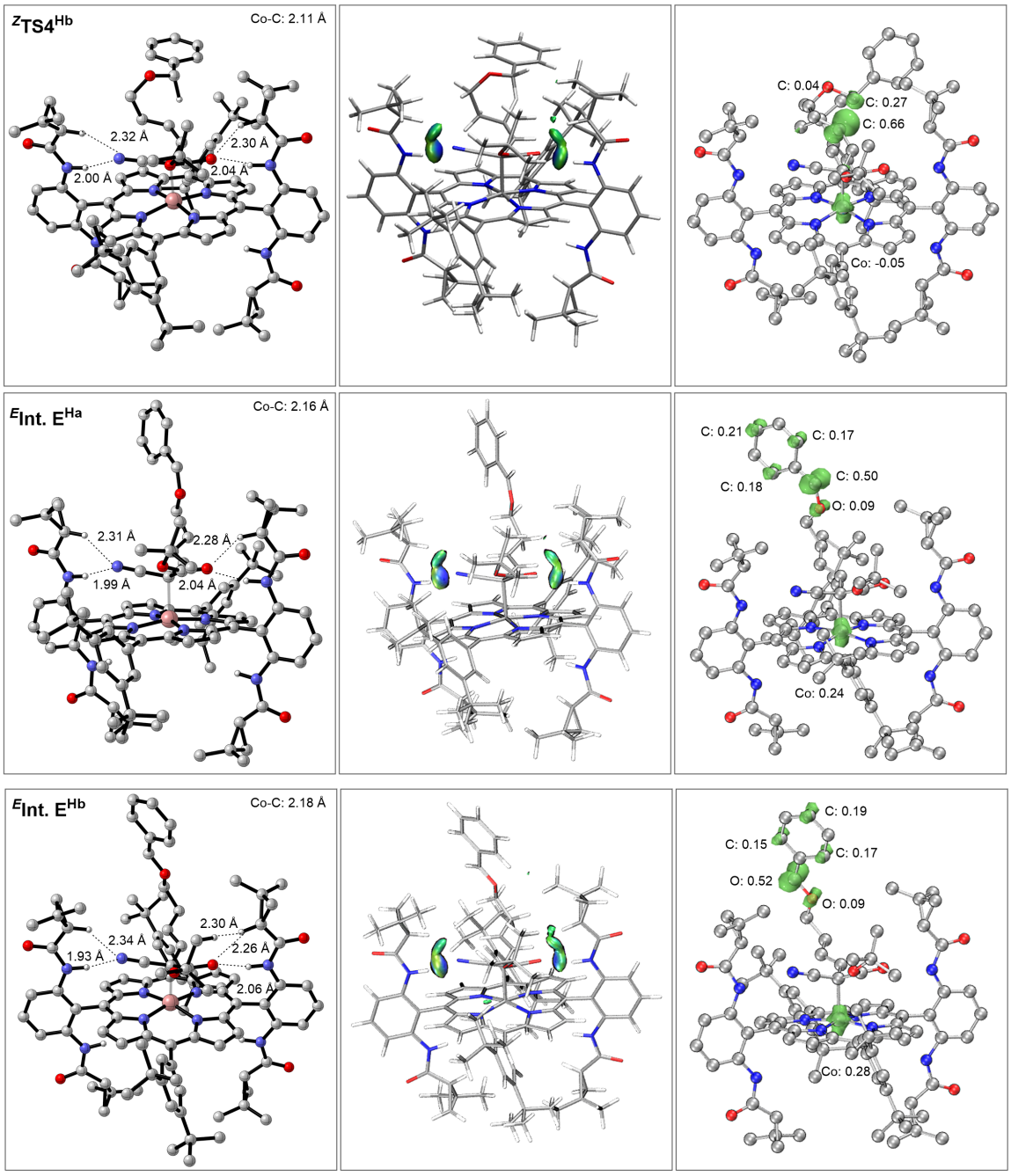

ReTS1
Co–C: 2.00 Å
2.48 Å
2.29 Å
2.04 Å
2.11 Å
N: 0.51
N: 0.13
C: 0.20
Co: 0.15
SiTS1
Co–C: 2.00 Å
2.47 Å
2.45 Å
2.24 Å
2.01 Å
N: 0.08
C: 0.20
N: 0.36
Co: 0.37
ReInt. C
Co–C: 1.88 Å
2.29 Å
2.13 Å
2.14 Å
2.46 Å
2.24 Å
N: 0.27
C: 0.60
O: 0.10
Co: 0.18

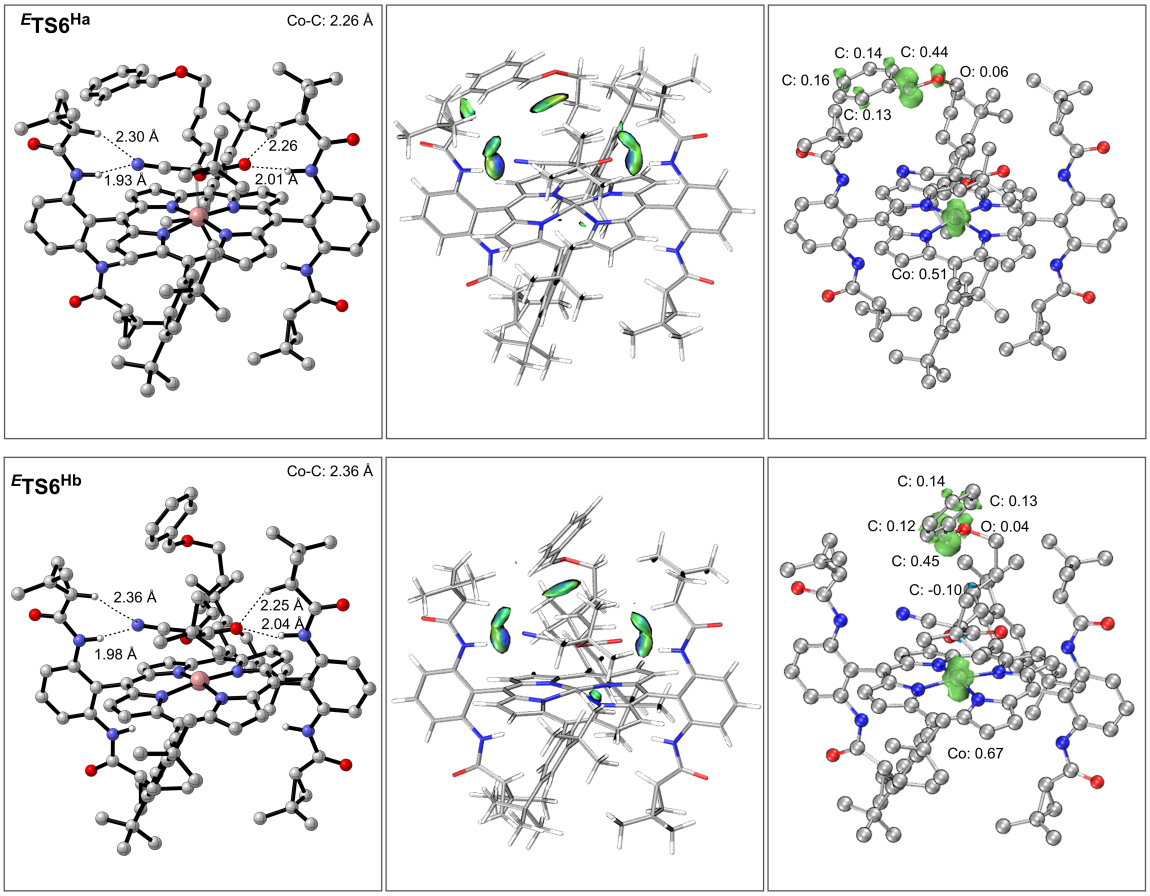

Si Int. C
Co-C: 1.89 Å
2.40 Å
2.18 Å
N: 0.32
O: 0.06
C: 0.69
Co: 0.10
TS2
Co-C: 1.95 Å
2.19 Å
2.29 Å
2.37 Å
2.00 Å
2.08 Å
C: 0.43
N: 0.11
C: 0.46
Co: 0.09
Z Int. D
Co-C: 2.10Å
2.33 Å
2.32 Å
2.31 Å
2.04 Å
2.01 Å
C: 0.97
C: 0.07
Co: 0.00


TS3
Co-C: 2.10 Å
2.37 Å
2.31 Å
2.29 Å
2.05 Å
1.99 Å
C: 1.00
Co: 0.00
EInt. D
Co-C: 2.10 Å
2.32 Å
2.29 Å
2.05 Å
1.98 Å
C: 1.03
Co: -0.05
TS3′
Co-C: 2.63 Å
2.31 Å
2.20 Å
1.94 Å
2.08 Å
C: 0.36
C: -0.11
Co: 0.97


^{E}TS4^{Ha}
Co-C: 2.12 Å
2.33 Å
1.98 Å
2.28 Å
2.08 Å
O: 0.05
C: 0.22
C: 0.66
Co: 0.02
^{E}TS4^{Hb}
Co-C: 2.13 Å
2.47 Å
2.45 Å
2.40 Å
2.00 Å
2.35 Å
2.31 Å
2.03 Å
O: 0.06
C: 0.21
C: 0.67
Co: 0.04
^{Z}TS4^{Ha}
Co-C: 2.14 Å
2.34 Å
1.94 Å
2.29 Å
2.02 Å
O: 0.03
C: 0.13
C: 0.66
Co: 0.24


ETS4Ha
Co-C: 2.12 Å
2.33 Å
2.28 Å
1.98 Å
2.08 Å
O: 0.05
C: 0.22
C: 0.66
Co: 0.02
ETS4Hb
Co-C: 2.13 Å
2.47 Å
2.45 Å
2.35 Å
2.40 Å
2.31 Å
2.00 Å
2.03 Å
O: 0.06
C: 0.21
C: 0.67
Co: 0.04
ZTS4Ha
Co-C: 2.14 Å
2.34 Å
1.94 Å
2.29 Å
2.02 Å
O: 0.03
C: 0.13
C: 0.66
Co: 0.24


ZTS4Hb
Co-C: 2.11 Å
2.32 Å
2.30 Å
2.00 Å
2.04 Å
C: 0.04
C: 0.27
C: 0.66
Co: -0.05
EInt. EHa
Co-C: 2.16 Å
2.31 Å
2.28 Å
1.99 Å
2.04 Å
C: 0.21
C: 0.17
C: 0.18
C: 0.50
O: 0.09
Co: 0.24
EInt. EHb
Co-C: 2.18 Å
2.30 Å
2.34 Å
1.93 Å
2.26 Å
2.06 Å
C: 0.19
C: 0.15
C: 0.17
O: 0.52
O: 0.09
Co: 0.28


^{E}TS6^{Ha}
Co-C: 2.26 Å
2.30 Å
1.93 Å
2.26
2.01 Å
C: 0.14
C: 0.44
C: 0.16
O: 0.06
C: 0.13
Co: 0.51
^{E}TS6^{Hb}
Co-C: 2.36 Å
2.36 Å
1.98 Å
2.25 Å
2.04 Å
C: 0.14
C: 0.13
C: 0.12
O: 0.04
C: 0.45
C: -0.10
Co: 0.67

Diazo **1a**
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.113978 Hartree
H_corr: 0.168238 Hartree
SCF: -587.068686 Hartree
S: 114.201 Cal/Mol-Kelvin
H: -586.900448 Hartree
G: -586.954708 Hartree

Cartesian Coordinates:

C	-1.74594600	0.12223900	0.00001200
C	-0.41335100	-0.55395700	-0.00015600
O	-0.28180500	-1.80008500	-0.00000300
O	0.59171500	0.40174700	-0.00014400
C	2.08062300	-0.00847500	-0.00007300
C	2.78089400	1.36322800	-0.00018400
C	2.37380600	-0.80727600	-1.28743200
C	2.37375500	-0.80704100	1.28744600
C	-2.96573400	-0.61446900	0.00023200
N	-3.97763600	-1.25585400	0.00038900
N	-1.79991800	1.46260900	-0.00003100
N	-1.79811000	2.63904900	0.00000800
H	2.50429900	1.94531400	0.89627700
H	3.87670700	1.21909500	-0.00015700
H	2.50432300	1.94515100	-0.89675200
H	1.84416700	-1.77342300	-1.28924600
H	3.46056600	-1.00202100	-1.35131600
H	2.07574300	-0.22948700	-2.18073800
H	3.46051800	-1.00175300	1.35142000
H	2.07563600	-0.22909200	2.18063600
H	1.84413200	-1.77320000	1.28941600

Alkyne **2a**
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.152995 Hartree
H_corr: 0.206997 Hartree
SCF: -501.773345 Hartree
S: 113.659 Cal/Mol-Kelvin
H: -501.566348 Hartree
G: -501.62035 Hartree

Cartesian Coordinates:

C	0.08671700	0.72178500	0.73101200
H	-0.11824500	1.79805500	0.52560500

H	-0.03534300	0.56188300	1.82742300
O	-0.87414000	-0.11169800	0.00088400
C	-2.26372700	0.18325500	0.37029500
H	-2.50973100	1.24458100	0.14839200
H	-2.42587600	0.00285700	1.45534900
C	-3.14469400	-0.76460700	-0.47373300
H	-2.84846200	-1.80860600	-0.25641400
H	-2.93120900	-0.58454000	-1.54467200
C	-4.58425900	-0.57818400	-0.20409700
C	-5.78591900	-0.41696900	0.02631900
H	-6.83431700	-0.28174500	0.22210800
C	1.50413000	0.36558100	0.30250900
C	2.59873200	1.05828000	0.88467200
C	1.75559000	-0.64024400	-0.66246500
C	3.92591300	0.74990200	0.50776300
H	2.41579500	1.84058100	1.63415500
C	3.08555600	-0.94871200	-1.03967100
H	0.90703500	-1.16879600	-1.10619000
C	4.17417500	-0.25690200	-0.45782100
H	4.76263500	1.29188400	0.96450100
H	3.26986600	-1.72920800	-1.78777600
H	5.20287800	-0.49733400	-0.75134500

Product **3a**

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.291467 Hartree
H_corr: 0.370103 Hartree
SCF: -979.428889 Hartree
S: 165.502 Cal/Mol-Kelvin
H: -979.058786 Hartree
G: -979.137422 Hartree

Cartesian Coordinates:

C	-3.04060600	-0.75840100	0.16863200
C	-1.76274600	-1.59096700	0.56234200
H	-3.84133600	-1.02668600	0.89544000
C	-2.16922900	-3.01781000	0.04031200
H	-2.69189600	-3.56041600	0.84837200
C	-0.53155200	-1.08414200	-0.13610900
H	-0.60101100	-0.89070600	-1.21678800
C	0.69038700	-0.85514800	0.44672500
C	0.91517100	-1.06541500	1.85494000
N	1.07254900	-1.25415900	3.02665800
C	1.82894000	-0.36936900	-0.41687600

O	1.73629200	-0.20412000	-1.66016100
O	2.95293800	-0.14510100	0.35627900
C	4.26723100	0.36686000	-0.26191600
C	4.77812300	-0.67425700	-1.28148100
C	4.01492600	1.75374000	-0.89206300
C	5.17948100	0.45495600	0.97590500
H	4.87195300	-1.66742500	-0.80636800
H	4.10193400	-0.75023000	-2.14805100
H	5.77906400	-0.36864300	-1.63970900
H	3.57779800	2.44311700	-0.14754000
H	4.97895600	2.17805800	-1.23004500
H	3.33790200	1.68253200	-1.75832900
H	6.18039400	0.81668400	0.67666200
H	4.75858500	1.15258300	1.72060100
H	5.28801400	-0.53547400	1.45107700
C	-3.12742500	-2.73856100	-1.16093600
H	-2.68315400	-2.98022700	-2.14165000
H	-4.08526000	-3.28324500	-1.05170800
O	-3.39398200	-1.27505600	-1.16788300
H	-1.61761400	-1.59669600	1.65671300
H	-1.29026400	-3.61625500	-0.25329900
C	-2.87317900	0.75357400	0.12029500
C	-2.74923900	1.44450300	-1.11094800
C	-2.82559700	1.48425600	1.33636100
C	-2.56914200	2.84819100	-1.12347000
H	-2.81207500	0.87775500	-2.04493300
C	-2.63928800	2.88573100	1.32301800
H	-2.93279200	0.96093600	2.29594100
C	-2.50989200	3.57277100	0.09098100
H	-2.47772600	3.37501000	-2.08072300
H	-2.59955100	3.43942800	2.26841900
H	-2.36992300	4.66014600	0.07915000

Product **3a** (diastereomer)
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.292375 Hartree
H_corr: 0.370216 Hartree
SCF: -979.427797 Hartree
S: 163.83 Cal/Mol-Kelvin
H: -979.057581 Hartree
G: -979.135422 Hartree

Cartesian Coordinates:

C	-2.22574400	0.65529700	0.62255700
C	-1.21309800	0.33365800	-0.53395400

H	-1.77807000	0.47024300	1.61759300
C	-1.73342800	1.29973100	-1.65957800
H	-2.55003800	0.79249700	-2.20246400
C	0.19231200	0.67172800	-0.11856500
H	0.35332900	1.63608400	0.38769300
C	1.30562200	-0.10936400	-0.31173100
C	1.23104000	-1.39905700	-0.95162700
N	1.13887600	-2.46715900	-1.48451000
C	2.64498600	0.39970500	0.16568900
O	2.80409200	1.51613000	0.72244800
O	3.63186400	-0.52973600	-0.10205300
C	5.10393900	-0.27678300	0.27805000
C	5.60923200	0.96651200	-0.48544500
C	5.20372300	-0.12448100	1.81125700
C	5.77878400	-1.56954300	-0.21699300
H	5.44877300	0.84539400	-1.57191600
H	5.09837800	1.88100700	-0.14392700
H	6.69513300	1.08192900	-0.30935300
H	4.76125800	-1.00148300	2.31708100
H	6.26986900	-0.06336600	2.09955400
H	4.69280900	0.78828400	2.15725000
H	6.86320800	-1.52813100	-0.00624700
H	5.35251900	-2.45122300	0.29226800
H	5.63376700	-1.69310800	-1.30425600
C	-2.25964300	2.53847600	-0.88540200
H	-1.55296200	3.38717100	-0.89355700
H	-3.24020100	2.87846600	-1.26762900
O	-2.40763200	2.12066200	0.54204100
H	-1.28478300	-0.71681100	-0.86199100
H	-0.94347300	1.55915400	-2.38450700
C	-3.54681900	-0.11801200	0.49435400
C	-4.78467500	0.57124700	0.45979400
C	-3.54609000	-1.53852300	0.45951500
C	-6.00220200	-0.14557700	0.37114700
H	-4.77928600	1.66470100	0.52448400
C	-4.76227300	-2.25478600	0.37383400
H	-2.59888500	-2.09200600	0.50681500
C	-5.99572700	-1.55994800	0.32467600
H	-6.95347800	0.39931400	0.34492500
H	-4.74768400	-3.35073600	0.34724100
H	-6.93853300	-2.11538800	0.25756700

Product **3a'**

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 0.283858 Hartree

H_corr: 0.36727 Hartree
SCF: -979.354692 Hartree
S: 175.556 Cal/Mol-Kelvin
H: -978.987422 Hartree
G: -979.070834 Hartree

Cartesian Coordinates:

C	2.32181000	-1.50032100	-0.02491000
C	2.35876100	-1.70642100	1.41894200
N	2.34771700	-1.91249100	2.59684800
C	3.12694800	-0.34118400	-0.59515000
O	3.16622800	-0.08109500	-1.82404600
O	3.77079400	0.34819500	0.41250900
C	4.66589500	1.56816900	0.11501600
C	5.83915600	1.11629700	-0.78084100
H	6.54771300	1.95709200	-0.90152800
H	6.38138200	0.27498900	-0.31285300
H	5.48531100	0.80835400	-1.77783900
C	5.13789400	1.96003300	1.52750400
H	4.27655600	2.21155900	2.17042000
H	5.80468800	2.83982800	1.46749600
C	3.80397300	2.67294900	-0.53299700
H	2.93589700	2.91278100	0.10728000
H	3.44555000	2.36745800	-1.52910400
H	5.68999300	1.12816300	1.99815400
H	4.41293100	3.58984400	-0.64267500
C	2.07469300	-2.72308800	-0.95824900
C	1.02873800	-1.93453800	-0.81709600
C	-0.35731300	-1.46568900	-1.08297900
H	-0.91337300	-2.24070000	-1.64096000
H	-0.31941800	-0.56013000	-1.72030000
C	-3.29007100	-0.26095500	0.91970400
C	-1.12152500	-1.11367700	0.21120700
H	-1.22571300	-2.00668400	0.86535900
H	-0.58437400	-0.32402300	0.78094600
O	-2.43798000	-0.63243200	-0.21743600
H	-3.43026700	-1.14285100	1.58579700
H	-2.78634600	0.53315500	1.51764000
H	2.59911900	-3.57320800	-1.37976600
C	-4.63642300	0.23531500	0.41052300
C	-4.90802800	0.35445200	-0.97445500
C	-5.64115700	0.59264800	1.34845200
C	-6.16899600	0.82586300	-1.41484500
H	-4.13042300	0.07503700	-1.69109700
C	-6.89903000	1.06409500	0.90816200
H	-5.44238200	0.50250200	2.42519500

C	-7.16760300	1.18255700	-0.47799500
H	-6.36992700	0.91389900	-2.48938100
H	-7.66663700	1.33666900	1.64220800
H	-8.14296400	1.54733700	-0.82110900

N_2
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: -0.013596 Hartree
H_corr: 0.008227 Hartree
SCF: -109.561471 Harree
S: 45.93 cal/mol-kelvin
H: -109.553244 Hartree
G: -109.575067 Hartree

Cartesian Coordinates:

N	0.00000	0.00000	0.57309
N	0.00000	0.00000	-0.57309

Intermediate A
[Co(**P3**)]
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.446285 Hartree
H_corr: 1.690496 Hartree
SCF: -5382.602472 Hartree
S: 513.986 Cal/Mol-Kelvin
H: -5380.911976 Hartree
G: -5381.156187 Hartree

Cartesian Coordinates:

N	1.42060900	1.40130100	-0.02479300
N	-1.39925000	-1.40102200	-0.01953400
N	-1.39923900	1.40103900	0.01966800
N	1.42060100	-1.40130400	0.02465600
C	1.24068100	-2.80247000	0.07292800
C	2.82353000	-1.22677600	0.06354400
C	2.82353300	1.22676400	-0.06382800
C	1.24069400	2.80246900	-0.07302600
C	-1.21845500	2.80232500	0.06239000
C	-2.80217900	1.22686700	0.06452500
C	-2.80219300	-1.22684000	-0.06427700
C	-1.21848100	-2.80231000	-0.06225300
C	-2.49813600	-3.48714500	-0.16693400
C	0.01097300	-3.48564400	0.00888800
C	2.52142100	-3.48671500	0.17172100

C 3.50970100 -0.00000900 -0.00018000
C -3.47450200 -2.51441900 -0.17566900
C -3.48957500 0.00001600 0.00014900
C -3.47446900 2.51445000 0.17598800
C 3.49761800 2.51374200 -0.17117600
C 0.01099700 3.48565100 -0.00885500
C -2.49809600 3.48716800 0.16718700
C 3.49761800 -2.51375800 0.17083600
C 2.52142800 3.48670600 -0.17194200
C 0.01015200 4.99584800 -0.01922900
C 0.00804600 7.82428200 -0.04069200
C -0.08166900 5.71062900 -1.25480400
C 0.10083200 5.72947600 1.20519900
C 0.09767900 7.15109400 1.19606800
C -0.08061600 7.13222400 -1.26706300
C 5.01438300 -0.00001500 -0.00025800
C 7.83407600 -0.00002100 -0.00040400
C 5.73047400 -0.50449400 -1.11469600
C 5.73059200 0.50445800 1.11410900
C 7.15026200 0.50805400 1.13607200
C 7.15014100 -0.50809800 -1.13680600
C 0.01011700 -4.99584100 0.01928500
C 0.00799200 -7.82427400 0.04079100
C 0.10063200 -5.72948800 -1.20514400
C -0.08154700 -5.71060300 1.25488300
C -0.08050200 -7.13219800 1.26716200
C 0.09746800 -7.15110600 -1.19599200
C -4.99361100 0.00002300 0.00020500
C -7.80744200 0.00004200 0.00031100
C -5.70809100 -0.55452000 1.09333900
C -5.70816600 0.55457300 -1.09287700
C -7.12645300 0.56054200 -1.11365400
C -7.12637600 -0.56046800 1.11422400
C -0.26635300 5.36339700 -3.77686300
N -0.16910700 4.93483600 -2.44569900
C 0.28547600 5.42015600 3.73220200
N 0.18918800 4.97170300 2.40757900
C -0.26587500 -5.36333200 3.77696200
N -0.16881300 -4.93479200 2.44577800
C 0.28492600 -5.42021300 -3.73217700
N 0.18883100 -4.97173600 -2.40754700
C 0.35626400 -4.30614100 -4.73687300
C 0.88885700 -4.62462900 -6.15397400
C -0.59024500 -4.27699000 -5.99719300
C -0.33709100 -4.23442600 4.76501100
C -0.86949800 -4.53238600 6.18665400

C	0.60950300	-4.18659300	6.02466800
C	0.35705400	4.30606600	4.73686100
C	0.88995400	4.62453600	6.15385100
C	-0.58917600	4.27687000	5.99739100
C	-0.33782400	4.23450400	-4.76491000
C	-0.87053900	4.53249900	-6.18643100
C	0.60848600	4.18665300	-6.02478100
C	-1.05000100	2.88257500	6.43609800
C	-1.63717500	5.37564400	6.18327300
C	1.06846800	2.78597400	-6.44365000
C	1.65702000	5.28215300	-6.22632600
C	-1.05119700	-2.88271400	-6.43582700
C	-1.63826400	-5.37579000	-6.18281400
C	1.06962900	-2.78592500	6.44341900
C	1.65804400	-5.28212700	6.22598300
C	-7.93858700	1.15281000	-2.29677000
C	-7.93842600	-1.15274700	2.29739200
C	-8.82956100	2.32583200	-1.77581200
C	-7.02492900	1.70354800	-3.42628900
C	-8.85194700	0.04215200	-2.90718100
C	-7.02468400	-1.70358600	3.42679400
C	-8.82951100	-2.32569900	1.77646500
C	-8.85167000	-0.04207300	2.90794700
C	7.89346100	-1.05464400	-2.38522900
C	7.89371500	1.05460000	2.38441600
C	9.43880300	0.99002700	2.23476400
C	7.48947500	0.20940600	3.63515900
C	7.48852500	2.54539500	2.61782700
C	7.48833300	-2.54547200	-2.61853300
C	9.43856600	-0.98997100	-2.23578800
C	7.48899800	-0.20951900	-3.63594700
H	1.56647300	3.89652400	6.61446500
H	4.57666600	2.63764600	-0.24089100
H	4.57667200	-2.63766800	0.24043800
H	-4.55259200	2.63928100	0.25572300
H	2.63593500	-4.56794200	0.23437200
H	2.63594300	4.56793300	-0.23458900
H	-4.55263300	-2.63924400	-0.25531300
H	-2.61178300	4.56851900	0.22894400
H	-2.61183700	-4.56849500	-0.22866800
Co	0.01068300	0.00000500	-0.00000200
H	0.16597400	7.68855800	2.14325900
H	-0.14972000	7.65528300	-2.22223300
H	0.00727900	8.92050400	-0.04906900
H	8.92651800	-0.00002400	-0.00046000
H	-0.14948400	-7.65524100	2.22235000

H 0.16563300 -7.68858400 -2.14318400
H 0.00721700 -8.92049700 0.04918500
H -8.90472500 0.00004600 0.00035100
O -0.28439300 6.58920900 -4.12108700
O 0.30235100 6.65097500 4.05810200
O -0.28381400 -6.58913900 4.12121100
O 0.30167600 -6.65103800 -4.05806200
H 0.60320700 -3.31703100 -4.32892300
H -0.58453800 -3.25149100 4.34280500
H -1.12531700 -5.58163800 6.36797500
H 0.60392900 3.31696900 4.32883700
H 1.14608400 5.67623800 6.31993000
H -0.58521100 3.25157300 -4.34266000
H -1.54607800 -3.79789100 6.63676900
H 0.17456800 -3.95528900 -2.27523500
H -1.94376100 2.56406800 5.86541400
H -1.31854800 2.88884300 7.51057300
H -0.25914300 2.12250900 6.29016100
H -2.57322700 5.12141800 5.64887800
H -1.27639400 6.34755700 5.80737600
H -1.87918600 5.48339700 7.25860800
H -1.12636200 5.58176200 -6.36768300
H -1.54724400 3.79803200 -6.63640300
H 1.33577800 2.77660100 -7.51840900
H 0.27742400 2.02847900 -6.28575600
H 1.96281100 2.47538200 -5.86950900
H 1.90023200 5.37333300 -7.30291700
H 2.59240800 5.03591900 -5.68705700
H 1.29617300 6.25985400 -5.86578000
H 1.56526000 -3.89661200 -6.61475200
H 1.14497300 -5.67632900 -6.32008700
H -0.26032200 -2.12262900 -6.29008600
H -1.94483300 -2.56421200 -5.86494800
H -1.31998700 -2.88901100 -7.51024200
H -2.57420300 -5.12156700 -5.64822000
H -1.27738100 -6.34768500 -5.80696700
H -1.88050800 -5.48357900 -7.25809200
H 0.27857500 -2.02840500 6.28570100
H 1.96385000 -2.47537000 5.86907000
H 1.33718700 -2.77655200 7.51811700
H 1.90149300 -5.37331400 7.30251900
H 2.59332000 -5.03592800 5.68650400
H 1.29708300 -6.25981800 5.86551900
H -0.15335300 3.92048500 -2.29843300
H 0.17490700 3.95525800 2.27525000
H -0.15306000 -3.92044300 2.29849600

H	5.16253200	-0.88365900	-1.97288600
H	5.16274000	0.88362800	1.97235600
H	-5.14029300	0.96859100	-1.93191200
H	-5.14016000	-0.96854800	1.93233100
H	-9.43281800	2.74378800	-2.60457400
H	-8.20624300	3.13863600	-1.35788200
H	-9.52599100	1.99227200	-0.98471600
H	-7.65133000	2.11163000	-4.24140700
H	-6.38580600	0.91135500	-3.86044200
H	-6.37189200	2.52092700	-3.06620300
H	-9.44256000	0.45410300	-3.74787600
H	-9.56086400	-0.36201300	-2.16133500
H	-8.24572600	-0.80034300	-3.28965800
H	-6.38547400	-0.91144700	3.86091800
H	-6.37172800	-2.52098400	3.06660500
H	-7.65102500	-2.11167100	4.24195700
H	-9.52600800	-1.99206300	0.98545900
H	-9.43270100	-2.74367100	2.60526700
H	-8.20627700	-3.13851100	1.35842500
H	-9.56064600	0.36215800	2.16219400
H	-8.24536800	0.80037600	3.29039800
H	-9.44221400	-0.45403400	3.74868500
H	9.79520800	1.59771900	1.38144700
H	9.79561300	-0.04840400	2.09774700
H	9.91502900	1.38837700	3.15026100
H	6.39924600	0.24098700	3.81466500
H	7.99434400	0.60086100	4.53928400
H	7.78148100	-0.84973300	3.50572900
H	6.39906800	2.65570300	2.76877000
H	7.77656600	3.17261900	1.75319200
H	7.99688100	2.94246300	3.51743700
H	6.39886400	-2.65585400	-2.76933200
H	7.77652500	-3.17264700	-1.75391300
H	7.99659800	-2.94254200	-3.51819500
H	9.79533400	0.04849100	-2.09889000
H	9.91469300	-1.38835400	-3.15132100
H	9.79512000	-1.59758400	-1.38247700
H	7.78096200	0.84964200	-3.50659800
H	6.39874600	-0.24116900	-3.81529700
H	7.99376300	-0.60098000	-4.54012900

^{Re}Intermediate B

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.575281 Hartree
H_corr: 1.85946 Hartree

SCF: -5969.691409 Hartree
S: 598.105 Cal/Mol-Kelvin
H: -5967.831949 Hartree
G: -5968.116128 Hartree

Cartesian Coordinates:

N	1.44688800	1.25361200	0.63134500
N	-1.63959000	-1.19220800	0.26082500
N	-1.31525300	1.58147900	0.26196600
N	1.15226800	-1.50629400	0.32636200
C	0.81667200	-2.87632800	0.24575200
C	2.56626800	-1.48041900	0.26257500
C	2.81649800	0.91980200	0.72918100
C	1.39531300	2.63586000	0.92656700
C	-0.99273200	2.94950100	0.42193900
C	-2.70587400	1.57403500	-0.00384400
C	-3.00839900	-0.85823300	0.14356100
C	-1.62654400	-2.60246200	0.36196500
C	-2.98343400	-3.13164300	0.36082700
C	-0.48062700	-3.42115600	0.34906200
C	2.00942200	-3.68779300	0.06468600
C	3.37921300	-0.34940600	0.48137100
C	-3.83325400	-2.05749700	0.20346700
C	-3.53280700	0.43498800	-0.04181800
C	-3.21670700	2.93557200	-0.07893900
C	3.59393500	2.08045100	1.14278900
C	0.25955100	3.46238400	0.82166200
C	-2.16337400	3.78354600	0.19429200
C	3.08656000	-2.82469500	0.05007200
C	2.71573400	3.13573100	1.27668100
C	0.36147700	4.91792300	1.21266600
C	0.49940400	7.63001800	2.02098600
C	0.82993000	5.92093300	0.30536600
C	-0.02495200	5.30722700	2.53805400
C	0.04368800	6.66700400	2.94399100
C	0.89400500	7.28300400	0.71304900
C	4.87426500	-0.50130400	0.51354700
C	7.68166500	-0.76206700	0.58856600
C	5.68847100	0.21821600	-0.40585100
C	5.49209900	-1.34343300	1.46880600
C	6.90629800	-1.48851900	1.52455100
C	7.09831100	0.09891500	-0.38542900
C	-0.62927500	-4.92004200	0.45818000
C	-0.82477000	-7.73319100	0.70502800
C	-0.88067800	-5.73170000	-0.69342900
C	-0.49695300	-5.54989100	1.73802600

C -0.59457900 -6.96187300 1.86337600
C -0.97108300 -7.14609000 -0.56864100
C -5.01999900 0.60969300 -0.20718700
C -7.79684100 0.93290700 -0.48974800
C -5.87404100 0.44652500 0.91400100
C -5.56975600 0.93750900 -1.47212000
C -6.97094300 1.10294000 -1.63287900
C -7.27793700 0.60789100 0.79224200
C 1.69540800 6.30408200 -2.05876300
N 1.22811500 5.50688000 -1.00083700
C -0.86577700 4.37239600 4.75992800
N -0.46642300 4.27876900 3.41893800
C -0.13507900 -5.03985300 4.21327700
N -0.27332200 -4.70103200 2.86027200
C -1.24641500 -5.63072700 -3.21814900
N -1.04364300 -5.07028800 -1.94363000
C -1.45403900 -4.61214300 -4.29580600
C -1.21421700 -5.03148300 -5.76711500
C -2.64563100 -4.73923800 -5.32530500
C 0.06117600 -3.85162000 5.11129600
C -0.26058900 -4.01057900 6.61735800
C 1.19693000 -3.82015000 6.20315400
C -1.25558300 3.05282700 5.36179600
C -1.25923000 2.92210200 6.90408800
C -2.59786600 2.88174000 6.17016400
C 2.06063700 5.53551900 -3.29474300
C 2.07191800 6.29186900 -4.64658500
C 3.40351800 5.81460700 -4.07186100
C -3.28727700 1.52246800 6.01042500
C -3.55839400 4.06479200 6.30454200
C 4.05431300 4.58265700 -4.71065600
C 4.39911900 6.84404700 -3.53447900
C -3.27238800 -3.40931000 -5.75764600
C -3.63652200 -5.89788700 -5.20070800
C 1.83541500 -2.44761400 6.44253700
C 2.16606700 -4.99764400 6.32434000
C -7.61402300 1.43829900 -3.00505800
C -8.24427300 0.44148400 1.99554900
C -8.47194800 2.73784800 -2.88034200
C -6.55320500 1.66338200 -4.11743300
C -8.53643600 0.25293500 -3.43767500
C -7.49782900 0.09287200 3.31304900
C -9.25737400 -0.70847900 1.69126700
C -9.02886200 1.77397800 2.21905600
C 8.01650000 0.86784700 -1.37246700
C 7.53648200 -2.41548900 2.59782100

C	9.08670900	-2.46512400	2.50608900
C	6.99048500	-3.86761300	2.41320000
C	7.14863200	-1.89491400	4.01927600
C	7.21338600	1.76127600	-2.35751000
C	8.85052800	-0.15458800	-2.20915900
C	8.98880100	1.78744900	-0.56566500
H	-0.85473900	1.99943600	7.33415400
H	4.66685100	2.06851400	1.32462000
H	4.14025300	-3.06487200	-0.07806800
H	-4.25523700	3.18771700	-0.28545600
H	2.00254800	-4.77121100	-0.04667400
H	2.92398000	4.16195300	1.57630300
H	-4.91853000	-2.05771100	0.12197000
H	-2.16137300	4.87121200	0.25234500
H	-3.22873700	-4.18997400	0.43904500
Co	-0.08884300	0.03273500	0.37055000
H	-0.25398400	6.93281500	3.95947000
H	1.24481300	8.03133700	0.00158300
H	0.55079200	8.68061900	2.32961200
H	8.77166000	-0.86107500	0.61548300
H	-0.49089100	-7.41586400	2.85008000
H	-1.14720800	-7.74470200	-1.46353700
H	-0.89607000	-8.82317700	0.79807300
H	-8.88136200	1.05684800	-0.60172200
O	1.80533200	7.57136200	-1.98749300
O	-0.89964100	5.46659700	5.41034000
O	-0.17159700	-6.23671000	4.64689500
O	-1.25895400	-6.88646900	-3.43200500
H	-1.19302200	-3.57752200	-4.04257400
H	-0.16543500	-2.87615300	4.66059900
H	-0.57363900	-5.01742500	6.91320900
H	-0.94966400	2.16476400	4.79285700
H	-1.00579400	3.84245300	7.44076500
H	1.73350200	4.49009300	-3.31584600
H	-0.79034300	-3.18849400	7.11071200
H	-1.04523800	-4.04642300	-1.89905100
H	-3.93091200	1.50917300	5.10972000
H	-3.92890000	1.31288200	6.88842200
H	-2.55610600	0.69659800	5.92171500
H	-4.24720400	4.11327500	5.43881900
H	-3.01462500	5.02193500	6.36853000
H	-4.17088900	3.94664700	7.21962600
H	1.84668100	7.36101600	-4.57421900
H	1.64772300	5.77885200	-5.51675600
H	4.69249400	4.88710000	-5.56322100
H	3.29897900	3.86937700	-5.09179600

H 4.69505700 4.05025800 -3.98111000
H 5.01087200 7.24242900 -4.36741500
H 5.08652400 6.38136400 -2.79959700
H 3.88335100 7.68582100 -3.04377400
H -0.69956100 -4.30924400 -6.40933300
H -0.93370200 -6.08096000 -5.90747100
H -2.52101500 -2.60147300 -5.81271500
H -4.06124600 -3.09564400 -5.04722000
H -3.74038400 -3.51698800 -6.75618300
H -4.45420800 -5.64196600 -4.49900500
H -3.14513600 -6.81742200 -4.84131500
H -4.09202900 -6.10513400 -6.18891500
H 1.09760600 -1.62793200 6.35243600
H 2.64988000 -2.25688600 5.71715200
H 2.27046400 -2.39978200 7.45985000
H 2.56698700 -5.04707100 7.35551700
H 3.02256100 -4.87615900 5.63277200
H 1.66916700 -5.95497500 6.09514900
H 1.17209900 4.49821900 -1.18050900
H -0.49604300 3.34098200 3.00728400
H -0.21379000 -3.70229300 2.63838200
H 5.19735700 0.86791600 -1.13737000
H 4.85649700 -1.87481700 2.18686600
H -4.89673500 1.03648900 -2.32913000
H -5.42612300 0.20101400 1.88229600
H -8.93989000 2.97740600 -3.85462900
H -7.84371300 3.59704600 -2.57859900
H -9.28180400 2.63053500 -2.13525600
H -7.06682700 1.89672100 -5.06933500
H -5.92191200 0.77252500 -4.28304800
H -5.88304200 2.51076600 -3.87902900
H -9.01872600 0.47972300 -4.40814300
H -9.33479600 0.06463700 -2.69592900
H -7.95084800 -0.67848500 -3.55154000
H -6.78487400 0.88816700 3.60259600
H -6.94331400 -0.86131400 3.23197100
H -8.23032200 -0.01505100 4.13491700
H -9.84794100 -0.50279600 0.77977500
H -9.96481500 -0.82739700 2.53456200
H -8.72990300 -1.66960400 1.54346000
H -9.61593300 2.05791000 1.32651100
H -8.33566900 2.60539300 2.44701500
H -9.73201400 1.66552400 3.06734400
H 9.54059100 -1.46874300 2.66665800
H 9.42878300 -2.85281200 1.52760700
H 9.48048800 -3.14049800 3.28846600

H	5.88930600	-3.90689500	2.50171600
H	7.41503100	-4.53575800	3.18679000
H	7.26728300	-4.26970800	1.42031500
H	6.05267900	-1.86906000	4.16077700
H	7.53587600	-0.87183600	4.18356600
H	7.57551000	-2.55669400	4.79719100
H	6.62062800	2.52888400	-1.82481400
H	6.52665800	1.16301600	-2.98628700
H	7.91332700	2.28760800	-3.03317300
H	9.47631200	-0.79760100	-1.56369600
H	9.52234500	0.38094500	-2.90727200
H	8.18720500	-0.81266100	-2.80167900
H	9.61835500	1.20588300	0.13223700
H	8.42605900	2.53339100	0.02640900
H	9.66181800	2.33029000	-1.25688900
C	-0.49075400	0.59559400	-3.75216900
N	0.13399000	1.57380000	-3.08343700
N	0.71286100	2.40940800	-2.49421800
C	-1.91075600	0.63698000	-3.84517800
N	-3.10324000	0.67033000	-3.92740200
C	0.30799100	-0.49342200	-4.38971600
O	-0.23175400	-1.45848900	-4.98545400
O	1.65635500	-0.25864300	-4.21734100
C	2.71928000	-1.24224600	-4.77566700
C	2.58984700	-1.27470100	-6.31268500
H	3.40835400	-1.89098200	-6.72870200
H	1.62999900	-1.71563100	-6.62607300
H	2.67749000	-0.25762100	-6.73523400
C	4.02729900	-0.57231200	-4.31877700
H	4.07287900	-0.51520400	-3.21748700
H	4.11180700	0.44736100	-4.73405900
C	2.51746100	-2.62159900	-4.11705700
H	1.57777300	-3.09506500	-4.44313000
H	2.52009000	-2.53497000	-3.01586300
H	4.88734100	-1.16850400	-4.67414600
H	3.35586900	-3.28173400	-4.40801300

^{Si}Intermediate B

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.57483 Hartree
H_corr: 1.859405 Hartree
SCF: -5969.677898 Hartree
S: 598.938 Cal/Mol-Kelvin
H: -5967.818493 Hartree
G: -5968.103068 Hartree

Cartesian Coordinates:

N	-1.19636700	-1.38558700	0.56143800
N	1.31828700	1.61357400	-0.02457200
N	1.59854000	-1.10741200	0.55833100
N	-1.46693000	1.38197300	0.25652400
C	-1.41104200	2.79481100	0.18624600
C	-2.83979100	1.08950800	0.42721800
C	-2.60925600	-1.35815800	0.47925000
C	-0.87696000	-2.75116700	0.74154800
C	1.55787000	-2.46637100	0.94882700
C	2.97654700	-0.79352700	0.51535200
C	2.72243700	1.54453700	-0.19136400
C	0.99819800	2.96821700	-0.27784700
C	2.18395100	3.71083300	-0.67581200
C	-0.26822000	3.56474000	-0.10436100
C	-2.73140600	3.37146400	0.38486200
C	-3.41193800	-0.19880800	0.46873600
C	3.24496300	2.82916400	-0.63498900
C	3.53561200	0.43239900	0.10474900
C	3.77328600	-1.93740200	0.93790100
C	-3.14379100	-2.71299000	0.51183700
C	0.40533100	-3.27342600	1.01328300
C	2.89900100	-2.96714900	1.21149500
C	-3.61222400	2.32066800	0.53295800
C	-2.07662000	-3.57021400	0.69001100
C	0.52849600	-4.70697800	1.47366200
C	0.75895900	-7.36567800	2.42814200
C	0.92982300	-5.76024500	0.59156700
C	0.25236600	-5.01977400	2.84668300
C	0.35977700	-6.35295600	3.32414500
C	1.04975600	-7.09314600	1.07667300
C	-4.90672100	-0.33391900	0.55719700
C	-7.71461600	-0.55843200	0.75692000
C	-5.74460300	0.17877000	-0.46676700
C	-5.50137200	-0.95961100	1.68341800
C	-6.91012300	-1.08249800	1.80341100
C	-7.15829600	0.07623900	-0.38536200
C	-0.38668800	5.06890600	-0.17830300
C	-0.59404100	7.89445700	-0.25450700
C	-0.84494000	5.73137600	-1.36181600
C	-0.04125700	5.85873400	0.96740100
C	-0.14052600	7.27575700	0.92821200
C	-0.95028100	7.14970400	-1.39710900
C	5.02991100	0.56225500	0.00498500
C	7.82541700	0.79925300	-0.18194600

C 5.73025300 1.44652700 0.86676800
C 5.74671400 -0.20326300 -0.95075600
C 7.15624000 -0.09178800 -1.06319800
C 7.14066200 1.57522600 0.79196700
C 1.78314900 -6.24713700 -1.75750800
N 1.17266100 -5.44068200 -0.77646900
C -0.47496700 -3.97012700 5.05672800
N -0.09724300 -3.93899300 3.70733600
C 0.80801800 5.68411200 3.36732500
N 0.37484800 5.16406900 2.13907200
C -1.75855700 5.32236900 -3.70147400
N -1.17157100 4.92427300 -2.49125900
C -2.00035200 4.19727300 -4.66643700
C -3.03907500 4.41300400 -5.79323400
C -1.56472800 4.30344400 -6.17725200
C 1.14027700 4.62906500 4.38232800
C 2.05040600 5.01362700 5.57371200
C 0.58130200 4.70570300 5.85465800
C -0.72934900 -2.60942300 5.63934900
C -1.57307900 -2.50607200 6.93241800
C -0.08400700 -2.17486400 7.01031400
C 1.85175200 -5.62049700 -3.11530900
C 3.00568600 -6.05980400 -4.05589800
C 1.58151700 -6.46383300 -4.42321000
C 0.32039700 -0.70000900 7.10318000
C 0.85548900 -3.13244200 7.74588300
C 0.89704300 -5.69980500 -5.56161700
C 1.16932900 -7.93382300 -4.32291400
C -1.08640100 2.99499500 -6.81587800
C -0.82870400 5.55007400 -6.67182100
C 0.23957200 3.35619400 6.49449700
C -0.35710100 5.84643600 6.25307200
C 7.96588200 -0.89276800 -2.11720800
C 7.94190500 2.52231300 1.72515000
C 9.05628300 -1.75054200 -1.39922800
C 7.06735000 -1.84784600 -2.95132400
C 8.66065800 0.10794000 -3.09619800
C 7.02893100 3.27838900 2.72987200
C 8.69828700 3.58198700 0.86118600
C 8.97964300 1.68883400 2.54331400
C -8.03608000 0.65859500 -1.52595700
C -7.51251500 -1.76943000 3.05820500
C -9.06533400 -1.81547300 3.02552400
C -7.07538500 -0.98478600 4.33689300
C -6.98277900 -3.23662600 3.14785600
C -7.75590600 2.18967500 -1.66257400

C	-9.55617600	0.46605600	-1.26730000
C	-7.67892400	-0.05218200	-2.87047800
H	-2.30659100	-1.69476200	6.99375100
H	-4.19961400	-2.96103100	0.42092900
H	-4.68523000	2.36095900	0.70951100
H	4.85894500	-1.93366100	1.01114100
H	-2.93762200	4.44075300	0.40141300
H	-2.08207300	-4.65548600	0.78255300
H	4.29016300	3.01524700	-0.87430500
H	3.12110500	-3.97968500	1.54523300
H	2.18485400	4.76652400	-0.94395500
Co	0.06295100	0.12423500	0.33975400
H	0.13531500	-6.56159300	4.37121800
H	1.37984400	-7.87594300	0.39326300
H	0.84924700	-8.39517100	2.79380900
H	-8.80088000	-0.64356800	0.83553400
H	0.13484900	7.85103100	1.81340700
H	-1.30987100	7.63064200	-2.30757100
H	-0.67342600	8.98731400	-0.28658500
H	8.91628300	0.89268500	-0.25640100
O	2.24243500	-7.40895700	-1.50672100
O	-0.58423800	-5.04300100	5.73437800
O	0.90391100	6.93081600	3.60899600
O	-2.06568500	6.52901600	-3.97237000
H	-1.93550500	3.18847700	-4.24220300
H	1.25049200	3.61003100	3.98821100
H	2.35782300	6.06452600	5.59403900
H	-0.84318500	-1.79555700	4.91082800
H	-1.89738800	-3.46718600	7.34532400
H	1.53652900	-4.57288100	-3.18454200
H	2.81727200	4.29220100	5.87588900
H	-0.95366200	3.92622300	-2.39867800
H	1.33025700	-0.54116100	6.67760200
H	0.34450300	-0.37564500	8.16187400
H	-0.38856900	-0.04308500	6.56466800
H	1.89544800	-3.02157100	7.38182000
H	0.55075600	-4.18320000	7.60885200
H	0.84896200	-2.90259000	8.82925300
H	3.66108300	-6.83682400	-3.64826500
H	3.50582000	-5.27210100	-4.62949200
H	1.16264800	-6.15607700	-6.53580100
H	1.19474900	-4.63668800	-5.58022700
H	-0.20436700	-5.74206300	-5.45481200
H	1.45427900	-8.46331100	-5.25345800
H	0.07196400	-8.02675600	-4.20341800
H	1.65394000	-8.43332600	-3.46833500

H -3.71633900 3.58281200 -6.02235200
H -3.49239700 5.40959700 -5.81349900
H -1.63628000 2.11906900 -6.42175700
H -0.00637500 2.83608800 -6.63103900
H -1.23934200 3.02618400 -7.91239900
H 0.26243200 5.45491000 -6.50829700
H -1.17895800 6.45789700 -6.15321400
H -0.99877100 5.67828000 -7.75865600
H 0.94529000 2.56222300 6.18534900
H -0.78367000 3.03643300 6.21713100
H 0.28178300 3.43490700 7.59838900
H -0.28886900 6.02133600 7.34454000
H -1.40862900 5.59312500 6.01522100
H -0.09972700 6.78312400 5.73147200
H 0.91451400 -4.49185800 -1.06581100
H -0.06316200 -3.01198900 3.27230900
H 0.35430000 4.14219100 2.06502300
H -5.27538400 0.65883200 -1.33420700
H -4.84571800 -1.33566300 2.47764500
H 5.18492700 -0.85893600 -1.62175600
H 5.16085600 2.01914700 1.60579400
H 9.64615600 -2.31647900 -2.14575600
H 8.59246100 -2.47566500 -0.70437700
H 9.75865400 -1.12438600 -0.81847300
H 7.69148700 -2.38562600 -3.68990100
H 6.28003400 -1.30413200 -3.50441400
H 6.57280800 -2.60545100 -2.31444600
H 9.25816200 -0.44560900 -3.84613000
H 9.33985800 0.79826000 -2.56214300
H 7.90930400 0.71695600 -3.63297400
H 6.48629000 2.58052700 3.39558000
H 6.28683700 3.91634300 2.21349900
H 7.64790600 3.93655700 3.36808700
H 9.39246200 3.10565300 0.14472600
H 9.29029000 4.25359300 1.51247000
H 7.98582100 4.20014600 0.28319400
H 9.68881100 1.15615200 1.88354300
H 8.47042900 0.93471600 3.17240700
H 9.56662400 2.35425400 3.20544600
H -9.44221900 -2.38673500 2.15587600
H -9.50693400 -0.80120600 2.99626200
H -9.43772600 -2.31520700 3.93929600
H -5.97537800 -0.95016800 4.43951600
H -7.48463900 -1.47341500 5.24191900
H -7.44696900 0.05676800 4.30659100
H -5.87977500 -3.27170200 3.21076600

H -7.29286300 -3.82239300 2.26186500
H -7.38781200 -3.73420600 4.04979200
H -6.69227500 2.39486400 -1.88321300
H -8.01807700 2.72239000 -0.72915900
H -8.36063100 2.61715800 -2.48535400
H -9.82947700 -0.60365500 -1.19301000
H -10.13055000 0.90020700 -2.10704900
H -9.88308400 0.97556000 -0.34118700
H -7.87902400 -1.13845000 -2.80641700
H -6.61341400 0.08398400 -3.13192400
H -8.28709600 0.36542100 -3.69591800
C 0.80569300 -0.47554200 -3.49073100
N 0.36901500 0.77200700 -3.27520800
N -0.09178500 1.83694400 -3.09155800
C 2.18920200 -0.77433700 -3.34153900
N 3.34671500 -1.05646700 -3.23682900
C -0.17026400 -1.52536800 -3.90927900
O 0.16227200 -2.72829700 -4.04877400
O -1.41744100 -0.97039800 -4.10691500
C -2.62092000 -1.84005200 -4.55475700
C -2.31068100 -2.40832400 -5.95496800
H -3.20260400 -2.94217800 -6.33234000
H -2.07195500 -1.59547900 -6.66412600
H -1.46926200 -3.11902700 -5.92215900
C -2.87366600 -2.93208500 -3.49646000
H -2.98031400 -2.48915100 -2.49057700
H -2.05931400 -3.67339200 -3.47789900
C -3.75339400 -0.79865500 -4.58947800
H -3.51979600 0.01312100 -5.30056400
H -3.90826300 -0.36124700 -3.58780800
H -3.81699100 -3.45487400 -3.74190600
H -4.69220300 -1.28557500 -4.90964000

***Re*TS1**

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -225.7012 cm-1
G_corr: 1.579225 Hartree
H_corr: 1.856372 Hartree
SCF: -5969.659788 Hartree
S: 583.304 Cal/Mol-Kelvin
H: -5967.803416 Hartree
G: -5968.080563 Hartree

Cartesian Coordinates:
N 1.38113100 1.43385900 0.26878000

N -1.43325100 -1.35448000 0.31101000
N -1.41036900 1.42180000 0.60520000
N 1.36209900 -1.33867100 -0.03733000
C 1.17970900 -2.74159100 -0.08994000
C 2.75612900 -1.16003100 -0.21760000
C 2.77058100 1.28083900 0.03534000
C 1.23001100 2.80780900 0.56712000
C -1.21083900 2.80274000 0.85192000
C -2.80705900 1.24926100 0.72938000
C -2.82914100 -1.18871900 0.46590000
C -1.26194100 -2.75403000 0.19806000
C -2.53779100 -3.44308900 0.30289000
C -0.04360100 -3.43011000 0.01762000
C 2.44759900 -3.42007100 -0.28575000
C 3.44058000 0.07043800 -0.21853000
C -3.50661100 -2.47524900 0.45055000
C -3.50465000 0.03213100 0.63209000
C -3.45832900 2.50874100 1.05215000
C 3.46165100 2.54948800 0.20662000
C 0.02395100 3.47408000 0.85862000
C -2.47178900 3.46625100 1.13903000
C 3.41796900 -2.44456200 -0.37813000
C 2.51180100 3.49016900 0.53916000
C 0.06847200 4.92437000 1.27678000
C 0.15666300 7.61241000 2.15945000
C -0.18516700 5.99231000 0.35627000
C 0.35847200 5.23522000 2.64691000
C 0.40526300 6.58323000 3.09066000
C -0.13788700 7.34252000 0.80831000
C 4.92856000 0.09946800 -0.43127000
C 7.71897000 0.19876600 -0.81166000
C 5.47579000 0.78878700 -1.54941000
C 5.79971000 -0.52785300 0.49038000
C 7.21143000 -0.48949300 0.31682000
C 6.87452000 0.84997700 -1.75678000
C -0.03759200 -4.93798000 -0.02376000
C 0.02046700 -7.76669000 -0.04956000
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C 0.32872800 -5.67165000 1.15231000
C 0.36350700 -7.09121000 1.13985000
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C -3.19804200 -4.44190900 -5.21699000
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C -2.00223700 6.58647100 -4.38434000
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H 3.84477000 -0.90446200 -5.68074000
H 3.05043900 -3.21457200 -4.78342000

^{Si}TS1

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -354.519 cm-1
G_corr: 1.578737 Hartree
H_corr: 1.856247 Hartree
SCF: -5969.657015 Hartree
S: 584.07 Cal/Mol-Kelvin
H: -5967.800768 Hartree
G: -5968.078278 Hartree

Cartesian Coordinates:
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N -1.50469000 1.34882000 0.13706000

C -1.47661000 2.75655000 0.31537000
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C -0.89716000 -2.80903000 0.23665000
C 1.53059000 -2.53620000 0.51599000
C 2.93697000 -0.79976000 0.49699000
C 2.69909000 1.63086000 0.25536000
C 0.96142000 3.03132000 0.23621000
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C -2.82026100 3.28897900 0.44244000
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C 3.50166000 0.48392000 0.38583000
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C 0.38992100 -3.35224000 0.41885000
C 2.86186100 -3.06332000 0.76737000
C -3.68918000 2.22791900 0.30610000
C -2.09321900 -3.62620000 0.14224000
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C -0.85247100 7.36663000 -0.23123000
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H -1.60643900 -3.87180000 -3.37654000
C -3.58212000 -1.18242100 -4.47992000
H -3.36953000 -0.16348100 -4.84769000
H -4.19678000 -1.11120100 -3.56619000
H -3.14124900 -3.92095100 -4.30409000
H -4.16147000 -1.72254100 -5.25098000

Re Intermediate C

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.574063 Hartree
H_corr: 1.848077 Hartree
SCF: -5860.140835 Hartree
S: 576.712 Cal/Mol-Kelvin
H: -5858.292758 Hartree
G: -5858.566772 Hartree

Cartesian Coordinates:
N 1.59443800 1.11760900 0.59590700
N -1.55097600 -1.19236700 0.33335200
N -1.17473200 1.51118800 0.70133400
N 1.20742200 -1.55011700 0.01754000
C 0.84215700 -2.90662600 -0.07904500
C 2.57526700 -1.51736600 -0.34950900
C 2.94248200 0.81368900 0.30342100
C 1.62619500 2.44117700 1.09092900

C -0.80065800 2.81835500 1.07991300
C -2.57466700 1.57812100 0.52103900
C -2.91794100 -0.83404500 0.30504300
C -1.55266200 -2.60608400 0.36040000
C -2.91383200 -3.11258000 0.43150800
C -0.43497900 -3.43940300 0.18284700
C 1.96806100 -3.71055900 -0.52370900
C 3.42035400 -0.39775600 -0.23567500
C -3.75490800 -2.02321400 0.34898700
C -3.42403200 0.47928300 0.29743500
C -3.05713200 2.92596800 0.78383500
C 3.80680900 1.91648900 0.69492200
C 0.50975000 3.26254600 1.33590300
C -1.96600200 3.68453700 1.15280900
C 3.02654700 -2.84811400 -0.72589900
C 2.99685500 2.91170800 1.20135600
C 0.72237100 4.65221100 1.88081600
C 1.12940200 7.21200200 3.01155100
C 0.91277400 5.78803100 1.02680000
C 0.73118200 4.83071800 3.30392500
C 0.93709100 6.11382900 3.87471300
C 1.11892400 7.07334400 1.60973900
C 4.86754900 -0.49715400 -0.62381600
C 7.58112200 -0.64378000 -1.36336800
C 5.36933400 0.32299500 -1.67269800
C 5.74505800 -1.38006800 0.04892900
C 7.11987000 -1.46680500 -0.30735000
C 6.72816300 0.25934900 -2.06175200
C -0.60614700 -4.93536400 0.17303500
C -0.87238100 -7.75001600 0.17537700
C -1.14539500 -5.60696400 -0.97140000
C -0.20959000 -5.70264900 1.31620700
C -0.34290400 -7.11673800 1.31894000
C -1.27407600 -7.02488600 -0.96509600
C -4.89938000 0.72226100 0.14242400
C -7.64829400 1.22441300 -0.16115700
C -5.80734500 0.35818900 1.16958400
C -5.38349100 1.34659000 -1.03531200
C -6.76785200 1.60385200 -1.20943100
C -7.19761700 0.60684600 1.03646400
C 1.01760900 6.59511300 -1.37965900
N 0.89144500 5.60346800 -0.38585800
C 0.48670700 3.55439000 5.50401200
N 0.52083500 3.67113200 4.10766400
C 0.73577000 -5.47636300 3.67772400
N 0.29848600 -4.98619500 2.43880100

C -2.26573800 -5.23450400 -3.21759600
N -1.54706000 -4.81414600 -2.08504300
C -2.70933100 -4.10958100 -4.10257500
C -3.05932800 -4.42281200 -5.57712500
C -4.19367500 -4.03299000 -4.63137300
C 1.18964800 -4.39937100 4.62117200
C 1.23393000 -4.72083200 6.13491600
C 2.55559800 -4.50767600 5.40037500
C 0.21743200 2.15464400 5.97962300
C 0.58438300 1.78936800 7.43743000
C -0.89354000 1.85368200 7.05626300
C 0.94734800 6.06645900 -2.77982200
C 0.52736700 7.04352900 -3.90601000
C 1.96731400 6.53631200 -3.88572900
C -1.64519400 0.53141100 6.86827100
C -1.75363300 2.99688500 7.59837000
C 2.36018500 5.45924000 -4.90273300
C 3.09502100 7.50729400 -3.53151600
C -4.77142700 -2.61822000 -4.74677600
C -5.21464500 -5.09243100 -4.21283200
C 3.29047900 -3.18057900 5.61820500
C 3.47484000 -5.70610700 5.15712700
C -7.33441000 2.28142000 -2.48560500
C -8.22001500 0.23391900 2.14323200
C -8.04448800 3.61601700 -2.08988900
C -6.22626100 2.61106600 -3.52381400
C -8.36968400 1.32784100 -3.16365000
C -7.54366500 -0.41695600 3.38172900
C -9.25997000 -0.77938600 1.56599000
C -8.96444000 1.52319800 2.61739500
C 7.30898600 1.13008500 -3.20720300
C 8.04876400 -2.43985900 0.46660100
C 9.51016300 -2.41360800 -0.06035300
C 7.50542300 -3.89776400 0.32372900
C 8.06806400 -2.04196800 1.97758600
C 6.23972300 2.05682800 -3.84854500
C 7.88280400 0.19954300 -4.32361500
C 8.45716000 2.02817300 -2.64412100
H 1.05151700 0.81425400 7.61302900
H 4.89163600 1.90525300 0.60845100
H 4.02846300 -3.08155200 -1.08031900
H -4.10221600 3.22466000 0.72726200
H 1.92731200 -4.78756800 -0.67952800
H 3.27751400 3.88656200 1.59708100
H -4.84272600 -2.00907600 0.33303400
H -1.92933700 4.73308500 1.44443200

H	-3.17107300	-4.16881200	0.49308600
Co	0.00628000	-0.00201500	0.23329200
H	0.94238200	6.21942100	4.96054700
H	1.25957100	7.92913900	0.94858500
H	1.28975600	8.20674100	3.44367500
H	8.63518600	-0.69913000	-1.65391600
H	-0.03808100	-7.67786200	2.20353100
H	-1.68657500	-7.51985800	-1.84507900
H	-0.97509500	-8.84147000	0.17236100
H	-8.72133200	1.42026100	-0.27935300
O	1.17322400	7.83463400	-1.12204900
O	0.65769100	4.53404700	6.29915100
O	0.75121500	-6.71322900	3.97966500
O	-2.53810600	-6.45460700	-3.46672300
H	-2.24937000	-3.13954300	-3.88321700
H	0.90319500	-3.37610600	4.34375600
H	0.95942900	-5.74952500	6.39129000
H	0.34754900	1.36604900	5.22629900
H	0.98943900	2.61827900	8.02749000
H	0.62524800	5.02557600	-2.87124100
H	0.87377500	-3.95116600	6.82608200
H	-1.33117100	-3.80776500	-2.04052700
H	-2.48823600	0.65244900	6.16071000
H	-2.06154400	0.18641000	7.83480100
H	-0.98445800	-0.26743300	6.48112200
H	-2.63143600	3.17315700	6.94655600
H	-1.18022200	3.93618600	7.66860300
H	-2.12735400	2.73713400	8.60800600
H	0.35409000	8.07543800	-3.58258400
H	-0.16521500	6.66425300	-4.66573100
H	2.68093500	5.92874800	-5.85390400
H	1.51757000	4.77805400	-5.12412100
H	3.20186000	4.84720600	-4.52455200
H	3.40602000	8.06717300	-4.43565600
H	3.97995600	6.96032200	-3.15068400
H	2.77734900	8.22994300	-2.76166900
H	-2.72835000	-3.70838200	-6.33907800
H	-2.97708800	-5.47910300	-5.85483500
H	-4.00851200	-1.88579200	-5.07096500
H	-5.17998500	-2.27871400	-3.77566900
H	-5.59472800	-2.60099000	-5.48788300
H	-5.69764000	-4.81634300	-3.25506900
H	-4.74372300	-6.08179600	-4.09100000
H	-6.00801200	-5.17084300	-4.98194100
H	2.58836600	-2.34390300	5.79507000
H	3.91482400	-2.92428800	4.74053700

H 3.95814100 -3.25266400 6.49879200
H 4.11054600 -5.87606200 6.04787000
H 4.14329000 -5.52143400 4.29361700
H 2.89783700 -6.62450000 4.95829600
H 0.74367600 4.64586700 -0.74472500
H 0.35965100 2.80507000 3.58474700
H 0.35006500 -3.97020500 2.31617600
H 4.67543400 0.99857000 -2.18240300
H 5.35133900 -1.98733900 0.87261900
H -4.66563900 1.62005100 -1.81490700
H -5.41246500 -0.10048700 2.08151200
H -8.46782200 4.10323300 -2.98921100
H -7.33072900 4.31833300 -1.61989900
H -8.87153400 3.44455600 -1.37663900
H -6.68268500 3.08822300 -4.41114800
H -5.70114000 1.69945700 -3.86698200
H -5.47547200 3.31417000 -3.11621500
H -8.79085900 1.80549800 -4.06908700
H -9.20996100 1.08613200 -2.48717100
H -7.89138500 0.37671700 -3.46406500
H -6.81428800 0.26565400 3.85763400
H -7.02316600 -1.35809300 3.12100300
H -8.31429000 -0.66093000 4.13663900
H -9.80349100 -0.35967500 0.69973700
H -10.00652000 -1.04161900 2.34007300
H -8.76267400 -1.71061000 1.23538000
H -9.50235300 2.01544100 1.78655600
H -8.25263800 2.25577100 3.04196200
H -9.70703800 1.26886400 3.39792700
H 9.96812200 -1.41197100 0.04663700
H 9.56973300 -2.71450700 -1.12361500
H 10.12468500 -3.12490700 0.52254200
H 6.47712000 -3.99325100 0.71850500
H 8.14876200 -4.60135800 0.88604900
H 7.49449200 -4.21231100 -0.73690400
H 7.05693000 -2.07541000 2.42302400
H 8.46337400 -1.01742900 2.11034600
H 8.71251400 -2.73886900 2.54709900
H 5.81212100 2.76299400 -3.11204600
H 5.41057100 1.47827800 -4.29809500
H 6.70522400 2.65500800 -4.65401700
H 8.68060100 -0.46086300 -3.93699300
H 8.31336600 0.80786600 -5.14210000
H 7.08798600 -0.44156900 -4.74918900
H 9.27144300 1.42510900 -2.20224600
H 8.07619400 2.71060800 -1.86130300

H 8.89254400 2.64211800 -3.45576600
C -0.01586300 0.38341800 -1.60155900
C 0.20277900 1.74081000 -1.87758600
N 0.37701100 2.93013700 -1.96893700
C -0.11902500 -0.60975400 -2.68967400
O -0.65250000 -1.75529400 -2.62170200
O 0.48018600 -0.07314000 -3.83914800
C 0.54014400 -0.81088700 -5.18424300
C -0.89388800 -0.91075000 -5.74429600
H -0.86482600 -1.35979700 -6.75470300
H -1.52563500 -1.54291500 -5.10060300
H -1.34828100 0.09308700 -5.82233200
C 1.40881900 0.14621400 -6.02399000
H 2.41729700 0.24114500 -5.58517100
H 0.95126700 1.14979900 -6.06651900
C 1.22178100 -2.18435400 -5.00402700
H 0.59821700 -2.87432400 -4.41525600
H 2.19737100 -2.06683200 -4.49885000
H 1.50653100 -0.24393900 -7.05389500
H 1.40133300 -2.63095800 -6.00012700

^{Si}Intermediate C
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.573232 Hartree
H_corr: 1.847438 Hartree
SCF: -5860.146487 Hartree
S: 577.115 Cal/Mol-Kelvin
H: -5858.299049 Hartree
G: -5858.573255 Hartree

Cartesian Coordinates:
N 1.23805000 -1.42609500 -0.22567900
N -1.25922400 1.58971700 -0.30826900
N -1.48251700 -1.16185000 -0.64376700
N 1.46405000 1.31282900 0.09615300
C 1.38207600 2.66763800 0.47871500
C 2.84708400 1.05897300 -0.04438300
C 2.64707200 -1.36915900 -0.29739900
C 0.93494600 -2.80277400 -0.12705600
C -1.47308800 -2.56997600 -0.52484200
C -2.79087100 -0.84225300 -1.06430500
C -2.60074200 1.58312100 -0.74444900
C -1.03862400 2.90338200 0.16264300
C -2.24151500 3.70775700 0.01386300
C 0.19635600 3.42090500 0.59814200

C 2.70925000 3.25424600 0.57311300
C 3.43002500 -0.19676800 -0.30429800
C -3.19473700 2.90152300 -0.57299400
C -3.32803300 0.45510700 -1.17066300
C -3.56099100 -2.05914600 -1.28178000
C 3.20821200 -2.71150000 -0.24913300
C -0.35486500 -3.36459100 -0.20407400
C -2.76185800 -3.12094100 -0.91228300
C 3.60844700 2.27651400 0.19903500
C 2.15469400 -3.59239000 -0.10465900
C -0.51808000 -4.86145400 -0.13375000
C -0.87448200 -7.66761500 -0.08123300
C -0.94639200 -5.50628100 1.07012100
C -0.27987800 -5.65086700 -1.30816100
C -0.45262200 -7.05935400 -1.28200600
C -1.12611100 -6.91962200 1.08563700
C 4.90955300 -0.31797500 -0.53930800
C 7.67473500 -0.56795800 -1.04541400
C 5.85587800 0.01718200 0.46187500
C 5.37144200 -0.79019400 -1.79489300
C 6.75752800 -0.91898600 -2.07131000
C 7.25109400 -0.10213000 0.22745100
C 0.27599600 4.85094200 1.07068700
C 0.44794900 7.52629000 1.96676700
C 0.11002300 5.15882100 2.45788600
C 0.51935300 5.91189500 0.14137600
C 0.60896000 7.25680200 0.59114100
C 0.19858500 6.50560400 2.90750300
C -4.74695400 0.63926000 -1.62896800
C -7.39802300 1.01223100 -2.47763800
C -5.01326900 1.26750800 -2.87190100
C -5.82163100 0.20805900 -0.80981400
C -7.16696100 0.39160700 -1.22024100
C -6.34551500 1.45835400 -3.32113300
C -1.92750100 -5.08368200 3.36512300
N -1.17166900 -4.71531100 2.23503100
C 0.42369400 -5.47475000 -3.75913000
N 0.10485100 -4.95968000 -2.49502500
C 0.89823700 6.37885600 -2.34107500
N 0.66305800 5.55500400 -1.23052000
C -0.37890600 4.10562800 4.72706900
N -0.15175300 4.07430900 3.34172000
C -0.68370200 2.76106000 5.31778700
C -0.58535900 2.59623100 6.85304300
C -1.96841200 2.53965400 6.20790000
C 0.96474300 5.62636000 -3.63903800

C	0.76389500	6.41357900	-4.95622500
C	2.14861100	5.84304100	-4.65714700
C	0.76665400	-4.41317600	-4.76590900
C	1.54820000	-4.82689500	-6.03536900
C	0.09407500	-4.38522400	-6.19104800
C	-2.02136000	-4.02054800	4.41615600
C	-3.25004300	-4.04750100	5.36114800
C	-1.87610100	-4.36079700	5.94774400
C	-0.17462500	-2.98750700	-6.75947200
C	-0.96709200	-5.42746600	-6.54882400
C	-1.20048400	-3.27739100	6.79467100
C	-1.55945200	-5.78990300	6.39240600
C	-2.63570300	1.16911900	6.05359100
C	-2.94414000	3.69680300	6.42942900
C	2.58915200	4.59031100	-5.42229300
C	3.28798900	6.79984500	-4.30131800
C	-8.36985900	-0.05220200	-0.34573200
C	-6.67842400	2.12809000	-4.68119400
C	-9.23271500	-1.08650100	-1.13767000
C	-7.92158800	-0.71230500	0.98759100
C	-9.24590000	1.19536200	-0.00258100
C	-5.40342900	2.55488100	-5.46040100
C	-7.54681100	3.40309700	-4.43332600
C	-7.47926400	1.12318800	-5.56999600
C	8.25041800	0.27168900	1.35514800
C	7.21453500	-1.43291500	-3.46270500
C	8.76115800	-1.50570700	-3.59324700
C	6.67710000	-0.47173300	-4.57127300
C	6.63747700	-2.86580200	-3.69776300
C	8.03942100	1.76612400	1.75939900
C	9.73209900	0.09212900	0.92295200
C	7.99203000	-0.63962600	2.59780400
H	2.34973300	-4.16209400	-6.37538600
H	4.27341800	-2.93252800	-0.28843200
H	4.68848500	2.35972200	0.09606900
H	-4.58367800	-2.07904000	-1.65280400
H	2.90416000	4.29193000	0.84011900
H	2.18102000	-4.67784800	-0.02088200
H	-4.22070400	3.14857600	-0.83942400
H	-2.99493700	-4.18462300	-0.92067000
H	-2.32025500	4.75355800	0.30763800
Co	-0.04128600	0.06354300	-0.10416800
H	-0.26262100	-7.63544200	-2.18893700
H	-1.47853800	-7.39562600	2.00082100
H	-1.01365900	-8.75467400	-0.05561300
H	8.74518000	-0.66228000	-1.24173200

H 0.79826800 8.04835700 -0.13559000
H 0.06999000 6.71811700 3.96982400
H 0.51647300 8.56329500 2.31556800
H -8.43398400 1.15667600 -2.80895200
O -2.50000300 -6.21699000 3.48180900
O 0.41848900 -6.71730200 -4.03735000
O 1.04584900 7.64084300 -2.26115000
O -0.34571100 5.17521600 5.41755100
H -0.40551400 1.89787600 4.69926500
H 0.56779100 4.60282900 -3.61269800
H 0.62373700 7.49200900 -4.82698700
H 0.99191000 -3.42214500 -4.34972600
H 1.76056600 -5.89855700 -6.11201300
H -1.63659200 -3.03769800 4.12651800
H 0.14809500 5.94811200 -5.73336800
H -0.21185300 3.15138300 2.89841200
H -1.14090700 -2.59037900 -6.39274400
H -0.22260700 -3.02673700 -7.86528800
H 0.62004900 -2.26935700 -6.48124000
H -1.97183600 -5.09465300 -6.22318400
H -0.75413700 -6.40048600 -6.07560000
H -0.99617800 -5.56992100 -7.64670900
H -3.93358800 -4.88841900 5.20374200
H -3.72593300 -3.08711300 5.58717400
H -1.52568500 -3.35864000 7.85065800
H -1.45512300 -2.26137100 6.43851200
H -0.09868900 -3.38696800 6.77062800
H -1.92852800 -5.95142500 7.42444800
H -0.46628200 -5.96935700 6.39118200
H -2.03282700 -6.53176200 5.72831500
H -0.13991300 1.67233800 7.23879300
H -0.31493300 3.51004800 7.39295000
H -1.88795900 0.35948500 5.95136600
H -3.28647400 1.13839200 5.16006600
H -3.25682800 0.94616600 6.94321100
H -3.69110000 3.74082900 5.61348700
H -2.42174200 4.66695600 6.47769500
H -3.49041200 3.54620300 7.38093100
H 1.73285700 3.93217900 -5.66320900
H 3.31957900 4.00289100 -4.83296500
H 3.07466600 4.87567800 -6.37595900
H 3.75595500 7.18488500 -5.22825000
H 4.07150400 6.27937500 -3.71678000
H 2.92655300 7.65771400 -3.71008700
H -0.75782000 -3.77108600 2.26140100
H 0.14658400 -3.93994200 -2.40862300

H 0.57833400 4.55306700 -1.42769200
H 5.49076700 0.35749900 1.43798900
H 4.62896600 -1.04430200 -2.56093000
H -5.59077300 -0.24747900 0.15784000
H -4.16813700 1.59393700 -3.48642900
H -10.10388300 -1.39857300 -0.53025200
H -8.64114700 -1.98884900 -1.38177100
H -9.61484200 -0.66405700 -2.08532100
H -8.81401900 -1.00848000 1.57012400
H -7.32882200 -0.01882900 1.61293000
H -7.31858800 -1.62367900 0.81483400
H -10.11599600 0.89183500 0.61073200
H -9.62958300 1.69098200 -0.91346200
H -8.66203700 1.94024600 0.56985400
H -4.75829100 1.68783000 -5.69844000
H -4.80348800 3.29262200 -4.89433700
H -5.69652400 3.02630500 -6.41717000
H -8.49059800 3.16112600 -3.91123500
H -7.80603400 3.88128800 -5.39751900
H -6.99820600 4.14043200 -3.81762700
H -8.42162900 0.80912700 -5.08497000
H -6.88266300 0.21375400 -5.77178400
H -7.73649000 1.59209400 -6.53931600
H 9.20451400 -2.19996700 -2.85441800
H 9.23237500 -0.51243700 -3.46721500
H 9.02831300 -1.87640600 -4.60050700
H 5.57371800 -0.40533100 -4.55626000
H 6.98144500 -0.83605800 -5.57128200
H 7.08036400 0.54957400 -4.43692100
H 5.53317700 -2.87684700 -3.64910000
H 7.01766500 -3.57375900 -2.93746200
H 6.93634100 -3.23835000 -4.69632100
H 7.01088200 1.95258300 2.11987000
H 8.22713400 2.43744900 0.90035200
H 8.73670000 2.04334400 2.57310000
H 9.95886000 -0.95732600 0.65550900
H 10.39661700 0.37358400 1.76114300
H 9.99046500 0.73661300 0.06141200
H 8.14938700 -1.70495900 2.34489600
H 6.95953800 -0.52951800 2.97744800
H 8.68566800 -0.37169600 3.41784100
C -0.46267800 -0.19248300 1.71557900
C -1.79928000 -0.06395500 2.10705300
N -2.95713900 0.09597300 2.43043600
C 0.48758100 -0.86561500 2.64613000
O 0.27859100 -2.03910400 3.08438000

O 1.55709100 -0.07125500 2.99552200
C 2.60491800 -0.53046700 4.04369300
C 1.88671100 -0.77412200 5.38762500
H 2.64418700 -0.97855100 6.16738300
H 1.31923600 0.12390800 5.69171700
H 1.20335500 -1.63578600 5.32872800
C 3.33516200 -1.78280400 3.51861600
H 3.77920800 -1.59098300 2.52643800
H 2.65121300 -2.64291300 3.44268500
C 3.52774200 0.69981100 4.11051200
H 2.97629700 1.58499000 4.47210000
H 3.93484300 0.93388200 3.11151900
H 4.15099900 -2.04288200 4.21935100
H 4.36603500 0.49994600 4.80309100

TS2

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -408.3699 cm-1
G_corr: 1.752081 Hartree
H_corr: 2.055588 Hartree
SCF: -6361.920272 Hartree
S: 638.785 Cal/Mol-Kelvin
H: -6359.864684 Hartree
G: -6360.168191 Hartree

Cartesian Coordinates:
N 0.94817700 1.55122900 0.96039700
N 0.44903000 -2.25663100 0.05841700
N -1.18354200 -0.27358900 1.14286700
N 2.52611600 -0.38689000 -0.25871300
C 3.21507000 -1.50747900 -0.77128700
C 3.42883500 0.69111900 -0.43645200
C 2.08180400 2.36730800 0.73856800
C 0.05944300 2.38096400 1.68294500
C -1.84571100 0.83120900 1.72475100
C -2.15853900 -1.29818600 1.13143000
C -0.68870500 -3.06836900 0.28398200
C 1.44223000 -3.16230600 -0.38275700
C 0.93650800 -4.52470300 -0.38254800
C 2.74348000 -2.83143700 -0.79687300
C 4.52185600 -1.12577000 -1.27814900
C 3.24022000 2.00580100 0.02602800
C -0.37952900 -4.46608300 0.02326300
C -1.94594000 -2.63127700 0.73987700
C -3.42129000 -0.81095400 1.66435100

C 1.91827100 3.65968000 1.38741400
C -1.26897300 2.07826900 2.02849900
C -3.22457900 0.50010500 2.04301100
C 4.64546400 0.23446800 -1.09072700
C 0.67299900 3.66475300 1.97715700
C -2.07842700 3.07288600 2.82515300
C -3.62223800 4.82342900 4.42753400
C -2.91190900 4.06167900 2.20691900
C -2.02539600 2.99597600 4.25759000
C -2.79695200 3.87340500 5.06343600
C -3.69255000 4.93063400 3.02506000
C 4.30721400 3.04009100 -0.19878100
C 6.28707700 5.00136400 -0.60870000
C 4.02838800 4.18258600 -0.99953000
C 5.58478200 2.90135900 0.39289900
C 6.59814300 3.88153400 0.20009800
C 5.01109600 5.17719300 -1.21850600
C 3.66097200 -3.92470800 -1.28035800
C 5.38700300 -5.98886200 -2.14721800
C 3.56656800 -4.42403300 -2.61897900
C 4.63179000 -4.48390900 -0.38760800
C 5.50188700 -5.51893800 -0.82227800
C 4.43918700 -5.46402200 -3.04930100
C -3.06790700 -3.62537200 0.85265900
C -5.16176900 -5.49687200 1.05777000
C -3.57394500 -3.99501200 2.12079700
C -3.62298400 -4.20839800 -0.31938700
C -4.67881500 -5.14719500 -0.23655100
C -4.62860700 -4.94205300 2.24651800
C -3.76342600 4.98529400 0.00055400
N -2.92142500 4.17472100 0.78592200
C -0.91632000 1.72473600 6.17668000
N -1.17248600 2.00498600 4.82734400
C 5.48352700 -4.35090800 2.01628300
N 4.66526400 -3.97254200 0.94273600
C 2.20365700 -4.29913000 -4.75504700
N 2.58503600 -3.85190500 -3.47881000
C 1.04999700 -3.54252900 -5.34279500
C 0.87775100 -3.54685800 -6.88224600
C -0.15302900 -4.28955900 -6.03506000
C 5.19691700 -3.59538700 3.28272500
C 5.65429300 -4.21575800 4.62536600
C 6.35230300 -2.94831400 4.13695600
C 0.06584300 0.60553000 6.37820300
C 0.78923100 0.50129300 7.74242100
C -0.22779300 -0.57790000 7.37644900

C	-3.39880400	5.01577400	-1.45055500
C	-4.46515600	5.45230200	-2.48264100
C	-3.28207200	6.38245600	-2.23382000
C	0.30548500	-1.94736400	6.94183200
C	-1.56256800	-0.62734700	8.12228500
C	-2.17008300	6.43074000	-3.28699600
C	-3.51637100	7.70703100	-1.50566100
C	-1.52378200	-3.63135900	-5.84352900
C	-0.18987200	-5.81822600	-6.07324800
C	5.99538000	-1.62502300	4.82269500
C	7.79877500	-3.03573800	3.64663600
H	1.85733900	0.25863300	7.73093800
H	2.67483100	4.44171100	1.39592500
H	5.48048500	0.87966600	-1.35613600
H	-4.32627200	-1.40994400	1.74332000
H	5.23102500	-1.82057600	-1.72555000
H	0.19325200	4.45235100	2.55637700
H	-1.08321400	-5.28466500	0.16128900
H	-3.92924200	1.19293700	2.50041100
H	1.52866600	-5.39660800	-0.65596900
Co	0.61715900	-0.29745000	0.28953500
H	-2.73585700	3.79072100	6.14958900
H	-4.34418800	5.65933200	2.54204300
H	-4.22671200	5.50045600	5.04245400
H	7.05427400	5.76551100	-0.76998300
H	6.23085900	-5.92998000	-0.12229000
H	4.34975100	-5.83720300	-4.07020100
H	6.05561200	-6.78851500	-2.48693000
H	-5.97653600	-6.22409500	1.13386800
O	-4.75236700	5.64216200	0.47621700
O	-1.45970600	2.35033400	7.14360800
O	6.38482400	-5.24663400	1.93338300
O	2.77198100	-5.26486000	-5.36367000
H	0.77366100	-2.62849200	-4.80618100
H	4.25146600	-3.03681000	3.29645300
H	6.19937800	-5.16071000	4.52926600
H	0.64667600	0.32061100	5.49075200
H	0.48462500	1.25217700	8.47910200
H	-2.68189100	4.25168400	-1.76317300
H	4.96174900	-4.15521900	5.47185700
H	2.09115300	-3.01623600	-3.13021600
H	-0.41042700	-2.45579100	6.26728000
H	0.45766500	-2.59736300	7.82552300
H	1.27411900	-1.86341500	6.41344600
H	-2.33585400	-1.13541700	7.51361900
H	-1.92526200	0.38453500	8.36822000

H -1.44375200 -1.19714700 9.06447000
H -5.43314900 5.74280600 -2.06274600
H -4.51828100 4.88076600 -3.41522300
H -2.41100500 7.18343300 -4.06372900
H -2.03923000 5.45374800 -3.78849600
H -1.20211300 6.71262300 -2.82904000
H -3.84859900 8.47800500 -2.22865600
H -2.58268300 8.06767500 -1.03089500
H -4.28631000 7.60592400 -0.72269000
H 0.59522300 -2.60391200 -7.36384800
H 1.61248500 -4.15143000 -7.42460700
H -1.45133600 -2.52814100 -5.80923300
H -1.99794900 -3.97080100 -4.90222500
H -2.19857000 -3.90272100 -6.67923700
H -0.65553800 -6.22362200 -5.15358300
H 0.82311800 -6.24375000 -6.16416400
H -0.79549600 -6.15634200 -6.93700400
H 4.94353300 -1.60928300 5.16585300
H 6.14533900 -0.76961100 4.13587600
H 6.64181400 -1.46567500 5.70771200
H 8.49054600 -2.96699500 4.50873600
H 8.03245900 -2.20146100 2.95673100
H 7.98971900 -3.98504700 3.11912000
H -2.24305400 3.60512100 0.24729300
H -0.67425100 1.42051400 4.14937900
H 3.98915900 -3.22732900 1.13643000
H 3.03440200 4.27242800 -1.44871800
H 5.77850000 2.02679800 1.02540800
H -3.22556500 -3.90219200 -1.29181600
H -3.12563800 -3.54748000 3.01604600
C -0.01928800 0.26577200 -1.46566500
C -0.68220800 1.51778600 -1.35250200
N -1.35295800 2.49122800 -1.15327900
C 0.83912000 0.01947000 -2.66998100
O 1.24875800 -1.11698700 -3.04408300
O 1.05814400 1.20744700 -3.36140900
C 1.75009600 1.26607100 -4.73932000
C 3.17938100 0.69676300 -4.63148800
H 3.70954100 0.87186300 -5.58675700
H 3.73844800 1.20571100 -3.82666600
H 3.16946400 -0.38477600 -4.42633000
C 1.76024900 2.78271600 -5.00983000
H 0.73314800 3.18701700 -5.00619600
H 2.21828300 2.98349700 -5.99584500
C 0.87292000 0.51221300 -5.76024700
H -0.16134200 0.89988000 -5.74385100

H 0.85862600 -0.56912000 -5.55233900
H 2.34555400 3.30824000 -4.23502900
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C -1.62533100 -1.00934400 -2.21956700
C -2.72179100 -0.46413200 -2.53258400
C -3.87025300 0.41858000 -2.79360800
H -4.57823900 -0.06966000 -3.49474700
H -3.52870300 1.34940100 -3.28922900
C -6.48557200 2.24501200 -0.81463800
H -0.99878800 -1.89364500 -2.20424500
C -4.64460000 0.80690600 -1.51231400
H -4.99582100 -0.10041900 -0.97357100
H -3.98886400 1.38920900 -0.83228500
O -5.78263600 1.61721700 -1.96032000
H -6.80226200 1.43860300 -0.11300500
H -5.79062700 2.91961200 -0.27394900
C -5.14405700 -5.32710700 3.65872500
C -3.96928800 -5.94069100 4.48643200
C -5.67295600 -4.04766300 4.38295500
C -6.29715800 -6.36726200 3.60873400
H -3.58312700 -6.85749800 4.00270800
H -3.12737400 -5.23191000 4.58997000
H -4.31700800 -6.20509500 5.50355200
H -6.51998300 -3.60228900 3.82783300
H -6.02370300 -4.30325700 5.40121100
H -4.88696100 -3.27643100 4.48076200
H -6.62502100 -6.60343000 4.63834000
H -7.17639800 -5.98066800 3.05911600
H -5.97650200 -7.31465600 3.13527100
C -5.31865400 -5.79517400 -1.49286000
C -6.83798200 -5.43361600 -1.54353700
C -4.65909600 -5.30815900 -2.81242900
C -5.16068900 -7.34773500 -1.41375700
H -7.37378400 -5.78891500 -0.64424500
H -6.98040500 -4.33883900 -1.61328700
H -7.31167500 -5.90195800 -2.42764200
H -3.58265400 -5.56181600 -2.85055000
H -5.14899000 -5.80011800 -3.67338900
H -4.76560300 -4.21505300 -2.94651000
H -5.62768500 -7.82301300 -2.29767900
H -4.09267600 -7.63512000 -1.39054000
H -5.64410400 -7.76432600 -0.51116900
C 7.98090400 3.69300600 0.87890100
C 7.79027000 3.63608100 2.42880900
C 8.62053200 2.35481800 0.38774600
C 8.96678700 4.84902500 0.55373700

H 7.35113200 4.57844100 2.80657100
H 7.12326100 2.80738800 2.72929200
H 8.76657700 3.48367700 2.92777200
H 8.78388800 2.37420500 -0.70631100
H 9.59905800 2.19650600 0.88026500
H 7.98087500 1.48387200 0.62128400
H 9.93301000 4.66213800 1.05856600
H 9.16694400 4.92591800 -0.53192800
H 8.58784000 5.82562000 0.91030600
C 4.74540900 6.43676900 -2.08512000
C 3.30265600 6.46872800 -2.65992200
C 4.94889600 7.71729500 -1.21261400
C 5.74985100 6.46389700 -3.28157000
H 3.10370400 5.60335900 -3.32047400
H 2.53984400 6.47667400 -1.85871000
H 3.16523800 7.38616500 -3.26222900
H 5.97242800 7.77413400 -0.79906700
H 4.77950900 8.62470600 -1.82353300
H 4.23853600 7.73382900 -0.36480100
H 5.58081900 7.36592500 -3.90058400
H 6.79943400 6.48298000 -2.93514600
H 5.62088600 5.57301000 -3.92467300
C -7.68677300 3.01558600 -1.32636500
C -8.62174300 2.39769800 -2.19821200
C -7.90379200 4.35423700 -0.90948900
C -9.76171700 3.10649500 -2.64161600
H -8.43993100 1.37089300 -2.53651300
C -9.05202400 5.05977100 -1.34525400
H -7.17302800 4.84500700 -0.25313400
C -9.98351100 4.43881400 -2.21132200
H -10.47710400 2.62385800 -3.31868700
H -9.21225500 6.09307300 -1.01512200
H -10.87050200 4.98690100 -2.55147100

[z]Intermediate D
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.756813 Hartree
H_corr: 2.058314 Hartree
SCF: -6361.94995 Hartree
S: 634.562 Cal/Mol-Kelvin
H: -6359.891636 Hartree
G: -6360.193137 Hartree

Cartesian Coordinates:
N 0.95532900 1.60672000 0.73515000

N 0.29707100 -2.23472000 0.00823000
N -1.21920000 -0.14444000 1.09353000
N 2.45812000 -0.47474900 -0.36627000
C 3.09036000 -1.64317900 -0.85388000
C 3.46068000 0.52343100 -0.45383000
C 2.14663900 2.34456100 0.53615000
C 0.09250900 2.51837000 1.38783000
C -1.82221000 1.00329000 1.66062000
C -2.20141000 -1.15277100 1.22631000
C -0.86868900 -2.98742000 0.28385000
C 1.20464100 -3.18206000 -0.51796000
C 0.61409100 -4.51064000 -0.54217000
C 2.52088100 -2.92548900 -0.93976000
C 4.46044000 -1.36791800 -1.24878000
C 3.33716900 1.86286100 -0.03937000
C -0.66602900 -4.39018000 -0.04642000
C -2.06468900 -2.49638100 0.83501000
C -3.39829000 -0.62712100 1.86404000
C 2.02014900 3.68648100 1.08783000
C -1.22441100 2.26803000 1.81105000
C -3.16164000 0.70278900 2.13894000
C 4.68699000 -0.03023800 -1.00890000
C 0.75058900 3.79431000 1.60926000
C -1.97916100 3.33389000 2.56967000
C -3.43710200 5.21518900 4.10411000
C -2.81905100 4.29402900 1.91763000
C -1.86886100 3.35728000 4.00091000
C -2.59770100 4.30006900 4.77209000
C -3.55857200 5.22779900 2.70112000
C 4.52054900 2.78543200 -0.14365000
C 6.72988900 4.53110200 -0.28596000
C 4.45803900 3.95862200 -0.94635000
C 5.70143900 2.50998200 0.58632000
C 6.82757900 3.37730200 0.52861000
C 5.55665800 4.84722200 -1.03021000
C 3.36731100 -4.07366900 -1.43080000
C 4.95826200 -6.24867800 -2.29023000
C 3.29932100 -4.51985900 -2.78976000
C 4.24023100 -4.74573900 -0.51408000
C 5.04307200 -5.83520800 -0.94456000
C 4.10398200 -5.61570900 -3.21543000
C -3.21815900 -3.44176100 1.03310000
C -5.37332800 -5.21623200 1.38880000
C -3.58539900 -3.86538100 2.33076000
C -3.94377900 -3.91765100 -0.09282000
C -5.03254900 -4.80804100 0.06657000

C	-4.66968900	-4.76555100	2.53203000
C	-3.75182200	5.06103900	-0.31482000
N	-2.87189100	4.31643900	0.49289000
C	-0.69887100	2.20989000	5.96100000
N	-1.00471100	2.39785000	4.60601000
C	4.97375100	-4.77158800	1.93224000
N	4.24967100	-4.28488900	0.83521000
C	2.08534100	-4.20147900	-4.99575000
N	2.41137100	-3.84460900	-3.67603000
C	1.03627100	-3.33031000	-5.62051000
C	0.95713100	-3.27141000	-7.16624000
C	-0.18057900	-3.95100000	-6.40718000
C	4.68397100	-4.04071800	3.21257000
C	5.01078100	-4.74907800	4.54982000
C	5.84152100	-3.53086800	4.15207000
C	0.27949000	1.09562000	6.20353000
C	1.05191000	1.07669000	7.54445000
C	0.01159000	-0.01265000	7.29115000
C	-3.42457200	5.01857900	-1.77428000
C	-4.53156200	5.35420900	-2.80096000
C	-3.37724200	6.33853900	-2.64071000
C	0.51546000	-1.41482000	6.93253000
C	-1.29517000	0.00504000	8.08632000
C	-2.29433200	6.36087900	-3.72480000
C	-3.64001200	7.69625900	-1.98723000
C	-1.50187900	-3.18708000	-6.26761000
C	-0.33963800	-5.46941000	-6.50286000
C	5.56240100	-2.20810800	4.87392000
C	7.30013100	-3.72709800	3.73462000
H	2.11648000	0.82084100	7.51078000
H	2.81643900	4.42749100	1.09246000
H	5.59447000	0.54254200	-1.18845000
H	-4.29081000	-1.21385100	2.07241000
H	5.14105100	-2.11317800	-1.65755000
H	0.28946900	4.64004000	2.11718000
H	-1.41043800	-5.16920000	0.10656000
H	-3.81417000	1.42673900	2.62453000
H	1.13306200	-5.40438000	-0.88494000
Co	0.54546000	-0.27132000	0.17157000
H	-2.49450100	4.29233900	5.85820000
H	-4.21975200	5.93113900	2.19420000
H	-4.00984200	5.94085900	4.69335000
H	7.58567800	5.21135200	-0.34329000
H	5.69826200	-6.32965800	-0.22581000
H	4.03512200	-5.94603900	-4.25255000
H	5.57457200	-7.09026800	-2.62756000

H -6.21210800 -5.90669200 1.52357000
O -4.74310200 5.72129900 0.15058000
O -1.19827100 2.90839000 6.90140000
O 5.79911200 -5.73864800 1.85930000
O 2.61825200 -5.18090900 -5.61476000
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H 3.79042100 -3.40236900 3.20079000
H 5.47675200 -5.73425800 4.44241000
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H 0.78211900 1.88004000 8.23809000
H -2.68876100 4.26246900 -2.06161000
H 4.27997100 -4.65916900 5.36079000
H 1.95355100 -2.99321900 -3.31713000
H -0.22963900 -1.95903000 6.32034000
H 0.69391100 -2.00500000 7.85257000
H 1.46486000 -1.37761900 6.36519000
H -2.09498000 -0.53458100 7.54256000
H -1.63917000 1.03566000 8.27459000
H -1.14709000 -0.49977000 9.06087000
H -5.49852200 5.63319800 -2.37110000
H -4.58743200 4.72523900 -3.69567000
H -2.57999200 7.05859900 -4.53681000
H -2.14394200 5.36102900 -4.17333000
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H -4.01797300 8.40973900 -2.74587000
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H -4.38548200 7.61641900 -1.17862000
H 0.78274100 -2.29315000 -7.62847000
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H 3.53550900 4.16272100 -1.49878000
H 5.72852900 1.61623200 1.22093000

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O 1.24604000 -1.08026900 -3.23304000
O 1.28303000 1.26162100 -3.17992000
C 2.11411900 1.45721100 -4.47584000
C 3.48468000 0.76803100 -4.34150000
H 4.09423000 1.01189100 -5.23233000
H 4.01805000 1.13233100 -3.44739000
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H -4.91992000 -0.28732100 -0.83962000
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C -5.85446800 -5.34310200 -1.13590000
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H -6.36988800 -7.29837200 -2.01136000
H -4.72808800 -7.24179100 -1.29311000
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C 7.72504900 2.98112300 2.87110000
C 8.64595900 1.64399300 0.90601000
C 9.22715900 4.08568300 1.16980000
H 7.34414900 3.95948200 3.21931000
H 6.94703900 2.22287200 3.07523000
H 8.61735900 2.72196300 3.47274000
H 8.93560900 1.65962300 -0.16165000
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H 7.89638000 0.84316300 1.04374000
H 10.10463900 3.79212300 1.77576000
H 9.55742900 4.15381300 0.11579000
H 8.91269800 5.09248300 1.50442000
C 5.52392800 6.14070200 -1.88729000
C 4.16532800 6.34038100 -2.61336000
C 5.76645800 7.37879200 -0.96483000
C 6.65078800 6.07473200 -2.96767000
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H 3.32299800 6.41520100 -1.89985000
H 4.19338800 7.27961100 -3.19683000
H 6.73849800 7.31790200 -0.44229000
H 5.76326700 8.30776200 -1.56675000
H 4.97337800 7.46103200 -0.19803000
H 6.64877800 6.99853200 -3.57757000
H 7.65177800 5.97361200 -2.50975000
H 6.49846800 5.21240200 -3.64379000
C -7.62861100 2.82092800 -1.12189000
C -8.63181100 2.12851700 -1.85086000
C -7.78886100 4.20663800 -0.86372000
C -9.78148100 2.80976700 -2.31105000
H -8.49883000 1.06117700 -2.06541000
C -8.94628200 4.88674700 -1.31621000

H -7.00796200 4.75415800 -0.31970000
C -9.94441100 4.19170700 -2.03983000
H -10.54998100 2.26835700 -2.87616000
H -9.06285200 5.95703700 -1.10821000
H -10.83902200 4.71979700 -2.39160000

TS3

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -63.8847 cm-1
G_corr: 1.755235 Hartree
H_corr: 2.056784 Hartree
SCF: -6361.945577 Hartree
S: 634.663 Cal/Mol-Kelvin
H: -6359.888793 Hartree
G: -6360.190342 Hartree

Cartesian Coordinates:
N 1.13427100 1.59226800 0.71019600
N 0.14496400 -2.19178500 0.07454800
N -1.19650100 0.05977000 1.06924500
N 2.45439500 -0.63924500 -0.33294300
C 2.98076600 -1.86826100 -0.79669700
C 3.54221200 0.26351700 -0.43424000
C 2.39433000 2.20993600 0.52464900
C 0.34925800 2.59411000 1.32865700
C -1.71324800 1.28129000 1.56115500
C -2.27273200 -0.84775400 1.19532300
C -1.07698000 -2.83465800 0.38007500
C 0.97289700 -3.23091400 -0.40884800
C 0.28018300 -4.50850400 -0.36906700
C 2.30299600 -3.09901100 -0.84411200
C 4.36921400 -1.72289300 -1.19568000
C 3.53934800 1.61355400 -0.03543300
C -0.98330900 -4.26463200 0.12367800
C -2.23830100 -2.21953800 0.88237100
C -3.44914500 -0.18120400 1.73454400
C 2.38815600 3.56458300 1.05965700
C -0.99993100 2.48485100 1.70863100
C -3.10065200 1.13223300 1.96787600
C 4.71409300 -0.40649700 -0.97841900
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C 2.95357900 -4.80439000 -2.64481700
C 3.85333100 -5.04983300 -0.35474500
C 4.56257900 -6.21543000 -0.74869400
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Co	0.56645500	-0.25444300	0.18702100
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H	5.16704100	-6.74490900	-0.01069700
H	3.57558400	-6.32676600	-4.06281800
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H	-6.66064700	-5.23747500	1.68970000
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H	7.43831600	6.72830300	-0.53796500
H	6.54726100	7.78890000	-1.66746600
H	5.69888100	7.04545200	-0.27400800
H	7.27492900	6.36658000	-3.66499000
H	8.18767400	5.26651800	-2.59067800
H	6.95084700	4.60269400	-3.69757200
C	-7.80875000	3.00654100	-1.56584200
C	-8.58929100	1.94217100	-2.08023500
C	-8.45340700	4.19884300	-1.14116600
C	-9.99708300	2.06968500	-2.17082900
H	-8.08534900	1.02512400	-2.39936600
C	-9.85834100	4.32586300	-1.23424200
H	-7.85699100	5.02705300	-0.73572700
C	-10.63657000	3.26007800	-1.75055800
H	-10.59315100	1.23947800	-2.56928400
H	-10.34438700	5.25121000	-0.90262200
H	-11.72651400	3.35733800	-1.82160100

[E]Intermediate D

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.754554 Hartree
H_corr: 2.058357 Hartree
SCF: -6361.947669 Hartree
S: 639.407 Cal/Mol-Kelvin
H: -6359.889312 Hartree
G: -6360.193115 Hartree

Cartesian Coordinates:

N	1.75064100	1.39854300	0.68093200
N	-0.37239400	-1.90658100	0.18616800
N	-0.86028000	0.59841500	1.34426300
N	2.20742900	-1.06655000	-0.55499400
C	2.27687600	-2.36474100	-1.11448900
C	3.49133000	-0.51735800	-0.79422800
C	3.10913300	1.62049600	0.34986100
C	1.38053000	2.55620500	1.40525000
C	-0.94220400	1.90969300	1.86898100
C	-2.12612300	0.03396800	1.62188600

C -1.65684000 -2.19802400 0.70324300
C 0.04231500 -3.11520800 -0.41959200
C -0.95888700 -4.15385400 -0.24406500
C 1.26938000 -3.34354400 -1.06755400
C 3.57793700 -2.60581000 -1.71167600
C 3.94501700 0.74547600 -0.36807100
C -2.00032700 -3.59231000 0.46215600
C -2.51293800 -1.29584300 1.36468100
C -2.99427700 1.01024800 2.26544300
C 3.57475200 2.88373000 0.90555700
C 0.11080400 2.84021400 1.93915000
C -2.26072100 2.16664000 2.42222700
C 4.32641700 -1.46481800 -1.51749500
C 2.50635400 3.46238200 1.55260400
C -0.08483900 4.10038400 2.74943600
C -0.45895800 6.37733100 4.39252600
C -0.48446900 5.34765200 2.16619400
C 0.13975800 4.03049600 4.16631800
C -0.04880600 5.16915400 4.99212700
C -0.67590000 6.48529500 3.00545500
C 5.36847500 1.15122000 -0.63367200
C 8.04081700 1.92673000 -1.08879700
C 5.65881900 2.30195000 -1.41885900
C 6.43654400 0.40591400 -0.07964000
C 7.79185400 0.78000600 -0.29663300
C 6.99354700 2.70709400 -1.65844100
C 1.54888500 -4.71227600 -1.63775900
C 2.07085200 -7.30545900 -2.64051900
C 1.13349300 -5.06734000 -2.96108400
C 2.22408400 -5.68474300 -0.82967900
C 2.49067400 -6.98578700 -1.33273800
C 1.39907300 -6.37544500 -3.45909300
C -3.85800000 -1.77413600 1.83601000
C -6.36574600 -2.69185200 2.73883700
C -4.15947700 -1.79228400 3.21880100
C -4.83549100 -2.22577700 0.90595900
C -6.10118400 -2.68678200 1.33878600
C -5.41746900 -2.25519300 3.69548400
C -1.11344600 6.53600500 0.01518900
N -0.67199600 5.42532600 0.75658100
C 0.89505300 2.44412600 6.02212100
N 0.56633100 2.77862300 4.70179600
C 3.21968300 -6.04583500 1.49434500
N 2.59510100 -5.29321400 0.49009900
C -0.14618600 -4.25938700 -4.99818500
N 0.45679900 -4.08495400 -3.74121400

C	-0.84382000	-3.03593800	-5.51590900
C	-1.09066000	-2.92450600	-7.04070600
C	-2.29592600	-3.11785600	-6.12267000
C	3.40778400	-5.29049900	2.77929700
C	3.61369800	-6.10248000	4.08140900
C	4.78683800	-5.28742400	3.54144100
C	1.34518700	1.01902500	6.18286900
C	2.19154100	0.65511900	7.42705700
C	0.77401500	0.09560300	7.32371500
C	-1.15743300	6.30097700	-1.46603500
C	-2.08570100	7.19728400	-2.32152100
C	-0.57458500	7.35691500	-2.47923200
C	0.61433400	-1.38208300	6.94998200
C	-0.30841500	0.63025200	8.26330100
C	0.08050200	6.76198500	-3.73064800
C	0.09867400	8.63005800	-1.96355300
C	-3.18638700	-1.90098100	-5.84844600
C	-3.04537300	-4.45122700	-6.14538100
C	5.13578100	-3.97718600	4.25577000
C	5.98849300	-6.01826300	2.93958100
H	3.04557100	-0.01476200	7.27928300
H	4.59452100	3.25330800	0.82388500
H	5.35018700	-1.26900100	-1.82985000
H	-4.02597200	0.82045700	2.55495200
H	3.86237300	-3.53297400	-2.20689500
H	2.46493300	4.40464100	2.09674100
H	-2.91409800	-4.06978700	0.80925300
H	-2.56234500	3.11298900	2.86839600
H	-0.84933300	-5.17667800	-0.60112300
Co	0.60250100	-0.17725900	0.23145100
H	0.13029900	5.08375000	6.06492900
H	-0.99565800	7.42196000	2.54744200
H	-0.61066700	7.26093500	5.02358400
H	9.07729000	2.23070900	-1.26692200
H	3.00483900	-7.70699400	-0.69567000
H	1.06880400	-6.63103600	-4.46653800
H	2.27195300	-8.30913000	-3.03306700
H	-7.34025800	-3.04967600	3.08613500
O	-1.44970300	7.65146400	0.53636700
O	0.82497500	3.25993300	6.99776200
O	3.59371500	-7.25344600	1.34061000
O	-0.11880000	-5.35549800	-5.64963600
H	-0.62544400	-2.11103200	-4.97250800
H	2.83470300	-4.35791500	2.86785800
H	3.64695500	-7.18812300	3.94168300
H	1.59197100	0.49342700	5.25072100

H 2.35701400 1.48318500 8.12434100
H -1.03644200 5.25935900 -1.77616400
H 3.08899300 -5.75852300 4.97929300
H 0.40908800 -3.13204500 -3.34981400
H -0.35439100 -1.56072500 6.44429800
H 0.64250000 -2.01299500 7.85983500
H 1.42150900 -1.72524200 6.27526700
H -1.31649100 0.47846900 7.83045900
H -0.17528400 1.70696500 8.46045100
H -0.26800100 0.08764400 9.22797100
H -2.61667300 7.97683400 -1.76490000
H -2.65987200 6.71267900 -3.11940200
H 0.05691300 7.49452700 -4.56175700
H -0.43930100 5.84568100 -4.06839200
H 1.13925100 6.50295100 -3.53570000
H 0.02940300 9.42823400 -2.72888800
H 1.17210600 8.45118200 -1.75626300
H -0.37748000 8.98869800 -1.03598900
H -0.92636300 -1.94843800 -7.51117600
H -0.76006800 -3.79028900 -7.62422000
H -2.60517400 -0.95950300 -5.83770900
H -3.70030100 -1.99914500 -4.87238100
H -3.96486900 -1.81127400 -6.63147300
H -3.59038600 -4.61299800 -5.19472500
H -2.35587900 -5.29806000 -6.29717800
H -3.78928600 -4.44895000 -6.96617500
H 4.23826400 -3.48707600 4.67837800
H 5.62184700 -3.26445900 3.56173800
H 5.83902800 -4.17090300 5.08913000
H 6.68977300 -6.31113400 3.74516600
H 6.53614900 -5.36267600 2.23465900
H 5.67843000 -6.92698200 2.39733300
H -0.46992700 4.57858100 0.19425900
H 0.65866600 2.02296600 4.01649100
H 2.35702600 -4.32797100 0.73792400
H 4.82253400 2.87333200 -1.83362000
H 6.19997300 -0.46450600 0.54378800
H -4.59138200 -2.20542400 -0.16034400
H -3.39264400 -1.45600300 3.92671600
C -0.25709500 0.52862600 -1.54980600
C -0.24645800 1.96845800 -1.35916900
N -0.33132400 3.13768800 -1.15005000
C 0.60753700 0.04862700 -2.71818600
O 0.47070700 -1.08768200 -3.24736800
O 1.43494800 1.04561700 -3.18415600
C 2.09715200 0.98457600 -4.58566100

C 3.07465000 -0.20203800 -4.67305300
H 3.61277900 -0.14755700 -5.63853500
H 3.81788000 -0.15499700 -3.85975800
H 2.54813500 -1.16708200 -4.61664100
C 2.83092700 2.33665800 -4.63112500
H 2.12466500 3.17142100 -4.48198400
H 3.32494700 2.45805900 -5.61268100
C 0.96759600 0.91145200 -5.63554800
H 0.25009000 1.73953700 -5.49436700
H 0.43158700 -0.05011800 -5.58252900
H 3.60031300 2.38120000 -3.84143100
H 1.40815200 1.00427800 -6.64550000
C -1.65645400 -0.01201600 -1.72356800
C -2.77922300 0.68474700 -1.48370400
C -4.25579500 0.59258000 -1.56929400
H -4.69738400 0.54938300 -0.55366400
H -4.56606200 -0.33950100 -2.09551500
C -7.06504700 2.64590000 -2.99746400
H -1.69160200 -1.03935500 -2.12743600
C -4.88160400 1.79731600 -2.30788700
H -4.60705800 2.74828100 -1.80200600
H -4.52200600 1.83961000 -3.35962500
O -6.33569800 1.59146400 -2.26689500
H -6.71819100 3.64097400 -2.63292100
H -6.83551300 2.58403300 -4.08401300
C -5.69743300 -2.26676000 5.22179600
C -4.64837300 -3.18140400 5.93195800
C -5.57705800 -0.81245500 5.78002000
C -7.11591600 -2.80111800 5.56305900
H -4.72042300 -4.22236400 5.56474500
H -3.61462100 -2.83126700 5.75685400
H -4.82432400 -3.18564300 7.02483300
H -6.32336100 -0.14607200 5.30787900
H -5.75229300 -0.80764500 6.87293800
H -4.57468600 -0.38372600 5.59711800
H -7.26125100 -2.78593400 6.65943200
H -7.91034800 -2.17609400 5.11270100
H -7.25555600 -3.84466800 5.22237300
C -7.18998800 -3.18588200 0.35220900
C -8.47885700 -2.31843400 0.51733000
C -6.73614000 -3.09601400 -1.13099700
C -7.52726200 -4.67820200 0.67126300
H -8.87373700 -2.36180000 1.54905100
H -8.27367900 -1.25987200 0.27199800
H -9.27101400 -2.68191700 -0.16481900
H -5.83761200 -3.71234800 -1.32562900

H	-7.54477100	-3.46993600	-1.78630700
H	-6.52369400	-2.05243200	-1.43085200
H	-8.31569000	-5.04421000	-0.01402300
H	-6.63513600	-5.32047000	0.54638900
H	-7.89365700	-4.80358600	1.70672800
C	8.92770100	-0.06312900	0.34143900
C	8.76898400	-0.04772000	1.89592500
C	8.83169800	-1.53507400	-0.17333200
C	10.34088000	0.48059000	-0.00705800
H	8.84694000	0.98301600	2.28967800
H	7.79226600	-0.45764400	2.21197400
H	9.56229700	-0.65995200	2.36625900
H	8.96087400	-1.57784500	-1.27130500
H	9.62269600	-2.15413200	0.29171500
H	7.85635300	-1.99356600	0.07283600
H	11.10874200	-0.15801700	0.46825800
H	10.52780000	0.47150200	-1.09778400
H	10.48823500	1.51215700	0.36529600
C	7.34892300	3.96004700	-2.50256300
C	6.08893900	4.70112900	-3.02825700
C	8.16765600	4.96021000	-1.62398300
C	8.21167300	3.52901200	-3.73188000
H	5.48267300	4.05910000	-3.69506200
H	5.44297600	5.05395300	-2.20218000
H	6.39923900	5.58801700	-3.61178700
H	9.10172300	4.50583200	-1.24613000
H	8.44169100	5.85264200	-2.21877900
H	7.57565700	5.29482400	-0.75150000
H	8.48598700	4.41587900	-4.33492900
H	9.14703300	3.02890200	-3.42053000
H	7.65206700	2.82846400	-4.37998000
C	-8.55552400	2.48255300	-2.75489600
C	-9.04135700	2.09550500	-1.47909300
C	-9.48195000	2.76053100	-3.79217600
C	-10.43238000	1.99490600	-1.24534200
H	-8.32209100	1.86305100	-0.68654600
C	-10.87473900	2.66771800	-3.55697100
H	-9.11705800	3.04846300	-4.78708100
C	-11.35418800	2.28477800	-2.28146600
H	-10.79846300	1.69245600	-0.25683000
H	-11.58088800	2.88632800	-4.36675200
H	-12.43250800	2.20911800	-2.09808800

TS3'

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm

Imaginary Frequency: -292.4063 cm-1
G_corr: 1.751314 Hartree
H_corr: 2.056367 Hartree
SCF: -6361.941508 Hartree
S: 642.038 Cal/Mol-Kelvin
H: -6359.885141 Hartree
G: -6360.190194 Hartree

Cartesian Coordinates:

N	-1.14338400	-1.36318100	1.10883200
N	-0.21739200	2.14895100	-0.50142400
N	0.87382900	0.55294500	1.53866700
N	-2.19084900	0.19855900	-0.97621700
C	-2.56824600	1.09080300	-2.00601300
C	-3.23083200	-0.75917900	-0.93874400
C	-2.27909300	-2.16089600	0.84389300
C	-0.46543100	-2.05017300	2.14054900
C	1.29165000	-0.37174900	2.52418800
C	1.72016200	1.67170500	1.72290000
C	0.75899100	3.07666100	-0.05731500
C	-0.81304700	2.77279100	-1.62283300
C	-0.20001500	4.06558000	-1.87971200
C	-1.90803300	2.28317700	-2.36187100
C	-3.83039400	0.68331900	-2.60430100
C	-3.30338100	-1.87327900	-0.07915400
C	0.76285000	4.25712000	-0.91013800
C	1.66797800	2.88144400	1.00157500
C	2.65917700	1.42842300	2.81003300
C	-2.27362000	-3.35434600	1.68094000
C	0.68499700	-1.60864300	2.82163200
C	2.40528700	0.16275500	3.29291300
C	-4.25380700	-0.43899400	-1.92547900
C	-1.15470800	-3.28464500	2.48159100
C	1.16478900	-2.37992900	4.03085600
C	2.01597700	-3.70556100	6.38839400
C	2.08518400	-3.47555000	3.94740500
C	0.66533300	-1.98739600	5.31965700
C	1.09080800	-2.64821400	6.50154300
C	2.51460900	-4.12789700	5.14106800
C	-4.52365300	-2.75444100	-0.10452200
C	-6.83129300	-4.37680000	-0.09535900
C	-4.85854300	-3.53334200	-1.24619200
C	-5.36283800	-2.80544900	1.03436100
C	-6.53216900	-3.61504800	1.05985600
C	-6.01123600	-4.35513800	-1.26018600
C	-2.50014600	3.15884400	-3.44118900

C -3.64737800 4.86829100 -5.38743500
C -1.99907000 3.15973900 -4.78283400
C -3.57756900 4.04335200 -3.09857400
C -4.15703700 4.89752300 -4.07342900
C -2.58345500 4.02171400 -5.75608900
C 2.61685100 3.99380100 1.35540800
C 4.38122200 6.09186800 2.01150400
C 2.12003100 5.20960000 1.88064900
C 4.01726800 3.84129100 1.15998400
C 4.91890400 4.88357400 1.48090400
C 2.99355800 6.28031700 2.22102200
C 3.43670300 -4.94445400 2.38463900
N 2.53414200 -3.90525000 2.66454600
C -0.92904100 -0.34818200 6.46056000
N -0.27437300 -0.91524500 5.35976300
C -5.03009100 4.80207400 -1.13867400
N -4.02637200 4.03523700 -1.74539700
C -0.18082400 2.26197900 -6.30724600
N -0.91168700 2.29471100 -5.10718200
C 0.96347500 1.29081900 -6.30730600
C 1.51268600 0.81111300 -7.67308500
C 2.39178000 1.71878500 -6.81422800
C -5.19837800 4.51381300 0.32639300
C -5.90823000 5.57110000 1.20587100
C -6.61791700 4.24214500 0.95363000
C -1.86276900 0.76947400 6.08837400
C -2.97069400 1.16672800 7.09289700
C -1.83058200 2.15230900 6.84185300
C 3.59513500 -5.24092900 0.92086200
C 4.85465100 -6.01150700 0.45596200
C 3.50184500 -6.71892000 0.38210300
C -2.12171800 3.37852100 5.96994000
C -0.79596100 2.39220100 7.94290800
C 2.84804500 -6.86770600 -0.99602300
C 3.20975800 -7.87290300 1.34278700
C 3.56677400 1.07708200 -6.06807600
C 2.65027600 3.15624200 -7.26922200
C -6.64383900 3.21587300 2.09150500
C -7.85329700 4.21582600 0.05171800
H -3.96580300 1.38324200 6.68921800
H -3.02862400 -4.13702500 1.64078700
H -5.17414000 -1.00312100 -2.06315200
H 3.39612000 2.14879100 3.15933800
H -4.32679300 1.21899500 -3.41207800
H -0.81186300 -3.98834500 3.23858700
H 1.43292100 5.10510200 -0.78260200

H	2.89360400	-0.36610200	4.11003900
H	-0.48733800	4.72901600	-2.69400900
Co	-0.59904800	0.33245500	0.21167000
H	0.69227500	-2.32435300	7.46421800
H	3.23040800	-4.94653500	5.05938600
H	2.35463800	-4.21766600	7.29675800
H	-7.72591700	-5.00783900	-0.09526500
H	-4.97433700	5.55889100	-3.78170400
H	-2.18394000	4.01404800	-6.77057300
H	-4.08934400	5.52581100	-6.14523500
H	5.06913200	6.90482700	2.26541400
O	4.06810300	-5.60395700	3.27744500
O	-0.75564400	-0.73094300	7.66316400
O	-5.73825000	5.65923000	-1.76020700
O	-0.44518100	2.99529200	-7.31735700
H	0.96404000	0.57148800	-5.48301000
H	-4.37810100	3.95415000	0.79520900
H	-6.27215100	6.44842000	0.66065600
H	-2.11759500	0.83716000	5.02231500
H	-2.95534900	0.60743300	8.03434900
H	3.17931100	-4.48828800	0.24470700
H	-5.48353300	5.77339400	2.19516100
H	-0.62646200	1.61026000	-4.39020400
H	-1.20171100	3.73074100	5.46456700
H	-2.50600800	4.20964900	6.59312800
H	-2.87882100	3.16023300	5.19288300
H	0.15658100	2.76026500	7.51434700
H	-0.58733100	1.46885900	8.50850500
H	-1.17057200	3.15991500	8.64786500
H	5.53175100	-6.31718600	1.26111800
H	5.33662600	-5.69144600	-0.47523300
H	3.19859700	-7.79600100	-1.48888200
H	3.09263000	-6.01713200	-1.65974400
H	1.74622800	-6.92593700	-0.90444500
H	3.61907200	-8.81641300	0.93092900
H	2.11833100	-8.00658100	1.47618600
H	3.66050100	-7.69632400	2.33340800
H	1.77124300	-0.24931500	-7.77191600
H	1.03128800	1.26201600	-8.54725500
H	3.34053000	0.03522800	-5.77050300
H	3.81218000	1.65392000	-5.15443800
H	4.46813000	1.05931300	-6.71204000
H	2.92439400	3.79882500	-6.40947200
H	1.76011100	3.58953300	-7.75441400
H	3.49117300	3.17681100	-7.99019800
H	-5.73510900	3.27569400	2.72016500

H -6.71950100 2.18575300 1.69295800
H -7.51997300 3.39161200 2.74592000
H -8.75402200 4.47118800 0.64342200
H -8.00475100 3.20684000 -0.37890000
H -7.76300900 4.93685300 -0.77773200
H 2.15735500 -3.41390200 1.83217400
H -0.49756600 -0.50296700 4.44896800
H -3.54348500 3.36972000 -1.13431700
H -4.19685800 -3.49763200 -2.11688600
H -5.09790000 -2.19401400 1.90522100
H 4.38490800 2.89900600 0.74172100
H 1.03863300 5.31059800 2.03226600
C 1.06575800 -0.71172400 -1.54272000
C 1.46919700 -1.75560300 -0.65846500
N 1.83955200 -2.60805800 0.09271500
C 0.23493300 -1.05590100 -2.73668600
O 0.00892100 -0.23053500 -3.66921800
O -0.18922100 -2.36970900 -2.70861200
C -0.83817800 -3.04969400 -3.93410600
C -2.12569600 -2.31090800 -4.34656000
H -2.65434900 -2.91465600 -5.10838000
H -2.79589000 -2.17817100 -3.48076200
H -1.90575800 -1.31895500 -4.76986400
C -1.12815800 -4.45676500 -3.37979700
H -0.19675900 -4.94196100 -3.04004100
H -1.58652500 -5.08096100 -4.16873200
C 0.21325600 -3.08241700 -5.06489900
H 1.13909600 -3.57945300 -4.72320800
H 0.44999300 -2.06513400 -5.41849700
H -1.82021900 -4.39981500 -2.52168400
H -0.19033800 -3.65727200 -5.91902900
C 2.00385500 0.47471000 -1.73814400
C 3.12282100 -0.07663600 -2.15122300
C 4.29808400 -0.88424100 -2.46781500
H 4.96812300 -0.32095000 -3.15437900
H 4.00116100 -1.79197800 -3.03645000
C 7.08035800 -2.66204900 -0.68946500
H 1.70819300 1.52240600 -1.64949700
C 5.10850200 -1.32248400 -1.22093700
H 5.46627000 -0.43378100 -0.65644300
H 4.48412100 -1.94546500 -0.54865700
O 6.23356200 -2.08751700 -1.75965600
H 7.40944700 -1.83707800 -0.01657100
H 6.48416000 -3.37793600 -0.08492500
C 2.40179000 7.59336000 2.79886200
C 1.40716700 8.21037100 1.76374800

C 1.63660700 7.27617500 4.12372500
C 3.49488100 8.65218800 3.11200300
H 1.92657600 8.46329900 0.82021800
H 0.58255800 7.51506200 1.52189000
H 0.95928600 9.13719900 2.17077300
H 2.31952000 6.84609400 4.88026100
H 1.19607400 8.20238400 4.54023700
H 0.81509400 6.55518700 3.95911700
H 3.01877500 9.56406400 3.51842300
H 4.21650400 8.28733800 3.86750900
H 4.05570700 8.94534100 2.20414400
C 6.45161100 4.75376500 1.27522200
C 7.17532300 4.93007600 2.64887400
C 6.85722000 3.37319900 0.68869400
C 6.93928700 5.86370000 0.28964200
H 6.95476100 5.91266700 3.10447200
H 6.86116000 4.14677600 3.36407800
H 8.27176800 4.85728400 2.51461500
H 6.40212400 3.20182700 -0.30561600
H 7.95566400 3.33287400 0.56545000
H 6.56457000 2.54164000 1.35780700
H 8.03449100 5.79149700 0.14512800
H 6.45104600 5.75691700 -0.69729500
H 6.71448100 6.87657800 0.67071400
C -7.41965400 -3.63383100 2.33261800
C -6.57171800 -4.13767700 3.54450300
C -7.93180500 -2.18748800 2.62755500
C -8.65489700 -4.56453300 2.18386400
H -6.21098600 -5.16911300 3.37138000
H -5.69021800 -3.49540000 3.72417400
H -7.18478200 -4.13604600 4.46615400
H -8.54502900 -1.80768400 1.78880100
H -8.55436000 -2.18320600 3.54286800
H -7.09558600 -1.48176000 2.78412000
H -9.24925700 -4.53944500 3.11633200
H -9.31625600 -4.24158000 1.35739900
H -8.35873300 -5.61580500 2.00566700
C -6.40425800 -5.22457100 -2.48429500
C -5.40819200 -5.07194900 -3.66655500
C -6.43322200 -6.72897500 -2.06280000
C -7.82254600 -4.80287400 -2.98671300
H -5.36063500 -4.02822100 -4.03126800
H -4.38681000 -5.39117200 -3.38519800
H -5.73733700 -5.70691000 -4.51040600
H -7.15619300 -6.91110800 -1.24679400
H -6.72663700 -7.36091100 -2.92316200

H -5.43710400 -7.05940300 -1.71303500
H -8.12247100 -5.42779700 -3.84987500
H -8.58893600 -4.92354700 -2.19950200
H -7.82928900 -3.74399000 -3.30694200
C 8.27814000 -3.35004500 -1.32077100
C 8.87023100 -2.84111200 -2.50531800
C 8.84417100 -4.49245300 -0.69847600
C 10.01408400 -3.46506000 -3.05573600
H 8.41895400 -1.97178600 -2.99497300
C 9.99409400 -5.11106500 -1.24399800
H 8.38709200 -4.90126500 0.21219300
C 10.58279600 -4.59876300 -2.42510600
H 10.46179100 -3.06838200 -3.97484300
H 10.42260000 -5.99292400 -0.75356000
H 11.47066700 -5.08014300 -2.85164300

^{E}TS4^{Ha}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -622.076 cm-1
G_corr: 1.758446 Hartree
H_corr: 2.053559 Hartree
SCF: -6361.948372 Hartree
S: 621.117 Cal/Mol-Kelvin
H: -6359.894813 Hartree
G: -6360.189926 Hartree

Cartesian Coordinates:
N 1.37891000 1.27089000 0.70354000
N -0.88296000 -1.92015000 0.12908000
N -1.38681000 0.77772000 0.66979000
N 1.87662000 -1.39018000 0.01447000
C 1.94889100 -2.76098000 -0.32608000
C 3.23025000 -0.98004000 0.08550000
C 2.79110000 1.32906000 0.79096000
C 0.95541000 2.55089000 1.13028000
C -1.46182000 2.16946000 0.91849000
C -2.73660000 0.35950000 0.62592000
C -2.27765000 -2.03849000 0.33286000
C -0.45355900 -3.24185000 -0.13359000
C -1.56261900 -4.17558000 -0.03718000
C 0.86450100 -3.65118000 -0.40471000
C 3.32698100 -3.18393000 -0.50050000
C 3.68876000 0.29322100 0.47365000
C -2.68325900 -3.43628000 0.27398000
C -3.18177000 -0.97497100 0.53469000

C -3.62993000 1.50139900 0.76242000
C 3.22164000 2.61895000 1.31231000
C -0.37127000 3.01534000 1.19340000
C -2.84302000 2.61726000 0.94926000
C 4.11837000 -2.08447900 -0.24632000
C 2.08875000 3.37352000 1.51814000
C -0.63566100 4.40376000 1.72500000
C -1.13474100 6.95835000 2.84494000
C -0.53754100 5.57809000 0.90919000
C -0.96438100 4.54594000 3.11575000
C -1.22105100 5.82415000 3.67736000
C -0.79578100 6.85809000 1.48164000
C 5.16611000 0.53667100 0.61237000
C 7.93060000 1.00482100 0.91387000
C 5.81676000 1.52885100 -0.17301000
C 5.92264000 -0.20669900 1.54978000
C 7.31765000 0.01441100 1.71880000
C 7.20347000 1.77735100 -0.03732000
C 1.13219100 -5.11079000 -0.67657000
C 1.59753100 -7.86465000 -1.12267000
C 1.08284100 -5.64068000 -2.00512000
C 1.42210100 -5.98807000 0.41887000
C 1.65926100 -7.37060000 0.19682000
C 1.31451100 -7.02946000 -2.22224000
C -4.64573000 -1.27355100 0.69583000
C -7.38949000 -1.84280100 1.03535000
C -5.32153000 -0.88368100 1.87766000
C -5.37087000 -1.96187100 -0.31784000
C -6.74657000 -2.25448100 -0.16739000
C -6.70306000 -1.16213100 2.06980000
C -0.01571100 6.45030000 -1.41341000
N -0.16704100 5.43431000 -0.45804000
C -1.20903000 3.21976000 5.28578000
N -0.99203000 3.36065000 3.90881000
C 1.65927100 -6.03800000 2.96114000
N 1.44922100 -5.41434000 1.72361000
C 0.58225100 -5.06906000 -4.42599000
N 0.79956100 -4.74410000 -3.07726000
C 0.26185100 -3.88850000 -5.29578000
C 0.51927100 -4.01366000 -6.81799000
C -0.92566900 -3.93201000 -6.32958000
C 1.57502100 -5.09575000 4.12821000
C 1.29653100 -5.69013000 5.53037000
C 2.67125100 -5.08239000 5.26001000
C -1.08948000 1.80099000 5.76764000
C -0.77656000 1.56338000 7.26582000

C	-2.15216000	1.16160000	6.73775000
C	0.45077900	5.96348000	-2.75437000
C	0.14947900	6.84069000	-3.99604000
C	1.59978900	6.70102000	-3.53865000
C	-2.42357000	-0.33051000	6.51761000
C	-3.37878000	1.97116900	7.16227000
C	2.51872900	5.78551000	-4.35499000
C	2.30638900	7.90662000	-2.91648000
C	-1.66846000	-2.60593000	-6.52500000
C	-1.81762900	-5.17107000	-6.42524000
C	2.97500100	-3.70506000	5.85954000
C	3.88596100	-6.00591900	5.15093000
H	-0.04704000	0.78431000	7.51240000
H	4.25663000	2.88719100	1.51291000
H	5.20383000	-2.01367900	-0.27664000
H	-4.71482000	1.44811900	0.70650000
H	3.62887100	-4.19460900	-0.77125000
H	2.00441900	4.38632000	1.90880000
H	-3.69232900	-3.79447100	0.46497000
H	-3.15136100	3.65354900	1.07773000
H	-1.46994900	-5.25282000	-0.16640000
Co	0.22776000	-0.27396000	0.17059000
H	-1.46614100	5.89907000	4.73787000
H	-0.72276100	7.73986000	0.84417000
H	-1.33109100	7.94893000	3.27189000
H	9.00359000	1.18921100	1.02843000
H	1.87558100	-8.01668000	1.04901000
H	1.26165100	-7.41876000	-3.23955000
H	1.77612100	-8.93173000	-1.29972000
H	-8.45375000	-2.06480100	1.16394000
O	-0.25251100	7.68508000	-1.18425000
O	-1.47488100	4.19268000	6.06389000
O	1.89862100	-7.28210000	3.09166000
O	0.64323100	-6.25708000	-4.88621000
H	0.43605100	-2.91069000	-4.83522000
H	1.12893100	-4.11563000	3.91312000
H	1.22445100	-6.78256000	5.55697000
H	-0.63943000	1.09643000	5.05564000
H	-0.71489000	2.47522000	7.86914000
H	0.43238900	4.87740000	-2.88693000
H	0.59011100	-5.15523000	6.17434000
H	0.77290100	-3.73907000	-2.84740000
H	-3.18957000	-0.48246100	5.73227000
H	-2.79982000	-0.79377000	7.45059000
H	-1.50981000	-0.87551000	6.21361000
H	-4.19745000	1.86262900	6.42420000

H -3.14025000 3.04337900 7.25881000
H -3.75075000 1.60284900 8.13832000
H -0.35479100 7.78873000 -3.78073000
H -0.17589100 6.33056000 -4.90982000
H 2.98340900 6.35139000 -5.18652000
H 1.96365900 4.93361000 -4.79138000
H 3.33274900 5.37897000 -3.72389000
H 2.71815900 8.55399000 -3.71572000
H 3.14920900 7.58105000 -2.27561000
H 1.61419900 8.50396000 -2.30036000
H 0.96164100 -3.15187000 -7.33043000
H 0.88429100 -4.99357000 -7.14323000
H -0.98752000 -1.73739000 -6.44728000
H -2.46638000 -2.48610000 -5.76548000
H -2.14598000 -2.57660000 -7.52418000
H -2.64689900 -5.11765000 -5.69260000
H -1.24562900 -6.09356000 -6.23206000
H -2.26282900 -5.23576000 -7.43756000
H 2.06844100 -3.07376000 5.92255000
H 3.72739100 -3.16569900 5.25215000
H 3.38240100 -3.81449000 6.88357000
H 4.28540100 -6.21937900 6.16160000
H 4.69264100 -5.52840900 4.56114000
H 3.62392100 -6.96219900 4.66842000
H -0.04826100 4.47152000 -0.82201000
H -0.80247000 2.49334000 3.39777000
H 1.27604100 -4.40484000 1.75490000
H 5.21817000 2.10055100 -0.88899000
H 5.40597000 -0.95269900 2.16520000
H -4.83994000 -2.26384100 -1.22518000
H -4.75087000 -0.37077100 2.66056000
C -0.05420000 0.17128000 -1.88288000
C -0.00835000 1.62063000 -1.90884000
N -0.01693000 2.81178000 -1.90850000
C 1.10470000 -0.48328000 -2.64652000
O 1.08694000 -1.68537000 -3.02710000
O 2.08337000 0.43141000 -2.96813000
C 3.14598000 0.15806000 -4.06233000
C 4.05659000 -1.01309900 -3.64994000
H 4.86183000 -1.11912900 -4.40167000
H 4.52208000 -0.81751900 -2.66955000
H 3.49785000 -1.95990900 -3.59411000
C 3.90590000 1.49634100 -4.08522000
H 3.22352000 2.33222000 -4.31634000
H 4.69921000 1.46014100 -4.85438000
C 2.40385000 -0.09882000 -5.39174000

H 1.70285000 0.72619000 -5.61252000
H 1.85109000 -1.05181000 -5.36521000
H 4.37331000 1.68798100 -3.10423000
H 3.14343000 -0.15178000 -6.21211000
C -1.34567000 -0.40956000 -2.38254000
C -2.51204000 0.22774000 -2.64882000
C -3.74228000 -0.30523100 -3.32047000
H -4.59390000 -0.33553100 -2.61204000
H -3.57361000 -1.33966100 -3.69705000
C -3.45482000 2.65928900 -3.42972000
H -1.27014000 -1.49161000 -2.59366000
C -4.16493000 0.59444900 -4.51975000
H -3.33736000 0.67153900 -5.25682000
H -5.06472000 0.19469900 -5.01574000
O -4.55603000 1.92747900 -4.03944000
H -2.84093000 1.80753000 -2.78457000
H -2.71162000 2.98972000 -4.18645000
C -7.39446000 -0.71998100 3.38674000
C -6.68640000 -1.40834100 4.59744000
C -7.28015000 0.83114900 3.53428000
C -8.90027000 -1.10120100 3.42596000
H -6.75983000 -2.50958100 4.52313000
H -5.61439000 -1.14303100 4.64941000
H -7.15986000 -1.09148100 5.54647000
H -7.79339000 1.34490900 2.69966000
H -7.74787000 1.15969900 4.48212000
H -6.22700000 1.16674900 3.54322000
H -9.34139000 -0.76100200 4.38148000
H -9.46788000 -0.61996200 2.60688000
H -9.04991000 -2.19573100 3.36046000
C -7.56524900 -3.00056100 -1.25452000
C -8.73760000 -2.08756100 -1.73779000
C -6.70499900 -3.38102100 -2.49111000
C -8.15257900 -4.31601100 -0.64908000
H -9.41337000 -1.81498200 -0.90664000
H -8.35145000 -1.15061100 -2.18150000
H -9.33876000 -2.61277200 -2.50471000
H -5.86801900 -4.05248100 -2.22078000
H -7.33439900 -3.91243100 -3.22915000
H -6.28819000 -2.48603100 -2.99140000
H -8.75558900 -4.84905100 -1.40908000
H -7.34373900 -4.99175100 -0.31309000
H -8.80597900 -4.11166100 0.21863000
C 8.10080000 -0.81958900 2.76723000
C 7.49212000 -0.56852900 4.18431000
C 7.98076000 -2.33694900 2.41476000

C	9.60941000	-0.45095900	2.81540000
H	7.57539000	0.49805100	4.46544000
H	6.42322000	-0.84698900	4.22617000
H	8.02954000	-1.17038900	4.94218000
H	8.42244000	-2.54724900	1.42241000
H	8.51608100	-2.94703900	3.16739000
H	6.92736000	-2.67177900	2.39622000
H	10.11707000	-1.07525800	3.57429000
H	10.10881000	-0.63369800	1.84488000
H	9.76548000	0.60797200	3.09616000
C	7.94725000	2.85104100	-0.87559000
C	7.00033900	3.61128100	-1.84427000
C	8.60055900	3.89743100	0.08377000
C	9.06414000	2.16231100	-1.72401000
H	6.53519000	2.93043100	-2.58223000
H	6.19490900	4.14122100	-1.30148000
H	7.57817900	4.36799100	-2.40721000
H	9.31652000	3.42497100	0.78078000
H	9.15055900	4.65894100	-0.50183000
H	7.83062900	4.41449100	0.68669000
H	9.61379000	2.91857100	-2.31684000
H	9.79644000	1.63487200	-1.08566000
H	8.62885000	1.42302100	-2.42257000
C	-3.96807100	3.77045900	-2.56832000
C	-3.16290100	4.91952900	-2.34031000
C	-5.24540100	3.68557900	-1.94731000
C	-3.61796100	5.96174900	-1.50130000
H	-2.18341100	5.00349000	-2.82513000
C	-5.70411100	4.73287900	-1.11794000
H	-5.87274000	2.81025900	-2.14459000
C	-4.89097100	5.87143900	-0.88635000
H	-2.98397100	6.83962900	-1.33309000
H	-6.69592100	4.66612900	-0.65420000
H	-5.24563100	6.68157900	-0.23848000

^{E}TS4^{Hb}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -723.1753 cm-1
G_corr: 1.757555 Hartree
H_corr: 2.053387 Hartree
SCF: -6361.94025 Hartree
S: 622.632 Cal/Mol-Kelvin
H: -6359.886863 Hartree
G: -6360.182695 Hartree

Cartesian Coordinates:

N	1.47714400	-0.18415800	-1.38160100
N	-1.64919400	1.13248600	0.67466500
N	-1.28007200	-0.75929900	-1.36342100
N	1.10470600	1.66710800	0.68457400
C	0.75011000	2.54693100	1.73438800
C	2.48303500	1.91572700	0.47684200
C	2.80540900	0.30457900	-1.34731200
C	1.47686000	-1.10061700	-2.45892400
C	-0.91863400	-1.64886900	-2.40162700
C	-2.69260200	-0.84191000	-1.30934300
C	-3.01223500	0.80759300	0.48678900
C	-1.65280900	2.04110300	1.75894500
C	-3.00290400	2.26169600	2.24754000
C	-0.53442900	2.71856600	2.27719800
C	1.89736000	3.31942200	2.17800200
C	3.30475800	1.29544200	-0.48267300
C	-3.84320900	1.50454400	1.45913300
C	-3.53429200	-0.08805700	-0.46867800
C	-3.18836800	-1.78136400	-2.30538900
C	3.60488400	-0.30007600	-2.40418000
C	0.37093000	-1.82279400	-2.94147800
C	-2.09309600	-2.29670200	-2.96185400
C	2.96648600	2.93187600	1.40048800
C	2.78610600	-1.17130900	-3.08596000
C	0.52585000	-2.66069300	-4.18895000
C	0.73574200	-4.15101100	-6.59049100
C	1.05814200	-3.99110900	-4.16544100
C	0.13999400	-2.08641300	-5.44826100
C	0.23889600	-2.83328500	-6.65122700
C	1.14888500	-4.73608600	-5.37803500
C	4.73122500	1.74985200	-0.63243600
C	7.39137600	2.62413300	-0.96207600
C	5.81426900	0.86001500	-0.39112300
C	5.00563500	3.07627200	-1.04327900
C	6.34004300	3.53728600	-1.21728200
C	7.15658900	1.28070400	-0.54973700
C	-0.74306900	3.74884900	3.35995900
C	-1.17810100	5.72642300	5.33551300
C	-0.72954400	3.39293600	4.74631100
C	-0.98196600	5.11248800	2.98785600
C	-1.19855500	6.10720000	3.97777600
C	-0.94914300	4.39467200	5.73569000
C	-5.02689800	-0.18193100	-0.63199800
C	-7.82343700	-0.29024700	-0.99227300
C	-5.75222300	0.97782800	-0.99978000

C	-5.72891600	-1.40584000	-0.44752700
C	-7.13186200	-1.47958300	-0.62276900
C	-7.16139900	0.94564800	-1.18747500
C	2.19427300	-5.73916200	-2.72753200
N	1.50441400	-4.53135500	-2.92528200
C	-0.73339200	0.06494300	-6.51574500
N	-0.31976400	-0.73629100	-5.44295900
C	-1.25777800	6.63553700	0.95604100
N	-0.99945100	5.41521600	1.59453600
C	-0.58268300	1.44582300	6.36513800
N	-0.50513600	2.02806800	5.08896100
C	-0.39103700	-0.04201600	6.37055300
C	0.06660100	-0.71769500	7.68694000
C	-1.35243000	-0.98492800	7.18909200
C	-1.21328200	6.54713100	-0.54337600
C	-1.93703500	7.64237300	-1.36402500
C	-0.41119700	7.59172500	-1.40813200
C	-1.11207400	1.46049600	-6.10661200
C	-1.11888100	2.56586800	-7.19004400
C	-2.45416400	2.12633000	-6.59230600
C	2.69260500	-5.93585200	-1.32590900
C	3.05213200	-7.37201000	-0.87590400
C	4.18692300	-6.36614300	-1.06180900
C	-3.12567100	3.05707800	-5.57681300
C	-3.43033100	1.32523500	-7.45578600
C	4.82410400	-5.76242000	0.19413700
C	5.15773600	-6.54532300	-2.23021600
C	-1.63667100	-2.34430700	6.54168400
C	-2.53710000	-0.39723200	7.95806000
C	0.24956400	7.02565200	-2.66977000
C	0.39155200	8.69434000	-0.71512400
H	-0.70392500	3.54257200	-6.91829300
H	4.64623300	-0.05683800	-2.60362400
H	3.99501500	3.28447900	1.44288000
H	-4.23976300	-1.99167600	-2.48729800
H	1.86656300	4.05706000	2.97846900
H	3.01856700	-1.79393200	-3.94837400
H	-4.92471400	1.40635400	1.52781100
H	-2.06369000	-3.01926400	-3.77574300
H	-3.25392100	2.91700600	3.08019600
Co	-0.06231200	0.30953500	-0.19972200
H	-0.06468300	-2.36936800	-7.59090300
H	1.54843400	-5.74992700	-5.33869600
H	0.81014300	-4.73594600	-7.51474900
H	8.42545700	2.96013000	-1.08946200
H	-1.38153400	7.13671600	3.66627900

H -0.94090300 4.10478400 6.78699000
H -1.34544000 6.48969500 6.10450700
H -8.90808700 -0.33680500 -1.13231800
O 2.41010100 -6.59544900 -3.64873800
O -0.78694700 -0.33922600 -7.72235600
O -1.50628500 7.71888900 1.57792100
O -0.80713800 2.10799200 7.43208400
H -0.02129200 -0.46778800 5.43212900
H -1.23157900 5.53017900 -0.95760600
H -2.39808300 8.43335400 -0.76310200
H -0.79159100 1.76114100 -5.10019900
H -0.87920800 2.21659200 -8.19994200
H 2.27628900 -5.25058500 -0.58035100
H -2.51016300 7.32148900 -2.24067900
H -0.23772100 1.39237800 4.32139900
H -3.76581800 2.48297900 -4.87921800
H -3.76725900 3.79430800 -6.09803100
H -2.38209300 3.61800400 -4.97916900
H -4.11799200 0.73025000 -6.82368800
H -2.89848600 0.63616700 -8.13275900
H -4.04300100 2.01625500 -8.06718200
H 2.93086100 -8.13850700 -1.64870600
H 2.76724500 -7.67992400 0.13625200
H 5.63797500 -6.41700300 0.56467200
H 4.08653700 -5.63663300 1.00875900
H 5.26144200 -4.76937500 -0.02594100
H 5.96171700 -7.25189700 -1.94407900
H 5.63337200 -5.58144100 -2.49829800
H 4.64524400 -6.93895600 -3.12347200
H 0.81840600 -1.51163600 7.61359800
H 0.18024300 -0.03763900 8.53784000
H -0.75814200 -2.73321000 5.99374100
H -2.48097600 -2.27064800 5.82802500
H -1.91407400 -3.08677900 7.31592100
H -3.42475600 -0.30286700 7.30201700
H -2.29918200 0.60018600 8.36290700
H -2.80667500 -1.06632200 8.79884000
H -0.36743500 6.23600600 -3.13901700
H 1.24202700 6.59349700 -2.43711400
H 0.39716300 7.82861800 -3.41813000
H 0.49790600 9.56259200 -1.39437200
H 1.40819100 8.33895400 -0.45689100
H -0.10262100 9.03209900 0.21095200
H 1.33160900 -3.97676300 -2.06745600
H -0.34467400 -0.28978800 -4.52159200
H -0.80392200 4.62074100 0.97772300

H 5.58782900 -0.16298800 -0.07529000
H 4.16147700 3.74658500 -1.24451600
H -5.16106900 -2.29755500 -0.16457900
H -5.19905700 1.91186500 -1.15364400
C 0.10760400 -1.24857700 1.24577000
C 0.60297100 -2.36333200 0.45819500
N 0.96310000 -3.27223900 -0.22405500
C 1.09613200 -0.76030700 2.30967100
O 0.75098800 -0.05571900 3.29685700
O 2.35182700 -1.28905300 2.11572200
C 3.43197100 -1.28968900 3.22761500
C 3.87616300 0.15396700 3.52820800
H 4.69384100 0.12815200 4.27347400
H 4.25481100 0.64549100 2.61597800
H 3.04717300 0.75225800 3.93732400
C 4.54714000 -2.11387900 2.55968300
H 4.19331300 -3.13198900 2.32391900
H 5.41438600 -2.18661000 3.24155100
C 2.85920900 -2.01259500 4.46557900
H 2.44433600 -2.99790600 4.18748600
H 2.07847500 -1.41206900 4.95872400
H 4.87260200 -1.63227500 1.62171800
H 3.67778700 -2.17735400 5.19099800
C -1.23241600 -1.49438100 1.88004900
H -1.57709800 -0.66413200 2.51868000
C -7.90762400 2.24413400 -1.59371200
C -7.68675500 3.33111200 -0.49319300
C -7.33936000 2.76356300 -2.95322000
C -9.43676700 2.02454200 -1.75971700
H -8.09735000 2.99773600 0.47853700
H -6.61447800 3.55831700 -0.34961100
H -8.19585900 4.27154100 -0.77867900
H -7.49116900 2.01715700 -3.75537900
H -7.85293700 3.69887200 -3.24763500
H -6.25695900 2.97860800 -2.88888400
H -9.91656000 2.97860700 -2.04747500
H -9.66279700 1.28526900 -2.55157000
H -9.90858900 1.68531600 -0.81793500
C -7.93283300 -2.79594800 -0.43743100
C -8.64078800 -3.16286400 -1.78152300
C -7.02909500 -3.98972800 -0.02601300
C -9.01142800 -2.59694000 0.67545900
H -9.32934600 -2.36431900 -2.11276400
H -7.89993400 -3.32716300 -2.58642200
H -9.23152600 -4.09104800 -1.65989500
H -6.52557200 -3.80327300 0.94149100

H -7.64746500 -4.89918300 0.08976900
H -6.25752800 -4.20591000 -0.78933400
H -9.59845600 -3.52604000 0.80759600
H -8.53850000 -2.34482400 1.64333500
H -9.71714000 -1.78495000 0.42210200
C 6.58908300 4.99807300 -1.67786800
C 5.91067100 5.22386700 -3.06725000
C 5.96891200 5.98129600 -0.63395400
C 8.10074700 5.32916200 -1.81734100
H 6.34073800 4.54822100 -3.83018000
H 4.82168000 5.03858800 -3.02668100
H 6.06502200 6.26783700 -3.40151300
H 6.44583700 5.85684900 0.35653600
H 6.11848200 7.02841500 -0.96022200
H 4.88256800 5.81741200 -0.51121300
H 8.21912300 6.37872000 -2.14563000
H 8.63692900 5.21810000 -0.85565600
H 8.59471500 4.68633700 -2.57053600
C 8.36465200 0.33965100 -0.29764800
C 7.92780300 -1.08845200 0.12935500
C 9.20839700 0.21777100 -1.60735400
C 9.25779000 0.93669100 0.83698300
H 7.35695800 -1.07677000 1.07709200
H 7.30888900 -1.57868900 -0.64590200
H 8.82425100 -1.71673600 0.28757700
H 9.58302000 1.20048000 -1.94734500
H 10.08390600 -0.43769300 -1.43639600
H 8.60536500 -0.21729600 -2.42635500
H 10.13254400 0.28273600 1.01764000
H 9.63518500 1.94200700 0.57473400
H 8.68878000 1.02392200 1.78171900
C -1.97888900 -2.62006400 1.78275400
C -1.43347700 -5.24879800 1.90384000
O -2.71793300 -5.36969300 2.57249600
H -1.33448300 -4.03292500 1.67369600
C -3.72147900 -4.43441300 2.03960500
H -1.45017800 -5.68784300 0.88463400
C -3.31586800 -2.97197500 2.37535800
H -3.82268200 -4.56460100 0.94129600
H -4.66518300 -4.71299300 2.53555700
H -4.09648300 -2.29142400 1.97727300
H -3.30752300 -2.85805800 3.47981900
C -0.32824500 -5.75454600 2.77440700
C -0.42547100 -5.67222600 4.19222200
C 0.84682700 -6.30552200 2.19310400
C 0.62958500 -6.13549900 5.00904900

H	-1.34290800	-5.27259700	4.63625100
C	1.90154200	-6.76608100	3.01345000
H	0.92661200	-6.38189200	1.10199700
C	1.79888100	-6.68274400	4.42405400
H	0.53875300	-6.07967600	6.10041400
H	2.79725800	-7.20453000	2.55768700
H	2.61477500	-7.04886800	5.05836800

^{Z}TS4^{Ha}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -169.2426 cm-1
G_corr: 1.756794 Hartree
H_corr: 2.055007 Hartree
SCF: -6361.940597 Hartree
S: 627.642 Cal/Mol-Kelvin
H: -6359.88559 Hartree
G: -6360.183803 Hartree

Cartesian Coordinates:

N	1.99301100	1.20609000	0.33312000
N	-1.14989000	-1.21470000	0.38957000
N	-0.72221900	1.48463000	1.02291000
N	1.55783000	-1.49770000	-0.25856000
C	1.16331000	-2.82008000	-0.56824000
C	2.96795000	-1.51719100	-0.37966000
C	3.34602100	0.86306900	0.09967000
C	2.03927100	2.57594000	0.68321000
C	-0.32988900	2.81674000	1.29594000
C	-2.05098900	1.40382100	1.50982000
C	-2.44595000	-0.94032900	0.87885000
C	-1.22958000	-2.54323000	-0.09223000
C	-2.57580000	-3.06824900	0.05775000
C	-0.14950000	-3.32359000	-0.54453000
C	2.31664900	-3.64691000	-0.88021000
C	3.83436000	-0.42138100	-0.20497000
C	-3.32438000	-2.08286900	0.66696000
C	-2.87678000	0.26187100	1.47913000
C	-2.46041900	2.67693100	2.08688000
C	4.21123100	2.01792900	0.29939000
C	0.95750100	3.36340000	1.11858000
C	-1.41011900	3.55512000	1.92898000
C	3.43086000	-2.84591100	-0.75523000
C	3.40293100	3.07792900	0.64425000
C	1.22521100	4.76340000	1.62490000
C	1.68513200	7.33719000	2.71927000

C 1.15152200 5.92406000 0.78701000
C 1.55576100 4.92533000 3.01377000
C 1.78516200 6.21324000 3.56429000
C 1.37652200 7.21484000 1.35100000
C 5.32015000 -0.64331100 -0.29375000
C 8.10694000 -1.05870200 -0.39881000
C 6.10007000 -0.02490100 -1.30947000
C 5.95997000 -1.46771100 0.66237000
C 7.36487000 -1.68855200 0.62924000
C 7.50009000 -0.22260200 -1.37989000
C -0.38571100 -4.78234000 -0.85320000
C -0.85567100 -7.53072000 -1.33677000
C -0.76145100 -5.22668000 -2.16124000
C -0.25390100 -5.74384000 0.20280000
C -0.48659100 -7.12354000 -0.03806000
C -0.99706100 -6.61264000 -2.39620000
C -4.22085000 0.28522100 2.15508000
C -6.70672000 0.27865200 3.49513000
C -4.47037000 -0.62690900 3.21042000
C -5.24391900 1.20180100 1.78382000
C -6.49602900 1.21605200 2.44313000
C -5.71461000 -0.64694900 3.89890000
C 0.68341200 6.77120000 -1.55720000
N 0.87127200 5.75934000 -0.59953000
C 1.95384100 3.61251000 5.17020000
N 1.64309100 3.74534000 3.81028000
C 0.25113900 -5.95221000 2.69821000
N 0.11062900 -5.25376000 1.49163000
C -1.35735100 -4.45970000 -4.50527000
N -0.89735100 -4.25328000 -3.19253000
C -1.44441000 -3.20826000 -5.32618000
C -1.38534000 -3.34107000 -6.86943000
C -2.69893000 -2.89922900 -6.22900000
C 0.62170900 -5.07262000 3.85906000
C 0.33623900 -5.58986000 5.29010000
C 1.79062900 -5.45517000 4.84356000
C 1.96575100 2.18568000 5.64238000
C 2.71333100 1.85336900 6.95553000
C 1.18962100 1.74321000 6.93974000
C 0.47894200 6.25824000 -2.95278000
C -0.24617800 7.17168000 -3.97159000
C 1.24153200 6.89242000 -4.17697000
C 0.57254000 0.34150000 6.88553000
C 0.35943100 2.76903000 7.71353000
C 1.63783200 5.90216000 -5.27768000
C 2.25039200 8.02088000 -3.95603000

C	-3.07742000	-1.41739900	-6.32930000
C	-3.89473100	-3.85300900	-6.24011000
C	2.59916900	-4.27288100	5.38871000
C	2.61357900	-6.71977100	4.59074000
H	3.31753100	0.93986900	6.97598000
H	5.29511100	1.99840900	0.20865000
H	4.47414000	-3.11015100	-0.91642000
H	-3.41781900	2.85678100	2.57067000
H	2.25926900	-4.69991000	-1.15201000
H	3.68467100	4.10179900	0.88515000
H	-4.37580000	-2.11011900	0.94619000
H	-1.33821900	4.59515000	2.24332000
H	-2.88271100	-4.06598900	-0.25241000
Co	0.37261000	0.04358000	0.17368000
H	2.03111200	6.30216000	4.62354000
H	1.29539200	8.08800000	0.70267000
H	1.85560200	8.33598000	3.13801000
H	9.18935000	-1.21662200	-0.44209000
H	-0.38210200	-7.83211000	0.78496000
H	-1.28872100	-6.93208000	-3.39730000
H	-1.03837200	-8.59448000	-1.52909000
H	-7.67215000	0.27818200	4.01091000
O	0.68480200	8.01833000	-1.28601000
O	2.19957100	4.59670000	5.94027000
O	0.08380900	-7.20987000	2.81017000
O	-1.67923100	-5.60369000	-4.96876000
H	-0.97631000	-2.32578000	-4.87891000
H	0.50002900	-3.99389000	3.69289000
H	-0.08606100	-6.59931000	5.33462000
H	2.00138100	1.42595000	4.85024000
H	3.15097100	2.71941900	7.46327000
H	0.31251200	5.18018000	-3.03356000
H	-0.07081100	-4.87576000	6.01423000
H	-0.60221000	-3.29070000	-2.96712000
H	-0.42320000	0.36683000	6.40186000
H	0.44233000	-0.06001000	7.90956000
H	1.21097000	-0.36623000	6.32299000
H	-0.66301900	2.84466000	7.29474000
H	0.82189100	3.76960000	7.68114000
H	0.27065100	2.45699000	8.77248000
H	-0.52238800	8.16039000	-3.58999000
H	-0.97683800	6.70348000	-4.64099000
H	1.74784200	6.42877000	-6.24630000
H	0.87962200	5.10687000	-5.40671000
H	2.60555200	5.41836900	-5.04217000
H	2.33581200	8.63310000	-4.87547000

H 3.25393200 7.61194900 -3.72635000
H 1.94493200 8.67567000 -3.12326000
H -0.78401000 -2.60756000 -7.41872000
H -1.32701100 -4.37025000 -7.23936000
H -2.18542000 -0.76278900 -6.31006000
H -3.74047000 -1.11990900 -5.49480000
H -3.62037000 -1.22541900 -7.27571000
H -4.60743100 -3.59629900 -5.43254000
H -3.57687100 -4.90024900 -6.10639000
H -4.43221100 -3.76568900 -7.20490000
H 1.96267000 -3.38451000 5.56274000
H 3.40512900 -3.98675100 4.68547000
H 3.07171900 -4.54414100 6.35292000
H 3.04108900 -7.08481100 5.54496000
H 3.45385900 -6.51173100 3.89995000
H 1.99654900 -7.52219000 4.15338000
H 0.79689100 4.79146000 -0.96408000
H 1.45455100 2.87066000 3.31198000
H 0.28277900 -4.24482000 1.53748000
H 5.59303000 0.60741900 -2.04477000
H 5.34908000 -1.92656100 1.44901000
H -5.05068900 1.90293100 0.96703000
H -3.67119000 -1.31870900 3.50154000
C -0.17754000 0.57125000 -1.82221000
C 0.20454100 1.96515000 -1.89134000
N 0.44169100 3.13300000 -1.90189000
C 0.62104000 -0.31670000 -2.78315000
O 0.24486000 -1.46543000 -3.13801000
O 1.72262000 0.34538000 -3.27975000
C 2.52717000 -0.16989100 -4.49868000
C 3.22449000 -1.49573100 -4.14149000
H 3.84724000 -1.81540100 -4.99850000
H 3.88137000 -1.36894100 -3.26435000
H 2.49184000 -2.28905100 -3.92548000
C 3.52901100 0.98115900 -4.70280000
H 3.00191100 1.92338900 -4.93185000
H 4.20787000 0.73995900 -5.54136000
C 1.56664000 -0.30164000 -5.70008000
H 0.99921000 0.63469000 -5.84926000
H 0.86330000 -1.13853000 -5.56669000
H 4.13095100 1.13552900 -3.79114000
H 2.16127000 -0.49124000 -6.61312000
C -1.66365000 0.33401000 -2.04420000
H -1.93126000 -0.73166900 -2.05613000
C -5.93300000 -1.66506900 5.04950000
C -5.77367000 -3.11587900 4.49171000

C -4.86629000 -1.42094900 6.16481000
C -7.34246000 -1.54366800 5.69195000
H -6.53188000 -3.32450800 3.71347000
H -4.77508000 -3.27757900 4.04598000
H -5.90324100 -3.85396900 5.30628000
H -4.96170000 -0.40239900 6.58565000
H -5.00134000 -2.15029900 6.98644000
H -3.83681000 -1.53392900 5.77839000
H -7.44341000 -2.29008800 6.50186000
H -7.50724000 -0.54393800 6.13691000
H -8.14754000 -1.73776800 4.95794000
C -7.63159900 2.20276200 2.06106000
C -8.03070900 3.04357200 3.31660000
C -7.21539900 3.18916200 0.93512000
C -8.87338900 1.39204200 1.56809000
H -8.37955900 2.40418200 4.14795000
H -7.17298900 3.63872200 3.68271000
H -8.85098900 3.74091200 3.05994000
H -6.97062900 2.66997200 -0.01049000
H -8.05471900 3.87706200 0.72197000
H -6.34683900 3.80792200 1.23303000
H -9.70111900 2.08121200 1.31321000
H -8.62677900 0.80169200 0.66582000
H -9.23934000 0.69349200 2.34297000
C 8.02081000 -2.59338200 1.70578000
C 7.74868000 -1.99126200 3.12170000
C 7.39963900 -4.02475200 1.62451000
C 9.55818000 -2.72077200 1.52059000
H 8.18823000 -0.98018200 3.21113000
H 6.66641000 -1.90923200 3.33108000
H 8.19747000 -2.63521200 3.90228000
H 7.59563900 -4.48405200 0.63727000
H 7.84069900 -4.67690200 2.40263000
H 6.30517900 -4.00626100 1.77924000
H 9.97151000 -3.37461200 2.31118000
H 9.81916000 -3.17211200 0.54447000
H 10.06463000 -1.74012200 1.60020000
C 8.38435000 0.43506800 -2.47264000
C 7.56298100 1.31869800 -3.45107000
C 9.46309100 1.33766800 -1.79161000
C 9.09582000 -0.68066200 -3.30363000
H 6.80223000 0.72836800 -3.99603000
H 7.05243100 2.14905800 -2.92724000
H 8.24091100 1.76499800 -4.20247000
H 10.10832000 0.75932800 -1.10540000
H 10.11326100 1.79928800 -2.55945000

H 8.98799100 2.14841800 -1.20795000
H 9.74133000 -0.22539200 -4.07919000
H 9.73260000 -1.32207200 -2.66733000
H 8.35502000 -1.33057200 -3.80635000
C -2.59307900 1.25527100 -2.35423000
C -5.32879900 0.93296100 -2.22462000
C -2.89416900 2.70518100 -2.47699000
O -5.38823900 2.37359100 -2.44735000
H -5.50362000 0.68287100 -1.15616000
C -4.26477900 3.08648100 -1.82632000
H -2.93376900 2.98945100 -3.54731000
H -2.11724900 3.33293100 -1.99140000
H -4.47394900 4.15502100 -1.99395000
H -4.22504900 2.88279100 -0.73670000
H -4.20500000 0.64438100 -2.42289000
C -6.25881000 0.19826200 -3.15090000
C -6.68447900 0.77269200 -4.37834000
C -6.69166000 -1.11283800 -2.81100000
C -7.53328000 0.04772200 -5.24610000
H -6.36151900 1.78834200 -4.62780000
C -7.53194000 -1.83934800 -3.68459000
H -6.37081000 -1.56402800 -1.86284000
C -7.95718000 -1.26053800 -4.90601000
H -7.86497000 0.50225200 -6.18723000
H -7.85839000 -2.84991800 -3.41273000
H -8.61210000 -1.82197800 -5.58248000

^{Z}TS4^{Hb}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -1078.0606 cm-1
G_corr: 1.75557 Hartree
H_corr: 2.053463 Hartree
SCF: -6361.926999 Hartree
S: 626.97 Cal/Mol-Kelvin
H: -6359.873536 Hartree
G: -6360.171429 Hartree

Cartesian Coordinates:
N 1.75141700 1.22335800 0.66456900
N -0.94908500 -1.64781300 0.29402600
N -1.01892900 1.03361600 1.10504700
N 1.80401200 -1.41827800 -0.24477700
C 1.65895300 -2.76824600 -0.64329100
C 3.18798700 -1.15865700 -0.40132300
C 3.14993200 1.13729700 0.46388600

C 1.56306100 2.51355800 1.21338300
C -0.87658900 2.39404600 1.47262200
C -2.38540900 0.75207500 1.33243000
C -2.29745200 -1.62946800 0.72431800
C -0.73249000 -2.98228100 -0.11996800
C -1.92466600 -3.78827000 0.08106300
C 0.47481700 -3.52307800 -0.59753700
C 2.93111000 -3.32804000 -1.06287500
C 3.84948300 0.03794100 -0.06680800
C -2.88270900 -2.95944100 0.62133600
C -3.00334600 -0.50877800 1.20588900
C -3.08718200 1.94609600 1.77993300
C 3.81337100 2.34616500 0.93274900
C 0.33536500 3.10519000 1.55895300
C -2.15512700 2.95910700 1.86903700
C 3.87410800 -2.33339100 -0.91869300
C 2.83288500 3.19664100 1.39154400
C 0.32583700 4.47634000 2.19307600
C 0.22996800 6.98374200 3.50724400
C 0.25657500 5.68570100 1.42687700
C 0.37831700 4.55829500 3.62591900
C 0.32799500 5.81325400 4.28691300
C 0.19692700 6.94163100 2.10003800
C 5.34152700 0.13299800 -0.22816300
C 8.14113900 0.33096300 -0.49753000
C 5.91241700 1.09847200 -1.10399100
C 6.19568100 -0.72055300 0.50990000
C 7.61079600 -0.63712100 0.38910600
C 7.31518400 1.21295200 -1.25264200
C 0.52541600 -4.98596800 -0.96437100
C 0.61660300 -7.74429100 -1.58608400
C 0.16959100 -5.43874500 -2.27494300
C 0.92015400 -5.94440600 0.02569200
C 0.96980000 -7.32919100 -0.28539900
C 0.21796800 -6.82928200 -2.58114500
C -4.42111100 -0.68285000 1.67360700
C -7.04360400 -1.09177000 2.62562600
C -4.74531100 -0.41773000 3.02693300
C -5.43749600 -1.15388100 0.79652200
C -6.75660800 -1.37484600 1.25901500
C -6.06244200 -0.61245400 3.52621500
C 0.12241000 6.66617600 -0.91037800
N 0.26747700 5.60604700 0.00391400
C 0.60603900 3.12623400 5.72965600
N 0.49267200 3.33361100 4.34837900
C 1.61194800 -6.15599200 2.47505200

N	1.24121500	-5.44846300	1.32322400
C	-0.73085700	-4.69806900	-4.52845400
N	-0.23041000	-4.46625900	-3.23669400
C	-1.14327700	-3.45175100	-5.25494400
C	-1.22249600	-3.49412600	-6.80083500
C	-2.52324200	-3.36749600	-6.01019800
C	1.83398900	-5.27623900	3.67245200
C	1.75708300	-5.92024900	5.07831000
C	3.11298000	-5.42438100	4.58045700
C	0.76046600	1.67951600	6.10638200
C	1.38773400	1.34551500	7.48201400
C	-0.09042700	1.03036700	7.26200000
C	0.28133200	6.26011900	-2.34565300
C	-0.36233500	7.15239900	-3.43629600
C	1.16114700	7.10649300	-3.34242800
C	-0.48341500	-0.43430000	7.04089300
C	-1.14645200	1.86513100	7.98879800
C	1.91695200	6.28646800	-4.39395100
C	1.91727900	8.34057700	-2.84737000
C	-3.20398800	-1.99524400	-5.96830100
C	-3.49306600	-4.54994800	-5.97467500
C	3.65453500	-4.11530000	5.16504700
C	4.19129400	-6.44541200	4.21274600
H	2.11201800	0.52467700	7.52126500
H	4.89043300	2.49863400	0.92652600
H	4.93916300	-2.37739900	-1.13709300
H	-4.15381300	1.98973500	1.99047300
H	3.06435400	-4.34925200	-1.41653000
H	2.93736000	4.18946000	1.82648200
H	-3.88938400	-3.21611300	0.94263500
H	-2.29728900	3.99287200	2.18043700
H	-1.98906800	-4.85244800	-0.14031700
Co	0.34699300	-0.14538300	0.25624800
H	0.36810800	5.84237600	5.37679500
H	0.11771100	7.85060500	1.50284300
H	0.18361400	7.95680800	4.01016700
H	9.22775900	0.41036200	-0.60438400
H	1.27172400	-8.03728300	0.48779700
H	-0.06136100	-7.15650600	-3.58329600
H	0.65187300	-8.81224900	-1.83129500
H	-8.06218100	-1.25566100	2.99173200
O	-0.12022800	7.87073400	-0.56675000
O	0.58482200	4.06521500	6.58995800
O	1.74918800	-7.42158600	2.51154100
O	-0.84115100	-5.85802300	-5.04721300
H	-0.81498100	-2.51459500	-4.79380500

H 1.45498200 -4.24957300 3.58156600
H 1.58365300 -7.00153800 5.07612000
H 1.00175400 0.99880500 5.27907400
H 1.63097600 2.21860300 8.09668200
H 0.30763500 5.18149600 -2.52482200
H 1.23529800 -5.36070800 5.86220600
H -0.13571500 -3.47623200 -2.96349100
H -1.41094900 -0.50983300 6.44069800
H -0.66793800 -0.93265800 8.01258900
H 0.31080600 -0.99888800 6.51657700
H -2.11421700 1.83142100 7.45123000
H -0.83629200 2.91960000 8.07703100
H -1.30915700 1.45916800 9.00630700
H -0.86019500 8.05283100 -3.06093200
H -0.86292300 6.64973100 -4.27165300
H 2.13387200 6.91051300 -5.28337500
H 1.33171800 5.40941100 -4.72863200
H 2.88160400 5.92169000 -3.99107700
H 2.08538400 9.03994400 -3.69001600
H 2.90737100 8.05766100 -2.43902000
H 1.35549700 8.86750000 -2.05851200
H -0.84360100 -2.62614200 -7.35211500
H -0.99964700 -4.46935300 -7.24650300
H -2.46828900 -1.16948200 -6.00192000
H -3.80397400 -1.88542300 -5.04334800
H -3.88654200 -1.87844400 -6.83296400
H -4.14272800 -4.50025500 -5.07876000
H -2.95423300 -5.51165800 -5.95738600
H -4.14597600 -4.52600600 -6.86925800
H 2.84059800 -3.41029900 5.41975900
H 4.33310900 -3.61241600 4.44908600
H 4.22853800 -4.31751100 6.09036500
H 4.74597900 -6.74742400 5.12251500
H 4.91923000 -6.01070300 3.50017300
H 3.75378400 -7.34739600 3.75345600
H 0.40737900 4.67416000 -0.42494900
H 0.51512700 2.48934100 3.76866600
H 1.17806600 -4.43087200 1.42479500
H 5.23949800 1.75675100 -1.66238000
H 5.74494400 -1.44394100 1.19966600
H -5.17974500 -1.33502200 -0.25125400
H -3.94930100 -0.07401500 3.69804000
C -0.18514800 0.47957100 -1.68484200
C 0.18140800 1.88279200 -1.65966300
N 0.38891300 3.05543300 -1.60795900
C 0.64965300 -0.34021900 -2.67847800

O 0.31725900 -1.49034800 -3.07201700
O 1.70429500 0.39320200 -3.17695400
C 2.43876100 0.00514300 -4.48782100
C 3.14487300 -1.35437100 -4.33164100
H 3.74978100 -1.54589100 -5.23835000
H 3.82067700 -1.34454200 -3.46030500
H 2.42211500 -2.17566400 -4.20994900
C 3.44579000 1.16132700 -4.62209700
H 2.92517400 2.13393600 -4.65117600
H 4.02705900 1.04022000 -5.55466600
C 1.39931600 0.01562100 -5.62897000
H 0.86116400 0.97979900 -5.65955200
H 0.67160100 -0.80443600 -5.51683600
H 4.14506400 1.16108600 -3.76838000
H 1.92260900 -0.11900800 -6.59377700
C -1.64899700 0.23526500 -2.00381500
H -1.82609500 -0.80033200 -2.32862500
C -6.36709100 -0.30749500 5.01695500
C -5.46806600 -1.20803200 5.92355000
C -6.05585900 1.19524200 5.30998600
C -7.85182800 -0.57633300 5.38782400
H -5.67576100 -2.27962400 5.74419400
H -4.39269100 -1.03518100 5.73429300
H -5.66356900 -0.98999600 6.99107900
H -6.69393000 1.85678400 4.69421000
H -6.24795700 1.42414300 6.37578900
H -5.00055300 1.44524500 5.09569300
H -8.01343900 -0.33922900 6.45603500
H -8.54365900 0.05435100 4.79774600
H -8.12847500 -1.63699600 5.23598300
C -7.88408000 -1.91917600 0.34241500
C -9.03259900 -0.86412800 0.25053200
C -7.38226400 -2.22213900 -1.09583500
C -8.44842700 -3.24478500 0.94799600
H -9.44840800 -0.62586700 1.24686500
H -8.66690700 0.07662500 -0.20120900
H -9.85791700 -1.25353400 -0.37663800
H -6.57738400 -2.98180200 -1.09832900
H -8.21864400 -2.62000100 -1.70121400
H -7.00842100 -1.31031500 -1.59697600
H -9.26141600 -3.63809900 0.30781900
H -7.65835100 -4.01622400 1.01592200
H -8.86151500 -3.09204700 1.96176800
C 8.50552600 -1.58867300 1.22708600
C 8.23262000 -1.34698800 2.74660200
C 8.16217700 -3.07028600 0.86968300

C 10.02076300 -1.36569100 0.96529400
H 8.48022600 -0.30703300 3.03074900
H 7.17299700 -1.52552600 3.00593500
H 8.85162000 -2.03084700 3.35861800
H 8.36466300 -3.27511700 -0.19853500
H 8.77774200 -3.76161100 1.47658800
H 7.09965600 -3.30419500 1.06583400
H 10.60892500 -2.06957800 1.58334100
H 10.28666200 -1.54868600 -0.09323700
H 10.33824000 -0.34034400 1.23433500
C 7.97424300 2.25658900 -2.19340300
C 6.92943900 3.14848700 -2.91876200
C 8.91015700 3.18870700 -1.35826300
C 8.82054200 1.51435600 -3.27709900
H 6.25783800 2.55261000 -3.56550400
H 6.30779800 3.72000900 -2.20385200
H 7.45255100 3.87814400 -3.56479300
H 9.70281800 2.61814800 -0.84074200
H 9.40186900 3.92645300 -2.02105300
H 8.33466400 3.74173100 -0.59232700
H 9.30782000 2.24739300 -3.94840100
H 9.61329800 0.89247900 -2.82236200
H 8.18109500 0.85285100 -3.89149100
C -2.67627700 1.12013600 -2.04553600
C -4.30086100 1.53769800 -4.05494900
C -2.93283200 2.57388100 -1.78255600
O -3.47299200 2.69667300 -4.28724400
C -2.91072500 3.40599700 -3.09825900
H -2.19772800 3.02068900 -1.08803400
H -3.92673200 2.66659300 -1.30104400
H -1.87113400 3.63656100 -3.38598600
H -3.46201000 4.35519200 -2.95351300
H -4.12364400 0.83359000 -4.88792800
H -3.74960800 0.95587400 -3.06106800
C -5.75496000 1.77756700 -3.77524800
C -6.26451000 3.07443100 -3.48481500
C -6.66321000 0.67939600 -3.80919200
C -7.64152200 3.26599100 -3.23023800
H -5.58759400 3.93454700 -3.50409500
C -8.03873700 0.87289300 -3.55681000
H -6.28987700 -0.32502100 -4.05051200
C -8.53501200 2.16756700 -3.26117200
H -8.01967700 4.27344900 -3.01987900
H -8.72566400 0.01939800 -3.59832700
H -9.60361400 2.31832400 -3.06927000

***E*Intermediate E^{Ha}**

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.756371 Hartree
H_corr: 2.058851 Hartree
SCF: -6361.982721 Hartree
S: 636.624 Cal/Mol-Kelvin
H: -6359.92387 Hartree
G: -6360.22635 Hartree

Cartesian Coordinates:

N	-1.61963700	-1.09168400	1.12136500
N	0.41725400	1.97974400	-0.33587100
N	0.89251500	0.05699100	1.65015300
N	-2.05365100	0.76340400	-0.92641500
C	-2.12261700	1.78728700	-1.90026700
C	-3.28885500	0.08274800	-1.05016900
C	-2.93238300	-1.50204400	0.79132700
C	-1.27187800	-1.90603900	2.22410000
C	0.98047600	-0.99640600	2.59008700
C	2.09857300	0.77392200	1.81485100
C	1.62622500	2.52821100	0.15522000
C	0.00778000	2.88164800	-1.34301300
C	0.93572900	3.99560100	-1.45169600
C	-1.16269600	2.79075100	-2.11851700
C	-3.37541500	1.72561800	-2.63292900
C	-3.72970200	-0.98668300	-0.24755200
C	1.92478900	3.78673700	-0.51570100
C	2.44794200	1.96938100	1.15369500
C	2.94644100	0.12913900	2.80872800
C	-3.39988400	-2.52691000	1.71572500
C	-0.04055900	-1.91390600	2.90301500
C	2.25381100	-0.96258500	3.28926100
C	-4.09364200	0.67110400	-2.11148400
C	-2.37280200	-2.77868400	2.59704700
C	0.13717400	-2.81191000	4.10506600
C	0.49269500	-4.36287700	6.44894200
C	0.64351800	-4.14944600	4.00986000
C	-0.20805700	-2.28523400	5.39580000
C	-0.02870000	-3.05878400	6.57208500
C	0.82622500	-4.91736100	5.19823400
C	-5.09985700	-1.56608800	-0.46797400
C	-7.67153200	-2.65945400	-0.84562200
C	-5.25280700	-2.93162600	-0.83813000
C	-6.25337700	-0.76690800	-0.28570800
C	-7.55998200	-1.29869400	-0.47083000

C -6.53501900 -3.49838500 -1.03215200
C -1.44953600 3.86875900 -3.13489600
C -2.00575600 5.93402100 -4.98757900
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C 3.87236000 3.14840800 2.87884300
C 4.74541600 2.92224900 0.60444400
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C 1.64773500 -6.23086500 0.97403200
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H 6.51823500 -1.29202900 -1.33050700
H 4.87220900 0.02104600 -0.08238200
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C 7.65768800 -4.64160000 -3.96939200
C 7.66375000 -3.93875300 -1.60299900
C 8.79651400 -5.42802900 -3.74000300
H 7.21203200 -4.60867000 -4.97199100
C 8.80348900 -4.73514500 -1.38984500
H 7.24386100 -3.39562500 -0.75395600
C 9.38537900 -5.48339300 -2.44672300
H 9.23218200 -6.00416300 -4.56455000
H 9.24402300 -4.78071100 -0.38683100
H 10.27323200 -6.09920500 -2.26696500

^{E}Intermediate E^{Hb}
Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.758016 Hartree
H_corr: 2.058574 Hartree
SCF: -6361.992839 Hartree
S: 632.577 Cal/Mol-Kelvin
H: -6359.934265 Hartree
G: -6360.234823 Hartree

Cartesian Coordinates:
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N 0.40774300 1.78214500 -0.85863300
N 0.80219900 0.67551000 1.69239200
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C -1.93078600 0.84201900 -2.44163900
C -3.09235100 -0.53275300 -1.12071500
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C 0.83816400 0.03519400 2.95261400
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C	4.26094000	-5.84045000	3.19207700
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H 5.54051700 8.28124500 0.71029100
C 7.01988700 3.77706100 2.01759900
C 7.34512400 4.34992400 3.43471800
C 7.23310800 2.23865700 2.05914800
C 8.01820900 4.37866400 0.97726300
H 7.24376300 5.45007800 3.46311600
H 6.66455300 3.92721800 4.19740200
H 8.38462100 4.09757500 3.71970500
H 7.04951200 1.77638600 1.06981600
H 8.27939800 2.01833700 2.34215300
H 6.57544600 1.75047200 2.80302000
H 9.05857300 4.11769900 1.25118500
H 7.81672500 3.98543700 -0.03716300
H 7.94768300 5.48061100 0.93199300
C -8.55307300 -0.79144300 -0.06754000
C -8.50506300 0.03221300 1.25937700
C -8.50995000 0.18688500 -1.28499700
C -9.90197700 -1.56125200 -0.11142700
H -8.54633900 -0.63606500 2.13982100
H -7.58087000 0.63390900 1.33476700
H -9.36661700 0.72559500 1.30900800
H -8.56386000 -0.36953000 -2.23972500
H -9.36717600 0.88606000 -1.24344900
H -7.58257500 0.78848700 -1.29461600
H -10.73944400 -0.84007500 -0.06648300
H -10.01320100 -2.14362200 -1.04585000
H -10.00949900 -2.25148800 0.74680000

C	-6.53131500	-5.54440900	-0.35865500
C	-5.19369400	-6.33327400	-0.39370600
C	-7.34980300	-6.02982500	0.88088500
C	-7.32608500	-5.87519000	-1.66272700
H	-4.57963200	-6.05925700	-1.27232800
H	-4.59173600	-6.16522700	0.51953000
H	-5.40613900	-7.41684200	-0.45864900
H	-8.33417000	-5.53100000	0.94344600
H	-7.52619300	-7.12084100	0.81722300
H	-6.80392400	-5.82182600	1.82026500
H	-7.50112700	-6.96582900	-1.73648600
H	-8.31033500	-5.37245700	-1.68105000
H	-6.76384900	-5.55245400	-2.55918800
C	3.36079500	-0.42652900	-0.60654900
C	6.85103700	-2.70338400	-1.08201000
O	5.85991700	-1.82627100	-1.48118700
H	3.47440700	-0.85646300	0.40081400
C	5.88917900	-0.47599600	-0.84728100
H	7.47084400	-2.41674000	-0.21979400
C	4.58349000	0.24308700	-1.20144800
H	5.99105400	-0.60536200	0.25043800
H	6.77234600	0.06702900	-1.23800900
H	4.67747400	1.28281700	-0.81886500
H	4.49005200	0.32372500	-2.30060400
C	7.01648000	-3.94850600	-1.75500000
C	8.02641000	-4.86934300	-1.29750600
C	6.20372100	-4.32363600	-2.88367800
C	8.21152500	-6.10422400	-1.94241200
H	8.65194000	-4.59934700	-0.43673500
C	6.40251600	-5.56314700	-3.51664500
H	5.43429100	-3.62934400	-3.23493400
C	7.40300200	-6.46231400	-3.05597900
H	8.98306700	-6.79516600	-1.58344500
H	5.77961800	-5.83927200	-4.37561500
H	7.55062800	-7.42614500	-3.55598100

^{Z}Intermediate E^{Ha}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.759372 Hartree
H_corr: 2.059383 Hartree
SCF: -6361.990137 Hartree
S: 631.426 Cal/Mol-Kelvin
H: -6359.930754 Hartree
G: -6360.230765 Hartree

Cartesian Coordinates:

N	-1.23966600	-1.63546400	0.40911500
N	0.24364600	2.04717800	0.23151500
N	1.31964300	-0.50134800	0.72657400
N	-2.30483800	0.90237400	-0.12229100
C	-2.67690100	2.24606400	-0.35873200
C	-3.52644600	0.18984800	-0.16565900
C	-2.59354200	-2.03267400	0.31765000
C	-0.55157200	-2.82514300	0.73583700
C	1.69503900	-1.84630300	0.95214800
C	2.50701100	0.23311900	0.93985400
C	1.55776000	2.46798200	0.53830900
C	-0.45215700	3.24581100	-0.03927900
C	0.42009400	4.40026300	0.11387100
C	-1.82039300	3.36182300	-0.34685200
C	-4.11134800	2.36041100	-0.56399100
C	-3.68963500	-1.19384800	0.04110400
C	1.65752800	3.92078400	0.48429400
C	2.64177600	1.63334400	0.86794900
C	3.61210600	-0.65819100	1.26497700
C	-2.73440800	-3.45345400	0.61117600
C	0.83107200	-2.95705800	0.95956300
C	3.11063800	-1.94318200	1.27235000
C	-4.63607600	1.09200100	-0.44421000
C	-1.47221200	-3.94428700	0.85892300
C	1.39175500	-4.29897100	1.36692800
C	2.52420300	-6.74551600	2.24285600
C	1.96106200	-5.20720800	0.42162200
C	1.38537600	-4.65495800	2.75779200
C	1.95295300	-5.87945500	3.19840500
C	2.53606900	-6.43046000	0.87008200
C	-5.07276000	-1.78547300	0.01779600
C	-7.66039800	-2.90824800	0.01099500
C	-5.42743600	-2.76800900	-0.94826000
C	-6.03251200	-1.38478600	0.97762400
C	-7.34293300	-1.93842600	0.99236700
C	-6.72076500	-3.34273700	-0.96797300
C	-2.40618400	4.73818500	-0.54879700
C	-3.50045900	7.33086500	-0.85254800
C	-2.36583500	5.39024900	-1.82279300
C	-2.99343500	5.41958600	0.56751300
C	-3.54789200	6.71816700	0.41677200
C	-2.91979900	6.69510500	-1.96820000
C	3.97433100	2.26002100	1.17772800
C	6.45037400	3.46802900	1.77670000
C	4.50165000	2.20095900	2.48882700

C	4.70841700	2.93323900	0.16301300
C	5.95334700	3.54501200	0.44322400
C	5.74817000	2.80618600	2.81320900
C	2.70245800	-5.43378300	-1.98196400
N	1.90278400	-4.88944900	-0.96992300
C	0.63869600	-3.82325800	5.05329600
N	0.79727500	-3.72691800	3.66462700
C	-3.43800100	5.18517500	3.07130700
N	-2.97703400	4.74575700	1.82406400
C	-1.48103500	5.21145700	-4.19300700
N	-1.75820200	4.70299300	-2.91370000
C	-0.74790100	4.25322900	-5.08564600
C	-0.83354200	4.46654700	-6.61692500
C	0.50517100	4.71168800	-5.92265400
C	-3.19975200	4.19760100	4.17901300
C	-3.19641000	4.71947500	5.63640300
C	-4.33783900	3.80552800	5.19442600
C	-0.06312900	-2.64041900	5.65769400
C	-0.71229100	-2.80628700	7.05264300
C	0.51108100	-1.90054900	6.92454600
C	2.28734300	-5.04808100	-3.37031700
C	3.32627300	-5.14643400	-4.51553300
C	2.15571300	-6.12857100	-4.51019500
C	0.28655500	-0.38486900	6.95320800
C	1.84073300	-2.35429000	7.52991300
C	1.01276400	-5.88527600	-5.50192000
C	2.42315600	-7.60424100	-4.20915200
C	1.60007500	3.65216500	-6.08881300
C	1.03060300	6.14310700	-5.79996300
C	-4.31433000	2.34976000	5.67274800
C	-5.74041600	4.39273300	5.02606500
H	-1.69927600	-2.35684500	7.20661400
H	-3.68284300	-3.98543700	0.64162800
H	-5.67425900	0.78012000	-0.53979200
H	4.63245000	-0.33141100	1.45580100
H	-4.62881800	3.29626700	-0.76956600
H	-1.17424200	-4.95795000	1.12335800
H	2.55757300	4.48541300	0.71921500
H	3.63324900	-2.87576800	1.47887000
H	0.10091900	5.43232500	-0.02349600
Co	-0.45608400	0.18359200	0.11615800
H	1.93620000	-6.11971700	4.26269200
H	2.98961700	-7.10325200	0.14168100
H	2.96581300	-7.69160300	2.57729300
H	-8.66400700	-3.34568200	0.00507200
H	-3.98814400	7.21251700	1.28411300

H -2.87434700 7.17852300 -2.94472500
H -3.92570900 8.33393400 -0.97545000
H 7.40917600 3.94363200 2.00780500
O 3.70558800 -6.19805900 -1.75615800
O 1.04819700 -4.81257900 5.74371800
O -4.00438800 6.31082300 3.25917700
O -1.80773900 6.38415700 -4.57575400
H -0.70310900 3.22189500 -4.72193500
H -2.49597000 3.38749500 3.94608800
H -3.41648300 5.78733500 5.73908100
H -0.58677200 -1.98824300 4.94632400
H -0.56571400 -3.79017500 7.51072400
H 1.54673700 -4.24410100 -3.42452200
H -2.42654300 4.32936000 6.31097400
H -1.49297100 3.71795100 -2.75547300
H 1.08038300 0.14388500 6.39077000
H 0.30589300 -0.01404500 7.99670500
H -0.68961300 -0.10590200 6.51316300
H 2.69288400 -1.85609000 7.02764700
H 1.97446600 -3.44509100 7.43831800
H 1.87465000 -2.08459700 8.60359400
H 4.30696800 -5.53827700 -4.22444300
H 3.33999500 -4.34110100 -5.25925000
H 1.23341500 -6.37704900 -6.46982900
H 0.85800600 -4.80711200 -5.69457900
H 0.06230200 -6.30263500 -5.11764900
H 2.73423000 -8.12502600 -5.13604700
H 1.50725300 -8.10041400 -3.83305500
H 3.21737900 -7.72432300 -3.45385000
H -0.95586200 3.57807500 -7.24687800
H -1.40638600 5.34689500 -6.92727900
H 1.17723400 2.63316900 -6.17120500
H 2.29570400 3.66475000 -5.22729900
H 2.19103900 3.85142400 -7.00469700
H 1.74413800 6.22955900 -4.95698900
H 0.20941500 6.85951600 -5.63238200
H 1.56545800 6.42744100 -6.72764600
H -3.28080100 1.97076300 5.78527900
H -4.84646800 1.69027600 4.96006500
H -4.81627300 2.26102400 6.65610300
H -6.26085800 4.40597200 6.00366400
H -6.34337600 3.77911600 4.32852300
H -5.70158900 5.42310200 4.63515200
H 1.22080600 -4.16831000 -1.27624300
H 0.43059600 -2.87438300 3.22975600
H -2.55386000 3.81257000 1.80608200

H -4.67310200 -3.07336600 -1.68006600
H -5.74049200 -0.64272900 1.73023000
H 4.28963300 2.96474600 -0.84719800
H 3.91935800 1.68848300 3.26400700
C 0.08565100 -0.03681400 -2.08308400
C 0.22014400 -1.46771200 -2.16513200
N 0.39487900 -2.64933100 -2.19839900
C -1.09900500 0.52254900 -2.83907900
O -1.24760600 1.75061700 -3.09716300
O -1.93138700 -0.48127800 -3.30454400
C -2.95141200 -0.24111800 -4.43835600
C -4.03326300 0.76273900 -3.99753100
H -4.80955200 0.82020000 -4.78437700
H -4.51184000 0.43116200 -3.06112500
H -3.61225100 1.76764300 -3.84092100
C -3.53052200 -1.65509900 -4.62984800
H -2.73038700 -2.37709100 -4.86837400
H -4.26489200 -1.64836400 -5.45636200
C -2.17477200 0.22838700 -5.68823500
H -1.36571300 -0.48316200 -5.93377500
H -1.74553900 1.23235400 -5.53881900
H -4.03873900 -1.98665700 -3.70819400
H -2.86791400 0.27472700 -6.54869300
C 1.29901100 0.80011500 -2.29207000
H 1.04656100 1.86492400 -2.36496900
C 6.27795300 2.72703200 4.26980400
C 5.25011800 3.40782600 5.22995900
C 6.44995800 1.22857000 4.67714500
C 7.64848600 3.43769600 4.44518200
H 5.11744800 4.47533300 4.97227800
H 4.25866800 2.92190900 5.17913200
H 5.60593000 3.34476900 6.27638700
H 7.18998000 0.72543600 4.02643300
H 6.80346600 1.15554700 5.72365500
H 5.49830600 0.67137700 4.60212400
H 7.97768200 3.34894000 5.49745400
H 8.43248400 2.98213500 3.81055400
H 7.58619200 4.51611600 4.20501900
C 6.77167900 4.30113400 -0.63766200
C 8.19122200 3.66220700 -0.76511800
C 6.09414700 4.25632900 -2.03523900
C 6.92087000 5.79825700 -0.21417100
H 8.74083200 3.68424900 0.19360700
H 8.11854800 2.60700300 -1.09186900
H 8.79226000 4.21290100 -1.51394300
H 5.09892700 4.73959000 -2.02389300

H 6.72006700 4.80094600 -2.76687300
H 5.97522300 3.21868600 -2.40113900
H 7.51425900 6.35118000 -0.96767100
H 5.93051100 6.28355400 -0.13015000
H 7.43142800 5.89870400 0.76119200
C -8.35629200 -1.47173200 2.07111700
C -7.78441400 -1.79399000 3.48912700
C -8.57738400 0.06939600 1.94127600
C -9.73651800 -2.17215000 1.93466000
H -7.63073500 -2.88234300 3.61362500
H -6.81423000 -1.29342700 3.66237300
H -8.48837300 -1.45072200 4.27157000
H -9.00246200 0.32444400 0.95220000
H -9.28031800 0.42135900 2.72065900
H -7.63257500 0.63078600 2.05996900
H -10.41773000 -1.80105600 2.72320600
H -10.21034900 -1.96017700 0.95729500
H -9.65445700 -3.26926500 2.05370700
C -7.14299000 -4.41795700 -2.00467200
C -5.99143400 -4.79169600 -2.97811000
C -7.58432900 -5.71644000 -1.25553900
C -8.34151600 -3.87838100 -2.84963100
H -5.65937300 -3.92135100 -3.57501700
H -5.11447500 -5.20074900 -2.44158100
H -6.34285100 -5.56648800 -3.68515000
H -8.42949600 -5.52734500 -0.56878800
H -7.90542400 -6.48569800 -1.98406100
H -6.74936900 -6.13099600 -0.65993600
H -8.66418300 -4.64053200 -3.58498400
H -9.21138200 -3.63091600 -2.21395200
H -8.05372200 -2.96364200 -3.40129500
C 2.62057200 0.46854500 -2.44239600
C 6.53824100 -0.62235800 -1.79034900
C 3.29245300 -0.89150500 -2.45576600
O 5.66321500 -0.11619700 -2.71650100
C 4.55558100 -0.90251200 -3.34318400
H 2.61167700 -1.67600400 -2.82927500
H 3.57720900 -1.19665400 -1.42752800
H 4.38291000 -0.36838700 -4.29157700
H 4.91296200 -1.92318700 -3.56075300
H 7.23530900 0.17377900 -1.50260300
H 3.30934400 1.31678900 -2.57531400
C 6.72830800 -1.92828800 -1.22810800
C 5.89002000 -3.09550100 -1.37507100
C 7.91838100 -2.06592600 -0.41343600
C 6.23995000 -4.31765300 -0.77245500

H	4.94977600	-3.05469300	-1.92795800
C	8.25442900	-3.28931900	0.18613100
H	8.57061900	-1.19388200	-0.27518000
C	7.42190100	-4.42757900	0.00661700
H	5.57472800	-5.17959400	-0.90636400
H	9.16363800	-3.36449600	0.79365400
H	7.68314900	-5.38271500	0.47531500

^{Z}Intermediate E^{Hb}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
G_corr: 1.756822 Hartree
H_corr: 2.058647 Hartree
SCF: -6361.985138 Hartree
S: 635.243 Cal/Mol-Kelvin
H: -6359.926491 Hartree
G: -6360.228316 Hartree

Cartesian Coordinates:

N	1.63980100	1.17201400	1.04240000
N	-0.47667800	-1.85522200	-0.40965300
N	-0.88208200	0.05823700	1.61122700
N	2.01861700	-0.71443800	-0.99593100
C	2.04666200	-1.72444400	-1.98665000
C	3.29597300	-0.11028100	-1.07901600
C	2.96479800	1.54022300	0.71167800
C	1.30401900	2.02379800	2.11960100
C	-0.91542800	1.07766800	2.59309800
C	-2.04105800	-0.71075700	1.86497000
C	-1.69667900	-2.37145800	0.08218300
C	-0.15873800	-2.69332100	-1.50188800
C	-1.18565100	-3.70430600	-1.69847800
C	1.02183200	-2.64652900	-2.26577600
C	3.32288400	-1.73612600	-2.68131100
C	3.76789900	0.95093300	-0.28266800
C	-2.13215900	-3.51017800	-0.71583200
C	-2.43360200	-1.87277100	1.17195500
C	-2.78126200	-0.16662300	2.99431600
C	3.44191100	2.59639200	1.59541200
C	0.09730000	2.02479800	2.84263000
C	-2.09782800	0.94940800	3.43101400
C	4.09448900	-0.74172200	-2.12063800
C	2.41272600	2.90182100	2.45679700
C	-0.04443000	2.93303800	4.04241400
C	-0.35538500	4.50003800	6.38274800
C	-0.57768100	4.26000800	3.95204700

C 0.35754900 2.42801700 5.32552500
C 0.20090000 3.20985900 6.49969100
C -0.74127100 5.03463000 5.13846600
C 5.18092400 1.43549100 -0.46245400
C 7.83813100 2.33361700 -0.75579300
C 5.44657200 2.77036300 -0.87655300
C 6.26614000 0.56719000 -0.19549700
C 7.61400700 1.00013200 -0.33633400
C 6.77312000 3.23960000 -1.02978800
C 1.24918300 -3.70383100 -3.31909300
C 1.68214200 -5.74556400 -5.23152700
C 0.73547500 -3.56422800 -4.64827200
C 1.97148400 -4.89233200 -2.96967400
C 2.19333400 -5.91605400 -3.92836500
C 0.95933200 -4.59537600 -5.60603400
C -3.64103700 -2.64164000 1.63722100
C -5.86355100 -4.12985100 2.52777700
C -3.46505400 -3.92735300 2.20157600
C -4.95326900 -2.10715800 1.52375500
C -6.08227300 -2.84083300 1.96168100
C -4.57193100 -4.69374400 2.66096700
C -1.56951800 6.00092300 2.39761000
N -0.91242300 4.78766300 2.67079600
C 1.38793600 0.38709300 6.46611700
N 0.91804000 1.11730100 5.36677700
C 3.11623600 -6.06029200 -1.00778800
N 2.43744000 -5.00251200 -1.62638900
C -0.70658900 -2.11575800 -6.15027700
N -0.00063800 -2.38660800 -4.96641800
C -1.46381400 -0.82070800 -6.12635800
C -1.84295900 -0.16717700 -7.47808800
C -2.96135000 -0.74079900 -6.60991400
C 3.41066300 -5.81400200 0.44525800
C 3.69221300 -7.03616500 1.35293400
C 4.84041200 -6.07458900 1.05280900
C 1.93090800 -0.96470900 6.09652100
C 2.87810800 -1.67294900 7.09414700
C 1.48900400 -2.26636700 6.86538900
C -1.67331600 6.32394100 0.93627000
C -2.78398600 7.30016300 0.47616900
C -1.33053600 7.76242000 0.39146000
C 1.38192800 -3.52921800 6.00388600
C 0.44440500 -2.17152000 7.97896400
C -0.66827200 7.78961700 -0.99057100
C -0.83641300 8.85120100 1.34547000
C -3.84256800 0.24593100 -5.83632100

C	-3.68947100	-2.00511800	-7.06971200
C	5.26787900	-5.10358700	2.15872000
C	5.97996000	-6.53546700	0.14205300
H	3.75493000	-2.18444500	6.68244400
H	4.44299300	3.02079700	1.56379100
H	5.10789800	-0.44531300	-2.38372700
H	-3.68874000	-0.60595700	3.40428500
H	3.57502800	-2.42278400	-3.48801900
H	2.39246900	3.63011700	3.26613300
H	-3.04925000	-4.06934100	-0.54052500
H	-2.33257400	1.61175200	4.26292500
H	-1.16096700	-4.45855200	-2.48350700
Co	0.48126900	-0.21005000	0.17402200
H	0.51114800	2.79487800	7.45987500
H	-1.17732500	6.03067800	5.05624100
H	-0.48656100	5.10802000	7.28563500
H	8.86845800	2.68558700	-0.87010100
H	2.74411700	-6.81042600	-3.63316200
H	0.55627000	-4.47307600	-6.61201200
H	1.84966000	-6.53270900	-5.97606900
H	-6.72908400	-4.70571700	2.87084600
O	-2.03962600	6.77249600	3.29936900
O	1.35959300	0.81570900	7.66535100
O	3.45552000	-7.13057800	-1.60957500
O	-0.72195500	-2.89550700	-7.16002400
H	-1.21631800	-0.15294500	-5.29507500
H	2.86578800	-4.97747800	0.90278300
H	3.69316100	-8.00014100	0.83323700
H	2.14022600	-1.11391500	5.02892600
H	3.04604700	-1.12834000	8.02932700
H	-1.40286100	5.50916800	0.25858300
H	3.24156900	-7.03884500	2.35138900
H	-0.01825800	-1.64049200	-4.25338300
H	0.39249900	-3.58735700	5.51024200
H	1.50152700	-4.43353000	6.63218800
H	2.16053700	-3.55764100	5.21802900
H	-0.58029900	-2.23617500	7.56376500
H	0.53333700	-1.22389900	8.53590800
H	0.57681500	-3.01087000	8.68935500
H	-3.39525300	7.71765600	1.28346300
H	-3.32326200	7.05476600	-0.44581100
H	-0.85718200	8.76175100	-1.48760500
H	-1.05781000	6.98947000	-1.64764900
H	0.42777500	7.65863200	-0.90514000
H	-1.07798800	9.85026700	0.93187900
H	0.26247100	8.79348100	1.47252900

H -1.30492300 8.75800100 2.33917800
H -1.73536000 0.92015500 -7.56357400
H -1.55049500 -0.74090900 -8.36395500
H -3.27746400 1.14345700 -5.52156800
H -4.26428100 -0.22734900 -4.92868700
H -4.68959700 0.57992100 -6.46756800
H -4.14655700 -2.53085500 -6.20851200
H -3.00289500 -2.70322000 -7.57656400
H -4.50250600 -1.73478700 -7.77203100
H 4.41397900 -4.80209000 2.79465200
H 5.71673600 -4.18721500 1.72895400
H 6.02590200 -5.57722500 2.81274500
H 6.73093300 -7.09296300 0.73524800
H 6.48932700 -5.66817700 -0.32157100
H 5.61182200 -7.19184500 -0.66389800
H -0.63750600 4.23896400 1.83532800
H 0.98788000 0.64817400 4.45875100
H 2.23468400 -4.19285300 -1.03203800
H 4.59798100 3.43238600 -1.07468900
H 6.04874600 -0.45290700 0.14303900
H -5.07361300 -1.11842800 1.07019300
H -2.44651000 -4.32447000 2.28718900
C -0.58357600 1.09186400 -1.23677700
C -0.50456800 2.36367300 -0.55648900
N -0.50085800 3.38956200 0.05196700
C 0.21036500 1.04818000 -2.53427000
O 0.04964900 0.16261900 -3.41866600
O 1.02801100 2.15294200 -2.66788500
C 1.62441000 2.57823400 -4.03003600
C 2.60834900 1.51149900 -4.54589800
H 3.09443200 1.88949000 -5.46549000
H 3.39252000 1.31072000 -3.79686900
H 2.09393000 0.56712600 -4.78136500
C 2.34428800 3.88473100 -3.64925100
H 1.63522500 4.61201500 -3.21759800
H 2.80947800 4.32909300 -4.54839700
C 0.45539800 2.83722900 -5.00521300
H -0.26870000 3.54644400 -4.56521100
H -0.06330100 1.90146800 -5.26866000
H 3.13412000 3.68227100 -2.90583900
H 0.85437300 3.28352000 -5.93504000
C -1.95088400 0.52753900 -1.44583700
H -1.94662200 -0.31879200 -2.14297000
C -4.32637200 -6.09649900 3.27710900
C -3.63627700 -7.01203700 2.21546300
C -3.39365500 -5.95732600 4.52284300

C -5.64241800 -6.78613700 3.73154100
H -4.28386400 -7.14469600 1.32838300
H -2.67371900 -6.59010700 1.87294900
H -3.43323100 -8.01070500 2.64750600
H -3.86175700 -5.32096100 5.29720600
H -3.19665800 -6.95318000 4.96417800
H -2.42001200 -5.50693100 4.25650100
H -5.40869500 -7.77754500 4.16259300
H -6.16713200 -6.19923200 4.50933800
H -6.33674400 -6.94655900 2.88486100
C -7.53303700 -2.30333400 1.83867100
C -8.19488000 -2.25487200 3.25314200
C -7.58799900 -0.87361300 1.23365700
C -8.35912500 -3.25473100 0.91441200
H -8.22566500 -3.25319700 3.72584100
H -7.63733700 -1.57813500 3.92775300
H -9.23596700 -1.88664700 3.17461300
H -7.16806800 -0.84458700 0.21004000
H -8.64111100 -0.54034200 1.17277400
H -7.04063100 -0.14685700 1.86527500
H -9.40274500 -2.89508300 0.82957300
H -7.92212200 -3.29546300 -0.10091900
H -8.38713200 -4.28536300 1.31247600
C 8.76919000 0.01219400 -0.02358300
C 8.66037600 -0.45446600 1.46366000
C 8.65566400 -1.22974400 -0.96466300
C 10.17094800 0.64996900 -0.22977900
H 8.75102600 0.40524800 2.15375300
H 7.69414100 -0.95114900 1.66748400
H 9.46821200 -1.17431000 1.69760600
H 8.75073100 -0.93025100 -2.02545600
H 9.45961300 -1.95589900 -0.73725500
H 7.68712800 -1.74871400 -0.84354100
H 10.95325600 -0.09609000 0.00449000
H 10.32430800 0.97698100 -1.27582700
H 10.32901000 1.51951500 0.43611900
C 7.10131800 4.68982900 -1.47479400
C 5.82513400 5.54267400 -1.71414700
C 7.95214400 5.39126500 -0.36743900
C 7.91922700 4.65087200 -2.80555400
H 5.19497500 5.12171300 -2.52033000
H 5.20895200 5.62921300 -0.79922200
H 6.11659900 6.56536800 -2.01858100
H 8.89726200 4.85227900 -0.17265500
H 8.20810600 6.42196400 -0.67986600
H 7.39124100 5.44762300 0.58435700

H	8.17199600	5.67930200	-3.12804900
H	8.86495500	4.09063400	-2.68870200
H	7.33635700	4.16768700	-3.61220100
C	-3.16510700	0.93613600	-0.96072600
C	-7.04425800	2.63247700	-0.98906500
C	-3.48929200	2.09645900	-0.03489800
O	-5.66593400	2.58177100	-1.02059300
H	-7.54810300	2.35155800	-0.05292200
C	-4.98204700	2.22199100	0.26149000
H	-3.14400900	3.05532100	-0.46555600
H	-2.96039200	1.99568100	0.93309200
H	-5.17848400	3.02729300	0.99453800
H	-5.41620100	1.26970300	0.62788900
H	-4.03241400	0.36060500	-1.31707900
C	-7.76511100	3.04476000	-2.14776000
C	-9.20476100	3.08791900	-2.10772500
C	-7.09820300	3.42257700	-3.36776300
C	-9.93820300	3.49149300	-3.23669400
H	-9.72701400	2.80404200	-1.18482000
C	-7.84763300	3.82346100	-4.48760600
H	-6.00441800	3.39182800	-3.40406300
C	-9.26804300	3.86211400	-4.43478600
H	-11.03304000	3.52125900	-3.19237900
H	-7.33128600	4.10964700	-5.41143100
H	-9.84382100	4.17638900	-5.31254200

TS5

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -50.0572 cm-1
G_corr: 1.758224 Hartree
H_corr: 2.057128 Hartree
SCF: -6361.983313 Hartree
S: 629.097 Cal/Mol-Kelvin
H: -6359.926185 Hartree
G: -6360.225089 Hartree

Cartesian Coordinates:

N	-1.91640400	-0.30654400	1.31850200
N	0.73394900	1.49363700	-1.00471700
N	0.66006200	0.75511400	1.69593200
N	-1.80241700	0.33290300	-1.39606900
C	-1.60215100	0.77512700	-2.72544500
C	-3.09392500	-0.24838500	-1.41606100
C	-3.22078200	-0.74164000	0.98381400
C	-1.84359400	-0.48904700	2.71941000

C 0.46241000 0.29842900 3.02070800
C 1.94484200 1.34320700 1.71809500
C 1.95674700 2.09698100 -0.62289300
C 0.58513500 1.83845900 -2.36721900
C 1.68540000 2.67602000 -2.81437700
C -0.49043500 1.48873900 -3.20341200
C -2.74438400 0.45018400 -3.56083200
C -3.78804300 -0.76061900 -0.30370500
C 2.52389200 2.84755500 -1.73483100
C 2.56253200 2.01997100 0.64658800
C 2.55318700 1.19660200 3.03312700
C -3.95514800 -1.13625200 2.17834600
C -0.72390900 -0.25566600 3.53687400
C 1.63486200 0.55612100 3.83849500
C -3.66097900 -0.19062800 -2.75543800
C -3.10369900 -0.98183500 3.24881800
C -0.84148300 -0.45865100 5.02920300
C -1.04096700 -0.68689800 7.84523600
C -0.55679600 -1.70986400 5.66876400
C -1.24870500 0.66101500 5.83112600
C -1.34772000 0.55012100 7.24245400
C -0.65305600 -1.80931200 7.08867600
C -5.18531800 -1.28886900 -0.47474400
C -7.81370000 -2.26878700 -0.75791100
C -5.48379500 -2.64508300 -0.16362400
C -6.22433700 -0.43736700 -0.92005200
C -7.55738200 -0.91161700 -1.06944600
C -6.79678300 -3.15531400 -0.29937900
C -0.50514300 1.99196600 -4.62583200
C -0.56590000 2.99840800 -7.26865500
C 0.08880300 1.24426400 -5.69180900
C -1.12493700 3.25232600 -4.91284700
C -1.15754100 3.75885300 -6.23914100
C 0.05351000 1.75703500 -7.02079400
C 3.87843100 2.70991800 0.87328400
C 6.33340800 4.03432700 1.29398000
C 3.98280500 3.74088300 1.83790100
C 5.02875500 2.35283700 0.11449700
C 6.26920300 3.00411300 0.31194600
C 5.21054400 4.42279200 2.06435400
C 0.21469700 -4.10188300 5.31870200
N -0.19384000 -2.83151100 4.86952900
C -2.00675300 3.09629800 5.67384600
N -1.55460500 1.87760800 5.15105000
C -2.32035100 5.21907900 -3.80599400
N -1.69277700 3.96562900 -3.81690200

C	1.38932600	-0.85923500	-6.25781300
N	0.70904100	-0.00068800	-5.37820600
C	1.99549000	-2.06087600	-5.59554300
C	2.27593300	-3.30962700	-6.46897300
C	3.46535800	-2.51953700	-5.92791500
C	-2.76852900	5.65219000	-2.43912700
C	-3.02166700	7.15968900	-2.19469500
C	-4.21955600	6.21237600	-2.18601500
C	-2.25959200	4.14060000	4.62268600
C	-3.20267800	5.31733400	4.97258400
C	-1.71725700	5.61162800	4.77241400
C	0.48577700	-5.08026900	4.21549300
C	1.42413500	-6.27624000	4.51180500
C	-0.05824700	-6.55805000	4.27680400
C	-1.29231000	6.28796200	3.46451000
C	-0.86206700	5.98641800	5.98426500
C	-0.46690600	-7.15351400	2.92490800
C	-0.92764200	-7.01044700	5.45121900
C	4.24044800	-3.11966500	-4.75031600
C	4.32794200	-1.70737500	-6.89541700
C	-4.83354800	5.84724600	-0.83018100
C	-5.22318600	6.26918700	-3.33919200
H	-3.92088200	5.63413000	4.20855900
H	-4.99245800	-1.46378900	2.18267200
H	-4.63658000	-0.58769600	-3.02832700
H	3.55045900	1.54497100	3.29412900
H	-2.81566300	0.68776400	-4.62110800
H	-3.29199800	-1.16718600	4.30517400
H	3.43259900	3.44262100	-1.67682600
H	1.72068500	0.28015500	4.88837600
H	1.77197400	3.08858400	-3.81838300
Co	-0.48600700	0.38844100	0.10409300
H	-1.65937000	1.41900100	7.82398800
H	-0.41242900	-2.76220100	7.56130400
H	-1.11032000	-0.78026800	8.93541000
H	-8.83323400	-2.65222300	-0.86701100
H	-1.63389400	4.72188600	-6.42894800
H	0.50951600	1.17369100	-7.82134000
H	-0.58805100	3.38402100	-8.29466700
H	7.28717600	4.54695700	1.45494700
O	0.34945900	-4.40844600	6.55009600
O	-2.19064900	3.30921500	6.91610800
O	-2.49830600	5.92760700	-4.84914700
O	1.49573300	-0.64731000	-7.51108100
H	1.68226700	-2.23037200	-4.56027800
H	-2.34619500	5.08271700	-1.60053300

H -2.88677700 7.79414200 -3.07705700
H -2.29843000 3.77118200 3.58920100
H -3.58080600 5.30886400 6.00031500
H 0.52047700 -4.65258100 3.20976600
H -2.66631200 7.58476500 -1.24976900
H 0.64198000 -0.32063700 -4.40019400
H -0.24878500 6.02547600 3.20319400
H -1.34902100 7.38937700 3.56610700
H -1.94194700 5.99243500 2.61880800
H 0.20643700 5.76267300 5.79735500
H -1.17788100 5.43626500 6.88620800
H -0.95162000 7.07206500 6.18422300
H 1.78779500 -6.33360800 5.54329100
H 2.15148000 -6.54699800 3.73834000
H -0.40775300 -8.25947300 2.95938200
H 0.19063200 -6.80254900 2.10769700
H -1.50833300 -6.87628200 2.67047600
H -0.83887900 -8.10693600 5.58326400
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H 3.57921700 -3.69453100 -4.07432300
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H -4.67174800 -3.28868500 0.18885700
H -5.98781500 0.61210800 -1.13207300
H 4.93544900 1.55825700 -0.63166500
H 3.08613200 4.02152200 2.40282400
C 0.52434000 -1.43179400 -0.30959200
C 0.17078500 -2.23172200 0.84807100
N 0.00171500 -2.83595800 1.86104300
C -0.02488800 -1.97091900 -1.63265200
O 0.40880500 -1.60296600 -2.75760000

O -0.94017200 -2.97936100 -1.42326200
C -1.32165000 -3.99867900 -2.52801300
C -2.00146500 -3.29172700 -3.71542800
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H -2.86315300 -2.69552900 -3.37231700
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C -2.30112100 -4.91322500 -1.77079600
H -1.82294900 -5.33969500 -0.87225700
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C -0.03357900 -4.74803600 -2.93087400
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H -3.19438000 -4.34451200 -1.46019700
H -0.29456900 -5.56688500 -3.62656500
C 2.00779300 -1.22122300 -0.43481400
H 2.32708700 -0.86337900 -1.42152400
C 5.27064800 5.55279100 3.12613700
C 4.26578200 6.68307100 2.73310200
C 4.87538200 4.97224000 4.52175000
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H 4.52967400 7.12178600 1.75254300
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H 4.28464100 7.48974300 3.49081900
H 5.58396100 4.18256600 4.83539200
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H 7.44406200 5.43652500 3.55126200
H 7.01237900 6.64626300 2.29590000
C 7.54101800 2.64021000 -0.49950900
C 8.66537700 2.17202900 0.47914000
C 7.28638700 1.50208800 -1.52605900
C 8.03222700 3.89997800 -1.28305000
H 8.92208300 2.95681900 1.21396900
H 8.35109600 1.27183700 1.04019900
H 9.58384800 1.92390900 -0.08650300
H 6.51831800 1.78324700 -2.27143100
H 8.22105400 1.28465900 -2.07574000
H 6.96713300 0.56551900 -1.03027600
H 8.94896300 3.65901900 -1.85466700
H 7.26114500 4.24693200 -1.99633600
H 8.26807700 4.73930600 -0.60362200
C -8.66431300 0.06286200 -1.55262500
C -8.78407200 1.24897700 -0.54244500
C -8.28298700 0.62070000 -2.96133300
C -10.05451900 -0.62228800 -1.66257100

H -9.06624700 0.88349900 0.46272100
H -7.83237300 1.80297100 -0.44627100
H -9.55897800 1.96258400 -0.88254700
H -8.20961500 -0.19732200 -3.70263700
H -9.05331600 1.33486500 -3.31027800
H -7.31380300 1.15228300 -2.94356600
H -10.80154400 0.11437500 -2.01279100
H -10.04516500 -1.45835900 -2.38751300
H -10.40065100 -1.00937000 -0.68541000
C -7.16034700 -4.62677300 0.03441900
C -5.94005900 -5.43991800 0.54755800
C -8.25938900 -4.65016300 1.14511600
C -7.71054100 -5.32701200 -1.24953500
H -5.13710400 -5.50061000 -0.21131500
H -5.51372000 -5.00526200 1.47137600
H -6.25717700 -6.47374500 0.78002800
H -9.17455400 -4.11666200 0.82951900
H -8.54049700 -5.69474600 1.37979700
H -7.89196300 -4.17433700 2.07368600
H -7.98870800 -6.37430700 -1.02322400
H -8.60831200 -4.81515300 -1.64198900
H -6.94774600 -5.33626800 -2.05080200
C 2.92391700 -1.50659400 0.53482100
C 5.58542800 -4.01730000 -0.97876100
O 4.95172000 -3.83288000 0.25845300
H 2.57819000 -1.87004500 1.51523600
C 5.21007700 -2.55092600 0.97894900
H 4.99829400 -3.75307100 -1.86963900
C 4.42133600 -1.36024000 0.38875300
H 4.89092900 -2.75890600 2.01536500
H 6.29845100 -2.34051900 0.96356200
H 4.75685000 -0.45883000 0.94933700
H 4.70706800 -1.20237900 -0.66957400
C 6.88226300 -4.61157700 -1.07294700
C 7.50095400 -4.78774500 -2.36421400
C 7.60787800 -5.05129500 0.09305500
C 8.77959400 -5.36044200 -2.47595800
H 6.96008400 -4.46548200 -3.26335600
C 8.88647300 -5.62263700 -0.03508800
H 7.13092200 -4.95805300 1.07515000
C 9.48607200 -5.77959600 -1.31468000
H 9.23542900 -5.48614800 -3.46538200
H 9.42354800 -5.95850500 0.86018800
H 10.48227700 -6.22705000 -1.40671700

^{E}TS6^{Ha}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -18.872 cm-1
G_corr: 1.762004 Hartree
H_corr: 2.057901 Hartree
SCF: -6361.987531 Hartree
S: 622.769 Cal/Mol-Kelvin
H: -6359.92963 Hartree
G: -6360.225527 Hartree

Cartesian Coordinates:

N	1.36723800	1.51130000	0.32489700
N	-0.69577200	-1.88550700	0.38465900
N	-1.30552900	0.82583800	0.81770800
N	1.98773800	-1.19378200	-0.09762000
C	2.12693100	-2.59001300	-0.27582800
C	3.31628300	-0.70627700	-0.10622900
C	2.76475500	1.67226600	0.18005500
C	0.88676100	2.82548900	0.52733000
C	-1.46192800	2.22724800	0.93582800
C	-2.57008200	0.30084300	1.16545800
C	-2.02818200	-2.07634000	0.81812500
C	-0.23050100	-3.18644800	0.09224400
C	-1.26941700	-4.17533100	0.33523900
C	1.08945200	-3.54071600	-0.24782500
C	3.52829000	-2.96205600	-0.38563000
C	3.70915500	0.64013300	0.02337600
C	-2.36888100	-3.49343000	0.81046700
C	-2.92122400	-1.06368900	1.22186300
C	-3.50816700	1.37651700	1.45990700
C	3.13054100	3.08138800	0.25025600
C	-0.44381100	3.19215500	0.80214600
C	-2.82561900	2.56503700	1.31153400
C	4.26287200	-1.80359700	-0.25256100
C	1.97083400	3.79228300	0.46821100
C	-0.76024200	4.62531600	1.16669700
C	-1.43548800	7.24841200	2.00653600
C	-1.14410900	5.61302300	0.20282400
C	-0.68976000	4.99729400	2.55251700
C	-1.02816900	6.30919800	2.97581000
C	-1.49651400	6.92477300	0.63744100
C	5.17419500	0.98363300	0.06057200
C	7.91797600	1.62660100	0.19454500
C	6.01987300	0.76197800	-1.06106500
C	5.72867800	1.52984700	1.24311900
C	7.10952000	1.85908300	1.33324300

C 7.39835600 1.08056400 -1.01438700
C 1.43347200 -5.00328500 -0.40157800
C 2.08688000 -7.75105600 -0.60549300
C 1.30900800 -5.68054000 -1.65668400
C 1.88082400 -5.73742400 0.74680200
C 2.21156500 -7.11469900 0.64647300
C 1.64283300 -7.06290300 -1.75201700
C -4.26954600 -1.44295400 1.77244200
C -6.76790600 -2.16335100 2.87149900
C -4.58059800 -1.13377300 3.11856700
C -5.23608400 -2.12230400 0.98075500
C -6.49541900 -2.48899300 1.51174400
C -5.83174100 -1.49080700 3.69354300
C -1.57000300 6.05883000 -2.25454200
N -1.12886000 5.27139800 -1.18072400
C -0.06261000 4.09659800 4.85931000
N -0.26438500 3.99827500 3.47699500
C 2.35223800 -5.49525800 3.24545200
N 1.96884400 -5.02951800 1.98101000
C 0.56536900 -5.43049600 -4.06844400
N 0.83655600 -4.94114500 -2.78059900
C -0.02125800 -4.41186700 -5.00198200
C 0.13604300 -4.63901100 -6.52609600
C -1.25818800 -4.75878800 -5.91354300
C 2.30022000 -4.43822700 4.31220700
C 2.24485800 -4.88942200 5.79128500
C 3.51121700 -4.19707900 5.29037500
C 0.44142100 2.82438500 5.48143500
C 1.17595200 2.91607700 6.84141000
C -0.19301500 2.23979200 6.79860800
C -1.22857900 5.49555100 -3.60477400
C -2.00765600 6.00556300 -4.84257700
C -0.53736800 6.39461500 -4.69987300
C -0.23651300 0.71000800 6.87944400
C -1.39122000 2.94089500 7.44127000
C 0.48455400 5.67011200 -5.58293300
C -0.17906200 7.84873000 -4.38820900
C -2.24074300 -3.60637400 -6.14704600
C -1.91964700 -6.13545800 -5.82669000
C 3.74055100 -2.73803100 5.69923300
C 4.79325500 -5.01543300 5.12601000
H 2.07375500 2.30252700 6.97372800
H 4.14452500 3.45994500 0.13750600
H 5.34490400 -1.68910600 -0.23967900
H -4.55179900 1.22689000 1.72976200
H 3.88362200 -3.98356500 -0.51244200

H	1.83976300	4.86732300	0.58307100
H	-3.31921400	-3.90233400	1.14688800
H	-3.19014000	3.58226200	1.44572300
H	-1.13977900	-5.24775200	0.19709000
Co	0.29423900	-0.17030400	0.17061000
H	-0.96534200	6.55816300	4.03625700
H	-1.81755300	7.65452100	-0.10658700
H	-1.70686300	8.26145400	2.32619900
H	8.98315200	1.87487700	0.24262800
H	2.54900800	-7.64625000	1.53760000
H	1.54383100	-7.56088200	-2.71708300
H	2.34173800	-8.81402900	-0.69025300
H	-7.73688800	-2.44613600	3.29540100
O	-2.19471500	7.16592300	-2.12101300
O	-0.27819900	5.15618000	5.53326700
O	2.71507800	-6.69420700	3.47711700
O	0.78255300	-6.63501400	-4.42993900
H	0.01056000	-3.37861100	-4.64243000
H	1.73572100	-3.53279600	4.05286300
H	2.28796700	-5.97358100	5.94002100
H	0.80709900	2.06635000	4.77608700
H	1.22694500	3.92448400	7.26548900
H	-0.89555600	4.45319200	-3.60295500
H	1.56580500	-4.34847500	6.45928000
H	0.68660500	-3.92901600	-2.64338600
H	-1.13824700	0.31226800	6.37471400
H	-0.26794500	0.38248700	7.93702400
H	0.65189200	0.24812700	6.40835300
H	-2.34091700	2.58703700	6.99456300
H	-1.33483400	4.03454600	7.31217400
H	-1.42047500	2.71444100	8.52505400
H	-2.75135500	6.78272800	-4.63533100
H	-2.29274300	5.27248000	-5.60626700
H	0.59006100	6.19177600	-6.55466200
H	0.18303000	4.62568900	-5.78786000
H	1.47954100	5.64949500	-5.09824100
H	-0.14367500	8.43541700	-5.32723600
H	0.81776000	7.91393000	-3.90995100
H	-0.91827900	8.31028600	-3.71273500
H	0.37596300	-3.76818500	-7.14670800
H	0.64277200	-5.56948500	-6.80317000
H	-1.72848400	-2.62681800	-6.18940000
H	-2.99572500	-3.56798300	-5.33639000
H	-2.78144300	-3.74908000	-7.10334700
H	-2.68537700	-6.15529000	-5.02622800
H	-1.17898900	-6.92393900	-5.61467600

H -2.42411100 -6.37006800 -6.78476900
H 2.78660600 -2.18911100 5.81476600
H 4.35380700 -2.20787800 4.94508800
H 4.27732000 -2.69108200 6.66696800
H 5.32704000 -5.07363500 6.09471000
H 5.47252900 -4.53969400 4.39201500
H 4.57624100 -6.04092700 4.78345400
H -0.74871300 4.34189100 -1.44531900
H -0.05998700 3.08495300 3.06004200
H 1.71535400 -4.03814800 1.92856000
H 5.58095400 0.34738200 -1.97352200
H 5.06856300 1.68633500 2.10461800
H -4.98939800 -2.35352300 -0.05932400
H -3.82389500 -0.62006400 3.72328100
C -0.32459600 0.02591700 -1.99416600
C -0.29483200 1.45648900 -2.14965100
N -0.39622600 2.63822300 -2.27313500
C 0.73717300 -0.71944400 -2.76577000
O 0.67302100 -1.95482700 -3.02278100
O 1.71362500 0.13642600 -3.23784400
C 2.69666100 -0.26599900 -4.35587600
C 3.57943700 -1.44595000 -3.90536900
H 4.37389800 -1.60679100 -4.65868200
H 4.05708500 -1.23001100 -2.93488400
H 2.99435500 -2.37294200 -3.80478900
C 3.50651000 1.03338200 -4.52533400
H 2.84479200 1.87022400 -4.80840500
H 4.26833300 0.89834600 -5.31511000
C 1.87291500 -0.59118100 -5.62122600
H 1.20001400 0.24775100 -5.87425500
H 1.27724000 -1.50865300 -5.48556800
H 4.01285300 1.30016200 -3.58155800
H 2.56223100 -0.75056000 -6.47121200
C -1.67159400 -0.57192300 -2.16048600
H -1.65783300 -1.64763200 -2.38393700
C -6.11703900 -1.13966600 5.17787400
C -5.05326700 -1.83641100 6.08586800
C -6.02575500 0.40826700 5.36908200
C -7.52629000 -1.60326500 5.63962900
H -5.10300200 -2.93622100 5.97846700
H -4.02597300 -1.51786100 5.83090100
H -5.23358000 -1.58242600 7.14812500
H -6.78570100 0.92669300 4.75447600
H -6.20000100 0.67274500 6.42973700
H -5.03281000 0.79957200 5.08148200
H -7.67588000 -1.32665900 6.70006800

H -8.33095300 -1.12084700 5.05262600
H -7.64455500 -2.70076400 5.56119600
C -7.57208400 -3.22861800 0.67348400
C -8.87352200 -2.36569500 0.62135700
C -7.11025900 -3.49600800 -0.78575700
C -7.89312300 -4.60467500 1.34081600
H -9.27845900 -2.17506300 1.63189500
H -8.67798500 -1.38638200 0.14500000
H -9.65509000 -2.88788700 0.03642000
H -6.20687200 -4.13409000 -0.82148300
H -7.91224500 -4.02191500 -1.33686200
H -6.89584500 -2.55299300 -1.32476700
H -8.67313400 -5.13689700 0.76296700
H -6.99203000 -5.24518000 1.37803700
H -8.26309500 -4.48073700 2.37489000
C 7.66805700 2.45301400 2.65364300
C 6.92993400 3.79381300 2.96801900
C 7.42243100 1.44320300 3.82030500
C 9.19241700 2.74416500 2.57776200
H 7.10205500 4.53576000 2.16559600
H 5.83875600 3.64790600 3.06727500
H 7.30213400 4.22060300 3.91917400
H 7.94332300 0.48609900 3.62945400
H 7.80198300 1.86147800 4.77240300
H 6.34702300 1.22413300 3.95189600
H 9.53574300 3.16358300 3.54197500
H 9.77779700 1.82480200 2.38590600
H 9.43130700 3.48280100 1.78908400
C 8.34948300 0.85986500 -2.22081300
C 7.62034100 0.25030200 -3.44962000
C 8.96649700 2.22958400 -2.65080200
C 9.49782200 -0.11491500 -1.80502300
H 7.18143600 -0.73880600 -3.21811600
H 6.81440200 0.91282400 -3.81798500
H 8.34302900 0.11072300 -4.27537300
H 9.53494900 2.69881800 -1.82710800
H 9.65945800 2.08561400 -3.50213300
H 8.17542700 2.93713900 -2.96280600
H 10.19375900 -0.26728700 -2.65239300
H 10.08251900 0.27928700 -0.95388000
H 9.09118900 -1.10041700 -1.50964000
C -2.86025100 0.10947700 -2.10836500
C -4.00342400 1.79000000 -4.28725900
O -4.05065300 0.50343200 -4.76803600
H -2.86687100 1.17037700 -1.82586000
C -4.51379300 -0.65496400 -3.94412800

H -3.11229300 2.31670600 -4.65017500
C -4.20234200 -0.52044800 -2.42163100
H -5.59514600 -0.81783300 -4.11564000
H -3.95069100 -1.49107800 -4.39132200
H -5.00243400 0.05470100 -1.92569000
H -4.24612800 -1.55578100 -2.02827200
C -5.01777000 2.50815200 -3.56880200
C -4.69295200 3.83748500 -3.11632800
C -6.34348900 2.00785800 -3.31308200
C -5.63673400 4.61343400 -2.42208700
H -3.69449000 4.24438100 -3.31477200
C -7.28195400 2.79900500 -2.62646100
H -6.64121400 1.02416300 -3.69117100
C -6.93664600 4.09934800 -2.16845700
H -5.36207100 5.61741700 -2.08108400
H -8.29243700 2.41159500 -2.45139600
H -7.67301500 4.70640300 -1.63002300

^{E}TS6^{Hb}

Temperature: 298.15 Kelvin
Pressure: 1.0 Atm
Imaginary Frequency: -76.3048 cm-1
G_corr: 1.761856 Hartree
H_corr: 2.057849 Hartree
SCF: -6361.996781 Hartree
S: 622.97 Cal/Mol-Kelvin
H: -6359.938932 Hartree
G: -6360.234925 Hartree

Cartesian Coordinates:
N -1.58622400 0.35689800 -1.30245500
N 1.32950300 -1.25821200 0.85859600
N 1.18365700 0.02420200 -1.63616900
N -1.45835100 -1.03441400 1.12491000
C -1.21292700 -1.73687100 2.32656000
C -2.86706900 -1.04861700 0.99131400
C -2.97610900 0.31470900 -1.04968000
C -1.47767100 1.06315100 -2.52204900
C 0.92554200 0.67107500 -2.86672500
C 2.53646100 -0.38376100 -1.72789100
C 2.69416100 -1.37417200 0.52263300
C 1.24151700 -1.76730700 2.17420000
C 2.55554800 -2.14003500 2.67164100
C 0.04981800 -2.02379900 2.87938800
C -2.45680600 -2.20658600 2.91558900
C -3.60999100 -0.40812200 -0.02021500

C 3.45281200 -1.90229300 1.64991100
C 3.27590000 -1.03819200 -0.72051500
C 3.08867600 -0.02271600 -3.02779700
C -3.70618700 1.06501300 -2.06396900
C -0.30730800 1.20955800 -3.28946500
C 2.10446700 0.65013700 -3.71808100
C -3.47496500 -1.80699500 2.07634400
C -2.77989400 1.52582000 -2.97418300
C -0.41469700 1.75261500 -4.69647600
C -0.57046700 2.62807400 -7.38832300
C -0.34046300 3.14992500 -5.00332500
C -0.59888400 0.81344300 -5.76805500
C -0.67606100 1.24890800 -7.11666700
C -0.40720800 3.57841200 -6.36221700
C -5.10770900 -0.55449500 -0.05342100
C -7.90793500 -0.88813800 -0.16698200
C -5.93442600 -0.05714900 0.99160000
C -5.71084600 -1.21813800 -1.14955100
C -7.11930200 -1.40007700 -1.22553400
C -7.34085900 -0.21209000 0.95138400
C 0.12152400 -2.80115700 4.17204800
C 0.25077200 -4.34464700 6.54219300
C 0.24916800 -2.15587300 5.44297200
C 0.06813300 -4.23387900 4.11779100
C 0.13226100 -5.01009100 5.30492100
C 0.30993200 -2.93976700 6.63198200
C 4.70580000 -1.42162600 -0.97999400
C 7.37616800 -2.19465200 -1.47999300
C 5.09684800 -2.77910600 -0.87291900
C 5.68177200 -0.45291300 -1.34961200
C 7.02431000 -0.81948800 -1.60264800
C 6.43539800 -3.19033800 -1.12174600
C -0.14907800 5.48388000 -4.03556500
N -0.22975900 4.08538700 -3.93387600
C -0.89201500 -1.67903900 -6.24919100
N -0.70395300 -0.56586600 -5.42045200
C -0.10017400 -6.19118400 2.48522300
N -0.05223100 -4.83438000 2.83051100
C 0.54183300 0.08062700 6.60048800
N 0.33262100 -0.73225400 5.47483200
C 0.70802200 1.53862700 6.28607500
C 0.43502500 2.56590700 7.41167400
C 1.87413300 2.37681700 6.93442500
C -0.22675000 -6.42627700 1.00639200
C 0.15350300 -7.81797700 0.44732000
C -1.31627900 -7.40197900 0.42068600

C	-0.95594800	-2.97863100	-5.49632800
C	-1.59535900	-4.20229200	-6.19450000
C	-0.09064400	-4.22124400	-5.92973500
C	-0.22041300	6.19794000	-2.71689800
C	0.34700700	7.63485800	-2.62312900
C	-1.16595600	7.44372500	-2.52497700
C	0.42425800	-5.09211700	-4.77873600
C	0.87562000	-4.09849400	-7.10943500
C	-1.81576800	7.56149700	-1.14215300
C	-2.05671300	7.92318900	-3.67250800
C	2.47662000	3.46060000	6.03488400
C	2.88559300	1.70300500	7.86360600
C	-1.91788100	-6.97794000	-0.92344100
C	-2.30322200	-8.09123900	1.36475700
H	-2.25353100	-4.84054500	-5.59489700
H	-4.78502300	1.20822600	-2.06556200
H	-4.54107300	-2.00493400	2.16755600
H	4.09192500	-0.27193000	-3.36550000
H	-2.51968300	-2.78808400	3.83422900
H	-2.94265300	2.11082000	-3.87811700
H	4.52928300	-2.06273800	1.64841400
H	2.14372400	1.07259100	-4.72087500
H	2.74389700	-2.54658500	3.66438800
Co	-0.10190500	-0.32014000	-0.15176100
H	-0.81463200	0.50934300	-7.90680900
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H	-8.99450000	-1.01609000	-0.20737500
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H	0.29845000	-4.93736000	7.46330800
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O	-0.04236000	6.11483800	-5.13998800
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CHAPTER 4

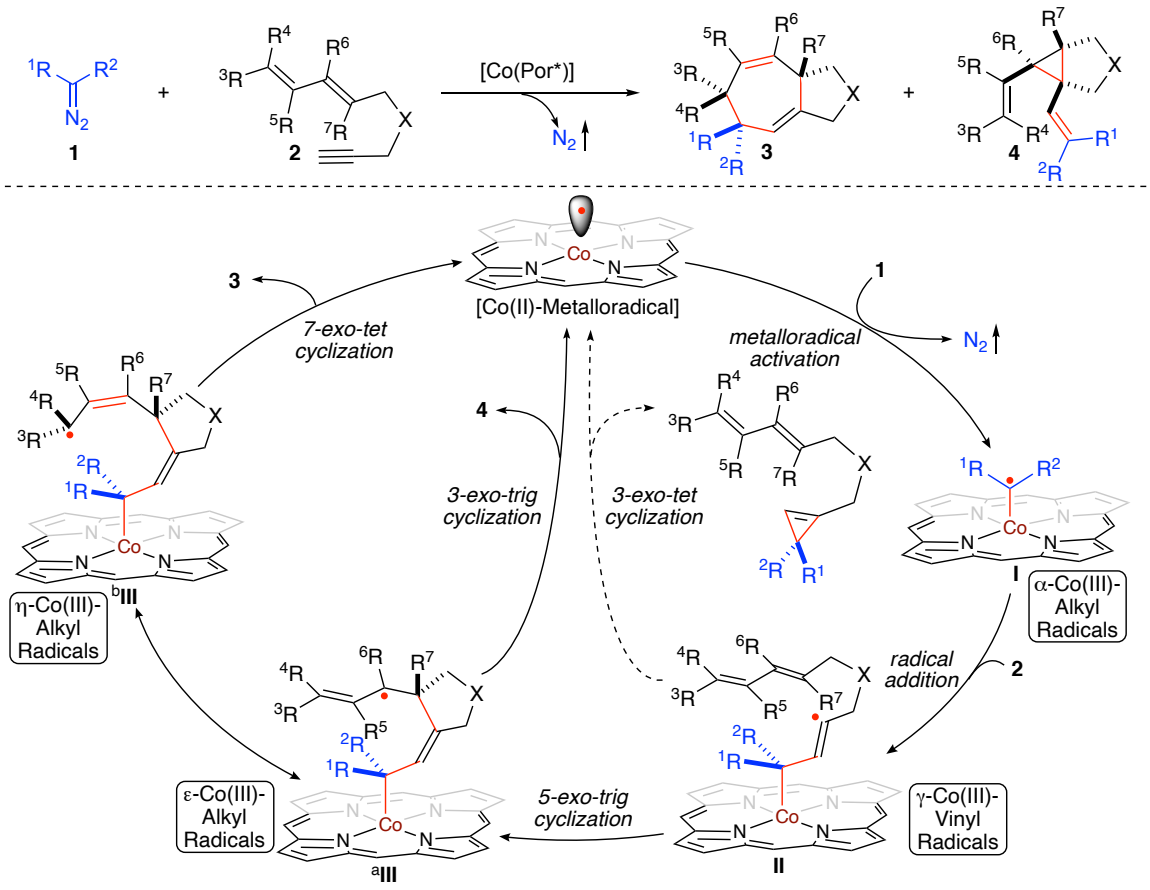
RADICAL CASCADE CYCLIZATION OF 1,6,8-DIENYNES WITH DIAZO COMPOUNDS VIA CO(II)-BASED METALLORADICAL CATALYSIS: STEREOSELECTIVE CONSTRUCTION OF BICYCLO[5.3.0]DECANE DERIVATIVES

4.1. INTRODUCTION

Radical cascade reactions have attracted much attention from organic chemists in the last decades.[1] These processes are quite appealing, not only for their high reactivity and tolerance of functional groups but also for their high efficiency in constructing complex molecules. However, control of stereoselectivity is still challenging for reactions involving free organic radicals. Over the past several decades, metalloradical catalysis (MRC) represents as a fundamentally novel approach by utilizing metal-supported organic radicals as key catalytic intermediates to control reactivity and selectivity.[1g, 2,3,4] As stable 15e-metalloradicals, Co(II) complexed of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have been demonstrated to homolytically activate diazo compounds for the generation of α-Co(III)-alkyl radicals as kinetically competent intermediates in various catalytic radical cyclization reactions.[5] Specifically, asymmetric radical cascade bicyclization of 1,6-enynes with diazo compounds, which involves the catalytic generation of γ-Co(III)-vinyl radicals,[6] have been successfully developed to construct multi-substituted cyclopropane-fused tetrahydrofurans.[6a] To further explore the possibilities of the Co-bonded vinyl radical intermediates for building complex molecules, we were interested to employ substrates containing multiple unsaturated bonds in the Co(III)-based metalloradical catalyzed radical cascade process (Scheme 4.1).

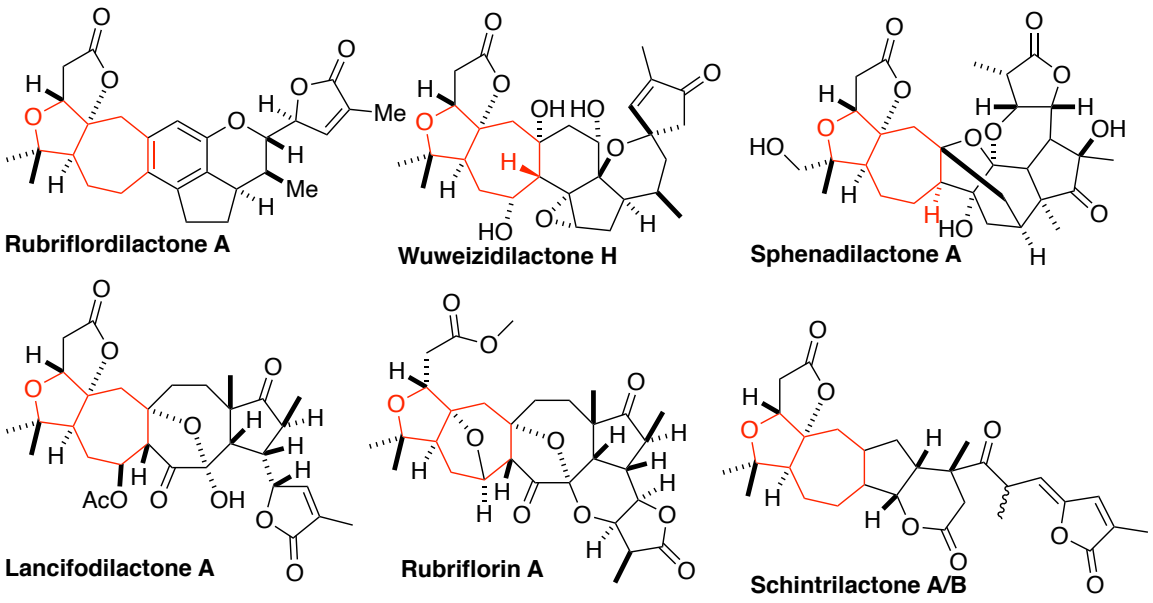
Specifically, we were interested in developing radical cascade bicyclization of 1,6,8-dienynes **2** with diazo compounds **1** for stereoselective construction of multi-substituted [5.3.0]decane structures. To avoid producing the undesired cyclopropenation product, the vinyl radical intermediate **II** would be required to undergo competitive *5-exo-trig* radical cyclization to form ε-Co(III)-alkyl radicals **^{a}III** over the previously demonstrated *3-exo-tet* radical cyclization. Furthermore, intermediate **III** might also face two competitive radical processes, which are *3-exo-trig* radical cyclization of intermediate **^{a}III** and *7-exo-tet* radical cyclization of intermediate **^{b}III**. Along with the breaking and forming multiple bonds, the proposed radical cascade transformation would create three stereogenic

Scheme 4.1. Working Proposal for Construction of Multi-Substituted [5.3.0]decane Derivatives by Radical Cascade Bicyclization via Co(II)-Based MRC



centers and two alkenes in the resulting multi-substituted [5.3.0]decane structures. Apart from the aforementioned reactivity issues, how to control diastereoselectivities in this radical cascade cyclization is an equally important question. We hoped to address these issues by designing and modifying the ligand structures as well as other reaction conditions to control the reactivity and selectivity of the desired catalytic process. If achieved, it would lead to the development of a new catalytic process for radical cascade cyclization to construct bicyclo[5.3.0]decane structures, which have found wide-ranging applications (Figure 4.1).[7]

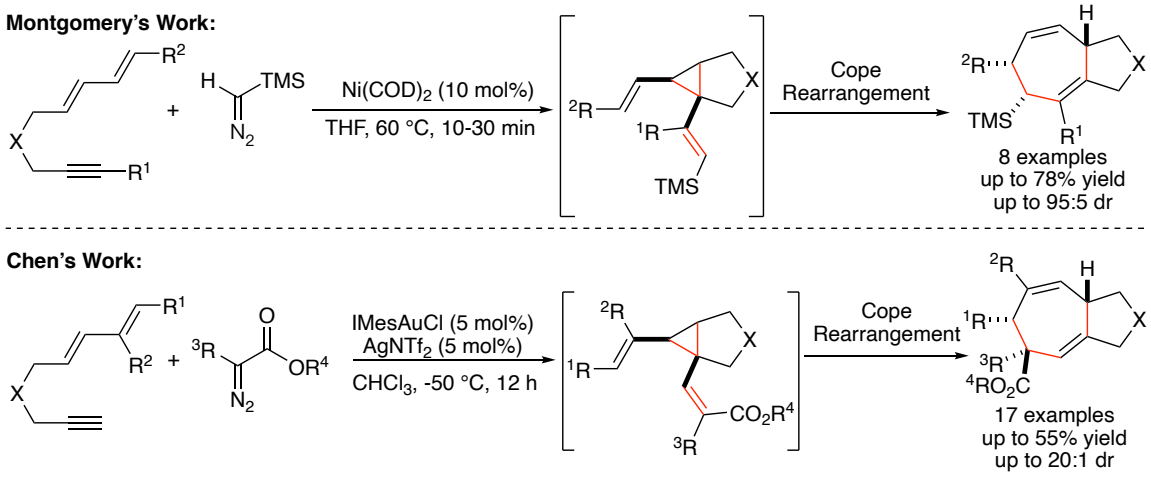
Figure 4.1. Selected Natural Products and Bioactive Compounds Containing Bicyclo[5.3.0]decane Frameworks



Catalytic bicyclization of 1,6,8-dienynes with diazo compounds represents an attractive method to construct multi-substituted [5.3.0]decane structures with potential control of stereoselectivities (Scheme 4.2). Among advances in the realm, Montgomery and Ni reported the first Ni-catalyzed [4+2+1] cycloadditions of (trimethylsilyl)-diazomethane with dienynes to construct the multi-substituted [5.3.0]decane structures.[8]

Very recently, Chen and coworkers described the Au-catalyzed [4+2+1] cycloaddition reactions to establish the bicyclo[5.3.0]decane structures by utilizing 1,6,8-dienyne and phenyl diazoacetate.[9] However, there has been no previous report on the synthesis of bicyclo[5.3.0]decane structures using acceptor/acceptor type diazo compounds presumably due to the less reactivity toward formation of metallocarbene intermediates.[10] We herein demonstrated the first Co(II)-based metalloradical system that is highly effective for radical cascade bicyclization of 1,6,8-dienyne with α-cyanodiazoacetate, enabling the construction of multi-substituted [5.3.0]decane structures in excellent diastereoselectivities. In addition, we revealed that the Co(II)-catalyzed bicyclization proceeds through an underlying stepwise radical mechanism, which is fundamentally different from existing catalytic systems involving Cope rearrangement of divinyl cyclopropane intermediates. Furthermore, we showed that the resulting multi-substituted [5.3.0]decane structures could serve as versatile intermediates for the construction of important molecules that may find interesting synthetic and biological applications.

Scheme 4.2. Previous Strategies for Constructing Multi-Substituted [5.3.0]decanes of 1,6,8-Dienynes with Diazo Compounds

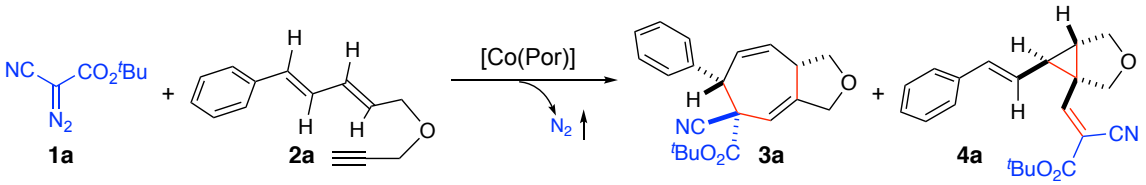


4.2. RESULTS AND DISCUSSION

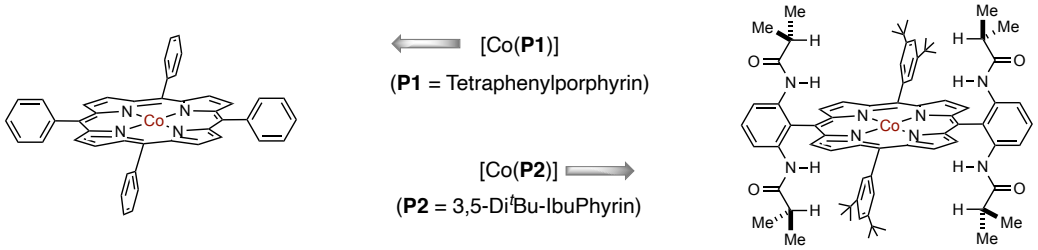
4.2.1. Condition Optimization for Radical Cascade Bicyclization of 1,6,8-Dienynes with α-Cyano Diazoacetate

At the outset of this project, phenyl substituted 1,6,8-dienyne **2a** was selected as the model substrate to explore the proposed radical cascade bicyclization process by Co(II)-based metalloradical catalysts with *tert*-butyl α-cyanodiazoacetate **1a** as the radical precursor (Scheme 4.3). It was found that the simple achiral catalyst [Co(**P1**)] (**P1**

Scheme 4.3. Optimization of Reaction Conditions on Co(II)-Catalyzed Radical Cascade Bicyclization of 1,6,8-Dienyne with *tert*-Butyl α-Cyanodiazoacetate[a]



entry	catalyst	solvent	time	**3a**	**4a**
1	[Co(**P1**)]	Toluene	24 h	5%	0%
2	[Co(**P2**)]	Toluene	24 h	10%	8%
3	[Co(**P2**)]	Benzene	24 h	17%	13%
4	[Co(**P2**)]	*n*-Hexane	24 h	18%	10%
5	[Co(**P2**)]	Acetonitrile	24 h	12%	11%
6	[Co(**P2**)]	Diethyl ether	24 h	14%	13%
7	[Co(**P2**)]	Dichloromethane	24 h	26%	20%
8	[Co(**P2**)]	Dichloromethane	48 h	30%	25%
9[b]	[Co(**P2**)]	Dichloromethane	48 h	41%	28%



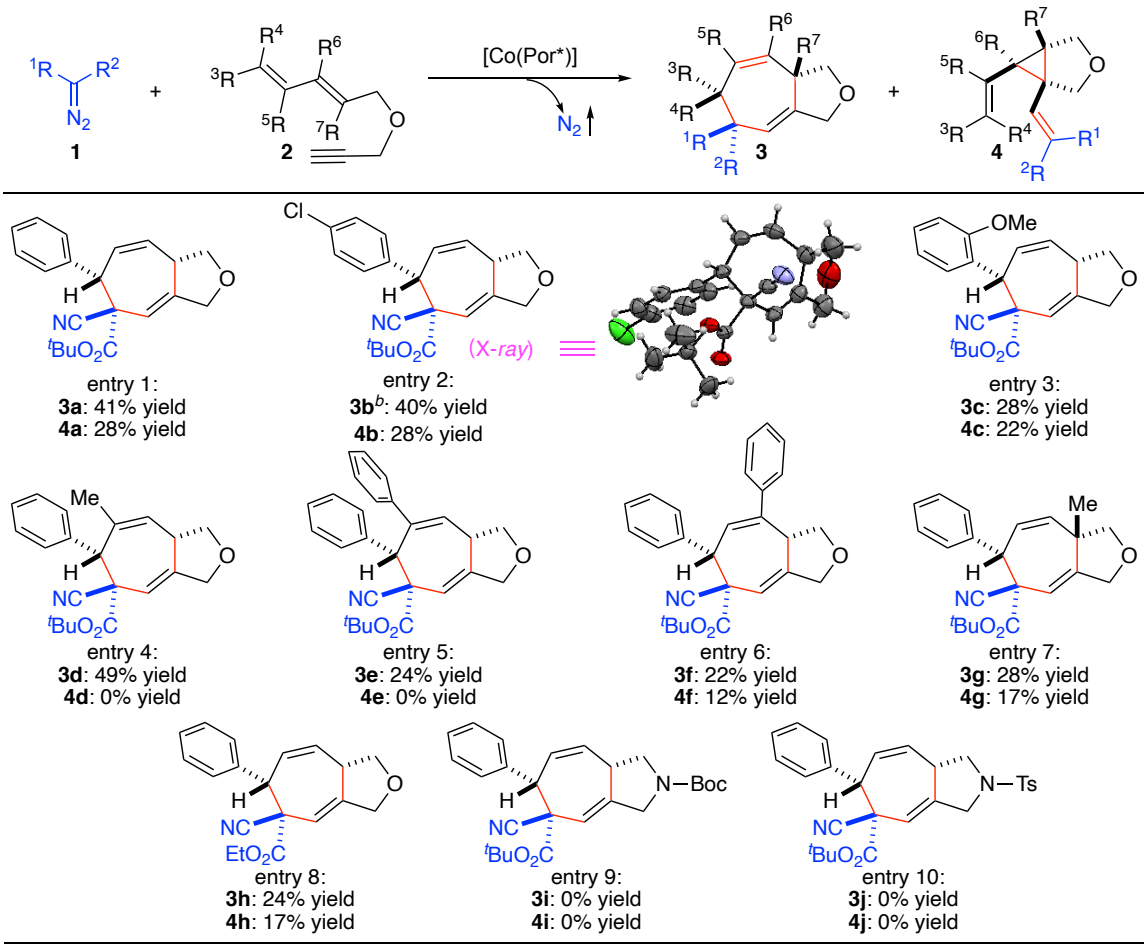
[a] Carried out with **1a** (0.1 mmol) and **2a** (0.12 mmol) by [Co(Por)] (5 mol %) in Solvent (0.5 mL) at 20 °C; isolated yields; diastereomeric ratio determined to be > 99:1.[b]Carried out at 40 °C.

= tetraphenylporphyrin) only produced trace amount of product **3a**. With the use of achiral catalyst [Co(**P2**)] (**P2** = 3,5-Di^{t}Bu-IbuPhyrin), which contains amide units in the supporting ligand, improvement of the yield of products **3a** was observed, together with the formation of bicyclo[3.1.0]hexane **4a**.[11] The difference in catalytic activity between [Co(**P1**)] and [Co(**P2**)] could be rationalized as the outcome of potential H-bonding stabilization of the corresponding Co-bonded alkyl radical intermediates. By solvent screening, DCM stood out as the optimal solvents, which furnished **3a** and **4a** in 26% and 20% yield, respectively. After that, the yields were further improved to 41% of **3a** and 28% of **4a** by increasing the reaction temperature and elongating the reaction time.

4.2.2. Radical Cascade Bicyclization of Different Substrates

Under the optimized reaction conditions, the Co(II)-based radical cascade bicyclization can be applied to a wide range of substrates (Table 4.1). For example, 1,6,8-dienynes bearing substitutions (R^3-R^7) on each carbon of the 1,3-diene motif participated in this process successfully to furnish the desired products. It is worth noting that the catalytic radical cascade process could be readily scaled up on a 2.0 mmol scale while maintaining equally good results. In addition to the phenyl substituted 1,6,8-dienyne **2a**, the metalloradical system could tolerate other aryl groups such as 4-Cl or 2-OMe substituted aryl groups to construct the multi-substituted [5.3.0]decanes in moderate to good yields (Table 4.1; entries 2 and 3). The relative configuration of stereogenic centers in **3b** was confirmed by X-ray crystallography. Notably, 1,6,8-dienynes containing R^5 substituents, such as Methyl or Phenyl groups (**2d** and **2e**), exhibited excellent chemoselectivity in affording cycloheptadiene-fused tetrahydrofurans **3d** and **3e** in moderate to good yields (Table 4.1; entries 4 and 5). Furthermore, dienyne substrates that

Table 4.1. Radical Cascade Bicyclization of Various 1,6,8-Dienynes with α-Cyanodiazoacetate Catalyzed by [Co(P2)][a]



[a] Carried out with **1** (0.1 mmol) and **2** (0.12 mmol) by [Co(**P2**)] (5 mol %) in Dichloromethane (0.5 mL) at 40 °C for 48 h; Isolated yields; diastereomeric ratio determined to be > 99:1. [b]Absolute configuration was determined by X-ray.

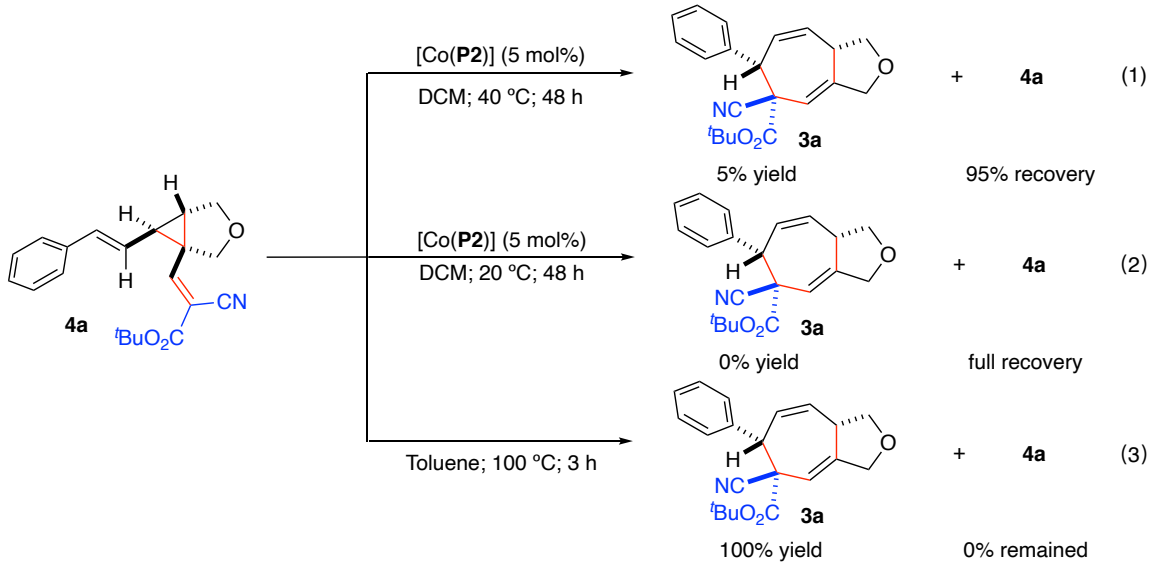
have a phenyl group at R^6 could be effective in delivering products **3f** and **4f**. More excitingly, the cascade process was also applicable for the generation of **3g** and **4g**, which were challenging to construct due to the existence of an additional quaternary stereogenic center at bridge carbon (Table 4.1; entry 7). Additionally, we discovered that not only *tert*-butyl α-cyanodiazoacetate but also ethyl α-cyanodiazoacetate could be used in the

radical cascade process, offering the desired products in good yield (Table 4.1; entry 8). N-linked 1,6,8-dienynes were also tested in the radical cascade bicyclization process (Table 4.1; entries 9 and 10). None of the cycloheptadiene-fused tetrahydrofurans or cyclopropane-fused tetrahydrofurans could be observed.

4.2.3. Mechanistic Studies for Radical Cascade Bicyclization of 1,6,8-Dienyne with *tert*-butyl α-Cyanodiazoacetate

The observation of compound **4** brought up another possibility for the formation of compound **3**. Based on reported literature,[8-9] a Cope rearrangement of divinyl cyclopropane compound **4** could occur to accomplish a ring-expansion of the 3-membered ring, which could form the 7-membered ring product **3**. To examine this possibility, cyclopropane-fused tetrahydrofuran **4a** was isolated and subjected into the standard reaction conditions in the absence of dienyne and diazo compound (Scheme 4.4; eq 1). However, **3a** was only obtained in 5% yield while 95% of substrate **4a** remained.

Scheme 4.4. Control Experiments for Radical Cascade Bicyclization of 1,6,8-Dienyne and *tert*-butyl α-Cyanodiazoacetate

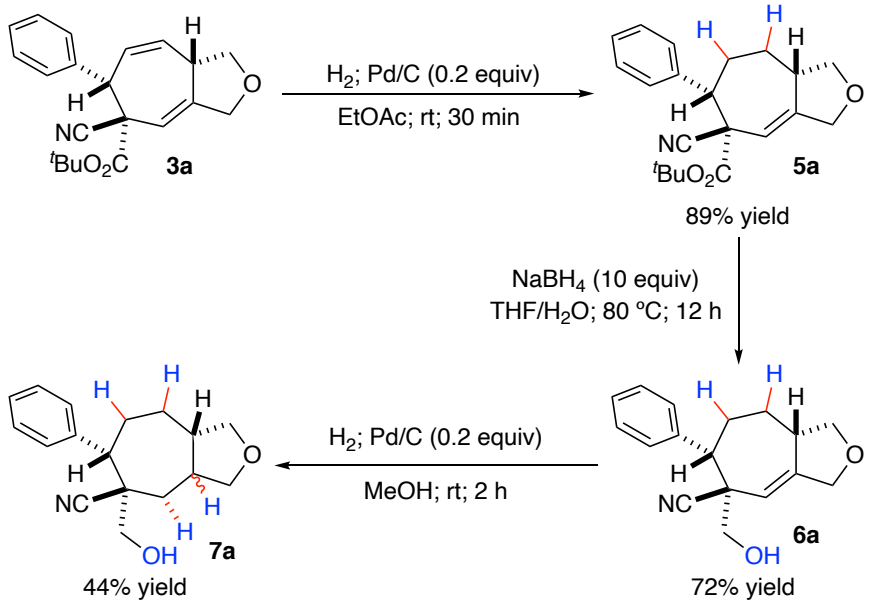


Then we conducted a similar reaction with lower reaction temperature, in which full recovery of compound **4a** was observed (Scheme 4.4; eq 2). These results indicate that the isomerization of **4a** is not the primary way for the formation of **3a** under the conditions of the radical cascade reaction. Of note, under harsher conditions, such as those shown in eq 3, the Cope rearrangement of **4a** proceeded efficiently to furnish **3a** in quantitative yield.

4.2.4. Synthetic Application of Resulting Multi-Substituted[5.3.0]decanes from Co(II)-Based Radical Cascade Bicyclization

By searching the literature, saturated 5,7-bicyclic ring system has been found in natural products, while the strategies for the construction of such architecture are limited.[12] We envisioned that, under appropriate conditions, product **3a** could be transformed into saturated bicyclo[5.3.0]decane structure in diastereoselective fashion

Scheme 4.5. Further Transformation of Resulting Multi-Substituted[5.3.0]decanes from Co(II)-Based Radical Cascade Bicyclization



(Scheme 4.5). To achieve this goal, the disubstituted alkene was subjected to hydrogenation by Pd/C, which furnished **5a** in 89% yield. After that, the *tert*-butyl ester was reduced to a hydroxy group, which served as a directing group to enable the hydrogenation of sterically more congested trisubstituted alkene and dictate the diastereoselectivity. As a result, saturated multi-substituted [5.3.0]decane **7a** was observed in practical yield as a single diastereoisomer.

4.3. CONCLUSIONS

In summary, we have demonstrated the application of metalloradical catalysis (MRC) for radical cascade bicyclization of 1,6,8-dienynes with diazo compounds. With the D_2-symmetric 3,5-Di^{t}Bu-IbuPhyrin as the optimal supporting ligand, the Co(II)-catalyzed radical cascade process enables activation of α-cyanodiazoacetate under mild conditions to react with different 1,6,8-dienynes for construction of multi-substituted cycloheptadiene-fused tetrahydrofurans and cyclopropane-fused tetrahydrofurans, in moderate to good yields with excellent diastereoselectivities. Mechanistic studies have shed light on the insight mechanism for the Co(II)-based cascade bicyclization. The resulting multi-substituted [5.3.0]decanes may serve as useful intermediates for stereoselective organic synthesis. Efforts are underway to explore the enantioselectivity of this radical cascade bicyclization process.

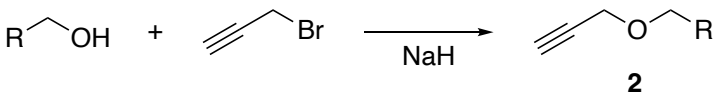
4.4. EXPERIMENT SECTION

4.4.1. General Considerations

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Gas tight syringes were used to transfer liquid reagents and solvents in catalytic reactions. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254), visualizing with UV-light 254 nm or ceriumammonium-molybdate (CAM) stain (ammonium pentamolybdate, cerium(IV) sulfate, sulfuric acid aqueous solution). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Inova600 (600 MHz), Inova500 (500 MHz), Inova400 (400 MHz) instrument with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. High resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight (ESI-TOF) or direct analysis in real time (DART). The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. Reagents [Co(3,5-Di^{t}Bu-IbuPhyrin)] was prepared by following the literature.[13] *tert*-Butyl 2-cyano-2-diazoacetate and ethyl 2-cyano-2-diazoacetate were synthesized according to reported procedure.[13]

4.4.2. Synthesis of Substrates

Procedure A and Characterization of 1,6,8-Dienyne



2

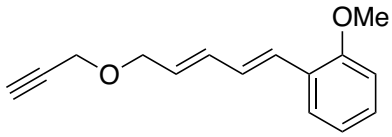
A solution of alcohol (1 equiv) in DMF (10 M) was added dropwise at 0 °C to a suspension of sodium hydride (1.5 equiv) in DMF (0.5 M). Keep reaction mixture stirring for 20 minutes and dropwise addition of 3- bromoprop-1-yne (2 equiv). The reaction mixture was stirred at room temperature and monitored by TLC. The reaction was quenched with water and extracted with Et_2O (3 × 5 mL/mmol). The organic layers were then combined and washed with brine and then dried over $MgSO_4$. The resulting organic layer was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica column (hexanes/ethyl acetate) to afford product.[14]

((1*E*,3*E*)-5-(Prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene 2a. Yellow oil; 65% Yield; R_f = 0.3 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.35 – 7.29 (m, 2H), 7.24 (qd, *J* = 7.5, 7.0, 1.3 Hz, 1H), 6.79 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.57 (d, *J* = 15.7 Hz, 1H), 6.50 – 6.39 (m, 1H), 5.87 (dt, *J* = 15.4, 6.4 Hz, 1H), 4.22 – 4.13 (m, 4H), 2.45 (td, *J* = 2.5, 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.20, 133.99, 133.28, 129.09, 128.75, 128.17, 127.82, 126.57, 79.84, 74.61, 70.01, 57.14. IR (neat, cm^{-1}): 3292.15, 3024.43, 2849.27, 1447.77, 1356.50, 1074.95, 988.54, 745.72. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{14}H_{18}NO^+$: 216.1383; Found: 216.1384.

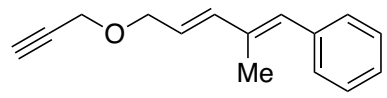
1-Chloro-4-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene 2b. Yellow solid; 62% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.25 (m, 2H), 6.75 (ddd, *J* = 15.6, 10.5, 0.7 Hz, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.43 (dddd, *J* = 15.3, 10.5, 2.2, 1.5 Hz, 1H), 5.88 (dtt, *J* = 15.3, 6.2, 0.9 Hz, 1H), 4.21 – 4.13 (m, 4H), 2.45 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.73,

133.53, 133.38, 131.85, 129.78, 128.93, 128.79, 127.71, 79.79, 74.66, 69.92, 57.22. IR (neat, cm^{-1}): 3296.16, 2851.00, 1490.82, 1356.28, 1114.18, 1070.92, 993.27, 821.15, 669.88.

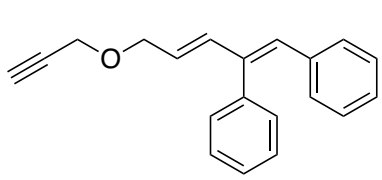
1-Methoxy-2-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene 2c. Yellow oil; 61% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.26 – 7.18 (m, 1H), 6.99 – 6.75 (m, 4H), 6.49 (ddt, *J* = 15.3, 10.3, 1.5 Hz, 1H), 5.85 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.23 – 4.13 (m, 4H), 3.86 (s, 3H), 2.46 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.93, 134.97, 128.83, 128.72, 128.33, 128.18, 126.65, 126.18, 120.79, 111.03, 79.90, 74.51, 70.07, 56.94, 55.57. IR (neat, cm^{-1}): 3289.44, 2837.20, 1594.81, 1486.62, 1462.79, 1241.02, 1025.83, 989.49, 747.91. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{15}H_{20}NO_2^+$: 246.1489; Found: 246.1495.



((1*E*,3*E*)-2-Methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene 2d. Yellow oil; 65% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.29 – 7.21 (m, 1H), 6.56 (s, 1H), 6.50 (dq, *J* = 15.7, 1.3 Hz, 1H), 5.86 (dt, *J* = 15.5, 6.4 Hz, 1H), 4.25 – 4.18 (m, 4H), 2.47 (t, *J* = 2.4 Hz, 1H), 2.03 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.03, 137.76, 135.06, 132.18, 129.33, 128.26, 126.82, 124.31, 79.93, 74.54, 70.49, 57.12, 13.99. IR (neat, cm^{-1}): 3290.84, 2850.81, 1356.03, 1076.85, 964.72, 698.13. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{15}H_{20}NO^+$: 230.1539; Found: 230.1547.

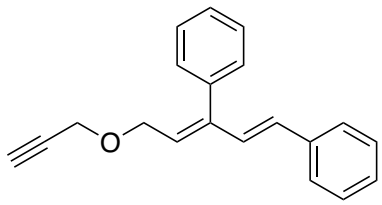


((1*Z*,3*E*)-5-(Prop-2-yn-1-yloxy)penta-1,3-diene-1,2-diyl)dibenzene 2e. Yellow oil; 55% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.38



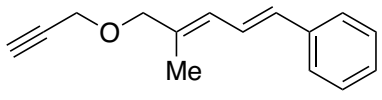
(td, *J* = 7.1, 1.3 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.19 – 7.14 (m, 2H), 7.08 (qd, *J* = 4.4, 2.1 Hz, 3H), 6.89 (dd, *J* = 6.4, 2.7 Hz, 2H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.61 (s, 1H), 5.38 (dt, *J* = 15.4, 6.2 Hz, 1H), 4.16 – 4.12 (m, 4H), 2.45 – 2.41 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.80, 138.64, 138.28, 136.74, 131.90, 129.60, 129.53, 128.99, 128.10, 127.84, 127.50, 127.10, 79.86, 74.60, 70.23, 57.28. IR (neat, cm^{-1}): 3293.44, 2848.53, 1443.57, 1355.49, 1079.08, 967.88, 705.69, 692.51. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{19}O^+$: 275.1430; Found: 275.1434.

((1*E*,3*Z*)-5-(Prop-2-yn-1-yloxy)penta-1,3-diene-1,3-diyl)dibenzene 2f. Yellow oil;



52% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.42 – 7.36 (m, 5H), 7.36 – 7.32 (m, 2H), 7.30 (dd, *J* = 16.0, 1.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 5.78 (tt, *J* = 7.0, 1.0 Hz, 1H), 4.50 (d, *J* = 6.9 Hz, 2H), 4.27 (d, *J* = 2.3 Hz, 2H), 2.52 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.74, 141.11, 137.27, 134.38, 128.90, 128.73, 128.29, 128.05, 127.64, 126.95, 126.80, 124.97, 79.99, 74.76, 65.75, 57.34. IR (neat, cm^{-1}): 3289.79, 3024.88, 2848.03, 1491.71, 1445.15, 1072.08, 963.37, 691.42. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{20}H_{19}O^+$: 275.1430; Found: 275.1433.

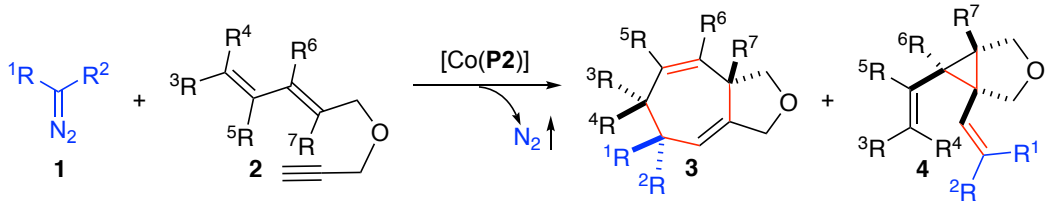
((1*E*,3*E*)-4-methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene 2g. Yellow oil;



39% Yield; R_f = 0.2 (hexanes/ethyl acetate, 12:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (dt, *J* = 8.1, 1.5 Hz, 2H), 7.31 (td, *J* = 7.8, 1.7 Hz, 2H), 7.22 (td, *J* = 7.3, 1.5 Hz, 1H), 7.01 (ddd, *J* = 15.6, 11.0, 1.6 Hz, 1H), 6.56 (d, *J* = 15.4 Hz, 1H), 6.25 (ddd, *J* = 11.0, 2.6, 1.2 Hz, 1H), 4.14 (t,

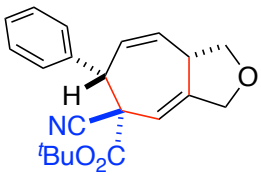
J = 2.0 Hz, 2H), 4.07 (s, 2H), 2.45 – 2.43 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.70, 134.69, 132.87, 128.75, 128.07, 127.62, 126.50, 124.63, 79.96, 75.39, 74.48, 56.91, 14.80. IR (neat, cm^{-1}): 3295.22, 3032.54, 2850.55, 1490.40, 1448.25, 1358.03, 1075.27, 965.79, 691.70. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{15}H_{17}O^+$: 213.1274; Found: 213.1271.

4.4.3. General Procedure for Radical Cascade Cyclization



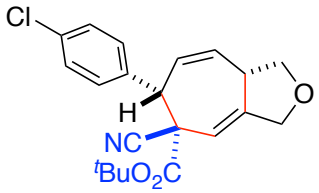
An oven dried Schlenk tube, that was previously charged with catalyst (5 mol %), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum, and 0.25 ml of anhydrous DCM and dienyne (0.10 mmol) were added followed by cyano diazoacetate (0.12 mmol, 1.2 equiv) and the remaining solvent (total 0.5 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. Following completion of the reaction (48 h), the reaction mixture was purified via flash column chromatography to afford compound **3**.

<u>Characterization of Bicyclo[5.3.0]decanes</u>

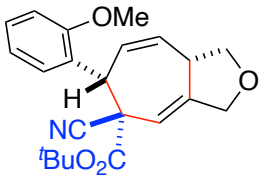


***tert*-Butyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3a.** Light yellow oil; 41% Yield (28% Yield of **4a**); R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 3H), 7.25 – 7.14 (m, 2H), 5.81 (q, J = 2.6 Hz, 1H), 5.77 – 5.59 (m, 2H), 4.55 (dd, J = 13.5, 2.1 Hz, 1H), 4.48 – 4.39 (m, 2H), 4.31 (t, J

= 4.2 Hz, 1H), 4.19 – 4.01 (m, 1H), 3.76 – 3.57 (m, 1H), 1.47 (t, *J* = 1.3 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.77, 148.39, 136.34, 130.15, 129.06, 128.43, 128.22, 125.76, 117.46, 113.66, 84.86, 74.95, 72.80, 50.96, 50.42, 42.21, 27.82. IR (neat, cm^{-1}): 2978.73, 2866.61, 1720.39, 1606.11, 1369.82, 1254.98, 1151.44, 839.29, 751.55. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{24}NO_3^+$: 338.1751; Found: 338.1763.



***tert*-Butyl (5*S*,8a*S*)-6-(4-chlorophenyl)-5-cyano-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3b.** 40% Yield (28% Yield of **4b**); R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 5.78 (d, *J* = 2.6 Hz, 1H), 5.77 – 5.59 (m, 2H), 4.55 (d, *J* = 14.1 Hz, 1H), 4.43 (q, *J* = 7.5, 6.1 Hz, 2H), 4.30 (t, *J* = 4.8 Hz, 1H), 4.20 – 4.04 (m, 1H), 3.66 (t, *J* = 9.0 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.69, 148.75, 134.91, 134.51, 131.47, 128.71, 128.50, 126.38, 117.26, 113.48, 85.21, 74.96, 72.85, 50.41, 50.21, 42.31, 27.92. IR (neat, cm^{-1}): 3016.65, 2979.68, 2851.57, 1743.02, 1370.63, 1250.90, 1150.19, 830.34, 750.98. HRMS (DART) ([M+H]$^+$) Calcd. for $C_{21}H_{23}NO_3Cl^+$: 372.1361; Found: 372.1356.



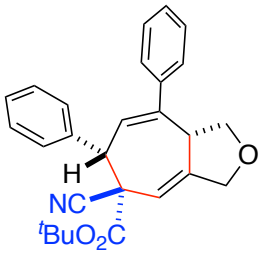
***tert*-Butyl (5*S*,8a*S*)-5-cyano-6-(2-methoxyphenyl)-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3c.** 38% Yield (22% Yield of 4c); R_f = 0.2 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.91 (d, *J* = 2.4 Hz, 1H), 5.68 (ddd, *J* = 11.7, 5.9, 2.9 Hz, 1H), 5.62 (d, *J* = 12.0 Hz, 1H), 5.01 (t, *J* = 5.0 Hz, 1H), 4.58 (d, *J* = 13.4 Hz, 1H), 4.51 – 4.44 (m, 1H), 4.41 (t, *J* = 8.6 Hz, 1H), 4.15 – 4.05 (m, 1H), 3.82 (s, 3H), 3.63

(t, J = 9.1 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.16, 157.06, 148.62, 130.48, 130.21, 129.17, 125.71, 125.26, 120.49, 117.90, 114.64, 110.58, 84.22, 77.41, 77.16, 76.91, 74.95, 72.94, 55.60, 50.18, 41.87, 41.56, 25.54. IR (neat, cm^{-1}): 2978.16, 2932.33, 2839.47, 1735.25, 1242.90, 1151.73, 1028.01, 840.02, 751.54. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{26}NO_4^+$: 368.1856; Found: 368.1859.

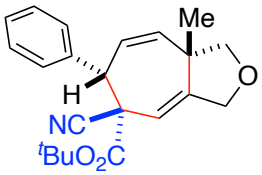
***tert*-Butyl (5*S*,8a*S*)-5-cyano-7-methyl-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3d.** 49% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 3H), 7.20 – 7.04 (m, 2H), 5.75 (q, J = 2.4 Hz, 1H), 5.52 (d, J = 1.6 Hz, 1H), 4.56 (dd, J = 13.7, 2.3 Hz, 1H), 4.49 – 4.37 (m, 2H), 4.05 (d, J = 2.4 Hz, 2H), 3.65 (dd, J = 9.8, 8.3 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.97, 147.42, 136.37, 134.73, 130.21, 128.43, 128.19, 120.87, 117.35, 113.19, 84.94, 75.44, 72.84, 55.17, 50.33, 42.39, 27.91, 26.71. IR (neat, cm^{-1}): 2977.54, 2936.22, 2850.92, 1742.73, 1370.25, 1253.16, 1149.17, 839.64, 701.13. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{22}H_{26}NO_3^+$: 352.1907; Found: 352.1897.

***tert*-Butyl (5*S*,8a*S*)-5-cyano-6,7-diphenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3e.** 24% Yield; R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 6H), 7.16 – 7.01 (m, 4H), 5.87 (d, J = 2.6 Hz, 1H), 5.78 (q, J = 2.4 Hz, 1H), 4.68 (d, J = 3.3 Hz, 1H), 4.62 (dt, J = 13.7, 1.5 Hz, 1H), 4.53 (t, J = 8.4 Hz, 1H), 4.46 (dt, J = 13.7, 2.3 Hz, 1H), 4.22 (d, J = 10.3 Hz, 1H), 3.77 (dd, J = 10.1, 8.3 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.95, 146.60, 144.49, 140.13, 135.97, 130.47, 128.37, 128.34, 128.17, 127.46, 127.32, 125.00, 117.19, 113.73,

85.20, 75.12, 72.92, 54.68, 50.81, 43.36, 27.94. IR (neat, cm^{-1}): 2978.92, 2932.26, 2849.38, 1742.77, 1370.51, 1252.80, 1150.87, 837.54, 700.04. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{27}H_{28}NO_3^+$: 414.2064; Found: 414.2064.

***tert*-Butyl (5*S*,8a*S*)-5-cyano-6,8-diphenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3f.** 

22% Yield (12% Yield); R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 (dd, *J* = 8.9, 6.5 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.26 – 7.19 (m, 1H), 7.18 – 7.13 (m, 2H), 6.21 (dd, *J* = 2.6, 1.2 Hz, 1H), 4.37 – 4.29 (m, 2H), 4.27 – 4.22 (m, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.86 (dd, *J* = 8.7, 3.4 Hz, 1H), 1.39 (d, *J* = 0.7 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.73, 160.04, 144.07, 139.94, 134.31, 128.96, 128.94, 128.54, 128.35, 127.73, 127.27, 126.40, 114.57, 109.65, 83.65, 78.29, 73.01, 62.38, 61.19, 57.06, 27.86. IR (neat, cm^{-1}): 2978.46, 2930.77, 2865.08, 1721.79, 1369.61, 1279.85, 1155.75, 761.13, 700.81. HRMS (DART) ($[M+NH_4]^+$) Calcd. for $C_{27}H_{28}NO_3^+$: 414.2064; Found: 414.2053.

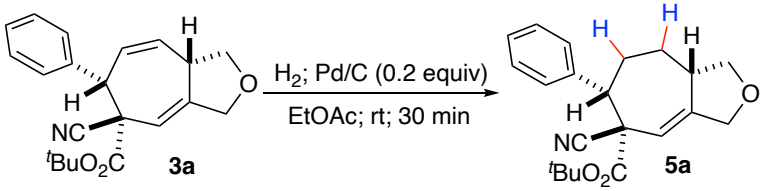
***tert*-Butyl (5*S*,8a*S*)-5-cyano-8a-methyl-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3g.** 

28% Yield (17% Yield of **4g**); R_f = 0.3 (hexanes/ethyl acetate, 4:1). For **3g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.21 – 7.14 (m, 2H), 5.90 – 5.76 (m, 2H), 5.69 (d, *J* = 12.2 Hz, 1H), 4.72 (dd, *J* = 13.8, 2.4 Hz, 1H), 4.52 – 4.42 (m, 1H), 4.36 (d, *J* = 7.1 Hz, 1H), 3.90 (d, *J* = 8.1 Hz, 1H), 3.75 (d, *J* = 8.1 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 9H). For **4g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.14 (m, 4H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.38 (dd, *J* = 15.8, 9.2 Hz, 1H), 4.50 – 4.40 (m,

2H), 4.13 (d, J = 8.8 Hz, 1H), 3.83 (d, J = 8.9 Hz, 1H), 2.37 (d, J = 9.2 Hz, 1H), 1.62 (s, 9H), 1.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.94, 161.01, 159.21, 149.78, 137.02, 136.50, 135.41, 130.49, 130.17, 128.73, 128.47, 128.29, 127.73, 126.97, 126.33, 121.53, 119.84, 115.50, 113.28, 84.99, 83.79, 81.66, 73.08, 72.71, 68.97, 51.25, 49.50, 48.60, 43.70, 43.08, 42.80, 28.07, 27.85, 22.41, 15.64. IR (neat, cm^{-1}): 2978.10, 2931.43, 2853.20, 1718.63, 1603.90, 1369.53, 1155.33, 1110.87, 838.95, 751.30. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{22}H_{26}NO_3^+$: 352.1907; Found: 352.1906.

Ethyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 3h. 24% Yield (17% Yield of **4h**); R_f = 0.3 (hexanes/ethyl acetate, 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 3H), 7.13 (dt, J = 7.8, 1.5 Hz, 2H), 5.85 – 5.77 (m, 1H), 5.77 – 5.66 (m, 2H), 4.59 – 4.51 (m, 1H), 4.48 – 4.40 (m, 2H), 4.33 (t, J = 4.1 Hz, 1H), 4.23 – 4.21 (m, 2H), 4.15 – 4.09 (m, 1H), 3.72 – 3.59 (m, 1H), 1.31 (td, J = 7.2, 1.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.22, 148.92, 136.15, 129.88, 128.69, 128.60, 128.43, 126.61, 126.10, 113.18, 75.02, 72.85, 63.48, 58.23, 51.29, 42.31, 14.06. IR (neat, cm^{-1}): 2980.12, 2922.74, 2850.50, 2240.03, 1491.56, 1220.32, 1190.40, 1078.73, 934.90, 700.12. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{19}H_{20}NO_3^+$: 310.1438; Found: 310.1424.

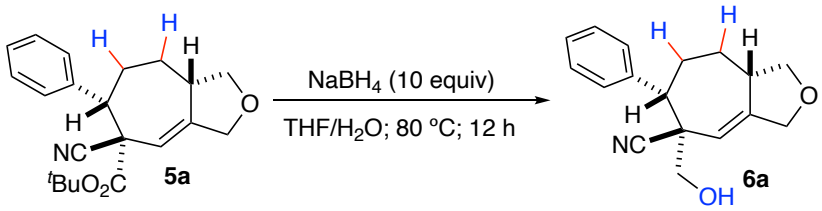
4.4.4. Further Transformations



A solution of **3a** (1.0 equiv) and Pd/C (0.2 equiv, 10% w/w) in EtOAc (10 mL/mmol) was subjected to 1 atm H_2-pressure (balloon) at r.t. until full conversion of the

3a was detected by TLC. Work-up by filtering through celite and evaporation yielded **5a**.

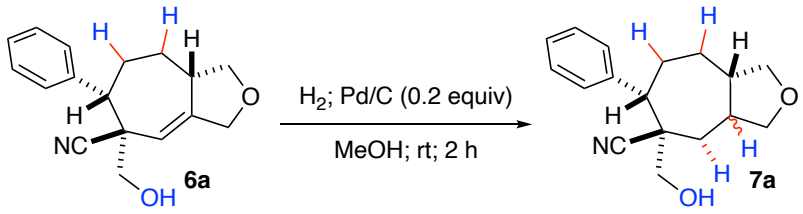
***tert*-Butyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,7,8,8a-hexahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate 5a.** Colorless oil; 89% Yield; R_f = 0.3 (hexanes/ethyl acetate, 8:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 5H), 6.27 – 6.10 (m, 1H), 4.48 (qt, *J* = 13.4, 1.7 Hz, 2H), 4.23 (t, *J* = 8.4 Hz, 1H), 3.75 (t, *J* = 4.7 Hz, 1H), 3.49 (t, *J* = 8.3 Hz, 1H), 3.27 – 3.13 (m, 1H), 2.66 (t, *J* = 13.6 Hz, 1H), 2.17 (dtd, *J* = 14.9, 5.5, 2.6 Hz, 1H), 1.64 (ddt, *J* = 13.2, 6.7, 3.3 Hz, 1H), 1.59 – 1.48 (m, 1H), 1.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.44, 150.64, 139.00, 129.57, 128.36, 127.51, 118.03, 113.63, 84.30, 75.54, 73.25, 50.75, 48.83, 43.21, 33.45, 27.44, 23.80. IR (neat, cm^{-1}): 2930.97, 1739.51, 1370.32, 1249.25, 1152.19, 840.63, 701.89. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{21}H_{26}NO_3^+$: 340.1907; Found: 340.1926.



A solution of **5a** (1 equiv) in THF/H_2O was added $NaBH_4$ (10 equiv) at r.t. The reaction mixture was heated at 80 °C for 12 h. The reaction was then concentrated and purified by flash column chromatograph over silica to give the product **6a**.

(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyl-3,5,6,7,8,8a-hexahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile 6a. white solid; 72% Yield; R_f = 0.3 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 5.38 (d, *J* = 2.4 Hz, 1H), 4.54 – 4.38 (m, 2H), 4.26 (t, *J* = 8.4 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.55 (t, *J* = 8.1 Hz, 1H), 3.47 (d, *J* = 11.0 Hz, 1H), 3.42 (t, *J* = 4.3 Hz, 1H), 3.30 (t, *J* = 7.9 Hz, 1H), 2.71 – 2.56 (m, 1H), 2.55 – 2.30 (m, 1H), 2.22 – 2.07 (m, 1H), 1.63 (dt, *J* = 8.8, 4.5 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.72, 139.45, 129.97, 128.61, 127.42, 121.10, 114.40, 75.70, 72.93, 66.88, 47.19, 44.82, 43.43, 33.76, 24.08. IR (neat, cm^{-1}): 3413.12, 2927.38, 2856.66, 1759.86, 1493.32, 1452.94, 1076.80, 918.01, 731.35, 703.27. HRMS (DART) ($[M–H]^-$) Calcd. for $C_{17}H_{18}NO_2^+$: 268.1332; Found: 268.1347.



A solution of **6a** (1.0 equiv) and Pd/C (0.2 equiv, 10% w/w) in MeOH (10 mL/mmol) was subjected to 1 atm H_2-pressure (balloon) at r.t. until full conversion of the **6a** was detected by TLC. The reaction was then filtered through celite and concentrated. Flash column chromatography was used to get the pure product **7a**.

(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyloctahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile 7a. white solid; 44% Yield; R_f = 0.3 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 4.18 – 4.05 (m, 2H), 3.53 (qd, *J* = 11.1, 6.1 Hz, 2H), 3.41 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.35 (ddd, *J* = 8.9, 7.3, 3.0 Hz, 2H), 2.84 (dddd, *J* = 17.5, 13.0, 7.7, 3.4 Hz, 1H), 2.69 – 2.54 (m, 1H), 2.28 (dddd, *J* = 14.7, 10.5, 6.4, 4.0 Hz, 1H), 2.06 (dd, *J* = 14.7, 12.5 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.84 (dddd, *J* = 16.3, 12.5, 9.8, 6.4 Hz, 1H), 1.71 (ddt, *J* = 14.8, 7.7, 3.9 Hz, 1H), 1.60 (t, *J* = 6.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.02, 129.22, 128.80, 127.85, 123.17, 75.24, 74.58, 65.64, 47.47, 46.82, 39.18, 38.43, 32.25, 28.40, 25.64. IR (neat, cm^{-1}): 3413.50, 2930.13, 2864.48, 1761.73, 1454.33, 1069.84, 915.16, 732.29, 703.93. HRMS (DART) ($[M+H]^+$) Calcd. for $C_{17}H_{22}NO_2^+$: 272.1645; Found: 272.1648.

4.4.5. X-ray Crystallographic Information

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (Cu K_α, λ = 1.54178 Å). Indexing was performed using *APEX2*[15] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[16] Absorption correction was performed by multi-scan method implemented in SADABS.[17] Space group were determined using XPREP implemented in APEX2.[15] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[18-20]program.

