MAIN GROUP LEWIS ACID CATALYZED FUNCTIONALIZATION OF 1,3-DIENES AND OTHER UNSATURATED COMPOUNDS

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by

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2018CYZ0005

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY ROPAR

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Gautam Kumar

Main Group Lewis Acid Catalyzed Functionalization of 1,3-dienes and Other Unsaturated Compounds

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Dedicated

to

My Mother

and

Memory of My Father

DECLARATION

I declare that this work entitled "**Main Group Lewis Acid Catalyzed Functionalization of 1,3-dienes and Other Unsaturated Compounds**" has not previously been accepted in substance for any degree and is not being simultaneously submitted in candidature for any other degree. This thesis is being submitted in partial fulfilment of the requirements for the degree of PhD in Chemistry. This thesis is the result of my own independent investigation, except where otherwise stated. I have acknowledged all the other sources by stating the references explicitly. I declare that any idea/data/fact/source stated in my thesis has not been fabricated/falsified/misrepresented. All the principles of academic honesty and integrity have been followed. I understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed. I hereby give consent for my thesis, if accepted, to be available online in the Institute's Open Access repository and for inter-library loan, and for the title and abstract to be made available to outside organizations.

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Gautam Kumar

CERTIFICATE

It is certified that the work contained in the thesis titled "**Main Group Lewis Acid Catalyzed Functionalization of 1,3-dienes and Other Unsaturated Compounds**" by **Gautam Kumar**" has been carried out under my/our supervision and that this work has not been submitted elsewhere for the award of any degree.

Signature of the Supervisor

Dr. Indranil Chatterjee

Department of Chemistry

IIT Ropar

LAY SUMMARY

In chapter 1, a thorough introductory discussion about the current work status and prior literature reports was carried out. This review process also provided the motivation to conduct the research program.

In chapter 2, a main group Lewis acid tris(pentaflurophenyl)borane was used for the synthesis of highly important classes of organic molecules such as primary and secondary allylic sulfides by reacting 1,3-dienes and thiol derivatives under transition-metal-free condition.

In chapter 3, we have depicted a mild method for the *para*-C–H bond functionalization of arylamines using main group Lewis acid tris(pentaflurophenyl)borane as catalyst.

In chapter 4, we have synthesized *β*-aminoacrylonitrile derivatives using main group Lewis acid catalysts from alkyne and arylamines with *N*-cyanosuccinimide.

In chapter 5, the novel combination of 1,3-benzodioxole and residual moisture is explored for hydrogenation of alkenes using $InBr_3$.

ABSTRACT

One of the main focuses of the present thesis is to carry out functionalization of various unsaturated C–C bonds under main group Lewis acids catalysis.

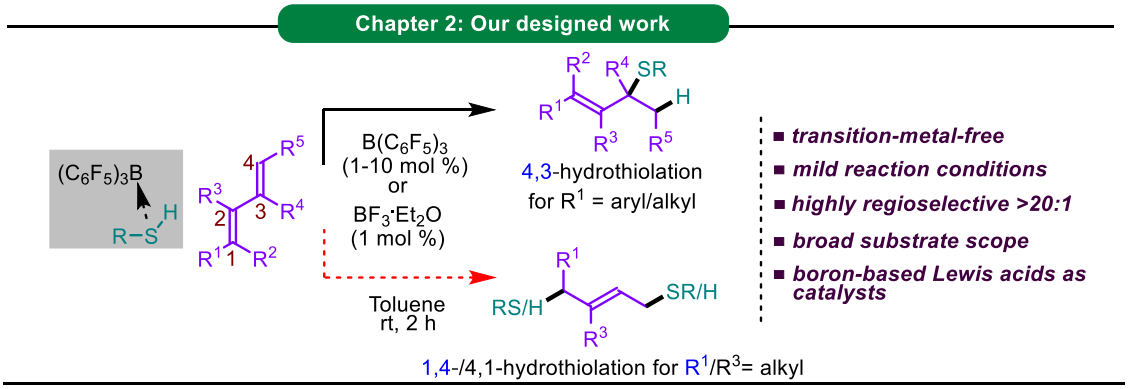
Keywords: Main Group Lewis acids; 1,3-dienes; transition-metal-free; hydrothiolation; hydroarylation; alkynes; aminocyanation; olefins; hydrogenation.

Chapter 1: Introduction

To pursue the above thought process, a detailed literature studies as well as vigorous surveys of previous reports on main group Lewis acid ($B(C_6F_5)_3$ and $InBr_3$)-catalyzed functionalization of unsaturated compounds was carried out in chapter 1, introduction part. The electron deficiency often leads to particular chemical reactions via the activation of several functional groups and unsaturated π-bonds. For example, several unsaturated bonds such as alkene, alkynes, conjugated dienes, allenes, and crucial functional groups, e.g., thiols, alcohols, carbonyl, halide, imines, etc., can be successfully activated by Lewis acids for further concomitant reactivity. $B(C_6F_5)_3$ and $InBr_3$ have played a significant role in the formation of several C–heteroatom and C–C bonds formation via the activation of electron-rich sites of the substrate partners.

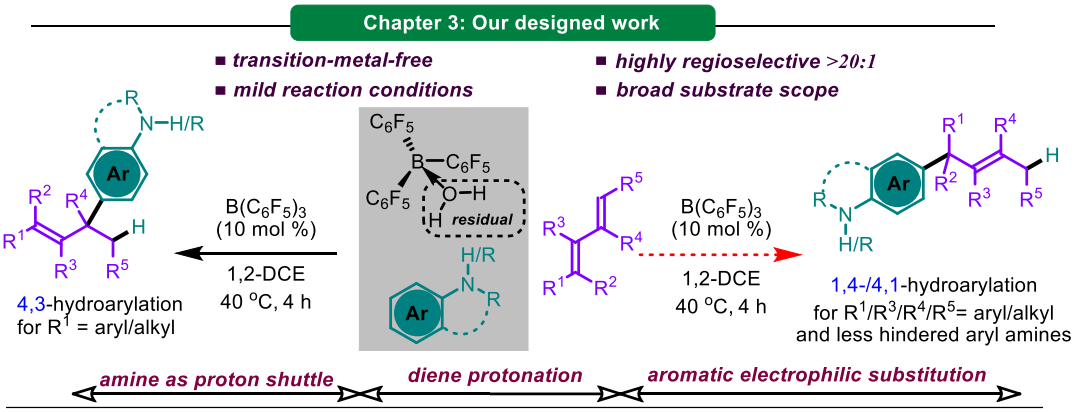
Chapter 2: Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated 1,3-Dienes with Thiols

In this chapter, we have exploited the transition-metal-free boron Lewis acids $B(C_6F_5)_3$, and $BF_3{\cdot}Et_2O$ catalyzed regioselective hydrothiolation of 1,3-dienes. Here synthesis of allylic sulfides is discussed by hydrothiolation of 1,3-dienes. The boron Lewis acids provded high 1,4-regioselectivity for a wide range of terminal 1-aryl-1,3-dienes. However, in the case of internal 1,3-dienes $B(C_6F_5)_3$ remains the superior catalyst because $BF_3{\cdot}Et_2O$ was unable to catalyze the hydrothiolation of highly substituted 1,3-dienes. The reaction conditions are milder, with a broad substrate scope of up to 35 examples. Also, the low catalyst loading and quick scalability make this methodology a prominent tool for allyl sulfide synthesis within 2 h. The extensive DFT calculations revealed that the protonation of 1,3-dienes with thiol-boron Lewis acid complexes is the rate-limiting step. The sulfide anion transfer to the resultant allyl cations furnishes the regioselective hydrothiolated products.



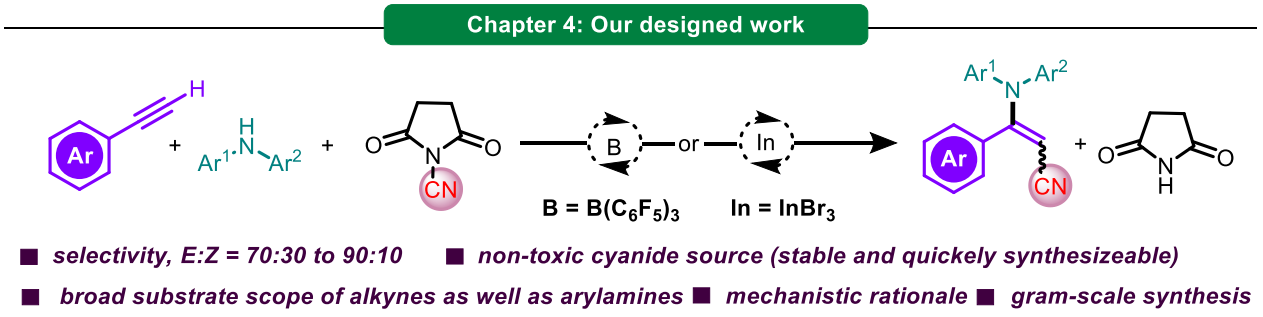
Chapter 3: Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines

In this chapter, we have represented tris(pentafluorophenyl)borane, $B(C_6F_5)_3$-catalyzed regioselective hydroarylation of 1,3-dienes with arylamines arylamine derivatives. This new protocol shows broad substrate scope for the highly regioselective functionalization of sterically hindered aniline derivatives. Experimental and extensive DFT mechanistic studies show that the complex of residual water and $B(C_6F_5)_3$ plays a crucial role in the aryl-assisted protonation of conjugated dienes, forming allyl cation intermediates that induce facile electrophilic aromatic substitution of aniline substrates.



Chapter 4: Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and *N*-cyanosuccinimide

In this chapter, a transition-metal-free aminocyanation of aryl alkynes has been achieved using indium tribromide ($InBr_3$) or $B(C_6F_5)_3$ as a Lewis acid. This aminocyanation protocol features with non-toxic cyanide source, a good substrate scope and valuable aminocyanation products. Mechanistic studies reveal the complex formation between Lewis acid and alkyne to produce *in situ* alkyne nitrile as a key intermediate. Further hydroamination of alkyne nitrile with arylamines affords the *E*-selective (majorly) *β*-aminoacrylonitrile derivatives.

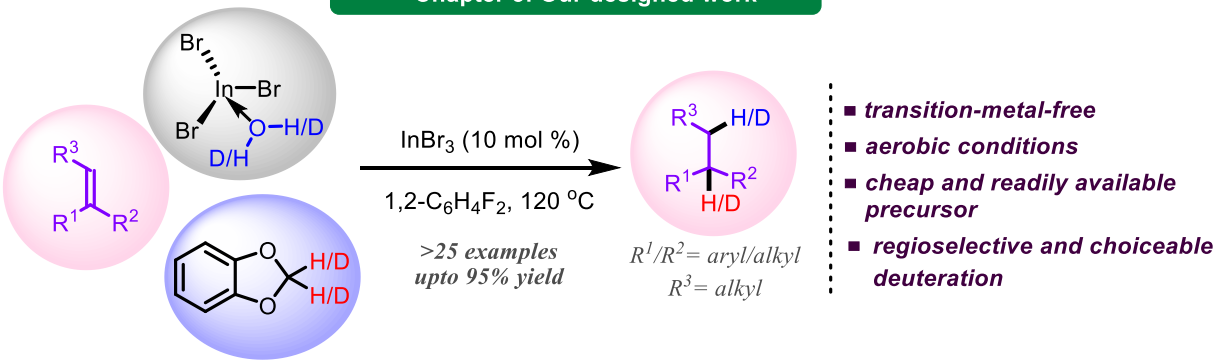


Chapter 5: Transition-metal-free Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins

In this last chapter, a unique and valuable methodology is developed for the hydrogenation of aromatic as well as aliphatic 1,1-di- and trisubstituted alkenes. In the presence of catalytic $InBr_3$, readily available 1,3-Benzodioxole and residual H_2O presents in the reaction mixture are utilized as a

hydrogen gas surrogate and proved to be a practical source of deuterium incorporation into the olefins on either side by varying the source of the deuterated starting 1,3-Benzodioxole or D_2O. Experimental studies show the transfer of hydride from 1,3-Benzodioxole to the carbocationic intermediate generated from the protonation of alkenes by H_2O–$InBr_3$ adduct is the critical step.

Chapter 5: Our designed work



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8. **Kumar, G.;** Bhattacharya, D.; Mistry, P.; Chatterjee, I. In-Catalyzed Transfer Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins. *J. Org. Chem.* **2023**, DOI:10.1021/acs.joc.3c00272.

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NOTATIONS AND ABBREVIATIONS

Ac	acetyl
ACN/MeCN	acetonitrile
aq	aqueous
atm	atmospheric
BINOL	1,1′-binaphthalene-2,2′-diol
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
brs	broad singlet
^{n}Bu	butyl
^{t}Bu	*tert*-butyl
calcd	calculated
CPA	chiral phosphoric acid
Cy	cyclohexyl
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
dd	doublet of a doublet
DKR	dynamic kinetic resolution
DMAP	4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	*N,N'*-dimethyl formamide
DMSO	dimethyl sulfoxide
dq	doublet of a quartet
dr	diastereomeric ratio
dt	doublet of a triplet
ee	enantiomeric excess
equiv	equivalents
ESI	electron spray ionization
FT-IR	Fourier-transform infrared spectroscopy
Gem	geminal
h	hour(s)
HFIP	1,1,1,3,3,3-hexafluoroisopropanol
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrum
Hz	Hertz
IBX	2-iodoxybenzoic acid
J	coupling constant
LDA	lithium diisopropylamide

m	multiplet
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mmol	millimole(s)
M.P	melting point
MS	molecular sieves
m/z	mass/charge
NMF	N-methylformamide
NMR	Nuclear Magnetic Resonance
ppm	parts per million
^{n}Pr	*n*-propyl
^{i}Pr	isopropyl
p-TSA	*para*-toluenesulfonic acid
q	quartet
rt	room temperature
s	singlet
sept	septet
t	triplet
td	triplet of a doublet
tert	tertiary
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
TMS	trimethylsilyl
TLC	thin layer chromatography

Chapter 1

Introduction

1. Introduction

1.1 Main Group Lewis Acid Mediated Functionalization of Unsaturated Compounds

Exploitation of Lewis Acids for the Construction of C–heteroatom and C–C bonds: The functionalization of unsaturated hydrocarbons *viz.* 1,3-dienes, alkynes, alkenes, and allenes, can be done using several methods available in the sea of literature.[1] These unsaturated hydrocarbons contains π-electron cloud which can be easily polarized using transition-metal catalysts,[2] Lewis acids,[3] or Brønsted acid catalysts[4] etc. Among all these systems, transitions metal catalysts are extensively studied for the functionalization of unsaturated hydrocarbon compounds. With the great potential of catalysis, transition-metal catalysis also associated with various shortcomings for example, including high cost for catalyst preparation, toxicity, not environmentally benign and sophisticated handling techniques.[5] An alternative method, if therefore highly desirable to solve the potential challenges associated with transition-metal catalysis.[6] However, main-group Lewis acids have the caliber to overcome most of the drawbacks of transition-metal catalysts.[7]

The main-group-based Lewis acid compounds are the game changer and play an important role in the functionalization of unsaturated compounds. In 1923, Pof. G. N. Lewis coined the term "*Lewis acidity*" for the first time when he observed the electron-pair donation and acceptance ability of some compounds called as Lewis base and Lewis acid respectively (Figure 1-a).[8] When Lewis acid and base interact each other in a system, they form classic Lewis-pair or Lewis acid-base adduct which is eventually coordinated with dative bond (Figure 1-b). However, if the Lewis acid and base possess steric congestion, which can prohibit them to form a classic Lewis acid-base pair, but both can come closer up to a specific space called the frustrated Lewis pairs (FLPs) (Figure 1-c).[9]

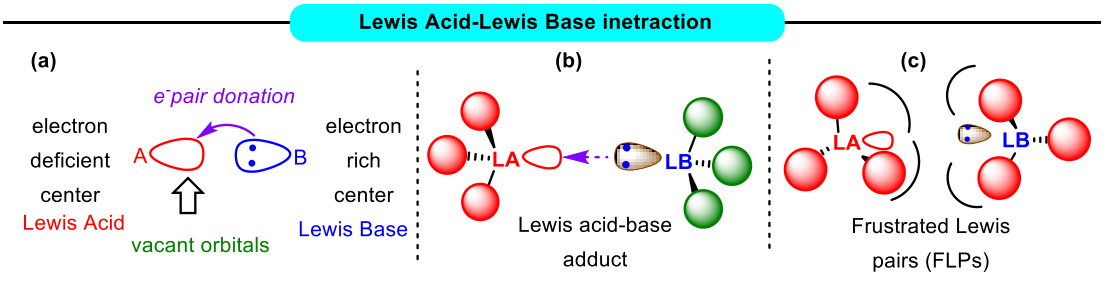


Figure 1: Lewis Acid-Lewis Base Interaction

The electron-deficient nature of Lewis acids is responsible for the functionalization of unsaturated hydrocarbons. These Lewis acids effortlessly interact with electron-rich site of the reaction substrates and activate them for nucleophilic attack. For example, if the substrate molecule contains a heteroatom having free lone pair of electrons, then Lewis acids coordinate with these electron pairs and form a σ-complex. Such types of Lewis acids are known as σ–electrophilic Lewis acids (Figure 2-a). Whereas, the coordination with π-electron cloud form a

π-complex and such Lewis acids are abbreviated as σ–electrophilic Lewis acids (Figure 2-b). Moreover, if there is any unsaturated hydrocarbon or unsaturated hydrocarbon along with heteroatoms in the reaction substrates, then Lewis acids can interact with the π-/σ- or both π- and σ-electron density (dual interaction) and form polarized intermediate (Figure 2-c). These intermediates are accountable for transformation of reaction partners to useful derivatives with new C–C and C–heteroatom bonds.[10]

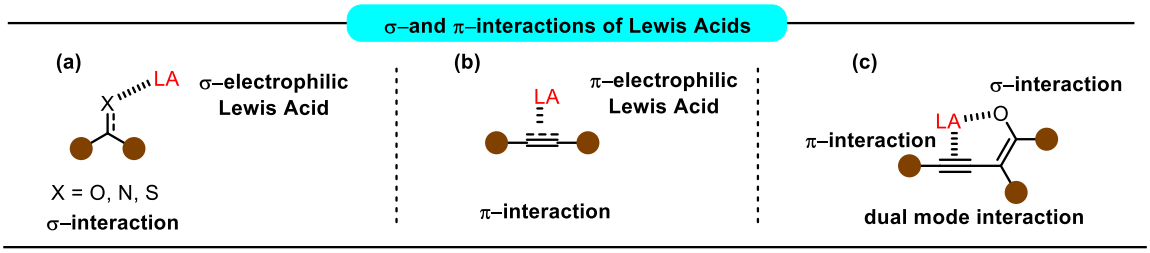


Figure 2: σ– and π–interactions of Lewis Acids

With great and incompatible properties of the entire main group based Lewis acids, we targeted only boron and indium based Lewis acids from group XIII elements in periodic table. Although, boron is very different from their rest of the family elements, like metalloid nature, low covalent and ionic radius and high melting point. Boron can be extracted from various ores present in the earth's crust but the most protrusive ore for the large-scale production of boron is borax ($Na_2B_4O_7$). Whereas, Indium is extracted as a side product of sulfidic zinc and sulfidic copper ores present in the earth's crust. The common outer shell electronic configuration of the boron family is ns^2, np^1. The halides and other compounds of group XIII elements possess empty orbitals acting as Lewis acids.[11]

1.2 Objectives

- Development of main group Lewis acid catalyzed methodologies.
- Exploration the catalytic reactivity of $B(C_6F_5)_3$ and $InBr_3$.
- Functionalization of 1,3-dienes for C−S/C−C bond formation via hydrothiolation/hydroarylation.
- Functionalization of alkynes via aminocyanation.
- Transfer hydrogenation of alkenes via $InBr_3$ catalysis.

1.3 Motivation and Scope

1.3.1 Boron and Indium based Lewis Acids, Their Reactivity

1.3.2 Boron Lewis Acids

The boron-based Lewis acids can be classified as boron halides and organo-boron compounds. The catalytic reactivity of boron Lewis acids for various C−heteroatom/C−C bond-forming reactions via the functionalization of unsaturated bonds has been extensively studied in the last few decades. We have exploited the catalytic reactions of organo-boron Lewis acid, e.g., tris(pentafluorophenyl)borane $B(C_6F_5)_3$, also abbreviated as BCF in short. $B(C_6F_5)_3$ was first

synthesized in 1963 by Massey and co-workers, but it remain unexplored in the territory of catalysis. In 1990s, Marks and co-workers utilized $B(C_6F_5)_3$ as a co-catalyst for the Zieglar-Natta polymerization of olefins with metallocenes.[12]

The $B(C_6F_5)_3$ is associated with trademark features as a) the Lewis acidity remains in between $BF_3{\cdot}Et_2O$ and BCl_3, b) it is thermally stable up to 270 ^oC, which provides compatibility for high-temperature reactions, c) the solubility in polar and non-polar solvents augments extra supremacy to perform the catalytic reactions in diverse solvents (Figure 3). [13]

The electron-withdrawing fluorine substitutions at aryl rings make B-center more electrons deficient so that this compound acts as a stronger Lewis acid. The $B(C_6F_5)_3$ acquired benefits in terms of handling and sensitivity, whereas the boron trihalides are highly volatile, which makes them difficult to handle. On the other hand boron trihalides are readily dissociated in presence of moisture because B−halogen bond is more prone towards hydrolysis. However, in the case of $B(C_6F_5)_3$, the B−C bonds are comparatively less cleavable by hydrolysis, which makes them an overwhelming candidate for various catalytic organic transformations in presence of moisture too.[13]

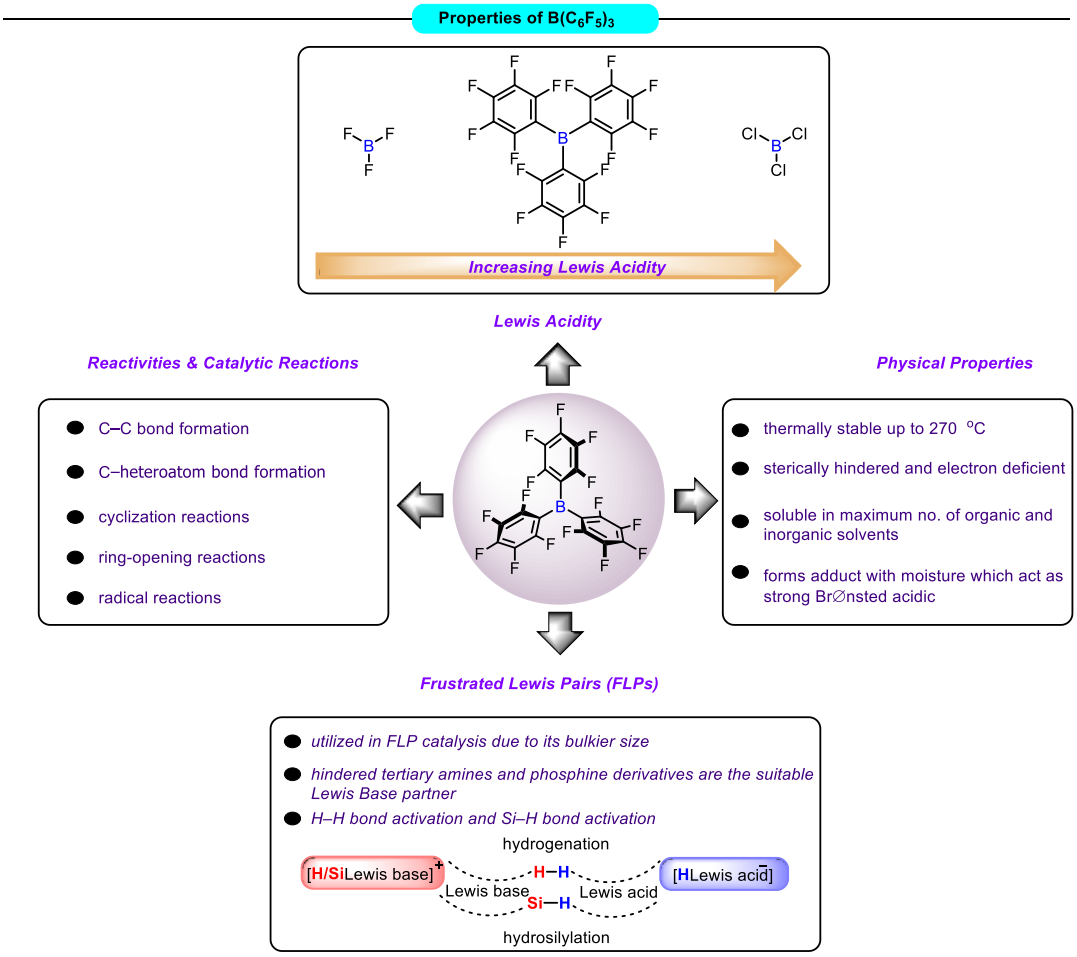


Figure 3: Exclusive Properties of Tris(pentafluorophenyl)borane

Tris(pentafluorophenyl)borane can be synthesized by the treatment of n-BuLi upon boron trihalides (BX_3) and 1-bromo-2,3,4,5,6-pentafluorobenzene (C_6F_5Br) **1**. This procedure requires -80 ^oC throughout the reaction because the C_6F_5Li **2** decomposes with paramount release of energy upon increase in reaction temperature. Another way to synthesize $B(C_6F_5)_3$ is by using Mg-Grignard (C_6F_5MgBr) **3** of C_6F_5Br **1** with boron trihalides (BX_3) (Figure 4). Both the procedures require high precautions to avoid $H_2O{\cdot}B(C_6F_5)_3$ adduct formation. Sublimation under reduced pressure and backfilled argon provides a nice white solid $B(C_6F_5)_3$ **4**, but to get high purity, the process of sublimation should be repeated for two to three times.[12a, 14]

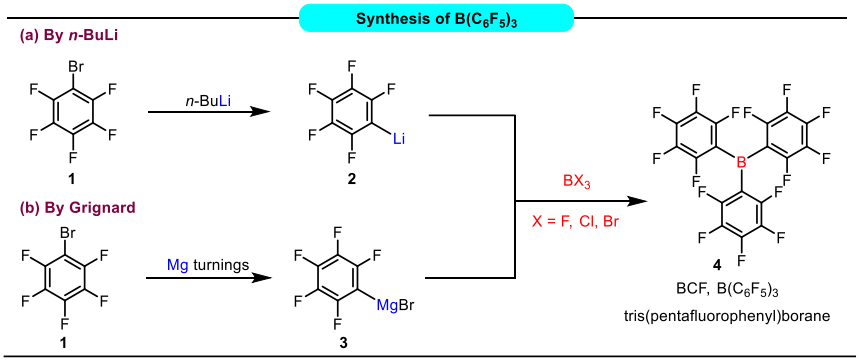


Figure 4: Synthesis of Tris(pentafluorophenyl)borane

1.3.3 Role of Tris(pentafluorophenyl)borane in Synthetic Organic Chemistry

In the arena of synthetic organic chemistry for the formation of C–heteroatom or C–C bonds, tris(pentafluorophenyl)borane has been extensively studied and applied for various novel methodology development. Owing to its strong Lewis acidity, $B(C_6F_5)_3$ has enabled to overcome several challenging transformations or reduced reaction steps to improve the economic factor. The abundant number of functional groups such as carbonyl, aldehyde, imines, C–F bonds, epoxide, alcohol, alkene, alkynes, allenes, etc., can be easily activated via FLPs or σ– and π–interaction with $B(C_6F_5)_3$ to accomplish novel methodologies (Figure 5).[13]

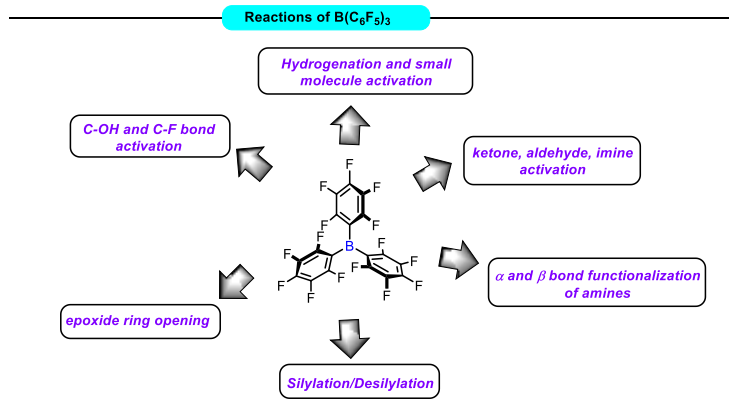


Figure 5: Functional Group Activation by $B(C_6F_5)_3$

1.3.4 Role of $B(C_6F_5)_3$ in functionalization of unsaturated bond

The easy synthesis of C–C unsaturated moieties has attracted ample attention of scientists for functionalizing them to construct new bonds. The reactivity of $B(C_6F_5)_3$ to functionalize C–C

unsaturated bonds are extensively studied in the literature through FLPs (associated with molecular congestion and high Lewis acidity) or σ– and π–interaction (associated with high Lewis acidity).

Reactivities of $B(C_6F_5)_3$-mediated FLPs: Here we would like to include a brief introduction of FLPs using $B(C_6F_5)_3$ with different base partner species (P–, N–, O–center). The energy level mismatch between LUMO of Lewis acid (acceptor) and HOMO of Lewis bases (donor) precludes the dative bond formation and produce FLP. Depending on the position of the donor and acceptor, they can be divided into two categories, a) if both are present in a single molecule, then it will be intramolecular FLPs; b) if both remain as a separate molecule, then it is intermolecular FLPs (Figure 6).[9, 15]

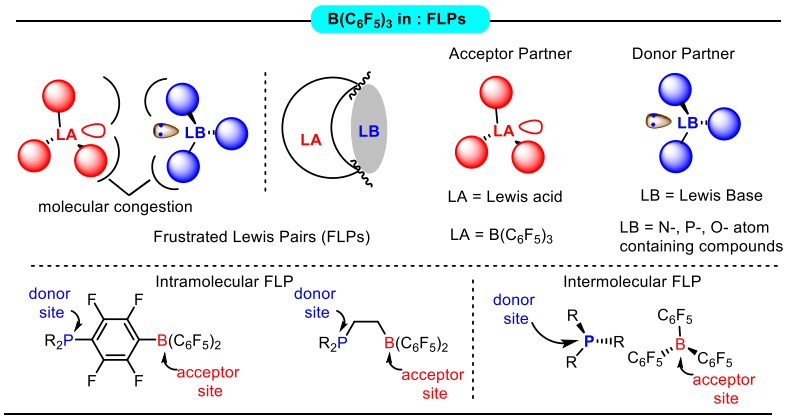


Figure 6: $B(C_6F_5)_3$-based FLPs Intramolecular and Intermolecular

FLP reactivity of $B(C_6F_5)_3$ is directly involved in the bi-functionalization of alkenes, alkynes and dienes molecules to form the zwitterions. This zwitterionic bi-functionalization can occur in intermolecular and intramolecular fashion across unsaturated compounds with P/B, N/B FLPs(Figure 7).[15, 16]

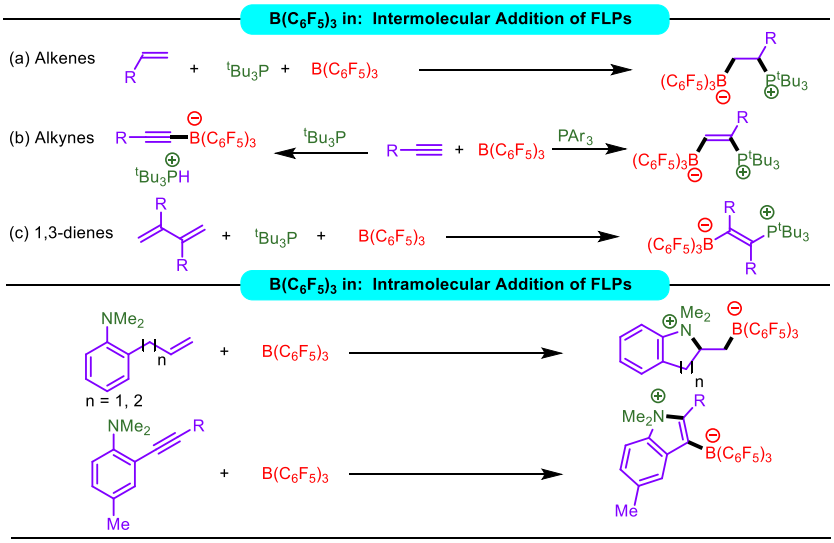


Figure 7: $B(C_6F_5)_3$-based FLPs Mediated Activation of Unsaturated Compounds

B(C_6F_5)$_3$-mediated FLPs Catalysis in Hydrogenation via H_2-activation: In 2006, Stephan and co-workers observed the B(C_6F_5)$_3$ and phosphine-derived reversible H_2 activation.[9a] Then later, Stephan and Erker introduced the catalytic activity of B(C_6F_5)$_3$ in FLPs for the activation of various small molecules and functionalization of unsaturated bonds. Numerous methodologies have been developed for the functionalization of π-bonds by using the B(C_6F_5)$_3$-based inter-/intramolecular FLPs. The initial investigations of B(C_6F_5)$_3$-based FLP catalysis were mainly focused on the heterolytic cleavage of dihydrogen gas (H_2) (Figure 8). This reactivity of B(C_6F_5)$_3$ based-FLPs was utilized for hydrogenation of numerous carbon–heteroatom, and carbon–carbon unsaturated bonds.[15, 17]

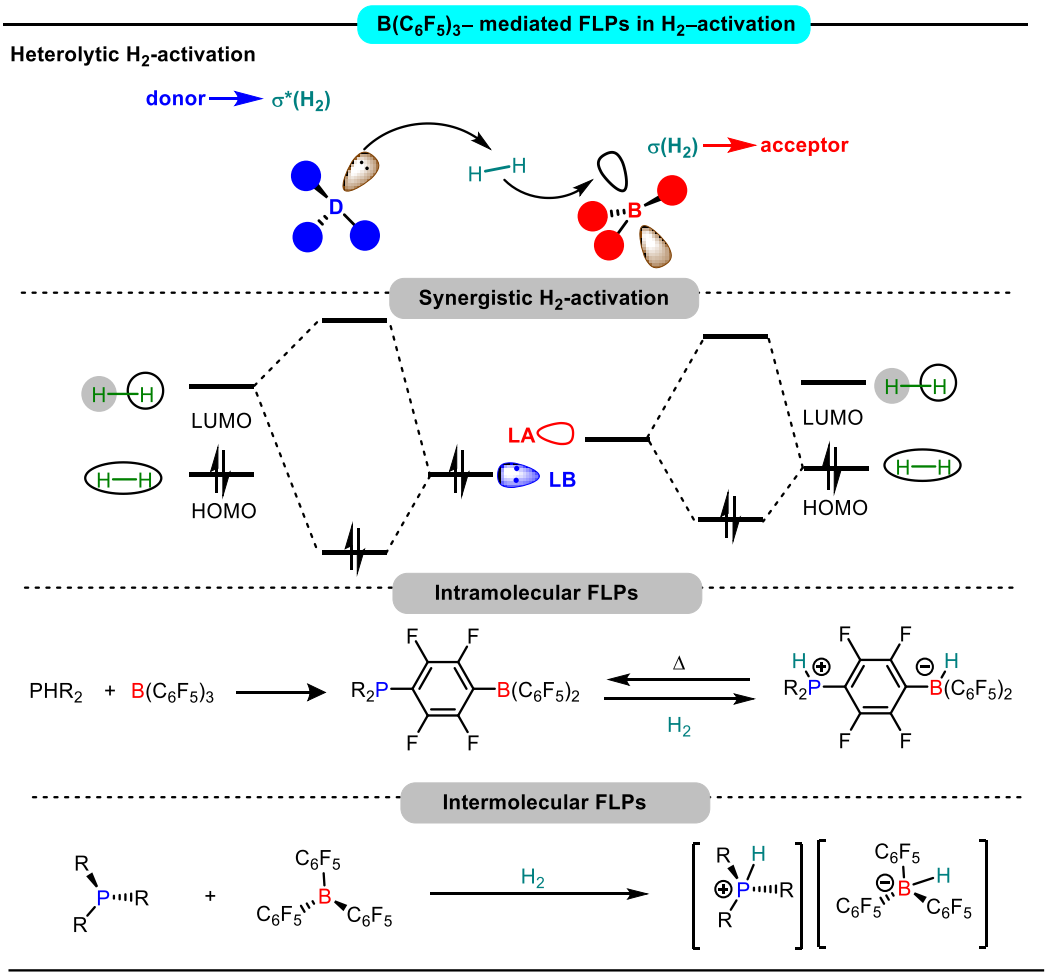
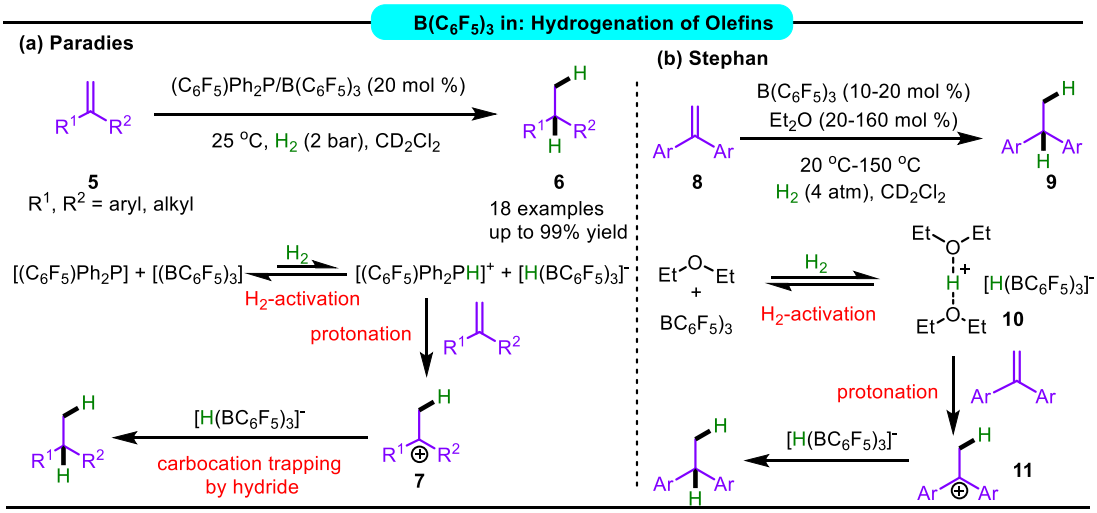


Figure 8: B(C_6F_5)$_3$–mediated FLPs in H_2-activation

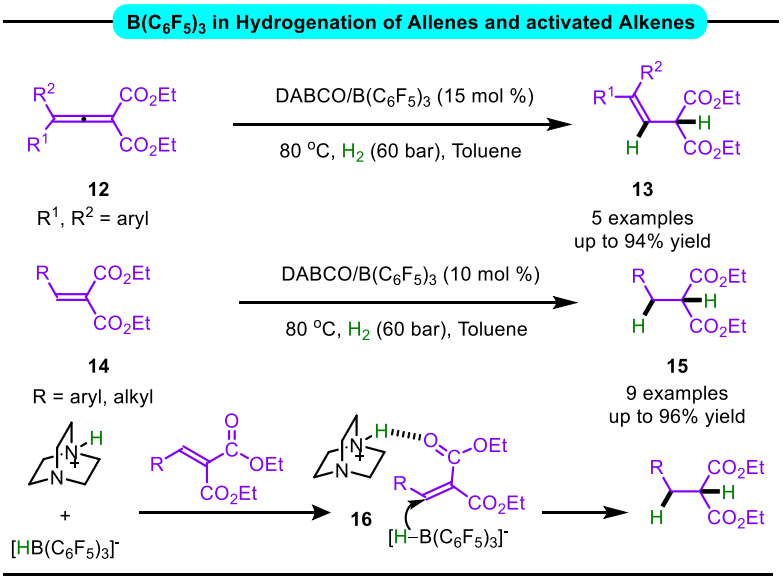
The FLP-catalyzed hydrogenations of olefins were extensively explored by different scientists after projection of state of art work by Paradies 2012 (Scheme 1-a).[18] In this study, Paradies utilized the P/B-FLP for the hydrogenation of 1,1-disubstituted olefin derivatives **5**. The Brønsted acidity of the cation partner was enhanced by using (C_6F_5)Ph_2P as a base partner with B(C_6F_5)$_3$. The combination of (C_6F_5)Ph_2P/B(C_6F_5)$_3$ is adequate enough for the hydrogenation of olefins as well as the regioselective hydrogenation of 1,3-dienes (few examples). The mechanistic pathway suggests the activation of olefin via proton transfer from cationic partner [(C_6F_5)Ph_2P–

$H]^+$, generate carbocationic intermediate **7**. The resulted carbocation is trapped with the hydride from anionic partner $[H–B(C_6F_5)_3]^-$ and furnishes the hydrogenation products **6** in good to excellent yields. In 2013 Stephan and co-workers introduced the diethyl ether as a base partner with $B(C_6F_5)_3$ for the FLP-catalyzed hydrogenation of 1,1-disubstituted olefins (Scheme 1-b).[19]



Scheme 1: $B(C_6F_5)_3$–based FLPs Catalyzed Hydrogenation of Olefins

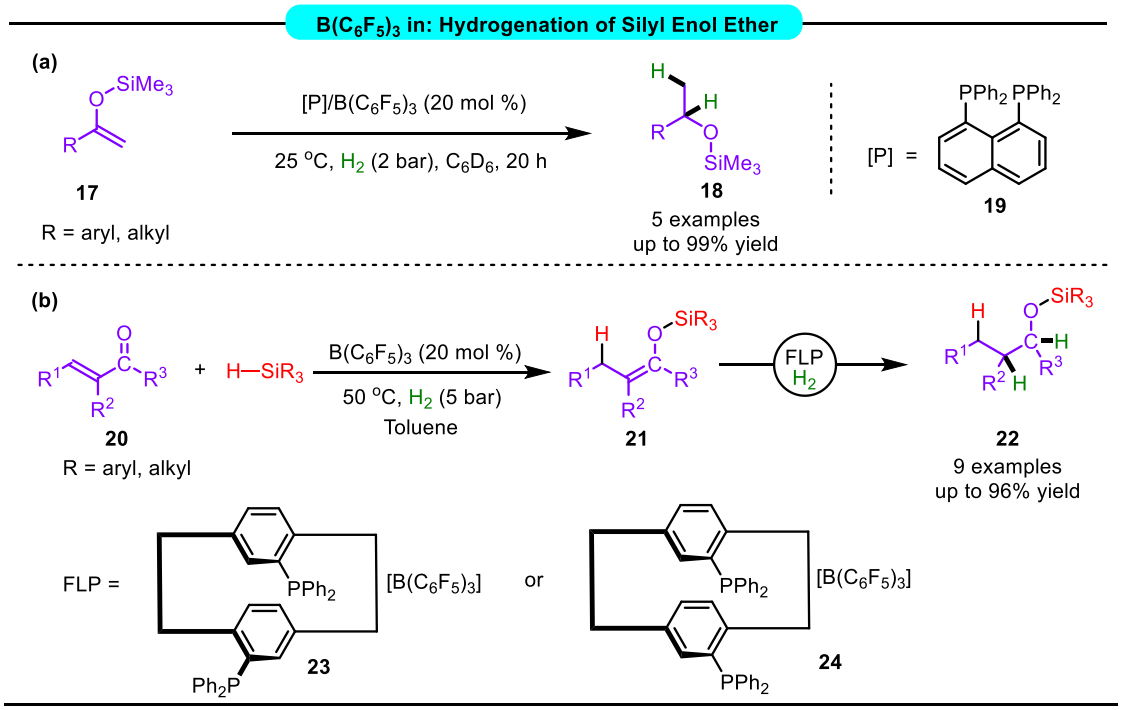
In 2012 Alcarazo conveyed the hydrogenation of electron-deficient allenes **12** and allylidene **14** malonates using DABCO/$B(C_6F_5)_3$ combination.[20] Here DABCO act as the donor partner along with acceptor partner $B(C_6F_5)_3$, for the heterolytic cleavage of H_2-gas. Authors have shown that $[HDABCO]^+$ activates the carbonyl functional group via hydrogen bonding **16** and hydride transfer from borohydride $[H–B(C_6F_5)_3]^-$ afforded the hydrogenated products **15** (Scheme 2).



Scheme 2: DABCO/$B(C_6F_5)_3$ FLP Catalyzed Hydrogenation of Activated Alkene, and Allene

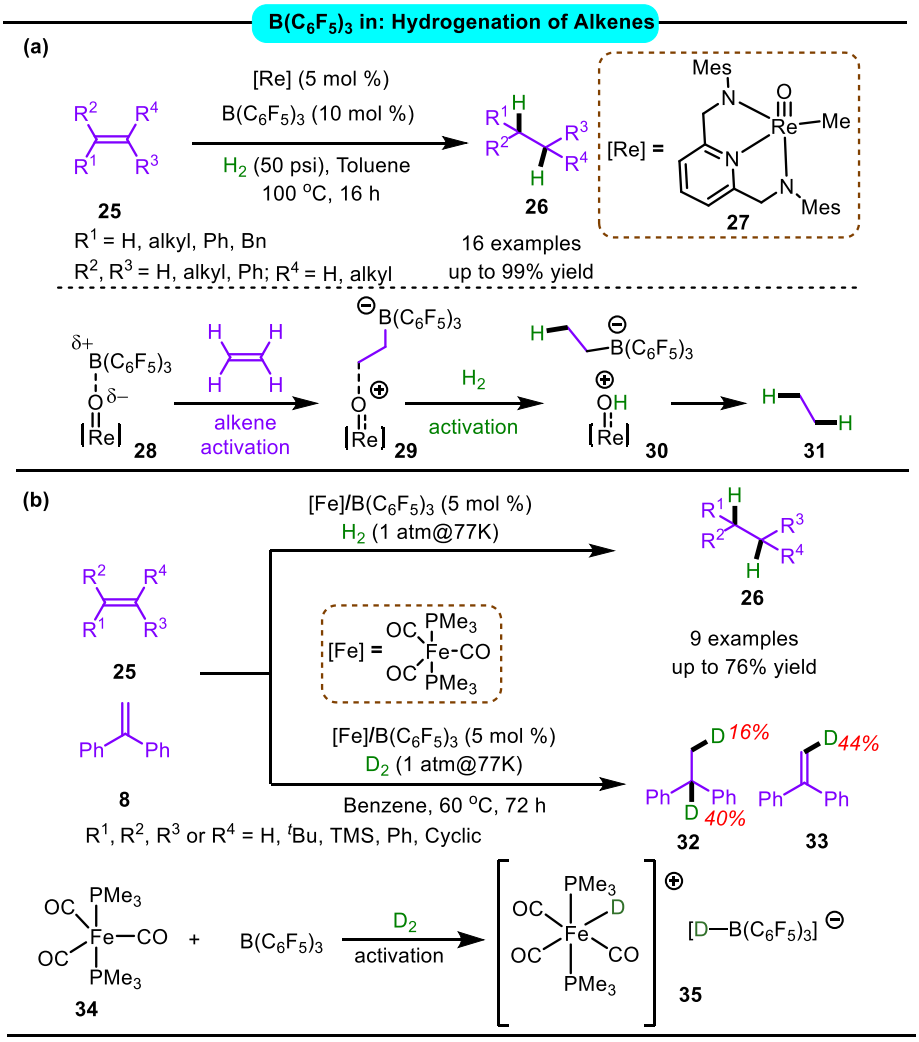
Likewise, in the line of P/B-based FLP-catalyzed hydrogenation, Erker introduced the 1,8-bis(diphenylphosphino)naphthalene/$B(C_6F_5)_3$ **19** combination for hydrogenation of silyl enol

ether **17** (Figure 3-a).[21] Later, in 2012, Paradies described intramolecular FLP for consecutive hydrosilylation and hydrogenation of enones **20**. In this reaction, first $B(C_6F_5)_3$ catalyzed hydrosilylation of enones gives silyl enol ethers **21** which undergo hydrogenation via FLP catalysis (Figure 3-b).[22]



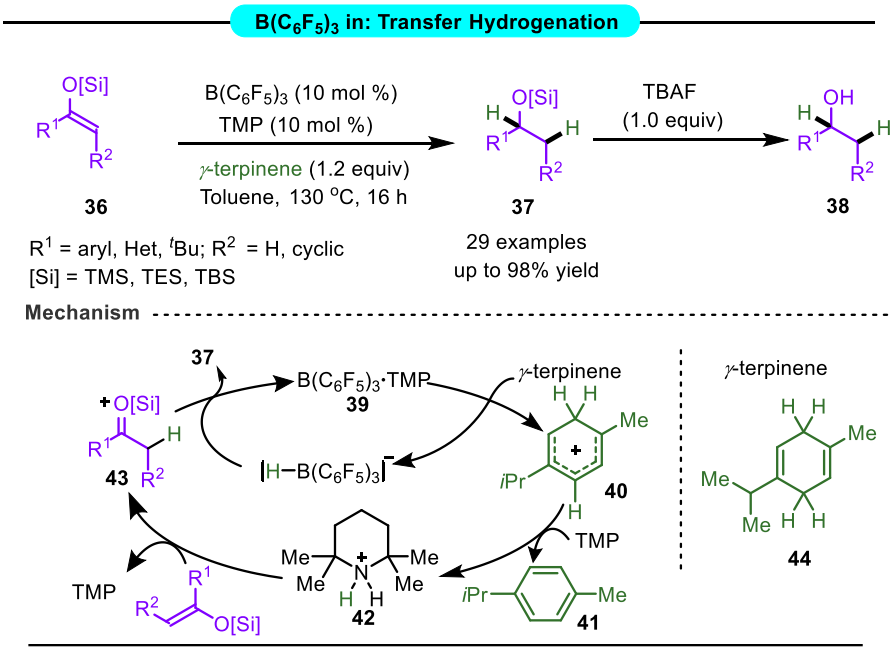
Scheme 3: $B(C_6F_5)_3$–based FLPs Catalyzed Hydrogenation of Enol Ether

It is also observed that various organometallic compounds can be utilized as a Lewis base partner with the $B(C_6F_5)_3$ to make an efficient FLP for the activation of hydrogen gas. The field of metal complex/$B(C_6F_5)_3$–based frustrated Lewis pairs have been studied by Wass[23] and Ison research groups independently. Among them, Ison exploited oxorhenium complexes **27** as a base partner in the FLP-catalyzed hydrogenation of alkene derivatives **25** (Scheme 4-a).[24] After extensive mechanistic studies the author suggested that the oxygen atom of these complexes is the active site to make FLP **28** with $B(C_6F_5)_3$. This FLP results in the electrophilic activation **29** of olefin followed by heterolytic cleavage of H_2-gas to afford hydrogenated products **26** in good yields. In 2020 Young and his team discovered the $Fe(CO)_3(PMe_3)_2/B(C_6F_5)_3$–based **35** FLP-catalyzed heterolytic activation of H_2 gas for the hydrogenation of alkenes. The mechanistic studies were done by using the D_2 gas in place of H_2 gas (Scheme 4-b).[25]



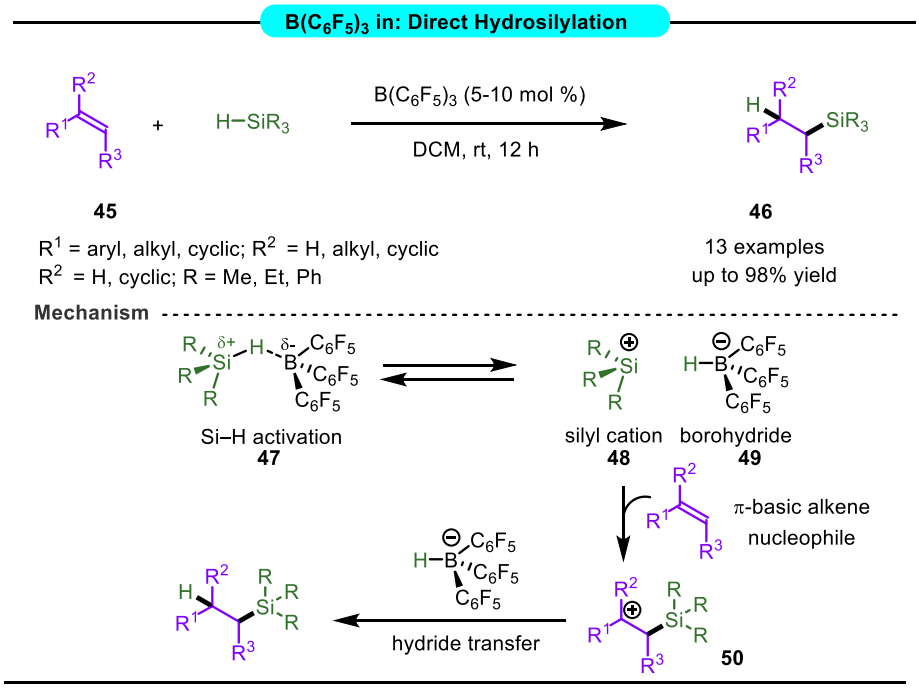
Scheme 4: Metal Complex/$B(C_6F_5)_3$ FLP Catalyzed Hydrogenation of Alkene

FLP Catalysis in Transfer Hydrogenation: Apart from the activation of molecular H_2 with $B(C_6F_5)_3$–mediated FLPs, several H_2-surrogates have been explored for the hydrogenation of unsaturated bonds.[26] In line with $B(C_6F_5)_3$–mediated FLP-catalyzed transfer hydrogenation of alkenes, the group of Gandon, and Oestreich exploited the cyclohexa-1,4-diene (1,4-CHD) as H_2-surrogates (for detailed discussion see chapter 5). Later in 2018 Morril and co-workers utilized γ-terpinine **44** as a hydrogen surrogate and TMP·$B(C_6F_5)_3$ catalyst **39**. The hydride abstraction from γ-terpinine by $B(C_6F_5)_3$ generate borohydride $[H–B(C_6F_5)_3]^-$ and cationic intermediate **40** (Scheme 5).[27] The proton abstraction from intermediate **40** by TMP form a $[TMP\text{-}H]^+$ **42**, which protonates the silyl enol ether **36** and generate intermediate **43**. The hydride transfer from $[H–B(C_6F_5)_3]^-$ to the intermediate **43** furnishes hydrogenated silyl ether derivatives **37**.



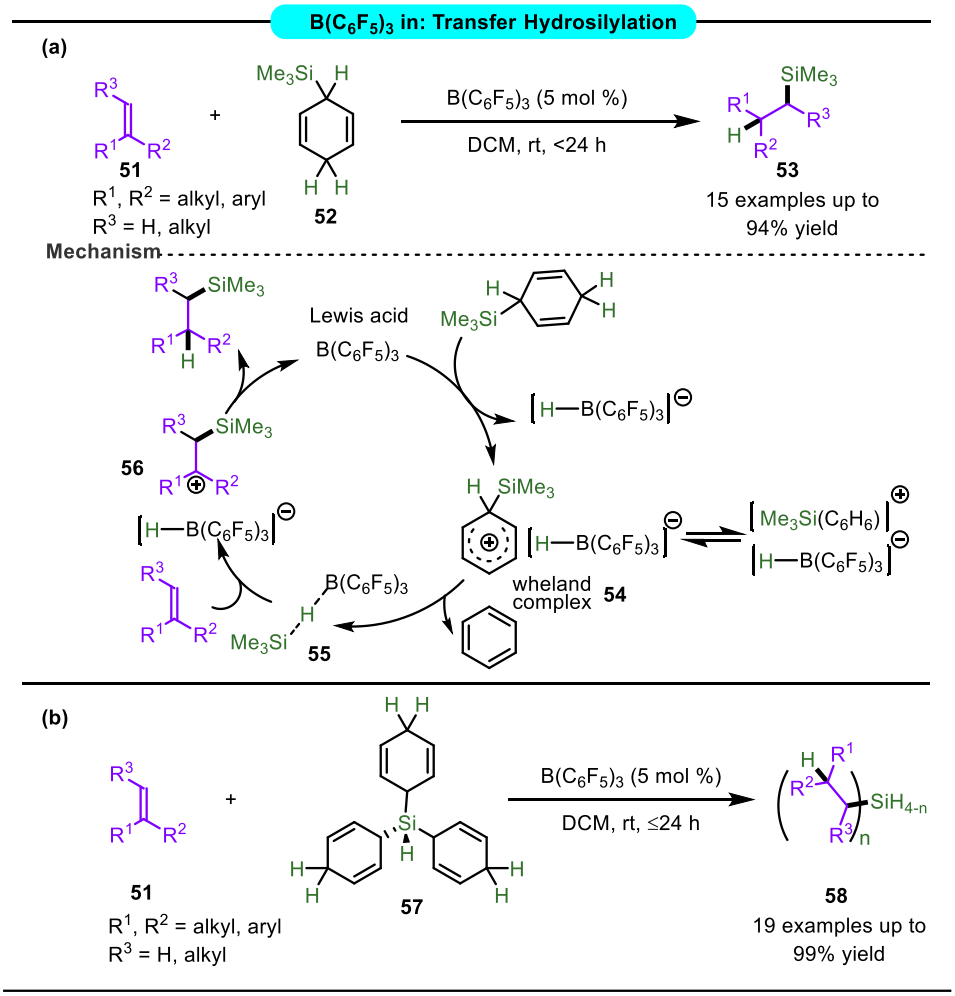
Scheme 5: TMP/$B(C_6F_5)_3$ FLP Catalyzed Transfer Hydrogenation of Silyl Enol Ether

$B(C_6F_5)_3$-catalyzed Direct and Transfer Hydrosilylation Reactions: In 1996, three decades later from the synthesis of $B(C_6F_5)_3$, Piers and his team first explored its catalytic property in the field of hydrosilylation of aldehydes, ketones, and esters.[28] However, at that time, the FLP chemistry of this Lewis acid was not invented. This finding of Piers for hydrosilylation was much ahead of its time of development in the field of metal-free Si–H bond activation with $B(C_6F_5)_3$. Then later, Si–H bond activation reactivity of $B(C_6F_5)_3$ was explored for the dehydrogenative coupling, and hydrogenation reactions of several heterocyclic compounds.[29] This reactivity of $B(C_6F_5)_3$ with silane also utilized in various defunctionalization[30, 13h] reactions, e.g., deoxygenations, hydrodefluorination, and desulfurization reactions under metal-free conditions. These are also utilized in silylation of unsaturated bonds, e.g., imines, enones, enamines, alkenes, alkynes, etc.[31-36] Gevorgyan, and co-workers realized the hydrosilaylation of alkenes **45** in 2002 (Scheme 6).[37] They proposed that the Si–H bond is first activated **47** by $B(C_6F_5)_3$, which generates borohydride **49** and silyl cation **48**. The resulted silyl cation **48** combines with π-basic alkenes and forms a *β*-silycarbenium ion **50** that can be trapped by borohydride to afford the hydrosilylated products **46**. Besides the hindered $i\text{Pr}_3\text{SiH}$, various hydrosilanes reacted well with styrene, and aliphatic alkenes, including cyclohexene and polymerizable indene also provided hydrosilylation products in good yields.



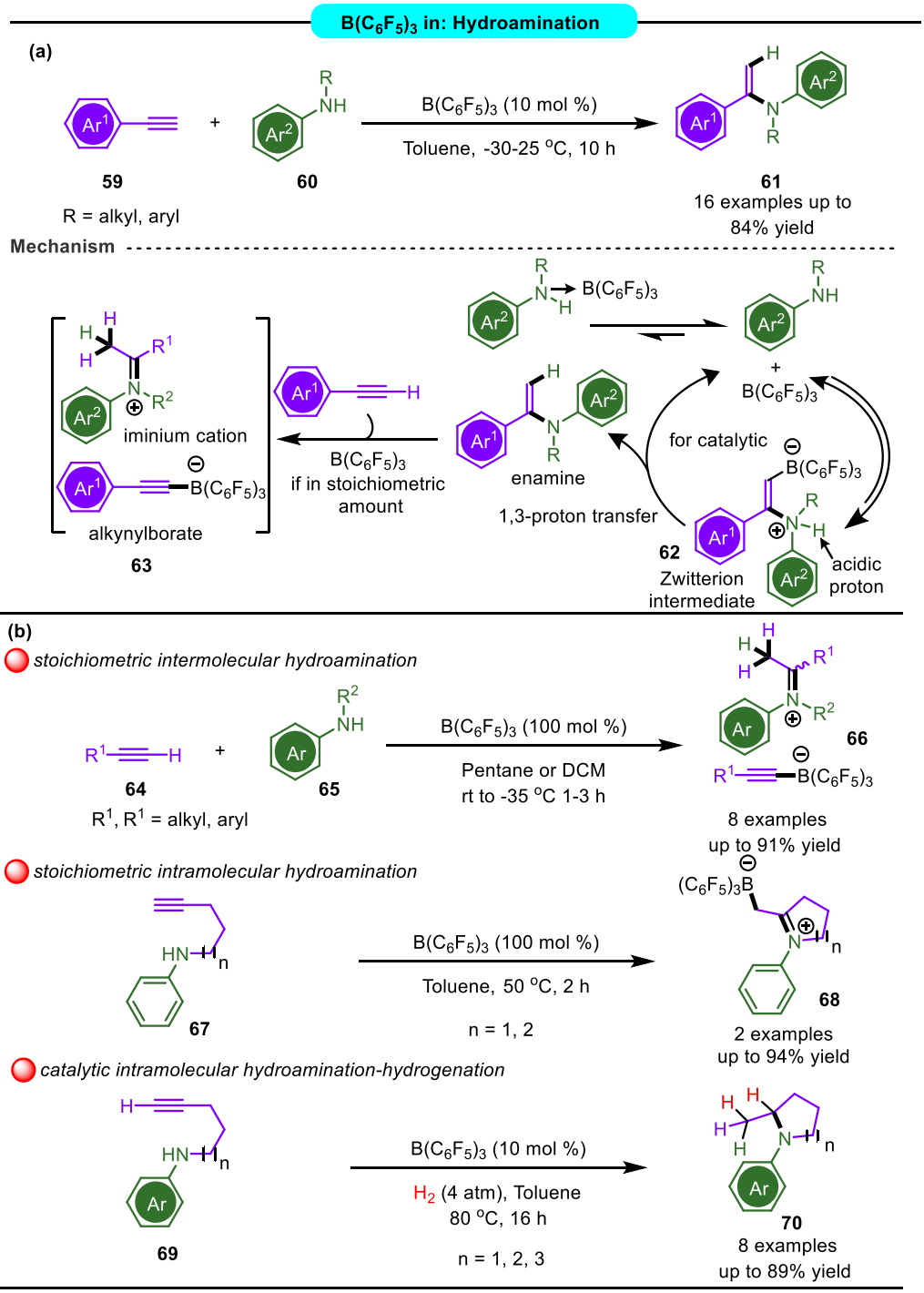
Scheme 6: $B(C_6F_5)_3$ Catalyzed Direct Hydrosilylation of Olefin

In the field of direct hydrosilylation reactions, the high flammability, volatility, and toxicity of hydrosilanes remain a major challenge for the scientists.[38] To avoid the use of these hydrosilanes Oestreich, and his team introduced silicon-substituted cyclohexa-1,4-diene as [Si]-H surrogates **52** for *in-situ* transfer hydrosilylation. By using the combination of $B(C_6F_5)_3$ as a catalyst and silicon-substituted cyclohexa-1,4-diene **52** as a hydrosilane source, various methodologies were developed for transfer hydrosilylation across the unsaturated bonds.[39] In 2013 they documented the $B(C_6F_5)_3$-catalyzed transfer hydrosilylation of olefin derivatives by using 3-silylated cyclohexa-1,4-diene **52** as hydrosilane surrogate (Scheme 7-a).[40] The theoretical and experimental mechanistic studies by Fujimoto and Oestreich show that hydride abstraction by $B(C_6F_5)_3$ from bisallylic position generates the silicon-stabilized cyclohexadienyl cation **54**. The aromatization of the cyclohexadienyl cation released a phenyl ring and resulted in $[R_3Si\cdots H\cdots B(C_6F_5)_3]$ **55**. Subsequently the π-Lewis base alkene coordinates with silyl part and generates a carbocationic intermediate. The hydride transfer from borohydride to the carbocationic intermediate **56** furnishes the *anti*-Markovnikov hydrolsilylated products **53**.[41] Later the group of Oestreich studied the effect of substituents at the cyclohexa-1,4-diene and different π- and σ-donating substrates.[42] In the year 2015 and 2018, consecutively they explored the SiH_4 surrogate **57** for the hydrosilylation of alkenes, and alkynes (Scheme 7-b).[43]



Scheme 7: $B(C_6F_5)_3$ Catalyzed Transfer Hydrosilylation of Alkene

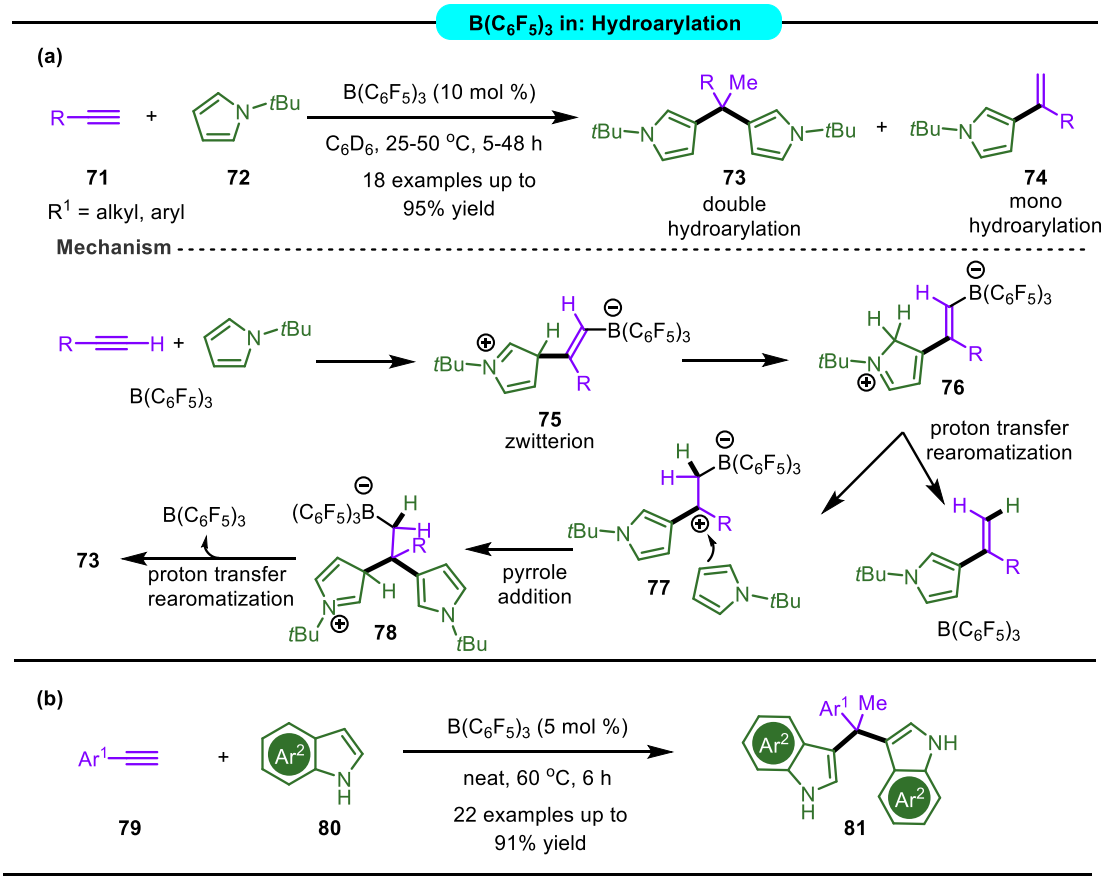
$B(C_6F_5)_3$-catalyzed Hydroamination Reactions: Since the development of $B(C_6F_5)_3$ mediated FLPs across unsaturated C–C bonds in presence of P/N-cantered bases, Stephan and co-workers explored the hydroamination of terminal alkynes by using catalytic and stoichiometric amount of $B(C_6F_5)_3$. In 2013, they explored the catalytic hydroamination of alkynes **59** for the synthesis of enamine derivatives **61** (Scheme 8-a).[44] In this study, sterically hindered, mainly diarylamines reacted well and provided good yield; however, *N*-isopropylaniline provided desired products in moderate yields. This reaction followed the zwitterionic **62** pathway via the addition of $B(C_6F_5)_3$ and arylamine across the C–C triple bond. Then 1,3-proton transfer from arylamonium cation, furnished enamine **61** and regenerate $B(C_6F_5)_3$. However, in the case of stoichiometric amount of $B(C_6F_5)_3$ with diphenylamine and phenylacetylene, a salt of iminium cation and alkynylborate $[Ph_2N{=}C(CH_3)Ph][PhCCB(C_6F_5)_3]$ **63** was obtained. Later in 2015, the same group extended their finding for inter-/intramolecular hydroamination under stoichiometric and catalytic conditions (Scheme 8-b). These hydroaminated products further undergo hydrogenation by using H_2- gas in a one-pot manner and various *N*-containing heterocyclic **70** compounds were synthesized.[16d]



Scheme 8: $B(C_6F_5)_3$ Catalyzed/Mediated Hydroamination of Alkyne

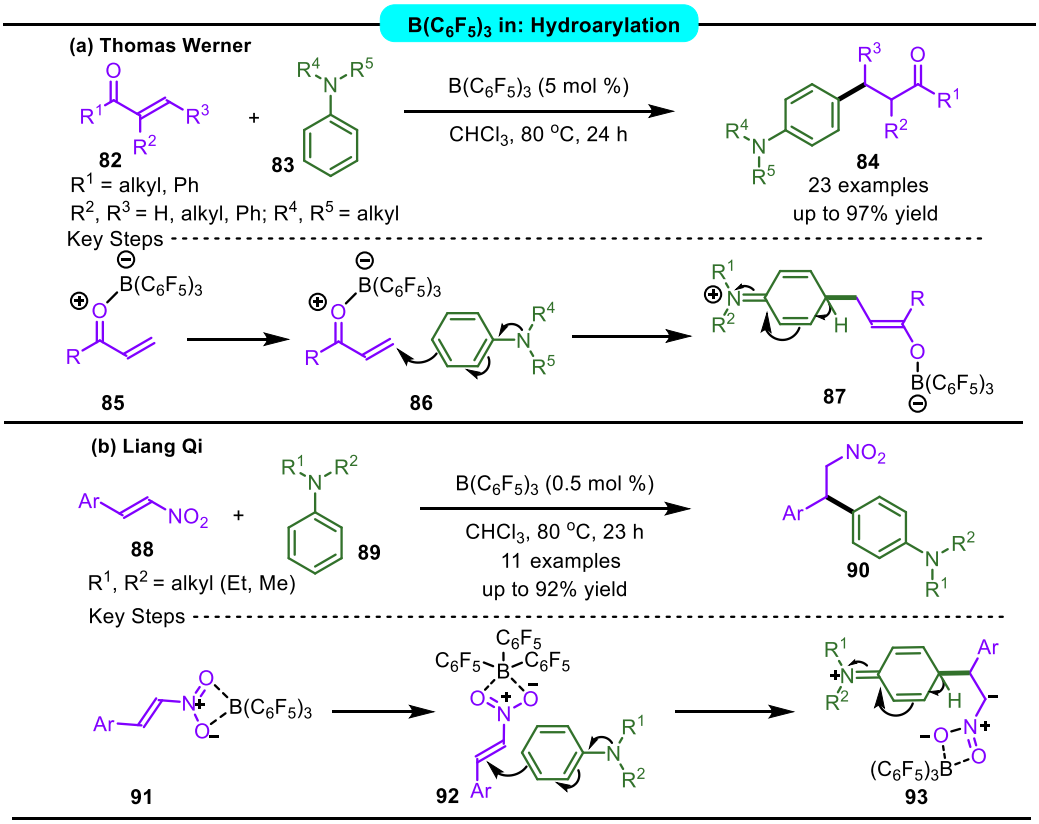
$B(C_6F_5)_3$-catalyzed Hydroarylation Reactions: The activation of alkynes is extensively studied by Stephan and co-workers in the field of FLP addition across the C–C triple bond. In 2010 they observed the zwitterion formation via the addition of pyrrole (through C-center) and $B(C_6F_5)_3$ across alkyne.[45] Then after ten years, in 2020, the same group explored this reactivity of pyrrole **72**, alkyne **71**, and $B(C_6F_5)_3$ in catalytic hydroarylation reactions (Scheme 9-a). The double hydroarylation of alkynes with *N*-protected pyrrole **73** was observed via $B(C_6F_5)_3$-mediated FLP catalysis. This reaction remains steric and electronically controlled in terms of mono **77** and

double hydroarylation **73**.[46] Similar to the Stephan's work, Zhong and co-workers introduced double hydroarylation of alkyne with indole **80**, for the synthesis of numerous bis(indolyl)alkanes as end products **81** (Scheme 9-b).[47]



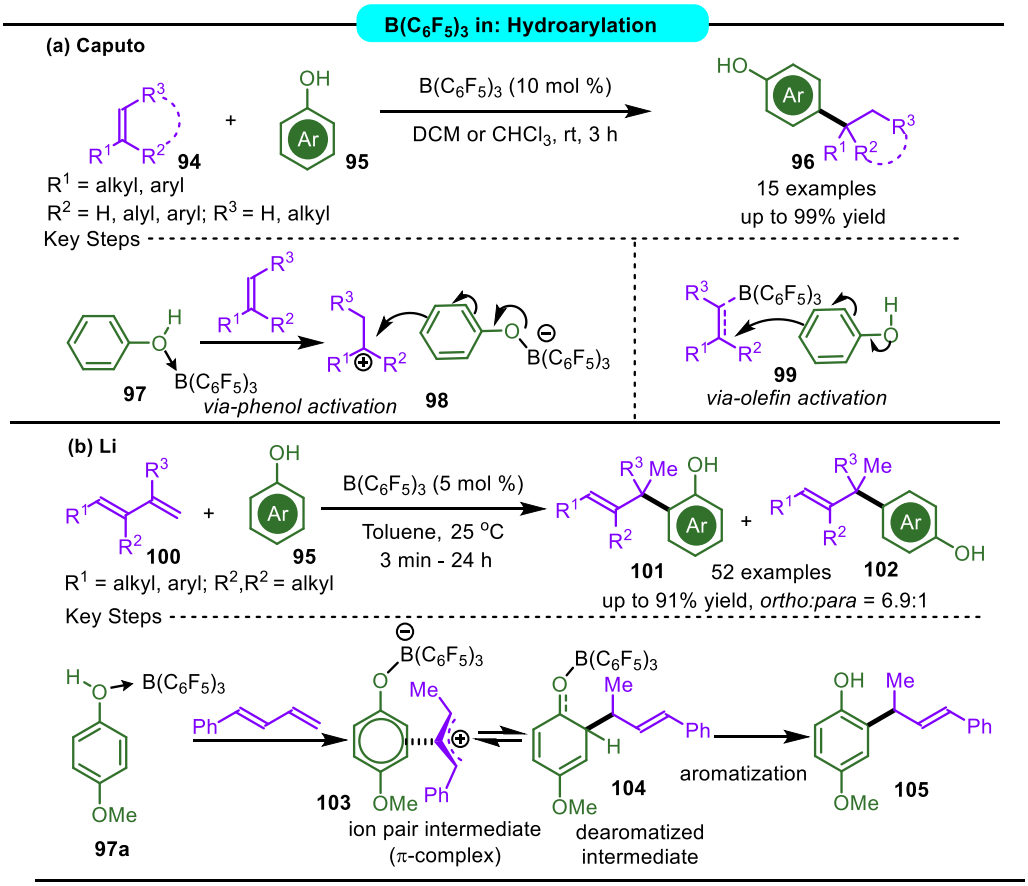
Scheme 9: $B(C_6F_5)_3$ Catalyzed Hydroarylation of Alkyne

In 2017, Werner and co-workers explored the $B(C_6F_5)_3$-catalyzed hydroarylation (Michael addition) of activated alkene **82** (α, β-unsaturated ketone) (Scheme 10-a).[48] In this reaction $B(C_6F_5)_3$ activates the carbonyl by increasing the electrophilicity of β-carbon **85**. Then the attacks by aniline derivative via para-C–H generate intermediate **87**. The resulted intermediate **87** furnished the desired products **84** through rearomatization and tautomerization. Similarly, Qi and his team developed a methodology for the hydroarylation **90** of electron-deficient alkenes **88** (nitroalkenes) with aniline derivatives **89** (Scheme 10-b).[49]



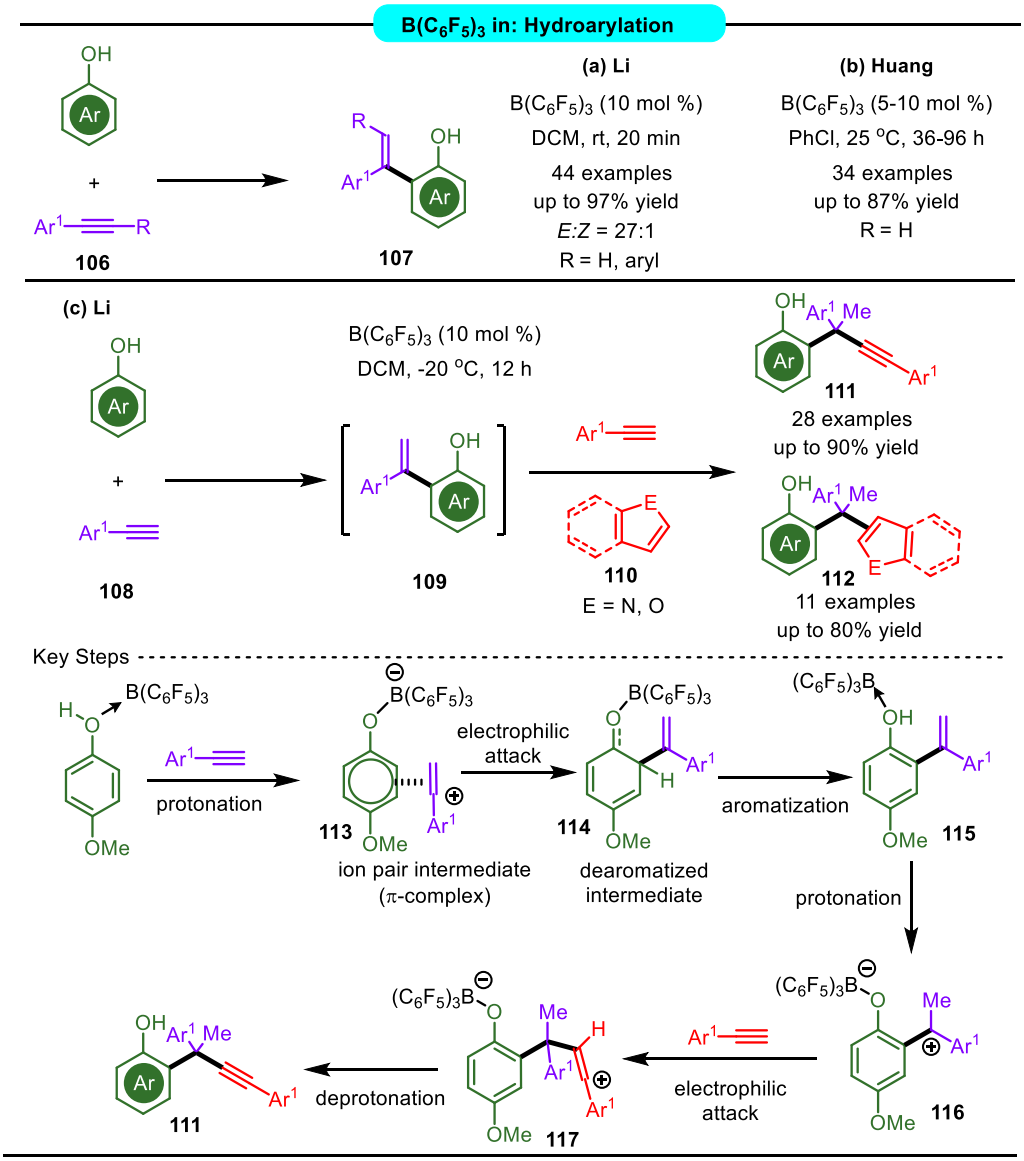
Scheme 10: $B(C_6F_5)_3$ Catalyzed Michael Addition/Hydroarylation Reactions

The hydroarylation of alkenes and 1,3-dienes with phenol were explored by two independent groups, Caputo[50] and Li[51], respectively, in 2018 and 2019. The initial study for hydroarylation of alkene with phenol was done by Caputo; where several alkenes **94** and phenol **95** partners were screened (Scheme 11-a). Interestingly, they obtained the *para*-selective Friedel-crafts products **96** beside the trisubstituted phenols. However, the *para*-substituted phenols furnished *ortho*-hydroarylation under their reaction conditions. In this study, authors proposed two possible pathways for the hydroarylation 1) through coordination of $B(C_6F_5)_3$ with the oxygen of phenol **97** resulting in the enhancement of Brønsted acidity 2) π-activation of alkenes with $B(C_6F_5)_3$ **99**. In contrast Li performed several controlled experiments and extensive DFT calculations for hydroarylation of 1,3-dienes **100** with phenol **95** (Scheme 11-b). On the basis of these results, they proposed that the activation of O–H through σ-complexation **97a** increases the Brønsted acidity, which is responsible for the protonation of 1,3-dienes and generates the ion pair intermediate **103** (π-complex between anion and carbocation). The resulted intermediate **103** experience Friedel–Crafts reaction through electrophilic attack between anion and carbocation ion pair and forms a new dearomatized intermediate **104**. The intermediate **104** transformed into the hydroarylated product **105** via rearomatization. In the case of *para*-substituted phenols, selectively *ortho* hydroarylation was observed, whereas in case of free phenol mixture of *ortho*/*para* products **101** + **103** were formed.



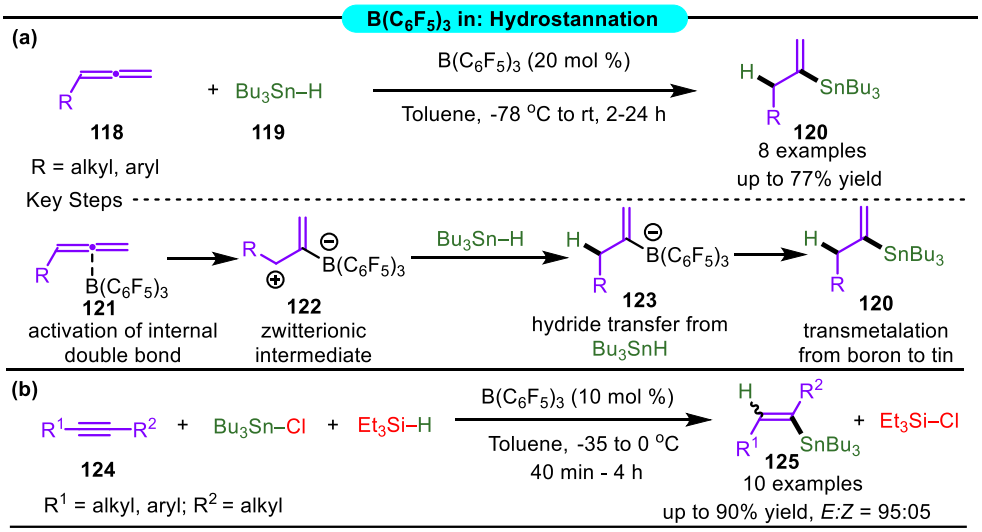
Scheme 11: $B(C_6F_5)_3$ Catalyzed Hydroarylation of Alkene and 1,3-diene

In 2021, Huang[52] and Li[53] independently introduced the $B(C_6F_5)_3$–catalyzed hydroarylation of alkynes with phenol to contrive the *ortho*-alkenylated phenol derivatives **107** (Scheme 12-a, 12-b). In the same year Li group published another work where they have synthesized *ortho*-propargylic alkylated phenols derivatives **111** via double hydroarylation of alkynes with phenol at -20 °C (Scheme 12-c). This work furthermore extended for the second hydroarylation with heterocyclic compounds (indole/pyrrole) to synthesize 1,1,1-triaryl ethanes **112**. The mechanism following first O–H activation through σ-complexation and protonation of alkyne generates the ion pair intermediate **113** (π-complex between anion and carbocation). The resulted intermediate **113** transformed into dearomatized intermediate **114** through electrophilic attack. This intermediate **113** furnished the *ortho*-propargylic alkylated phenols derivatives **115** via rearomatization. This compound **115** further undergoes intramolecular protonation of vinyl via O–H activation with $B(C_6F_5)_3$ and generate carbocationic intermediate **116**. The electrophilic attack between this carbocation **116** and alkyne generates the vinyl carbocationic intermediate **117**, which further furnishes *ortho*-propargylic alkylated phenols **111** via aromatization.



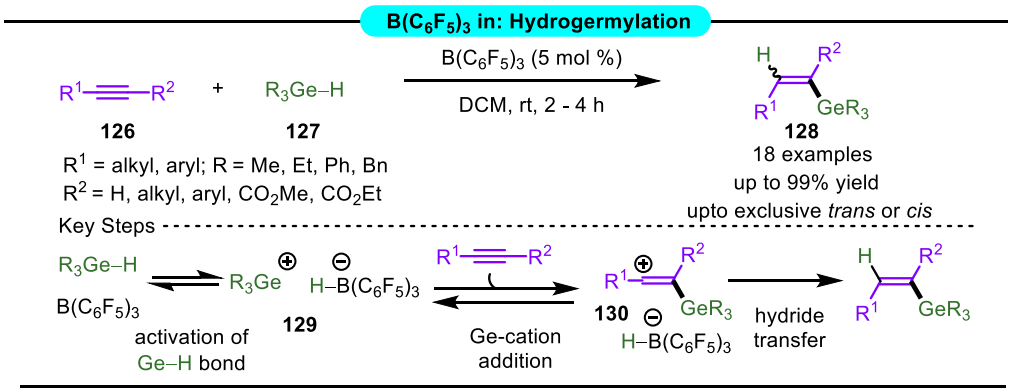
Scheme 12: $B(C_6F_5)_3$ Catalyzed Hydroarylation of Alkynes with Phenols

$B(C_6F_5)_3$-catalyzed Other Hydrofunctionalization Reactions: Besides the above-mentioned hydrogenation, hydrosilylation, hydroamination, and hydroarylation, $B(C_6F_5)_3$ also displays catalytic reactivity in other hydrofunctionalization (e.g., hydroelementation) reactions across the unsaturated C–C bonds.[54] In 1997, Yamamoto and his team first time introduced the $B(C_6F_5)_3$-catalyzed hydrostannation of allene derivatives **118** with Bu_3SnH **119** for the synthesis of vinylstannanes **120** (Scheme 13-a). The activation of internal double bond of allene with $B(C_6F_5)_3$ **121** generate Zwitterionic intermediate **122**. The resulted intermediate **122** transformed into product **120** via hydride and transmetalation. Then later in 1998, they utilized *in-situ* prepared Bu_3SnH (from Bu_3SnCl and Et_3SiH) for the hydrostannation **125** of alkynes **124** (eight examples), alkene (one example), and allene (one example) (Scheme 13-b).[55]



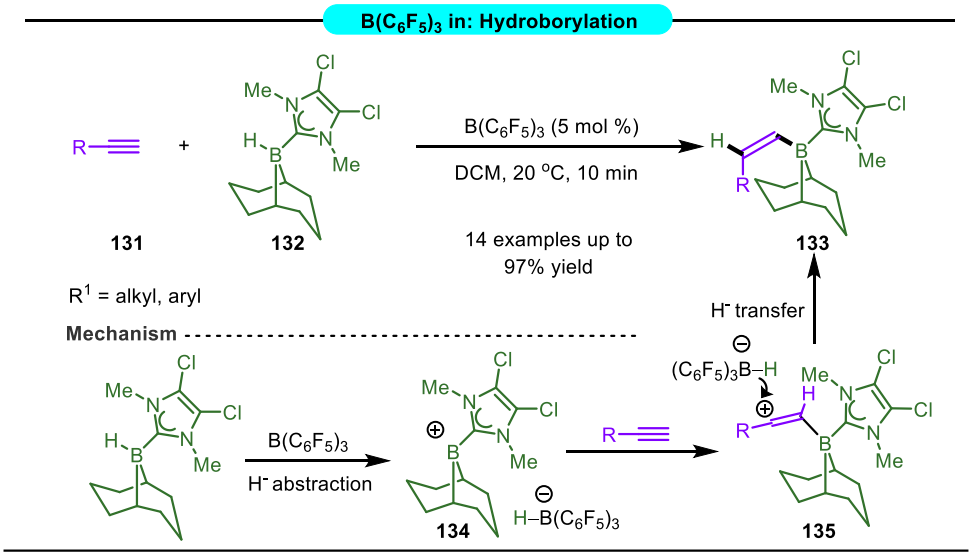
Scheme 13: $B(C_6F_5)_3$ Catalyzed Hydrostnnation of Allene and Alkyne

In 2005, Gevorgyan and co-workers described the $B(C_6F_5)_3$-catalyzed hydrogermylation across C–C triple bonds. This reaction follows similar pathways as hydrosilylation, where first, the activation of Ge–H bonds generates germyl cation **129** and borohydride species $[H–B(C_6F_5)_3]^-$. Later the addition of germyl cation across alkyne generates a cationic vinyl intermediate **130** into which addition of hydride from the borohydride through less hindered site furnishes (*Z*)-vinylgermanes **128**. However, in the case of propiolates, the *cis*-addition of hydrogermane was perceived (Scheme 14).[56]



Scheme 14: $B(C_6F_5)_3$ Catalyzed Hydrogermylation of Alkyne

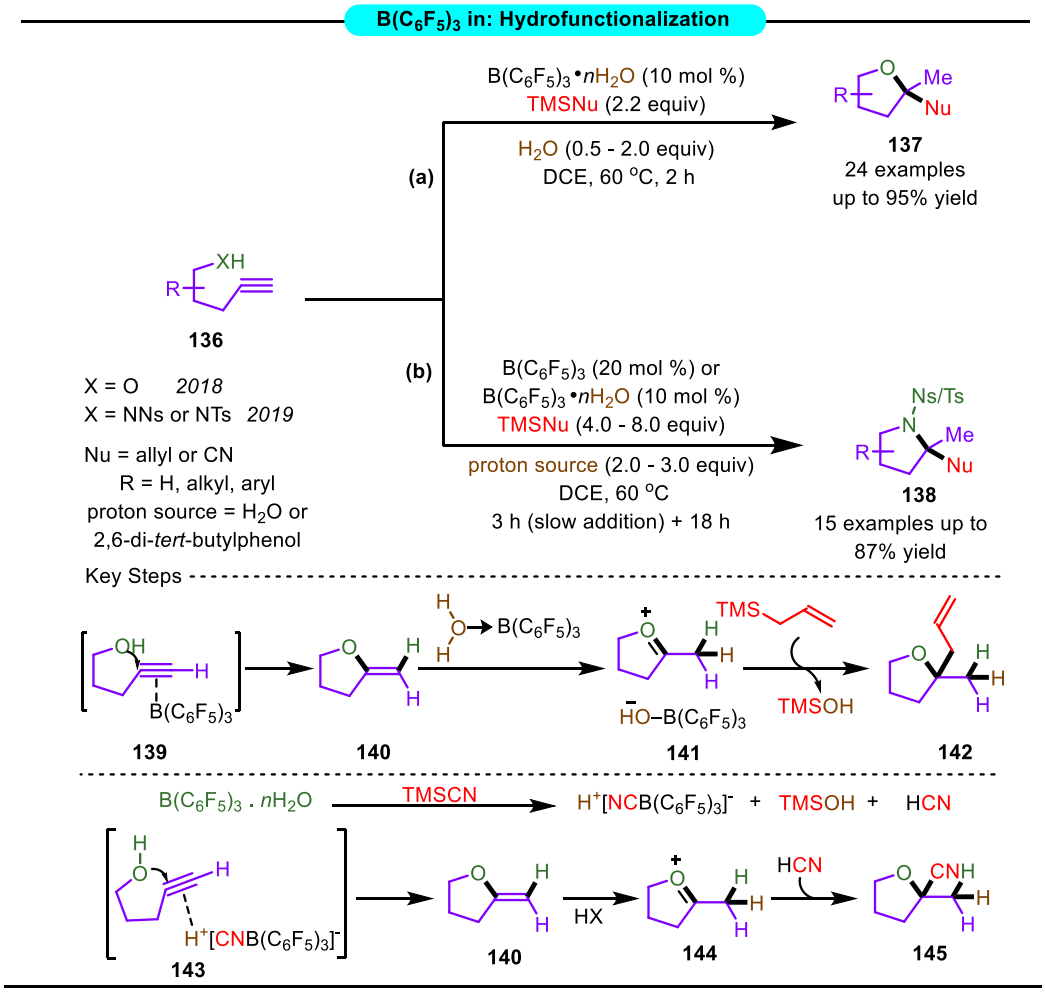
In 2016, Ingleson introduced a $B(C_6F_5)_3$ catalyzed hydroboration of alkynes with 2-((1*R*,5*S*)-9λ^4-borabicyclo[3.3.1]nonan-9-yl)-4,5-dichloro-1,3-dimethyl-2,3-dihydro-1*H*-imidazole (9-BBN(H)(I-DCDM)) **132** (Scheme 15).[57] This reaction furnished *trans*-hydroborated products **133** with high selectivity. Authors performed several experiments for the mechanistic pathway and suggested that the $B(C_6F_5)_3$ abstract hydride from 9-BBN(H)(I-DCDM) **132** to generate the borenium [9-BBN (I-DCDM)][$HB(C_6F_5)_3$] **134**. This borenium **134** reacts with alkyne **131** and generates the vinyl cation intermediate **135**. The hydride transfer from borohydride $[H–B(C_6F_5)_3]^-$ to vinyl cation **135** afforded the products **133** in good yields.



Scheme 15: $B(C_6F_5)_3$ Catalyzed Hydroboration of Alkyne

H_2O–$B(C_6F_5)_3$-catalyzed Reactions: The high Lewis acidity of $B(C_6F_5)_3$ is accountable for the σ-complexation with H_2O molecules because of that it can form stable H_2O–$B(C_6F_5)_3$ adduct and this adduct acts as a Brønsted acid. The Brønsted acidity of this H_2O–$B(C_6F_5)_3$ complex always remains variable in particular solvents. Therefore, the catalytic reactivity of H_2O–$B(C_6F_5)_3$ adduct was also explored in numerous reactions by different research groups.[58]

In this regard, Yamamoto reported two consecutive methods for the partially intra-and intermolecular double hydrofunctionalization of alkynes by using $B(C_6F_5)_3{\cdot}nH_2O$ as a catalyst. In 2018 they studied the hydroalkoxylation/hydroallylation **142** and hydroalkoxylation/hydrocyanation **145** by using allylsilane and TMSCN as a source of allyl and CN nucleophiles, respectively (Scheme 16-a).[59] In the case of hydroalkoxylation/hydroallylation, $B(C_6F_5)_3$ activates **139** the alkyne that undergoes intramolecular hydroalkoxylation **140** followed by protonation **141**. Finally, nucleophile (allyl from allylsilane) addition furnishes functionalized cyclic ethers **142**. However, in the case of hydroalkoxylation/hydrocyanation, the Brønsted acidic species $H^+[NCB(C_6F_5)_3]^-$ is responsible for the activation **143** of alkyne and experiences hydroalkoxylation **140** step. Then later followed by protonation and cyanide addition furnishes the functionalized cyclic ethers **145** having cyanide functional group. Later in 2019, the same group utilized this reactivity of $B(C_6F_5)_3{\cdot}nH_2O$ for hydroamination/hydroallylation and hydroamination/hydrocyanation (Scheme 16-b).[60]



Scheme 16: $B(C_6F_5)_3{\cdot}nH_2O$ Catalyzed Hydrofunctionalization of Alkyne

1.3.5 Indium Lewis Acids

Indium also belongs to group XIII having oxidation states +1 and +3; however, +3 is the stable oxidation state for the Indium compounds represented by In(III). The commonly used Lewis acids of In(III) are the halides (Cl, Br, I) and triflates (OTf).[61]

In comparison with boron-based Lewis acids, In(III) remains less reactive owing to the high ionic radius of In. Interestingly the lower reactivity of In-Lewis acids makes them highly functional group tolerant, e.g., amide, hydroxyl, etc.[62] In(III), Lewis acids display σ– and π–interaction with carbonyl and unsaturated C–C bonds, respectively. The π–Lewis acidity of In(III) makes them pleasant for C–heteroatom, and C–C bond formation via functionalization of C–C unsaturated bonds, e.g., hydroamination, hydrothiolation, and hydroalkoxylation, enyne polycyclization reactions (Figure 9). We have explored the reactivity of $InBr_3$ for the functionalization of alkynes (chapter 4) and alkene (chapter 5). The $InBr_3$ can be synthesized upon treatment of In-metal with Br_2.[62, 63]

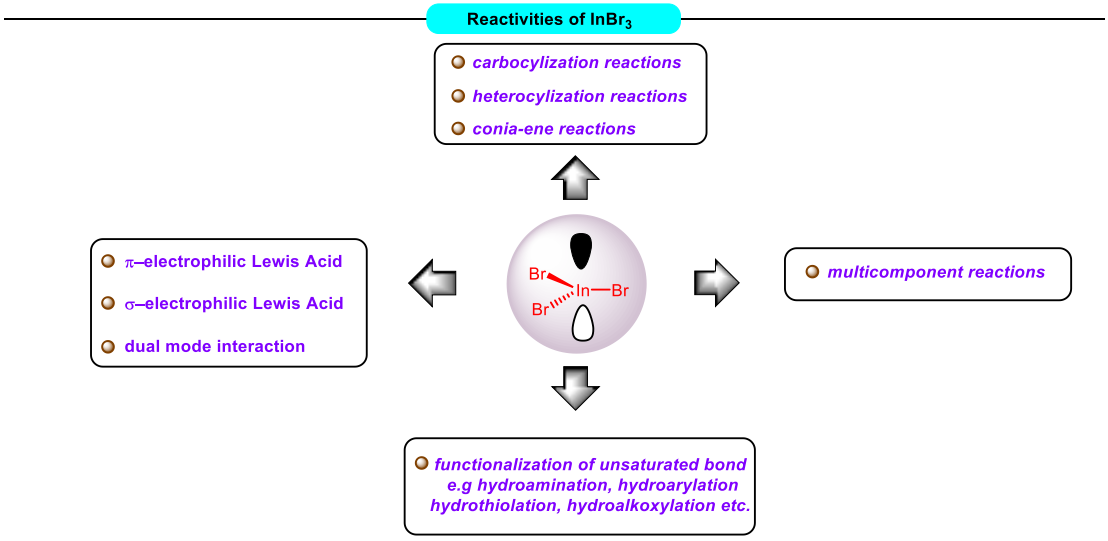
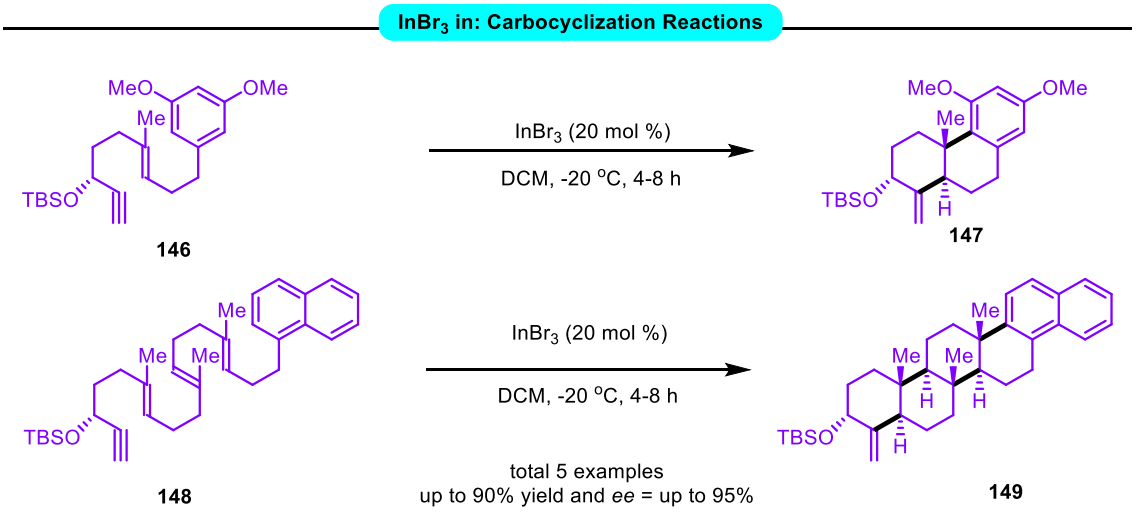


Figure 9: Reactivities of $InBr_3$

$InBr_3$-catalyzed Carbocyclization/Intramoleuclar Hydroarylation Reactions: The $InBr_3$ catalyst can activate the substrate molecules through σ– and π–Lewis acidity, because of that, this catalyst has been extensively explored in numerous cyclization reactions, including carbo- and heterocyclization. These types of reactions can follow the hydroarylation, Friedel–Crafts, and Diels alder pathway.[62, 63]

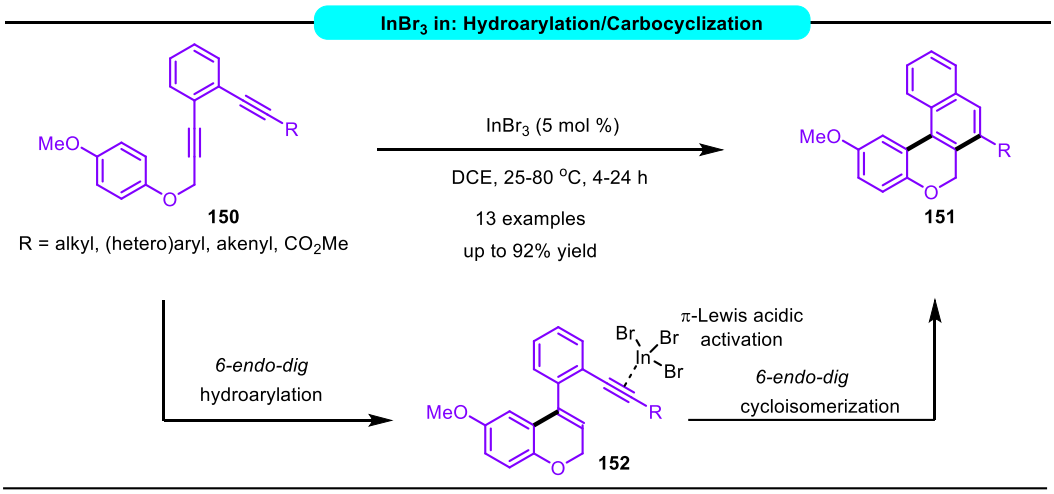
In 2011, Corey and co-workers exploited the $InBr_3$ catalyst for the cyclization of enyne **146** to synthesize cyclic compounds **147**. The cyclization of polyenynes **148** delivers polycyclic compounds **149** with tolerance of silyl ether and methoxy groups. This reaction can afford up to four new C– C bonds via cycloisomerization and intramolecular hydroarylation (Scheme 17).[64]



Scheme 17: $InBr_3$ Catalyzed Carbocyclization of Alkene and Alkyne

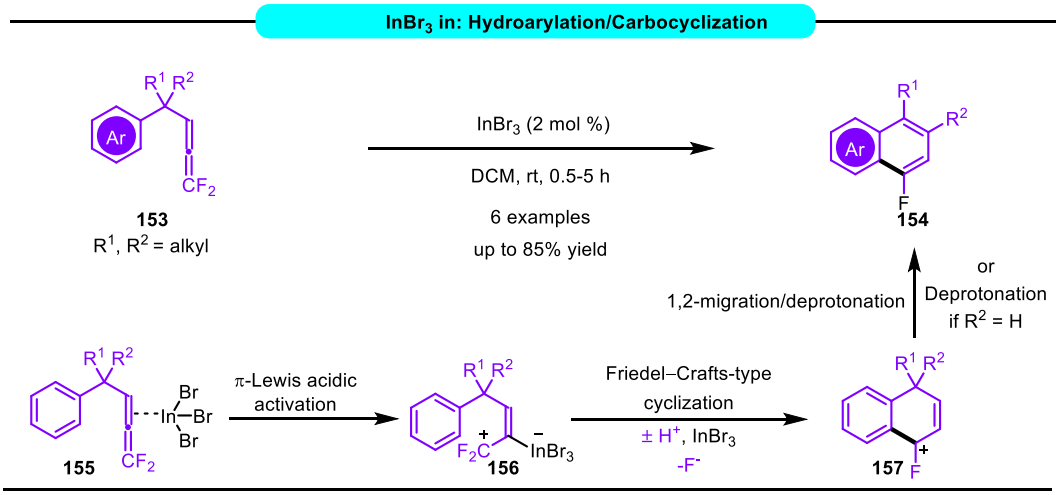
In 2018, Sestelo and his team presented the $InBr_3$-catalyzed hydroarylation/cycloisomerization of arylpropargyl ether **150** for delivering a series of fused chromene derivatives **151** (Scheme 18).

The π-activation of triple bond with $InBr_3$ generates 4-aryl-2H-chromene intermediate **152**, which undergo cycloisomerization to furnish the polycyclic compounds **151**.[65]



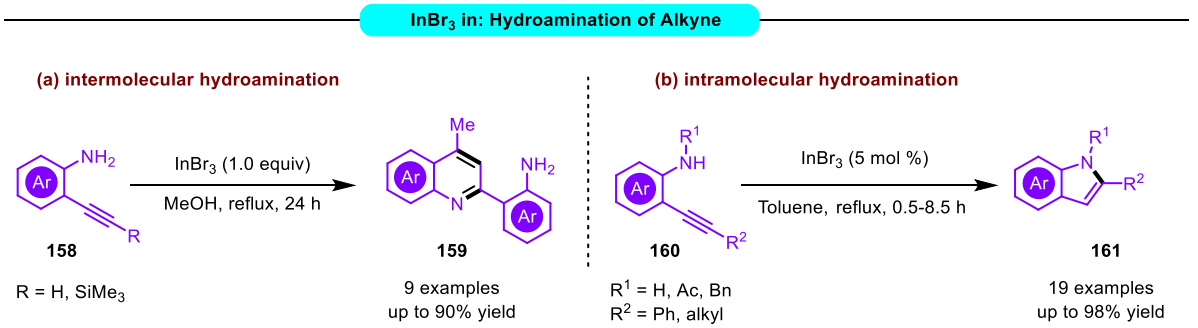
Scheme 18: $InBr_3$ Catalyzed Carbocyclization of Alkyne

In 2013 and 2014, Ichikawa and co-workers explored the catalytic reactivity of $InBr_3$ in cationic cyclization of 1,1-difluoroallenes **153** to deliver various fluorine-substituted polycyclic hydrocarbons **154** in a regioselective manner. The π-activation **155** of allene by $InBr_3$ generates the allylic carbocation **156** that undergoes intramolecular Friedel–Crafts-type cyclization **157** followed by rearomatization to deliver the polycyclic compounds (Scheme 19).[66]



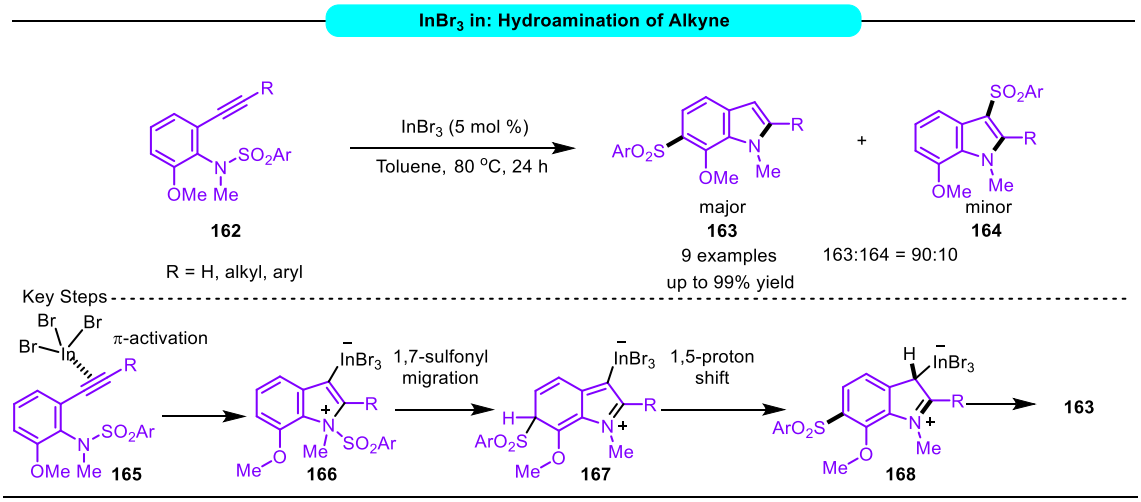
Scheme 19: $InBr_3$ Catalyzed Hydroarylation/Carbocyclization of Alllene

<u>$InBr_3$-catalyzed Intramoleuclar Heterocyclization/Hydroamination and Multicomponent Reactions:</u> The strong σ-, π- and dual activation of the substrates by $InBr_3$ open a door for several heterocyclization and multicomponent reactions. In 2006, Konakahara and co-workers employed $InBr_3$ for the synthesis of indole derivatives **161** via intramolecular hydroamination of aryl alkynes **160** (Scheme 20-b). However, the terminal or trimethyl silly substituted internal alkynes **158** with an stoichiometric amount of $InBr_3$ undergo intermolecular hydroamination (dimerization) reactions to generate quinoline derivatives **159** (Scheme 20-a).[67]



Scheme 20: $InBr_3$ Catalyzed Hydroamination of Alkyne

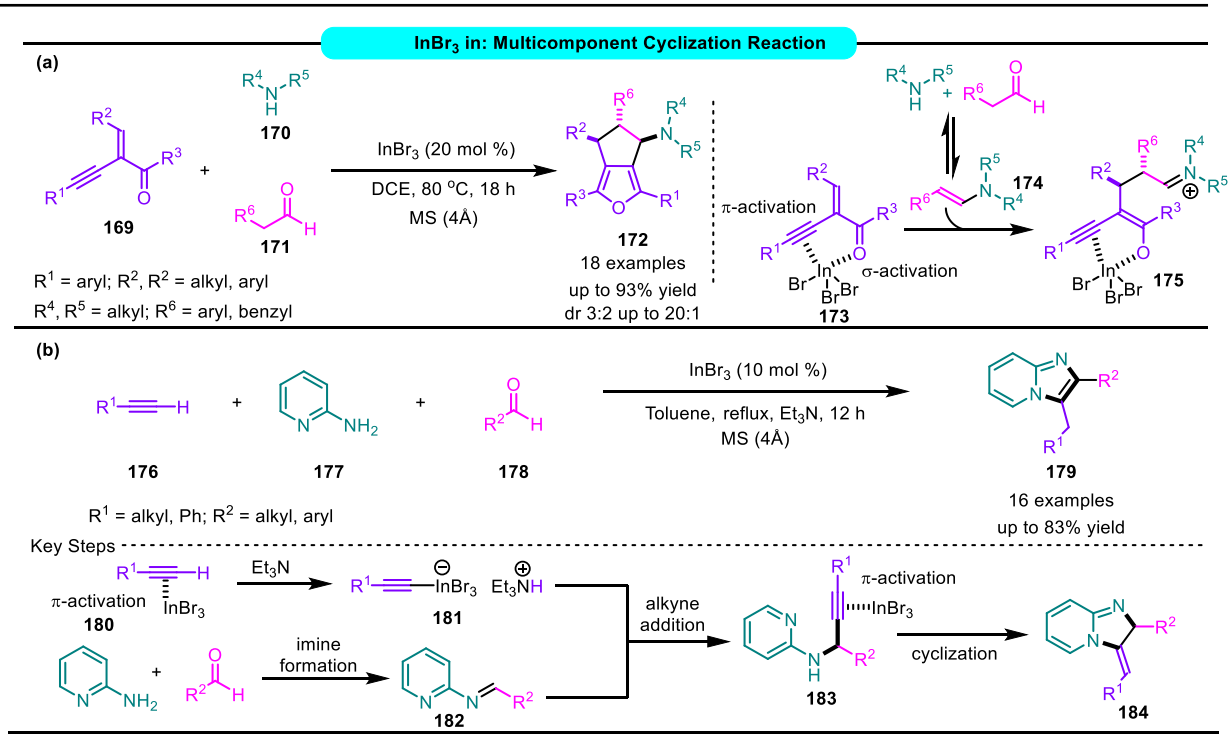
Later in 2007, the group of Yamamoto documented intramolecular hydroamination of 2-alkynyl-6-methoxy-*N*-sulfonylanilines **162** by using $InBr_3$ in catalytic amount. The Lewis acidic $InBr_3$ forms a π-complex **165** with the alkyne, and the nucleophilic attack by *N*-atom to the activated C–C triple bond forms a cyclic intermediate **166**. Then consecutive 1,7-sulfonyl **167** and 1,5-proton transfers **168** furnish 6-sulfonylindoles derivatives **16**3 in an unprecedented fashion (Scheme 21).[68]



Scheme 21: $InBr_3$ Catalyzed Intramolecular Hydroamination of Alkyne

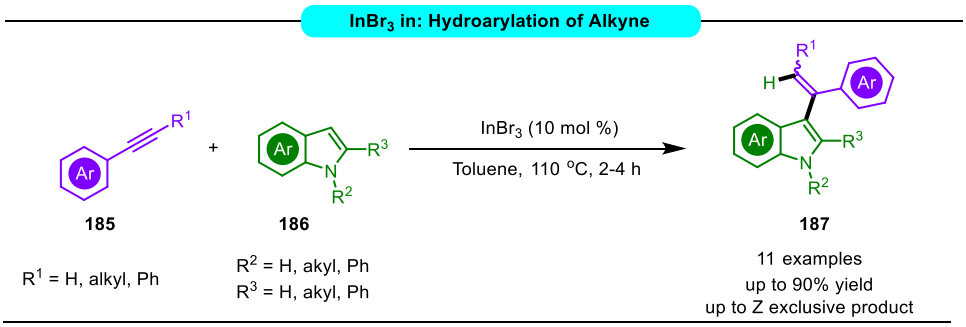
In 2016, Selander and co-workers employed $InBr_3$ as catalyst in a three-component cyclization reaction for the synthesis of highly substituted cyclopenta[c]furans **172** with a good diastereomeric ratio. The dual activation of $InBr_3$ to the σ- and π- sites plays an important role in such multi component reactions. The *in situ* formed enamine **174** from amine **170** and aldehyde **171** performed a nucleophilic attack on activated alkynyl enone **173** and produced intermediate **175**. The intermediate **175** can undergo cyclization to furnish the highly substituted fused furan derivatives **172** (Scheme 22-a).[69]

Reddy and his team also developed $InBr_3$-catalyzed three-component reaction for the synthesis of imidazo[1,2-a]pyridines **179**. The aminopyridine **177** and aldehyde **178** form *in situ* imine **182**, followed by the alkyne addition **183** (deprotonated through π-activation **180** with $InBr_3$ and Et_3N of alkyne) and cyclization (Scheme 22-b).[70]



Scheme 22: $InBr_3$ Catalyzed Multicomponent Cyclization Reaction

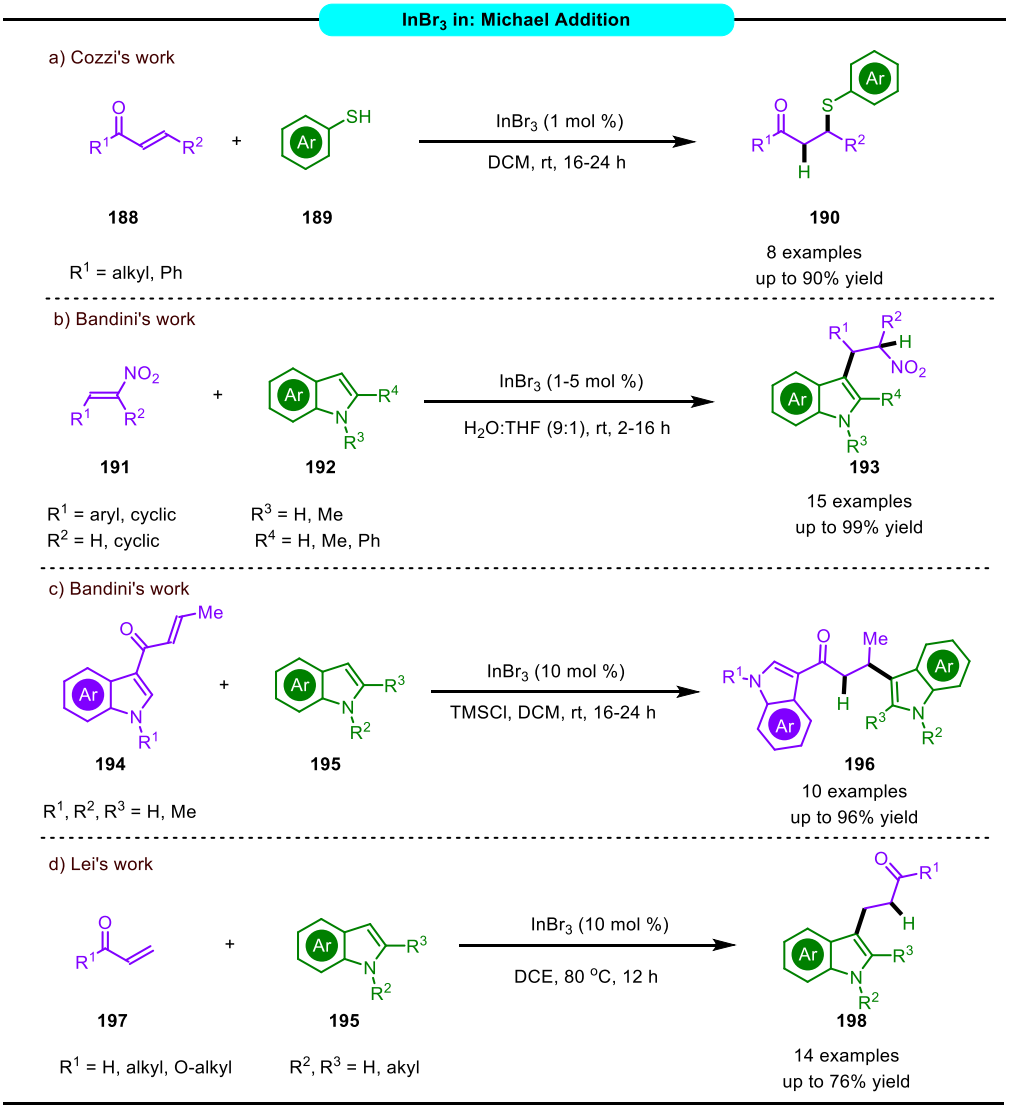
$InBr_3$-catalyzed Intermolecular Hydroarylation/Michael Addition Reactions: Perumal and his team reported an $InBr_3$-catalyzed, intermolecular hydroarylation **187** of alkynes **185** with indole **186** (Scheme 23).[71]



Scheme 23: $InBr_3$ Catalyzed Hydroarylation of Alkyne

Michael addition reactions of α-, β-unsaturated ketones are the easiest approach to construct C–C and C–heteroatom bonds. The $InBr_3$ remains one of the most noticeable candidates as the main group Lewis acid catalyst to accomplish these atom-economic reactions in the easiest manner. With respect to this kind of catalytic reactivity of $InBr_3$, different C–C and C–heteroatom bond-forming reactions were explored by Cozzi,[72] Bandini,[73] and Lei[74]. Cozzi presented the addition of aryl thiols **189** to enones **188** for the construction of C–S bonds **190** (Scheme 24-a). Bandini and co-workers documented the addition of indoles **192** onto nitroalkenes **191** by using $InBr_3$ under aqueous conditions (Scheme 24-b). Then Later, they synthesized various 1,3-Bis(indolyl) compounds **196** by using $InBr_3$/TMSCl catalyst (Scheme 24-c). In 2010, Lei

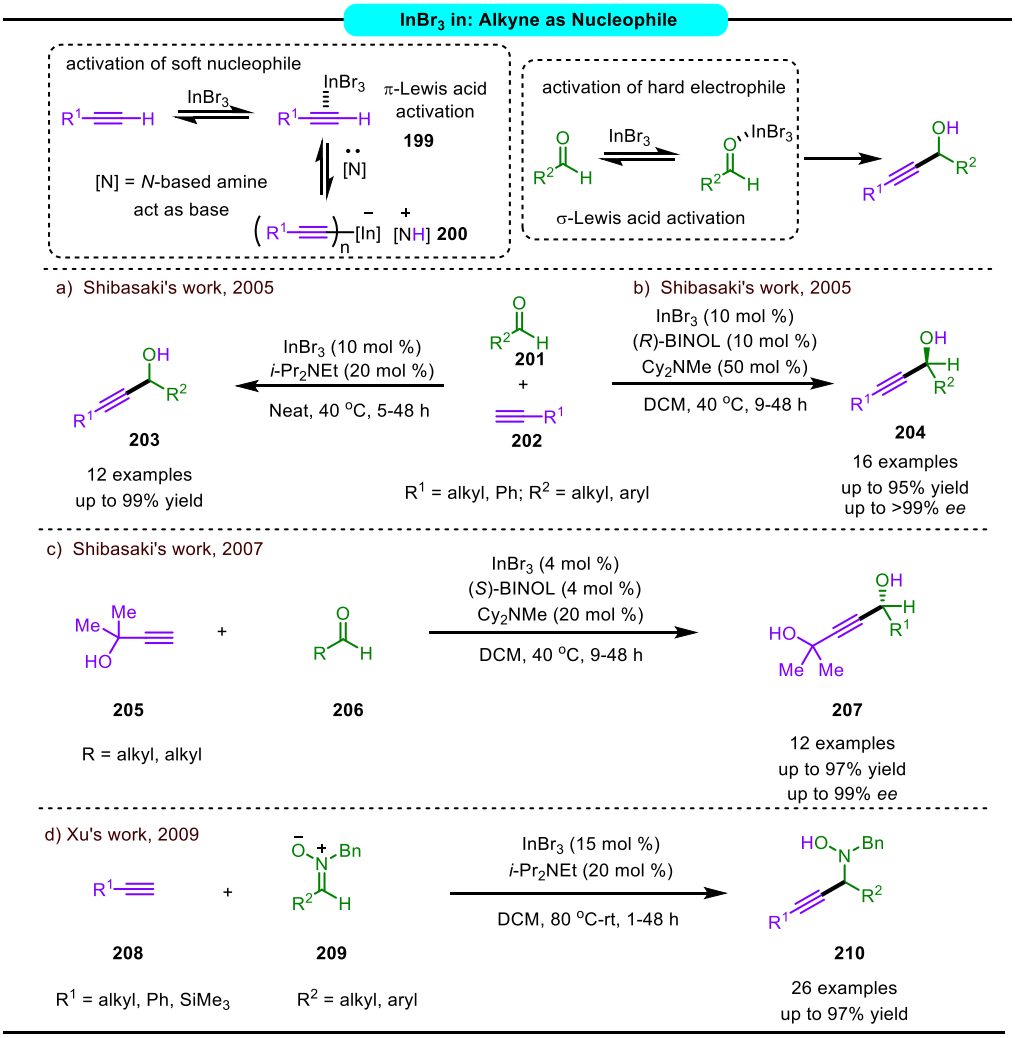
similarly explored the addition of indole **195** to the acrylate derivatives **197** without using any additive (Scheme 24-d).



Scheme 24: $InBr_3$ Catalyzed Michael Addition/Hydroarylation Reactions

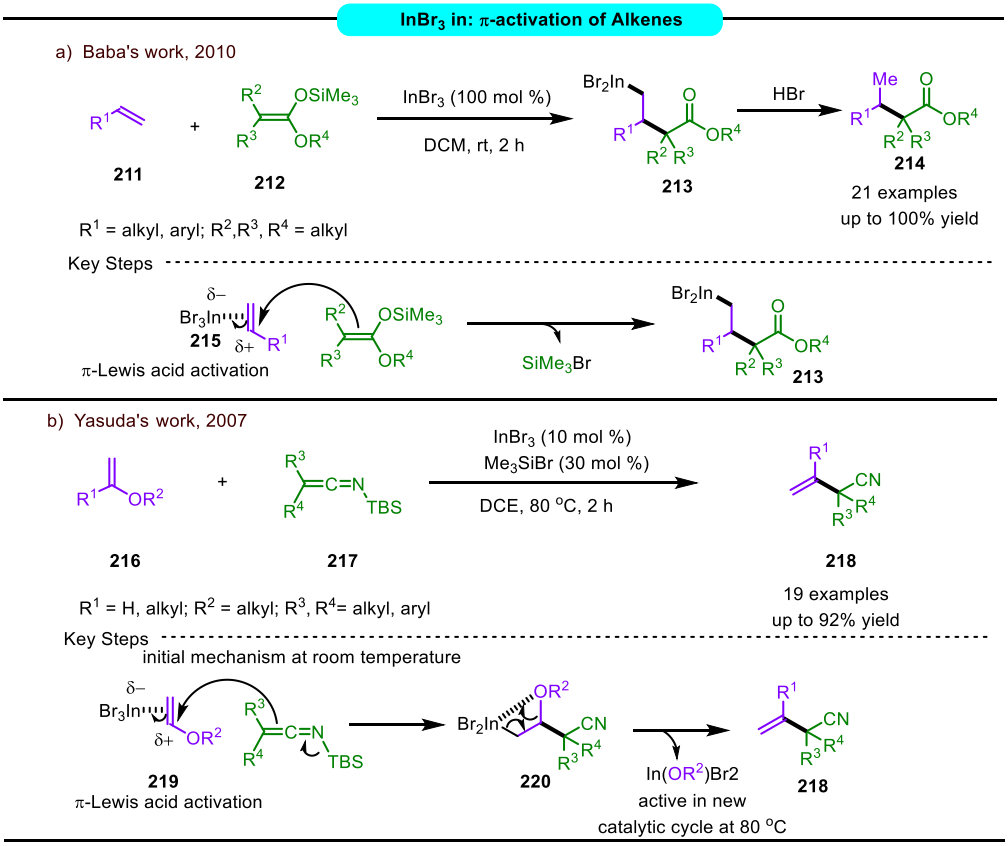
$InBr_3$-catalyzed Reactions Involving Terminal Alkynes as Nucleophiles: Numerous approaches are available for the alkynylation reactions in literature by using diverse procedures. Among them, $InBr_3$, with a mild base such as amines, remains one of the prominent candidates in the last two decades. $InBr_3$ transforms alkyne into indium acetylide **199** via π-activation of C–C triple bonds followed by proton abstraction **200** in presence of base. These indium acetylides can be employed in nucleophilic addition to the carbonyl group as well as in transmetallation for coupling reactions. In 2005, Shibasaki and co-workers exploited the combination of $InBr_3$/*i*-Pr_2NEt as a catalyst for the alkynylation of aldehydes **201** (Scheme 25-a). In this study, they have showed the dual activity of $InBr_3$ in the activation of hard electrophiles (carbonyl, via σ-Lewis acidity) and soft nucleophiles (alkyne, via π-Lewis acidity). Then later in the same year, they advanced the enantioselective alkynylation of aldehydes **201** by using chiral ligand (*R*-BINOL)

with $InBr_3$ and mild base *N*,*N*-dicyclohexylmethylamine (Scheme 25-b).[75] After two years, in 2007, the same group utilized a similar reactivity for the 2-methyl-3-butyn-2-ol **205** as an alkyne partner (Scheme 25-c).[76] The group of Xu also contributed to this field as the alkynylation of nitrons **209** and synthesized numerous *N*-hydroxy-propargyl amine derivatives **210** (Scheme 25-d).[77]



Scheme 25: $InBr_3$ Catalyzed Alkyne Addition Reactions

$InBr_3$-catalyzed Reactions Involving Electrophilic Activation of C–C Double Bonds: The activation of C–C double bond remains a prominent method that unlocks door for new C–heteroatom/C–C bonds formation to create molecular complexity. The $InBr_3$ likewise exploited by Baba's group for carboindation **213** of alkene **211** with ketene silyl acetals **212** in 2010 (Scheme 26-a).[78] In this work, the stoichiometric amount of $InBr_3$ was used, and the addition of 1M HBr furnished the demetalated product **214** in good yields. Later in 2015, Yasuda and his team employed this π-activation **219** by catalytic $InBr_3$ into the coupling of enol ethers **216** with silyl ketene imines **217** for the synthesis of nitrile derivatives **218** (Scheme 26-b).[79]



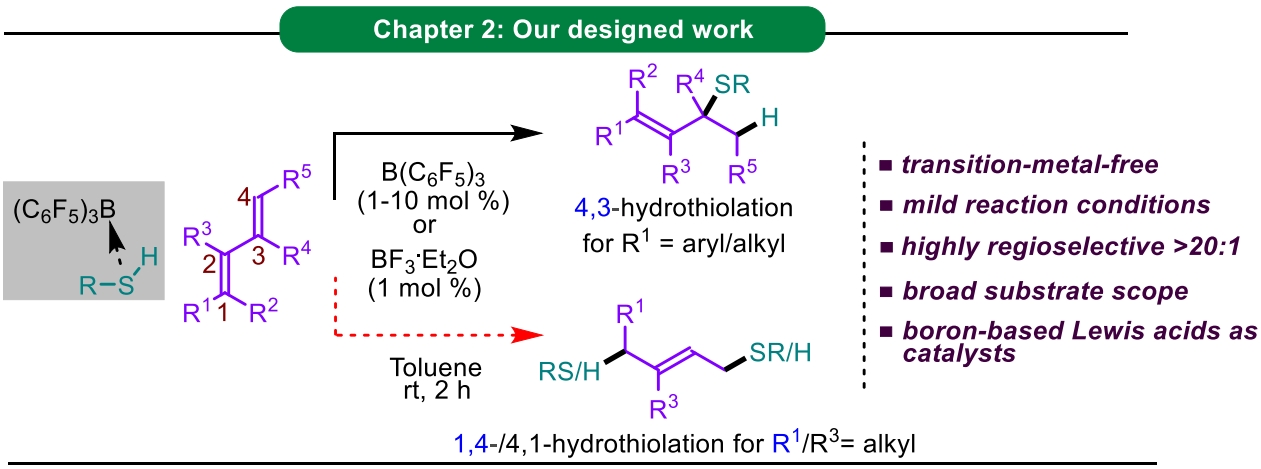
Scheme 26: $InBr_3$ Catalyzed/Mediated Reactions Involving π-activation of Alkene

1.4. Conclusion

In this chapter, we have explored several interesting features such as; a) a brief overview of Lewis acids, b) a short survey of main group Lewis acids and their reactivities, c) various important roles of unsaturated C–C bonds in organic transformations, d) applications of $B(C_6F_5)_3$ in several organic transformations for functionalization of unsaturated C–C bonds, and finally e) the chemistry of $InBr_3$ in functionalization of unsaturated compounds. These robust discussions of fundamental chemistry as well as extensive literature studies will provide a suitable platform to understand the chemistry involved in the upcoming chapters.

Chapter 2

Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated 1,3-Dienes with Thiols



❖ This work was published in ACS Catalysis (a journal of ACS). Please see the citation as: "**Kumar, G.;** Qu, Z-W.; Ghosh, S.; Grimme, S.; Chatterjee, I. *ACS Catal.* **2019**, *9*, 11627−11633."