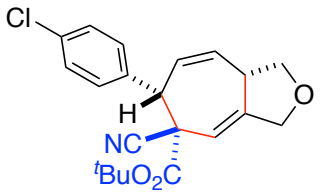
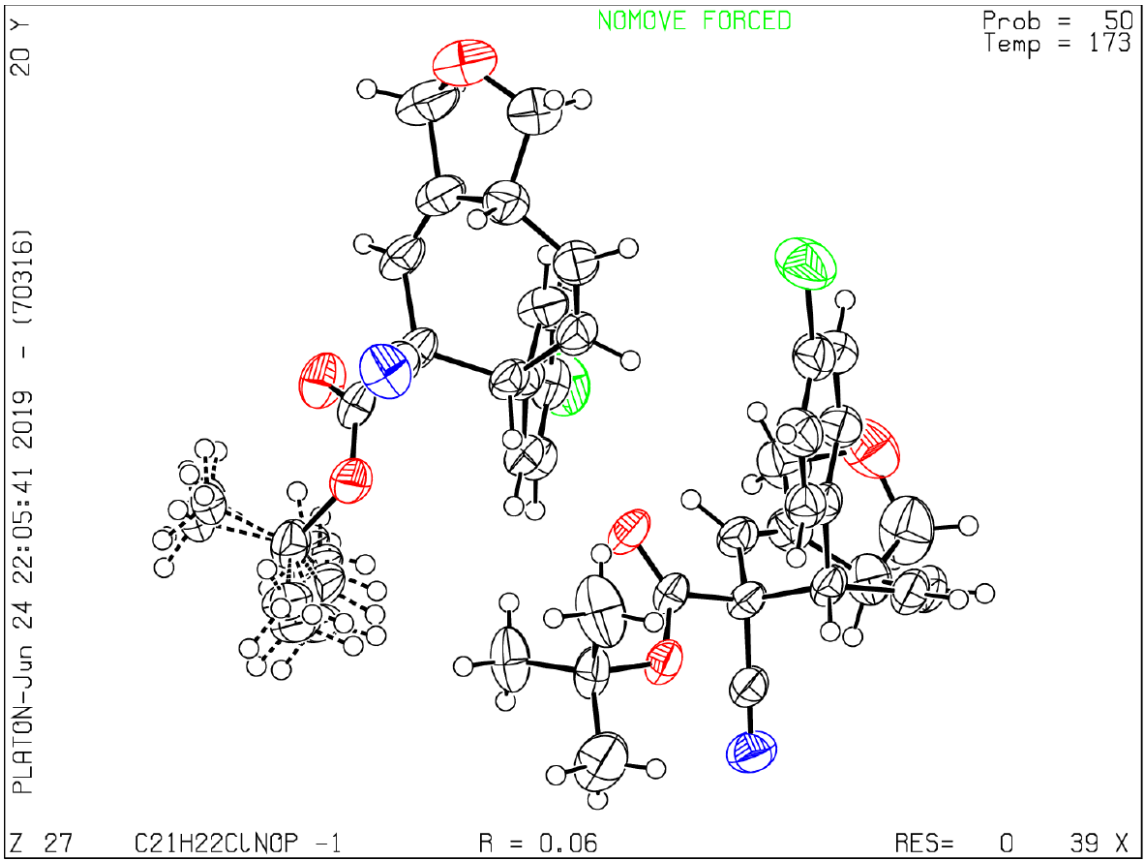


Table 1. Crystal data and structure refinement for **3b**.		
Identification code	**3b**	
Empirical formula	C21 H22 Cl N O3	
Formula weight	371.84	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6912(13) Å	α= 105.525(3) °.
	b = 12.6072(14) Å	β= 91.308(4) °.
	c = 13.7780(11) Å	γ = 91.957(3)°.
Volume	1054.5(3) $Å^3$	
Z	4	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	1.888 mm^{-1}	
F(000)	784	
Crystal size	0.560 x 0.360 x 0.190 mm^3	
Theta range for data collection	3.331 to 66.985°.	
Index ranges	-13<=h<=13, -14<=k<=14, -15<=l<=16	
Reflections collected	33697	
Independent reflections	6828 [R(int) = 0.0784]	
Completeness to theta = 67.679°	98.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6168	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6828 / 19 / 490	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R_1 = 0.0551, wR_2 = 0.1362	
R indices (all data)	R_1 = 0.0929, wR_2 = 0.156	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.558 and -0.292 $e.Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 173
20 Y
PLATON-Jun 24 22:05:41 2019 - (70316)
Z 27 C21H22ClNOP -1 R = 0.06 RES= 0 39 X

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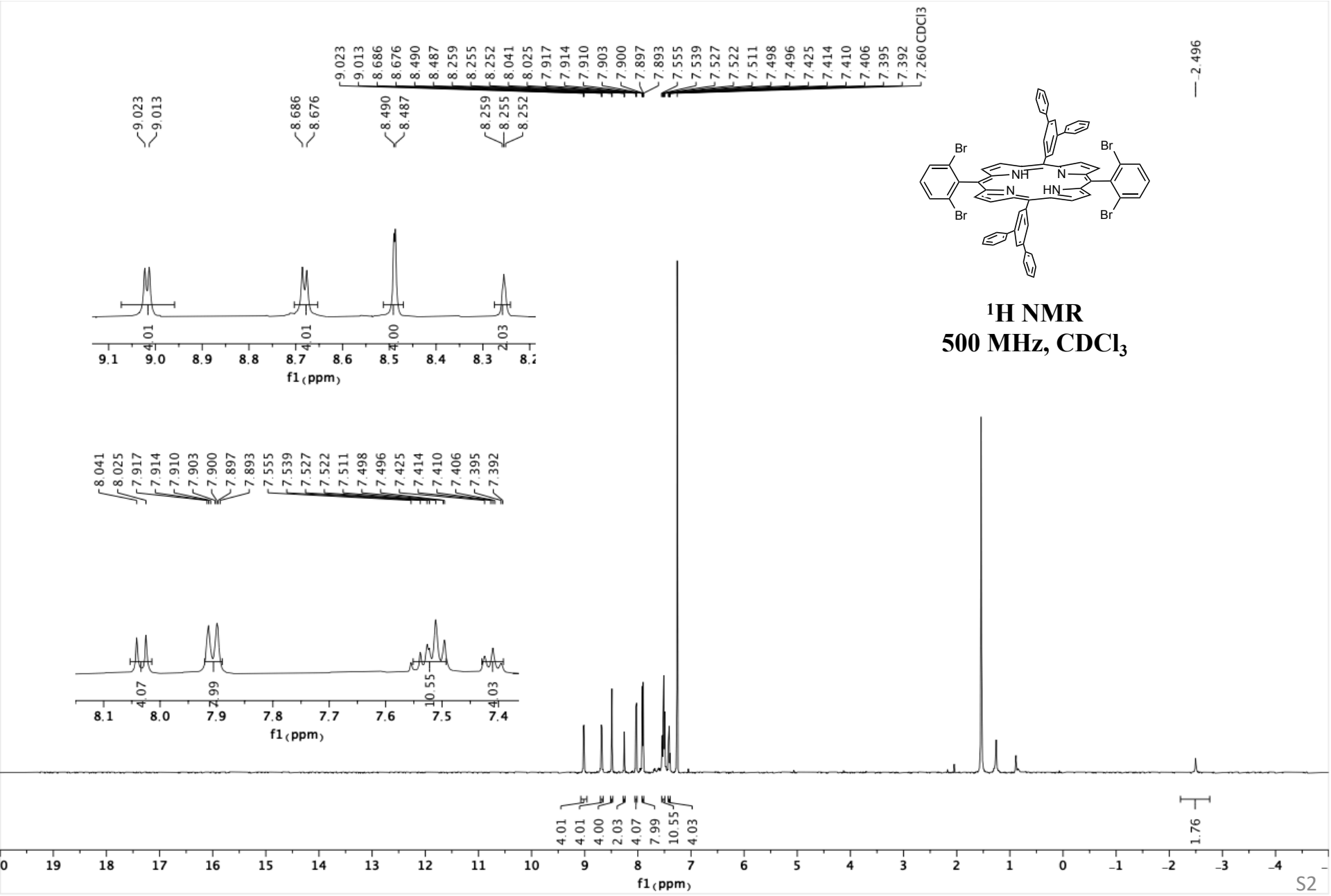
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Chapter 5

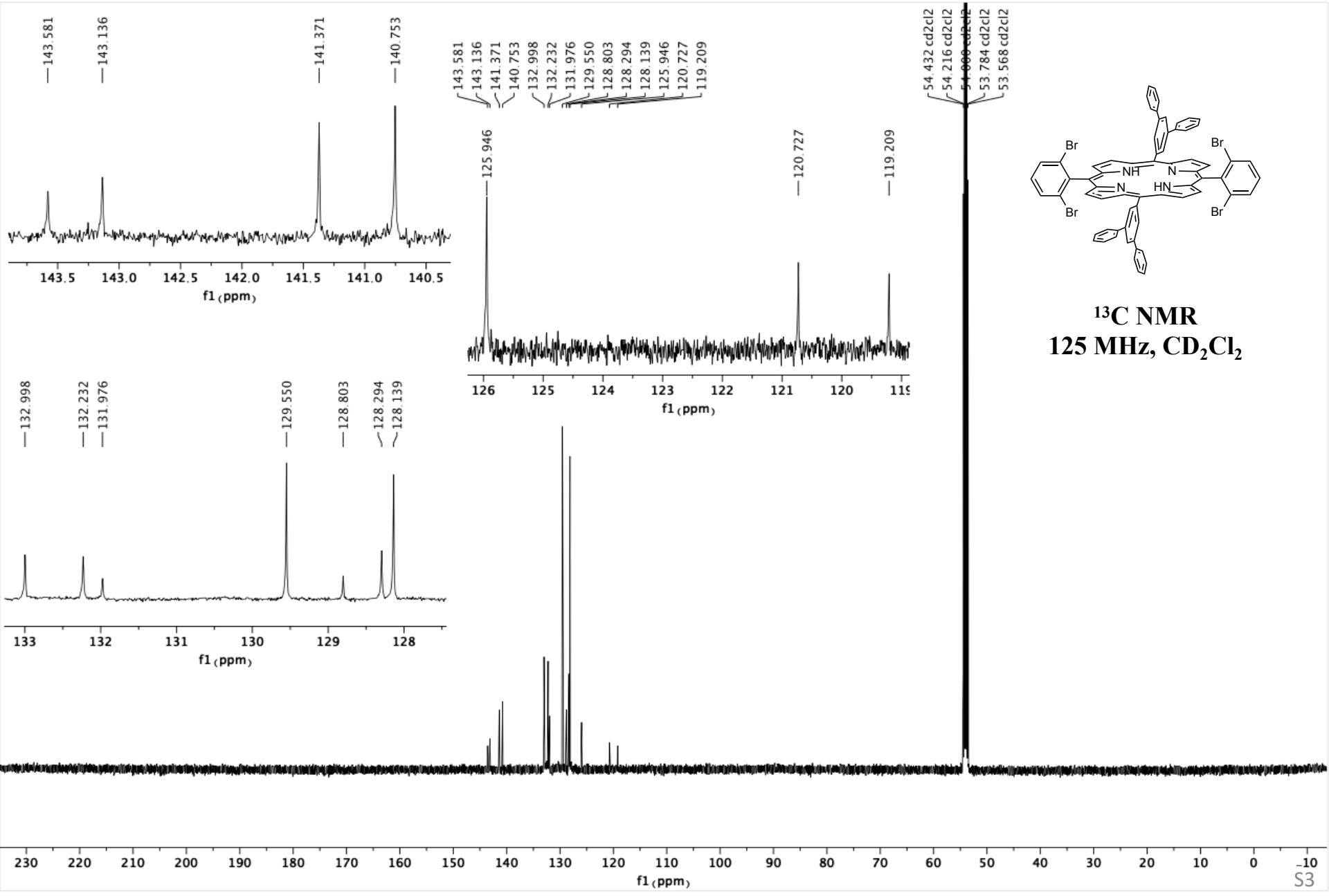
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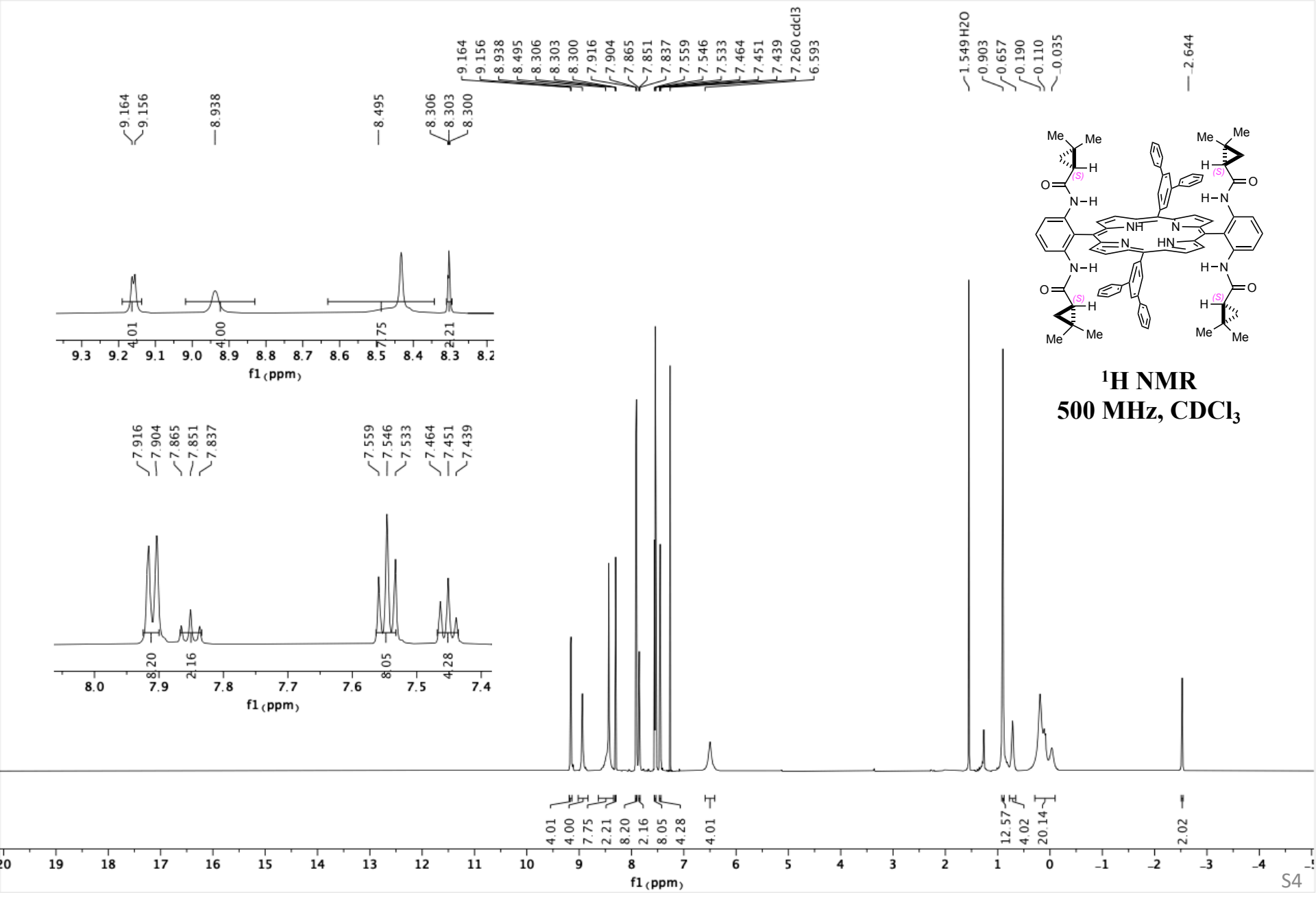
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500 MHz, $CDCl_3$

5,15-di([1,1':3',1"-terphenyl]-5'-yl)-10,20-bis(2,6-dibromophenyl)porphyrin



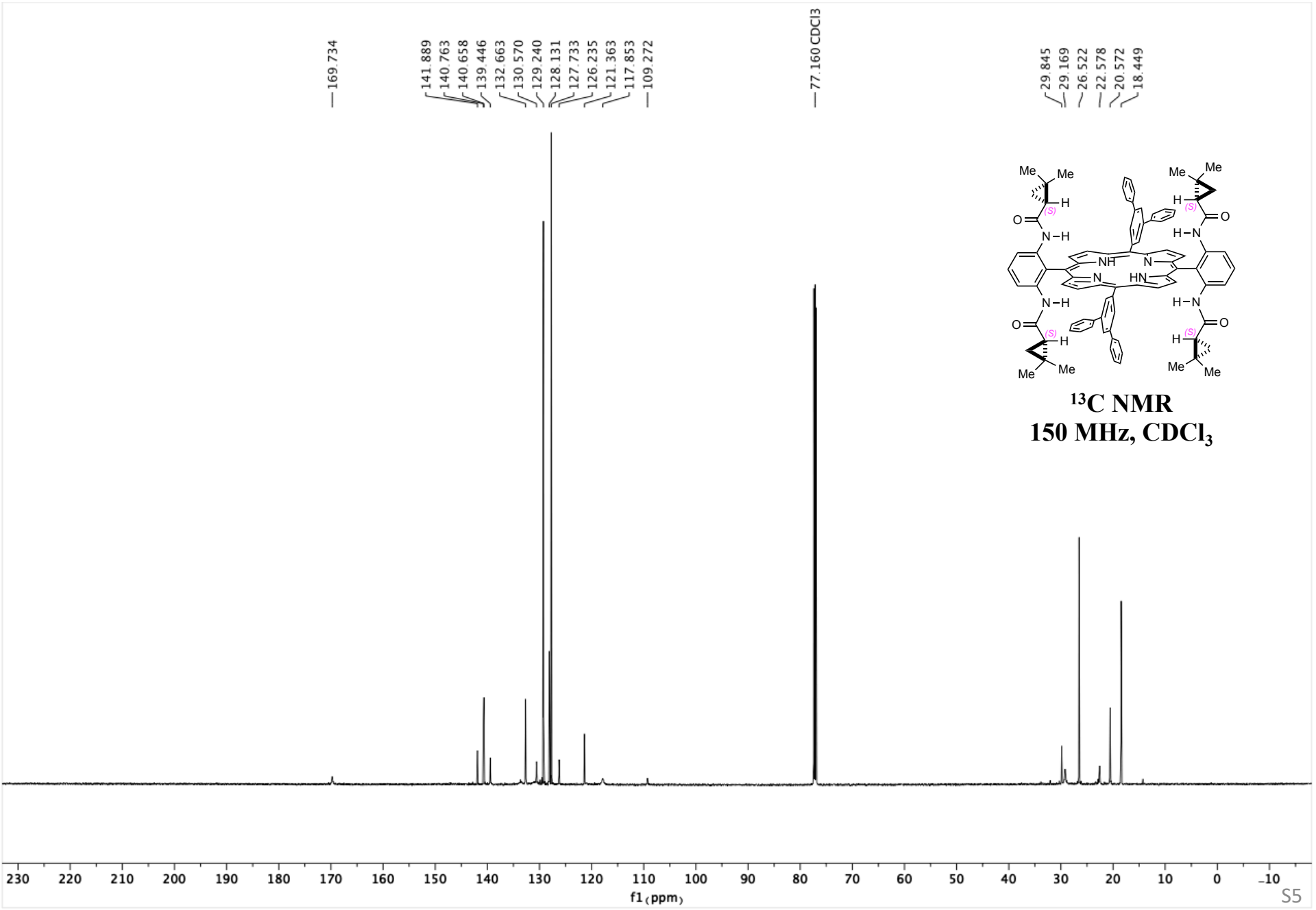
^{13}C NMR
125 MHz, CD_2Cl_2

H_2P5



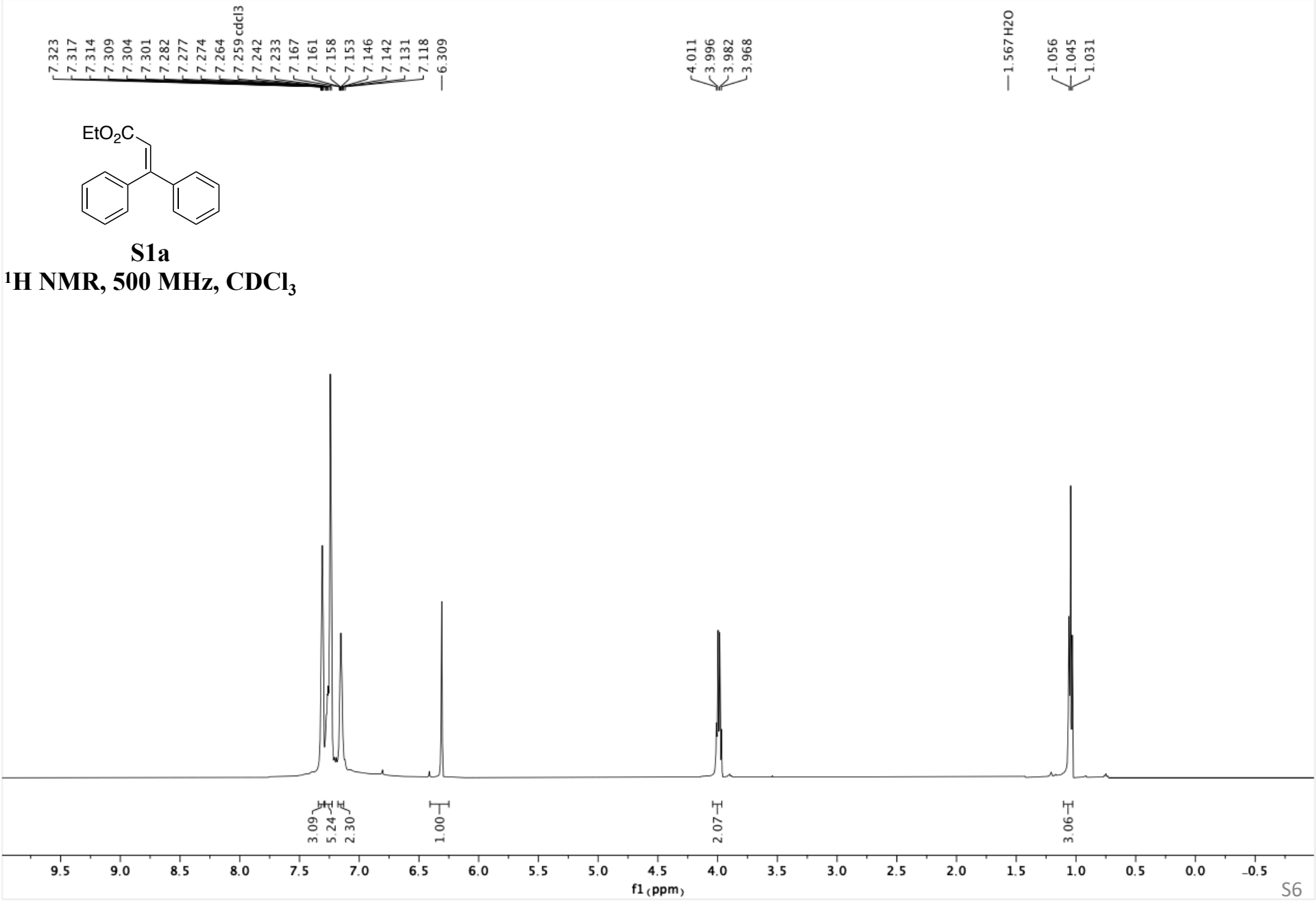
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500 MHz, $CDCl_3$

H_2P5



^{13}C NMR
150 MHz, $CDCl_3$

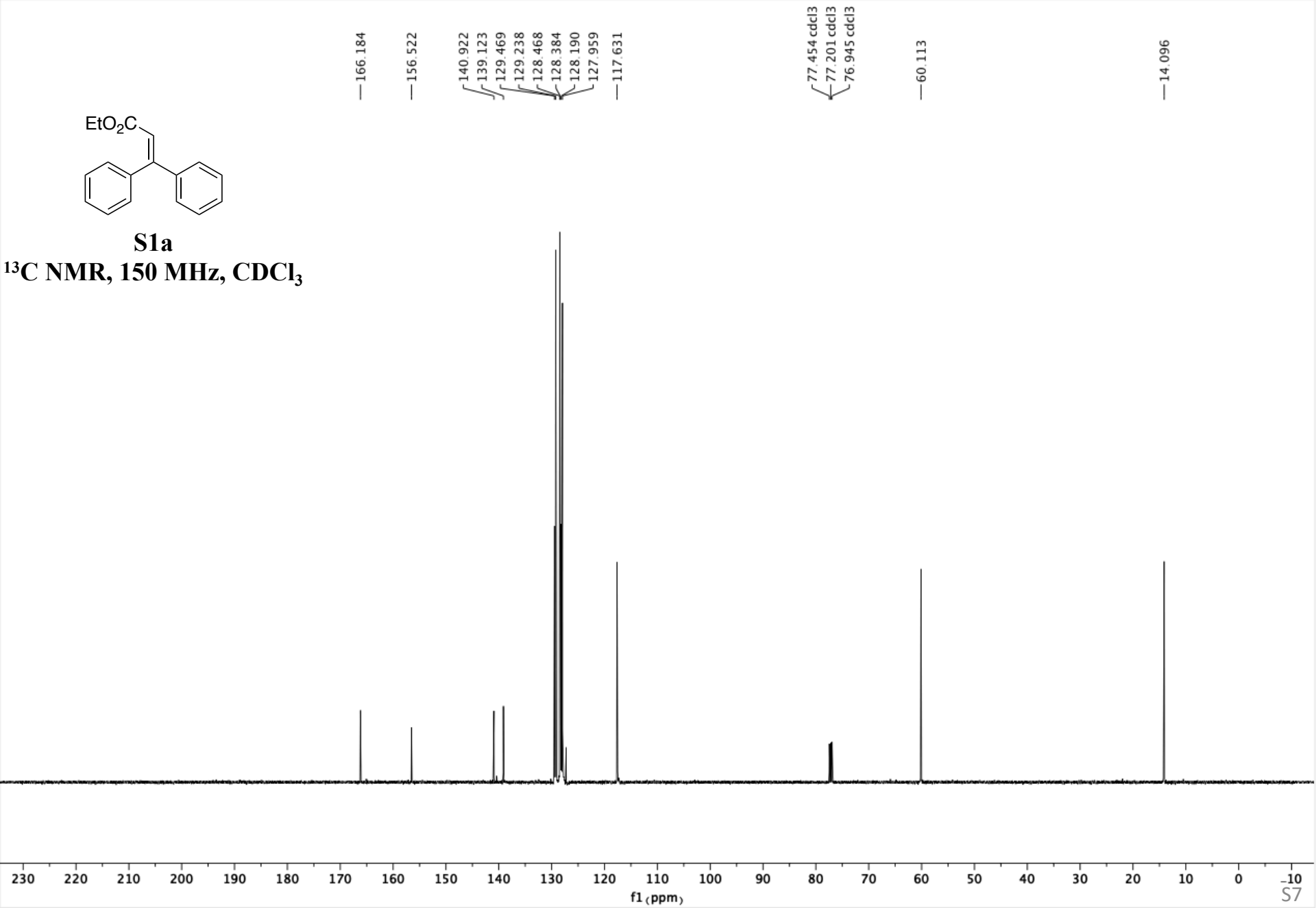
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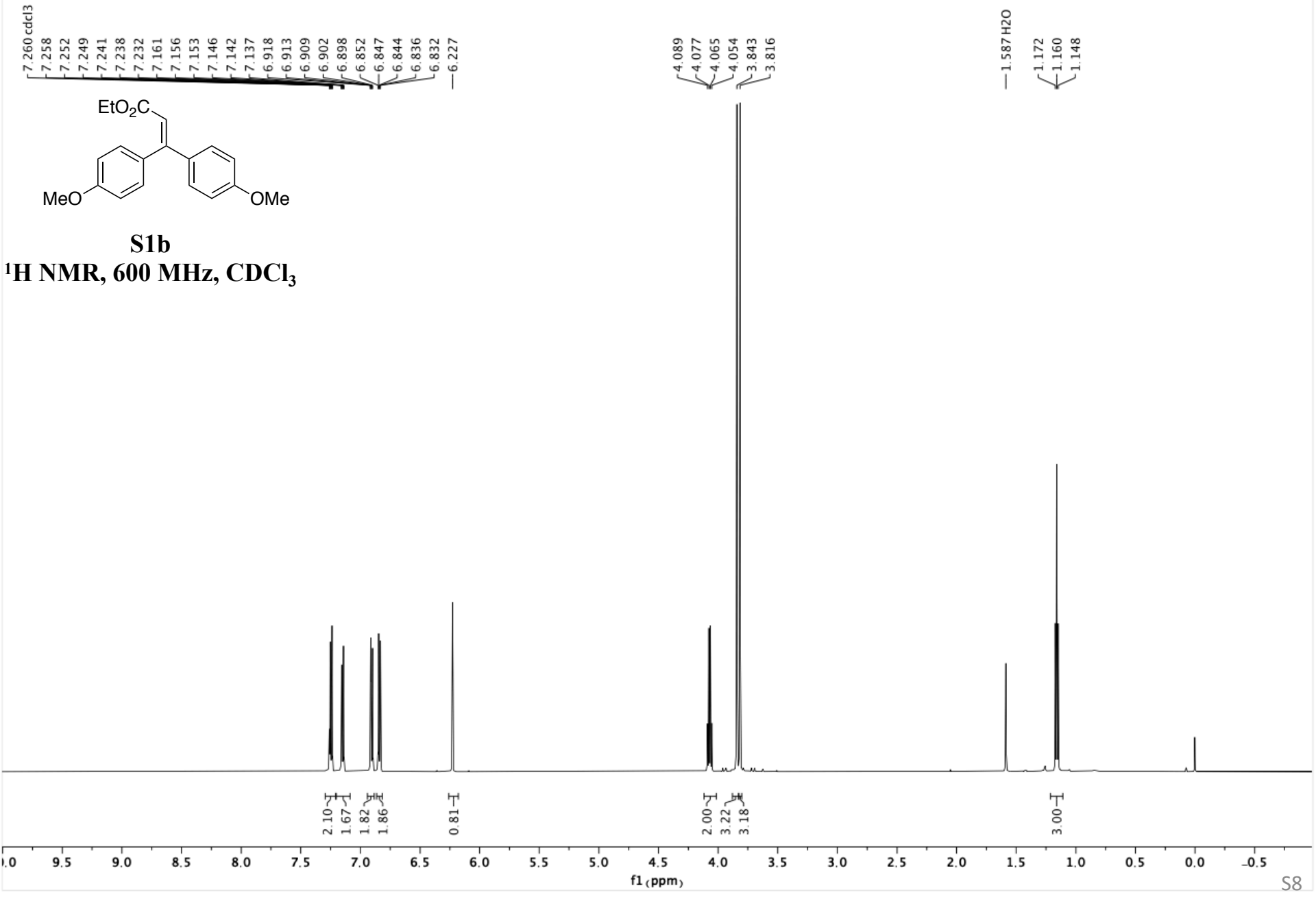
S1a

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Ethyl 3,3-diphenylacrylate



Ethyl 3,3-bis(4-methoxyphenyl)acrylate



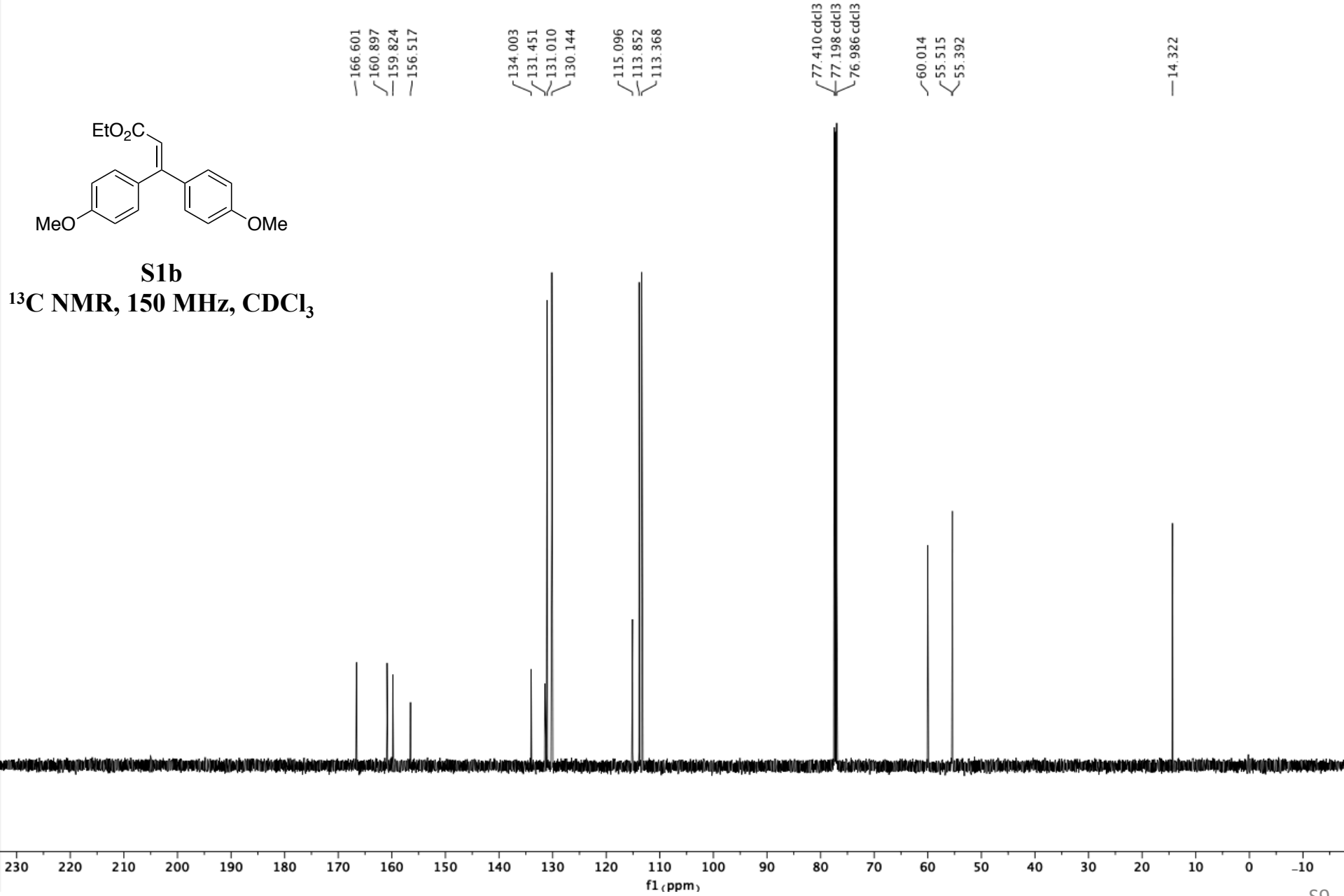
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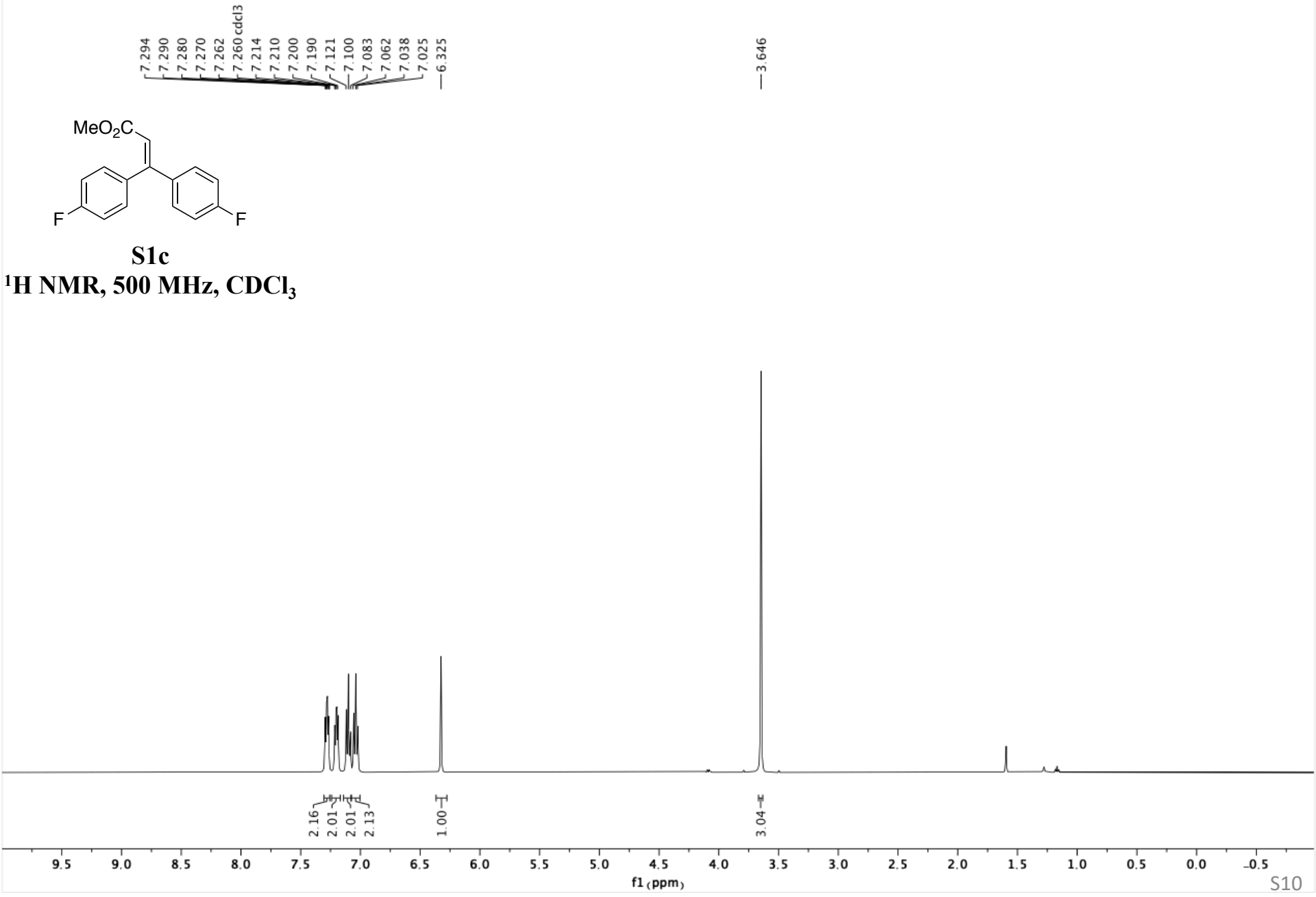
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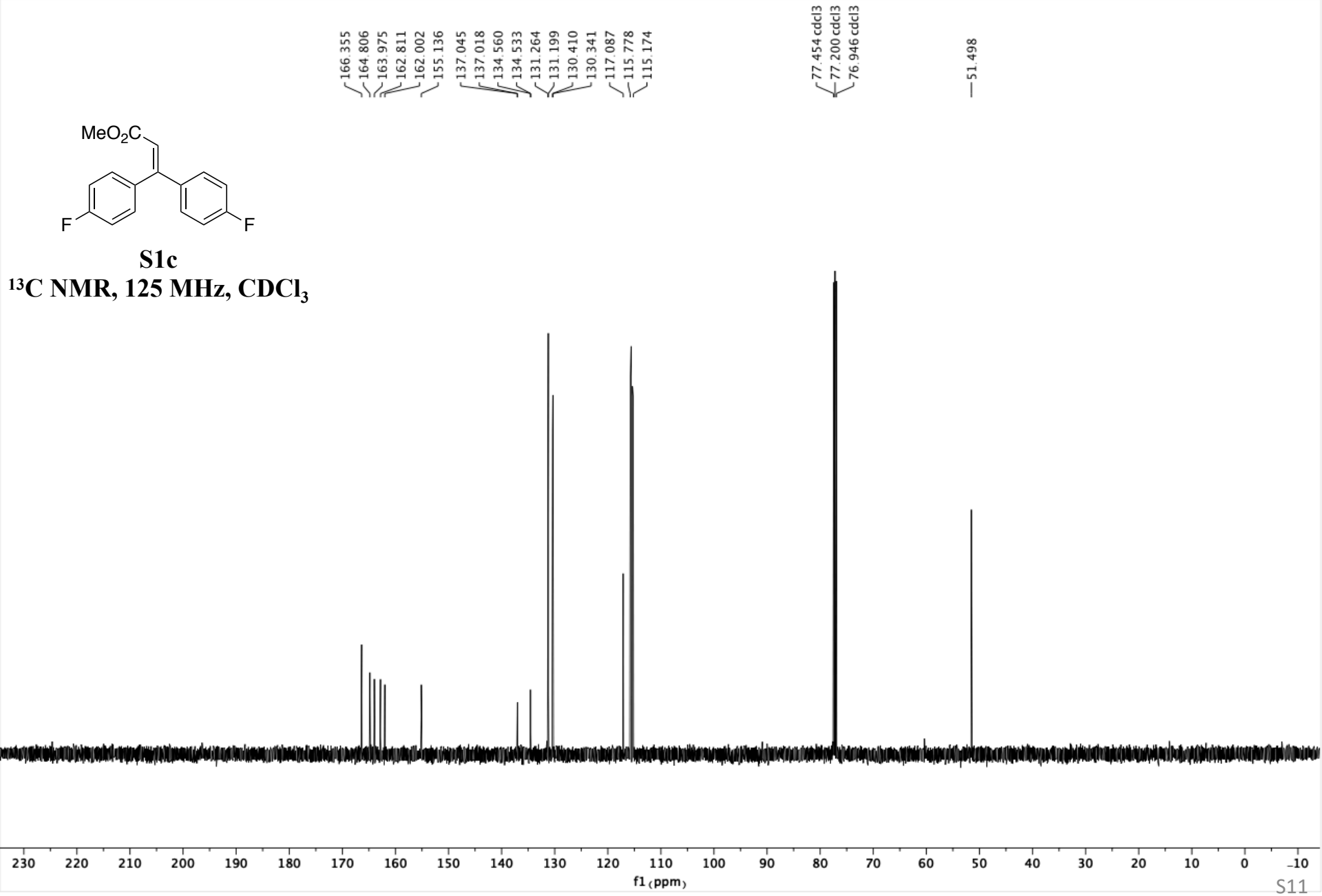
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S1c

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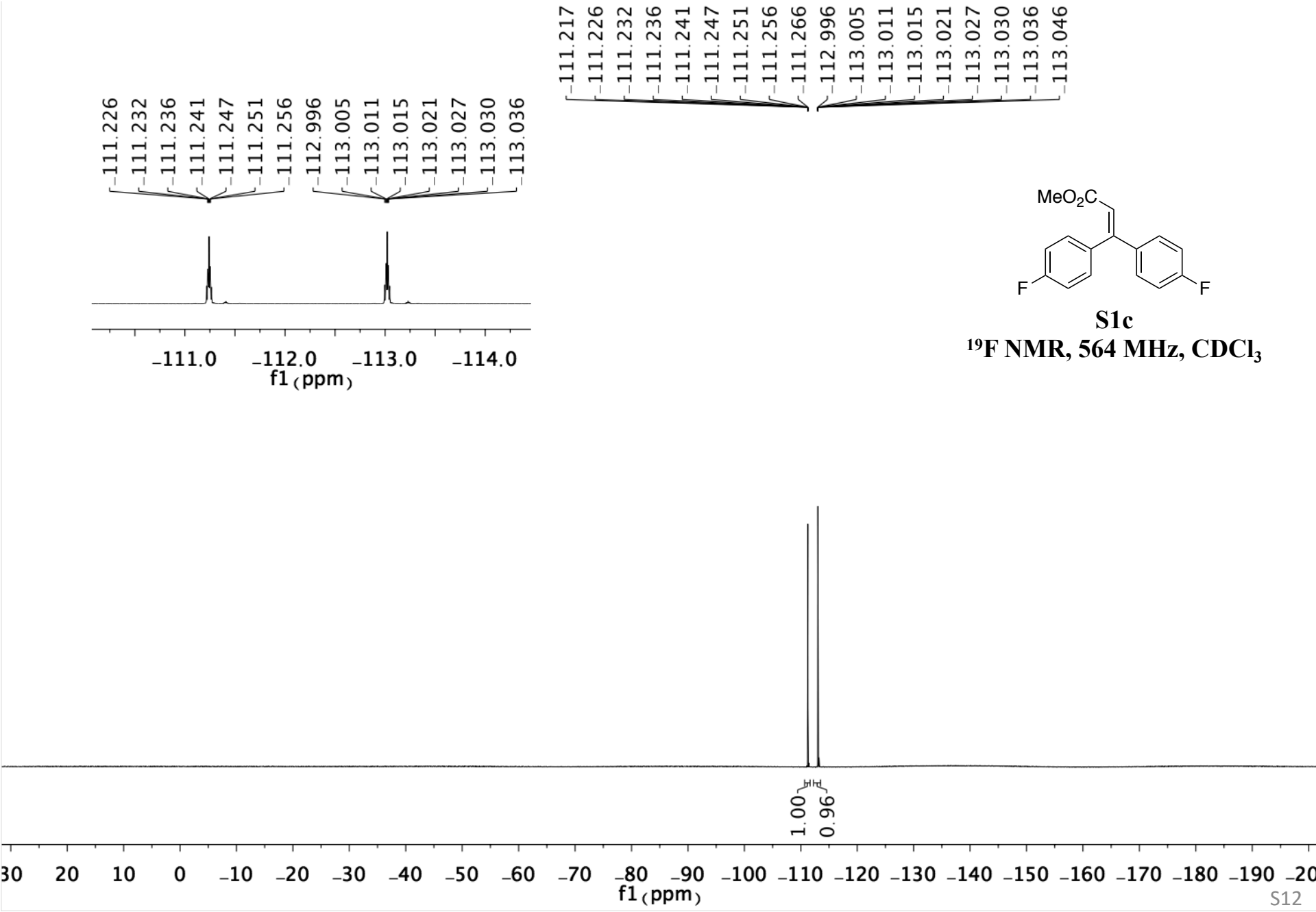
Methyl 3,3-bis(4-fluorophenyl)acrylate



S1c

^{13}C NMR, 125 MHz, $CDCl_3$

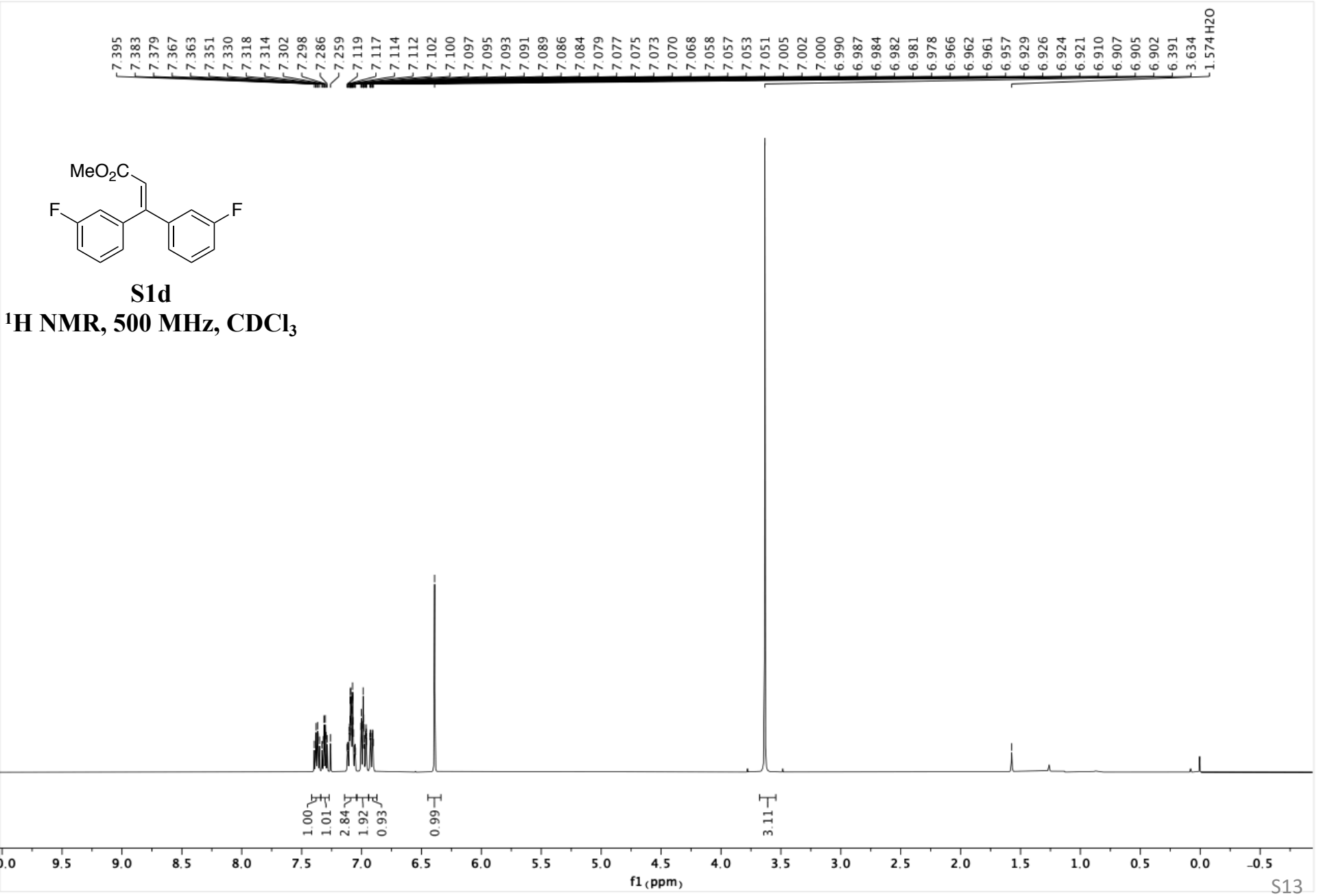
Methyl 3,3-bis(4-fluorophenyl)acrylate



S1c

^{19}F NMR, 564 MHz, $CDCl_3$

Methyl 3,3-bis(3-fluorophenyl)acrylate



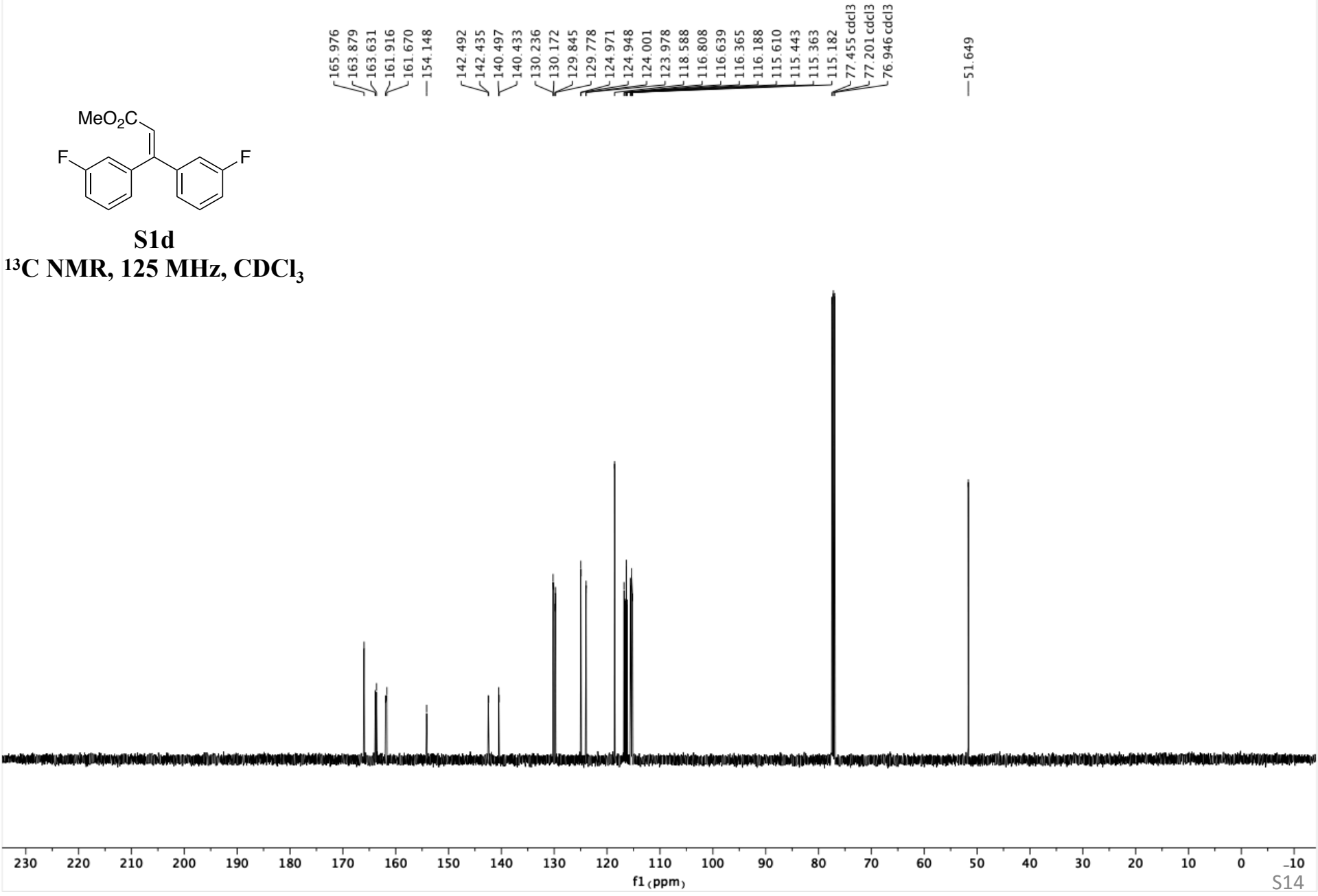
S1d

^{1}H NMR, 500 MHz, $CDCl_3$

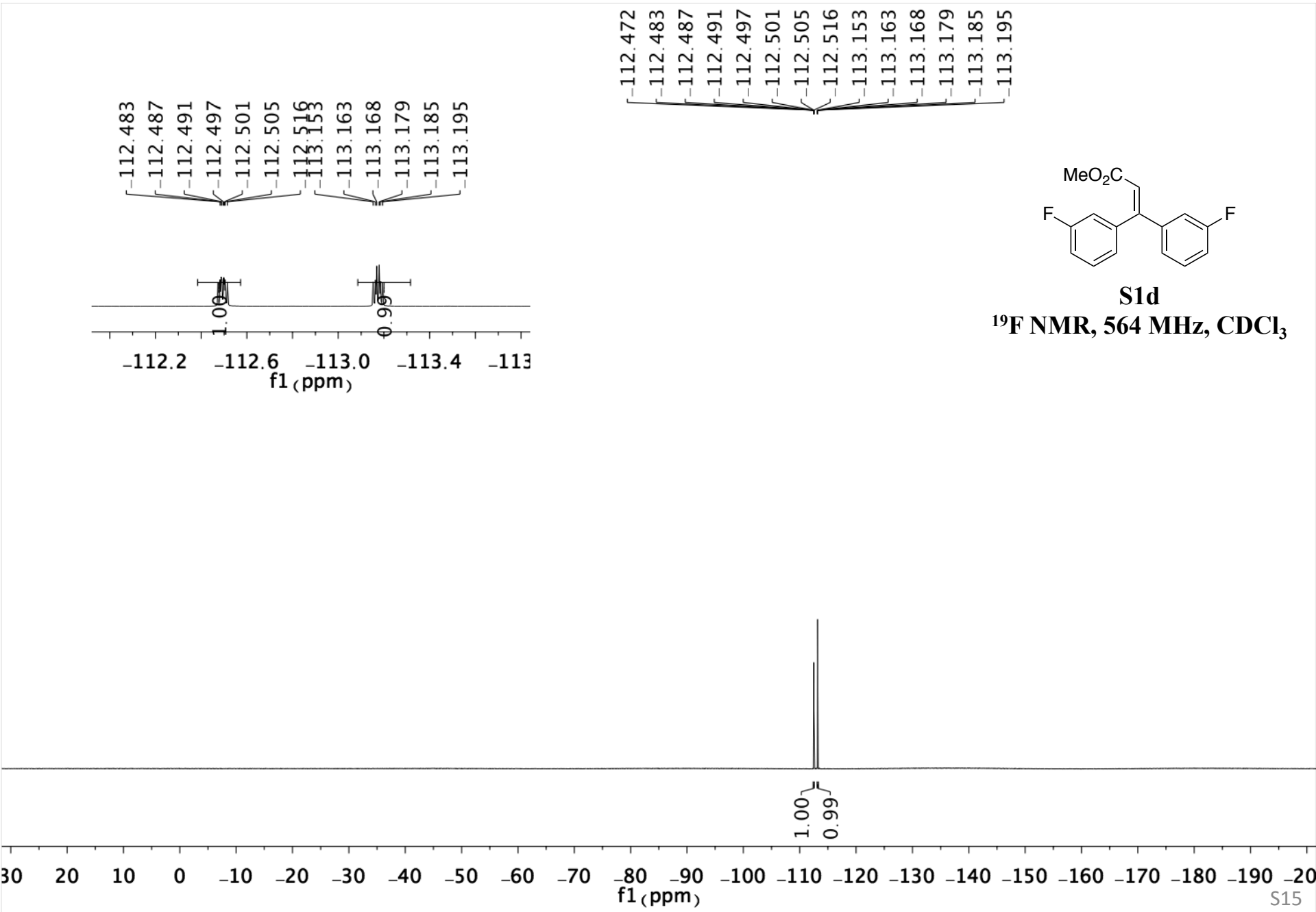
Methyl 3,3-bis(3-fluorophenyl)acrylate

S1d

^{13}C NMR, 125 MHz, $CDCl_3$



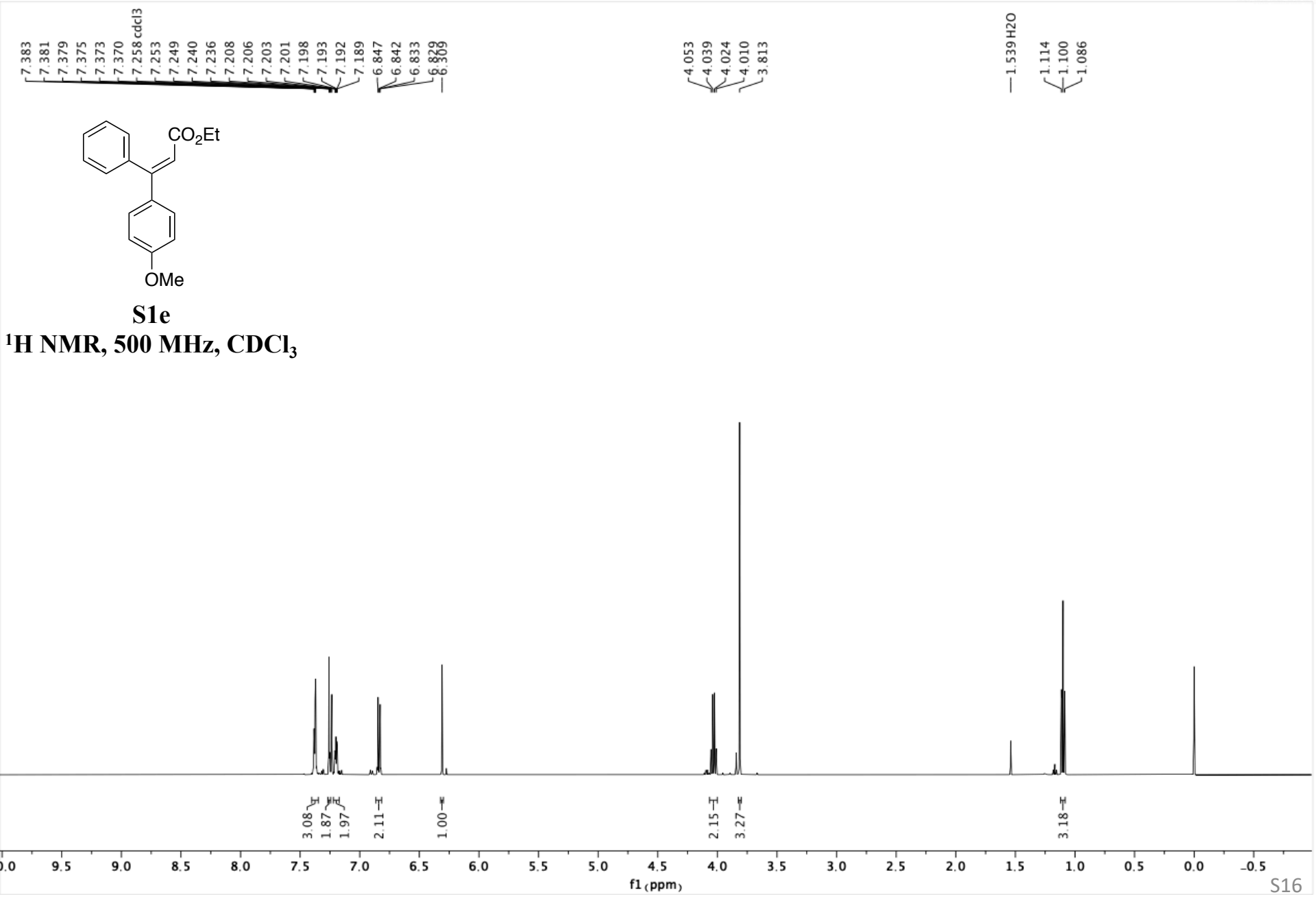
Methyl 3,3-bis(3-fluorophenyl)acrylate



S1d

^{19}F NMR, 564 MHz, $CDCl_3$

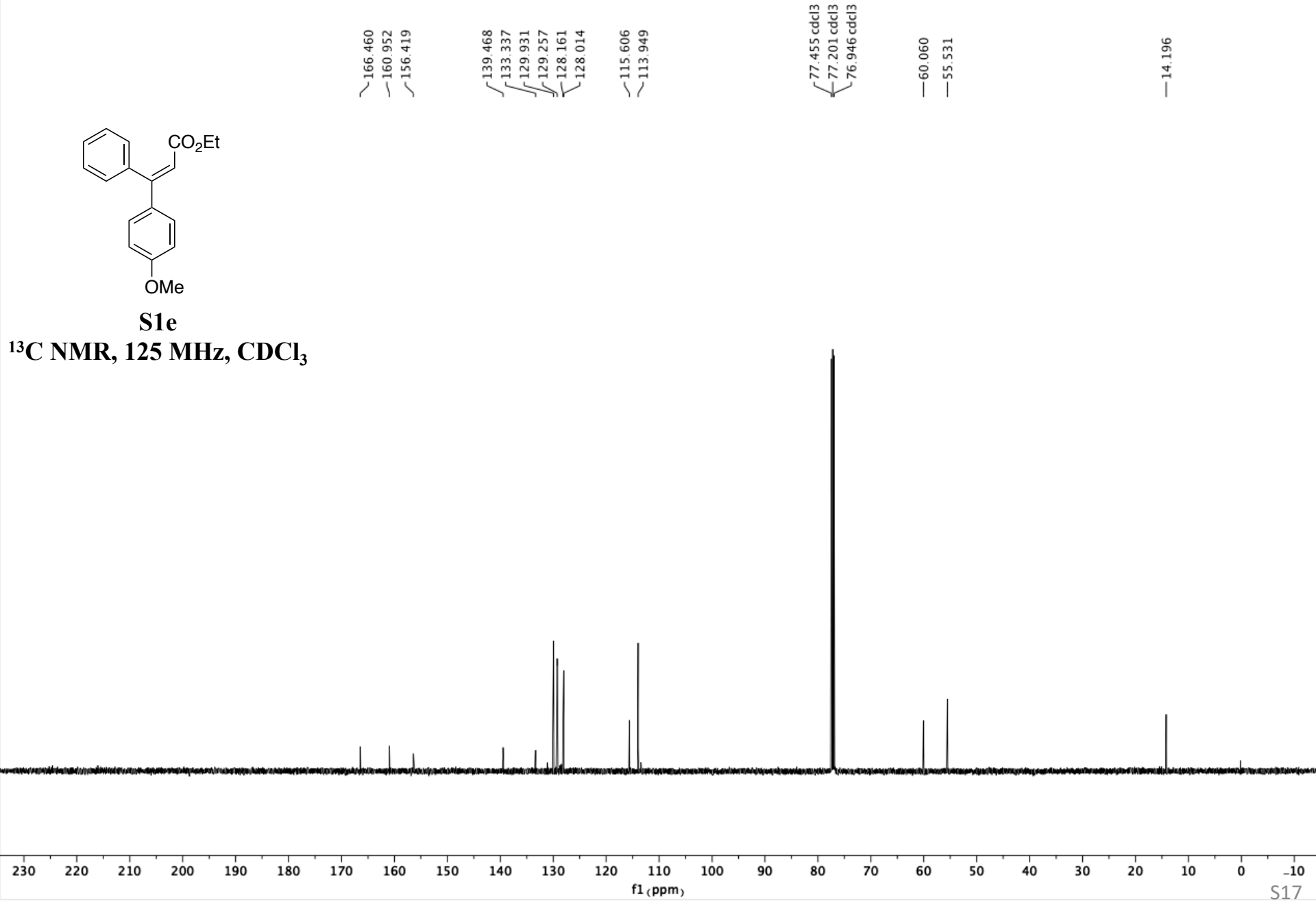
Ethyl (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate



S1e

^{1}H NMR, 500 MHz, $CDCl_3$

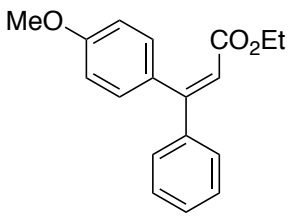
Ethyl (*E*)-3-(4-methoxyphenyl)-3-phenylacrylate



S1e

^{13}C NMR, 125 MHz, $CDCl_3$

Ethyl (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate



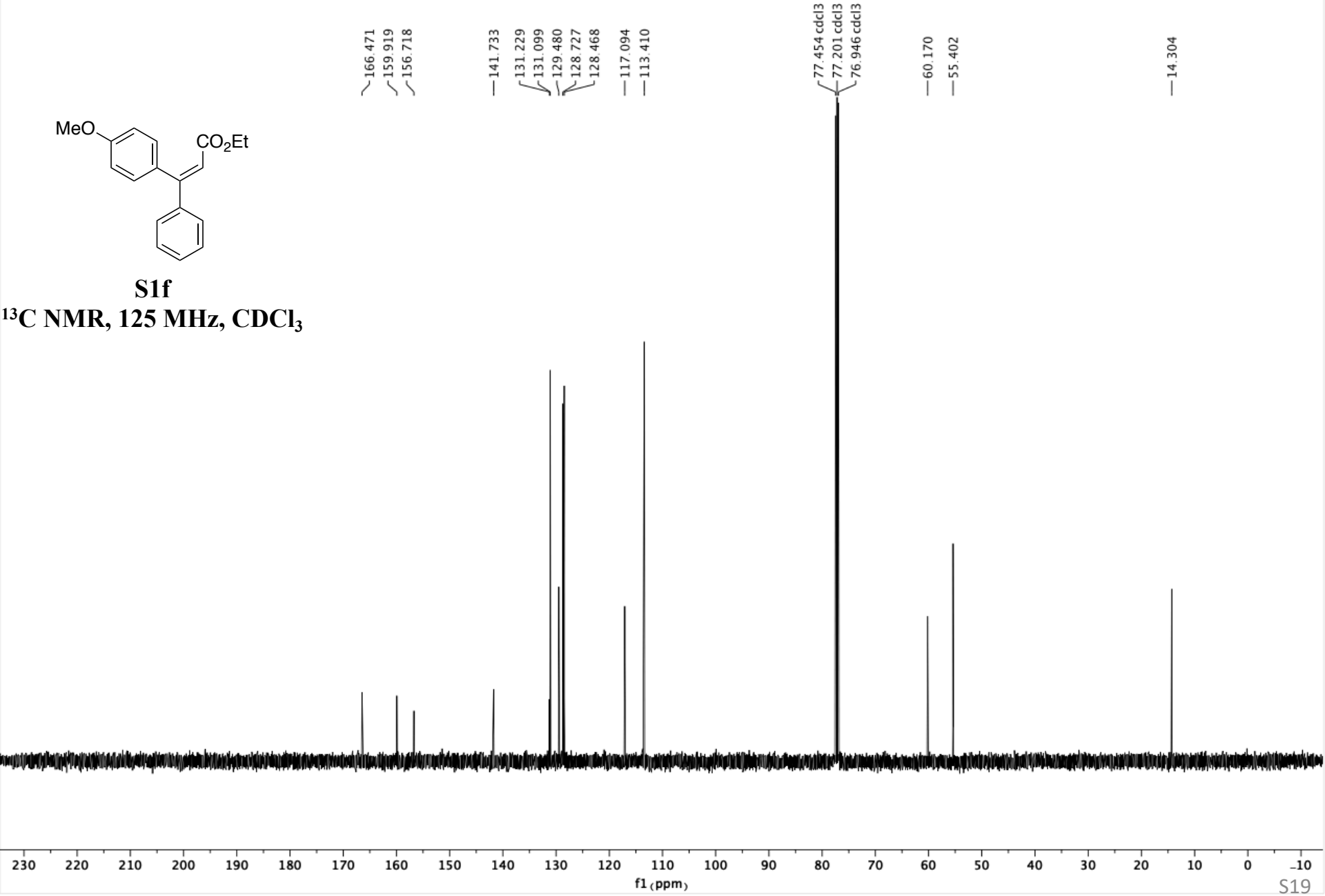
S1f

^{1}H NMR, 500 MHz, $CDCl_3$

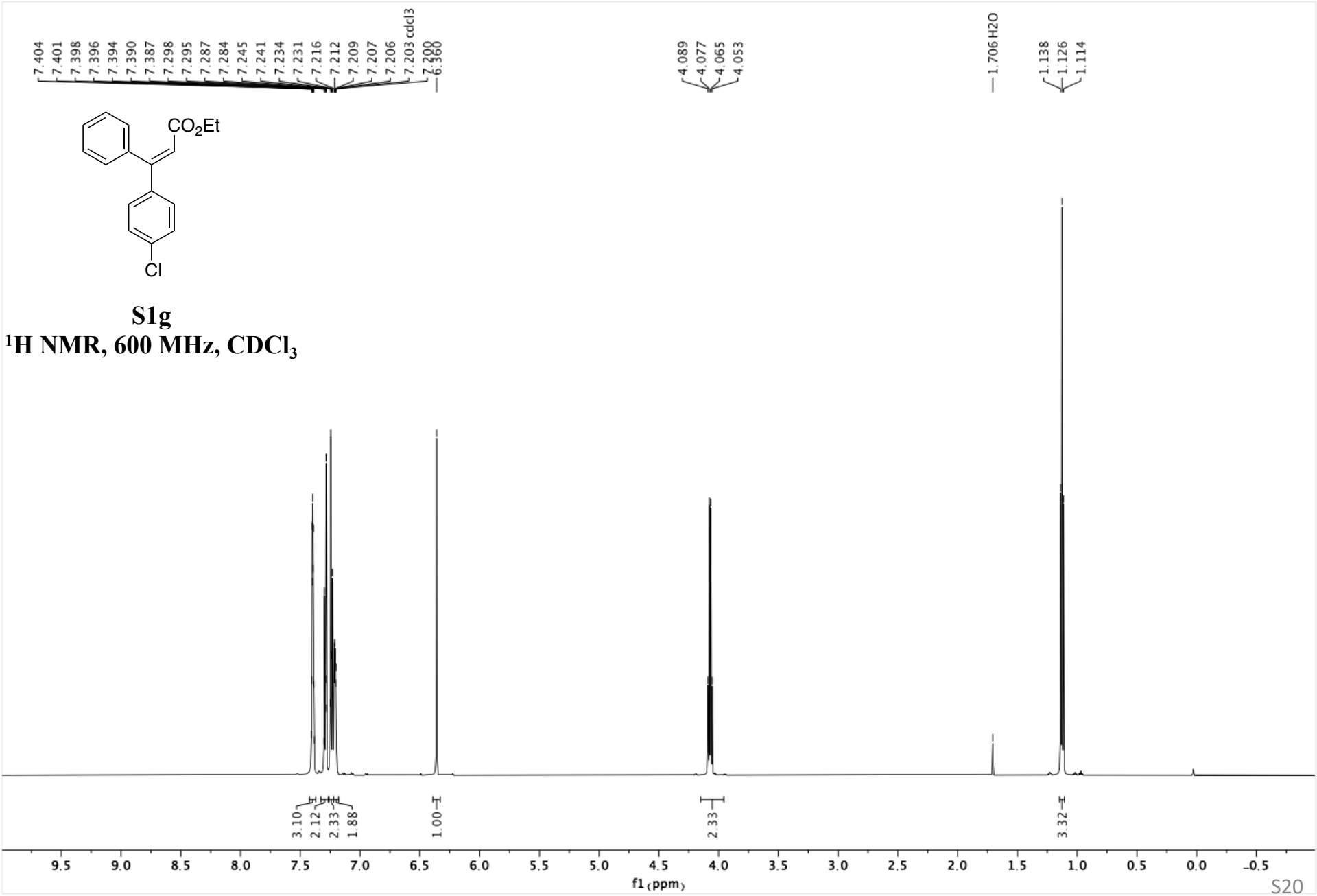
Ethyl (*Z*)-3-(4-methoxyphenyl)-3-phenylacrylate

S1f

^{13}C NMR, 125 MHz, $CDCl_3$



Ethyl (*E*)-3-(4-chlorophenyl)-3-phenylacrylate



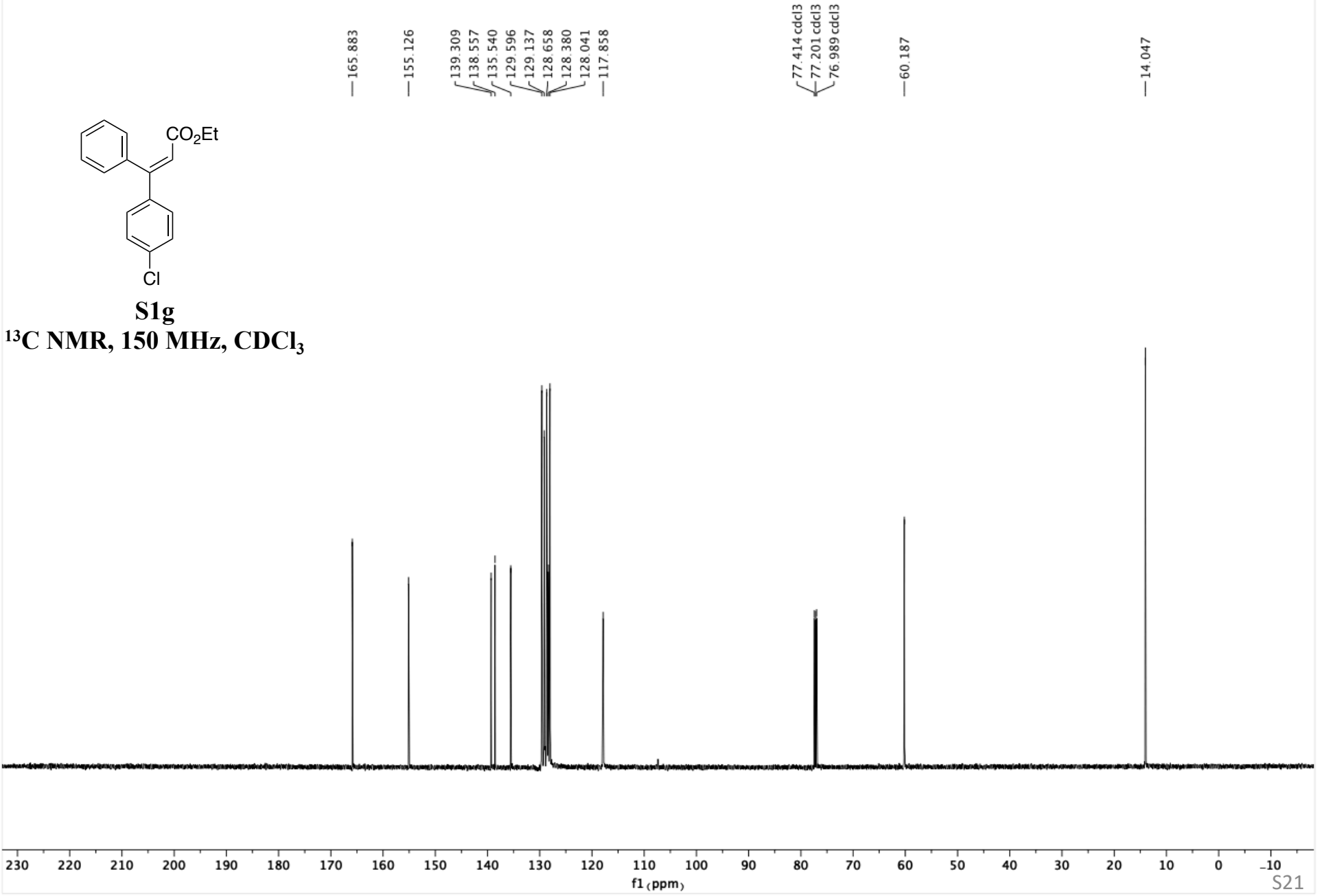
S1g

^{1}H NMR, 600 MHz, $CDCl_3$

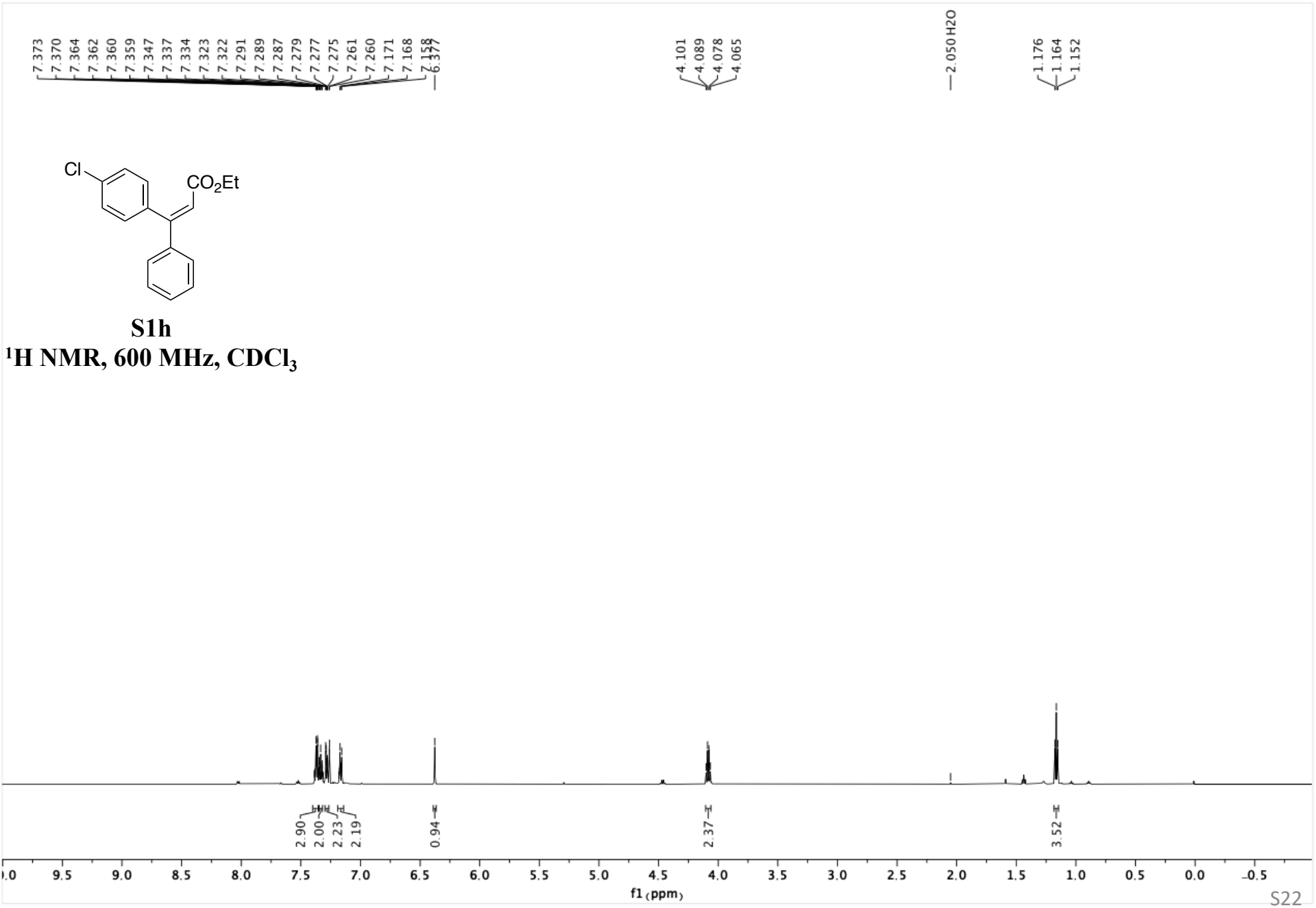
Ethyl (*E*)-3-(4-chlorophenyl)-3-phenylacrylate

S1g

^{13}C NMR, 150 MHz, $CDCl_3$



Ethyl (*Z*)-3-(4-chlorophenyl)-3-phenylacrylate



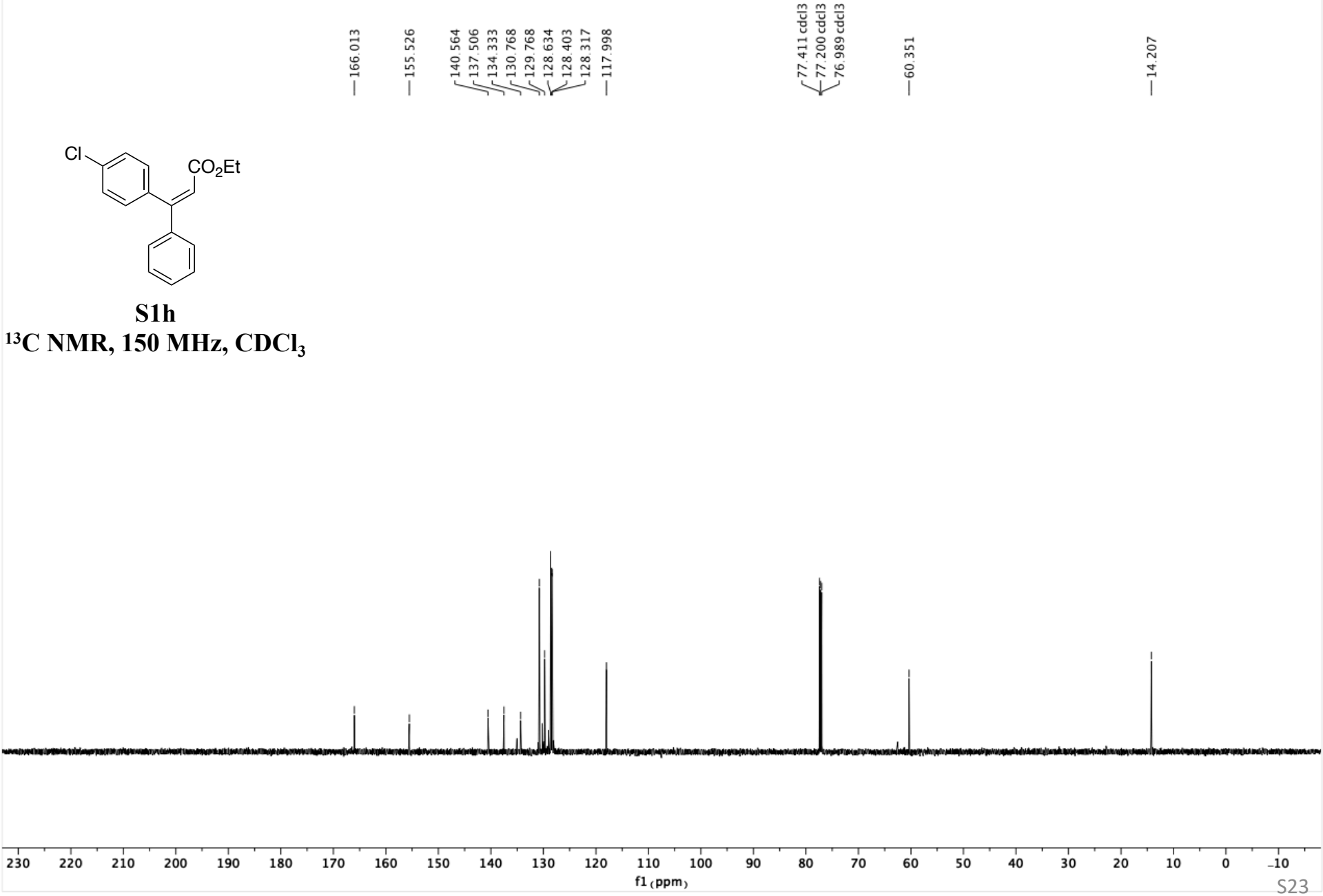
S1h

^{1}H NMR, 600 MHz, $CDCl_3$

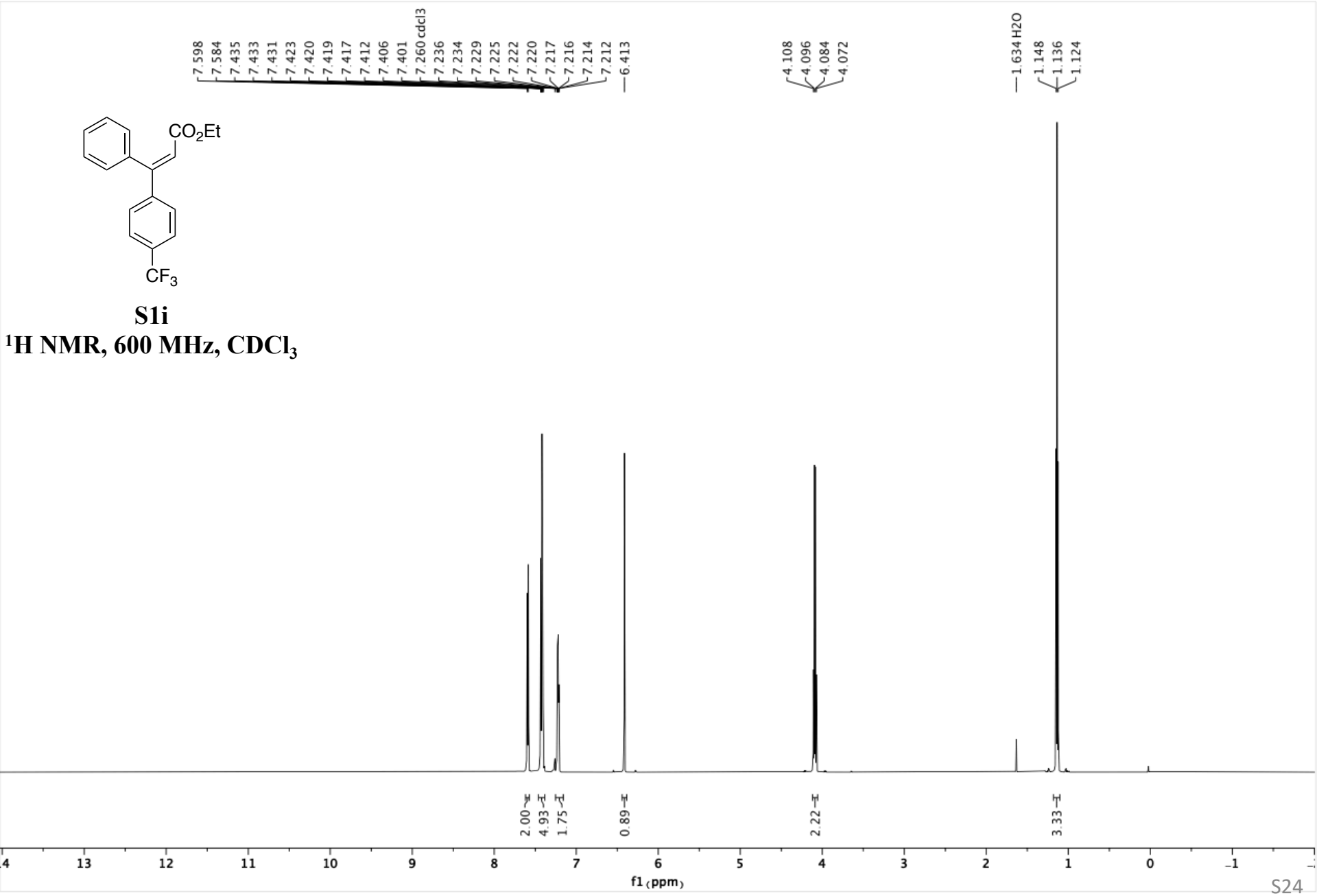
Ethyl (*Z*)-3-(4-chlorophenyl)-3-phenylacrylate

S1h

^{13}C NMR, 150 MHz, $CDCl_3$



Ethyl (*E*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)acrylate



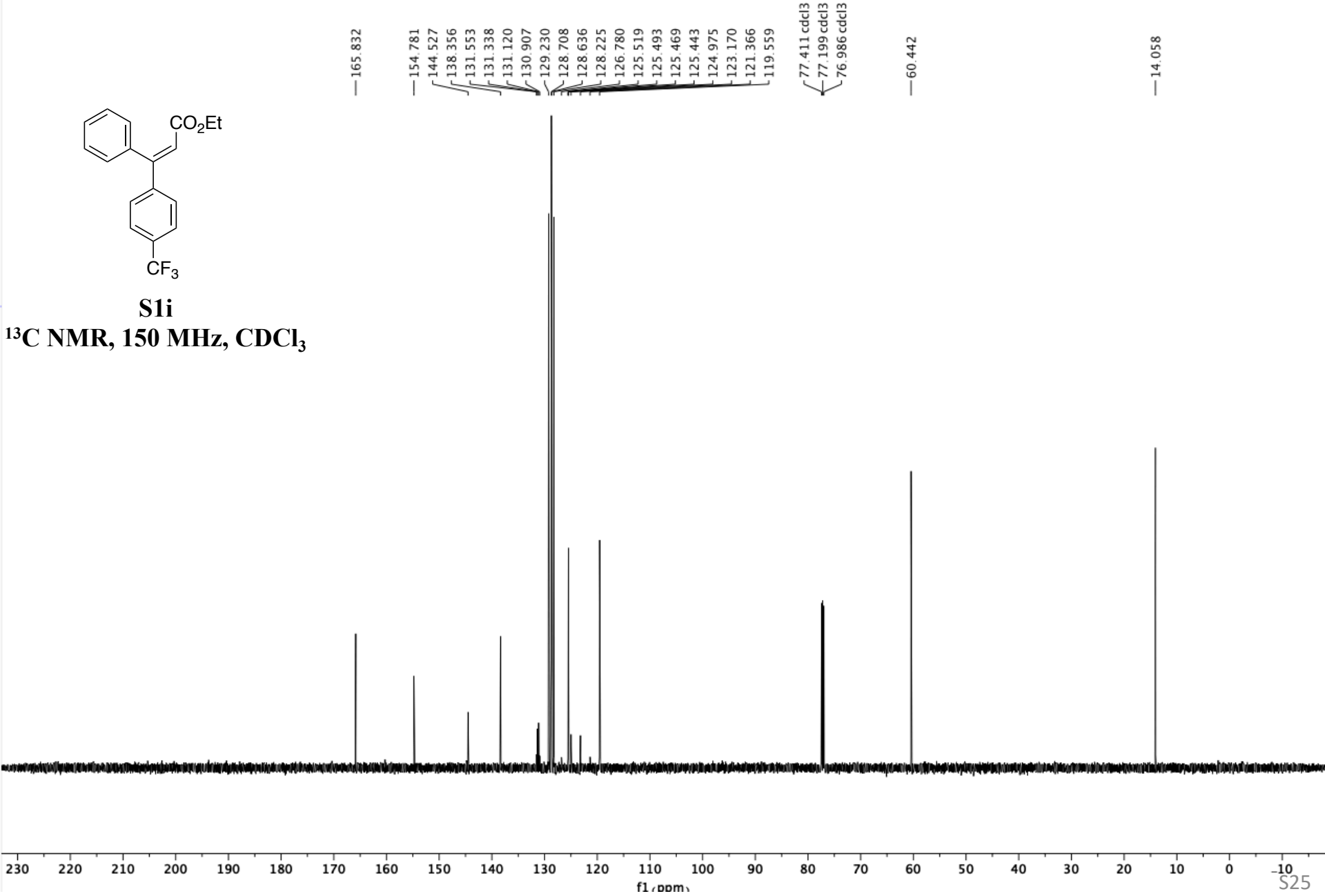
S1i

^{1}H NMR, 600 MHz, $CDCl_3$

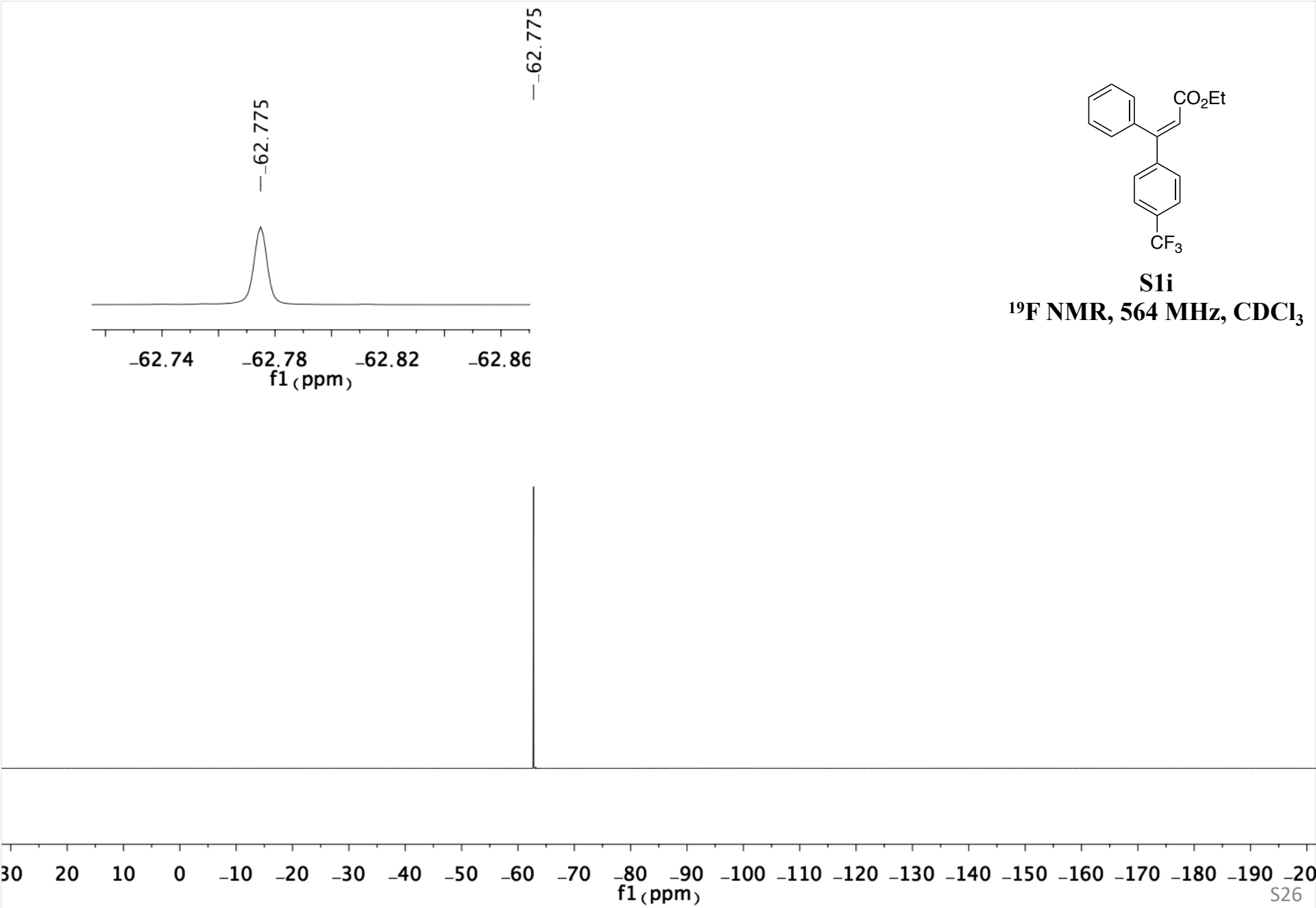
Ethyl (*E*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)acrylate

S1i

^{13}C NMR, 150 MHz, $CDCl_3$



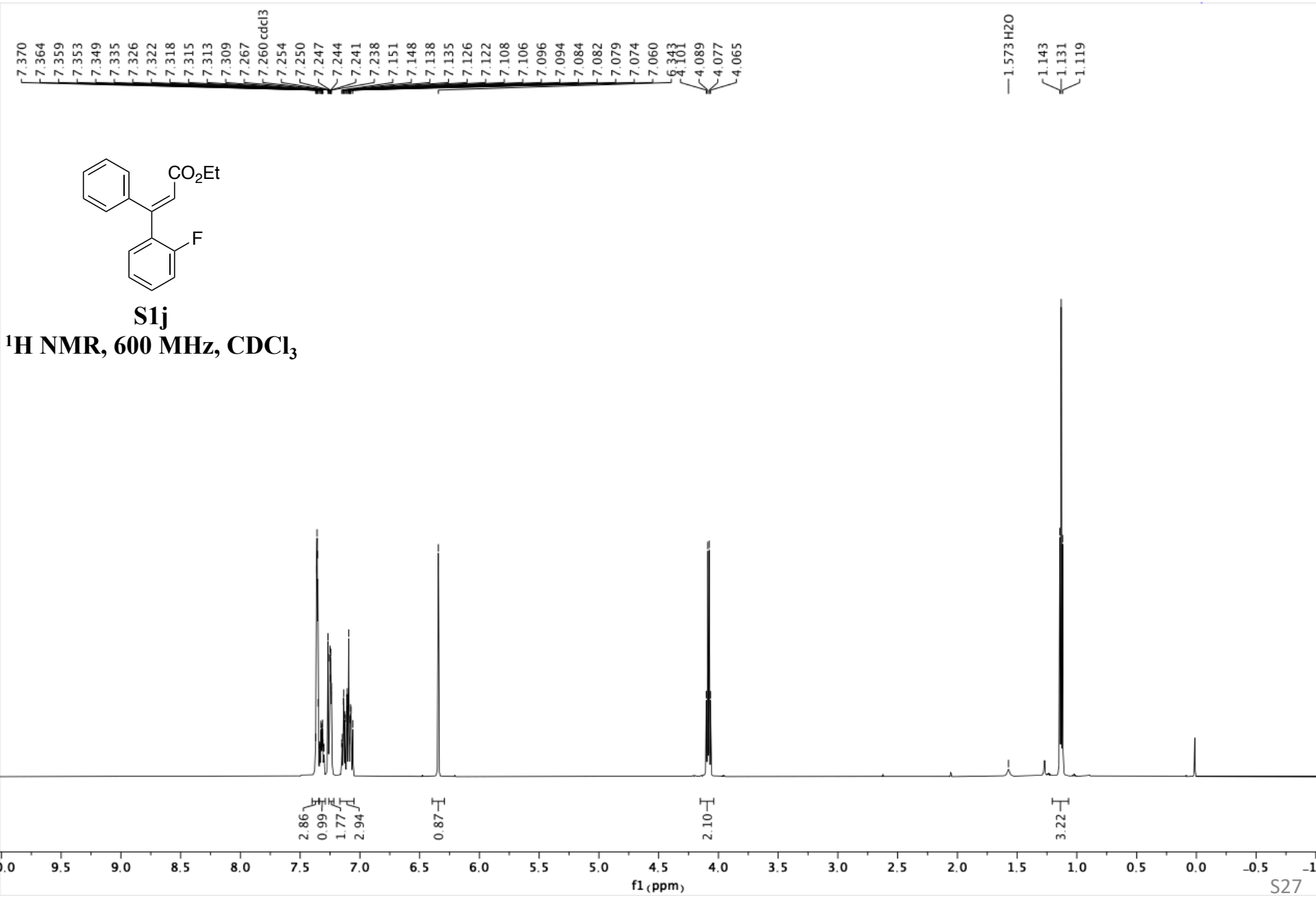
Ethyl (*E*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)acrylate



S1i

^{19}F NMR, 564 MHz, $CDCl_3$

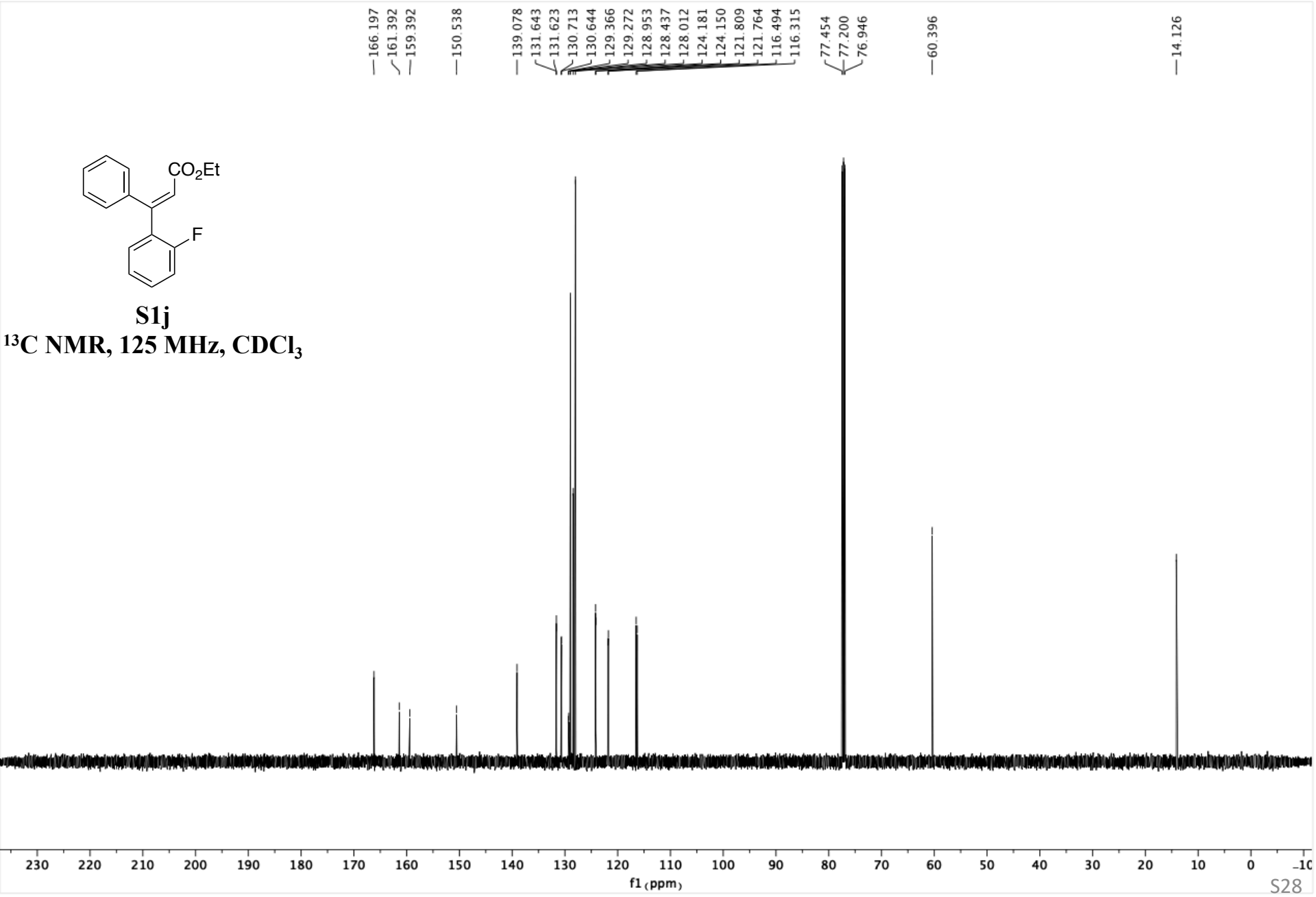
Ethyl (*E*)-3-(2-fluorophenyl)-3-phenylacrylate



S1j

^{1}H NMR, 600 MHz, $CDCl_3$

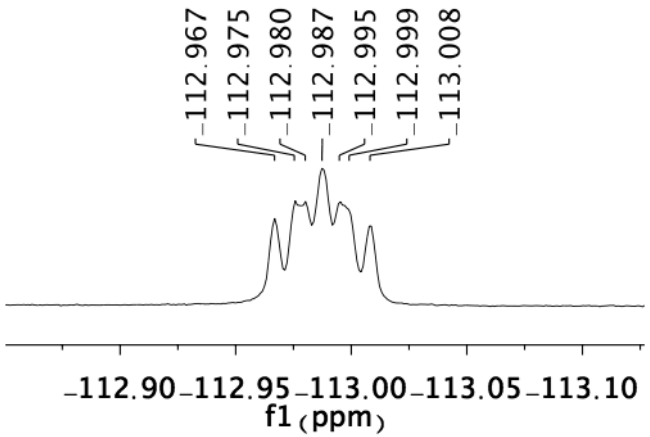
Ethyl (*E*)-3-(2-fluorophenyl)-3-phenylacrylate

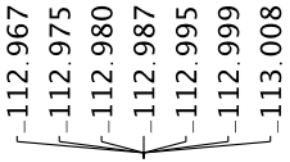


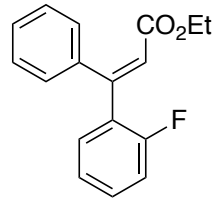
S1j

^{13}C NMR, 125 MHz, $CDCl_3$

Ethyl (*E*)-3-(2-fluorophenyl)-3-phenylacrylate

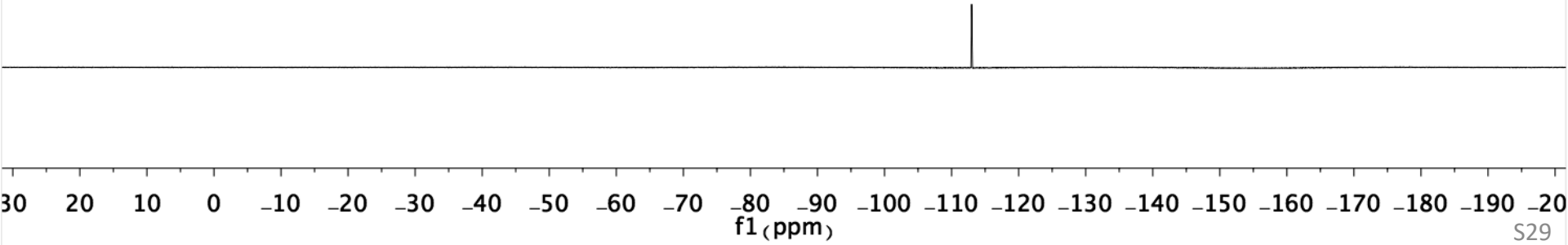




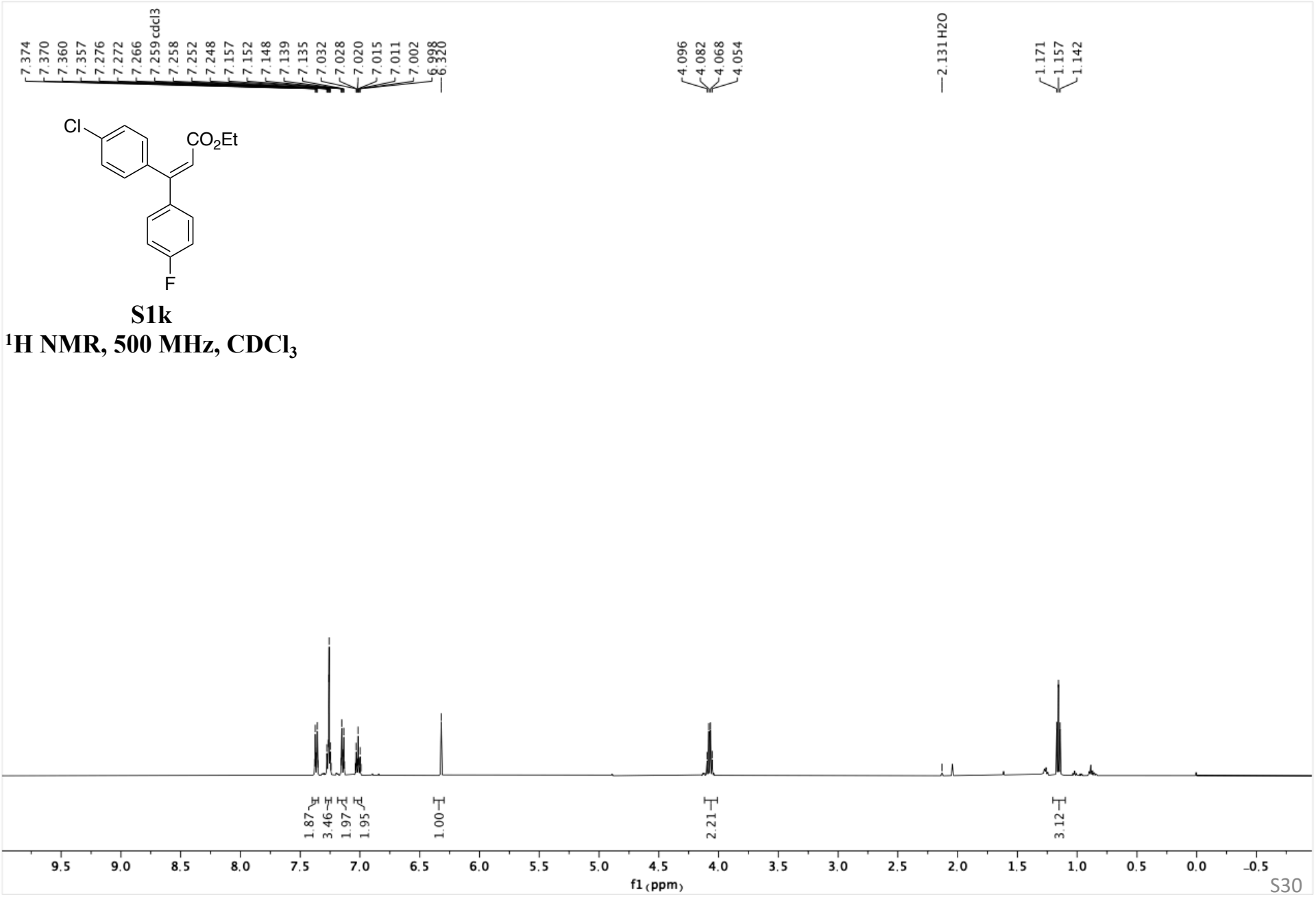


S1j

^{19}F NMR, 564 MHz, $CDCl_3$



Ethyl (*Z*)-3-(4-chlorophenyl)-3-(4-fluorophenyl)acrylate



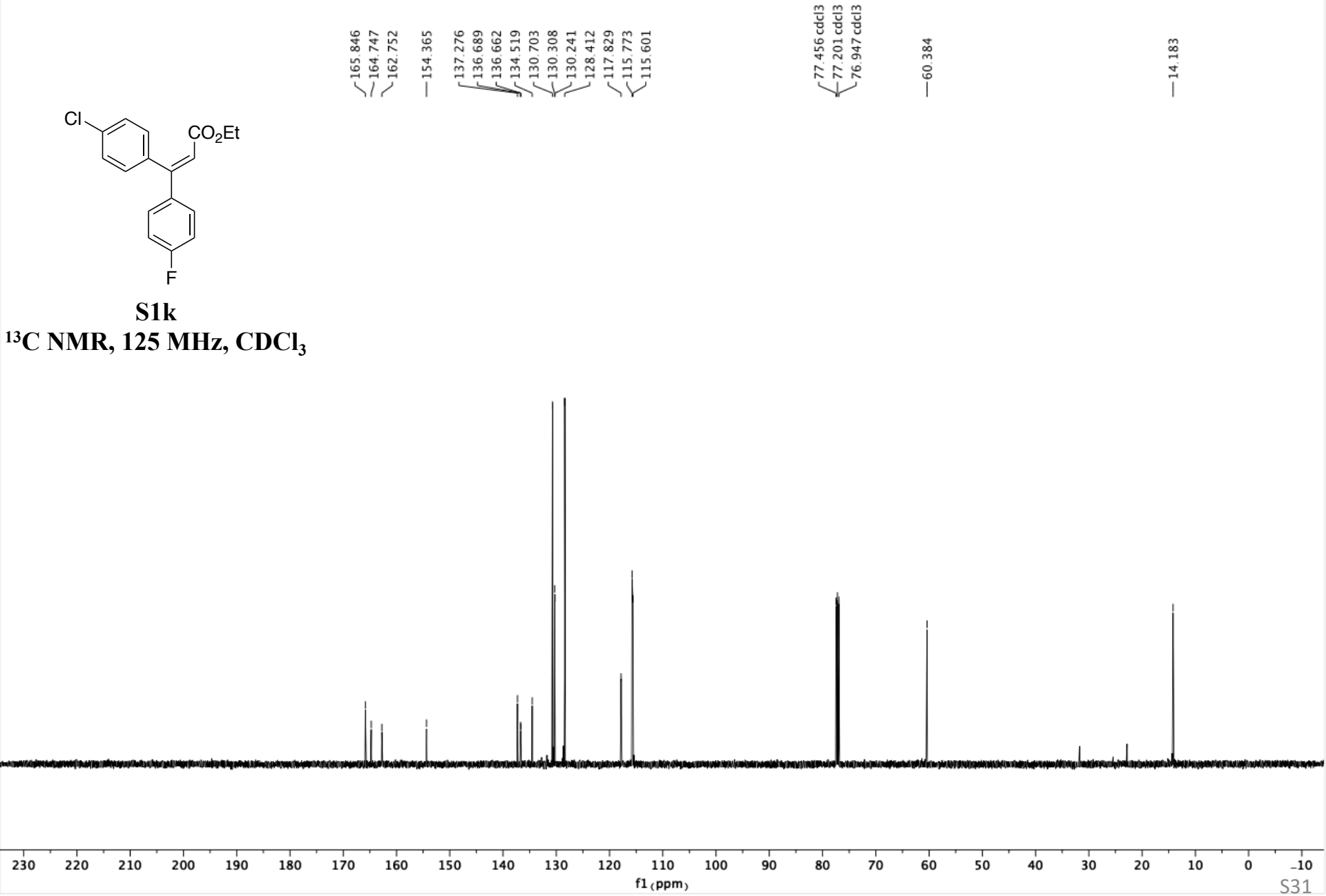
S1k

^{1}H NMR, 500 MHz, $CDCl_3$

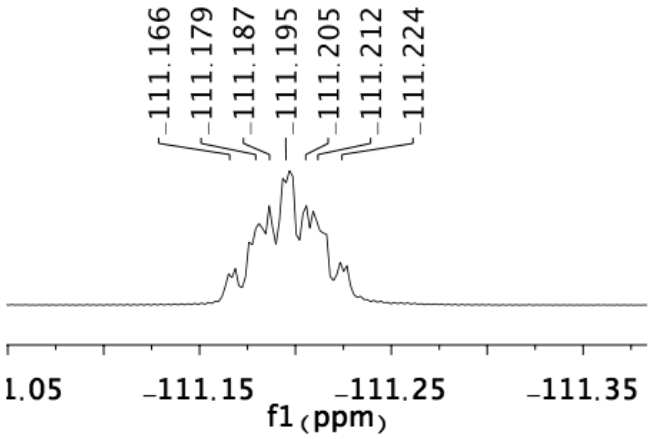
Ethyl (*Z*)-3-(4-chlorophenyl)-3-(4-fluorophenyl)acrylate

S1k

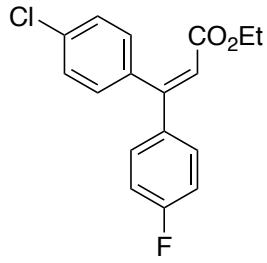
^{13}C NMR, 125 MHz, $CDCl_3$



Ethyl (*Z*)-3-(4-chlorophenyl)-3-(4-fluorophenyl)acrylate

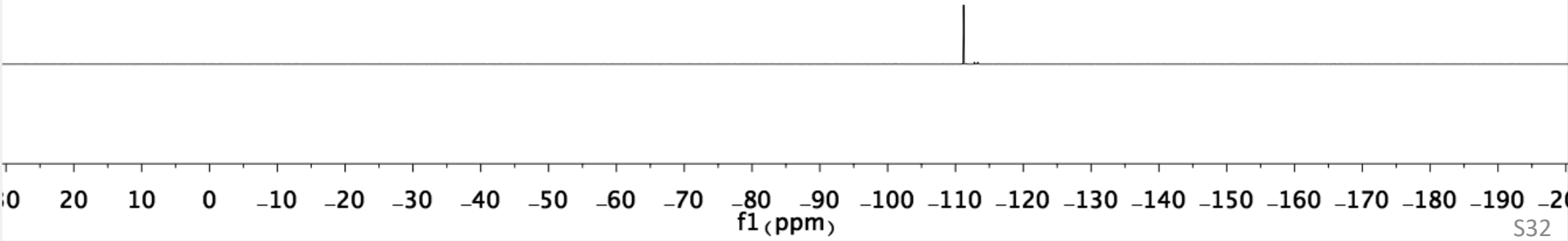




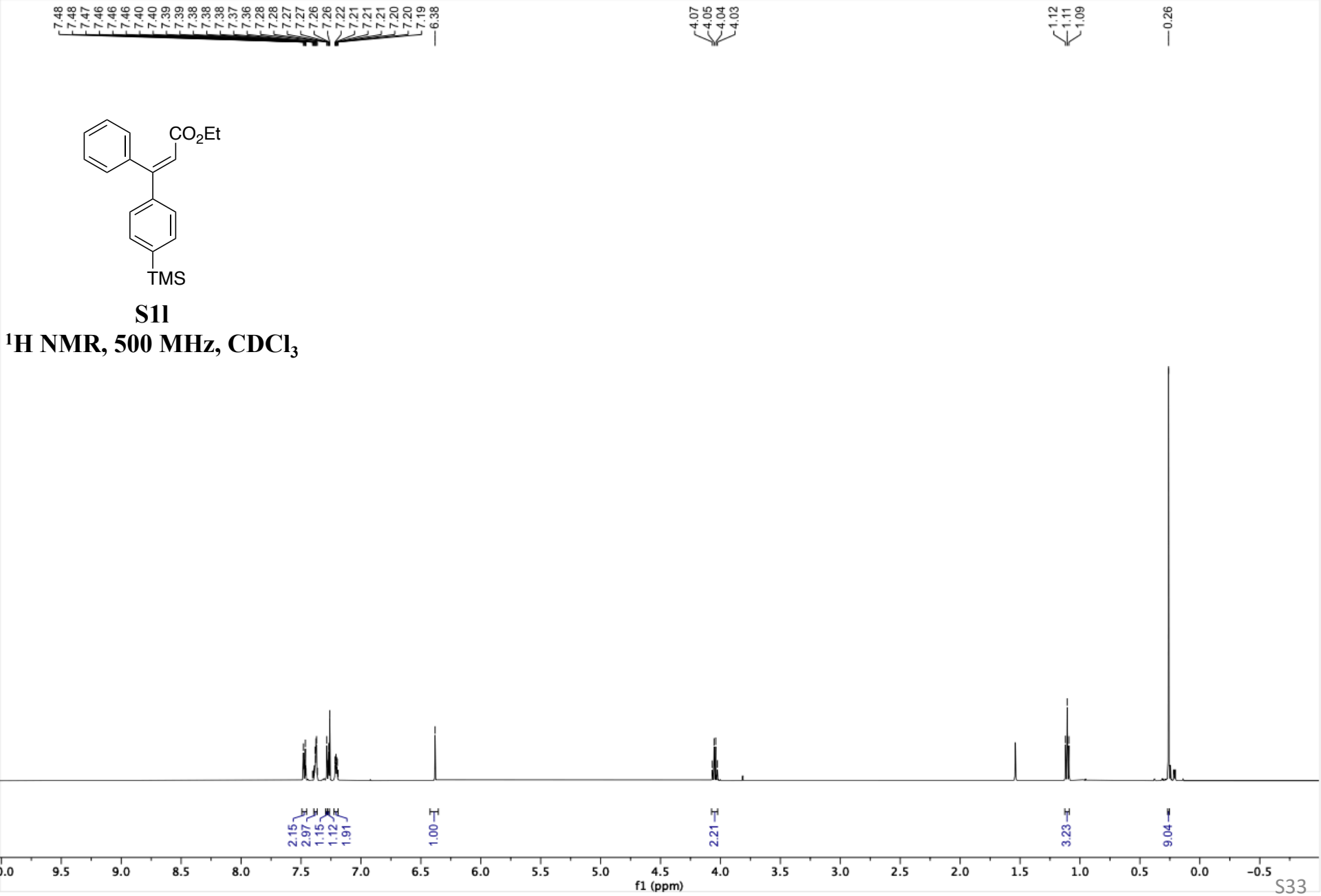


S1k

^{19}F NMR, 564 MHz, $CDCl_3$



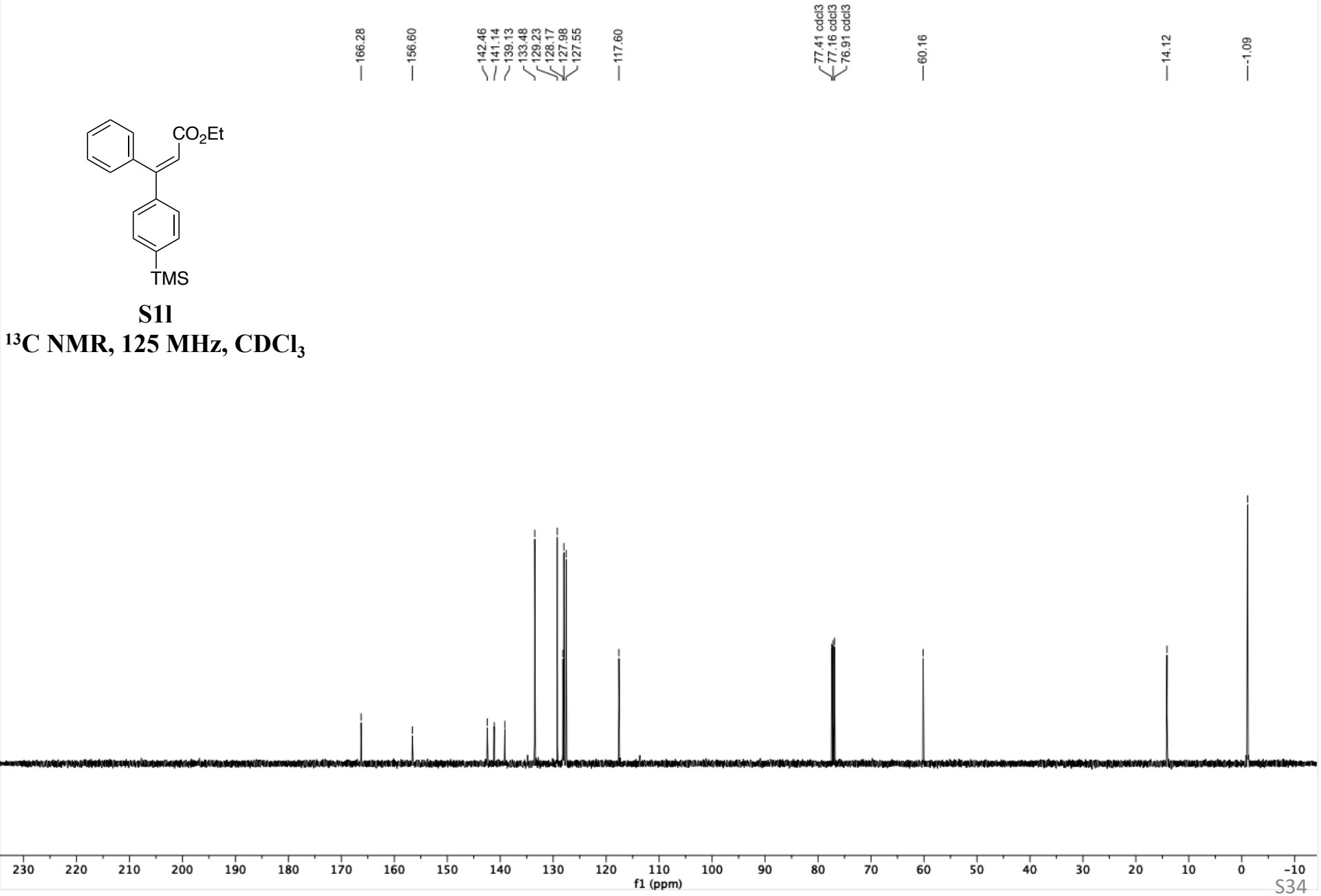
Ethyl (*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)acrylate



S11

^{1}H NMR, 500 MHz, $CDCl_3$

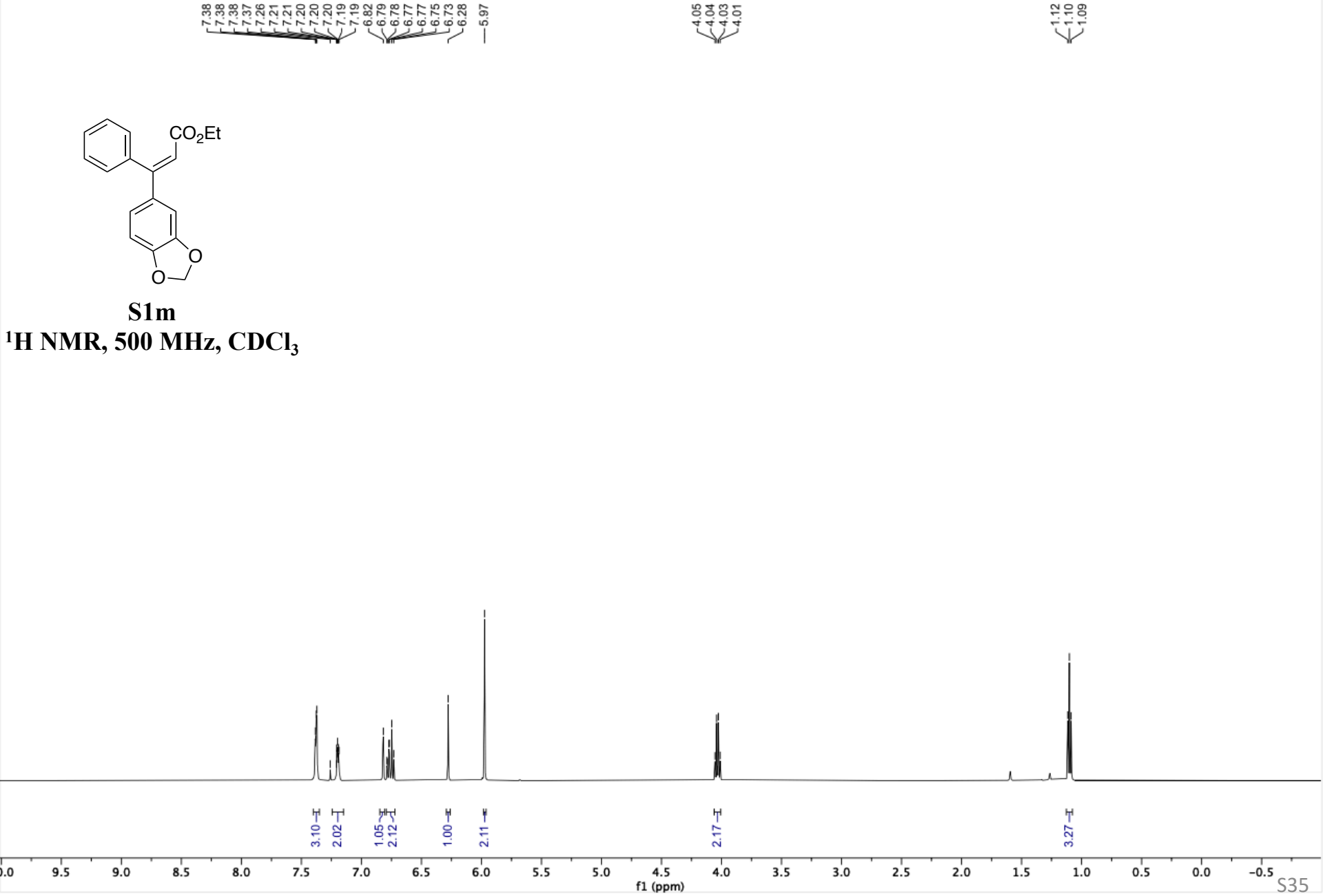
Ethyl (*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)acrylate



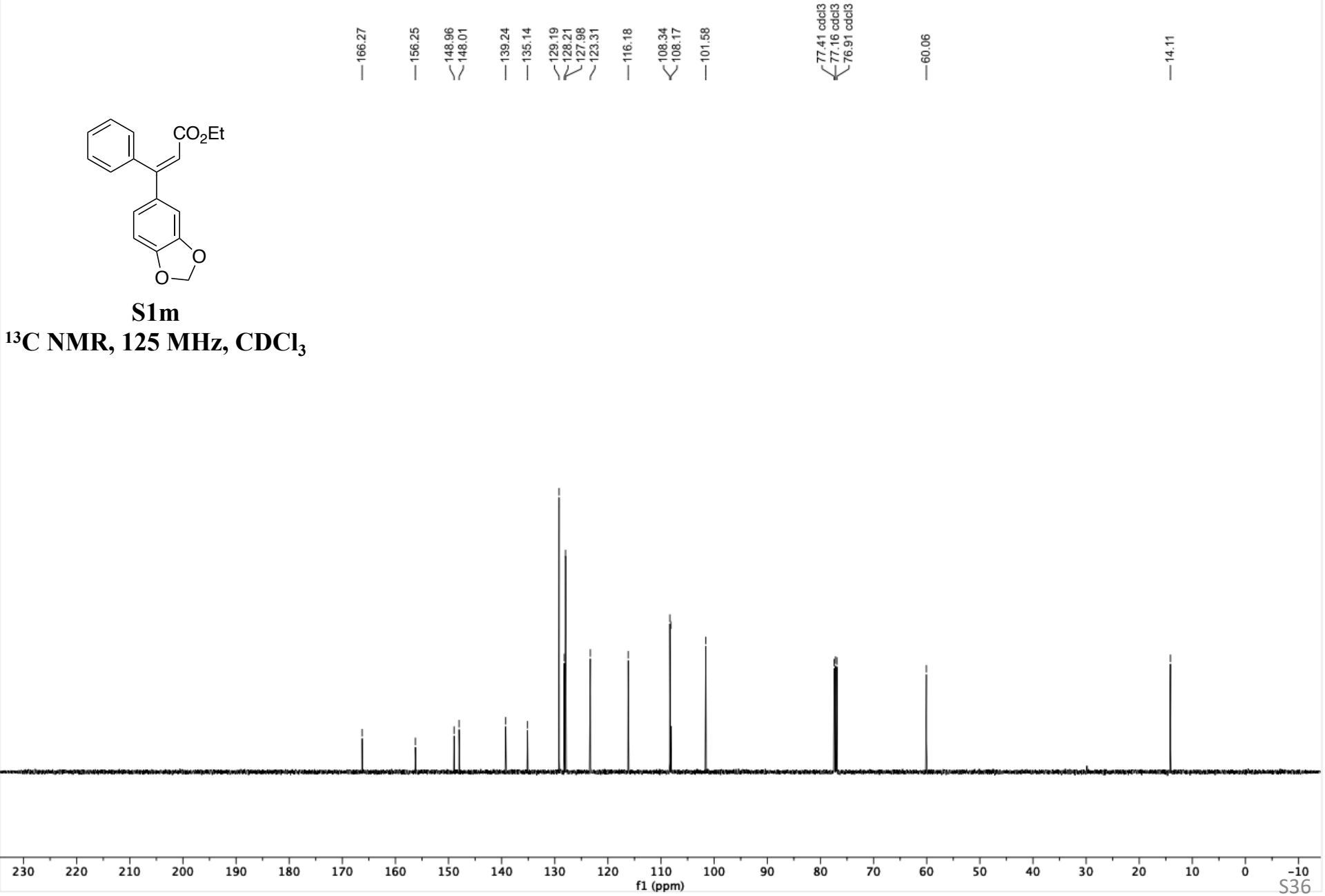
S11

^{13}C NMR, 125 MHz, $CDCl_3$

Ethyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylacrylate



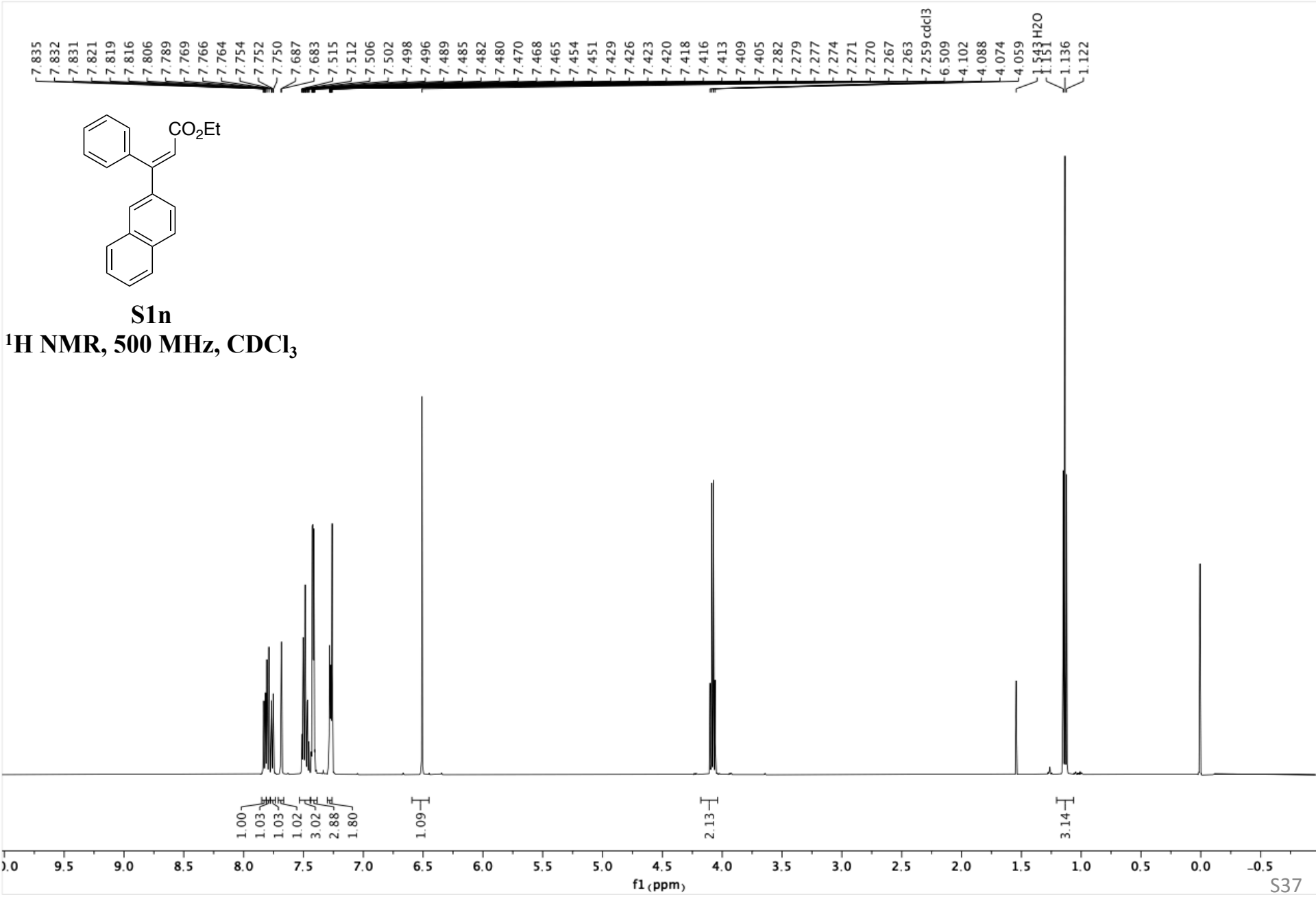
Ethyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylacrylate



S1m

^{13}C NMR, 125 MHz, $CDCl_3$

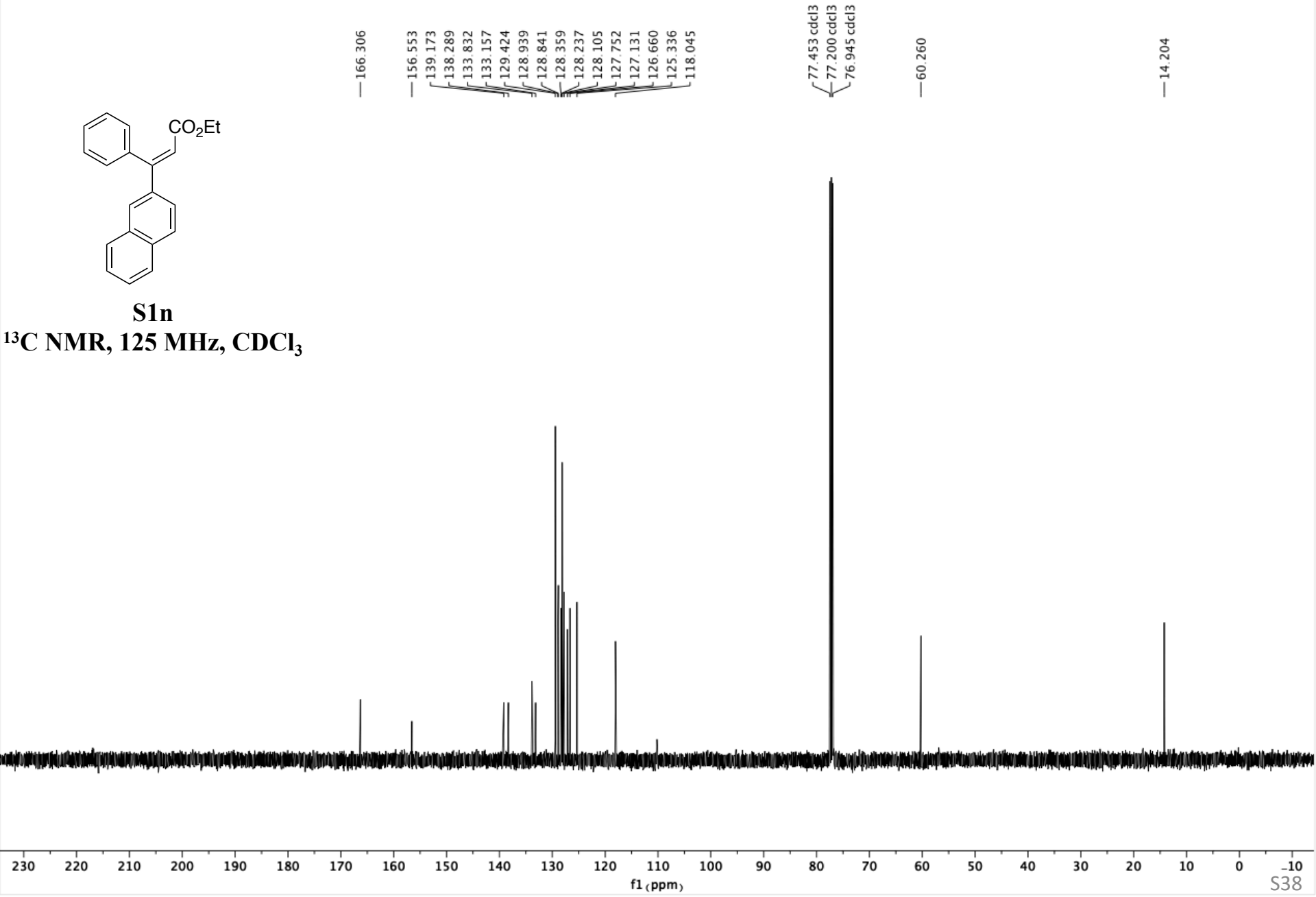
Ethyl (*E*)-3-(naphthalen-2-yl)-3-phenylacrylate



S1n

^{1}H NMR, 500 MHz, $CDCl_3$

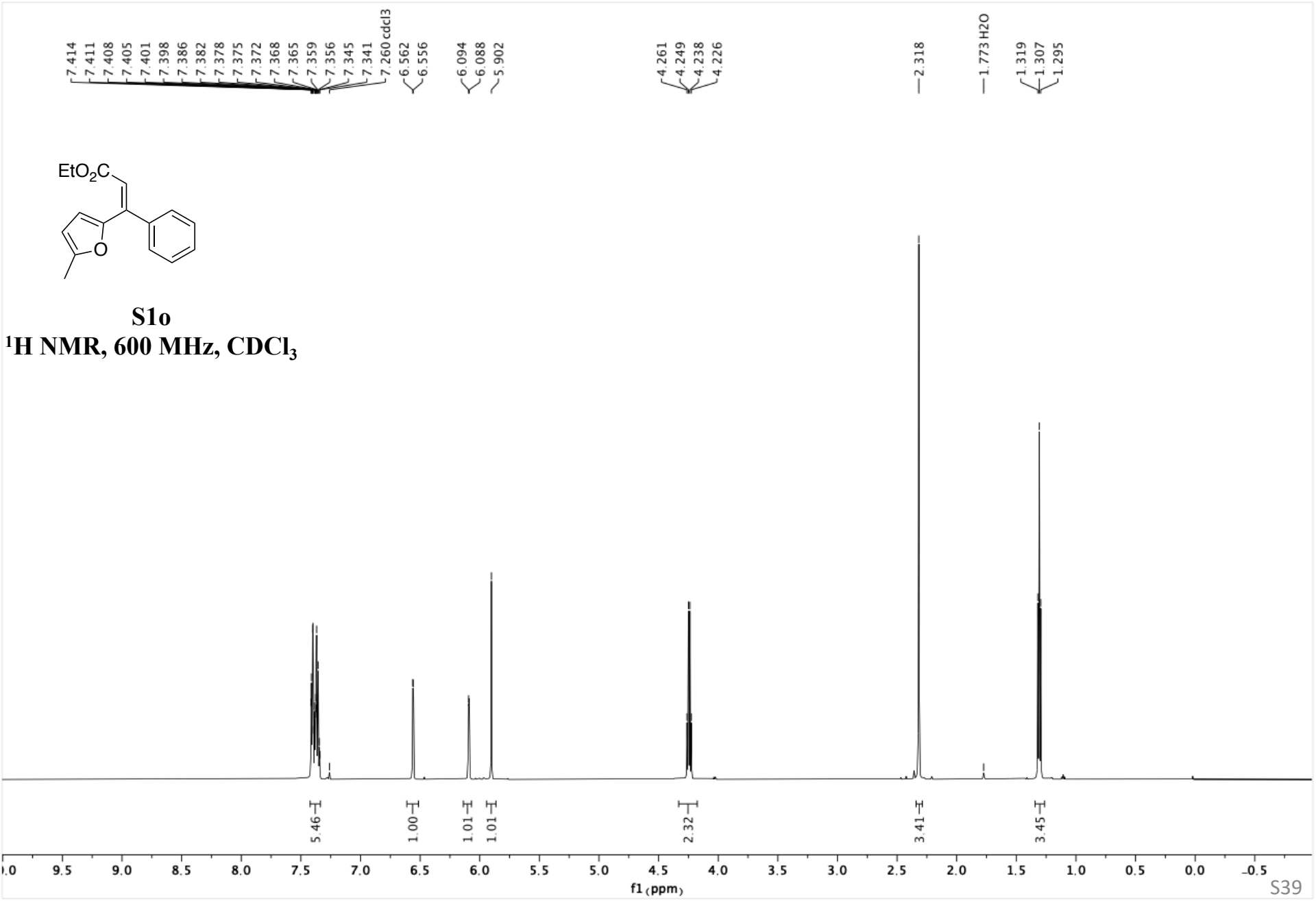
Ethyl (*E*)-3-(naphthalen-2-yl)-3-phenylacrylate



S1n

^{13}C NMR, 125 MHz, $CDCl_3$

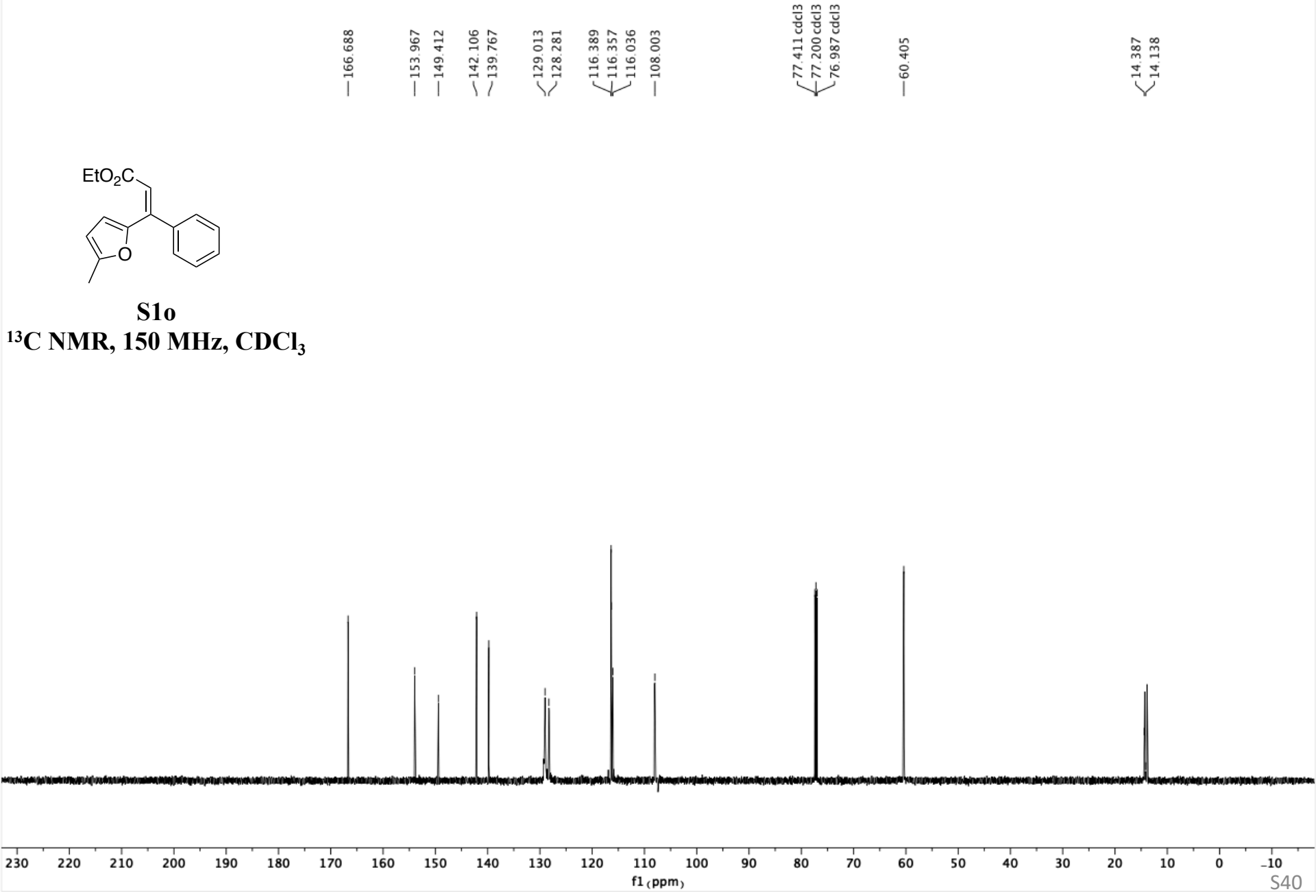
Ethyl (*Z*)-3-(5-methylfuran-2-yl)-3-phenylacrylate



S1o

^{1}H NMR, 600 MHz, $CDCl_3$

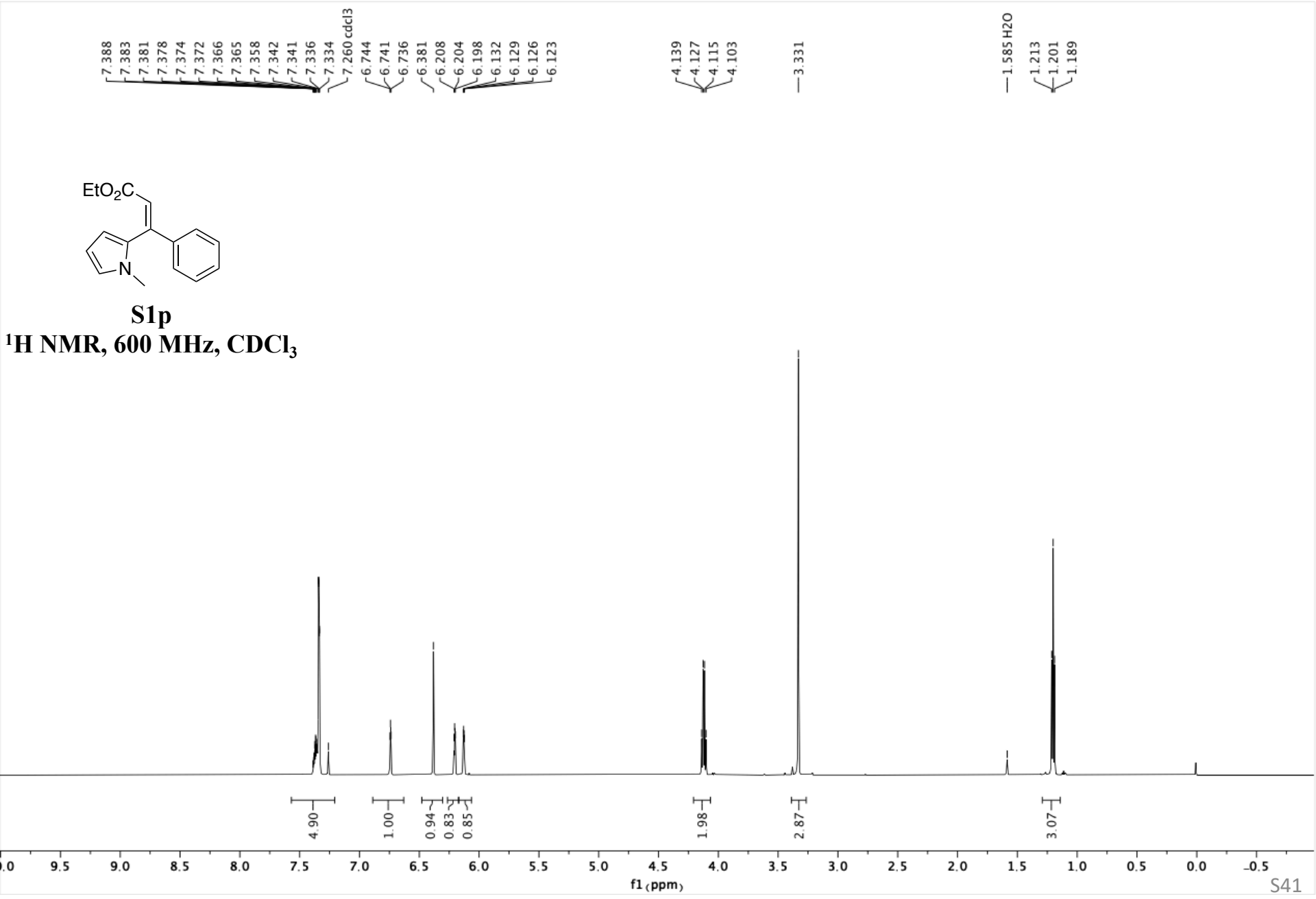
Ethyl (*Z*)-3-(5-methylfuran-2-yl)-3-phenylacrylate



S1o

^{13}C NMR, 150 MHz, $CDCl_3$

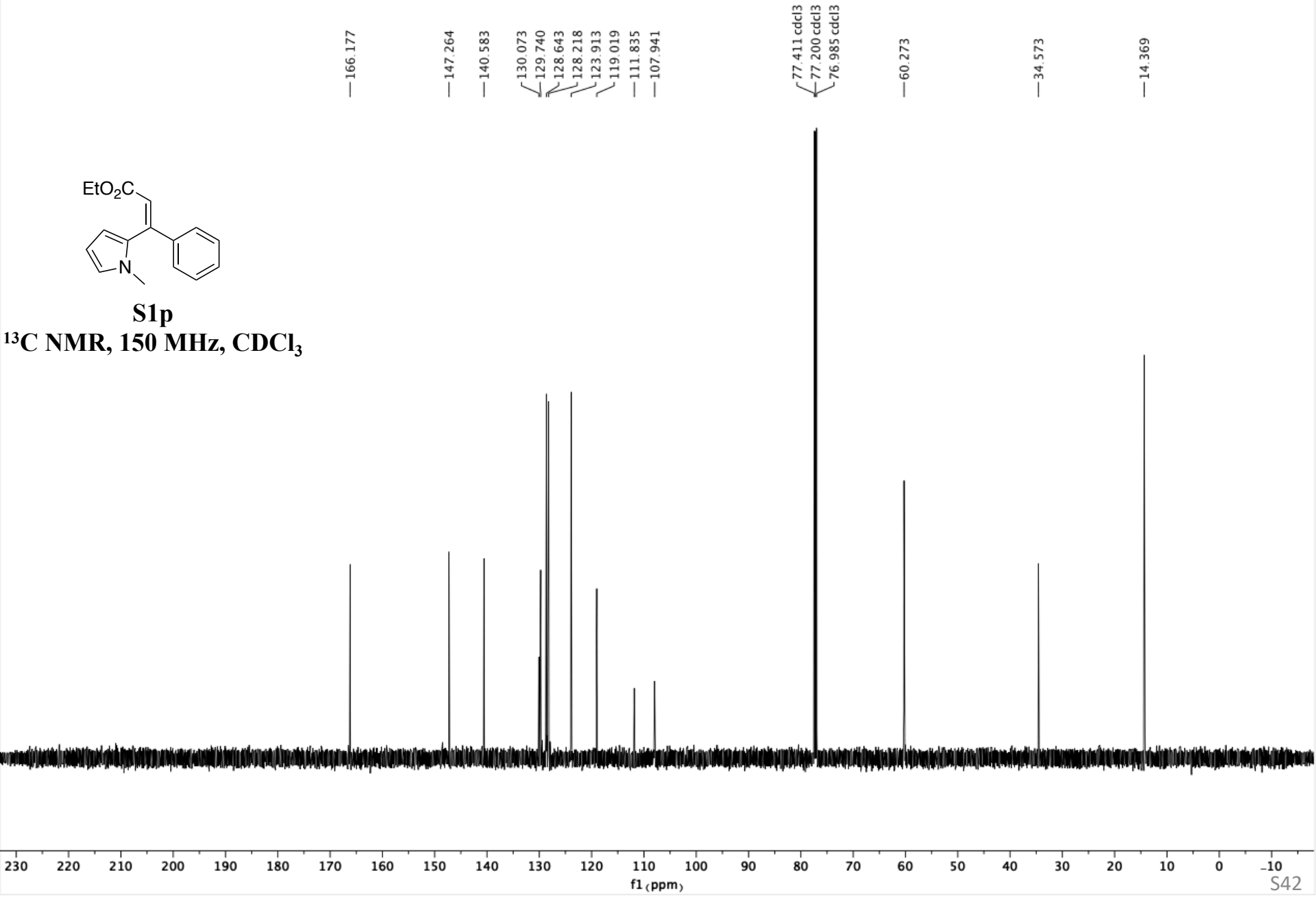
Ethyl (*Z*)-3-(1-methyl-1*H*-pyrrol-2-yl)-3-phenylacrylate



S1p

^{1}H NMR, 600 MHz, $CDCl_3$

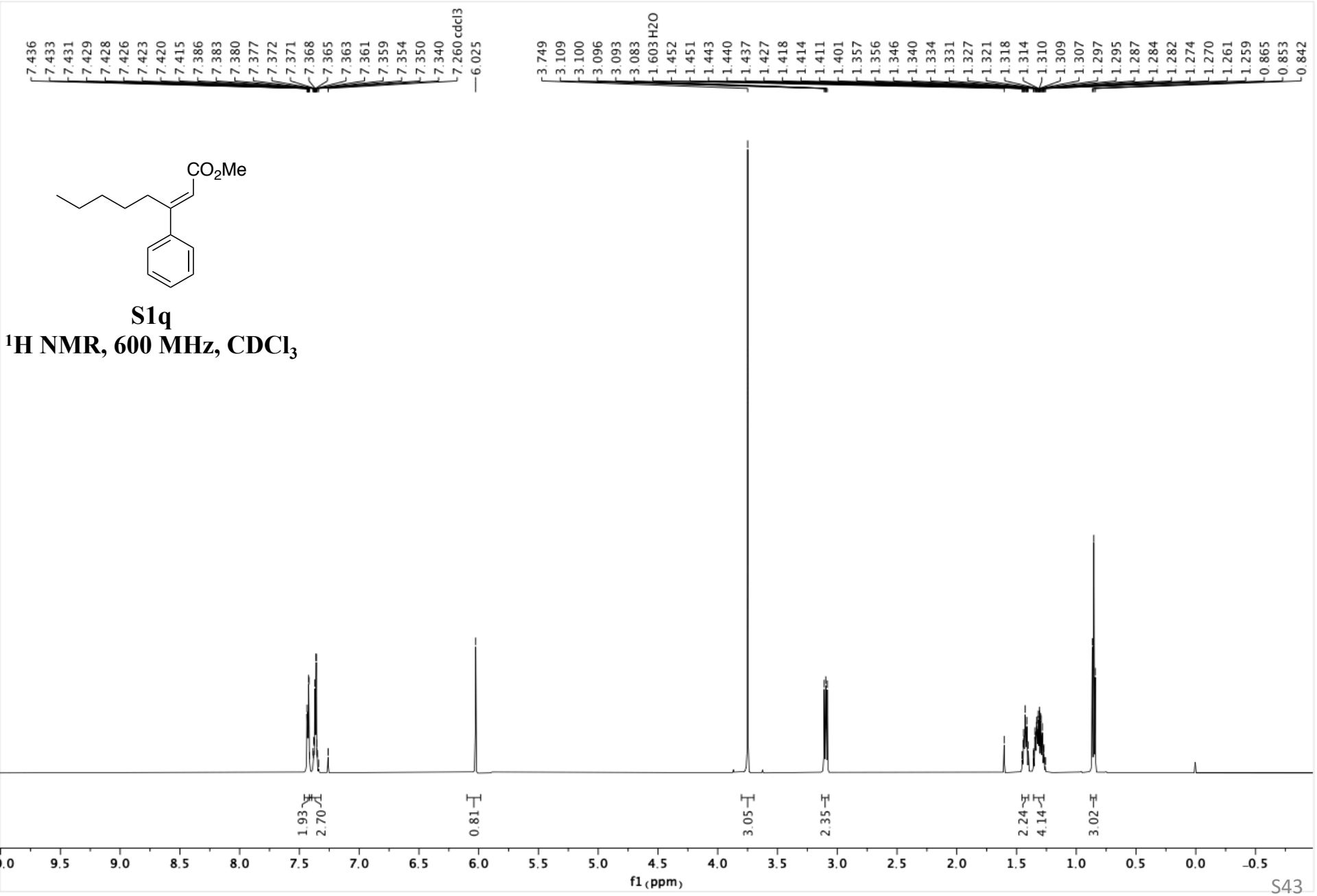
Ethyl (*Z*)-3-(1-methyl-1*H*-pyrrol-2-yl)-3-phenylacrylate



S1p

^{13}C NMR, 150 MHz, $CDCl_3$

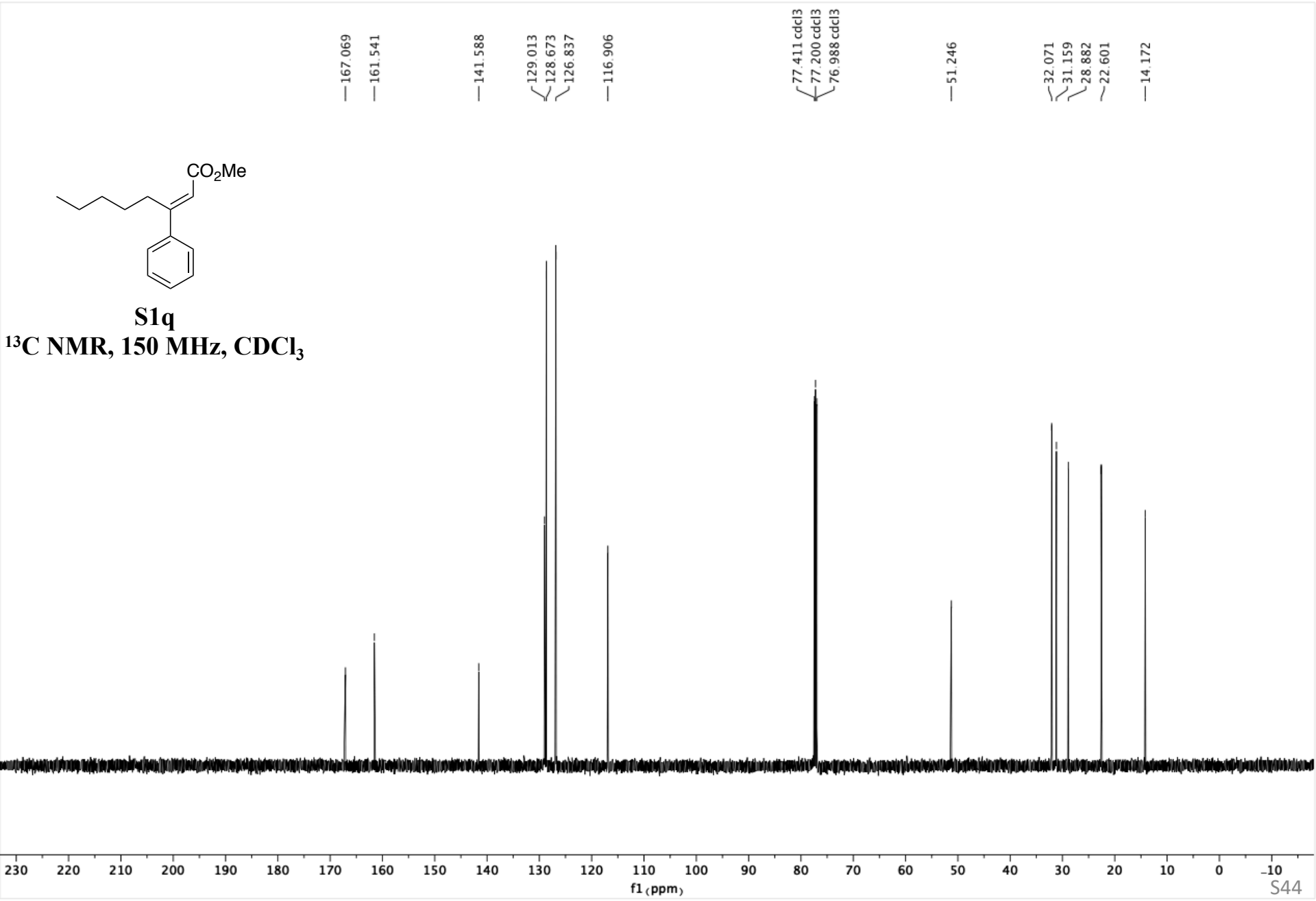
Methyl (*E*)-3-phenyloct-2-enoate



S1q

^{1}H NMR, 600 MHz, $CDCl_3$

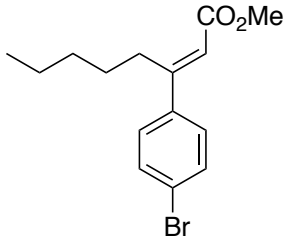
Methyl (*E*)-3-phenyloct-2-enoate



S1q

^{13}C NMR, 150 MHz, $CDCl_3$

Methyl (*E*)-3-(4-bromophenyl)oct-2-enoate



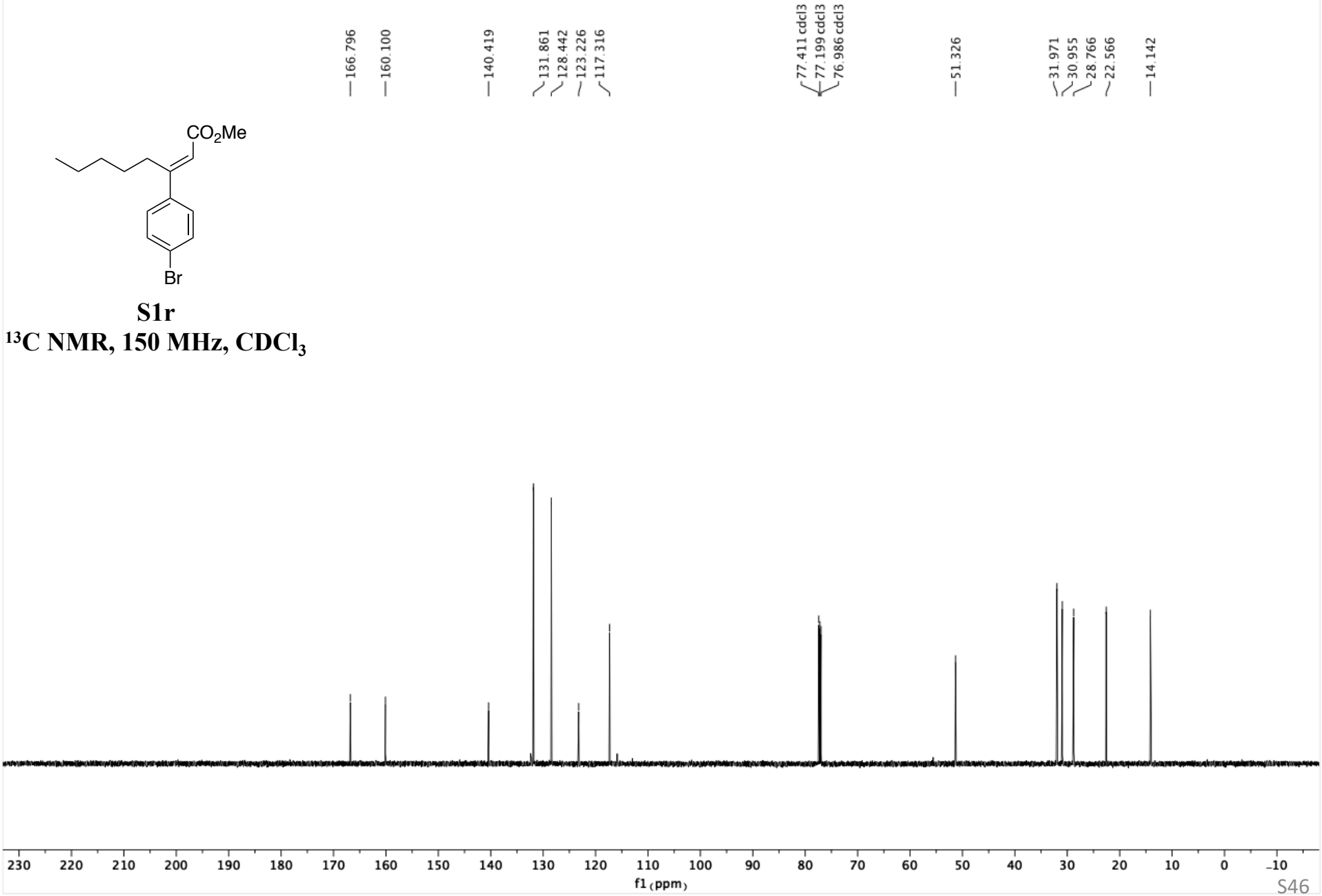
S1r

^{1}H NMR, 600 MHz, $CDCl_3$

Methyl (*E*)-3-(4-bromophenyl)oct-2-enoate

S1r

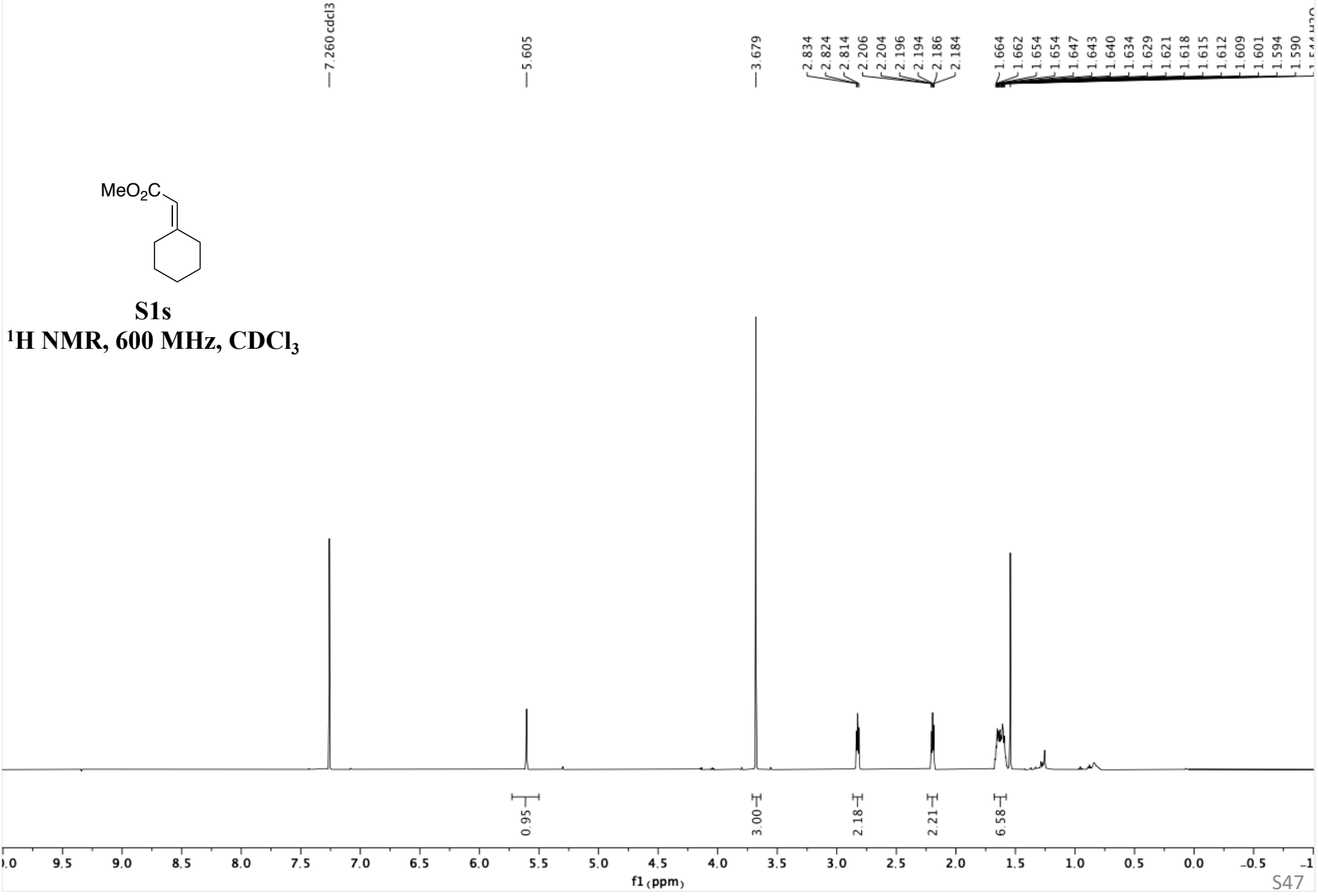
^{13}C NMR, 150 MHz, $CDCl_3$



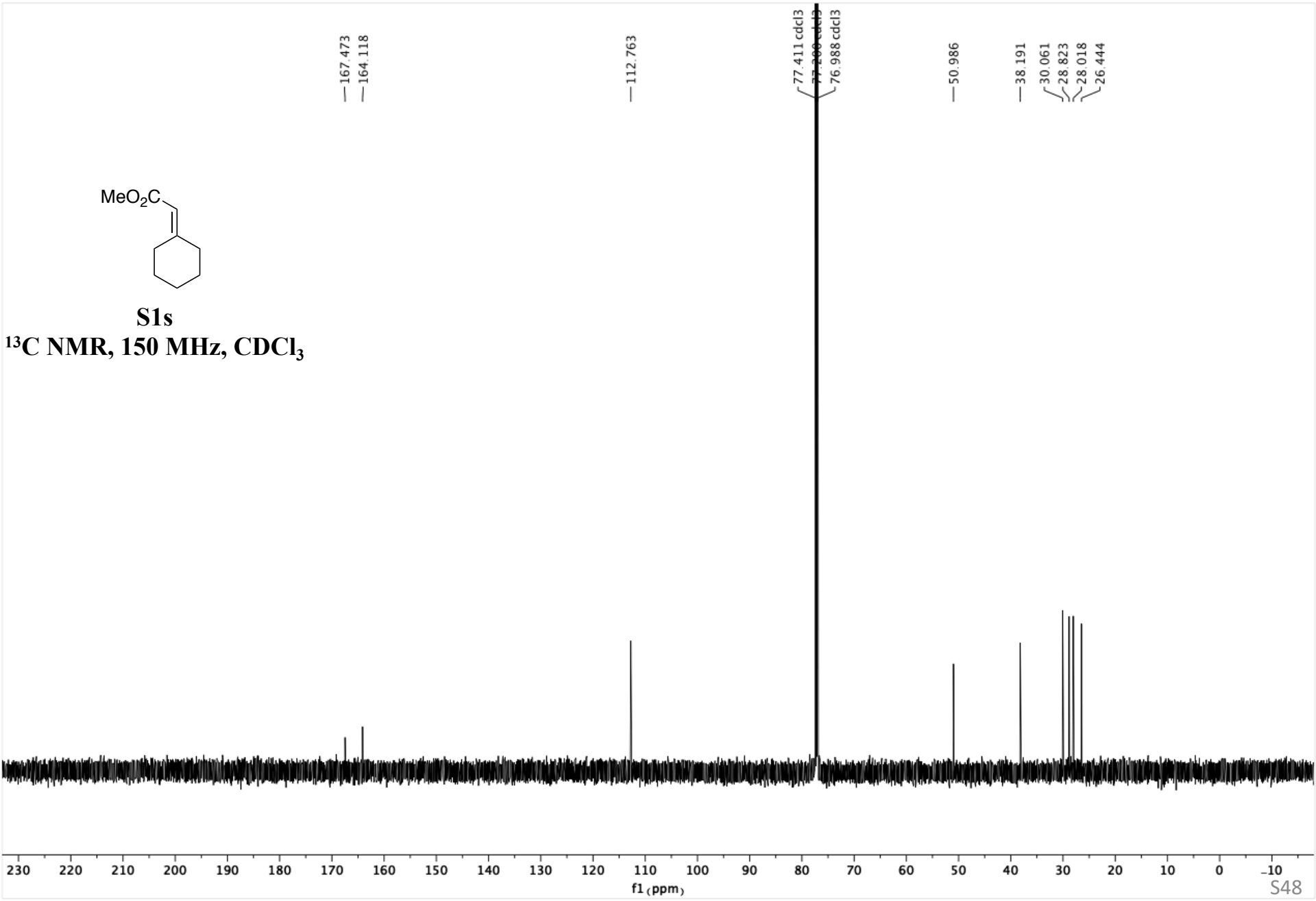
Methyl 2-cyclohexylideneacetate

S1s

^{1}H NMR, 600 MHz, $CDCl_3$



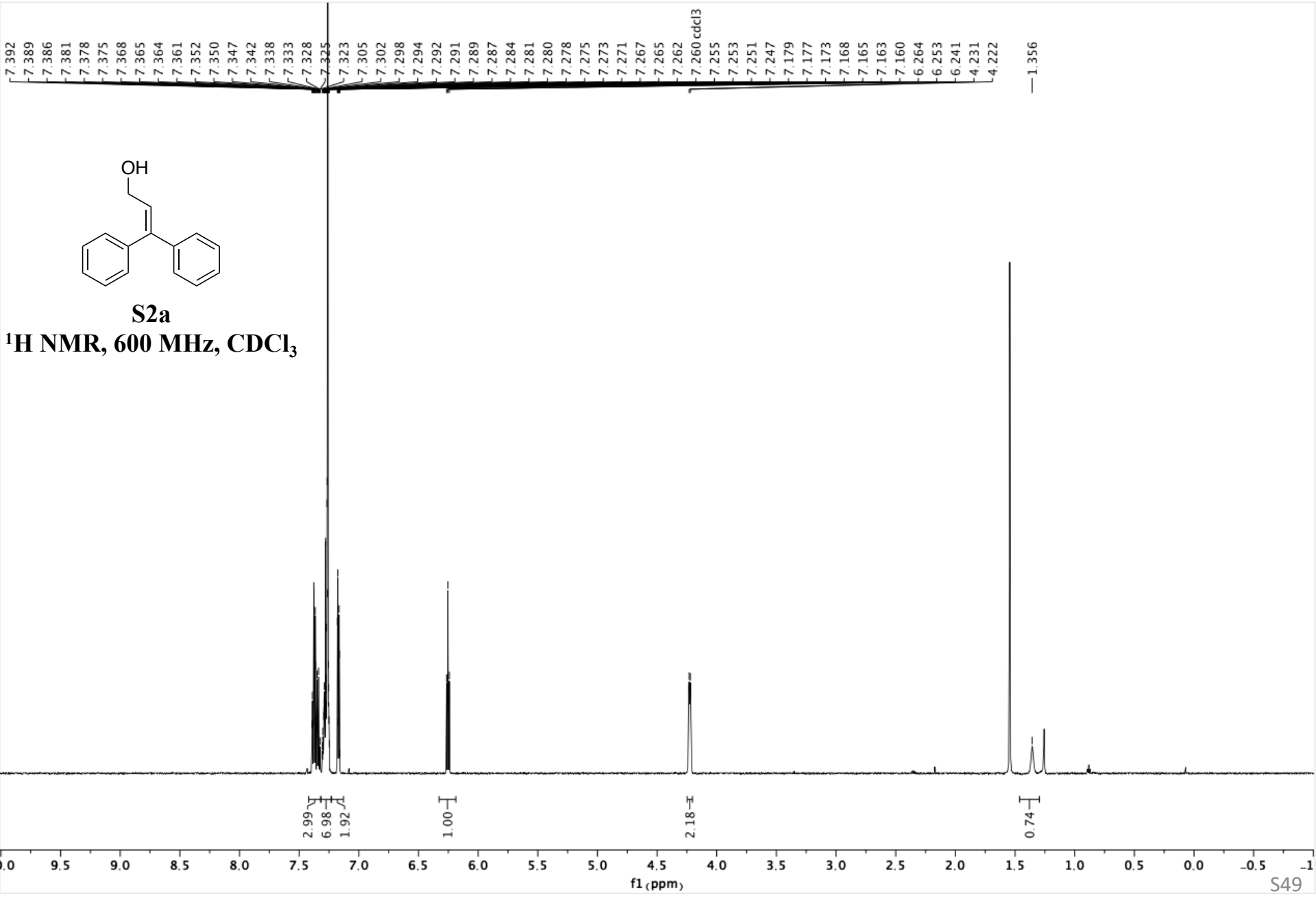
Methyl 2-cyclohexylideneacetate



S1s

^{13}C NMR, 150 MHz, $CDCl_3$

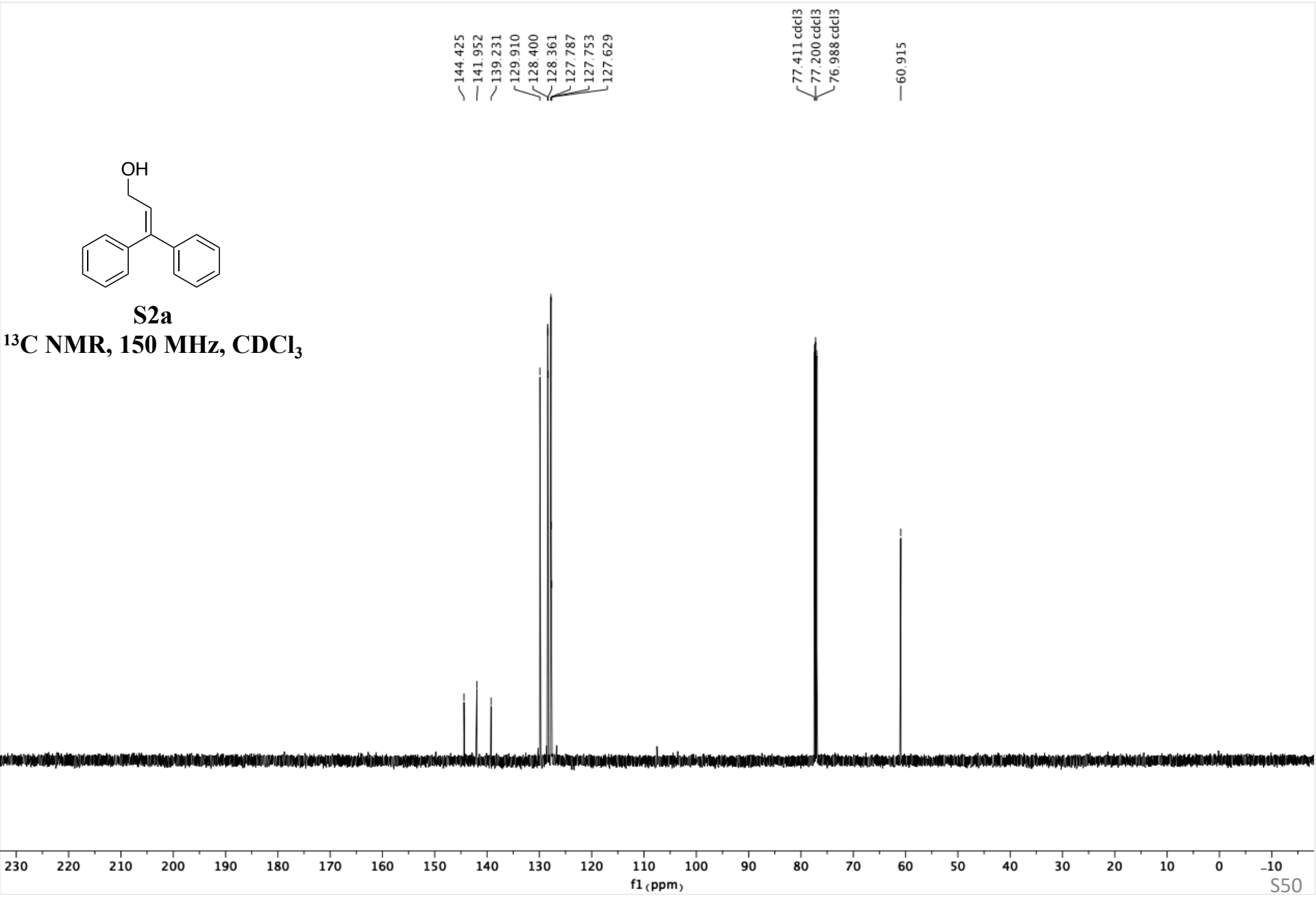
3,3-Diphenylprop-2-en-1-ol



S2a

^{1}H NMR, 600 MHz, $CDCl_3$

3,3-Diphenylprop-2-en-1-ol



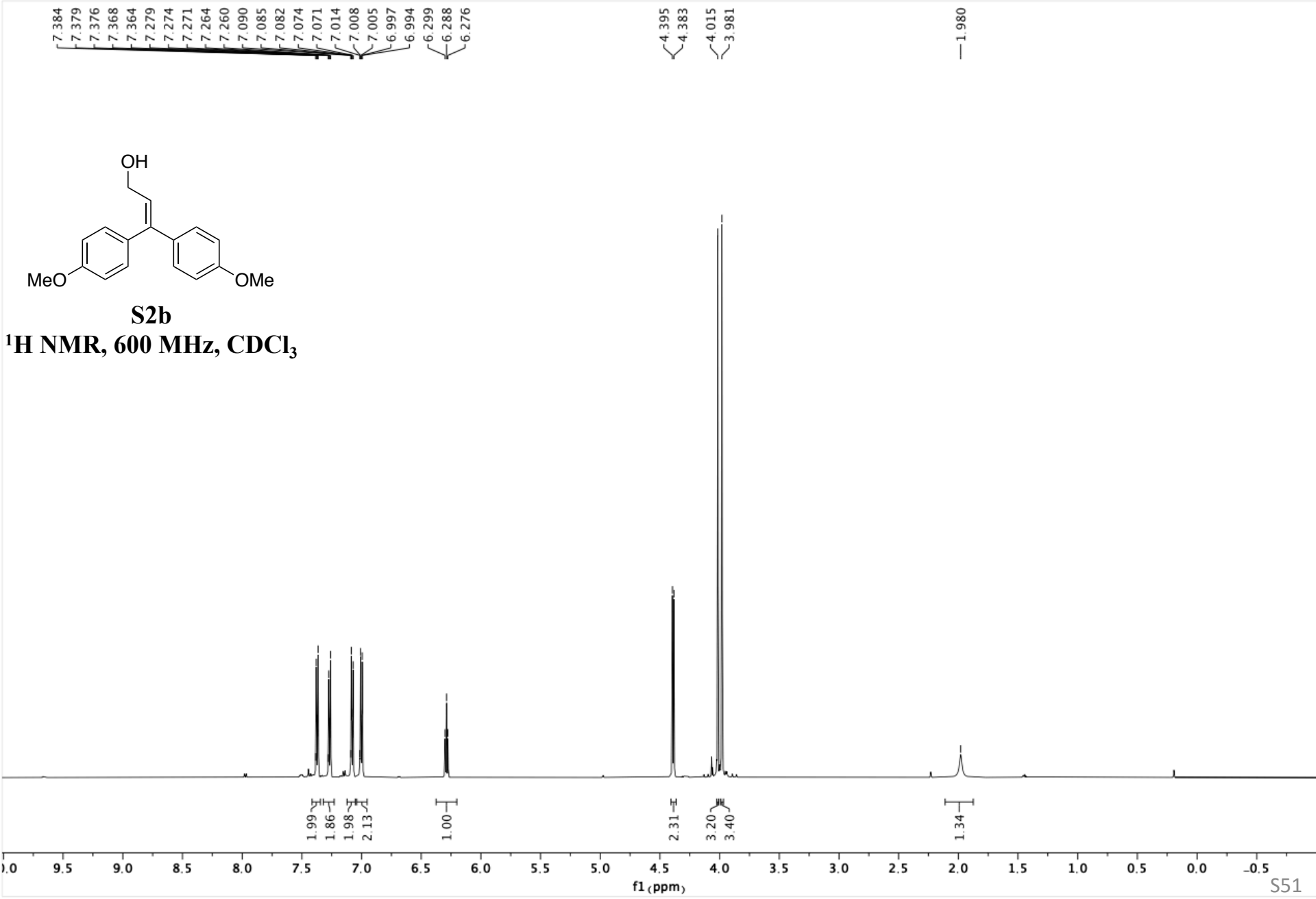
S2a

^{13}C NMR, 150 MHz, $CDCl_3$

3,3-Bis(4-methoxyphenyl)prop-2-en-1-ol

S2b

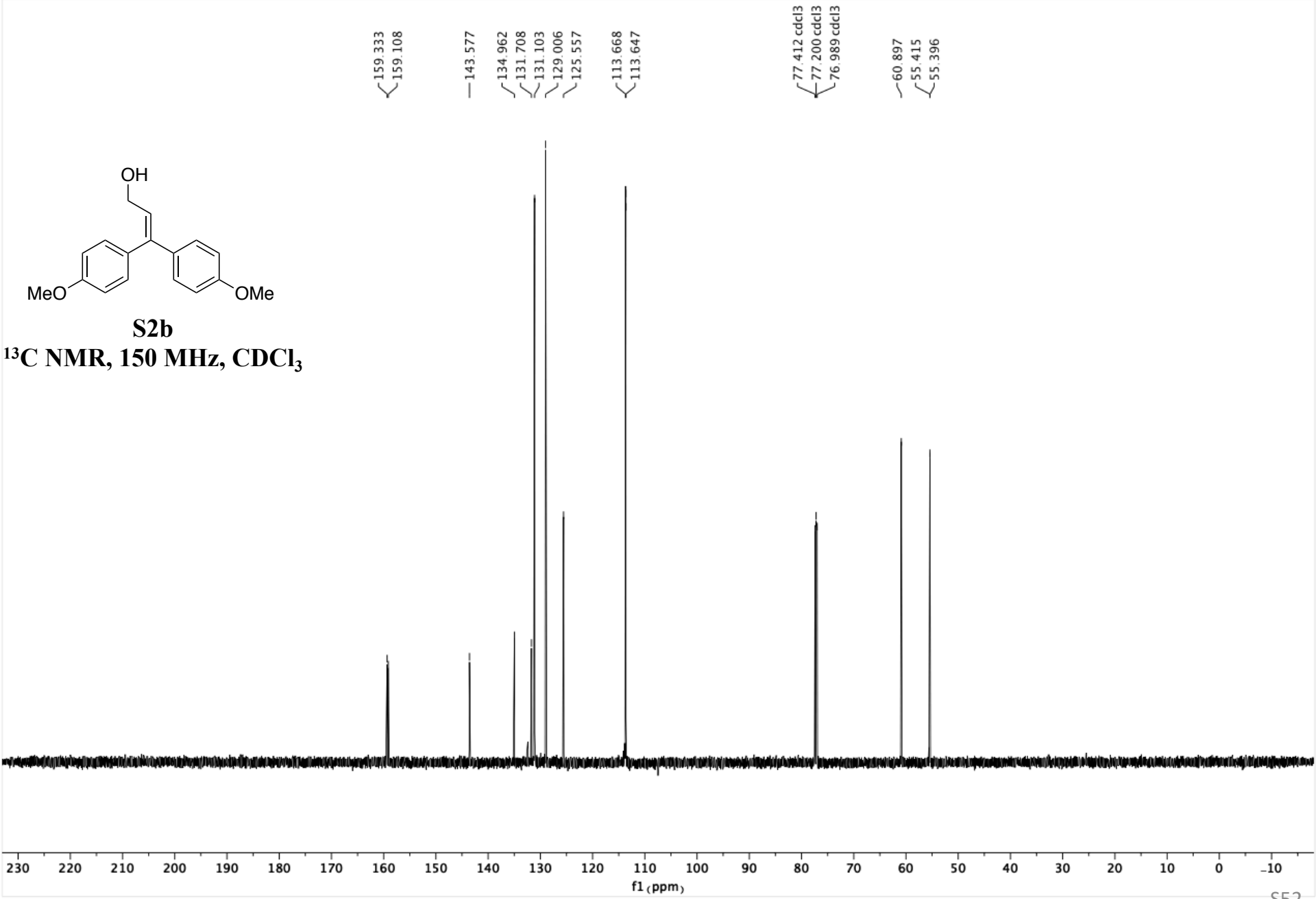
^{1}H NMR, 600 MHz, $CDCl_3$



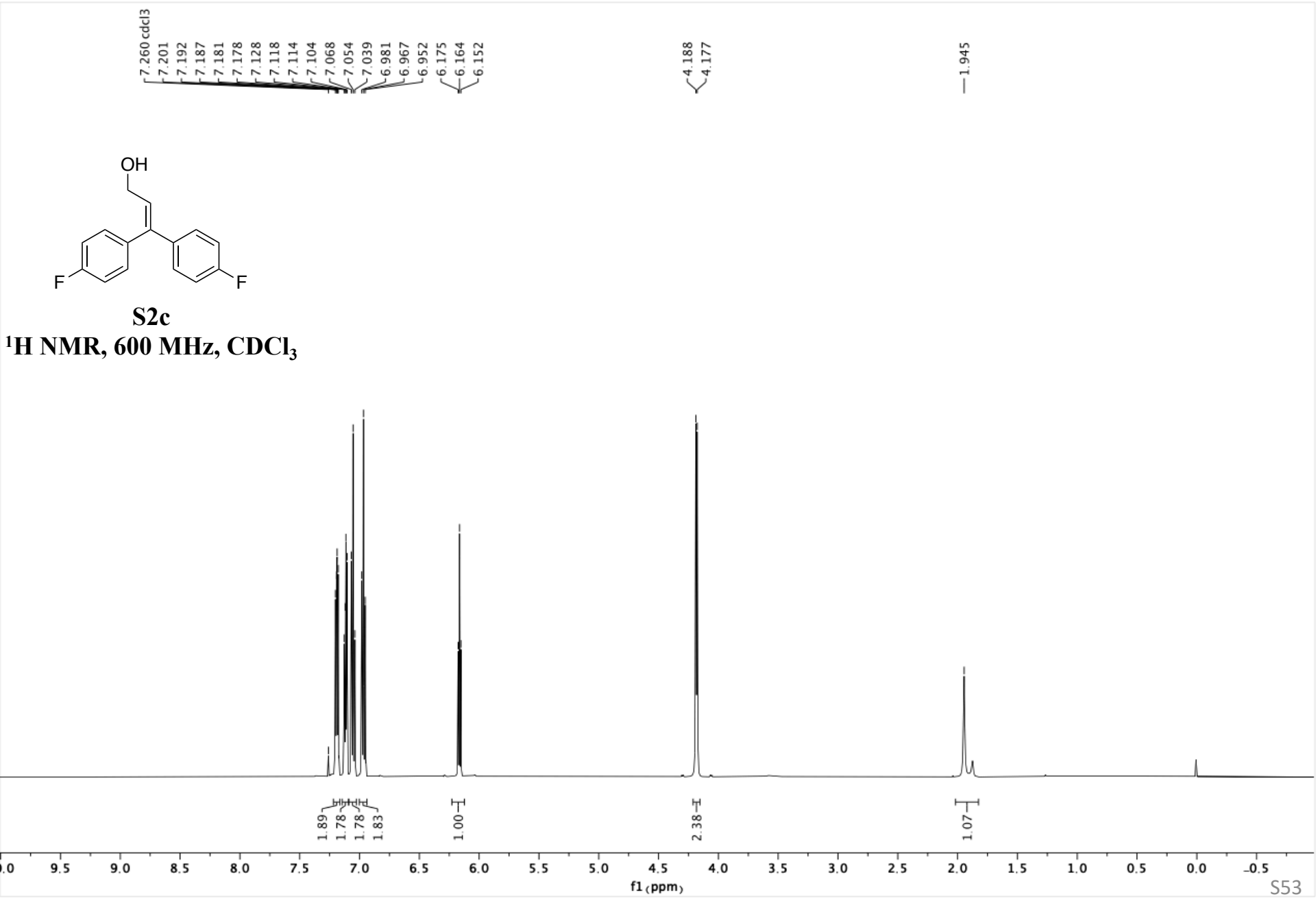
3,3-Bis(4-methoxyphenyl)prop-2-en-1-ol

S2b

^{13}C NMR, 150 MHz, $CDCl_3$



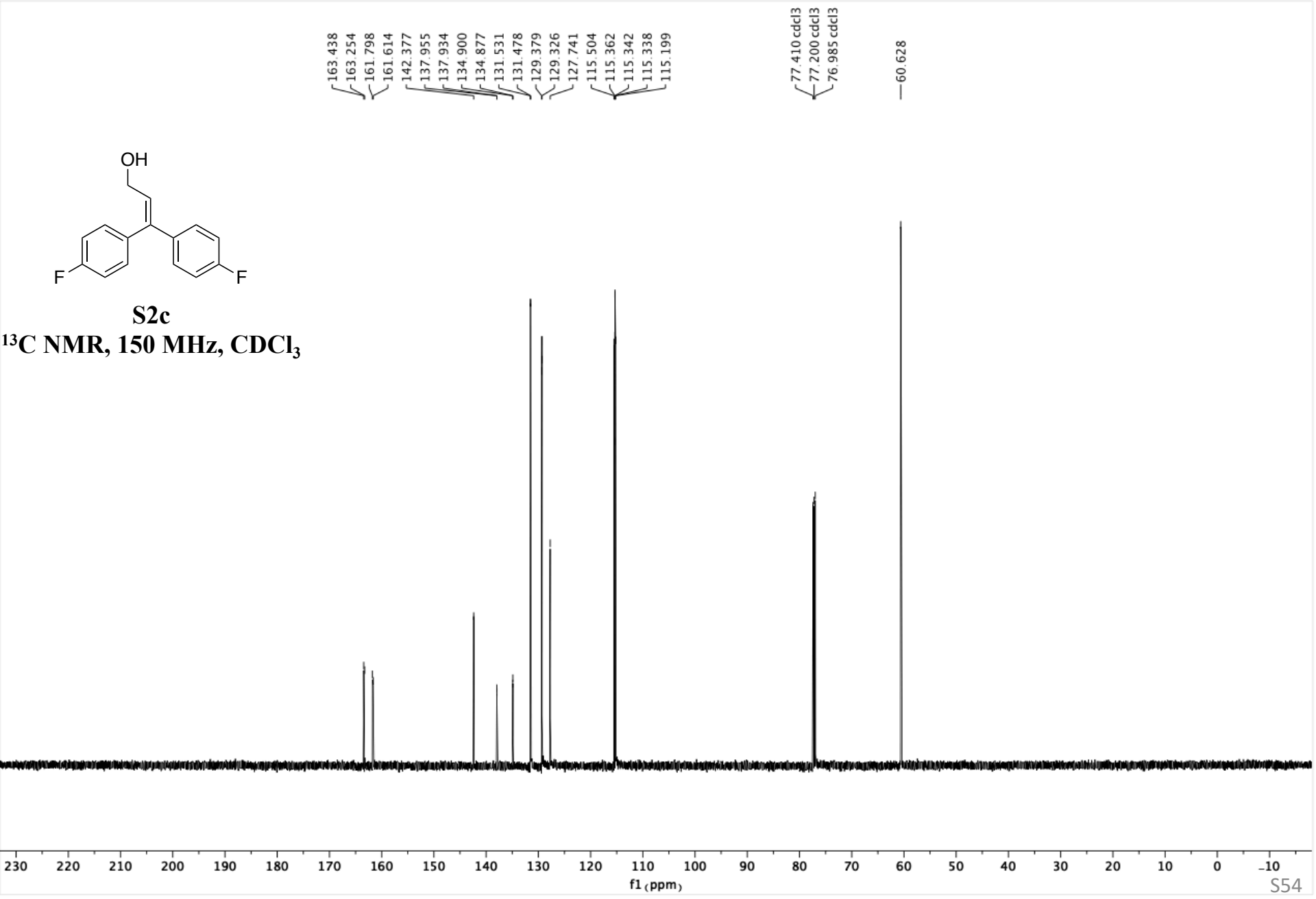
3,3-Bis(4-fluorophenyl)prop-2-en-1-ol



S2c

^{1}H NMR, 600 MHz, $CDCl_3$

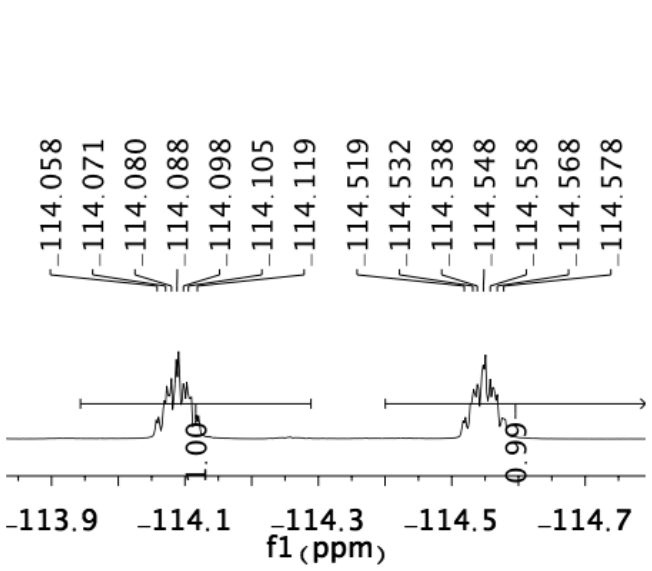
3,3-Bis(4-fluorophenyl)prop-2-en-1-ol



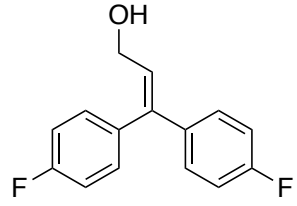
S2c

^{13}C NMR, 150 MHz, $CDCl_3$

3,3-Bis(4-fluorophenyl)prop-2-en-1-ol

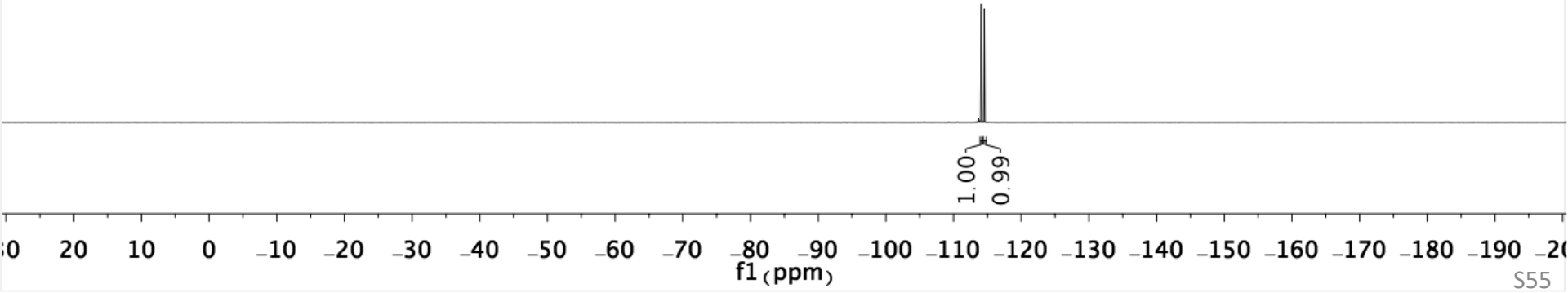




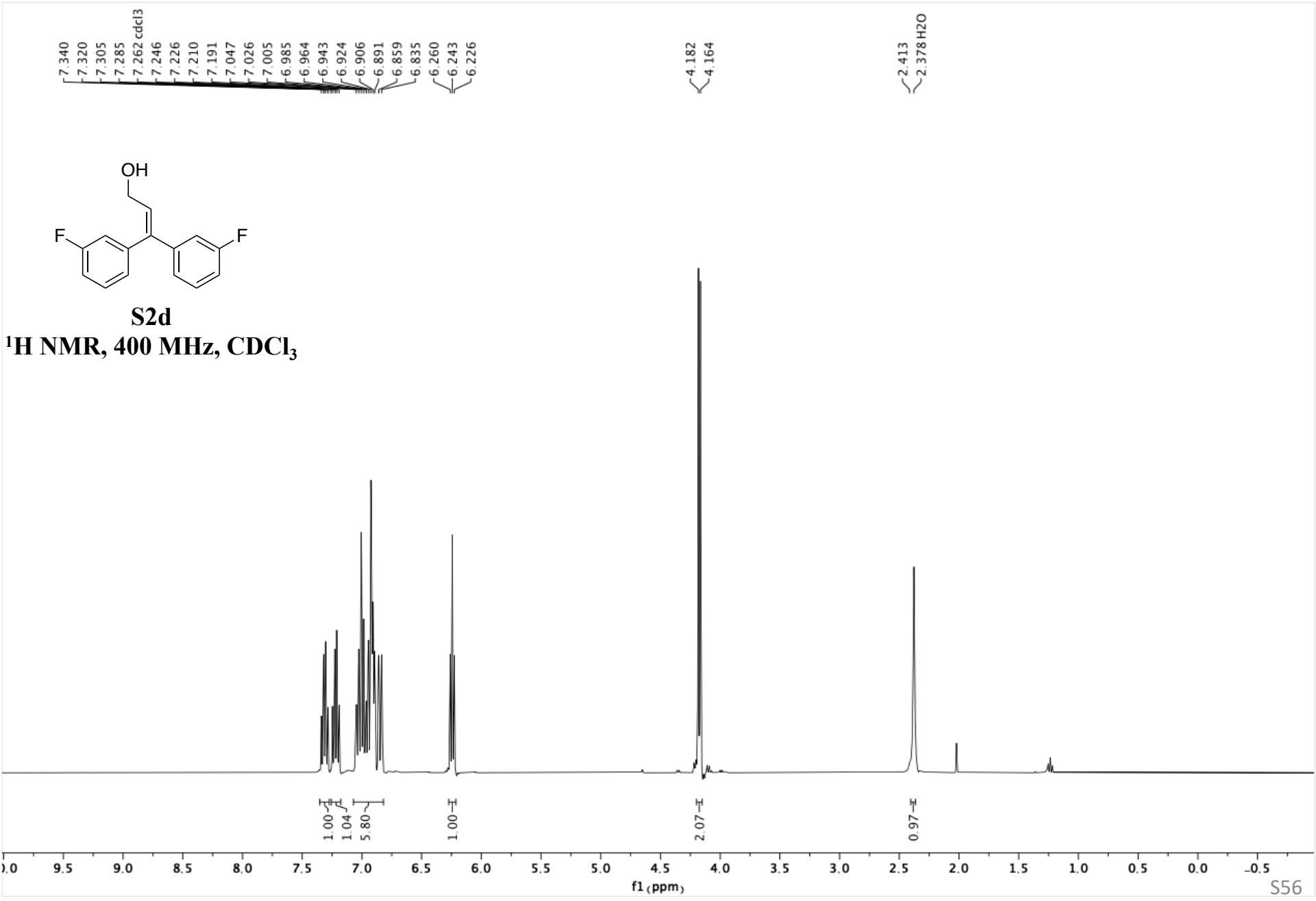


S2c

^{19}F NMR, 564 MHz, $CDCl_3$



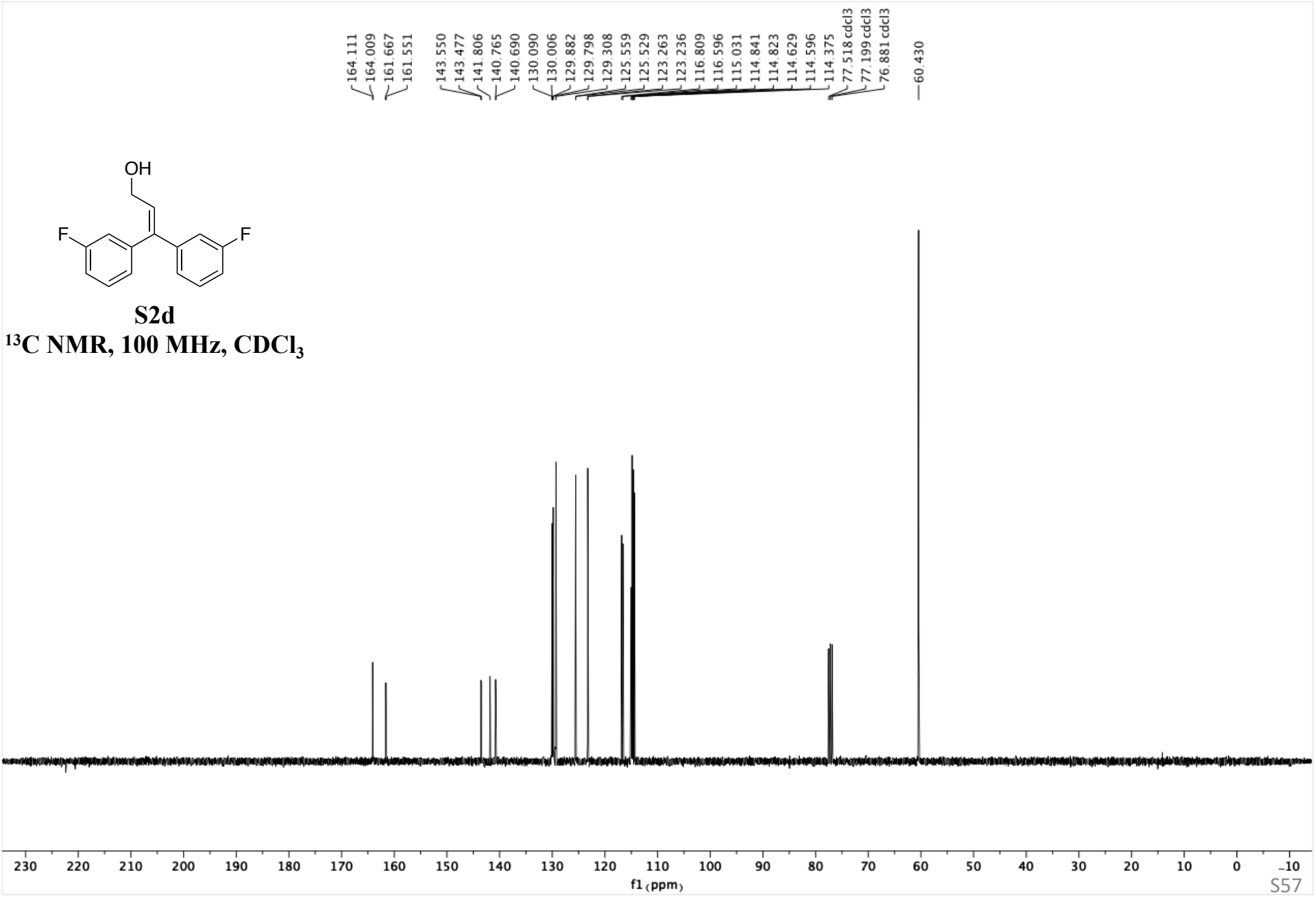
3,3-Bis(3-fluorophenyl)prop-2-en-1-ol



S2d

^{1}H NMR, 400 MHz, $CDCl_3$

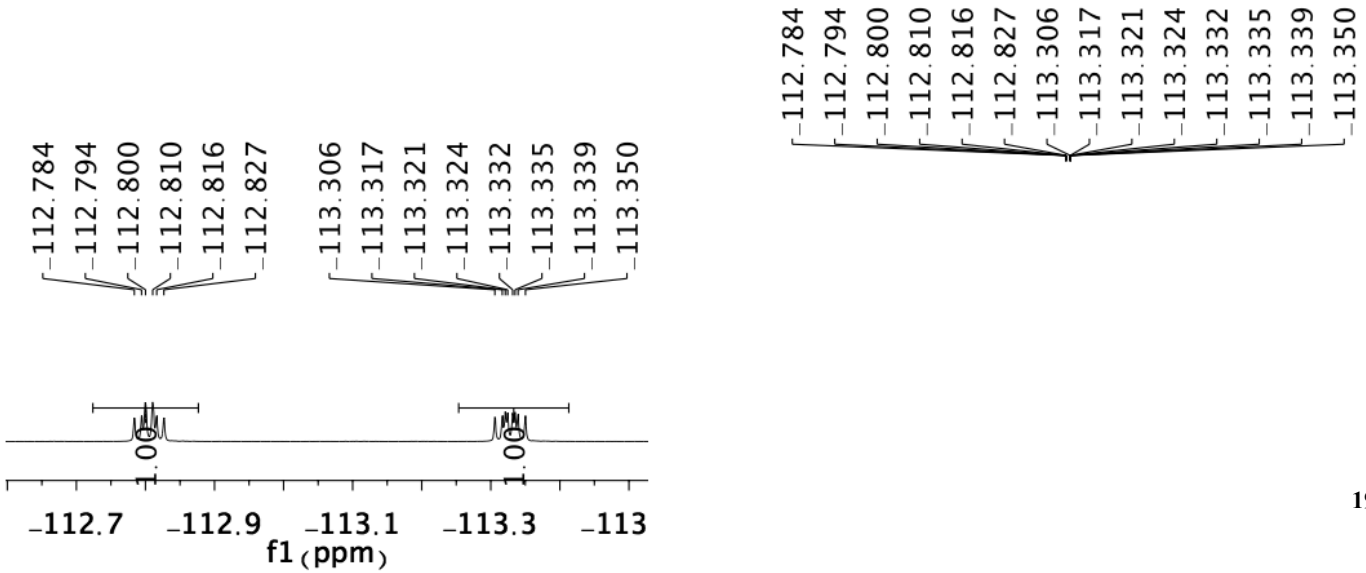
3,3-Bis(3-fluorophenyl)prop-2-en-1-ol

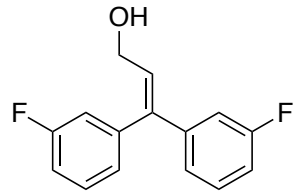


S2d

^{13}C NMR, 100 MHz, $CDCl_3$

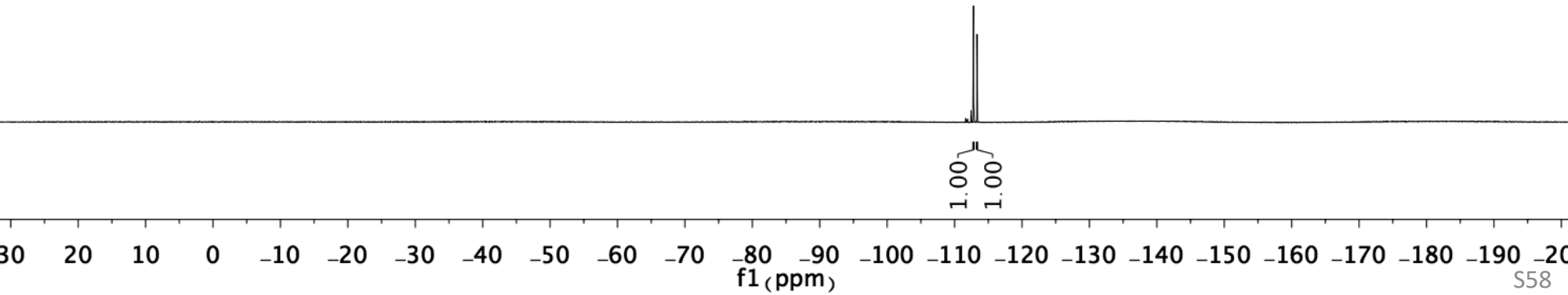
3,3-Bis(3-fluorophenyl)prop-2-en-1-ol



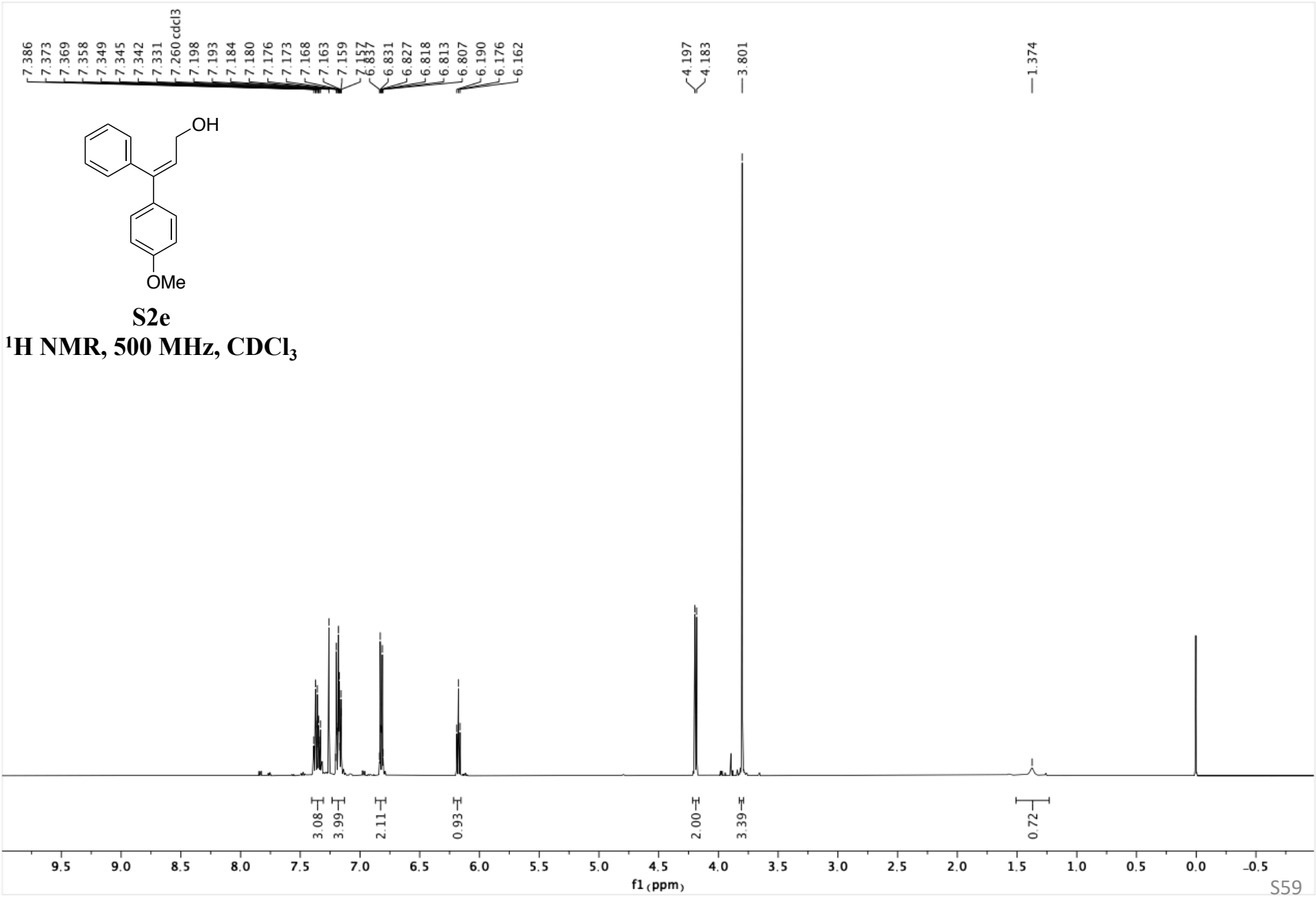


S2d

^{19}F NMR, 564 MHz, $CDCl_3$



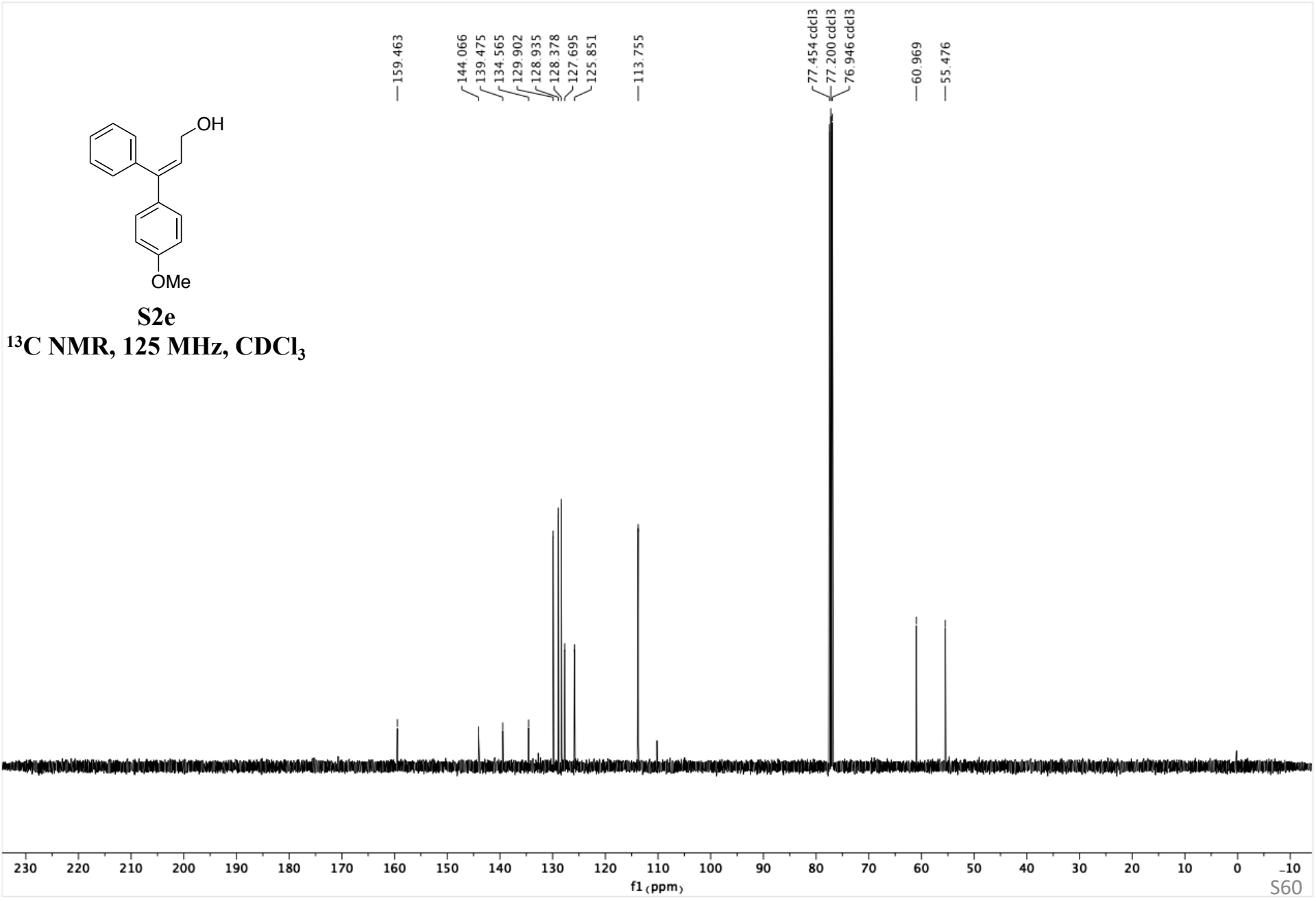
(*E*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol



S2e

^{1}H NMR, 500 MHz, $CDCl_3$

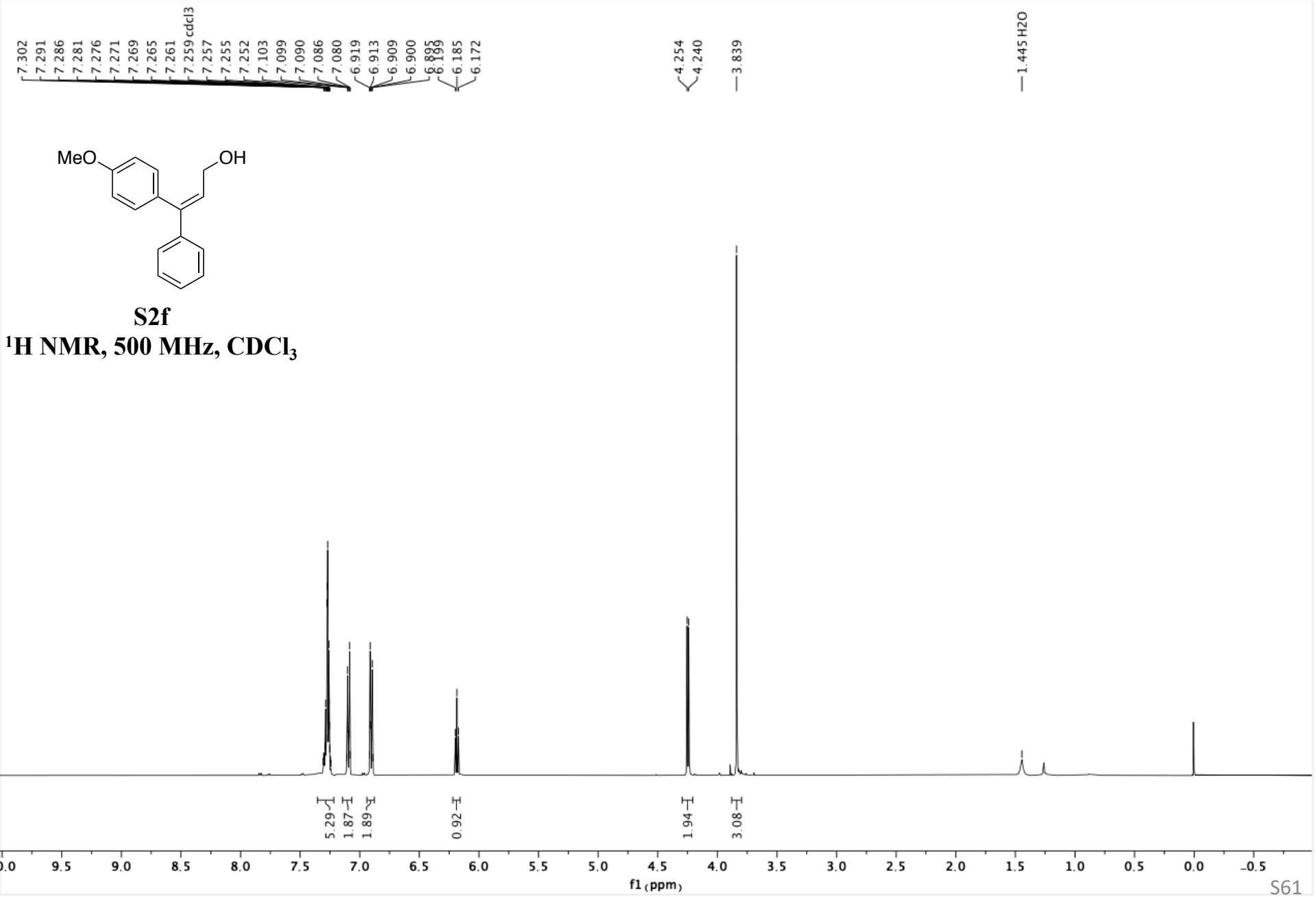
(*E*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol



S2e

^{13}C NMR, 125 MHz, $CDCl_3$

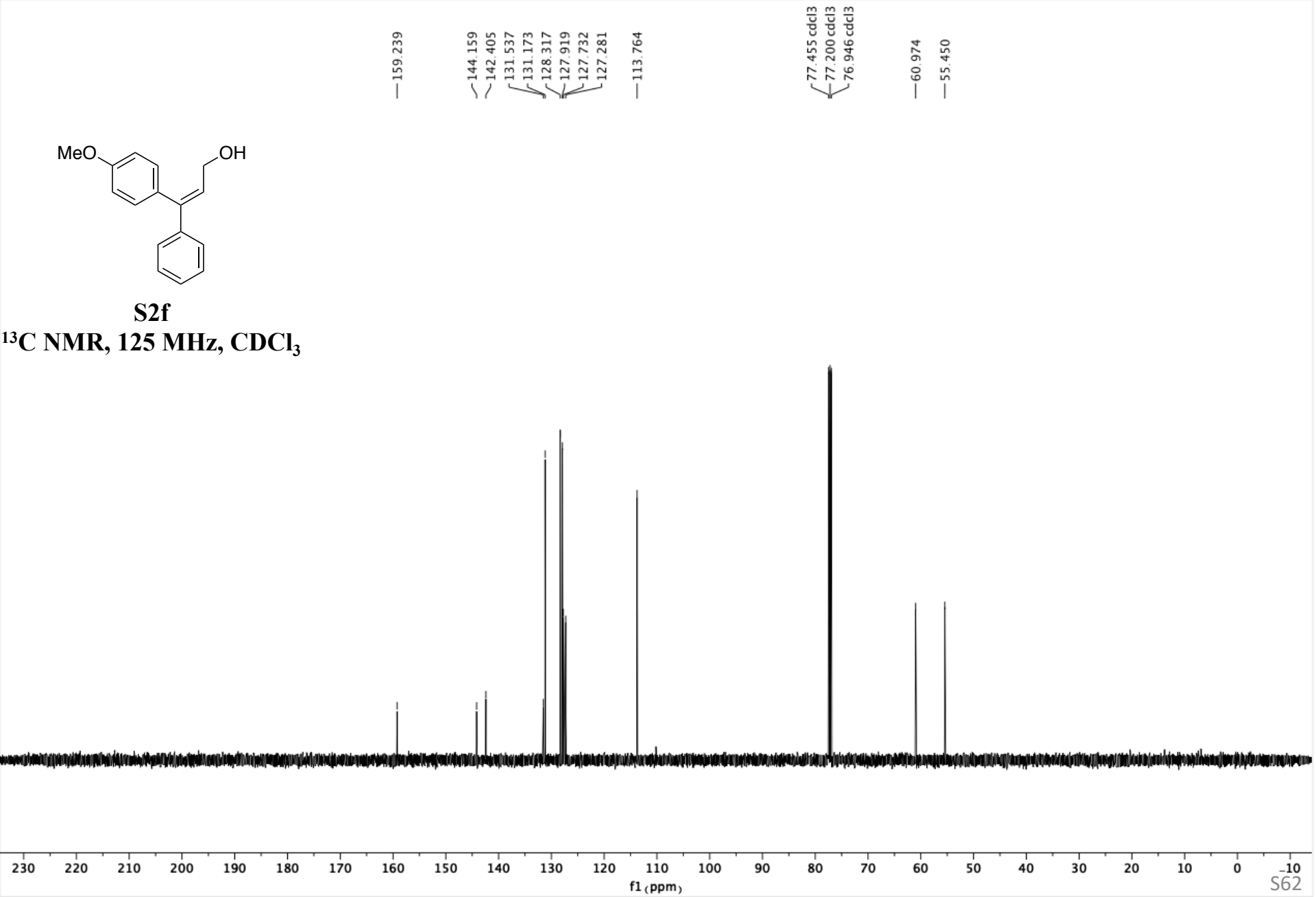
(*Z*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol



S2f

^{1}H NMR, 500 MHz, $CDCl_3$

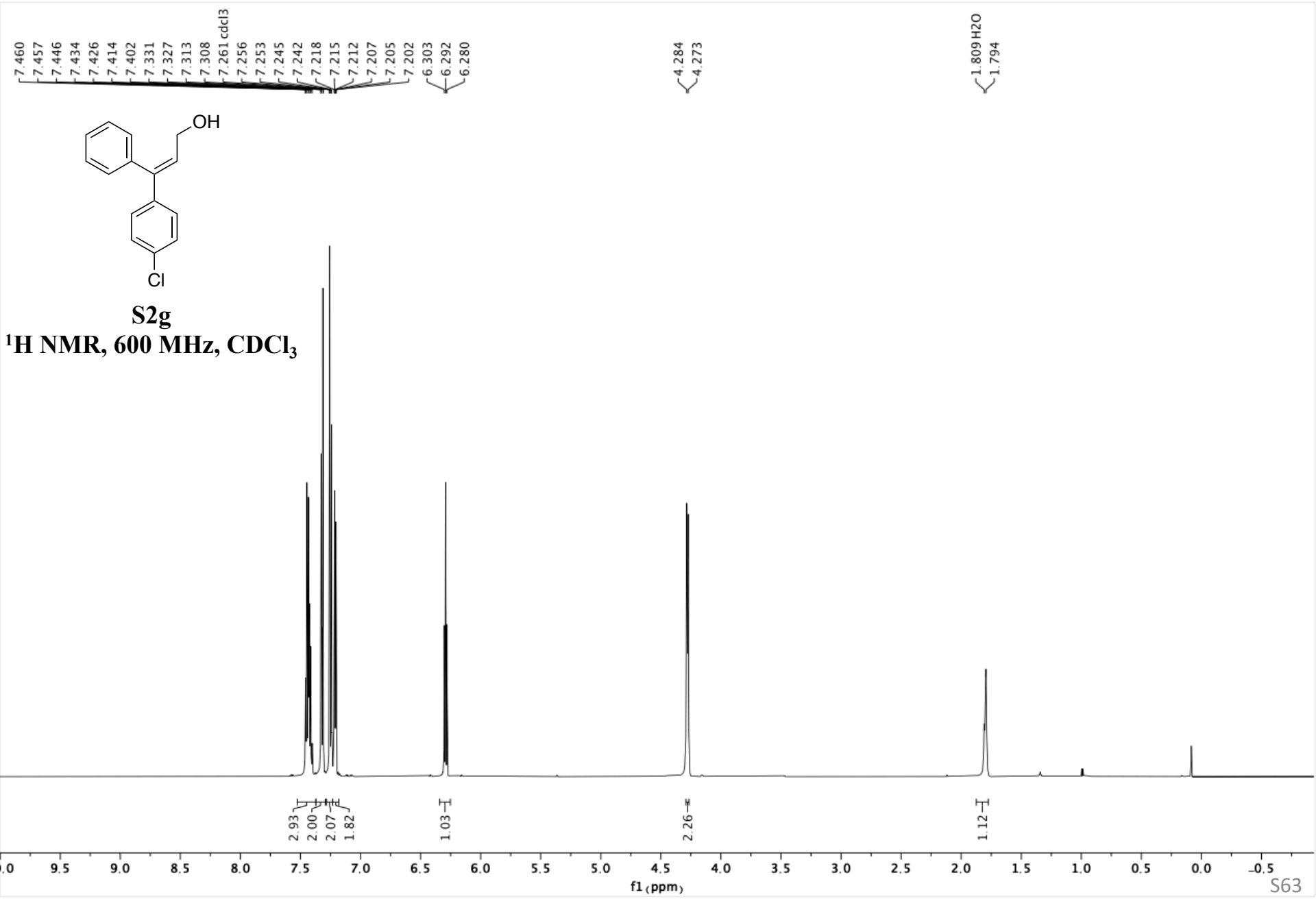
(*Z*)-3-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol



S2f

^{13}C NMR, 125 MHz, $CDCl_3$

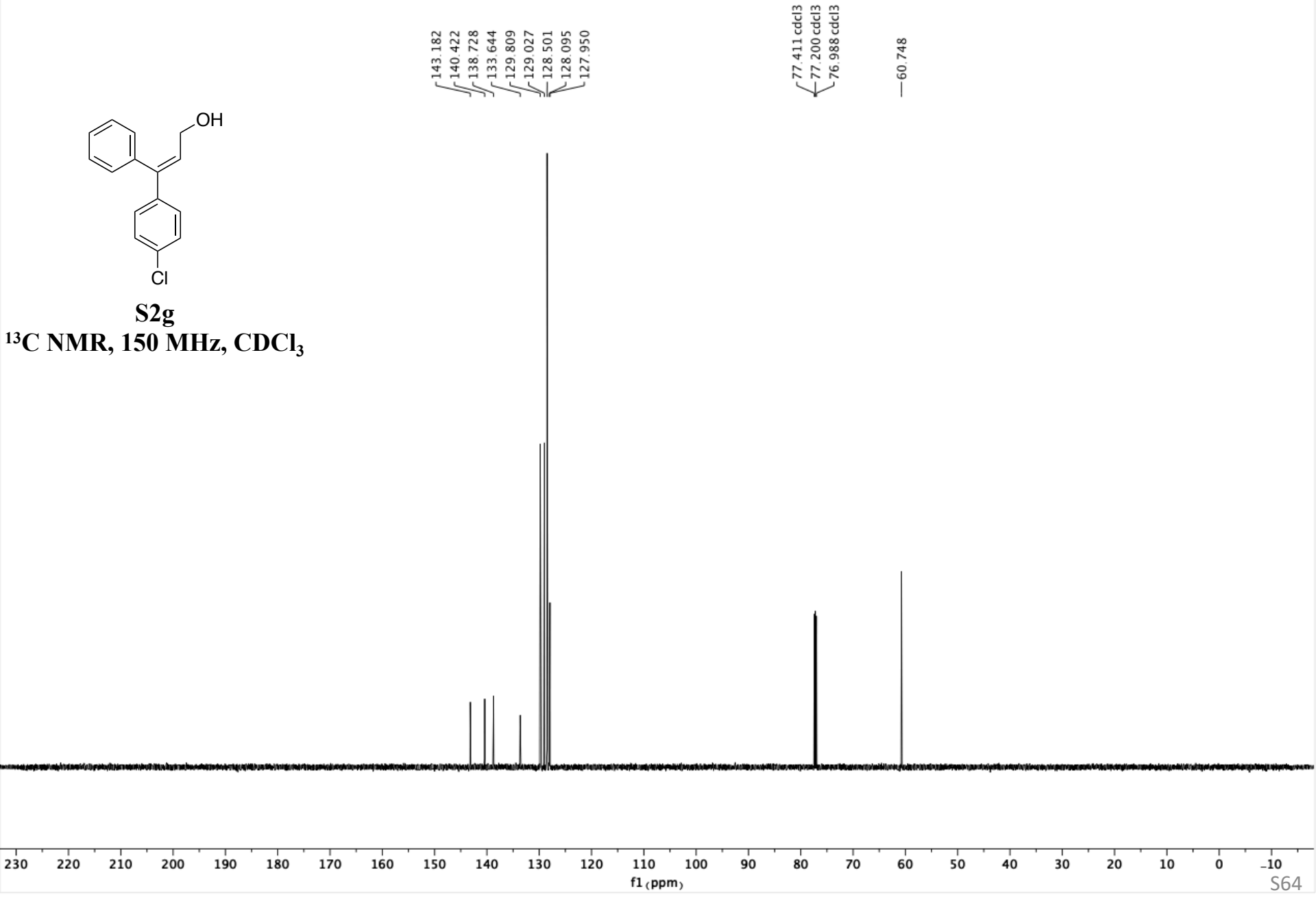
(*E*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol



S2g

^{1}H NMR, 600 MHz, $CDCl_3$

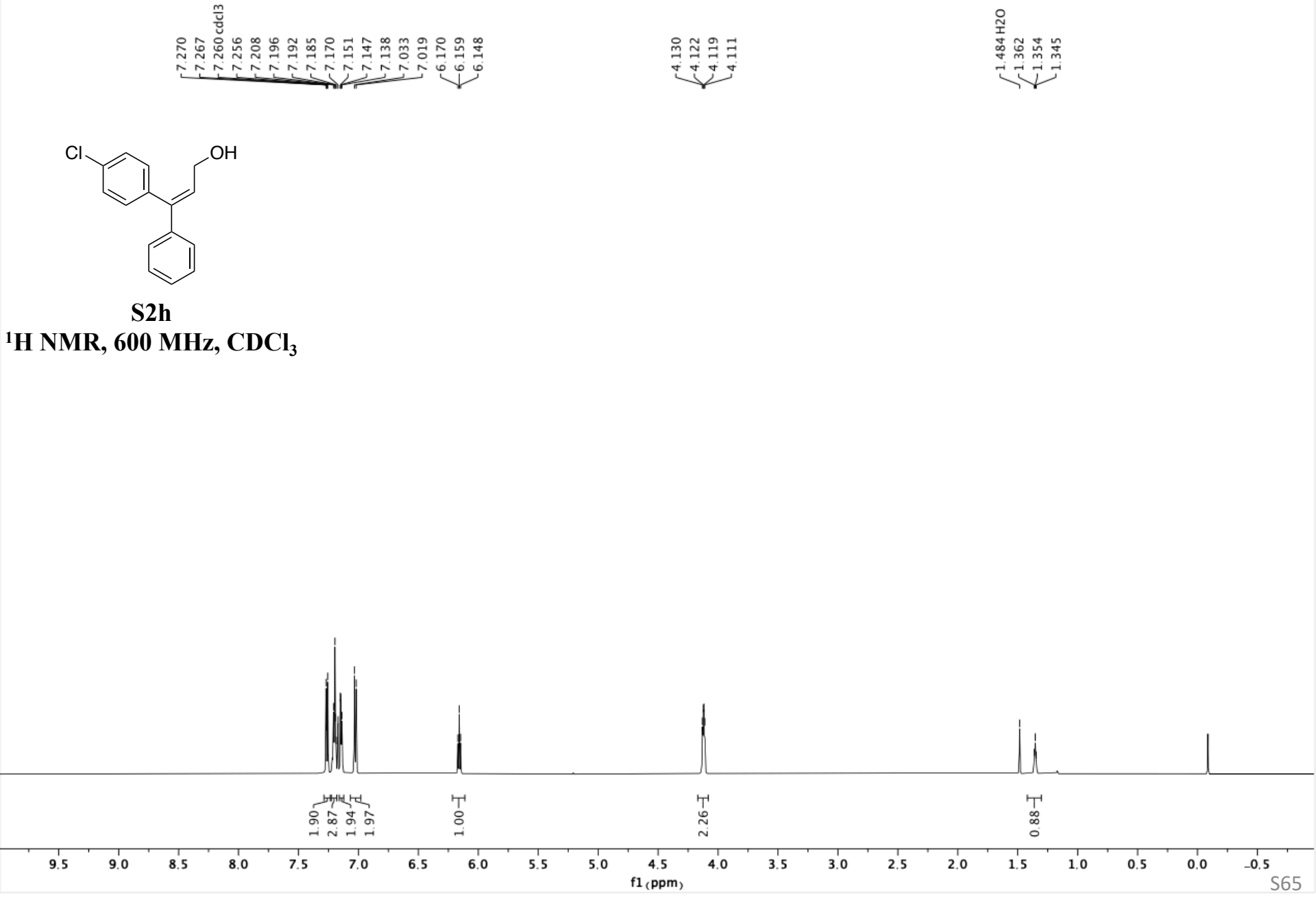
(*E*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol



S2g

^{13}C NMR, 150 MHz, $CDCl_3$

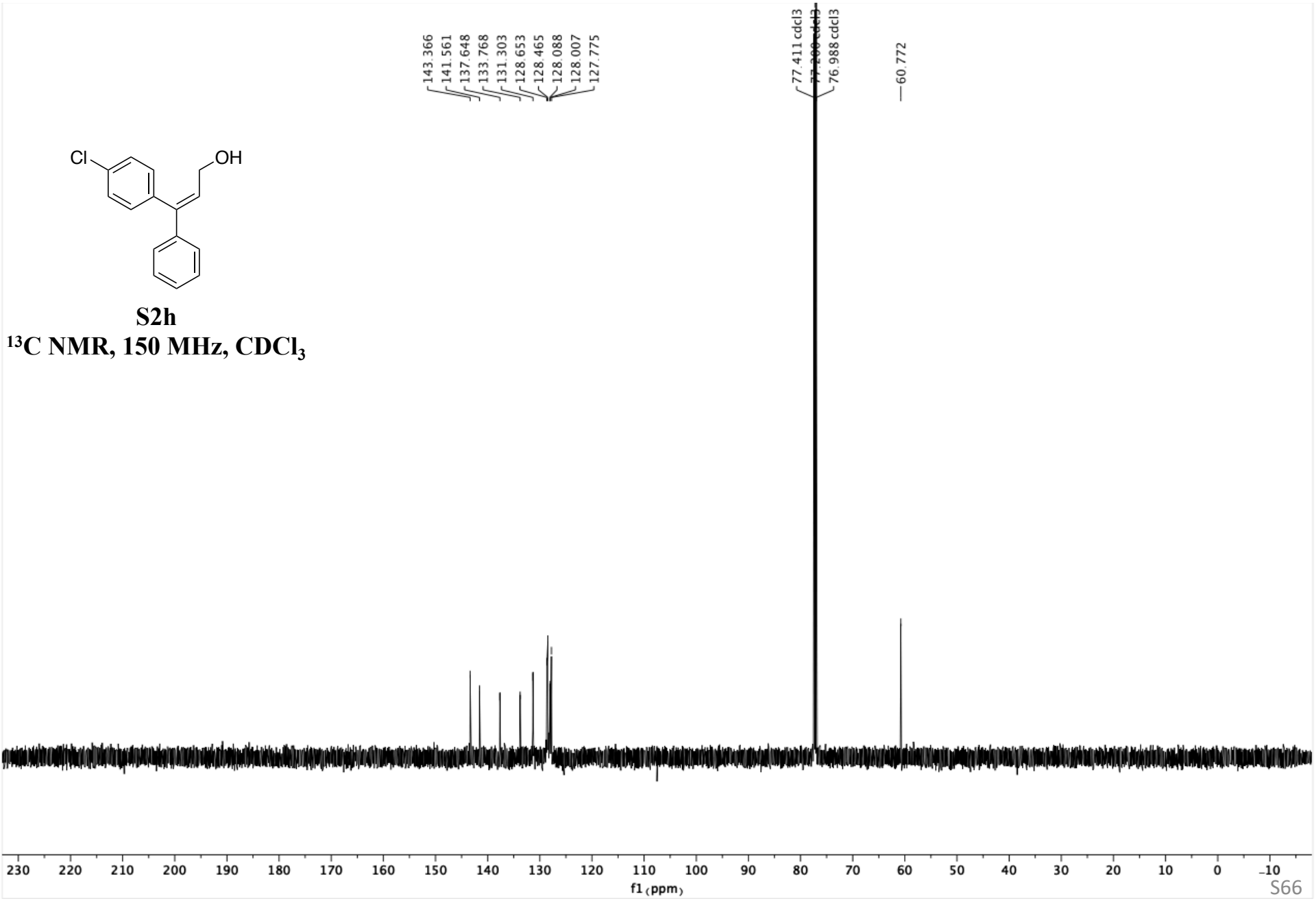
(*Z*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol



S2h

^{1}H NMR, 600 MHz, $CDCl_3$

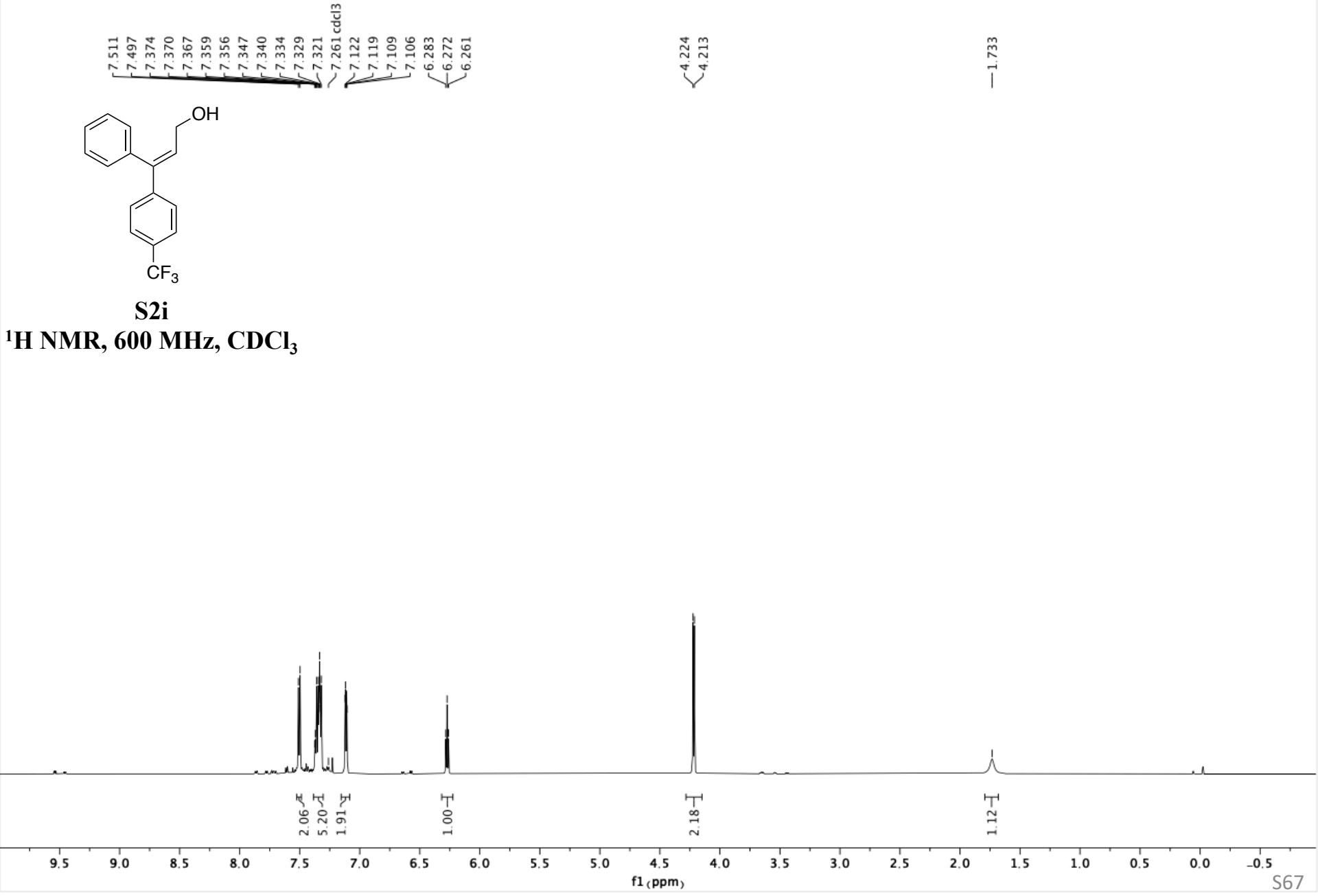
(*Z*)-3-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol



S2h

^{13}C NMR, 150 MHz, $CDCl_3$

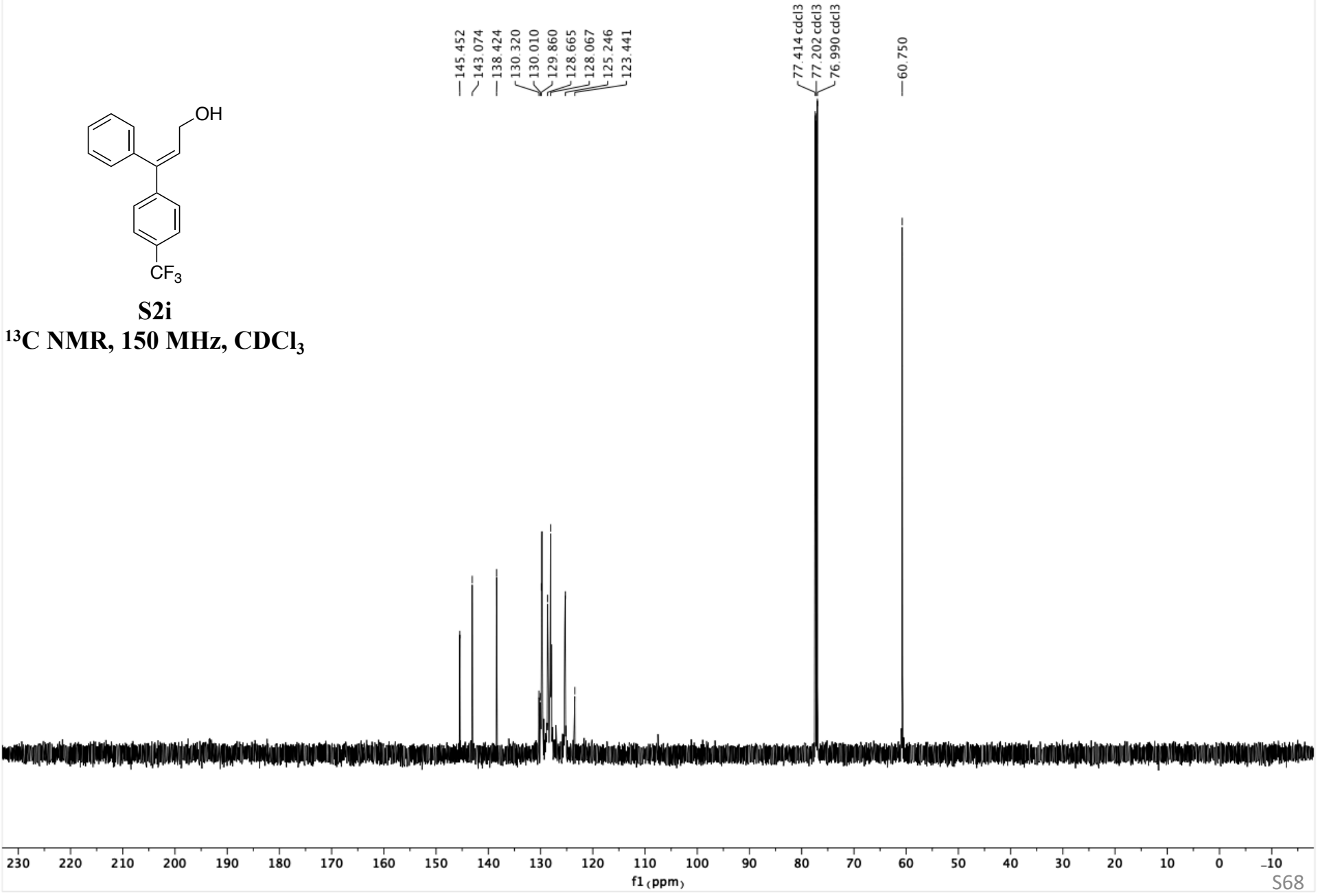
(*E*)-3-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol



S2i

^{1}H NMR, 600 MHz, $CDCl_3$

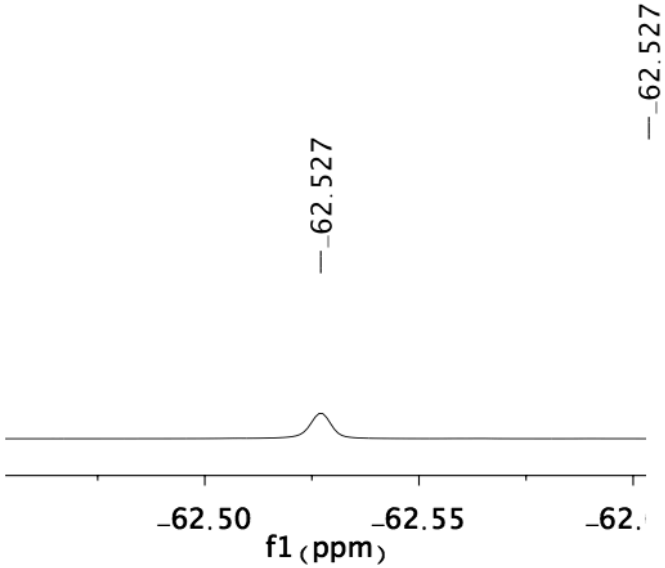
(*E*)-3-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol

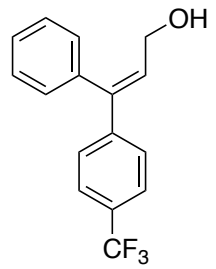


S2i

^{13}C NMR, 150 MHz, $CDCl_3$

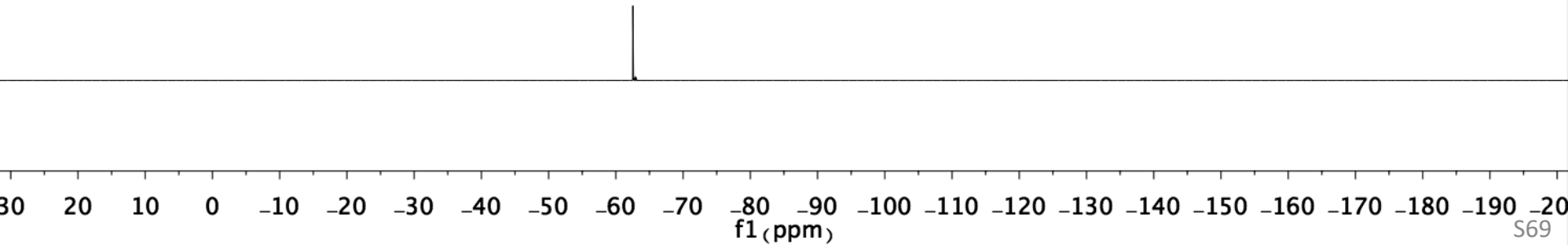
(*E*)-3-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol



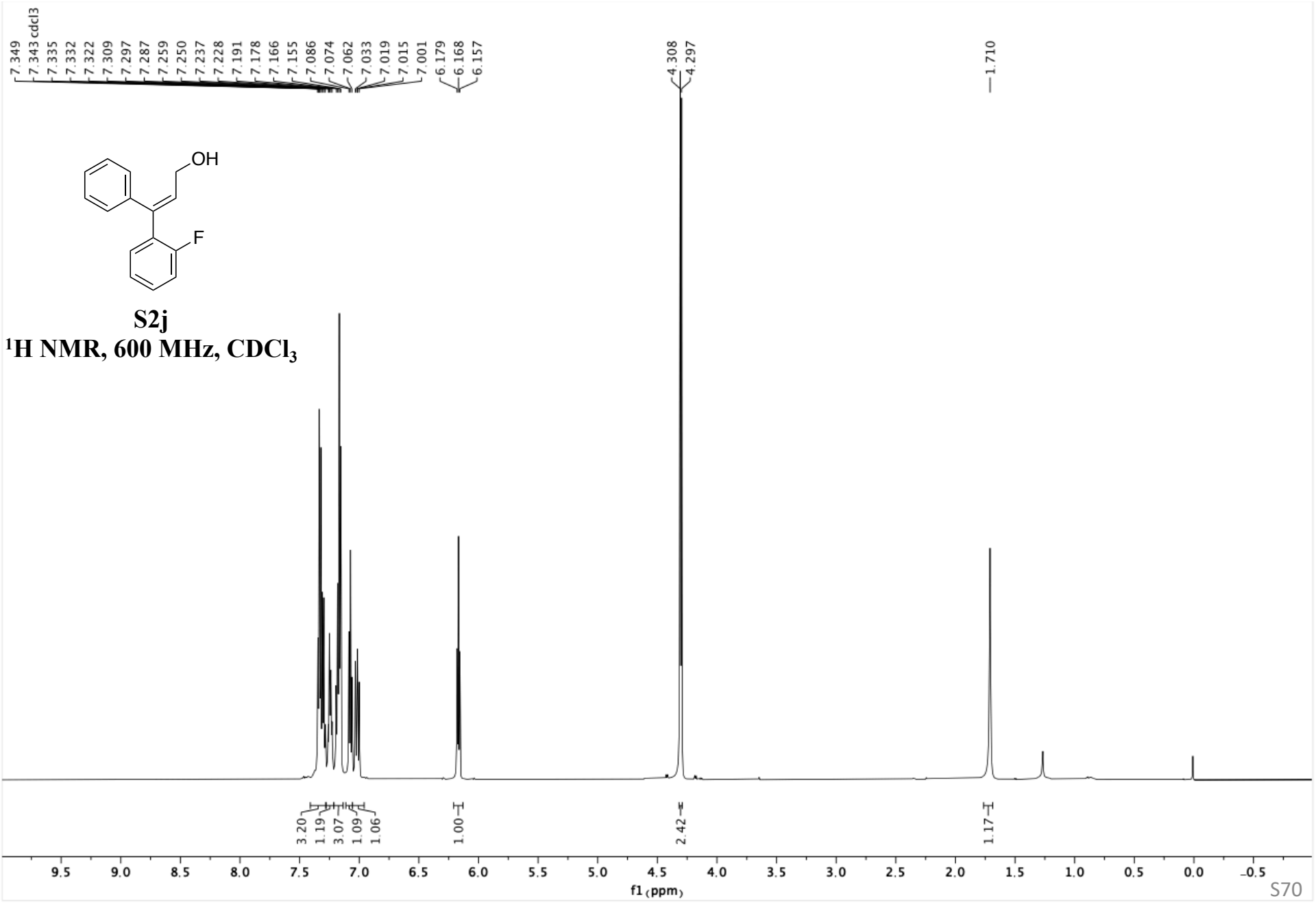


S2i

^{19}F NMR, 470 MHz, $CDCl_3$



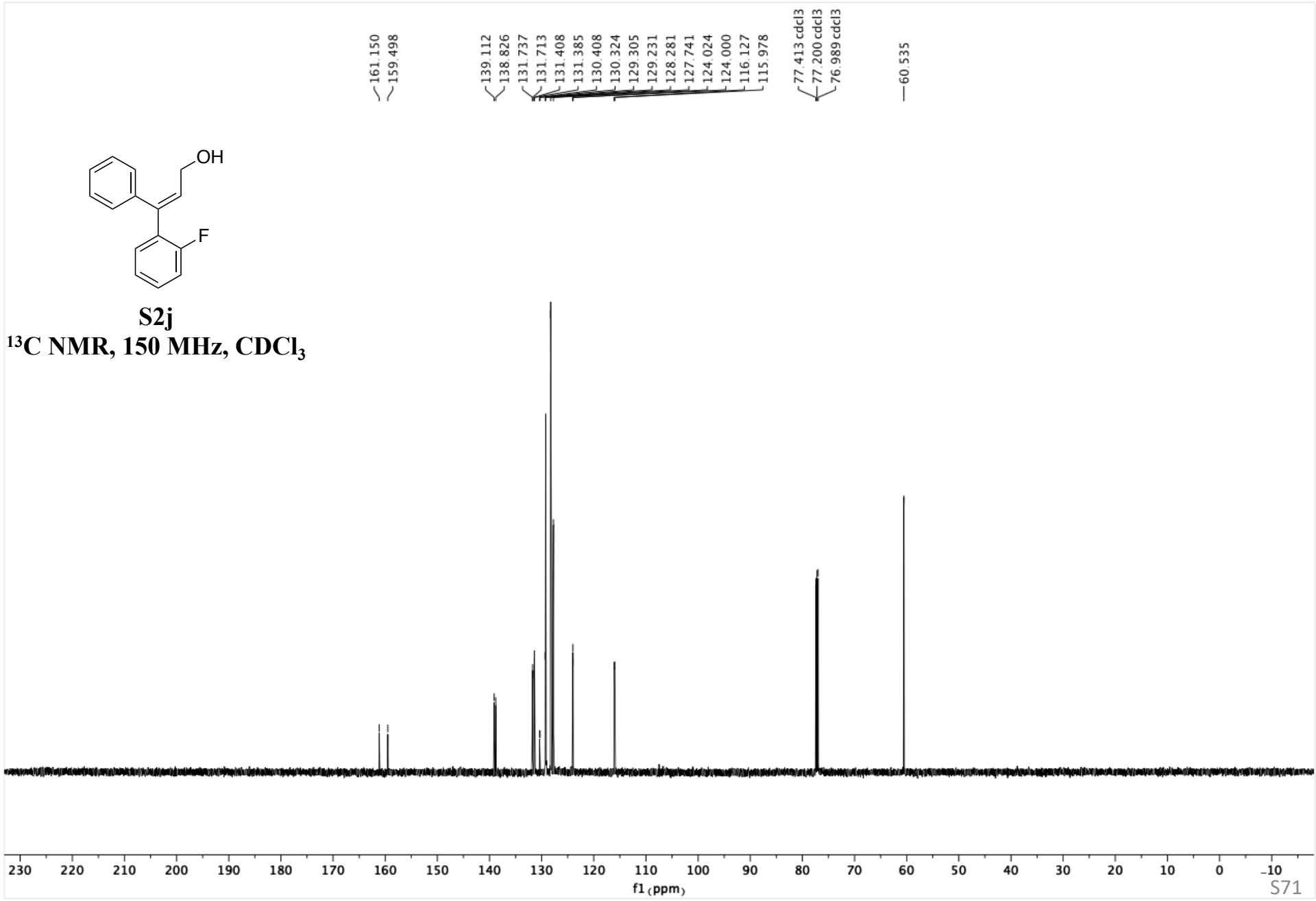
(*E*)-3-(2-Fluorophenyl)-3-phenylprop-2-en-1-ol



S2j

^{1}H NMR, 600 MHz, $CDCl_3$

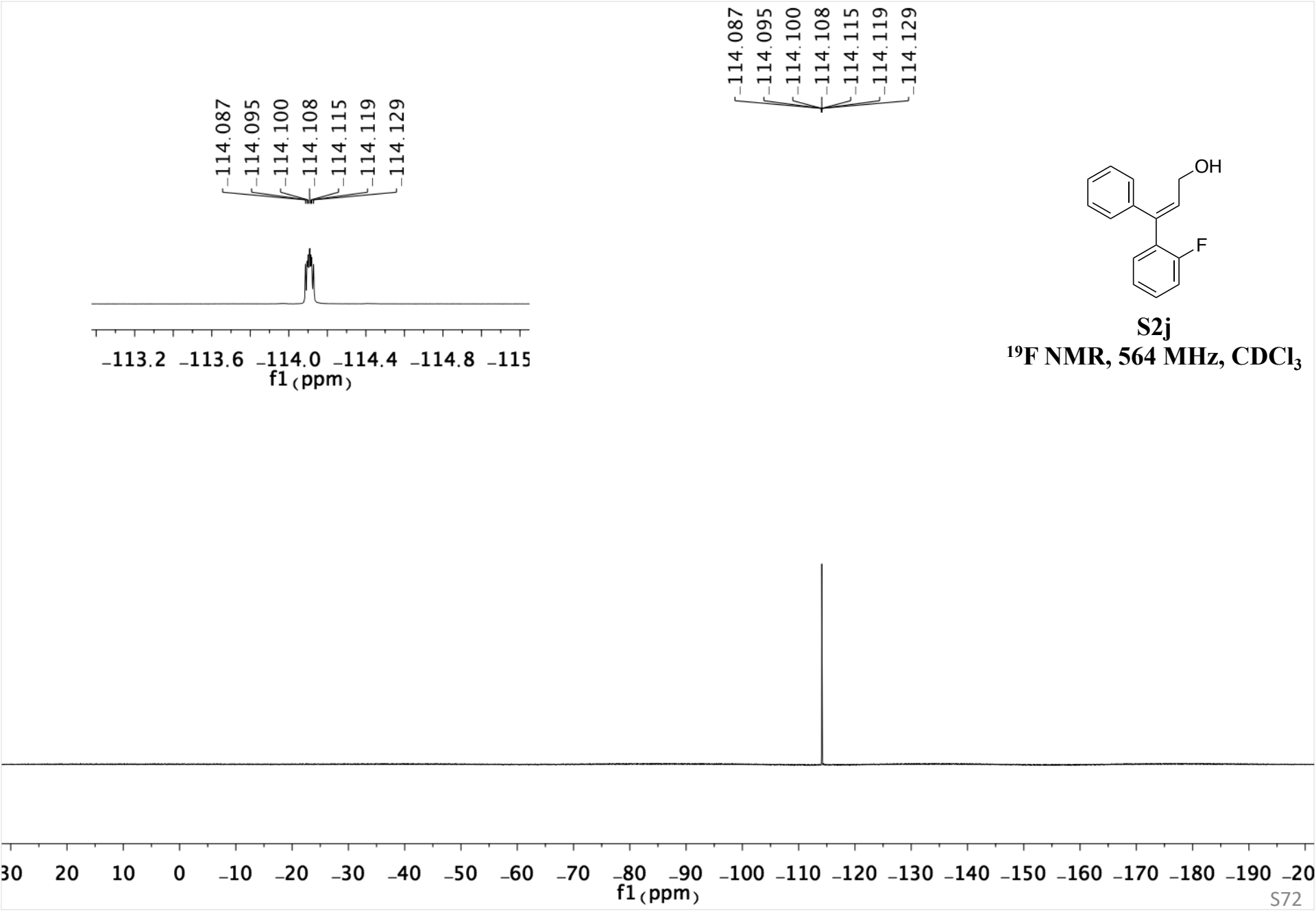
(*E*)-3-(2-Fluorophenyl)-3-phenylprop-2-en-1-ol



S2j

^{13}C NMR, 150 MHz, $CDCl_3$

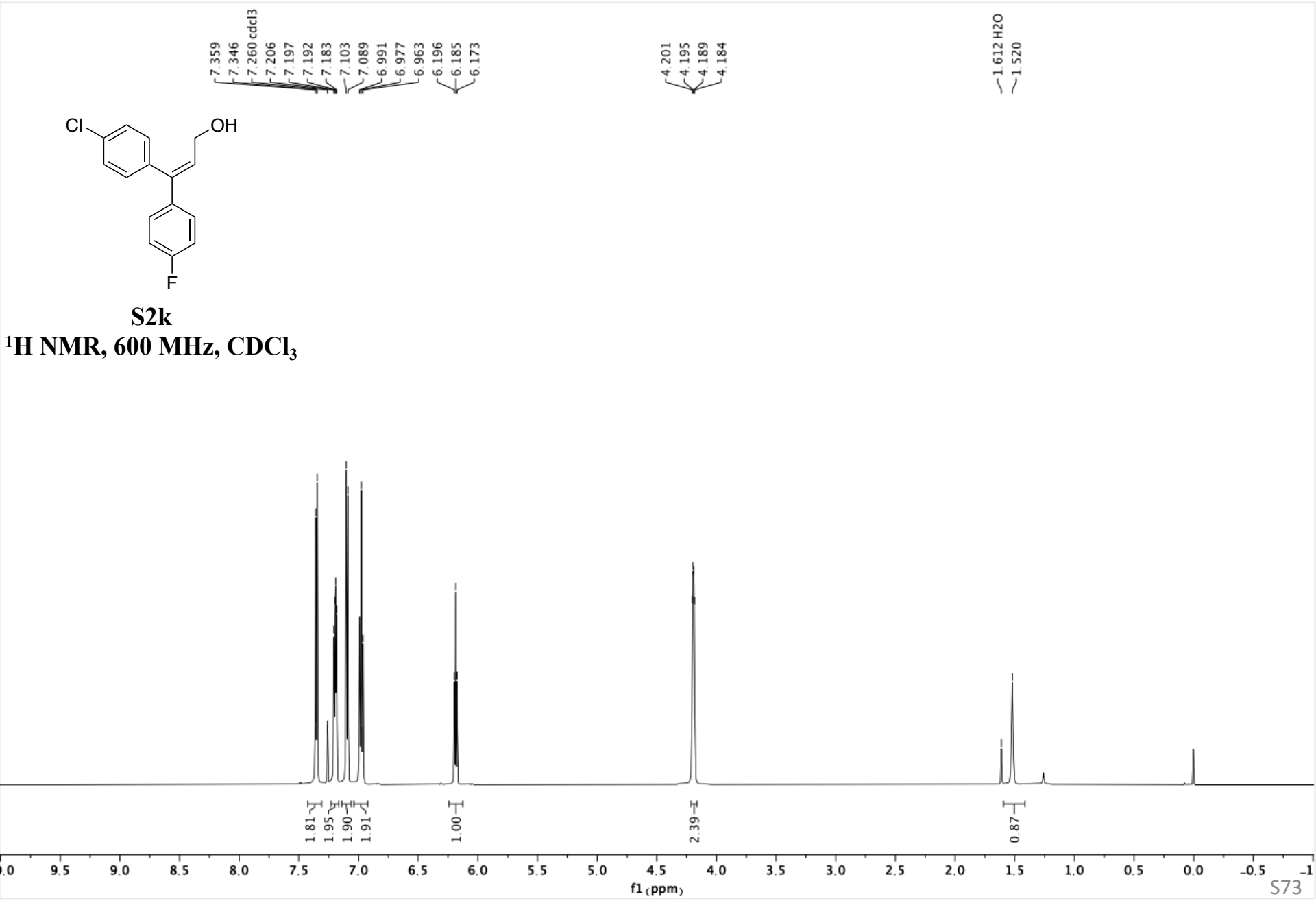
(*E*)-3-(2-Fluorophenyl)-3-phenylprop-2-en-1-ol



S2j

^{19}F NMR, 564 MHz, $CDCl_3$

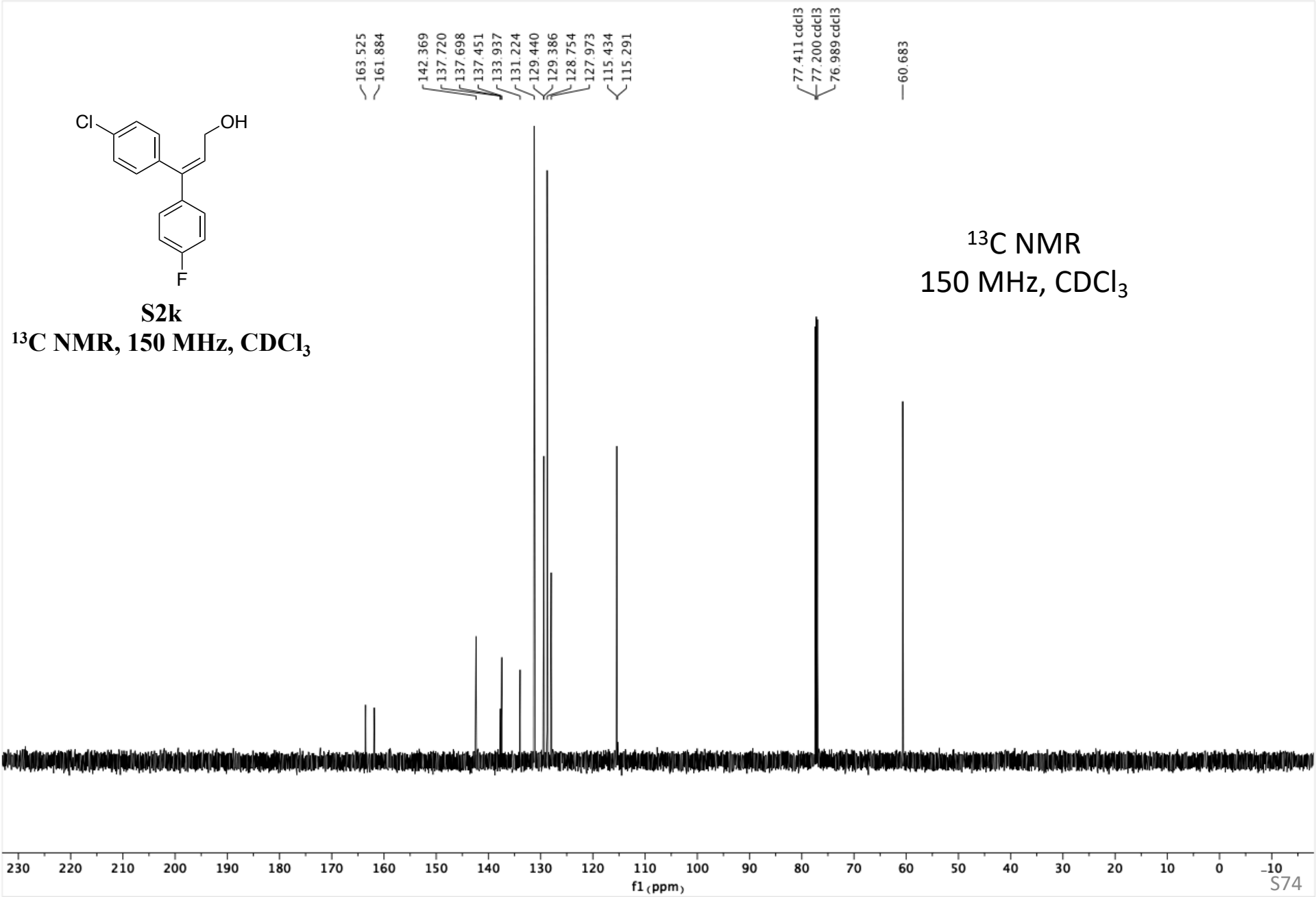
(*Z*)-3-(4-Chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-ol



S2k

^{1}H NMR, 600 MHz, $CDCl_3$

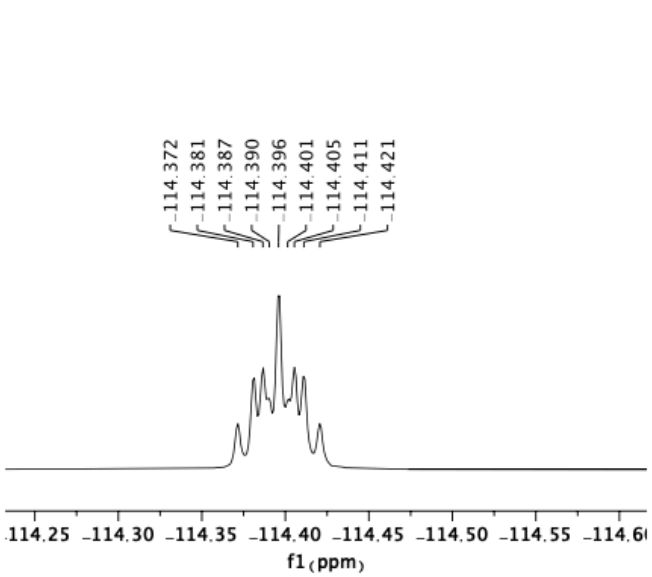
(*Z*)-3-(4-Chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-ol



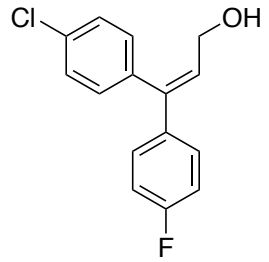
S2k

^{13}C NMR, 150 MHz, $CDCl_3$

(*Z*)-3-(4-Chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-ol

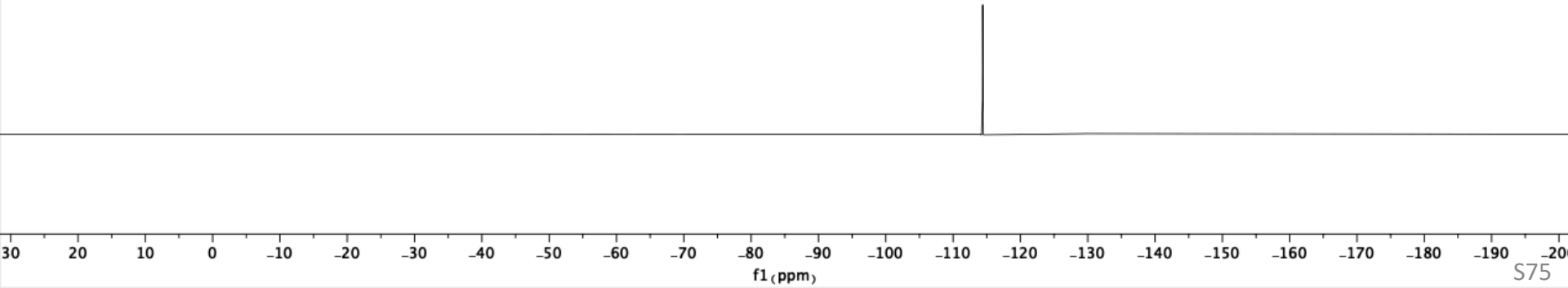




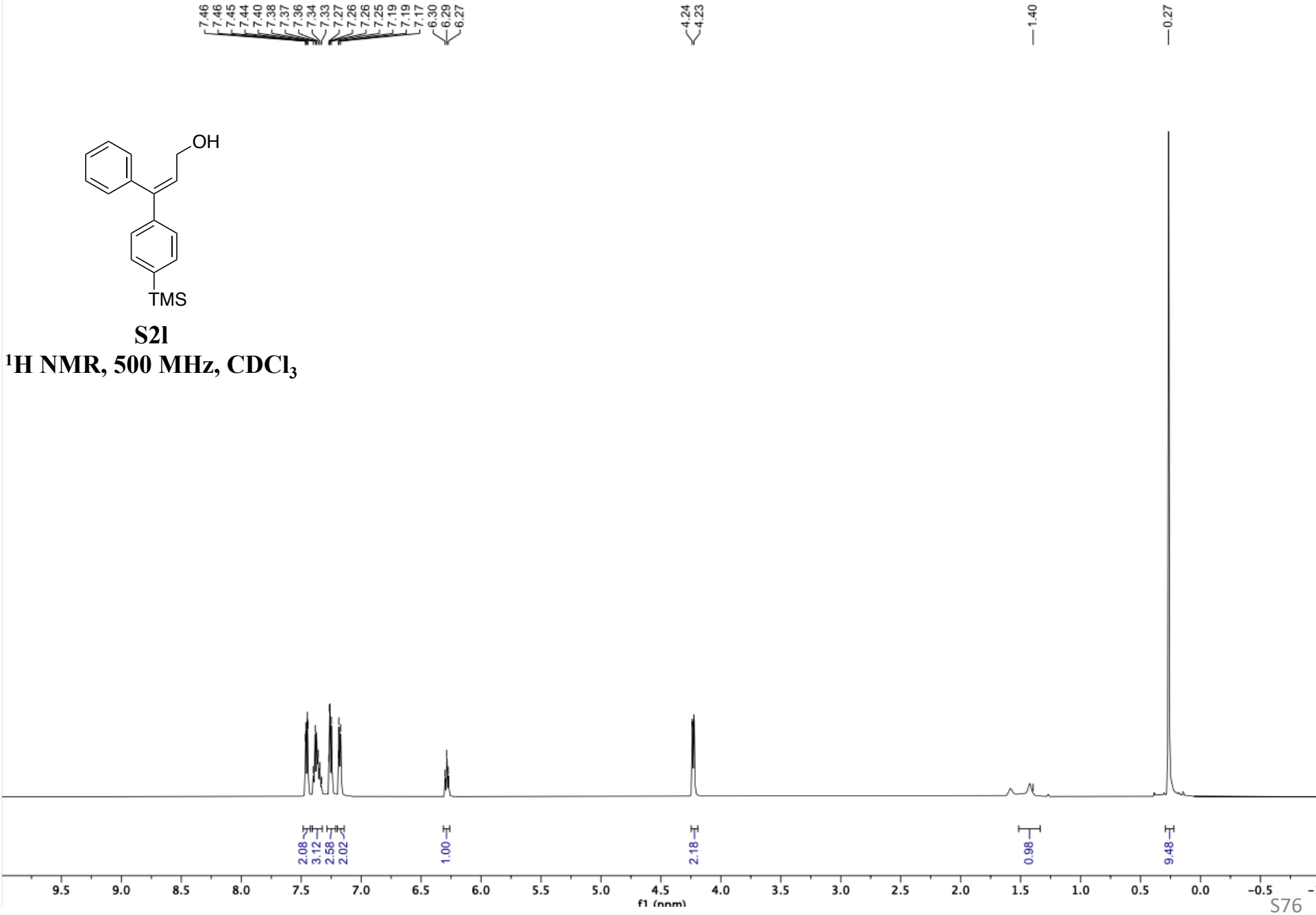


S2k

^{19}F NMR, 564 MHz, $CDCl_3$



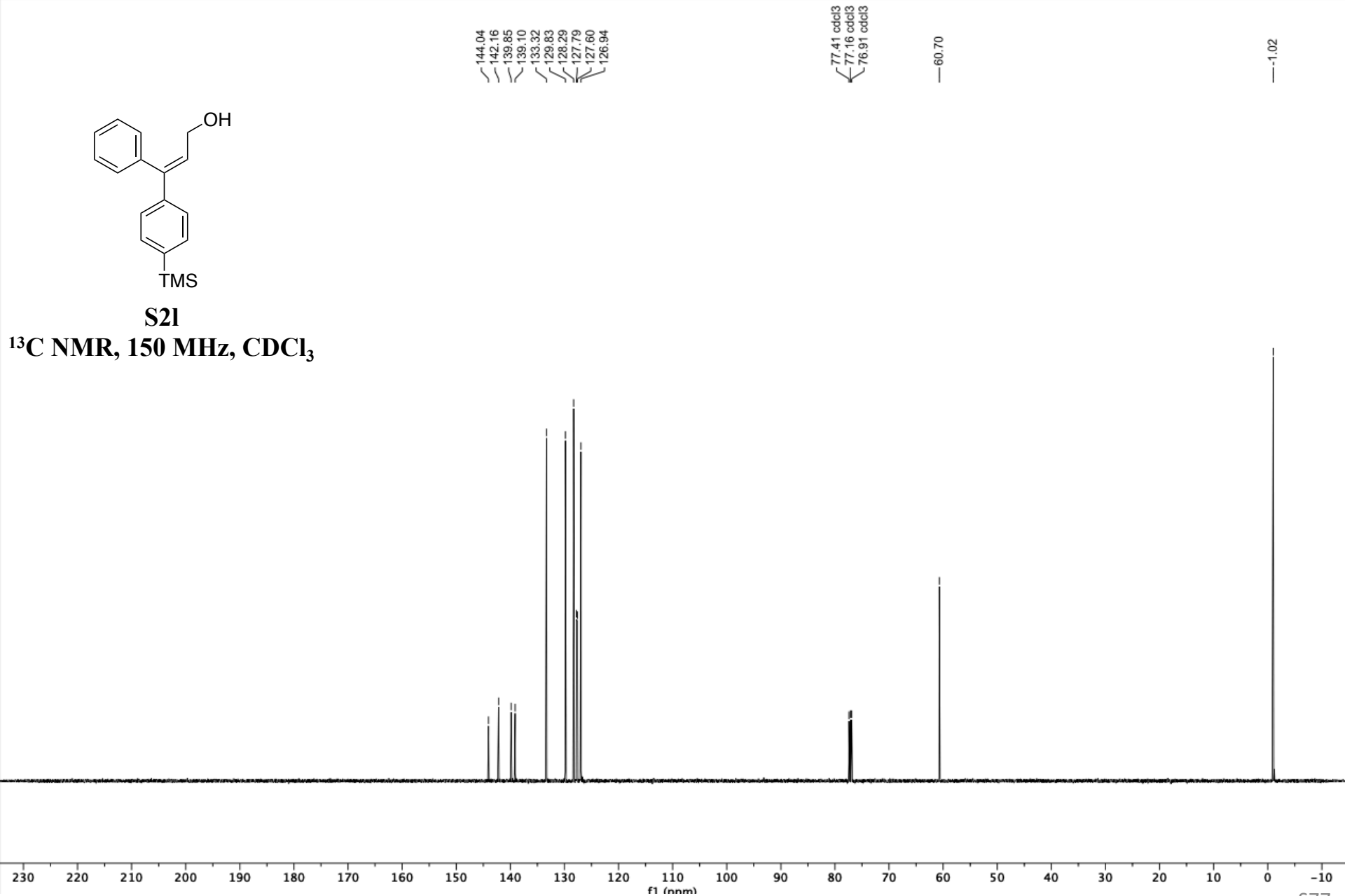
(*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)prop-2-en-1-ol



S21

^{1}H NMR, 500 MHz, $CDCl_3$

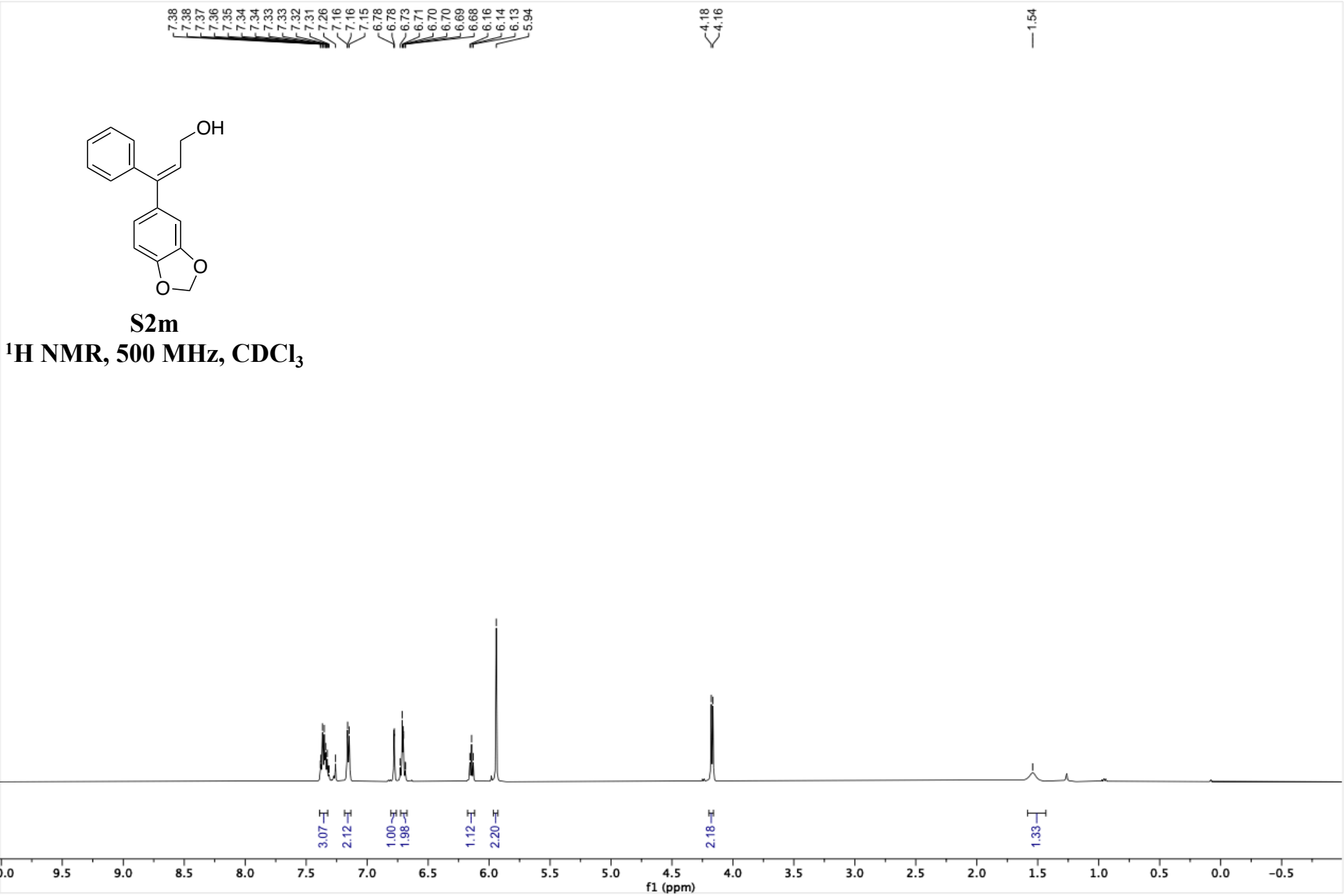
(*E*)-3-phenyl-3-(4-(trimethylsilyl)phenyl)prop-2-en-1-ol



S2l

^{13}C NMR, 150 MHz, $CDCl_3$

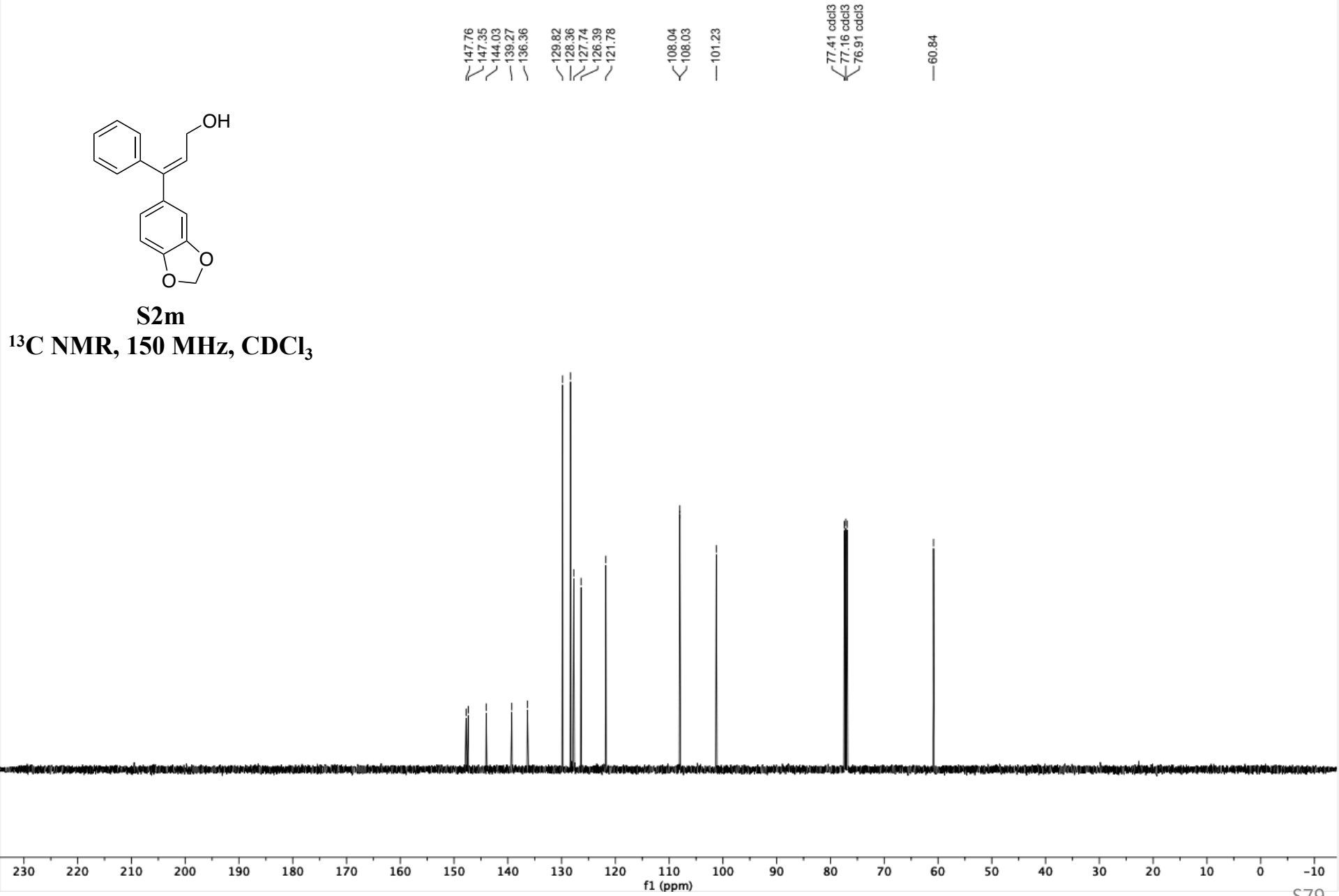
(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-ol



S2m

^{1}H NMR, 500 MHz, $CDCl_3$

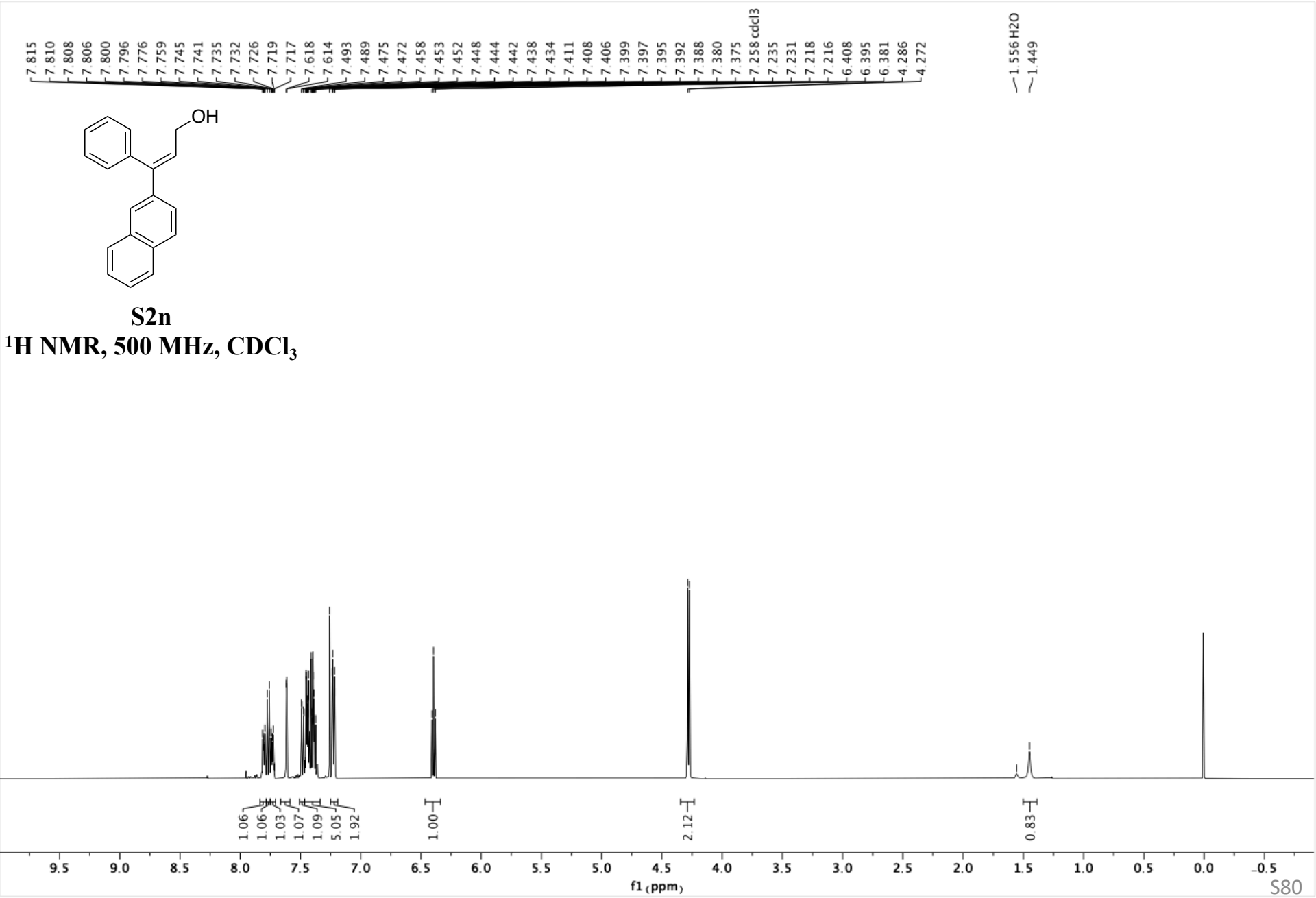
(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-ol



S2m

^{13}C NMR, 150 MHz, $CDCl_3$

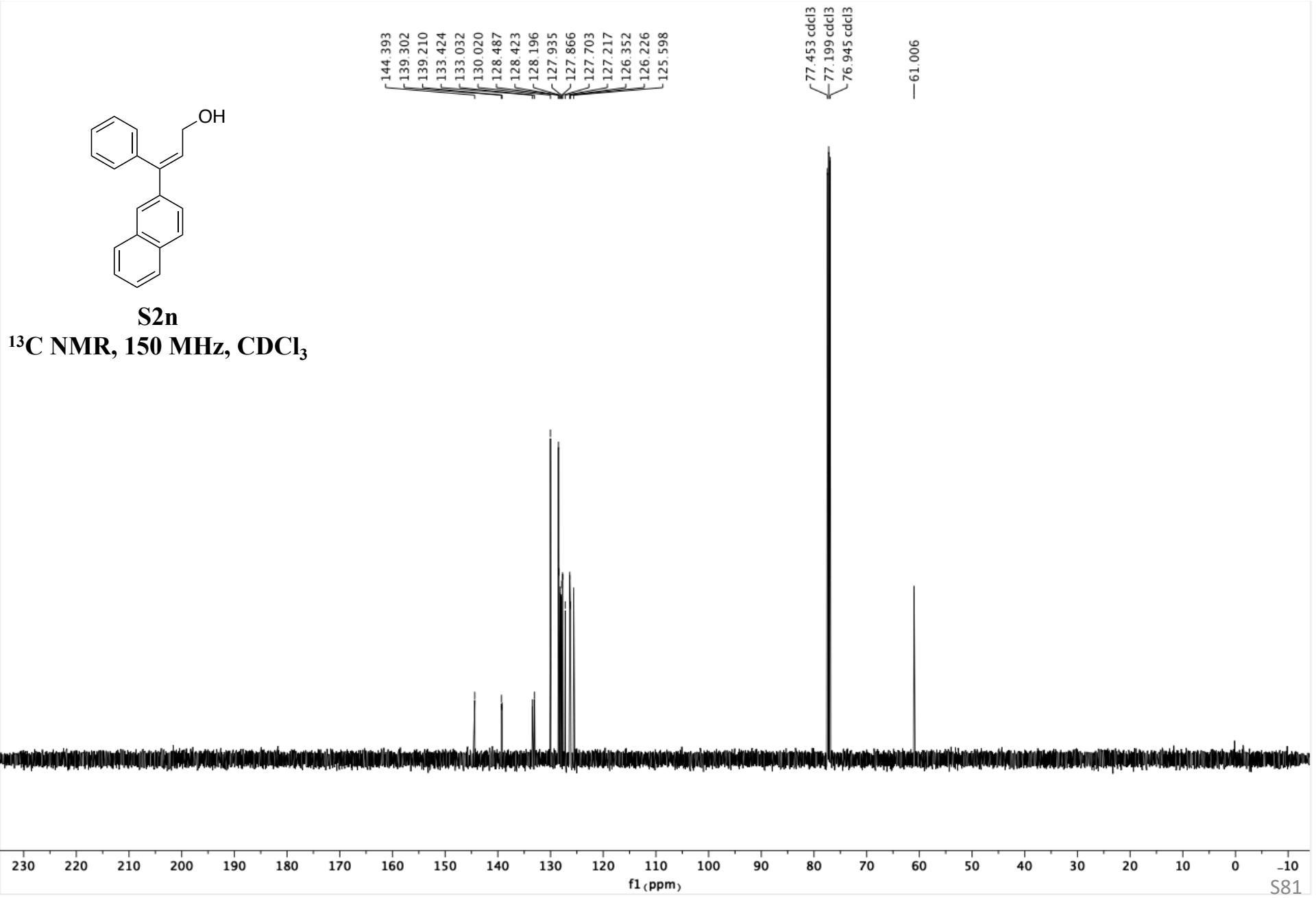
(*E*)-3-(Naphthalen-2-yl)-3-phenylprop-2-en-1-ol



S2n

^{1}H NMR, 500 MHz, $CDCl_3$

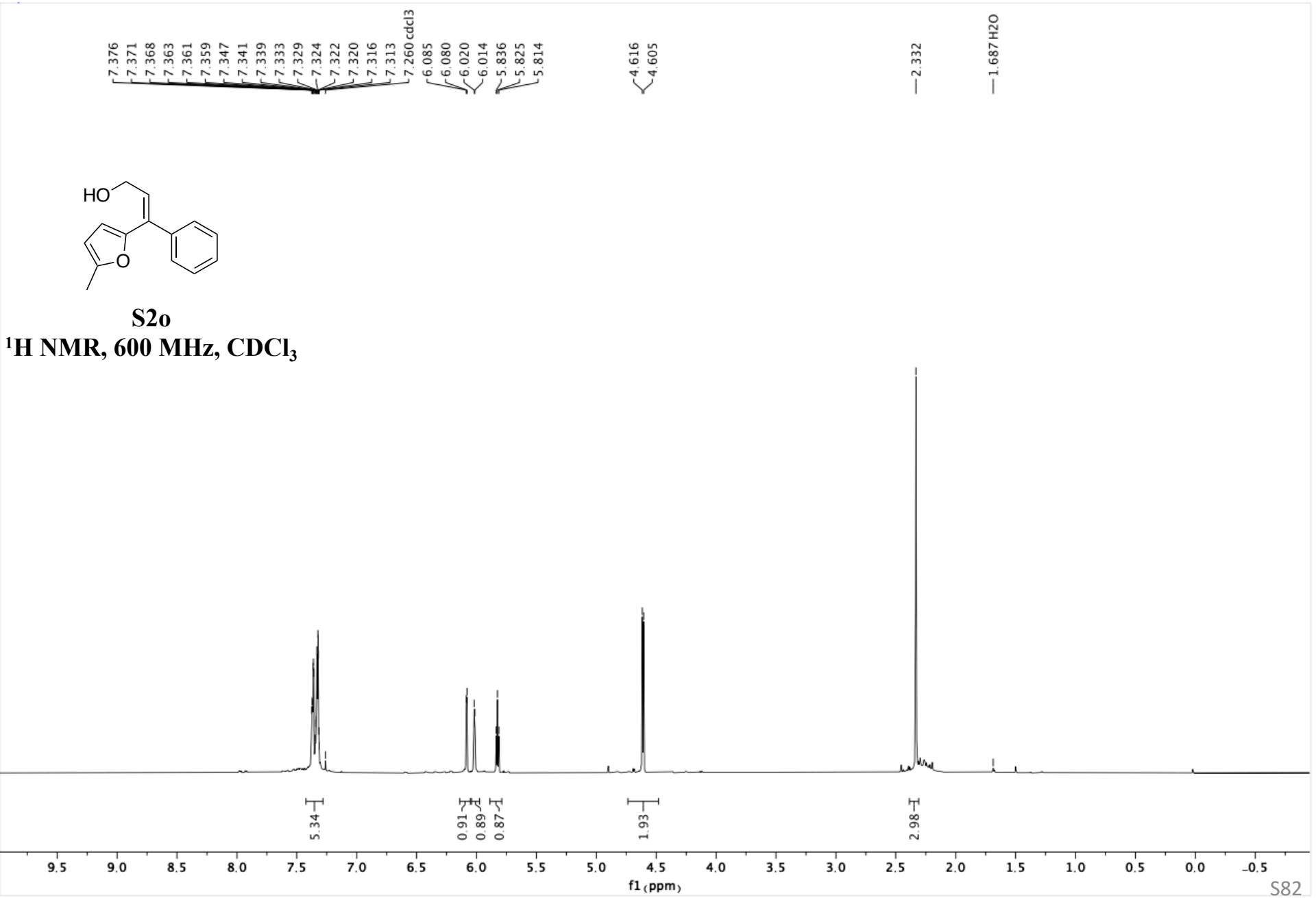
(*E*)-3-(Naphthalen-2-yl)-3-phenylprop-2-en-1-ol



S2n

^{13}C NMR, 150 MHz, $CDCl_3$

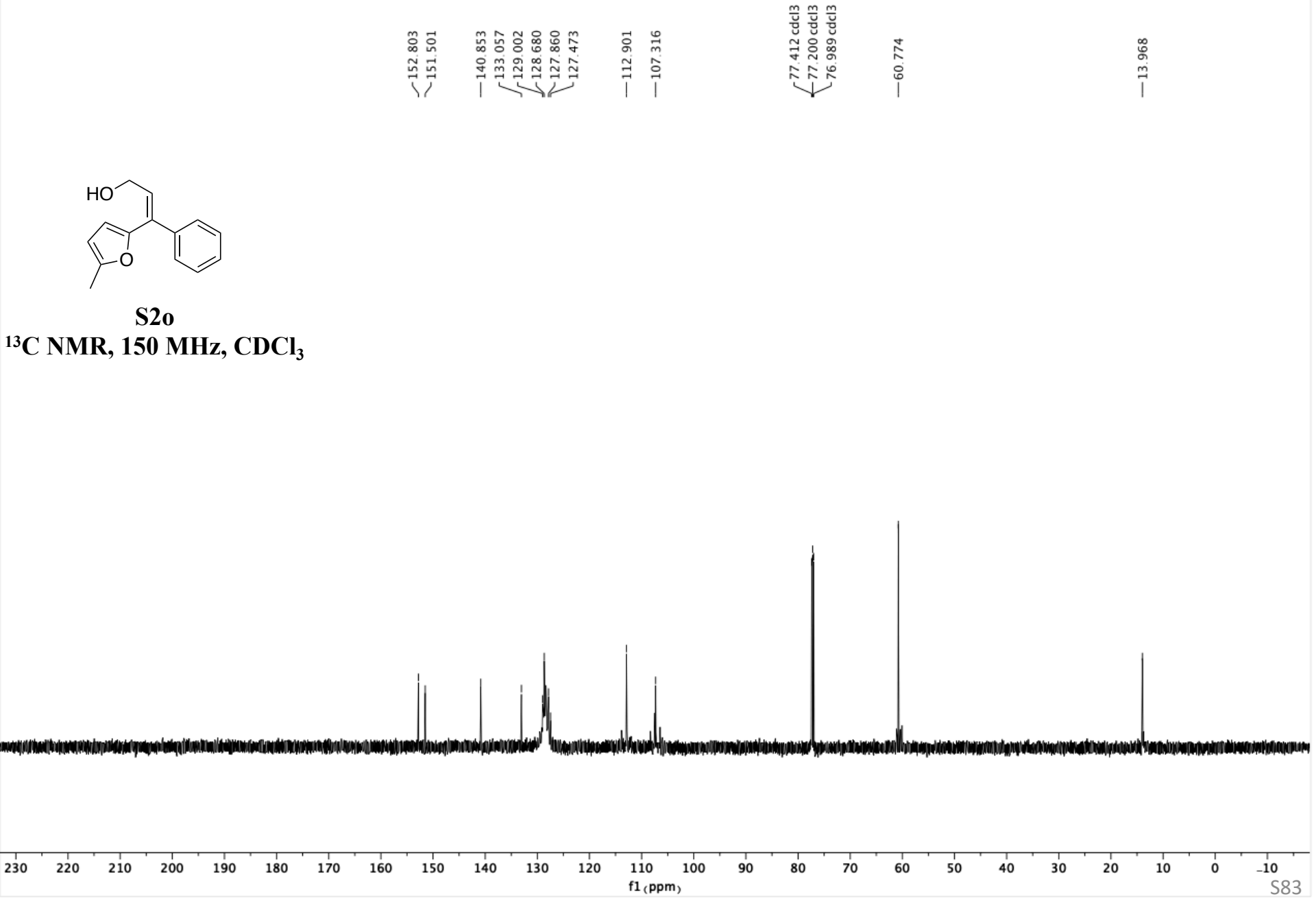
(*Z*)-3-(5-Methylfuran-2-yl)-3-phenylprop-2-en-1-ol



S2o

^{1}H NMR, 600 MHz, $CDCl_3$

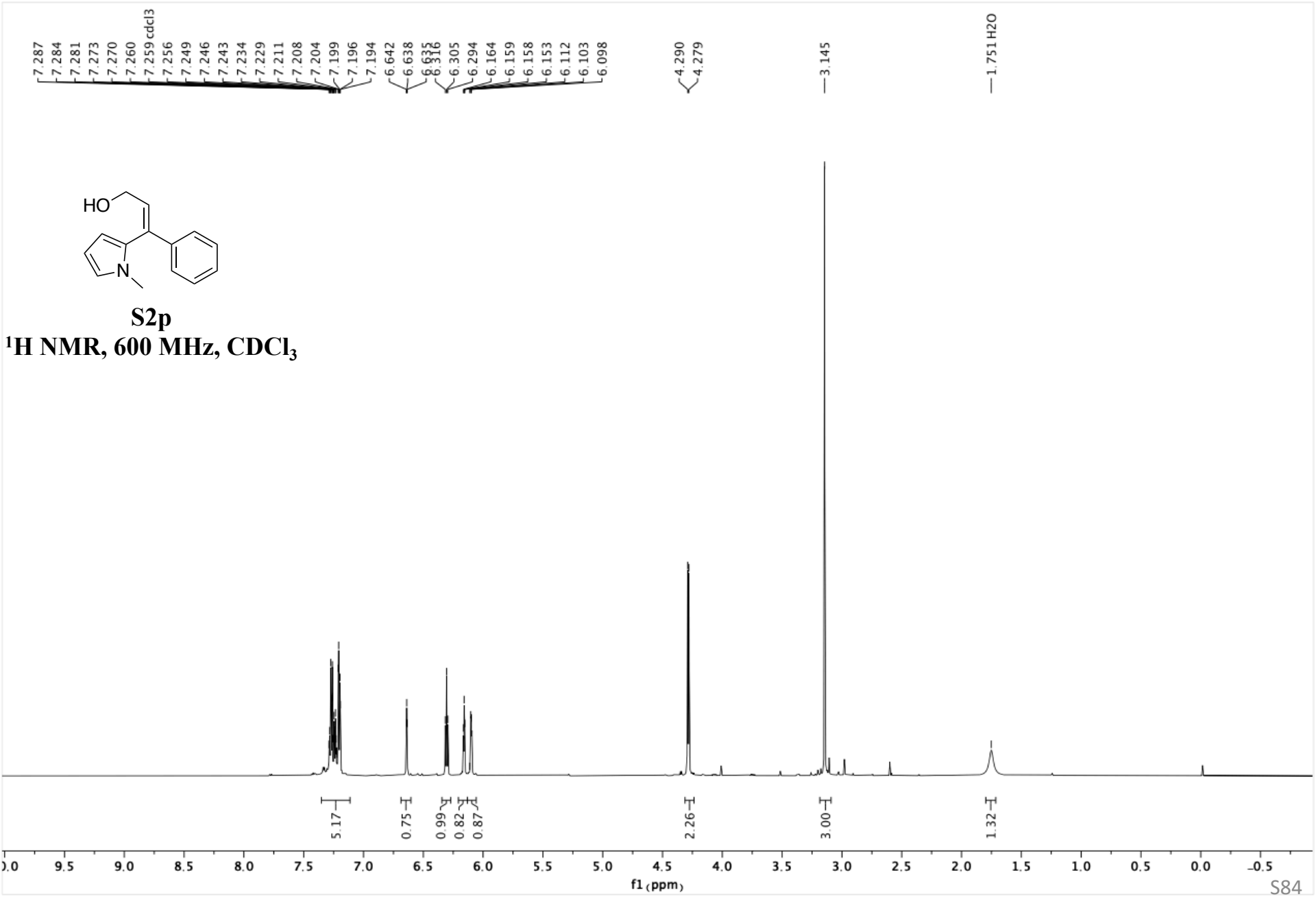
(*Z*)-3-(5-Methylfuran-2-yl)-3-phenylprop-2-en-1-ol



S2o

^{13}C NMR, 150 MHz, $CDCl_3$

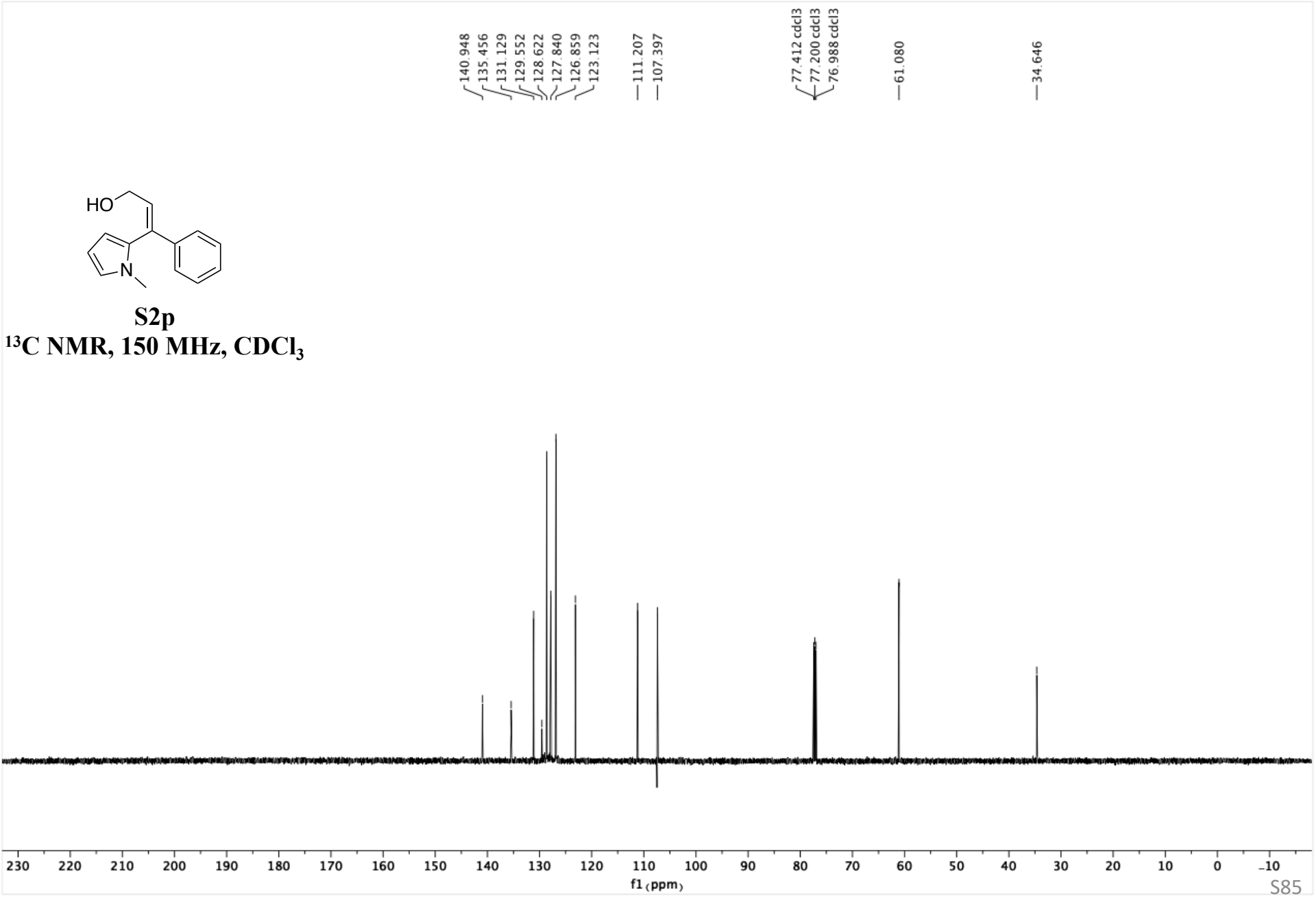
(*Z*)-3-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-en-1-ol