2. Abstract

In this chapter, a transition-metal-free regioselective hydrothiolation of 1,3-conjugated dienes with thiols for procuring allylic sulfide derivatives is documented. Boron-based catalysts tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, and $BF_3{\cdot}Et_2O$ catalyze the reaction, low catalyst loading (1 mol %) for terminal 1-aryl-1,3-dienes. In the case of substituted internal 1,3-conjugated dienes, $B(C_6F_5)_3$ emerged as a worthier catalyst than $BF_3{\cdot}Et_2O$. This protocol has certain trademarks, which include low catalyst loading and mild reaction conditions with short reaction time. The DFT inquisition and ^{11}B NMR appraisal reveal that the reaction proceeds via allylic carbocationic intermediate formation from the borane-thiol complex.

2.1. Introduction

As discussed in chapter 1, the boron Lewis acids can interact with the lone pair of electrons of heteroatom and form the σ–complex. In this regard, the Lewis acid-catalyzed hydrothiolation reactions remain very important via σ–complex formation of thiols with Lewis acids. By using this Lewis acid-thiol complexation strategy, several important structural motifs containing C–S bond can be synthesized. This chapter will discuss an interesting and spacious method for contriving the C–S bond to accomplish allylic sulfide derivatives. We have displayed the synthesis of such value-added allylic sulfide via hydrothiolation of 1,3-conjugated dienes.

Organosulfur compounds, especially allylic sulfides and their derivatives remain highly important and value-added building blocks, serving as key synthons for synthetic organic chemists. These compounds show numerous bioactivities for different biological purposes (Figure 10). Also, these allylsulfides play a significant role in pharmaceuticals industries. However, organosulphur compounds contributed 20% to the FDA-approved drugs.[80]

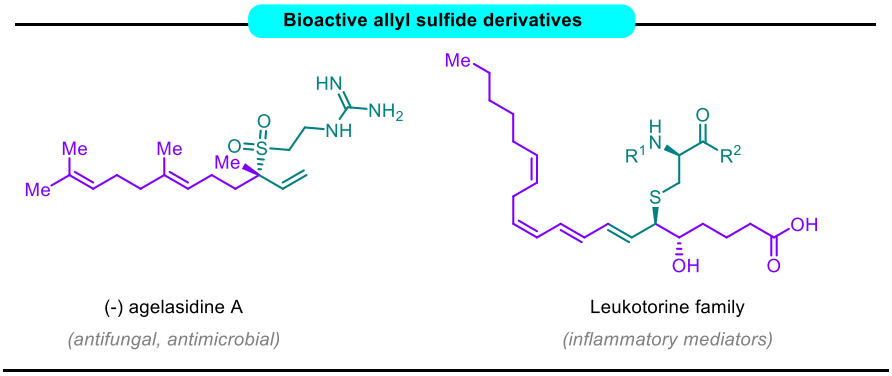


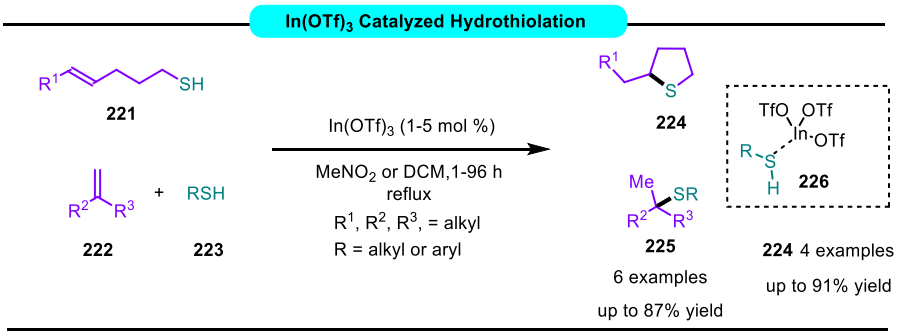
Figure 10: Allyl Sulfide/Sulfone Containing Bio-active Candidates

In recent years, the development of a worthwhile approach for the construction of C−S bonds gained the significant attention of synthetic chemists from all over the globe. The C−S bond-forming reactions involving thiol addition onto olefin is a straightforward and atom-economical approach for the synthesis of organosulfur compounds.[81] A plethora of reports is there in the literature on transition-metal-catalyzed hydrothiolation of olefin; however, the transition-metal-

free hydrothiolation remains less explored.[82] Moreover, the synthesis of allylic sulfides from 1,3-dienes via main-group Lewis acid-catalyzed hydrothiolation is yet to be explored. However, using a radical initiator, the thiol addition to the 1,3-dienes is achieved albeit with a mixture of regioisomers and other side products.[83] Brønsted acid-catalyzed hydrothiolation of dienes was also reported in the literature by different scientists.[84] The transition-metal catalyzed regioselective hydrothiolation of conjugated 1,3-dienes was commenced by He and co-workers in 2007[85], and Dong group in 2018-2019.[86] Here we have showcased the Lewis acid catalyzed and other literature reports for the hydrothiolation of olefin systems.

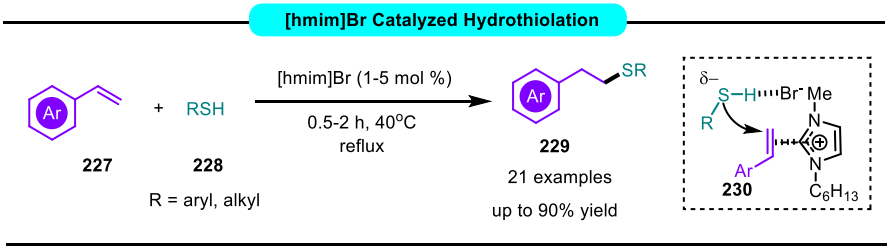
2.1.1 Literature Reports for the Transition-Metal-Free Hydrothiolation of Olefins

In 2006, Duñach and co-workers developed a Markovnikov hydrothiolation of non-activated olefin derivatives **222** with the combination of $In(OTf)_3$ and thiols derivatives **223** (Scheme 27).[87] This methodology featured the regioselectivity and inter-/interamolecular hydrothiolation for the synthesis of cyclic/acyclic thioether derivatives **224**, **225**. The catalyst loading was 5 mol % in some cases, but they have claimed that without solvent, 1 mol % catalyst is enough for this reaction. The successful hydrothiolation of symmetrical internal conjugated 1,3-diene (e.g., 2,5-dimethyl-2,4-hexadiene) was also achieved. The Lewis acidic $In(OTf)_3$ forms complex **226** with thiol moiety, which induces the $[In(RS)(OTf)_3]^-H^+$ with a key feature of Brønsted acidity for the protonation of olefins. This complex **226** also enhances the nucleophilicity of thiolate.



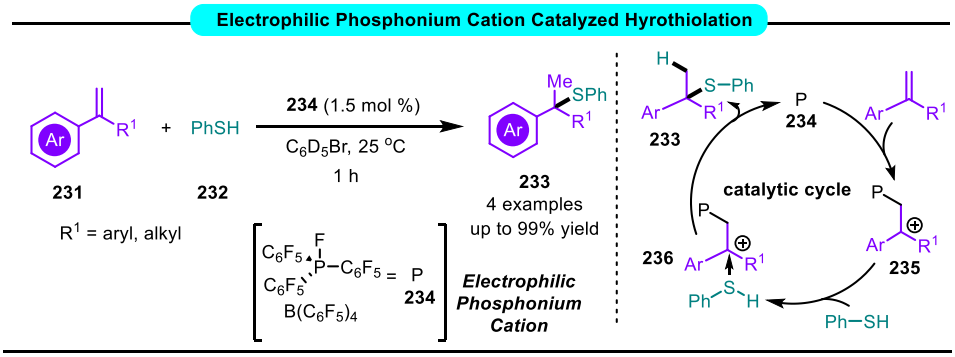
Scheme 27: Duñach's Hydrothiolation of Olefins

In 2015, Sinha and co-workers utilized ionic liquids for the hydrothiolation of olefins **227** with thiols **228** (Scheme 28).[88] They have synthesized selectively anti-Markovnikov hydrothiolated linear thioether derivatives **229**. In this reaction, ionic liquid simultaneously activates the olefin and thiols at the same time. The counter anion Br^- of the ionic liquid undergoes hydrogen bond (H–B) formation with the S–H group (nucleophilic activation). At the same time, the C-2 hydrogen of the hmim cation interacts with π–electron density of olefin through the H–B bond (electrophilic activation) **230**. The nucleophilic attack of thiols onto alkenes leads to the formation of hydrothiolated products.



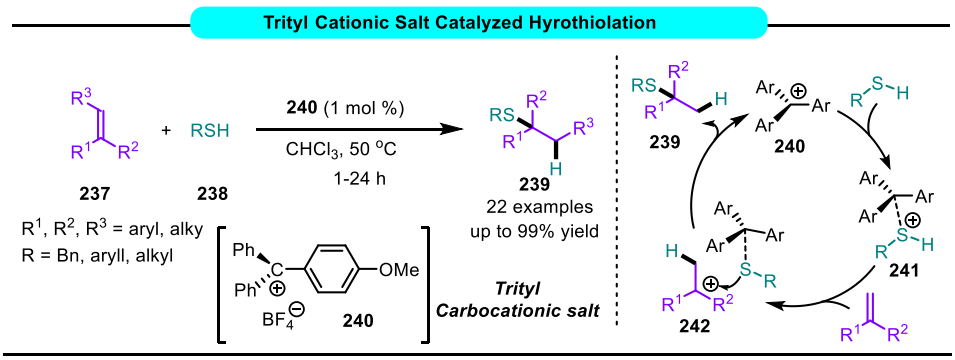
Scheme 28: Sinha's Hydrothiolation of Olefins

In the same year, Stephan research group projected electrophilic phosphonium cations catalyzed hydrothiolation of olefin derivative **231** (Scheme 29).[89] Very few examples have been depicted using this method. They proposed a catalytic pathway where phosphonium cation **234** first activates the olefin to generate carbocationic intermediate **235**. The addition of thiol to this carbocationic intermediate **235** via nucleophilic attack furnishes the hydrothiolated products **233** in good yield.



Scheme 29: Stephan's EPC-Catalyzed Hydrothiolation

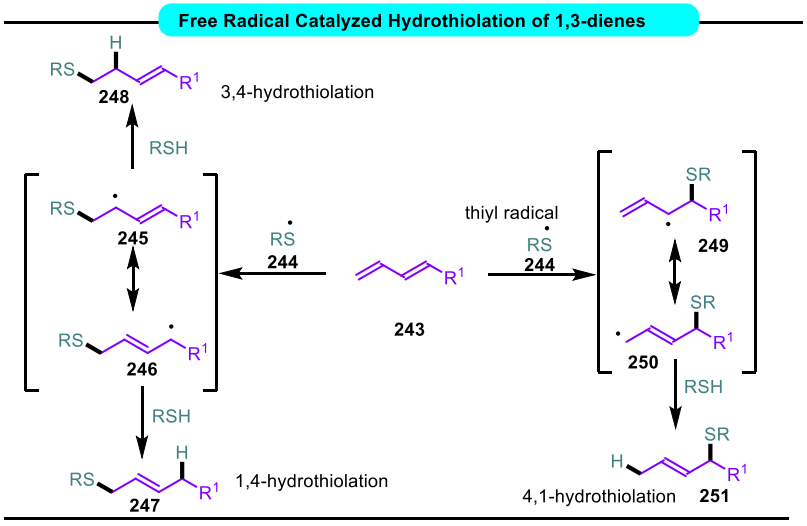
In the next year, the same group introduced the trityl cation (carbocationic salts) **240** catalyzed hydrothiolation of olefins **237** (Scheme 30).[90] In this protocol, the trityl carbocations form a complex **241** with thiol, which prompts the protonation of olefin, and generates the carbocationic intermediate **242**. This carbocationic intermediate **242** is accessible for the thiolate transfer to furnish the hydrothiolated products **239** in a Markovnikov manner and release the trityl cation to regenerate the catalyst.



Scheme 30: Stephan's Trityl Cationic Salt Catalyzed Hydrothiolation

2.1.2 Literature Reports for the Hydrothiolation of 1,3-Dienes

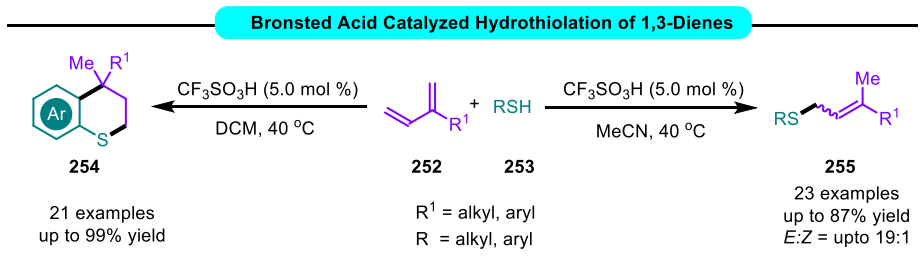
Till the 1970s, various hydrothiolation reactions of conjugated olefins was developed using radical initiator. The major issue associated with them is the polymerization and regioisomer formation which was difficult to separate.[83] In 1973, Wallis and co-workers achieved various hydrothiolation at diene and triene systems using 0.05 mol % benzoylperoxide as a radical initiator. All the products were isolated by distillation and preparatory G.L.C; still, high boiling bi-adducts and oligomers were observed in many cases. The thiyl radical **244** addition on diene **243** constructs the C–S bond in different regioisomeric manner, e.g., 3,4-(**248**)/1,4-(**247**)/4,1-(**251**) hydrothiolation (Scheme **31**).[91]



Scheme 31: Wallis's Free Radical Mediated Hydrothiolation Pathways

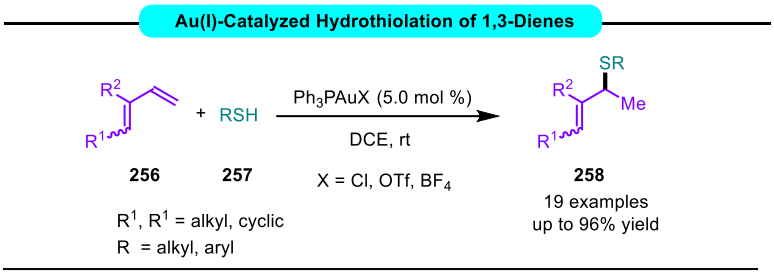
In 1962, Saville documented perchloric acid catalyzed hydrothiolation of 2-methylpenta-l,3-diene with alkyl thiols. The major problem in the Brønsted acid-catalyzed hydrothiolation of conjugated dienes is the dimerization of diene. Therefore, to minimize the dimerization of diene under 78 % perchloric acid conditions, slow addition of dienes at 5-15 ^{o}C was performed.[84]

In 2021, Chen and co-workers introduced triflic acid-catalyzed hydrothiolation of 1,3-dienes **252** (Scheme 32)[92]. They have synthesized various allyl sulfides **255** and thiochromane **254** derivatives in MeCN and DCM solvents, respectively. This reaction featured the effect of solvents in the end product formation. A milder reaction condition with 5 mol % of triflic acid is sufficient to afford good yield and selectivity.



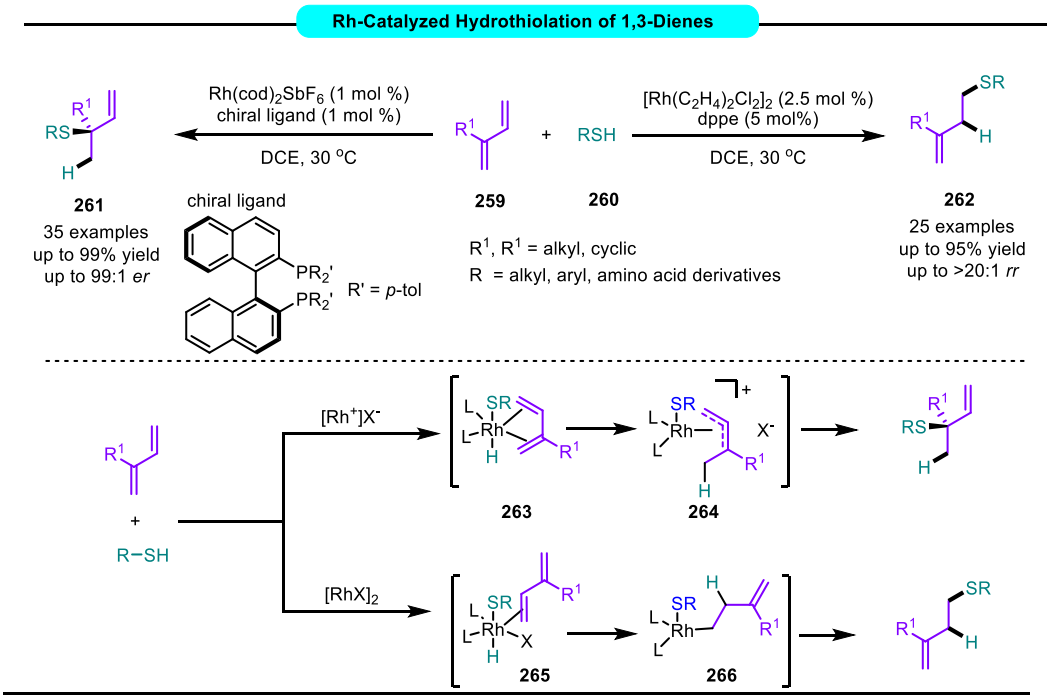
Scheme 32: Chen's Hydrothiolation of 1,3-deiens

However, He and co-workers demonstrated Gold (I)-catalyzed hydrothiolation of 1,3-dienes **256**, to furnish the allylic sulfide **258** derivatives at a 5 mol % catalyst loading (Scheme 33)[85]. This reaction shows high functional group tolerance, e.g., alcohol, amide, carbonyl, nitro, and also both aromatic and aliphatic thiols furnish good yield. The milder reaction conditions make this methodology interesting for the hydrothiolation of 1,3-dienes. The only drawback of this reaction is the formation of mixture of Markovnikov and anti-Markovnikov products in some cases. The mechanistic pathway remains unclear for this reaction, but author suggested that at first cationic Gold (I)-catalyst polarizes to the π-electron density of the diene, which undergoes nucleophilic attack by thiols.



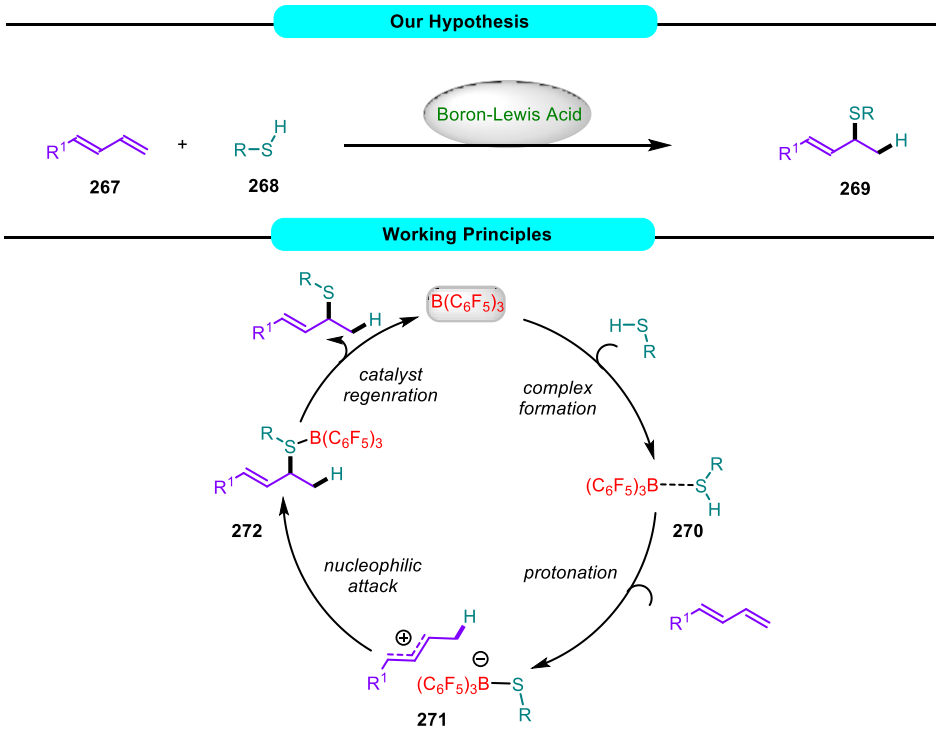
Scheme 33: He's Hydrothiolation of 1,3-deiens

In the same line, Dong and co-workers explored the Rh-catalyzed hydrothiolation of 1,3-dienes **259** in regio- **261** and enantioselective **262** fashion. In two consecutive years, 2018, and 2019 they published two works for selectively *R* or *S* enantiomer synthesis by changing the counter anion of the Rh-complex (Scheme 34)[86].



Scheme 34: Dong's Hydrothiolation of 1,3-deiens

From the above-discussed literature reports, it is well evident that the prior works for the synthesis of allylic sulfides majorly depend on the radical initiator-mediated, Brønsted acid, and transition-metal-catalysis and associated with handling and economic issues. Therefore, in search of milder and simpler reaction conditions, we have developed a borane-catalyzed reaction conditions to carry out the hydrothiolation of 1,3-dienes for the synthesis of allylic sulfides. Previously, in the introduction part, we have discussed σ- and π- activation modes of the main group Lewis acid in heteroatom and unsaturated bonds containing compounds, respectively. On the basis of our literature survey, we have hypothesized our reaction for the hydrothiolation of 1,3-diene, where borane can form a σ-complex **270** with thiol (through S-atom) and make the thiolic proton (S−H) enough Brønsted acidic to protonate 1,3-diene and generate a carbocationic intermediate **271**. This carbocation can be trapped by thiolate to furnish the regioselective hydrothiolation products **269** (Scheme 35).



Scheme 35: Chapter 2: Our Proposed Working Hypothesis

2.1.3 Challenges for the Hydrothiolation of 1,3-dienes

The hydrothiolation of 1,3-diene molecules can be associated with different challenges, e.g., oligomerization, polymerization, and regioselectivity issues. The possible regioisomers in hydrothiolation of 1,3-dienes are depicted here in figure 11.

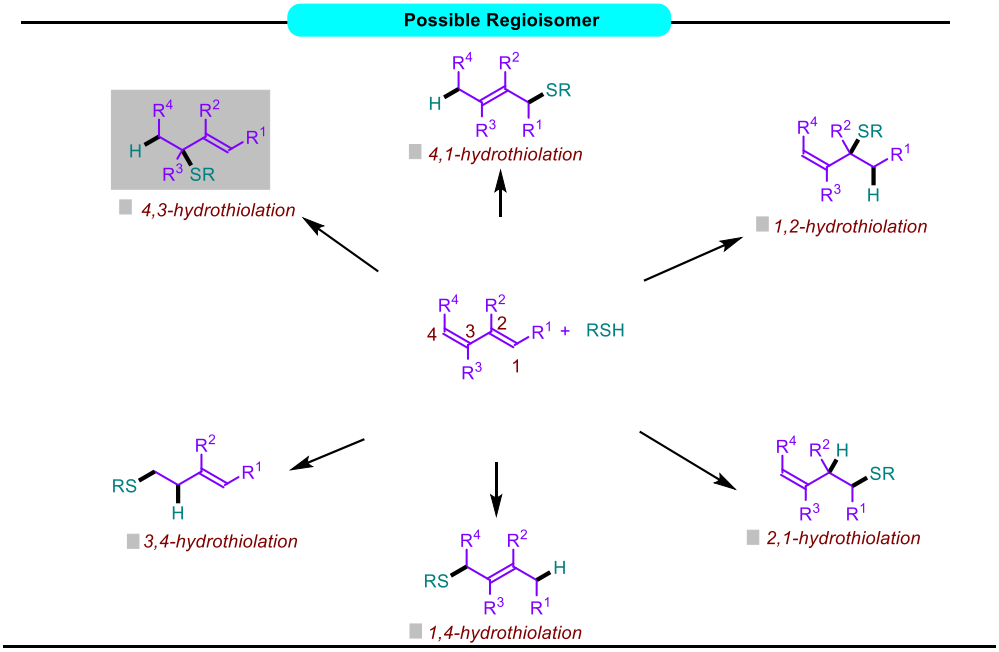


Figure 11: Chapter 2: Regioselectivity Challenges in Hydrothiolation of 1,3-dienes

2.2. Result and Discussion

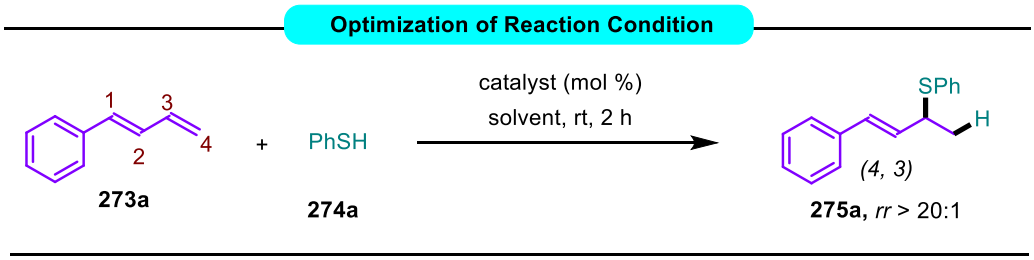
2.2.1 Optimization of the Reaction Condition

As per our proposed hypothesis (in Scheme 35), we sought for a unique transition-metal-free Lewis acid catalyzed regioselective hydrothiolation protocol for the synthesis of diverse array of primary and secondary allyl sulfide derivatives. In pursuit of checking the feasibility of our proposal, we commenced our enquiry by reacting (*E*)-buta-1,3-dien-1-ylbenzene (**273a**, 1.2 equiv) with thiophenol (**274a**, 1.0 equiv) as the model substrates in various solvents (1.5 M), and in the presence of catalyst $B(C_6F_5)_3$ (10 mol %). catalyst at rt for 2 h (Table 1)

While solvents like dioxane, THF and EtOH provided no conversion, $MeNO_2$ promoted the reaction with 20% ^1H NMR yield (Table 1, entries 1–4). However, the reaction in dichloromethane (DCM) resulted in a drastic improvement of the reactivity delivering **275a** in 61% yield and complete regioselectivity for 4,3-hydrothiolation (Table 1, entry 5). 1,2-difluorobenzene also showed similar reactivity like DCM (Table 1, entry 6). To our delight, using toluene as a solvent, the desired product **275a** was obtained in excellent isolated yield and regioselectivity (>20:1 *rr*). The catalyst loading can be lowered to 1 mol % without affecting the yield (Table 1, entries 7–11). Interestingly, $BF_3{\cdot}Et_2O$ also furnished the desired product **275a** in high yield (Table 1, entry 12). Other boron Lewis acid, BCl_3, provided **3** with 83% isolated yield (Table 1, entry 13). Tf_2NH and transition-metal based catalyst $Cu(OTf)_2$ were also able to catalyze the reaction, albeit in lower yield (Table 1, entry 14–15). Interestingly, using excess (10 mol %) $BF_3{\cdot}Et_2O$ and Tf_2NH we obtained a lower yield of **275a** owing to the oligomerization of

273a. Notably, the reactions conducted with the catalysts $B(C_6F_5)_3$ and $BF_3{\cdot}Et_2O$ were much clean and easy to purify.

Table 1. Chapter 2: Optimization Study and Reaction Set Up



Entry	Catalyst (mol %)	Solvent	Yield 275a (%)[a]
1	$B(C_6F_5)_3$ (10)	1,4-dioxane	nr
2	$B(C_6F_5)_3$ (10)	THF	nr
3	$B(C_6F_5)_3$ (10)	EtOH	nr
4	$B(C_6F_5)_3$ (10)	$MeNO_2$	20
5	$B(C_6F_5)_3$ (10)	DCM	61
6	$B(C_6F_5)_3$ (10)	1,2-$C_6F_4F_2$	64
7	$B(C_6F_5)_3$ (10)	Toluene	99
8	$B(C_6F_5)_3$ (5)	Toluene	99
9	$B(C_6F_5)_3$ (2.5)	Toluene	99
10	**$B(C_6F_5)_3$ (1)**	**Toluene**	**>99/98[b]**
11	$B(C_6F_5)_3$ (0.5)	Toluene	66
12	**$BF_3{\cdot}Et_2O$ (1)**	**Toluene**	**88[b]**
13	BCl_3[c] (1)	Toluene	83[b]
14	Tf_2NH (1)	Toluene	75[b]
15	$Cu(OTf)_2$ (1)	Toluene	78[b]

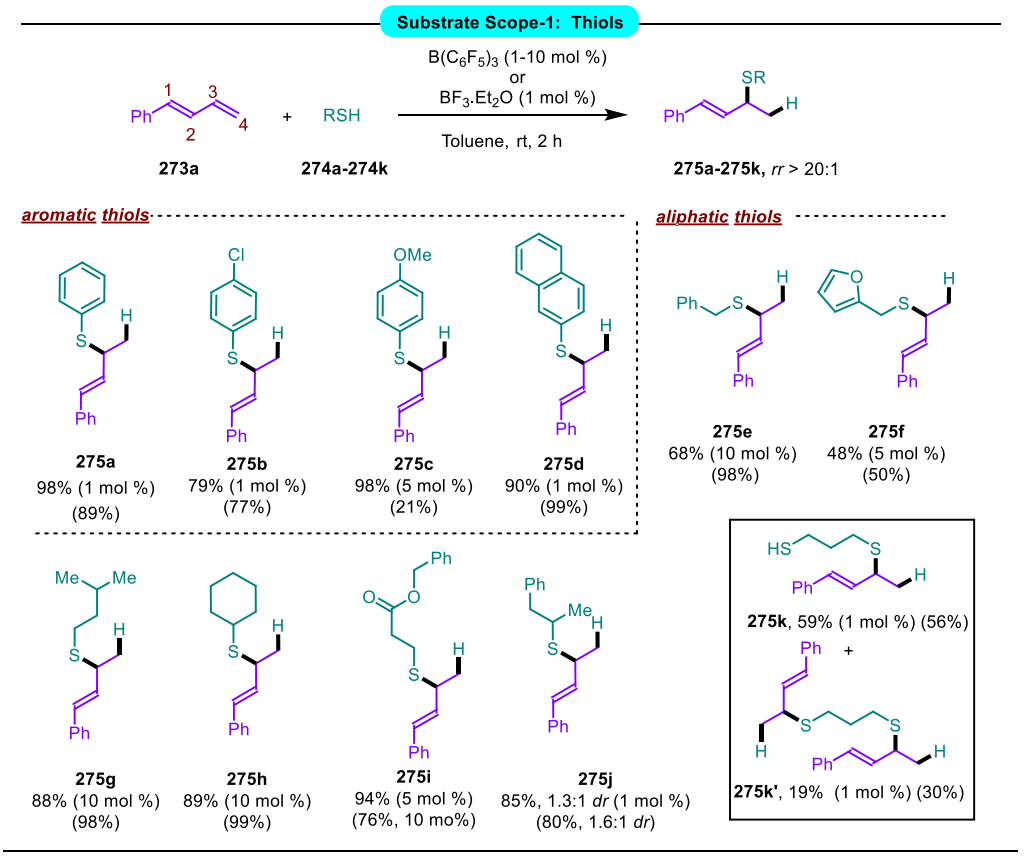
[a] Reaction condition **273a** (1.2 equiv) and **274a** (1.0 equiv) stirred in solvent at rt for 2 h. Yield determined by ^1H NMR using CH_2Br_2 as internal standard. Reaction scale for 1 mol % catalyst (0.58 mmol) and for 5 or 10 mol % (0.12 mmol); with $BF_3{\cdot}Et_2O$: for 1 mol % (0.90 mmol) [b] Isolated yield. [c] Used as 1M solution in DCM. nr = no reaction. *rr* = regiomeric ratio, determined by ^1H NMR of crude reaction mixture.

2.2.2 Substrate Scope Evaluation

After through screening of solvents and catalysts during optimization we have found $B(C_6F_5)_3$ and $BF_3{\cdot}Et_2O$ almost giving equal results. So, by utilizing these two optimized conditions (Table 1, entries 10 and 12) we started to explore the substrate scope for the hydrothiolation of 1,3-dienes with thiols.

Variation of thiols: In our initial substrate scope studies, we have checked several thiol derivatives (aliphatic and aromatic) by reacting them with (*E*)-buta-1,3-dien-1-ylbenzene (**273a**)

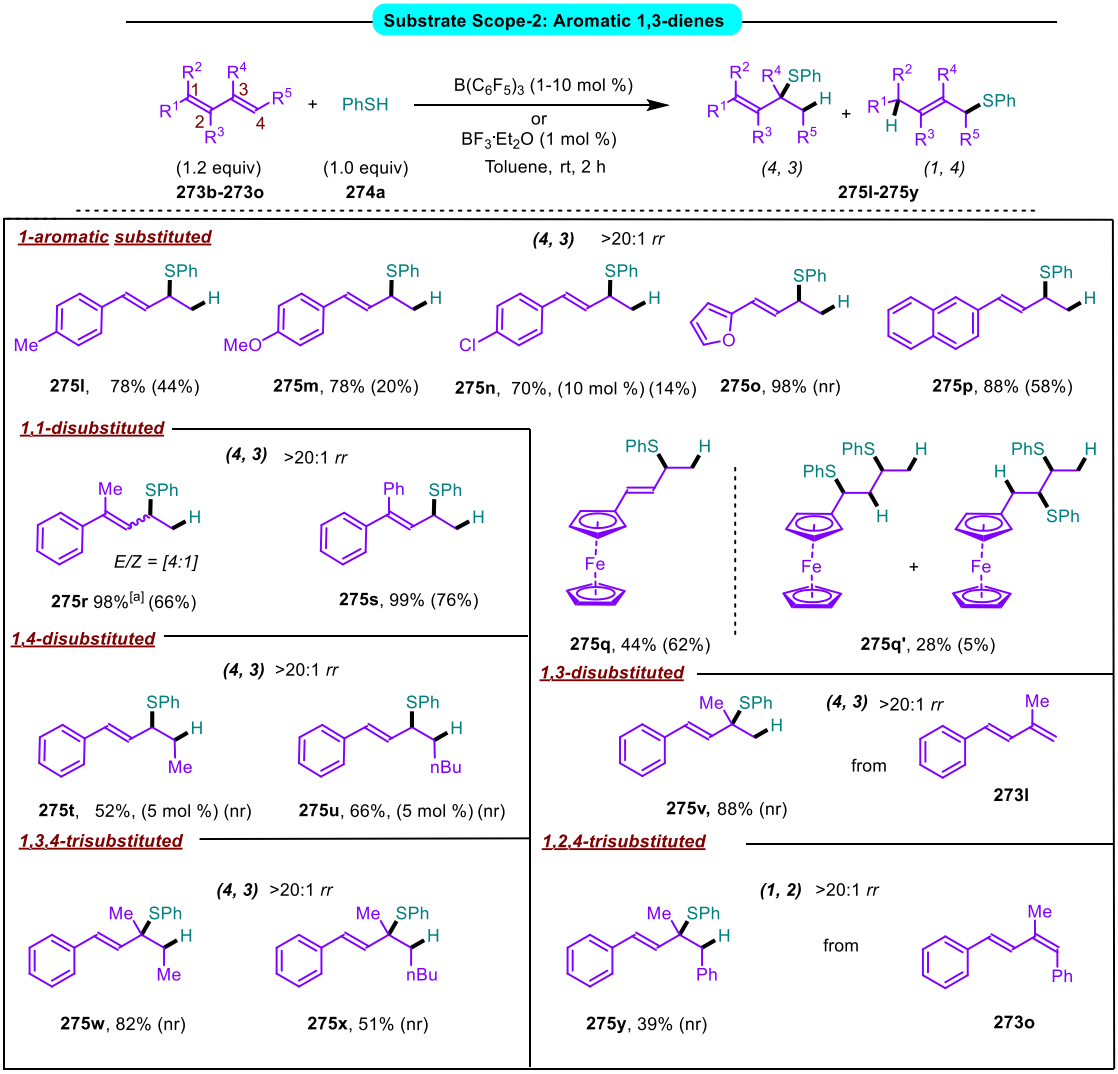
under reaction conditions 10 and 12. First we started with thiophenol and its *para*-substituted derivatives, e.g.; 4-chlorothiophenol, and 4-methoxythiophenol. These thiol partners worked smoothly and furnished allylic sulfides derivatives in excellant yields **275a–275c** with >20:1 *rr* using $B(C_6F_5)_3$. Using $BF_3{\cdot}Et_2O$ as a catalyst similar reactivity was observed except for the product **275c**. While naphthalene-2-thiol remained sufficiently reactive (Scheme 36, entry **275d**), aliphatic thiols were found to be less reactive, requiring higher catalyst loading of $B(C_6F_5)_3$. Aliphatic thiols having benzyl, heteroarene, and isobutyl group provided products **275e–275g** in good yields. Moreover, $BF_3{\cdot}Et_2O$ exhibited higher reactivity for aliphatic thiols (**275e–275h**) requiring only 1 mol % catalyst loading. High yield and regioselectivity were also observed for secondary thiol (**275h**). Thiol having ester functionality (**275i**) also worked smoothly in the presence of $B(C_6F_5)_3$, whereas high catalyst loading (10 mol %) of $BF_3{\cdot}Et_2O$ was required for a good yield of **275i**. Tertiary thiols such as Ph_3CSH remained unreactive probably due to steric effects. The employment of a racemic thiol led to the formation of allylic sulfide **275j** in *dr* = 1.3:1 and 1.6:1 in the presence of $B(C_6F_5)_3$ and $BF_3{\cdot}Et_2O$ respectively. Additionally, using propane-1,3-dithiol, an intermolecular di-hydrothiolation product **275k′** was detected along with the desired hydrothiolation product **275k**, which were easily separable.



Scheme 36: Substrate Scope of Thiols Variation for Hydrothiolation

Variation of aromatic 1,3-dienes: Next, we investigated the scope of various substituted 1,3-dienes using thiophenol **274a** as a model thiol substrate, as depicted in Scheme 37. Terminal 1-

aryl 1,3-dienes with Me, OMe and Cl substituents (**275l–275n**) worked well with high regioselectivity for the 4,3-hydrothiolation. Both 1-heteroaryl and 2-naphthalenyl 1,3-dienes were found to be equally reactive (**275o** and **275p**).

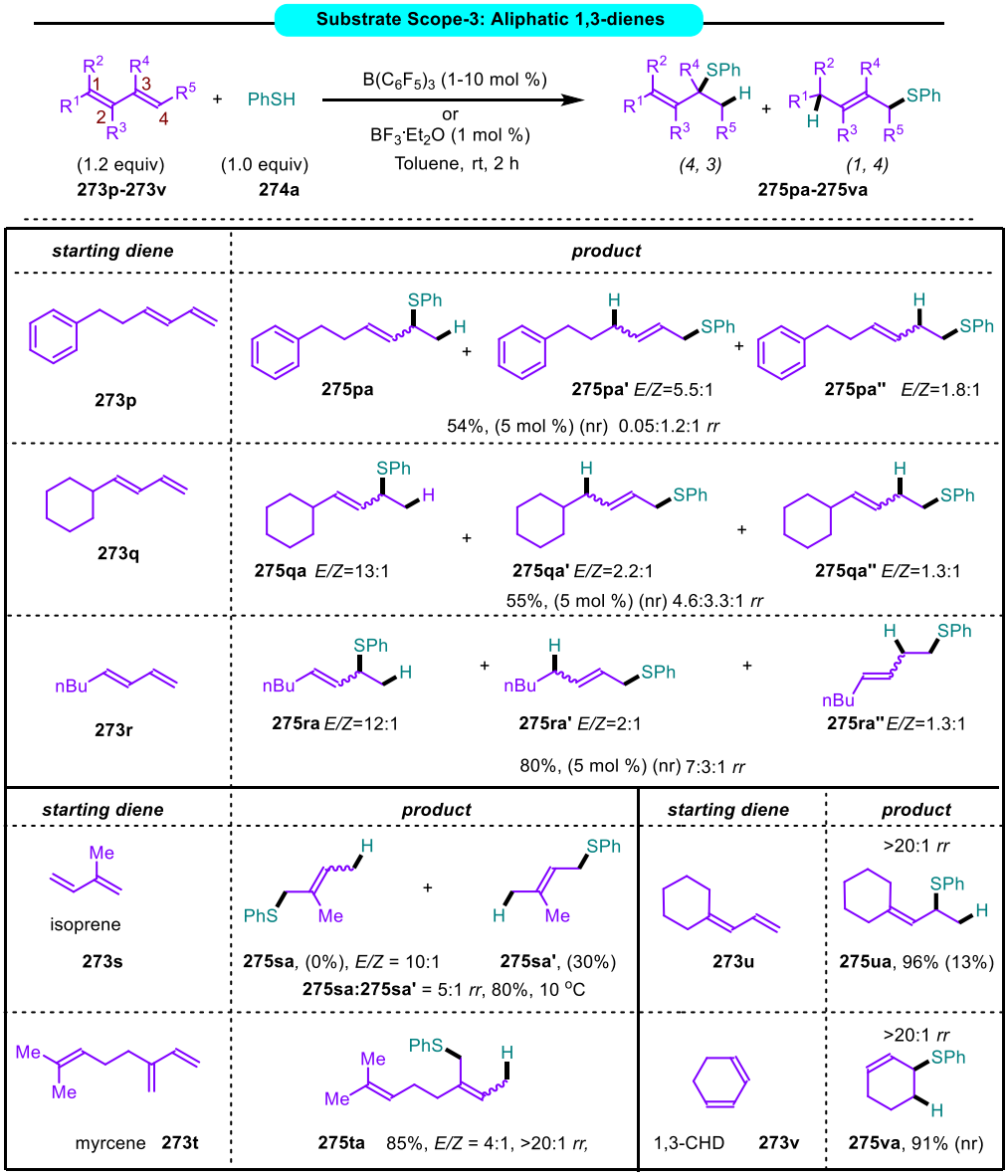


Scheme 37: Chapter-2 Substrate Scope for the aromatic 1,3-dienes. **Reaction scale**: 0.58 mmol with 1 mol % $B(C_6F_5)_3$, 0.12 mmol with 5 or 10 mol % $B(C_6F_5)_3$, 0.90 mmol with 1 mol % $BF_3{\cdot}Et_2O$, isolated yields unless otherwise mentioned. *rr* = regioisomeric ratio determined by ^1H NMR analysis of crude reaction mixture. The yields with $BF_3{\cdot}Et_2O$ are shown in parentheses. nr = no reaction. *rr* = regiomeric ratio, determined by ^1H NMR of crude reaction mixture. nd = not determined.

Using $BF_3{\cdot}Et_2O$ as a catalyst instead led to moderate to low yields for the above substrates. Interestingly, 1-ferrocenyl 1,3-diene delivered a mixture of both the singly and doubly hydrothiolated products **275q** and **275q′** in the presence of $B(C_6F_5)_3$ but in the presence of $BF_3{\cdot}Et_2O$ mainly the expected 4,3-hydrothiolation product **275q** was obtained. Then we checked with 1,1-disubstituted dienes and exhibited high efficiency for the selective 4,3-hydrothiolations to deliver products **275r–275s**. 1,4-disubstituted internal dienes having a methyl or butyl group as

a substituent at the 4-position (R^5 = Me or *n*-butyl) showed moderate to good reactivity (**275t–275u**). In the case of 1,3- disubstituted diene we obtained good yield and high regioselectivity for our 4,3-hydrothiolation with $B(C_6F_5)_3$ whereas using $BF_3{\cdot}Et_2O$, we were not able to obtain hydrothiolated product **275v**. To our delight, internal 1,3,4-trisubstituted 1,3-dienes reacted smoothly to produce tertiary allylic sulfides with moderate to good yields and complete regioselectivity (**275w**–**275x**). Also 1,2,4-trisubstituted 1,3-diene provided high yield and regioselectivity with $B(C_6F_5)_3$ as catalyst (**275y**).

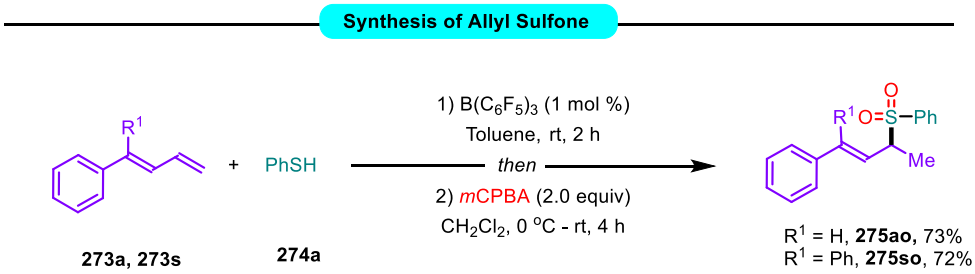
Variation of aliphatic 1,3-dienes: The reactions of terminal 1-alkyl 1,3-dienes were relatively less regioselective: aliphatic 1,3-dienes having 1-phenethyl-1,3-diene furnished the homoallylic sulfide **275pa″** as a main product instead of the expected 4,3-hydrothiolation product **275pa** in addition to the 1,4-hydrothiolation product **275pa′**. The reason behind the formation of homoallylic product is proved by our DFT calculation as the π-electron cloud of benzene ring stabilizes the terminal carbocation. Unfortunately, *n*-butyl and cyclohexyl group at site 1 provided both 4,3- and (less favored) 1,4-hydrothiolation products (**275qa**–**275ra**) and **275qa′**–**275ra′**, respectively) as well as with minor homoallylic sulfides (**275qa″**–**275ra″**). Isoprene (feedstock diene) furnished mainly the 4,1- along with minor 1,4-hydrothiolation products (**275sa**:**275sa′**=5:1) in the presence of $B(C_6F_5)_3$. Using $BF_3{\cdot}Et_2O$ instead we obtained exclusively **275sa′** albeit in low yield. The commercially available 1,3-diene, myrcene, was also provided the 4,1-hydrothiolation product **275ta** with high regioselectivity. Also, the 1,1-disubstituted aliphatic cyclohexyl 1,3-diene afforded 4,3-hydrothiolation with high regioselectivity **275ua**. To our delight, cyclic-1,3-diene readily furnished 4,3-hydrothiolation product **275va** with excellent yield. As such, highly regioselective 4,3-hydrothiolation (*rr* >20:1) was achieved for 1-aryl-substituted 1,3-dienes while 1,4-hydrothiolation was additionally obtained for 1-alkyl substituted 1,3-dienes in the presence of $B(C_6F_5)_3$ as catalyst. $BF_3{\cdot}Et_2O$ remained a less effective catalyst for internal 1,3-dienes as well as terminal 1-alkyl 1,3-dienes.



Scheme 38: Chapter-2 Substrate Scope for the aliphatic 1,3-dienes. **Reaction scale**: 0.58 mmol with 1 mol % $B(C_6F_5)_3$, 0.12 mmol with 5 or 10 mol % $B(C_6F_5)_3$, 0.90 mmol with 1 mol % $BF_3{\cdot}Et_2O$, isolated yields unless otherwise mentioned. *rr* = regioisomeric ratio determined by ^1H NMR analysis of crude reaction mixture. The yields with $BF_3{\cdot}Et_2O$ are shown in parentheses. nr = no reaction. *rr* = regiomeric ratio, determined by ^1H NMR of crude reaction mixture. nd = not determined.

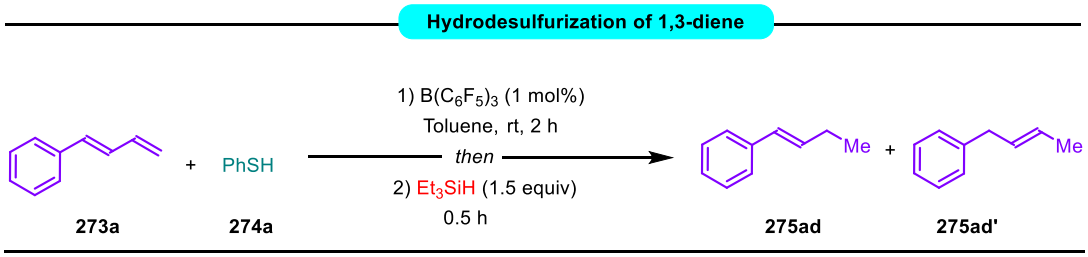
2.2.3 Synthetic Appication of the Developed Methodology

To check the synthetic potential of the developed methodology, we have functionalized our synthesized hydrothiolated product. For that, we have converted allyl sulfide into allyl sulfone via the oxidation of sulfur with the help of oxidising agent, *m*-CPBA (*m*-chloroperbenzoic acid). This reaction has been performed after successful isoltion of allyl sulfide, which was treated with *m*-CPBA in dichloromethane solvent. After full conversion of allyl sulfide, allyl sulfone **275go-275ho** was isolated in good yield (Scheme 39).



Scheme 39: Chapter 2: Application: Synthesis of Allyl Sulfone

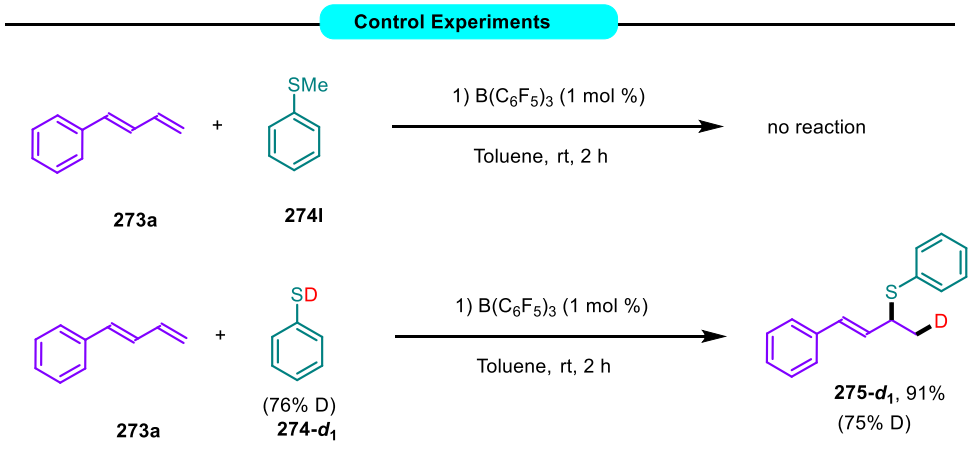
The one pot hydrothiolation and desulfurization was also performed to get the formally mono hydrogenated products of 1,3-diene. The reaction was set-up under standard conditions and after 2 h triethylsilane was added which furnishes the good isolated yield of alkene as mixture of isomers **275ad** and **275ad'** (Scheme 40).



Scheme 40: Chapter 2: Application: Hydrodesulfurization of Dienes

2.2.4 Control Experiments

To check the role of thiolic hydrogen (S–H), we have performed reaction with thioanisole **275l** and deuterated thiophenol (S–D) **274-*d*$_1$**. In case of thioanisole we did not observe any hydrothiolated product **275-*d*$_1$** formation (Scheme 41). However, interestingly we have observed the significant deuterium addition to the dienes in case of deuterated thiophenol, which suggests the proton source is the thiol partner. Also, to check the role of moisture we did titration with H_2O, which completely shut down the reaction even up to the 10 mol % ammount of H_2O.



Scheme 41: Chapter 2: Control Experiments- Role of S–H Proton

2.2.5 Time Dependant NMR Experiment

In order to get a clear picture of the reaction progress with time, we have performed a time dependant NMR experiment. This indicates the starting 1,3-diene **273a** and thiophenol **274a** peaks are diminishing with time and the peak for hydrothiolated product is increasing. Ultimatly within 2 h time, the complete starting substrate peaks vanished and only product peaks are visible. For this experiment we have performed a reaction under standard condition in toluene-d_8 solvent inside a glove-box. Aliquots has been taken at a 30 minutes time interval and NMR recorded in $CDCl_3$.

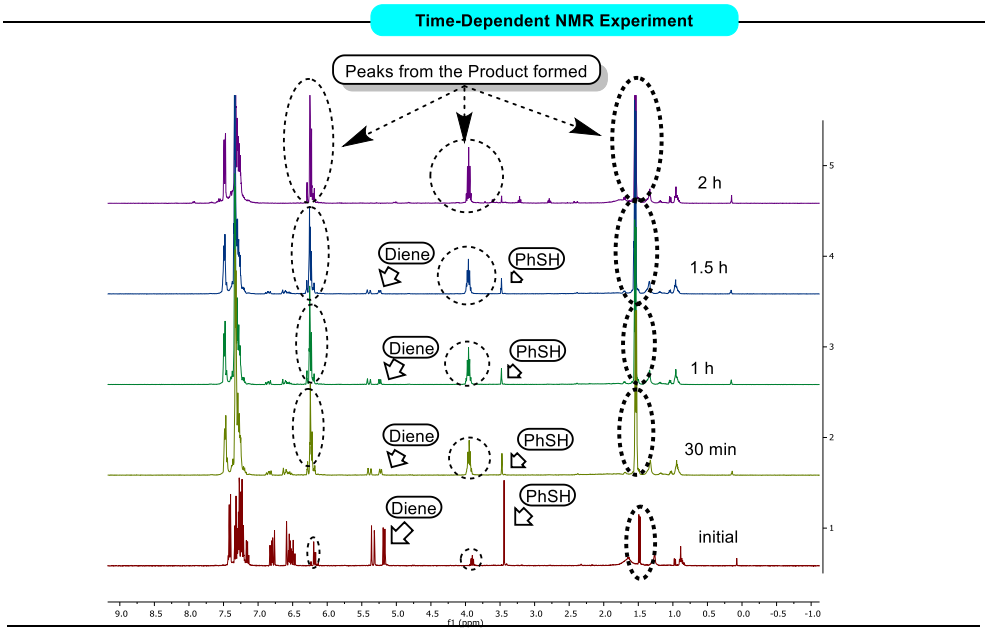


Figure 12: Chapter 2: Control Experiments- NMR Titration

2.2.6 ^{11}B-NMR of the PhSH–B(C_6F_5)$_3$ Adduct

To check the PhSH–B(C_6F_5)$_3$ adduct formation we have recorded the ^{11}B-NMR for the mixture of PhSH and B(C_6F_5)$_3$ in toluene-d_8 at two different temperatures. This NMR study shows that at low temperature (-30 ^{o}C), peak for ^{11}B of B(C_6F_5)$_3$ completely shifted at 1.51 ppm due to the adduct formation with PhSH. This result completely matched with our high-level DFT calculations.

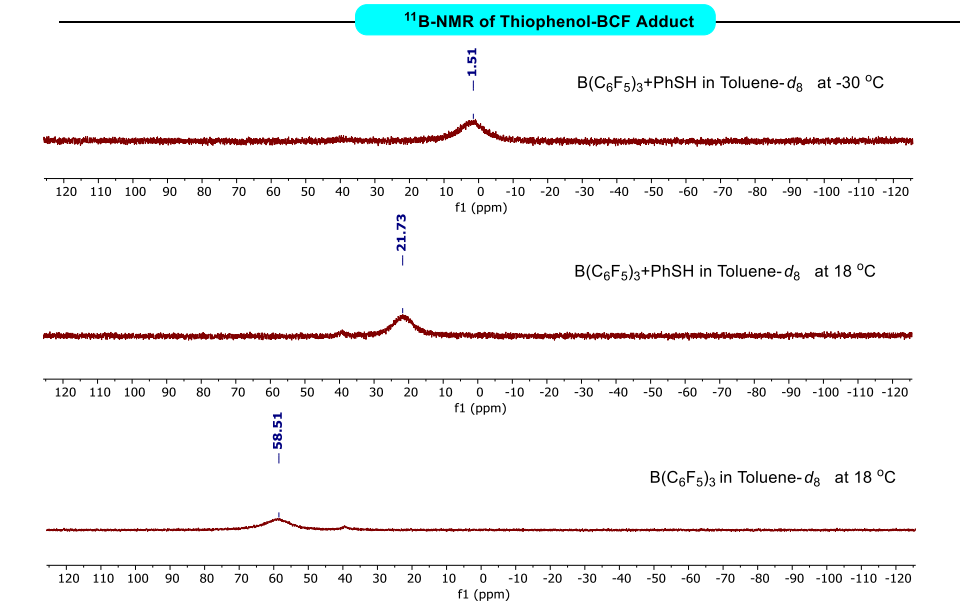


Figure 13: Chapter 2: ^{11}B-NMR of the PhSH–$B(C_6F_5)_3$ Adduct

2.2.7 DFT Studies for Mechanistic Proof

To gain deeper mechanistic insight, the 1,3-diene **273** and thiophenol **274a** were chosen as model substrate in the DFT studies at the PW6B95-D3/def2-QZVP + COSMO-RS(toluene)// TPSS-D3/def2-TZVP + COSMO(toluene) level of theory.[93] The lowest-lying reaction free energy paths (at 298 K and 1mol/L reference state) are shown in Figure 14. It is shown that thiophenol **274a** and $B(C_6F_5)_3$ may reversely form a weak B···S adduct **A** that is 2.1 kcal/mol higher in free energy at room temperature but should be observable at low temperatures. ^{11}B NMR of $B(C_6F_5)_3$ alone in toluene-d8 at room temperature (δ = 58.51 ppm) and $B(C_6F_5)_3$ + **274a** in toluene-d_8 (δ = 21.73 ppm at room temperature and δ = 1.51 ppm at – 30 °C) also indicate the formation of B···S adduct **A**.

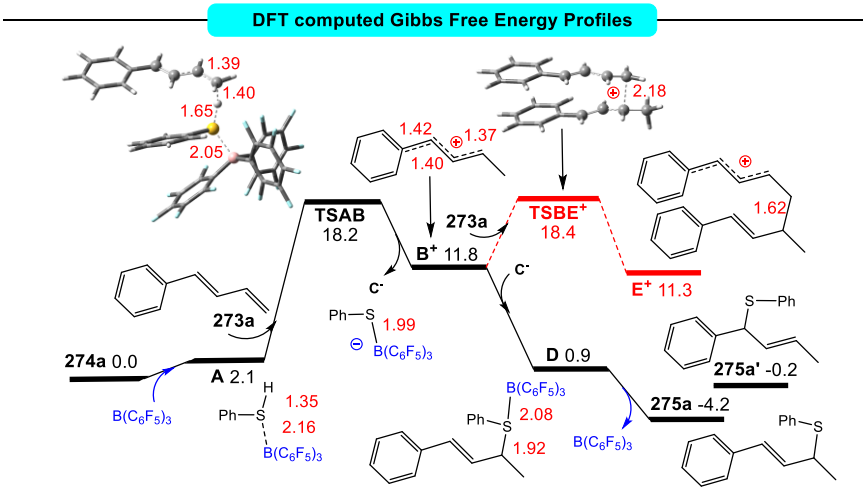


Figure 14: Chapter 2: DFT computed Gibbs free energy reaction profiles (in kcal/mol at 298 K and 1 mol/L reference state) for $B(C_6F_5)_3$ catalyzed hydrothiolation of 1,3-diene PhCH=CHCH=CH_2 (**273a**) with thiol PhSH (**274a**).

In contrast, the formation of an adduct of 1,3-diene **273a** and $B(C_6F_5)_3$ is 13.2 kcal/mol endergonic and thus much less favorable. Proton transfer from the S–H bond of **274a** via adduct **A** is highly selective (by 11.4 kcal/mol) to the carbon site 4 rather than the Ph-substituted site 1 of **273a**, which is 11.8 kcal/mol endergonic over a moderate barrier of 18.2 kcal/mol via the transition structure **TSAB**, forming two separated ionic species of $\mathbf{B}^+$ and $\mathbf{C}^-$ in solution.[18, 19] The high regioselectivity is mainly due to conjugation effects of the site-1 phenyl to stabilize the allyl cation intermediate. Further addition of anion $\mathbf{C}^-$ to the carbon 3 of cation $\mathbf{B}^+$ is almost barrier less to form the adduct **D** with a new C–S bond, followed by rapid $B(C_6F_5)_3$ elimination to form the main product **275**. Similar addition of $\mathbf{C}^-$ to the carbon 1 of $\mathbf{B}^+$ is thermodynamically 4.0 kcal/mol less favorable to form the adduct **275'**, which should be rapidly converted into more stable **275** over a barrier of 12.0 kcal/mol (via ionic $\mathbf{B}^+$ and $\mathbf{C}^-$) when catalyzed by $B(C_6F_5)_3$. At high substrate concentration, trapping of $\mathbf{B}^+$ with 1,3-diene **273a** may also occur selectively (by 3.0 kcal/mol) at the respective carbon sites 3 and 4 of $\mathbf{B}^+$ and **273a**, which is –0.5 kcal/mol exergonic over a barrier of 6.6 kcal/mol (Figure 14, reaction channel denoted in red) to form the allyl cation $\mathbf{E}^+$, followed by either sulfide anion transfer from $\mathbf{C}^-$ or further oligomerization of 1,3-dienes. Catalyzed by Lewis acid $B(C_6F_5)_3$, the reaction is thus directed by the stabilizing 1-aryl π-conjugation for the initial 1,3-diene protonation and the thermodynamic control of subsequent sulfide anion transfer, leading to selective 4,3-hydrothiolation. An analogous mechanism was previously proposed by the group of Stephan, which began with an interaction between Lewis acidic cationic salt and thiols followed by protonation and finally sulfide transfer to release the catalyst for hydrothiolation olefins.[89, 90]

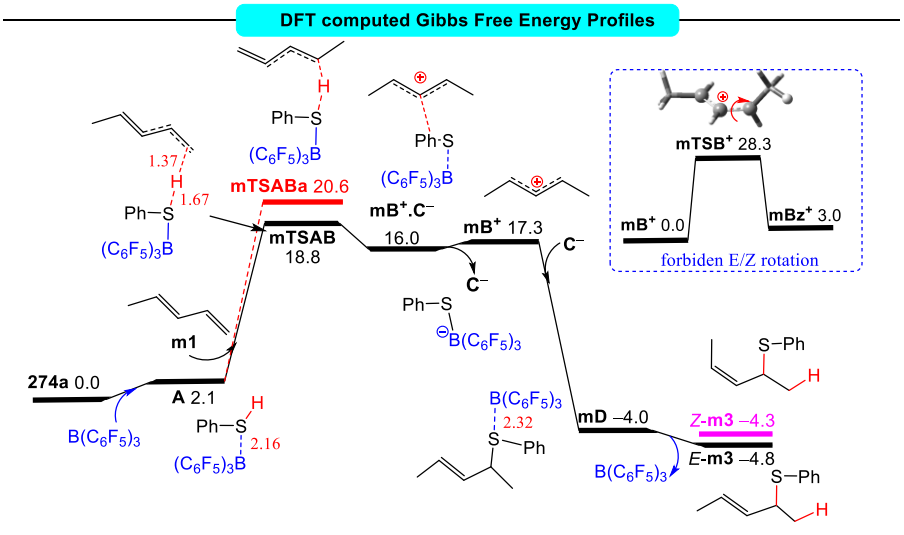


Figure 15: Chapter 2: DFT computed Gibbs free energy reaction profiles (in kcal/mol at 298 K and 1 mol/L reference state) for $B(C_6F_5)_3$ catalyzed hydrothiolation of 1-methyl 1,3-diene **m1** using thiol PhSH (**274a**), computed at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-P + COSMO level of theory.

The reduced 4,3-hydrothiolation selectivity observed for 1-alkyl 1,3-dienes is due to relatively weaker hyperconjugation (instead of π-conjugation) by 1-alkyl groups for initial 1,3-diene protonation. This is supported by our DFT calculations showing that the protonation of 1-methyl 1,3-diene by adduct **A** is kinetically only 1.9 kcal/mol more favorable at site 4 than at site 1 (Figure 15).

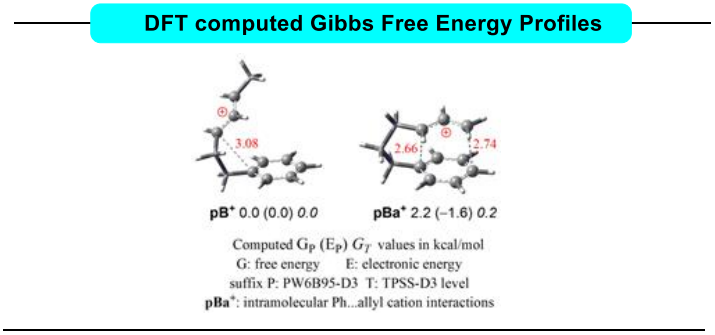


Figure 16: Chapter 2: DFT-supported intramolecular Ph...allyl cation interaction model (**pBa**$^{+}$) that may enhance the obseverved site 1 protonation.

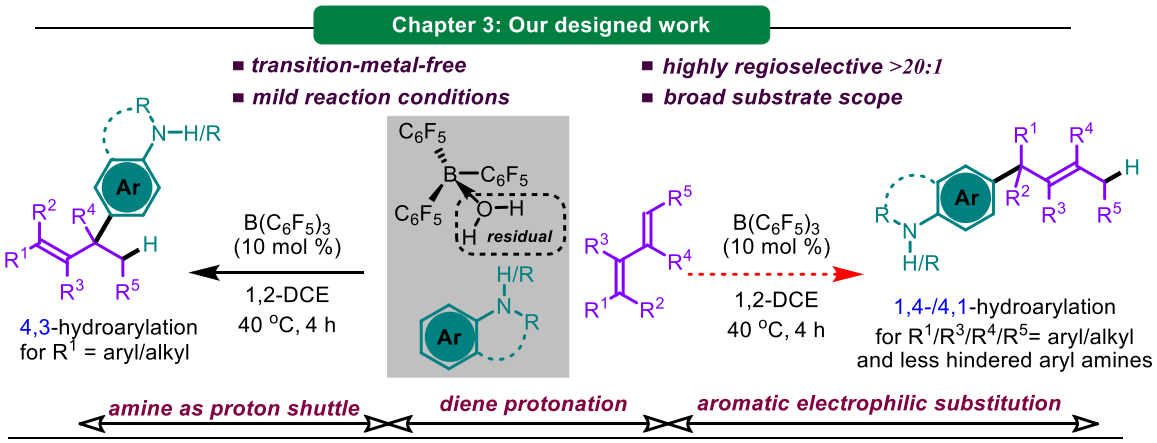
The dominant 4,1-hydrothiolation observed for 2-alkyl 1,3-dienes is likely due to steric effects during sulfide anion transfer from **C**$^{-}$, while the unusual formation of homoallylic sulfide **275pa″** instead of the expected 4,3-hydrothiolation in the case of 1-phenethyl-1,3-diene is likely directed by the flexible 1-phenethyl that may favor intramolecular phenyl-carbocation π-adducts.

2.3 Conclusion

In this chapter we have exhibited a rarely investigated transition-metal-free regioselective hydrothiolation strategy employing primary and seconadry allylic sulfide derivatives. Here, boron-based Lewis acids $B(C_6F_5)_3$, and $BF_3{\cdot}Et_2O$ are utilized as catalysts upto a very Low catalyst loadings. Remarkably, various aromatic, aliphatic thiol derivatives, and dienes even upto trisubstituted 1,3-dienes successfully utilized for the hydrothiolated product formation. Interestingly in case of highly substituted 1,3-dienes $B(C_6F_5)_3$ remains by far superior catalyst. Complete mechanistic pathway is investigated with high-level DFT calculation supported by ^{11}B-NMR and deuterium-lebelling experiments.

Chapter 3

Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines



This work was published in Organic Letters (a journal of ACS). Please see the citation as: "**Kumar, G.;** Qu, Z-W.; Grimme, S.; Chatterjee, I. *Org. Lett.* **2021**, *23*, 8952–8957."

3 Abstract

Boron-catalyzed chemo- along with regioselective hydroarylation of 1,3-dienes with arylamines to contrive C–C bond is depicted here. The process is felicitous to broad range of hindered amines and highly substituted 1,3-dienes, in addition to mild reaction conditions. Our experimental and throughput DFT mechanistic investigation bestows a clear catalytic pathway with $B(C_6F_5)_3$ where residual moisture plays a crucial role. The complex formation between Lewis acidic $B(C_6F_5)_3$ and residual H_2O induces the aryl-assisted protonation of conjugated dienes, forming allyl cation intermediates. These allyl cationic intermediates undergo facile electrophilic aromatic substitution with aryl amine derivatives through *para*-C–H bonds.

3.1 Introduction

After successful functionalization of 1,3-dienes to devise carbon-heteroatom bonds (C–S) using boron Lewis acids in chapter-1, we started our investigation in order to cast new C–C bonds. In this regard, we have gone through seminal literature reports, and perceived that opting aryl amine as a partner substrate for the functionalization of 1,3-dienes under boron-Lewis acid catalysis will be a worthier choice. The profound applications of arylamine in numerous bio-active, pharmaceuticals, agrochemicals, and optoelectronics make their functionalization a topic of interest for the synthetic organic chemists. Few examples of the arylamine-containing bioactive compounds have been portrayed in figure **17**.[94]

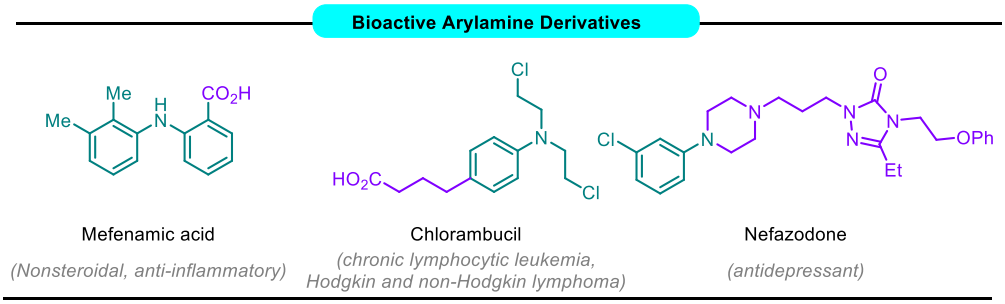


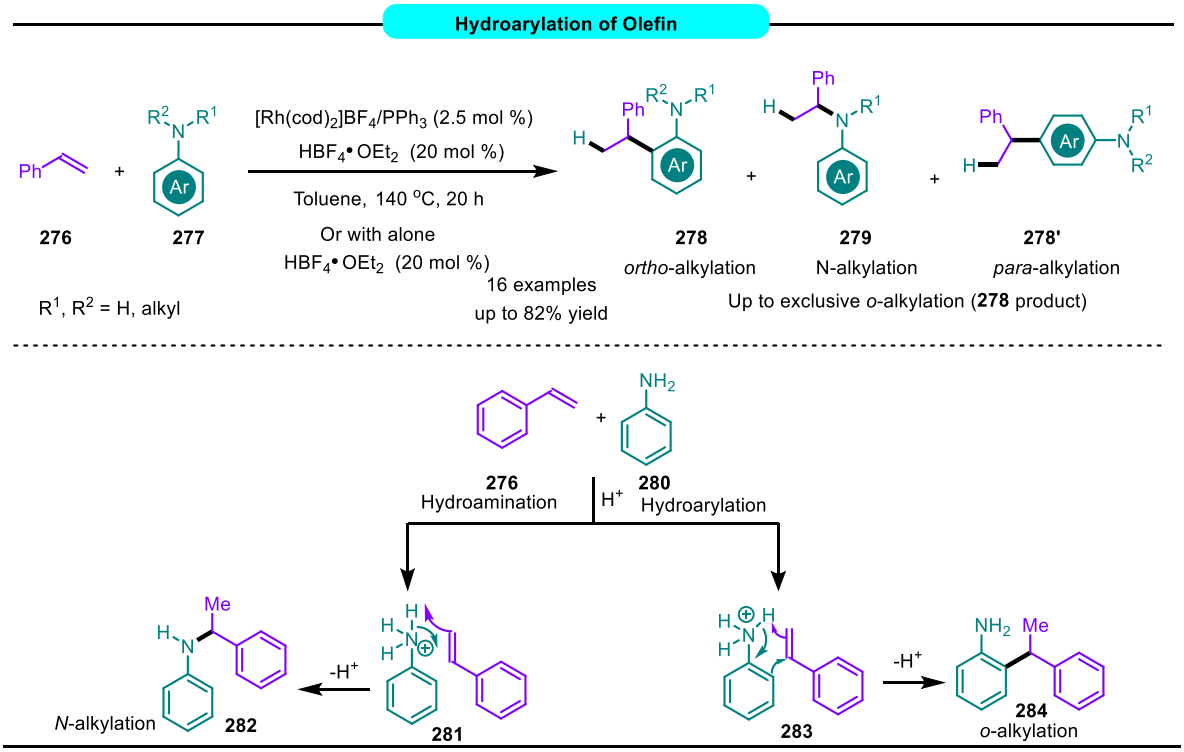
Figure 17: Arylamine Containing Bio-active Candidates

However, the Friedel-Crafts reaction of arylamines are challenging on account of the amine coordination with Lewis acids. Although, other methods are possible i.e. functionalization of C–H bonds of arylamines via transition-metal catalysis and visible-light photoredox protocols; but the atom and step-economy invariably remain a great challenge.[95] So, to get the atom economic pathway for the functionalization of arylamines, the hydroarylation of unsaturated bonds remains an elegant protocol. Interestingly, distinct transition-metal catalysts, Brønsted acid and Lewis acid catalyzed methods are documented in the literature, nevertheless, these processes are always associated with the *ortho*-/*para*-selectivity, and hydroarylation (C–C bond formation) *vs.* hydroamination (C–N bond formation) issues. However, the hydroarylation of olefins, and alkynes are somehow explored with main group Lewis acids. While the hydroarylation of 1,3-

dienes with arylamines under main group Lewis acid catalysis remains unplumbed in the literature. Here we have highlighted our extensive literature investigation for hydroarylation across the unsaturated C–C bonds with different catalytic systems.[96]

3.1.1 Literature Reports for the Hydroarylation of Olefins with Arylamines

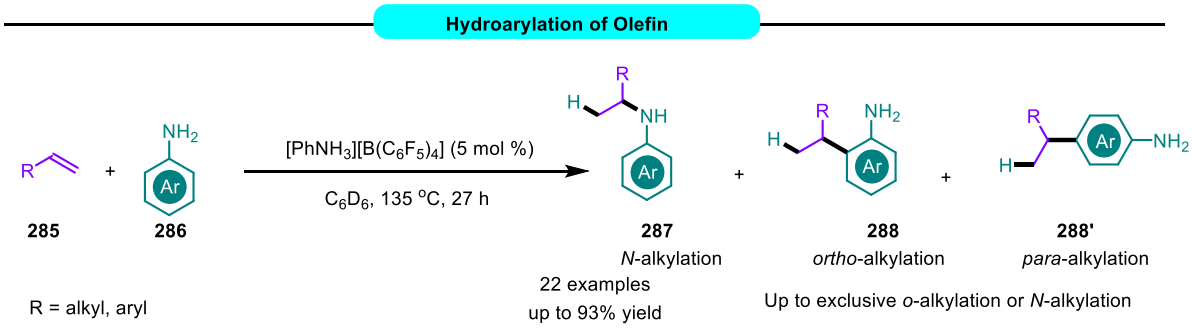
In 1999, Beller and co-workers foremost introduced a Friedel Crafts reaction of arylamines with olefin derivatives catalyzed by the combination of $[Rh(cod)_2]BF_4/PPh_3$ and $HBF_4{\cdot}OEt_2$ catalyst (Scheme 42). However, in case of electron-rich arylamine, $HBF_4{\cdot}OEt_2$ alone is sufficient to catalyze the reaction. Also, to check the role of $HBF_4{\cdot}OEt_2$, they performed reaction with other conventional Brønsted acids, e.g., HCl, CF_3CO_2H, CF_3SO_3H, *p*-$CH_3C_6H_4SO_3H$, out of all these, only CF_3SO_3H was able to give comparable results. But this process associated with chemoselectivity issue, the mixture of hydroarylated **278, 278'** and hydroaminated **279** products have been obtained. According to the authors' mechanistic proposal, protonation of aniline derivative with $HBF_4{\cdot}OEt_2$ generate anilinium ion. This anilinium ion form six-membered transition states **283** with olefin and furnish *ortho*-alkylation as a major product. At the same time, four-membered transition states **281** provided *N*-alkylation products (hydroamination).[97]



Scheme 42: Beller's Hydroarylation of Olefins

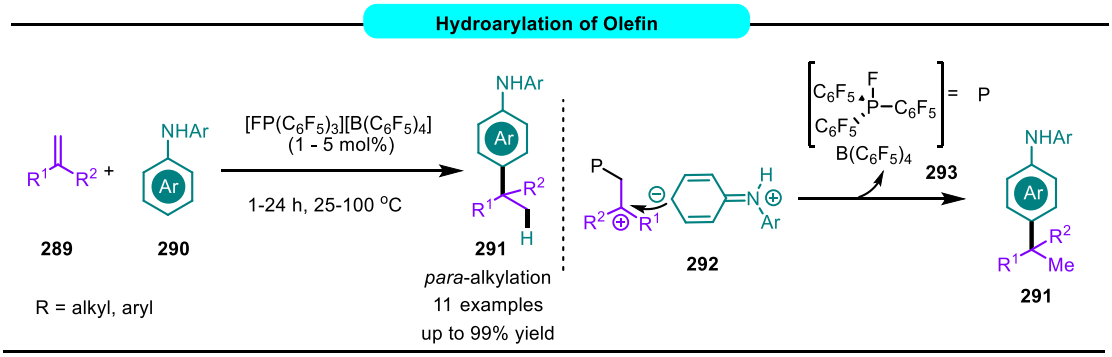
Similarly, in 2005, Bergman and co-workers documented the Lewis acid-induced protic borane-aniline compounds for the hydoarylation and hydroamination of alkene **285** with arylamines **286**. In this report, they observed the electron-withdrawing group at aniline partner and electron-donating group at styrene enhanced the productivity of the reaction. It was also

revealed that a shorter reaction time provided better yield of hydroaminated products **287**, whereas a longer time furnished hydroarylated products **288** with good yields. The transformation from hydroaminated to hydroarylated products via Hofmann-Martius rearrangement was also achieved. This methodology is associated with a mixture of *N*-alkylated and C-alkylated (*ortho*- and *para*-ArC–H alkylation) products **287, 288, 288'** formation issue (Scheme 43).[98]



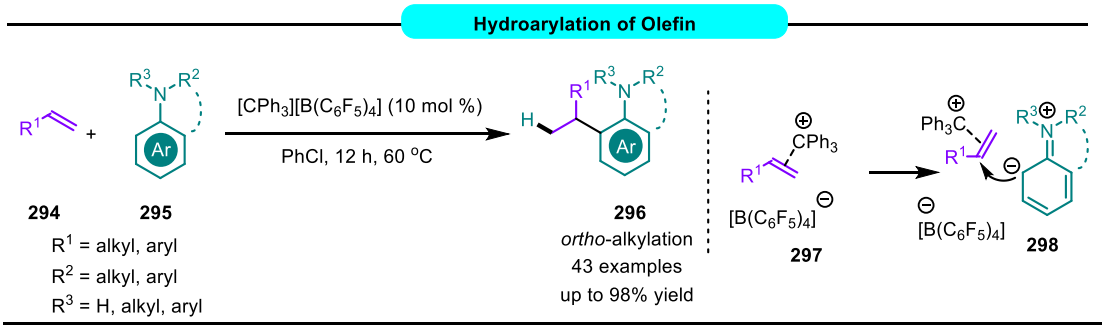
Scheme 43: Bergman's Hydroarylation of Olefins

In 2015, Stephan and co-workers introduced electrophilic phosphonium cations **293** (EPCs) catalyzed hydroarylation of alkenes **289**. This process provides metal free *p*ara-selective hydroarylation of alkenes with arylamines **290**. In this work author claimed that first EPCs coordinate with alkene and generate carbocationic intermediate **292**, and the carbocation trapping with arylamine through carbon center furnish addition products **291** (Scheme 44).[99]



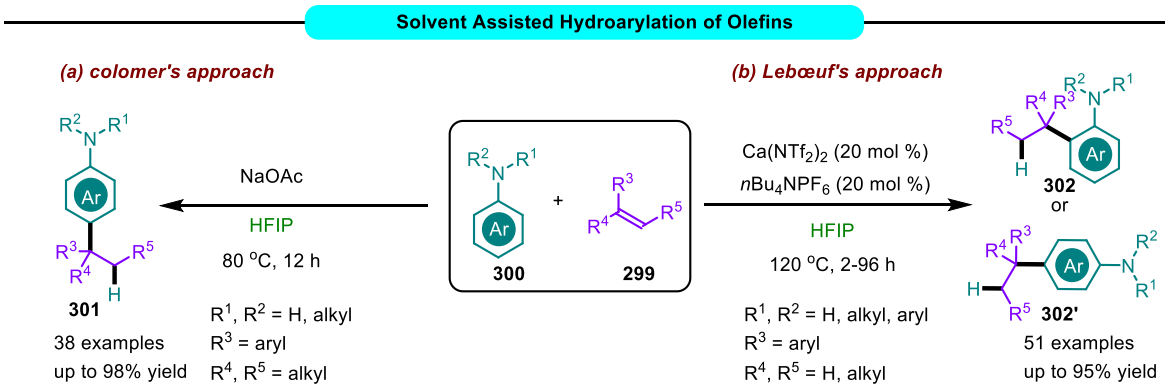
Scheme 44: Stephan's Hydroarylation of Olefins

In 2018, Yao and his team documented the trityl cation-catalyzed hydroarylation of alkenes **294** with arylamine **295** derivatives. This process remains exclusively chemo selective for the C–C bond formation via addition of arylamines onto alkenes. They utilized 1,2,3,4-tetrahydroquinoline, and aniline derivatives as amine partner with aromatic and aliphatic alkenes for the hydroarylation. Authors suggested that trityl cation first interacts with alkene **297** and subsequently, nucleophilic attack **298** by arylamine followed by proton transfer and regeneration of trityl cations furnishes addition products **296** (Scheme 45).[100] Later in 2019, the Patureau group utilized the $AgBF_4$ and $HBF_4{\cdot}OEt_2$ for the hydroarylation of styrene with diaryl amine derivatives to get exclusively *ortho*-selective C–C bond formation.[101]



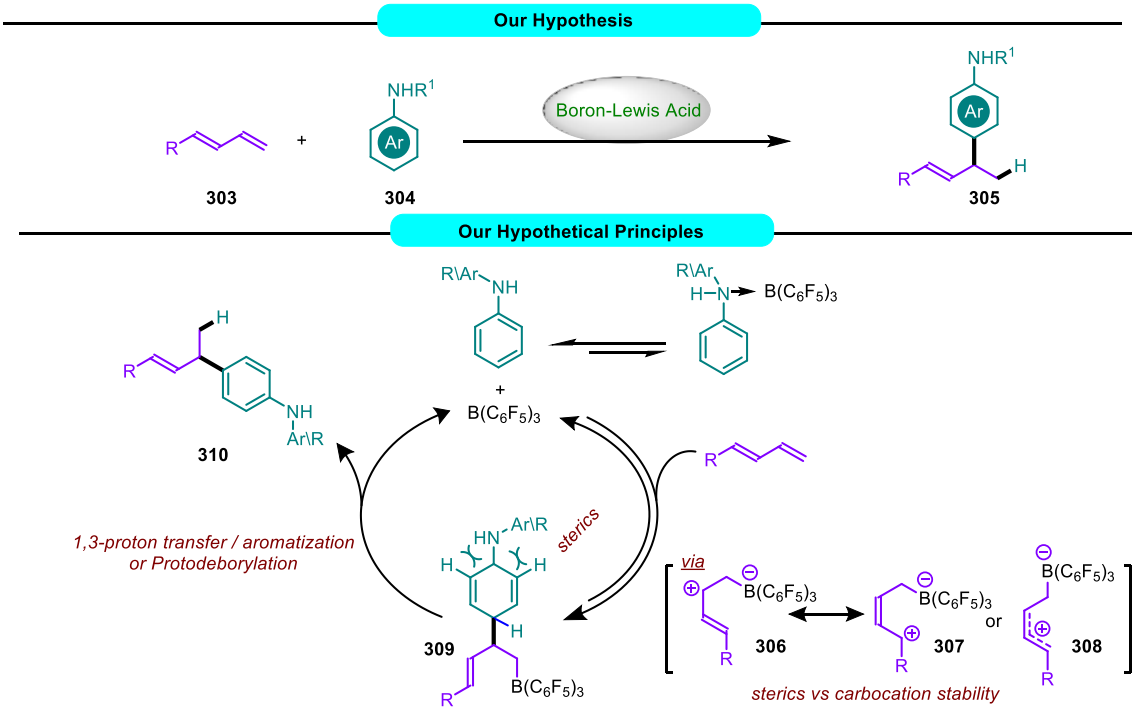
Scheme 45: Yao's Hydroarylation of Olefins

In 2020, consecutively, two reports appeared in the literature by Colomer (Scheme 46-a) and Leboeuf (Scheme 46-b) groups on hydroarylation of olefin **299** with arylamine **300** derivatives. They were able to get regioselectively *ortho*-or *para*-alkylated products. Both reports have broad substrate scope and extensive mechanistic studies. Mechanistic pathway shows that the fluorinated alcoholic solvents (HFIP) promote anilinium ion formation, which transfers a proton to the olefin partner and generates carbocationic intermediate. This intermediate can be easily trapped via electrophilic aromatic substitution with aryl amine partner.[102]



Scheme 46: Colomer and Leboeuf's Hydroarylation of Olefins

After doing an extensive literature survey we did not find any prominent report for the hydroarylation of 1,3-dienes with aniline derivatives under main group Lewis acid catalysis. So that we thought to explore boron-catalyzed hydroarylation reactions of 1,3-dienes with arylamine derivatives. We have discussed in the first chapter about the catalytic efficiency of the boron-based Lewis acid, $B(C_6F_5)_3$ in functionalization of unsaturated bonds via FLP and Lewis acidic chemistry. Mainly the hydroamination reaction of alkyne with diphenylamine and other seminal work of Stephan on hydroarylation of alkenes motivated us to explore such reactions with 1,3-dienes (Scheme 8, in chapter 1). So, we hypothesized that the arylamine **304** and 1,3-dienes **303** could be activated via FLP using $B(C_6F_5)_3$ as shown in scheme 47 lower part. If $B(C_6F_5)_3$ activate to 1,3-diene via Zwitterionic intermediate **306, 307, 308** followed by carbocation trapping with arylamine through *para*-C–H bonds **309** (due to steric) and aromatization/protodeborylation could afford the hydroarylated products.



Scheme 47: Chapter 3: Our Proposed Working Hypothesis

3.1.2 Challenges for the Hydroarylation of 1,3-dienes

As we already discussed in chapter 2 about the regioselectivity issue with hydrothiolation of 1,3-dienes. Similarly the hydroarylation reactions are also associated with regioisomeric challenges.

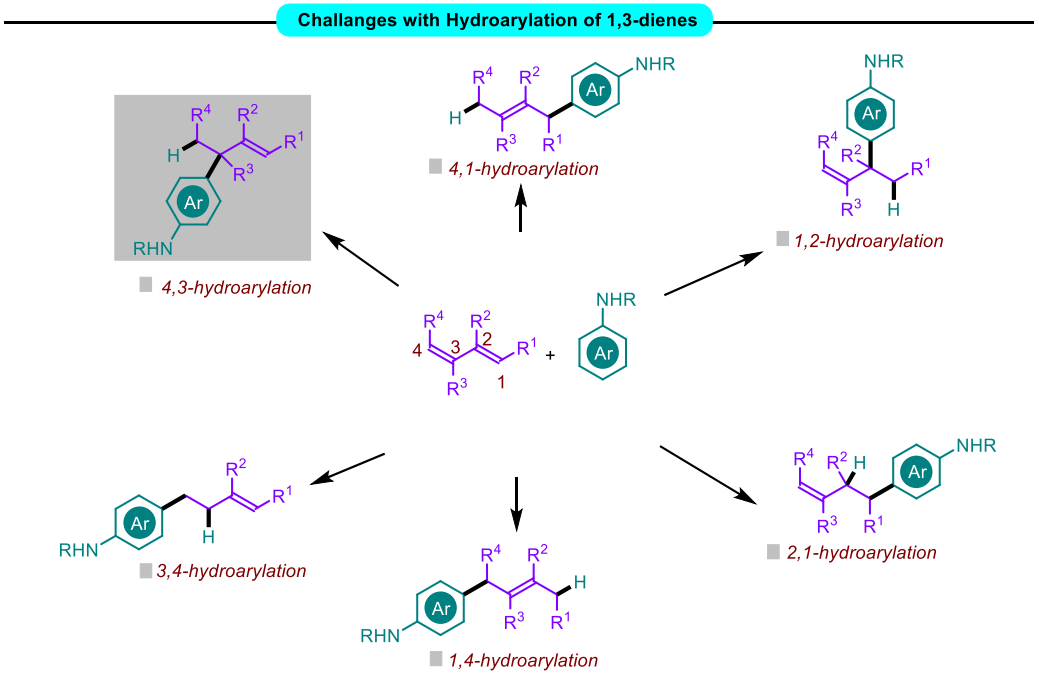


Figure 18: Chapter 3: Regioselectivity Challenges Across 1,3-diene

However, besides the regiomeric hydroarylation at diene side, there are another issues, e.g., the *ortho*- **311** or *para*-alkylated **312** formation. Also, the hydroamination **313** (C–N bond formation)

vs. hydroarylation **314** (C–C bond formation) is another challenge in case of arylamine containing starting substrates.

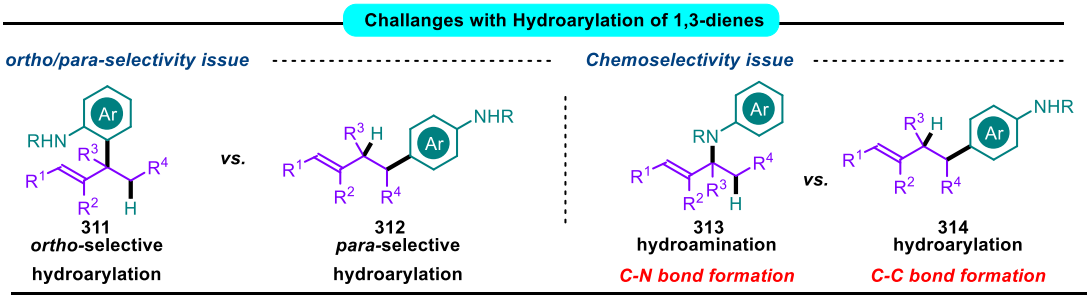


Figure 19: Chapter 3: Regio-/Chemoselectivity Challenges

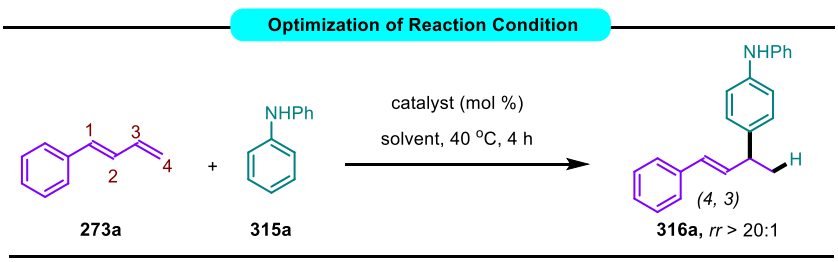
3.2. Results and Discussion

3.2.1 Optimization of the Reaction Condition

As per our hypothesis (described in Scheme 47), we started looking for a unique transition-metal-free and Lewis acid catalyzed regioselective hydroarylation of 1,3-dienes protocol for the C–C bond formation. To check the feasibility of our proposal, we commenced our study by reacting (*E*)-buta-1,3-dien-1-ylbenzene (**273a**, 1.0 equiv) with diphenylamine (**315a**, 1.5 equiv) as the model substrates in various solvents (0.15 M) and in the presence of catalyst $B(C_6F_5)_3$ (10 mol %) (Table 2).

While THF as a solvent provided only traces of conversion (Table 2, entry 1), MeCN, $MeNO_2$ and $CHCl_3$ lead to moderate ^{1}H NMR yields (Table 2, entries 2–4). The use of toluene and dichloromethane (DCM) resulted in a drastically improved 62% and 72% yields of **316a**, respectively, with complete regioselectivity for 4,3-hydroarylation (Table 2, entries 5–6). To our delight, the solvent 1,2-dichloroethane (DCE) led to excellent isolated yield (90%) and regioselectivity (>20:1 *rr*) of the desired product **316a** (Table 2, entry 7). Lower catalyst loading provided low yield of **316a** (Table 2, entry 8). Transition-metal-based catalysts $Cu(OTf)_2$, $Fe(OTf)_3$ and $Yb(OTf)_3$ were unable to catalyze the reaction (Table 2, entries 9–11), whereas $In(OTf)_3$, $Sc(OTf)_3$ catalyzed the reaction only in lower yield (Table 2, entries 12–13). Brønsted acid Tf_2NH and other boron Lewis acids such as BCl_3 and $BF_3{\cdot}Et_2O$ provided **316a** with lower ^{1}H NMR yields (Table 2, entries 14–16).

Table 2. Chapter 3: Optimization Study and Reaction Set Up



Entry	Catalyst (mol %)	Solvent	Yield 316a (%)[a]
1	$B(C_6F_5)_3$ (10)	THF	trace
2	$B(C_6F_5)_3$ (10)	MeCN	18
3	$B(C_6F_5)_3$ (10)	$MeNO_2$	50
4	$B(C_6F_5)_3$ (10)	$CHCl_3$	40
5	$B(C_6F_5)_3$ (10)	Toluene	62
6	$B(C_6F_5)_3$ (10)	DCM	72
7	**$B(C_6F_5)_3$ (10)**	**1,2-DCE**	**>99/90[b]**
8	$B(C_6F_5)_3$ (5)	1,2-DCE	40
9	$Cu(OTf)_2$ (10)	1,2-DCE	nr
10	$Fe(OTf)_3$ (10)	1,2-DCE	trace
11	$Yb(OTf)_3$ (10)	1,2-DCE	nr
12	$In(OTf)_3$ (10)	1,2-DCE	27
13	$Sc(OTf)_3$ (10)	1,2-DCE	19]
14	Tf_2NH	1,2-DCE	30
15	BCl_3[c] (10)	1,2-DCE	45
16	$BF_3 \cdot Et_2O$ (10)	1,2-DCE	26

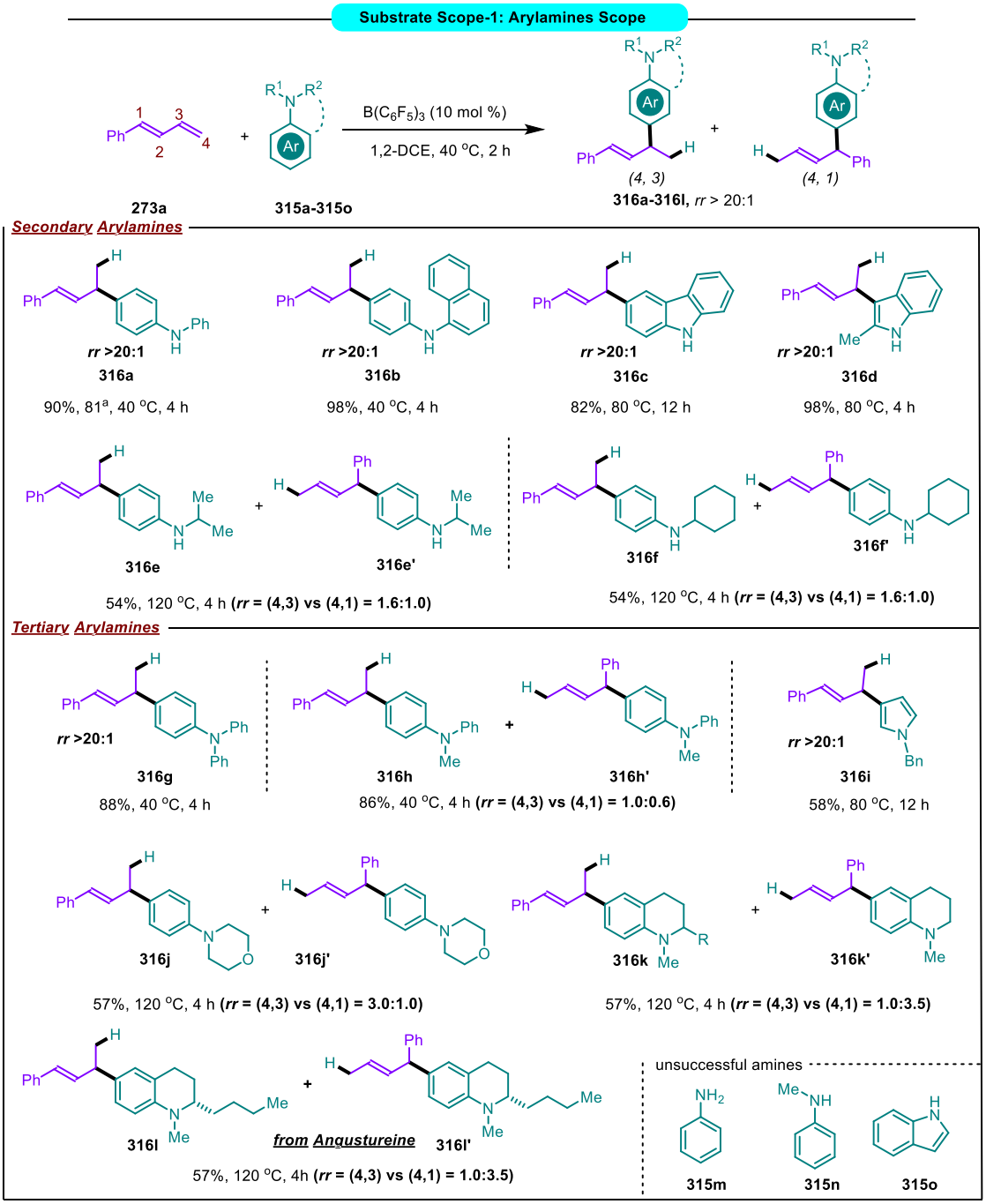
[a] Reaction condition **273a** (1.0 equiv) and **315a** (1.5 equiv) stirred in solvent at rt for 4 h. Yield determined by ^1H NMR using CH_2Br_2 as internal standard. [b] Isolated yield. [c] Used as 1M solution in DCM. nr = no reaction. rr = regioisomeric ratio, determined by ^1H NMR of crude reaction mixture.

3.2.2 Substrate Scope Evaluation

After thorough put optimization of solvent, and catalyst we found an optimized reaction condition for further studies and we moved on the substrate scope to check the practicalability of the developed methodology.

Variation of arylamines: In our initial substrate scope studies, we have checked several arylamine derivatives **315a–315o** (seconadry and tertiary) by reacting them with (*E*)-buta-1,3-dien-1-ylbenzene (**273a**) under reaction conditions (Table 2, entry 7). In some cases we have observed that high temperatur (80 or 120 ^oC) as well as additional time (up to 12 h) were required (Scheme 48). Sterically less-hindered primary amines remain unreactive under this reaction conditions. Secondary amines like diphenylamine **315a** and *N*-phenylnaphthalen-1-amine **315b** worked well to form 4,3-hydroarylated products (entries **316a–316b**) in high yield and complete regioselectivity. To our delight, carbazole **315c** also remained sufficiently reactive at a temperature of 80 ^oC and 12 h reaction time to furnish *para*-selective product **316c**. 2-methyl indole **315d** produced highly C3-selective hydroarylated product **316d** at a 80 ^oC. However, arylalkylamines *N*-isopropylaniline **315e** and *N*-cyclohexylaniline **315f** provided products **316e**

and **316f** in moderate yields at elevated temperature of 120 °C with lower regioselectivity. Moreover, triphenyl amine **135g** displayed higher reactivity to produce product **316g** in high yield and with high 4,3-regioselectivity. *N*-methyl-*N*-phenylaniline **315h** delivered hydroarylated product **316h** in good yield but with lower regioselectivity due to competing 4,1-hydroarylation under standard reaction conditions.



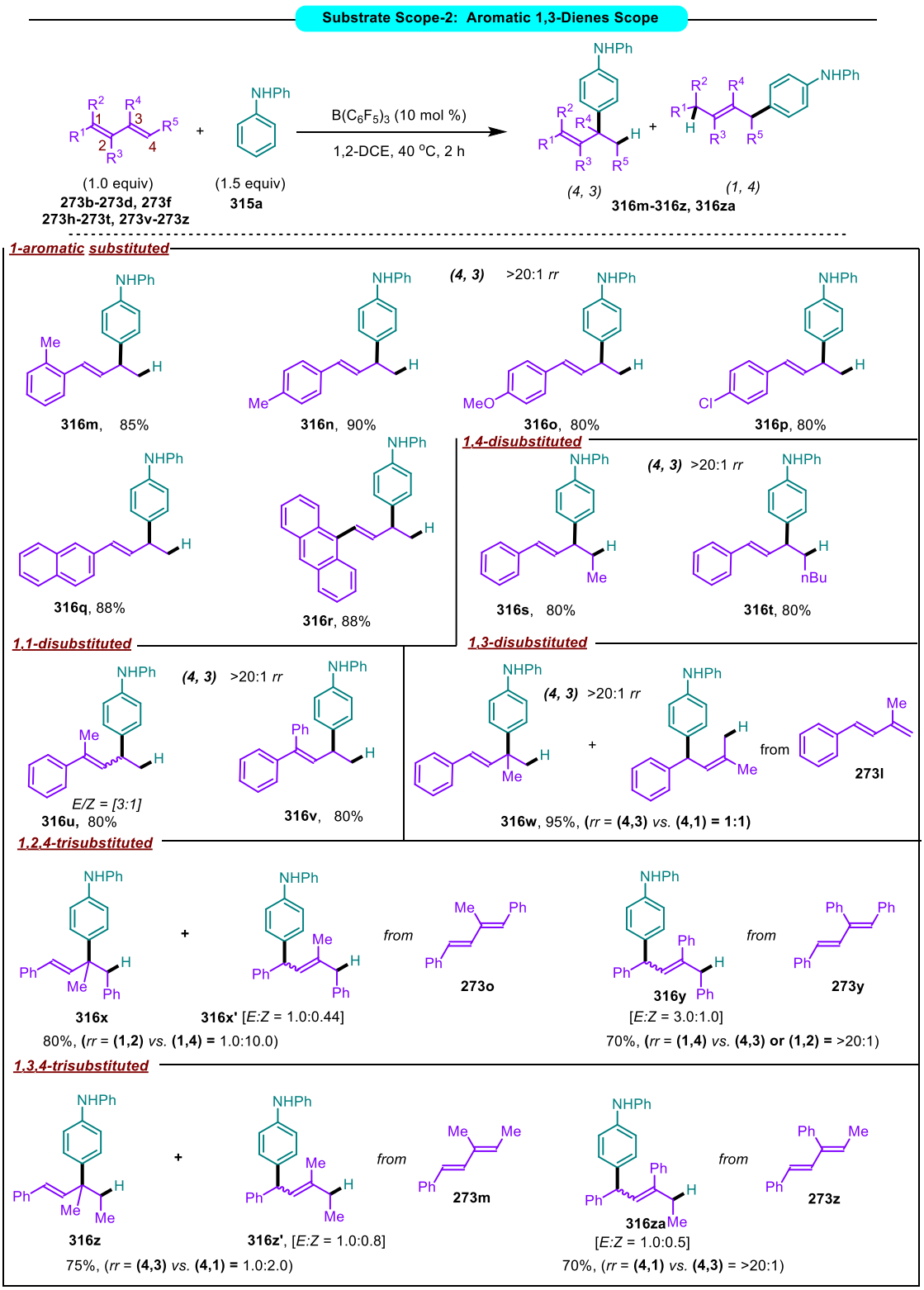
Scheme 48: Substrate Scope for Arylamines. **Reaction scale**: 0.12 mmol, isolated yields unless otherwise mentioned. [a] Reaction scale 4.22 mmol, 1.02 g of **316a** was obtained. *rr* = regioisomeric ratio, determined by ^{1}H NMR of crude reaction mixture.

Interestingly, 1-benzyl-1*H*-pyrrole **315i** produced hydroarylated product **316i** in moderate yield at higher temperature of 80 °C. *N*-phenyl morpholine **315j** and tertiary amine **315k** (derived

from tetrahydroquinoline) produced hydroarylated products **316j** and **316k** with modest regioselectivity at elevated temperature of 120 ^{o}C. A natural product, Angustureine **315l**, provided the hydroarylated product **316l** in moderate yield at elevated temperature of 120 ^{o}C but with moderate regioselectivity. In case of **316k** and **316l**, (4,1)-hydroarylaed products **316k′** and **316l′** were formed as major product as judged by the crude ^{1}H NMR of the respective reaction mixtures.

Variation of aromatic 1,3-dienes: After succsseful evaluation of arylamines scope we have explored the variation of different substituted aromatic 1,3-dienes in scheme **49**. For the scope of dienes, we have used diphenylamine **315a** as a model arylamine partner under optimized condition (Table 2, entry 7). Terminal 1-aryl-1,3-dienes with the respective Me, OMe and Cl substituent at the phenyl ring (**316m–316p**) also led to a high regioselectivity for the 4,3-hydroarylation. Both 1-naphthalenyl **273f** and 1-anthracenyl **273x** 1,3-dienes were found to be equally reactive (**316q** and **316r**). We also checked the substituted 1,3-dienes, and observed that 1,4-disubstituted, e.g., 1-phenyl-4-methyl **273j**, and 1-phenyl-4-*n*-butyl **273k** 1,3-dienes furnishes good isolated yields with high regioselectivity (>20:1) (**316s–316t**). Following this substrates 1,1-disubstituted dienes also selectively led to 4,3-hydroarylated products (**316u–316v**). Moreover, the 1,3-disubstituted 1,3-diene having methyl group at 3-position delivered the 4,3- and 4,1-hydroarylation products in almost equal ratios (**316w:316w′** = 1:1**)**. Also, the 1,2,4-trisubstituted 1,3-dienes works smoothly and provided good yields of hydroarylated products. However, in case of 1-phenyl-2-methyl-4-phenyl 1,3-diene the moderate regioslectivity for 1,2-hydroarylation **316x** in competition with 1,4-hydroarylation **316x'** was observed. Moreover, 1-phenyl-2-phenyl-4-phenyl **273y** 1,3-diene furnishes highly regioselective (>20:1) 1,4-hydroarylated product (**316y**). Both 1,3,4-trisubstituted 1,3-dienes were reacted equally and provided up to 75% yields (**316z–316za**). In case of 1-phenyl-3-methyl-4-methyl **273m** 1,3-diene mixture of regiosiomer of 4, 3- and 4, 1-hydroarylation was obtained (**316z & 316z'**). Interestingly in the case of 1-phenyl-3-phenyl-4-methyl **273z** 1,3-diene highly regioselective 4,1-hydroarylated product was obtained **316za**.

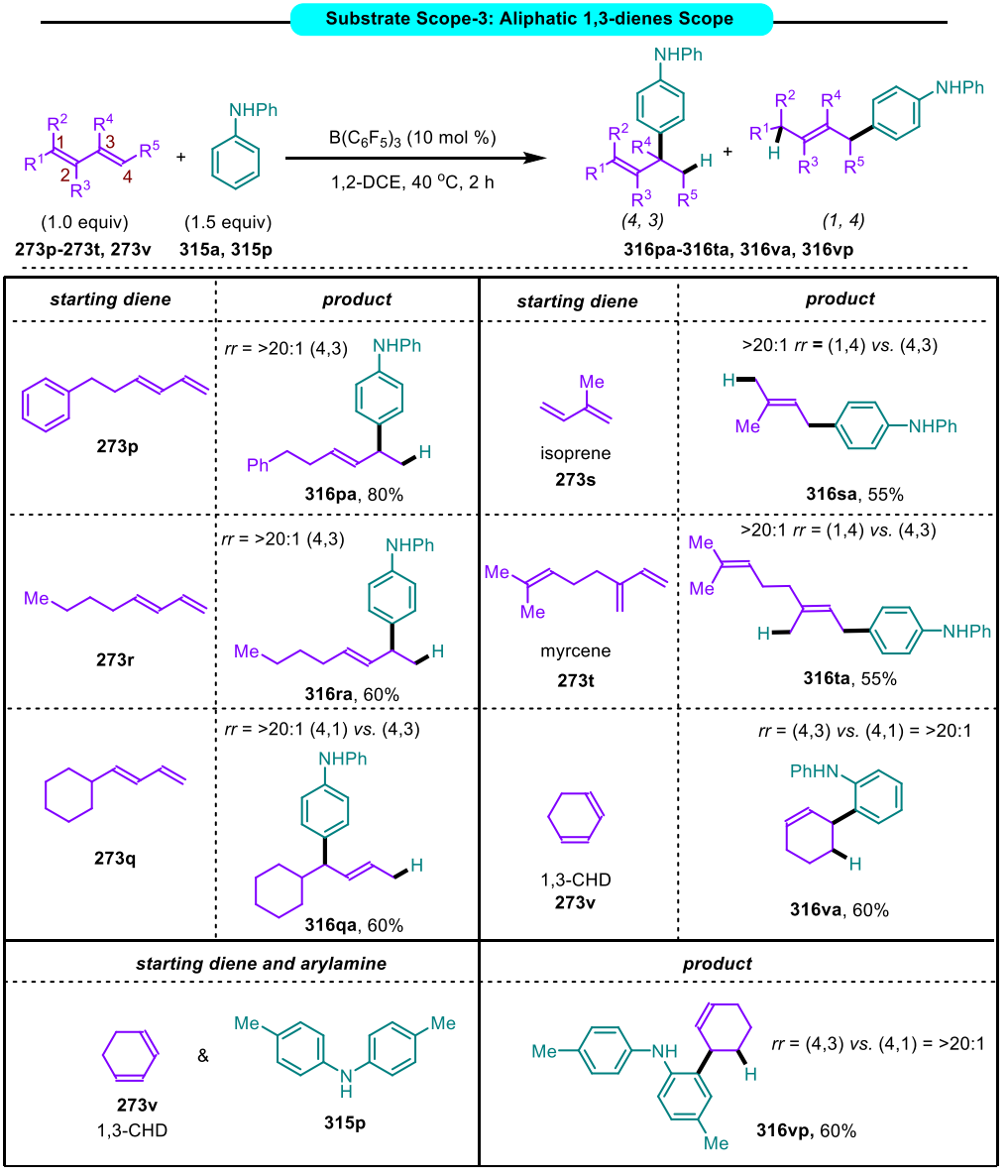
Variation of aliphatic 1,3-dienes: After successful screening of aromatic 1,3-dienes, we have exhibited the reactions with aliphatic and feed stock 1,3-dienes (Scheme 50). Aliphatic 1,3-dienes with 1-phenethyl **273p** or 1-*n*-butyl **273r** group also provided exclusively 4,3-hydroarylated products (**316pa** & **316ra**) in good yields. Surprisingly, 1-cyclohexyl-1,3-diene **273q** furnished the 4,1-hydroarylated product **316qa** with high regioselectivity instead of the expected 4,3-hydroarylation, likely due to the stabilization of the secondary carbocation by the cyclohexyl group. Commercially available 1,3-dienes of isoprene **273r** and myrcene **273s** also provided 1,4-hydroarylated products (**316ra–316sa**) with high regioselectivity (>20:1) and moderate yields.



Scheme 49: Chapter-3 Substrate Scope for the Aromatic 1,3-dienes. **Reaction scale**: 0.12 mmol, isolated yields unless otherwise mentioned. *rr* = regioisomeric ratio, determined by ^{1}H NMR of crude reaction mixture.

Interestingly, cyclohexa-1,3-diene **273v** furnished 4,3-hydroarylation products **316va** and **316vp** in good yield but with a surprising *ortho*- rather than expected *para*-selectivity with respect

to aniline substrate. In this way, highly regioselective 4,3-hydroarylation (*rr* >20:1) was achieved for site 1-substituted 1,3-dienes while 1,4-hydroarylation was reached for feedstock 1,3-dienes, indicating the dependency of the reactivity on additional steric and substituent effects. Our experimental results showed that less hindered or alkyl substituted arylamines mainly afforded the 4,1- along with 4,3-hydroarylated products, 1-aryl substituted dienes furnished 4,3-hydroarylated products, while 1-alkyl substituted dienes mainly provided either 4,1- or 4,3-hydroarylated product. On the other hand, 2-alkyl substituted dienes mainly provided 1,4-hydroarylated products. Depending on the nature of the substituents, highly substituted dienes may undergo 1,2-, 1,4- or 4,1- along with 4,3-hydroarylation.



Scheme 50: Chapter- 3 Substrate Scope for the Aliphatic 1,3-dienes. **Reaction scale**: 0.12 mmol, isolated yields unless otherwise mentioned. *rr* = regioisomeric ratio, determined by ^{1}H NMR of crude reaction mixture.

3.2.3 Mechanistic Studies: Theoretical and Experimental

According to the most prominant outcome of the DFT studies we have performed several control experiment to verify our mechanistic pathway, which shows the residual moisture present in the reaction medium is sufficient to catalyze the reaction via making complex with Lewis acidic $B(C_6F_5)_3$ catalyst. Unfortunately our hypothetical mechanism (discussed above in section 3.1) not the actual pathway for this developed hydroarylation methodology. In the next part of this chapter we will discuss the DFT studies and experimental results to provide the overviw of the actual catalytic pathway for this developed methodology.

3.2.3.1 Theoretical Studies for the Mechanistic Pathway

To gain deeper mechanistic insights, the reactions of diene substrate **273a** with Ph_2NH **315a** and with Ph_3N **315g** were chosen in our extensive DFT studies at the PW6B95-D3/def2-QZVP + COSMO-RS // TPSS-D3/def2-TZVP + COSMO level of theory in 1,2-dichloroethane solution.[93] The computed reaction free energy paths (at 298 K and 1mol/L concentration) are shown in figure 20. Lewis-acidic $B(C_6F_5)_3$ (or Bf_3 for simplicity) itself cannot induce efficient proton transfer from **315a** to another **315a** as the most basic acceptor, which is already 21.6 kcal/mol endergonic. Proton transfer from *N*-protonated ammonium **315a**H^+ to the preferred C4-postion of **273a** is 1.2 kcal/mol endergonic over an additional barrier of 12.0 kcal/mol (via transition state **TS1**$^+$) to form the allyl cation **273a**H^+, which is kinetically inefficient due to a high overall barrier of 33.6 kcal/mol. In contrast, in the presence of residual water, **315a** can be rapidly protonated (over a rather low barrier of 3.5 kcal/mol via **TS0**) by the stable protic complex $H_2O{\cdot}Bf_3$ into the H-bonded contact ion pair of **315a**$H^+HOBf_3^-$ that is 9.0 kcal/mol more stable than the separated ammonium **315a**H^+ and borate $HOBf_3^-$. Further proton transfer from **315a**H^+ to **273a** is 1.2 kcal/mol endergonic over low addition barrier of 13.2 kcal/mol (via **TS1**) to form **273a**H^+. Facile electrophilic aromatic substitution between reactive allyl cation **273a**H^+ and electron-rich amine **315a** is now possible: the electrophilic attack of **273a**H^+ via the C3-position on one *para*-position of **315a** is 4.2 kcal/mol endergonic over a low barrier of 9.9 kcal/mol (via **TS2**$^+$) to form the arenium **316a**H^+, followed by facile deprotonation of **316a**H^+ with neutral amine **315a** that is –7.8 kcal/mol exergonic over a low barrier of 7.0 kcal/mol (via **TS3**$^+$) to form the observed 4,3-hydroarylation product **316a**. Both competing ways of arenium **316a**H^+ deprotonation with less basic **273a** (via **TS3a**$^+$) and with low-concentration of $HOBf_3^-$ are kinetically less efficient. The released ammonium **315a**H^+ can be stabilized by $HOBf_3^-$ into more stable **315a**$H^+HOBf_3^-$ as the actual catalyst to complete the catalytic cycle. The overall **315a**$H^+HOBf_3^-$-catalyzed electrophilic aromatic substitution between **273a** and **315a** is thus –2.4 kcal/mol exergonic over a barrier of 22.2 kcal/mol, rate-limited by the 1,3-diene **273a** protonation step (via **TS1**$^+$) with neutral **315a** as efficient *N*-centred proton shuttle. This mechanism is supported by the deuterium-labelling experiments as well as moderate heating needed in experiment.

Note that in the case of **273a** and **315a**, the three catalytic steps via **TS1**$^+$, **TS2**$^+$ and **TS3**$^+$ are kinetically competing with each other over similar barrier height within 2 kcal/mol for the formation of main product **316a**, with the actual rate-limiting step being dependent on the detailed nature of both diene and amine substrates. Similar electrophilic attack of allyl cation **273a**H$^+$ on one *ortho*-position of **315a** (via **TS2a**$^+$) is kinetically 2.1 kcal/mol less favorable. Moreover, facile electrophilic attack of **273a**H$^+$ via the C1-position on the p*ara*-position of **315a** is kinetically only 1.0 kcal/mol less favorable due to less efficient deprotonation with **315a** (via **TS3b**$^+$). Thus, our DFT calculations suggest that the actual rate-determining step and regioselectivity observed in experiment is due to a subtle competition between several possible product channels, dependent on substituents on both 1,3-diene and aniline substrates, as indeed observed in experiment (See Schemes 48-50 for broad substrate scope).

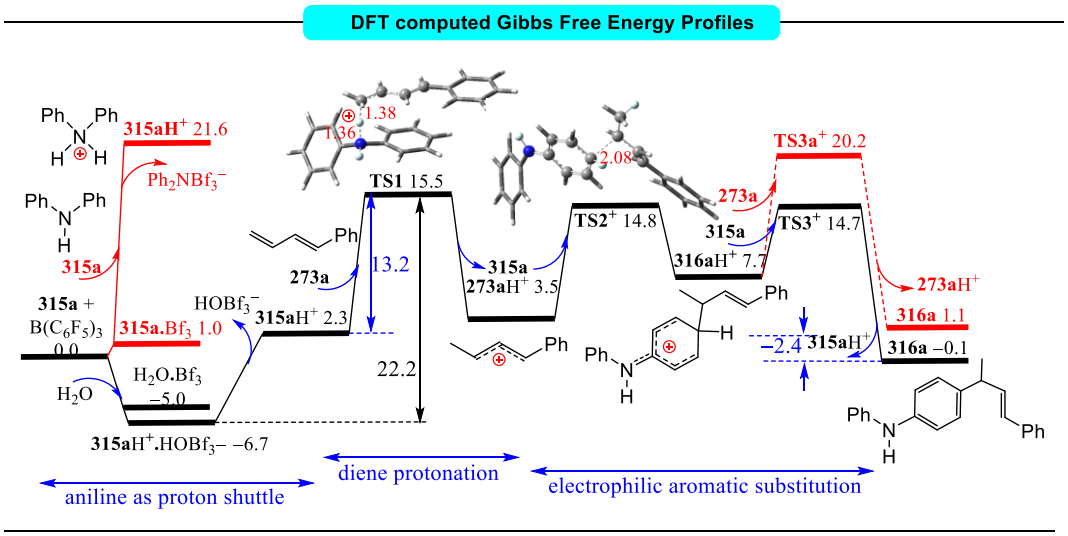


Figure 20: DFT computed Gibbs free energy profiles (in kcal/mol at 298 K and 1 mol/L reference state) for $B(C_6F_5)_3$ induced electrophilic aromatic substitution of 1,3-diene $PhCH{=}CHCH{=}CH_2$ (**273a**) with diphenylamine Ph_2NH (**315a**). Selected bond lengths are shown in Å.

For example, the extensive DFT calculations show that the *N*-methylation of **315a** leads to a 3.8 kcal/mol higher proton affinity with also increased steric hindrance at the *N*-center of tertiary amine **315h**. As a result, the electrophilic attack of **273a**H$^+$ via the 1-postion becomes comparable with the 3-position on more electron-rich phenyl-rings of **315h**, leading to reduced 4,3-hydroarylation selectivity; moreover, deprotonation of arenium **316h**H$^+$ with $HOBf_3^-$ becomes kinetically more favorable than that with neutral **315h** to form the final products **316h** and **316h′** (Figure 21).

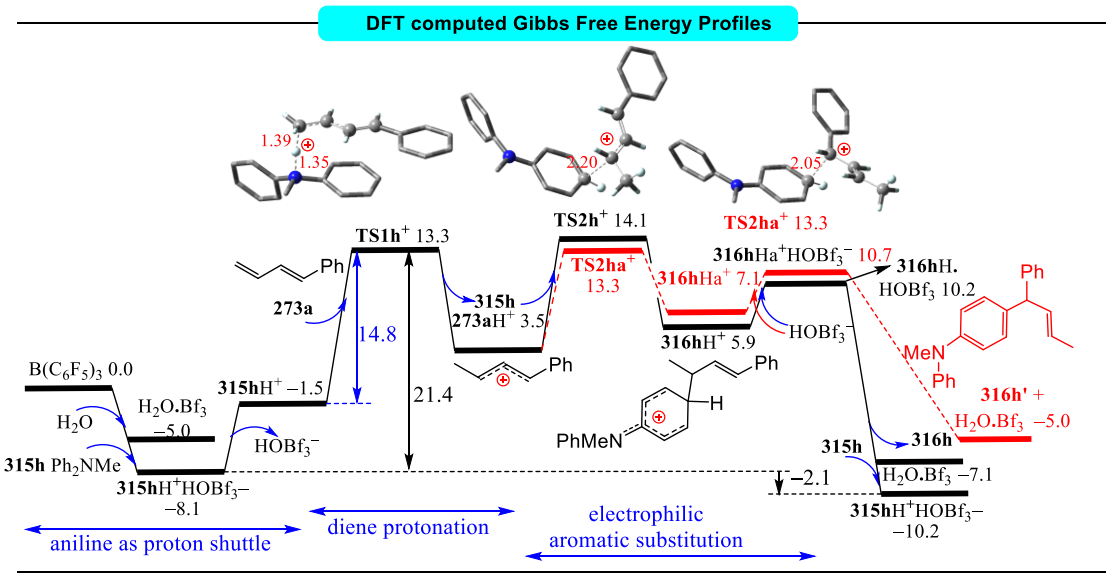


Figure 21: DFT computed Gibbs free energy profiles (in kcal/mol at 298 K and 1 mol/L reference state) for $B(C_6F_5)_3$ induced electrophilic aromatic substitution of 1,3-diene PhCH=CHCH=CH_2 (**273a**) with triphenylamine Ph_2NMe (**315h**). Selected bond lengths are shown in Å.

In contrast, the DFT calculations show that further *N*-arylation of **315a** leads to 4.3 kcal/mol lower proton affinity with increased steric hindrance at the *N*-center of Ph_3N (**315g**). As a result, as shown in figure 22, the 4-position of 1,3-diene substrate **273a** is selectively protonated by acidic $H_2O{\cdot}Bf_3$ complex at first, which is 2.6 kcal/mol endergonic over a barrier of 14.8 kcal/mol (via **TS1g**) to form the contact ion pair **273a**$H^+HOBf_3^-$ that is 5.9 kcal/mol more stable than the separated allyl cation **273a**H^+ and borate anion $HOBf_3^-$. Further electrophilic aromatic substitution of **273a**H^+ via 3-position on one *para*-position of **315g** is 5.6 kcal/mol endergonic over a low barrier of 11.5 kcal/mol (via **TS2g**$^+$) to form the arenium **316g**H^+, followed by facile deprotonation with $HOBf_3^-$ via the H-bonded complex **273a**$H^+HOBf_3^-$ to form the main 4,3-hydroarylation product **316g** along with regenerated $H_2O{\cdot}Bf_3$ as actual protic acid catalyst. The overall $H_2O{\cdot}Bf_3$ catalyzed electrophilic aromatic substitution of **273a** and **315g** is thus –3.0 kcal/mol exergonic over a barrier of 20.4 kcal/mol, rated-limited by the arenium **316g**H^+ deprotonation with $HOBf_3^-$, with phenyl *para*-H as actual proton source for the protonation of 1,3-diene substrate **273a** during the catalysis. Though very similar kinetic barriers are computed for the catalytic steps of electrophilic aromatic addition (**TS2g**$^+$) and subsequent arenium **316g**H^+ deprotonation with $HOBf_3^-$, the latter is very likely the actual rate-limiting step according to our KIE experiment.

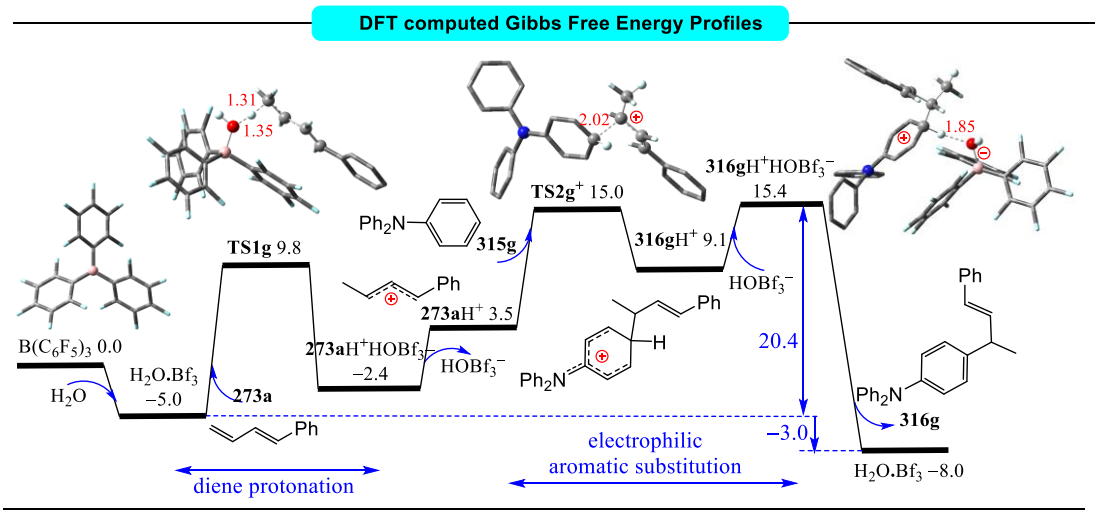
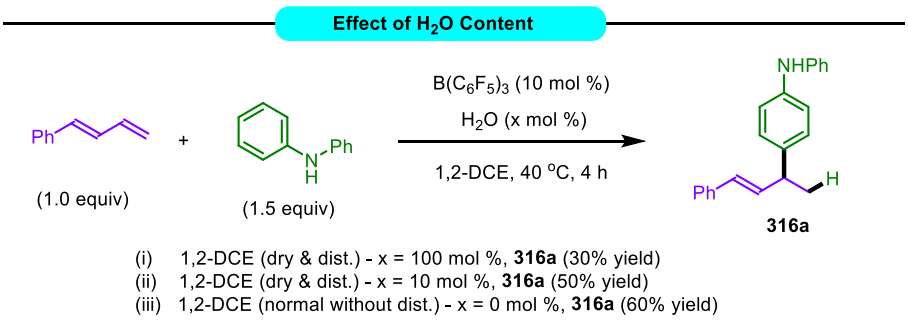


Figure 22: DFT computed Gibbs free energy profiles (in kcal/mol at 298 K and 1 mol/L reference state) for $B(C_6F_5)_3$ induced electrophilic aromatic substitution of 1,3-diene PhCH=CHCH=CH_2 (**273a**) with triphenylamine Ph_3N (**315g**). Selected bond lengths are shown in Å.

3.2.3.2 Control Experiments for Mechanistic Pathway

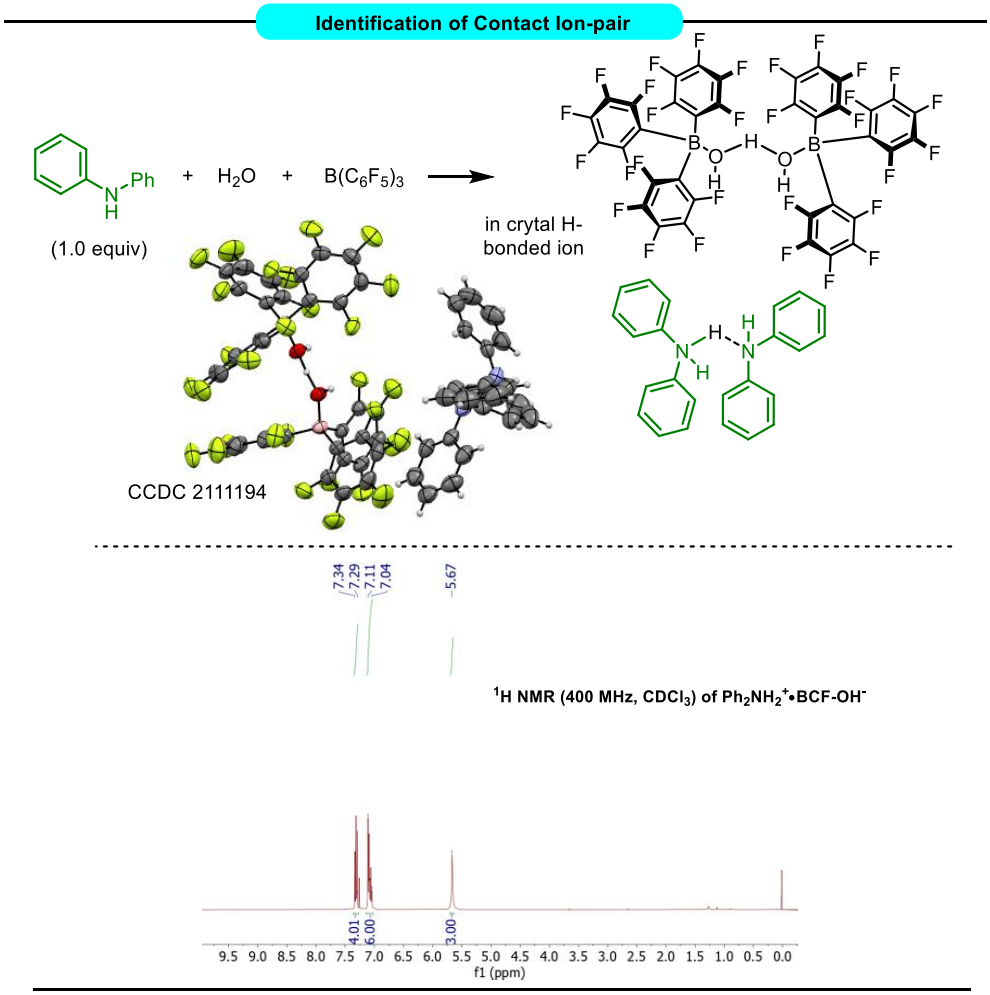
DFT calculations suggest that the formed protic complex between residual H_2O and $B(C_6F_5)_3$ actually protonate the substrate **315a**. To check the effect of H_2O in the hydroarylation we have performed several controlled experiments with H_2O. We obtained the product **316a** in 30% and 50% isolated yields, when 100 mol % and 10 mol % H_2O was added, respectively under our optimized conditions. Interestingly the normal 1,2-DCE (without drying and distillation), without the addition of extra H_2O (0 mol %) **316a** was furnished in 60% yield (Scheme 51-ii). So as a result, these experiments suggest that water content did not shut down the reaction even up to 100 mol % amount. However, excess water diminished the isolated yield of product **316a**. Hence, residual amount of water content is enough to initiate the reaction.



Scheme 51: Chapter 3: Control Experiment- Effect of Water Content

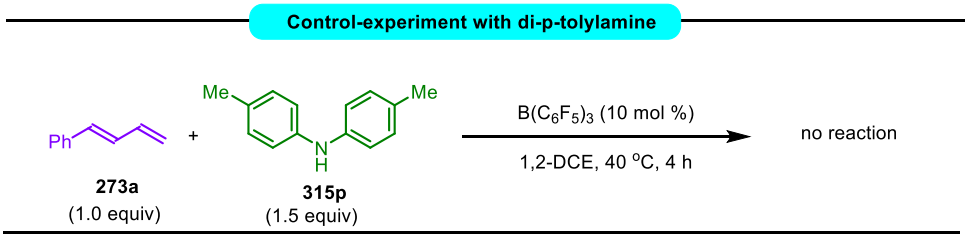
An extensive DFT studies show the contact ion pair **315a**$H^+HOB(C_6F_5)_3^-$ formation from $B(C_6F_5)_3$, residual H_2O and amine substrate. From a separate experiment of mixing $B(C_6F_5)_3$, H_2O and amine substrates (2^o or 3^o) we observed the formation of contact ion pair **315a**$H^+HOBf_3^-$ in the case of diphenyl amine **315a** which was confirmed by ^{19}F, ^{11}B and ^1H NMR in solution (in

crystal, H-bonded ions of $(\mathbf{315a})_2H^+$ and $(HOB(C_6F_5)_3)_2H^-$ are formed instead CCDC 2111194)[103] (Scheme 52). The formation of $H_2O{\cdot}B(C_6F_5)_3$ adduct in case of triphenyl amine was also confirmed by ^{19}F and ^{11}B NMR study.