S2p

^{1}H NMR, 600 MHz, $CDCl_3$

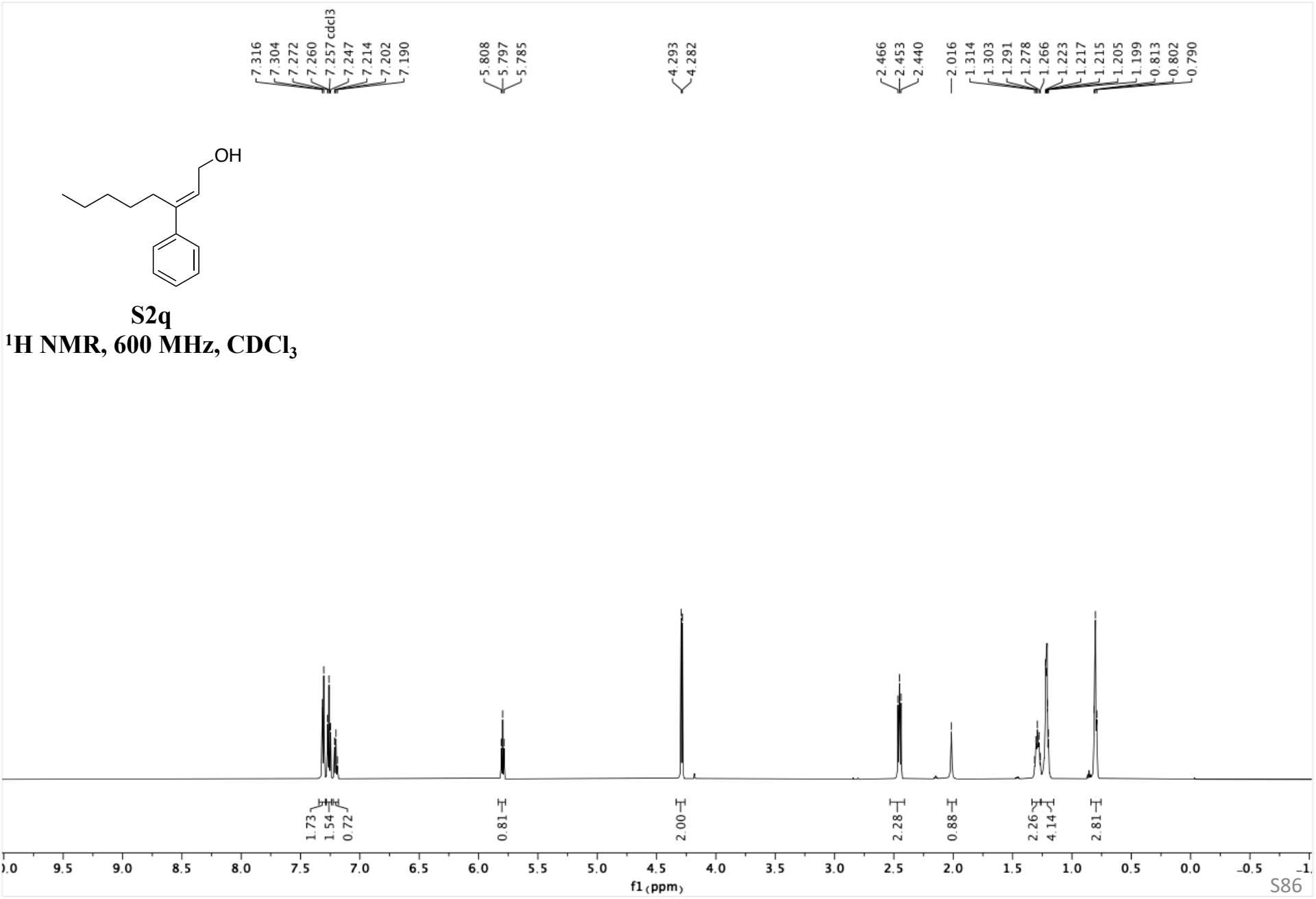
(*Z*)-3-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-en-1-ol



S2p

^{13}C NMR, 150 MHz, $CDCl_3$

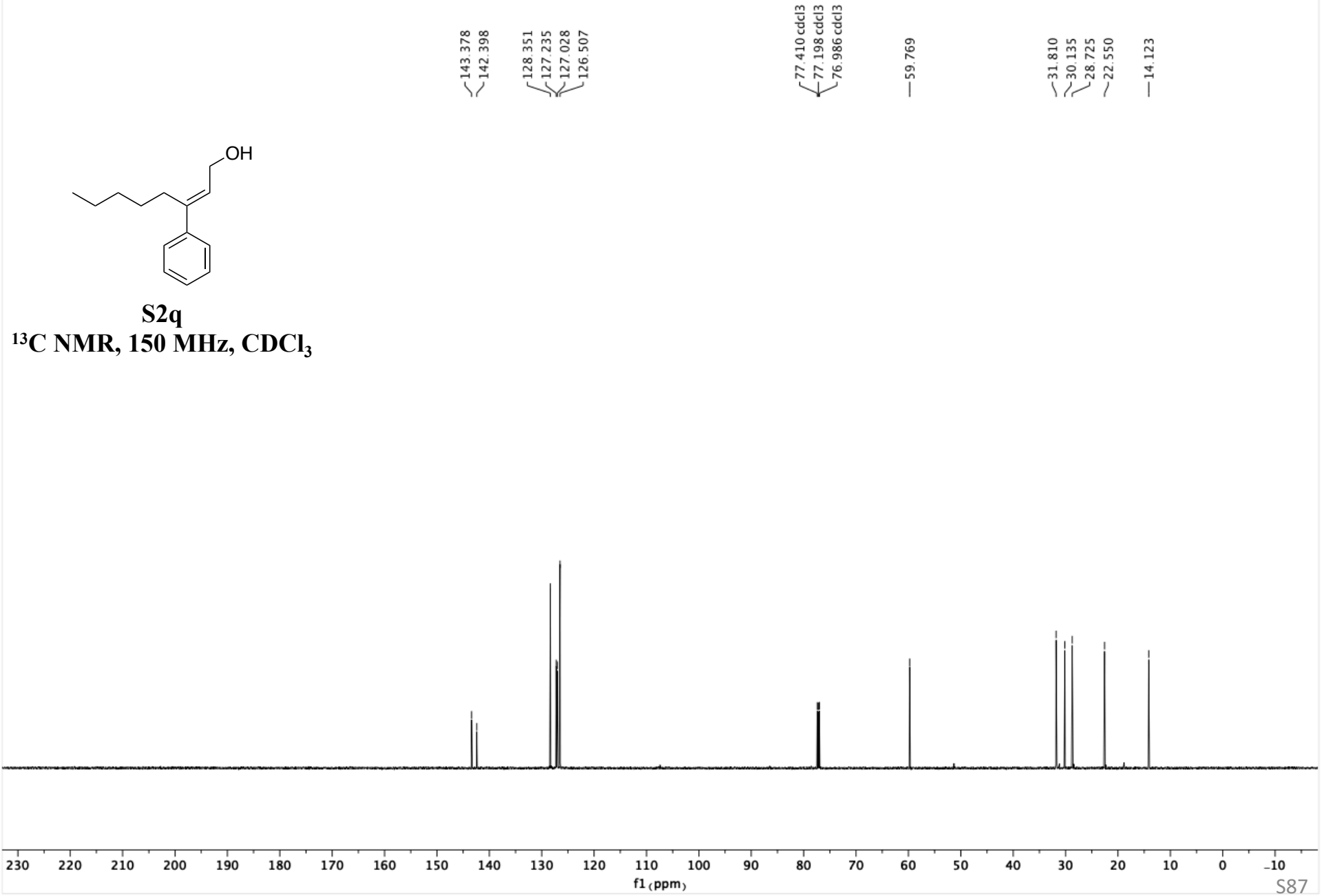
(*E*)-3-Phenyloct-2-en-1-ol



S2q

^{1}H NMR, 600 MHz, $CDCl_3$

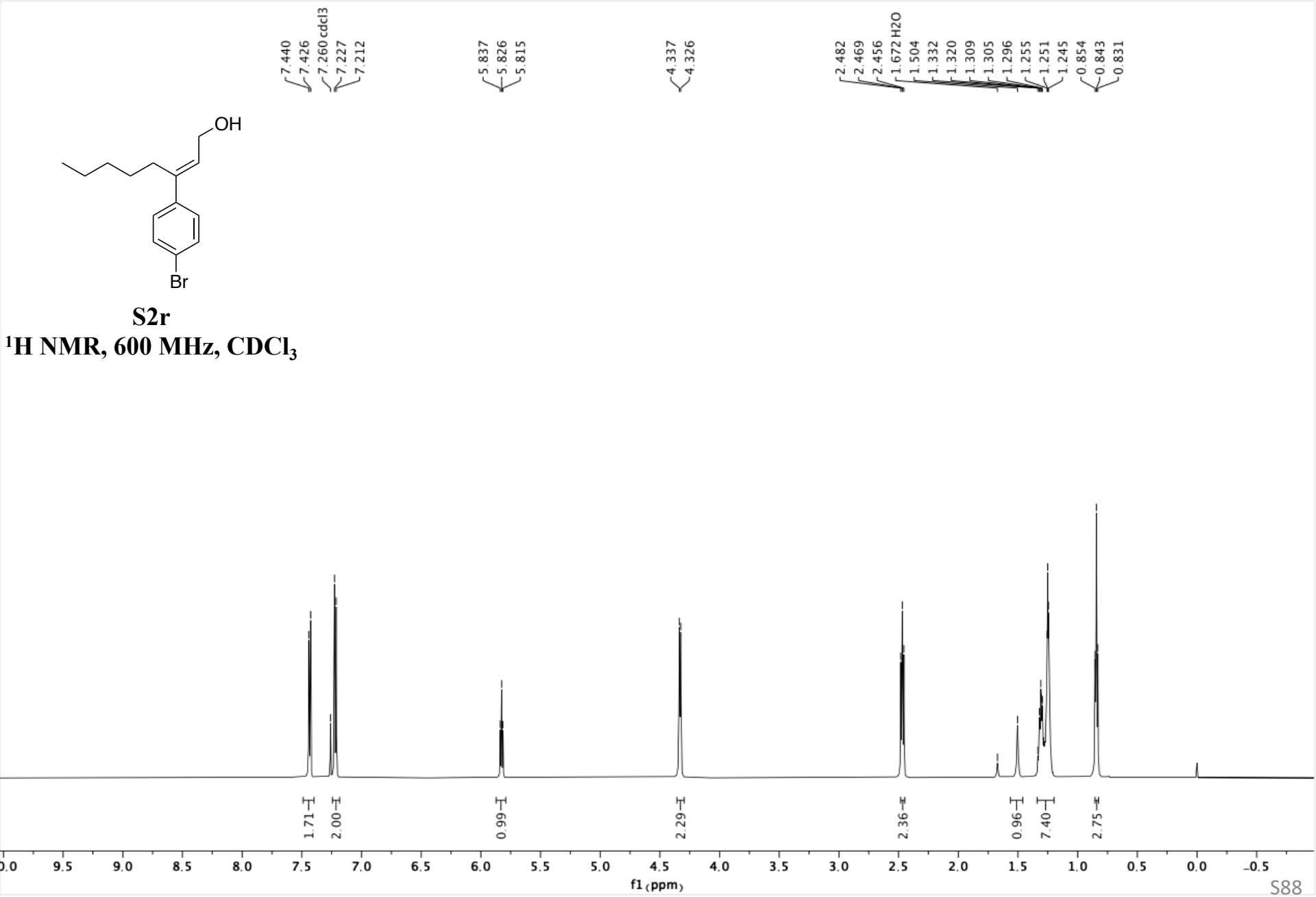
(*E*)-3-Phenyloct-2-en-1-ol



S2q

^{13}C NMR, 150 MHz, $CDCl_3$

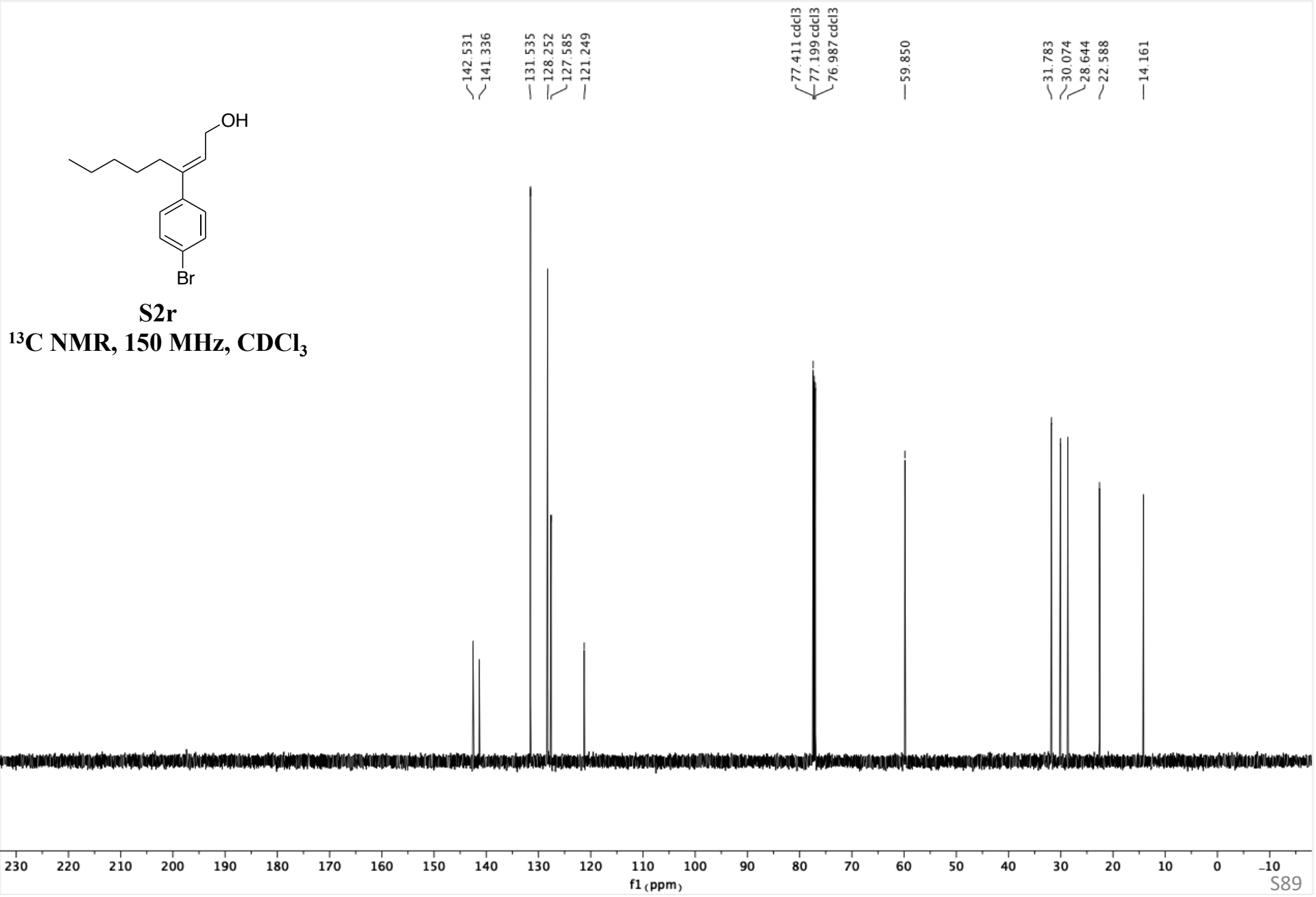
(*E*)-3-(4-Bromophenyl)oct-2-en-1-ol



S2r

^{1}H NMR, 600 MHz, $CDCl_3$

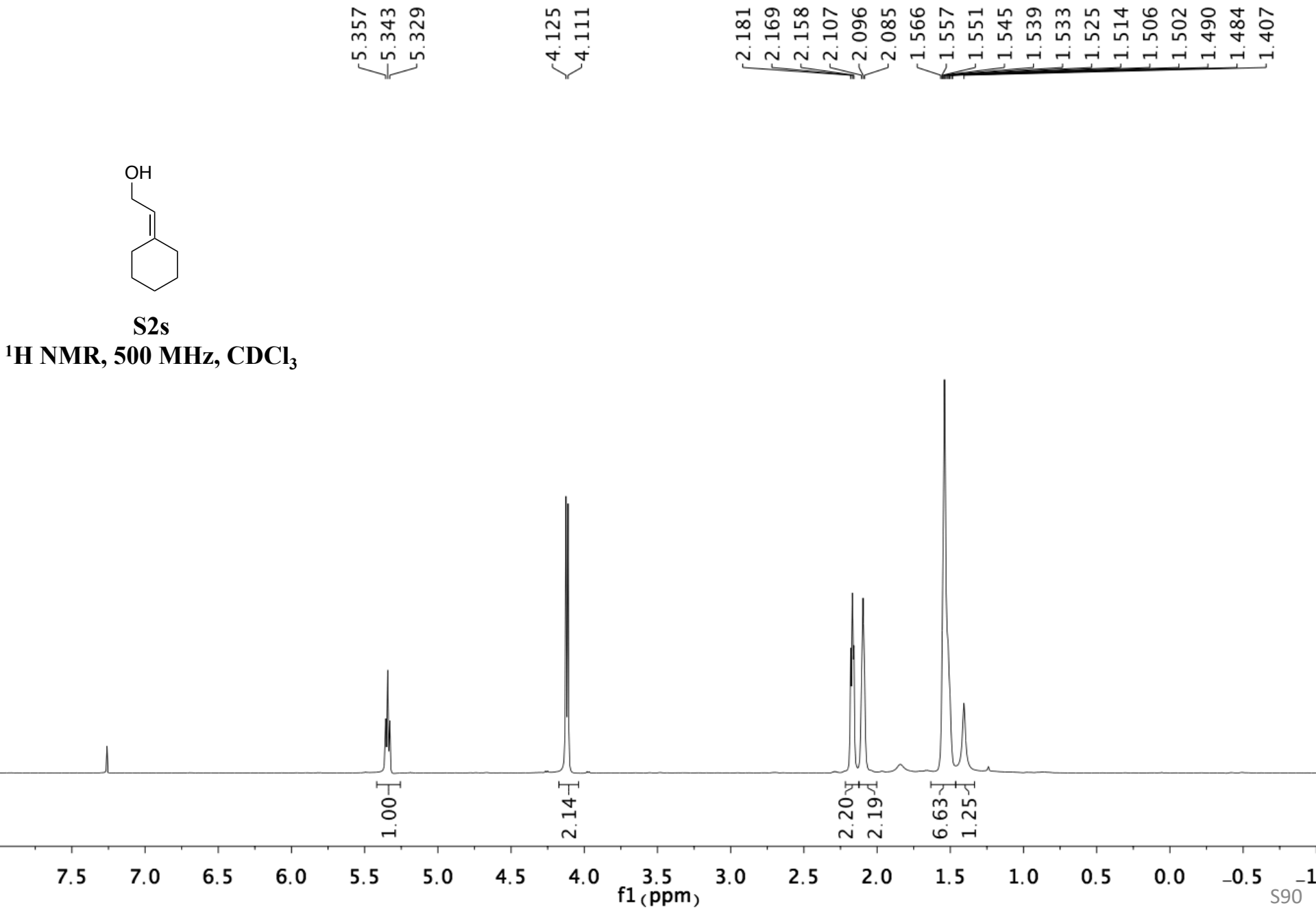
(*E*)-3-(4-Bromophenyl)oct-2-en-1-ol



S2r

^{13}C NMR, 150 MHz, $CDCl_3$

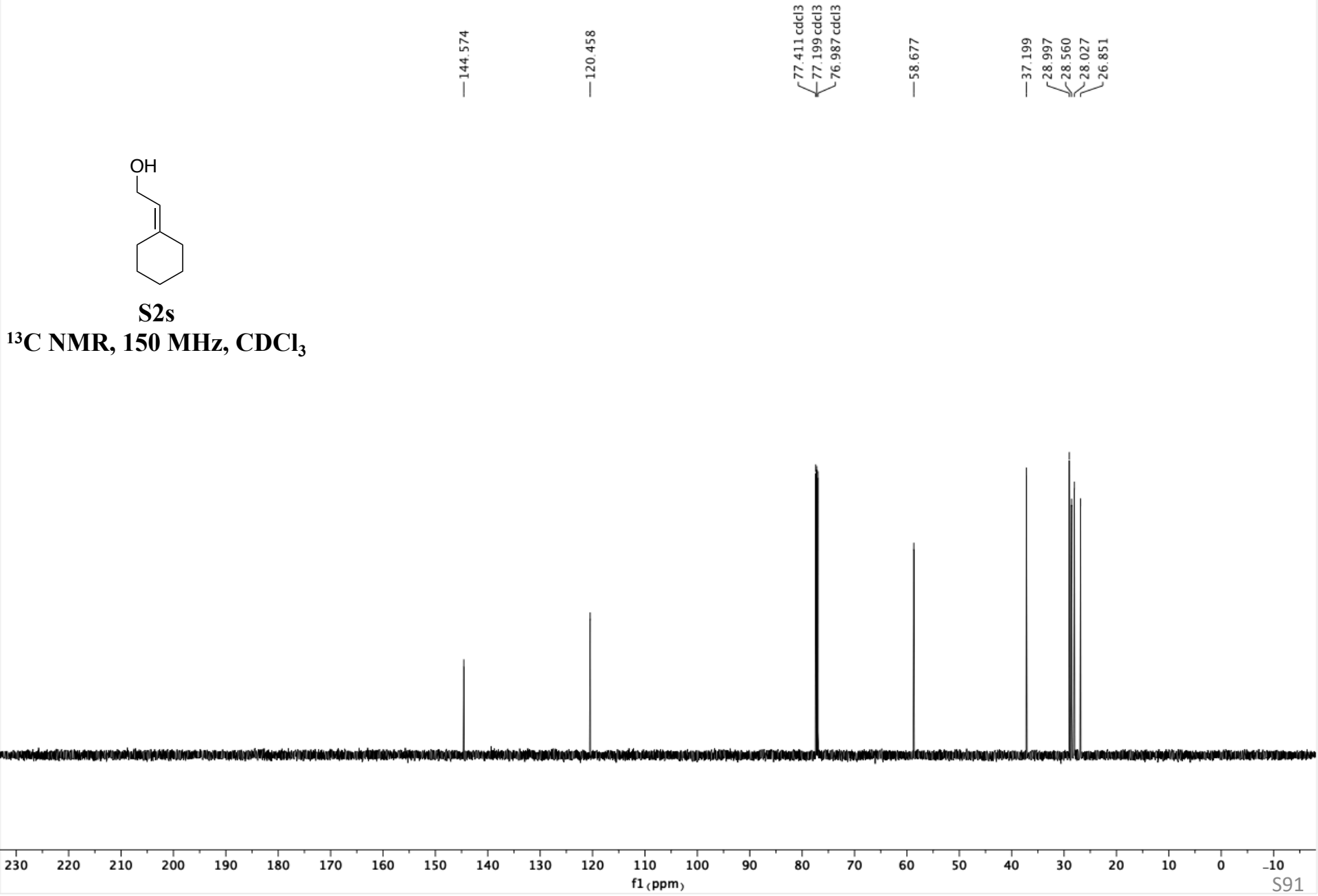
2-Cyclohexylideneethan-1-ol



S2s

^{1}H NMR, 500 MHz, $CDCl_3$

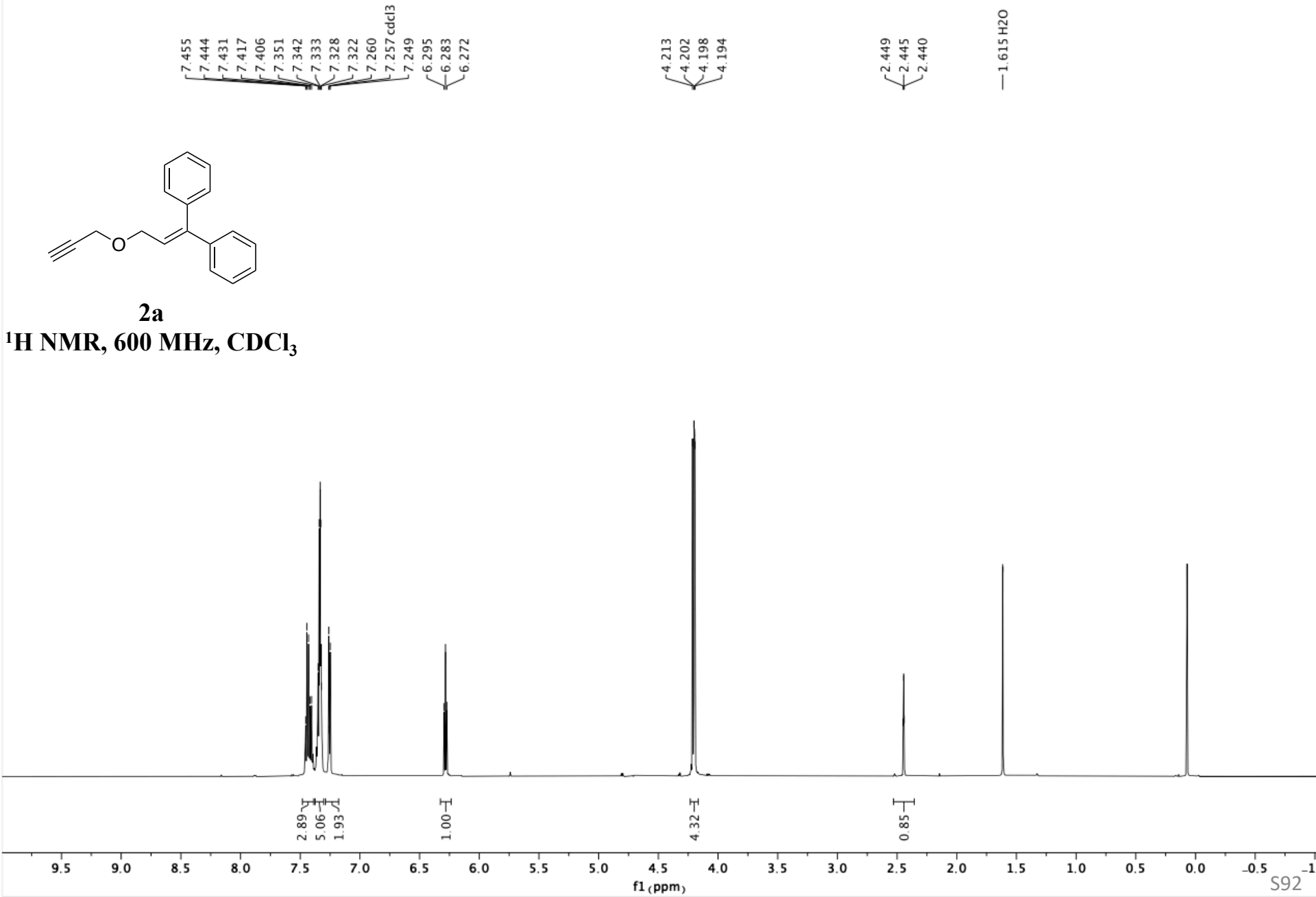
2-Cyclohexylideneethan-1-ol



S2s

^{13}C NMR, 150 MHz, $CDCl_3$

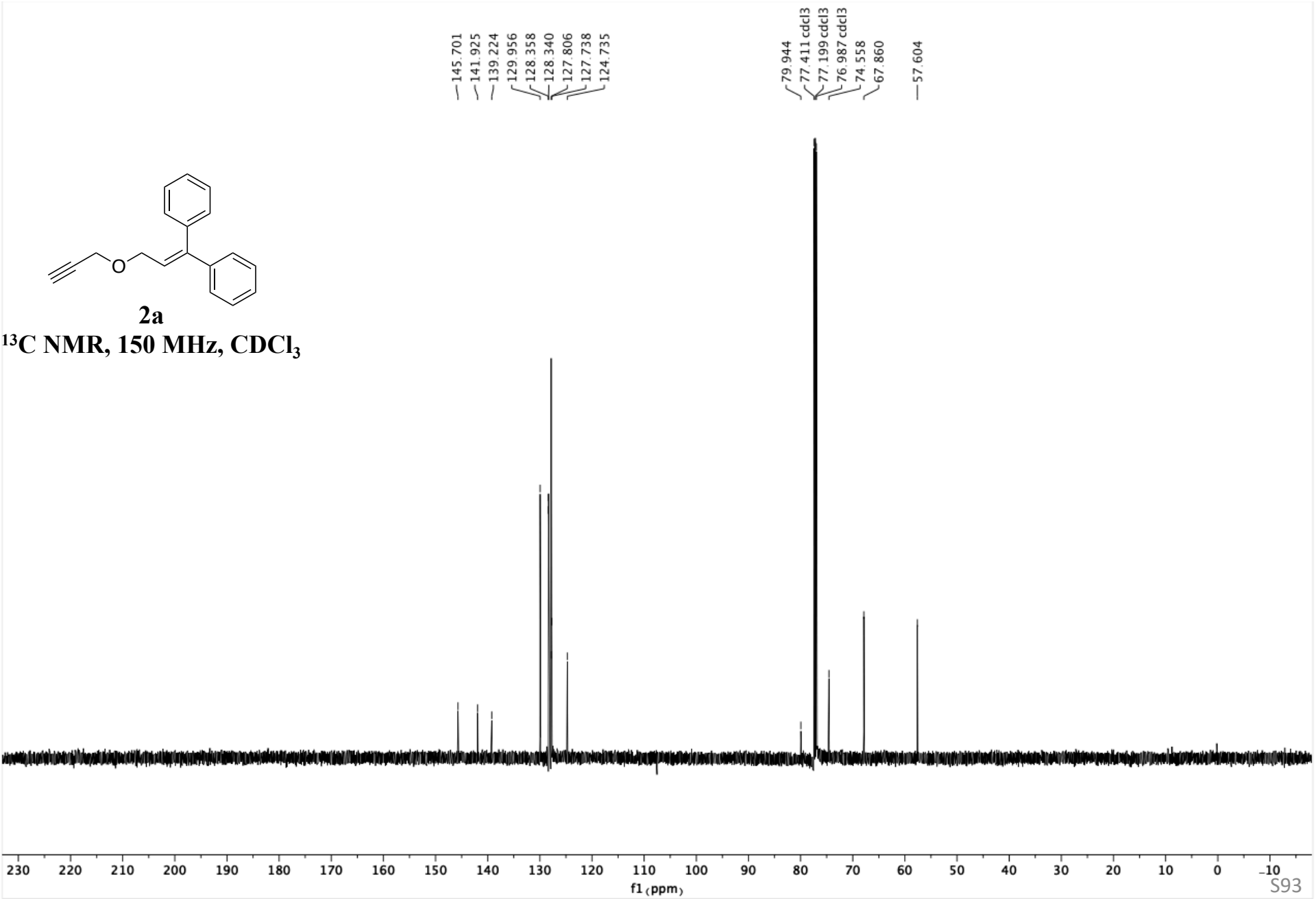
(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)dibenzene



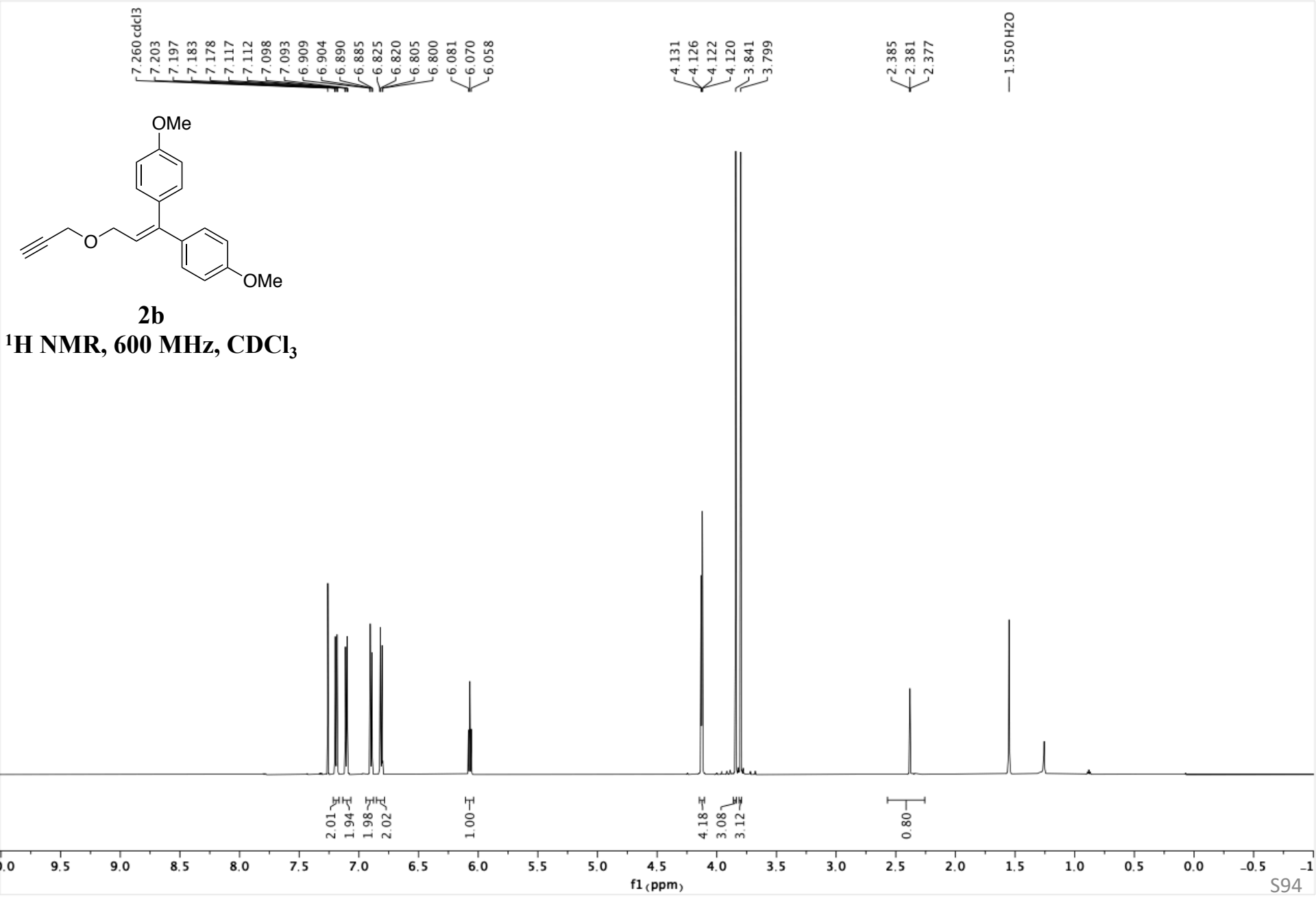
2a

^{1}H NMR, 600 MHz, $CDCl_3$

(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)dibenzene



4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(methoxybenzene)



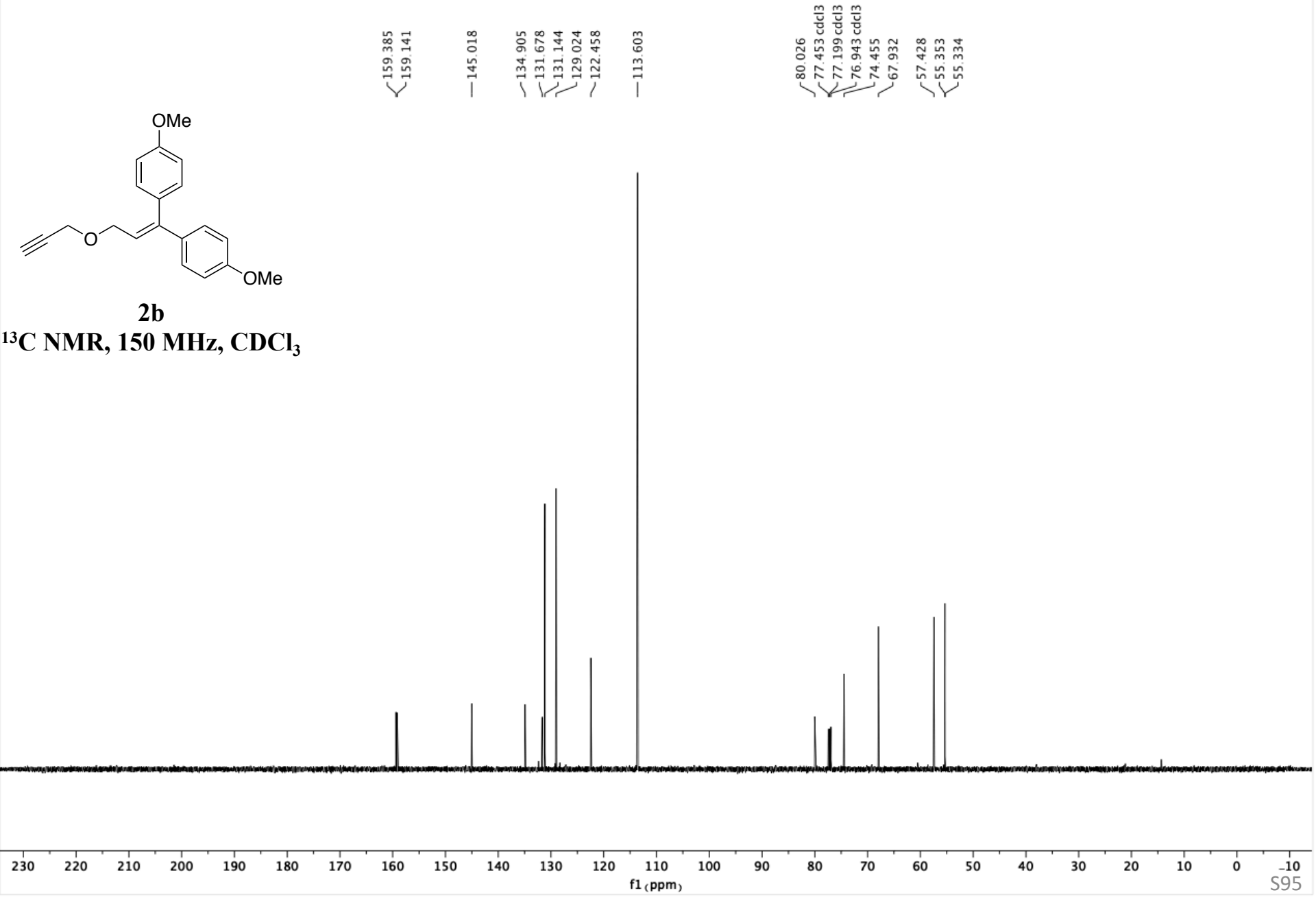
2b

^{1}H NMR, 600 MHz, $CDCl_3$

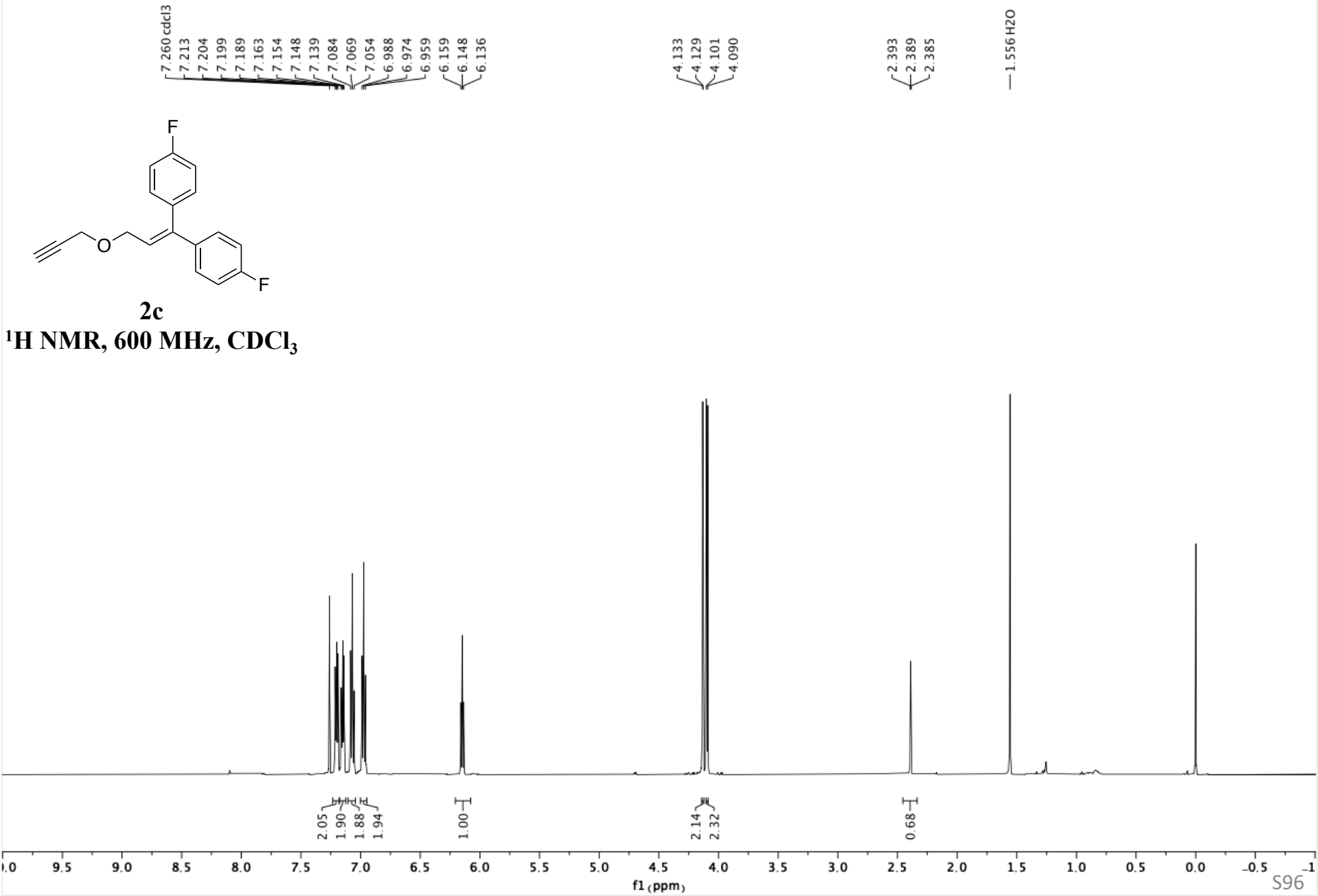
4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(methoxybenzene)

2b

^{13}C NMR, 150 MHz, $CDCl_3$



4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)



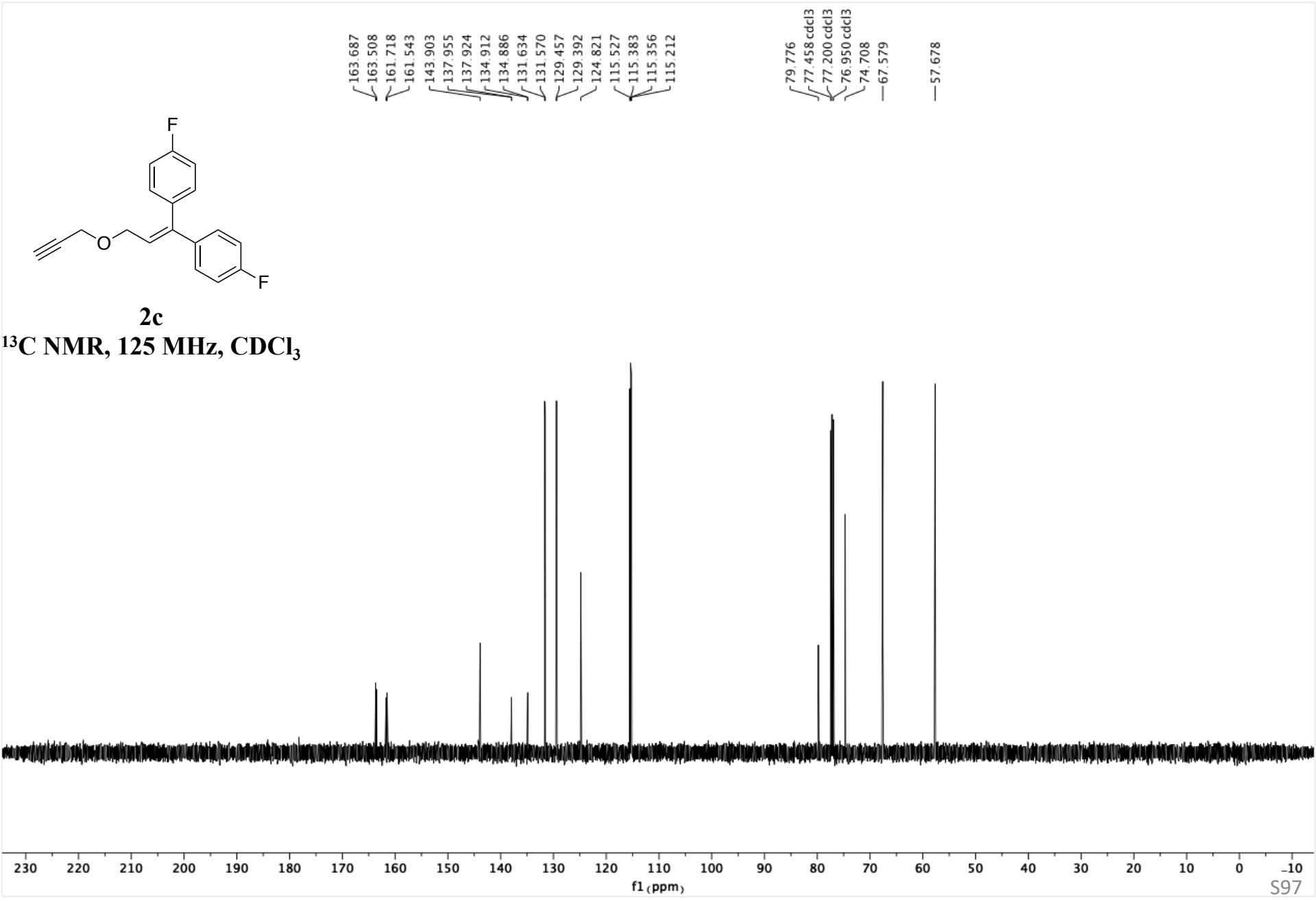
2c

^{1}H NMR, 600 MHz, $CDCl_3$

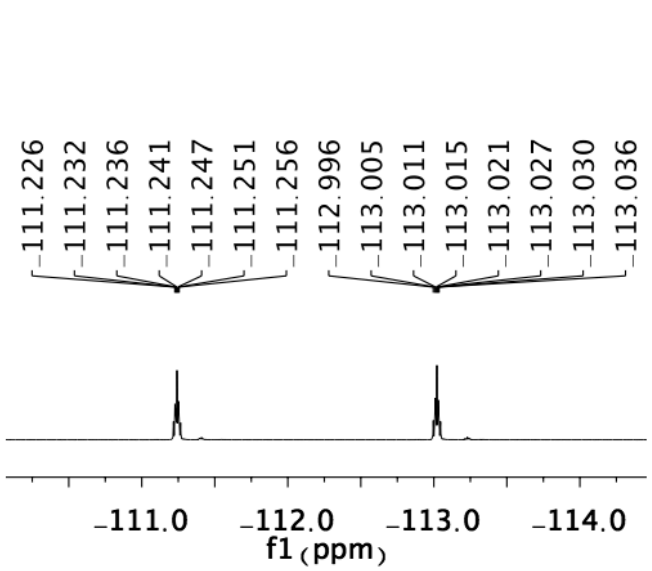
4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)

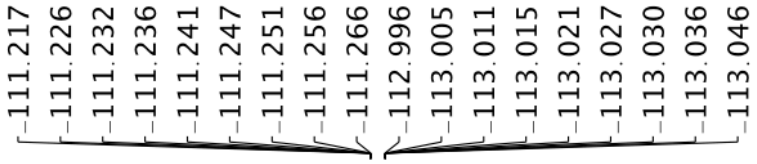
2c

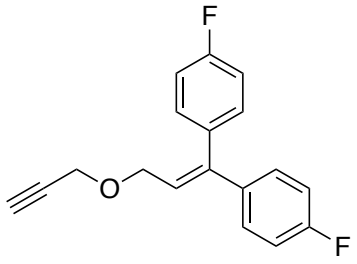
^{13}C NMR, 125 MHz, $CDCl_3$



4,4'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)

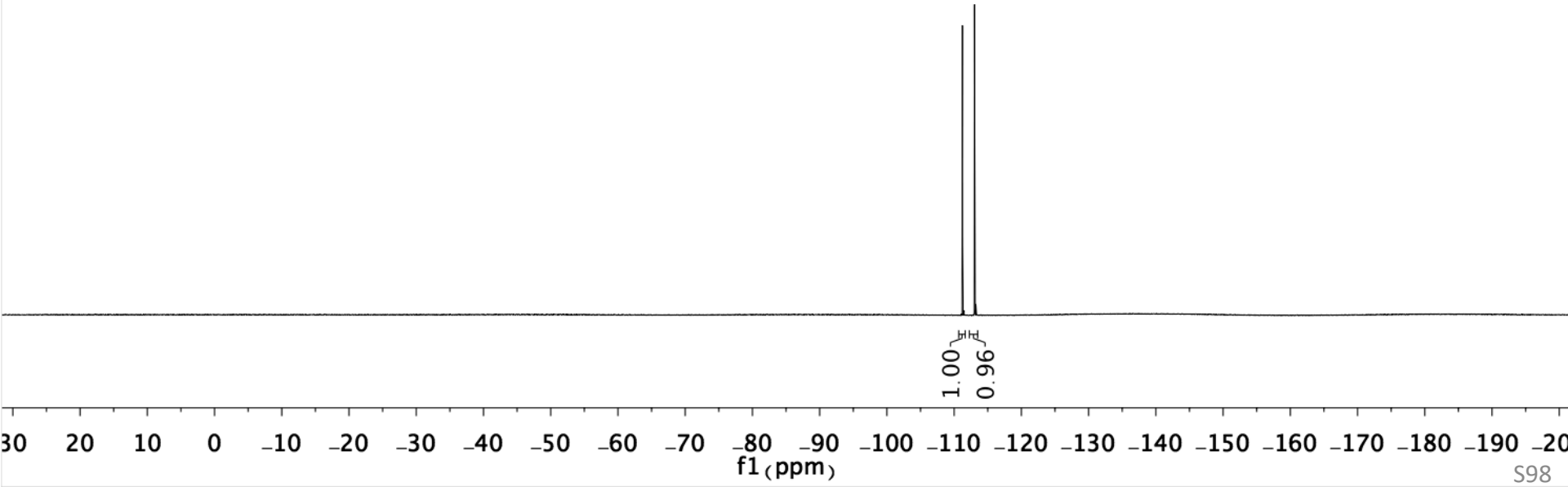




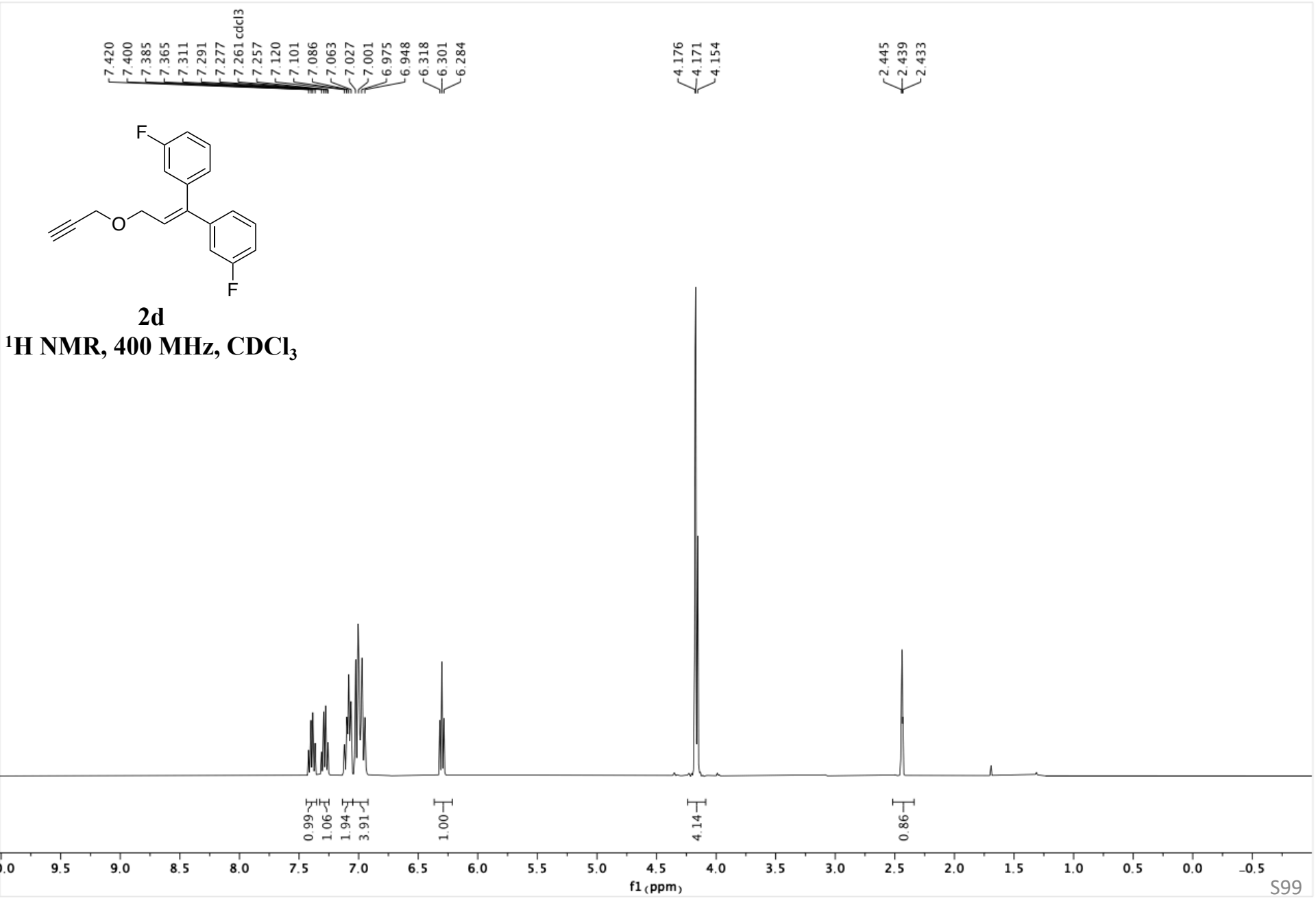


2c

^{19}F NMR, 564 MHz, $CDCl_3$



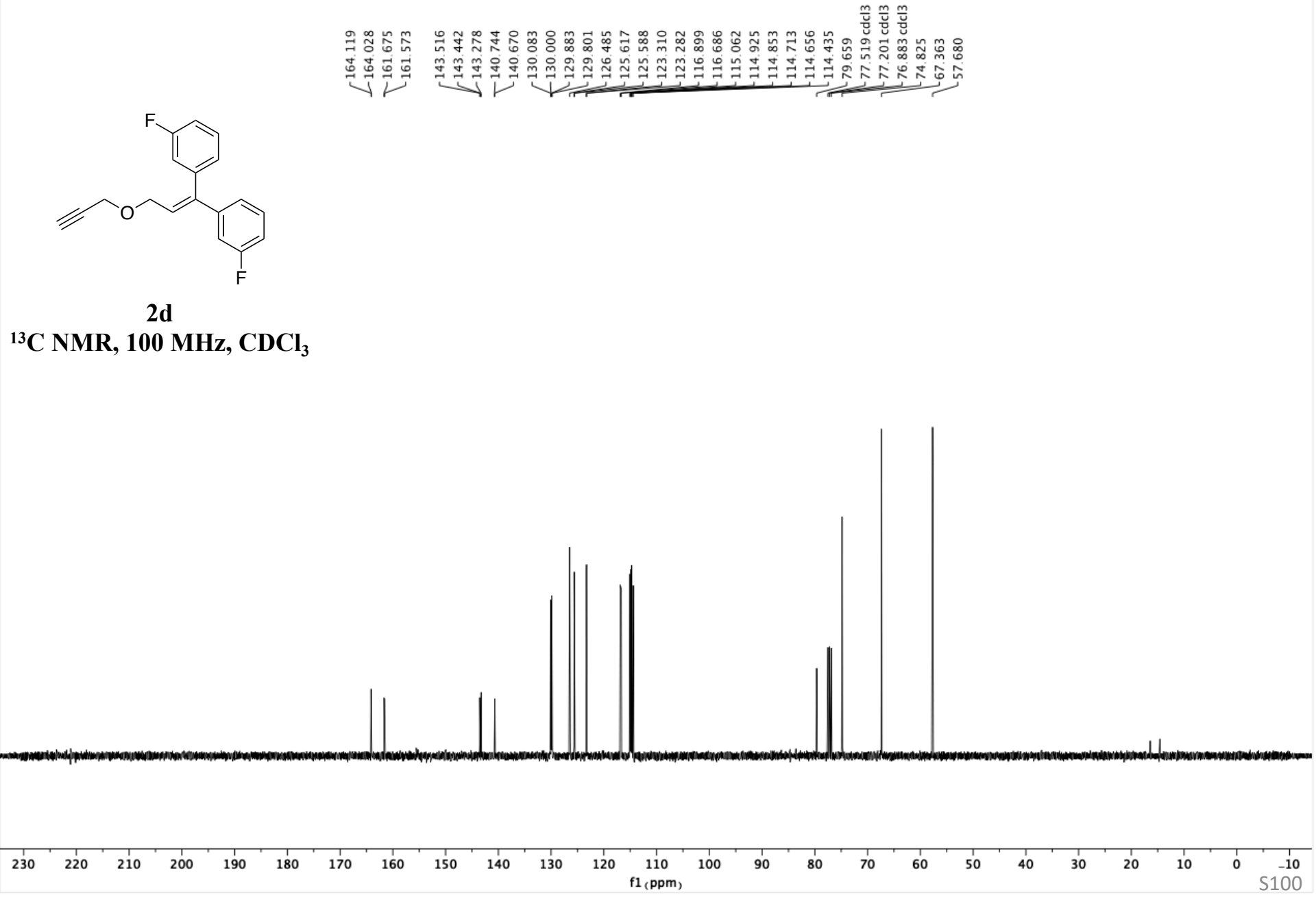
3,3'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)



2d

^{1}H NMR, 400 MHz, $CDCl_3$

3,3'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)

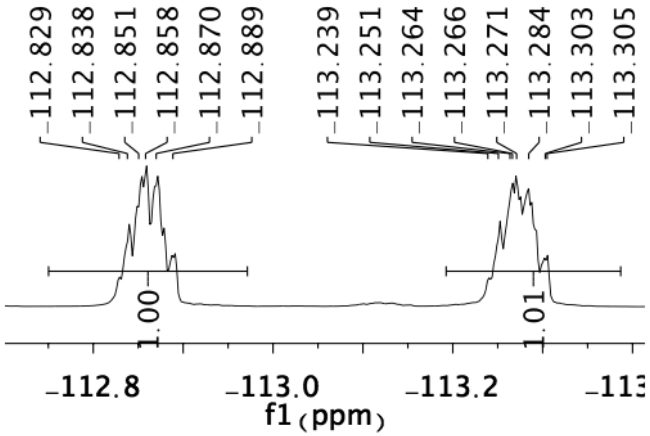


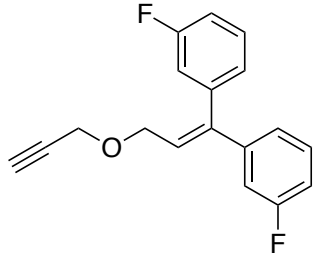
2d

^{13}C NMR, 100 MHz, $CDCl_3$

3,3'-(3-(Prop-2-yn-1-yloxy)prop-1-ene-1,1-diyl)bis(fluorobenzene)

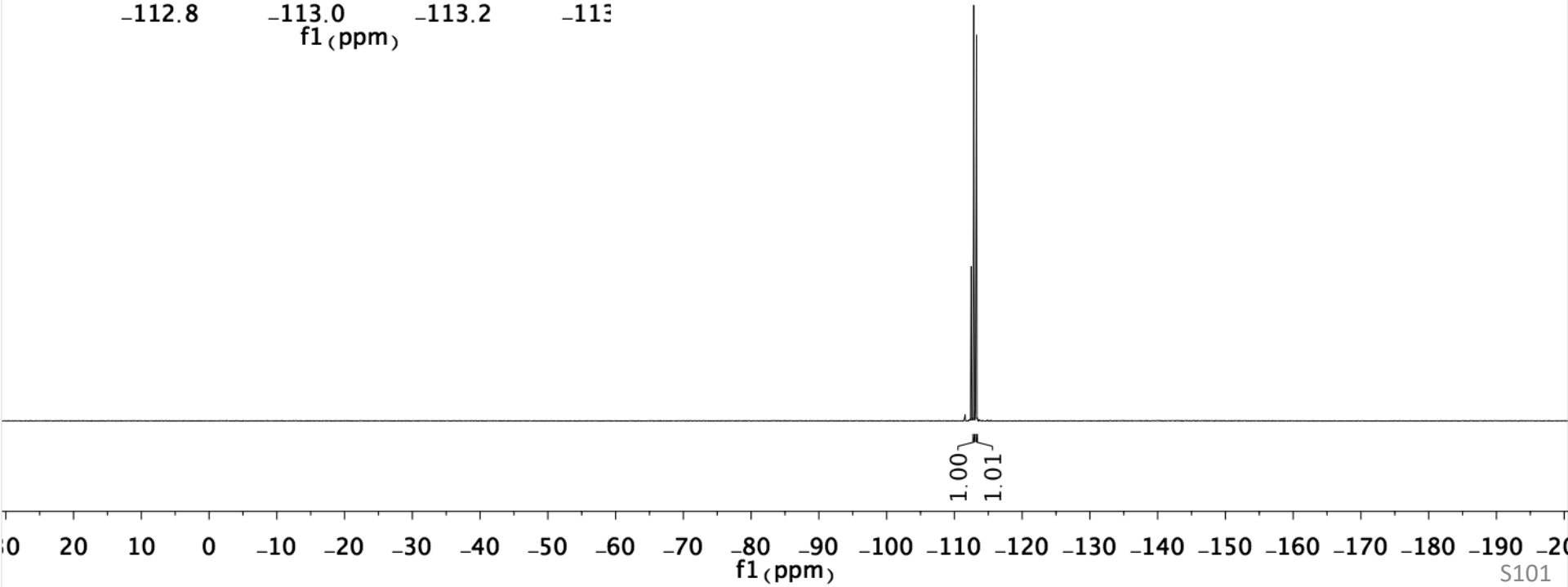




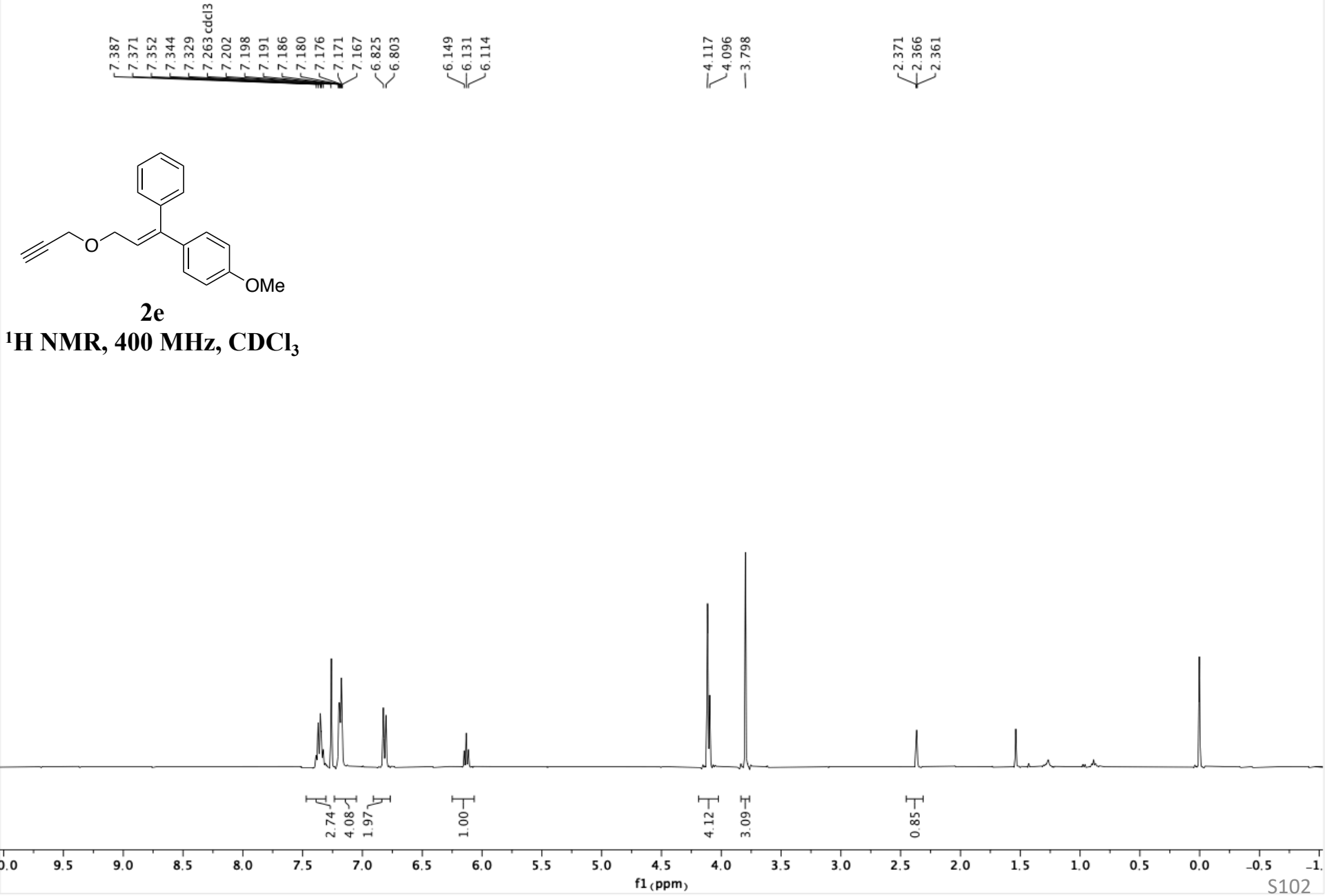


2d

^{19}F NMR, 470 MHz, $CDCl_3$



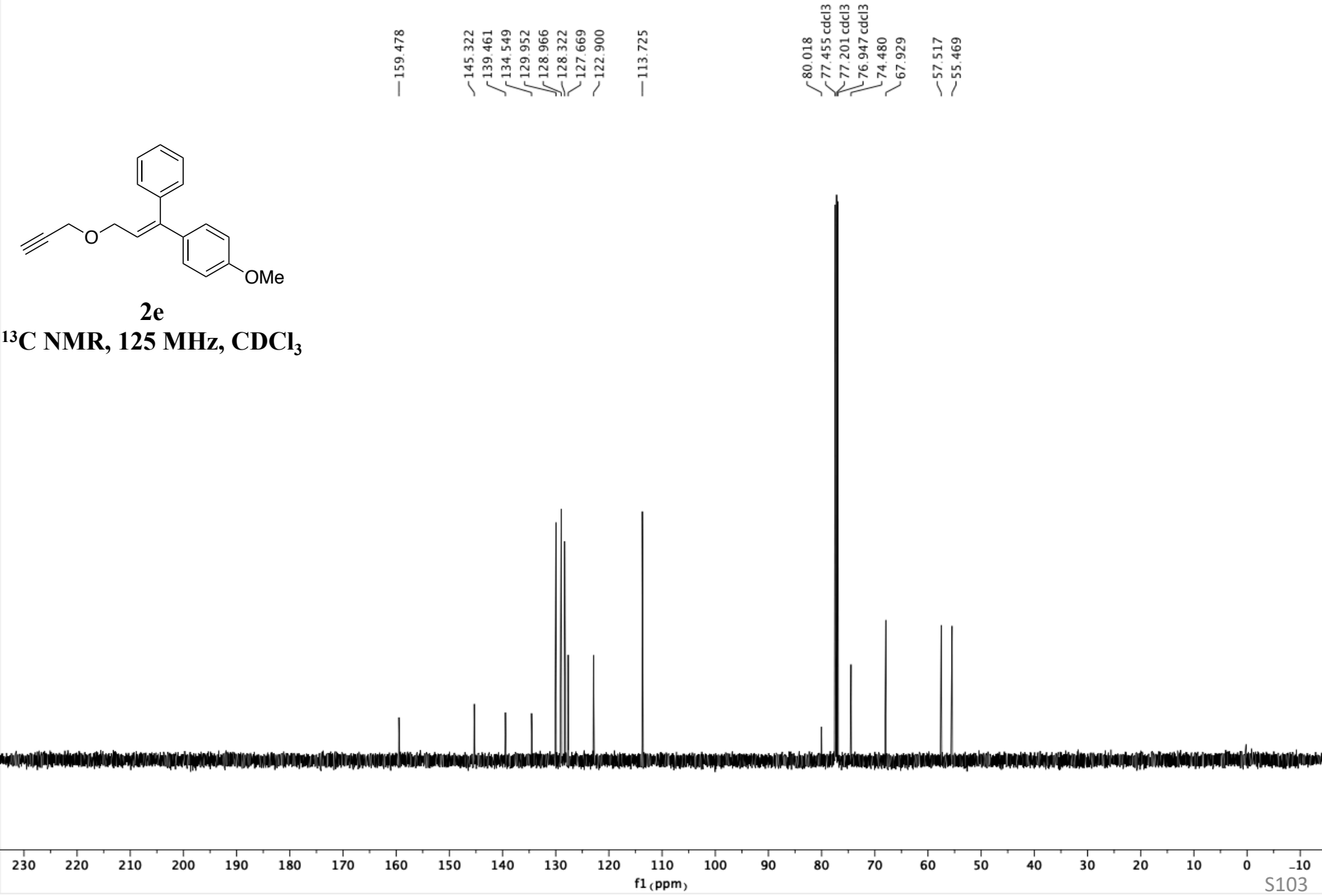
(*E*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2e

^{1}H NMR, 400 MHz, $CDCl_3$

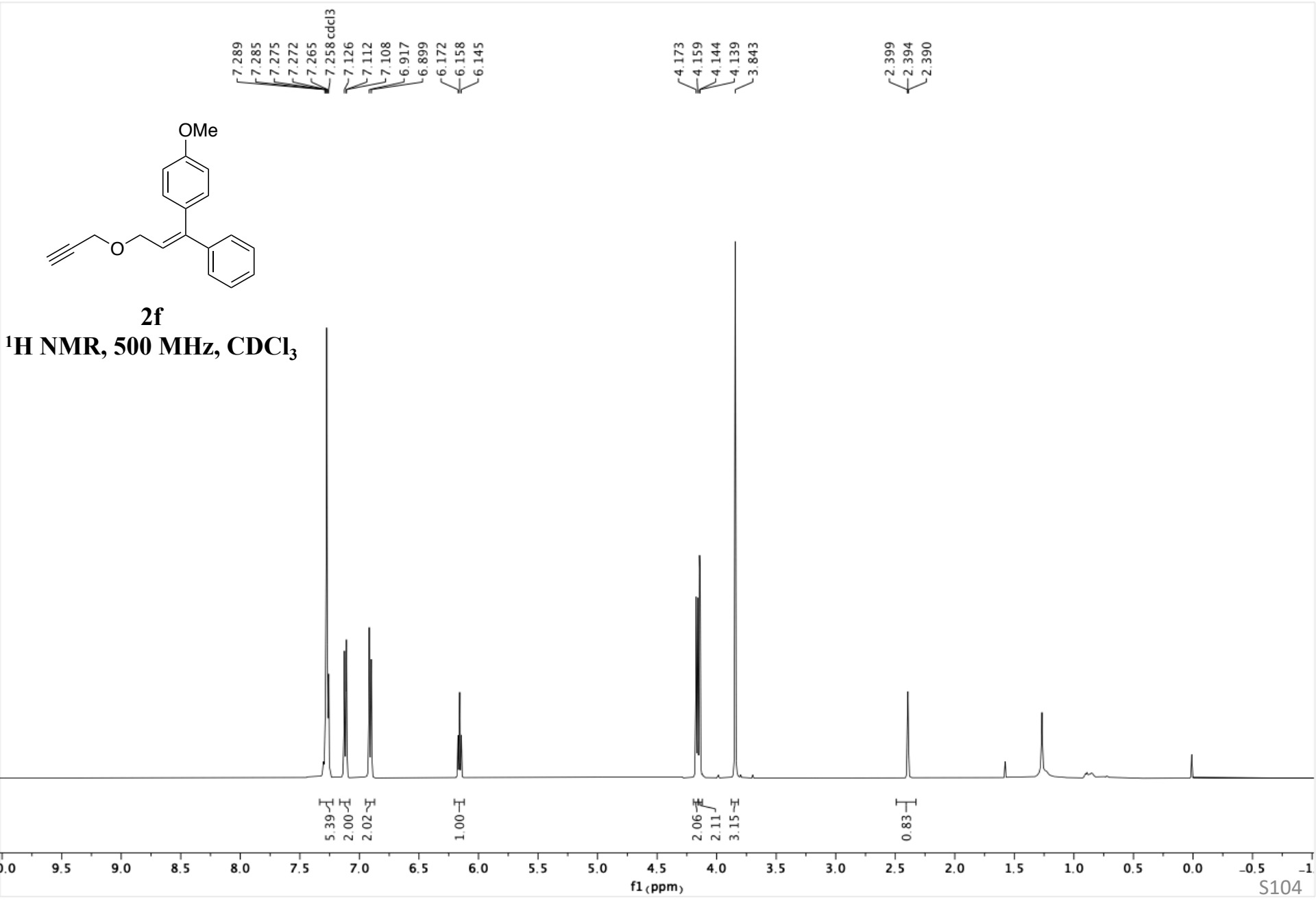
(*E*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2e

^{13}C NMR, 125 MHz, $CDCl_3$

(*Z*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



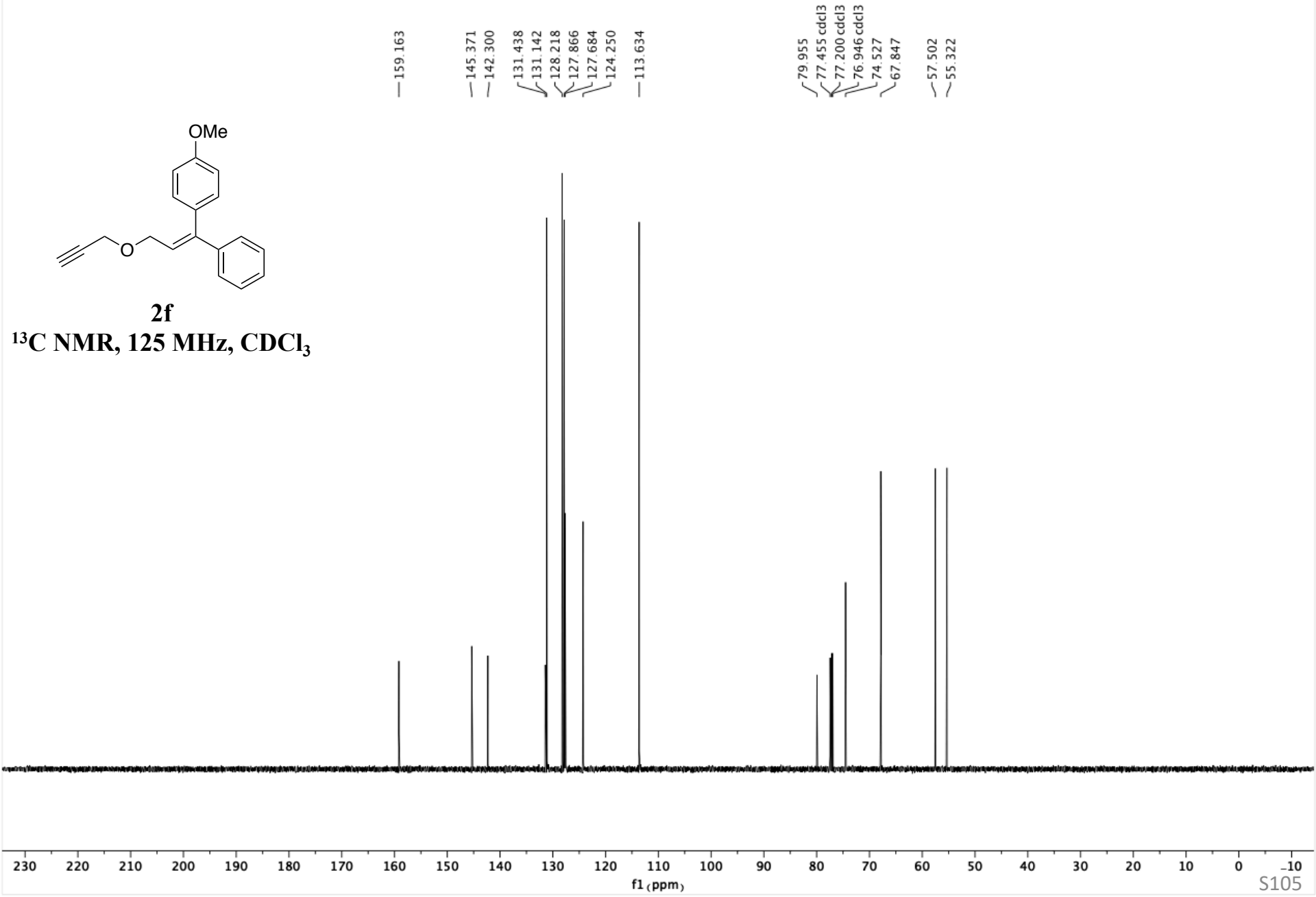
2f

^{1}H NMR, 500 MHz, $CDCl_3$

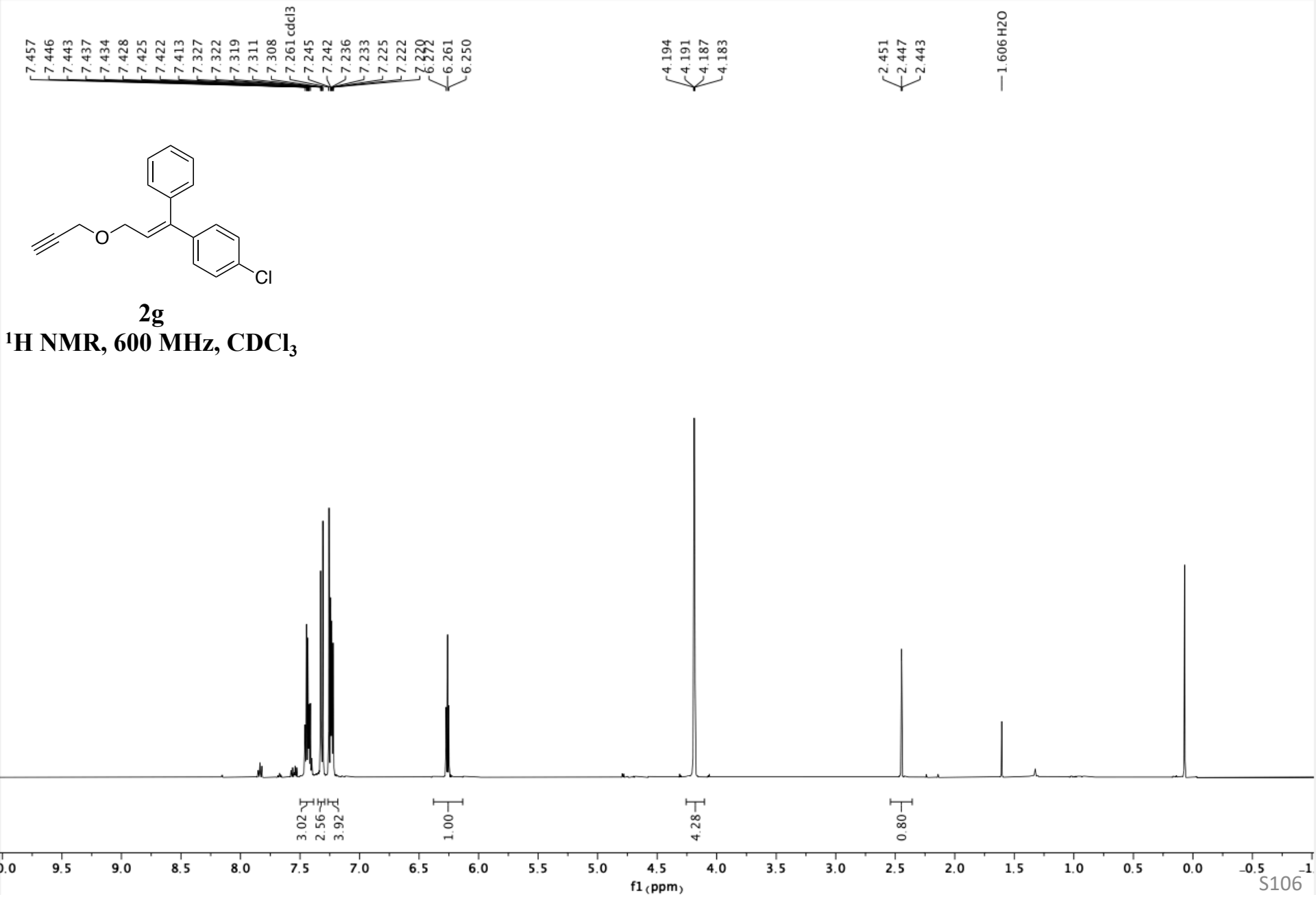
(*Z*)-1-Methoxy-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene

2f

^{13}C NMR, 125 MHz, $CDCl_3$



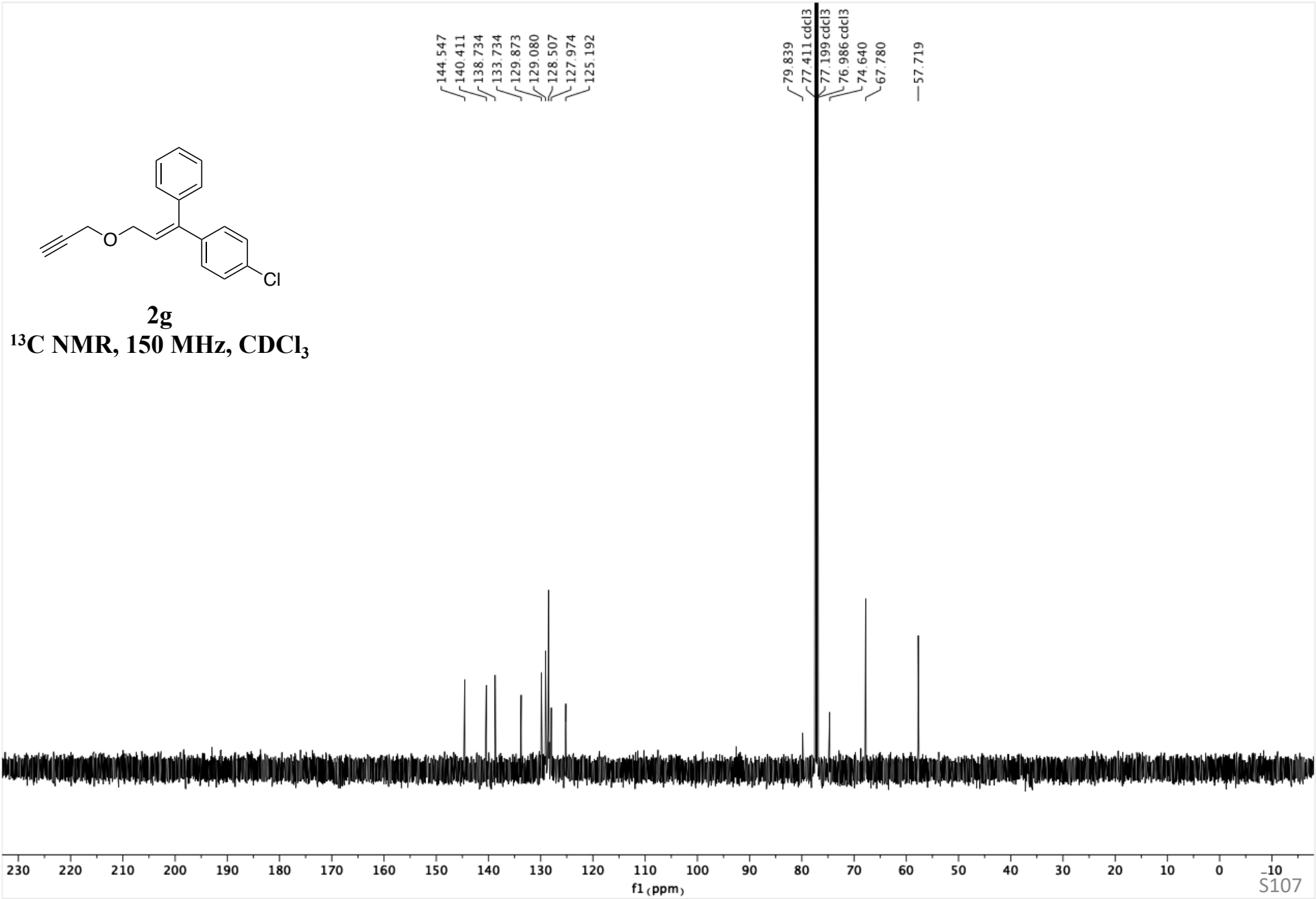
(*E*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2g

^{1}H NMR, 600 MHz, $CDCl_3$

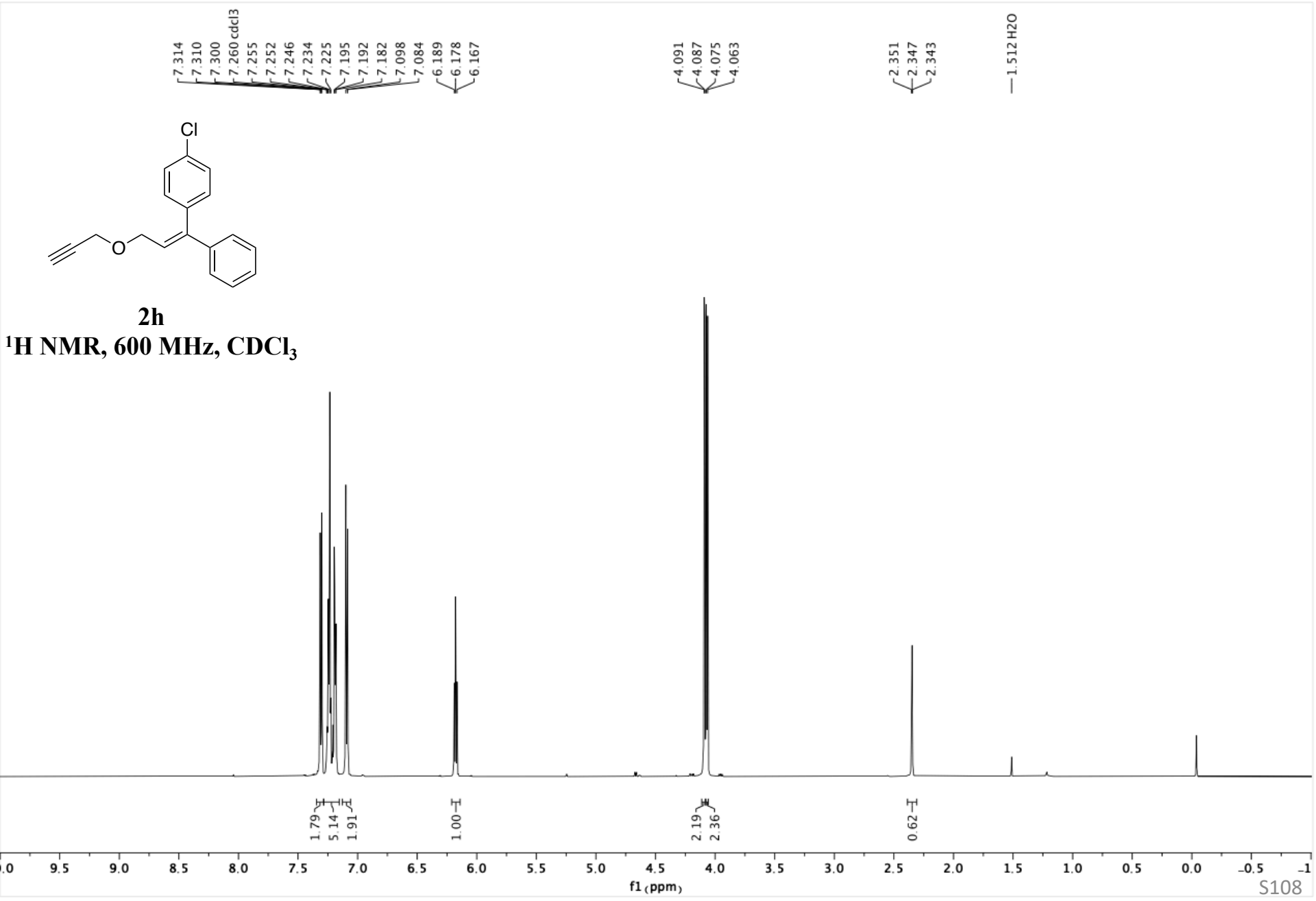
(*E*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2g

^{13}C NMR, 150 MHz, $CDCl_3$

(*Z*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



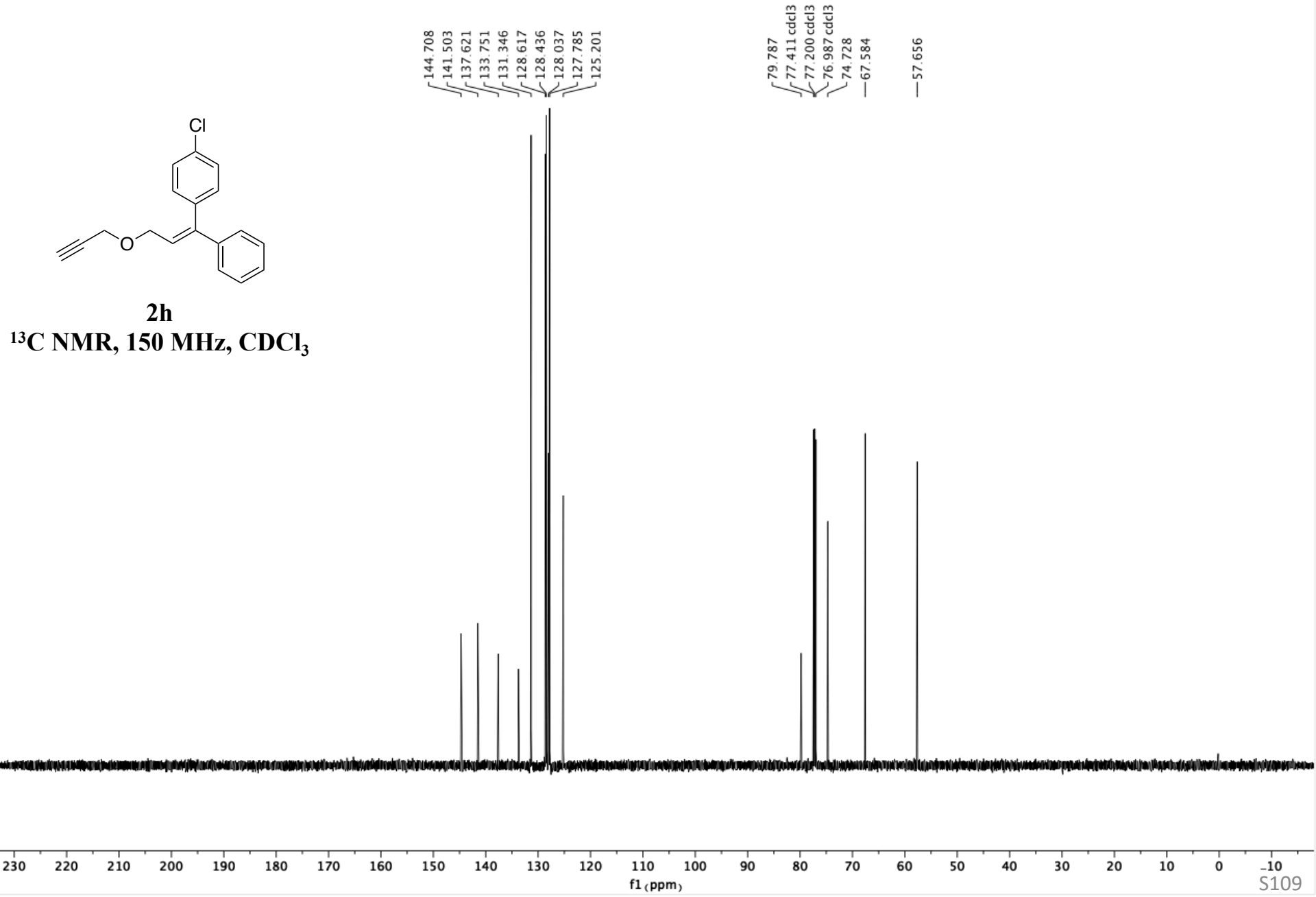
2h

^{1}H NMR, 600 MHz, $CDCl_3$

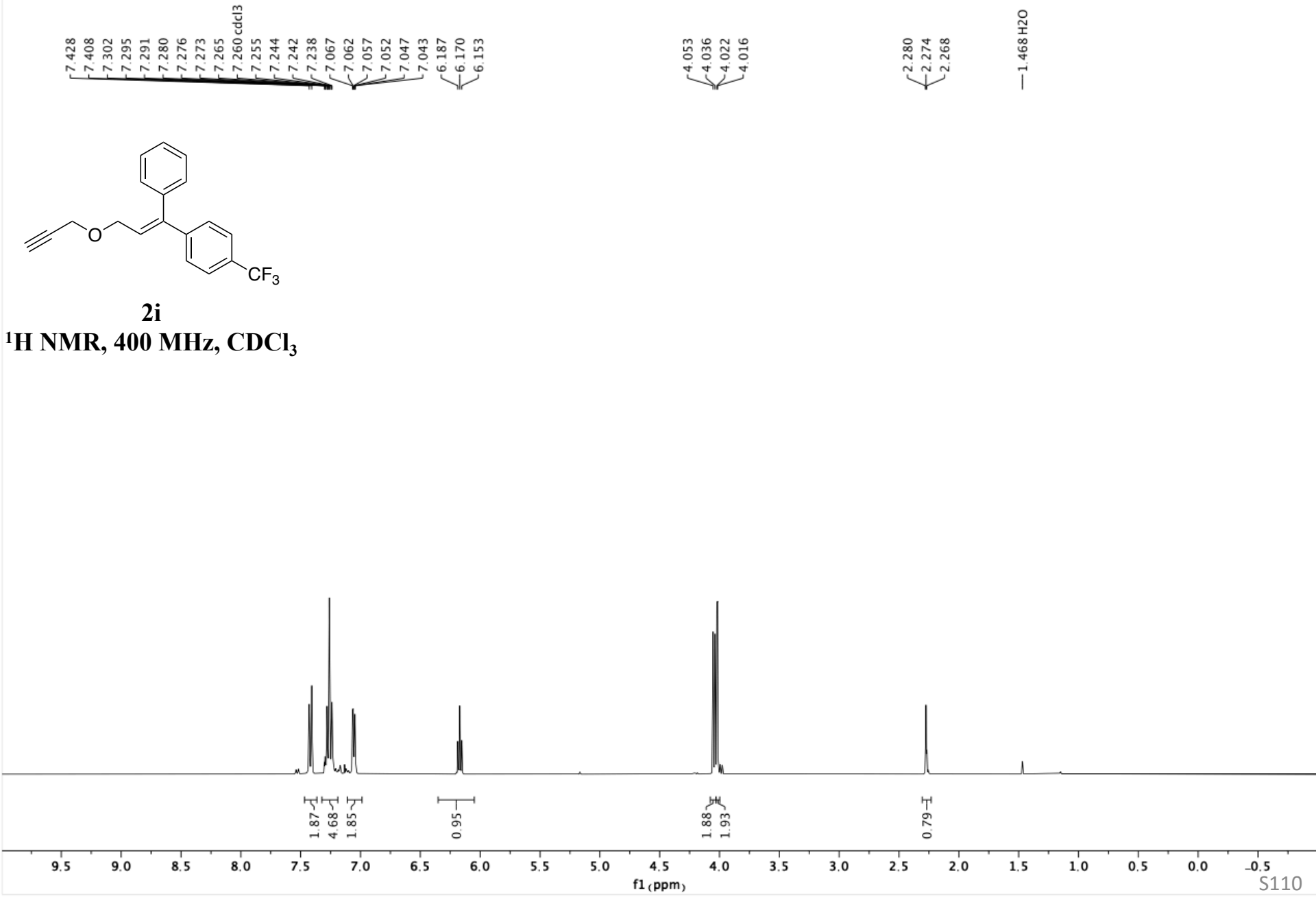
(*Z*)-1-Chloro-4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene

2h

^{13}C NMR, 150 MHz, $CDCl_3$



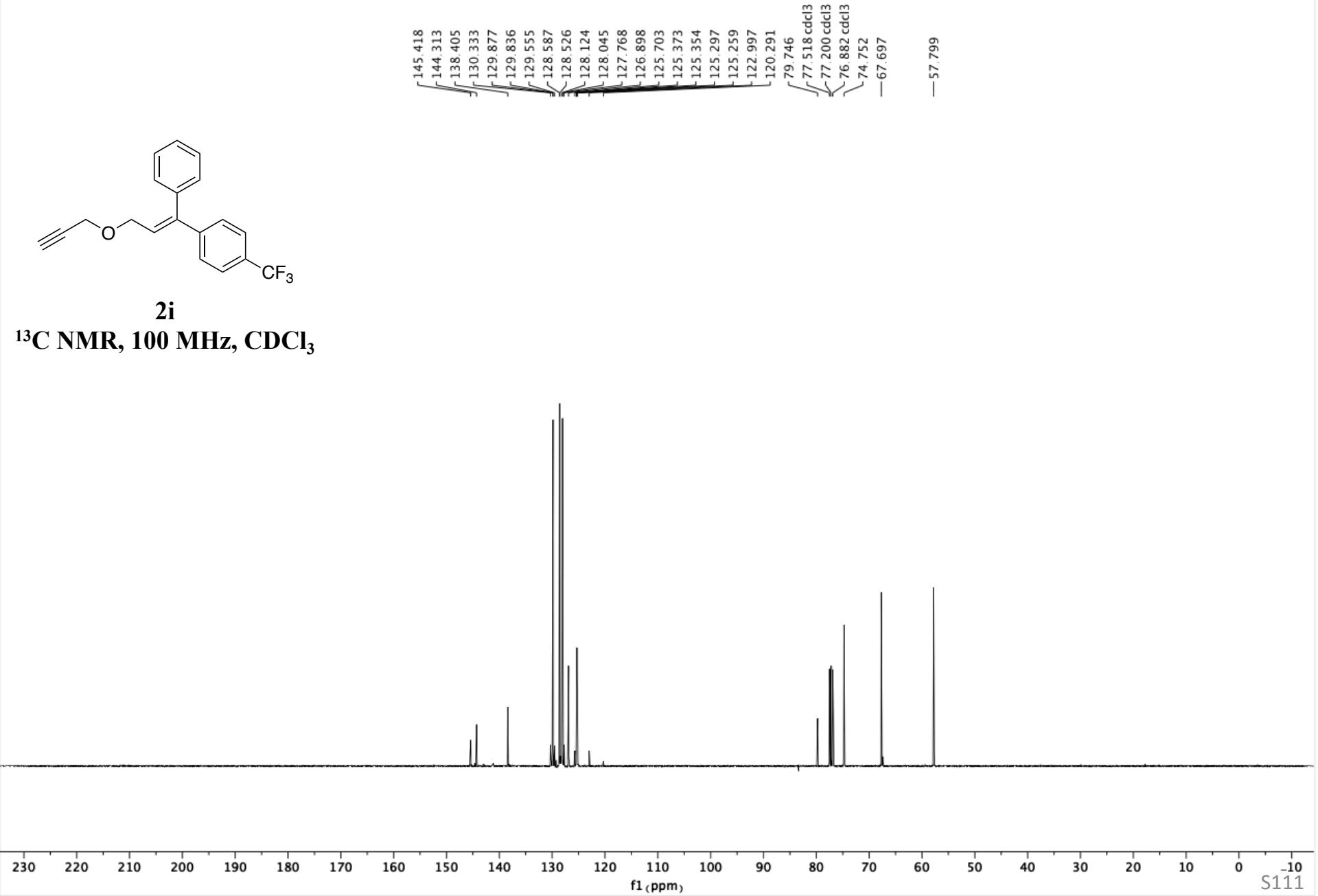
(*E*)-1-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene



2i

^{1}H NMR, 400 MHz, $CDCl_3$

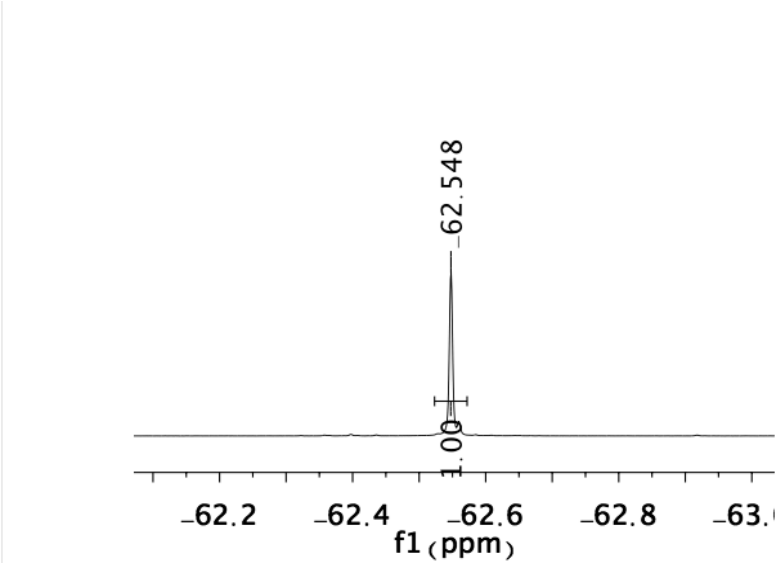
(*E*)-1-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene

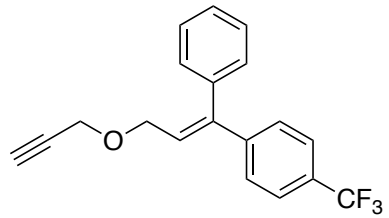


2i

^{13}C NMR, 100 MHz, $CDCl_3$

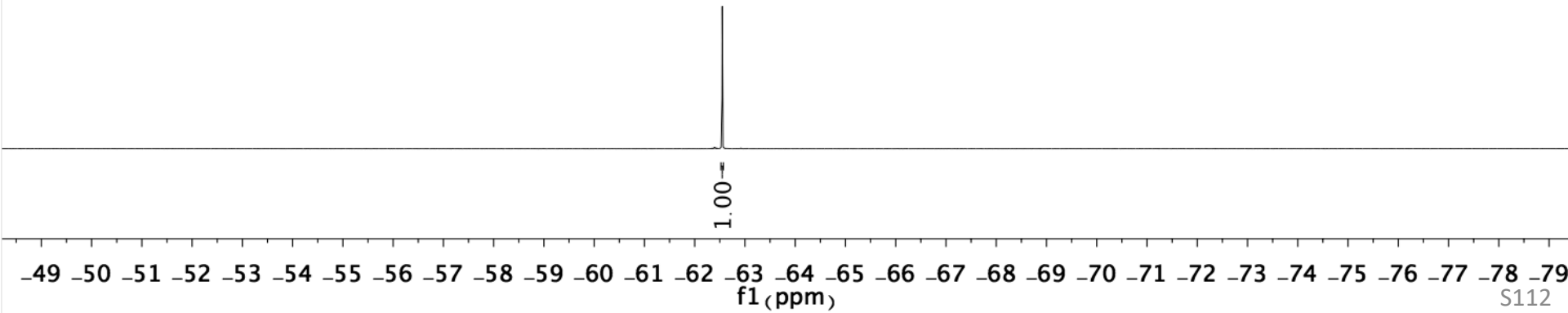
(*E*)-1-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene



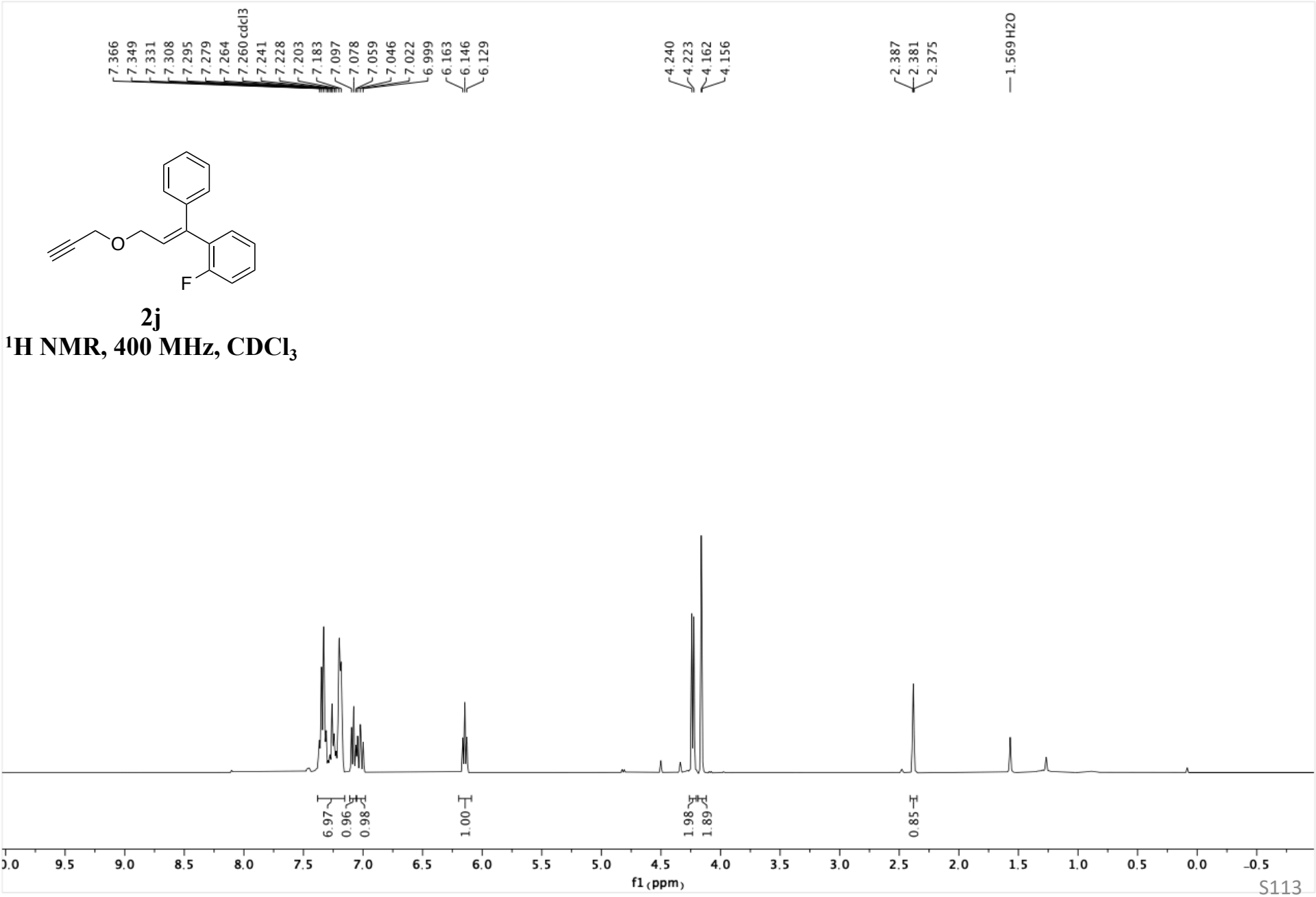


2i

^{19}F NMR, 470 MHz, $CDCl_3$



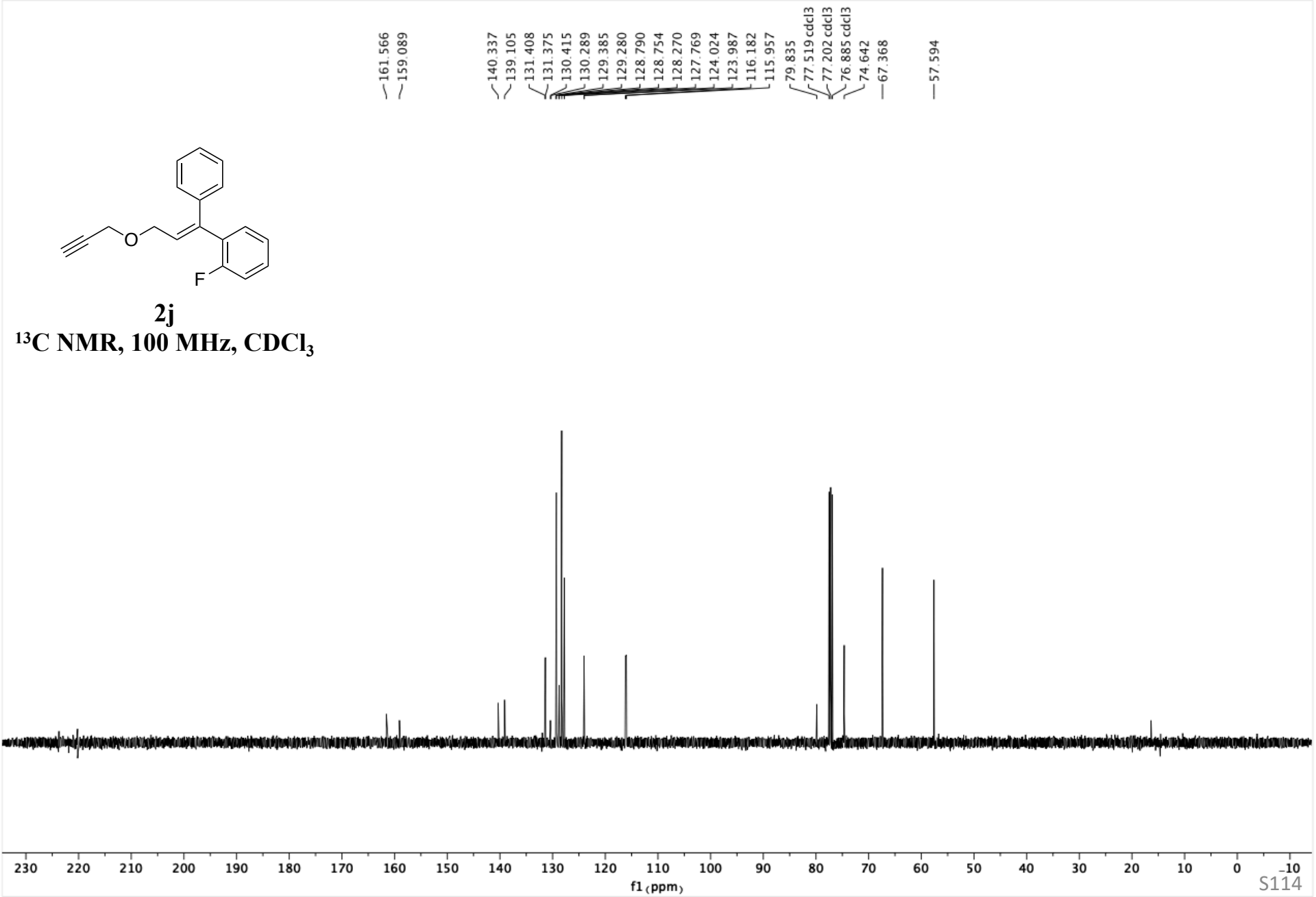
(*E*)-1-Fluoro-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2j

^{1}H NMR, 400 MHz, $CDCl_3$

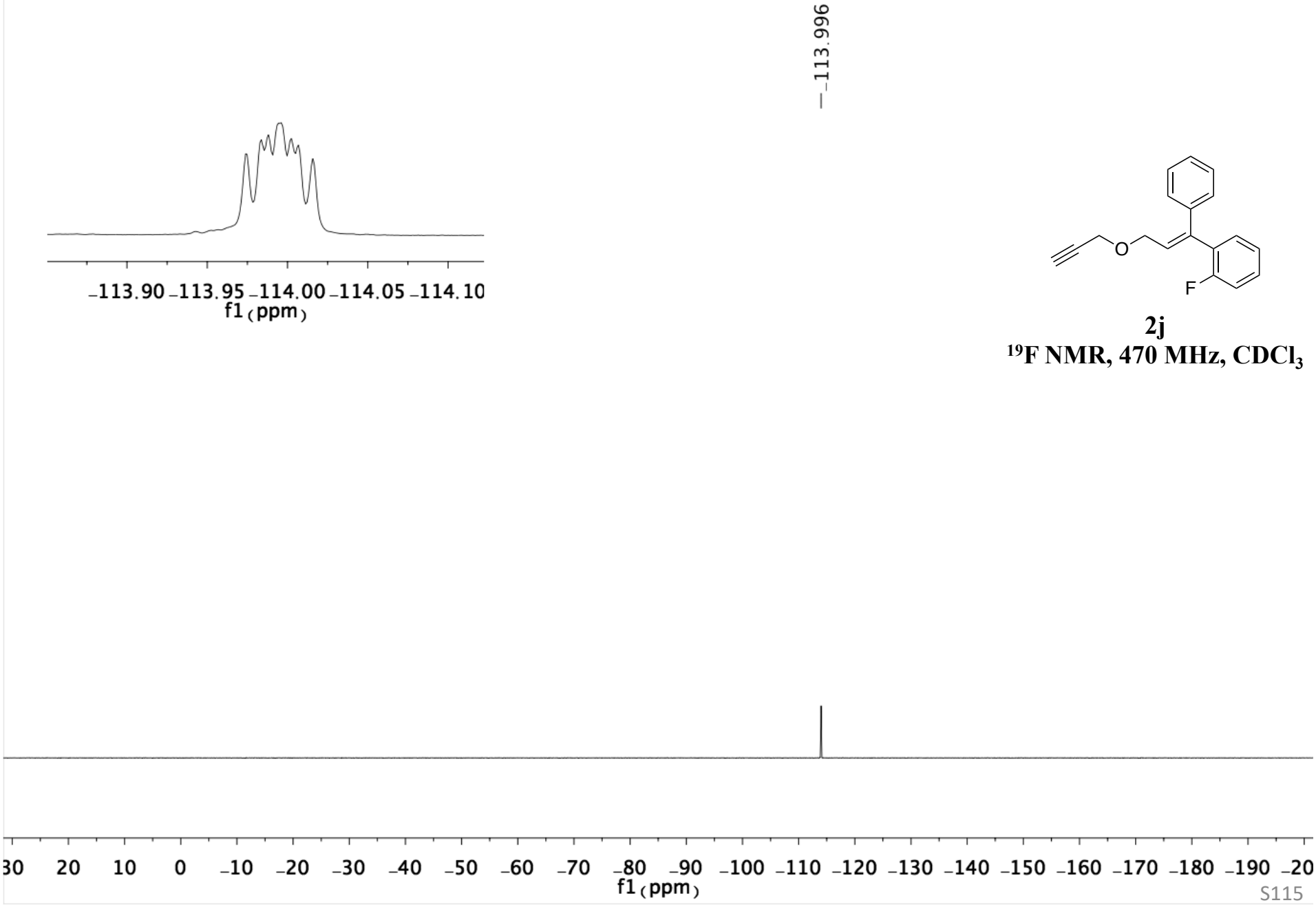
(*E*)-1-Fluoro-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2j

^{13}C NMR, 100 MHz, $CDCl_3$

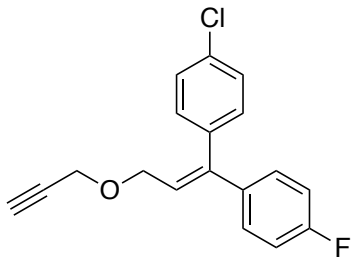
(*E*)-1-Fluoro-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2j

^{19}F NMR, 470 MHz, $CDCl_3$

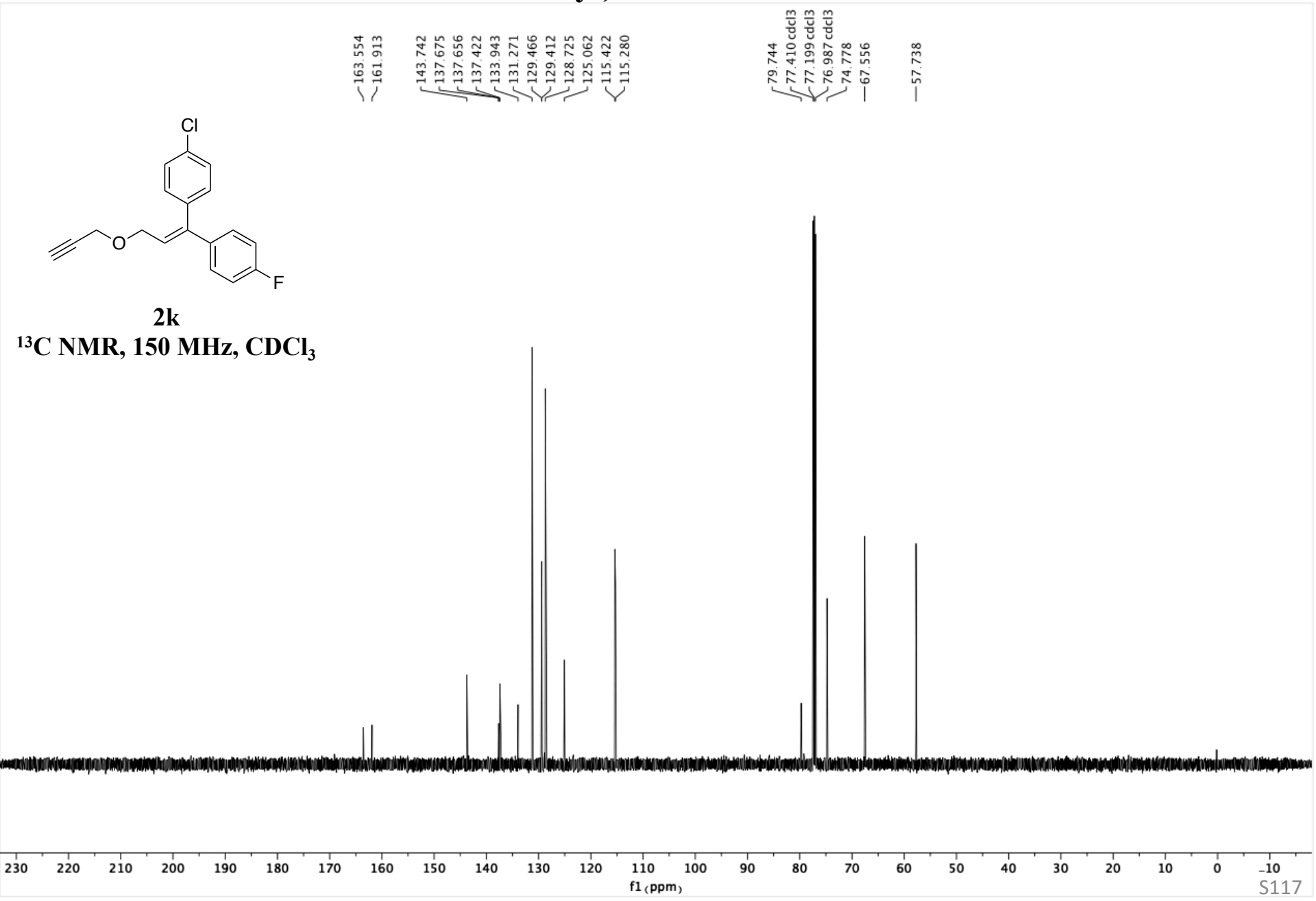
(*Z*)-1-Chloro-4-(1-(4-fluorophenyl)-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2k

^{1}H NMR, 600 MHz, $CDCl_3$

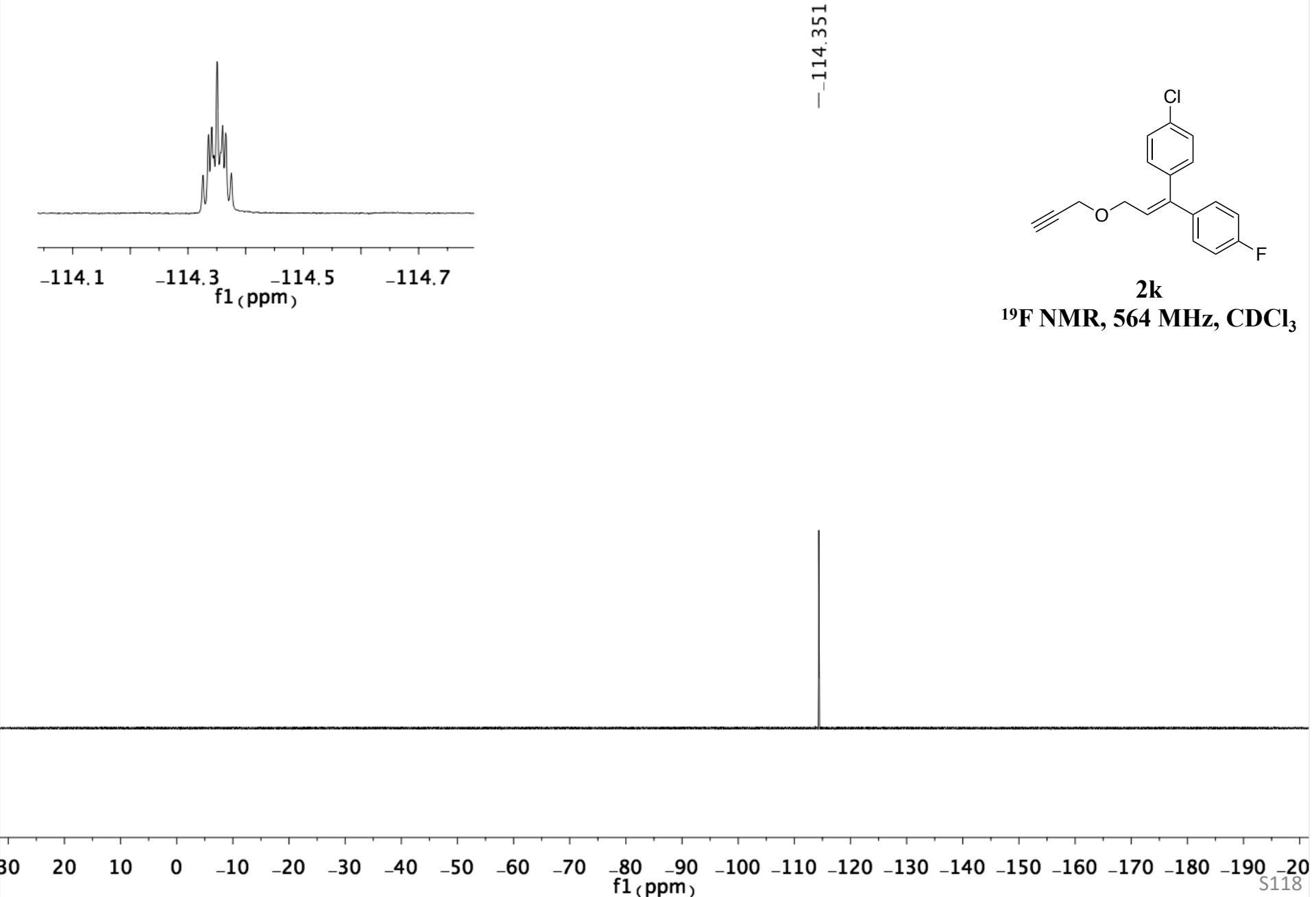
(*Z*)-1-Chloro-4-(1-(4-fluorophenyl)-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2k

^{13}C NMR, 150 MHz, $CDCl_3$

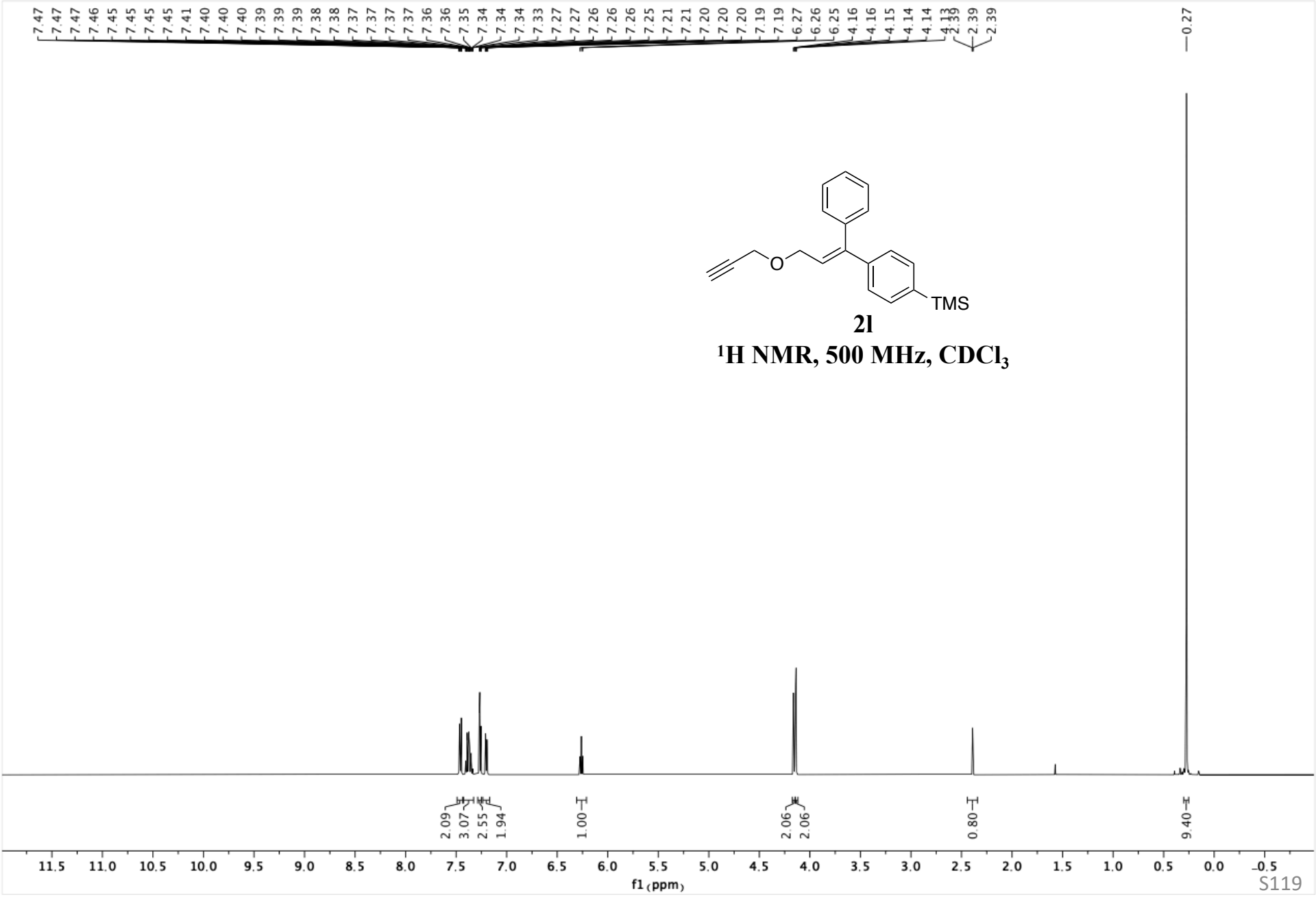
(*Z*)-1-Chloro-4-(1-(4-fluorophenyl)-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



2k

^{19}F NMR, 564 MHz, $CDCl_3$

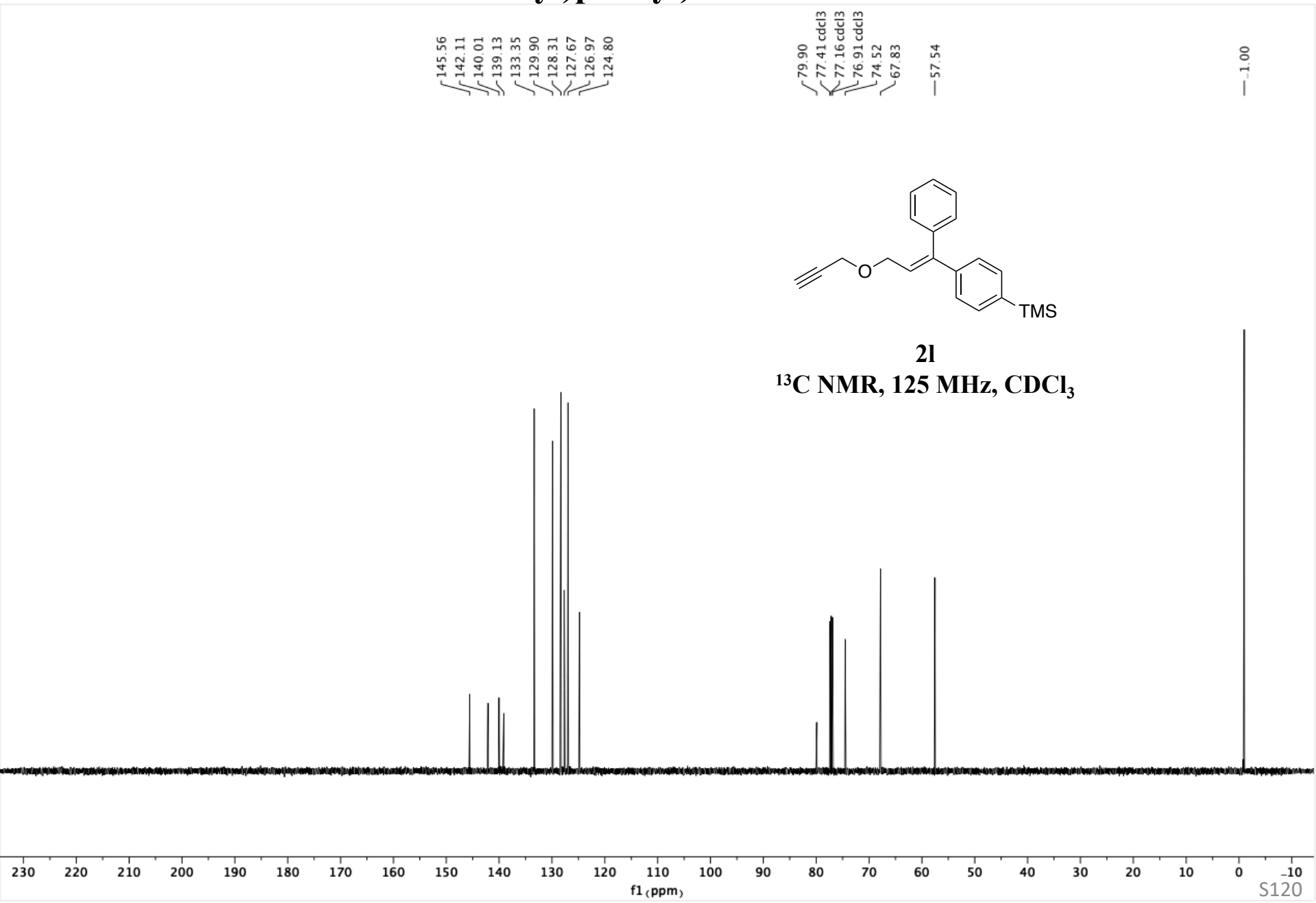
(*E*)-trimethyl(4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)phenyl)silane



2l

^{1}H NMR, 500 MHz, $CDCl_3$

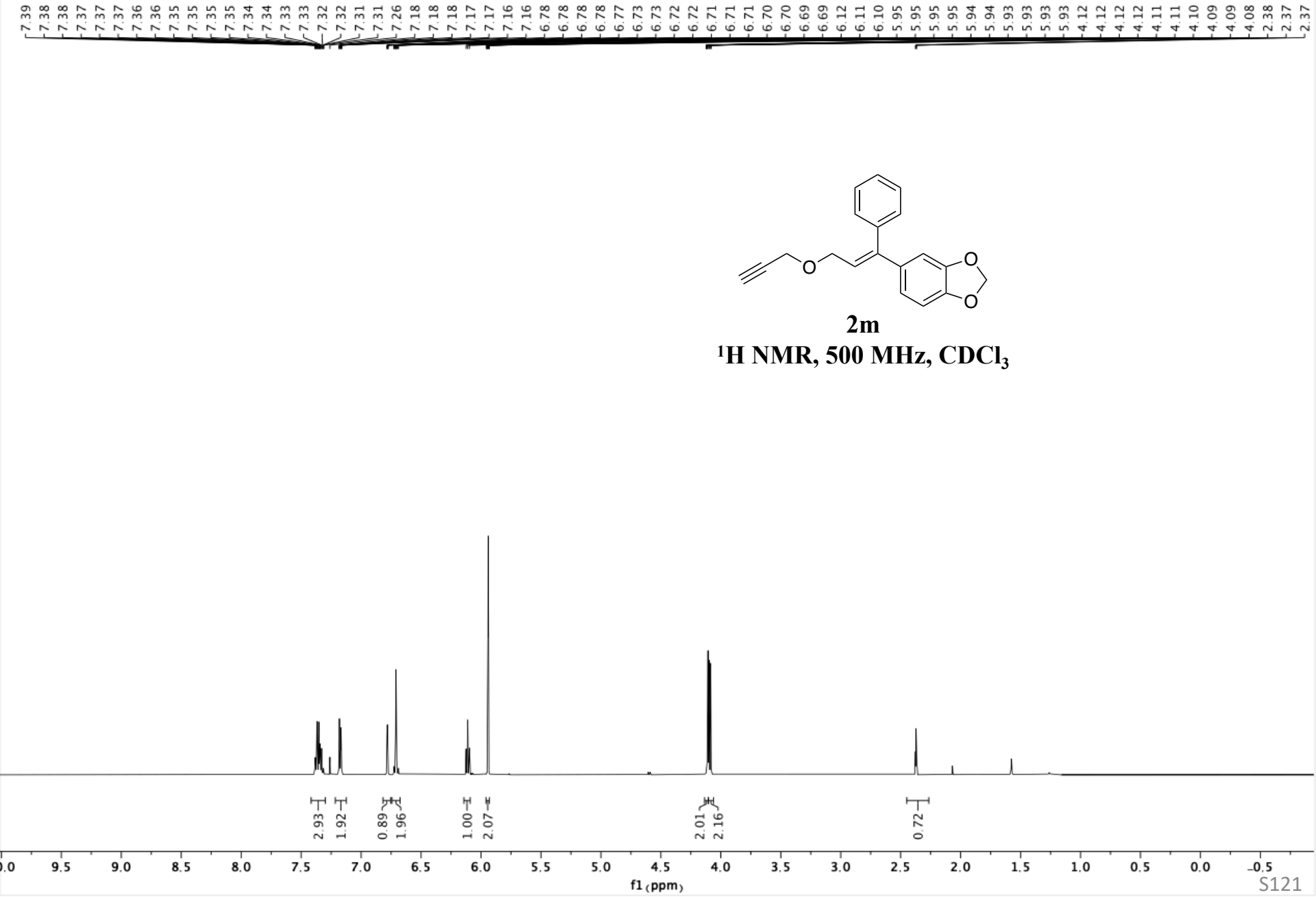
(*E*)-trimethyl(4-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)phenyl)silane



2l

^{13}C NMR, 125 MHz, $CDCl_3$

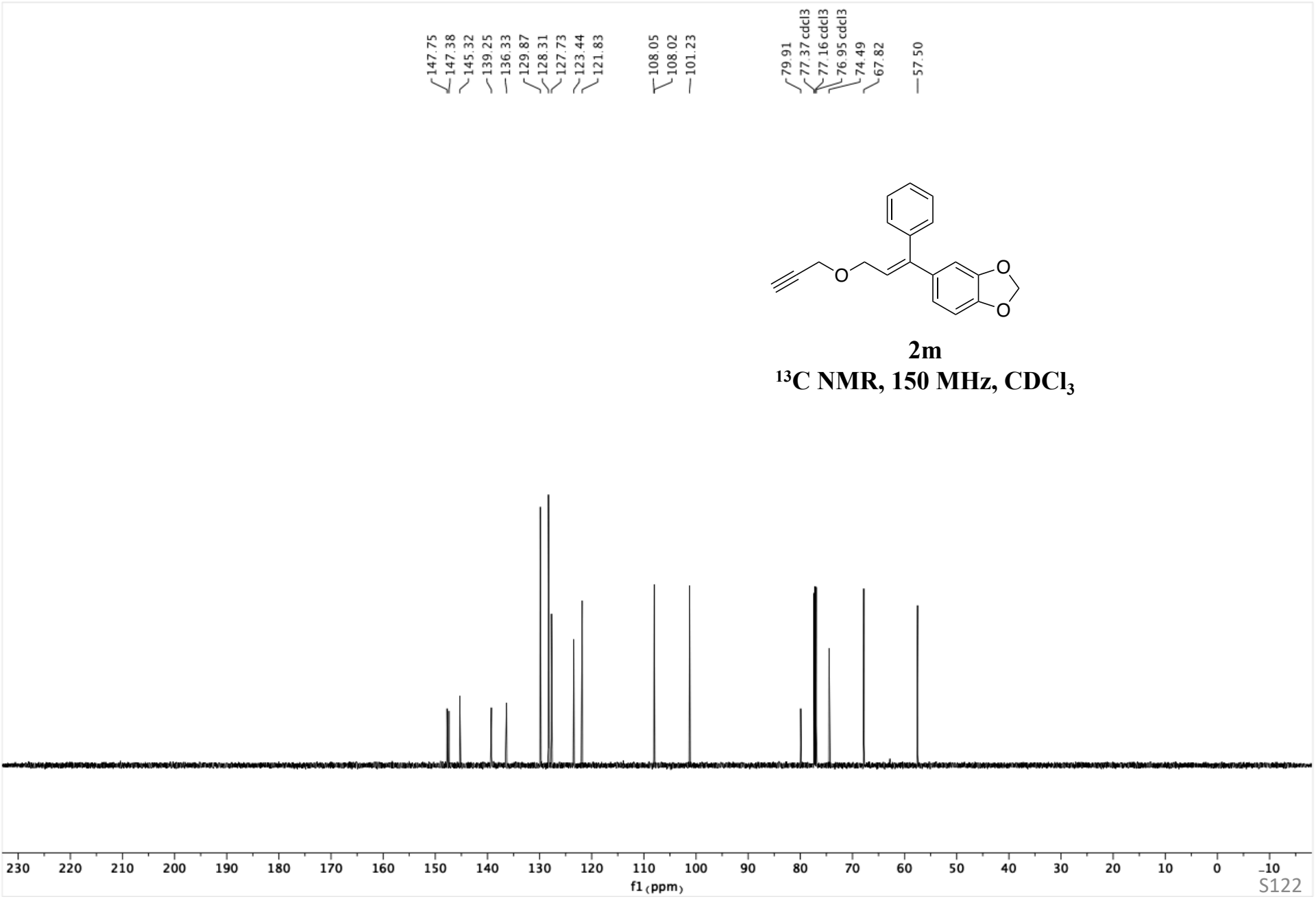
(*E*)-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzo[*d*][1,3]dioxole



2m

^{1}H NMR, 500 MHz, $CDCl_3$

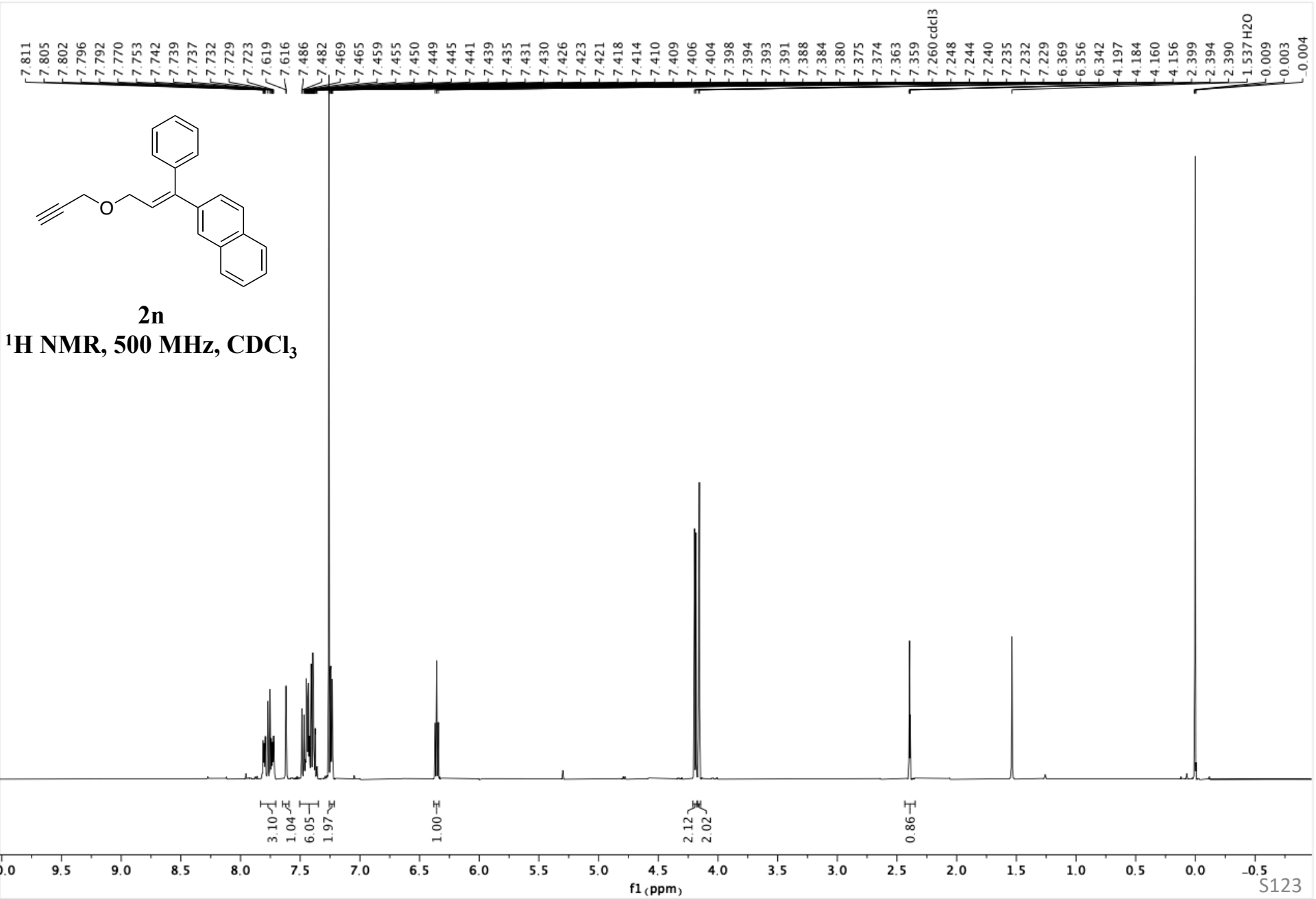
(*E*)-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzo[*d*][1,3]dioxole



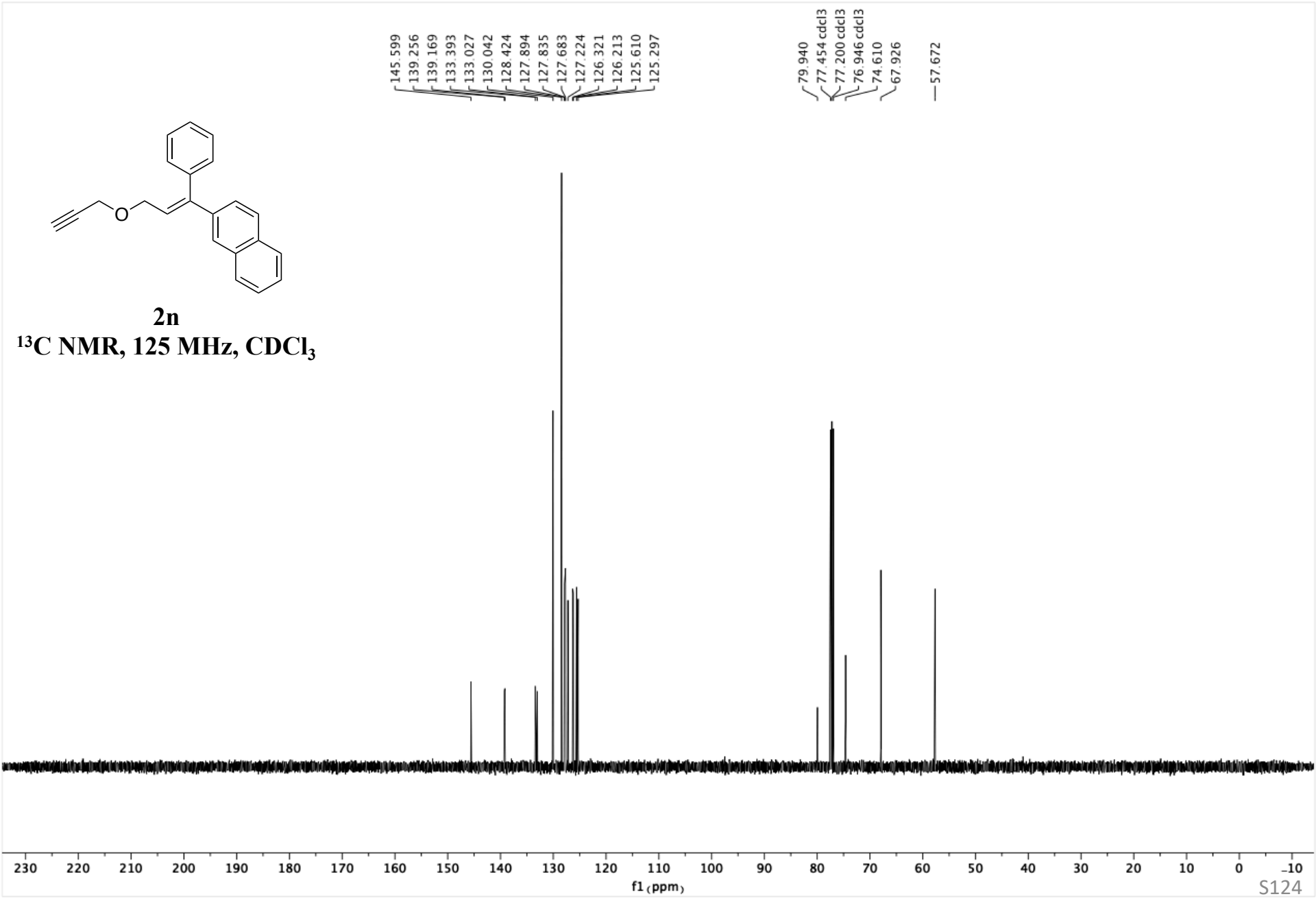
2m

^{13}C NMR, 150 MHz, $CDCl_3$

(*E*)-2-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)naphthalene



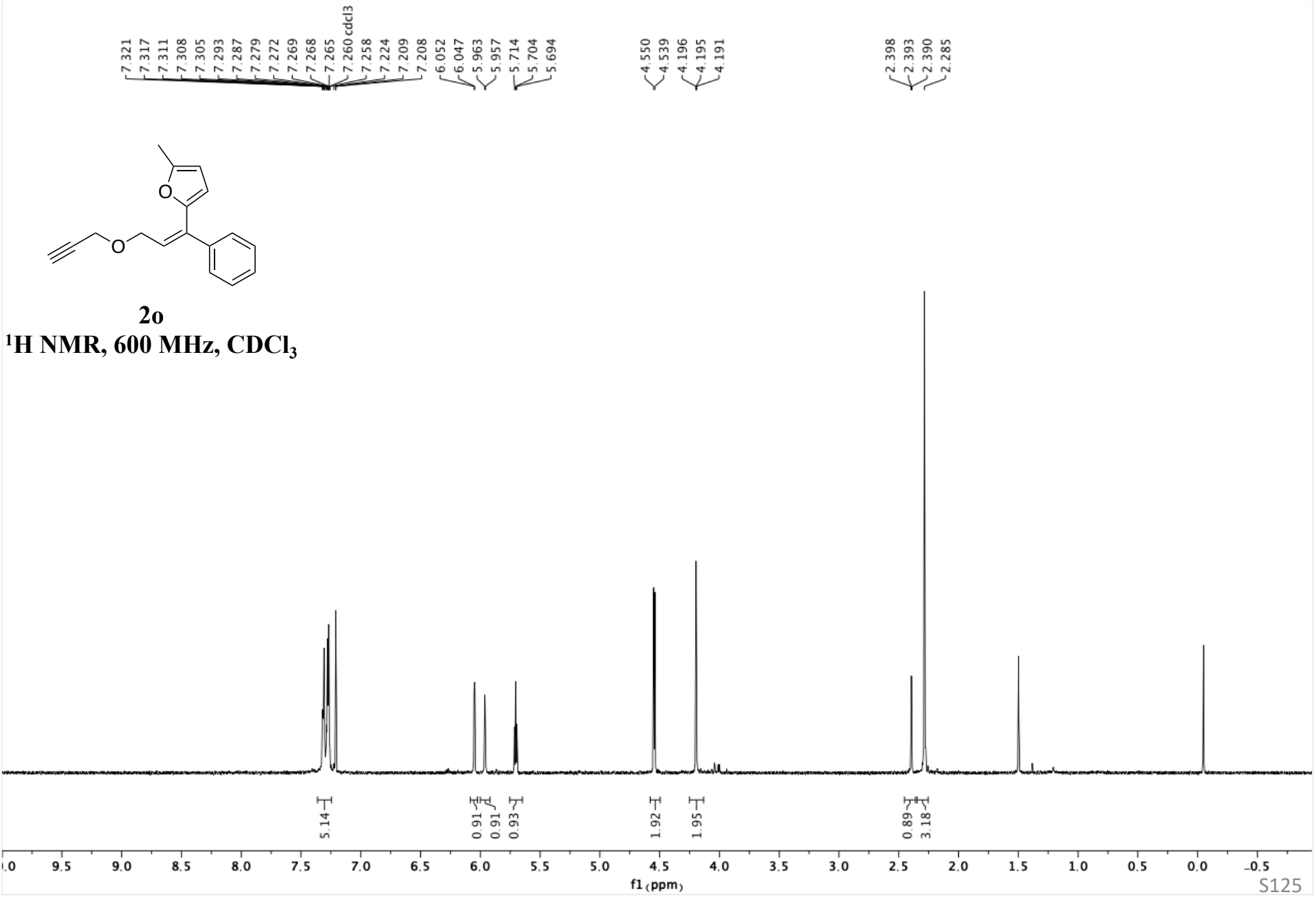
(*E*)-2-(1-Phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)naphthalene



2n

^{13}C NMR, 125 MHz, $CDCl_3$

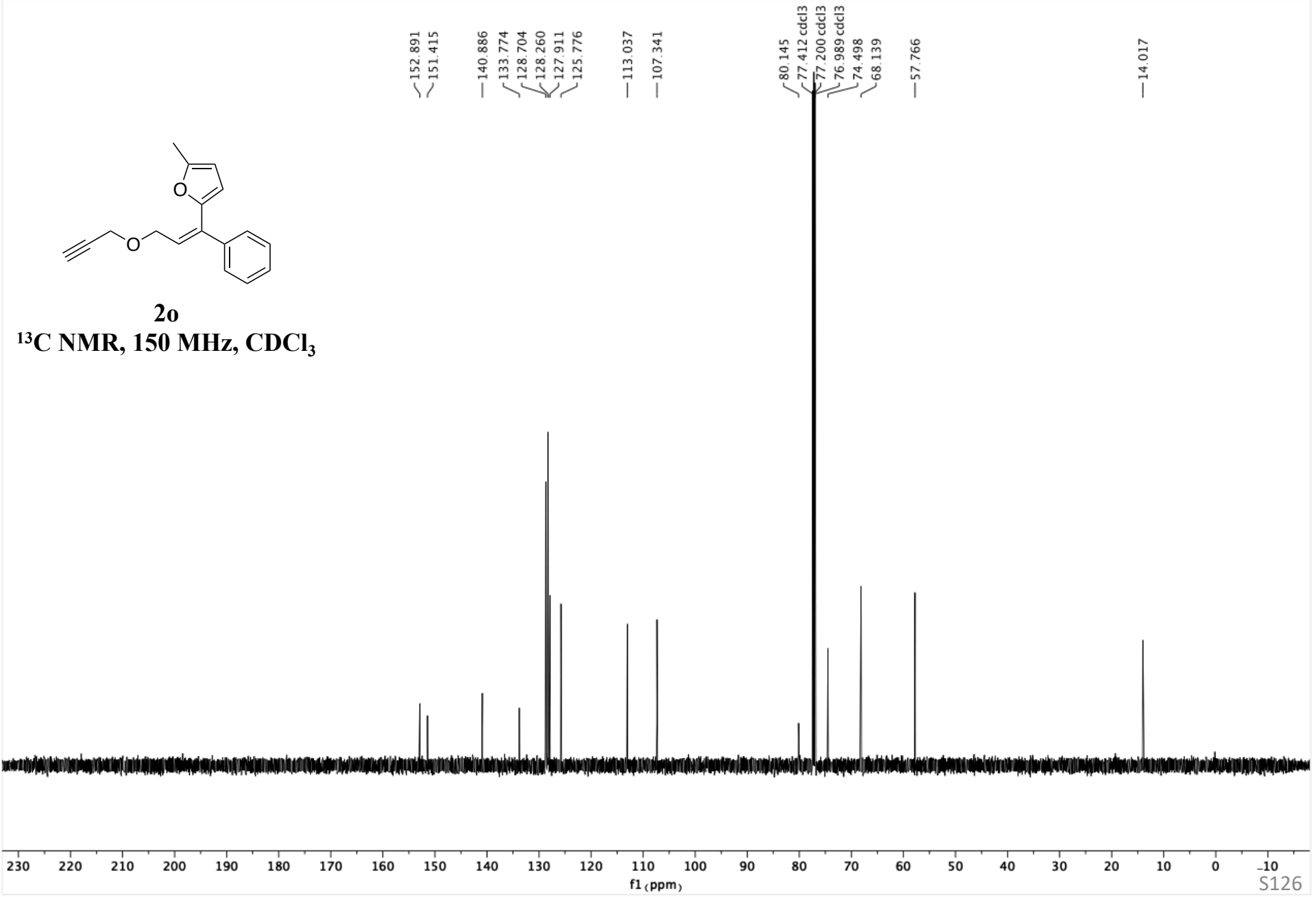
(*Z*)-2-Methyl-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)furan



2o

^{1}H NMR, 600 MHz, $CDCl_3$

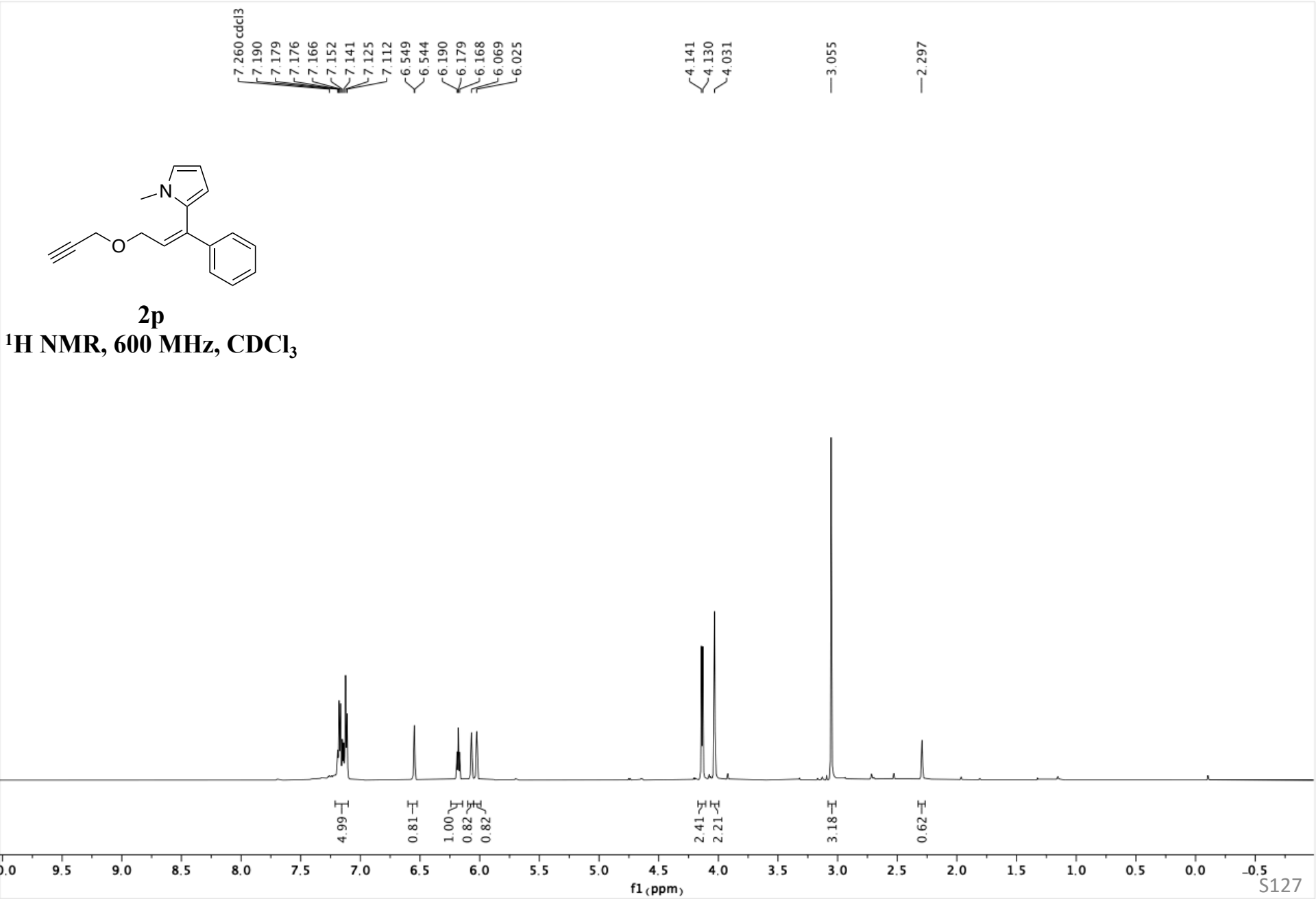
(*Z*)-2-Methyl-5-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)furan



2o

^{13}C NMR, 150 MHz, $CDCl_3$

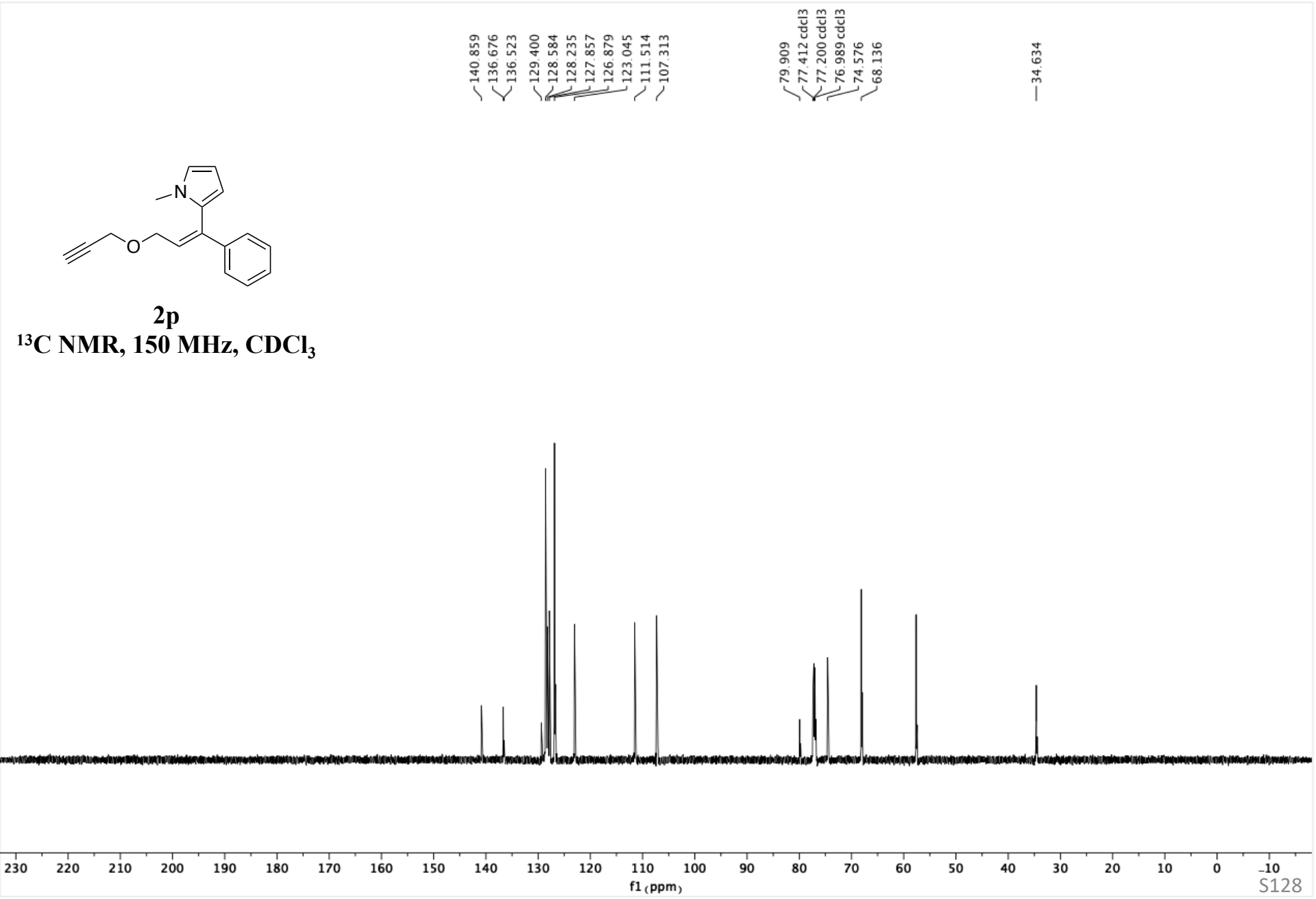
(*Z*)-1-Methyl-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-1*H*-pyrrole



2p

^{1}H NMR, 600 MHz, $CDCl_3$

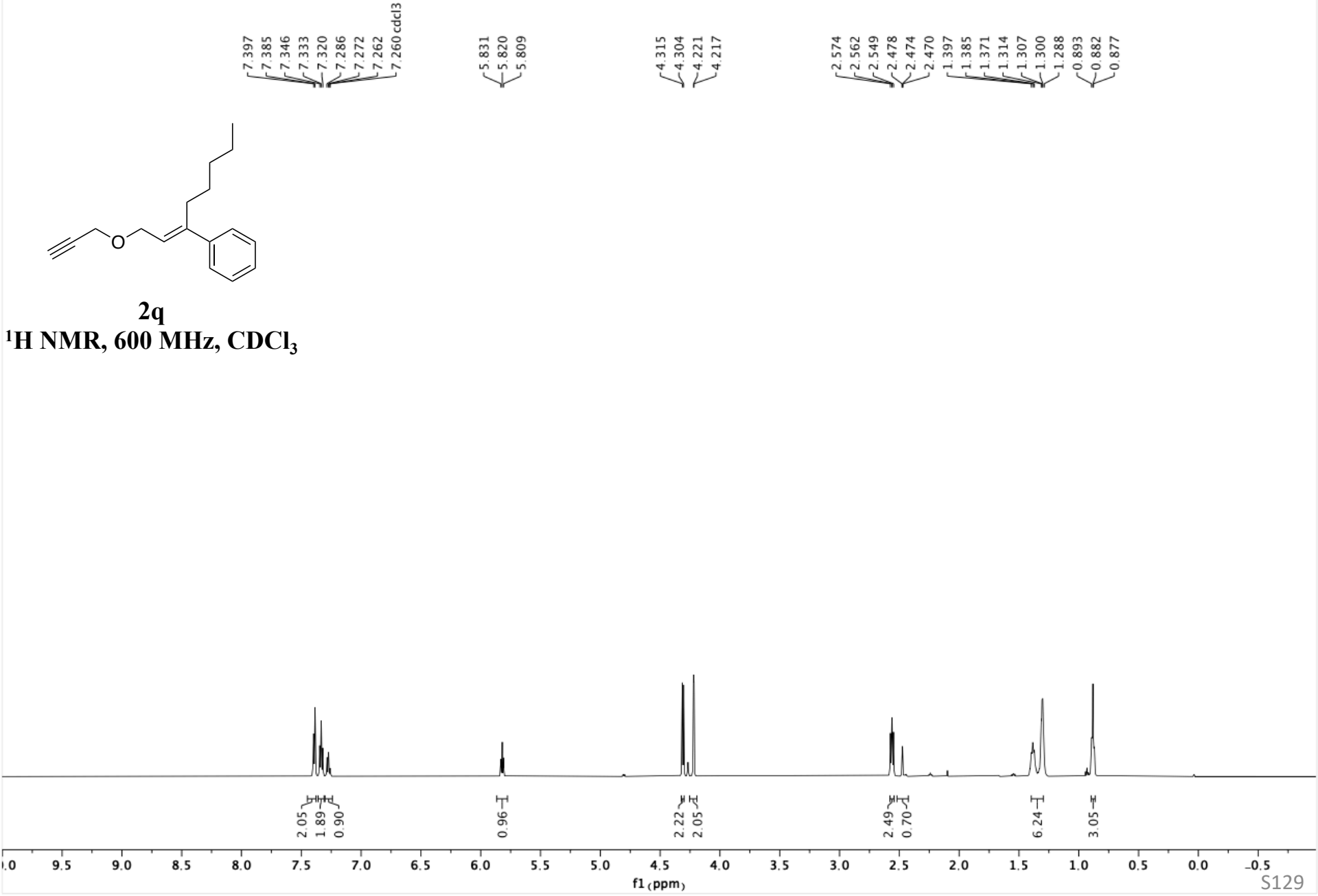
(*Z*)-1-Methyl-2-(1-phenyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)-1*H*-pyrrole



2p

^{13}C NMR, 150 MHz, $CDCl_3$

(*E*)-(1-(Prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene



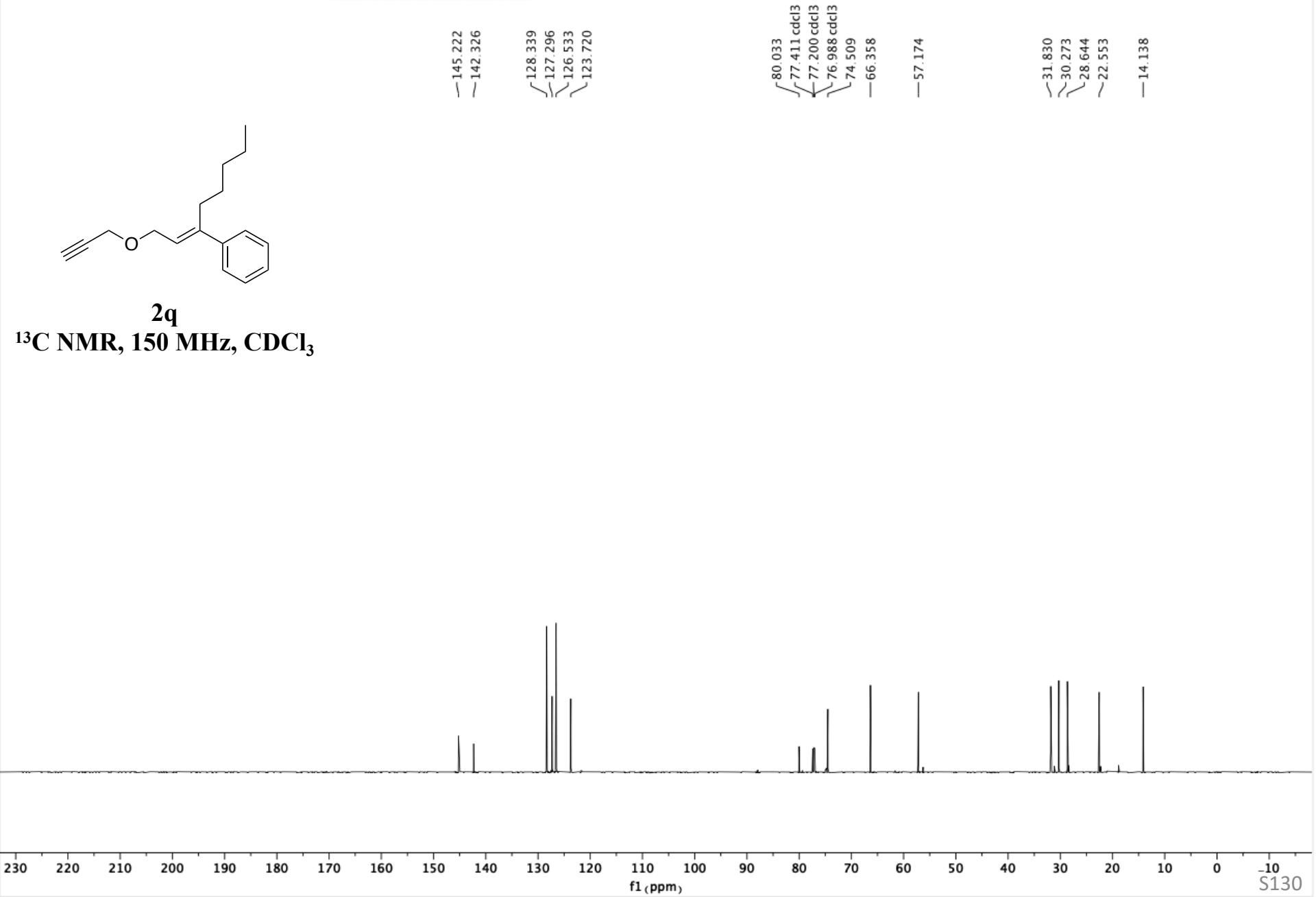
2q

^{1}H NMR, 600 MHz, $CDCl_3$

(*E*)-(1-(Prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene

2q

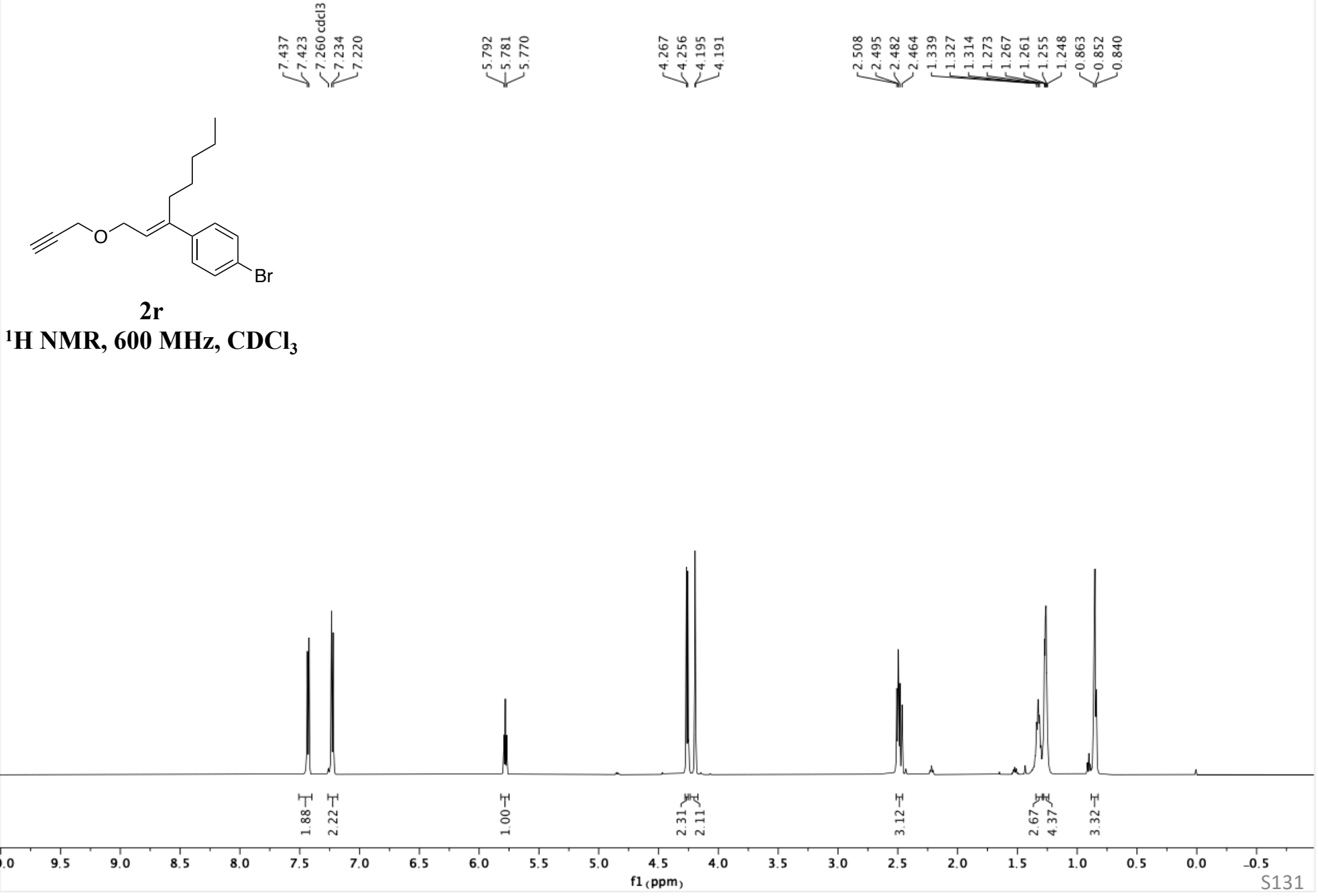
^{13}C NMR, 150 MHz, $CDCl_3$



(*E*)-1-Bromo-4-(1-(prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene

2r

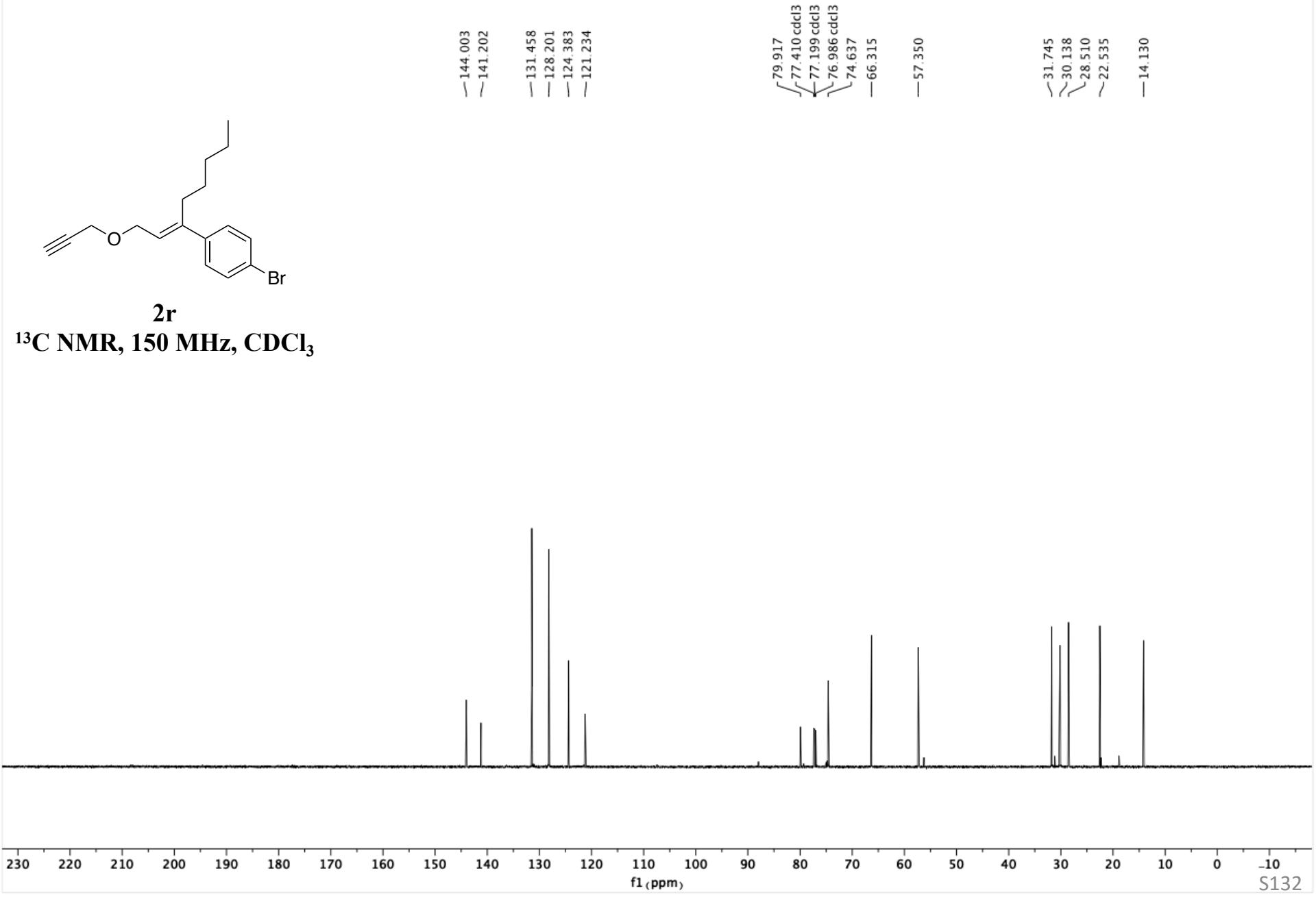
^{1}H NMR, 600 MHz, $CDCl_3$



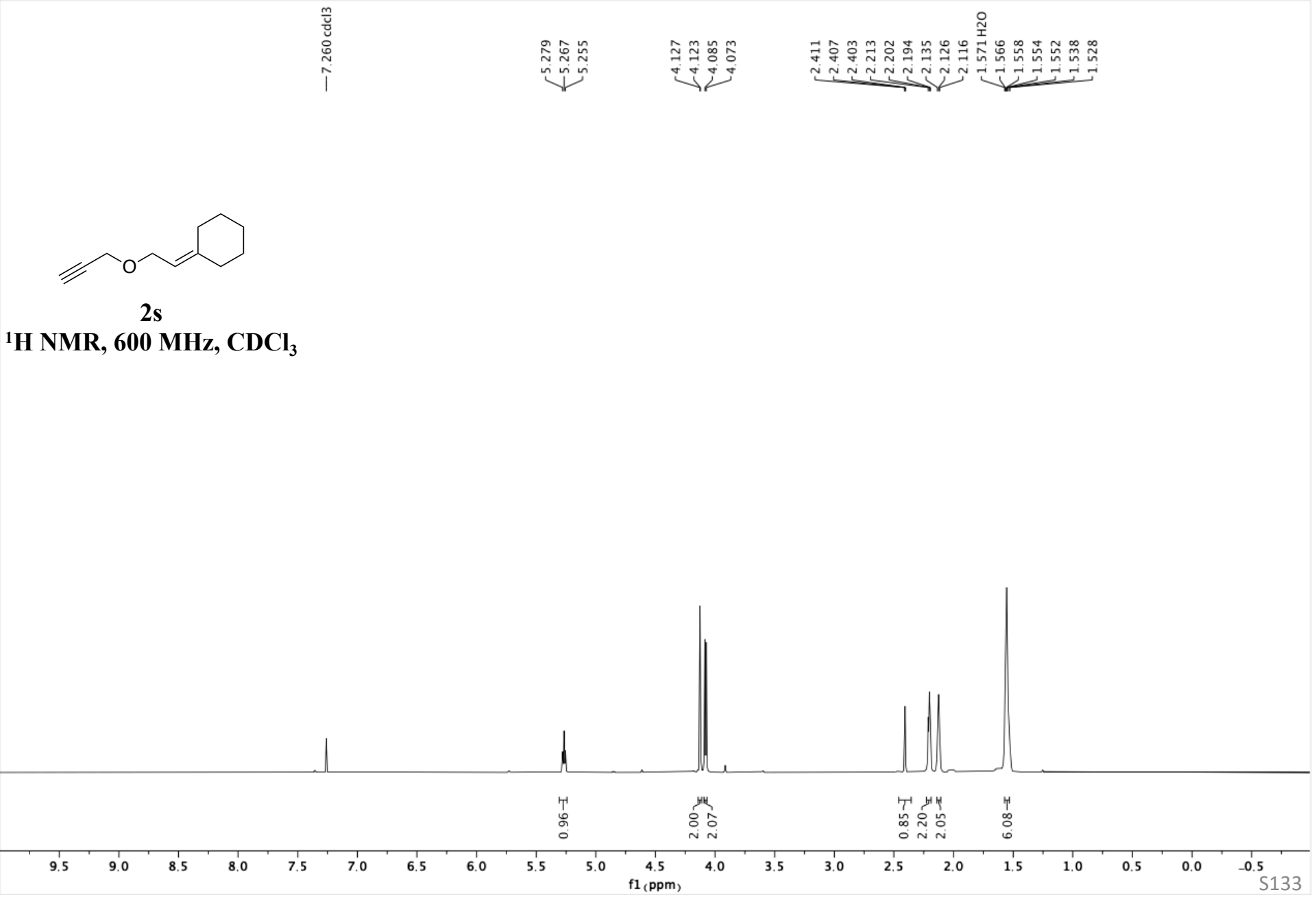
(*E*)-1-Bromo-4-(1-(prop-2-yn-1-yloxy)oct-2-en-3-yl)benzene

2r

^{13}C NMR, 150 MHz, $CDCl_3$



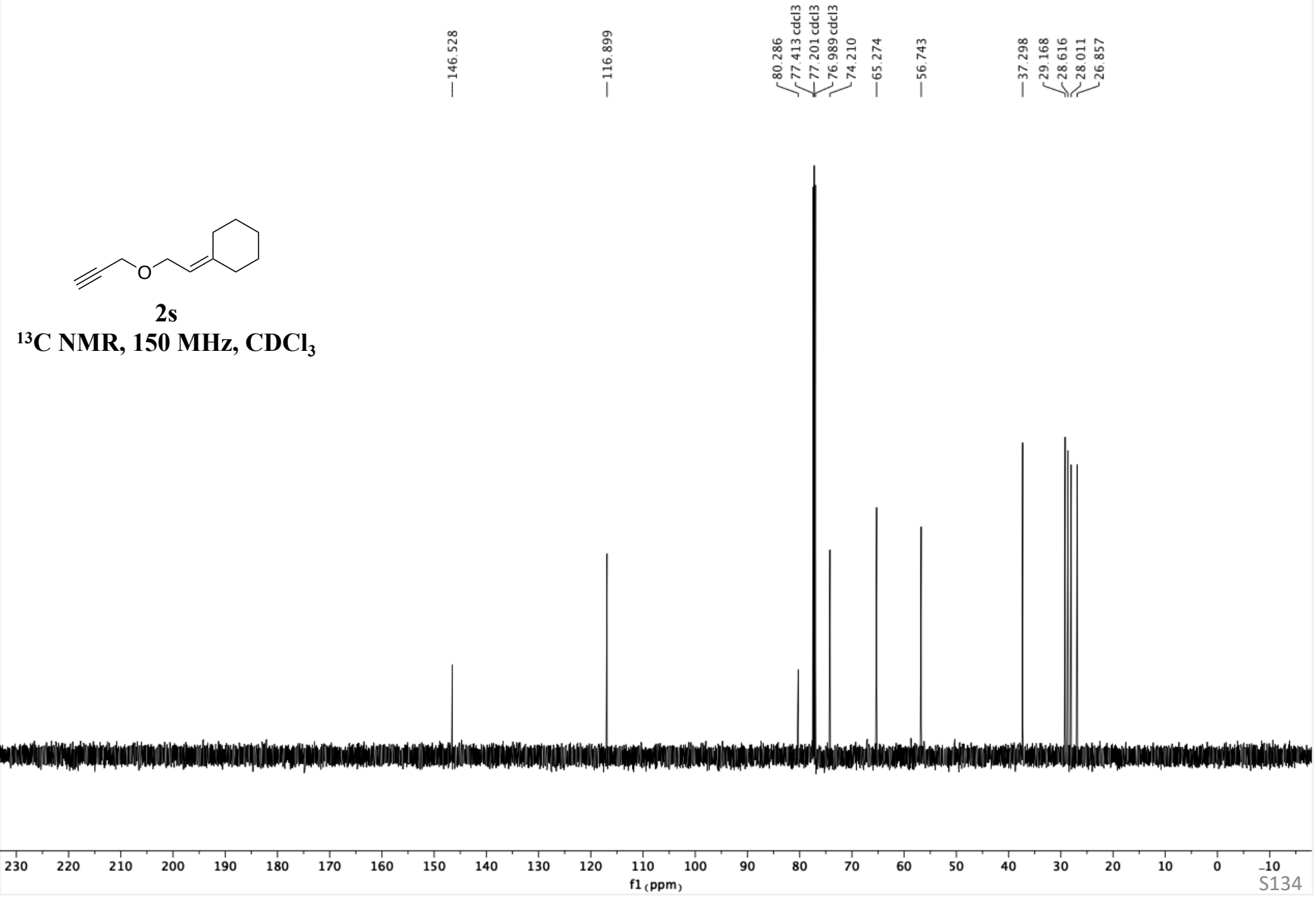
(2-(Prop-2-yn-1-yloxy)ethylidene)cyclohexane



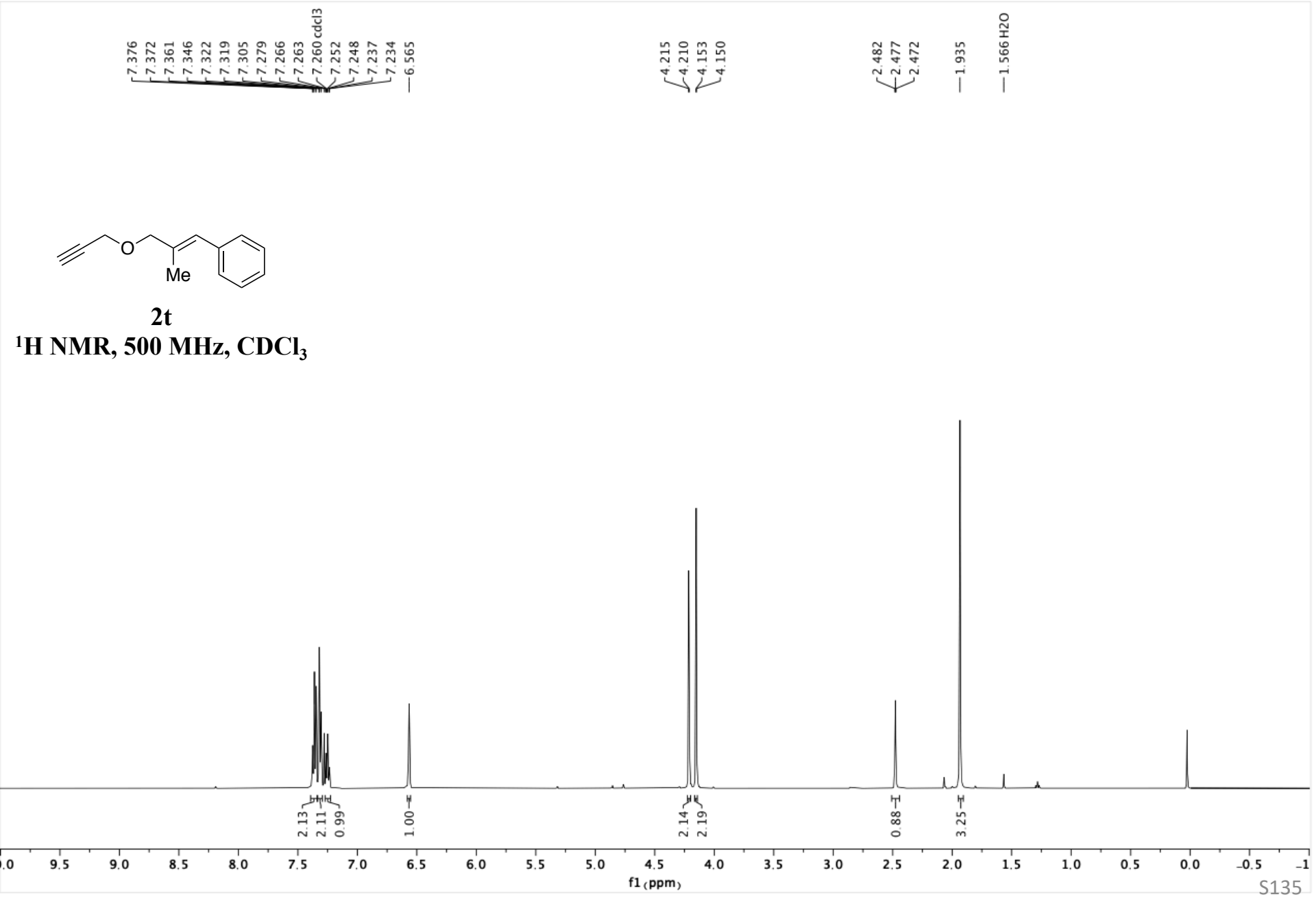
2s

^{1}H NMR, 600 MHz, $CDCl_3$

(2-(Prop-2-yn-1-yloxy)ethylidene)cyclohexane



(*E*)-(2-Methyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



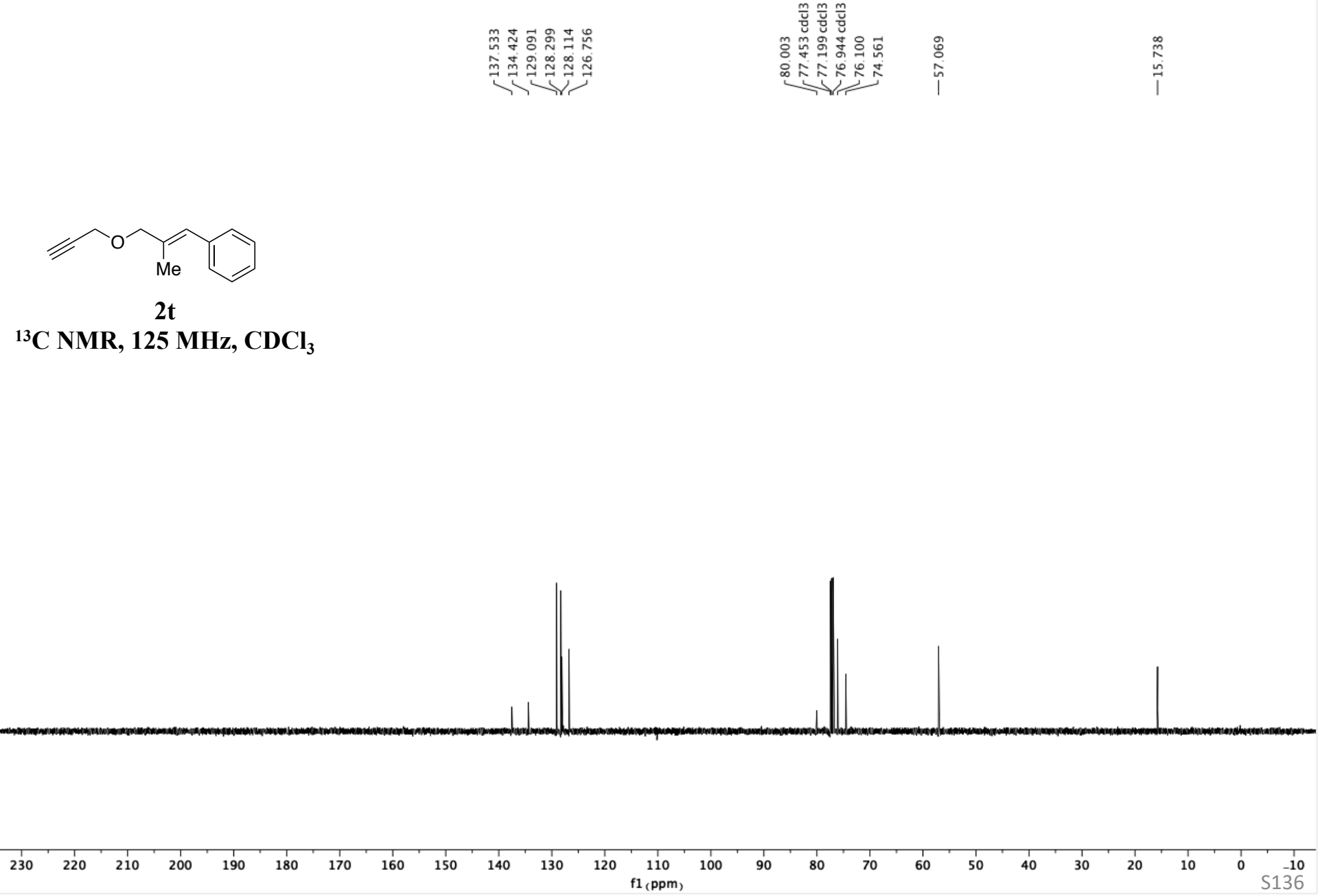
2t

^{1}H NMR, 500 MHz, $CDCl_3$

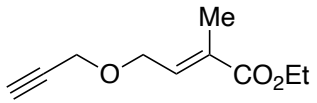
(*E*)-(2-Methyl-3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene

2t

^{13}C NMR, 125 MHz, $CDCl_3$



Ethyl (*E*)-2-methyl-4-(prop-2-yn-1-yloxy)but-2-enoate



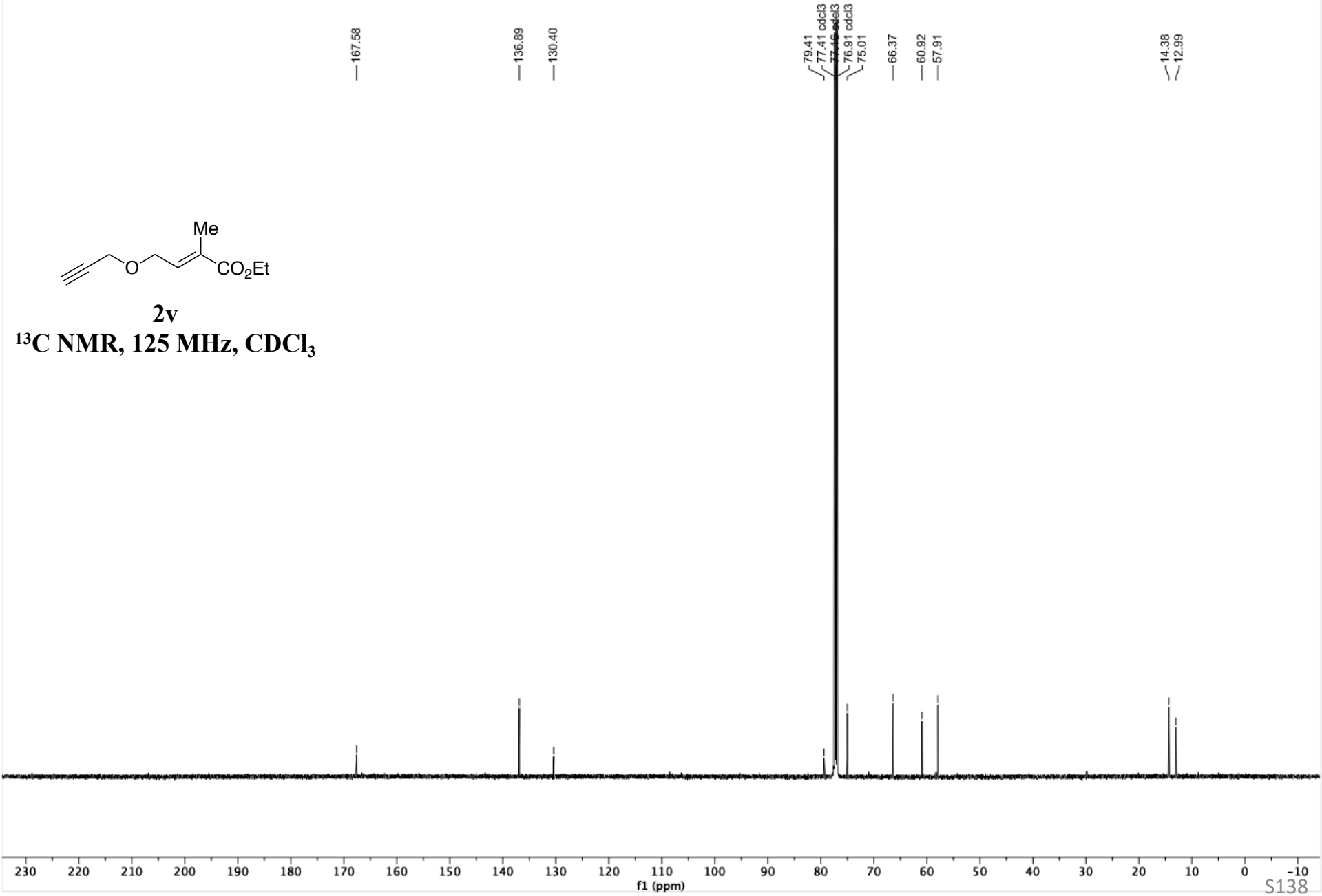
2v

^{1}H NMR, 400 MHz, $CDCl_3$

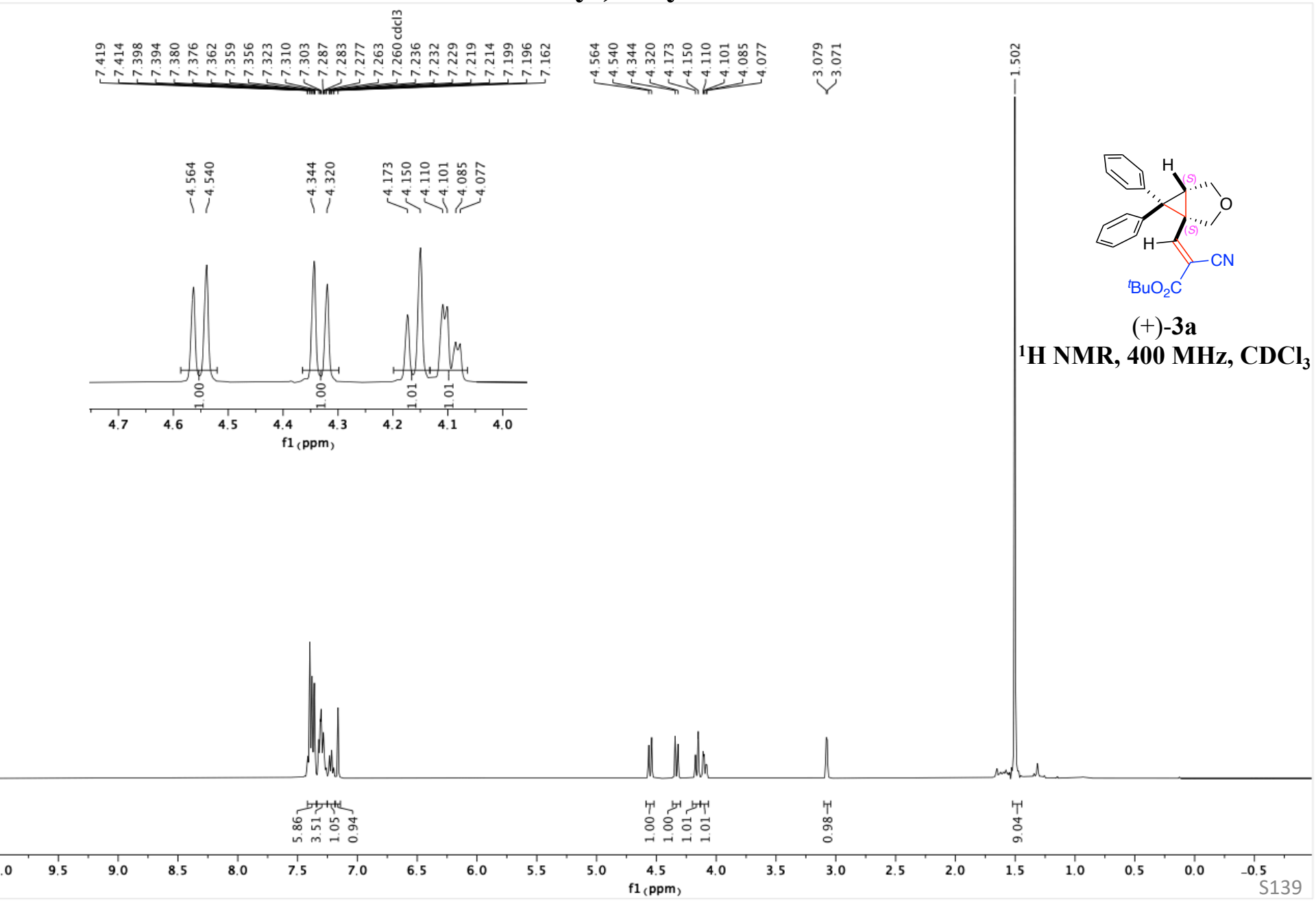
Ethyl (*E*)-2-methyl-4-(prop-2-yn-1-yloxy)but-2-enoate

2v

^{13}C NMR, 125 MHz, $CDCl_3$



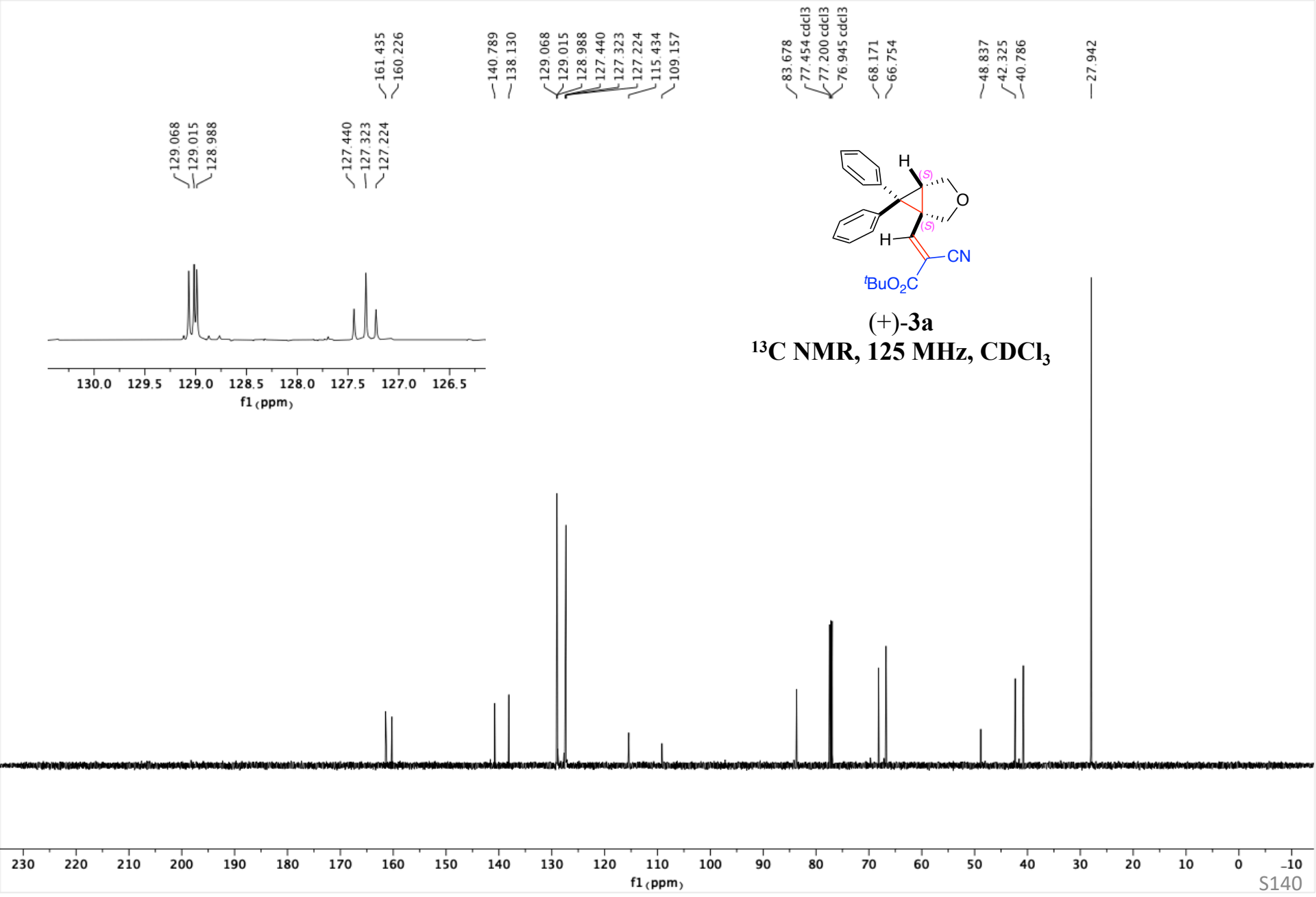
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3a**

^{1}H NMR, 400 MHz, $CDCl_3$

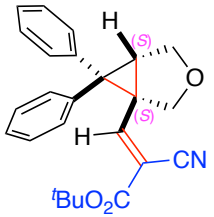
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

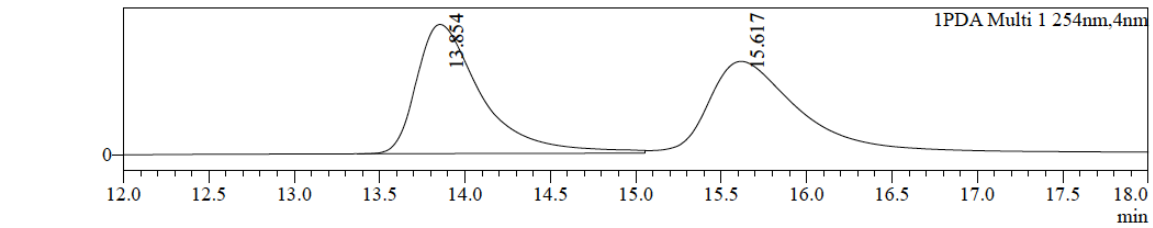
Sample Information

Sample Name	: CZZ-1250-ID-5%-1mL
Sample ID	: CZZ-1250-ID-5%-1mL
Data File	: CZZ-1250-ID-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

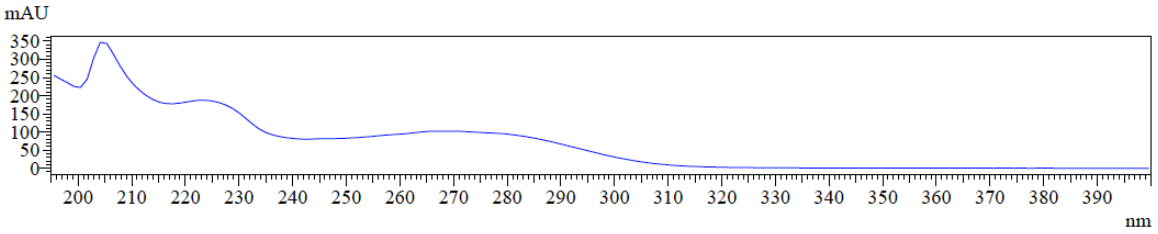


(±)-**3a**

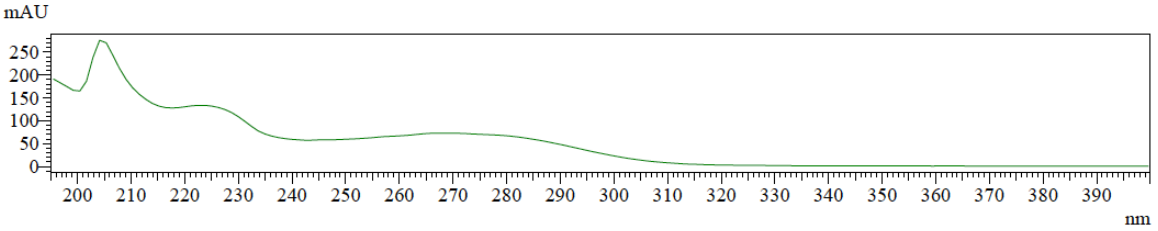
Chromatogram



UV Spectrum
Retention time = 13.854



UV Spectrum
Retention time = 15.617

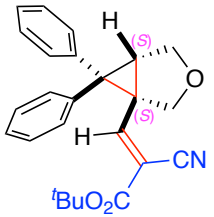


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.854	2282386	50.125
2	15.617	2271015	49.875
Total		4553401	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

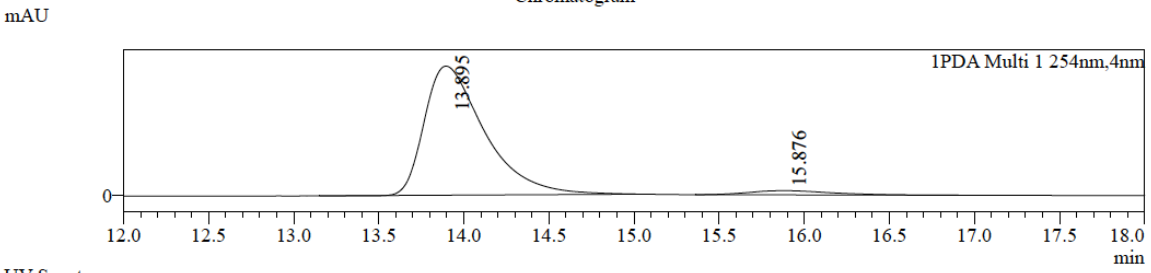


(+)-**3a**

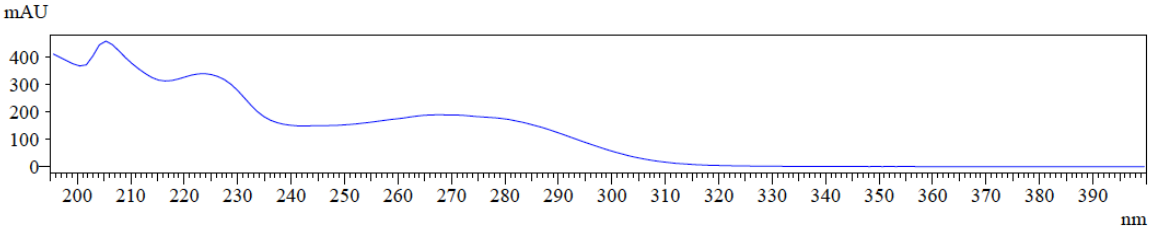
Sample Information

Sample Name	: CZZ-1256-ID-5%-1mL
Sample ID	: CZZ-1256-ID-5%-1mL
Data File	: CZZ-1256-ID-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

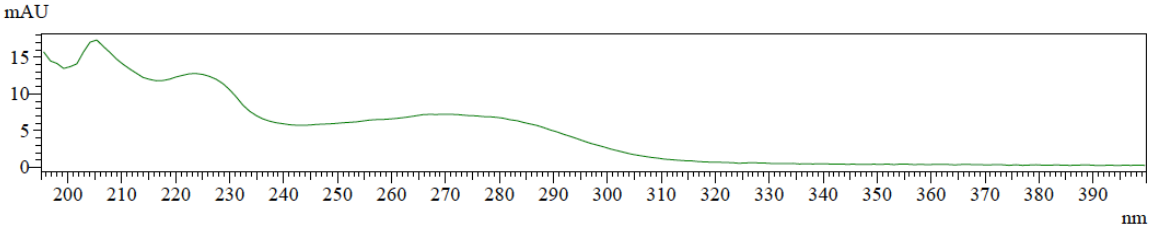
Chromatogram



UV Spectrum
Retention time = 13.895



UV Spectrum
Retention time = 15.876

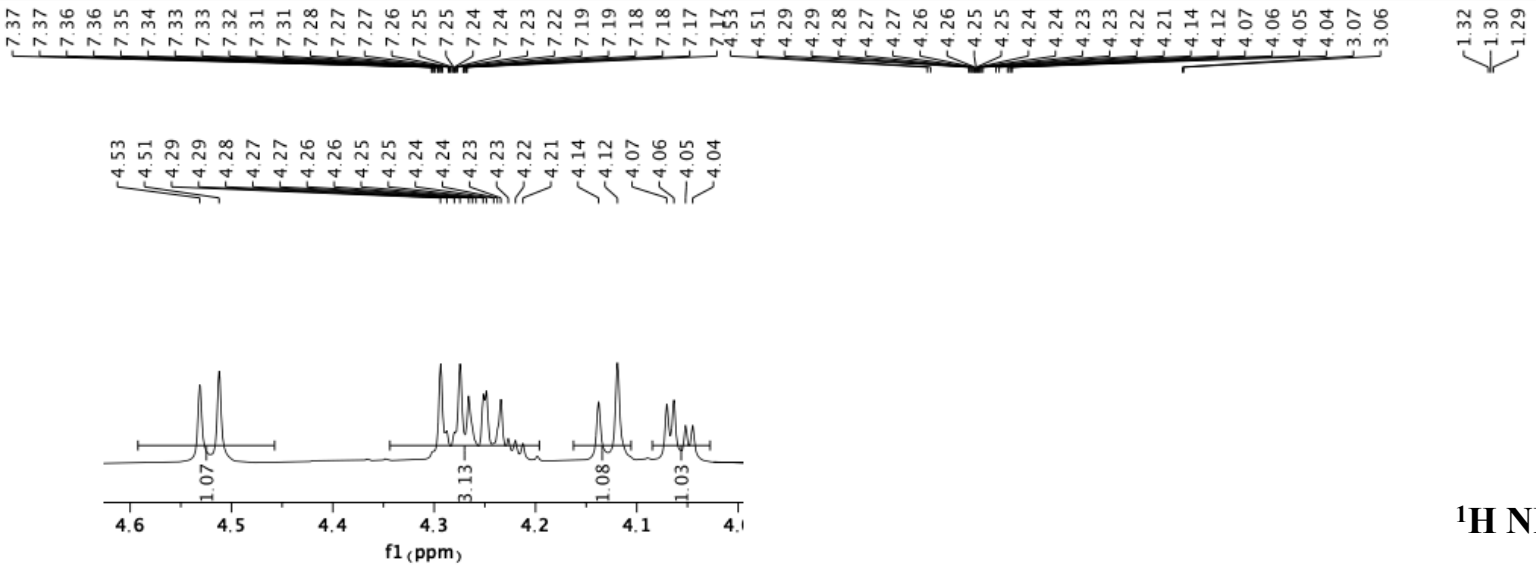


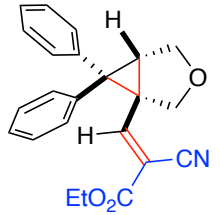
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.895	3945477	95.747
2	15.876	175259	4.253
Total		4120736	100.000

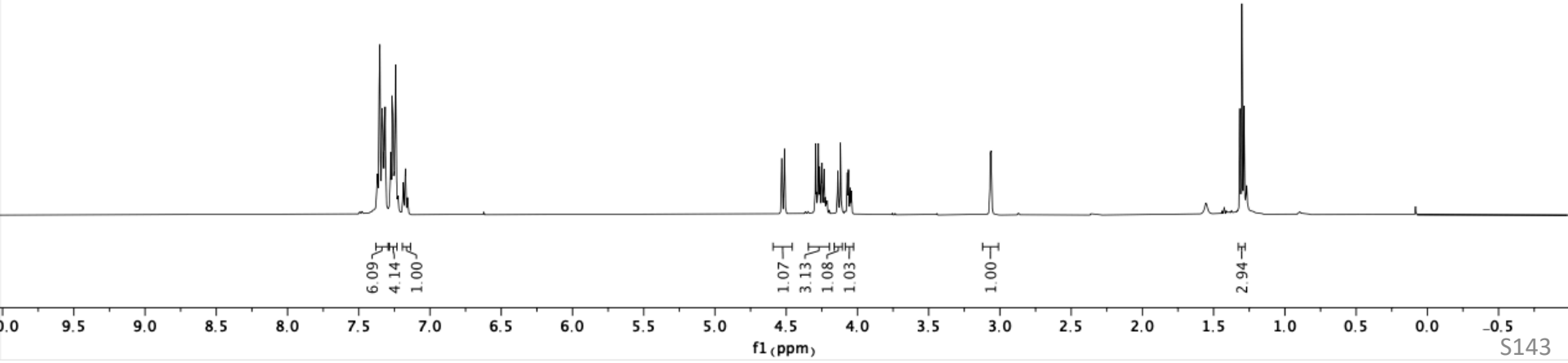
Ethyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



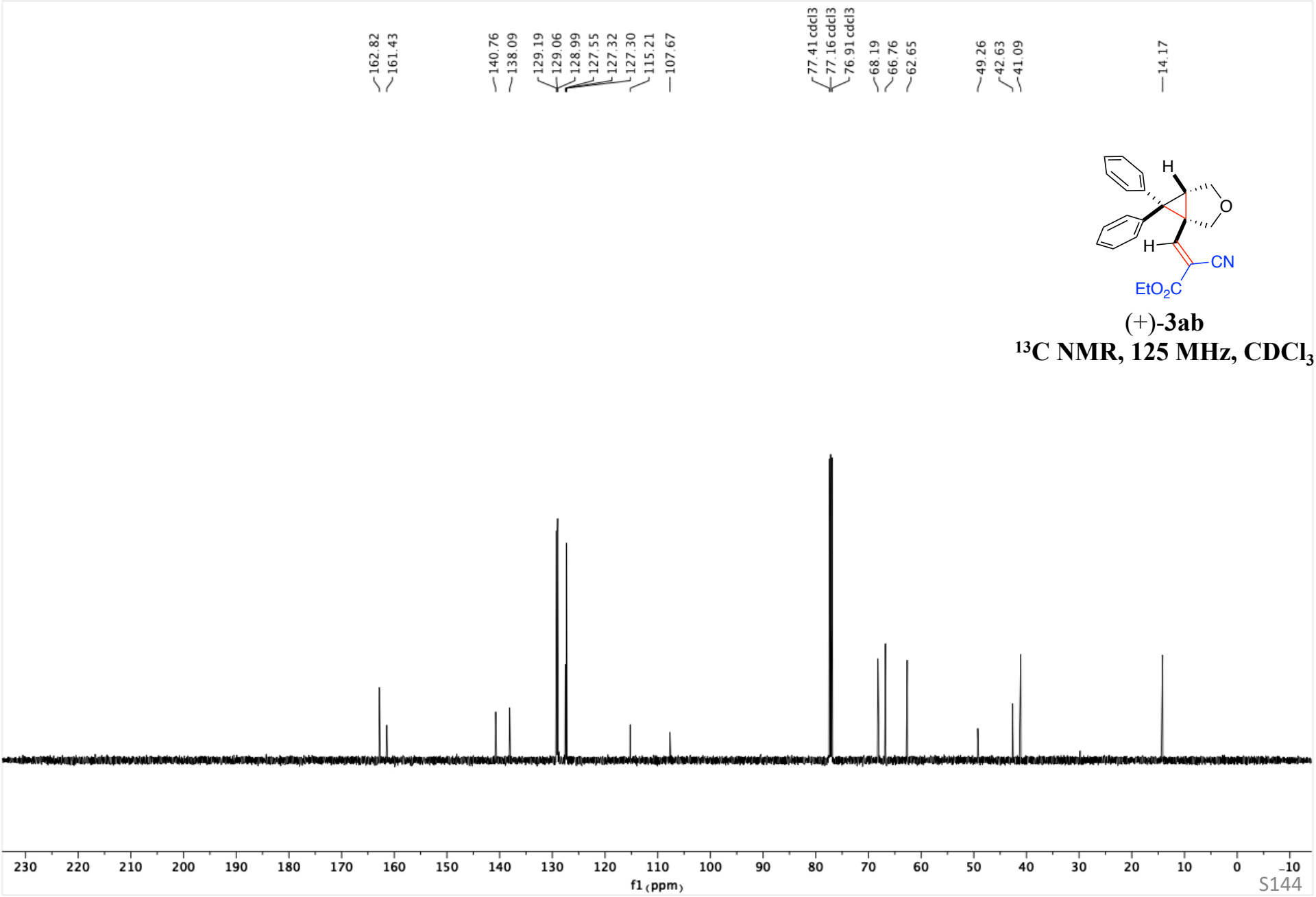


(+)-**3ab**

^{1}H NMR, 500 MHz, $CDCl_3$



Ethyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3ab**

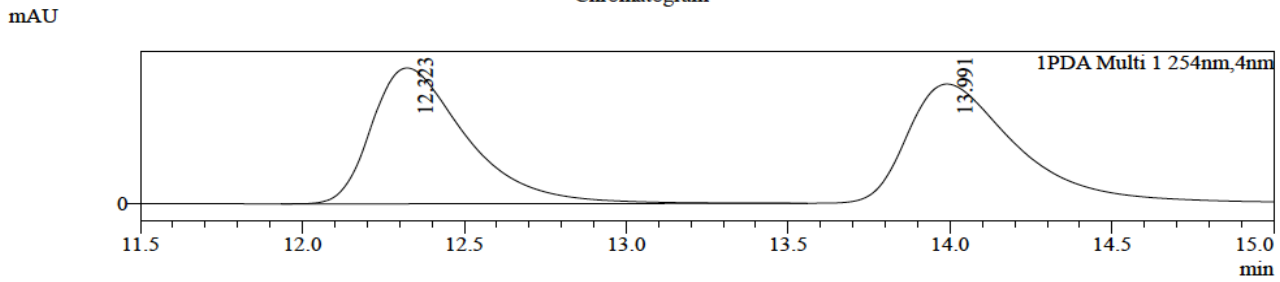
^{13}C NMR, 125 MHz, $CDCl_3$

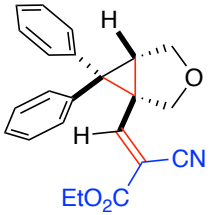
Ethyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2741-5%-IA-0.8mL
Sample ID	: CZZ-2741-5%-IA-0.8mL
Data File	: CZZ-2741-5%-IA-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

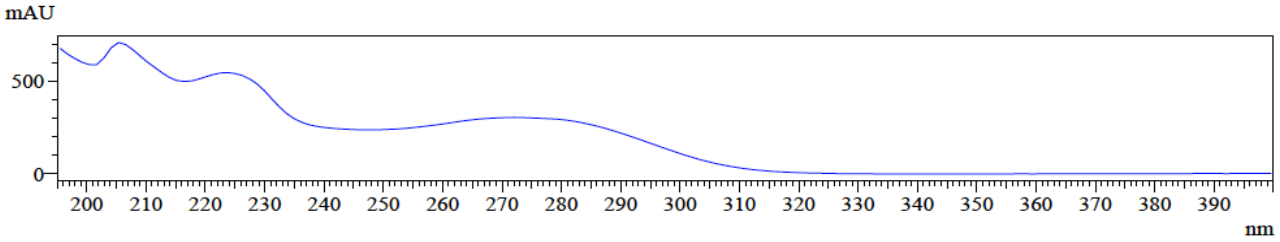
Chromatogram



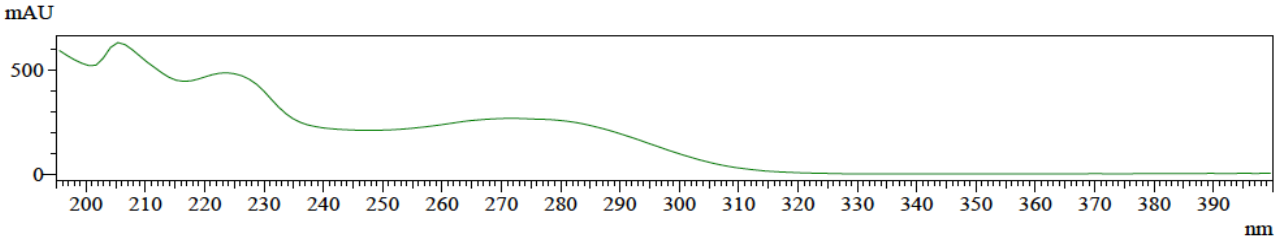


(±)-**3ab**

UV Spectrum
Retention time = 12.323



UV Spectrum
Retention time = 13.991



Peak Table

PDA Ch1 254nm

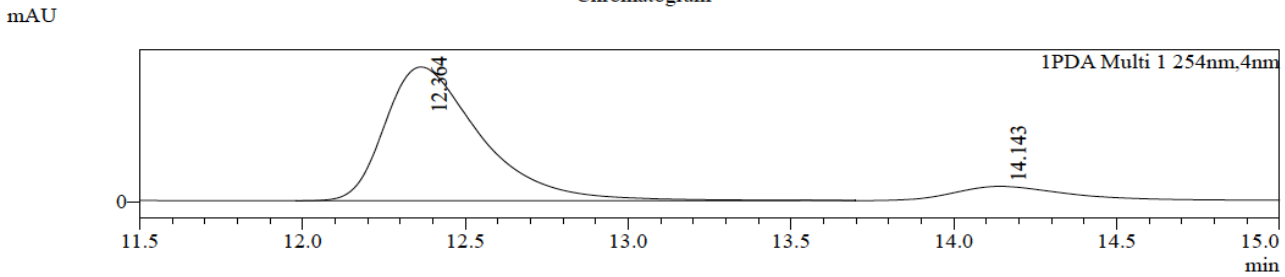
Peak#	Ret. Time	Area	Area%
1	12.323	5072109	50.195
2	13.991	5032710	49.805
Total		10104820	100.000

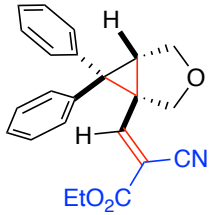
Ethyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2742-5%-IA-0.8mL
Sample ID	: CZZ-2742-5%-IA-0.8mL
Data File	: CZZ-2742-5%-IA-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

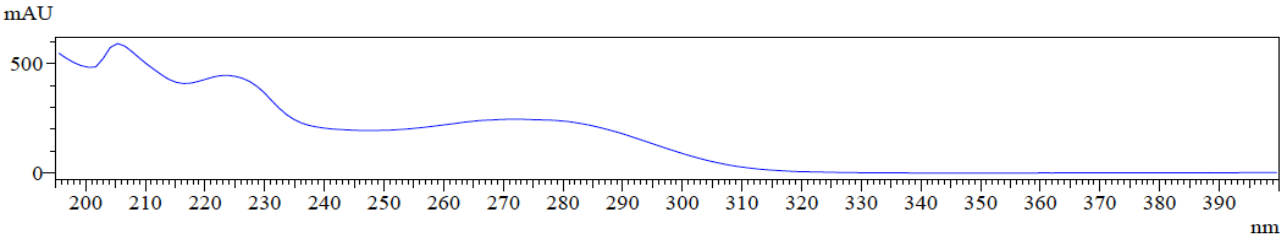
Chromatogram



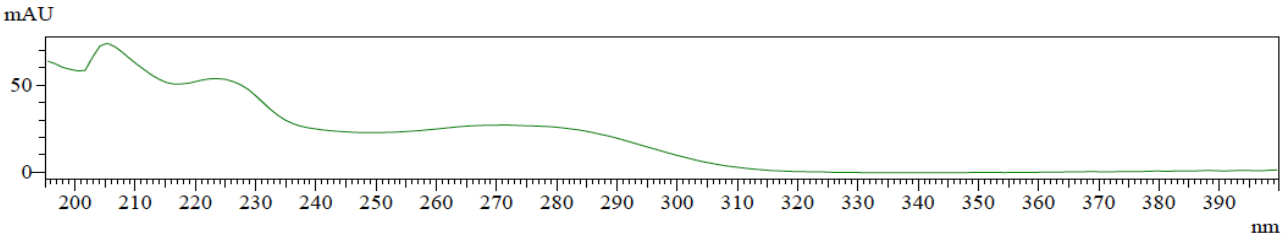


(+)-**3ab**

UV Spectrum
Retention time = 12.364



UV Spectrum
Retention time = 14.143

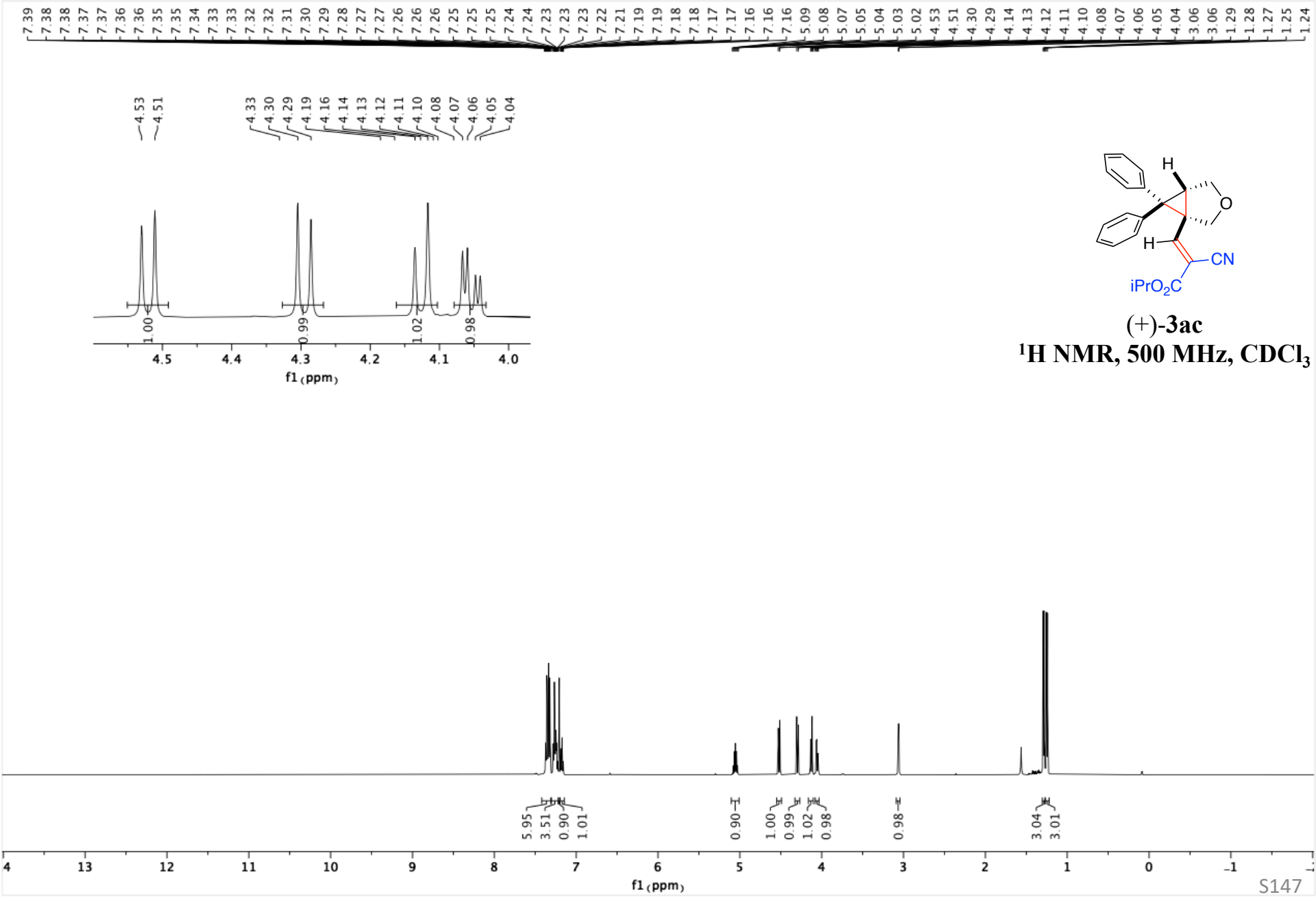


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.364	4091443	89.089
2	14.143	501101	10.911
Total		4592544	100.000

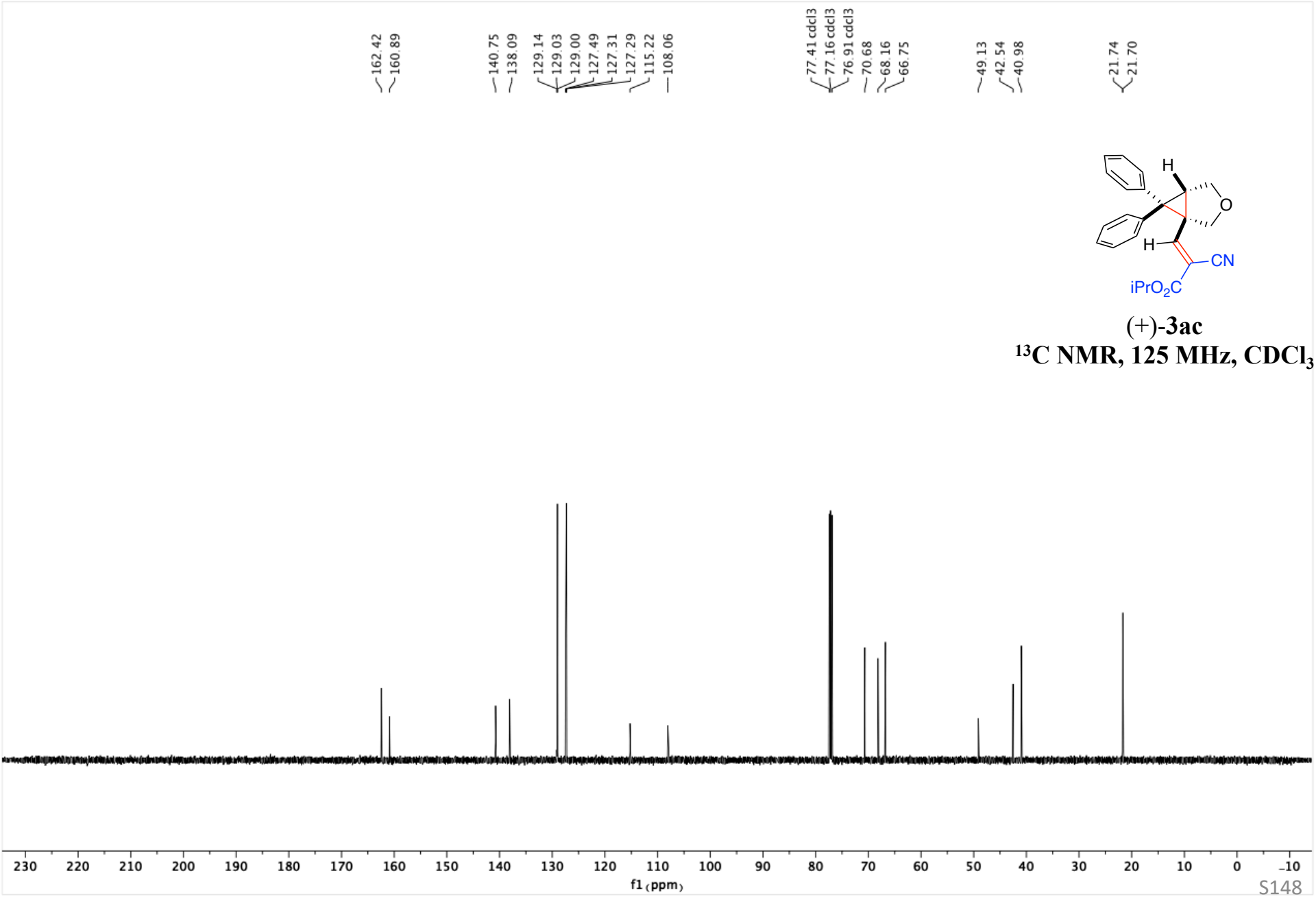
Isopropyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3ac**

^{1}H NMR, 500 MHz, $CDCl_3$

Isopropyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3ac**

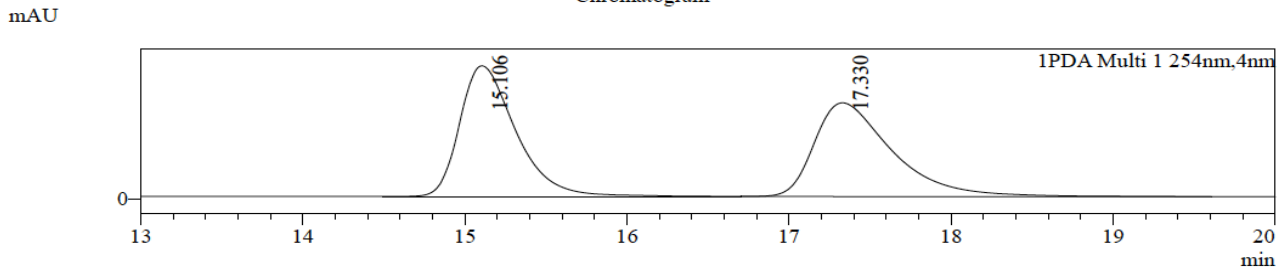
^{13}C NMR, 125 MHz, $CDCl_3$

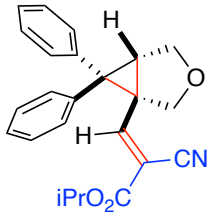
Isopropyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2746-ID-10%-0.8mL
Sample ID	: CZZ-2746-ID-10%-0.8mL
Data File	: CZZ-2746-ID-10%-0.8mL.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

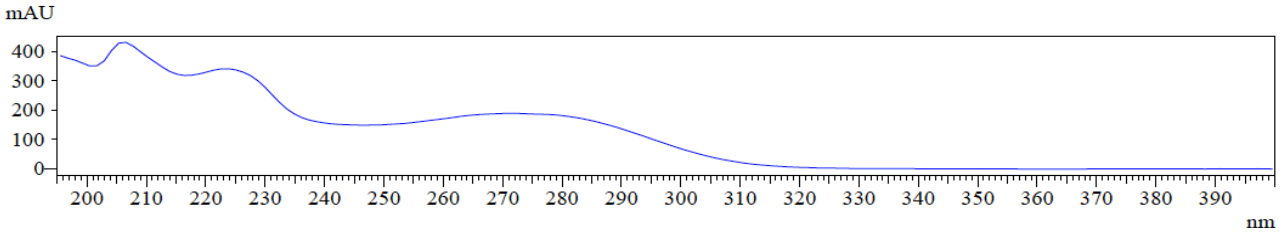
Chromatogram



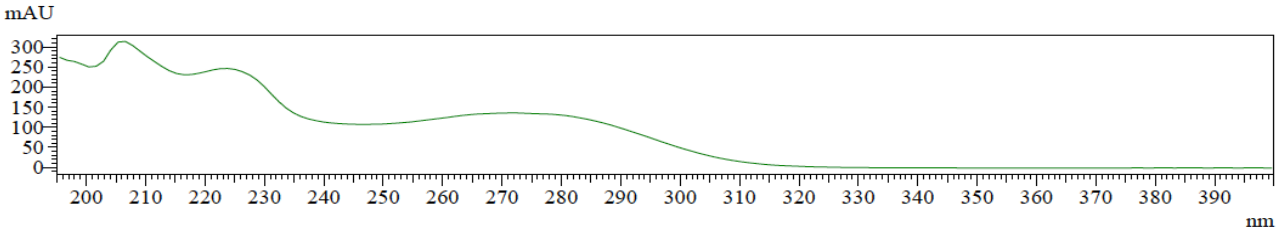


(±)-**3ac**

UV Spectrum
Retention time = 15.106



UV Spectrum
Retention time = 17.330



Peak Table

PDA Ch1 254nm

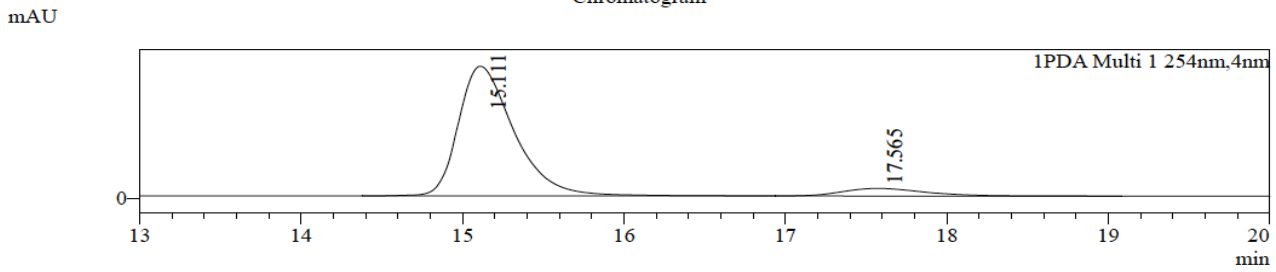
Peak#	Ret. Time	Area	Area%
1	15.106	3708108	50.138
2	17.330	3687746	49.862
Total		7395854	100.000

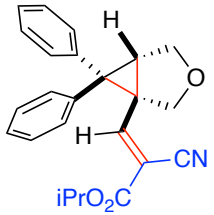
Isopropyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2747-ID-10%-0.8mL
Sample ID	: CZZ-2747-ID-10%-0.8mL
Data File	: CZZ-2747-ID-10%-0.8mL001.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

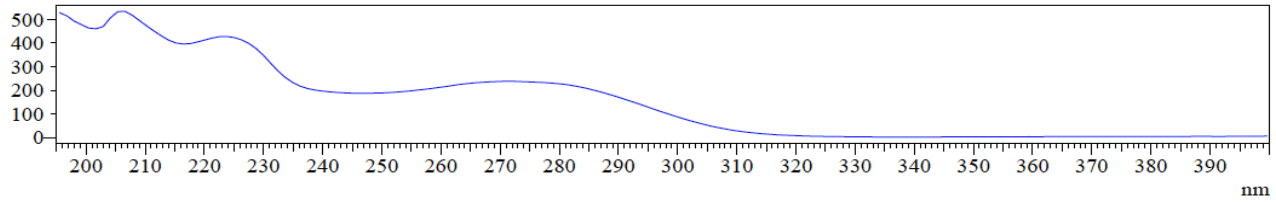
Chromatogram



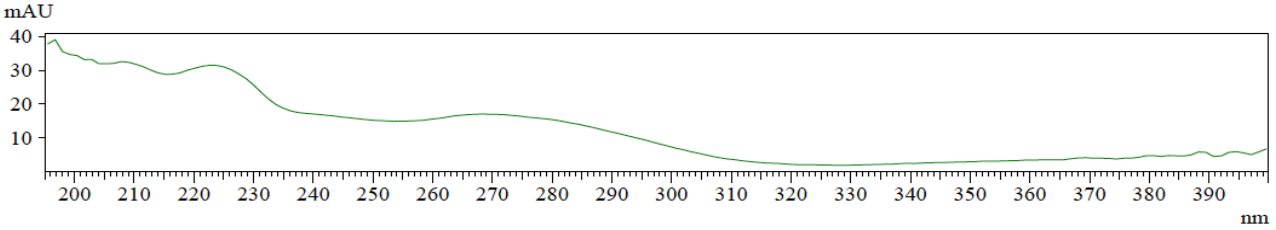


(+)-**3ac**

UV Spectrum
Retention time = 15.111



UV Spectrum
Retention time = 17.565

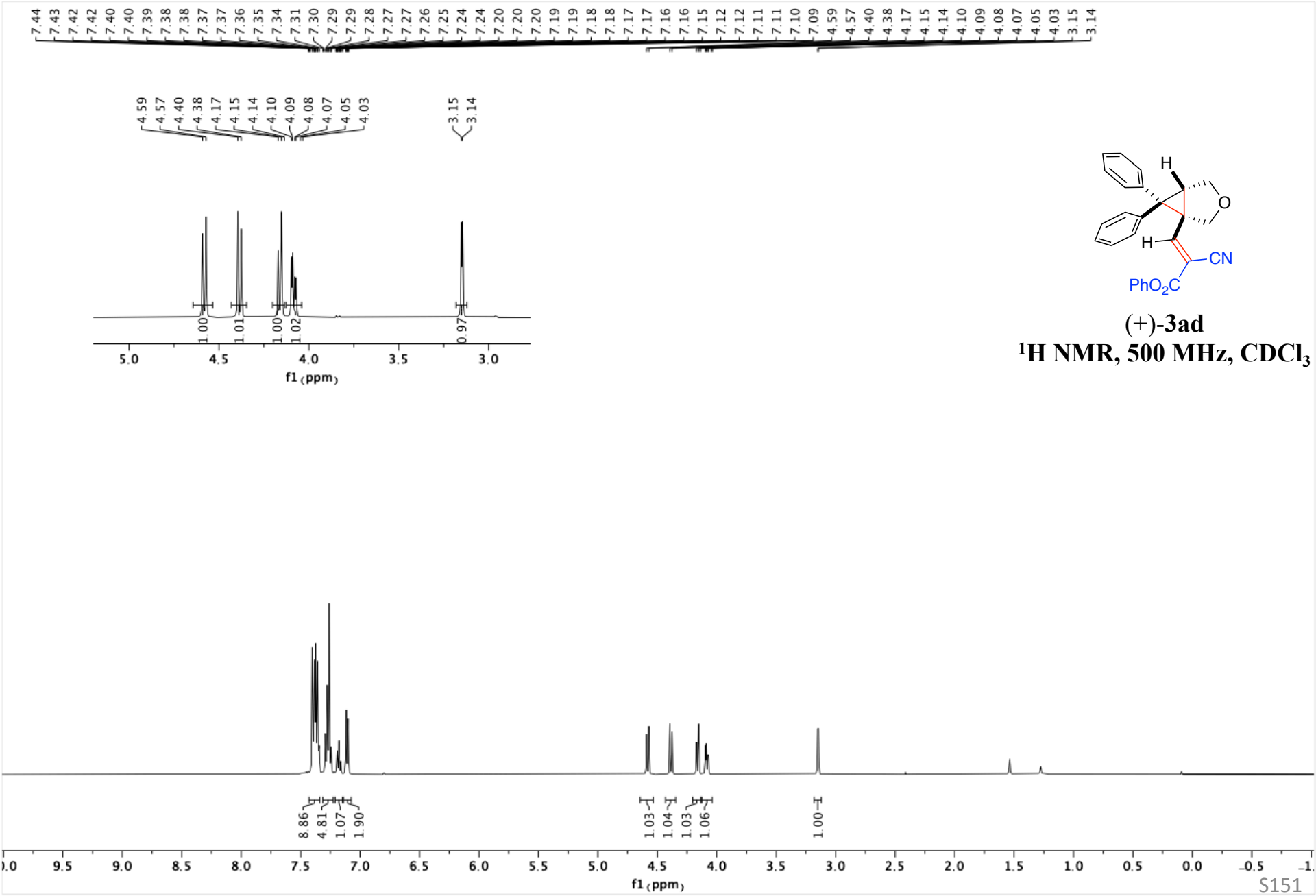


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.111	4639918	91.832
2	17.565	412682	8.168
Total		5052601	100.000

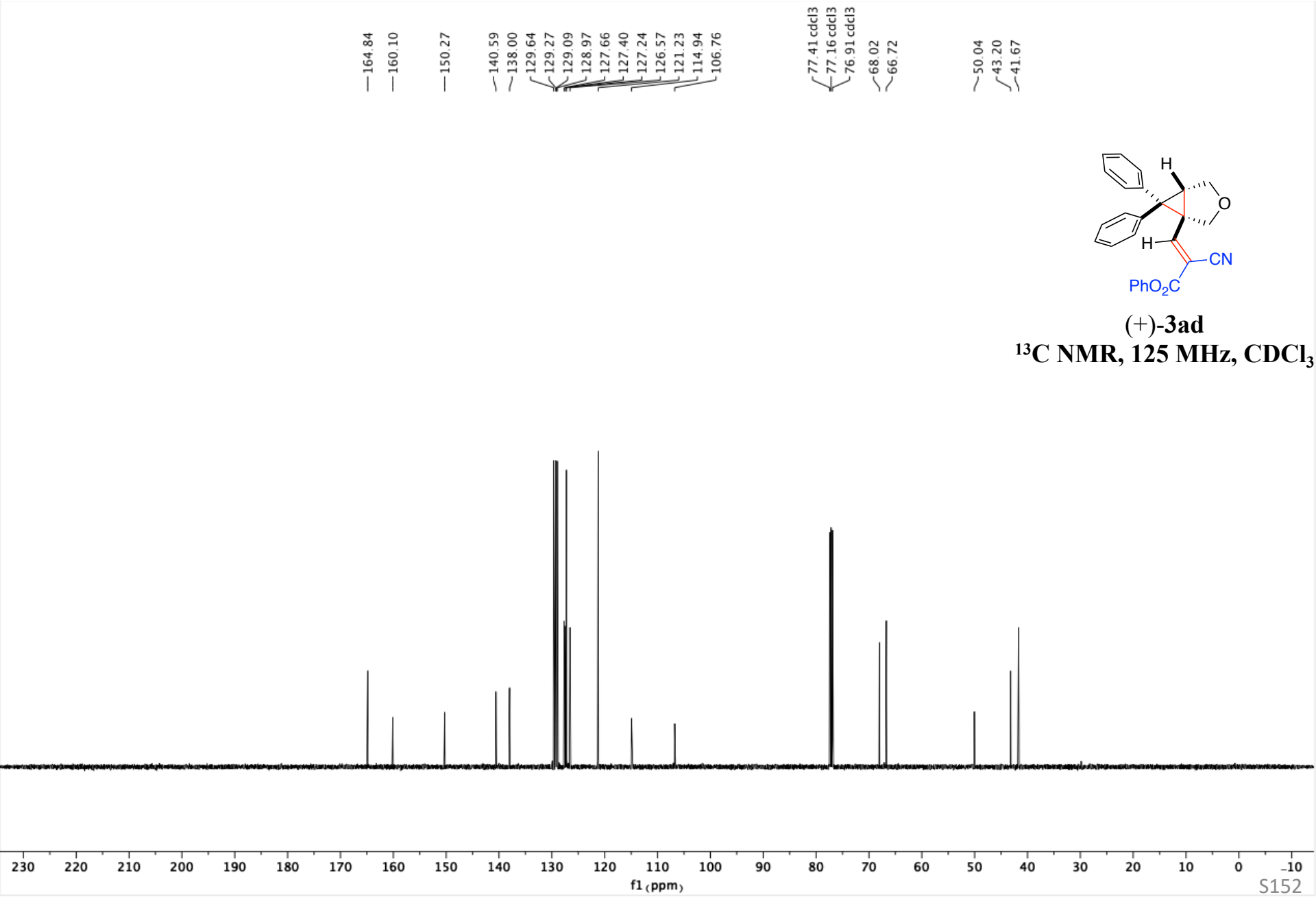
Phenyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3ad**

^{1}H NMR, 500 MHz, $CDCl_3$

Phenyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3ad**

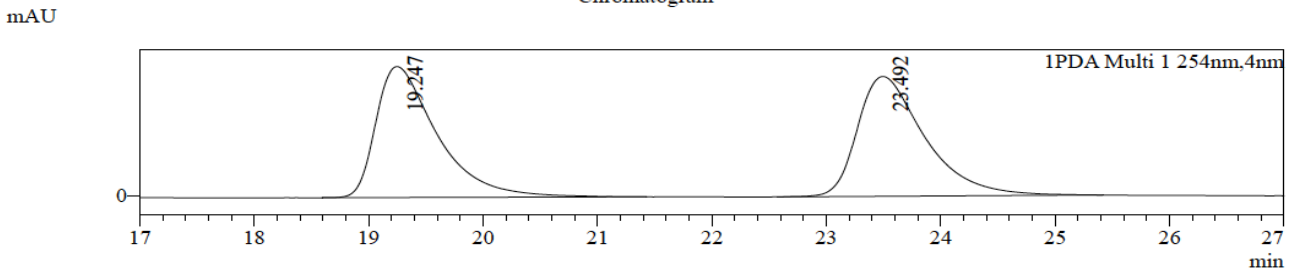
^{13}C NMR, 125 MHz, $CDCl_3$

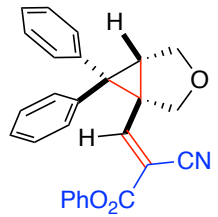
Phenyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2743-5%-IA-0.8mL
Sample ID	: CZZ-2743-5%-IA-0.8mL
Data File	: CZZ-2743-5%-IA-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

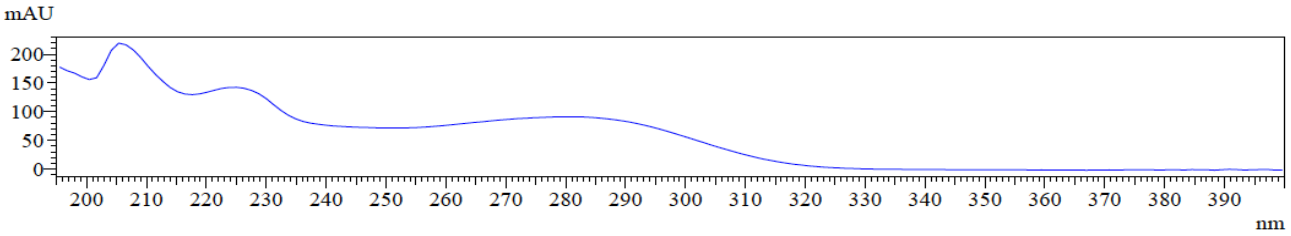
Chromatogram



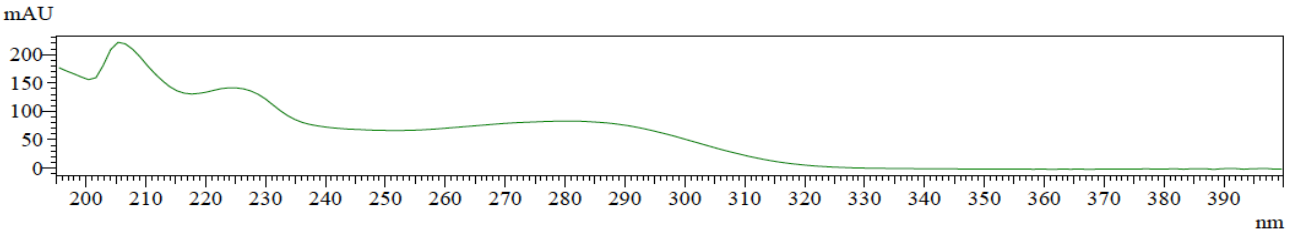


(±)-**3ad**

UV Spectrum
Retention time = 19.247



UV Spectrum
Retention time = 23.492



Peak Table

PDA Ch1 254nm

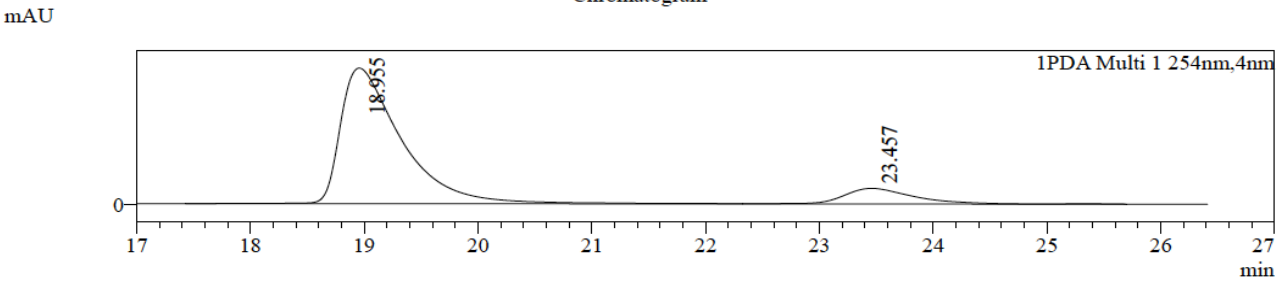
Peak#	Ret. Time	Area	Area%
1	19.247	2728985	49.785
2	23.492	2752552	50.215
Total		5481537	100.000

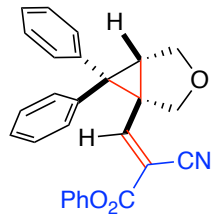
Phenyl (*E*)-2-cyano-3-(6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

Sample Information

Sample Name	: CZZ-2744-5%-IA-0.8mL
Sample ID	: CZZ-2744-5%-IA-0.8mL
Data File	: CZZ-2744-5%-IA-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

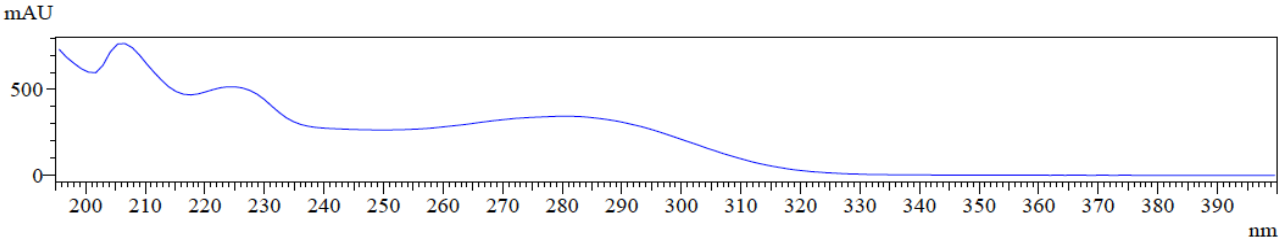
Chromatogram



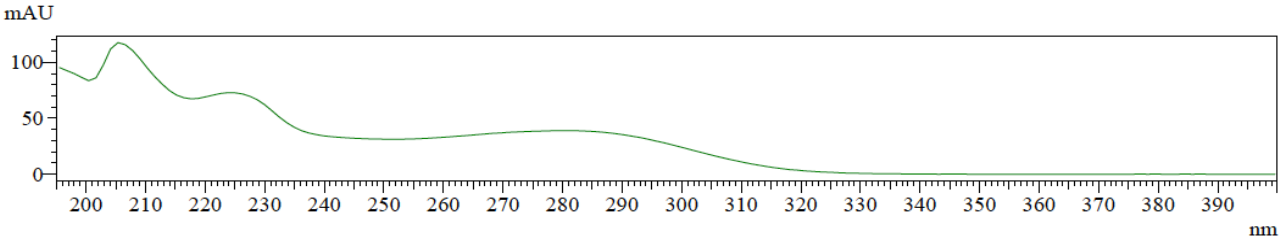


(+)-**3ad**

UV Spectrum
Retention time = 18.955



UV Spectrum
Retention time = 23.457

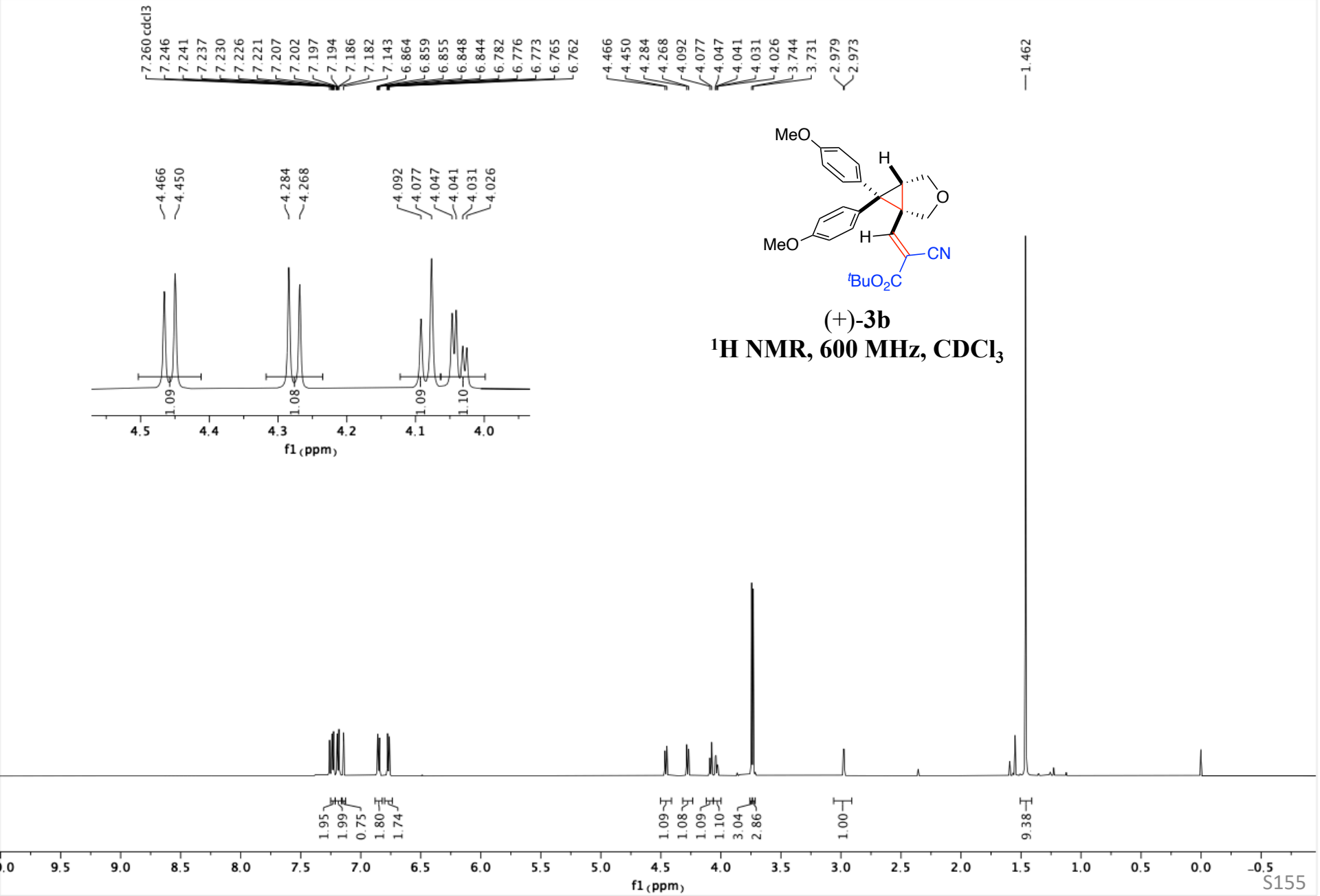


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.955	9974195	88.198
2	23.457	1334639	11.802
Total		11308834	100.000

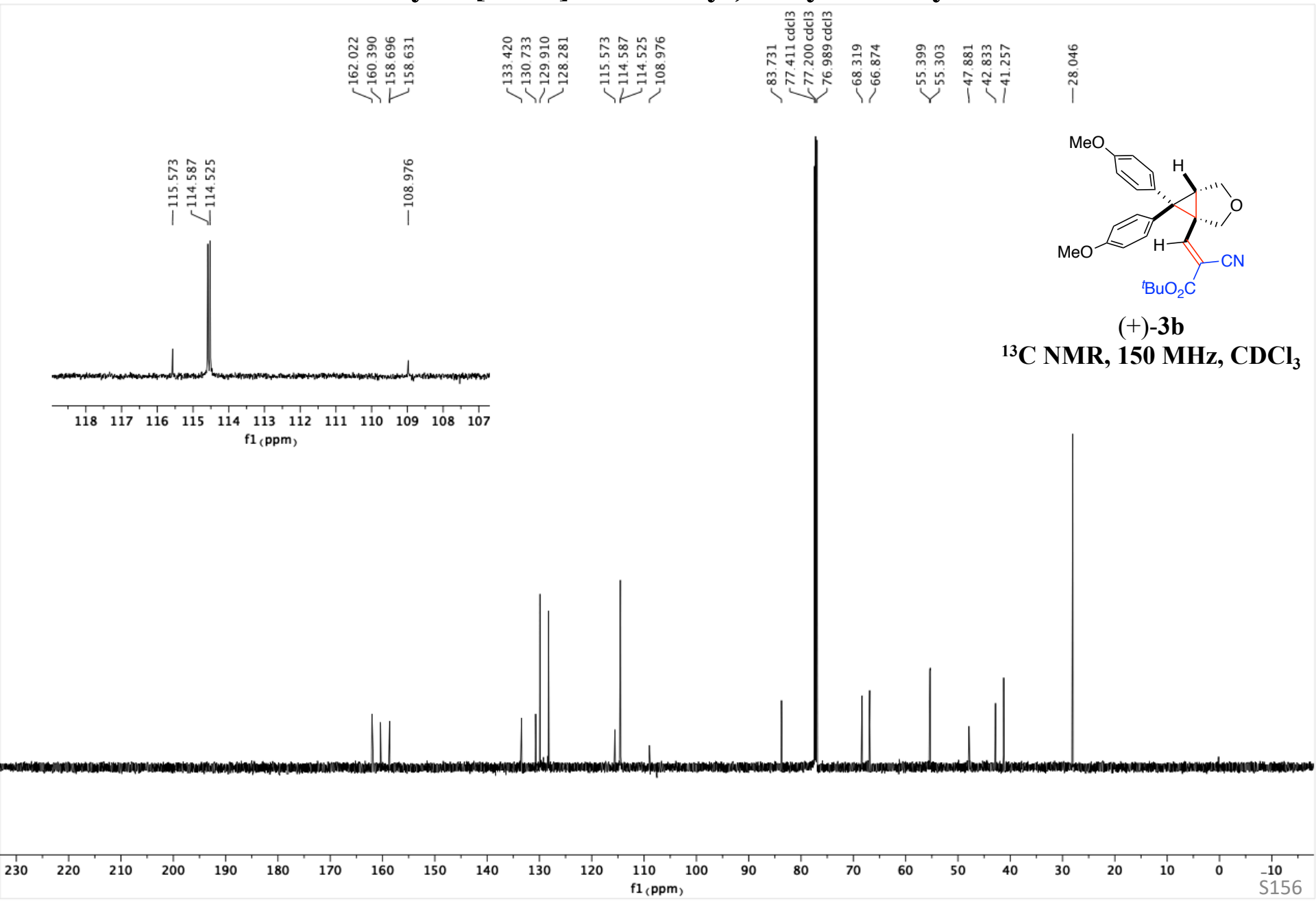
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3b**

^{1}H NMR, 600 MHz, $CDCl_3$

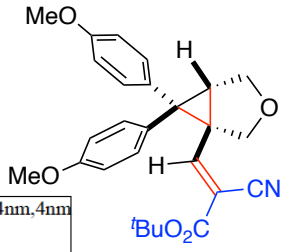
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3b**

^{13}C NMR, 150 MHz, $CDCl_3$

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate (±)-3b

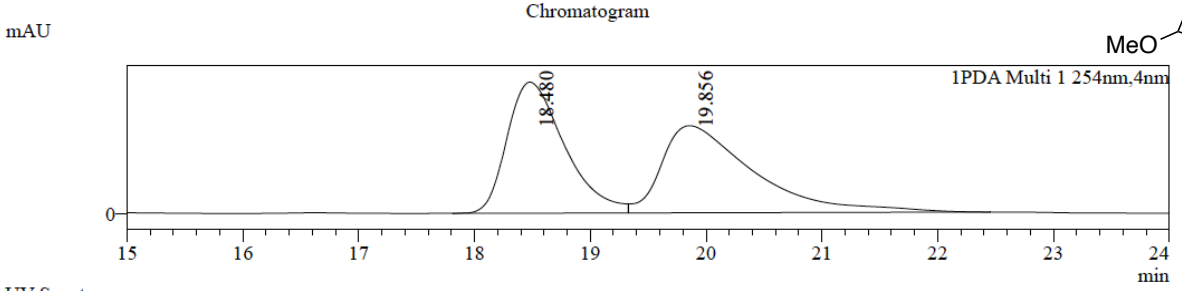


(±)-**3b**

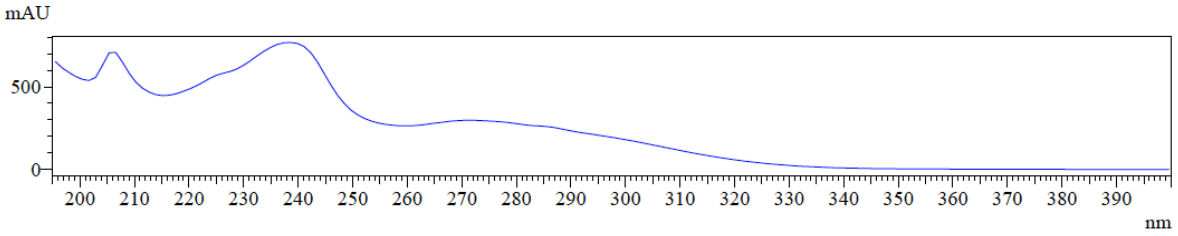
Sample Information

Sample Name	: CZZ-1371-25%-iD-0.8mL
Sample ID	: CZZ-1371-25%-iD-0.8mL
Data File	: CZZ-1371-25%-iD-0.8mL.lcd
Method File	: CZZ-25%-0.8ml-1.lcm

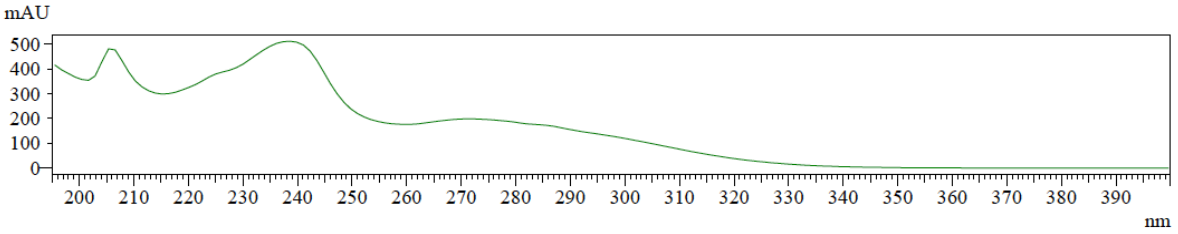
Chromatogram



UV Spectrum
Retention time = 18.480



UV Spectrum
Retention time = 19.856

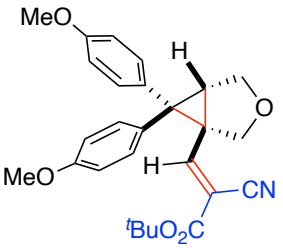


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.480	10055683	48.626
2	19.856	10624160	51.374
Total		20679844	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

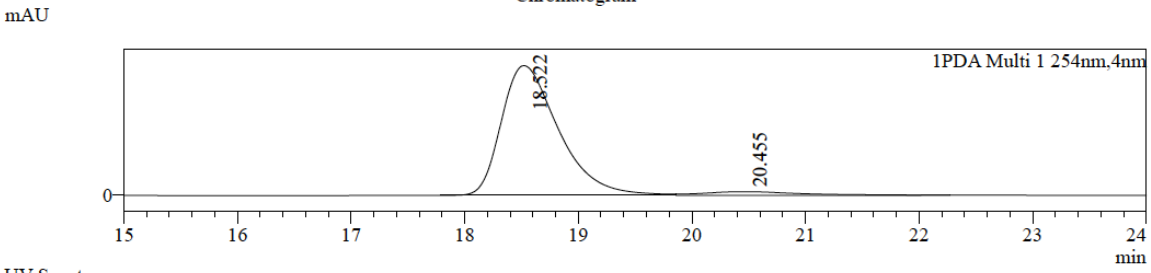


(+)-**3b**

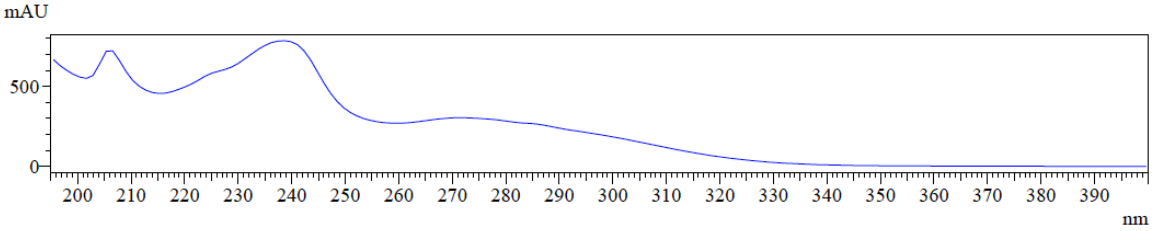
Sample Information

Sample Name	: CZZ-1308-25%-iD-0.8mL
Sample ID	: CZZ-1308-25%-iD-0.8mL
Data File	: CZZ-1308-25%-iD-0.8mL.lcd
Method File	: CZZ-25%-0.8ml-1.lcm

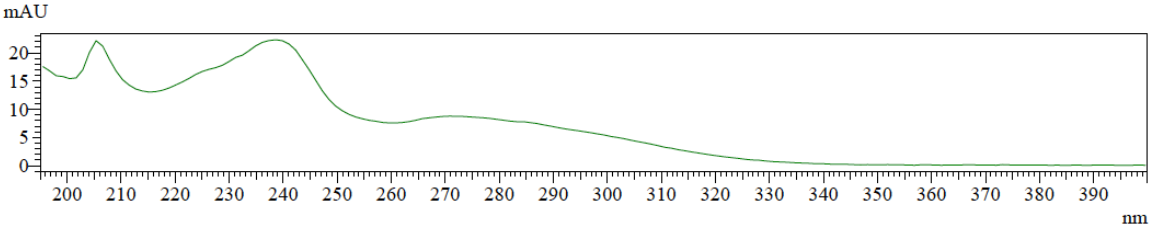
Chromatogram



UV Spectrum
Retention time = 18.522



UV Spectrum
Retention time = 20.455

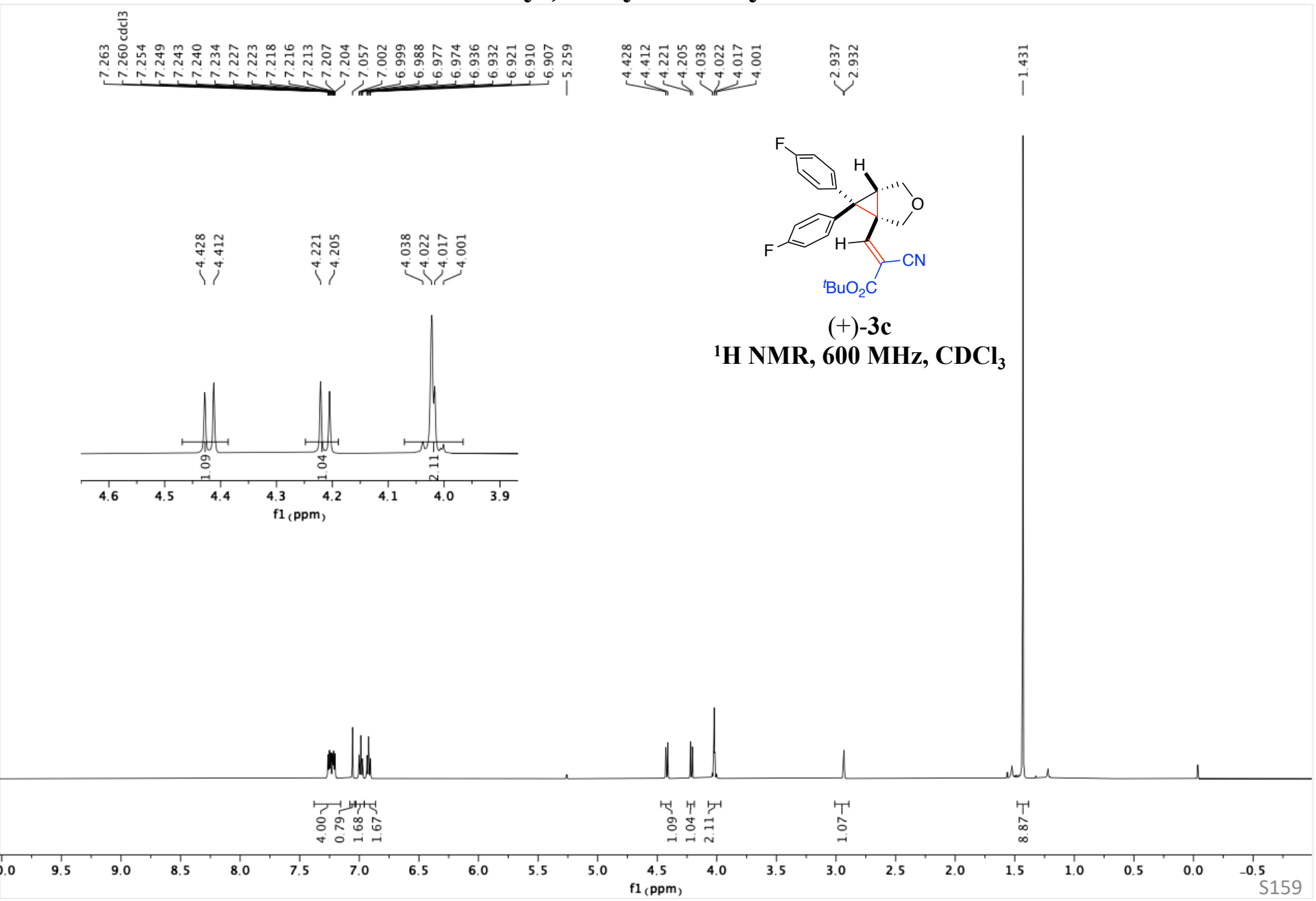


Peak Table

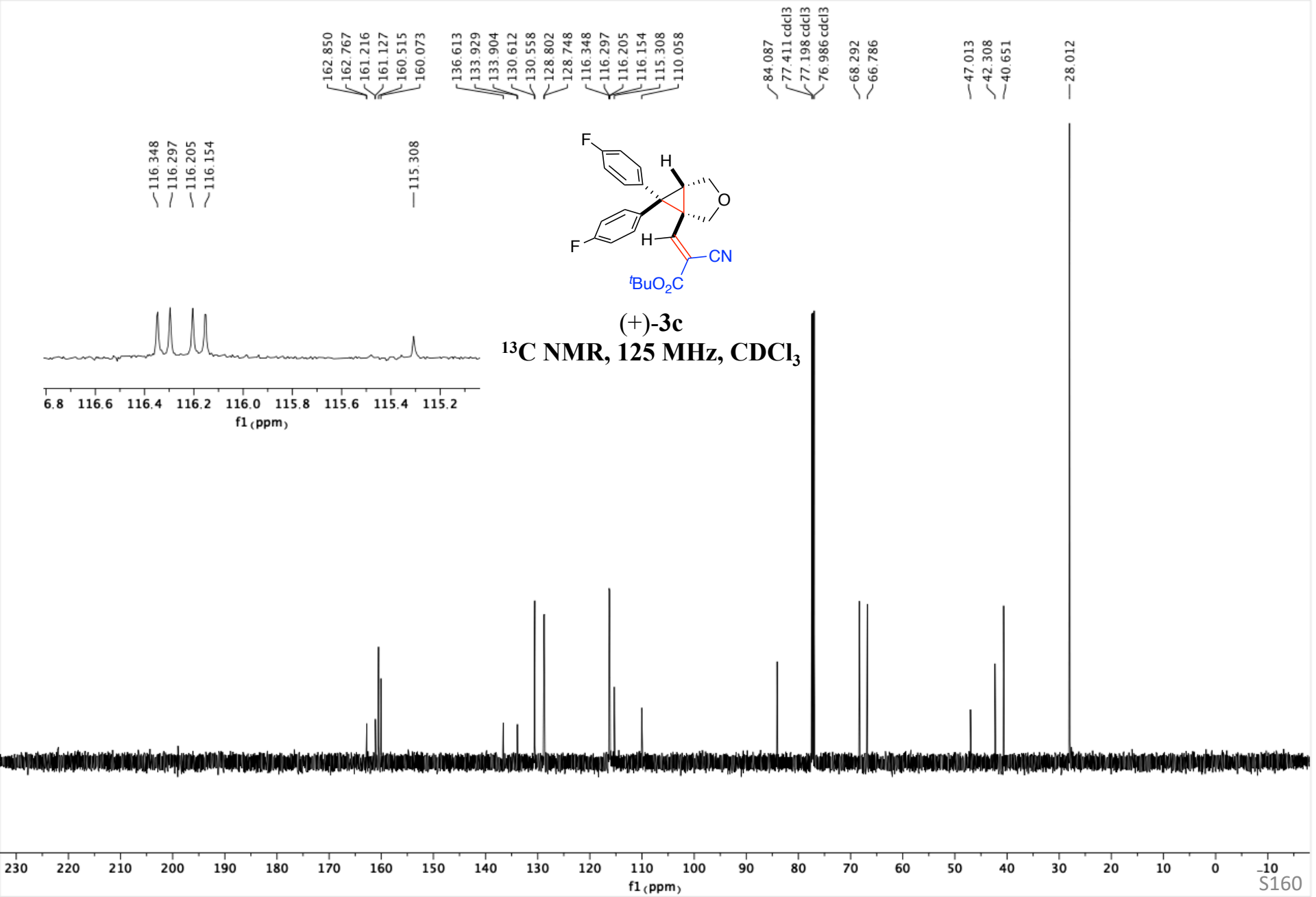
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.522	10428363	95.466
2	20.455	495240	4.534
Total		10923603	100.000

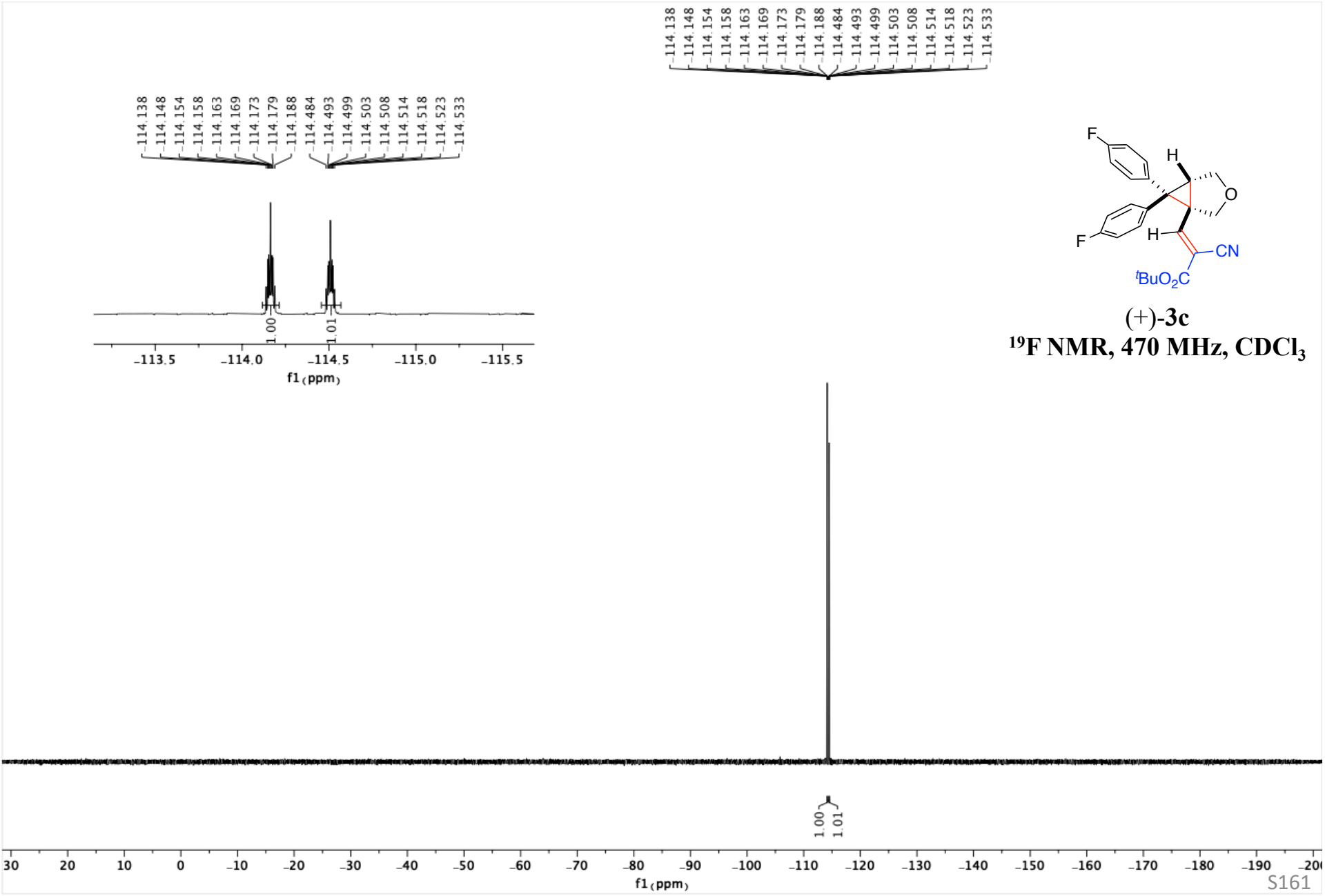
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



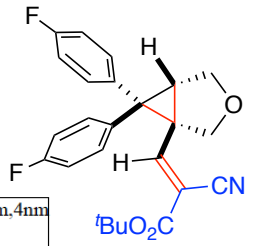
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3c**

^{19}F NMR, 470 MHz, $CDCl_3$

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

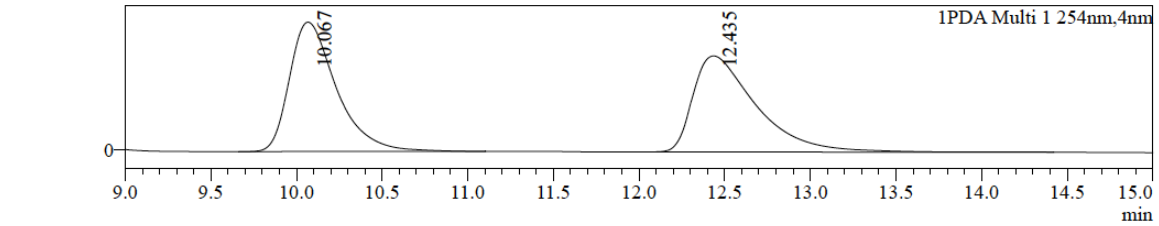


(±)-**3c**

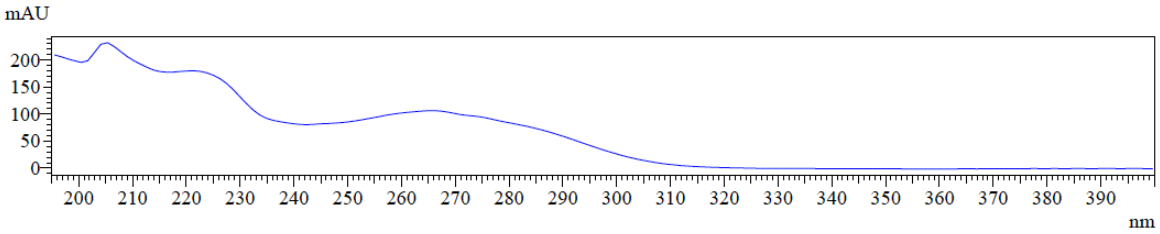
Sample Information

Sample Name	: CZZ-1284-IB-5%-1mL
Sample ID	: CZZ-1284-IB-5%-1mL
Data File	: CZZ-1284-IB-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

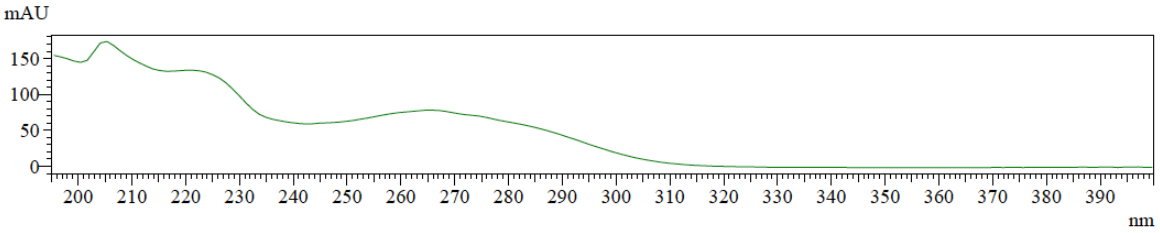
Chromatogram



UV Spectrum
Retention time = 10.067



UV Spectrum
Retention time = 12.435

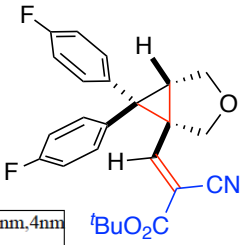


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.067	1778131	50.036
2	12.435	1775606	49.964
Total		3553737	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

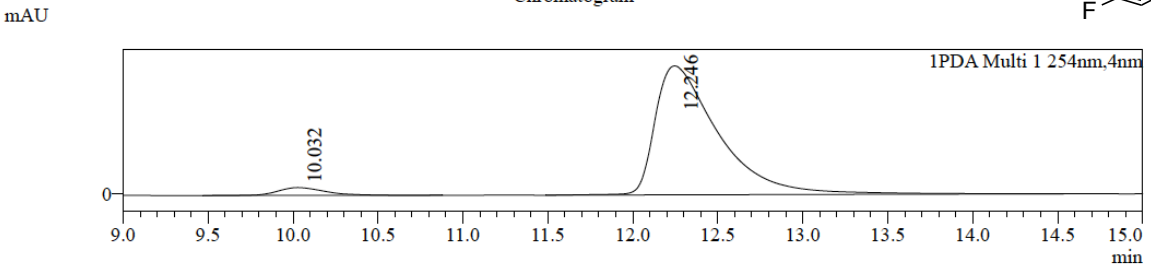


(+)-**3c**

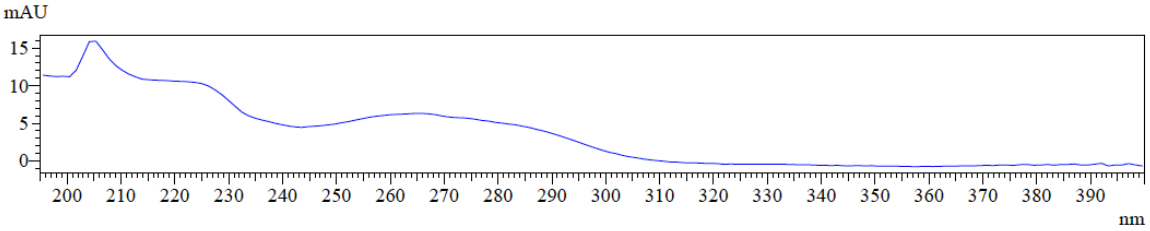
Sample Information

Sample Name	: CZZ-1285-IB-5%-1mL
Sample ID	: CZZ-1285-IB-5%-1mL
Data File	: CZZ-1285-IB-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

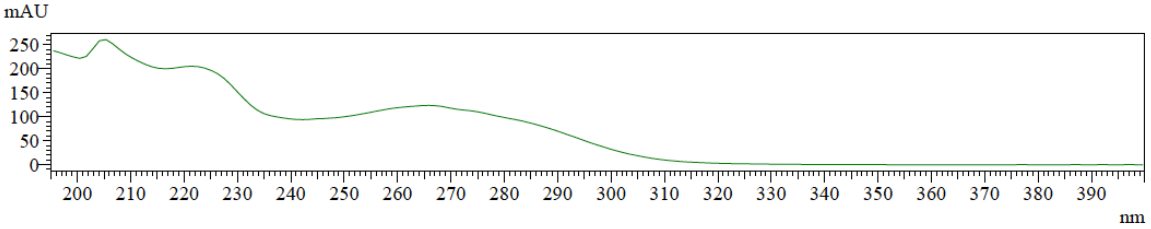
Chromatogram



UV Spectrum
Retention time = 10.032



UV Spectrum
Retention time = 12.246

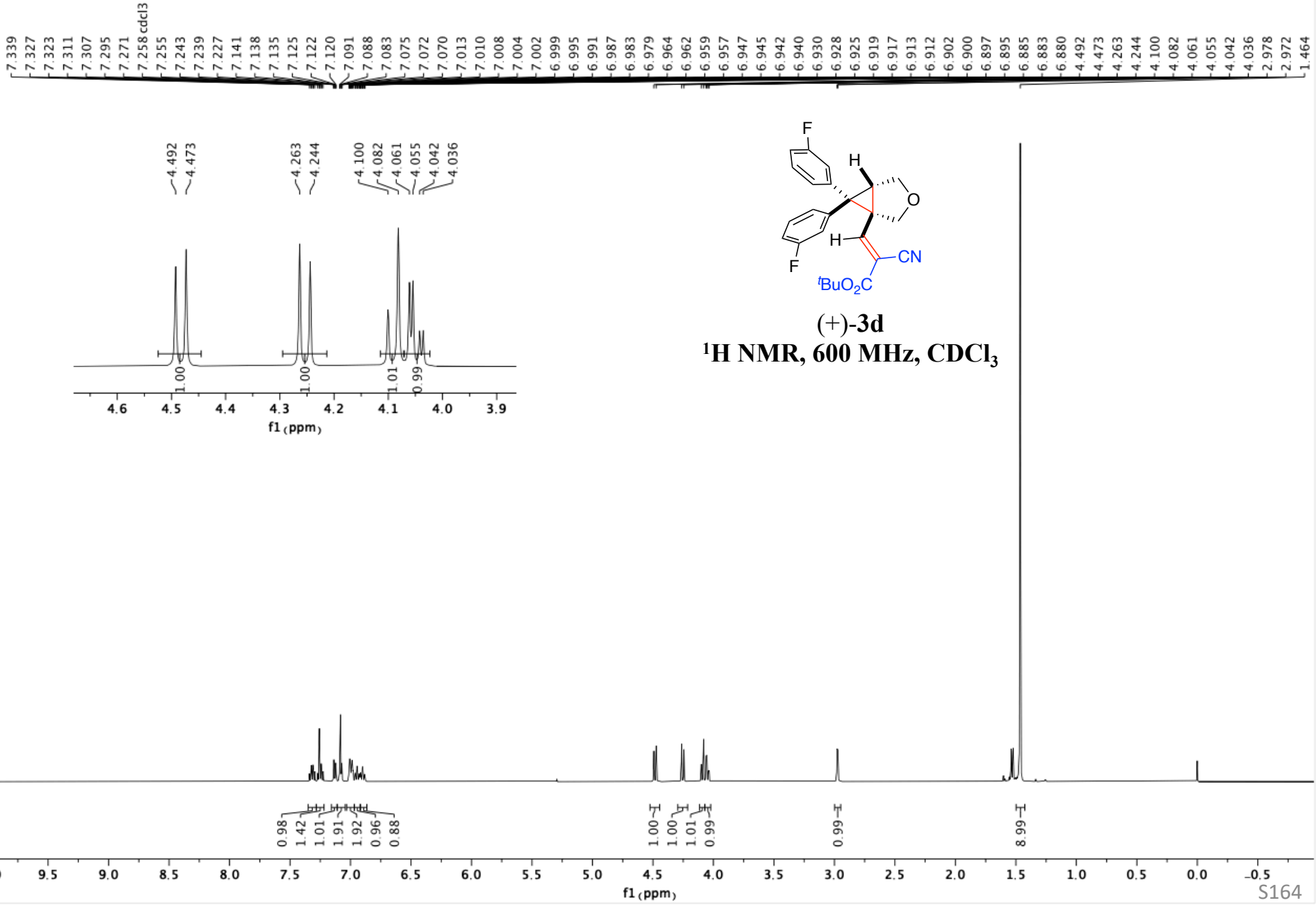


Peak Table

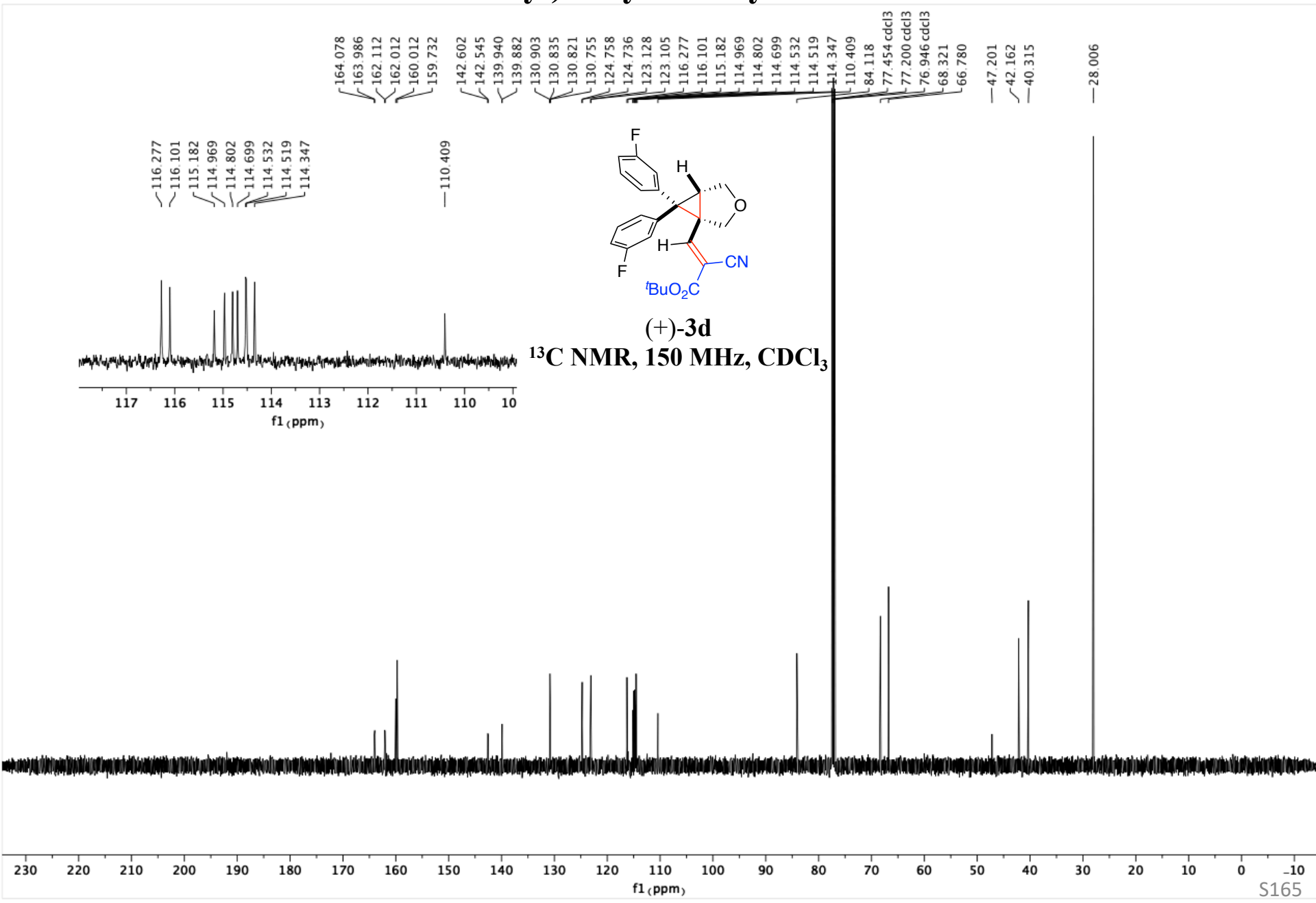
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.032	124340	4.222
2	12.246	2820943	95.778
Total		2945283	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



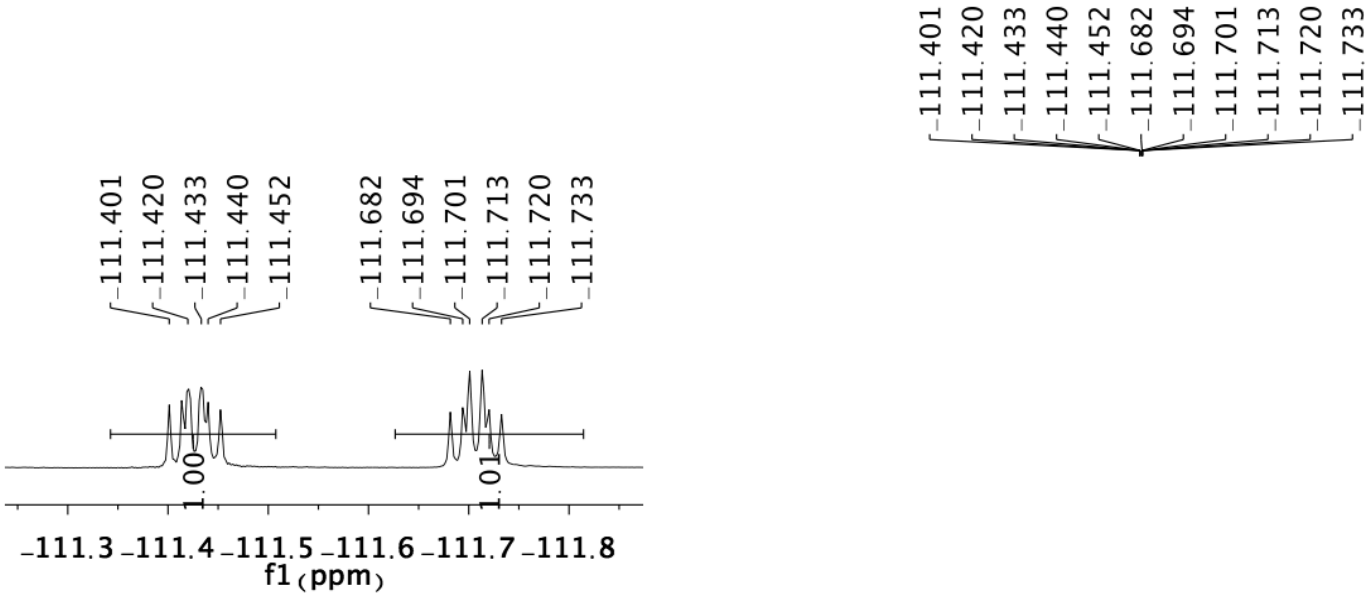
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

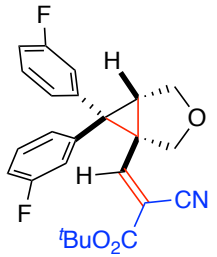


(+)-3d

^{13}C NMR, 150 MHz, $CDCl_3$

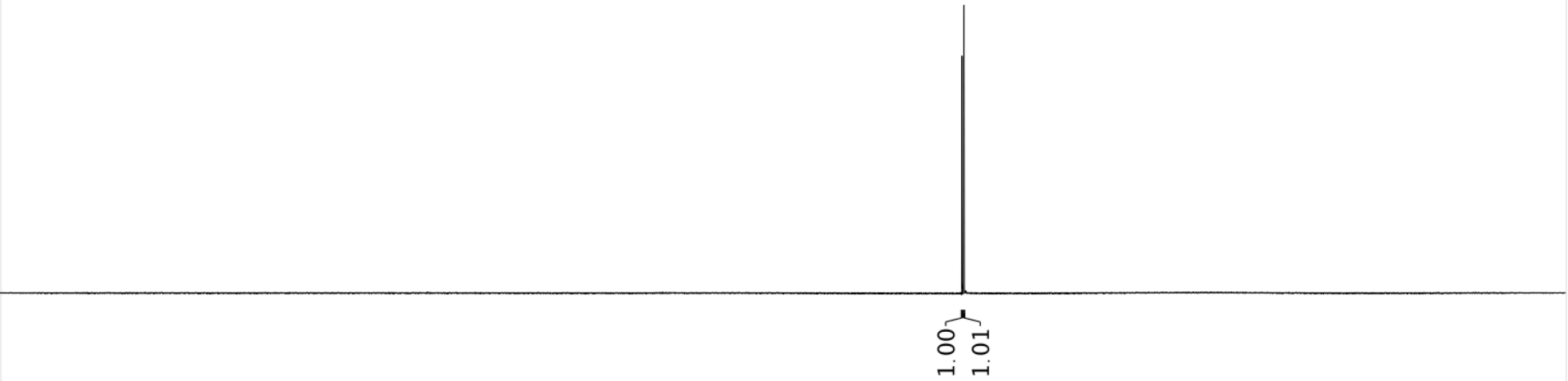
tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



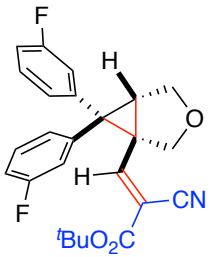


(+)-3d

^{19}F NMR, 470 MHz, $CDCl_3$



tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

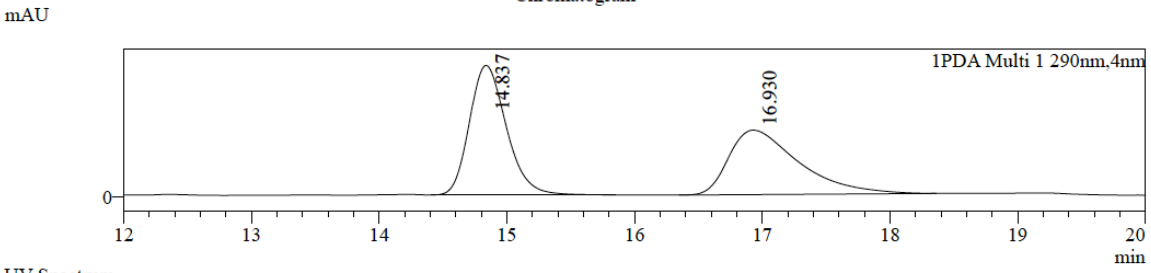


(±)-**3d**

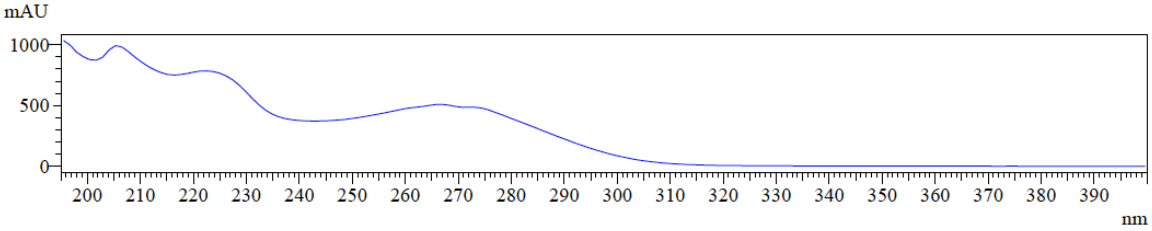
Sample Information

Sample Name	: CZZ-0781-IF-5%-1ML
Sample ID	: CZZ-0781-IF-5%-1ML
Data File	: CZZ-0781-IF-5%-1ML.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