Scheme 52: Chapter 3: Control Experiment- Identification of Contact-ion Pair

Moreover, in the case of *para*-substituted arylamine e.g., di-*p*-tolylamine we did not observe any hydroarylated product formation. (Scheme 53)

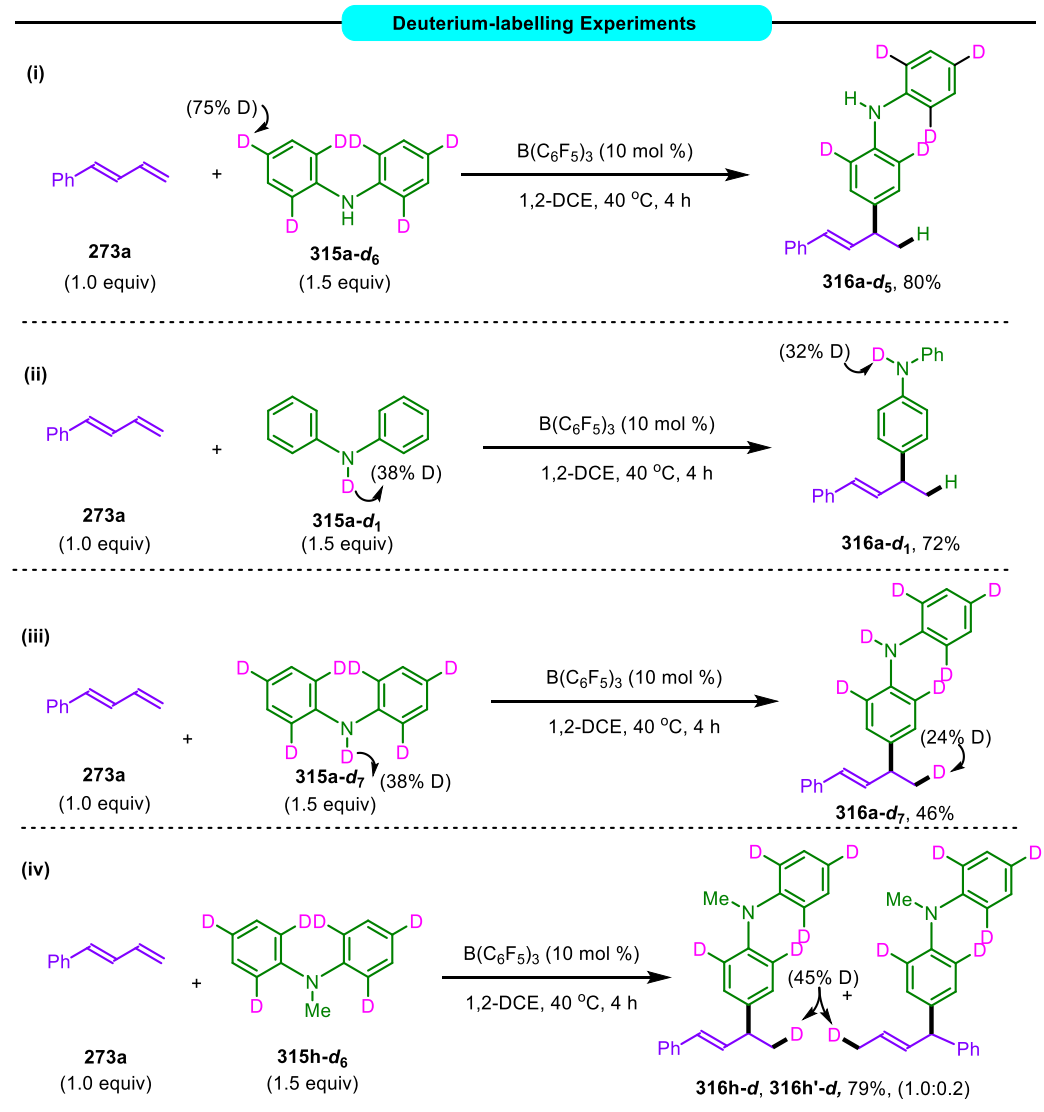


Scheme 53: Chapter 3: Control Experiments- Reaction with *para*-substituted Arylamine

To check the role of aryl C–H or Ph_2N–H proton in this hydroarylation reaction we have performed several deuterium-labelling experiments. First we performed the reaction of 1,3-diene **273a** with deuterated aryl C–D (diphenylamine-d_6) **315a-*d*$_6$** or Ph_2N–D (diphenylamine-d_1) **315a-*d*$_1$**, but no deuterium transfer into hydroarylated products was observed (Scheme 54-i and 54-ii).

This observation is in accordance with our proposed mechanism in figure 20. Then after we tried our reaction with fully deuterated diphenylamine-d_7 **315a-*d*$_7$** and 1,3-diene **273a**. Interestingly this reaction provided regioselective deuterium transfer **316a-*d*$_7$** (Scheme 54-iii). Moreover, in case of tertiary amine, deuterium transfer from the *para*-C–D bond is confirmed by the C–D bond formation in **316h-*d*, 316h′-*d*** (Scheme 54-iv).

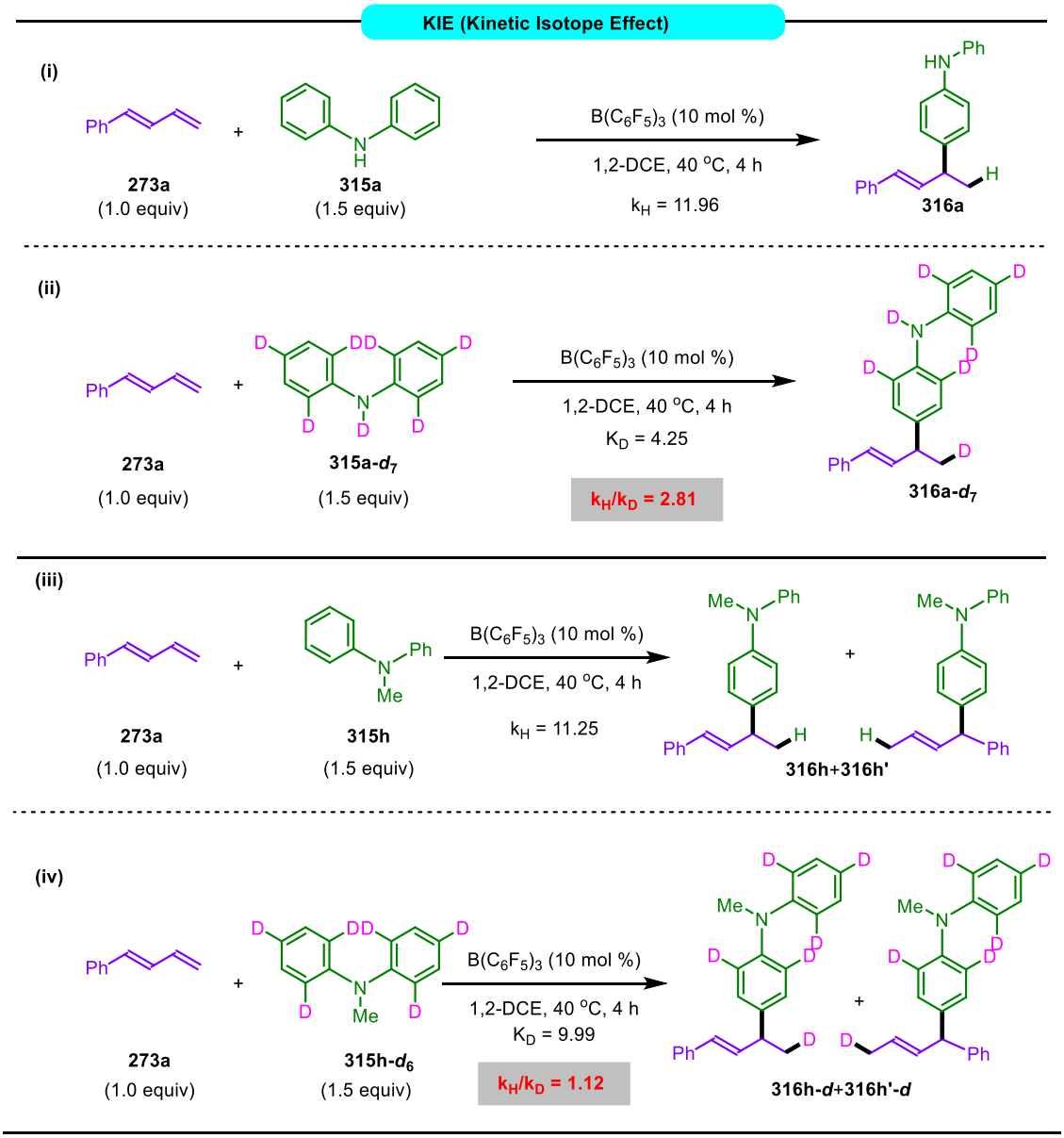
These deuterium-labelling experiments clearly show that only fully deuterated (N–D and C–D) diphenylamine able to provide the deuterium incorporation into the hydroarylation product. The proton can come from either N–H or *para*-C–H of arylamine which indicates that the secondary arylamine acts as the proton shuttle in presence of $H_2O{\cdot}B(C_6F_5)_3$ complex.



Scheme 54: Chapter 3: Control Experiment- Deuterium-Labelling Experiment

Furthermore, the independent kinetic isotope effect (KIE) has been measured for both secondary and tertiary arylamines separately (Scheme 55), revealing a k_H/k_D value of 2.81 and 1.12, respectively. These results suggest that proton transfer is involved in the rate-limiting

catalytic step for secondary arylamine substrates but is much less involved for tertiary arylamines, as also supported by our DFT calculations shown above.



Scheme 55: Chapter 3: Control Experiment- KIE Study

3.3 Conclusion

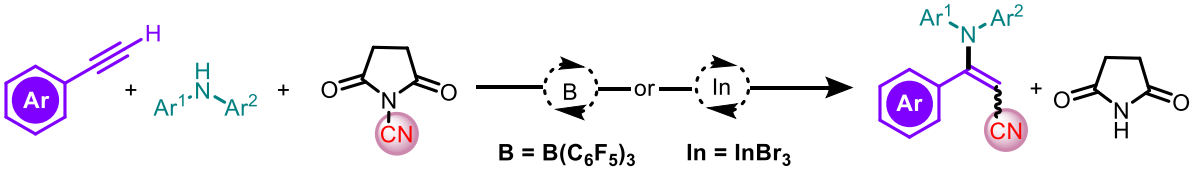
In this chapter we have explored a rarely investigated transition-metal-free regioselective hydroarylation of 1,3-dienes with seconadry, and tertiary arylamine derivatives. Here, boron-based Lewis acid $B(C_6F_5)_3$ and residual moisture utilized as catalyst for the ptotonation of 1,3-dienes followed by nucleophilic attack by arene ring of arylamines. Remarkably, various seconadry, tertiary arylamine derivatives, and dienes even upto trisubstituted 1,3-dienes were successfully utilized for the *para*-selective hydroarylated product formation. Complete

mechanistic pathway is investigated with high-level DFT calculation supported by ^{11}B and ^{19}F-NMR, SC-XRD and deuterium-lebelling experiments.

Chapter 4

Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and *N*-cyanosuccinimide

Chapter 4: Our designed work



■ *selectivity, E:Z = 70:30 to 90:10* ■ *non-toxic cyanide source (stable and quickely synthesizeable)*

■ *broad substrate scope of alkynes as well as arylamines* ■ *mechanistic rationale* ■ *gram-scale synthesis*

❖ This work was published in Advanced Synthesis and Catalysis (a journal of Wiley). Please see the citation as: "**Kumar, G.;** Bhattacharya, D.; Chatterjee, I. *Adv. Synth. Catal*. **2022**, *364*, 2416–2421."

4. Abstract

In this chapter, transition-metal-free Lewis acid-assisted aminocyantion of alkyne for the synthesis of *β*-aminoacrylonitrile derivatives is documented. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) and indium tribromide ($InBr_3$) both were utilized separately as a main group Lewis acid for this transformation. The proposed methodology featured with non-toxic electrophilic cyanide surrogate and provides value added *β*-aminoacrylonitrile derivatives. Our experimental studies show that the complex formation between Lewis acid and π-electron density of alkyne exhibited the *in situ* alkyne nitrile intermediate. Subsequent hydroamination of this intermediate furnishes the aminocyanted products.

4.1. Introduction

After the successful functionalization of 1,3-dienes to construct carbon-heteroatom (C–S), and carbon-carbon (C–C) bonds in chapters 2 and 3, we planned for the functionalization of alkynes to construct C–N and C–C bonds using main group Lewis acids. In this regard, we have initiated literature analysis and realized that the aminocyanation of alkynes would be an interesting transformation because the cyanide-containing compounds possess profound applications in numerous bio-active, pharmaceuticals, agrochemicals, materials, and catalysis. Also, the easy transformation of cyano group into another functionality, e.g., amide, acid, aldehyde, ester, ketone, tetrazole etc. makes them interesting for creating molecular complexity. Acrylonitrile derivatives act as the intermediate for various pharmaceuticals, polymers, and fine chemicals. A few of the acrylonitrile unit containing bioactive compounds is depicted in figure **23**.[104]

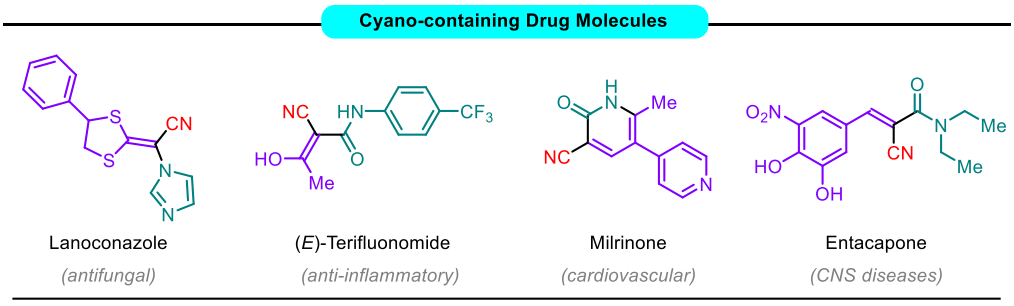


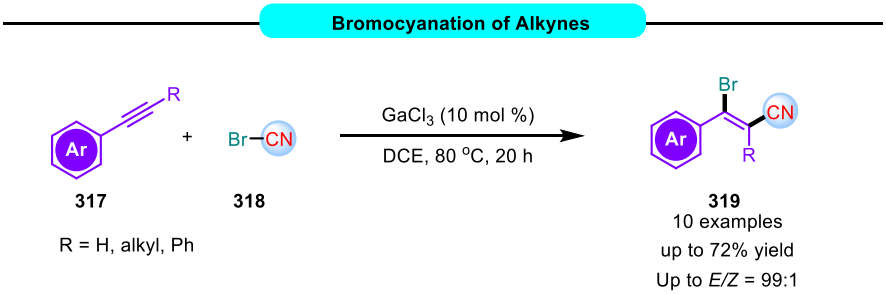
Figure 23: Cyano Containing Drug Candidates

The synthesis of acrylonitrile derivatives is challenging because this reaction requires a special setup to control the release of hazardous HCN gas. So, the cyanofunctionalization of acetylene by using a non-toxic cyanide source remains a significant and most prominent method to achieve acrylonitrile derivatives.[105] Moreover, cyanofunctionalization can be done by using cyanide source along with other functional partners from a single molecule or from two separate molecules. The addition of both these two functional groups across the triple bond provides cyanofunctionalized alkene derivatives (acrylonitrile). A plethora of cyanofunctionalizations is known, e.g., carbocyanation, cyanothiolation, chlorocyanation, bromocyanation, cyanotriflation,

cyanosilylation, cyanogermylation, aminocyanation, etc. However, in the cyanofunctionalization of alkynes, mainly transition metal catalysts are extensively studied, whereas reports based on the main group Lewis acids are scarce.[106] We have chosen the aminocyanation of alkynes to target the valuable β-aminoacrylonitile derivatives, which can be easily converted into natural and unnatural amino acids. After an extensive literature search, several reports for aminocyanation reactions are described below, where we mainly focused on main group Lewis acid-catalyzed reactions.

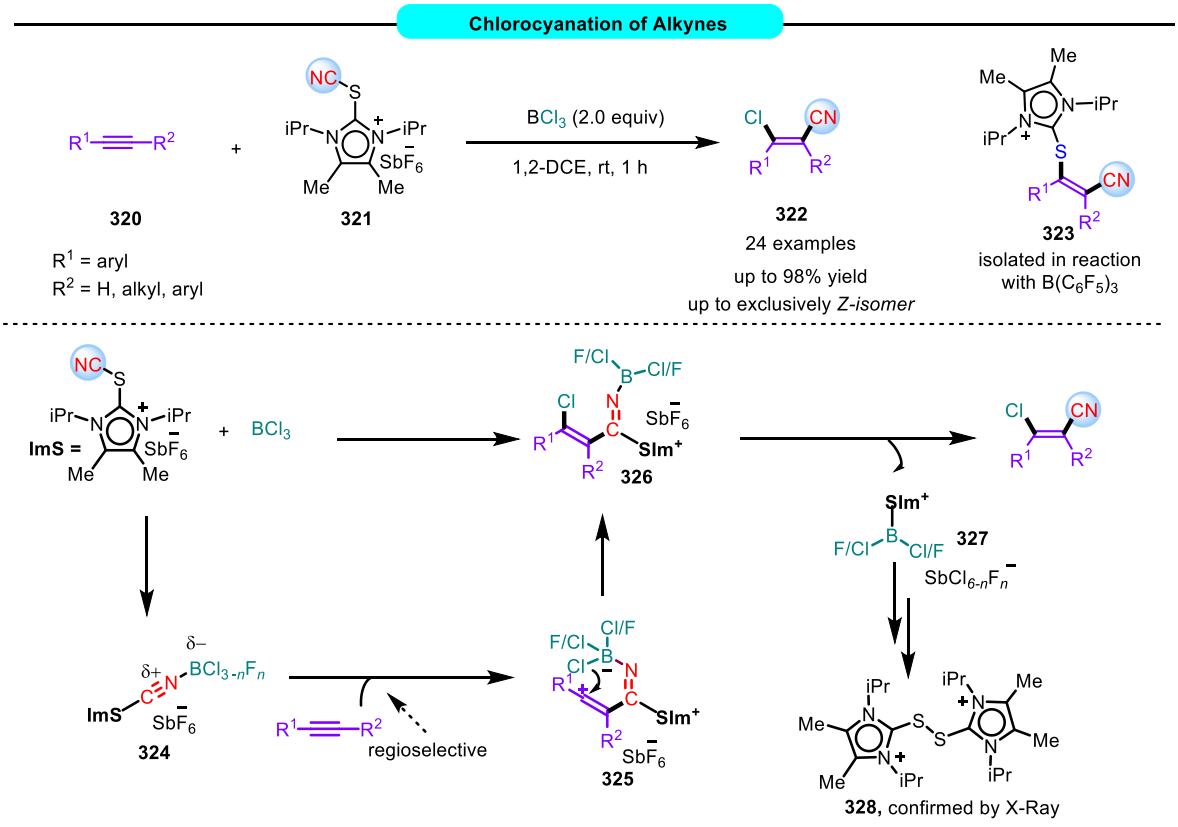
4.1.1 Literature Reports for the Cyanofunctionalization of Alkynes

In 2011, Ohe and co-workers introduced a $GaCl_3$-catalyzed bromocyanation of alkynes **317** using cyanogen bromide **318** as the source of Br and CN functional groups. This methodology generates (*Z*)-*β*-bromoacrylonitrile derivatives **319**, which is important from the synthetic chemistry point of view as both the groups attached across double a bond can easily be participated in various coupling reactions and other value-added transformations. This reaction remains regioselective in terms of addition of Br and CN groups across alkyne (Scheme 56).[107]



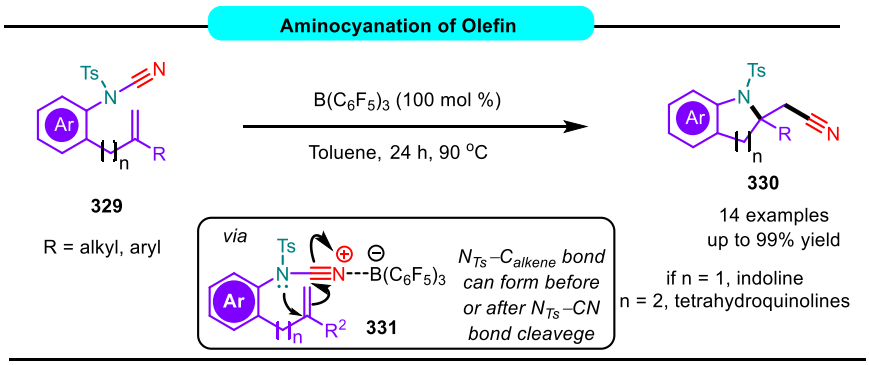
Scheme 56: Ohe's Bromocyanation of Alkynes

Similarly, in 2017, Alcarazo and co-workers documented the BCl_3-mediated chlorocyanation of alkyne **320** derivatives. They utilized thioimidazolium salt **321** as the electrophilic cyanating reagent and the boron trichloride as a chloride source (Scheme 57). This process remains remarkably regio- and stereoselective for chlorocyanation **322** via *syn* addition pathway. Both internal and terminal alkynes worked well under their standard reaction conditions. Interestingly in the case of $B(C_6F_5)_3$, they isolated the cyanothiolated product **323**. According to their plausible mechanism, Lewis acidic BCl_3 activates the CN through *N*-atom (via σ-activation) **324** and increases its electrophilicity. Alkyne **320** performs a nucleophilic attack at the activated CN through C-atom, giving vinyl carbocationic intermediate **325**. This carbocation is trapped by chloride from BCl_3 to provide chlorocyanated products **322**.[108]



Scheme 57: Alcarazo's Chlorocyanation of Alkynes

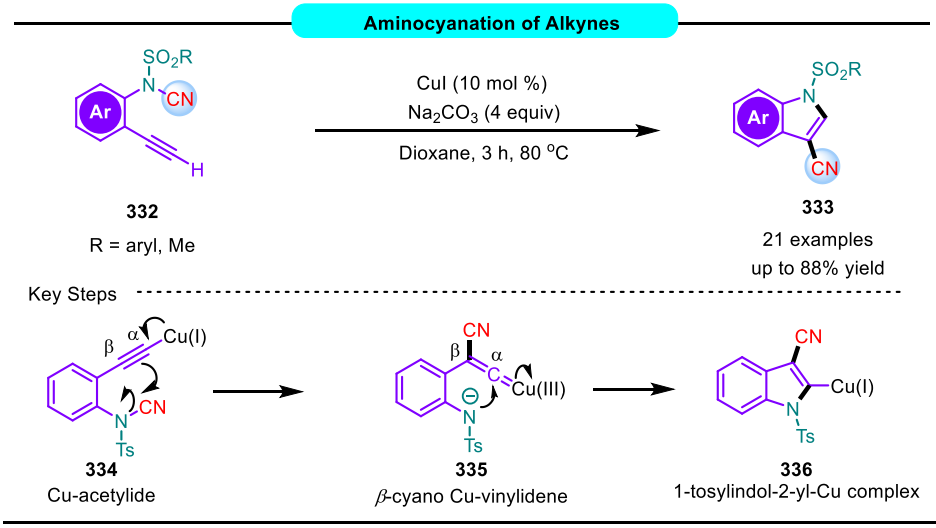
In 2014, Douglas and co-workers reported $B(C_6F_5)_3$ promoted intramolecular aminocyanation of alkenes **329**. The N–CN bond cleavage becomes easier by activation of *N*-sulfonyl cyanamides with Lewis acidic $B(C_6F_5)_3$ **331**. This is the only report in the literature we have found for the $B(C_6F_5)_3$-assisted aminocayanation of alkenes. In this process, 100 mol % of $B(C_6F_5)_3$ was used to get the *N*-heterocyclic aminocyanation for the synthesis of indolines and tetrahydroquinolines derivatives **330**. So, to reduce the amount of costly $B(C_6F_5)_3$ they have shown one reaction with 20 mol % with good yield at an extended time of up to 48 h (Scheme 58).[109]



Scheme 58: Douglas's Intramolecular Aminocyanation of Olefins

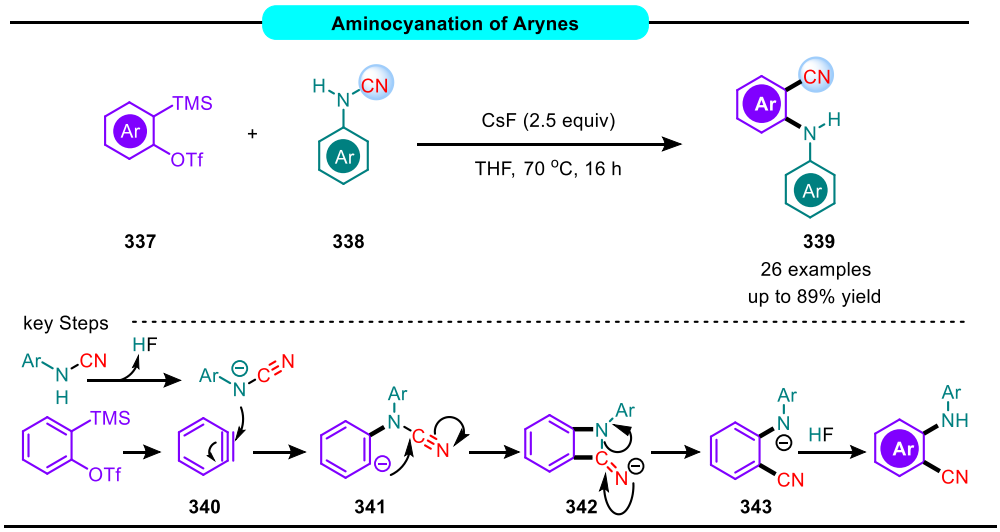
In 2016, Chien and his team documented CuI-catalyzed intramolecular aminocyanation of alkynes **332** to synthesize 3-cyanoindole derivatives **333**. The Cu-acetylide **334** is the key intermediate for this reaction, which increases the electron density at *β*-carbon that can perform

nucleophilic attack at CN group resulting the *β*-cyano Cu-vinylidene **335**. Further attack by tosylamide at *α*-carbon generate 1-tosylindol-2-yl–Cu complex **336**, the protonation of this complex furnishing 3-cyano-indole derivatives **333** (Scheme 59).[110]



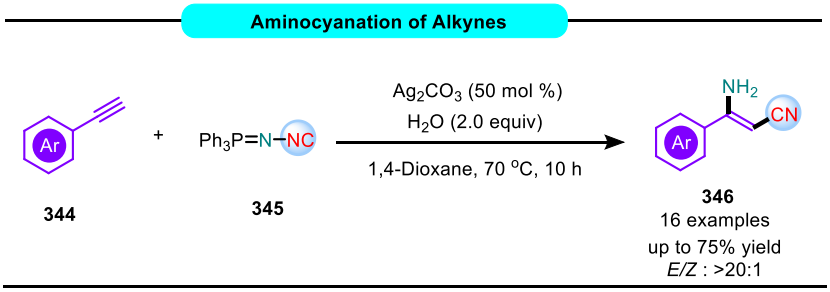
Scheme 59: Chien's Intramolecular Aminocyanation of Alkynes

In 2014, Zeng and Rao explored aminocyanation of *in situ* generated arynes **340** for the synthesis of aminobenzonitrile derivatives **339**. Aryl cyanamides **338** were utilized for the addition across aryne bonds to give bifunctional aminobenzonitrile derivatives **339**. AgF plays a decisive role for the generation of benzyne **340** and deprotonation of cyanamide. This deprotonated cyanamide performs a nucleophilic attack at benzyne, leading to the formation of phenyl anion **341**. This phenyl anion **341** attacks the carbon center of the cyano group and forms a four-membered cyclic intermediate **342**. The ring opening **343** of these four-membered cyclic intermediates **342**, followed by protonation leads to the desired product (Scheme 60).[111]



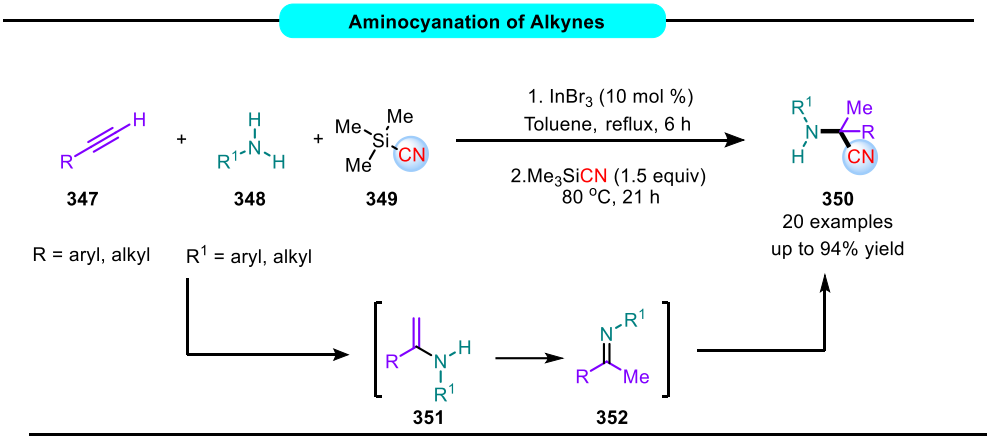
Scheme 60: Zeng's Aminocyanation of Arynes

In 2019, Wang and his team documented intermolecular aminocyanation of alkynes **344** for the synthesis of *β*-aminoacrylonitrile derivatives **346**. *N*-isocyanoiminotriphenylphosphorane (NIITP) **345** was utilized as a source of both amine and cyano groups for the addition across alkyne bonds to give bifunctional aminocyanated products **346** (Scheme 61).[112]



Scheme 61: Wang's Aminocyanation of Alkynes

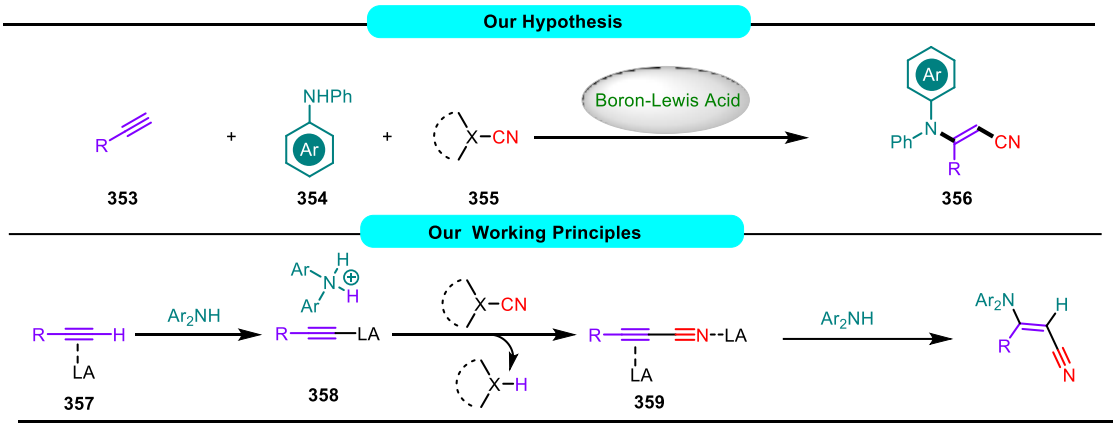
In 2016, Sakai and co-workers introduced the $InBr_3$-catalyzed three-component reaction for the aminocyanation of alkynes. They have utilized TMSCN **349** as a nucleophilic cyanide source along with 1° and 2° amine derivatives **348** as an amine source. Authors claimed that this reaction works via the generation of imine intermediate **352** from hydroamination of alkynes **347** with amines **348**. The resulting intermediate **352** underwent hydrocyanation with nucleophilic cyanide reagent TMSCN and furnished quaternary *α*-aminonitrile derivatives **350** (Scheme 62).[113]



Scheme 62: Sakai's Aminocyanation of Alkynes

By doing this thorough literature search and our knowledge on the main group Lewis acid catalysis, we speculated the reaction for the synthesis of *β*-aminoacrylonitrile derivatives. Also, in the view of non-hazardous cyanide sources, *N*-cyanosuccinimide remains very less explored.[114] We got motivation from the Alcarazo work, where they also observed the thiocyanated product **323** in their chlorocyanation reactions in presence of $B(C_6F_5)_3$ (Scheme 57); and from Douglas's work on the intramolecular aminocyanation of alkenes (Scheme 58). We speculated utilizing the N–CN bond activation ability of $B(C_6F_5)_3$ to release electrophilic CN^+ and parallel generation of alkynyl-borane **358** via deprotonation of alkyne C–H with an amine. So, we planned to combine

these reactivities of $B(C_6F_5)_3$ for aminocyanation of alkynes by utilizing *N*-cyanosuccinimide as the electrophilic cyanide[115] source (Scheme 63).



Scheme 63: Chapter 4: Our Proposed Working Hypothesis

4.1.2 Challenges for the Aminocynation of Alkynes

As per the discussion in chapter 1 and beginning of this chapter about the reactivities of Lewis acids with alkynes, we can analyze the challenges. In the case of aminocyanation of alkynes with arylamines, different side reactions are possible, e.g., 1) cyanation of electron-rich arylamine via aryl ring or *N*-center, 2) hydroarylation of alkynes with arylamines (already reported by Stephan and Erker), 3) regioselectivity for amine and cyano group addition across alkyne. Besides these challenges, the selection of non-toxic electrophilic cyanide is another issue. Mainly the organic compounds containing cyanide or amide groups are utilized as the non-hazardous cyanide sources in the literature, e.g., 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzyl cyanide, acetonitrile, *N*,*N*-dimethylformamide (DMF), azobisisobutyronitrile (AIBN), trimethylsilylcyanide (TMSCN), aryl(cyano)iodonium triflates, *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS), bis(dialkylamino)cyanoboranes, malononitrile, and so on. But *N*-cyanosuccinimide remains very less explored, so we are curious to inspect it in our aminocyanation reaction.[114, 115]

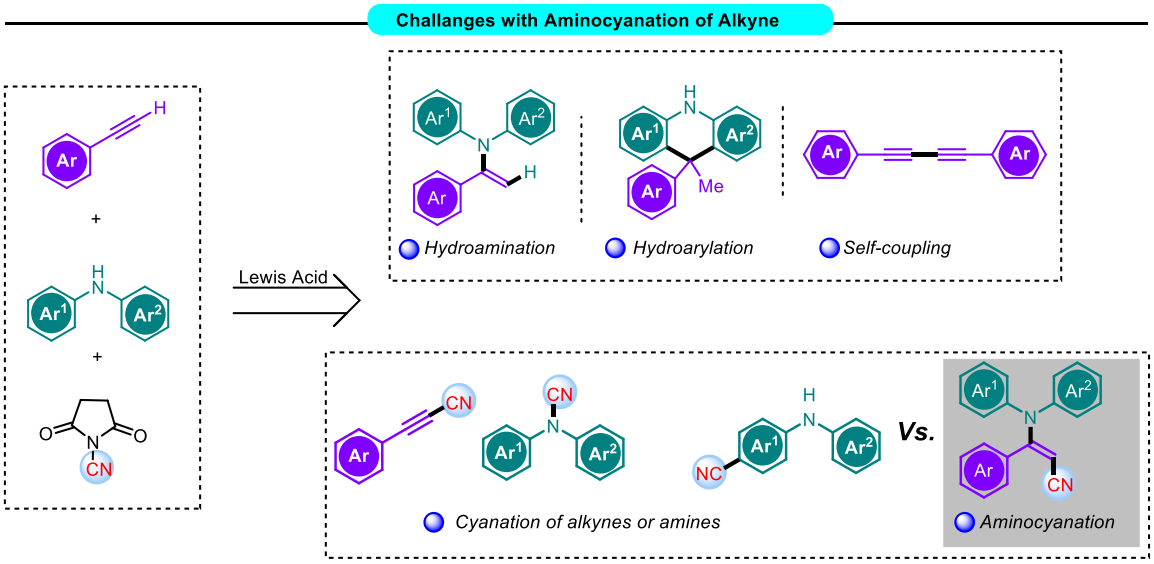


Figure 24: Chapter 4: Possible Challenges

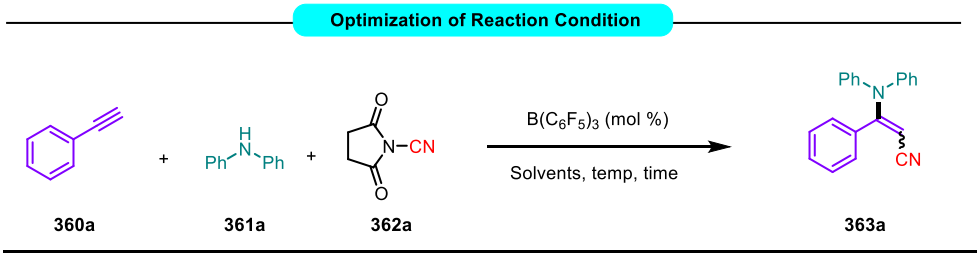
4.2. Result and Discussion

4.2.1 Optimization of the Reaction Condition

As per our speculation (described in Scheme 63), we started our investigation for the development of unique transition-metal-free Lewis acid catalyzed aminocyanation of alkynes. To check the feasibility of our proposal, we started our enquiry by reacting ethynylbenzene (**360a**, 2.4 equiv) with diphenylamine (**361a**, 1.0 equiv) and *N*-cyanosuccinimide (**362a**, 1.6 equiv) as the model substrates in various solvents (0.24 M) and in the presence of catalyst $B(C_6F_5)_3$ (10 mol %) at different temperatures and time.

After screening of a series of solvents using $B(C_6F_5)_3$ (10 mol %) at 80 ^oC (Table 3 entries 1–7), it was observed that toluene is the compatible solvent. On increasing the reaction temperature the yield of product **363a** improved (Table 3 entries 8–9). Then by increasing the mol % of $B(C_6F_5)_3$, we quickly realized that higher catalyst loading was necessary to obtain good isolated yield of product **363a** (Table 3, entries 10–12). However, further increase of $B(C_6F_5)_3$ mol % (up to 100 mol %) and reaction time (up to 24 h) did not show significant improvement in terms of yield of **363a** (Table 3, entries 13–16). However, even with in 8 h reaction time the similiar result was obtained (Table 3, entry 17). So by keeping this as best conditions we further screened several other Lewis acids shown in table 4.

Table 3. Chapter 4: Optimization Study: Screening of Solvents, Time, Temperature, and Catalyst Loading

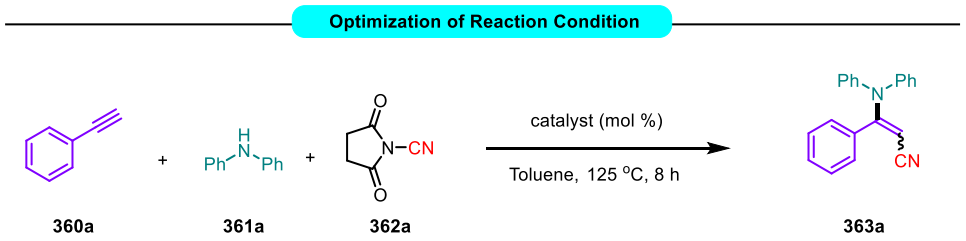


Entry	Catalyst (mol %)	Solvents	Time (h)	Temp (^{o}C)	Yield 363a (%)	*E/Z*[a]
1	$B(C_6F_5)_3$ (10)	THF	12	80	n.r	-
2	$B(C_6F_5)_3$ (10)	CH_3CN	12	80	<2	-
3	$B(C_6F_5)_3$ (10)	CH_3Cl	12	80	<2	-
4	$B(C_6F_5)_3$ (10)	$MeNO_2$	12	80	n.r	-
5	$B(C_6F_5)_3$ (10)	Toluene	12	80	6	75:25
6	$B(C_6F_5)_3$ (10)	DCM	12	80	n.r	-
7	$B(C_6F_5)_3$ (10))	1,2-DCE	12	80	4	75:25
8	$B(C_6F_5)_3$ (10)	Toluene	12	100	12	74:26
9	$B(C_6F_5)_3$ (10)	Toluene	12	120	26	72:28
10	$B(C_6F_5)_3$ (20)	Toluene	12	120	31	72:28
11	$B(C_6F_5)_3$ (30)	Toluene	12	120	44	71:29
12	**$B(C_6F_5)_3$ (40)**	**Toluene**	**12**	**120**	**70**	**70:30**
13	$B(C_6F_5)_3$ (50)	Toluene	12	120	70	70:30
14	$B(C_6F_5)_3$ (60)	Toluene	12	120	70	70:30
15	$B(C_6F_5)_3$ (100)	Toluene	12	120	70	70:30
16	$B(C_6F_5)_3$ (40)	Toluene	24	120	70	70:30
17	**$B(C_6F_5)_3$ (40)**	**Toluene**	**8**	**120**	**70**	**70:30**

Reaction condition: **360a** (2.4 equiv., 0.144 mmol), **361a** (1.0 equiv., 0.06 mmol) and **362a** (1.6 equiv., 0.096 mmol). [a] *E/Z*, determined by the ^{1}H NMR analysis of crude reaction mixtures. n.r. = no reaction.

Other Lewis acids such as BCl_3, $BF_3{\cdot}Et_2O$ and $GaCl_3$ were unable to initiate the reaction, whereas, $In(OTf)_3$, $InCl_3$ catalyzed the reaction albeit in a lower yield (Table 4, entries 1–5). In the case of $InBr_3$, reaction occurred smoothly and provided product **363a** in very good yield (Table 4, entry 6). Further the halides and triflates of Ag(I), Zn(II), Cu(I), Cu(II), Fe(III) remains unreactive or very less reactive under optimized reaction conditions (Table 4, entries 7-14). Upon lowering the amount of $InBr_3$ the yield of product **363a** also lowered (Table 4, entry 15).

Table 4. Chapter 4: Optimization Study: Screening of Catalysts

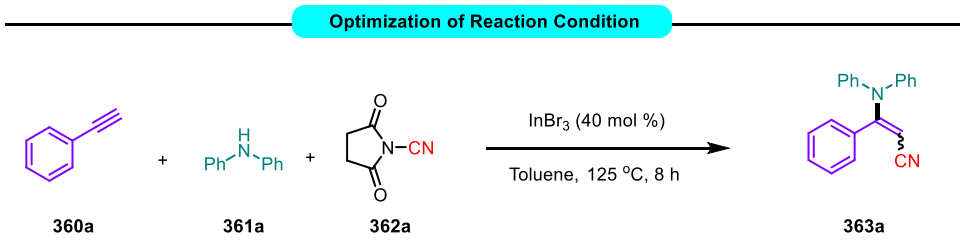


Entry	Catalyst (mol %)	Yield 363a (%)	*E/Z*[a]
1	BCl_3[b] (40)	n.r	-
2	$BF_3{\cdot}Et_2O$ (40)	n.r	-
3	$GaCl_3$ (40)	n.r	-
4	$In(OTf)_3$ (40)	27	70:30
5	$InCl_3$ (40)	20	70:30
6	**$InBr_3$ (40)[c]**	**70**	**70:30**
7	AgF (40)	n.r	-
8	AgOTf (40)	n.r	-
9	$ZnCl_2$ (40)	n.r	-
10	$Zn(OTf)_2$ (40)	n.r	-
11	CuI (40)	<5	-
12	CuOTf (40)	<5	-
13	$Cu(OTf)_2$ (40)	n.r	-
14	$FeCl_3$	n.r	-
15	$InBr_3$ (30)	55	70:30

Reaction condition: **360a** (2.4 equiv., 0.144 mmol), **361a** (1.0 equiv., 0.06 mmol) and **362a** (1.6 equiv., 0.096 mmol). [a] *E/Z*, determined by the ^{1}H NMR analysis of crude reaction mixtures. [b] Used as 1 M solution in DCM. n.r. = no reaction. [c] 6 mmol scale reaction provided 50% isolated yield of **363a**.

Further the screening of substrates and *N*-cyanosuccinimide equivalencies shown in table 5, where the entry 10 remains as an optimized reaction condition for our aminocyanation reaction.

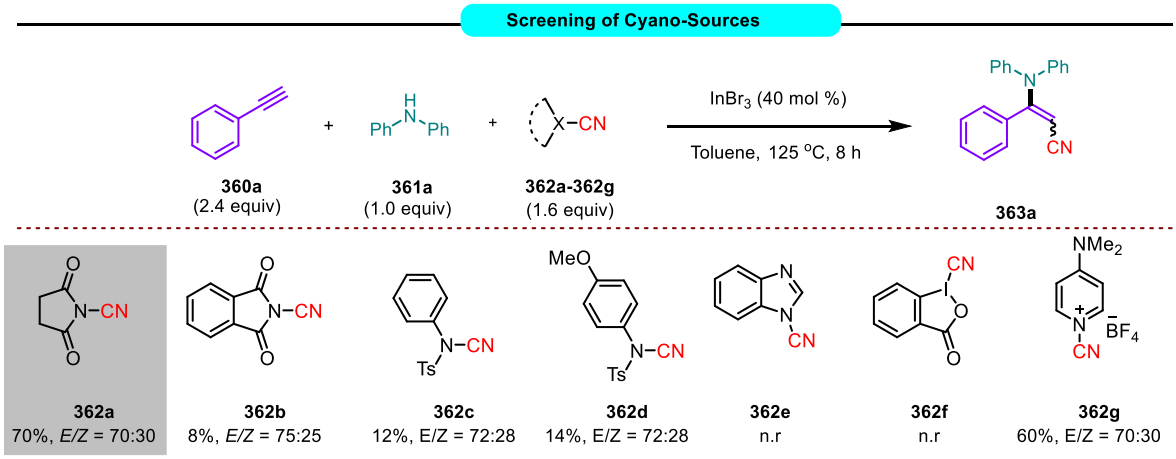
Table 5. Chapter 4: Optimization Study: Screening of Equivalencies



Entry	360a (equiv)	361a (equiv)	362a (equiv)	Yield 363a (%)	*E/Z*[a]
1	1.0	1.0	1.0	20	70:30
2	1.2	1.0	1.0	30	70:30
3	1.5	1.0	1.0	35	70:30
4	2.0	1.0	1.0	40	70:30
5	1.0	1.0	1.5	30	70:30
6	1.5	1.0	1.5	40	70:30
7	2.0	1.0	1.5	55	70:30
8	2.2	1.0	1.5	60	70:30
9	2.4	1.0	1.5	65	70:30
10	**2.4**	**1.0**	**1.6**	**70**	**70:30**
11	2.6	1.0	1.6	70	70:30
12	2.4	1.0	1.8	70	70:30
13	1.0	1.2	1.0	20	70:30
14	1.0	2.4	1.6	30	70:30

[a] *E/Z*, determined by the ^{1}H NMR analysis of crude reaction mixtures.

Screening of Electrophilic Cyanide Sources: We also varied several electrophilic cyanide sources shown in scheme 64, but the *N*-cyanosuccinimide **362a** remain as a remarkable candidate for the developed aminocyanation reaction.



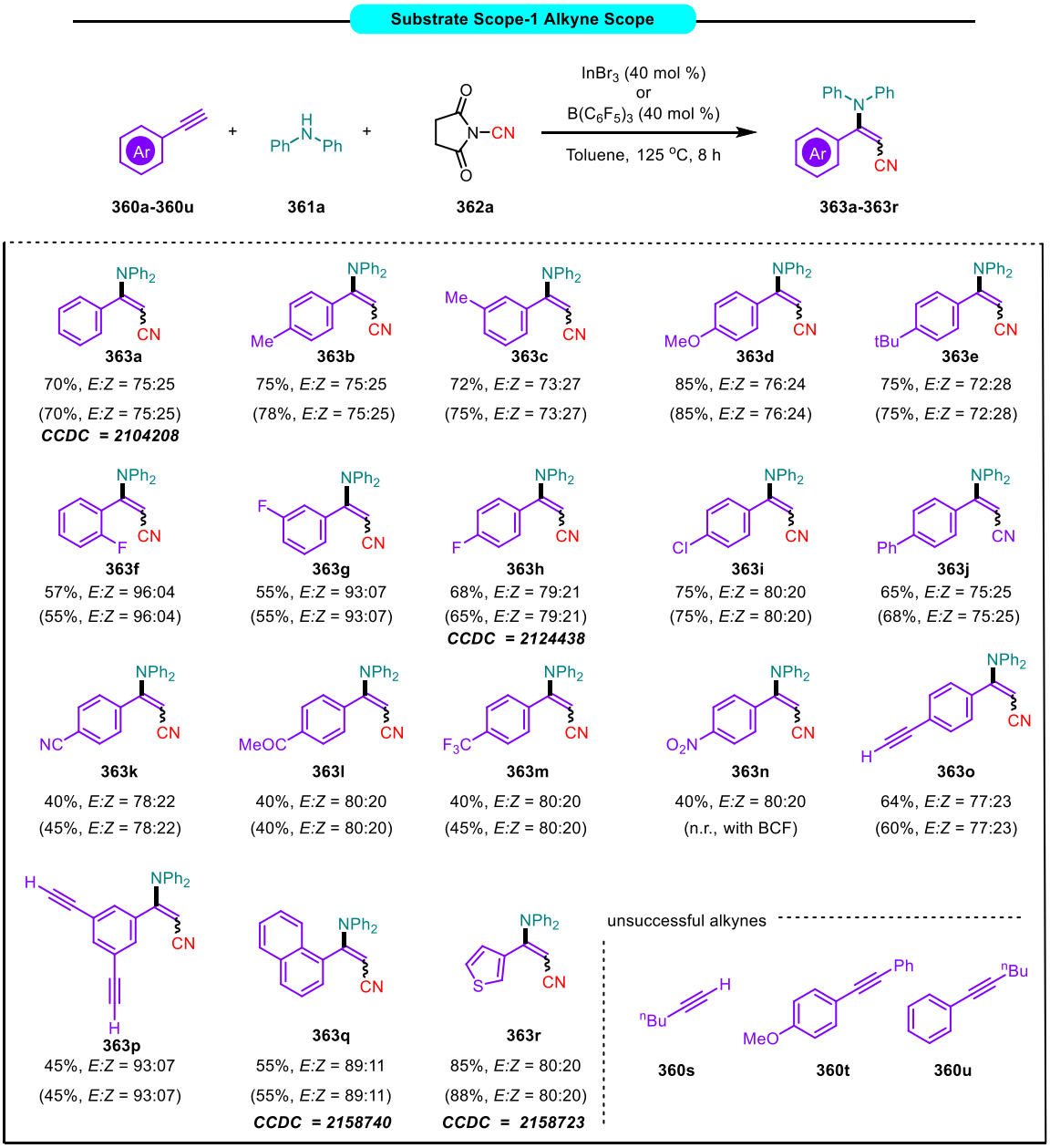
Scheme 64: Screening of Cyanide Sources. *E/Z*, determined by the ^{1}H NMR analysis of crude reaction mixtures.

The optimization results indicate that $B(C_6F_5)_3$ (Table 3 entry 17) and $InBr_3$ (Table 4 entry 6) are the two best Lewis acids for the aminocyanation reaction. We have done further substrate scope, and mechanistic studies with both $B(C_6F_5)_3$ and $InBr_3$ as Lewis acid for comparative study.

4.2.2 Substrate Scope Evaluation

After thorough optimization of catalysts we found an optimized reaction condition for further studies and started substrate scope to check the practicalability of the developed methodology.

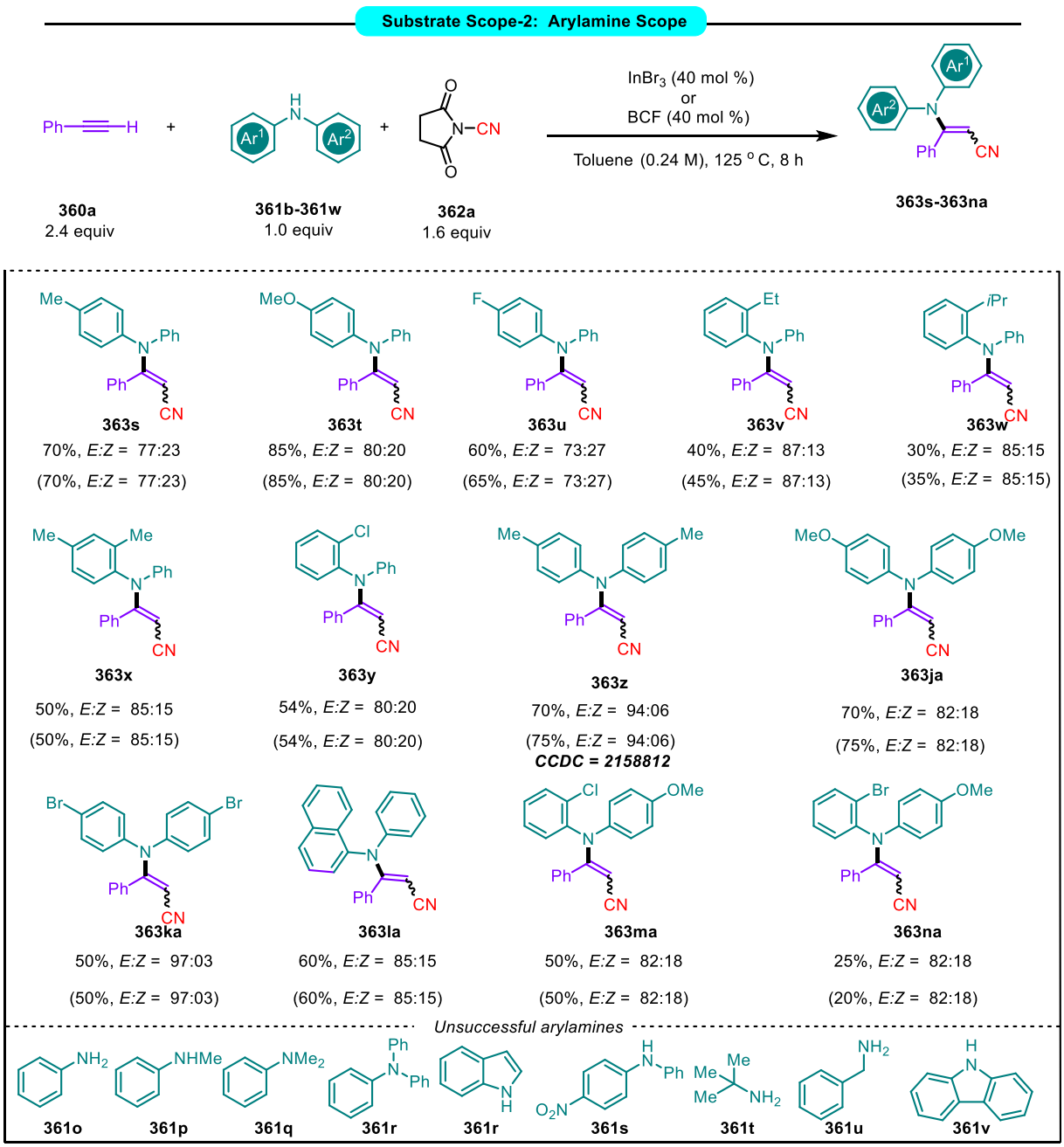
Variation of aryl alkynes: The optimized reaction condition (Table 3, entry 17, and Table 4, entry 6) was applied to test the reactivity of various alkynes **360a–360u** with diphenylamine **361a**, as summarized in scheme 65. The electron-donating groups such as –Me, –OMe, –*t*Bu, at *para* position worked smoothly and provided aminocyanated products **363b–363e** in good yields. When fluorine is substituted at the *ortho* and *meta* position, the yields were decreased, and *E/Z* ratio improved, which might be due to the electronic and steric effects (**363f–363g**). However, fluorine-atom as a substituent at the *para* position provided a comparatively higher yield of product **363h**.



Scheme 65: Substrate Scope for Alkynes. Yields in brackets are for 40 mol % of $B(C_6F_5)_3$. Reaction scale: 0.06 mmol. CCDC for **363a** = 2104208, **363h** = 2124438, **363q** = 2158740, **363r** = 2158723.[116]

Chloro and phenyl substitution at the *para* position also worked smoothly to afford the aminocyanated product **363i–363j** in good yield. Yet, electron-withdrawing group such as –CN, –COMe, $–CF_3$ and $–NO_2$ at the *para* position suppressed the reactivity and lowered the product formation **363k–363n**. The possible reason might be the lack of participation of electron-poor alkynes in the hydroamination step. However, in case of $–NO_2$ with $B(C_6F_5)_3$ no product formation was observed. Di- and tri- ethynyl substituted alkyne systems also underwent aminocyanation smoothly (**363o–363p**). The naphthyl and heterocyclic ethynyl molecules provided aminocyanated products in average to good yields **363q–363r**. $B(C_6F_5)_3$ as Lewis acid also provided comparable yield for the products **363a–363r** and is mentioned in scheme 65 (in brackets). Unfortunately, internal alkynes and aliphatic terminal alkynes remain unreactive under this protocol **361s–361u**.

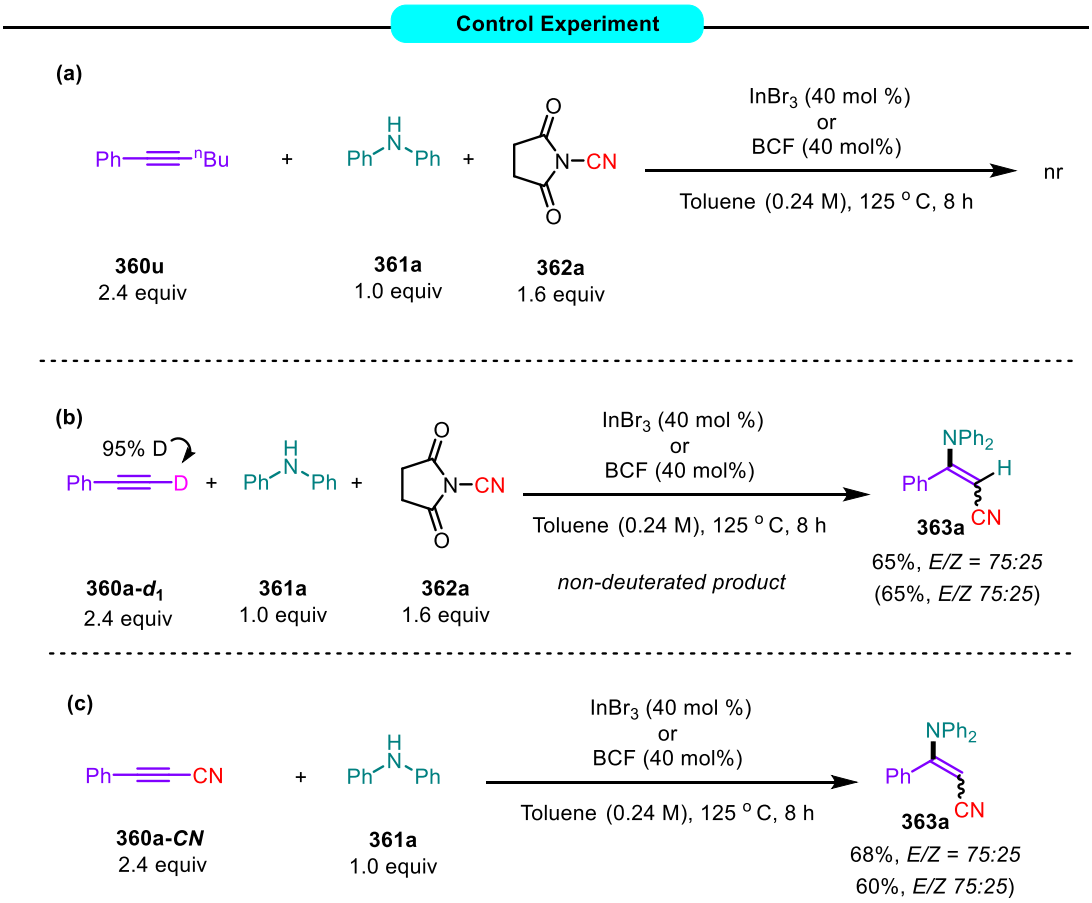
Variation of aryl amines: Next, we investigated the aminocyanation reactivity for various arylamines **361b–361w** with **360a** (Scheme 66). The electron-donating groups, such as –Me, –OMe, substituted at the *para* position of unsymmetrical arylamines provided higher yields **363s–363u**. Fluorine-atom at the *para* position worked smoothly as the steric effect remains ineffective. When the alkyl groups are substituted at the *ortho* position, steric effect plays a crucial role; as a result, –*o*-Et, –*o*-*i*Pr gave lower yield (**363v–363w**). 2,4-Me_2 substitution at the aromatic ring also gave moderate yield **363x**. In addition, 2-chloro substituted arylamine afforded aminocyanated product in average yield (Scheme 66, **363y**). Me, –OMe and –Br group at the *para* position of symmetrical arylamines worked smoothly and afforded aminocyanated products in good yields (Scheme 66, **363z**, **363ja–363ka**). *N*-phenylnaphthalen-1-amine also underwent aminocyanation in moderate yield **363la**. Apart from that, sterically hindered unsymmetrical arylamines underwent aminocyanation in lower yields (Scheme 66, **363ma–363na**). However, the yield is much lower in the case of Br-substituted amine might be due to the steric effect (**363na**). Primary amines, aliphatic secondary amines and tertiary amines remain unreactive under this protocol (**361o–361w**). A similar substrate scope and limitations was observed in case of $B(C_6F_5)_3$.



Scheme 66: Substrate Scope for the Arylamines. Yields in brackets are for 40 mol % of $B(C_6F_5)_3$. Reaction scale: 0.06 mmol. CCDC for **363z** = 2158812.[117]

4.2.3 Mechanistic Studies: Experimental

Several controlled experiments were executed to acquire the complete mechanistic pathway for aminocyanation reaction (Scheme 67). The aminocyanation reaction did not work with internal alkynes (Scheme 67-a). To check the fate of the terminal alkyne C–H bond, we performed a reaction with a deuterium-labelled alkyne **360a-*d*$_1$**(alkyne C–H was replaced with C–D); the reaction worked well and afforded a non-deuterated product **363a** (Scheme 67-b). This indicated that the alkyne C–H bond is playing an important role in this reaction for the acetylide formation.



Scheme 67: Chapter 4: Control Experiments.

[1]H-NMR Analysis of Crude Reaction Mixture: We performed the [1]H-NMR analysis of our crude reaction mixture for the measurement of *E:Z* ratio and side products formation. The comparison of [1]H-NMR for crude reaction mixture, *N*-cyanosuccinimide **362a**, and succinimide **362** indicates the formation of succinimide **362** as a side product (Figure 25).

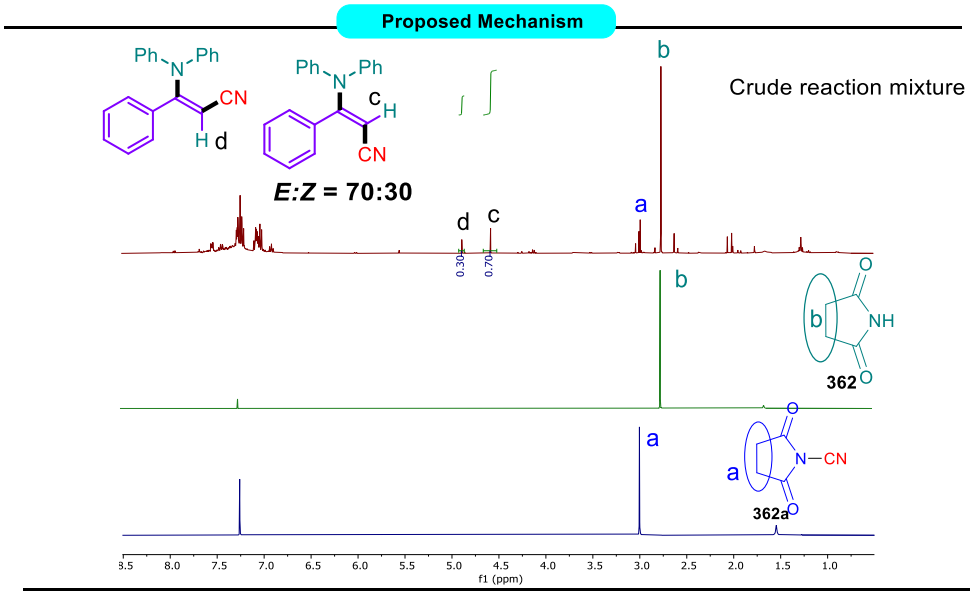
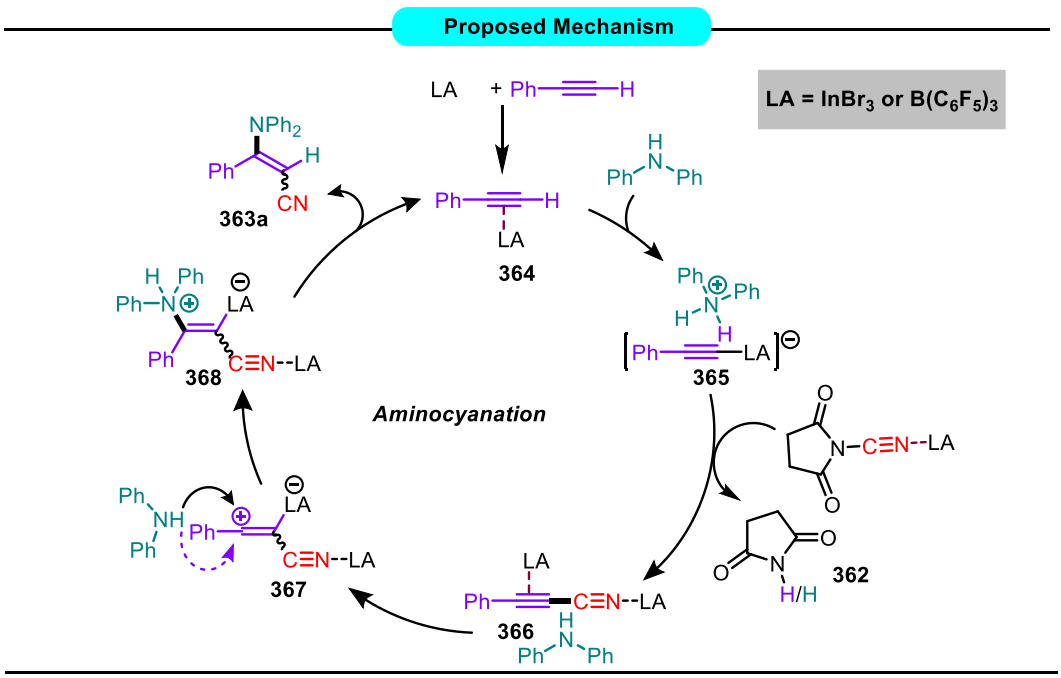


Figure 25: Chapter 4: Identification of Succinimide **362** by [1]H-NMR

4.2.4 Mechanistic Pathway

Based on previous reports we postulate a π-interactions of $InBr_3$ with terminal alkynes, which makes alkyne C–H proton acidic enough such that can be abstracted by a mild base to form bimolecular alkynyl indium bromide salt.[70, 75] Based on control experiments we have proposed a mechanism where initially $InBr_3$ forms a complex **364** with phenylacetylene **360a**. Then diphenylamine **361a** abstracts a proton to form intermediate **365**.

Next, we treated alkyne nitrile **360a-CN** in the absence of external cyanide source under our standard reaction conditions; we observed the formation of product **363a** in good yield (Scheme 67-c). This indicates the formation of **366** as a potent intermediate via alkyne transfer from **365** to the activated cyanide with the release of succinimide **362** as a side product (Scheme 68). Internal alkynes remained unreactive due to the unavailability of terminal proton which hampered the formation of intermediate **366**. The formation of succinimide **362** was confirmed by ^{1}H-NMR analysis of crude reaction mixture (Figure 25). Further activation of alkyne nitrile via π-interactions with $InBr_3$ facilitates the formation of vinyl carbocation **367**. Nucleophilic attack of diphenylamine **361a** at vinyl carbocation afforded zwitterionic intermediate **368**. Following a proton transfer process the desired product **363a** was released along with $InBr_3$. The generation of intermediate **368** from **367** resulted in the formation of mixture of *E*:*Z* stereoisomers having thermodynamically controlled *E* as major product. The instability of the intermediate **367** in the case of terminal aliphatic alkynes rendered the product formation. On the other hand, the electron donating substituents at aryl rings provides higher yields (Scheme 65 entries **363b–363e**) compare to the neutral and electron withdrawing substituents (Scheme 65 entries **363k–363m**) due to the stabilization of intermediate **367**.



Scheme 68: Chapter 4: Proposed Mechanism for Aminocyanation

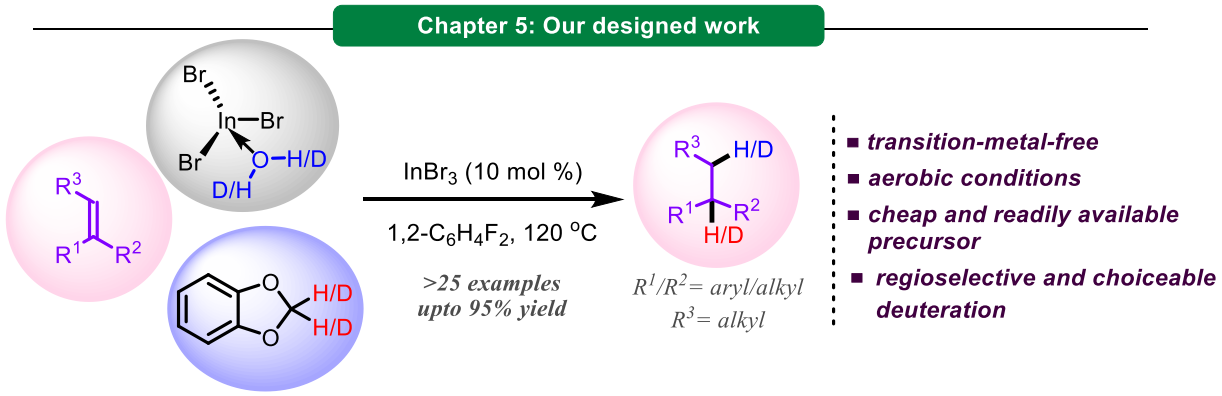
It is noteworthy to mention that the control experiments conducted using $B(C_6F_5)_3$ as Lewis acid also displayed similar observation. A mechanistic proposal comparable to the mechanism proposed using $InBr_3/B(C_6F_5)_3$ as Lewis acid is depicted (Scheme 68). The possible reason for low turn-over is the dual-mode of interaction nature of $InBr_3$ towards σ and π-activation.

4.3 Conclusion

In this chapter, we have explored a rarely investigated transition-metal-free aminocyanation of aryl alkynes with secondary arylamine derivatives. Here, main group-based Lewis acid $B(C_6F_5)_3$ and $InBr_3$ remain equally reactive under our developed, optimized reaction conditions. A series of *β*-amioacrylonitrile derivatives were synthesized in moderate to good yields and fully characterized with NMR, HR-MS, and SC-XRD. The mechanistic pathway was depicted by means of deuterium-lebeling and control experiments. The π-activation of alkyne with $InBr_3$ increases the acidity of acetylenic (C–H) proton, which was abstracted by basic amine derivatives followed by the *in situ* alkyne nitrile intermediate formation and hydroamination.

Chapter 5

Transition-metal-free Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins



❖ This work was published in Journal of Organic Chemistry (a journal of ACS). Please see the citation as: "**Kumar, G.;** Bhattacharya, D.; Mistry, P.; Chatterjee, I. In-Catalyzed Transfer Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins. *J. Org. Chem.* **2023**, DOI:10.1021/acs.joc.3c00272."

5. Abstract

Transition-metal-free Lewis acid catalyzed hydrogenation and regioselective hydrogen-deuterium addition to olefin is explored by using a combination of deuterated or non-deuterated 1,3-benzodioxole and H_2O/D_2O. This developed methodology involves the usage of cheap and readily available precursor as a hydrogen expedient and facile reaction set-up under aerobic conditions. The experimental studies show that the complex of Lewis acid-moisture H_2O–$InBr_3$ plays a crucial role in the protonation of olefin, which generates a carbocationic intermediate. The hydride transfer from 1,3-benzodioxole to this carbocationic intermediate is responsible for the hydrogenated product formation.

5.1 Introduction

After the successful functionalization of 1,3-dienes and alkynes to construct carbon-heteroatom (C–S/N), and carbon-carbon bonds in chapters 2, 3, and 4; we have explored the hydrogenation of 1,1-disubstituted alkenes for the synthesis of 1,1-disubstituted alkane derivatives in this chapter. Mainly the 1,1-diarylalkane were synthesized by using the main group based Lewis acid $InBr_3$ as a catalyst with 1,3-benzodioxole and moisture as hydrogen surrogate. 1,1-diarylalkane scaffolds play a significant role in numerous pharmaceutical and natural products. The bioactive unsymmetrical 1,1-diarylethanes utilized for the treatment of different diseases are depicted in figure **26**.[118]

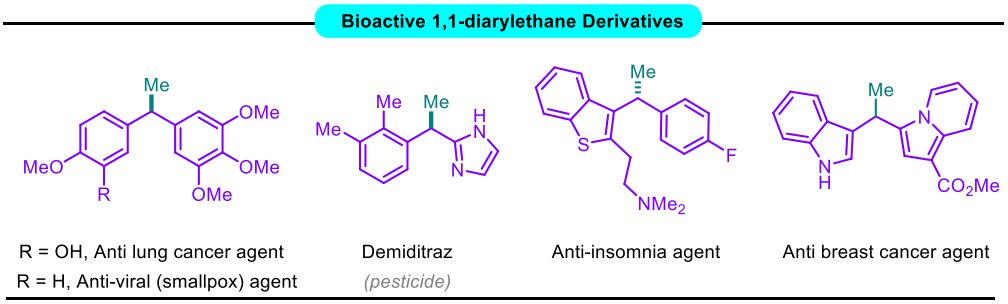


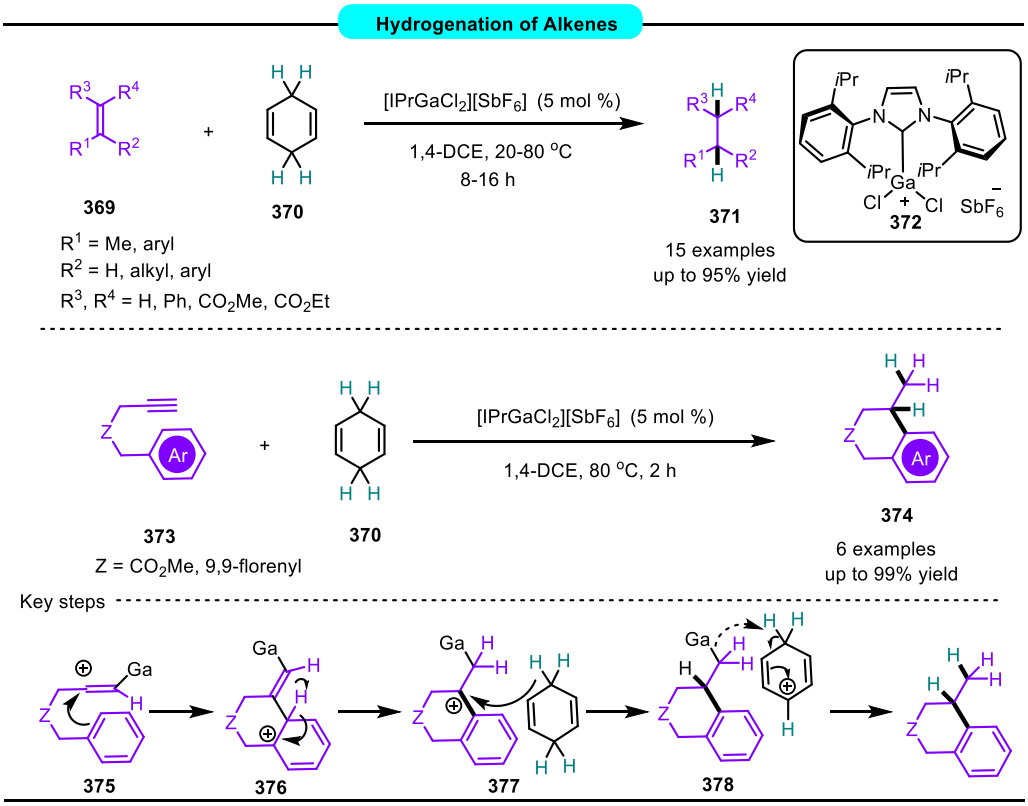
Figure 26: 1,1-diaryalethanes as Bio-active Candidates

We started searching the literature for the hydrogenation of olefins and observe that conventional methods require special reaction set-up to handle the highly flammable and pressurized hydrogen gas. However, majority of these reactions are catalyzed by transition metal catalysts and associated with cost and environmental issues.[119] So, the developments of easy and economical methods for hydrogenation always remain an area of interest for scientists. In this regard, various main group-based FLP-mediated hydrogenation methodologies have been developed by using H_2 gas. So, in order to replace the flammable hydrogen gas, transfer hydrogenating reagents, e.g., alcohols, formic acid, amine, hydrazines, boranes, silanes, and many more, have been developed in past years by using different methods.[120]

Though, the hydrogenation of unsaturated compounds using main group Lewis acid catalysts and cyclohexa-1,4-diene derivatives as H_2-gas surrogates was comprehensively explored by different independent research groups, e.g., Gandon, Oestreich, Hilt, and others. In the same sequence, dihydropyridine derivatives (Hantzsch ester type of compounds) were explored by List and MacMillan research groups. This type of hydrogenation is completely motivated by the biological reaction of organic hydride reduction cofactors such as NADH, NADPH, and $FADH_2$.[121-124, 127-132] However, Akiyama and co-workers extensively explored the transfer hydrogenation reactions of unsaturated bonds by using indolines and benzothiazoles as H_2-gas surrogates.[125] But the choiceable hydrogen-deuterium additions to the alkenes remain very less explored due to the regioselectivity issue and unavailability of suitable H–D source.[126, 129-132] We started our literature search regarding hydrogenation reactions with different catalytic systems, but our main focus was on the main group Lewis acid-catalyzed methods.

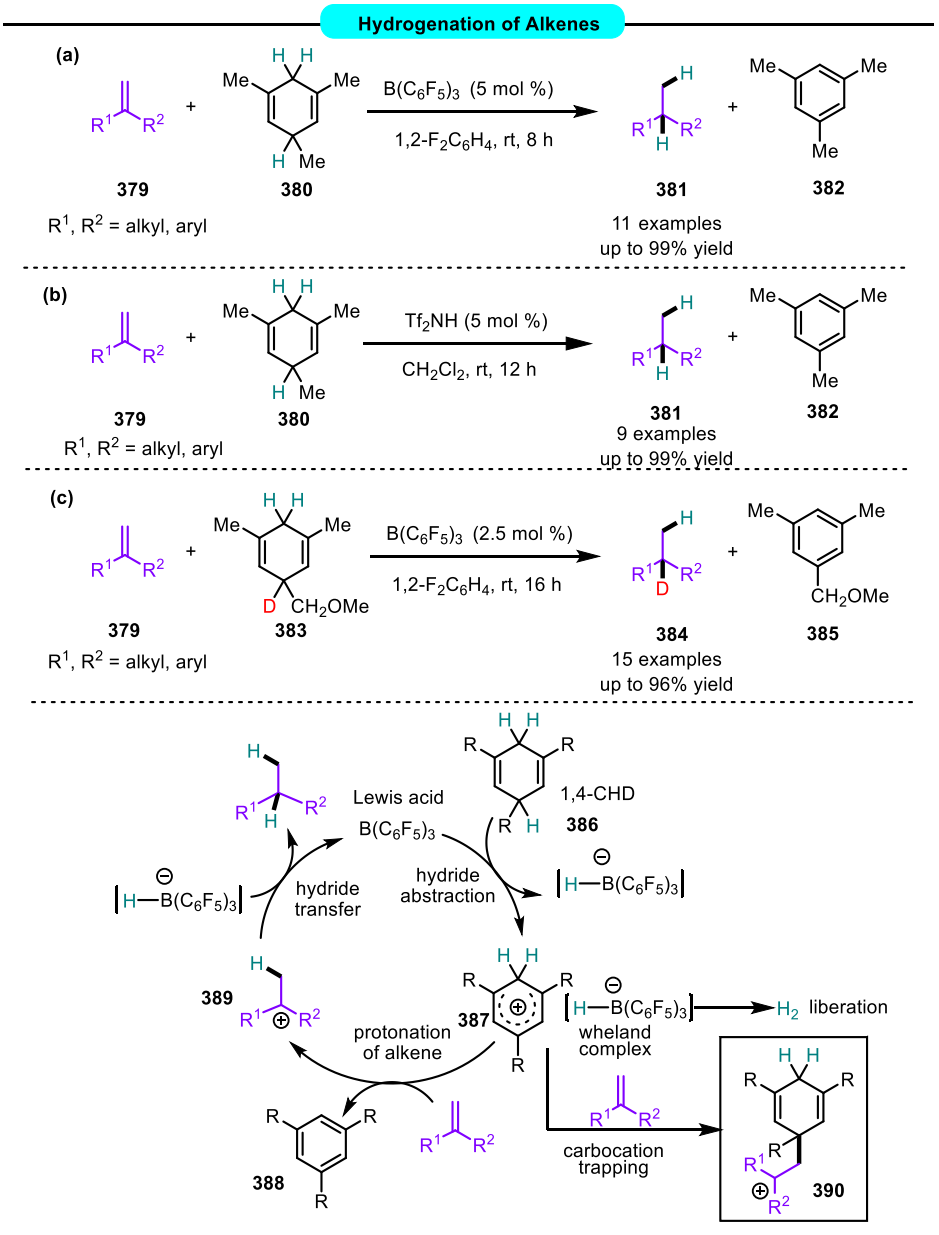
5.1.1 Literature Reports for the Hydrogenation of Alkenes

In 2014, the group of Gandon exploited cyclohexa-1,4-diene (1,4-CHD) **370** for the main group-catalyzed transfer hydrogenation of alkenes **369** and hydrogenative carbocyclization of arenyne **373**. They have used cationic NHC gallium complex $[IPrGaCl_2][SbF_6]$ **372** in this reaction. The authors also showed the reactivity of combined $BF_3{\cdot}Et_2O$ (5 mol %) and TfOH (15 mol %), which provided lower yield of the desired hydrogenation products **371** (Scheme 69).[127]



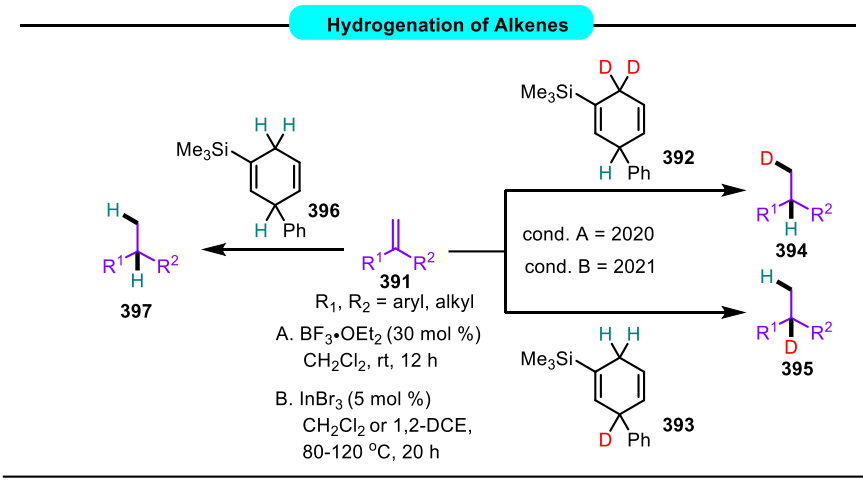
Scheme 69: Gandon's Hydrogenation of Alkenes

Later in 2015, Oestreich and co-workers introduced $B(C_6F_5)_3$-catalyzed transfer hydrogenation of alkenes using cyclohexa-1,4-diene (1,4-CHD) as a hydrogen surrogate (Scheme 70-a). Authors proposed that the hydride abstraction from 1,4-CHD by $B(C_6F_5)_3$ generates Wheland type intermediate **387** which is enough Brønsted acidic to protonate the alkenes and resulting a carbocationic intermediate **389**. The borohydride $H–B(C_6F_5)_3^-$, transfers hydride to the carbocation **389** that resulted in the formation of hydrogenated products **381** from alkenes **379**. They also revealed that carbocation trapping by the starting substrate generates undesirable side product **390**.[128] In continuation of transfer hydrogenation using 1,4-CHD, in the very next year, they utilized Brønsted acid in place of Lewis acidic $B(C_6F_5)_3$ to catalyze this reaction (Scheme 70-b).[129] Then later, in 2018, the same group was able to achieve regioselective hydrodeuteration **384** of alkenes using modified deuterated 1,4-CHD at C1-position **383** (Scheme 70-c).[130]



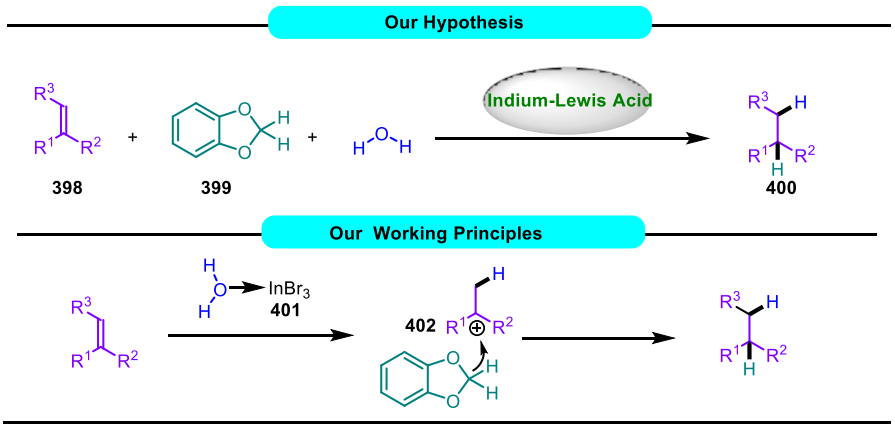
Scheme 70: Oestreich's Hydrogenation of Alkenes

Similarly, in 2020, Hilt and co-workers documented the $BF_3{\cdot}Et_2O$ catalyzed hydrogenation **397** and regioselective hydrodeuteration **394, 395** of alkene **391** derivatives using the deuterated 1,4-CHD **392, 393**. Interestingly by changing the position of deuterium at 1,4-CHD, the HD or DH addition can be tuned.[131] In the next year, the same group employed $InBr_3$ to catalyze this reaction, and the substrate scope expanded for the regioselective HD or DH addition at the alkenes (Scheme 71).[132]



Scheme 71: Hilt's Hydrogenation of Alkenes

So, motivated from Oestreich and Hilt's work, they have led the hydrogenation reactions in the presence of $B(C_6F_5)_3$, $BF_3{\cdot}Et_2O$ and $InBr_3$ using hydrogen surrogates, we planned to employ the combination of 1,3-benzodioxole **399** and $InBr_3$-moisture complex **401** as hydride and proton donor respectively.



Scheme 72: Chapter 5: Our Proposed Working Hypothesis

5.2. Result and Discussion

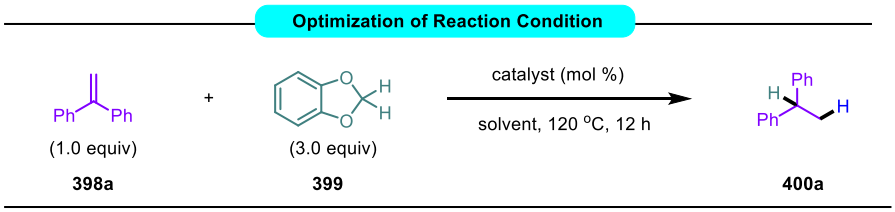
5.2.1 Optimization of the Reaction Condition

As per our hypothesis (described in Scheme 72), we started investigation to explore the development of unique transition-metal-free Lewis acid-catalyzed hydrogenation of alkenes. To check the feasibility of our proposal, we started our inquiry by reacting 1,1-diphenylethene (**398a**,

2.4 equiv) with 1,3-benzodioxole (**399**, 1.0 equiv) in various solvents (0.4 M) in the presence of catalyst $InBr_3$ (10 mol %) followed by other Lewis acids at 120 °C for 12 h.

While THF as a solvent provided no reaction, MeCN, and 1,2-DCE led to lower ^{1}H NMR yields of **400a** (Table 6, entries **1–3**). However, toluene resulted in a drastically improved 68% yield of **400a** (Table 6, entry **4**). To our delight, using 1,2-difluorobenzene (1,2-$C_6H_4F_2$) as a solvent led to excellent isolated yield (90%) of the desired product **400a** (Table 6, entry **5**). Boron-based Lewis acids such as $B(C_6F_5)_3$, BCl_3, and $BF_3{\cdot}Et_2O$ were unable to deliver product **400a** (Table 6, entries **6–8**). Other Lewis acids such as $InCl_3$, $In(OTf)_3$, and $Sc(OTf)_3$ were also able to catalyze the reaction albeit in lower yields of **400a** (Table 6, entries **9–11**). Also, Brønsted acid, Tf_2NH provided **400a** with lower ^{1}H NMR yields (Table 1, entry **12**). We found no reaction or lower ^{1}H NMR yield of **400a** by lowering the reaction temperature (Table 1, entries **13–14**).

Table 6. Chapter 5: Optimization Study and Reaction Set Up



Entry	Catalyst (mol %)	Solvents	Yield 400a (%)[a]
1	$InBr_3$ (10)	THF	nr
2	$InBr_3$ (10)	CH_3CN	18
3	$InBr_3$ (10)	1,2-DCE	42
4	$InBr_3$ (10)	Toluene	68
5	**$InBr_3$ (10)**	**1,2-$C_6H_4F_2$**	**>98 (90)[b]**
6	$B(C_6F_5)_3$ (10)	1,2-$C_6H_4F_2$	trace
7	$BF_3{\cdot}Et_2O$ (10)	1,2-$C_6H_4F_2$	-
8	BCl_3 (10)[c]	1,2-$C_6H_4F_2$	-
9	$InCl_3$ (10)	1,2-$C_6H_4F_2$	23
10	$In(OTf)_3$ (10)	1,2-$C_6H_4F_2$	55
11	$Sc(OTf)_3$ (10)	1,2-$C_6H_4F_2$	64
12	Tf_2NH (10)	1,2-$C_6H_4F_2$	30
13	$InBr_3$ (10)	1,2-$C_6H_4F_2$	nr[d]
14	$InBr_3$ (10)	1,2-$C_6H_4F_2$	60[e]

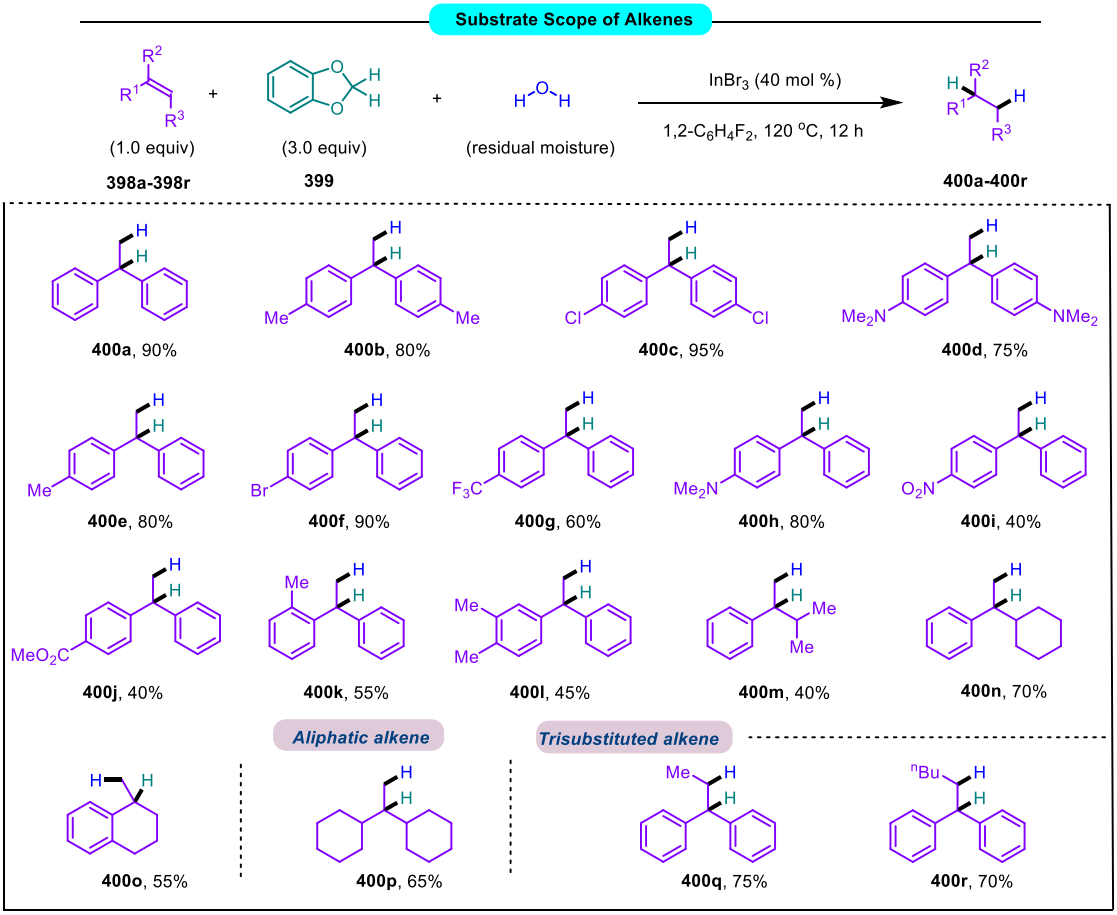
Reaction condition: 0.1 mmol scale. a) Yield from crude ^{1}H NMR using dibromomethane as internal standard. b) Isolated yield. c) BCl_3 used as 1M solution in DCM. d) Reaction temperature was 80 °C. e) Reaction temperature was 110 °C. nr = no reaction.

5.2.2 Substrate Scope Evaluation

After successful optimization of catalysts and solvents, we found a optimize reaction condition for further studies and started substrate scope to check the scope of the developed methodology.

Variation of olefins: By utilizing the optimized reaction conditions (Table 6, entry 5), we examined the reactivity of several alkene derivatives (Scheme 73). In the case of 1,1-disubstituted aromatic alkenes, firstly, we checked for symmetrical substrates, Me, Cl, and NMe_2 substituents at *para*-position afforded good yields (entries **400b–400d**). Unfortunately, the OMe substituent did not furnish any desired hydrogenation product despite of the complete conversion of starting olefin. The possible reason could be the tendency of polymerization of electron-rich olefins; as a result, only decomposition of olefin was noticed.

To our delight, unsymmetrical olefins also remained sufficiently reactive as Me, Br, CF_3, and NMe_2 at *para*-position of one of the phenyl rings furnished hydrogenation products in good to moderate yields (entries **400e–400h**).



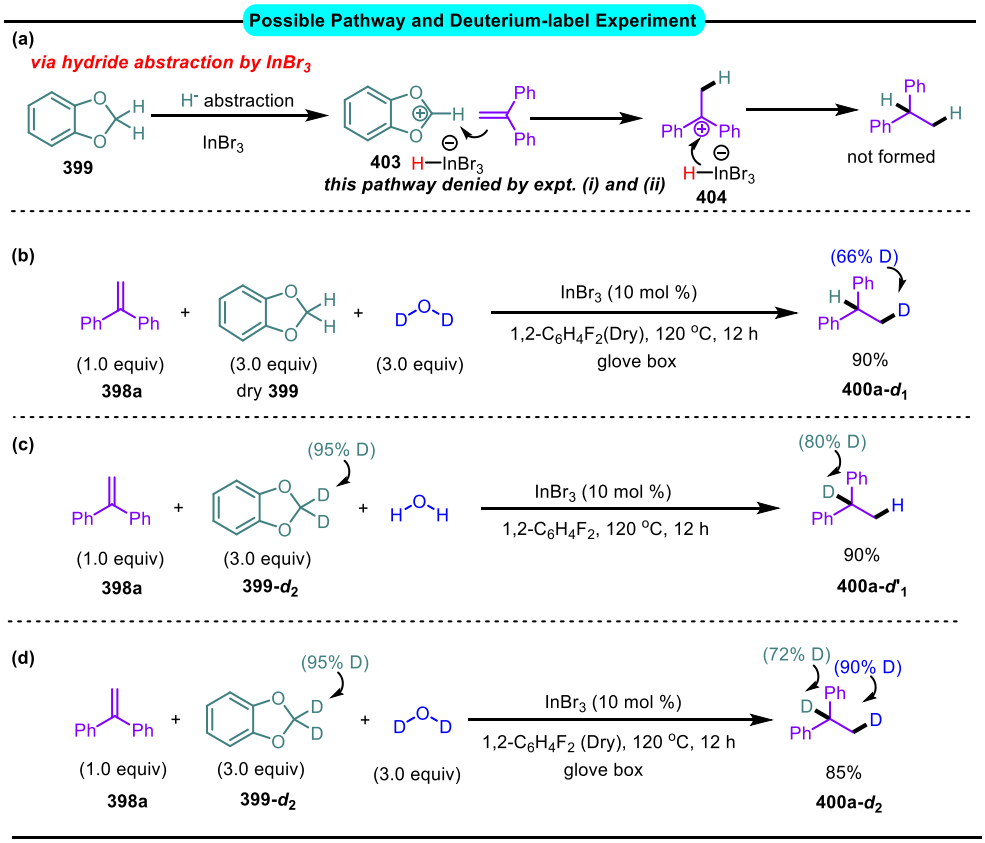
Scheme 73: Substrate Scope for Alkenes. 0.10 mmol, isolated yields unless otherwise mentioned. All the reactions setup under aerobic conditions using non-drying **399** and 1,2-difluorobenzene.

However, NO_2 and CO_2Me substituted olefins afforded comparatively lower yields of the products might be due to the higher electron-withdrawing nature (entry **400i–400j**). However, other functional groups like CN, amide, and ketones did not furnish any desired product. Interestingly, Me at the *ortho* position of one aryl ring produced the hydrogenation product in

moderate yield, which might be due to the steric and electronic factor affecting the reactivity (entry **400k**). 3,4-di-Me_2 substitution also afforded lesser yield of hydrogenation product (entry **400l**). 1-aryl-1-aliphatic substituted olefins also underwent hydrogenation and afforded alkyl-substituted benzene derivatives in moderate yields (entries **400m–400o**). 1,1-disubstituted aliphatic alkene, provided the hydrogenation product **400p** in good yield. To our delight, the scope of 1,1,2-trisubstituted olefins were studied and found to be equally reactive (entries **400q–400r**). Internal alkenes, non-activated olefins remained either less or unreactive in our reaction conditions.

5.2.3 Mechanistic Studies: Experimental

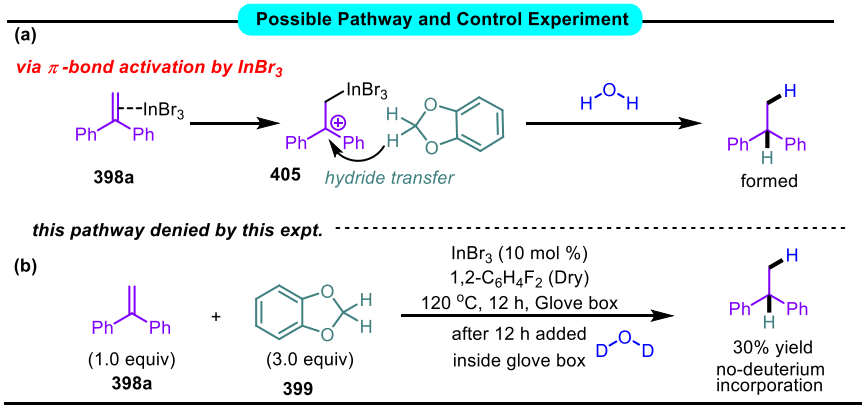
To establish the mechanistic pathway, various deuterium-labelling and KIE (kinetic isotope exchange) experiments were performed for substrate **398a** with **399** in the presence of $InBr_3$. We have performed various experiments to confirm every possible pathway for these reactions. The first possible pathway might be via hydride abstraction by $InBr_3$, followed by protonation and hydride transfer from $H–InBr_3^-$ (Scheme 74-a). However, the deuterium-labelling experiments in scheme 74-b and 74-c denied this pathway.



Scheme 74: Chapter 5: Deuterium Labelling Experiments

Another possible way is through the carbocationic **405** intermediate generation due to the activation of olefin by the Lewis acidic $InBr_3$ followed by hydride transfer from **399** to deliver product **400a** after hydrolysis (Scheme 75-a). Nevertheless, this pathway was also denied by an experiment done using dry and freshly distilled solvent and dry **399** under argon atmosphere using

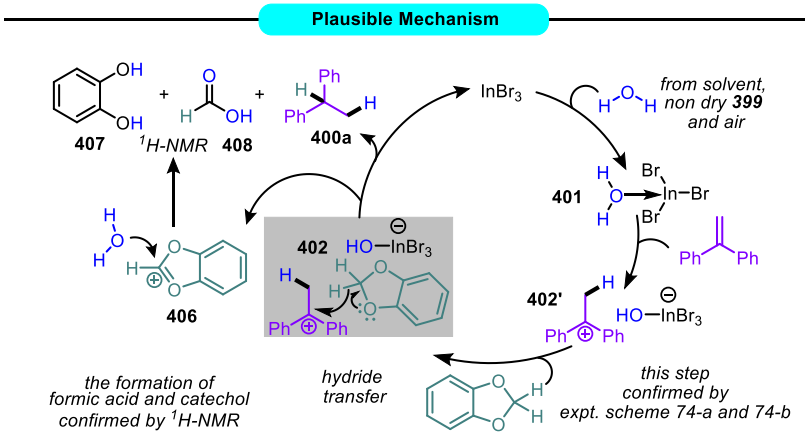
standard conditions (reaction was set up inside glove box). After 12 h, the reaction was tube again taken inside glove box and quenched with D_2O, but no deuterium transfer was observed (Scheme 75-b), which suggests the π-bond activation might not be the actual process. However, there is still formation of hydrogenation product might be due to the presence of residual moisture from solvent, olefin **398a**, and glassware.



Scheme 75: Chapter 5: Control Experiment for π-activation Path

Subsequently, from the outcome of deuterium-labelling experiments scheme 74-b, 74-c, 74-d, and 75-b, we have postulated the most prominent mechanism (Scheme 76). The addition of D_2O in our standard reaction condition provided deuterium transfer in the Markovnikov fashion (Scheme 74-b), which clearly indicates that one hydrogen atom is coming from the residual water content of the reaction mixture. However, when 1,3-benzodioxole-2,2-d_2 (**399-*d*$_2$**) was used, the product **400a-*d*$_1$**' formed, which indicates that 1,3-benzodioxole moiety is the source of another hydrogen atom (Scheme 74-c). If **399-*d*$_2$** and D_2O have been used, then fully deuterated product **400a-*d*$_2$** was obtained (Scheme 74-d). Consequently, all these experiments prove that the dihydrogen source is a combination of 1,3-benzodioxole and residual water content in the reaction mixture.

Therefore, we proposed a convincing mechanism where, Lewis acidic $InBr_3$ forms an adduct with residual H_2O **401**, the proton of H_2O becomes enough Brønsted acidic to protonate olefin. The protonation of olefin generates carbocationic intermediate **402** (Scheme **76**). Hydride transfers from 1,3-benzodioxole **399** to the carbocationic intermediate **402** affords the hydrogenation product **400a** and intermediate **406** (Scheme 76). The intermediate **406** can be hydrolyzed and produce formic acid **408** and catechol **407** as a side product confirmed by the ^{1}H-NMR (Figure 27) of crude reaction mixture. The isolation of catechol **407** was also done smoothly which can again be used to generate 1,3-benzodioxole.



Scheme 76: Chapter 5: Plausible Mechanism

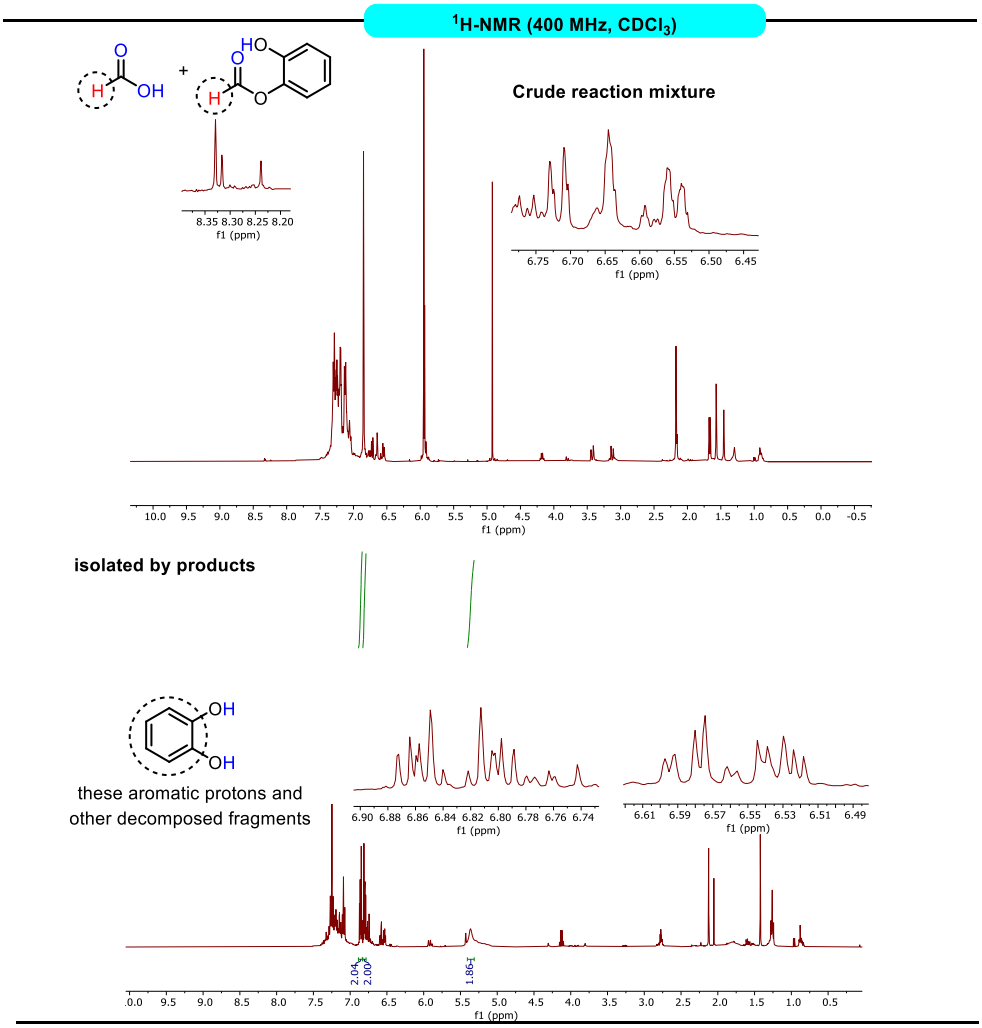
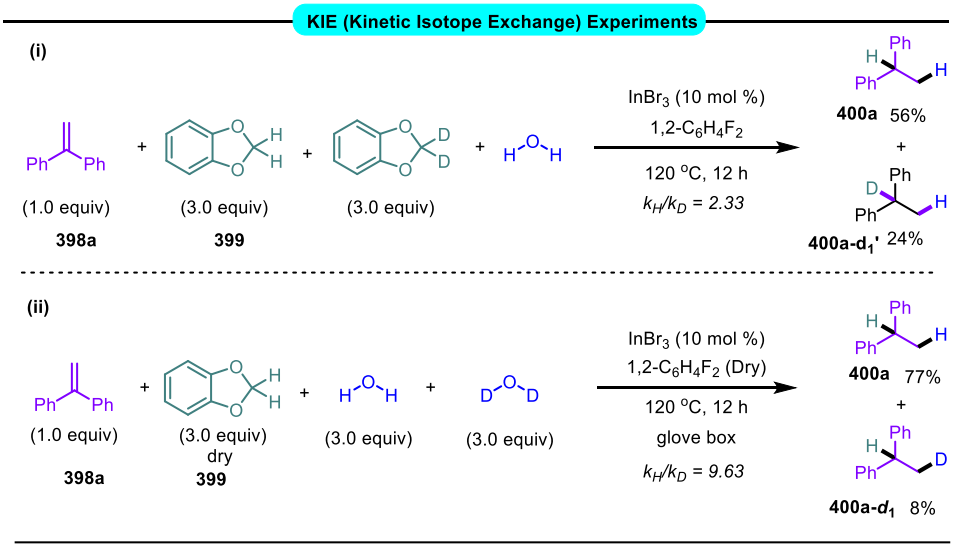


Figure 27: ^{1}H-NMR of Crude Reaction Mixture and Isolated Side Products

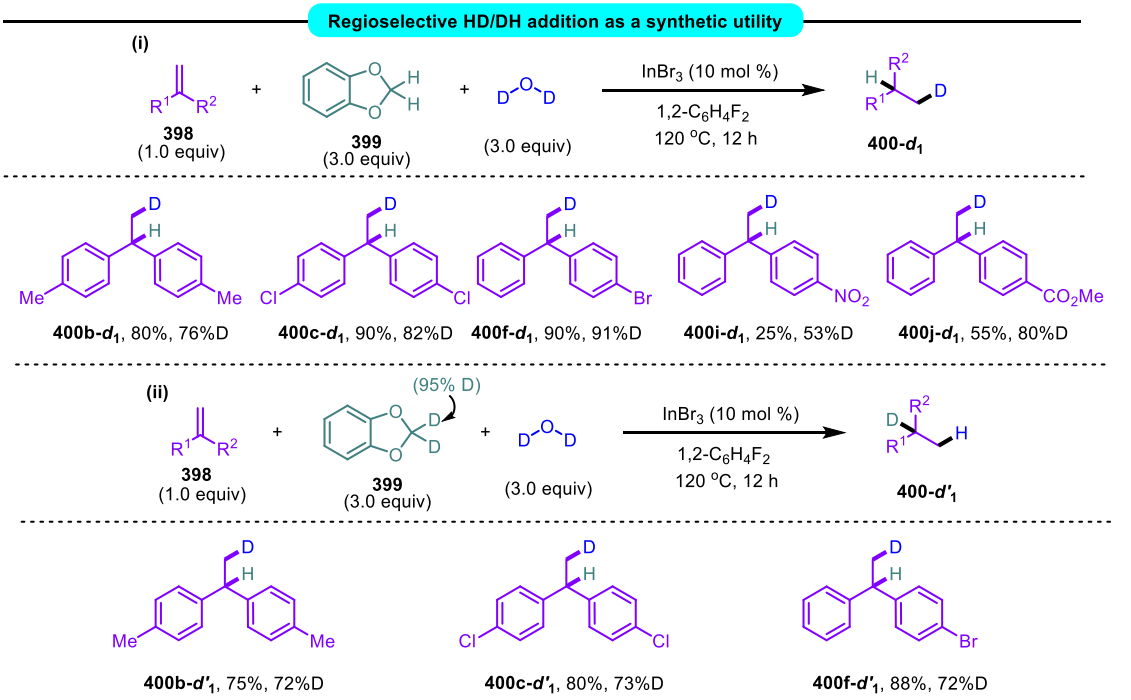
Furthermore, the kinetic isotope effect (KIE) has been measured for both **399-*d*$_2$** and D_2O separately, revealing a k_H/k_D value of 2.33 and 9.63 respectively (Scheme 77). These results suggest that the protonation of olefins involved in the rate-limiting step.



Scheme 77: Chapter 5: KIE (Kinetic Isotope Exchange) Study

5.2.4. Application of the Current Methodology

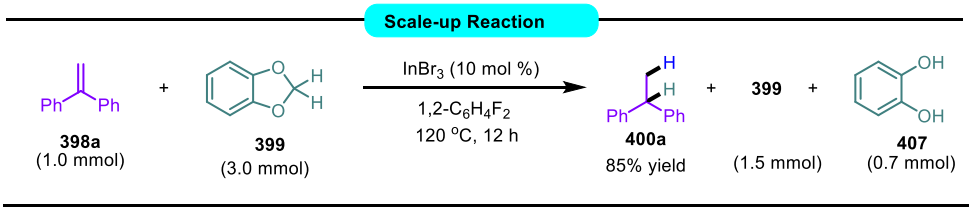
Selective hydro-deuteration remains an attractive process to install H/D group across multiple bond using suitable HD surrogates.[126, 130-132] We have utilized our methodology for the selective hydrogen-deuterium addition for the synthesis of various deuterated aromatic hydrocarbons with good yields and high deuterium incorporation (Scheme 78). This methodology remains a powerful and choiceable protocol to obtain regioselectively DH/HD or DD addition to the olefins.



Scheme 78: Chapter 5: Regioselective HD/DH Addition Across Alkene

5.2.5. Scale-up Reaction

The practicability of the methodology is further extended by conducting a 1 mmol scale reaction which had also been found equally efficient in terms of reactivity. In addition, the excess **399** was recovered along with the isolated side product catechol (Scheme **79**).



Scheme 79: Chapter 5: Scale-up Reaction

5.3 Conclusion

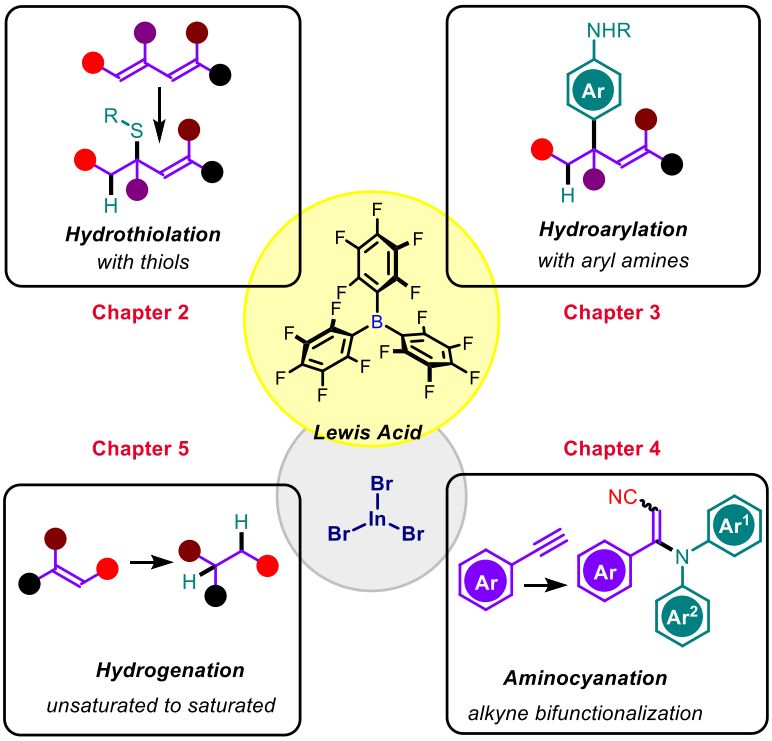
In this chapter, transition-metal-free hydrogenation of 1,1-substituted alkene derivatives using a combination of 1,3-benzodioxole and H_2O as H_2 gas surrogate is explored. This approach shows good substrate scope and functional group compatibility and can be applied for the mono and di-deuteration selectively. Moreover, a strong mechanistic outline is provided by deuterium-labelling experiments, pointing to the crucial role of Lewis-acidic H_2O–$InBr_3$ catalyst in the protonation of olefins to produce secondary carbocation intermediate to induce facile hydride transfer from 1,3-benzodioxole. This exquisite combination of 1,3-benzodioxole and H_2O for hydrogenation reactions can be further explored in another unsaturated system, particularly focusing on selective deuterium transfer process.

Chapter 6

Conclusion

6.1 Conclusion

Title of the thesis is "*Main Group Lewis Acid Catalyzed Functionalization of 1,3-dienes and Other Unsaturated Compounds"*. In this thesis various distinct methodologies have been revealed in pursuit the functionalization of 1,3-dienes, alkyne and alkenes for step economic construction of various new carbon-heteroatom (C−S/N) and C−C bonds. The exhibited works are based on the versatile catalytic reactivity of main group Lewis acids ($B(C_6F_5)_3$ and $InBr_3$). The thesis is divided into five chapters where all the detailed work aspect is discussed.



The significant applications of sulphur containing compounds in pharma and agrochemicals attracted us to develop a methodology for the C−S bond-forming reactions. So we have chosen thiols and conjugated dienes along with the boron base Lewis acid catalyst $B(C_6F_5)_3$ for the formation of C−S bonds. Another boron Lewis acid $BF_3{\cdot}Et_2O$ also shows equal reactivity for the hydrothiolation of conjugated 1,3-dienes. This methodology is associated with the following challenges a) regioselectivity issues of hydrothiolation, and b) high polymerization ability of dienes under Lewis acidic conditions. We have overcome the challenge of unnecessary regioisomer formation along with high yield, and short reaction time at room temperature. Here we have synthesized more than 35 examples with significant variations of thiol moiety, e.g., aliphatic and aromatic, along with substituted aromatic and aliphatic dienes. During the reaction scope of substituted dienes $B(C_6F_5)_3$ remains superior than $BF_3{\cdot}Et_2O$. The extensive DFT calculations and ^{11}B-NMR experiment claim for the boron-thiol complex formation, which is responsible for the protonation of 1,3-diene and generate carbocationic intermediate. The thiolate

transfer towards this carbocationic intermediate afforded the hydrothiolated products in good yields.

In the third chapter, reactivity of dienes with $B(C_6F_5)_3$ is further explored with the aniline derivatives featured with new C−C bond formation. This is the first methodology developed for the regioselective hydroarylation of conjugated dienes with aniline derivative under boron Lewis acid catalysis. This reaction is also associated with challenges, e.g., regioisomer formation along with polymerization of dienes. Another challenge for this reaction is the hydroarylation *vs.* hydroamination in the case of secondary amines and *ortho vs. para* selectivity in the case of both secondary and tertiary arylamine derivatives. The throughput DFT calculations suggested the residual amount of moisture is sufficient to form an complex with $B(C_6F_5)_3$. Thereafter, this $H_2O{-}B(C_6F_5)_3$ complex protonates the secondary amine and forms ammonium ion; now, this ammonium ion initiates protonation of dienes. Thereafter, aromatic electrophilic substitution with aniline derivatives generates the hydroarylated products. However, in the case of tertiary arylamines $H_2O{-}B(C_6F_5)_3$ is responsible for the protonation of dienes. The developed hydroarylation featured with broad substrate scope for arylamines, and various substituted dienes.

After these two seminal works on hydrofunctionalization of conjugated dienes we have functionalized alkyne derivatives in the fourth chapter. In this chapter we have developed a methodology for the aminocyanation of alkyne derivatives which afforded the value added *β*-aminoacrylonitrile derivatives. This reaction featured with the incorporation of two new functional moieties incorporation onto alkynes which end up with the new C−N and C−C bond formation. In this reaction $B(C_6F_5)_3$ and $InBr_3$ remains equally reactive and all the experiments and substrates scope were continued with both the Lewis acids. Here *N*-cyanosuccinimide used as an electrophilic cyanide source which featured with non-toxic reagent. This reaction associated with following disadvantages- a) high catalyst loading which is the 40 mol %, b) high reaction temperature at 120 ^{o}C. The complete mechanistic pathway proposed on the basis of controlled experiments and previous literature regarding reactivity of alkyne, diarylamines with Lewis acidic $B(C_6F_5)_3$ and $InBr_3$.

In the fifth chapter we have developed a unique strategy for the hydrogenation of olefin derivatives. In this reaction the combination of 1,3-benzodioxole and H_2O was utilized as the H_2-source. Also the regioselective hydrogen-deuterium addition at alkenes was achieved by tuning the deuterium source, e.g., 1,3-benzodioxole-2,2-d_2 or D_2O. The controlled experiments with 1,3-benzodioxole-2,2-d_2 and D_2O suggested the mechanistic pathway for this reaction. Based on the results of controlled experiments we have proposed a mechanism where first H_2O from moisture and air forms an-adduct with $InBr_3$ i.e. $H_2O{-}InBr_3$. This adduct protonates the alkenes and generates carbocationic intermediate followed by the hydride transfer from 1,3-benzodioxole to afford hydrogenated products. This methodology remains useful in terms of readily available hydrogen source; easy reaction setup under air, no need for dried solvents.

Chapter 7

Experimental Part of Chapter 2, 3,4 and 5

Annexure 1

Experimental part of Chapter 2: **Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated Dienes with Thiols**

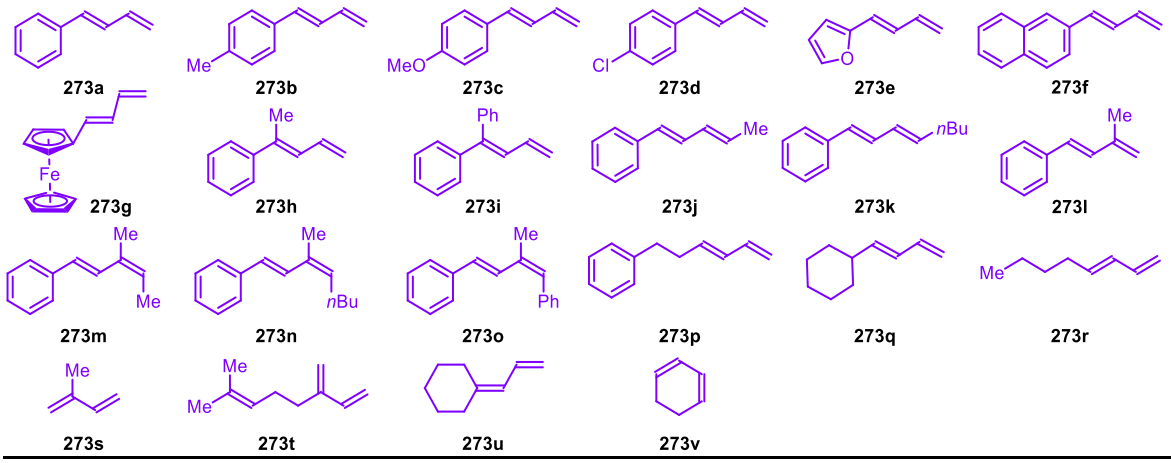
1. General Information

Reactions were performed in flame-dried glassware under argon atmosphere unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled prior to use. $CDCl_3$ was stored over 4Å molecular sieves. Used chemicals were purchased from *Sigma-Aldrich*, *TCI*, *A*lfa-*A*esar and *Sisco Research Laboratories (SRL)* used without further purification. All the liquid chemicals distilled freshly prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from *Merck* using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ unless otherwise stated on JEOL JNM ECS-400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for **^{1}H NMR** and $CDCl_3$: δ = 77.16 ppm for **^{13}C NMR**;.1,2-Dibromomethane was used as an internal standard to calculate NMR yields. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2-XS QTOF. All the X-ray data were recorded on Bruker D8 venture instrument. Dienes **273a-273r, 273u**[133]**,** and thiols **274a-*d*$_1$**[134]**, 274i**[135]**, 274j**[136] were synthesized according to the procedure in the literature.

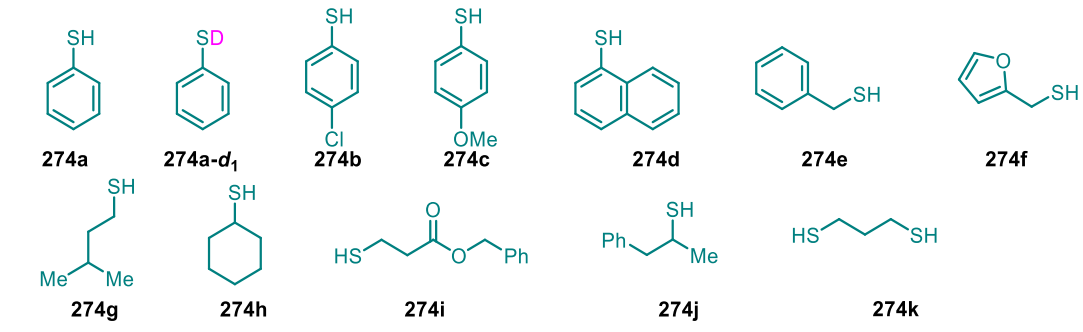
Computational Details: The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.3 suite of programs[93a] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(Toluene) level of theory, which combines the TPSS meta-GGA density functional[93f, 93l] with the BJ-damped DFT-D3 dispersion correction[93m] and the def2-TZVP basis set,[93d, 93i] using the Conductor-like Screening Model (COSMO) continuum solvation model[93b] for toluene solvent (dielectric constant ε = 2.38 and solvent diameter R_{solv} = 3.48 Å). The density-fitting RI-J approach[93c, 93d, 93k] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[93h] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model.[93n]

The final solvation free energies in toluene are computed with the COSMO-RS solvation model[93e] (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package[93o]on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol^{-1} to account for higher reference solute concentration of 1 mol·L^{-1} usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the TPSS-D3[2] and hybrid PW6B95-D3[S25] levels are performed using a larger def2-QZVP basis set.[93i, 93g] The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. The computed reaction free energies from both DFT functionals are in good mutual agreement of 0.6 ± 1.4 kcal/mol for reaction energies but the barriers at PW6B95-D3 level are usually 3.5 ± 2.4 kcal/mol higher (average ± standard deviations). In our discussion, the higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L reference concentration) will be used in our discussion unless specified otherwise

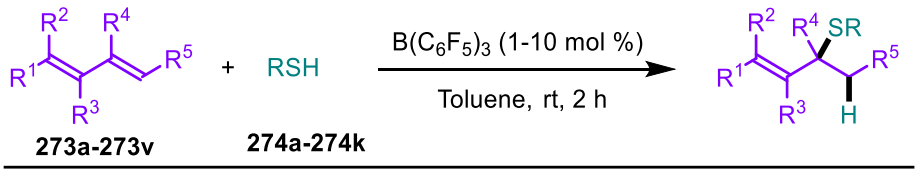
2. List of the Dienes



3. List of the Thiols



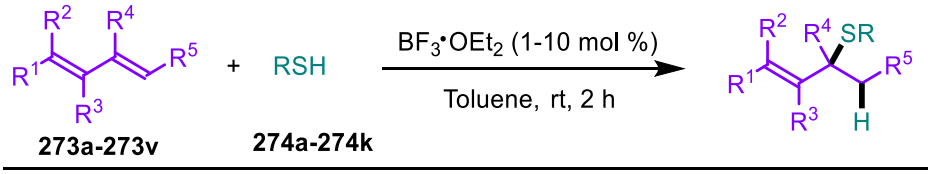
4. General Procedure for the Reaction of 1,3-Dienes and Thiols with $B(C_6F_5)_3$ (GP-1)



273a-273v **274a-274k**

In an argon filled glove box, an oven-dried glass vial is charged with a magnetic stir bar, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (1.0-10.0 mol %) and toluene. Thiol **274a-274k** (1.0 equiv) and diene **273a-273v** (1.2 equiv) simultaneously added to the mixture. The vial has been taken out from the glove box and stirred for two hours at room temperature. The crude reaction mixture is used to measure the regiomeric ratio (*rr*), *E*/*Z* ratio and diastereomeric ratio (*dr*) by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

5. General Procedure for the Reaction of 1,3-Dienes and Thiols with $BF_3{\cdot}Et_2O$ (GP-2)

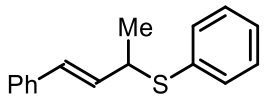


273a-273v **274a-274k**

In an argon filled glove box, an oven-dried glass vial is charged with a magnetic stir bar, thiol **274a-2274k** (1.0 equiv), diene **173a-173v** (1.2 equiv) mixed in toluene, Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.0-10.0 mol %) added to the mixture. The vial has been taken out from the glove box and stirred for two hours at room temperature. The crude reaction mixture is used to measure the regiomeric ratio (*rr*), *E*/*Z* ratio and diastereomeric ratio (*dr*) by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

6. Experimental Details for the Synthesized Compounds

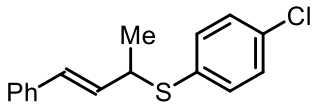
6.1 (*E*)-phenyl(4-phenylbut-3-en-2-yl)sulfane (275a)



$C_{16}H_{16}S$
M = 240.10 g/mol

Prepared according to **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275a** (137.0 mg, 98%) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275a** (190.0 mg, 88%) was obtained as colorless liquid**. MS-MS (ESI)**: for $C_{16}H_{17}S^+$ [$(M+H)^+$]: calculated 241.11, found 241.08 along with the other fragments 163.05, 130.07, 105.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.30–7.28 (m, 5H), 7.27–7.22 (m, 3H), 6.26–6.15 (m, 2H), 3.96–3.89 (m, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 134.6, 133.4, 131.7, 130.0, 128.8, 128.6, 127.5, 127.4, 126.4, 46.6, 20.7.

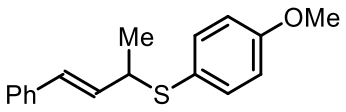
6.2 (*E*)-(4-chlorophenyl)(4-phenylbut-3-en-2-yl)sulfane (275b)



$C_{16}H_{15}ClS$
M = 274.06 g/mol

Prepared according to the **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274b** (84.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275b** (126.0, 79%) was obtained as colorless liquid**.** Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274b** (130.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275b** (190.0 mg, 77%) was obtained as colorless liquid**. MS-MS (ESI)**: for $C_{16}H_{16}ClS^+$ [$(M+H)^+$]: calculated 275.07, found 275.27 along with the other fragments 130.07, 105.05, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2H), 7.30–7.21 (m, 7H), 6.22–6.10 (m, 2H), 3.90–3.83 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 134.9, 133.7, 133.1, 131.4, 130.3, 129.0, 128.7, 127.7, 126.4, 47.0, 20.6.

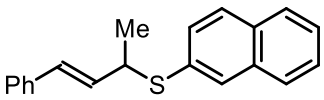
6.3 (*E*)-(4-methoxyphenyl)(4-phenylbut-3-en-2-yl)sulfane (275c)



$C_{17}H_{18}OS$
M = 270.11 g/mol

Prepared according to the **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274c** (167.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275c** (32.0 mg, 98%) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274c** (126.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275c** (51.0 mg, 21%) was obtained as colorless liquid. **HRMS (ESI)**: for $C_{17}H_{19}OS^+$ [$(M+H)^+$]: calculated 271.1157, found 271.1147. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.29–7.26 (m, 4H), 7.23–7.21 (m, 1H), 6.82–6.80 (m, 2H), 6.18–6.08 (m, 2H), 3.78 (s, 3H), 3.77–3.69 (m, 1H), 1.44 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 137.1, 136.8, 131.9, 129.8, 128.6, 127.5, 126.4, 124.6, 114.3, 55.4, 47.7, 20.5.