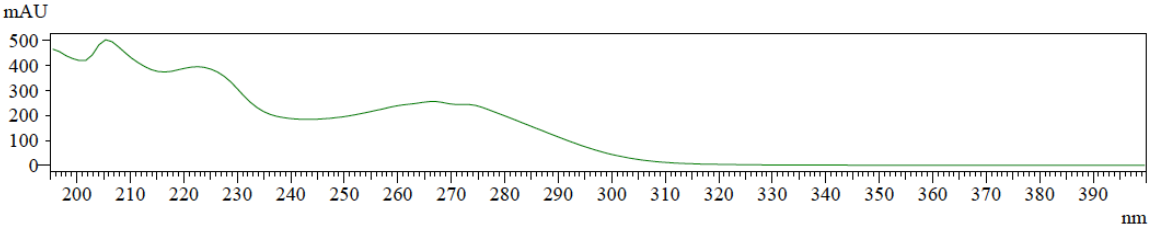
Chromatogram



UV Spectrum
Retention time = 14.837



UV Spectrum
Retention time = 16.930

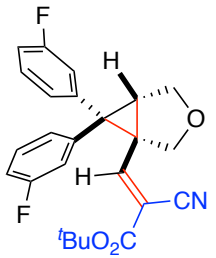


Peak Table

PDA Ch1 290nm

Peak#	Ret. Time	Area	Area%
1	14.837	4445953	51.509
2	16.930	4185397	48.491
Total		8631351	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*)-6,6-bis(3-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

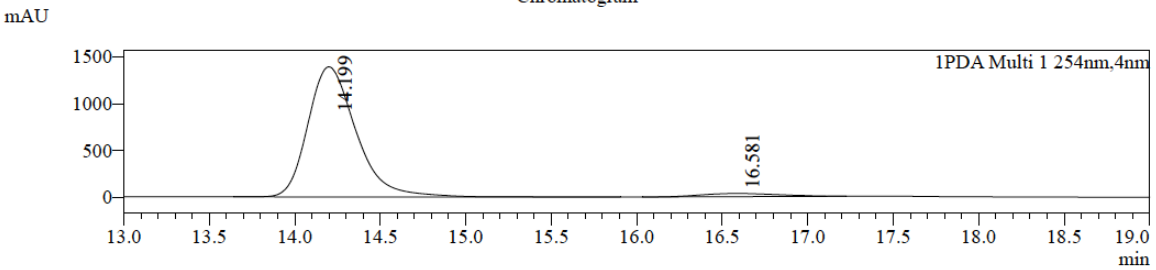


(+)-**3d**

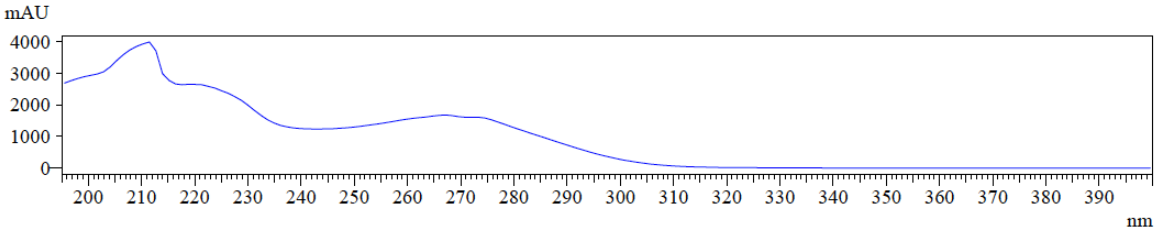
Sample Information

Sample Name	: CZZ-1061-if-5%1.0mL
Sample ID	: CZZ-1061-if-5%1.0mL
Data File	: CZZ-1061-if-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

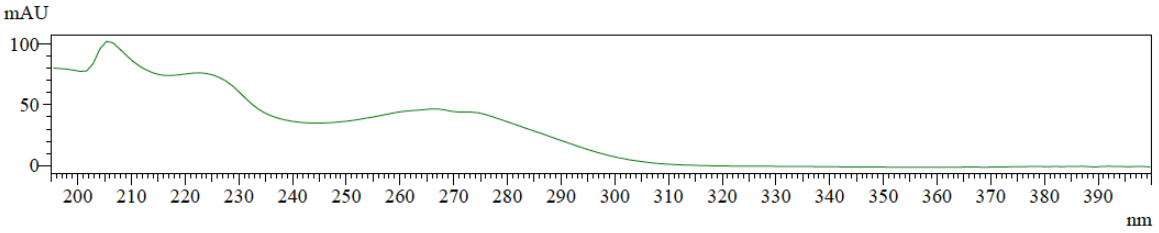
Chromatogram



UV Spectrum
Retention time = 14.199



UV Spectrum
Retention time = 16.581

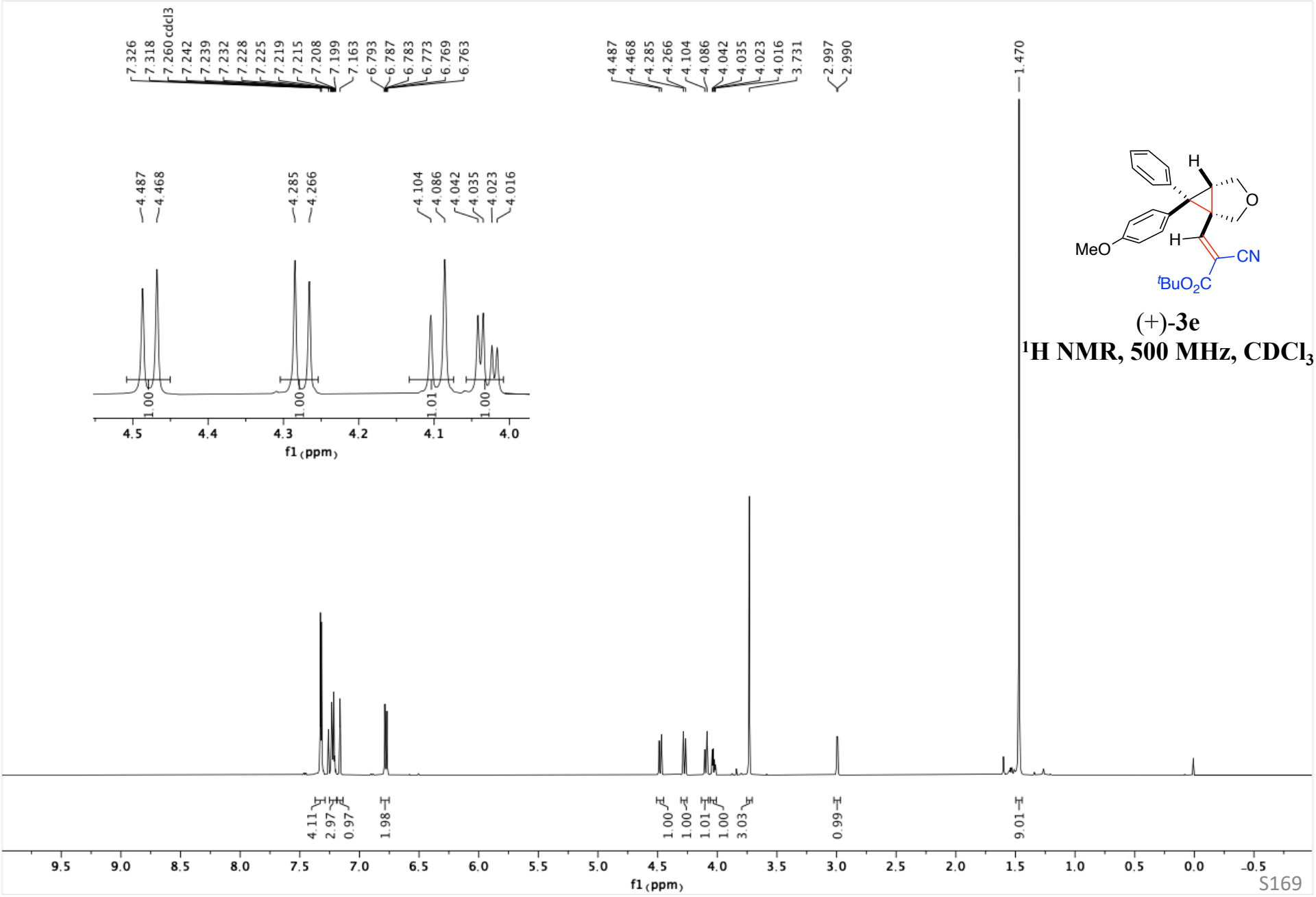


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.199	27302424	96.136
2	16.581	1097464	3.864
Total		28399887	100.000

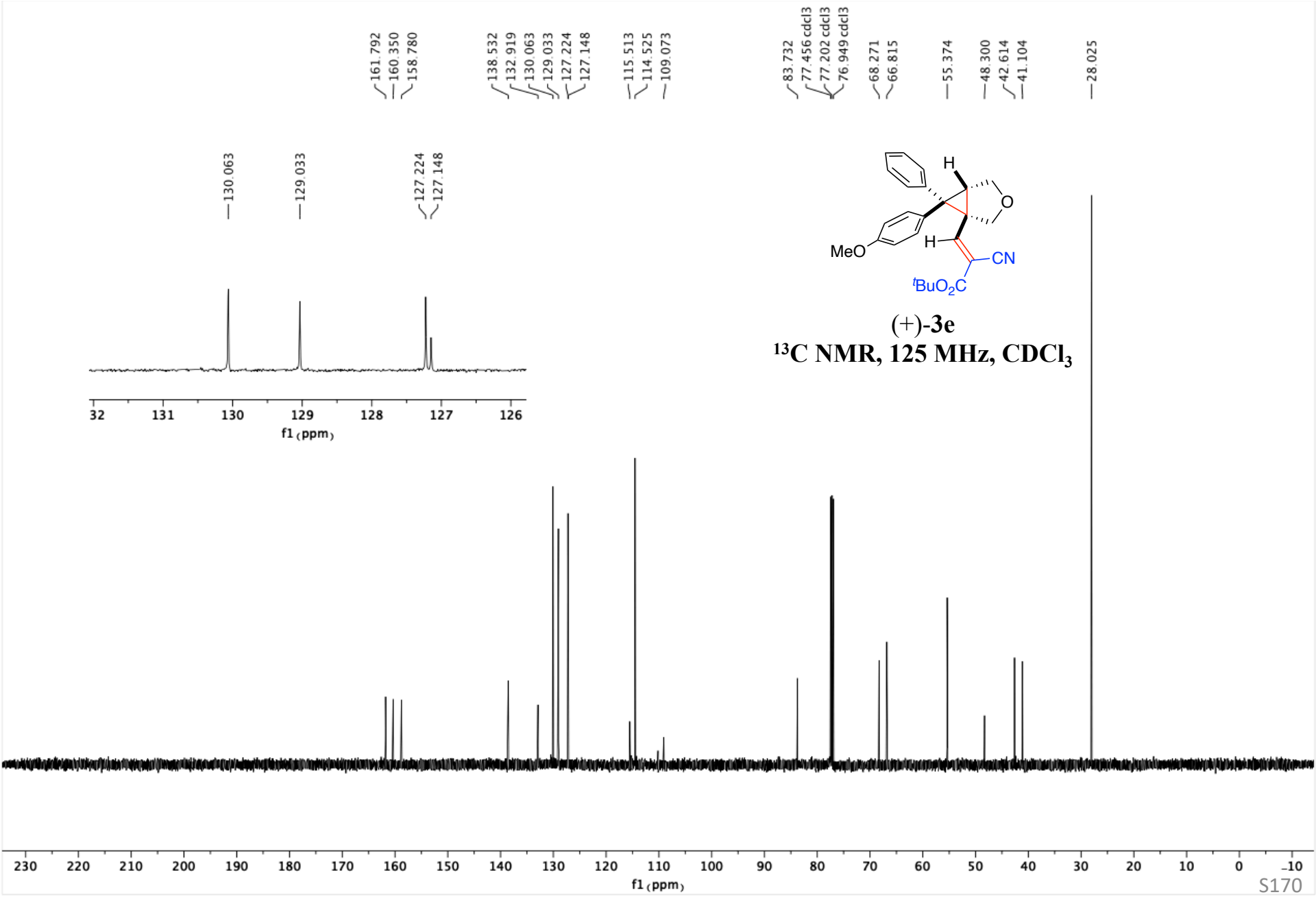
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3e**

^{1}H NMR, 500 MHz, $CDCl_3$

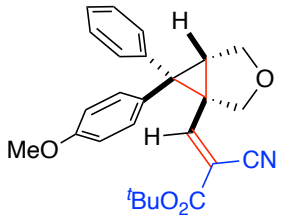
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-3e

^{13}C NMR, 125 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

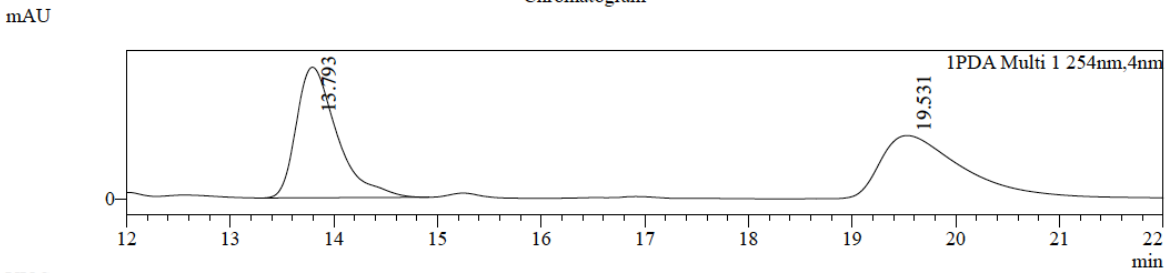


(±)-**3e**

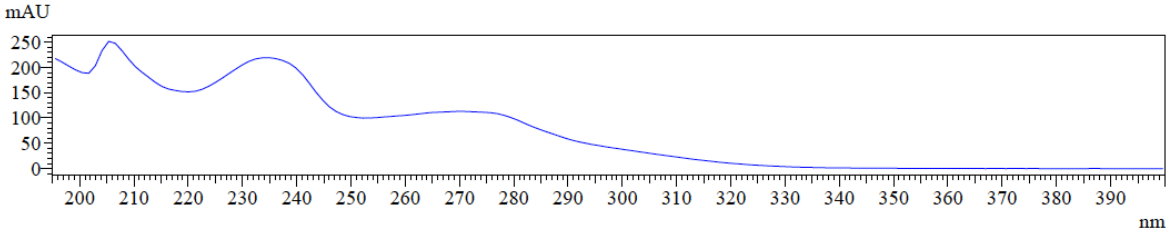
Sample Information

Sample Name	: CZZ-1336-ID-10%-1mL
Sample ID	: CZZ-1336-ID-10%-1mL
Data File	: CZZ-1336-ID-10%-1mL.lcd
Method File	: CZZ-10%-1.0ml.lcm

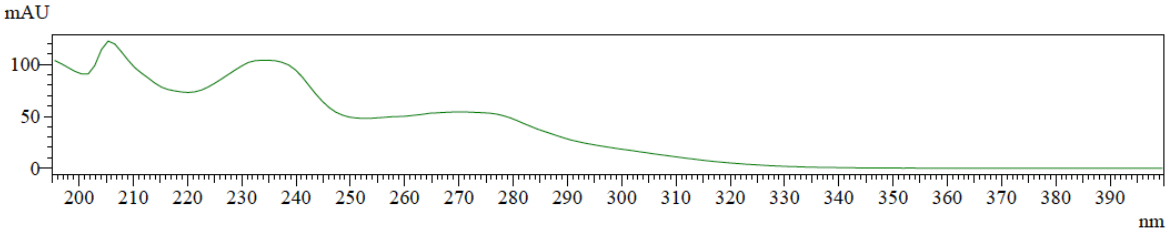
Chromatogram



UV Spectrum
Retention time = 13.793



UV Spectrum
Retention time = 19.531

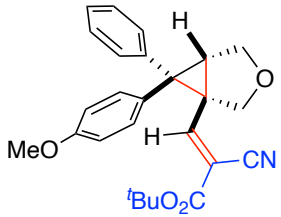


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.793	2735230	50.301
2	19.531	2702526	49.699
Total		5437757	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

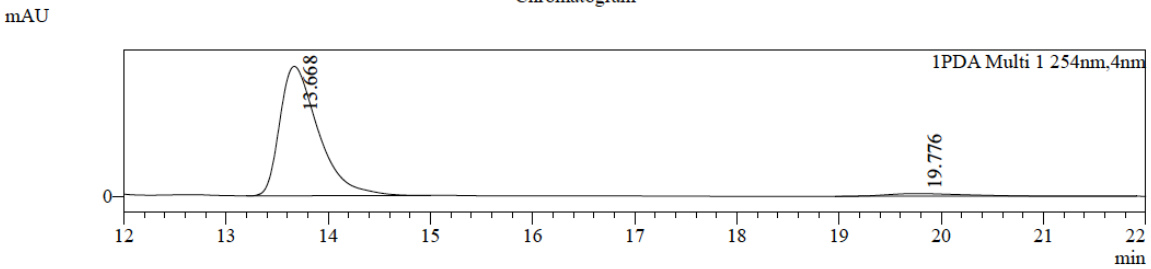


(+)-**3e**

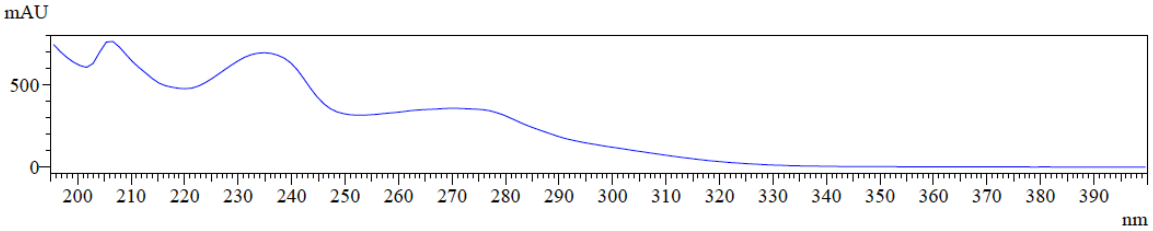
Sample Information

Sample Name	: CZZ-1337-ID-10%-1mL
Sample ID	: CZZ-1337-ID-10%-1mL
Data File	: CZZ-1337-ID-10%-1mL.lcd
Method File	: CZZ-10%-1.0ml.lcm

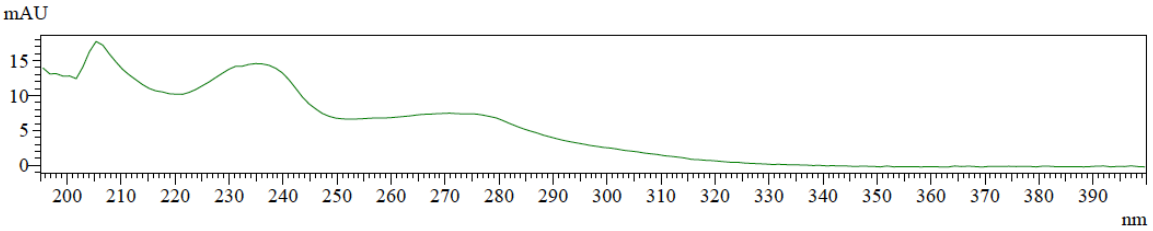
Chromatogram



UV Spectrum
Retention time = 13.668



UV Spectrum
Retention time = 19.776

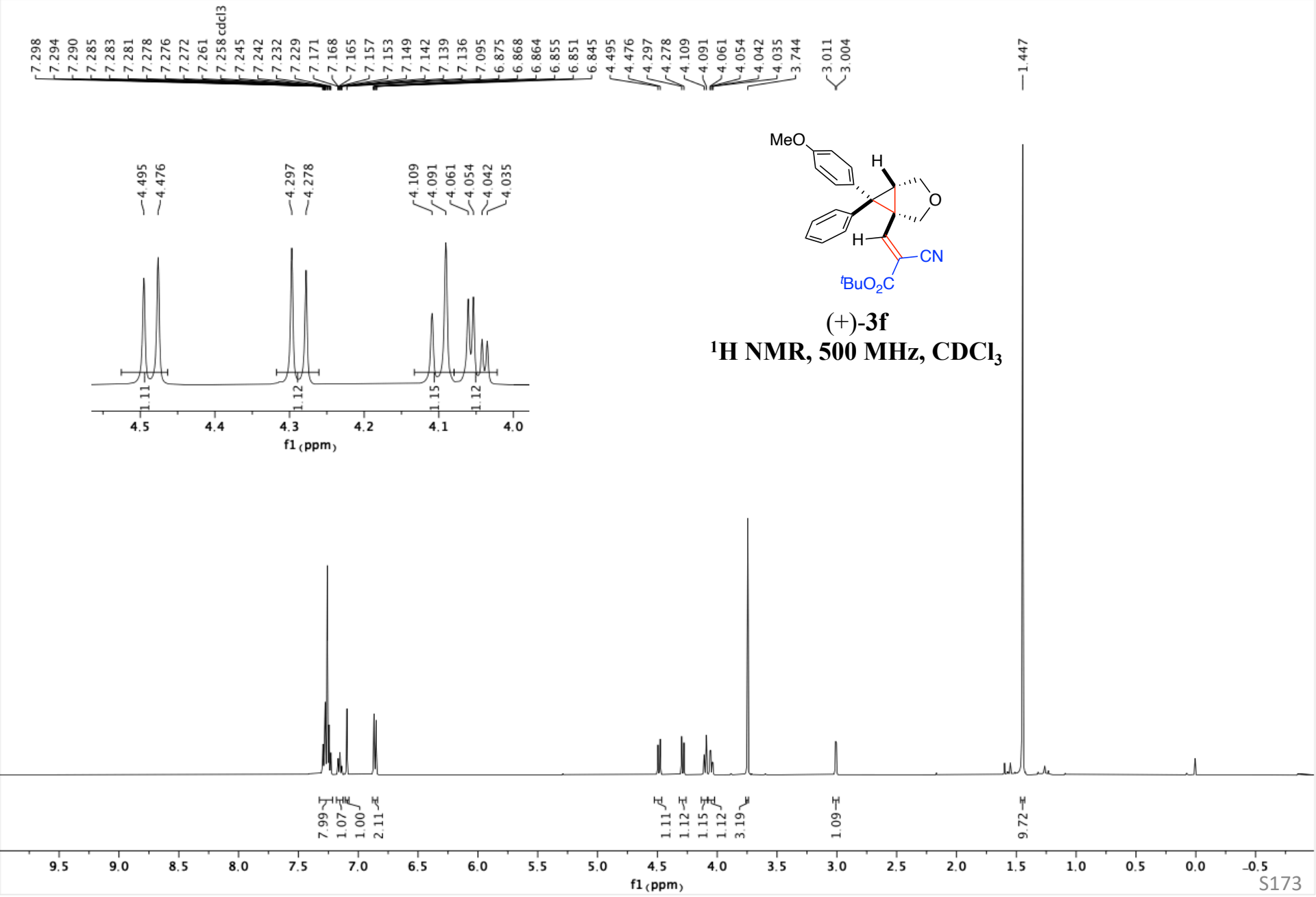


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.668	8362253	95.789
2	19.776	367658	4.211
Total		8729911	100.000

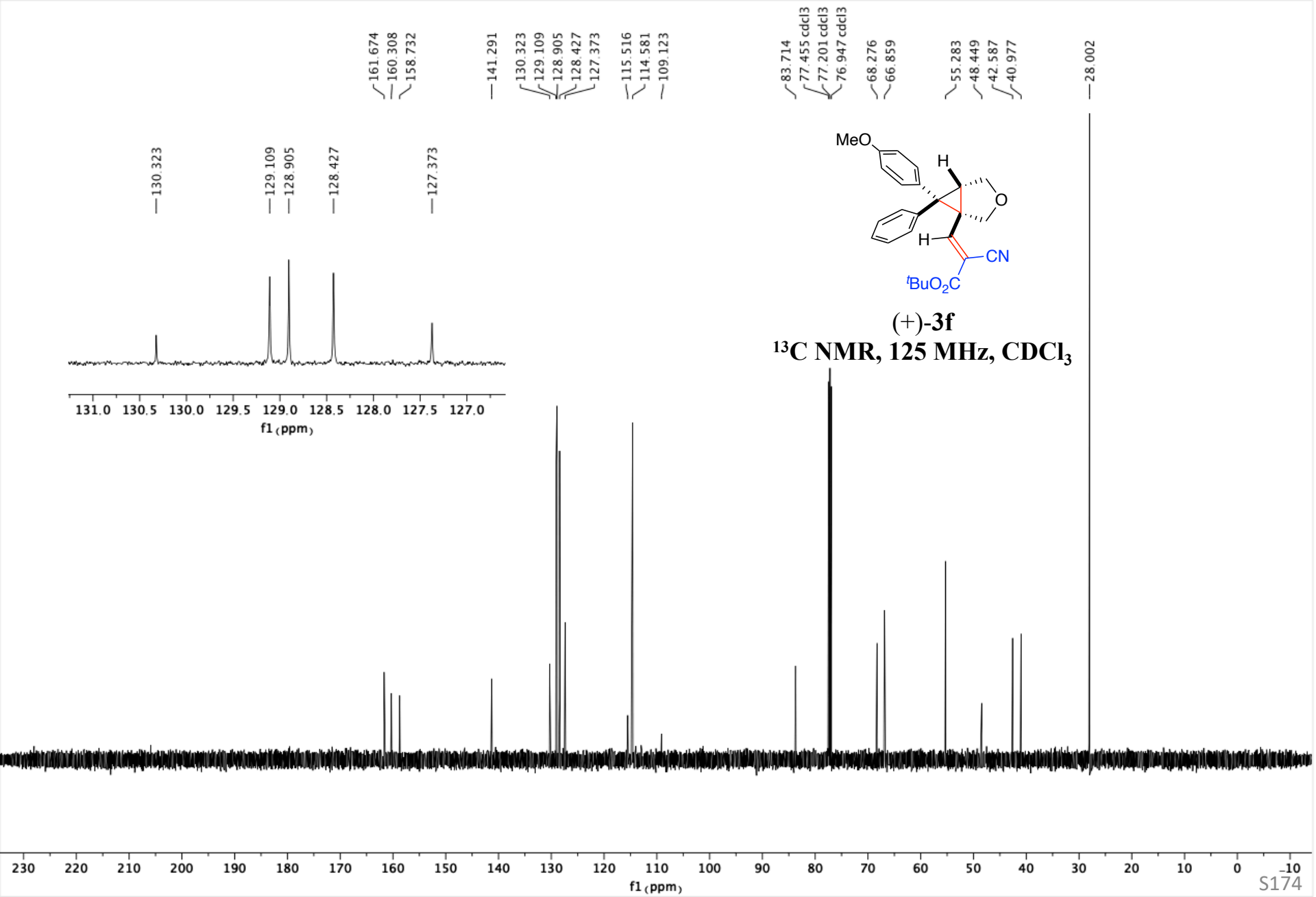
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



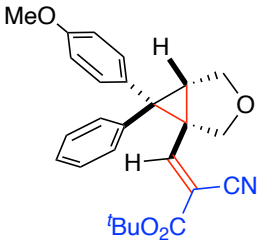
(+)-**3f**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

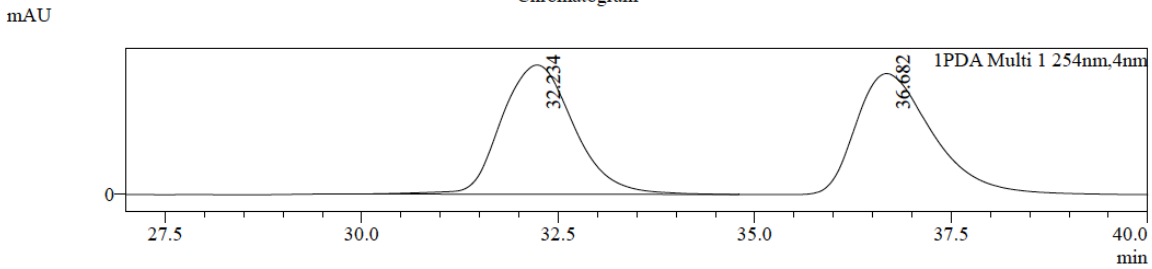


(±)-**3f**

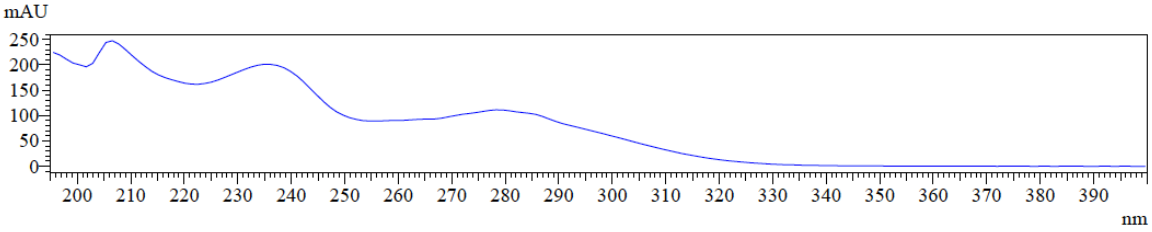
Sample Information

Sample Name	: CZZ-1357-5%-iB-1mL
Sample ID	: CZZ-1357-5%-iB-1mL
Data File	: CZZ-1357-5%-iB-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

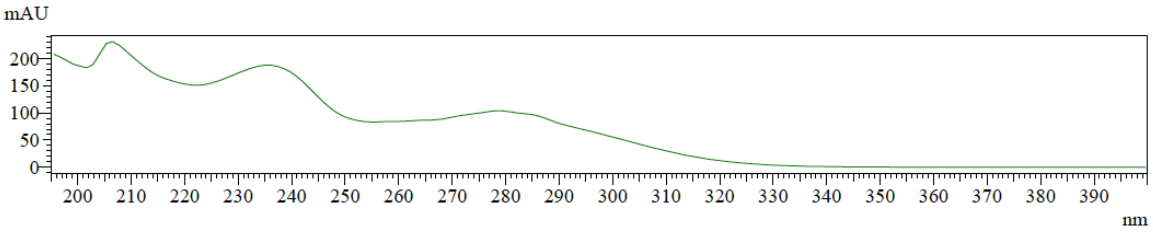
Chromatogram



UV Spectrum
Retention time = 32.234



UV Spectrum
Retention time = 36.682

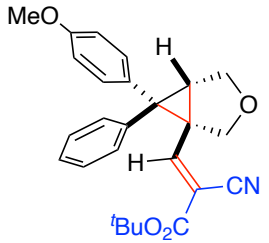


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	32.234	5842617	50.211
2	36.682	5793626	49.789
Total		11636243	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(4-methoxyphenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

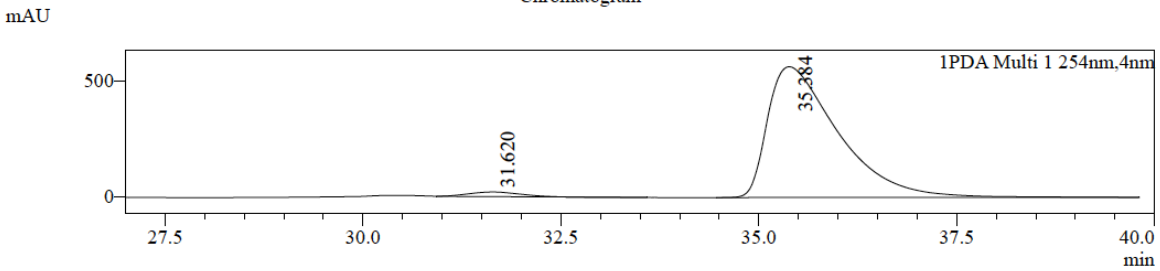


(+)-**3f**

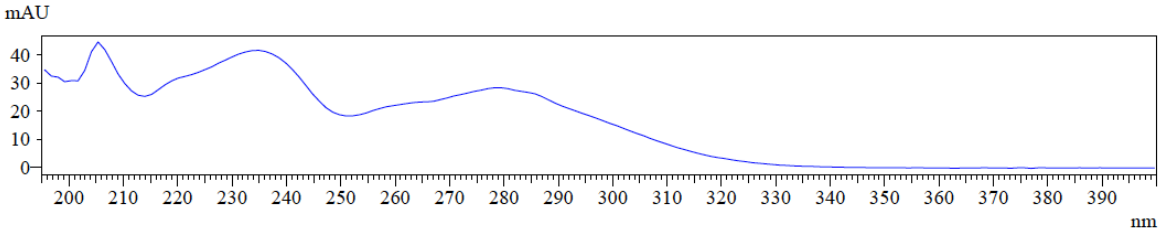
Sample Information

Sample Name	: CZZ-1358-5%-iB-1mL
Sample ID	: CZZ-1358-5%-iB-1mL
Data File	: CZZ-1358-5%-iB-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

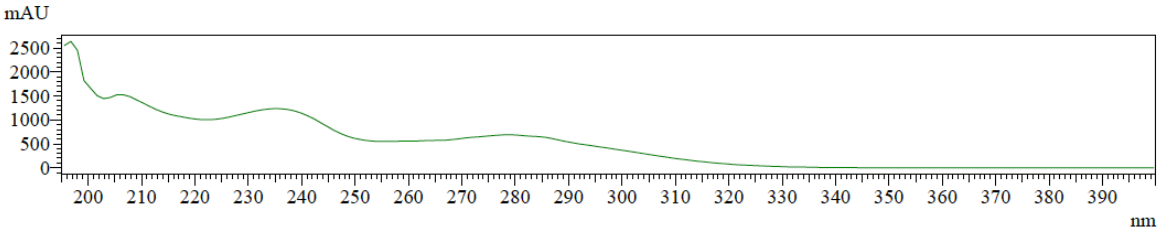
Chromatogram



UV Spectrum
Retention time = 31.620



UV Spectrum
Retention time = 35.384

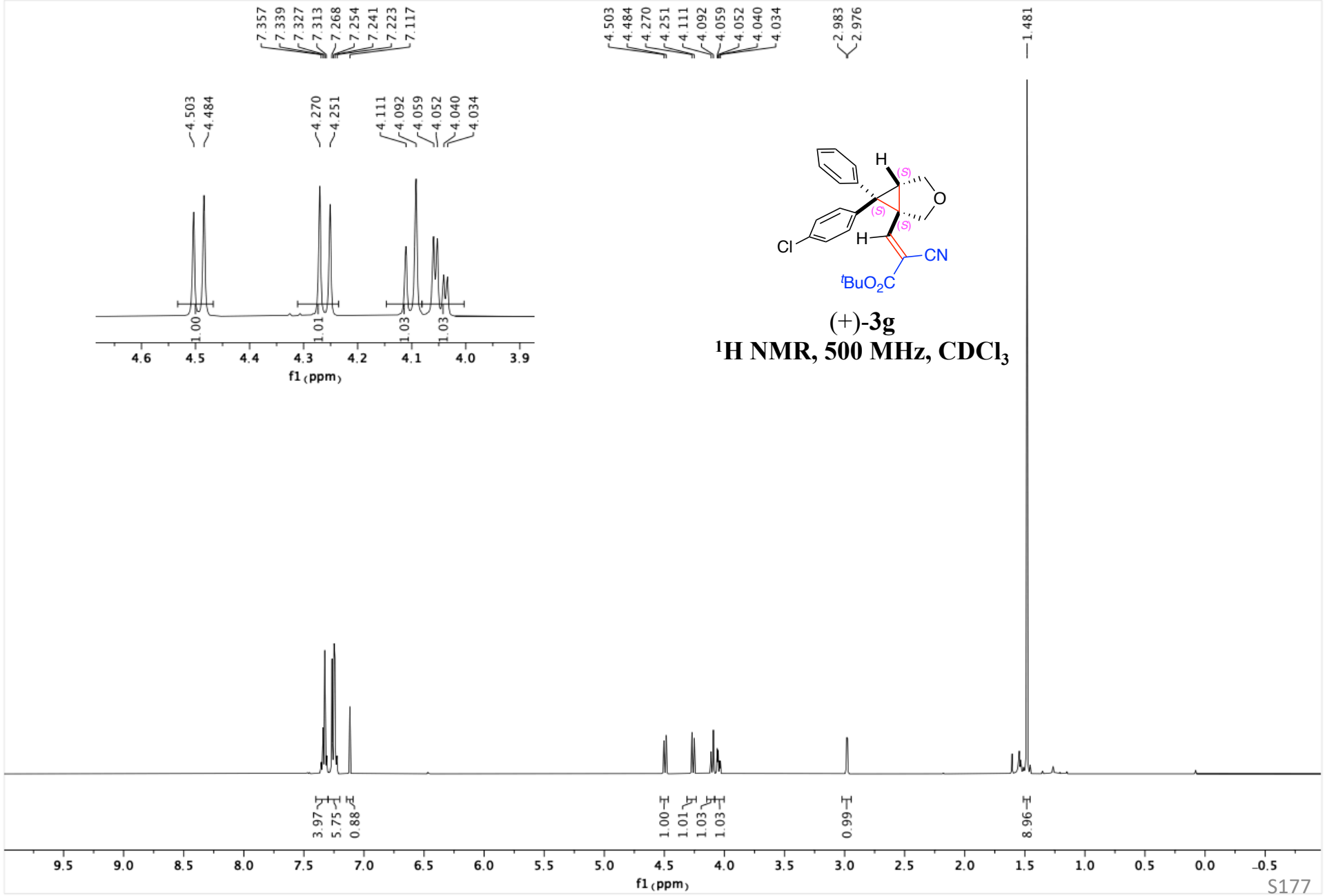


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	31.620	869560	2.428
2	35.384	34944944	97.572
Total		35814504	100.000

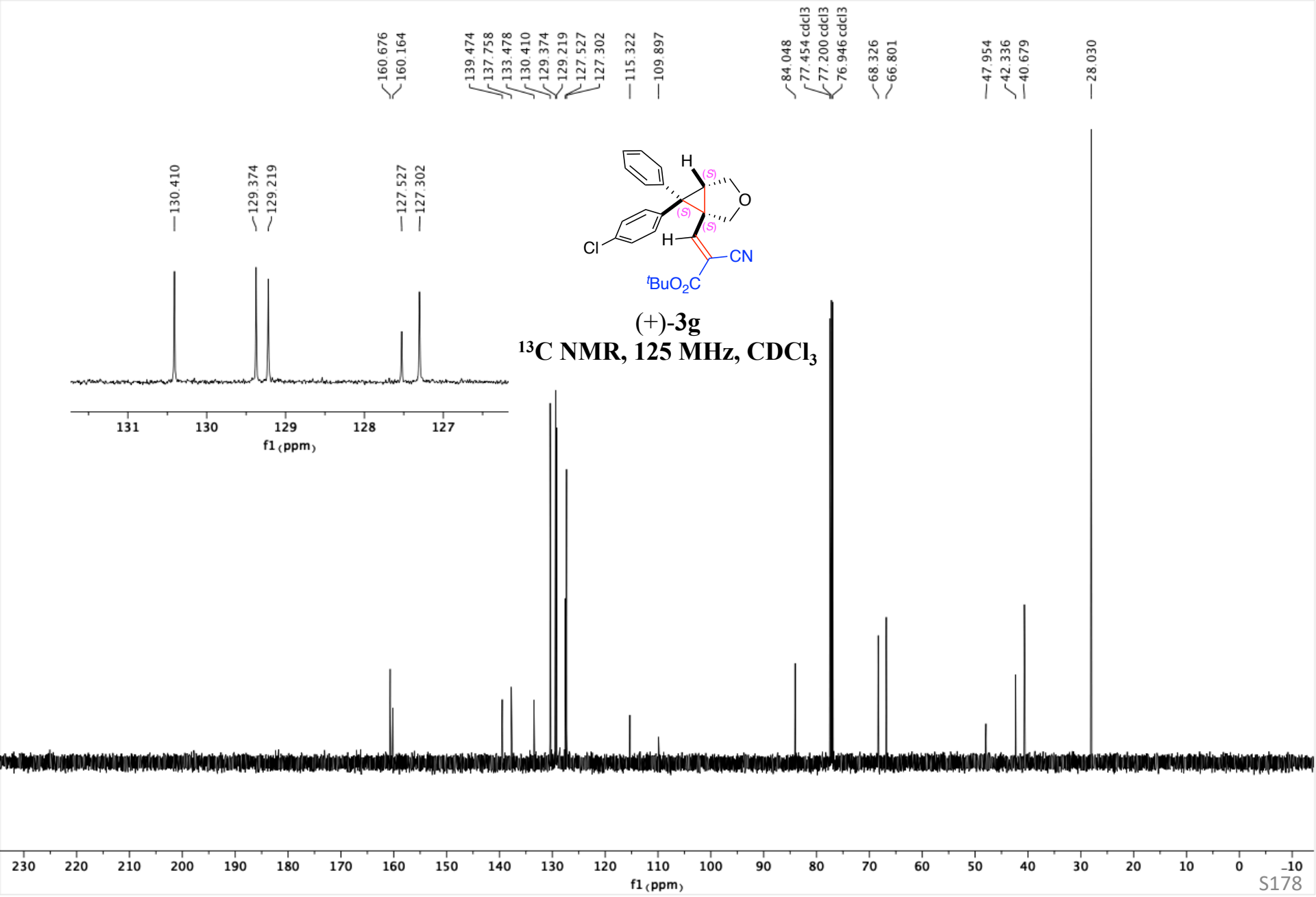
tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3g**

^{1}H NMR, 500 MHz, $CDCl_3$

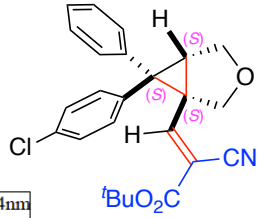
tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

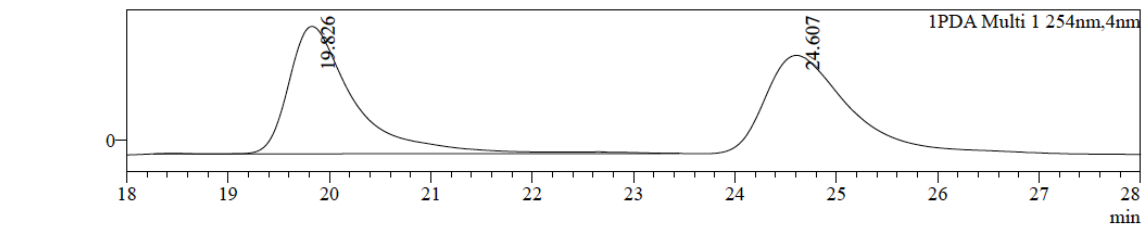
Sample Information

Sample Name	: CZZ-921-ID-5%1.0mL
Sample ID	: CZZ-921-ID-5%1.0mL
Data File	: CZZ-921-ID-5%1.0mL001.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

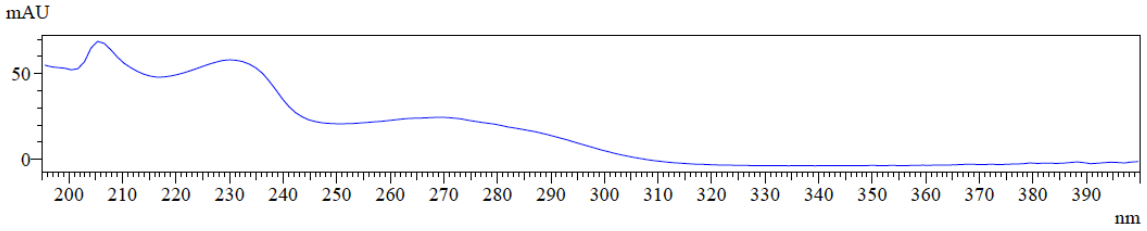


(±)-**3g**

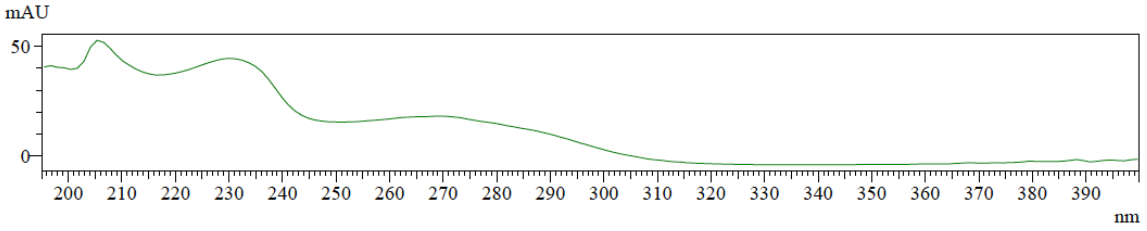
Chromatogram



UV Spectrum
Retention time = 19.826



UV Spectrum
Retention time = 24.607

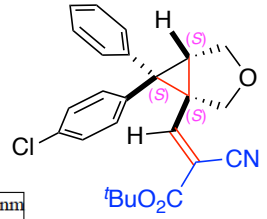


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.826	1060070	49.958
2	24.607	1061859	50.042
Total		2121929	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

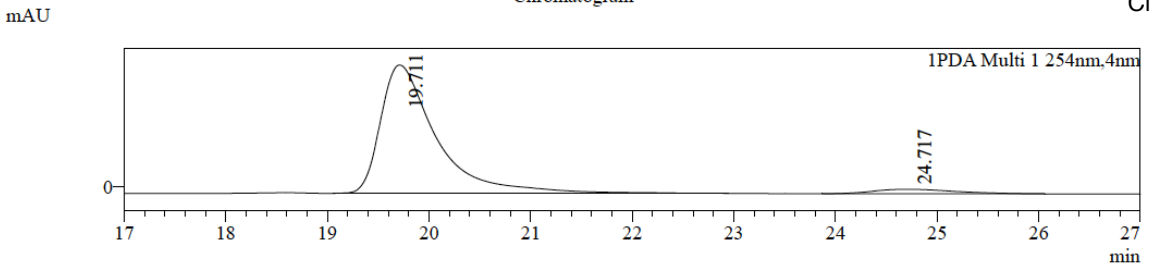


(+)-**3g**

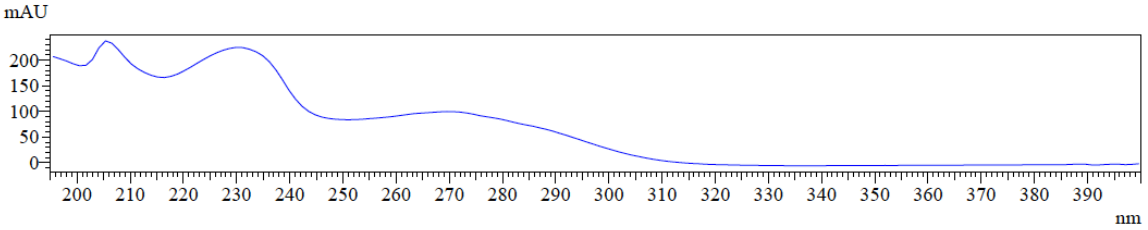
Sample Information

Sample Name	: CZZ-1049-id-5%1.0mL
Sample ID	: CZZ-1049-id-5%1.0mL
Data File	: CZZ-1049-id-5%1.0mL001.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

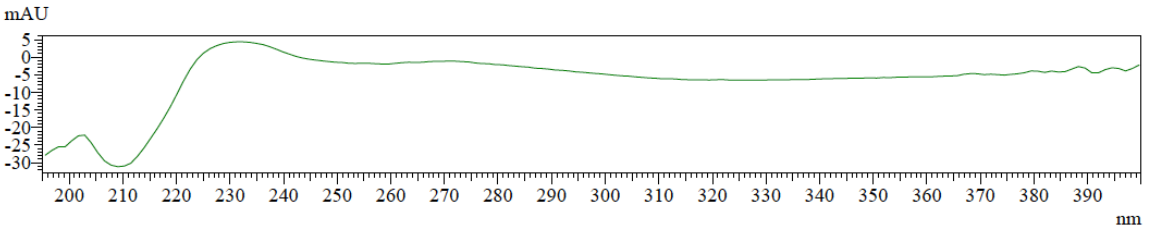
Chromatogram



UV Spectrum
Retention time = 19.711



UV Spectrum
Retention time = 24.717

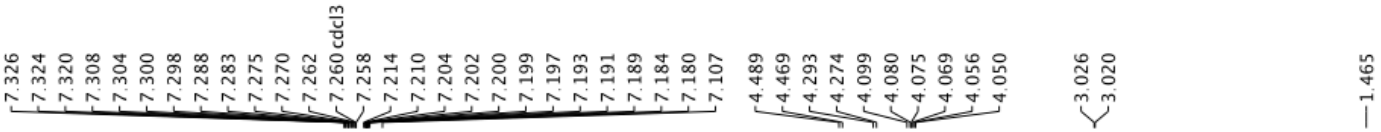


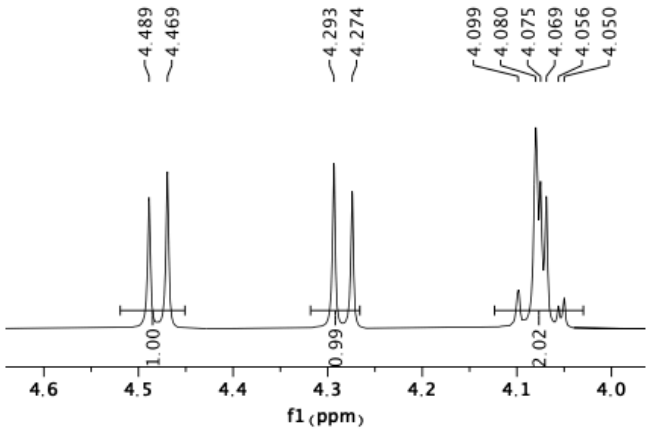
Peak Table

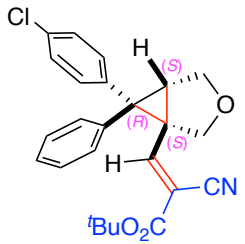
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.711	3436593	95.222
2	24.717	172426	4.778
Total		3609019	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

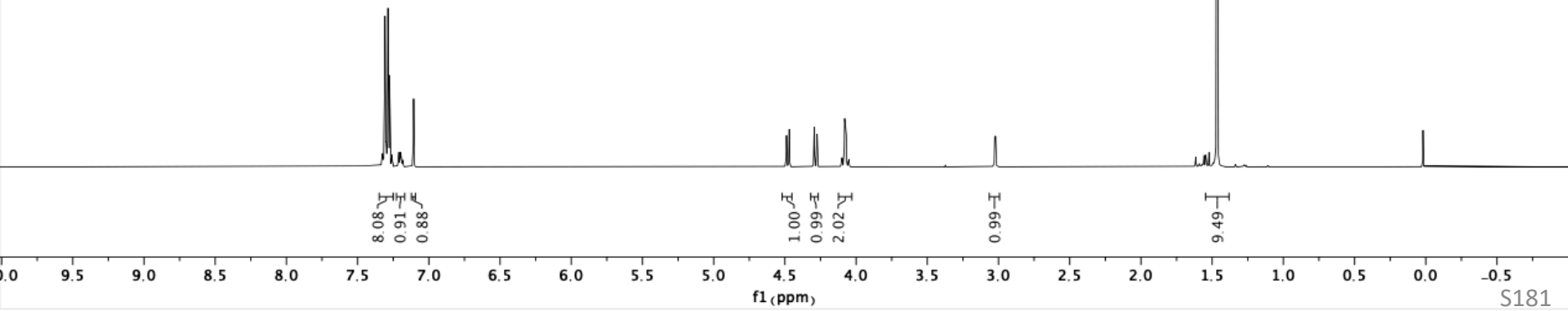




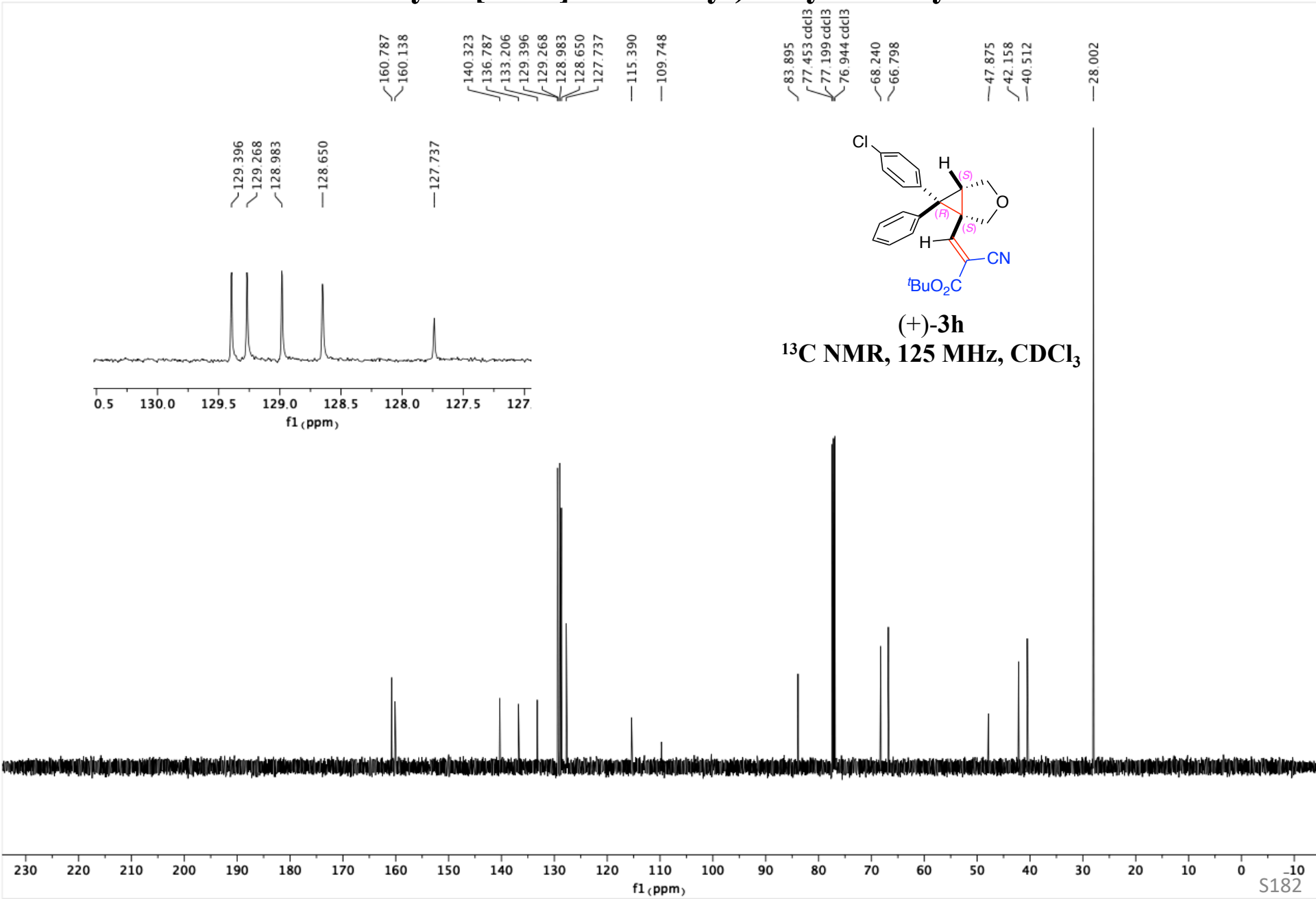


(+)-**3h**

^{1}H NMR, 500 MHz, $CDCl_3$



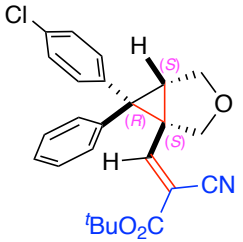
tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

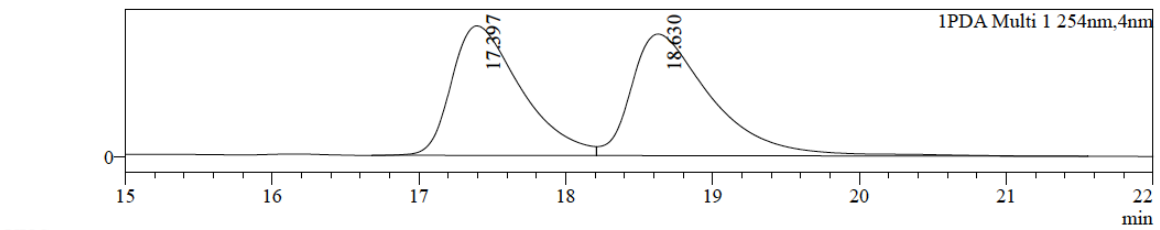
Sample Information

Sample Name	: CZZ-1095-IE-5%-1mL
Sample ID	: CZZ-1095-IE-5%-1mL
Data File	: CZZ-1095-IE-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

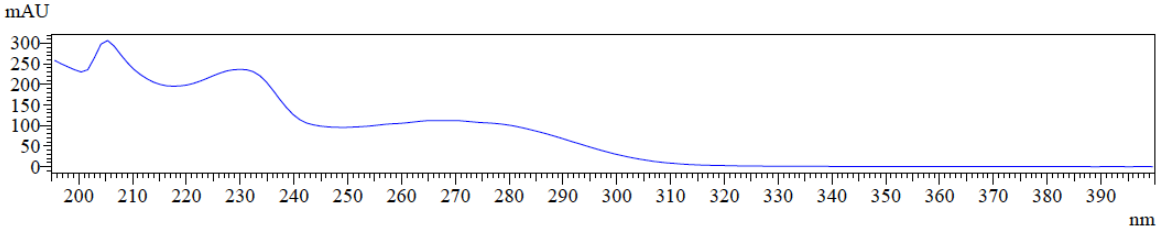


(±)-**3h**

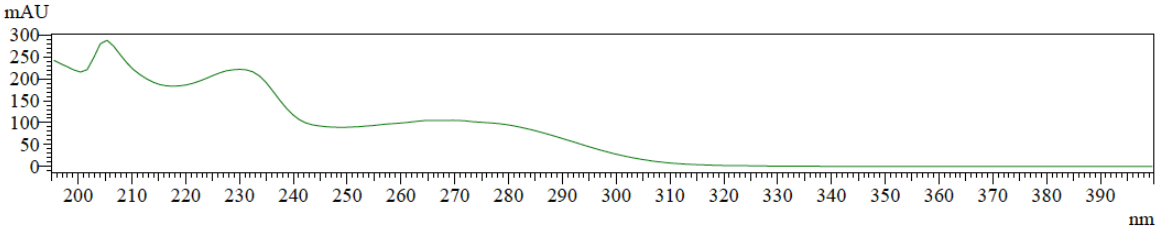
Chromatogram



UV Spectrum
Retention time = 17.397



UV Spectrum
Retention time = 18.630

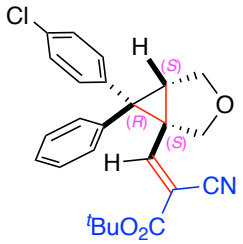


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.397	3232573	48.052
2	18.630	3494605	51.948
Total		6727178	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

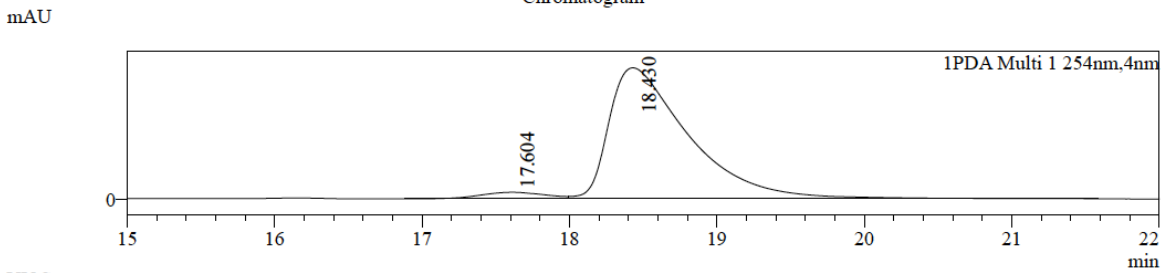


(+)-**3h**

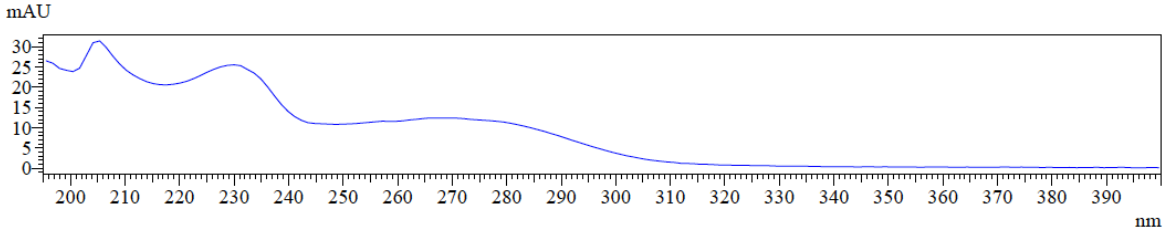
Sample Information

Sample Name	: CZZ-1386-IE-5%-1mL
Sample ID	: CZZ-1386-IE-5%-1mL
Data File	: CZZ-1386-IE-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

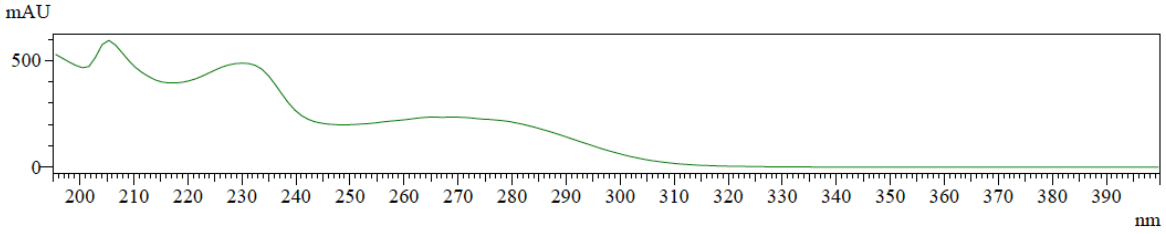
Chromatogram



UV Spectrum
Retention time = 17.604



UV Spectrum
Retention time = 18.430

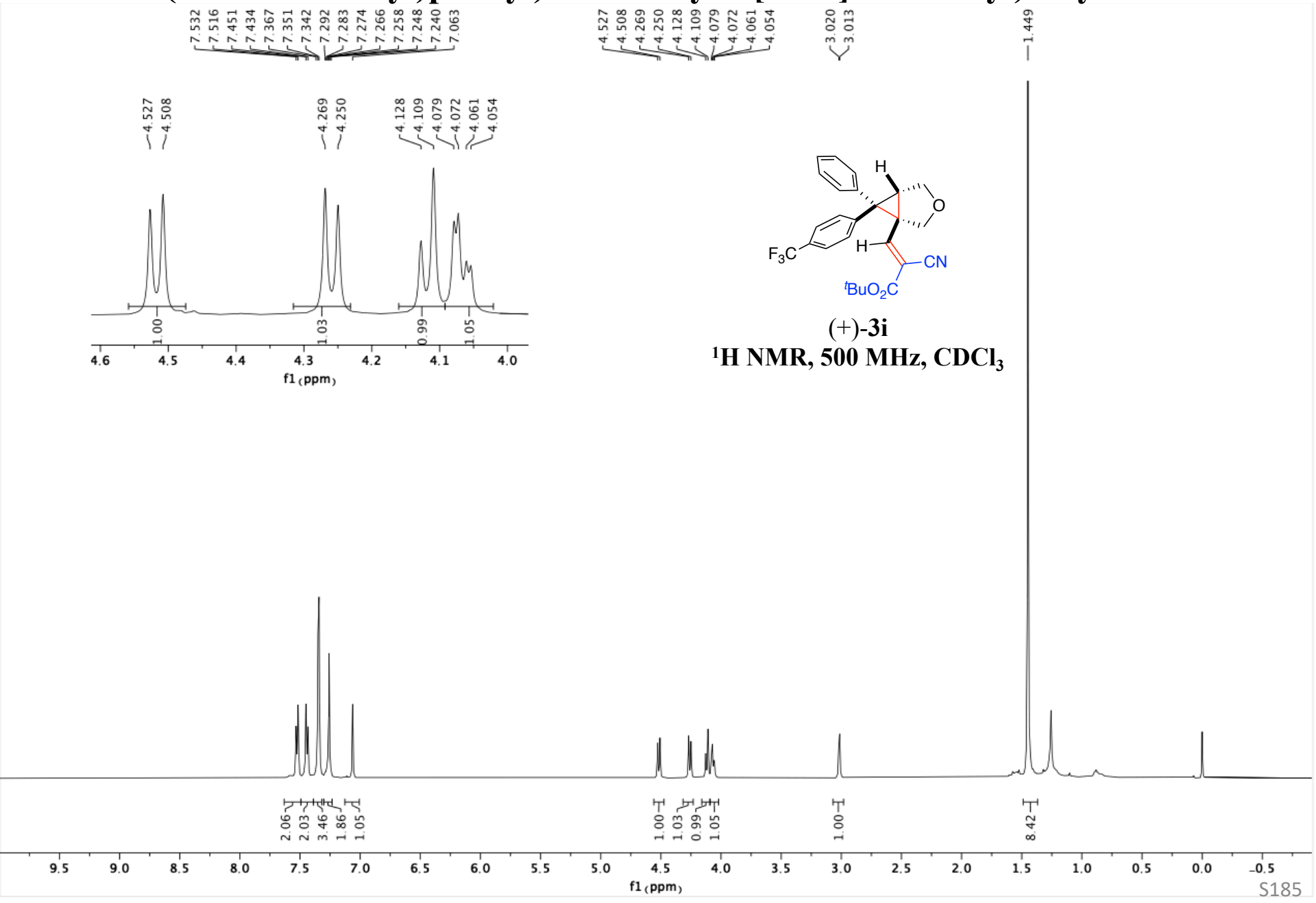


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.604	319907	3.957
2	18.430	7765471	96.043
Total		8085378	100.000

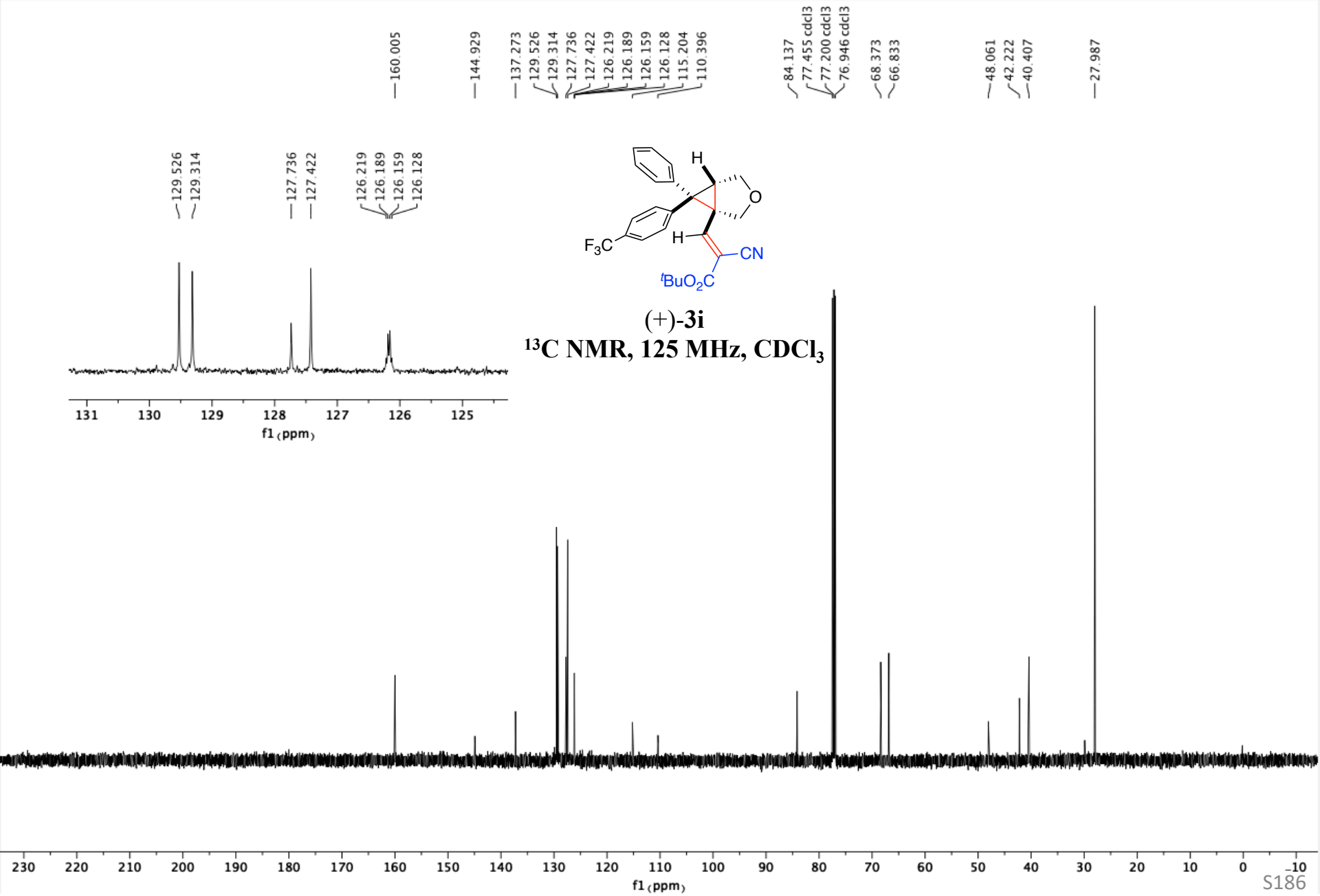
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



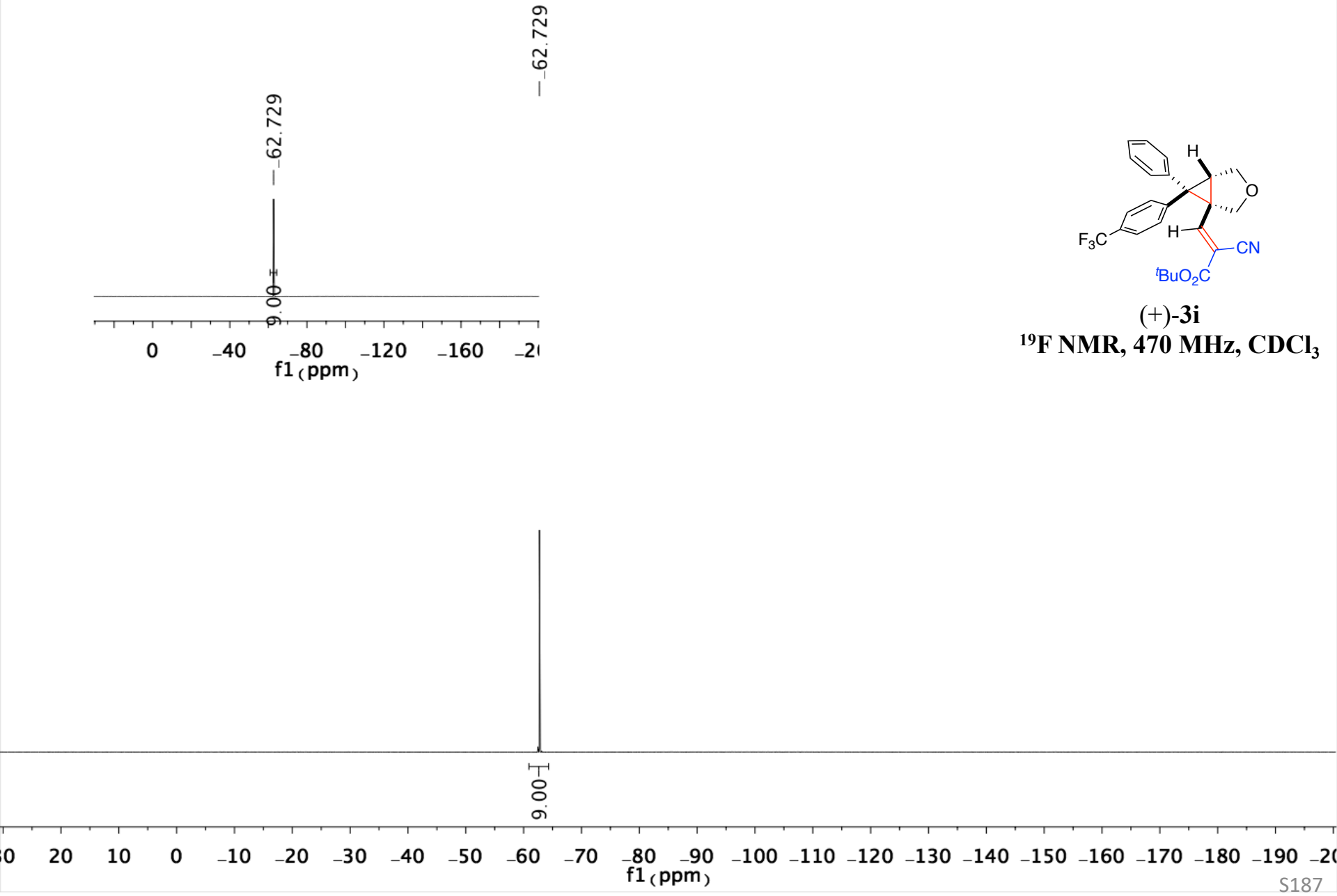
(+)-**3i**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



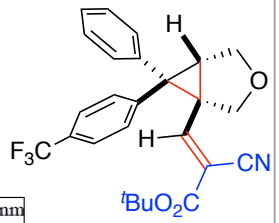
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3i**

^{19}F NMR, 470 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate (±)-3i

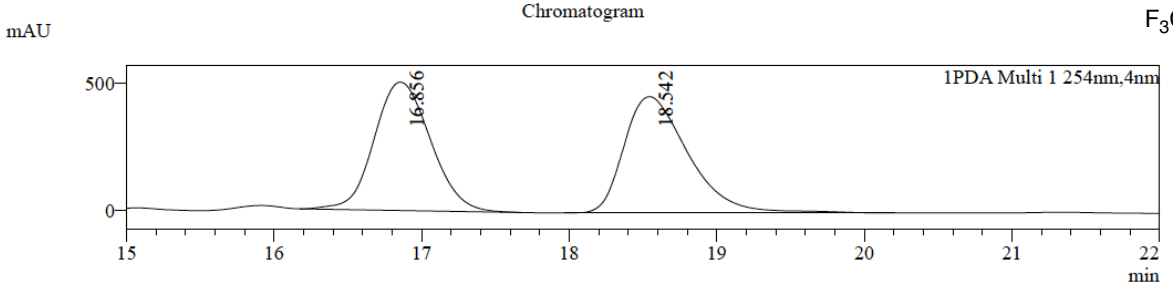


(±)-**3i**

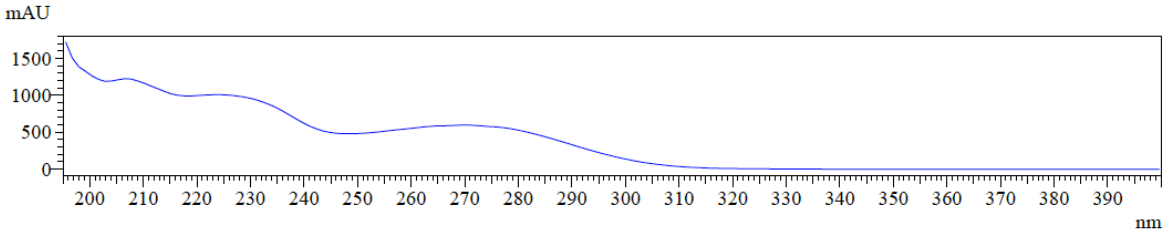
Sample Information

Sample Name	: CZZ-1067-ie-5%1.0mL
Sample ID	: CZZ-1067-ie-5%1.0mL
Data File	: CZZ-1067-ie-5%1.0mL001.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

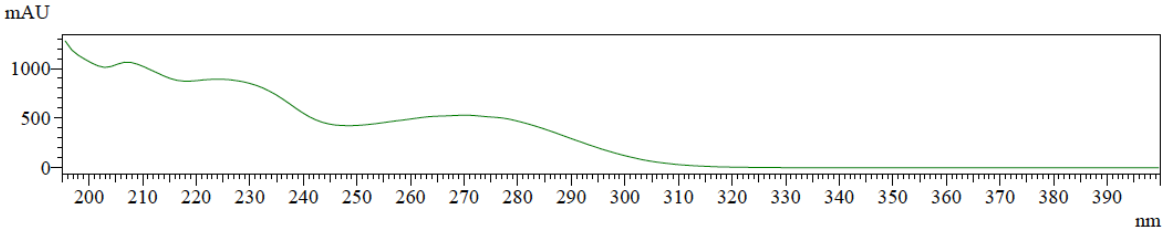
Chromatogram



UV Spectrum
Retention time = 16.856



UV Spectrum
Retention time = 18.542

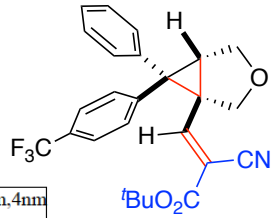


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.856	13435273	49.280
2	18.542	13827656	50.720
Total		27262929	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

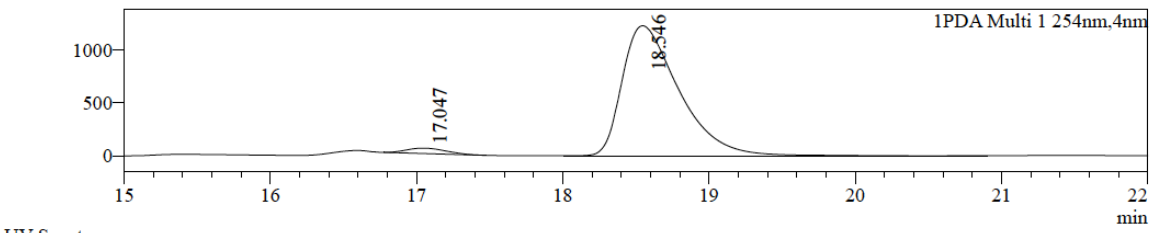


(+)-**3i**

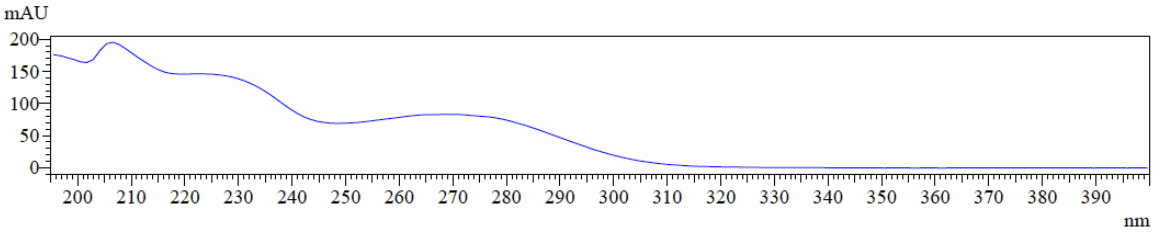
Sample Information

Sample Name	: CZZ-1068-ie-5%1.0mL
Sample ID	: CZZ-1068-ie-5%1.0mL
Data File	: CZZ-1068-ie-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

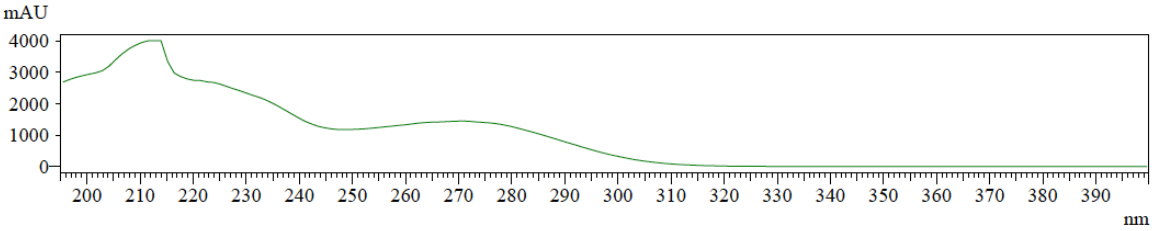
Chromatogram



UV Spectrum
Retention time = 17.047



UV Spectrum
Retention time = 18.546

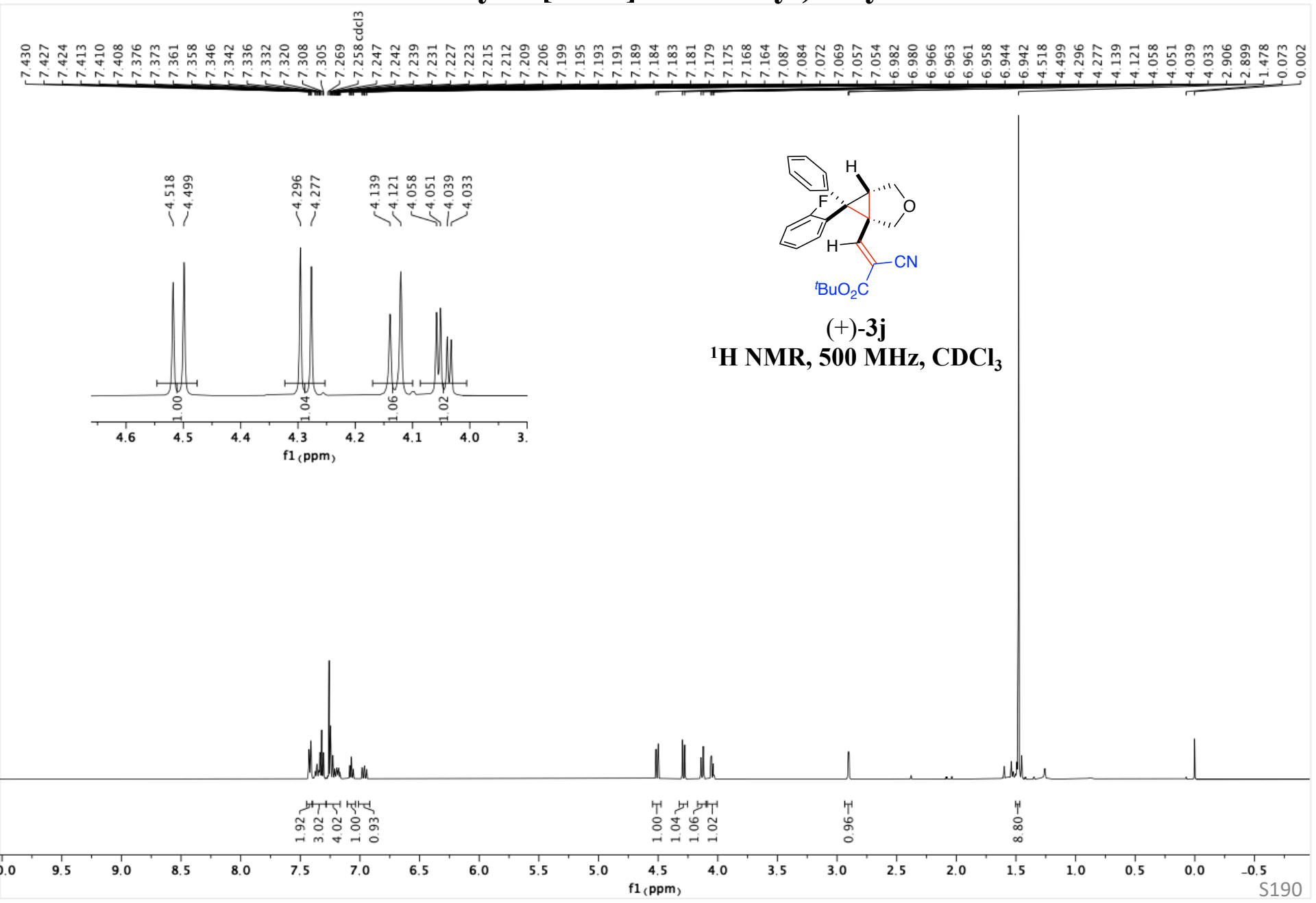


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.047	952056	2.787
2	18.546	33205926	97.213
Total		34157982	100.000

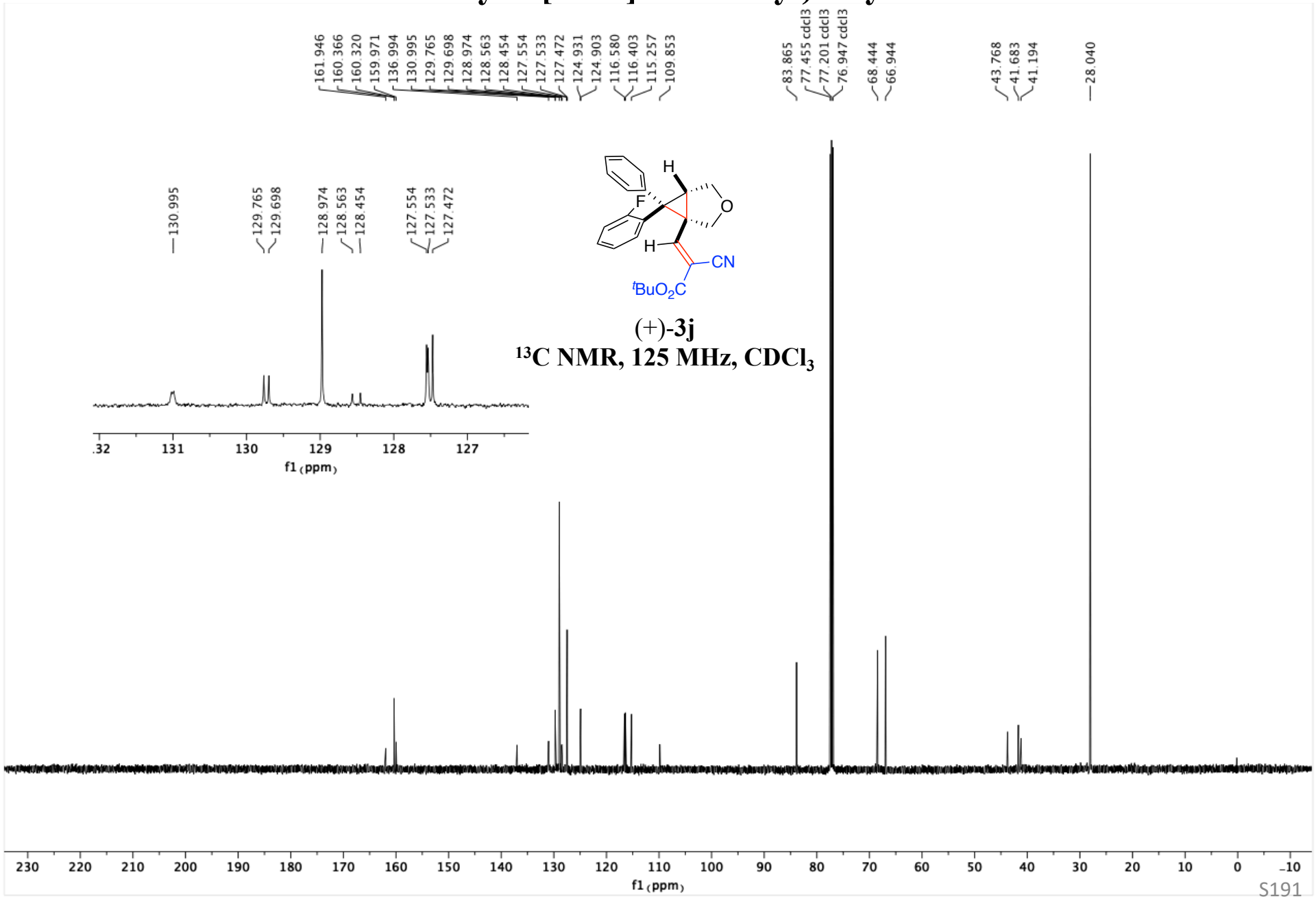
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3j**

^{1}H NMR, 500 MHz, $CDCl_3$

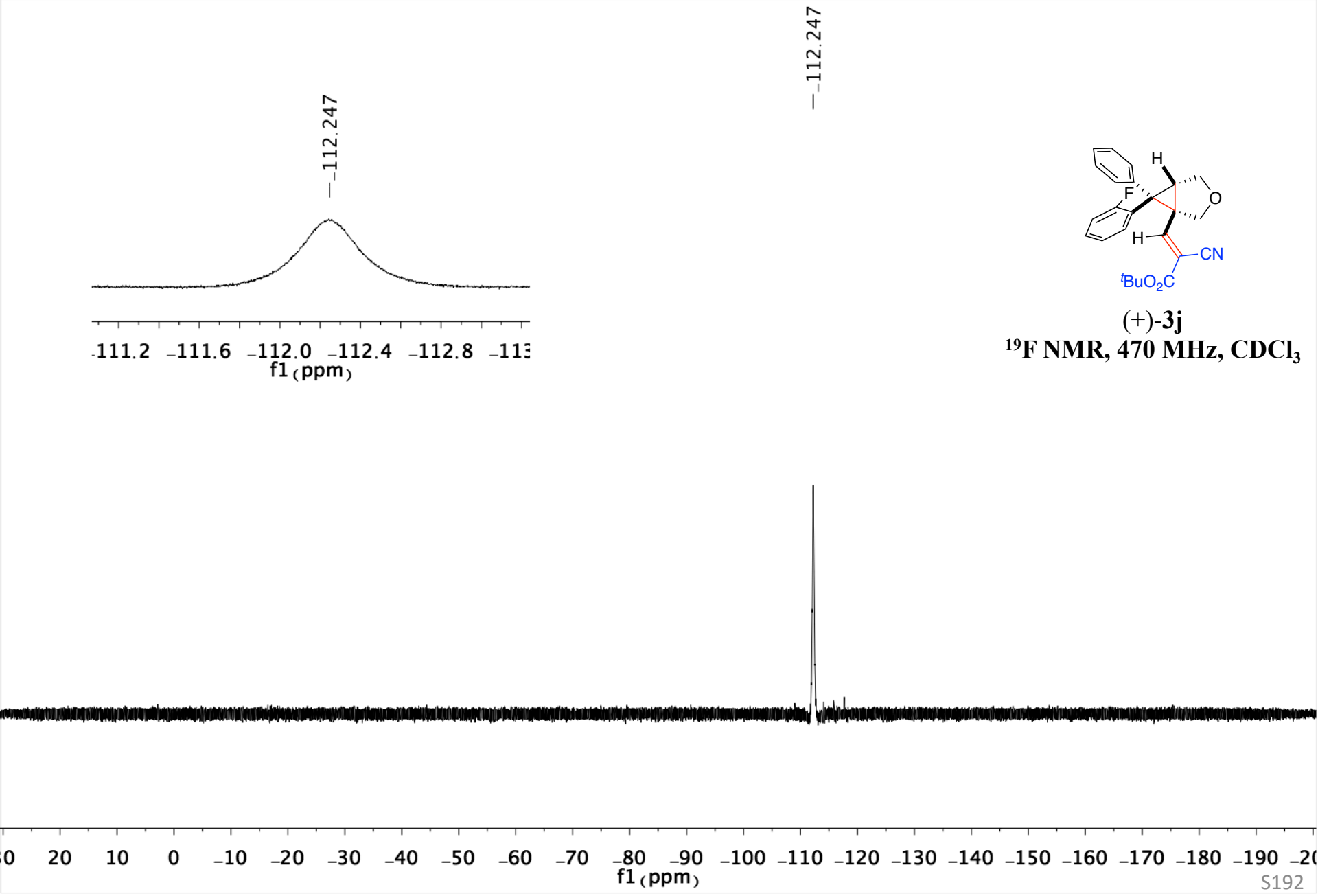
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3j**

^{13}C NMR, 125 MHz, $CDCl_3$

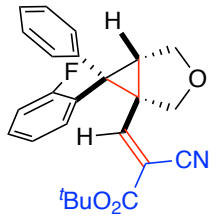
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3j**

^{19}F NMR, 470 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

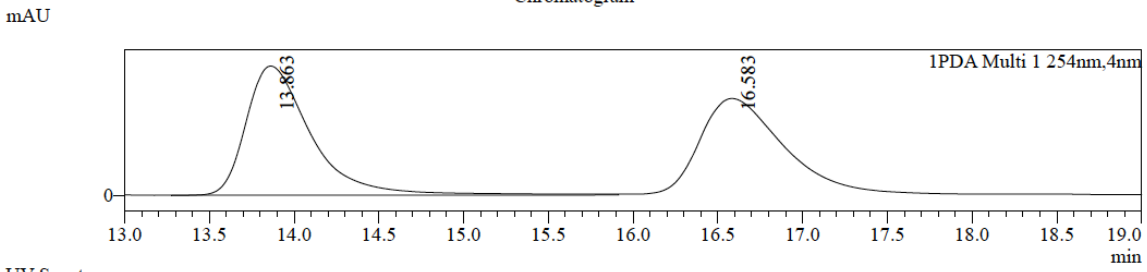


(±)-**3j**

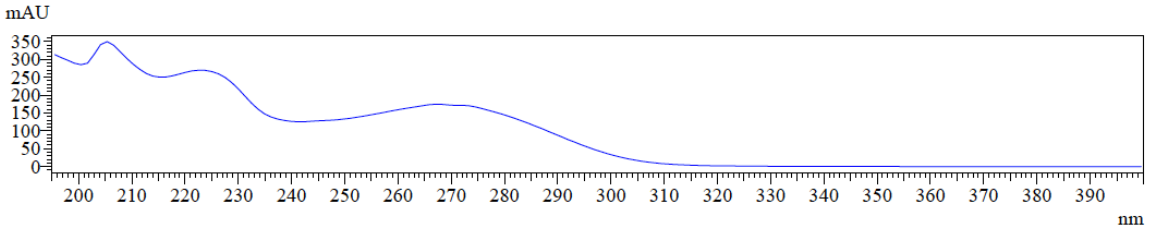
Sample Information

Sample Name	: CZZ-1103-5%-iD-1mL
Sample ID	: CZZ-1103-5%-iD-1mL
Data File	: CZZ-1103-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

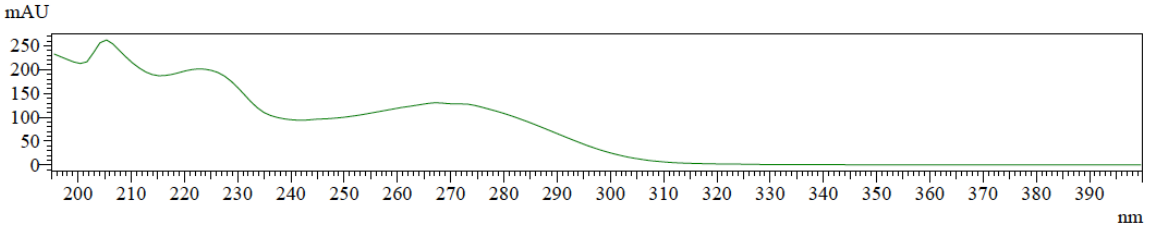
Chromatogram



UV Spectrum
Retention time = 13.863



UV Spectrum
Retention time = 16.583

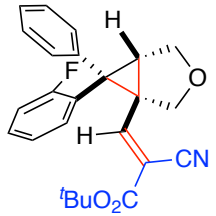


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.863	3834121	50.508
2	16.583	3756990	49.492
Total		7591111	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-(2-fluorophenyl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

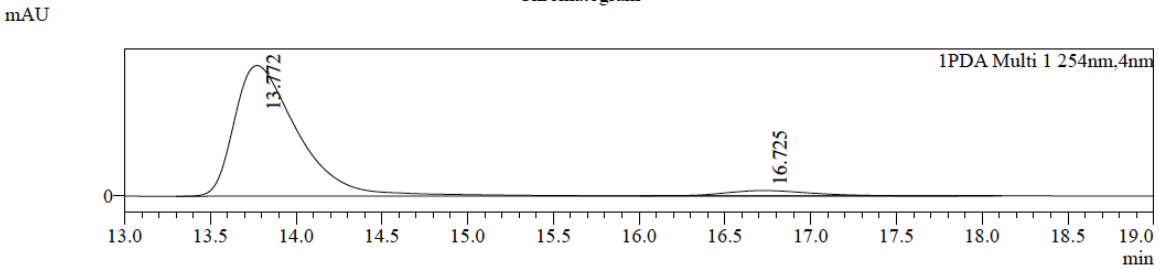


(+)-**3j**

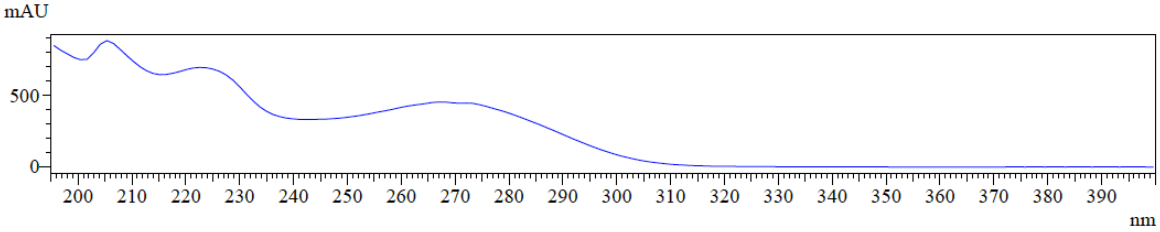
Sample Information

Sample Name	: CZZ-1335-5%-iD-1mL
Sample ID	: CZZ-1335-5%-iD-1mL
Data File	: CZZ-1335-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

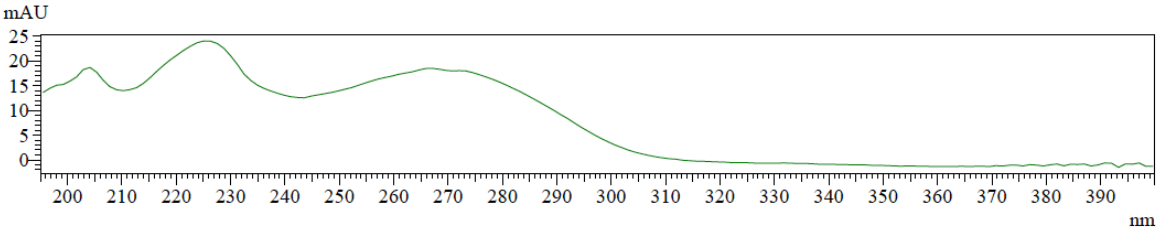
Chromatogram



UV Spectrum
Retention time = 13.772



UV Spectrum
Retention time = 16.725



Peak Table

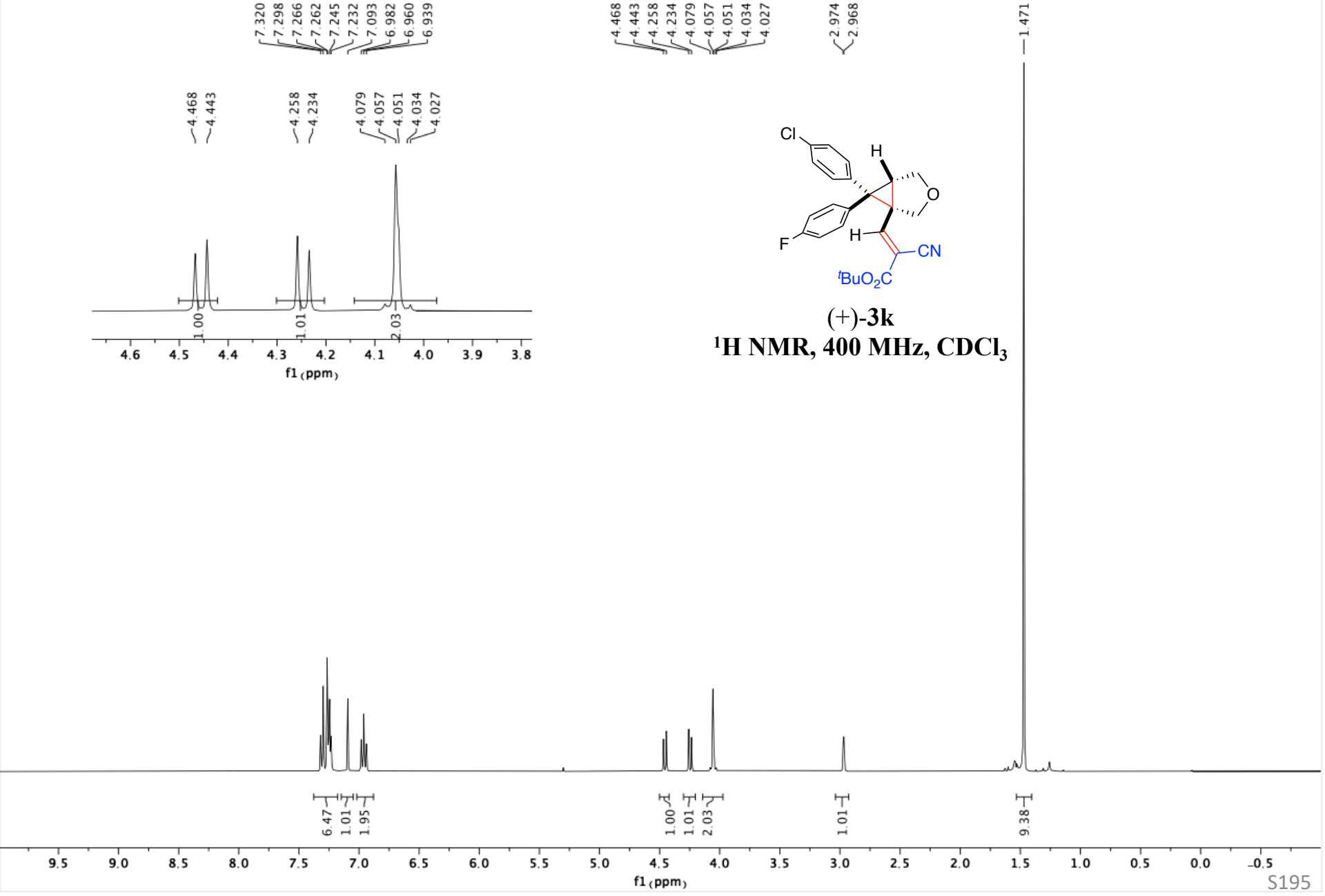
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.772	9691536	94.910
2	16.725	519790	5.090
Total		10211326	100.000

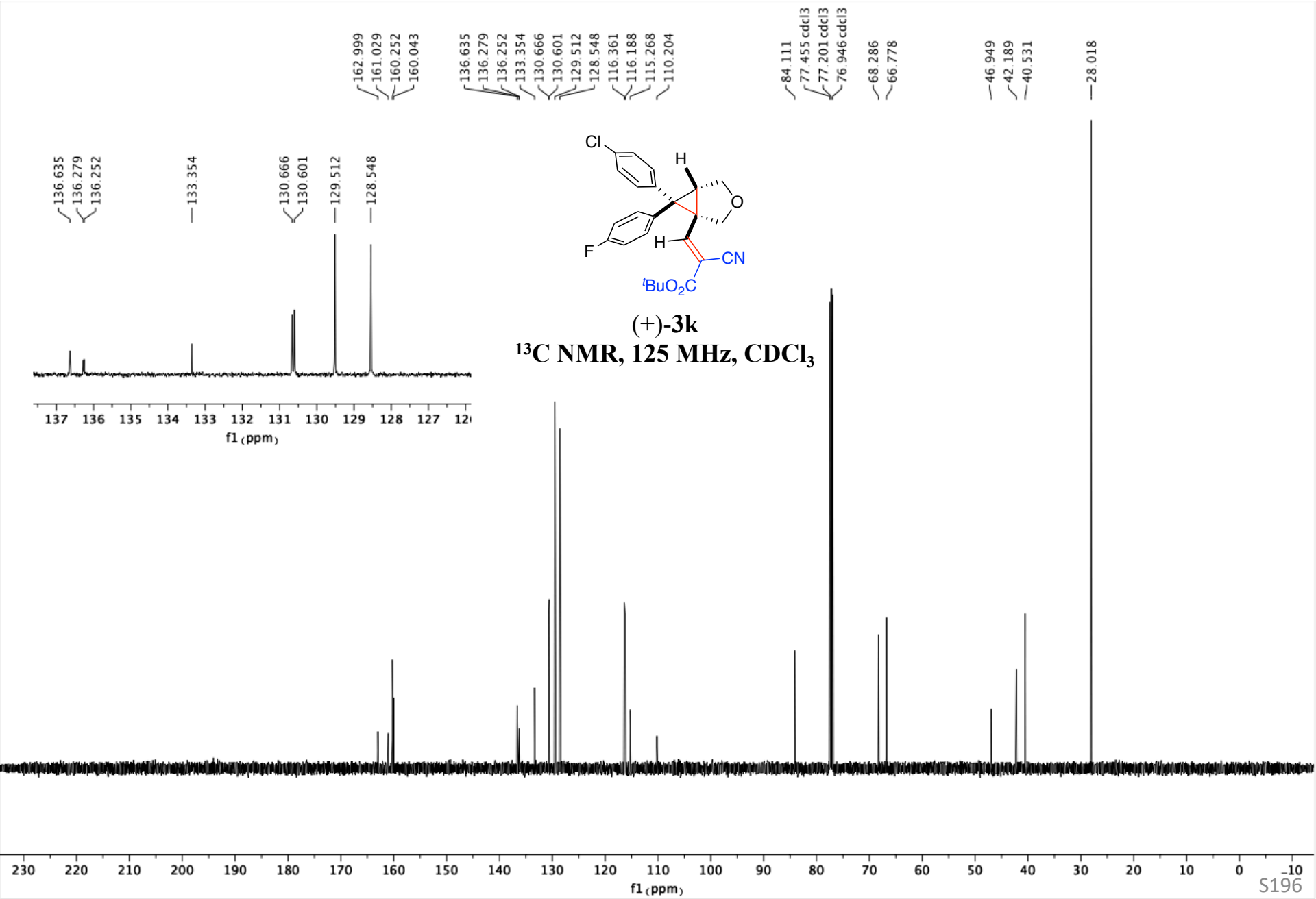
tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

(+)-**3k**

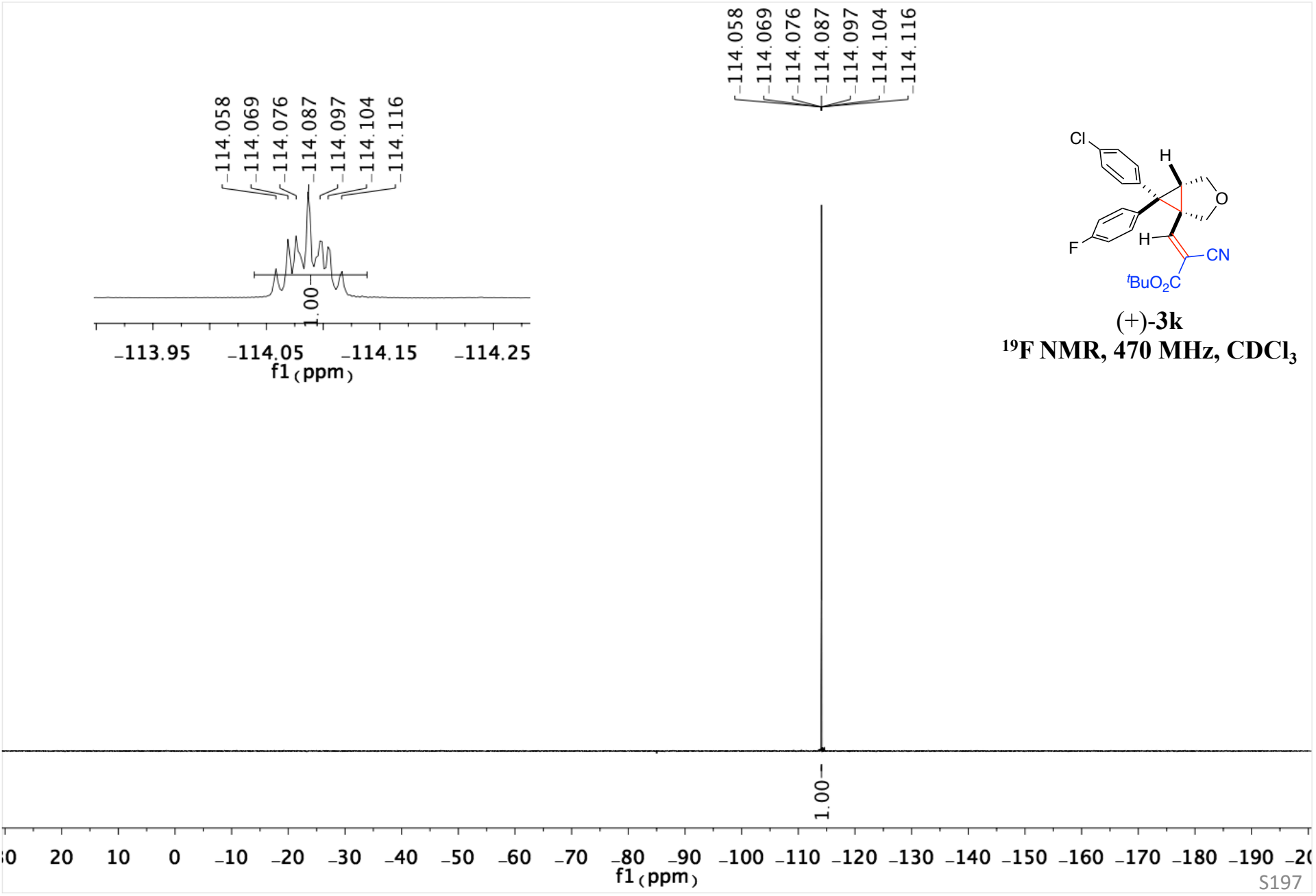
^{1}H NMR, 400 MHz, $CDCl_3$



tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3k**

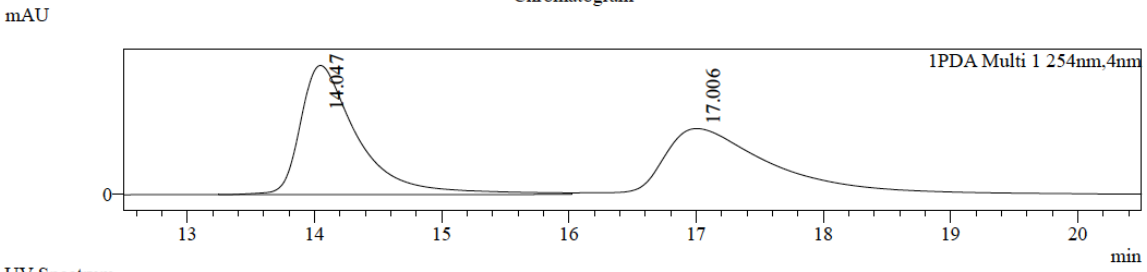
^{19}F NMR, 470 MHz, $CDCl_3$

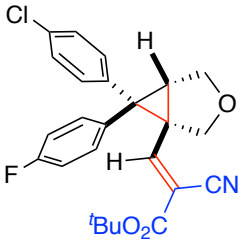
tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

Sample Information

Sample Name	: CZZ-1114-5%-iD-1mL
Sample ID	: CZZ-1114-5%-iD-1mL
Data File	: CZZ-1114-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

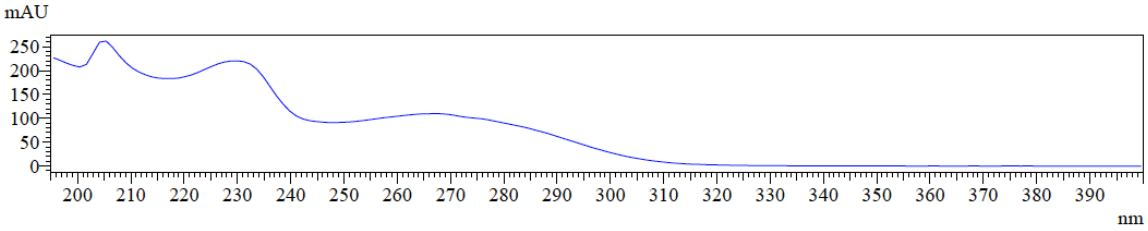
Chromatogram



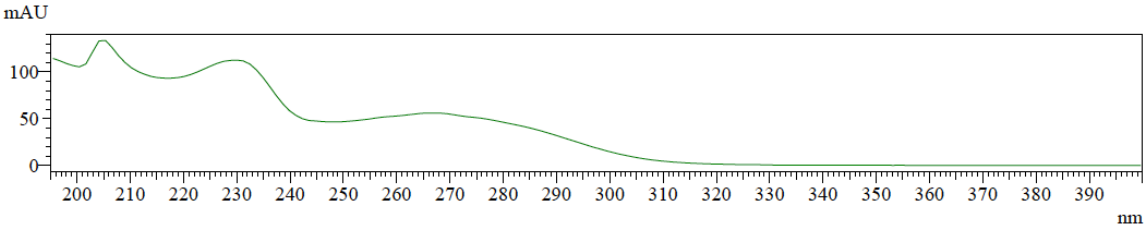


(±)-**3k**

UV Spectrum
Retention time = 14.047



UV Spectrum
Retention time = 17.006

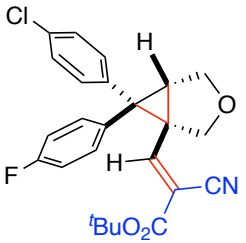


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.047	3030440	50.955
2	17.006	2916838	49.045
Total		5947278	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-chlorophenyl)-6-(4-fluorophenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

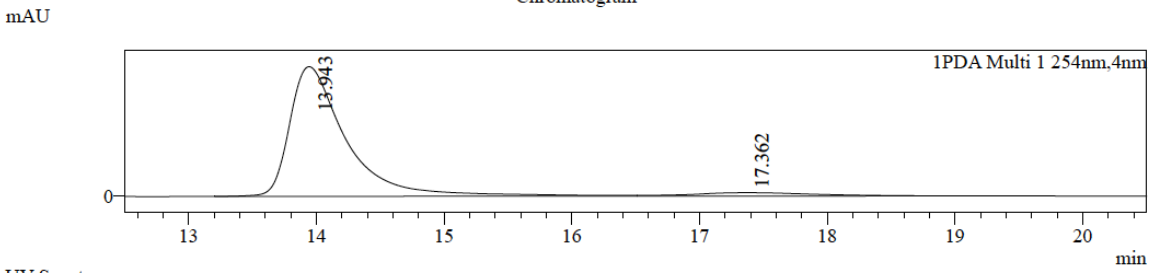


(+)-**3k**

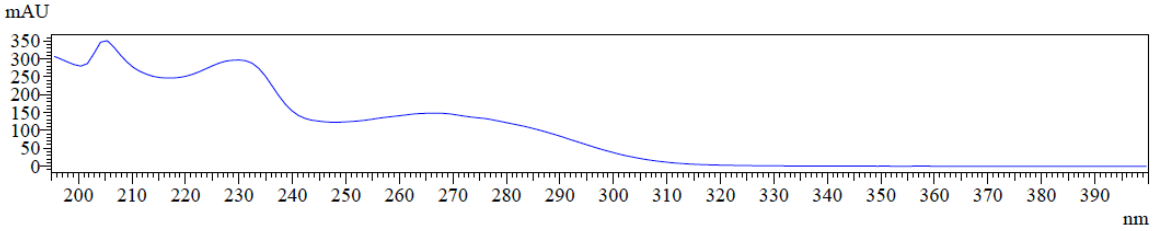
Sample Information

Sample Name	: CZZ-1294-5%-iD-1mL
Sample ID	: CZZ-1294-5%-iD-1mL
Data File	: CZZ-1294-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

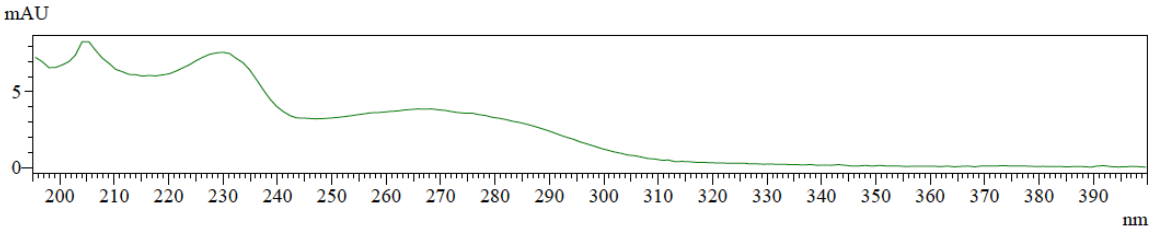
Chromatogram



UV Spectrum
Retention time = 13.943



UV Spectrum
Retention time = 17.362

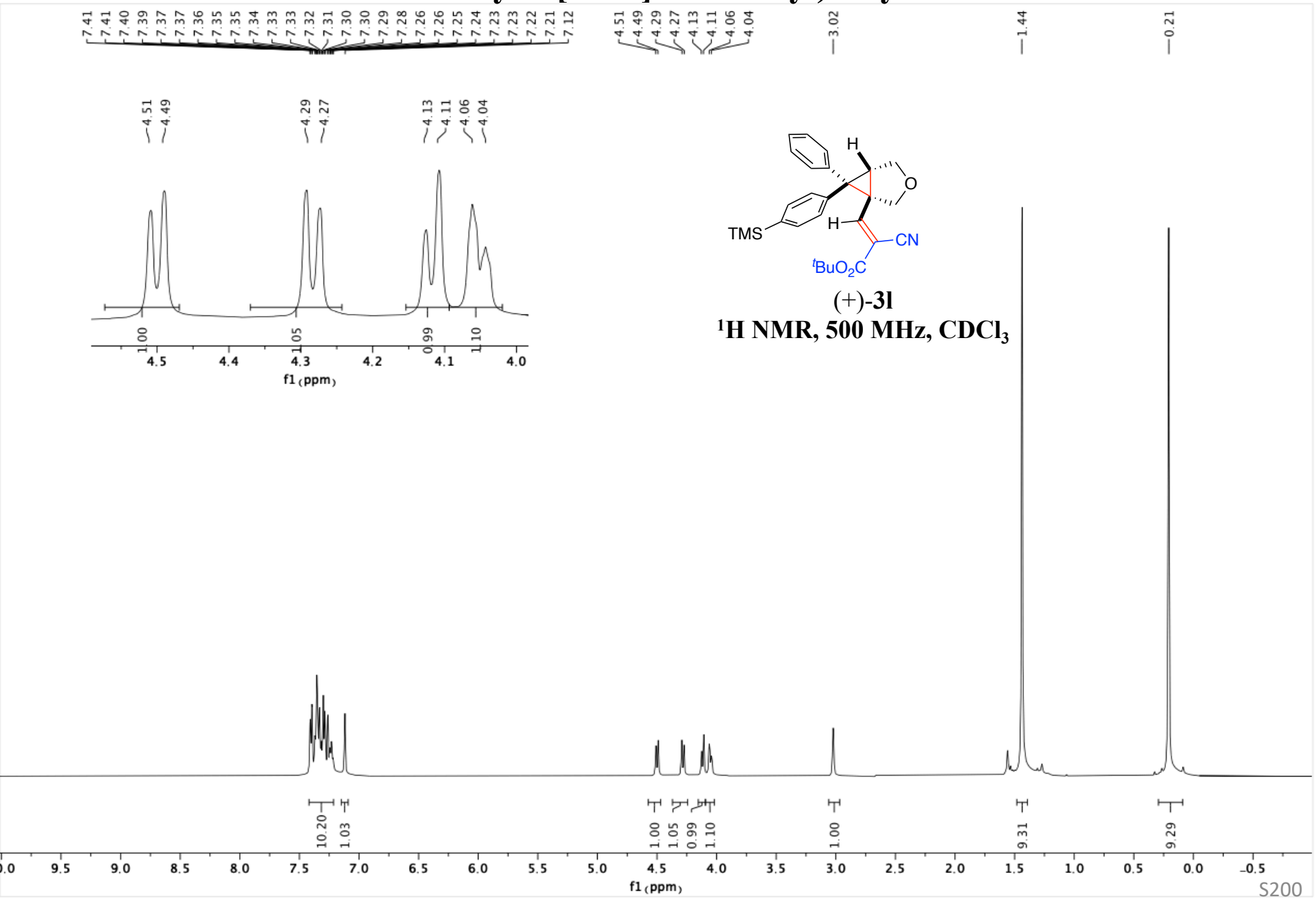


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.943	4025134	94.649
2	17.362	227581	5.351
Total		4252714	100.000

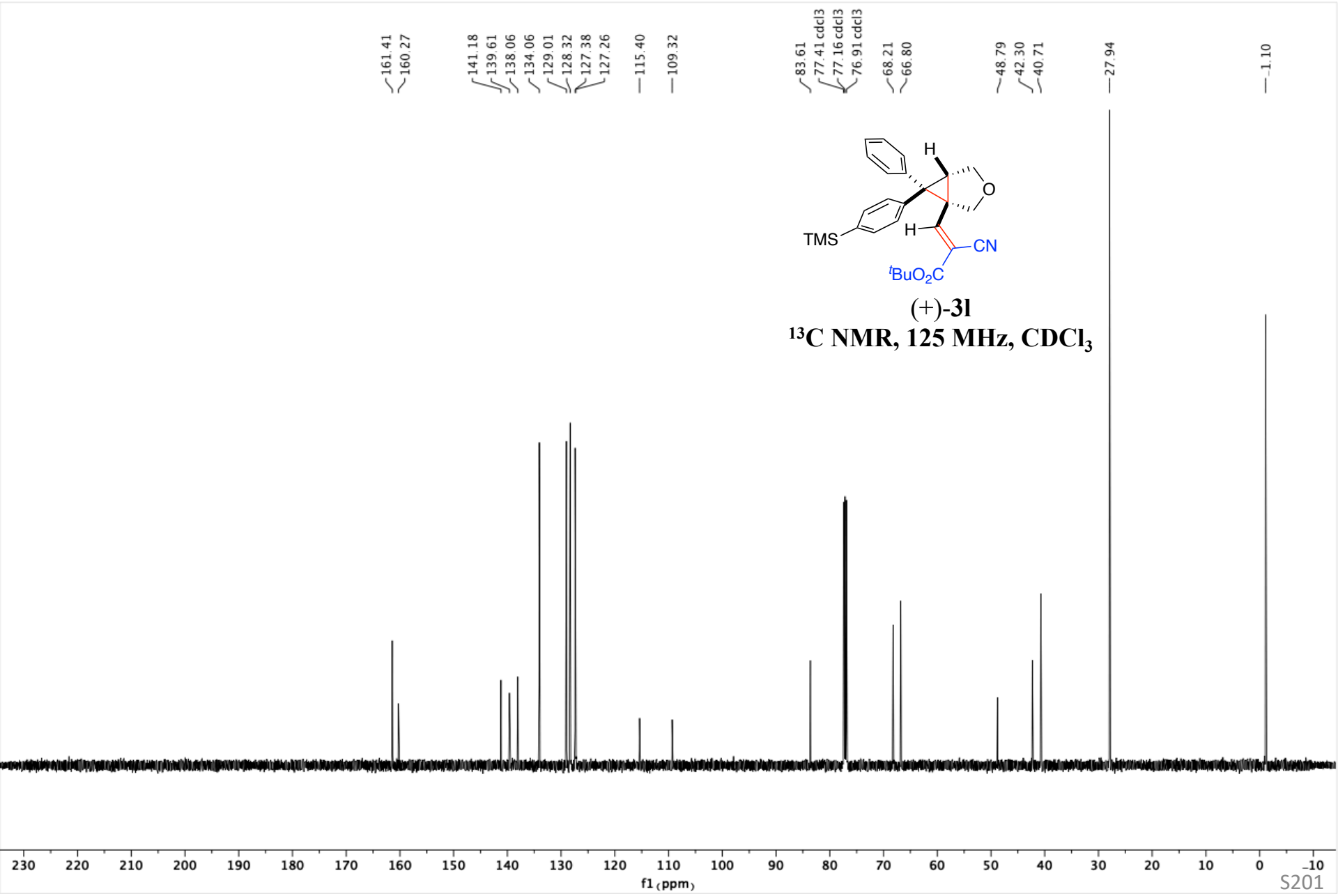
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trimethylsilyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



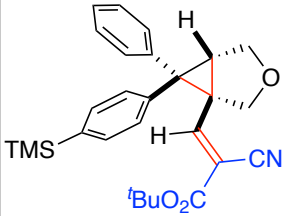
(+)-**3l**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trimethylsilyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

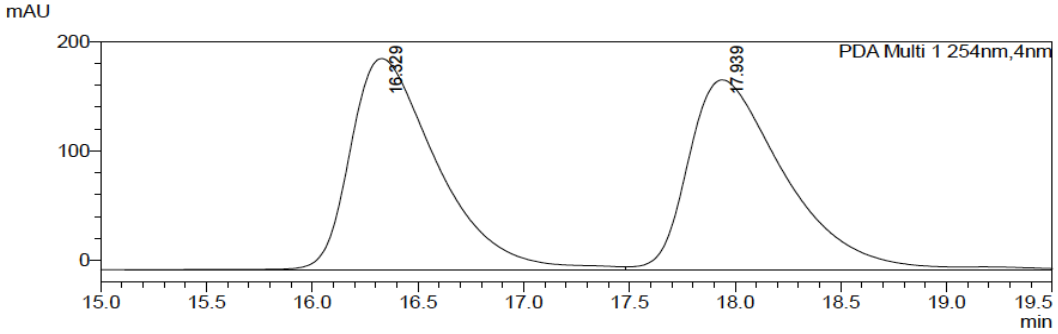


tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trimethylsilyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



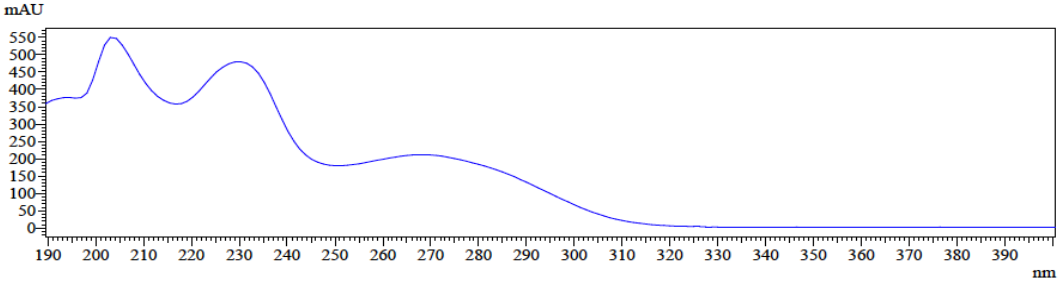
(±)-**3l**

CZZ-2781-IE-5%0.8mL



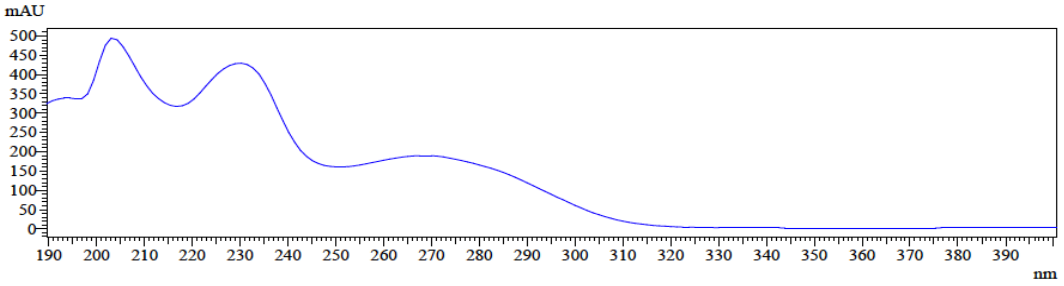
UV Spectrum

Retention Time: 16.329 min



UV Spectrum

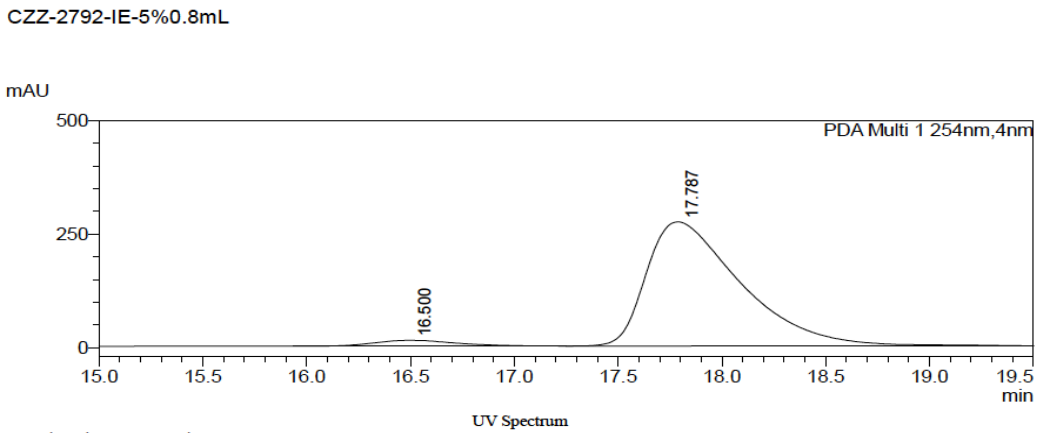
Retention Time: 17.939 min



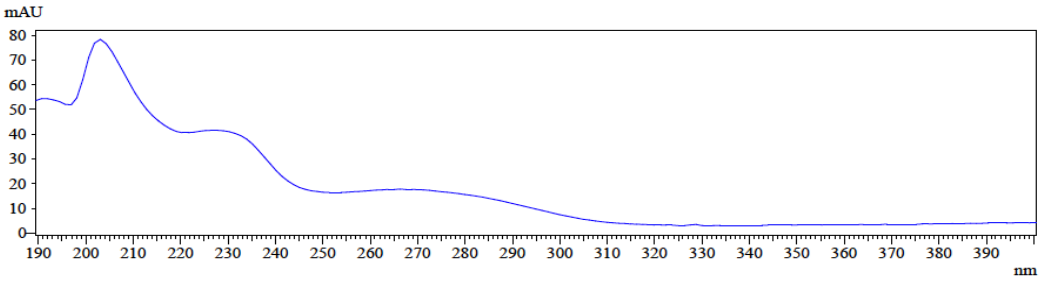
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	16.329	49.545
2	17.939	50.455
Total		100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-phenyl-6-(4-(trimethylsilyl)phenyl)-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

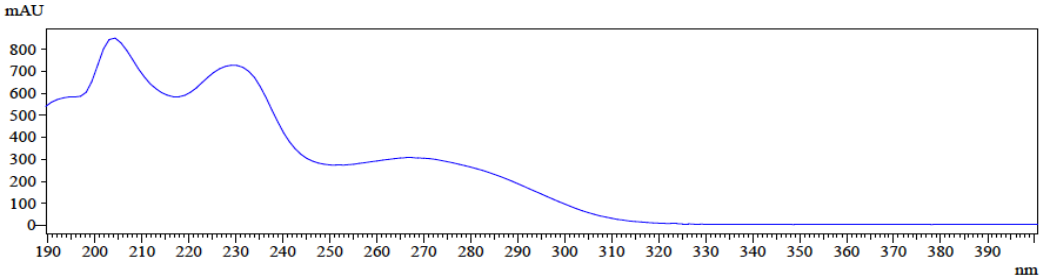


Retention Time: 16.500 min



UV Spectrum

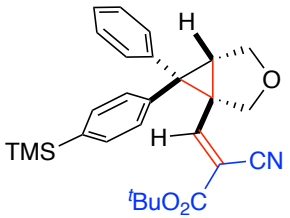
Retention Time: 17.787 min



Peak Table

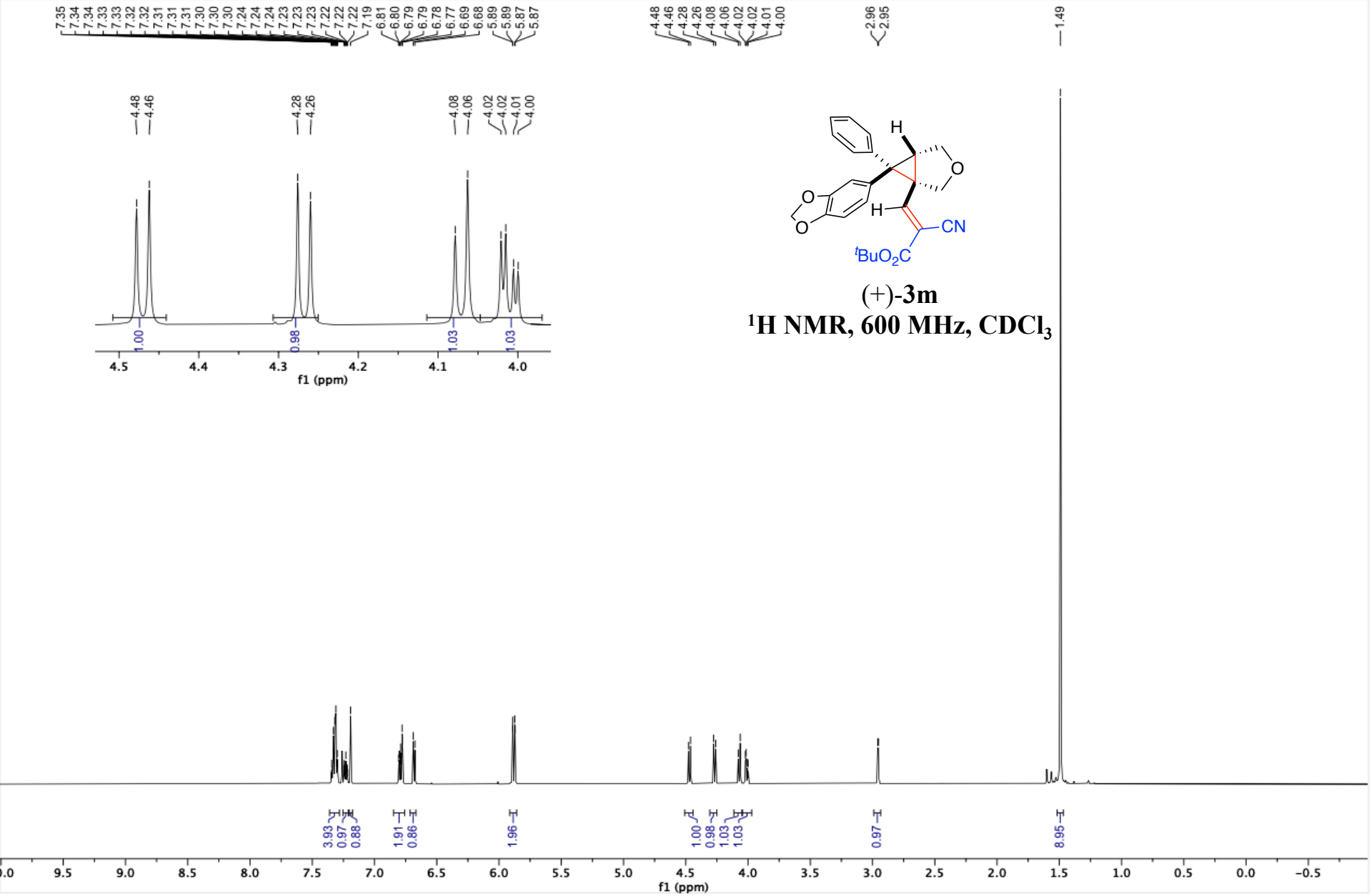
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	16.500	3.857
2	17.787	96.143
Total		100.000

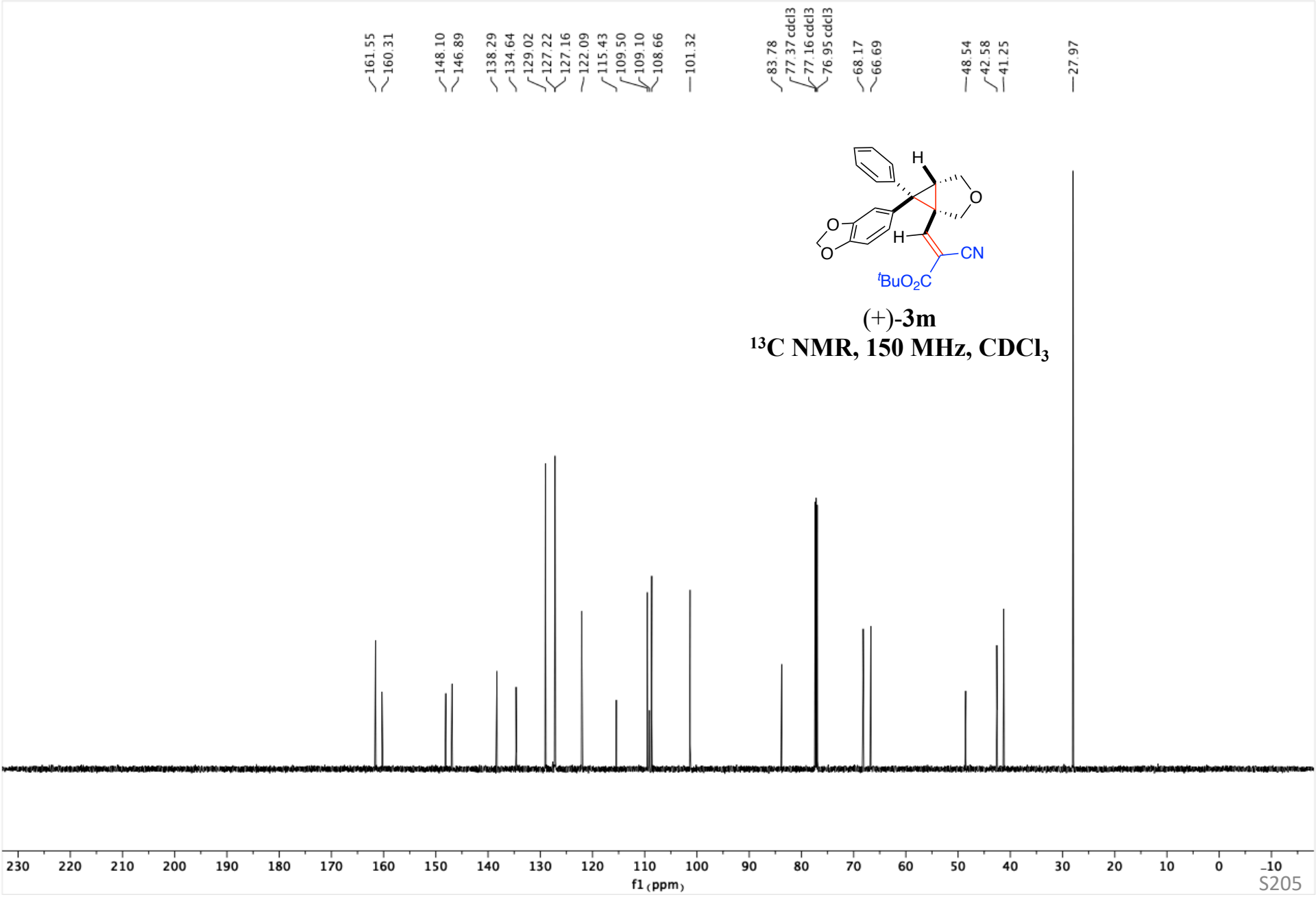


(+)-**3l**

tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3m**

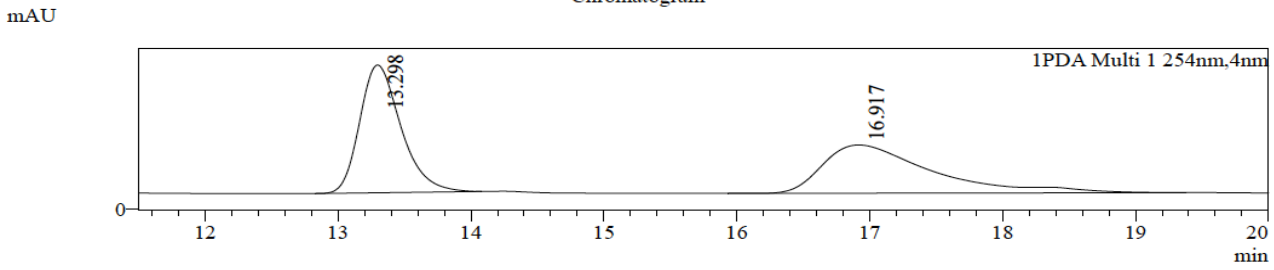
^{13}C NMR, 150 MHz, $CDCl_3$

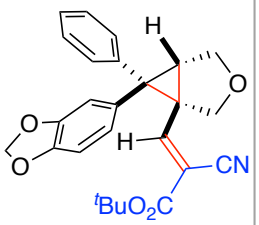
tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

Sample Information

Sample Name	: CZZ-2812-IF--10%-0.8mL
Sample ID	: CZZ-2812-IF--10%-0.8mL
Data File	: CZZ-2812-IF--10%-0.8mL.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

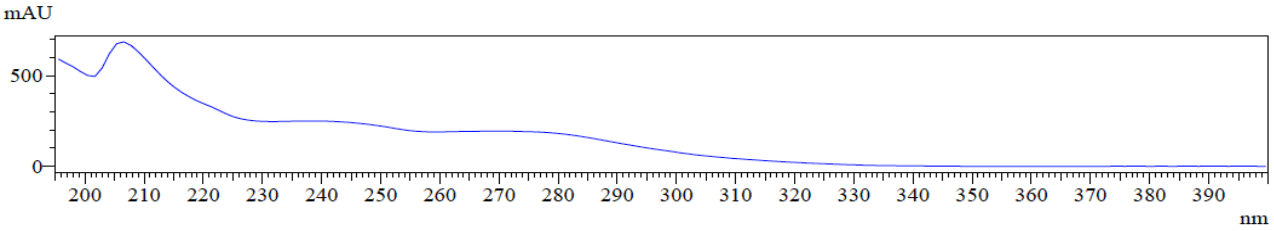
Chromatogram



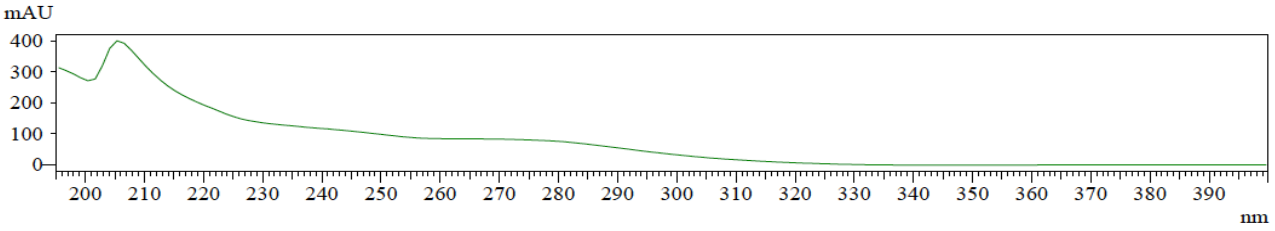


(±)-**3m**

UV Spectrum
Retention time = 13.298



UV Spectrum
Retention time = 16.917



Peak Table

PDA Ch1 254nm

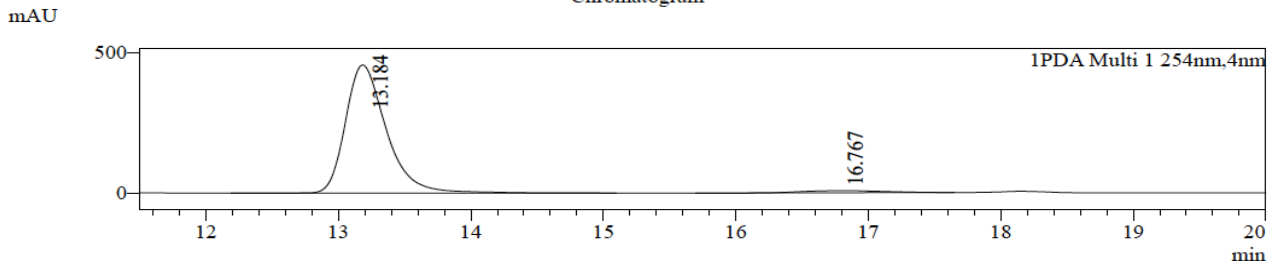
Peak#	Ret. Time	Area	Area%
1	13.298	3854450	50.051
2	16.917	3846546	49.949
Total		7700996	100.000

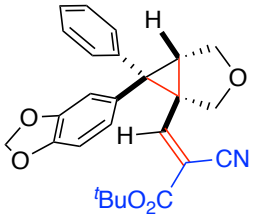
tert-Butyl (*E*)-3-((1*S*,5*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

Sample Information

Sample Name	: CZZ-2813-IF--10%-0.8mL
Sample ID	: CZZ-2813-IF--10%-0.8mL
Data File	: CZZ-2813-IF--10%-0.8mL.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

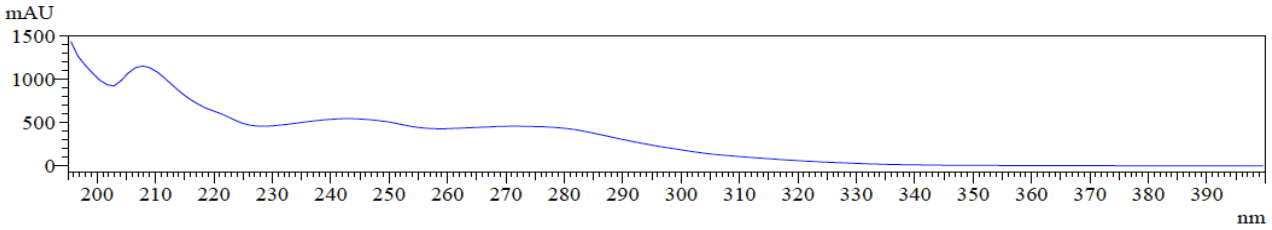
Chromatogram



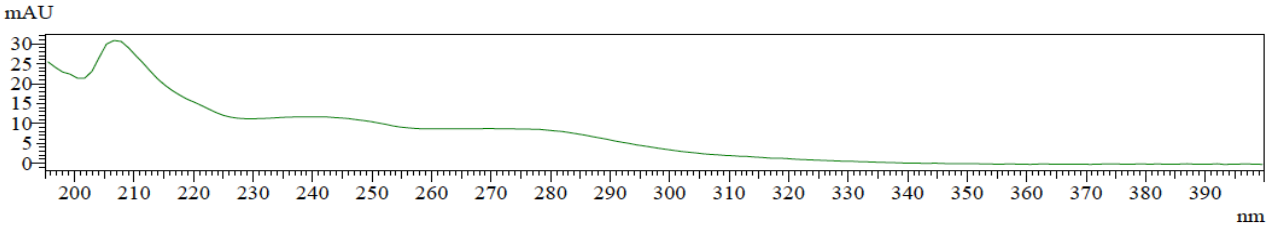


(+)-**3m**

UV Spectrum
Retention time = 13.184



UV Spectrum
Retention time = 16.767

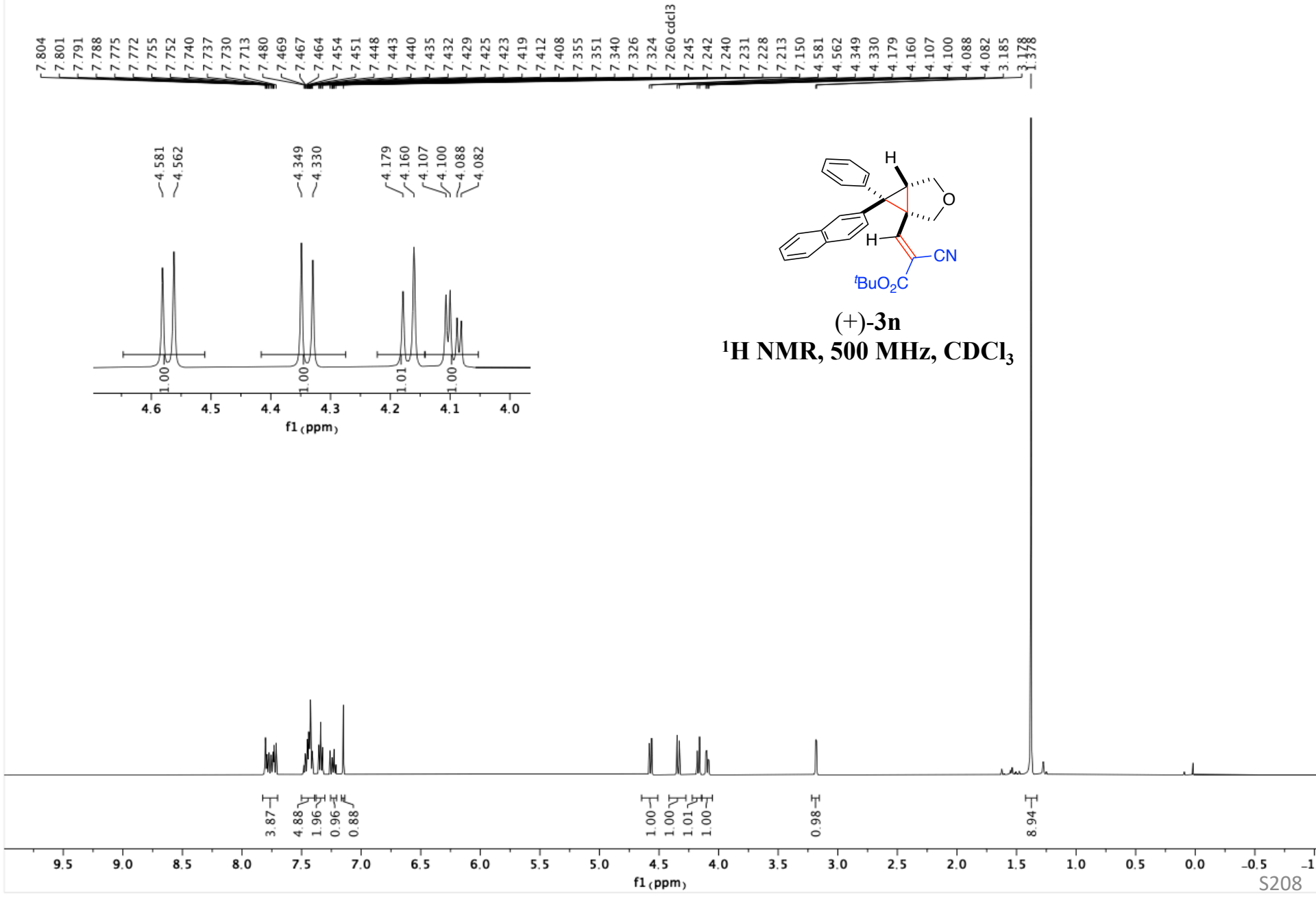


Peak Table

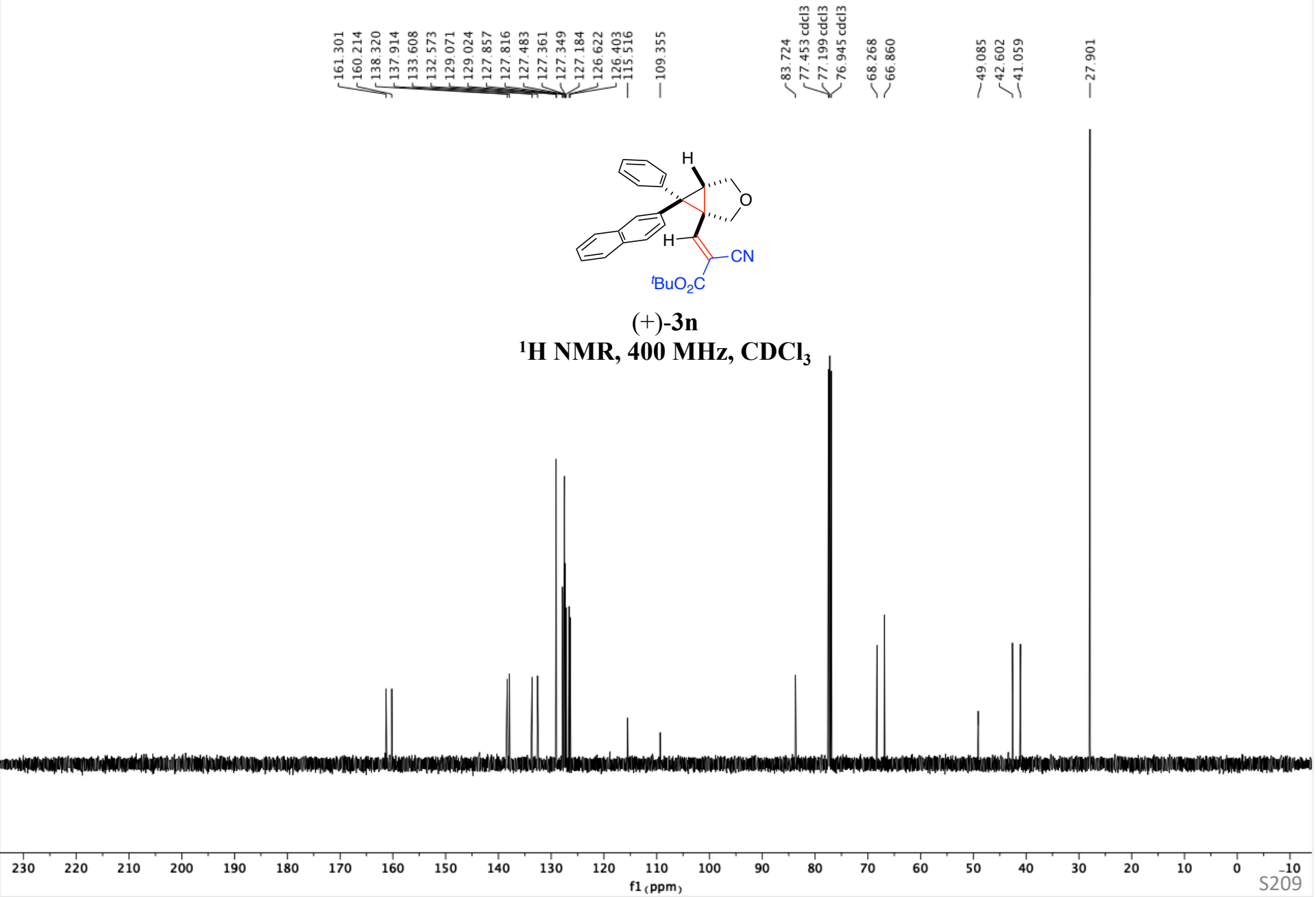
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.184	9801099	96.986
2	16.767	304605	3.014
Total		10105704	100.000

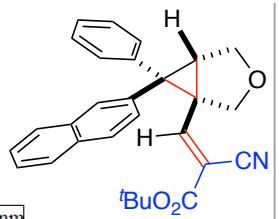
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(naphthalen-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(naphthalen-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(naphthalen-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

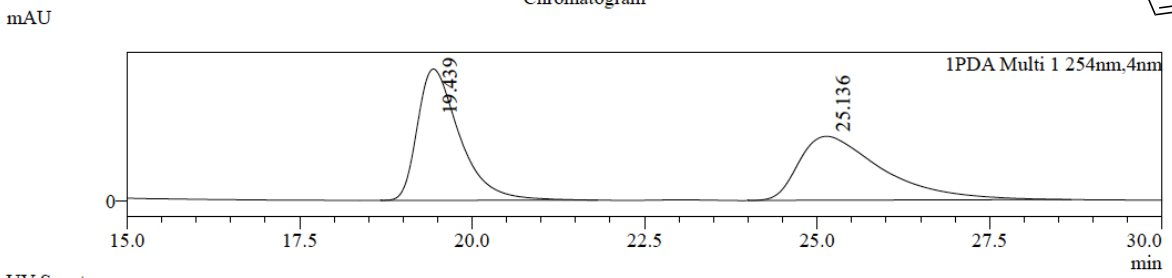


(±)-**3n**

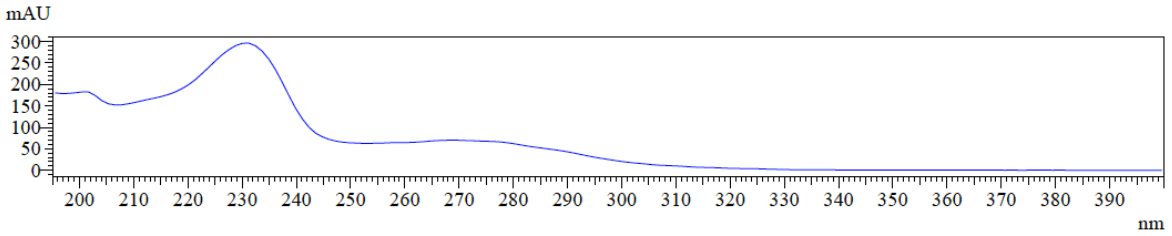
Sample Information

Sample Name	: CZZ-1288-5%-iD-1mL
Sample ID	: CZZ-1288-5%-iD-1mL
Data File	: CZZ-1288-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

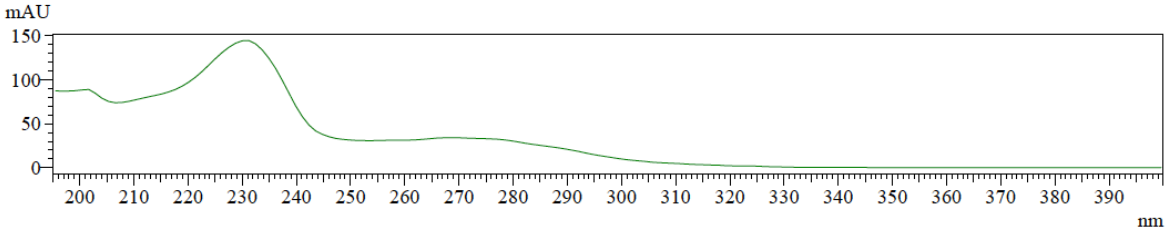
Chromatogram



UV Spectrum
Retention time = 19.439



UV Spectrum
Retention time = 25.136

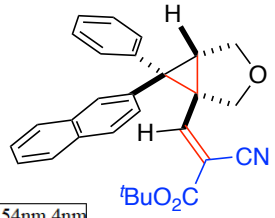


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.439	2668096	50.996
2	25.136	2563870	49.004
Total		5231966	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(naphthalen-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

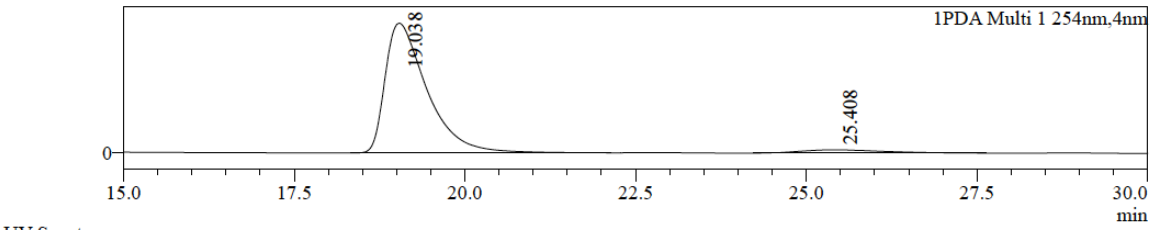


(+)-**3n**

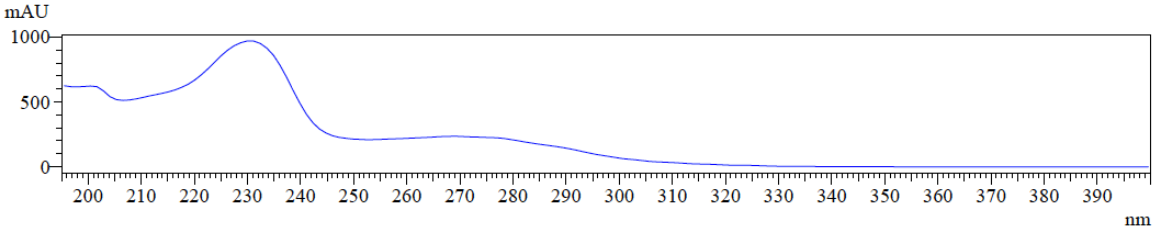
Sample Information

Sample Name	: CZZ-1289-5%-iD-1mL
Sample ID	: CZZ-1289-5%-iD-1mL
Data File	: CZZ-1289-5%-iD-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

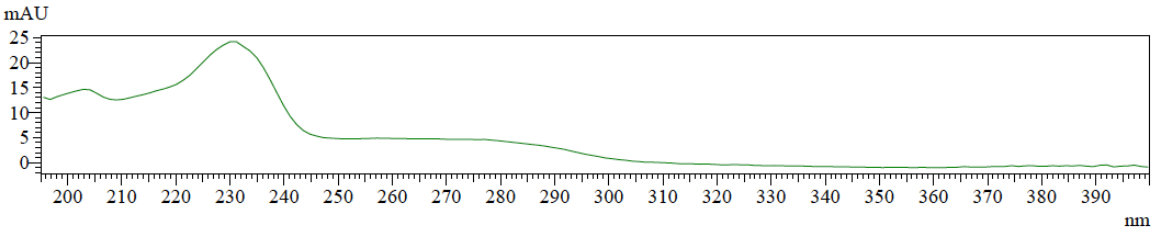
Chromatogram



UV Spectrum
Retention time = 19.038



UV Spectrum
Retention time = 25.408



Peak Table

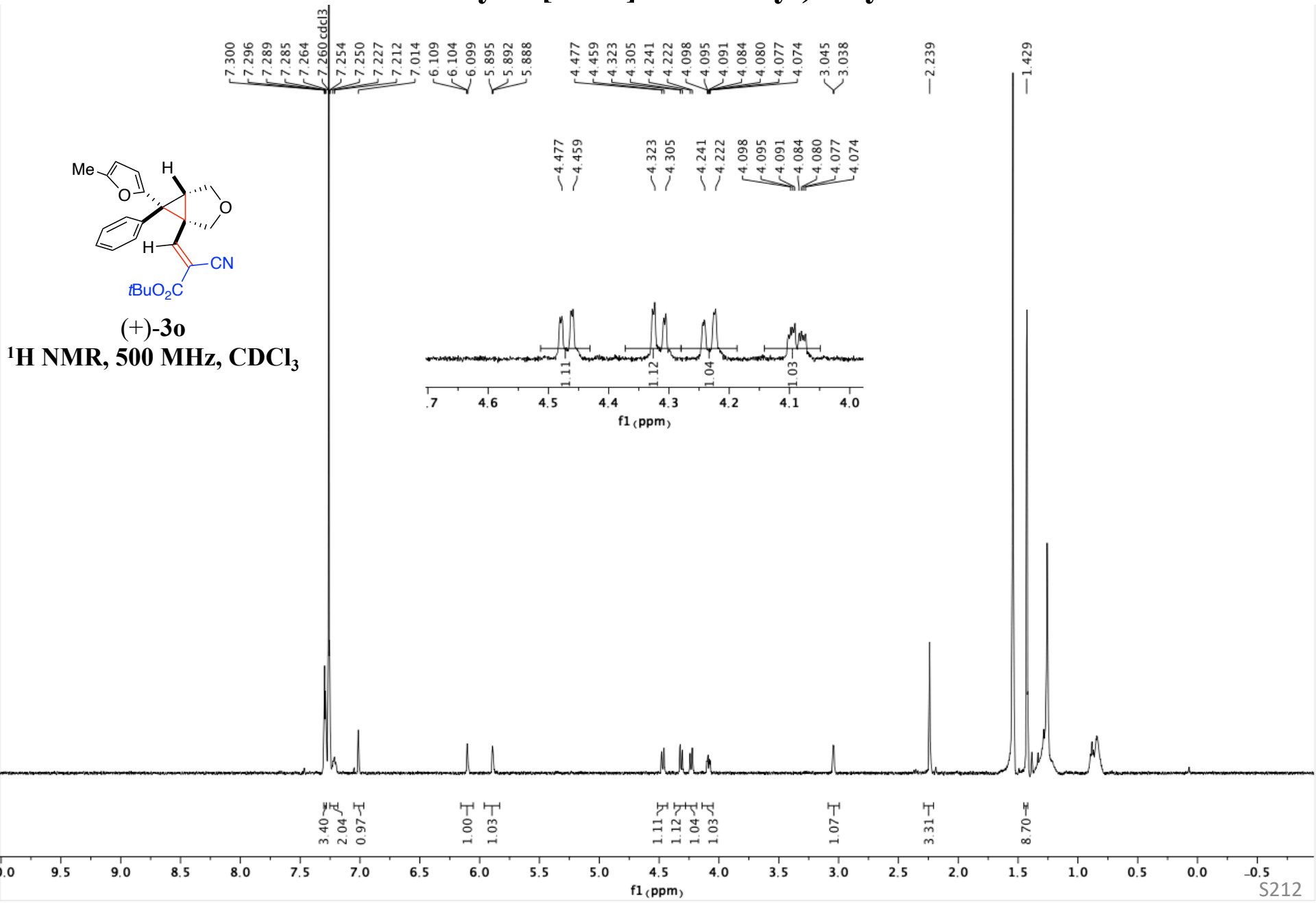
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.038	8998864	95.487
2	25.408	425290	4.513
Total		9424153	100.000

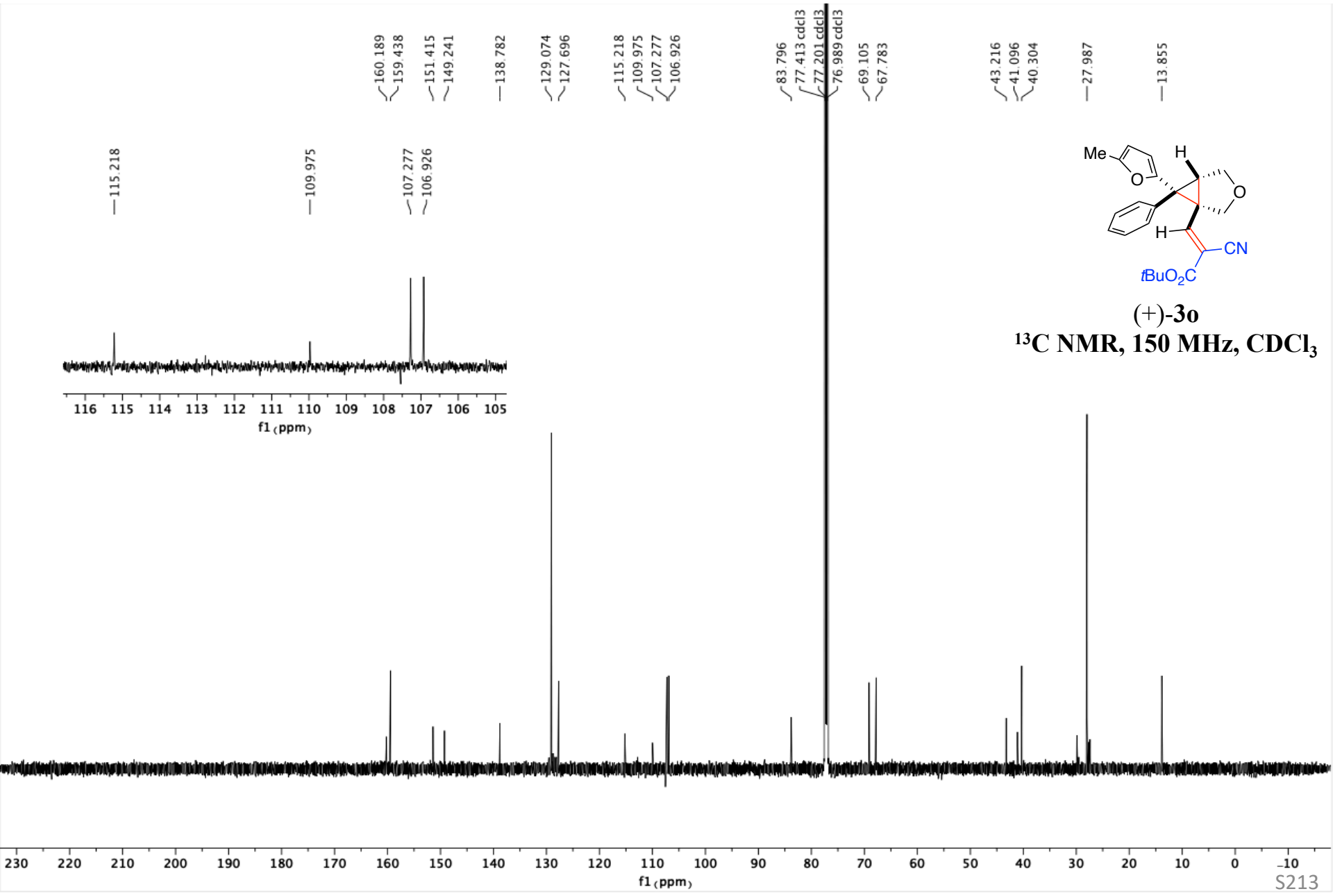
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*R*,6*S*)-6-(5-methylfuran-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

(+)-**3o**

^{1}H NMR, 500 MHz, $CDCl_3$



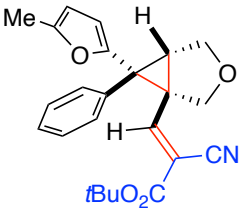
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*R*,6*S*)-6-(5-methylfuran-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(+)-**3o**

^{13}C NMR, 150 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*R*,6*S*)-6-(5-methylfuran-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

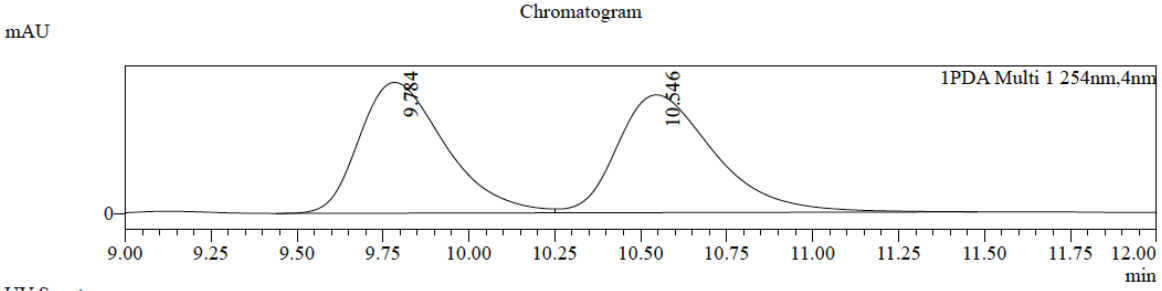


(±)-**3o**

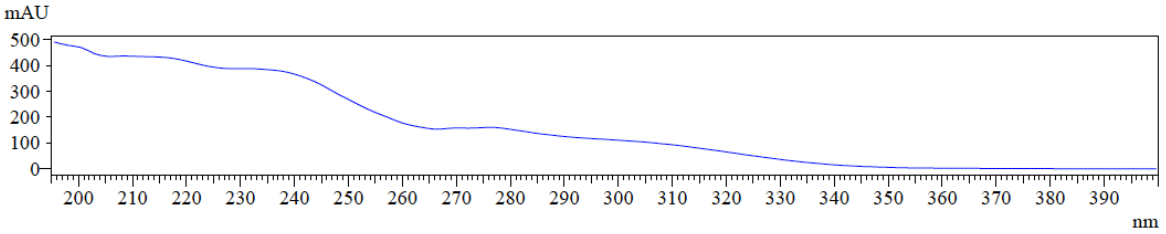
Sample Information

Sample Name	: CZZ-1379-IA-1%-1ML
Sample ID	: CZZ-1379-IA-1%-1ML
Data File	: CZZ-1379-IA-1%-1ML.lcd
Method File	: CZZ-1%-1.0ml.lcm

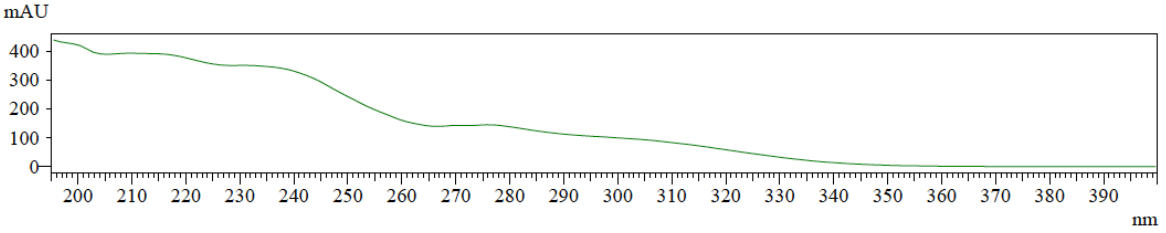
Chromatogram



UV Spectrum
Retention time = 9.784



UV Spectrum
Retention time = 10.546

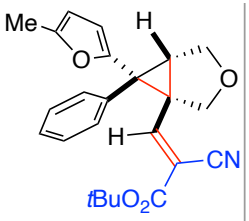


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.784	3948796	49.595
2	10.546	4013212	50.405
Total		7962008	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*R*,6*S*)-6-(5-methylfuran-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

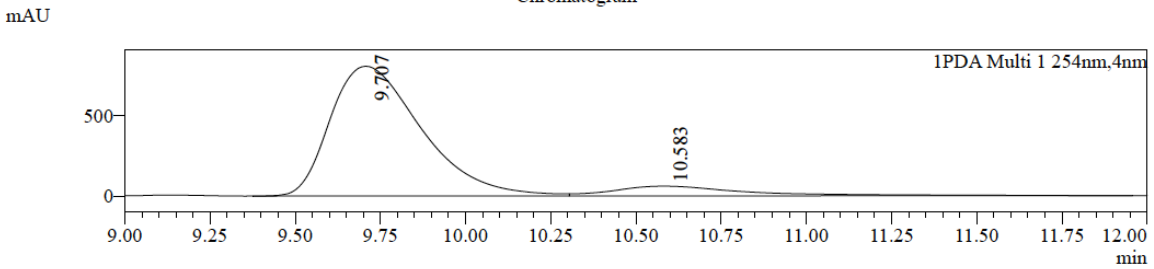


(+)-**3o**

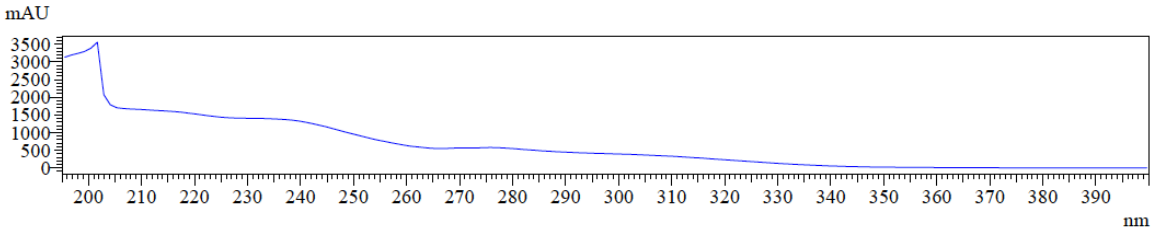
Sample Information

Sample Name	: CZZ-1380-IA-1%-1ML
Sample ID	: CZZ-1380-IA-1%-1ML
Data File	: CZZ-1380-IA-1%-1ML.lcd
Method File	: CZZ-1%-1.0ml.lcm

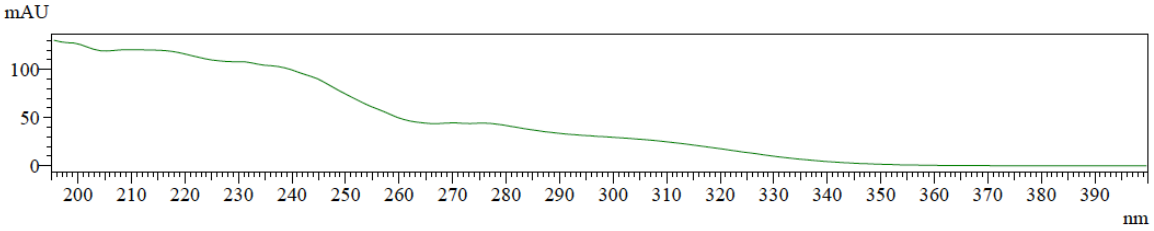
Chromatogram



UV Spectrum
Retention time = 9.707



UV Spectrum
Retention time = 10.583

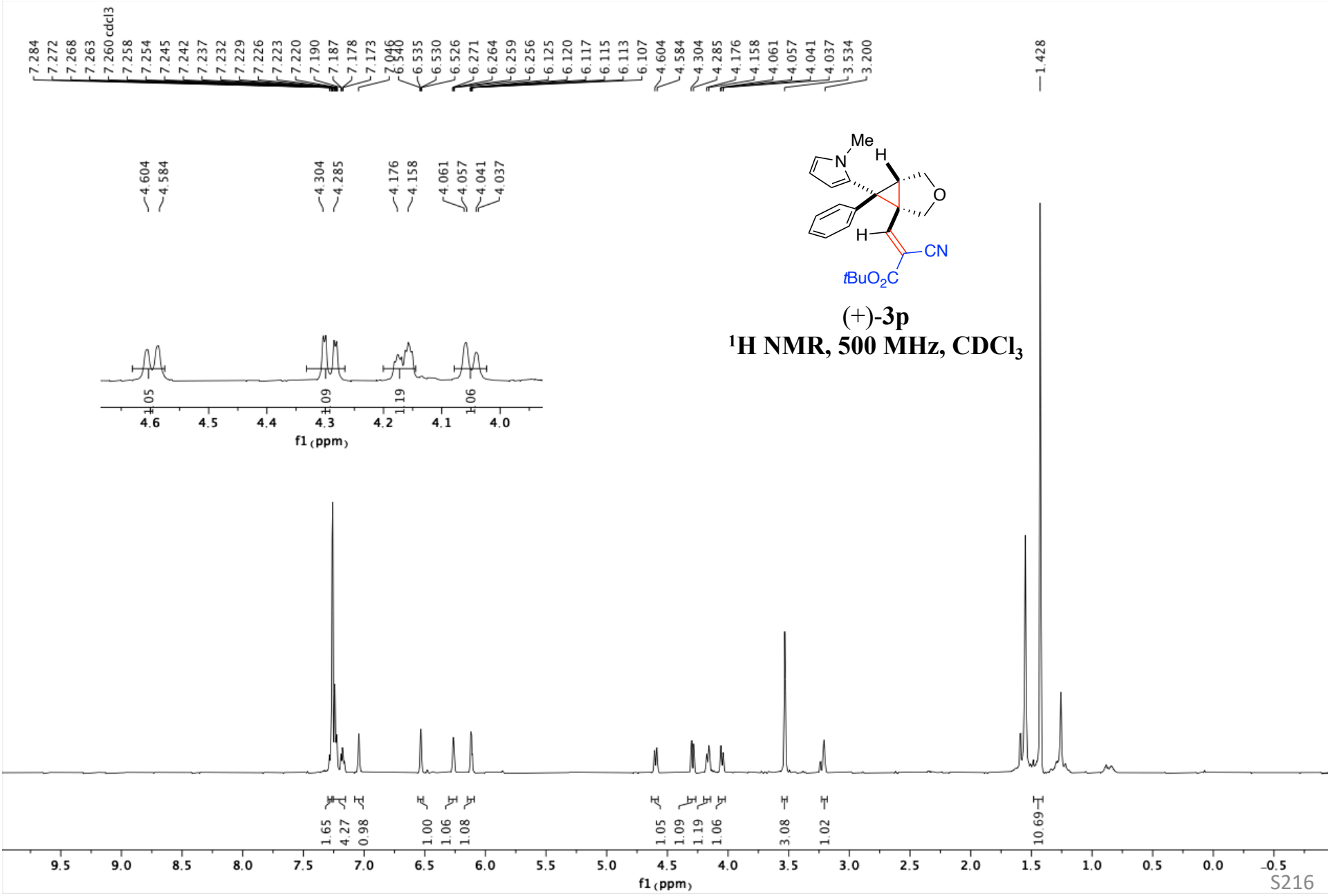


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.707	14975807	90.024
2	10.583	1659534	9.976
Total		16635341	100.000

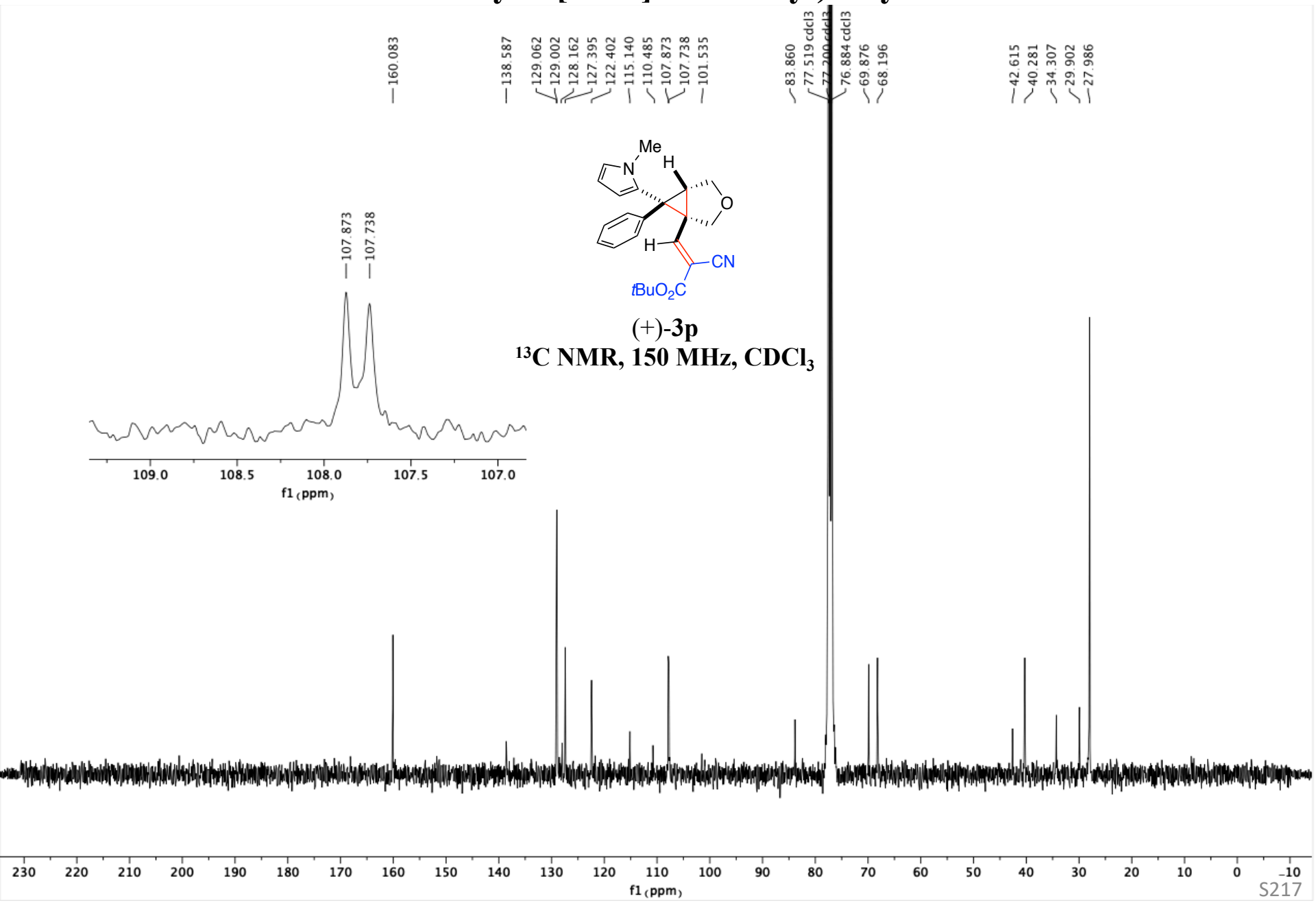
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(1-methyl-1*H*-pyrrol-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



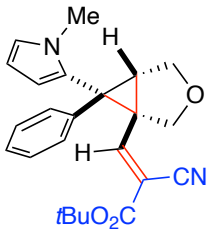
(+)-**3p**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(1-methyl-1*H*-pyrrol-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(1-methyl-1*H*-pyrrol-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

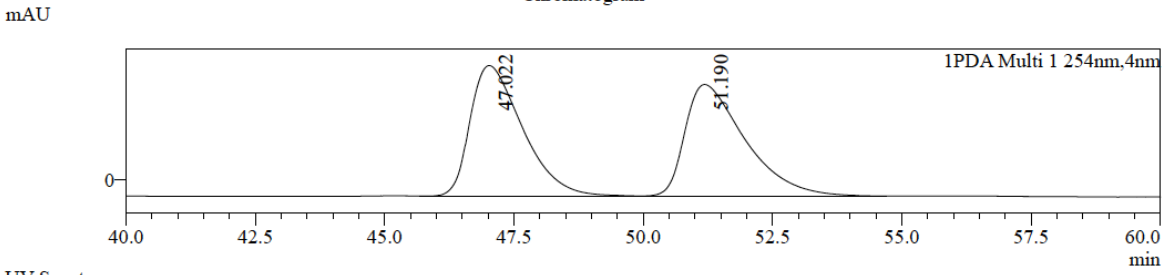


(±)-**3p**

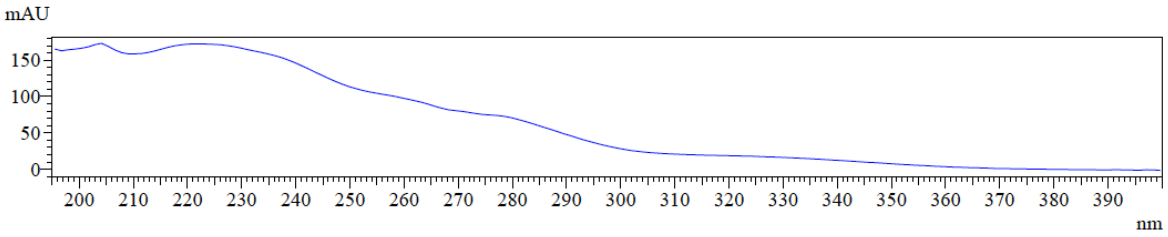
Sample Information

Sample Name	: CZZ-1111-iE-5%1.0mL
Sample ID	: CZZ-1111-iE-5%1.0mL
Data File	: CZZ-1111-iE-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

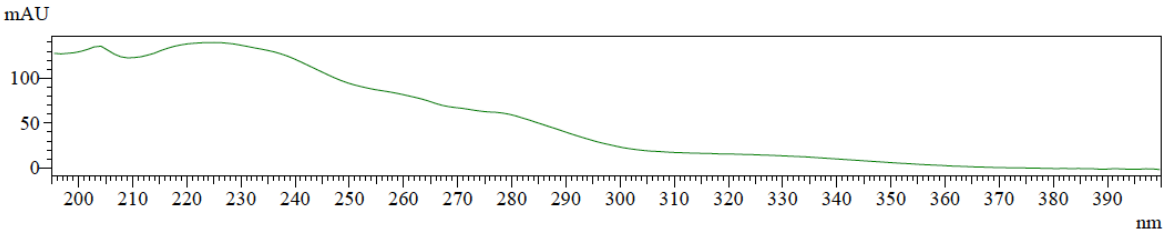
Chromatogram



UV Spectrum
Retention time = 47.022



UV Spectrum
Retention time = 51.190

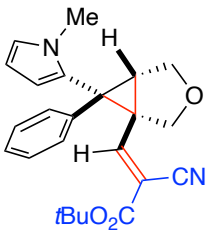


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	47.022	8533892	50.461
2	51.190	8378066	49.539
Total		16911958	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*S*)-6-(1-methyl-1*H*-pyrrol-2-yl)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

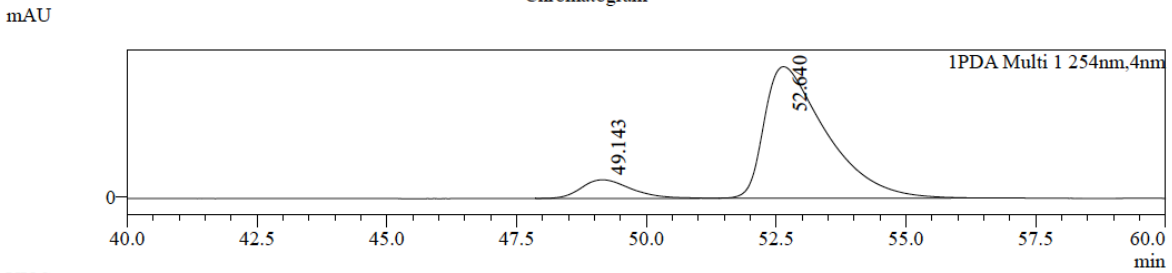


(+)-**3p**

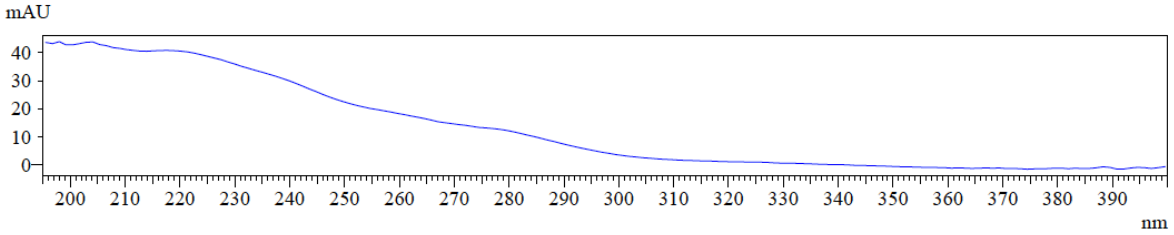
Sample Information

Sample Name	: CZZ-1112-iE-5%1.0mL
Sample ID	: CZZ-1112-iE-5%1.0mL
Data File	: CZZ-1112-iE-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

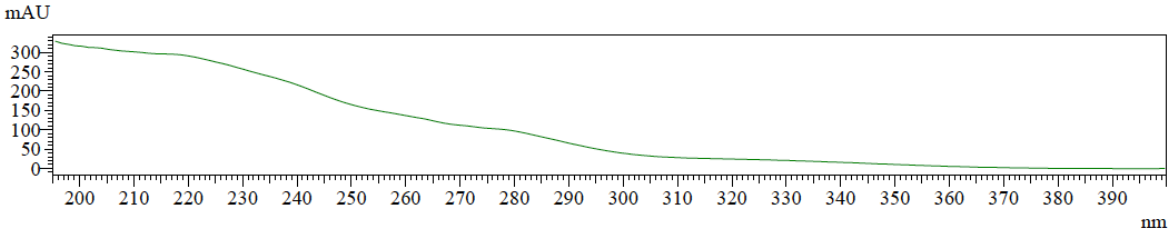
Chromatogram



UV Spectrum
Retention time = 49.143



UV Spectrum
Retention time = 52.640

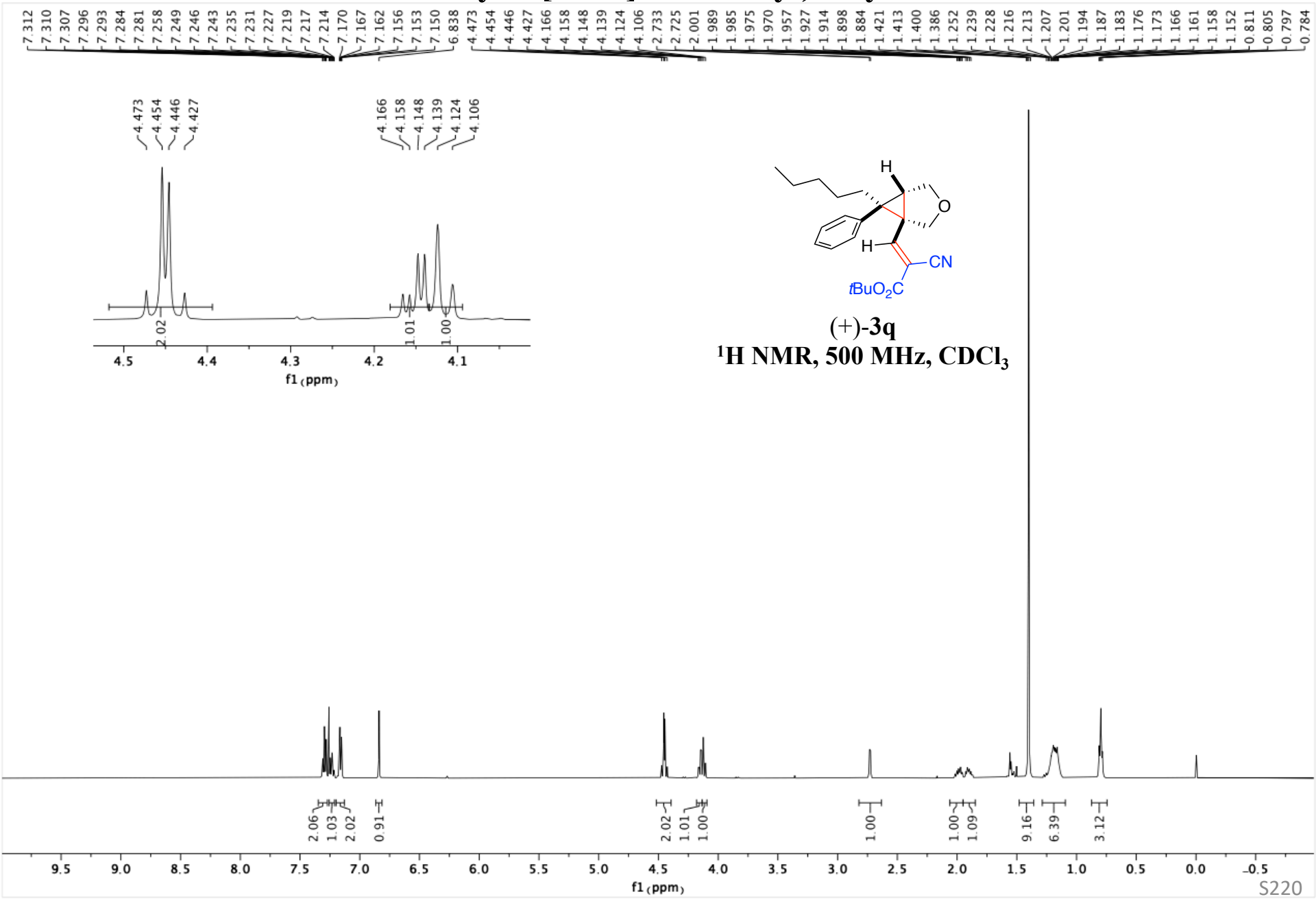


Peak Table

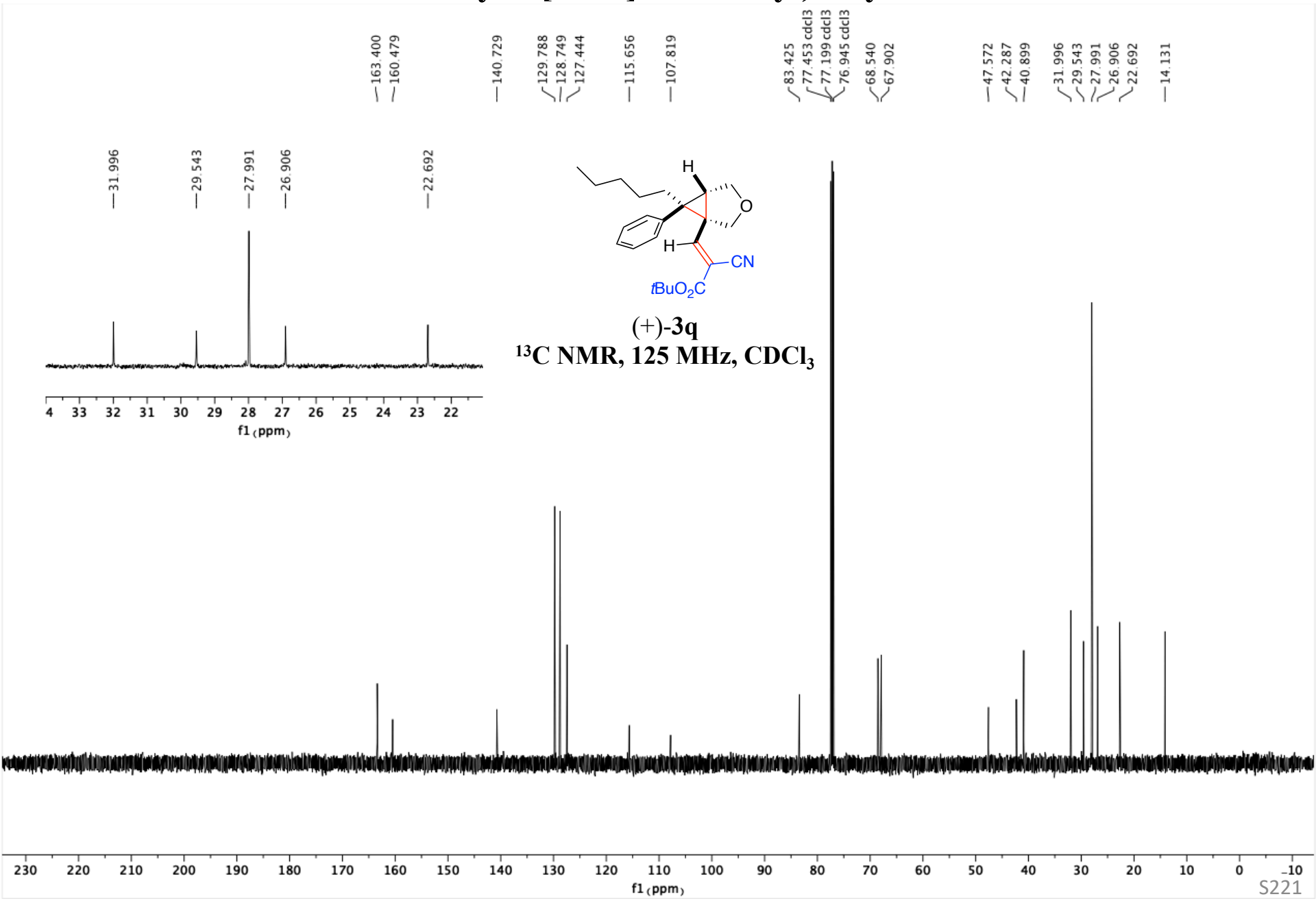
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	49.143	1449824	10.260
2	52.640	12680437	89.740
Total		14130261	100.000

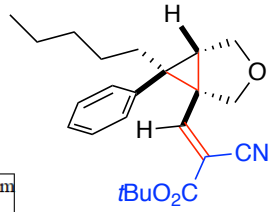
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-pentyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-pentyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-pentyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

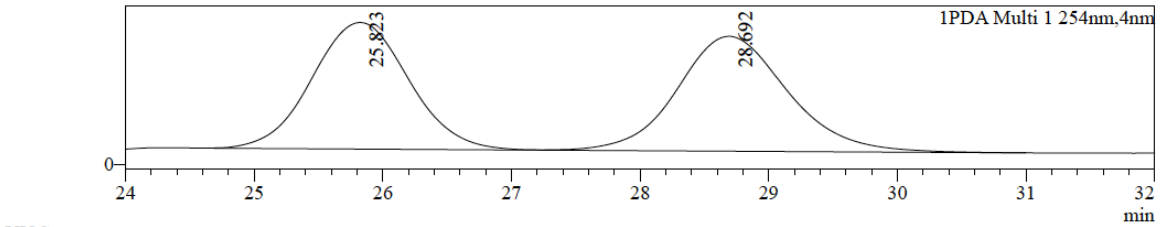


(±)-**3q**

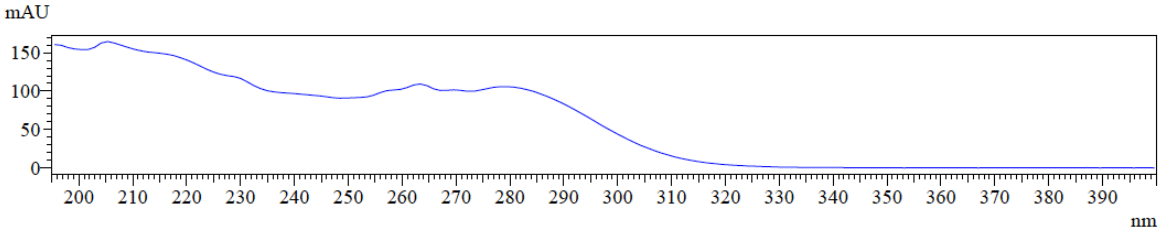
Sample Information

Sample Name	: CZZ-1064-whelk-5%1.0mL
Sample ID	: CZZ-1064-whelk-5%1.0mL
Data File	: CZZ-1064-whelk-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

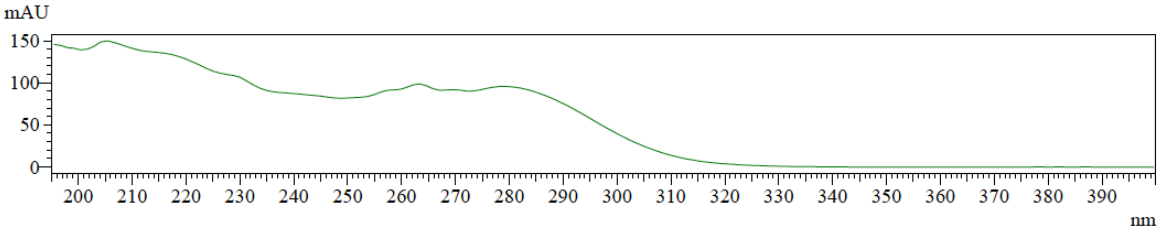
Chromatogram



UV Spectrum
Retention time = 25.823



UV Spectrum
Retention time = 28.692

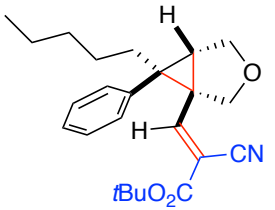


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.823	4423890	49.129
2	28.692	4580676	50.871
Total		9004566	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*,6*R*)-6-pentyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

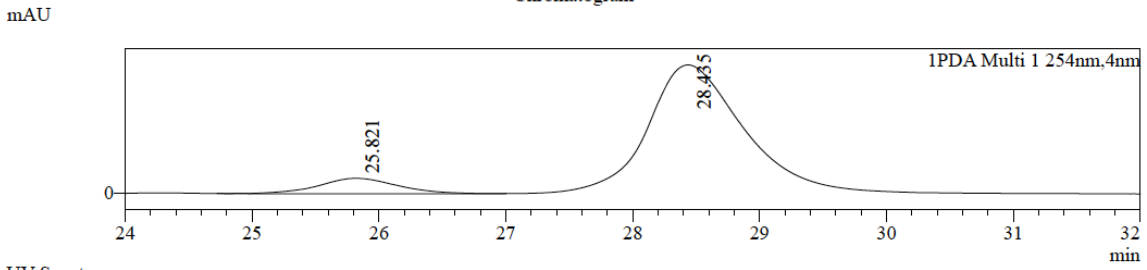


(+)-**3q**

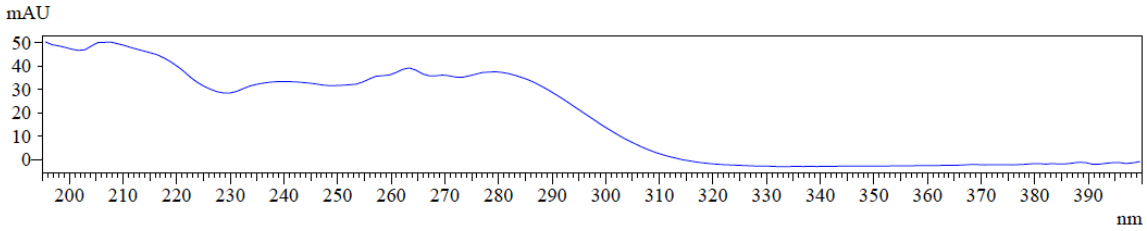
Sample Information

Sample Name	: CZZ-1065-whelk-5%1.0mL
Sample ID	: CZZ-1065-whelk-5%1.0mL
Data File	: CZZ-1065-whelk-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

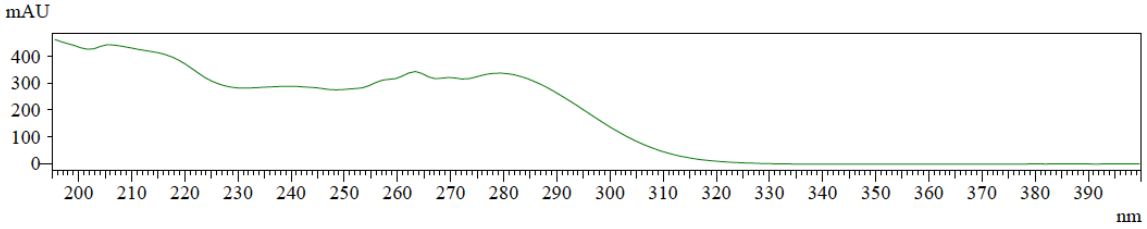
Chromatogram



UV Spectrum
Retention time = 25.821



UV Spectrum
Retention time = 28.435

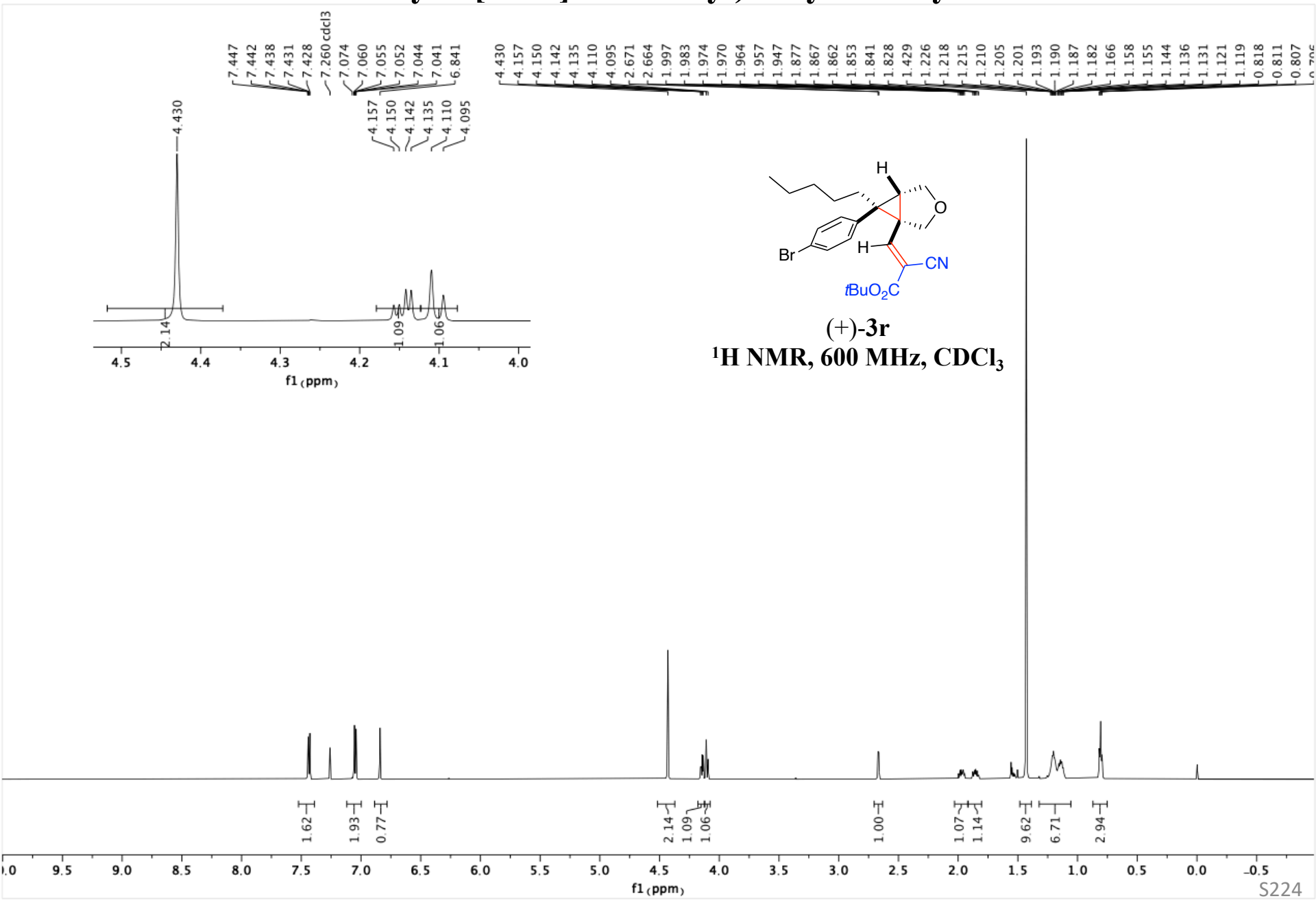


Peak Table

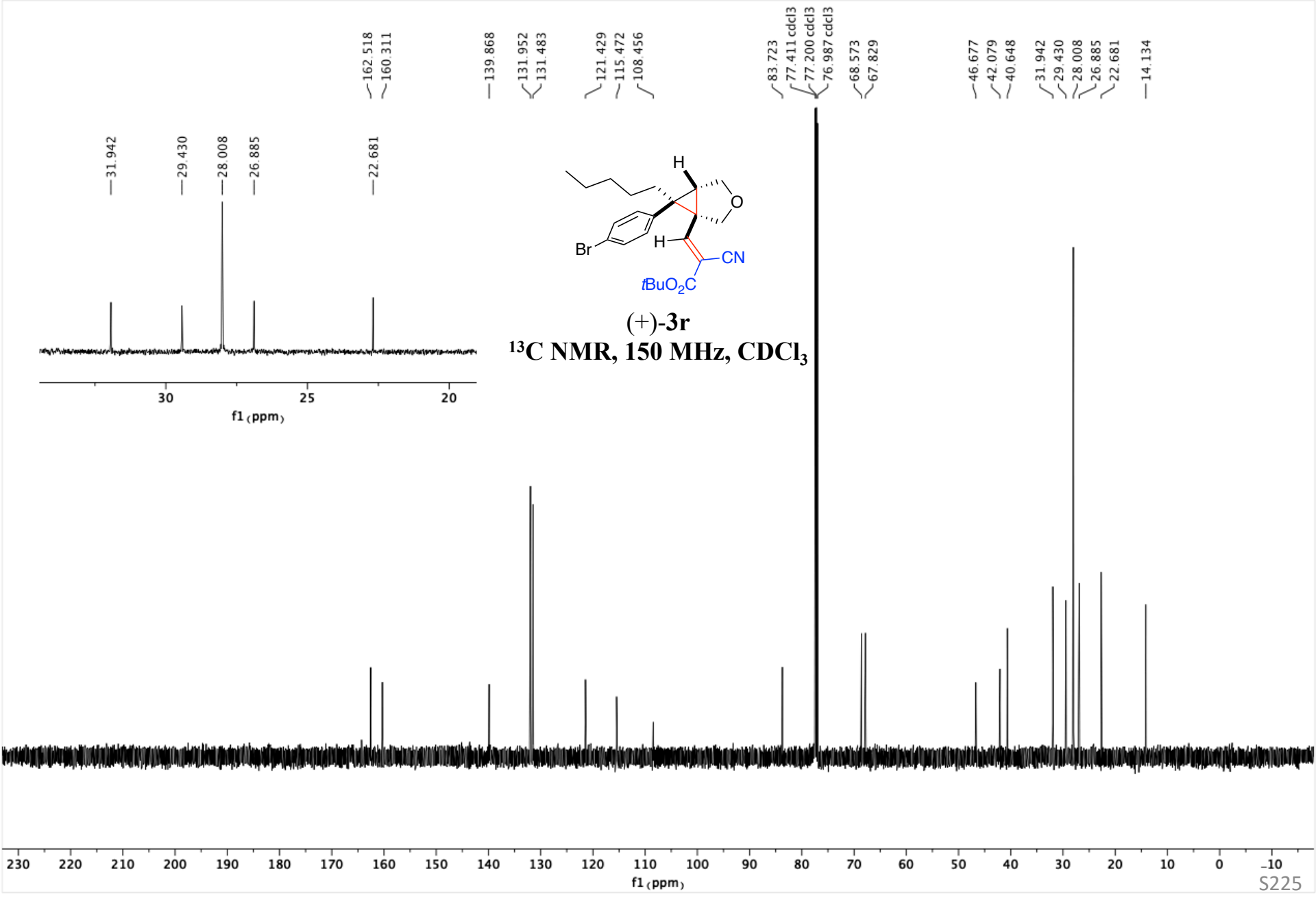
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.821	1501644	8.720
2	28.435	15719687	91.280
Total		17221331	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-bromophenyl)-6-pentyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



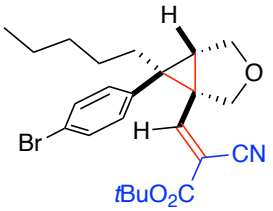
tert-butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-bromophenyl)-6-pentyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate



(+)-**3r**

^{13}C NMR, 150 MHz, $CDCl_3$

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-bromophenyl)-6-pentyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

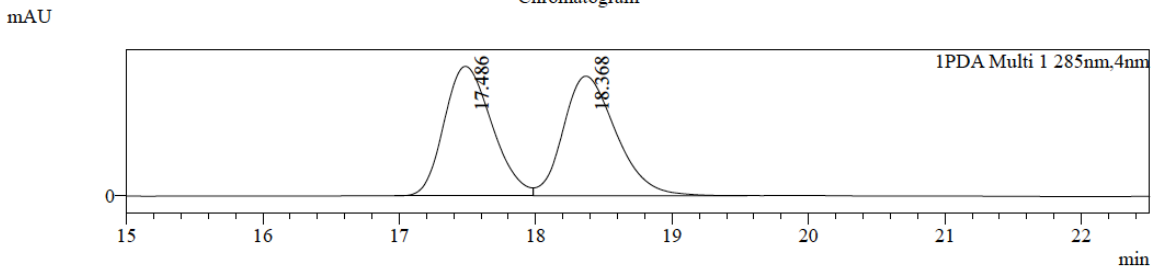


(±)-**3r**

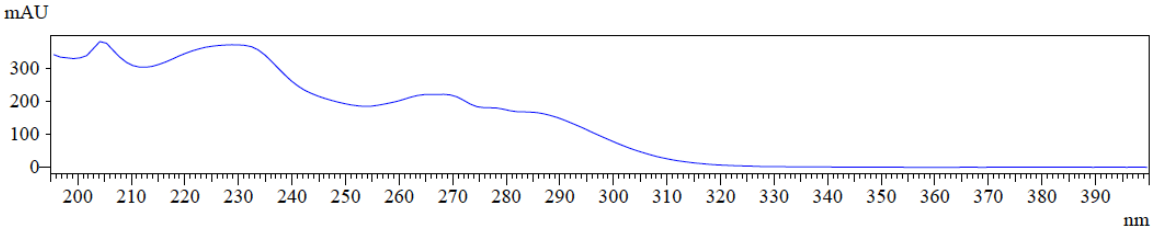
Sample Information

Sample Name	: CZZ-1095-IE-3%-1ML
Sample ID	: CZZ-1095-IE-3%-1ML
Data File	: CZZ-1095-IE-3%-1ML001.lcd
Method File	: CZZ-3.0%-1.0ml.lcm

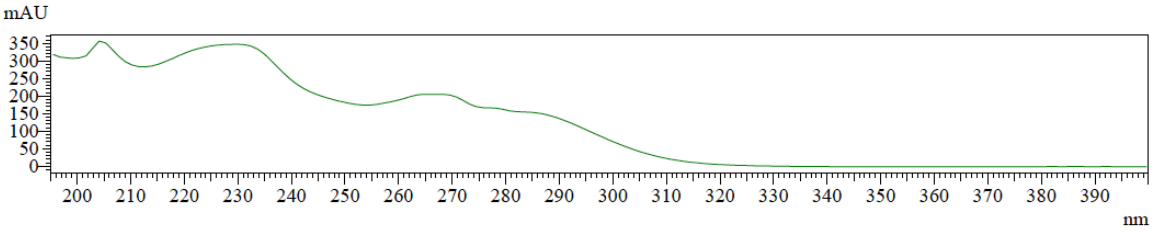
Chromatogram



UV Spectrum
Retention time = 17.486



UV Spectrum
Retention time = 18.368



Peak Table

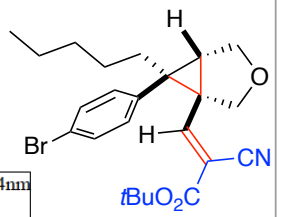
PDA Ch1 285nm

Peak#	Ret. Time	Area	Area%
1	17.486	4012718	49.574
2	18.368	4081638	50.426
Total		8094356	100.000

tert-Butyl (*E*)-3-((1*S*,5*S*,6*R*)-6-(4-bromophenyl)-6-pentyl-3-oxabicyclo[3.1.0]hexan-1-yl)-2-cyanoacrylate

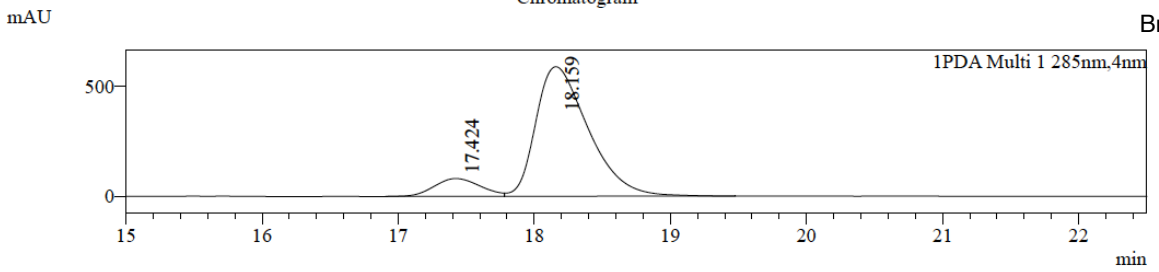
Sample Information

Sample Name	: CZZ-1096-IE-3%-1ML
Sample ID	: CZZ-1096-IE-3%-1ML
Data File	: CZZ-1096-IE-3%-1ML.lcd
Method File	: CZZ-3.0%-1.0ml.lcm

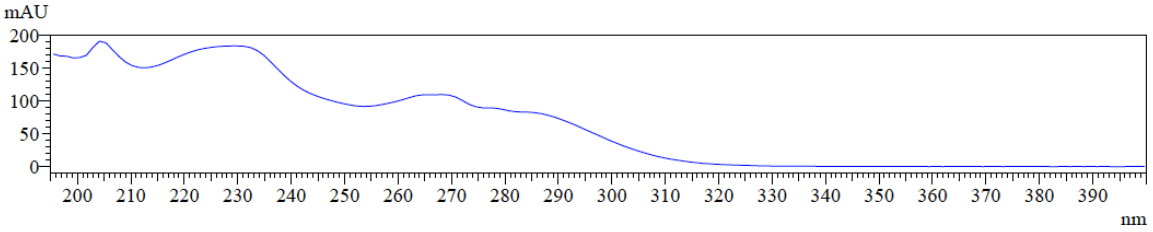


(+)-**3r**

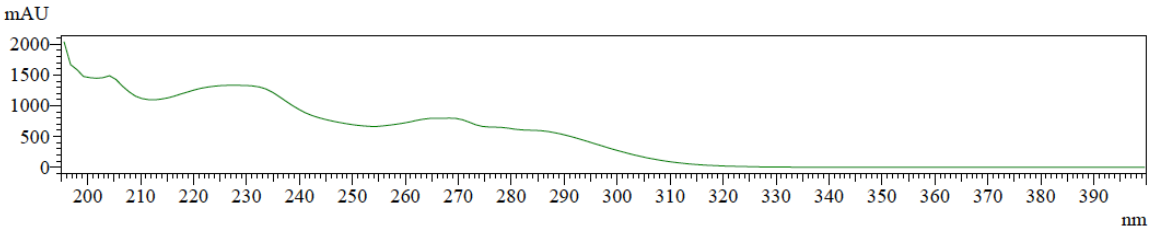
Chromatogram



UV Spectrum
Retention time = 17.424



UV Spectrum
Retention time = 18.159

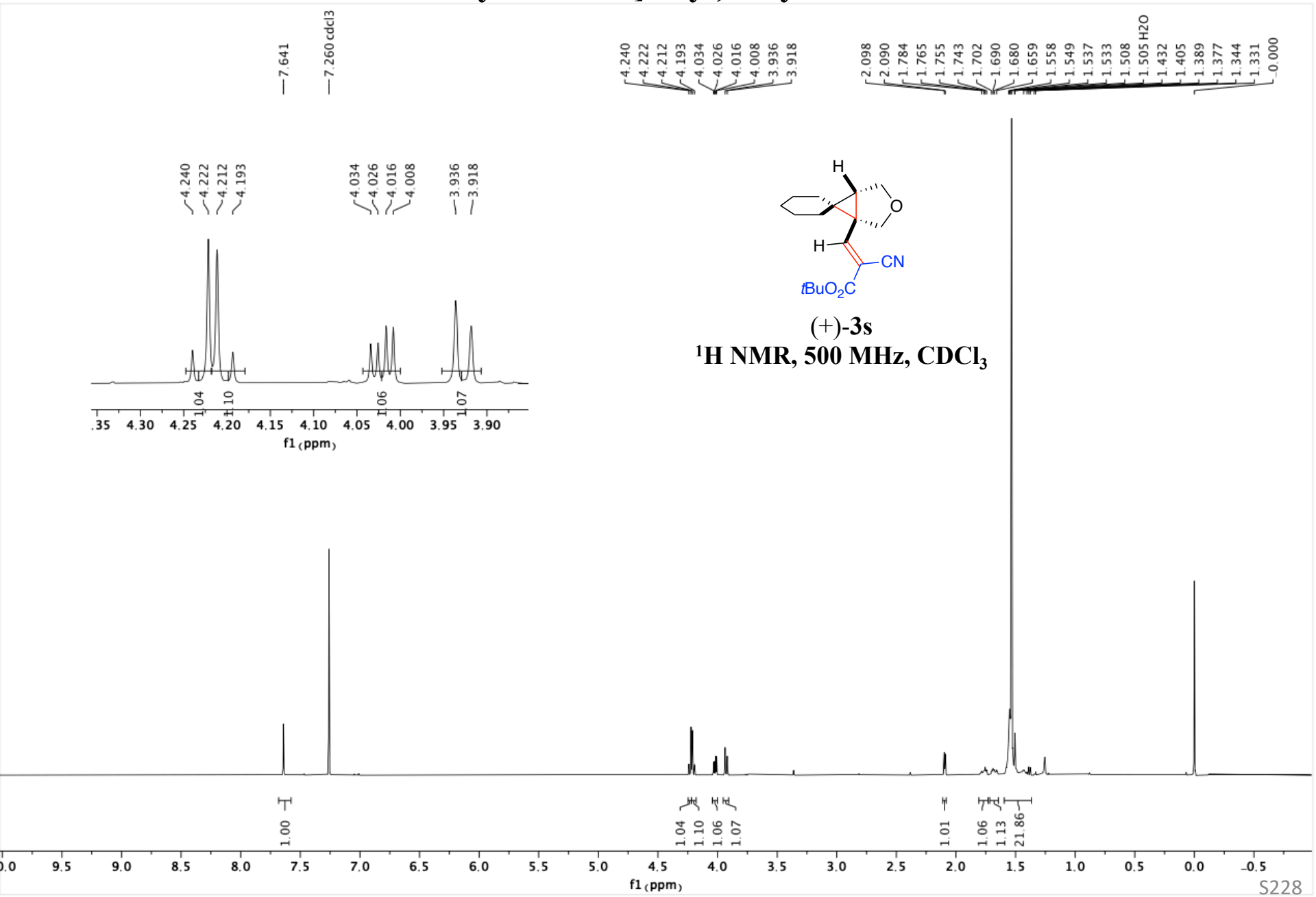


Peak Table

PDA Ch1 285nm

Peak#	Ret. Time	Area	Area%
1	17.424	1905659	10.783
2	18.159	15767824	89.217
Total		17673483	100.000

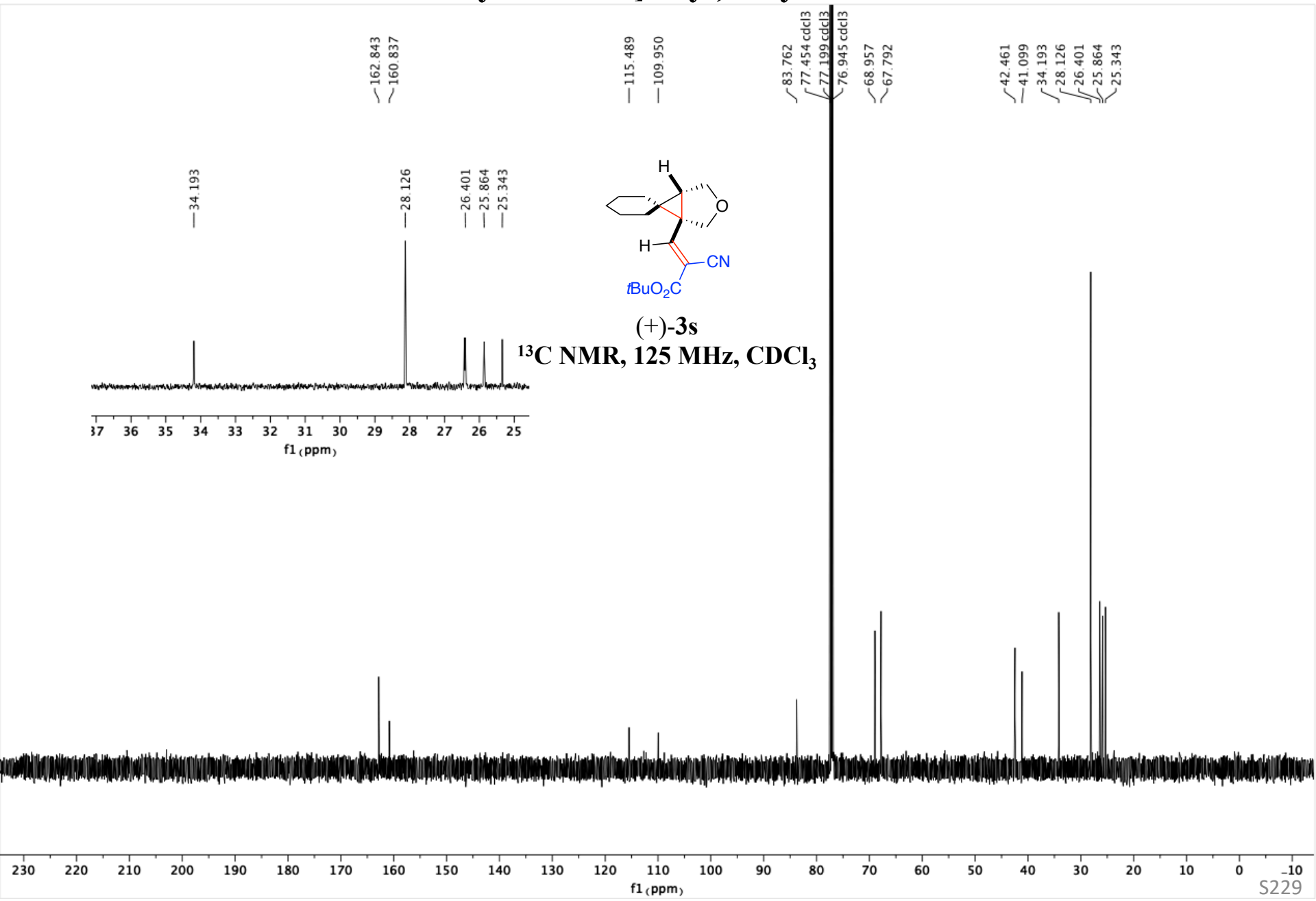
tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-3-oxaspiro[bicyclo[3.1.0]hexane-6,1'-cyclohexan]-1-yl)acrylate



(+)-**3s**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-3-oxaspiro[bicyclo[3.1.0]hexane-6,1'-cyclohexan]-1-yl)acrylate



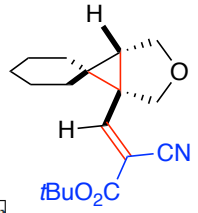
(+)-**3s**

^{13}C NMR, 125 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-3-oxaspiro[bicyclo[3.1.0]hexane-6,1'-cyclohexan]-1-yl)acrylate

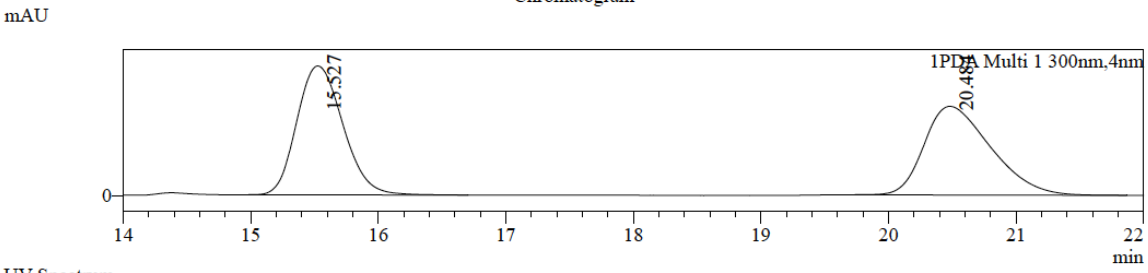
Sample Information

Sample Name	: CZZ-1116-iD-5%1.0mL
Sample ID	: CZZ-1116-iD-5%1.0mL
Data File	: CZZ-1116-iD-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

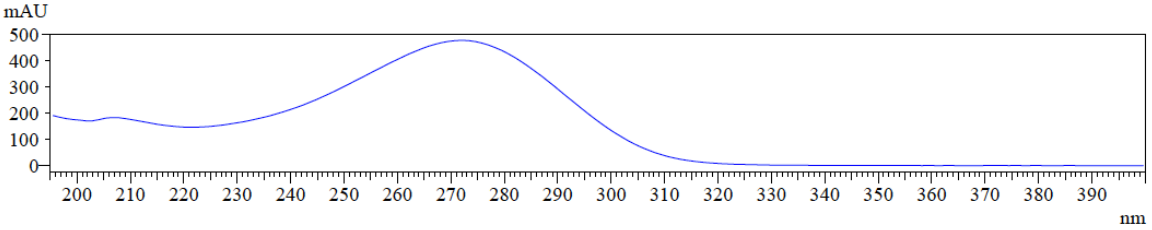


(±)-**3s**

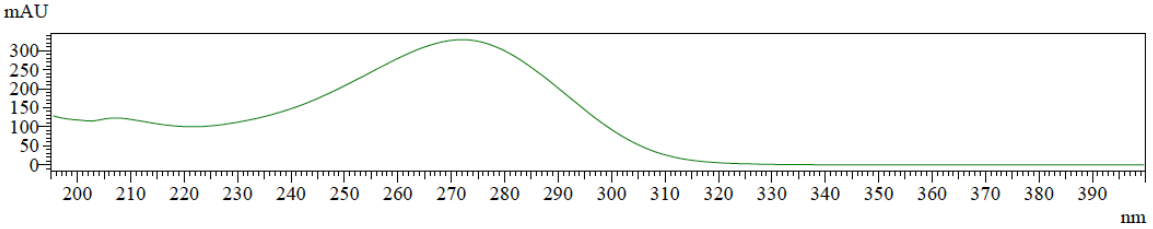
Chromatogram



UV Spectrum
Retention time = 15.527



UV Spectrum
Retention time = 20.484

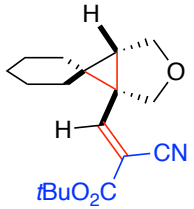


Peak Table

PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%
1	15.527	3386234	50.172
2	20.484	3363019	49.828
Total		6749253	100.000

tert-Butyl (*E*)-2-cyano-3-((1*S*,5*S*)-3-oxaspiro[bicyclo[3.1.0]hexane-6,1'-cyclohexan]-1-yl)acrylate

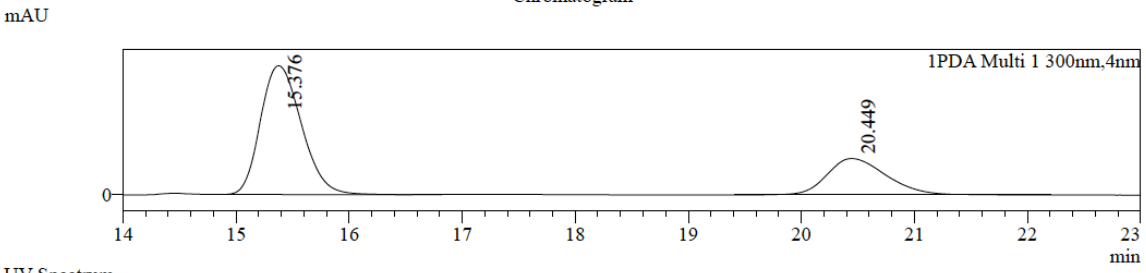


(+)-**3s**

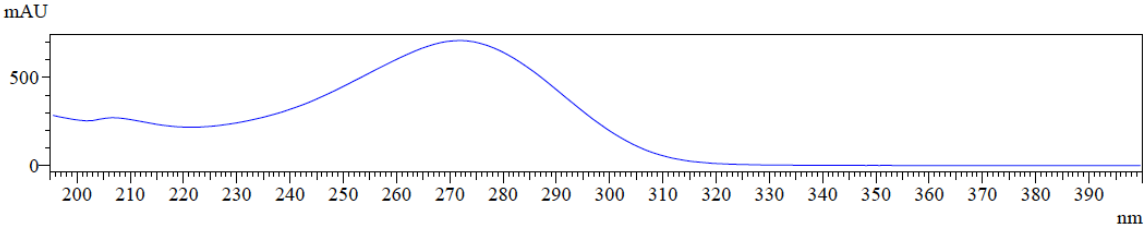
Sample Information

Sample Name	: CZZ-1117-iD-5%1.0mL
Sample ID	: CZZ-1117-iD-5%1.0mL
Data File	: CZZ-1117-iD-5%1.0mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

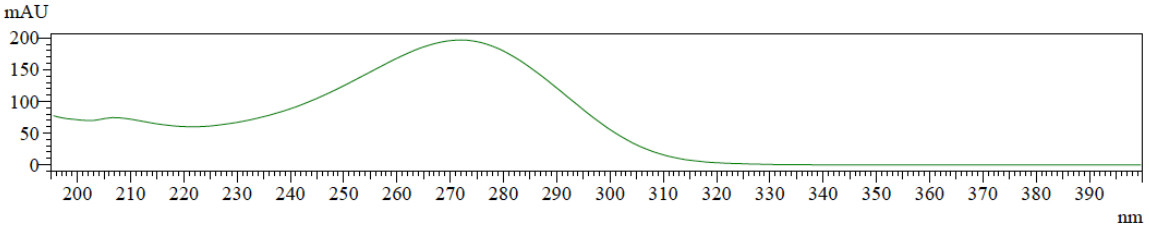
Chromatogram



UV Spectrum
Retention time = 15.376



UV Spectrum
Retention time = 20.449

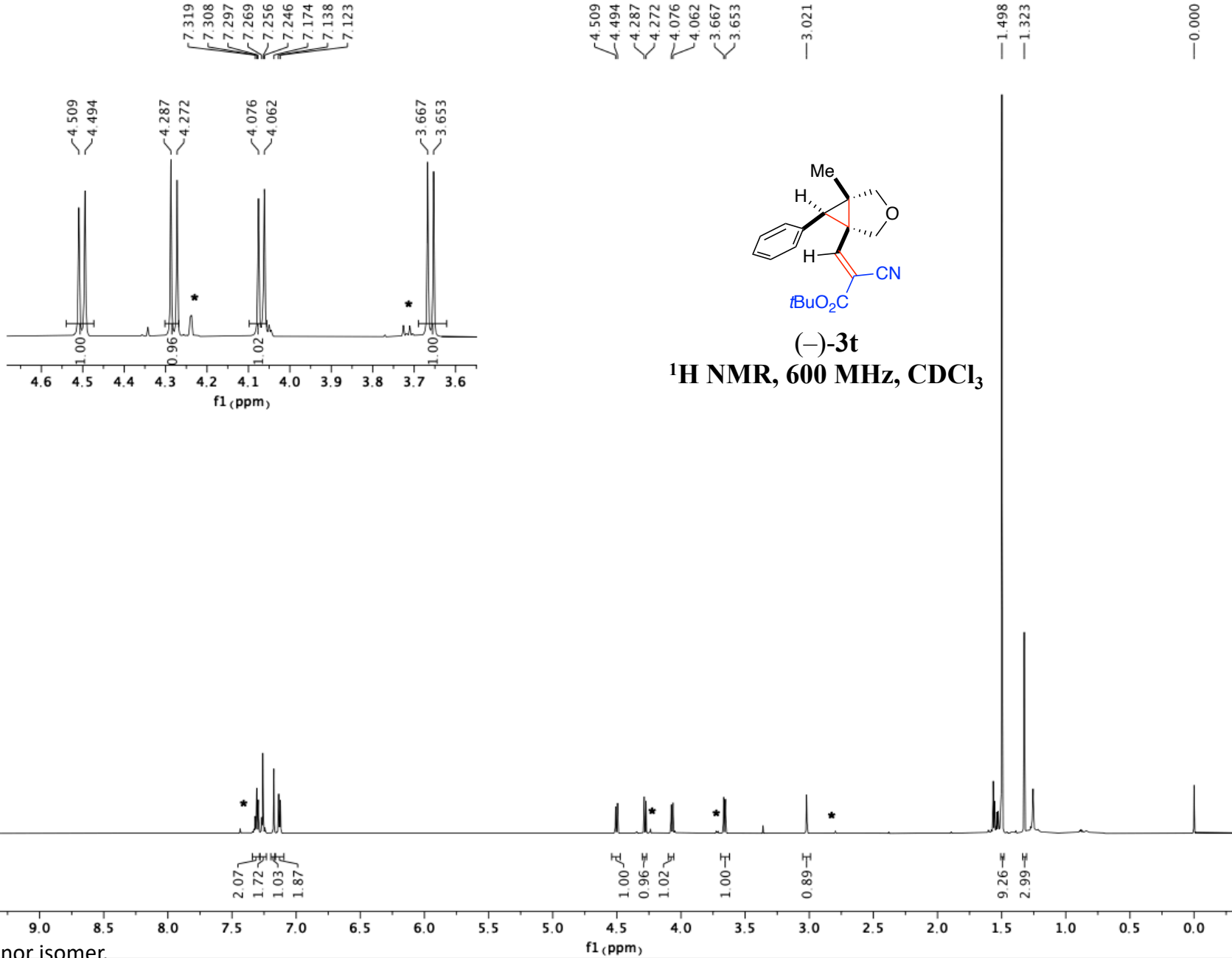


Peak Table

PDA Ch1 300nm

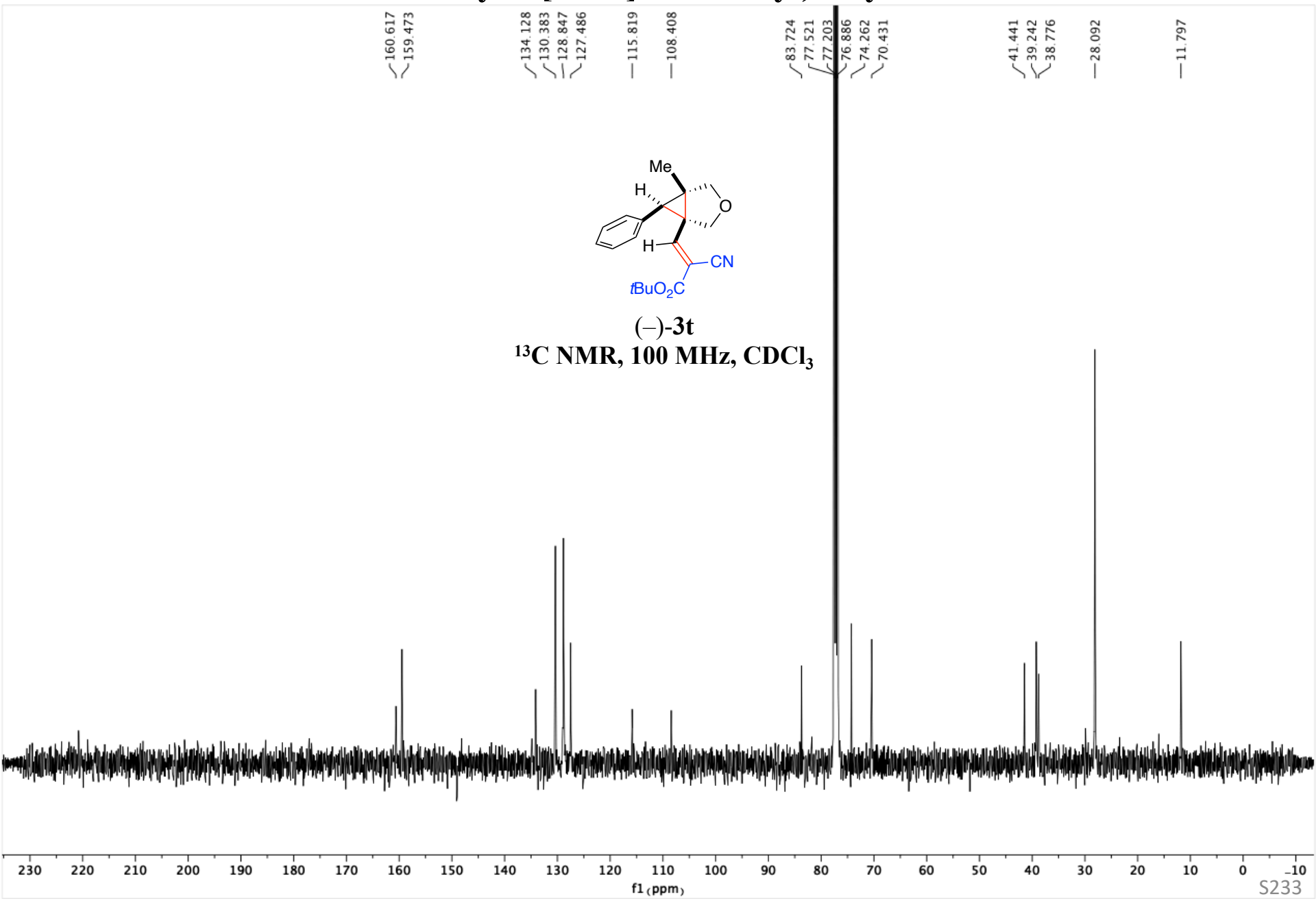
Peak#	Ret. Time	Area	Area%
1	15.376	4979177	70.780
2	20.449	2055582	29.220
Total		7034759	100.000

tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



* are minor isomer.

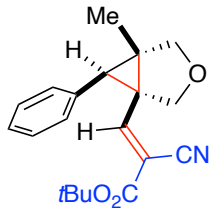
tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



(–)-**3t**

^{13}C NMR, 100 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

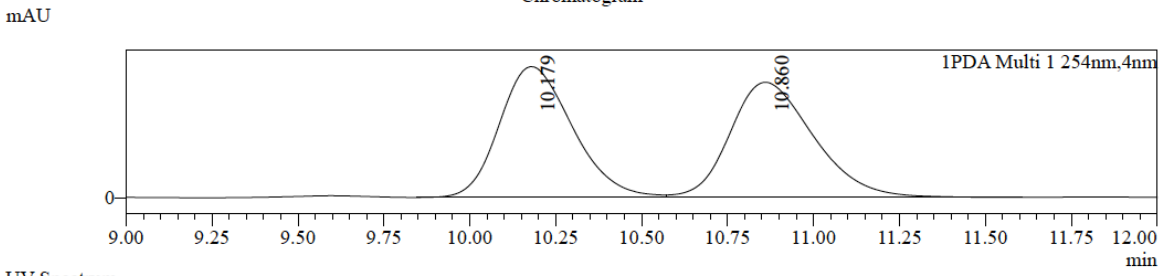


(±)-**3t**

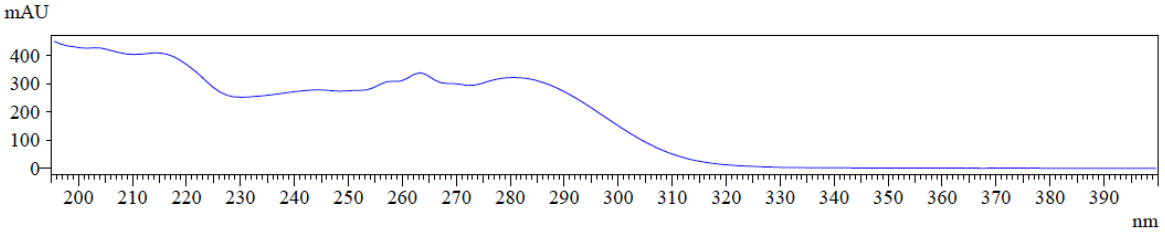
Sample Information

Sample Name	: CZZ-1425-ID-5%-1mL
Sample ID	: CZZ-1425-ID-5%-1mL
Data File	: CZZ-1425-ID-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

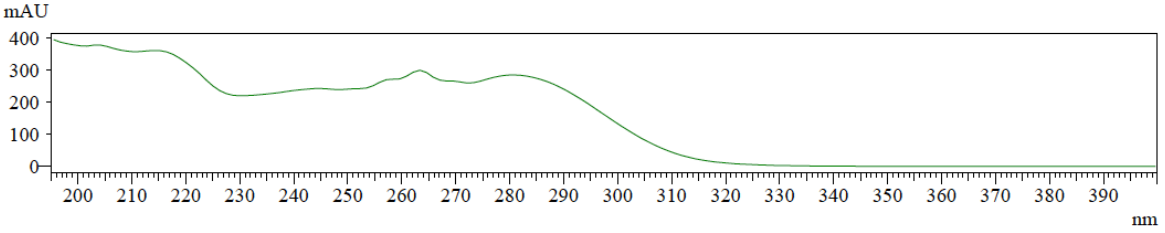
Chromatogram



UV Spectrum
Retention time = 10.179



UV Spectrum
Retention time = 10.860

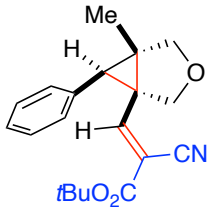


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.179	4227717	49.885
2	10.860	4247177	50.115
Total		8474894	100.000

tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate

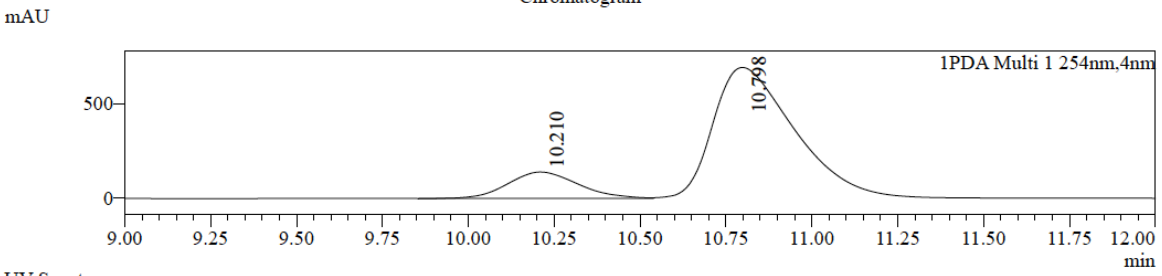


(–)-**3t**

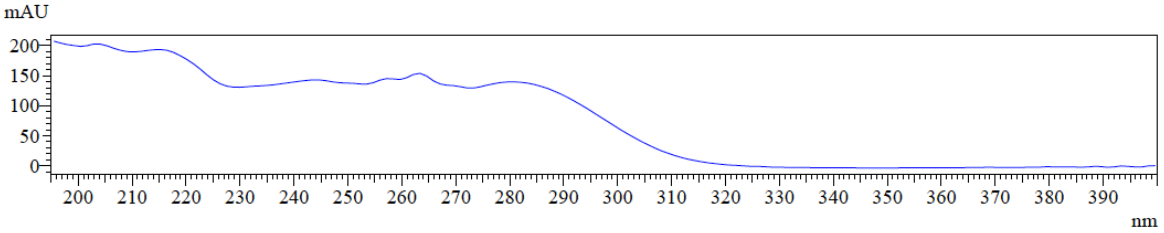
Sample Information

Sample Name	: CZZ-1426-ID-5%-1mL
Sample ID	: CZZ-1426-ID-5%-1mL
Data File	: CZZ-1426-ID-5%-1mL.lcd
Method File	: CZZ-5.0%-1.0ml.lcm

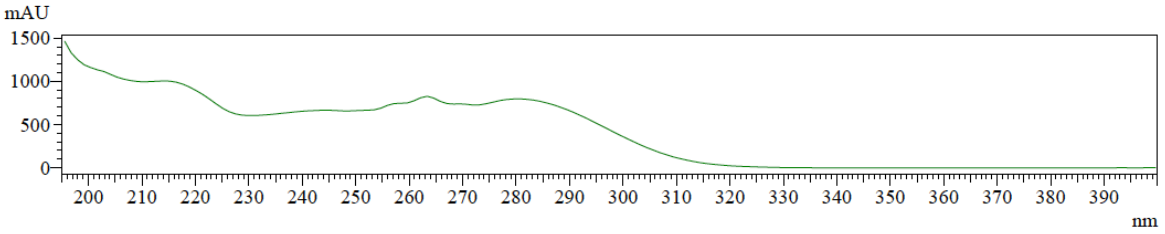
Chromatogram



UV Spectrum
Retention time = 10.210



UV Spectrum
Retention time = 10.798

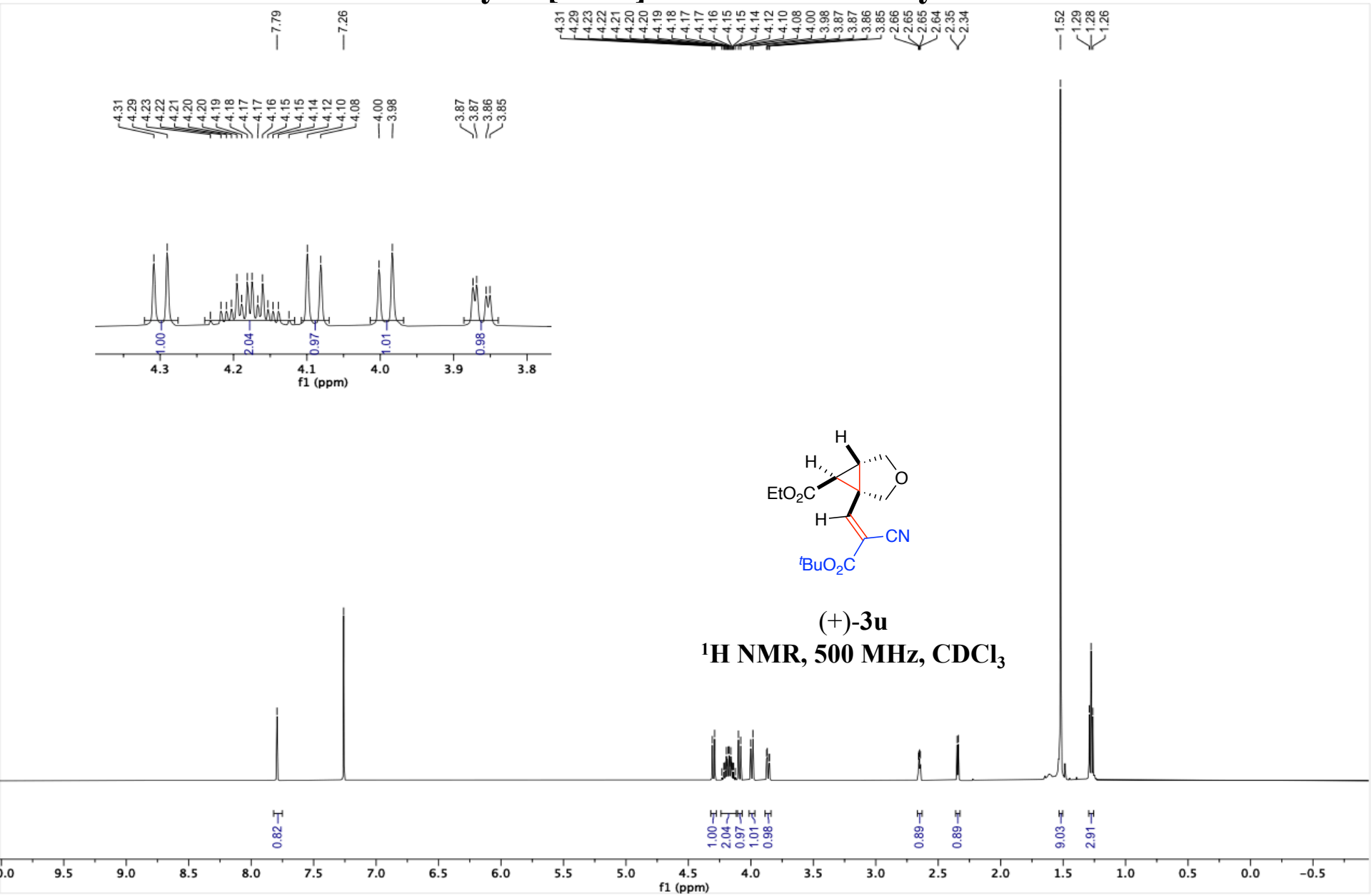


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.210	2006925	14.870
2	10.798	11489273	85.130
Total		13496198	100.000

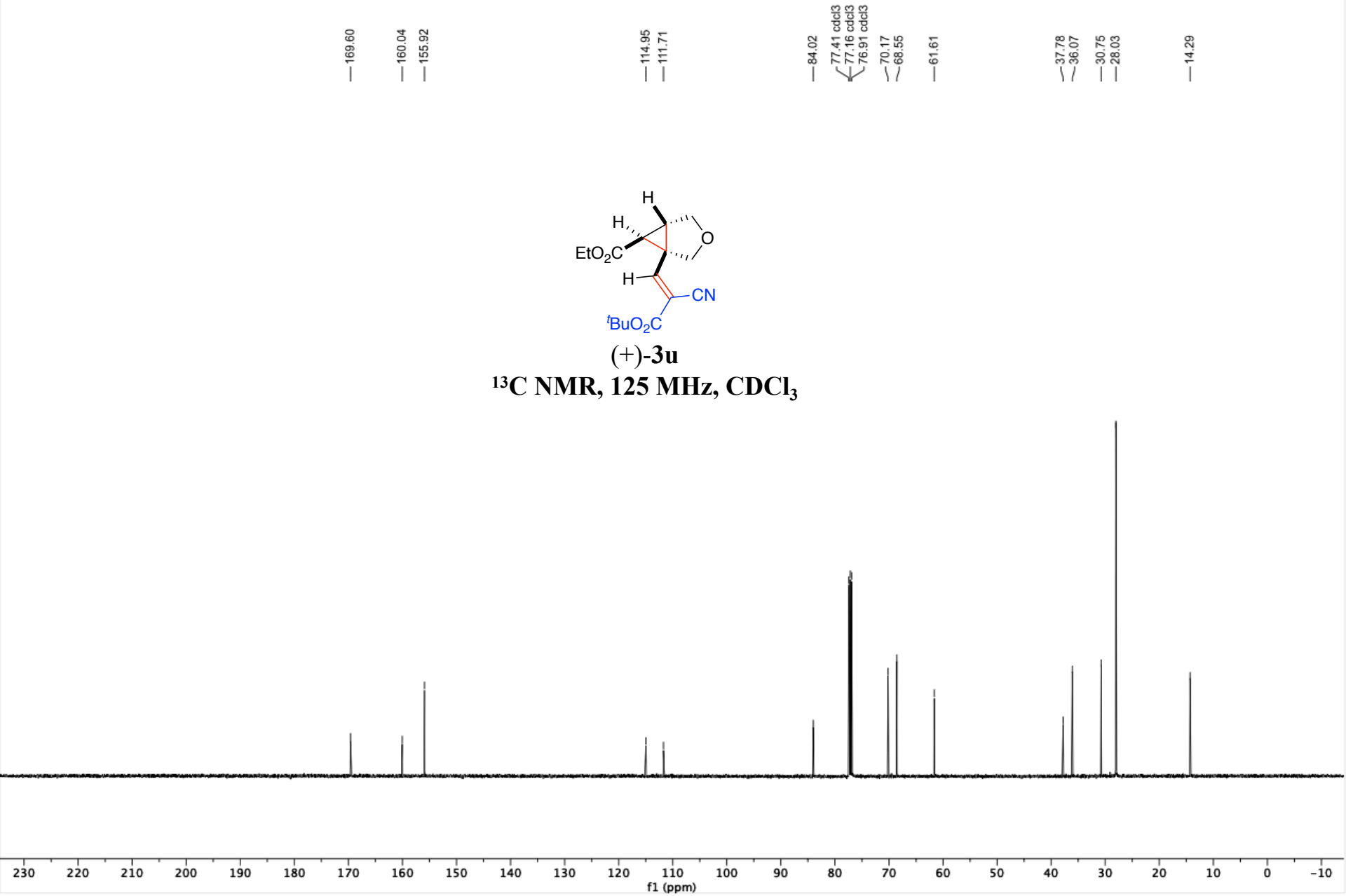
Ethyl (1*S*,5*S*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-6-carboxylate



(+)-**3u**

^{1}H NMR, 500 MHz, $CDCl_3$

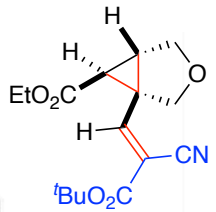
Ethyl (1*S*,5*S*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-6-carboxylate



(+)-**3u**

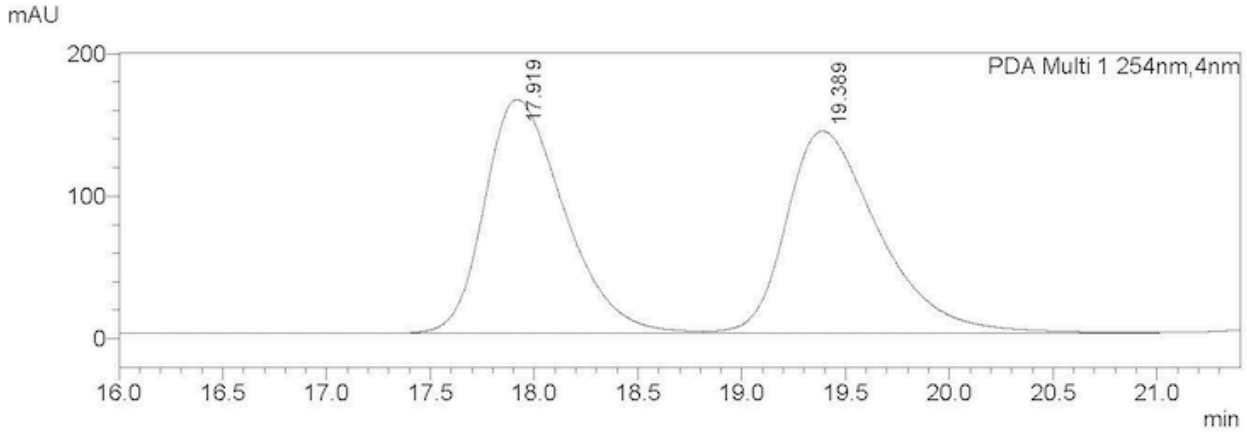
^{13}C NMR, 125 MHz, $CDCl_3$

Ethyl (1*S*,5*S*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-6-carboxylate



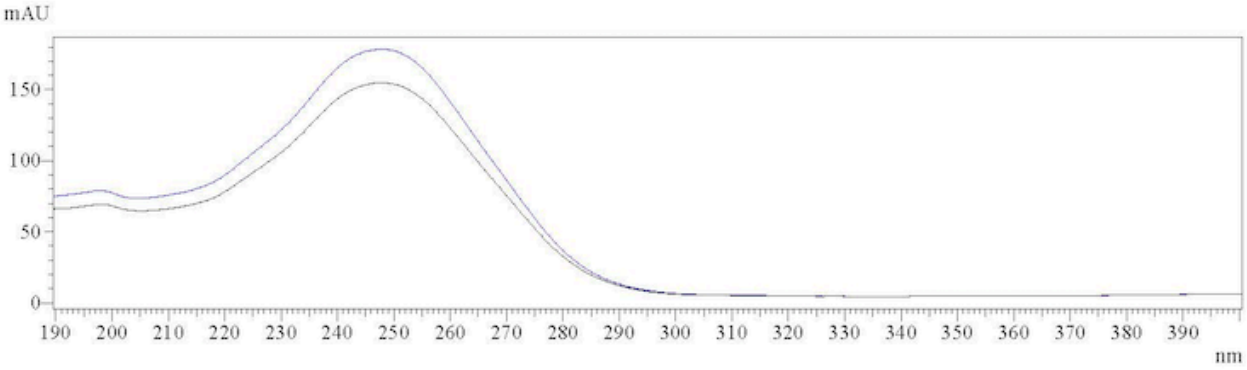
(±)-**3u**

DSW-2958-IE-5%0.8mL
DSW-5%-60min0.8mL.lcm



UV Spectrum

DSW-2958-IE-5%0.8mL_001.lcd

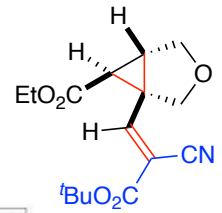


Peak Table

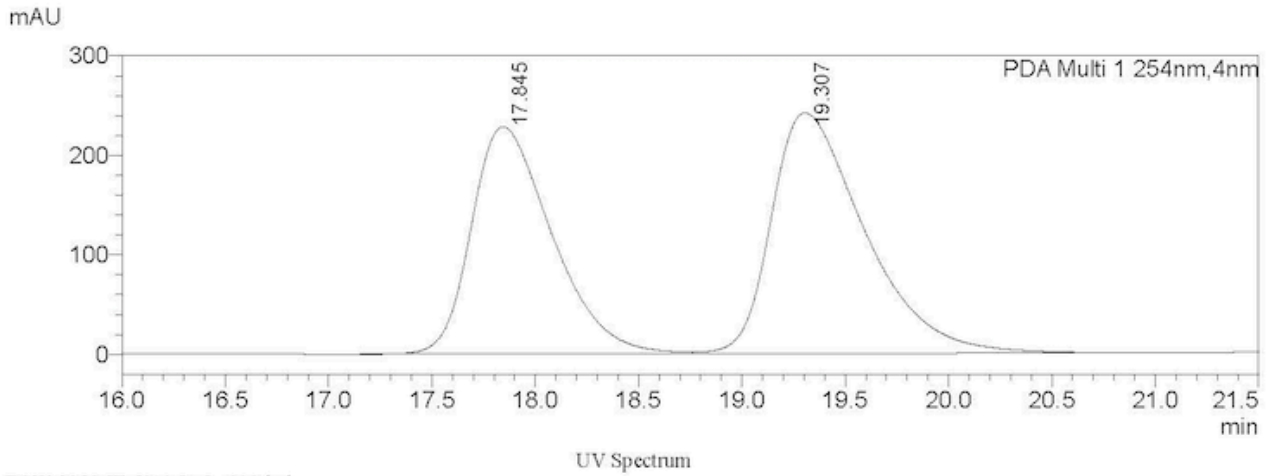
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	17.919	49.762
2	19.389	50.238
Total		100.000

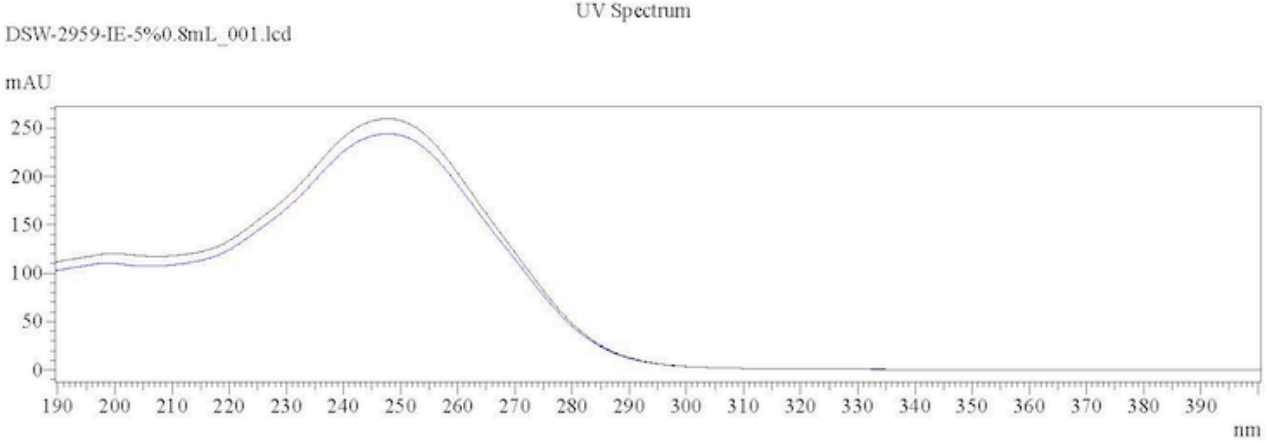
Ethyl (1*S*,5*S*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-6-carboxylate



(+)-**3u**



UV Spectrum

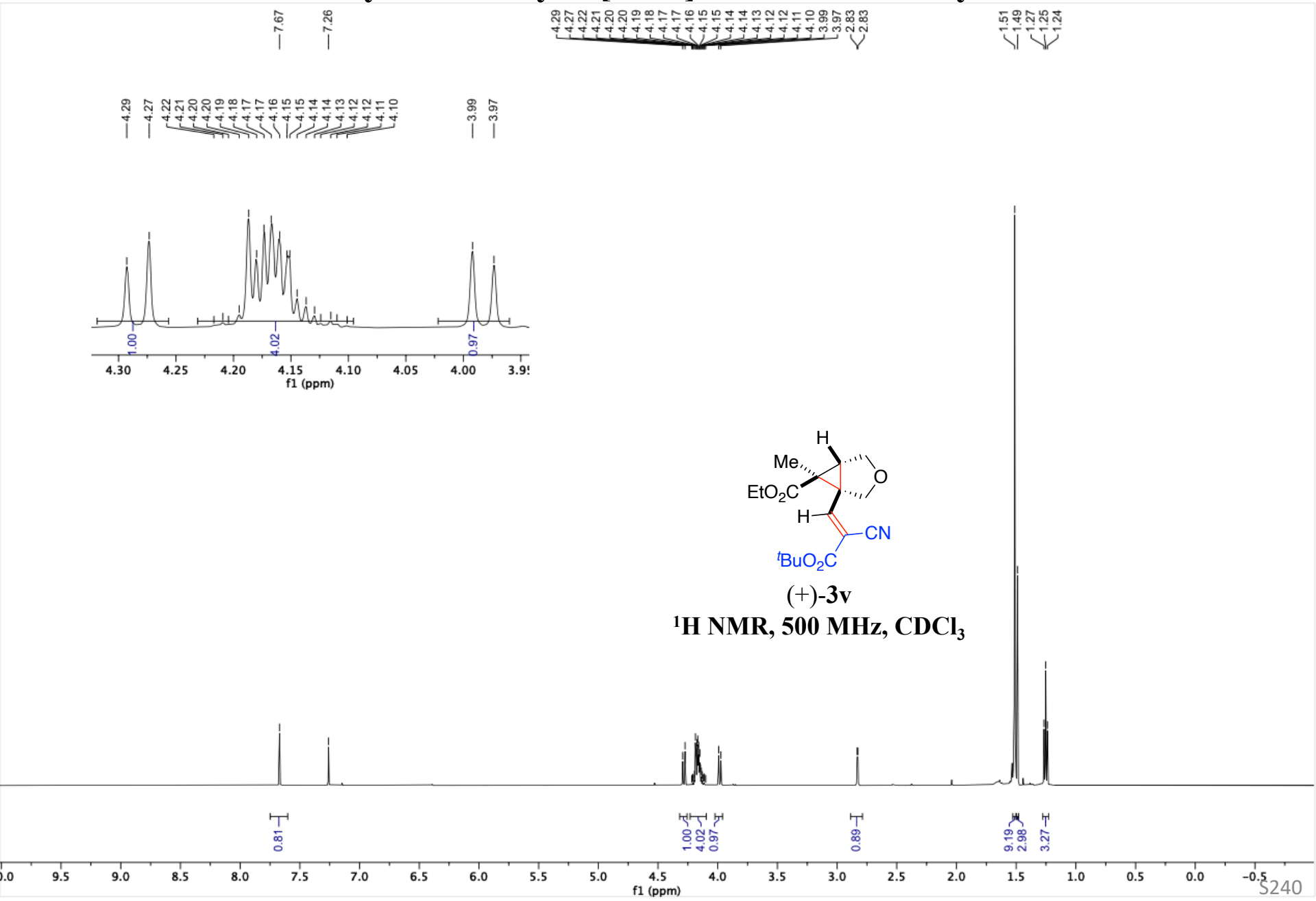


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	17.845	44.791
2	19.307	55.209
Total		100.000

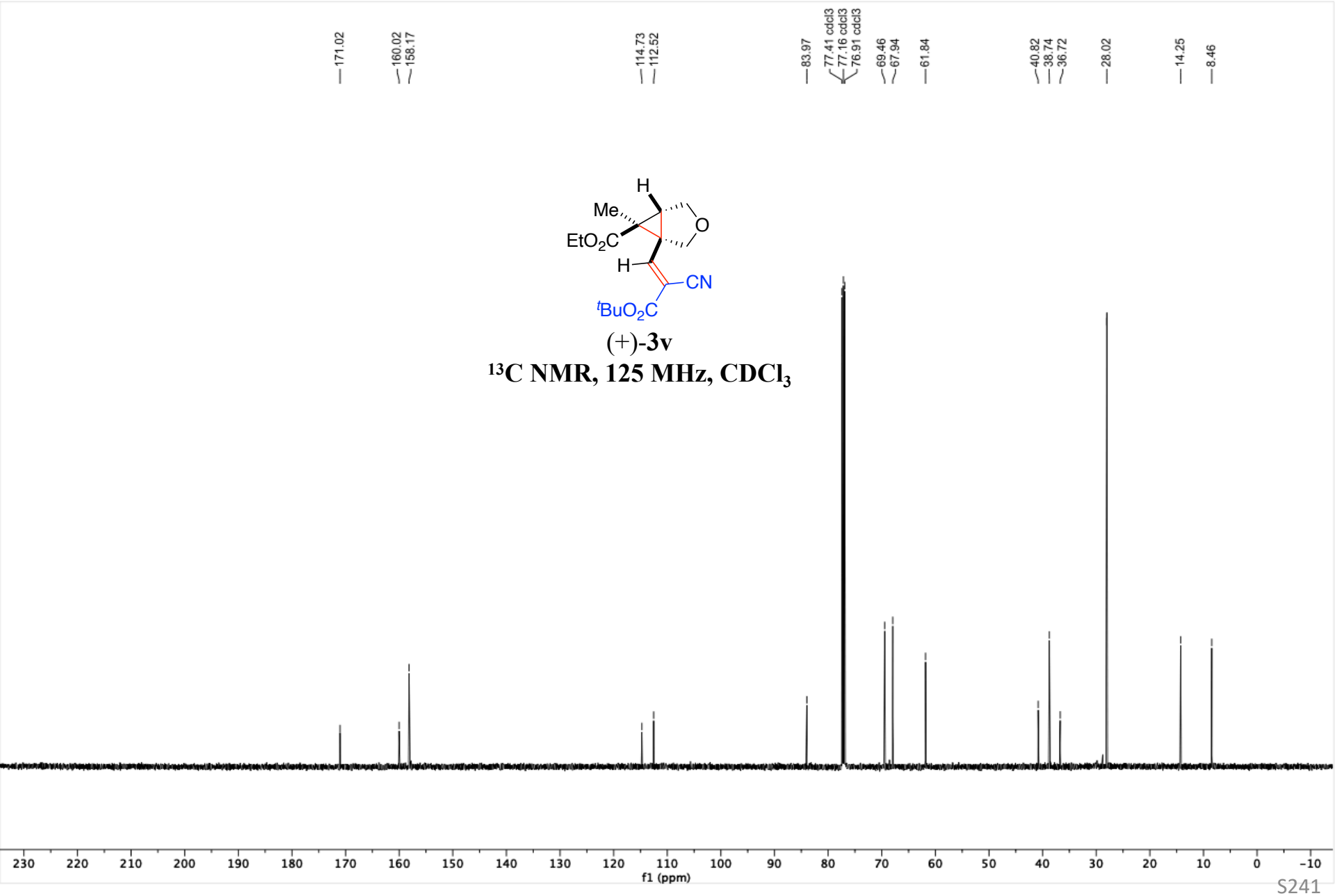
Ethyl (1*S*,5*R*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-6-methyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate



(+)-**3v**

^{1}H NMR, 500 MHz, $CDCl_3$

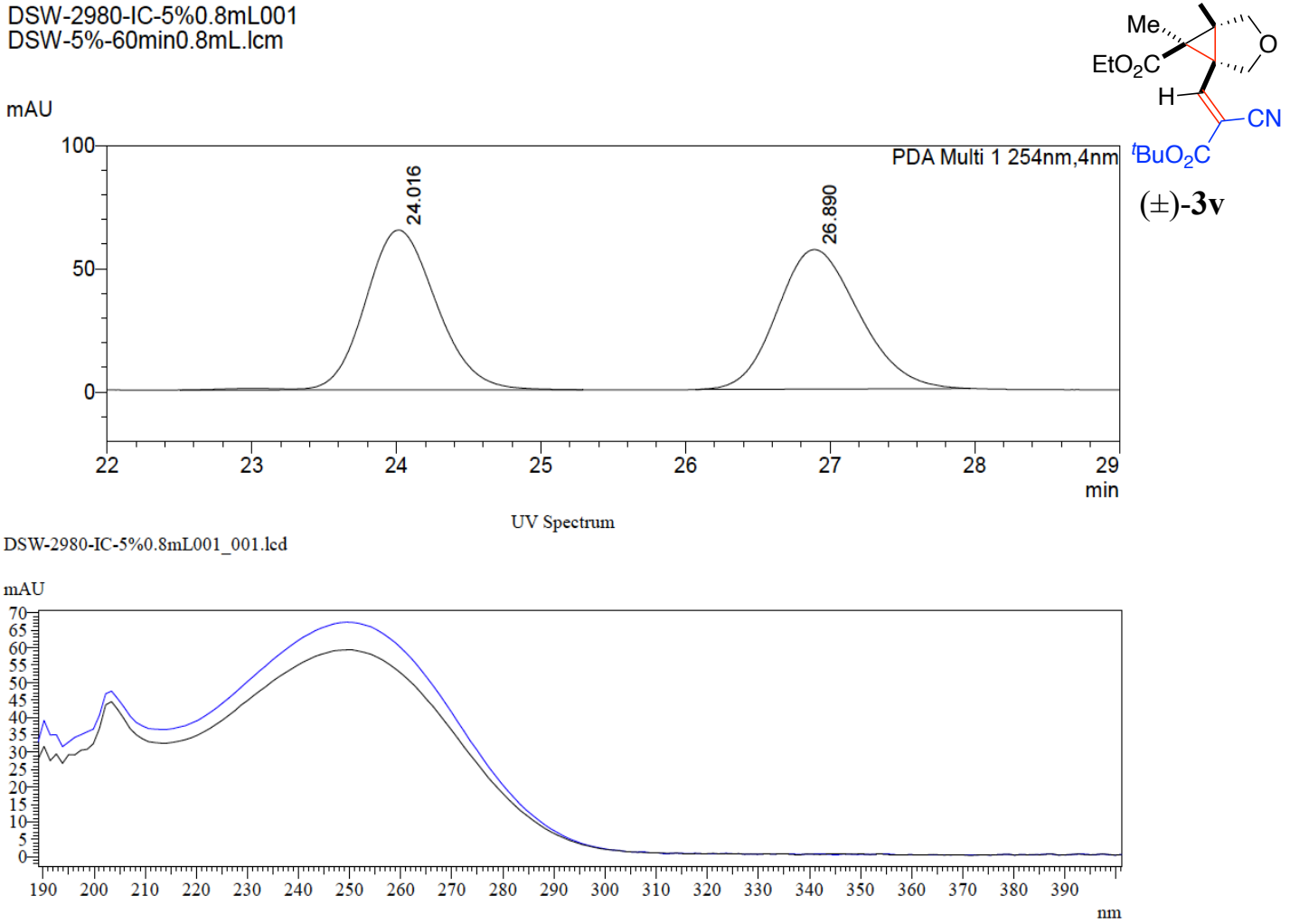
Ethyl (1*S*,5*R*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-6-methyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate

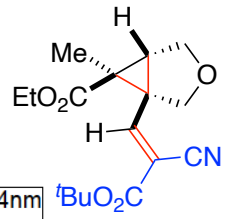


(+)-**3v**

^{13}C NMR, 125 MHz, $CDCl_3$

Ethyl (1*S*,5*R*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-6-methyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate





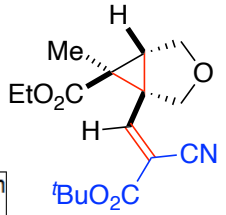
(±)-**3v**

Peak Table

PDA Ch1 254nm

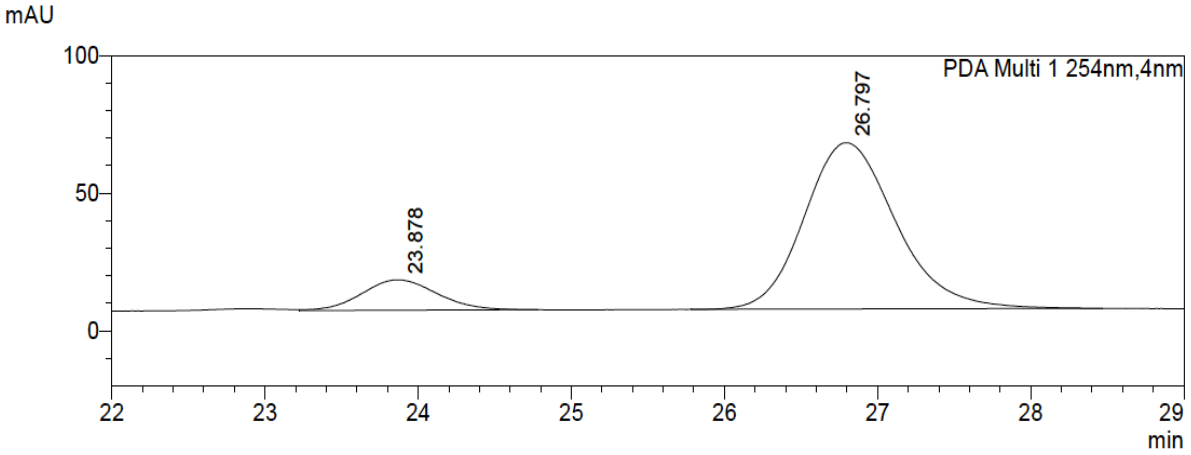
Peak#	Ret. Time	Area%
1	24.016	49.881
2	26.890	50.119
Total		100.000

Ethyl (1*S*,5*R*,6*S*)-1-((*E*)-3-(*tert*-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-6-methyl-3-oxabicyclo[3.1.0]hexane-6-carboxylate



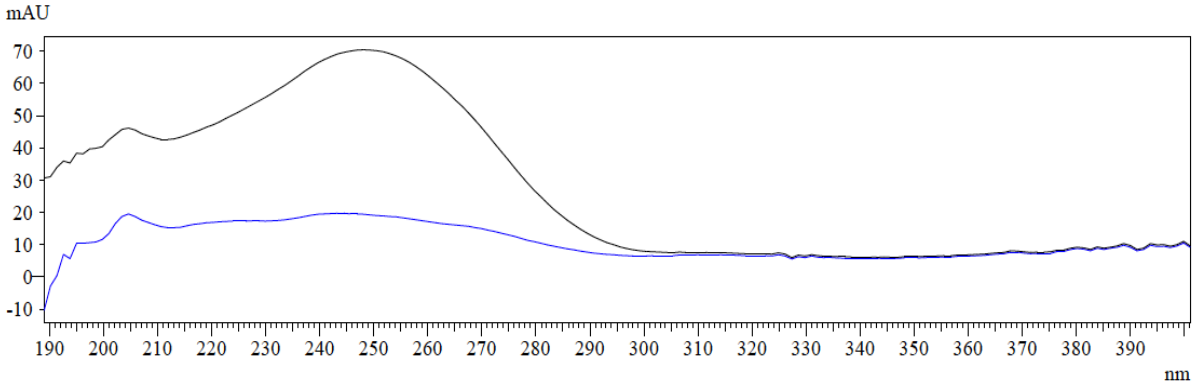
(+)-**3v**

DSW-2981-IC-5%0.8mL
DSW-5%-60min0.8mL.lcm



UV Spectrum

DSW-2981-IC-5%0.8mL_001.lcd

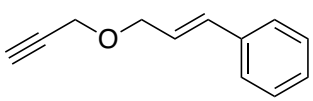


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	23.878	13.021
2	26.797	86.979
Total		100.000

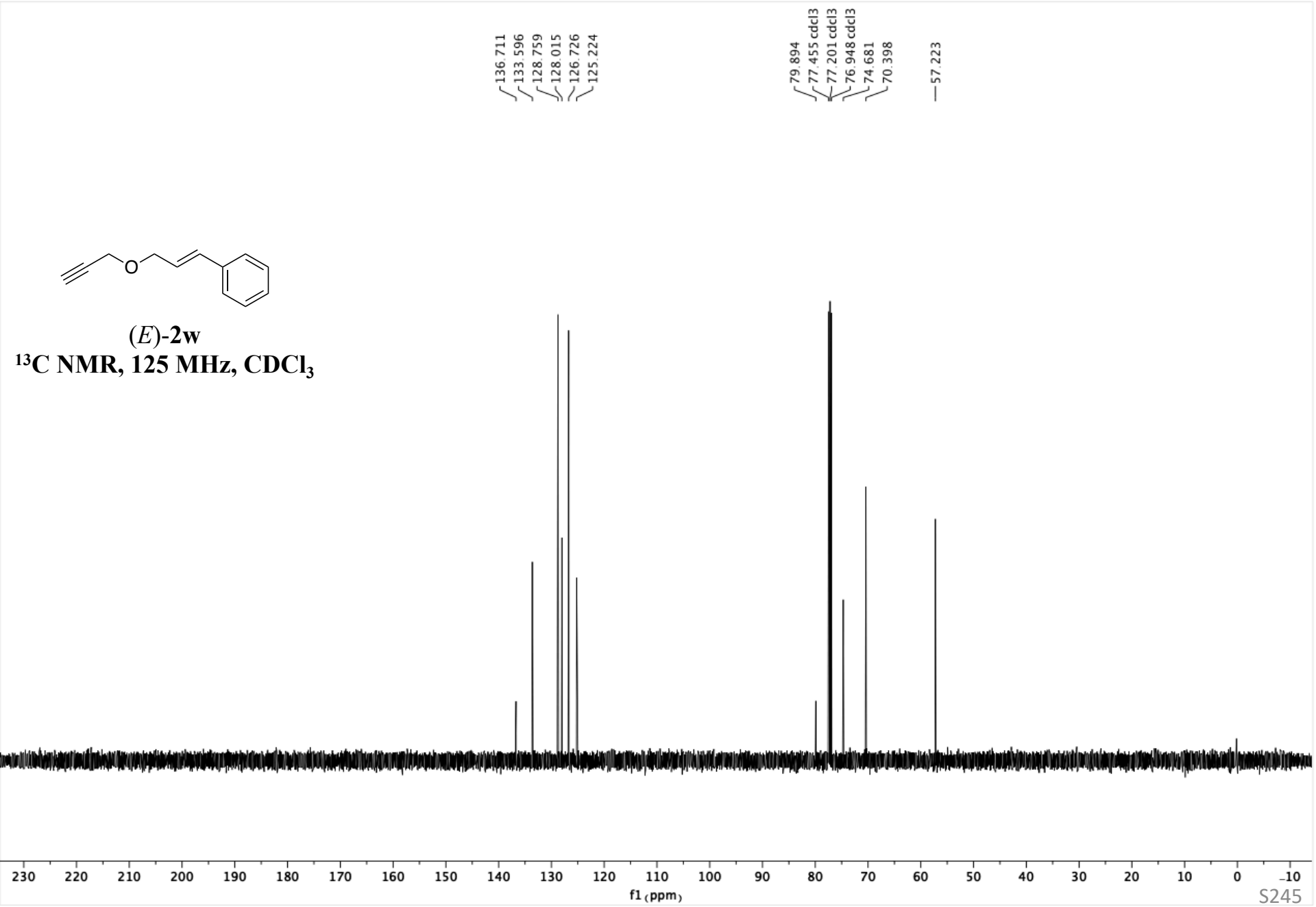
(*E*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



(*E*)-**2w**

^{1}H NMR, 500 MHz, $CDCl_3$

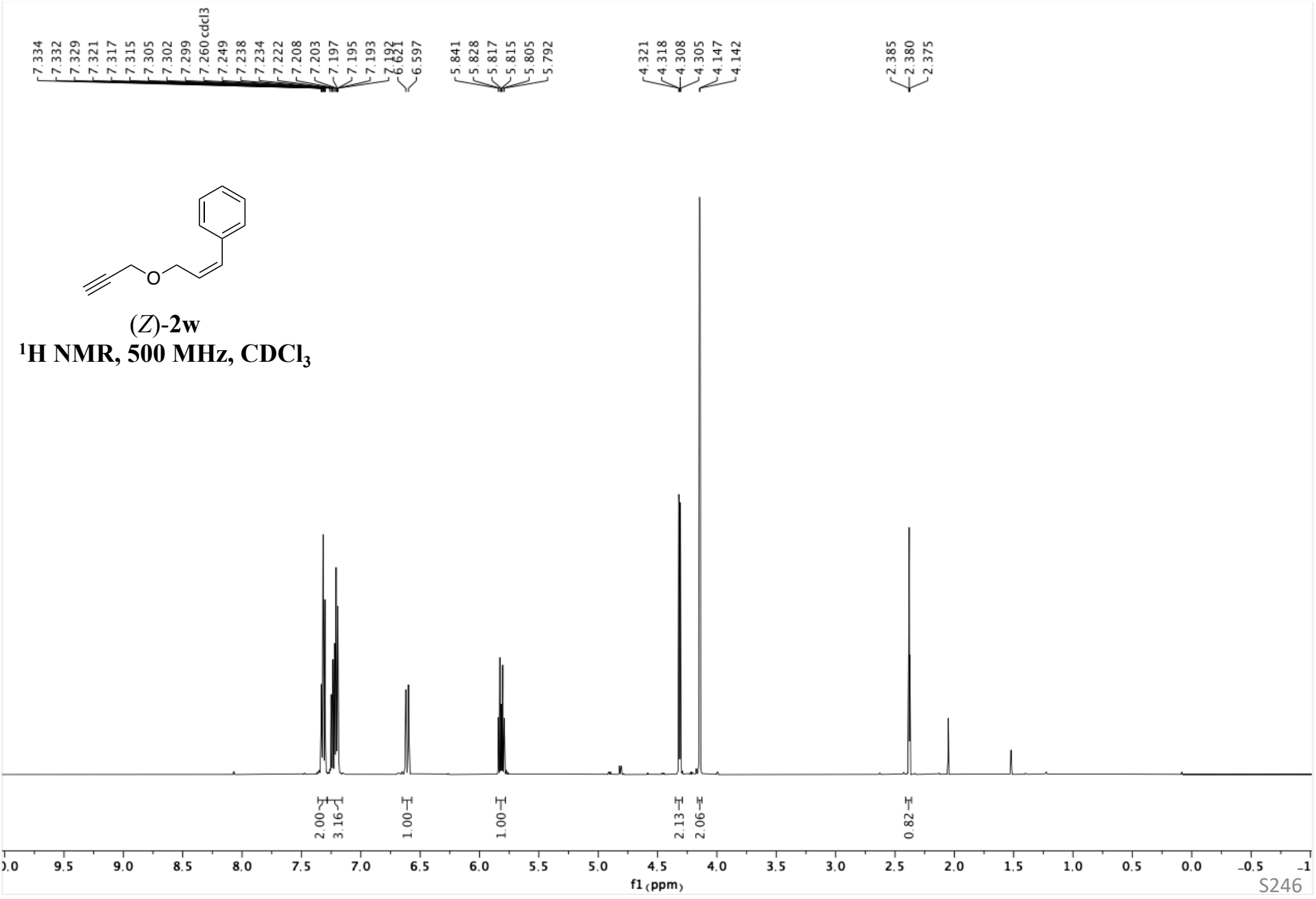
(*E*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



(*E*)-**2w**

^{13}C NMR, 125 MHz, $CDCl_3$

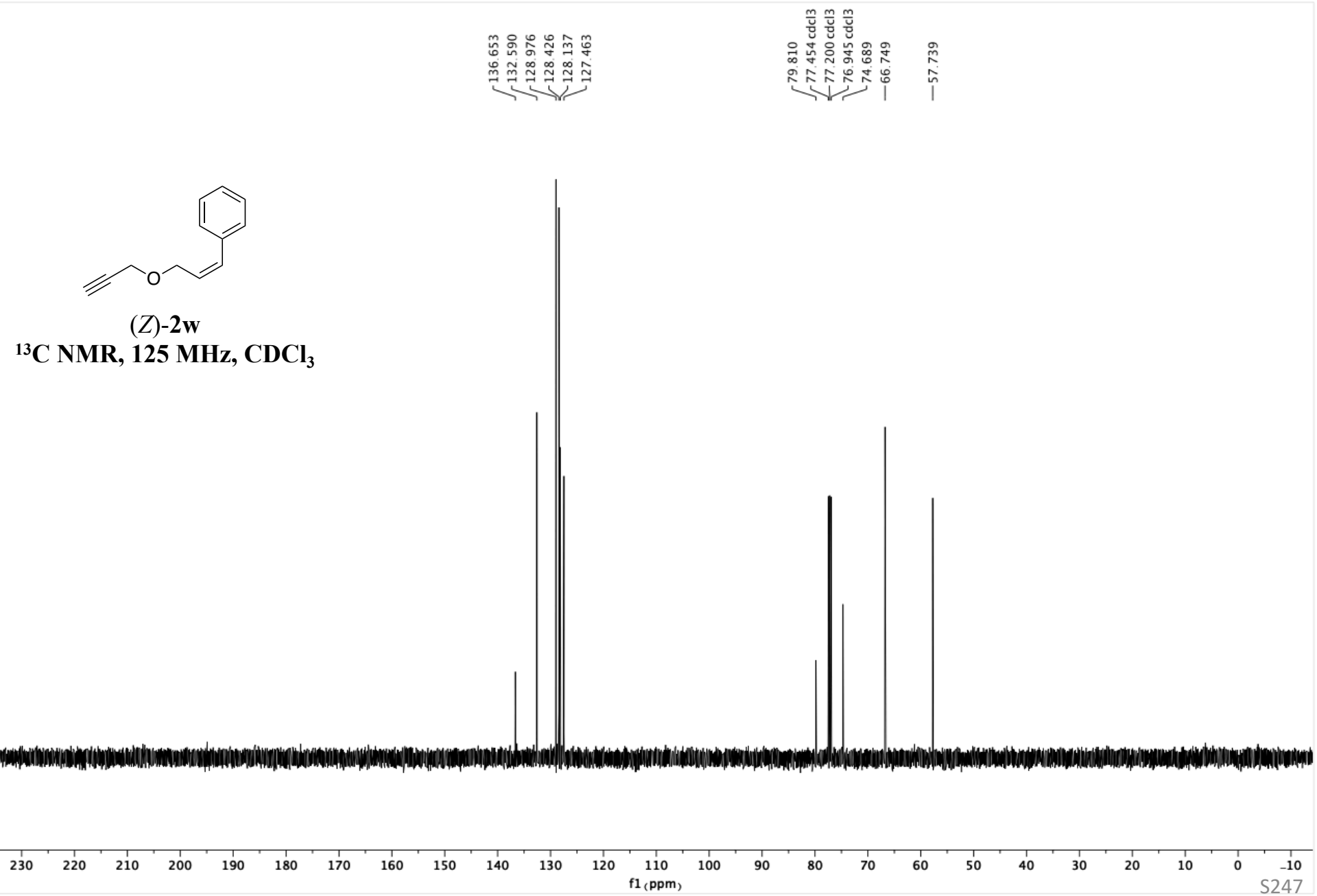
(*Z*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



(*Z*)-**2w**

^{1}H NMR, 500 MHz, $CDCl_3$

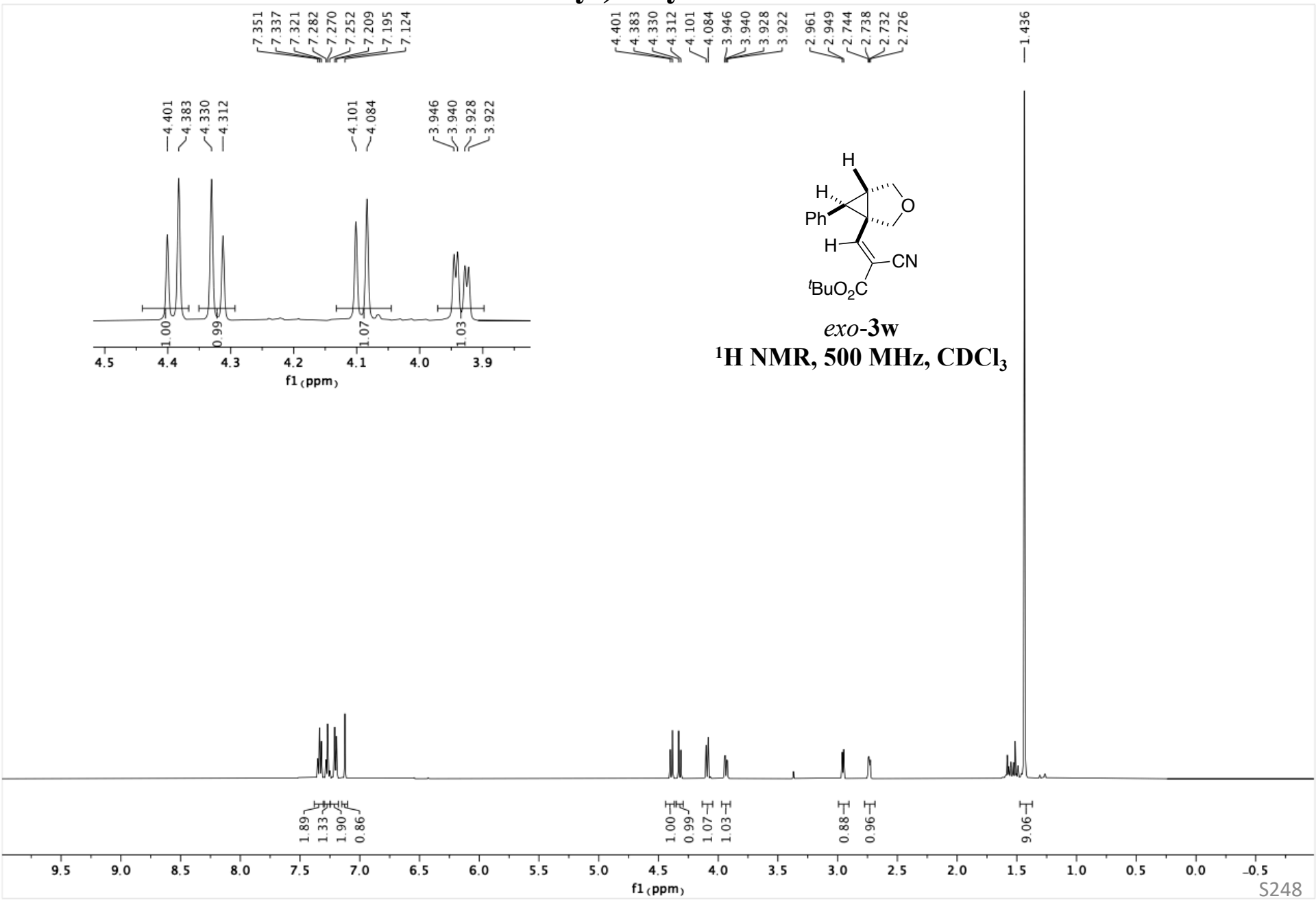
(*Z*)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene



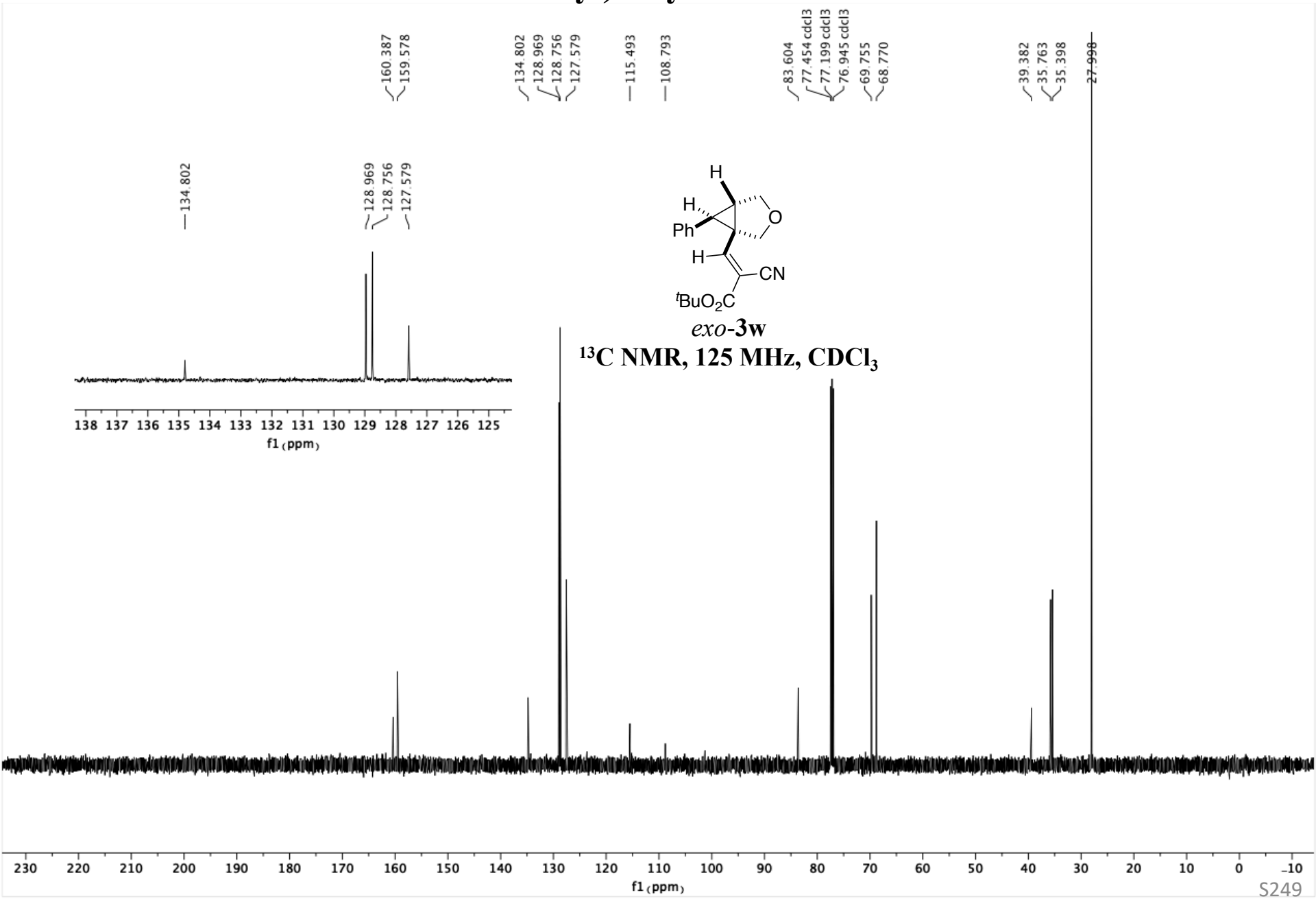
(*Z*)-**2w**

^{13}C NMR, 125 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*R*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



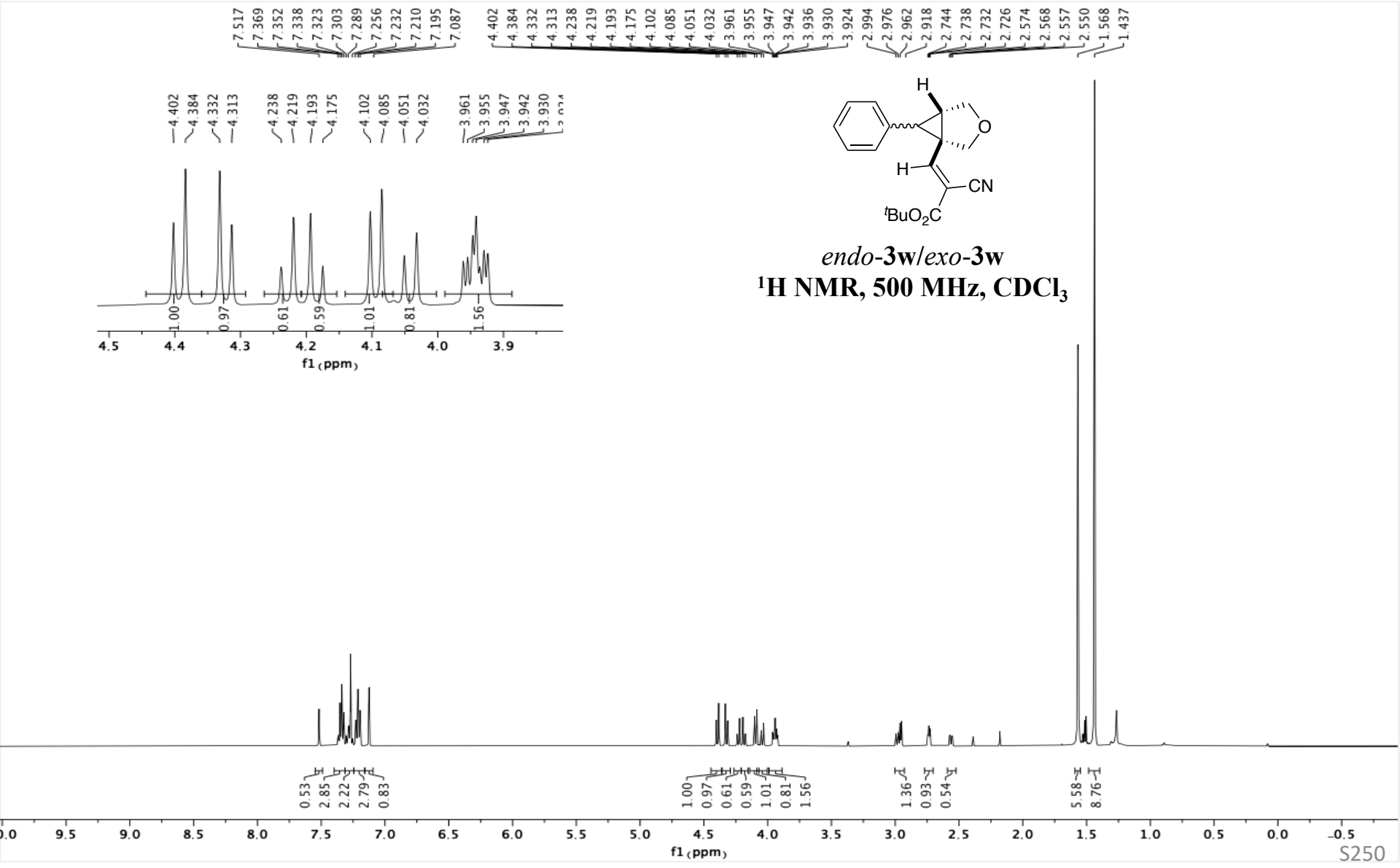
tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*R*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