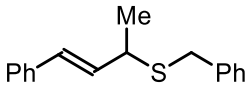
6.4 (*E*)-naphthalen-1-yl(4-phenylbut-3-en-2-yl)sulfane (275d)



$C_{20}H_{18}S$
M = 290.11 g/mol

Prepared according to the **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274d** (91.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275d** (151.0 mg, 90%) as yellow solid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274d** (144.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275d** (259.0 mg, 99%) was obtained as yellow solid. M.P- 60-61 ^oC. **MS-MS (ESI)**: for $C_{20}H_{19}S^+$ [$(M+H)^+$]: calculated 291.12, found 291.08 along with the other fragments 212.06, 187.05, 130.07, 129.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.81–7.74 (m, 3H), 7.53–7.44 (m, 3H), 7.28–7.19 (m, 5H), 6.32–6.21 (m, 2H), 4.08–4.01 (m,1H), 1.55 (d, *J* = 8.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 133.7, 132.5, 132.1, 132.0, 131.7, 130.6, 130.2, 128.6, 128.3, 127.8, 127.6(2C), 126.5, 126.4, 126.2, 46.5, 20.8.

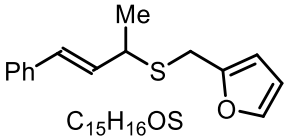
6.5 (*E*)-benzyl(4-phenylbut-3-en-2-yl)sulfane (275e)



$C_{17}H_{18}S$
M = 254.11 g/mol

Prepared according to the **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **275e** (15.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg,12.0 µmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275e** (21.0 mg, 68%) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274e** (112.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275e** (224.0 mg, 98%) was obtained as colorless liquid. **MS-MS (ESI):** for $C_{17}H_{19}S^+$ [$(M+H)^+$]: calculated 255.12, found 255.09 along with the other fragments 241.10, 179.08, 131.08, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.38–7.32 (m, 6H), 7.29–7.24 (m, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.12 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.71 (s, 2H), 3.47–3.39 (m, 1H), 1.41 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 136.8, 132.3, 130.0, 129.0, 128.7, 128.6, 127.6, 127.0, 126.4, 42.2, 35.4, 20.6.

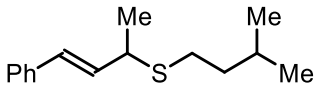
6.6 (*E*)-2-(((4-phenylbut-3-en-2-yl)thio)methyl)furan (275f)



$C_{15}H_{16}OS$
M = 244.09 g/mol

Prepared according to the **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274f** (14.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275f** (14.0 mg, 48%) as yellow liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274f** (103.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275f** (110.0 mg, 50%) was obtained as yellow liquid. **MS-MS (ESI):** for $C_{15}H_{17}OS^+$ [$(M+H)^+$]: calculated 245.10, found 245.09 along with the other fragments 141.03, 131.08, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.37 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27–7.23 (m, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.16 (d, *J* = 3.3 Hz, 1H), 6.06 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.73–3.62 (m, 2H), 3.57–3.50 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 142.1, 136.7, 131.8, 130.3, 128.7, 127.7, 126.5, 110.5, 107.3, 42.5, 27.5, 20.4.

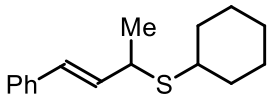
6.7 (*E*)-isopentyl(4-phenylbut-3-en-2-yl)sulfane (275g)



$C_{15}H_{22}S$
M = 234.14 g/mol

Prepared according to the **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274g** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg,12.0 µmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275g** (25.0 mg, 88%) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274g** (94.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275g** (207.0, 98%) was obtained as colorless liquid. **MS-MS (ESI):** for $C_{15}H_{23}S^+$ $[(M+H)^+]$: calculated 235.15, found 235.15 along with the other fragments 204.06, 179.07, 130.04, 129.04, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.33–7.30 (m, 2H), 7.25–7.21 (m, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.05 (dd, *J* = 15.6, 9.1 Hz, 1H), 3.54–3.47 (m, 1H), 2.54–2.39 (m, 2H), 1.67–1.61(m, 1H), 1.46 (q, *J* = 7.5 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 6.7, 4.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 132.7, 129.4, 128.7, 127.5, 126.4, 42.6, 38.9, 28.9, 27.7, 22.4, 20.8.

6.8 (*E*)-cyclohexyl(4-phenylbut-3-en-2-yl)sulfane (275h)

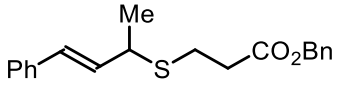


$C_{16}H_{22}S$
M = 246.14 g/mol

Prepared according to the **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274h** (14.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg,12.0 µmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275h** (26.0 mg, 89%) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274h** (105.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275h** (219.0 mg, 99%) was obtained as colorless liquid. **MS-MS (ESI):** for $C_{16}H_{23}S^+$ $[(M+H)^+]$: calculated 247.15, found 247.09 along with the other fragments 218.11, 143.09, 131.08, 129.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.34–1.30 (m, 2H), 7.25–7.21 (m, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 6.08 (dd, *J* = 15.6, 9.1 Hz, 1H), 3.66–3.59 (m, 1H), 2.65–2.58 (m, 1H), 2.04–1.99 (m, 1H), 1.88–1.83 (m, 1H), 1.78–1.68 (m, 2H), 1.39 (d, *J* =

6.9 Hz, 3H), 1.37 – 1.21 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0, 133.3, 128.9, 128.7, 127.5, 126.4, 42.5, 41.1, 34.3, 33.6, 26.3, 26.0, 21.1.

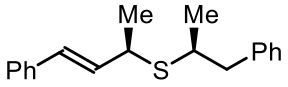
6.9 (*E*)-benzyl 3-((4-phenylbut-3-en-2-yl)thio)propanoate (275i)



$C_{20}H_{22}O_2S$
M = 326.13 g/mol

Prepared according to the **GP-1**, at 80 °C temperature, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274i** (24.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as eluent afforded the product **275i** (37.0 mg, 94%) as colorless liquid. Reaction was also performed by **GP-2**, at 80 °C temperature using **273a** (14.0 mg, 0.11 mmol, 1.2 equiv), **274i** (18.0 mg, 0.09 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 10.0 mol %). The product **275i** (22.0 mg, 76%) was obtained as colorless liquid. **HRMS (ESI):** for $C_{20}H_{22}O_2SNa^+$ [$(M+Na)^+$]: calculated 349.1238, found 349.1245. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 9H),7.25–7.23 (m, 1H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.04 (dd, *J* = 15.7, 9.1 Hz, 1H), 5.13 (s, 2H), 3.57–3.49 (m, 1H), 2.79–2.74 (m, 2H), 2.66–2.62 (m, 2H), 1.40 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 136.7, 135.9, 132.2, 129.8, 128.7(2C), 128.4(2C), 127.7, 126.5(2C), 66.6, 43.0, 35.1, 25.9, 20.7.

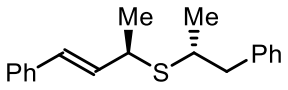
6.10 (*E*)-(4-phenylbut-3-en-2-yl)(1-phenylpropan-2-yl)sulfane (275j)



$C_{19}H_{22}S$
M = 282.14 g/mol

Prepared according to the **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274j** (83.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275j + 275j'** (139.0 mg, 85%, *dr* = 1.3:1 from crude) as colorless liquid. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274j** (137.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275j + 275j'** (203.0 mg, 80%, *dr* = *1.6:1* from crude) obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29–7.21 (m, 4H), 7.18–7.15 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J*= 15.7, 9.3 Hz, 1H), 3.52–3.44 (m, 1H), 3.08 (dd, *J*= 13.3, 5.5 Hz, 1H), 2.99–2.90 (m, 1H), 2.65 (dd, *J* = 13.2, 8.7

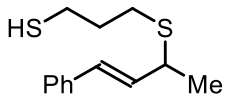
Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 136.8, 133.1, 129.5, 129.4, 128.8, 128.4, 127.6, 126.4(2C), 44.5, 42.1, 40.3, 20.9, 20.6.



$C_{19}H_{22}S$
M = 282.14 g/mol

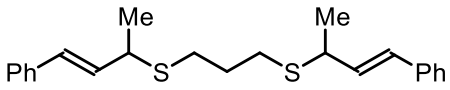
^{1}H NMR (400 MHz, $CDCl_3$)δ 7.38–7.31 (m, 4H), 7.26–7.17 (m, 4H),7.13 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.04 (dd, *J* = 15.7, 9.2 Hz, 1H), 3.61–3.56 (m, 1H), 2.99–2.90 (m, 2H), 2.70–2.62 (m, 1H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.6, 136.9, 133.1, 129.4, 129.2, 128.7, 128.3, 127.6, 126.5, 126.4, 43.6, 42.0, 40.5, 21.4, 21.0.

6.11 (*E*)-3-((4-phenylbut-3-en-2-yl)thio)propane-1-thiol and ((*E*)-4-phenylbut-3-en-2-yl)(3-(((E)-5-phenylpent-4-en-2-yl)thio)propyl)sulfane (275k + 275k')



$C_{13}H_{18}S_2$
M = 238.08 g/mol

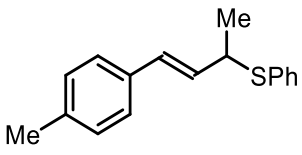
Prepared according to the **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274k** (63.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275k** (82.0 mg, 59%) and **275k' (**42.0 mg, 19%), as colorless liquids. Reaction was also performed by **GP-2**, using **273a** (141.0 mg, 1.08 mmol, 1.2 equiv), **274k** (97.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275k** (120.0 mg, 56%) and **275k' (**103.0 mg, 30%) are obtained as colorless liquids. **MS-MS (ESI)**: for $C_{13}H_{19}S_2^+$ [$(M+H)^+$]: calculated 239.09, found 239.08 along with the other fragments 130.07, 129.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.21 (m, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.04 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.54–3.45 (m, 1H), 2.66–2.50 (m, 4H), 1.90–1.83 (m, 2H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.33 (t, *J* = 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 132.4, 129.7, 128.8, 127.7, 126.4, 42.8, 33.6, 29.2, 23.7, 20.8.



$C_{24}H_{30}S_2$
M = 382.17 g/mol

MS-MS (ESI): for $C_{24}H_{31}S_2^+$ [$(M+H)^+$]: calculated 369.17, found 369.39 along with the other fragments 131.08, 129.07, 117.07. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 4H), 7.32–7.28 (m, 4H), 7.25–7.21 (m, 2H), 6.33 (dd, *J* = 15.7, 2.9 Hz, 2H), 6.02 (dd, *J* = 15.7, 9.1 Hz, 2H), 3.50–3.43 (m, 2H), 2.63–2.43 (m, 4H), 1.87–1.80 (m, 2H), 1.38 (d, *J* = 3.6 Hz, 3H), 1.37 (d, *J* = 3.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 132.5, 129.6, 128.7, 127.6, 126.5, 42.7, 29.9, 29.8, 20.8.

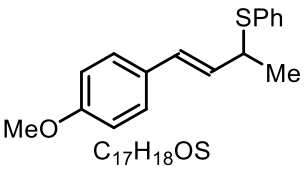
6.12 (*E*)-phenyl(4-(p-tolyl)but-3-en-2-yl)sulfane (275l)



$C_{17}H_{18}S$
M = 254.11 g/mol

Prepared according to the **GP-2**, using **273b** (100.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275l** (115.0 mg, 78%) as colorless liquid. Reaction was also performed by **GP-2**, using **273b** (156.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275l** (101.0, 44%) was obtained as colorless liquid. **MS-MS (ESI)**: for $C_{17}H_{19}S^+$ [$(M+H)^+$]: calculated 255.12, found 255.08 along with the other fragments, 146.07, 145.07, 144.06. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.31–7.24 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.23–6.10 (m, 2H), 3.96–3.88 (m, 1H), 2.34 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.3, 134.7, 134.2, 133.4, 130.7, 130.0, 129.3, 128.8, 127.4, 126.3, 46.7, 21.3, 20.8.

6.13 (*E*)-(4-(4-methoxyphenyl)but-3-en-2-yl)(phenyl)sulfane (275m)

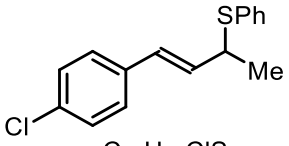


$C_{17}H_{18}OS$
M = 270.10 g/mol

Prepared according to the **GP-1**, using **273c** (112.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275m** (122.0 mg, 78%) as colorless liquid. Reaction was also performed by **GP-2**, using **273c** (173.0 mg,

1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate (BF_3·Et_2O) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275m** (47.0 mg, 20%) was obtained as colorless liquid. **MS-MS (ESI)**: for $C_{17}H_{19}OS^+$ [$(M+H)^+$]: calculated 271.12, found 271.09 along with the other fragments 242.07, 161.09, 160.08, 145.06, 144.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.31–7.22 (m, 5H), 6.86–6.83 (m, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.6, 8.2 Hz, 1H), 3.95–3.88 (m, 1H), 3.82 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 134.8, 133.4, 129.7, 129.5, 128.8, 127.6 (2C), 127.4, 114.0, 55.4, 46.7, 20.9.

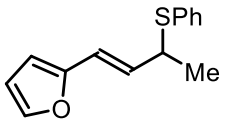
6.14 (*E*)-(4-(4-chlorophenyl)but-3-en-2-yl)(phenyl)sulfane (275n)



$C_{16}H_{15}ClS$
M = 274.06 g/mol

Prepared according to the **GP-1**, using **273d** (23.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg,12.0 µmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275n** (23.0 mg, 70%) as colorless liquid. Reaction was also performed by **GP-2**, using **273d** (178.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate (BF_3·Et_2O) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275n** (34.0 mg, 14%) was obtained as colorless liquid. **MS-MS (ESI):** for $C_{16}H_{16}ClS^+$ [$(M+H)^+$]: calculated 275.07, found 275.09 along with the other fragments, 165.03, 163.03, 135.07, 129.07, 128.06, 125.01. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.28–7.16 (m, 7H), 6.12–6.11 (m, 2H), 3.90–3.83 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.4, 134.4, 133.6, 133.1, 132.3, 128.8 (2C), 128.8, 127.6, 127.6, 46.6, 20.6.

6.15 (*E*)-2-(3-(phenylthio)but-1-en-1-yl)furan (275o)

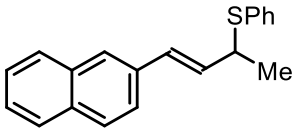


$C_{14}H_{14}OS$
M = 230.08 g/mol

Prepared according to the **GP-1**, using **273e** (83.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275o** (131.0 mg, 98%) as yellow liquid. Reaction was also performed by **GP-2**, using **273e** (130.0 mg, 1.08 mmol, 1.2

equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3 \cdot Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275o** was not detected. **MS-MS (ESI)**: for $C_{14}H_{15}OS^+$ [$(M+H)^+$]: calculated 231.08, found 231.07 along with the other fragments 162.04, 120.05, 105.07, 95.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.32–7.21 (m, 4H), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.18–6.04 (m, 3H), 3.90–3.83 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 142.0, 134.6, 133.2, 130.3, 128.9, 127.4, 118.5, 111.4, 107.8, 46.3, 20.7.

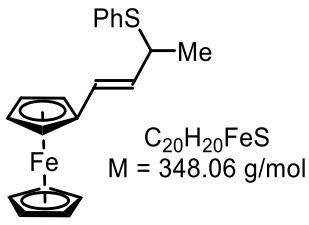
6.16 (*E*)-(4-(naphthalen-2-yl)but-3-en-2-yl)(phenyl)sulfane (275p)



$C_{20}H_{18}S$
M = 290.11 g/mol

Prepared according to the **GP-1**, using **273f** (125.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275p** (149.0, 88%) as yellow solid. Reaction was also performed by **GP-2**, using **273f** (195.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3 \cdot Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275p** (151.0 mg, 58%) was obtained as yellow solid. M.P. = 40-41 °C. **MS-MS (ESI)**: for $C_{20}H_{19}S^+$ [$(M+H)^+$]: calculated 291.12, found 291.08 along with the other fragments 180.09, 166.07, 155.08, 141.07. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83–7.68 (m, 3H), 7.51–7.39 (m, 6H), 7.33–7.25 (m, 3H), 6.87 (d, *J* = 15.3 Hz, 1H), 6.14 (dd, *J* = 15.5, 8.6 Hz, 1H), 4.08–4.00 (m, 1H), 1.58 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.0, 134.8, 134.6, 133.9, 133.6, 131.2, 129.0, 128.5, 127.9, 127.6, 127.4, 125.9, 125.8, 125.7, 124.1, 124.0, 47.3, 20.6.

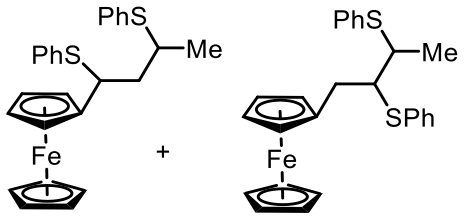
6.17 (*E*)-(4-(ferrocene-2-yl)but-3-en-2-yl)(phenyl)sulfane (275q) and (1-(ferrocene-2-yl)butane-1,3-diyl)bis(phenylsulfane) (275q')



$C_{20}H_{20}FeS$
M = 348.06 g/mol

Prepared according to the **GP-1**, using **273g** (139.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %).

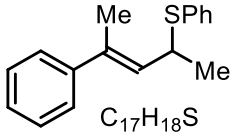
Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275q** (89.0 mg, 44%) and **19'** (74.0 mg, 28%) as yellow liquids. Reaction was also performed by **GP-B**, using **273g** (259.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The products **275q** (194.0 mg, 62%) and **275q'** (21.0 mg, 5%) were obtained as yellow liquids. **HRMS (ESI)**: for $C_{20}H_2FeS^+$ [M^+]: calculated 348.0635, found 348.0618. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.32 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.24–7.20 (m, 1H), 6.06 (d, *J* = 15.7 Hz, 1H), 5.76 (dd, *J* = 15.6, 8.4 Hz, 1H), 4.28–4.10 (m, 5H), 3.95 (s, 4H), 3.93–3.85 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.2, 132.5, 129.4, 128.9, 127.7, 127.2, 82.7, 69.2, 68.8, 68.6, 67.4, 66.1, 46.3, 21.0.



$C_{26}H_{26}FeS_2$
M = 458.08 g/mol

HRMS (ESI): for $C_{26}H_{26}FeS_2^+$ [M^+]: calculated 458.0825, found 458.0824 **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 3H), 7.33–7.27 (m, 4H), 7.25–7.20 (m, 8H), 4.37 (dd, *J* = 10.9, 3.2 Hz, 1H), 4.16 (s, 5H), 4.12 (d, *J* = 10.0 Hz, 7H), 4.02–3.93(m ,3H) 3.81–3.72 (m, 1H), 3.62–3.53 (m, 1H), 2.32–2.25 (m, 1H), 2.17 – 2.03 (m, 2H), 1.96–1.89 (m, 1H), 1.38 (d, *J* = 6.7 Hz, 3H), 1.32 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.4, 134.3, 133.9, 132.5, 132.0, 129.1, 129.0, 128.8, 128.7, 127.7, 127.6, 127.2, 126.9, 69.0 (2C), 68.0, 67.9, 67.5 (2C), 67.3, 66.4, 47.8, 47.0, 42.3, 42.2, 41.6, 40.5, 23.1, 20.7.

6.18 (*E*)-phenyl(4-phenylpent-3-en-2-yl)sulfane (275r)

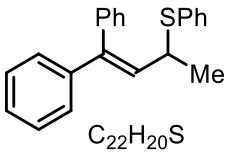


$C_{17}H_{18}S$
M = 254.11 g/mol

Prepared according to the **GP-1**, using **273h** (21.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12.0 µmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275r** (30.0 mg, 98%, *E*/*Z* = 4:1) as colorless liquid. Reaction was also performed by **GP-2**, using **273h** (155.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275r** (151.0 mg, 66%) was obtained as colorless

liquid. **MS-MS (ESI)**: for $C_{17}H_{19}S^+$ [$(M+H)^+$]: calculated 255.12, found 255.09 along with the other fragments 240.10, 128.06, 105.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.31 (d, *J* = 4.2 Hz, 4H), 7.29–7.22 (m, 4H), 5.66 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.20–4.13 (m, 1H), 1.76 (d, *J* = 1.6 Hz, 3H), 1.44 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 136.1, 134.7, 134.4, 130.4, 128.8, 128.3, 127.7, 127.1, 125.9, 43.1, 21.4, 16.0.

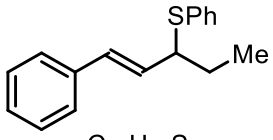
6.19 (4,4-diphenylbut-3-en-2-yl)(phenyl)sulfane (275s)



$C_{22}H_{20}S$
M = 316.13 g/mol

Prepared according to the **GP-1**, using **273i** (154.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %) Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275s** (182.0 mg, 99%) as colorless liquid. Reaction was also performed by **GP-2**, using **273i** (221.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275s** (216.0 mg, 76%) was obtained as colorless liquid. **MS-MS (ESI)**: for $C_{22}H_{21}S^+$ [$(M+H)^+$]: calculated 317.14, found 317.15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 5H), 7.30–7.25 (m, 6H), 7.19–7.17 (m, 2H), 6.96–6.93 (m, 2H), 6.04 (d, *J* = 10.6 Hz, 1H), 4.04–3.97 (m, 1H), 1.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 139.3, 134.4, 133.7, 131.5, 129.8, 128.7, 128.2 (2C), 127.5, 127.4 (3C), 127.3, 43.5, 21.4.

6.20 (*E*)-phenyl(1-phenylpent-1-en-3-yl)sulfane (275t)

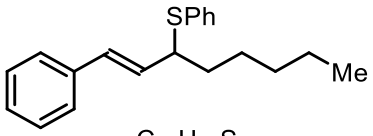


$C_{17}H_{18}S$
M = 254.11 g/mol

Prepared according to the **GP-1**, using **273j** (21.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275t** (16.0 mg, 52%) as colorless liquid. Reaction was also performed by **GP-2**, using **273j** (156.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %) The product **275t** was not detected. **MS-MS (ESI)**: for $C_{17}H_{19}S^+$ [$(M+H)^+$]:

calculated 255.12, found 255.09 along with the other fragments 240.09, 130.07, 129.07, 128.06, 115.05, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.29–7.20 (m, 8H), 6.18 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 15.8, 8.9 Hz, 1H), 3.68–3.62(m, 1H), 1.90–1.82 (m,1H), 1.78–1.68 (m,1H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0, 134.6, 133.5, 131.2, 130.6, 128.8, 128.6, 127.5, 127.4, 126.4, 54.1, 28.0, 12.2.

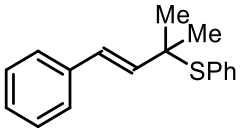
6.21 (*E*)-phenyl(1-phenyloct-1-en-3-yl)sulfane (275u)



$C_{20}H_{24}S$
M = 296.16 g/mol

Prepared according to the **GP-1**, using **273k** (27.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275u** (23.0 mg, 66%) as colorless liquid. Reaction was also performed by **GP-2**, using **273k** (201.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %) The product **275u** was not detected. **MS-MS (ESI)**: for $C_{20}H_{25}S^+$ $[(M+H)^+]$: calculated 297.17, found 297.10 along with the other fragments 167.04, 129.04, 117.04, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.27–7.17 (m, 8H), 6.14–6.00 (m, 2H), 3.72–3.66 (m, 1H), 1.83–1.63 (m, 2H), 1.48–1.41 (m, 2H), 1.30–1.26 (m, 4H), 0.89–0.82 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 134.7, 133.5, 131.0, 130.9, 128.8, 128.6, 127.5, 127.4, 126.4, 52.6, 34.8, 31.7, 27.3, 22.7, 14.2.

6.22 (*E*)-(2-methyl-4-phenylbut-3-en-2-yl)(phenyl)sulfane (275v)

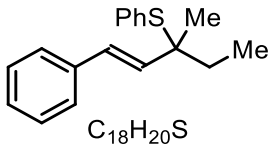


$C_{17}H_{18}S$
M = 254.11 g/mol

Prepared according to the **GP-1**, using **273l** (100.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %) Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275v** (130.0 mg, 88%) as colorless liquid. Reaction was also performed by **GP-2**, using **273l** (156.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %) The product **273l** was not detected. **MS-MS (ESI)**: for

$C_{17}H_{19}S^+$ [$(M+H)^+$]: calculated 255.12, found 255.11 along with the other fragments 240.09, 179.08, 129.07, 128.06, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.30–7.28 (m, 5H), 7.24–7.20 (m, 3H), 6.31 (d, *J* = 16.1 Hz, 1H), 5.98 (d, *J* = 16.1 Hz, 1H), 1.45 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$ δ 137.6, 137.3, 136.8, 132.4, 128.9, 128.7, 128.5, 127.4, 127.1, 126.4, 50.2, 28.0.

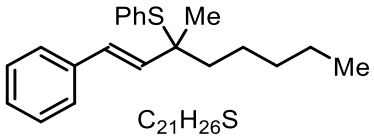
6.23 (*E*)-(3-methyl-1-phenylpent-1-en-3-yl)(phenyl)sulfane (275w)



$C_{18}H_{20}S$
M = 268.13 g/mol

Prepared according to the **GP-1**, using **273m** (110.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 μmol, 1.0 mol %) Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275w** (128.0 mg, 82%) as colorless liquid. Reaction was also performed by **GP-2**, using **273m** (178.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 μmol, 1.0 mol %). The product **275m** was not detected. **MS-MS (ESI)**: for $C_{18}H_{21}S^+$ [$(M+H)^+$]: calculated 269.14, found 269.13 along with the other fragments 255.12, 158.10, 143.08, 129.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.31–7.30 (m, 4H), 7.26–7.21 (m, 4H), 6.25 (d, *J* = 16.1 Hz, 1H), 5.96 (d, *J* = 16.3 Hz, 1H), 1.81–1.72(m, 2H), 1.38 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.7, 137.4, 135.7, 132.1, 128.8, 128.7, 128.4, 128.1, 127.3, 126.3, 54.4, 33.7, 23.4, 9.4.

6.24 (*E*)-(3-methyl-1-phenyloct-1-en-3-yl)(phenyl)sulfane (275x)

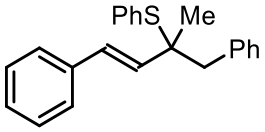


$C_{21}H_{26}S$
M = 310.18 g/mol

Prepared according to the **GP-1**, using **273n** (139.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 μmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275x** (92.0 mg, 51%) as colorless liquid. Reaction was also performed by **GP-2**, using **273n** (216.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 μmol, 1.0 mol %). The product **275x** was not detected. **MS-MS (ESI)**: for $C_{21}H_{27}S^+$ [$(M+H)^+$]: calculated 311.18, found 311.18 along with the other fragments 143.08, 130.07,

129.07, 91.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.40 (m, 2H), 7.30–7.29 (m, 5H), 7.25 – 7.20 (m, 3H), 6.25 (d, *J* = 16.1 Hz, 1H), 5.92 (d, *J* = 16.1 Hz, 1H), 1.73–1.68 (m, 2H), 1.51–1.41 (m, 2H), 1.38 (s, 3H), 1.32–1.26 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.7, 137.4, 136.0, 132.1, 128.8, 128.7, 128.4, 127.8, 127.3, 126.3, 54.1, 41.2, 32.4, 24.7, 24.0, 22.7, 14.2.

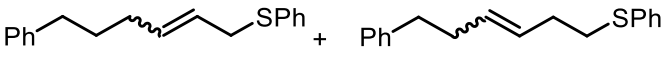
6.25 (*E*)-(2-methyl-1,4-diphenylbut-3-en-2-yl)(phenyl)sulfane (275y)



$C_{23}H_{22}S$
M = 330.14 g/mol

Prepared according to the **GP-1**, using **273o** (153.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275y** (65.0 mg, 39%) was obtained as colorless liquid. Reaction was also performed by **GP-2**, using **273o** (238.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %) The product **275y** was not detected. **MS-MS (ESI)**: for $C_{23}H_{23}S^+$ [$(M+H)^+$]: calculated 331.15, found 331.13. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.32–7.30 (m, 2H), 7.28–7.27 (m, 3H), 7.25–7.18 (m, 8H), 6.39 (d, *J* = 16.1 Hz, 1H), 5.83 (d, *J* = 16.1 Hz, 1H), 3.18 (d, *J* = 13.4 Hz, 1H), 3.03 (d, *J* = 13.4 Hz, 1H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 137.3, 137.1, 135.2, 133.7, 131.8, 130.8, 129.0, 128.7, 128.5, 128.0, 127.4, 126.7, 126.4, 77.5, 48.2, 23.7.

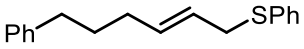
6.26 phenyl(6-phenylhex-2-en-1-yl)sulfane and phenyl(6-phenylhex-3-en-1-yl)sulfane (275pa + 275pa')



$C_{18}H_{20}S$
M = 268.12 g/mol

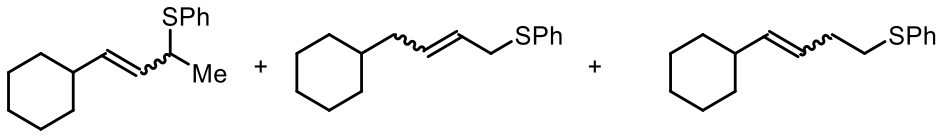
Prepared according to the **GP-1**, using **273p** (23.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the products **275pa+275pa'** (27.0 mg, 85%, 22 : 22' = 1 : 1, rr, 22'-*E*/*Z* = 3 : 1,) as colorless liquid mixture. Reaction was also performed by **GP-2**, using **273p** (171.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol,

1.0 equiv) and Boron trifluoride ethyl etherate (BF_3·Et_2O) (1.3 mg, 9.0 µmol, 1.0 mol %). The products **275pa+275a'** were not detected. **HRMS (ESI)**: for $C_{18}H_{21}S^+$ [$(M+H)^+$]: calculated 269.1364, found 269.1350. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 12H), 7.22–7.14 (m, 8H), 5.99–5.37 (m, 4H), 3.55 (d, *J* = 5.5 Hz, 2H), 2.96–2.93 (m, 1.32H), 2.85–2.81 (m, 0.51H), 2.68 (q, *J* = 7.9 Hz, 2H), 2.56–2.52 (m, 2H), 2.34 (q, *J* = 7.0 Hz, 3.70H), 2.04 (q, *J* = 6.9 Hz, 2H), 1.68– 1.61 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 142.0, 136.8, 136.2, 134.0, 132.9, 131.6, 130.8, 129.9, 129.2, 129.0, 128.8, 128.6 (2C), 128.5, 128.4, 126.2, 125.9, 125.8, 125.6, 36.6, 36.0, 35.2, 34.5, 33.6, 32.4, 31.8, 30.9.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5H), 7.24–7.10 (m, 5H), 5.58–5.46 (m, 2H), 3.52 (d, *J* = 5.7 Hz, 2H), 2.52 (t, *J* = 8.4 Hz, 2H), 2.01 (q, *J* = 6.6 Hz, 2H), 1.64–1.60 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 136.3, 134.1, 130.0, 128.9, 128.6, 128.4, 126.2, 125.8, 125.6, 36.6, 35.3, 31.8, 30.9.

6.27 (4-cyclohexylbut-3-en-2-yl)(phenyl)sulfane (4-cyclohexylbut-2-en-1-yl)(phenyl)sulfane & (4-cyclohexylbut-3-en-1-yl)(phenyl)sulfane (275qa+275qa'+275qa'')

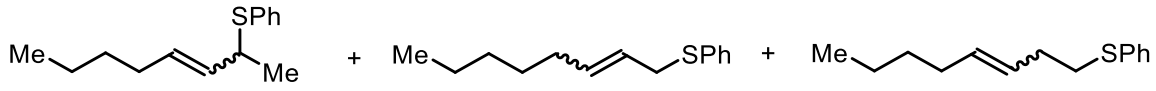


$C_{16}H_{22}S$
M = 246.14 g/mol

Prepared according to the **GP-1**, using **273q** (19.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the products **275qa+275qa'+275qa''** (16.0 mg, 55%, **275qa:275qa':275qa''** = 1 : 1 : 0.75 *rr*, 275qa-*E*/*Z* = 5 : 1, 275qa'-*E*/*Z* = 10 : 1, 275qa''-*E*/*Z* = 1.3 : 1) as colorless liquid mixture. Reaction was also performed by **GP-2**, using **273q** (147.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate (BF_3·Et_2O) (1.3 mg, 9.0 µmol, 1.0 mol %). The products **275qa+275qa'+275qa''** were not detected. **HRMS (ESI)**: for $C_{16}H_{23}S^+$ [$(M+H)^+$]: calculated 247.1520, found 247.1506. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.43 (m, 1H), 7.39–7.32 (m, 6H), 7.30–7.24 (m, 8H), 7.21–7.15 (m, 4H), 5.54–5.39 (m, 3H), 5.36–5.13 (m, 5H), 3.74–3.67 (m, 1H), 3.52 (d, *J* = 6.2 Hz, 2H), 2.41–2.36 (m, 1.86H), 2.34–2.29 (m, 1.66H), 2.21–2.12 (m, 1.47H), 1.90–1.83 (m, 3.30H), 1.74–1.62 (m, 9H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.28–1.02 (m, 18H), 0.96–0.86 (m, 2H), 0.83–0.73 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.6, 138.2, 137.5, 133.3 (2C), 132.9, 130.1, 129.2, 129.0 (2C), 128.8, 128.6 (2C), 127.6, 127.1, 126.8,

126.2, 125.9, 125.9, 125.2, 58.9, 46.4, 42.2, 40.8, 40.4, 38.0, 36.7, 33.7, 33.4, 33.1 (2C), 32.9, 32.6, 31.5, 30.3, 27.3, 26.6, 26.4, 26.3, 26.2, 20.9.

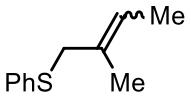
6.28 oct-3-en-2-yl(phenyl)sulfane, oct-2-en-1-yl(phenyl)sulfane & oct-3-en-1-yl(phenyl)sulfane (275ra+275ra'+275ra'')



$C_{14}H_{20}S$
M = 220.13 g/mol

Prepared according to the **GP-1**, using **273r** (15.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275ra+275ra'+275ra''** (21.13 mg, 80%, **275ra:275ra':275ra''**= 1 : 0.6 : 0.5 rr, 275ra-*E*/*Z* = 10 : 1, 275ra'-*E*/*Z* = 3 : 1, 275ra"-*E*/*Z* = 1.3 : 1) as colorless liquid mixture. Reaction was also performed by **GP-2**, using **273r** (119.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The products **275ra+275ra'+275ra''** were not detected. **MS-MS (ESI)**: for $C_{14}H_{21}S^+$ [$(M+H)^+$]: calculated 221.14, found 221.14. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.32 (m, 5H), 7.30–7.15 (m, 9H), 5.57–5.40 (m, 3H), 5.38–5.28 (m, 3H) 3.77–3.71 (m, 1H), 3.56 (d, *J* = 6.2 Hz, 0.32H). 3.52 (d, *J* = 6.2 Hz, 1H), 2.96–2.90 (m, 1H), 2.41–2.30 (m, 1.H), 2.02–1.87 (m, 4 H), 1.69–1.59 (m, 4H), 1.36 (d, *J* = 6.8 Hz, 3H).1.33–1.14 (m, 14H), 0.91–0.82 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.3, 135.2, 134.8, 133.0, 132.9, 132.7, 132.2, 131.9, 131.7, 130.0, 129.2(2C), 128.8, 128.7, 128.6, 127.1, 127.0, 126.9, 126.2, 125.9, 125.9 (2C), 51.8, 46.1, 36.7, 34.6, 33.7, 32.4, 32.0, 31.5, 31.4, 29.9, 29.6, 29.0, 27.2, 22.6, 22.6, 22.2, 20.9, 17.8, 14.2, 14.1.

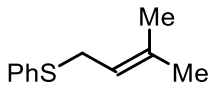
6.29 (2-methylbut-2-en-1-yl)(phenyl)sulfane (275sa) and (3-methylbut-2-en-1-yl)(phenyl)sulfane (275sa')



$C_{11}H_{14}S$
M = 178.08 g/mol

Prepared according to the **GP-1**, using **273s** (47.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %) reaction performed at -10^{o}C. Purification by column chromatography on silica gel using petroleum ether as eluent

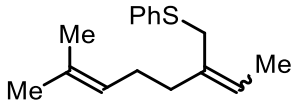
afforded the products **275sa + 275sa'** (83.0 mg, 90%, *E/Z* = 10 : 1, *rr = 5 : 1*) as colorless liquid mixture. Reaction was also performed by **GP-B**, using **273s** (74.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3 \cdot Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275sa'** (48.0 mg, 30%) was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.26 (m, 4H), 7.20–7.12 (m, 1H), 5.33 (q, *J* = 7.0 Hz, 1H), 3.51 (s, 2H), 1.74 (s, 3H), 1.56 (d, *J* = 8.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 131.1, 130.2, 128.8, 126.2, 123.3, 44.2, 15.1, 13.5.



$C_{11}H_{14}S$
M = 178.08 g/mol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.2 Hz, 2H), 7.28–7.24 (m, 2H), 7.19–7.15 (m, 1H), 5.32–5.28 (m, 1H), 3.54 (d, *J* = 7.7 Hz, 2H), 1.71 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 136.6, 129.8, 128.9, 126.1, 119.4, 32.3, 25.8, 17.8.

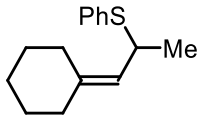
6.30 (2-ethylidene-6-methylhept-5-en-1-yl)(phenyl)sulfane (275ta)



E/*Z* = 4:1
$C_{16}H_{22}S$
M = 246.14 g/mol

Prepared according to the **GP-1**, using **273t** (95.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluenta afforded the product **275ta** (121.0 mg, 85%, *E/Z* = 4 : 1) as colorless liquid. Reaction was also performed by **GP-2**, using **273t** (147.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3 \cdot Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275ta** was not obtained **HRMS (ESI)**: for $C_{16}H_{23}S^+$ [$(M+H)^+$]: calculated 247.1520, found 247.1521 **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 2H), 7.29–7.24 (m, 2H), 7.19–7.15 (m, 1H), 5.37 (q, *J* = 6.9 Hz, 1H), 5.15–5.10 (m, 1H), 3.54 (s, 2H), 2.24–2.18 (m, 2H), 2.13–2.07 (m, 2H), 1.69 (s, 3H), 1.62 (s, 3H), 1.58 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 135.0, 132.1, 130.0, 128.8, 126.1, 124.1, 123.9, 41.8, 28.9, 26.8, 25.9, 17.8, 13.6.

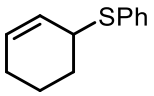
6.31 (1-cyclohexylidenepropan-2-yl)(phenyl)sulfane (275ua)



$C_{15}H_{20}S$
M = 232.13 g/mol

Prepared according to the **GP-1**, using **273u** (19.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275ua** (27.0 mg, 96%) was obtained as colorless liquid. Reaction was also performed by **GP-2**, using **273u** (147.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol). The product **275ua** (27.0 mg, 13%) was obtained as colorless liquid. **MS-MS (ESI)**: for $C_{15}H_{21}S^+$ [$(M+H)^+$]: calculated 233.14, found 233.12. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.29–7.21 (m, 3H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.11–4.04 (m, 1H), 2.01 (dd, *J* = 7.1, 4.8 Hz, 2H), 1.96–1.89 (m, 2H), 1.52–1.34 (m, 6H), 1.32 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 135.4, 133.7, 128.7, 127.2, 124.1, 41.4, 37.1, 29.1, 28.5, 27.6, 26.8, 21.8.

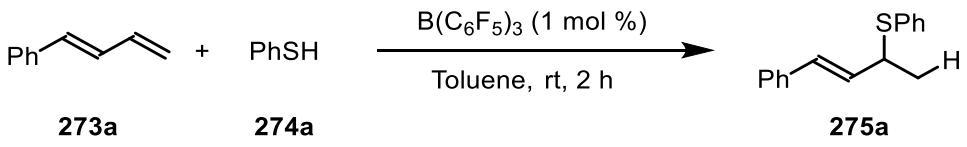
6.32 Cyclohex-2-en-1-yl(phenyl)sulfane (275va)



$C_{12}H_{14}S$
M = 190.08 g/mol

Prepared according to the **GP-1**, using **273v** (56.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %) Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275va** (110.0 mg, 91%) as colorless liquid. Reaction was also performed by **GP-2**, using **273v** (87.0 mg, 1.08 mmol, 1.2 equiv), **274a** (99.0 mg, 0.90 mmol, 1.0 equiv) and Boron trifluoride ethyl etherate ($BF_3{\cdot}Et_2O$) (1.3 mg, 9.0 µmol, 1.0 mol %). The product **275va** was not detected. **MS-MS (ESI)**: for $C_{12}H_{15}S^+$ [$(M+H)^+$]: calculated 191.09, found 191.05. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.31–7.27 (m, 2H), 7.24–7.19 (m, 1H), 5.86–5.82 (m, 1H), 5.79–5.75 (m, 1H), 3.88–3.84 (m, 1H), 2.08–2.00 (m, 2H), 1.97–1.86 (m, 2H), 1.82–1.76 (m, 1H), 1.66–1.59 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 131.4, 130.6, 129.0, 127.0, 126.7, 44.0, 28.9, 25.1, 19.6.

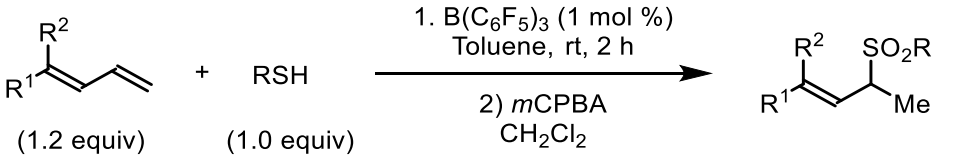
7. Gram scale synthesis:



273a **274a** **275a**

Gram scale synthesis has been done by using the **GP-1, 273a** (1310.0 mg, 10.08 mmol, 1.2 equiv), **274a** (924.0 mg, 8.4 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (43.0 mg, 0.084 mmol, 1.0 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275a** (1.56 g, 93%) as colorless liquid.

8. Derivatization of the sulfide to sulfone

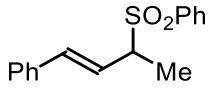


(1.2 equiv) (1.0 equiv)

Procedure A

First step has been done by following the **GP-1,** after isolation of the, oxidation was carried out via reported method in the literature.[137] To a stirred solution of sulfide (0.1 mmol, 1.0 equiv) in 1ml DCM was added *m*CPBA (0.2 mmol, 2 equiv) at 0 ^oC, reaction kept for stirring for 4 hours at the same temperature. After completion the reaction was quenched with aqueous solution of $NaHCO_3$, extracted with ethyl acetate, and the organic layer passed over anhydrous Na_2SO_4. Pure compound was isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent afforded the respected products.

8.1 (*E*)-((4-phenylbut-3-en-2-yl)sulfonyl)benzene (275ao)

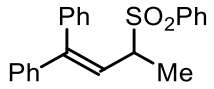


$C_{16}H_{16}O_2S$
M = 272.09 g/mol

Prepared according to the procedure **A**, by using **275a** (24.0 mg, 0.1 mmol, 1.0 equiv), *m*CPBA (34 mg, 0.2 mmol, 2equiv) in DCM at 0 ^oC for 4 hours. Purification by column chromatography on silica gel

using petroleum ether/ethyl acetate (10:1) as eluent afforded the product **275ao** (20.0 mg, 73%) as white solid. M.P - 60-61 °C **HRMS (ESI)**: for $C_{16}H_{16}O_2SNa^+$ [(M+Na)$^+$]: calculated 295.0769, found 295.0756. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.82 (m, 2H), 7.63–7.60 (m, 1H), 7.52–7.48 (m, 2H) 7.32–7.25 (m, 5H), 6.30 (d, *J* = 15.7 Hz, 1H), 6.07 (dd, *J* = 16.0, 8.2 Hz, 1H), 3.89–3.81 (m, 1H), 1.55 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0, 136.6, 135.9, 133.8, 129.4, 129.0, 128.8, 128.5, 126.7, 122.2, 64.2, 13.6.

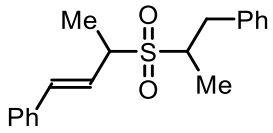
8.2 (3-(phenylsulfonyl)but-1-ene-1,1-diyl)dibenzene (275so)



$C_{22}H_{20}O_2S$
M = 348.12 g/mol

Prepared according to the procedure **A**, by using **275s** (32.0 mg, 0.1 mmol, 1.0 equiv), *m*CPBA (34.0 mg, 0.2 mmol, 2 equiv) in DCM at 0 °C for 4 hours. Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (10 : 1) as eluent afforded the product **275so** (23.0 mg, 72%) as white solid. M. P. – 91–92 °C. **HRMS (ESI)**: for $C_{22}H_{20}O_2SNa^+$ [(M+Na)$^+$]: calculated 371.1082, found 371.1076. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75–7.73 (m, 2H), 7.63–7.59 (m, 1H), 7.49–7.45 (m, 2H), 7.27–7.19 (m, 6H), 7.14–7.12 (m, 2H), 6.57 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.01 (d, *J* = 10.9 Hz, 1H), 3.89–3.81 (m, 1H), 1.58 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 140.7, 138.2, 133.6, 129.1, 129.0 (3C), 128.4(2C), 128.3, 127.8, 127.4, 121.6, 61.0, 13.7.

8.3 (*E*)-(2-((4-phenylbut-3-en-2-yl)sulfonyl)propyl)benzene (275jo)

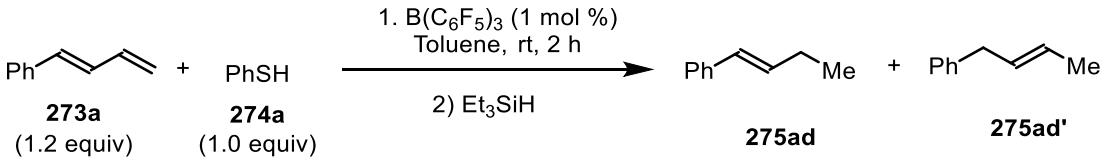


$C_{19}H_{22}O_2S$
M = 314.13 g/mol

Prepared according to the procedure **A**, by using **275j** (28.21 mg, 0.1 mmol, 1.0 equiv), *m*CPBA (34.0 mg, 0.2 mmol, 2 equiv) in DCM at 0 °C for 4 hours. Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (10 : 1) as eluent afforded the product **275jo** (21.0 mg, 68%, *dr* = 1:1) as gummy liquid (mixture of diastereomer). **HRMS (ESI)**: for $C_{19}H_{22}O_2S^+$ [(M+Na)$^+$]: calculated 337.1238, found 337.1244. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 4H), 7.37–7.34 (m, 3H), 7.33–7.26 (m, 6H), 7.25–7.21 (m, 1H), 7.17–7.12 (m, 3H), 6.57 (dd, *J* = 43.9, 16.0 Hz, 2H), 6.22 (dd, *J* = 25.9, 14.9 Hz, 2H), 3.99–3.92 (m, 1H), 3.88–3.81 (m, 1H), 3.51–3.30 (m, 4H), 2.77–2.66 (m, 2H), 1.62 (d, *J* =

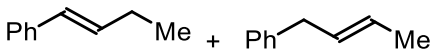
6.9 Hz, 3H), 1.59 (d, *J* = 6.9 Hz, 3H) 1.30 (d, *J* = 6.9 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 136.1, 135.9, 135.6, 129.6, 129.4, 129.0 (2C), 128.9 (2C), 128.8 (2C), 127.3, 127.1, 126.8 (2C), 123.4, 123.3, 59.9, 59.3, 56.3, 56.0, 36.5, 33.5, 13.2, 13.0, 12.9, 11.6.

9. Hydrodesulfurization of the synthesized sulfide



273a (1.2 equiv) + **274a** (1.0 equiv) → **275ad** + **275ad'**

9.1 (*E*)-but-1-en-1-ylbenzene and (*E*)-but-2-en-1-ylbenzene (275ad + 275ad')

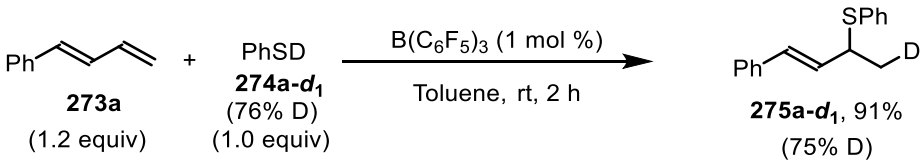


$C_{10}H_{12}$
M = 132.09 g/mol

According to **GP-1**, using **273a** (19.0 mg, 0.14 mmol, 1.2 equiv), **274a** (13.0 mg, 0.12 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 6.0 µmol, 5.0 mol %). Then after two hours triethylsilane (21.0 mg, 0.18 mmol, 1.5 equiv) was added to the reaction mixture and stirred for additional 30 minutes.[138] Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **275ad+275ad'** (15.53 mg, 98%) as colorless liquid. The ratio of **275ad : 275ad'** from crude is 1.6 : 1, and the isolated ratio is 1 : 1.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 1H), 7.28 (dd, *J* = 8.5, 6.9 Hz, 3H), 7.20–7.16 (m, 4H), 6.39–6.34 (m, 1H), 6.29–6.22 (m, 1H), 5.62–5.46 (m, 2H), 3.31 (d, *J* = 6.2 Hz, 2H), 2.26–2.19 (m, 2H), 1.68 (dd, *J* = 6.0, 1.5 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.8, 130.2, 128.9, 128.6, 128.5, 126.9, 126.5, 126.0(2C), 39.2, 26.2, 18.1, 13.8.

10. Deuterium labelling

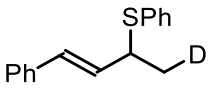


273a (1.2 equiv) + **274a-d_1** (76% D) (1.0 equiv) → **275a-d_1**, 91% (75% D)

According to **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274a-d_1** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %). Purification by

column chromatography on silica gel using petroleum ether as eluent afforded the product 3-d (127.0 mg, yield 91%,) as colorless liquid. 75% deuterium labelling has been confirmed by the ^{1}H NMR.

10.1. (*E*)-phenyl(4-phenylbut-3-en-2-yl)sulfane-d_1 (375a-d_1)

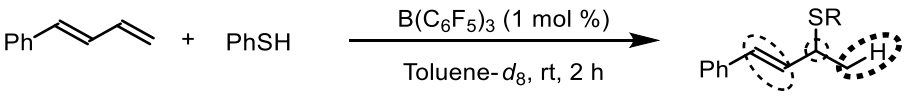


$C_{16}H_{15}DS$
M = 241.10 g/mol

D-MASS (ESI): for $C_{16}H_{15}DS^{+}$ [$(M+H)^{+}$]: calculated 242.11, found 242.10. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.42 (m, 2H), 7.29–7.27 (m, 5H), 7.25–7.19 (m, 3H), 6.24–6.13 (m, 2H), 3.93–3.87 (m, 1H), 1.50–1.45 (m, 2.25H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0, 134.6, 133.5, 131.7, 130.0, 128.8, 128.6, 127.5 (2C), 126.4, 46.6, 20.7 (20.7, 20.5, 20.3 for **CH_2D**). **^{13}C DEPT-135** NMR (101 MHz, $CDCl_3$) δ 137.0, 134.6, 133.5, 131.7, 130.0, 128.8, 128.6, 127.5(2C), 126.4, 46.5, 20.7 (20.6, 20.4, 20.2 for **CH_2D**).

11. Time-Dependent ^{1}H-NMR Measurement of Model Reaction

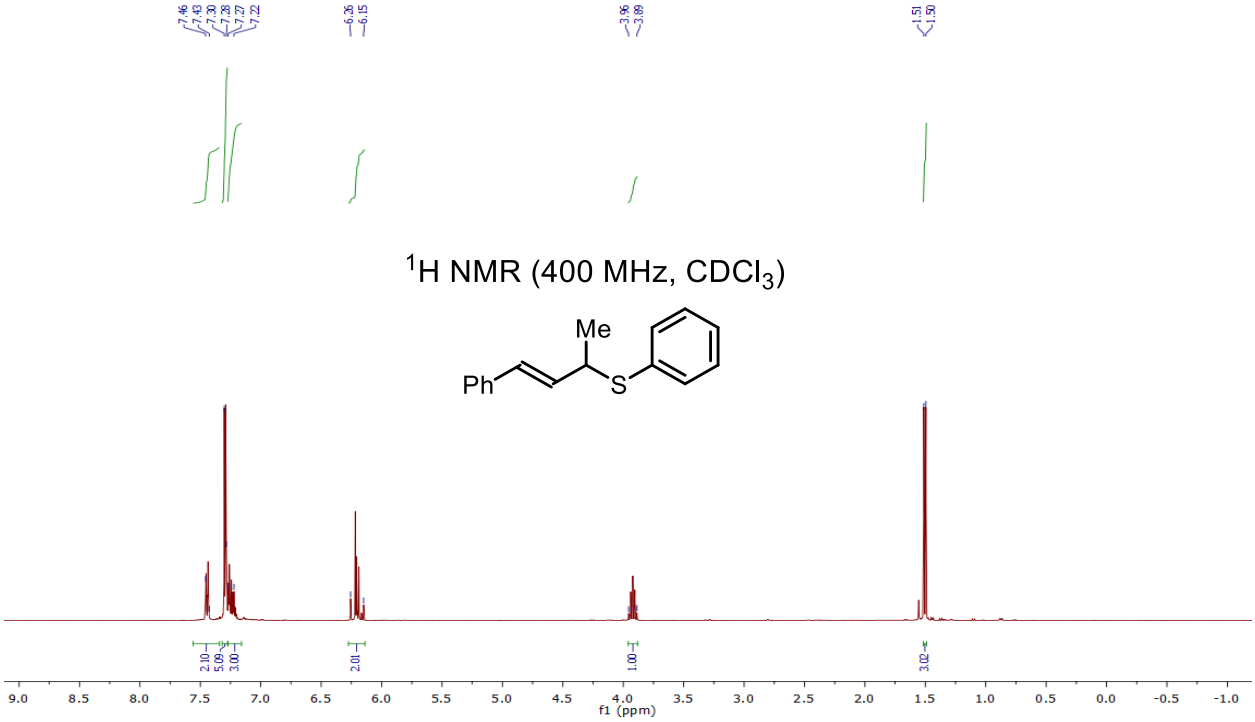
According to **GP-1**, using **273a** (91.0 mg, 0.69 mmol, 1.2 equiv), **274a** (64.0 mg, 0.58 mmol, 1.0 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (3.0 mg, 5.8 µmol, 1.0 mol %) in toluene-d_8. Complete reaction performed inside the glove box and the NMR samples prepared inside the glove box by taking aliquots from reaction mixture at every 30 minutes interval time. First NMR recorded for the initial aliquot which has been taken just after reaction setup. In similar manner all the NMR has been recorded.



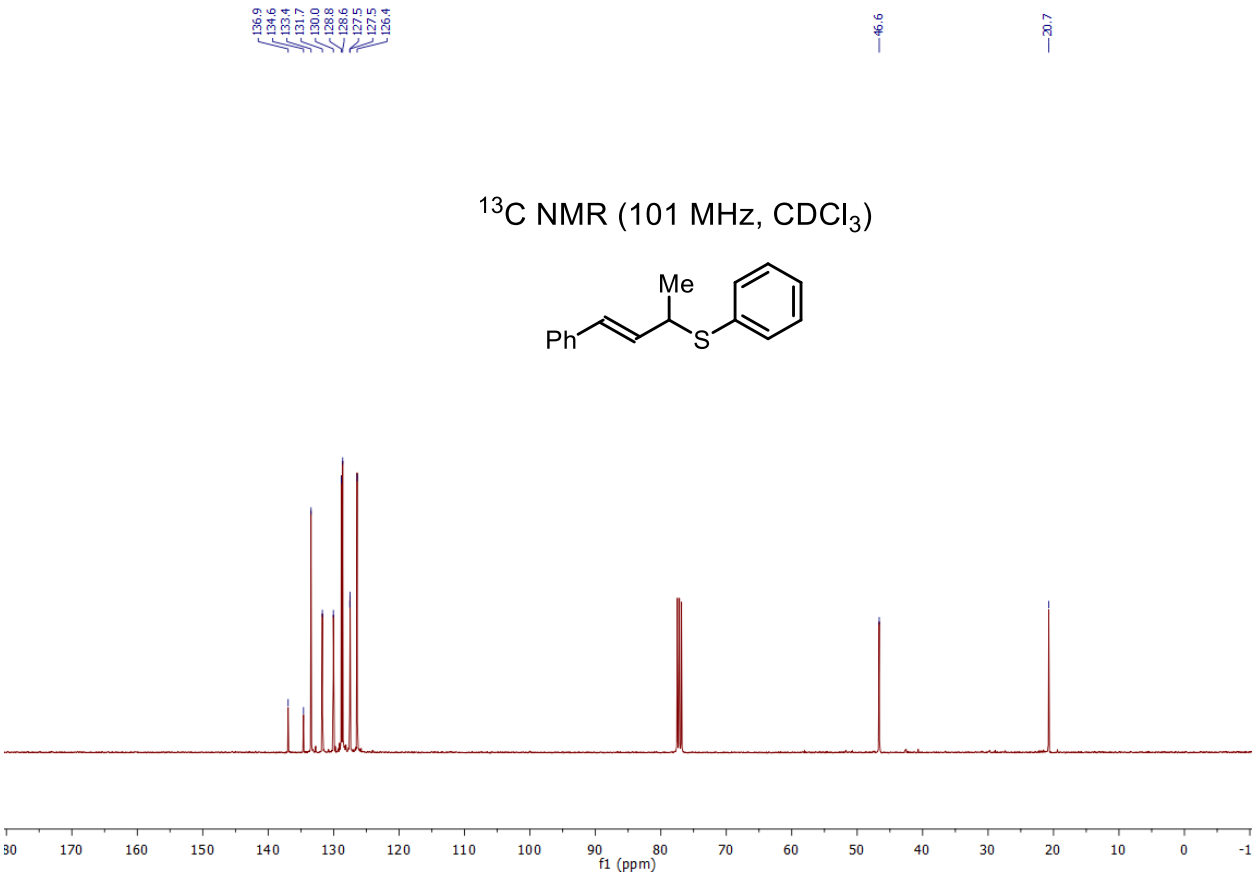
273a **274a** **275a**

12. Experimental NMR Data

(*E*)-phenyl(4-phenylbut-3-en-2-yl)sulfane (275a)

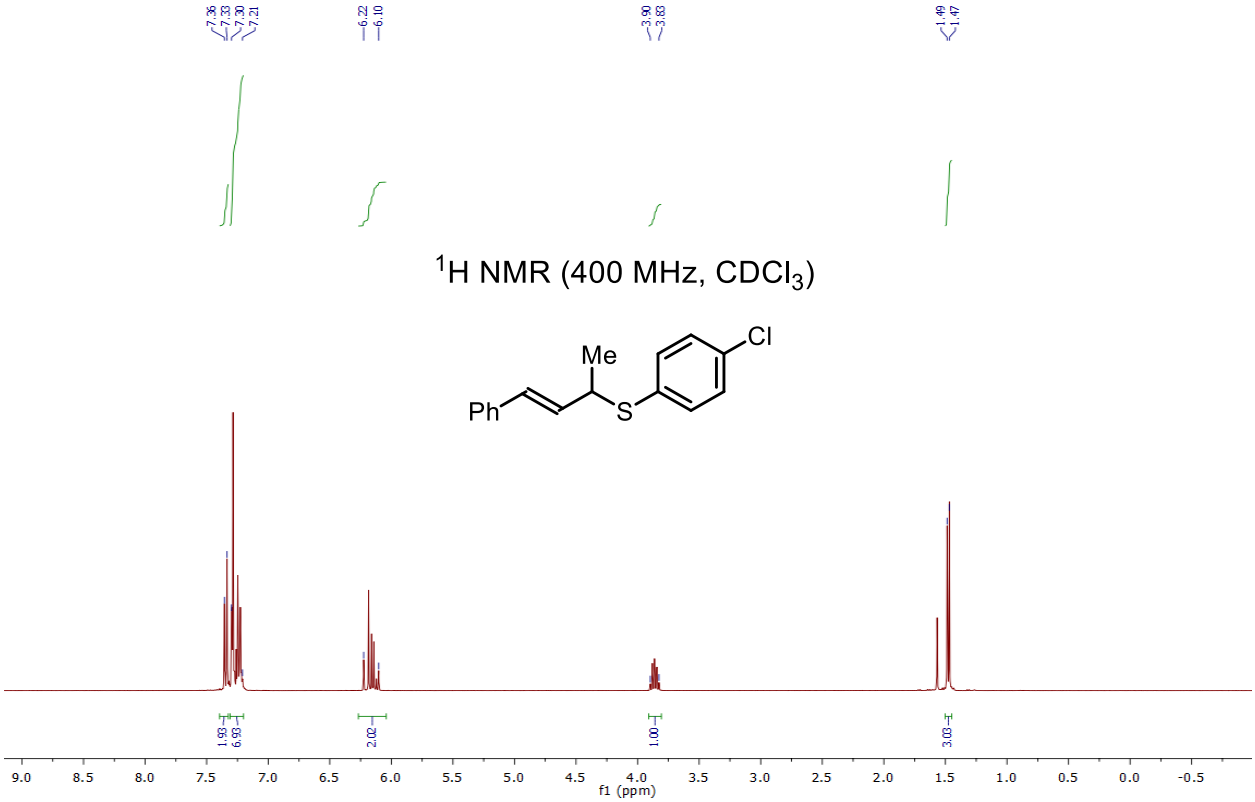


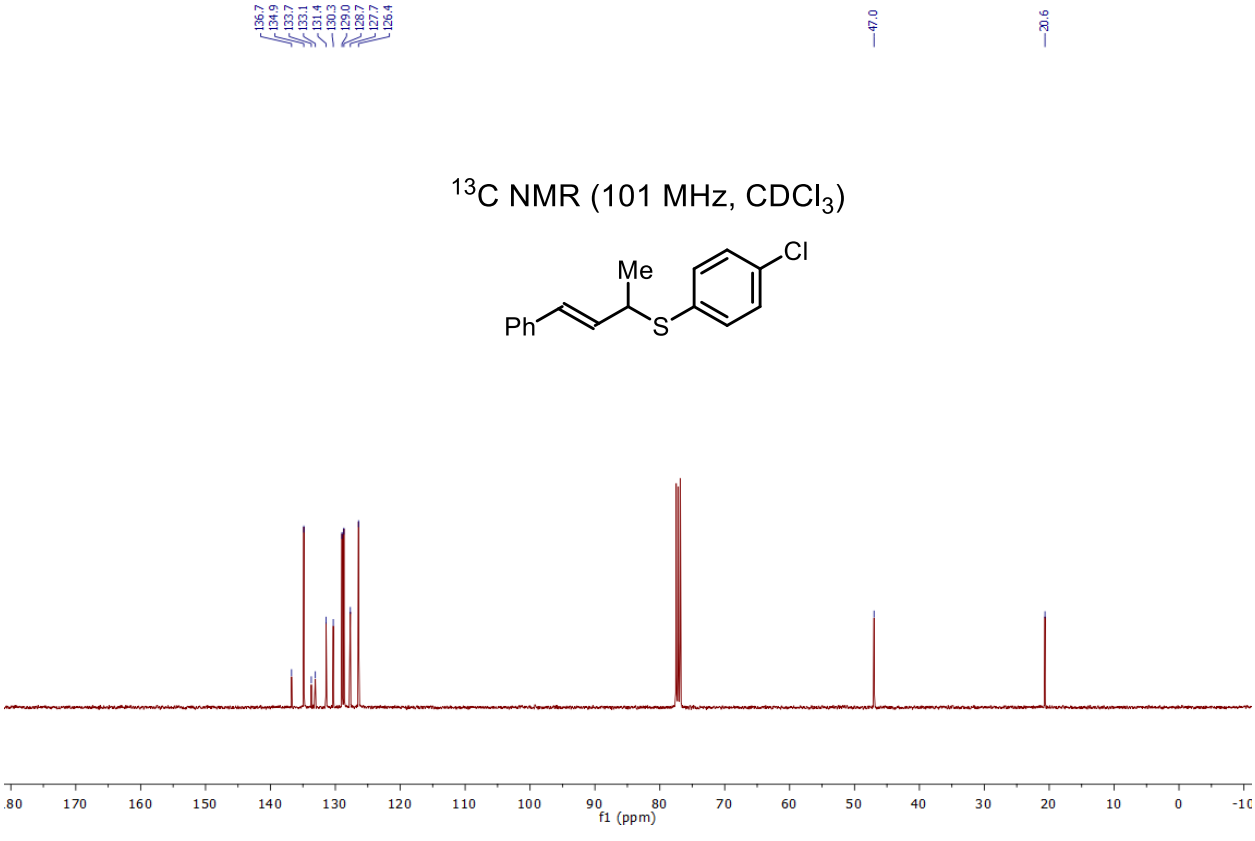
^{1}H NMR (400 MHz, $CDCl_3$)



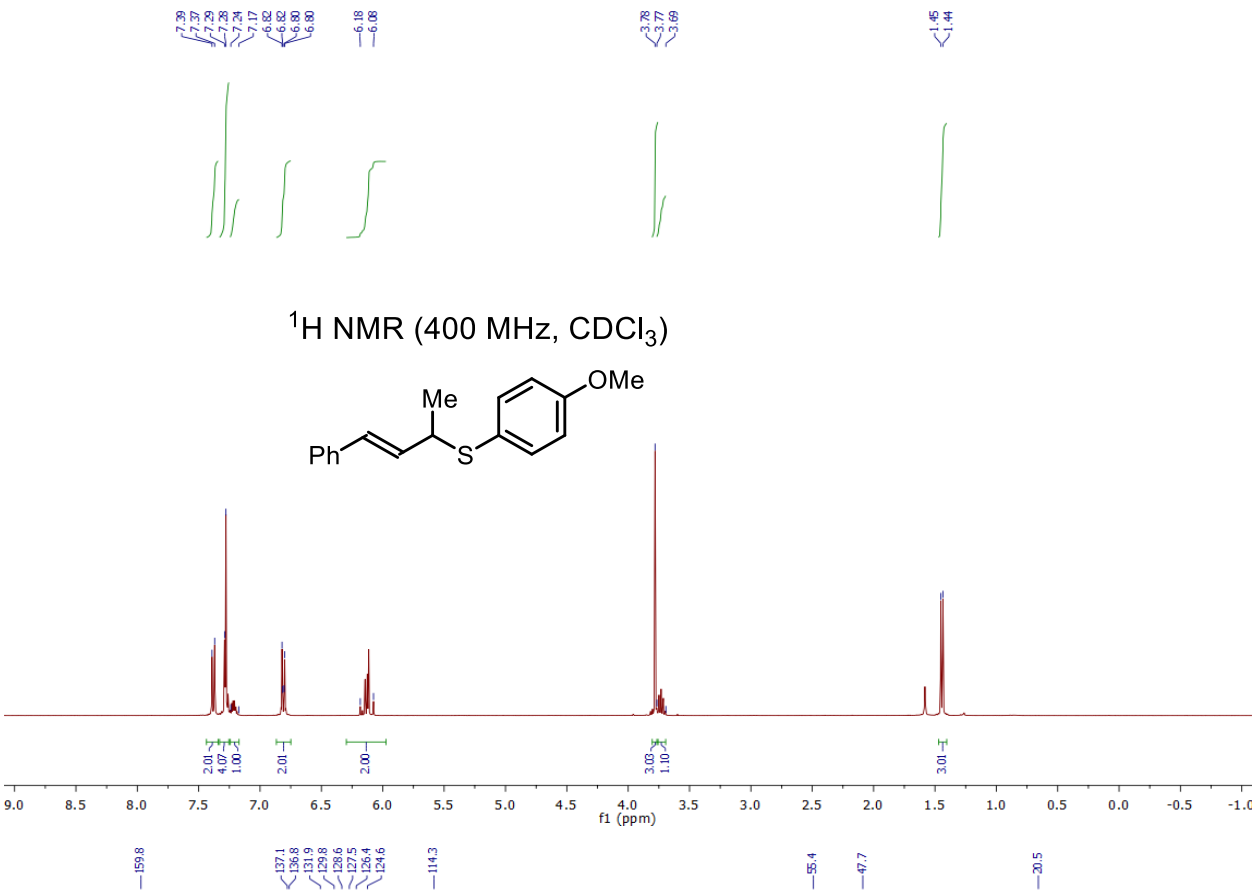
^{13}C NMR (101 MHz, $CDCl_3$)

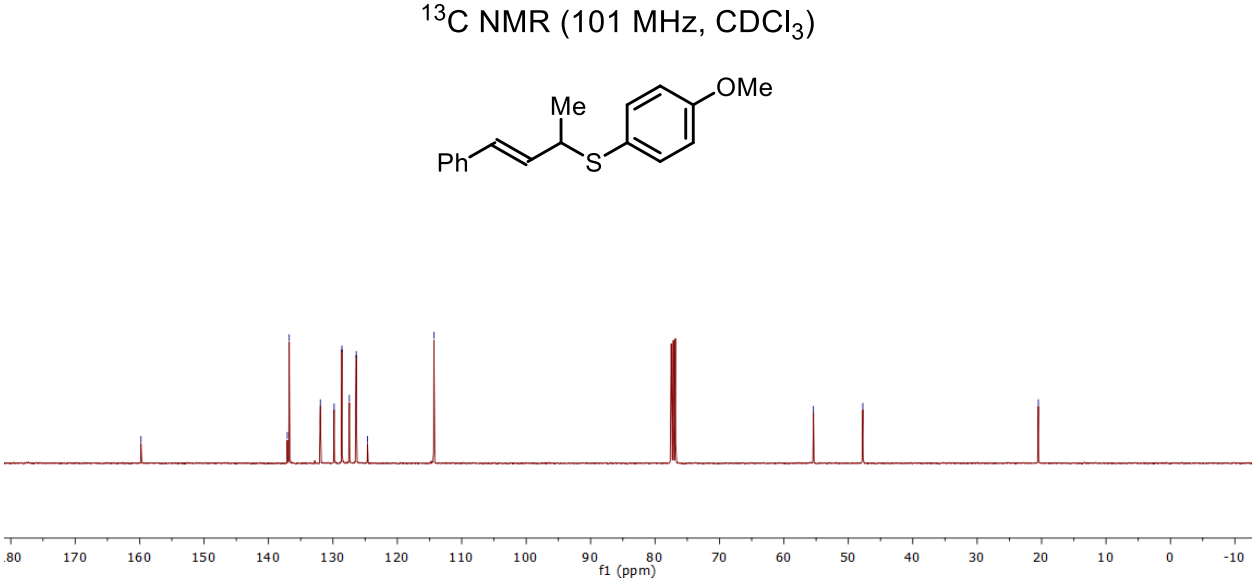
(*E*)-(4-chlorophenyl)(4-phenylbut-3-en-2-yl)sulfane (275b)



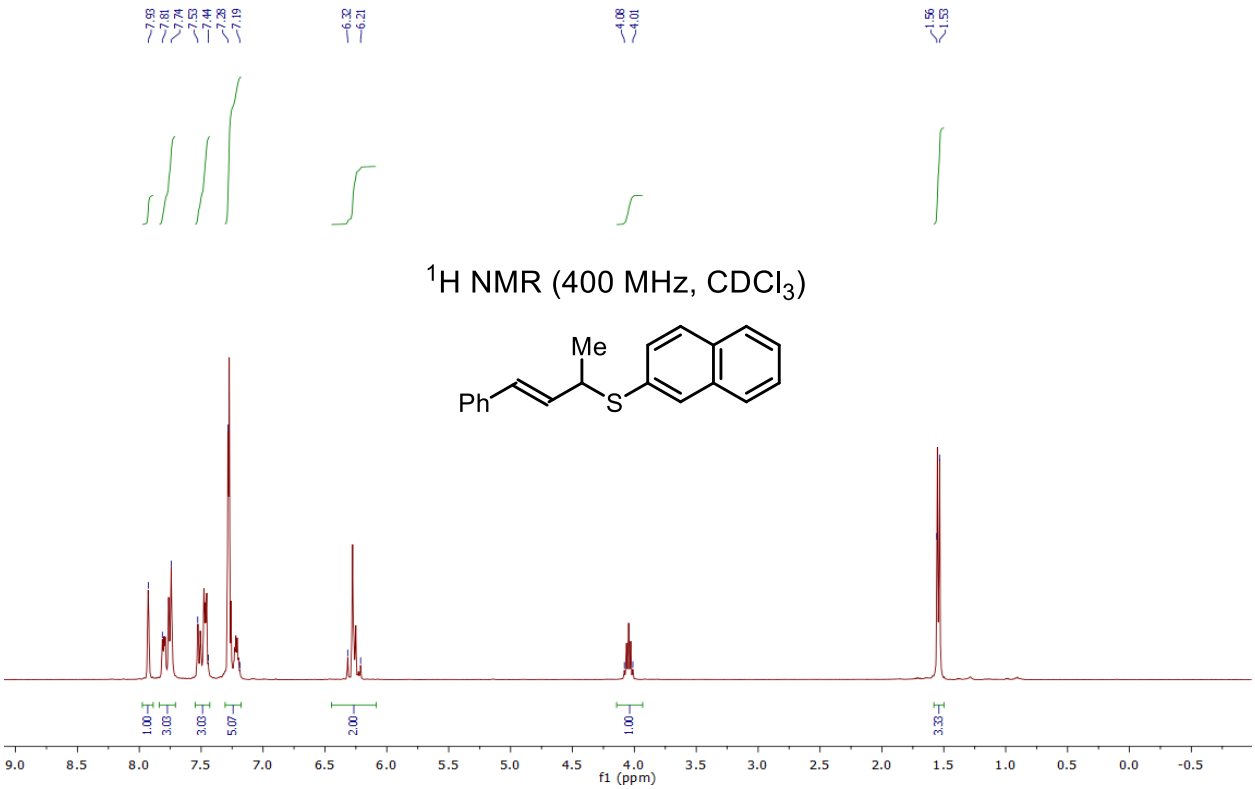


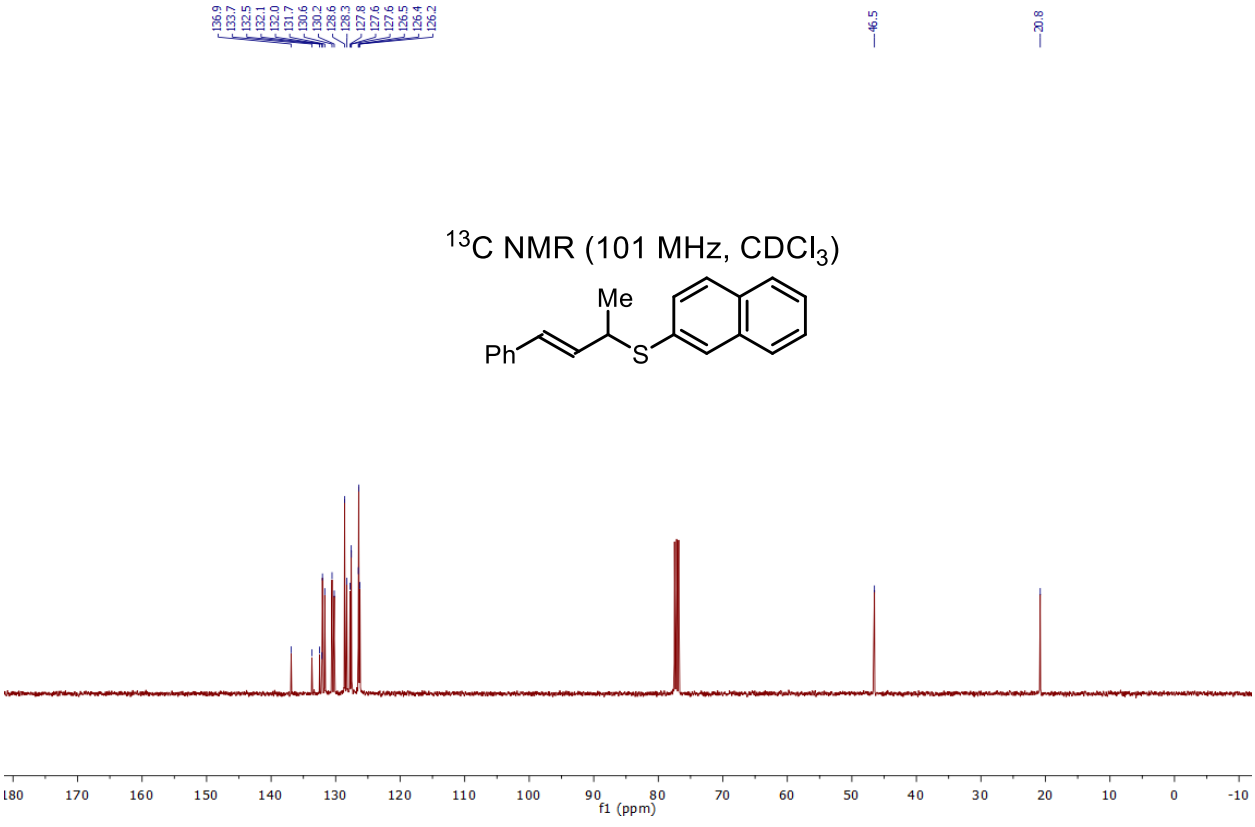
(*E*)-(4-methoxyphenyl)(4-phenylbut-3-en-2-yl)sulfane (275c)



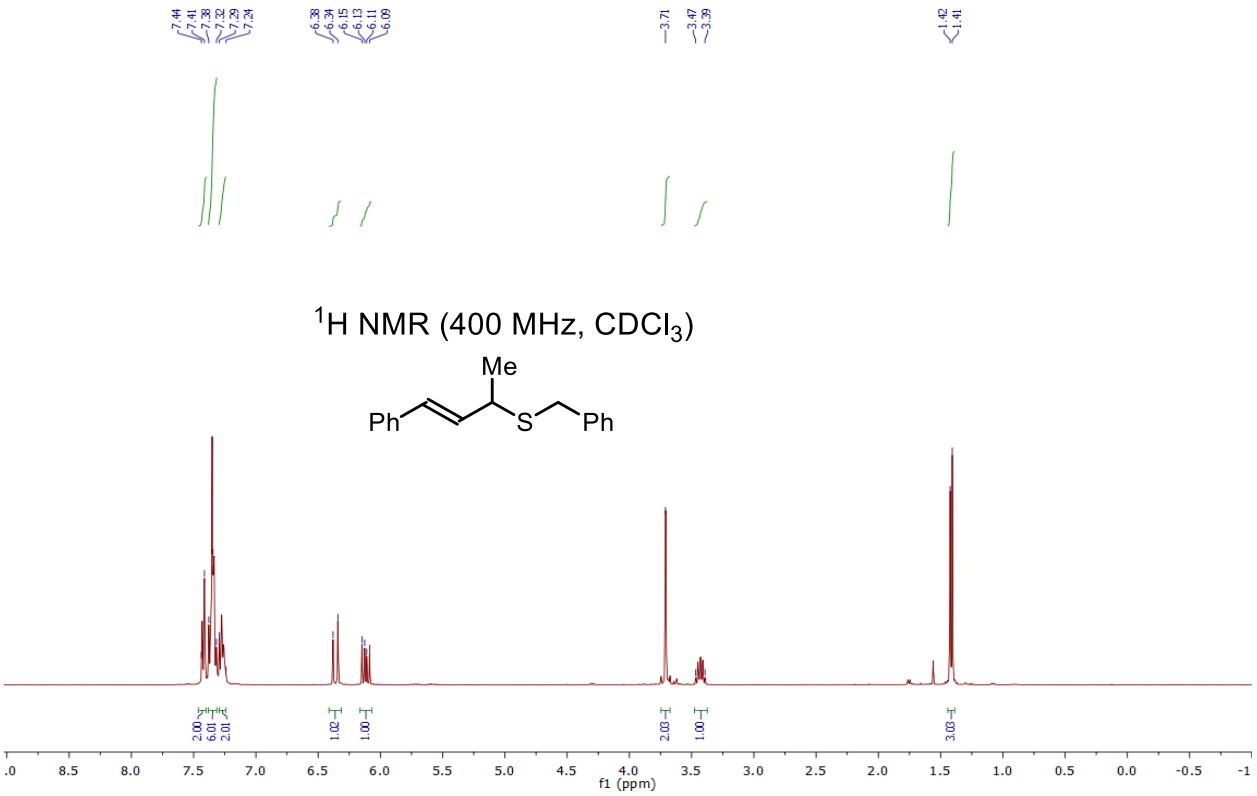


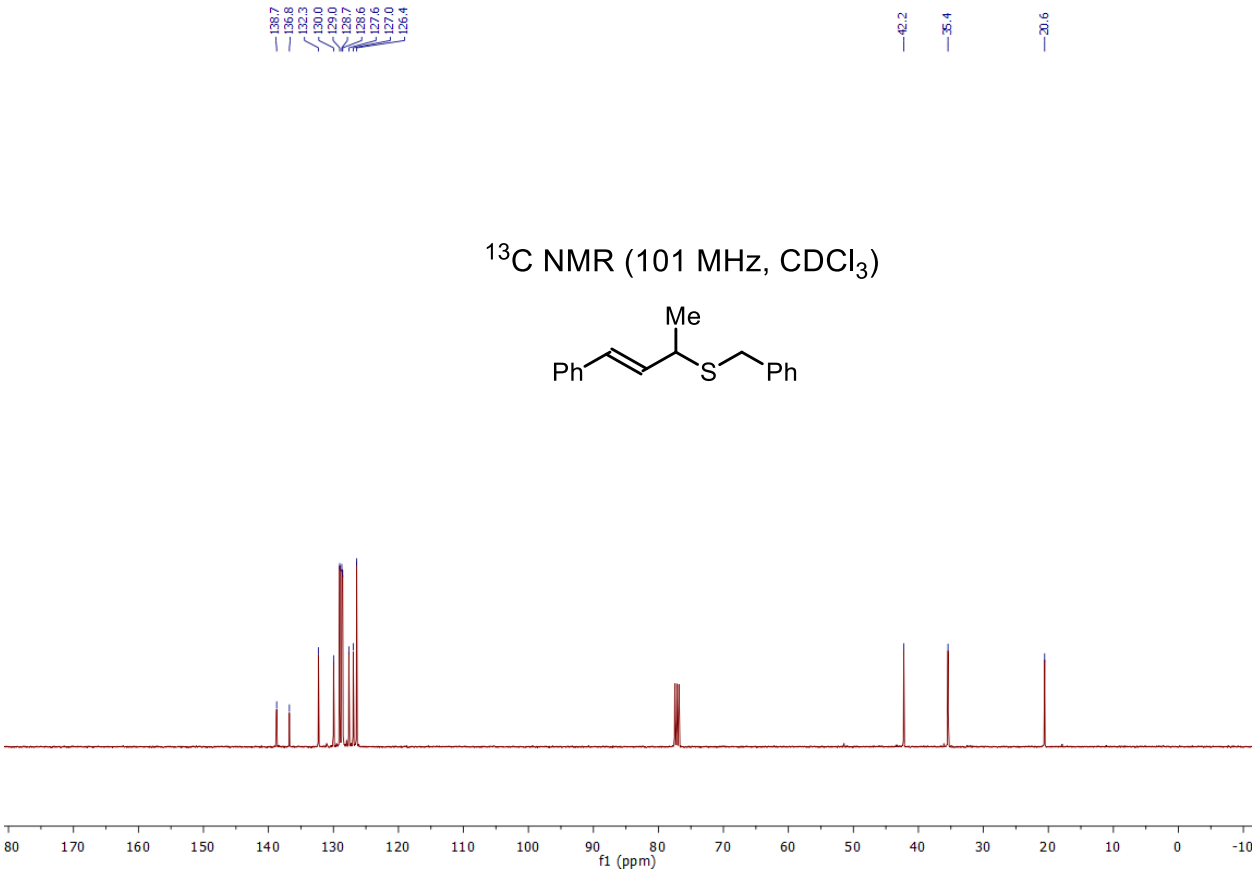
(*E*)-naphthalen-1-yl(4-phenylbut-3-en-2-yl)sulfane (275d)



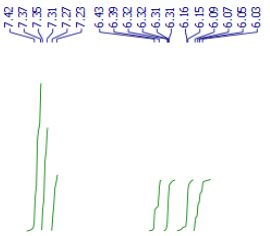


(*E*)-benzyl(4-phenylbut-3-en-2-yl)sulfane (275e)

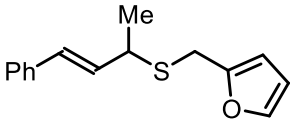


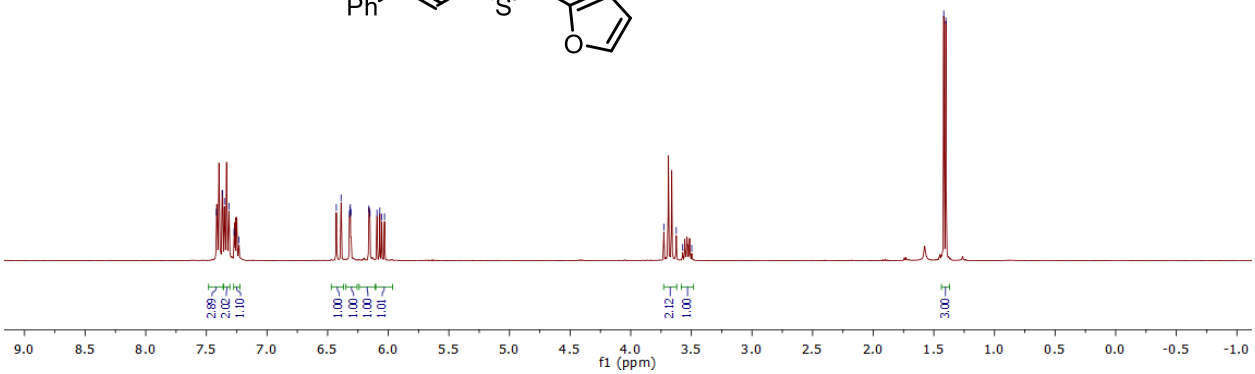


(*E*)-2-(((4-phenylbut-3-en-2-yl)thio)methyl)furan (275f)

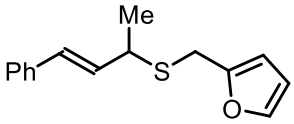


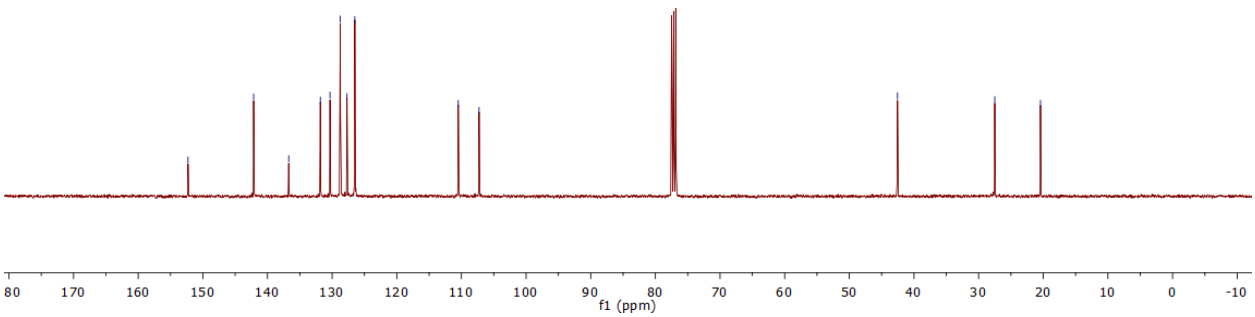
^{1}H NMR (400 MHz, $CDCl_3$)



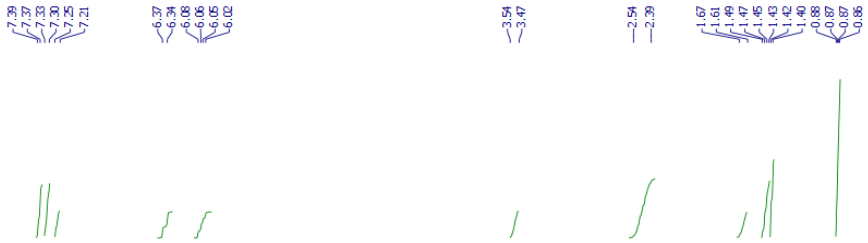


^{13}C NMR (101 MHz, $CDCl_3$)

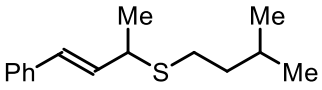


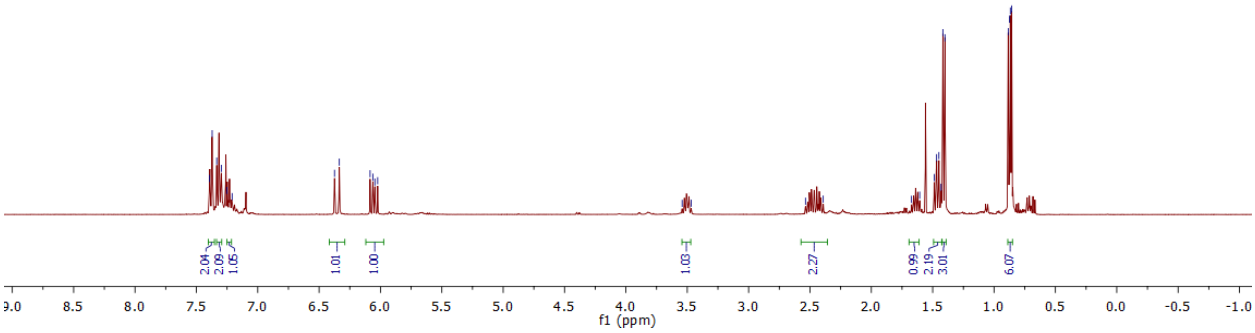


(*E*)-isopentyl(4-phenylbut-3-en-2-yl)sulfane (275g)

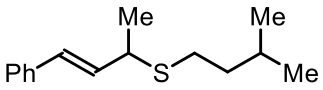


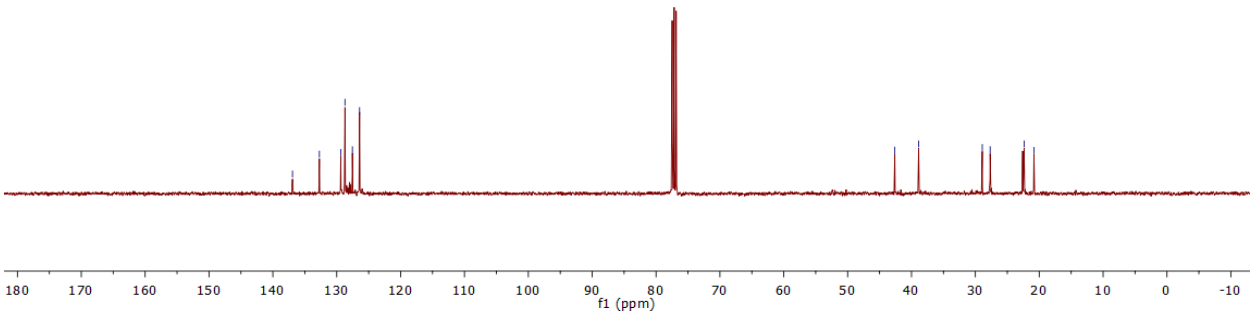
^{1}H NMR (400 MHz, $CDCl_3$)



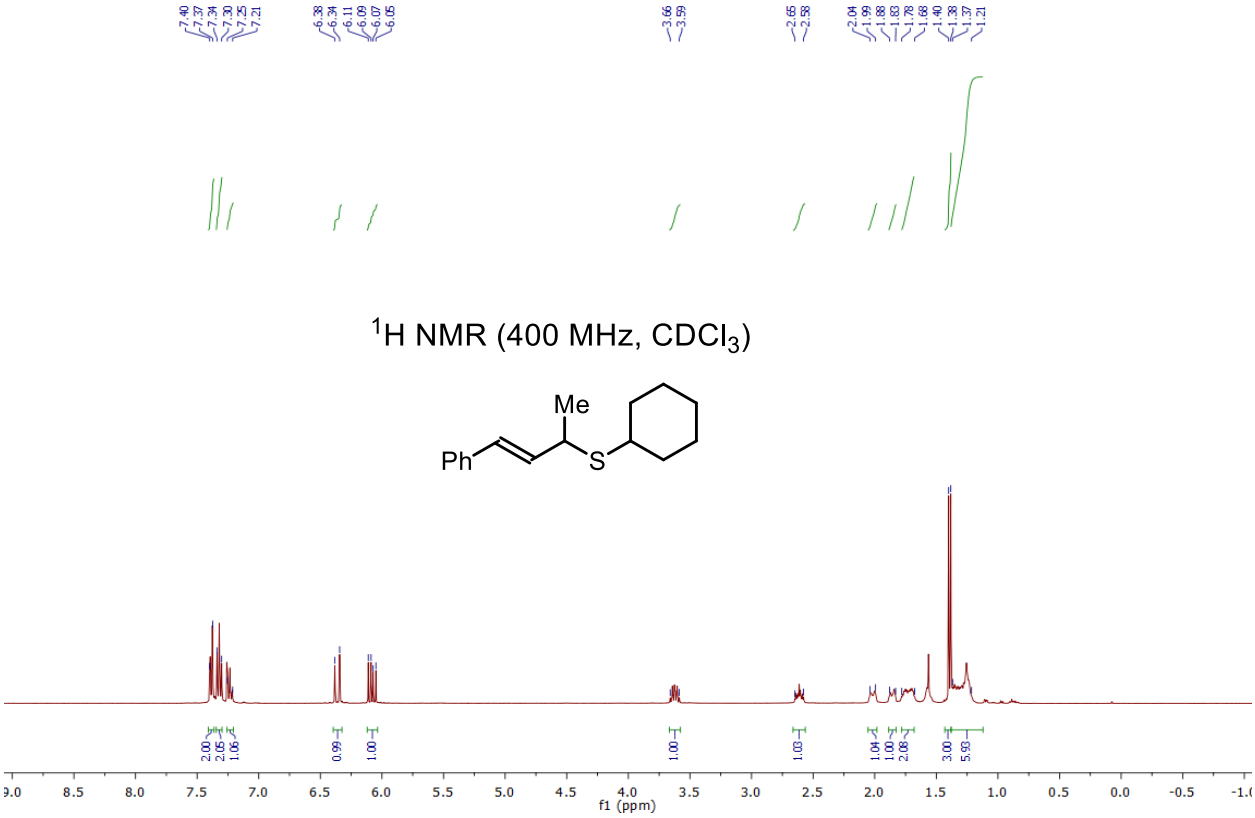


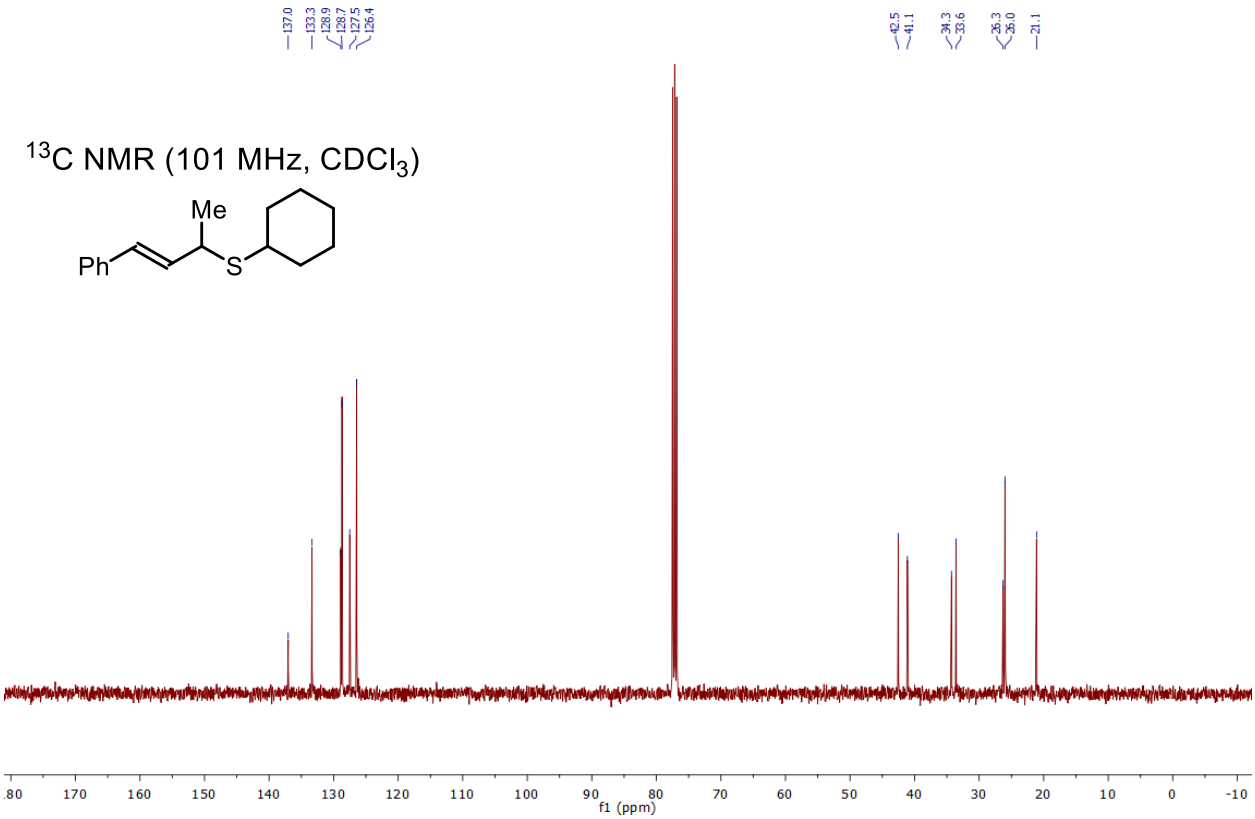
^{13}C NMR (101 MHz, $CDCl_3$)



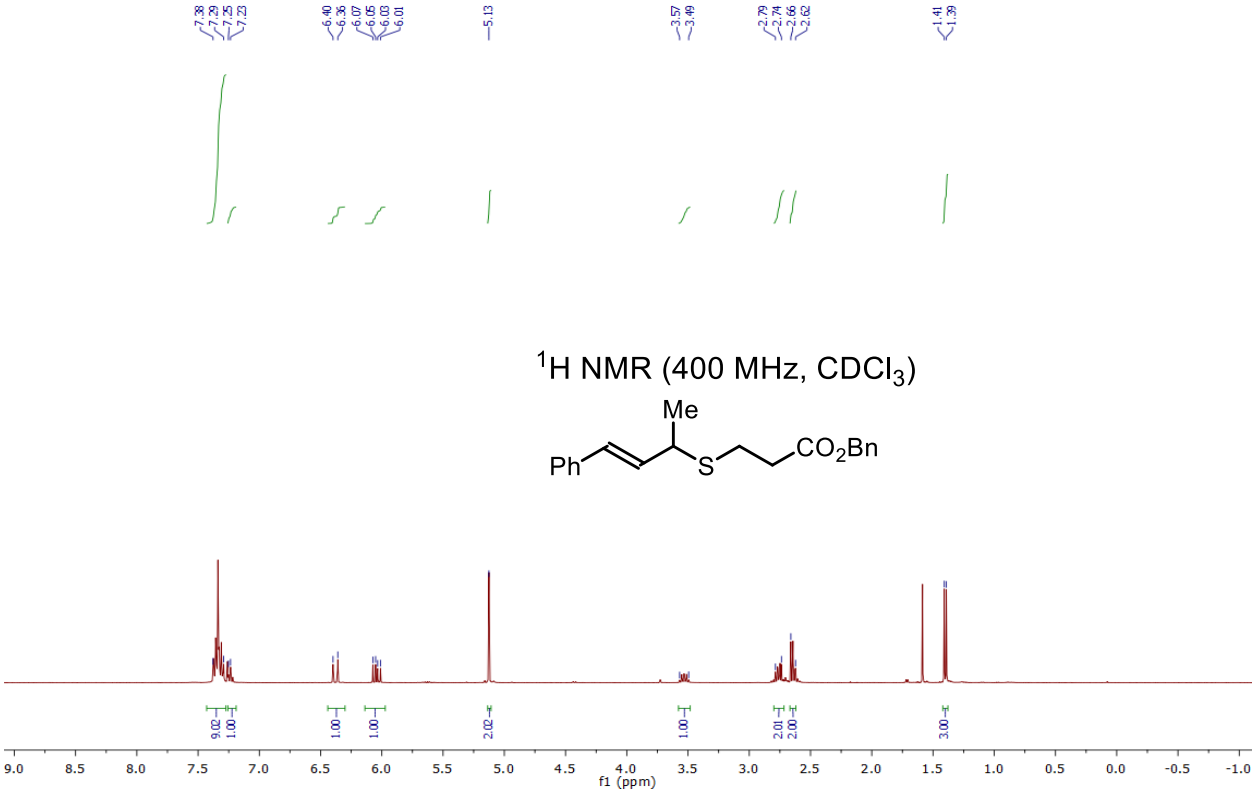


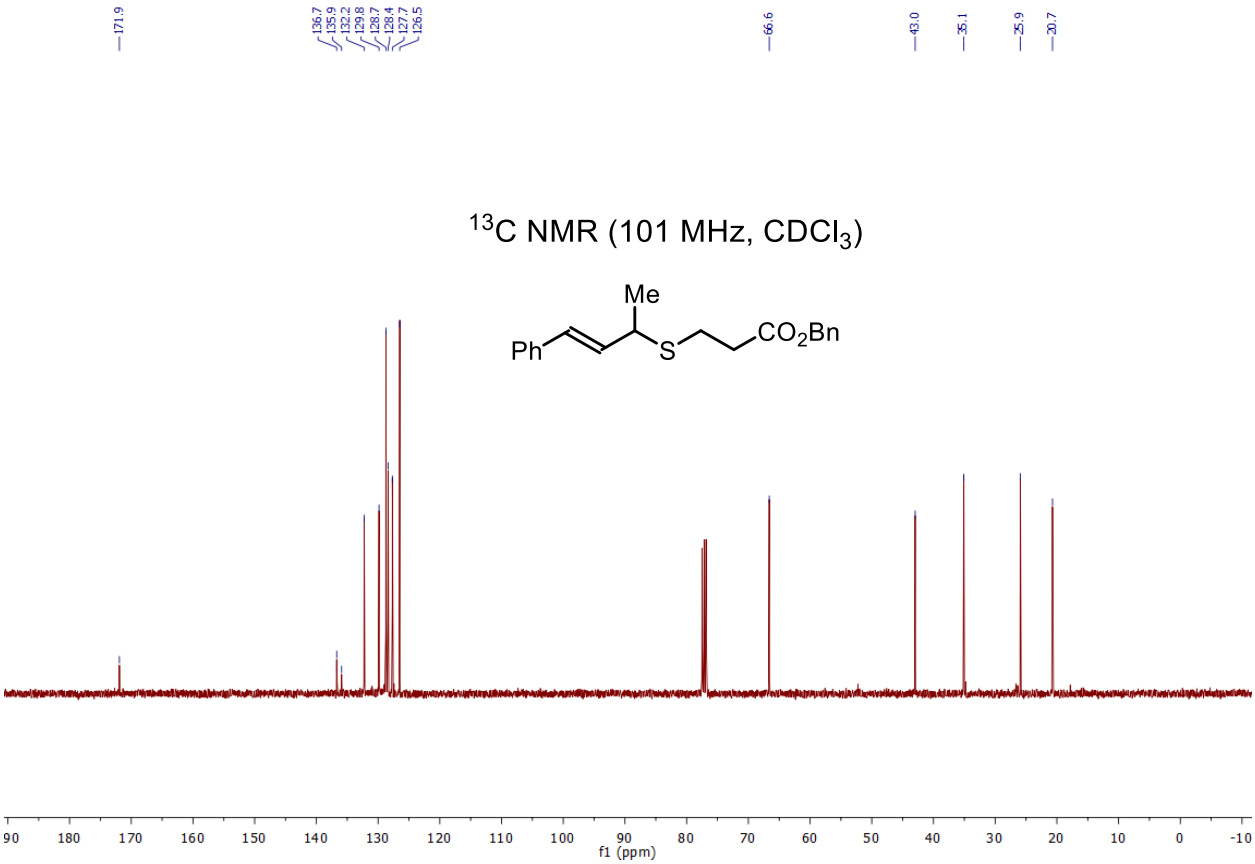
(*E*)-cyclohexyl(4-phenylbut-3-en-2-yl)sulfane (275h)



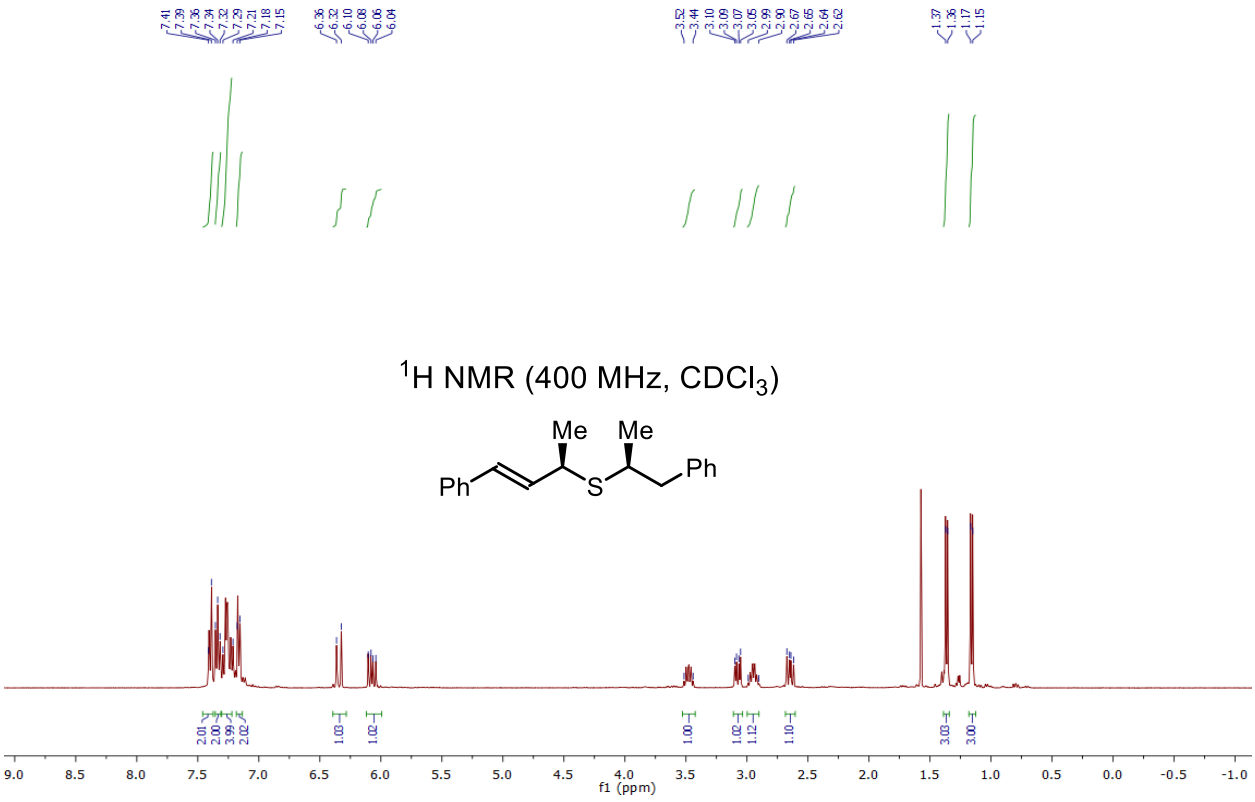


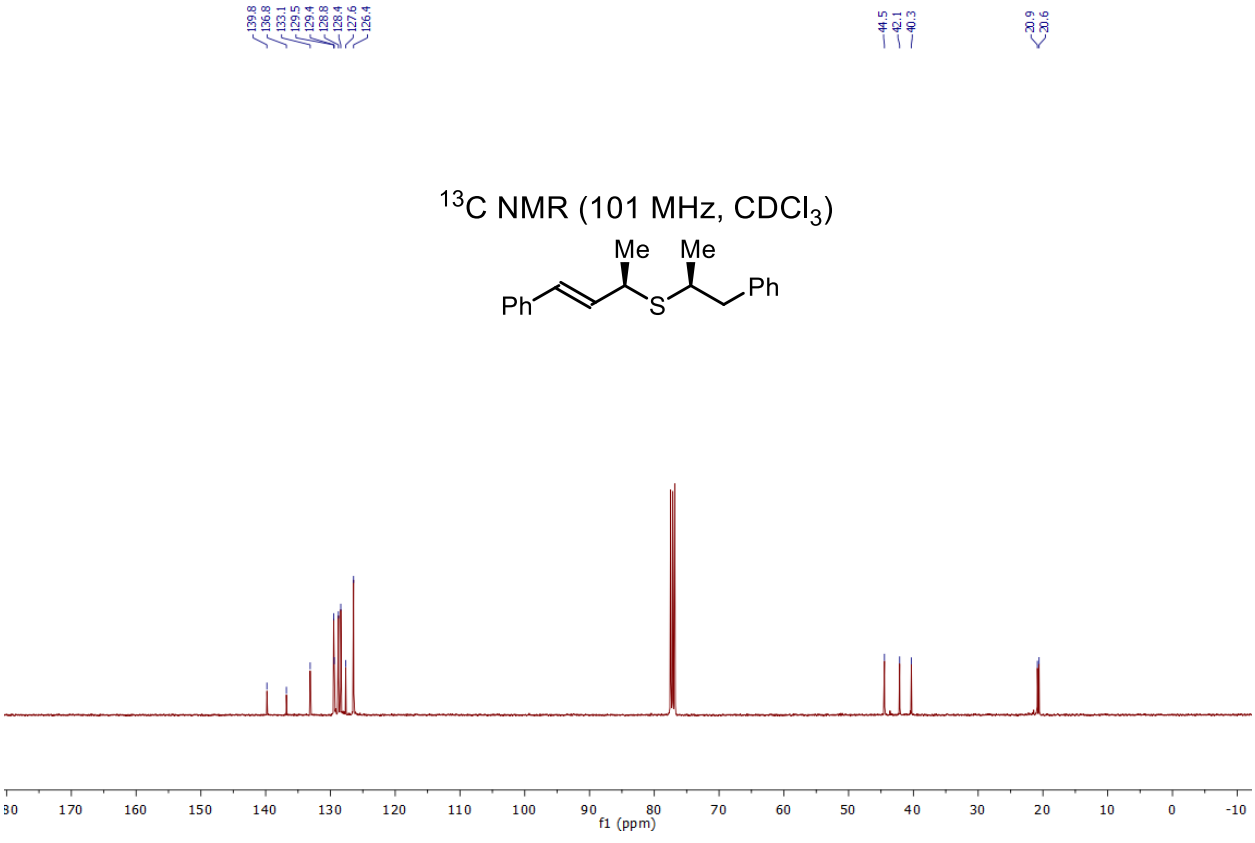
(*E*)-benzyl 3-((4-phenylbut-3-en-2-yl)thio)propanoate (275i)



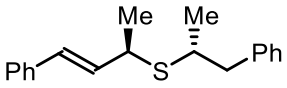


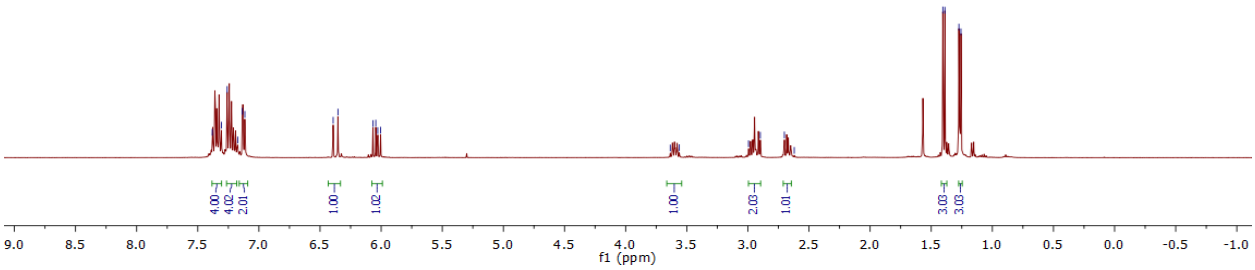
(*E*)-(4-phenylbut-3-en-2-yl)(1-phenylpropan-2-yl)sulfane (275j)



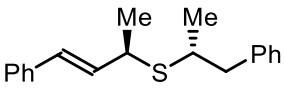


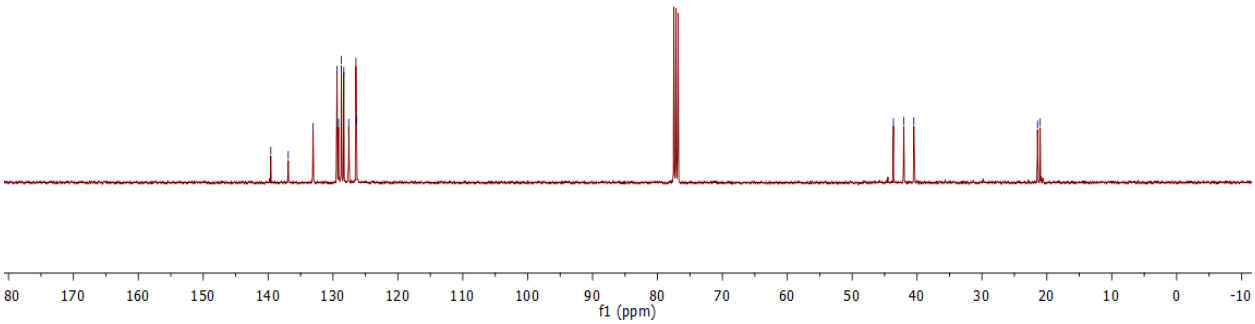
^{1}H NMR (400 MHz, $CDCl_3$)



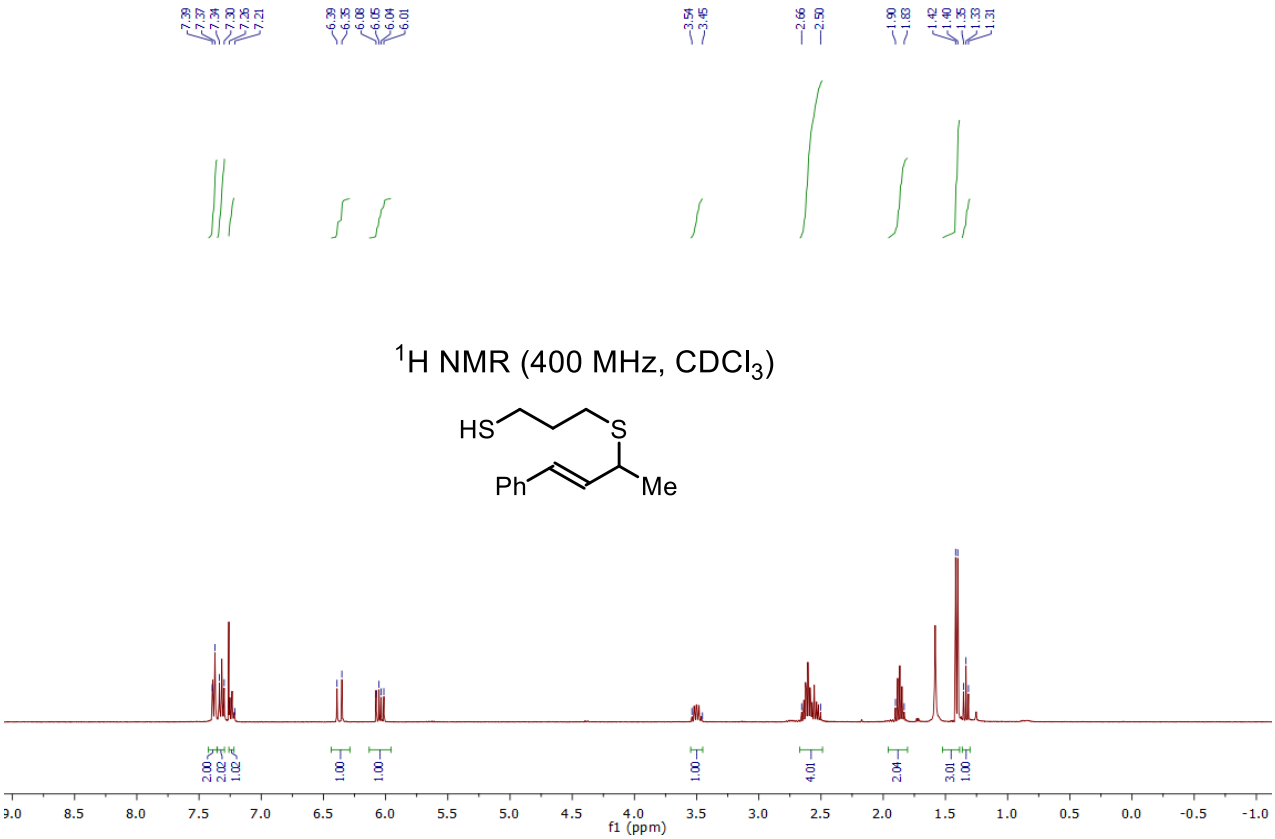


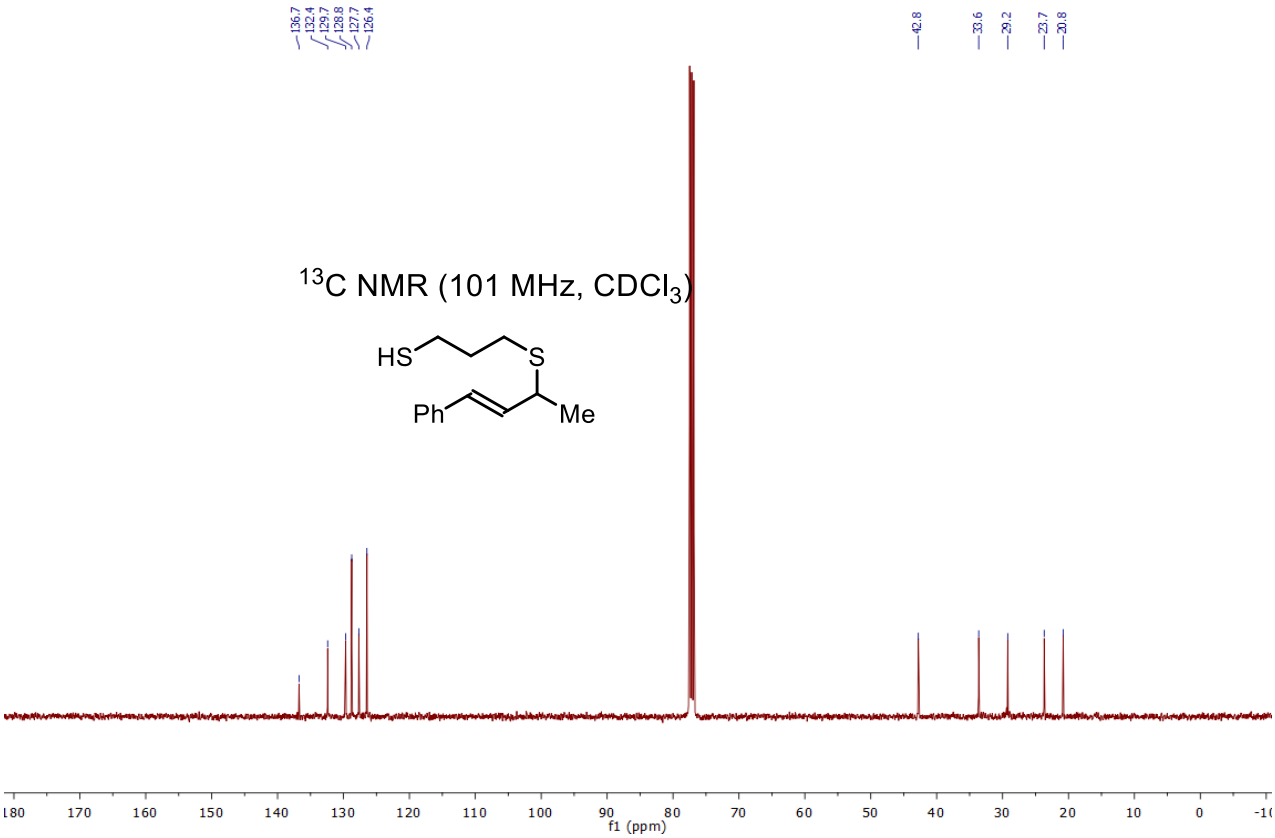
^{13}C NMR (101 MHz, $CDCl_3$)



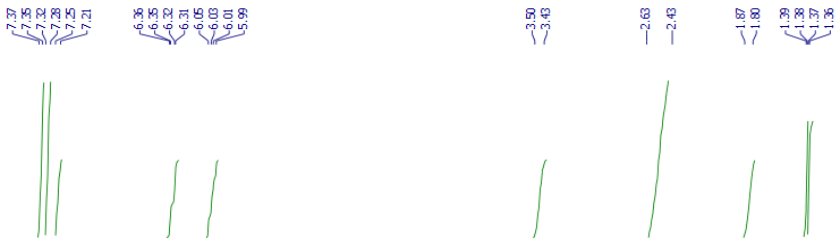


(*E*)-3-((4-phenylbut-3-en-2-yl)thio)propane-1-thiol (275k)

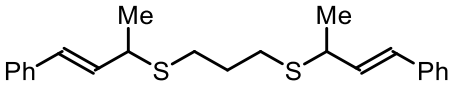


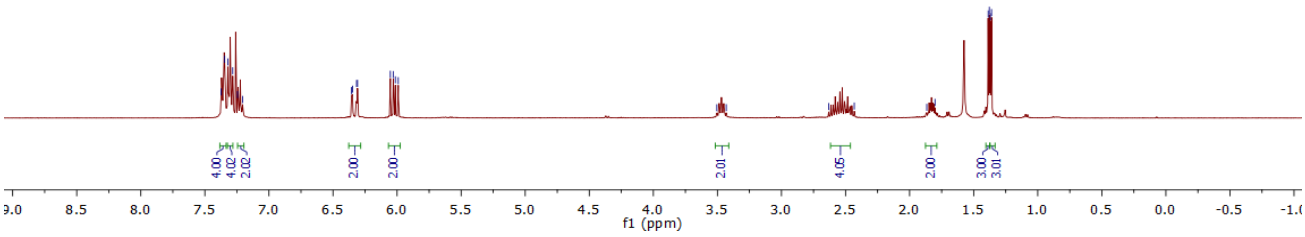


((*E*)-4-phenylbut-3-en-2-yl)(3-(((E)-5-phenylpent-4-en-2-yl)thio)propyl)sulfane (275k')

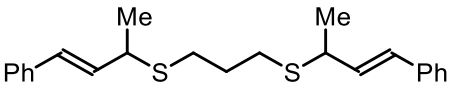


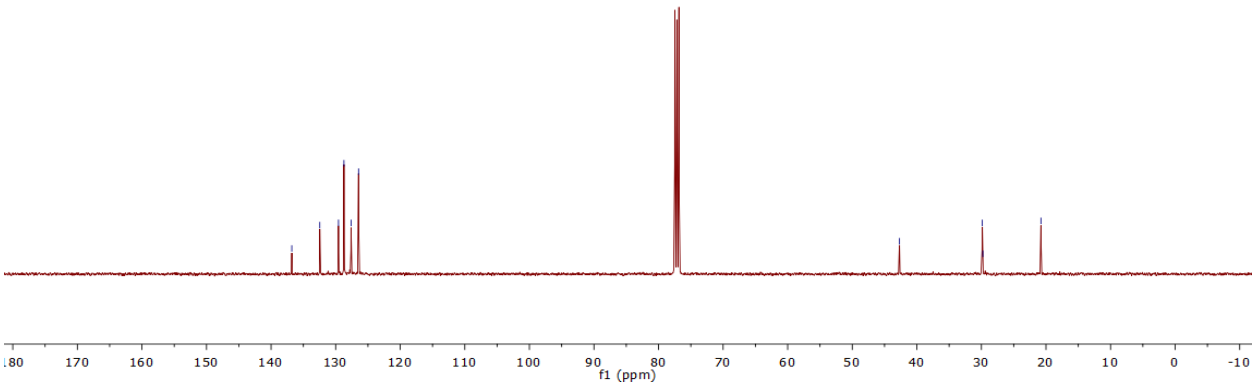
^{1}H NMR (400 MHz, $CDCl_3$)



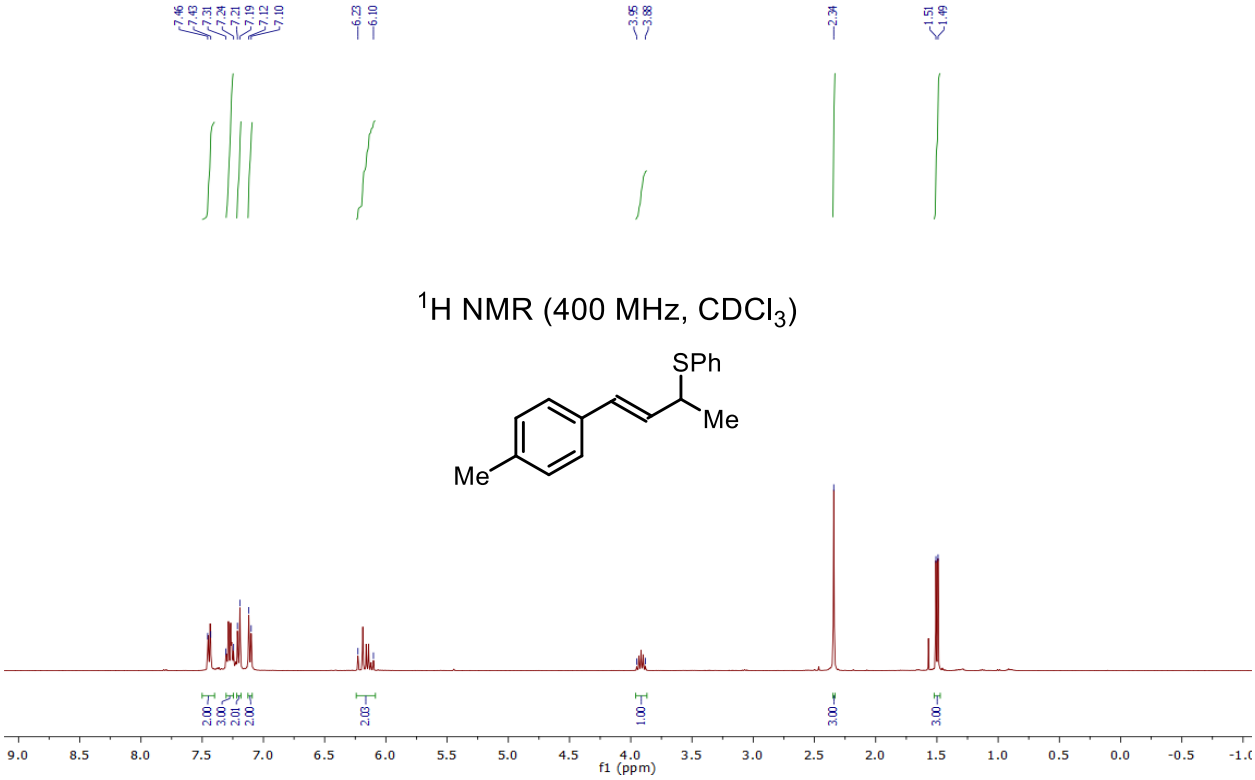


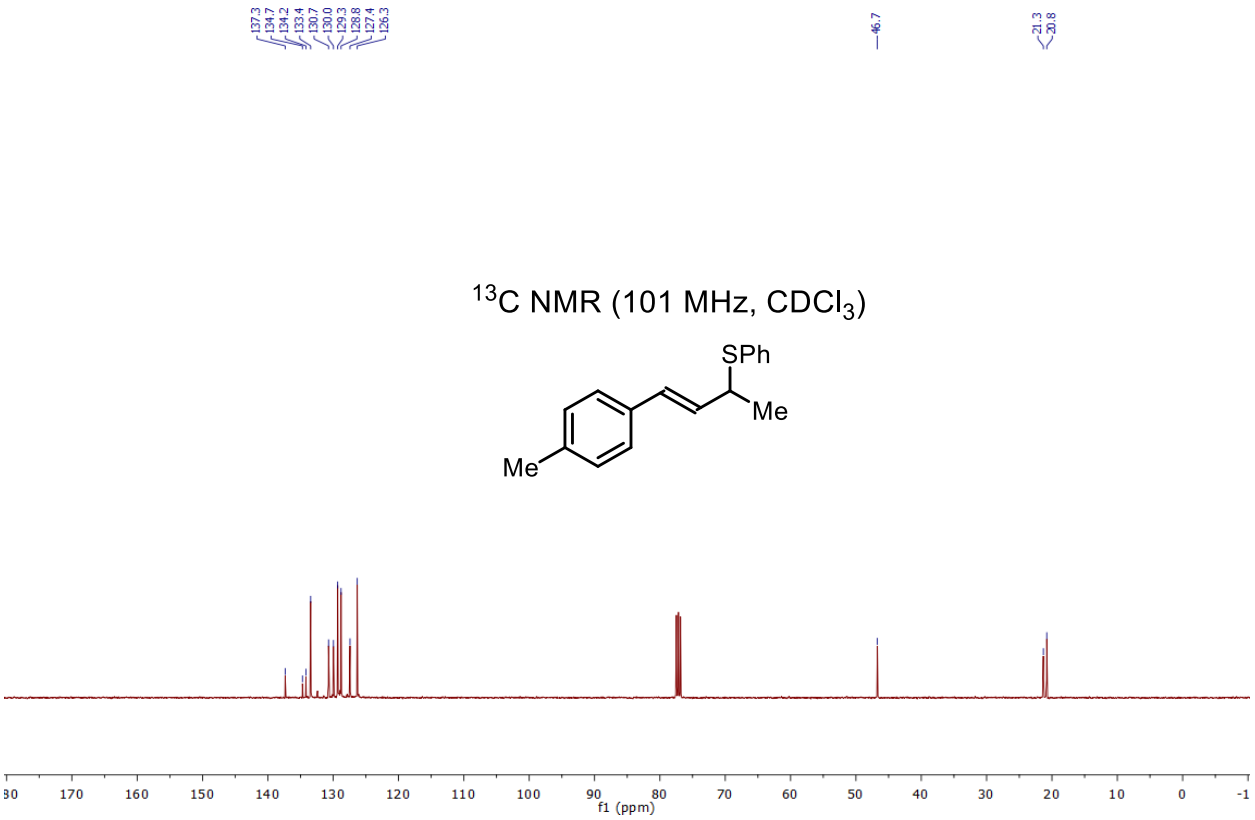
^{13}C NMR (101 MHz, $CDCl_3$)



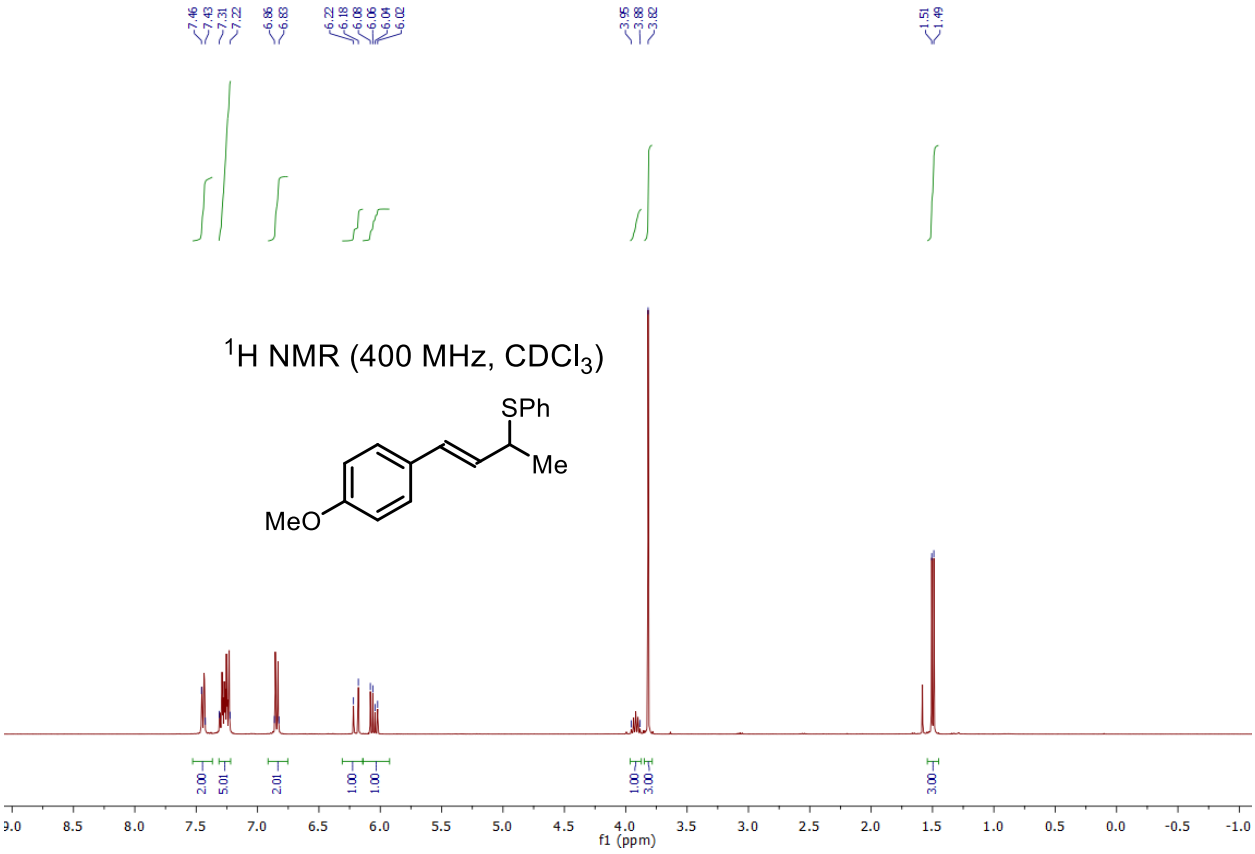


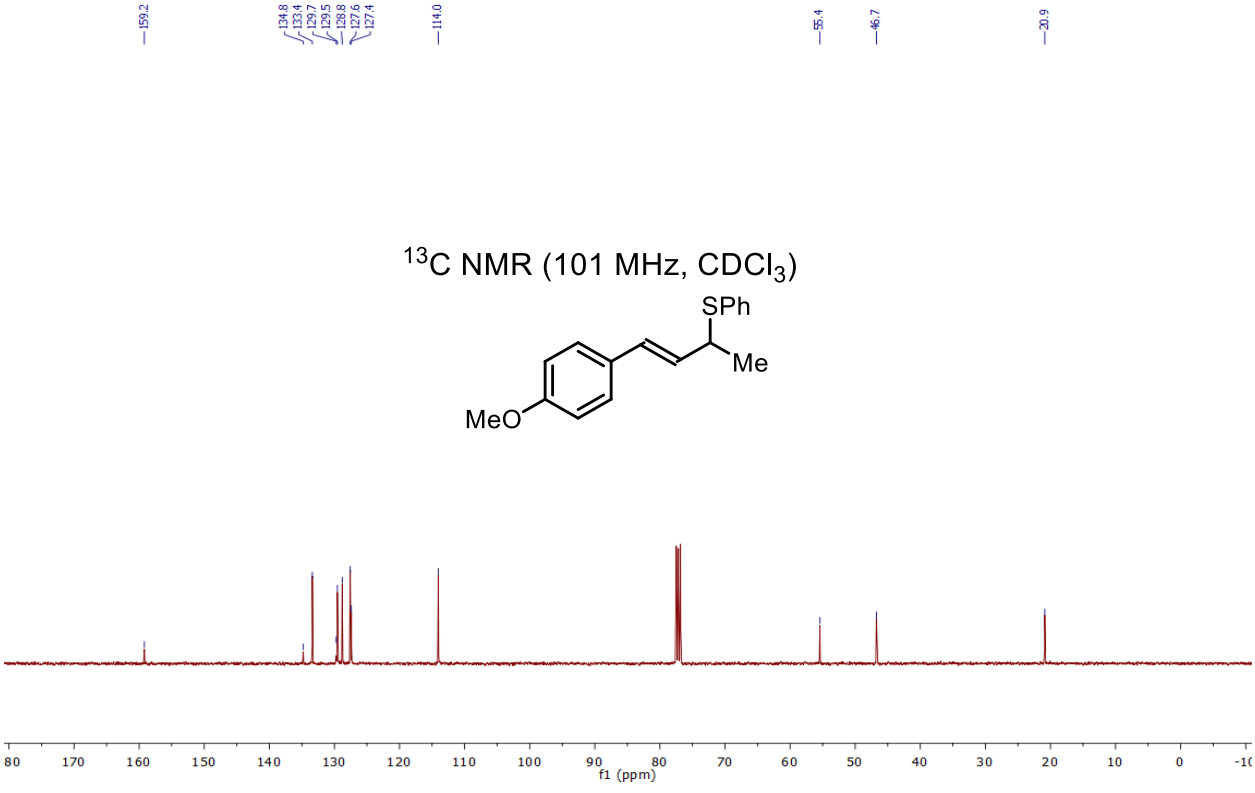
(*E*)-phenyl(4-(p-tolyl)but-3-en-2-yl)sulfane (275l)



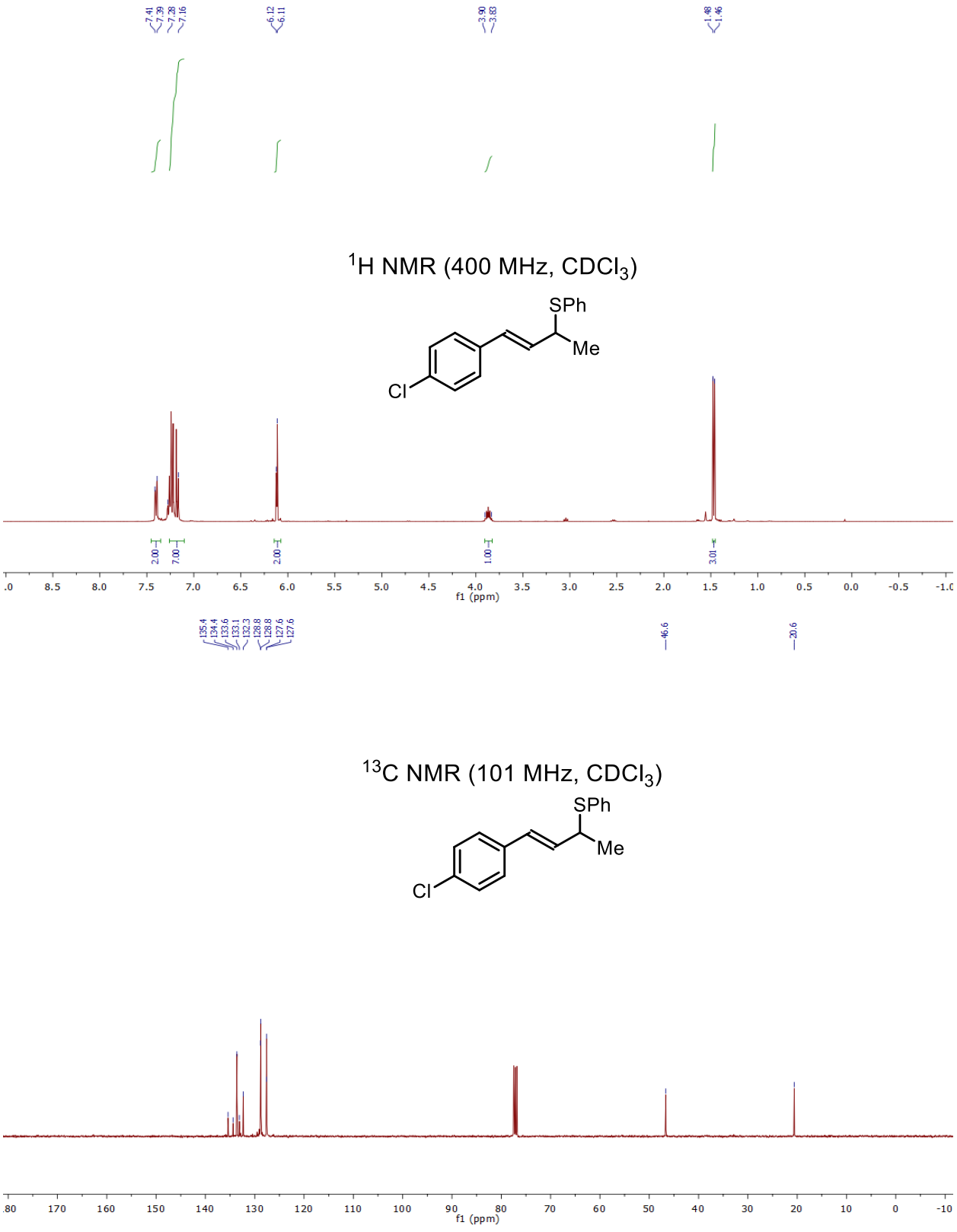


(*E*)-(4-(4-methoxyphenyl)but-3-en-2-yl)(phenyl)sulfane (275m)

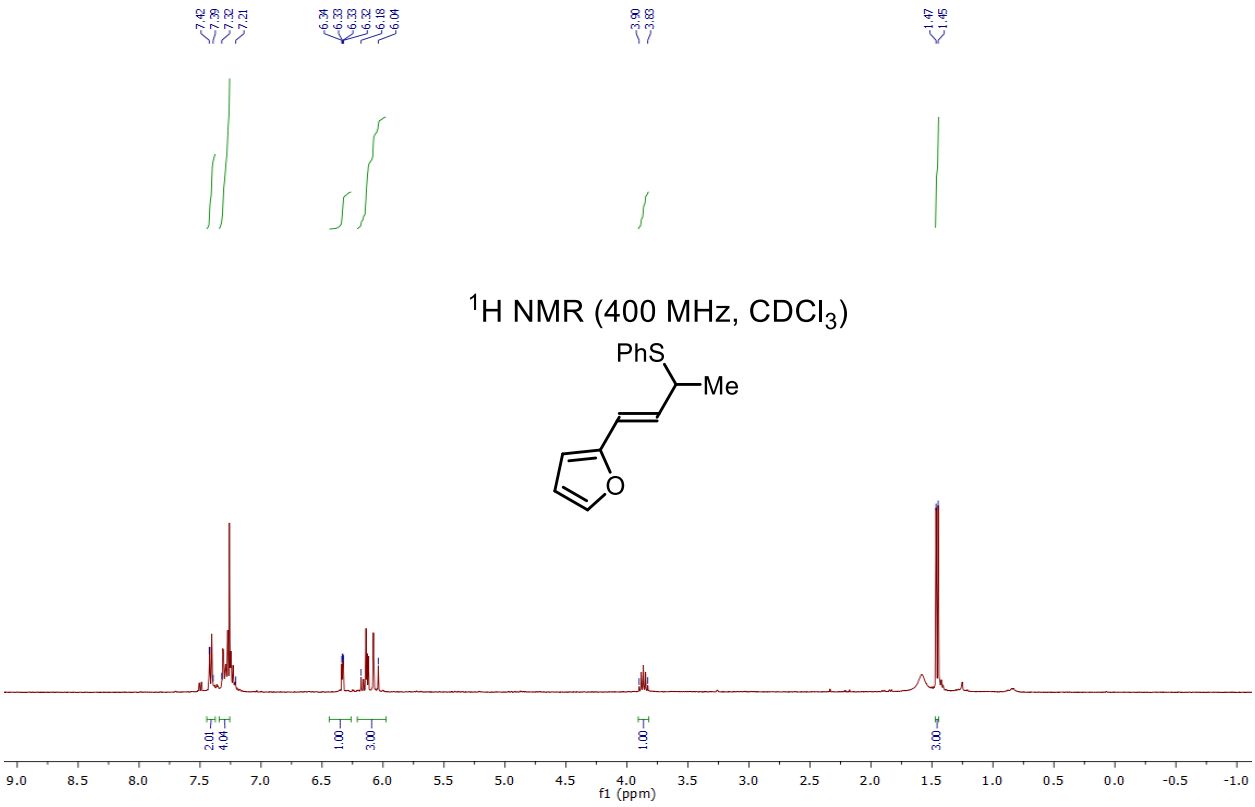


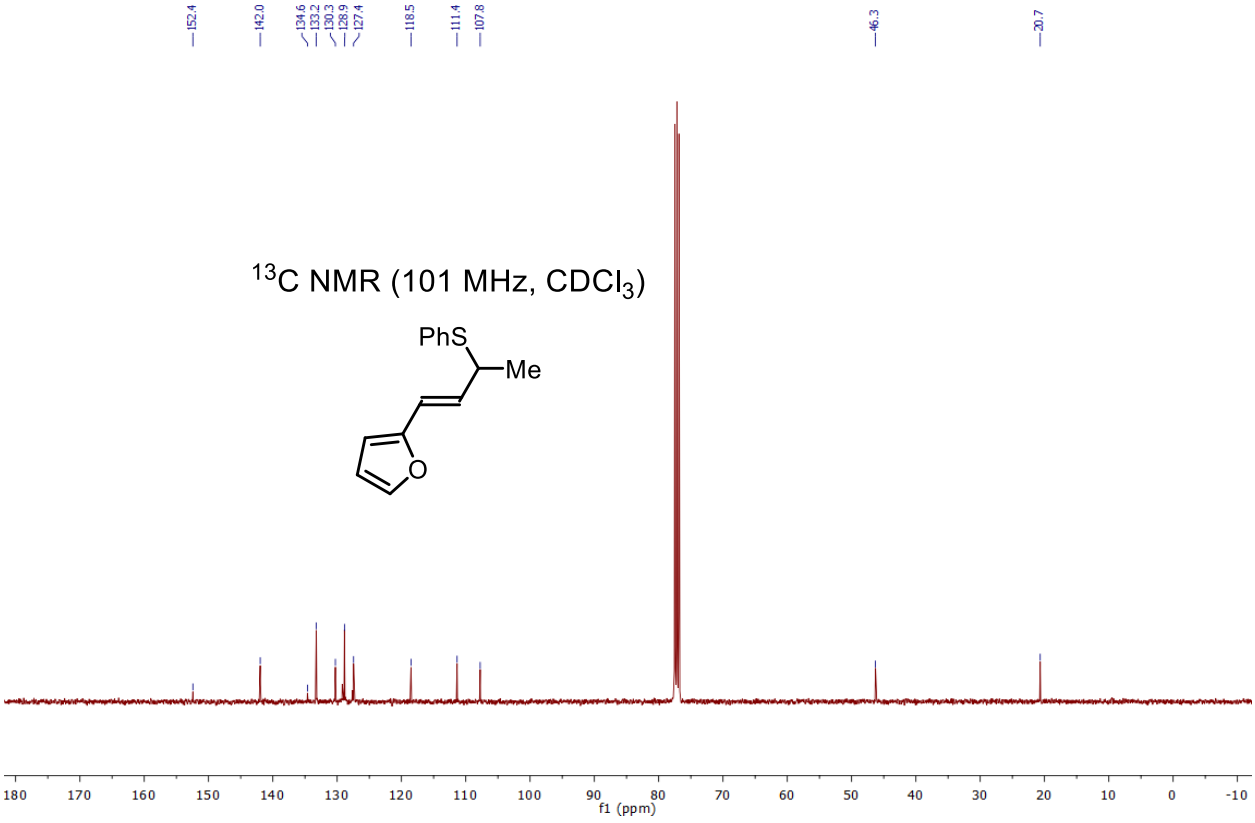


(*E*)-(4-(4-chlorophenyl)but-3-en-2-yl)(phenyl)sulfane (275n)

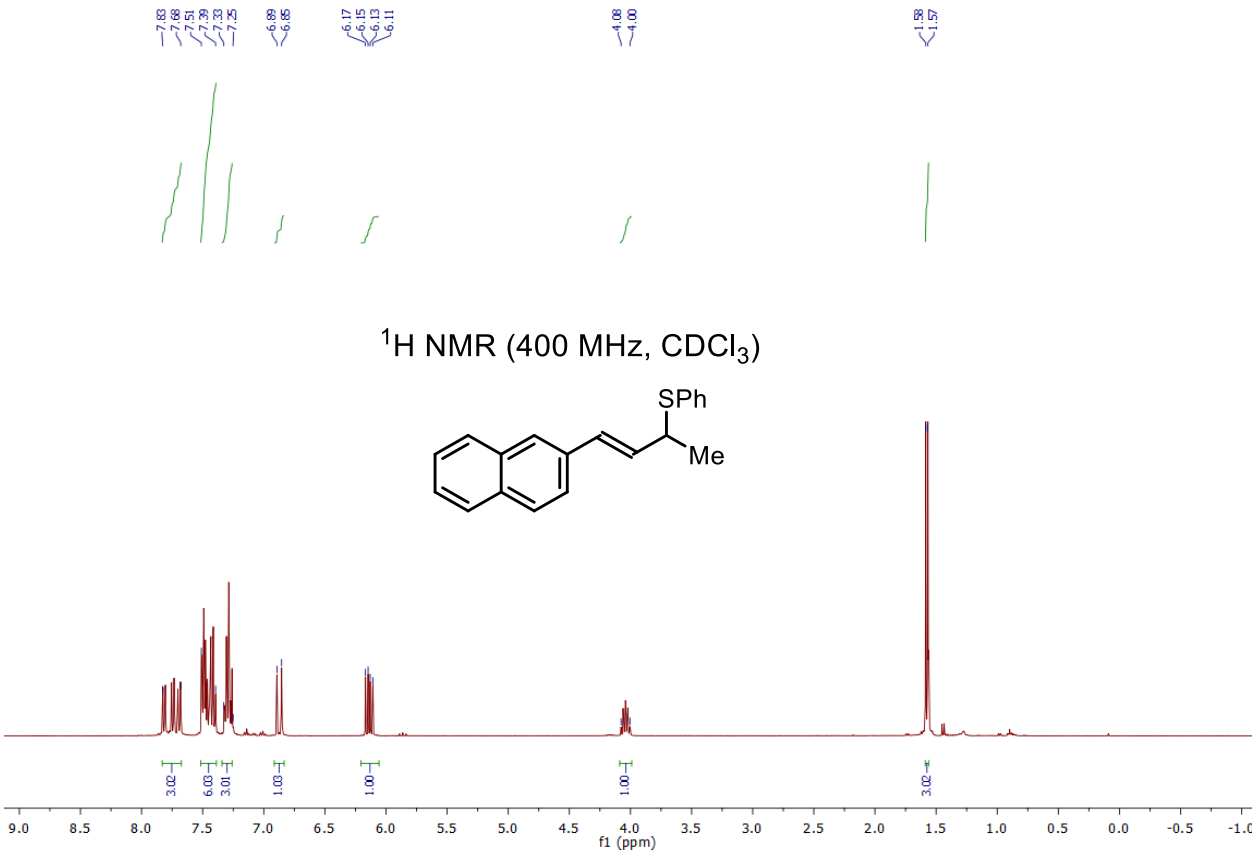


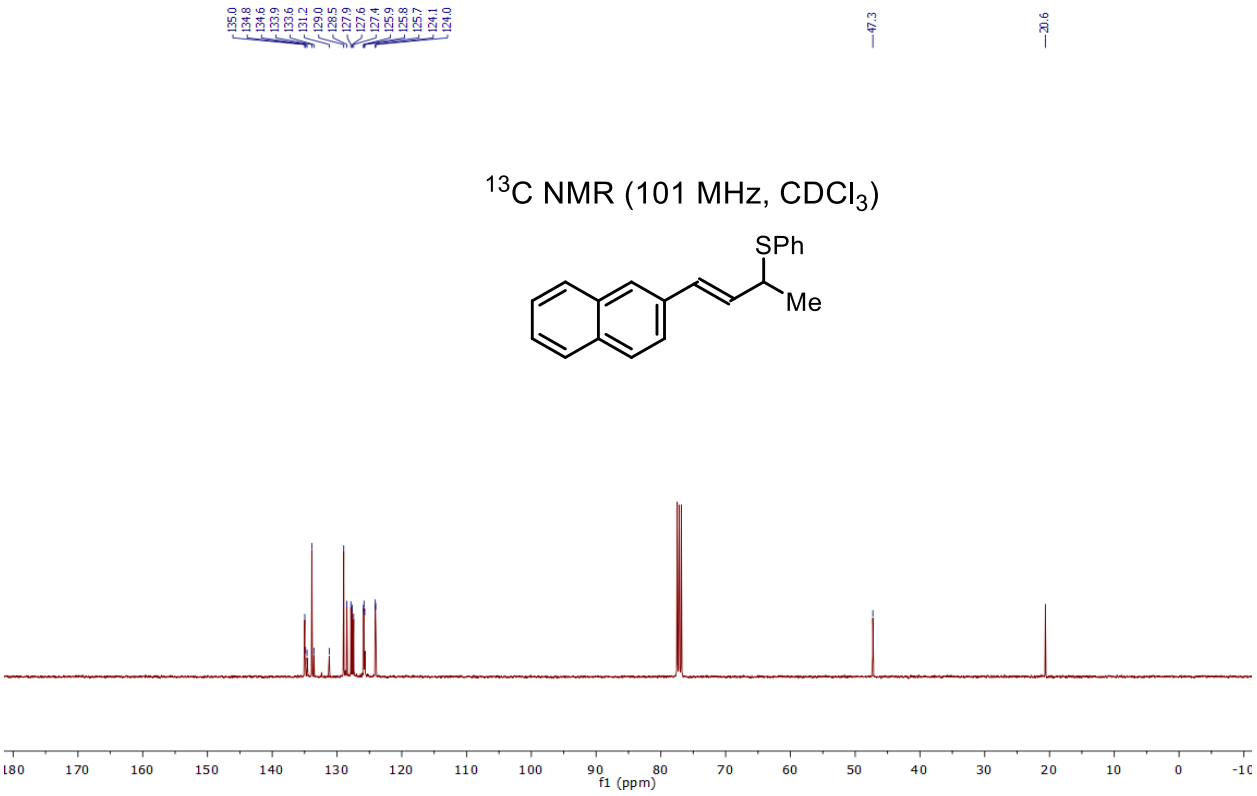
(*E*)-2-(3-(phenylthio)but-1-en-1-yl)furan (275o)



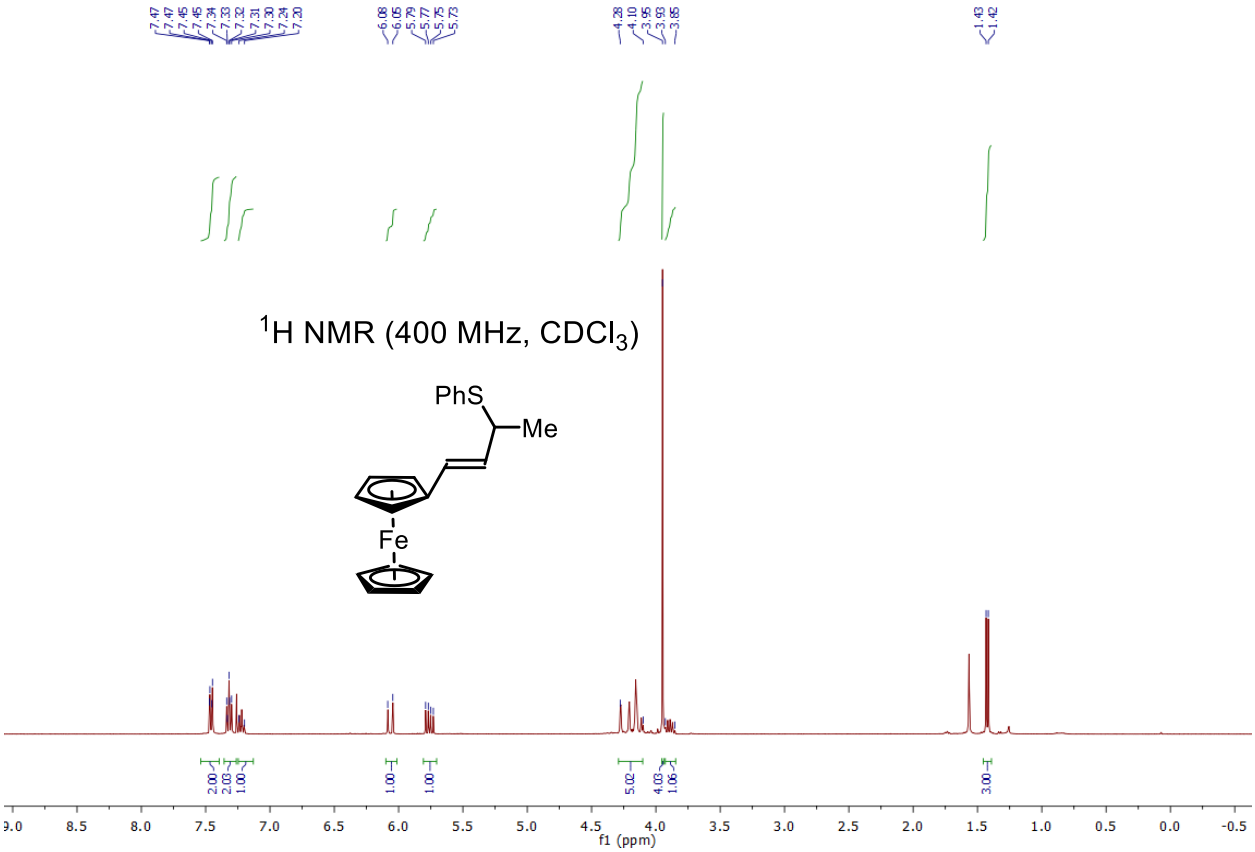


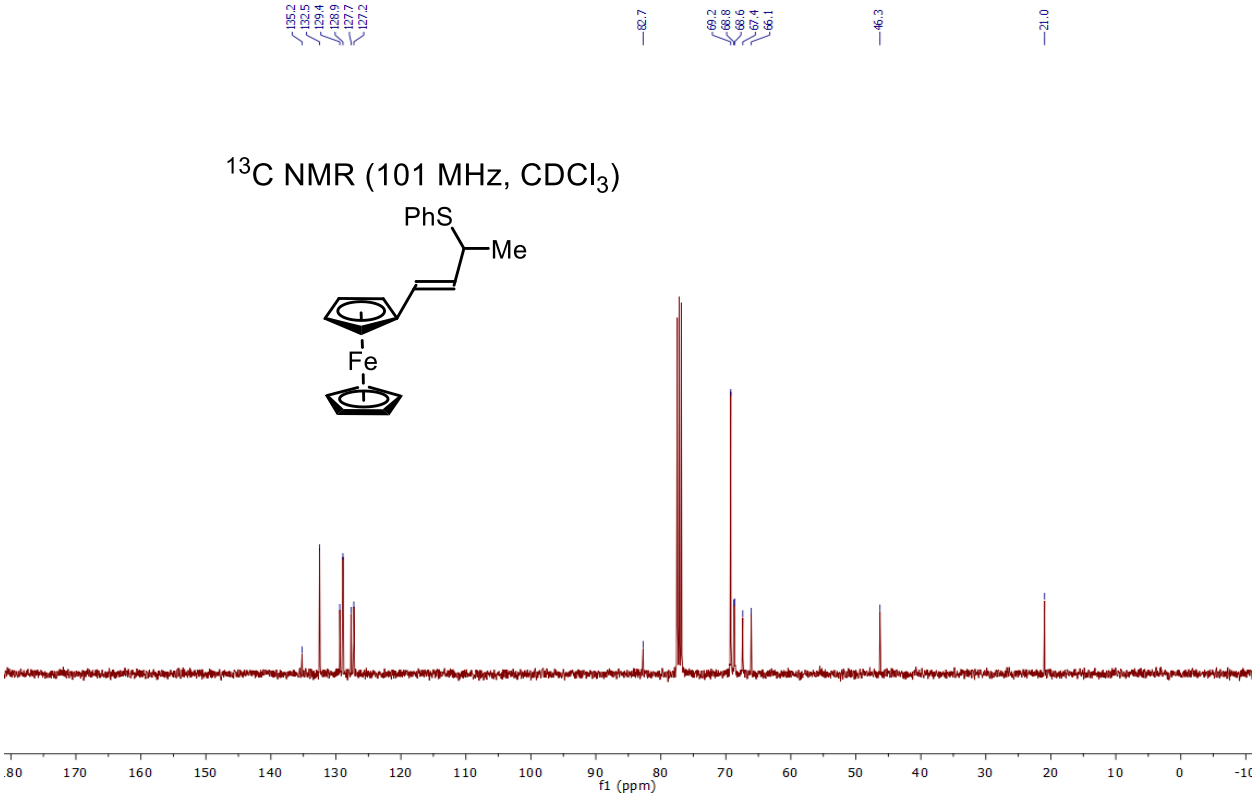
(*E*)-(4-(naphthalen-2-yl)but-3-en-2-yl)(phenyl)sulfane (275p)



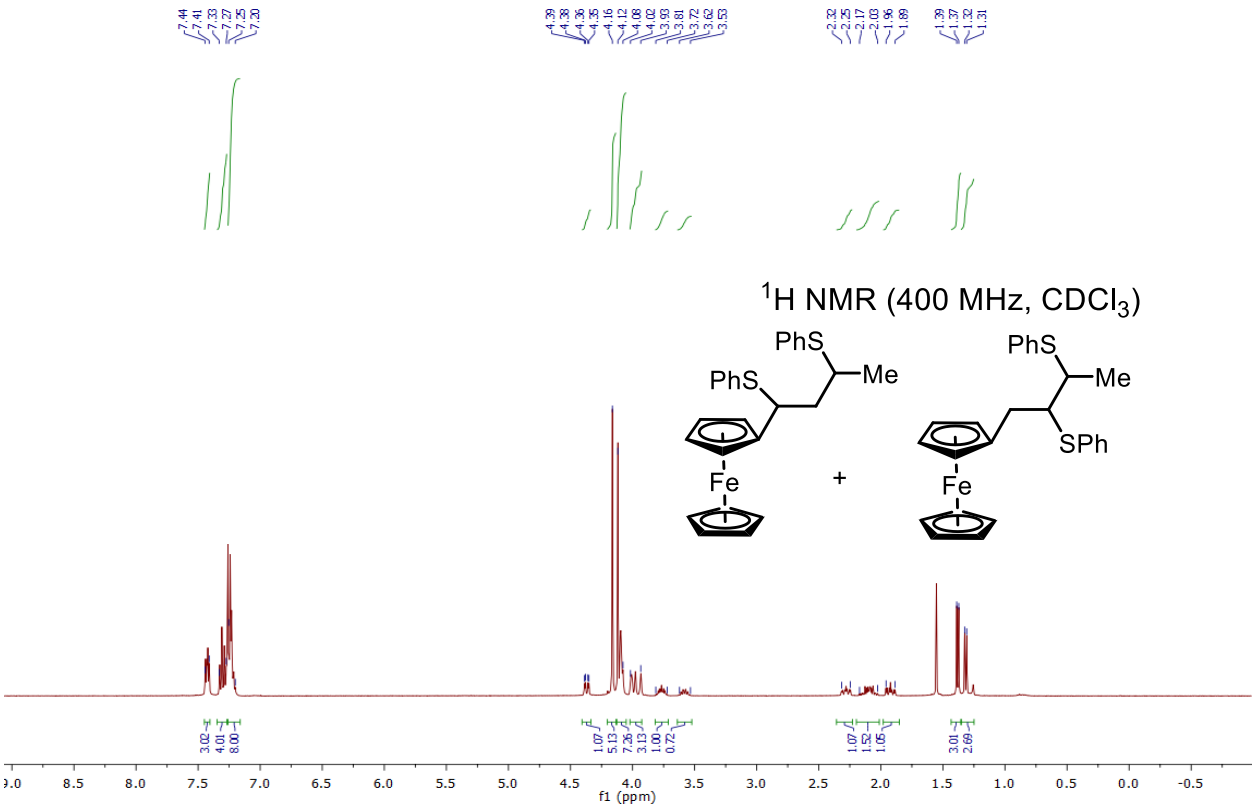


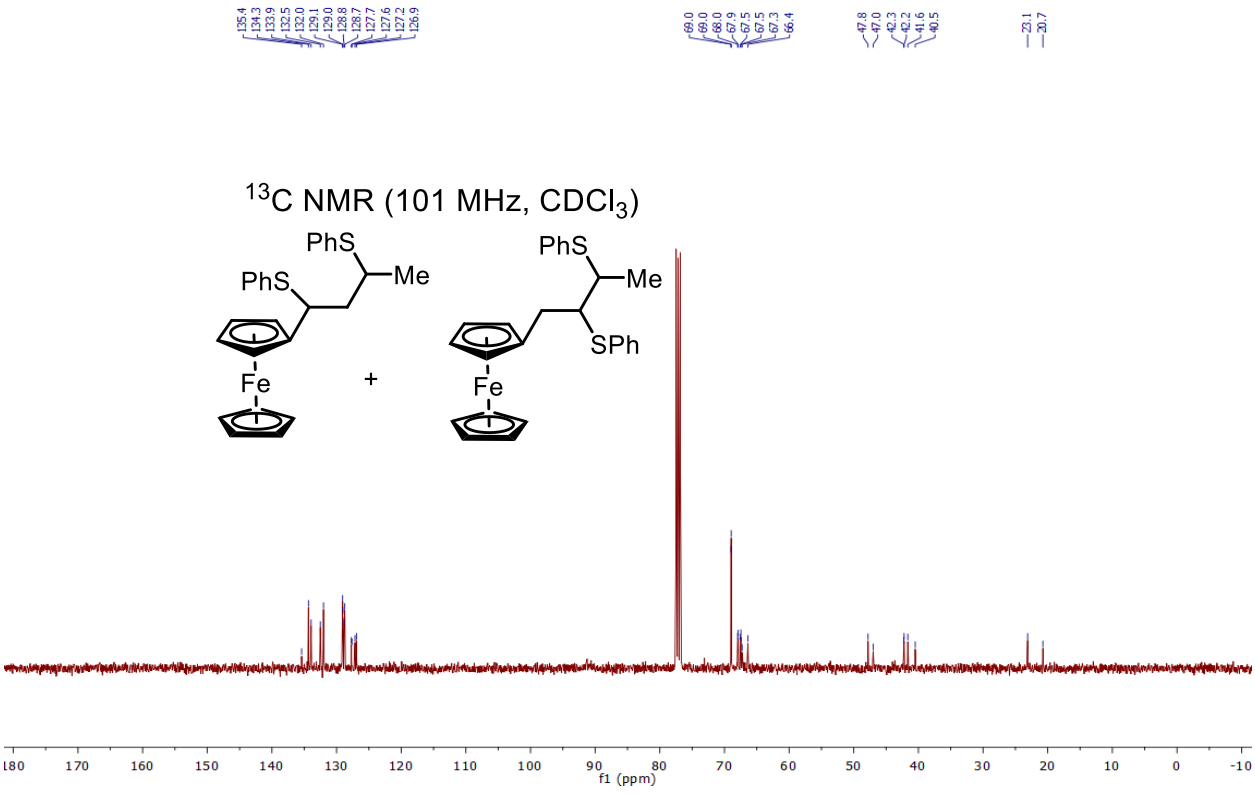
(*E*)-(4-(ferrocene-2-yl)but-3-en-2-yl)(phenyl)sulfane (275q)



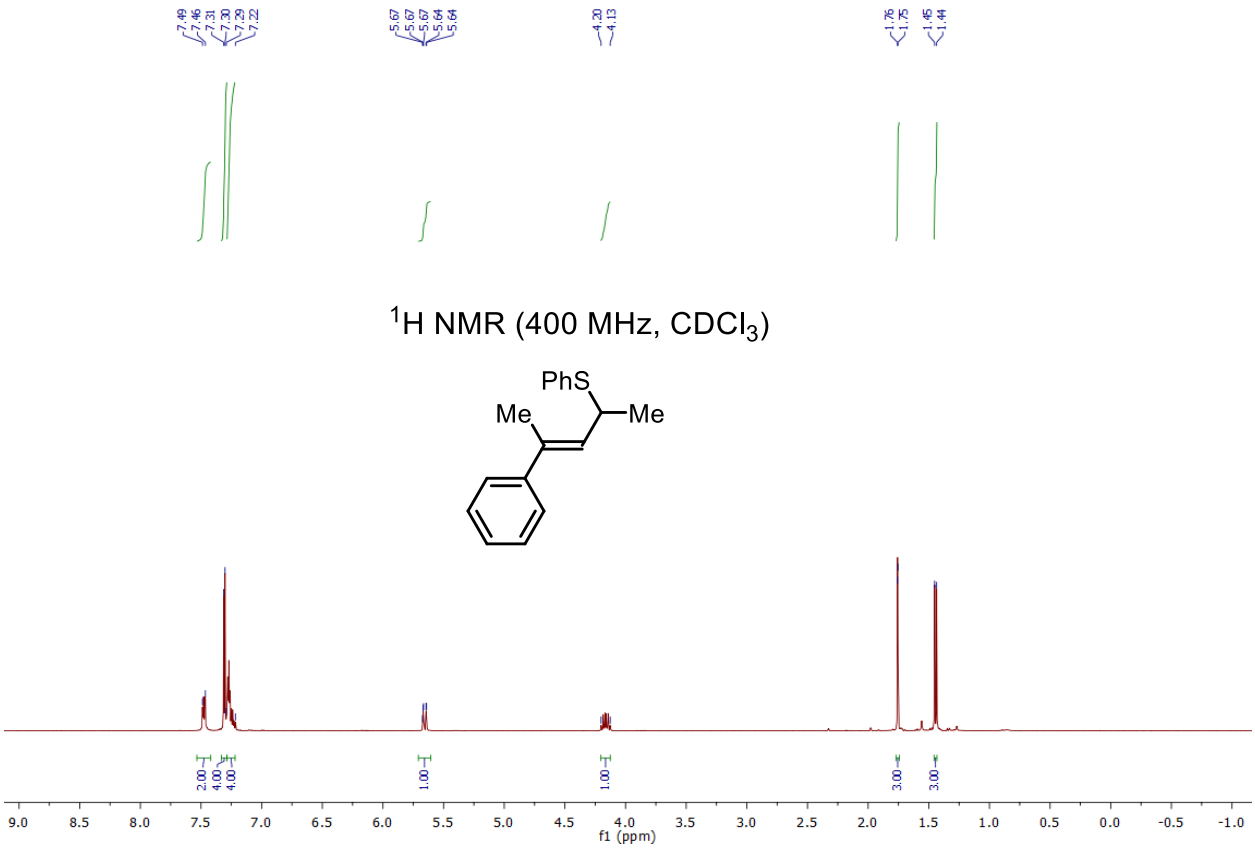


(1-(ferrocene-2-yl)butane-1,3-diyl)bis(phenylsulfane) (275q')

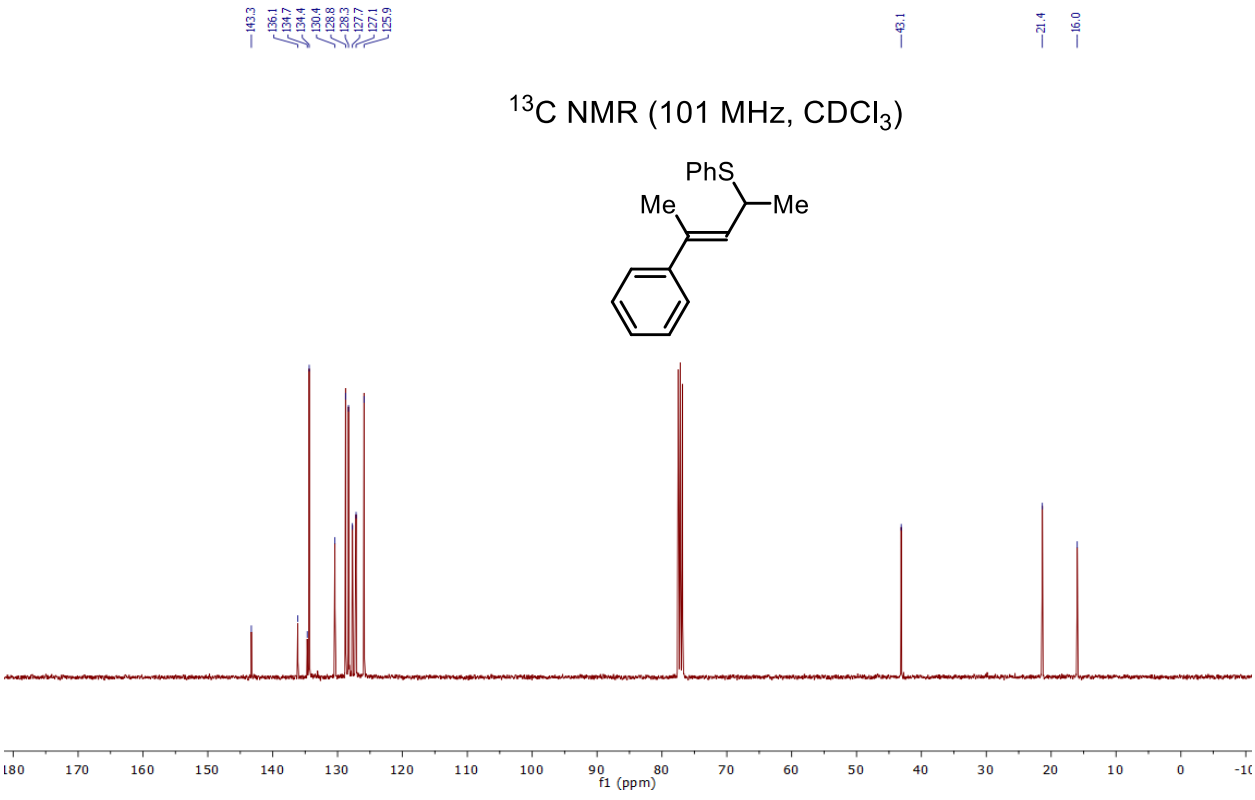




(*E*)-phenyl(4-phenylpent-3-en-2-yl)sulfane (275r)

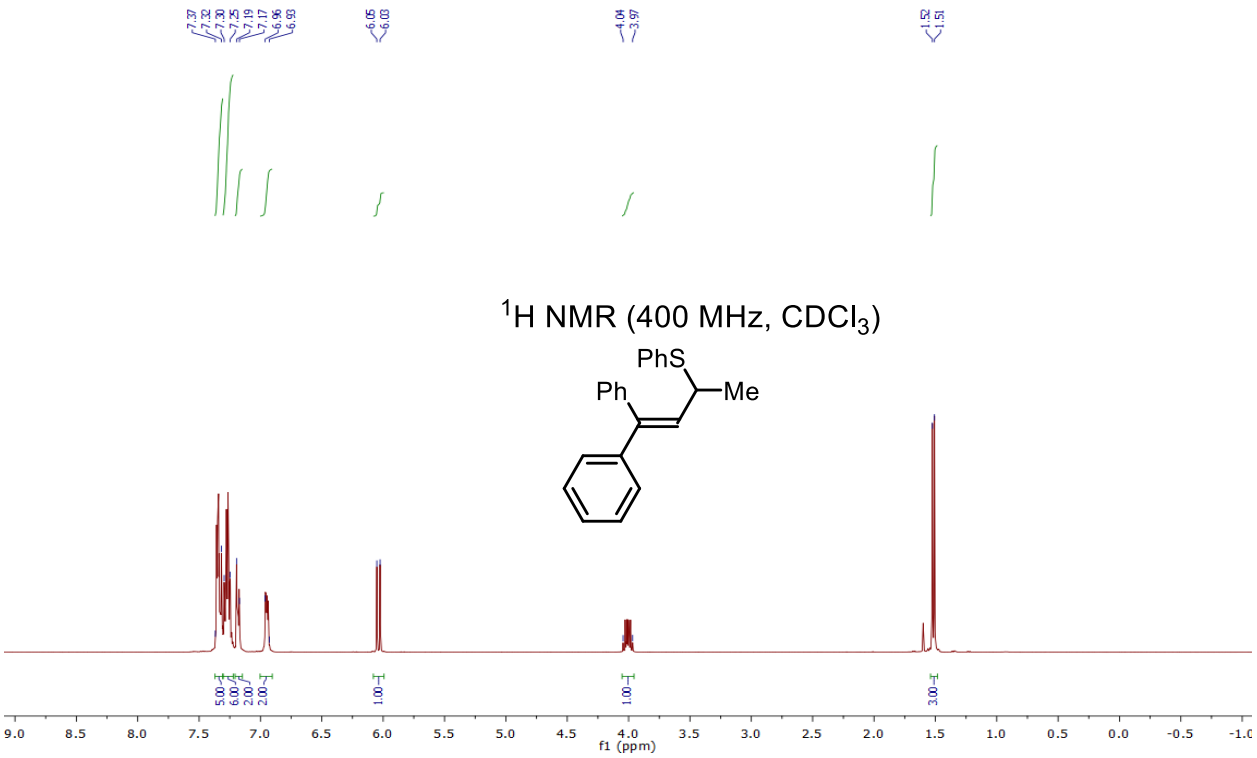


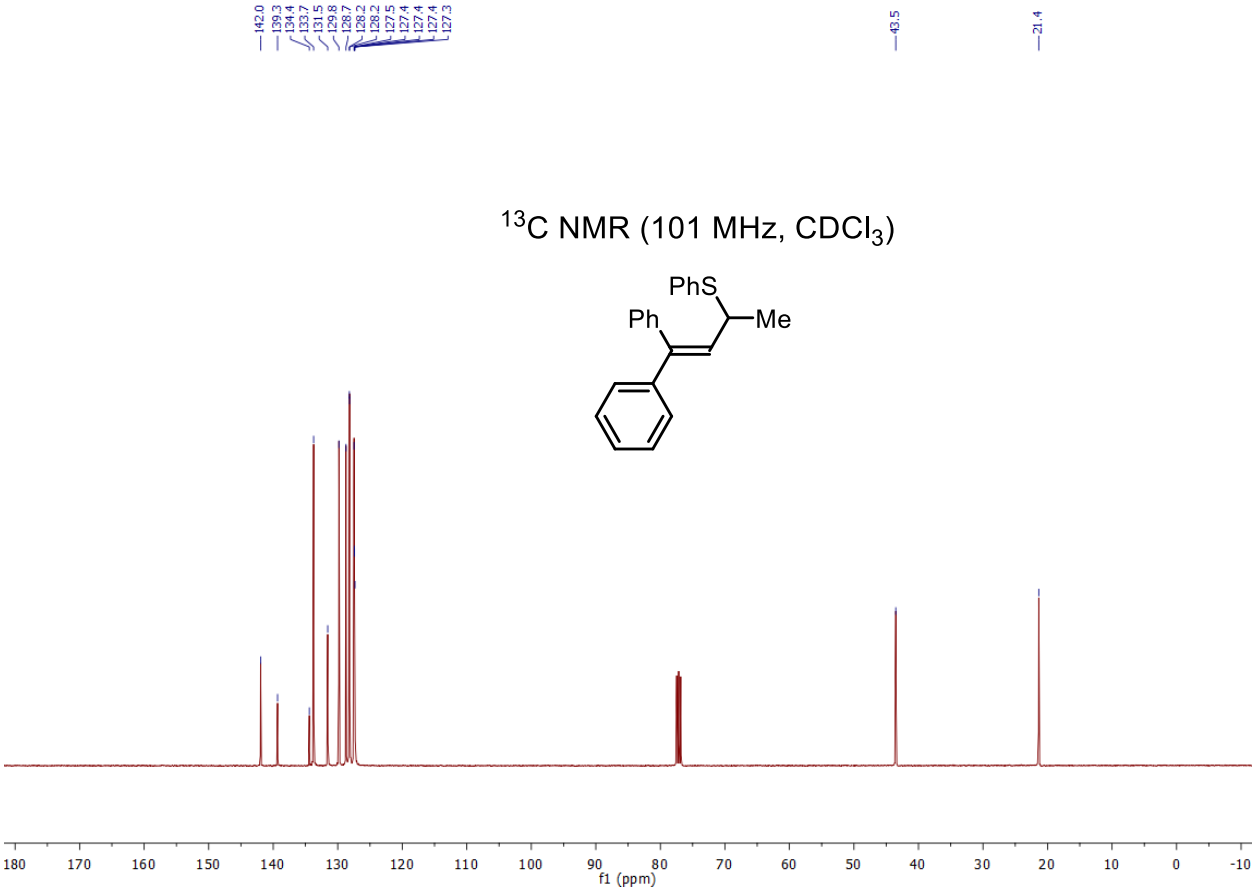
^{1}H NMR (400 MHz, $CDCl_3$)



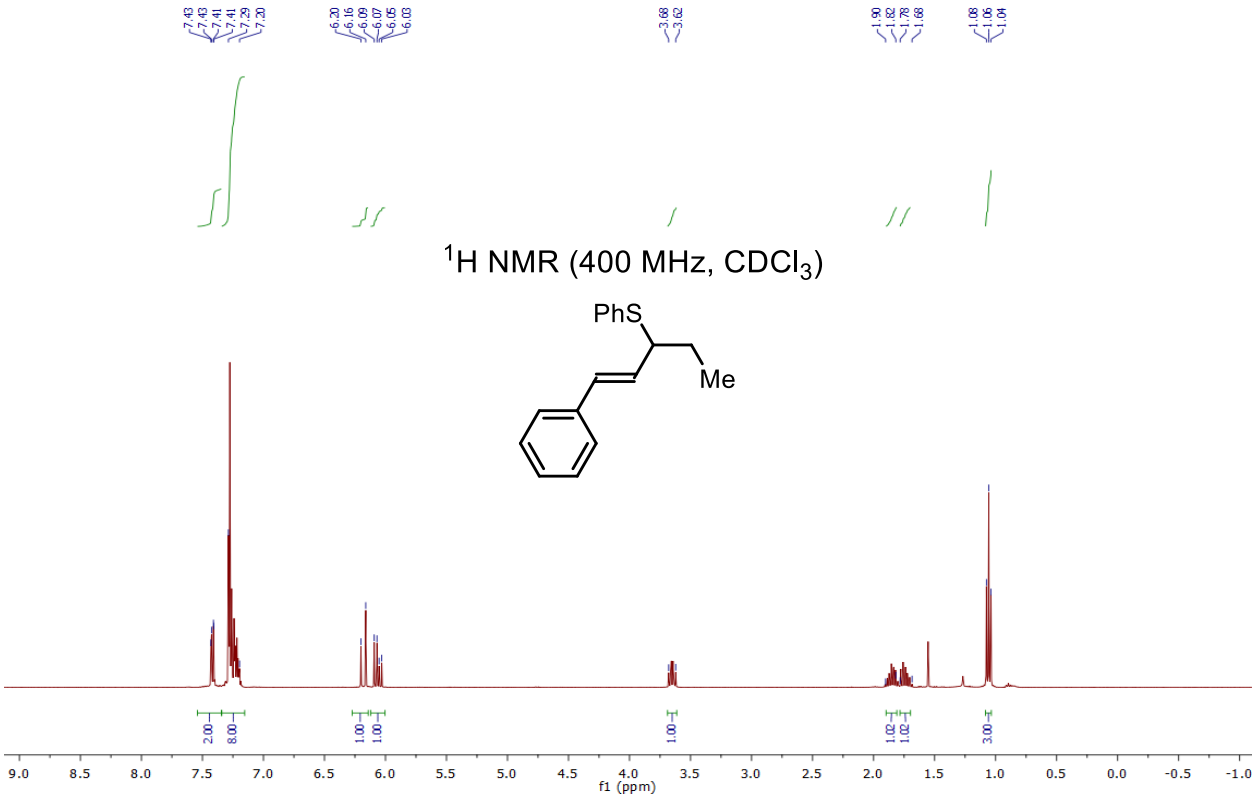
^{13}C NMR (101 MHz, $CDCl_3$)

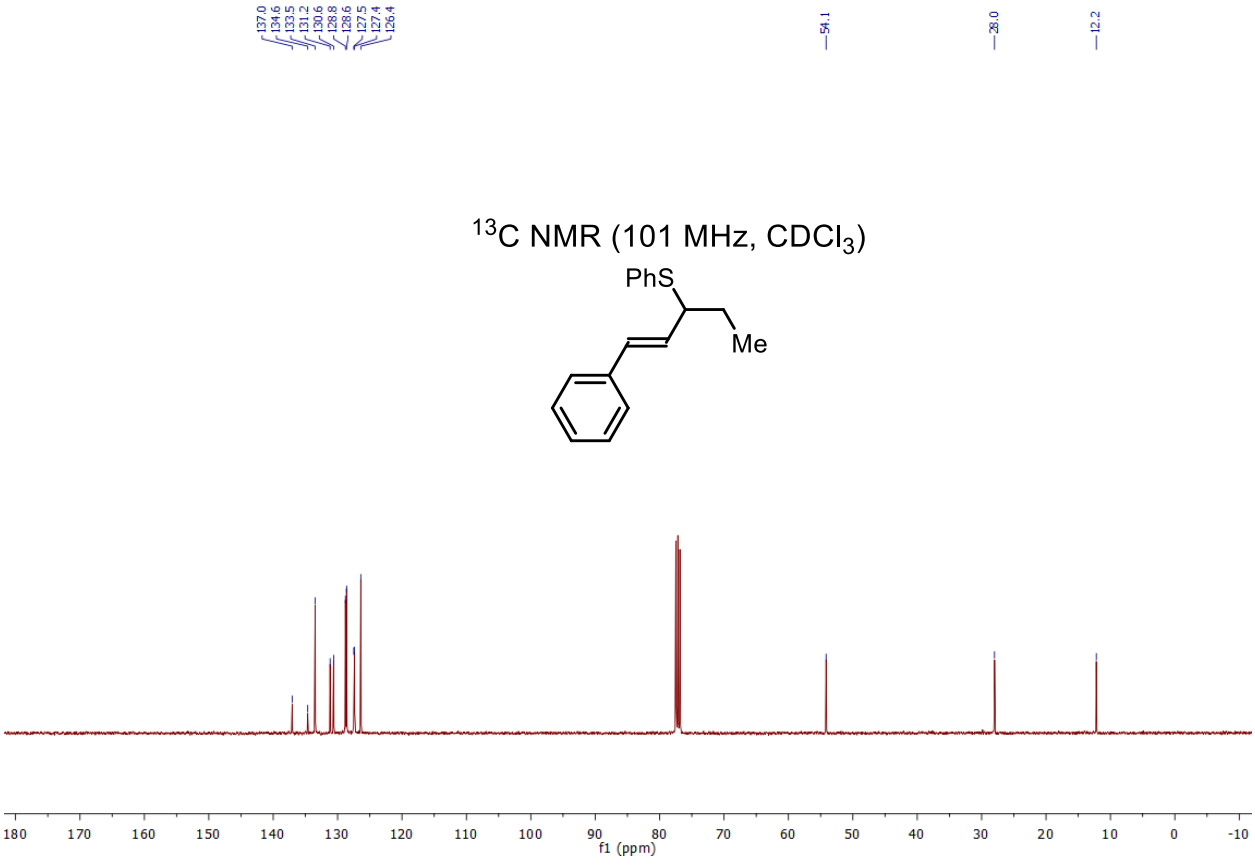
(4,4-diphenylbut-3-en-2-yl)(phenyl)sulfane (275s)



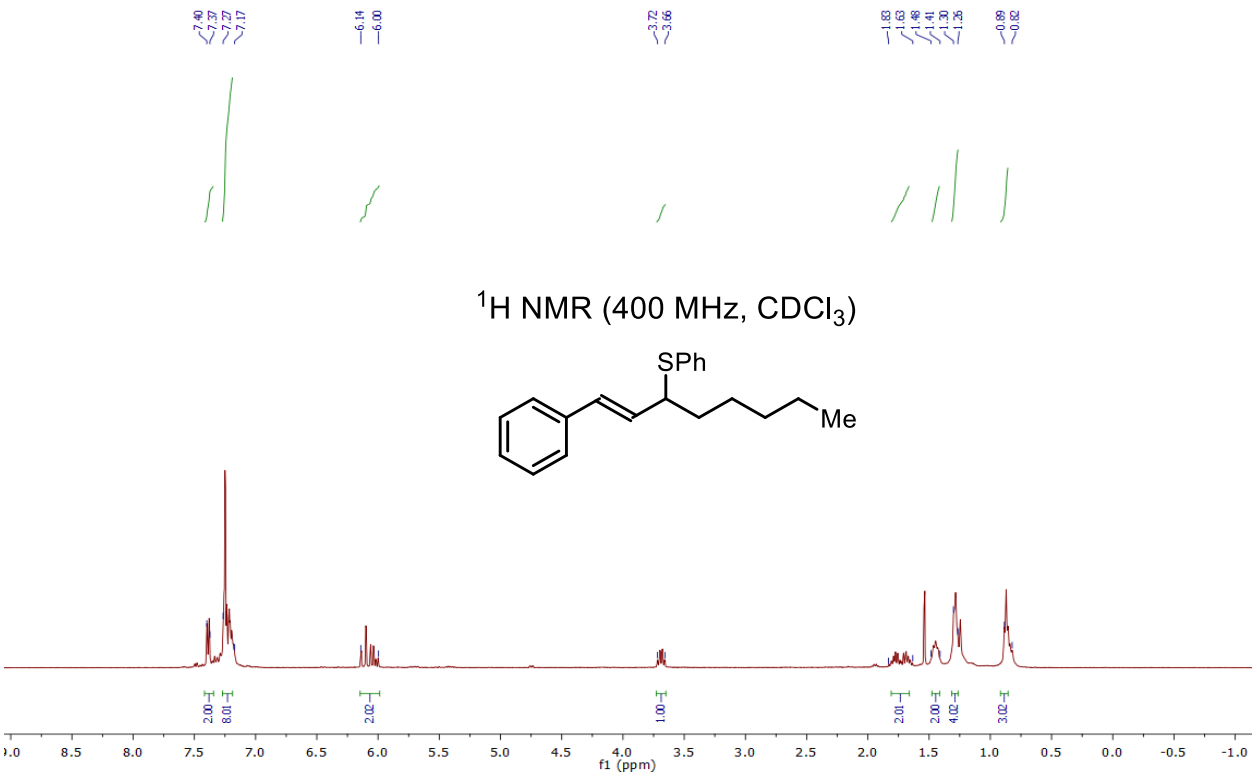


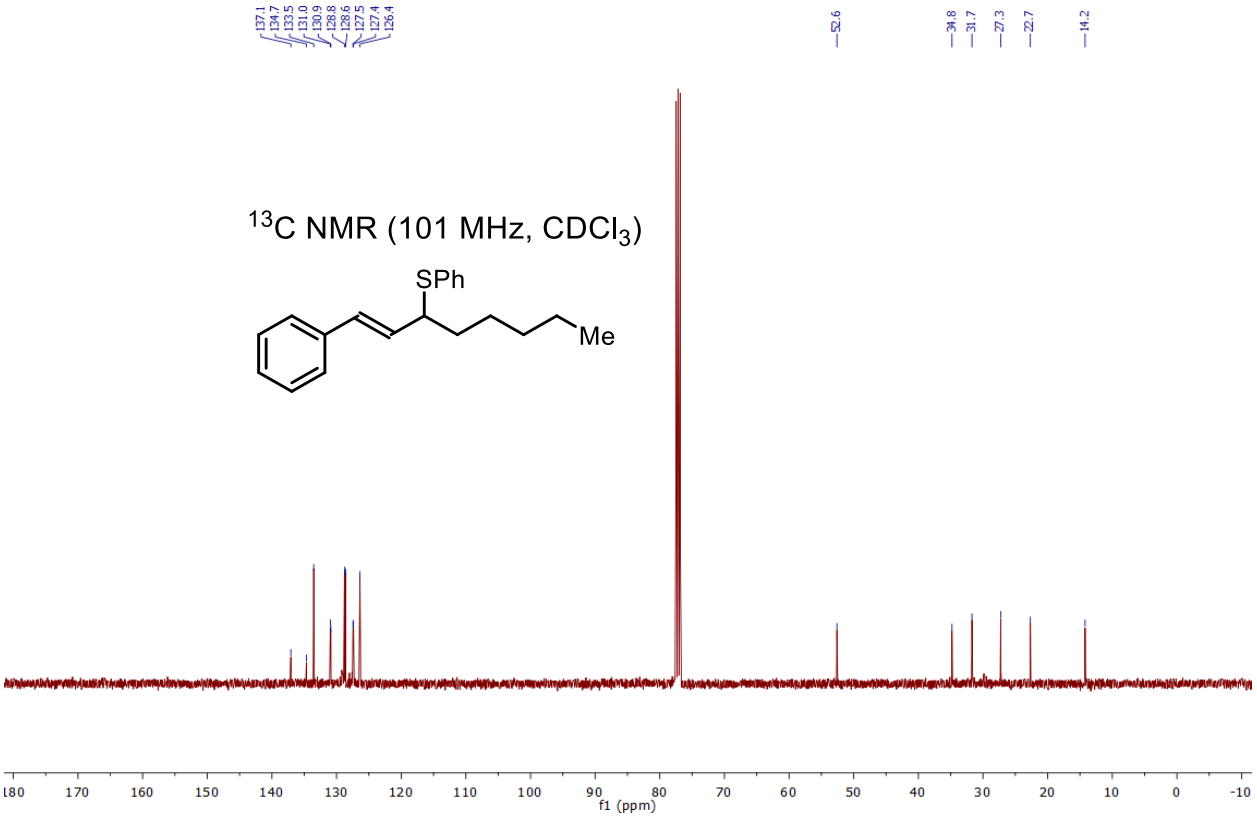
(*E*)-phenyl(1-phenylpent-1-en-3-yl)sulfane (275t)



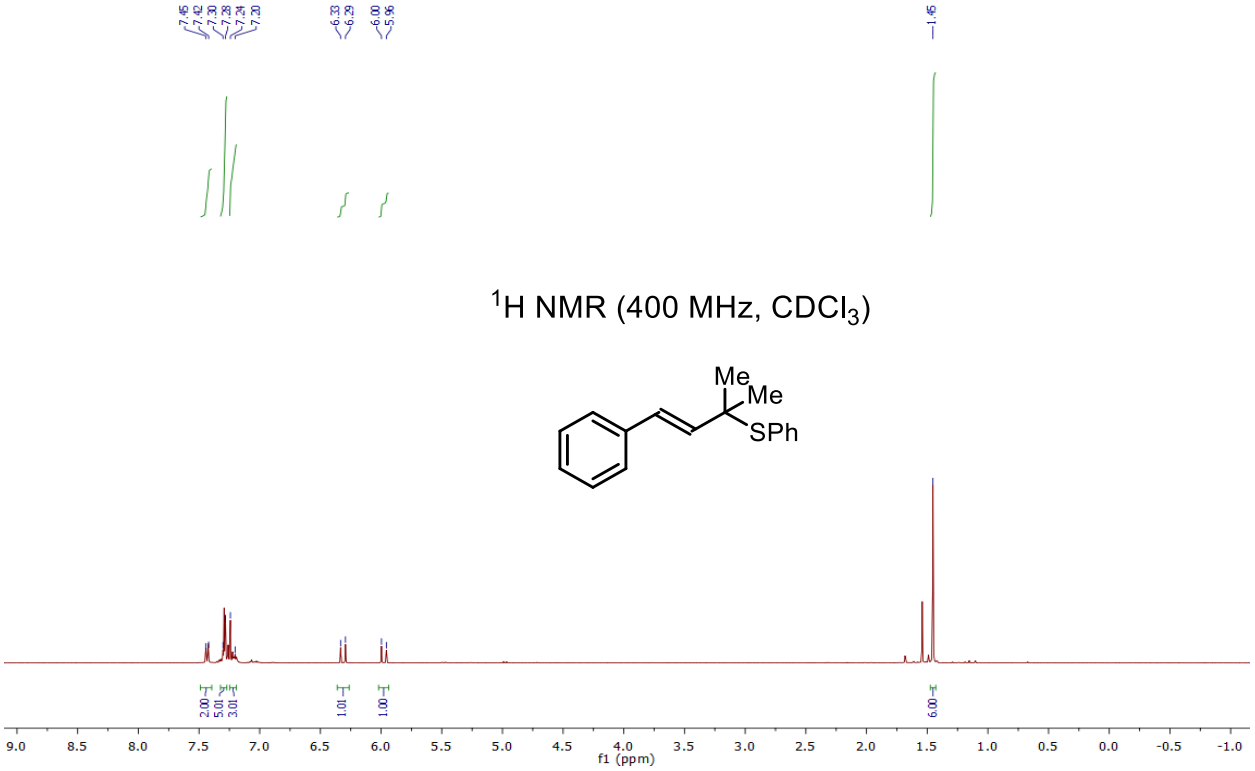


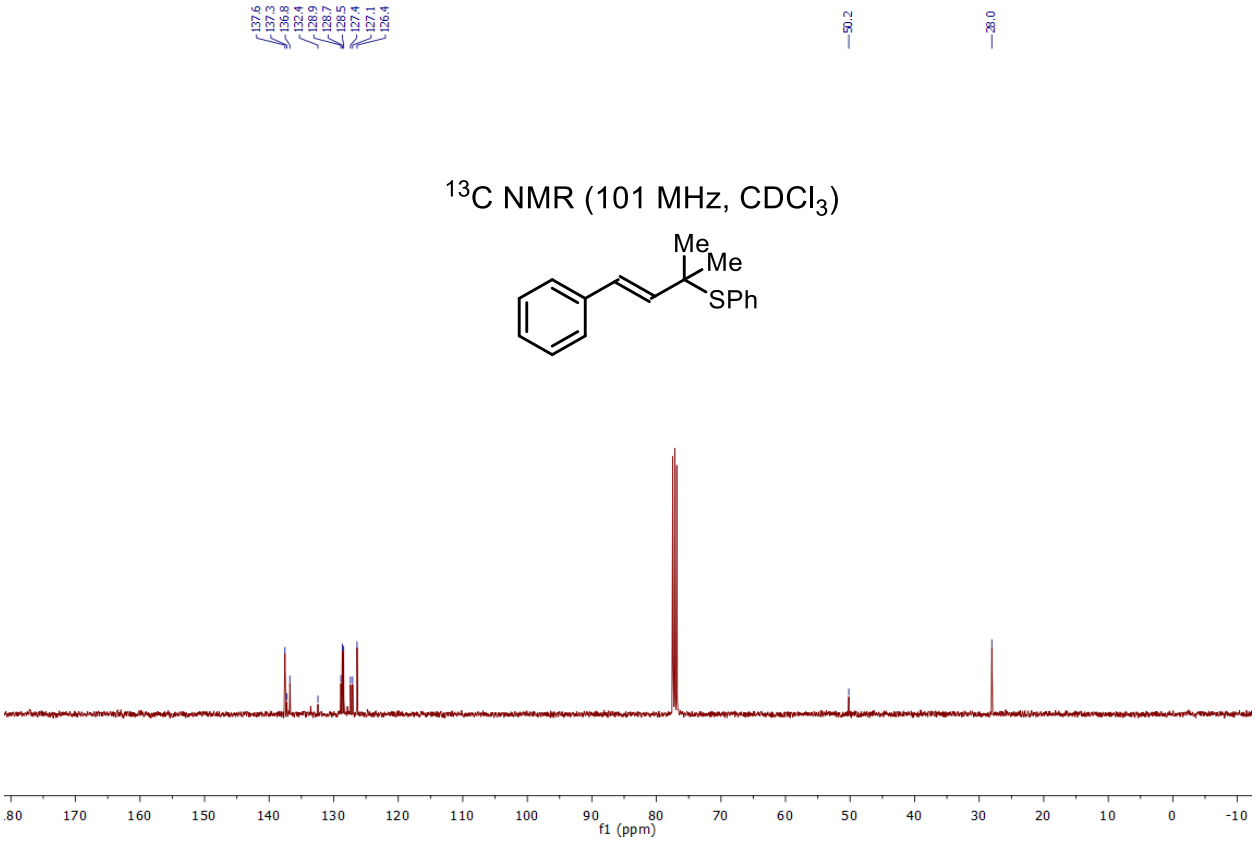
(*E*)-phenyl(1-phenyloct-1-en-3-yl)sulfane (275u)



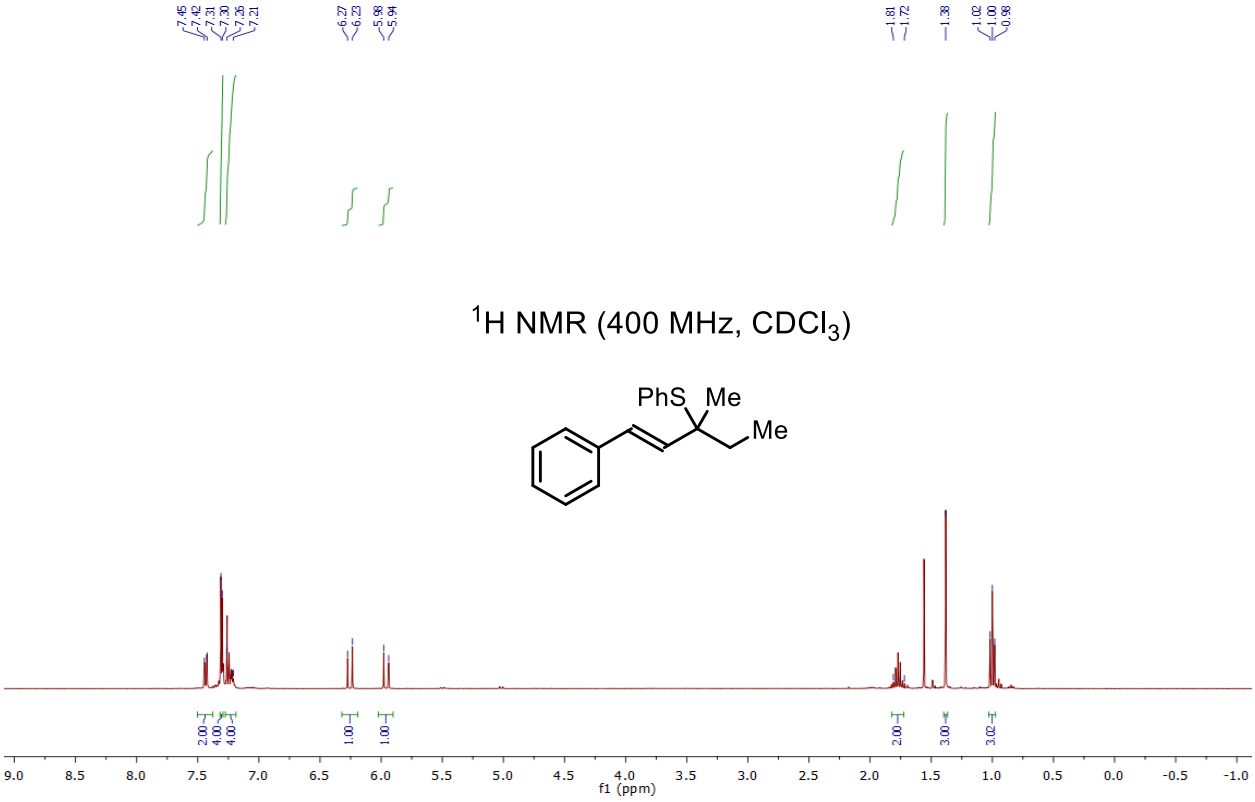


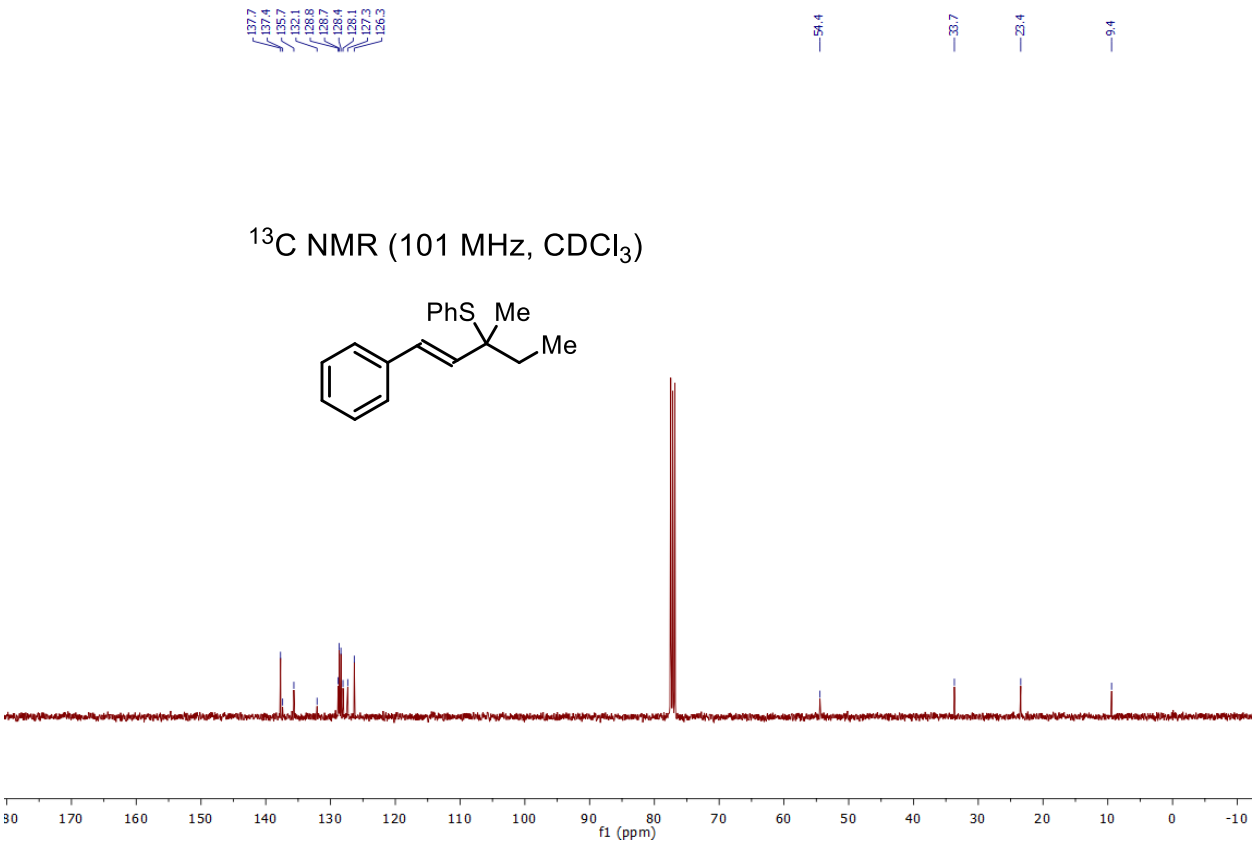
(*E*)-(2-methyl-4-phenylbut-3-en-2-yl)(phenyl)sulfane (275v)



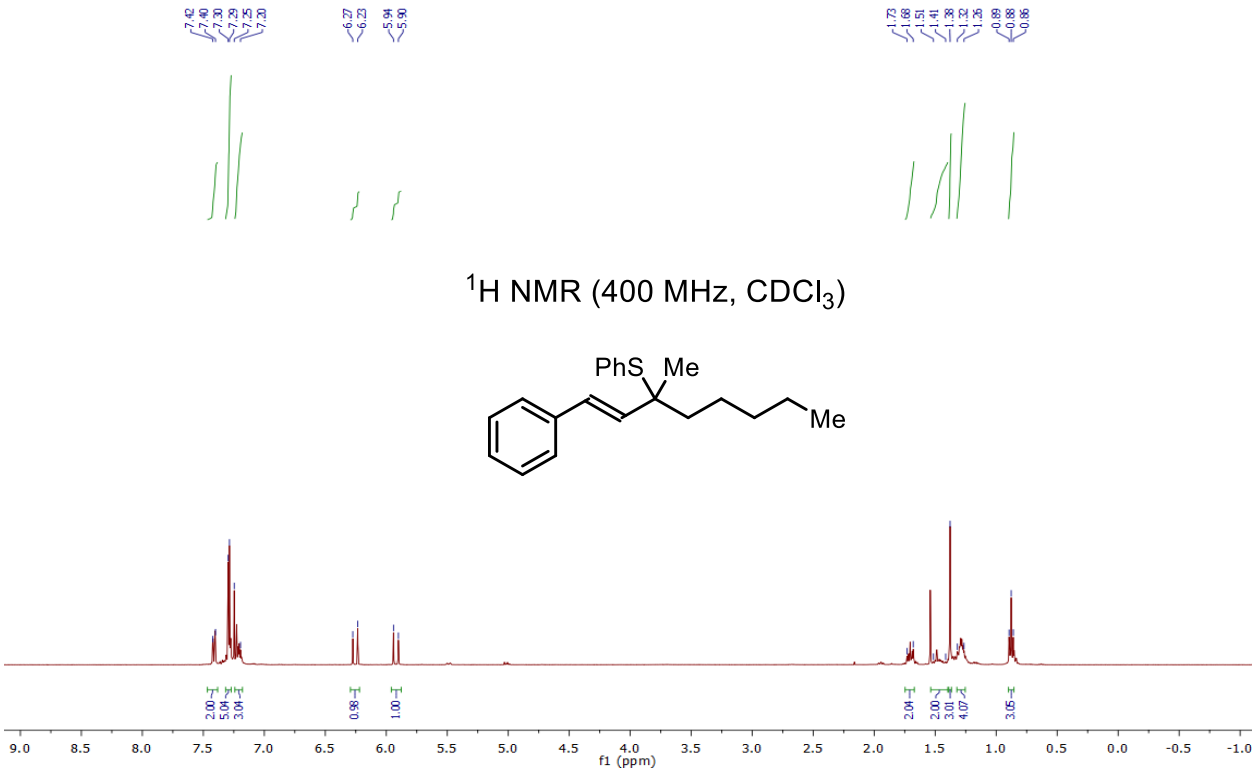


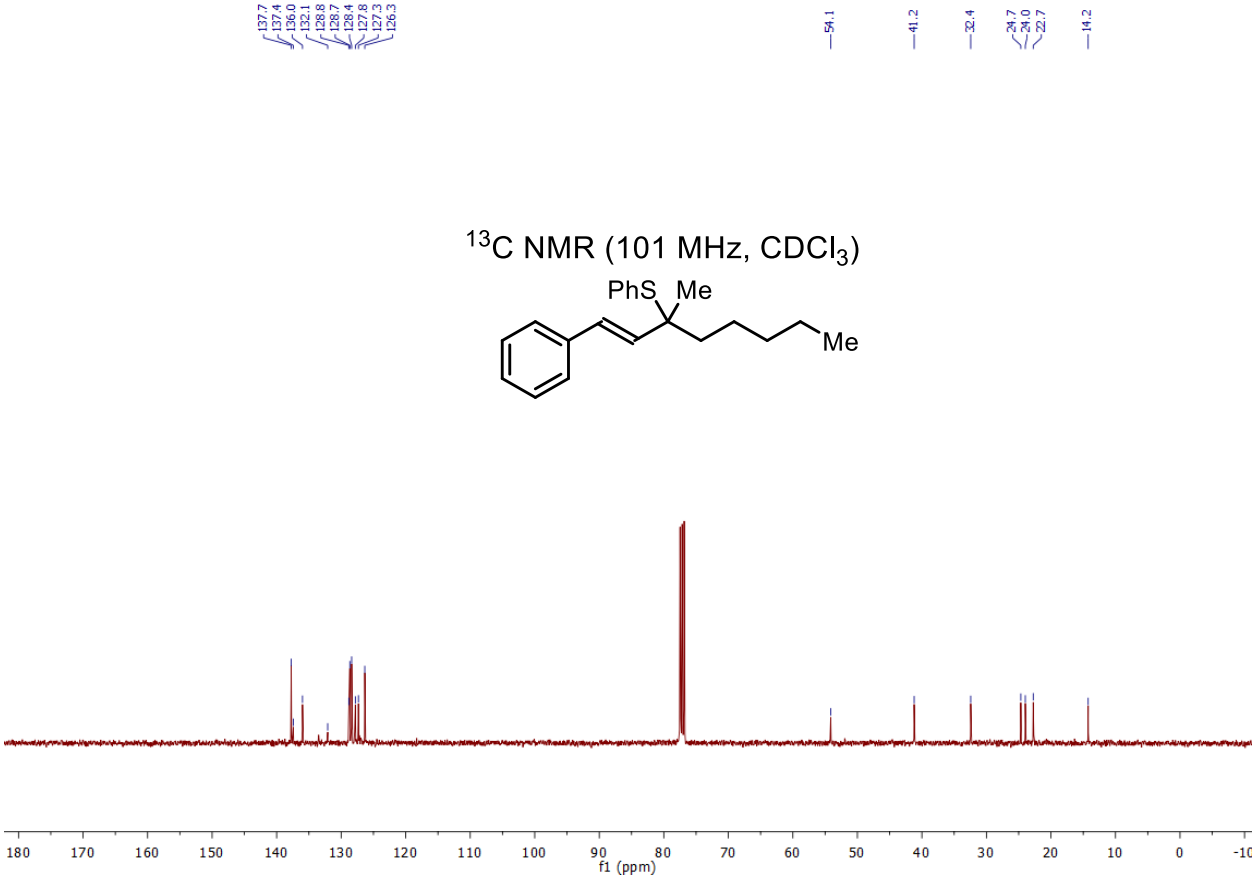
(*E*)-(3-methyl-1-phenylpent-1-en-3-yl)(phenyl)sulfane (275w)



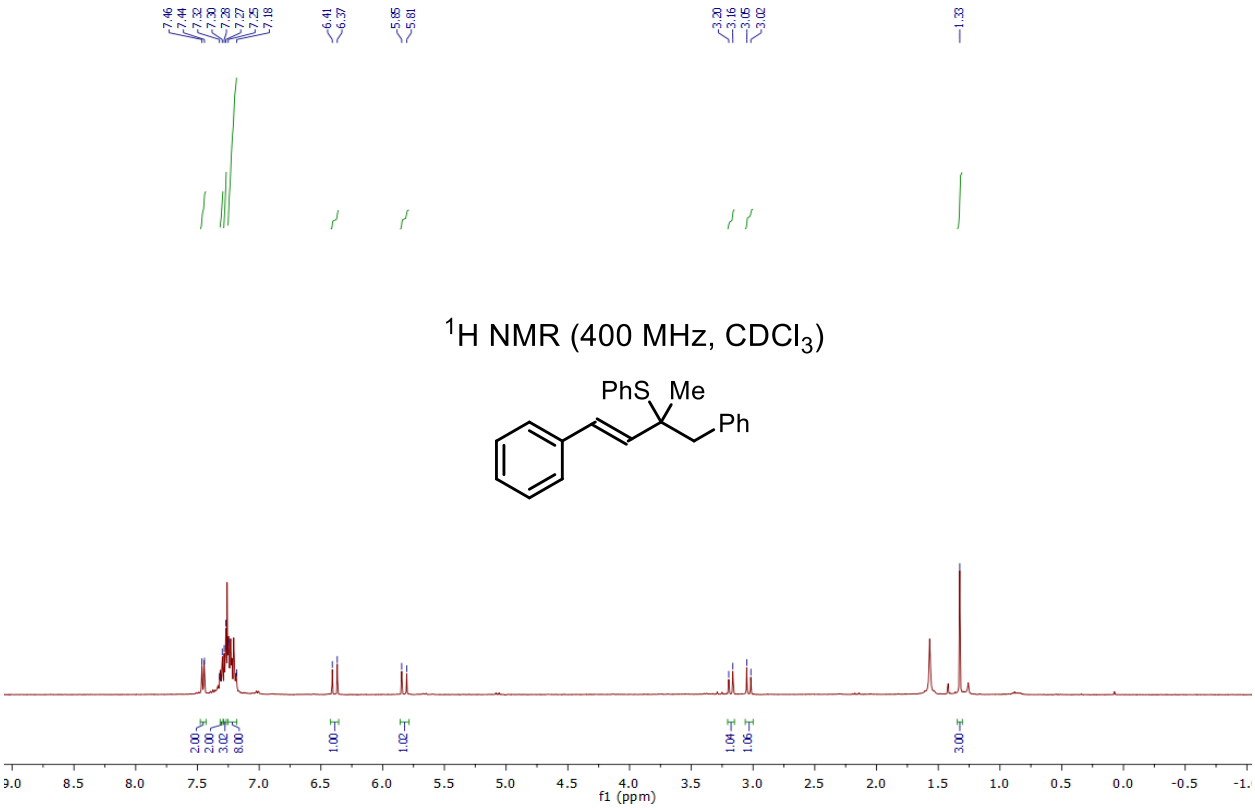


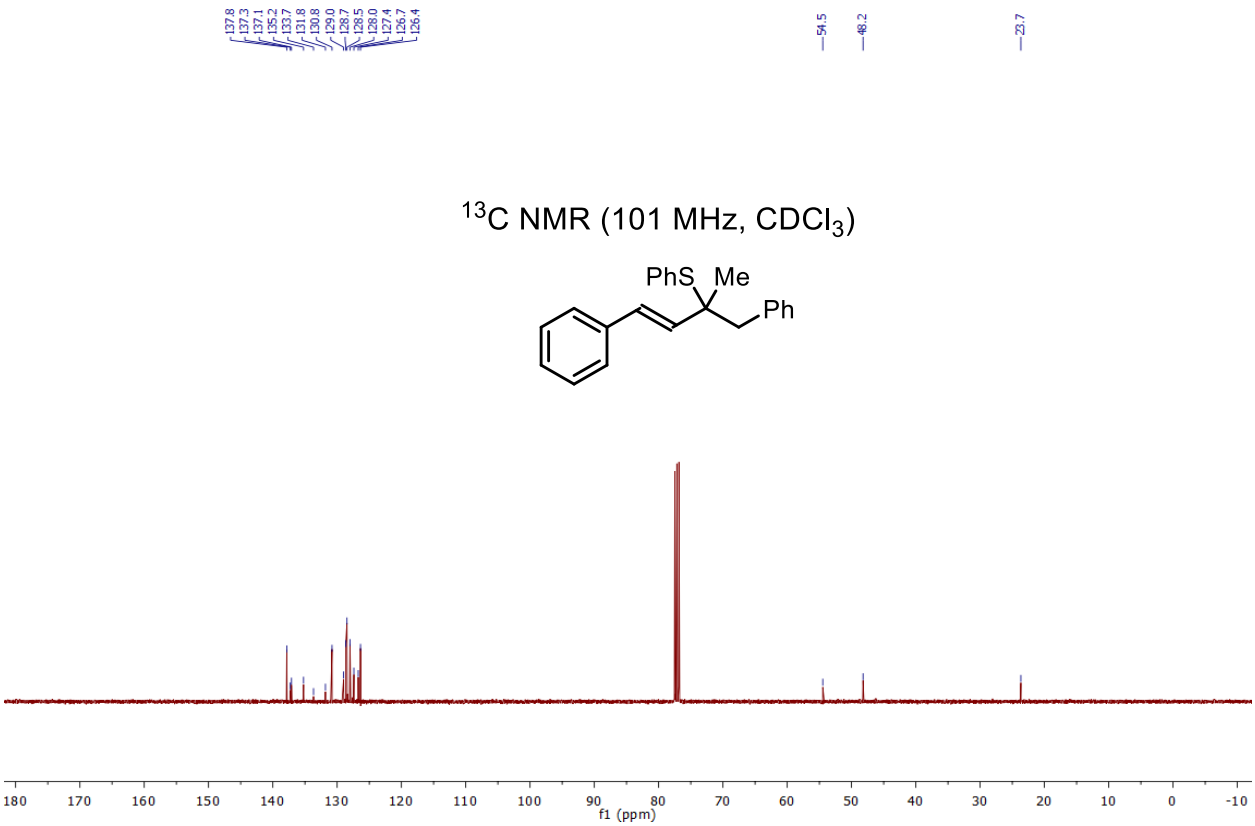
(*E*)-(3-methyl-1-phenyloct-1-en-3-yl)(phenyl)sulfane (275x)



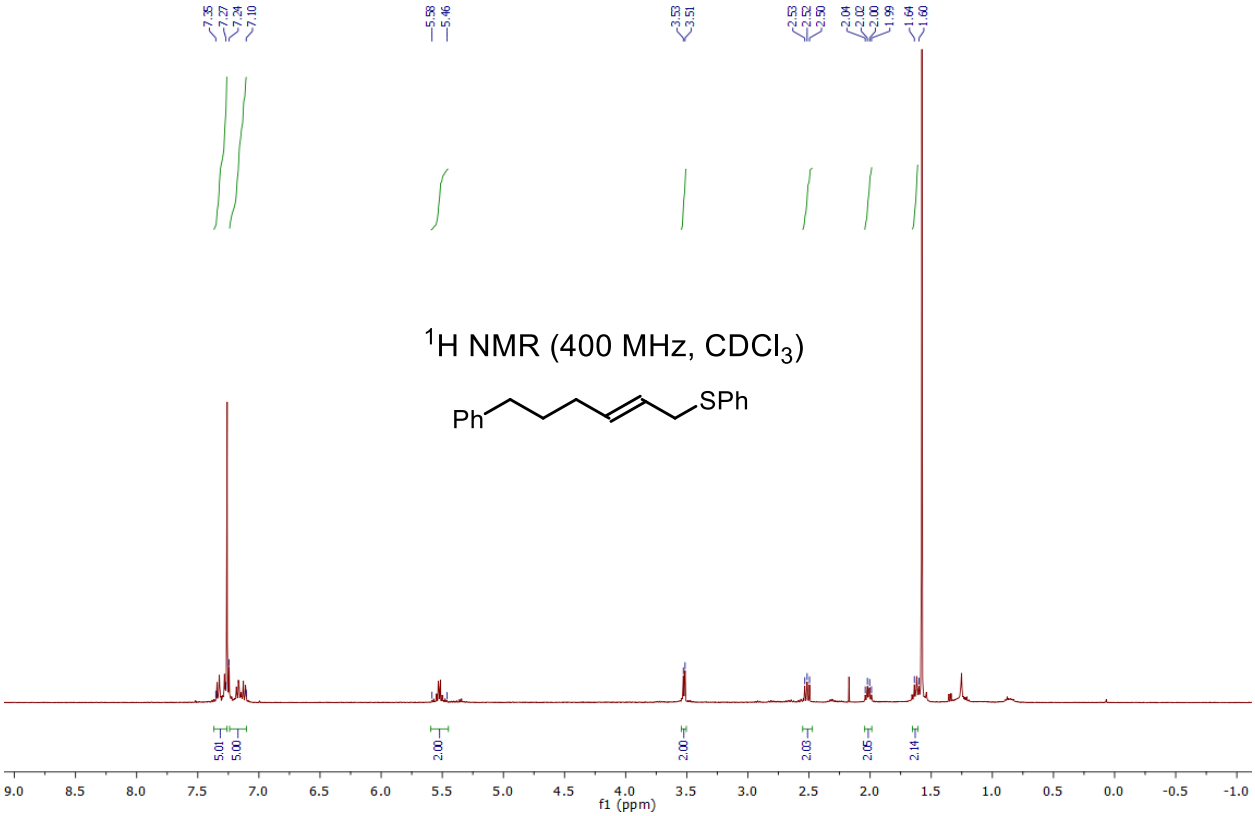


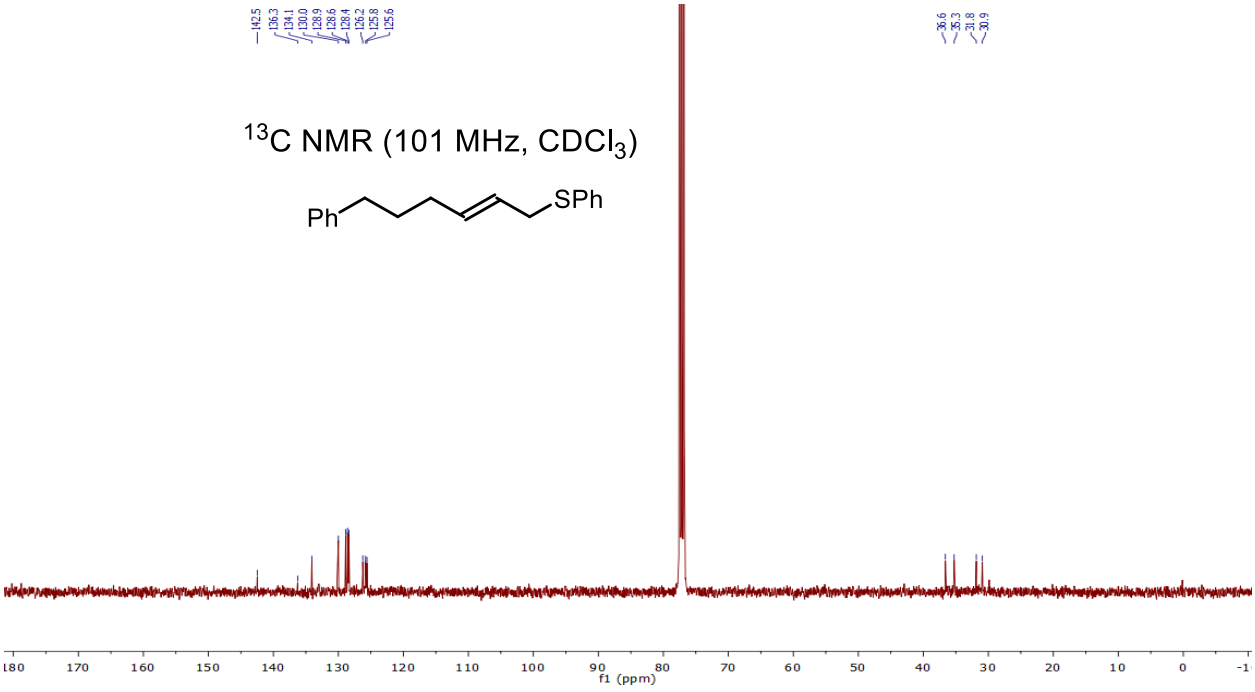
(*E*)-(2-methyl-1,4-diphenylbut-3-en-2-yl)(phenyl)sulfane (275y)

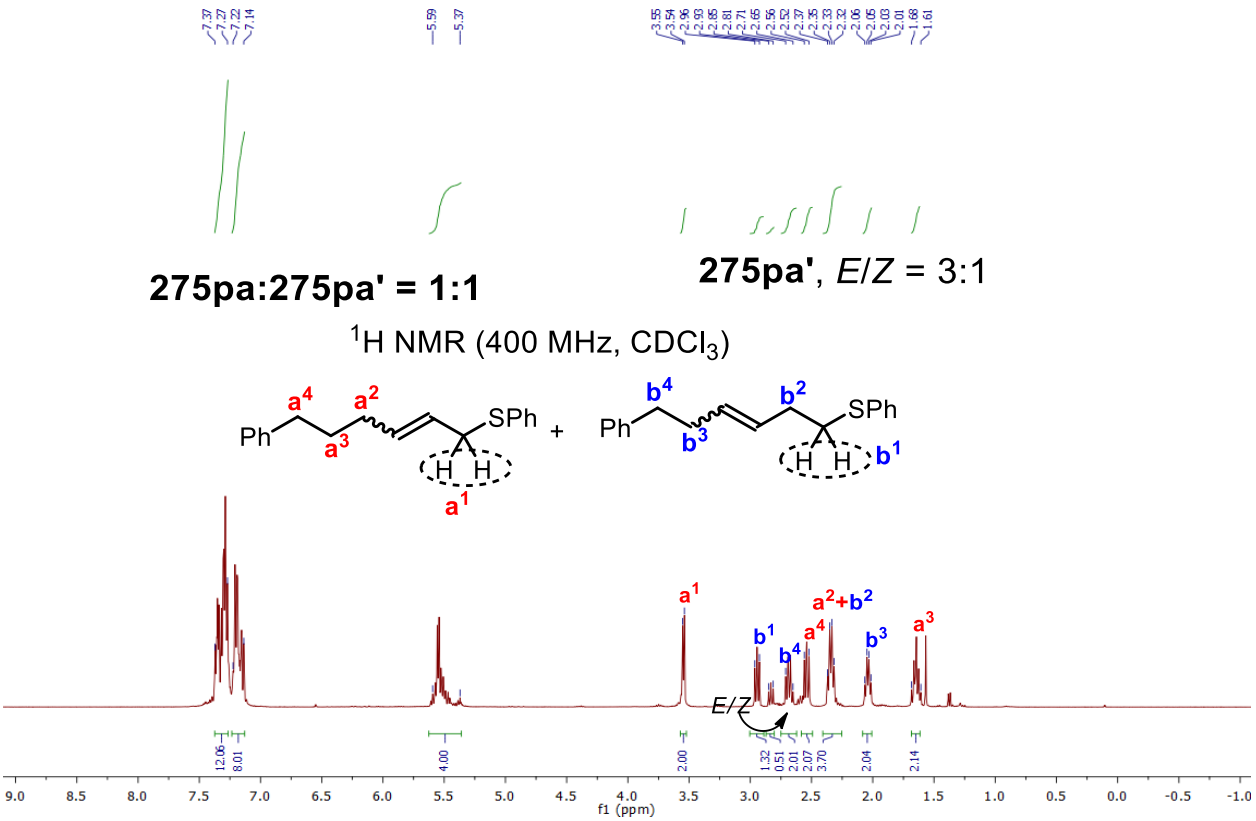


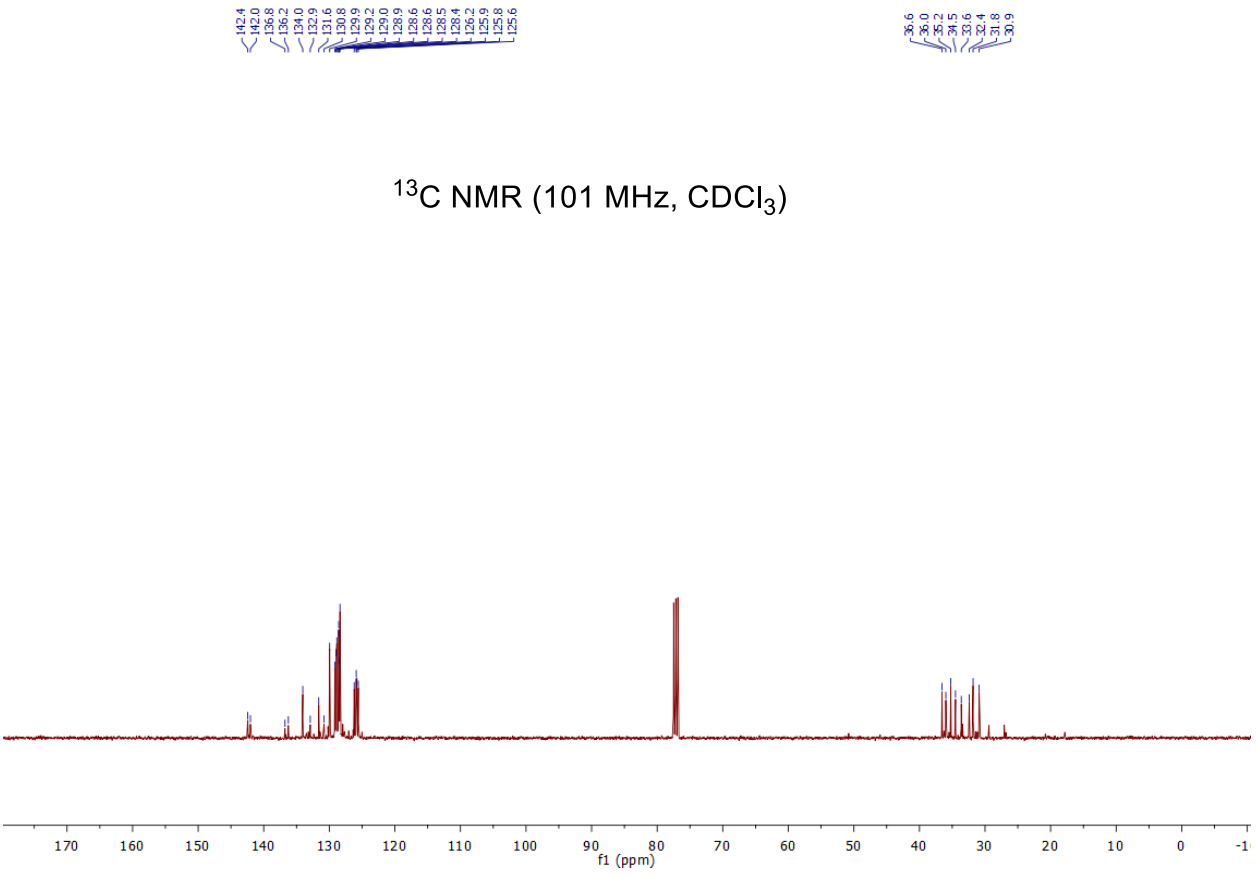


phenyl(6-phenylhex-2-en-1-yl)sulfane and phenyl(6-phenylhex-3-en-1-yl)sulfane (275pa + 275pa')

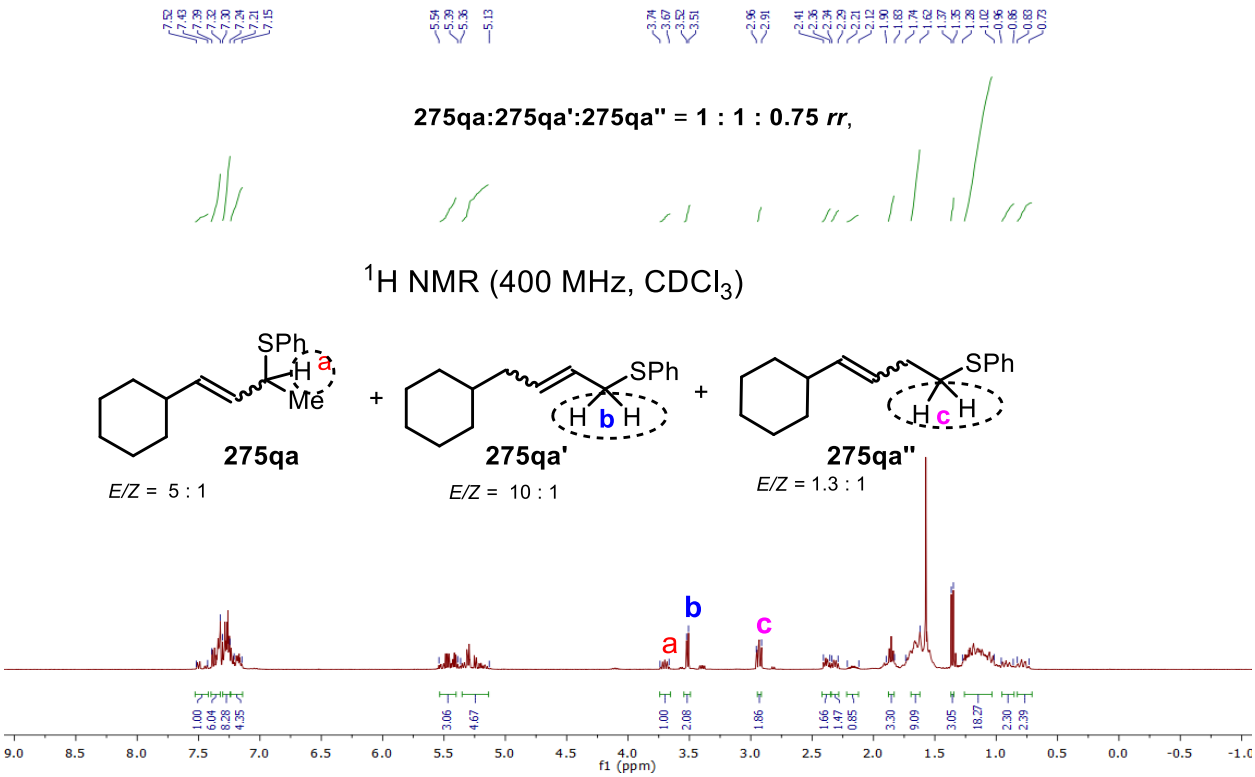


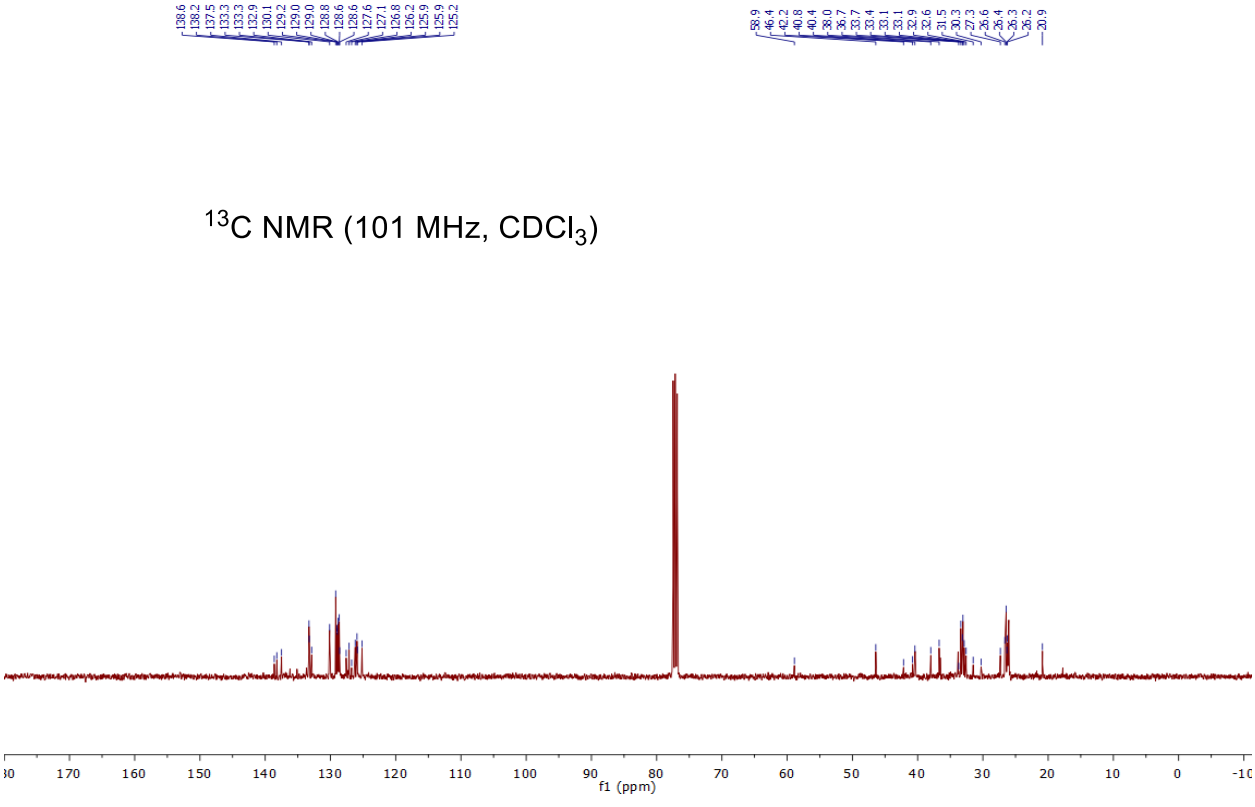



7.37
7.27
7.22
7.14
5.59
5.37
3.55
3.54
2.96
2.93
2.85
2.81
2.71
2.65
2.56
2.52
2.37
2.35
2.33
2.32
2.06
2.05
2.03
2.01
1.68
1.61
275pa:275pa' = 1:1
275pa', E/Z = 3:1
1H NMR (400 MHz, CDCl3)
Ph
SPh
a4
a2
a3
a1
b4
b2
b3
b1
E/Z
12.06
8.01
4.00
2.00
1.32
0.51
2.01
2.07
3.70
2.04
2.14
f1 (ppm)

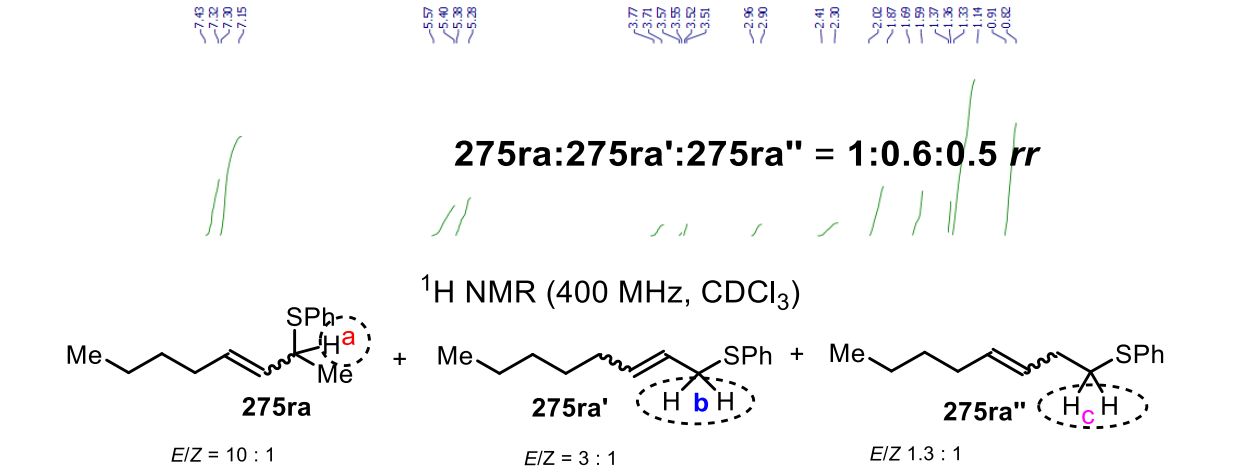

142.4
142.0
136.8
136.2
134.0
132.9
131.6
130.8
129.9
129.2
129.0
128.9
128.6
128.6
128.5
128.4
126.2
125.9
125.8
125.6
36.6
36.0
35.2
34.5
33.6
32.4
31.8
30.9
13C NMR (101 MHz, CDCl3)
f1 (ppm)

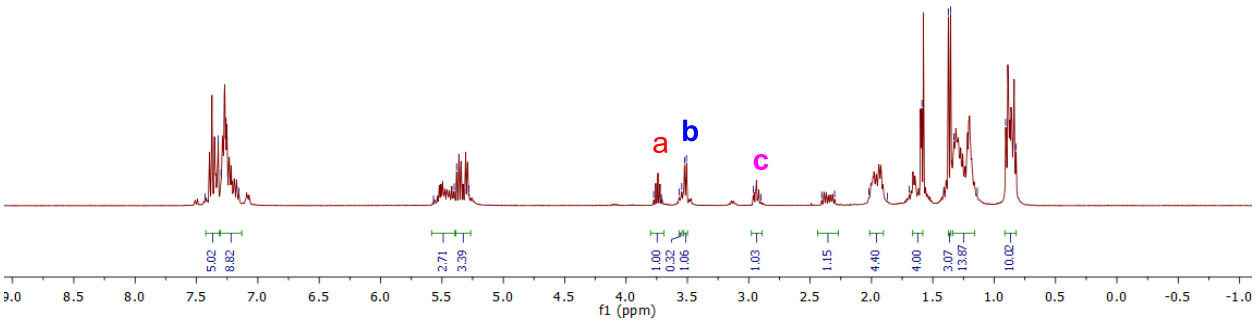
(4-cyclohexylbut-3-en-2-yl)(phenyl)sulfane (4-cyclohexylbut-2-en-1-yl)(phenyl)sulfane & (4-cyclohexylbut-3-en-1-yl)(phenyl)sulfane (275qa+275qa'+275qa'')

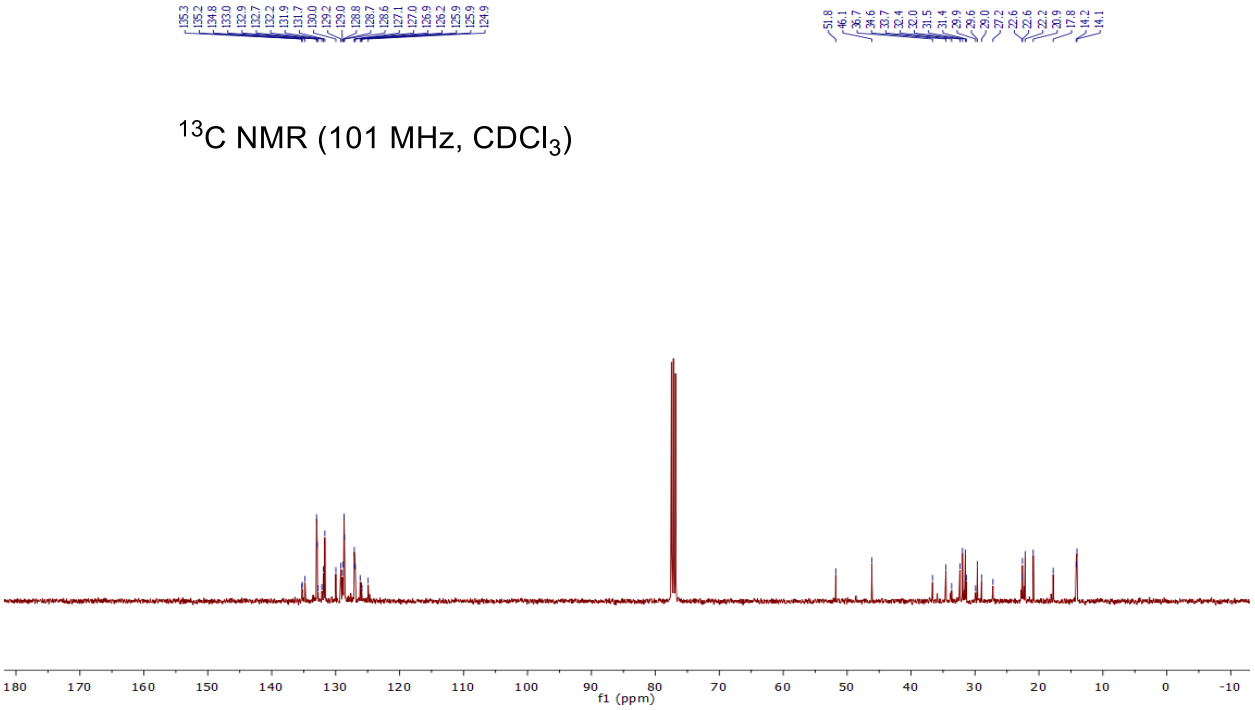




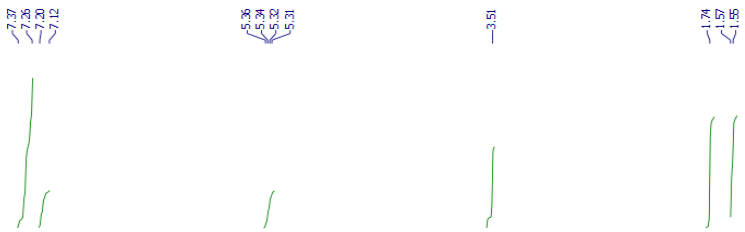
oct-3-en-2-yl(phenyl)sulfane, oct-2-en-1-yl(phenyl)sulfane & oct-3-en-1-yl(phenyl)sulfane (275ra+275ra'+275ra'')



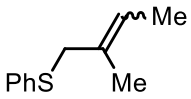




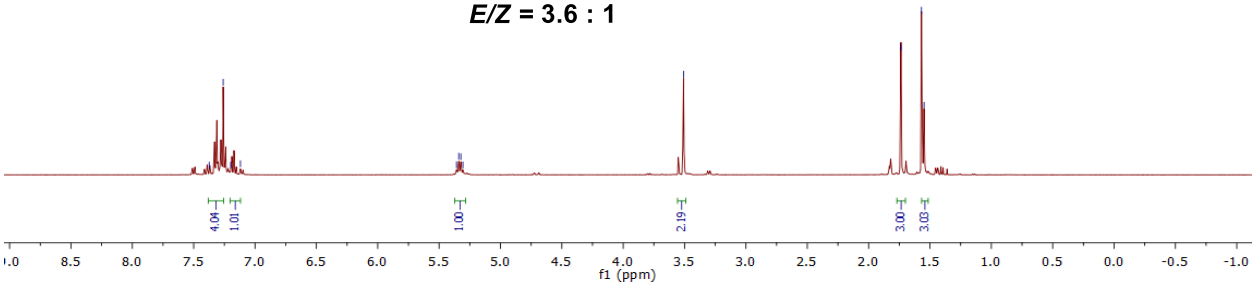
(2-methylbut-2-en-1-yl)(phenyl)sulfane (275sa)



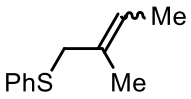
^{1}H NMR (400 MHz, $CDCl_3$)



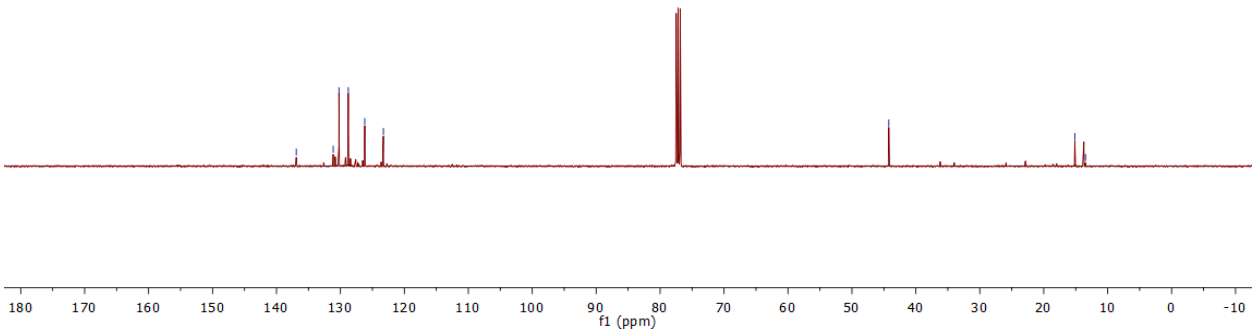
***E/Z* = 3.6 : 1**



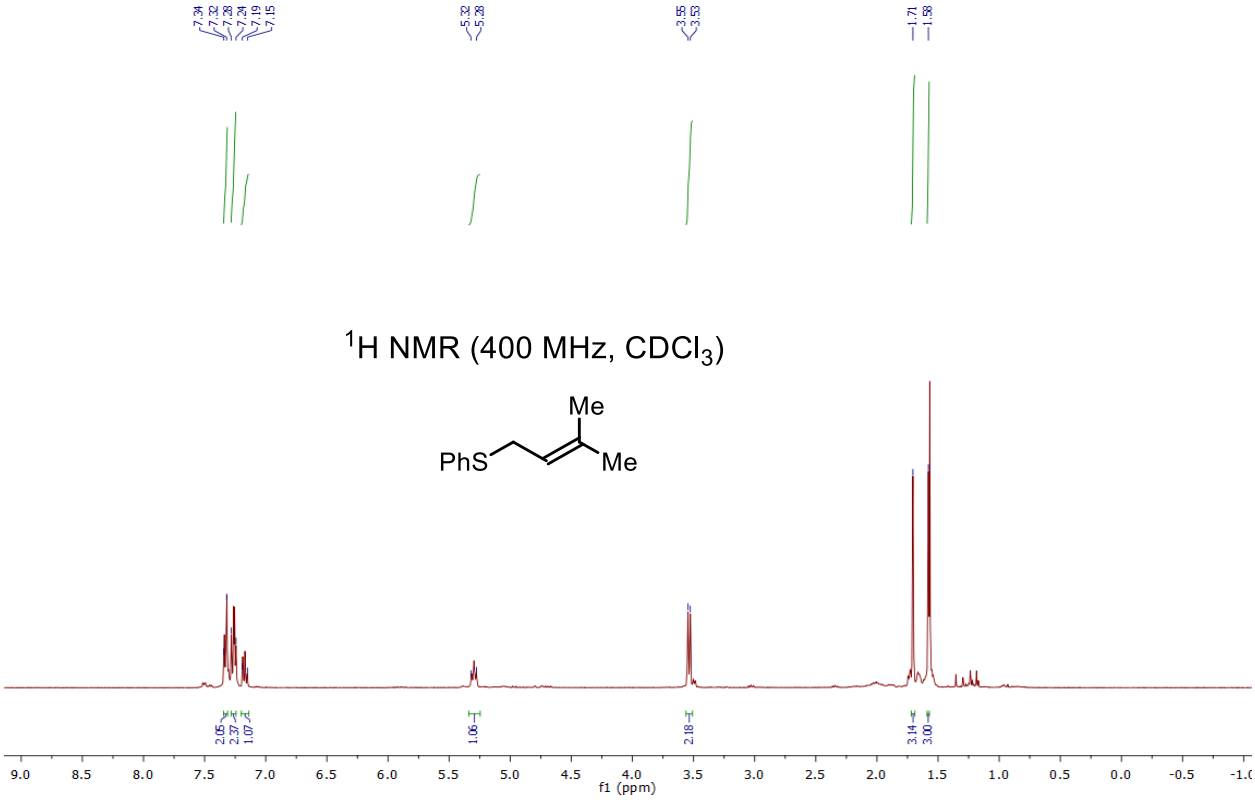
^{13}C NMR (101 MHz, $CDCl_3$)

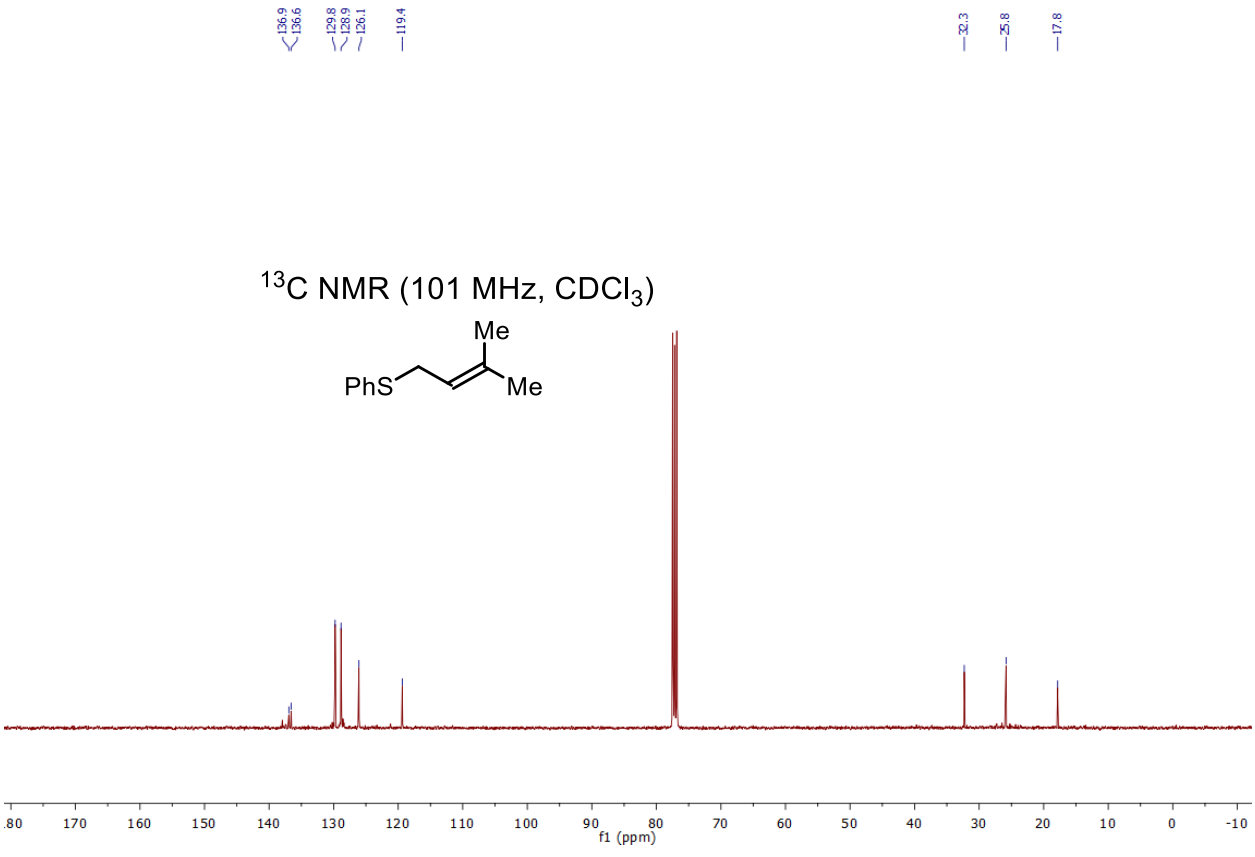


***E/Z* = 3.6 : 1**

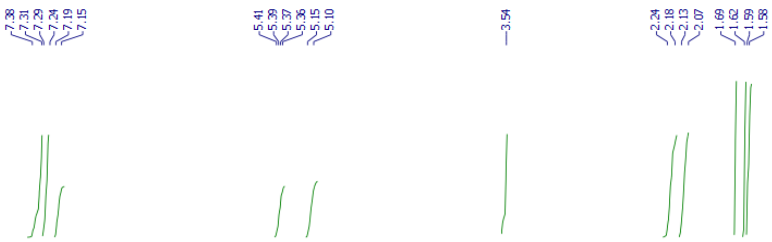


(3-methylbut-2-en-1-yl)(phenyl)sulfane (275sa')

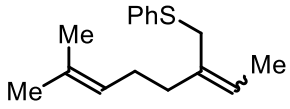




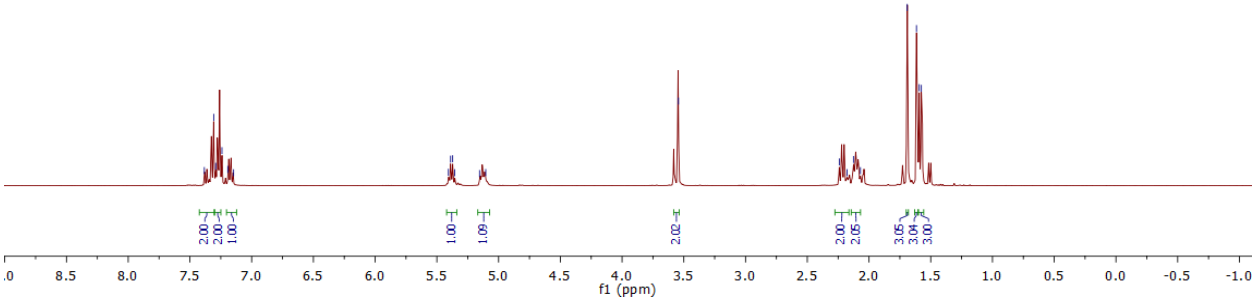
(2-ethylidene-6-methylhept-5-en-1-yl)(phenyl)sulfane (275ta)



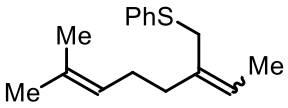
^{1}H NMR (400 MHz, $CDCl_3$)



E/*Z* = 3.2:1



^{13}C NMR (101 MHz, $CDCl_3$)



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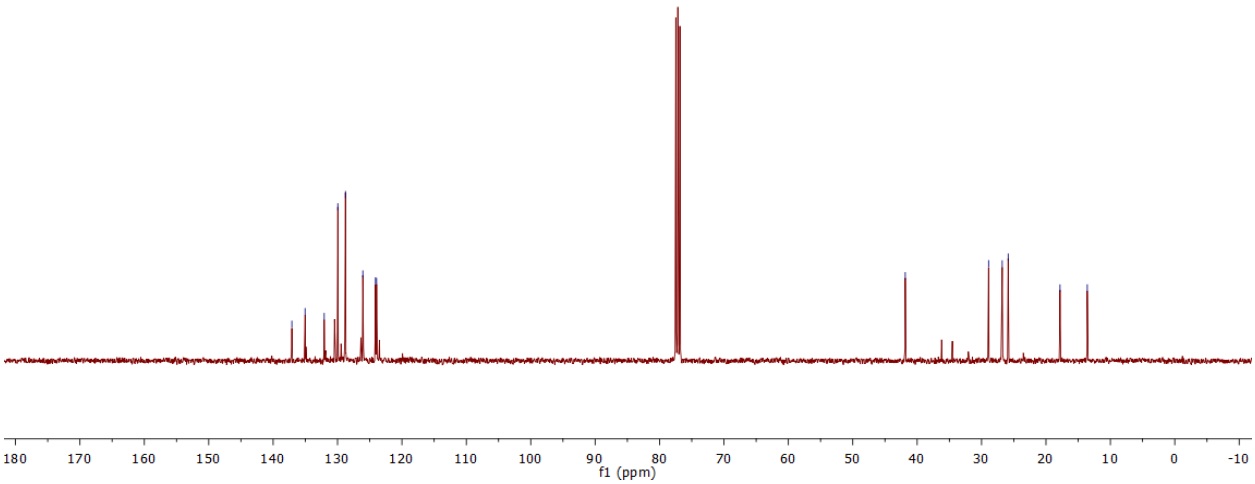
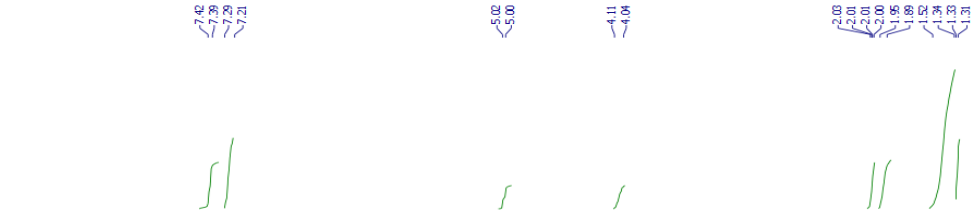
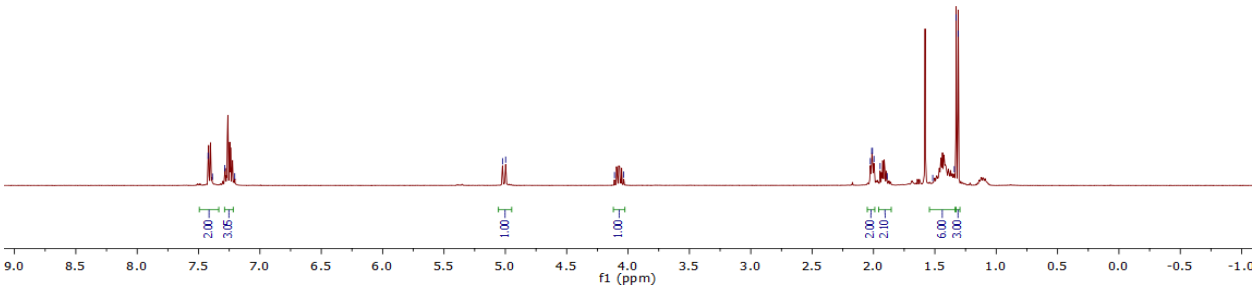


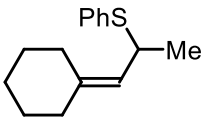
(1-cyclohexylidenepropan-2-yl)(phenyl)sulfane (275ua)