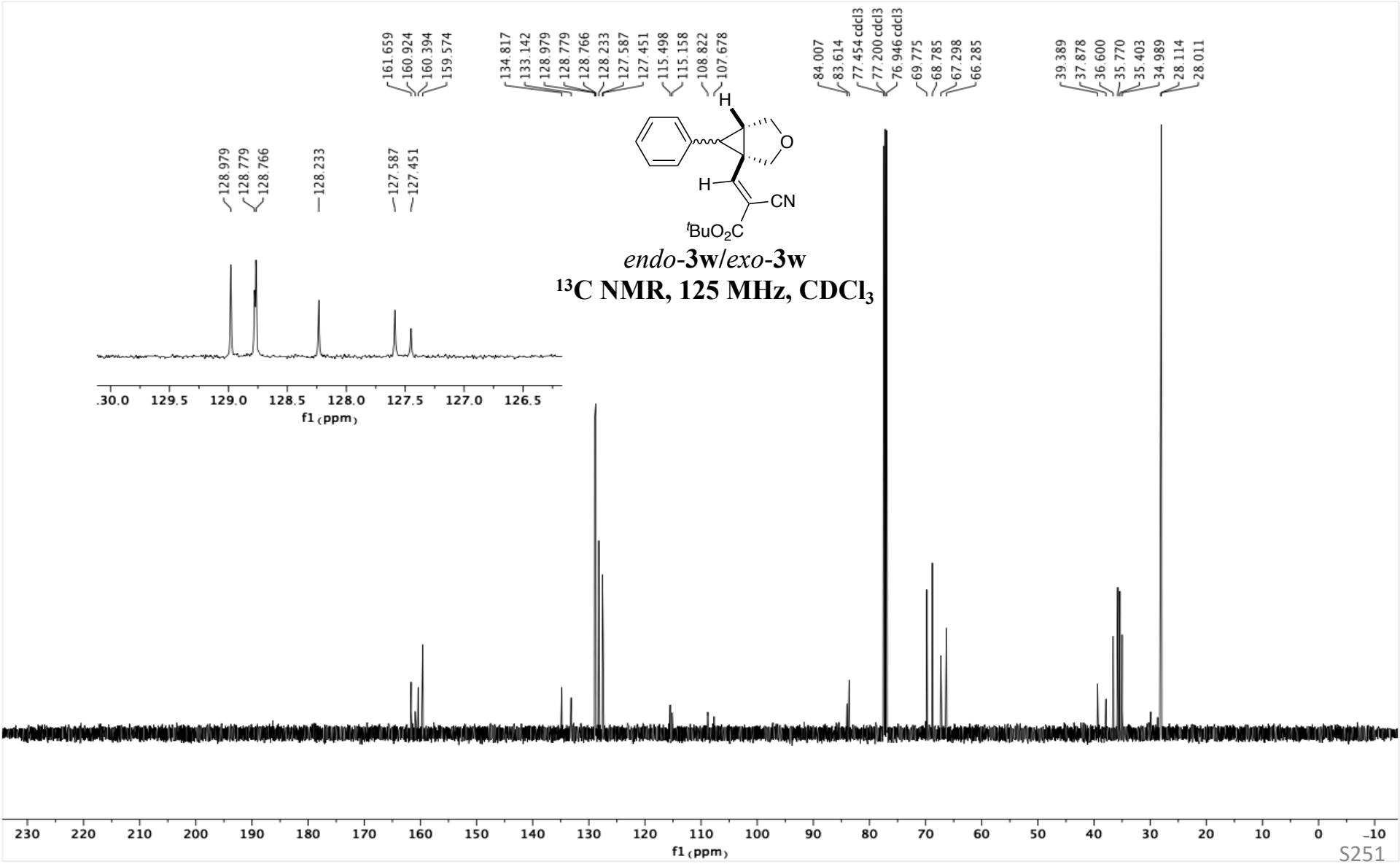
exo-**3w**

^{13}C NMR, 125 MHz, $CDCl_3$

tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate
tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*R*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



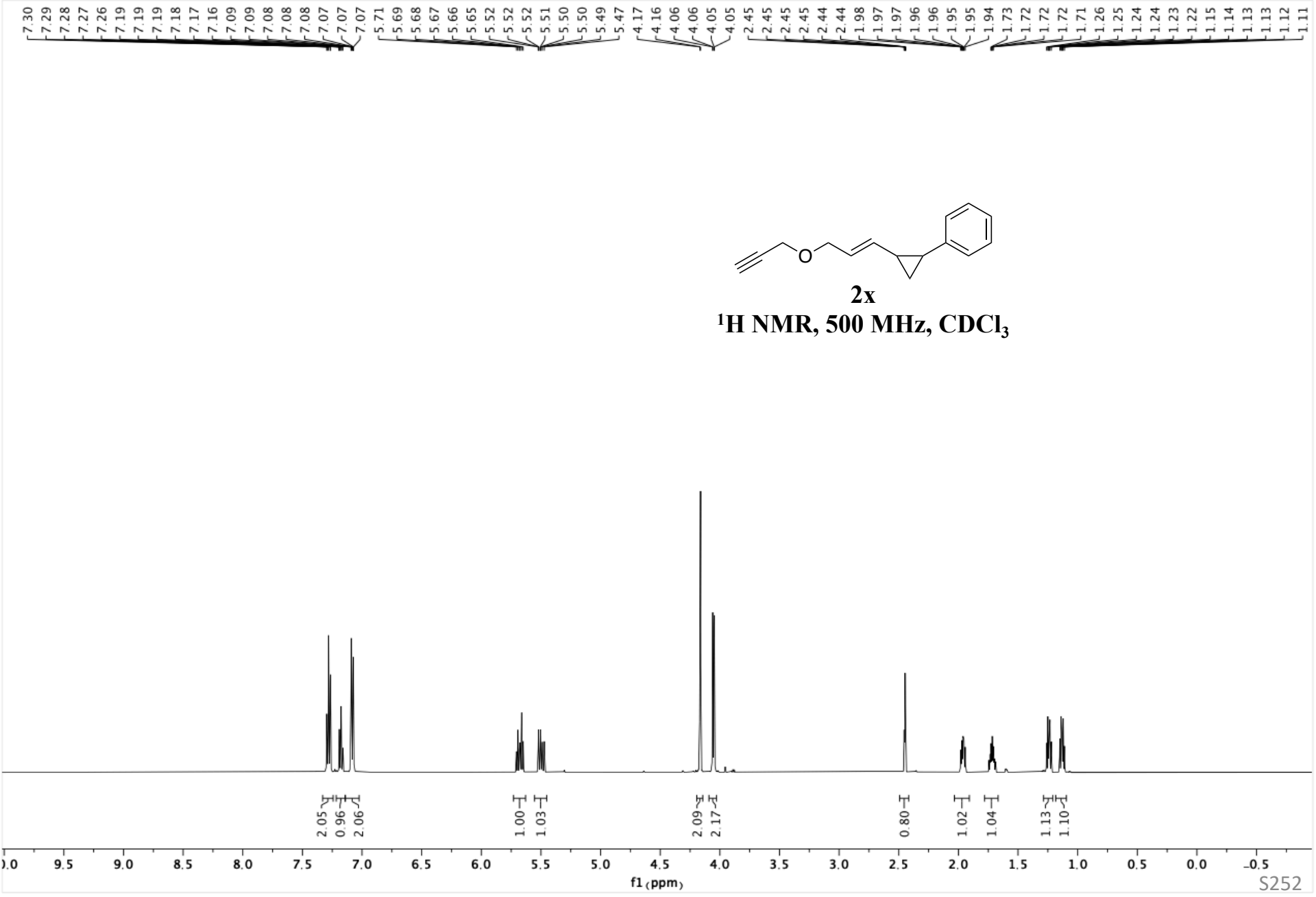
tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*S*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate
tert-Butyl (*E*)-2-cyano-3-((1*R*,5*S*,6*R*)-6-phenyl-3-oxabicyclo[3.1.0]hexan-1-yl)acrylate



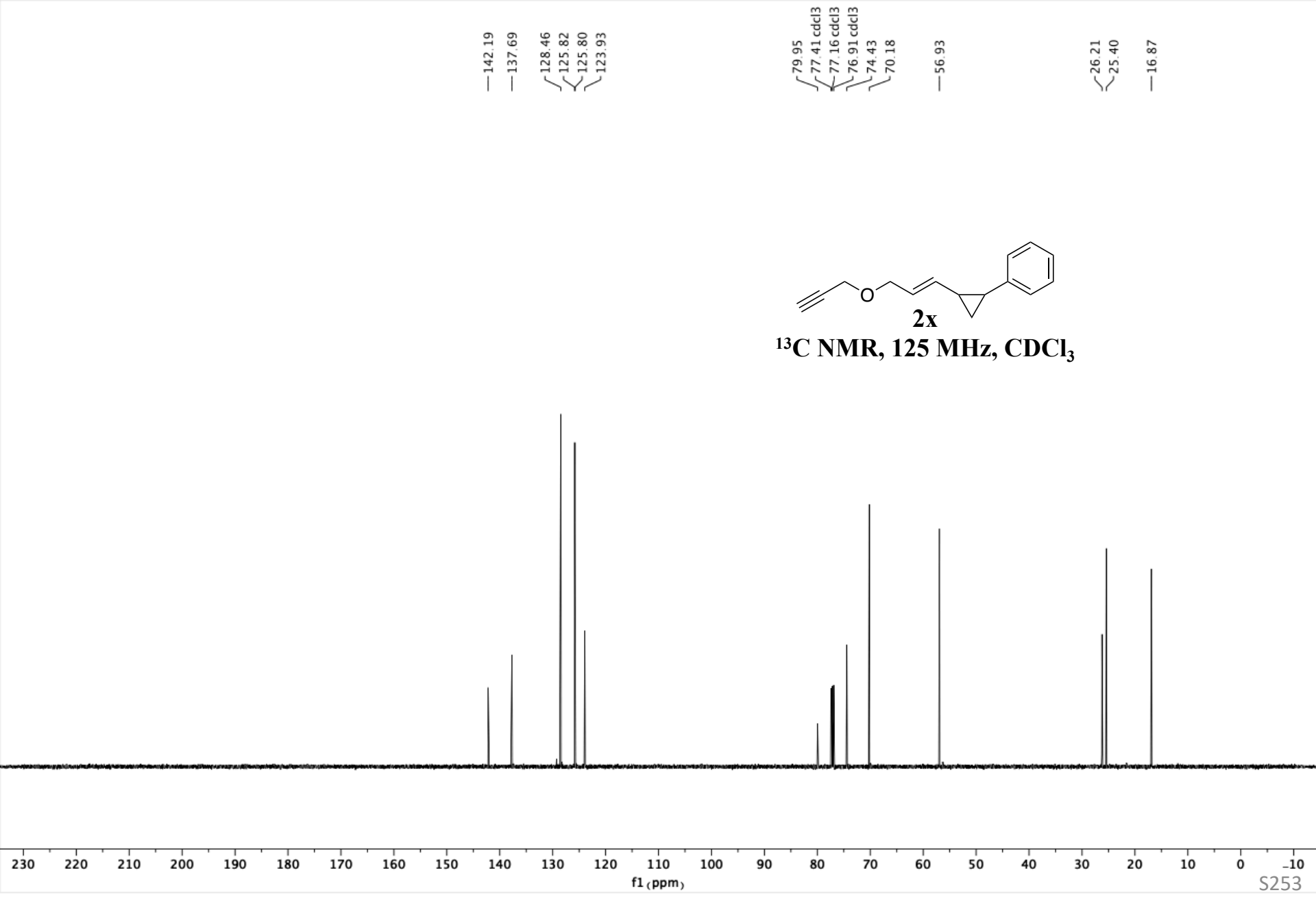
endo-**3w**/*exo*-**3w**

^{13}C NMR, 125 MHz, $CDCl_3$

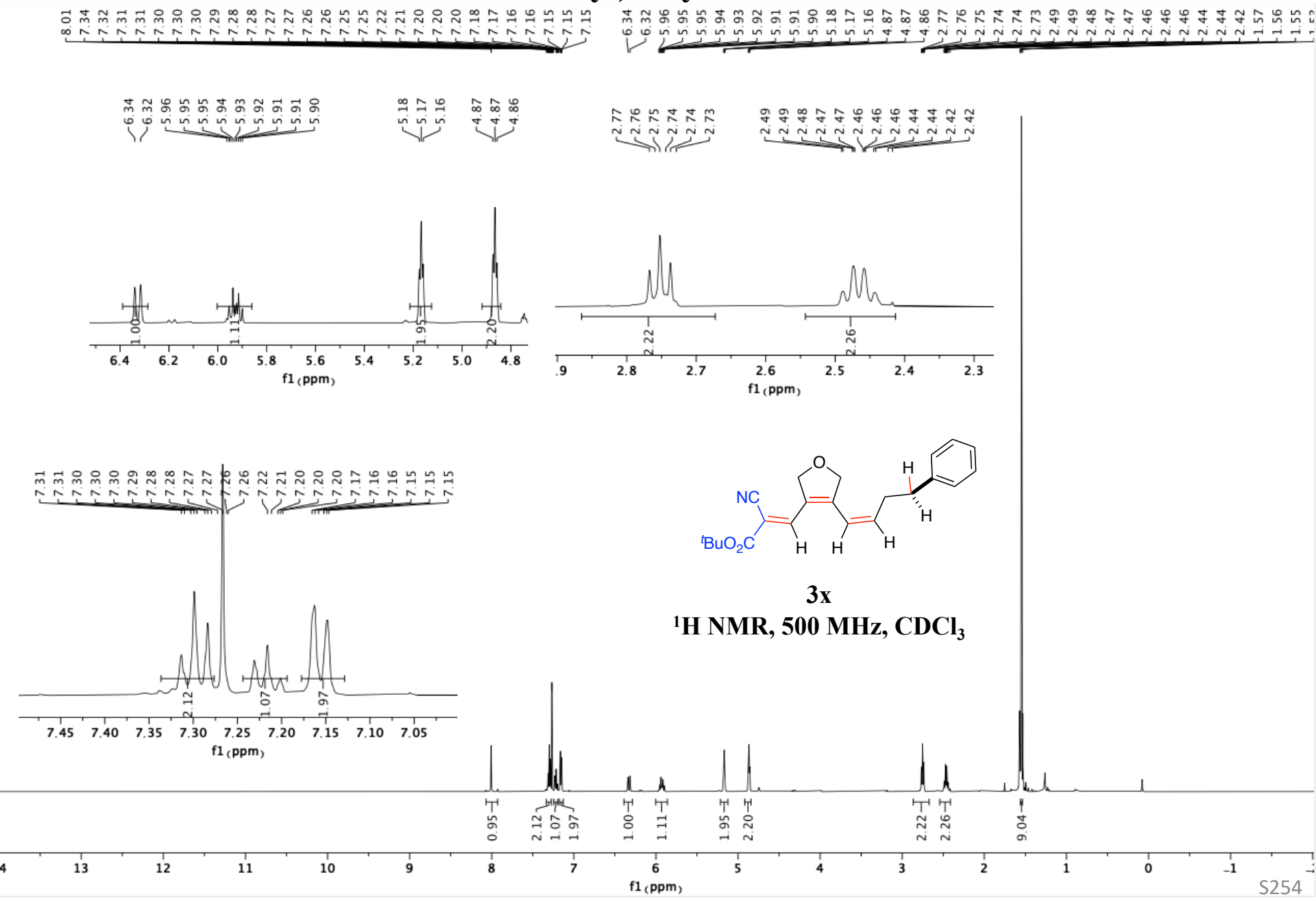
(*E*)-(2-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)cyclopropyl)benzene



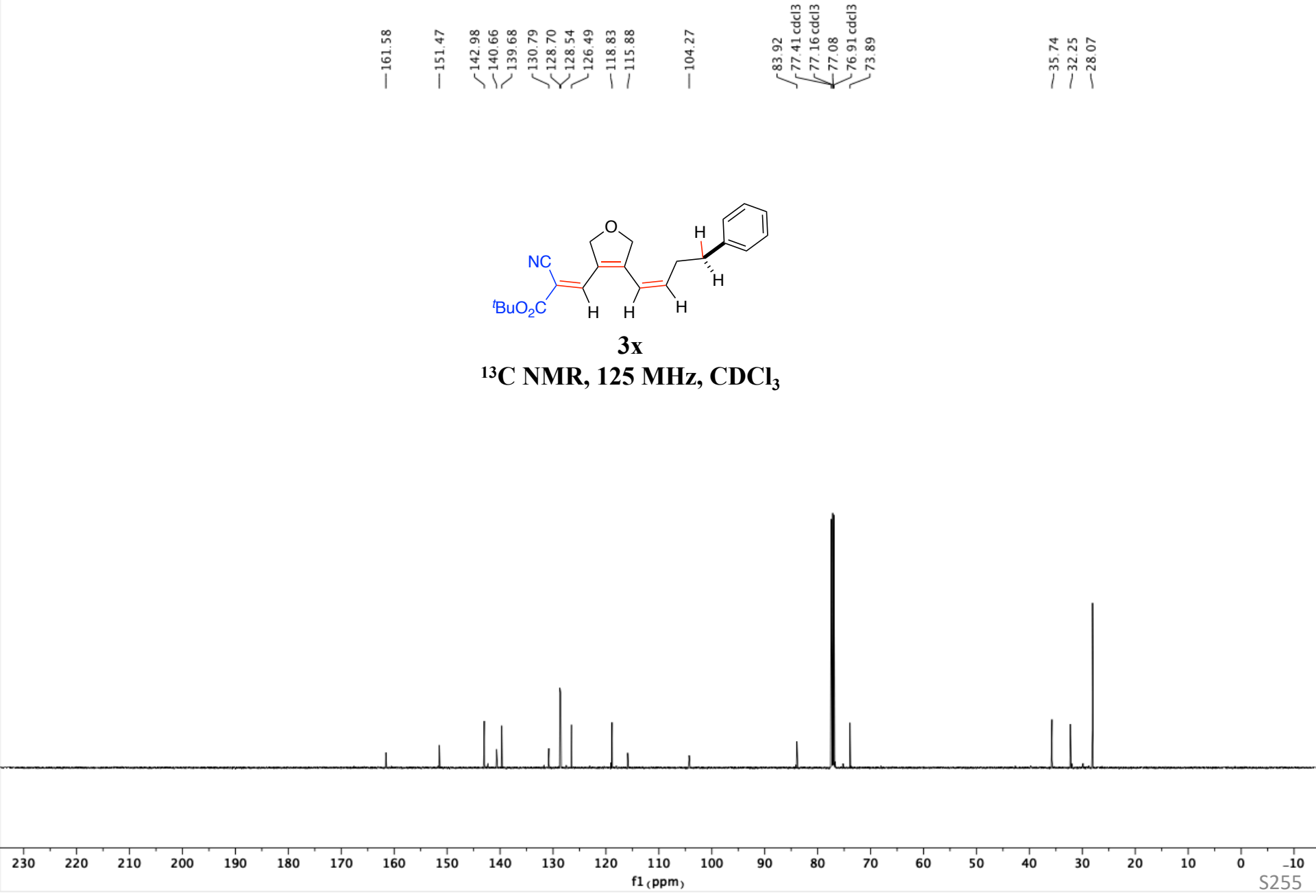
(*E*)-(2-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)cyclopropyl)benzene



tert-Butyl (*E*)-2-cyano-3-(4-((*Z*)-4-phenylbut-1-en-1-yl)-2,5-dihydrofuran-3-yl)acrylate



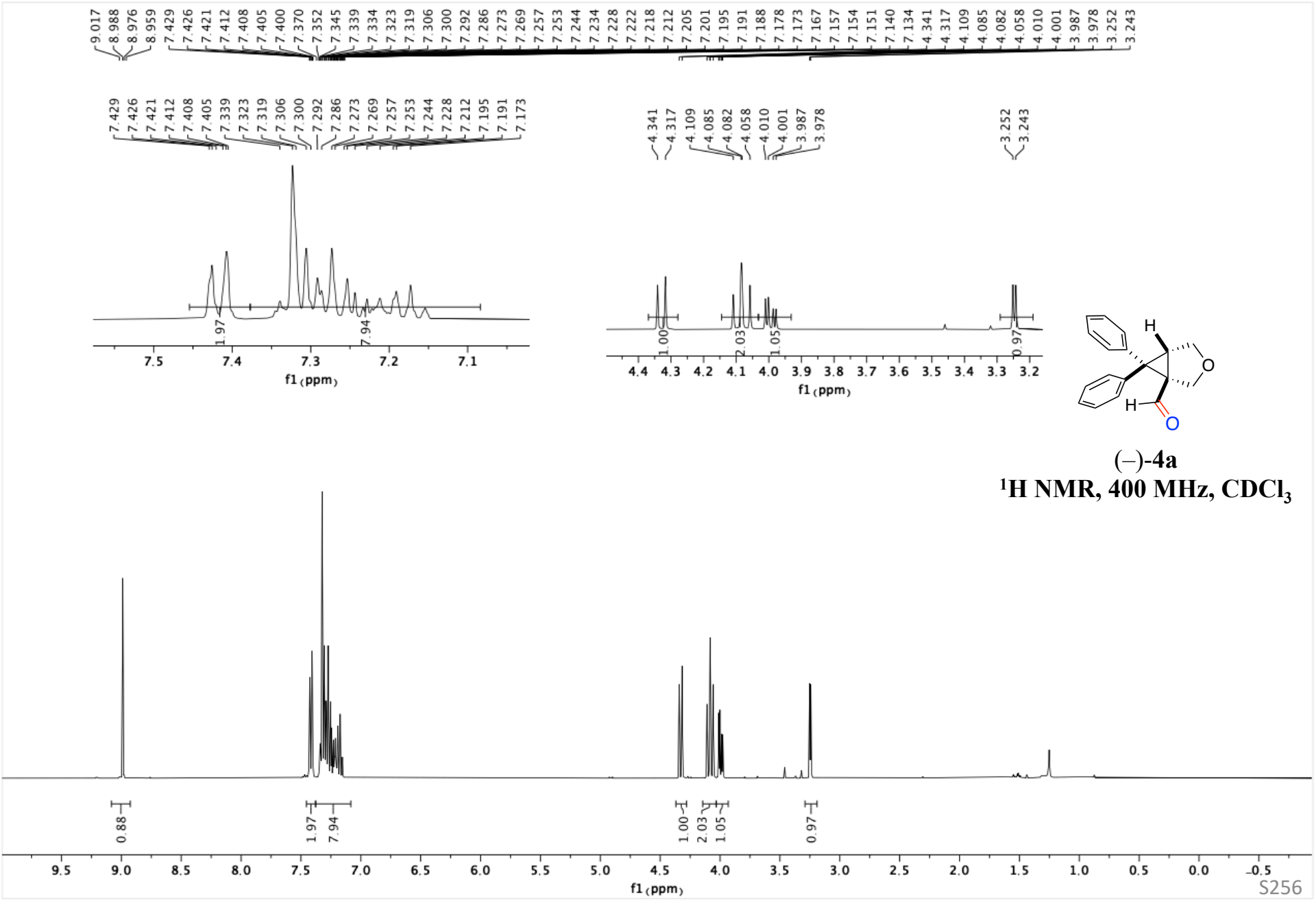
tert-Butyl (*E*)-2-cyano-3-(4-((*Z*)-4-phenylbut-1-en-1-yl)-2,5-dihydrofuran-3-yl)acrylate



3x

^{13}C NMR, 125 MHz, $CDCl_3$

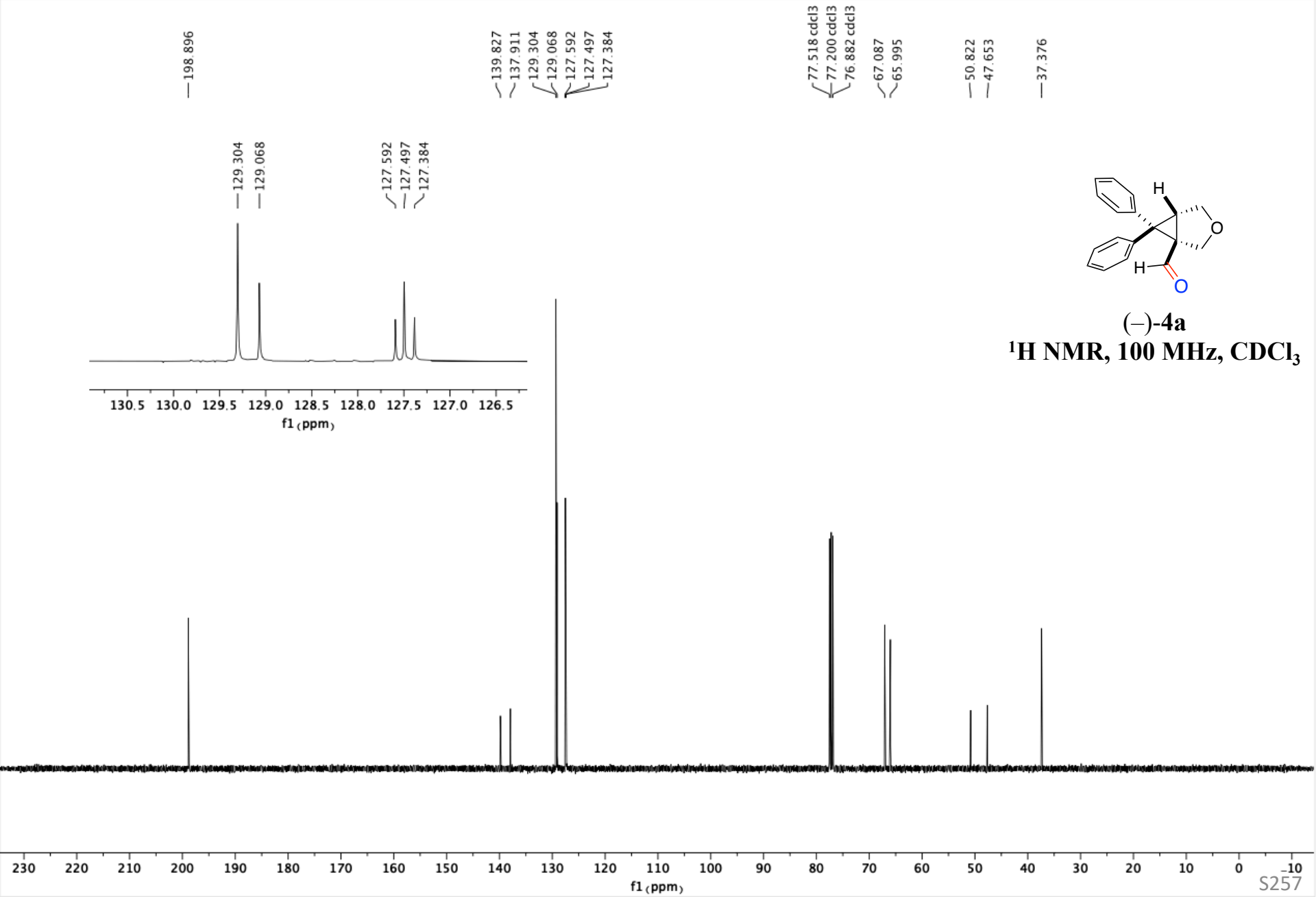
(1*R*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde



(–)-4a

^{1}H NMR, 400 MHz, $CDCl_3$

(1*R*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde



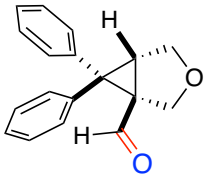
(–)-**4a**

^{1}H NMR, 100 MHz, $CDCl_3$

(1*R*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde

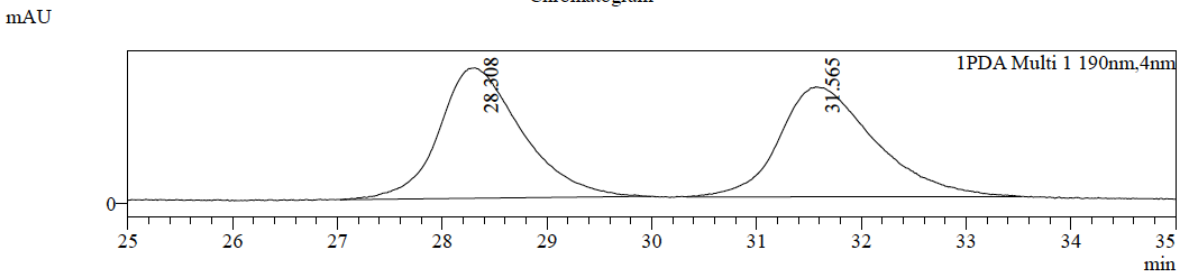
Sample Information

Sample Name	: CZZ-2223-WHELK-10%-0.8mL
Sample ID	: CZZ-2223-WHELK-10%-0.8mL
Data File	: CZZ-2223-WHELK-10%-0.8mL002.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

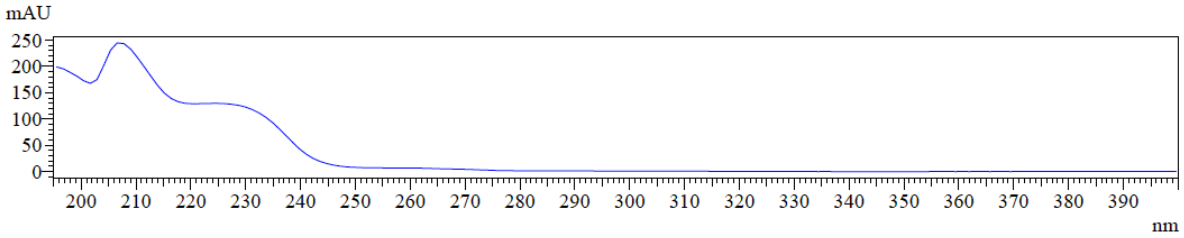


(±)-4a

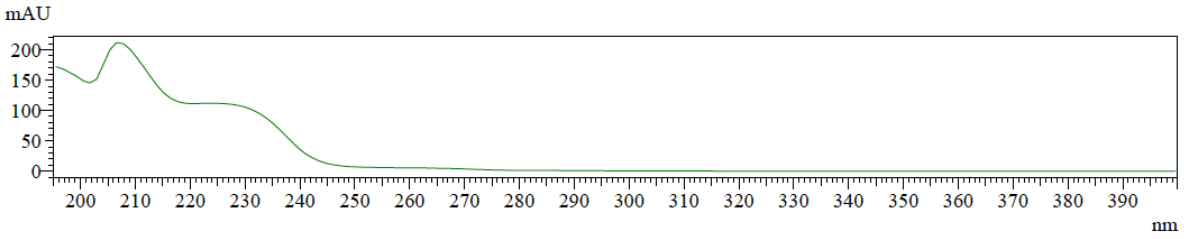
Chromatogram



UV Spectrum
Retention time = 28.308



UV Spectrum
Retention time = 31.565



Peak Table

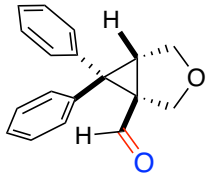
PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	28.308	10245574	50.577
2	31.565	10011849	49.423
Total		20257423	100.000

(1*R*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde

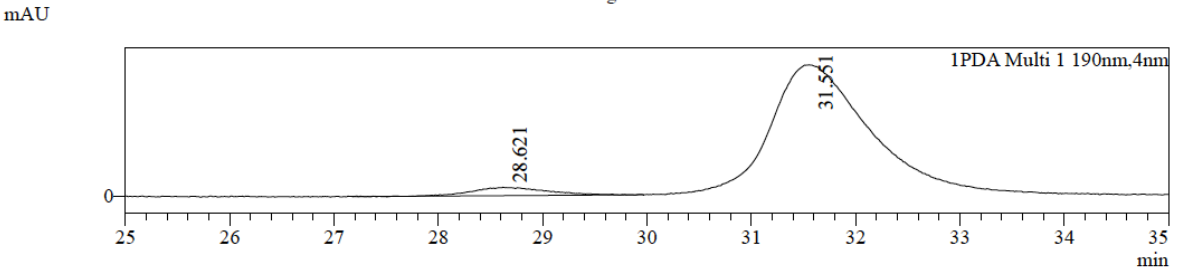
Sample Information

Sample Name	: CZZ-2234-WHELK-10%-0.8mL
Sample ID	: CZZ-2234-WHELK-10%-0.8mL
Data File	: CZZ-2234-WHELK-10%-0.8mL.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

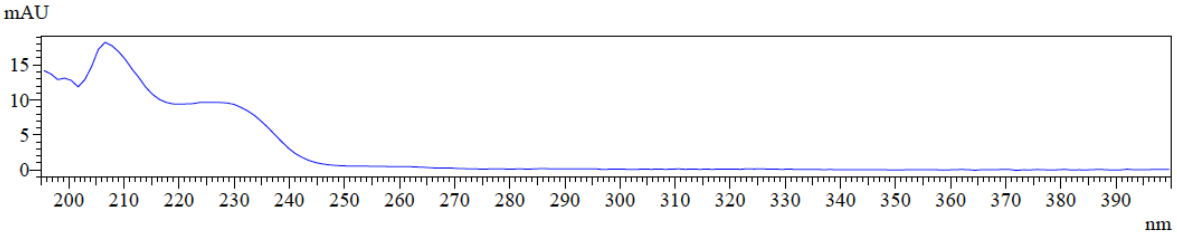


(–)-4a

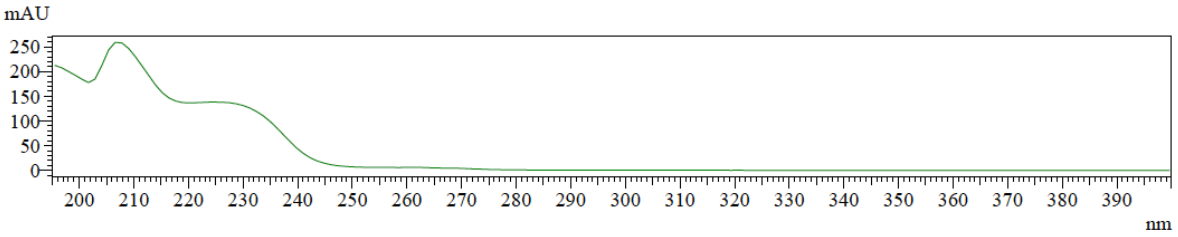
Chromatogram



UV Spectrum
Retention time = 28.621



UV Spectrum
Retention time = 31.551

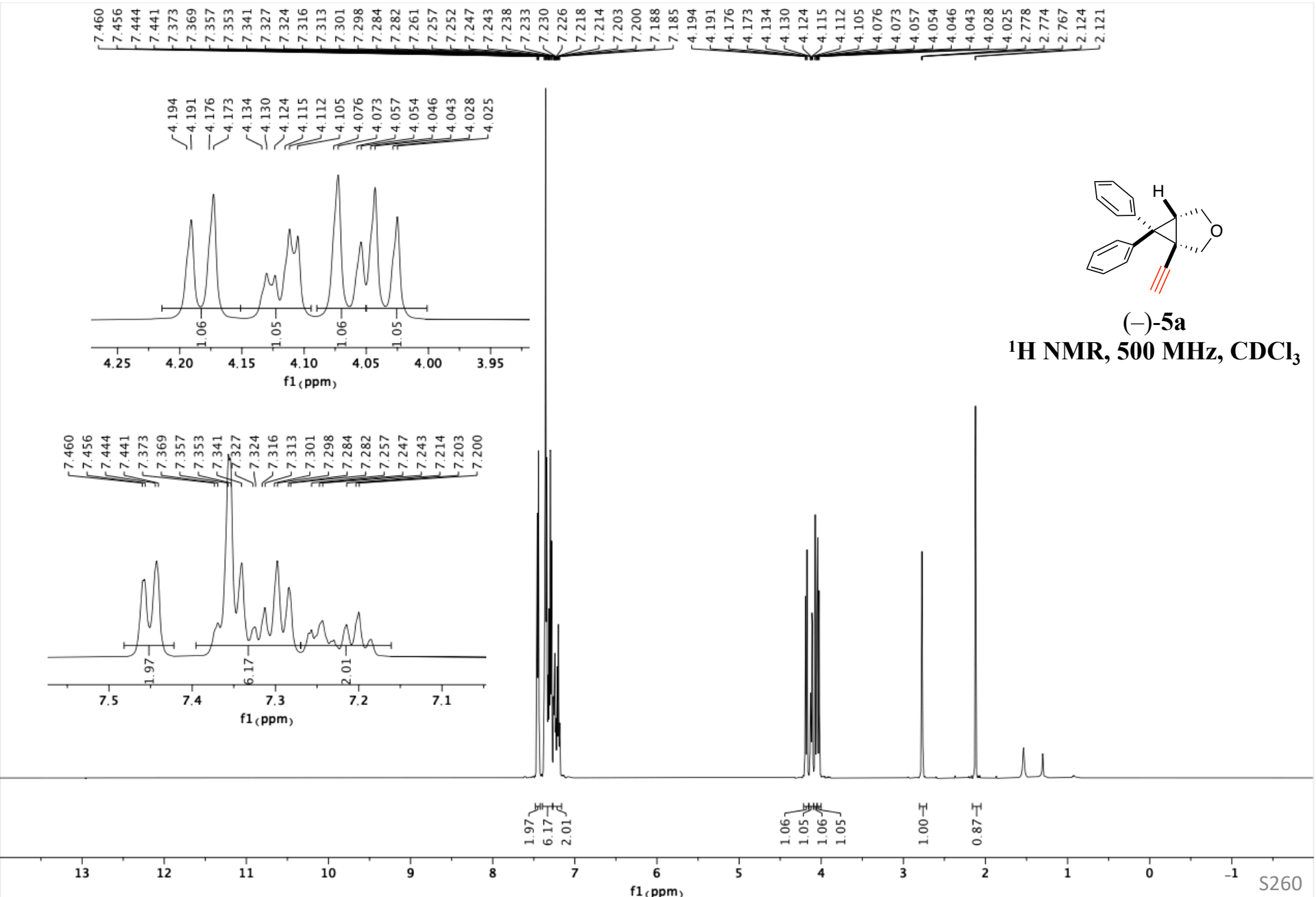


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	28.621	660577	4.458
2	31.551	14157034	95.542
Total		14817611	100.000

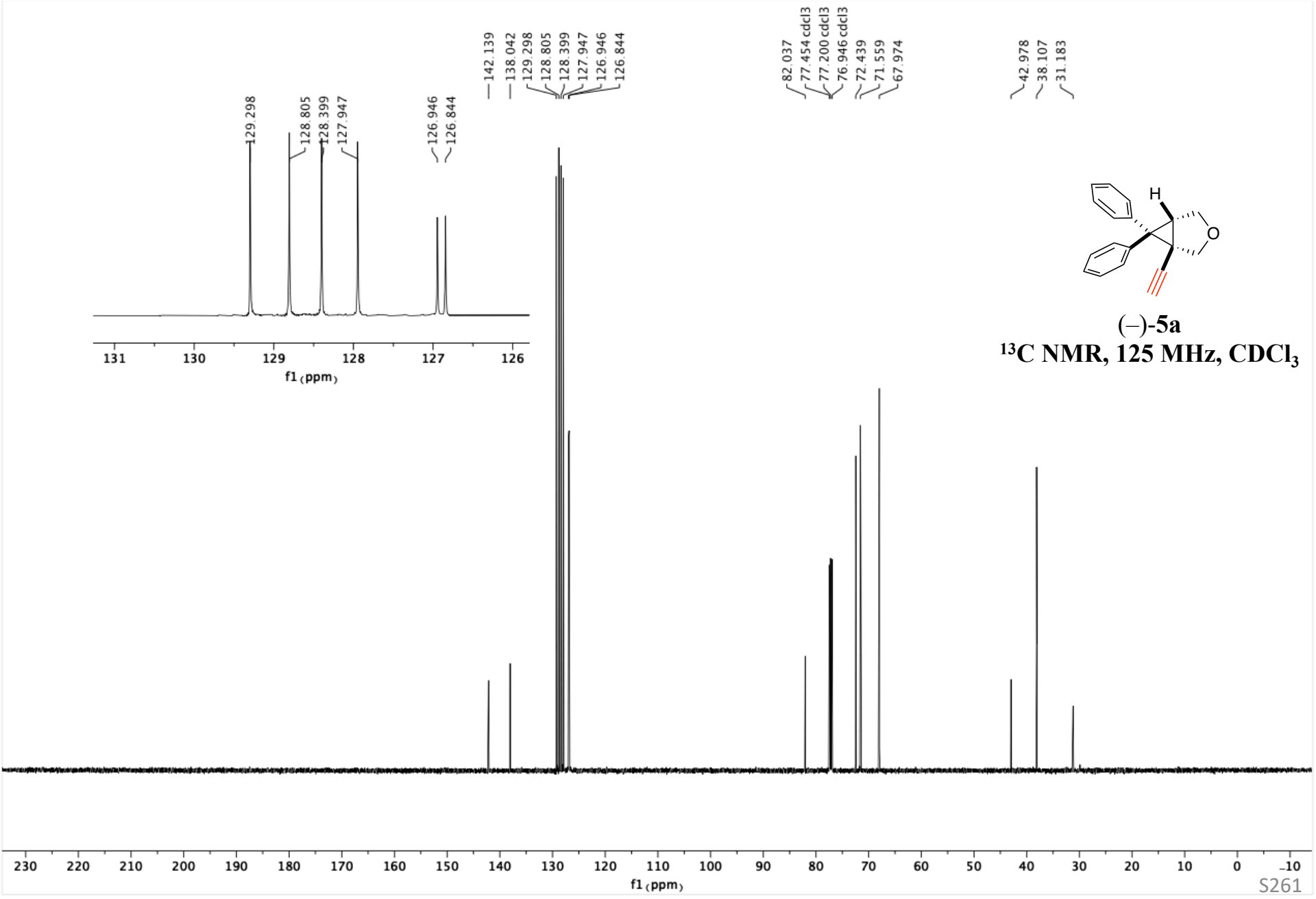
(1*R*,5*S*)-1-Ethynyl-6,6-diphenyl-3-oxabicyclo[3.1.0]hexane



(–)-5a

^{1}H NMR, 500 MHz, $CDCl_3$

(1*R*,5*S*)-1-Ethynyl-6,6-diphenyl-3-oxabicyclo[3.1.0]hexane



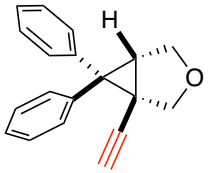
(–)-5a

^{13}C NMR, 125 MHz, $CDCl_3$

(1*R*,5*S*)-1-Ethynyl-6,6-diphenyl-3-oxabicyclo[3.1.0]hexane

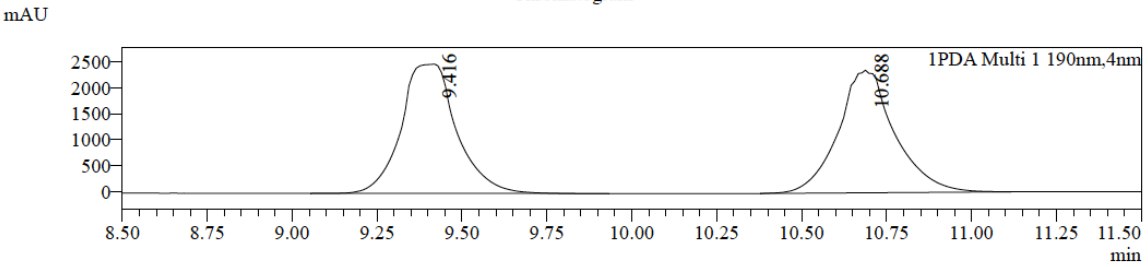
Sample Information

Sample Name : CZZ-2228-5%-IC-0.8mL
Sample ID : CZZ-2228-5%-IC-0.8mL
Data File : CZZ-2228-5%-IC-0.8mL001.lcd
Method File : CZZ-5.0%-0.8ml.lcm

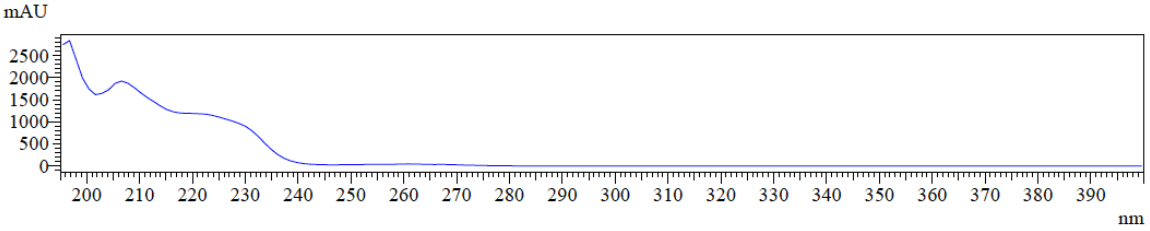


(±)-**5a**

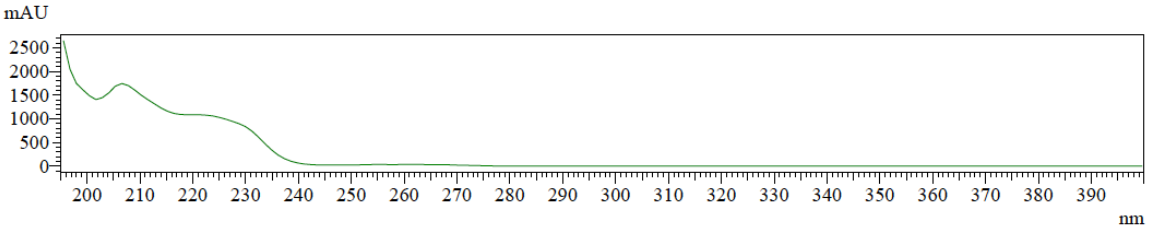
Chromatogram



UV Spectrum
Retention time = 9.416



UV Spectrum
Retention time = 10.688

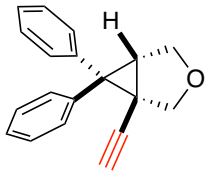


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	9.416	28322099	50.851
2	10.688	27374396	49.149
Total		55696494	100.000

(1*R*,5*S*)-1-Ethynyl-6,6-diphenyl-3-oxabicyclo[3.1.0]hexane

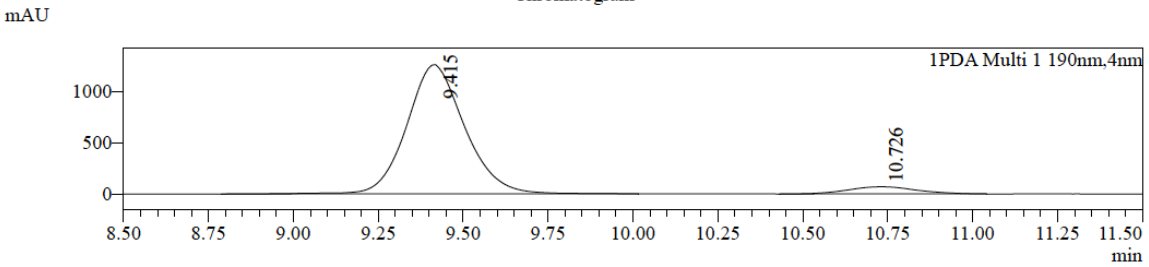


(–)-**5a**

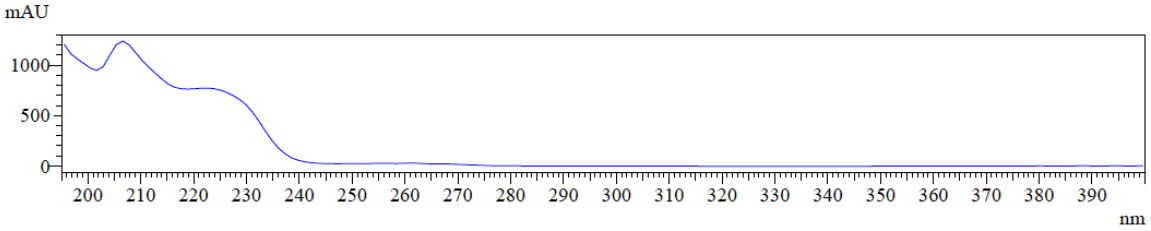
Sample Information

Sample Name	: CZZ-2243-5%-IC-0.8mL
Sample ID	: CZZ-2243-5%-IC-0.8mL
Data File	: CZZ-2243-5%-IC-0.8mL001.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

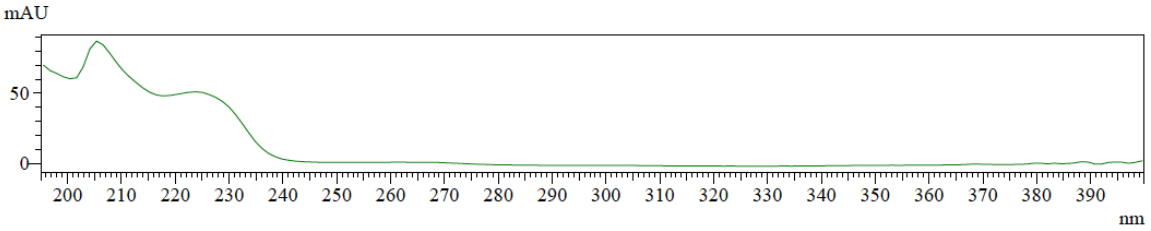
Chromatogram



UV Spectrum
Retention time = 9.415



UV Spectrum
Retention time = 10.726

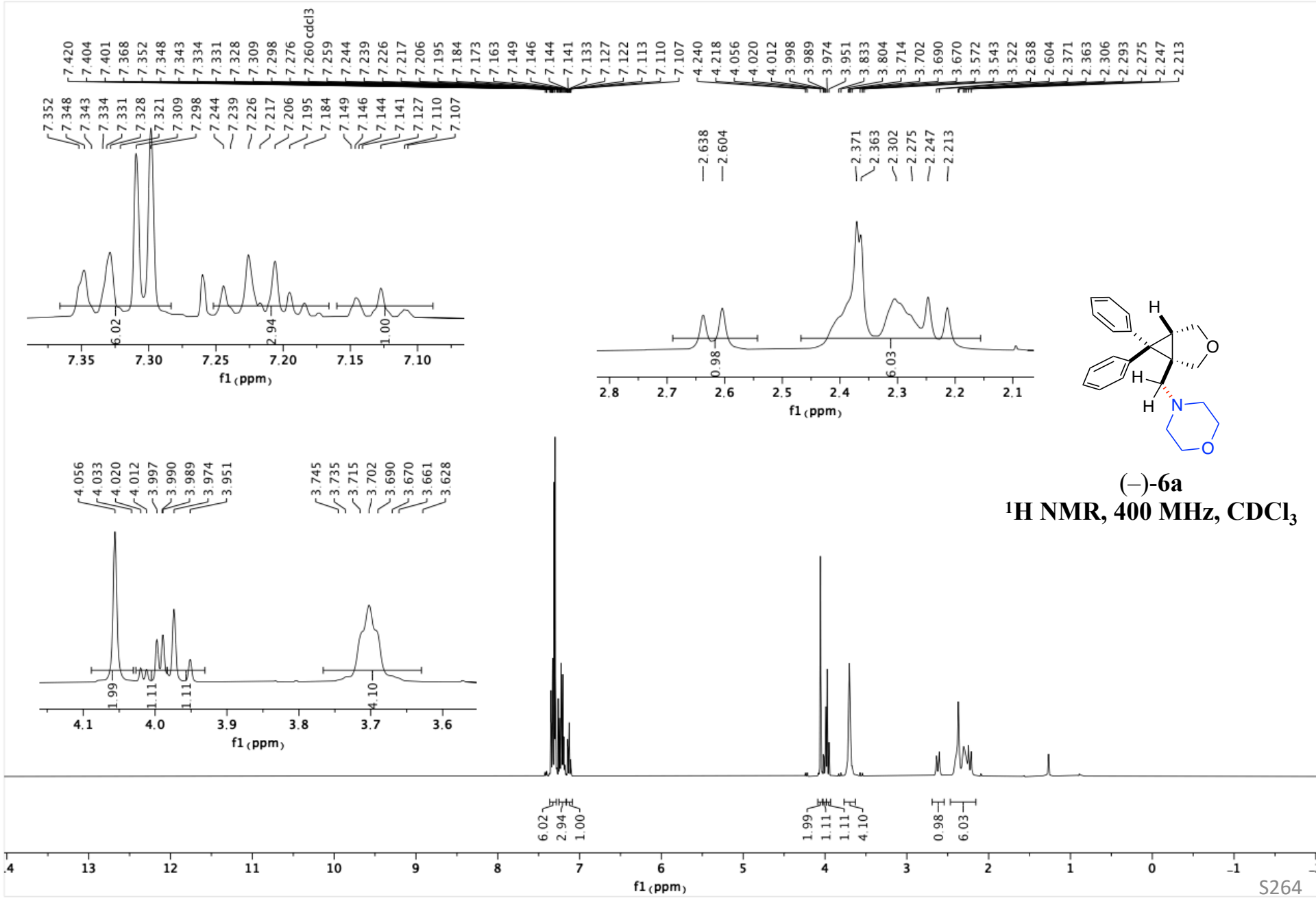


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	9.415	14935912	93.952
2	10.726	961479	6.048
Total		15897391	100.000

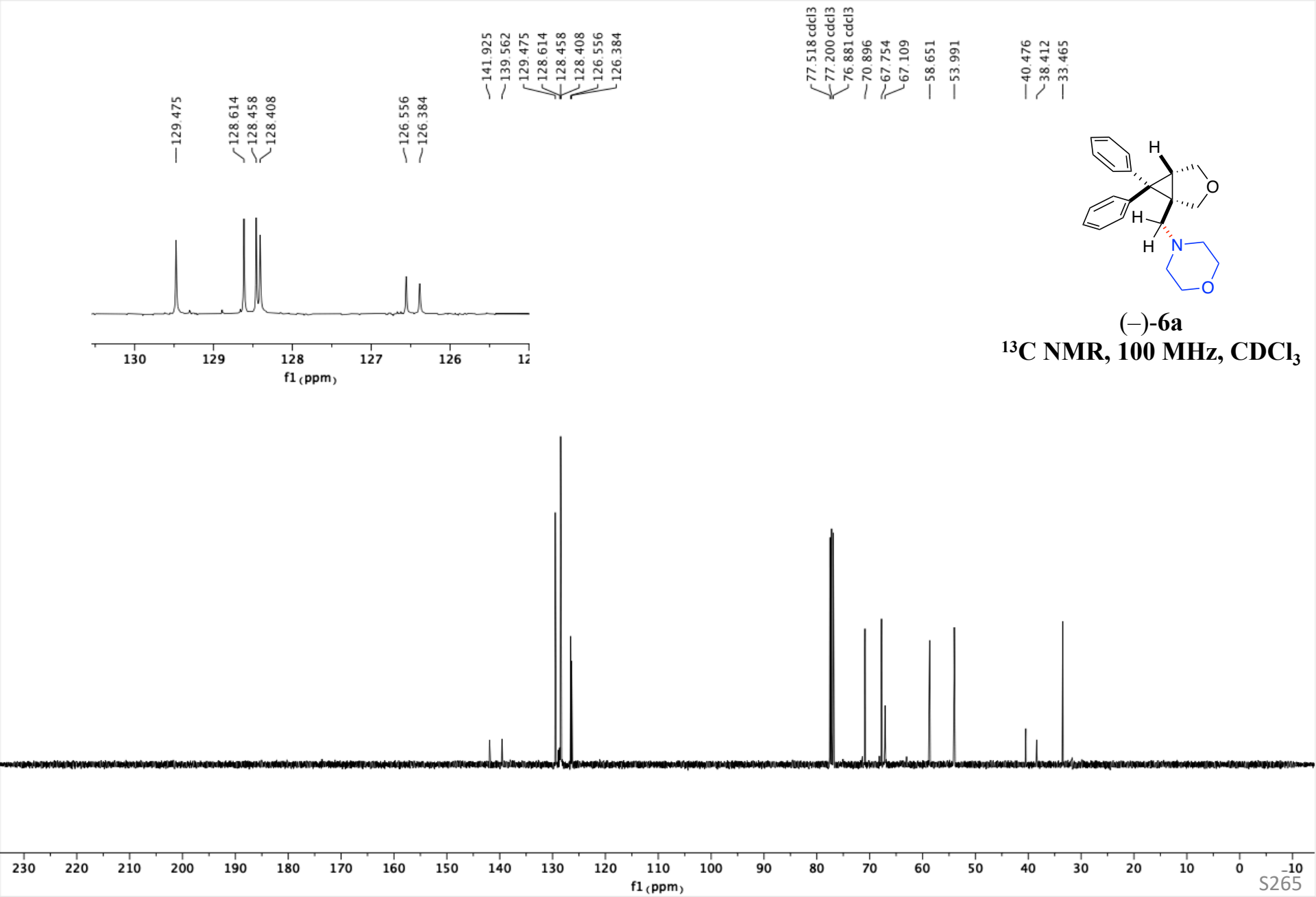
4-(((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)methyl)morpholine



(–)-6a

^{1}H NMR, 400 MHz, $CDCl_3$

4-(((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)methyl)morpholine



(–)-6a

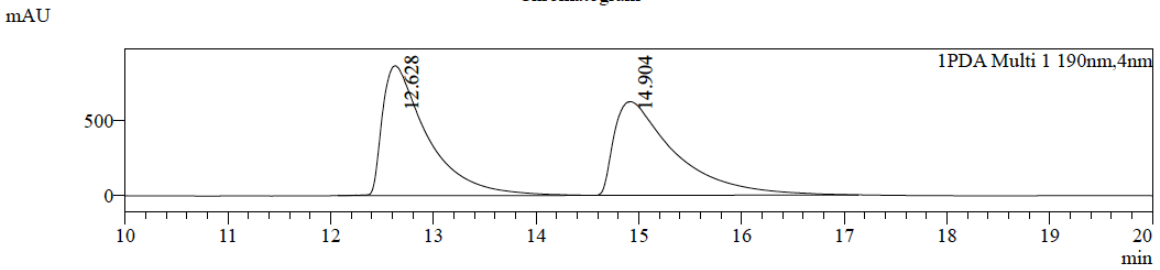
^{13}C NMR, 100 MHz, $CDCl_3$

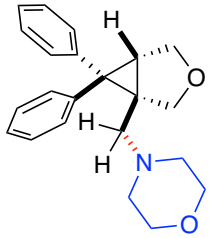
4-(((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)methyl)morpholine

Sample Information

Sample Name	: CZZ-2229-IE-10%-0.8mL
Sample ID	: CZZ-2229-IE-10%-0.8mL
Data File	: CZZ-2229-IE-10%-0.8mL002.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

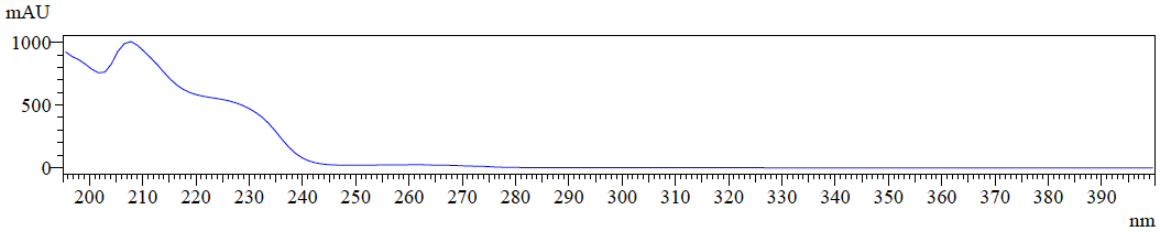
Chromatogram



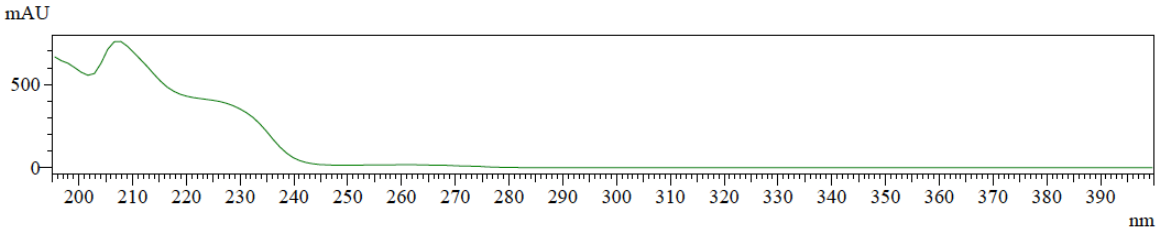


(±)-**6a**

UV Spectrum
Retention time = 12.628



UV Spectrum
Retention time = 14.904

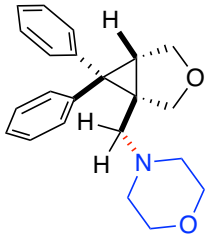


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	12.628	26455941	50.790
2	14.904	25632658	49.210
Total		52088599	100.000

4-(((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)methyl)morpholine

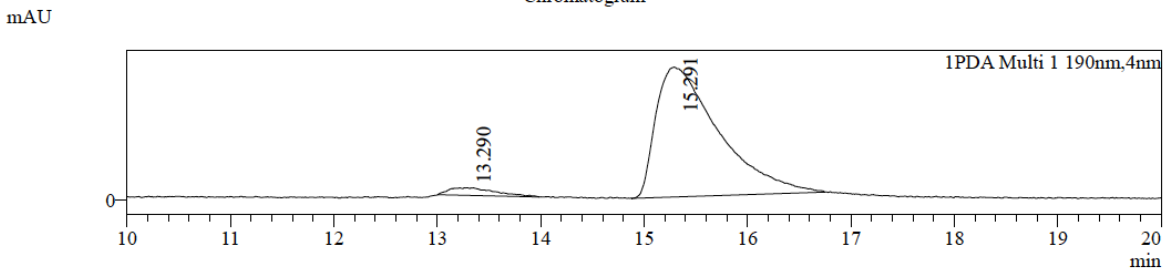


(–)-6a

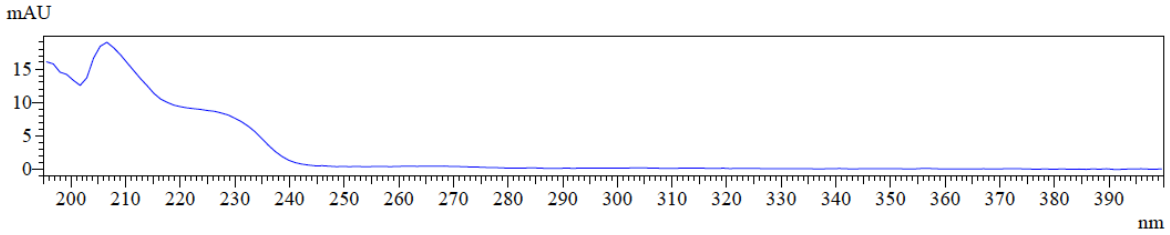
Sample Information

Sample Name	: CZZ-2242-IE-10%-0.8mL
Sample ID	: CZZ-2242-IE-10%-0.8mL
Data File	: CZZ-2242-IE-10%-0.8mL.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

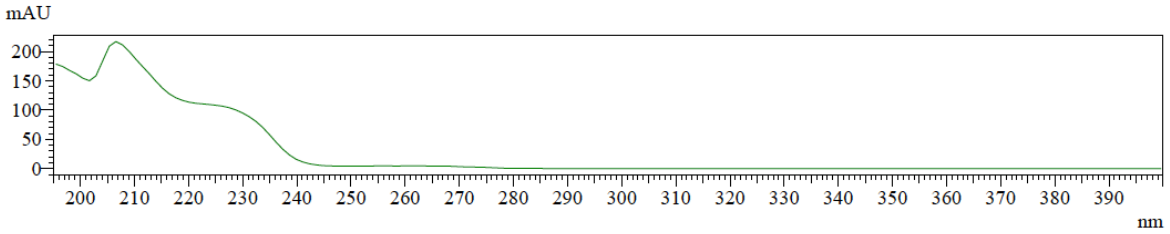
Chromatogram



UV Spectrum
Retention time = 13.290



UV Spectrum
Retention time = 15.291

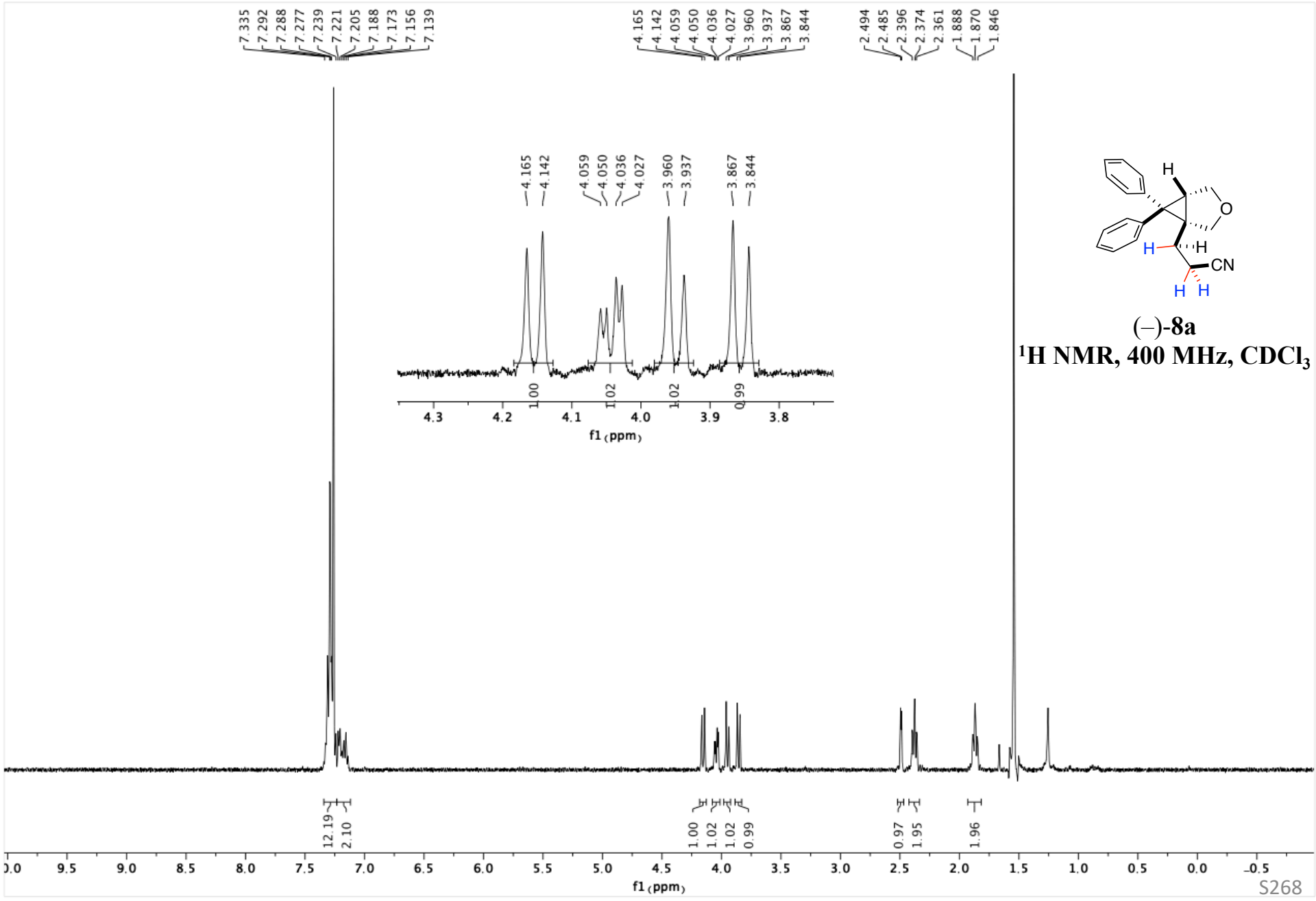


Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%
1	13.290	313964	4.160
2	15.291	7233863	95.840
Total		7547827	100.000

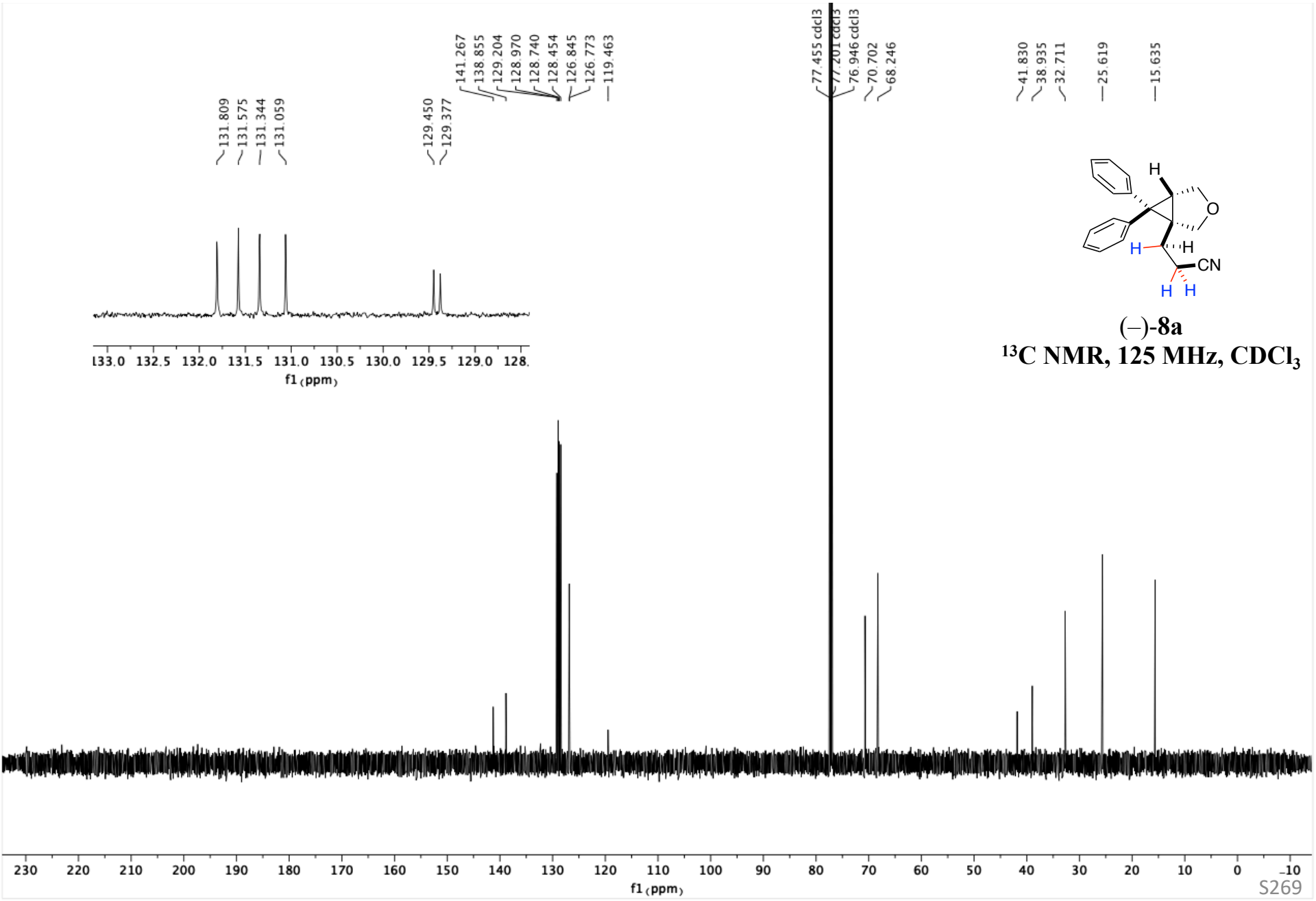
3-((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)propanenitrile



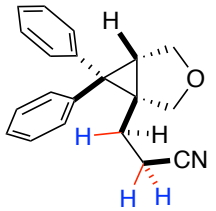
(–)-**8a**

^{1}H NMR, 400 MHz, $CDCl_3$

3-((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)propanenitrile



3-((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)propanenitrile

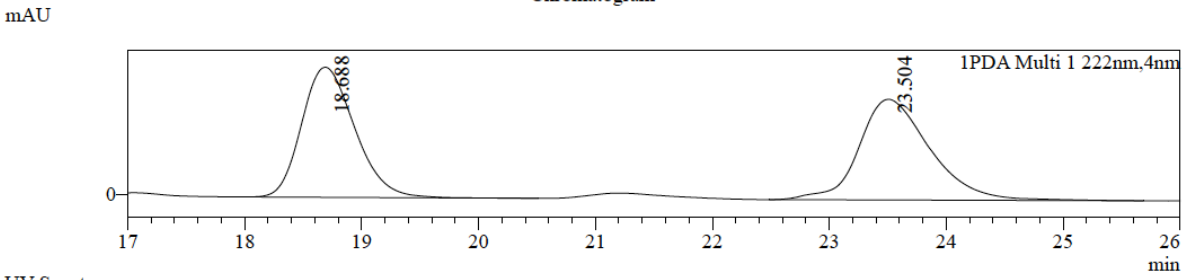


(±)-**8a**

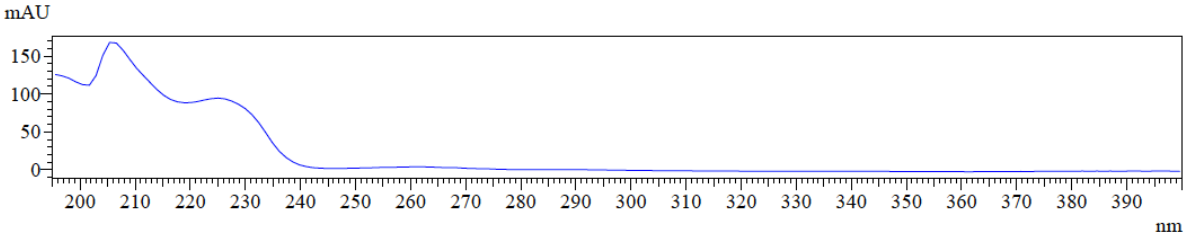
Sample Information

Sample Name	: CZZ-1519-IE-10%-1mL
Sample ID	: CZZ-1519-IE-10%-1mL
Data File	: CZZ-1519-IE-10%-1mL.lcd
Method File	: CZZ-10%-1.0ml.lcm

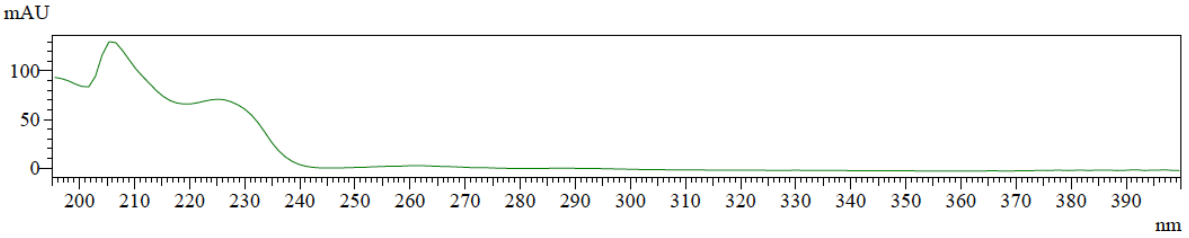
Chromatogram



UV Spectrum
Retention time = 18.688



UV Spectrum
Retention time = 23.504



Peak Table

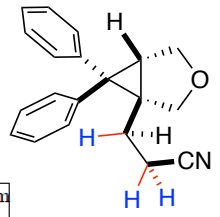
PDA Ch1 222nm

Peak#	Ret. Time	Area	Area%
1	18.688	2944269	49.085
2	23.504	3054067	50.915
Total		5998337	100.000

3-((1*S*,5*S*)-6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)propanenitrile

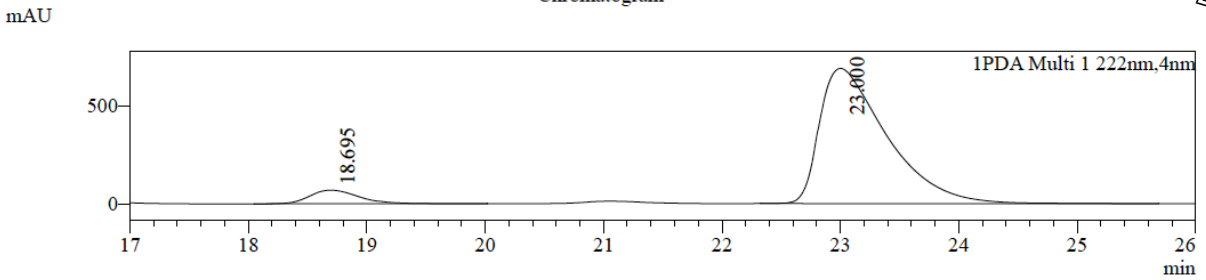
Sample Information

Sample Name	: CZZ-1522-IE-10%-1mL
Sample ID	: CZZ-1522-IE-10%-1mL
Data File	: CZZ-1522-IE-10%-1mL001.lcd
Method File	: CZZ-10%-1.0ml.lcm

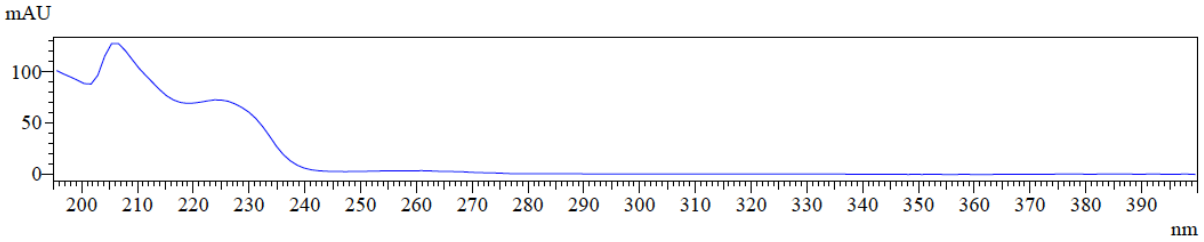


(–)-**8a**

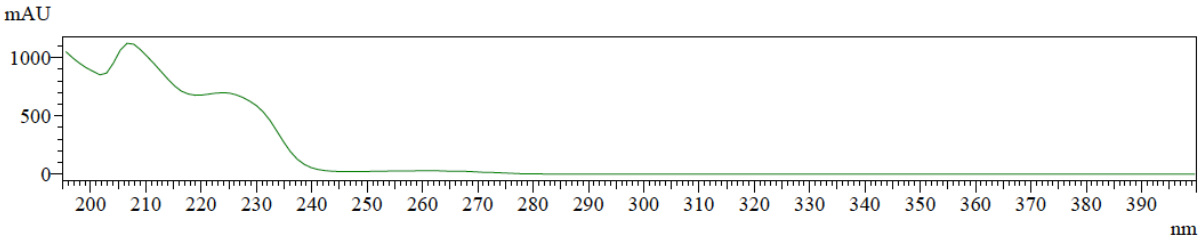
Chromatogram



UV Spectrum
Retention time = 18.695



UV Spectrum
Retention time = 23.000

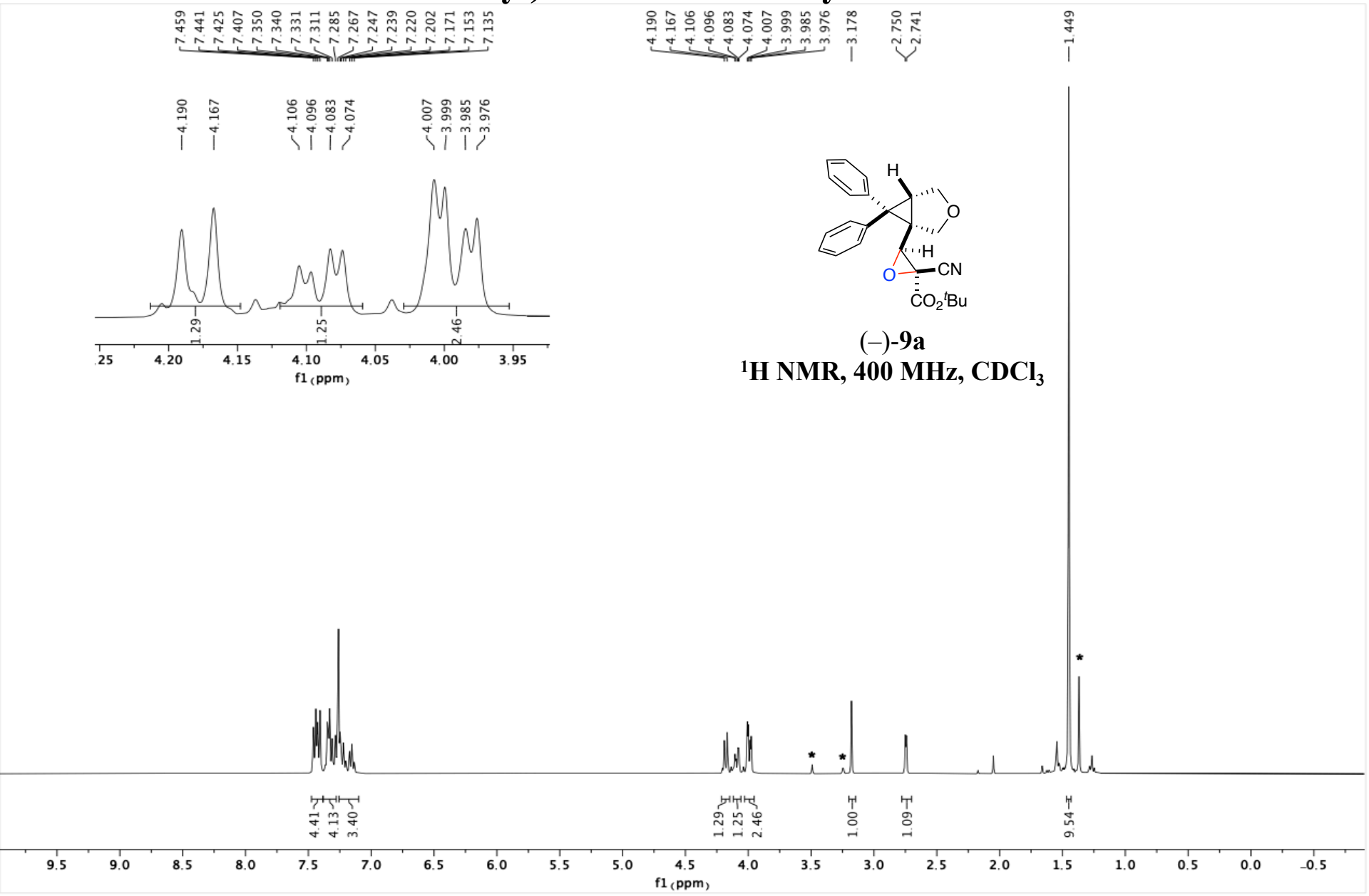


Peak Table

PDA Ch1 222nm

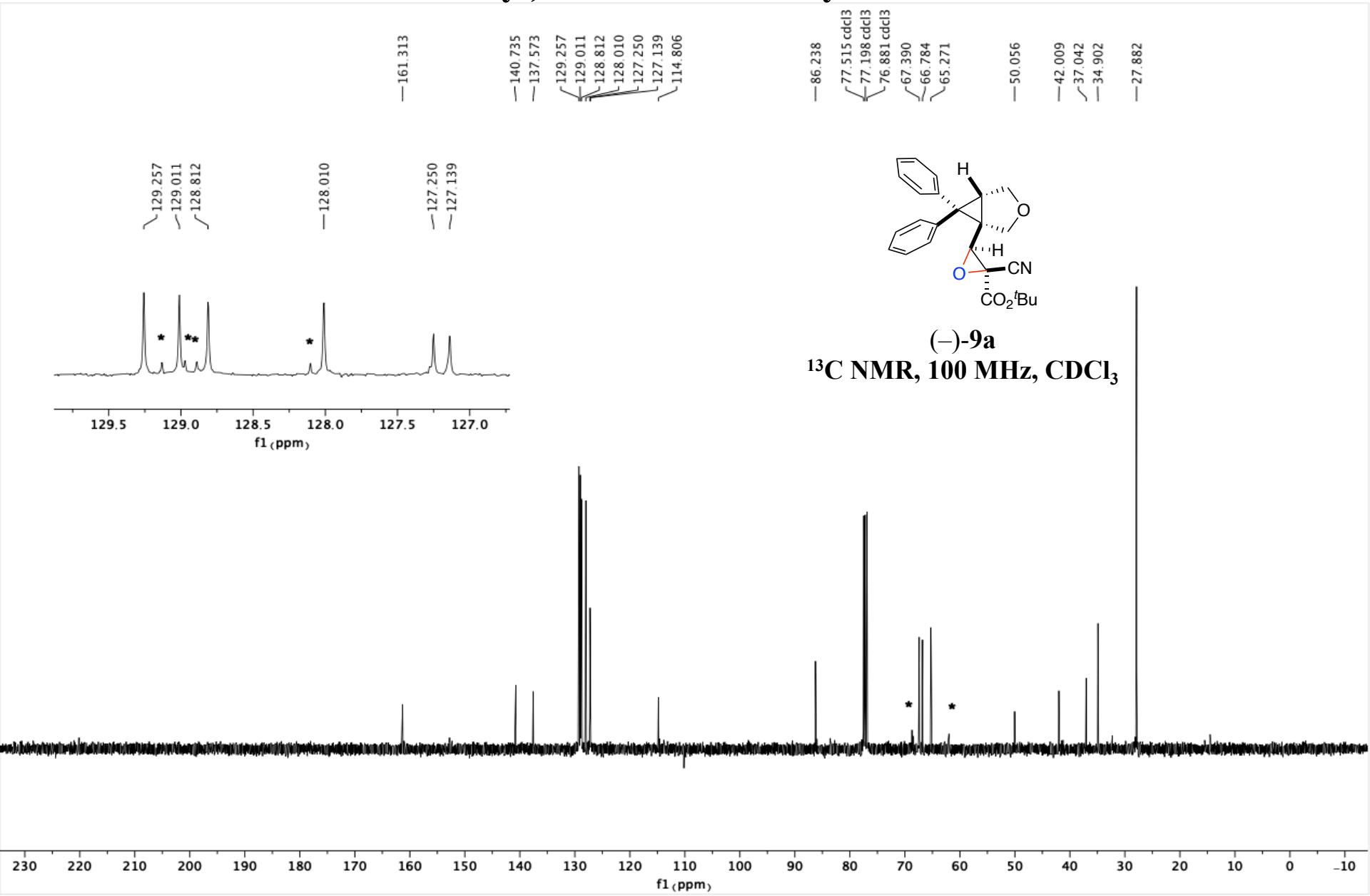
Peak#	Ret. Time	Area	Area%
1	18.695	1999199	6.863
2	23.000	27130216	93.137
Total		29129415	100.000

tert-Butyl (3*S*)-2-cyano-3-((1*R*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)oxirane-2-carboxylate



* is minor diastereomer.

tert-Butyl (3*S*)-2-cyano-3-((1*R*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)oxirane-2-carboxylate

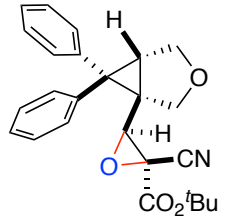


* is minor diastereomer.

tert-Butyl (3*S*)-2-cyano-3-((1*R*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)oxirane-2-carboxylate

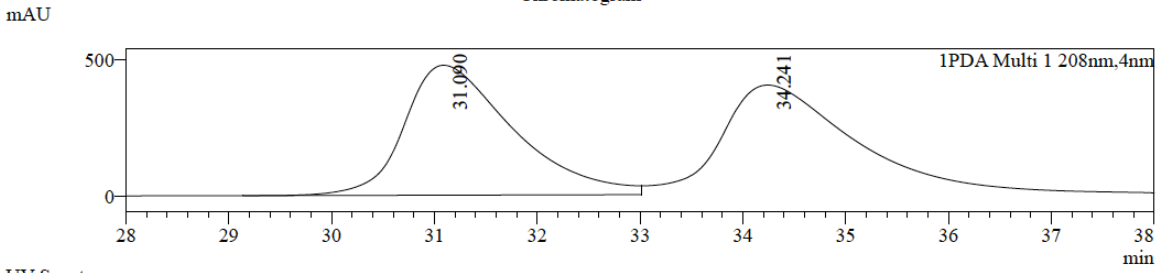
Sample Information

Sample Name : CZZ-1527-WHELK-3%-1mL
Sample ID : CZZ-1527-WHELK-3%-1mL
Data File : CZZ-1527-WHELK-3%-1mL.lcd
Method File : CZZ-3.0%-1.0ml.lcm

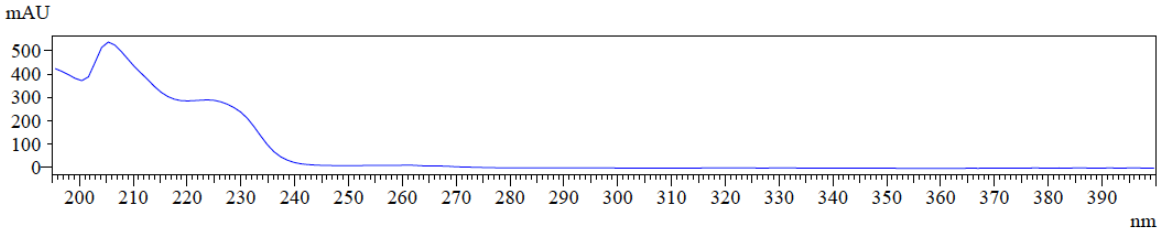


(±)-**9a**

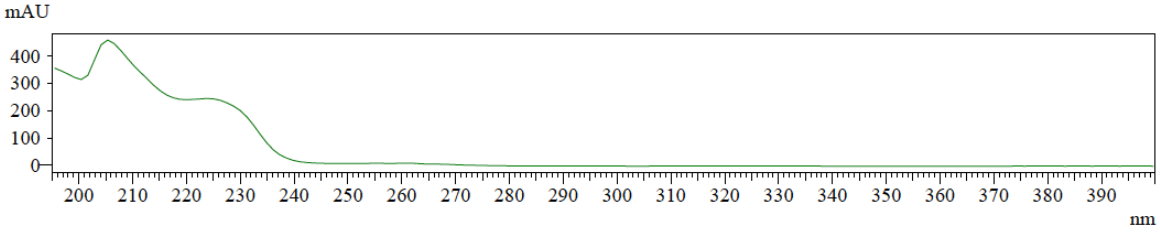
Chromatogram



UV Spectrum
Retention time = 31.090



UV Spectrum
Retention time = 34.241



Peak Table

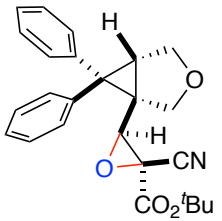
PDA Ch1 208nm

Peak#	Ret. Time	Area	Area%
1	31.090	35230039	49.120
2	34.241	36491966	50.880
Total		71722005	100.000

tert-Butyl (3*S*)-2-cyano-3-((1*R*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)oxirane-2-carboxylate

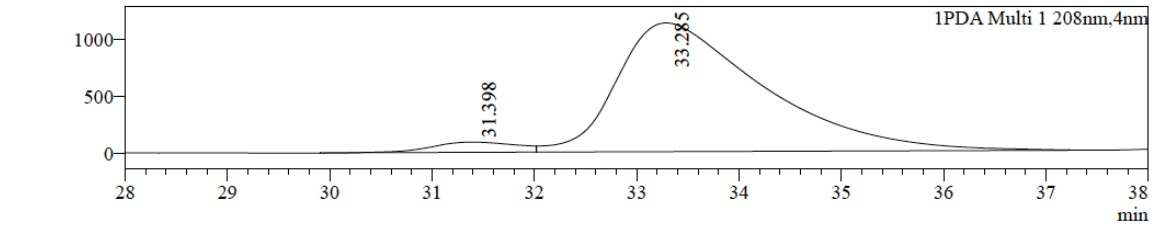
Sample Information

Sample Name	: CZZ-1528-WHELK-3%-1mL
Sample ID	: CZZ-1528-WHELK-3%-1mL
Data File	: CZZ-1528-WHELK-3%-1mL.lcd
Method File	: CZZ-3.0%-1.0ml.lcm

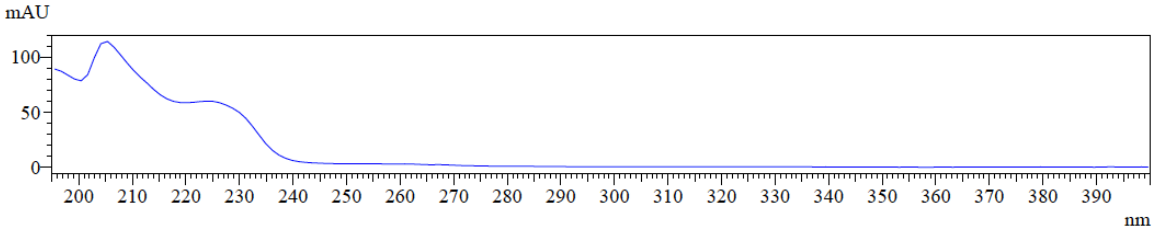


(–)-**9a**

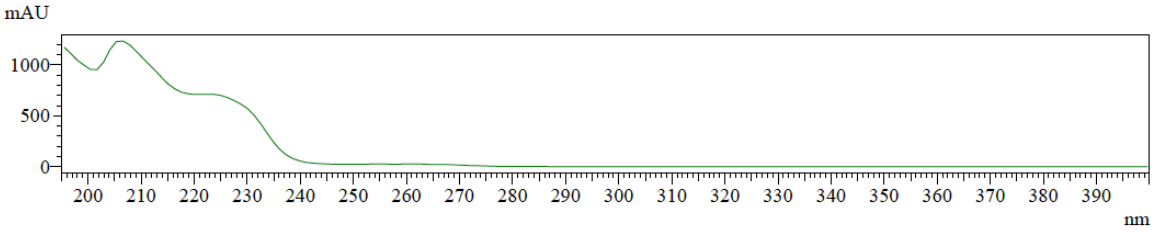
Chromatogram



UV Spectrum
Retention time = 31.398



UV Spectrum
Retention time = 33.285

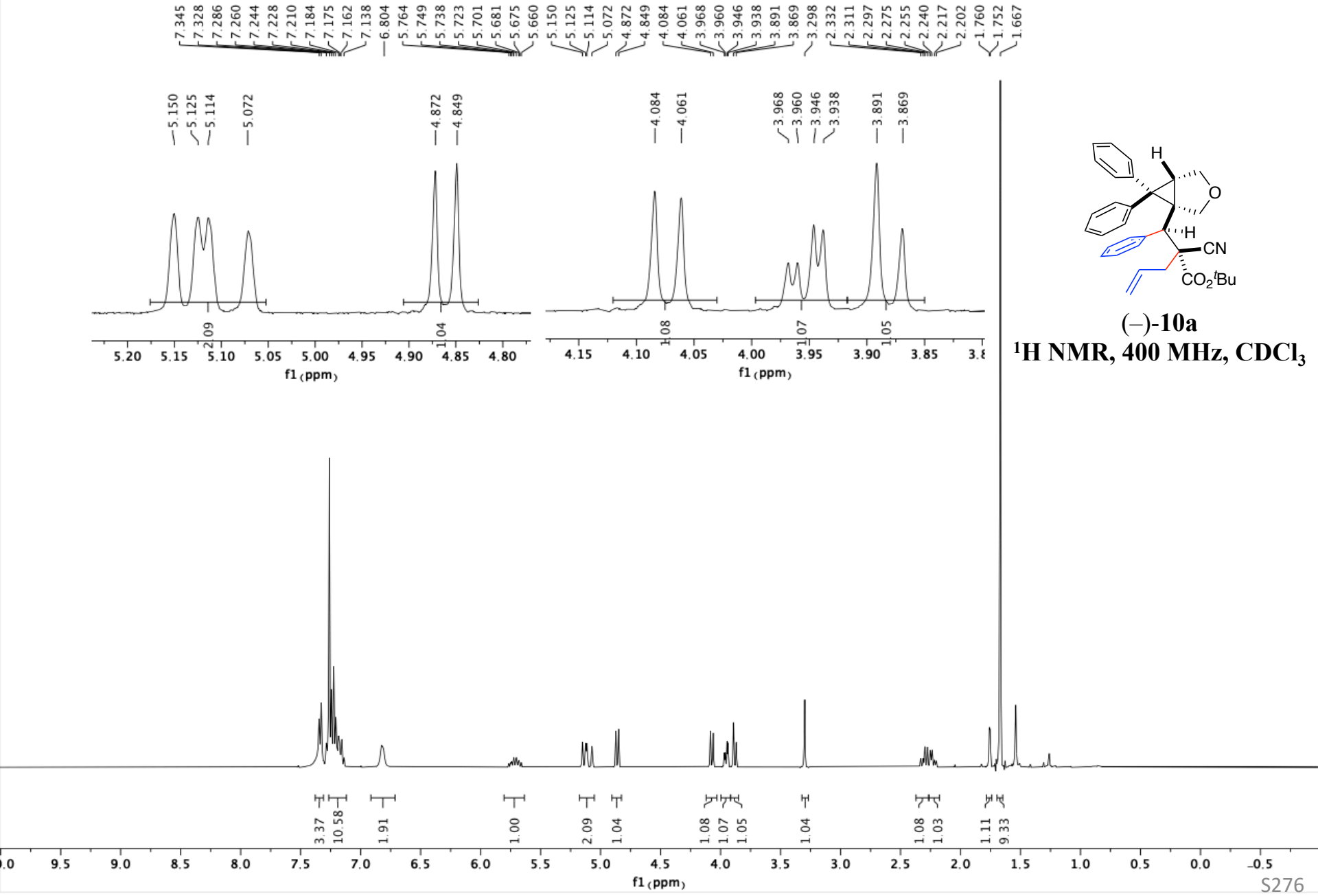


Peak Table

PDA Ch1 208nm

Peak#	Ret. Time	Area	Area%
1	31.398	5251673	4.431
2	33.285	113273862	95.569
Total		118525535	100.000

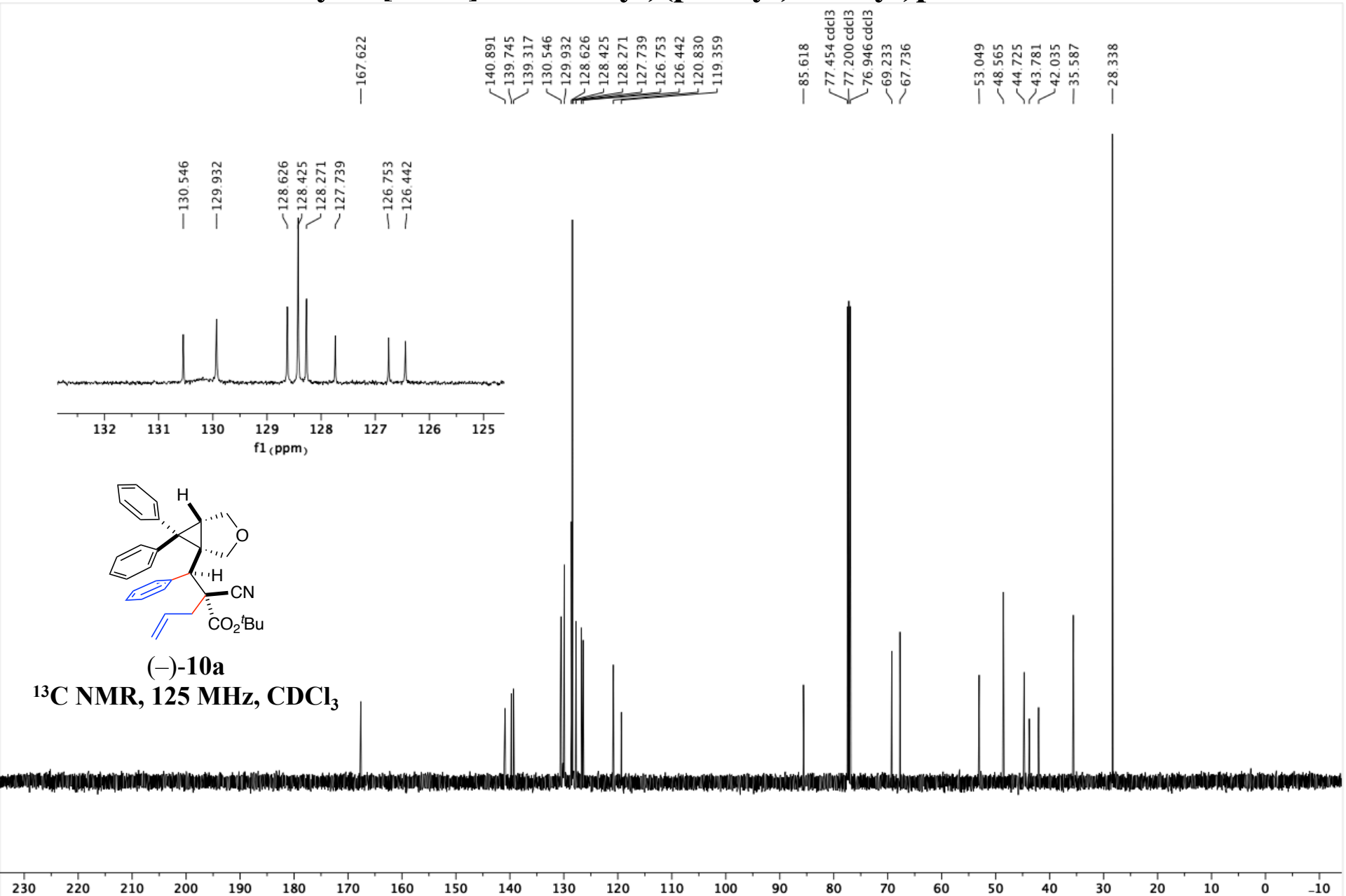
tert-Butyl (*R*)-2-cyano-2-((*S*)-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methyl)pent-4-enoate



(–)-10a

^{1}H NMR, 400 MHz, $CDCl_3$

tert-Butyl (*R*)-2-cyano-2-((*S*)-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methyl)pent-4-enoate



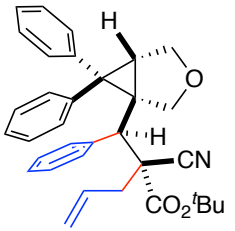
(–)-10a

^{13}C NMR, 125 MHz, $CDCl_3$

tert-Butyl (*R*)-2-cyano-2-((*S*)-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methyl)pent-4-enoate

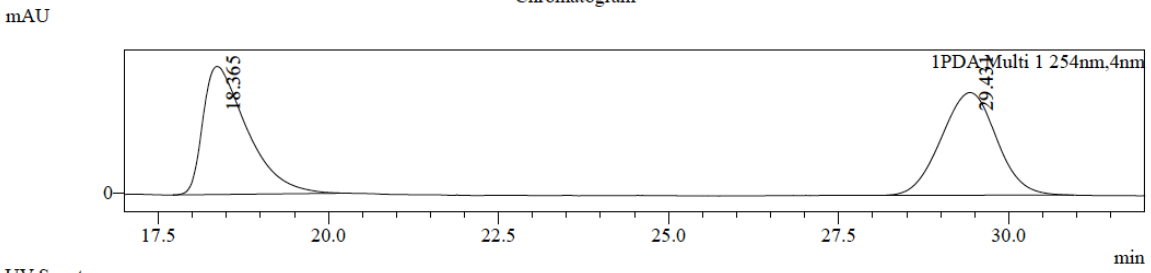
Sample Information

Sample Name	: CZZ-1516-IE-10%-1mL
Sample ID	: CZZ-1516-IE-10%-1mL
Data File	: CZZ-1516-IE-10%-1mL.lcd
Method File	: CZZ-10%-1.0ml.lcm

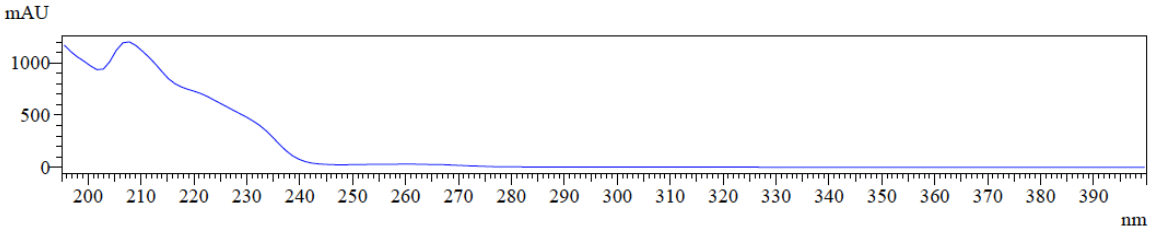


(±)-**10a**

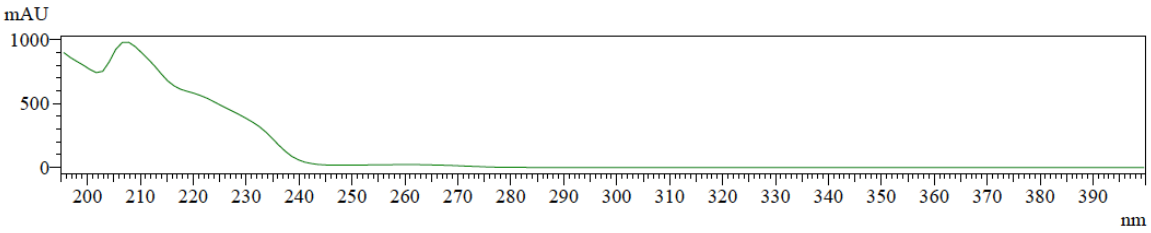
Chromatogram



UV Spectrum
Retention time = 18.365



UV Spectrum
Retention time = 29.431

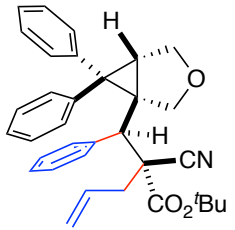


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.365	1201619	49.957
2	29.431	1203687	50.043
Total		2405306	100.000

tert-Butyl (*R*)-2-cyano-2-((*S*)-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methyl)pent-4-enoate

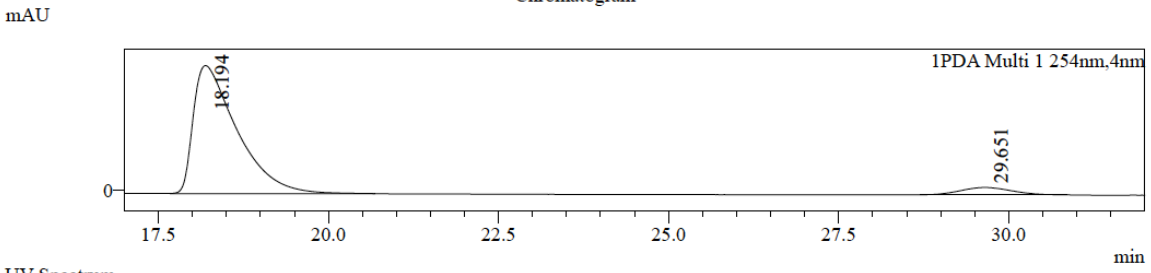


(–)-**10a**

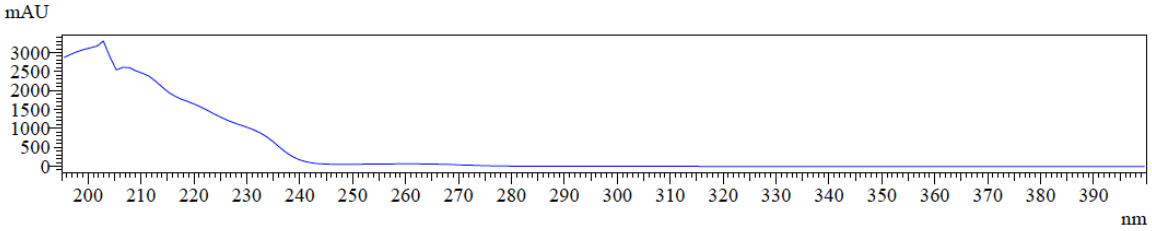
Sample Information

Sample Name	: CZZ-1521-IE-10%-1mL
Sample ID	: CZZ-1521-IE-10%-1mL
Data File	: CZZ-1521-IE-10%-1mL001.lcd
Method File	: CZZ-10%-1.0ml.lcm

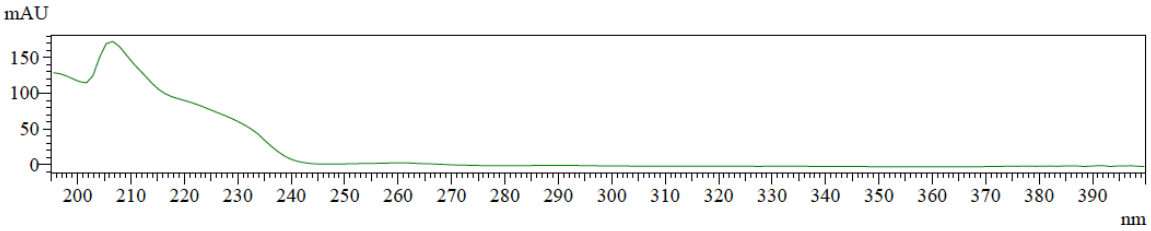
Chromatogram



UV Spectrum
Retention time = 18.194



UV Spectrum
Retention time = 29.651

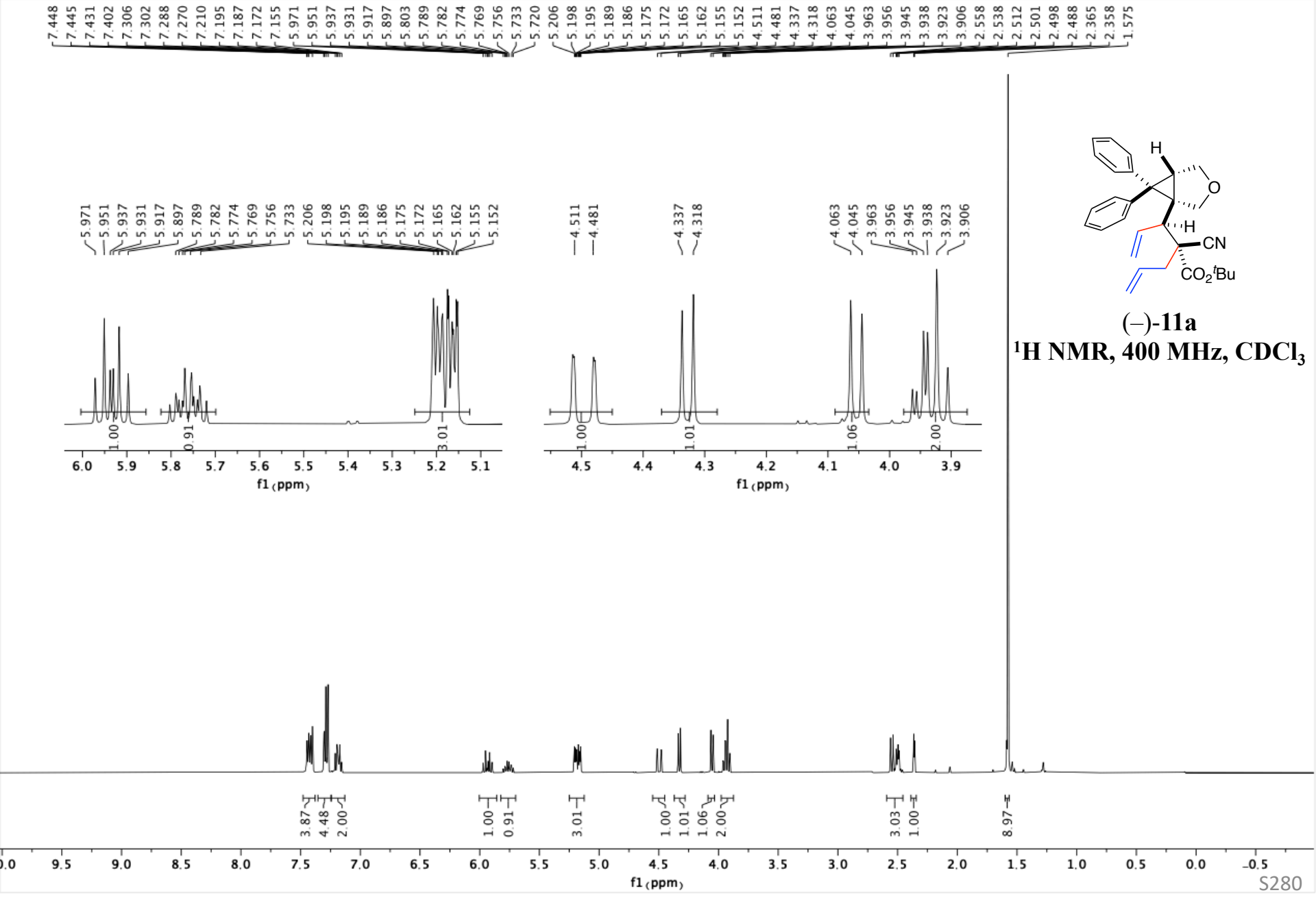


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.194	2709887	93.671
2	29.651	183111	6.329
Total		2892998	100.000

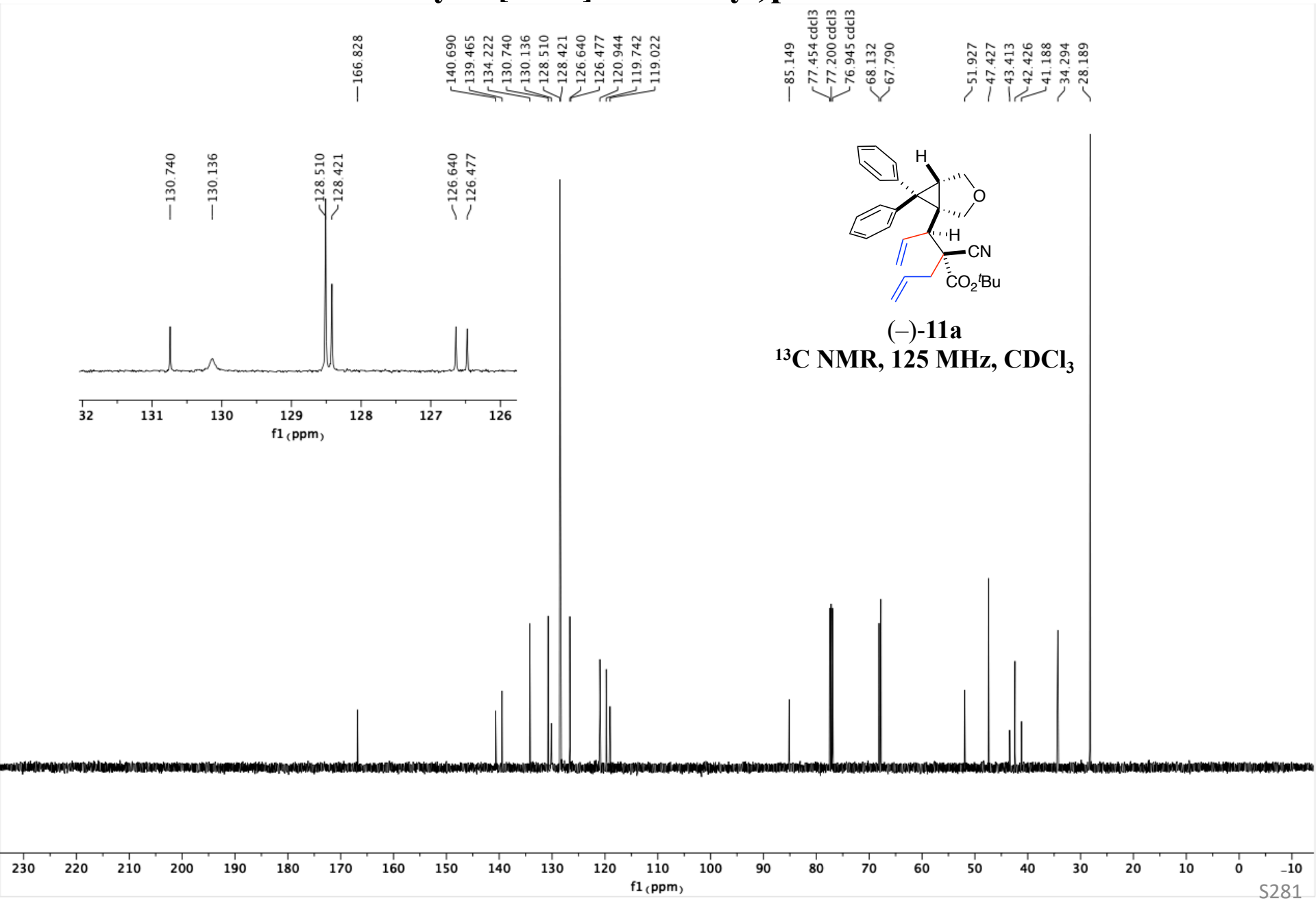
tert-Butyl (2*R*,3*S*)-2-allyl-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)pent-4-enoate



(–)-11a

^{1}H NMR, 400 MHz, $CDCl_3$

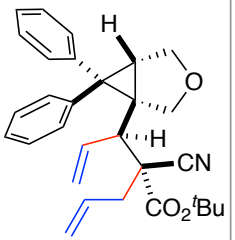
tert-Butyl (2*R*,3*S*)-2-allyl-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)pent-4-enoate



tert-Butyl (2*R*,3*S*)-2-allyl-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)pent-4-enoate

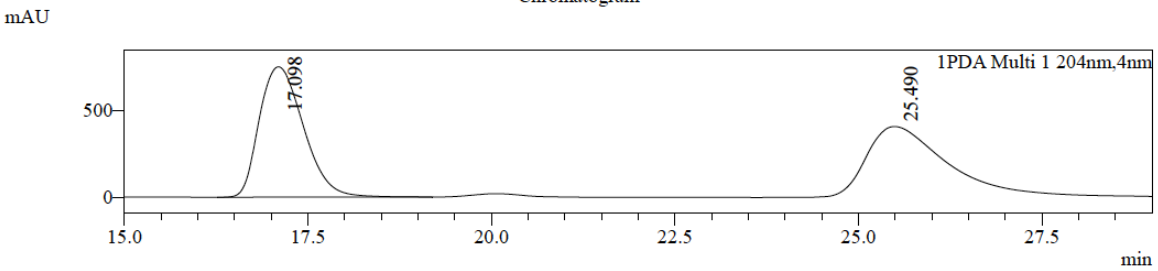
Sample Information

Sample Name	: CZZ-1974-ID-10%-0.8mL
Sample ID	: CZZ-1974-ID-10%-0.8mL
Data File	: CZZ-1974-ID-10%-0.8mL002.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

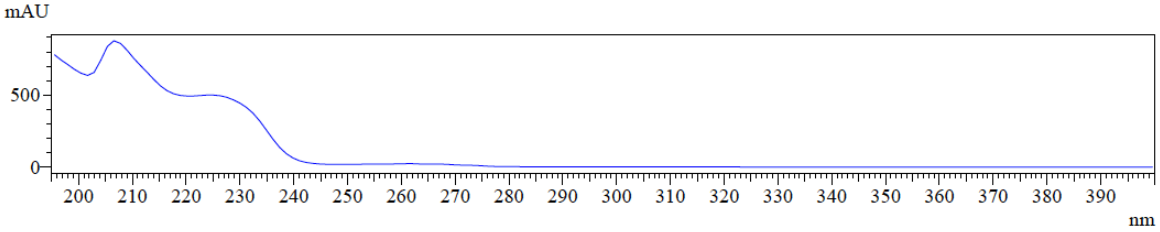


(±)-**11a**

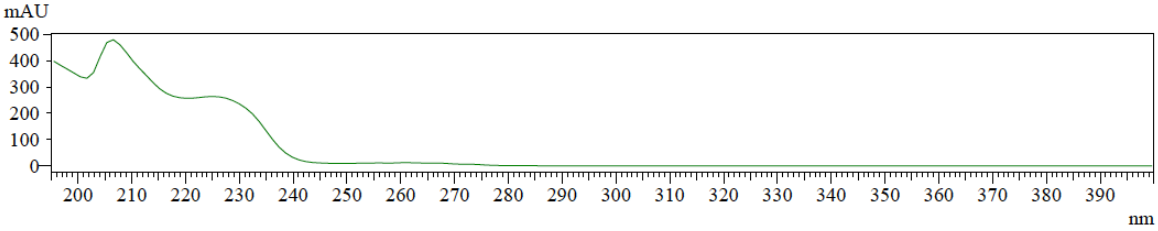
Chromatogram



UV Spectrum
Retention time = 17.098



UV Spectrum
Retention time = 25.490

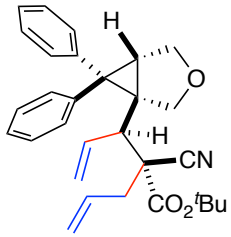


Peak Table

PDA Ch1 204nm

Peak#	Ret. Time	Area	Area%
1	17.098	31380772	49.910
2	25.490	31494097	50.090
Total		62874870	100.000

tert-Butyl (2*R*,3*S*)-2-allyl-2-cyano-3-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)pent-4-enoate

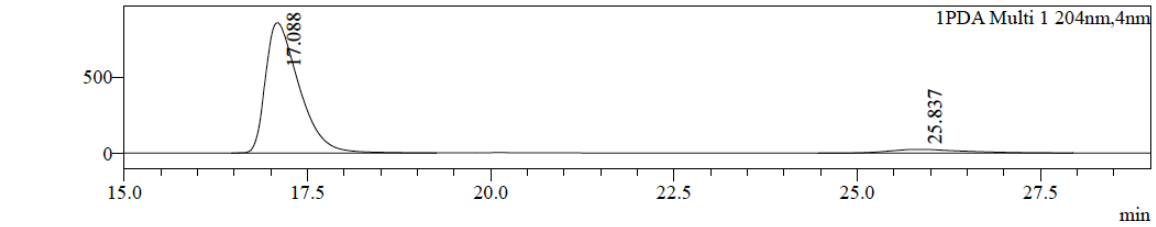


(–)-11a

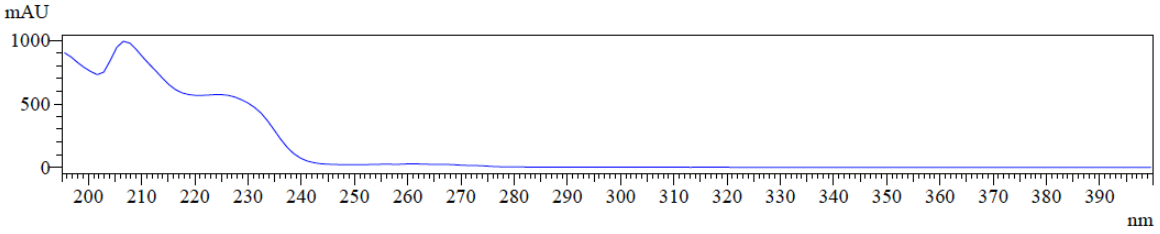
Sample Information

Sample Name	: CZZ-1975-ID-10%-0.8mL
Sample ID	: CZZ-1975-ID-10%-0.8mL
Data File	: CZZ-1975-ID-10%-0.8mL003.lcd
Method File	: CZZ-10.0%-0.8ml.lcm

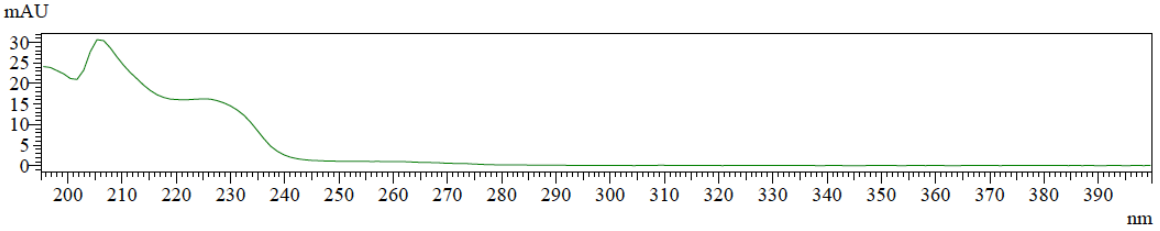
Chromatogram



UV Spectrum
Retention time = 17.088



UV Spectrum
Retention time = 25.837

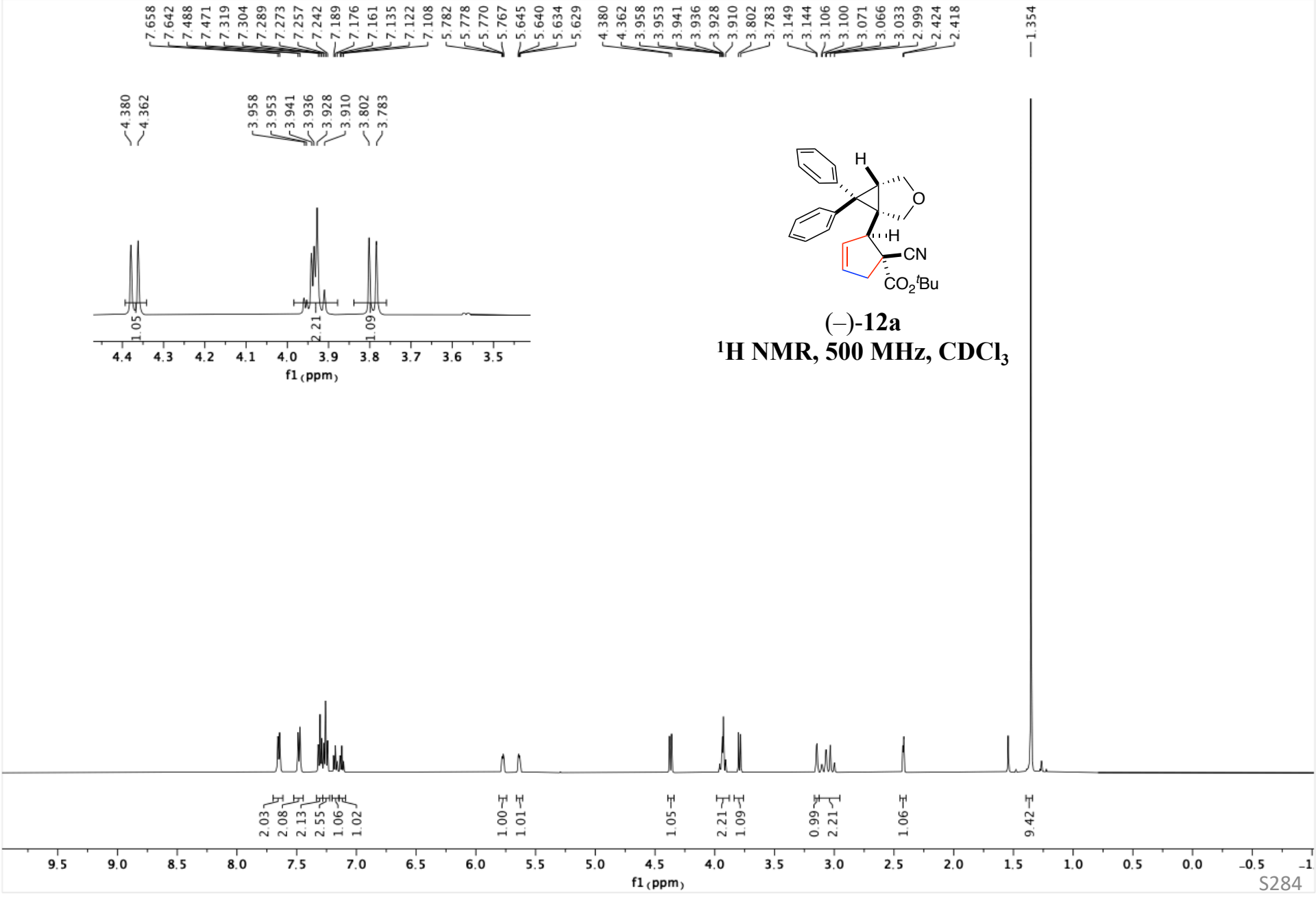


Peak Table

PDA Ch1 204nm

Peak#	Ret. Time	Area	Area%
1	17.088	27278568	94.356
2	25.837	1631599	5.644
Total		28910167	100.000

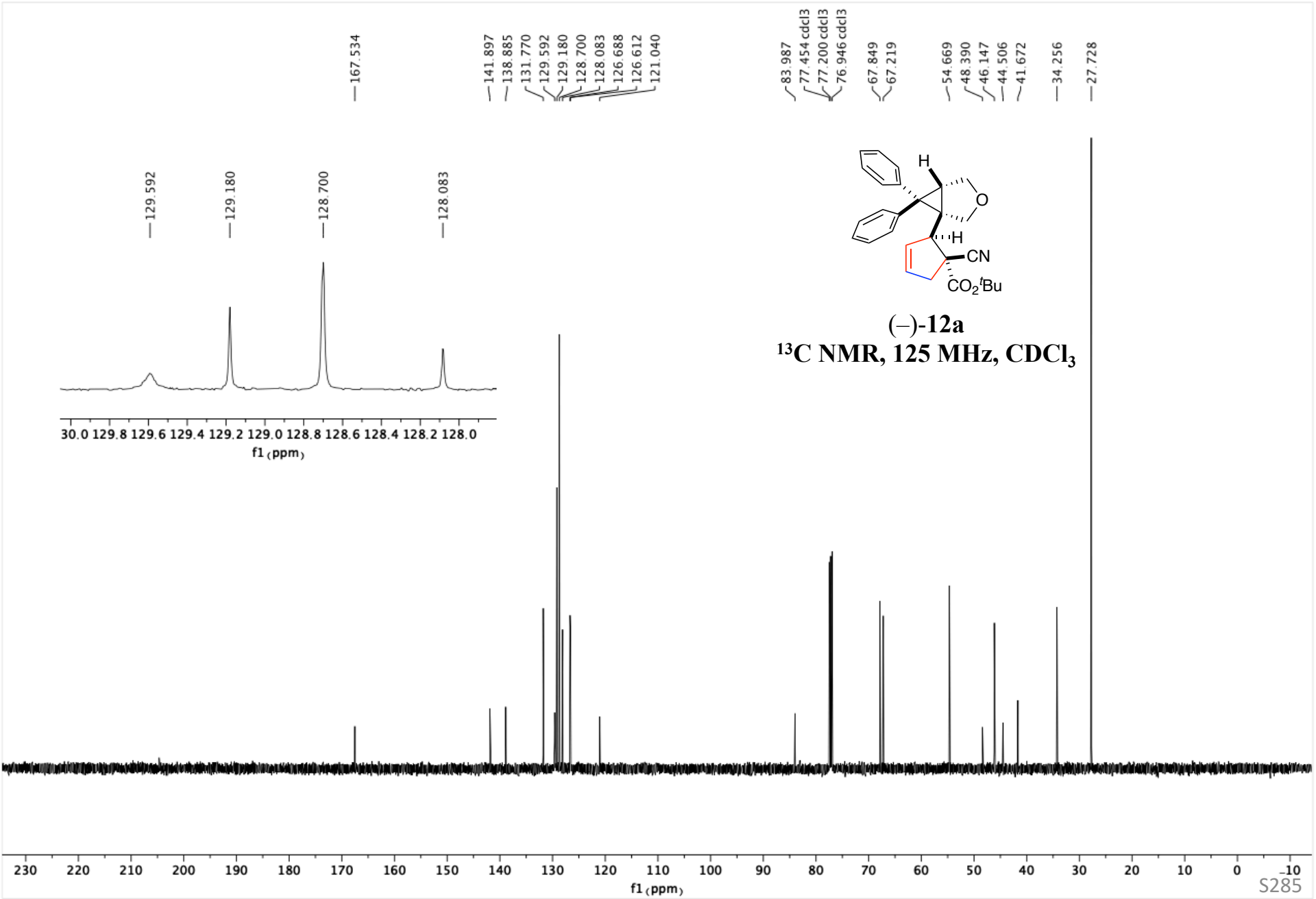
tert-Butyl (1*R*)-1-cyano-2-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)cyclopent-3-ene-1-carboxylate



(–)-**12a**

^{1}H NMR, 500 MHz, $CDCl_3$

tert-Butyl (1*R*)-1-cyano-2-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)cyclopent-3-ene-1-carboxylate

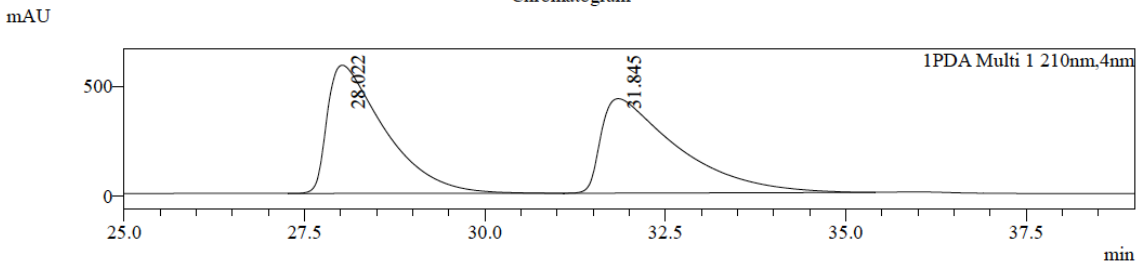


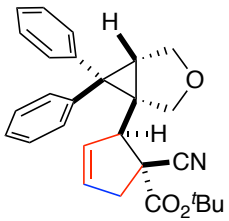
tert-Butyl (1*R*)-1-cyano-2-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)cyclopent-3-ene-1-carboxylate

Sample Information

Sample Name	: CZZ-2027-5%-IE-0.8mL
Sample ID	: CZZ-2027-5%-IE-0.8mL
Data File	: CZZ-2027-5%-IE-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

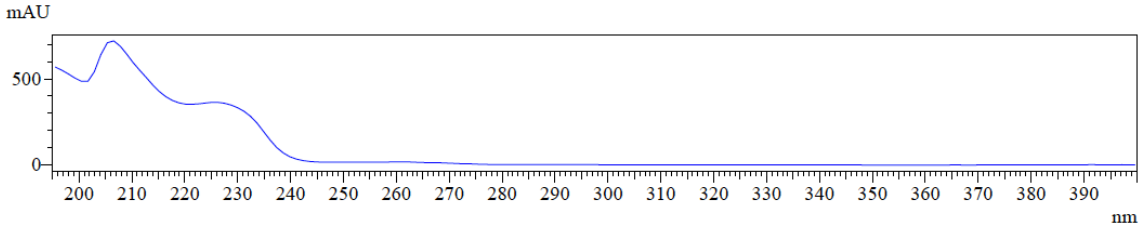
Chromatogram



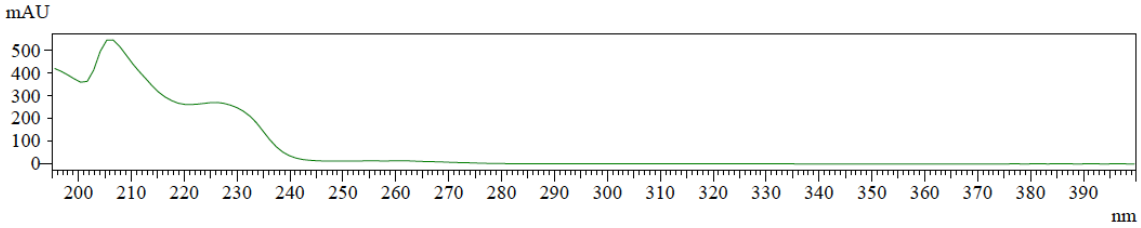


(±)-**12a**

UV Spectrum
Retention time = 28.022



UV Spectrum
Retention time = 31.845

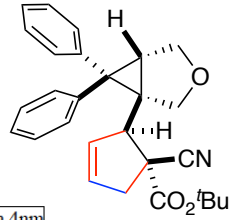


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	28.022	32260154	50.569
2	31.845	31533775	49.431
Total		63793929	100.000

tert-Butyl (1*R*)-1-cyano-2-((1*S*,5*S*)-6,6-diphenyl-3-oxabicyclo[3.1.0]hexan-1-yl)cyclopent-3-ene-1-carboxylate

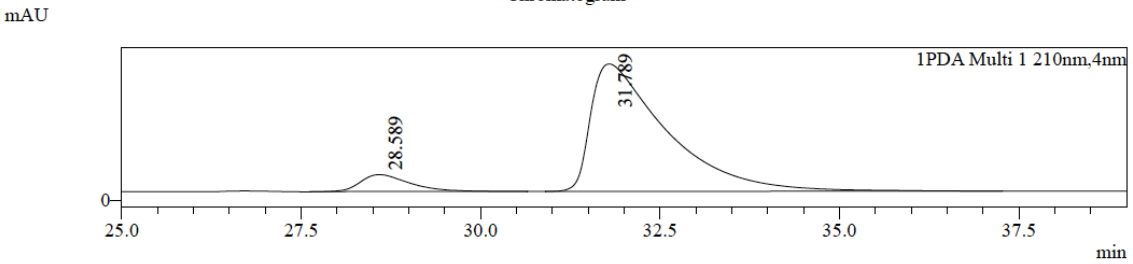


(–)-**12a**

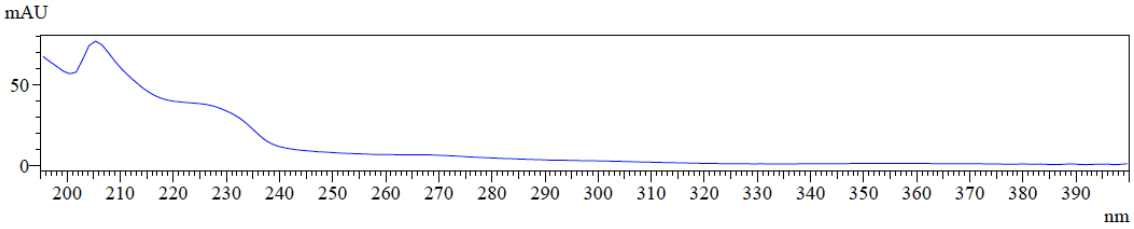
Sample Information

Sample Name	: CZZ-2034-5%-IE-0.8mL
Sample ID	: CZZ-2034-5%-IE-0.8mL
Data File	: CZZ-2034-5%-IE-0.8mL.lcd
Method File	: CZZ-5.0%-0.8ml.lcm

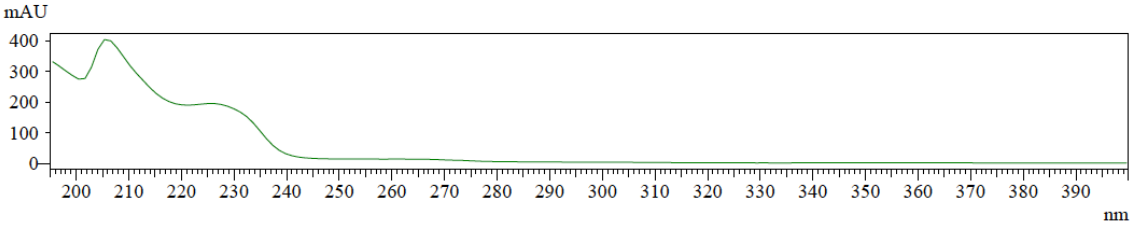
Chromatogram



UV Spectrum
Retention time = 28.589



UV Spectrum
Retention time = 31.789

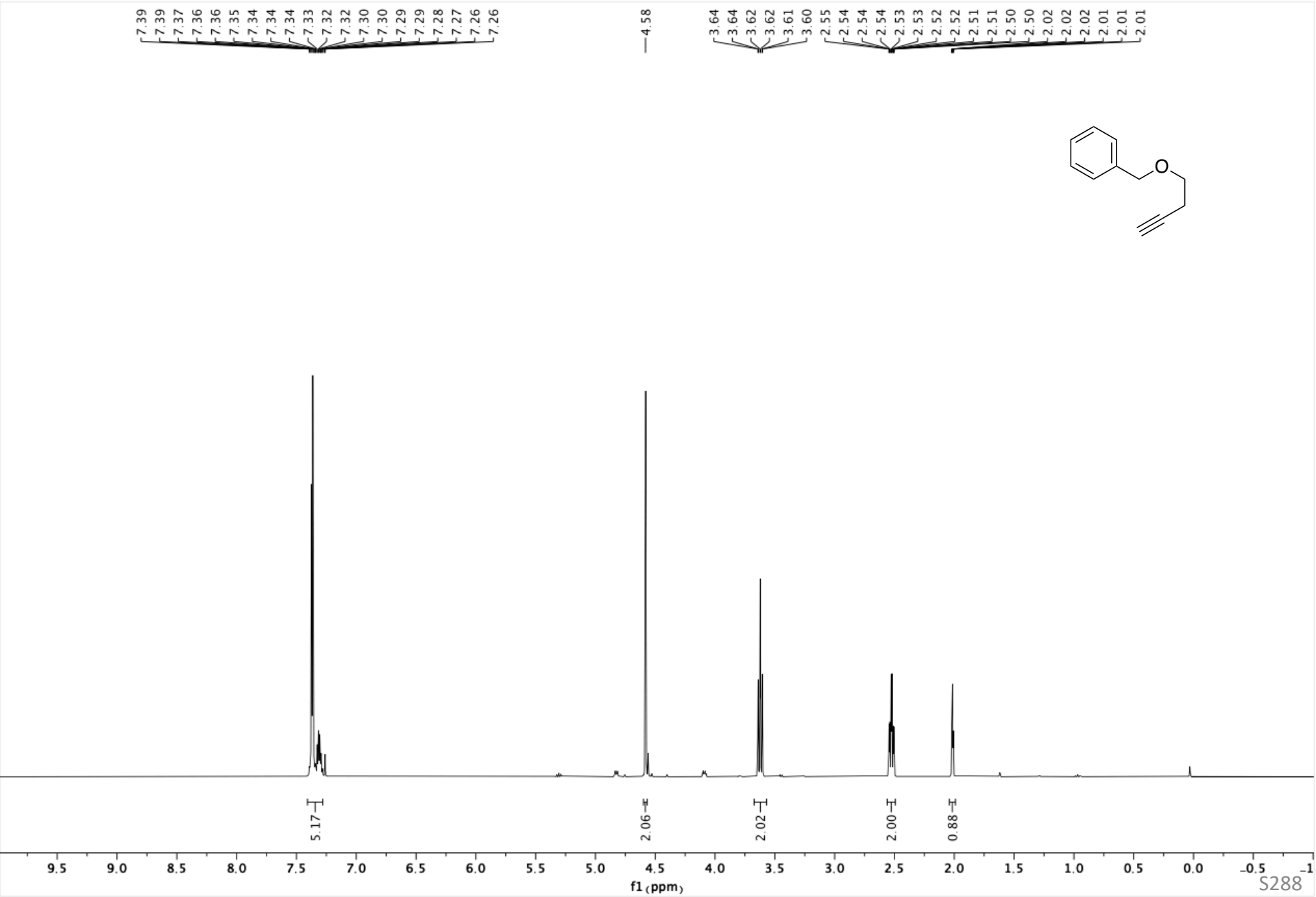


Peak Table

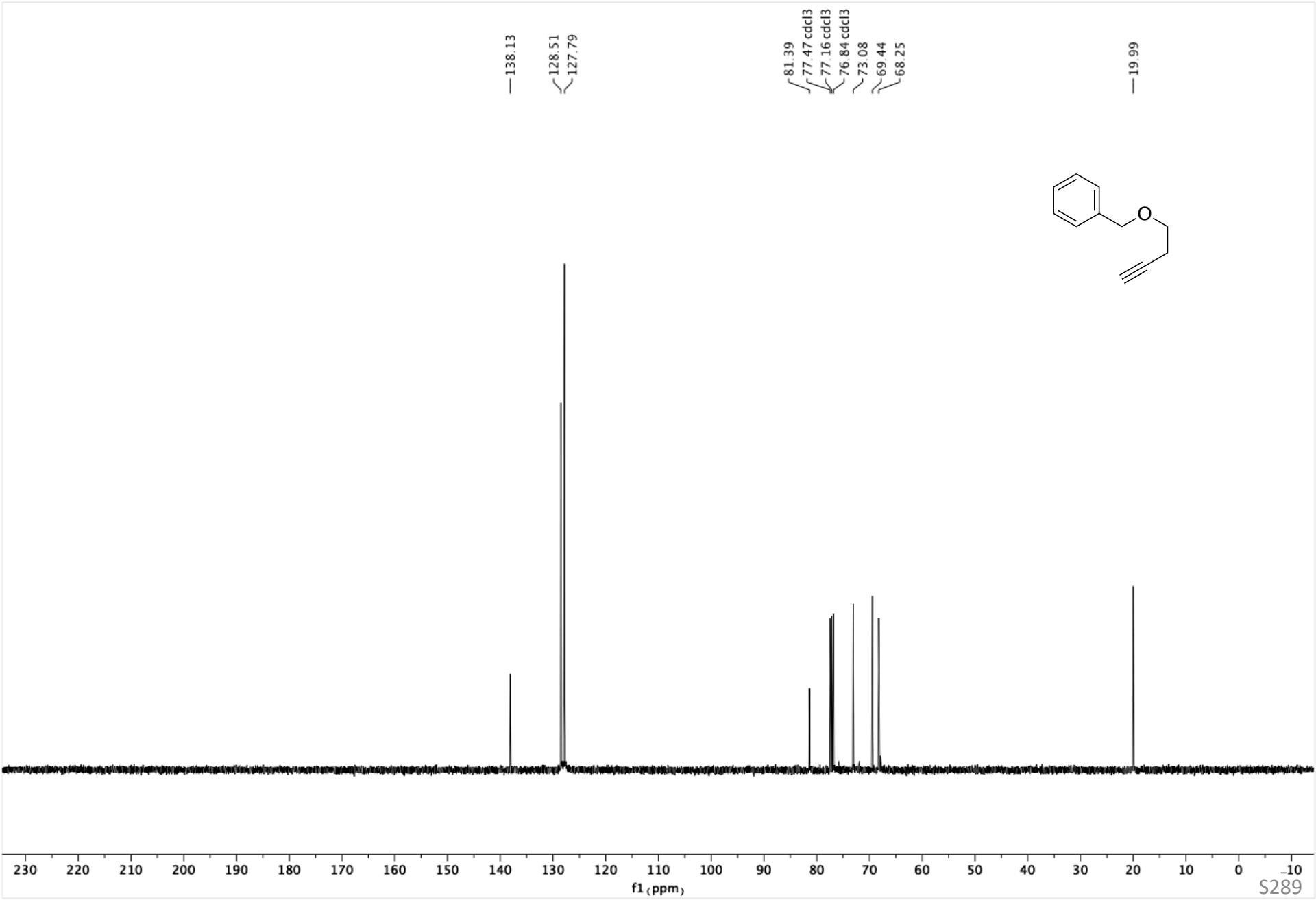
PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	28.589	1889767	7.869
2	31.789	22125275	92.131
Total		24015041	100.000

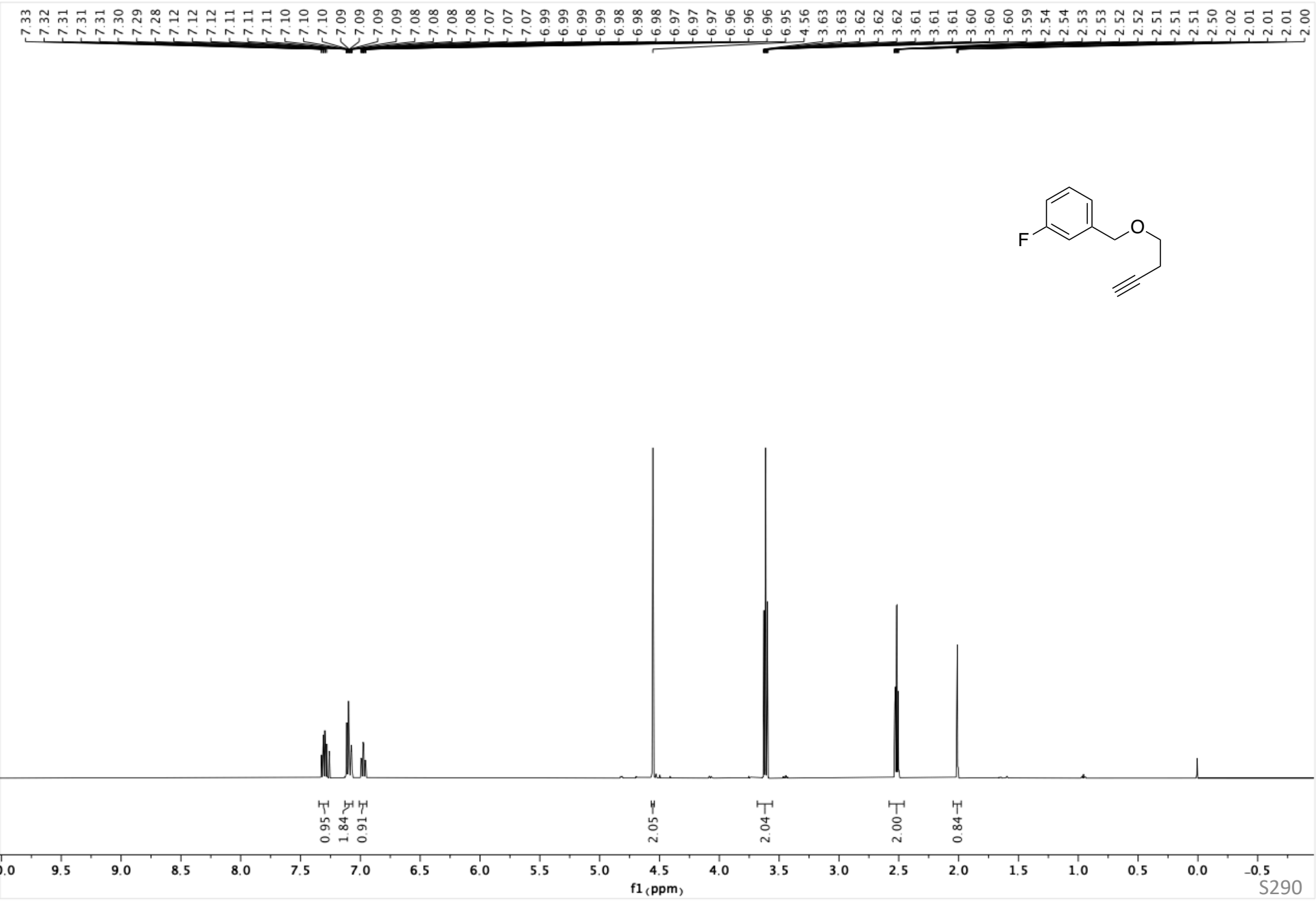
((But-3-yn-1-yloxy)methyl)benzene



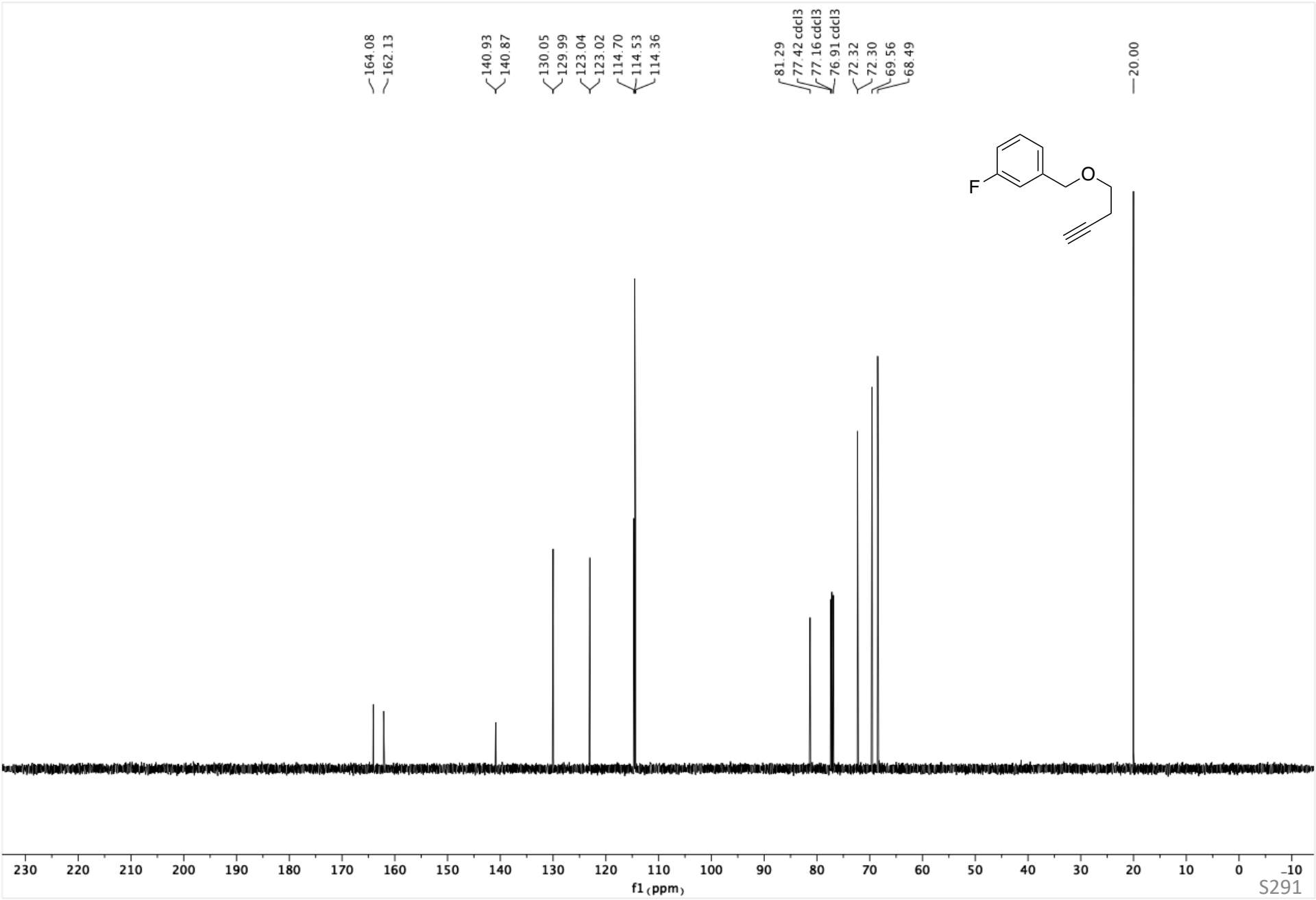
((But-3-yn-1-yloxy)methyl)benzene



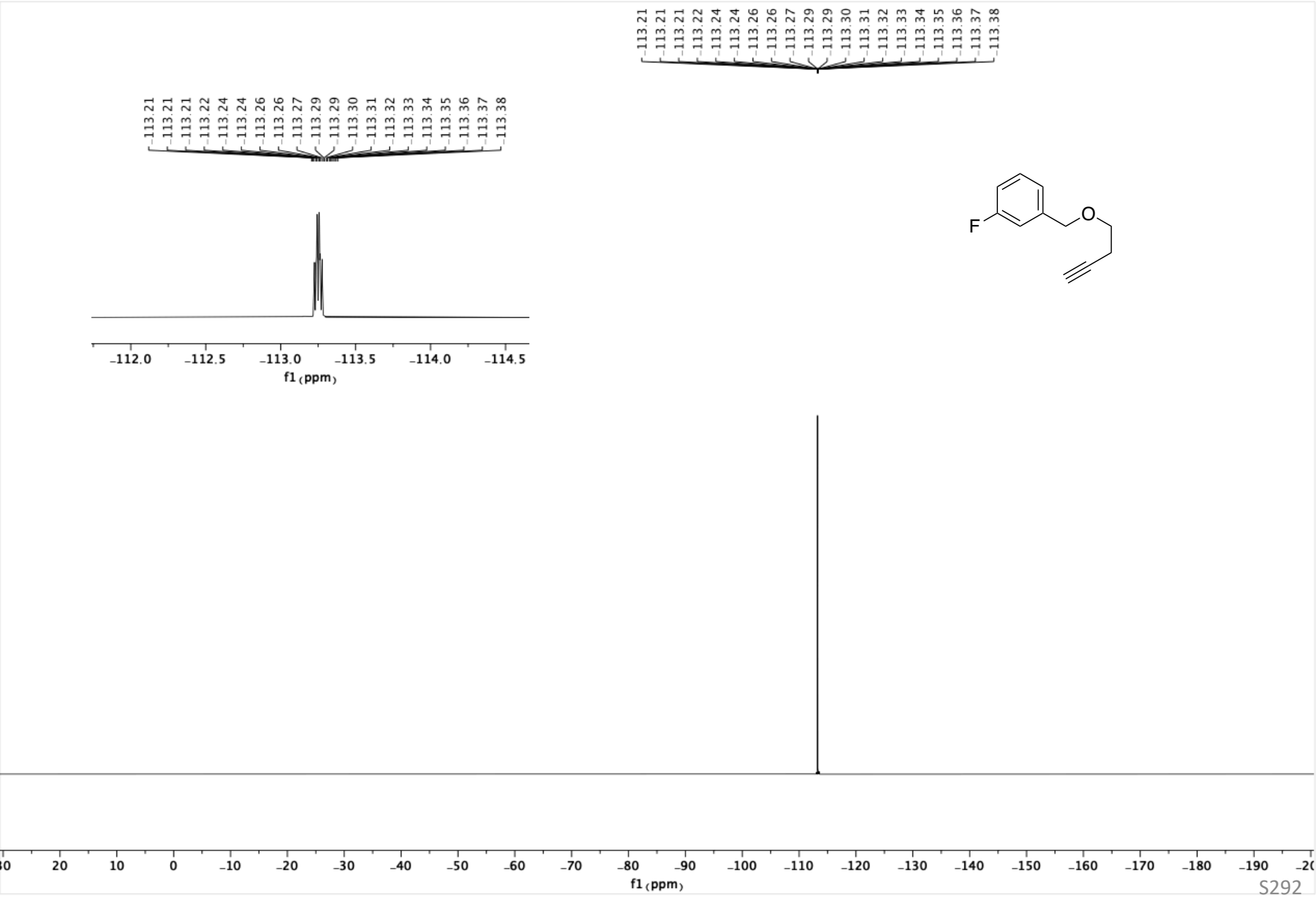
1-((But-3-yn-1-yloxy)methyl)-3-fluorobenzene



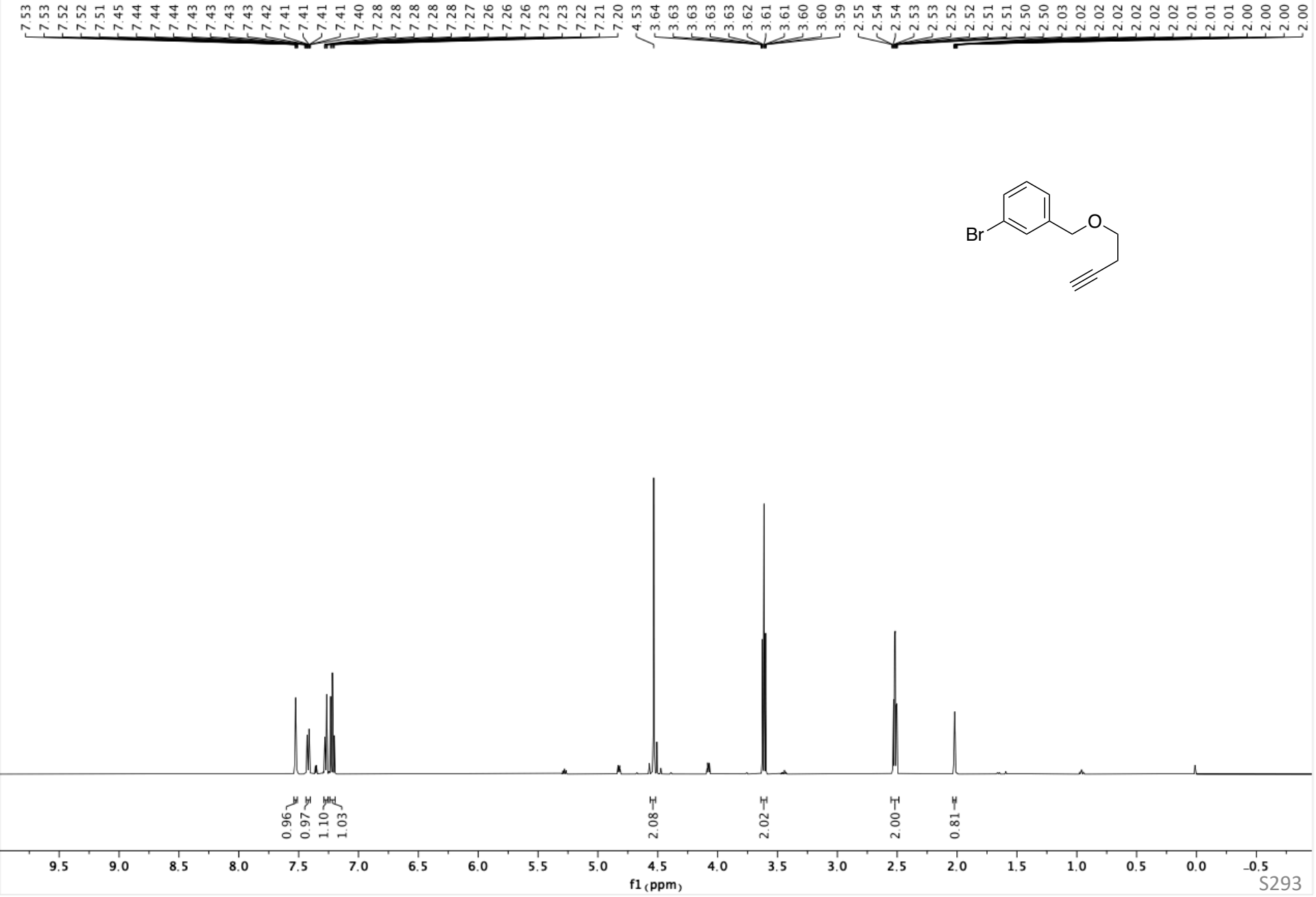
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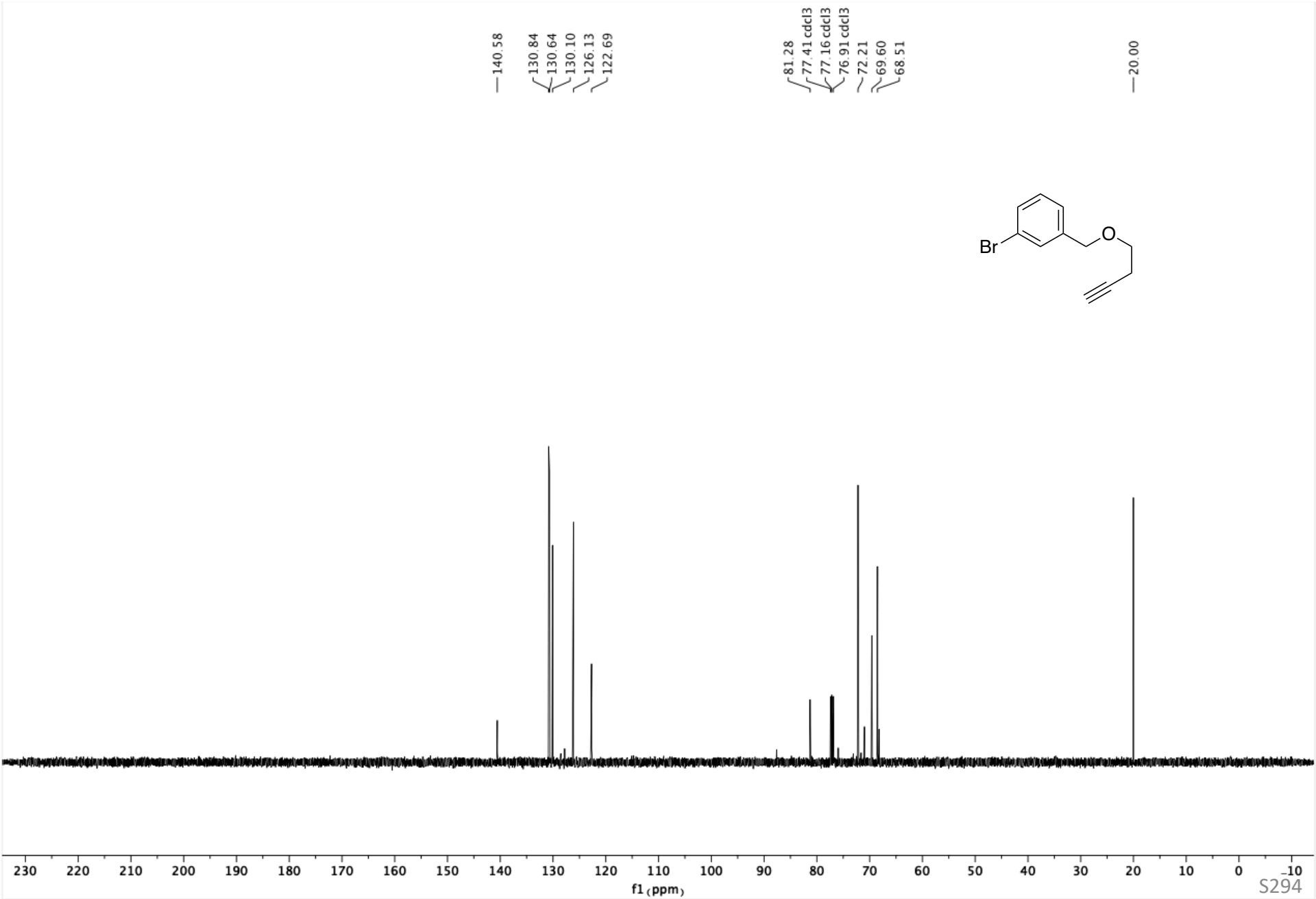
1-((But-3-yn-1-yloxy)methyl)-3-fluorobenzene



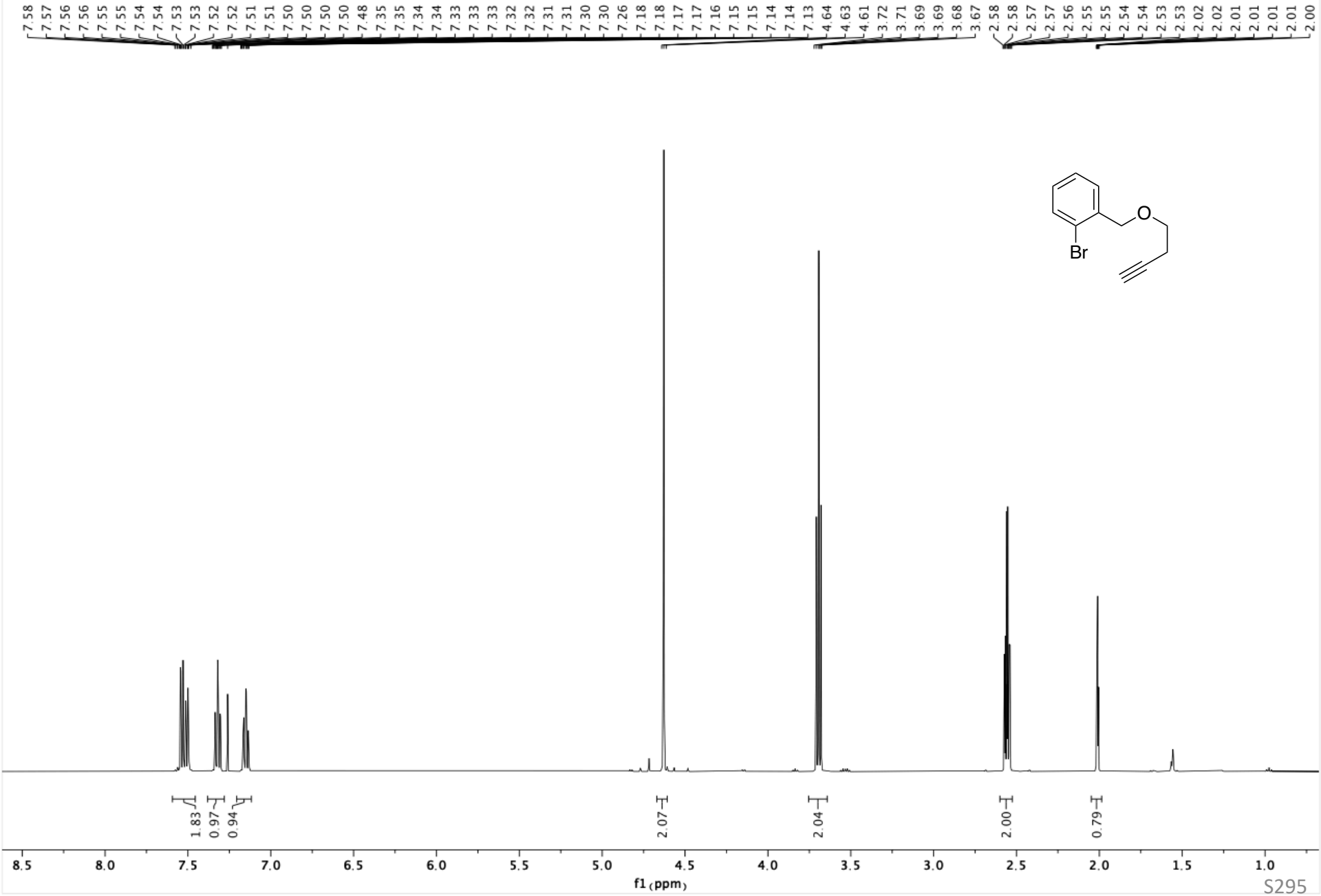
1-Bromo-3-((but-3-yn-1-yloxy)methyl)benzene



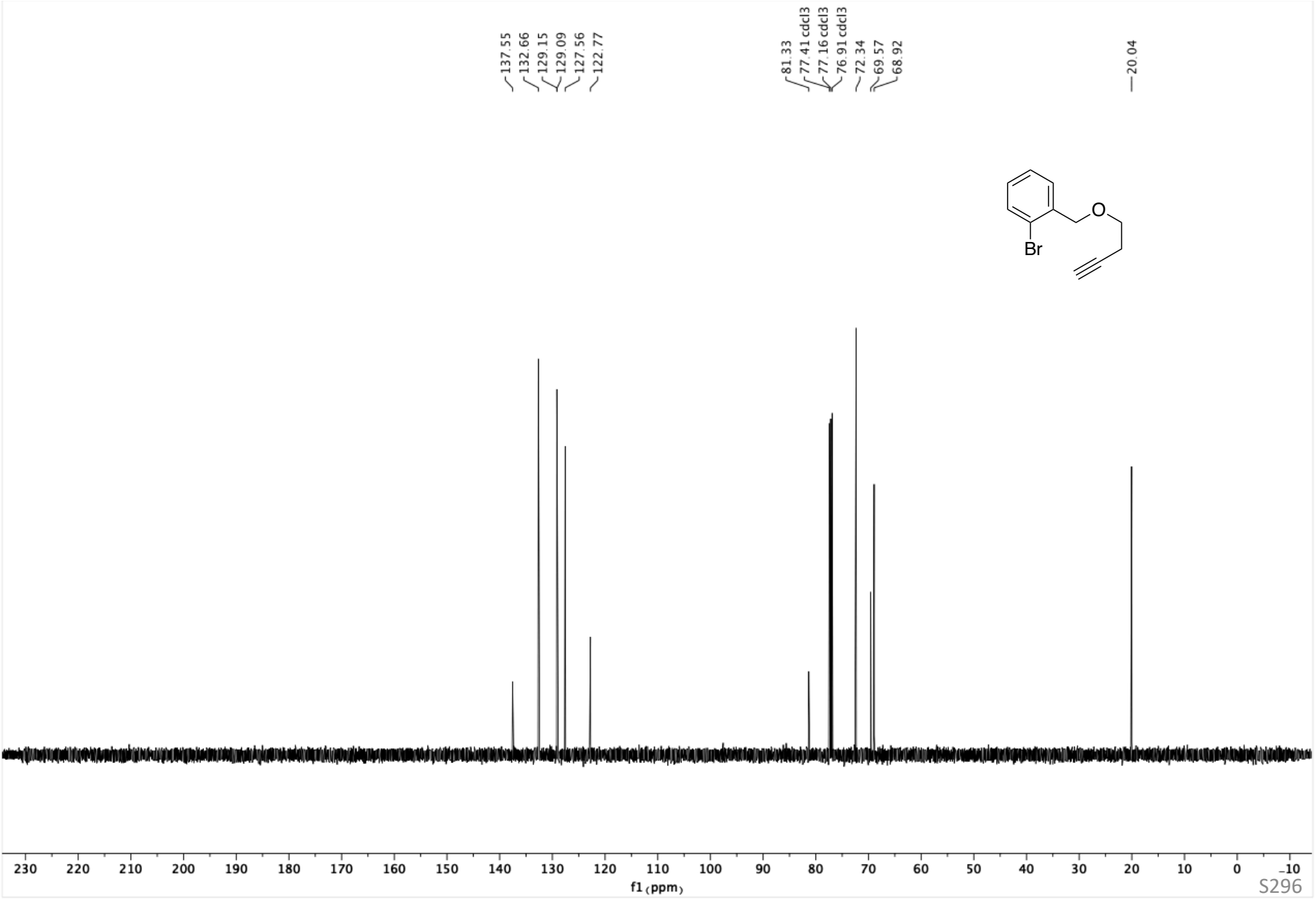
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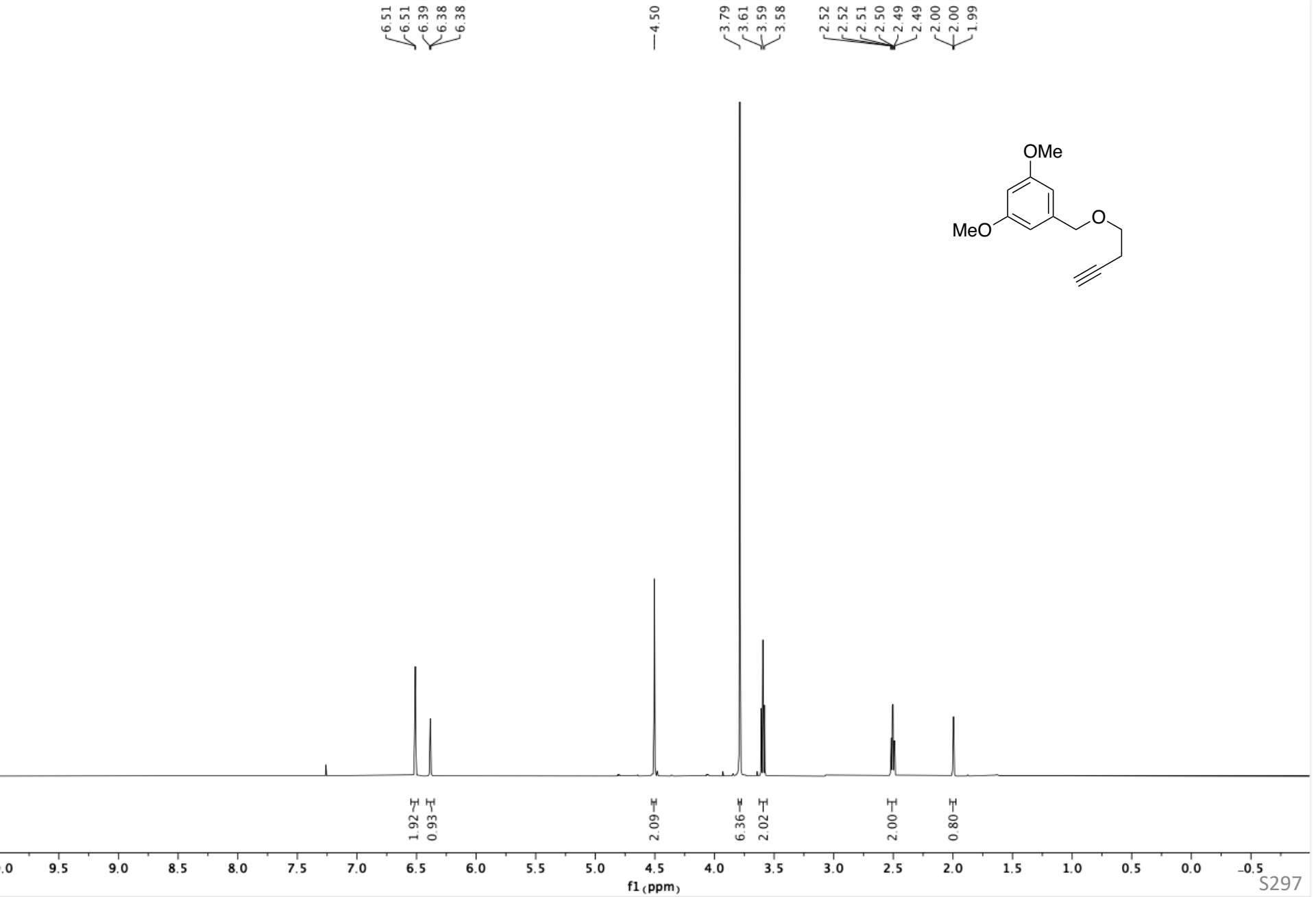
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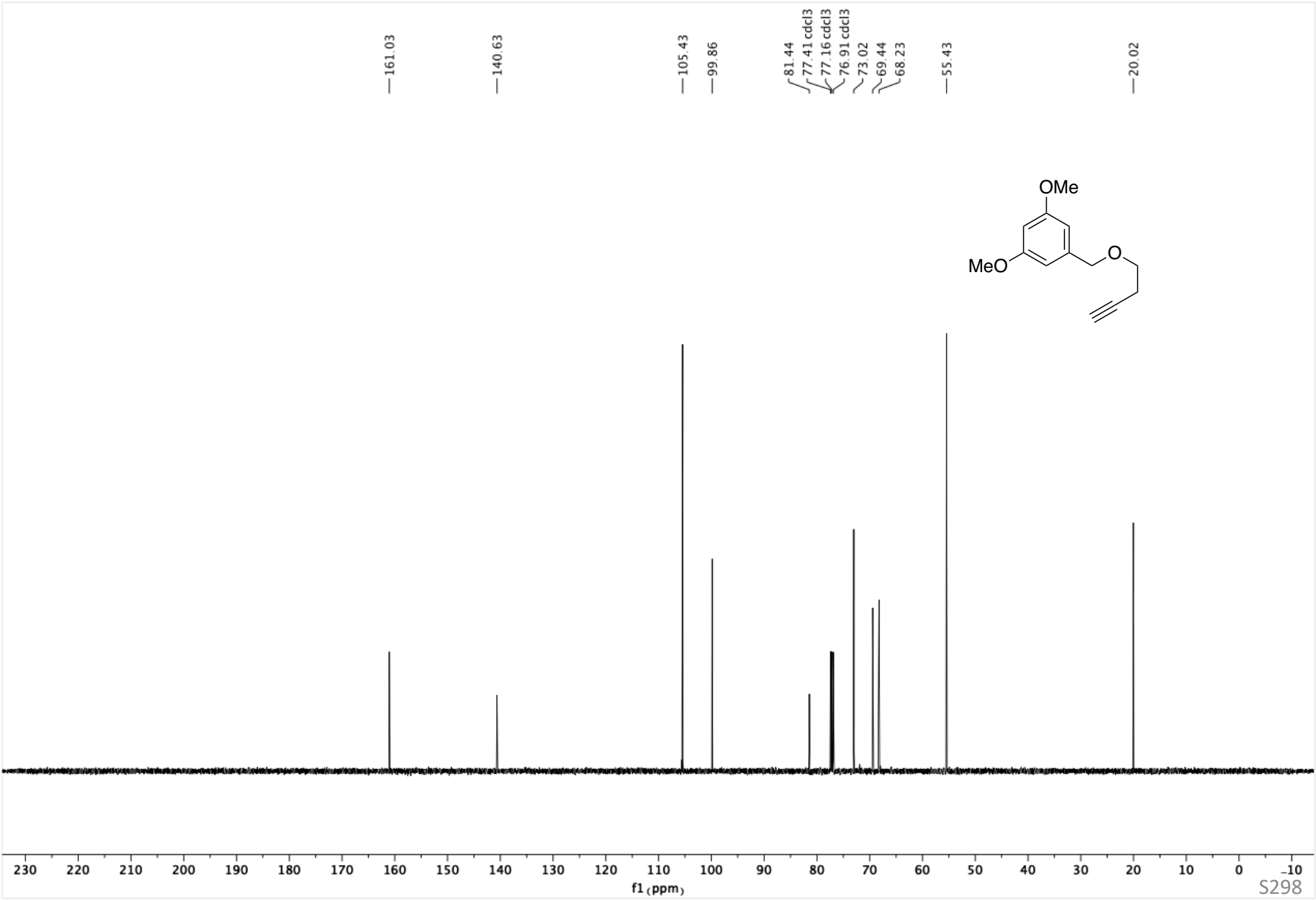
1-Bromo-2-((but-3-yn-1-yloxy)methyl)benzene



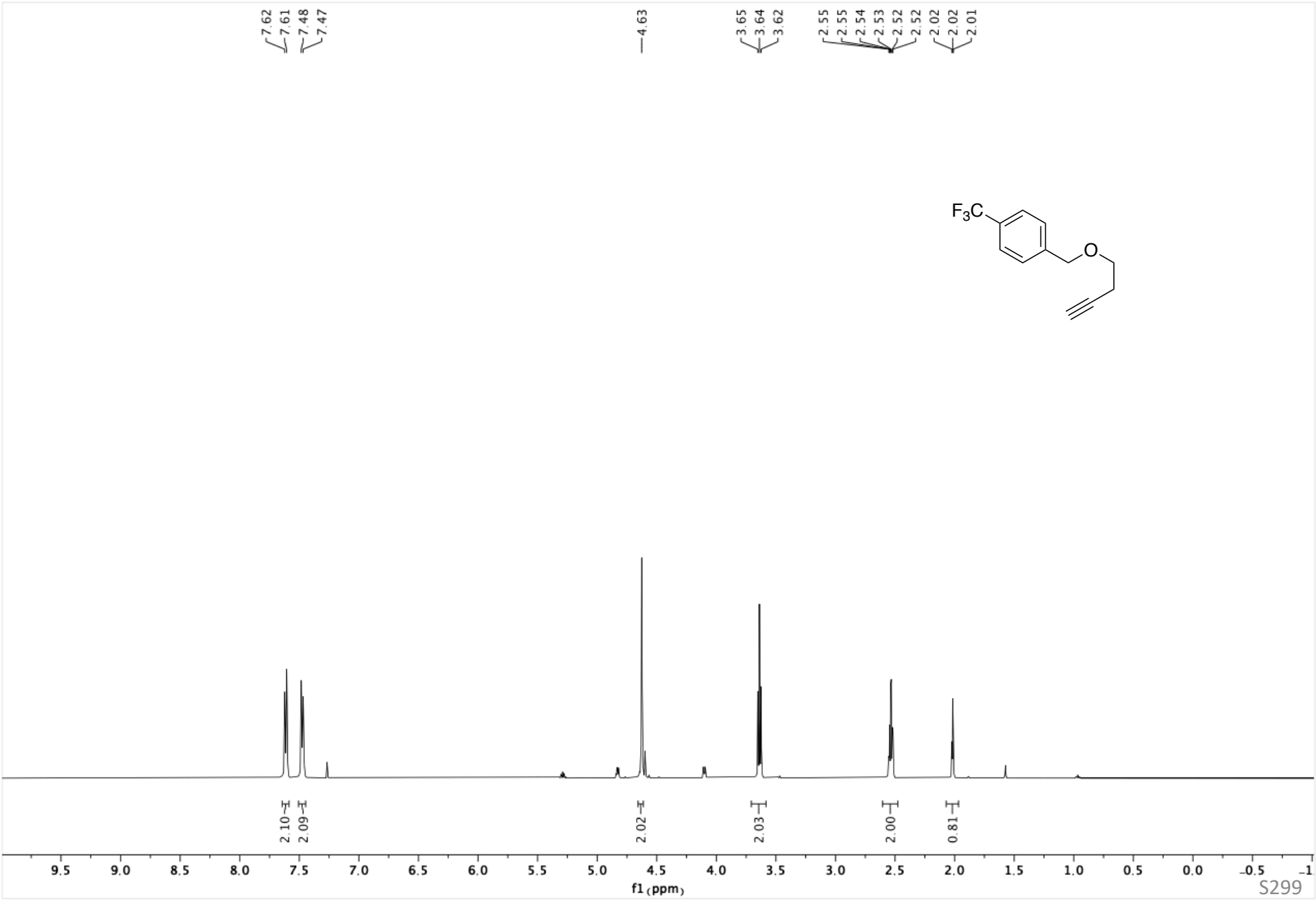
1-((But-3-yn-1-yloxy)methyl)-3,5-dimethoxybenzene



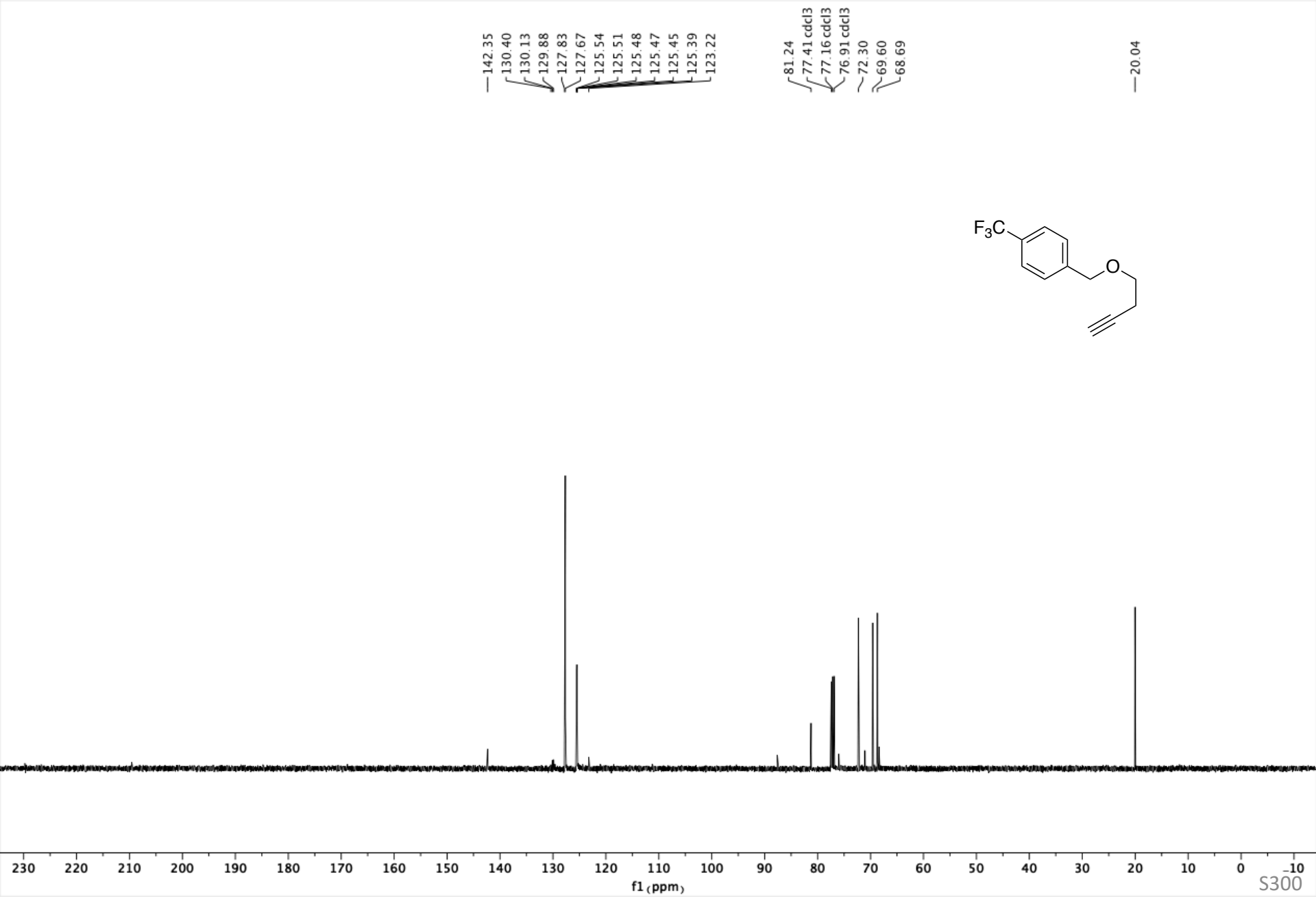
1-((But-3-yn-1-yloxy)methyl)-3,5-dimethoxybenzene



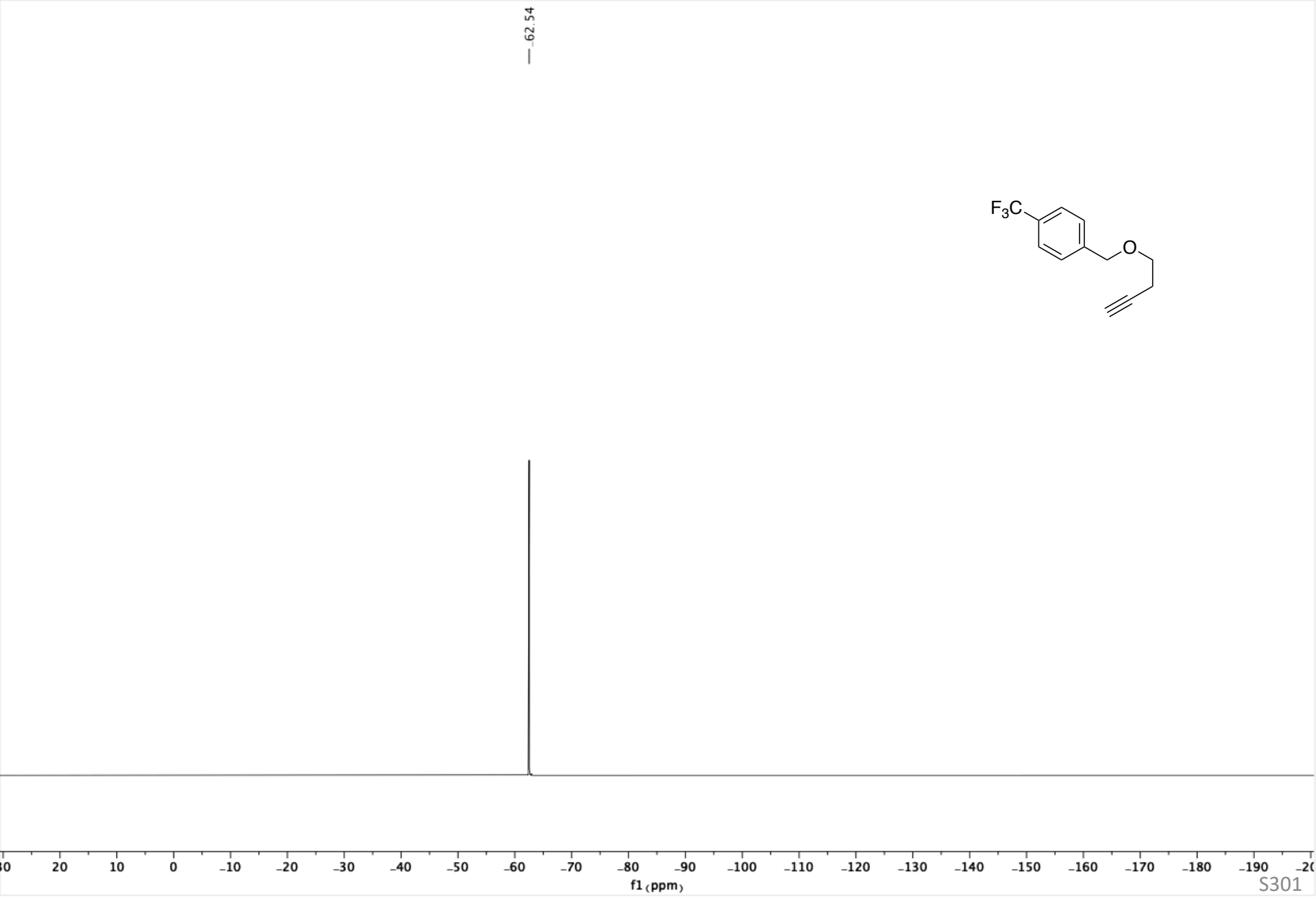
1-((But-3-yn-1-yloxy)methyl)-4-(trifluoromethyl)benzene



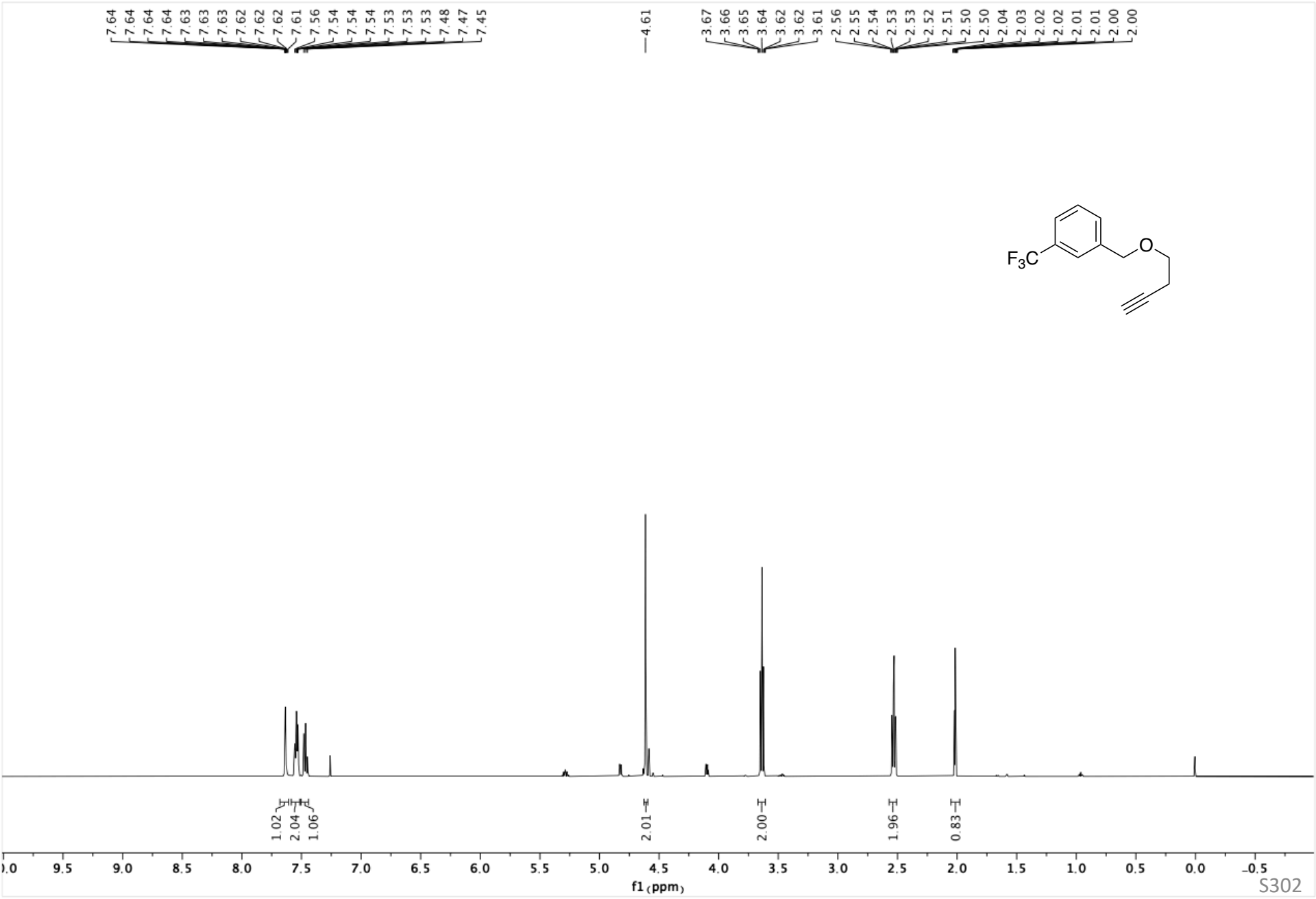
1-((But-3-yn-1-yloxy)methyl)-4-(trifluoromethyl)benzene



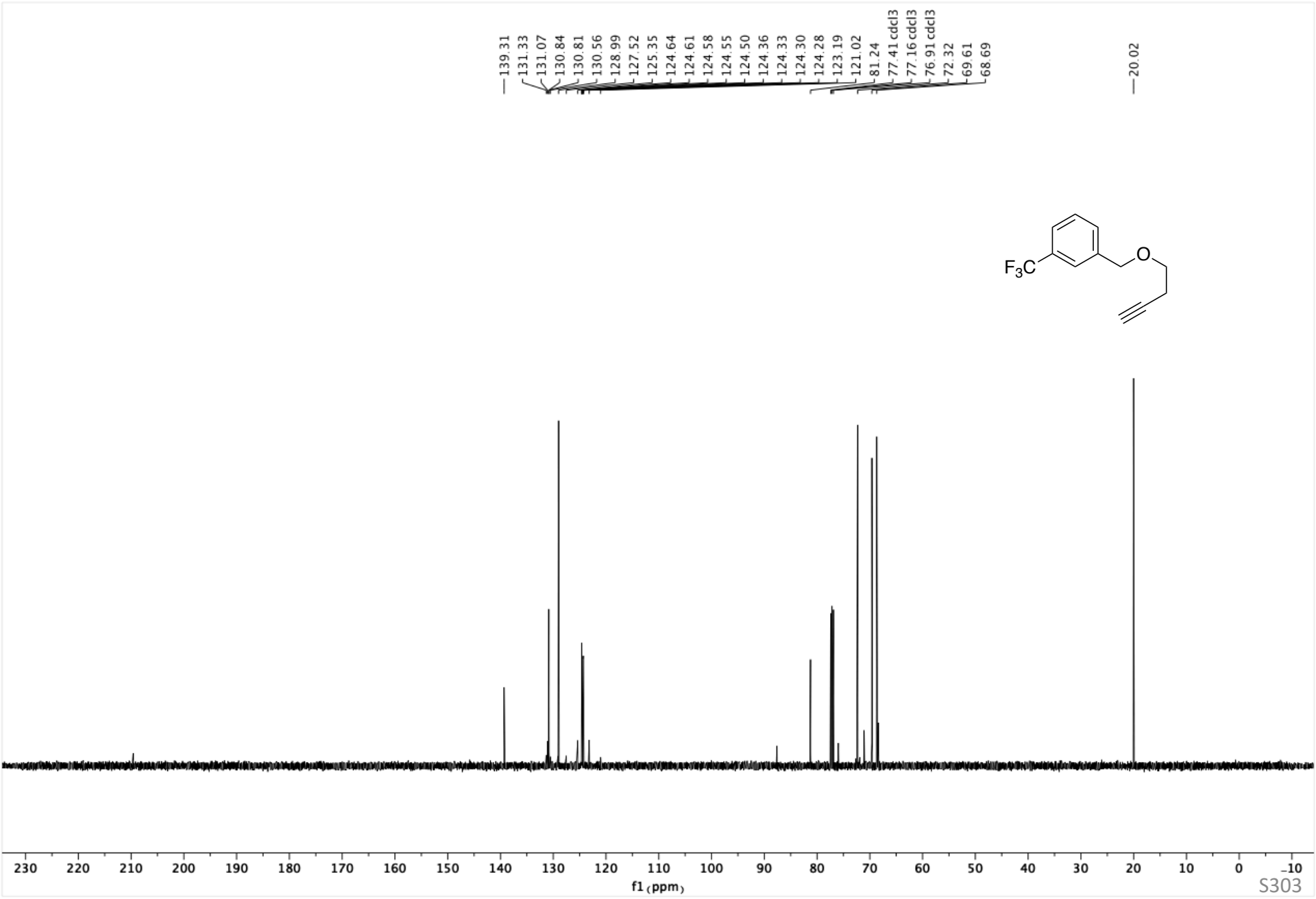
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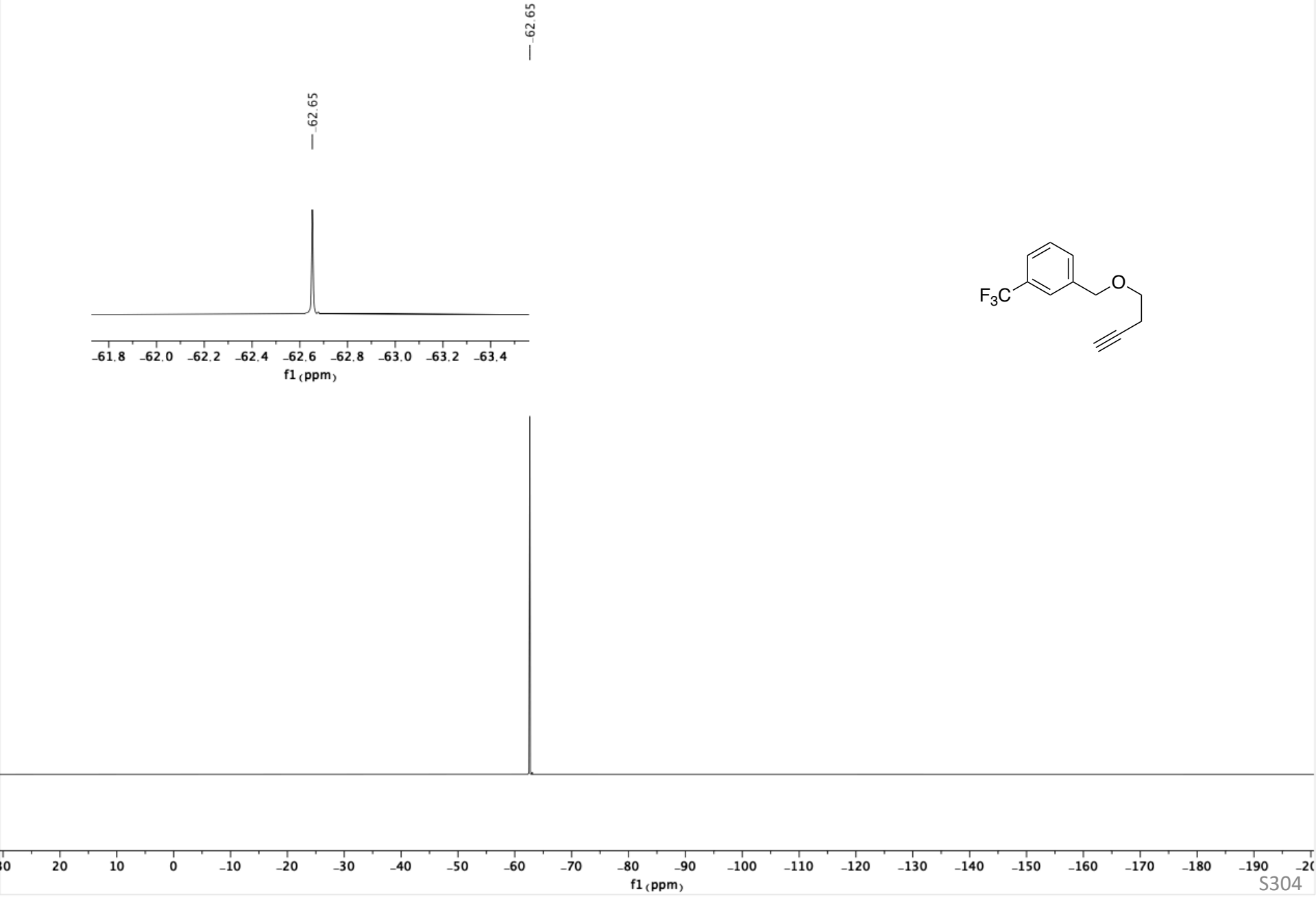
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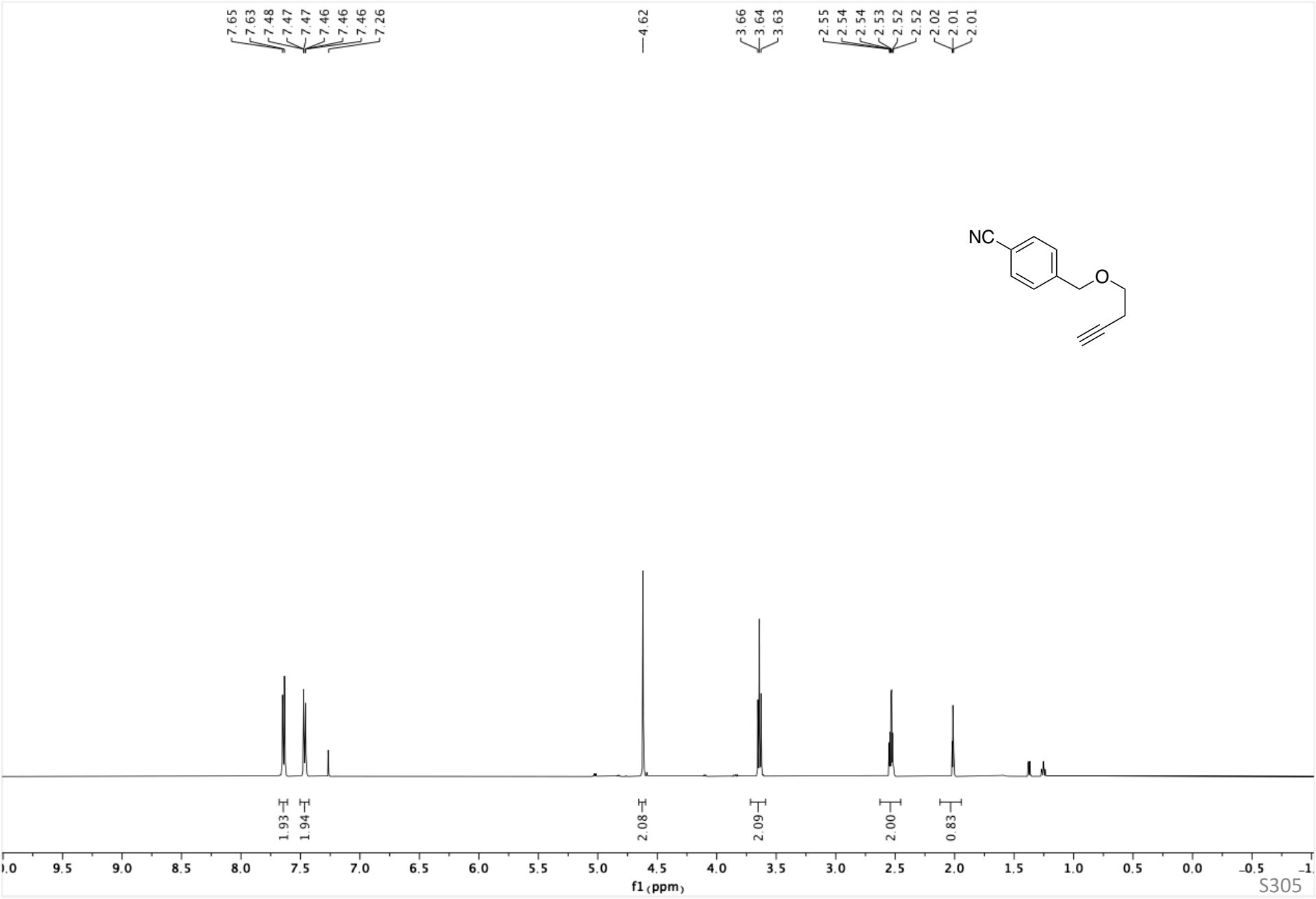
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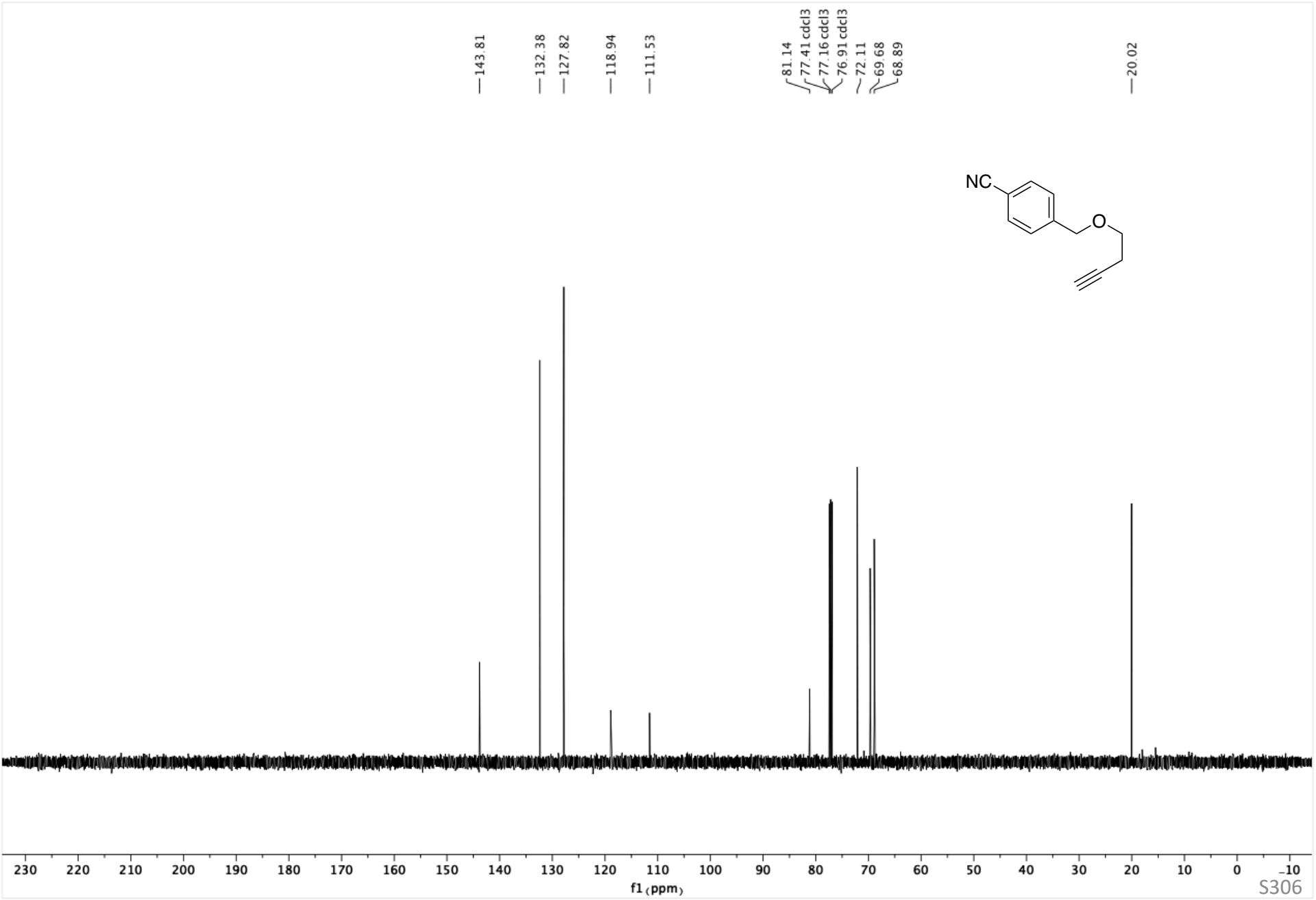
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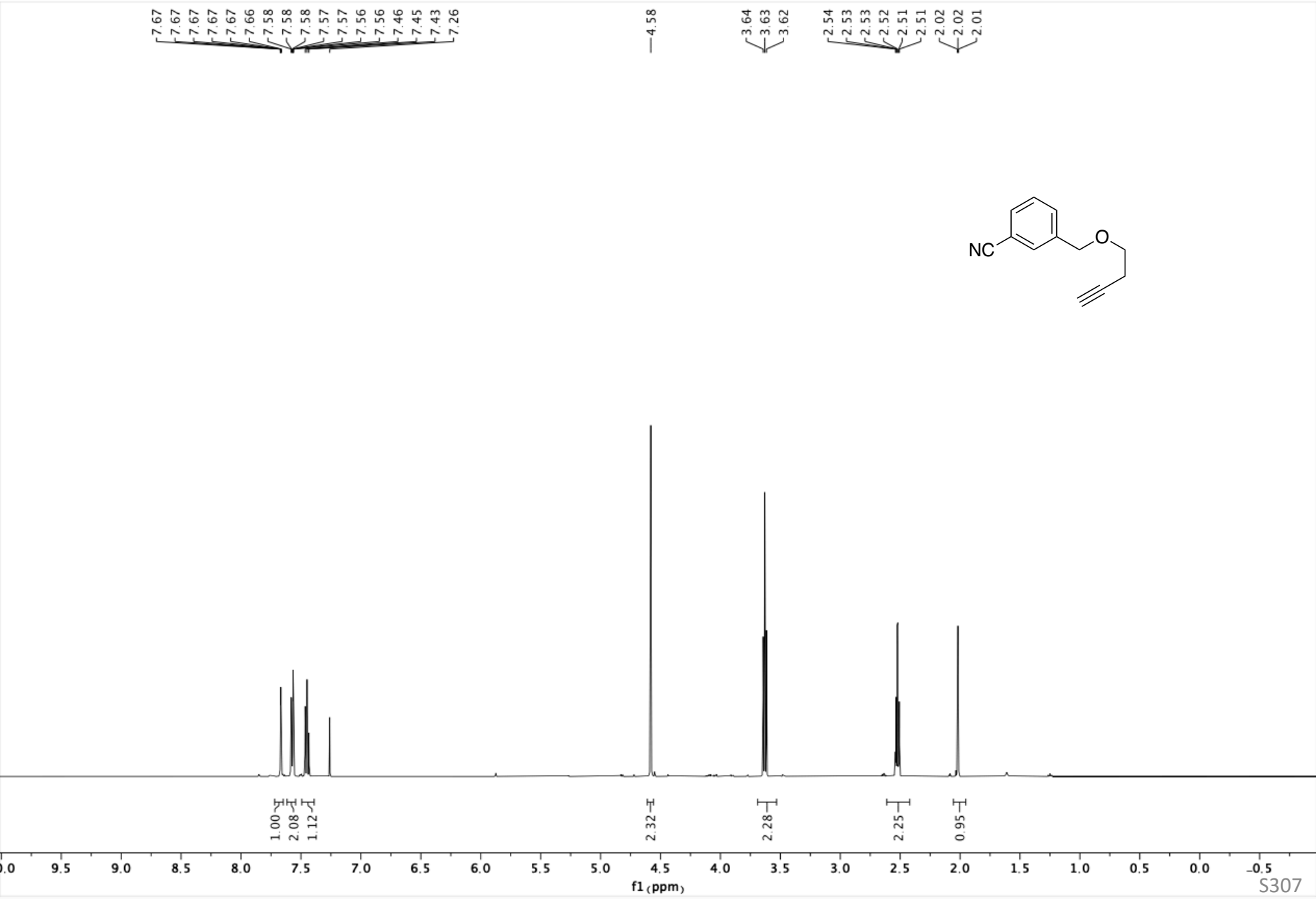
4-((But-3-yn-1-yloxy)methyl)benzonitrile



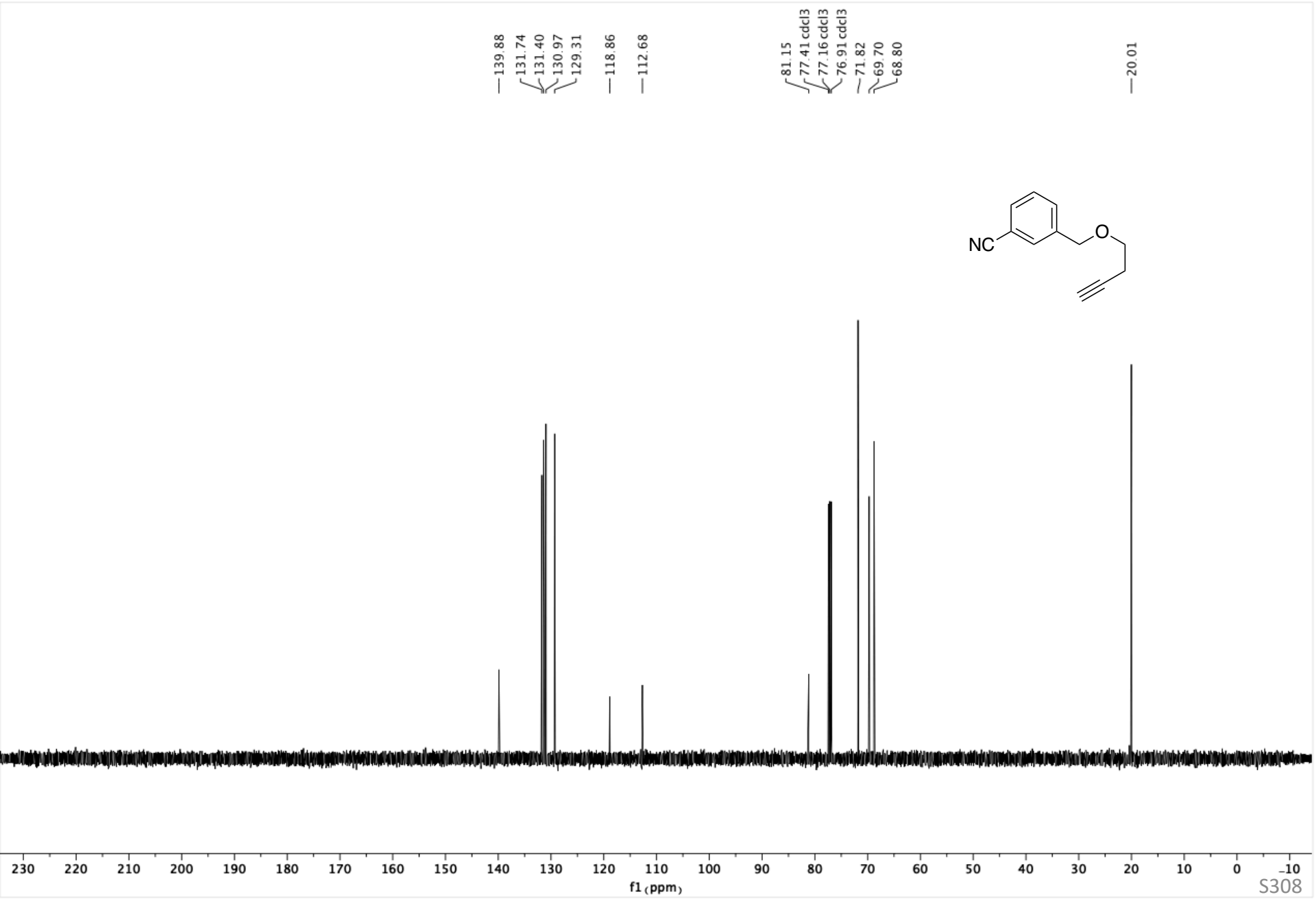
4-((But-3-yn-1-yloxy)methyl)benzonitrile



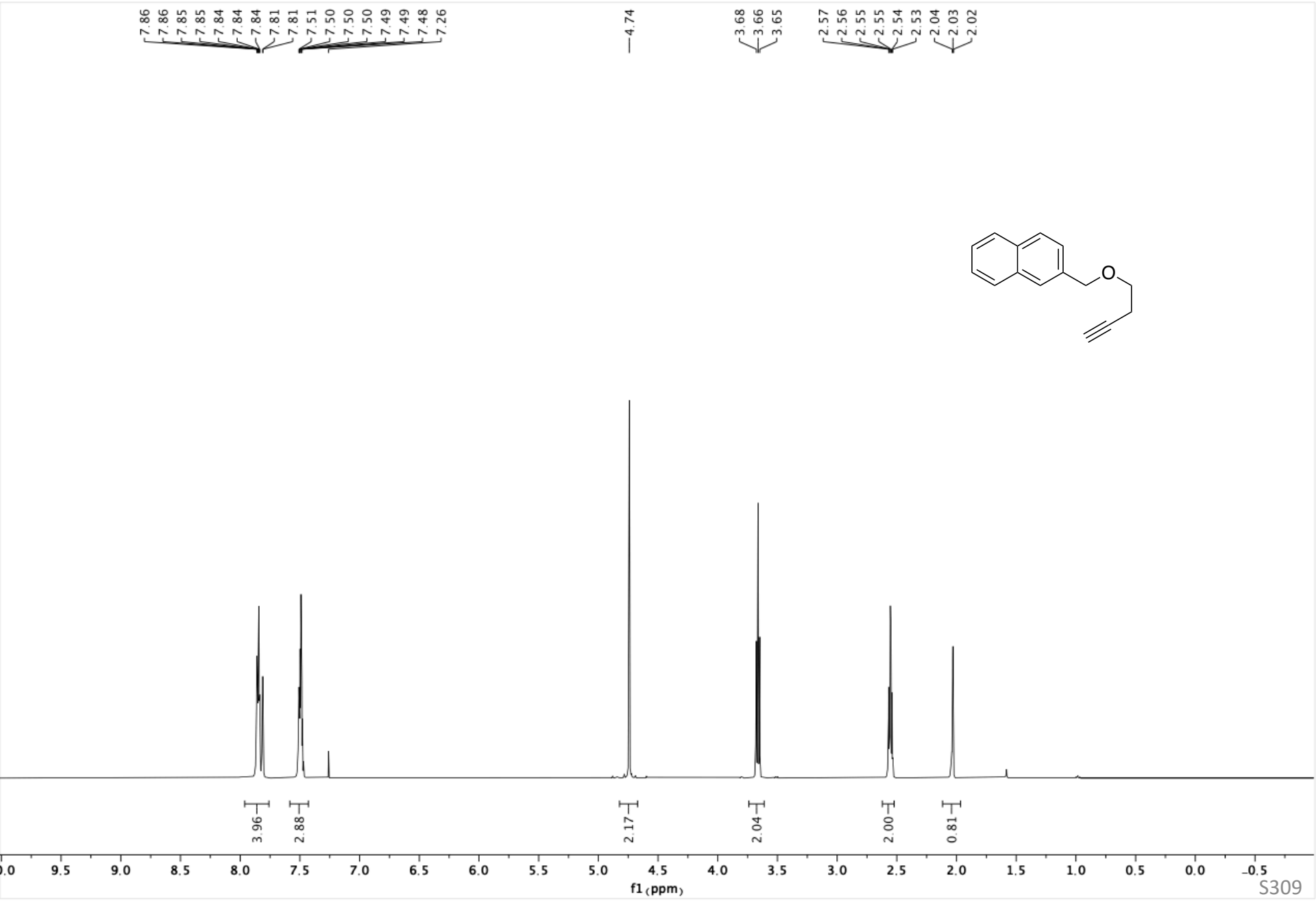
3-((But-3-yn-1-yloxy)methyl)benzonitrile



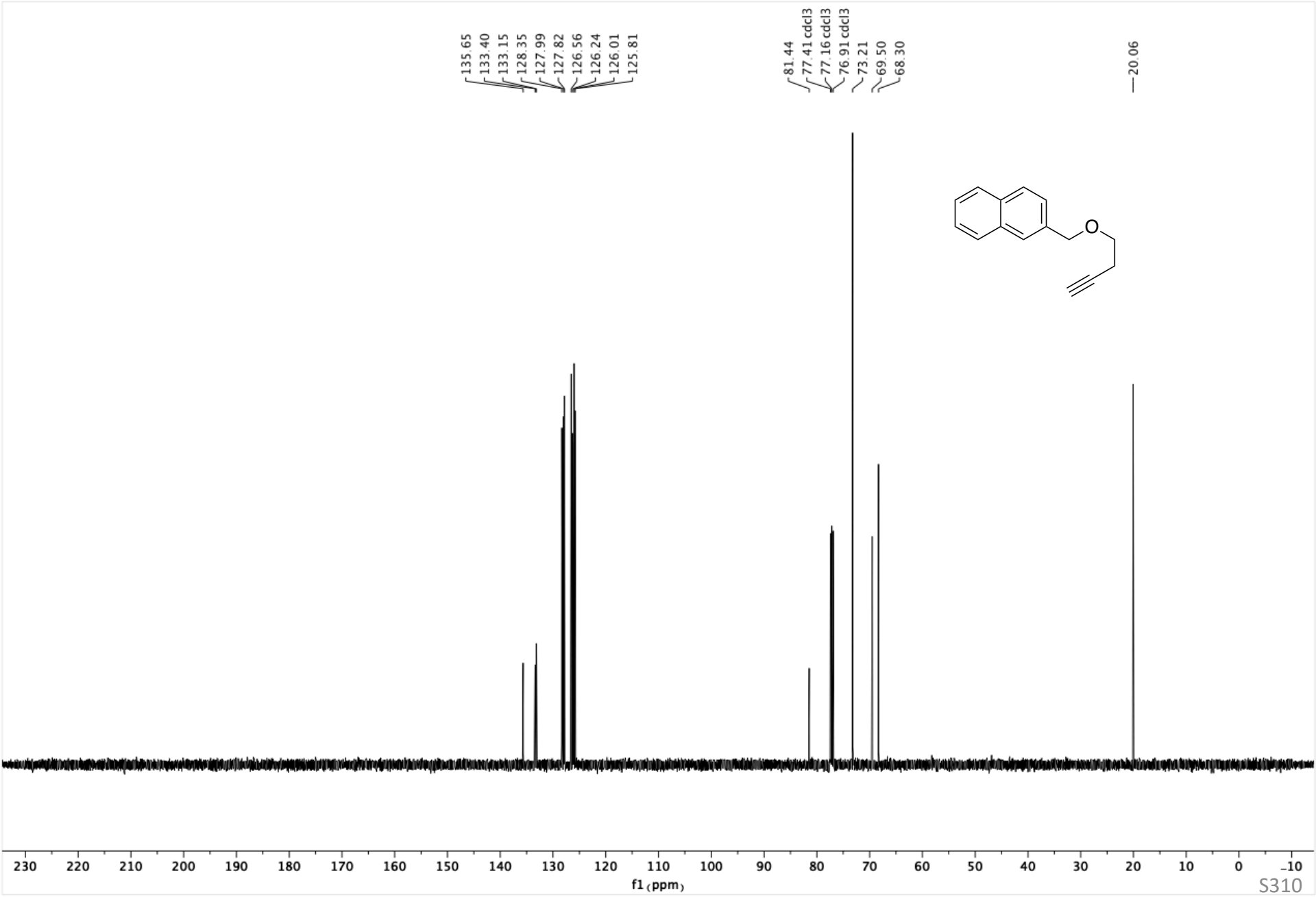
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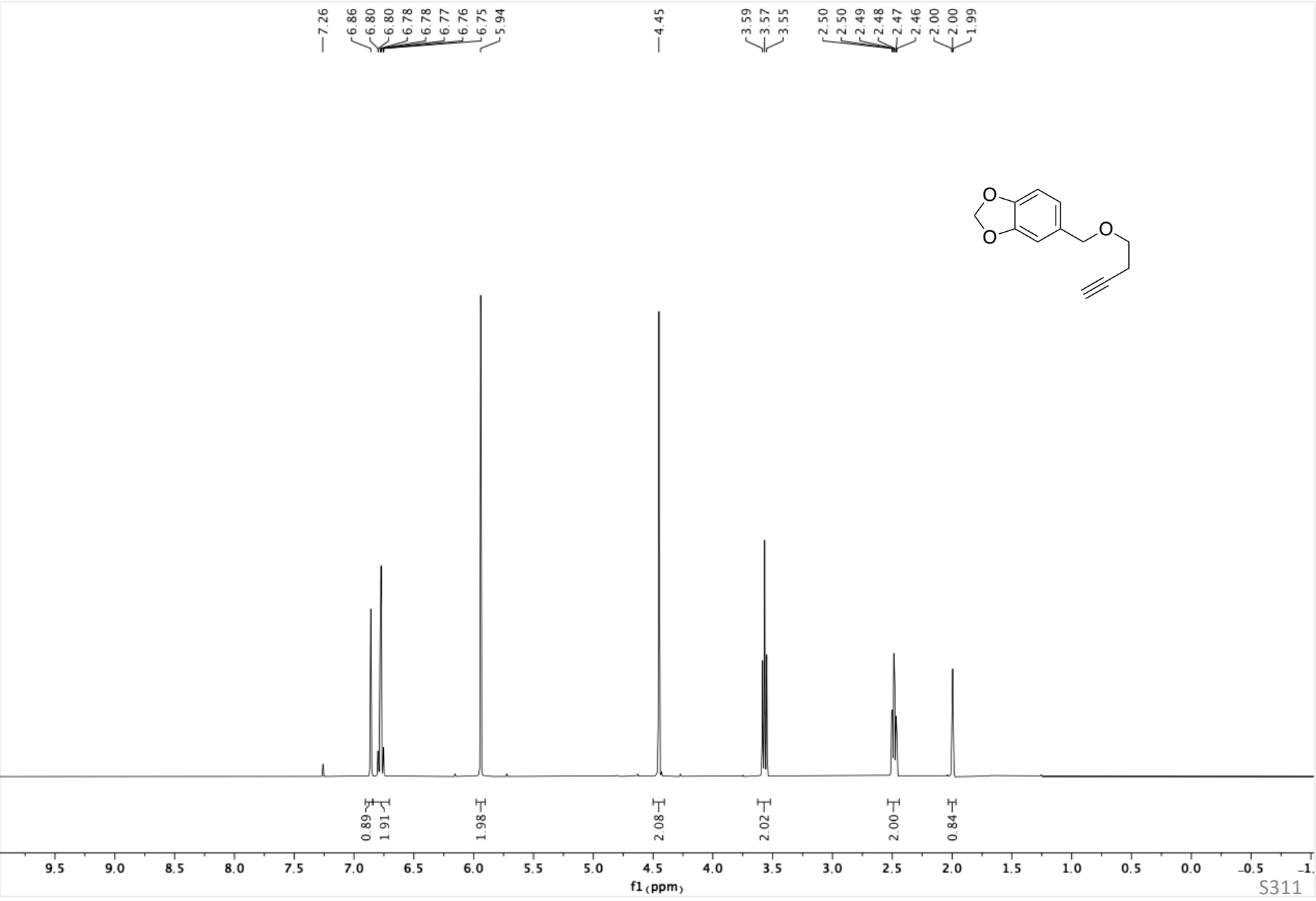
2-((But-3-yn-1-yloxy)methyl)naphthalene



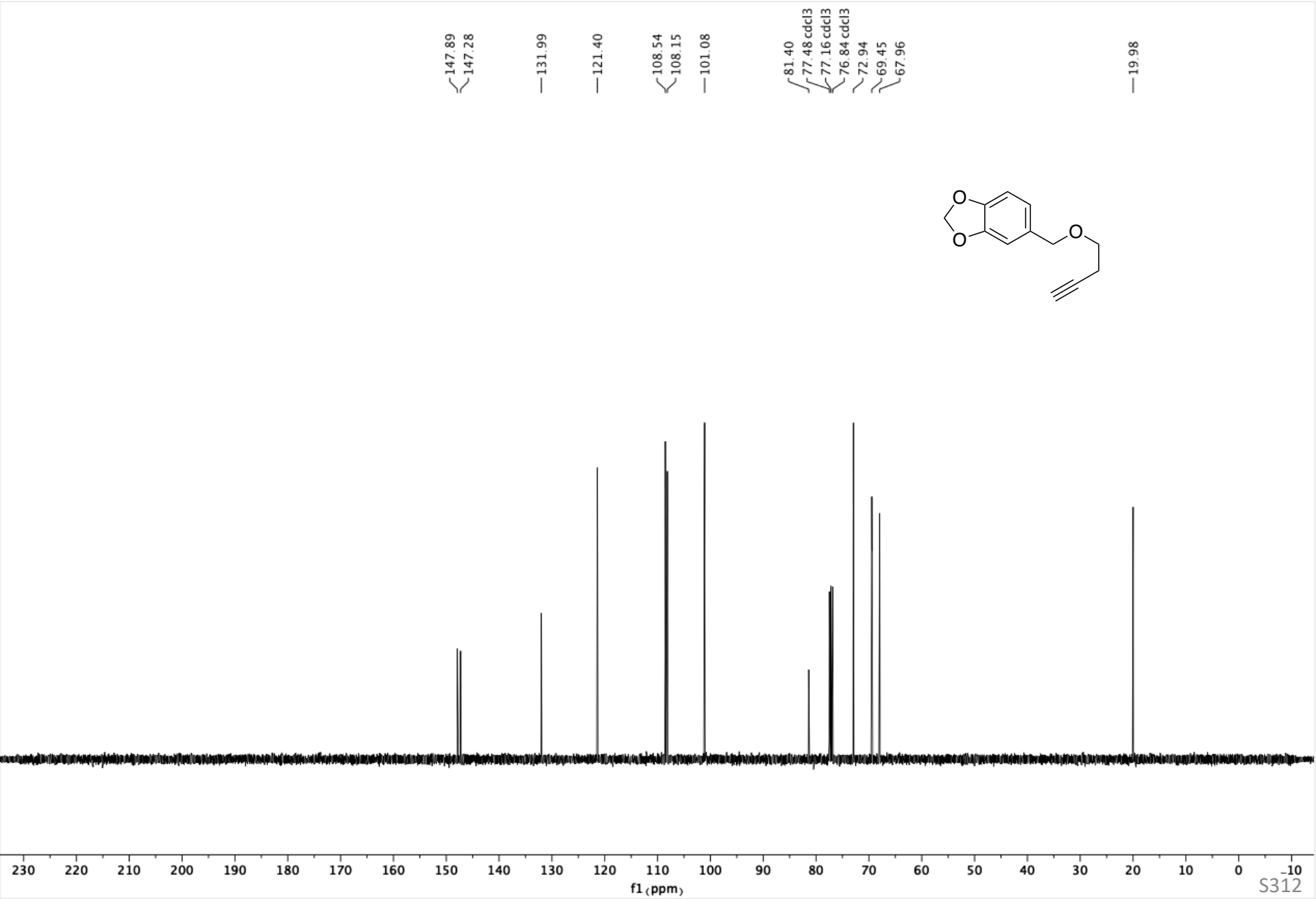
2-((But-3-yn-1-yloxy)methyl)naphthalene



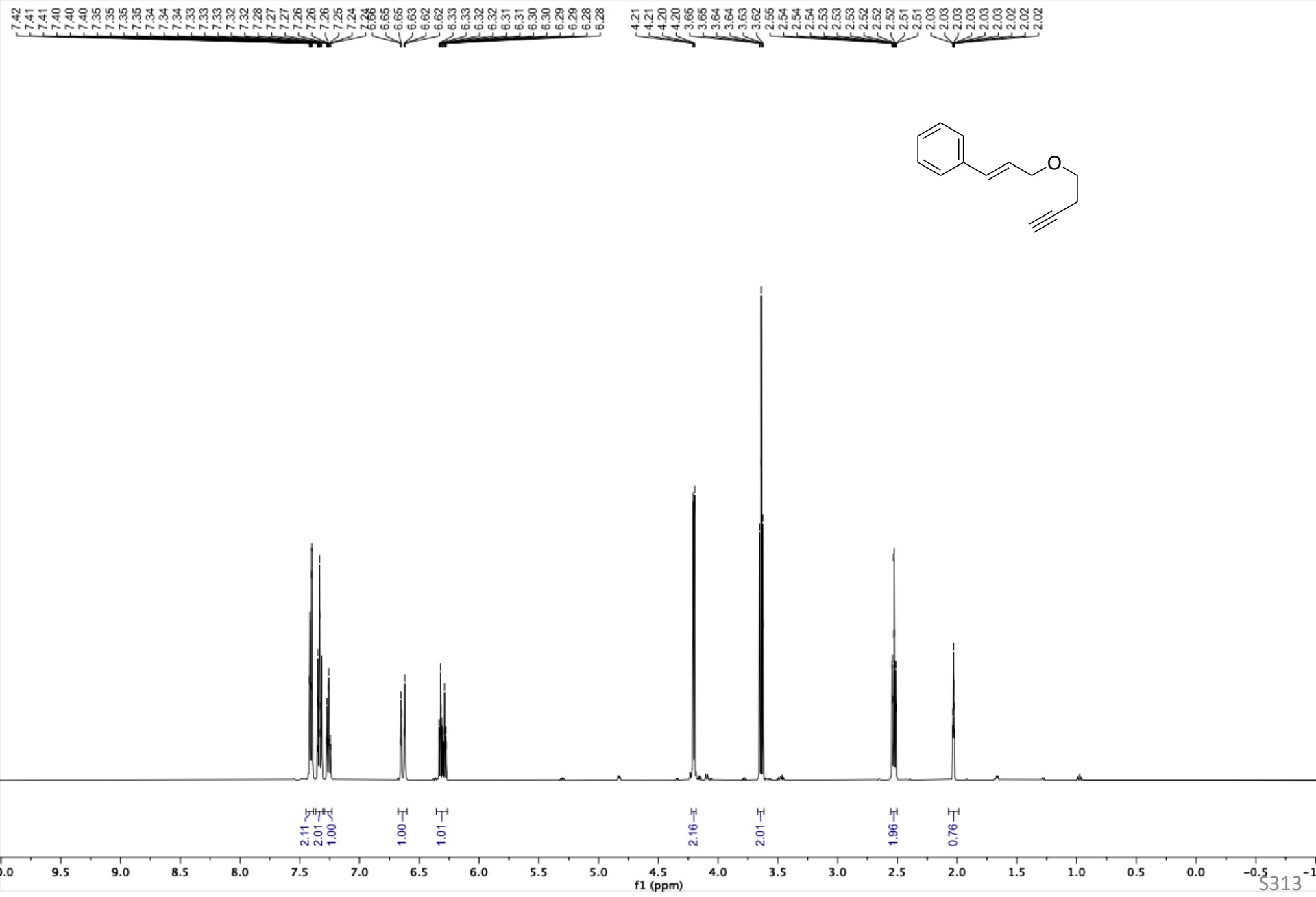
5-((But-3-yn-1-yloxy)methyl)benzo[*d*][1,3]dioxole



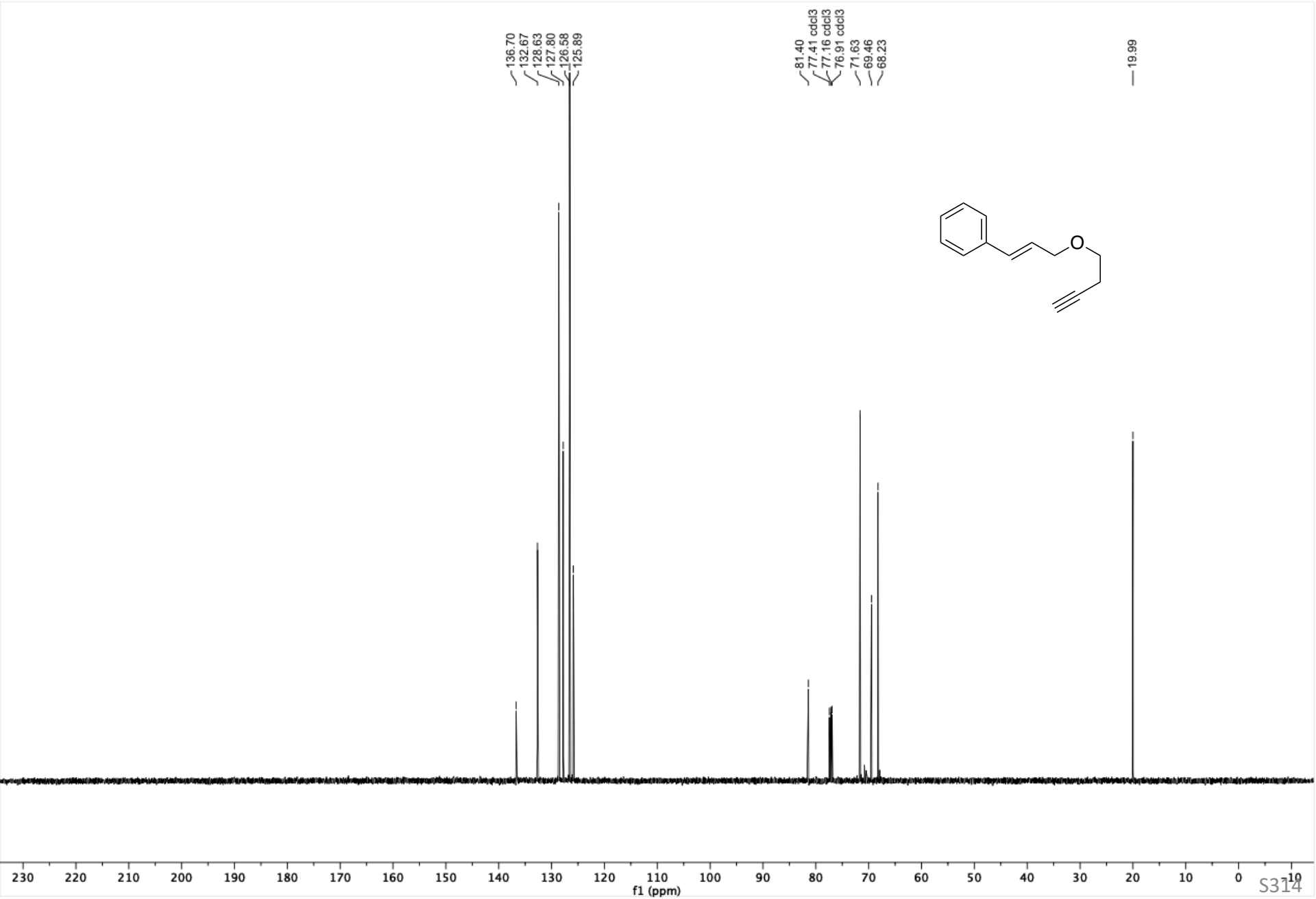
5-((But-3-yn-1-yloxy)methyl)benzo[*d*][1,3]dioxole



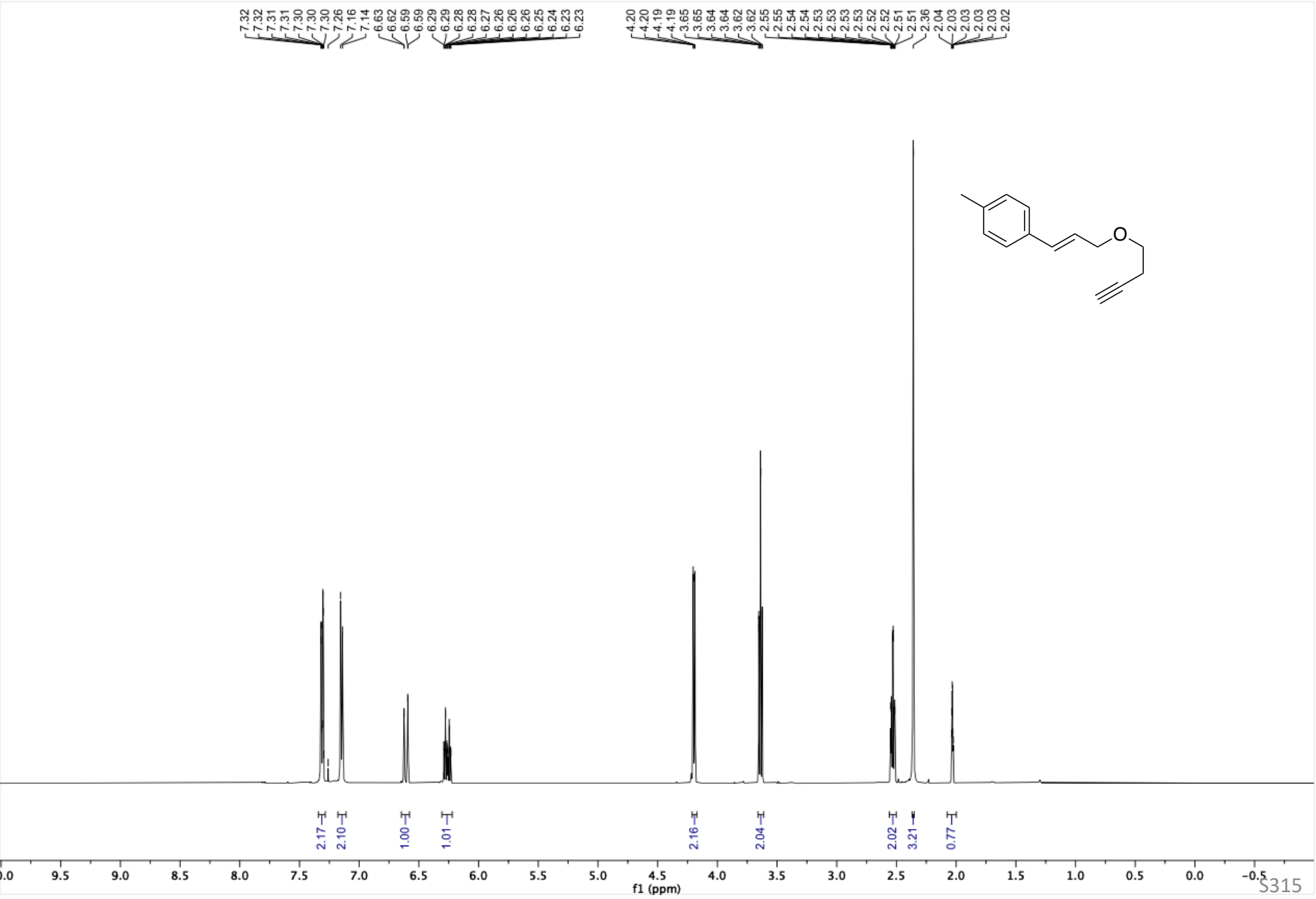
(*E*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene



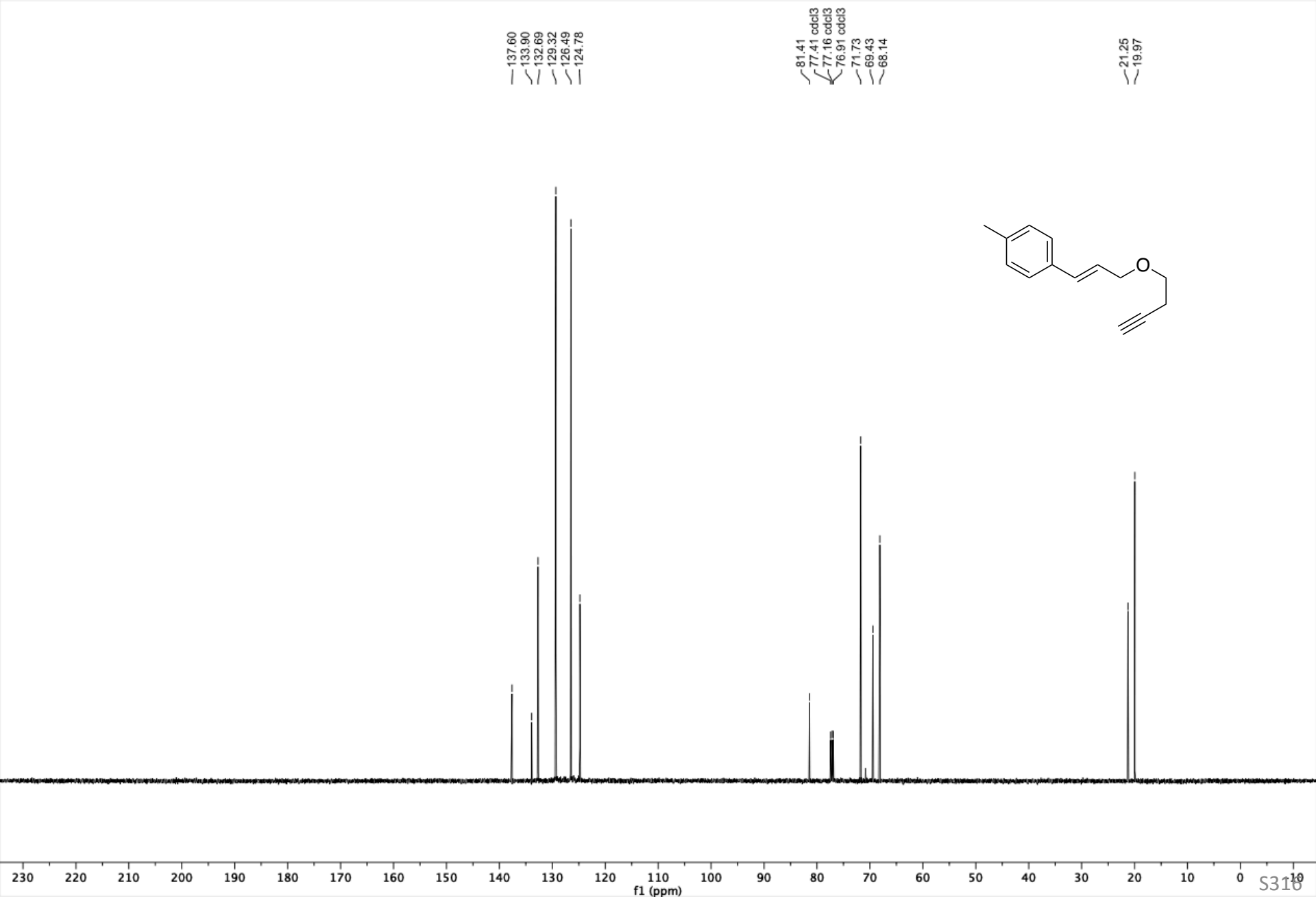
(*E*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene



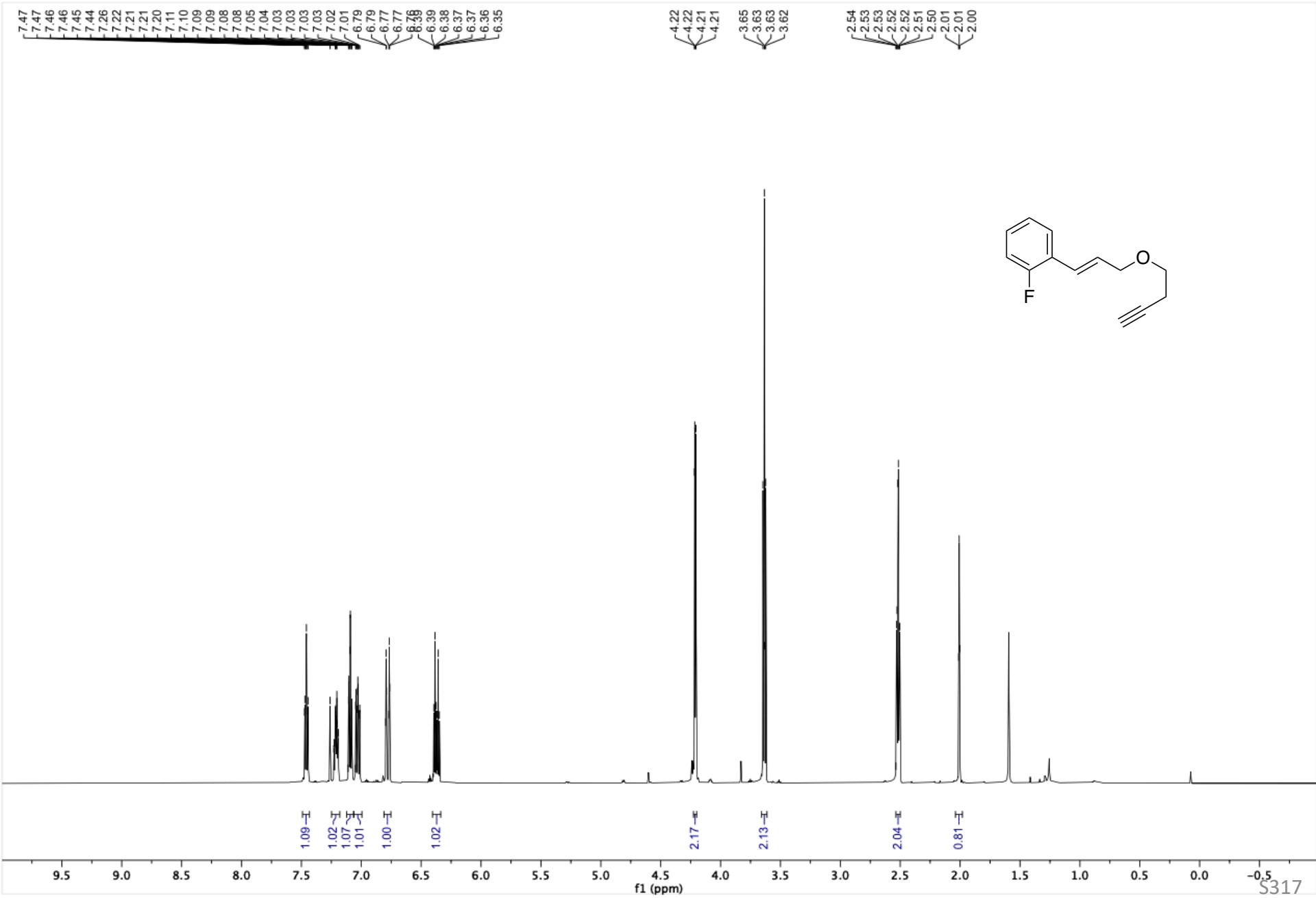
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-methylbenzene



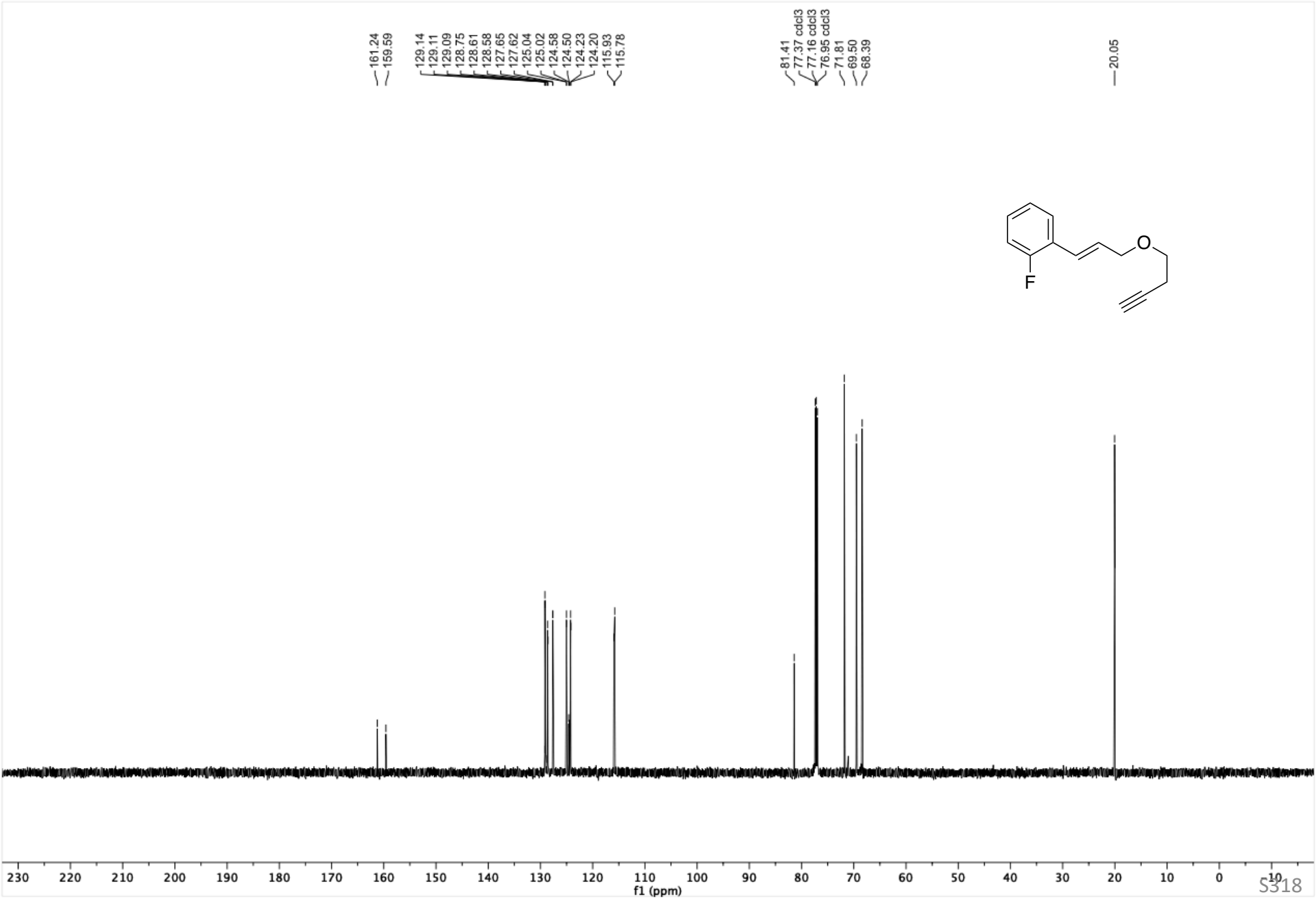
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-methylbenzene



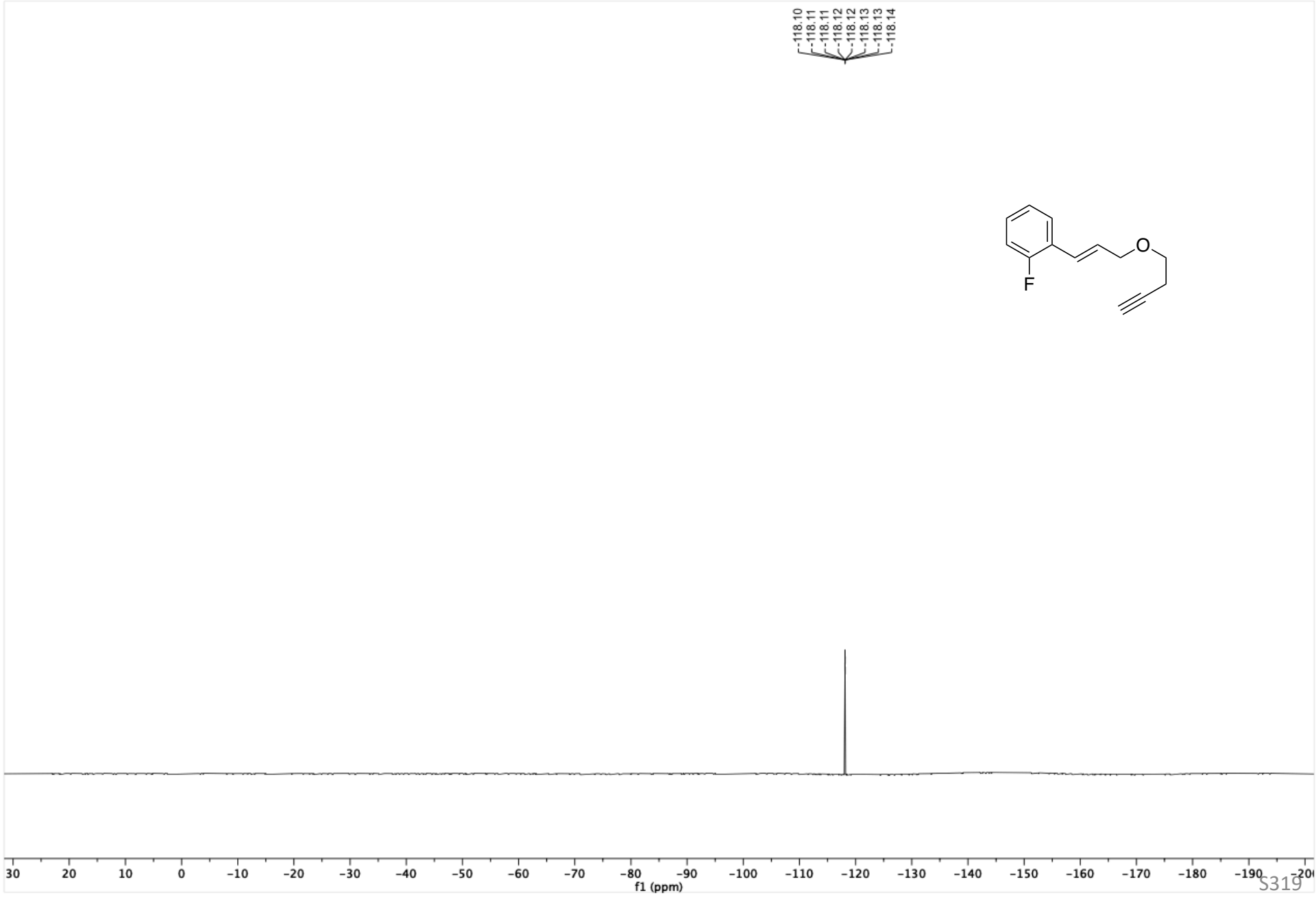
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-2-fluorobenzene



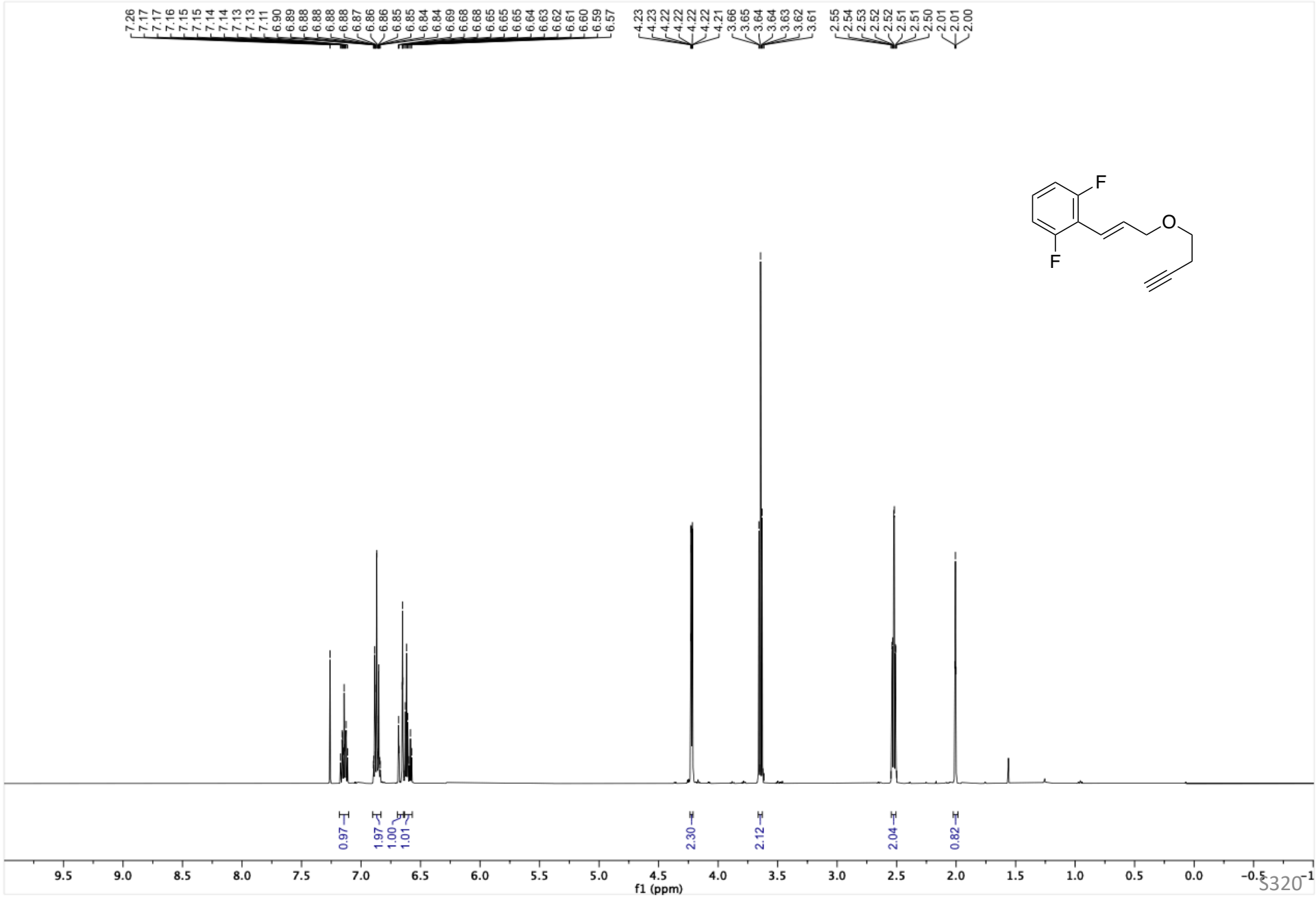
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-2-fluorobenzene



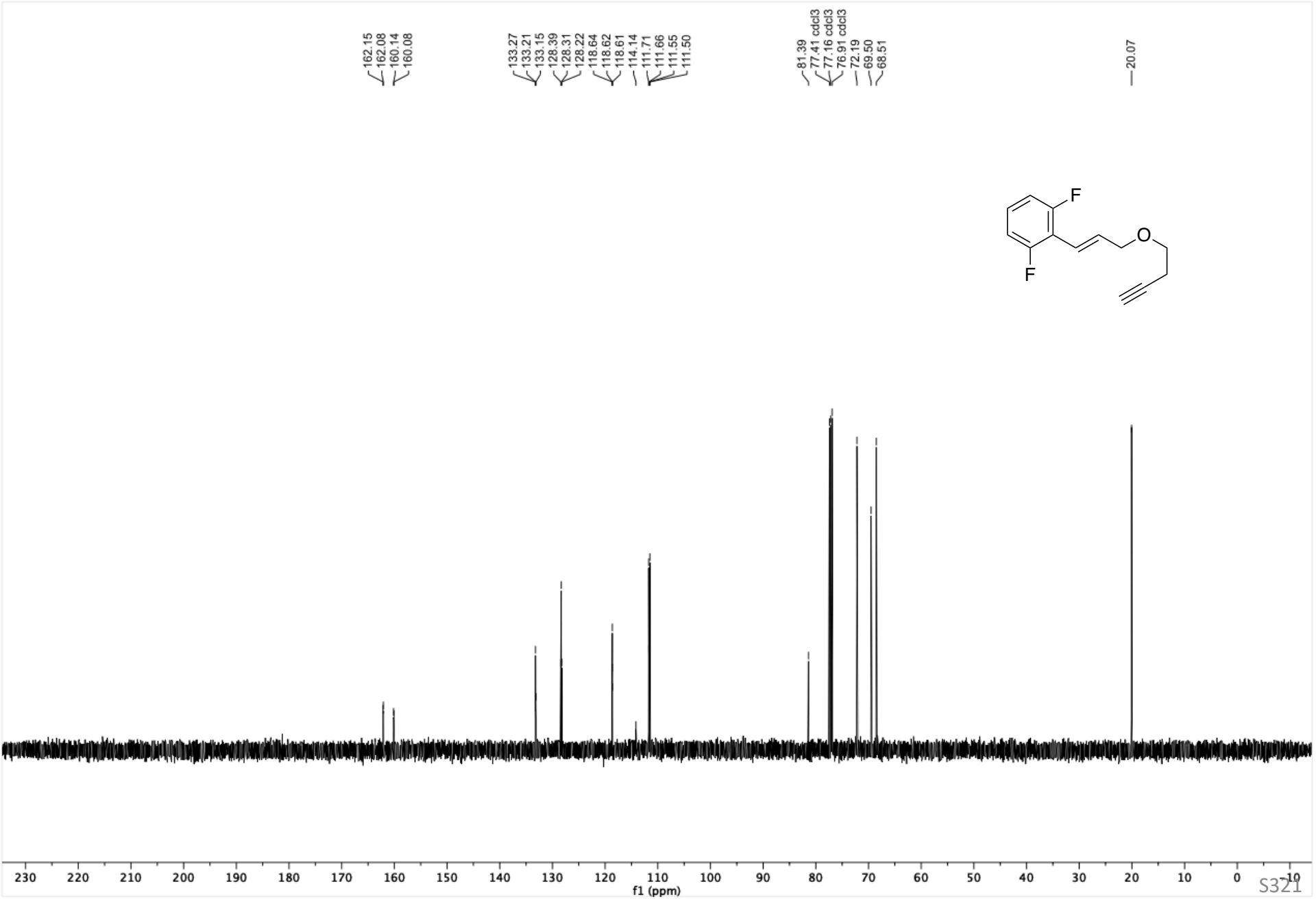
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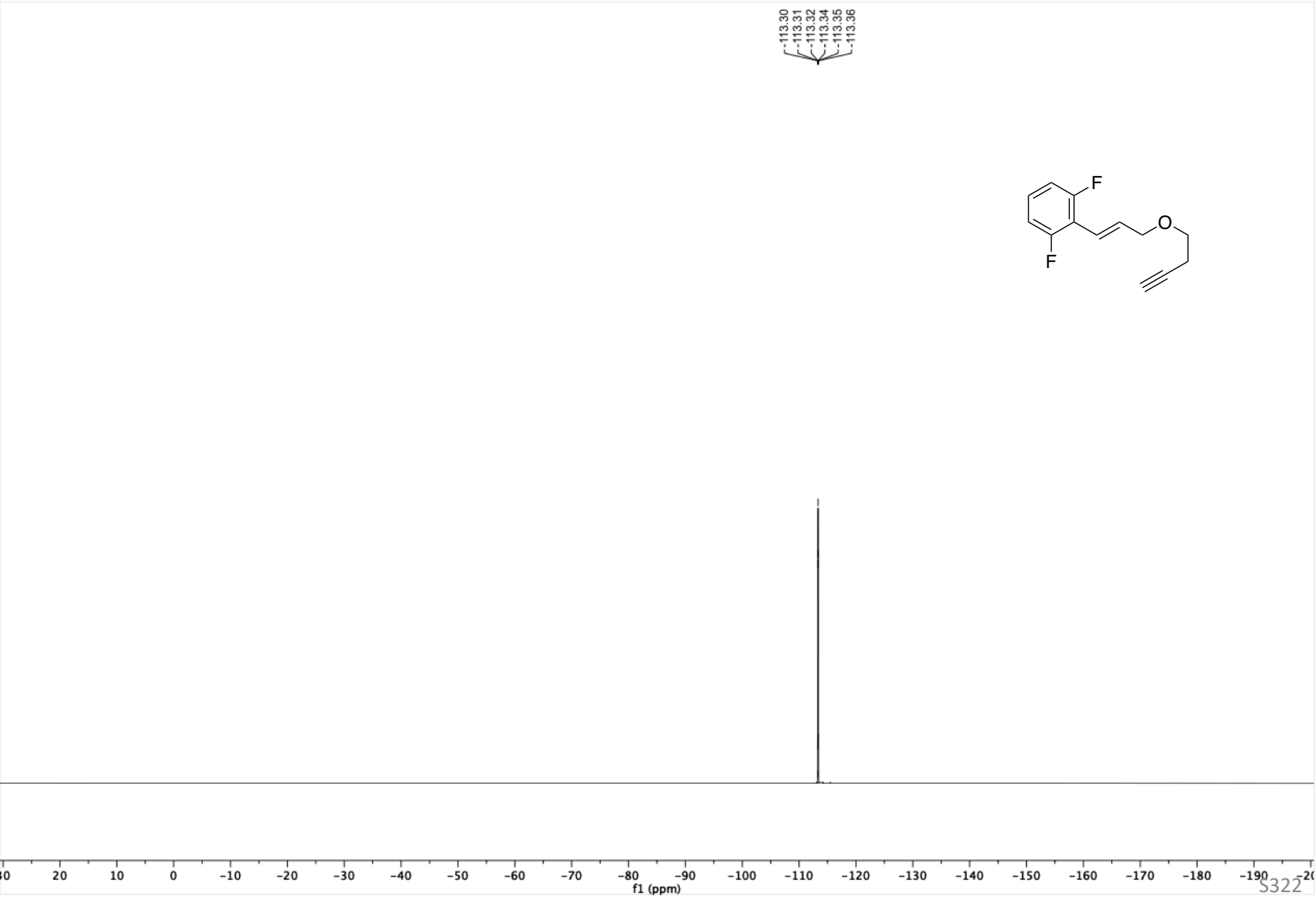
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-1,3-difluorobenzene



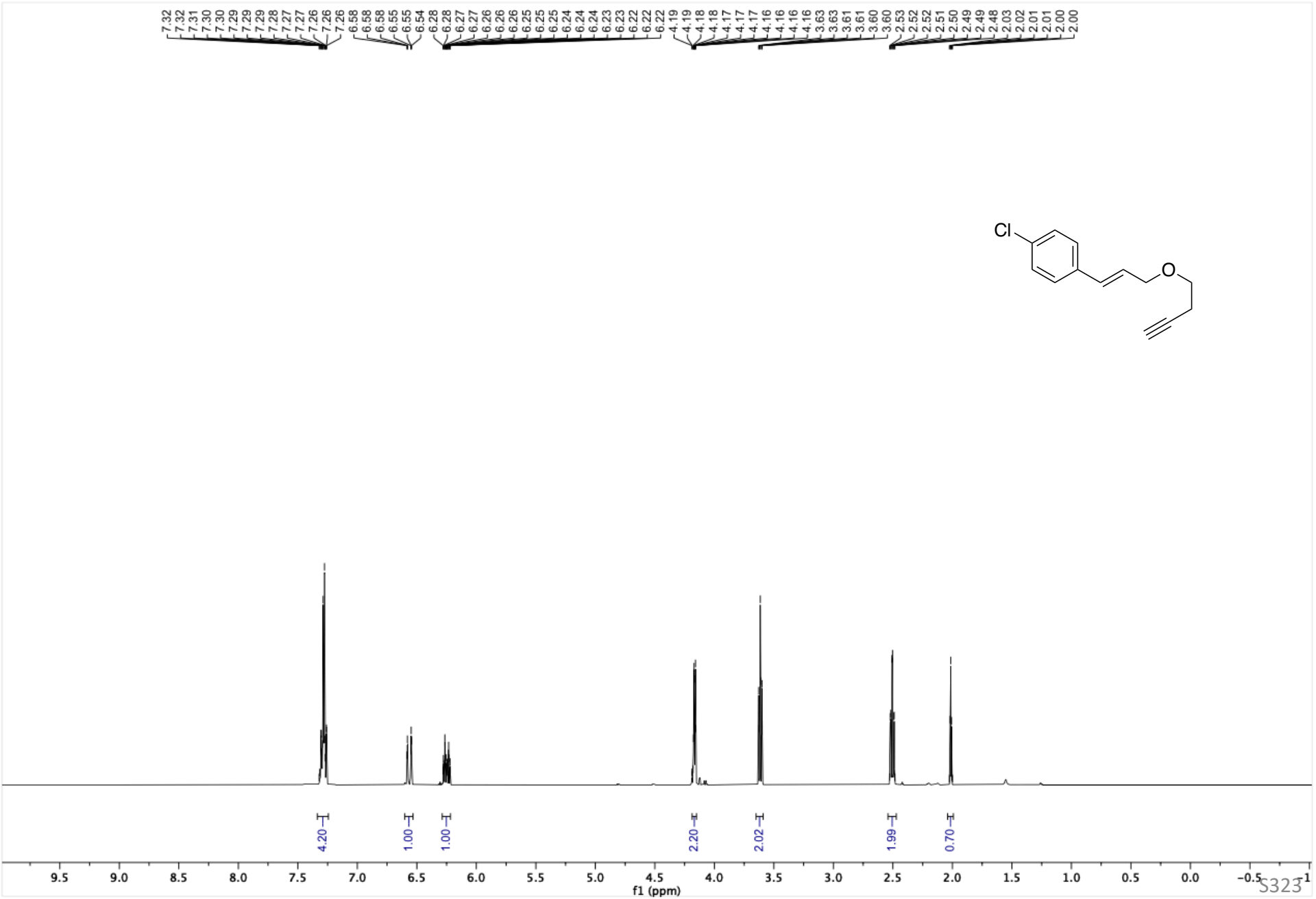
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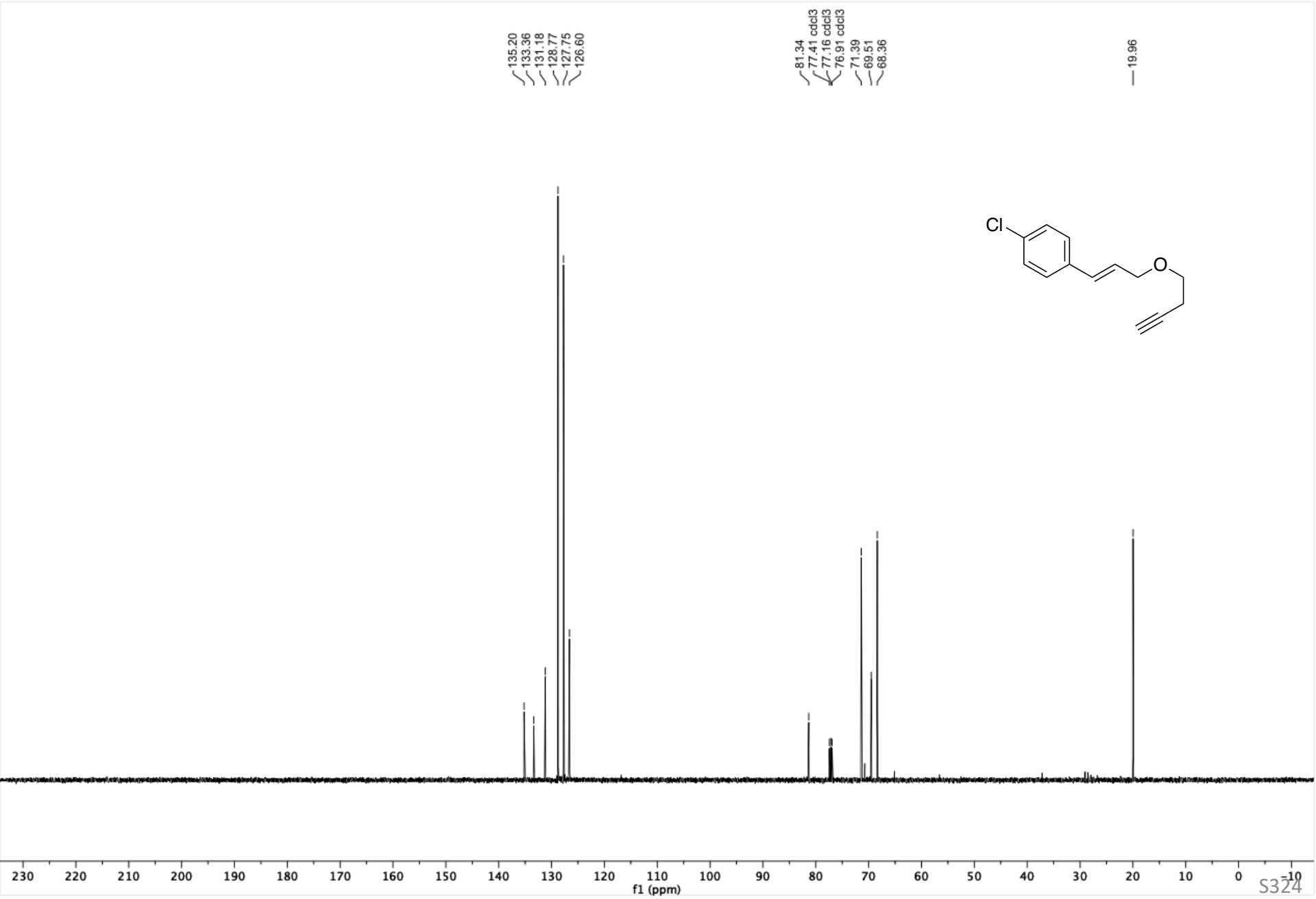
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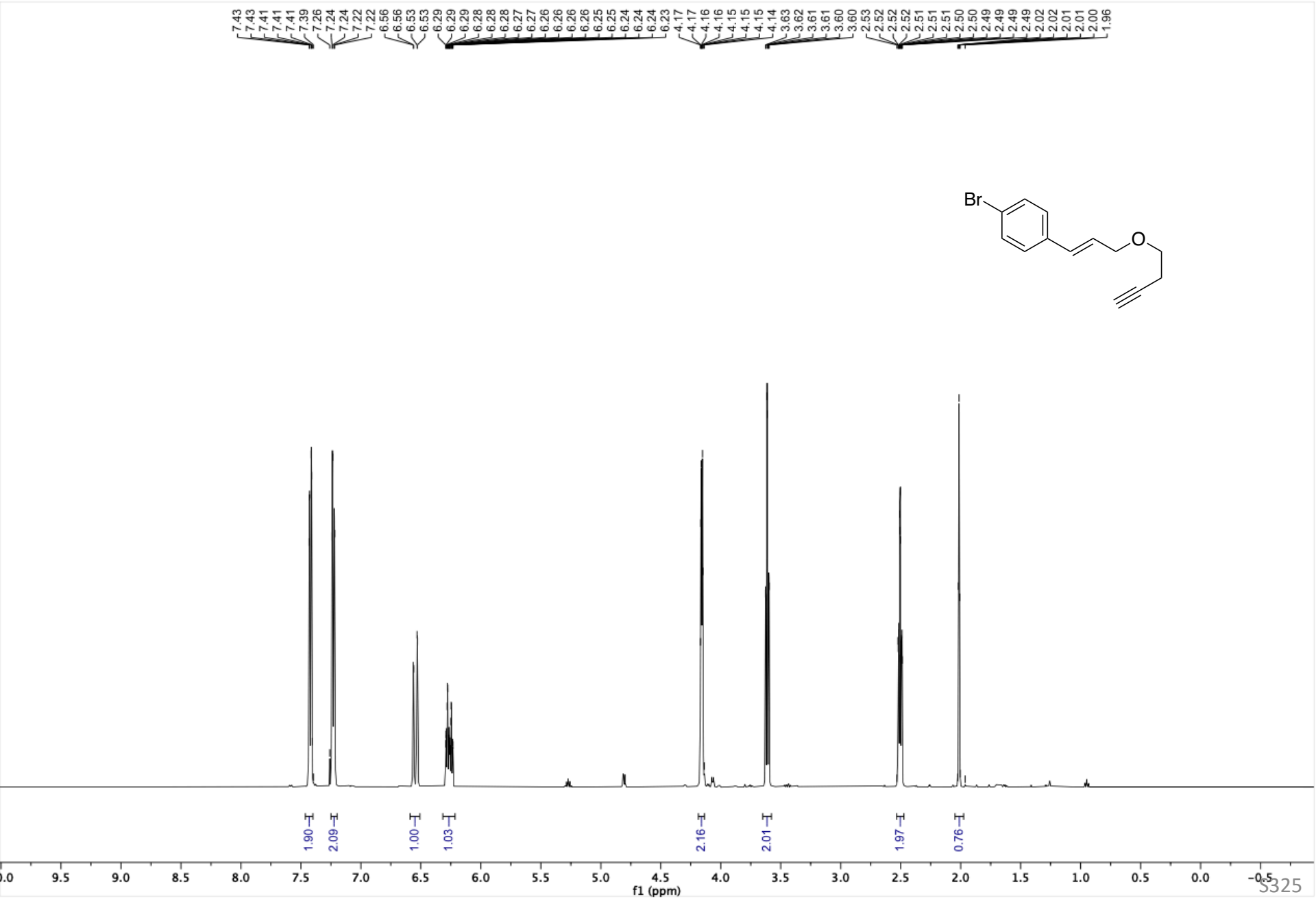
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-chlorobenzene



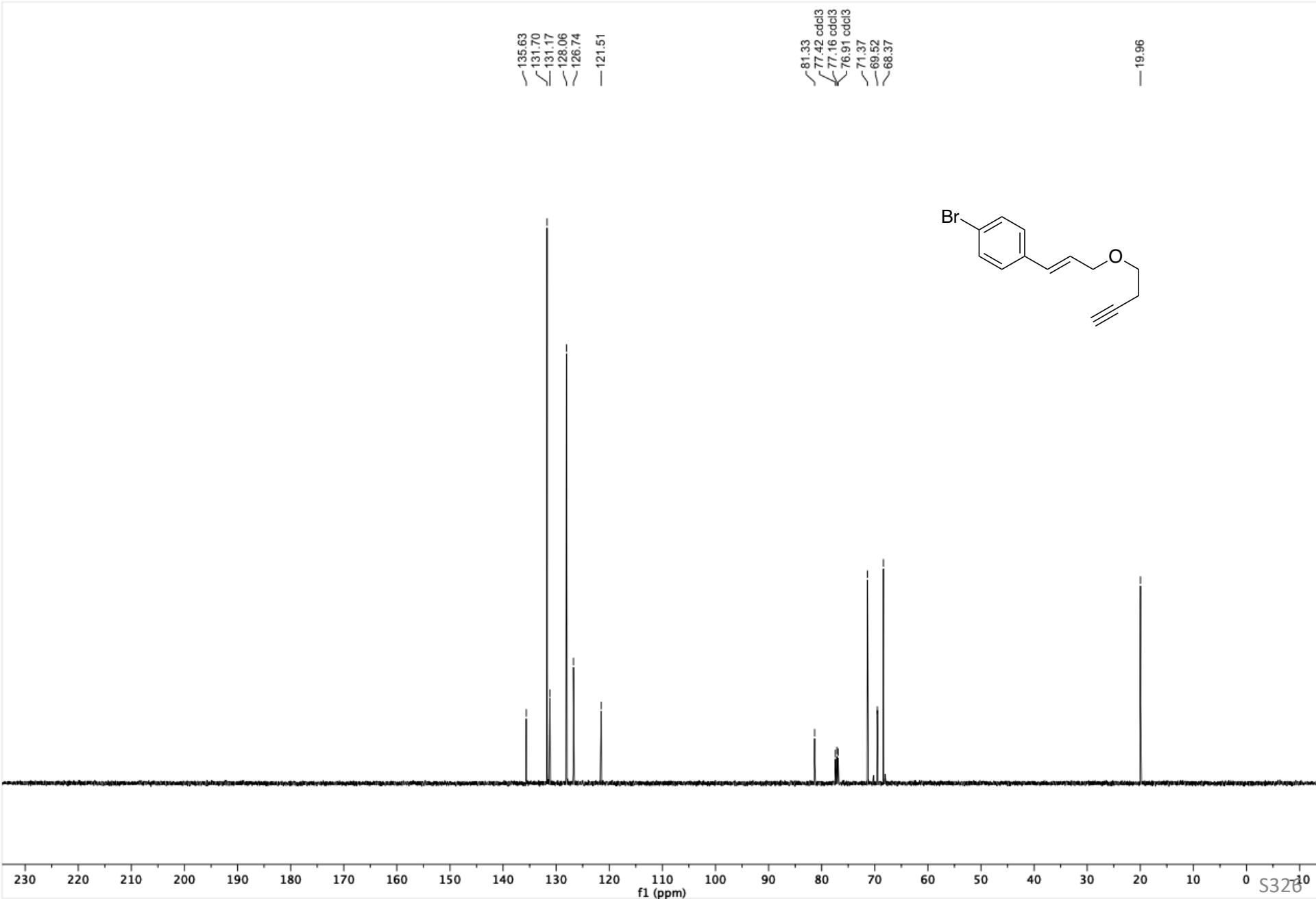
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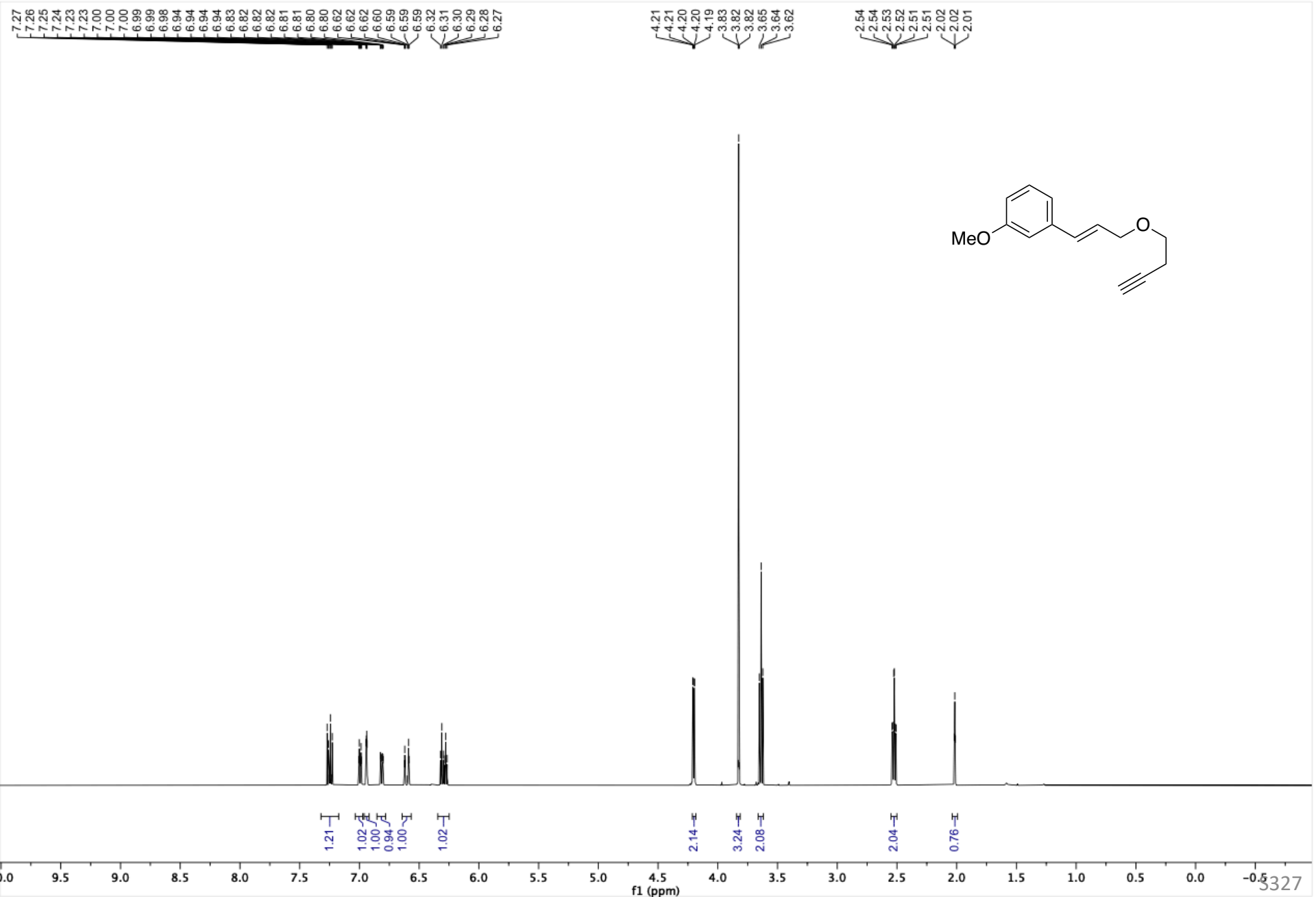
(*E*)-1-Bromo-4-(3-(but-3-yn-1-yloxy)prop-1-en-1-yl)benzene



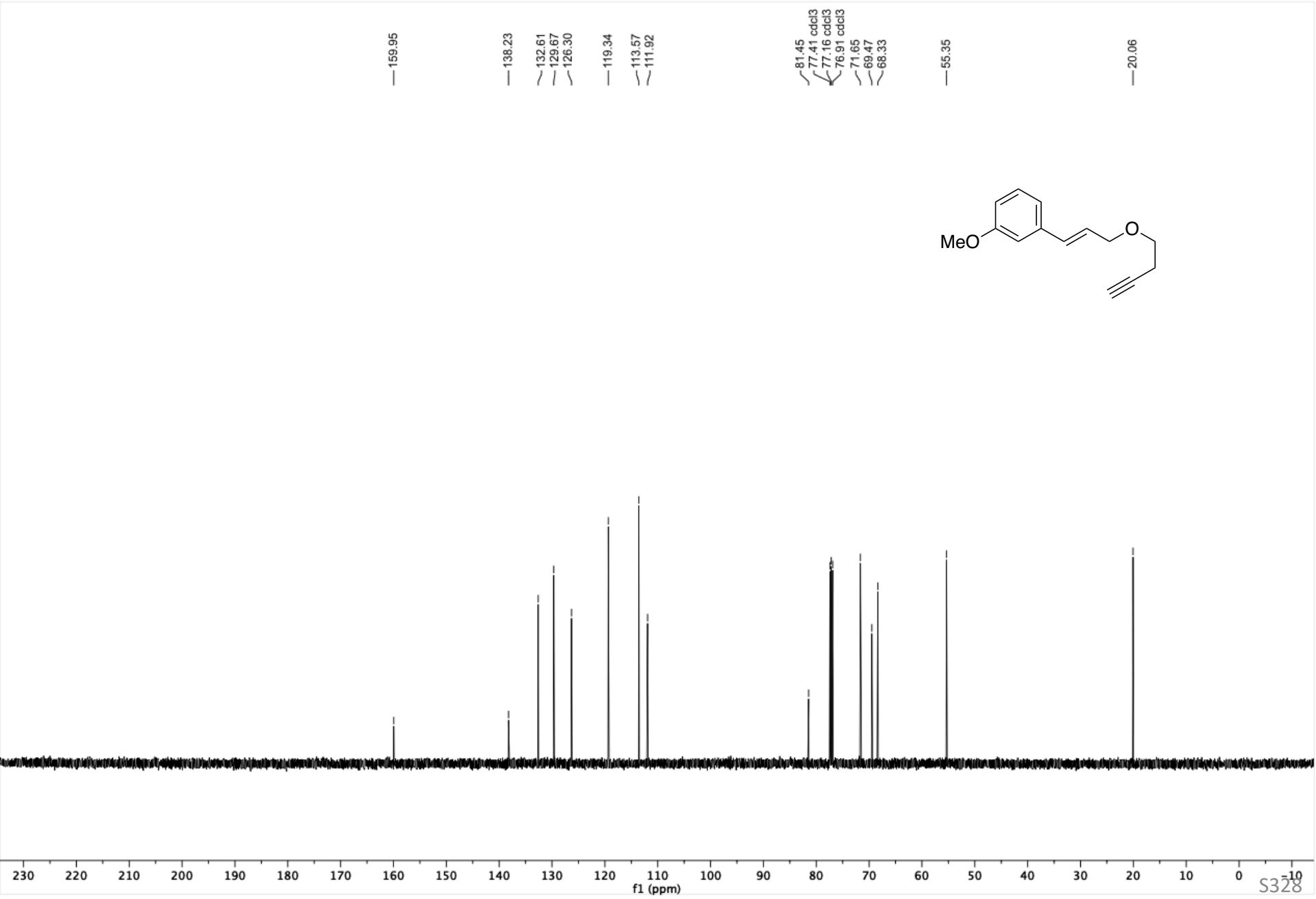
(*E*)-1-Bromo-4-(3-(but-3-yn-1-yloxy)prop-1-en-1-yl)benzene



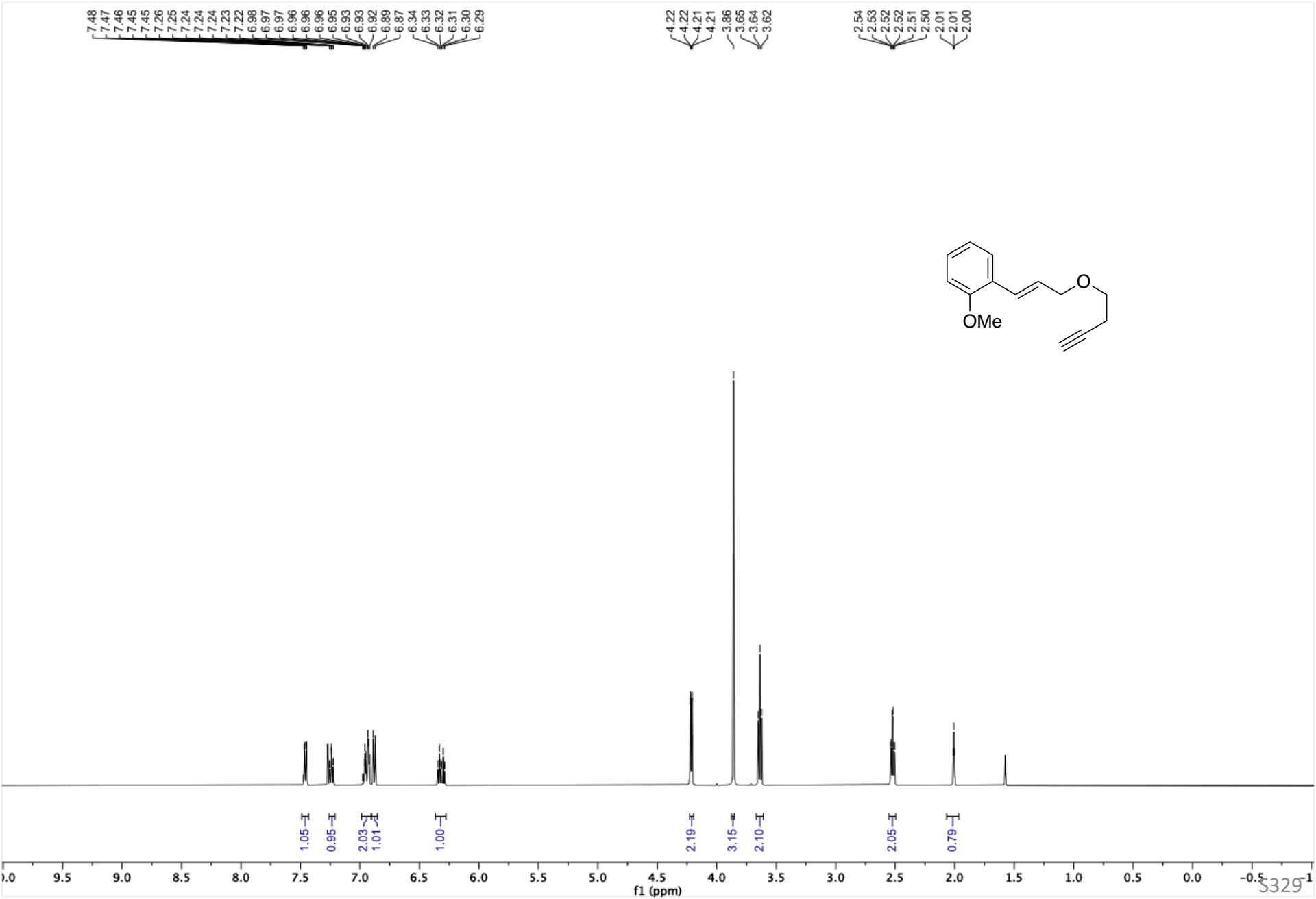
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-3-methoxybenzene



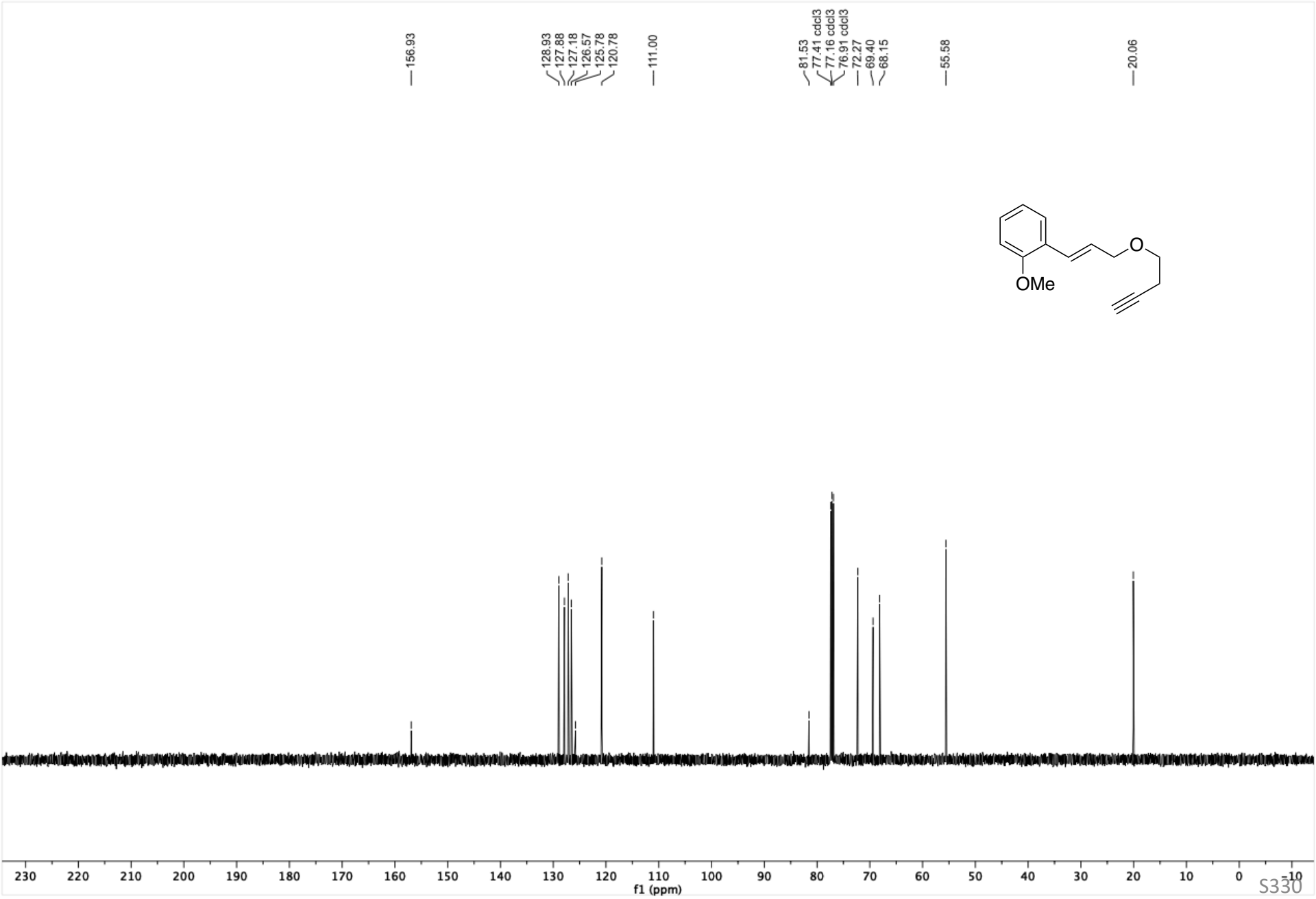
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-3-methoxybenzene



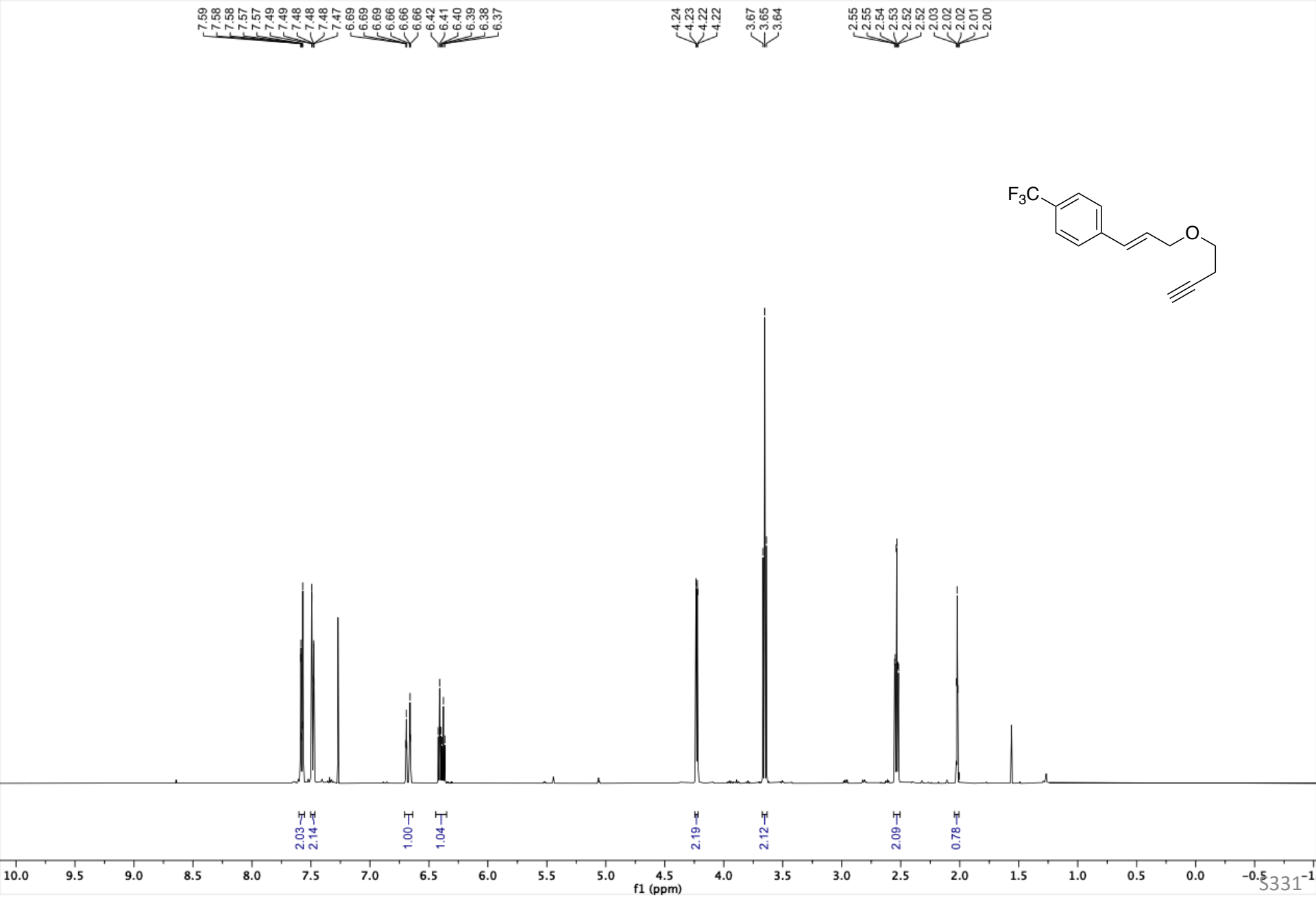
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-2-methoxybenzene