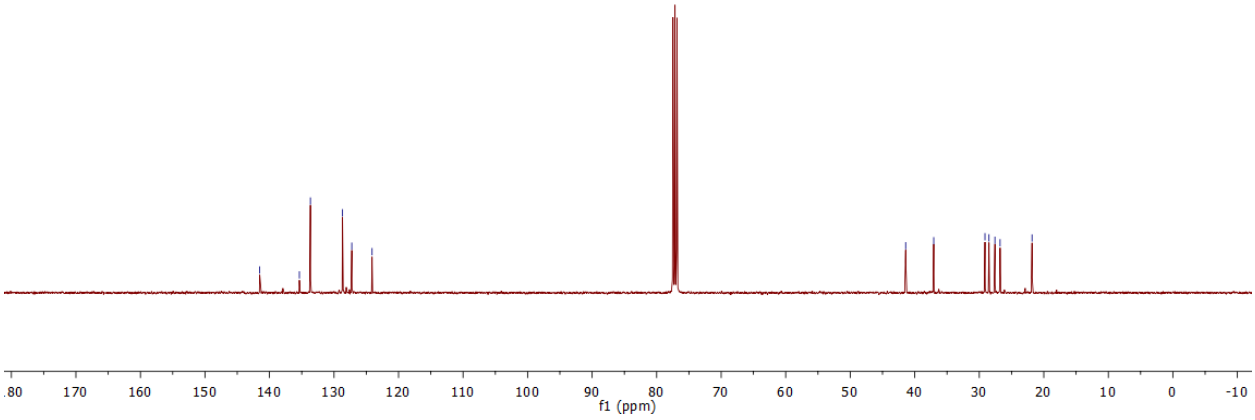


^{1}H NMR (400 MHz, $CDCl_3$)

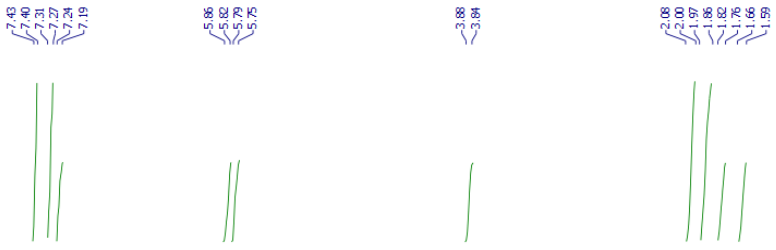


^{13}C NMR (101 MHz, $CDCl_3$)

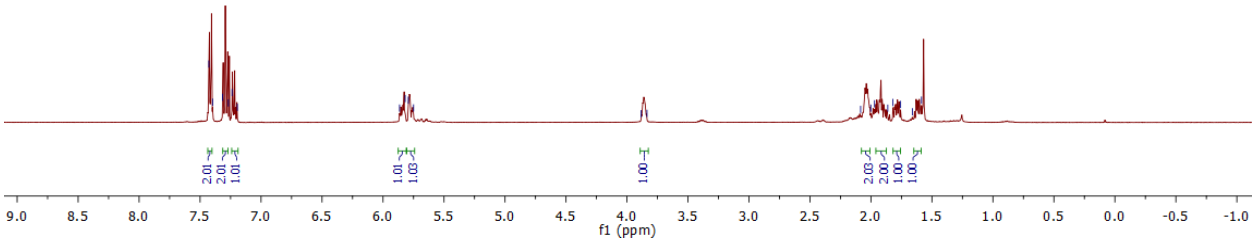




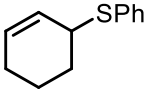
Cyclohex-2-en-1-yl(phenyl)sulfane (275va)

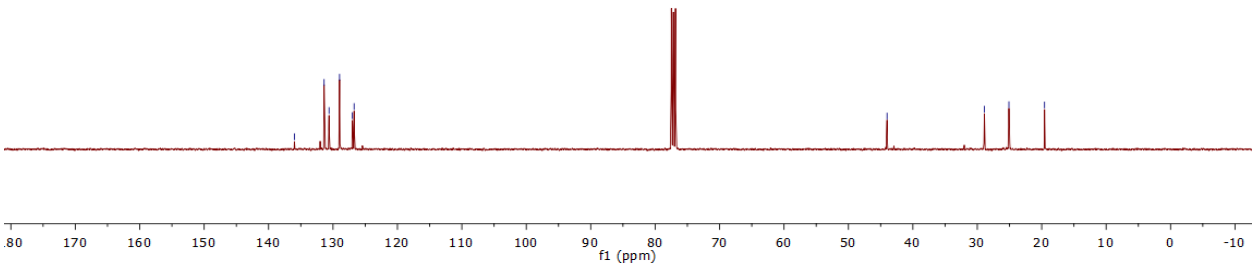


^{1}H NMR (400 MHz, $CDCl_3$)

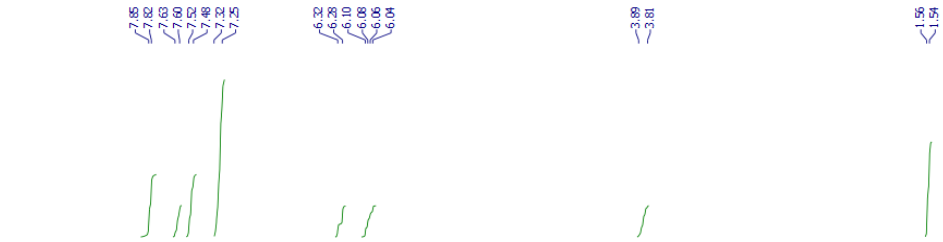


^{13}C NMR (101 MHz, $CDCl_3$)

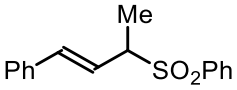


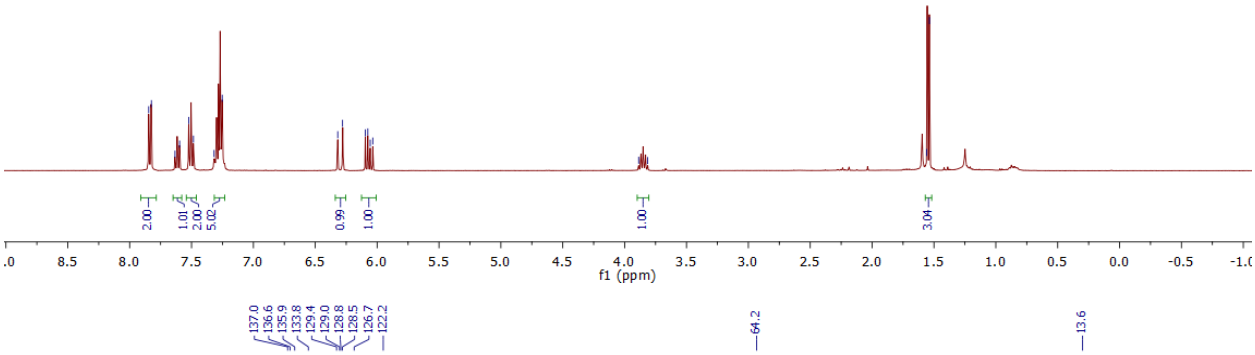


(*E*)-((4-phenylbut-3-en-2-yl)sulfonyl)benzene (275ao)

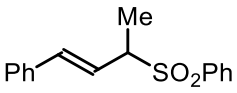


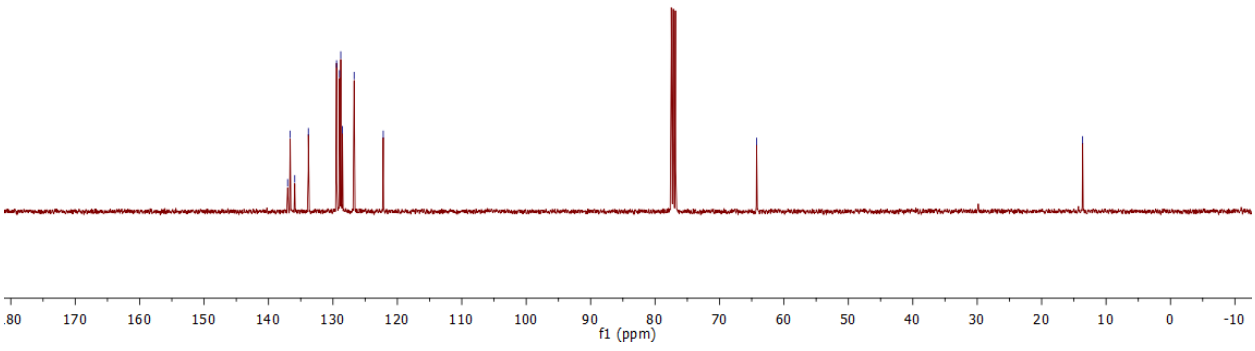
^{1}H NMR (400 MHz, $CDCl_3$)





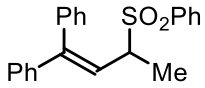
^{13}C NMR (101 MHz, $CDCl_3$)

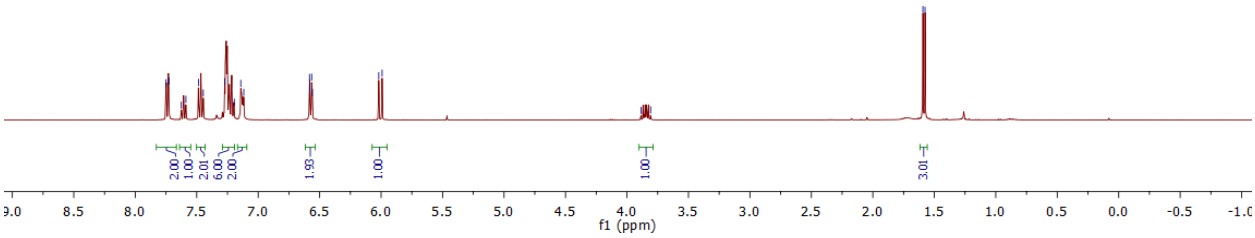




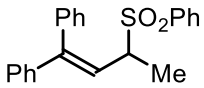
(3-(phenylsulfonyl)but-1-ene-1,1-diyl)dibenzene (275so)

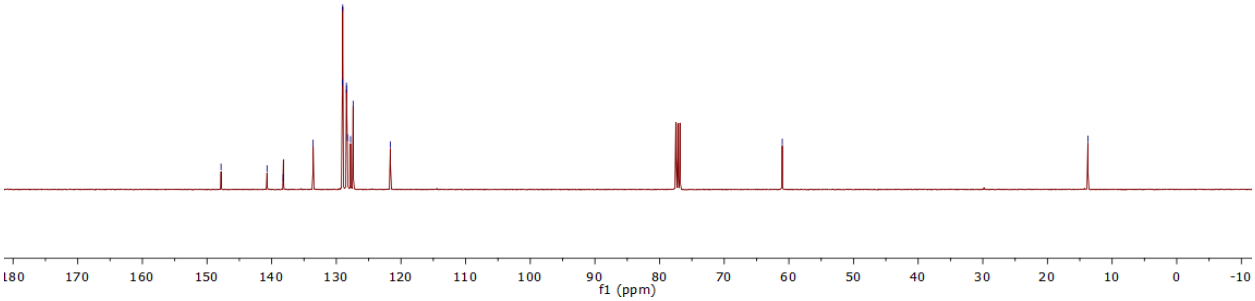
^{1}H NMR (400 MHz, $CDCl_3$)



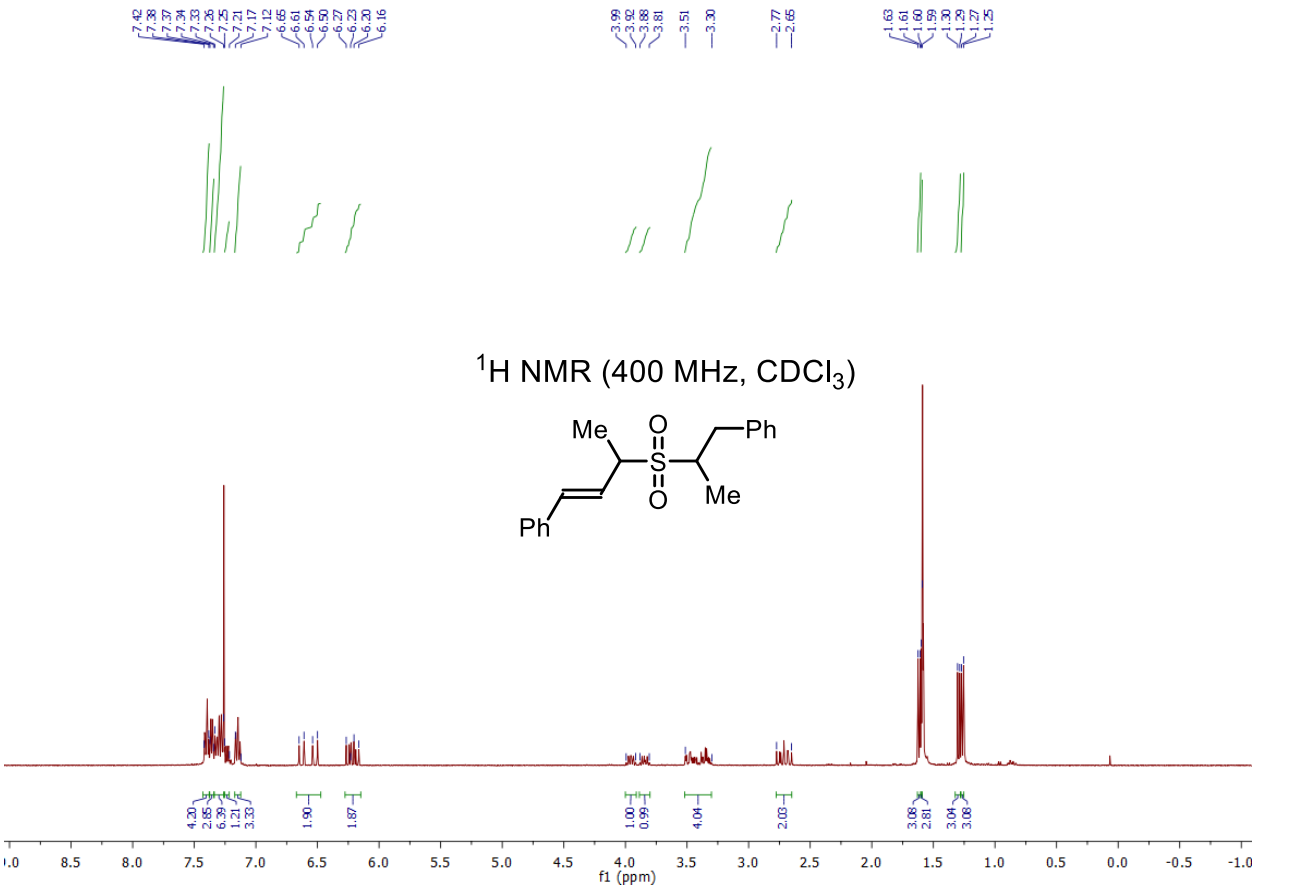


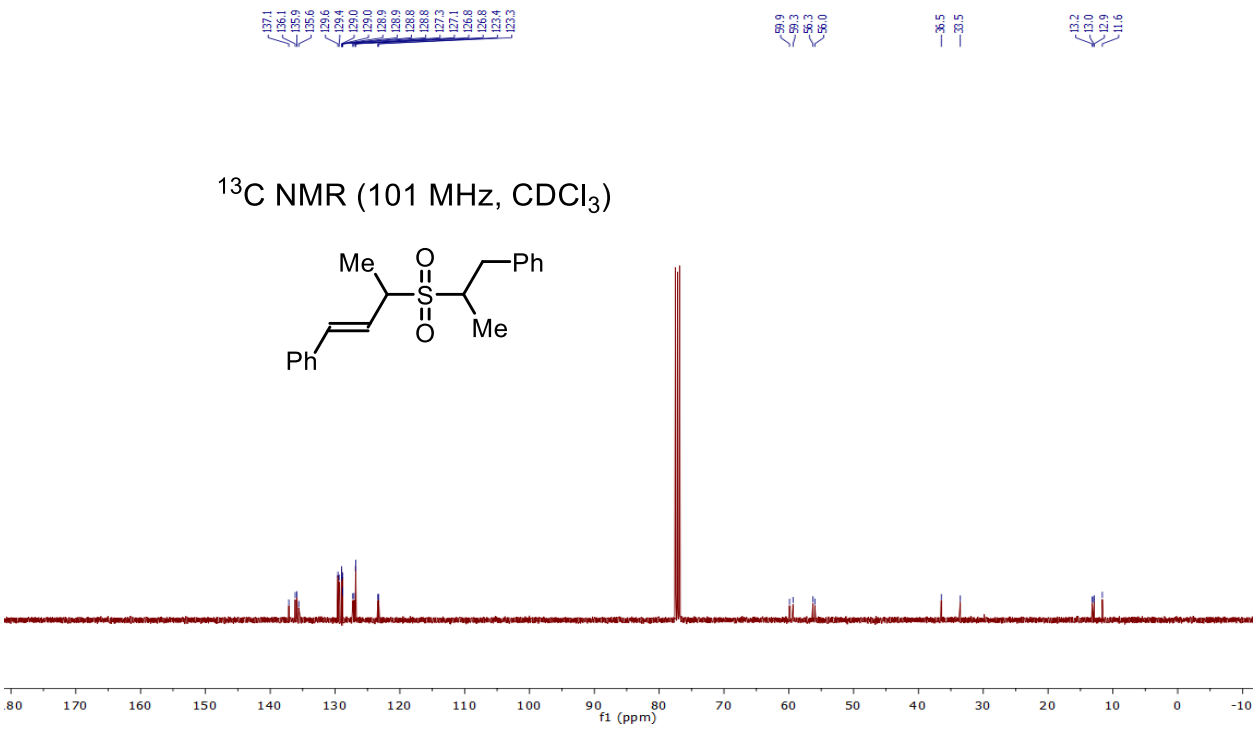
^{13}C NMR (101 MHz, $CDCl_3$)



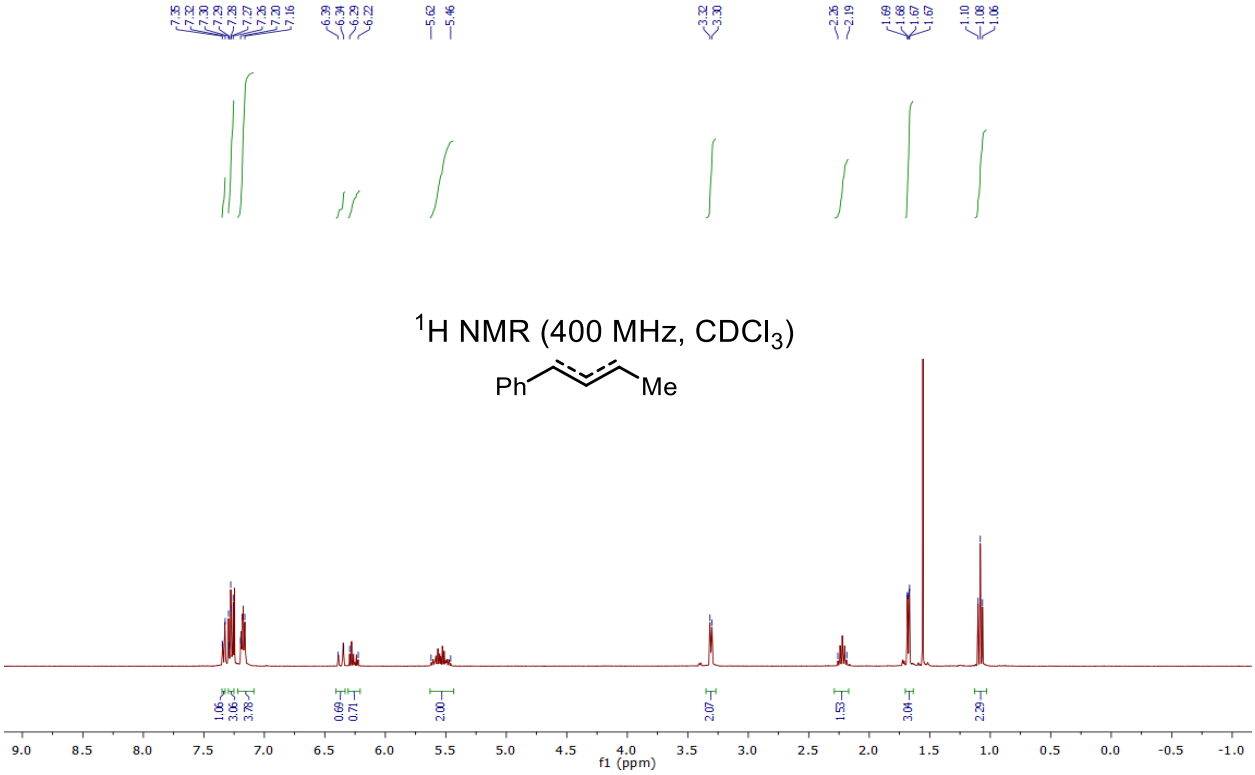


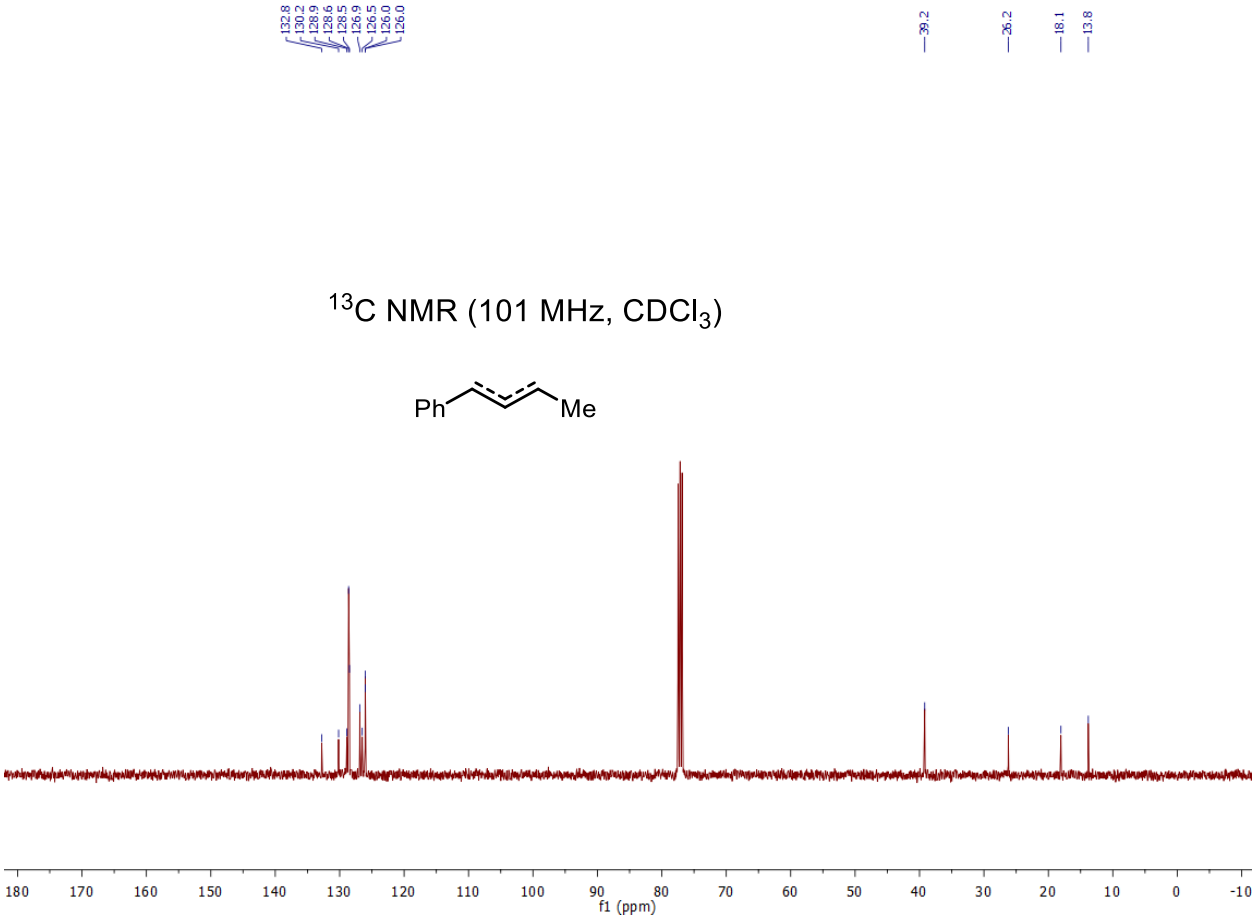
(*E*)-(2-((4-phenylbut-3-en-2-yl)sulfonyl)propyl)benzene(mixture of diastereomer) (275jo)



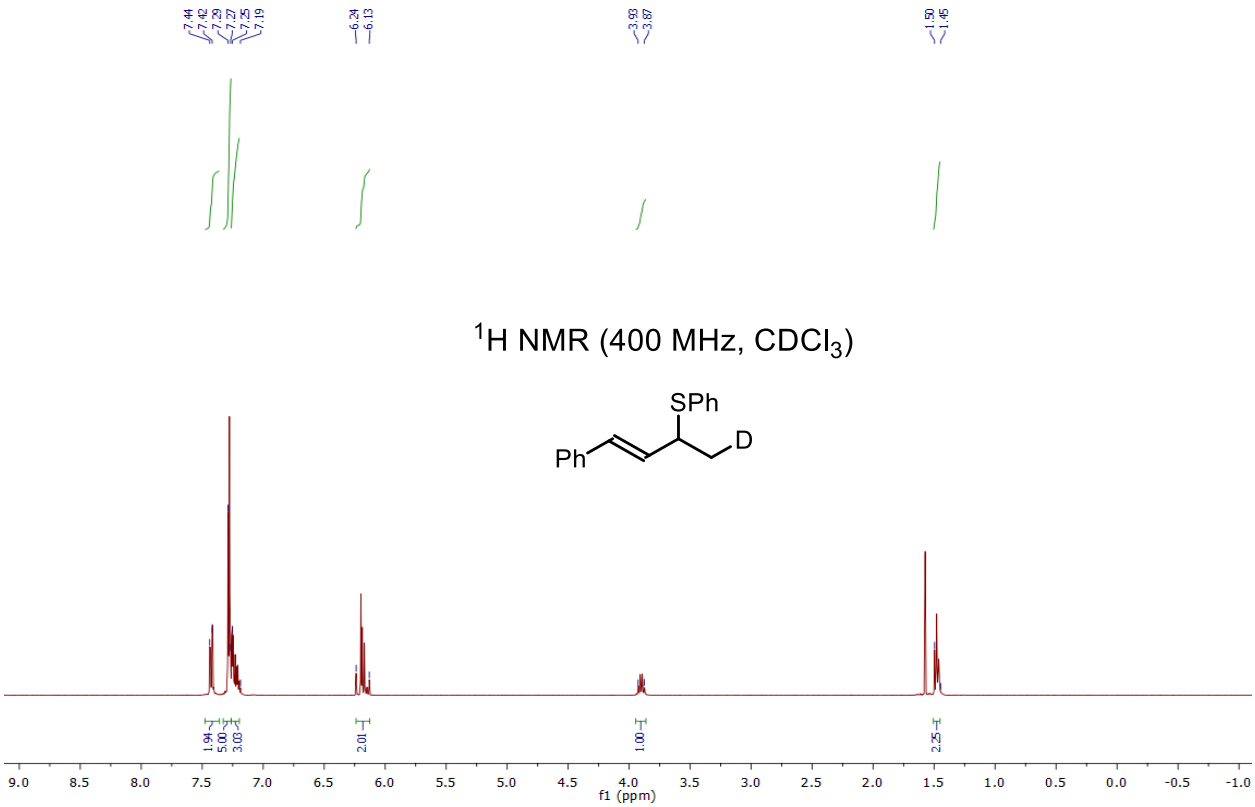


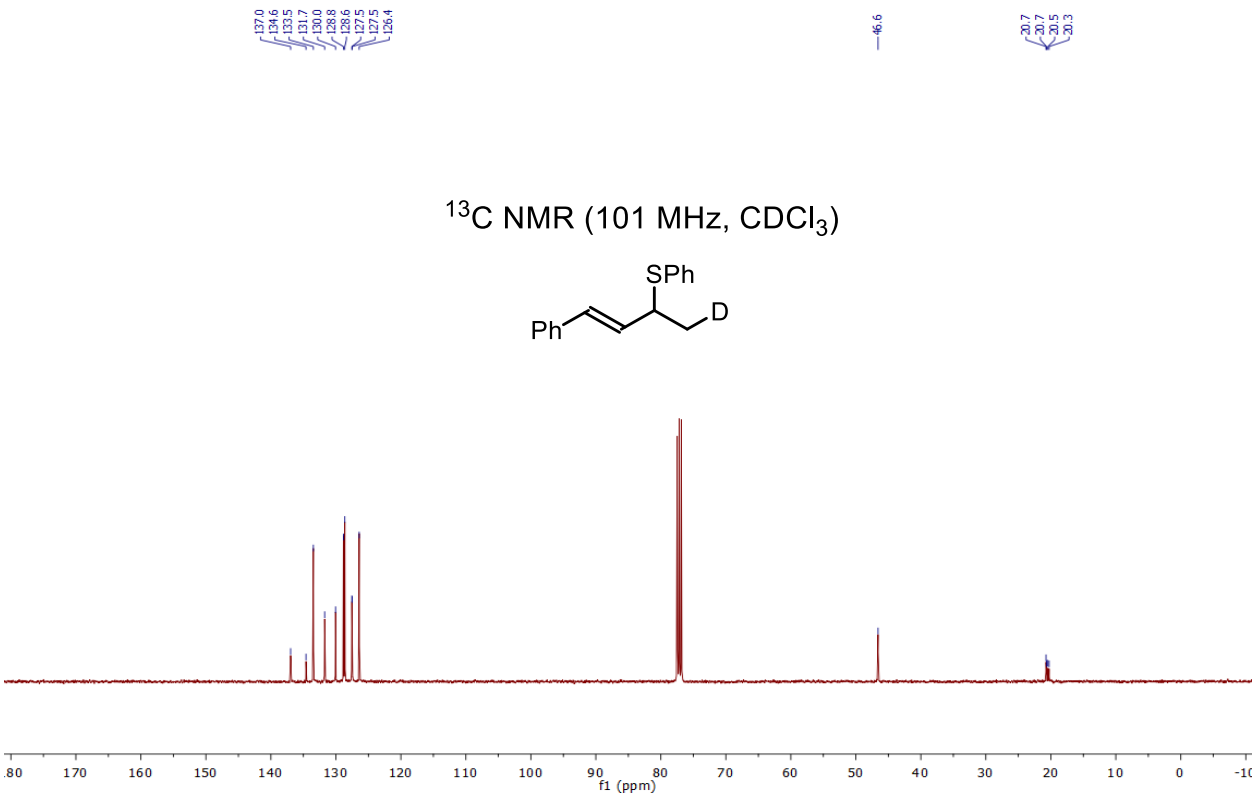
(*E*)-but-1-en-1-ylbenzene and (*E*)-but-2-en-1-ylbenzene (275ad + 275ad')

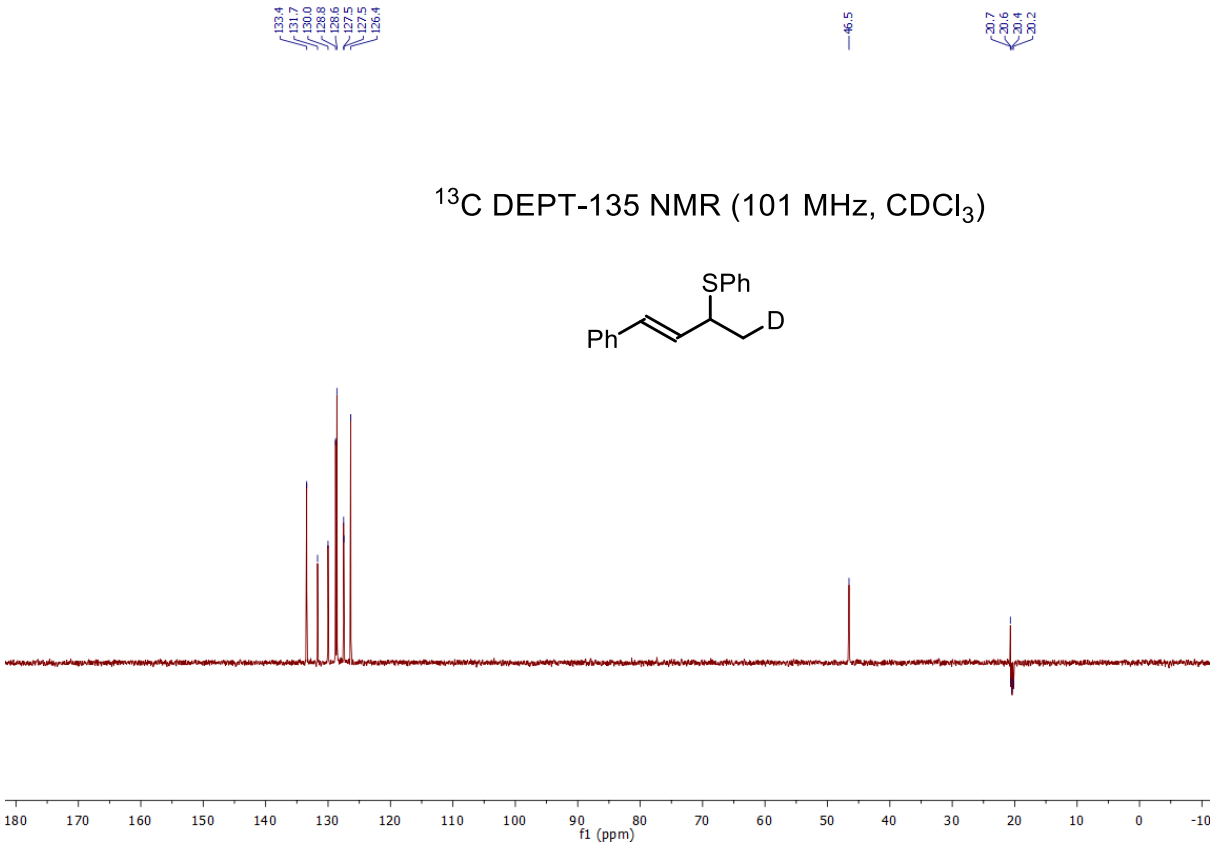




(*E*)-phenyl(4-phenylbut-3-en-2-yl)sulfane-d_1 (275a-d_1)






133.4
131.7
130.0
128.8
128.6
127.5
127.5
126.4
46.5
20.7
20.6
20.4
20.2
^{13}C DEPT-135 NMR (101 MHz, $CDCl_3$)
SPh
D
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Annexure-2

Experimental part of Chapter 3: **Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines**

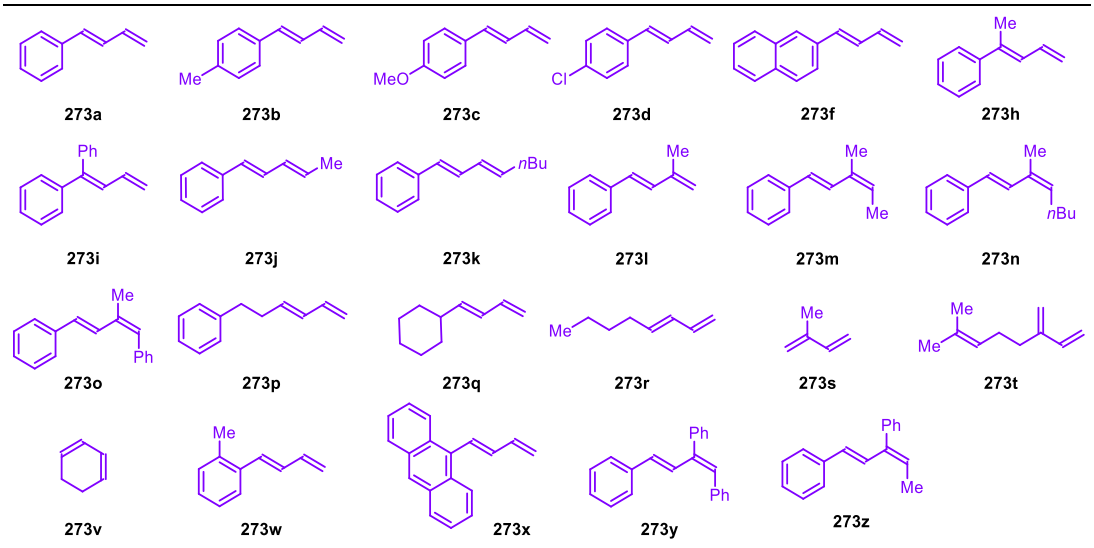
1. General Information

Reactions were performed in flame-dried glassware under aerobic condition unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled prior to use. $CDCl_3$ was stored over 4Å molecular sieves. Used chemicals were purchased from *Sigma-Aldrich*, *TCI*, *A*lfa-*A*esar and *Sisco Research Laboratories (SRL)* used without further purification. All the liquid chemicals and solvents were distilled freshly prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from *Merck* using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 unless otherwise stated on JEOL JNM ECS-400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for **^{1}H NMR** and $CDCl_3$: δ = 77.16 ppm for **^{13}C NMR**; DMSO-d_6: δ = 2.50 ppm for **^{1}H NMR** and DMSO-d_6: δ = 39.52 ppm for **^{13}C NMR**). Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2-XS QTOF. All the X-ray data were recorded on Bruker D8 venture instrument. Dienes **273s, 273t, 273v** and arylamines **315a, 315b, 315c, 315d, 315g, 315h, 315j** has been obtained from commercial sources. Dienes **273a-273r**, **273u**[133] and arylamines **315a-*d*$_1$, 315a-*d*$_6$, 315a-*d*$_7$ 315e, 315f, 315h, 315h-*d*$_6$, 315i, 315k, 315l** [139, 140, 141] were synthesized according to the procedure in the literature.

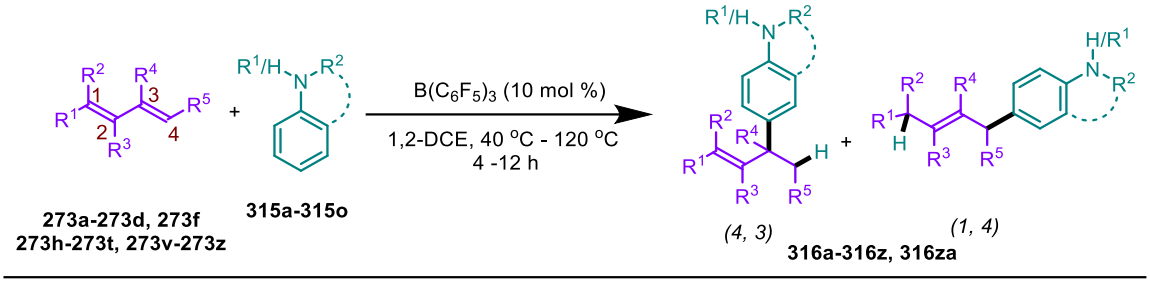
Computational Details: The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.4 suite of programs[93a] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(DCE) level of theory, which combines the TPSS meta-GGA density functional[93f] with the BJ-damped DFT-D3 dispersion correction[93l, 93m] and the def2-TZVP basis set, [93d, 93i] using the Conductor-like Screening Model (COSMO) continuum solvation model[93b] for 1,2-dichloroethane (DCE) solvent (dielectric constant ε = 10.5 and solvent diameter R_{solv} = 3.36 Å). The density-fitting RI-J approach[93c, 93d, 93k] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[93h] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima

and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model. [93n] This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in DCE solution are computed with the COSMO-RS solvation model[93e] (parameter file: BP_TZVP_19.ctd) using the COSMOtherm program package[93o] on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol^{-1} to account for higher reference solute concentration of 1 mol·L^{-1} usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at both the meta-GGA TPSS-D3[93f] and hybrid-meta-GGA PW6B95-D3[93o] levels are performed using a larger def2-QZVP basis set. [93g, 93i] The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. The computed reaction free energies from both DFT functionals are in good mutual agreement with the mean, mean absolute and standard deviations being 0.2, 1.0 and 1.5 kcal/mol for reaction energies and 4.3, 4.3 and 1.2 kcal/mol for transition barriers, respectively, with about 4.3 kcal/mol higher barriers found at the PW6B95-D3 level. In our discussion, higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L concentration) will be used in our discussion unless specified otherwise. The applied DFT methods in combination with the large AO basis set provide usually accurate electronic energies leading to errors for chemical energies (including barriers) on the order of typically 1-2 kcal/mol. This has been tested thoroughly for the huge data base GMTKN55[148] which is the common standard in the field of DFT benchmarking.



2. General Procedure for the Reaction of 1,3-Dienes and Arylamines (GP):



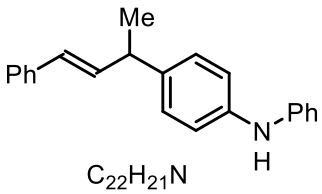
Procedure A : In an argon filled glove box, an oven-dried glass vial is charged with a magnetic stir bar, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (10.0 mol %) and 1,2-DCE (0.15 M) (dry and distilled). Arylamine **315a-315o** (1.5 equiv) and diene **273a-273z** (1.0 equiv) simultaneously added to the mixture. The vial has been taken out from the glove box and stirred for four hours at preheated oil bath at 40 ^{o}C temperature. The crude reaction mixture is used to measure the regiomeric ratio (*rr*) and *E*/*Z* ratio by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and dichloromethane (DCM) or EtOAc as eluent.

Procedure B: In an argon filled glove box, an oven-dried glass vial is charged with a magnetic stir bar, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (10.0 mol %) and 1,2-DCE (0.15 M) (dry and distilled). Arylamine **315a-315o** (1.5 equiv) and diene **273a-273z** (1.0 equiv) simultaneously added to the mixture. The vial has been taken out from the glove box and stirred for four to twelve hours at preheated oil bath at 80 ^{o}C temperature. The crude reaction mixture is used to measure the regiomeric ratio (*rr*) and *E*/*Z* ratio by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and dichloromethane (DCM) or EtOAc as eluent.

Procedure C: In an argon filled glove box, an oven-dried sealed tube is charged with a magnetic stir bar, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (10.0 mol %) and 1,2-DCE (0.15 M) (dry and distilled). Arylamine **315a-315o** (1.5 equiv) and diene **273a-273z** (1.0 equiv) simultaneously added to the mixture. The vial has been taken out from the glove box and stirred for four hours at preheated oil bath at 120 ^{o}C temperature. The crude reaction mixture is used to measure the regiomeric ratio (*rr*) and *E*/*Z* ratio by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and dichloromethane (DCM) or EtOAc as eluent.

3. Experimental Details for the Synthesized Compounds

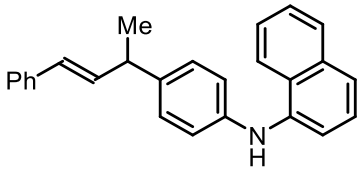
3.1 (*E*)-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline (316a)



$C_{22}H_{21}N$
M = 299.41 g/mol

Prepared according to the **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a** (32.0 mg, 90%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{22}H_{22}N^+$ 300.1747; found 300.1771. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.32–7.25 (m, 4H), 7.23–7.17 (m, 3H), 7.09–7.06 (m, 4H), 6.94–6.90 (m, 1H), 6.46–6.36 (m, 2H), 3.65–3.58 (m, 1H), 1.47 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 141.1, 138.8, 137.7, 135.6, 129.5, 128.6, 128.4, 128.3, 127.1, 126.3, 120.9, 118.7, 117.5, 42.0, 21.4.

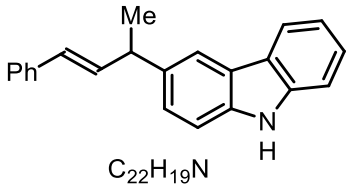
3.2 (*E*)-*N*-(4-(4-phenylbut-3-en-2-yl)phenyl)naphthalen-1-amine (316b)



$C_{26}H_{23}N$
M = 349.18 g/mol

Prepared according to the **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315b** (39.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316b** (41.0 mg, 98%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{26}H_{24}N^+$ 350.1903; found 350.1883. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.19–8.16 (m, 1H), 8.14 (s, 1H), 7.89–7.85 (m, 1H), 7.52–7.46 (m, 3H), 7.41–7.39 (m, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28 (q, *J* = 7.4 Hz, 3H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.18–7.14 (m, 2H), 7.04 (m, 2H), 6.49–6.39 (m, 2H), 3.60–3.54 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 142.9, 139.9, 137.2, 136.8, 135.8, 134.4, 128.6, 128.1, 127.7, 127.5, 127.0, 126.6, 126.2, 126.0 (2C), 124.9, 122.7, 120.8, 117.8, 112.9, 41.4, 21.4.

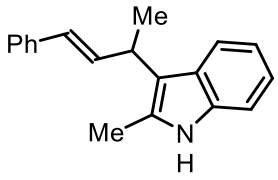
3.3 (*E*)-3-(4-phenylbut-3-en-2-yl)-9*H*-carbazole (316c)



$C_{22}H_{19}N$
M = 297.40 g/mol

Prepared according to the **GP-B**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315c** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %) stirred for 12 h. Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316d** (29.0 mg, 82%) as white solid. **Melting point:** 142-143 ^oC. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{22}H_{20}N^+$ 298.1590; found 298.1589. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 1H), 8.00 (s, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.44–7.37 (m, 5H), 7.35–7.32 (m, 1H), 7.31–7.27 (m, 2H), 7.24–7.18 (m, 2H), 6.55–6.44 (m, 2H), 3.87–3.80 (m, 1H), 1.58 (d, *J* = 7.8 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 138.3, 137.8, 136.9, 136.2, 128.6, 128.2, 127.1, 126.3, 125.9, 125.8, 123.6, 123.4, 120.4, 119.4, 118.7, 110.7, 110.6, 42.7, 21.9.

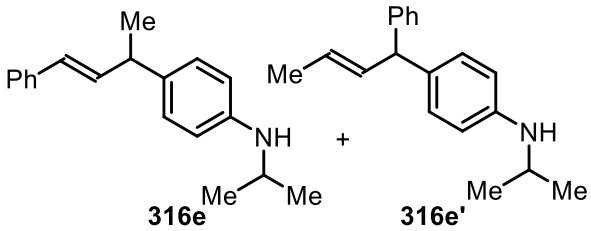
3.4 (*E*)-2-methyl-3-(4-phenylbut-3-en-2-yl)-1*H*-indole (316d)



$C_{19}H_{19}N$
M = 261.37 g/mol

Prepared according to the **GP-B**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315d** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %) stirred for 4 h. Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316d** (31.0 mg, 98%) as colorless gel turned into blue colored at rt. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{19}H_{20}N^+$ 262.1590; found 262.1598. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29–7.26 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.61 (dd, *J* = 16.0, 5.5 Hz, 1H), 6.45 (dd, *J* = 16.2, 1.8 Hz, 1H), 3.95–3.89 (m, 1H), 2.42 (s, 3H), 1.58 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 135.4, 135.3, 130.4, 128.6, 127.9, 127.7, 126.9, 126.2, 120.9, 119.4, 119.1, 114.9, 110.4, 33.7, 20.4, 12.4.

3.5 (*E*)-*N*-isopropyl-4-(4-phenylbut-3-en-2-yl)aniline and (*E*)-*N*-isopropyl-4-(1-phenylbut-2-en-1-yl)aniline (316e + 316e')



316e **316e'**

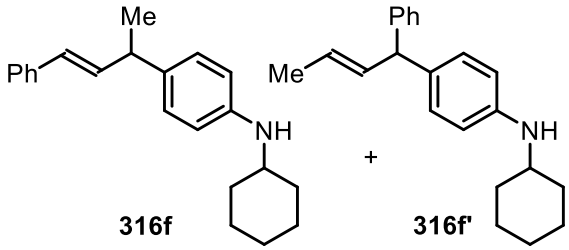
(316e:316e' = 1.6:1.0 from crude)

$C_{19}H_{23}N$

M = 265.00 g/mol

Prepared according to the **GP-C**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **316e** (24.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.7:0.3 v/v) as eluent afforded the product **316e + 316e'** (17.0 mg, 54%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{19}H_{24}N^+$ 266.1903; found 266.1917. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.34 (m, 2H), 7.32–7.25 (m, 5H), 7.22–7.16 (m, 3H), 7.11–7.07 (m, 2H), 7.01–6.97 (m, 2H), 6.63 (dd, *J* = 20.5, 8.1 Hz, 3H), 6.46–6.32 (m, 2H), 5.91–5.85 (m, 1H), 5.44–5.38 (m, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 3.63–3.51 (m, 3H), 1.73–1.70 (m, 3H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.21 (t, *J* = 6.3 Hz, 11H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 137.8, 136.0, 134.2, 129.4, 128.6, 128.4, 128.3, 128.0, 127.0, 126.5, 126.2, 126.1, 114.6, 114.2, 53.3, 41.8, 29.9, 22.8 (2C), 21.4, 21.1, 18.2.

3.6 (*E*)-*N*-cyclohexyl-4-(4-phenylbut-3-en-2-yl)aniline and (*E*)-*N*-cyclohexyl-4-(1-phenylbut-2-en-1-yl)aniline (316f + 316f')



316f **316f'**

(316f:316f' = 1.6:1.0 from crude)

$C_{22}H_{27}N$

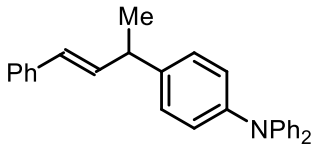
M = 305.47 g/mol

Prepared according to the **GP-C**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315f** (32.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %).

Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.7:0.3 v/v) as eluent afforded the product **316f + 316f'** (20.0 mg, 54%,) as colorless oil.

HRMS (ESI) *m/z*: [(M+H)$^+$] calcd for $C_{22}H_{28}N^+$ 306.2216; found 306.2209. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.23 (m, 4H), 7.21–7.14 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 0.44H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.70–6.58 (m, 3H), 6.41–6.31 (m, 0.48H), 5.91–5.84 (m, 1H), 5.46–5.37 (m, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 3.57–3.51 (m, 0.30H), 3.24–3.16 (m, 1H), 2.06–2.01 (m, 3H), 1.77–1.70 (m, 7H), 1.64–1.60 (m, 2H), 1.42 (d, *J* = 7.0 Hz, 1H), 1.38–1.27 (m, 4H), 1.24–1.13 (m, 4H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 136.0, 134.2, 129.9, 129.4, 128.7, 128.6, 128.4, 128.3, 127.0, 126.5, 126.2, 126.1, 114.5, 114.4, 53.4, 41.8, 33.2, 25.9, 25.1, 18.1.

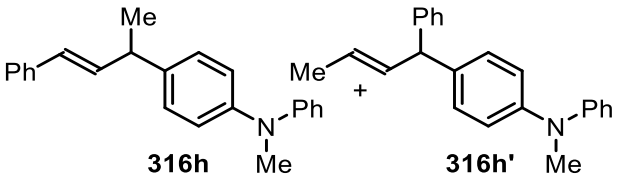
3.7 (*E*)-*N*,*N*-diphenyl-4-(4-phenylbut-3-en-2-yl)aniline (316g)



$C_{28}H_{25}N$
M = 375.52 g/mol

Prepared according to the **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315g** (44.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316g** (40.0 mg, 88%) as colorless gel. **HRMS** (ESI) *m/z*: [(M+H)$^+$] calcd for $C_{28}H_{26}N^+$ 376.2060; found 376.2030. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27–7.21 (m, 5H), 7.18–7.15 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 4H), 7.07–7.04 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.47–6.36 (m, 2H), 3.65–3.58 (m, 1H), 1.48 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.0, 140.2, 137.7, 135.5, 129.3, 128.6, 128.4, 128.1, 127.2, 126.3, 124.6, 124.0, 122.5, 42.2, 21.3.

3.8 (*E*)-*N*-methyl-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline and (*E*)-*N*-methyl-*N*-phenyl-4-(1-phenylbut-2-en-1-yl)aniline (316h + 316h′)

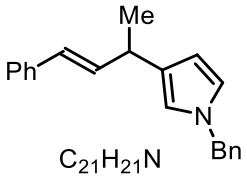


(316:316h' = 1.0:0.6 from crude)

$C_{23}H_{23}N$
M : 313.44 g/mol

Prepared according to the **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315h** (33.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316h + 316h'** (32.0 mg, 86%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{23}H_{24}N^+$ 314.1903; found 314.1904. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.32–7.18 (m, 7H), 7.04–6.97 (m, 4H), 6.94–6.90 (m, 1H), 6.46–6.36 (m, 2H), 3.65–3.59 (m, 1H), 3.32 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 147.3, 139.2, 137.8, 135.6, 129.2, 128.6, 128.4, 128.2, 127.1, 126.3, 121.7, 120.6, 119.4, 42.1, 40.4, 21.4.

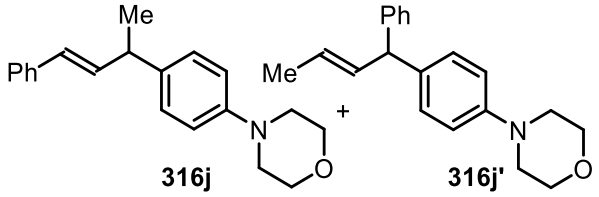
3.9 (*E*)-1-benzyl-3-(4-phenylbut-3-en-2-yl)-1*H*-pyrrole (316i)



$C_{21}H_{21}N$
M : 287.41 g/mol

Prepared according to the **GP-B**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315i** (29.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %) stirred for 12 h. Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316i** (20.0 mg, 58%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{21}H_{22}N^+$ 288.1747; found 288.1750. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.18 (m, 8H), 6.98–6.95 (m, 2H), 6.66–6.60 (m, 1H), 6.26–6.17 (m, 3H), 6.10–6.08 (m, 1H), 5.17–5.02 (m, 2H), 3.51–3.44 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 137.4, 136.0, 134.7, 128.8, 128.7, 128.6, 127.4, 127.2, 126.4, 126.3, 121.8, 107.2, 105.5, 50.4, 34.8, 20.6.

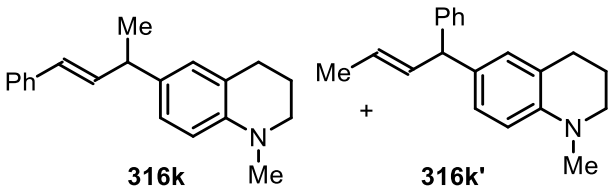
3.10 (*E*)-4-(4-(4-phenylbut-3-en-2-yl)phenyl)morpholine and (*E*)-4-(4-(1-phenylbut-2-en-1-yl)phenyl)morpholine (316j + 316j')



(316j:316j' = 3.0:1.0 from crude)
$C_{20}H_{23}NO$
M = 293.41 g/mol

Prepared according to the **GP-C**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315j** (29.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316j + 316j'** (19 mg, 57%,) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{20}H_{24}NO^+$ 294.1853; found 294.1845. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2H), 7.31–7.28 (m, 2H), 7.21–7.17 (m, 3.54H), 7.10–7.08 (m, 0.50H), 6.90–6.88 (m, 2H), 6.86–6.84 (m, 0.49H), 6.43–6.33 (m, 2H), 5.92–5.86 (m, 0.31H), 5.45–5.40 (m, 0.31H), 4.60 (d, *J* = 7.7 Hz, 0.26H), 3.87–3.84 (m, 4.60H), 3.61–3.55 (m, 1H), 3.15–3.11 (m, 4.64H), 1.73–1.71 (m, 0.71H), 1.44 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 137.8, 137.3, 135.8, 133.9, 129.3, 128.6 (2C), 128.4, 128.3, 128.1, 127.1, 126.7, 126.2 (2C), 116.0, 115.8, 67.1, 53.3, 49.7, 49.6, 41.8, 21.3.

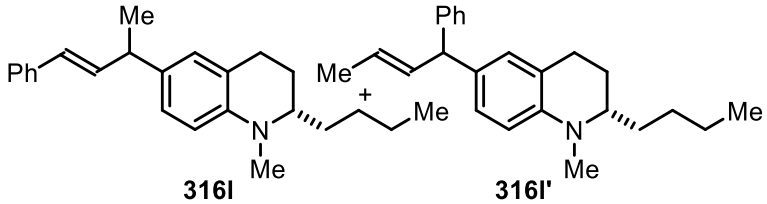
3.11 (*E*)-1-methyl-6-(4-phenylbut-3-en-2-yl)-1,2,3,4-tetrahydroquinoline and (*E*)-1-methyl-6-(1-phenylbut-2-en-1-yl)-1,2,3,4-tetrahydroquinoline (316k + 316k')



(316k:316k' = 1.0:3.5 from Crude)
$C_{20}H_{23}N$
M = 277.41 g/mol

Prepared according to the **GP-C**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315k** (28.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316k + 316k'** (19 mg, 57%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{20}H_{24}N^+$ 278.1903; found 278.1896. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 0.31H), 7.32–7.28 (m, 2.14H), 7.23–7.16 (m, 3H), 7.01 (dd, *J* = 8.5, 2.3 Hz, 0.16H), 6.90 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 0.11H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 0.19H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.58–6.56 (m, 0.30H), 5.94–5.88 (m, 1H), 5.59–5.40 (m, 1H), 4.55 (d, *J* = 7.8 Hz, 1H), 3.56–3.50 (m, 0.16H), 3.23–3.19 (m, 2.61H), 2.89 (s, 0.47H), 2.87 (s, 3H), 2.80–2.70 (m, 2.32H), 2.04–1.95 (m, 2.76H), 1.76–1.73 (m, 3H), 1.44 (d, *J* = 7.2 Hz, 0.48H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 138.0, 136.3, 134.4, 132.2, 129.0, 128.6, 128.3, 128.0, 127.8, 127.0, 126.2 (2C), 126.0, 125.8, 125.6, 123.2, 123.0, 111.5, 111.2, 53.4, 51.4, 41.7, 40.1, 39.4, 38.6, 34.2, 27.9, 22.8, 22.6, 21.4, 18.2.

3.12 1-((2S)-1-methyl-6-((*E*)-4-phenylbut-3-en-2-yl)-1,2,3,4-tetrahydroquinolin-2-yl)butan-2-ylium and (2S)-2-butyl-1-methyl-6-((*E*)-1-phenylbut-2-en-1-yl)-1,2,3,4-tetrahydroquinoline (316l + 316l')



316l **316l'**

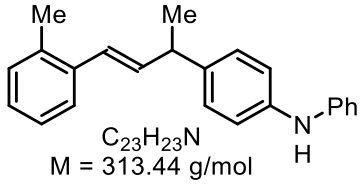
(316l:316l' = 1.0:3.5 from crude)

$C_{24}H_{31}N$

M = 333.52 g/mol

Prepared according to the **GP-C**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315m** (34.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (7:3 v/v) as eluent afforded the product **316l'** (19 mg, 57%) as Yellow oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{24}H_{32}N^+$ 334.2530; found 334.2537. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.22–7.16 (m, 3H), 6.87 (d, *J* = 6.8 Hz, 1H), 6.78 (t, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 5.93–5.87 (m, 1H), 5.48–5.39 (m, 1H), 4.53 (d, *J* = 7.9 Hz, 1H), 3.20 (d, *J* = 8.3 Hz, 1H), 2.90 (s, 3H), 2.80–2.72 (m, 1H), 2.60 (d, *J* = 16.5 Hz, 1H), 1.89–1.85 (m, 2H), 1.72 (dd, *J* = 6.6, 1.4 Hz, 3H), 1.44–1.22 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 143.9, 134.5, 130.9, 128.8, 128.6, 128.3, 127.0, 126.0 (2C), 121.9, 110.3, 59.1, 53.4, 38.1, 31.0, 28.4, 24.6, 23.8, 23.0, 18.2, 14.3.

3.13 (*E*)-*N*-phenyl-4-(4-(o-tolyl)but-3-en-2-yl)aniline (316m)



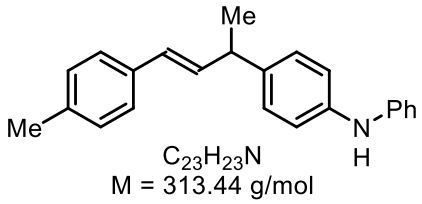
$C_{23}H_{23}N$

M = 313.44 g/mol

Prepared according to the **GP-A**, using **273w** (17.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316m** (33.0 mg, 85%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{23}H_{24}N^+$ 314.1903, found 314.1903. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.39 (m, 1H), 7.23–7.20 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.11–7.09 (m, 3H), 7.03–7.00 (m, 4H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.24–6.19 (m, 1H), 5.62 (s, 1H), 3.62–3.56 (m, 1H), 2.31 (s, 3H), 1.44 (d, *J*

= 7.0 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.7, 141.2, 138.7, 137.1, 136.9, 135.2, 130.3, 129.4, 128.2, 127.1, 126.2, 126.1, 125.6, 120.7, 118.6, 117.4, 42.3, 21.5, 20.0.

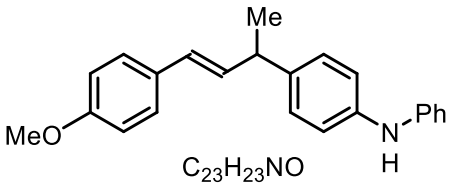
3.14 (*E*)-*N*-phenyl-4-(4-(*p*-tolyl)but-3-en-2-yl)aniline (316n)



$C_{23}H_{23}N$
M = 313.44 g/mol

Prepared according to the **GP-A**, using **273b** (17.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316n** (34.0 mg, 90%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{23}H_{24}N^+$ 314.1903; found 314.1910. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 4H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.09–7.06 (m, 4H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.42–6.30 (m, 2H), 3.63–3.57 (m, 1H), 2.34 (s, 3H), 1.46 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 141.0, 138.9, 136.8, 134.9, 134.6, 129.5, 129.3, 128.3, 128.2, 126.1, 120.8, 118.7, 117.4, 42.0, 21.4, 21.3.

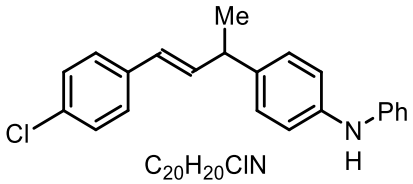
3.15 (*E*)-4-(4-(4-methoxyphenyl)but-3-en-2-yl)-*N*-phenylaniline (316o)



$C_{23}H_{23}NO$
M = 329.44 g/mol

Prepared according to the **GP-A**, using **273c** (19.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316o** (32.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{23}H_{24}NO^+$ 330.1853; found 330.1855. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 4H), 7.20–7.15 (m, 2H), 7.10–7.03 (m, 4H), 6.93–6.90 (m, 1H), 6.86–6.82 (m, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.27–6.21 (m, 1H), 3.80 (s, 3H), 3.62–3.55 (m, 1H), 1.45 (d, *J* = 7.0, 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 143.6, 141.0, 139.1, 133.6, 130.6, 129.5, 128.3, 127.7, 127.4, 120.9, 118.7, 117.5, 114.0, 55.4, 42.0, 21.5.

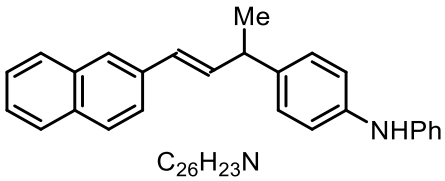
3.16 ((*E*)-4-(4-(4-chlorophenyl)but-3-en-2-yl)-*N*-phenylaniline (316p)



$C_{20}H_{20}ClN$
M = 333.86 g/mol

Prepared according to the **GP-A**, using **273d** (20.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316p** (32.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{20}H_{21}ClN^+$ 334.1357; found 334.1361. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 6H), 7.18–7.15 (m, 2H), 7.10–7.04 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.40–6.31 (m, 2H), 3.63–3.56 (m, 1H), 1.46 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 141.3, 138.3, 136.4, 136.2, 132.6, 129.5, 128.7, 128.3, 127.5, 127.2, 120.9, 118.6, 117.5, 42.0, 21.3.

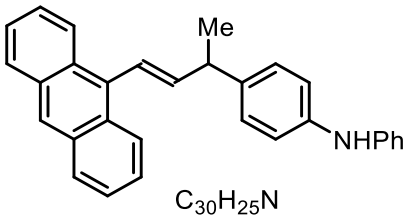
3.17 (*E*)-4-(4-(naphthalen-2-yl)but-3-en-2-yl)-*N*-phenylaniline (316q)



$C_{26}H_{23}N$
M = 349.48 g/mol

Prepared according to the **GP-A**, using **273f** (22.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316q** (36.0 mg, 85%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{26}H_{24}N^+$ 350.1903; found 350.1901. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 3H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.47–7.40 (m, 2H), 7.30–7.19 (m, 4H), 7.14–7.03 (m, 4H), 6.95–6.91 (m, 1H), 6.60–6.48 (m, 2H), 3.70–3.63 (m, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 141.1, 138.8, 136.1, 135.2, 133.8, 132.8, 129.5, 128.5, 128.3, 128.2, 128.0, 127.8, 126.3, 125.9, 125.7, 123.8, 121.0, 118.7, 117.6, 42.2, 21.4.

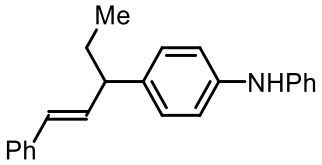
3.18 (*E*)-4-(4-(anthracen-9-yl)but-3-en-2-yl)-*N*-phenylaniline (316r)



$C_{30}H_{25}N$
M = 399.54 g/mol

Prepared according to the **GP-A**, using **273x** (28.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (7:3 v/v) as eluent afforded the product **316r** (41.0 mg, 85%) as yellow oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{30}H_{26}N^+$ 400.2060; found 400.2065. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.51 (s, 1H), 8.26–8.22 (m, 2H), 8.09–8.05 (m, 2H), 7.52–7.48 (m, 4H), 7.34–7.30 (m, 2H), 7.23–7.18 (m, 3H), 7.14 (s, 1H), 7.12–7.09 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.13 (dd, *J* = 16.1, 6.9 Hz, 1H), 3.93–3.86 (m, 1H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 144.3, 143.8, 141.5, 136.6, 132.7, 131.0, 129.2, 128.9, 128.6, 127.9, 125.8, 125.7, 125.6, 125.3, 123.2, 119.3, 117.4, 116.3, 42.1, 21.4.

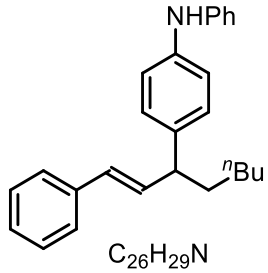
3.19 (*E*)-*N*-phenyl-4-(1-phenylpent-1-en-3-yl)aniline (316s)



$C_{23}H_{23}N$
M = 313.44 g/mol

Prepared according to the **GP-A**, using **273j** (24.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316s** (30.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{23}H_{24}N^+$ 314.1903; found 314.1895. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–735 (m, 2H), 7.31–7.24 (m, 4H), 7.21–7.08 (m, 7H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.42–6.28 (m, 2H), 3.27 (q, *J* = 7.5 Hz, 1H), 1.85–1.77 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 140.7, 138.1, 137.8, 134.5, 129.5, 129.3, 128.7, 128.6, 127.1, 126.2, 121.3, 118.9, 117.8, 50.4, 28.9, 12.5.

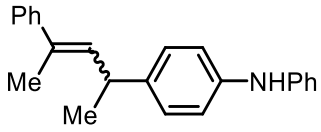
3.20 (*E*)-*N*-phenyl-4-(1-phenyloct-1-en-3-yl)aniline (316t)



$C_{26}H_{29}N$
M = 355.52 g/mol

Prepared according to the **GP-A**, using **273k** (22.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316t** (34.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{26}H_{30}N^+$ 356.2373; found 356.2378. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.34–7.26 (m, 4H), 7.24–7.17 (m, 3H), 7.11–7.06 (m, 4H), 6.96–6.91 (m, 1H), 6.45–6.32 (m, 2H), 3.42–3.36 (m, 1H), 1.86–1.78 (m, 2H), 1.40–1.29 (m, 6H), 0.94–0.90 (m, 3H).). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 141.1, 137.8 (2C), 134.9, 129.4, 129.1, 128.6 (2C), 127.1, 126.2, 120.7, 118.6, 117.4, 48.6, 36.0, 32.0, 27.5, 22.7, 14.3.

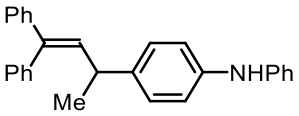
3.21 *N*-phenyl-4-(4-phenylpent-3-en-2-yl)aniline (316u)



[*E:Z* = 3:1] from crude
$C_{23}H_{23}N$
M = 313.44 g/mol

Prepared according to the **GP-A**, using **273h** (17.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316u** (30.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{23}H_{24}N^+$ 314.1903; found 314.1907. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.34–7.19 (m, 7H), 7.04–7.01 (m, 4H), 6.93–6.89 (m, 1H), 5.92–5.90 (m, 1H), 3.87–3.79 (m, 1H), 2.12 (d, *J* = 1.5 Hz, 3H), 1.42 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 143.7, 140.9, 139.7, 133.8, 133.8, 129.4, 128.3, 127.9, 126.8, 125.9, 120.7, 118.7, 117.4, 38.1, 22.5, 16.2.

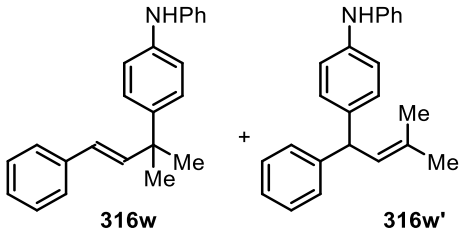
3.22 4-(4,4-diphenylbut-3-en-2-yl)-*N*-phenylaniline (316v)



$C_{28}H_{25}N$
M = 375.51 g/mol

Prepared according to the **GP-A**, using **273** (25.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316v** (36.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{28}H_{26}N^+$ 376.2060; found 376.2071. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 3H), 7.28–7.19 (m, 9H), 7.13–7.09 (m, 2H), 7.06–7.01 (m, 4H), 6.92–6.88 (m, 1H), 6.20 (d, *J* = 10.3 Hz, 1H), 5.64 (s, 1H), 3.60–3.52 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 140.2, 140.0, 134.5, 130.0, 129.8, 129.5, 128.8, 128.4, 128.2, 128.0, 127.4, 127.2, 127.1, 126.0, 121.3, 119.0, 117.8, 38.7, 22.4.

3.23 (*E*)-4-(2-methyl-4-phenylbut-3-en-2-yl)-*N*-phenylaniline and 4-(3-methyl-1-phenylbut-2-en-1-yl)-*N*-phenylaniline (316w + 316w')

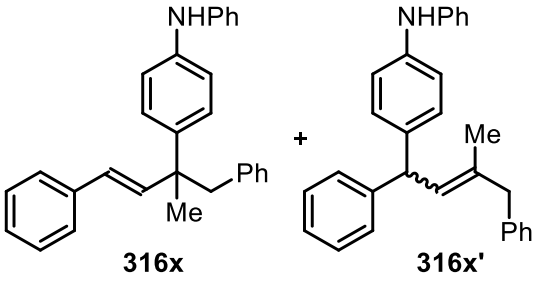


316w **316w'**

(316w:316w' = 1:1 from crude)
$C_{23}H_{23}N$
M = 313.44 g/mol

Prepared according to the **GP-A**, using **273l** (17.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316w + 316w'** (36.0 mg, 95%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{23}H_{24}N^+$ 314.1903; found 314.1905. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.33–7.17 (m, 14H), 7.11–7.02 (m, 10H), 6.94–6.90 (m, 2H), 6.46-6.38 (m, 2H), 5.64–5.60 (m, 1H), 4.84 (d, *J* = 9.5 Hz, 1H), 1.80 (d, *J* = 1.5 Hz, 3H), 1.74 (d, *J* = 1.6 Hz, 3H), 1.51 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 143.2, 141.9, 140.8, 140.7, 140.5, 138.5, 137.8, 132.4, 129.5, 129.2, 128.7, 128.5, 128.3, 127.6, 127.3, 127.1, 126.3, 126.1, 126.0, 121.1 (2C), 118.6, 118.2, 117.7 (2C), 48.9, 40.4, 28.9, 26.1, 18.2.

3.24 (*E*)-4-(2-methyl-1,4-diphenylbut-3-en-2-yl)-*N*-phenylaniline and 4-(3-methyl-1,4-diphenylbut-2-en-1-yl)-*N*-phenylaniline (316x+316x')



316x **316x'**

316x:316x' = 1.0:10.0 from crude

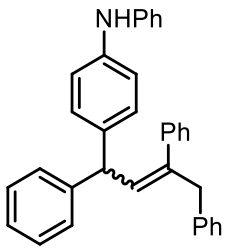
[316x' *E:Z* = 1.0:0.44] from crude

$C_{29}H_{27}N$

M = 389.54 g/mol

Prepared according to the **GP-A**, using **273o** (26.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316x + 316x'** (37.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{29}H_{28}N^+$ 390.2216; found 390.2224. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 1H), 7.33–7.26 (m, 6H), 7.25–7.15 (m, 9H), 7.13–7.03 (m, 7H), 6.96–6.89 (m, 2H), 6.53 (d, *J* = 16.1 Hz, 0.26H), 6.35 (d, *J* = 16.3 Hz, 0.27H), 5.81–5.77 (m, 1.10H), 5.00 (d, *J* = 9.7 Hz, 0.10H), 4.88 (d, *J* = 9.5 Hz, 1H), 3.49 (s, 0.20H), 3.39 (s, 2H), 3.14 (d, *J* = 3.1 Hz, 0.50H), 1.72 (d, *J* = 0.9 Hz, 0.31H), 1.65 (d, *J* = 0.9 Hz, 3H), 1.42 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 145.4, 143.5, 141.2 (2C), 141.1, 140.8, 140.5, 140.2, 139.7, 139.4, 138.3, 138.0, 137.9 (2C), 135.2, 134.6, 130.9, 129.7, 129.5 (2C), 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5 (2C), 128.4 (2C), 128.2 (2C), 128.1, 127.6, 127.2 (2C), 126.3, 126.2 (3C), 126.1, 125.9, 120.8, 118.4, 118.3, 118.1, 117.9, 117.5 (2C), 117.4, 48.9, 48.8, 48.5, 46.5, 44.5, 38.2, 25.1, 23.7, 16.3.

3.25 *N*-phenyl-4-(1,3,4-triphenylbut-2-en-1-yl)aniline (316y)



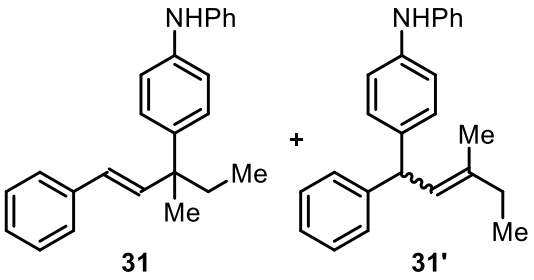
[*E:Z* = 3.0:1.0] from crude

$C_{34}H_{29}N$

M = 451.61 g/mol

Prepared according to the **GP-A**, using **273y** (34.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316y** (38.0 mg, 70%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{34}H_{30}N^+$ 452.2373; found 452.2381. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.11 (s, 1H), 7.31–7.25 (m, 4.80H), 7.24–7.16 (m, 7.18H), 7.13–7.09 (m, 5.34H), 7.07–7.02 (m, 5.33H), 7.01–6.96 (m, 3.65H), 6.78 (t, *J* = 7.3 Hz, 1.12H), 6.53 (d, *J* = 10.1 Hz, 0.12H), 6.16 (d, *J* = 10.6 Hz, 1H), 5.15 (d, *J* = 10.1 Hz, 0.12H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.03 (s, 0.24H), 3.76 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 145.1, 143.6, 141.5, 139.6, 139.4, 139.3, 135.8, 130.9, 129.1, 128.7, 128.5, 128.4, 128.2, 128.1, 127.7, 127.0, 126.4, 126.0 (2C), 119.4, 117.1, 116.4, 48.9, 44.8.

3.26 (*E*)-4-(3-methyl-1-phenylpent-1-en-3-yl)-*N*-phenylaniline and 4-(3-methyl-1-phenylpent-2-en-1-yl)-*N*-phenylaniline (316z + 316z')



31 **31'**

31:31' = 1.0:2.0 from crude

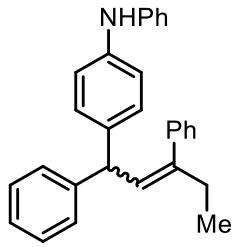
[31' *E:Z* = 1.0:0.8] from crude

$C_{24}H_{25}N$

M = 327.47 g/mol

Prepared according to the **GP-A**, using **273m** (19.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316z + 316z'** (29.0 mg, 75%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{24}H_{26}N^+$ 328.2060; found 328.2068. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2.33H), 7.33–7.17 (m, 26.25H), 7.10–7.01 (m, 18.59H), 6.93–6.89 (m, 3.16H), 6.41 (d, *J* = 2.7 Hz, 2H), 5.63–5.60 (m, 1.69H), 5.57 (d, *J* = 9.9 Hz, 0.89H), 4.86 (dd, *J* = 9.7, 3.4 Hz, 2.58H), 2.16 (q, *J* = 7.6 Hz, 1.82H), 2.10 (q, *J* = 7.5 Hz, 3.64H), 1.95–1.83 (m, 2H), 1.79 (d, *J* = 1.6 Hz, 2.57H), 1.72 (d, *J* = 1.6 Hz, 5.24H), 1.45 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 5.32H), 0.99 (t, *J* = 7.6 Hz, 2.55H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 143.4, 140.9, 140.8, 140.7, 139.6, 138.5, 138.4, 138.0, 137.9, 137.8, 129.4, 129.2, 128.7, 128.5, 128.4, 127.9, 127.1 (2C), 127.0, 126.3, 126.1 (2C), 120.9, 118.5, 118.1, 117.6, 48.6, 48.4, 43.8, 34.0, 32.6, 25.2, 25.1, 23.3, 16.5, 12.9, 9.3.

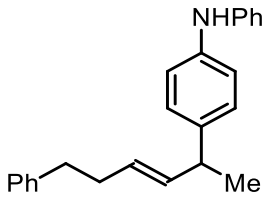
3.27 4-(1,3-diphenylpent-2-en-1-yl)-*N*-phenylaniline (316za)



[*E:Z* = 1.0:0.5] from crude
$C_{29}H_{27}N$
M = 389.54 g/mol

Prepared according to the **GP-A**, using **273z** (26.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316za** (32.0 mg, 70%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{29}H_{28}N^+$ 390.2216; found 390.2149. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69–7.66 (m, 1.14H), 7.61–7.43 (m, 14.77H), 7.41–7.38 (m, 5.13H), 7.33–7.27 (m, 4.47H), 7.18–7.14 (m, 1.56H), 6.35 (d, *J* = 9.8 Hz, 0.58H), 6.15 (dt, *J* = 10.4, 1.4 Hz, 1H), 5.92 (s, 1H), 5.30 (d, *J* = 9.8 Hz, 0.56H), 4.86 (d, *J* = 10.5 Hz, 1H), 2.90 (q, *J* = 7.6 Hz, 1H), 2.72–2.66 (m, 2H), 1.27 (dt, *J* = 12.4, 7.5 Hz, 4.62H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 145.2, 143.5 (2C), 143.1, 142.7, 141.9, 141.3, 141.2, 141.1, 138.0, 137.7, 130.6, 129.4, 129.3, 129.2, 128.6, 128.5, 128.4 (3C), 128.3, 128.2, 127.9, 127.0, 126.8, 126.7, 126.3, 126.1, 120.8 (2C), 118.3, 118.2, 117.5 (2C), 49.2, 49.0, 32.4, 23.4, 13.7, 13.1.

3.28 (*E*)-*N*-phenyl-4-(6-phenylhex-3-en-2-yl)aniline (316pa)

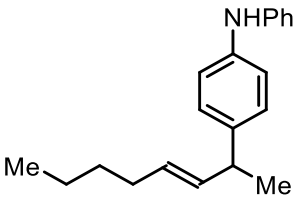


$C_{24}H_{25}N$
M = 327.47 g/mol

Prepared according to the **GP-A**, using **273p** (15.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316pa** (31.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{24}H_{26}N^+$ 328.2060; found 328.2054. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 4H), 7.21–7.17

(m, 3H), 7.13–7.05 (m, 6H), 6.92 (t, *J* = 7.3 Hz, 1H), 5.63–5.57 (m, 1H), 5.53–5.44 (m, 1H), 3.20 (q, *J* = 7.4 Hz, 1H), 2.66–2.52 (m, 2H), 2.00 (q, *J* = 7.8 Hz, 2H), 1.70 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 142.6, 140.9, 138.3, 135.3, 129.5, 128.6, 128.5, 128.4, 125.8, 124.9, 120.8, 118.7, 117.5, 47.8, 37.8, 33.9, 18.2.

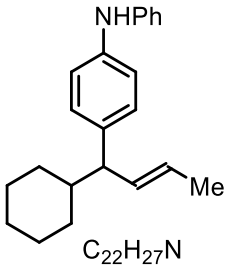
3.29 (*E*)-4-(oct-3-en-2-yl)-*N*-phenylaniline (316ra)



$C_{20}H_{25}N$
M = 279.43 g/mol

Prepared according to the **GP-A**, using **273r** (13.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316ra** (20.0 mg, 60%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{20}H_{26}N^+$ 280.2060; found 280.2044. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.03 (s, 1H), 7.21–7.16 (m, 2H), 7.05–6.94 (m, 6H), 6.76 (t, *J* = 7.3 Hz, 1H), 5.56–5.49 (m, 1H), 5.42–5.34 (m, 1H), 3.11–3.04 (m, 1H), 1.62–1.53 (m, 5H), 1.29–1.09 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 143.9, 141.1, 136.6, 136.0, 129.1, 127.8, 123.2, 119.1, 117.3, 116.0, 47.6, 35.4, 29.4, 22.1, 17.7, 14.0.

3.30 (*E*)-4-(1-cyclohexylbut-2-en-1-yl)-*N*-phenylaniline (316qa)

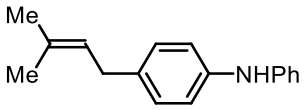


$C_{22}H_{27}N$
M = 305.47 g/mol

Prepared according to the **GP-A**, using **273q** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316qa** (22.0 mg, 60%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for

$C_{22}H_{28}N^+$ 306.2216; found 306.2212. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.08–7.01 (m, 6H), 6.90 (t, J = 7.3 Hz, 1H), 5.63–5.56 (m, 1H), 5.47–5.38 (m, 1H), 2.84 (t, J = 9.0 Hz, 1H), 1.91–1.86 (m, 1H), 1.77–1.63 (m, 5H), 1.54–1.43 (m, 2H), 1.34–1.10 (m, 4H), 0.95–0.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 140.6, 138.3, 134.2, 129.4, 128.8, 125.2, 120.7, 118.7, 117.3, 55.8, 42.7, 31.6, 31.5, 26.7, 26.6, 18.2.

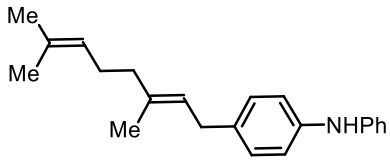
3.31 4-(3-methylbut-2-en-1-yl)-*N*-phenylaniline (316sa)



$C_{17}H_{19}N$
M = 237.34 g/mol

Prepared according to the **GP-A**, using **273s** (8.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316sa** (16.0 mg, 55%) as colorless oil. **HRMS** (ESI) *m/z*: [(M+H)$^+$] calcd for $C_{17}H_{20}N^+$ 238.1590; found 238.1597. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.11–7.08 (m, 2H), 7.05 – 7.03 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 1H), 5.36–5.31 (m, 1H), 3.31 (d, *J* = 7.3 Hz, 2H), 1.75 (d, *J* = 10.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 140.7, 135.1, 132.4, 129.4, 129.3, 123.6, 120.6, 119.0, 117.2, 33.8, 25.9, 18.0.

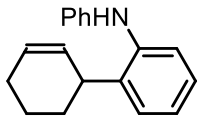
3.32 (*E*)-4-(3,7-dimethylocta-2,6-dien-1-yl)-*N*-phenylaniline (316ta)



$C_{27}H_{27}N$
M = 305.47 g/mol

Prepared according to the **GP-A**, using **273t** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316ta** (20.0 mg, 55%) as colorless oil. **HRMS** (ESI) *m/z*: [(M+H)$^+$] calcd for $C_{27}H_{28}N^+$ 306.2216; found 306.2225. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.11–7.08 (m, 2H), 7.04–7.00 (m, 4H), 6.91–6.87 (m, 1H), 5.62 (s, 1H), 5.35–5.31 (m, 1H), 5.18–5.11 (m, 1H), 3.31 (d, *J* = 7.3 Hz, 2H), 2.19–2.08 (m, 4H), 1.76 (d, *J* = 1.3 Hz, 3H), 1.70 (s, 3H), 1.63 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 140.8, 136.1, 135.0, 131.9, 129.4, 129.3, 124.4, 124.3, 120.5, 118.9, 117.1, 33.5, 32.1, 26.8, 25.9, 23.6, 17.8.

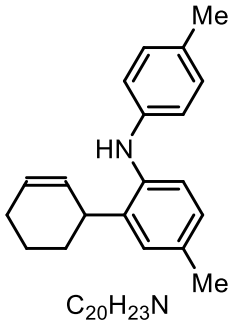
3.33 *N*-phenyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-amine (316ua)



$C_{18}H_{19}N$
M = 249.36 g/mol

Prepared according to the **GP-A**, using **273u** (10.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316ua** (18.0 mg, 60%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{18}H_{20}N^+$ 250.1590; found 250.1591. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.26–7.21 (m, 3H), 7.18–7.14 (m 1H), 7.01–6.93 (m, 3H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.01–5.96 (m, 1H), 5.76–5.72 (m, 1H), 3.61–3.55 (m, 1H), 2.12–2.07 (m, 2H), 2.00–1.91 (m, 1H), 1.80–1.72 (m, 1H), 1.68–1.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 140.6, 136.5, 130.1, 129.8, 129.4, 129.4, 127.0, 122.5, 120.8, 120.2, 116.8, 38.6, 29.7, 25.1, 21.6.

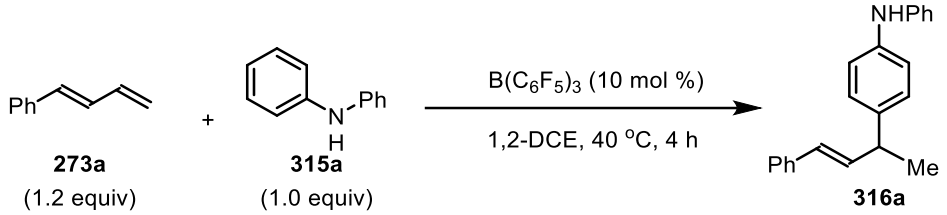
3.34 5-methyl-*N*-(*p*-tolyl)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-amine (316up)



$C_{20}H_{23}N$
M = 277.41 g/mol

Prepared according to the **GP-A**, using **273u** (10.0 mg, 0.12 mmol, 1.0 equiv), **315p** (35.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316up** (20.0 mg, 60%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{20}H_{24}N^+$ 278.1903; found 278.1916. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1H), 7.04–7.01 (m, 3H), 6.98–6.96 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 2H), 5.98–5.93 (m, 1H), 5.74–5.70 (m, 1H), 3.60–3.54 (m, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.12–2.05 (m, 2H), 1.98–1.91 (m, 1H), 1.79–1.72 (m, 1H), 1.67–1.57 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 138.4, 136.8, 131.9, 130.3, 130.2, 129.9, 129.1 (2C), 127.6, 121.3, 116.6, 38.4, 30.0, 25.1, 21.7, 21.0, 20.7.

4. Gram scale synthesis



Gram scale synthesis has been done by using the **GP-A, 273a** (550.0 mg, 4.22 mmol, 1.0 equiv), **315a** (1057.11 mg, 6.33 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$ 197.0 mg, 0.38 mmol, 10.0 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a** (1.02 g, 81%) as colorless oil.

5. Detection of the contact ion pair 315aH^+HOBCF^- and H_2O·BCF adduct

To identify the contact ion pair (in case of secondary amine) and H_2O-BCF adduct formation (in case of tertiary amine). Two separate experiments have been performed as follows-

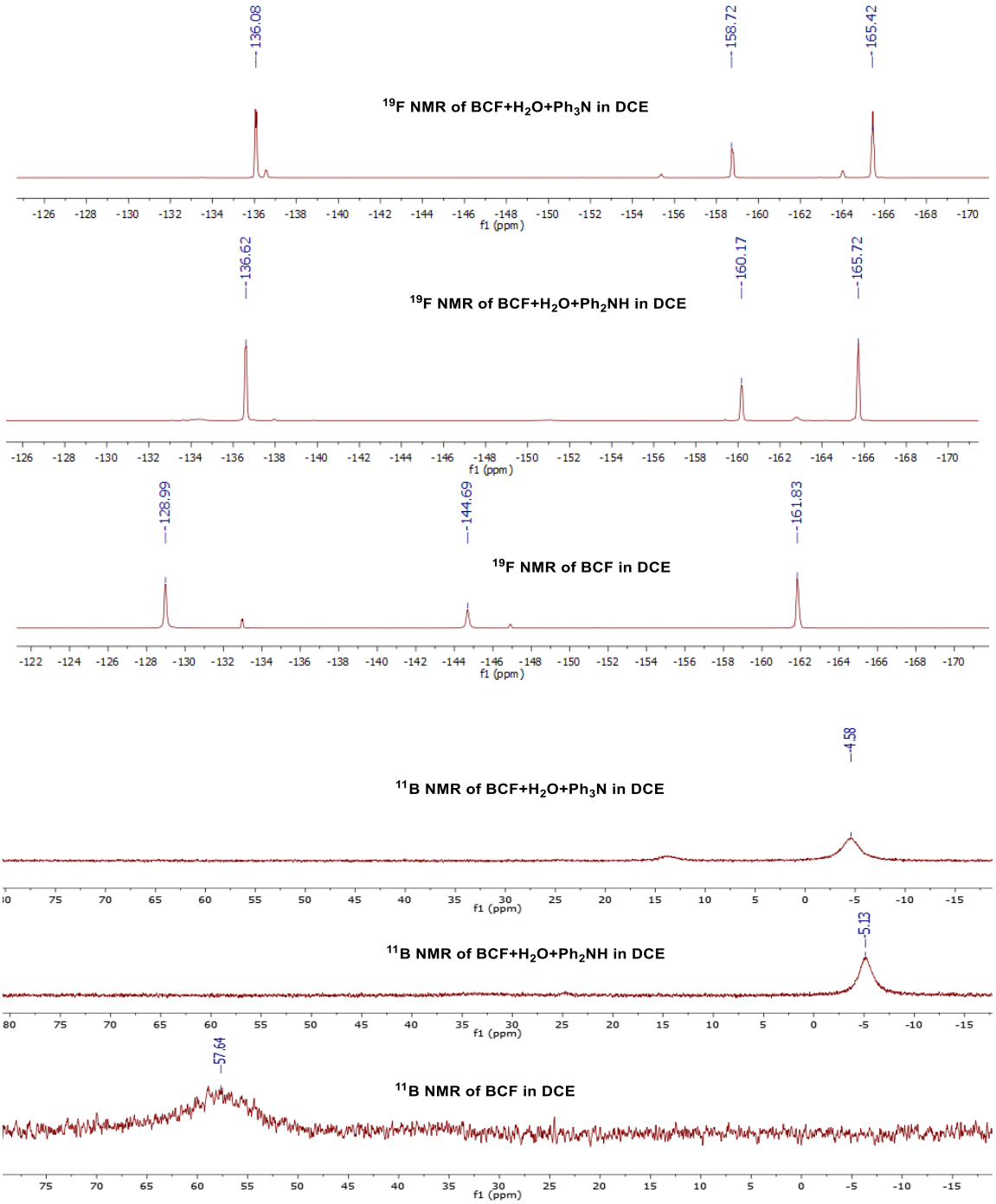
(i) BCF+H_2O+**315a** (Ph_2NH) as 1:1:1 dissolved into DCE and recorded the ^{19}F, ^{11}B NMR with no solvent locking system in 400 MHz JEOL JNM ECS400. ^1H NMR recorded in the $CDCl_3$ solvent to check the shifting of -OH and –NH peaks. The peak for-OH and –NH is coming together at 5.67 ppm. The crystal for SC-XRD grown in DCE/n-pentane at room temperature for 12 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 7.11–7.01 (m, 6H), 5.67 (s, 3H).**^{19}F NMR** (376 MHz, NONE) δ -136.62, -160.17, -165.72. **^{11}B NMR** (128 MHz, NONE) δ -5.13.

(ii) Similarly, for BCF+H_2O+315g (Ph_3N) recorded the ^{19}F, ^{11}B NMR to check the H_2O·BCF adducts formation.

^{19}F NMR (376 MHz, NONE) δ -136.08, -158.72, -165.42, **^{11}B NMR** (128 MHz, NONE) δ -4.58.

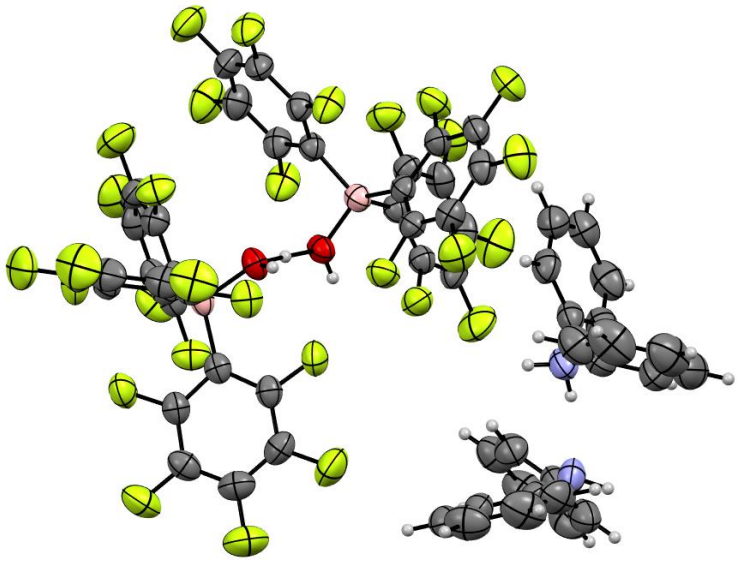
Note- reference for spectral data of BCF-OH and BCF-OH_2[142]



6. Crystal Data and Structure Refinement for Complex $((315a)_2H^+(HOBCF)_2H^-)$ (CCDC2111194):

For the determination of X-ray crystal structures of **$((315a)_2H^+(HOBCF)_2H^-)$** a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293K on

a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[143] was used. Absorption correction was done applying SADABS program.[144] The crystal structure was solved by SIR 92[145] and refined by full matrix least square method using SHELXL-97[146] WinGX system, Ver 1.70.01.[147] All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: **$((315a)_2H^+(HOBCF)_2H^-$): CCDC 2111194**.

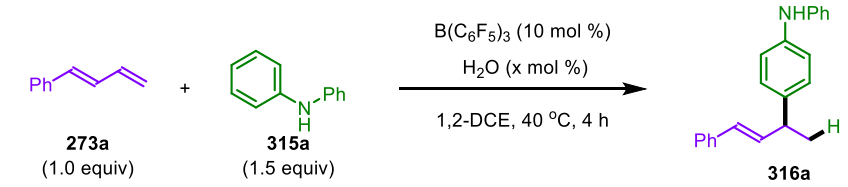


Atom color code: grey = carbon atom, white = hydrogen atom, blue = nitrogen atom, green = fluorine, salmon = boron atom and red = oxygen atom. ORTEP drawing of $((315a)_2H^+(HOBCF)_2H^-)$ showing thermal ellipsoids at the 50% probability.

Crystal data and structure refinement for Complex $((315a)_2H^+(HOBCF)_2H^-)$ (CCDC2111194)	
Identification Code	icgk_03_409_0m-sr
Ccdc no.	2111194
Empirical formula	$C_{30}H_{13}BF_{15}NO$
Formula weight	699.22
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	12.9009(7)

b/Å	14.2446(6)
c/Å	16.8164(9)
α/°	102.2630(10)
β/°	108.067(2)
γ/°	95.055(2)
Volume/Å^3	2831.2(2)
Z	4
ρ_{calc}g/cm^3	1.640
μ/mm^{-1}	0.167
F(000)	1392.0
Crystal size/mm^3	0.259× 0.215 × 0.189
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.438 to 52.888
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	62353
Independent reflections	11625 [R_{int} = 0.0502, R_{sigma} = 0.0362]
Data/restraints/parameters	11625/0/877
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1111
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1240
Largest diff. peak/hole / e Å^{-3}	0.32/-0.22

7. Effect of Water content



273a (1.0 equiv) **315a** (1.5 equiv) **316a**

(i) 1,2-DCE (dry & dist.) - x = 100 mol %, **316a** (30% yield)
(ii) 1,2-DCE (dry & dist.) - x = 10 mol %, **316a** (50% yield)
(iii) 1,2-DCE (normal without dist.) - x = 0 mol %, **316a** (60% yield)

(i) Following modified (first H_2O (2.2 mg, 0.12 mmol, 1.0 equiv) taken into vial) **GP-A,** using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a** (11.0 mg, 30%).

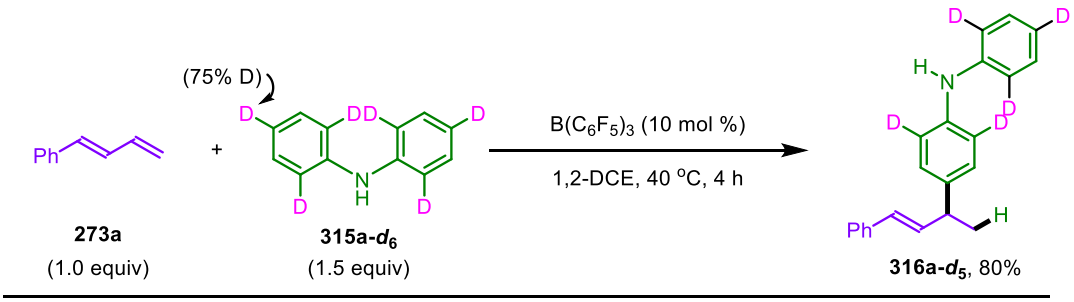
(ii) Following modified (first H_2O (0.2 mg, 12 µmmol, 10 mol %) taken into vial) **GP-A,** using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a** (18.0 mg, 50%).

Note: H_2O was used as:- 0.47 M-H_2O solution in DCE, added 25µl (0.2 mg H_2O).

(iii) Following modified (the normal without distilled DCE has been used) **GP-A,** using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a** (22.0 mg, 60%).

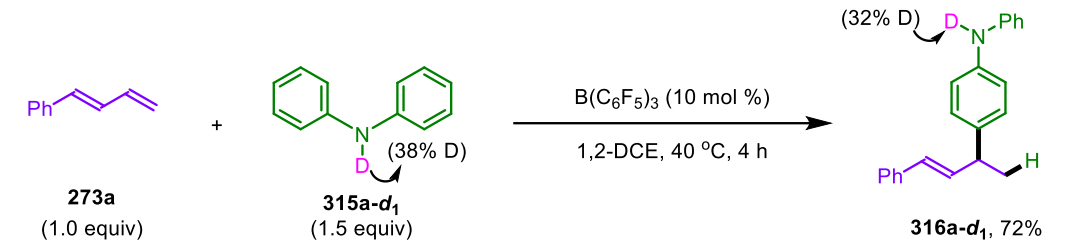
8. Deuterium labeling

8.1 (*E*)-*N*-(4-(4-phenylbut-3-en-2-yl)phenyl-2,6-d_2)benzen-2,4,6-d_3-amine (316a-d_5)



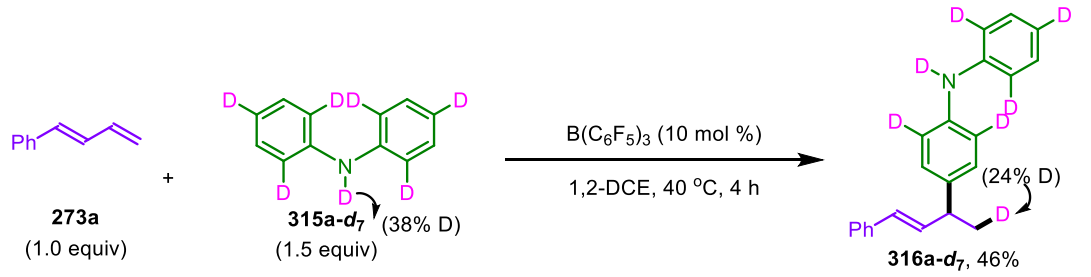
According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a-d_6** (31.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a-d_5** (22.0 mg, 80%) as colorless oil. **HRMS** (ESI) *m/z*: [$(M+H)^+$] calcd for $C_{22}H_{17}D_5N^+$ 305.2061; found 305.2047. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.31–7.23 (m, 4H), 7.22–7.16 (m, 3H), 7.06–7.03 (m, 1H), 6.90 (t, *J* = 7.3 Hz, 0.34H), 6.44–6.35 (m, 2H), 5.66 (s, 1H), 3.63–3.57 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 143.5, 141.2, 141.1, 138.5, 137.7, 135.7, 129.4, 129.3, 129.2, 128.6, 128.3, 128.2 (2C), 127.1, 126.3, 120.7, 118.5, 117.3, 42.0,41.9, 21.4.

8.2 (*E*)-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline-*d* (316a-d_1)



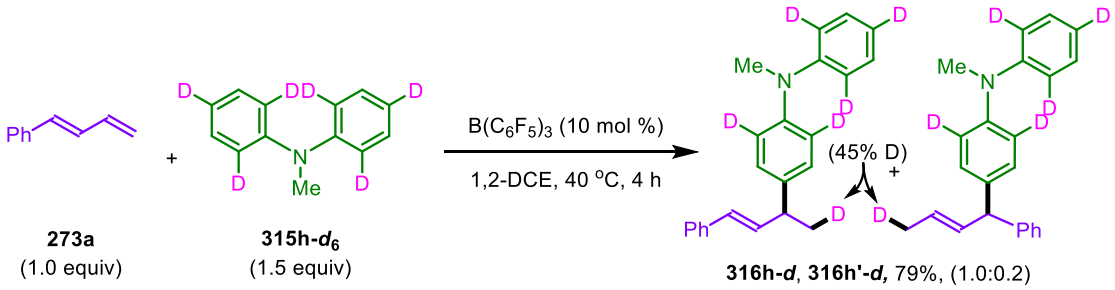
According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a-d_1** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 μmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **(316a-d_1)** (26.0 mg, 72%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{22}H_{21}D_1N^+$ 301.1810; found 301.1803. **1H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 2H), 7.30–7.22 (m, 4H), 7.20–7.15 (m, 3H), 7.05–7.02 (m, 4H), 6.89–6.87 (m, 1H), 6.43–6.33 (m, 2H), 5.66 (s, 0.68H), 3.59 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 141.2, 138.6, 137.7, 135.7, 129.4, 128.6, 128.4, 128.3, 127.1, 126.3, 120.7, 118.6, 117.4, 42.0, 21.4.

8.3 (*E*)-*N*-(4-(4-phenylbut-3-en-2-yl-1-*d*)phenyl-2,6-d_2)benzen-2,3,4,5,6-d_5-amine-*d* (316a-d_7)



According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a-d_7** (31.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 μmol, 10 mol %) stirred for 8 h. Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **(316a-d_7)** (17.0 mg, 46%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{22}H_{15}D_7N^+$ 307.2187; found 307.2206. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.31–7.23 (m, 4H), 7.22–7.17 (m, 3H), 7.05 (d, *J* = 8.7 Hz, 0.89H), 6.90 (t, *J* = 7.4 Hz, 0.21H), 6.45–6.35 (m, 2H), 5.66 (s, 0.62H), 3.64–3.57 (m, 1H), 1.45 (t, *J* = 6.8 Hz, 2.76H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 143.5, 141.2, 141.1, 138.5, 137.8, 135.7, 129.3, 129.2, 128.6, 128.4, 128.3, 128.2, 127.1, 126.3, 120.7, 118.5, 118.2, 117.9, 117.4, 117.3, 116.8, 42.0, 41.9, 21.4, 21.2, 21.1, 20.9.

8.4 (*E*)-*N*-methyl-*N*-(4-(4-phenylbut-3-en-2-yl-1-d)phenyl-2,6-d_2)aniline-2,4,6-d_3 and (*E*)-*N*-methyl-*N*-(4-(1-phenylbut-2-en-1-yl-4-d)phenyl-2,6-d_2)aniline-2,4,6-d_3 (316h-d_1 + 316h′-d_1)



According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315h-d_6** (34.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316h-d_1 + 316h′-d_1** (30.0 mg, 79%) as colorless oil. **HRMS** (ESI) *m/z*: $[(M+H)^+]$ calcd for $C_{23}H_{18}D_6N^+$ 320.2280; found 320.2190. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.32–7.18 (m, 7H), 7.03–6.98 (m, 0.92H), 6.91 (t, *J* = 7.3 Hz, 0.21H), 6.46–6.36 (m, 2H), 3.65–3.58 (m, 1H), 3.31 (s, 3H), 1.46 (t, *J* = 6.8 Hz, 2.55H). **^{13}C NMR** δ 149.2, 149.1, 147.2 (2C), 139.1, 137.7, 135.6, 129.1, 129.0, 128.6, 128.3, 128.1, 128.0, 127.1, 126.2, 121.6, 121.2, 121.0, 120.5, 120.3, 120.0, 119.4, 119.0, 118.8, 42.0 (2C), 40.4, 21.3, 21.2, 21.0, 20.8.

Note: 315h-d_6 has been synthesized by following procedure [141d] using the **316a-d_6**. 90% yield, colorless liquid. Deuterium labeling measured by **^{1}H NMR**

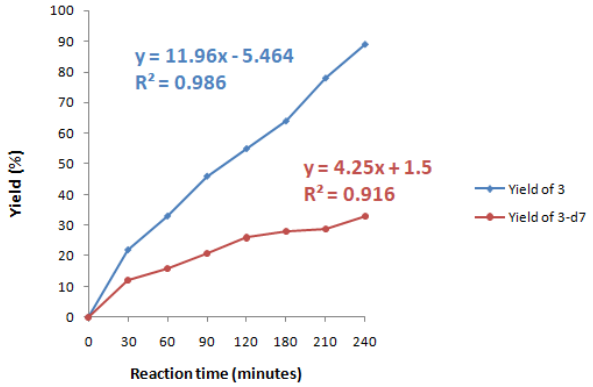
9.0 Independent Kinetic isotope exchange (KIE) study

Procedure: Following **GP-A**, eight sets of reactions was setup and stopped at 30, 60, 90, 120, 150, 180, 210, and 240 minutes. The products have been isolated to calculate the yields at particular time. All the reactions repeated three times to minimize the error and average taken, graph plotted for yield versus time in excel. These experiments performed for non-deuterated and deuterated secondary as well as tertiary amines independently. And the k_H/k_D ratio has been calculated.

9.1 Independent Kinetic isotope exchange (KIE) study for secondary amine

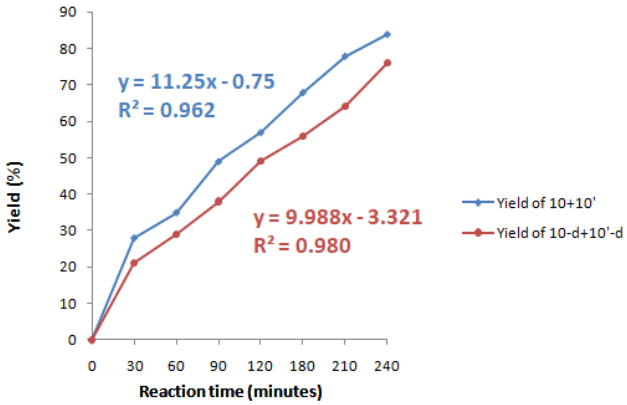
According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a** (30.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Total eight sets of reactions performed each one has stopped at the particular time as 30, 60, 90, 120, 150, 180, 210, and 240 minutes. Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a**. Similarly, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315a-d_7** (31.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12

µmol, 10 mol %). Total eight sets of reactions performed each one has stopped at the particular time as 30, 60, 90, 120, 150, 180, 210, and 240 minutes. Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **(316a-d_7).** Hence the k_H/k_D = 2.81.



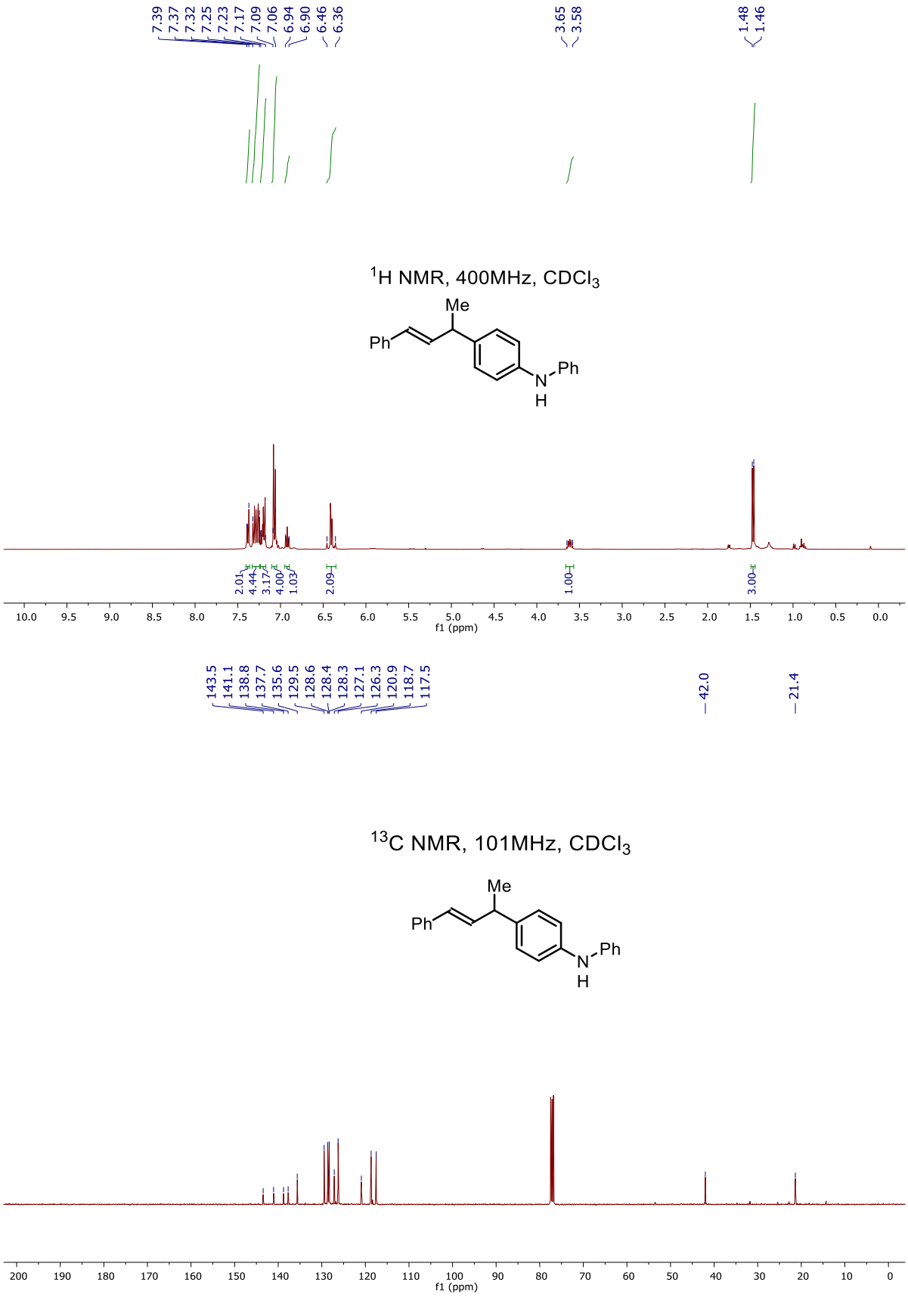
9.2 Independent Kinetic isotope exchange (KIE) study for tertiary amine

According to **GP-A**, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315h** (33.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Total eight sets of reactions performed each one has stopped at the particular time as 30, 60, 90, 120, 150, 180, 210, and 240 minutes. Purification by column chromatography on silica gel using petroleum ether/DCM (8:2 v/v) as eluent afforded the product **316h + 316h'**. Similiarly, using **273a** (16.0 mg, 0.12 mmol, 1.0 equiv), **315h-d_6** (34.0 mg, 0.18 mmol, 1.5 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (6.0 mg, 12 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether/DCM (9:1 v/v) as eluent afforded the product **316a-*d* + 316a′-*d***. Hence the k_H/k_D = 1.12.