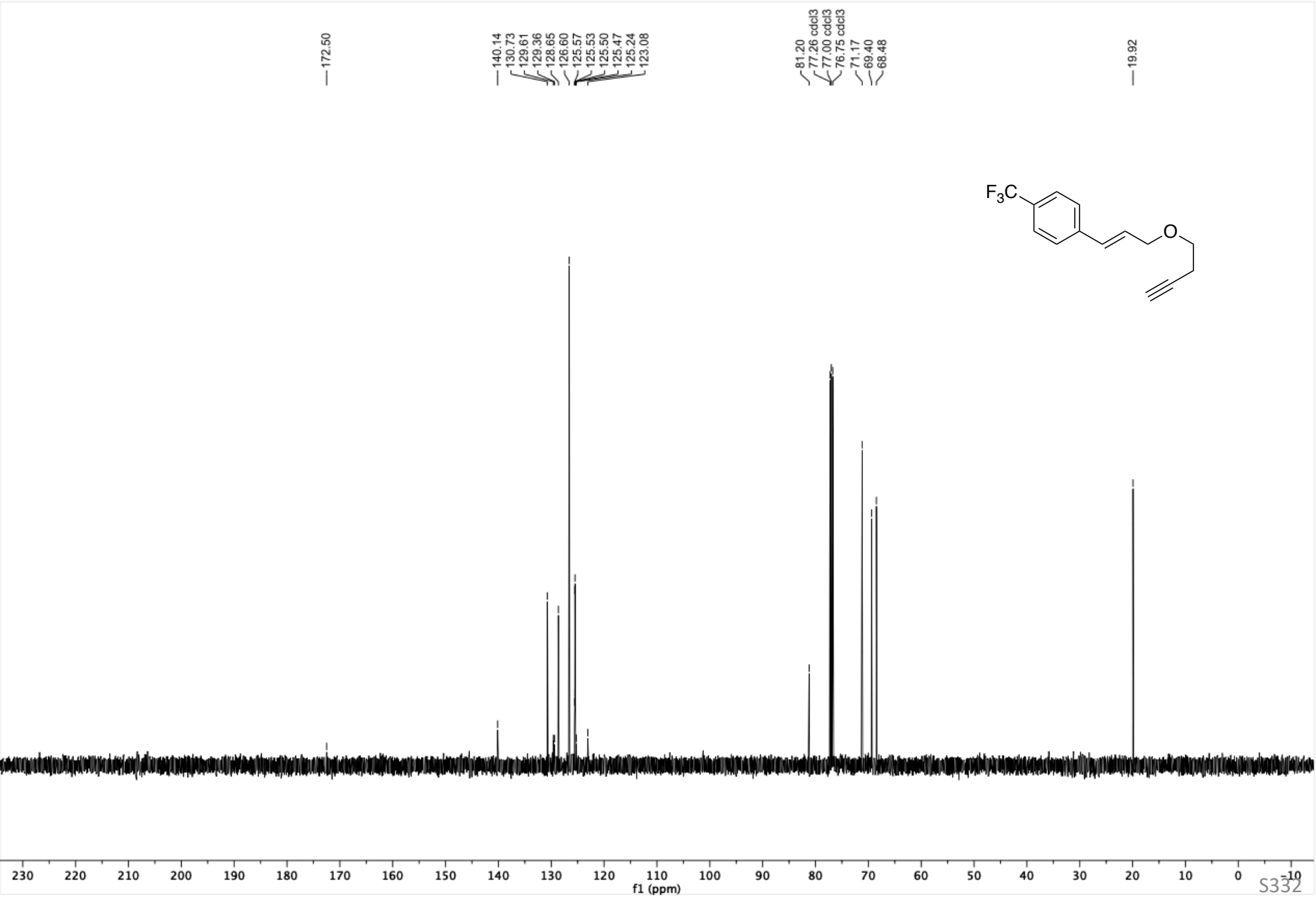
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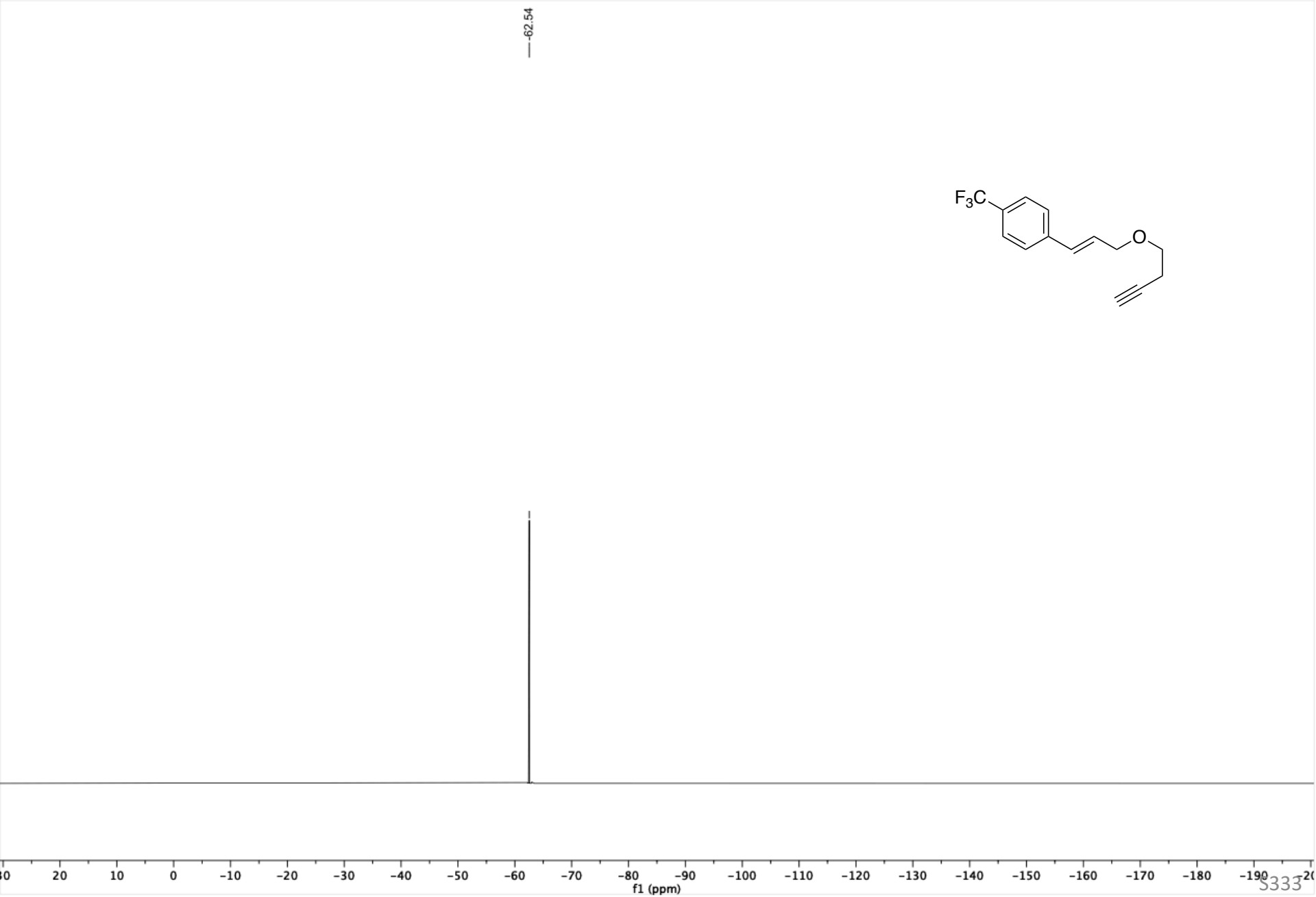
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene



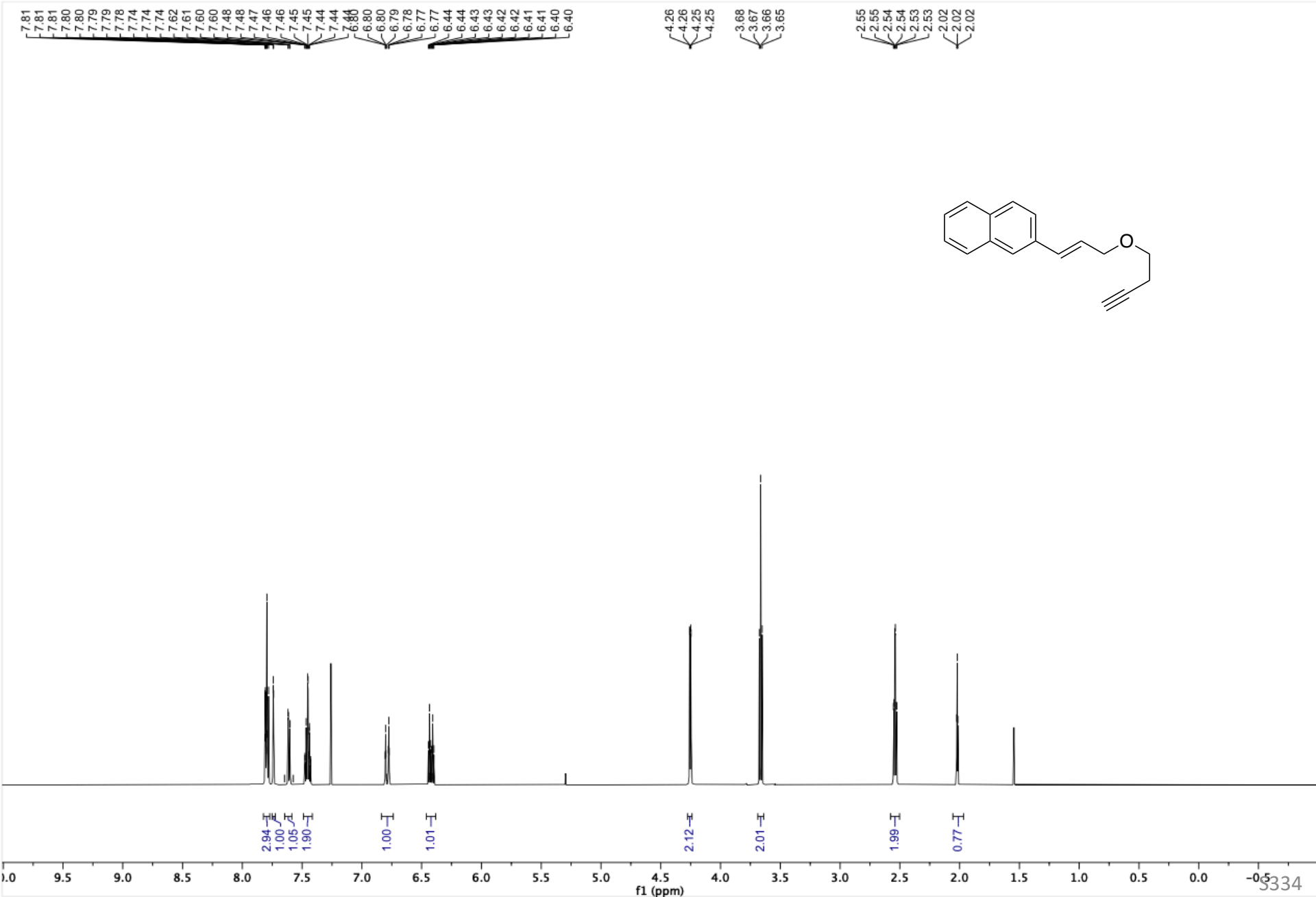
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene



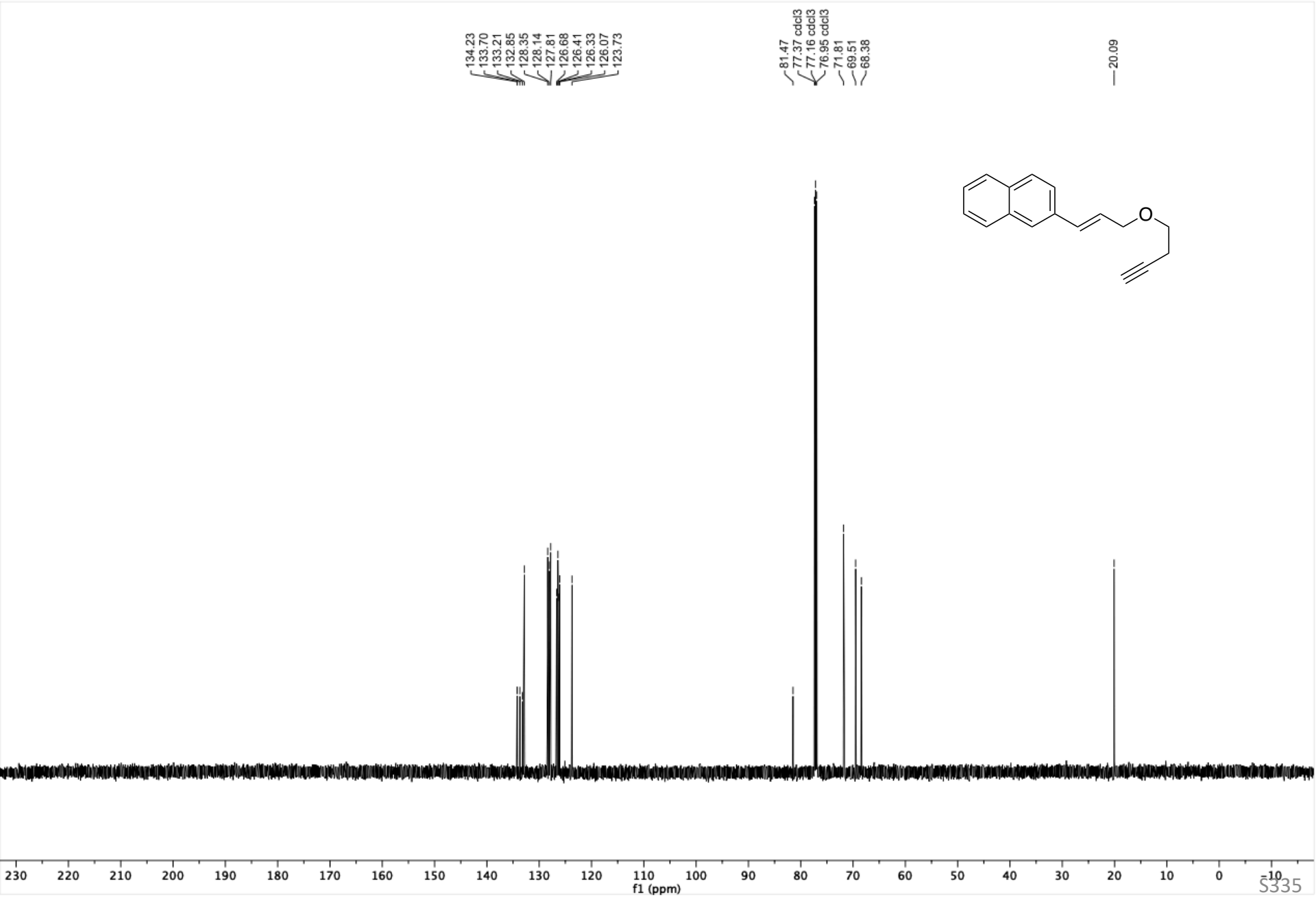
(*E*)-1-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene



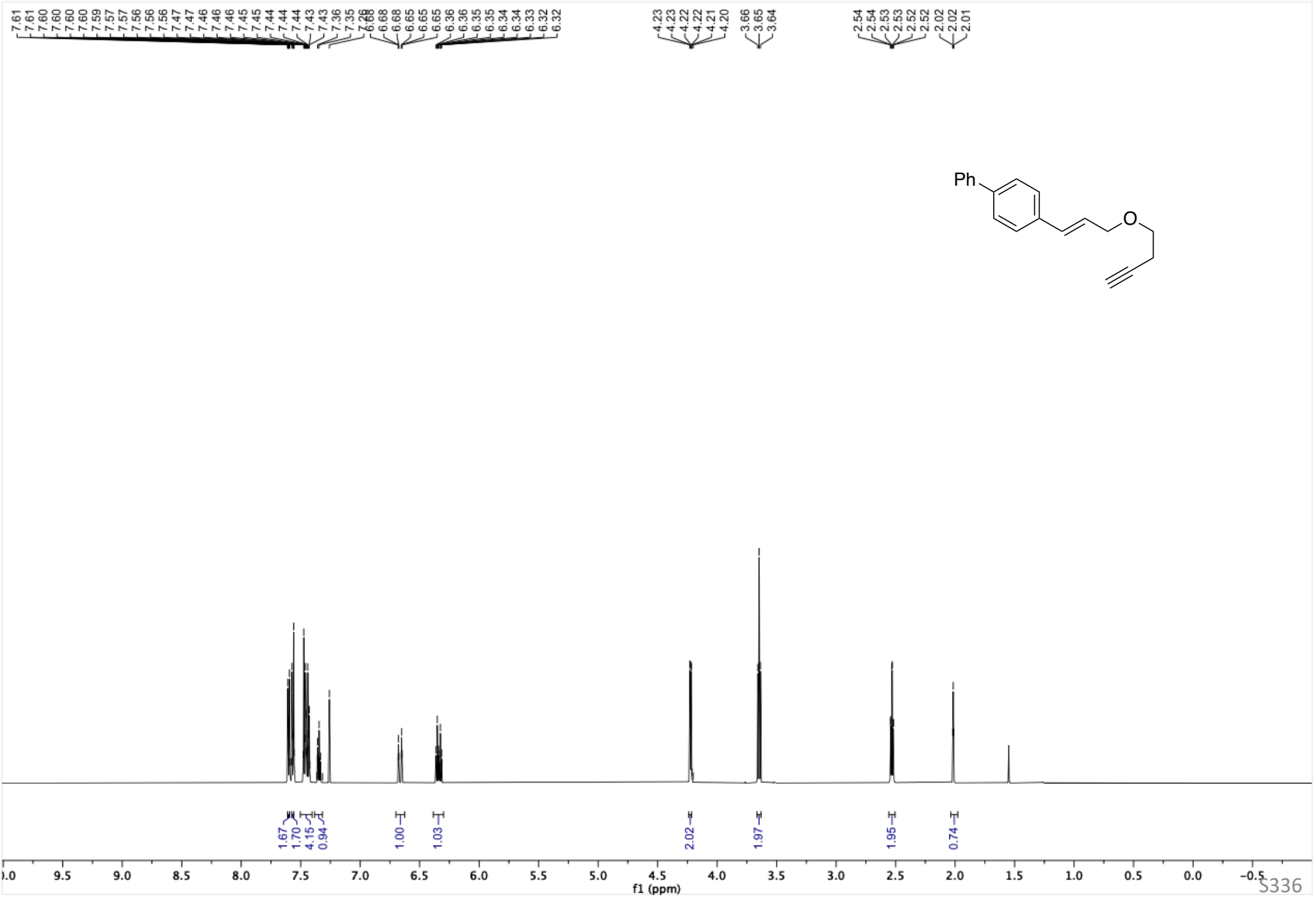
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)naphthalene



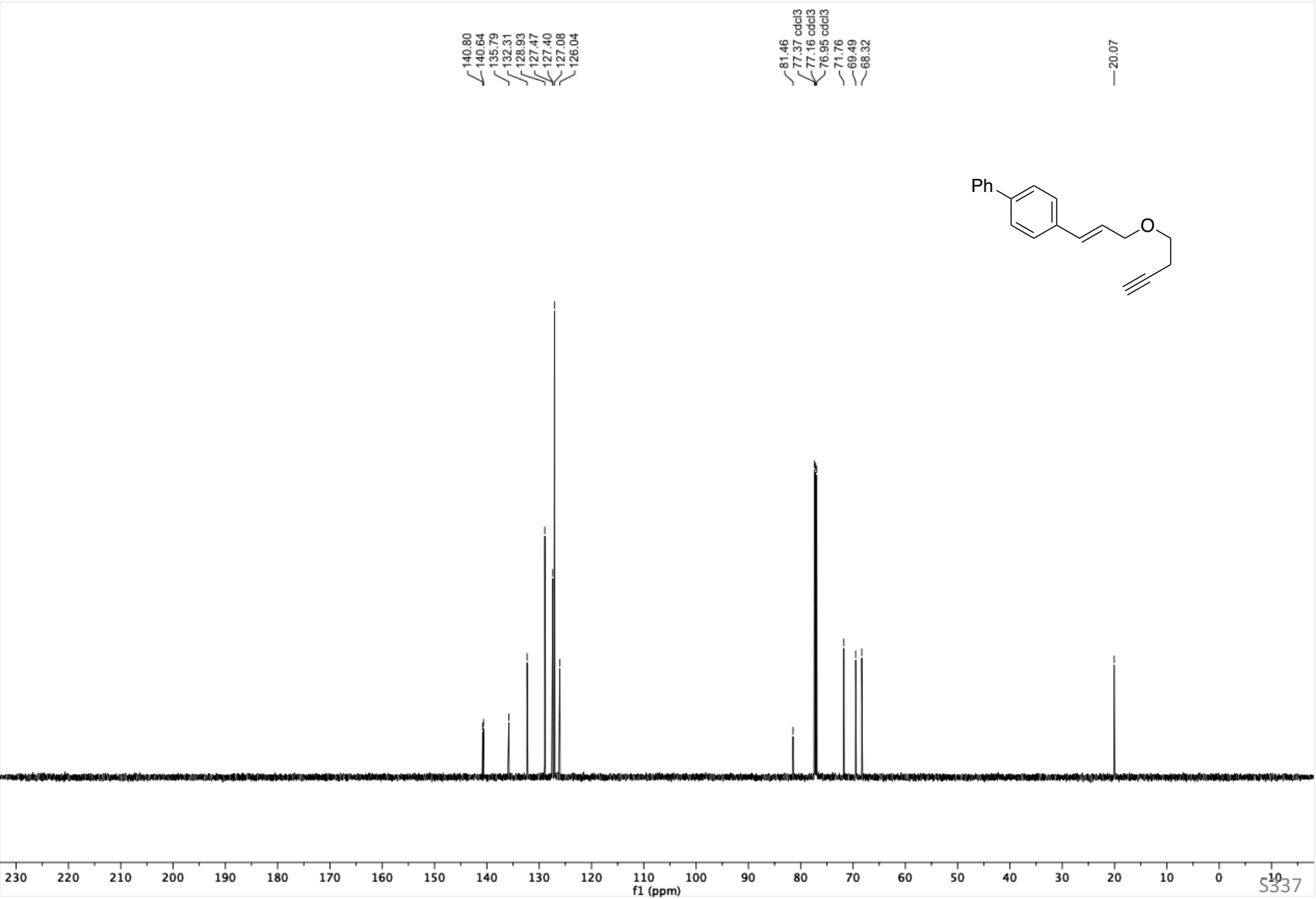
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)naphthalene



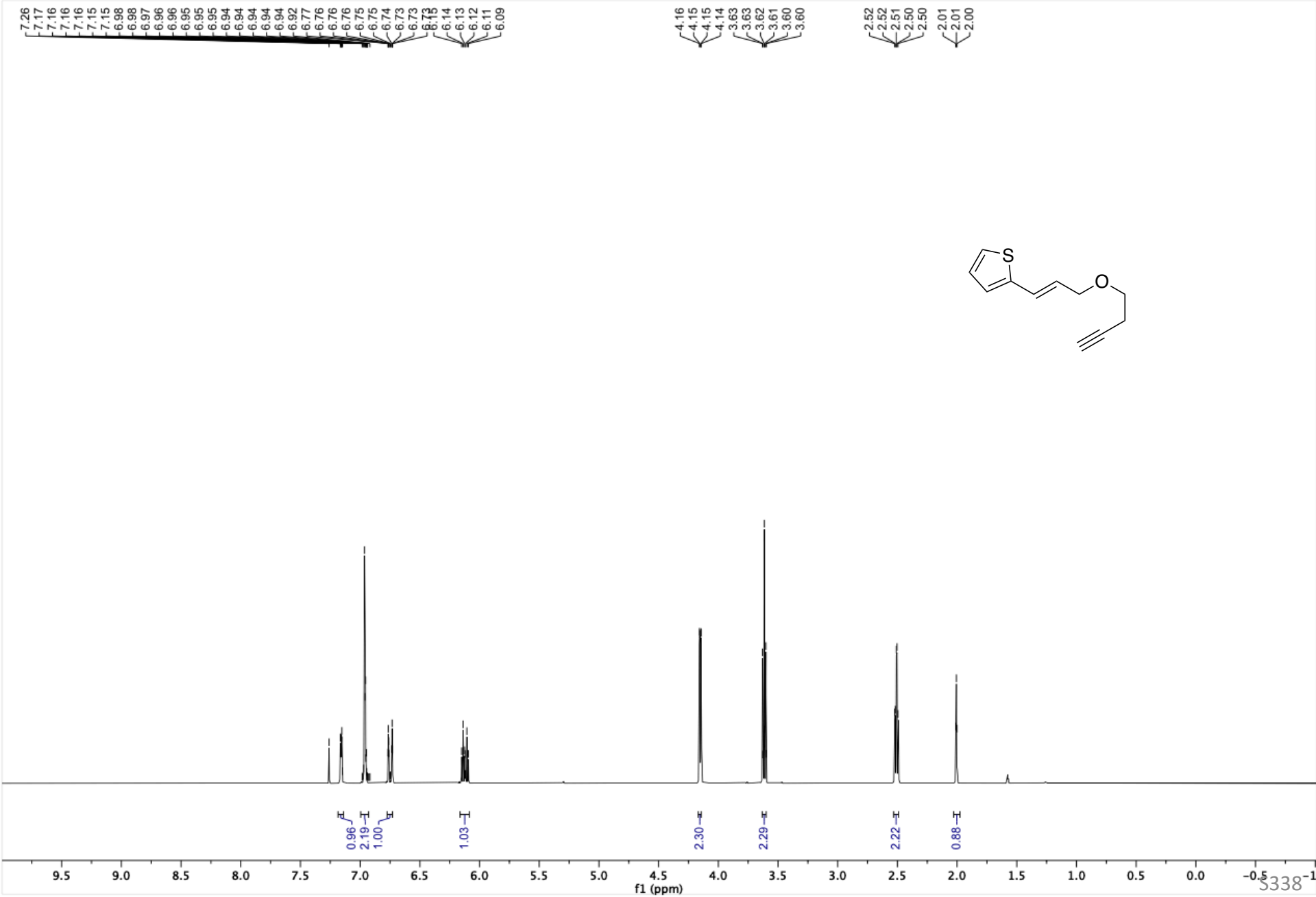
(*E*)-4-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-1,1’-biphenyl



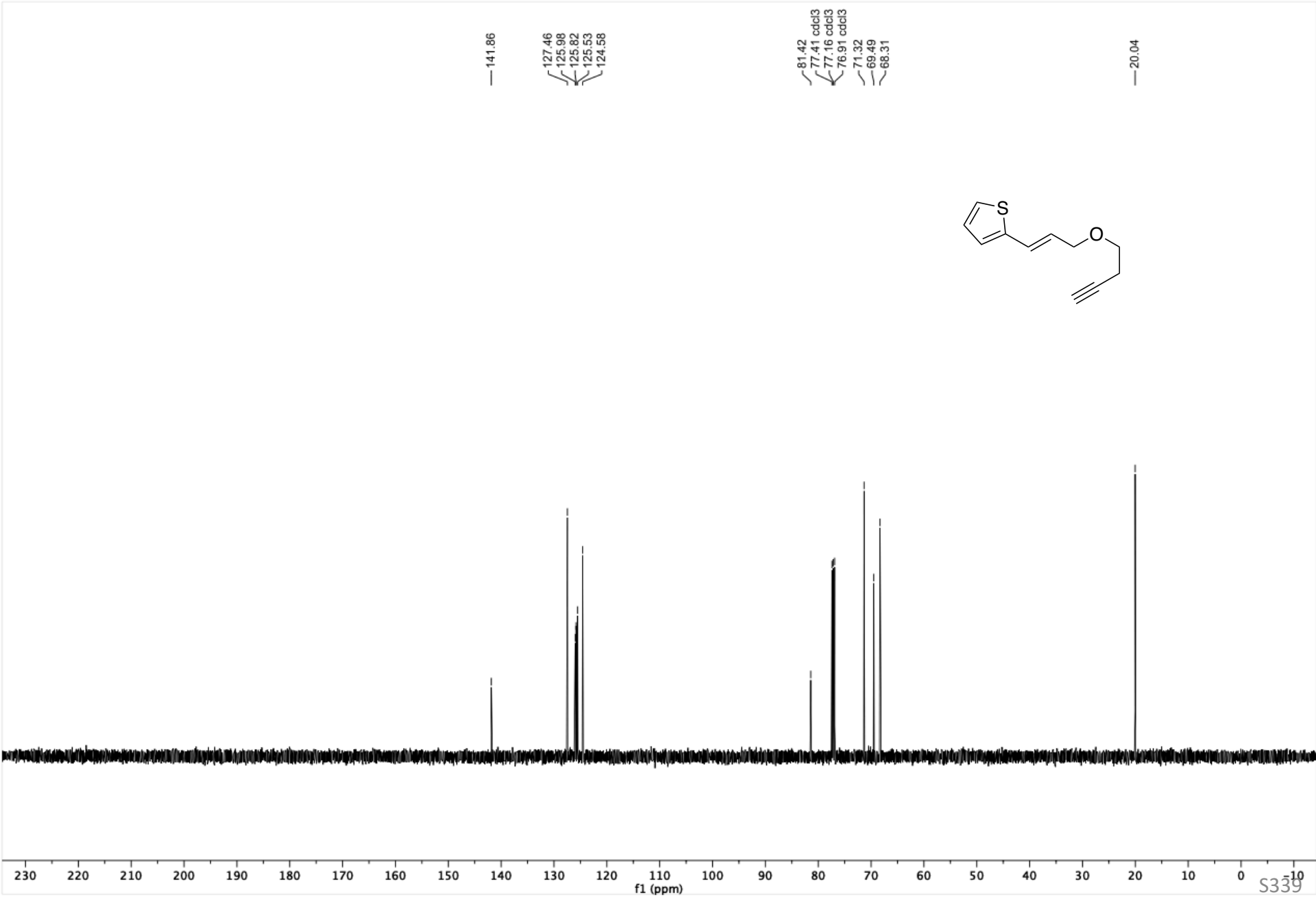
(*E*)-4-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)-1,1’-biphenyl



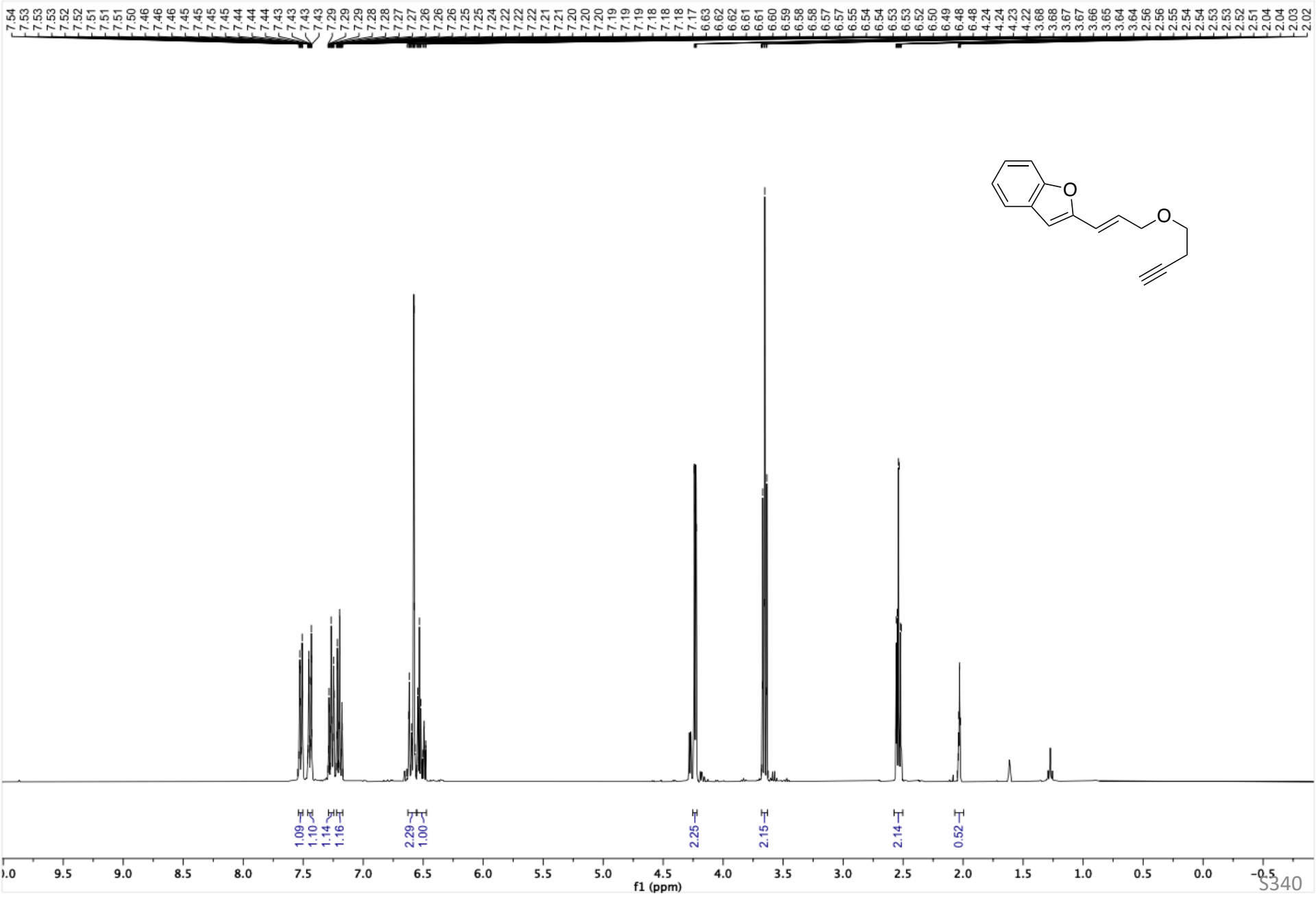
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)thiophene



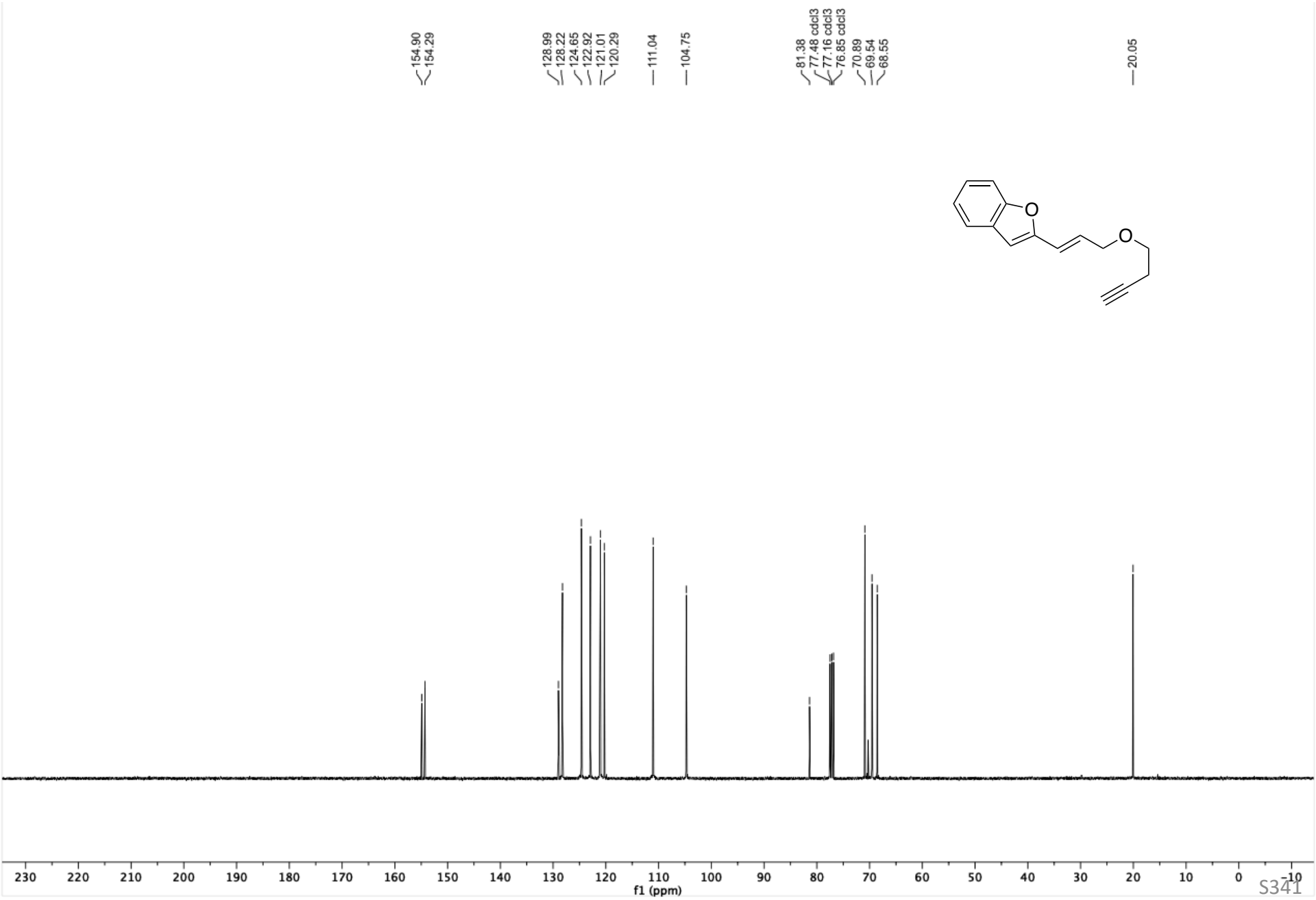
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)thiophene



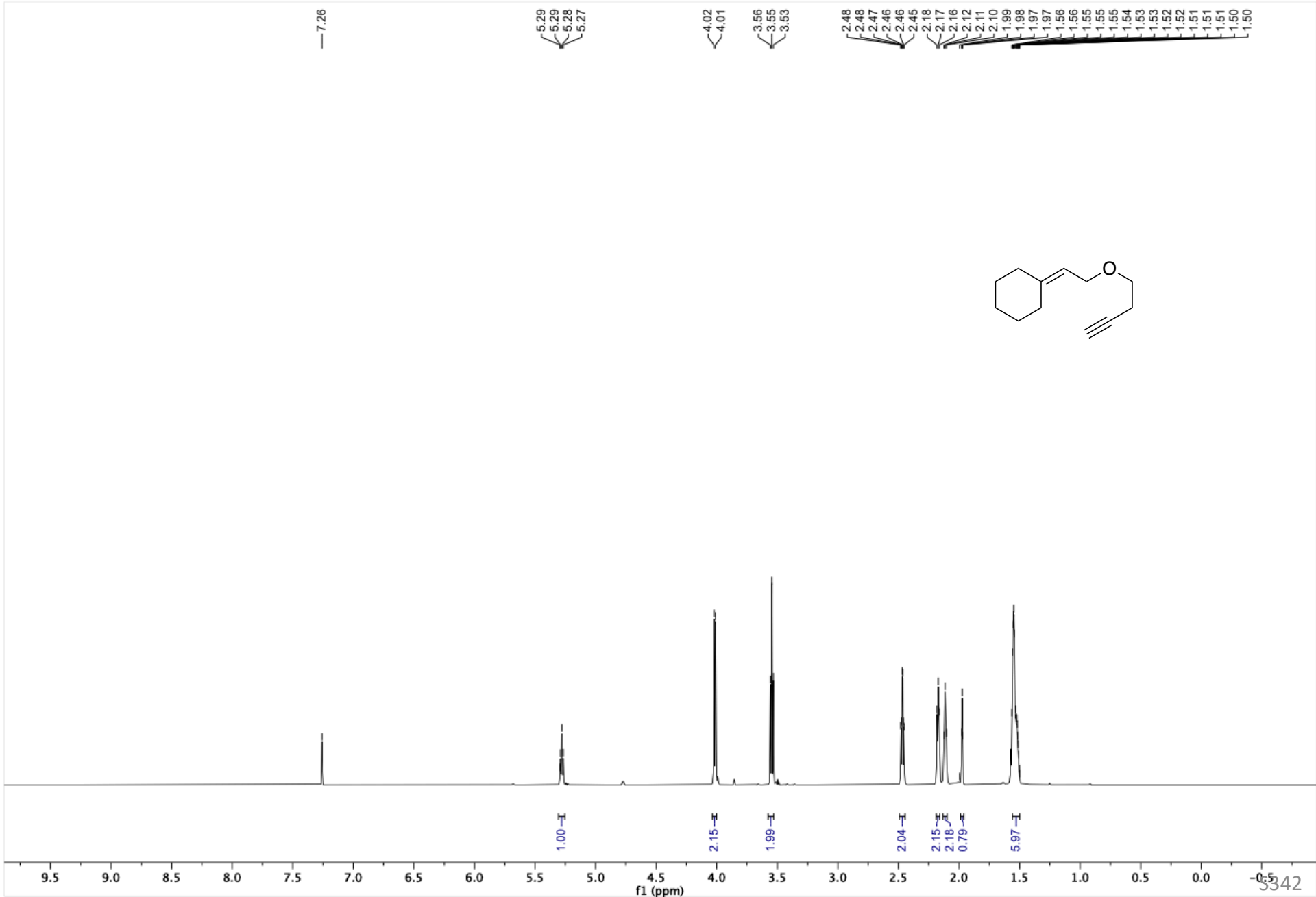
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzofuran



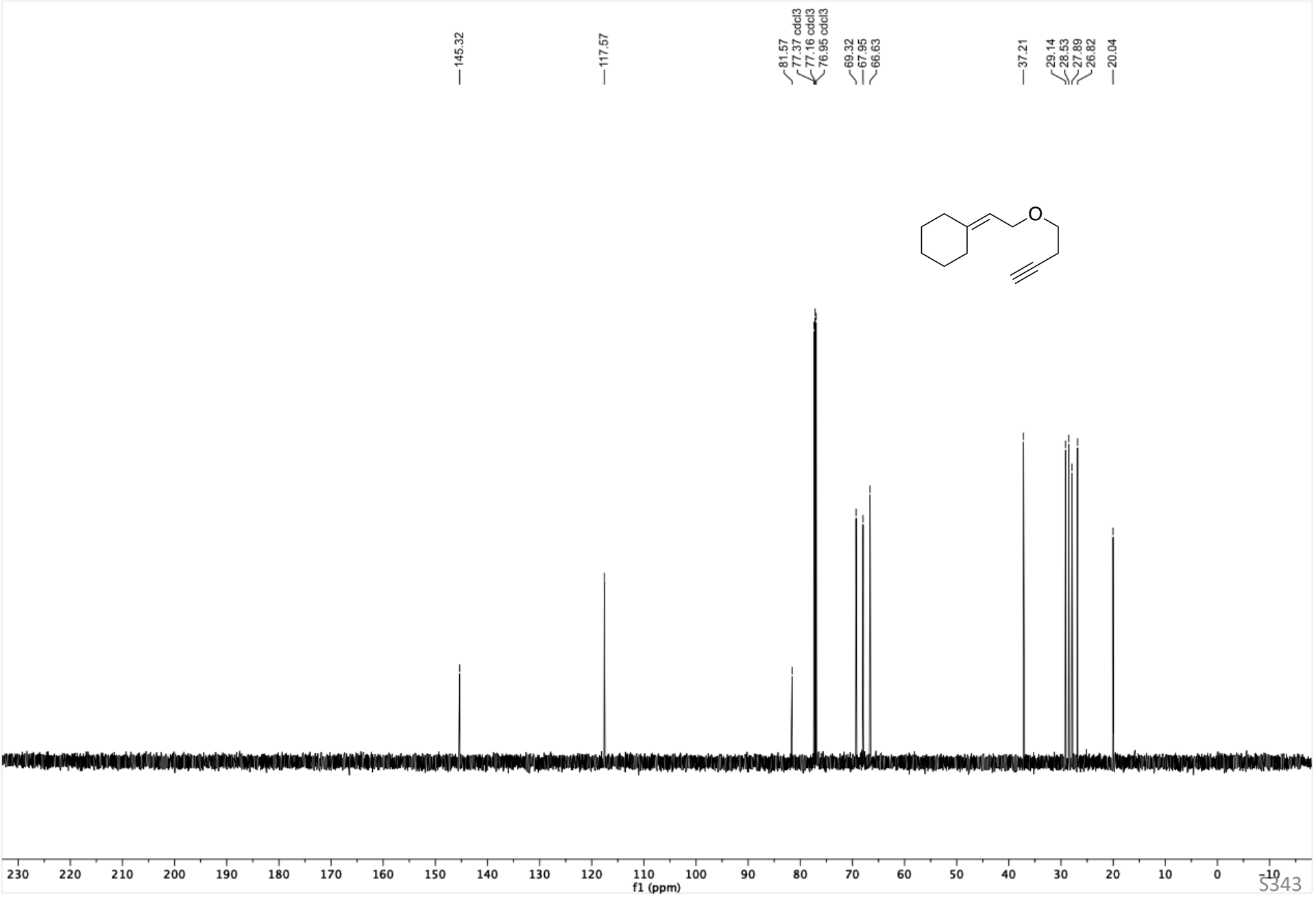
(*E*)-2-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzofuran



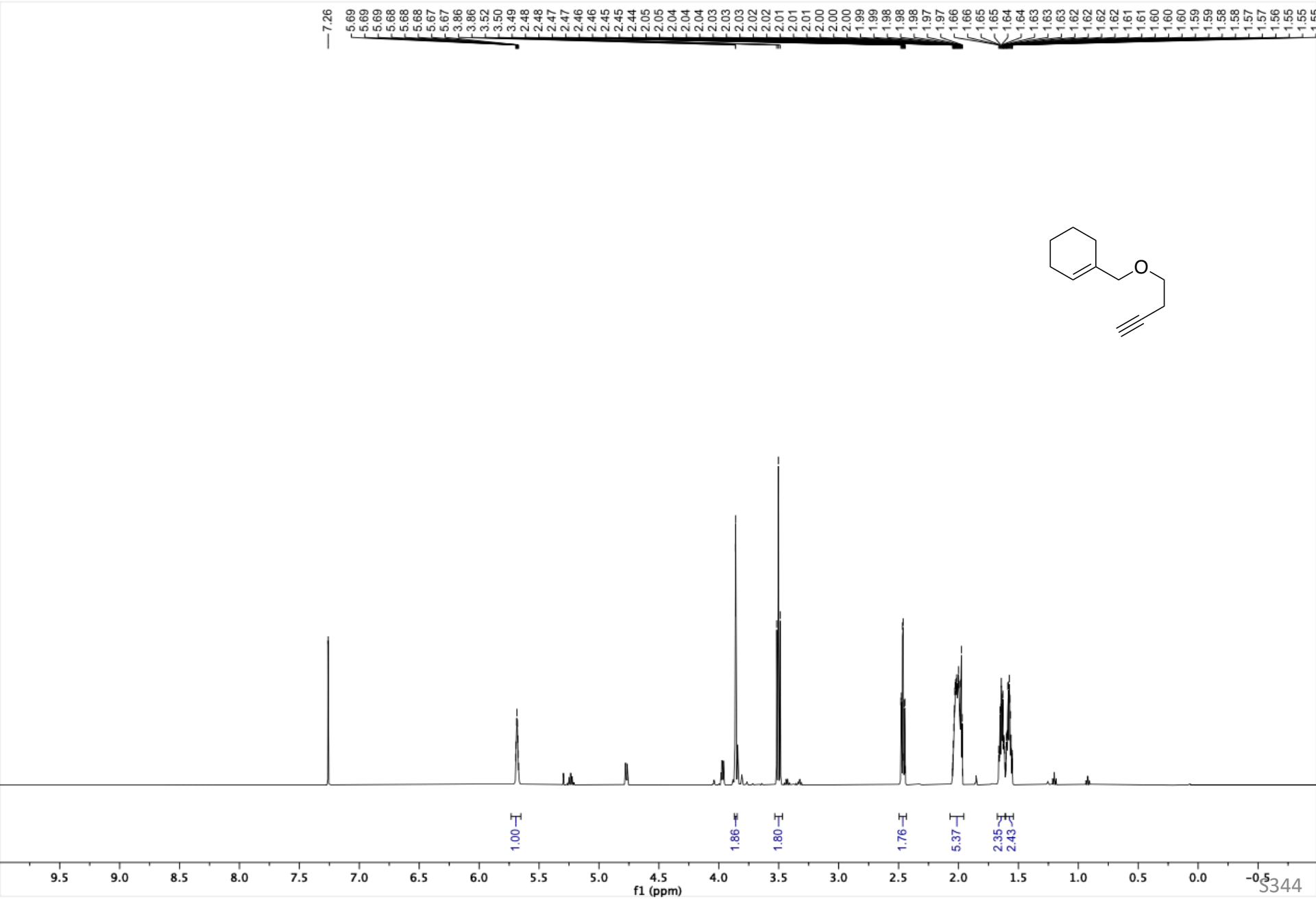
(2-(But-3-yn-1-yloxy)ethylidene)cyclohexane



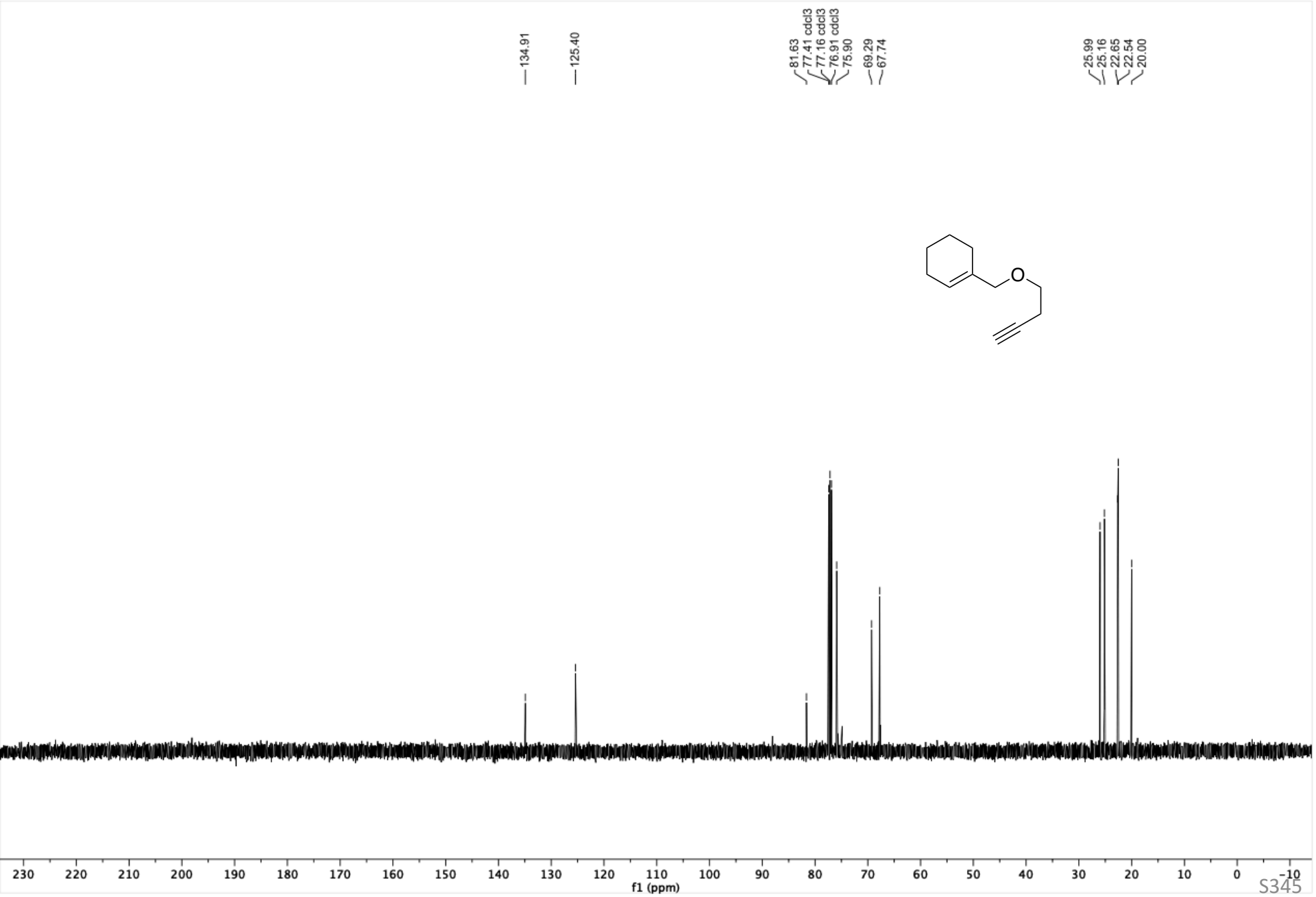
(2-(But-3-yn-1-yloxy)ethylidene)cyclohexane



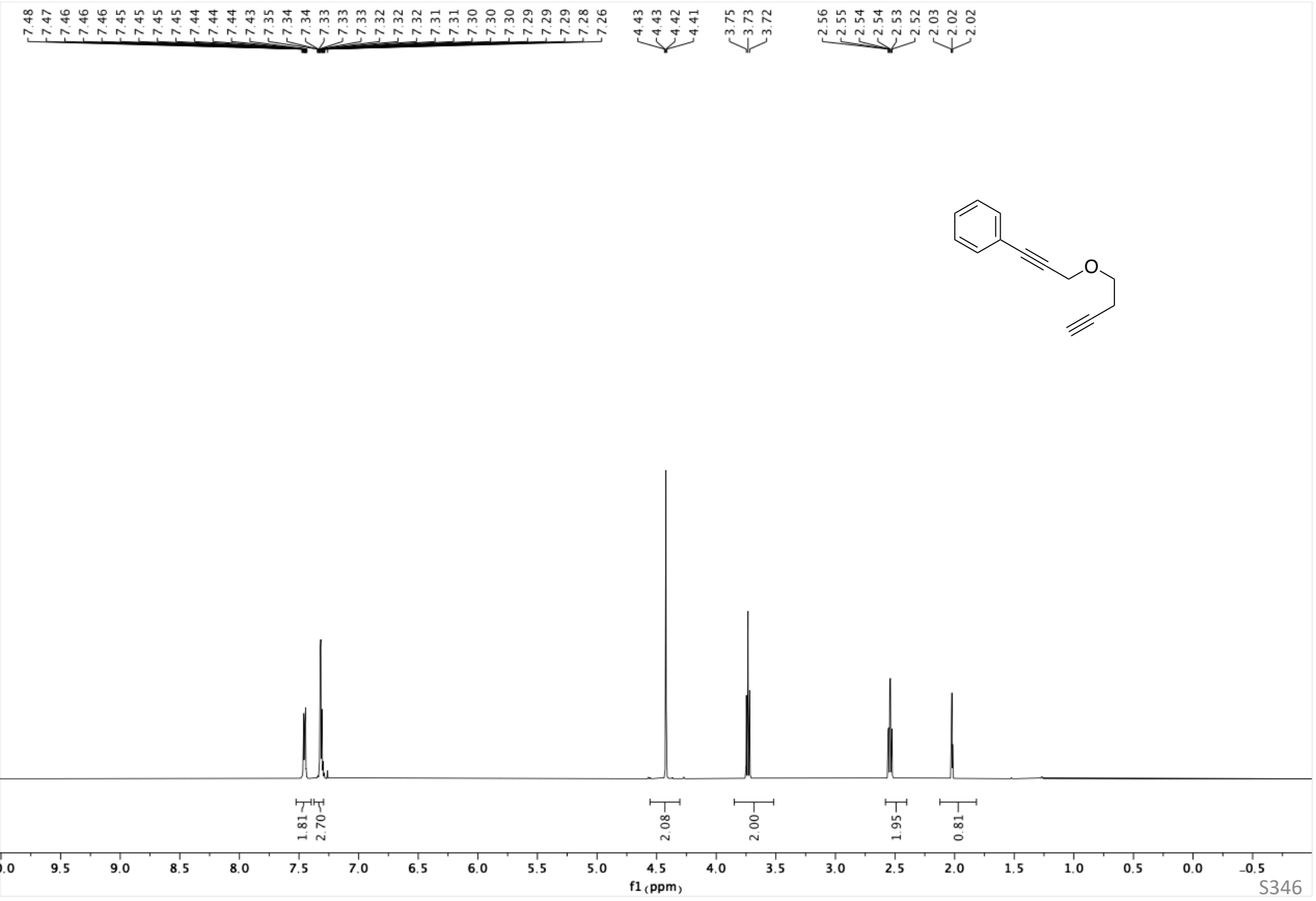
1-((But-3-yn-1-yloxy)methyl)cyclohex-1-ene



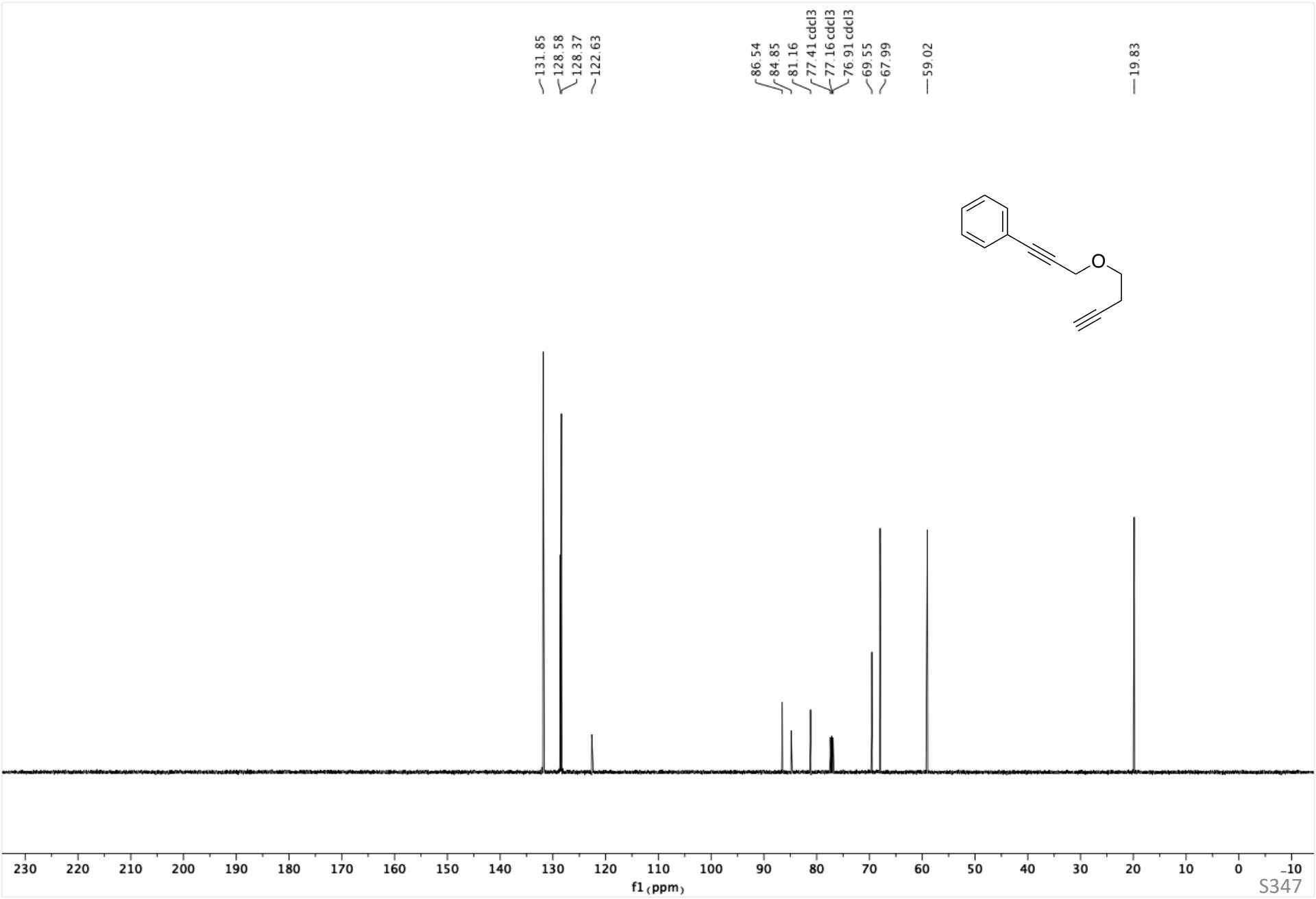
1-((But-3-yn-1-yloxy)methyl)cyclohex-1-ene



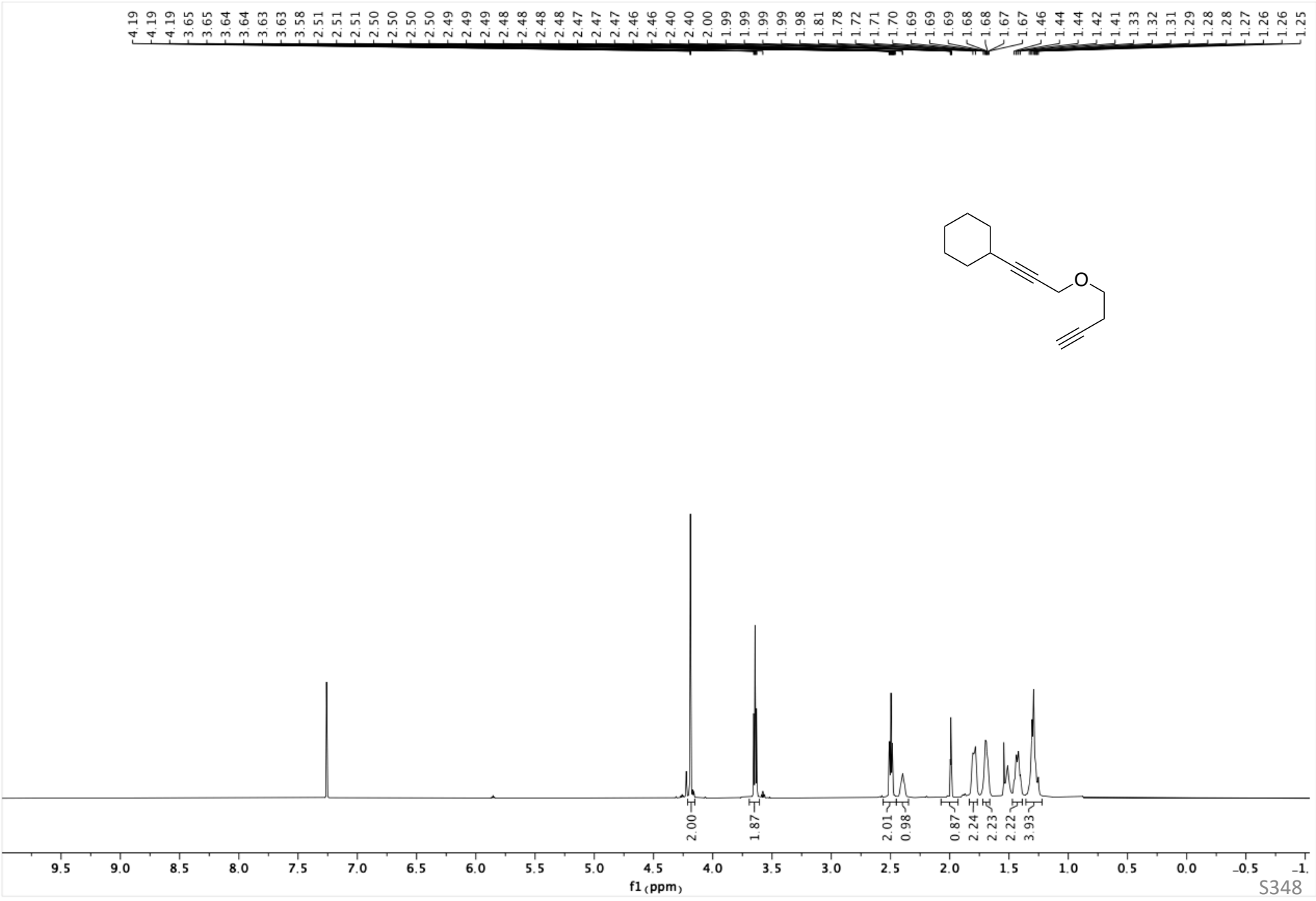
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)benzene



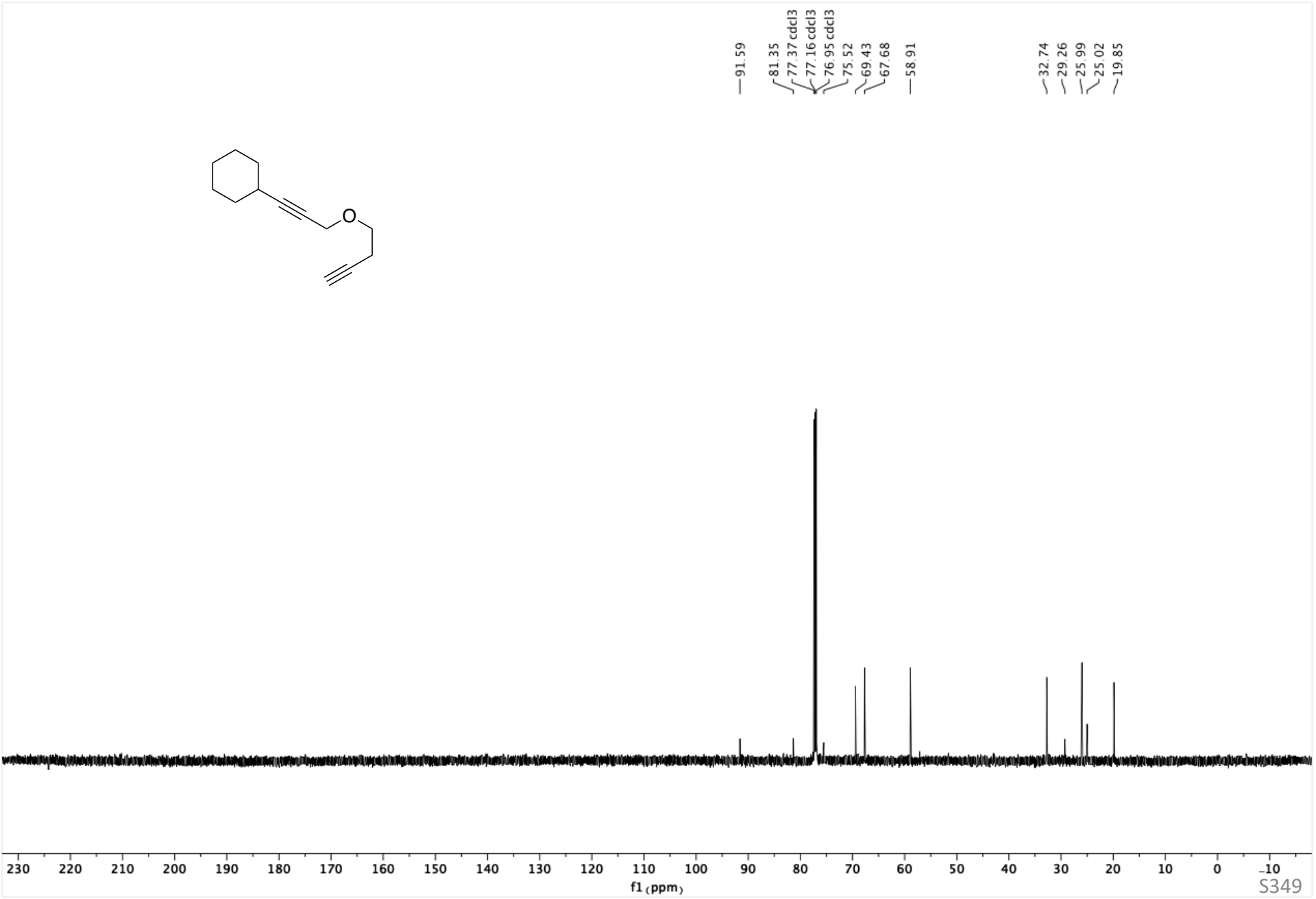
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)benzene



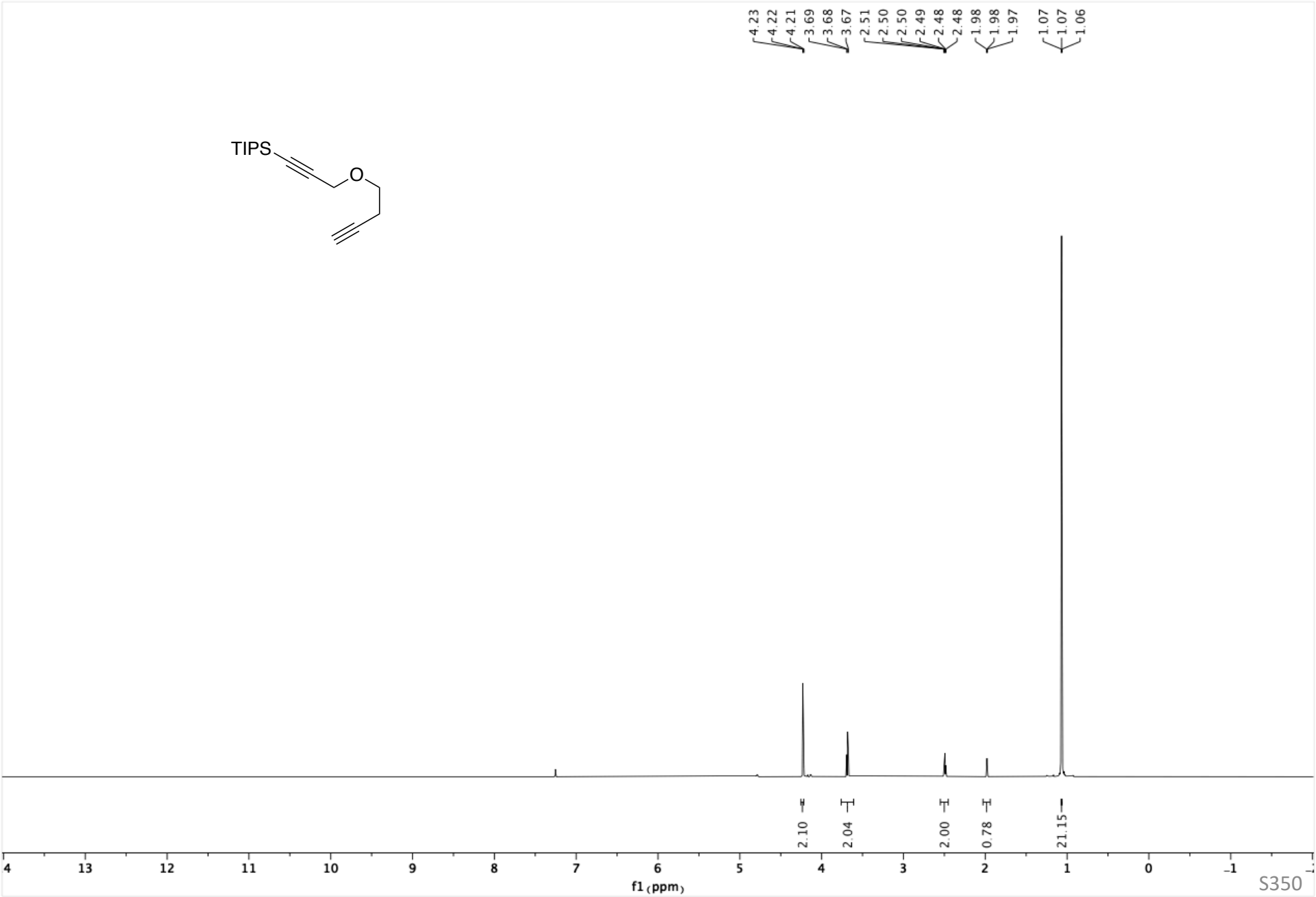
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)cyclohexane



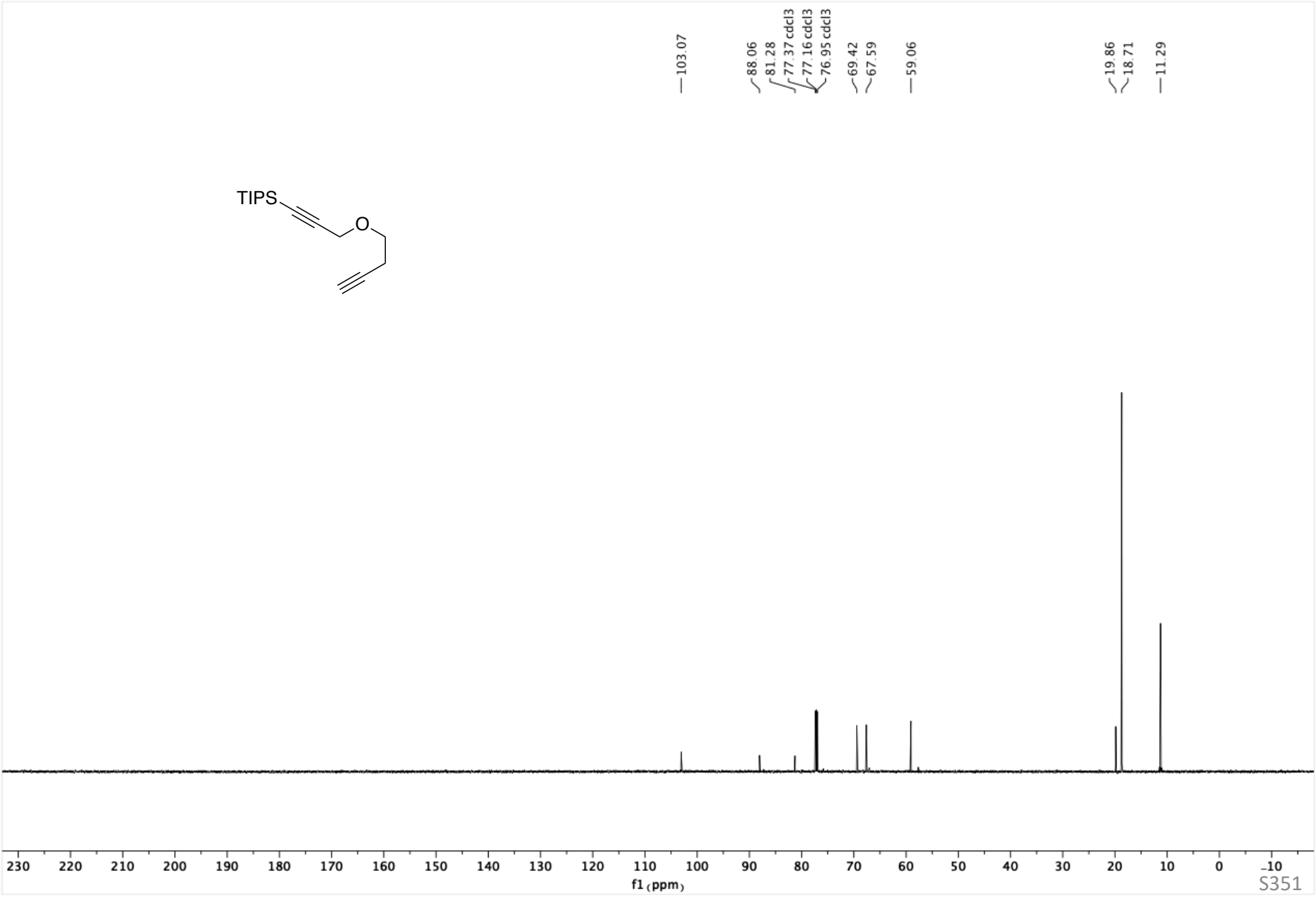
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)cyclohexane



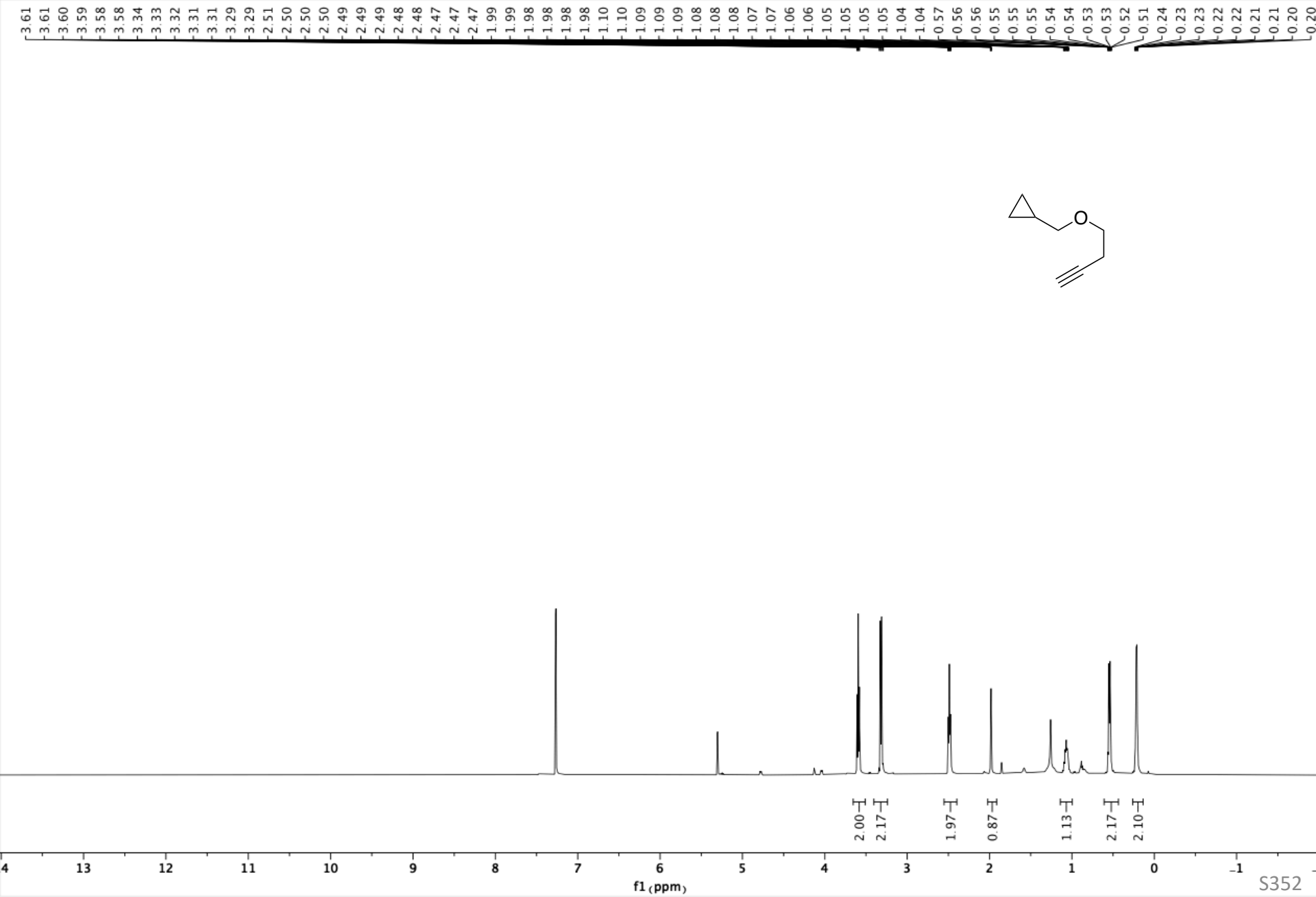
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)triisopropylsilane



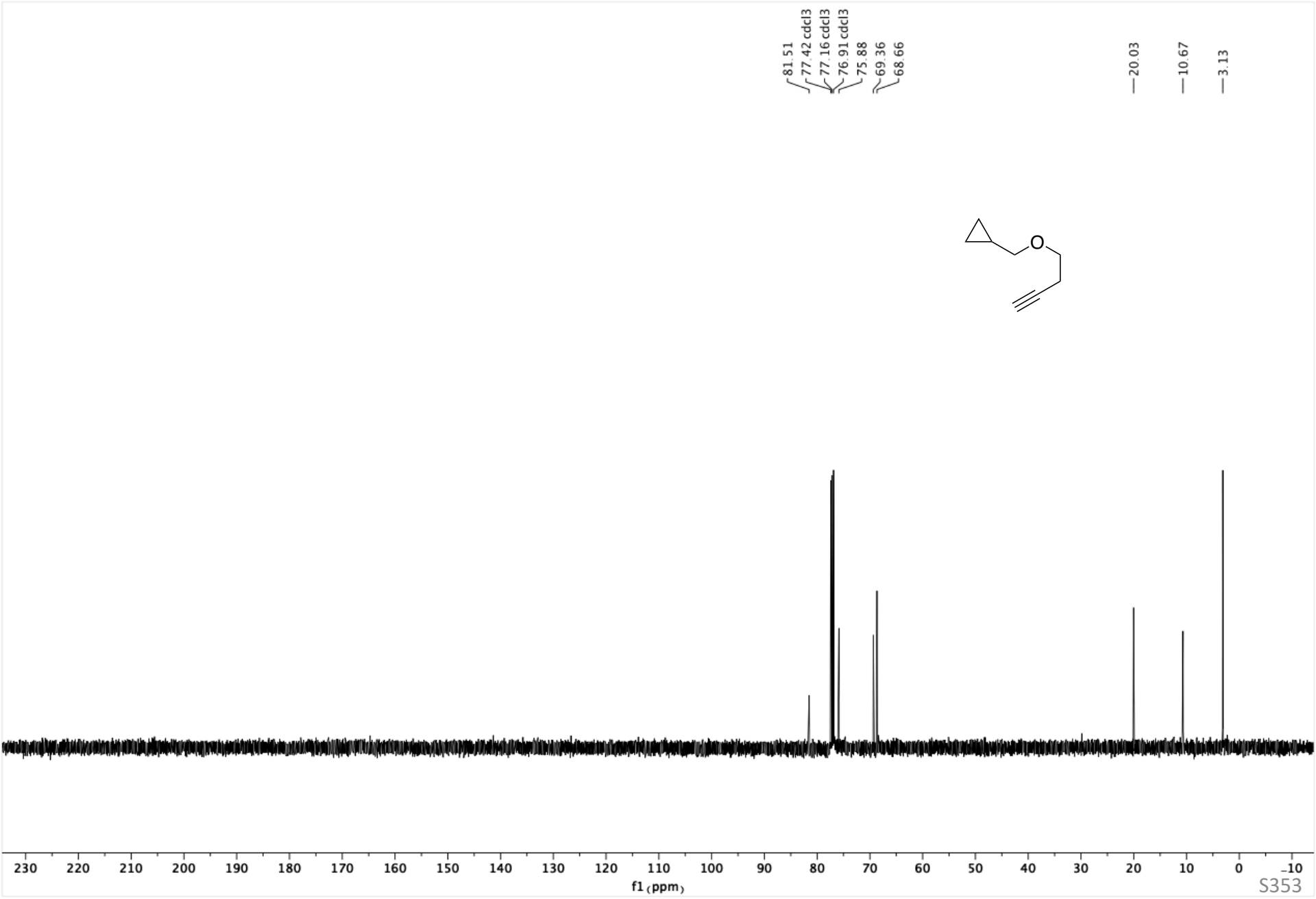
(3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)triisopropylsilane



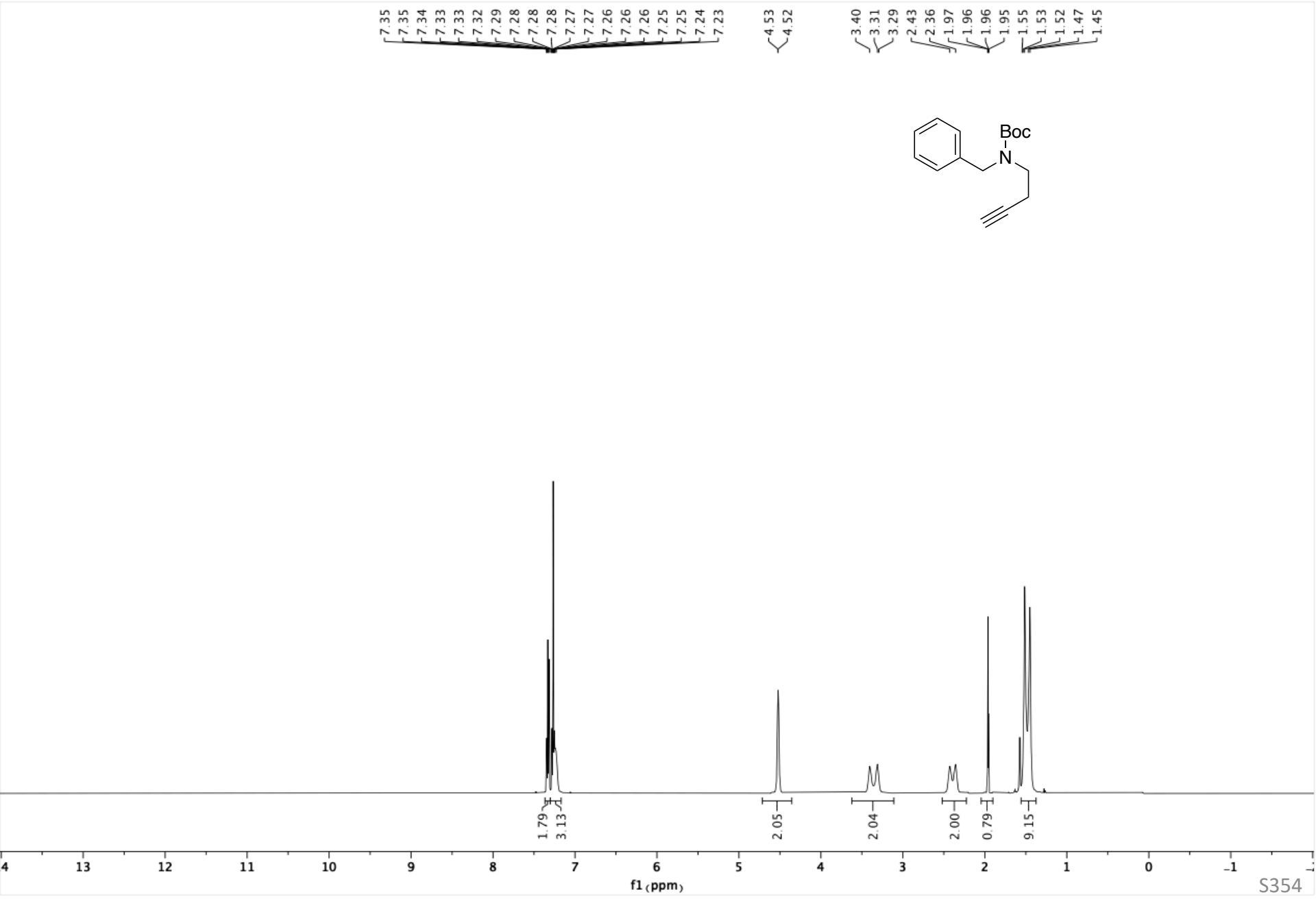
((But-3-yn-1-yloxy)methyl)cyclopropane



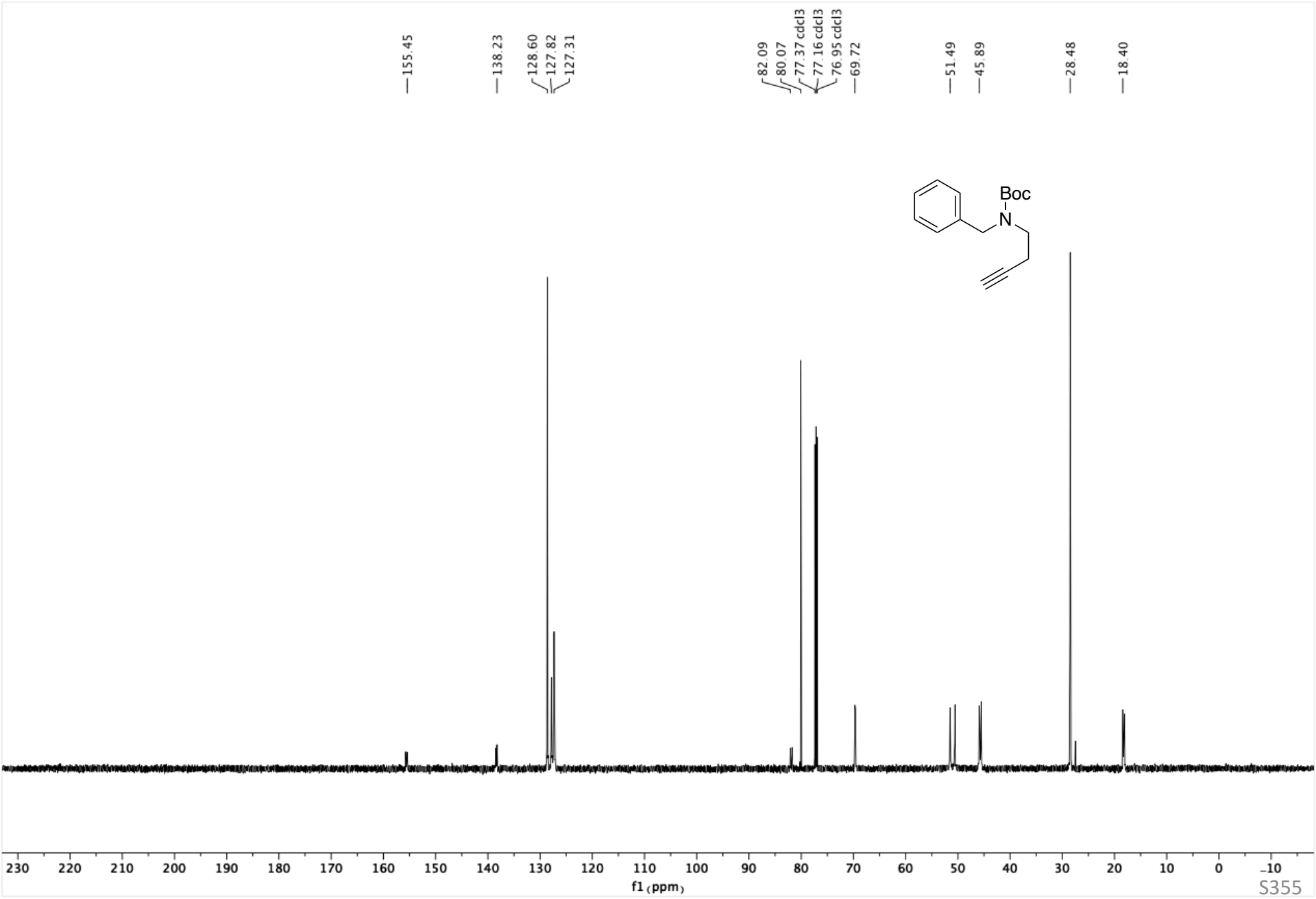
((But-3-yn-1-yloxy)methyl)cyclopropane



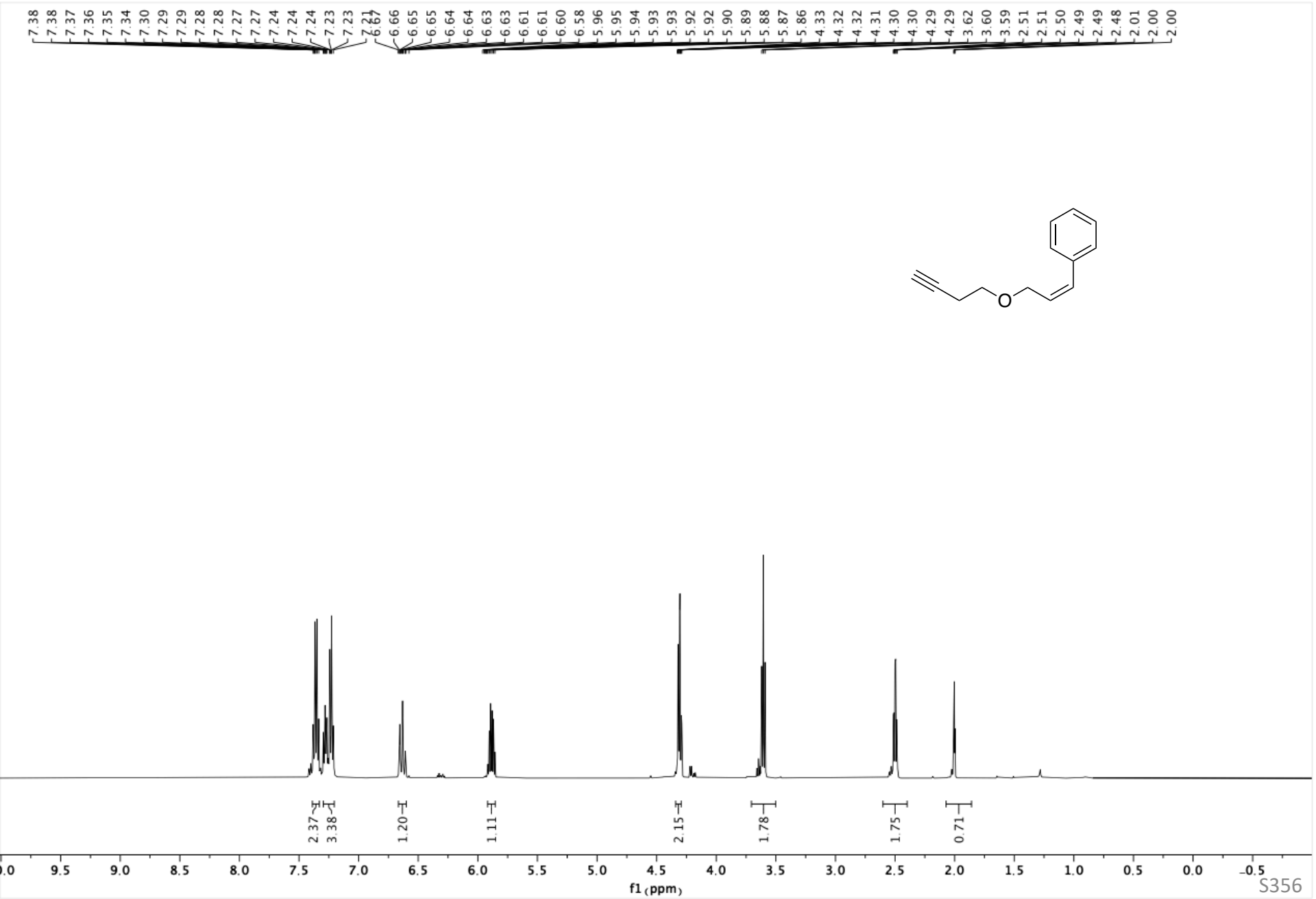
tert-Butyl benzyl(but-3-yn-1-yl)carbamate



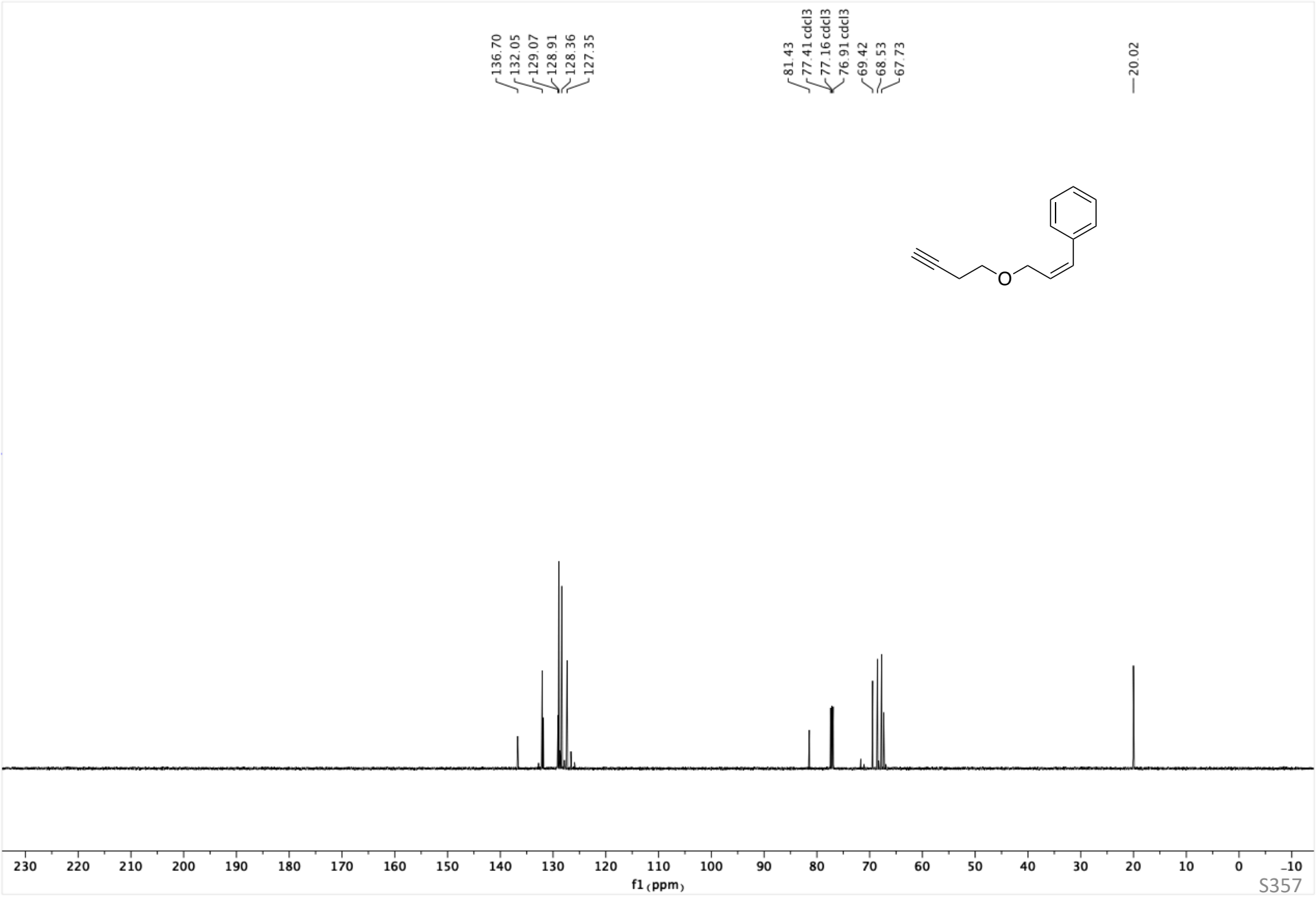
tert-Butyl benzyl(but-3-yn-1-yl)carbamate



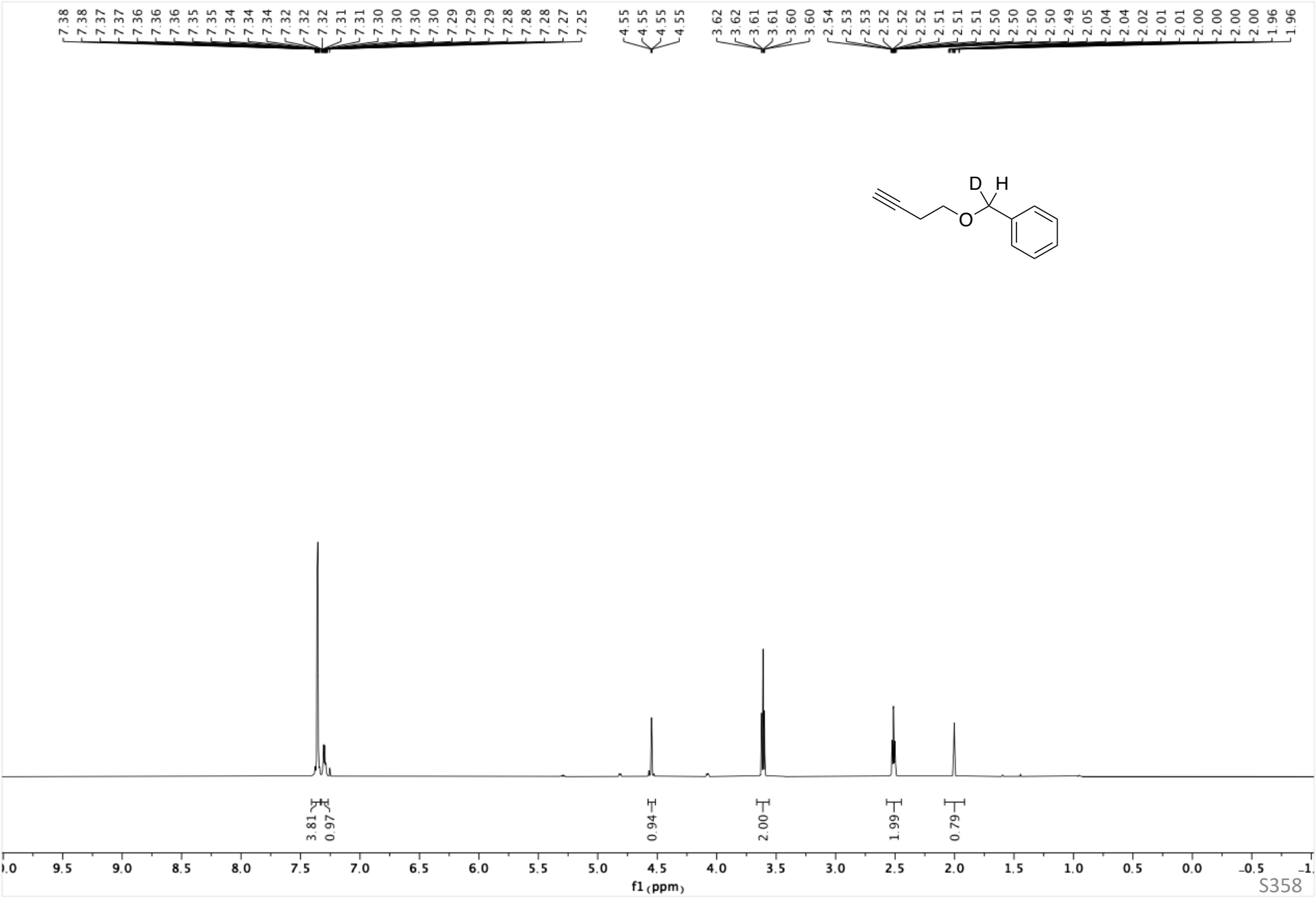
(*Z*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene



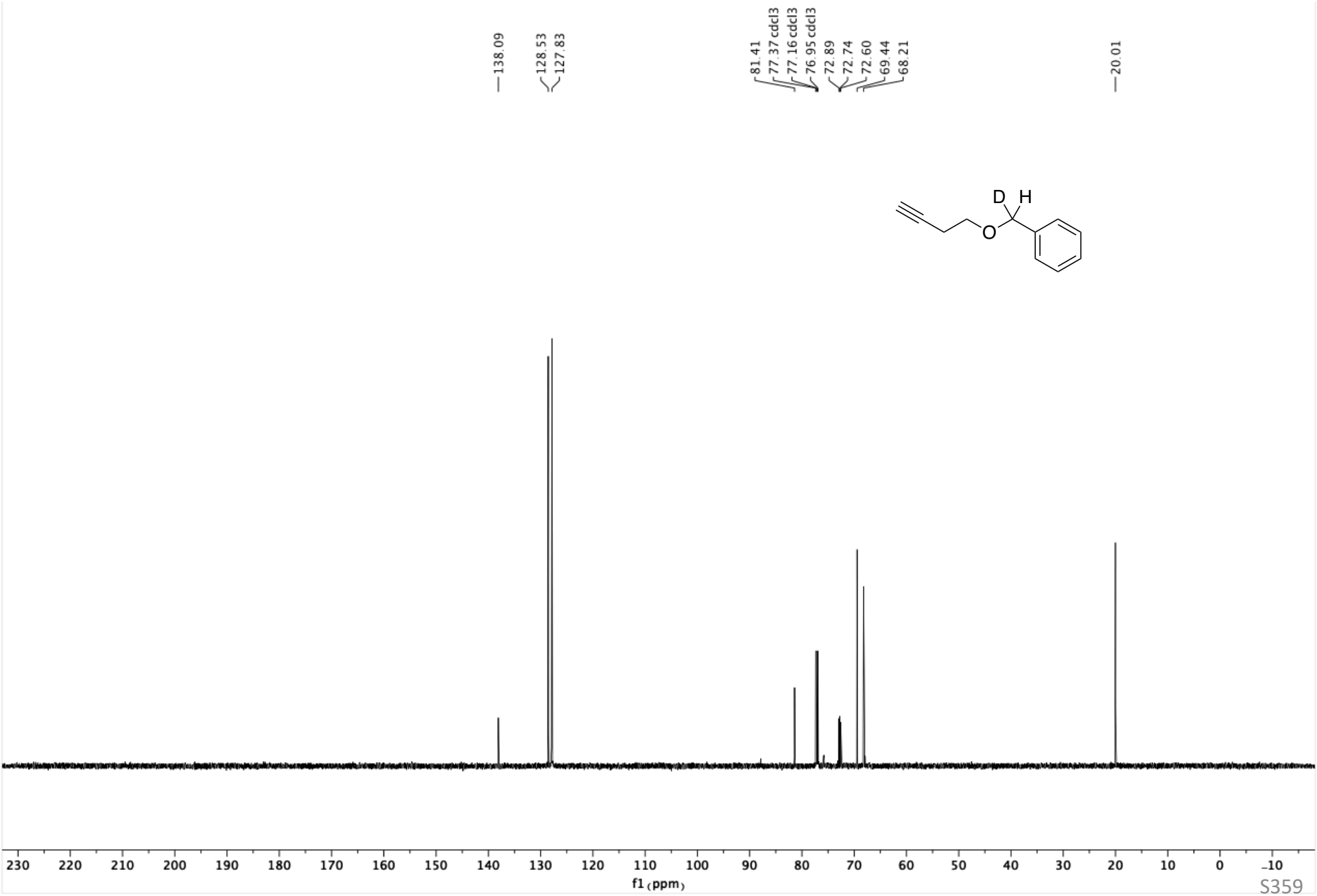
(*Z*)-(3-(But-3-yn-1-yloxy)prop-1-en-1-yl)benzene



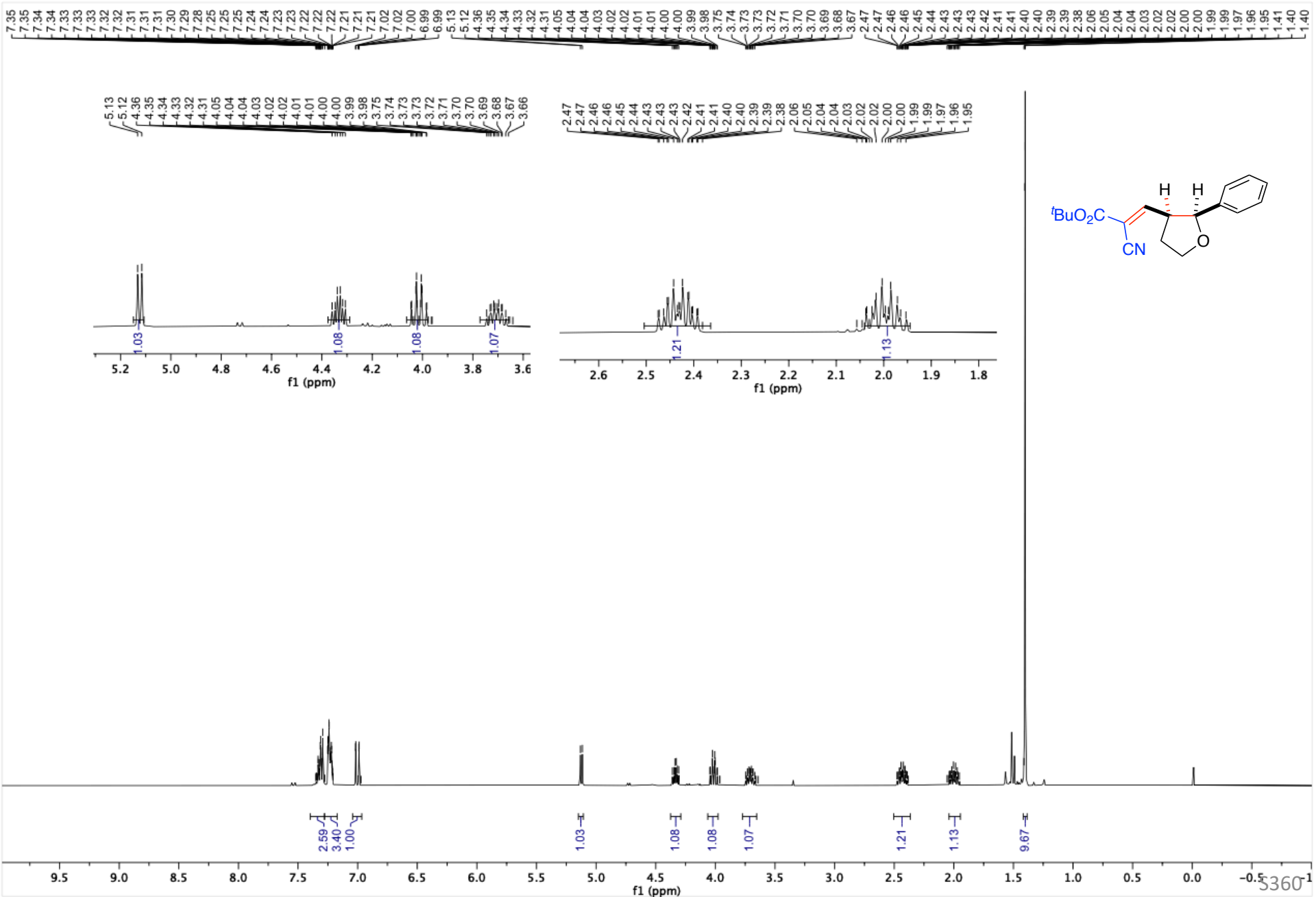
((But-3-yn-1-yloxy)methyl-d)benzene



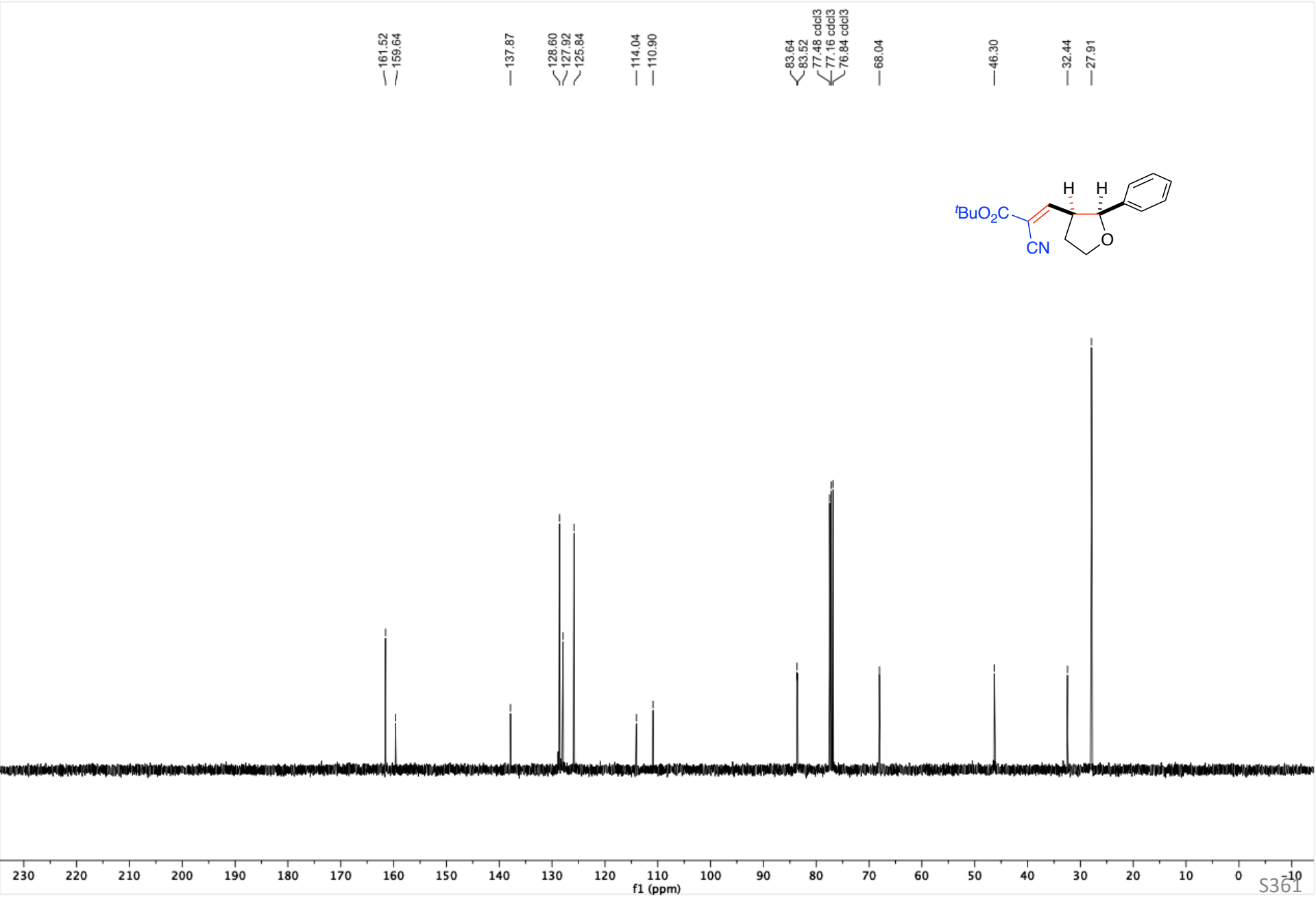
((But-3-yn-1-yloxy)methyl-d)benzene

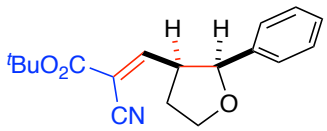


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)acrylate

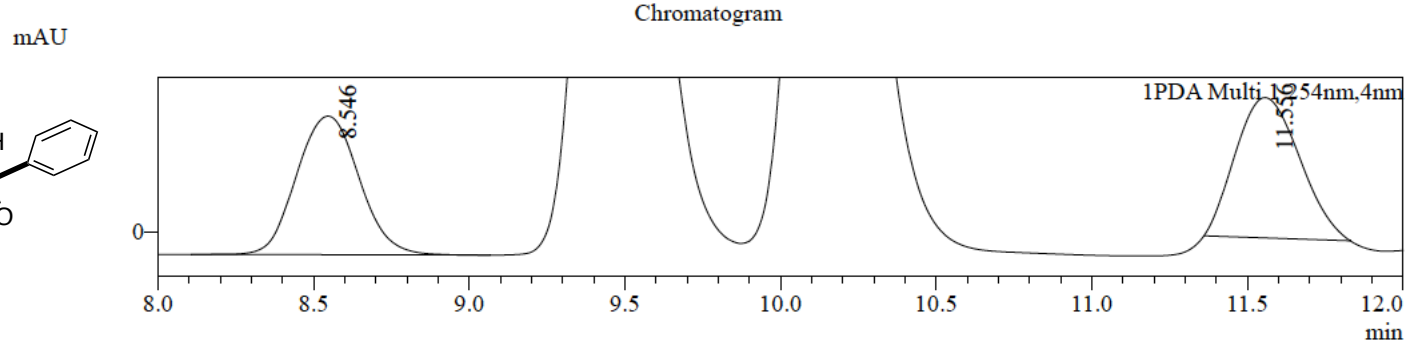


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)acrylate

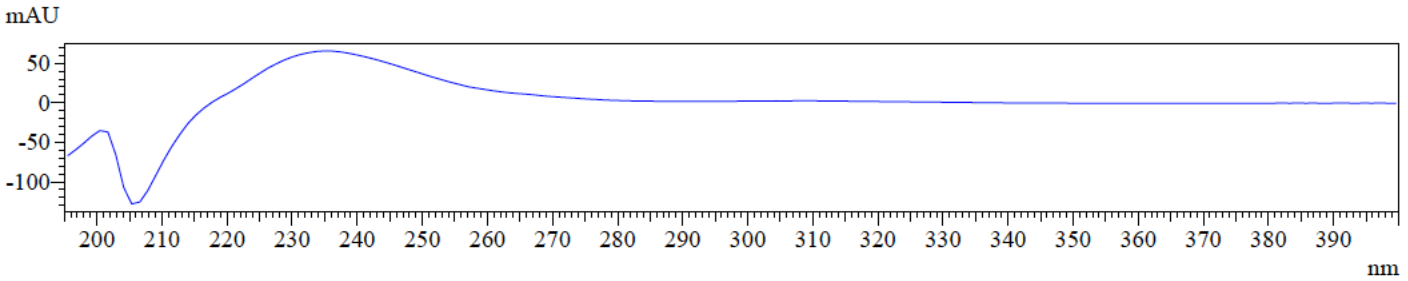




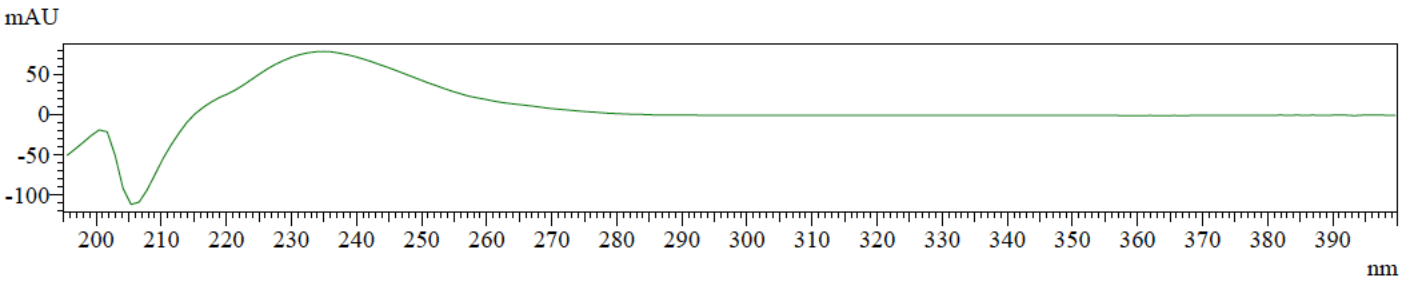
Chromatogram



UV Spectrum
Retention time = 8.546



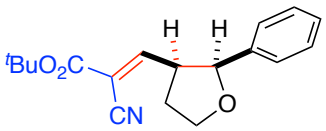
UV Spectrum
Retention time = 11.556



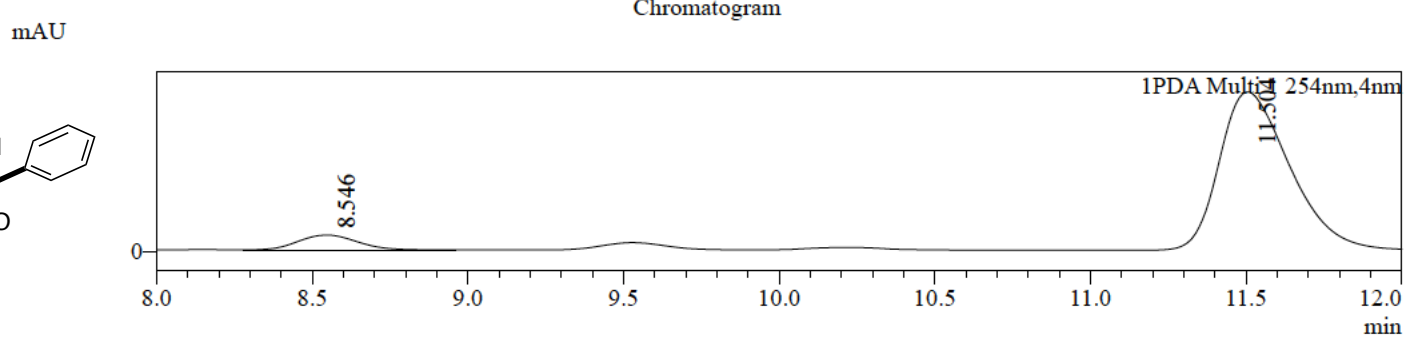
Peak Table

PDA Ch1 254nm

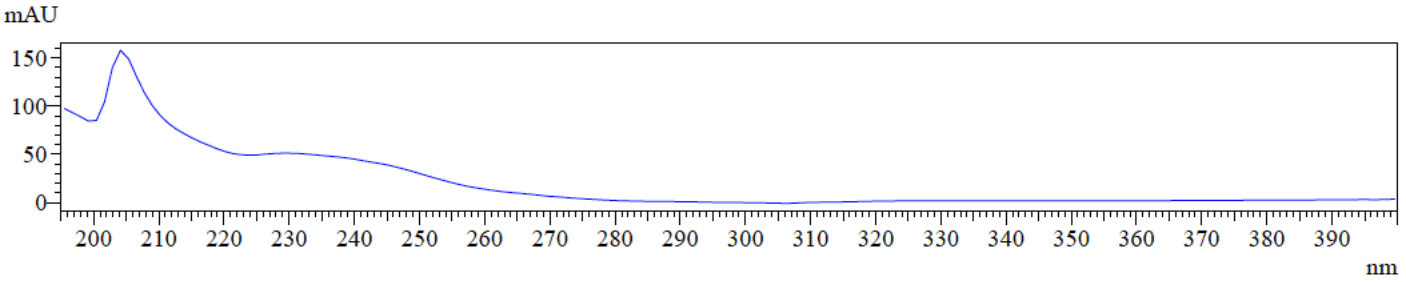
Peak#	Ret. Time	Area	Area%
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2	11.556	462320	50.861
Total		908980	100.000



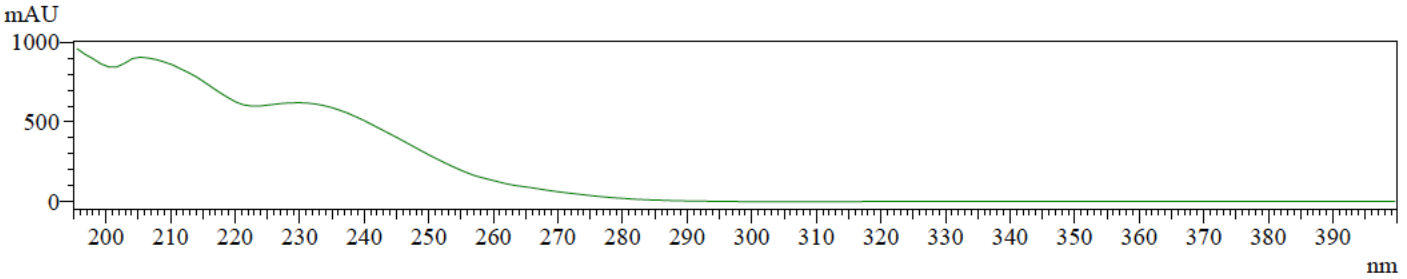
Chromatogram



UV Spectrum
Retention time = 8.546



UV Spectrum
Retention time = 11.504

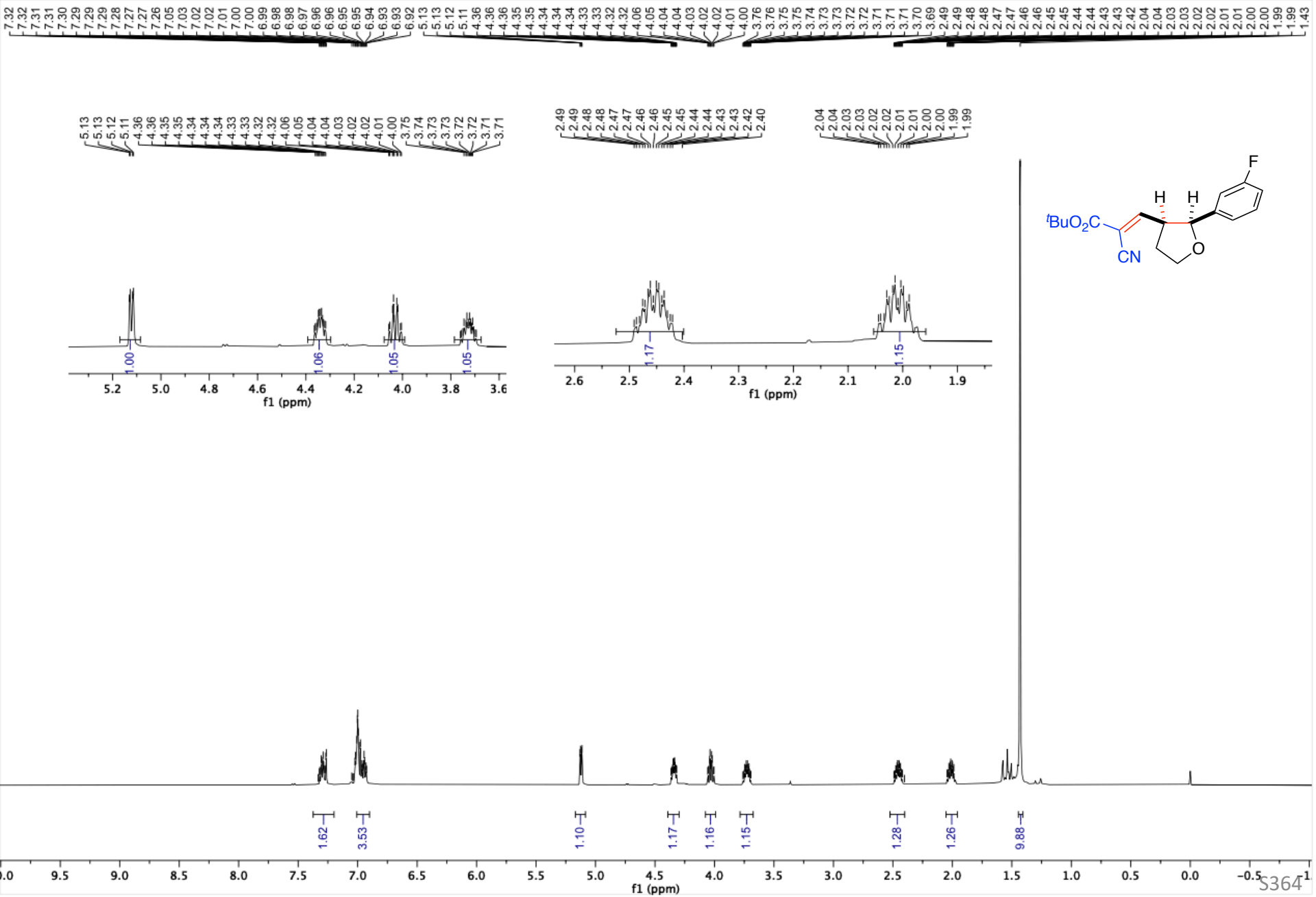


Peak Table

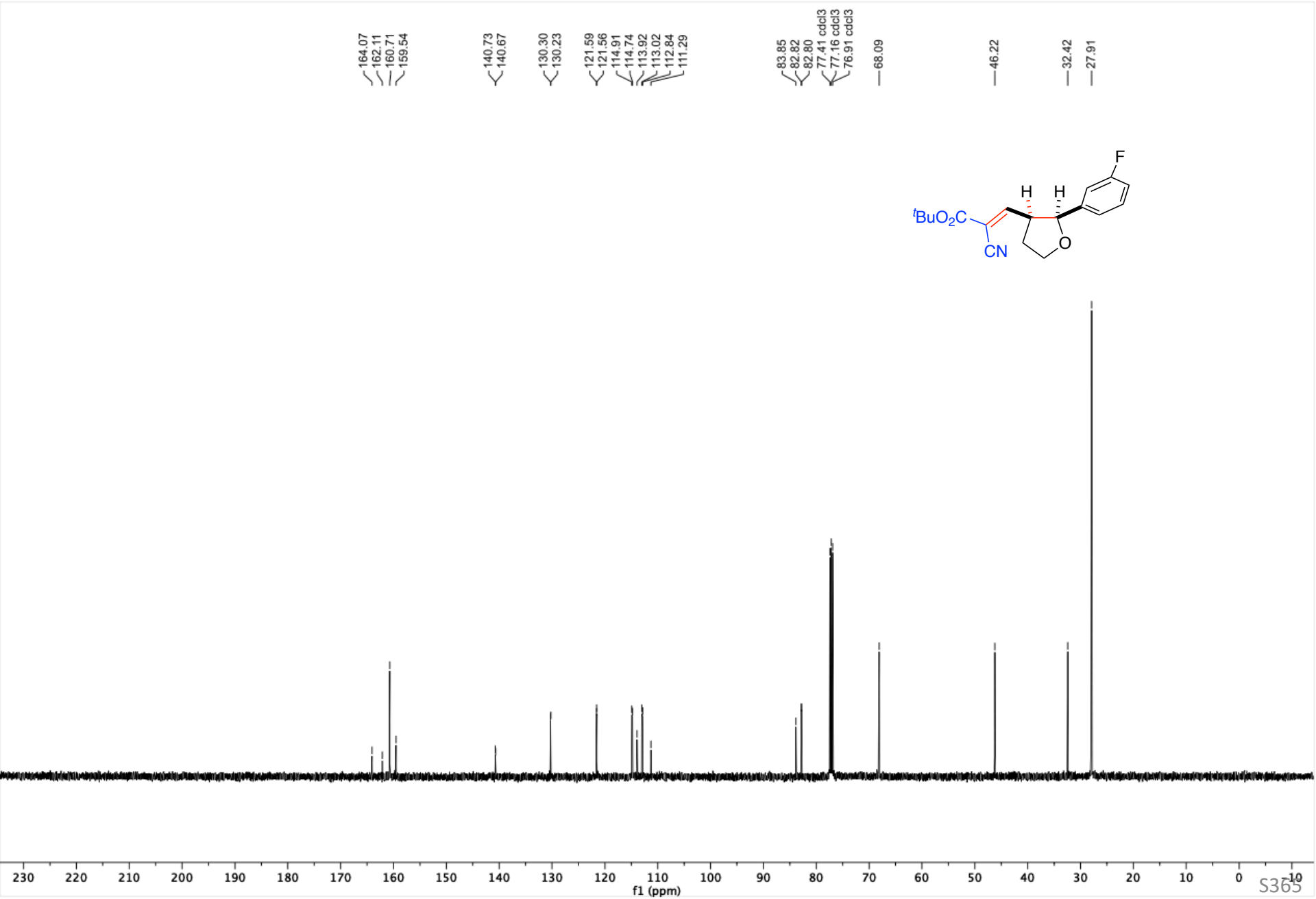
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.546	263921	7.244
2	11.504	3379286	92.756
Total		3643207	100.000

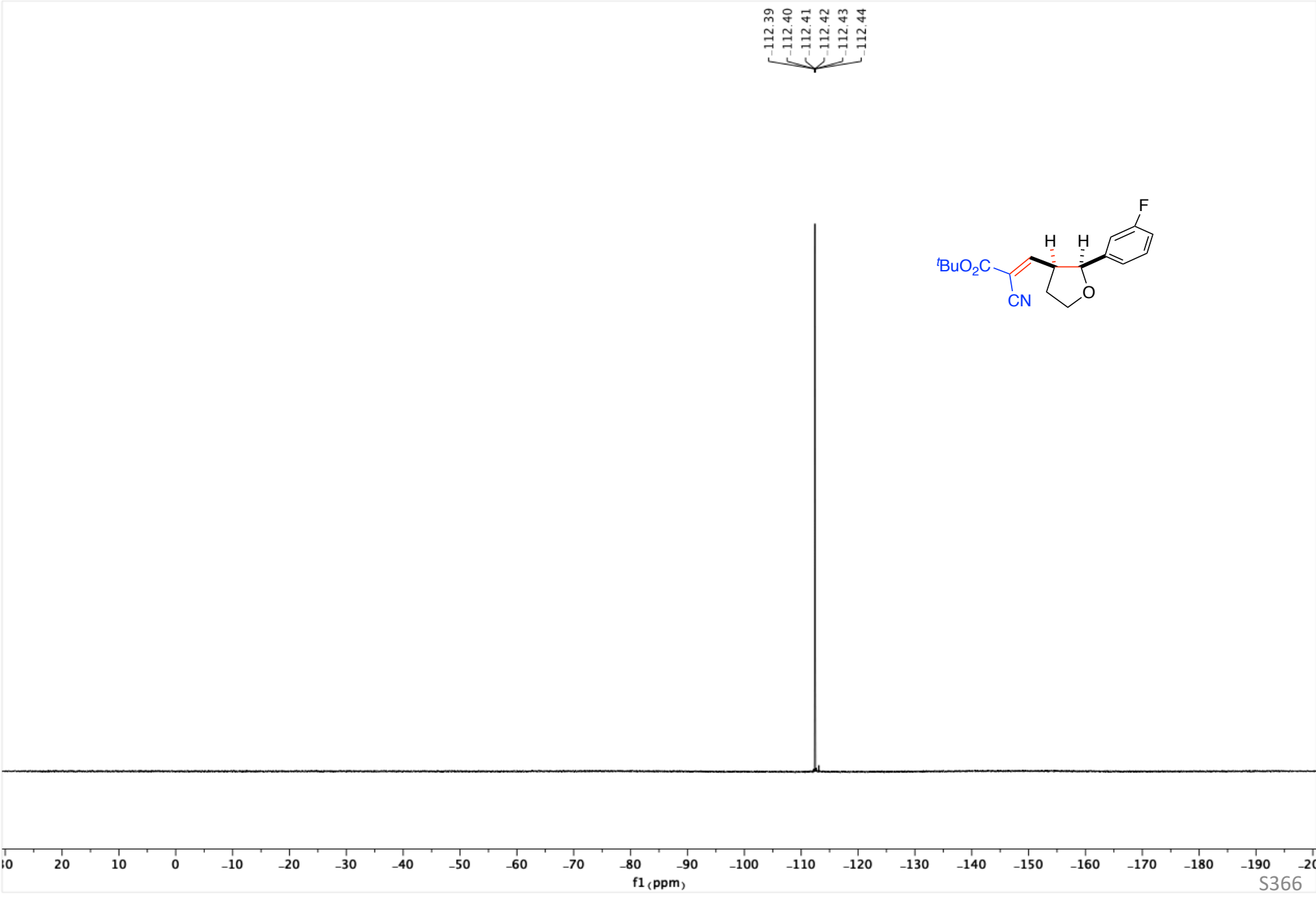
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-fluorophenyl)tetrahydrofuran-3-yl)acrylate

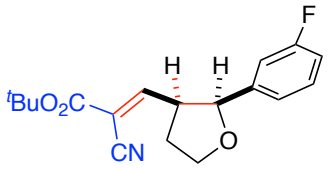


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-fluorophenyl)tetrahydrofuran-3-yl)acrylate

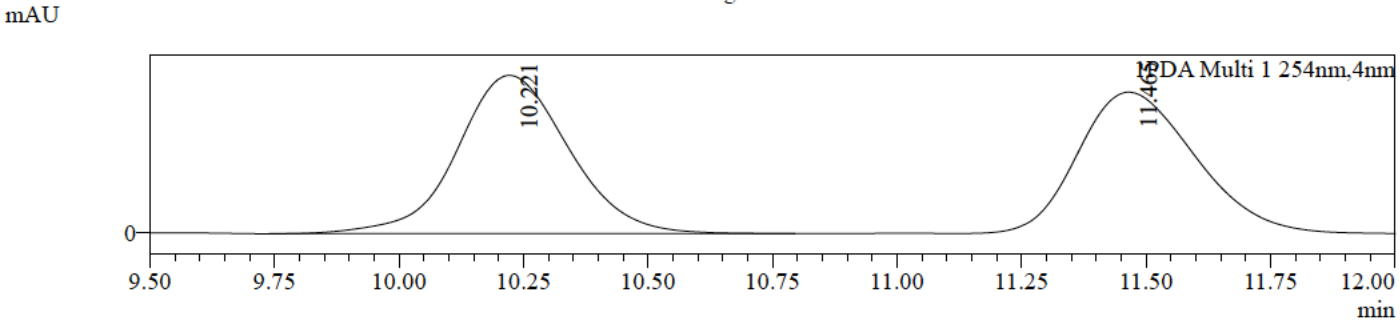


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-fluorophenyl)tetrahydrofuran-3-yl)acrylate

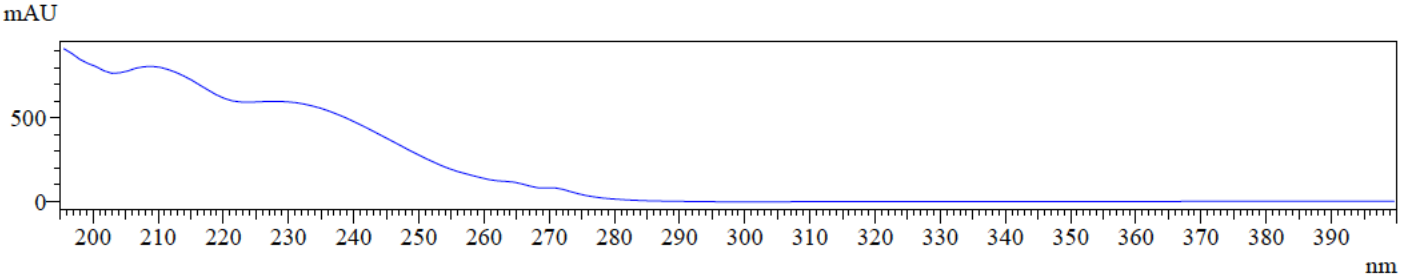




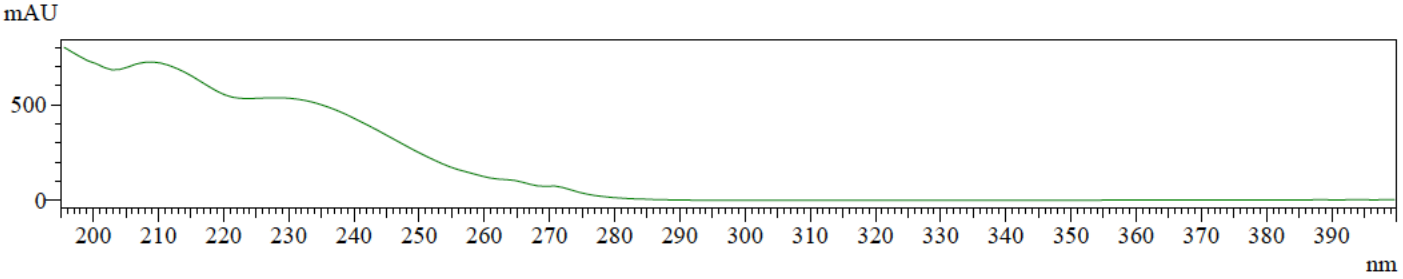
Chromatogram



UV Spectrum
Retention time = 10.221



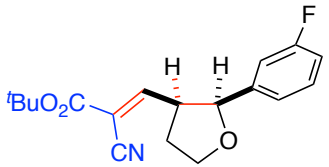
UV Spectrum
Retention time = 11.465



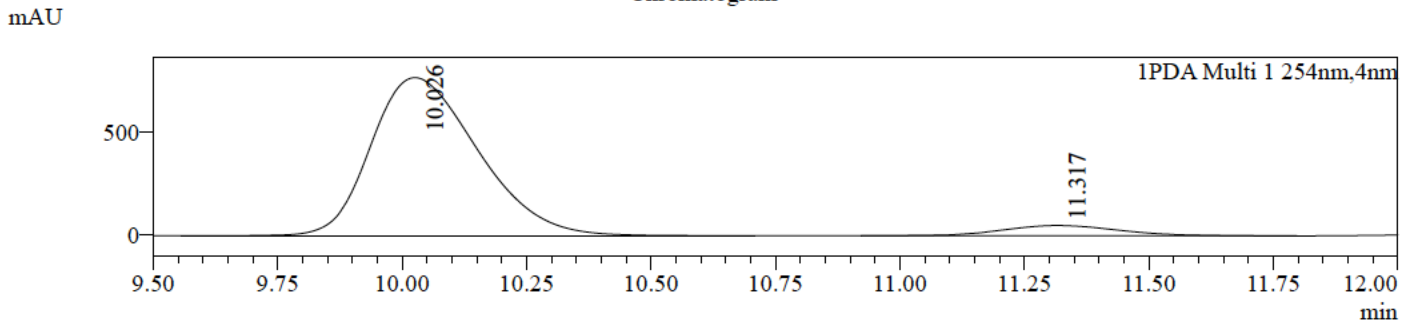
Peak Table

PDA Ch1 254nm

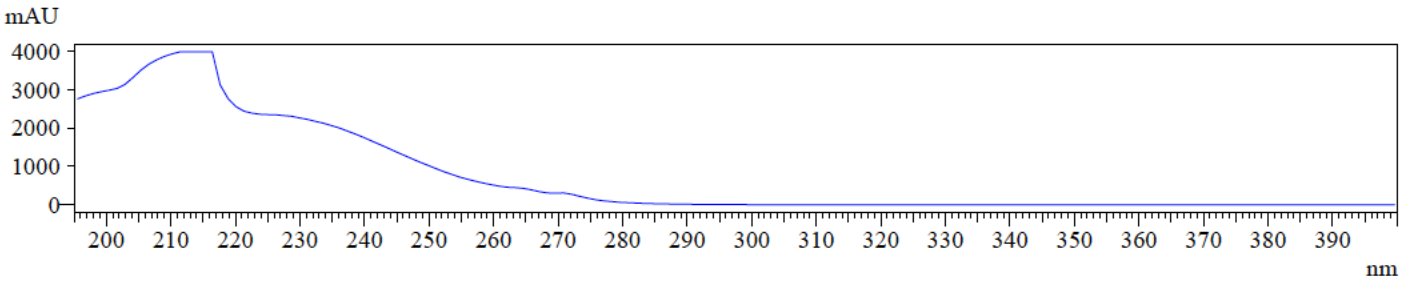
Peak#	Ret. Time	Area	Area%
1	10.221	3283241	51.703
2	11.465	3066944	48.297
Total		6350185	100.000



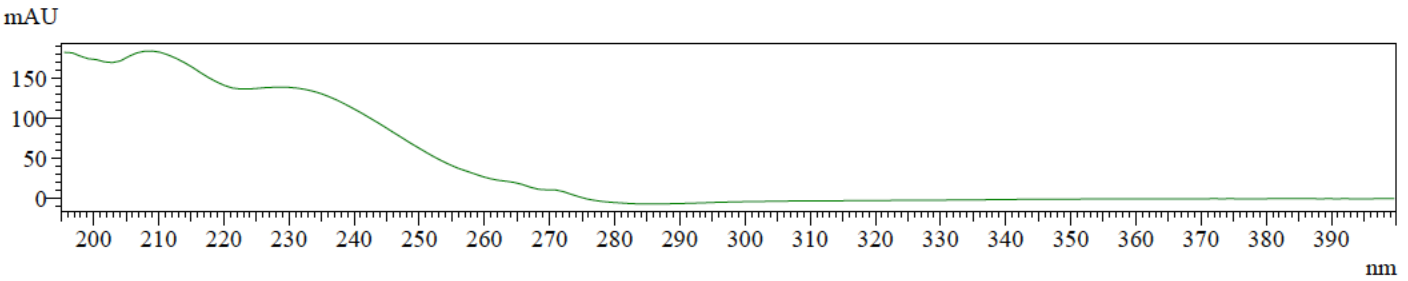
Chromatogram



UV Spectrum
Retention time = 10.026



UV Spectrum
Retention time = 11.317

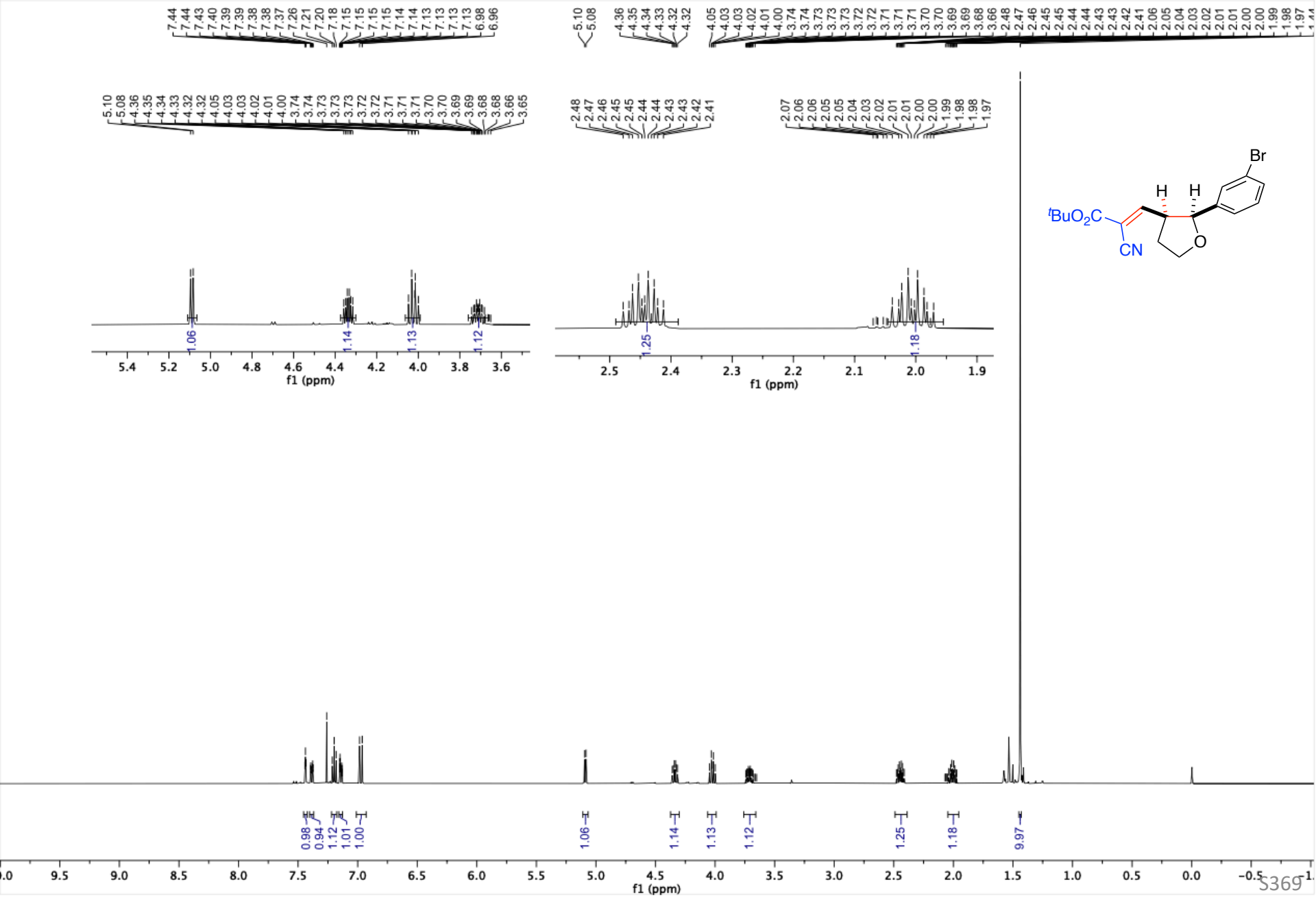


Peak Table

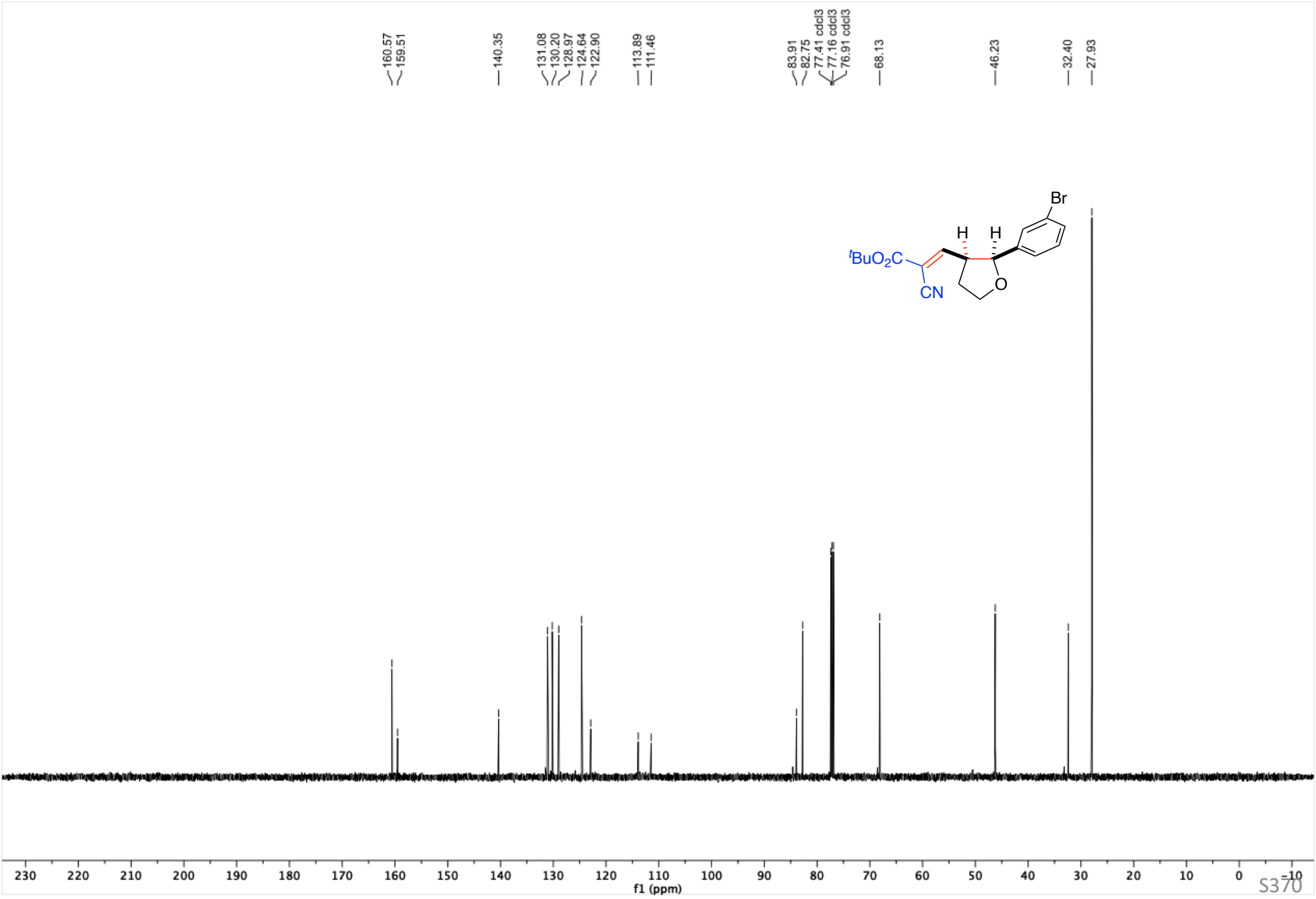
PDA Ch1 254nm

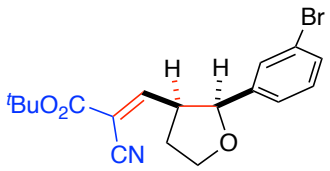
Peak#	Ret. Time	Area	Area%
1	10.026	11568244	93.489
2	11.317	805635	6.511
Total		12373880	100.000

tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(3-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

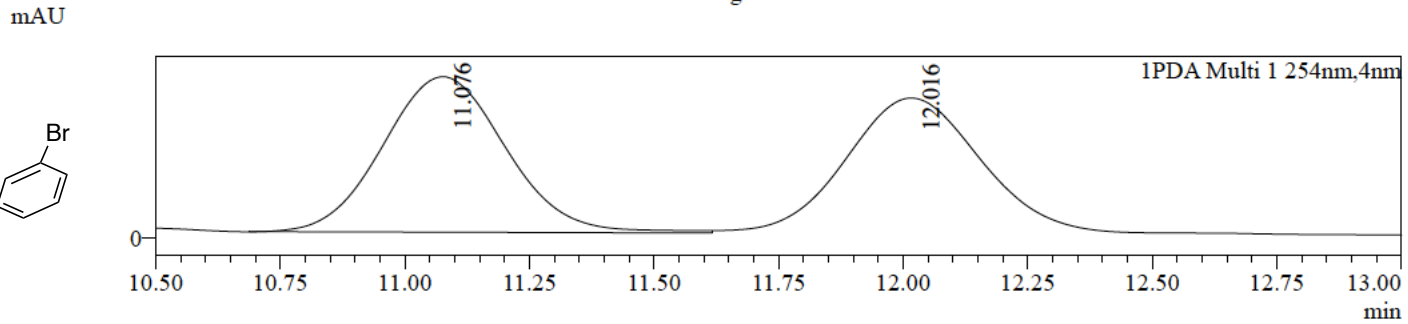


tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(3-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

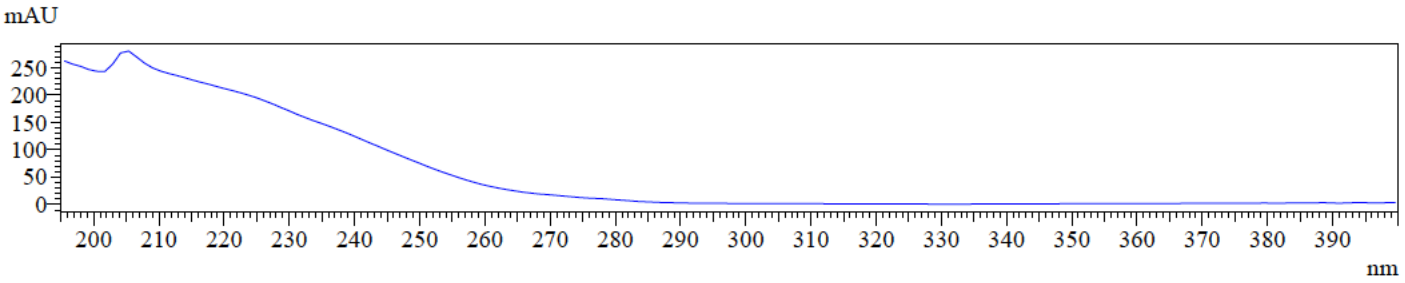




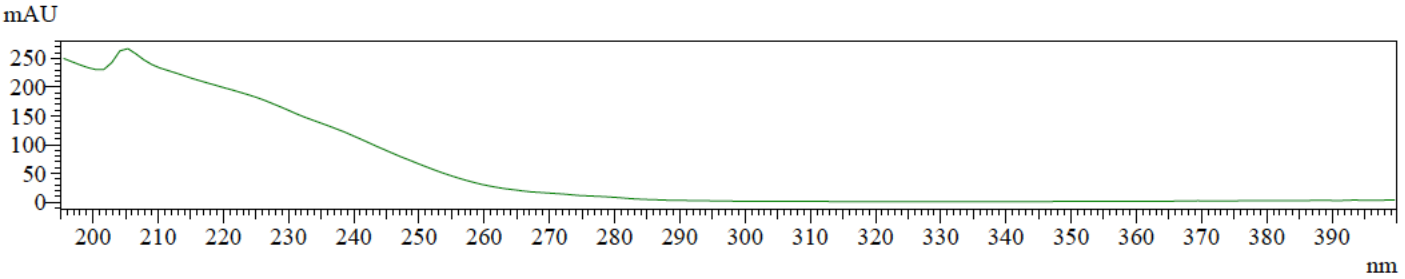
Chromatogram



UV Spectrum
Retention time = 11.076



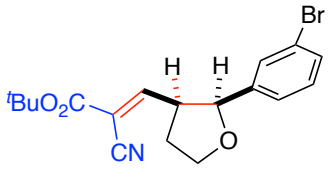
UV Spectrum
Retention time = 12.016



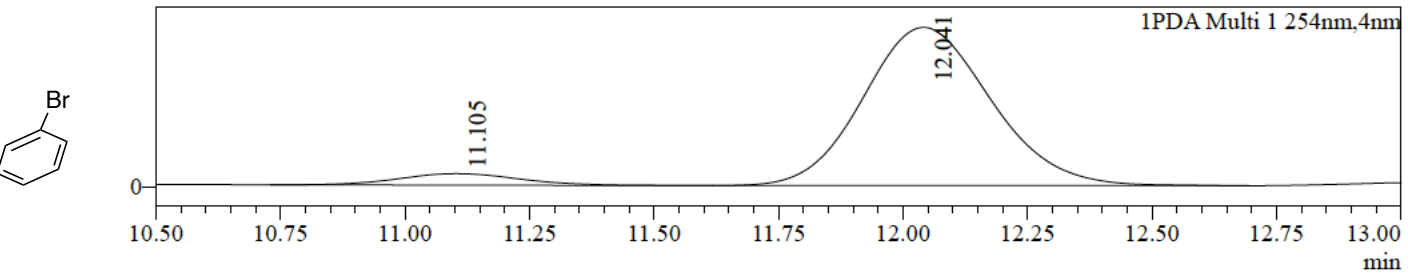
Peak Table

PDA Ch1 254nm

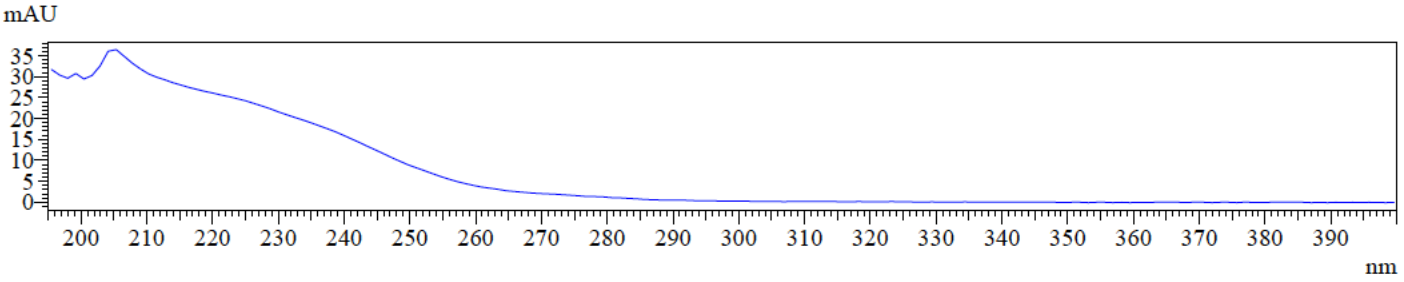
Peak#	Ret. Time	Area	Area%
1	11.076	947649	50.832
2	12.016	916617	49.168
Total		1864266	100.000



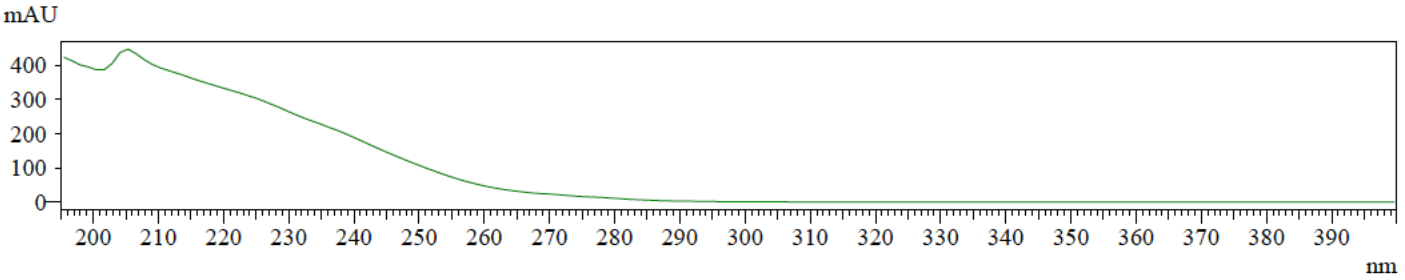
Chromatogram



UV Spectrum
Retention time = 11.105



UV Spectrum
Retention time = 12.041

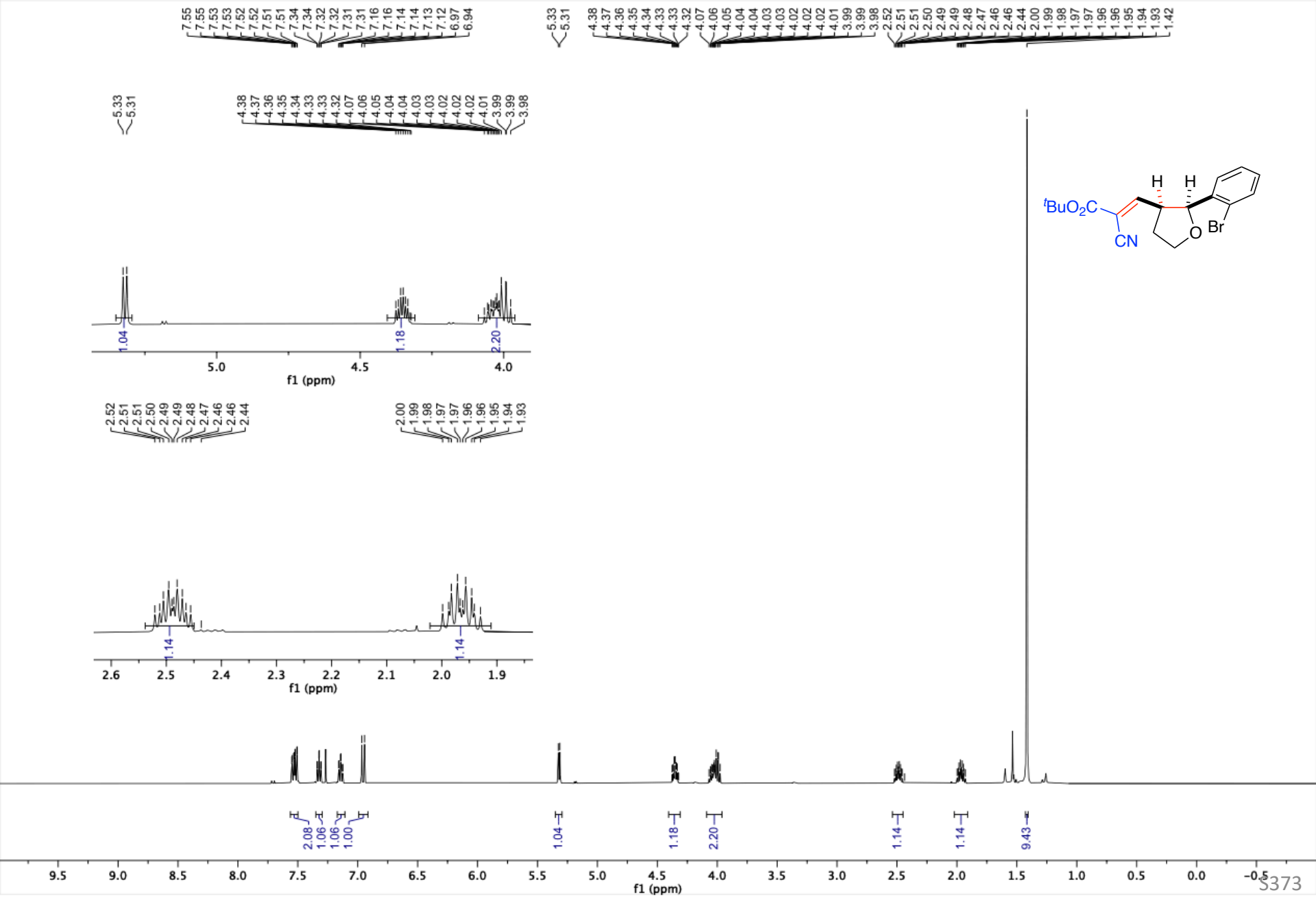


Peak Table

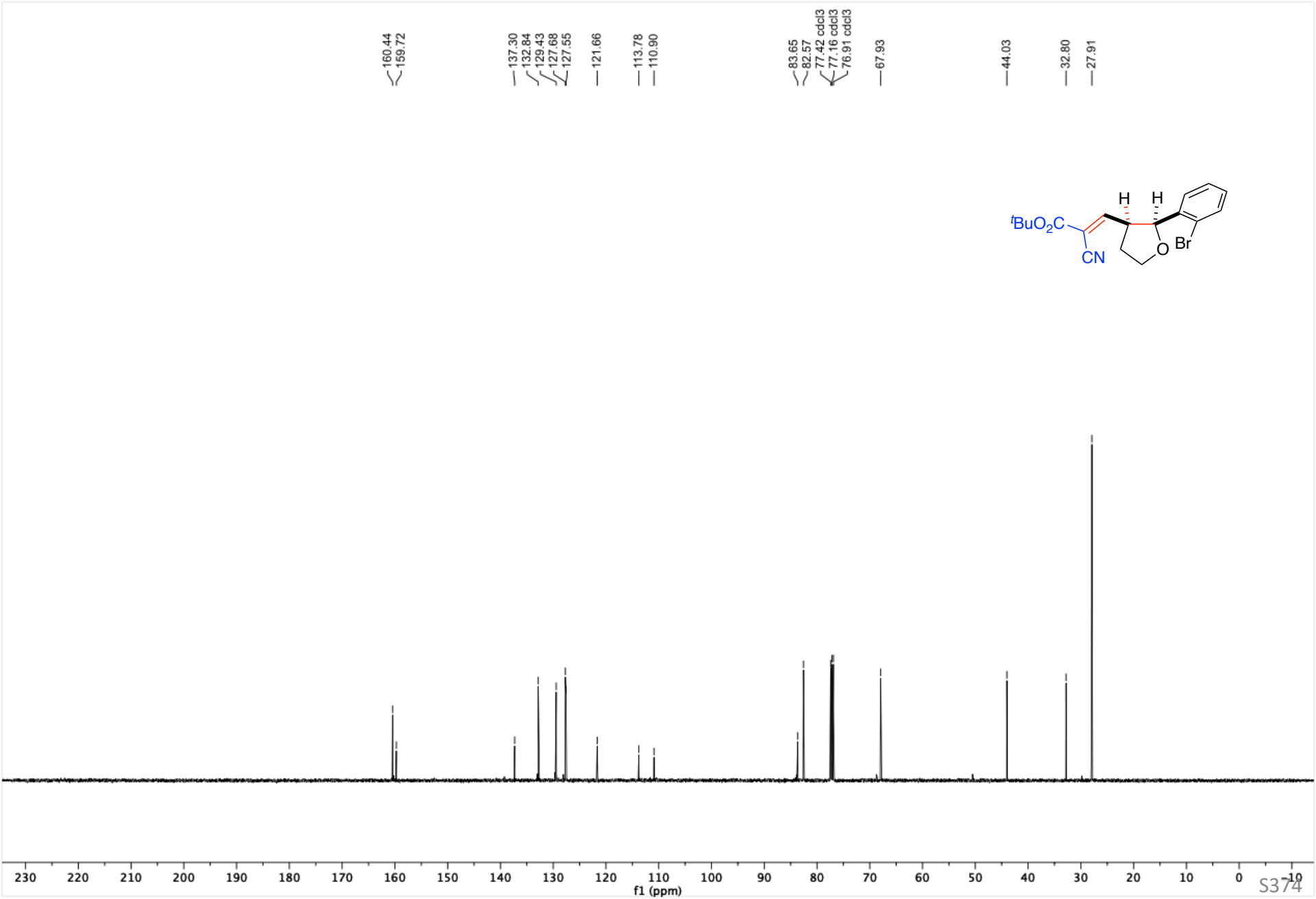
PDA Ch1 254nm

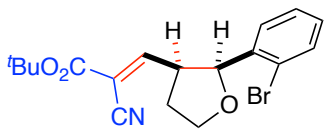
Peak#	Ret. Time	Area	Area%
1	11.105	96537	6.403
2	12.041	1411044	93.597
Total		1507581	100.000

tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(2-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

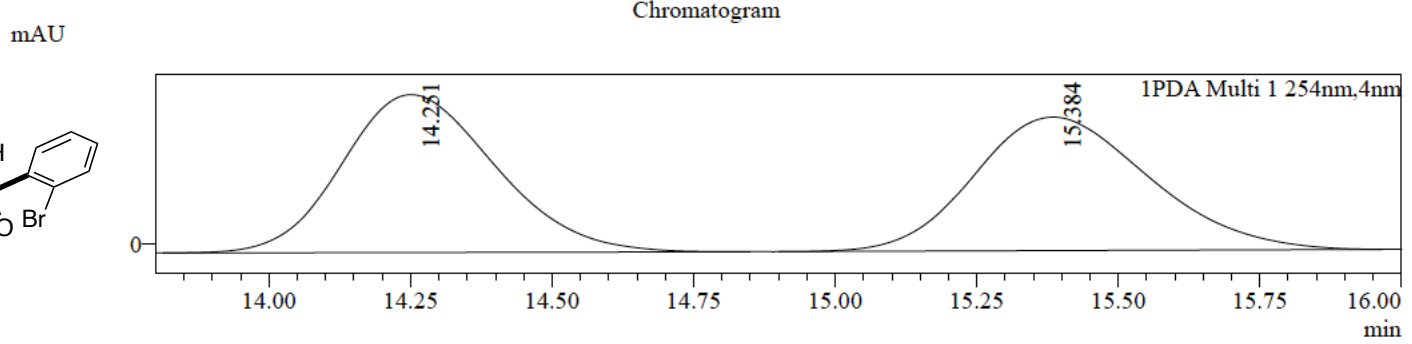


tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(2-bromophenyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

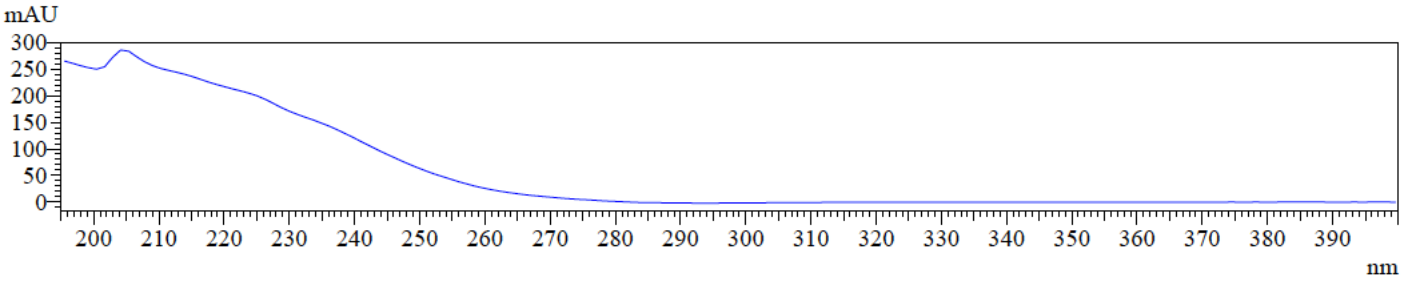




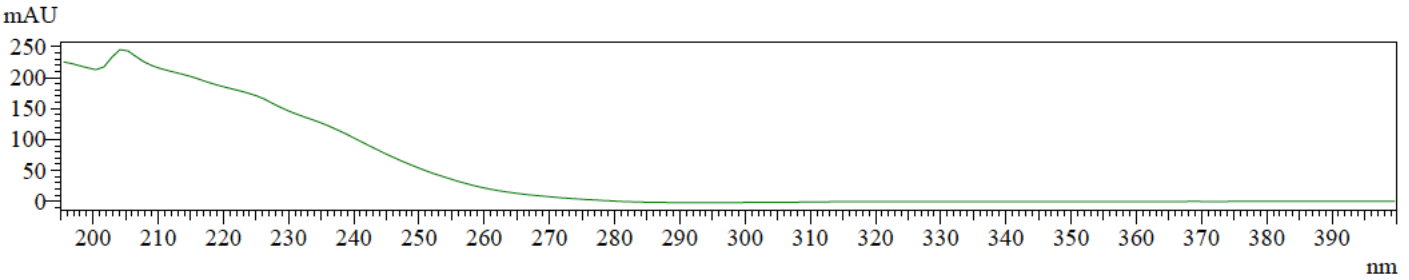
Chromatogram



UV Spectrum
Retention time = 14.251



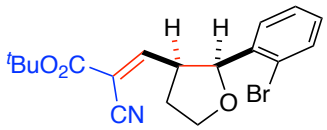
UV Spectrum
Retention time = 15.384



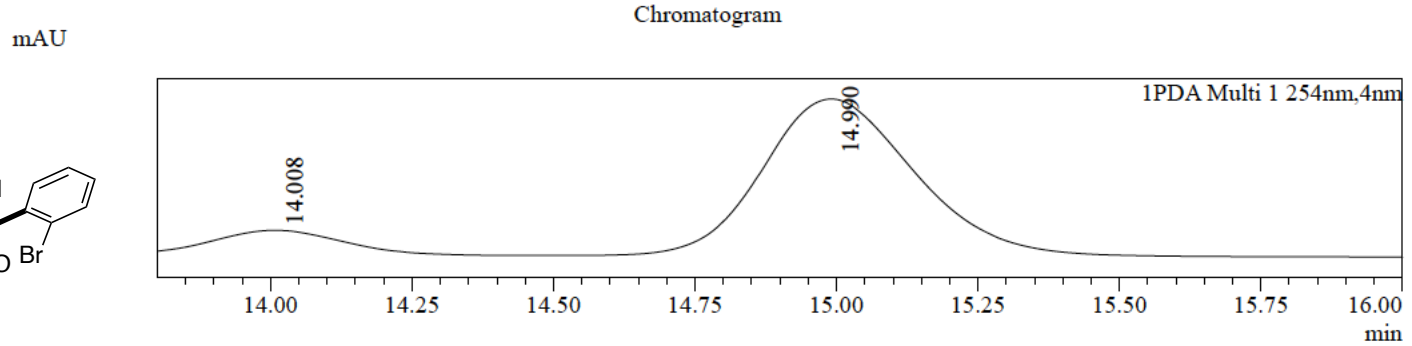
Peak Table

PDA Ch1 254nm

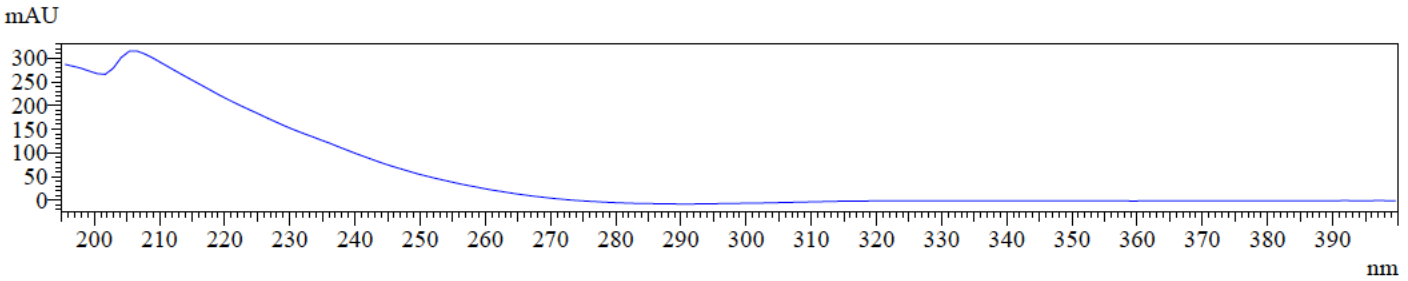
Peak#	Ret. Time	Area	Area%
1	14.251	915853	50.836
2	15.384	885723	49.164
Total		1801577	100.000



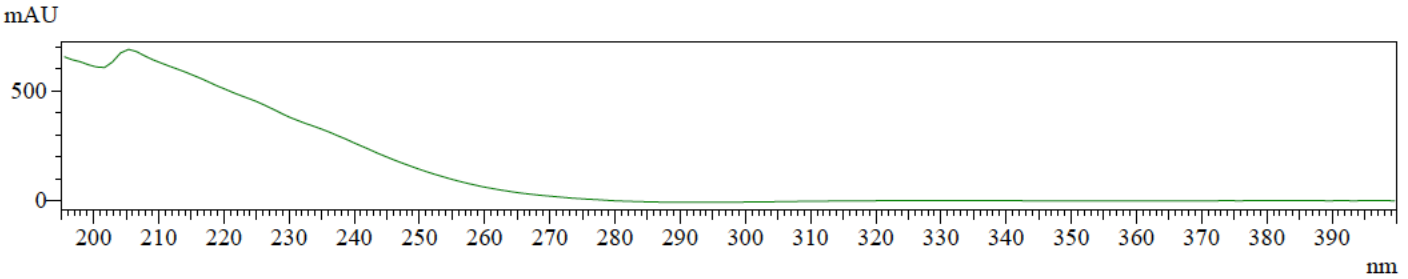
Chromatogram



UV Spectrum
Retention time = 14.008



UV Spectrum
Retention time = 14.990

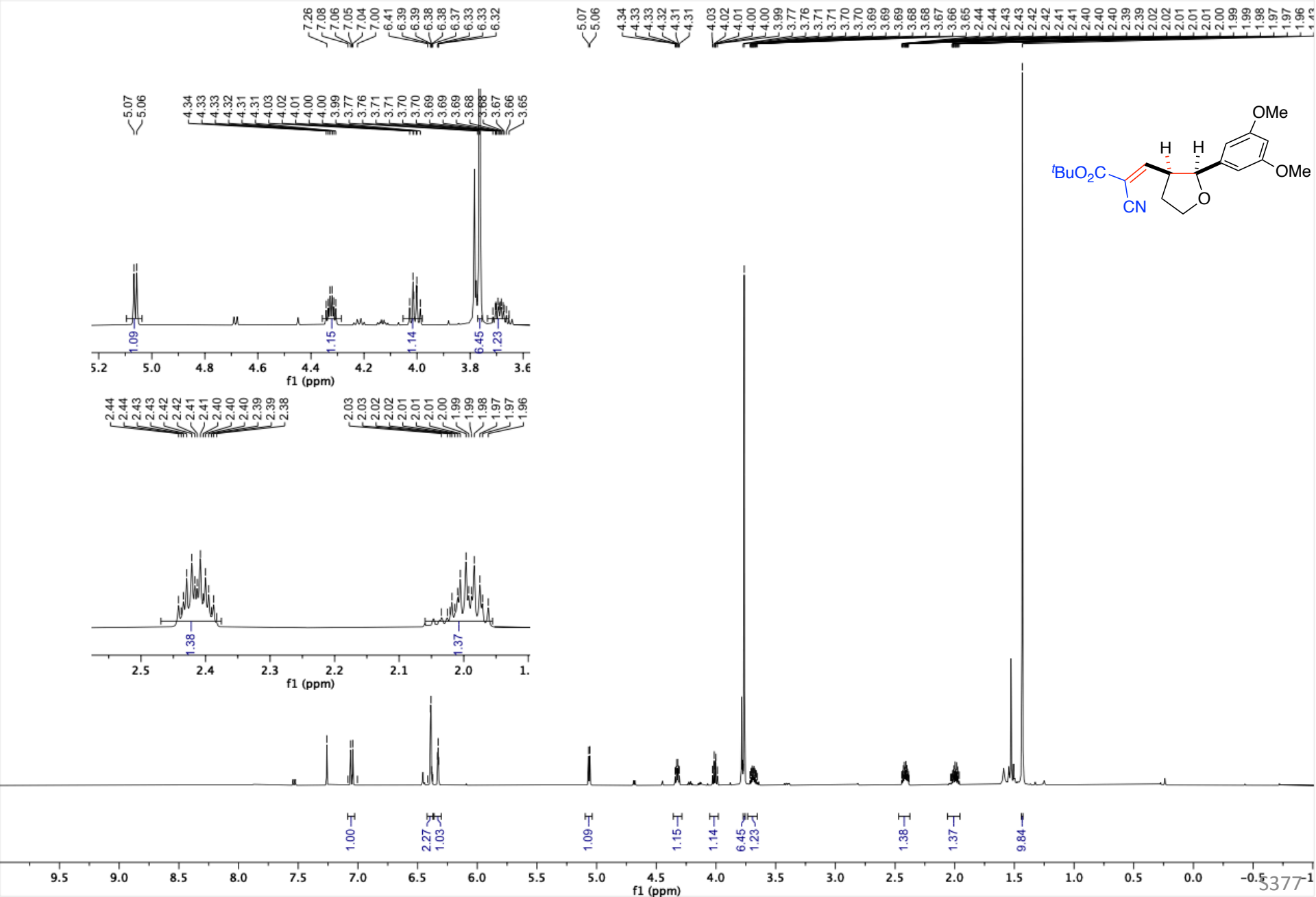


Peak Table

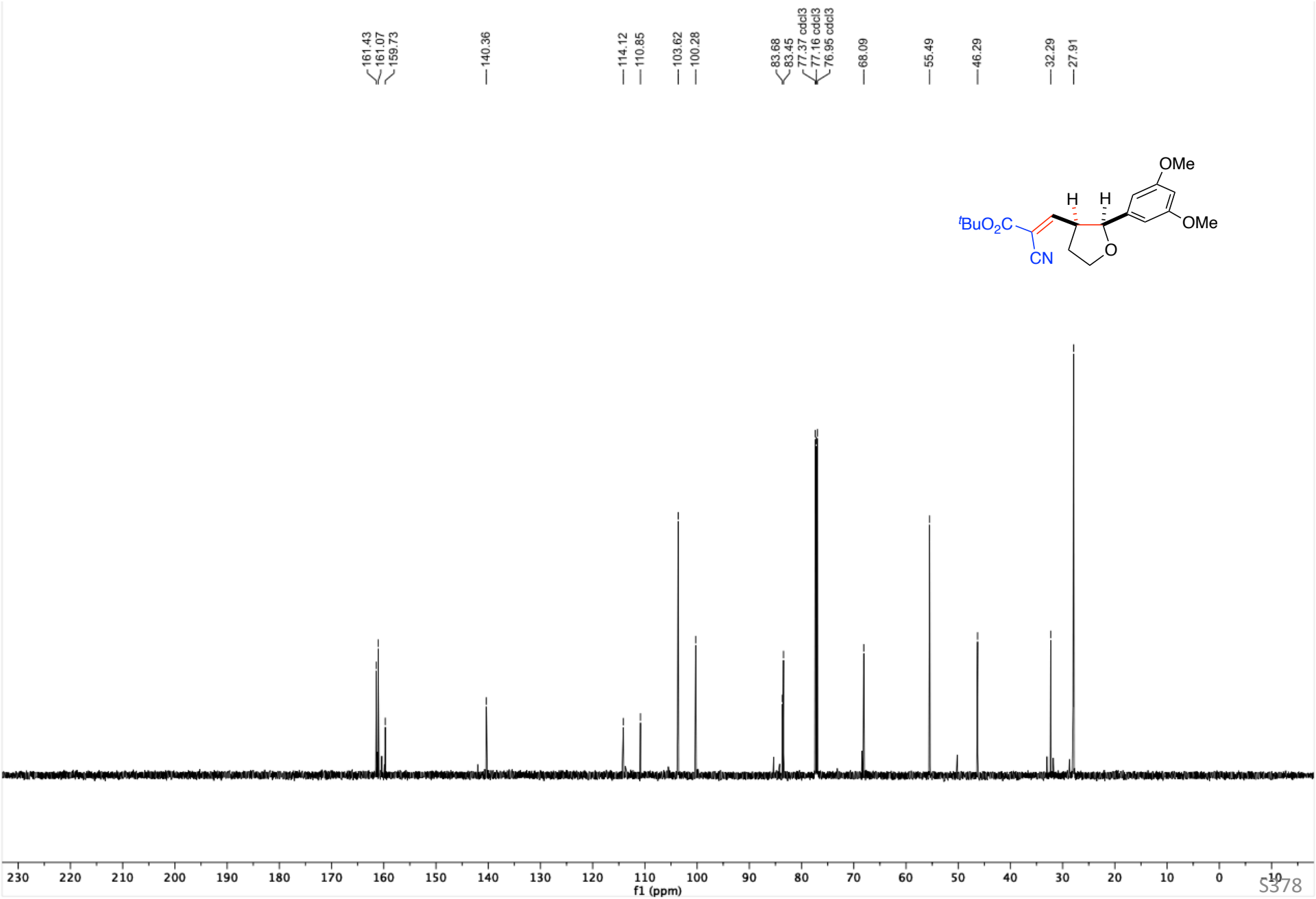
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.008	189671	11.628
2	14.990	1441559	88.372
Total		1631230	100.000

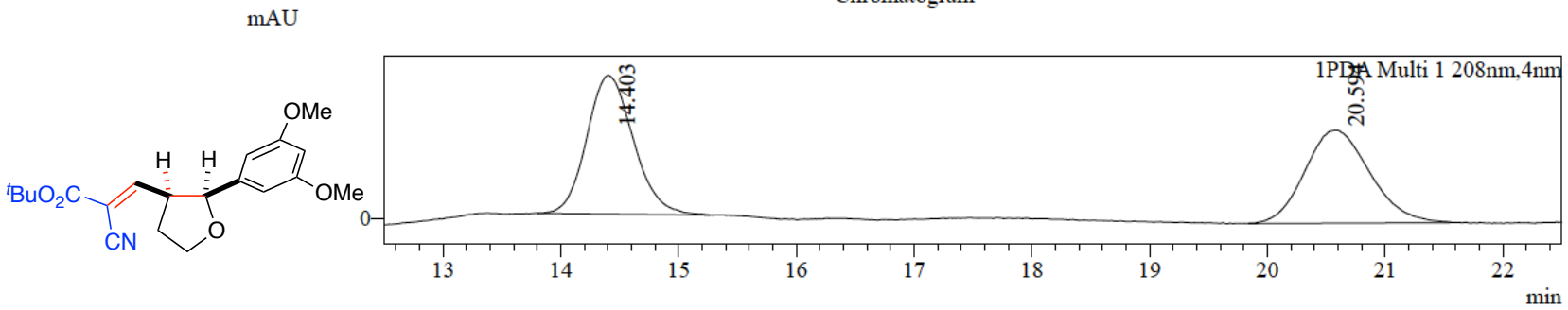
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3,5-dimethoxyphenyl)tetrahydrofuran-3-yl)acrylate



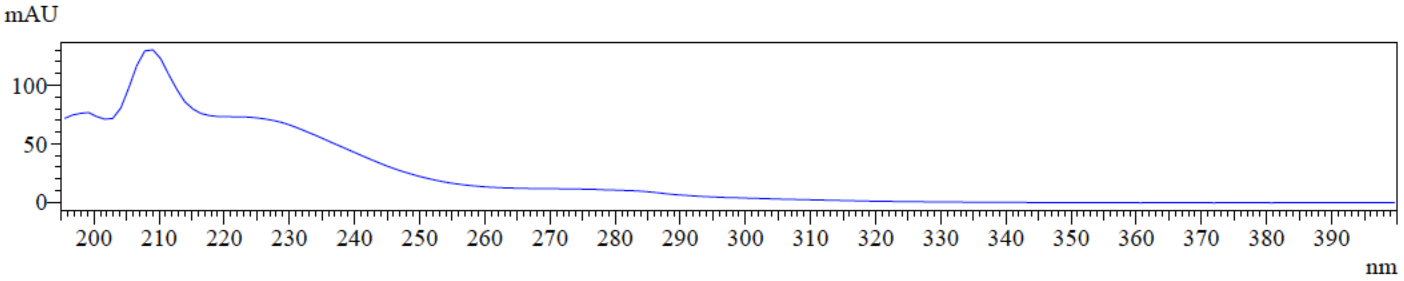
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3,5-dimethoxyphenyl)tetrahydrofuran-3-yl)acrylate



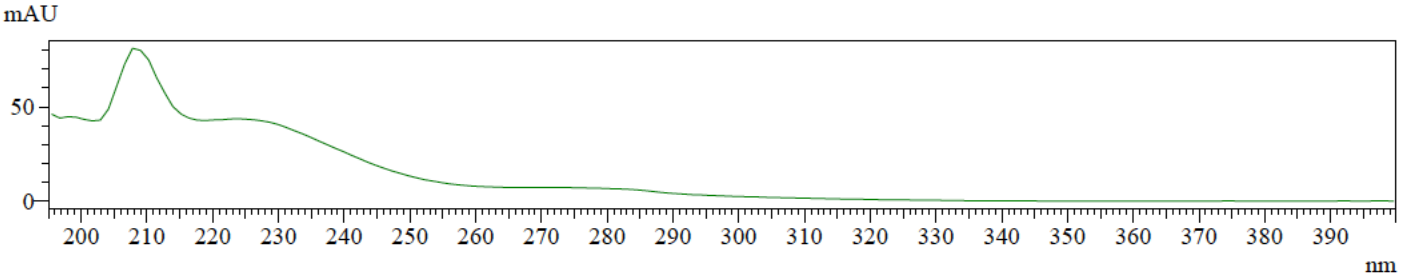
Chromatogram



UV Spectrum
Retention time = 14.403



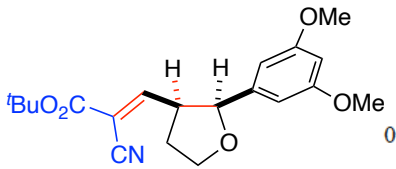
UV Spectrum
Retention time = 20.594



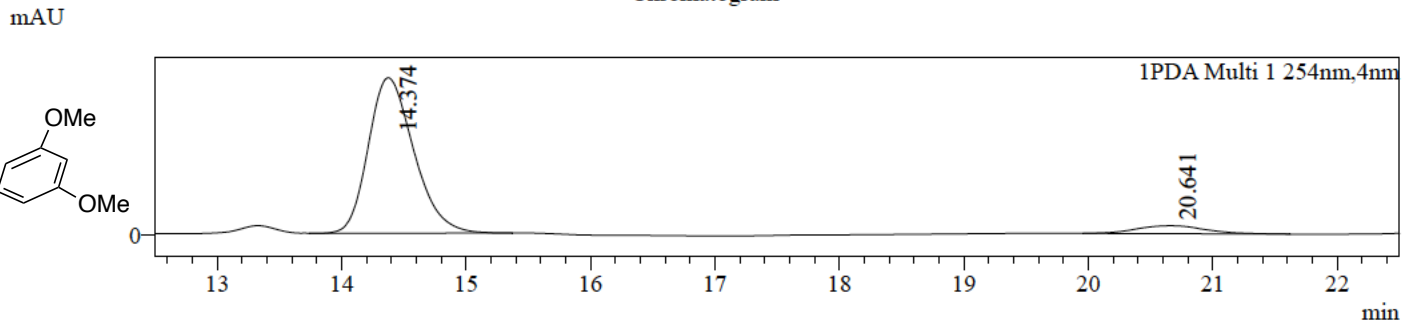
Peak Table

PDA Ch1 208nm

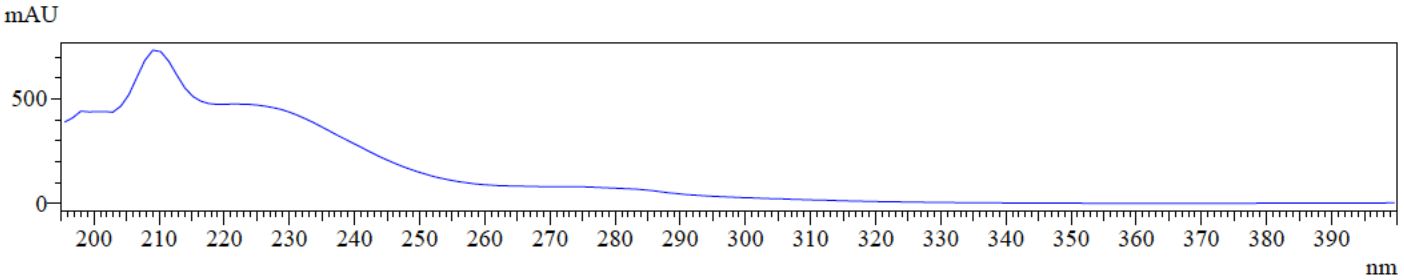
Peak#	Ret. Time	Area	Area%
1	14.403	3004297	51.667
2	20.594	2810409	48.333
Total		5814706	100.000



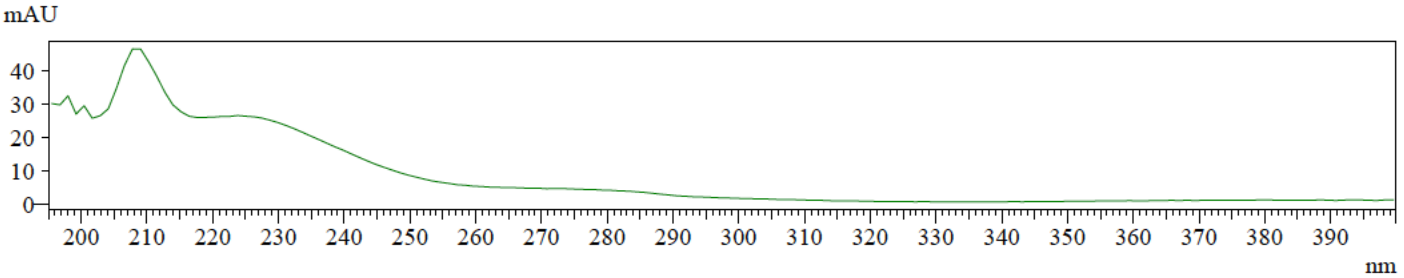
Chromatogram



UV Spectrum
Retention time = 14.374



UV Spectrum
Retention time = 20.641

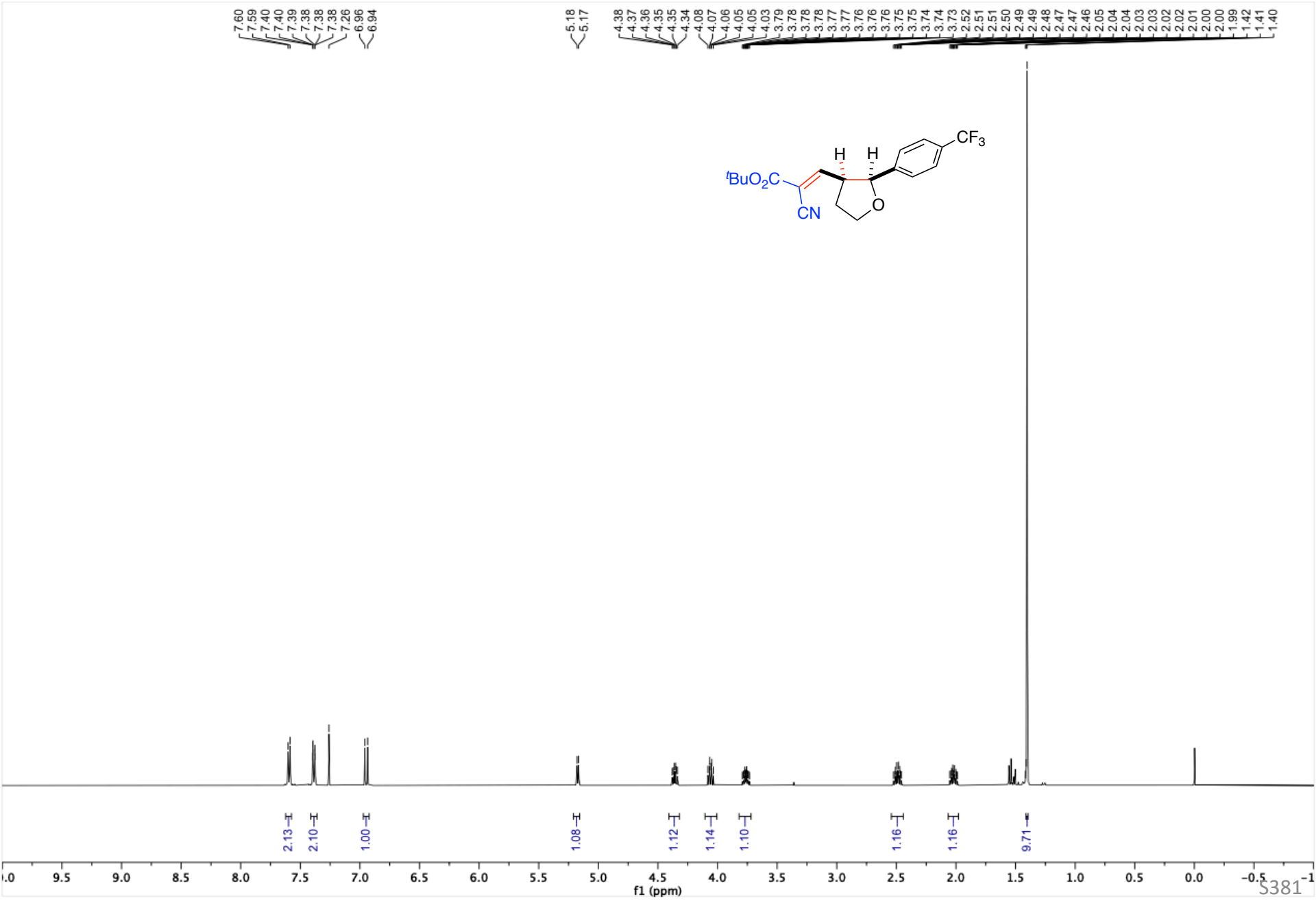


Peak Table

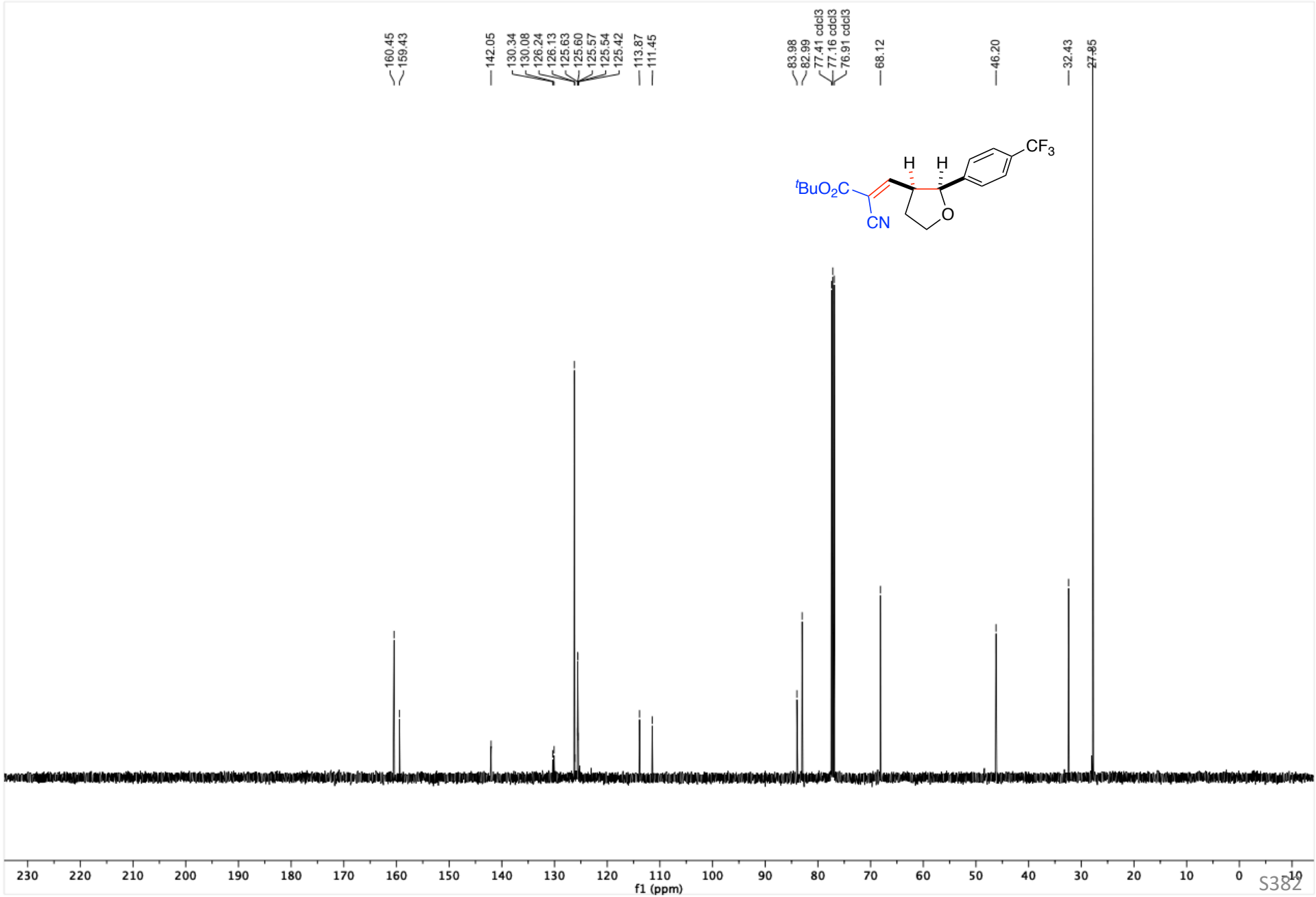
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.374	2949744	92.925
2	20.641	224577	7.075
Total		3174321	100.000

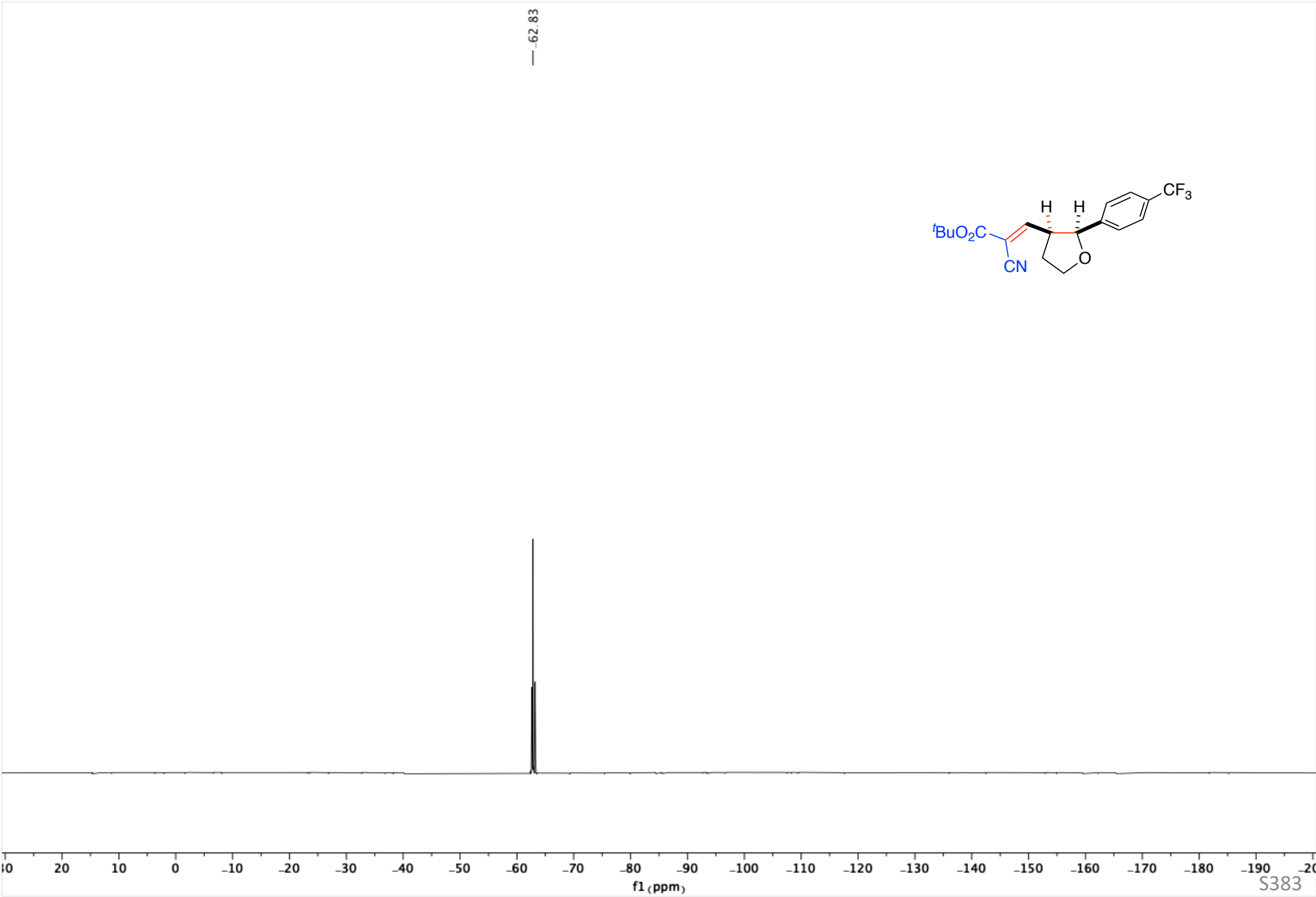
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

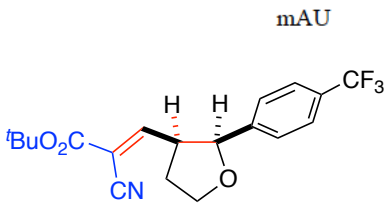


tert-Butyl (_E_)-2-cyano-3-((2_S_,3_S_)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

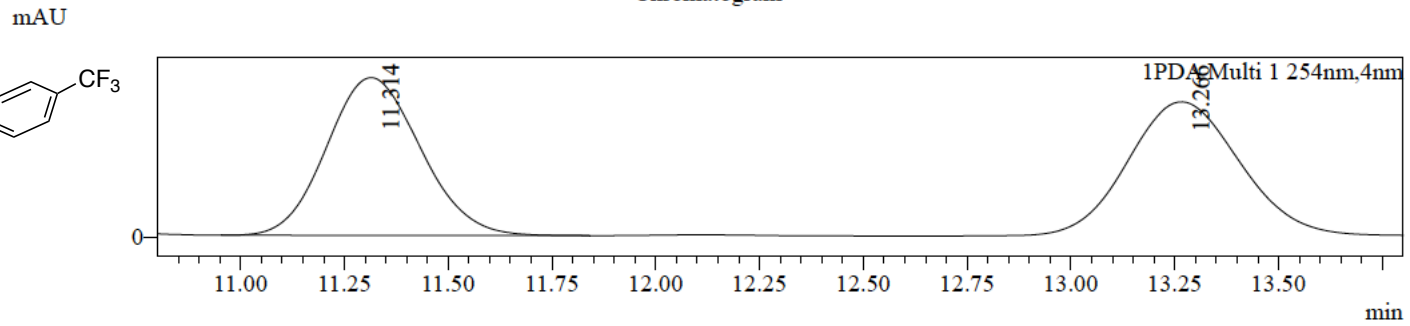


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

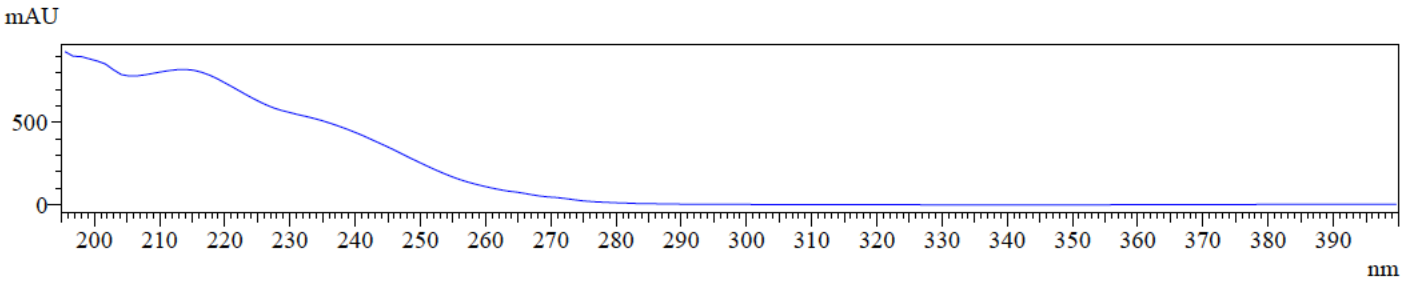




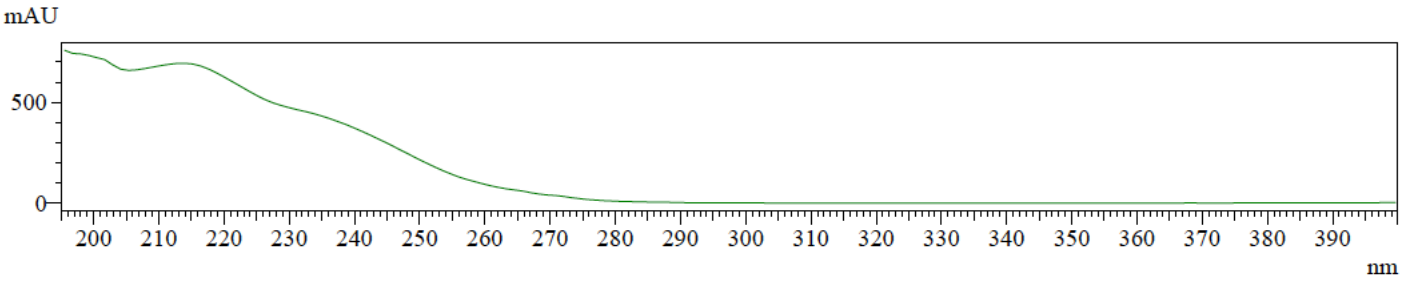
Chromatogram



UV Spectrum
Retention time = 11.314



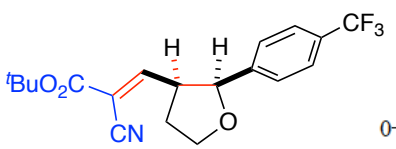
UV Spectrum
Retention time = 13.266



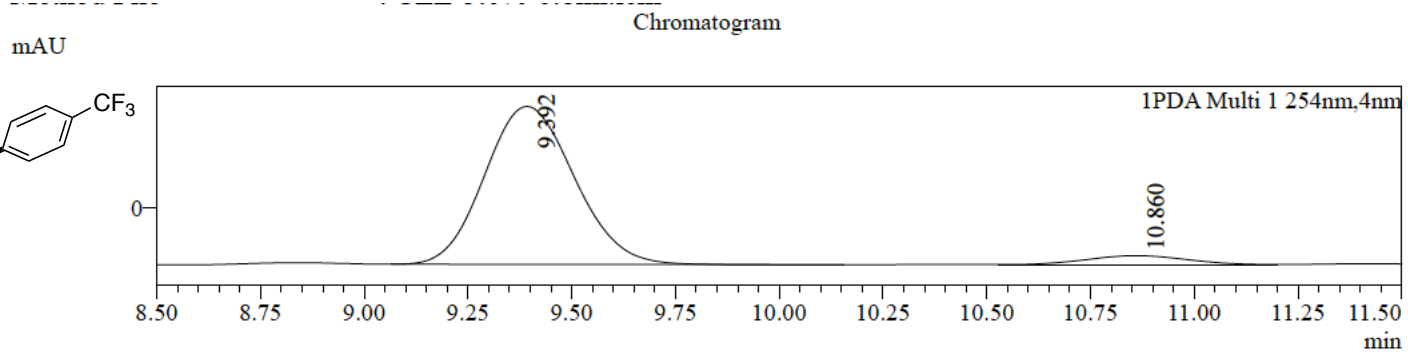
Peak Table

PDA Ch1 254nm

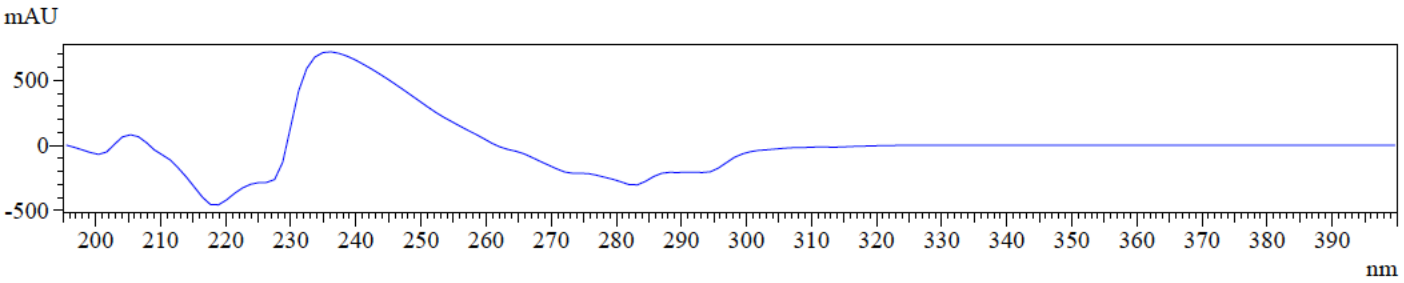
Peak#	Ret. Time	Area	Area%
1	11.314	2865138	49.804
2	13.266	2887677	50.196
Total		5752815	100.000



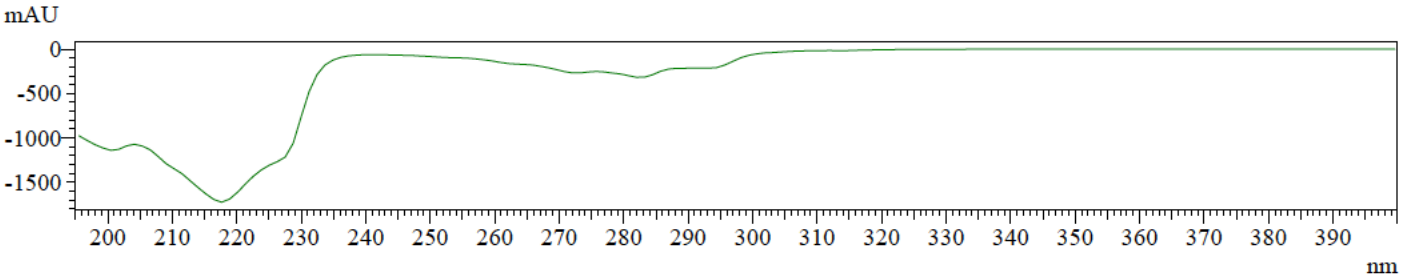
Chromatogram



UV Spectrum
Retention time = 9.392



UV Spectrum
Retention time = 10.860

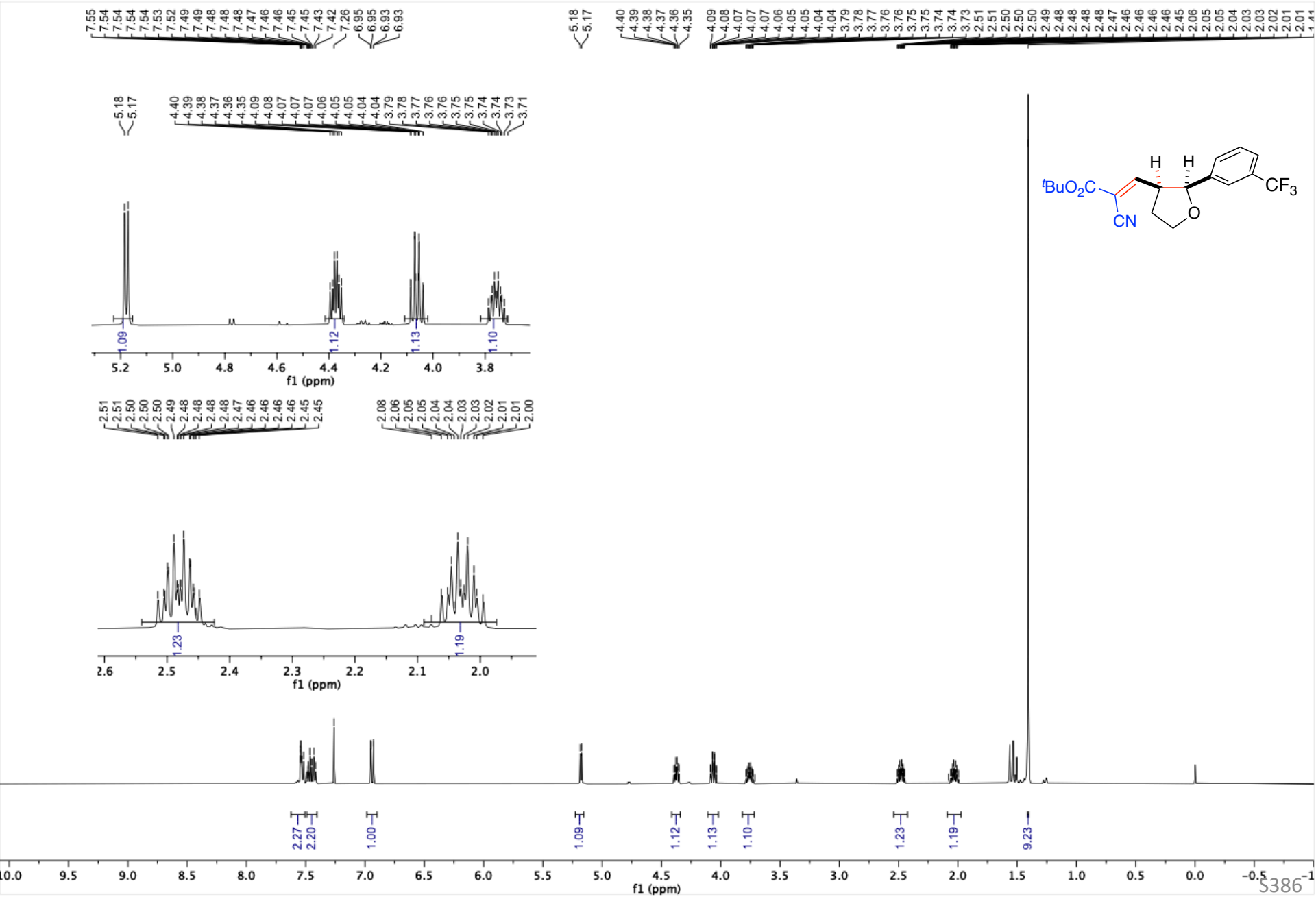


Peak Table

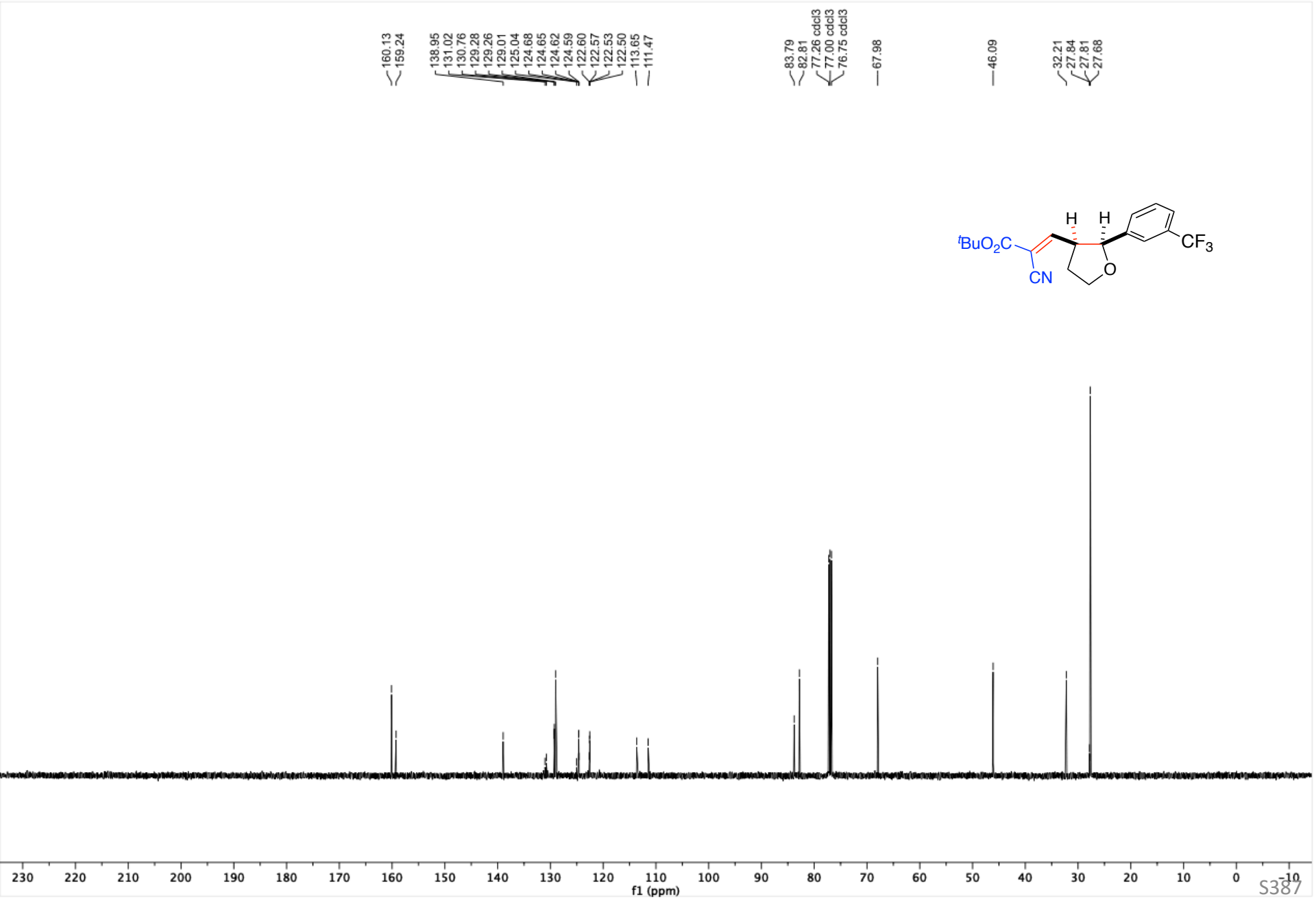
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.392	4777798	94.245
2	10.860	291748	5.755
Total		5069546	100.000

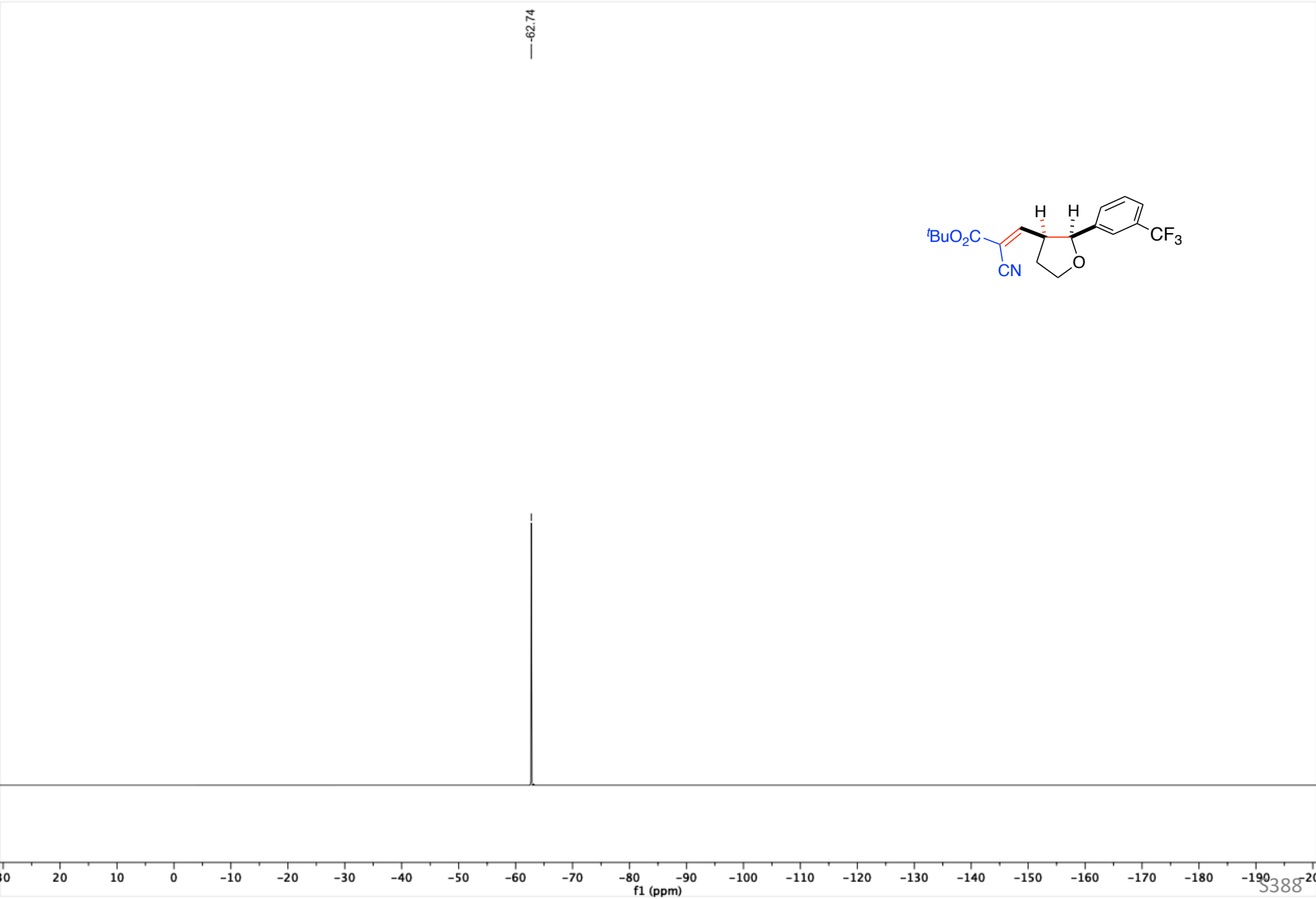
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

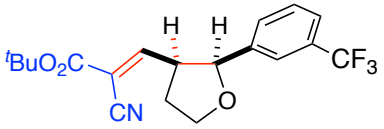


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

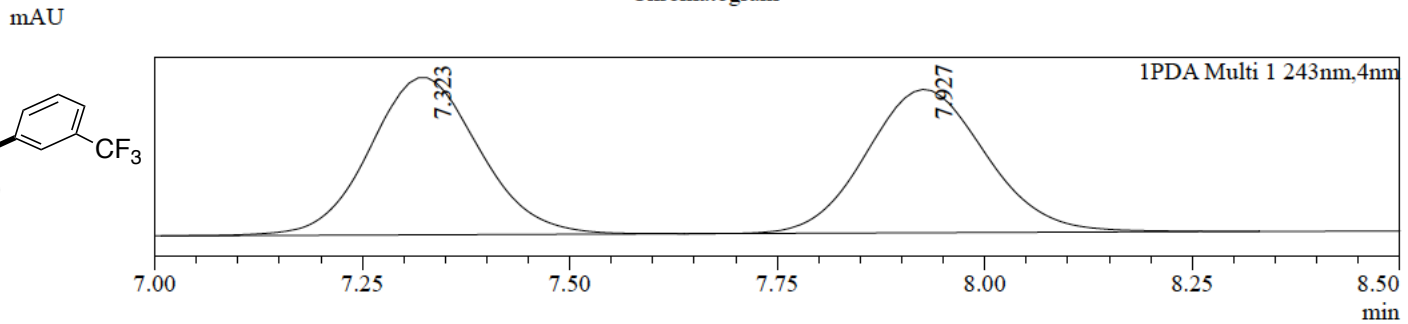


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-3-yl)acrylate

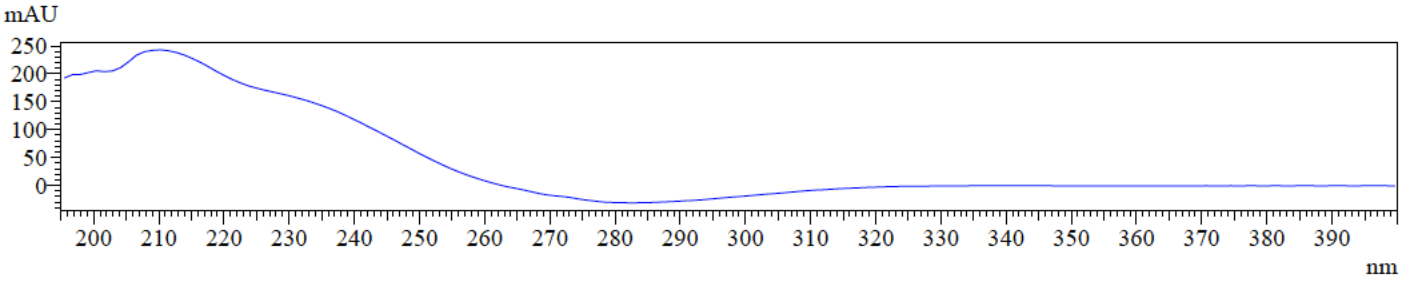




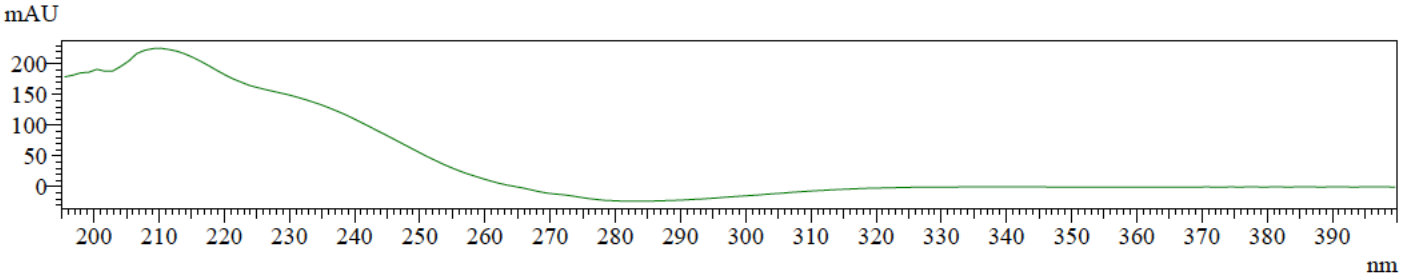
Chromatogram



UV Spectrum
Retention time = 7.323



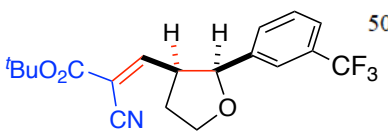
UV Spectrum
Retention time = 7.927



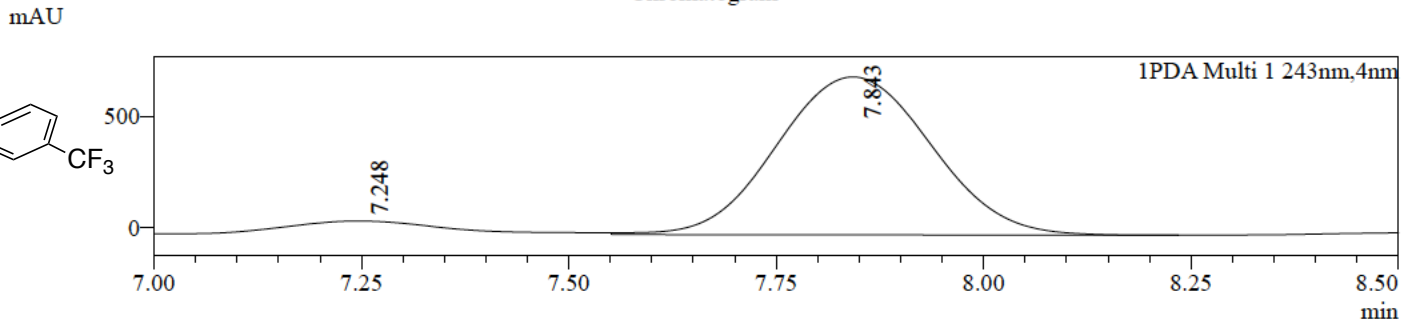
Peak Table

PDA Ch1 243nm

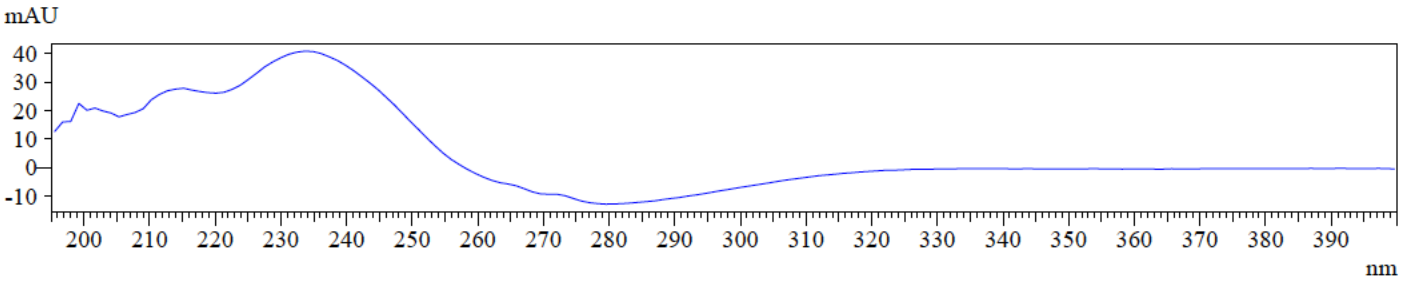
Peak#	Ret. Time	Area	Area%
1	7.323	809875	50.162
2	7.927	804641	49.838
Total		1614516	100.000



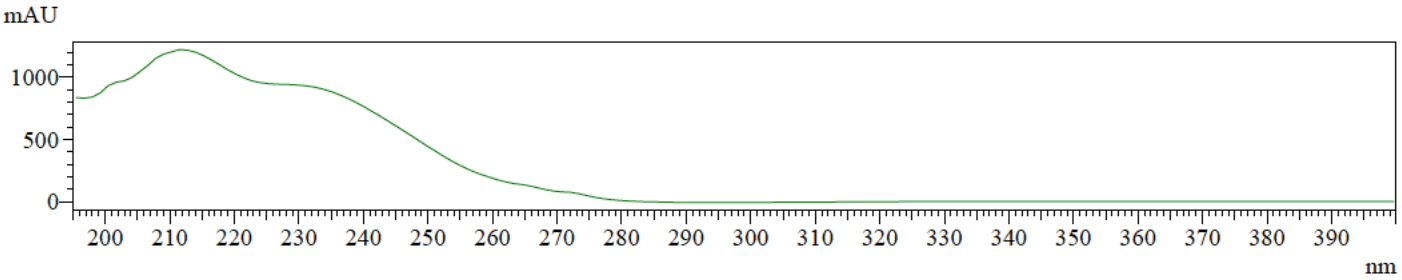
Chromatogram



UV Spectrum
Retention time = 7.248



UV Spectrum
Retention time = 7.843

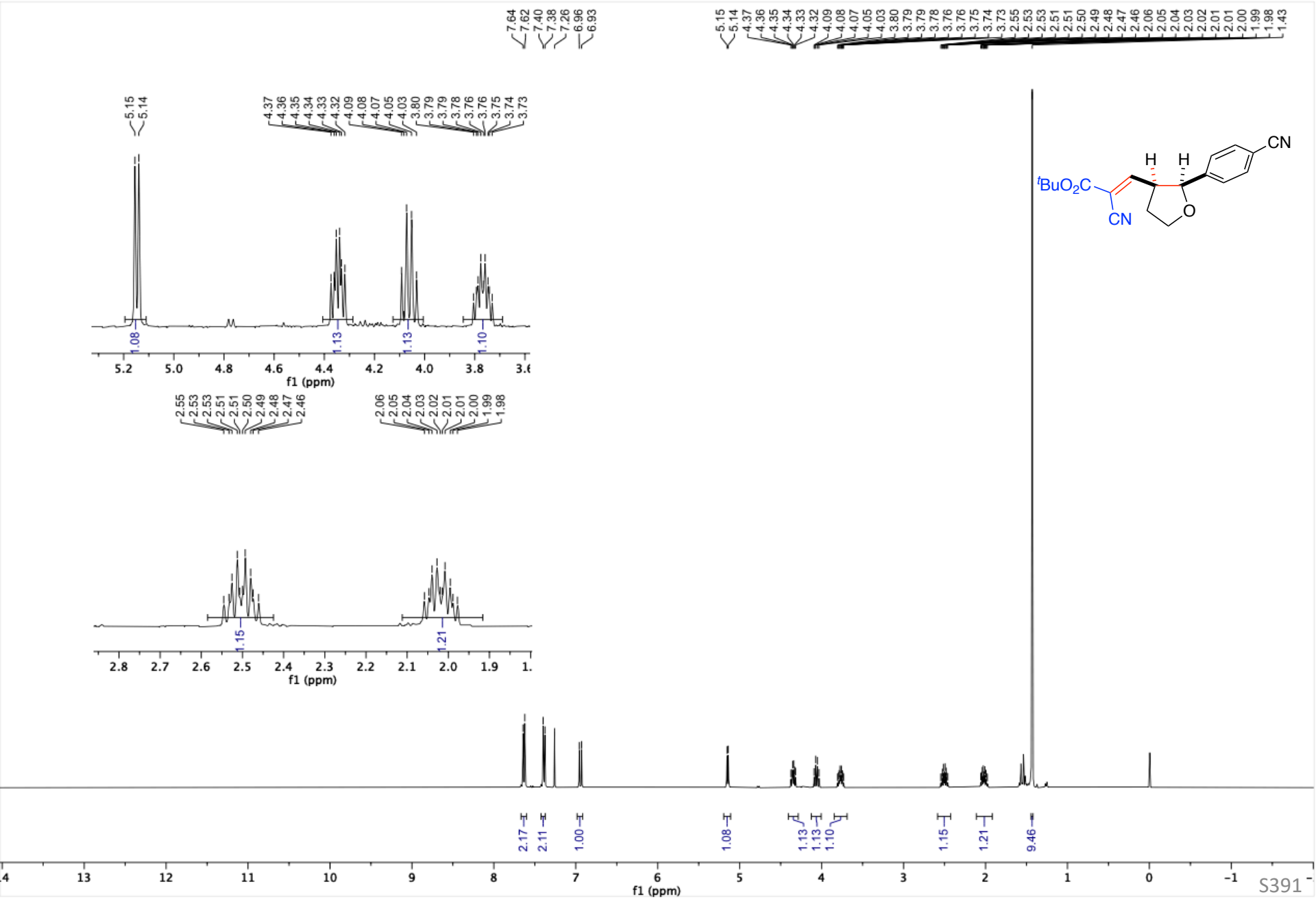


Peak Table

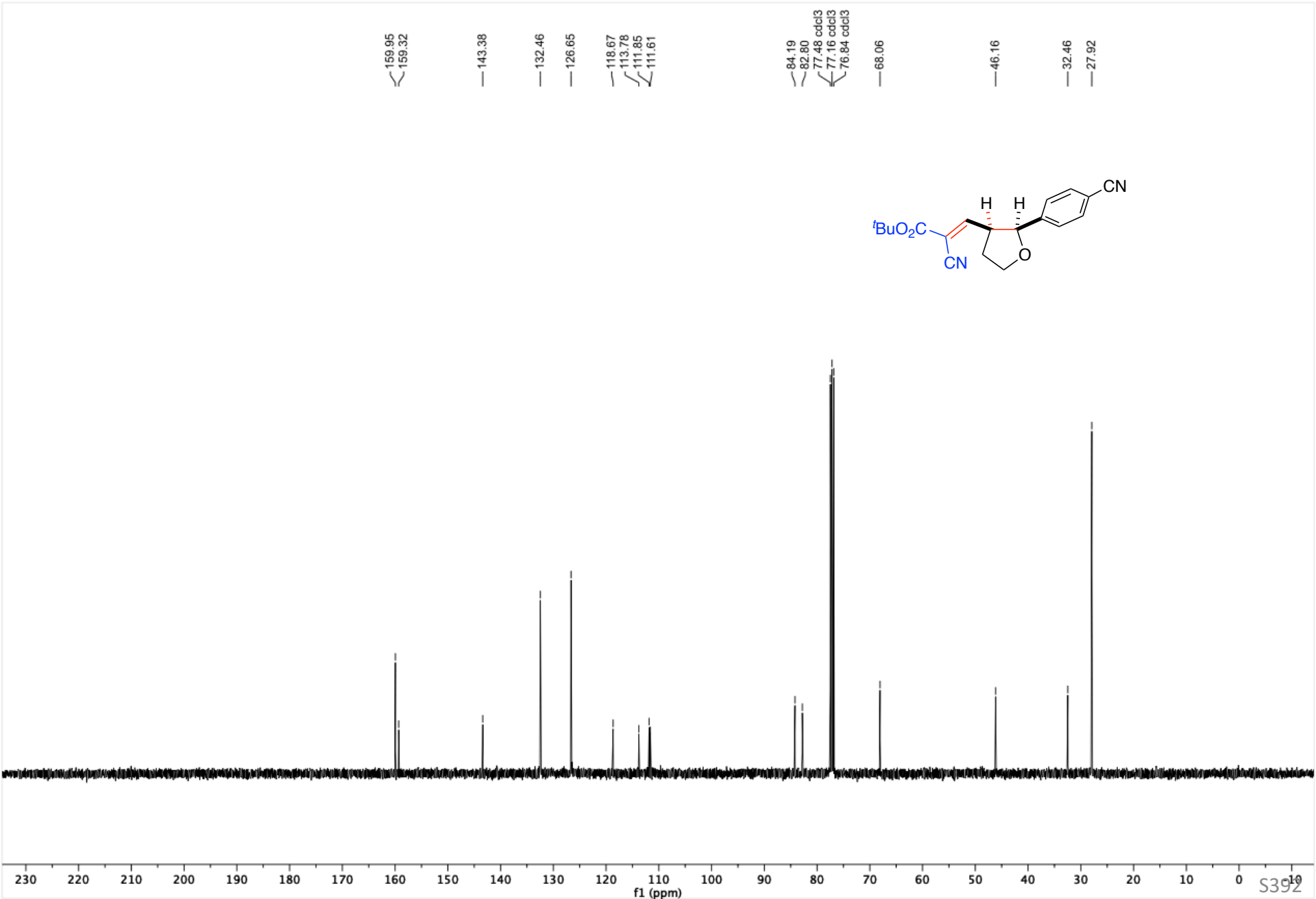
PDA Ch1 243nm

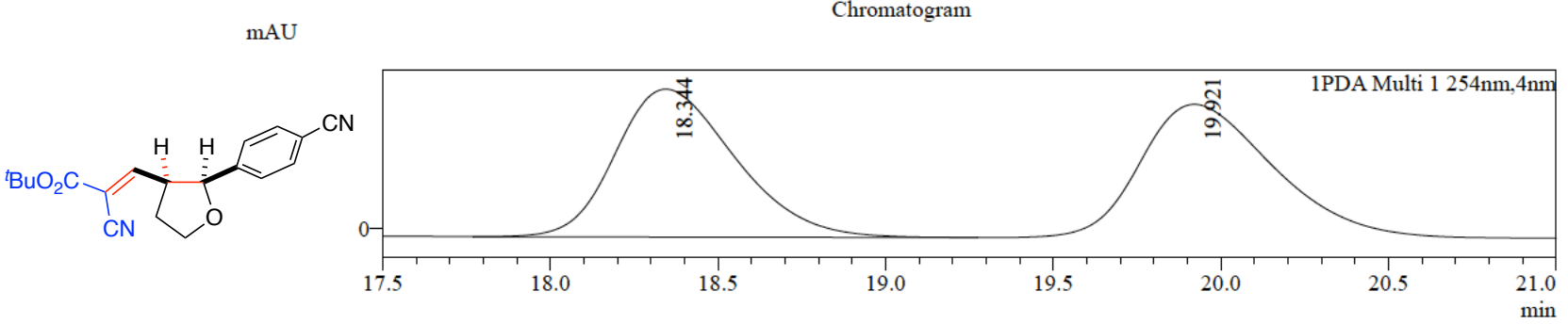
Peak#	Ret. Time	Area	Area%
1	7.248	793680	7.972
2	7.843	9162090	92.028
Total		9955770	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-cyanophenyl)tetrahydrofuran-3-yl)acrylate

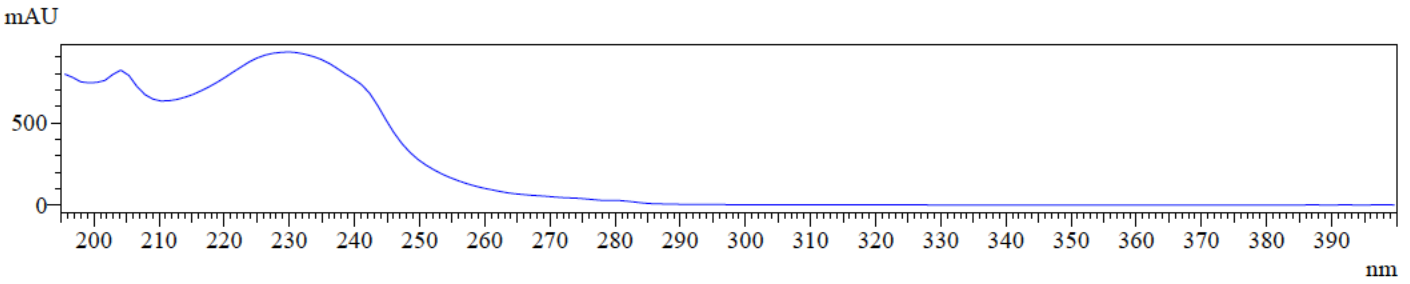


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(4-cyanophenyl)tetrahydrofuran-3-yl)acrylate

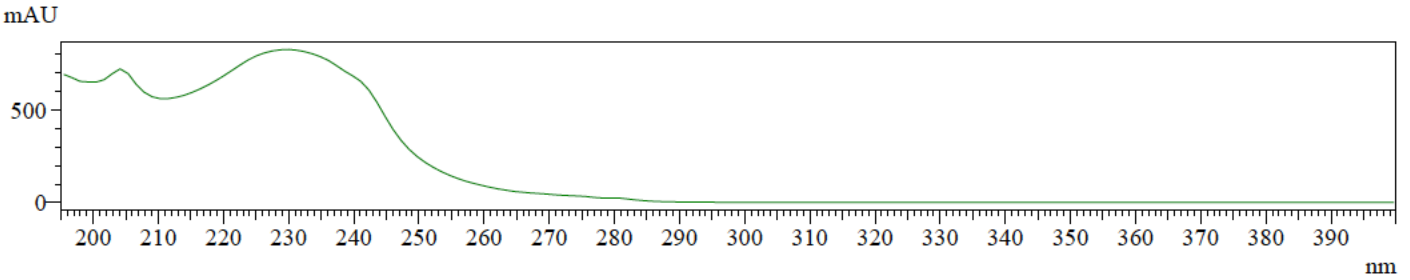




UV Spectrum
Retention time = 18.344



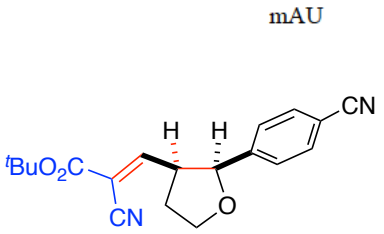
UV Spectrum
Retention time = 19.921



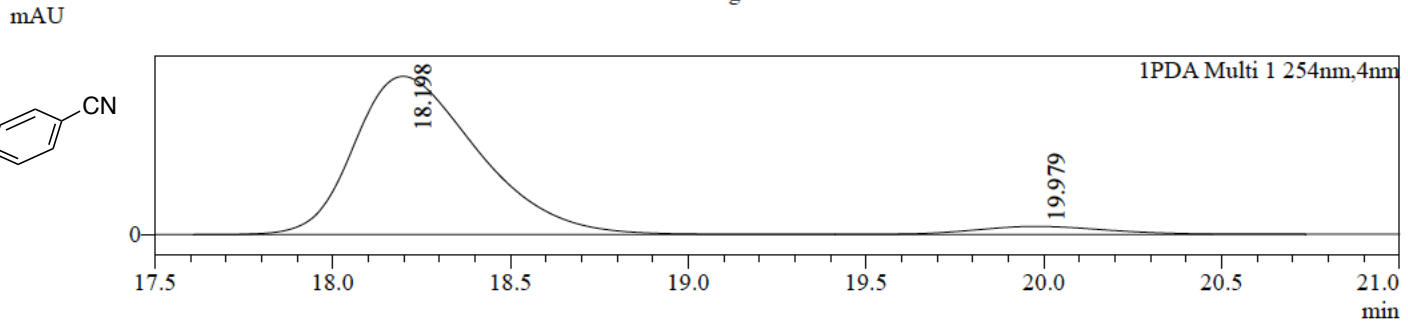
Peak Table

PDA Ch1 254nm

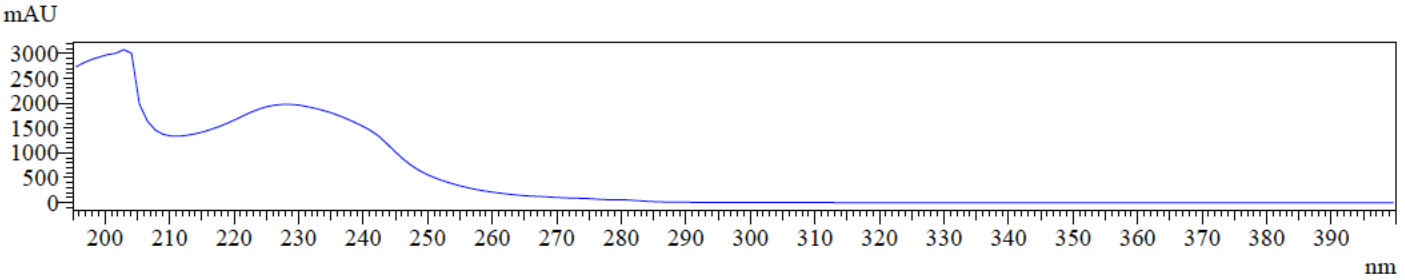
Peak#	Ret. Time	Area	Area%
1	18.344	4770844	49.905
2	19.921	4788975	50.095
Total		9559819	100.000



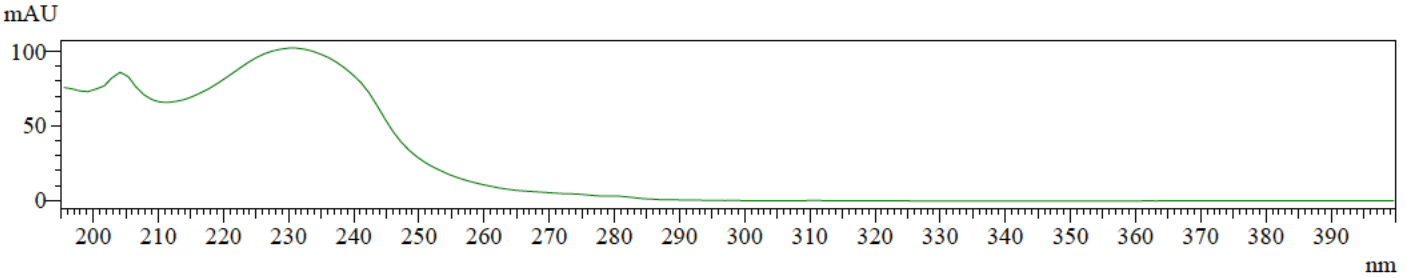
Chromatogram



UV Spectrum
Retention time = 18.198



UV Spectrum
Retention time = 19.979

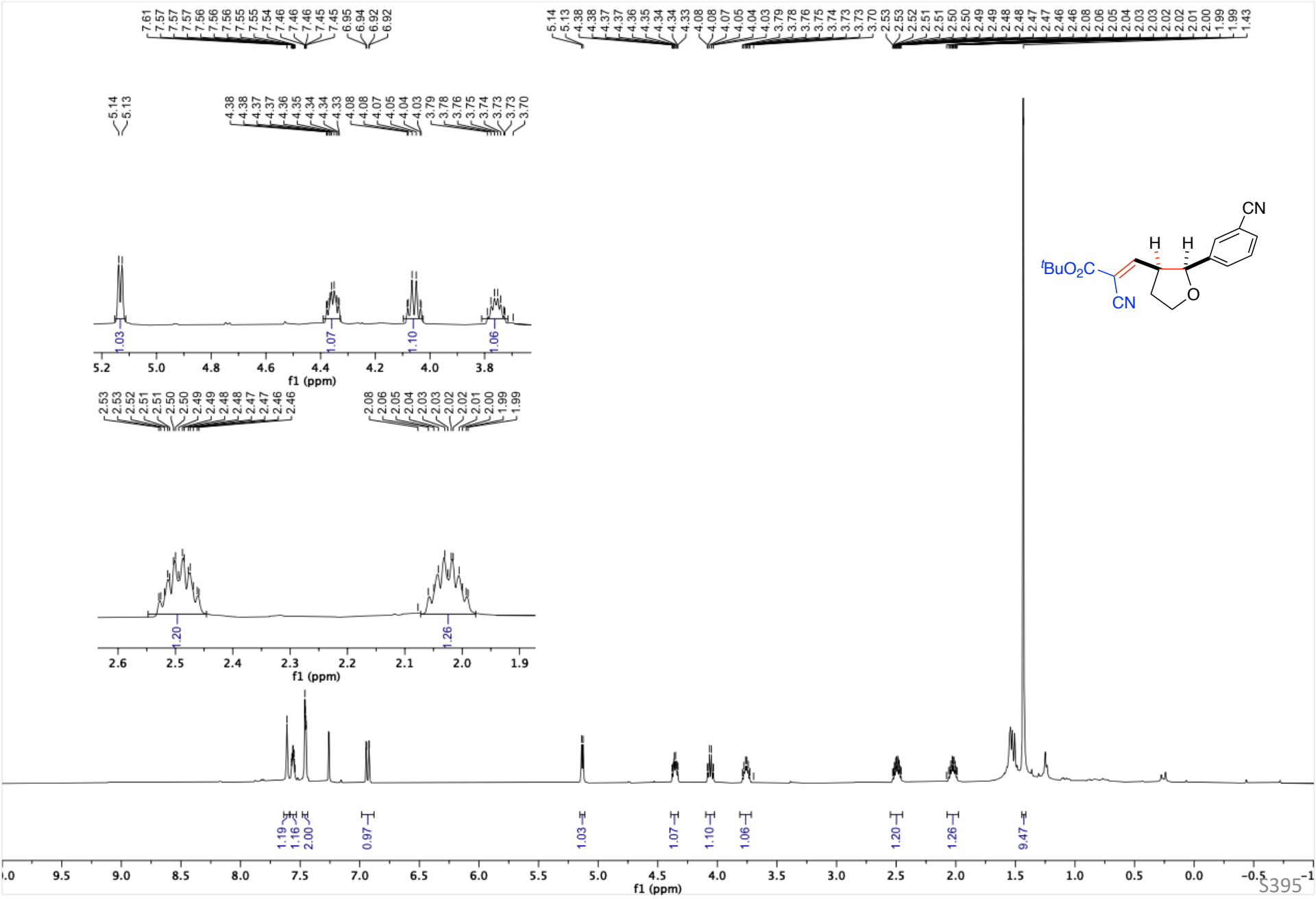


Peak Table

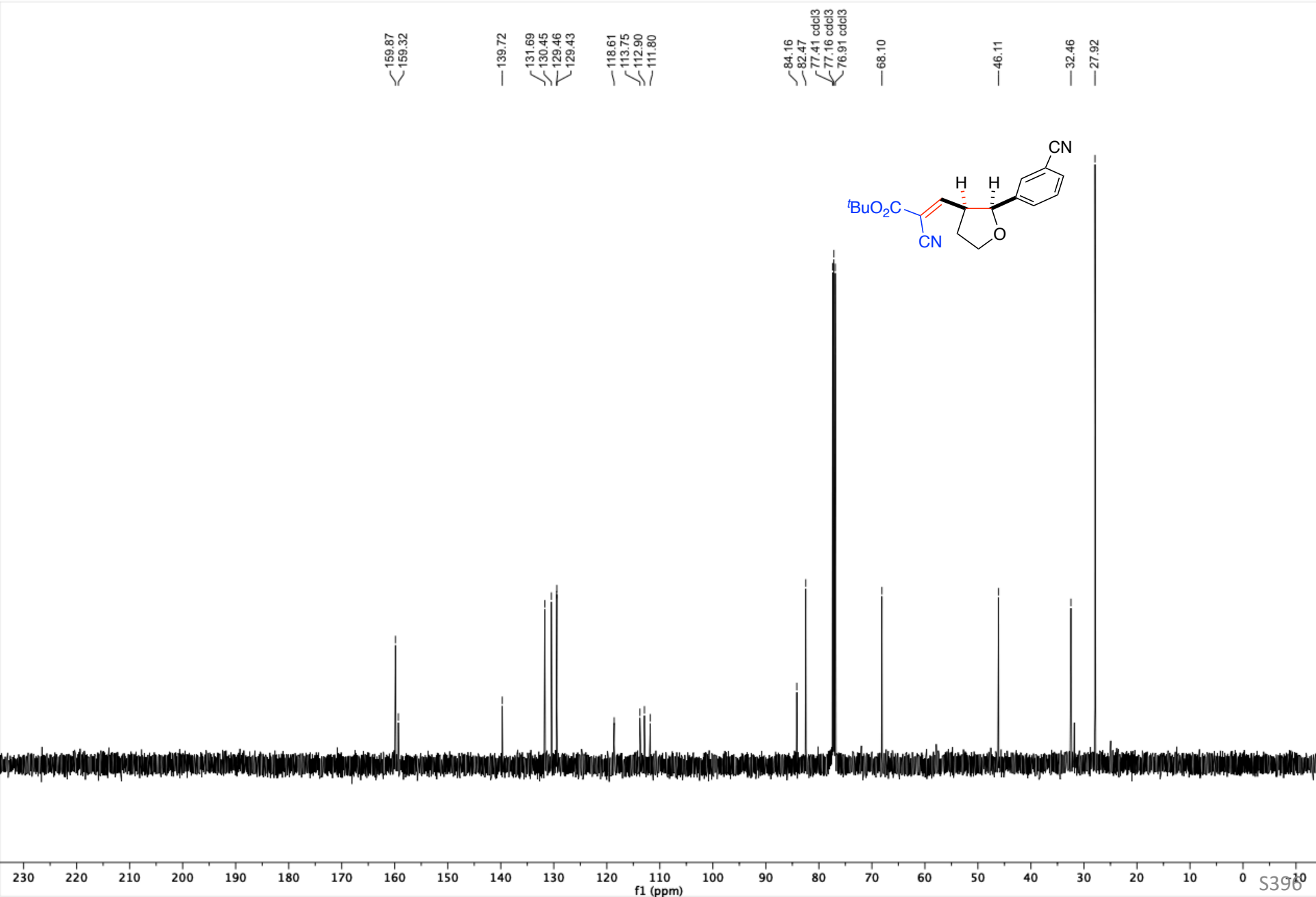
PDA Ch1 254nm

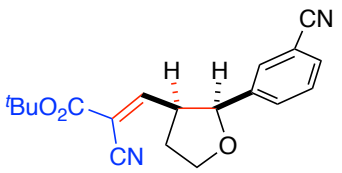
Peak#	Ret. Time	Area	Area%
1	18.198	9211583	94.829
2	19.979	502265	5.171
Total		9713848	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-cyanophenyl)tetrahydrofuran-3-yl)acrylate

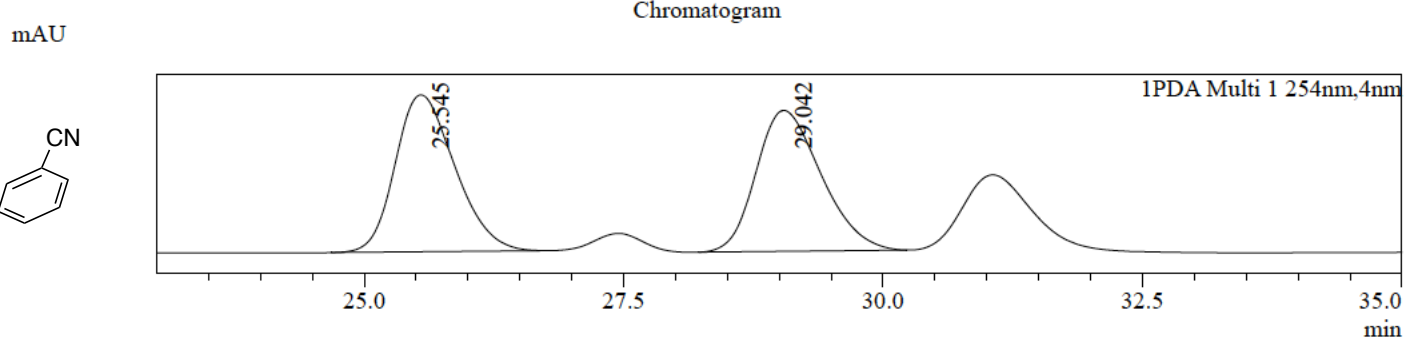


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(3-cyanophenyl)tetrahydrofuran-3-yl)acrylate

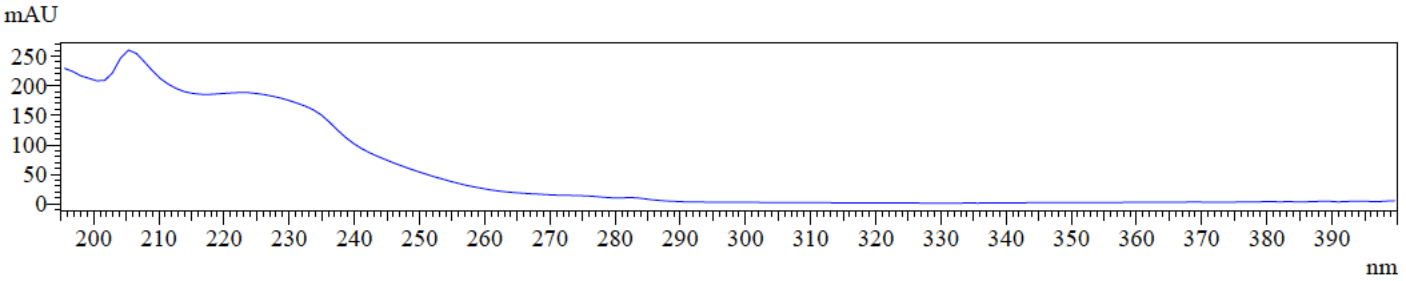




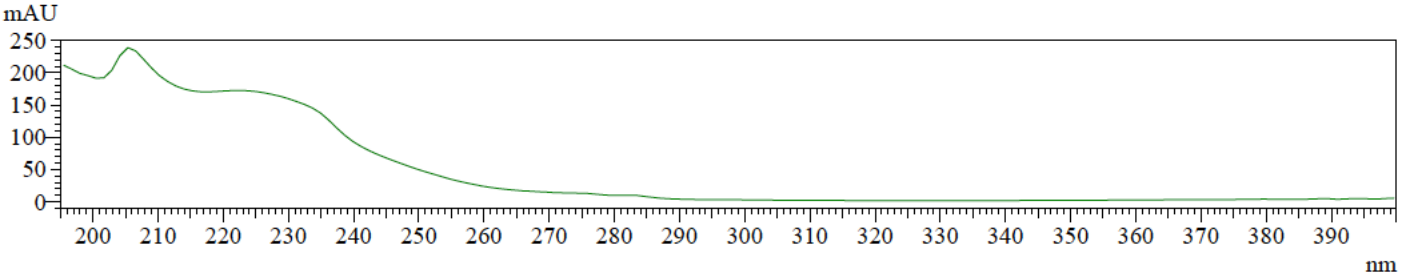
Chromatogram



UV Spectrum
Retention time = 25.545



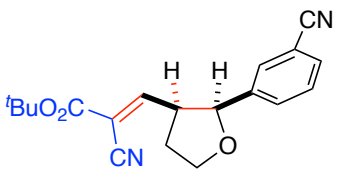
UV Spectrum
Retention time = 29.042



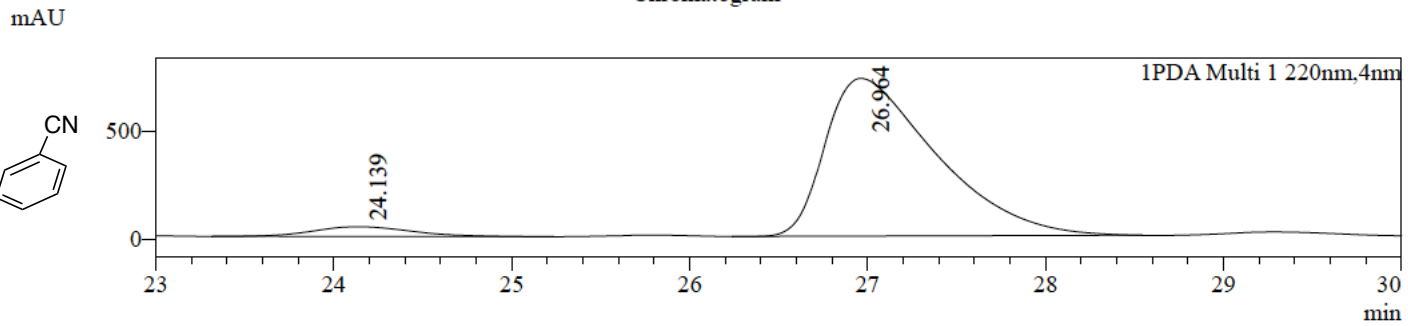
Peak Table

PDA Ch1 254nm

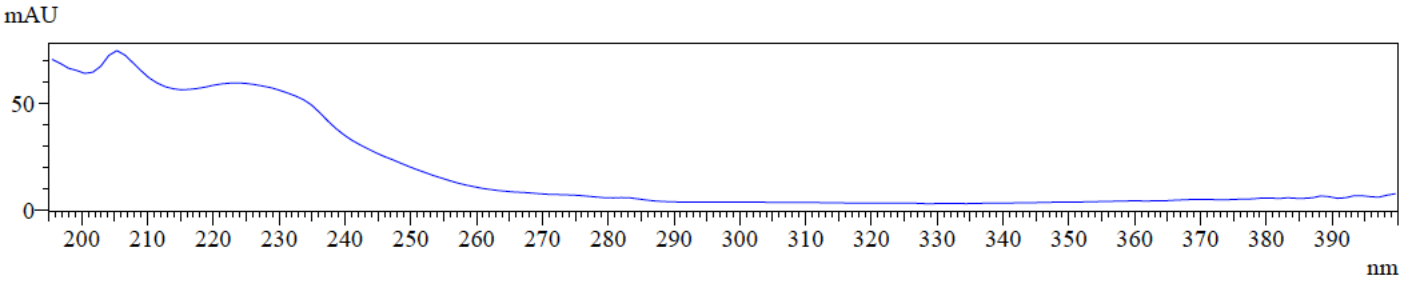
Peak#	Ret. Time	Area	Area%
1	25.545	1281651	50.525
2	29.042	1254996	49.475
Total		2536648	100.000



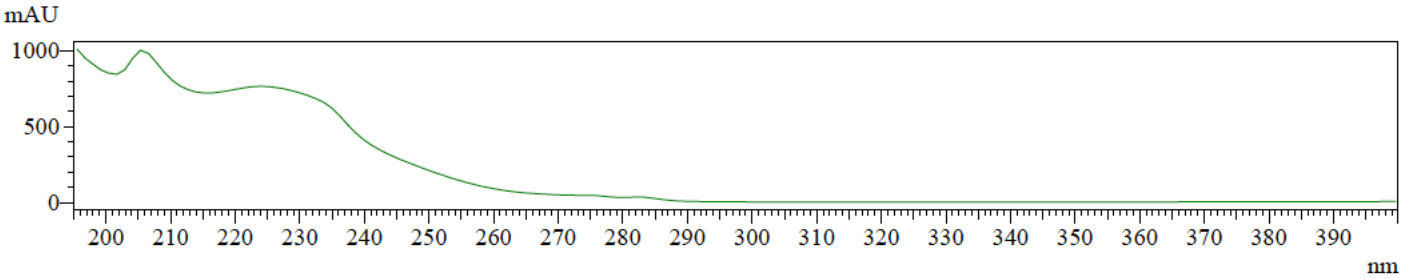
Chromatogram



UV Spectrum
Retention time = 24.139



UV Spectrum
Retention time = 26.964

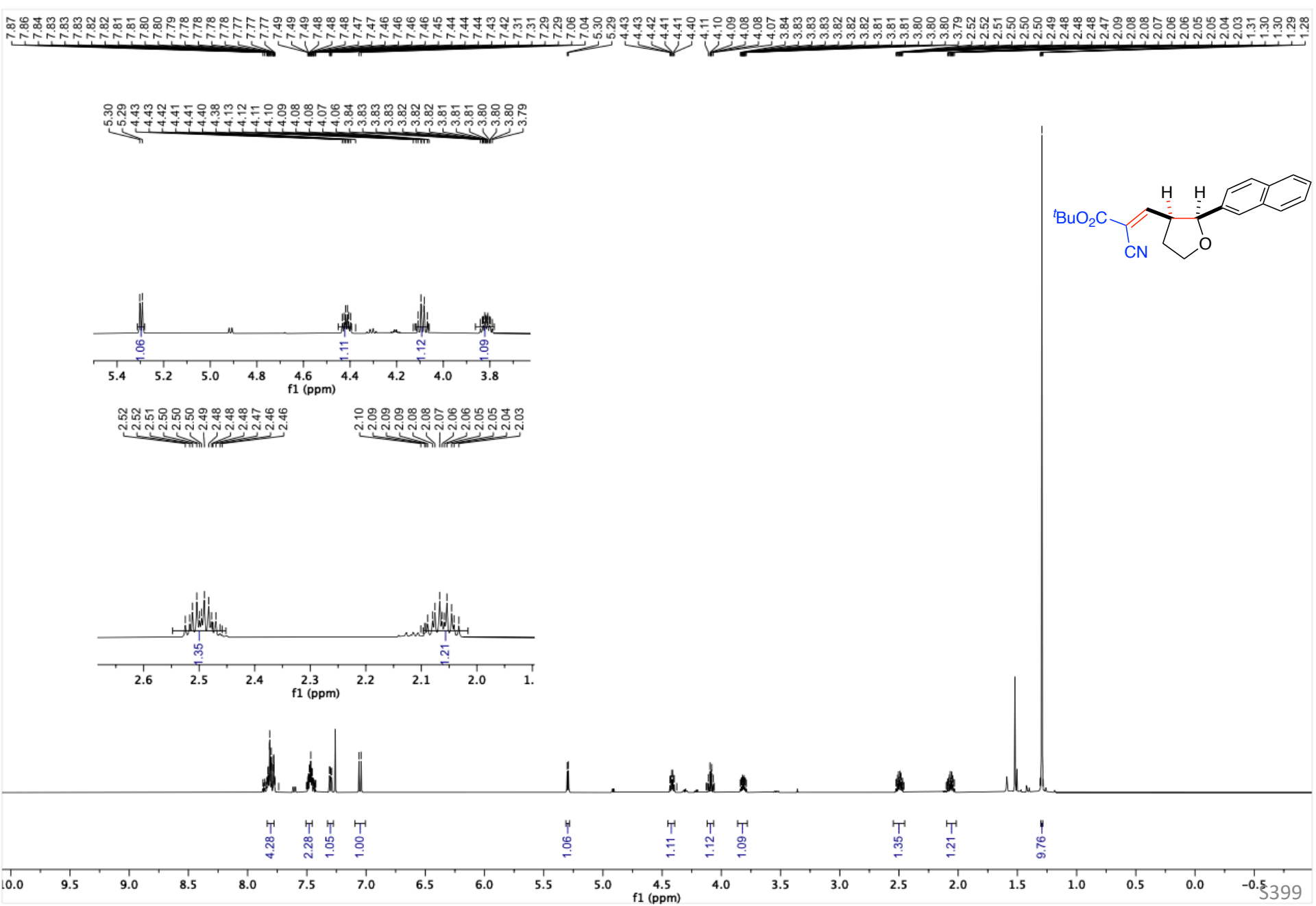


Peak Table

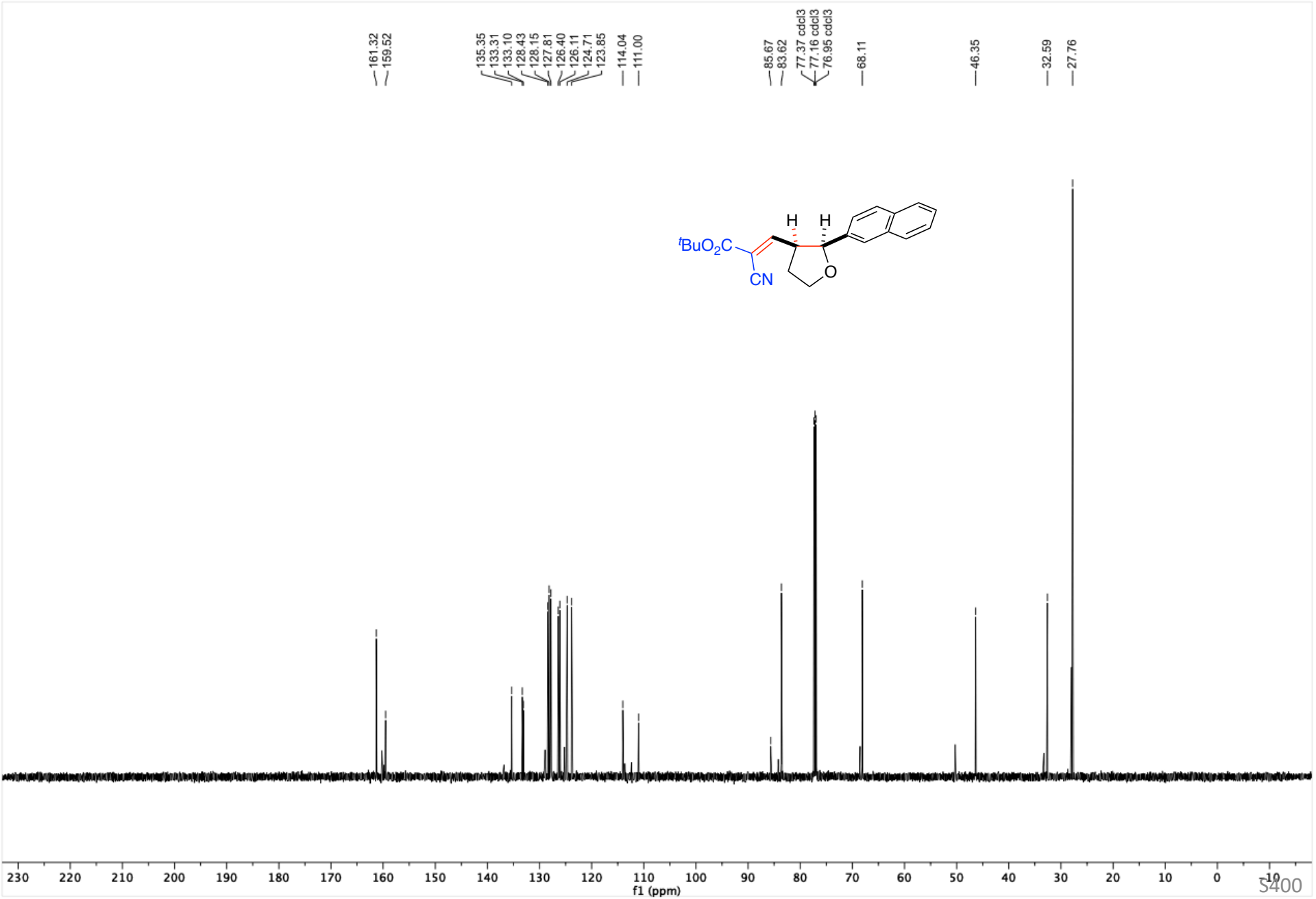
PDA Ch1 220nm

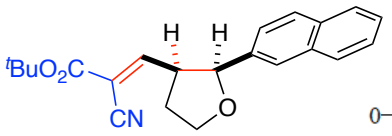
Peak#	Ret. Time	Area	Area%
1	24.139	1715177	5.148
2	26.964	31602797	94.852
Total		33317975	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(naphthalen-2-yl)tetrahydrofuran-3-yl)acrylate

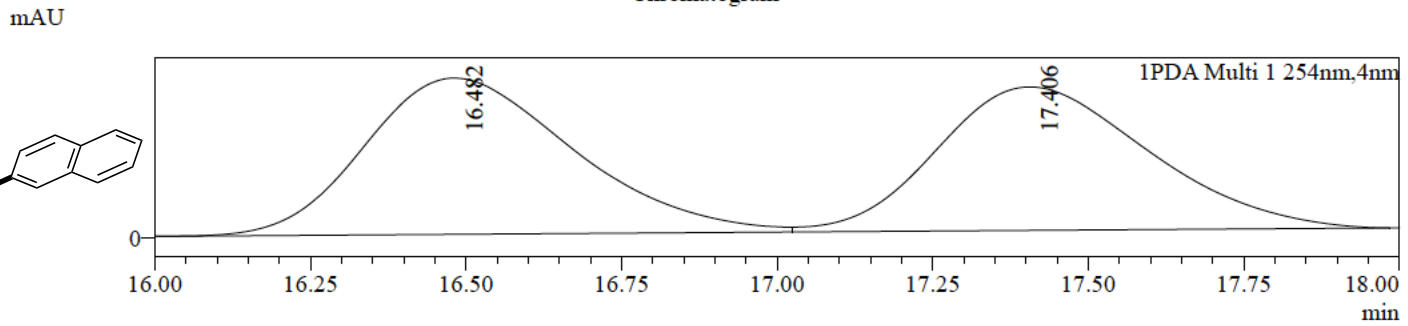


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(naphthalen-2-yl)tetrahydrofuran-3-yl)acrylate

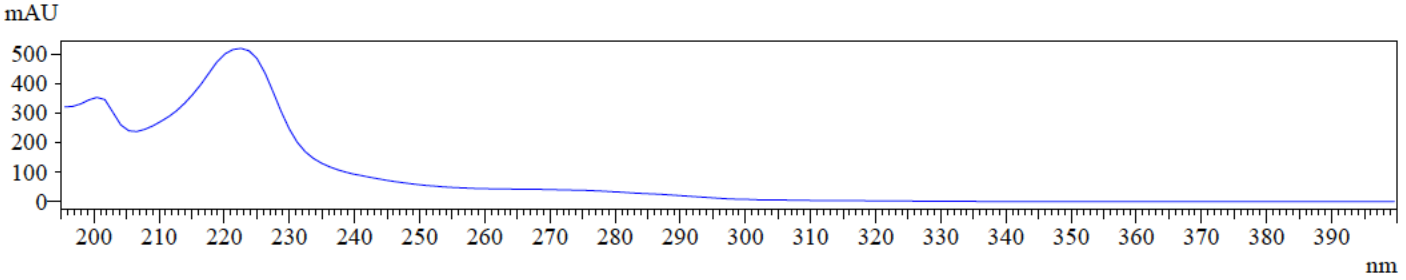




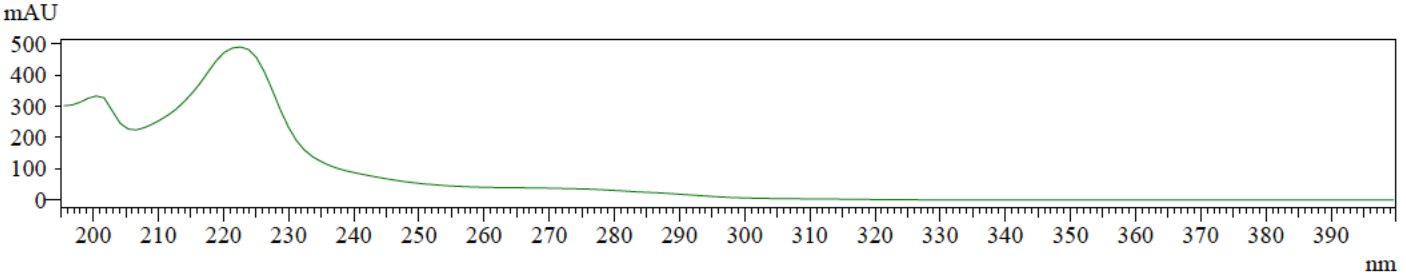
Chromatogram



UV Spectrum
Retention time = 16.482



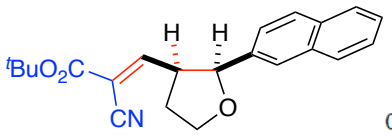
UV Spectrum
Retention time = 17.406



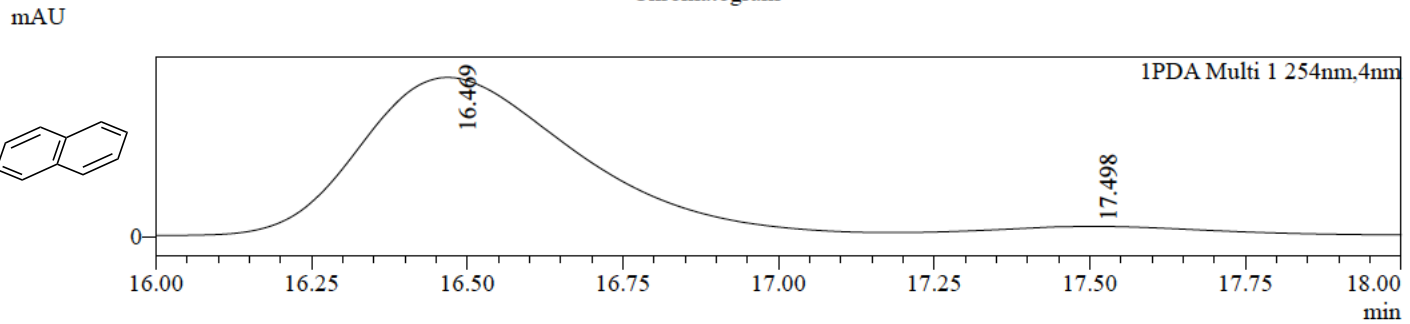
Peak Table

PDA Ch1 254nm

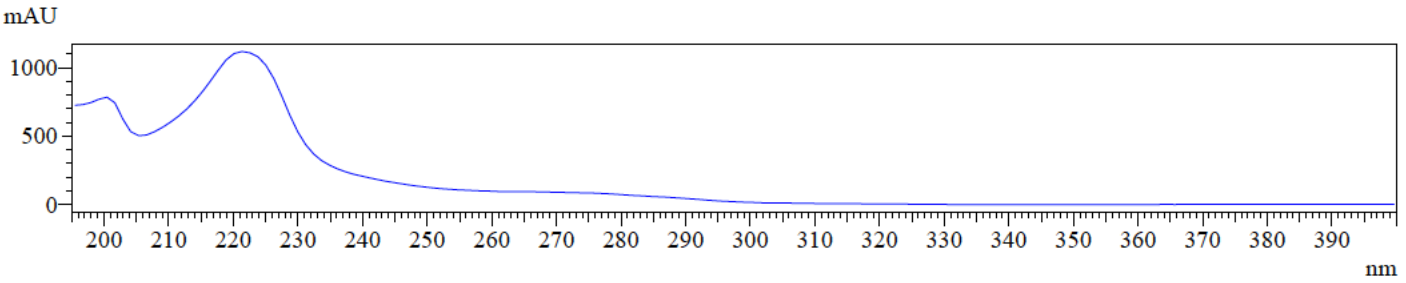
Peak#	Ret. Time	Area	Area%
1	16.482	1123179	51.775
2	17.406	1046146	48.225
Total		2169325	100.000



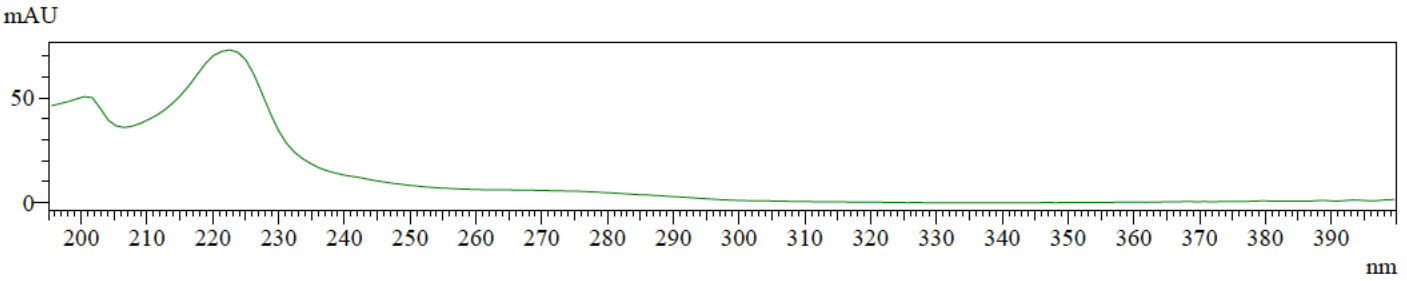
Chromatogram



UV Spectrum
Retention time = 16.469



UV Spectrum
Retention time = 17.498

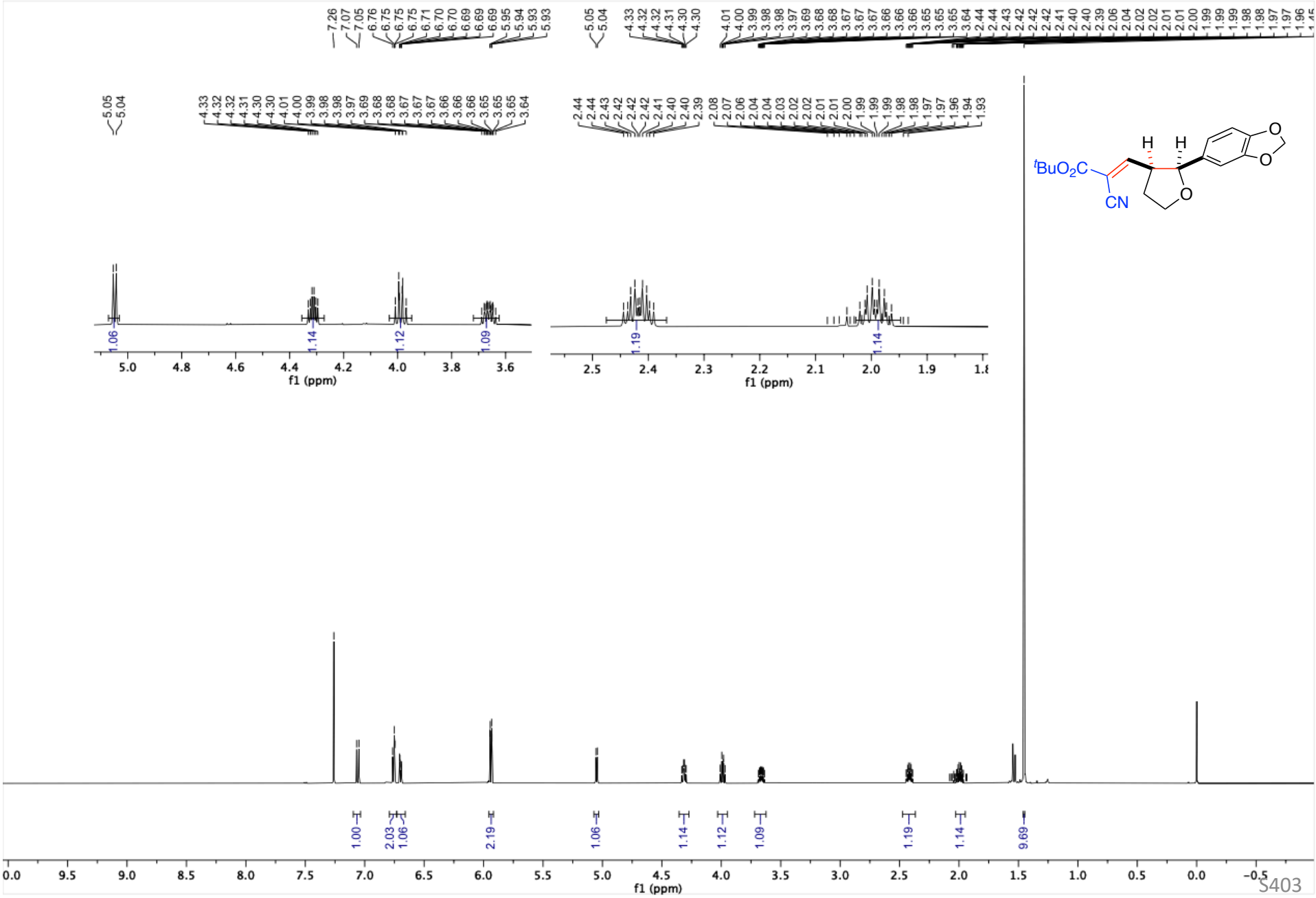


Peak Table

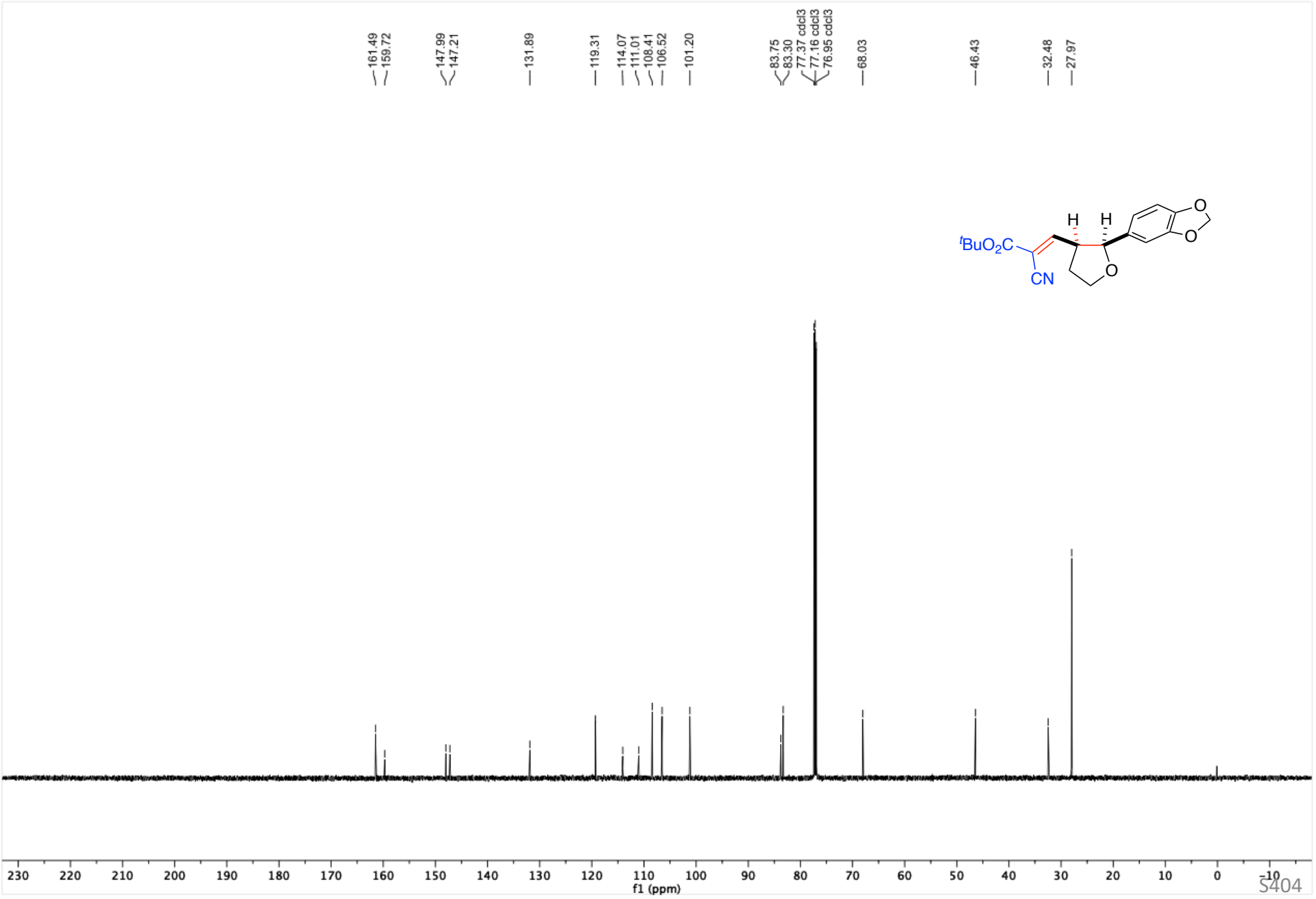
PDA Ch1 254nm

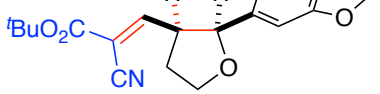
Peak#	Ret. Time	Area	Area%
1	16.469	2640708	94.732
2	17.498	146846	5.268
Total		2787554	100.000

tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(benzo[d][1,3]dioxol-5-yl)tetrahydrofuran-3-yl)-2-cyanoacrylate

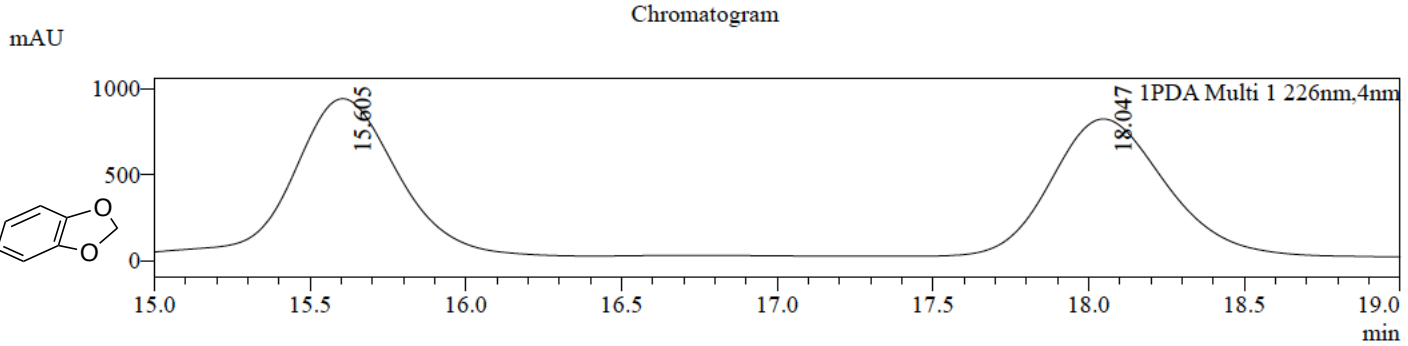


tert-Butyl (*E*)-3-((2*S*,3*S*)-2-(benzo[d][1,3]dioxol-5-yl)tetrahydrofuran-3-yl)-2-cyanoacrylate

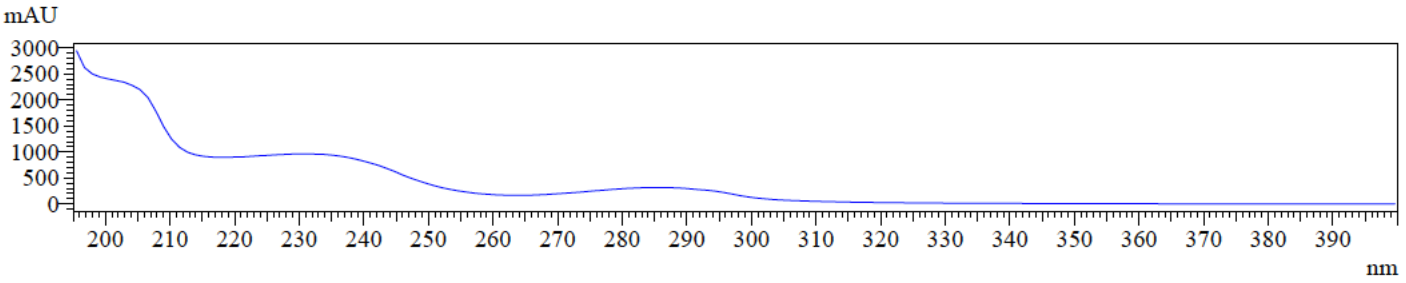




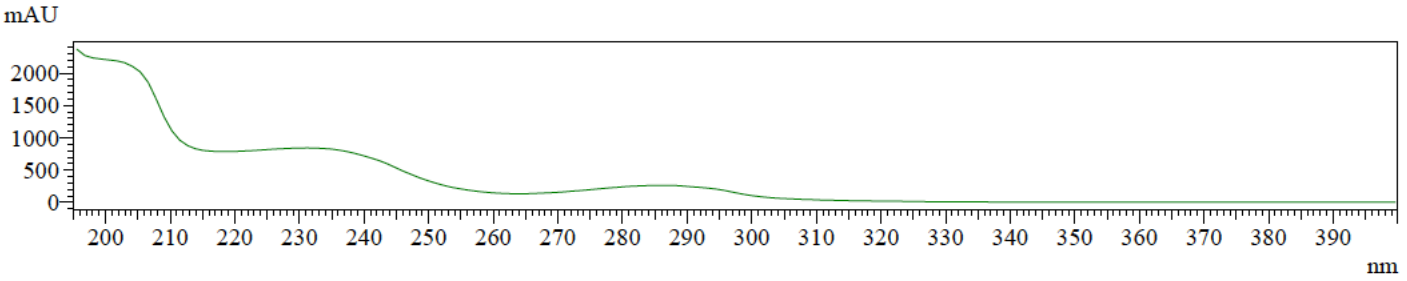
Chromatogram



UV Spectrum
Retention time = 15.605



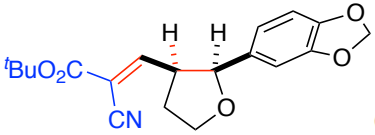
UV Spectrum
Retention time = 18.047



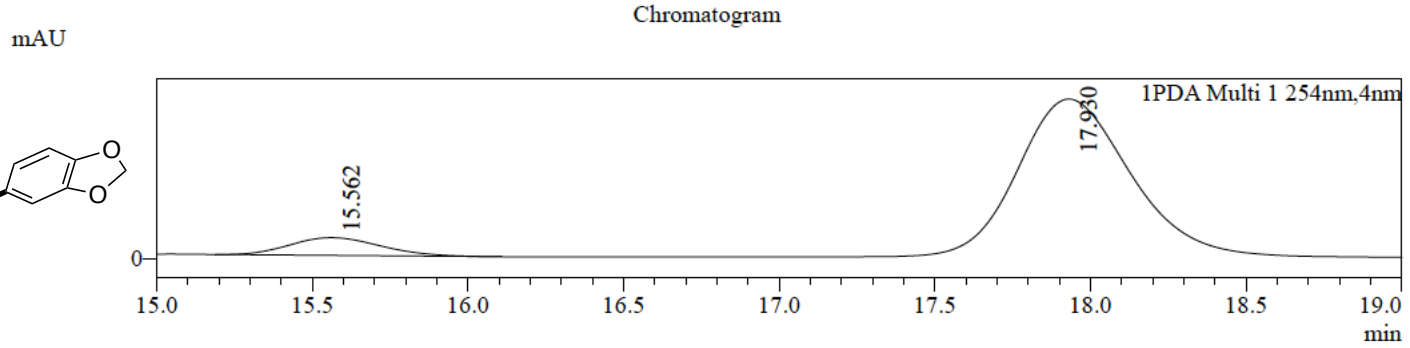
Peak Table

PDA Ch1 226nm

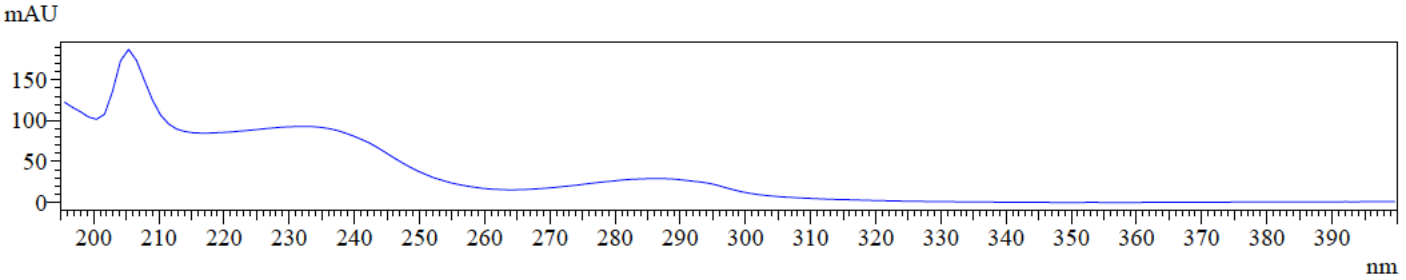
Peak#	Ret. Time	Area	Area%
1	15.605	21741265	51.299
2	18.047	20640382	48.701
Total		42381647	100.000