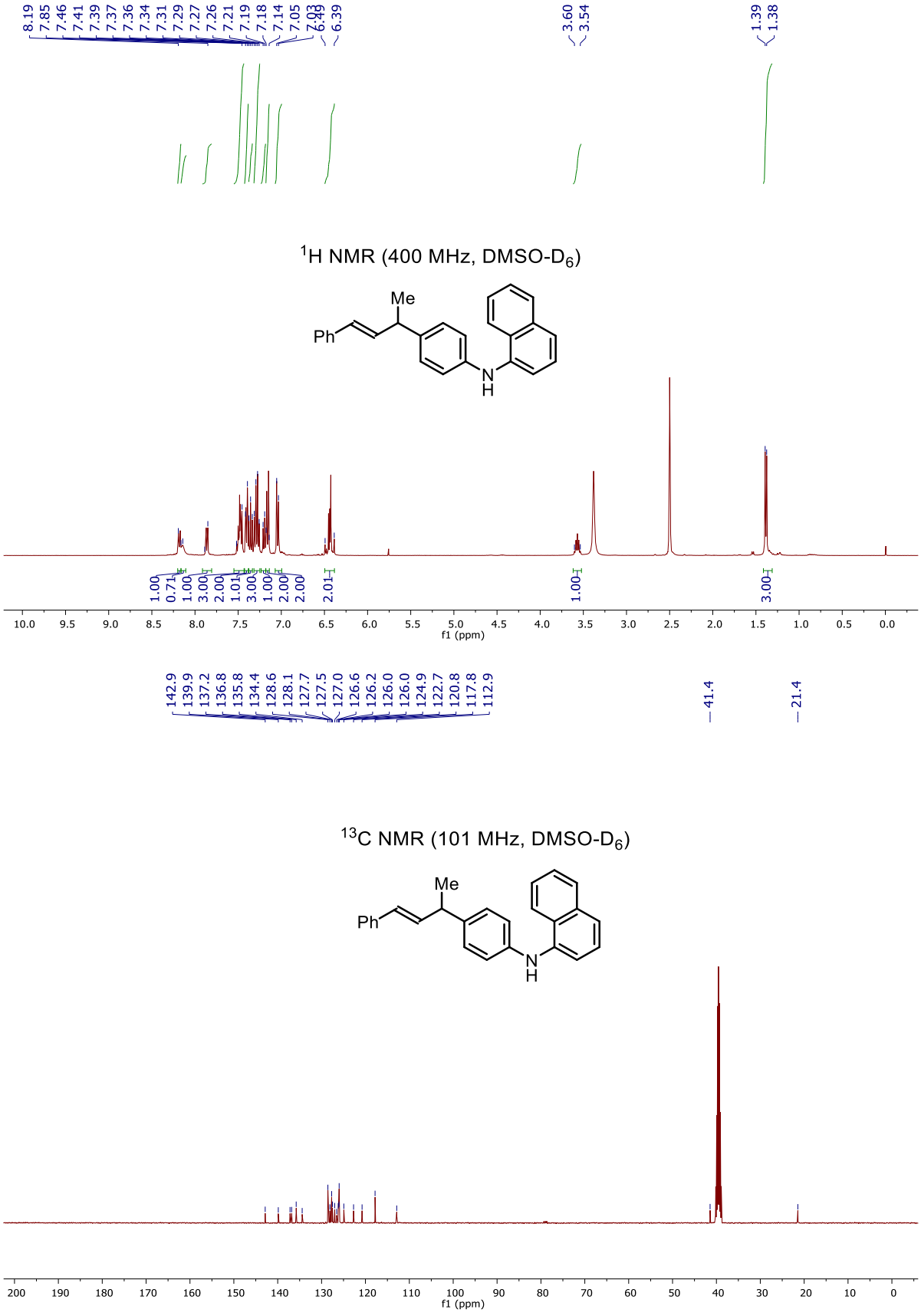


10. Experimental NMR Data

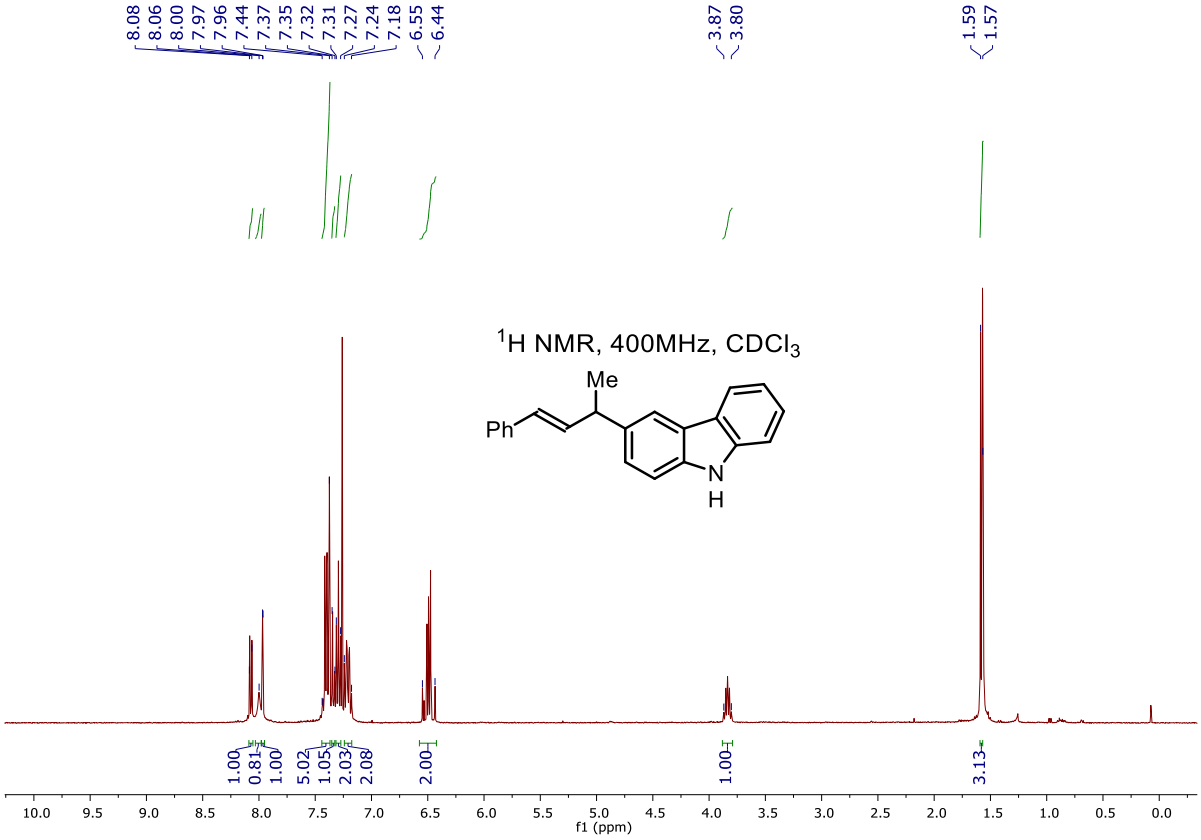
(*E*)-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline (316a)

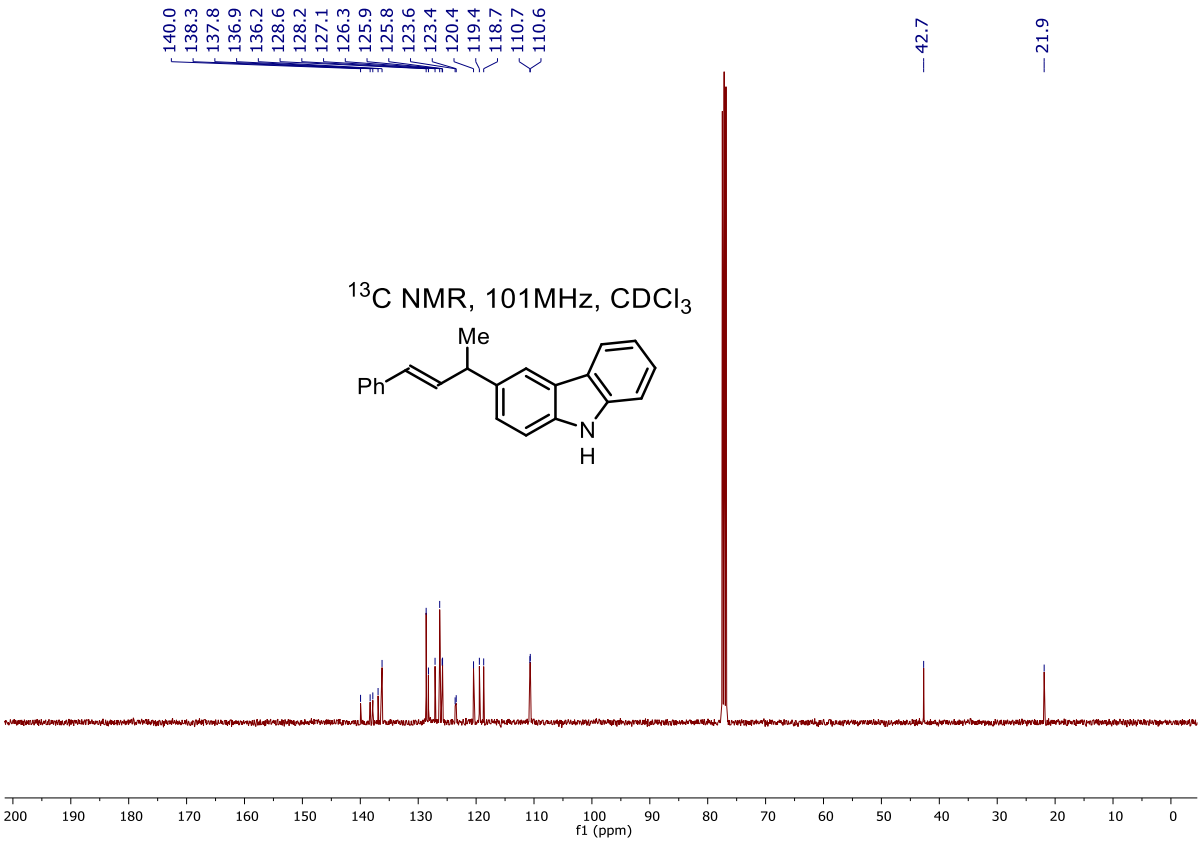


(*E*)-*N*-(4-(4-phenylbut-3-en-2-yl)phenyl)naphthalen-1-amine (316b)

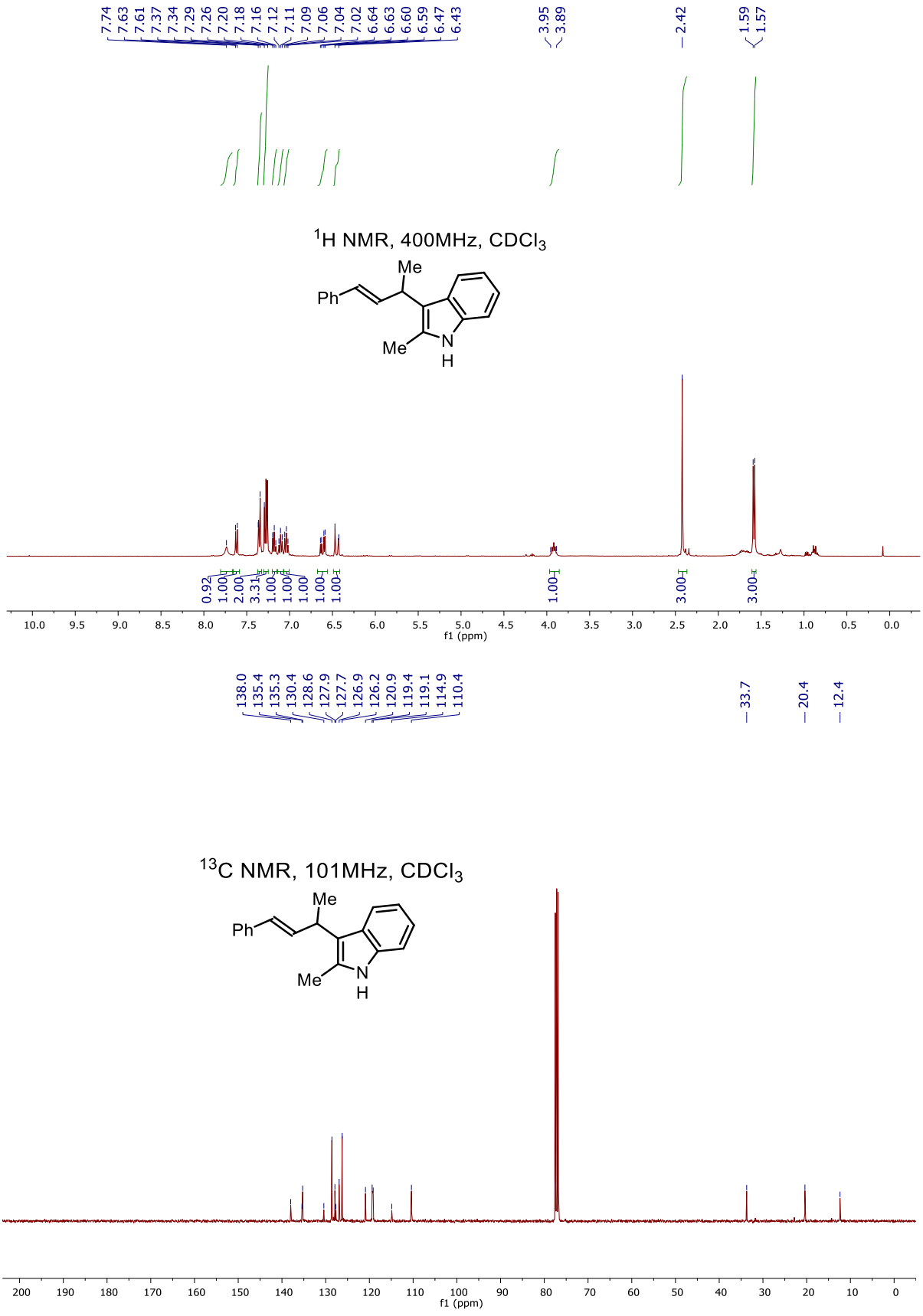


(*E*)-3-(4-phenylbut-3-en-2-yl)-9*H*-carbazole (316c)

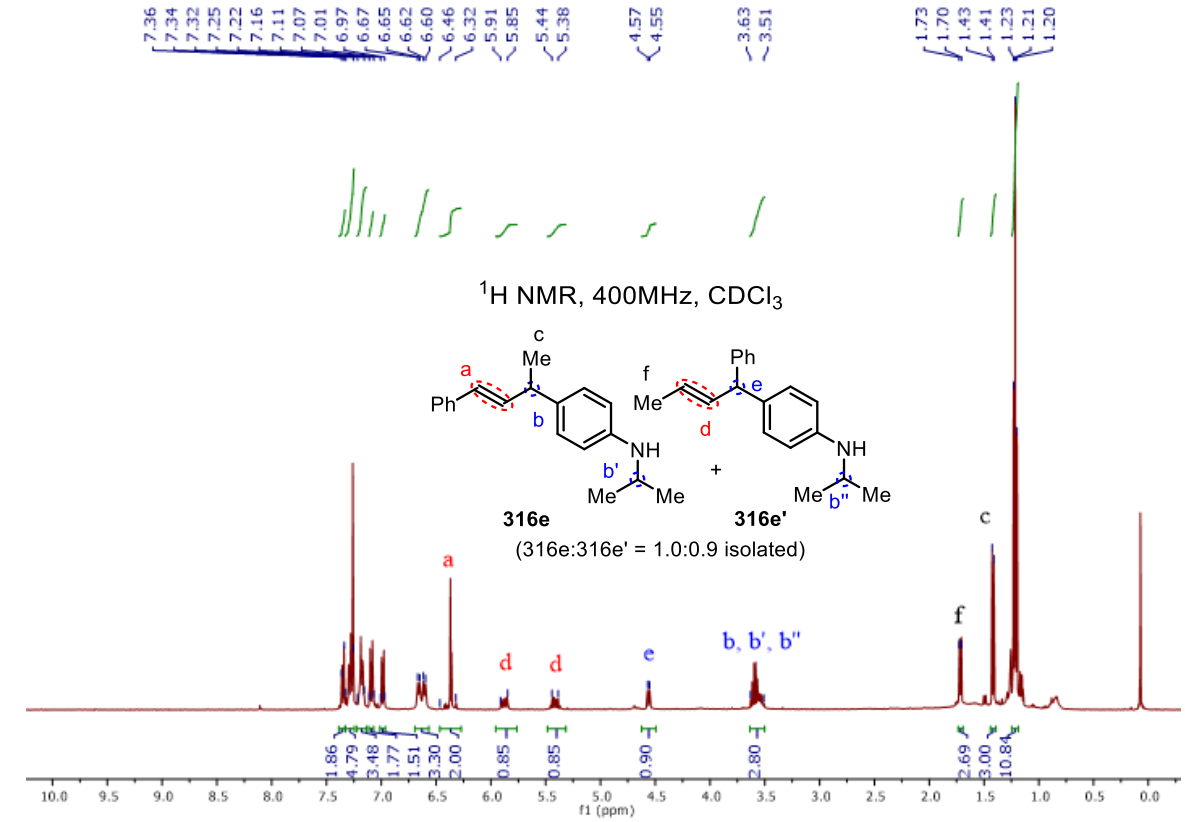


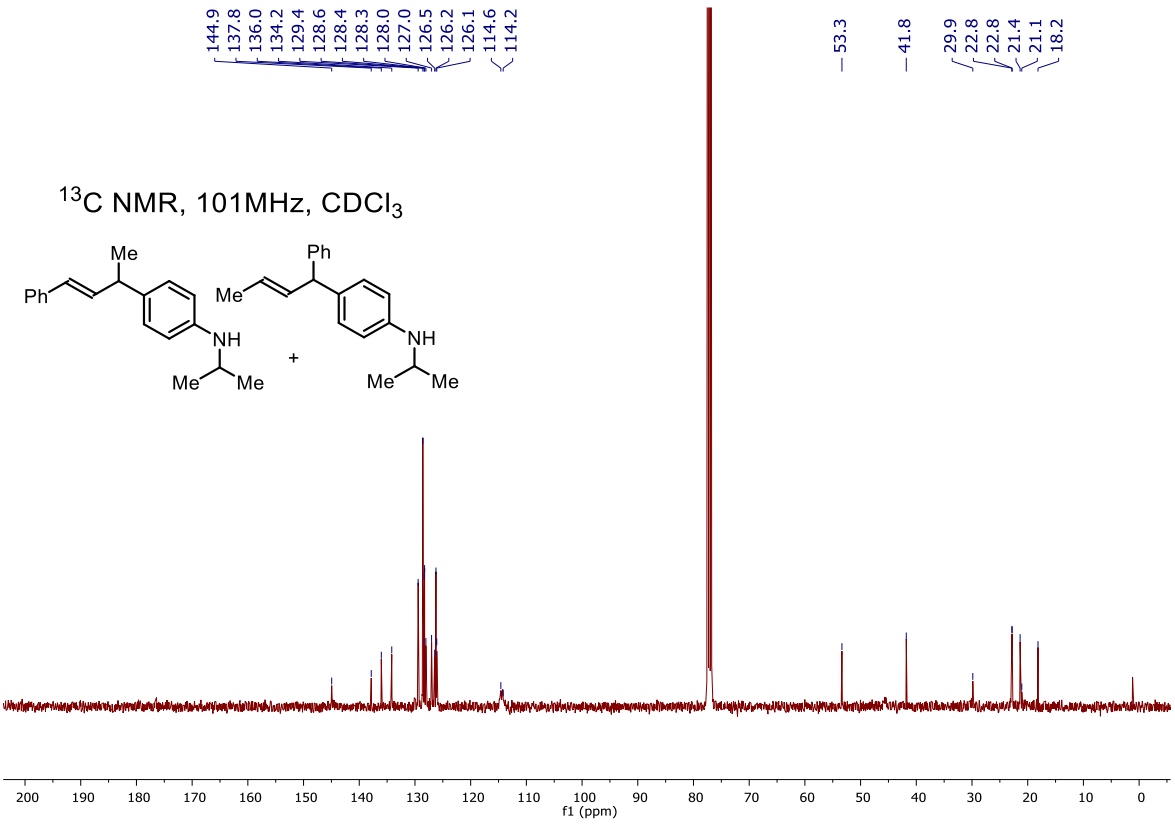


(*E*)-2-methyl-3-(4-phenylbut-3-en-2-yl)-1*H*-indole (316d)

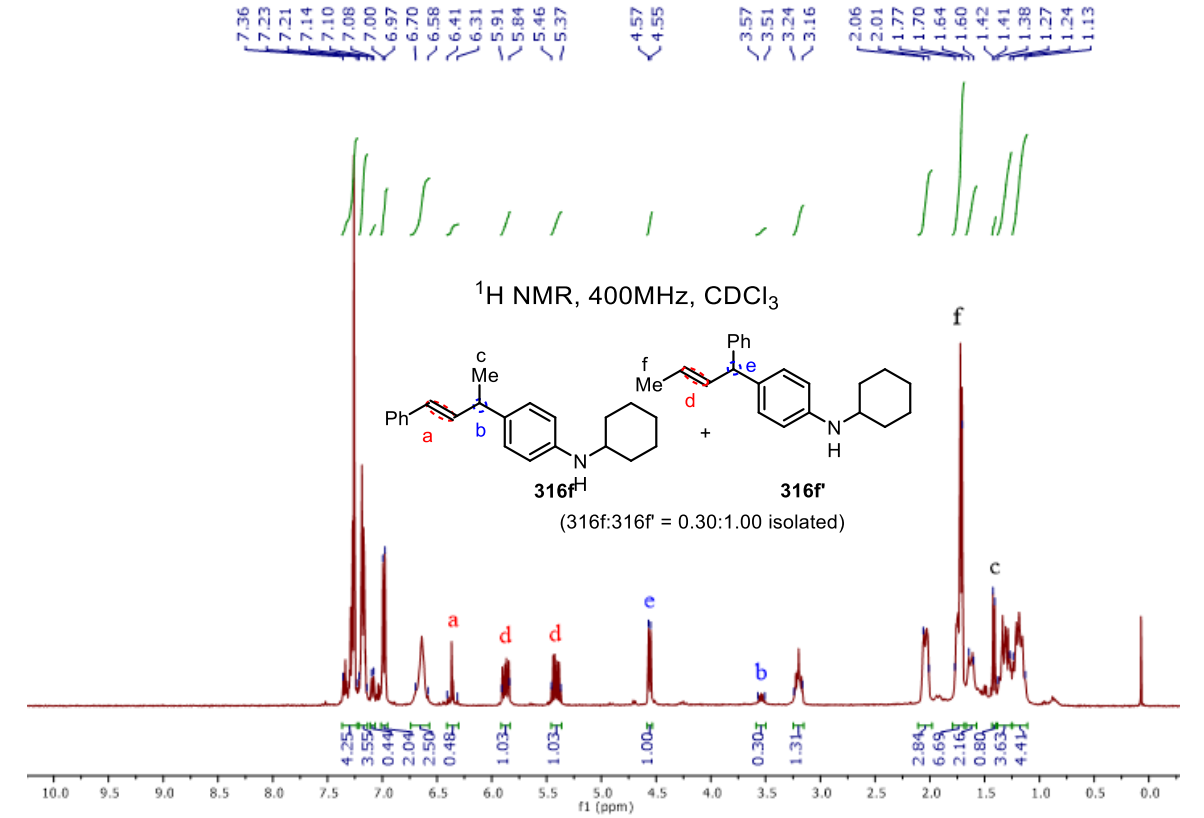


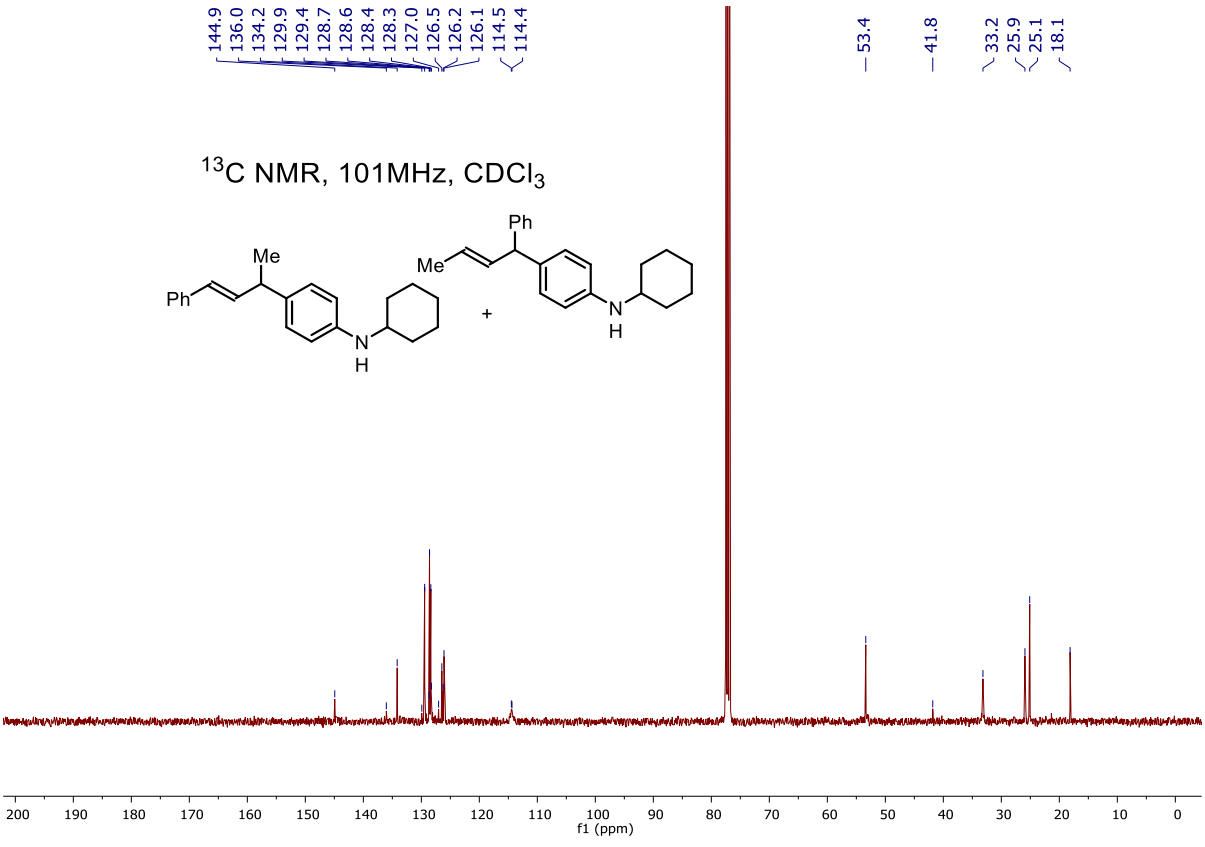
(*E*)-*N*-isopropyl-4-(4-phenylbut-3-en-2-yl)aniline and (*E*)-*N*-isopropyl-4-(1-phenylbut-2-en-1-yl)aniline (316e + 316e')



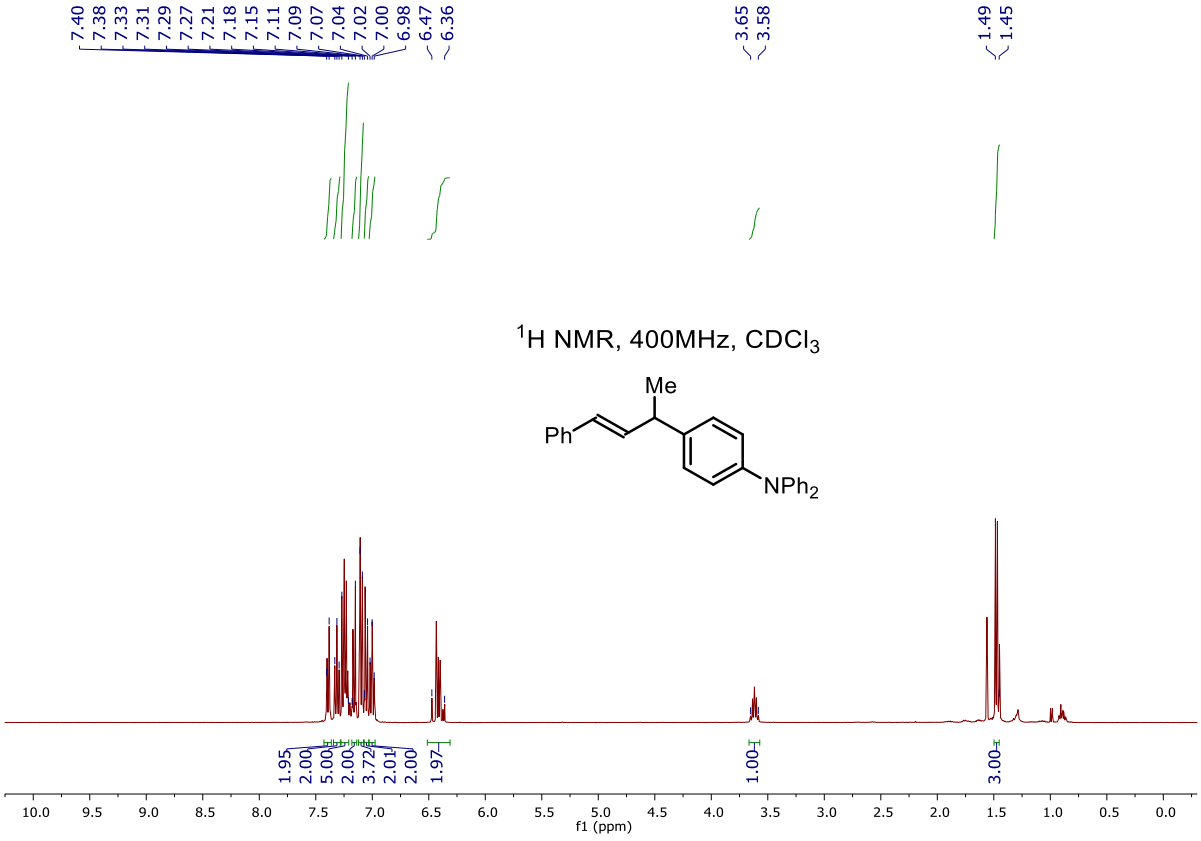


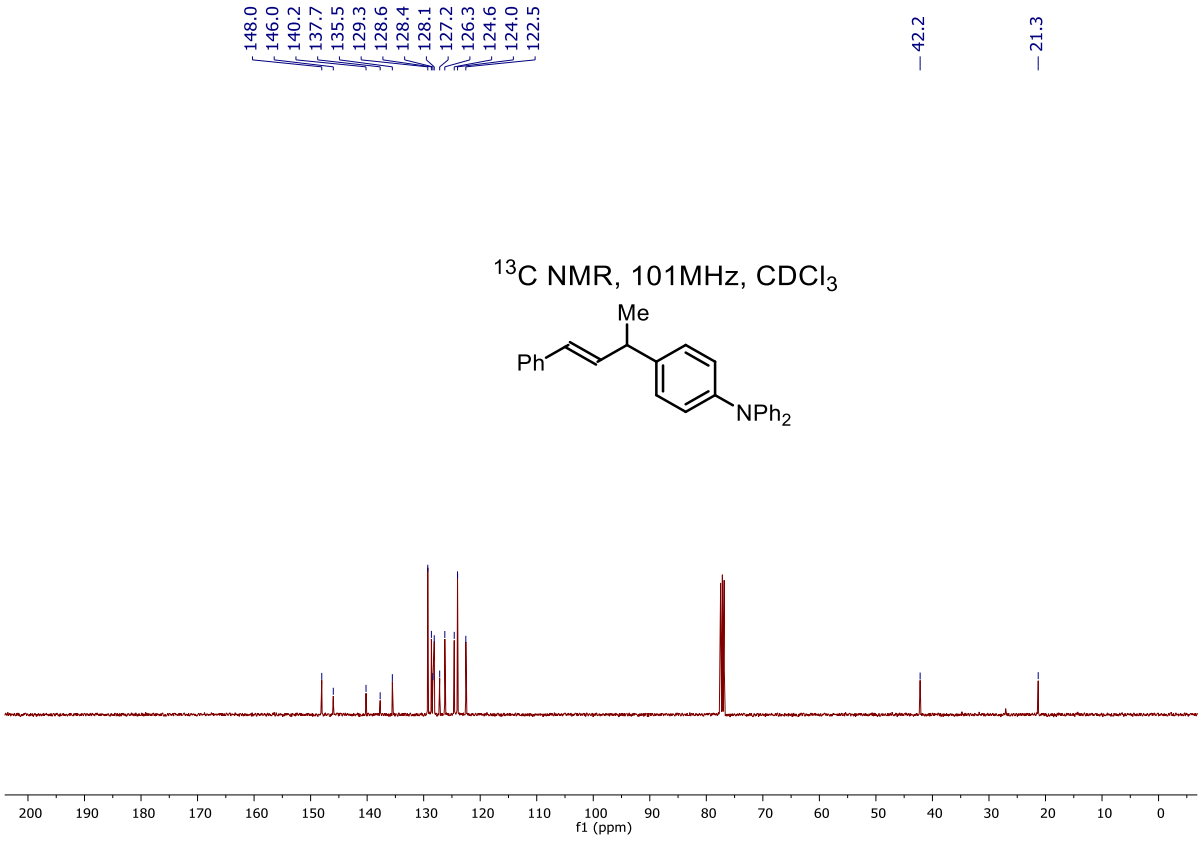
(*E*)-*N*-cyclohexyl-4-(4-phenylbut-3-en-2-yl)aniline and (*E*)-*N*-cyclohexyl-4-(1-phenylbut-2-en-1-yl)aniline (316f + 316f')



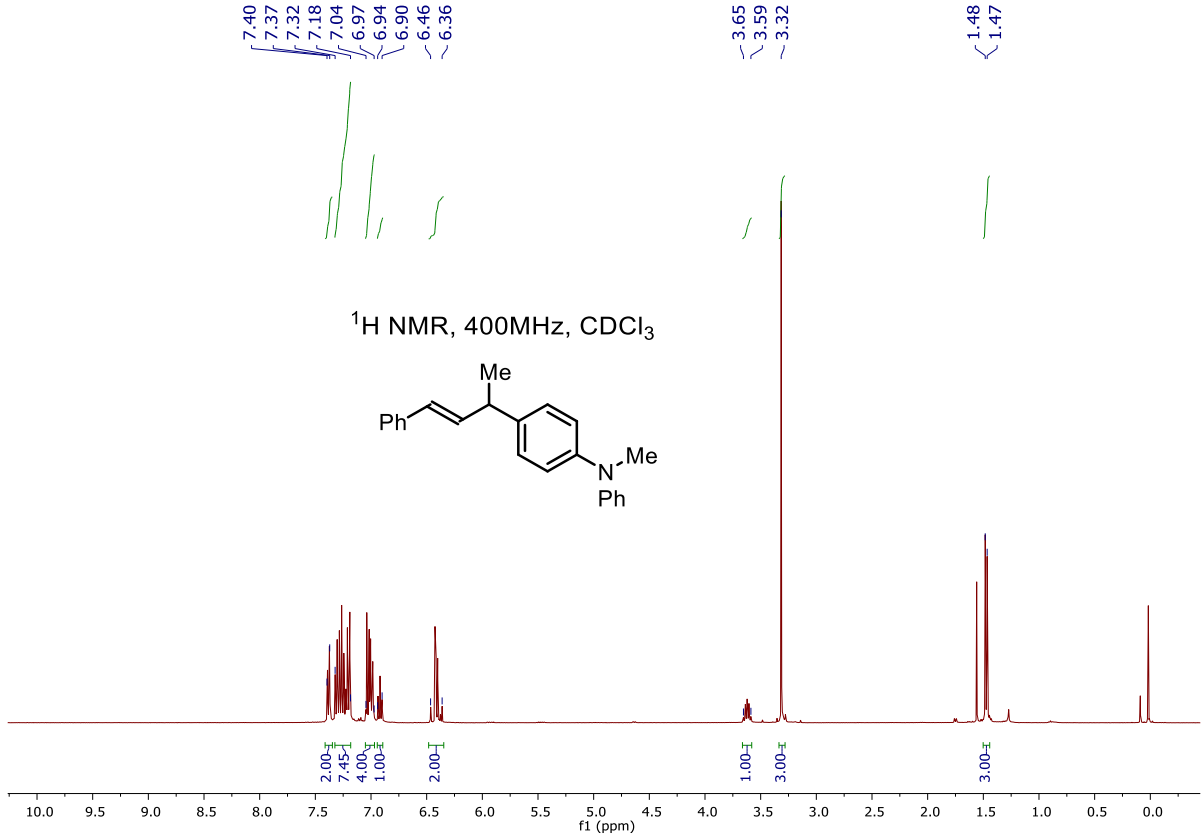


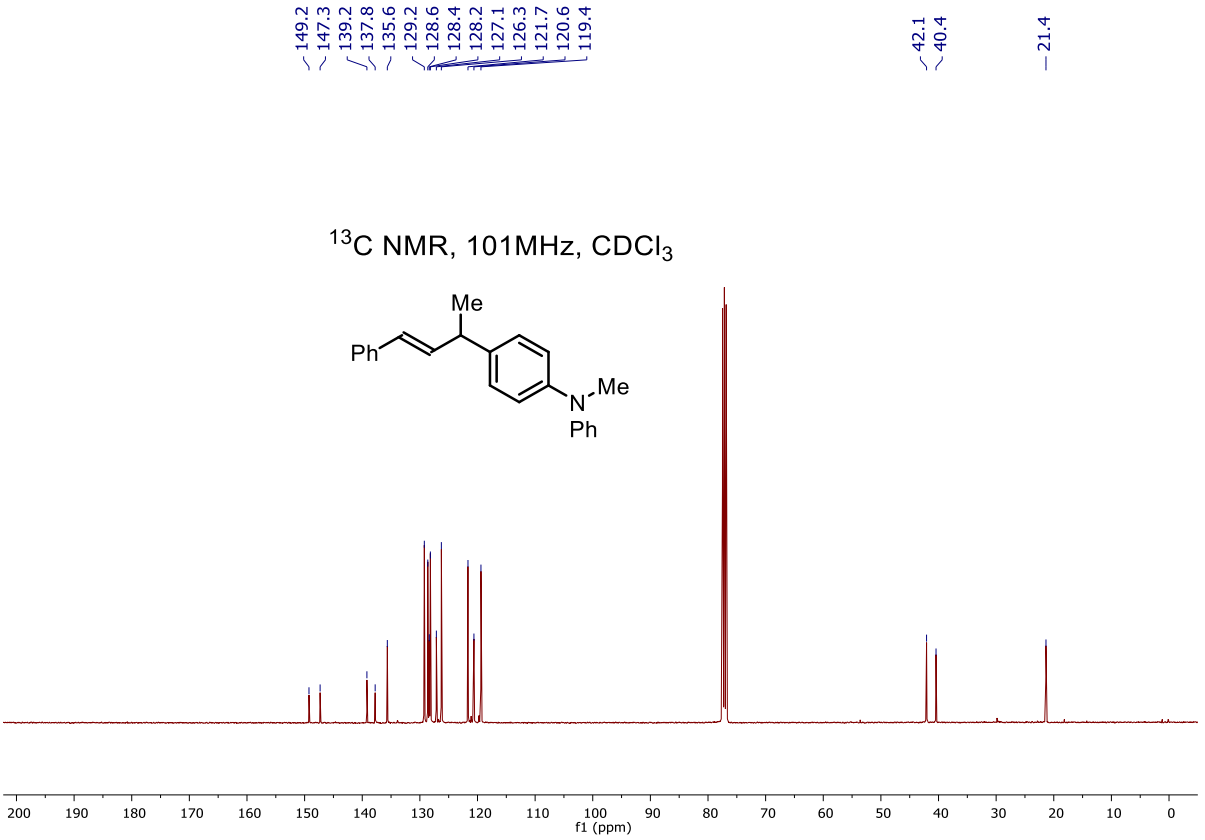
(*E*)-*N*,*N*-diphenyl-4-(4-phenylbut-3-en-2-yl)aniline (316g)



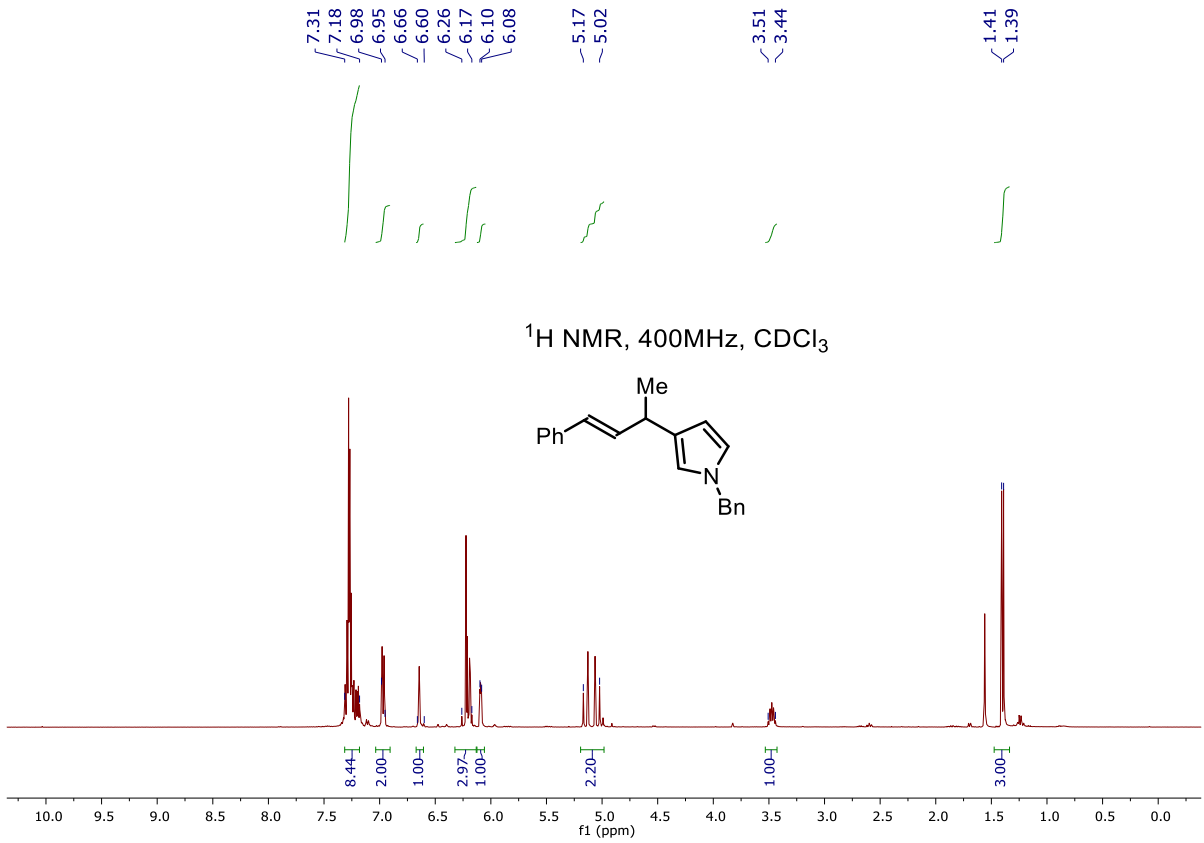


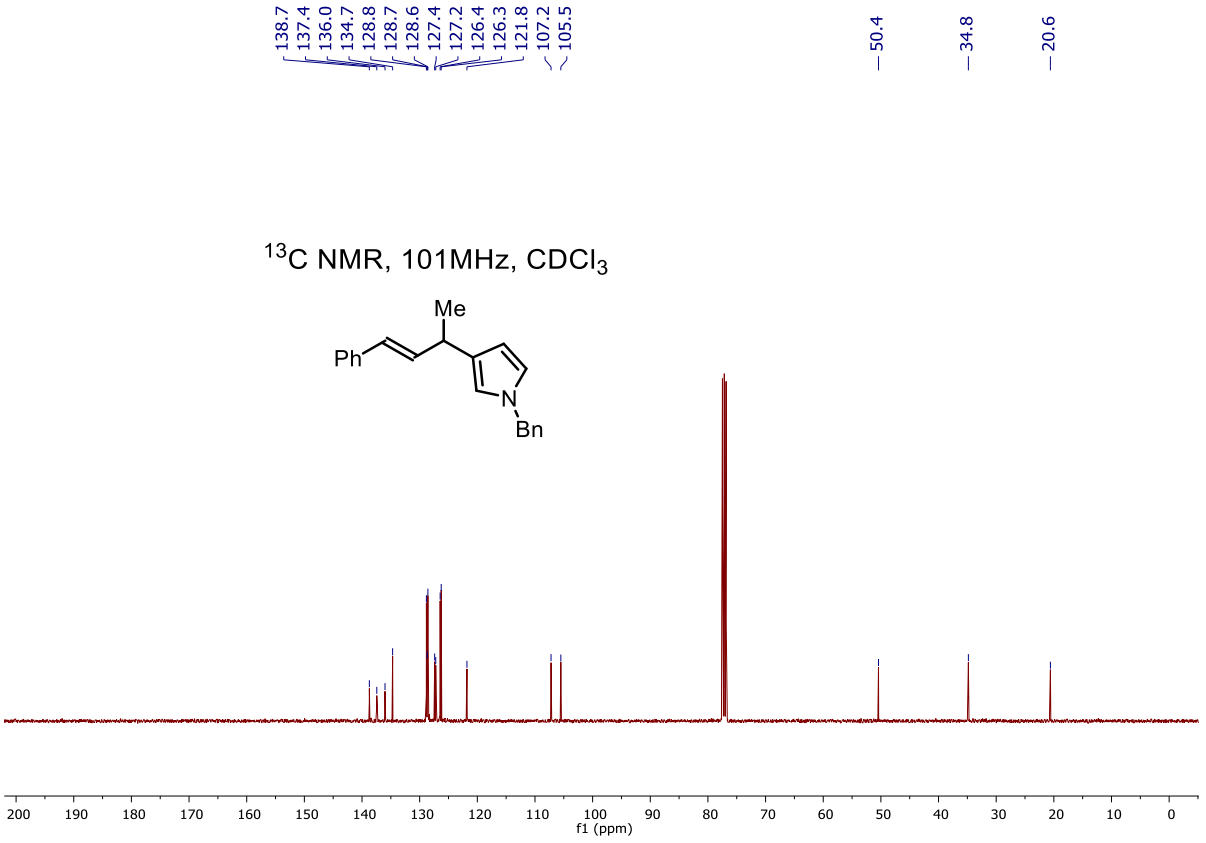
(*E*)-*N*-methyl-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline (316h)



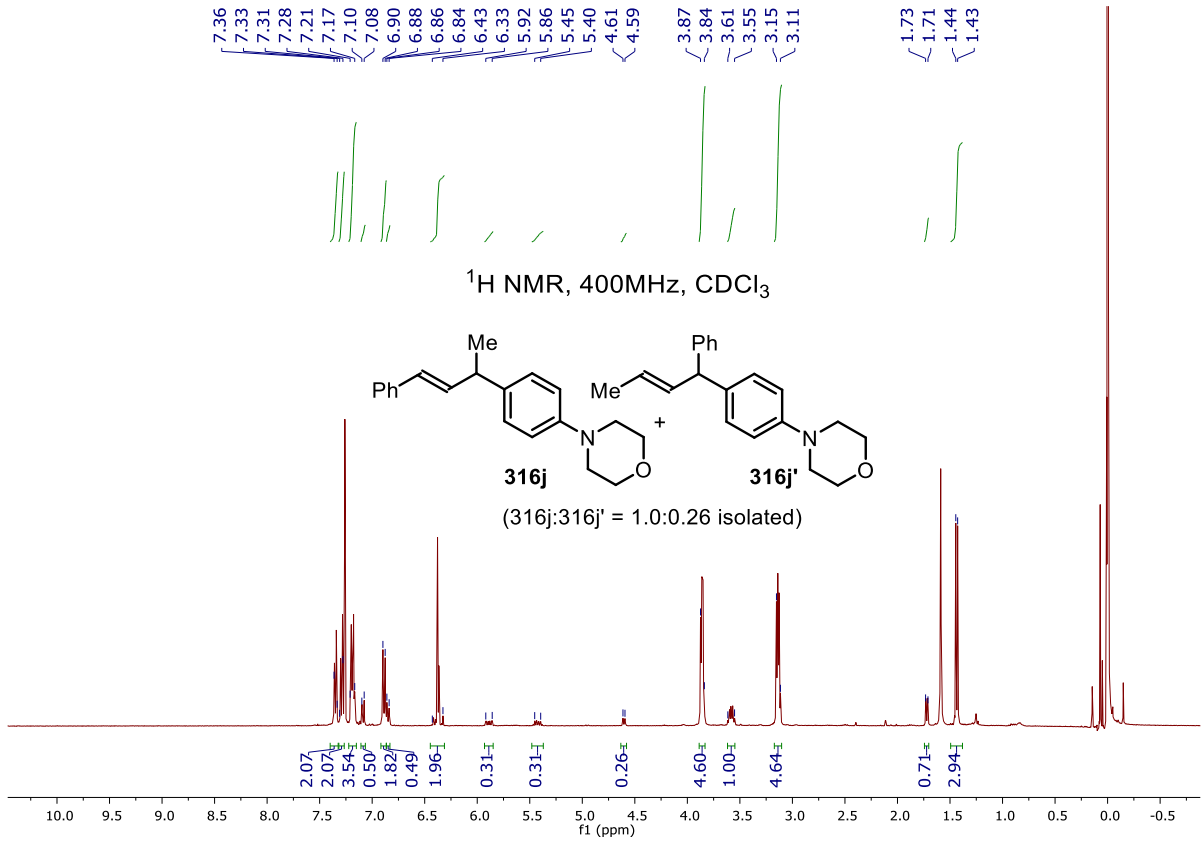


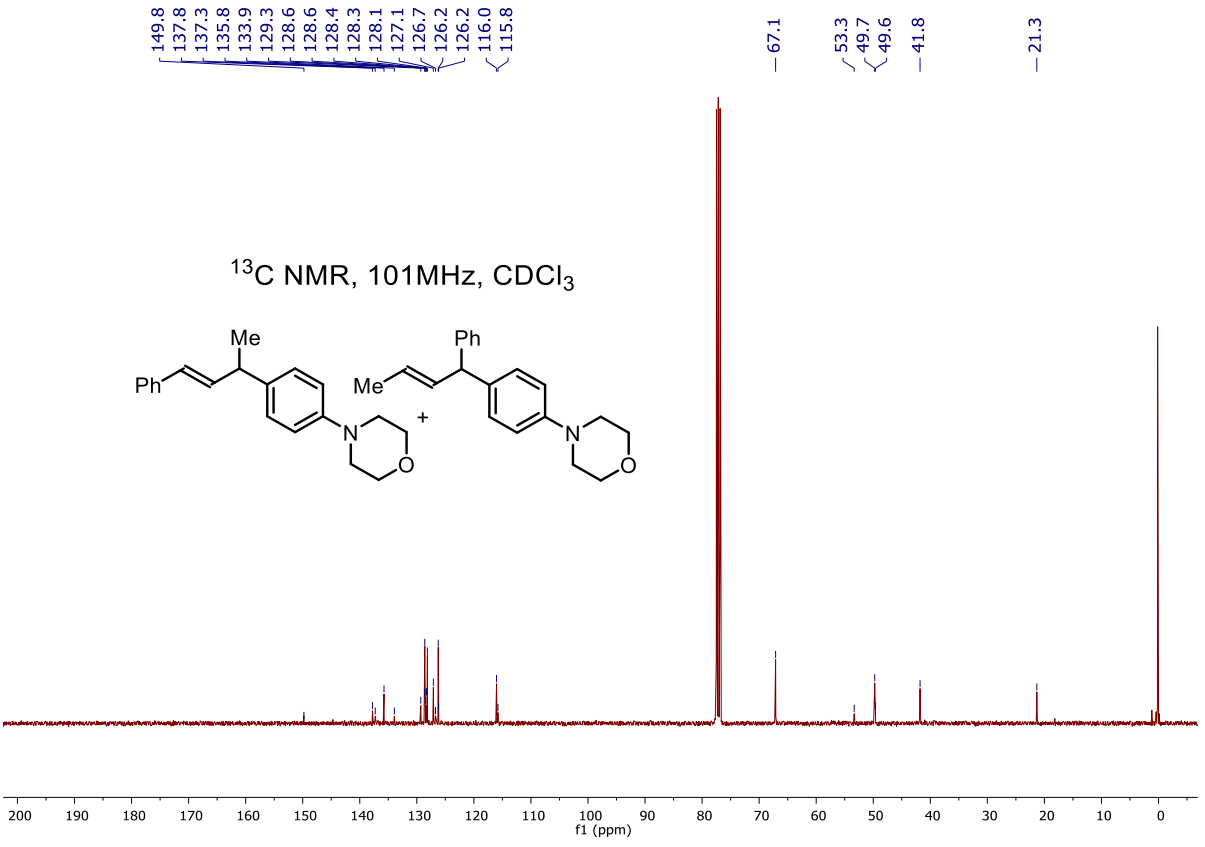
(*E*)-1-benzyl-3-(4-phenylbut-3-en-2-yl)-1*H*-pyrrole (316i)



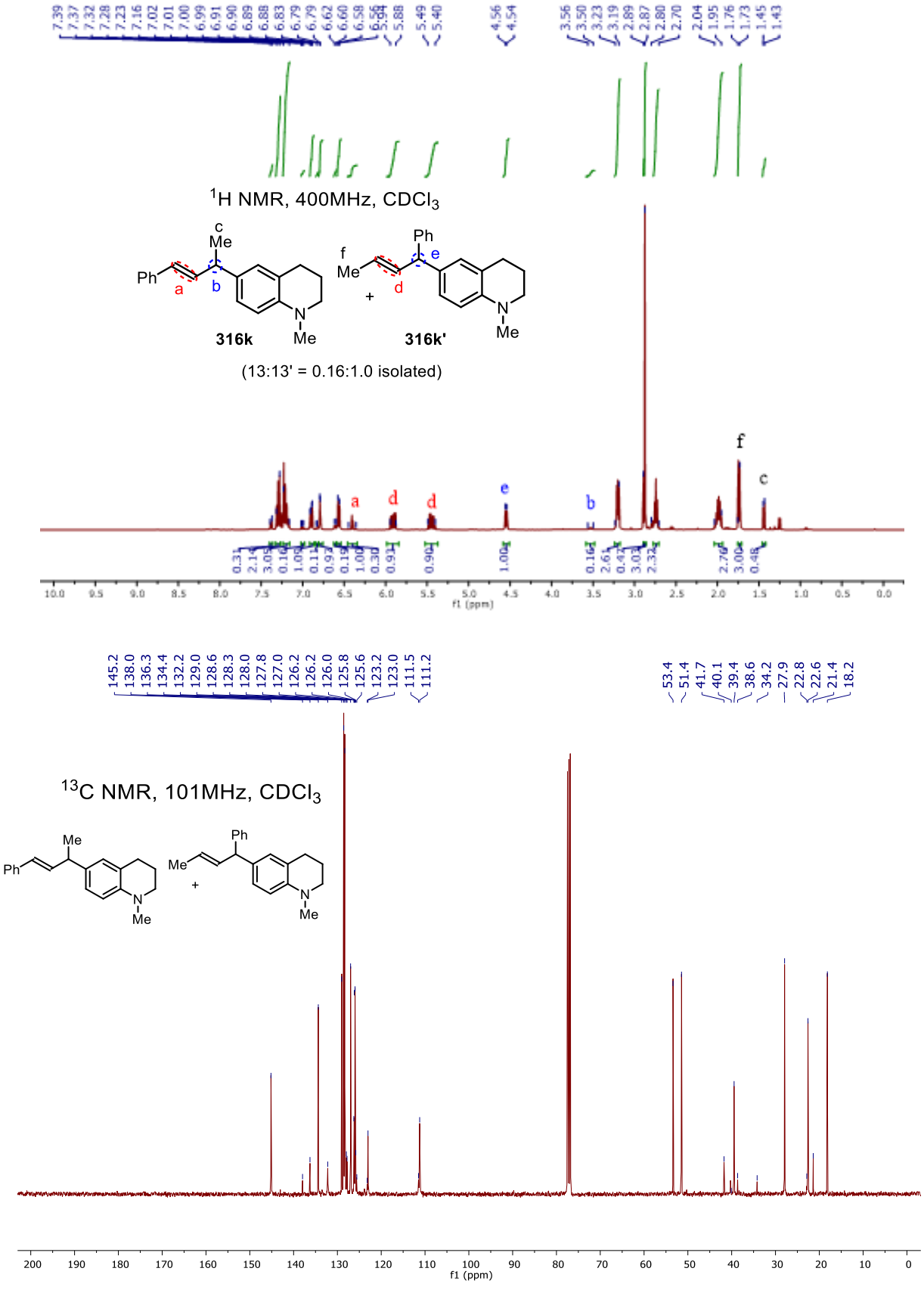


(*E*)-4-(4-(4-phenylbut-3-en-2-yl)phenyl)morpholine and (*E*)-4-(4-(1-phenylbut-2-en-1-yl)phenyl)morpholine (316j + 316j')

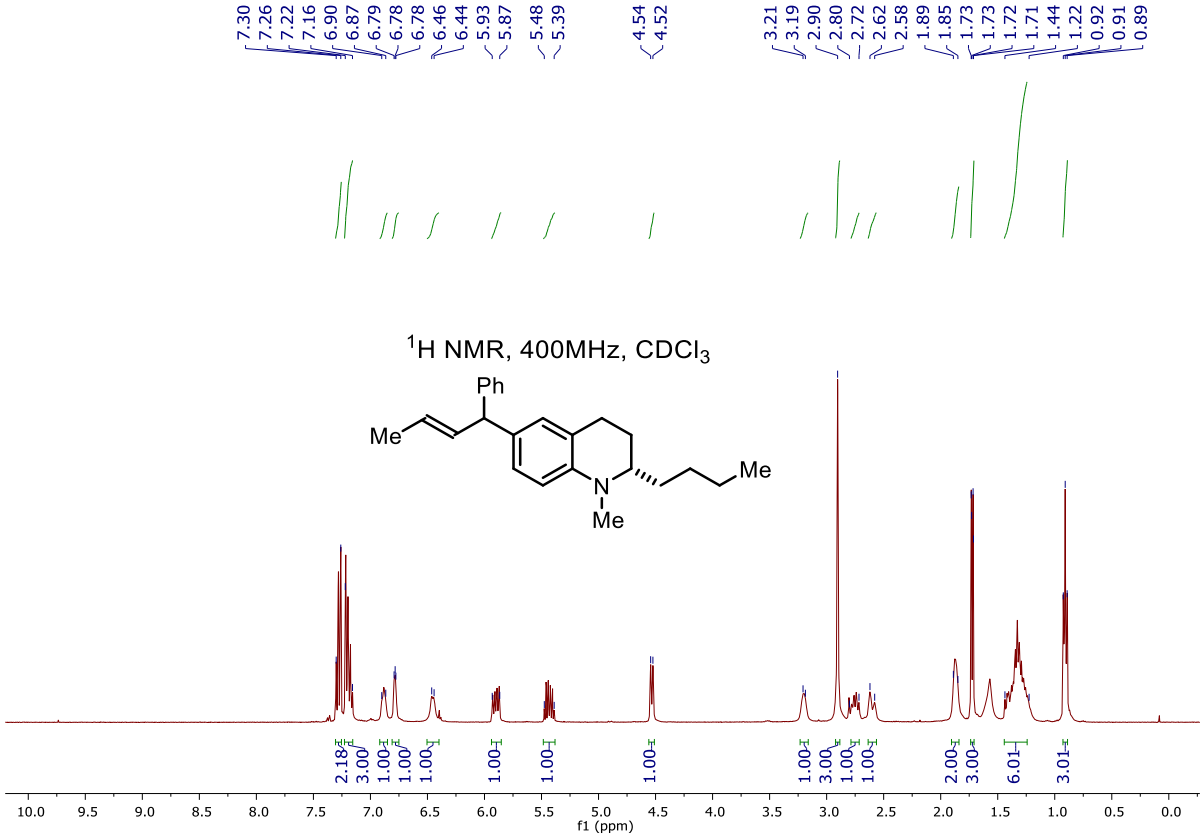


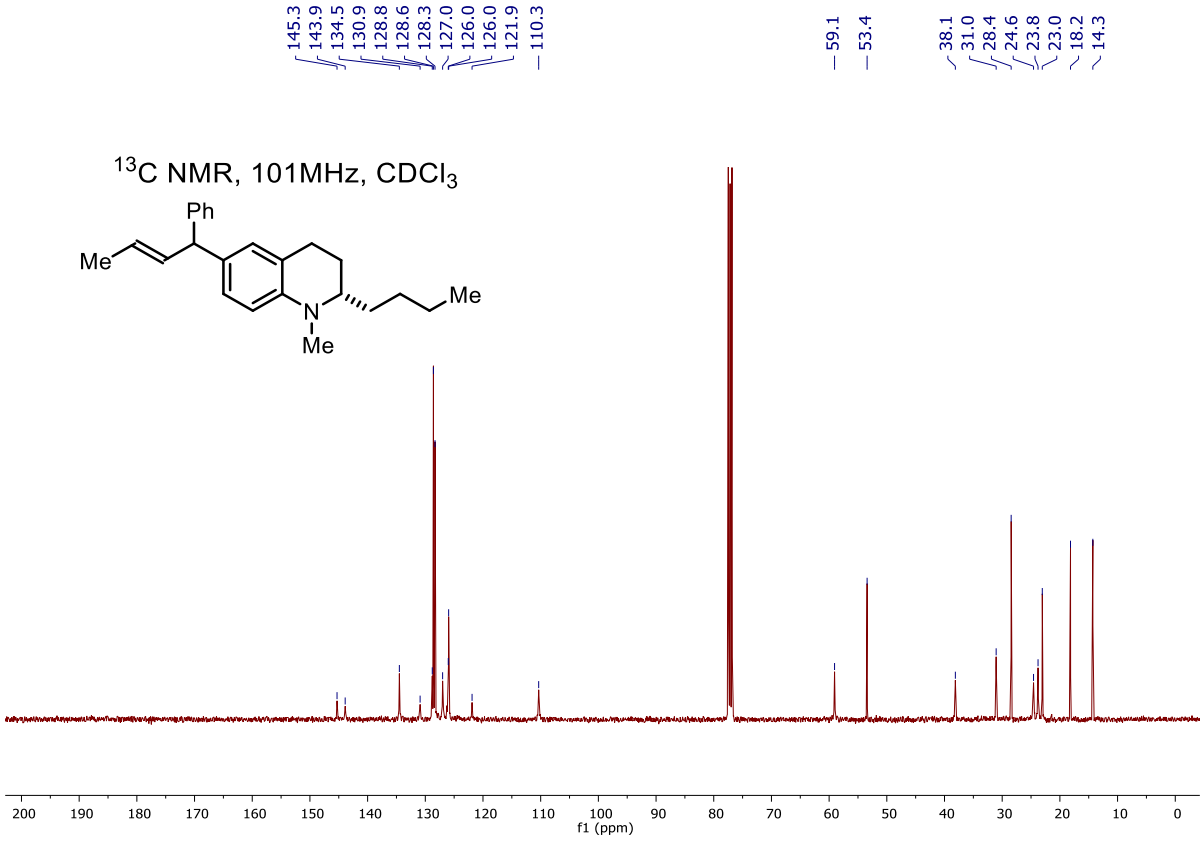


(*E*)-1-methyl-6-(4-phenylbut-3-en-2-yl)-1,2,3,4-tetrahydroquinoline and (*E*)-1-methyl-6-(1-phenylbut-2-en-1-yl)-1,2,3,4-tetrahydroquinoline (316k + 316k′)

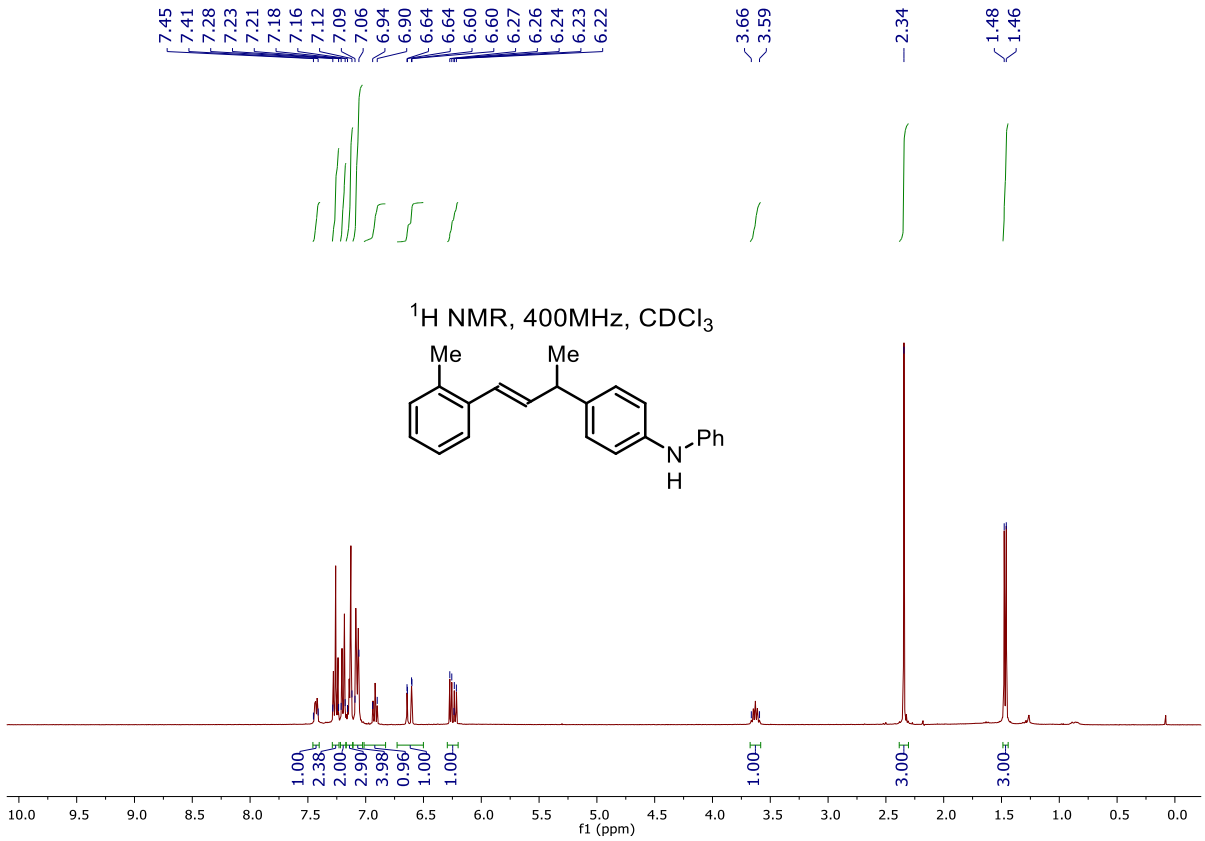


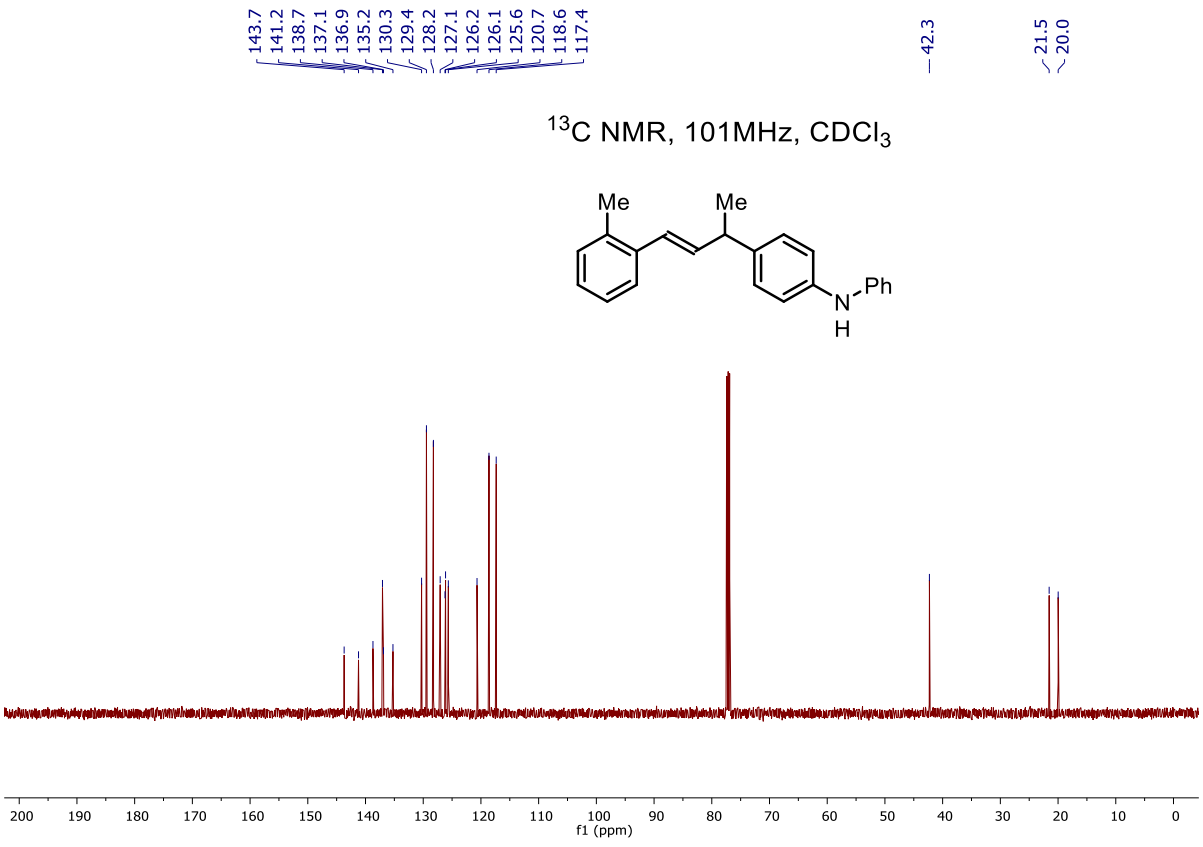
(2S)-2-butyl-1-methyl-6-((*E*)-1-phenylbut-2-en-1-yl)-1,2,3,4-tetrahydroquinoline (316l')



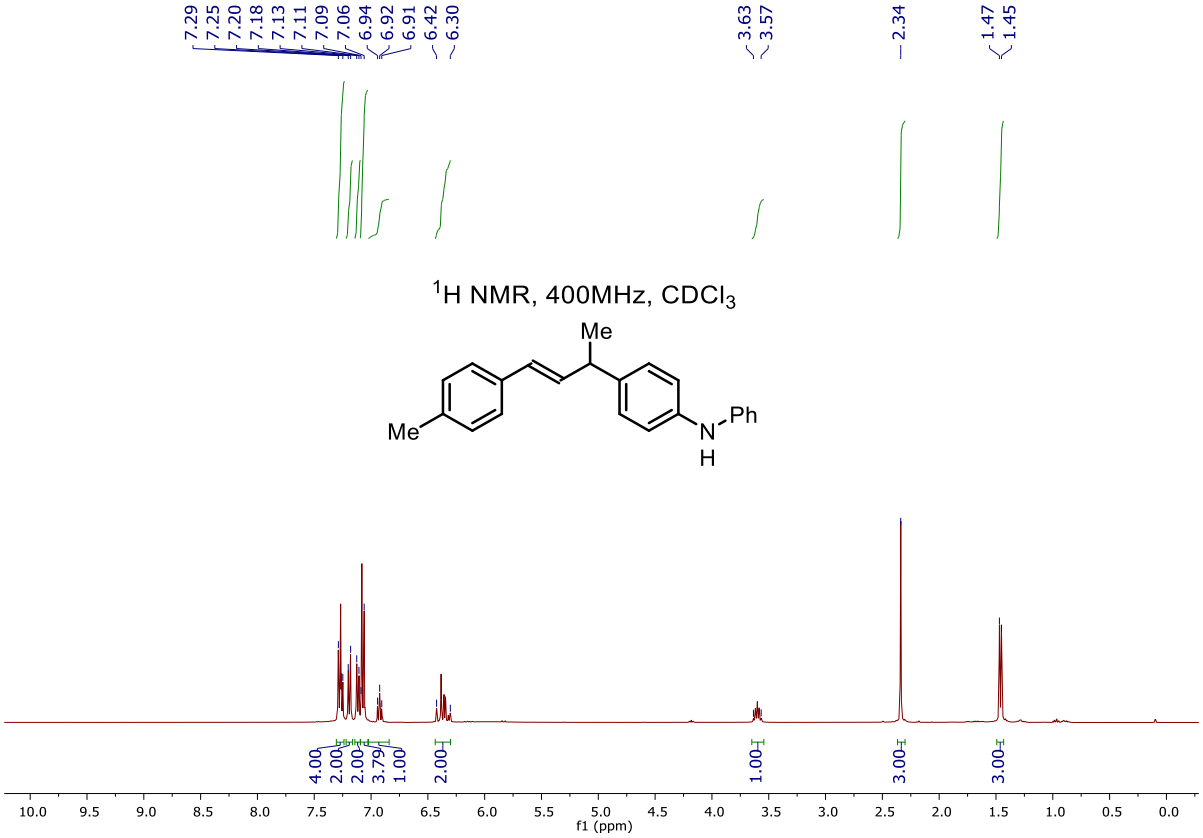


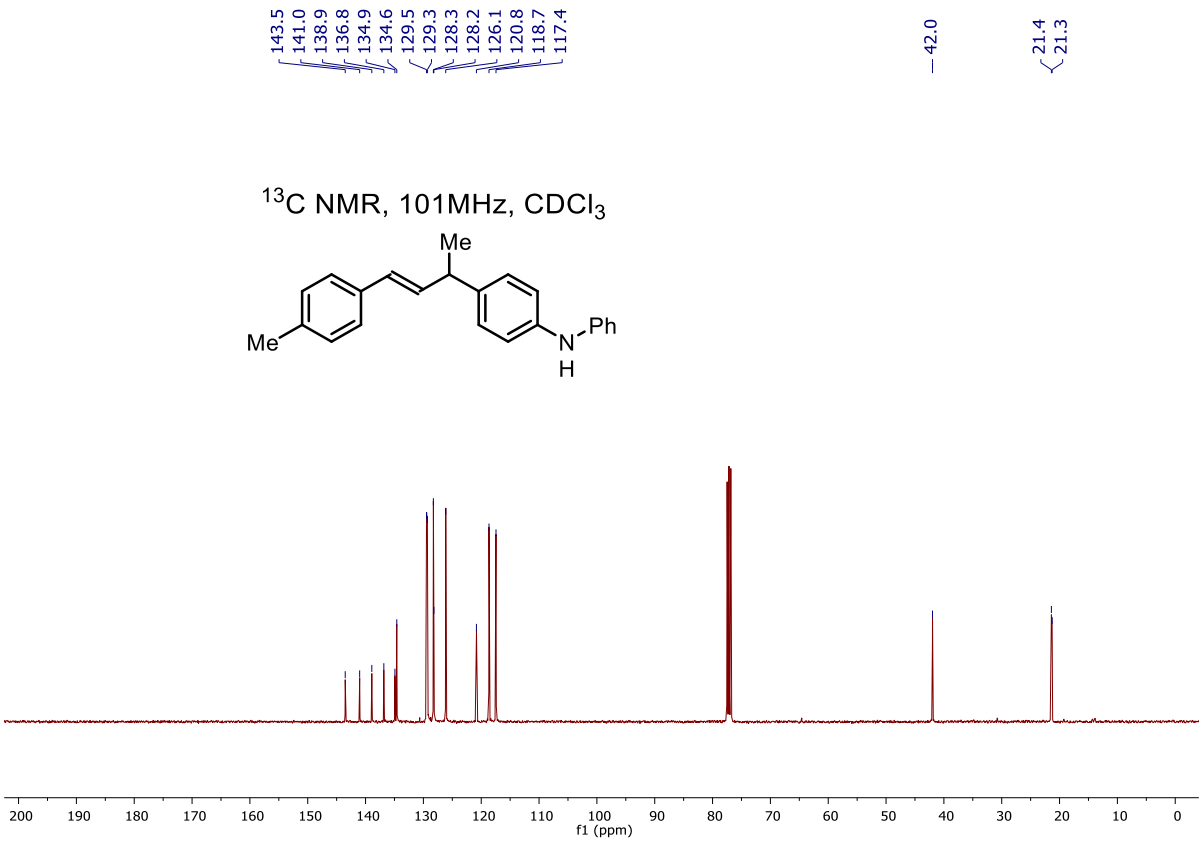
(*E*)-*N*-phenyl-4-(4-(o-tolyl)but-3-en-2-yl)aniline (316m)



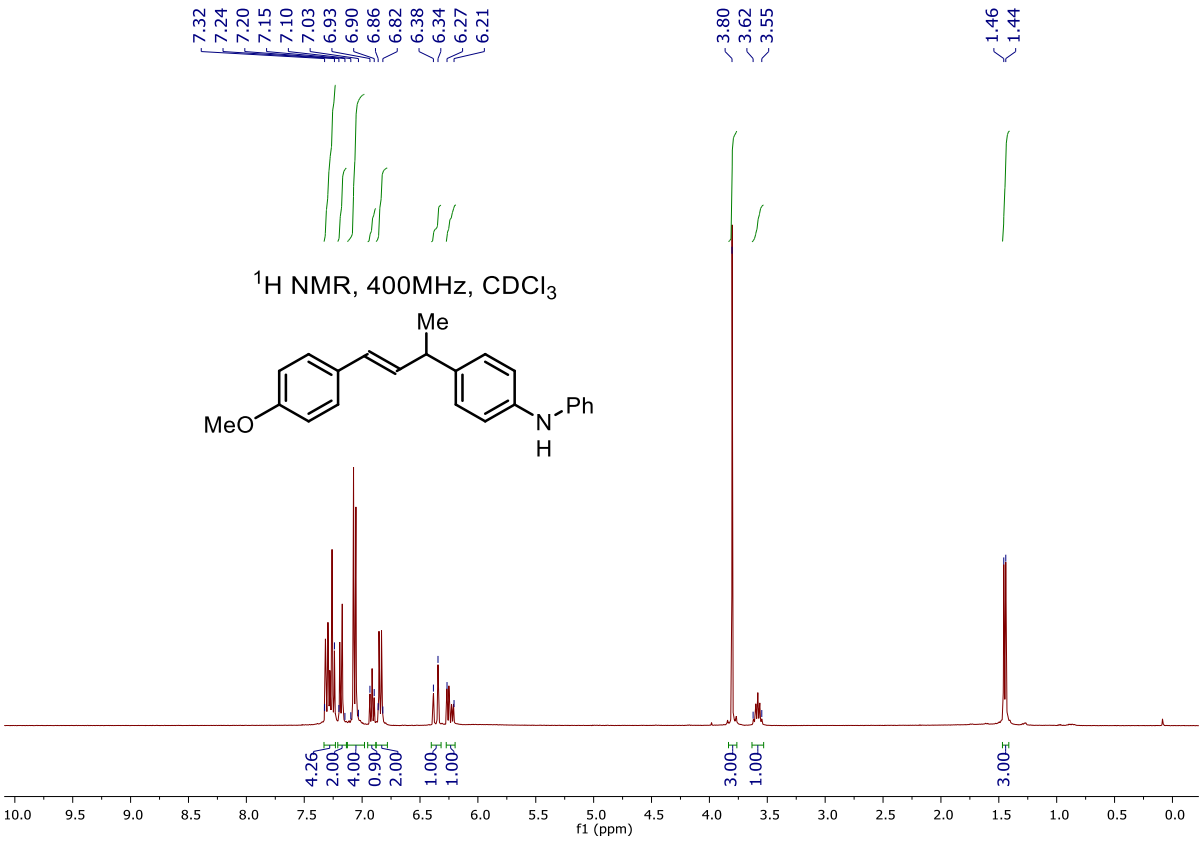


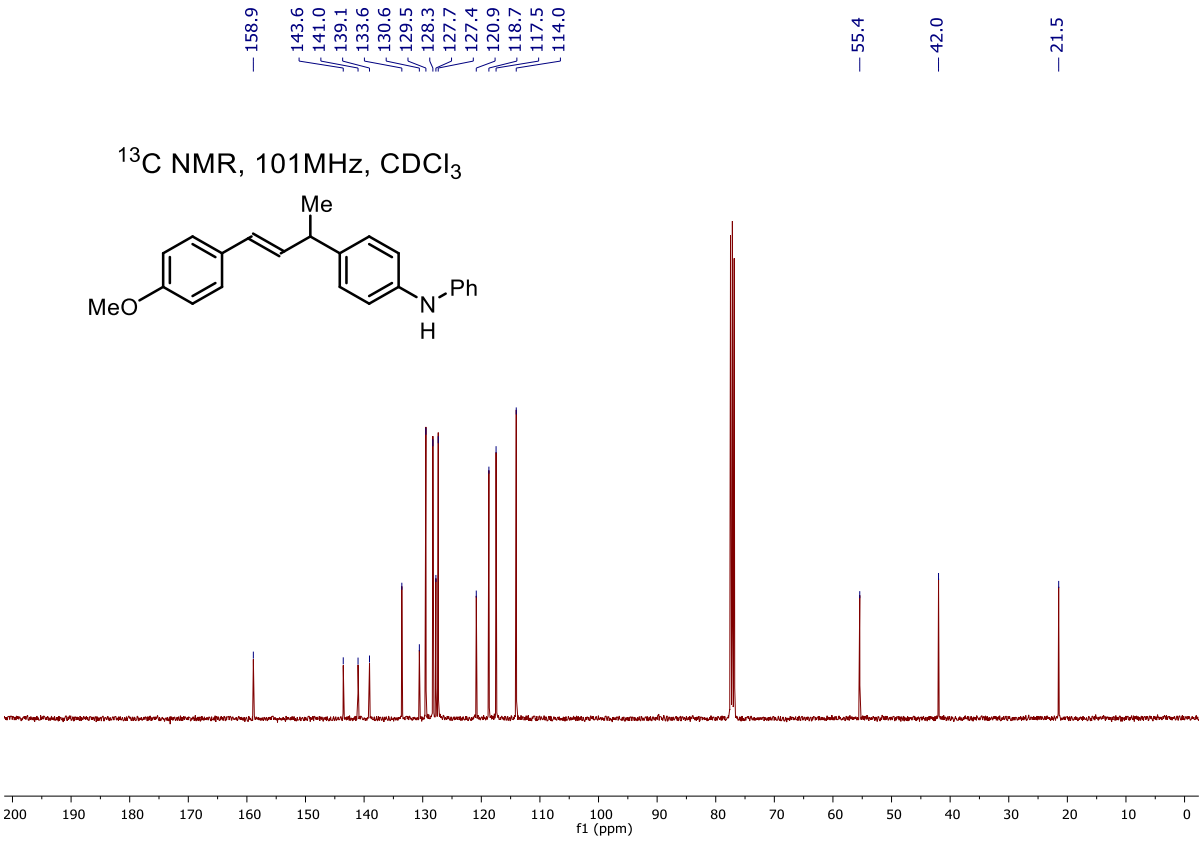
(*E*)-*N*-phenyl-4-(4-(p-tolyl)but-3-en-2-yl)aniline (316n)



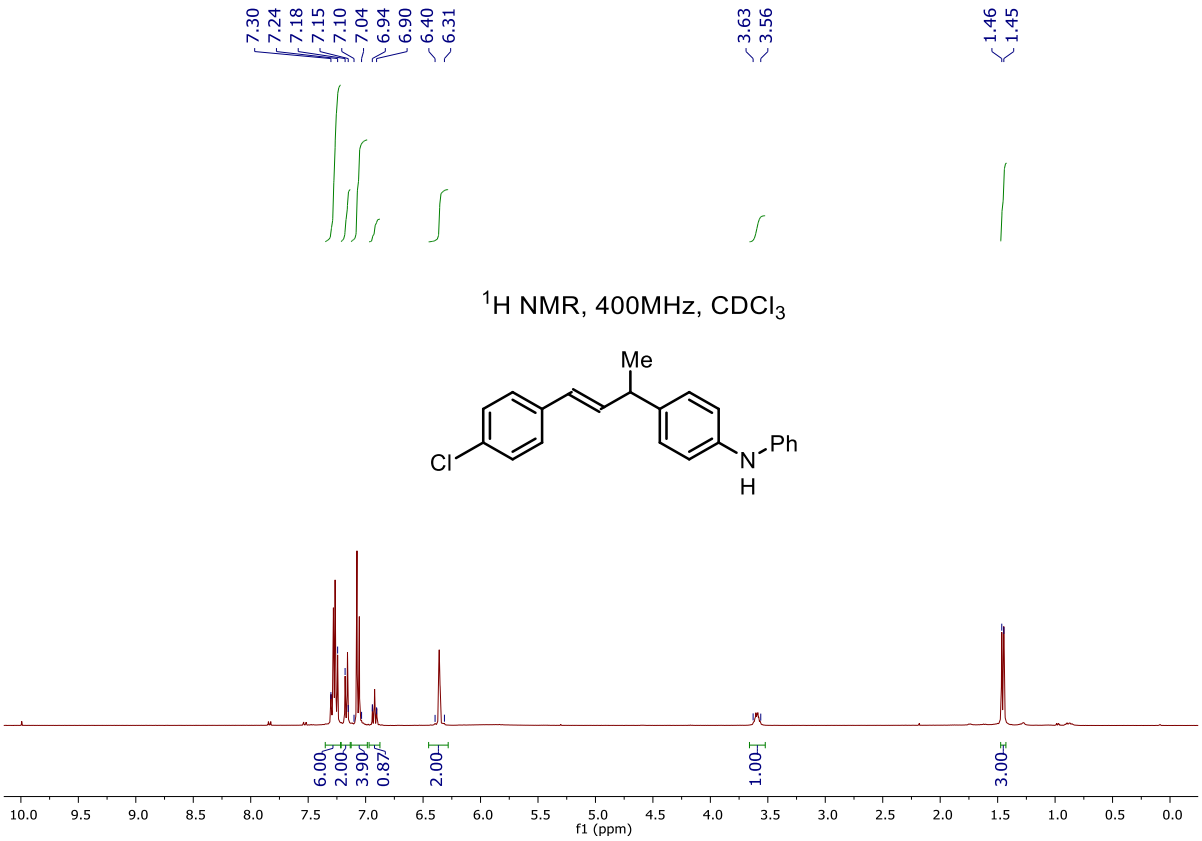


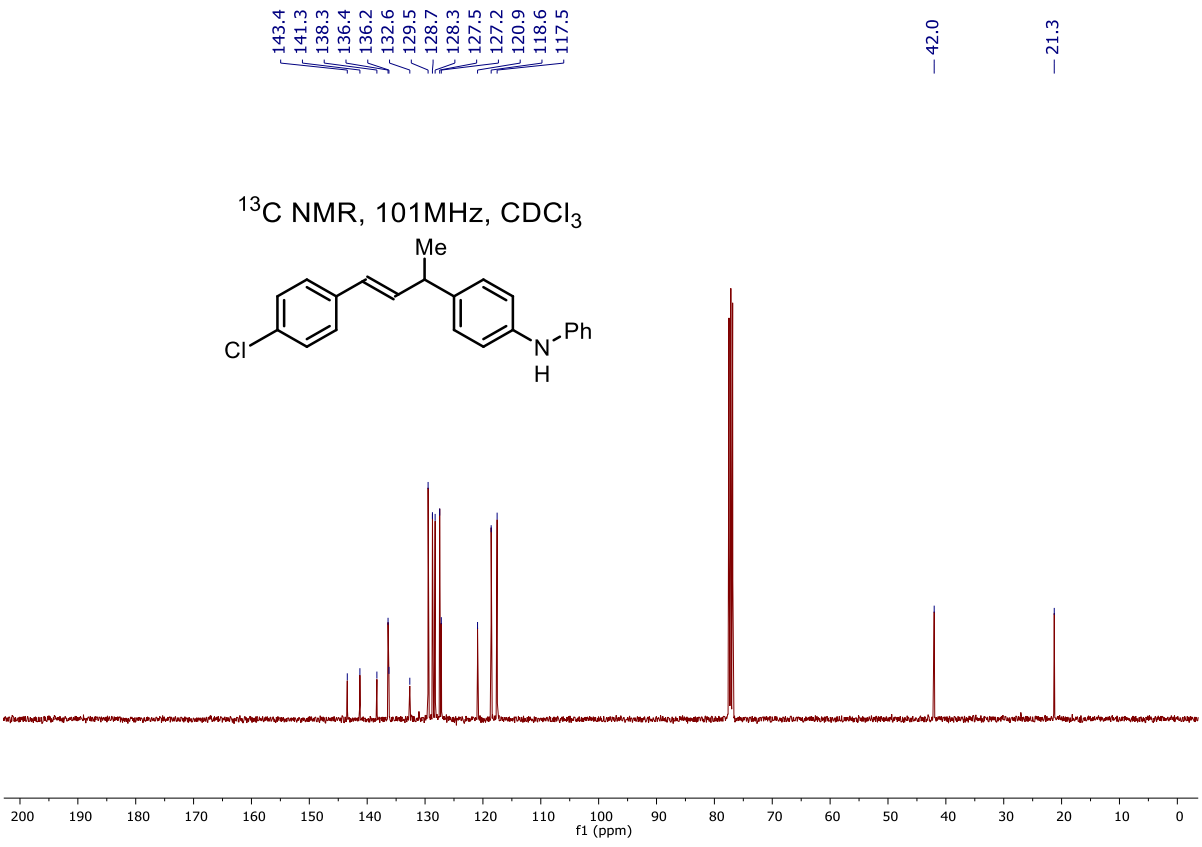
(*E*)-4-(4-(4-methoxyphenyl)but-3-en-2-yl)-*N*-phenylaniline (316o)



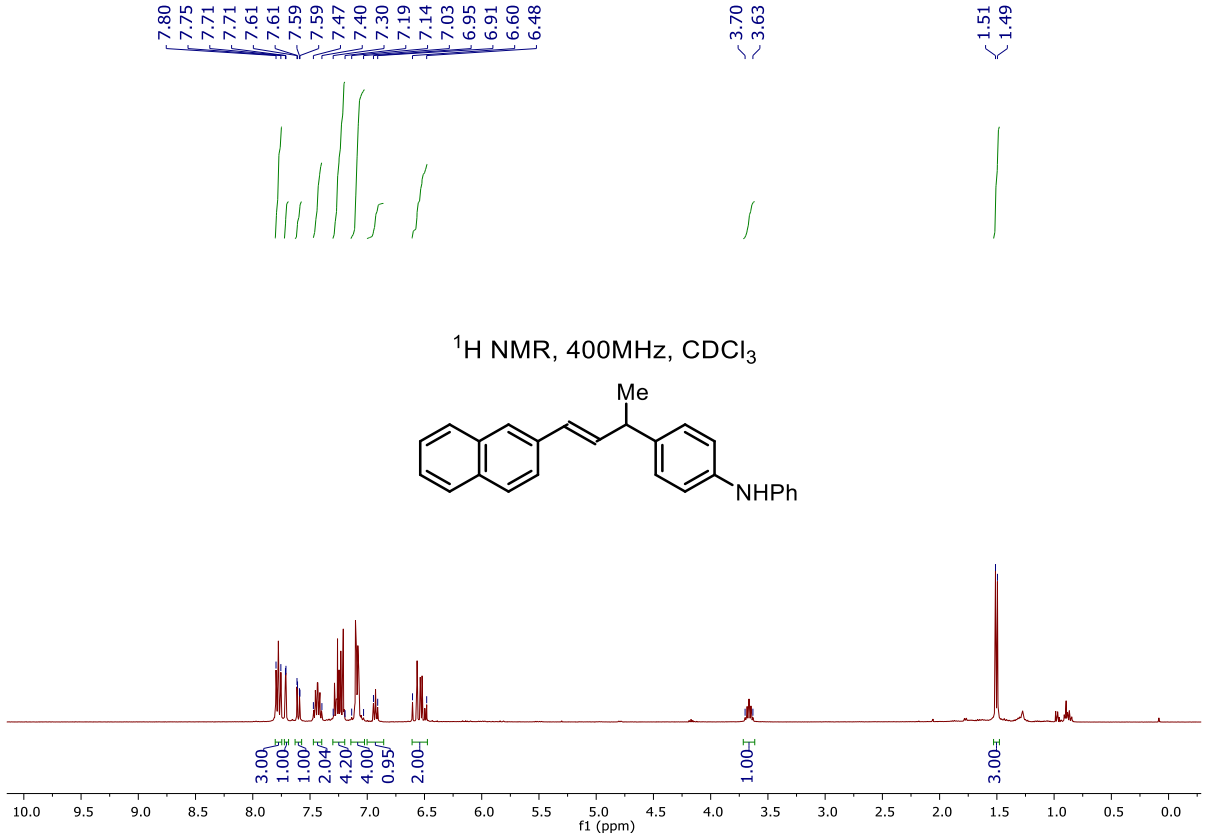


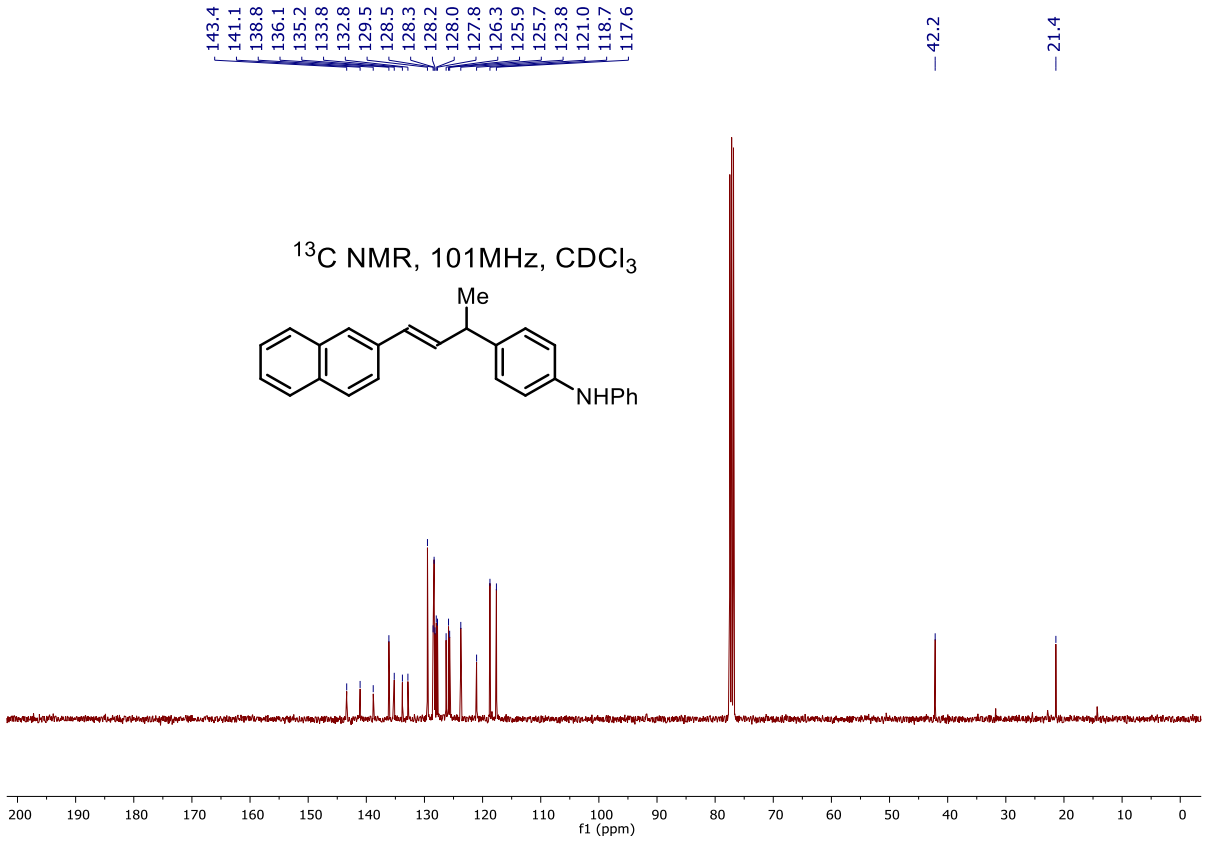
((*E*)-4-(4-(4-chlorophenyl)but-3-en-2-yl)-*N*-phenylaniline (316p)



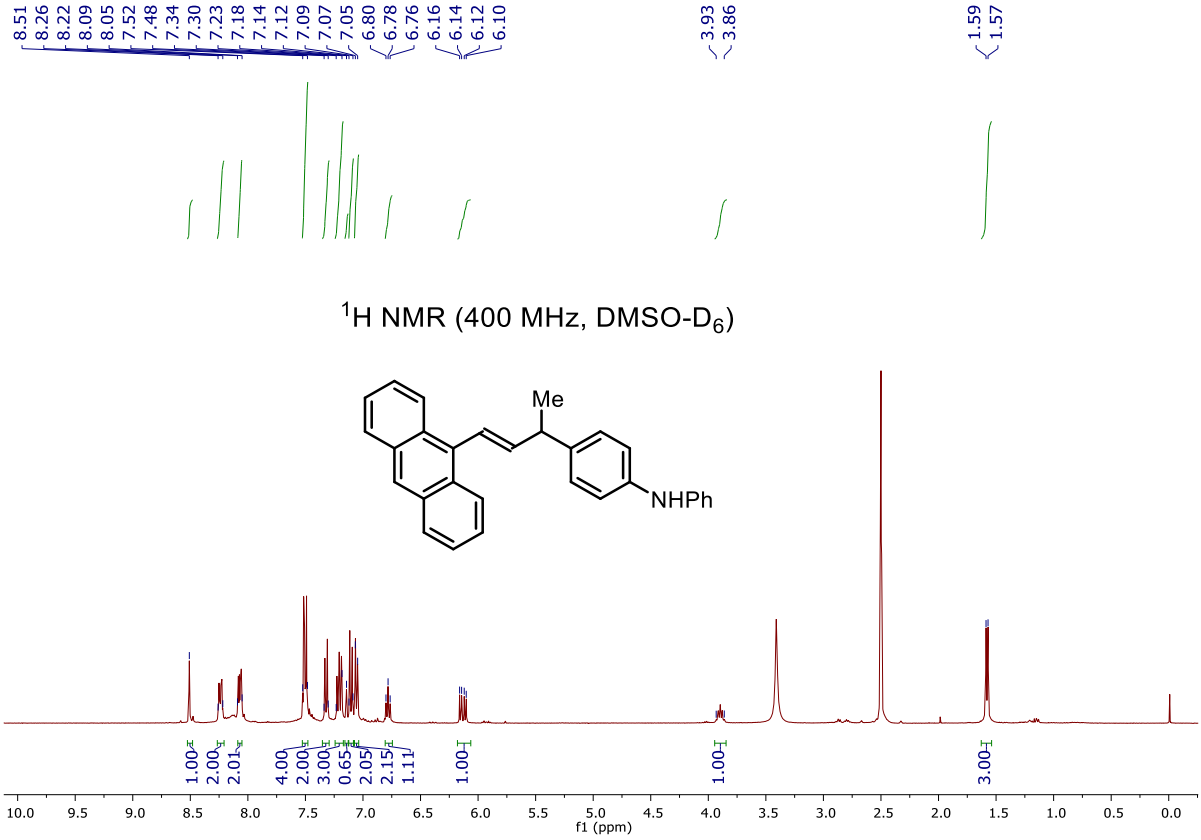


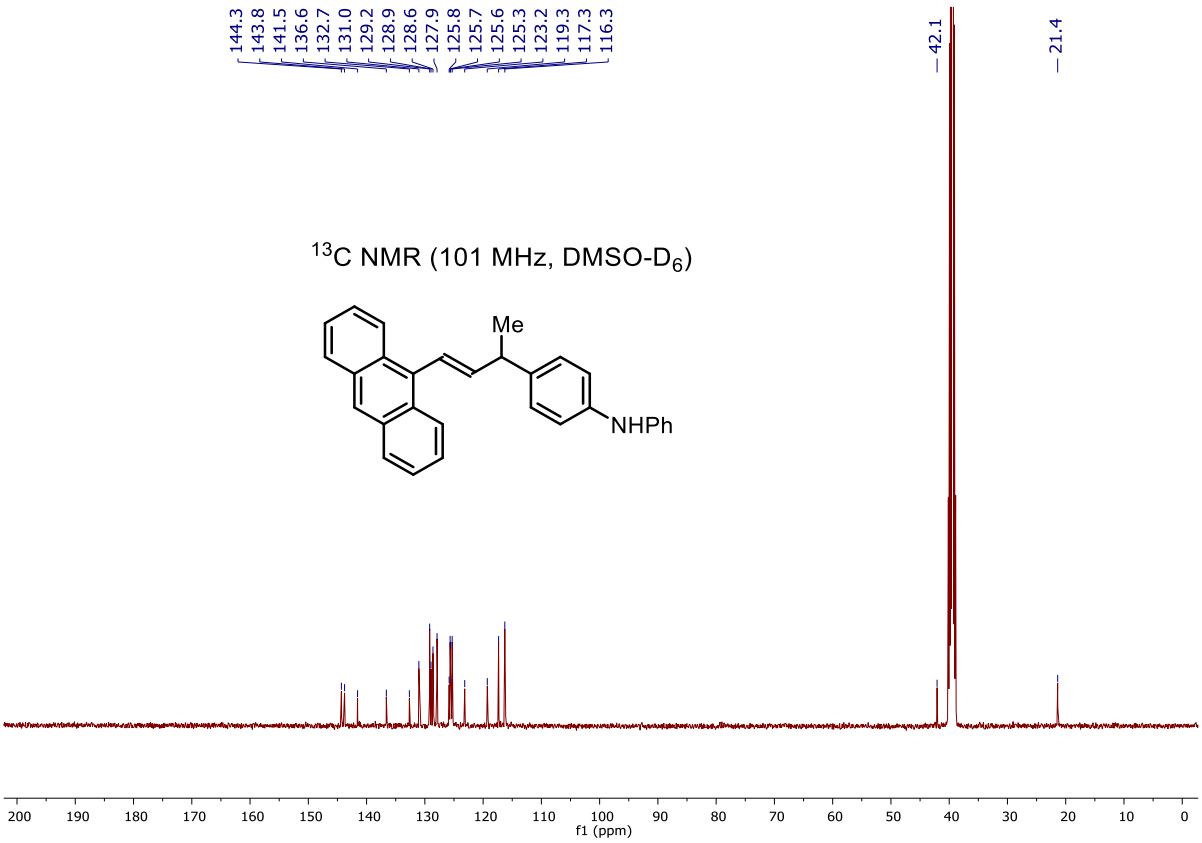
(*E*)-4-(4-(naphthalen-2-yl)but-3-en-2-yl)-*N*-phenylaniline (316q)



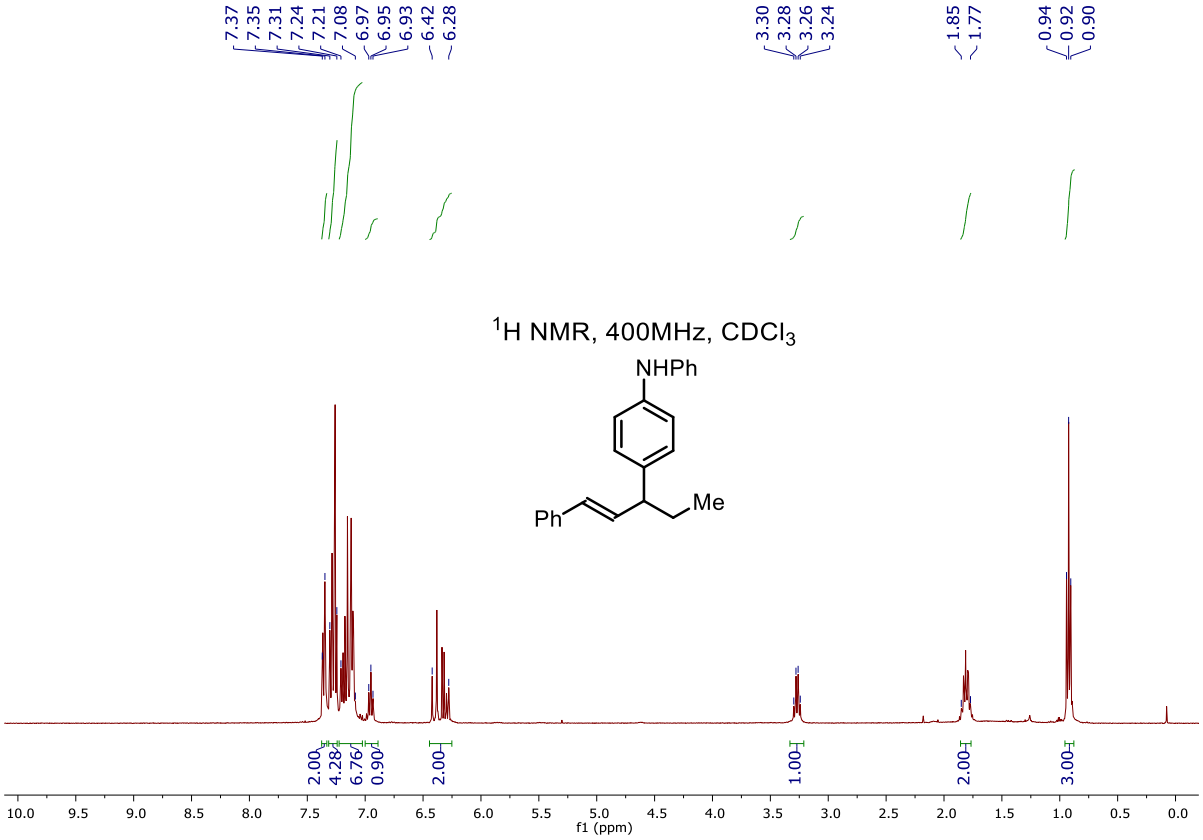


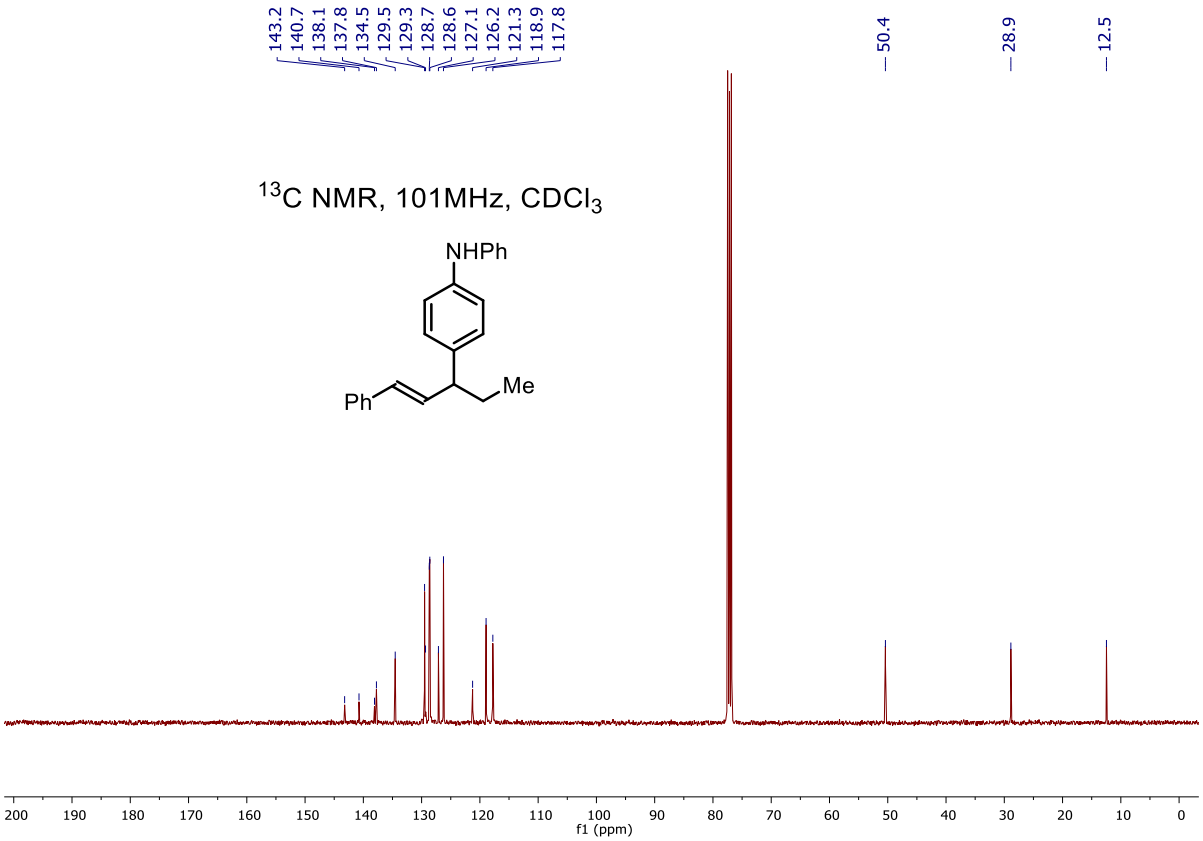
(*E*)-4-(4-(anthracen-9-yl)but-3-en-2-yl)-*N*-phenylaniline (316r)



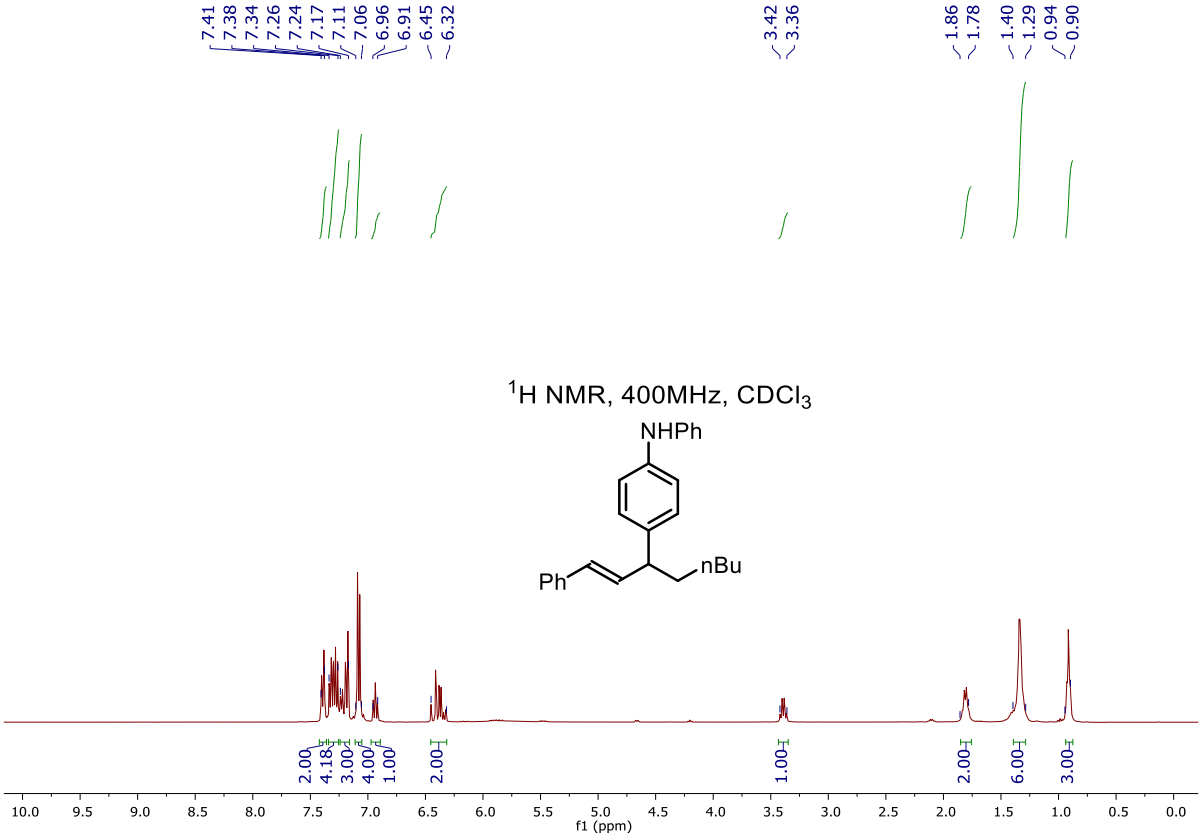


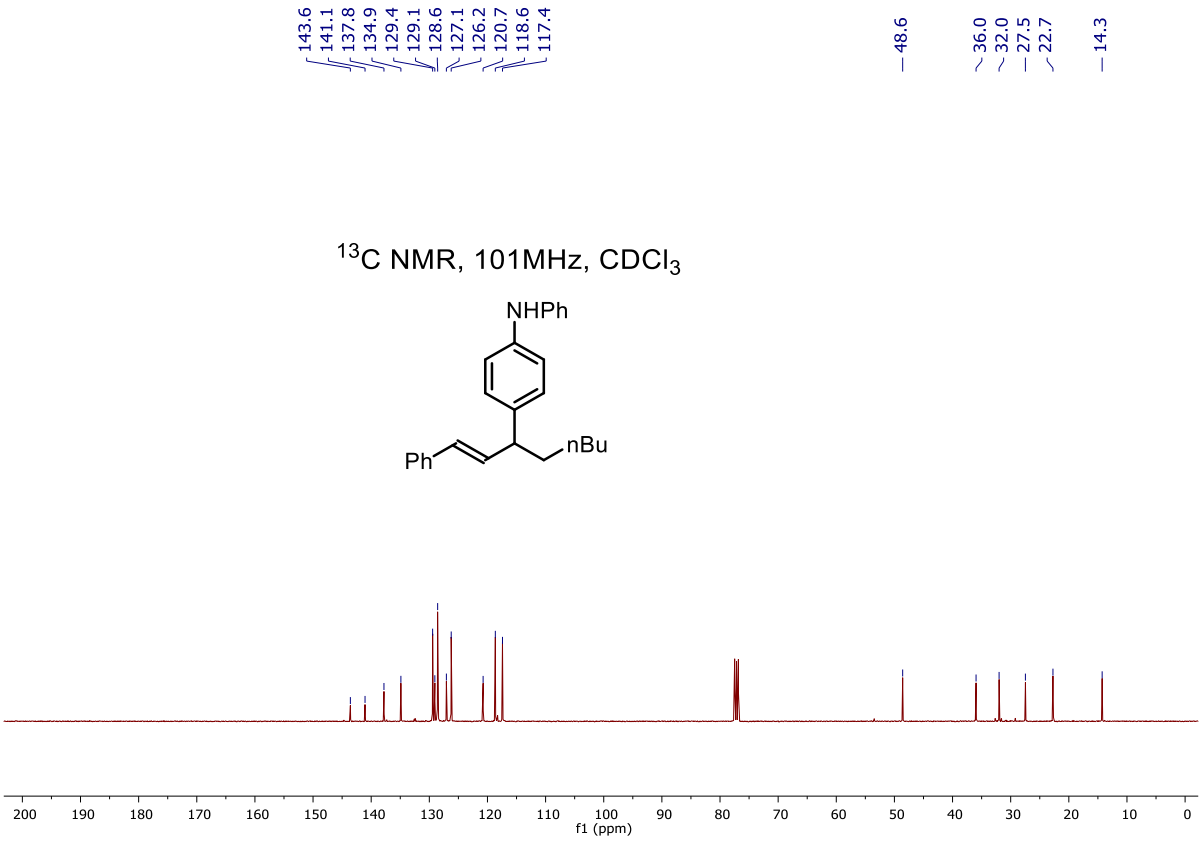
(*E*)-*N*-phenyl-4-(1-phenylpent-1-en-3-yl)aniline (316s)



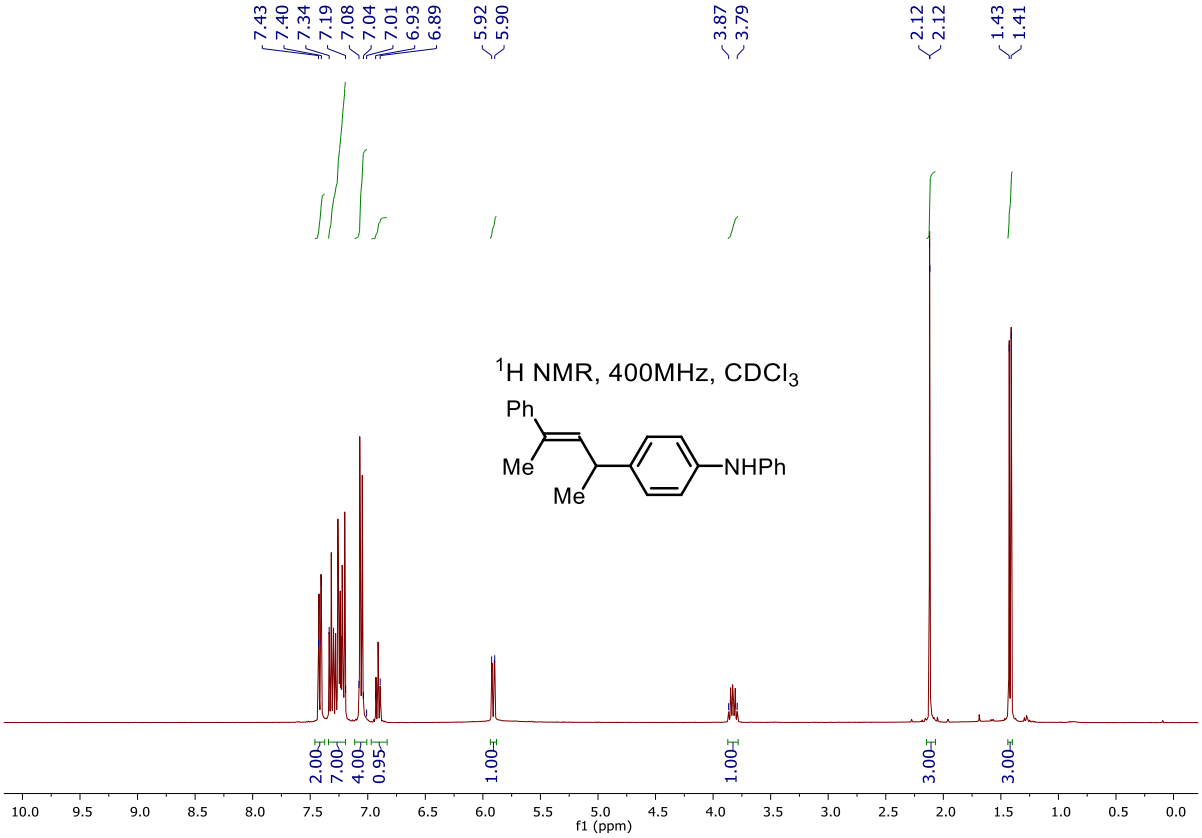


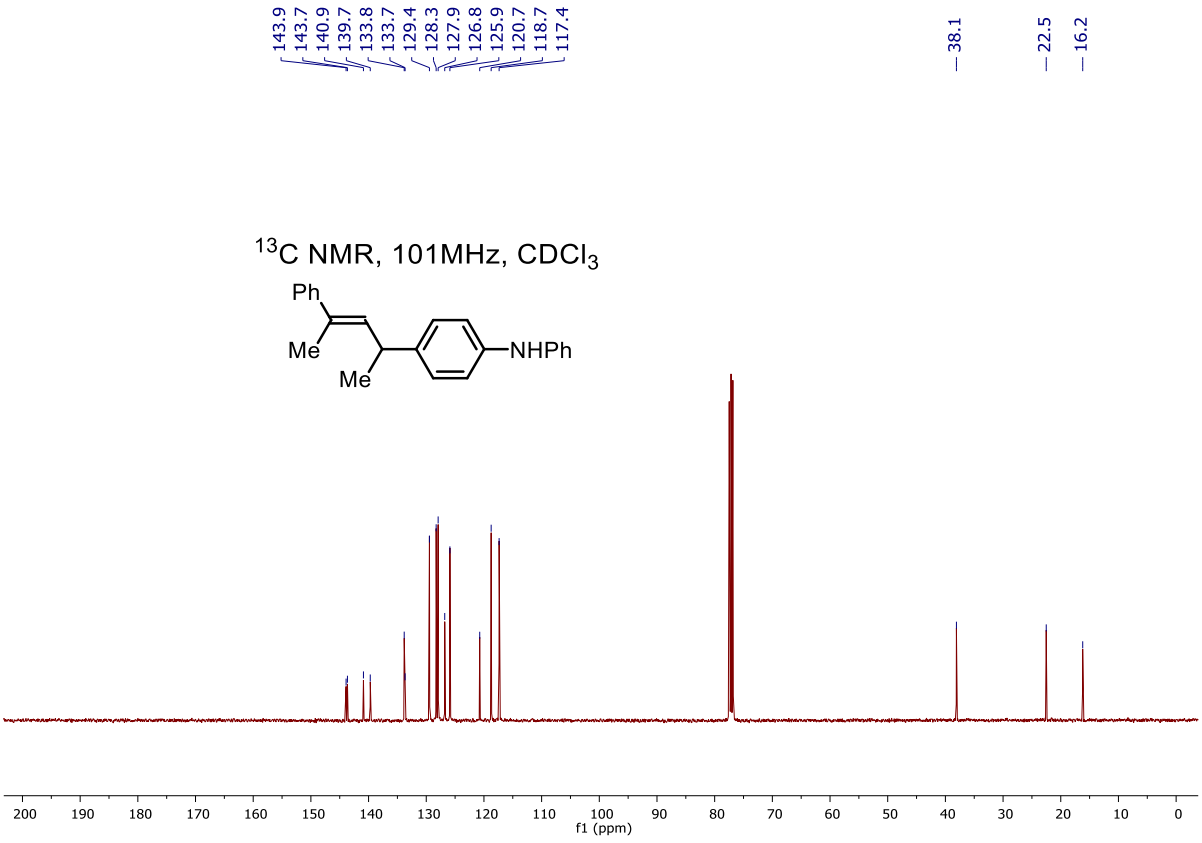
(*E*)-*N*-phenyl-4-(1-phenyloct-1-en-3-yl)aniline (316t)



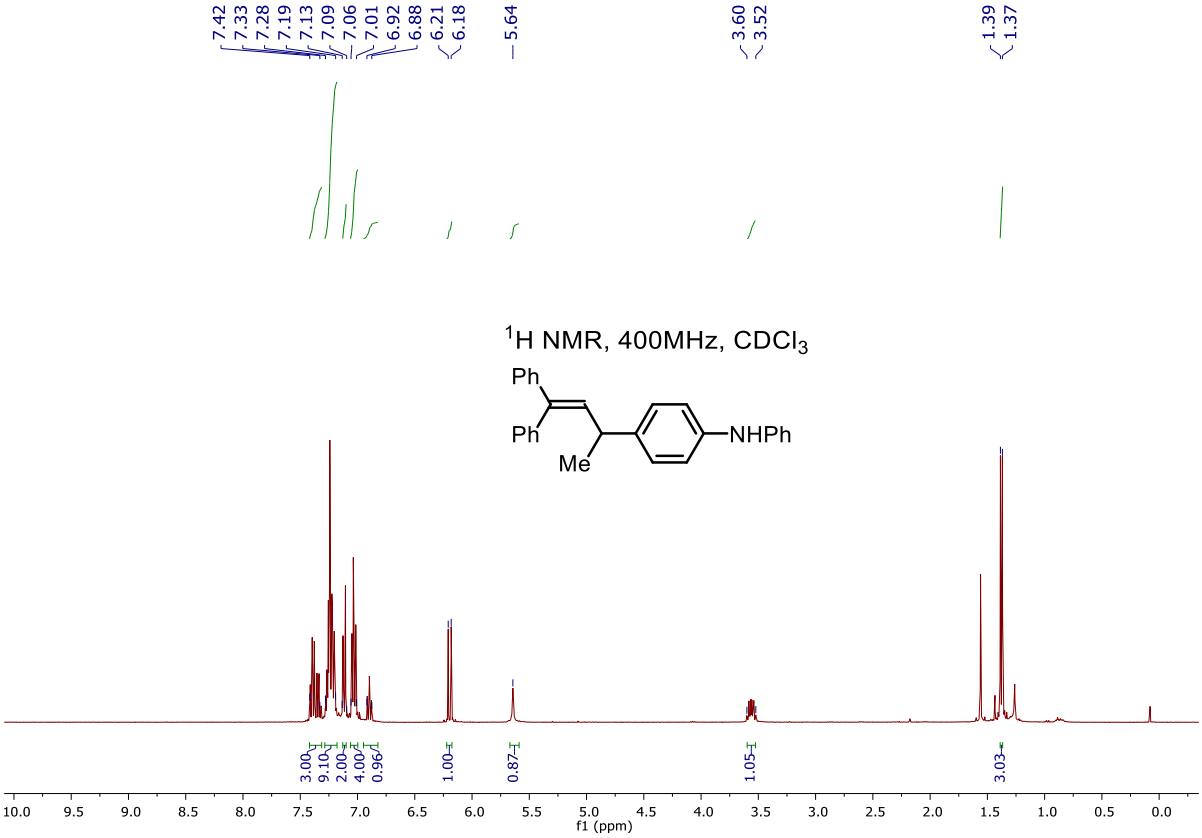


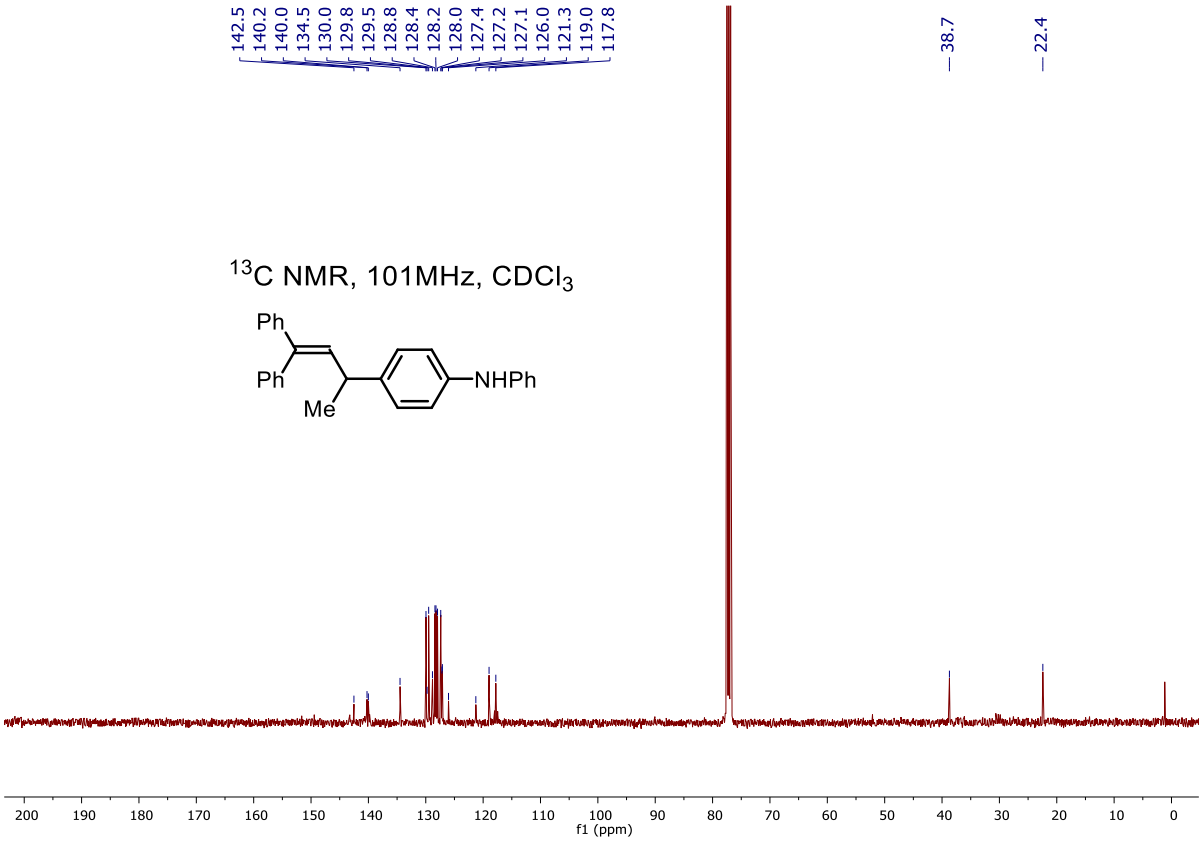
(*E*)-*N*-phenyl-4-(4-phenylpent-3-en-2-yl)aniline (316u)



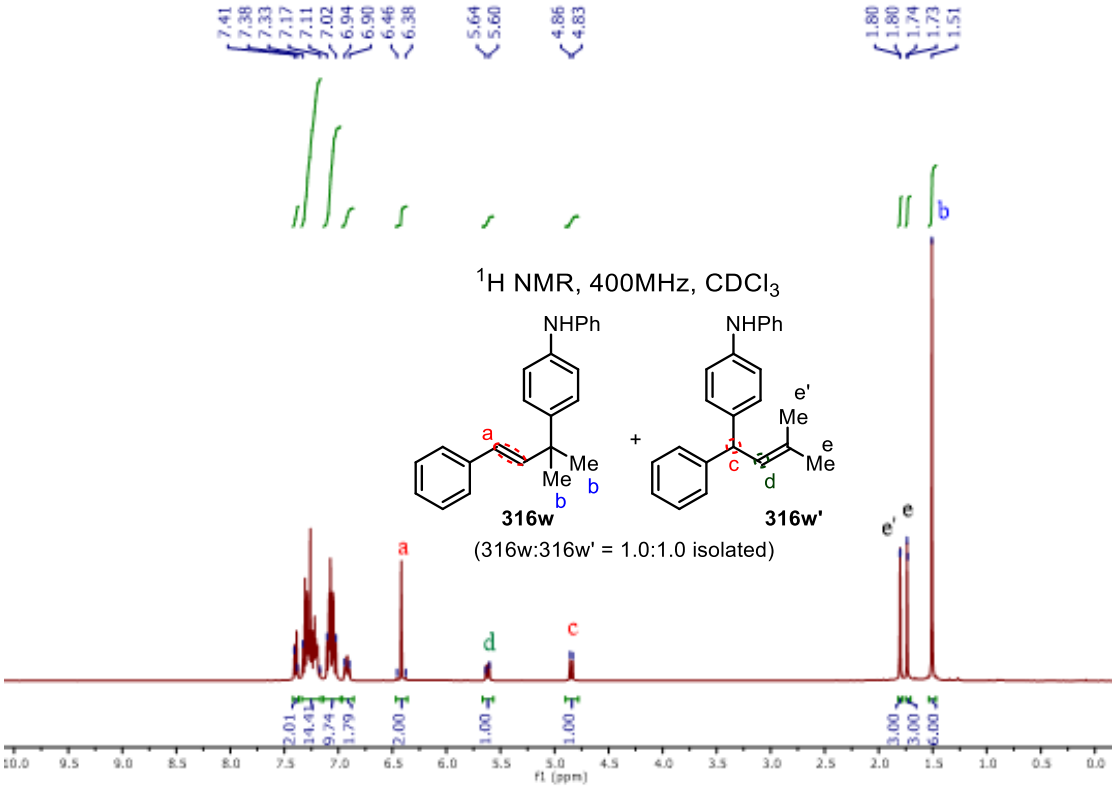


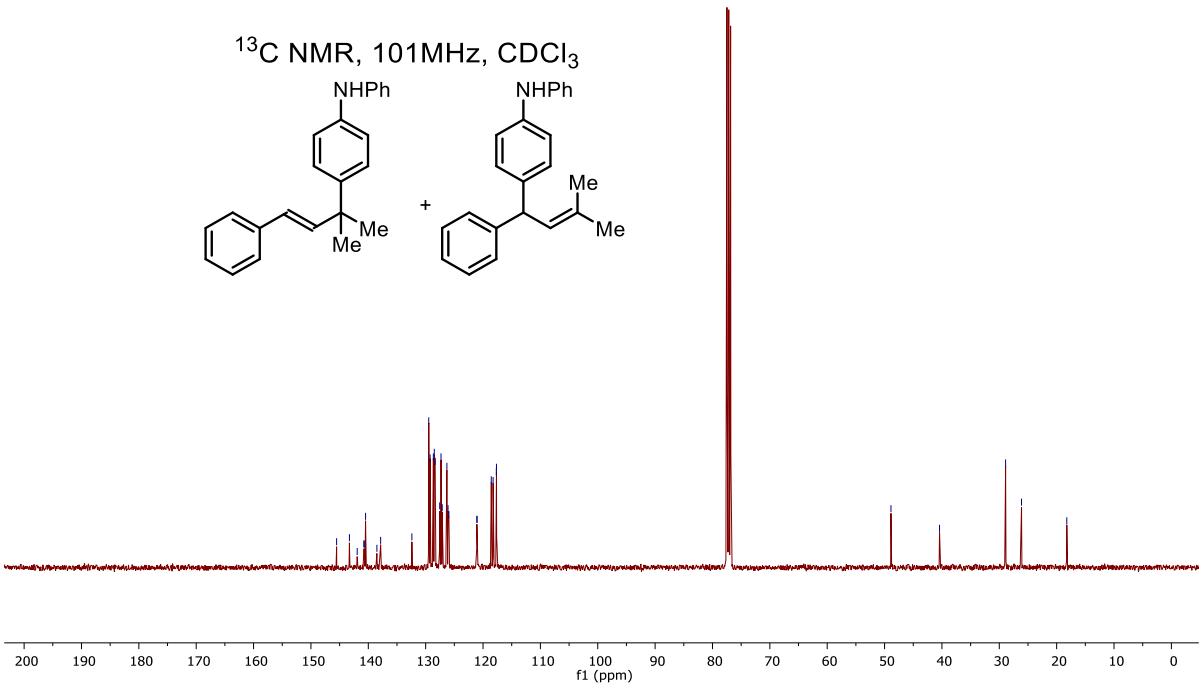
4-(4,4-diphenylbut-3-en-2-yl)-*N*-phenylaniline (316v)



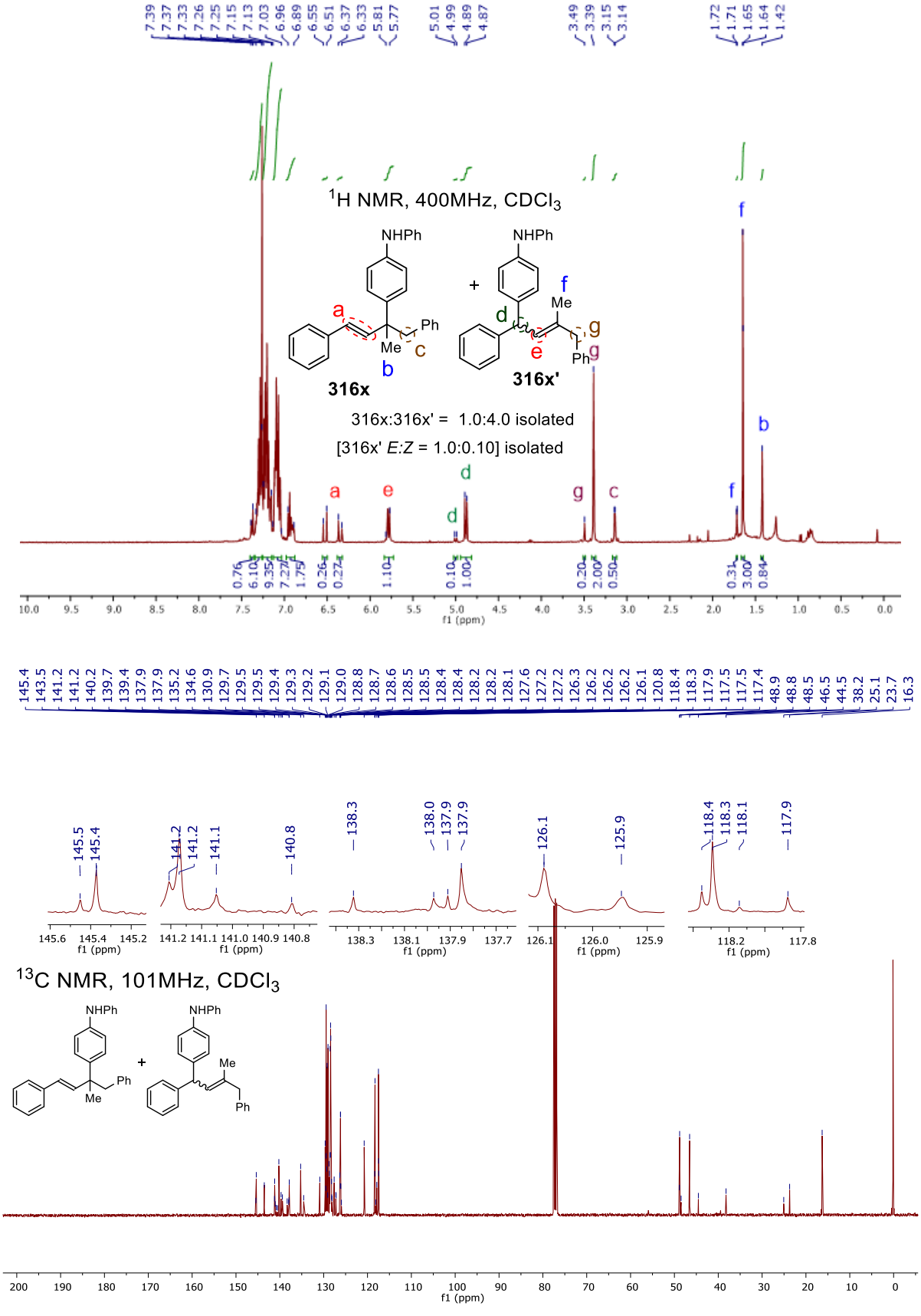


(*E*)-4-(2-methyl-4-phenylbut-3-en-2-yl)-*N*-phenylaniline and 4-(3-methyl-1-phenylbut-2-en-1-yl)-*N*-phenylaniline (316w + 316w')



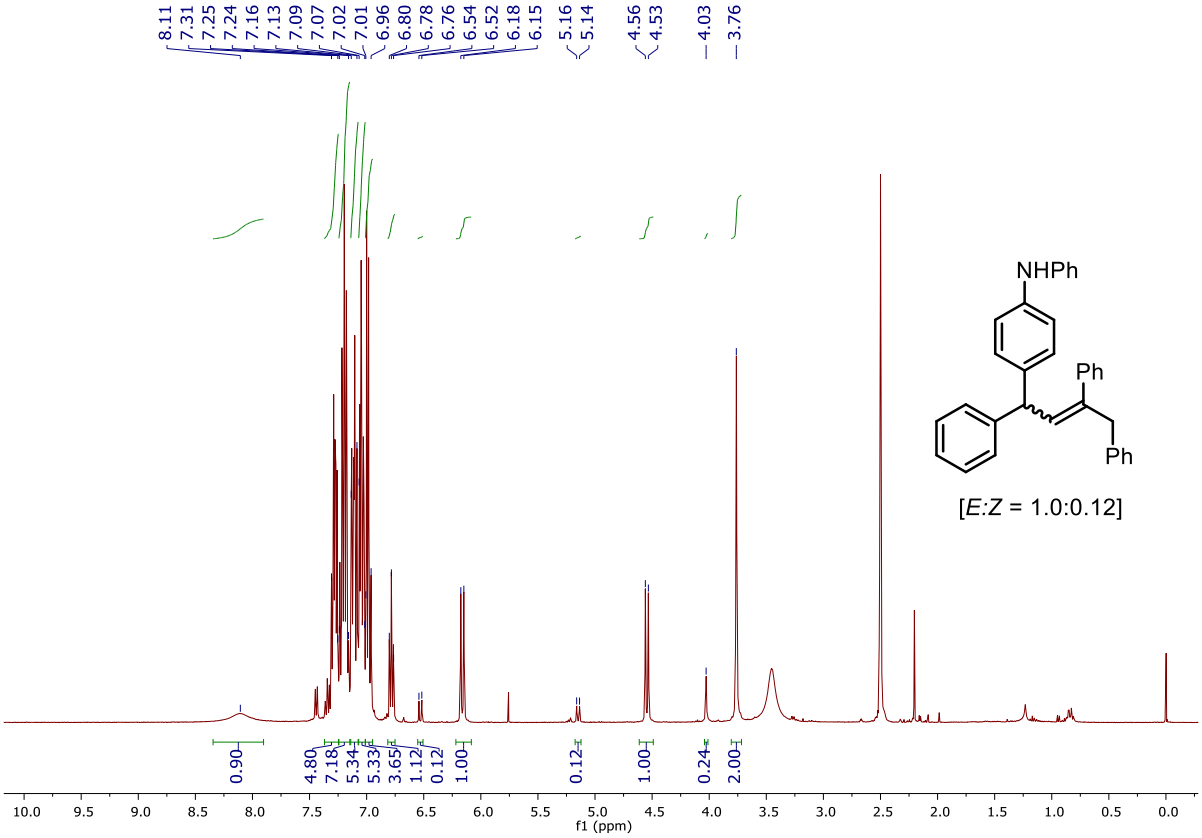


(*E*)-4-(2-methyl-1,4-diphenylbut-3-en-2-yl)-*N*-phenylaniline and 4-(3-methyl-1,4-diphenylbut-2-en-1-yl)-*N*-phenylaniline (316x+316x')



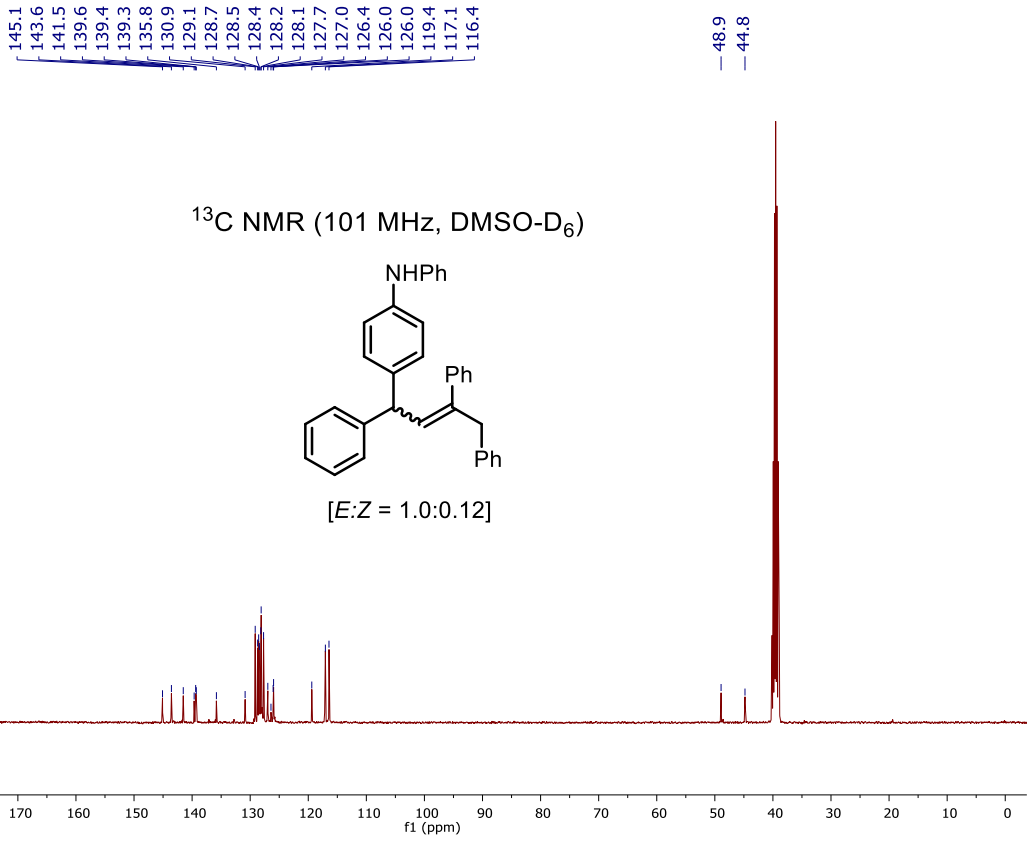
_N_-phenyl-4-(1,3,4-triphenylbut-2-en-1-yl)aniline (316y)

^{1}H NMR (400 MHz, DMSO-D$_6$)



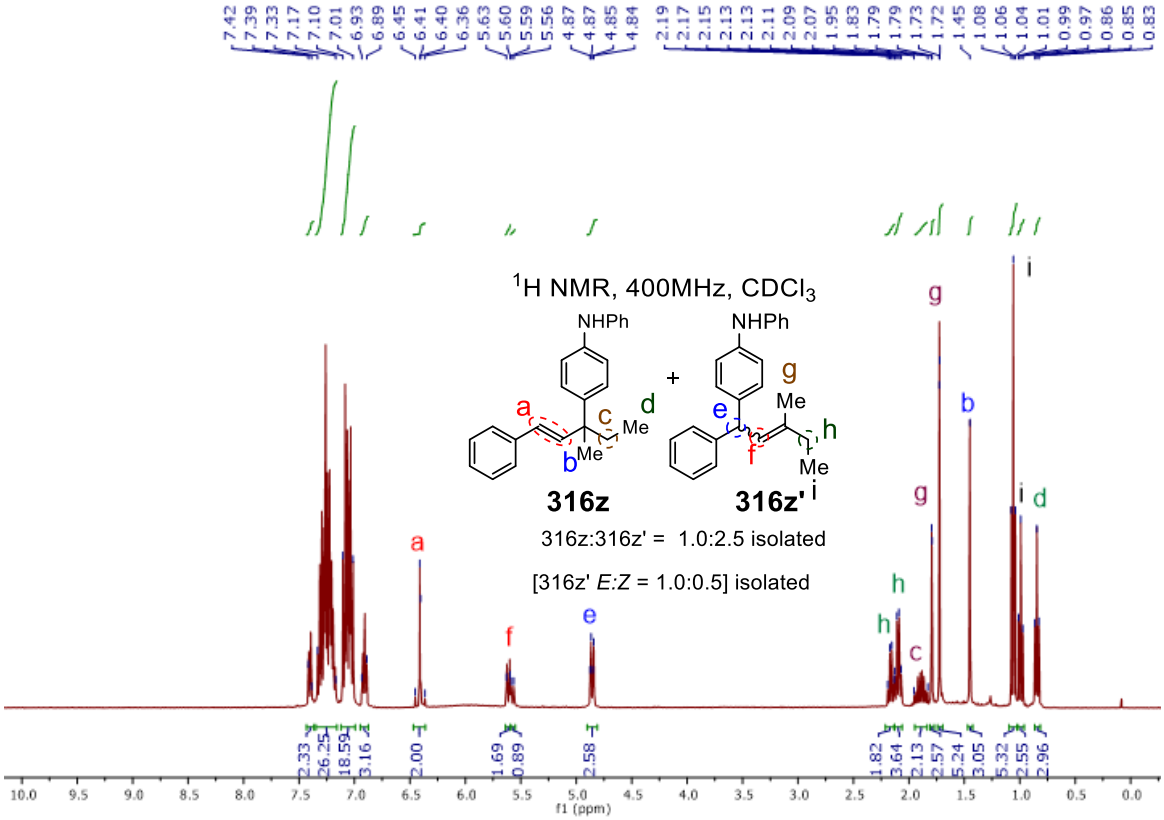
[*E*:*Z* = 1.0:0.12]

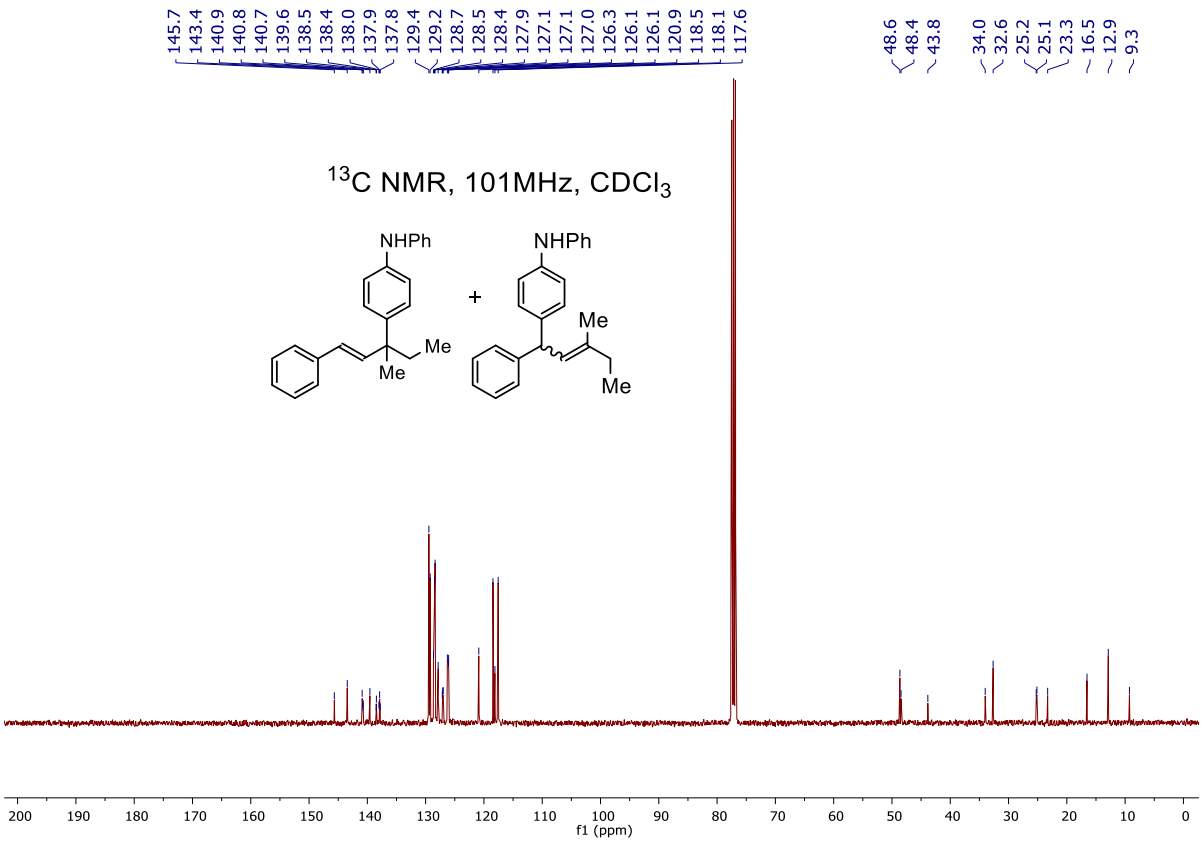
^{13}C NMR (101 MHz, DMSO-D$_6$)