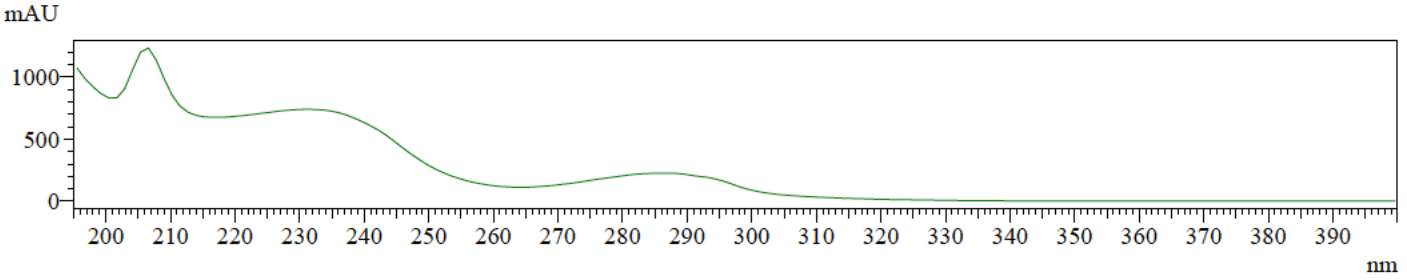
Chromatogram



UV Spectrum
Retention time = 15.562



UV Spectrum
Retention time = 17.930

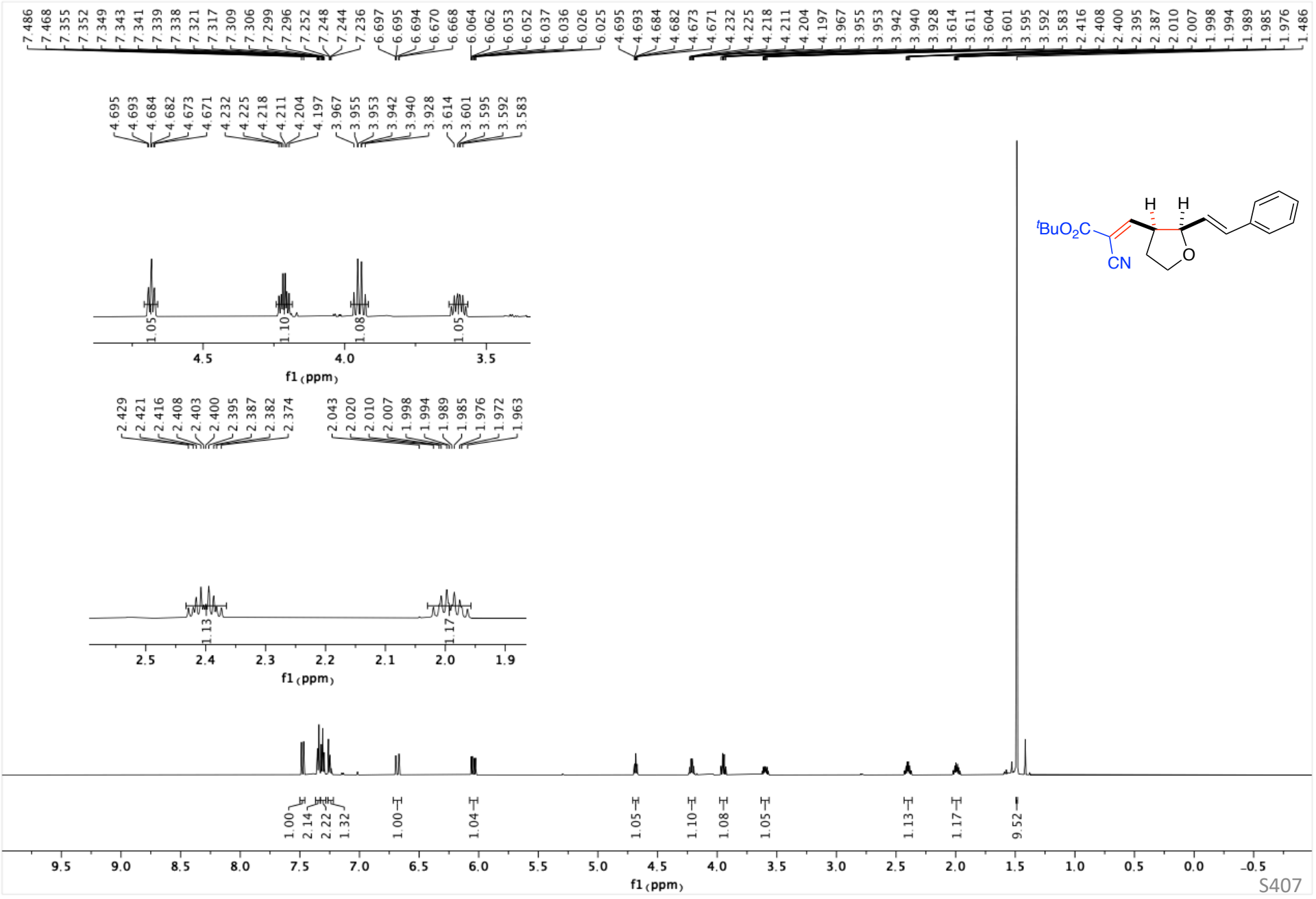


Peak Table

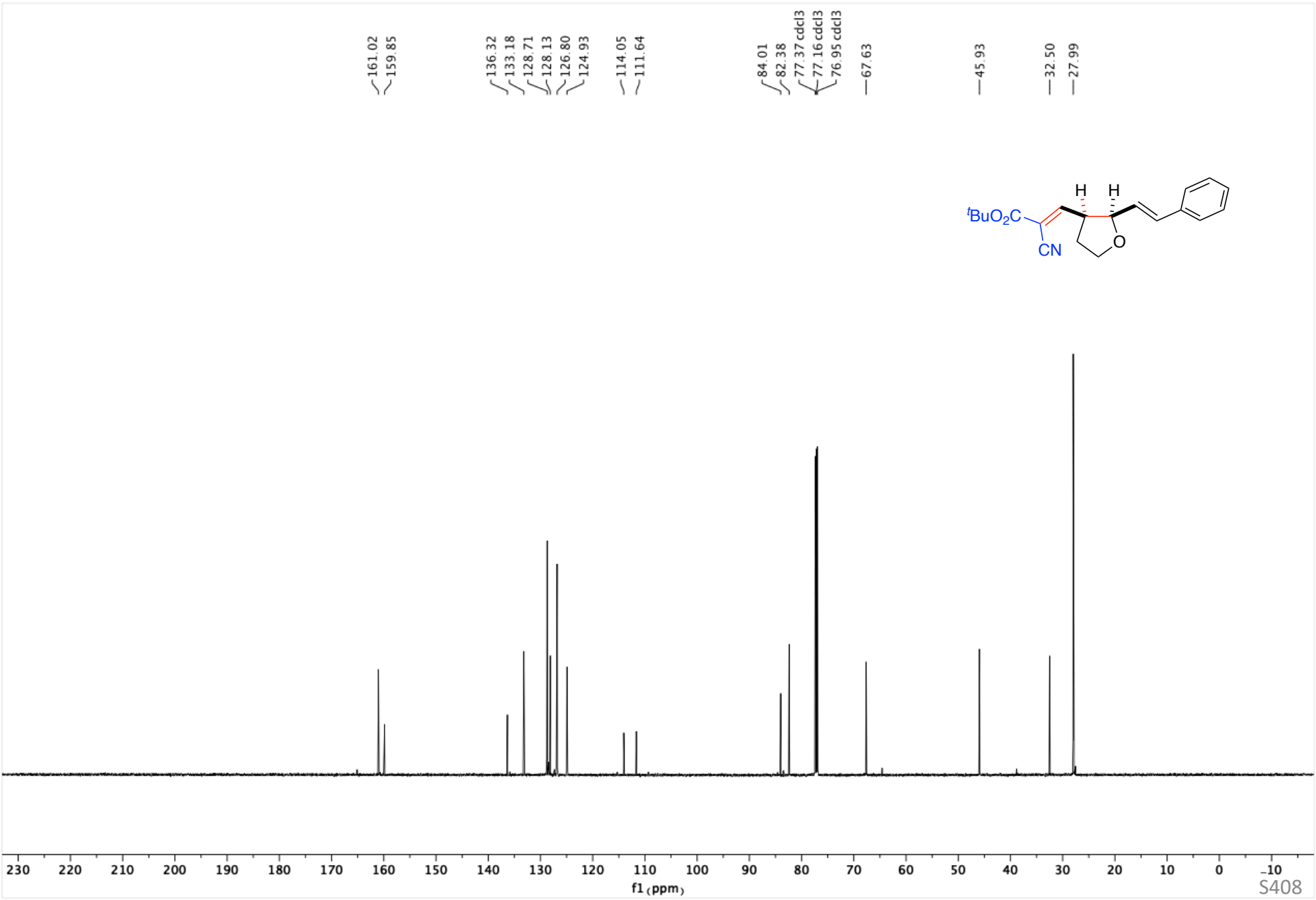
PDA Ch1 254nm

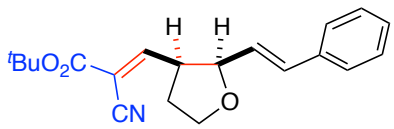
Peak#	Ret. Time	Area	Area%
1	15.562	446900	8.209
2	17.930	4996977	91.791
Total		5443877	100.000

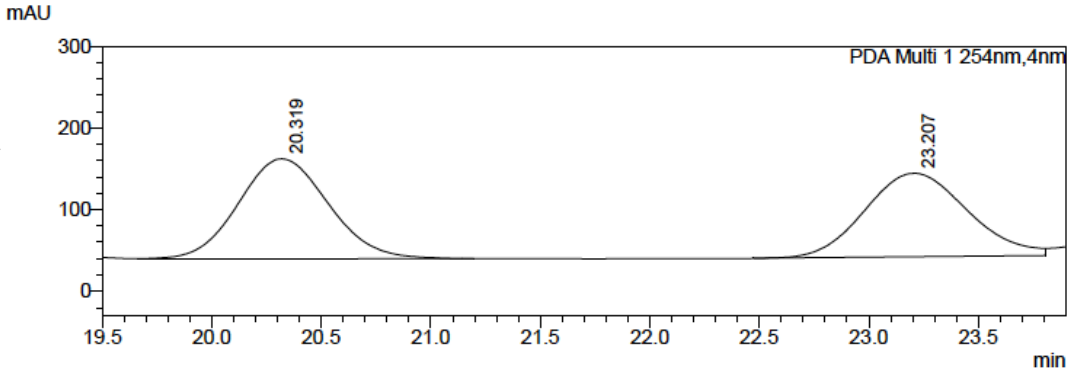
tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)acrylate



tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)acrylate

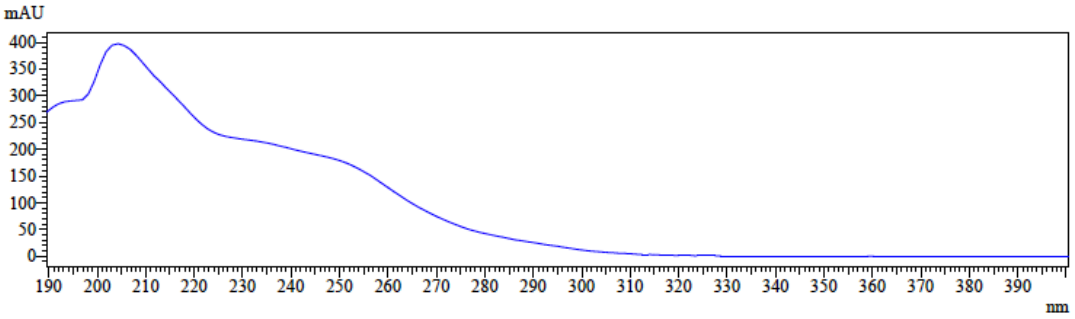






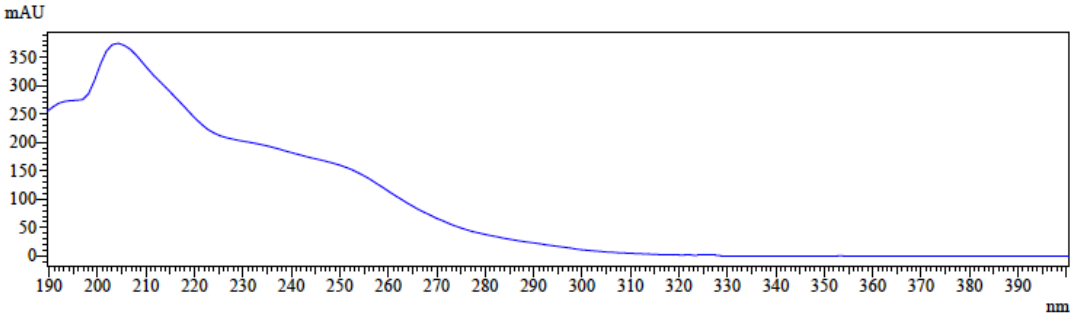
UV Spectrum

Retention Time: 20.319 min



UV Spectrum

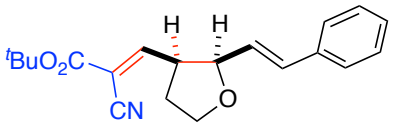
Retention Time: 23.207 min

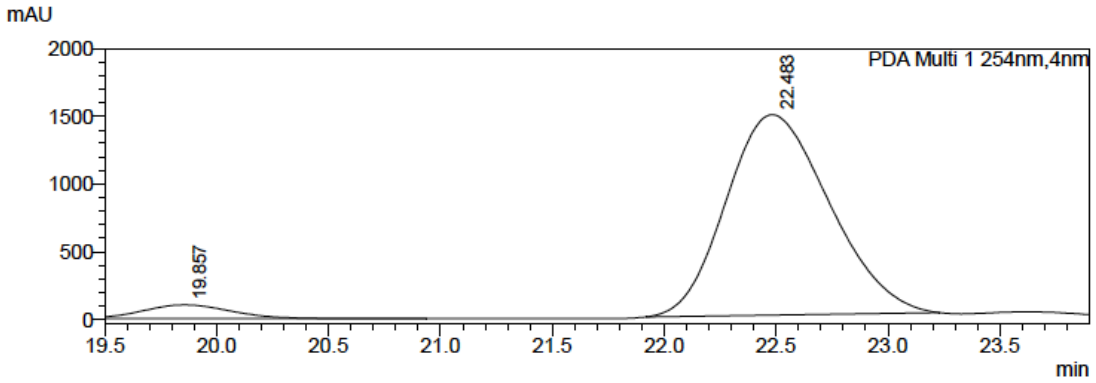


Peak Table

PDA Ch1 254nm

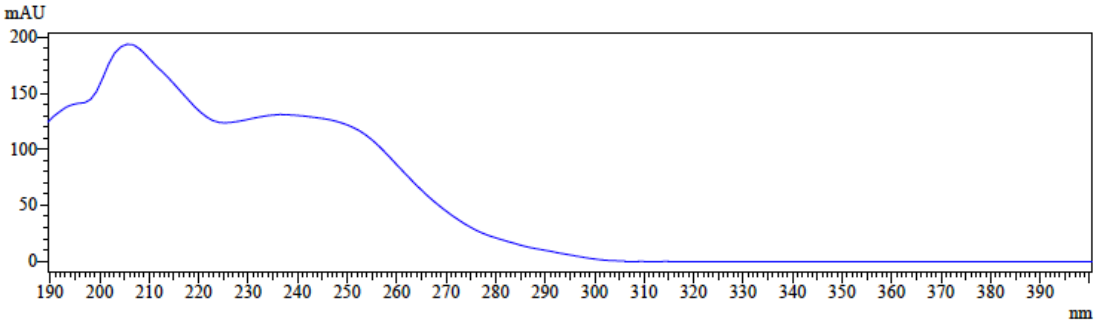
Peak#	Ret. Time	Area%
1	20.319	51.316
2	23.207	48.684
Total		100.000





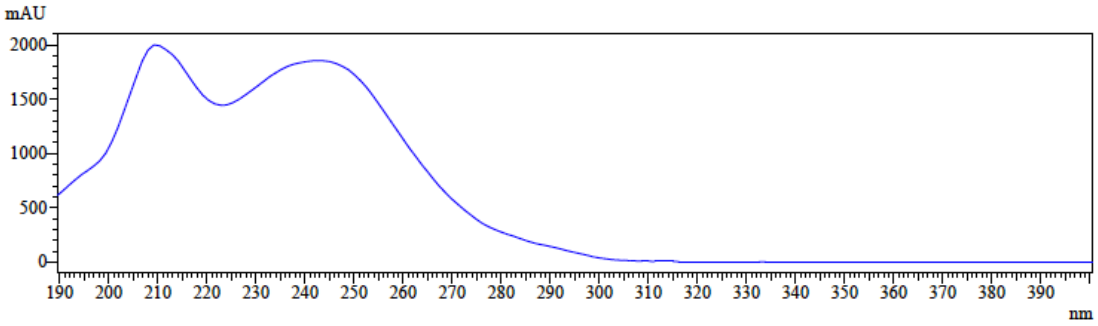
UV Spectrum

Retention Time: 19.857 min



UV Spectrum

Retention Time: 22.483 min

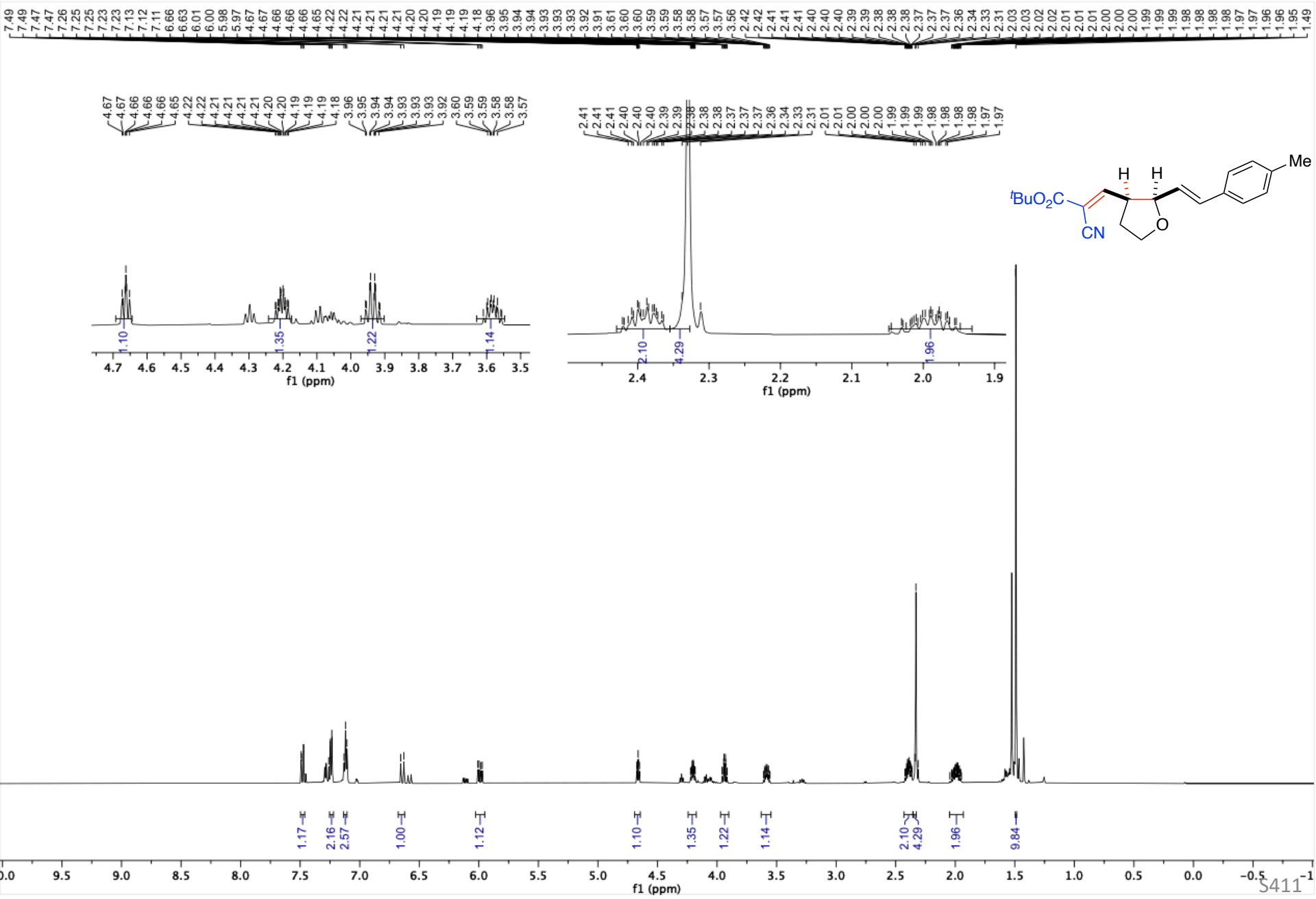


Peak Table

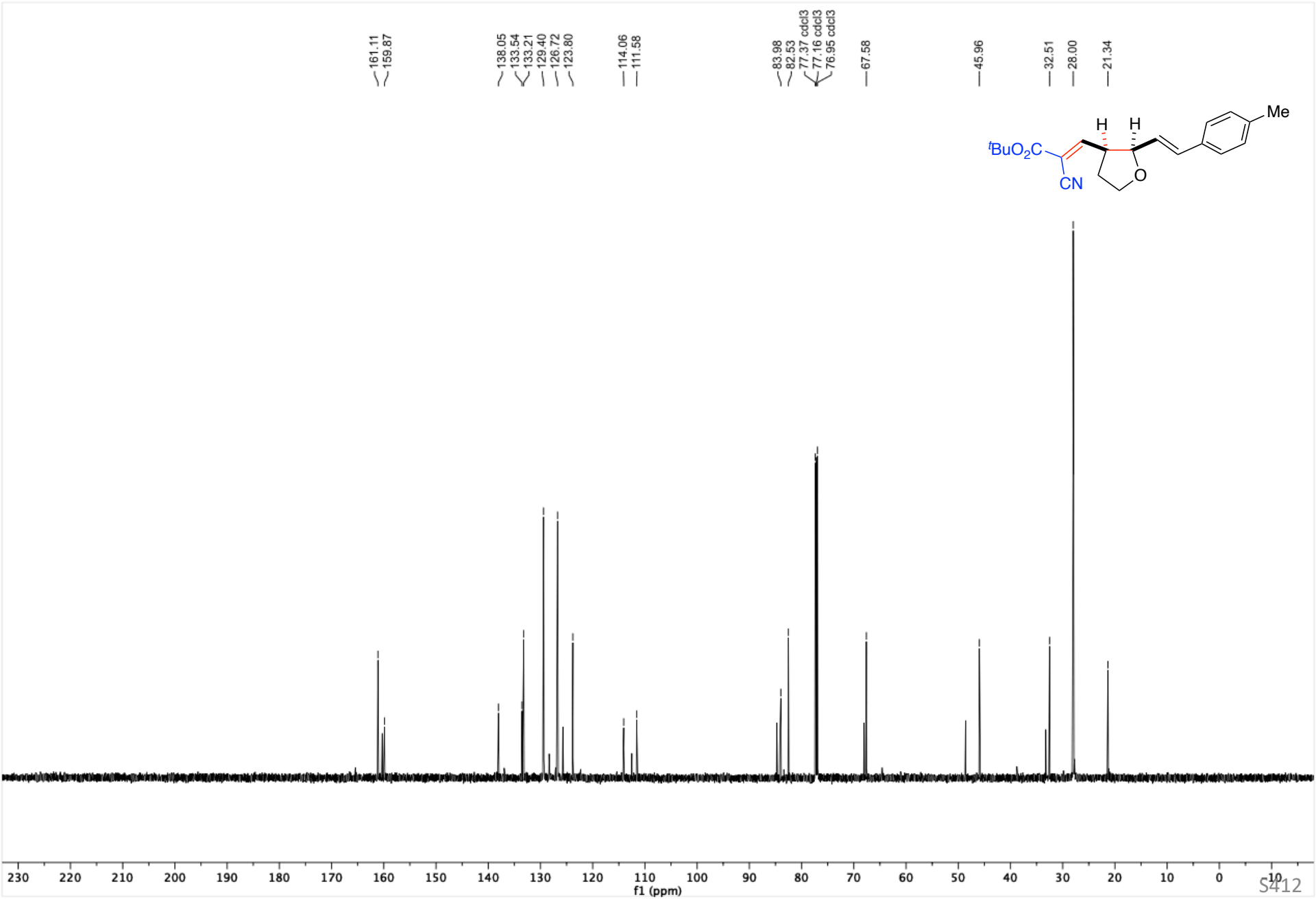
PDA Ch1 254nm

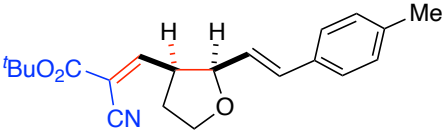
Peak#	Ret. Time	Area%
1	19.857	5.406
2	22.483	94.594
Total		100.000

tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-4-methylstyryl)tetrahydrofuran-3-yl)acryla

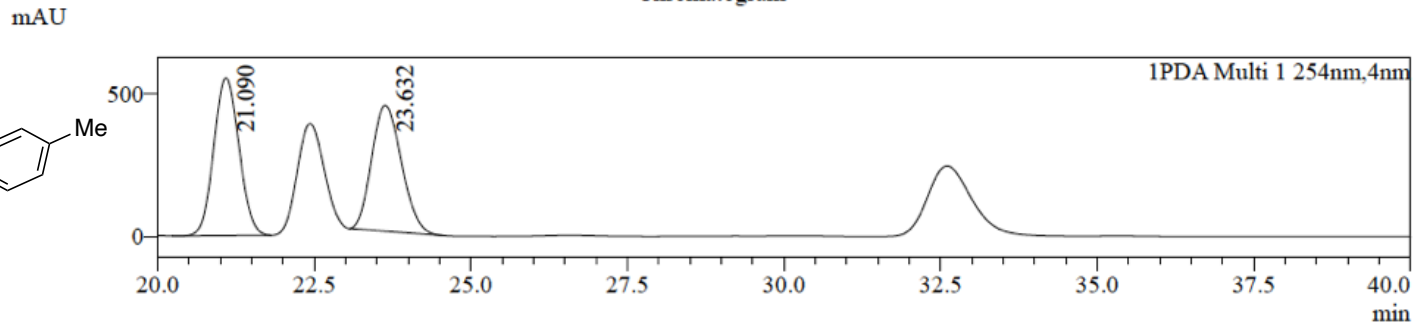


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-4-methylstyryl)tetrahydrofuran-3-yl)acryla

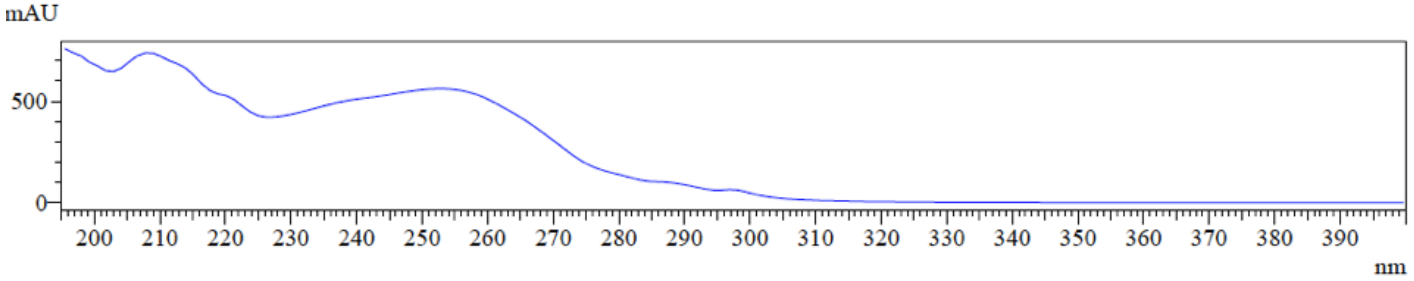




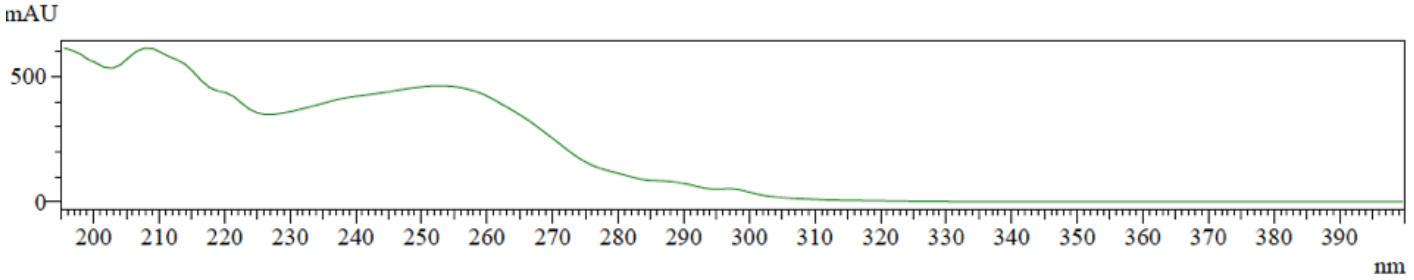
Chromatogram



UV Spectrum
Retention time = 21.090



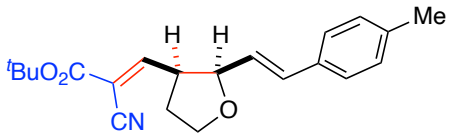
UV Spectrum
Retention time = 23.632



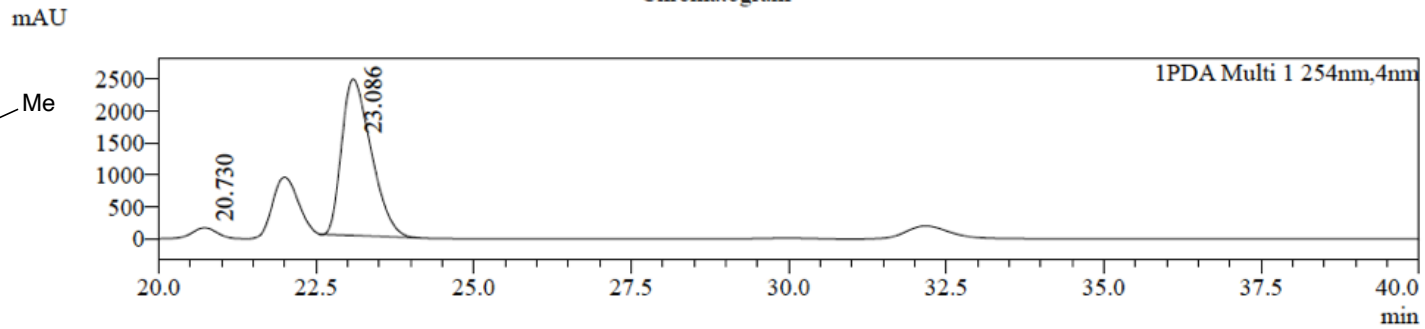
Peak Table

PDA Ch1 254nm

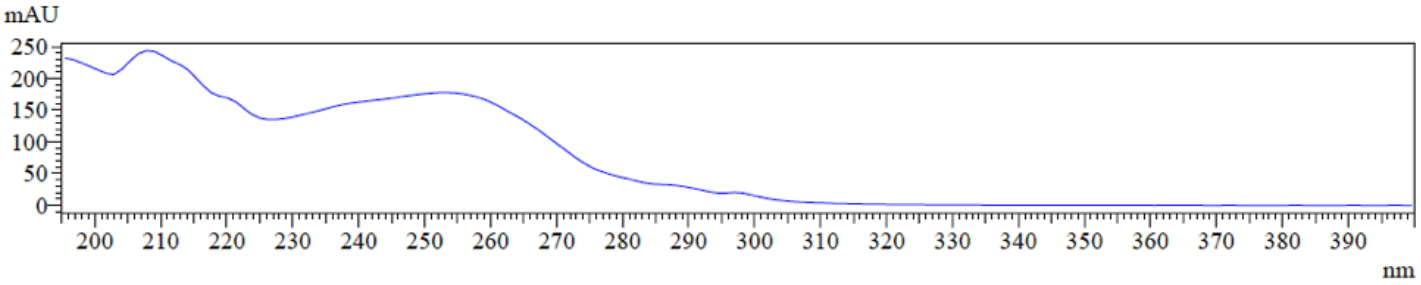
Peak#	Ret. Time	Area	Area%
1	21.090	15516154	51.517
2	23.632	14602528	48.483
Total		30118682	100.000



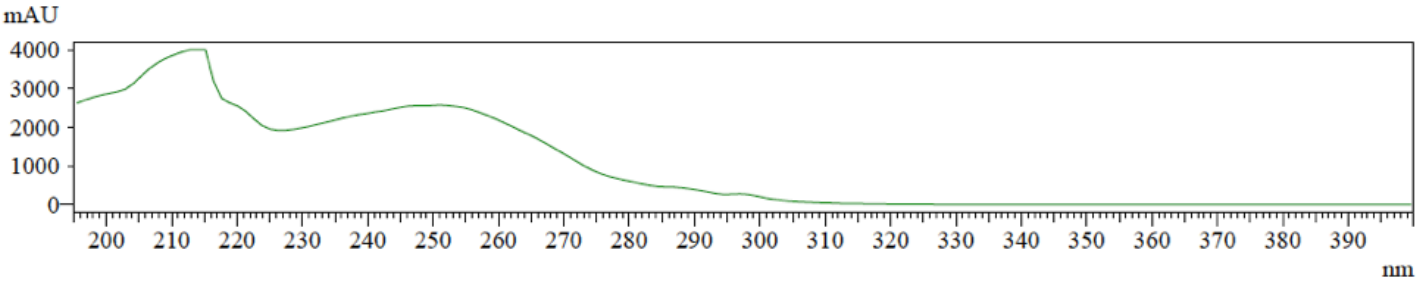
Chromatogram



UV Spectrum
Retention time = 20.730



UV Spectrum
Retention time = 23.086

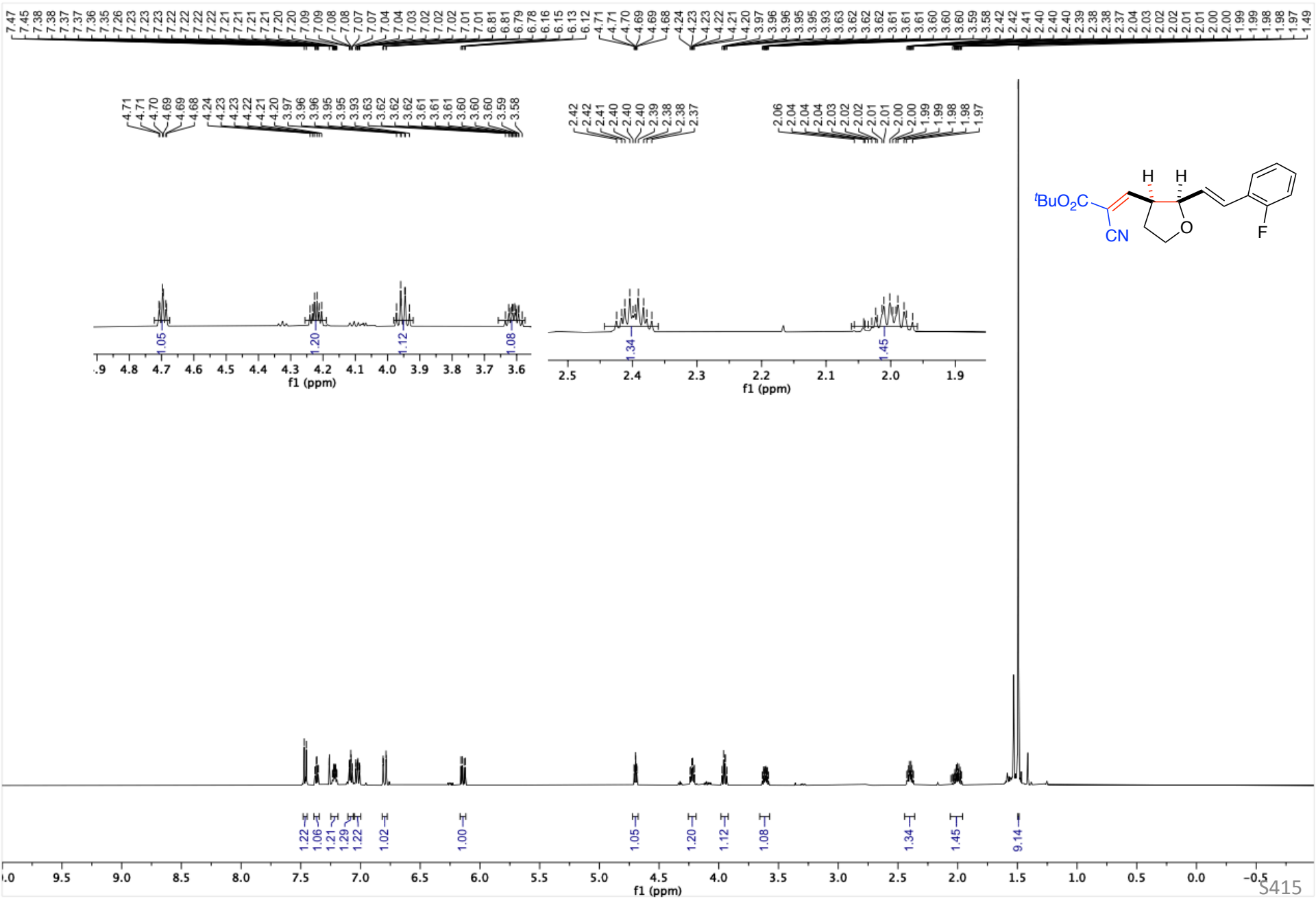


Peak Table

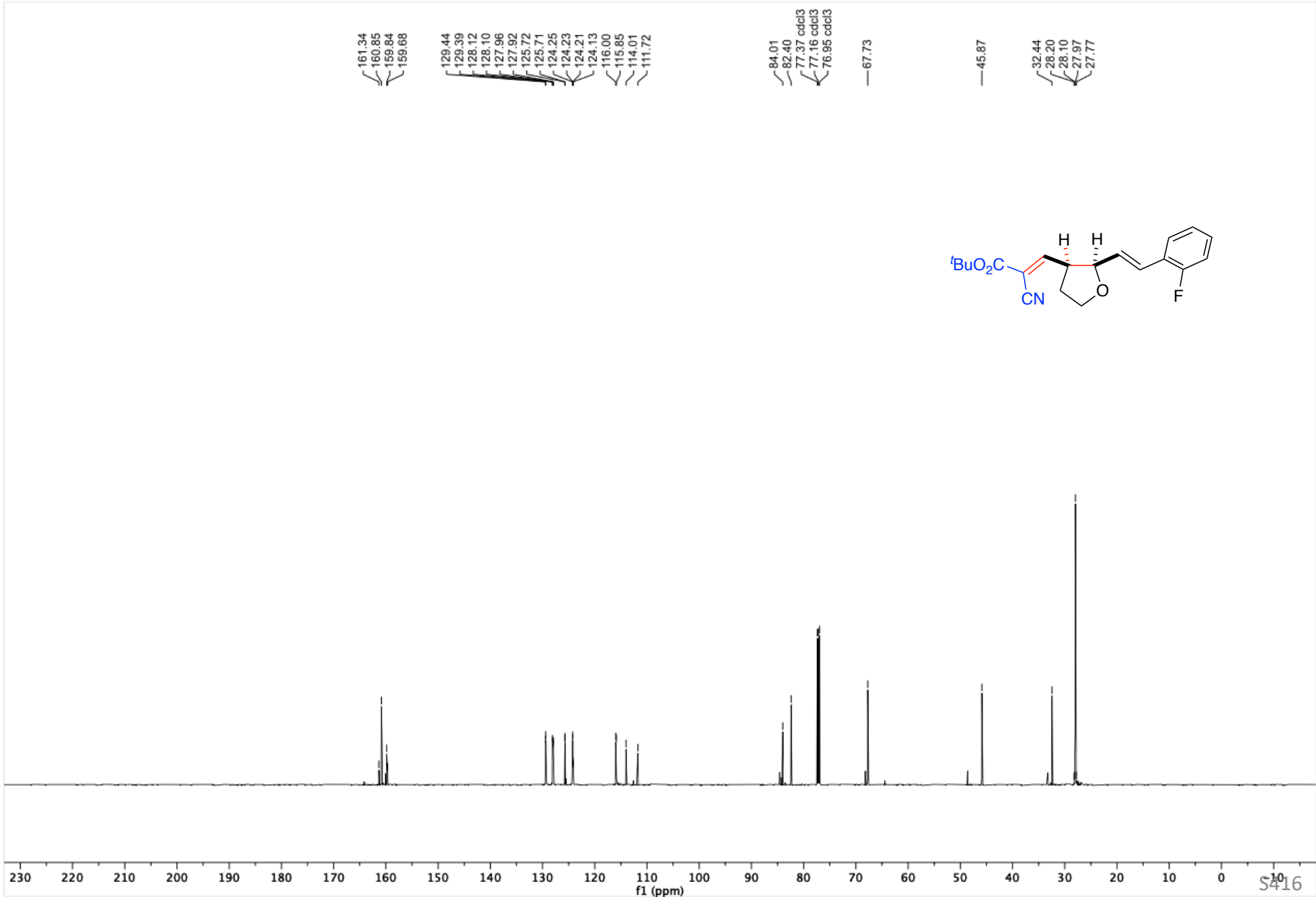
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.730	4863533	5.739
2	23.086	79888035	94.261
Total		84751568	100.000

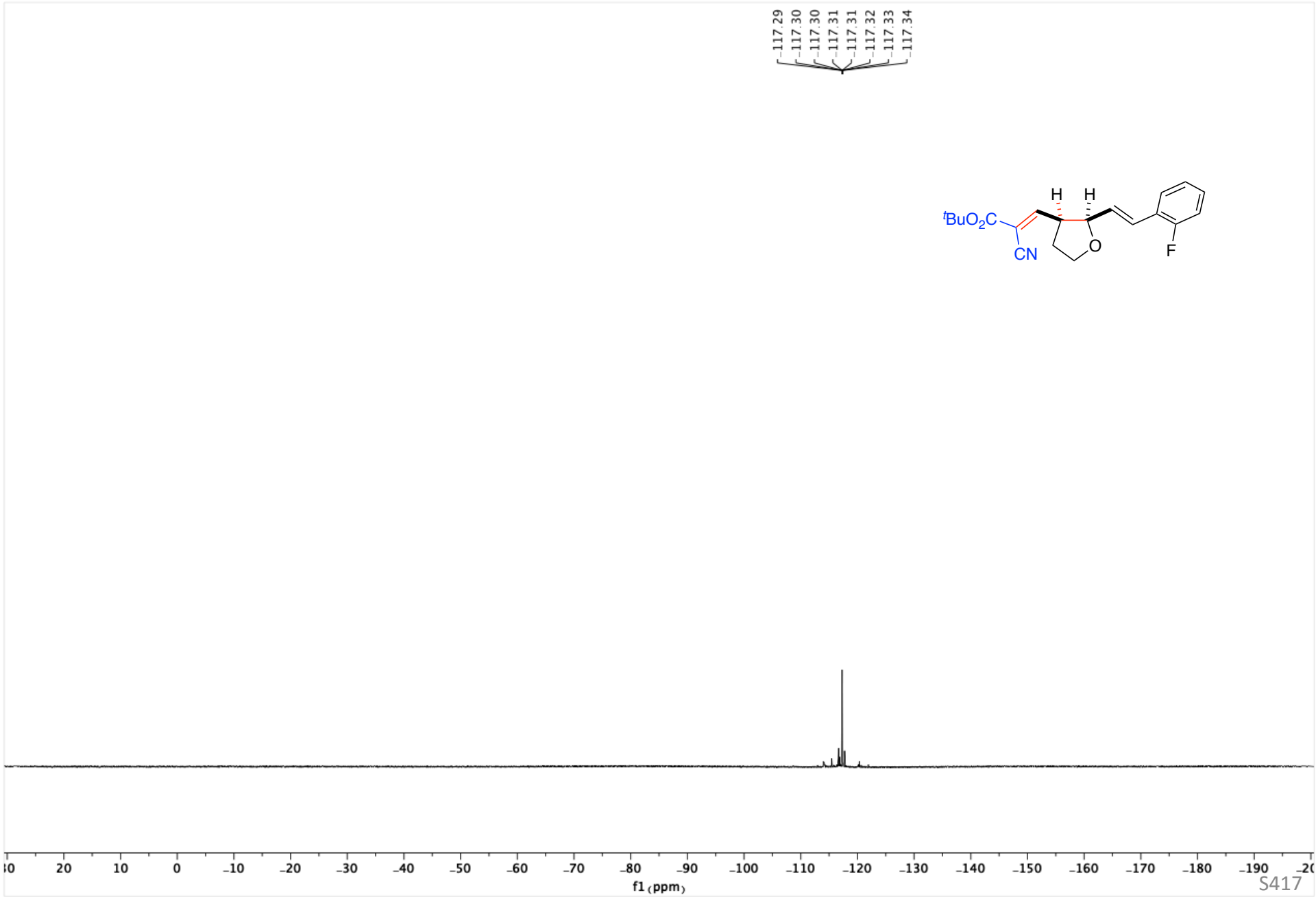
tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-fluorostyryl)tetrahydrofuran-3-yl)acrylate

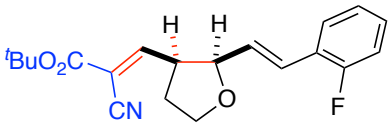


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-fluorostyryl)tetrahydrofuran-3-yl)acrylate

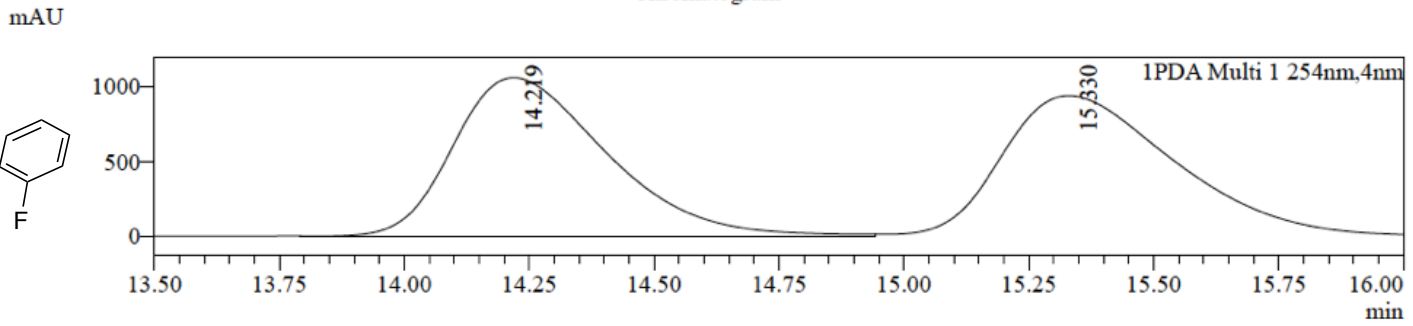


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-fluorostyryl)tetrahydrofuran-3-yl)acrylate

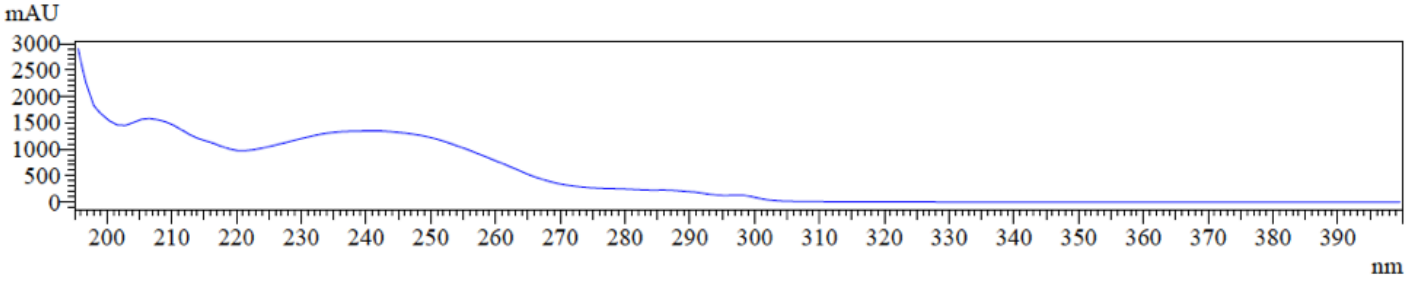




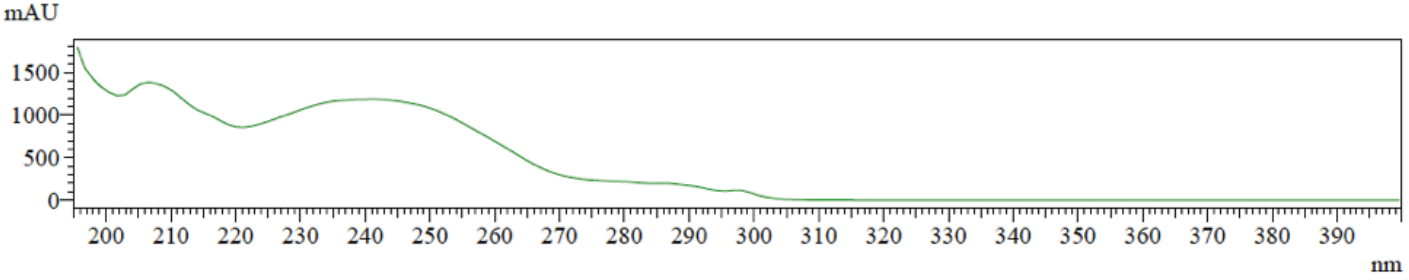
Chromatogram



UV Spectrum
Retention time = 14.219



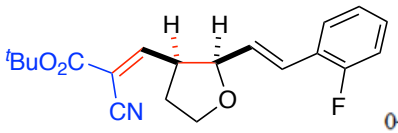
UV Spectrum
Retention time = 15.330



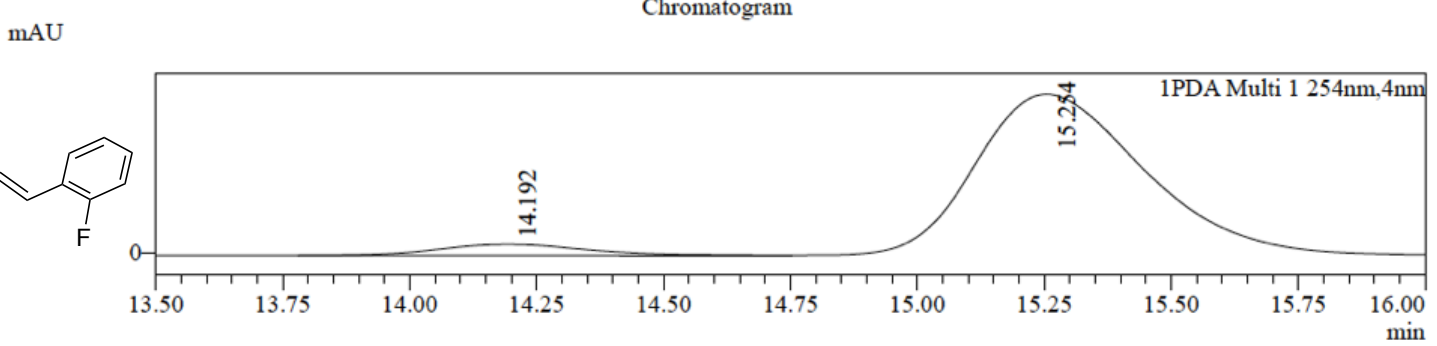
Peak Table

PDA Ch1 254nm

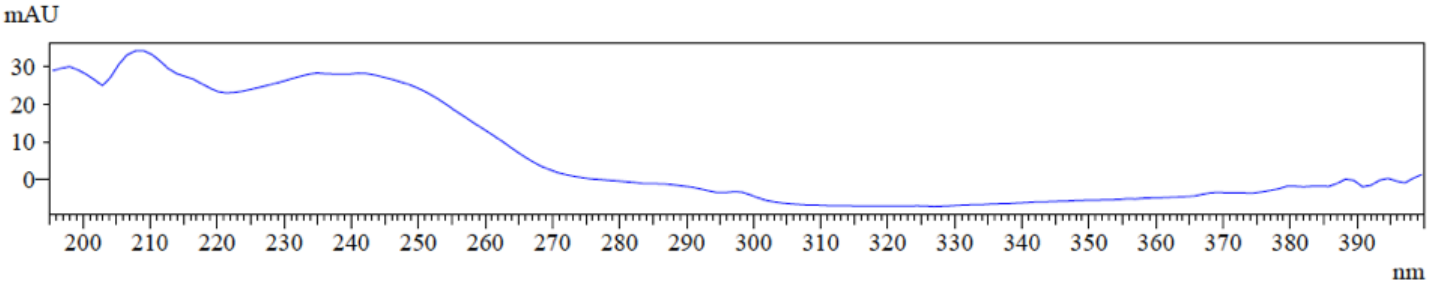
Peak#	Ret. Time	Area	Area%
1	14.219	22559171	49.912
2	15.330	22638300	50.088
Total		45197471	100.000



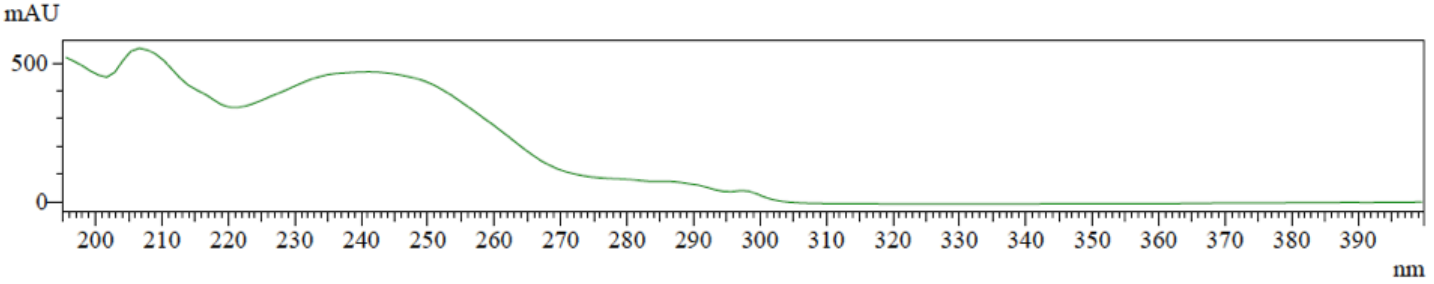
Chromatogram



UV Spectrum
Retention time = 14.192



UV Spectrum
Retention time = 15.254

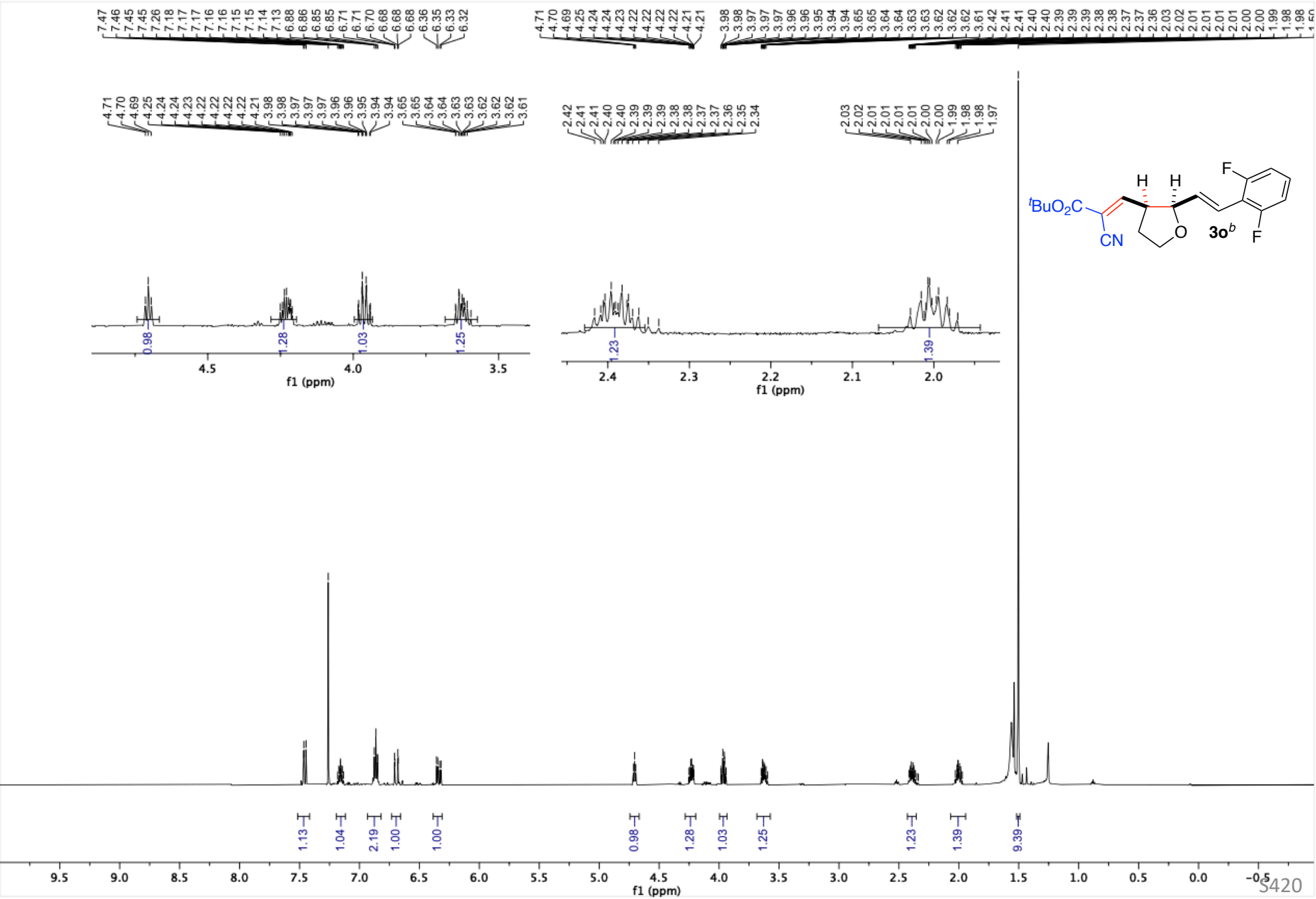


Peak Table

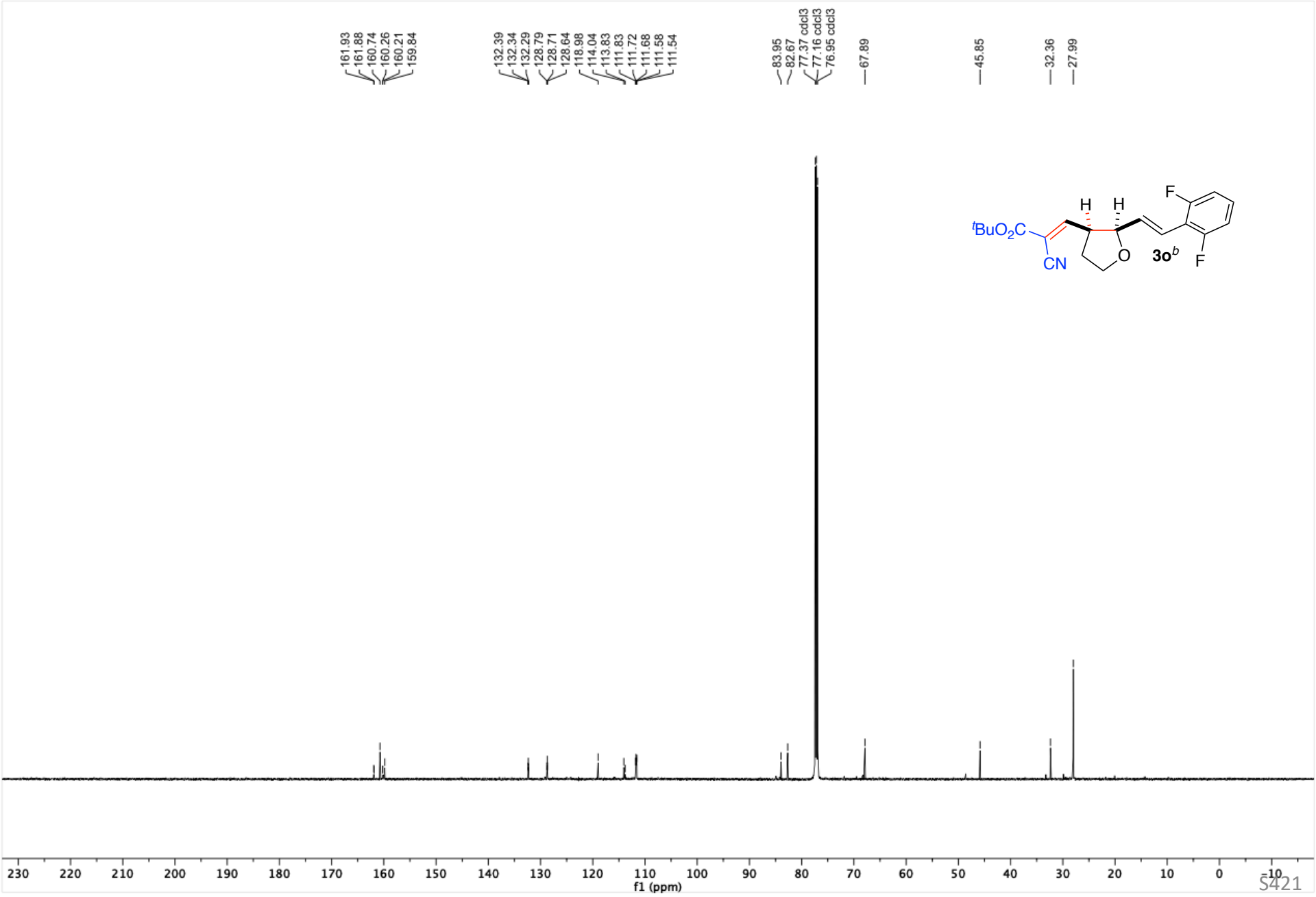
PDA Ch1 254nm

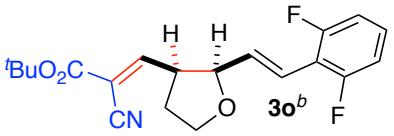
Peak#	Ret. Time	Area	Area%
1	14.192	528865	5.644
2	15.254	8841014	94.356
Total		9369880	100.000

tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2,6-difluorostyryl)tetrahydrofuran-3-yl)acrylate

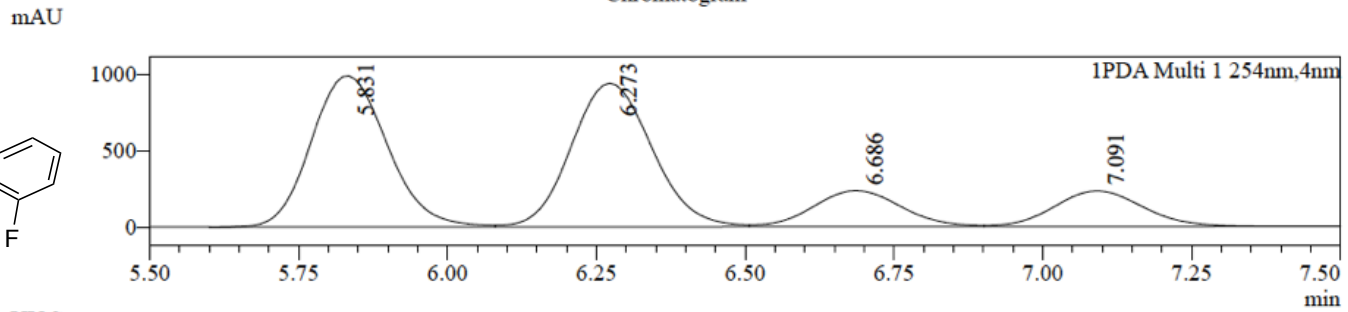


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2,6-difluorostyryl)tetrahydrofuran-3-yl)acrylate

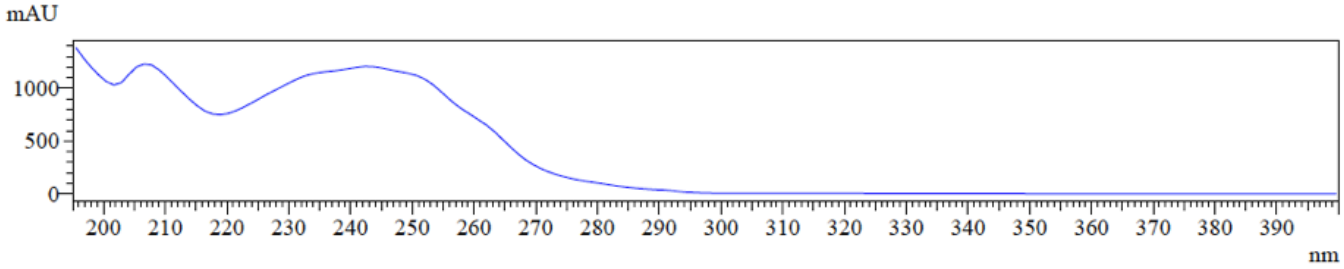




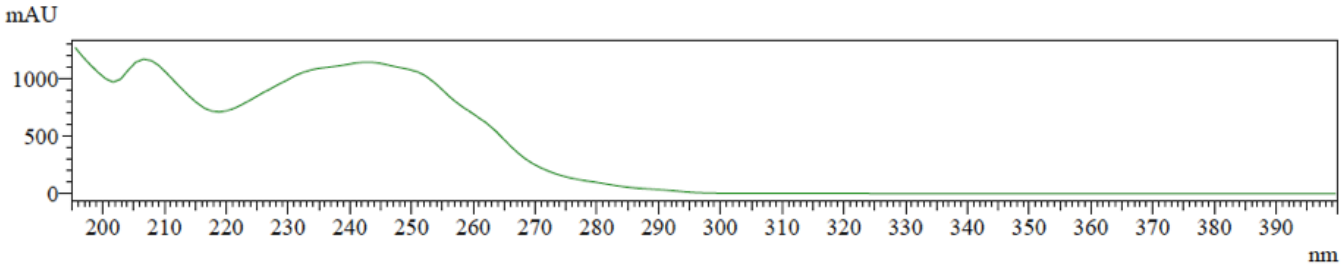
Chromatogram



UV Spectrum
Retention time = 5.831



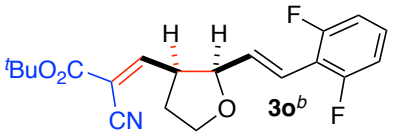
UV Spectrum
Retention time = 6.273



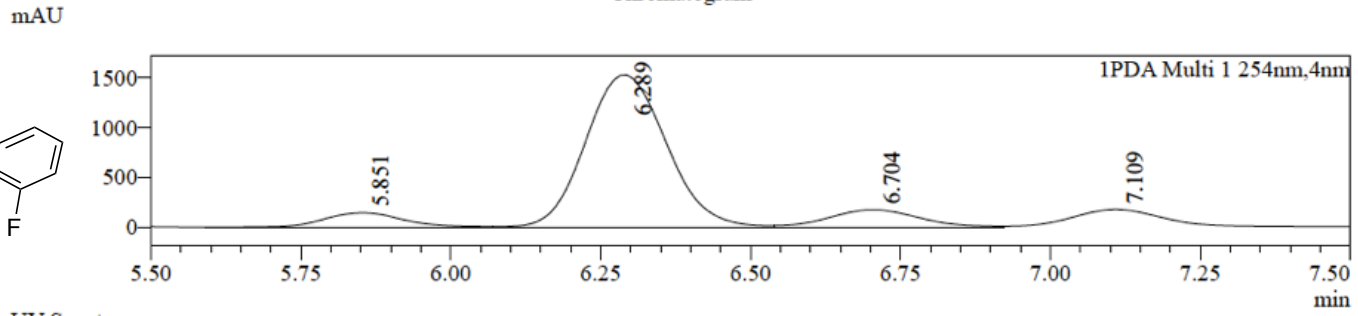
Peak Table

PDA Ch1 254nm

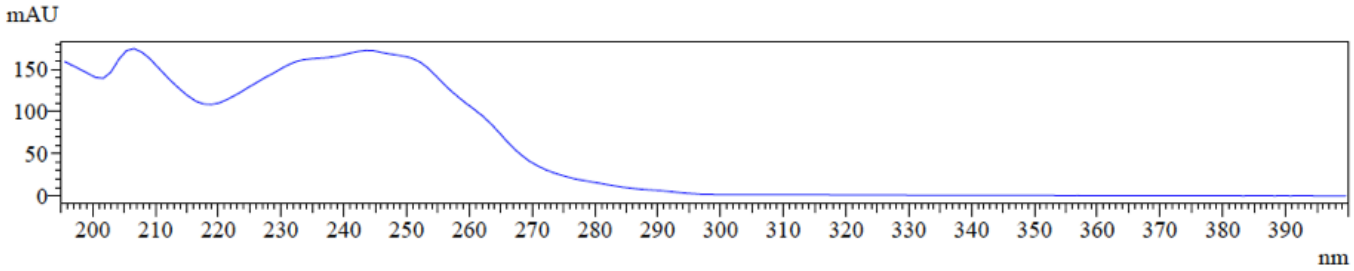
Peak#	Ret. Time	Area	Area%
1	5.831	8812009	39.045
2	6.273	8869281	39.299
3	6.686	2438902	10.807
4	7.091	2448379	10.849
Total		22568570	100.000



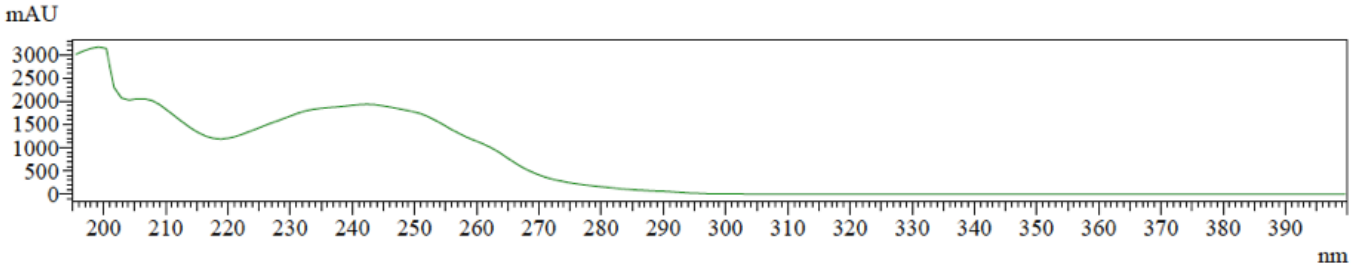
Chromatogram



UV Spectrum
Retention time = 5.851



UV Spectrum
Retention time = 6.289

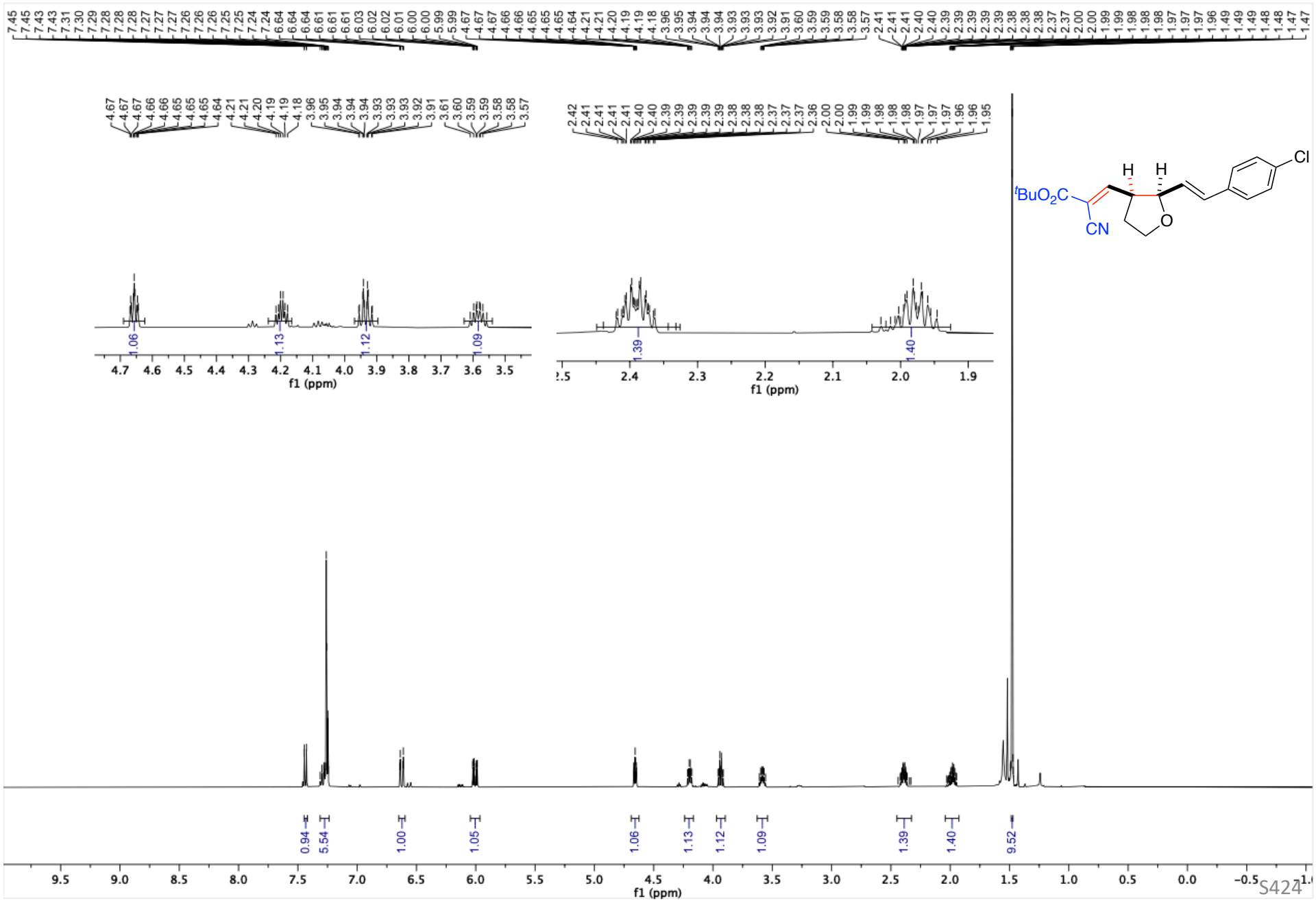


Peak Table

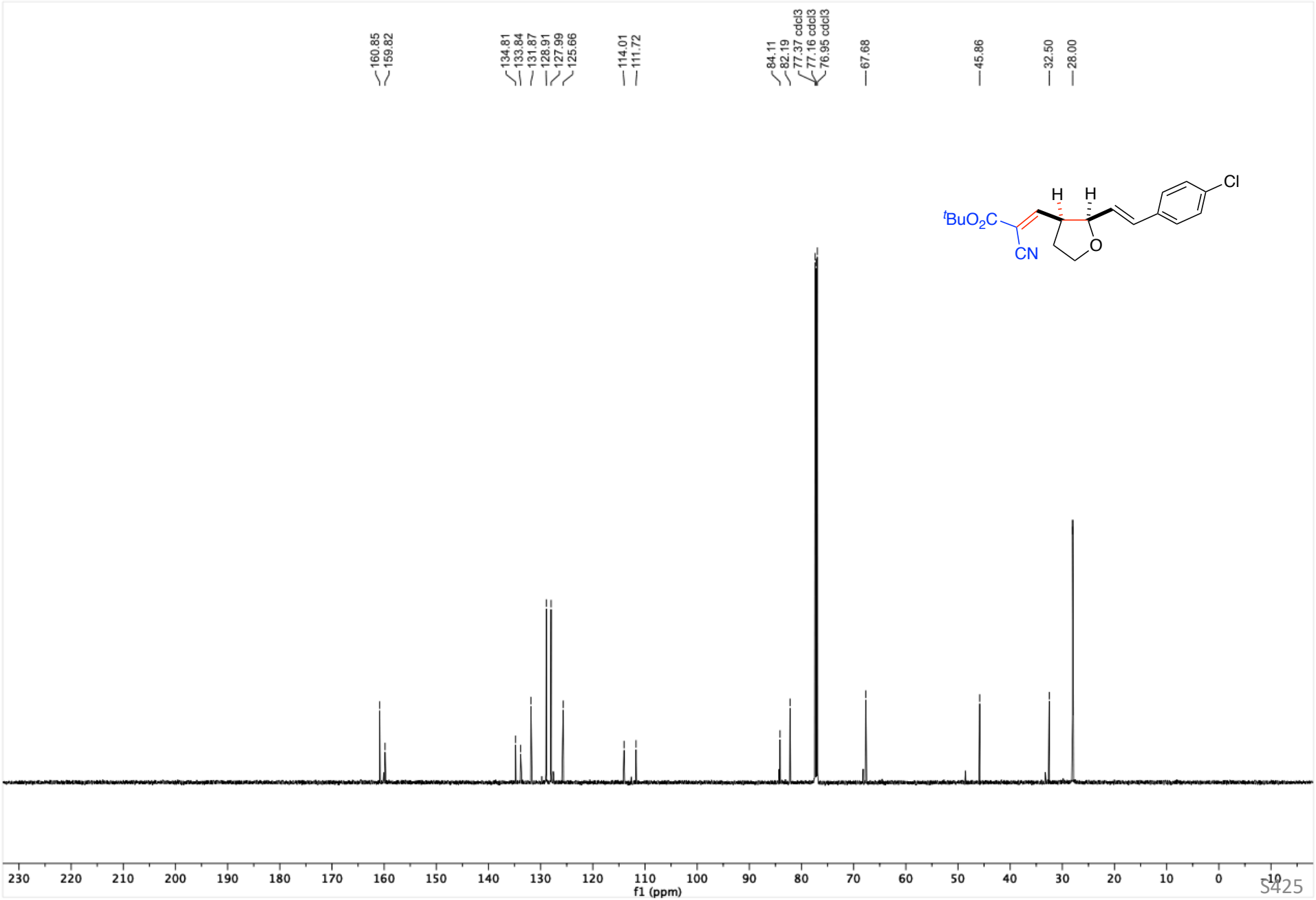
PDA Ch1 254nm

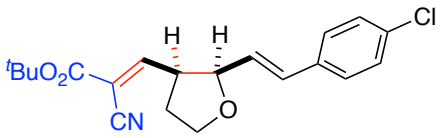
Peak#	Ret. Time	Area	Area%
1	5.851	1290144	6.693
2	6.289	14277338	74.065
3	6.704	1793257	9.303
4	7.109	1916051	9.940
Total		19276791	100.000

tert-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-chlorostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate

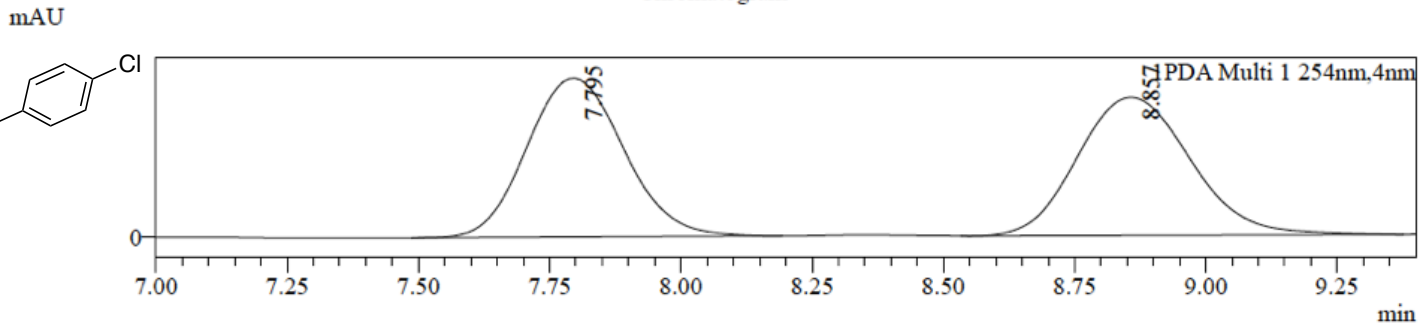


tert-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-chlorostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate

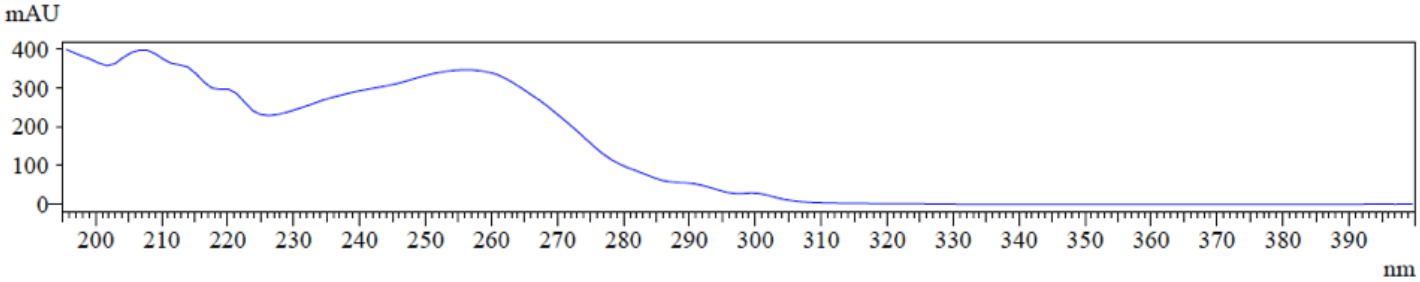




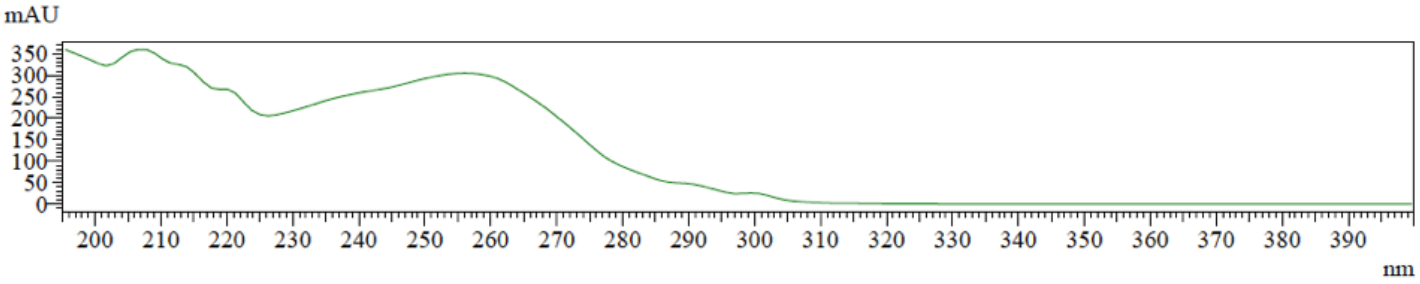
Chromatogram



UV Spectrum
Retention time = 7.795



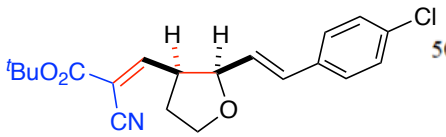
UV Spectrum
Retention time = 8.857



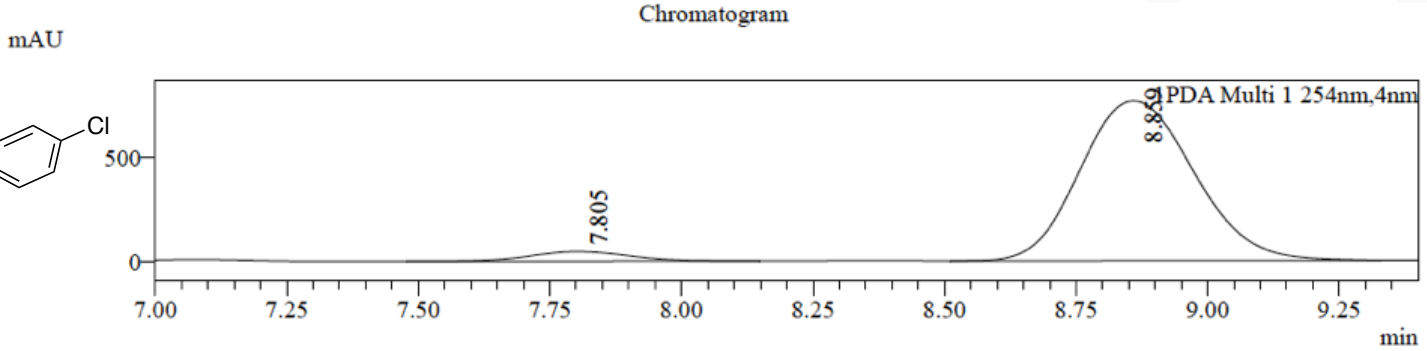
Peak Table

PDA Ch1 254nm

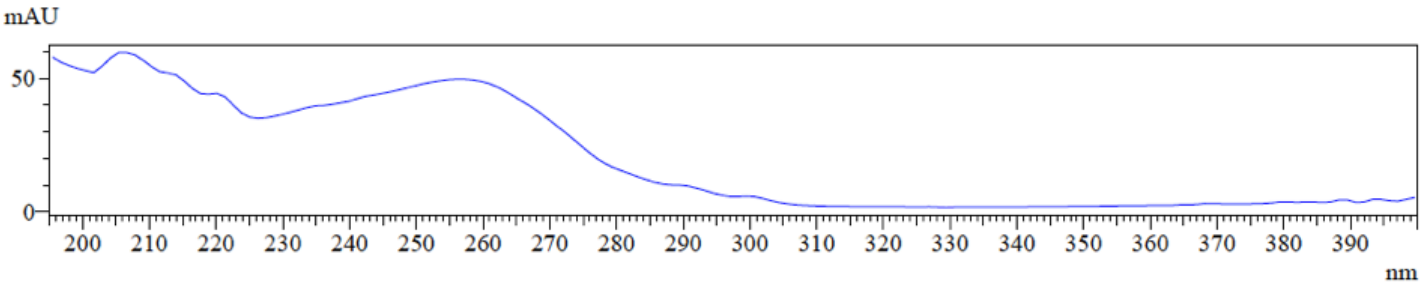
Peak#	Ret. Time	Area	Area%
1	7.795	4410753	49.658
2	8.857	4471482	50.342
Total		8882235	100.000



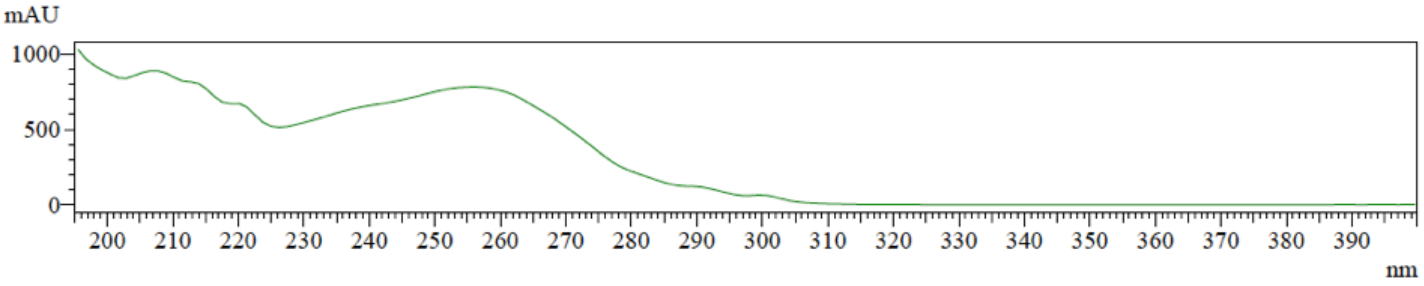
Chromatogram



UV Spectrum
Retention time = 7.805



UV Spectrum
Retention time = 8.859

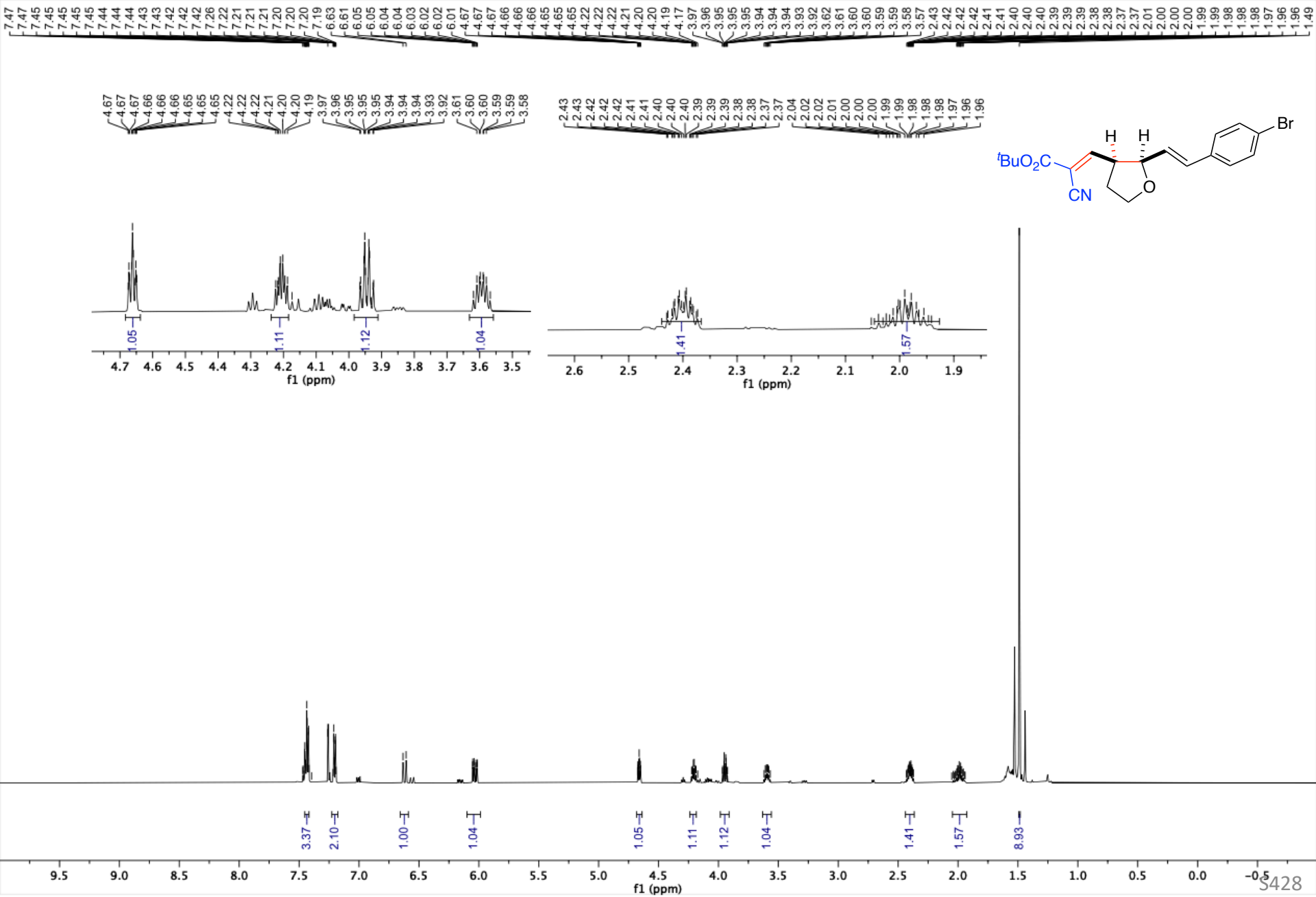


Peak Table

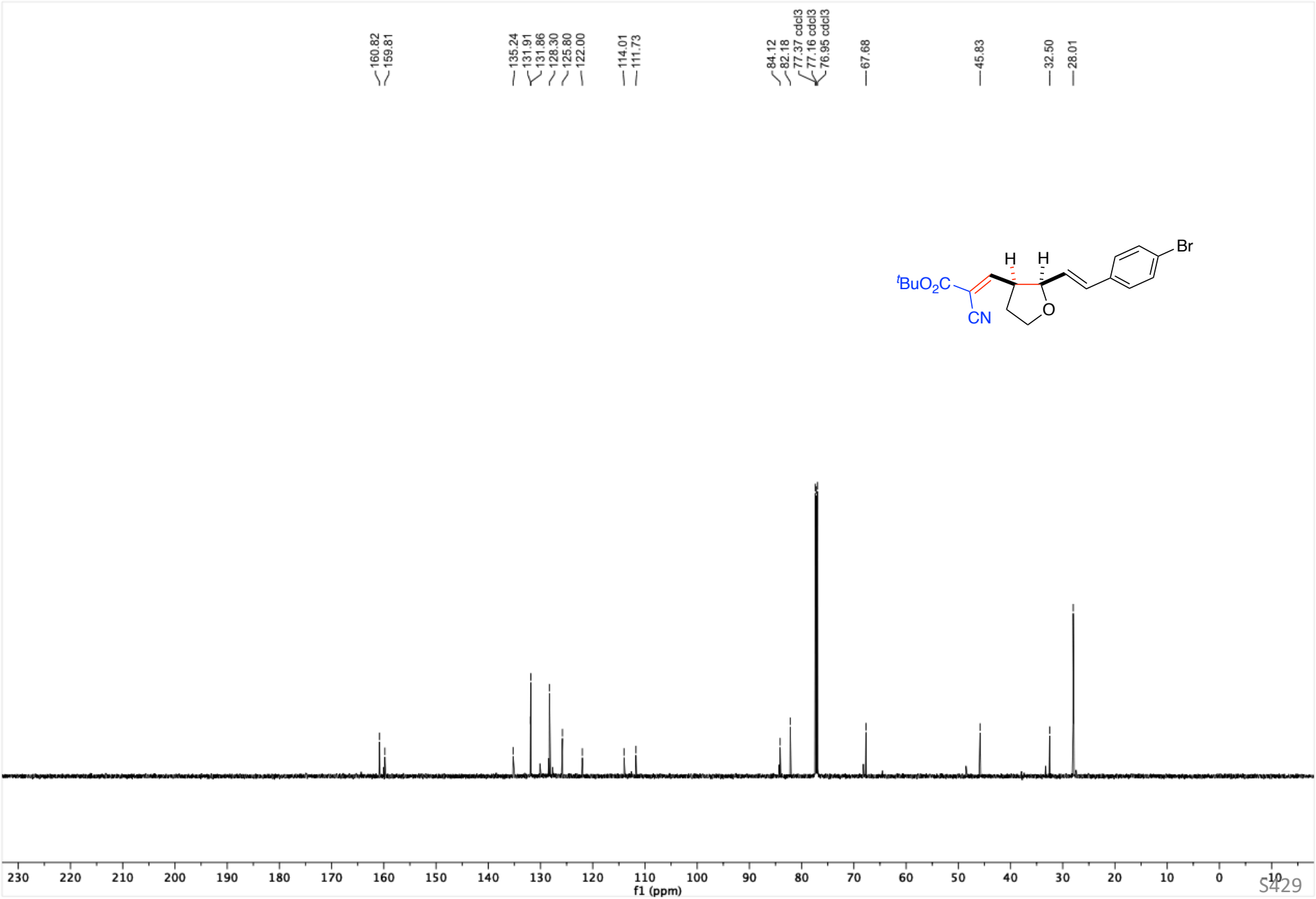
PDA Ch1 254nm

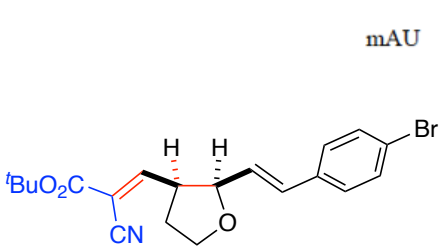
Peak#	Ret. Time	Area	Area%
1	7.805	603233	4.935
2	8.859	11620383	95.065
Total		12223616	100.000

tert-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-bromostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate

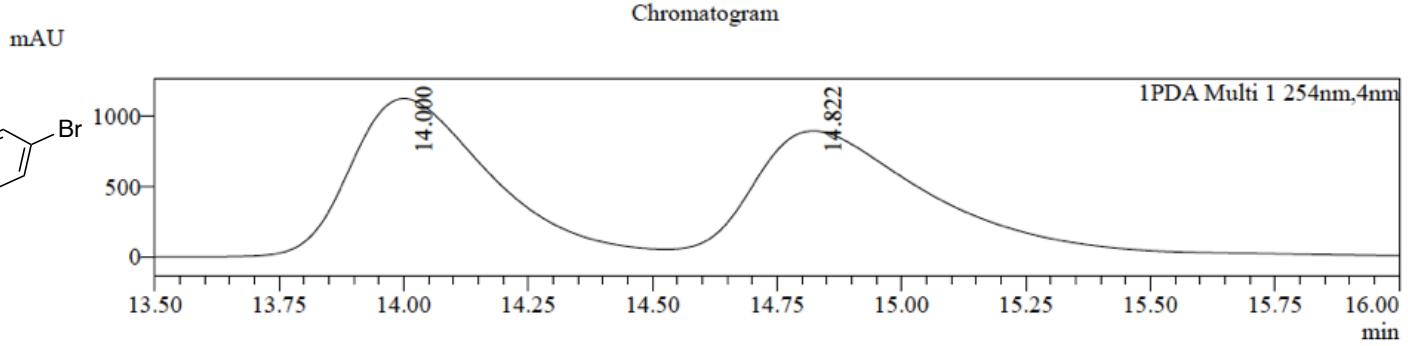


tert-Butyl (*E*)-3-((2*R*,3*S*)-2-((*E*)-4-bromostyryl)tetrahydrofuran-3-yl)-2-cyanoacrylate

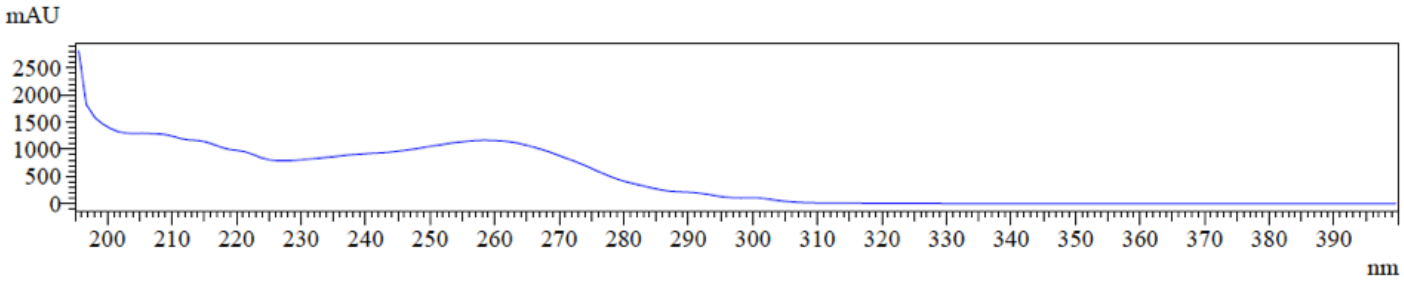




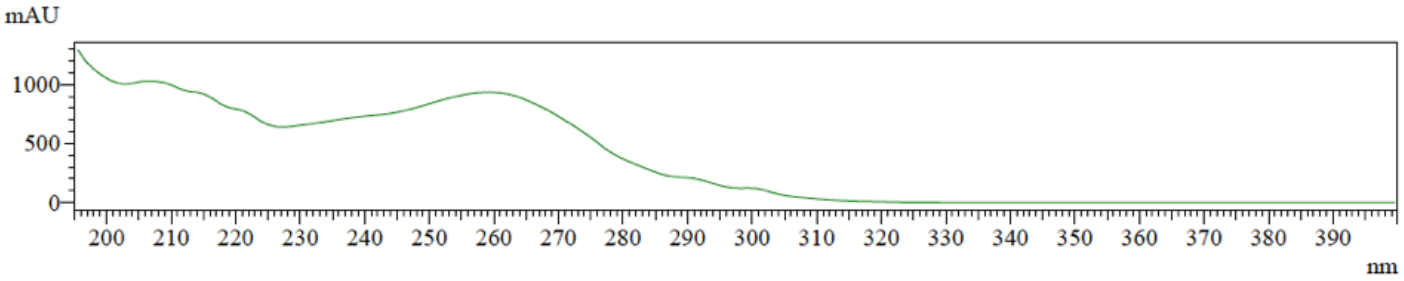
Chromatogram



UV Spectrum
Retention time = 14.000



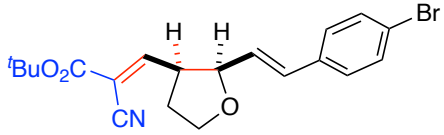
UV Spectrum
Retention time = 14.822



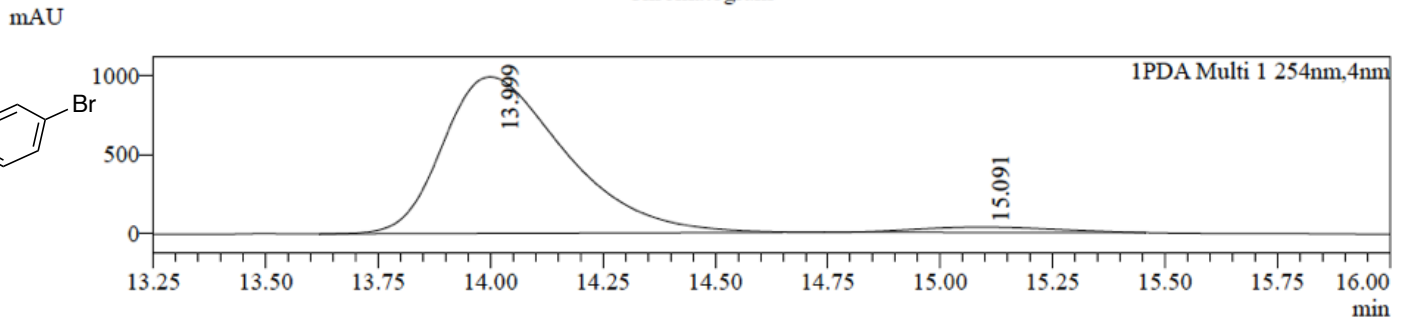
Peak Table

PDA Ch1 254nm

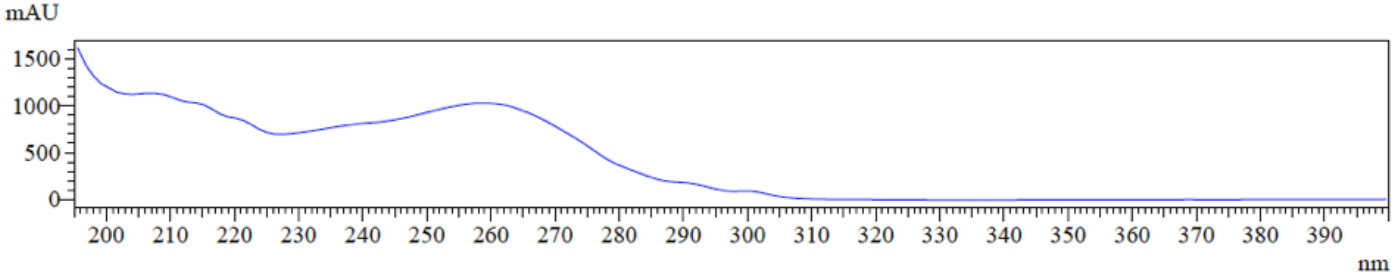
Peak#	Ret. Time	Area	Area%
1	14.000	22135789	49.275
2	14.822	22787511	50.725
Total		44923300	100.000



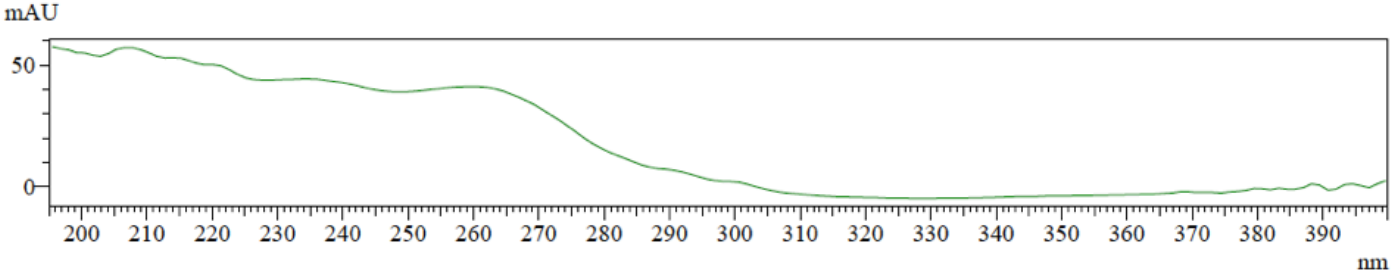
Chromatogram



UV Spectrum
Retention time = 13.999



UV Spectrum
Retention time = 15.091

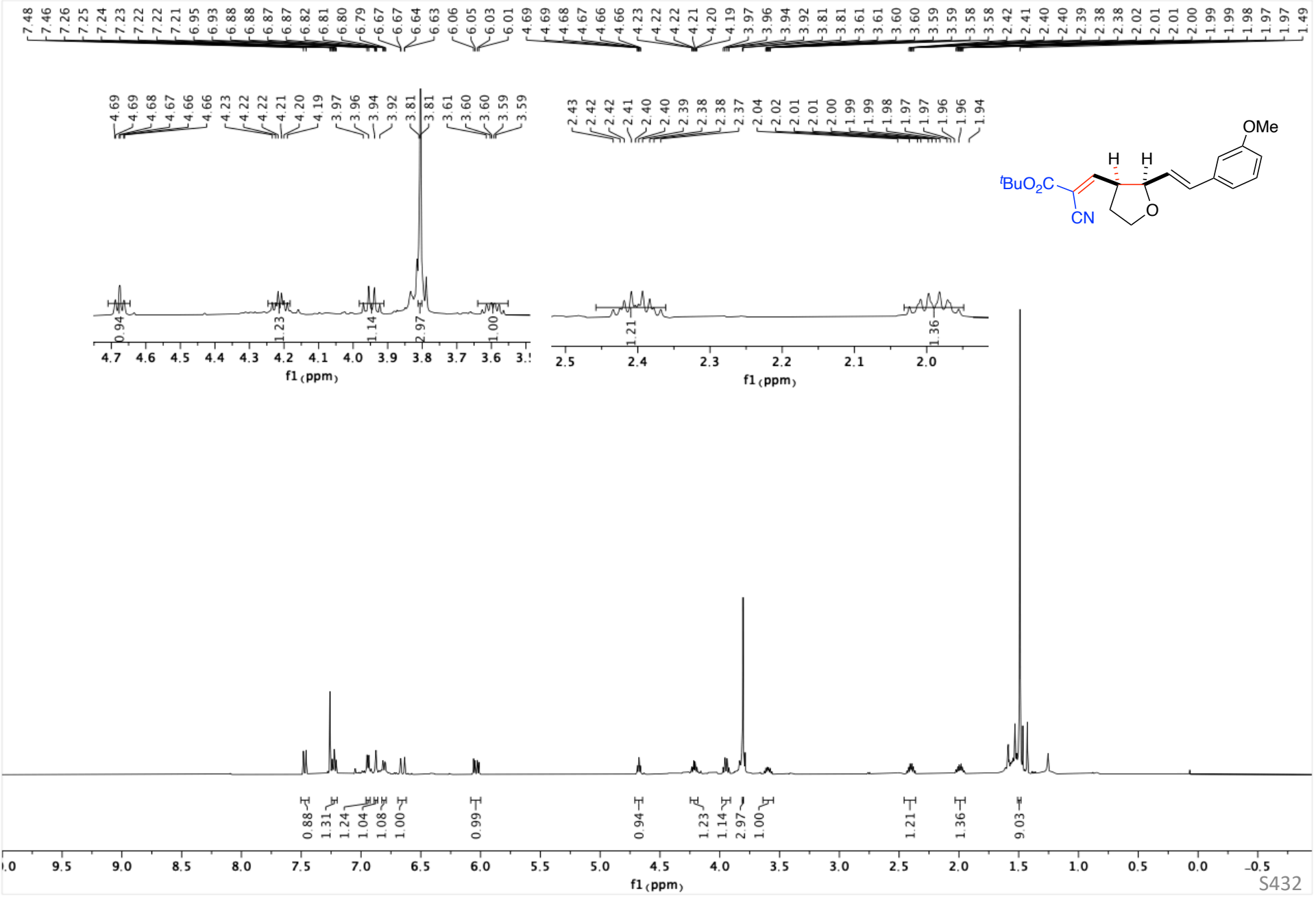


Peak Table

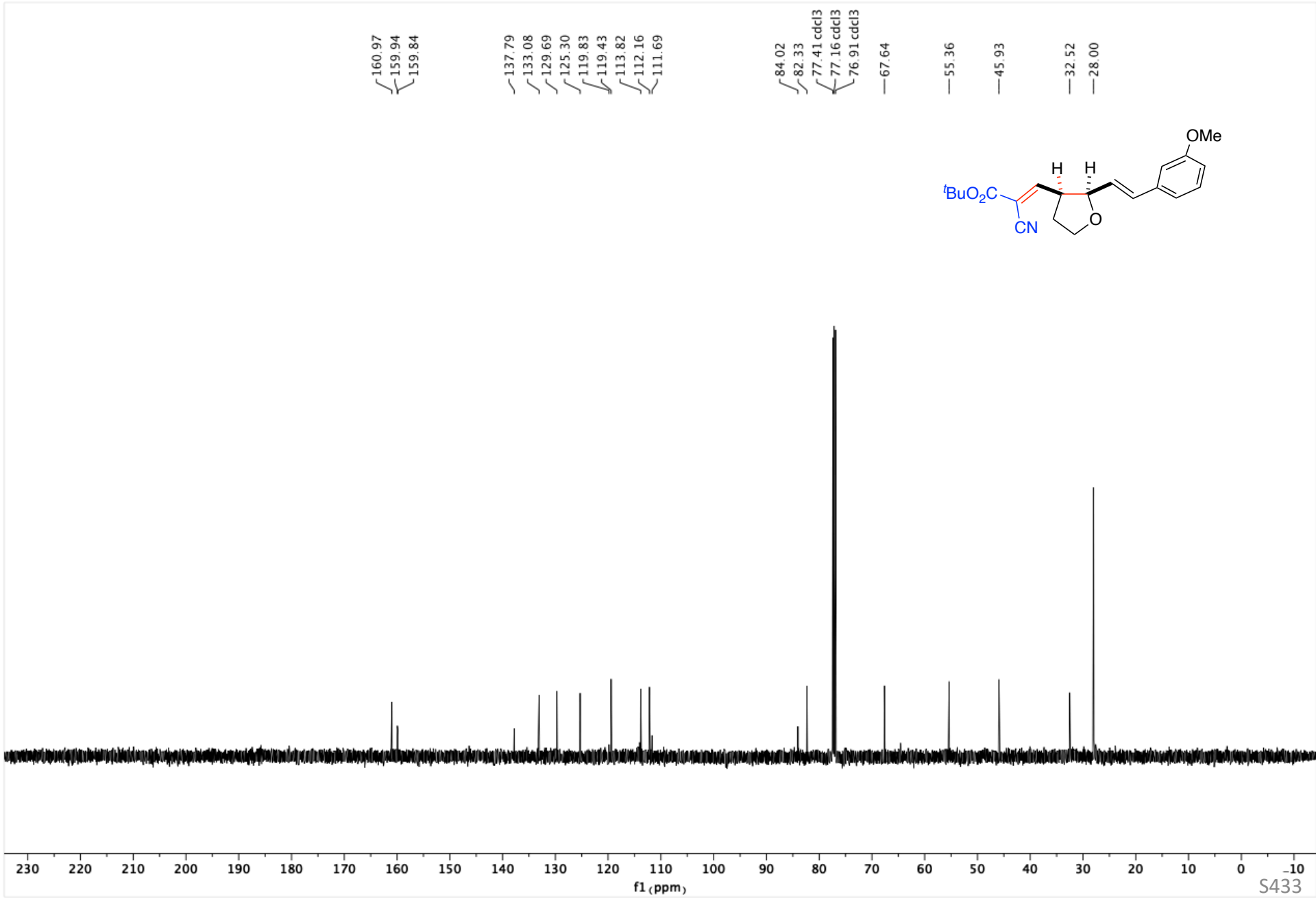
PDA Ch1 254nm

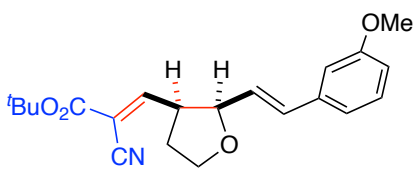
Peak#	Ret. Time	Area	Area%
1	13.999	18742466	96.366
2	15.091	706831	3.634
Total		19449297	100.000

tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-3-methoxystyryl)tetrahydrofuran-3-yl)acrylate

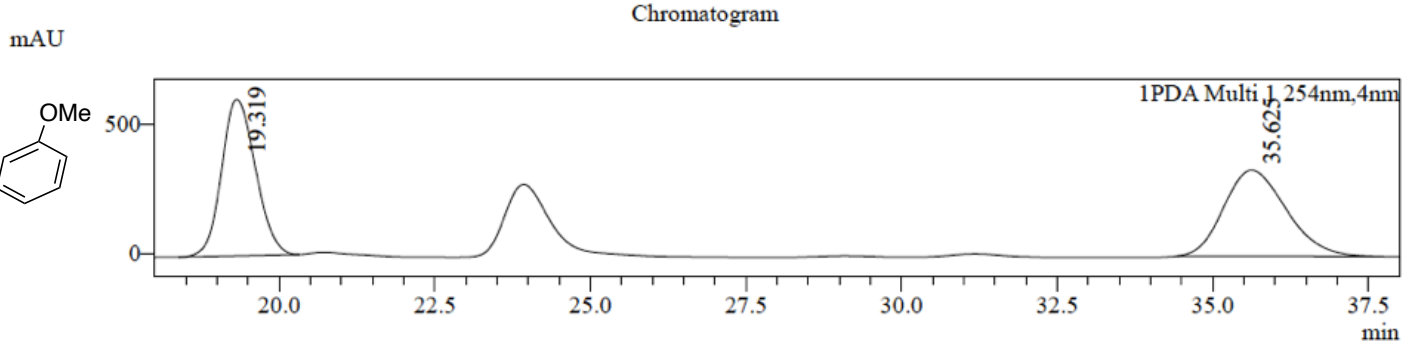


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-3-methoxystyryl)tetrahydrofuran-3-yl)acrylate

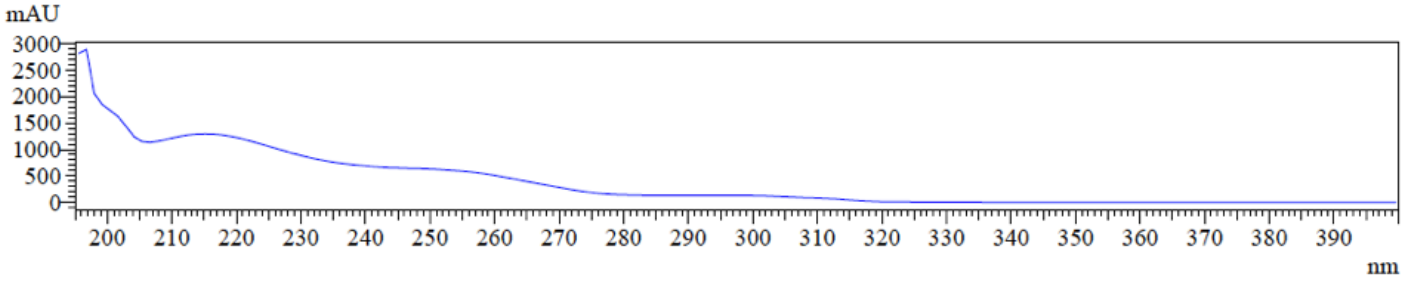




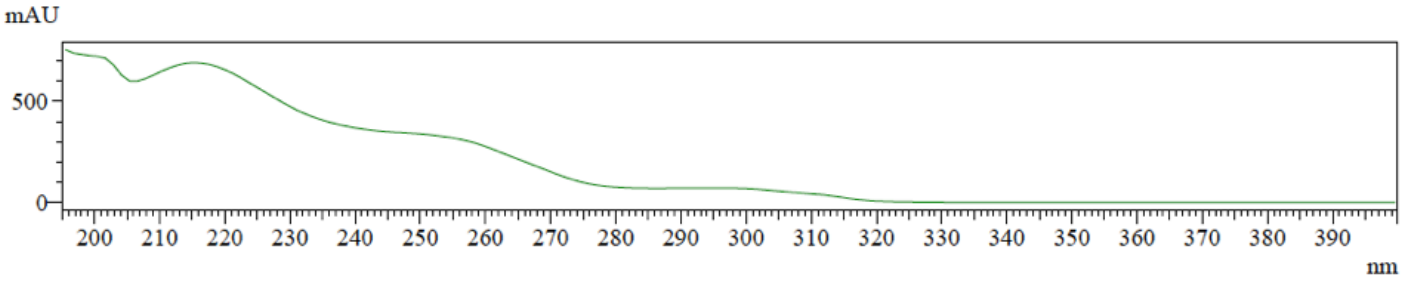
Chromatogram



UV Spectrum
Retention time = 19.319



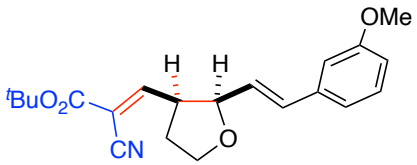
UV Spectrum
Retention time = 35.625



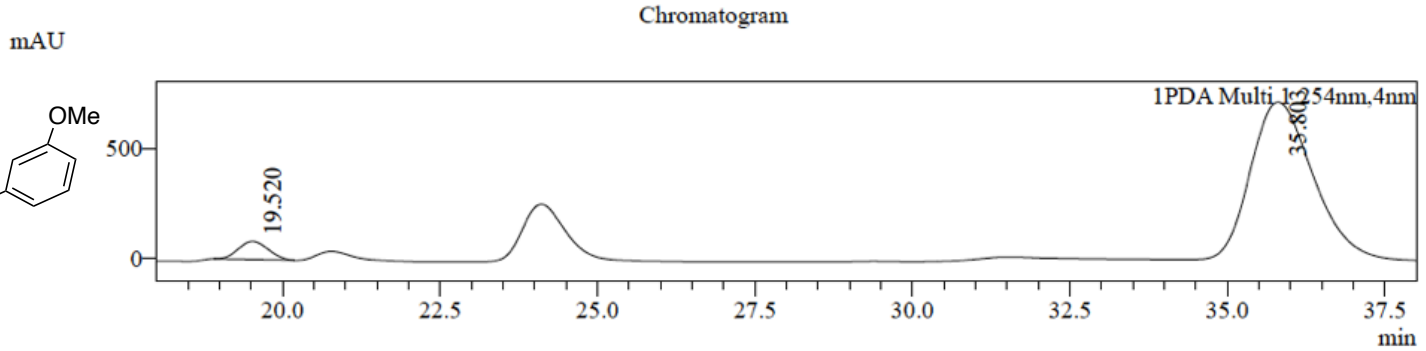
Peak Table

PDA Ch1 254nm

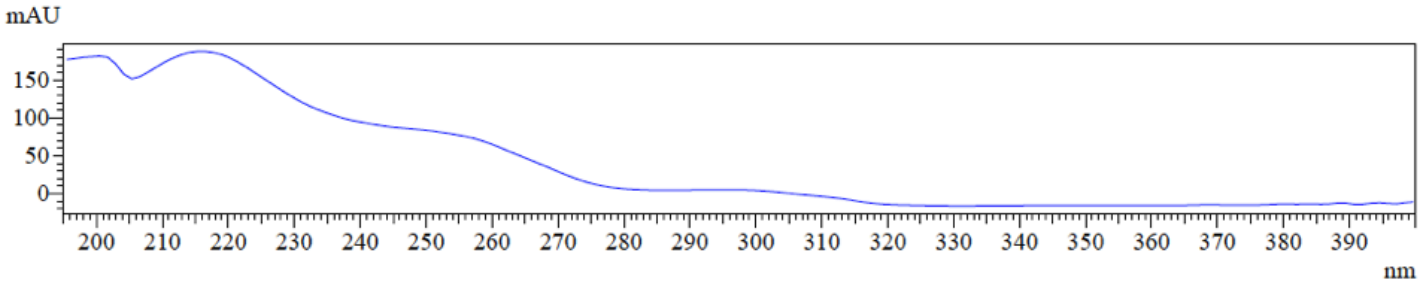
Peak#	Ret. Time	Area	Area%
1	19.319	22938220	49.738
2	35.625	23179474	50.262
Total		46117694	100.000



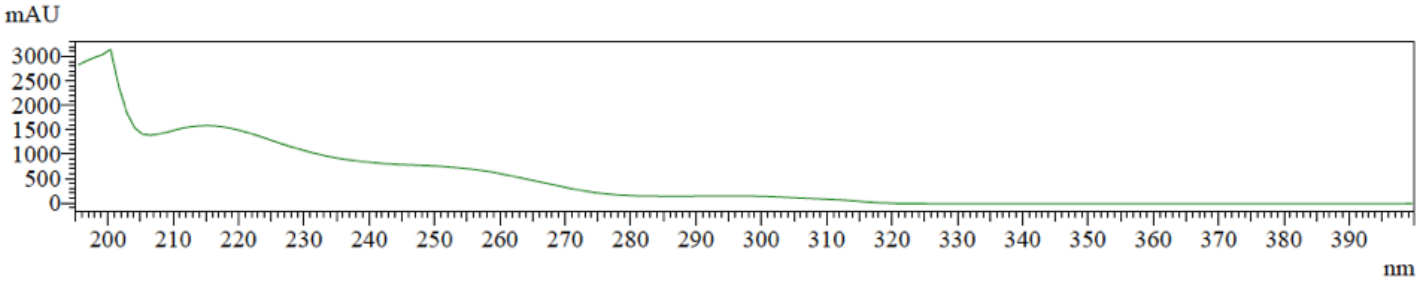
Chromatogram



UV Spectrum
Retention time = 19.520



UV Spectrum
Retention time = 35.803

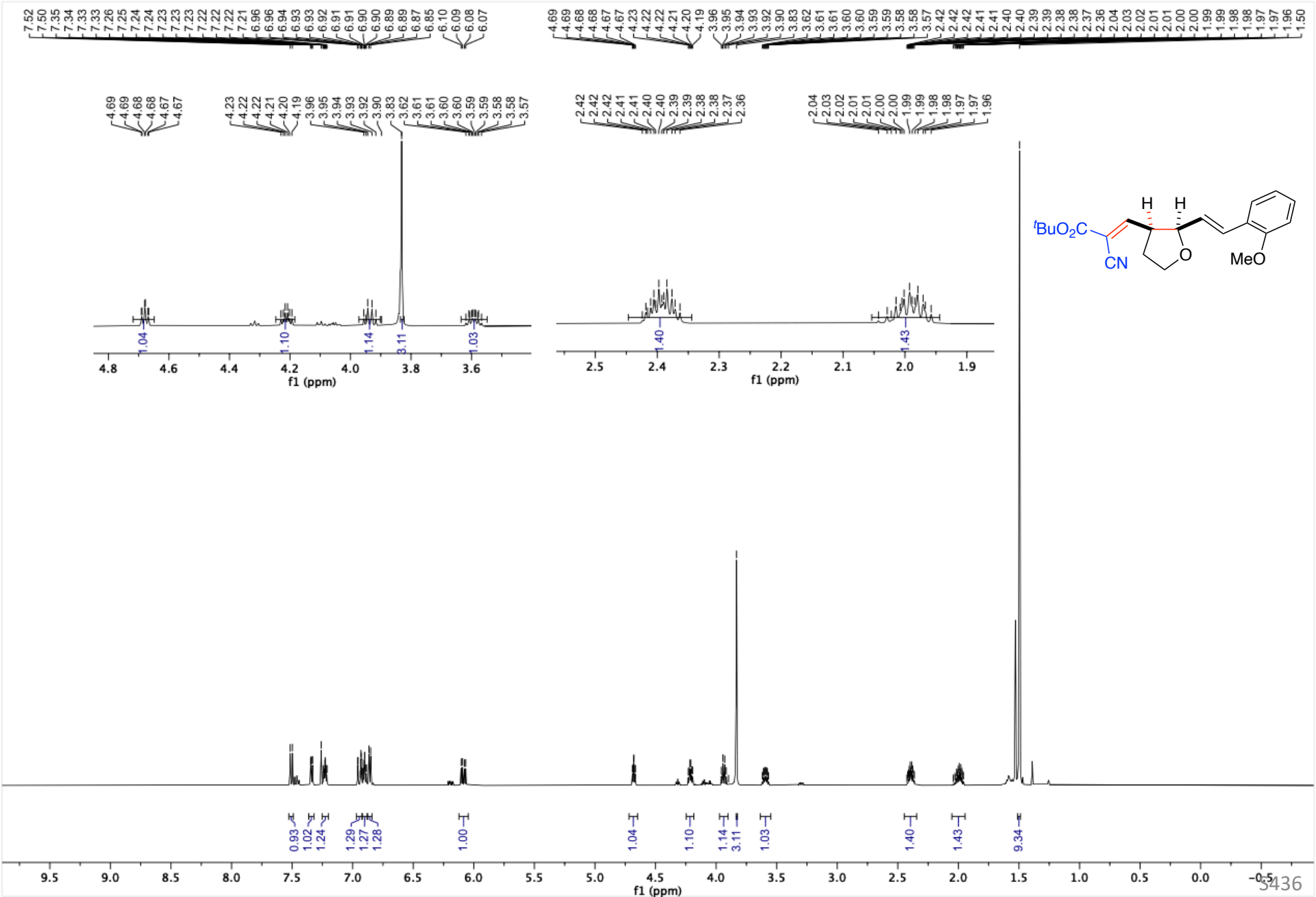


Peak Table

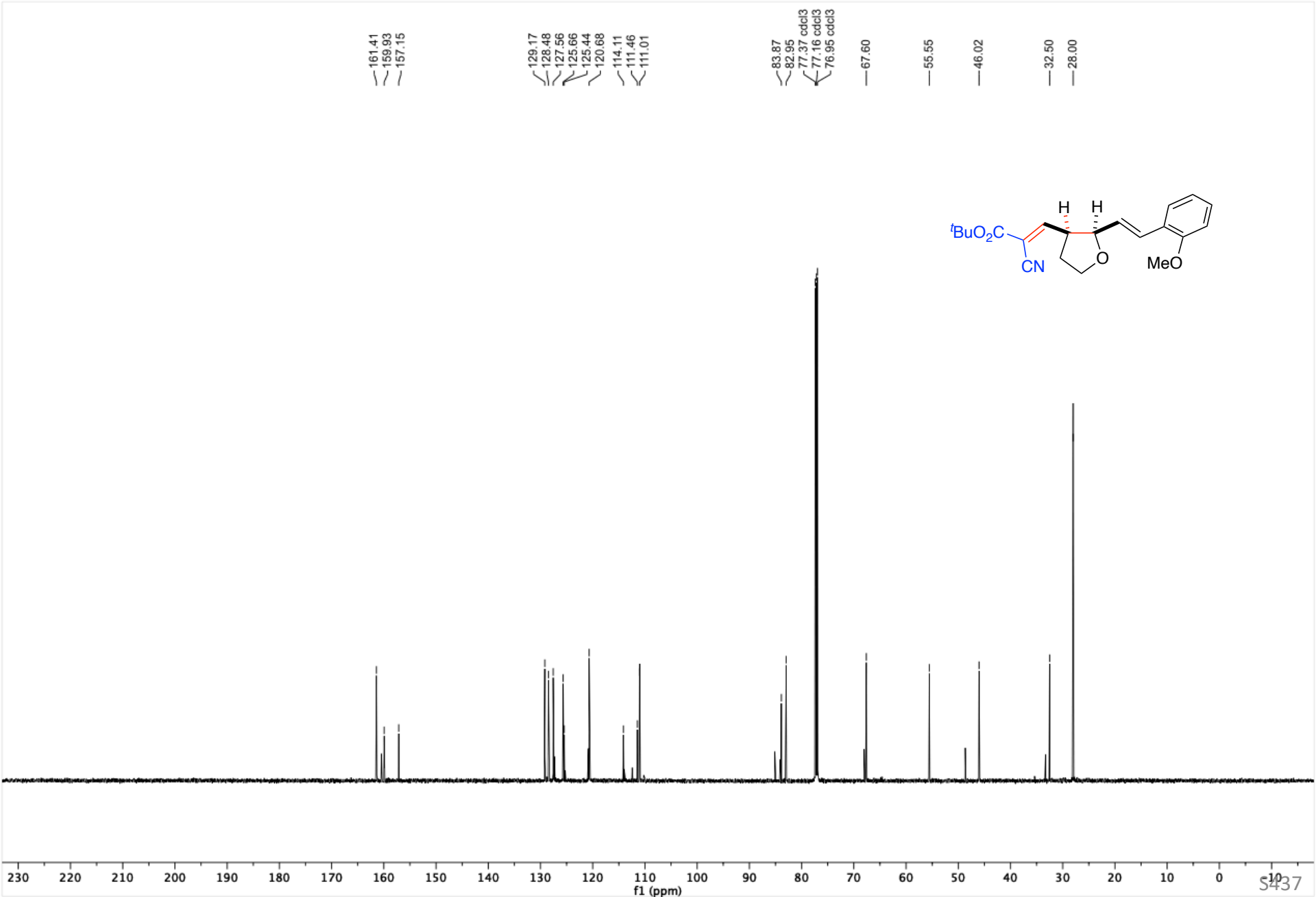
PDA Ch1 254nm

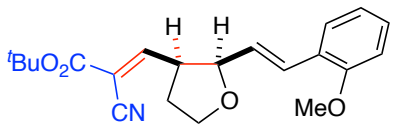
Peak#	Ret. Time	Area	Area%
1	19.520	2700900	5.135
2	35.803	49899618	94.865
Total		52600518	100.000

tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-methoxystyryl)tetrahydrofuran-3-yl)acrylate

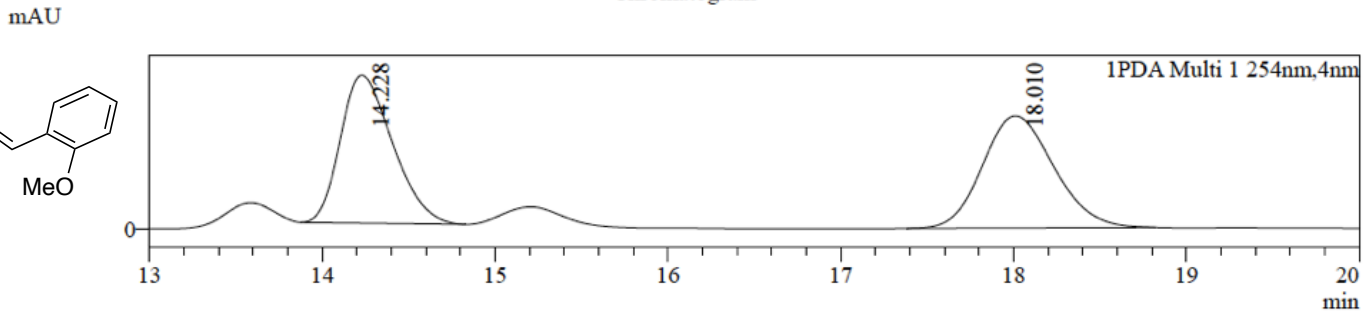


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-methoxystyryl)tetrahydrofuran-3-yl)acrylate

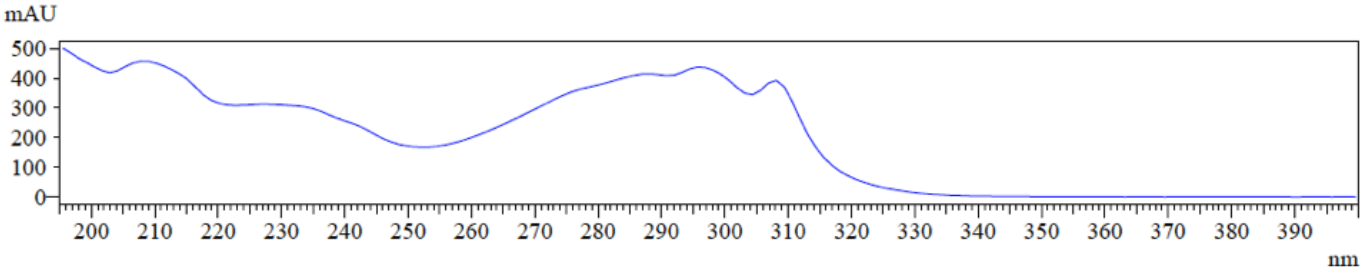




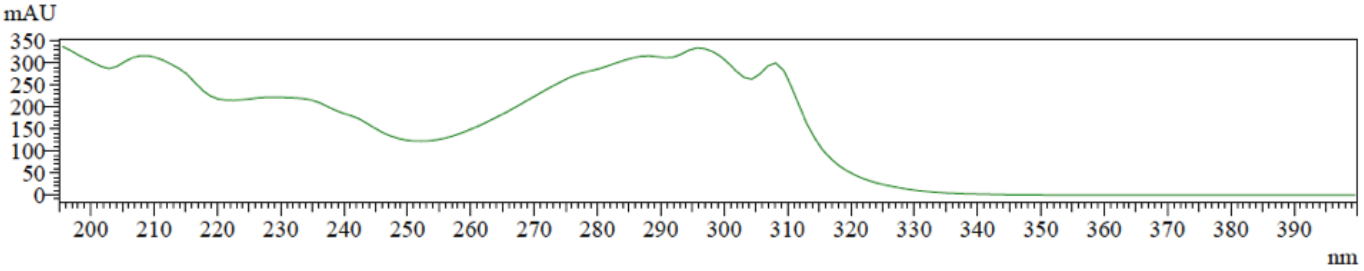
Chromatogram



UV Spectrum
Retention time = 14.228



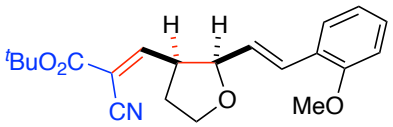
UV Spectrum
Retention time = 18.010



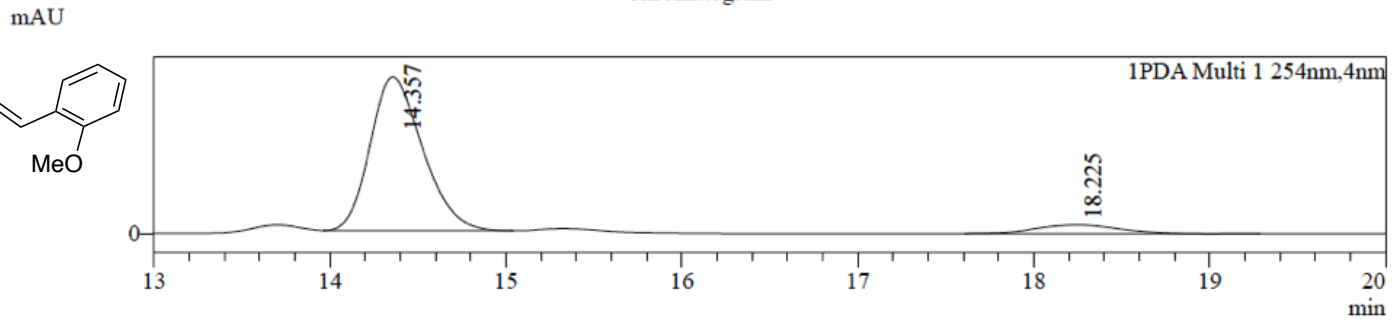
Peak Table

PDA Ch1 254nm

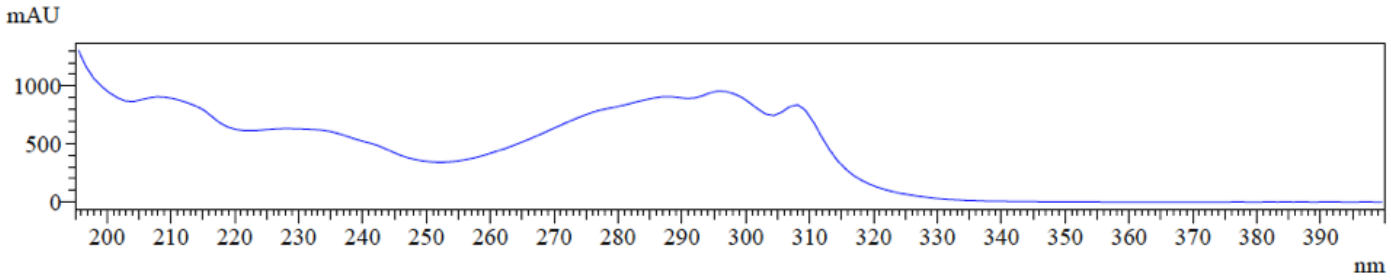
Peak#	Ret. Time	Area	Area%
1	14.228	3439676	49.083
2	18.010	3568145	50.917
Total		7007821	100.000



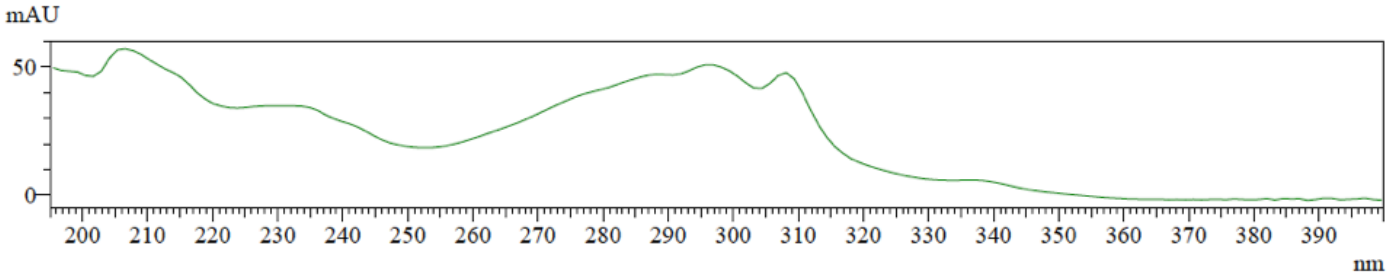
Chromatogram



UV Spectrum
Retention time = 14.357



UV Spectrum
Retention time = 18.225

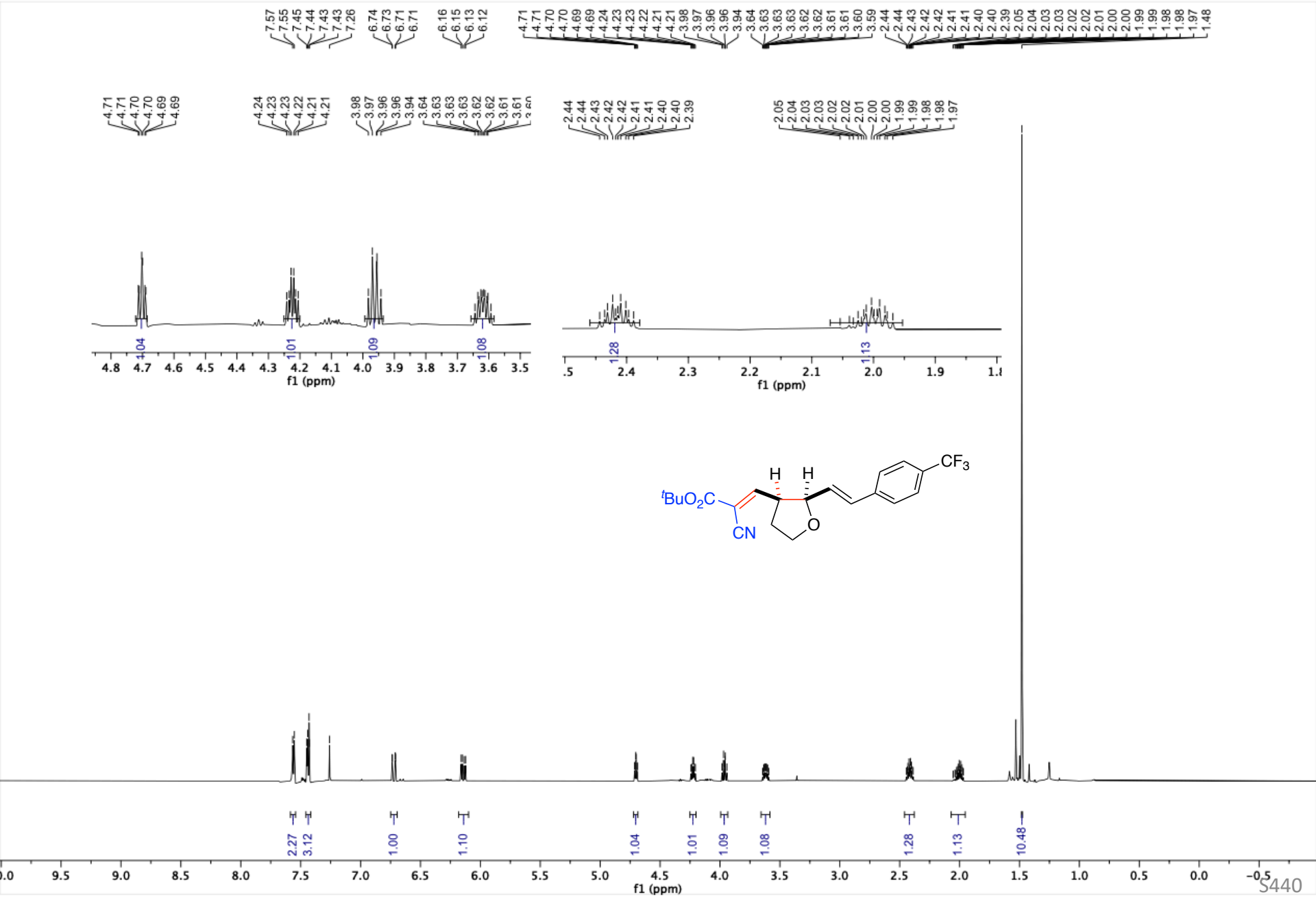


Peak Table

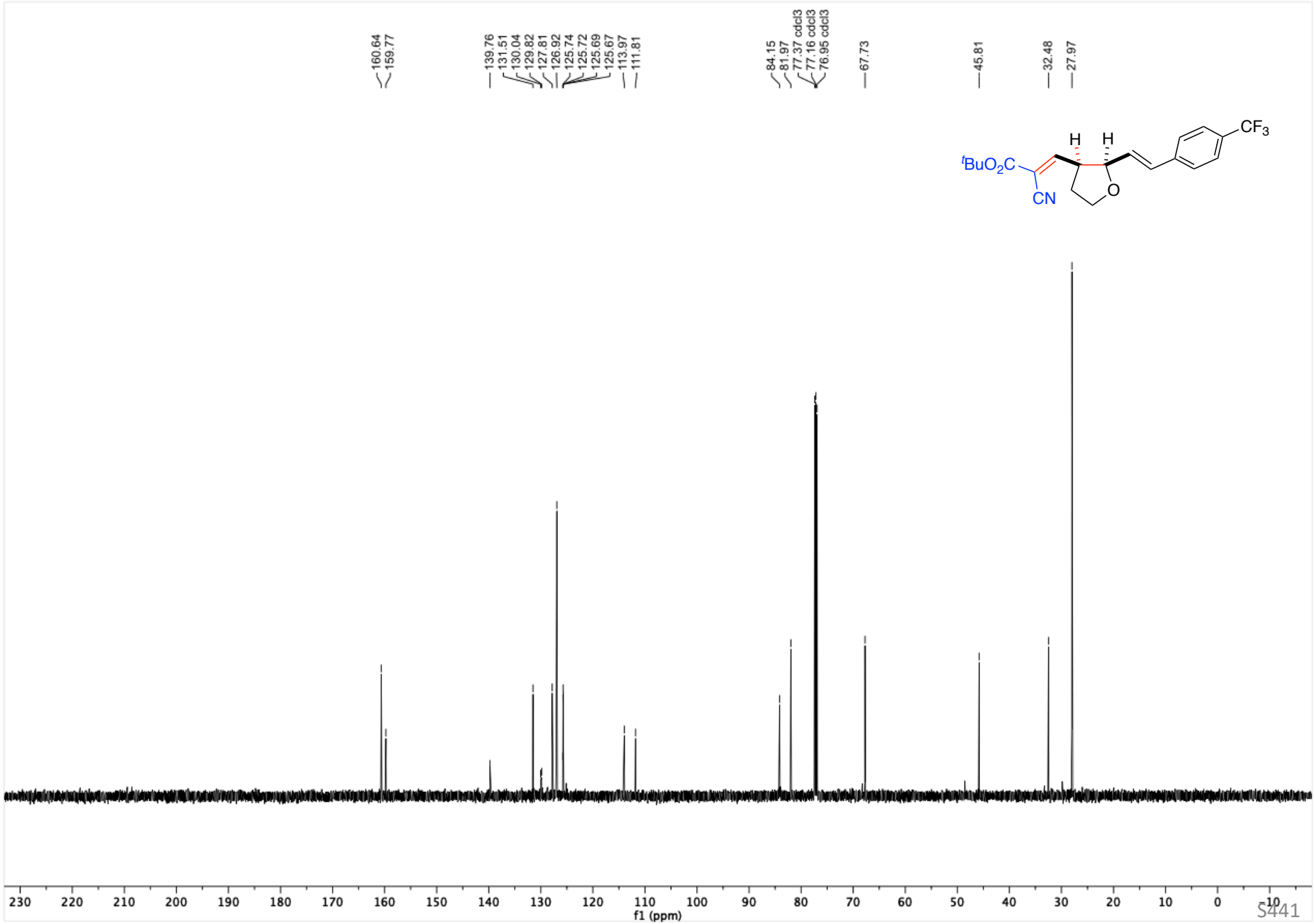
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.357	7207433	92.169
2	18.225	612374	7.831
Total		7819807	100.000

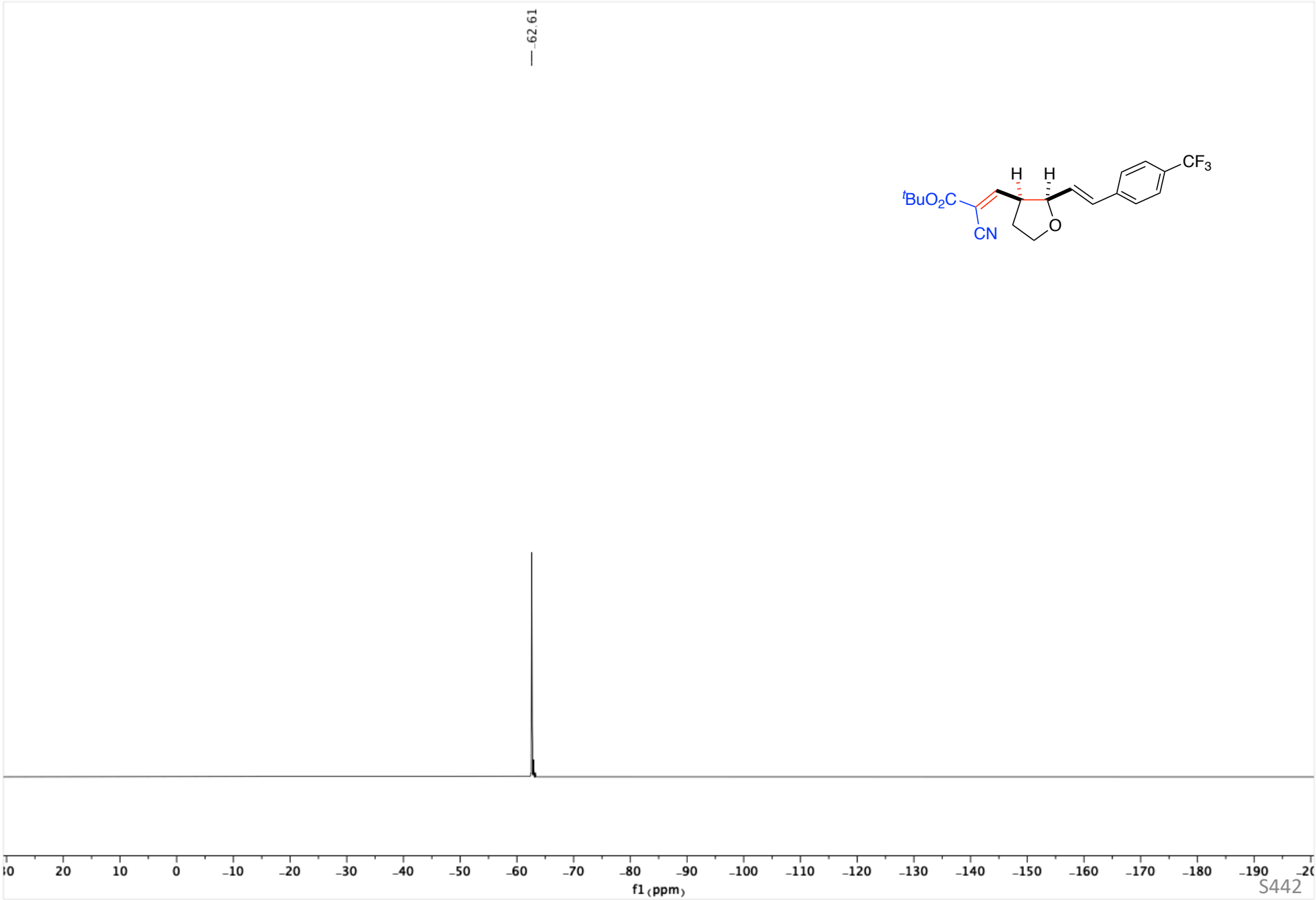
tert-Butyl (_E_)-2-cyano-3-((2_R_,3_S_)-2-((_E_)-4-(trifluoromethyl)styryl)tetrahydrofuran-3-yl)acrylate

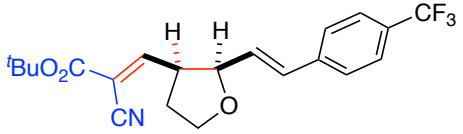


tert-Butyl (_E_)-2-cyano-3-((2_R_,3_S_)-2-((_E_)-4-(trifluoromethyl)styryl)tetrahydrofuran-3-yl)acrylate

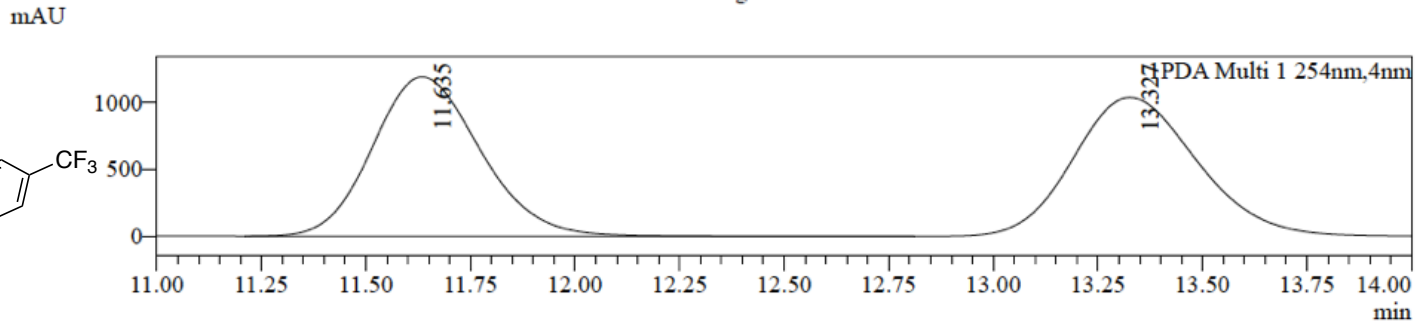


tert-Butyl (_E_)-2-cyano-3-((2_R_,3_S_)-2-((_E_)-4-(trifluoromethyl)styryl)tetrahydrofuran-3-yl)acrylate

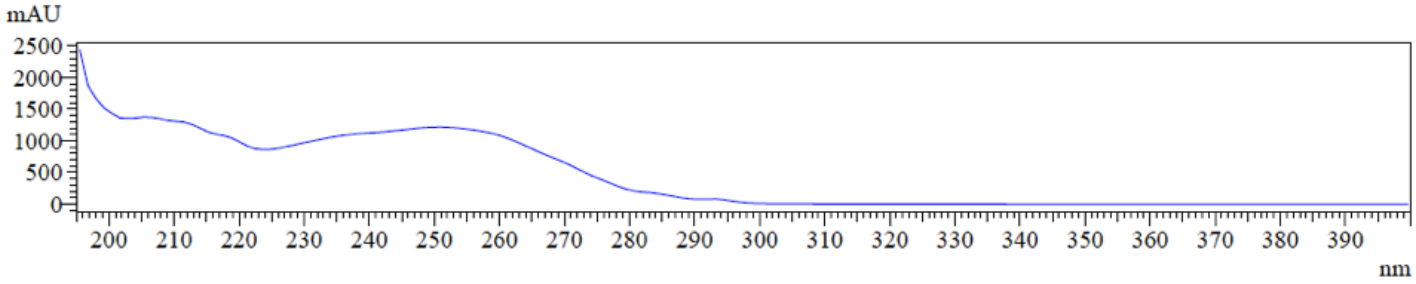




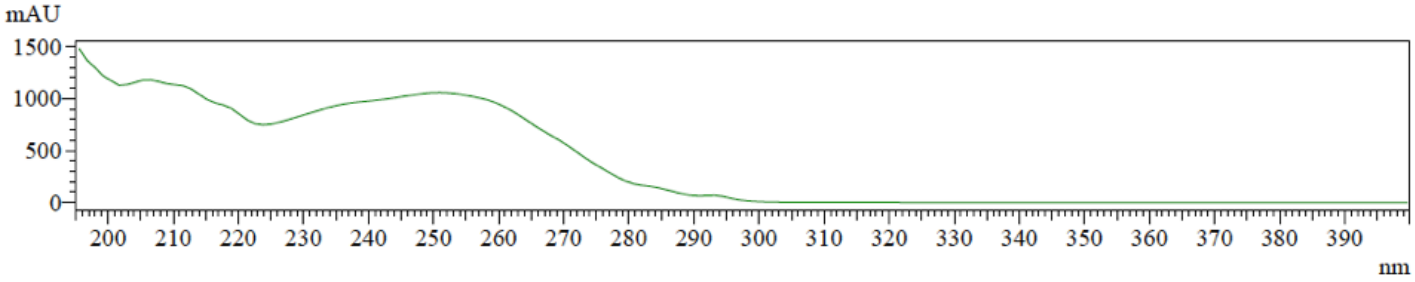
Chromatogram



UV Spectrum
Retention time = 11.635



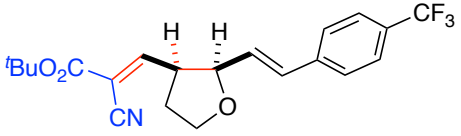
UV Spectrum
Retention time = 13.327



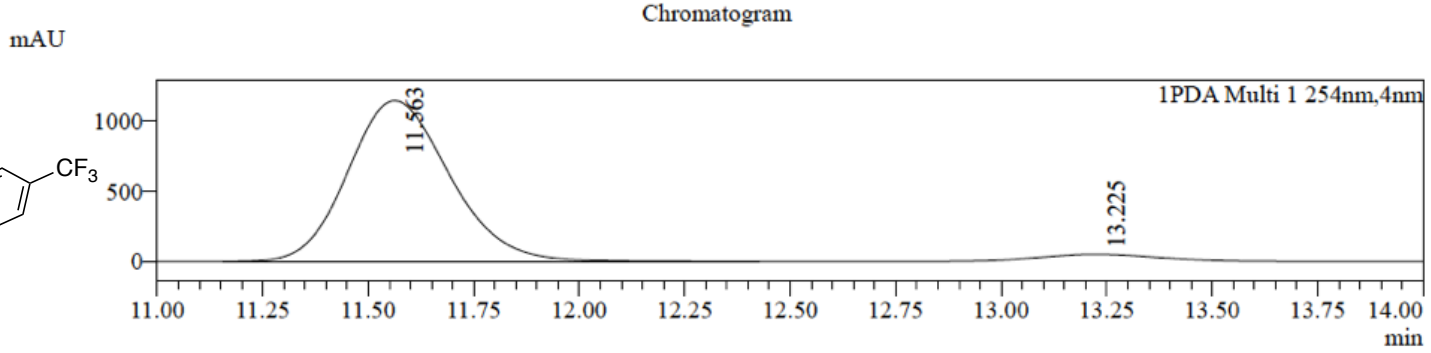
Peak Table

PDA Ch1 254nm

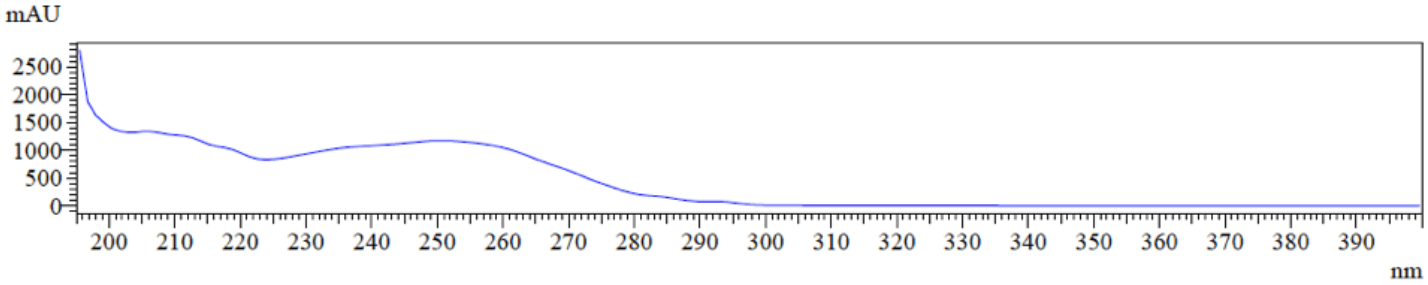
Peak#	Ret. Time	Area	Area%
1	11.635	21416691	49.903
2	13.327	21500234	50.097
Total		42916925	100.000



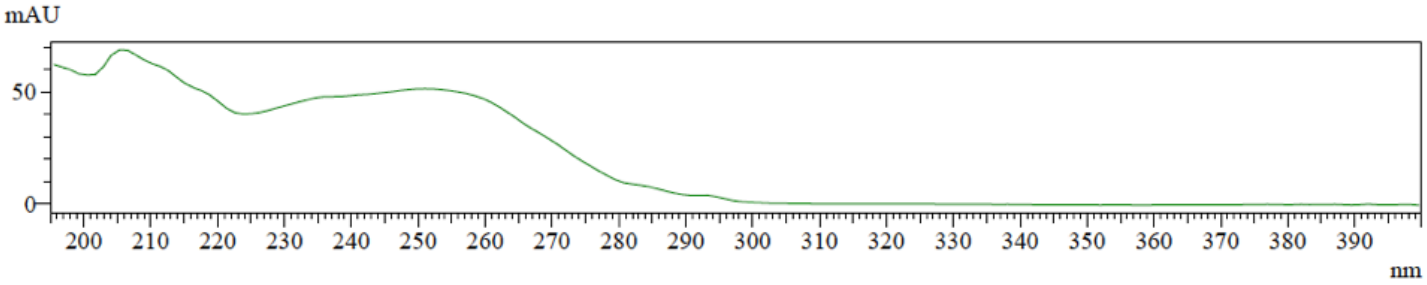
Chromatogram



UV Spectrum
Retention time = 11.563



UV Spectrum
Retention time = 13.225

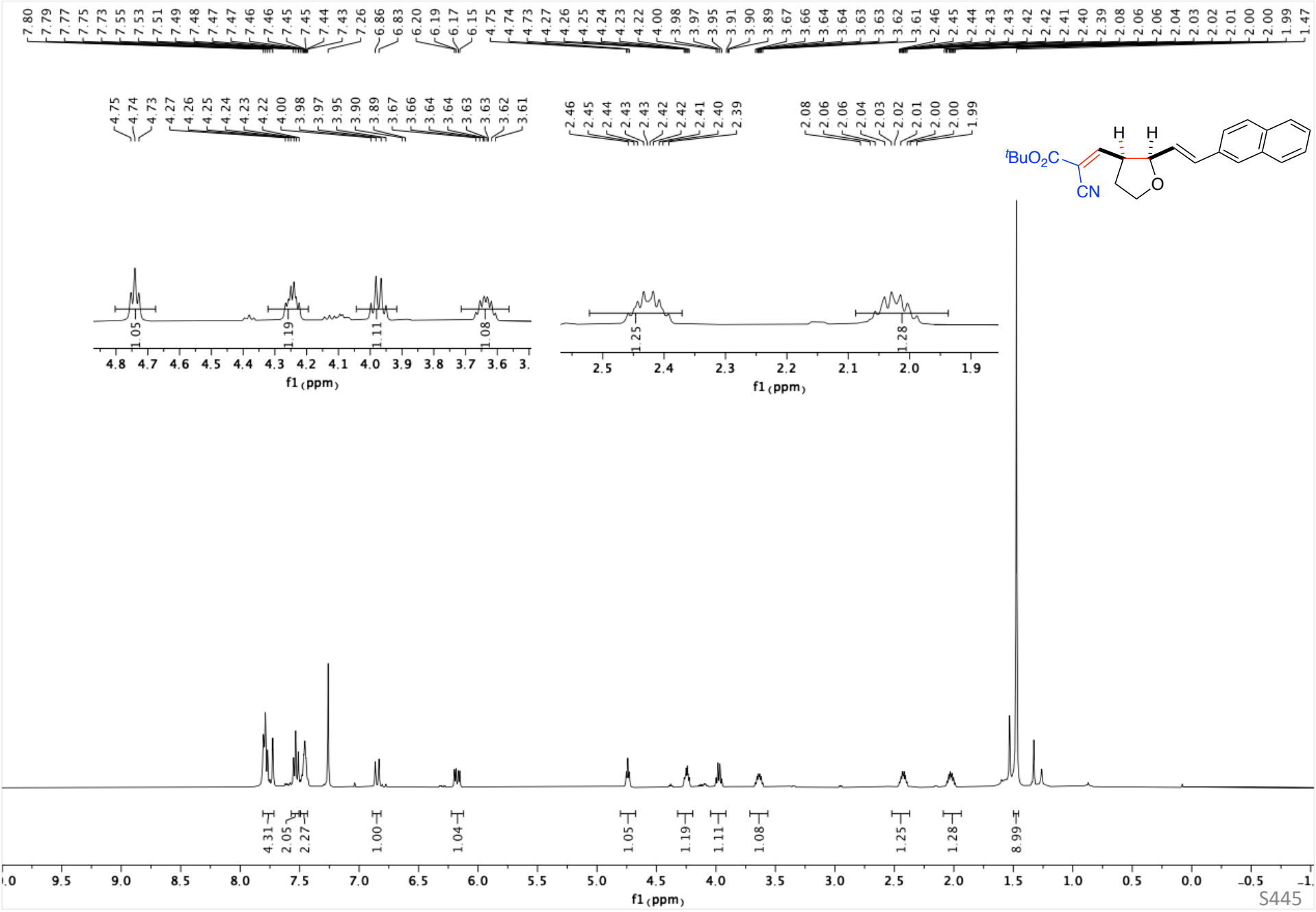


Peak Table

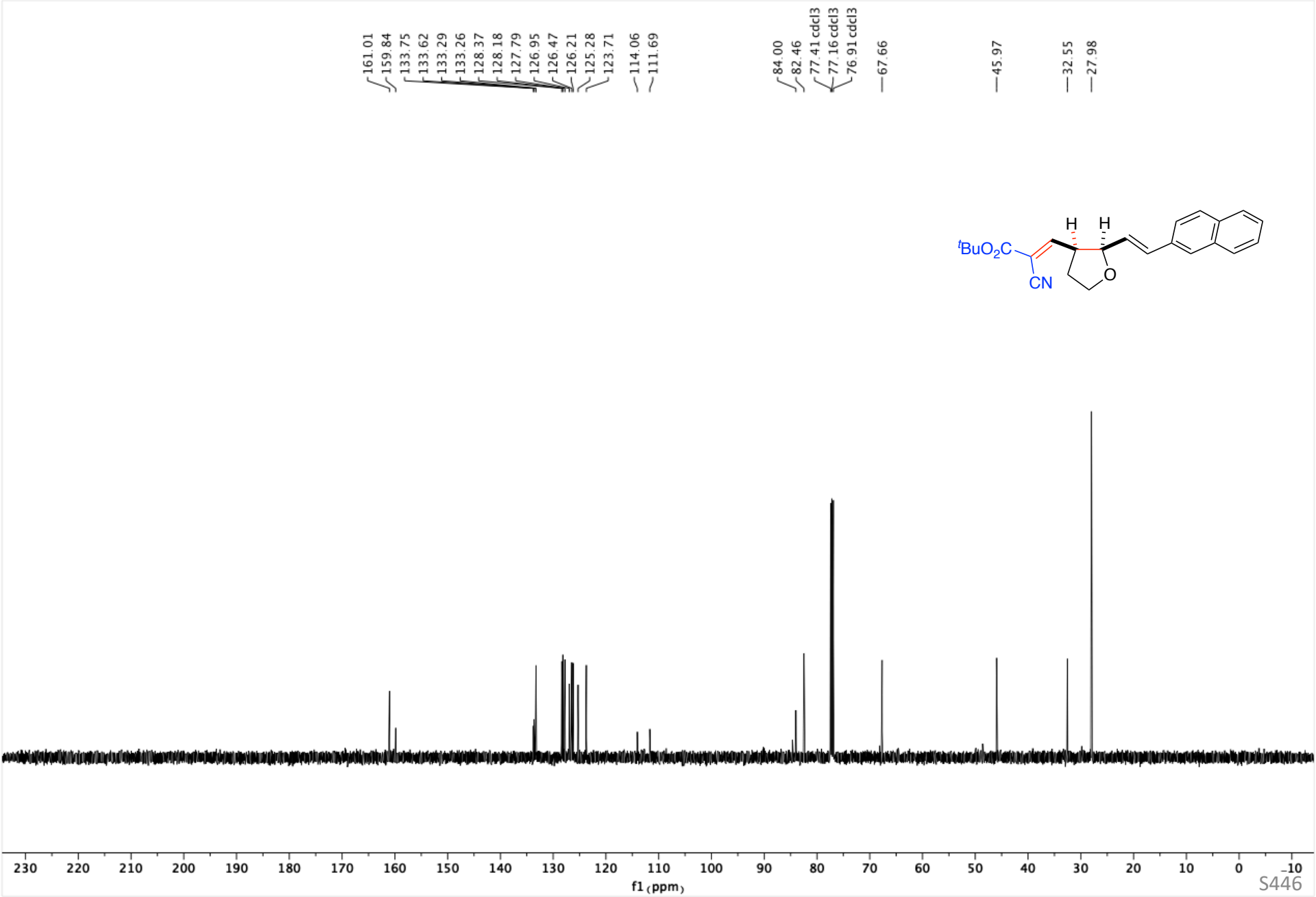
PDA Ch1 254nm

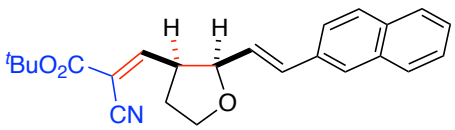
Peak#	Ret. Time	Area	Area%
1	11.563	19249126	95.061
2	13.225	1000070	4.939
Total		20249196	100.000

tert-Butyl (_E_)-2-cyano-3-((2_R_,3_S_)-2-((_E_)-2-(naphthalen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate

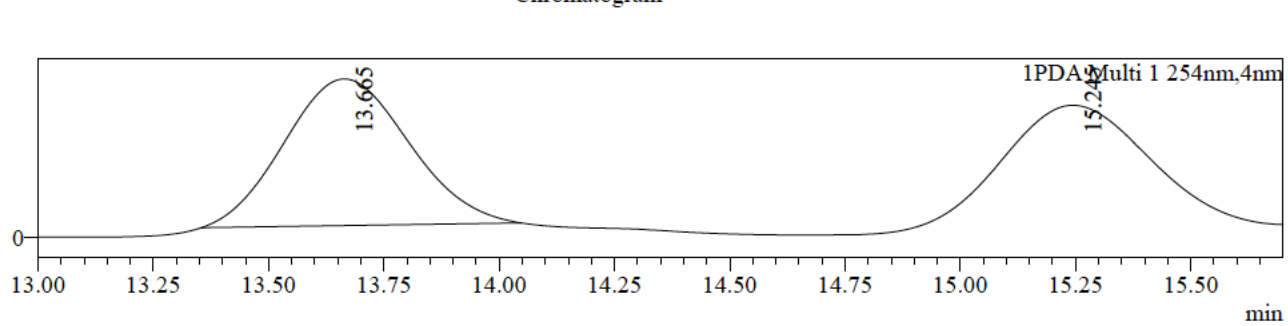


tert-Butyl (_E_)-2-cyano-3-((2_R_,3_S_)-2-((_E_)-2-(naphthalen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate

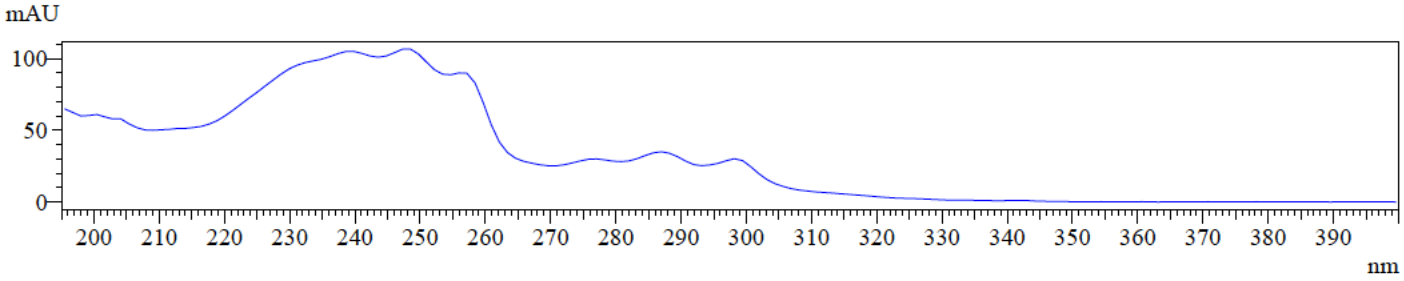




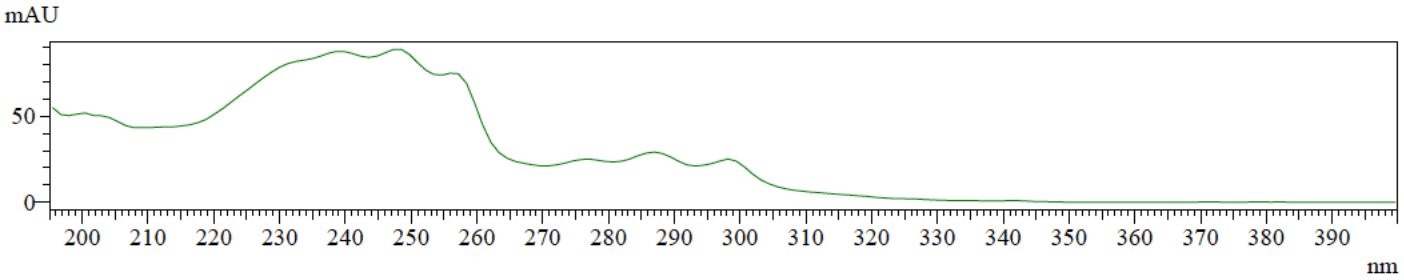
Chromatogram



UV Spectrum
Retention time = 13.665



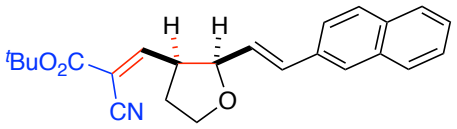
UV Spectrum
Retention time = 15.245



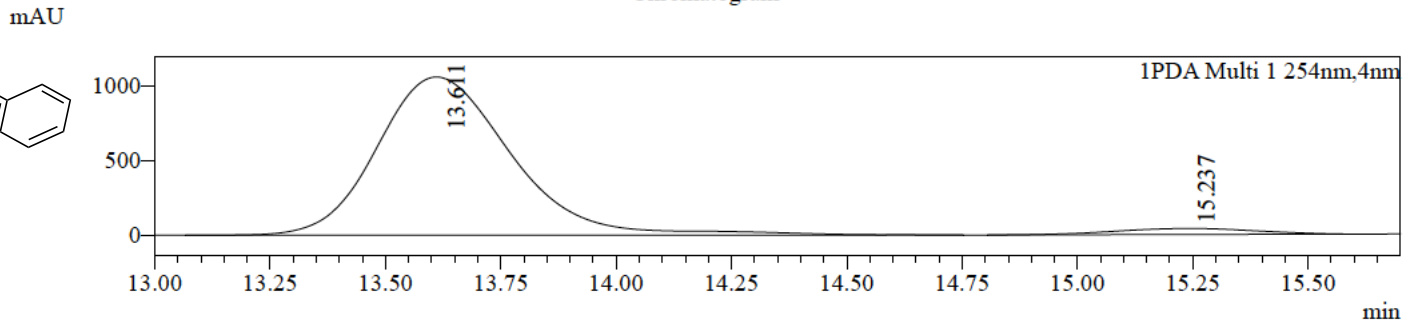
Peak Table

PDA Ch1 254nm

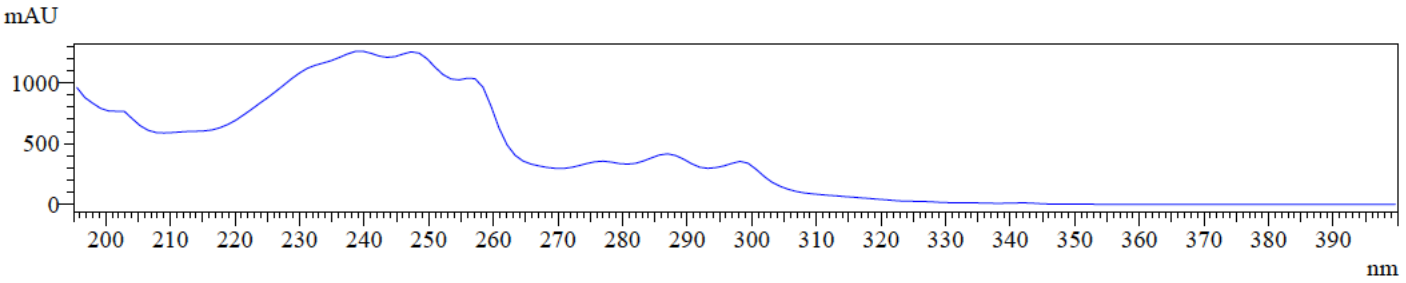
Peak#	Ret. Time	Area	Area%
1	13.665	1584201	49.813
2	15.245	1596080	50.187
Total		3180281	100.000



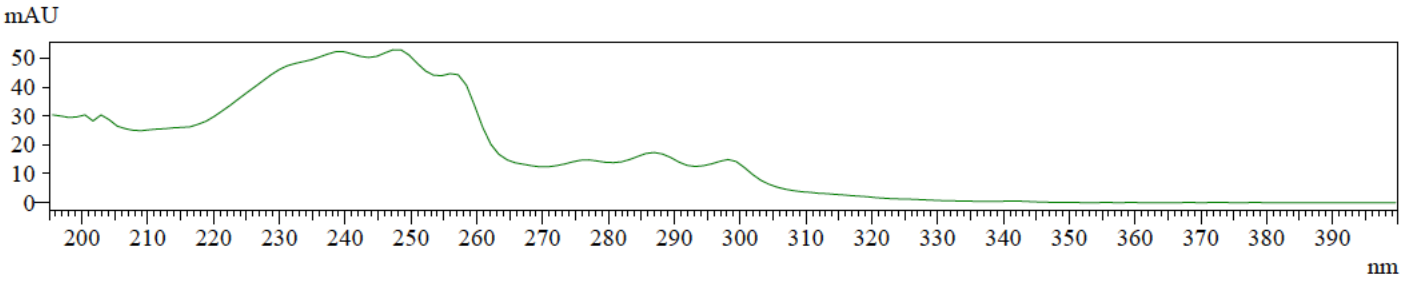
Chromatogram



UV Spectrum
Retention time = 13.611



UV Spectrum
Retention time = 15.237

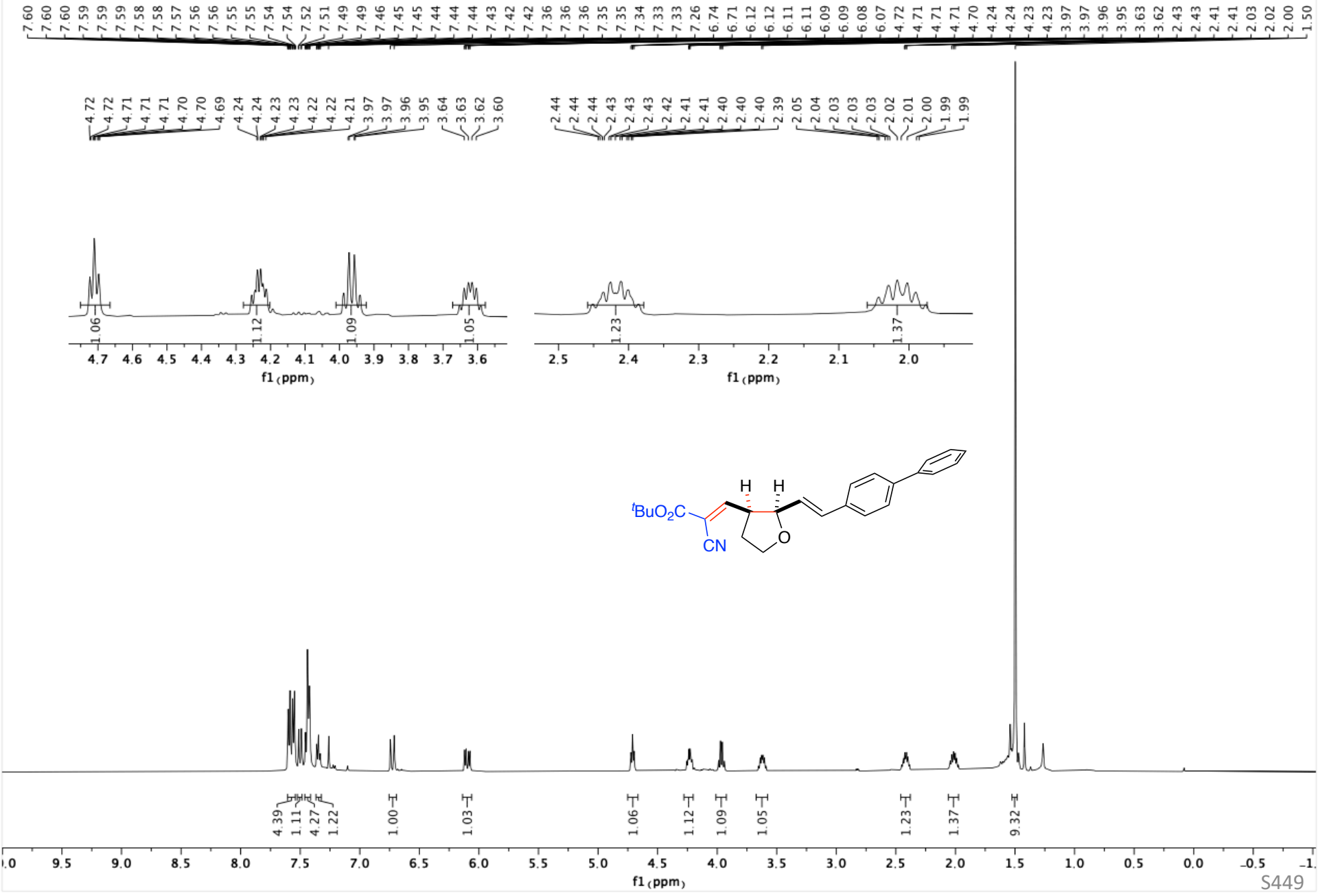


Peak Table

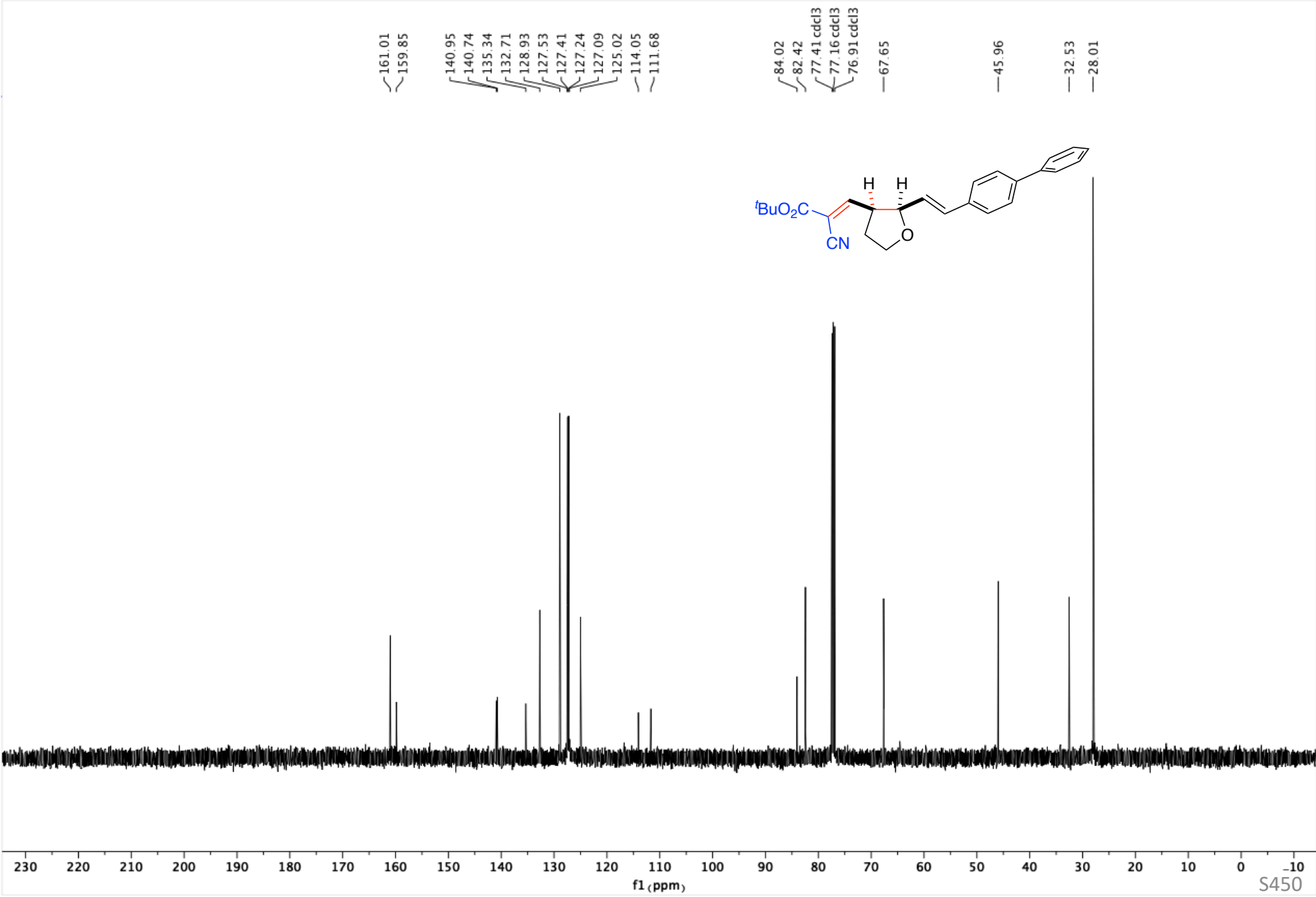
PDA Ch1 254nm

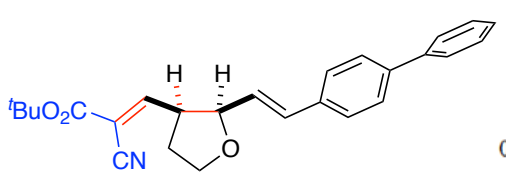
Peak#	Ret. Time	Area	Area%
1	13.611	21356304	96.132
2	15.237	859370	3.868
Total		22215674	100.000

tert-Butyl (_E_)-3-((2_R_,3_S_)-2-((_E_)-2-([1,1‘-biphenyl]-4-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

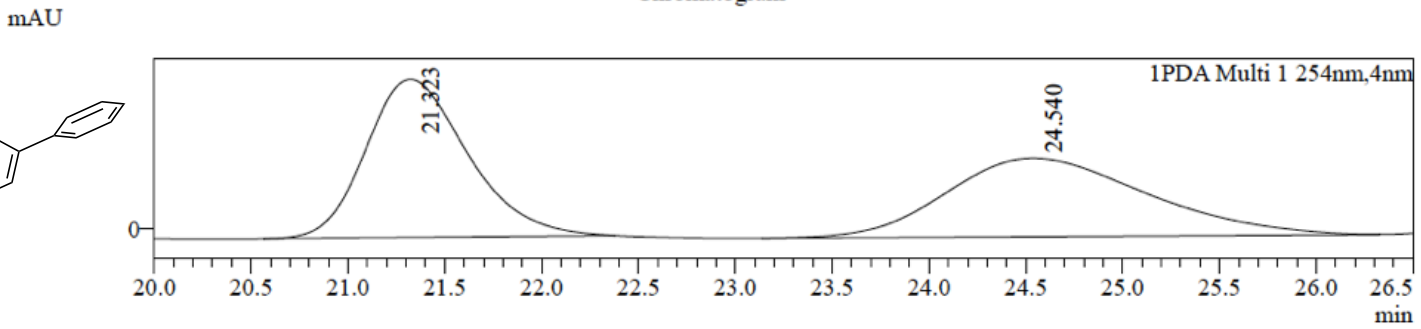


tert-Butyl (_E_)-3-((2_R_,3_S_)-2-((_E_)-2-([1,1‘-biphenyl]-4-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

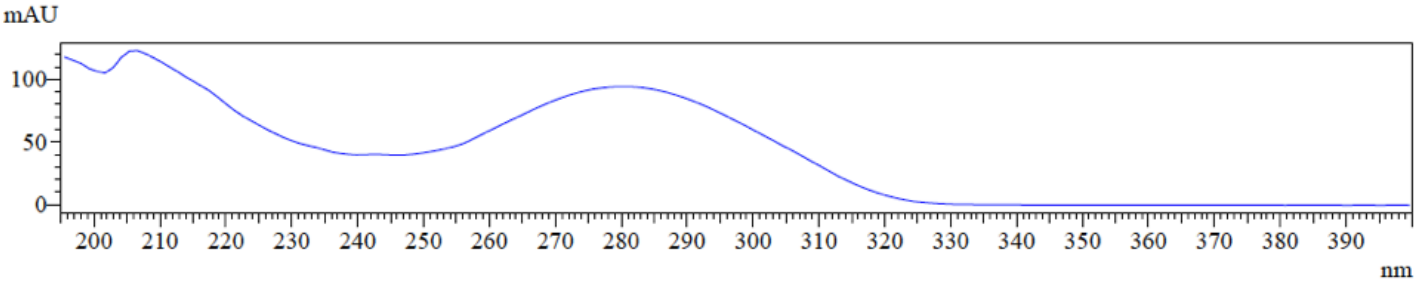




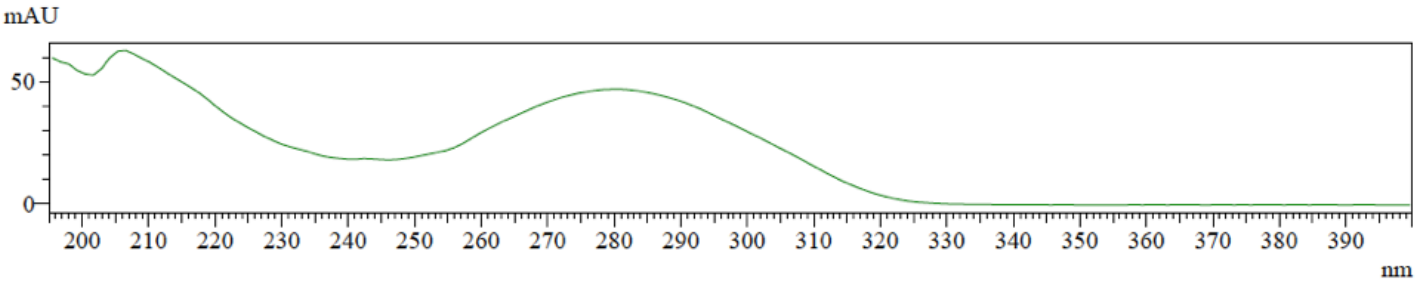
Chromatogram



UV Spectrum
Retention time = 21.323



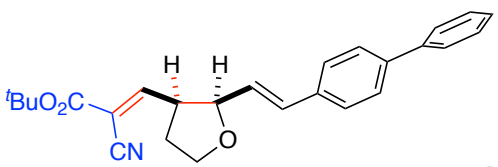
UV Spectrum
Retention time = 24.540



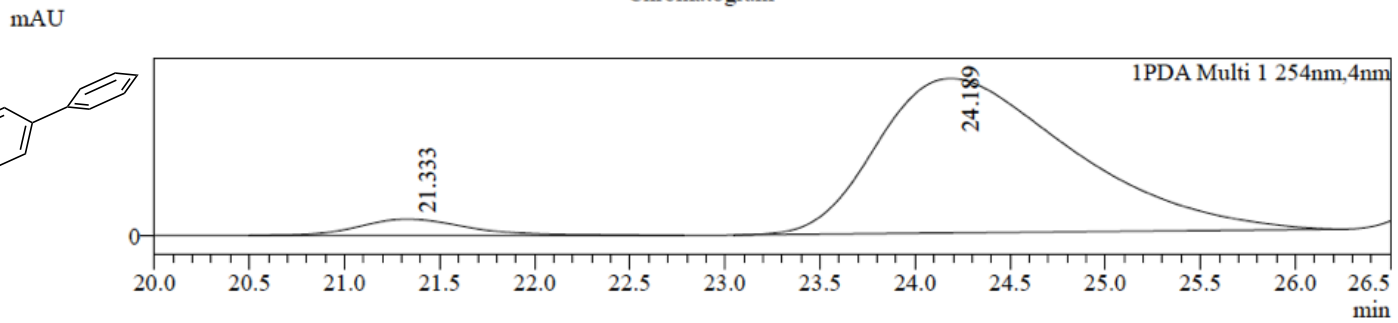
Peak Table

PDA Ch1 254nm

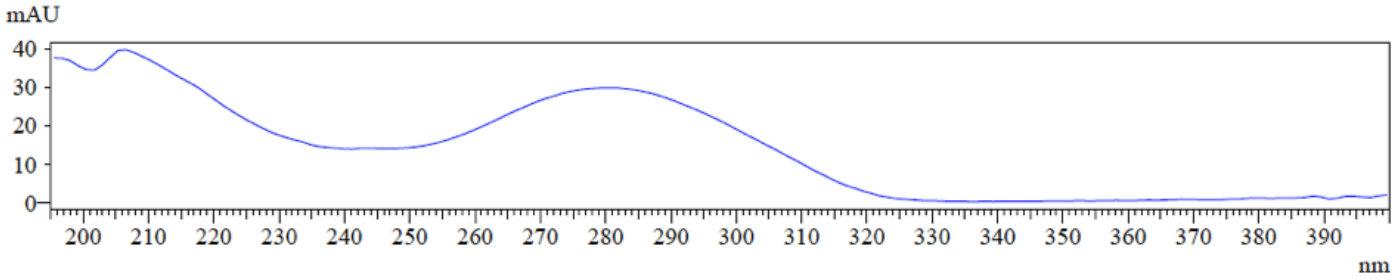
Peak#	Ret. Time	Area	Area%
1	21.323	1782875	50.559
2	24.540	1743430	49.441
Total		3526305	100.000



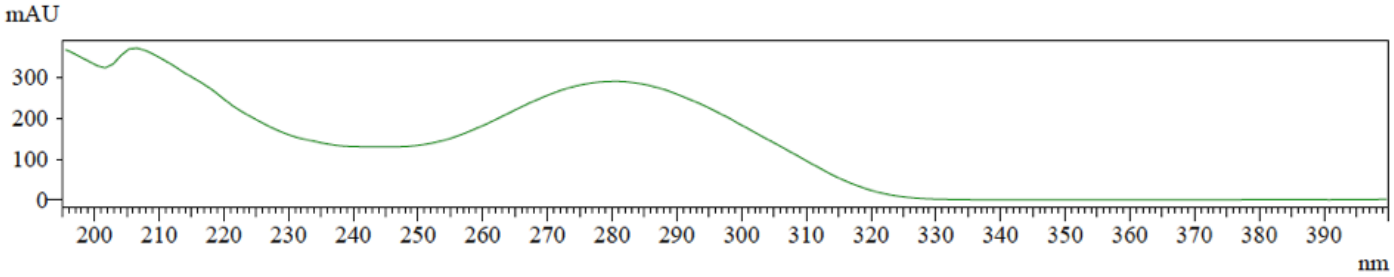
Chromatogram



UV Spectrum
Retention time = 21.333



UV Spectrum
Retention time = 24.189

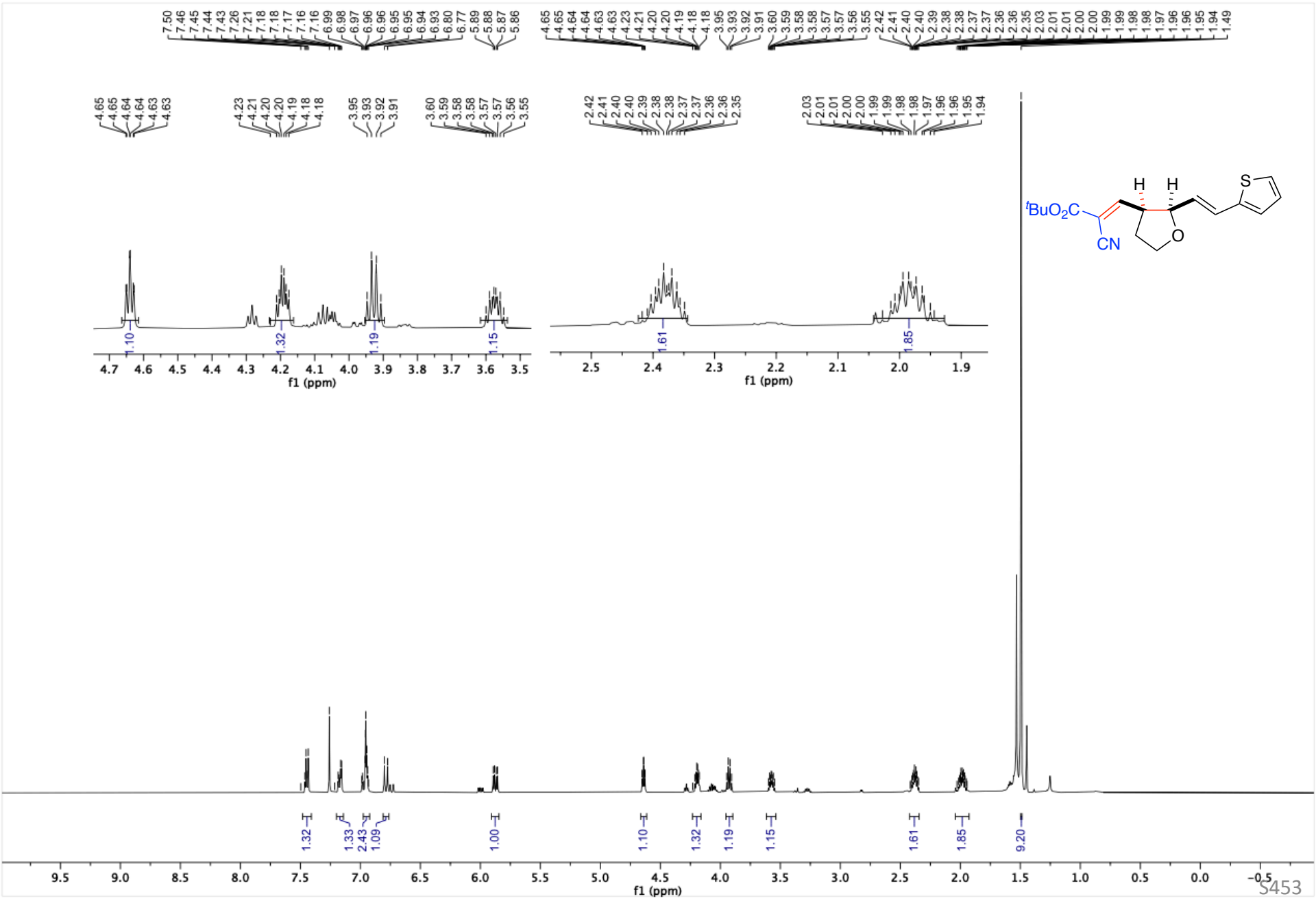


Peak Table

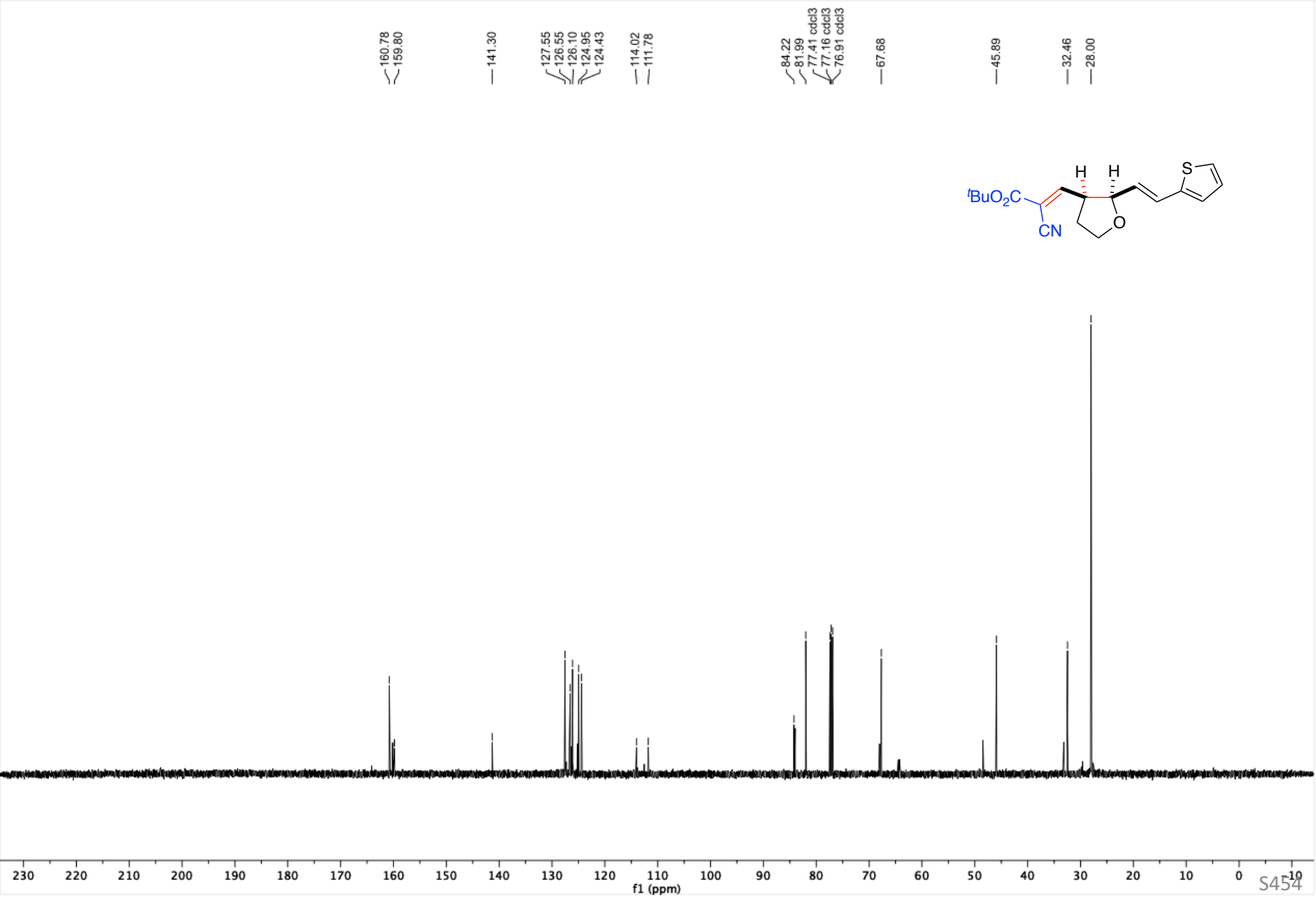
PDA Ch1 254nm

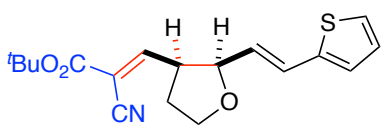
Peak#	Ret. Time	Area	Area%
1	21.333	597118	5.456
2	24.189	10347211	94.544
Total		10944328	100.000

tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-(thiophen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate

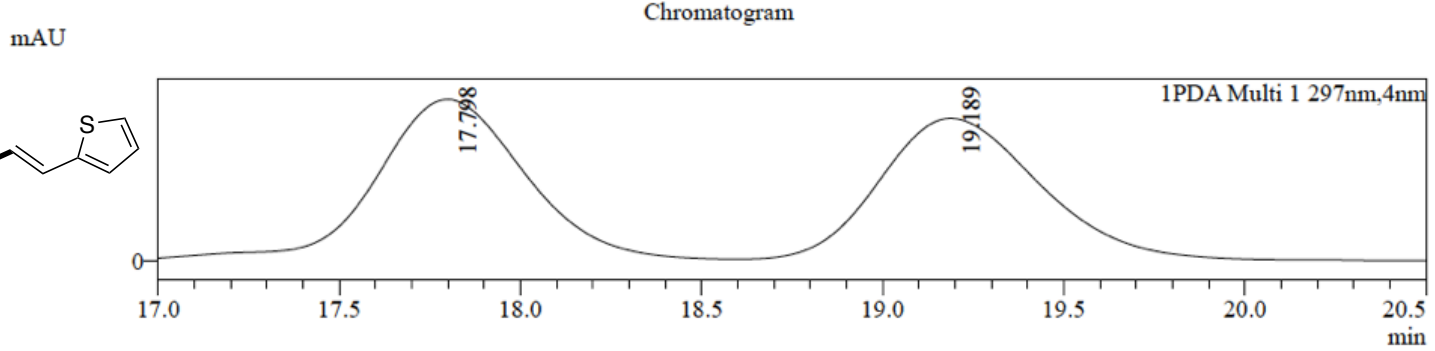


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*E*)-2-(thiophen-2-yl)vinyl)tetrahydrofuran-3-yl)acrylate

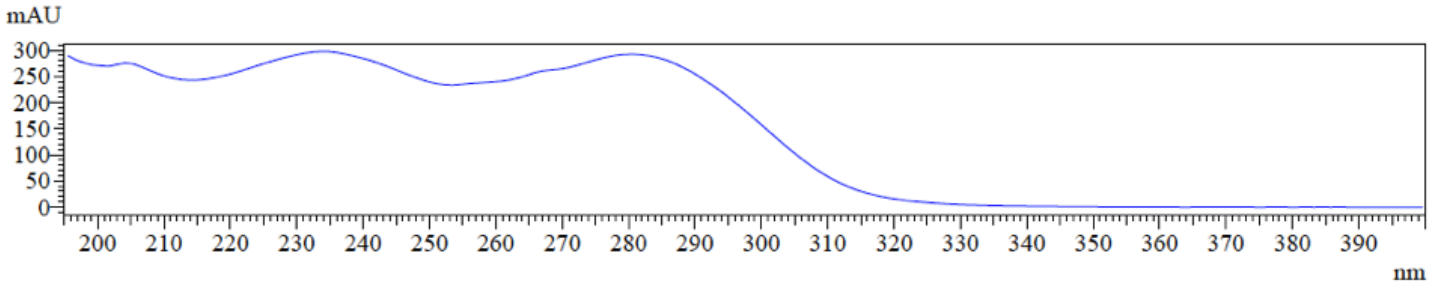




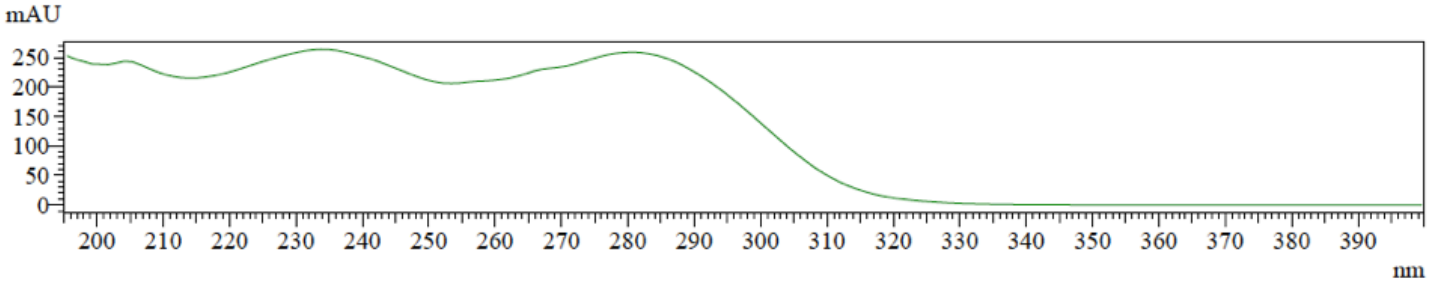
Chromatogram



UV Spectrum
Retention time = 17.798



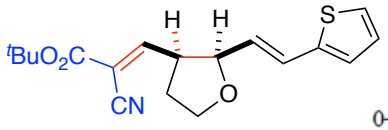
UV Spectrum
Retention time = 19.189



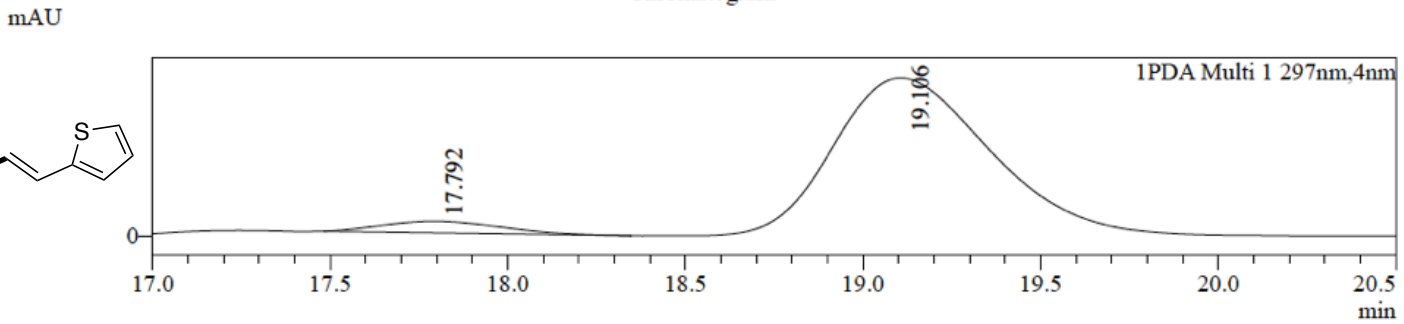
Peak Table

PDA Ch1 297nm

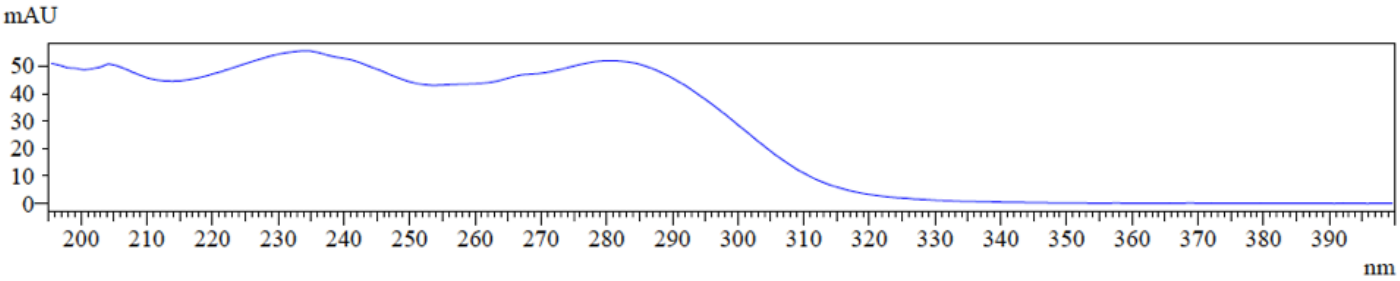
Peak#	Ret. Time	Area	Area%
1	17.798	5500202	51.492
2	19.189	5181559	48.508
Total		10681761	100.000



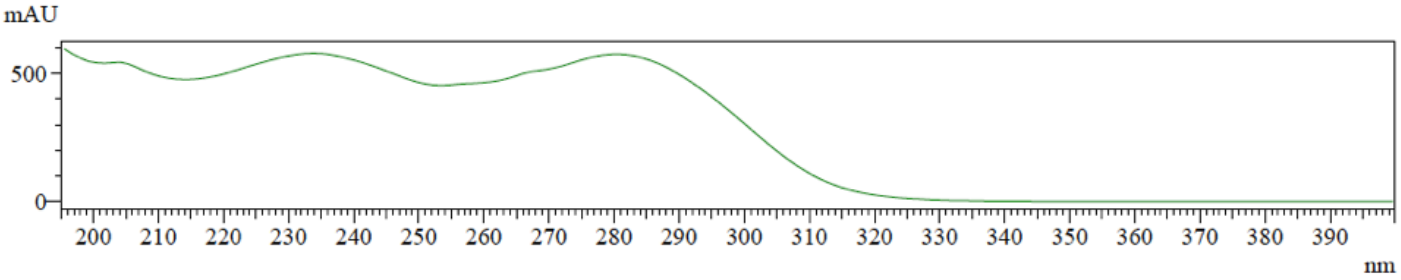
Chromatogram



UV Spectrum
Retention time = 17.792



UV Spectrum
Retention time = 19.106

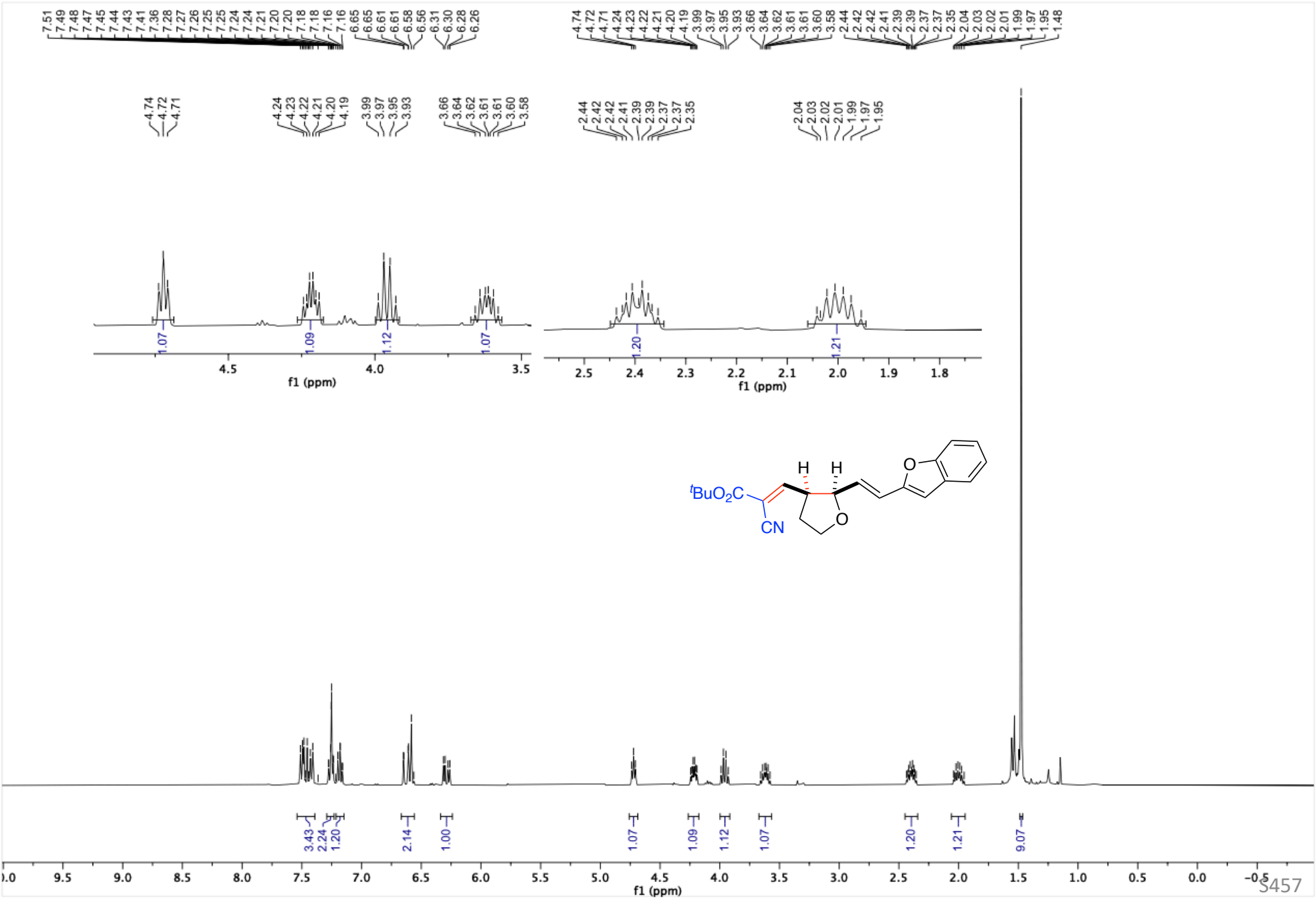


Peak Table

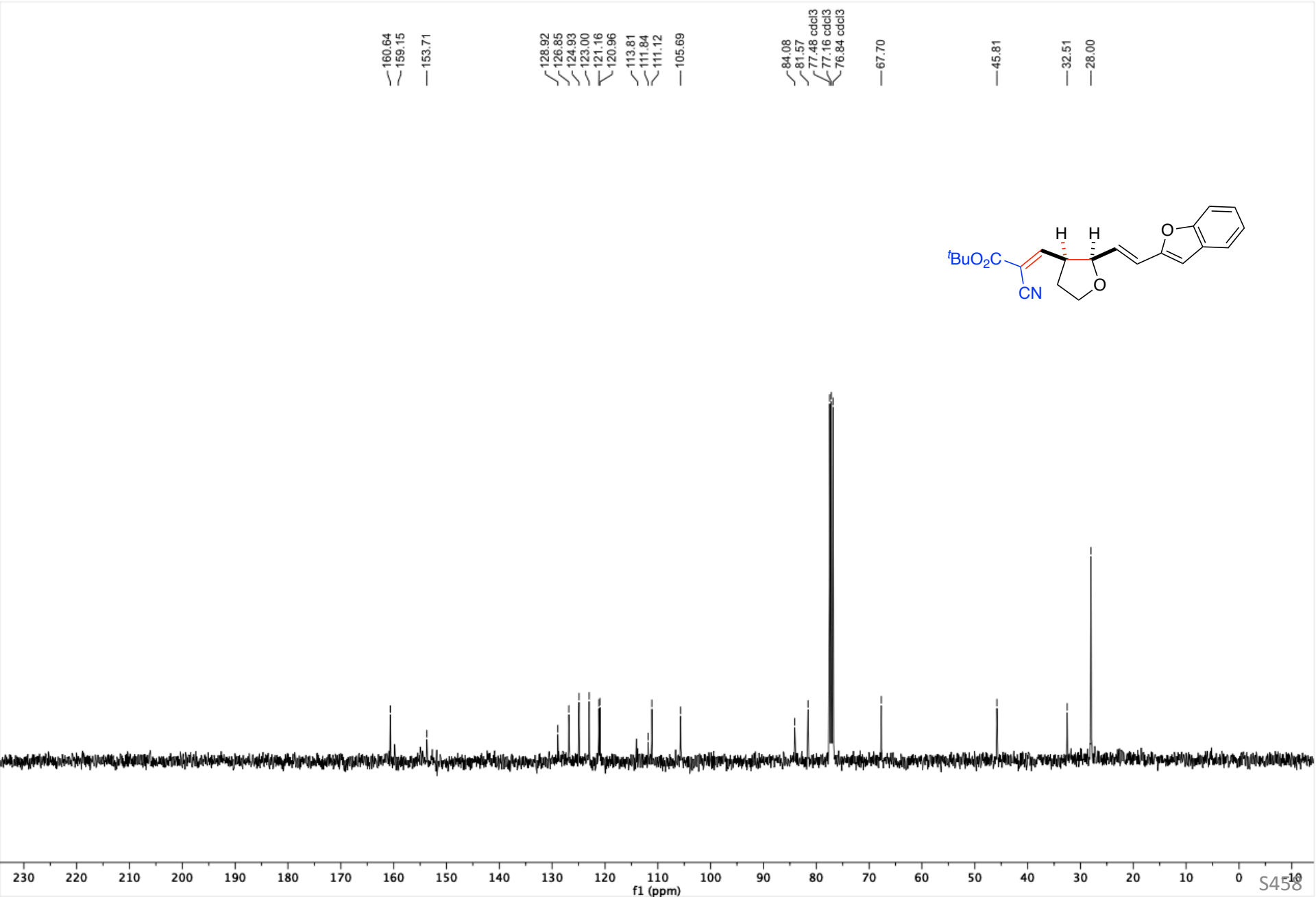
PDA Ch1 297nm

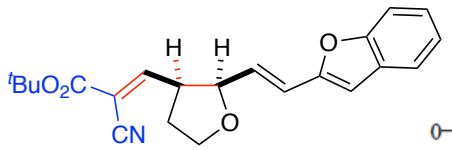
Peak#	Ret. Time	Area	Area%
1	17.792	611249	5.121
2	19.106	11324105	94.879
Total		11935354	100.000

tert-Butyl (_E_)-3-((2_R_,3_S_)-2-((_E_)-2-(benzofuran-2-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

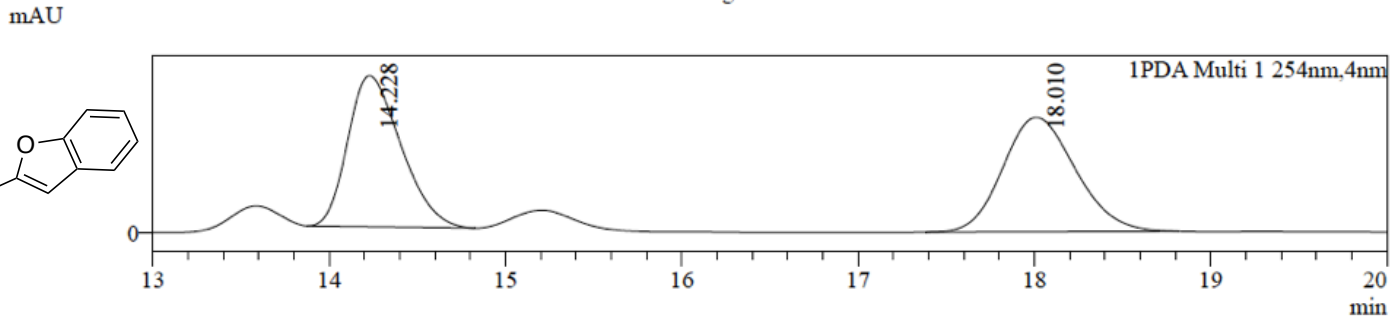


tert-Butyl (_E_)-3-((2_R_,3_S_)-2-((_E_)-2-(benzofuran-2-yl)vinyl)tetrahydrofuran-3-yl)-2-cyanoacrylate

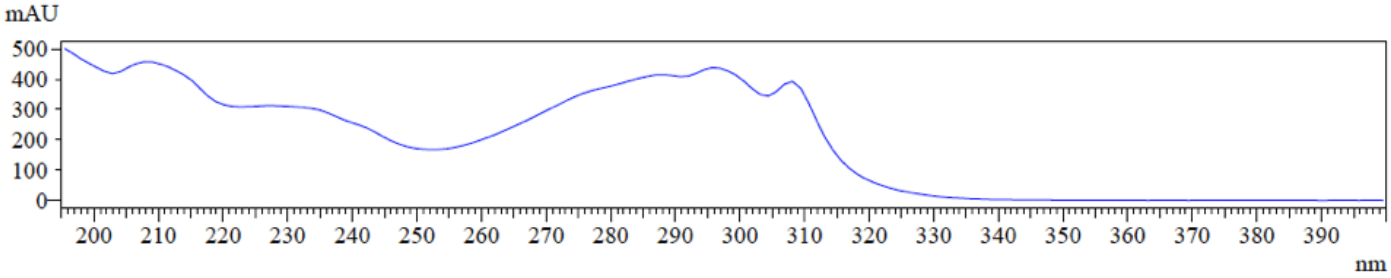




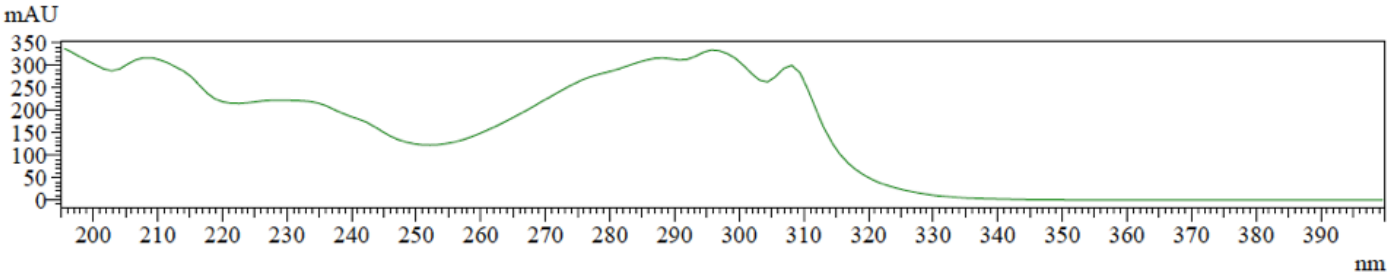
Chromatogram



UV Spectrum
Retention time = 14.228



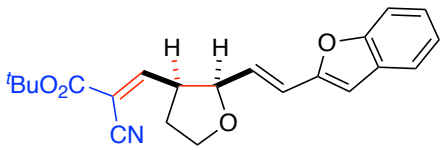
UV Spectrum
Retention time = 18.010



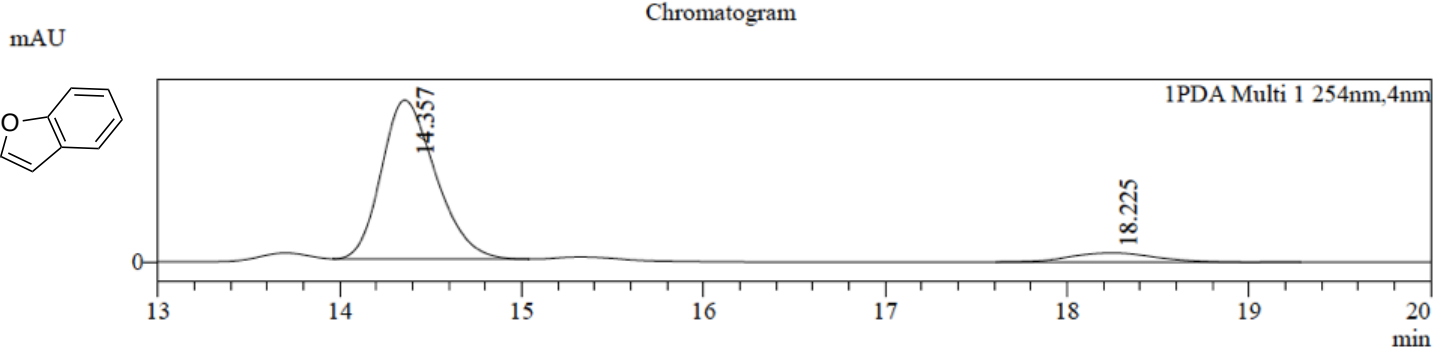
Peak Table

PDA Ch1 254nm

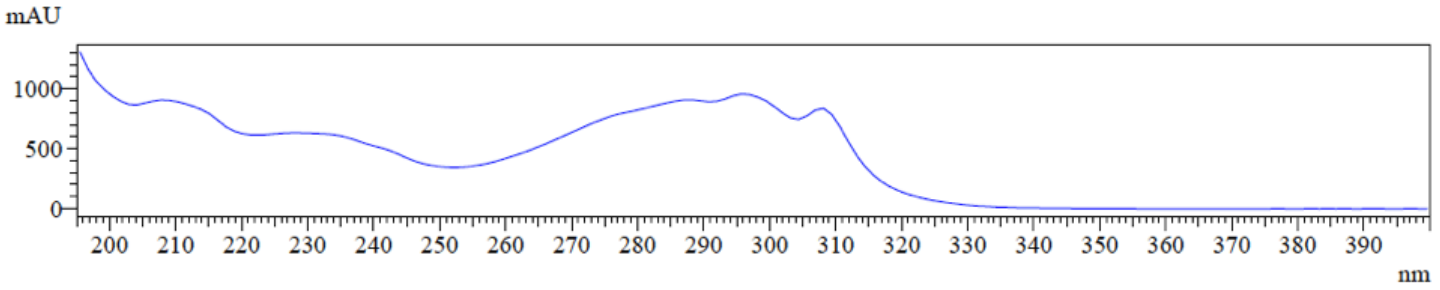
Peak#	Ret. Time	Area	Area%
1	14.228	3439676	49.083
2	18.010	3568145	50.917
Total		7007821	100.000



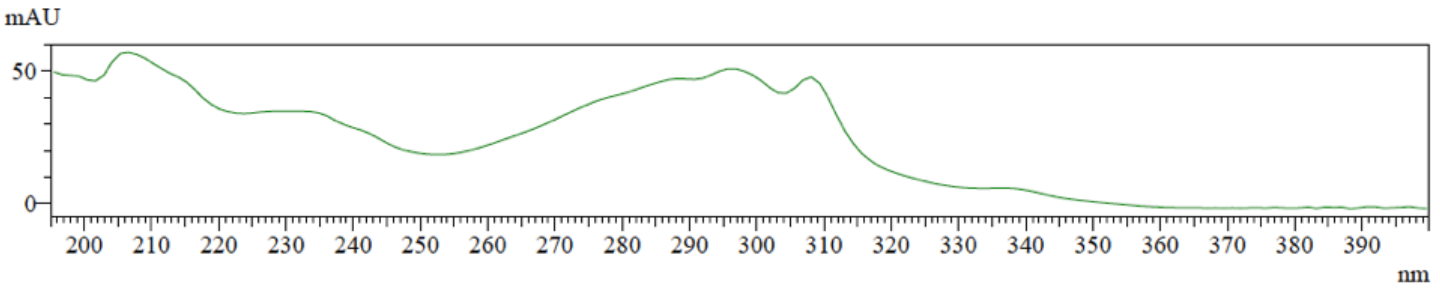
Chromatogram



UV Spectrum
Retention time = 14.357



UV Spectrum
Retention time = 18.225

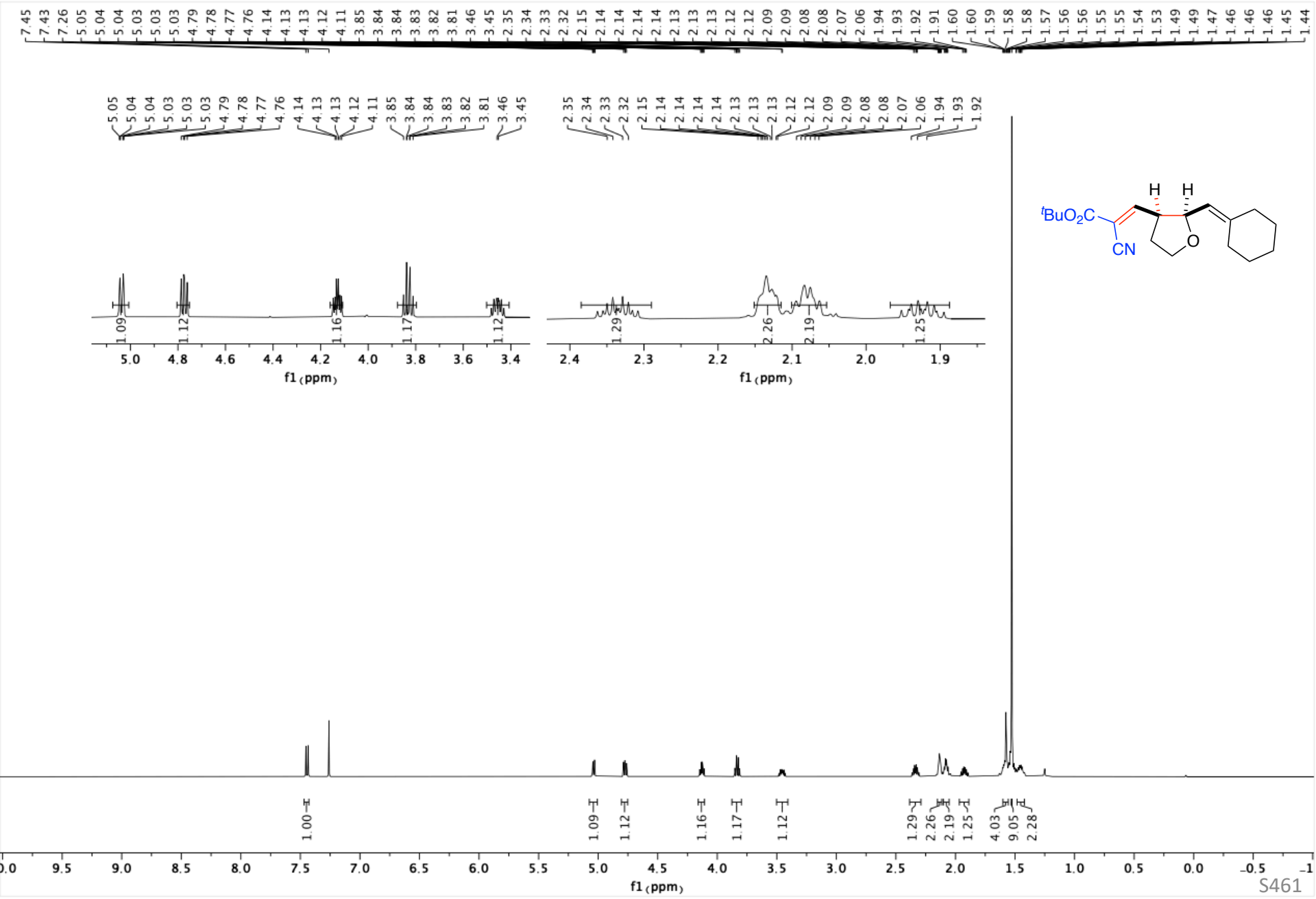


Peak Table

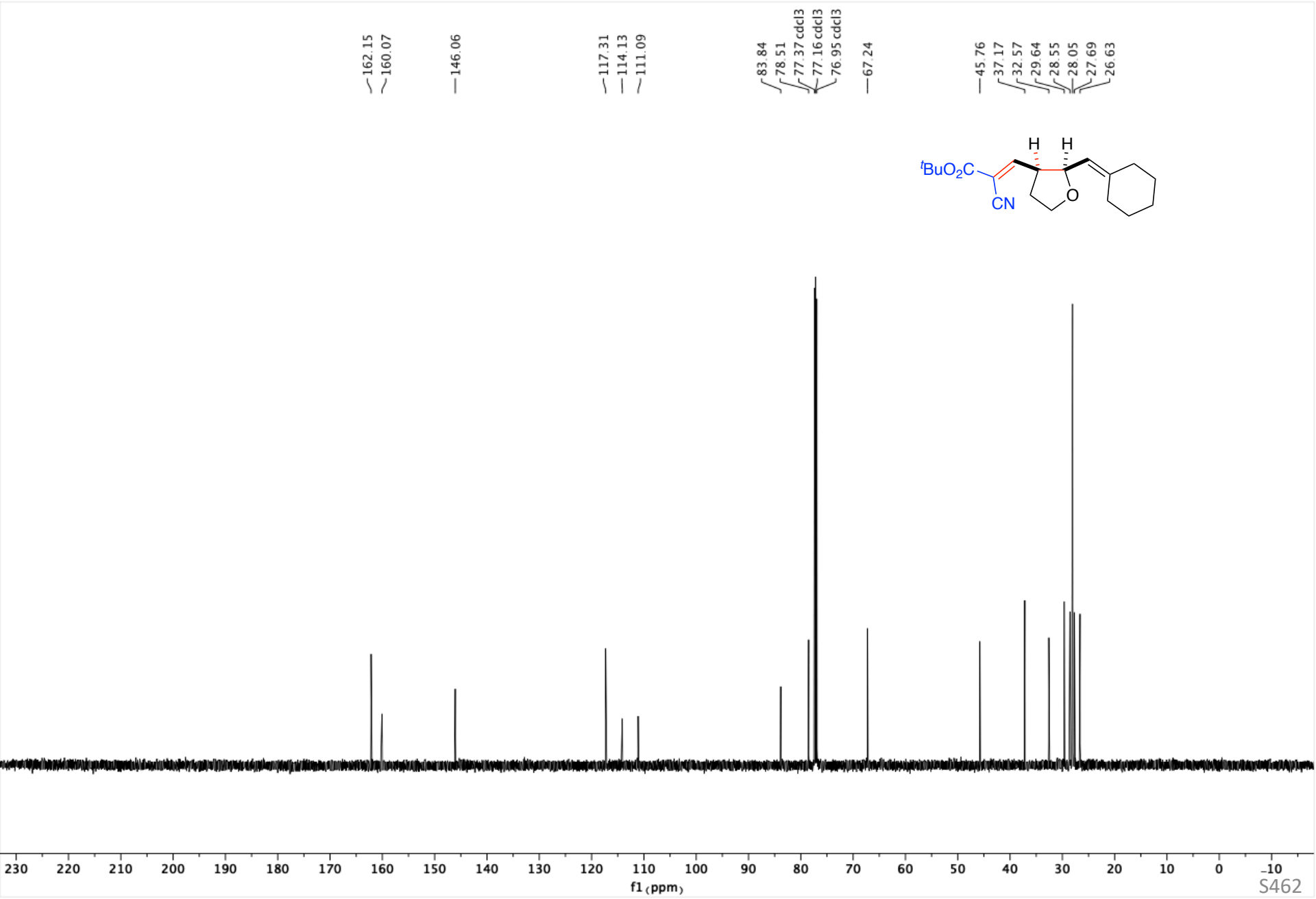
PDA Ch1 254nm

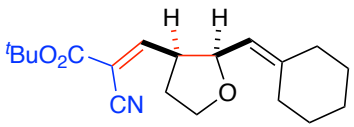
Peak#	Ret. Time	Area	Area%
1	14.357	7207433	92.169
2	18.225	612374	7.831
Total		7819807	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylidenemethyl)tetrahydrofuran-3-yl)acrylate

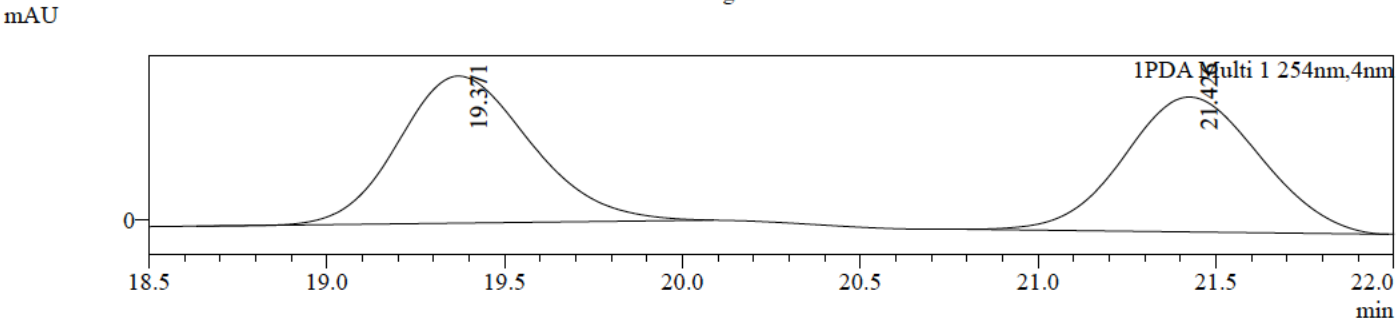


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylidenemethyl)tetrahydrofuran-3-yl)acrylate

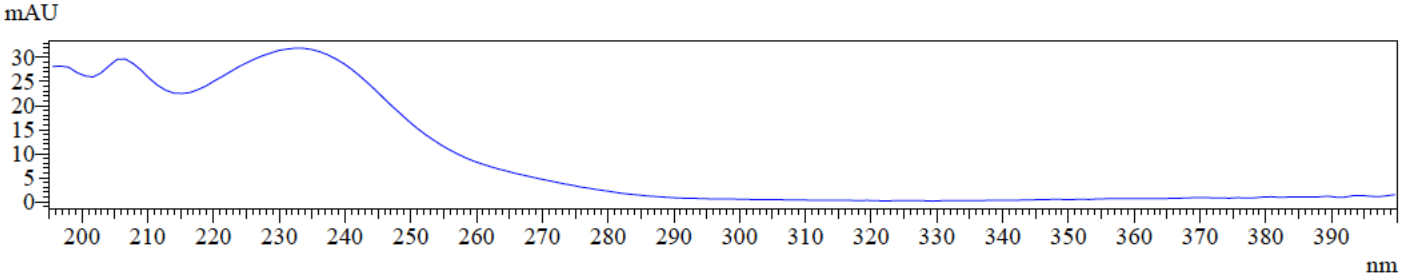




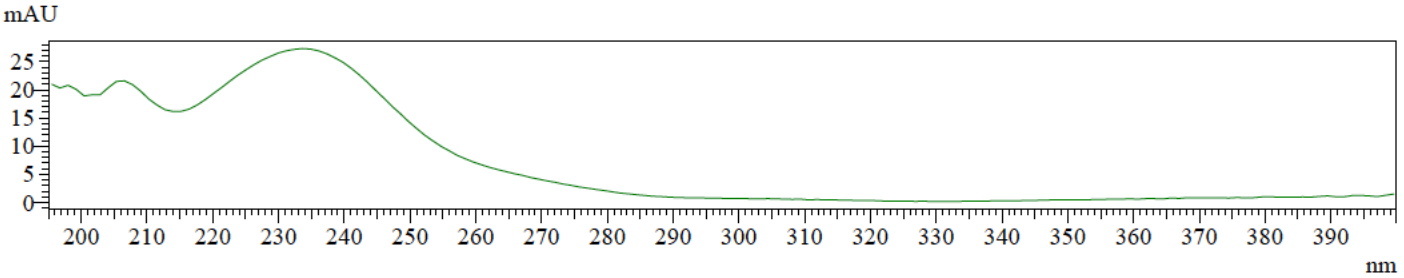
Chromatogram



UV Spectrum
Retention time = 19.371



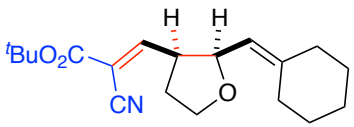
UV Spectrum
Retention time = 21.426



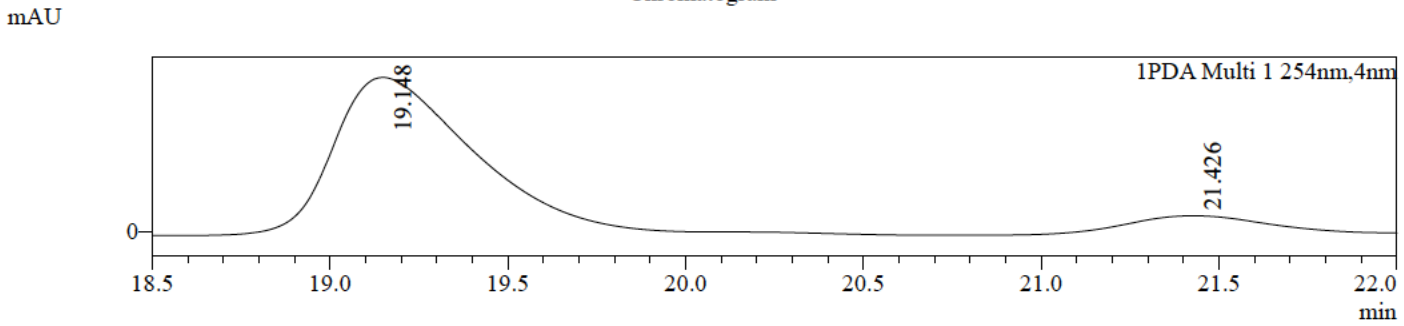
Peak Table

PDA Ch1 254nm

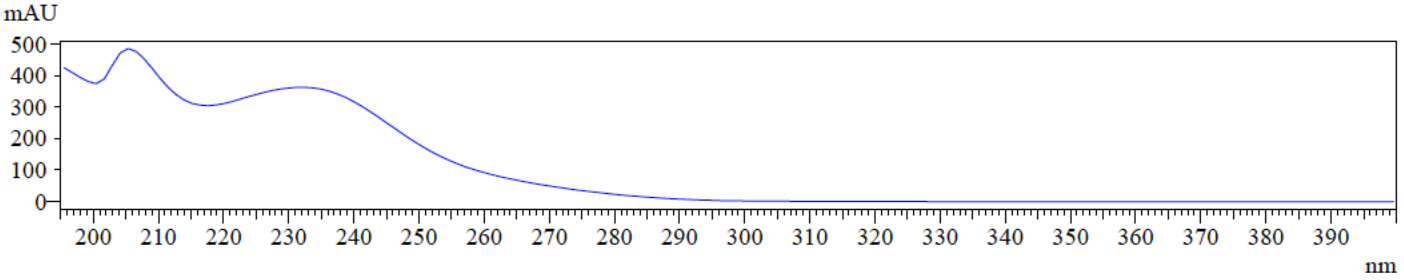
Peak#	Ret. Time	Area	Area%
1	19.371	329249	51.506
2	21.426	309994	48.494
Total		639243	100.000



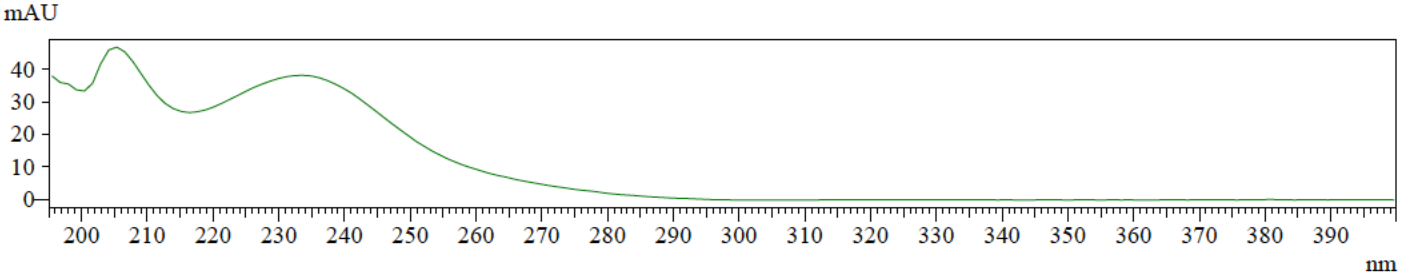
Chromatogram



UV Spectrum
Retention time = 19.148



UV Spectrum
Retention time = 21.426

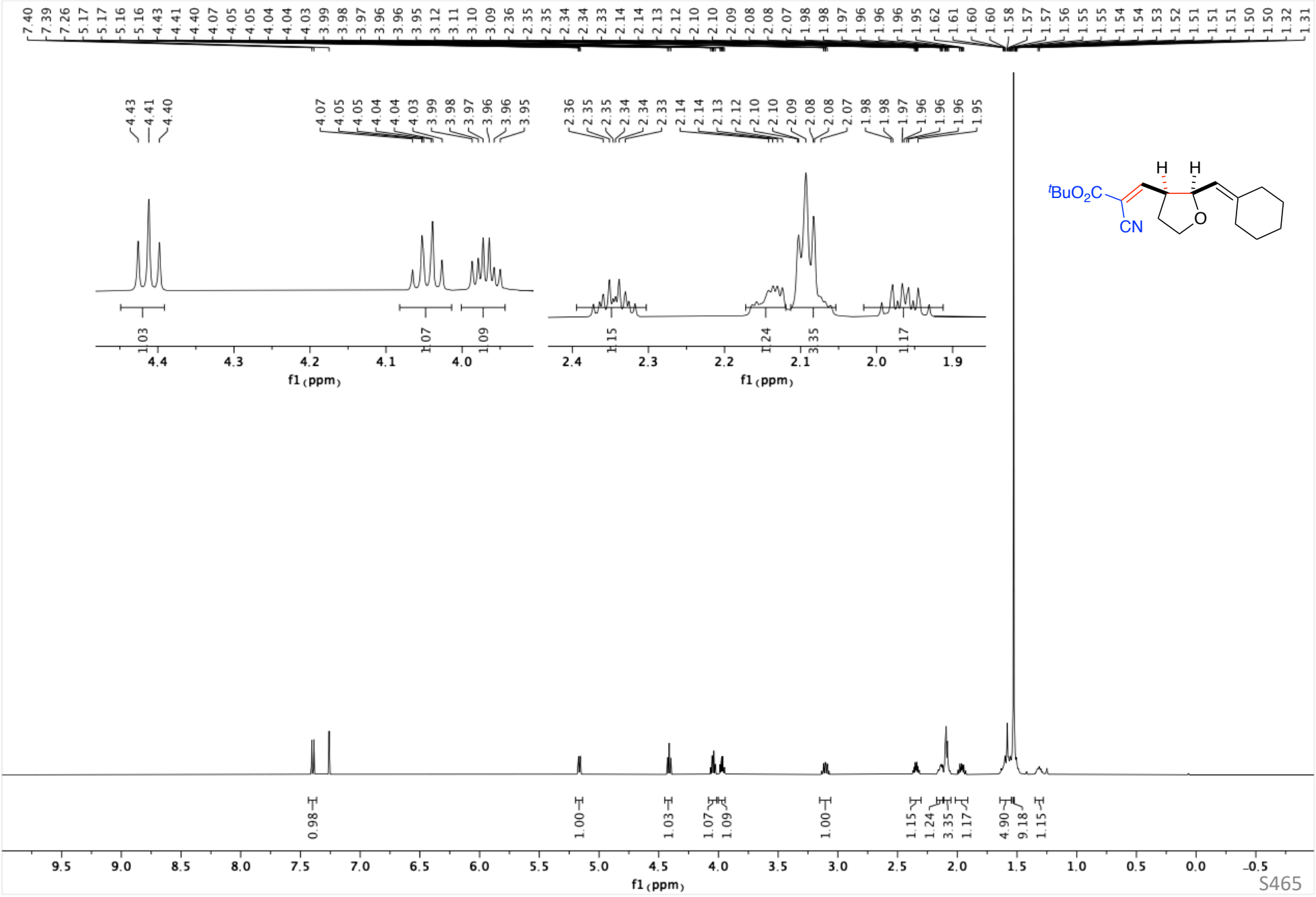


Peak Table

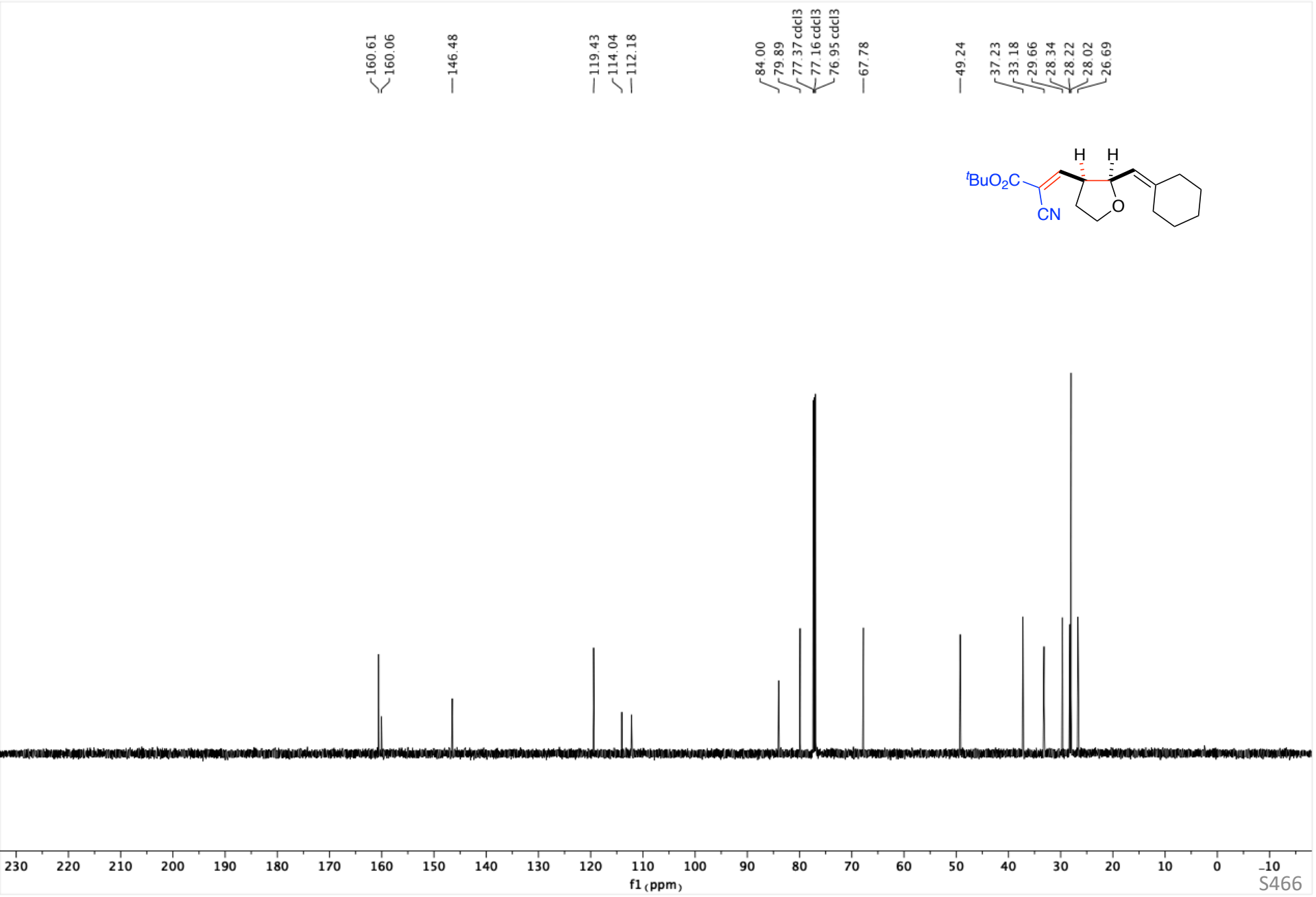
PDA Ch1 254nm

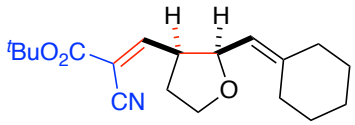
Peak#	Ret. Time	Area	Area%
1	19.148	4014793	89.795
2	21.426	456254	10.205
Total		4471047	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylidenemethyl)tetrahydrofuran-3-yl)acrylate

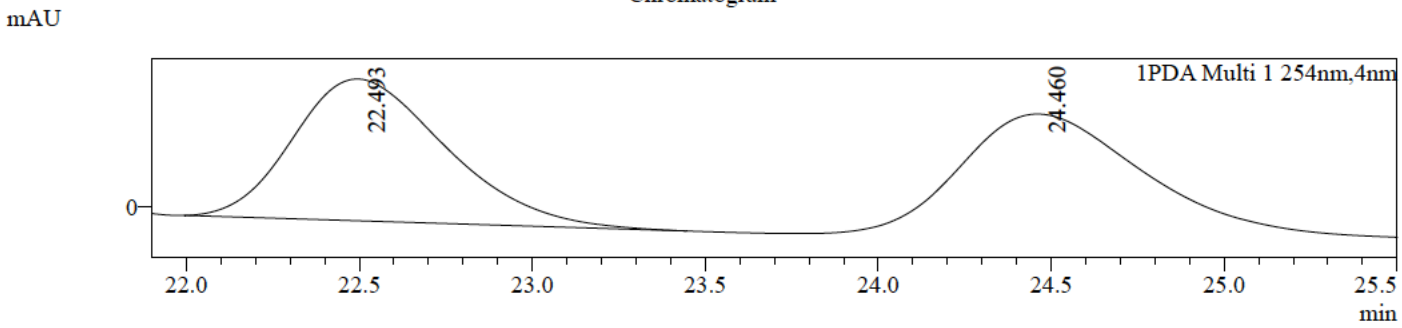


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylidenemethyl)tetrahydrofuran-3-yl)acrylate

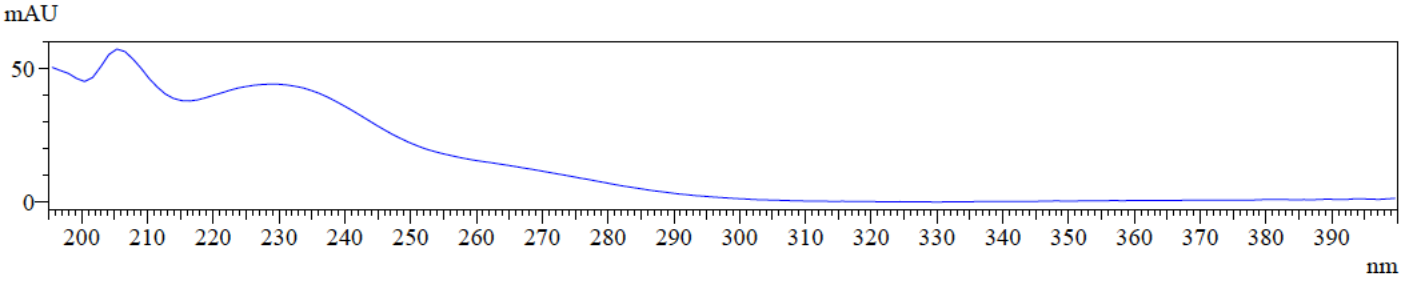




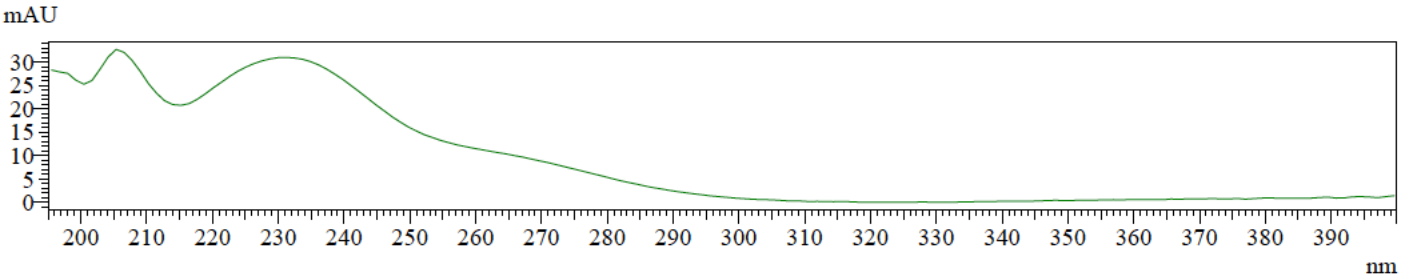
Chromatogram



UV Spectrum
Retention time = 22.493



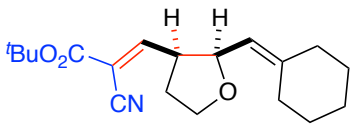
UV Spectrum
Retention time = 24.460



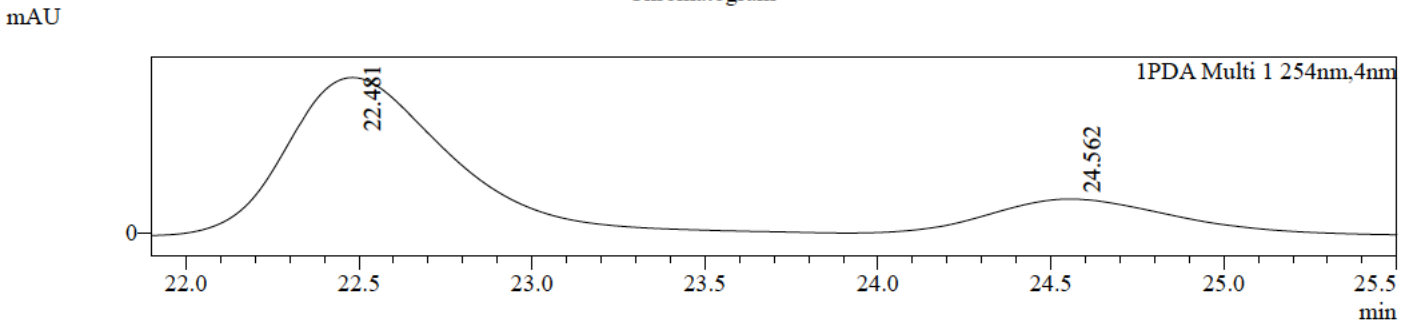
Peak Table

PDA Ch1 254nm

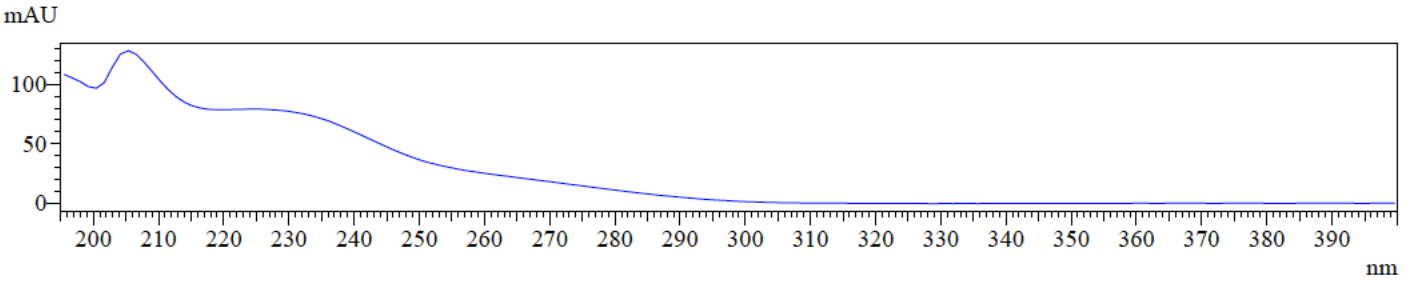
Peak#	Ret. Time	Area	Area%
1	22.493	641520	49.378
2	24.460	657671	50.622
Total		1299191	100.000



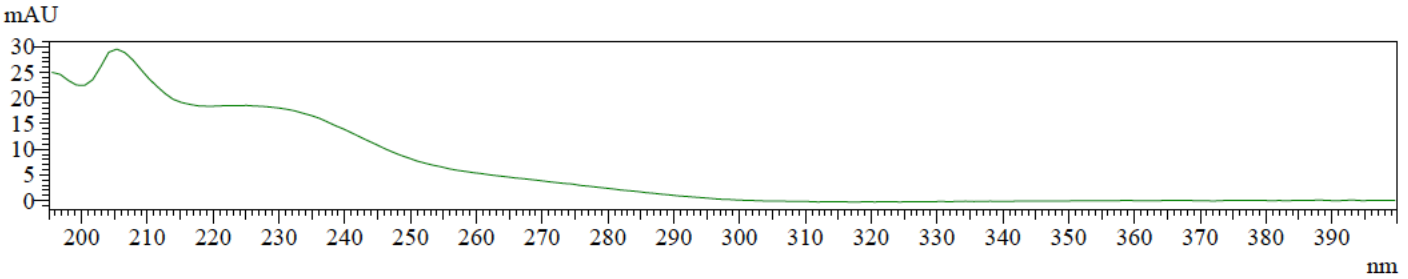
Chromatogram



UV Spectrum
Retention time = 22.481



UV Spectrum
Retention time = 24.562

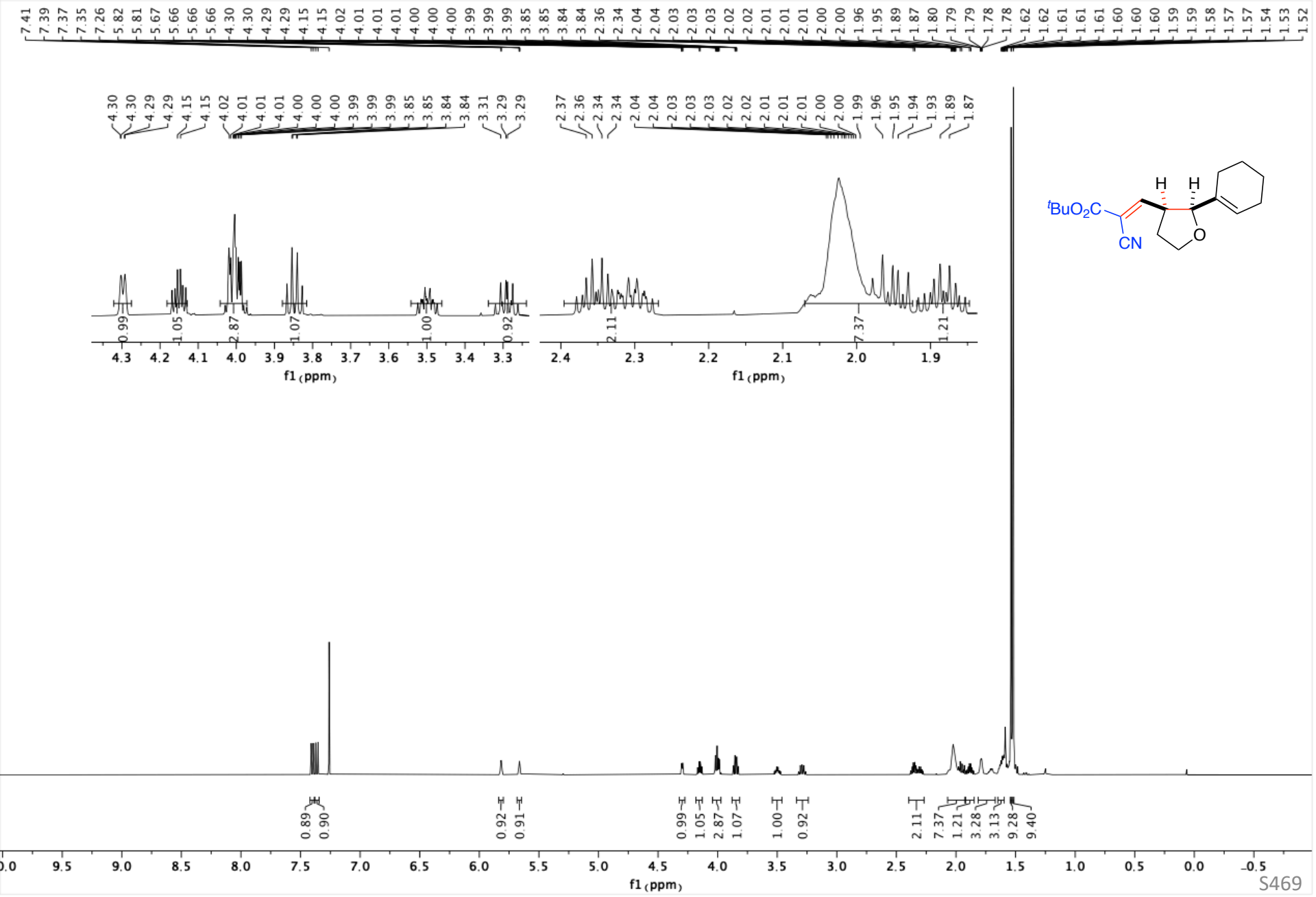


Peak Table

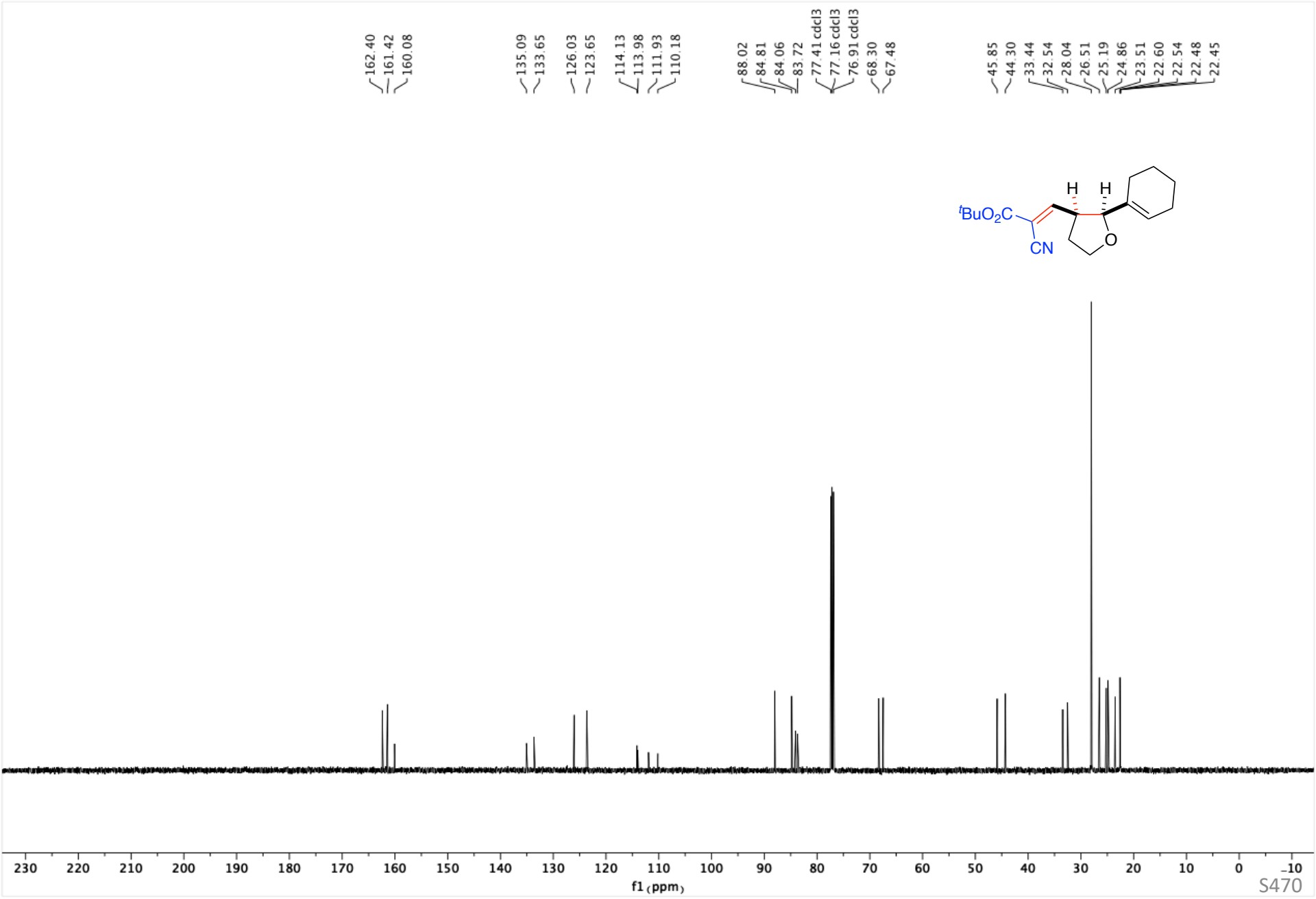
PDA Ch1 254nm

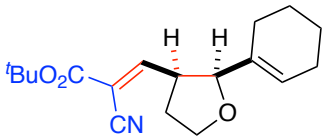
Peak#	Ret. Time	Area	Area%
1	22.481	1074412	78.769
2	24.562	289587	21.231
Total		1363998	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohex-1-en-1-yl)tetrahydrofuran-3-yl)acrylate

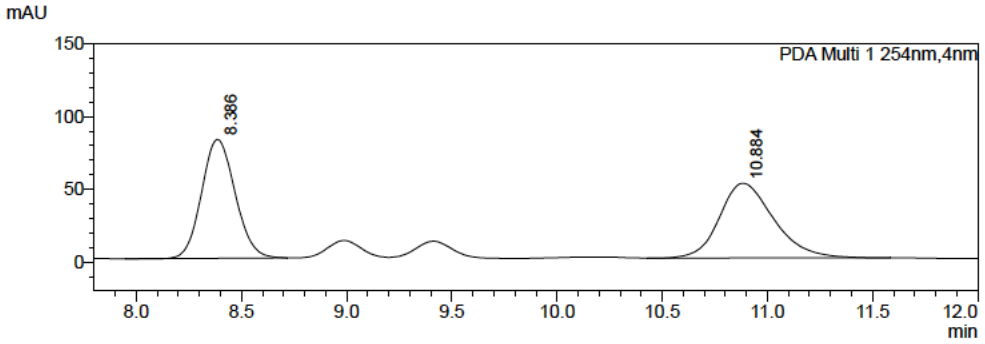


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohex-1-en-1-yl)tetrahydrofuran-3-yl)acrylate



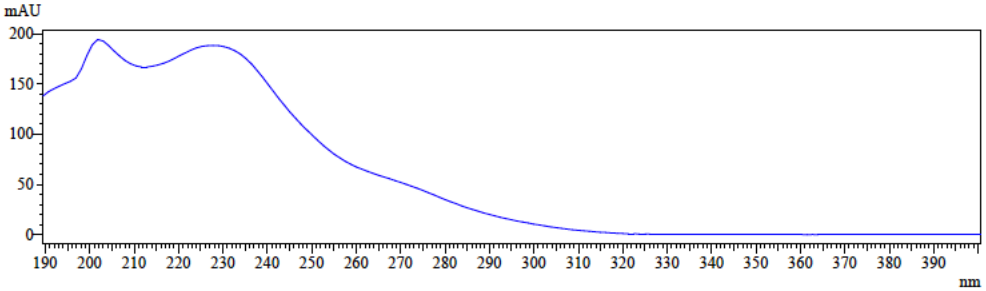


CZZ-EndoVinyl-Rac-IE-5%-0.8mL



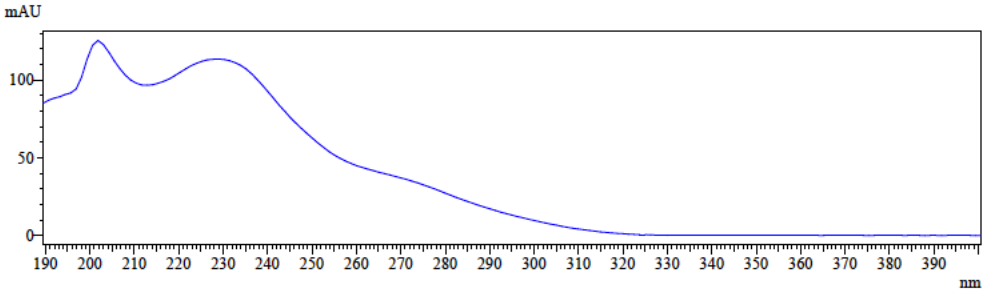
UV Spectrum

Retention Time: 8.386 min



UV Spectrum

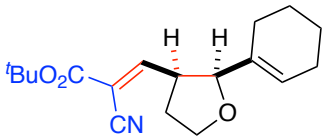
Retention Time: 10.884 min



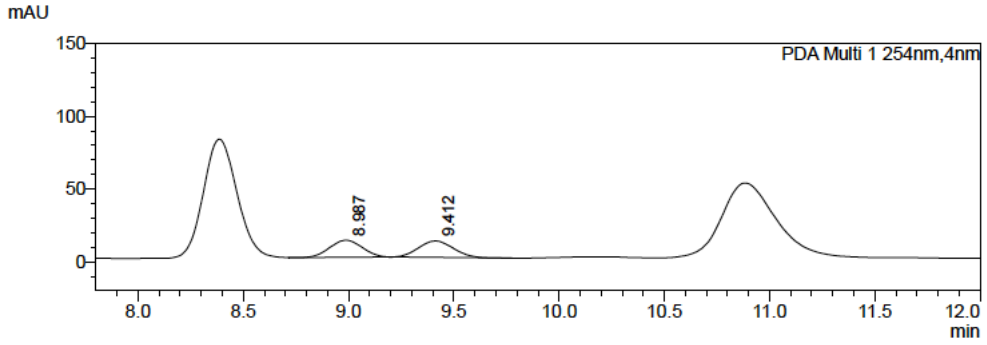
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.386	49.511
2	10.884	50.489
Total		100.000

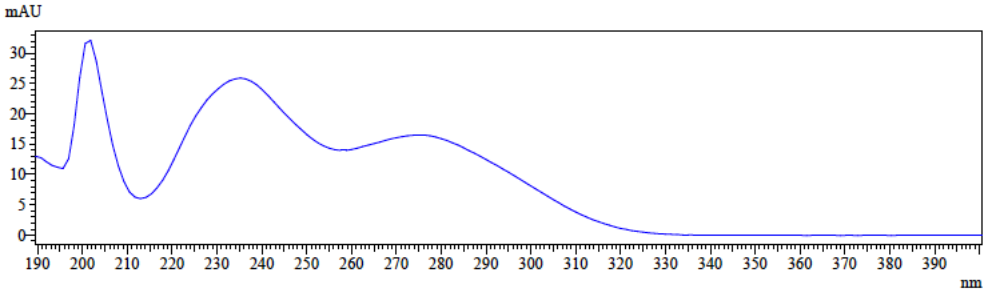


CZZ-EndoVinyl-Rac-IE-5%-0.8mL



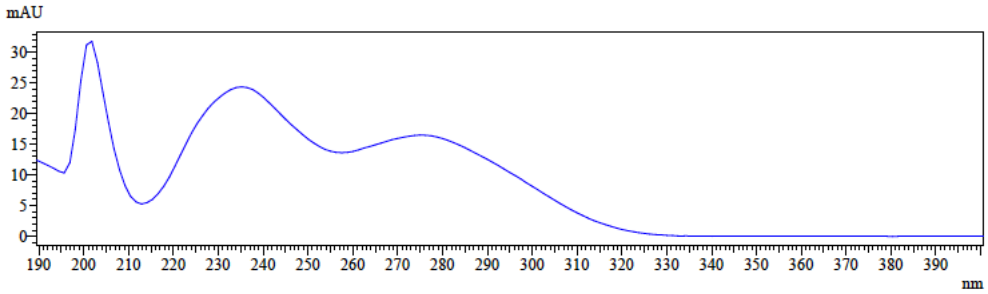
UV Spectrum

Retention Time: 8.987 min



UV Spectrum

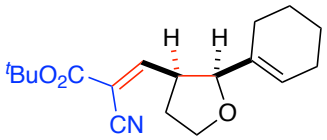
Retention Time: 9.412 min



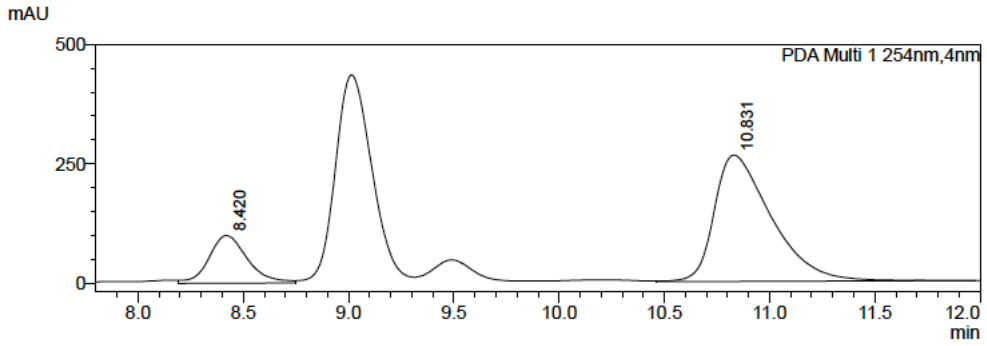
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.987	49.302
2	9.412	50.698
Total		100.000

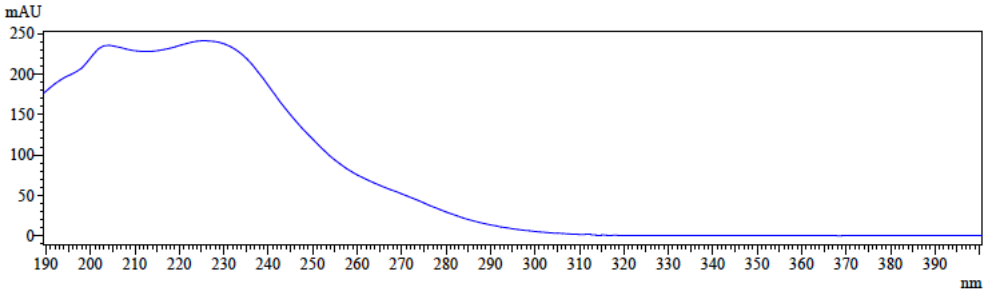


CZZ-EndoVinyl-Chiral-IE-5%-0.8mL



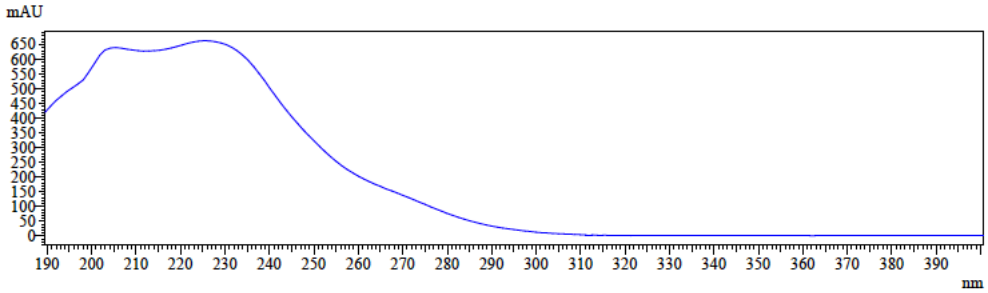
UV Spectrum

Retention Time: 8.420 min



UV Spectrum

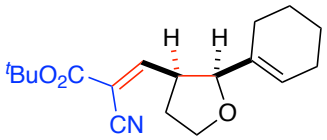
Retention Time: 10.831 min



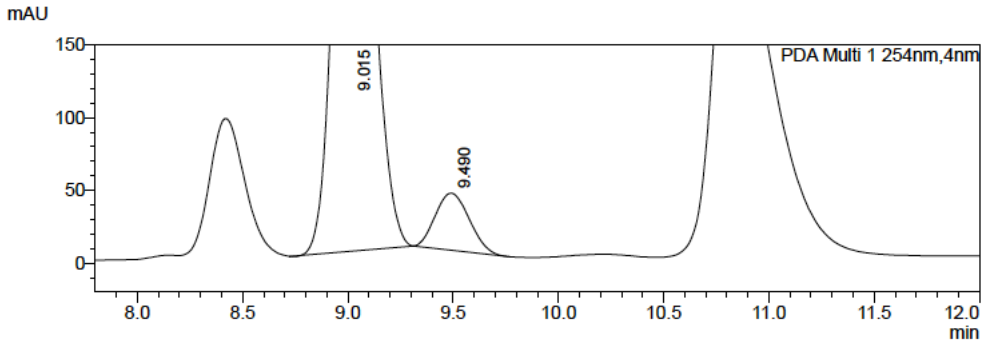
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.420	20.370
2	10.831	79.630
Total		100.000

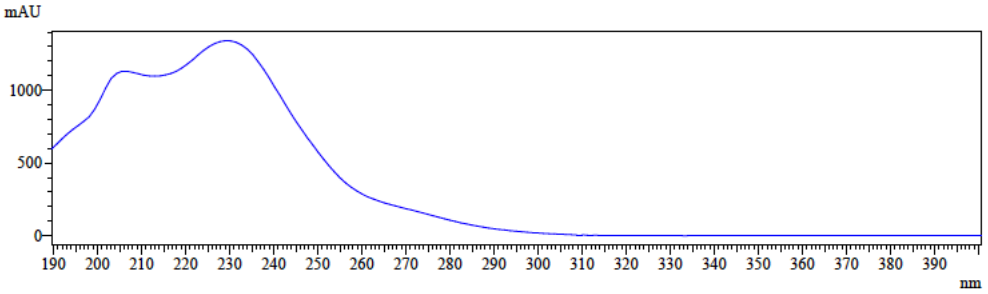


CZZ-EndoVinyl-Chiral-IE-5%-0.8mL



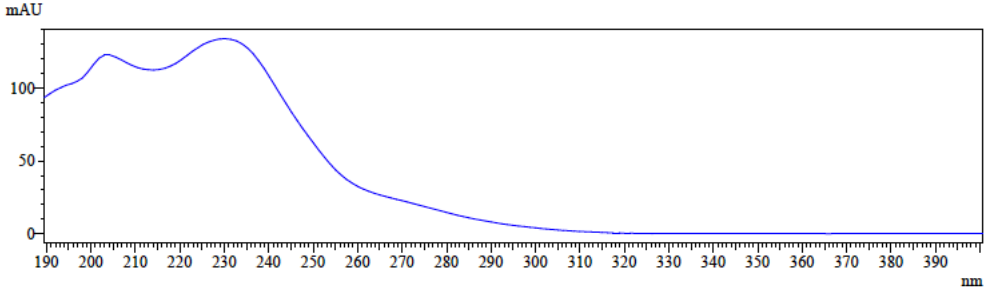
UV Spectrum

Retention Time: 9.015 min



UV Spectrum

Retention Time: 9.490 min

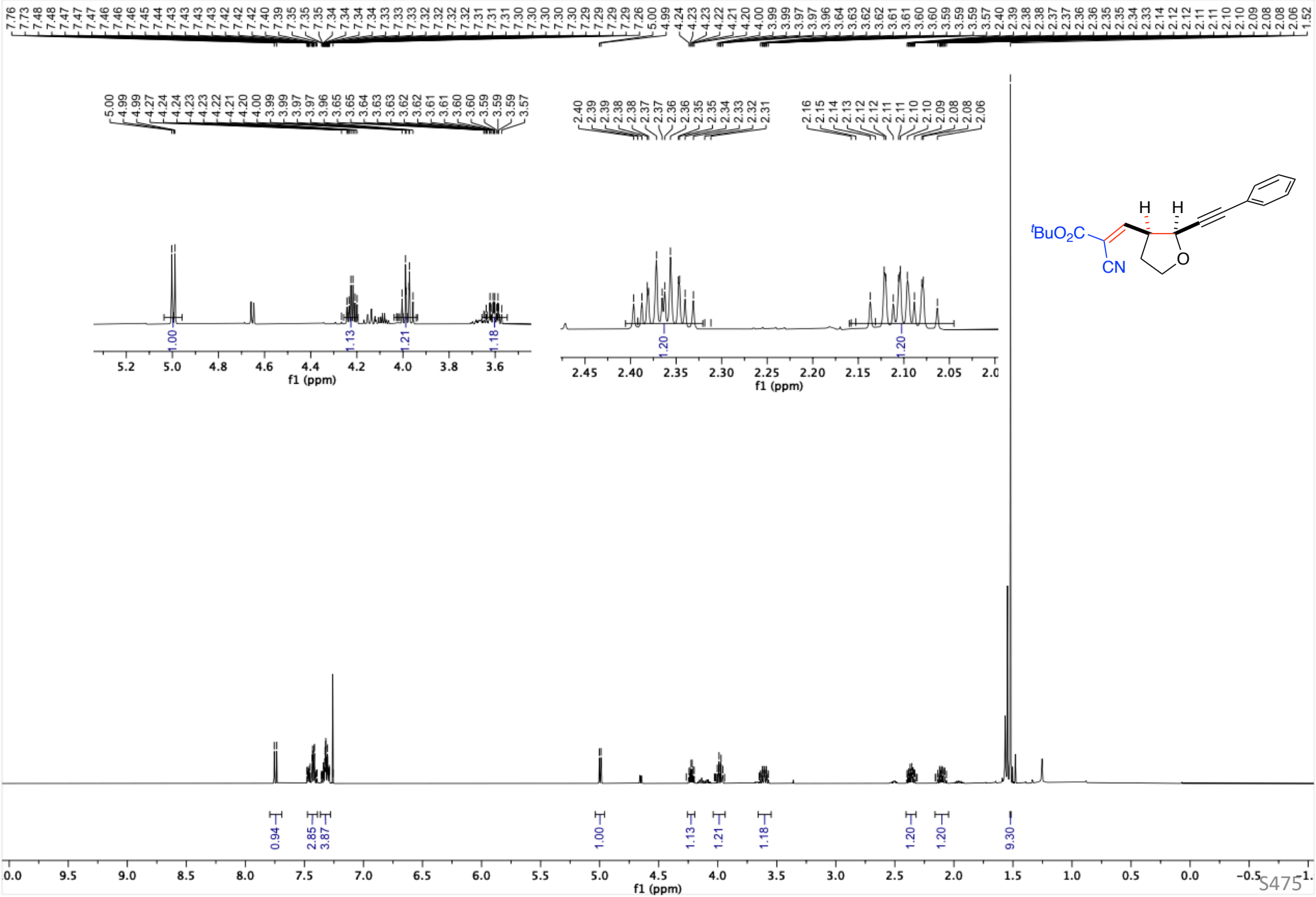


Peak Table

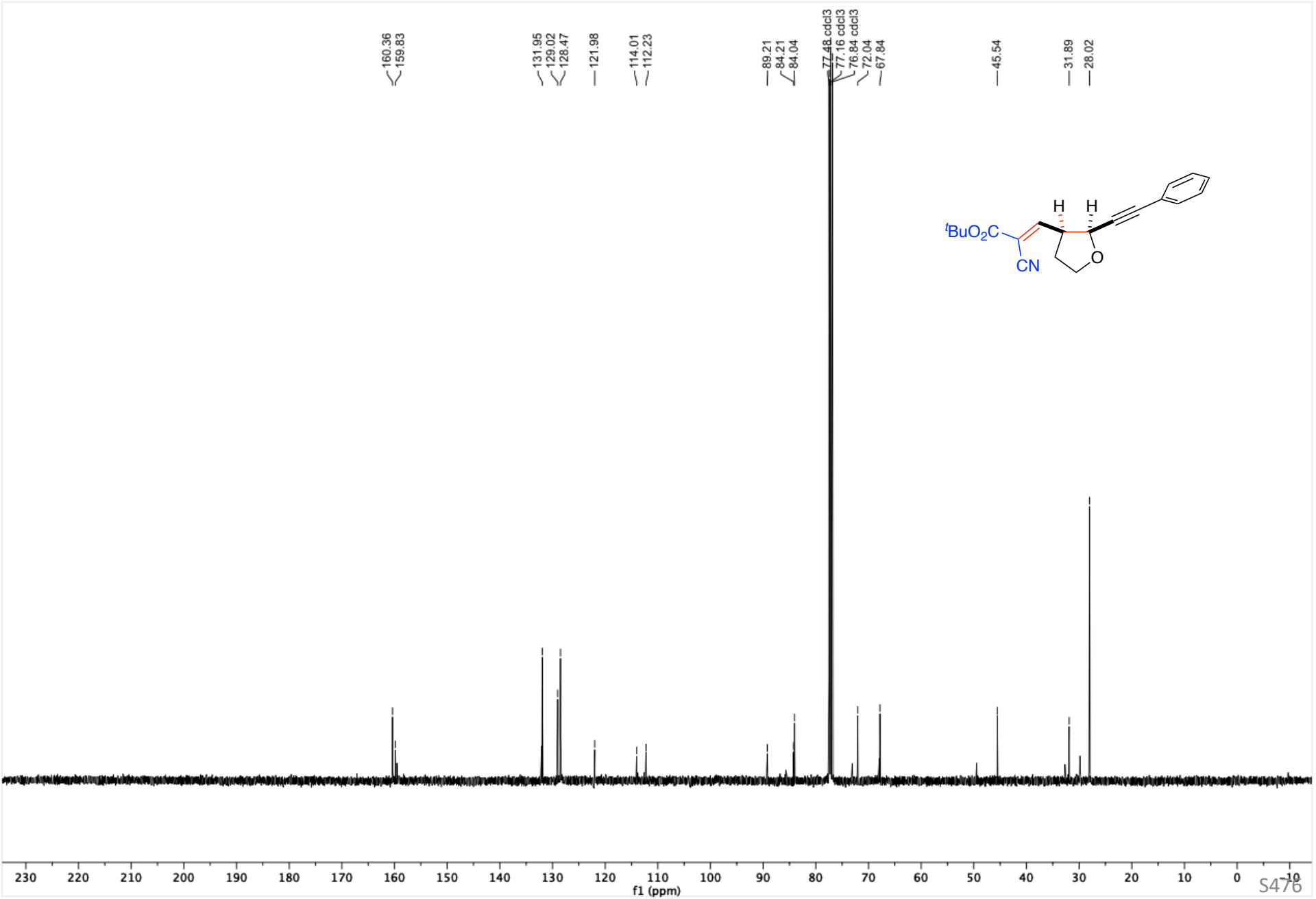
PDA Ch1 254nm

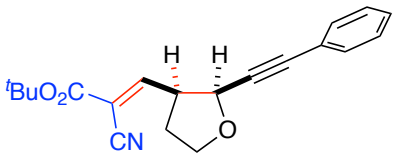
Peak#	Ret. Time	Area%
1	9.015	91.981
2	9.490	8.019
Total		100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(phenylethynyl)tetrahydrofuran-3-yl)acrylate

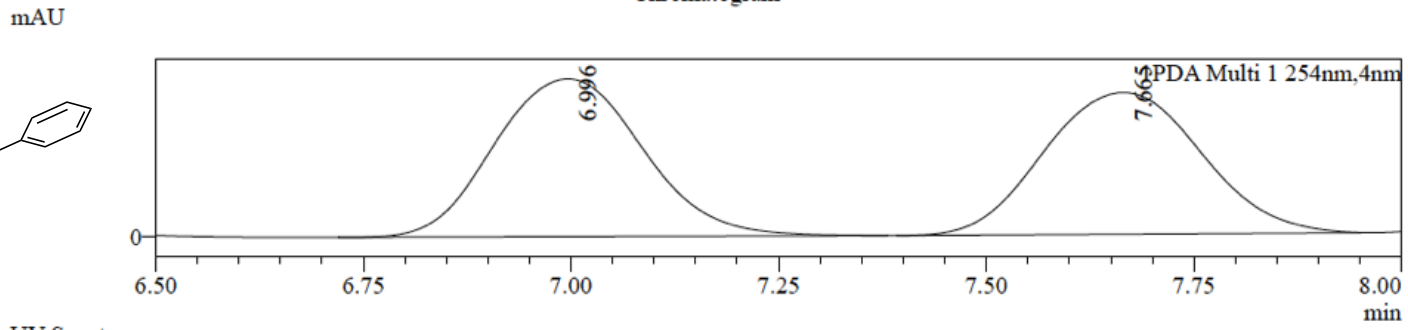


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(phenylethynyl)tetrahydrofuran-3-yl)acrylate

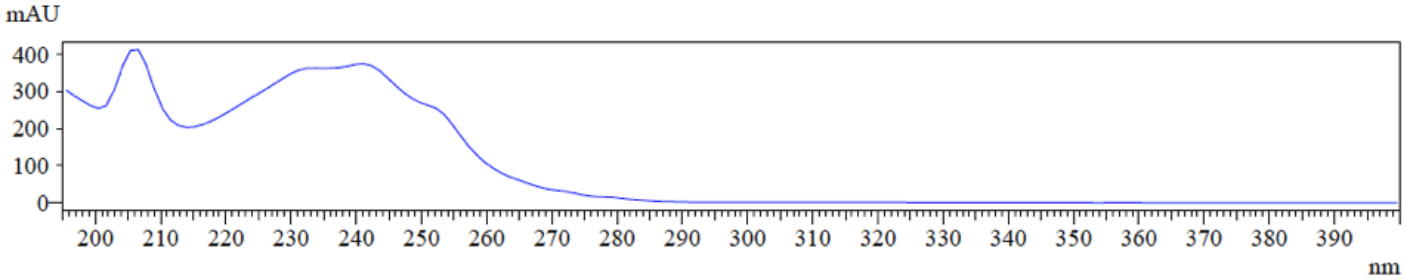




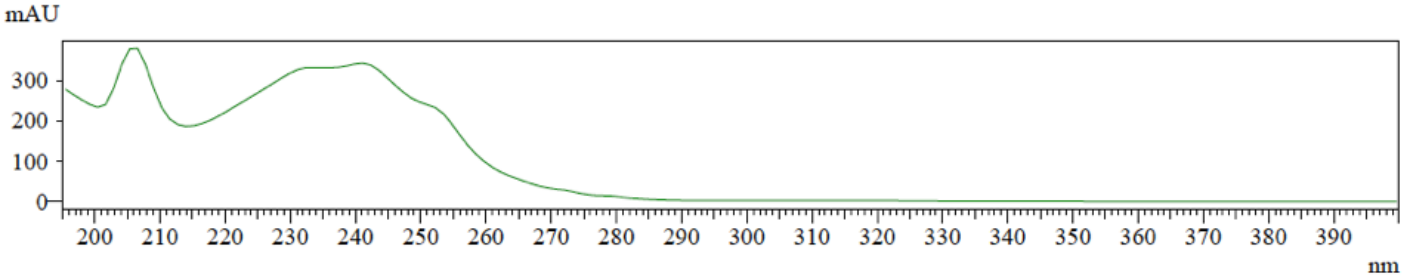
Chromatogram



UV Spectrum
Retention time = 6.996



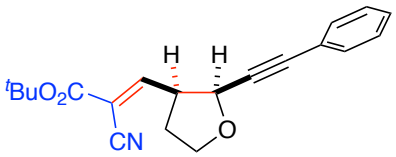
UV Spectrum
Retention time = 7.665



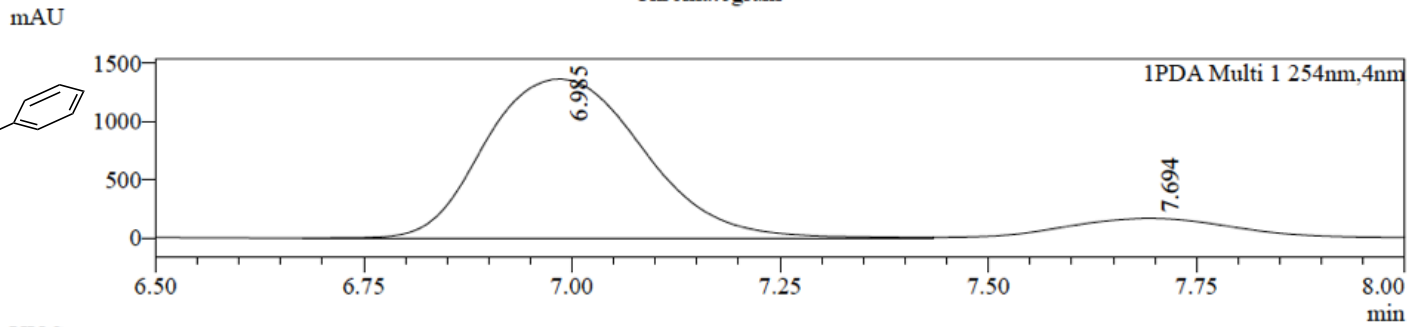
Peak Table

PDA Ch1 254nm

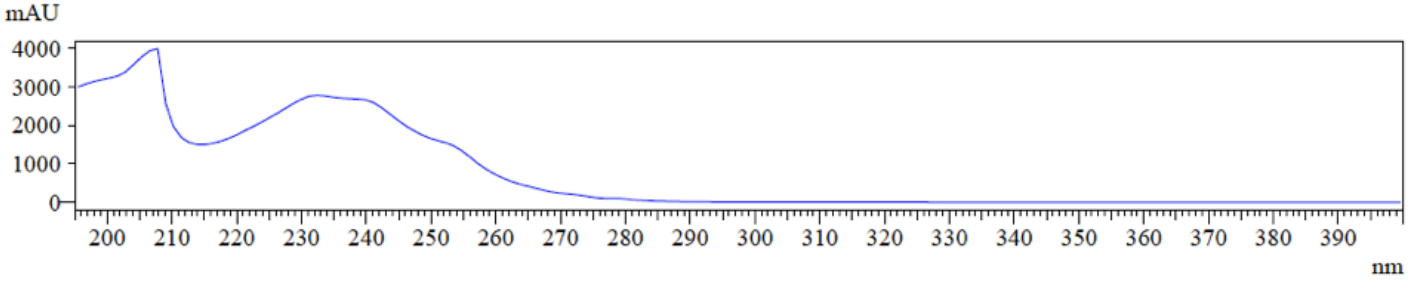
Peak#	Ret. Time	Area	Area%
1	6.996	2703902	51.203
2	7.665	2576844	48.797
Total		5280746	100.000



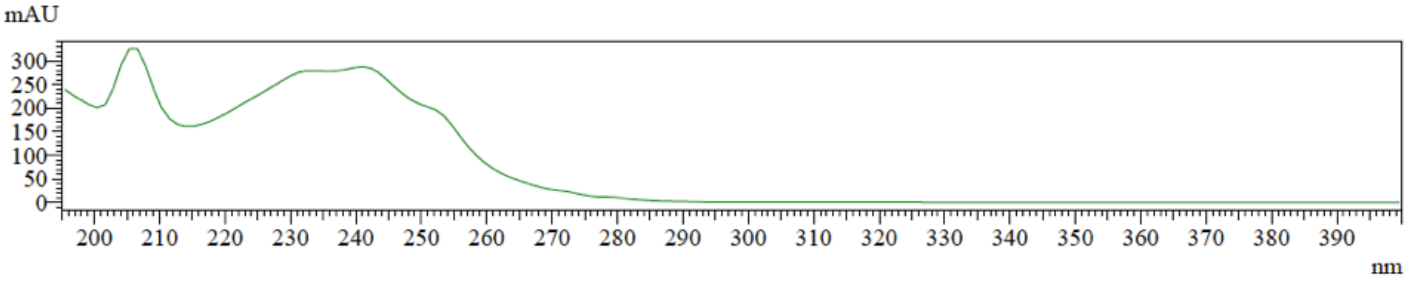
Chromatogram



UV Spectrum
Retention time = 6.985



UV Spectrum
Retention time = 7.694

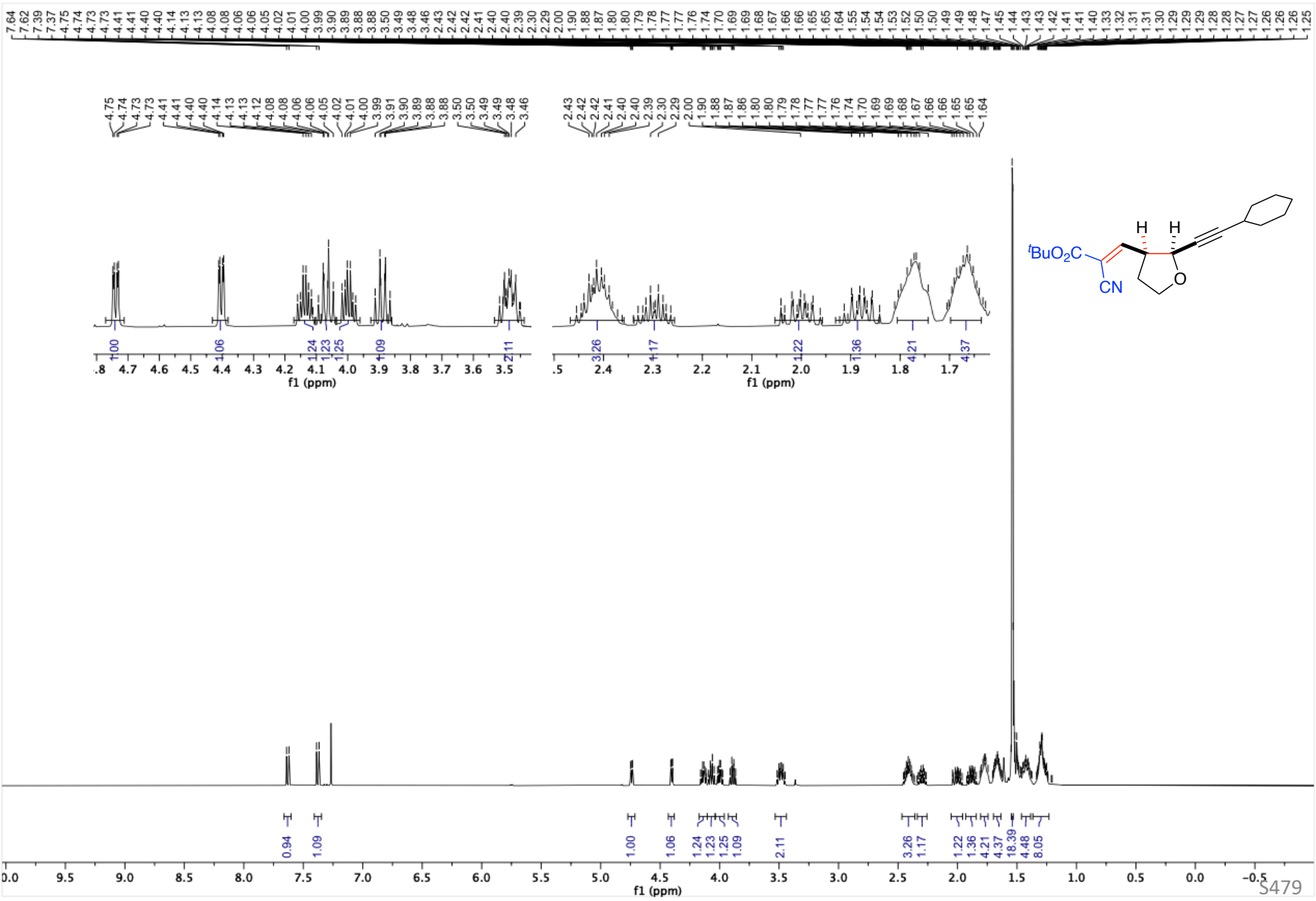


Peak Table

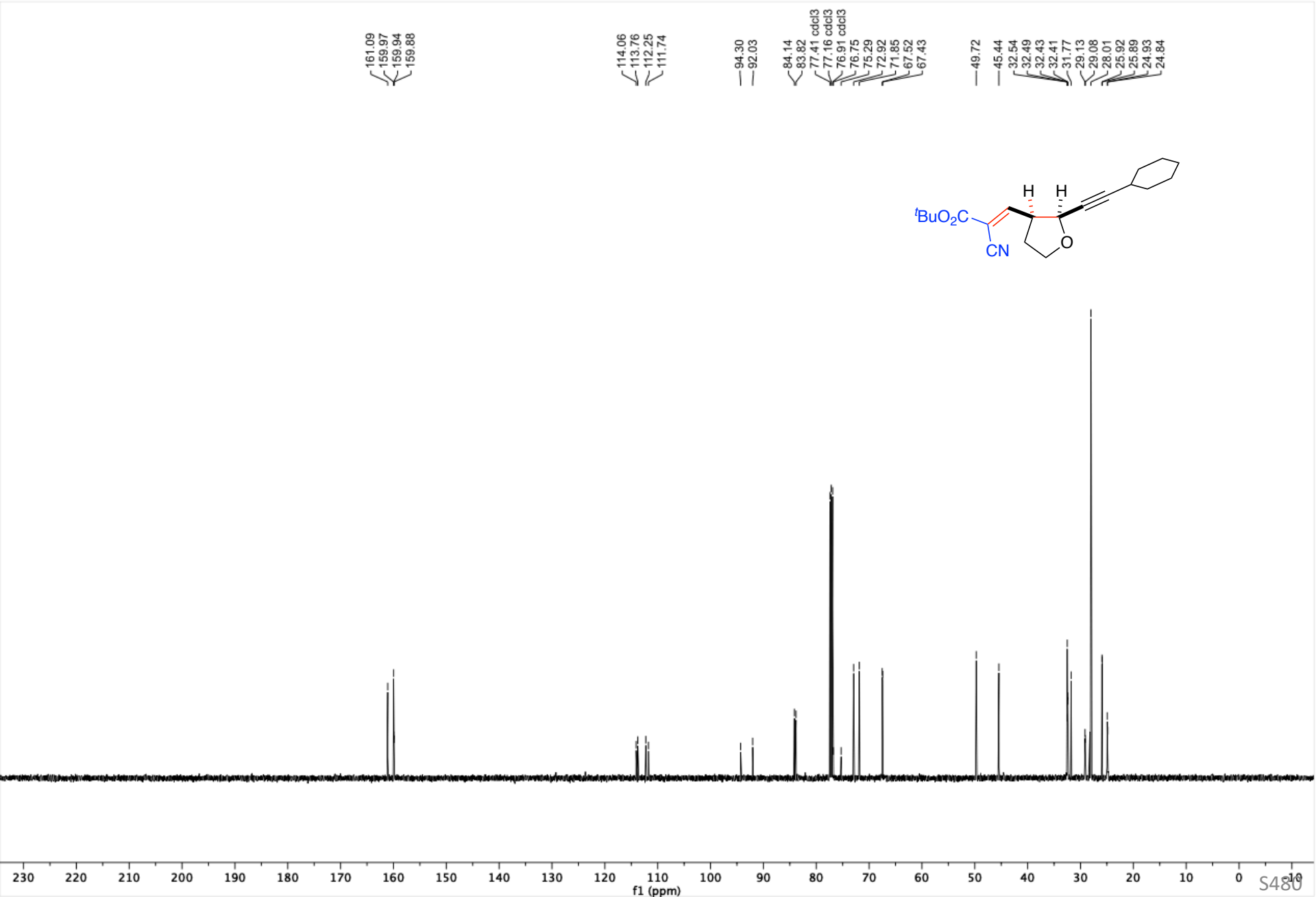
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.985	17969345	88.454
2	7.694	2345471	11.546
Total		20314816	100.000

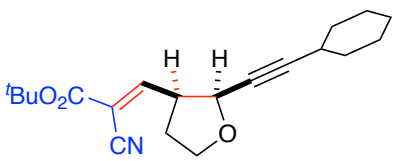
tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-(cyclohexylethynyl)tetrahydrofuran-3-yl)acrylate

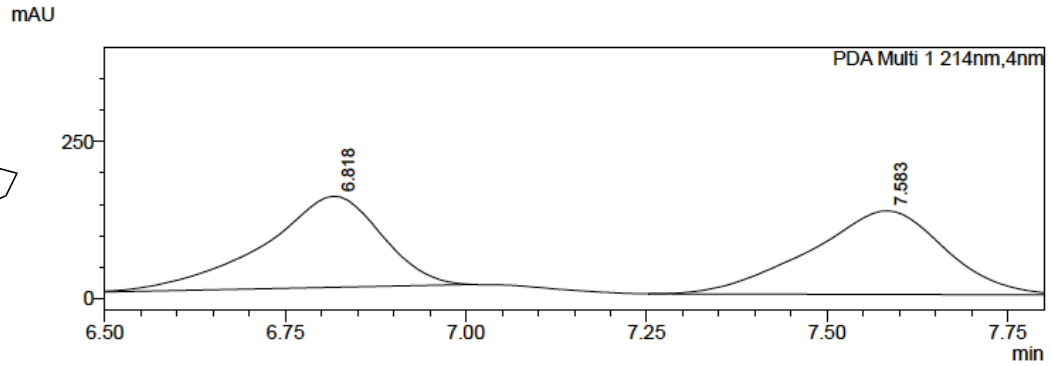


tert-Butyl (_E_)-2-cyano-3-((2_S_,3_S_)-2-(cyclohexylethynyl)tetrahydrofuran-3-yl)acrylate



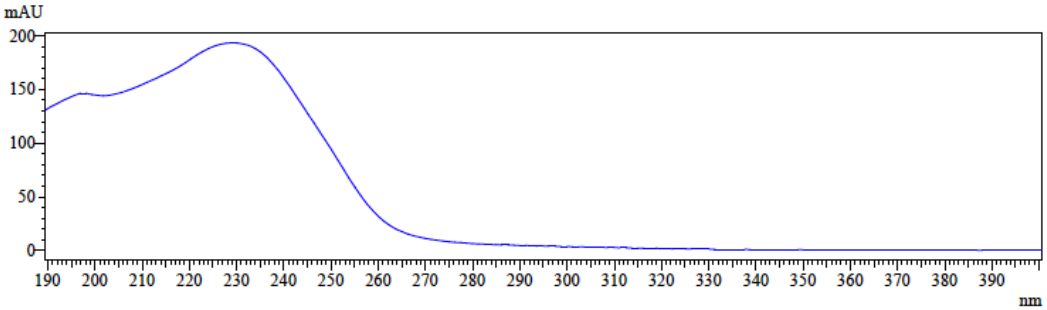
CZZ-HexAlkyne-Rac-IB-2%-0.8mL





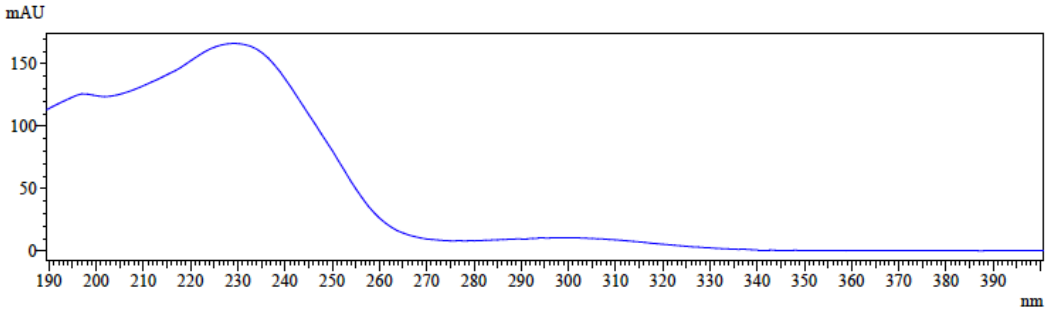
UV Spectrum

Retention Time: 6.818 min



UV Spectrum

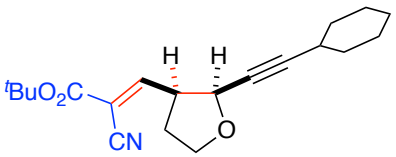
Retention Time: 7.583 min



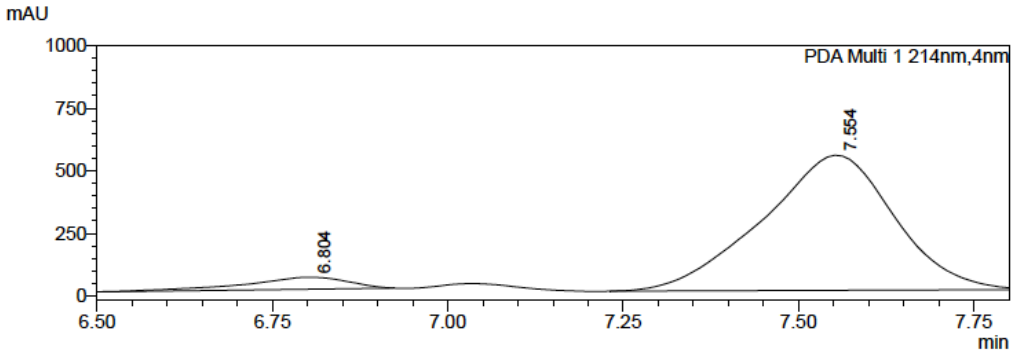
Peak Table

PDA Ch1 214nm

Peak#	Ret. Time	Area%
1	6.818	48.747
2	7.583	51.253
Total		100.000

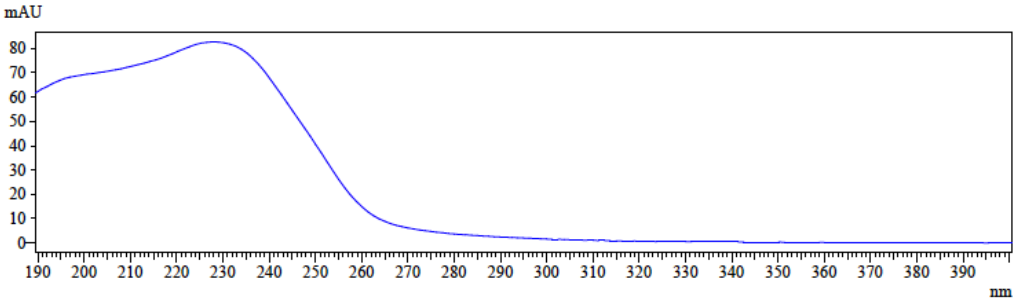


CZZ-HexAlkyne-Chrial-IB-2%-0.8mL



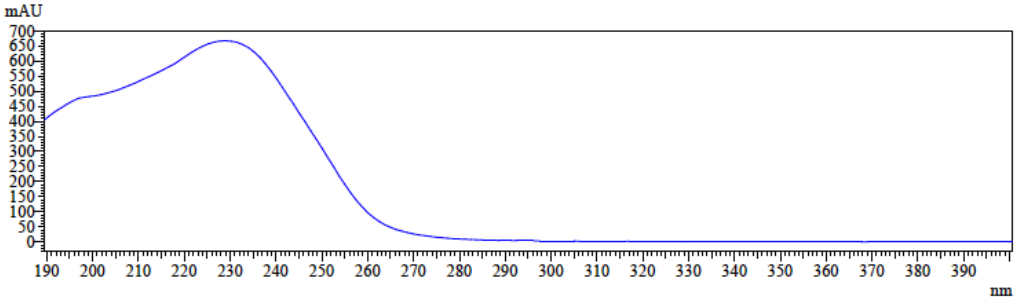
UV Spectrum

Retention Time: 6.804 min



UV Spectrum

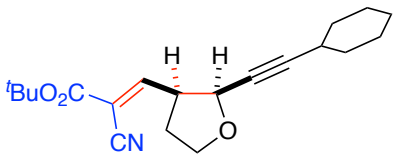
Retention Time: 7.554 min



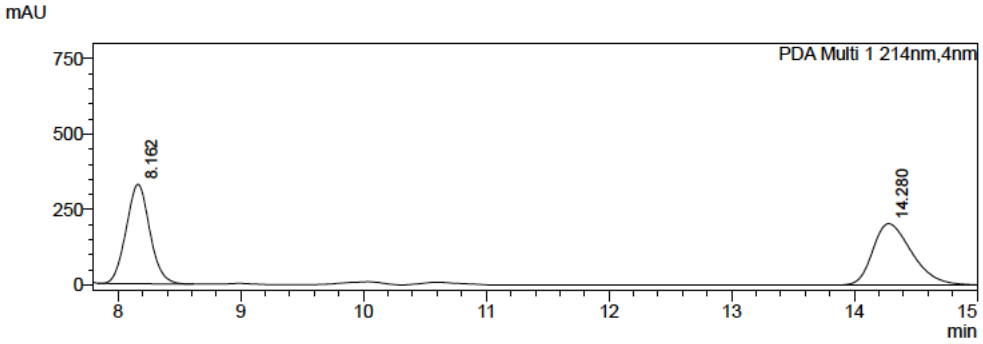
Peak Table

PDA Ch1 214nm

Peak#	Ret. Time	Area%
1	6.804	6.557
2	7.554	93.443
Total		100.000

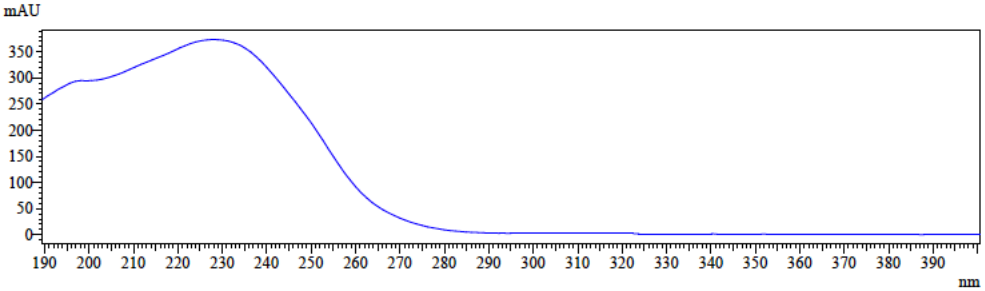


CZZ-HexAlkyne-Rac-IB-2%-0.8mL



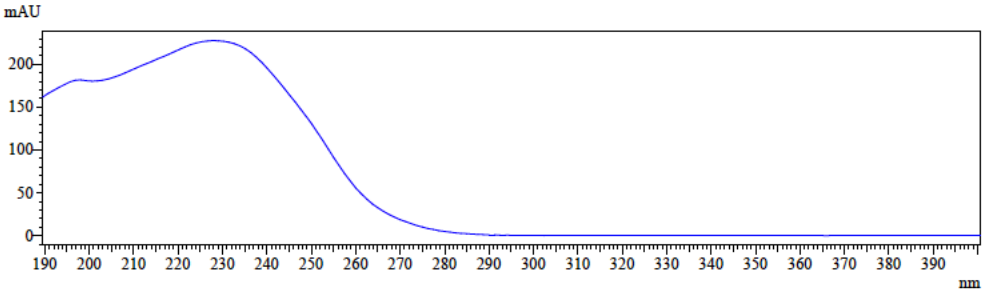
UV Spectrum

Retention Time: 8.162 min



UV Spectrum

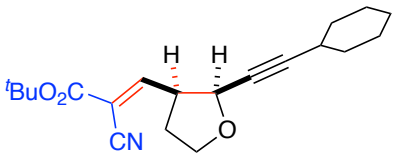
Retention Time: 14.280 min



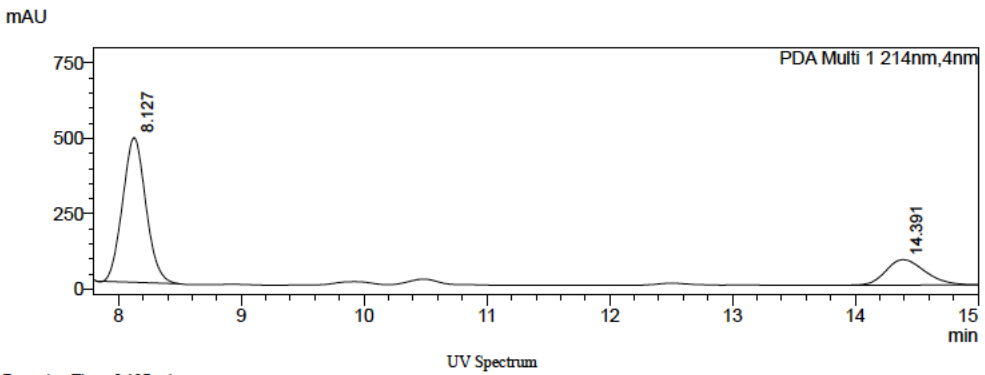
Peak Table

PDA Ch1 214nm

Peak#	Ret. Time	Area%
1	8.162	49.513
2	14.280	50.487
Total		100.000

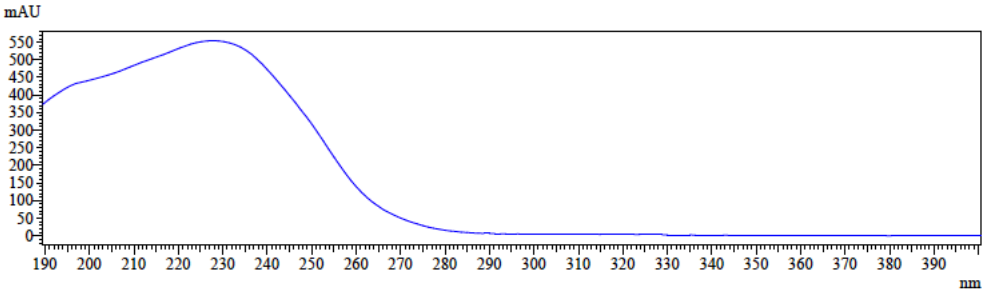


CZZ-HexAlkyne-Chrial-IB-2%-0.8mL



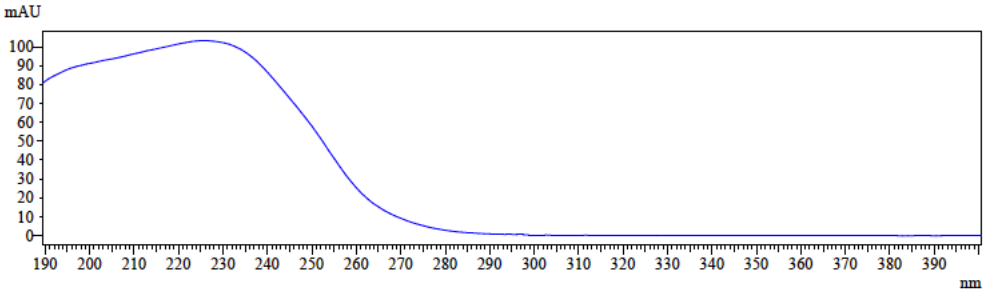
UV Spectrum

Retention Time: 8.127 min



UV Spectrum

Retention Time: 14.391 min

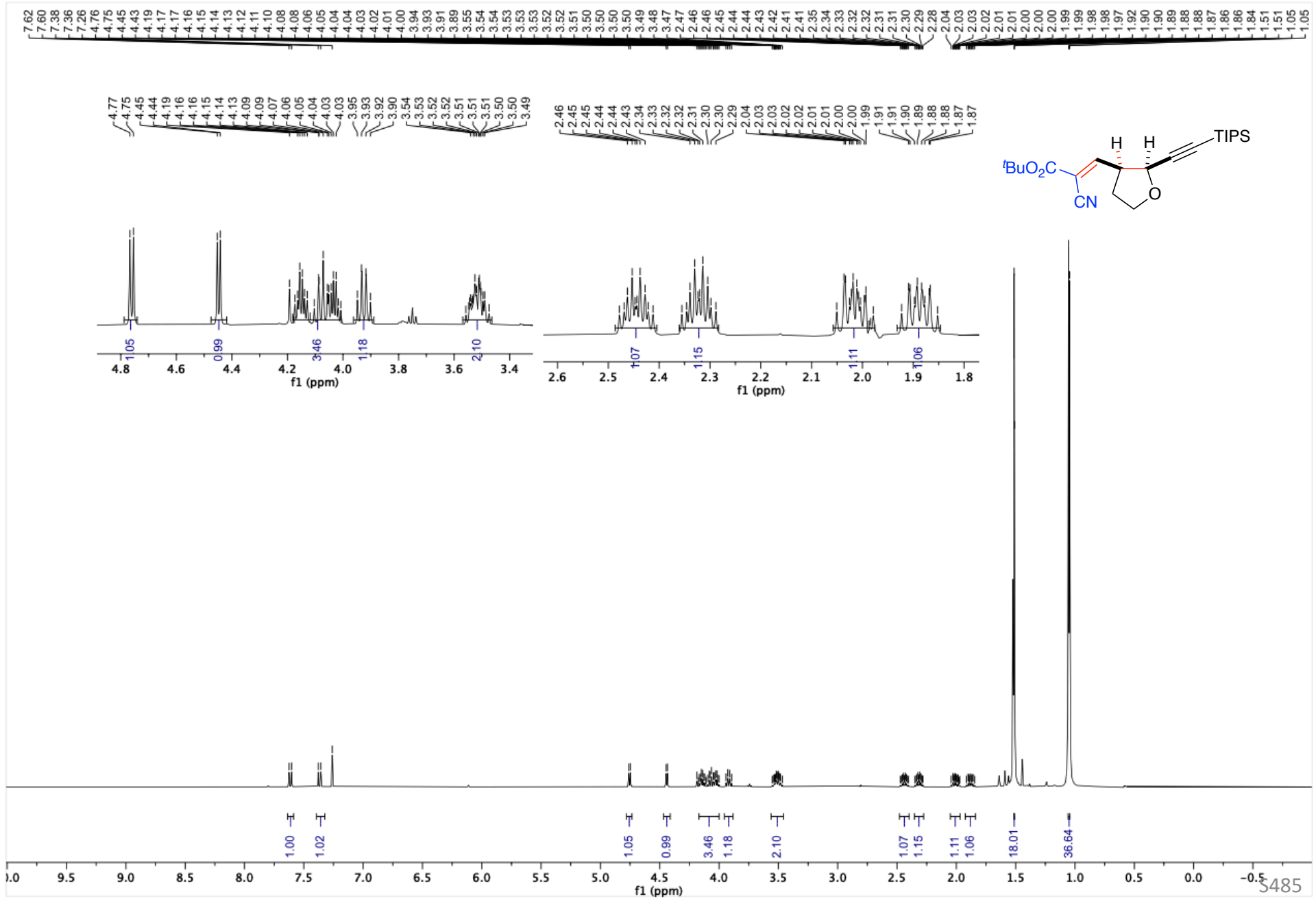


Peak Table

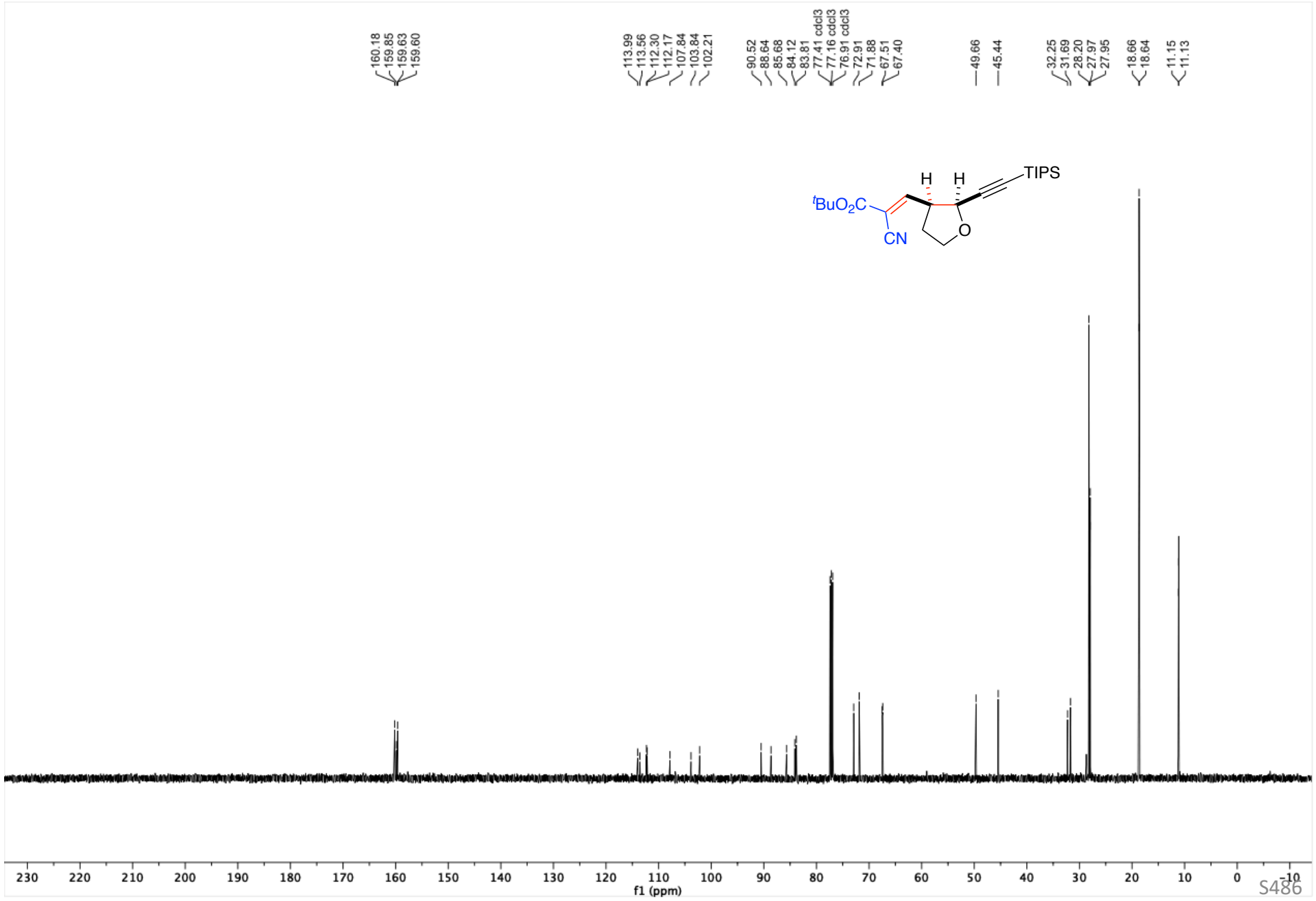
PDA Ch1 214nm

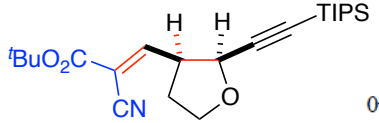
Peak#	Ret. Time	Area%
1	8.127	76.935
2	14.391	23.065
Total		100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((triisopropylsilyl)ethynyl)tetrahydrofuran-3-yl)acrylate

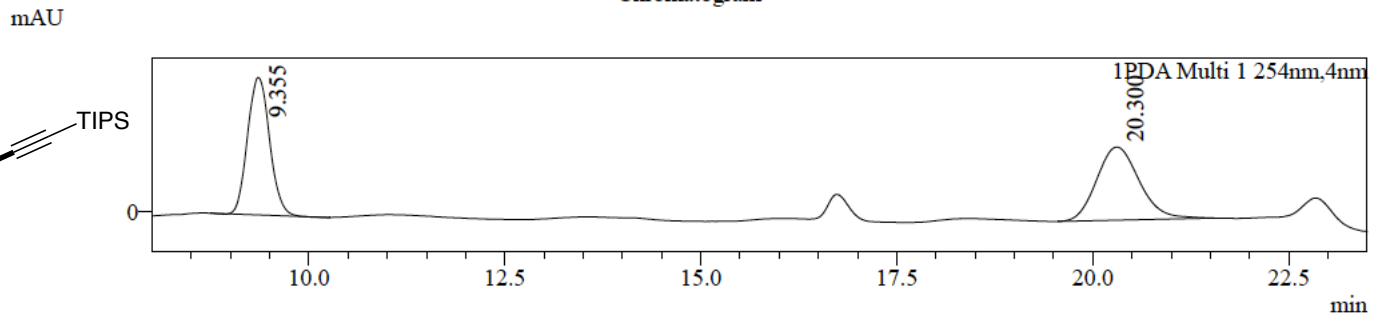


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((triisopropylsilyl)ethynyl)tetrahydrofuran-3-yl)acrylate

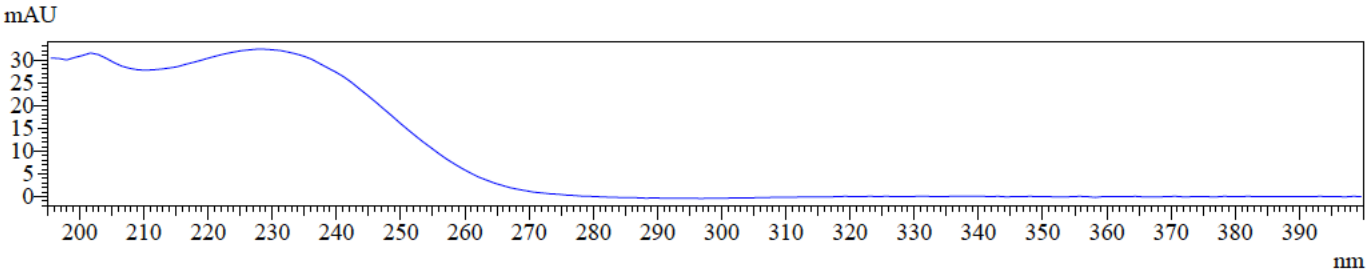




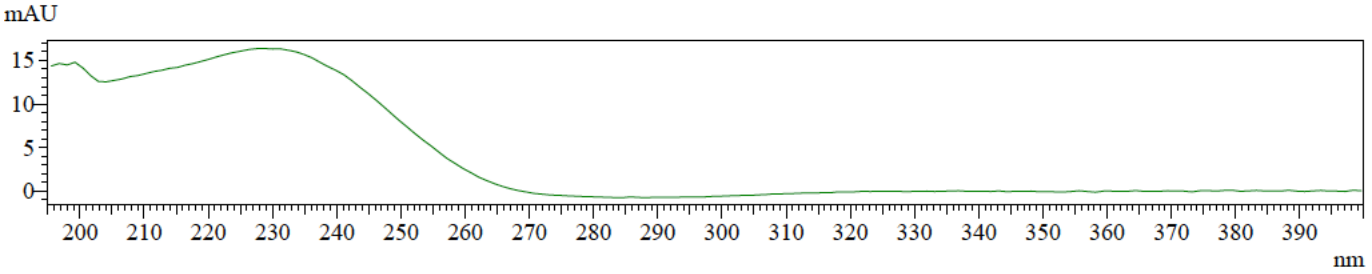
Chromatogram



UV Spectrum
Retention time = 9.355



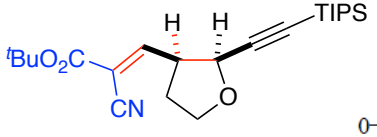
UV Spectrum
Retention time = 20.300



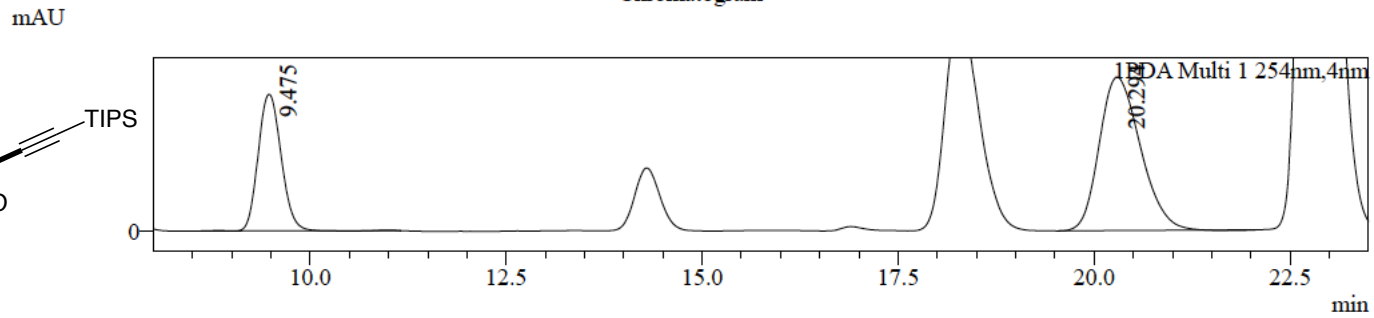
Peak Table

PDA Ch1 254nm

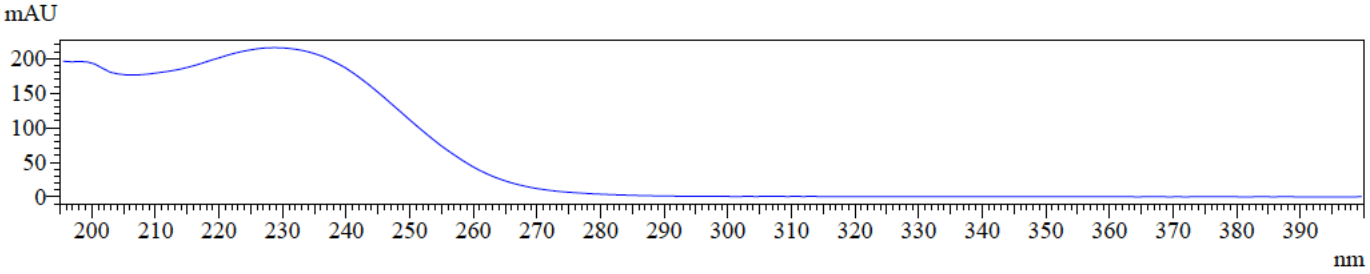
Peak#	Ret. Time	Area	Area%
1	9.355	230003	49.379
2	20.300	235790	50.621
Total		465792	100.000



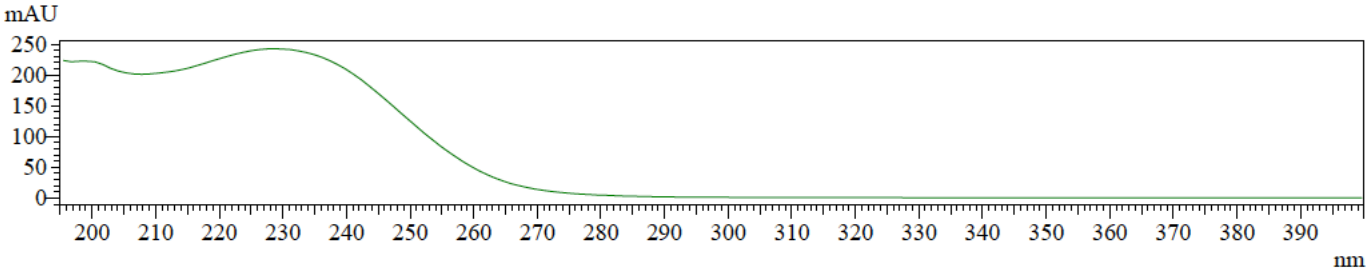
Chromatogram



UV Spectrum
Retention time = 9.475



UV Spectrum
Retention time = 20.294

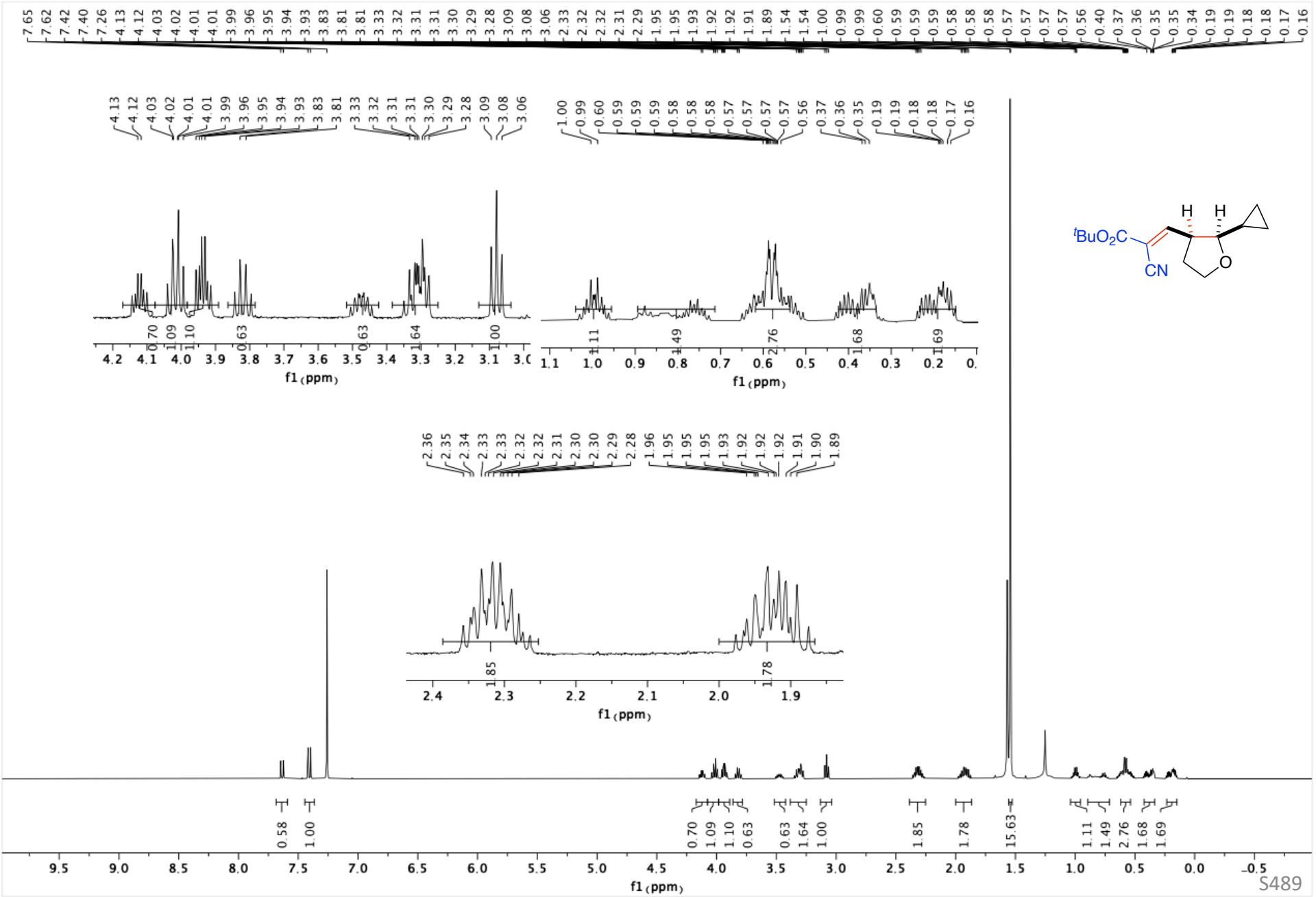


Peak Table

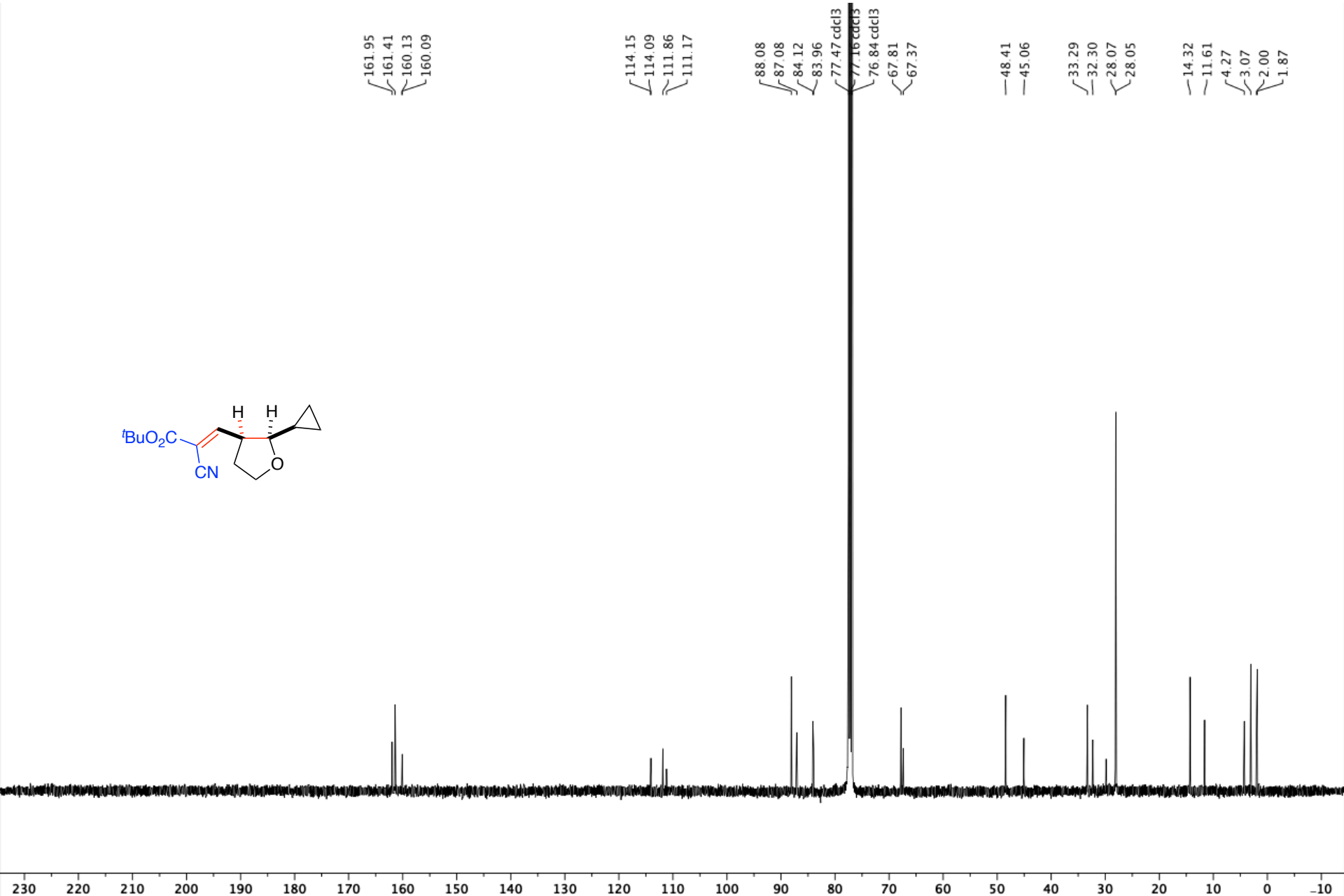
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.475	1640000	33.328
2	20.294	3280819	66.672
Total		4920820	100.000

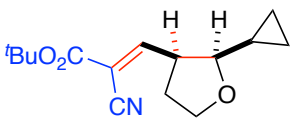
tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-cyclopropyltetrahydrofuran-3-yl)acrylate

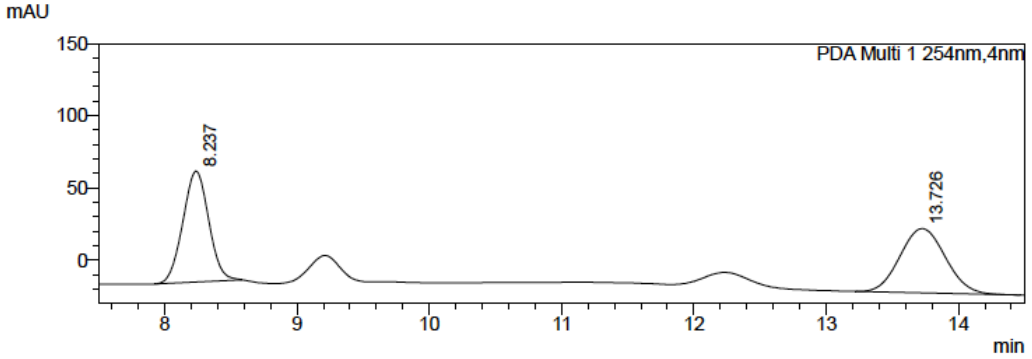


tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-cyclopropyltetrahydrofuran-3-yl)acrylate



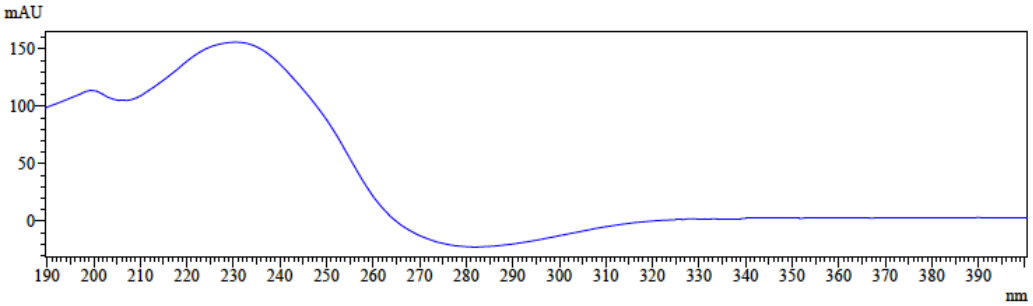
CZZ-2844-IF-5%0.8mL





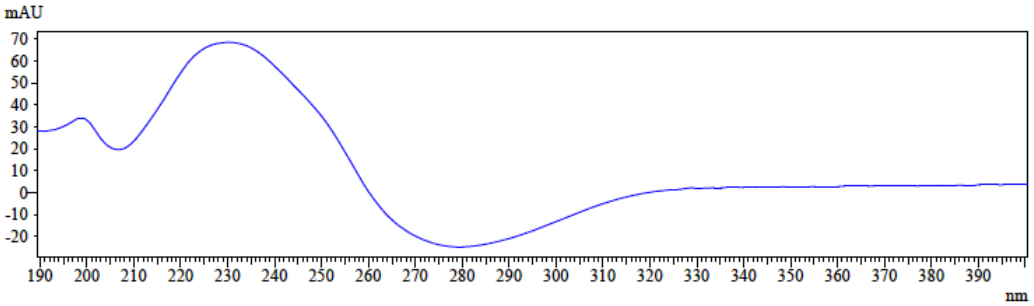
UV Spectrum

Retention Time: 8.237 min



UV Spectrum

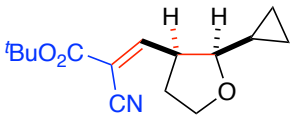
Retention Time: 13.726 min



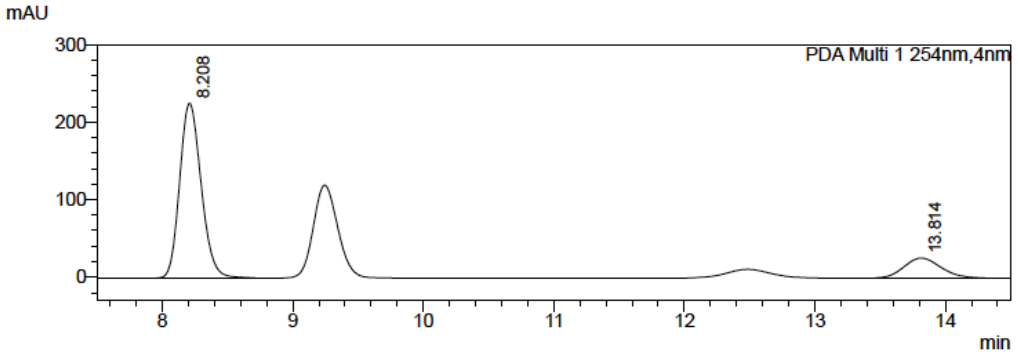
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.237	49.517
2	13.726	50.483
Total		100.000

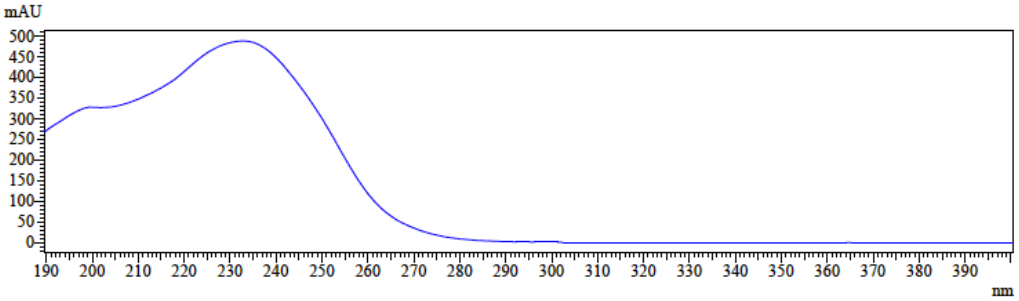


CZZ-CyclopropanePDT-Chiral-IF-5%-0.8mL



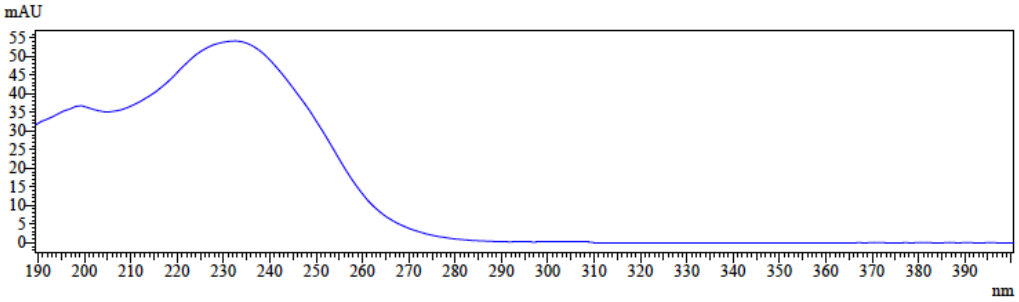
UV Spectrum

Retention Time: 8.208 min



UV Spectrum

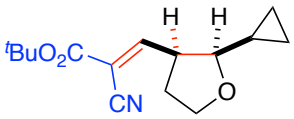
Retention Time: 13.814 min



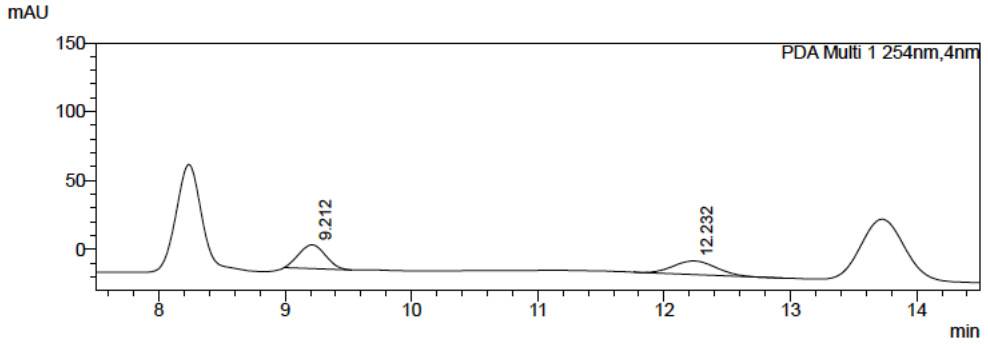
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	8.208	83.087
2	13.814	16.913
Total		100.000

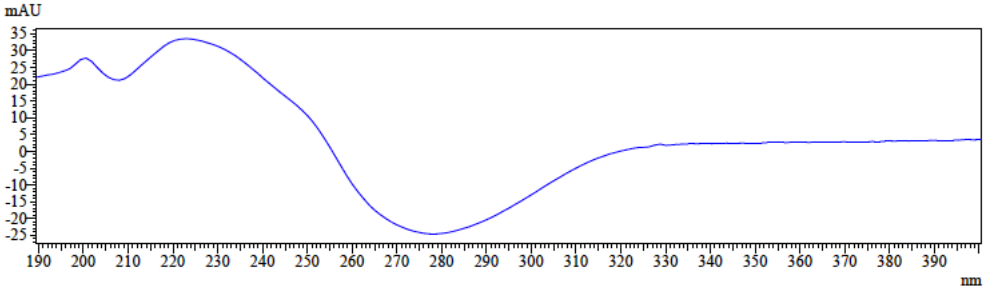


CZZ-2844-IF-5%0.8mL



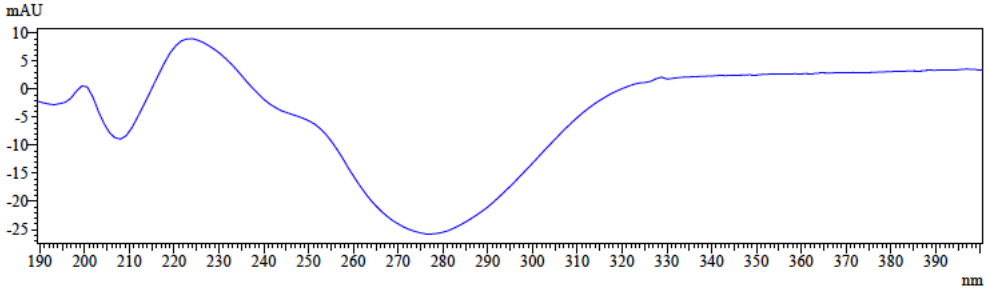
UV Spectrum

Retention Time: 9.212 min



UV Spectrum

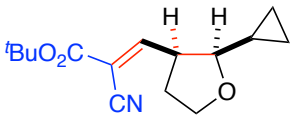
Retention Time: 12.232 min



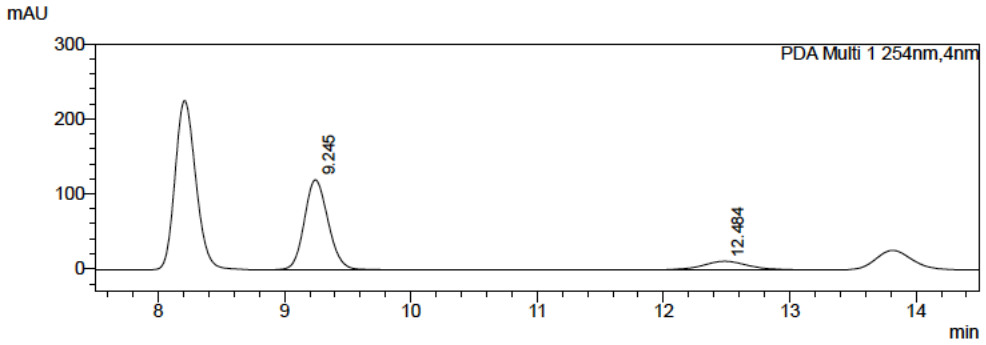
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.212	52.089
2	12.232	47.911
Total		100.000

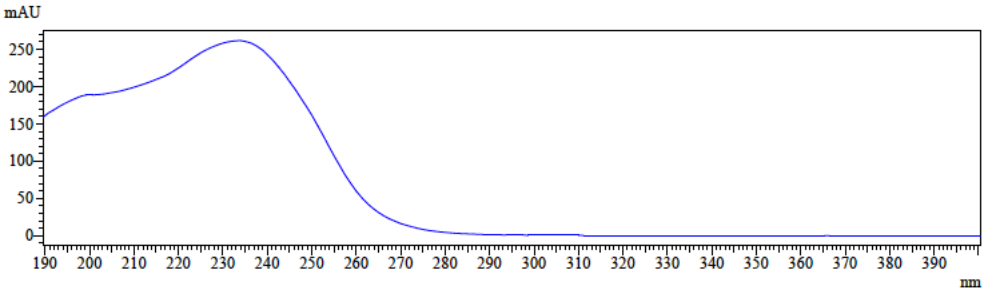


CZZ-CyclopropanePDT-Chiral-IF-5%-0.8mL



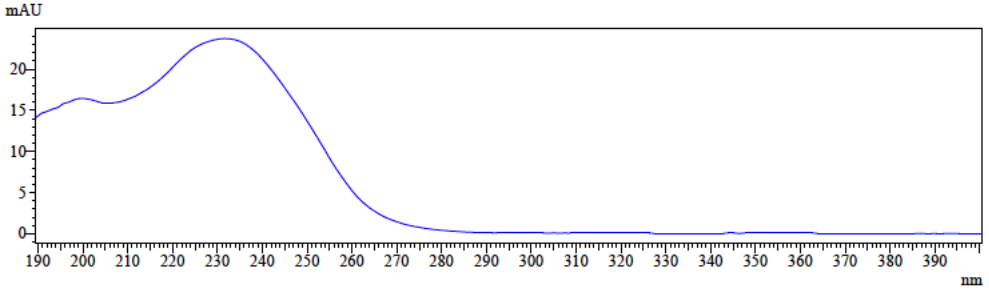
UV Spectrum

Retention Time: 9.245 min



UV Spectrum

Retention Time: 12.484 min

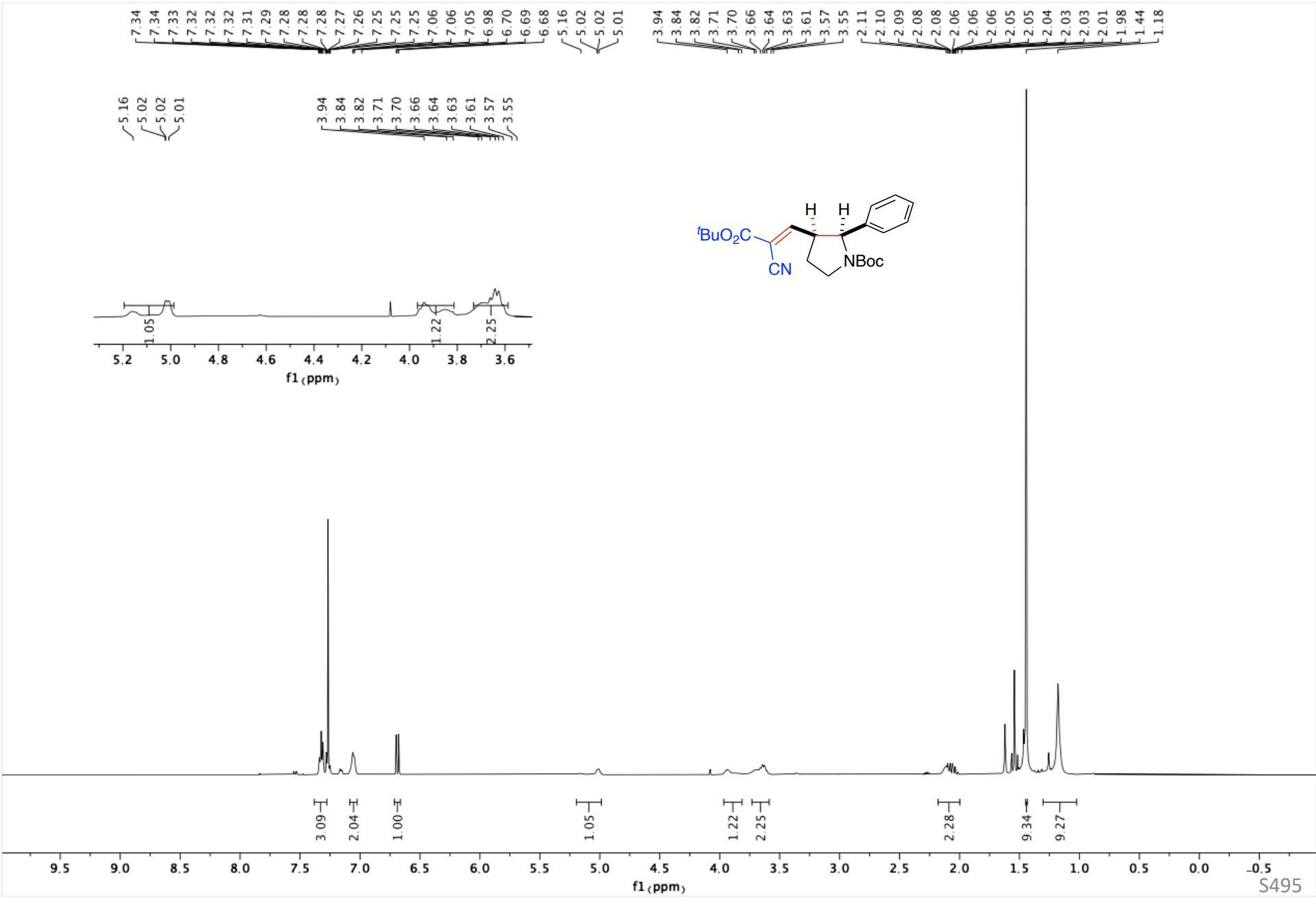


Peak Table

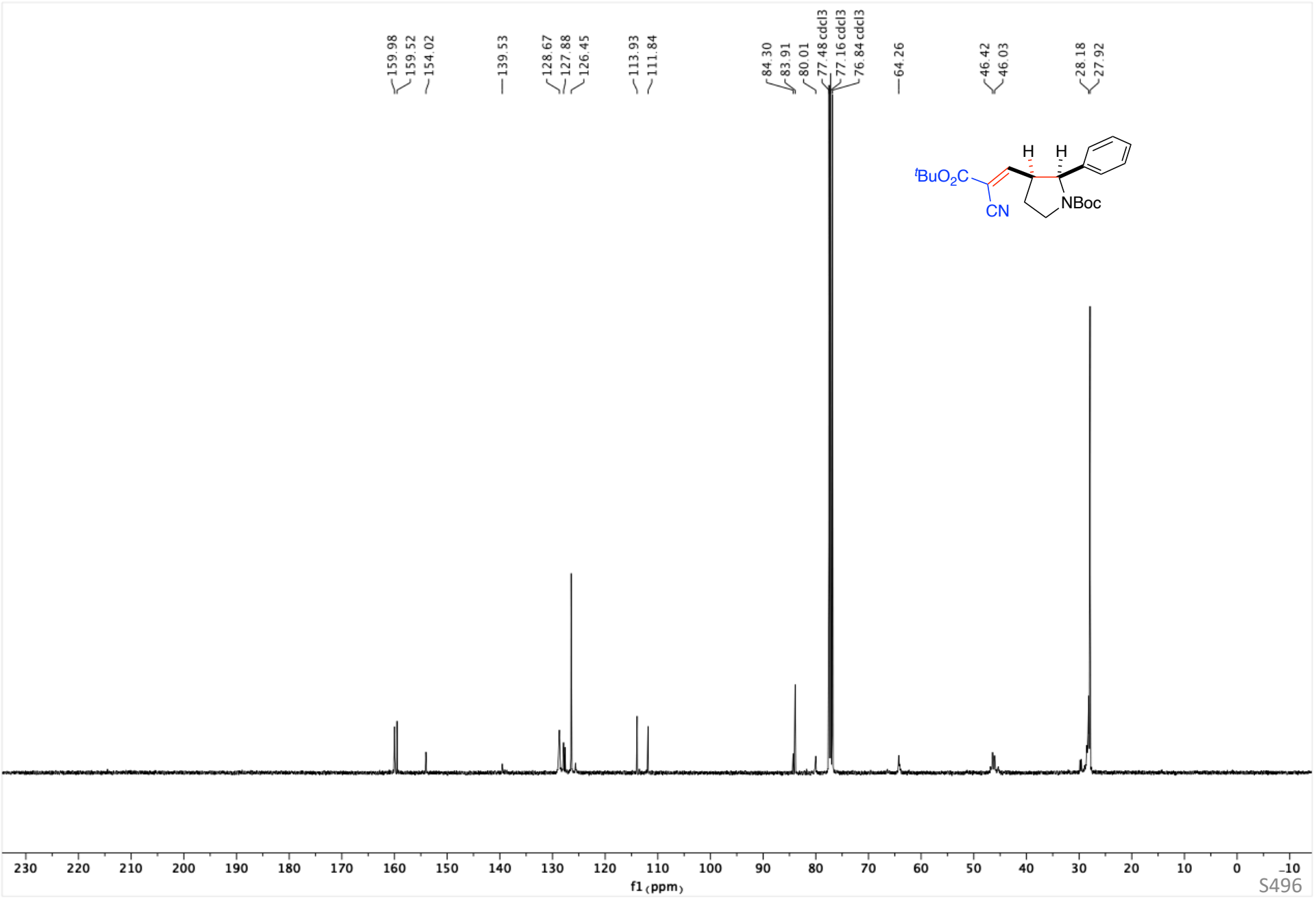
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.245	84.647
2	12.484	15.353
Total		100.000

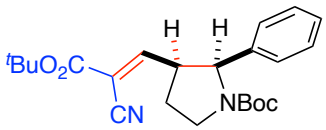
tert-Butyl (2_S_,3_S_)-3-((_E_)-3-(tert-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-2-phenylpyrrolidine-1-carboxylate

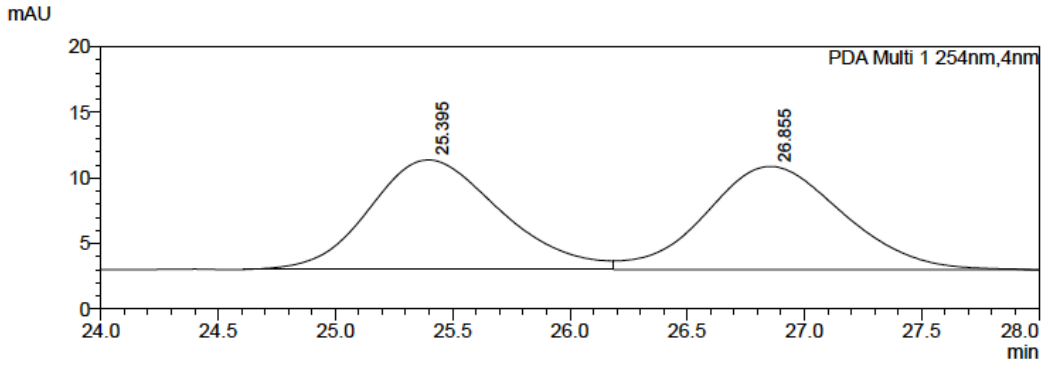


***tert*-Butyl (2*S*,3*S*)-3-((*E*)-3-(tert-butoxy)-2-cyano-3-oxoprop-1-en-1-yl)-2-phenylpyrrolidine-1-carboxylate**



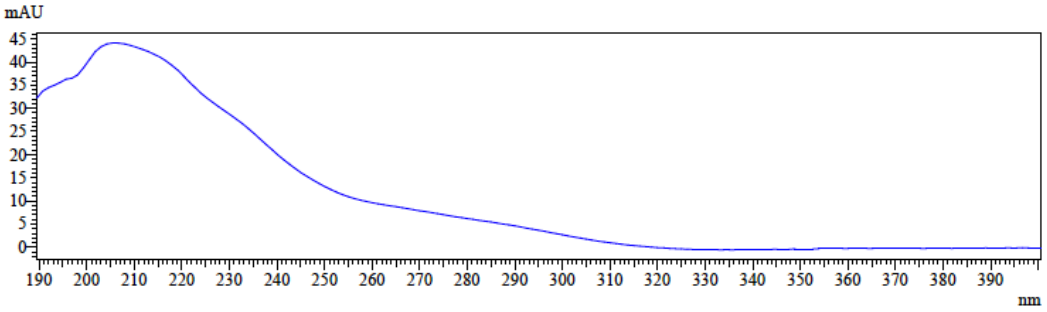
CZZ-NBoc-Rac-IE-5%-0.8mL





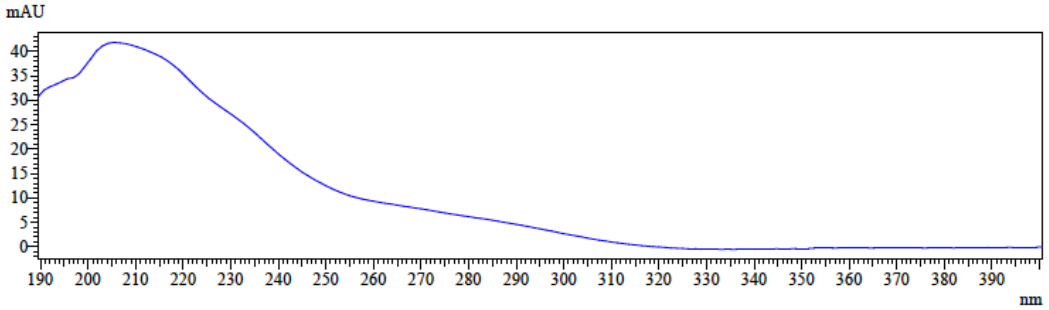
UV Spectrum

Retention Time: 25.395 min



UV Spectrum

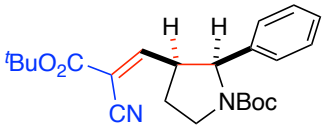
Retention Time: 26.855 min



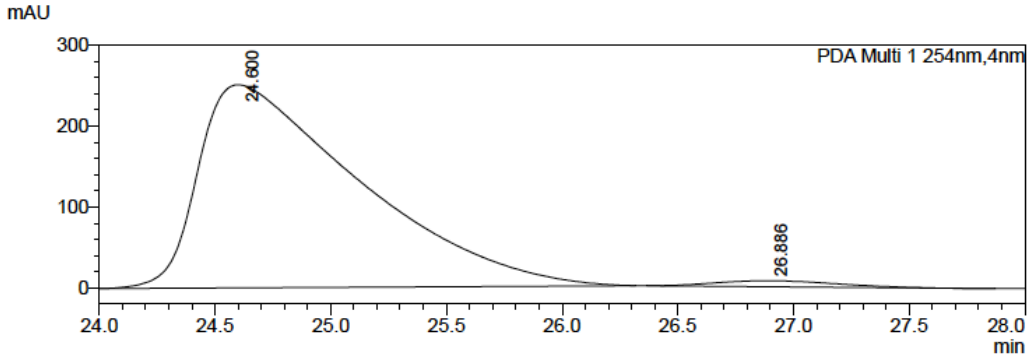
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	25.395	50.313
2	26.855	49.687
Total		100.000

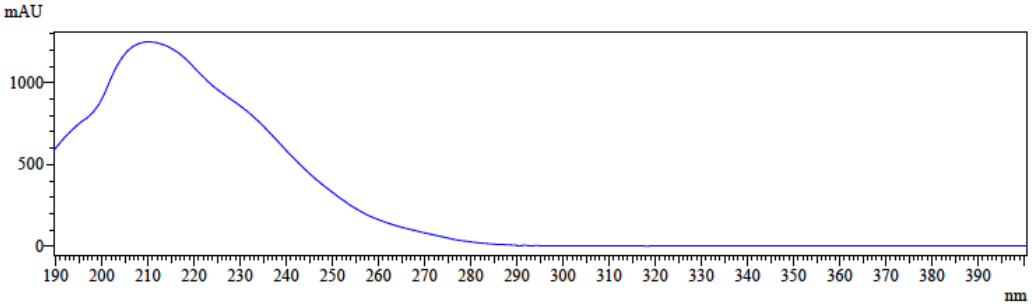


CZZ-NBoc-Chrial-IE-5%-0.8mL



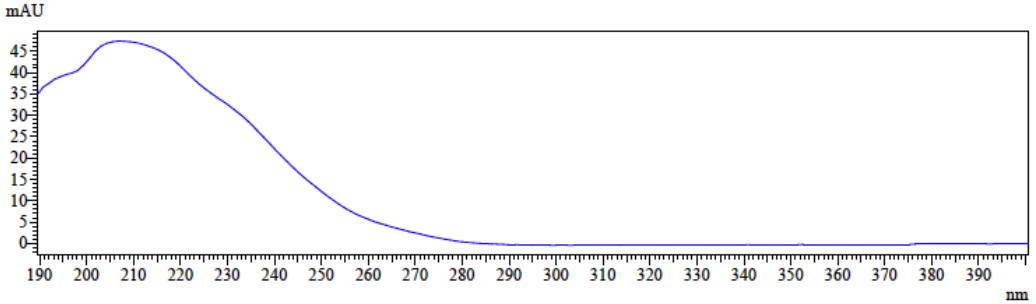
UV Spectrum

Retention Time: 24.600 min



UV Spectrum

Retention Time: 26.886 min

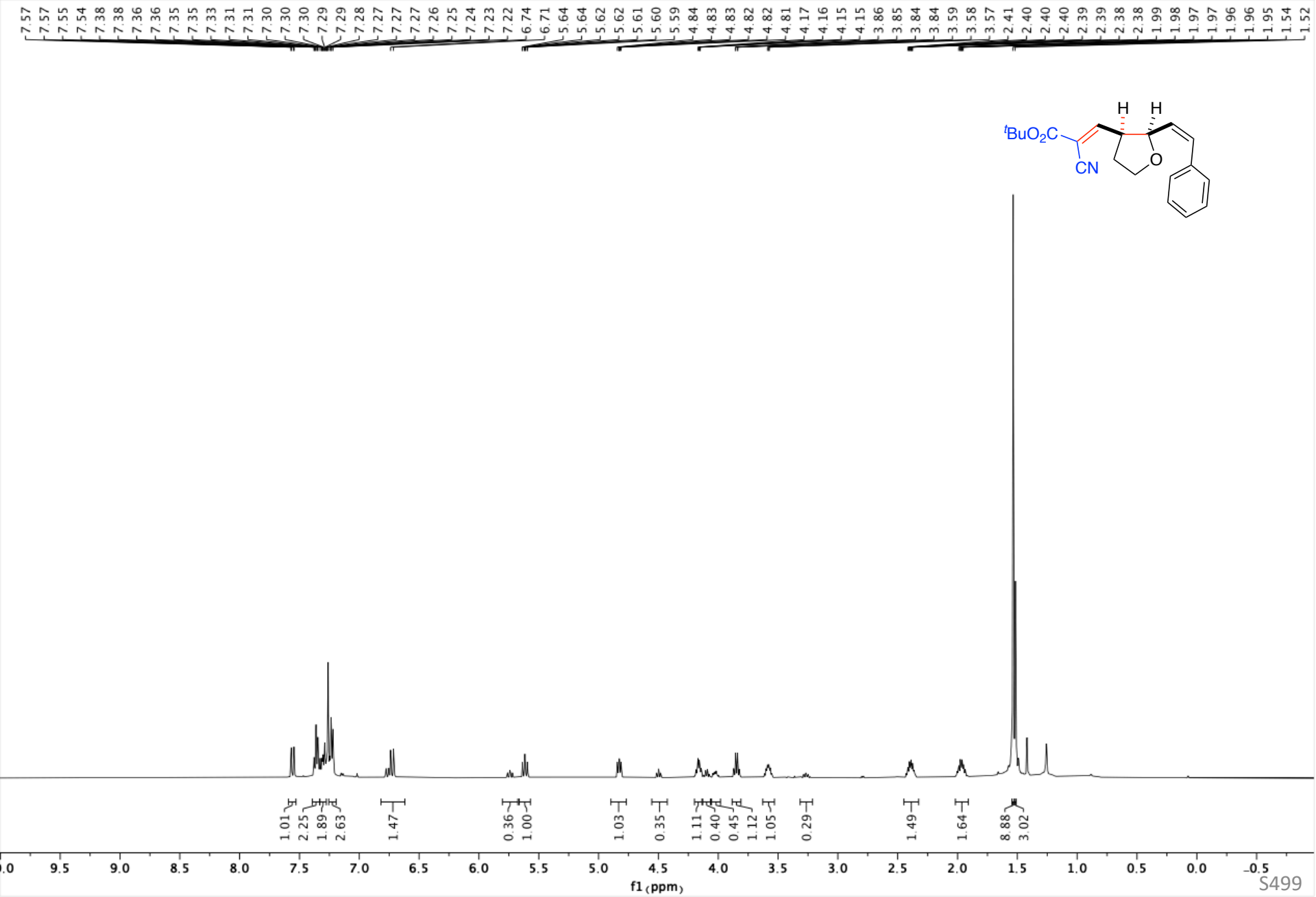


Peak Table

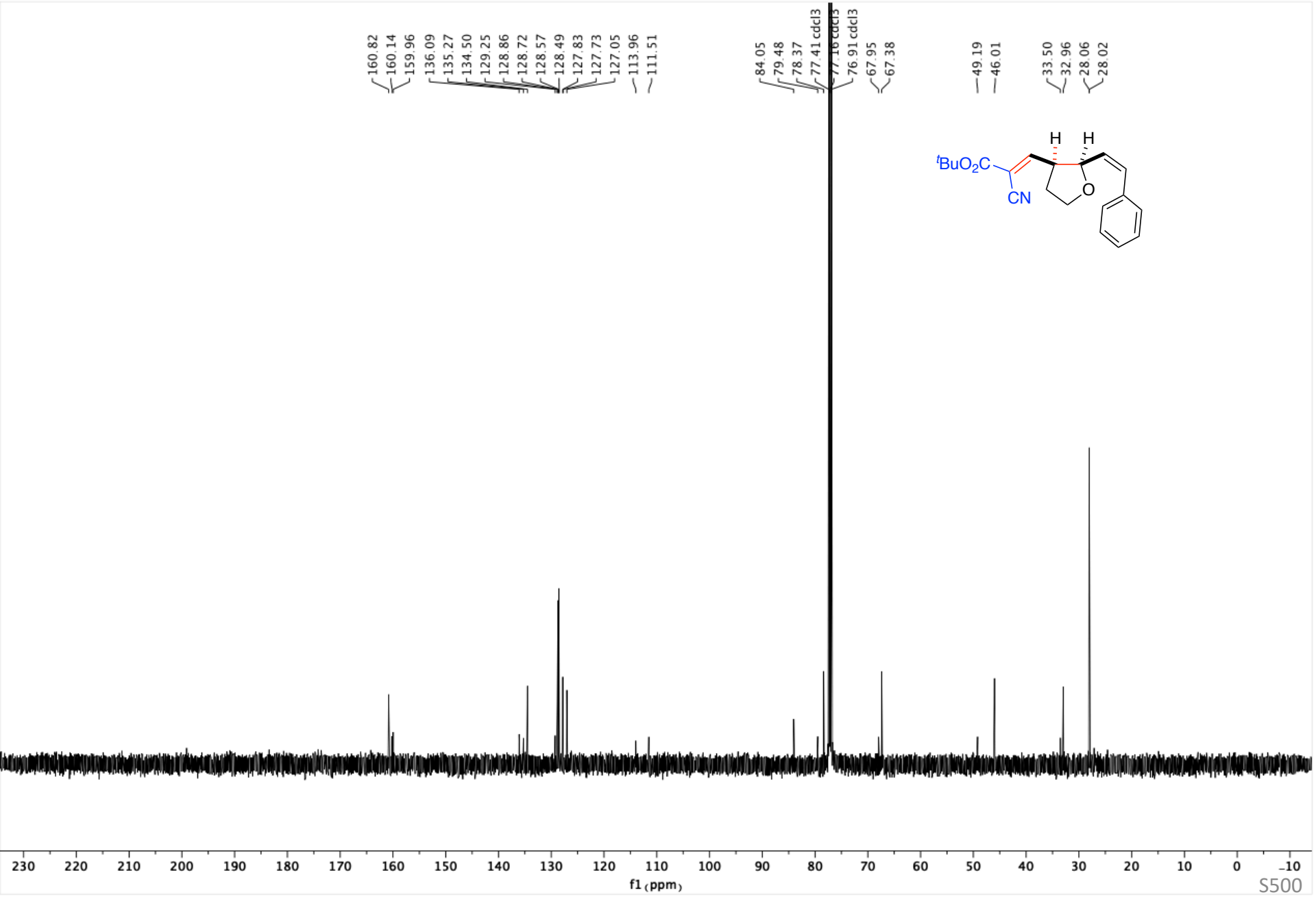
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	24.600	97.817
2	26.886	2.183
Total		100.000

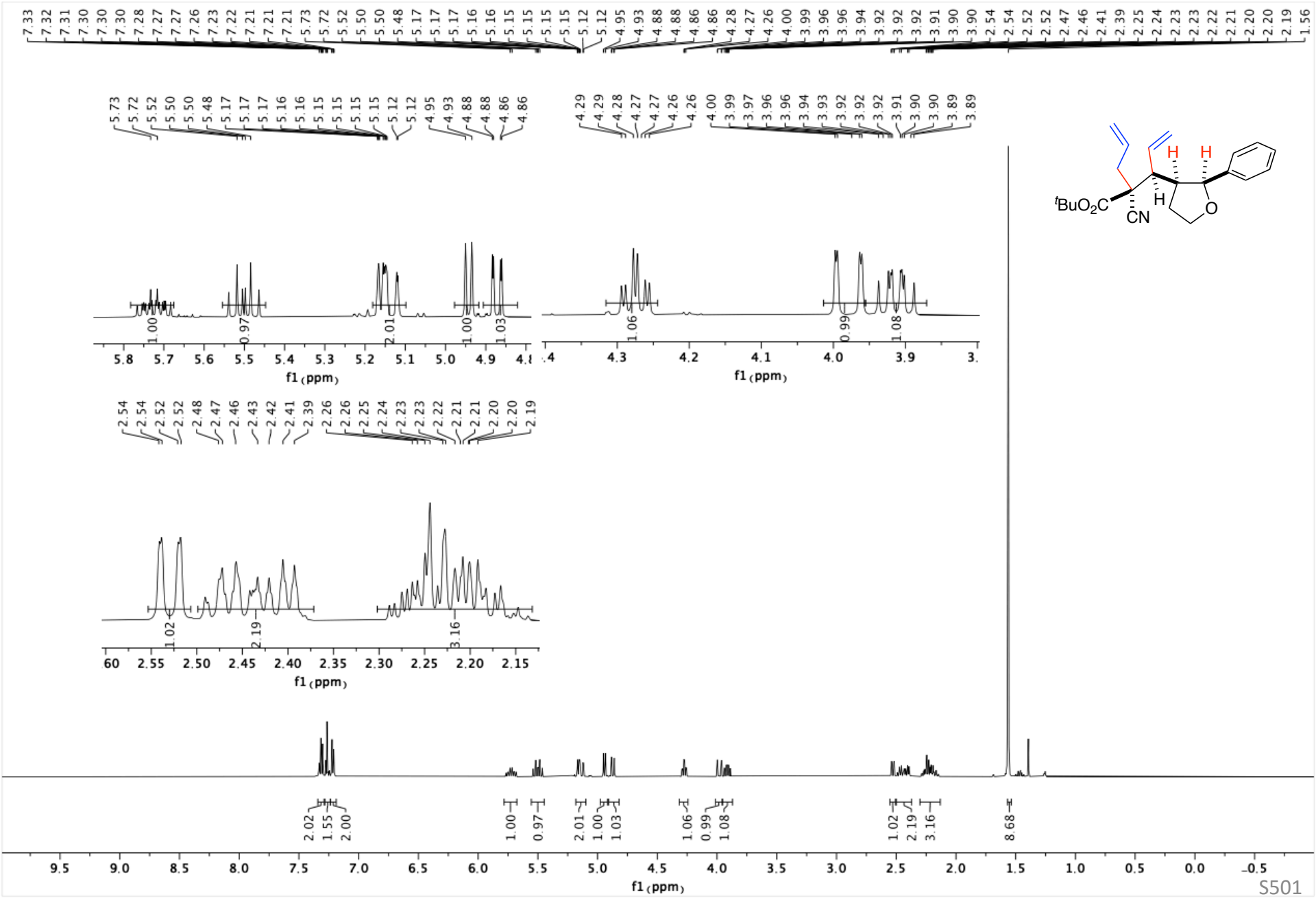
tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*Z*)-styryl)tetrahydrofuran-3-yl)acrylate



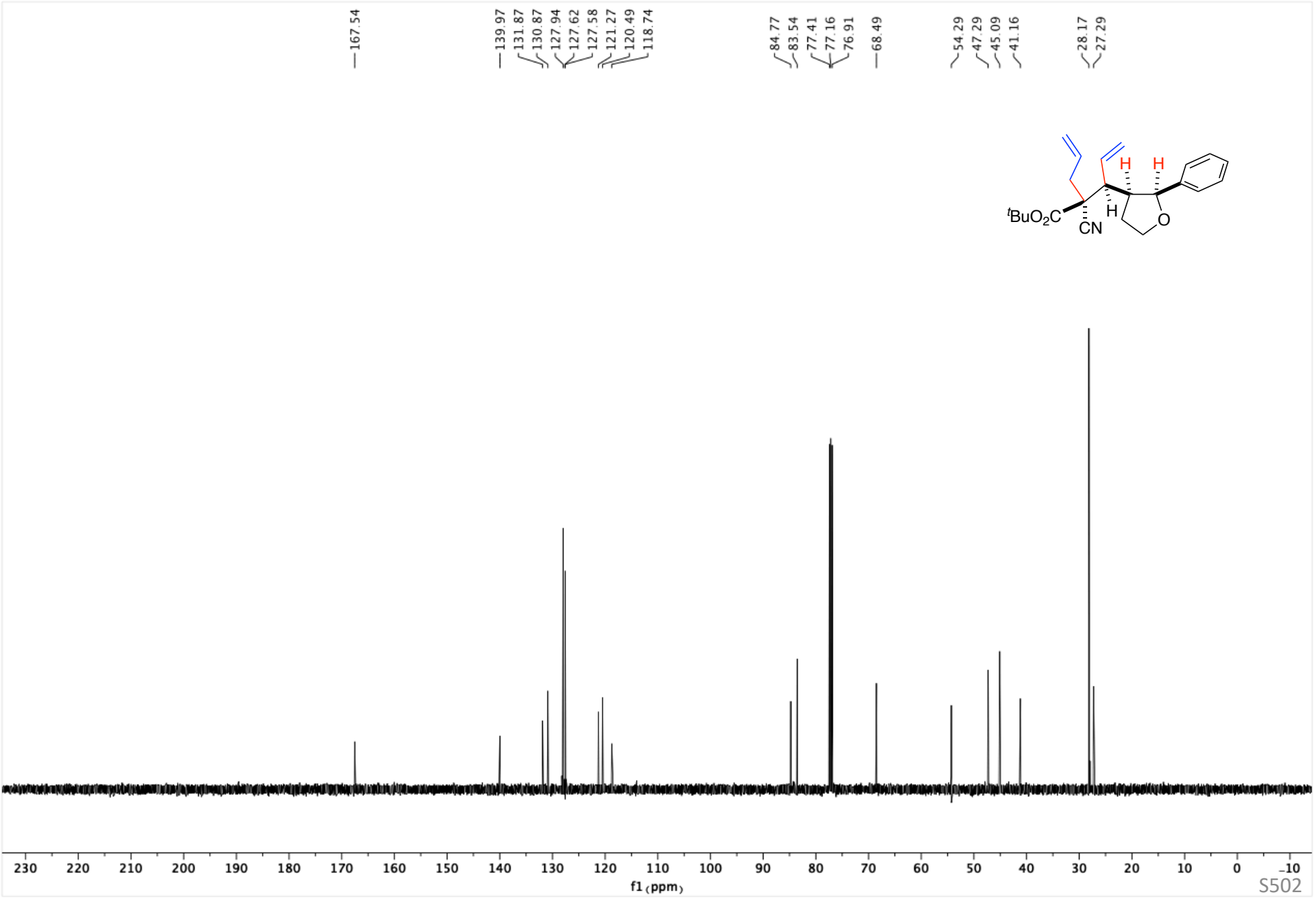
tert-Butyl (*E*)-2-cyano-3-((2*R*,3*S*)-2-((*Z*)-styryl)tetrahydrofuran-3-yl)acrylate

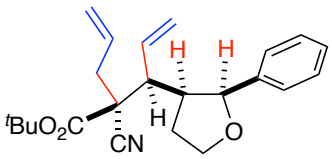


tert-Butyl (2*S*,3*S*)-2-allyl-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)pent-4-enoate

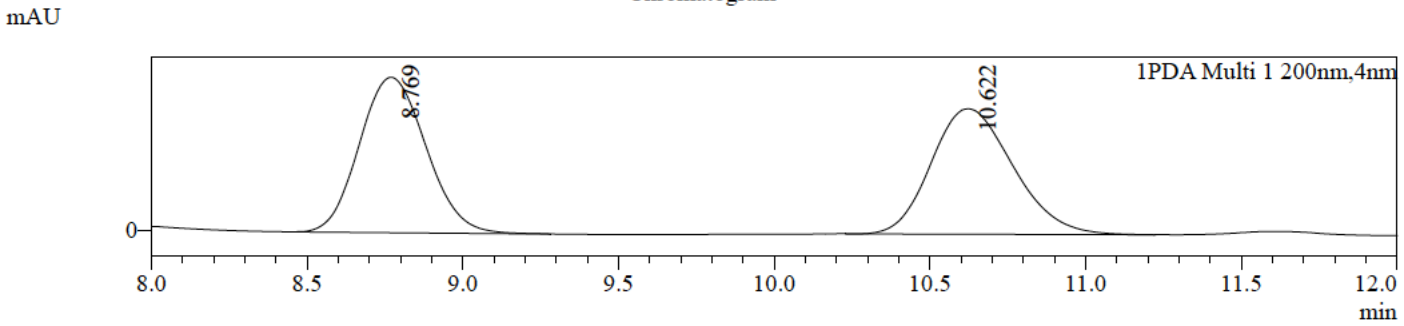


tert-Butyl (2*S*,3*S*)-2-allyl-2-cyano-3-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)pent-4-enoate

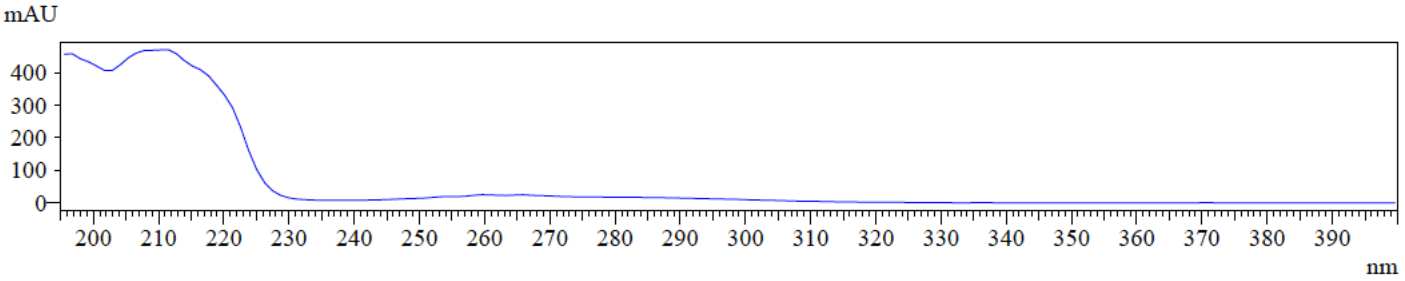




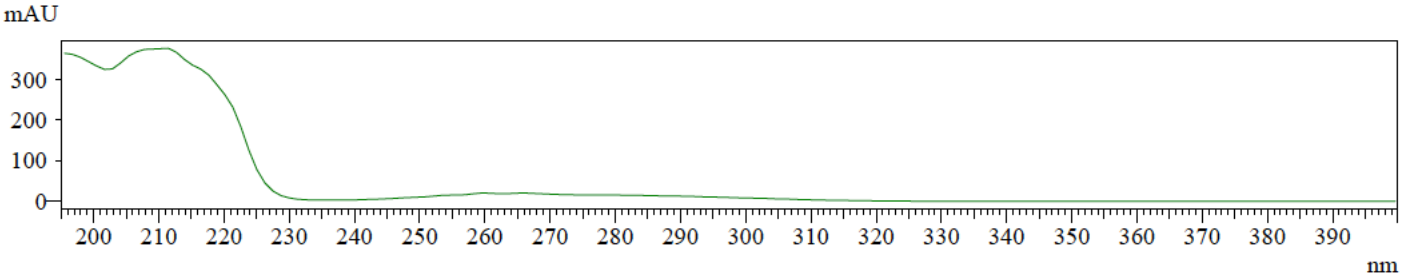
Chromatogram



UV Spectrum
Retention time = 8.769



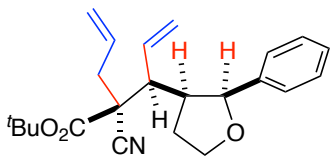
UV Spectrum
Retention time = 10.622



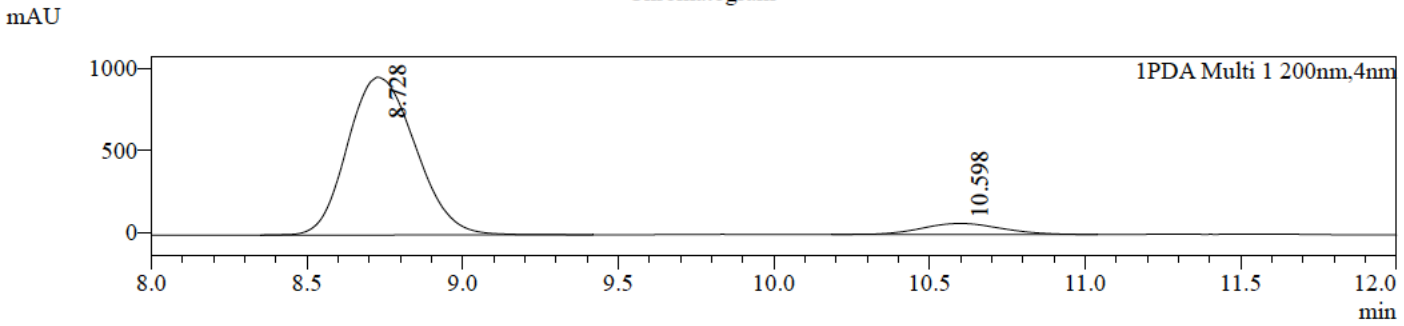
Peak Table

PDA Ch1 200nm

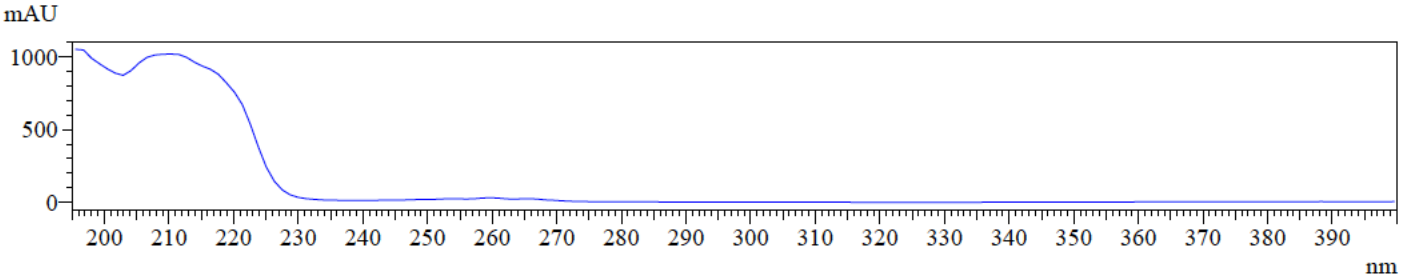
Peak#	Ret. Time	Area	Area%
1	8.769	6498163	50.238
2	10.622	6436595	49.762
Total		12934759	100.000



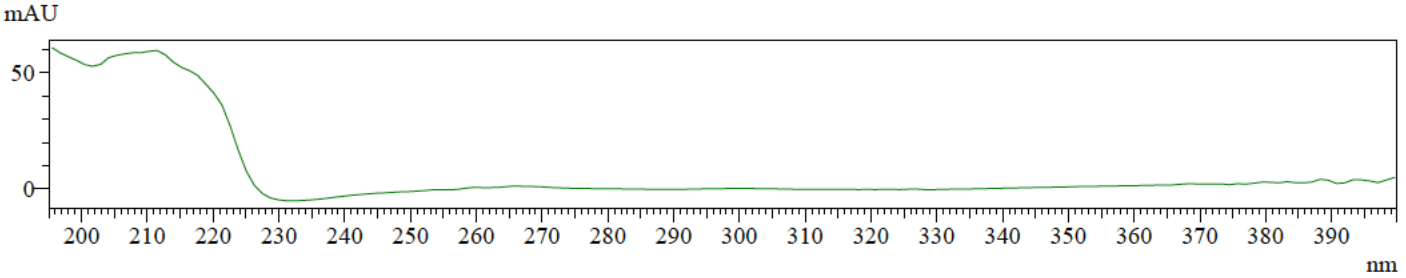
Chromatogram



UV Spectrum
Retention time = 8.728



UV Spectrum
Retention time = 10.598

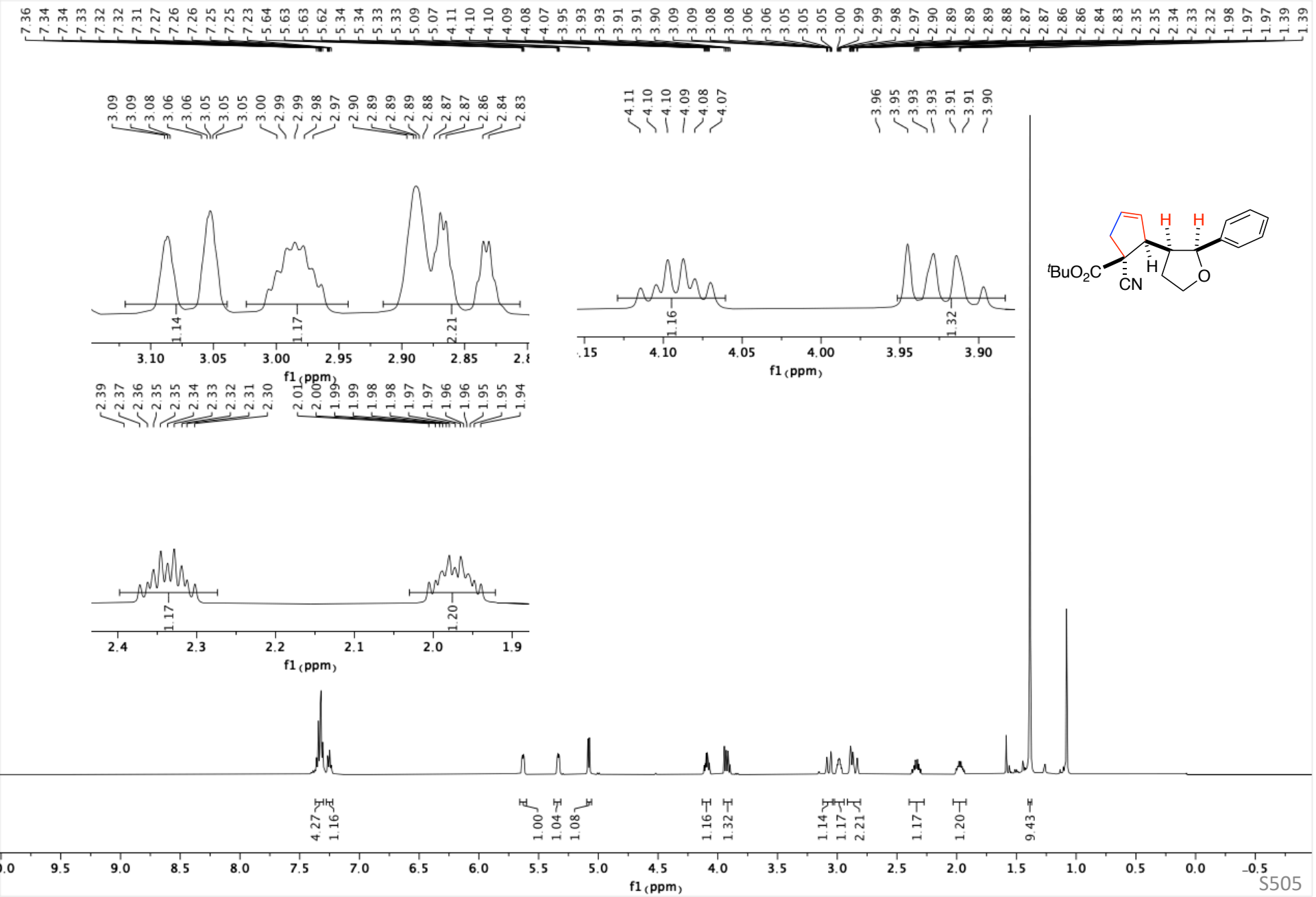


Peak Table

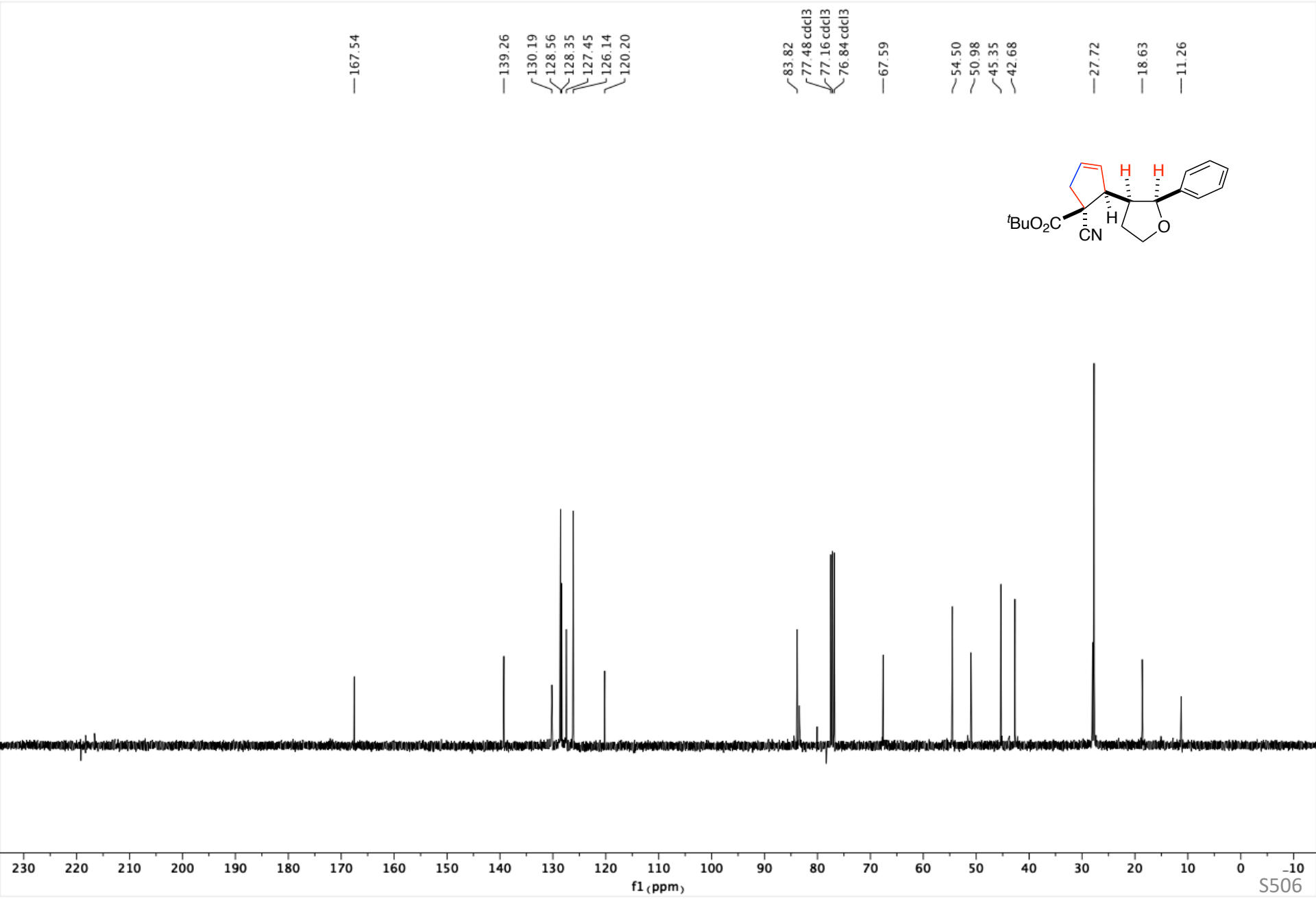
PDA Ch1 200nm

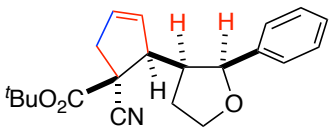
Peak#	Ret. Time	Area	Area%
1	8.728	14602590	92.484
2	10.598	1186799	7.516
Total		15789389	100.000

tert-Butyl (1*S*,2*S*)-1-cyano-2-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)cyclopent-3-ene-1-carboxylate

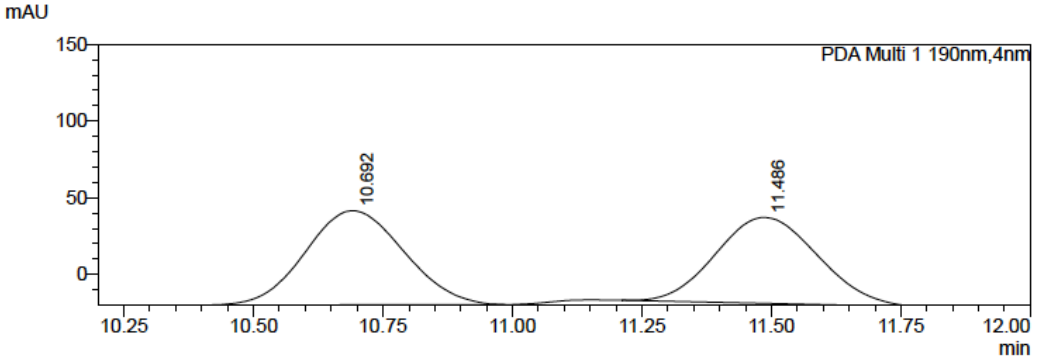


***tert*-Butyl (1*S*,2*S*)-1-cyano-2-((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)cyclopent-3-ene-1-carboxylate**



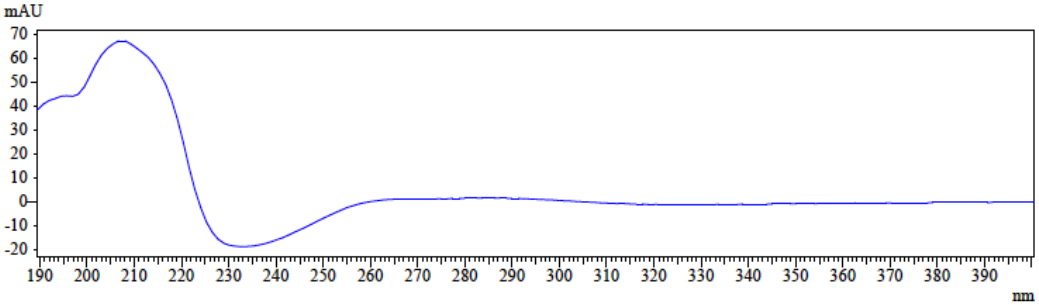


CZZ-2990-IE-5%-0.8mL



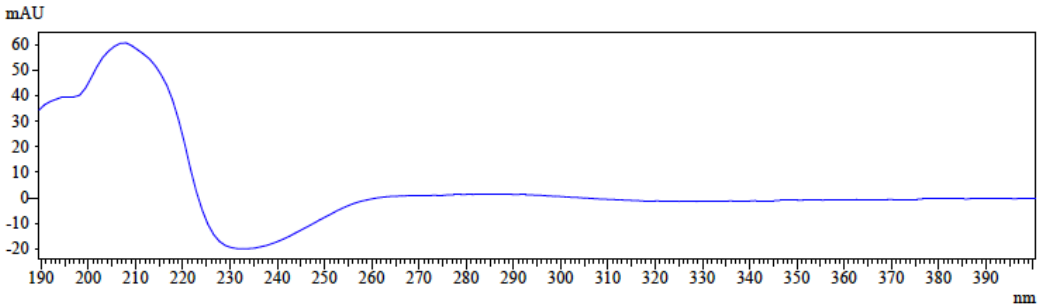
UV Spectrum

Retention Time: 10.692 min



UV Spectrum

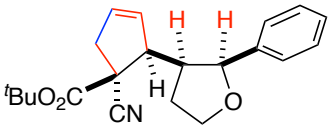
Retention Time: 11.486 min



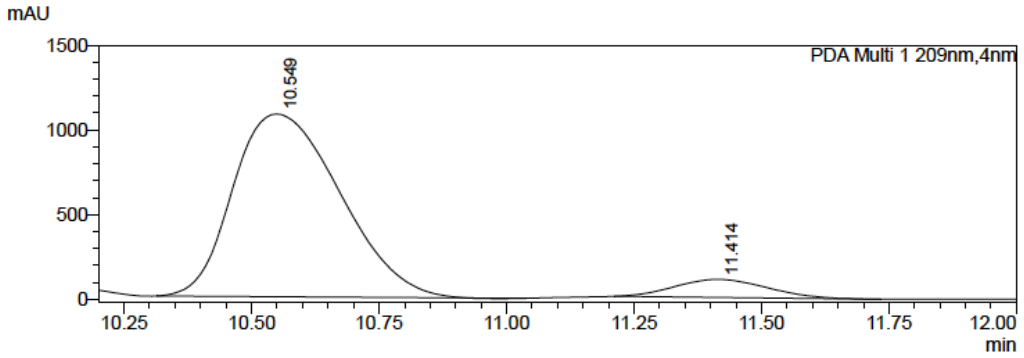
Peak Table

PDA Ch1 190nm

Peak#	Ret. Time	Area%
1	10.692	51.539
2	11.486	48.461
Total		100.000

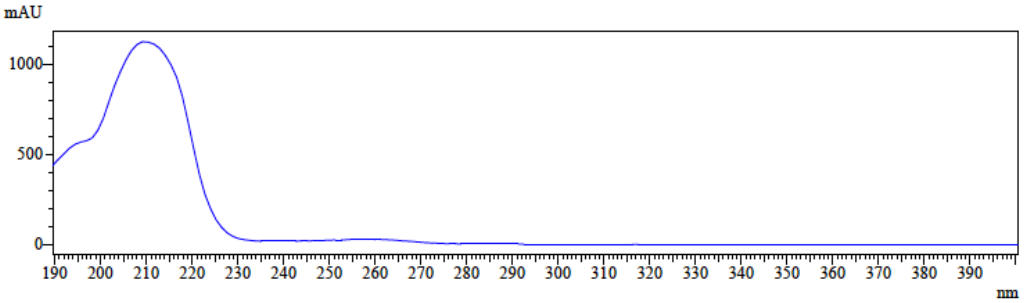


CZZ-3003-IE-5%-0.8mL



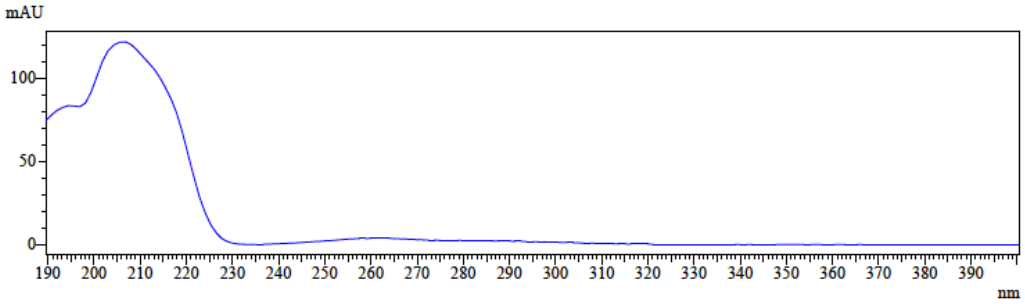
UV Spectrum

Retention Time: 10.549 min



UV Spectrum

Retention Time: 11.414 min

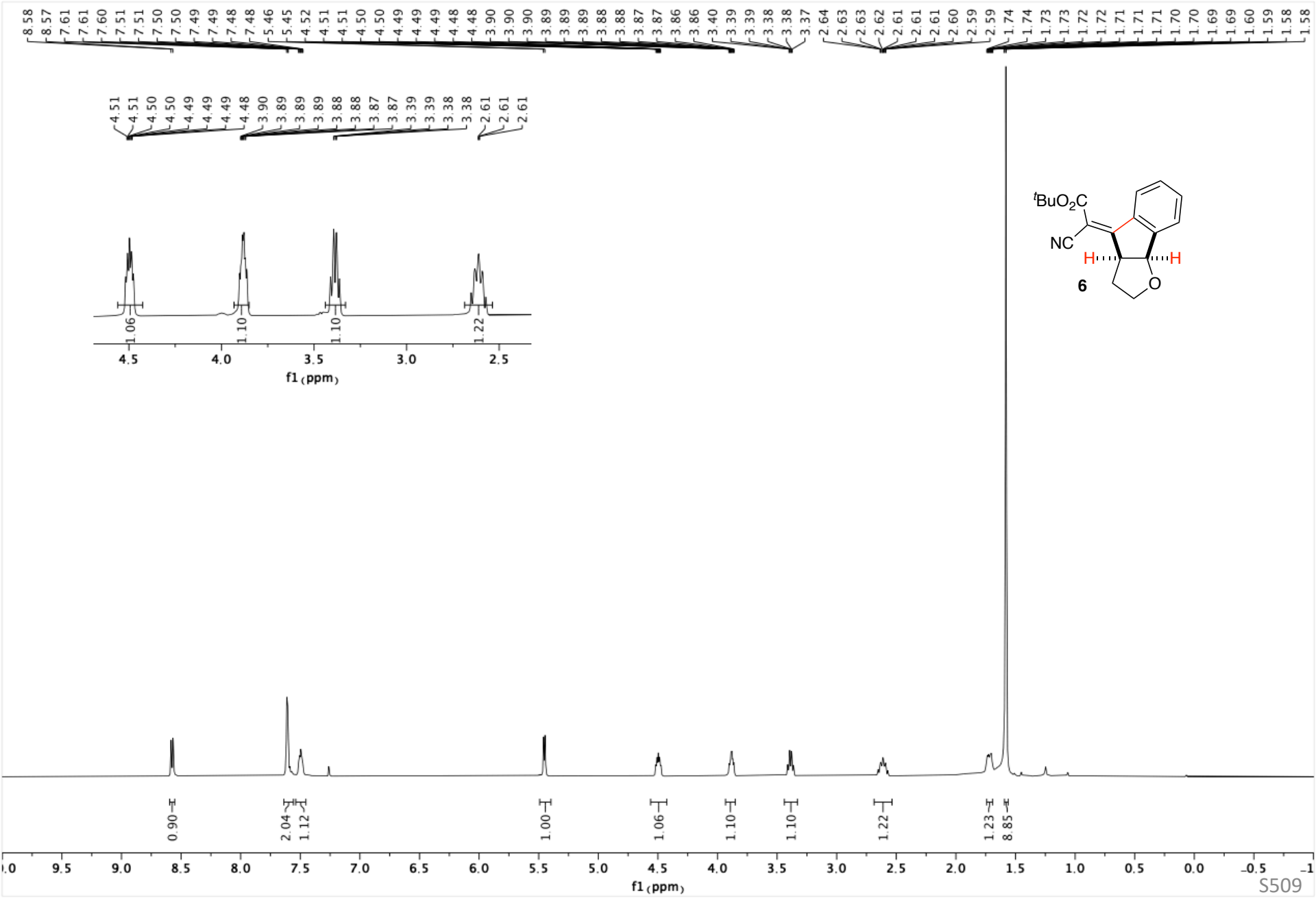


Peak Table

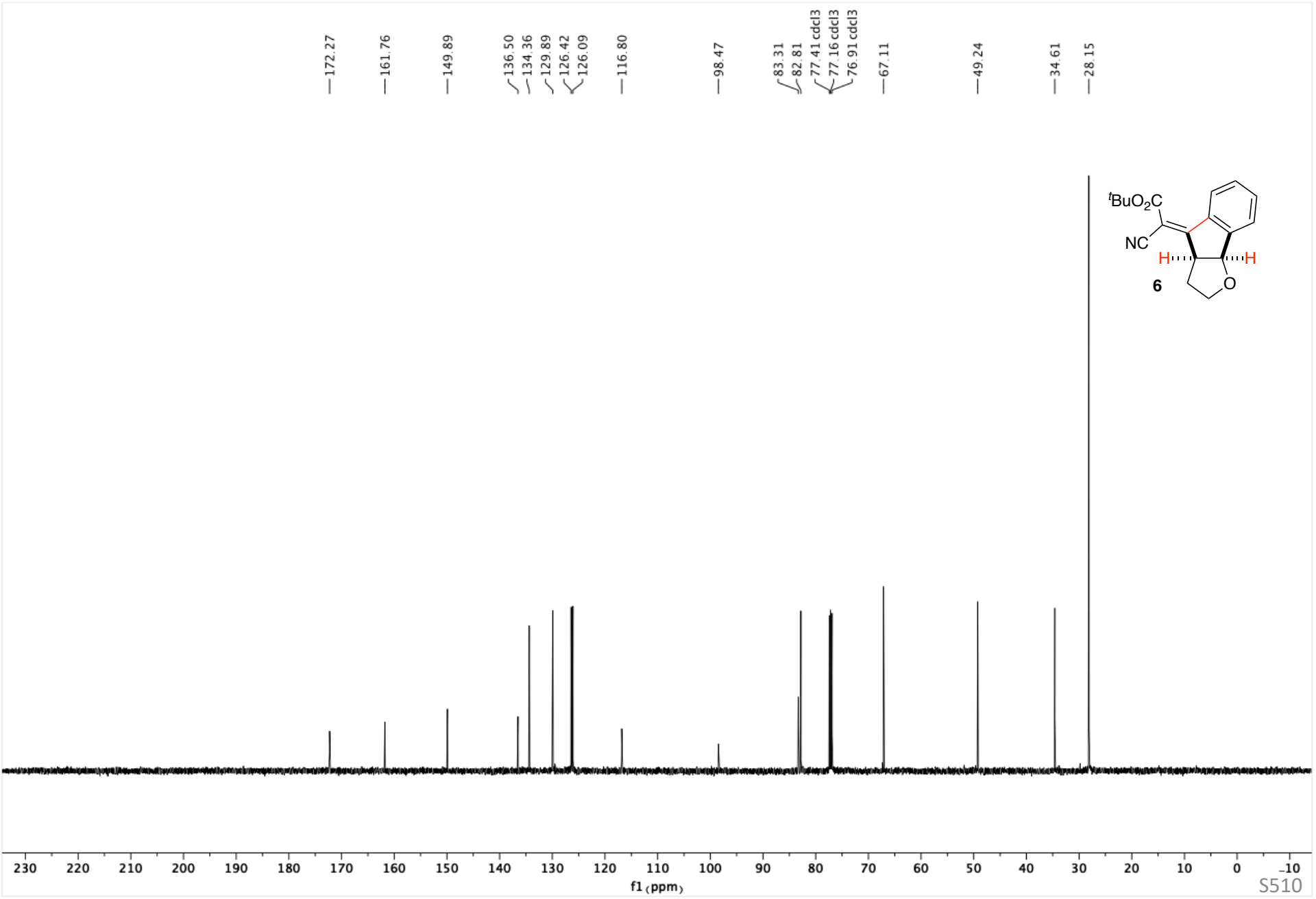
PDA Ch1 209nm

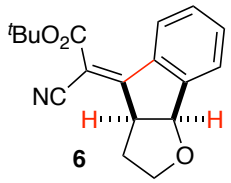
Peak#	Ret. Time	Area%
1	10.549	92.165
2	11.414	7.835
Total		100.000

tert-Butyl (_Z_)-2-cyano-2-((3a_S_,8b_S_)-2,3,3a,8b-tetrahydro-4_H_-indeno[1,2-_b_]furan-4-ylidene)acetate



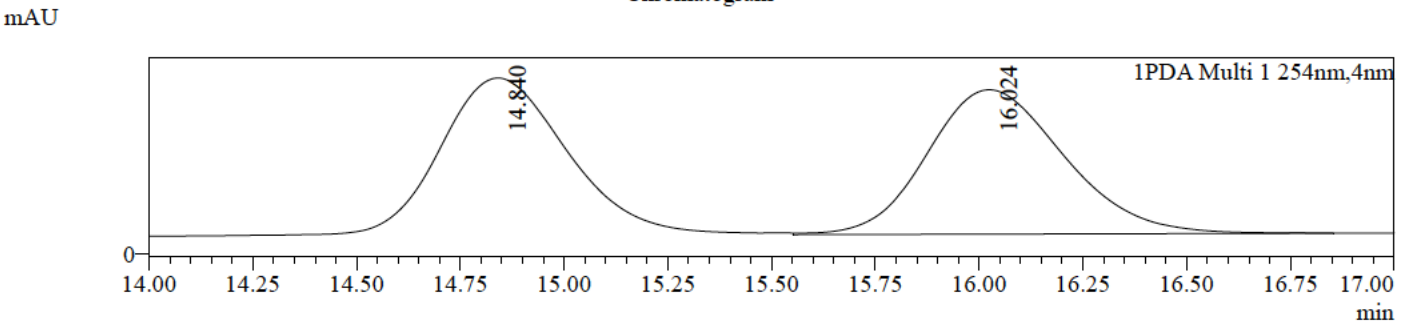
tert-Butyl (_Z_)-2-cyano-2-((3a_S_,8b_S_)-2,3,3a,8b-tetrahydro-4_H_-indeno[1,2-_b_]furan-4-ylidene)acetate



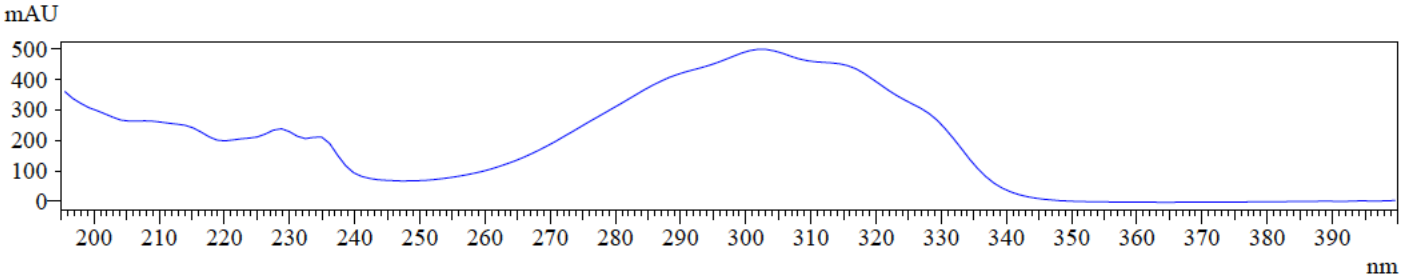


6

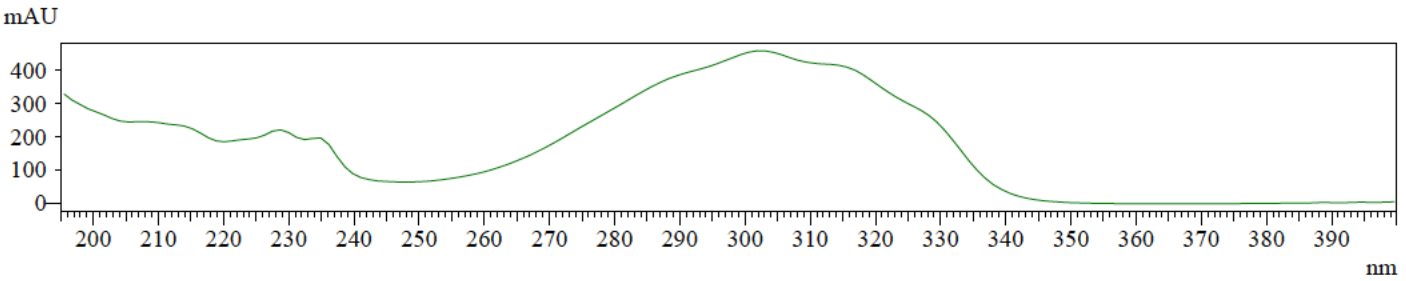
Chromatogram



UV Spectrum
Retention time = 14.840



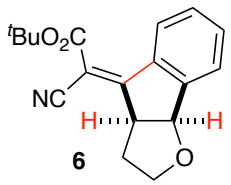
UV Spectrum
Retention time = 16.024



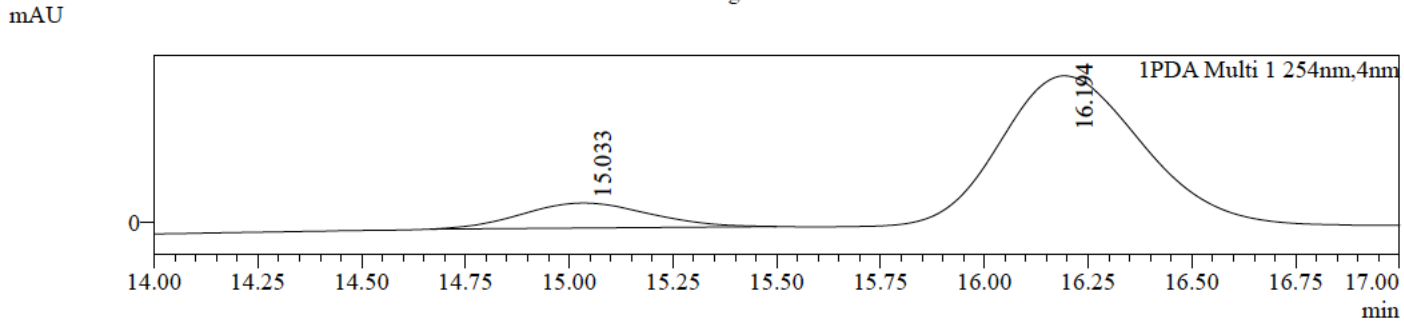
Peak Table

PDA Ch1 254nm

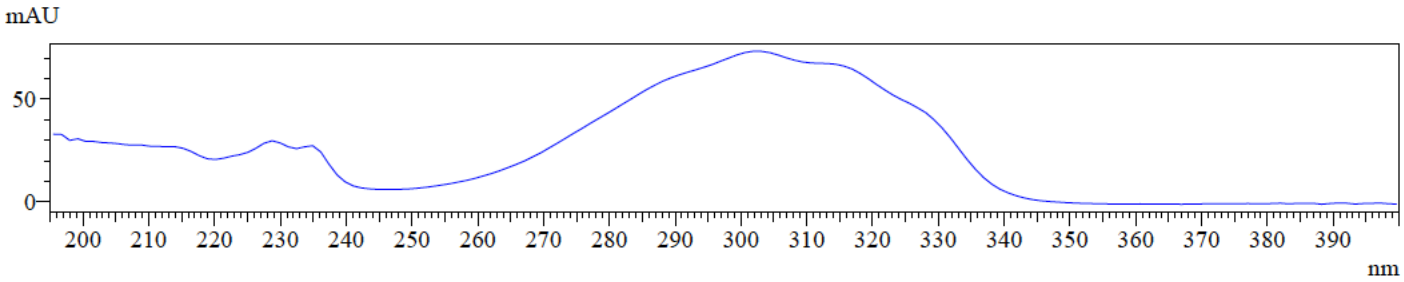
Peak#	Ret. Time	Area	Area%
1	14.840	1481782	50.394
2	16.024	1458591	49.606
Total		2940373	100.000



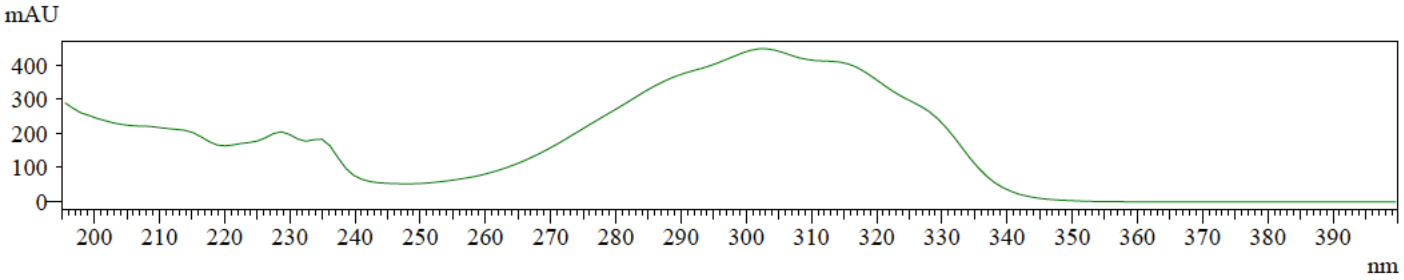
Chromatogram



UV Spectrum
Retention time = 15.033



UV Spectrum
Retention time = 16.194

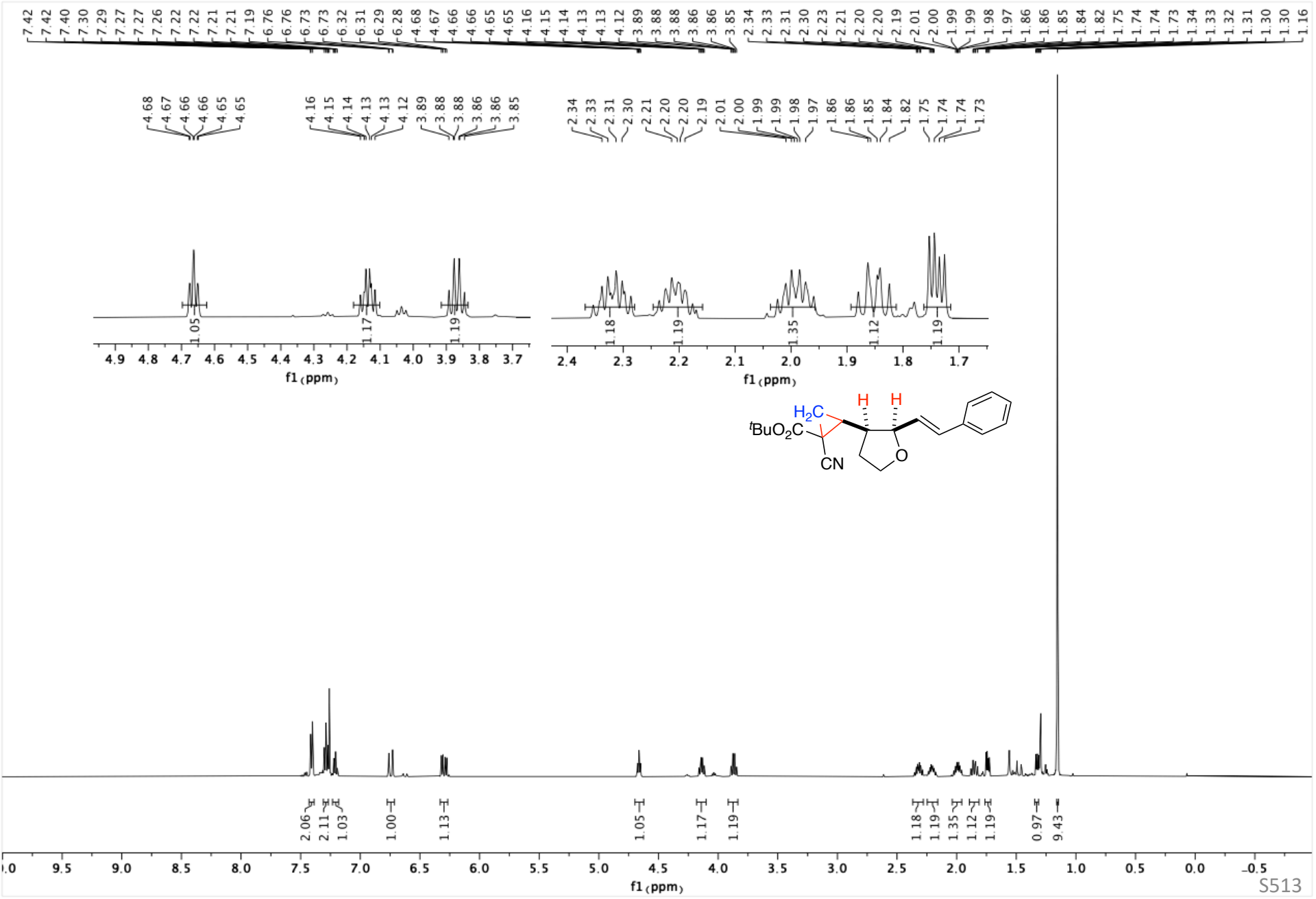


Peak Table

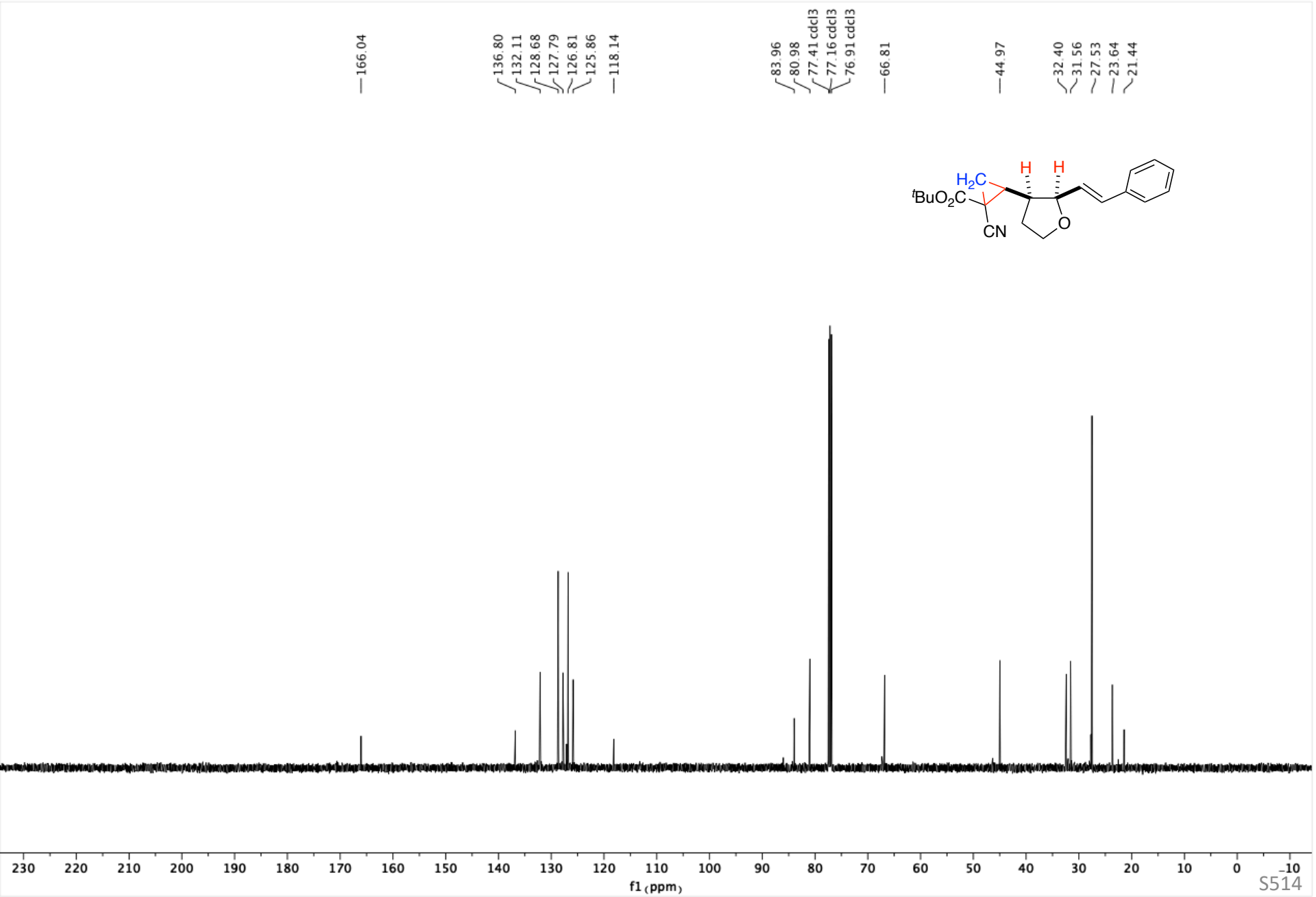
PDA Ch1 254nm

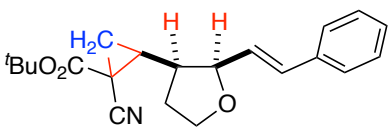
Peak#	Ret. Time	Area	Area%
1	15.033	221645	12.897
2	16.194	1496932	87.103
Total		1718577	100.000

tert-Butyl (2*S*)-1-cyano-2-((2*R*,3*S*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)cyclopropane-1-carboxylate

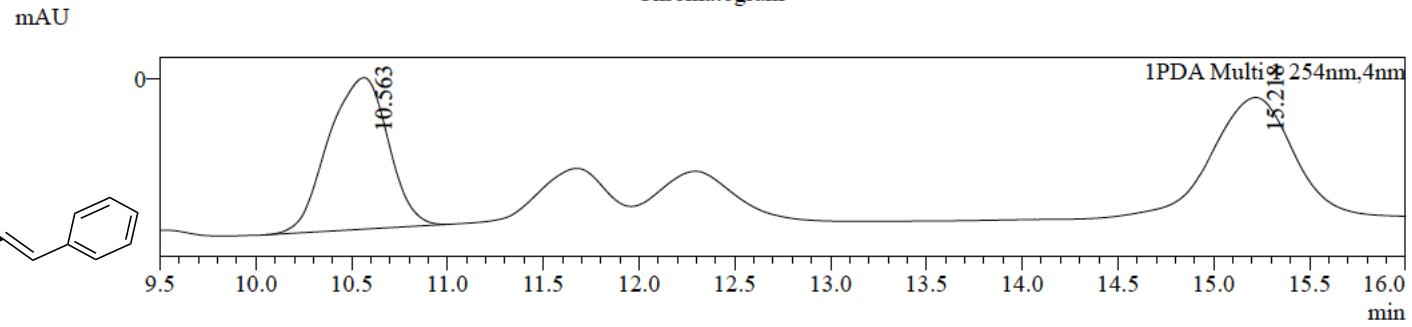


tert-Butyl (2_S_)-1-cyano-2-((2_R_,3_S_)-2-((_E_)-styryl)tetrahydrofuran-3-yl)cyclopropane-1-carboxylate

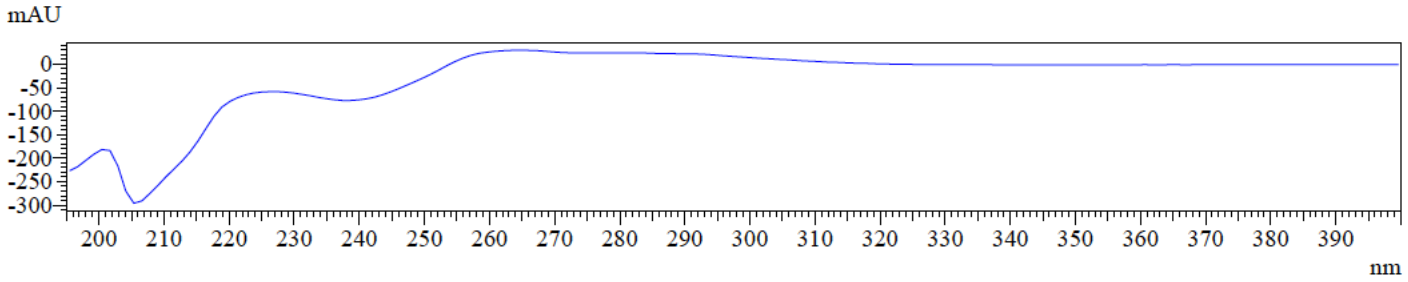




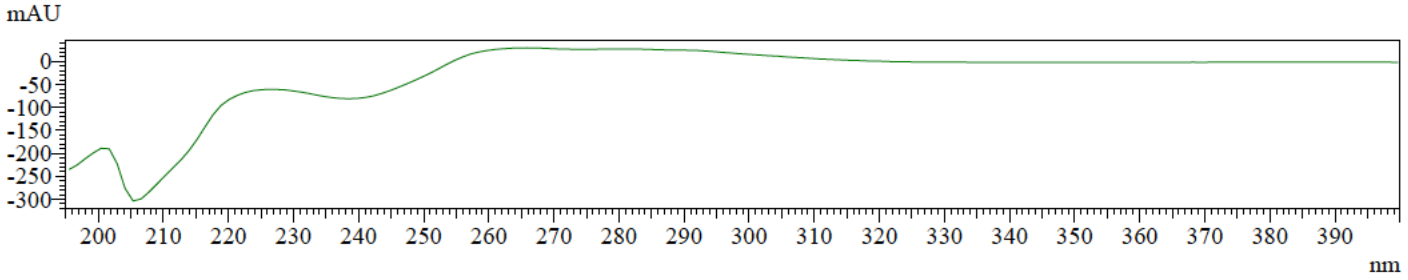
Chromatogram



UV Spectrum
Retention time = 10.563



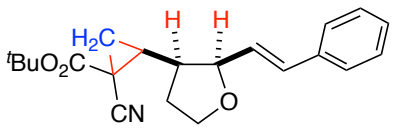
UV Spectrum
Retention time = 15.218



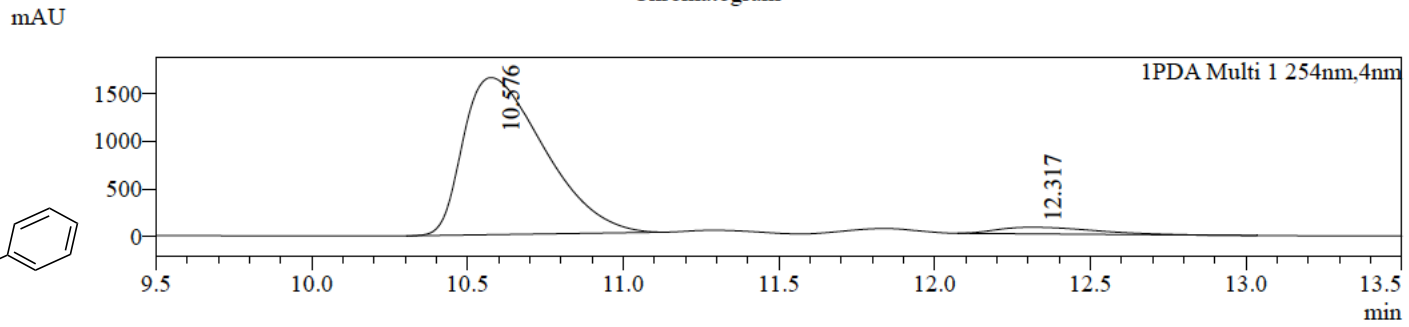
Peak Table

PDA Ch1 254nm

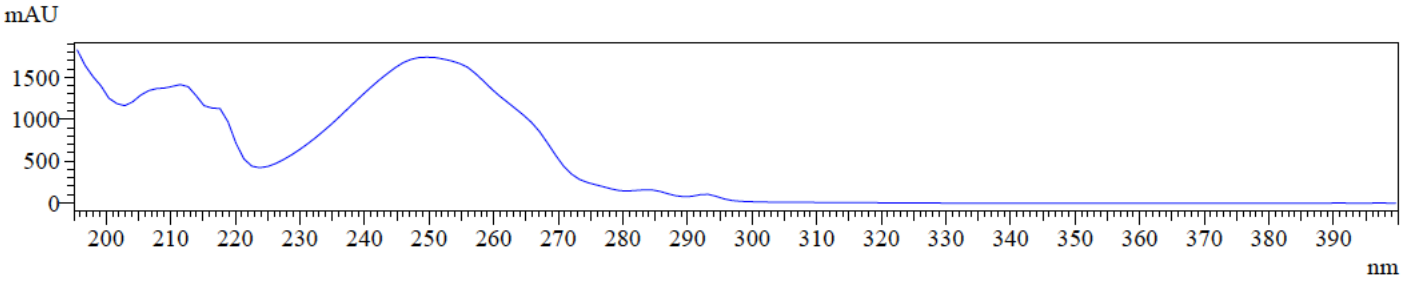
Peak#	Ret. Time	Area	Area%
1	10.563	532714	49.563
2	15.218	542113	50.437
Total		1074826	100.000



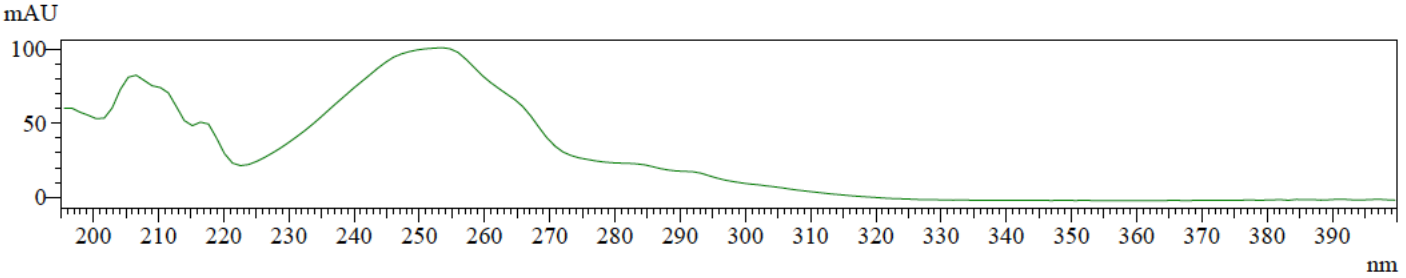
Chromatogram



UV Spectrum
Retention time = 10.576



UV Spectrum
Retention time = 12.317

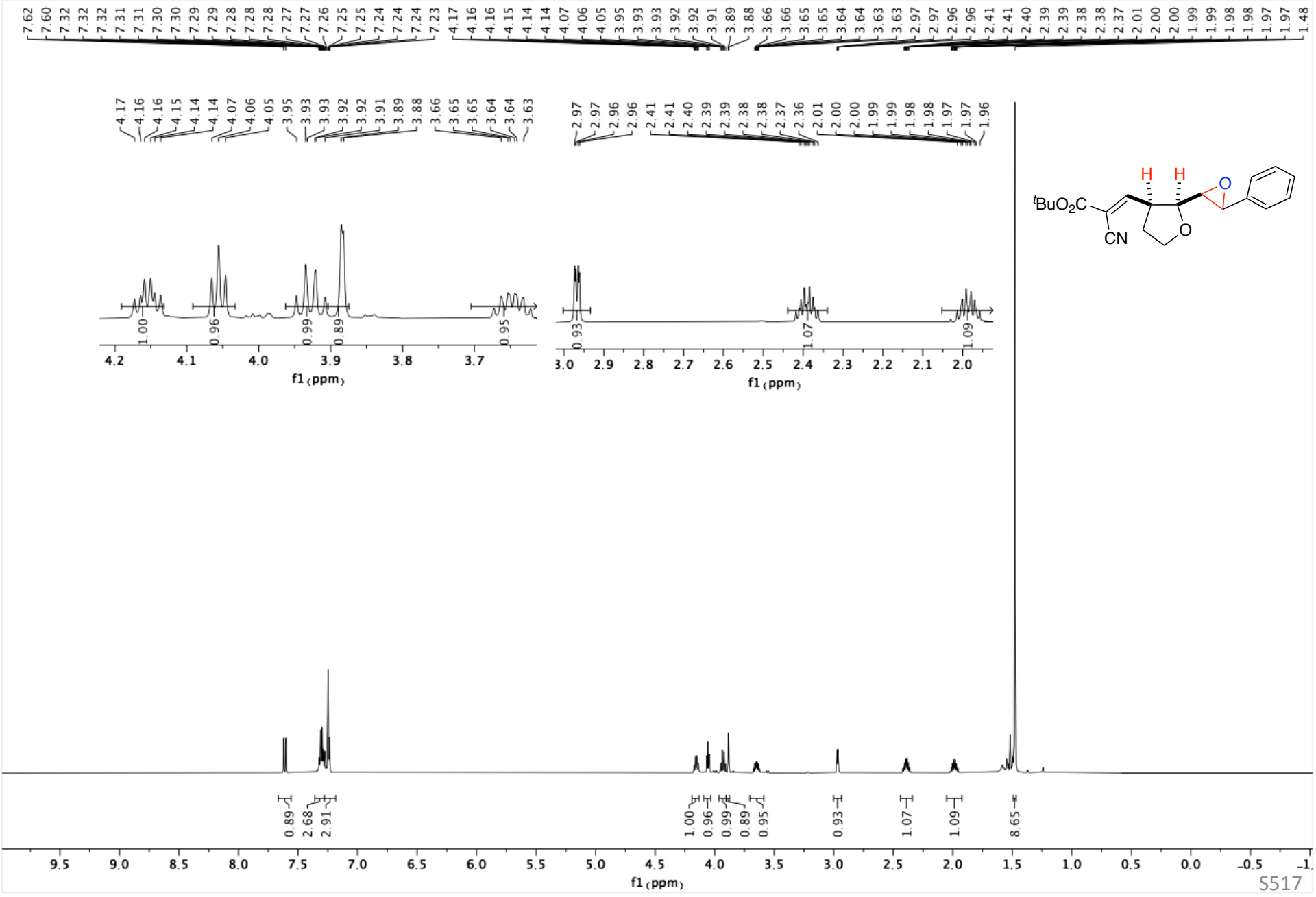


Peak Table

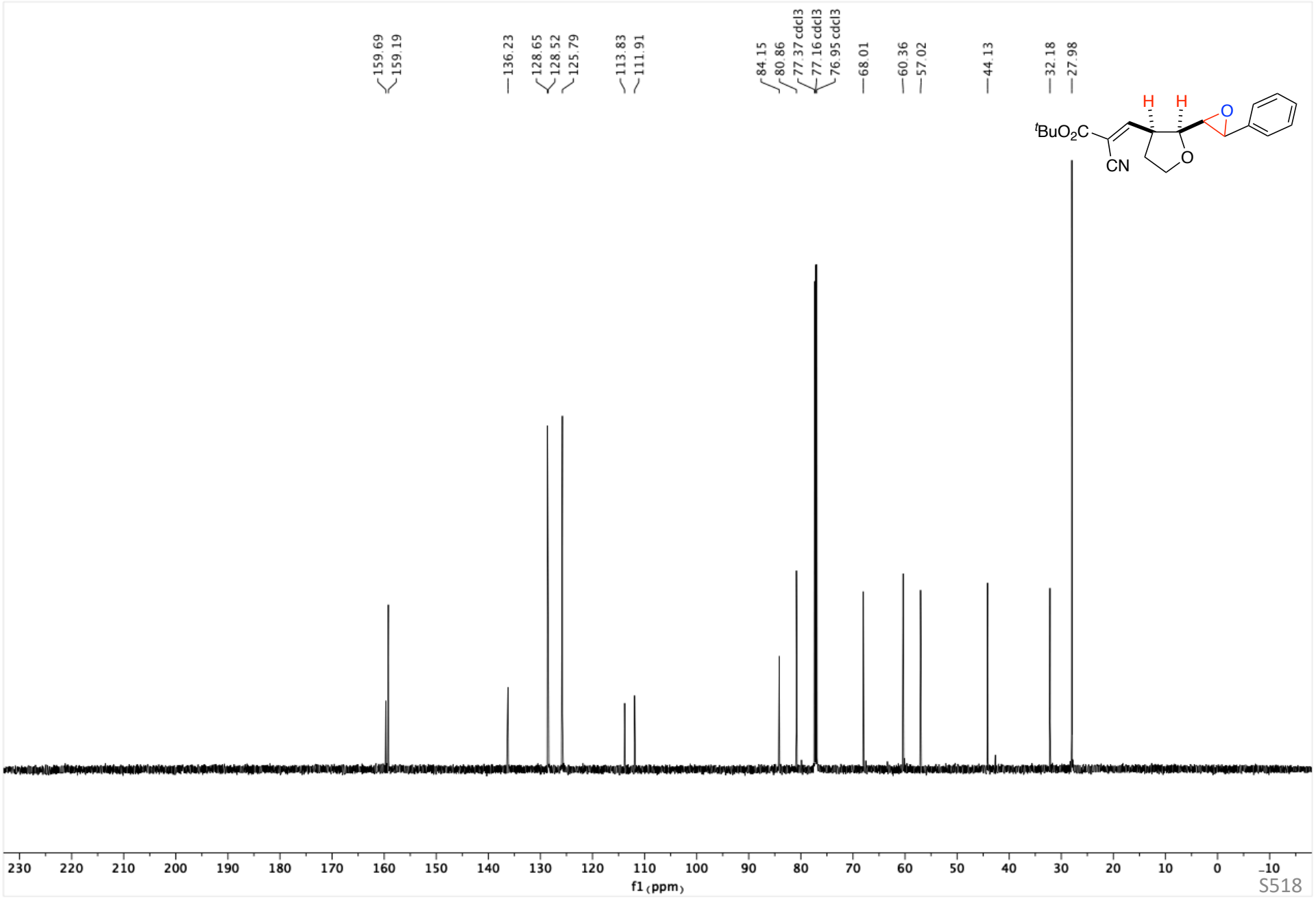
PDA Ch1 254nm

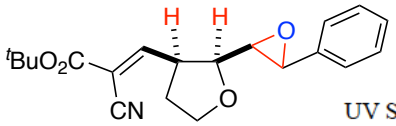
Peak#	Ret. Time	Area	Area%
1	10.576	29774540	95.169
2	12.317	1511543	4.831
Total		31286084	100.000

tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((2*S*)-3-phenyloxiran-2-yl)tetrahydrofuran-3-yl)acrylate

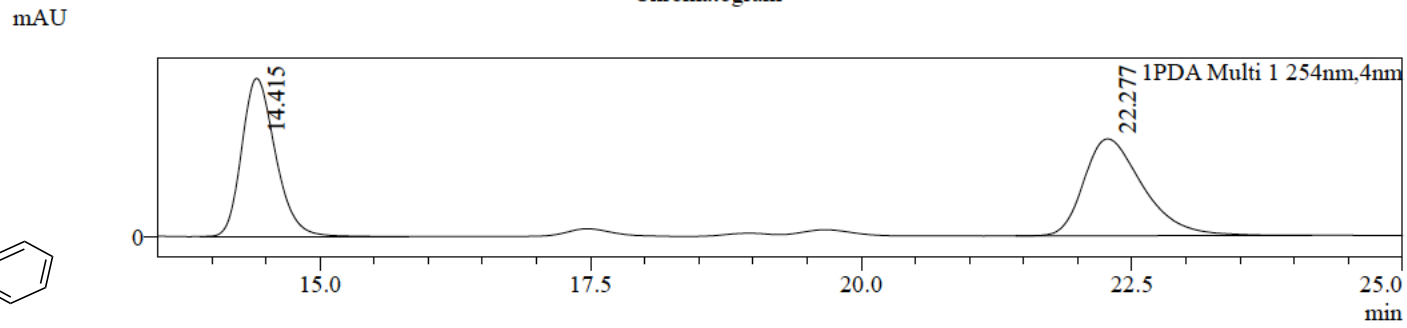


tert-Butyl (*E*)-2-cyano-3-((2*S*,3*S*)-2-((2*S*)-3-phenyloxiran-2-yl)tetrahydrofuran-3-yl)acrylate

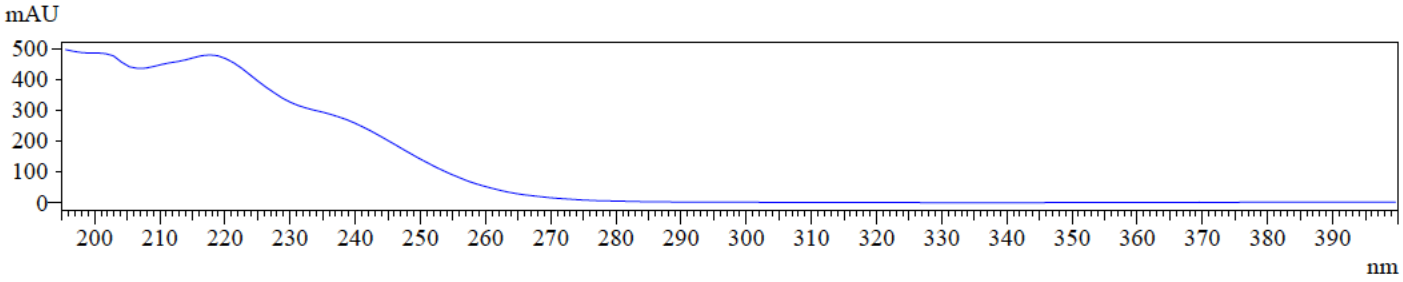




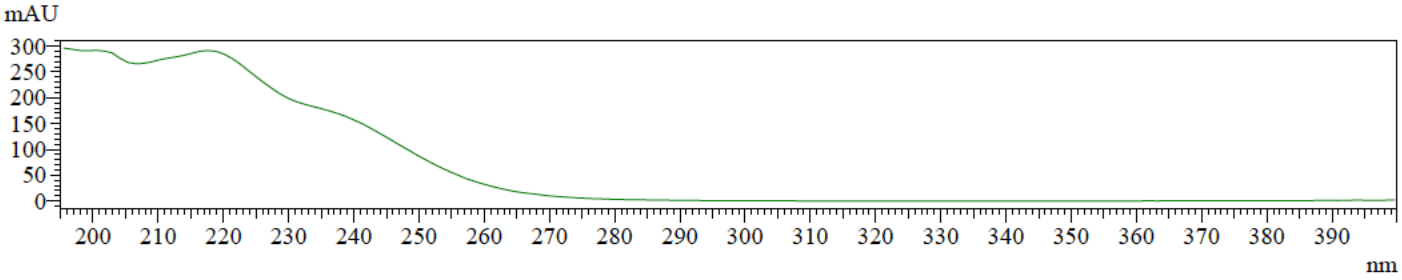
Chromatogram



UV Spectrum
Retention time = 14.415



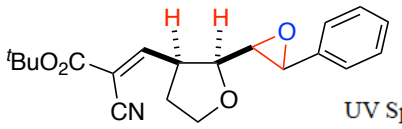
UV Spectrum
Retention time = 22.277



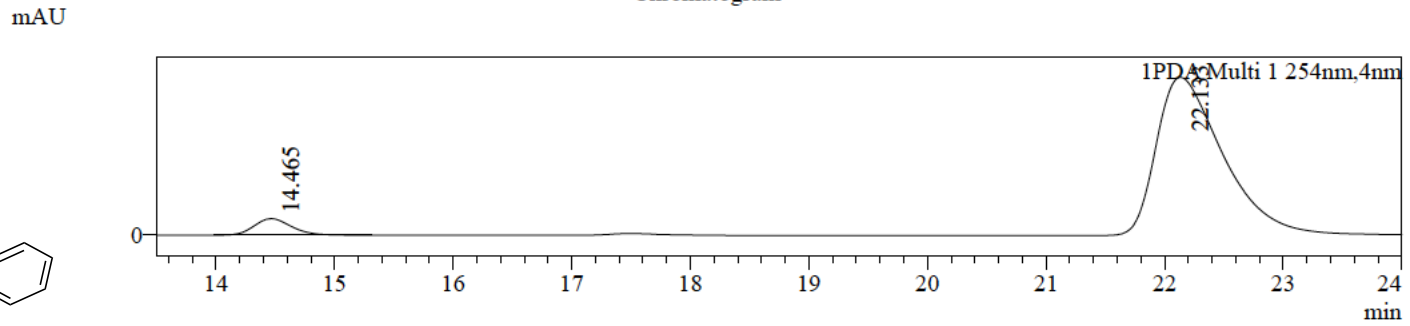
Peak Table

PDA Ch1 254nm

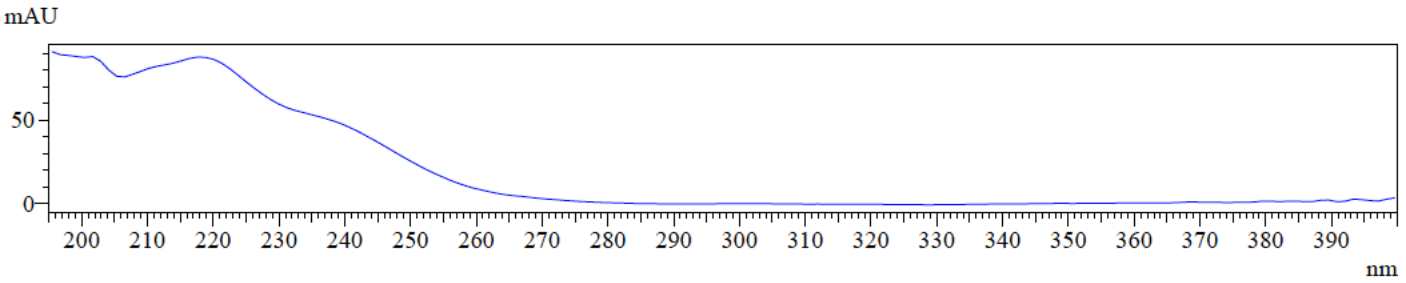
Peak#	Ret. Time	Area	Area%
1	14.415	2146579	48.334
2	22.277	2294592	51.666
Total		4441172	100.000



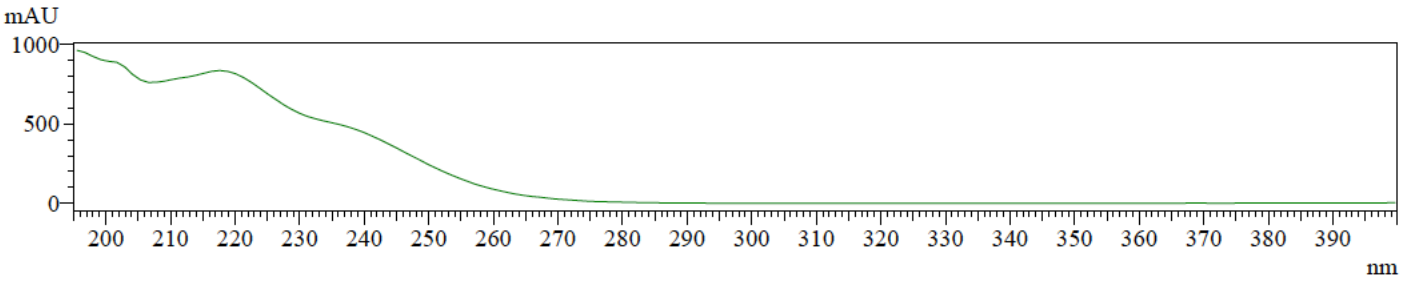
Chromatogram



UV Spectrum
Retention time = 14.465



UV Spectrum
Retention time = 22.133

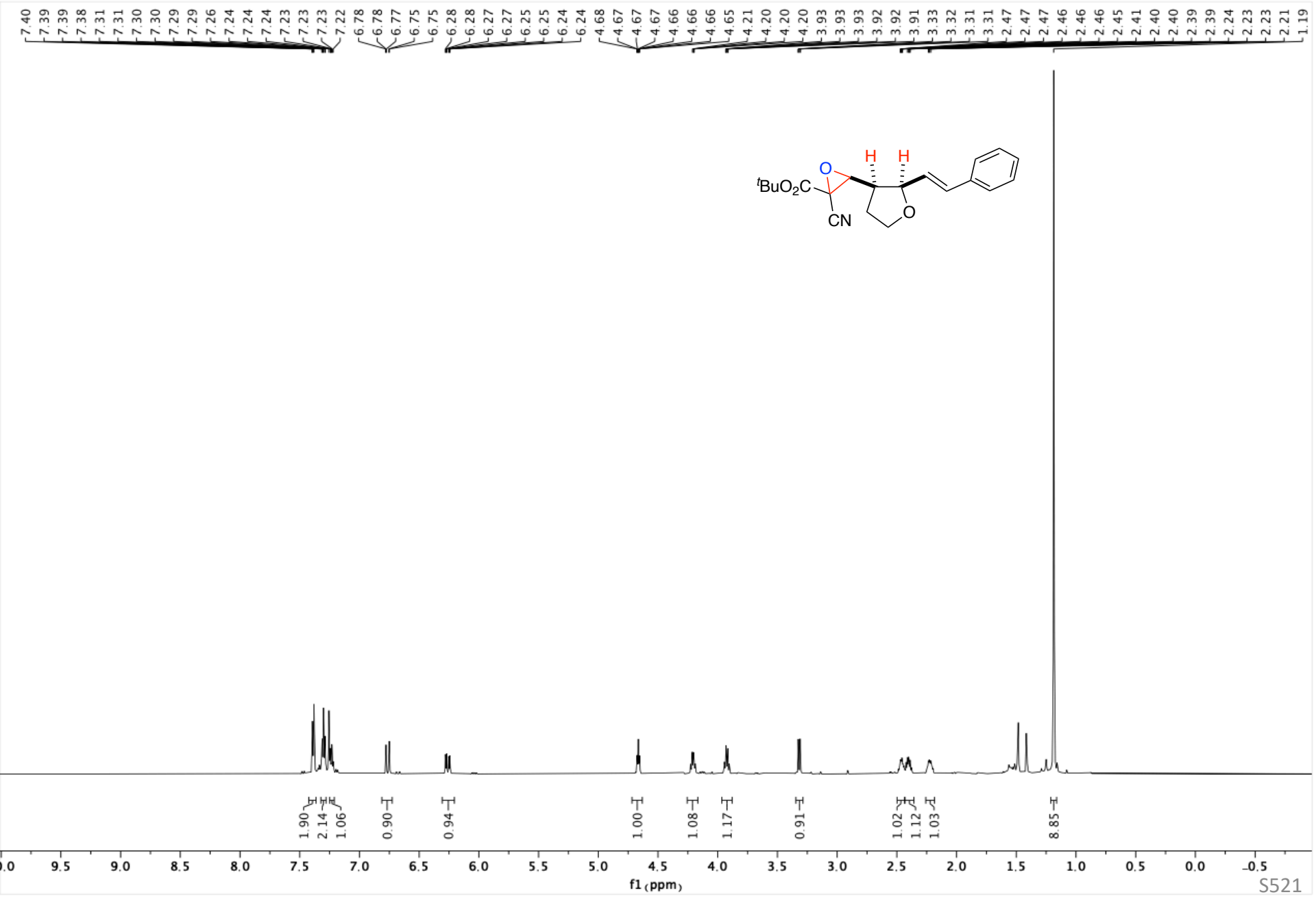


Peak Table

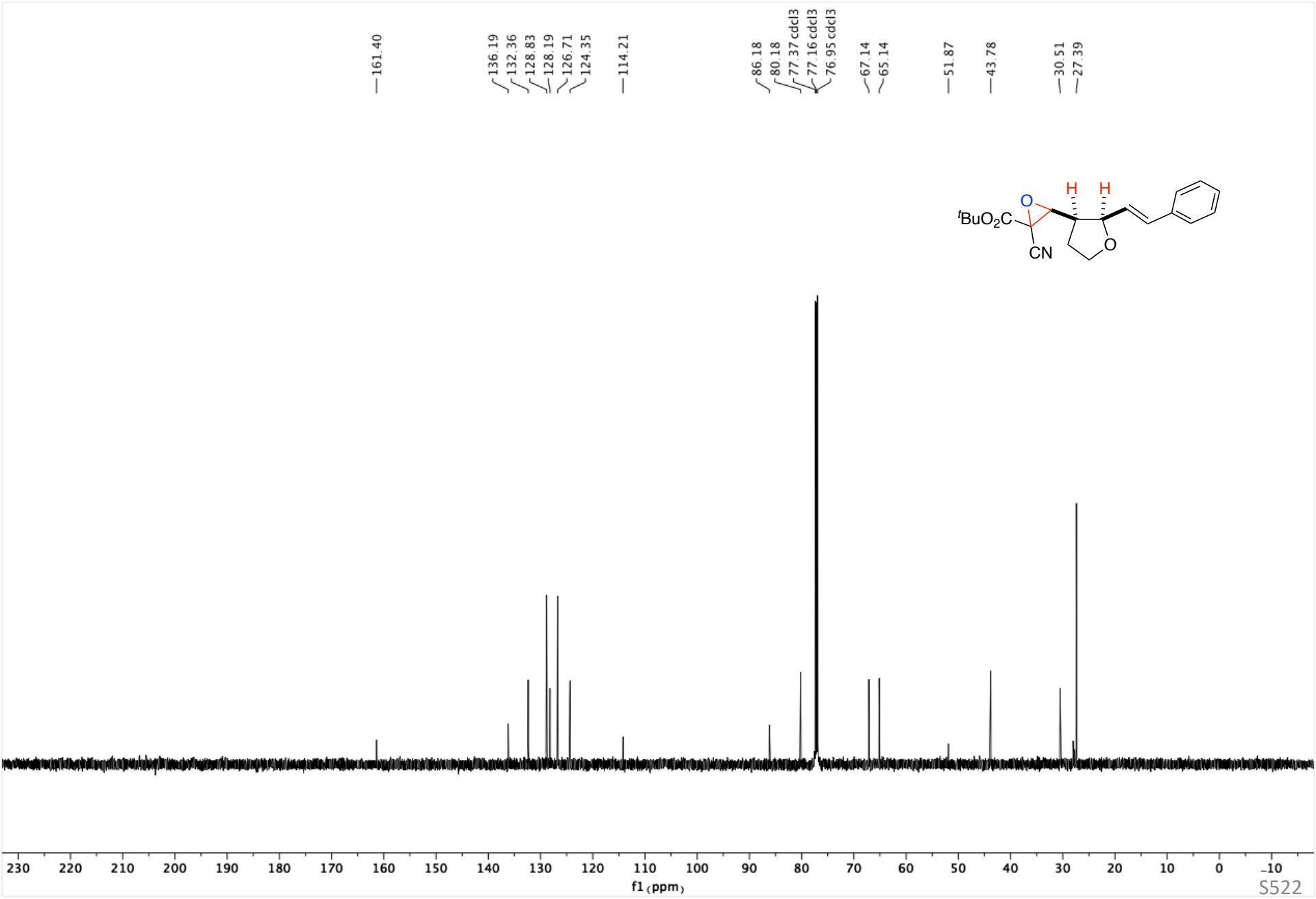
PDA Ch1 254nm

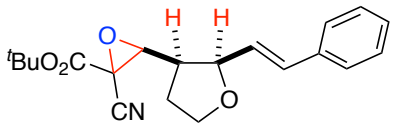
Peak#	Ret. Time	Area	Area%
1	14.465	391852	5.555
2	22.133	6662682	94.445
Total		7054534	100.000

tert-Butyl (3*S*)-2-cyano-3-((2*R*,3*R*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)oxirane-2-carboxylate

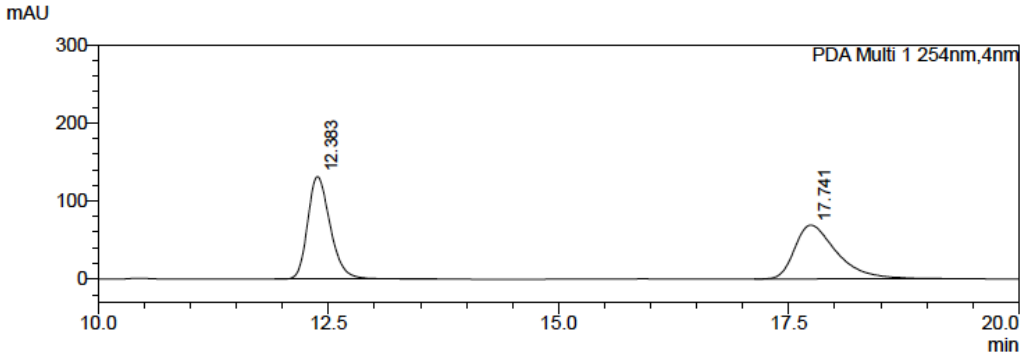


tert-Butyl (3*S*)-2-cyano-3-((2*R*,3*R*)-2-((*E*)-styryl)tetrahydrofuran-3-yl)oxirane-2-carboxylate



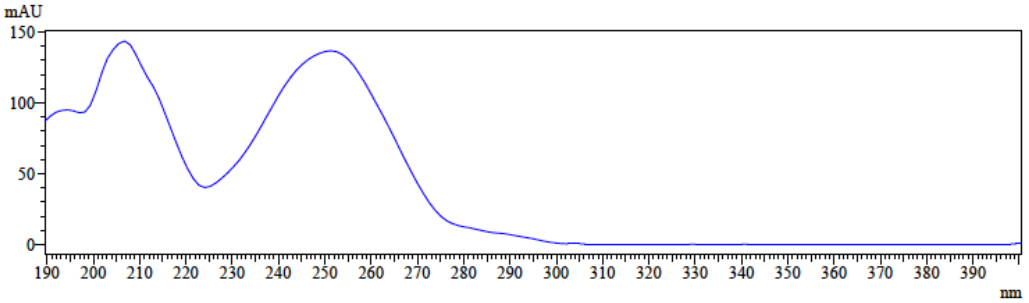


CZZ-3058-Rac-ID-5%-0.8mL-1



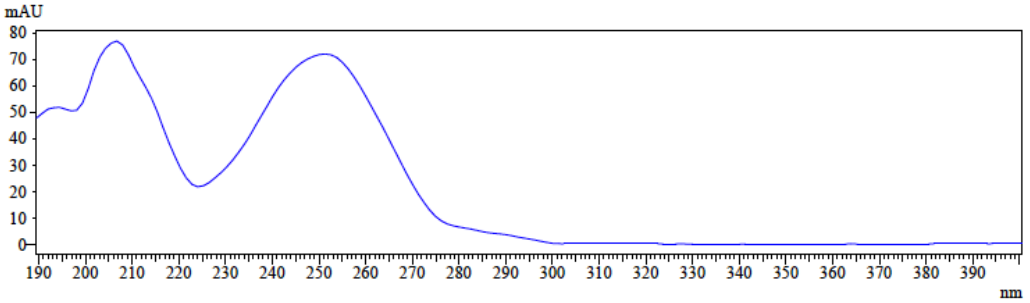
UV Spectrum

Retention Time: 12.383 min



UV Spectrum

Retention Time: 17.741 min

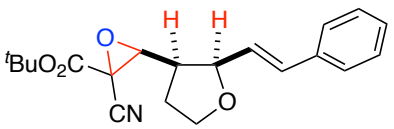


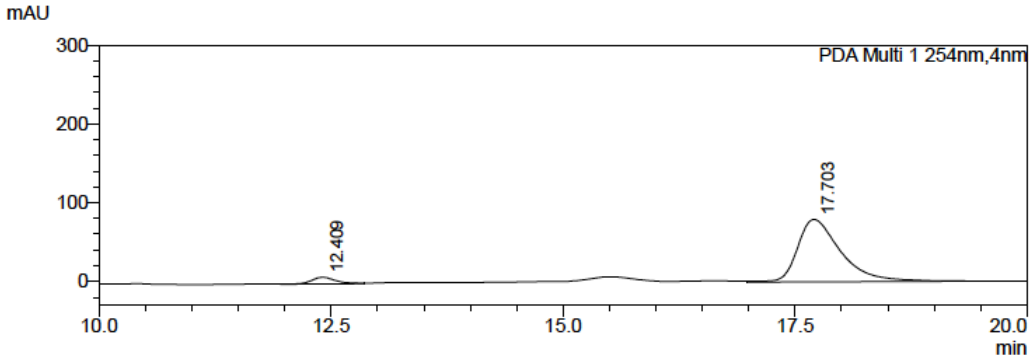
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	12.383	50.508
2	17.741	49.492
Total		100.000

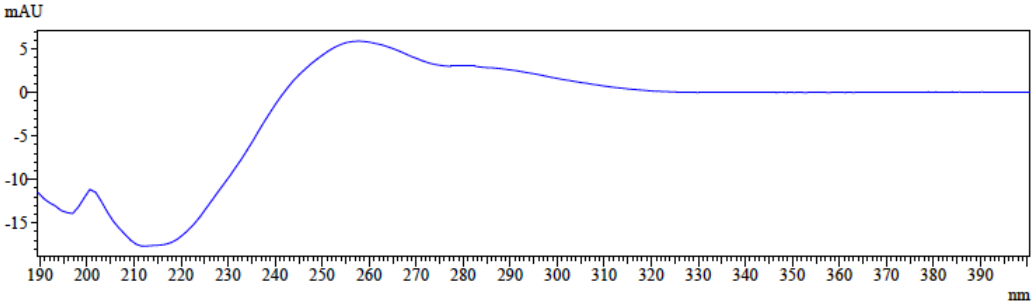
CZZ-3060-Chiral-ID-5%-0.8mL





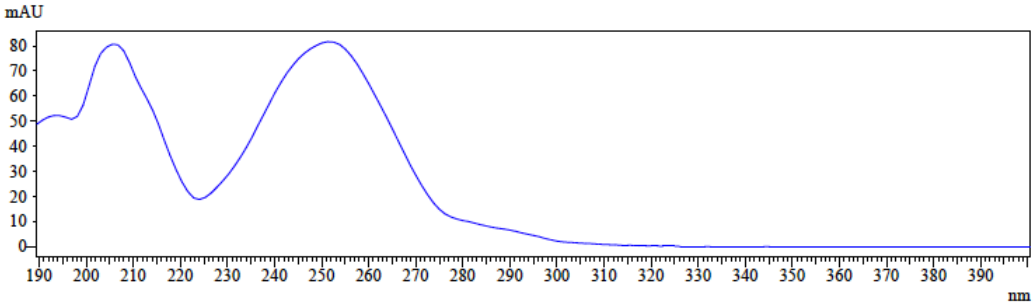
UV Spectrum

Retention Time: 12.409 min



UV Spectrum

Retention Time: 17.703 min

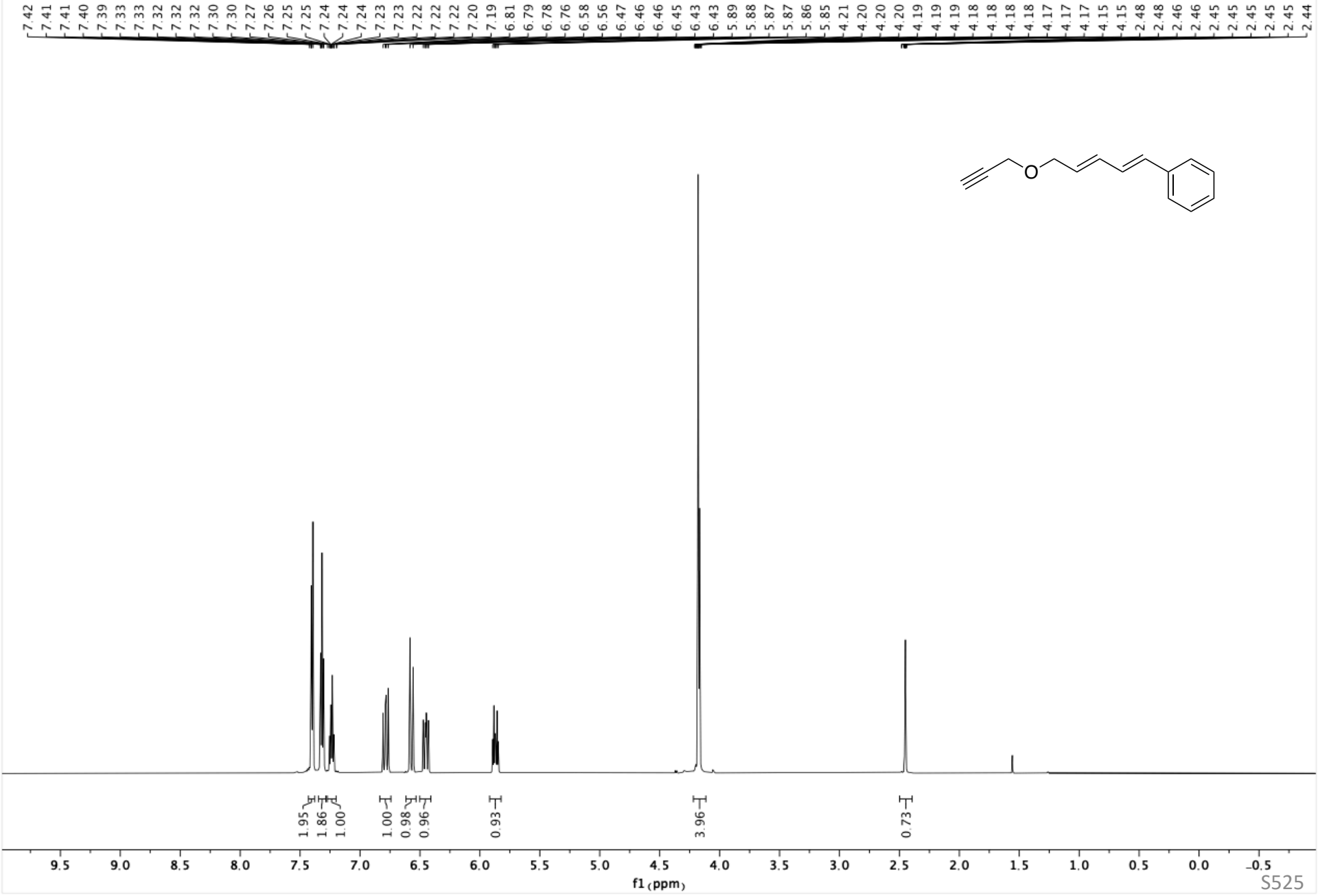


Peak Table

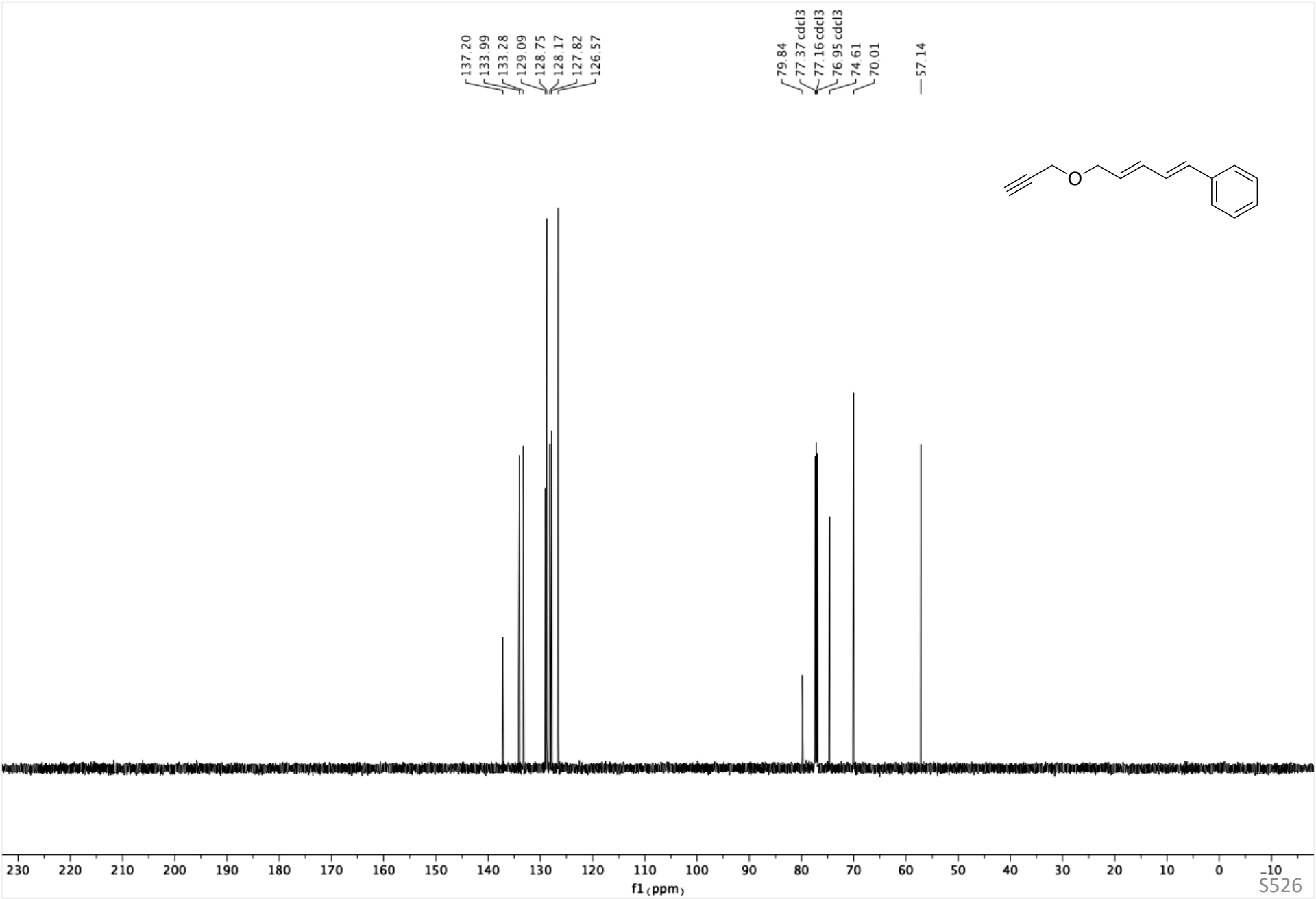
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	12.409	5.693
2	17.703	94.307
Total		100.000

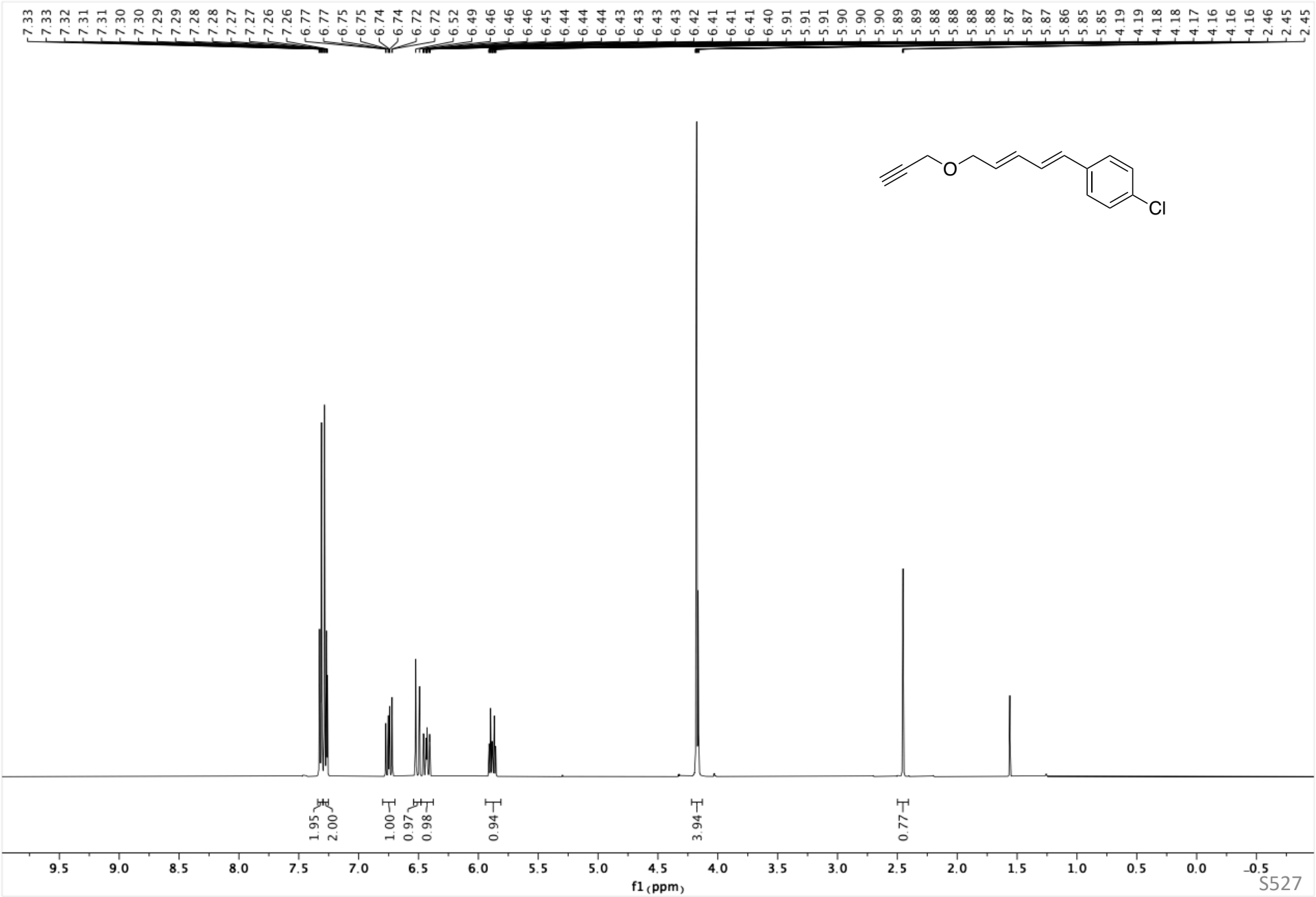
((1*E*,3*E*)-5-(Prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



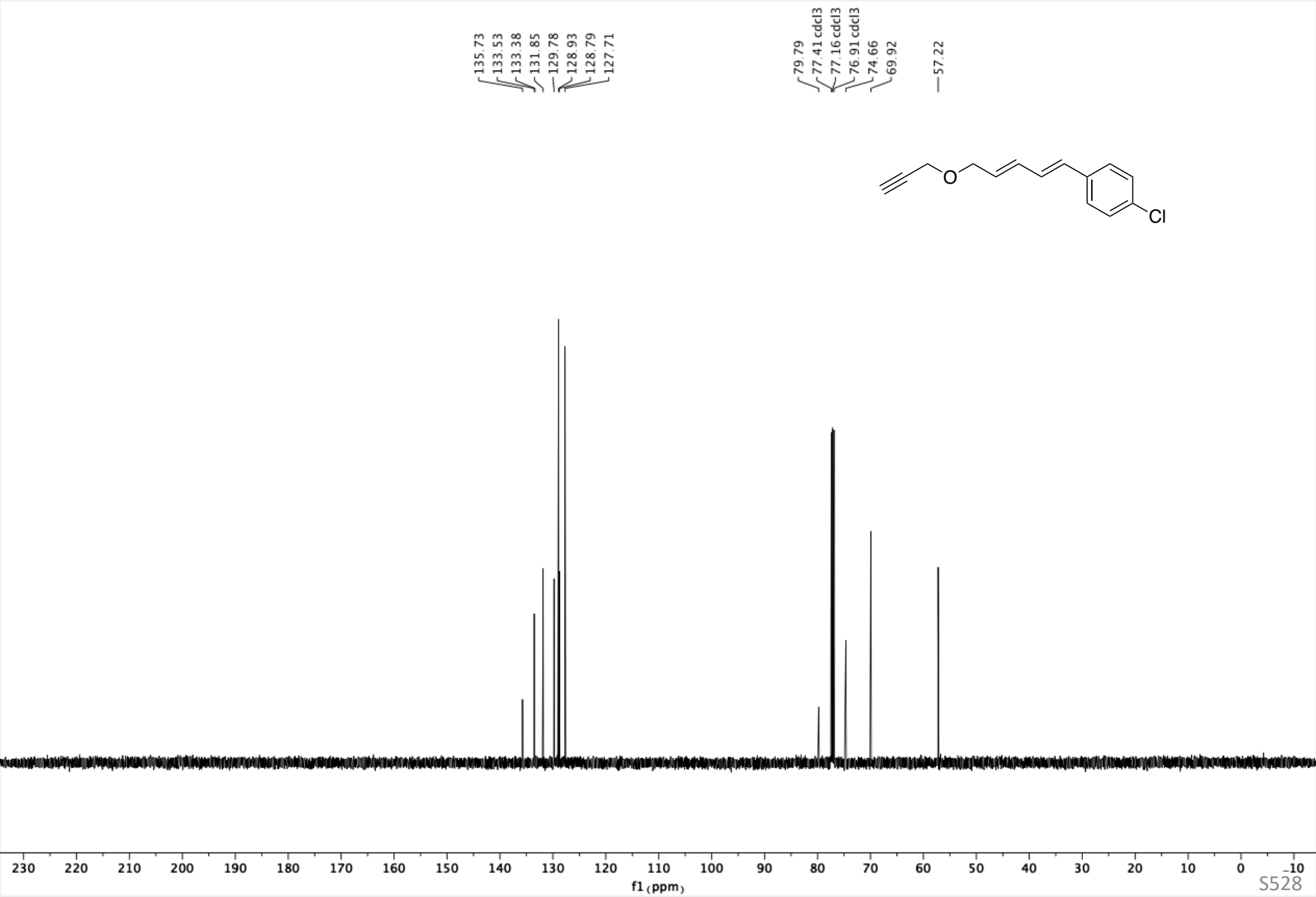
((1*E*,3*E*)-5-(Prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



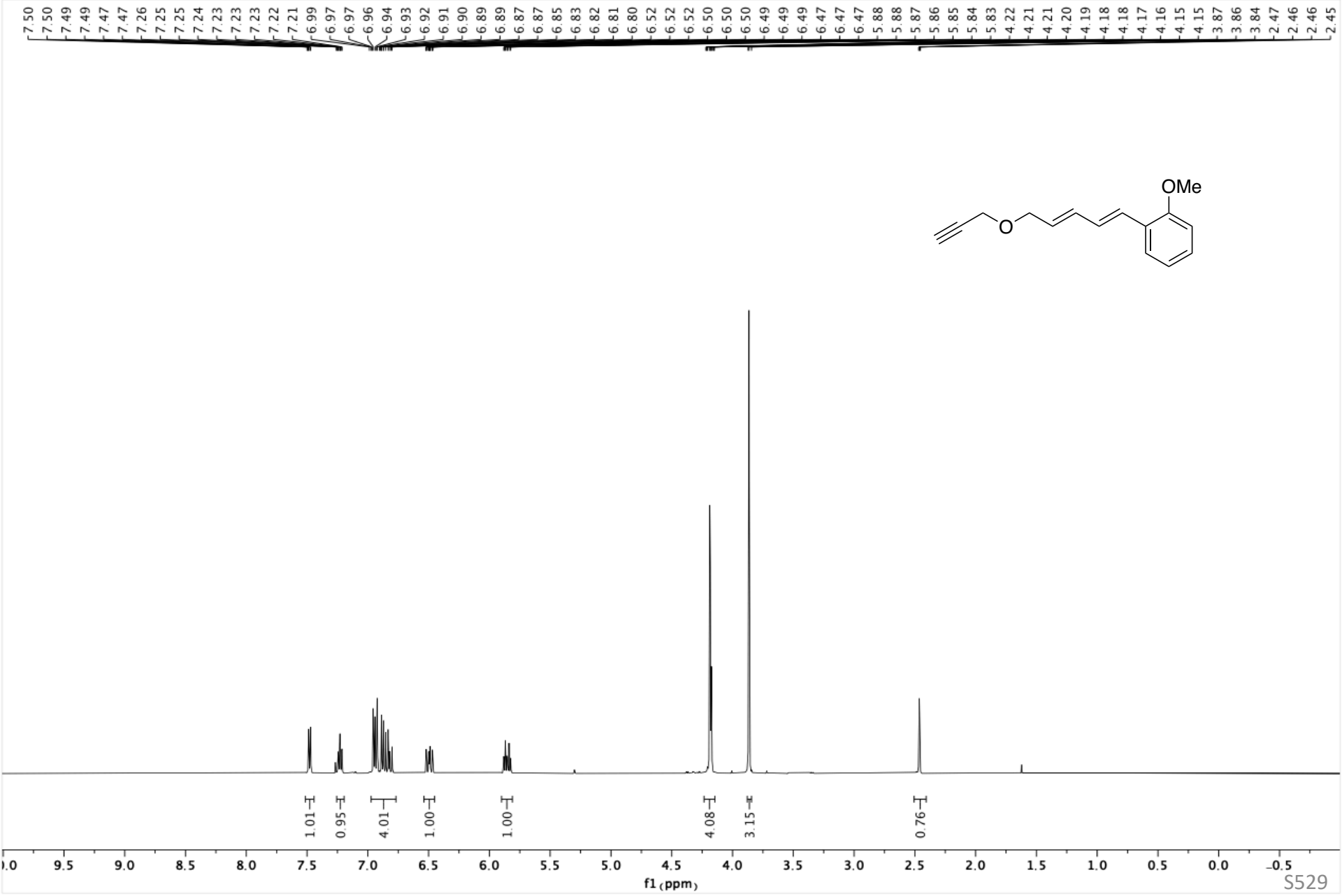
1-Chloro-4-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



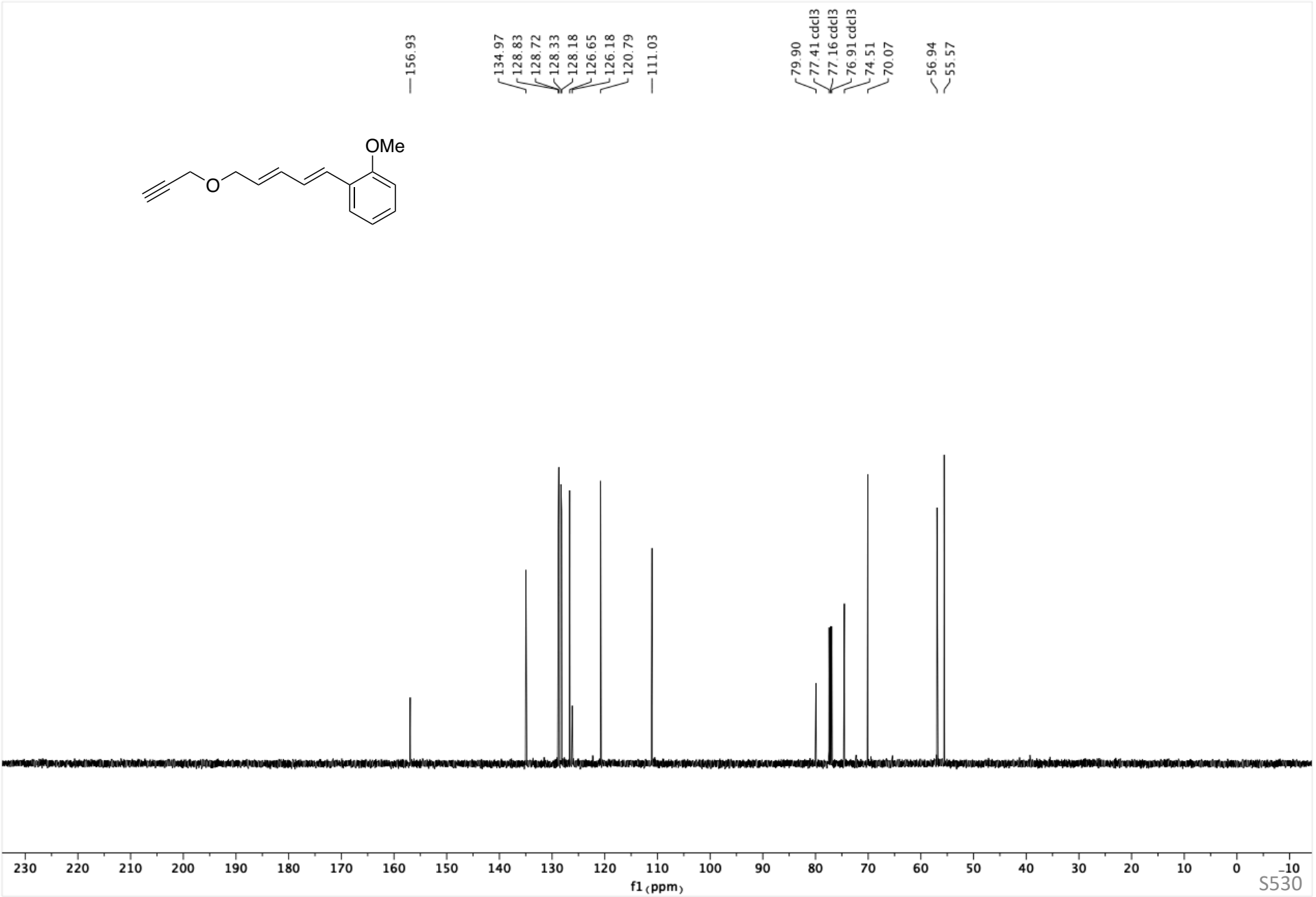
1-Chloro-4-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



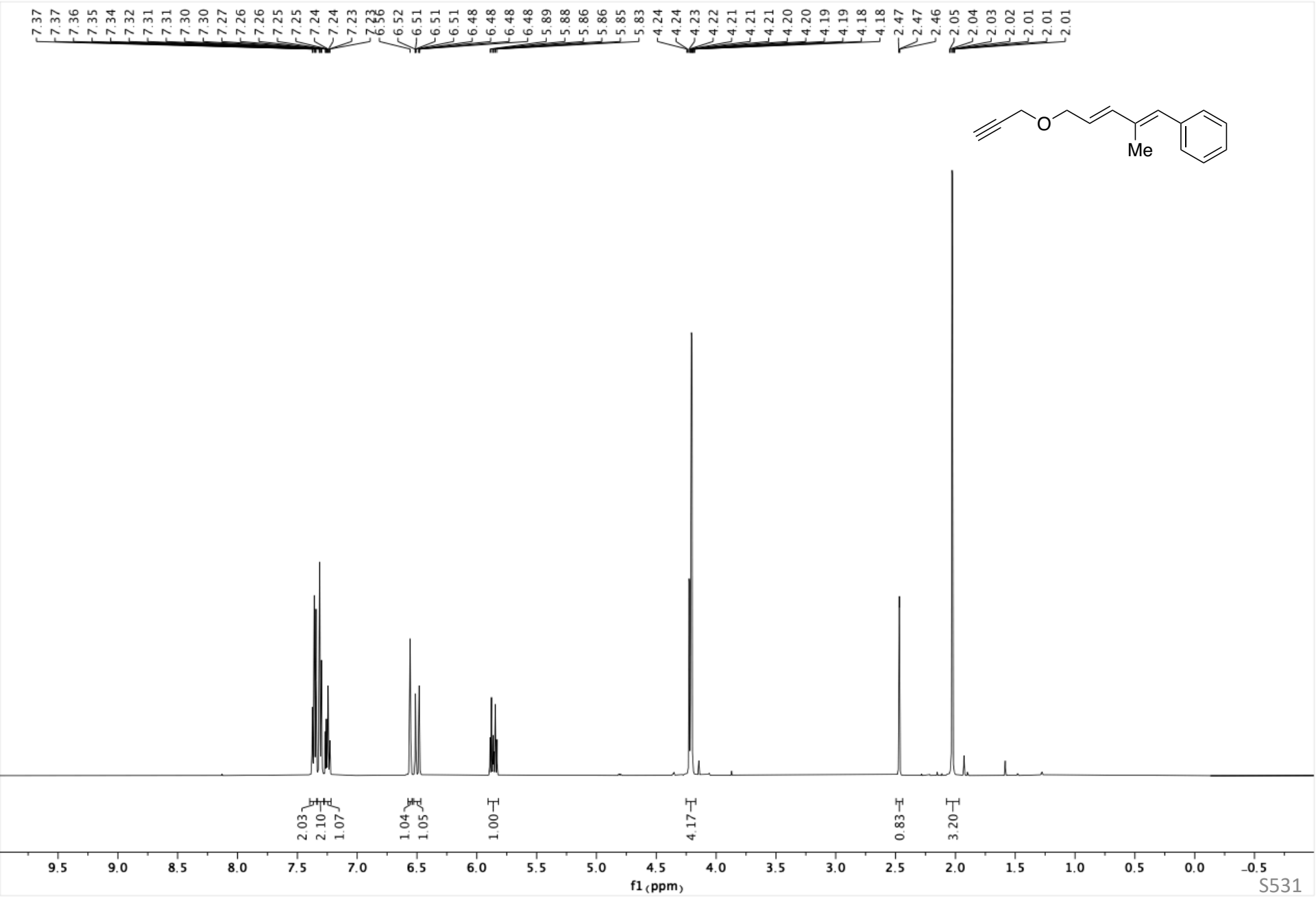
1-Methoxy-2-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



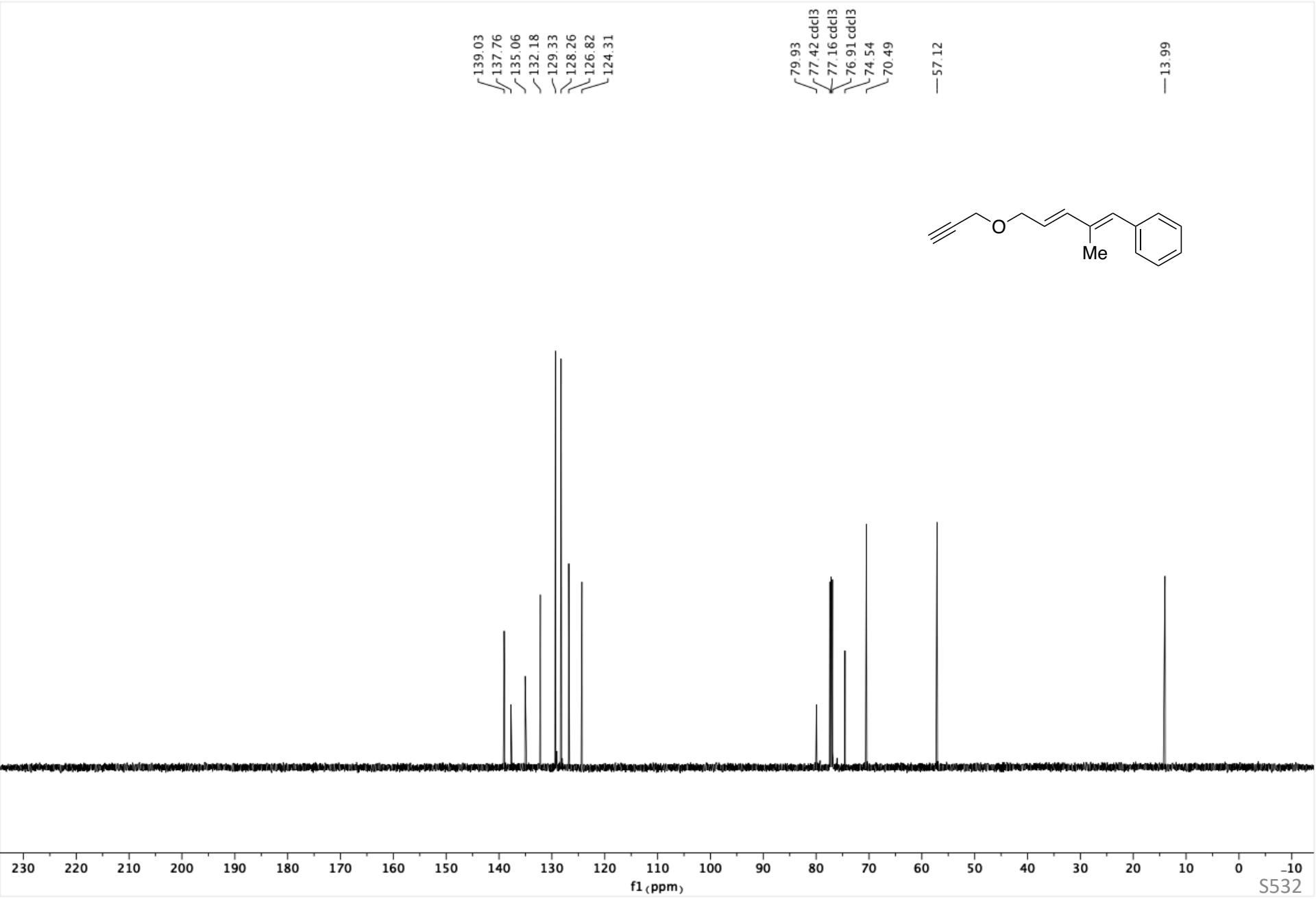
1-Methoxy-2-((1*E*,3*E*)-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



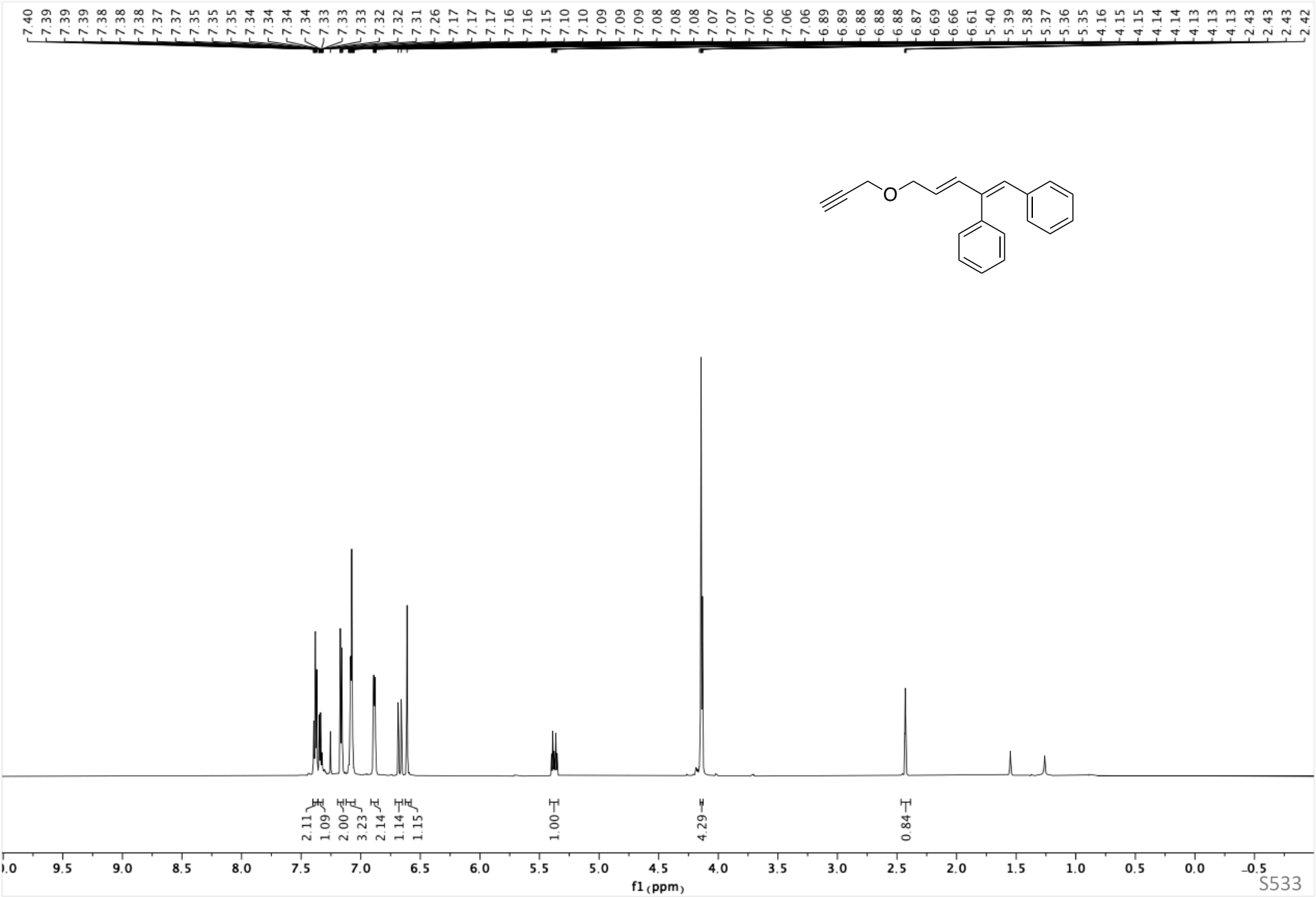
((1*E*,3*E*)-2-Methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



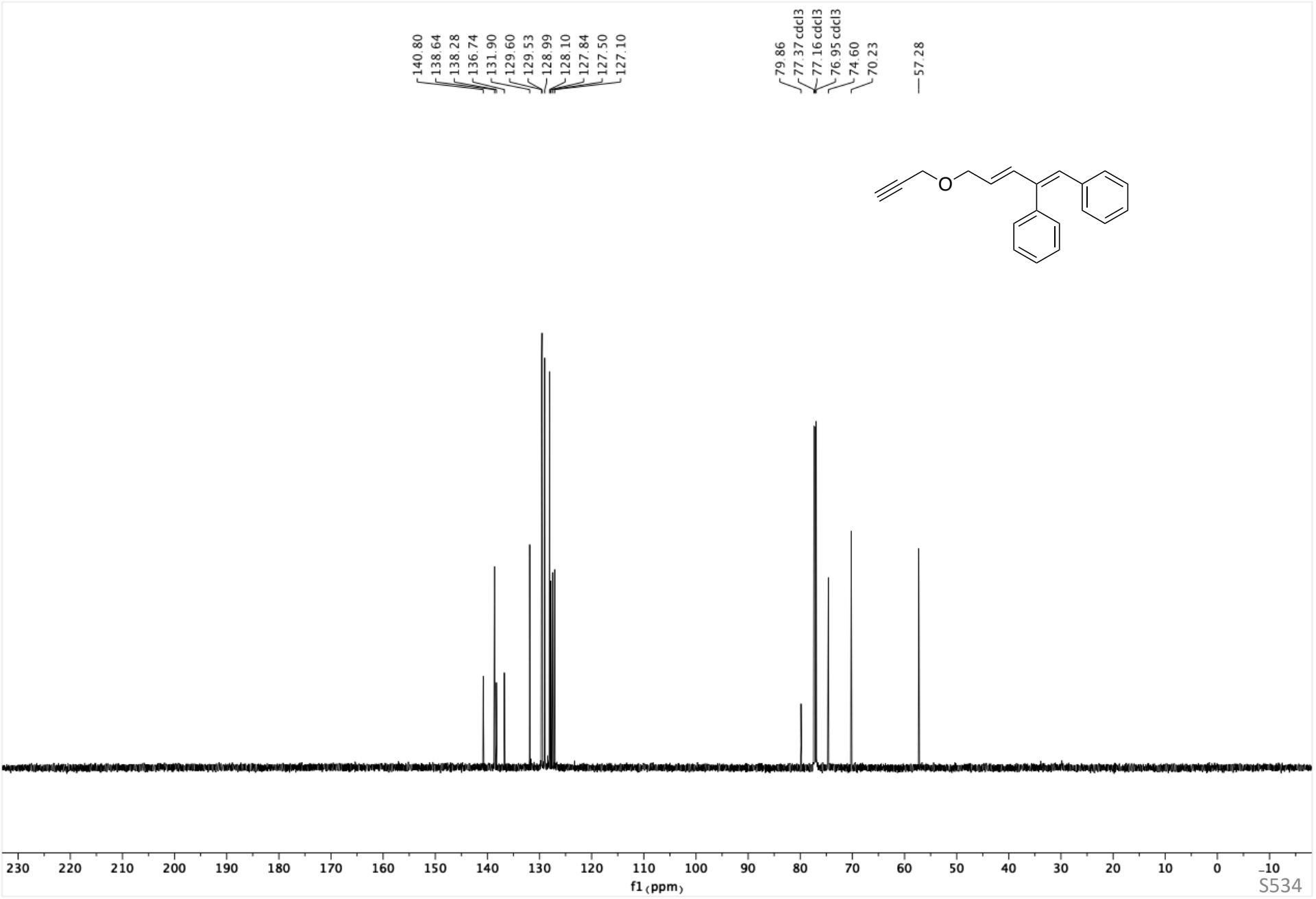
((1*E*,3*E*)-2-Methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



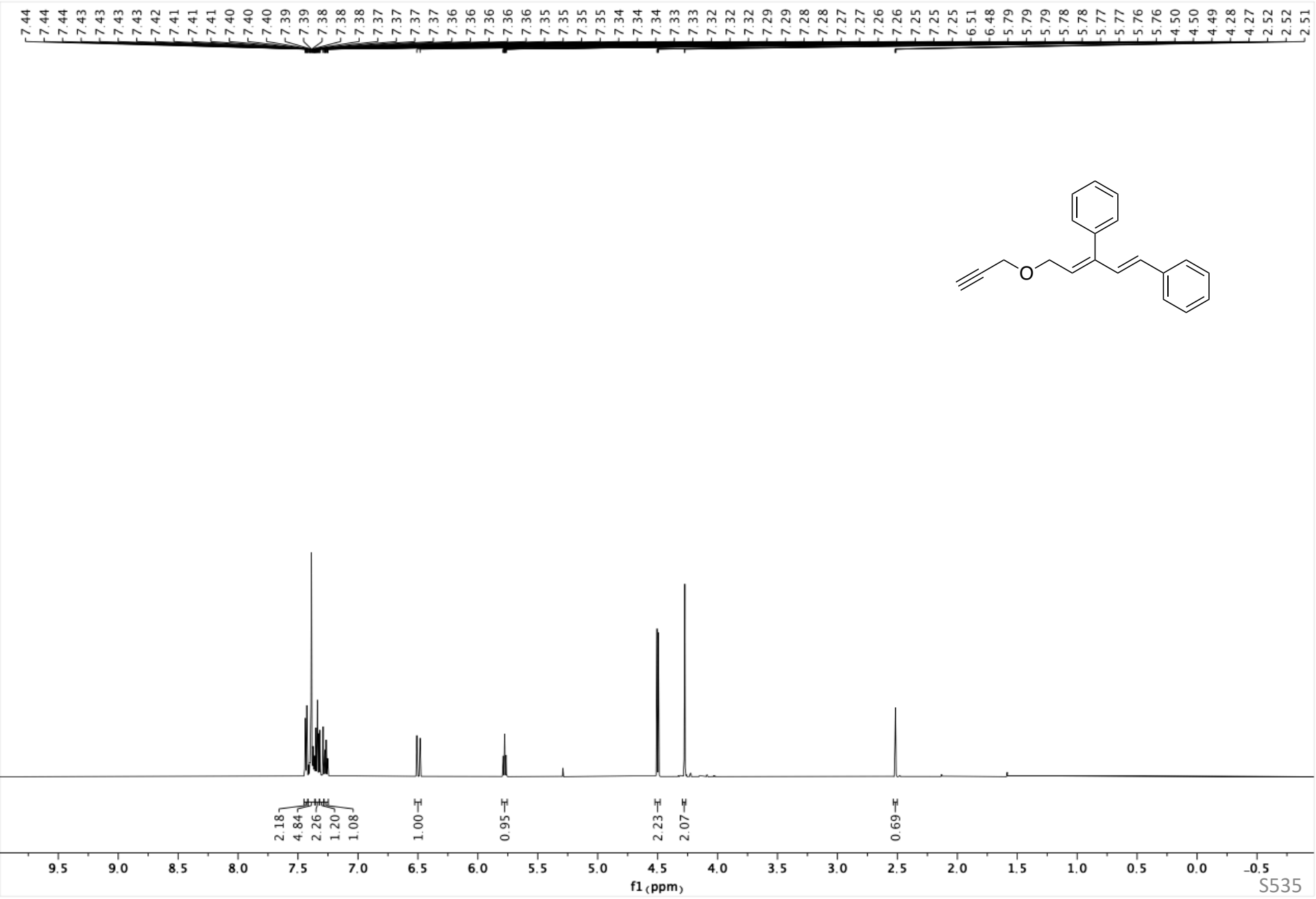
((1*Z*,3*E*)-5-(Prop-2-yn-1-yloxy)penta-1,3-diene-1,2-diyl)dibenzene



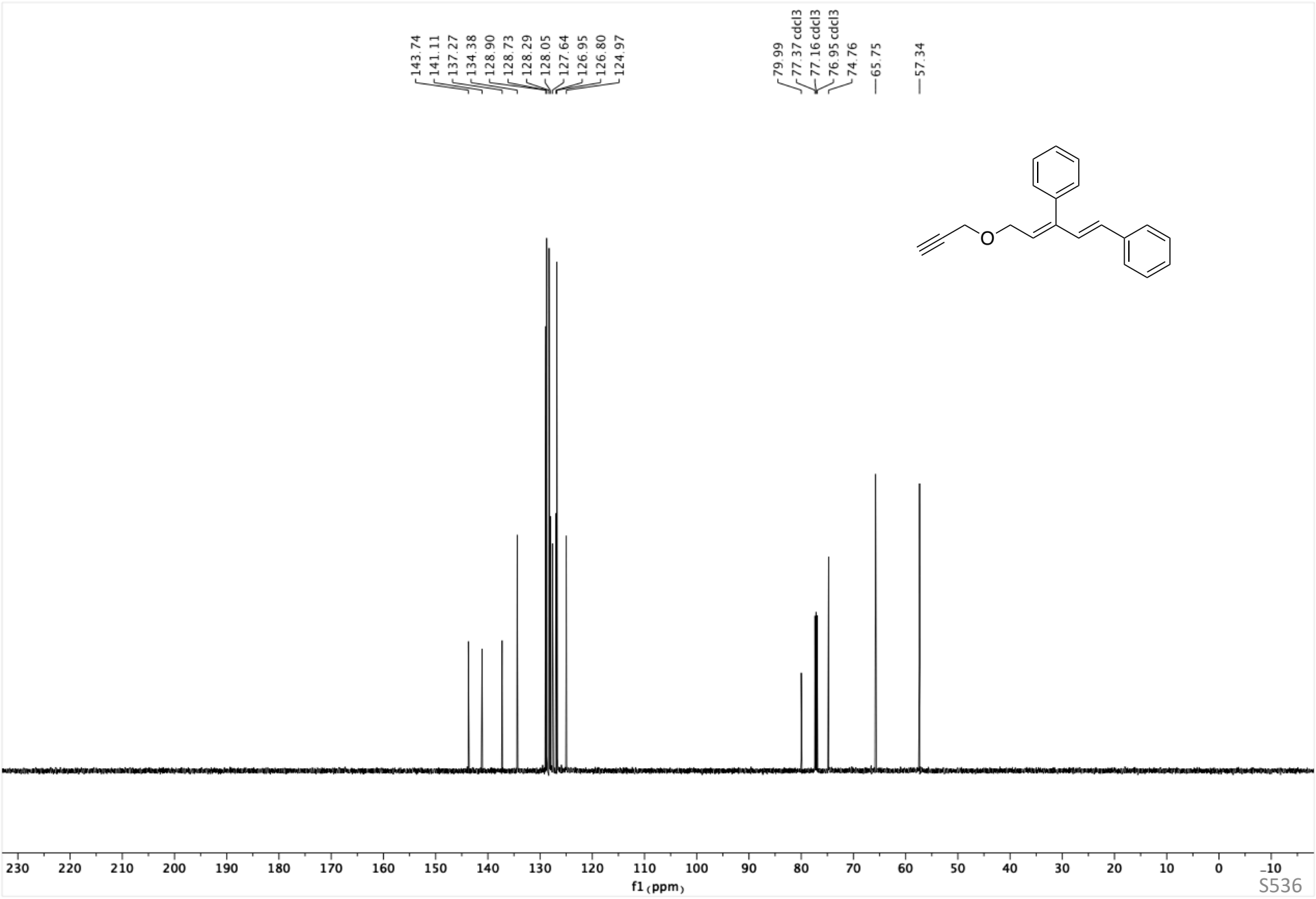
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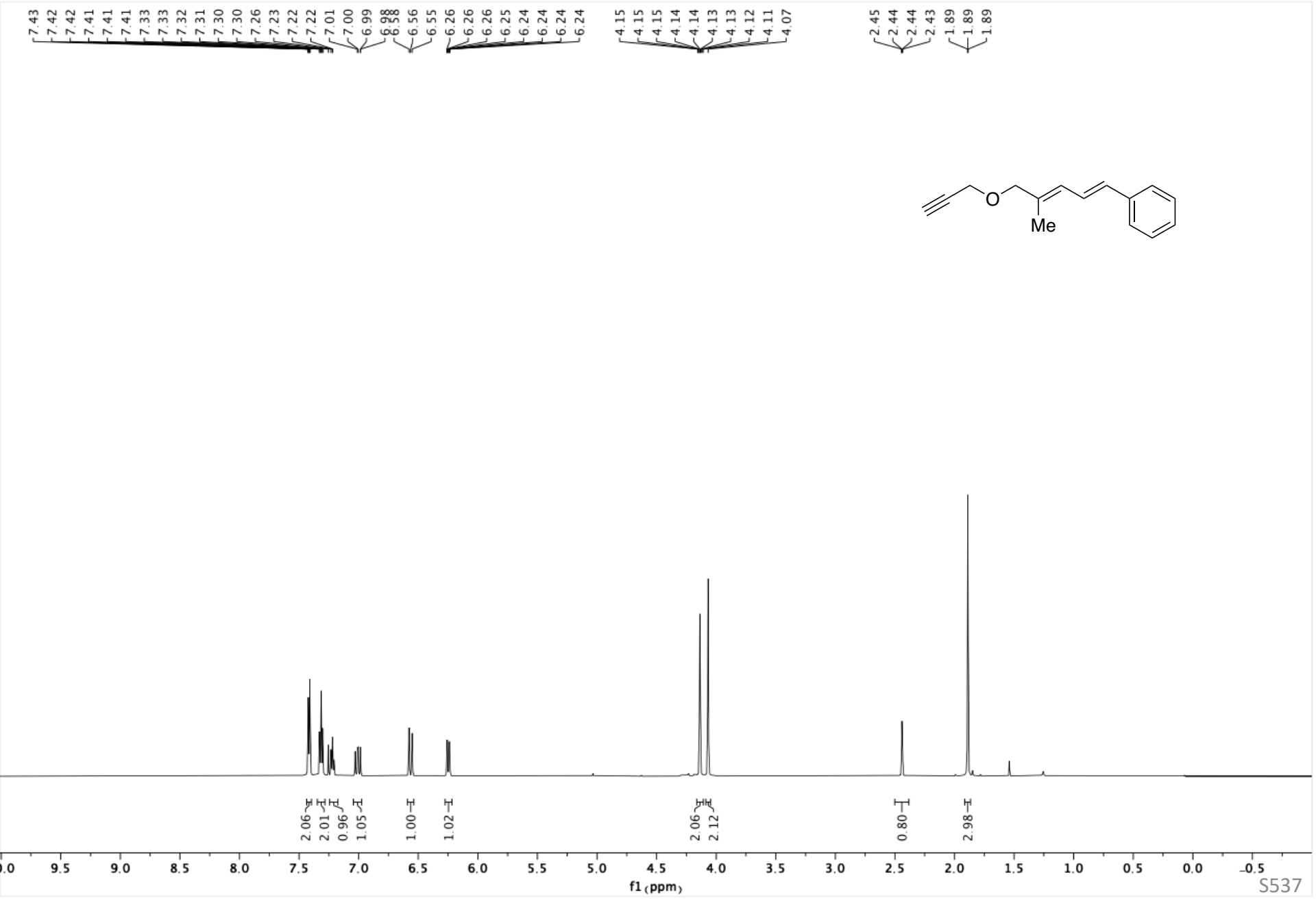
((1*E*,3*Z*)-5-(Prop-2-yn-1-yloxy)penta-1,3-diene-1,3-diyl)dibenzene



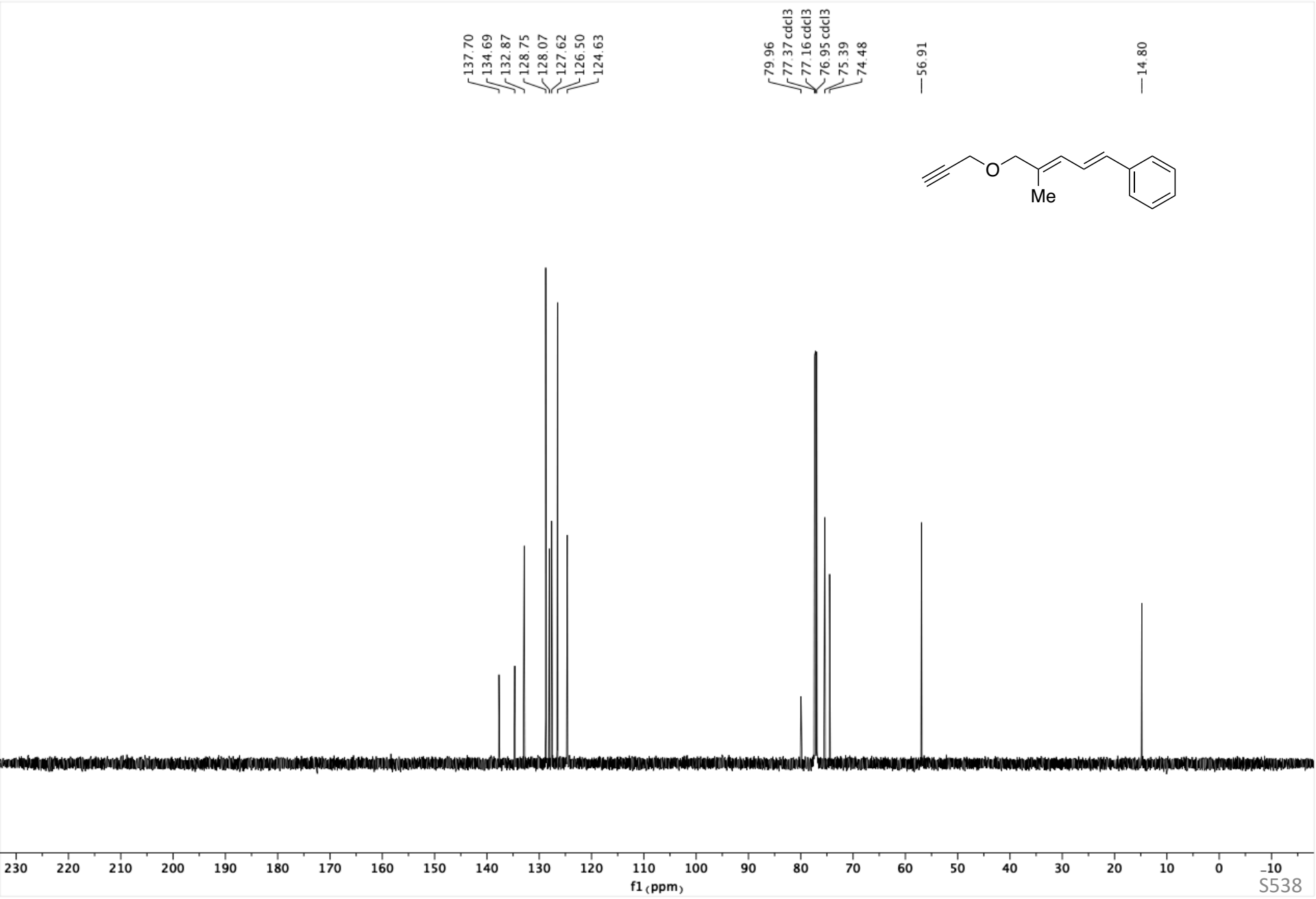
((1*E*,3*Z*)-5-(Prop-2-yn-1-yloxy)penta-1,3-diene-1,3-diyl)dibenzene



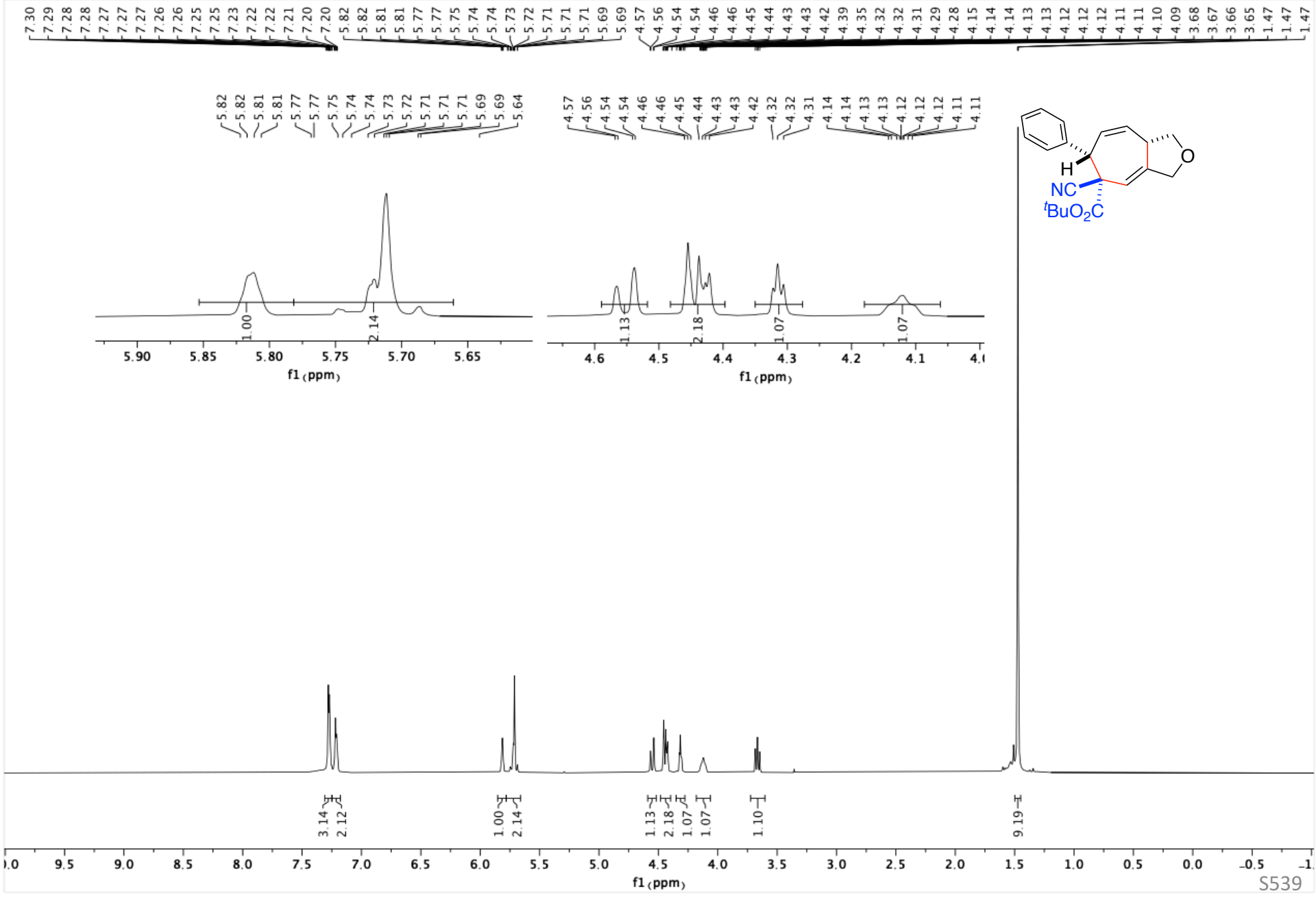
((1*E*,3*E*)-4-methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



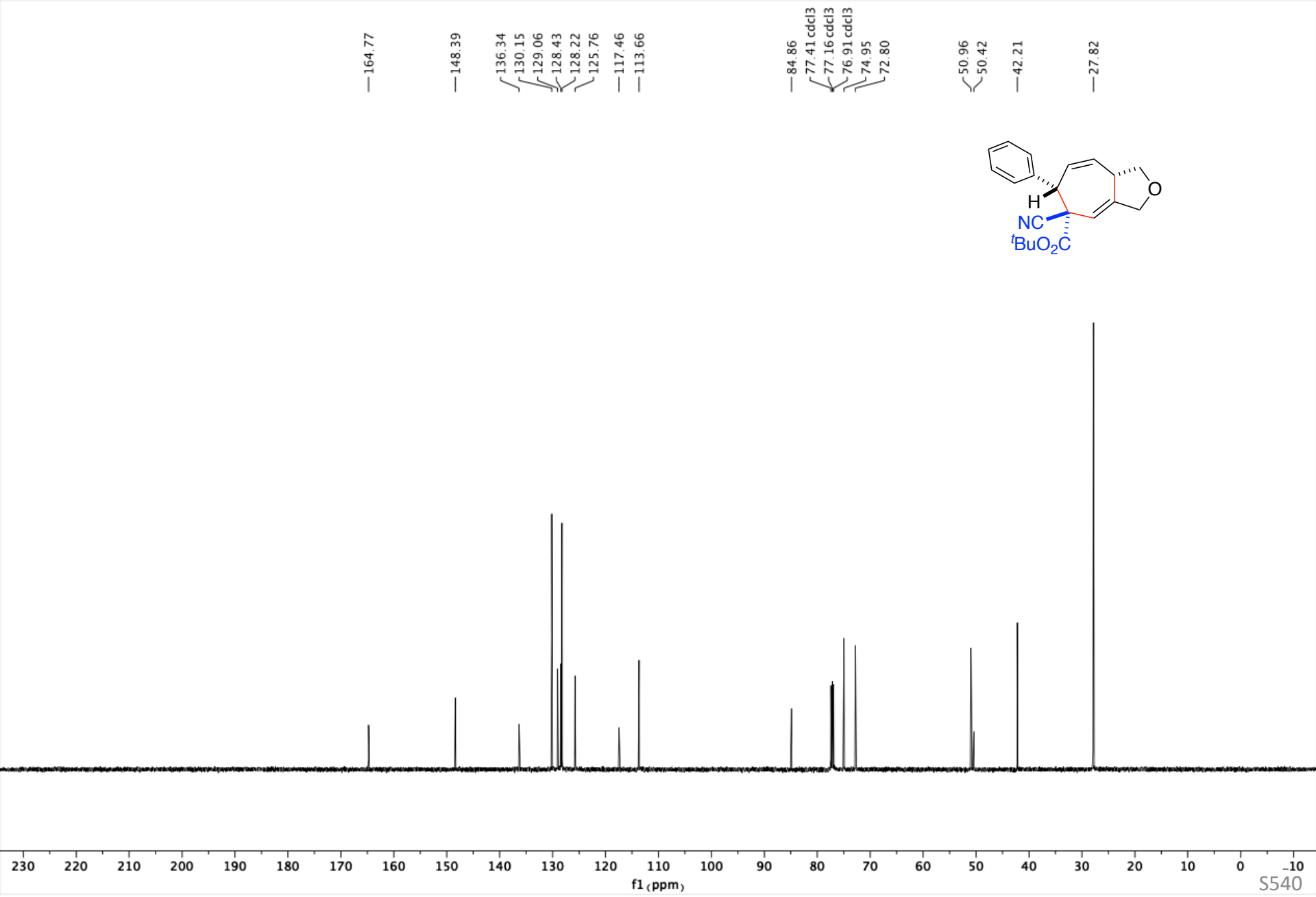
((1*E*,3*E*)-4-methyl-5-(prop-2-yn-1-yloxy)penta-1,3-dien-1-yl)benzene



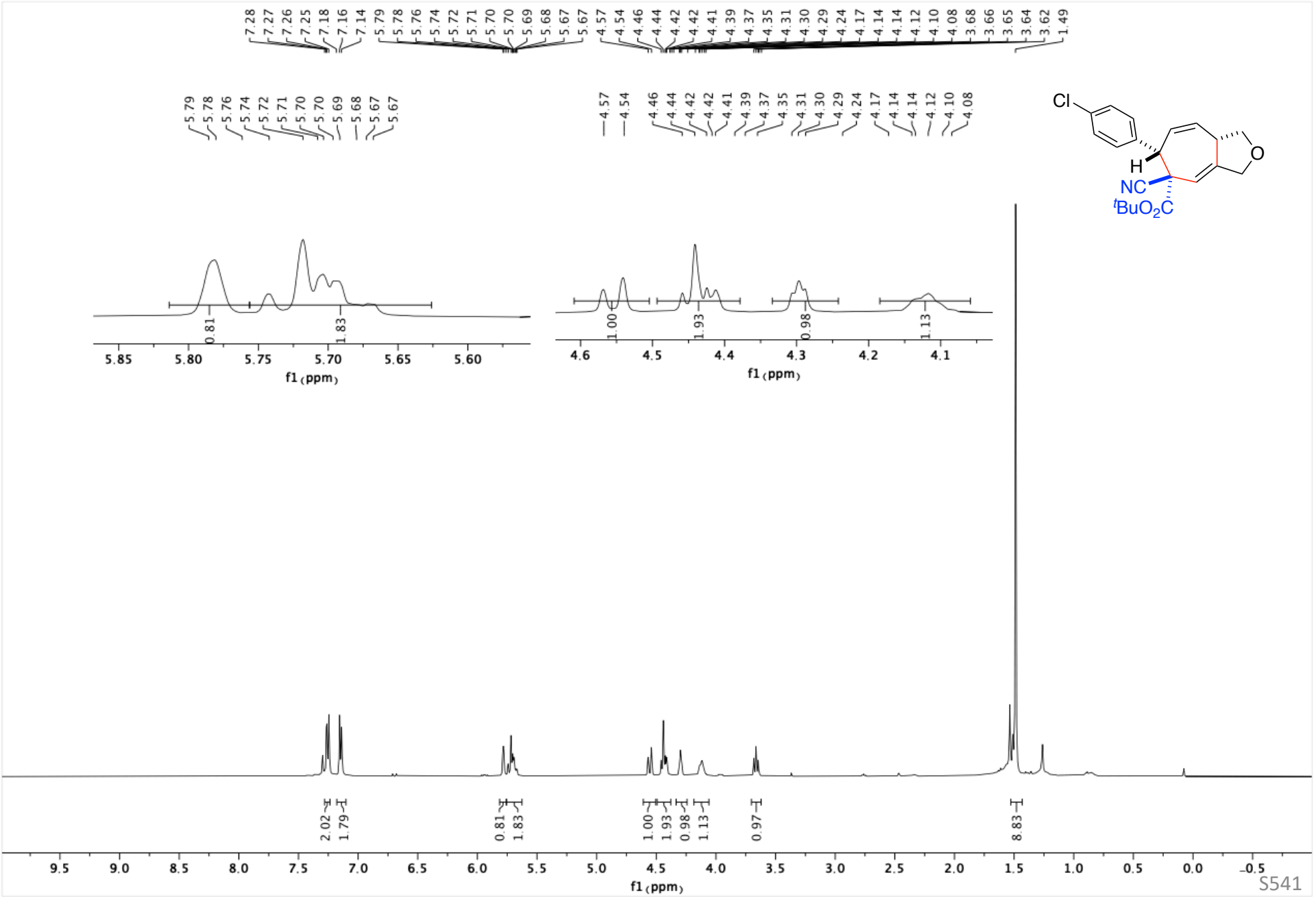
tert-Butyl (5_S_,8a_S_)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



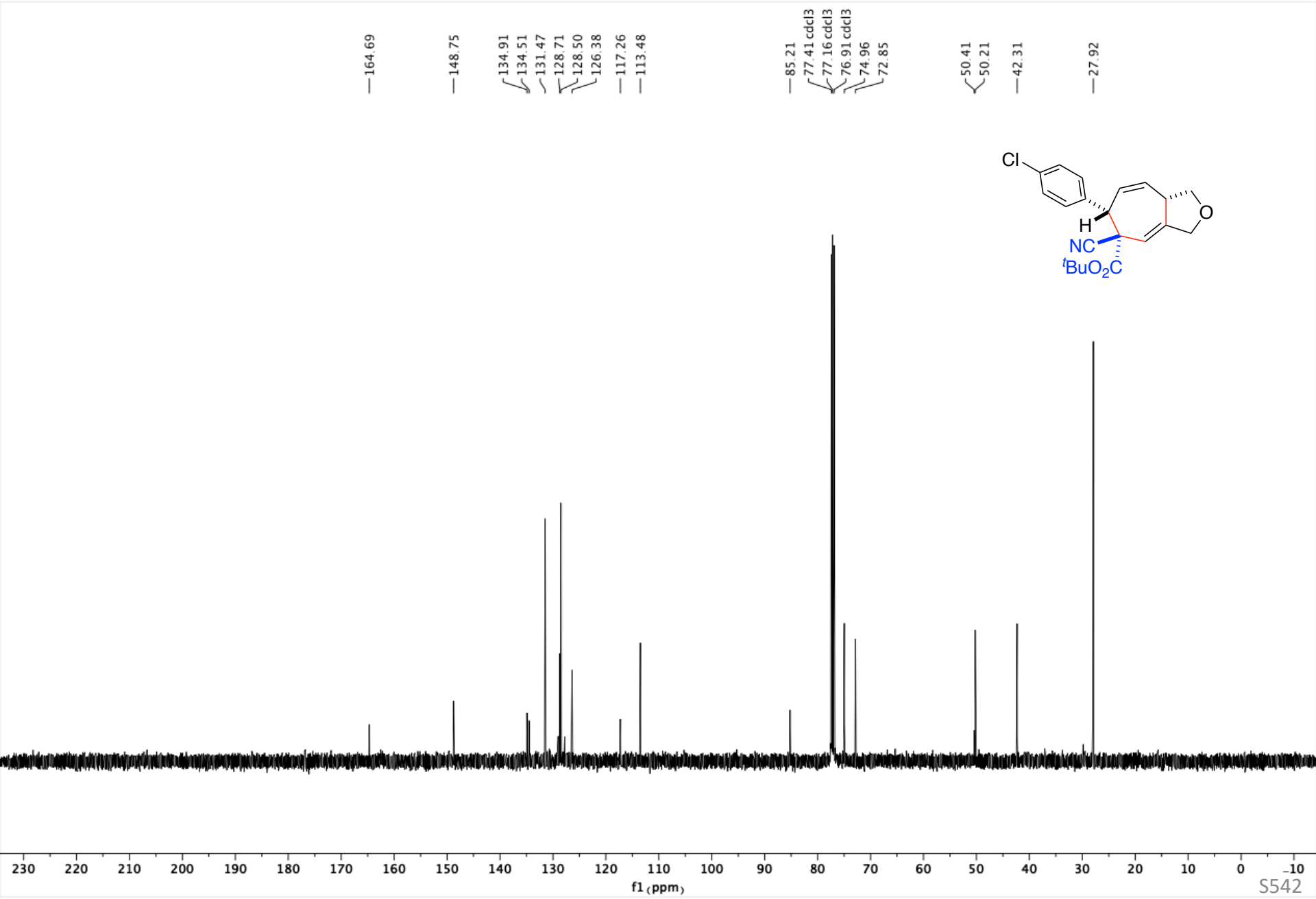
tert-Butyl (5_S_,8a_S_)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



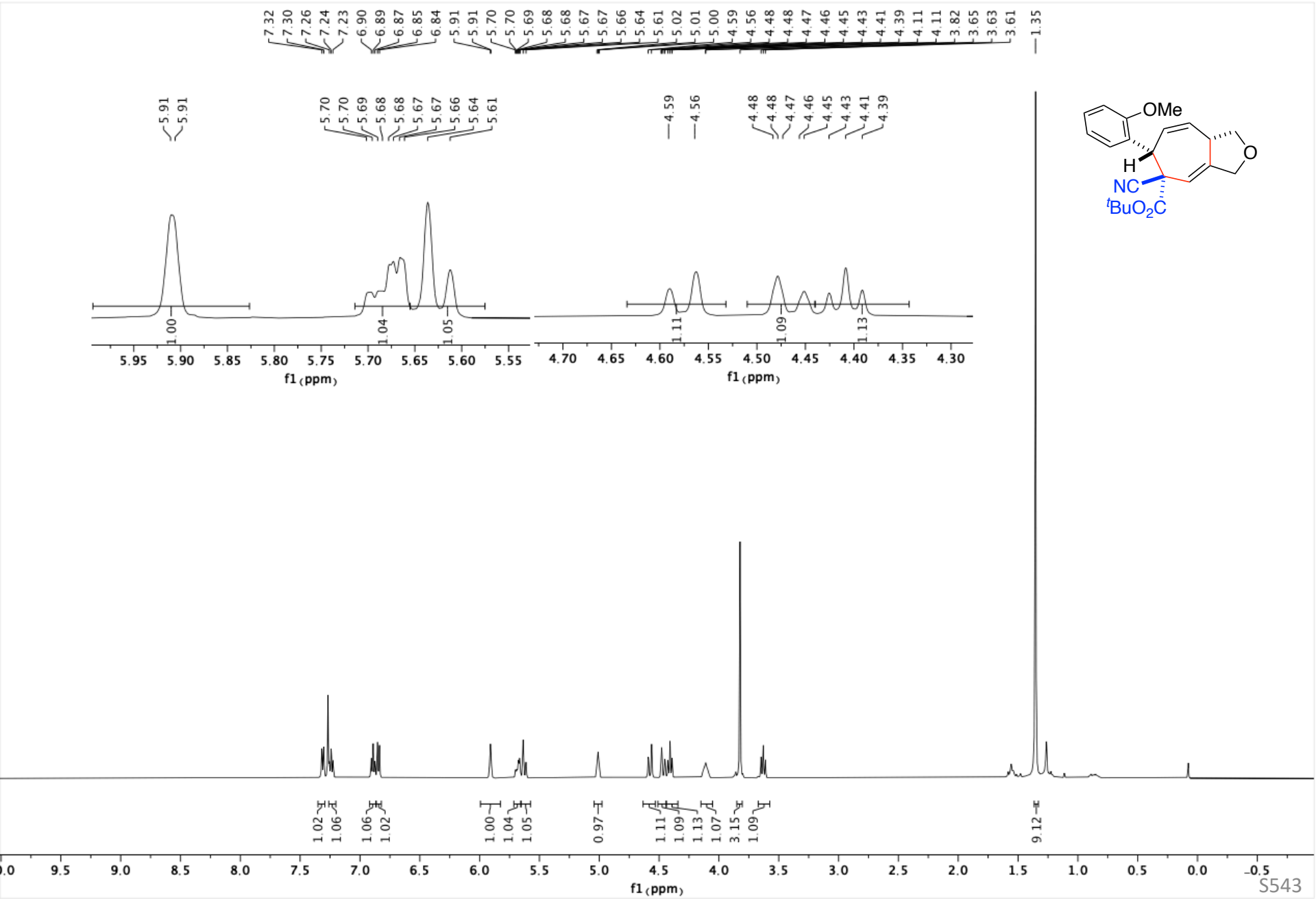
tert-Butyl (5_S_,8a_S_)-6-(4-chlorophenyl)-5-cyano-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



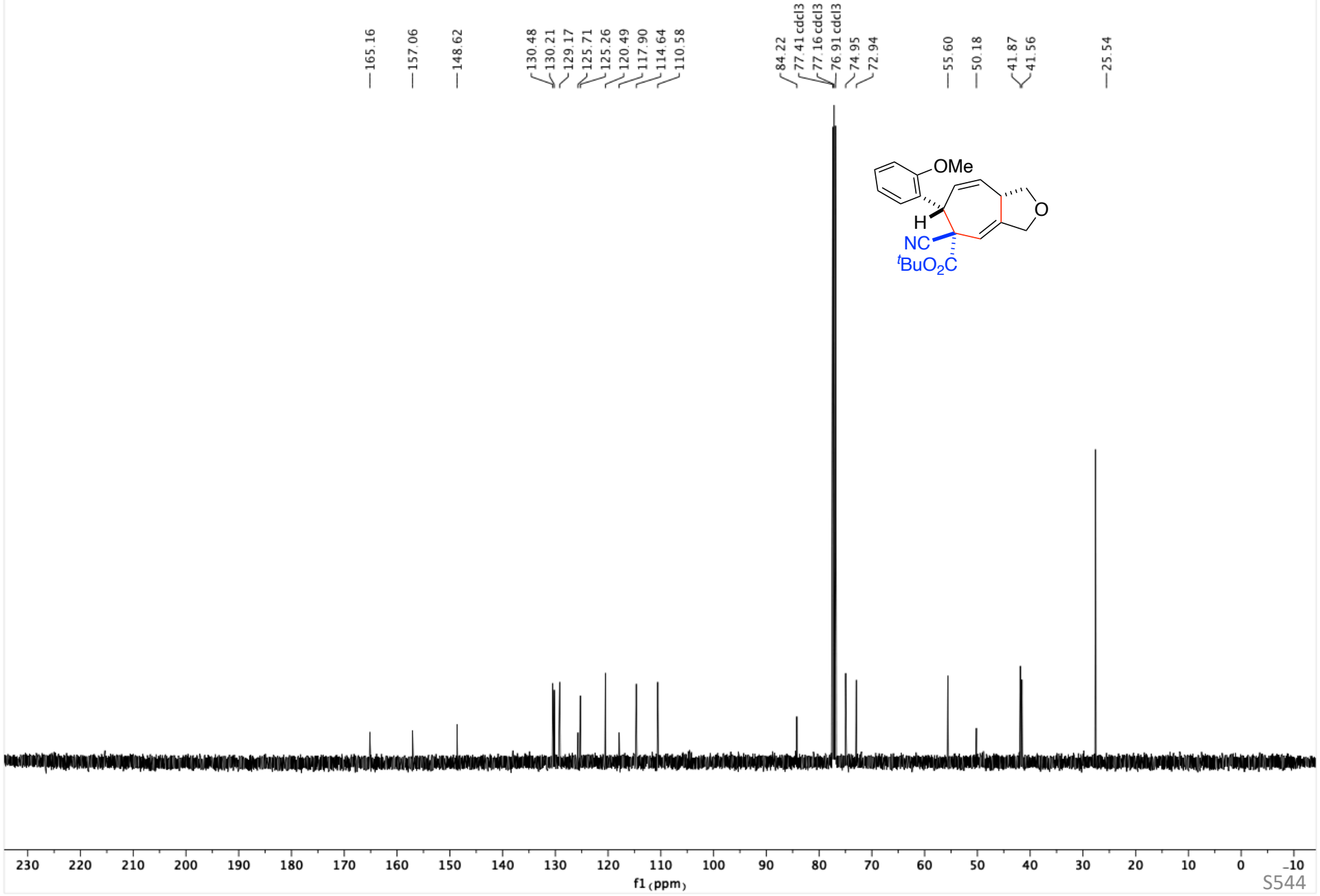
***tert*-Butyl (5*S*,8a*S*)-6-(4-chlorophenyl)-5-cyano-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate**



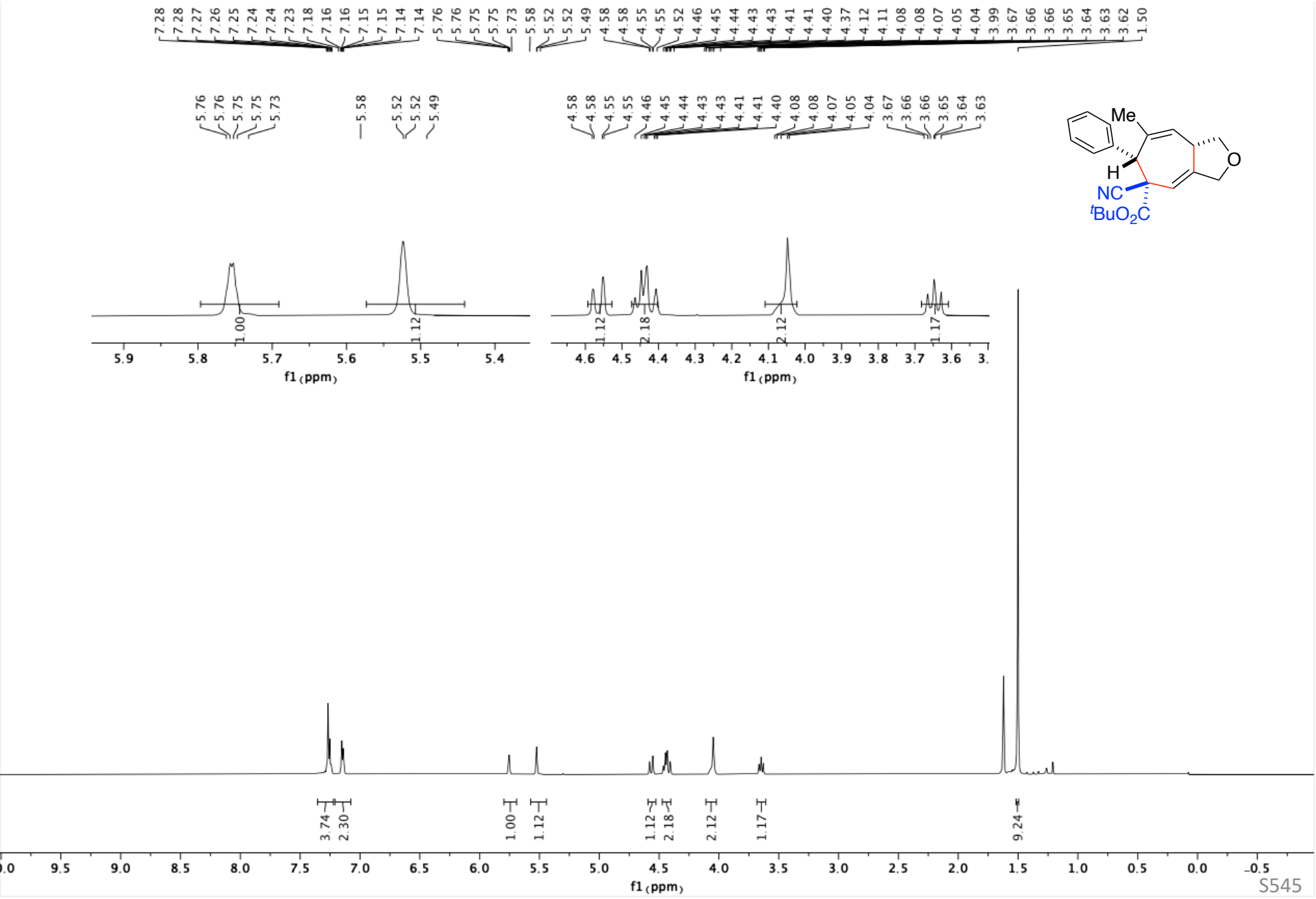
tert-Butyl (5_S_,8a_S_)-5-cyano-6-(2-methoxyphenyl)-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



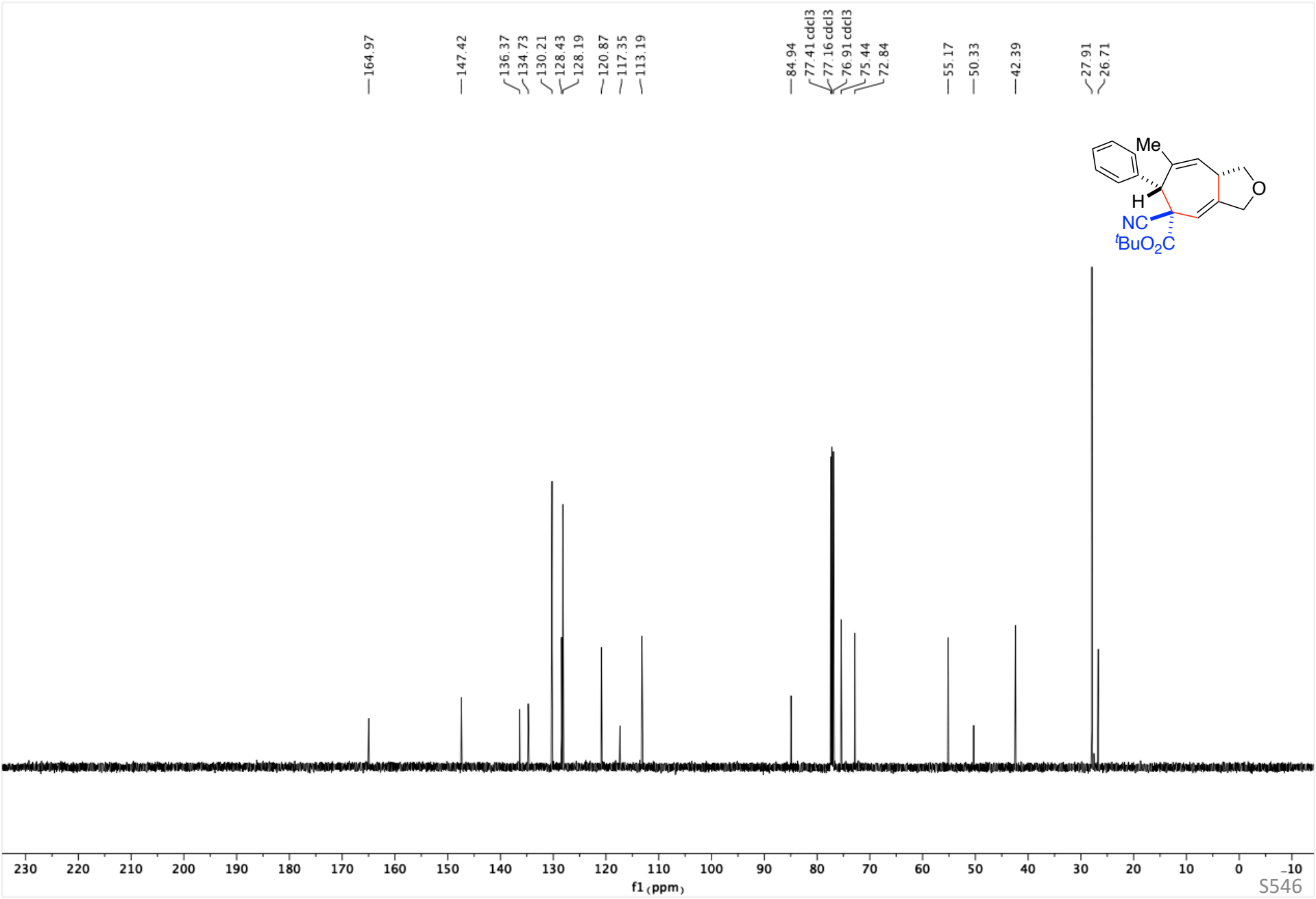
tert-Butyl (5_S_,8a_S_)-5-cyano-6-(2-methoxyphenyl)-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



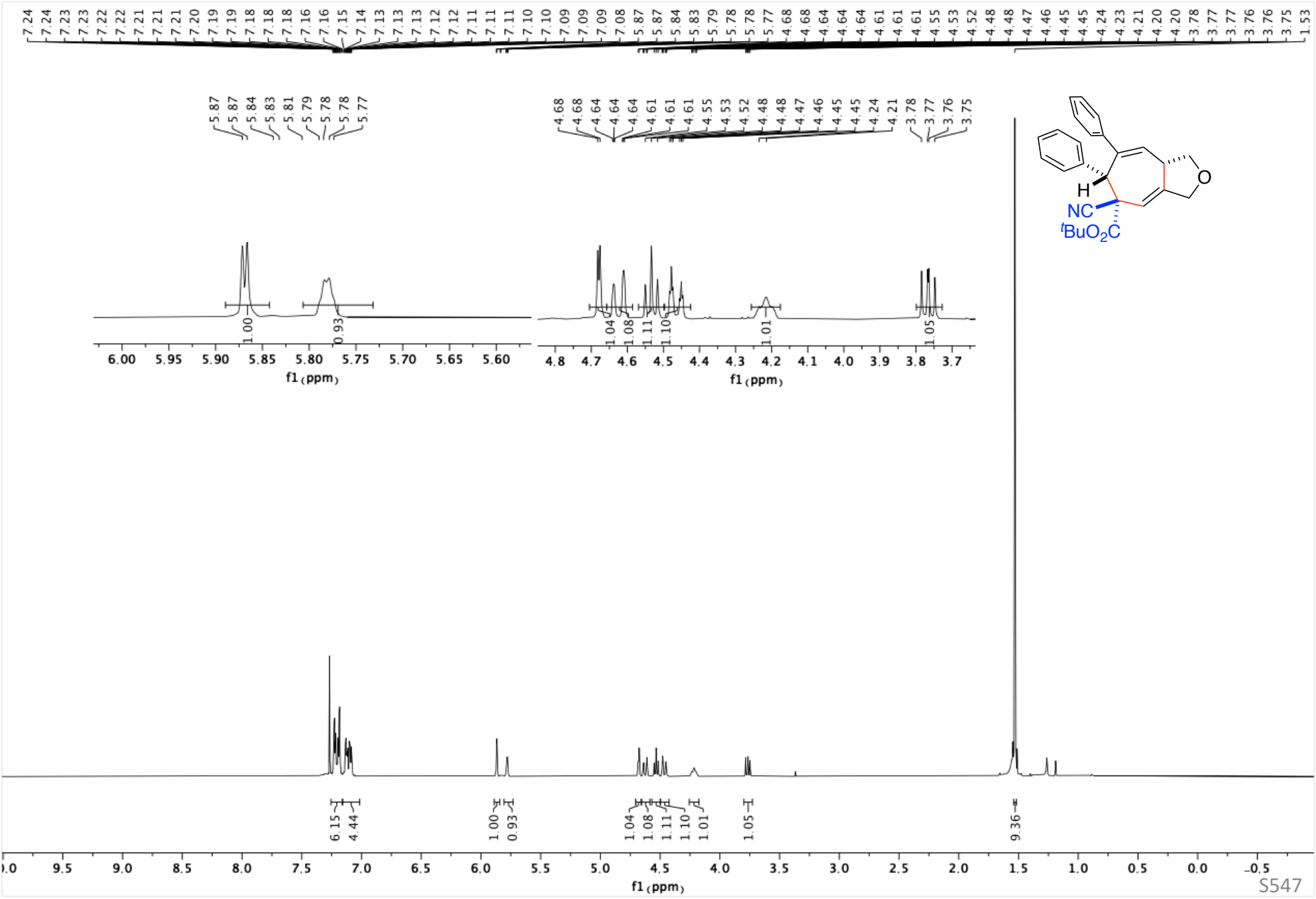
tert-Butyl (5*S*,8a*S*)-5-cyano-7-methyl-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



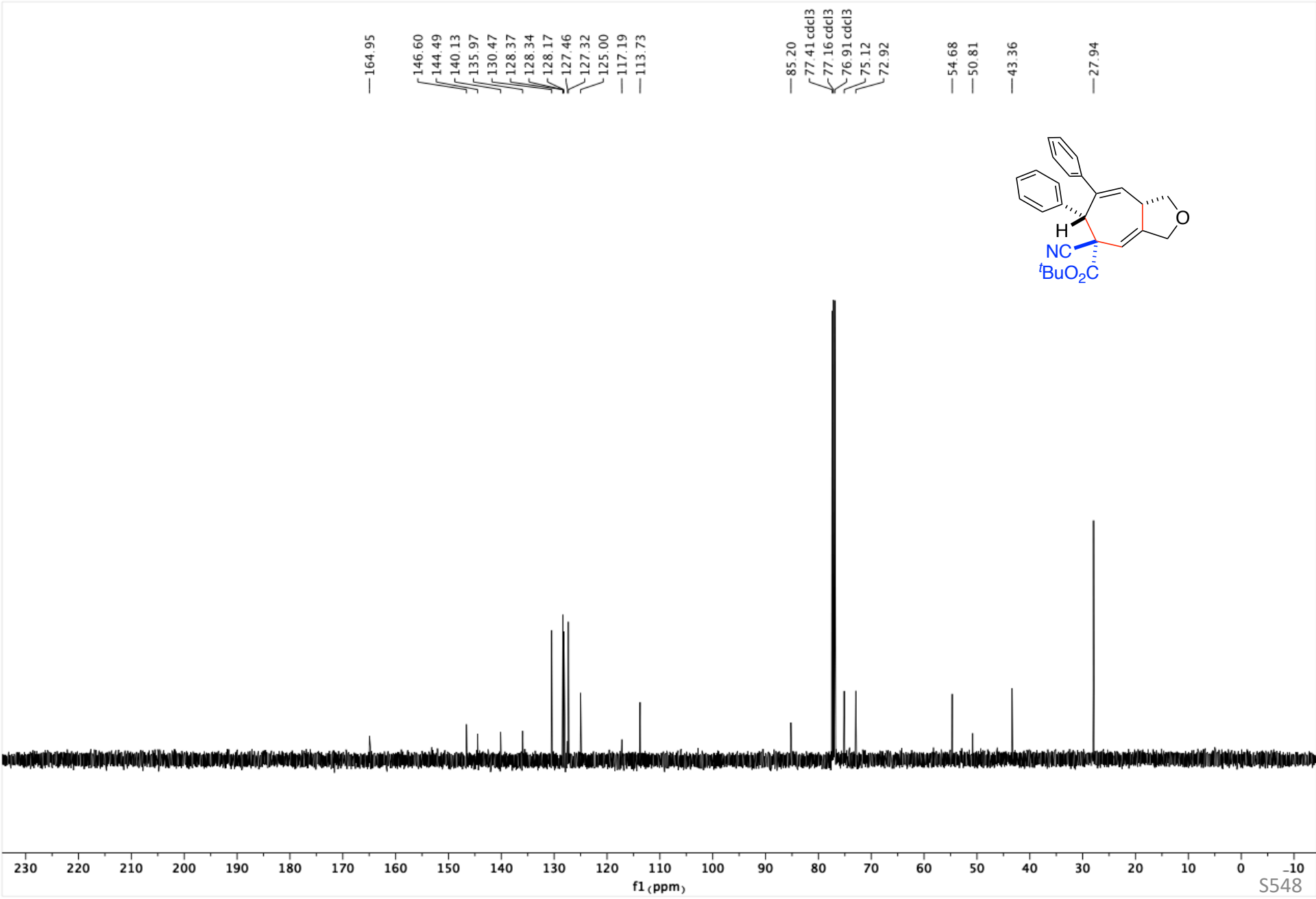
tert-Butyl (5_S_,8a_S_)-5-cyano-7-methyl-6-phenyl-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



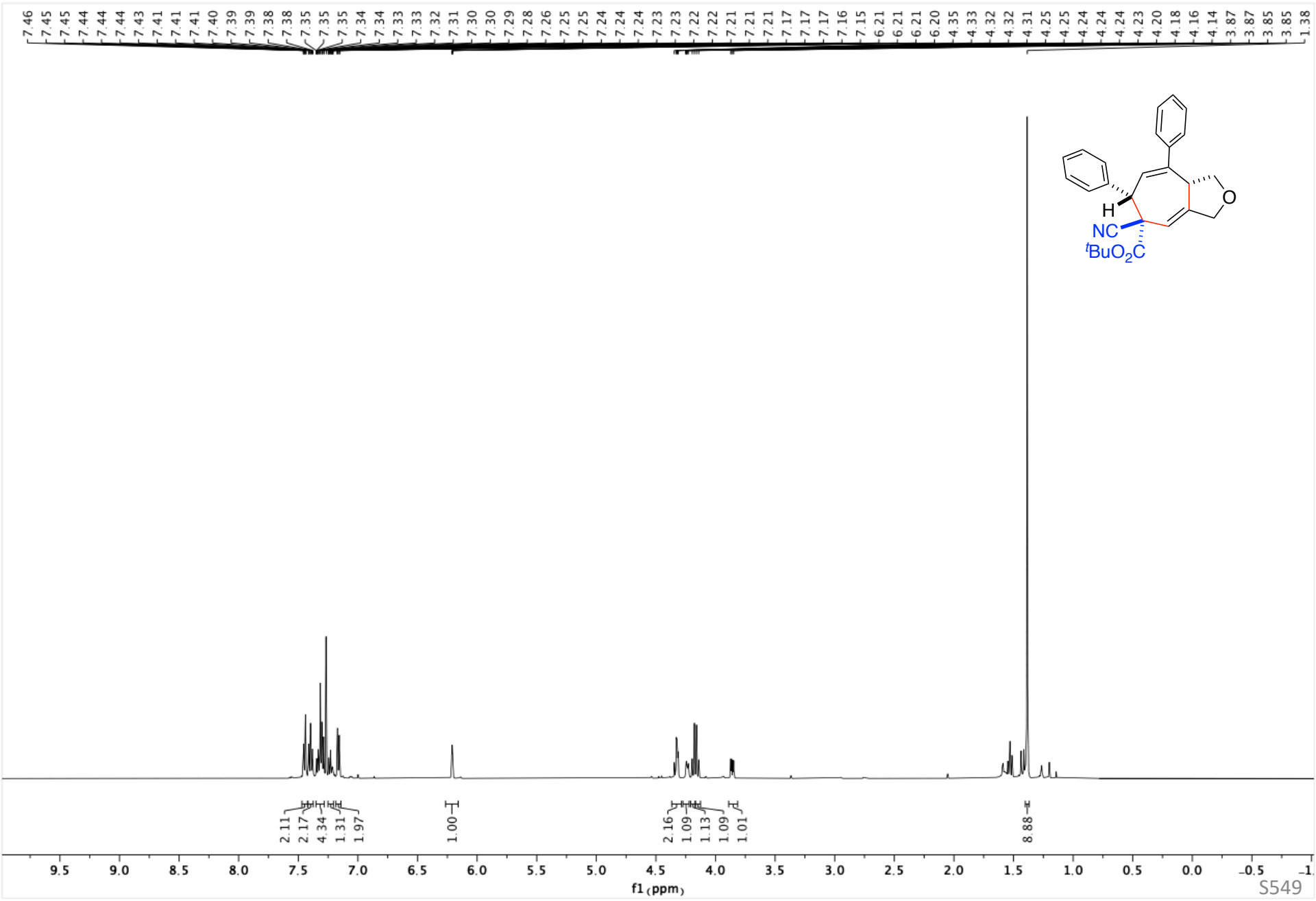
tert-Butyl (5*S*,8a*S*)-5-cyano-6,7-diphenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



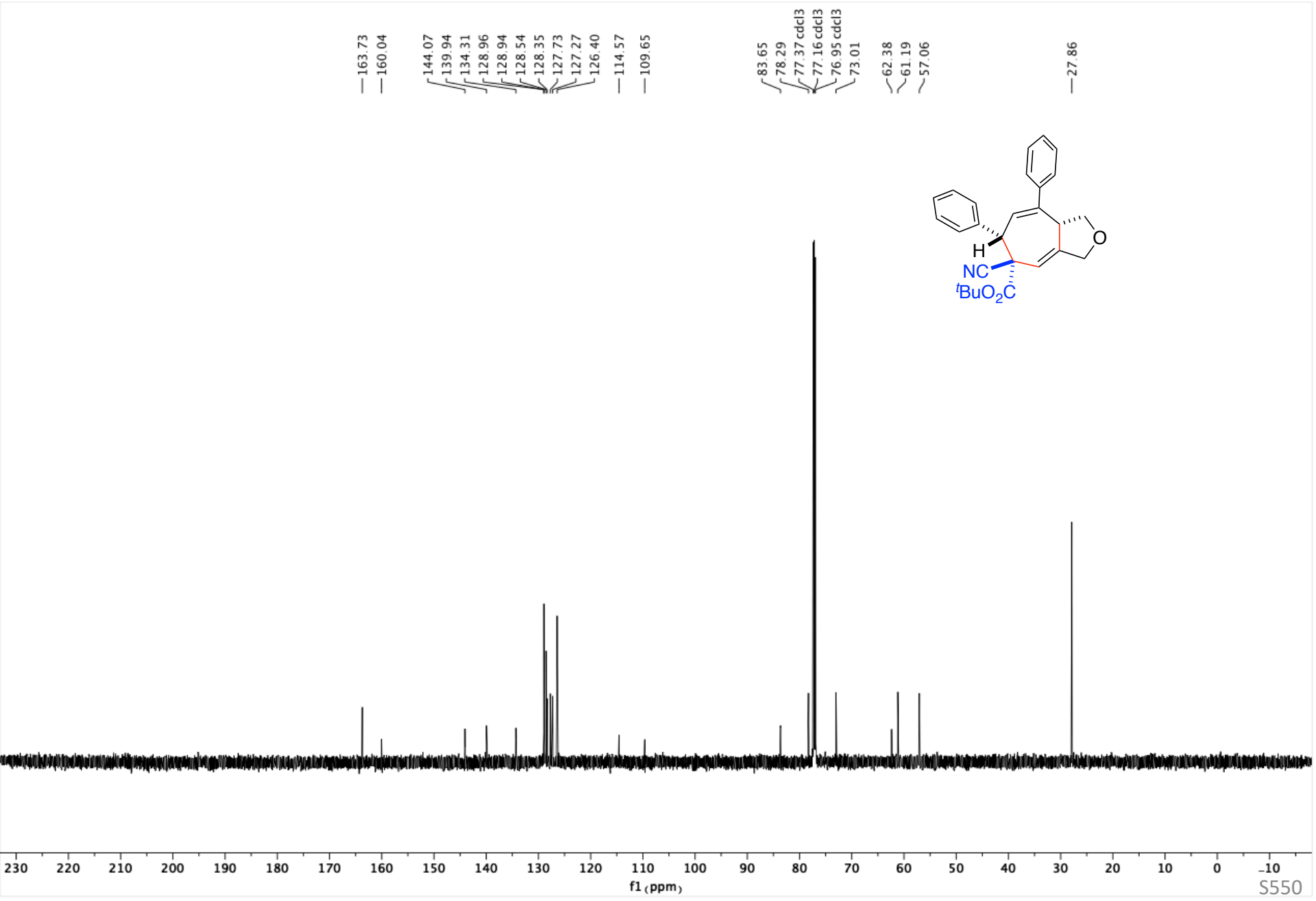
tert-Butyl (5_S_,8a_S_)-5-cyano-6,7-diphenyl-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



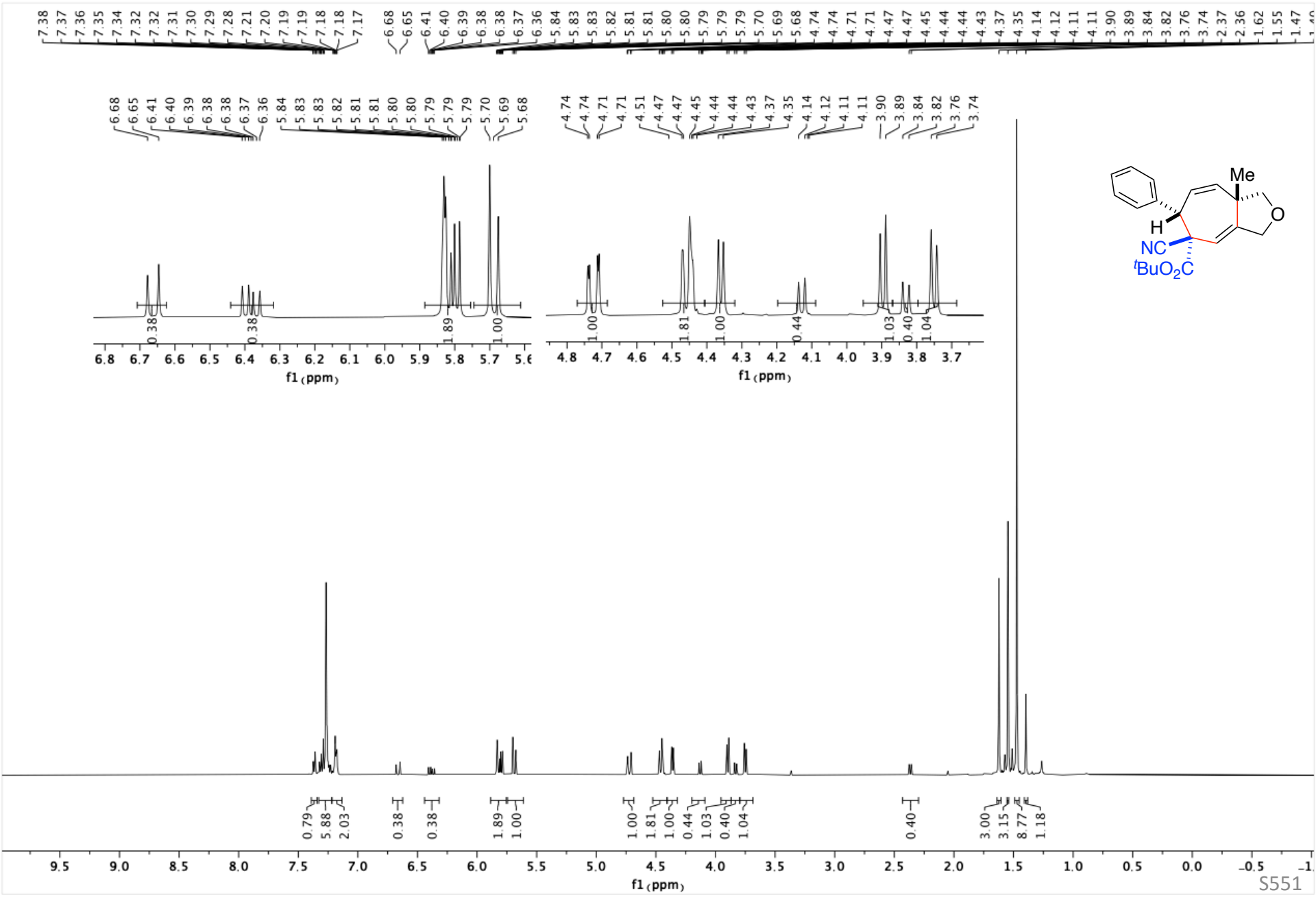
tert-Butyl (5*S*,8a*S*)-5-cyano-6,8-diphenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



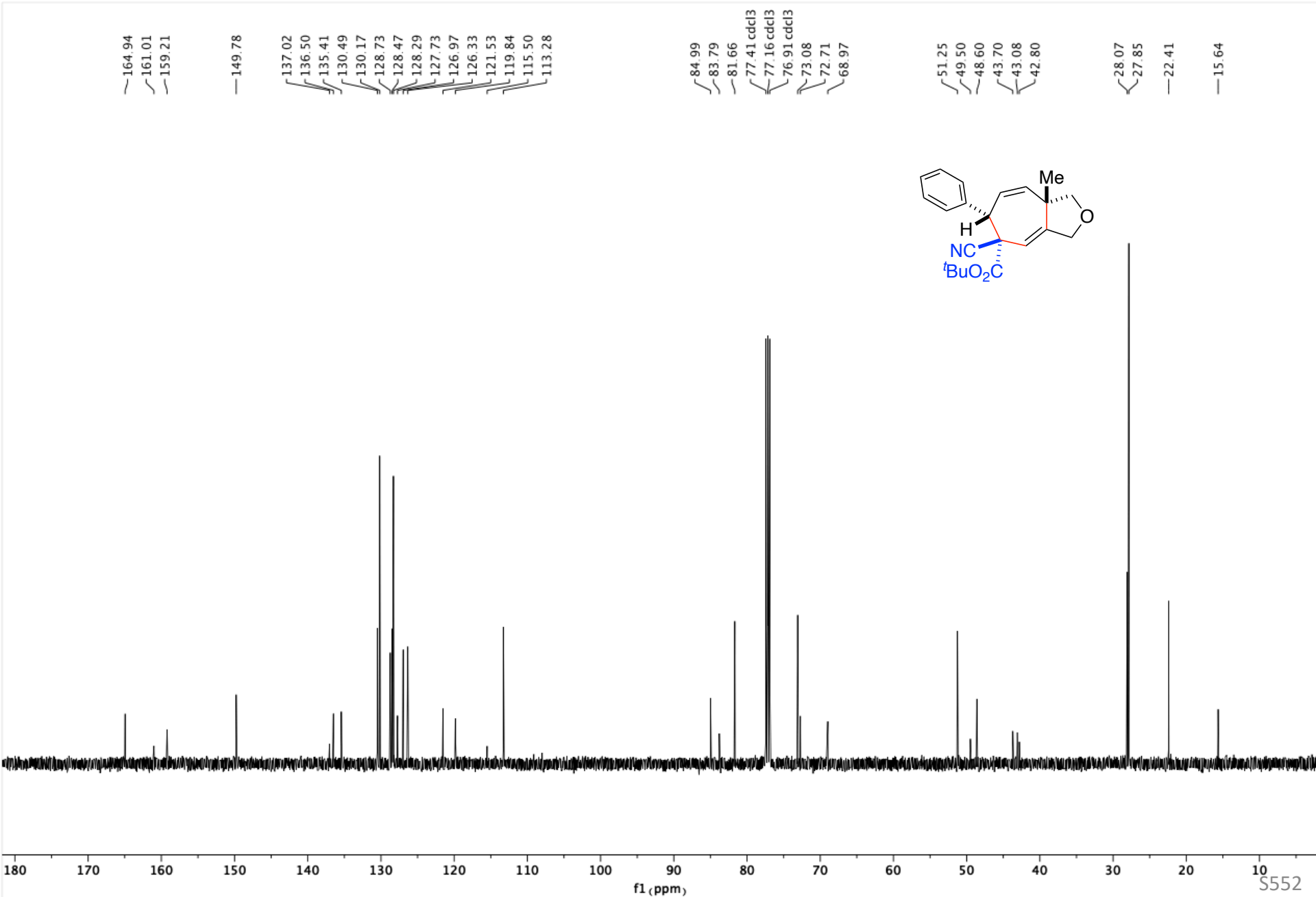
tert-Butyl (5*S*,8a*S*)-5-cyano-6,8-diphenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



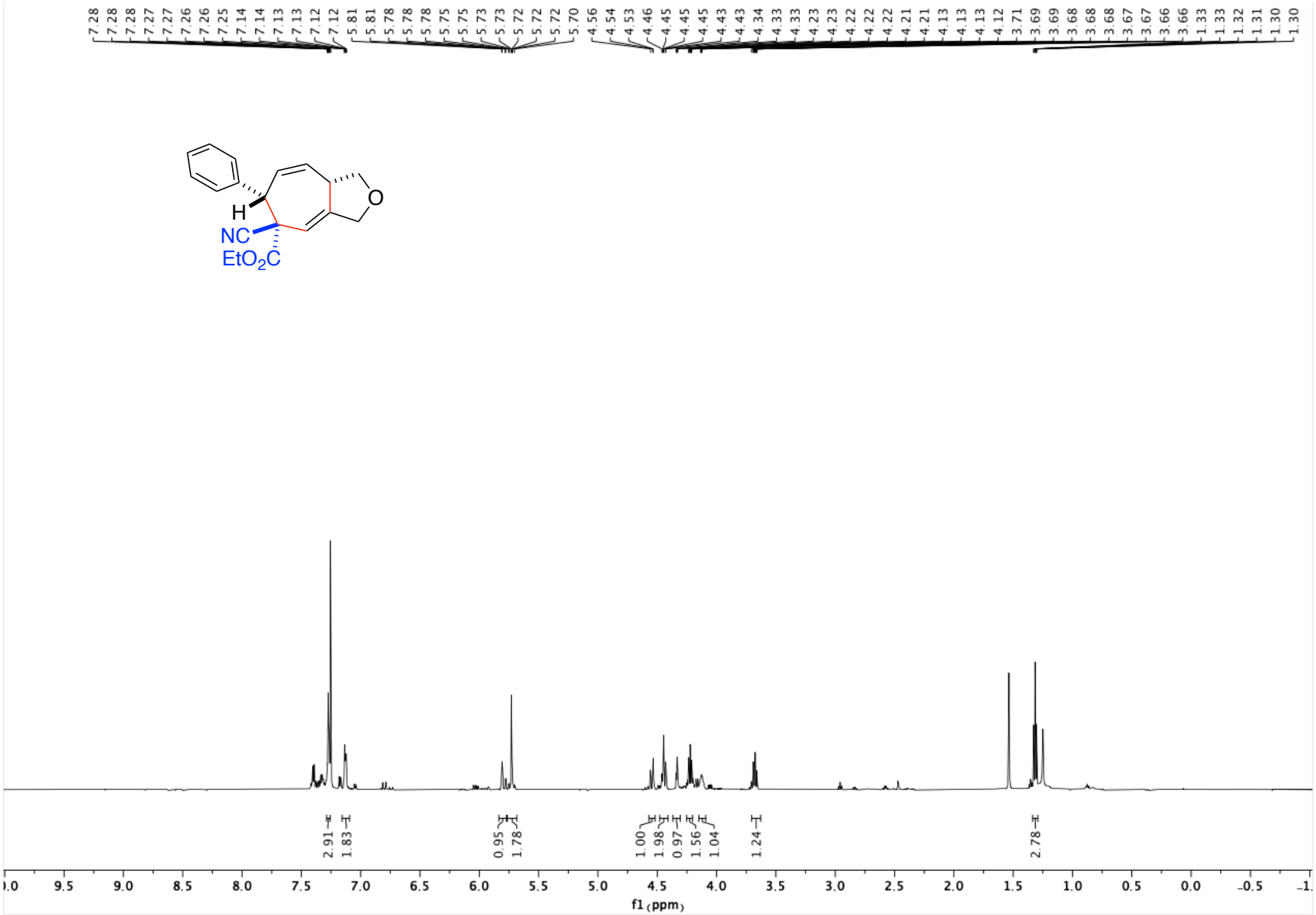
***tert*-Butyl (5*S*,8a*S*)-5-cyano-8a-methyl-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate**



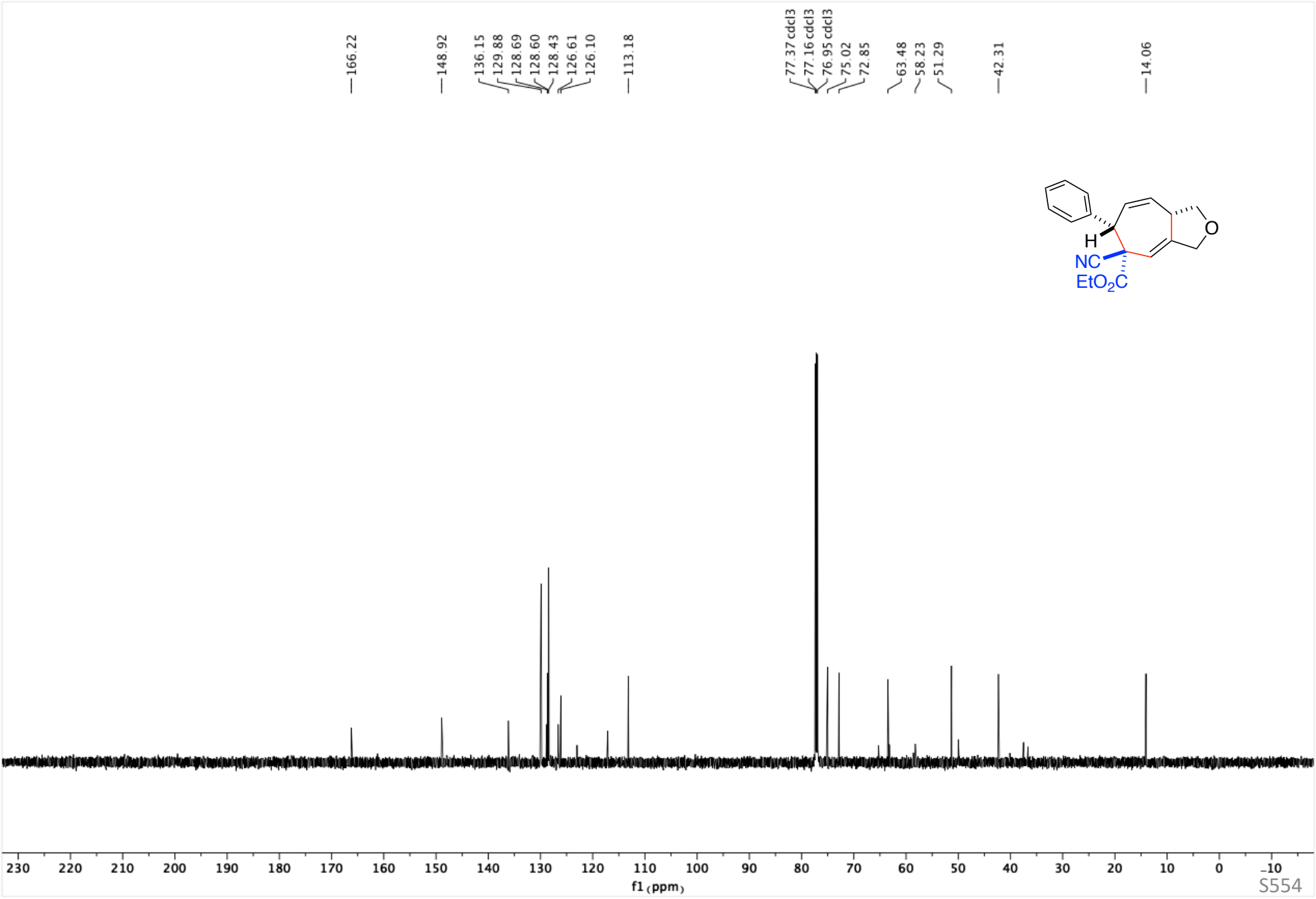
tert-Butyl (5_S_,8a_S_)-5-cyano-8a-methyl-6-phenyl-3,5,6,8a-tetrahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



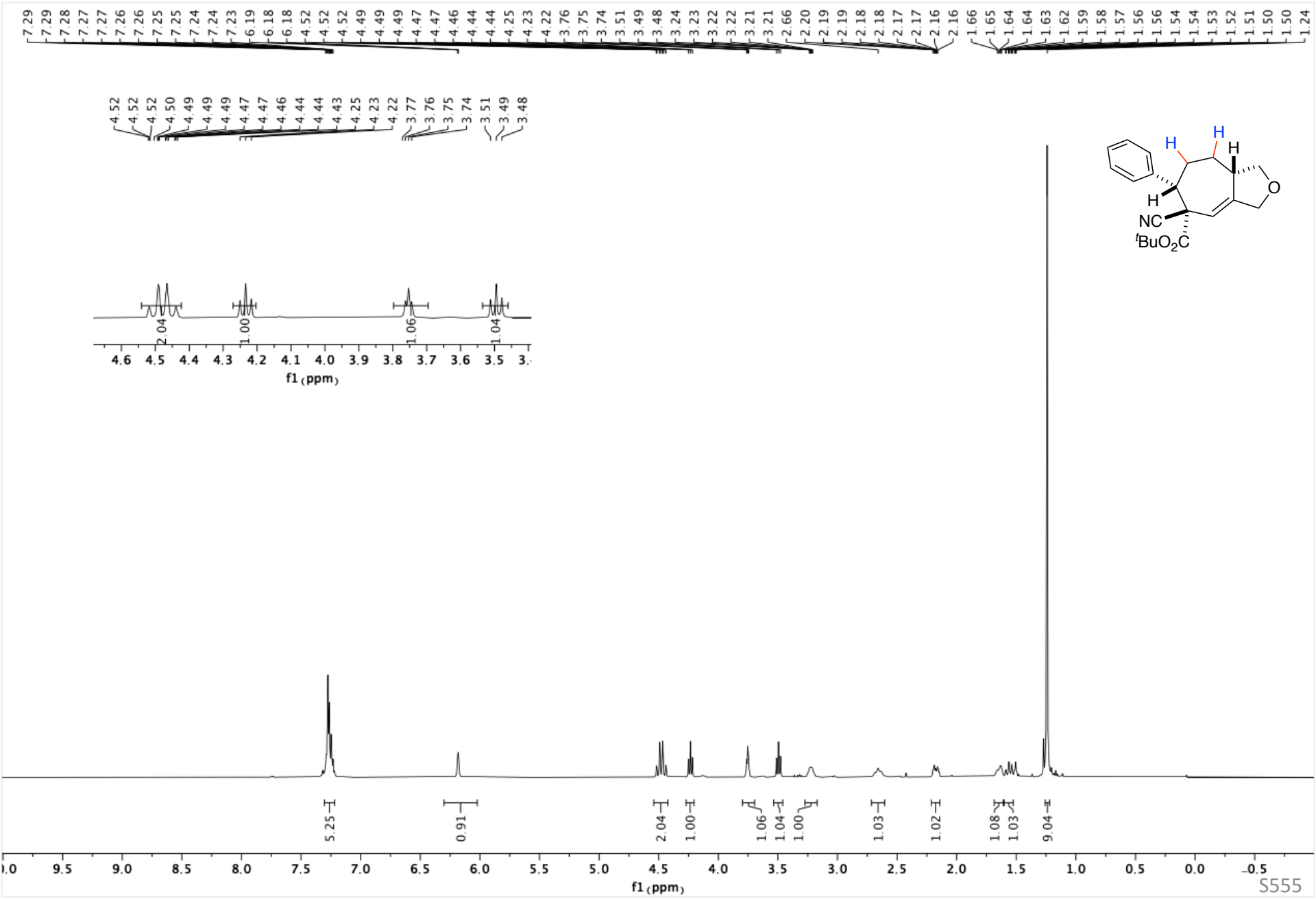
Ethyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



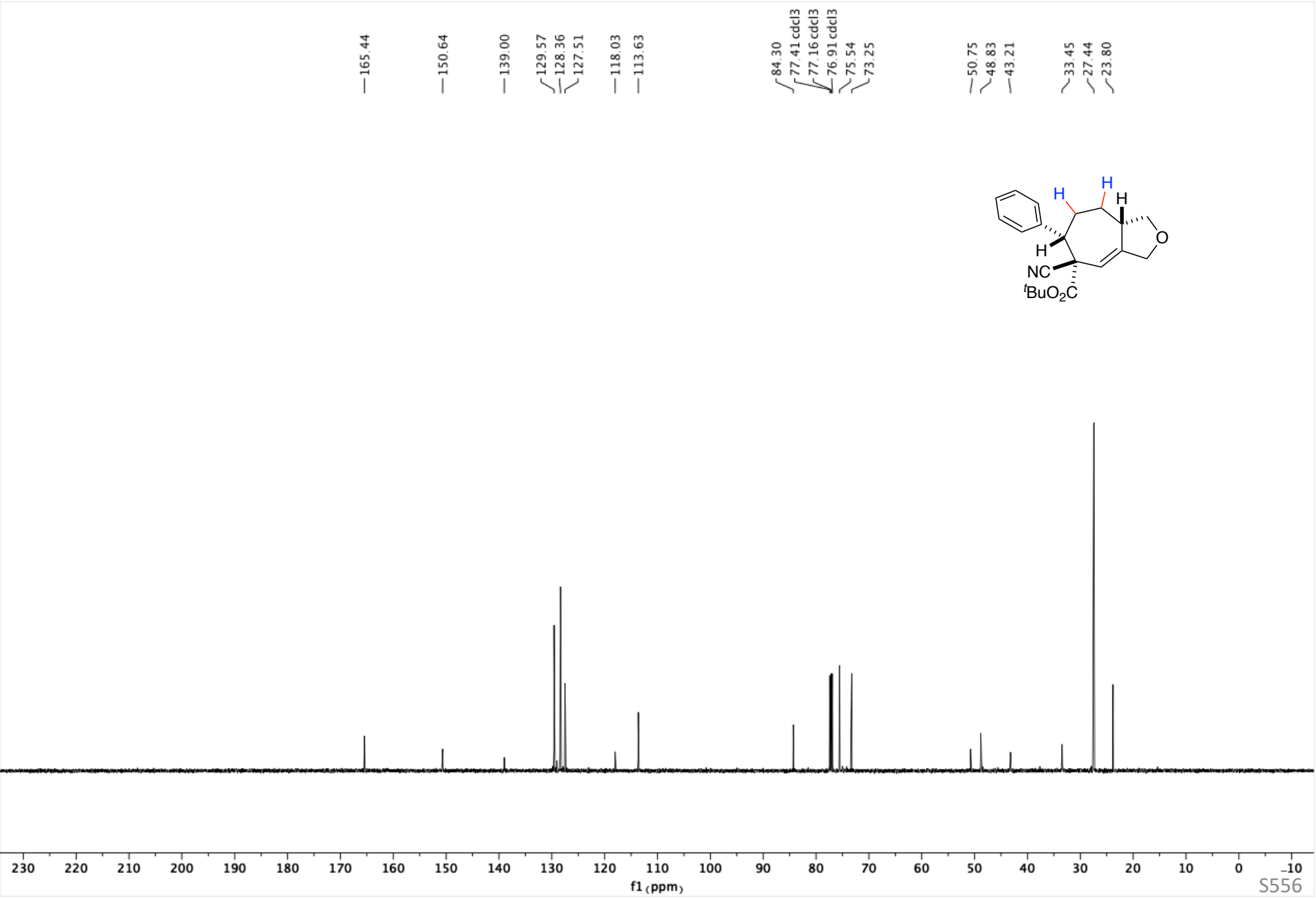
Ethyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



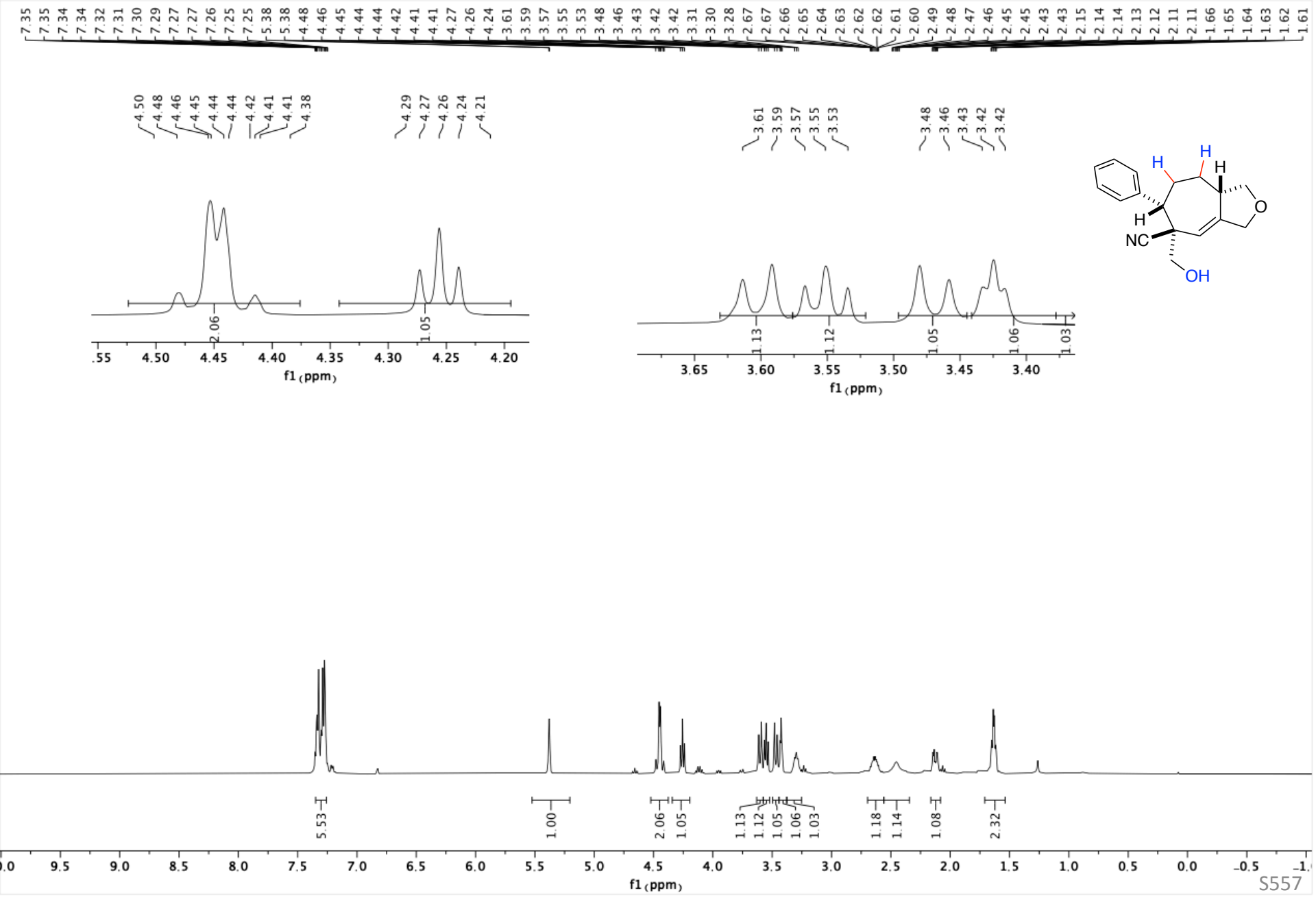
tert-Butyl (5*S*,8a*S*)-5-cyano-6-phenyl-3,5,6,7,8,8a-hexahydro-1*H*-cyclohepta[*c*]furan-5-carboxylate



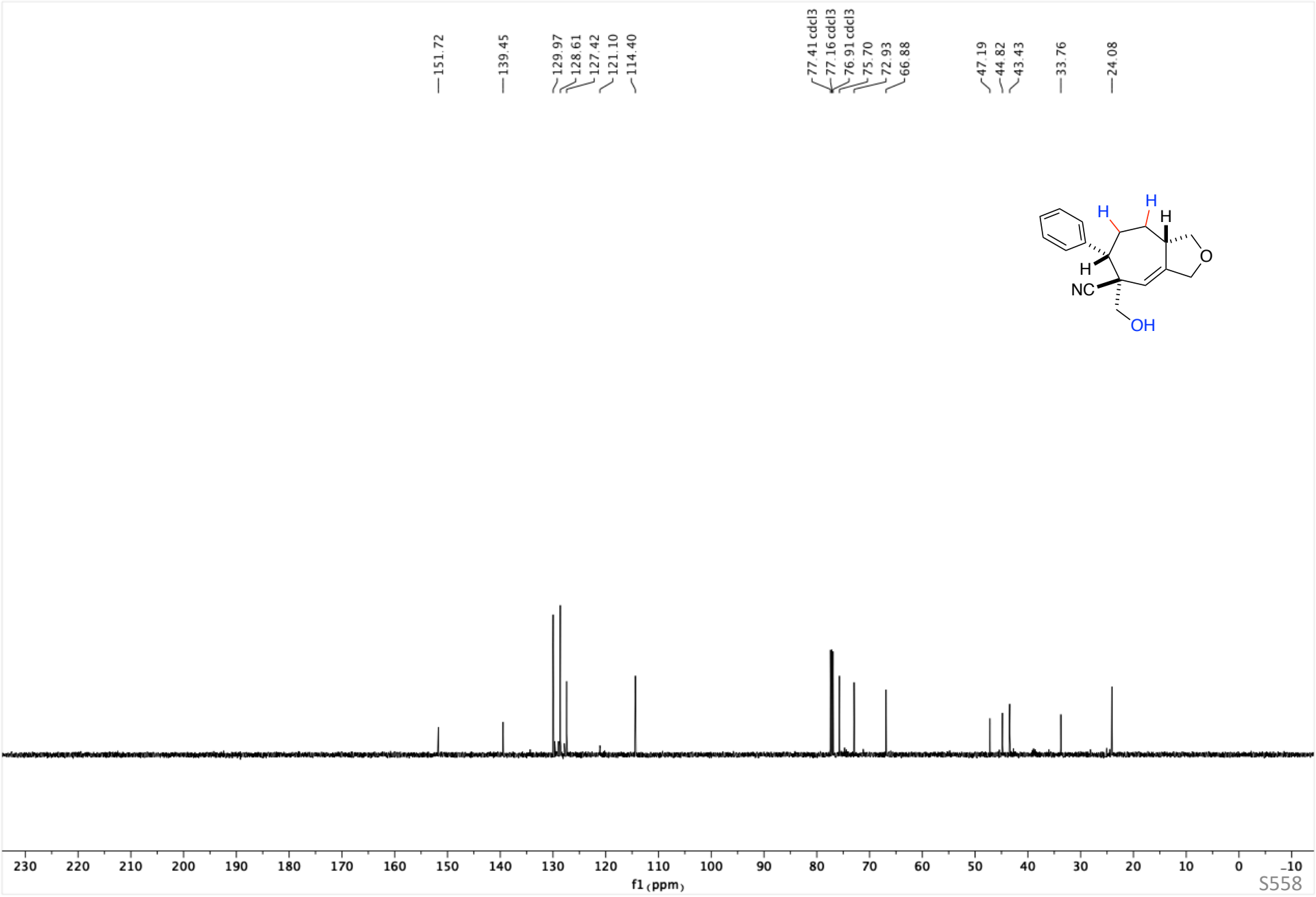
tert-Butyl (5_S_,8a_S_)-5-cyano-6-phenyl-3,5,6,7,8,8a-hexahydro-1_H_-cyclohepta[_c_]furan-5-carboxylate



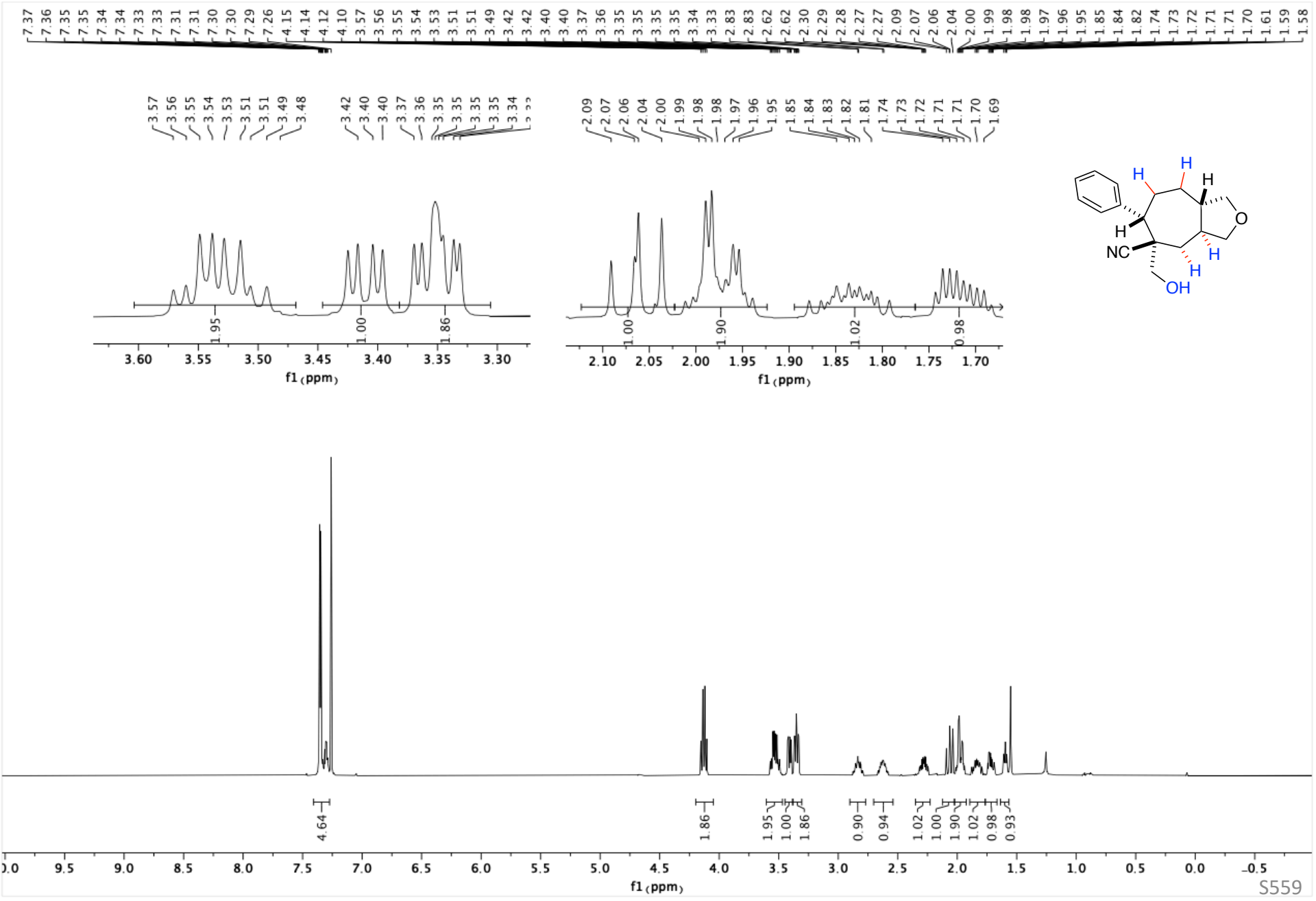
(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyl-3,5,6,7,8,8a-hexahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile



(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyl-3,5,6,7,8,8a-hexahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile



(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyloctahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile



(5*S*,8a*S*)-5-(Hydroxymethyl)-6-phenyloctahydro-1*H*-cyclohepta[*c*]furan-5-carbonitrile