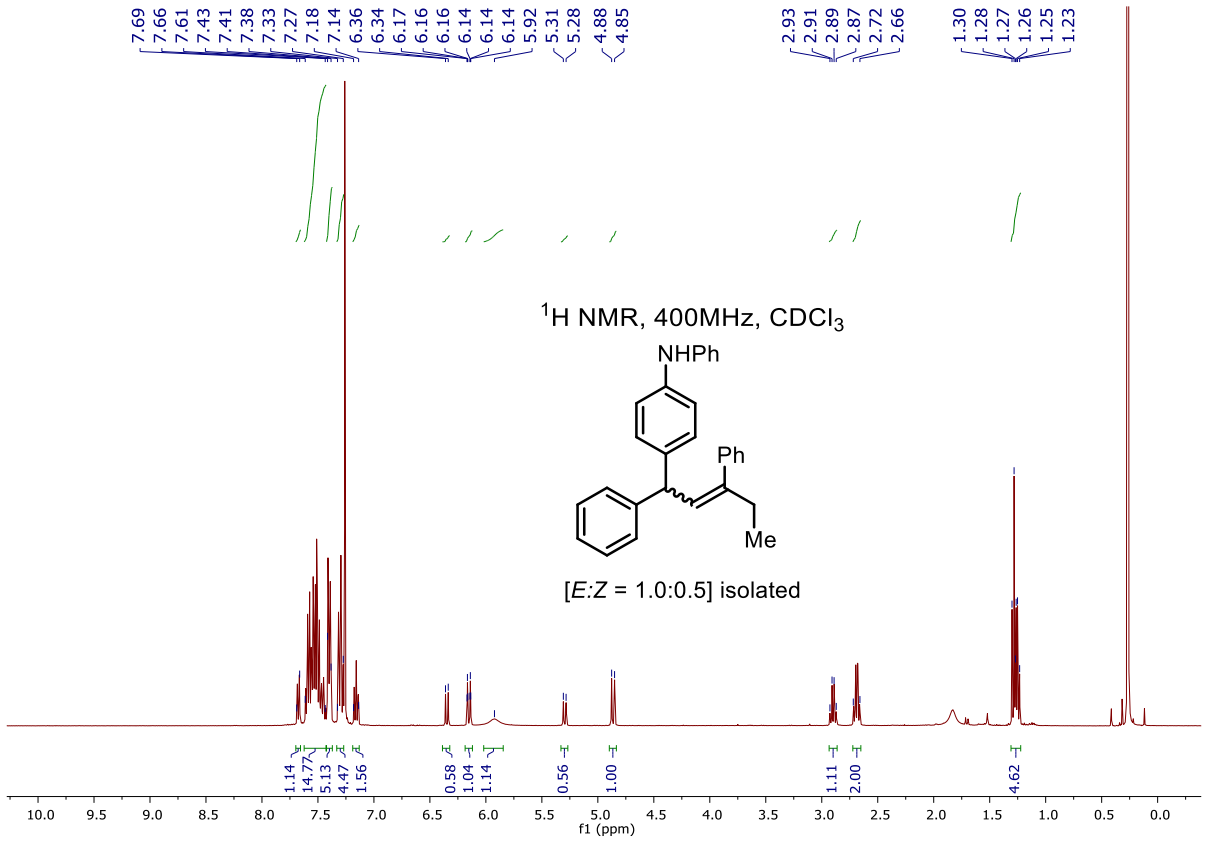
[*E*:*Z* = 1.0:0.12]

(*E*)-4-(3-methyl-1-phenylpent-1-en-3-yl)-*N*-phenylaniline and 4-(3-methyl-1-phenylpent-2-en-1-yl)-*N*-phenylaniline (316z + 316z')



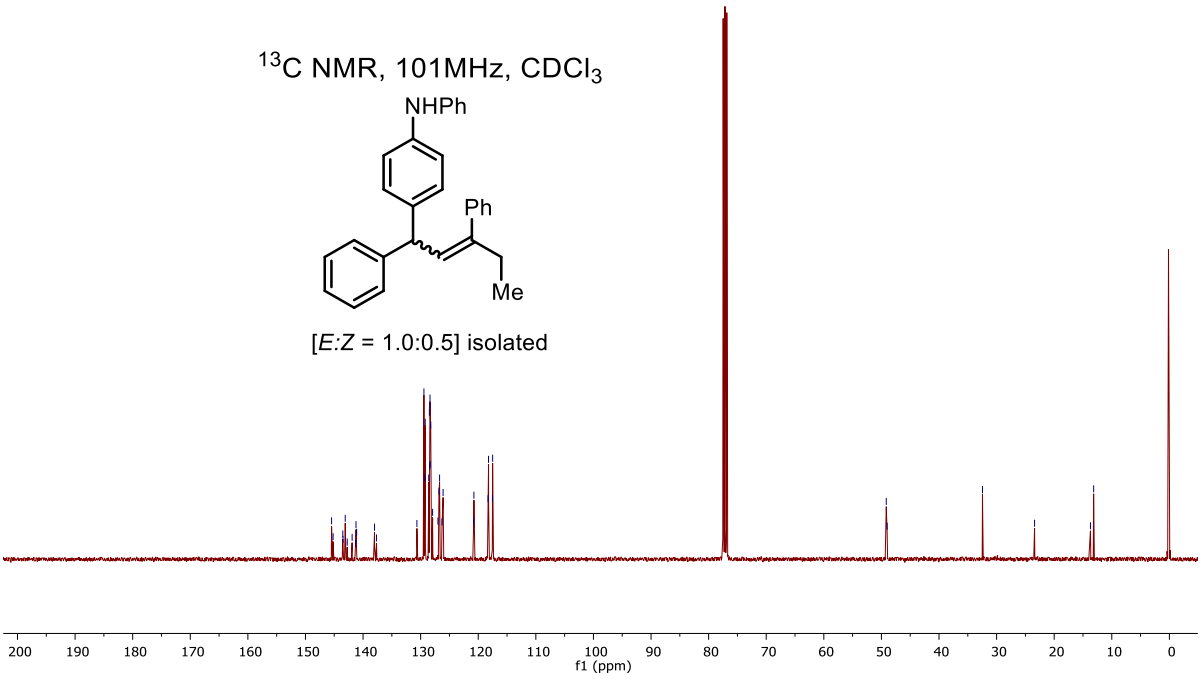


4-(1,3-diphenylpent-2-en-1-yl)-*N*-phenylaniline (316za)



^{1}H NMR, 400MHz, $CDCl_3$

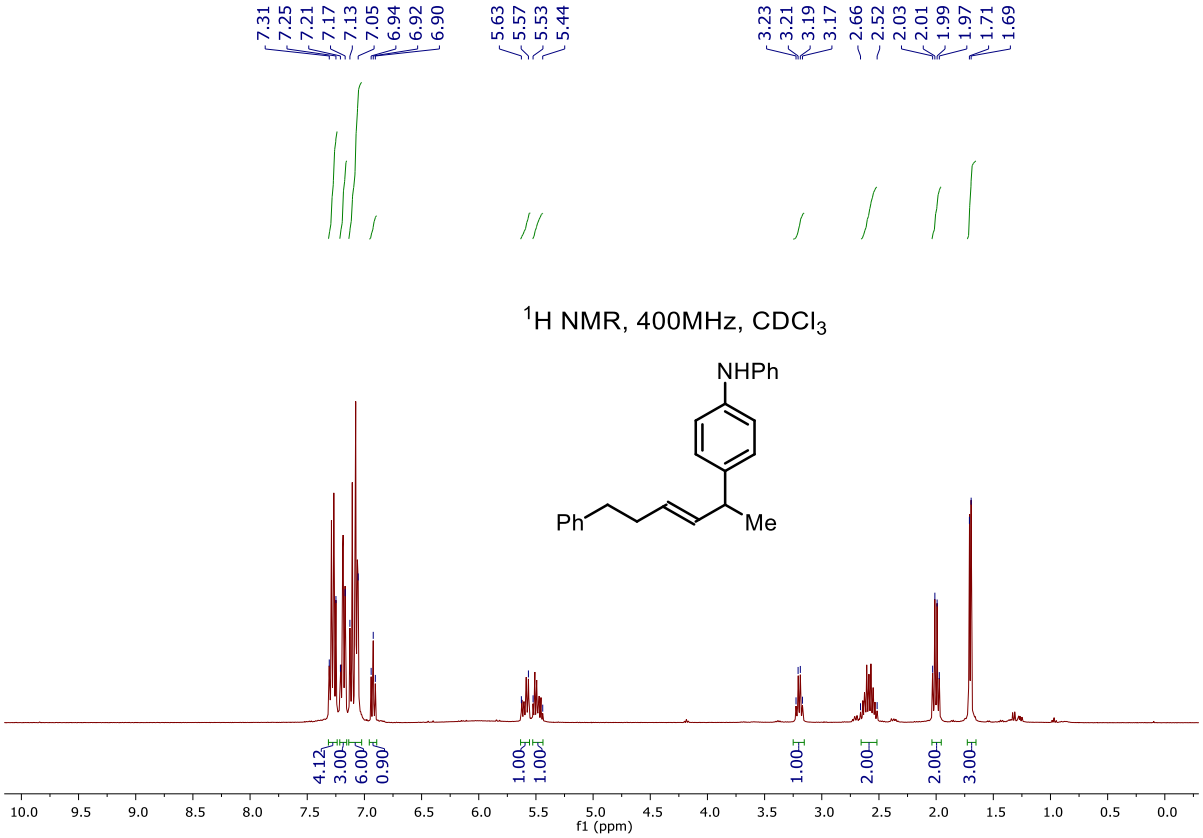
[*E*:*Z* = 1.0:0.5] isolated

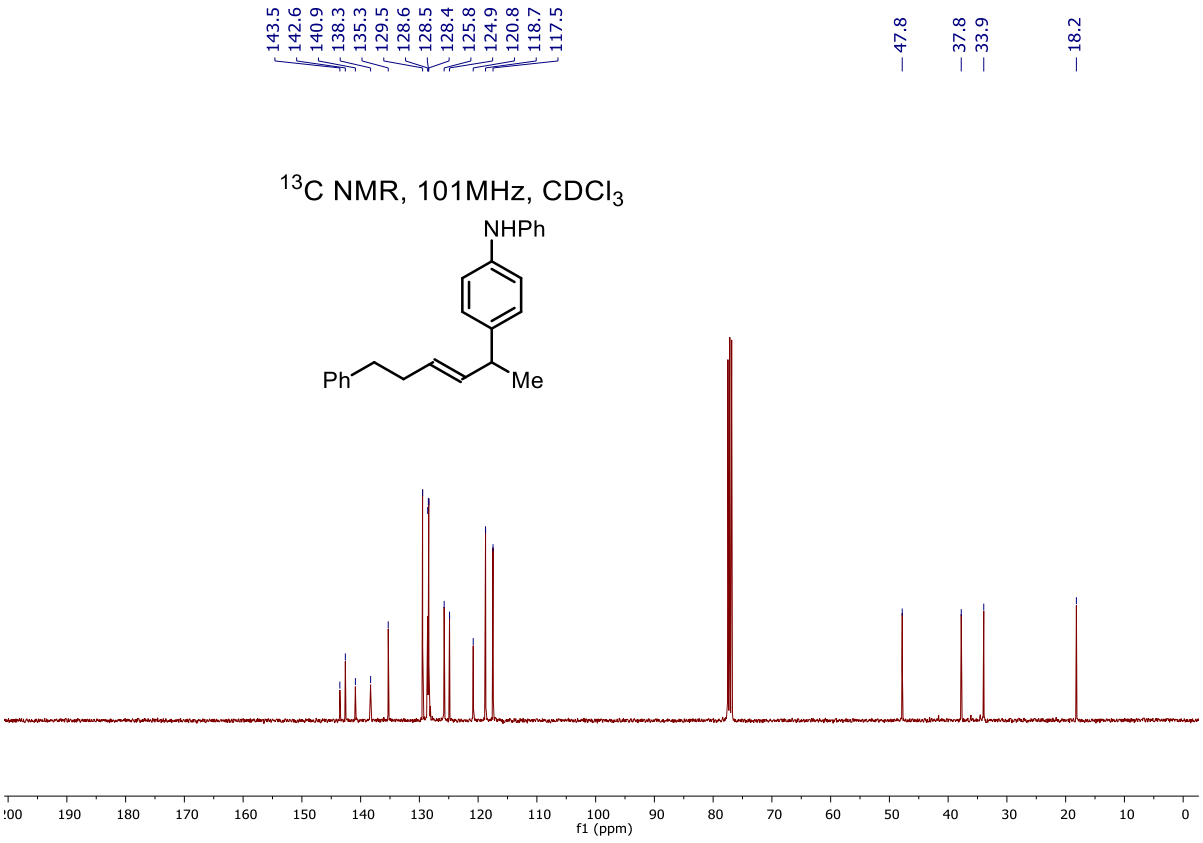


^{13}C NMR, 101MHz, $CDCl_3$

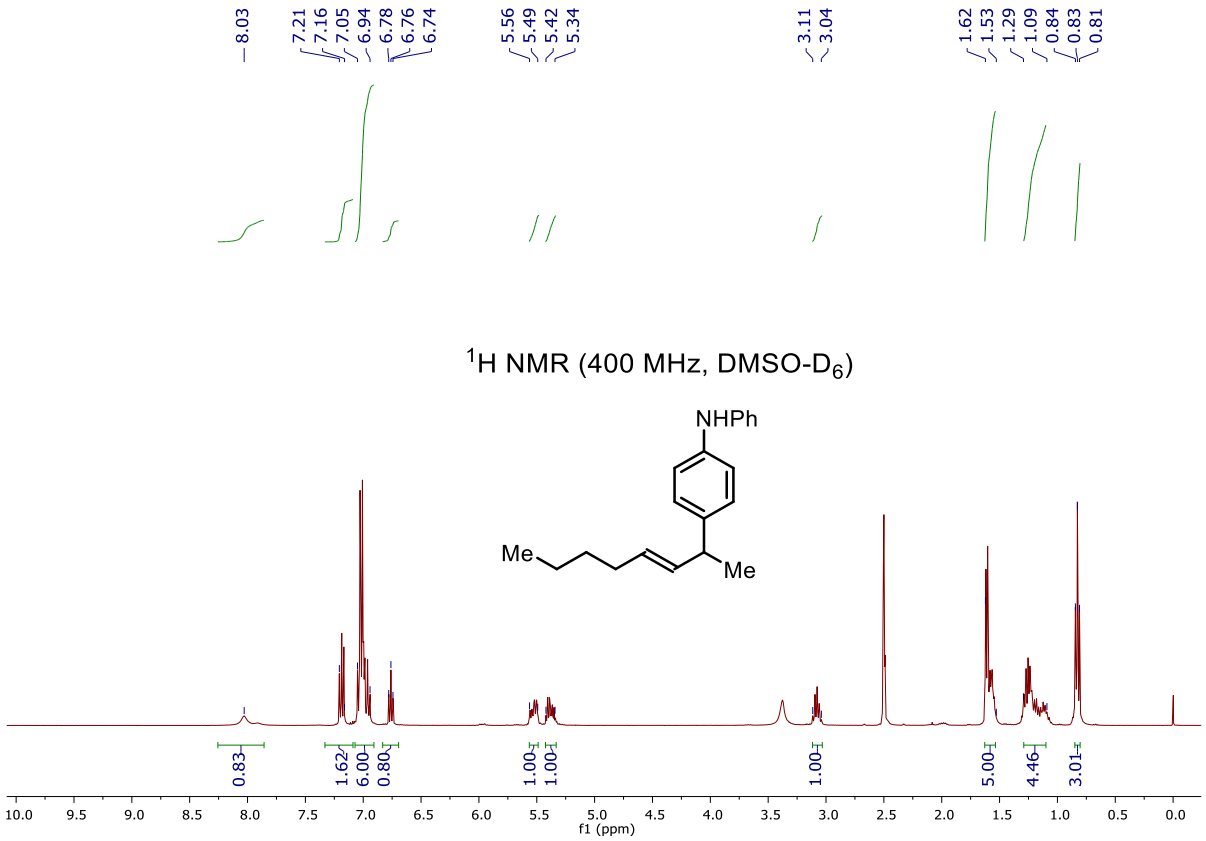
[*E*:*Z* = 1.0:0.5] isolated

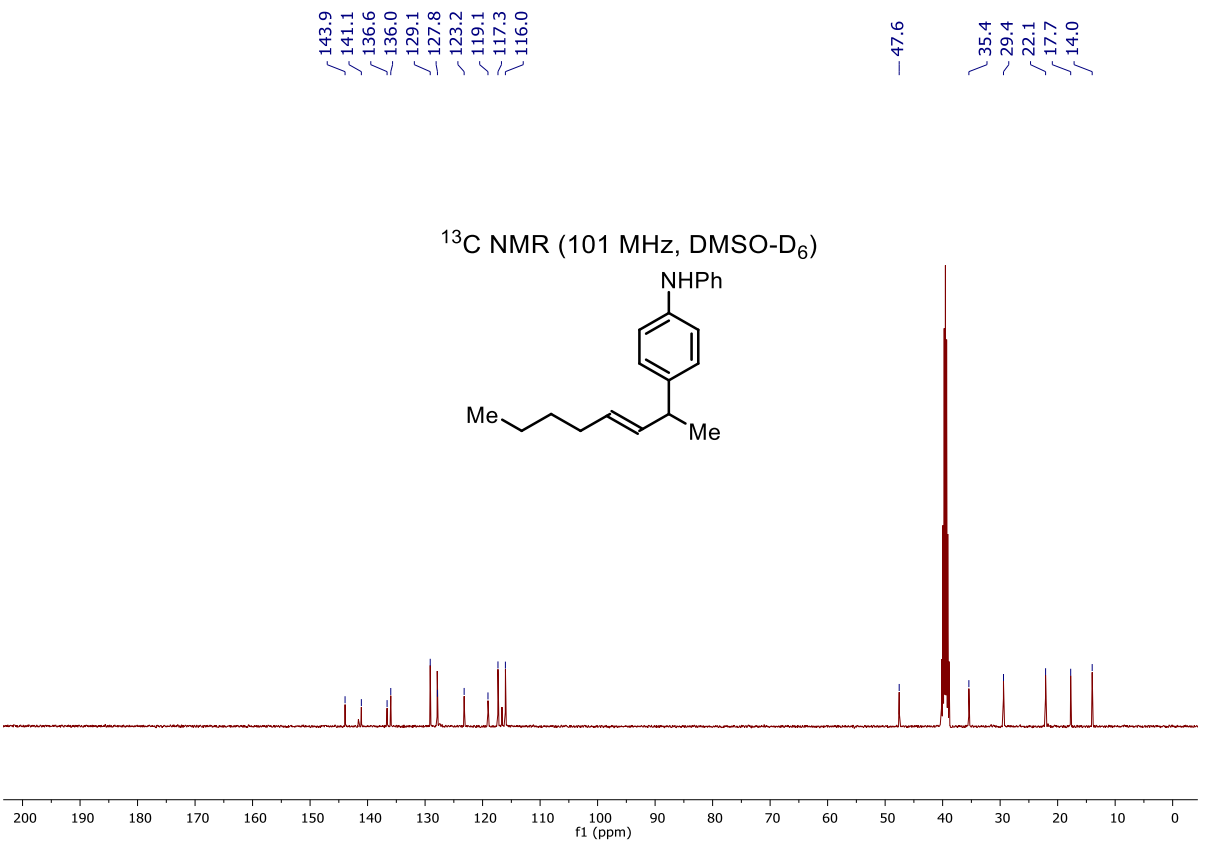
(*E*)-*N*-phenyl-4-(6-phenylhex-3-en-2-yl)aniline (316pa)



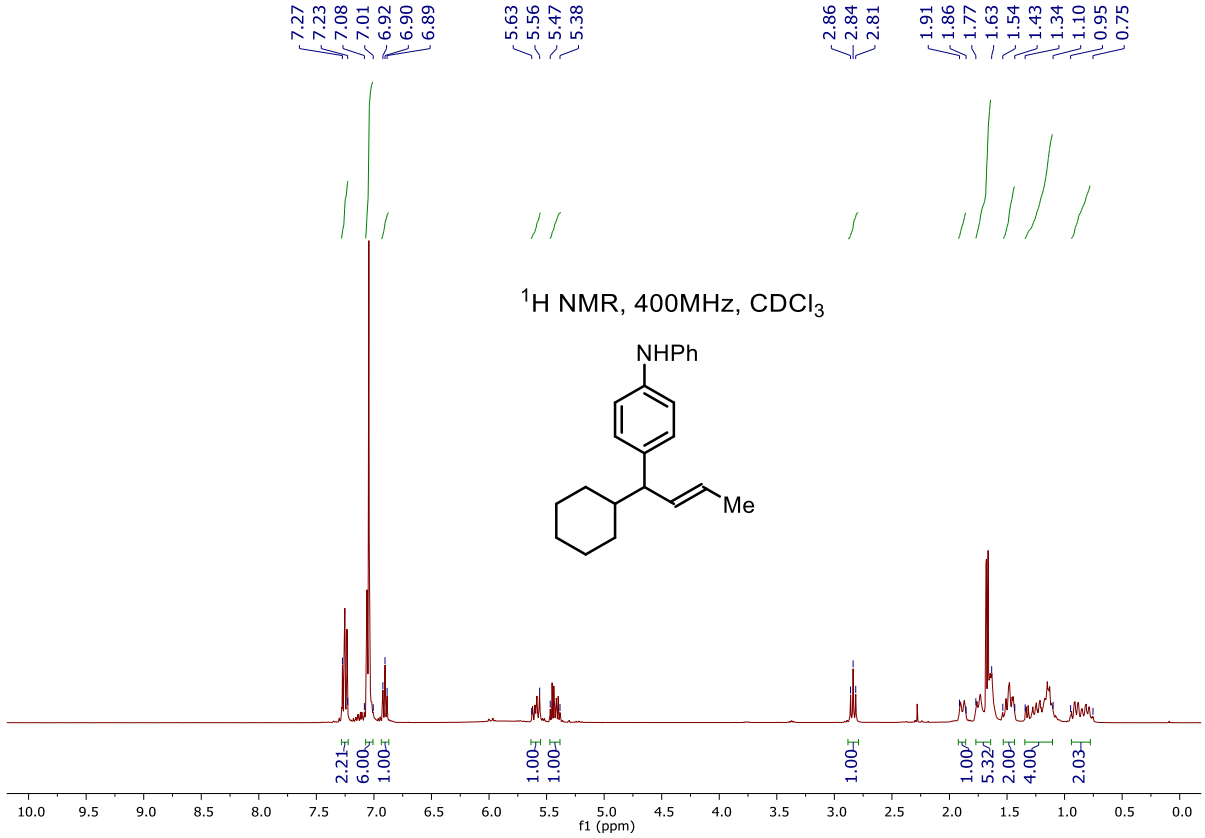


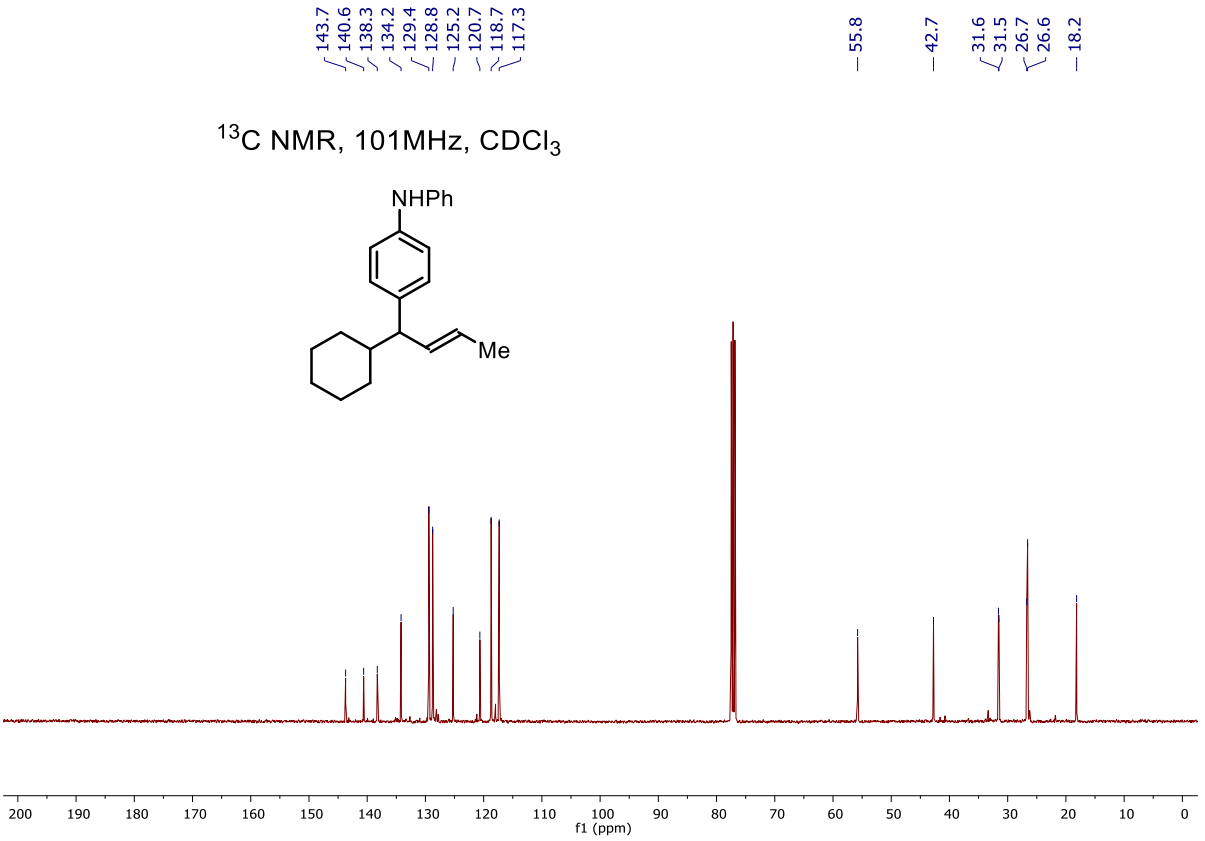
(*E*)-4-(oct-3-en-2-yl)-*N*-phenylaniline (316ra)



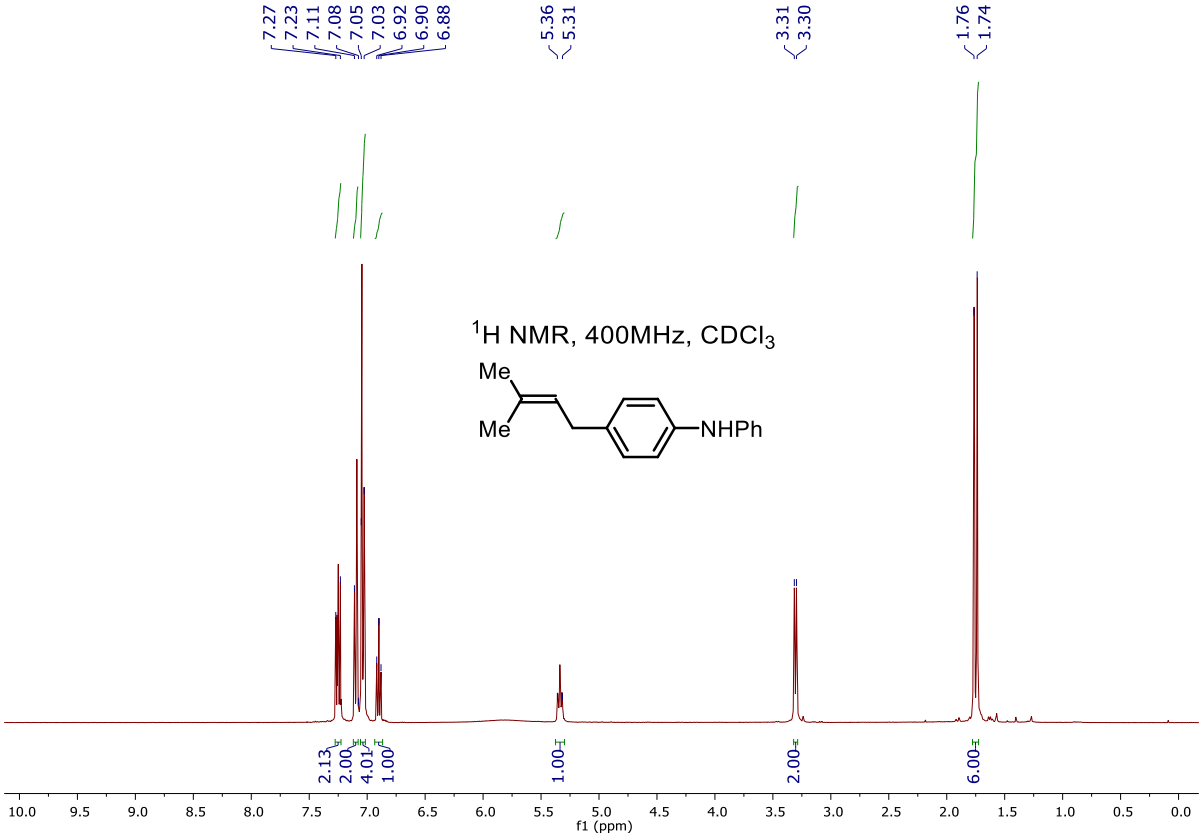


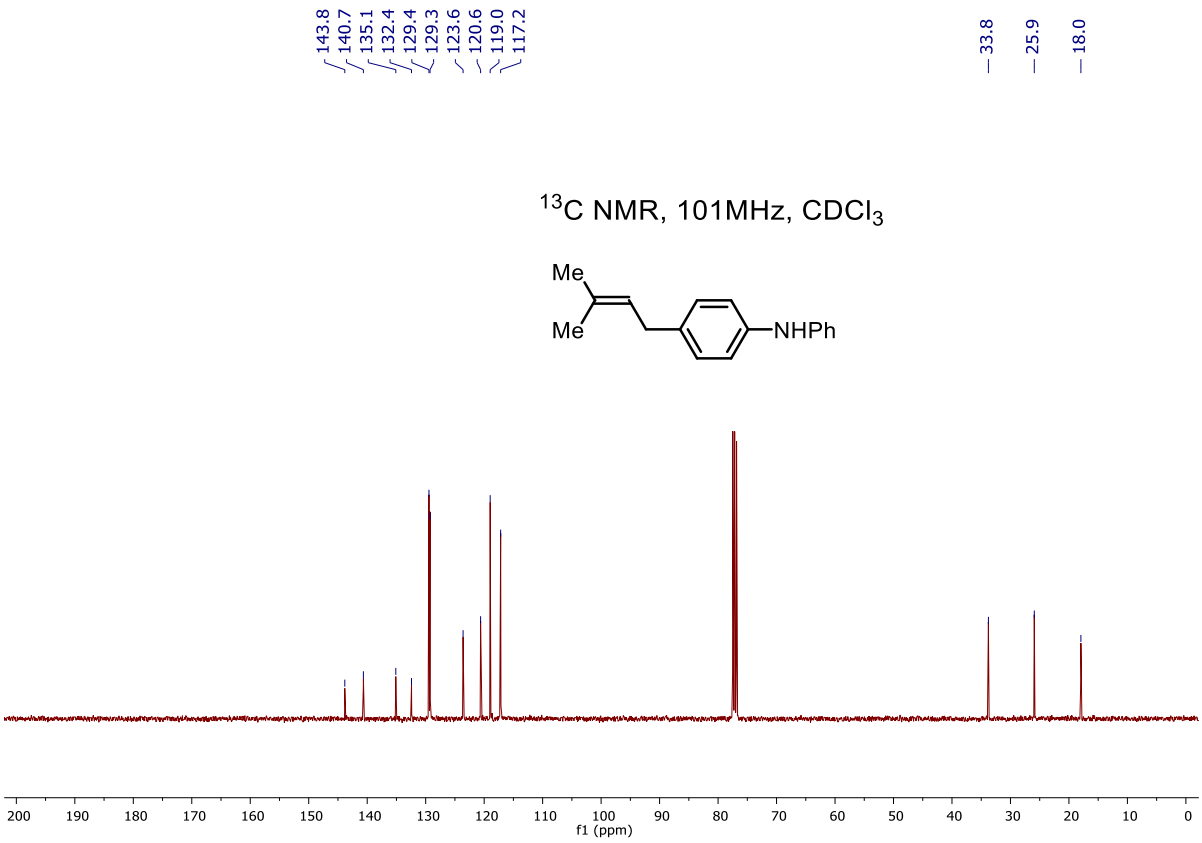
(*E*)-4-(1-cyclohexylbut-2-en-1-yl)-*N*-phenylaniline (36qa)



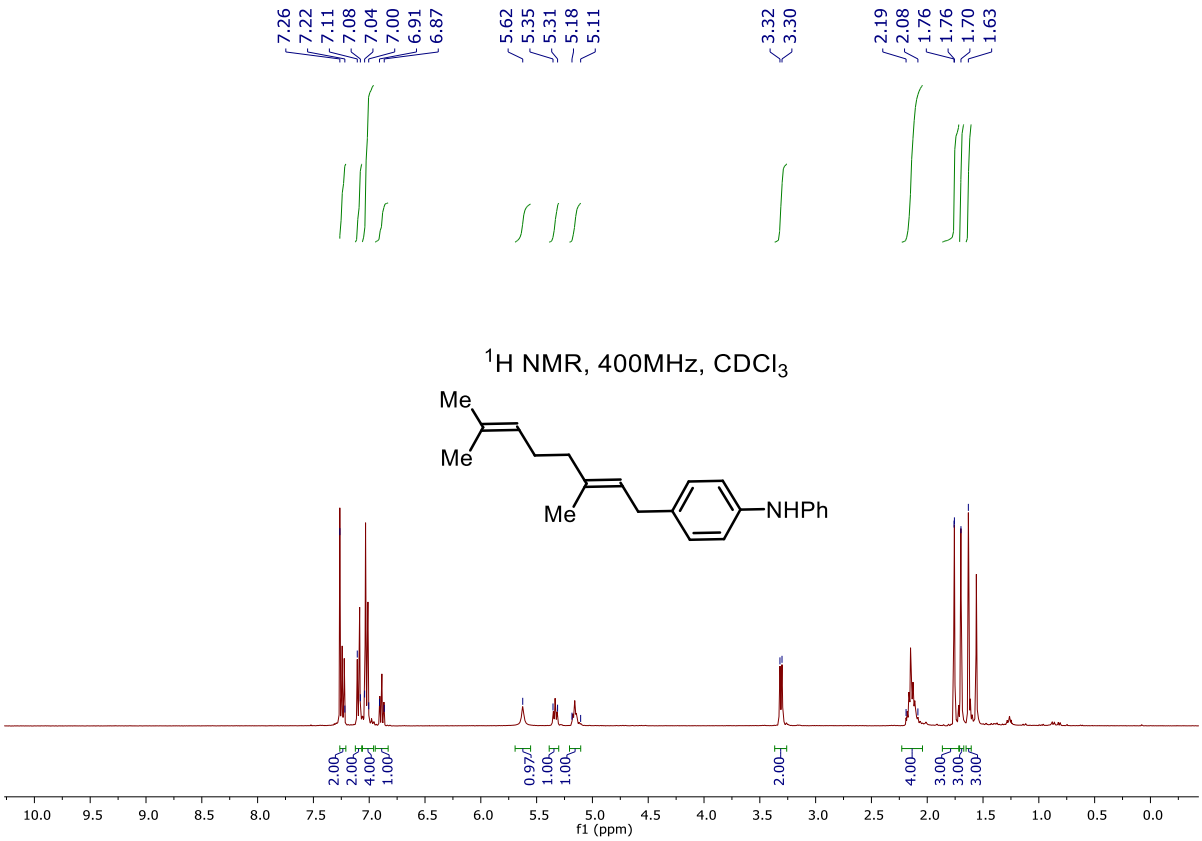


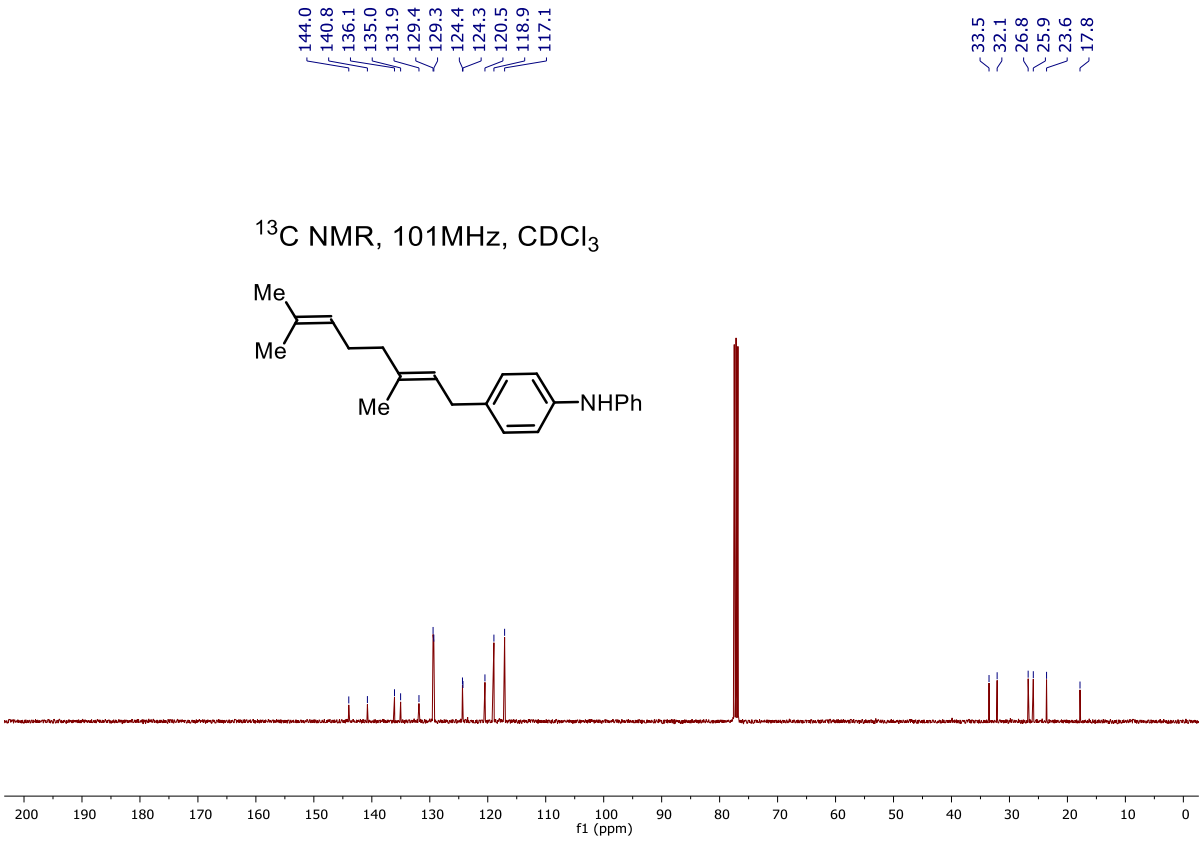
4-(3-methylbut-2-en-1-yl)-*N*-phenylaniline (316sa)



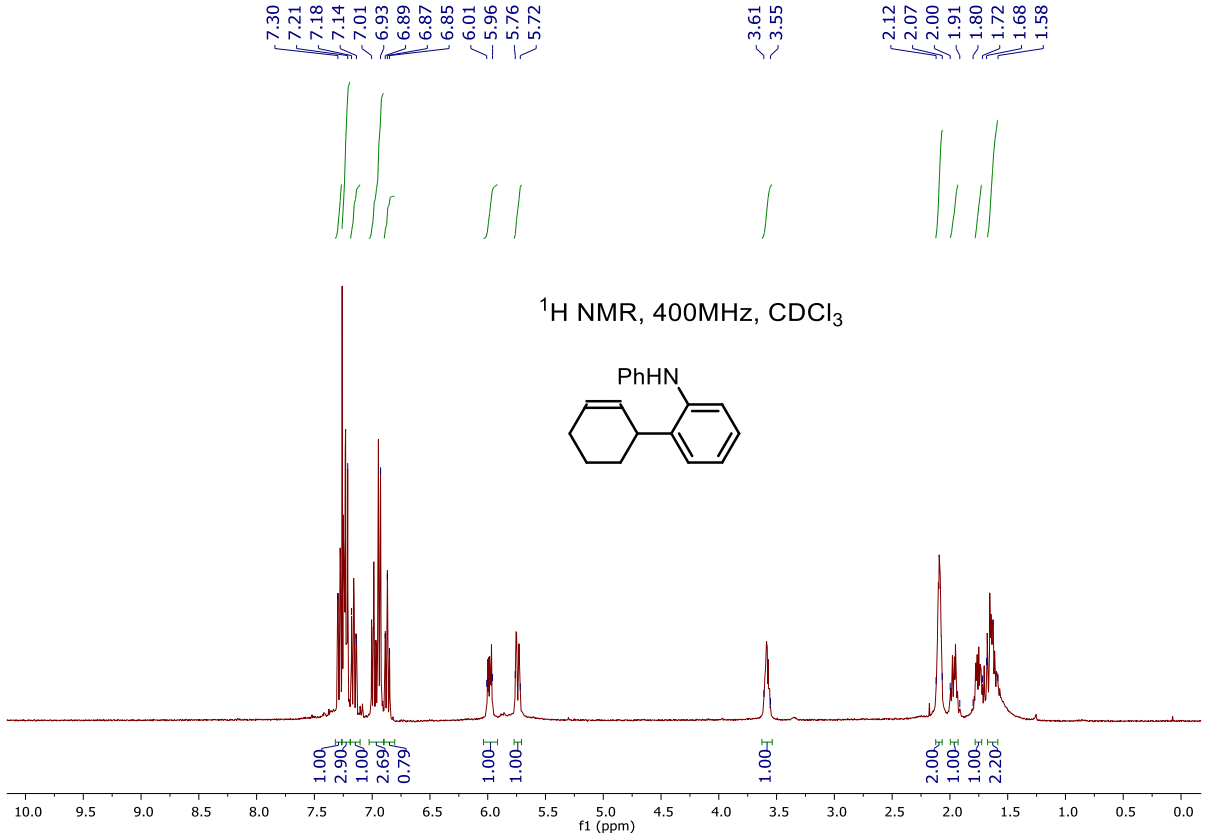


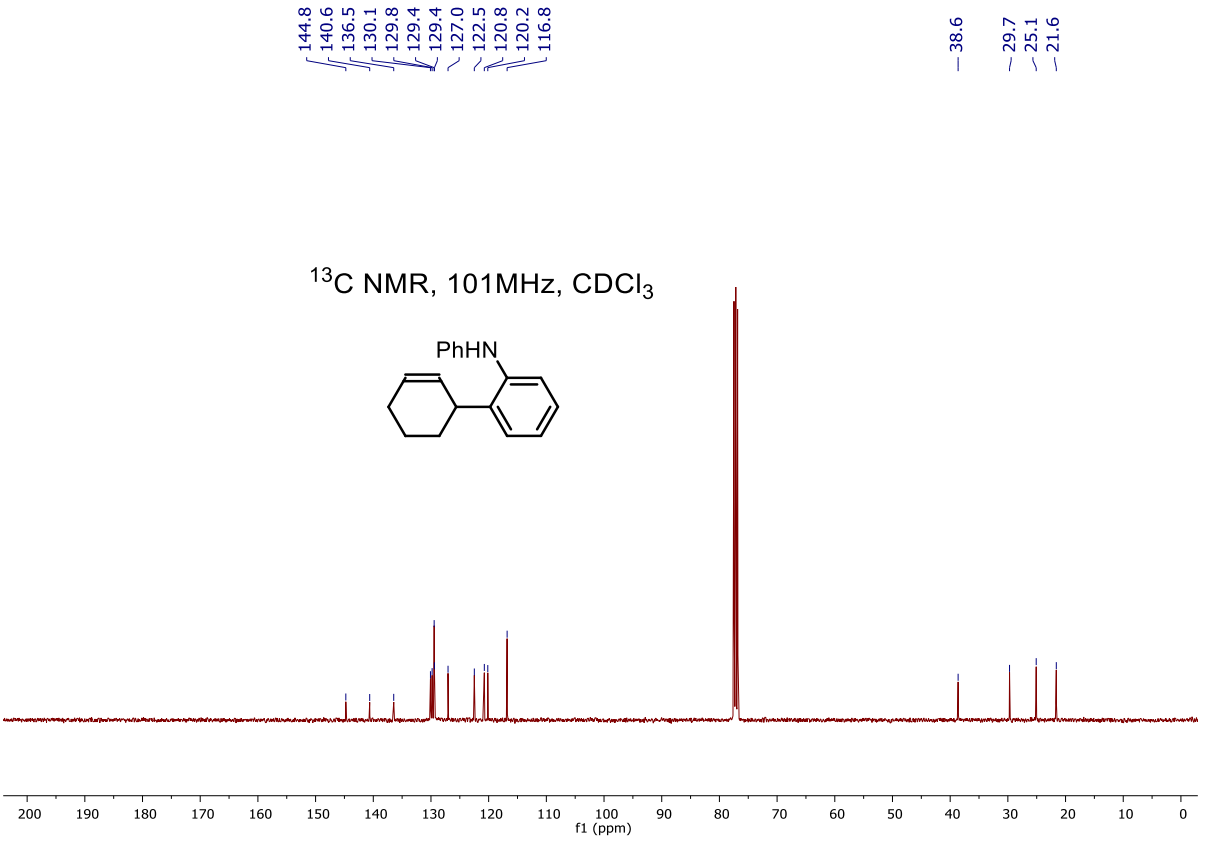
(*E*)-4-(3,7-dimethylocta-2,6-dien-1-yl)-*N*-phenylaniline (316ta)



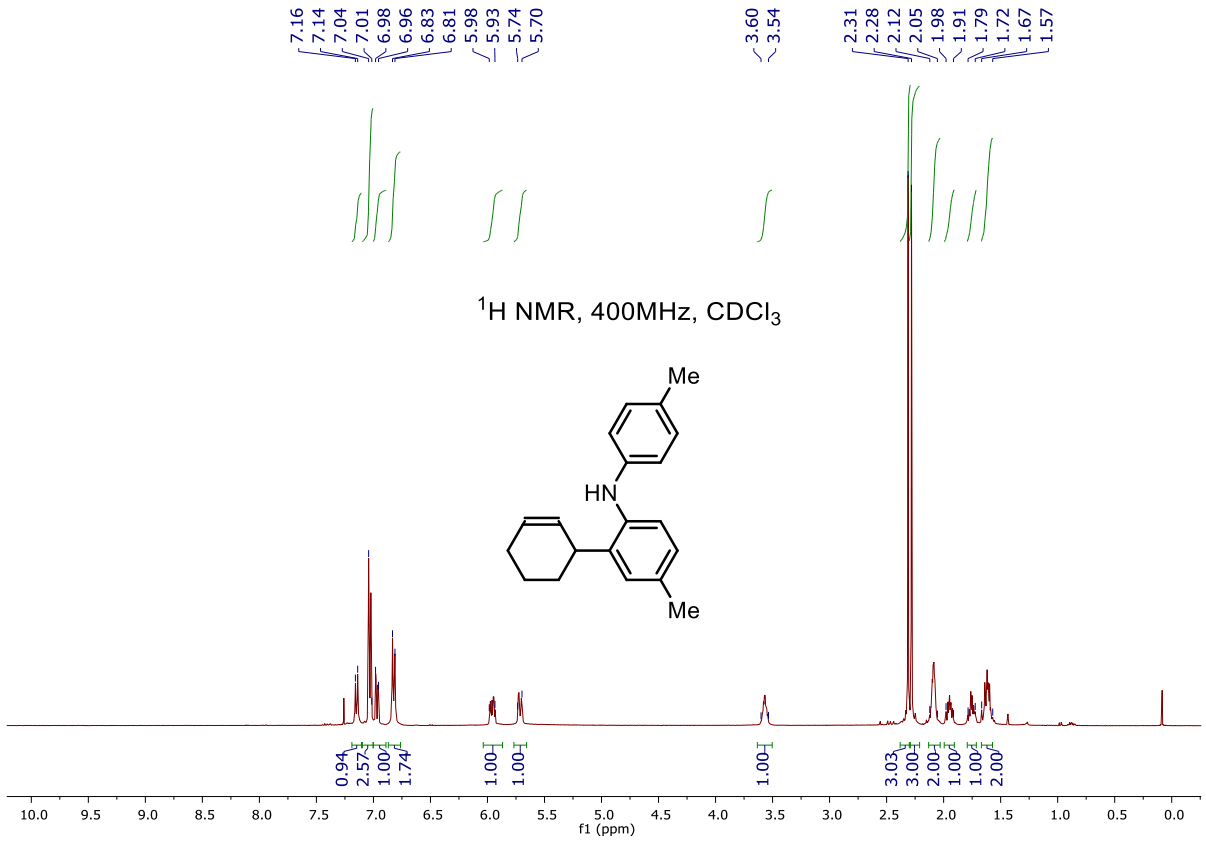


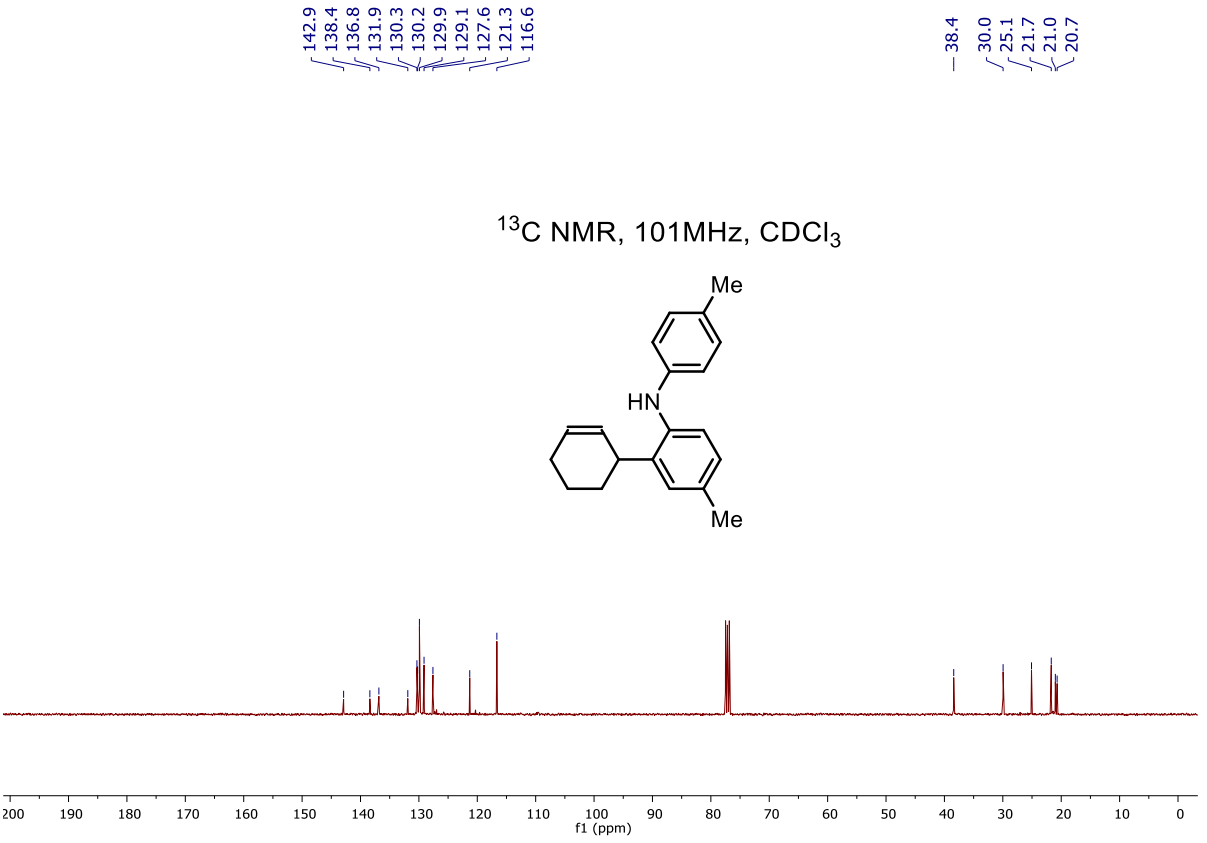
_N_-phenyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-amine (316ua)



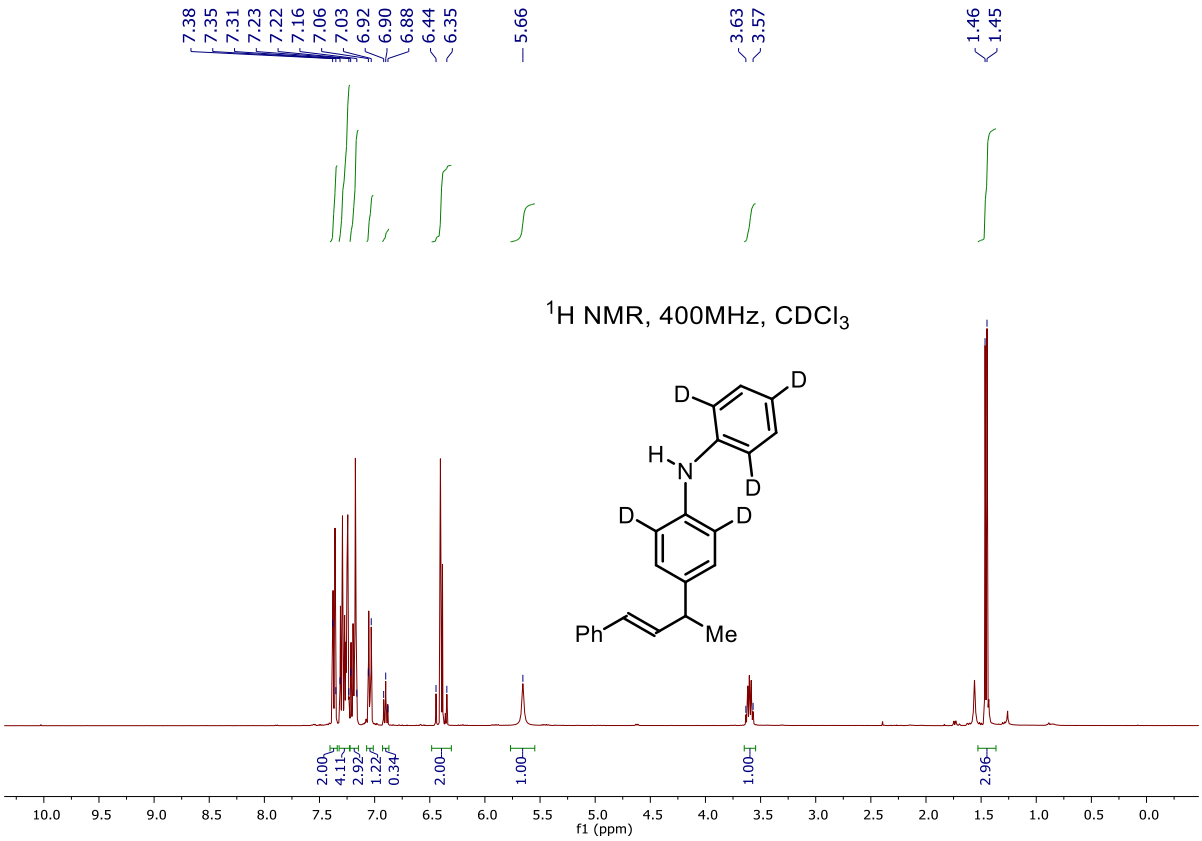


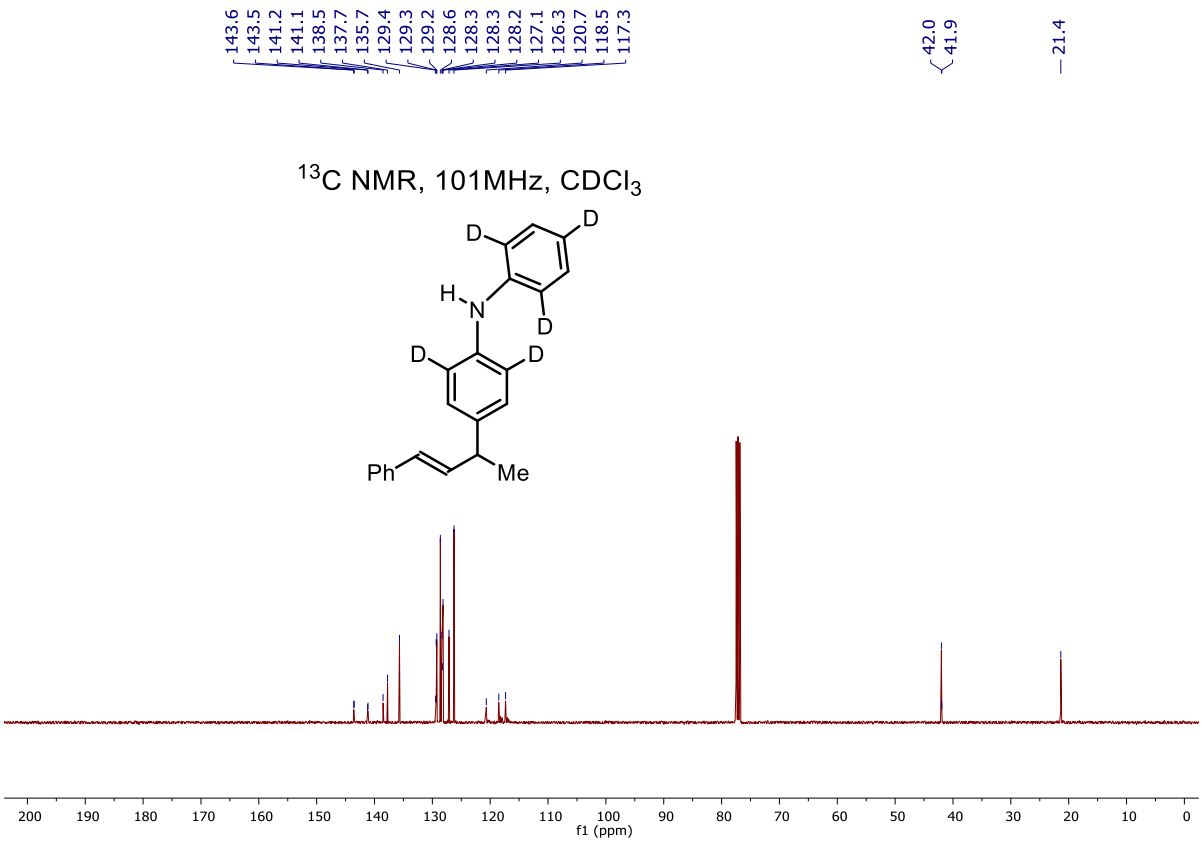
5-methyl-*N*-(p-tolyl)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-amine (316up)





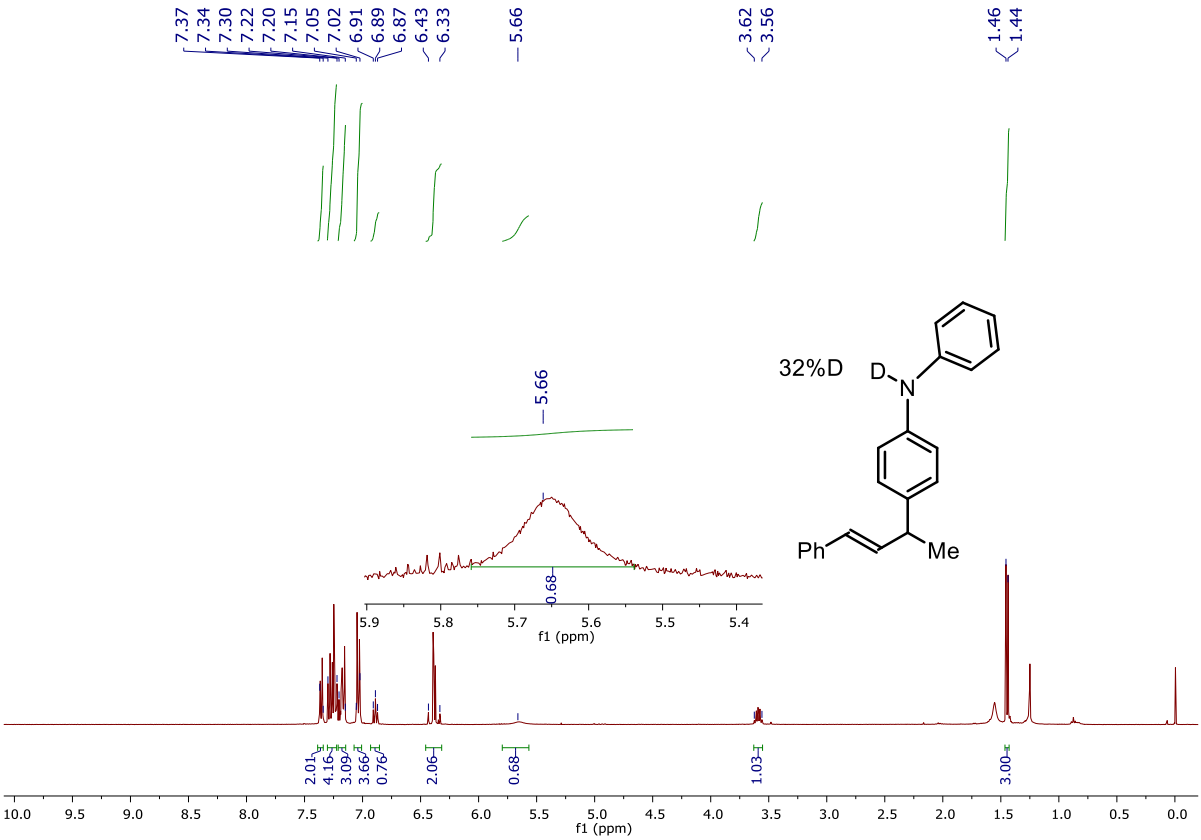
(*E*)-*N*-(4-(4-phenylbut-3-en-2-yl)phenyl-2,6-d_2)benzen-2,4,6-d_3-amine (316a-d_5)



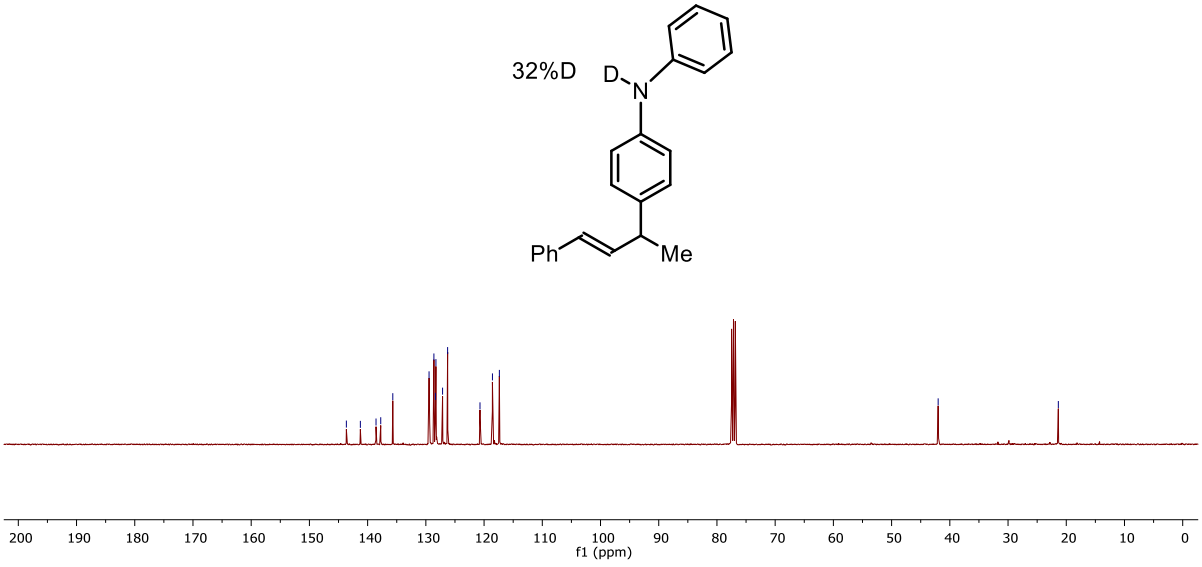


(*E*)-*N*-phenyl-4-(4-phenylbut-3-en-2-yl)aniline-d *(316a-d_1)*

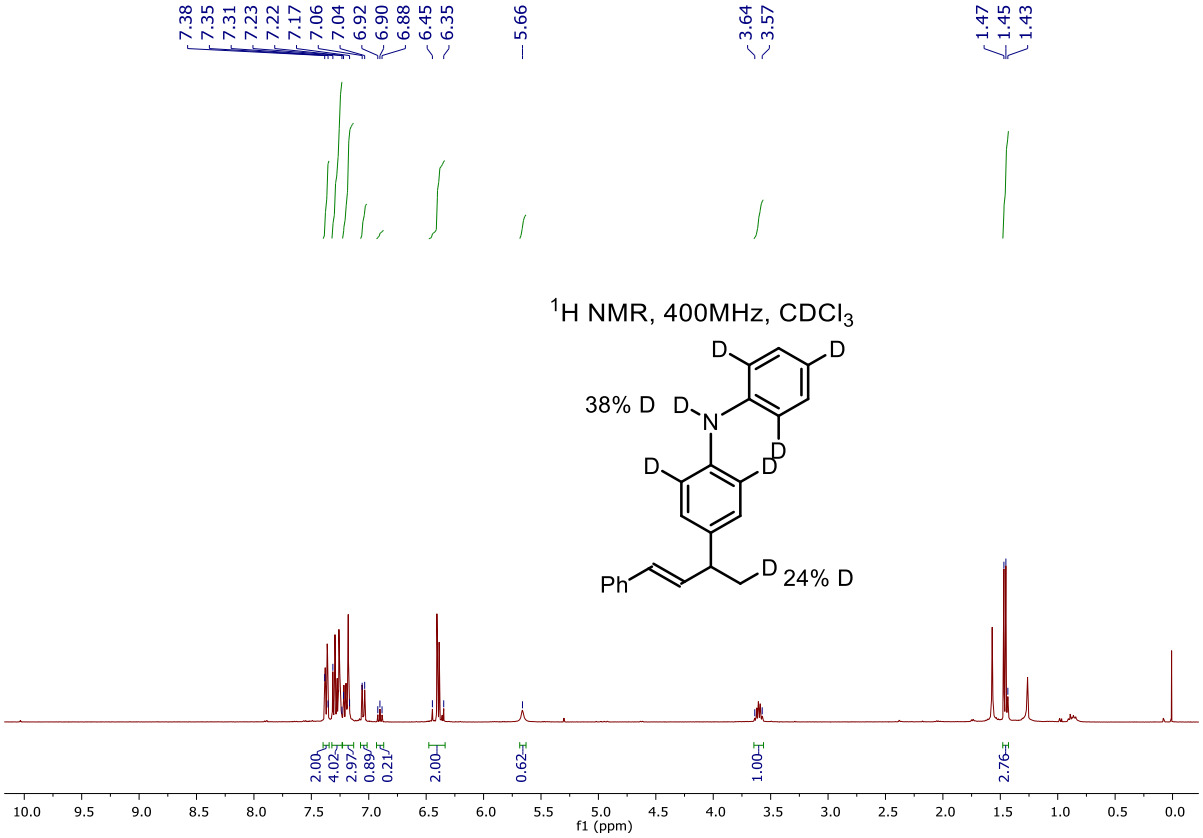
^{1}H NMR, 400MHz, $CDCl_3$

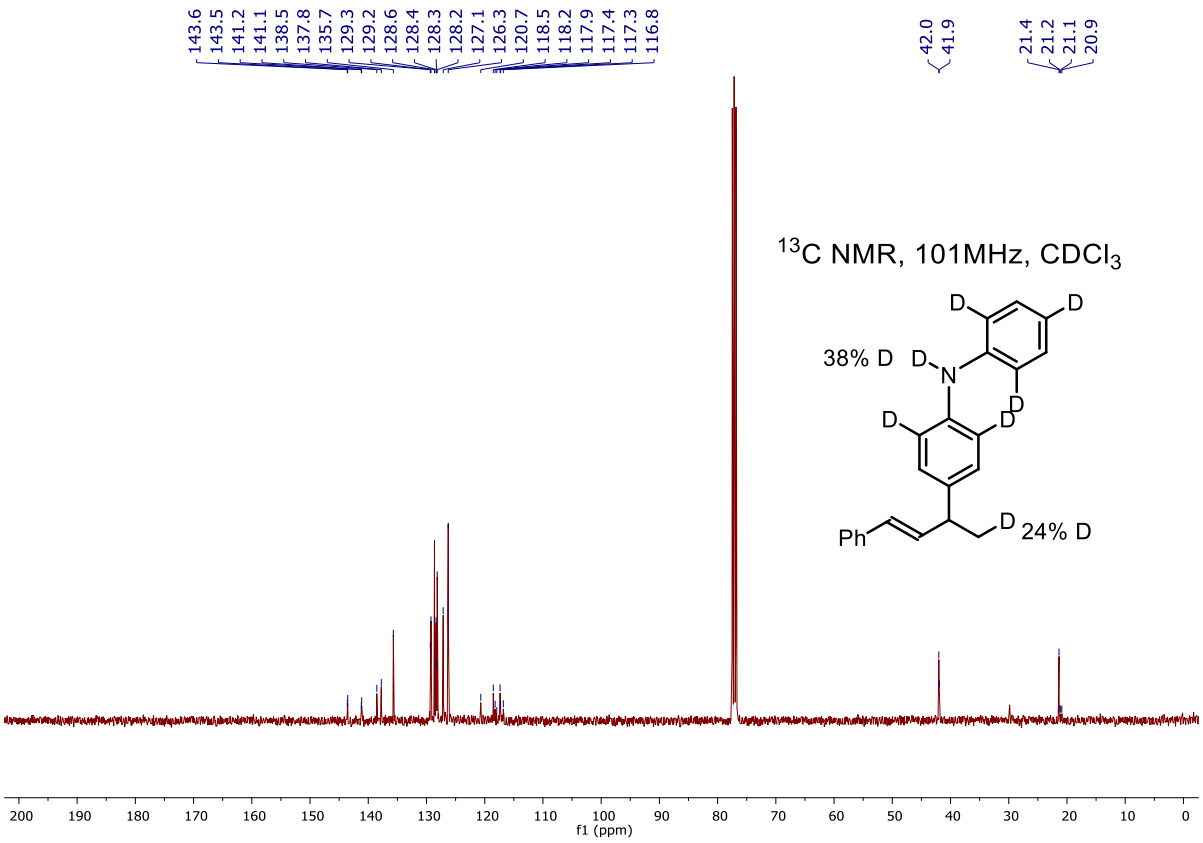


^{13}C NMR, 101MHz, $CDCl_3$

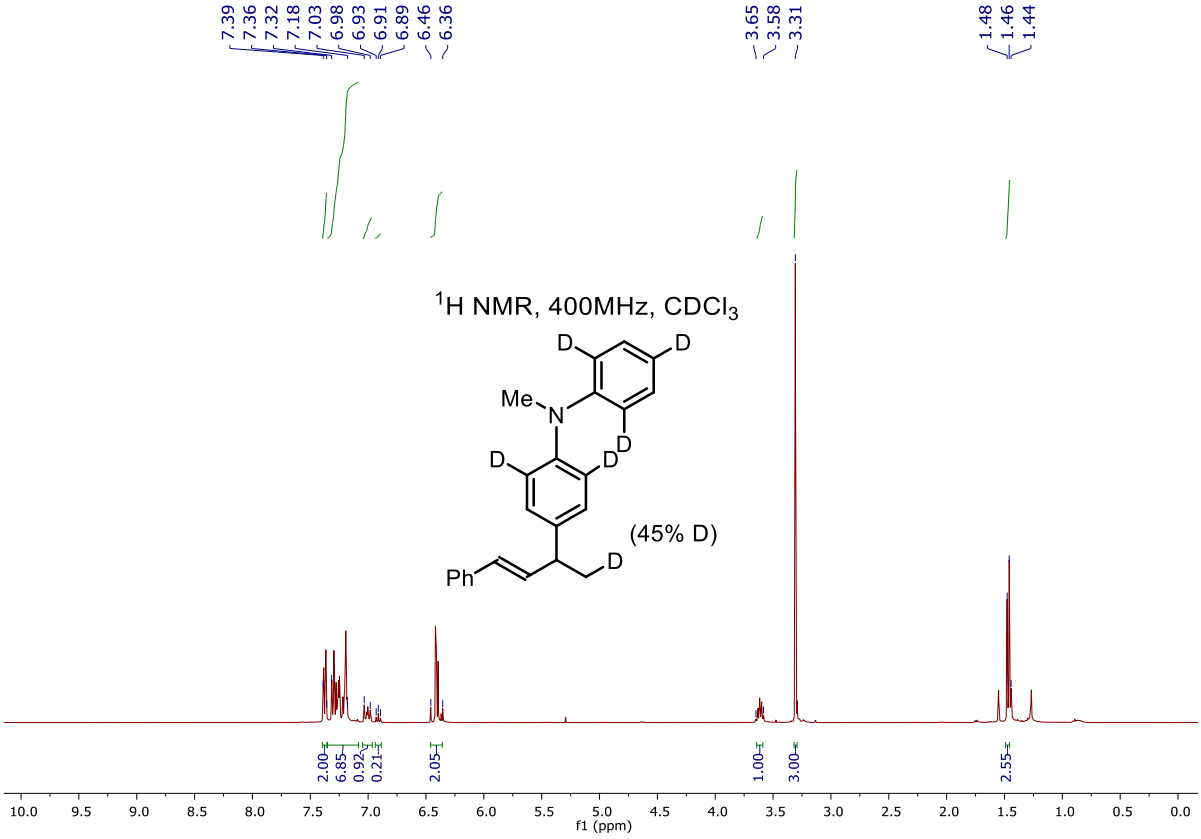


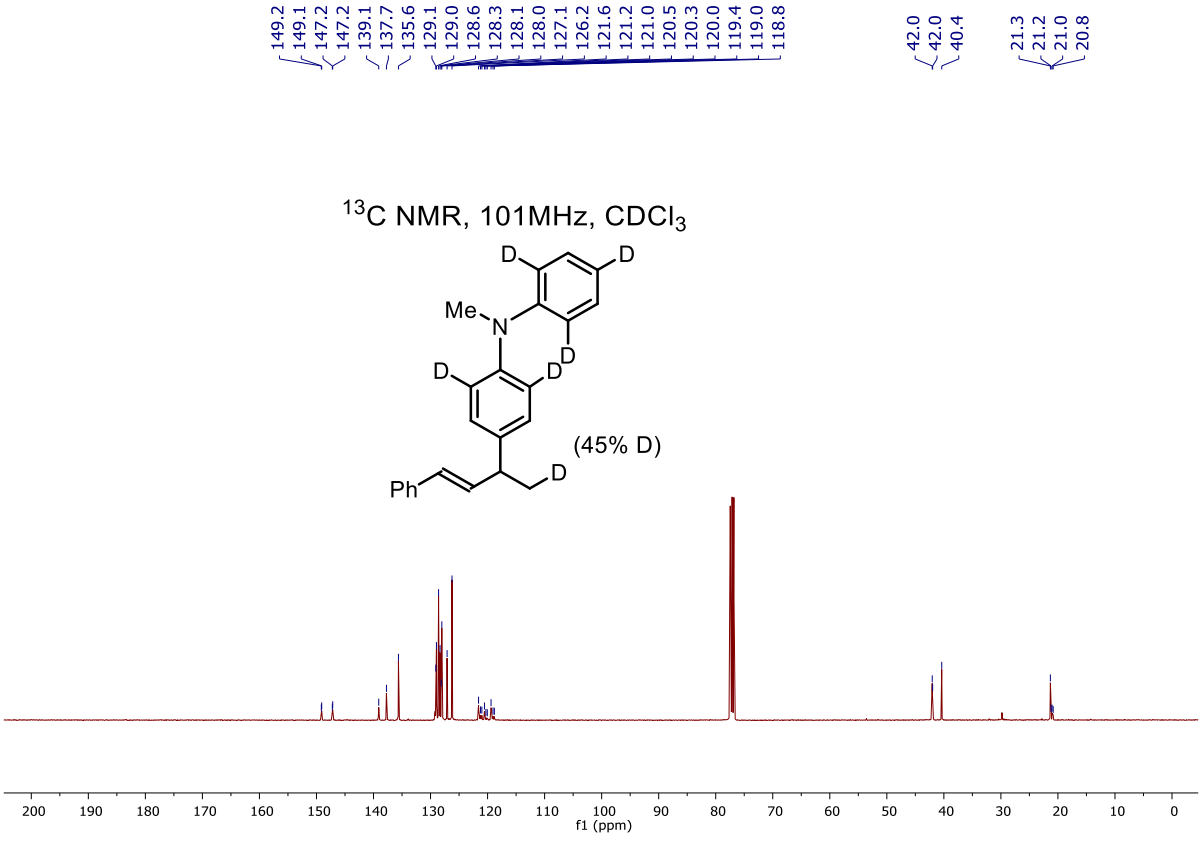
(*E*)-*N*-(4-(4-phenylbut-3-en-2-yl-1-*d*)phenyl-2,6-d_2)benzen-2,3,4,5,6-d_5-amine-*d* (316a-d_7)





(*E*)-*N*-methyl-*N*-(4-(4-phenylbut-3-en-2-yl-1-d)phenyl-2,6-d_2)aniline-2,4,6-d_3 (316h-*d*)





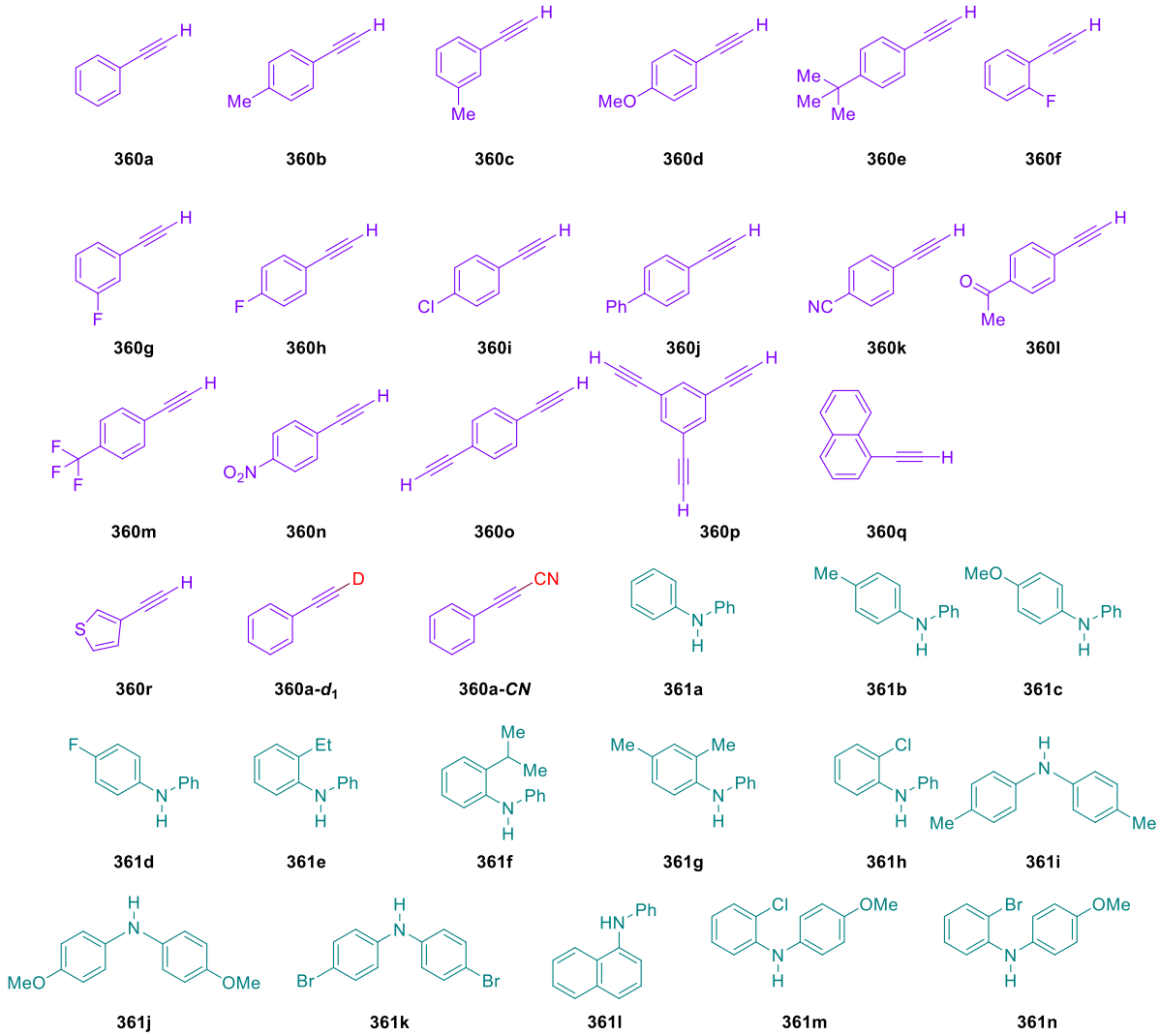
Annexure 3

Experimental part of Chapter 4: **Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and *N*-cyanosuccinimide**

1. General Information

Reactions were performed in flame-dried glassware under aerobic condition unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled prior to use. $CDCl_3$ was stored over 4Å molecular sieves. Used chemicals were purchased from *Sigma-Aldrich*, *TCI*, *A*lfa-*A*esar and *Sisco Research Laboratories (SRL)* used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from *Merck* using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ unless otherwise stated on JEOL JNM ECS-400, Bruker AVANCE NEO 400 MHz FT-NMR and Bruker AVANCE NEO 500 MHz FT-NMR instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for **^{1}H NMR** and $CDCl_3$: δ = 77.16 ppm for **^{13}C NMR**; CD_3OD: δ = 3.31 ppm for **^{1}H NMR** and CD_3OD: δ = 49.00 ppm for **^{13}C NMR**. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2-XS QTOF. Alkynes **360a-360r** and arylamines **361a, 361i, 361j, 361k, 361l,** has been obtained from commercial sources. Alkynes **360a-*d*$_1$**, **360a-*CN***, **360s-360v**[149] and arylamines **361b-361h, 361m-361n**[150] were synthesized according to the procedure in the literature.

2. List of the Alkynes and Arylamines Used



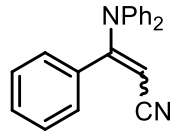
3. General Procedure for the Reaction of Alkynes and Arylamines (GP):

Procedure A: In an argon filled glove box, an oven-dried sealed tube is charged with a magnetic stir bar, indium tribromide ($InBr_3$) (40.0 mol %), arylamine **361a-361n** (1.0 equiv), **362a** (1.6 equiv), toluene (0.25 ml), and alkynes **360a-360r** (2.4 equiv) simultaneously added. The sealed tube has been taken out from the glove box and stirred for eight hours in a preheated oil bath at 125 ^{o} C temperature. The crude reaction mixture is used to measure the *E/Z* ratio by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and EtOAc as eluent.

Procedure B: In an argon filled glove box, an oven-dried sealed tube is charged with a magnetic stir bar, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (40.0 mol %), arylamine **361a-361n** (1.0 equiv), **362a** (1.6 equiv), toluene (0.25 ml), and alkynes **360a-360r** (2.4 equiv) simultaneously added. The sealed tube has been taken out from the glove box and stirred for eight hours in a preheated oil bath at 125 ^{o}C temperature. The crude reaction mixture is used to measure the *E/Z* ratio by ^{1}H NMR. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and EtOAc as eluent.

4. Experimental Details for the Synthesized Compounds

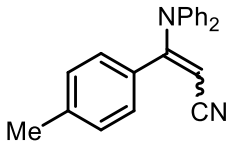
4.1 3-(diphenylamino)-3-phenylacrylonitrile (363a)



$C_{21}H_{16}N_2$
M = 296.37 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (12.0 mg, 70% yield). ***E:Z* ratio** (isolated)**:** 75:25. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B**, afforded the product **363a** (12.0 mg, 70% yield), ***E:Z* ratio** (isolated)**:** 75:25. White to yellow solid. **M.P:** 115 ^{o}C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{17}N_2^+$ 297.1392; found 297.1392. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2.48H), 7.46–7.44 (m, 0.90H), 7.30–7.26 (m, 5H), 7.25–7.19 (m, 8H), 7.10–7.06 (m, 5H), 7.05–7.01 (m, 5H), 4.88 (s, 0.34H), 4.58 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 162.2, 146.3, 145.8, 137.3, 134.4, 130.3, 130.2, 129.8, 129.5, 129.3, 128.7, 128.7, 128.5, 126.9, 125.7, 125.6, 124.9, 120.4, 117.1, 83.2, 79.6. **IR (neat):** ν 3056, 2195, 1584, 1551, 1484, 1379, 759, 724 cm^{-1}.

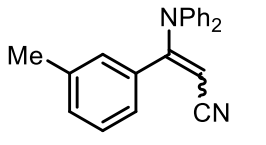
4.2 3-(diphenylamino)-3-(*p*-tolyl)acrylonitrile (363b)



$C_{22}H_{18}N_2$
M = 310.40 g/mol

Prepared according to the **GP-A**, using **360b** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.2:0.8 v/v) as eluent afforded the product **363b** (14.0 mg, 75% yield). ***E:Z* ratio** (isolated)**:** 75:25. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B,** afforded the product **363b** (14.5 mg, 78% yield), ***E:Z* ratio** (isolated)**:** 75:25. White to yellow solid. **M.P:** 162 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{22}H_{19}N_2^+$ 311.1548; found 311.1548. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2.45H), 7.34–7.32 (m, 0.81H), 7.26–7.20 (m, 7H), 7.10–7.06 (m, 7.41H), 7.04–7.00 (m, 6H), 4.87 (s, 0.33H), 4.54 (s, 1H), 2.28 (s, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 162.3, 146.4, 146.0, 140.6, 140.4, 134.3, 131.5, 129.7, 129.4, 129.3, 129.2, 128.6, 126.9, 125.5, 125.4, 124.7, 120.6, 117.3, 82.9, 79.5, 21.5, 21.5. **IR (neat):** ν 3055, 3033, 2192, 1582, 1550, 1485, 1449, 1383, 748, 669 cm^{-1}.

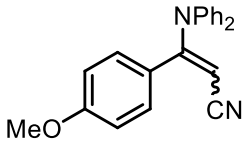
4.3 3-(diphenylamino)-3-(*m*-tolyl)acrylonitrile (363c)



$C_{22}H_{18}N_2$
M = 310.40 g/mol

Prepared according to the **GP-A**, using **360c** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.2:0.8 v/v) as eluent afforded the product **363c** (13.0 mg, 72% yield). ***E:Z* ratio** (isolated)**:** 73:27. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B**, afforded the product **363c** (14.0 mg, 75% yield), ***E:Z* ratio** (isolated)**:** 73:27. White to yellow solid. **M.P:** 149 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{22}H_{19}N_2^+$ 311.1548; found 311.1549. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 2H), 7.26–7.21 (m, 8H), 7.15 (dd, J = 14.4, 6.9 Hz, 2H), 7.10–7.06 (m, 7H), 7.04–7.01 (m, 5H), 4.88 (s, 0.38H), 4.55 (s, 1H), 2.28 (s, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 162.4, 146.3, 145.8, 138.4, 138.1, 137.2, 134.3, 131.1, 130.9, 130.3, 129.4, 129.3, 129.3, 128.5, 128.3, 127.0, 126.9, 125.9, 125.6, 125.4, 124.8, 120.4, 117.1, 83.2, 79.5, 21.5. **IR (neat):** ν 3055, 2921, 2196, 1597, 1550, 1485, 1449, 1383, 749, 669 cm^{-1}.

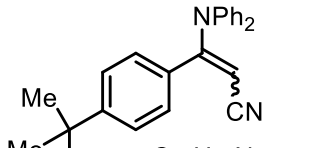
4.4 3-(diphenylamino)-3-(4-methoxyphenyl)acrylonitrile (363d)



$C_{22}H_{18}N_2O$
M = 326.39 g/mol

Prepared according to the **GP-A**, using **360d** (19.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363d** (17.0 mg, 85% yield. ***E:Z* ratio** (isolated)**:** 76:24. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B**, afforded the product **363d** (17.0 mg, 85% yield), ***E:Z* ratio** (isolated)**:** 76:24. Yellow solid. **M.P:** 135 ^{o}C. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{22}H_{19}N_2O^+$ 327.1497; found 327.1489. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2.46H), 7.38–7.35 (m, 1H), 7.25–7.19 (m, 7H), 7.08–7.04 (m, 5H), 7.01–6.98 (m, 5.48H), 6.79–6.74 (m, 4H), 4.83 (s, 0.31H), 4.50 (s, 1H), 3.74 (s, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 162.2, 161.3, 161.0, 146.6, 146.2, 131.5, 130.4, 129.6, 129.4, 126.9, 126.7, 125.6, 125.5, 124.8, 120.9, 117.5, 114.2, 114.0, 82.5, 79.3, 55.5, 55.5. **IR (neat):** ν 3055, 2928, 2201, 1586, 1490, 1370, 1263, 732, 701 cm^{-1}.

4.5 3-(4-(*tert*-butyl)phenyl)-3-(diphenylamino)acrylonitrile (363e)

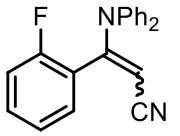


$C_{25}H_{24}N_2$
M = 352.48 g/mol

Prepared according to the **GP-A**, using **360e** (26.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363e** (16.0 mg, 75% yield). ***E:Z* ratio** (isolated)**:** 72:28. ***E:Z* ratio** (crude mixture)**:** 73:27. **GP-B**, afforded the product **363e** (16.0 mg, 75% yield), ***E:Z* ratio** (isolated)**:** 72:28. Yellow gel. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{25}H_{25}N_2^+$ 353.2018; found 353.2018. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.41–7.39 (m, 1H), 7.31–7.28 (m, 4H), 7.26–7.22 (m, 7H), 7.11–7.07 (m, 5H), 7.04–7.02 (m, 5H), 4.92 (s, 0.39H), 4.56 (s, 1H), 1.27 (s, 3H) 1.26 (s, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 162.3, 153.4, 149.8, 146.1, 129.5, 129.4, 129.3, 128.4,

126.8, 125.7, 125.4, 125.3, 124.7, 120.6, 79.7, 34.9, 31.2. **IR (neat):** ν 3061, 3037, 2961, 2905, 2868, 2200, 1574, 1488, 1368, 1263, 843, 754, 695 cm^{-1}.

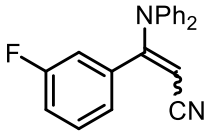
4.6. 3-(diphenylamino)-3-(2-fluorophenyl)acrylonitrile (363f)



$C_{21}H_{15}FN_2$
M = 314.36 g/mol

Prepared according to the **GP-A**, using **360f** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363f** (11.0 mg, 57% yield). ***E:Z* ratio** (isolated)**:** 96:04. ***E:Z* ratio** (crude mixture)**:** 90:10. **GP-B,** afforded the product **363f** (10.0 mg, 55% yield), ***E:Z* ratio** (isolated)**:** 96:04. Yellow solid. **M.P:** 126 ^{o}C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}FN_2^+$ 315.1298; found 315.1298. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 1H), 7.30–7.21 (m, 9H), 7.13–7.08 (m, 3H), 7.04–7.01 (m, 5H), 6.99–6.96 (m, 1H), 4.88 (s, 0.05H), 4.60 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 163.0, 161.3, 146.0, 145.5, 136.6, 136.5, 130.2, 130.2, 129.7, 129.5, 126.8, 126.0, 125.8, 125.5, 125.2, 119.9, 117.4, 117.2, 116.9, 116.7, 80.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.94. **IR (neat):** ν 3056, 2982, 2925, 2202, 1565, 1488, 1371, 1264, 733, 697 cm^{-1}.

4.7 3-(diphenylamino)-3-(3-fluorophenyl)acrylonitrile (363g)

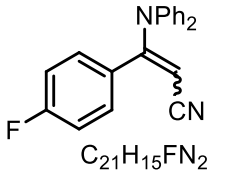


$C_{21}H_{15}FN_2$
M = 314.36 g/mol

Prepared according to the **GP-A**, using **360g** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363g** (11.0 mg, 55% yield). ***E:Z* ratio** (isolated)**:** 93:07. ***E:Z* ratio** (crude mixture)**:** 82:18. **GP-B,** afforded the product **363g** (11.0 mg, 55% yield), ***E:Z* ratio** (isolated)**:** 93:07. Yellow solid. **M.P:** 125 ^{o}C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}FN_2^+$ 315.1298; found 315.1299. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 1.27H), 7.44–7.40 (m, 0.19H), 7.30–7.22 (m, 8H), 7.12–7.08 (m, 10H), 6.96–6.91 (m, 1H), 4.72 (s, 0.08H), 4.62 (s, 1H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ 160.6, 158.9, 158.1, 145.7, 145.0, 132.2, 132.1, 131.8, 129.5, 129.2, 127.0, 126.2, 126.0, 125.5, 124.3, 124.3, 122.8, 122.7, 119.8, 116.3, 116.1, 78.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.71, -113.84. **IR (neat):** ν 3040, 2919, 2851, 2199, 1582, 1562, 1486, 1450, 1374, 756, 694 cm^{-1}.

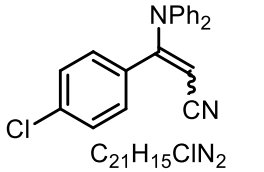
4.8 3-(diphenylamino)-3-(4-fluorophenyl)acrylonitrile (363h)



$C_{21}H_{15}FN_2$
M = 314.36 g/mol

Prepared according to the **GP-A**, using **360h** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363h** (13.0 mg, 68% yield). ***E:Z* ratio** (isolated)**:** 79:21. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B,** afforded the product **363h** (12.0 mg, 65% yield), ***E:Z* ratio** (isolated)**:** 79:21. Yellow solid. **M.P:** 162 ^{o}C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}FN_2^+$ 315.1298; found 315.1299. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 3H), 7.45–7.42 (m, 1H), 7.28–7.22 (m, 7H), 7.12–7.05 (m, 5H), 7.03–6.92 (m, 9H), 4.83 (s, 0.27H), 4.57 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 163.5, 162.3, 161.2, 146.2, 145.7, 132.0, 131.9, 130.9, 130.8, 130.6, 130.5, 129.7, 129.5, 127.0, 125.9, 125.7, 125.2, 120.4, 116.1, 116.0, 115.9, 115.8, 83.1, 79.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.29. **IR (neat):** ν 3062, 2922, 2850, 2196, 1597, 1555, 1487, 1380, 1227, 756, 669 cm^{-1}.

4.9 3-(4-chlorophenyl)-3-(diphenylamino)acrylonitrile (363i)

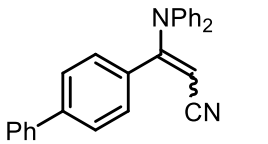


$C_{21}H_{15}ClN_2$
M = 330.81 g/mol

Prepared according to the **GP-A**, using **360i** (20.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.8:1.2 v/v) as eluent afforded the product **363h** (15.0 mg, 75% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B,** afforded the product **363h** (15.0 mg, 75% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellow solid. **M.P:** 154 ^{o} C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}ClN_2^+$

331.1002; found 331.1002. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.39–7.35 (m, 1H), 7.27–7.21 (m, 10H), 7.12–7.03 (m, 4H), 7.02–6.99 (m, 5H), 4.84 (s, 0.26H), 4.58 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3, 161.0, 146.1, 145.5, 136.3, 136.1, 135.8, 132.9, 131.1, 130.0, 129.6, 129.5, 129.0, 128.9, 126.9, 125.9, 125.6, 125.2, 120.1, 116.8, 83.3, 79.9. **IR (neat):** ν 3054, 2983, 2202, 1580, 1557, 1488, 1374, 1262, 731, 702 cm^{-1}.

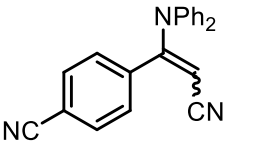
4.10 3-([1,1'-biphenyl]-4-yl)-3-(diphenylamino)acrylonitrile (363j)



$C_{27}H_{20}N_2$
M = 372.47 g/mol

Prepared according to the **GP-A**, using **360j** (26.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.8:1.2 v/v) as eluent afforded the product **363j** (15.0 mg, 65% yield). ***E:Z* ratio** (isolated)**:** 75:25. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B,** afforded the product **363j** (16.0 mg, 68% yield), ***E:Z* ratio** (isolated)**:** 75:25. Yellow gel. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{27}H_{21}N_2^+$ 373.1705; found 373.1703. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.55–7.48 (m, 8H), 7.42–7.38 (m, 4H), 7.35–7.30 (m, 2H), 7.29–7.22 (m, 7H), 7.12–7.09 (m, 4H), 7.08–7.04 (m, 6H), 4.95 (s, 0.33H), 4.61 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 161.9, 146.3, 145.9, 143.0, 142.7, 140.0, 139.8, 136.1, 133.2, 130.2, 129.5, 129.4, 129.2, 128.9, 128.9, 128.0, 127.8, 127.3, 127.1, 127.1, 126.8, 125.6, 125.4, 124.9, 120.5, 117.1, 83.4, 79.8. **IR (neat):** ν 3055, 2987, 2202, 1588, 1572, 1488, 1375, 1264, 731, 700 cm^{-1}.

4.11 4-(2-cyano-1-(diphenylamino)vinyl)benzonitrile (363k)

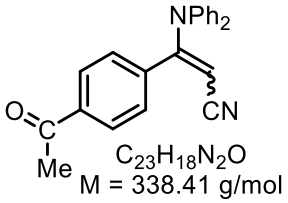


$C_{22}H_{15}N_3$
M = 321.38 g/mol

Prepared according to the **GP-A**, using **360k** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363k** (7.7 mg, 40% yield). ***E:Z* ratio** (isolated)**:** 78:22. ***E:Z***

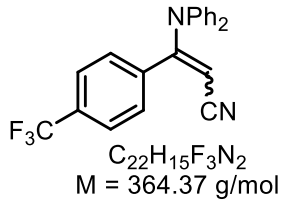
ratio (crude mixture)**:** 73:27. **GP-B,** afforded the product **363k** (8.5 mg, 45% yield), ***E:Z* ratio** (isolated)**:** 78:22. Yellow solid. **M.P:** 146 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{22}H_{16}N_3^+$ 322.1344; found 322.1344. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68–7.66 (m, 3H), 7.60–7.58 (m, 3H), 7.30–7.27 (m, 4H), 7.25–7.24 (m, 2H), 7.15–7.10 (m, 3H), 7.07–7.05 (m, 1H), 7.03–7.01 (m, 5H), 4.89 (s, 0.29H), 4.68 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 145.1, 139.1, 132.5, 132.4, 130.5, 129.8, 129.6, 129.3, 126.8, 126.3, 125.6, 119.5, 118.2, 113.7, 80.6. **IR (neat):** ν 3054, 2982, 2230, 2202, 1576, 1490, 1372, 1263, 732, 701 cm^{-1}.

4.12 3-(4-acetylphenyl)-3-(diphenylamino)acrylonitrile (363l)



Prepared according to the **GP-A**, using **360l** (21.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363l** (7.0 mg, 40% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 77:23. **GP-B,** afforded the product **363l** (7.0 mg, 40% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellow solid. **M.P:** 160 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{23}H_{19}N_2O^+$ 339.1497; found 339.1497. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.85–7.83 (m, 1H), 7.67–7.65 (m, 2H), 7.57–7.53 (m, 1H), 7.29–7.27 (m, 3H), 7.25–7.22 (m, 4H), 7.13–7.07 (m, 5H), 7.05–7.02 (m, 5H), 4.92 (s, 0.27H), 4.65 (s, 1H), 2.57 (s, 3H), 2.56 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4, 163.2, 146.0, 145.4, 139.1, 138.0, 130.1, 129.7, 129.5, 129.0, 128.6, 128.5, 126.9, 126.1, 125.6, 125.3, 119.9, 84.1, 80.3, 26.8. **IR (neat):** ν 3072, 2979, 2901, 2202, 1682, 1584, 1489, 1375, 1263, 756, 696 cm^{-1}.

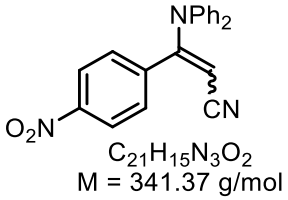
4.13 3-(diphenylamino)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (363m)



Prepared according to the **GP-A**, using **360m** (24.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24

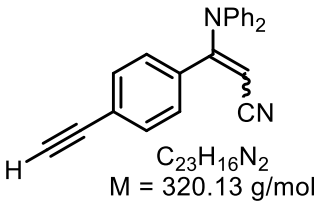
μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.7:1.3 v/v) as eluent afforded the product **363m** (8.0 mg, 40% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 70:30. **GP-B,** afforded the product **363m** (9.0 mg, 45% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellow solid. **M.P:** 135 ^{o}C. **HRMS** (ESI) *m/z*: [(M+H)$^{+}$]: calcd for $C_{22}H_{16}F_3N_2^{+}$ 365.1266; found 365.1266. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 3H), 7.58–7.51 (m, 4H), 7.29–7.23 (m, 8H), 7.14–7.06 (m, 5H), 7.04–7.02 (m, 5H), 4.89 (s, 0.27H), 4.65 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 146.0, 145.4, 138.2, 130.3, 129.8, 129.7, 129.1, 127.0, 126.2, 125.7, 125.5, 119.9, 84.3, 80.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.76. **IR (neat):** ν 3056, 2984, 2204, 1590, 1490, 1322, 1264, 732, 702 cm^{-1}.

4.14 3-(diphenylamino)-3-(4-nitrophenyl)acrylonitrile (363n)



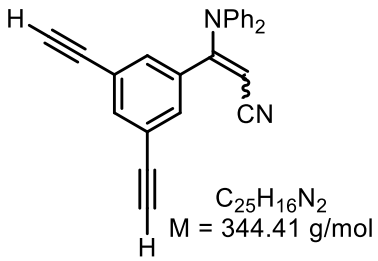
Prepared according to the **GP-A**, using **360n** (21.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363n** (8.0 mg, 40% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 80:20. By following **GP-B,** no reaction was observed. Yellow solid. **M.P:** 155 ^{o}C. **HRMS** (ESI) *m/z*: [(M+H)$^{+}$]: calcd for $C_{21}H_{16}N_3O_2^{+}$ 342.1243; found 342.1242. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16–8.13 (m, 2H), 8.12–8.09 (m, 0.62H), 7.75–7.72 (m, 2H), 7.63–7.61 (m, 0.61H), 7.29–7.23 (m, 6H), 7.15–7.11 (m, 3H), 7.08–7.01 (m, 6H), 4.91 (s, 0.28H), 4.69 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 148.4, 145.0, 140.9, 130.9, 129.9, 129.7, 129.6, 126.9, 126.4, 125.7, 124.0, 123.9, 80.8. **IR (neat):** ν 2926, 2854, 2200, 1569, 1519, 1489, 1344, 1108, 857, 753, 796 cm^{-1}.

4.15 3-(diphenylamino)-3-(4-ethynylphenyl)acrylonitrile (363o)



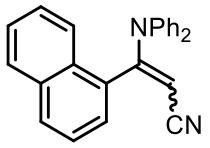
Prepared according to the **GP-A**, using **360o** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.6:1.4 v/v) as eluent afforded the product **363o** (12.0 mg, 64% yield). ***E:Z* ratio** (isolated)**:** 77:23. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B,** afforded the product **18** (11.0 mg, 60% yield), ***E:Z* ratio** (isolated)**:** 77:23. Yellow solid. **M.P:** 139 °C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{23}H_{17}N_2^+$ 321.1392; found 321.1392. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.41–7.34 (m, 4H), 7.27–7.20 (m, 7H), 7.11–7.04 (m, 5H), 7.02–6.99 (m, 5H), 4.87 (s, 0.29H), 4.59 (s, 1H), 3.11 (s, 0.24H), 3.09 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 161.2, 146.1, 145.6, 137.7, 134.8, 132.4, 132.3, 129.7, 129.6, 129.4, 128.6, 126.8, 125.9, 125.5, 125.1, 124.0, 123.9, 120.0, 116.8, 83.6, 83.0, 82.9, 80.0, 79.4, 79.0. **IR (neat):** ν 3295, 3057, 2995, 2202, 2135, 1572, 1489, 1372, 1264, 732, 698 cm^{-1}.

4.16 3-(3,5-diethynylphenyl)-3-(diphenylamino)acrylonitrile (363p)



Prepared according to the **GP-A**, using **360p** (22.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363p** (9.0 mg, 45% yield). ***E:Z* ratio** (isolated)**:** 70:30. ***E:Z* ratio** (crude mixture)**:** 80:20. **GP-B,** afforded the product **363p** (9.0 mg, 45% yield), ***E:Z* ratio** (isolated)**:** 70:30. Brown gel, after pentane wash and high vacuum becomes solid. **M.P:** 60 °C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{25}H_{17}N_2^+$ 345.1392; found 345.1392. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 1.6 Hz, 2H), 7.52–7.50 (m, 3H), 7.29–7.26 (m, 6H), 7.24–7.22 (m, 3H), 7.14–7.10 (m, 4H), 7.08–6.99 (m, 8H), 4.85 (s, 0.42H), 4.61 (s, 1H), 3.09 (s, 0.81H), 3.08 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 145.8, 145.2, 138.2, 137.0, 135.3, 133.3, 132.3, 129.7, 129.6, 126.9, 126.1, 125.6, 125.4, 123.2, 123.1, 119.5, 83.8, 81.9, 81.7, 80.3, 79.1, 79.1. **IR (neat):** ν 3285, 3050, 2991, 2185, 2141, 1589, 1565, 1489, 1376, 1238, 730, 703 cm^{-1}.

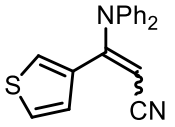
4.17 3-(diphenylamino)-3-(naphthalen-1-yl)acrylonitrile (363q)



$C_{25}H_{18}N_2$
M = 346.43 g/mol

Prepared according to the **GP-A**, using **360q** (22.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363q** (10.0 mg, 55% yield). ***E:Z* ratio** (isolated)**:** 89:11. ***E:Z* ratio** (crude mixture)**:** 88:12. **GP-B,** afforded the product **363q** (10.0 mg, 55% yield), ***E:Z* ratio** (isolated)**:** 89:11. Brown solid. **M.P:** 180 ^oC. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{25}H_{19}N_2^+$ 347.1548; found 347.1548. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 0.15H), 8.31 (d, *J* = 8.6 Hz, 1H), 7.78–7.69 (m, 4H), 7.60–7.53 (m, 2H), 7.45–7.40 (m, 3H), 7.22–7.15 (m, 11H), 7.06–7.00 (m, 3H), 4.78 (s, 1H), 4.75 (s, 0.13H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 145.8, 145.0, 133.5, 131.4, 130.7, 130.6, 129.9, 129.3, 129.2, 128.7, 127.2, 127.0, 126.2, 126.2, 125.6, 124.9, 124.6, 120.2, 80.8, 77.8. **IR (neat):** ν 3062, 2922, 2852, 2196, 1559, 1487, 1360, 1301, 1258, 800, 704, 698, 649 cm^{-1}.

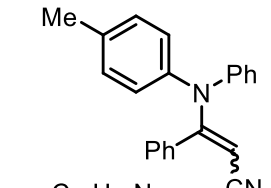
4.18 3-(diphenylamino)-3-(thiophen-3-yl)acrylonitrile (363r)



$C_{19}H_{14}N_2S$
M = 302.39 g/mol

Prepared according to the **GP-A**, using **360r** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.1:0.9 v/v) as eluent afforded the product **363r** (15.0 mg, 85% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B,** afforded the product **363r** (16.0 mg, 88% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellow solid. **M.P:** 136 ^{o} C. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{19}H_{15}N_2S^+$ 303.0956; found 303.0955. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 3.1, 1.3 Hz, 0.29H), 7.25–7.19 (m, 6H), 7.13–7.11 (m, 1H), 7.09–7.03 (m, 5H), 7.00–6.96 (m, 5H), 4.92 (s, 0.26H), 4.49 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 145.8, 135.4, 129.5, 129.4, 128.1, 126.6, 125.8, 125.6, 125.3, 124.9, 120.5, 78.9. **IR (neat):** ν 3055, 2200, 1564, 1489, 1422, 1264, 732, 699 cm^{-1}.

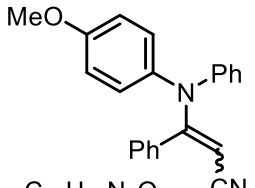
4.19 3-phenyl-3-(phenyl(*p*-tolyl)amino)acrylonitrile (363s)



$C_{22}H_{18}N_2$
M = 310.40 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361b** (11.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.2:0.8 v/v) as eluent afforded the product **363s** (13.0 mg, 70% yield). ***E:Z* ratio** (isolated)**:** 77:23. ***E:Z* ratio** (crude mixture)**:** 75:25. **GP-B,** afforded the product **363s** (13.0 mg, 70% yield), ***E:Z* ratio** (isolated)**:** 77:23. Brownish gel. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{22}H_{19}N_2^+$ 311.1548; found 311.1548. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 3H), 7.46–7.43 (m, 1H), 7.30–7.28 (m, 5H), 7.24–7.19 (m, 5H), 7.08–7.04 (m, 6H), 6.99 (t, *J* = 7.9 Hz, 4H), 6.94 (d, *J* = 8.3 Hz, 3H), 4.83 (s, 0.29H), 4.55 (s, 1H), 2.29 (s, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 145.9, 143.3, 135.7, 134.5, 130.2, 130.1, 130.0, 129.8, 129.4, 129.3, 128.8, 128.7, 128.5, 126.9, 126.8, 125.7, 125.4, 124.7, 120.6, 78.9, 21.1. **IR (neat):** ν 3055, 2205, 1581, 1482, 1422, 1363, 1237, 727, 700 cm^{-1}.

4.20 3-((4-methoxyphenyl)(phenyl)amino)-3-phenylacrylonitrile (363t)

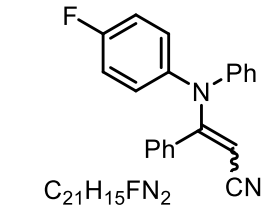


$C_{22}H_{18}N_2O$
M = 326.14 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361c** (12.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363t** (16.6 mg, 85% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 75:25. **GP-B,** afforded the product **363t** (16.6 mg, 85% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellowish gel. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{22}H_{19}N_2O^+$ 327.1497; found 327.1497. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.42–7.40 (m, 1H), 7.27–7.23 (m, 5H), 7.20–7.15 (m, 3H), 7.03–6.94 (m, 8H), 6.78–6.74 (m, 3H), 4.75 (s, 0.26H), 4.48 (s, 1H), 3.74 (s, 5H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 164.7, 162.3, 157.6, 157.0, 146.6, 145.9, 139.4, 138.7, 137.5, 134.5, 130.1, 130.0, 129.8, 129.3, 129.2, 128.8, 128.6, 128.5, 128.4, 127.4, 126.6, 125.3, 125.2, 124.5, 120.7, 117.4, 114.8, 114.6, 81.5, 78.2, 55.6. **IR (neat):** ν 3055, 2983, 2200, 1587, 1562, 1507, 1376, 1264, 731, 701 cm^{-1}.

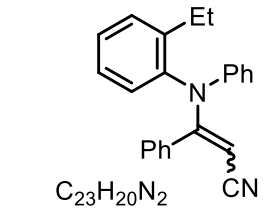
4.21 3-((4-fluorophenyl)(phenyl)amino)-3-phenylacrylonitrile (363u)



$C_{21}H_{15}FN_2$
M = 314.36 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361d** (11.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363u** (11.0 mg, 60% yield). ***E:Z* ratio** (isolated)**:** 73:27. ***E:Z* ratio** (crude mixture)**:** 75:25. **GP-B,** afforded the product **363u** (12.0 mg, 65% yield), ***E:Z* ratio** (isolated)**:** 73:27. Yellowish gel. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}FN_2^+$ 315.1298; found 315.1297. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.43–7.40 (m, 1H), 7.30–7.21 (m, 9H), 7.10–7.05 (m, 2H), 7.03–6.96 (m, 6H), 6.94–6.88 (m, 3H), 4.85 (s, 0.35H), 4.53 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 162.2, 161.5, 159.0, 146.2, 145.7, 142.4, 141.8, 137.1, 134.2, 130.4, 130.3, 129.8, 129.6, 129.4, 128.8, 128.6, 128.5, 127.3, 127.3, 126.8, 125.8, 125.3, 125.0, 120.2, 116.6, 116.4, 116.4, 116.2, 82.9, 79.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -29.52, -29.58, -29.82, -29.89, -31.36, -31.42, -31.48, -31.54, -31.60, -31.67. **IR (neat):** ν 3056, 2986, 2204, 1563, 1502, 1422, 1375, 1263, 730, 703 cm^{-1}.

4.22 3-((2-ethylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363v))

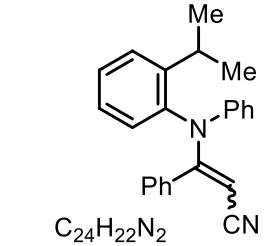


$C_{23}H_{20}N_2$
M = 324.42 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361e** (12.0 mg, 0.06 mmol, 1.0 equiv), **3a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0

v/v) as eluent afforded the product **363v** (7.7 mg, 40% yield). ***E:Z* ratio** (isolated)**:** 87:13. ***E:Z* ratio** (crude mixture)**:** 87:13. **GP-B,** afforded the product **363v** (9.0 mg, 45% yield), ***E:Z* ratio** (isolated)**:** 87:13. Yellowish solid. **M.P:** 130 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{23}H_{21}N_2^+$ 325.1705; found 325.1705. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57–7.54 (m, 3H), 7.43–7.42 (m, 1H), 7.34–7.27 (m, 9H), 7.25–7.19 (m, 3H), 7.11–7.06 (m, 5H), 6.96–6.93 (m, 2H), 6.82–6.80 (m, 3H), 4.66 (s, 0.15H), 4.31 (s, 1H), 2.71–2.64 (m, 4H), 1.18 (t, *J* = 7.5 Hz, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 145.4, 143.3, 140.9, 134.2, 130.2, 130.1, 129.7, 129.3, 128.9, 128.9, 128.5, 128.0, 127.7, 125.8, 125.1, 124.5, 120.6, 77.6, 23.9, 14.1. **IR (neat):** ν 3054, 2982, 2201, 1588, 1561, 1490, 1374, 1264, 730, 703 cm^{-1}.

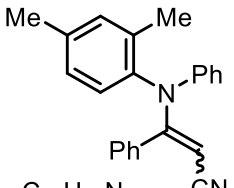
4.23 3-((2-isopropylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363w)



$C_{24}H_{22}N_2$
M = 338.45 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361f** (13.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363w** (6.0 mg, 30% yield). ***E:Z* ratio** (isolated)**:** 85:15. ***E:Z* ratio** (crude mixture)**:** 90:10. **GP-B,** afforded the product **363w** (7.0 mg, 35% yield), ***E:Z* ratio** (isolated)**:** 85:15. White to brown solid. **M.P:** 160 °C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{24}H_{23}N_2^+$ 339.1861; found 339.1861. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 3H), 7.43–7.40 (m, 0.55H), 7.38–7.35 (m, 2H), 7.32–7.28 (m, 5H), 7.24–7.17 (m, 2H), 7.13–7.06 (m, 4H), 6.98–6.92 (m, 1H), 6.88–6.85 (m, 0.49H), 6.83–6.81 (m, 2H), 4.62 (s, 0.18H), 4.33 (s, 1H), 3.31–3.23 (m, 1.52H), 1.26 (d, *J* = 6.8 Hz, 6H), 0.96 (d, *J* = 6.8 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 146.0, 145.7, 142.4, 134.2, 130.2, 129.8, 129.5, 129.3, 128.9, 128.6, 128.4, 128.2, 127.9, 127.6, 127.5, 127.0, 125.9, 125.6, 124.5, 124.4, 120.6, 78.3, 77.8, 28.1, 28.0, 24.1, 23.4. **IR (neat):** ν 3050, 2984, 2204, 1574, 1558, 1485, 1365, 1261, 733, 701 cm^{-1}.

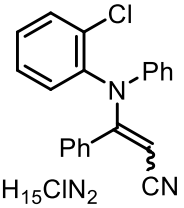
4.24 3-((2,4-dimethylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363x)



$C_{23}H_{20}N_2$
M = 324.42 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361g** (13.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.7:1.3 v/v) as eluent afforded the product **363x** (8.0 mg, 50% yield). ***E:Z* ratio** (isolated)**:** 85:15. ***E:Z* ratio** (crude mixture)**:** 88:12. **GP-B,** afforded the product **363x** (8.0 mg, 50% yield), ***E:Z* ratio** (isolated)**:** 85:15. White to Yellowish powder. **M.P:** 123 ^{o}C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{23}H_{21}N_2^+$ 325.1705; found 325.1705. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.44–7.42 (m, 0.42H), 7.31–7.28 (m, 4H), 7.15–7.07 (m, 4H), 7.04–6.99 (m, 2H), 6.96–6.92 (m, 3H), 6.83–6.80 (m, 3H), 4.69 (s, 0.16H), 4.31 (s, 1H), 2.32 (s, 4H), 2.28 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 161.7, 146.2, 145.2, 141.7, 141.2, 137.5, 137.4, 137.1, 135.2, 134.8, 134.2, 132.6, 132.3, 130.1, 130.0, 129.6, 128.9, 128.7, 128.5, 128.4, 128.0, 125.8, 124.7, 124.5, 124.0, 120.8, 117.0, 79.0, 76.7, 21.2, 21.1, 18.7, 18.2. **IR (neat):** ν 3062, 2975, 2921, 2200, 1588, 1559, 1492, 1377, 1304, 753, 725, 693 cm^{-1}.

4.25 3-((2-chlorophenyl)(phenyl)amino)-3-phenylacrylonitrile (363y)

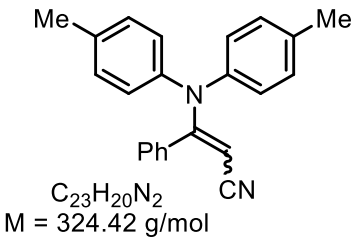


$C_{21}H_{15}ClN_2$
M = 330.09 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361h** (12.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.7:1.3 v/v) as eluent afforded the product **363y** (11.0 mg, 54% yield). ***E:Z* ratio** (isolated)**:** 80:20. ***E:Z* ratio** (crude mixture)**:** 80:20. **GP-B,** afforded the product **363y** (11.0 mg, 54% yield), ***E:Z* ratio** (isolated)**:** 80:20. Yellowish gel. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{21}H_{16}ClN_2^+$ 331.1002; found 331.1001. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.60 (m, 3H), 7.52–7.50 (m, 1H), 7.47–7.39 (m, 2H),

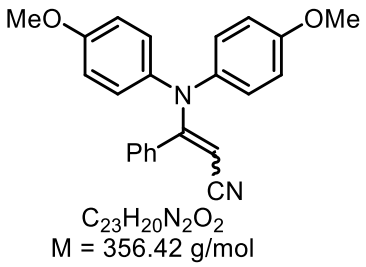
7.31–7.28 (m, 5H), 7.24–7.11 (m, 12H), 7.04 (t, *J* = 7.4 Hz, 2H), 6.96–6.91 (m, 3H), 4.80 (s, 0.24H), 4.41 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 144.6, 142.3, 133.9, 133.3, 132.3, 131.3, 130.8, 130.3, 130.2, 129.9, 129.8, 129.6, 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 127.5, 126.2, 125.4, 125.4, 122.7, 120.5, 120.3, 120.2, 115.6, 80.0, 78.2. **IR (neat):** ν 3055, 2987, 2202, 1588, 1563, 1491, 1375, 1262, 731, 702 cm^{-1}.

4.26 3-(di-*p*-tolylamino)-3-phenylacrylonitrile (363z)



Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361i** (12.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.0:1.0 v/v) as eluent afforded the product **363z** (14.0 mg, 70% yield). ***E:Z* ratio** (isolated)**:** 94:06. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B,** afforded the product **363z** (15.0 mg, 75% yield), ***E:Z* ratio** (isolated)**:** 94:06. Pink solid. **M.P:** 191 °C. **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{23}H_{21}N_2^+$ 325.1705; found 325.1706. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.45–7.43 (m, 0.17H), 7.31–7.27 (m, 4H), 7.04–7.02 (m, 5H), 6.92–6.89 (m, 5H), 4.78 (s, 0.06H), 4.51 (s, 1H), 2.27 (s, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 143.3, 135.4, 134.7, 130.1, 130.0, 129.9, 129.8, 128.4, 126.7, 125.5, 120.8, 78.1, 21.1. **IR (neat):** ν 3052, 3029, 2919, 2849, 2197, 1586, 1557, 1505, 1368, 1314, 1281, 811, 778, 763, 723, 696 cm^{-1}.

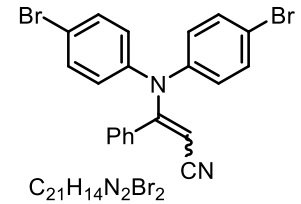
4.27 3-(bis(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363ja)



Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361j** (14.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24

μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363ja** (15.0 mg, 70% yield). ***E:Z* ratio** (isolated)**:** 82:18. ***E:Z* ratio** (crude mixture)**:** 78:22. **GP-B,** afforded the product **363ja** (16.0 mg, 75% yield), ***E:Z* ratio** (isolated)**:** 82:18. Yellow gel after pentane wash and high vacuum become solid. **M.P:** 40 ^{o}C. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{23}H_{21}N_2O_2^+$ 357.1603; found 357.1603. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.41–7.39 (m, 0.51H), 7.28–7.23 (m, 5H), 6.98–6.92 (m, 6H), 6.76–6.71 (m, 6H), 4.64 (s, 0.21H), 4.41 (s, 1H), 3.73 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.9, 157.3, 156.8, 139.8, 138.8, 137.7, 134.5, 129.8, 129.8, 128.8, 128.5, 128.4, 128.0, 127.0, 120.9, 114.6, 114.5, 79.5, 76.6, 55.5. **IR (neat):** ν 3055, 2987, 2201, 1588, 1562, 1377, 1263, 732, 703 cm^{-1}.

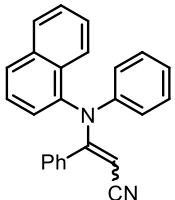
4.28 3-(bis(4-bromophenyl)amino)-3-phenylacrylonitrile (363ka)



$C_{21}H_{14}N_2Br_2$
M = 454.16 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361k** (20.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363ka** (14.0 mg, 50% yield). ***E:Z* ratio** (isolated)**:** 97:03. ***E:Z* ratio** (crude mixture)**:** 77:23. **GP-B,** afforded the product **363ka** (14.0 mg, 50% yield), ***E:Z* ratio** (isolated)**:** 97:03. Yellow solid. **M.P:** 165 ^{o}C. **HRMS** (ESI) *m/z*: $[(M+H)^+]$: calcd for $C_{21}H_{15}N_2Br_2^+$ 454.9582; found 454.9600. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.38–7.30 (m, 9H), 6.91–6.88 (m, 5H), 5.02 (s, 0.03H), 4.66 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 144.9, 144.5, 133.7, 132.9, 132.7, 130.8, 130.7, 129.7, 129.0, 128.8, 128.6, 128.2, 126.6, 119.6, 119.2, 81.8. **IR (neat):** ν 3054, 2984, 2204, 1586, 1564, 1488, 1372, 1262, 732, 703 cm^{-1}.

4.29 3-(naphthalen-1-yl(phenyl)amino)-3-phenylacrylonitrile (363la)

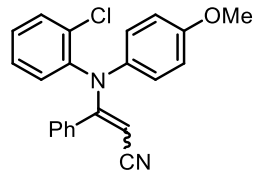


$C_{25}H_{18}N_2$
M = 346.43 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361l** (13.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24

μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.8:1.2 v/v) as eluent afforded the product **363la** (14.0 mg, 60% yield). ***E:Z* ratio** (isolated)**:** 85:15. ***E:Z* ratio** (crude mixture)**:** 88:12. **GP-B,** afforded the product **363la** (14.0 mg, 60% yield), ***E:Z* ratio** (isolated)**:** 85:15. Brown gel. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{25}H_{19}N_2^+$ 347.1548; found 347.1548. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–8.08 (m, 1H), 7.88–7.86 (m, 1.40H), 7.76 (d, *J* = 8.3 Hz, 1.42H), 7.66–7.64 (m, 3H), 7.56–7.49 (m, 3H), 7.42–7.39 (m, 2H), 7.30–7.25 (m, 4H), 7.15–7.10 (m, 3H), 7.03–6.95 (m, 5H), 4.75 (s, 0.16H), 4.36 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 146.0, 141.4, 135.0, 134.3, 130.2, 129.6, 129.2, 128.8, 128.5, 128.1, 127.5, 127.3, 126.7, 126.0, 125.1, 123.0, 120.5, 78.4. **IR (neat):** ν 3062, 2922, 2852, 2196, 1559, 1487, 1360, 1301, 1258, 800, 704, 698, 649 cm^{-1}.

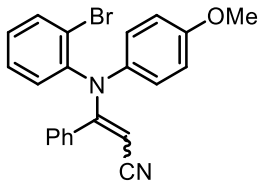
4.30 3-((2-chlorophenyl)(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363ma)



$C_{22}H_{17}ClN_2O$
M = 360.84 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361m** (14.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 μmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363ma** (11.0 mg, 50% yield). ***E:Z* ratio** (isolated)**:** 82:18. ***E:Z* ratio** (crude mixture)**:** 80:20. **GP-B,** afforded the product **363ma** (11.0 mg, 50% yield), ***E:Z* ratio** (isolated)**:** 82:18. Brown solid. **M.P:** 55 ^{o}C. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{22}H_{18}ClN_2O^+$ 361.1108; found 361.1109. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2.54H), 7.49 (dd, *J* = 8.0, 1.6 Hz, 0.57H), 7.44 (d, *J* = 8.0 Hz, 0.31H), 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29–7.27 (m, 4H), 7.23–7.13 (m, 4H), 7.11 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.71 (dd, *J* = 11.1, 5.5 Hz, 3H), 4.70 (s, 0.23H), 4.33 (s, 1H), 3.73 (s, 3H) 3.72 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 161.0, 157.3, 156.9, 142.9, 142.4, 138.8, 137.5, 137.1, 134.0, 132.0, 131.4, 131.2, 130.8, 130.6, 130.1, 130.1 130.0, 129.7, 129.0, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.0, 120.5, 116.9, 114.5, 114.3, 78.3, 76.6, 55.5. **IR (neat):** ν 3055, 2983, 2203, 1590, 1564, 1506, 1372, 1265, 731, 703 cm^{-1}.

4.31 3-((2-bromophenyl)(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363na)



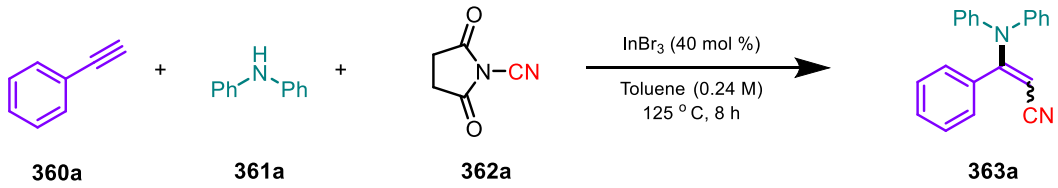
$C_{22}H_{17}BrN_2O$
M = 404.29 g/mol

Prepared according to the **GP-A**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361n** (17.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (8.5:1.5 v/v) as eluent afforded the product **363na** (6.0 mg, 25% yield). ***E:Z* ratio** (isolated)**:** 82:18. ***E:Z* ratio** (crude mixture)**:** 80:20. **GP-B,** afforded the product **363na** (5.0 mg, 20% yield), ***E:Z* ratio** (isolated)**:** 82:18. Brown gel. **HRMS** (ESI) *m/z*: [(M+H)$^+$]: calcd for $C_{22}H_{18}BrN_2O^+$ 405.0603; found 405.0602. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.60 (m, 4H), 7.52 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.29–7.27 (m, 5H), 7.24–7.19 (m, 2H), 7.13–7.08 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 1H) 6.70 (dd, *J* = 9.1, 2.6 Hz, 3H), 4.70 (s, 0.27H), 4.30 (s, 1H), 3.72 (s, 5H). **^{13}C NMR** (101 MHz, DMSO-D_6) δ 163.4, 160.0, 156.9, 156.3, 143.1, 138.5, 136.9, 134.1, 133.8, 131.2, 130.9, 129.9, 129.5, 129.4, 129.2, 128.9, 128.4, 128.2, 127.9, 126.8, 121.6, 121.1, 120.0, 116.5, 114.4, 114.3, 78.5, 75.1, 55.2. **IR (neat):** ν 3053, 2986, 2200, 1598, 1562, 1503, 1365, 1270, 730, 701 cm^{-1}.

Note: *In some cases we have taken no. of protons after decimal points in ^{1}H-NMR e.g. 0.25, 1.45 like that, because mixture of E/Z isomers present.*

5. Additional experiments

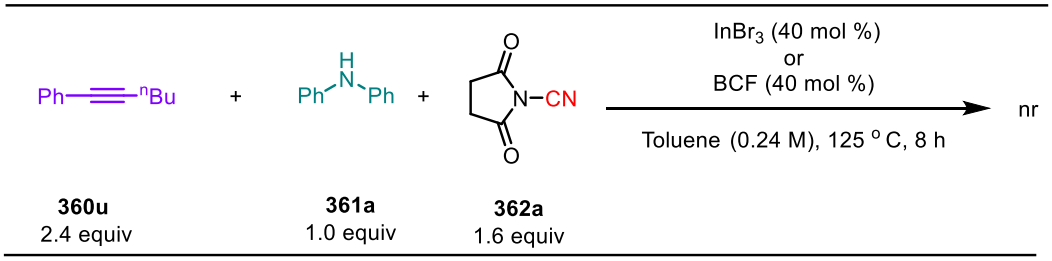
5.1 Gram scale synthesis



360a **361a** **362a** **363a**

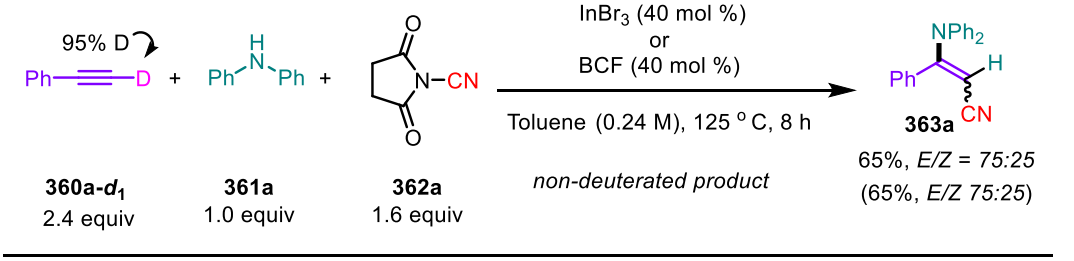
Gram scale synthesis has been done by using the **GP-A, 360a** (1.5 gm, 14.4 mmol, 2.4 equiv), **361a** (1.0 gm, 6.0 mmol, 1.0 equiv), **362a** (1.2 gm, 9.6 mmol, 1.6 equiv), toluene (25.0 ml) and indium tribromide ($InBr_3$) (0.8 gm, 2.4 mmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (0.9 g, 50%).

5.2 Control experiments



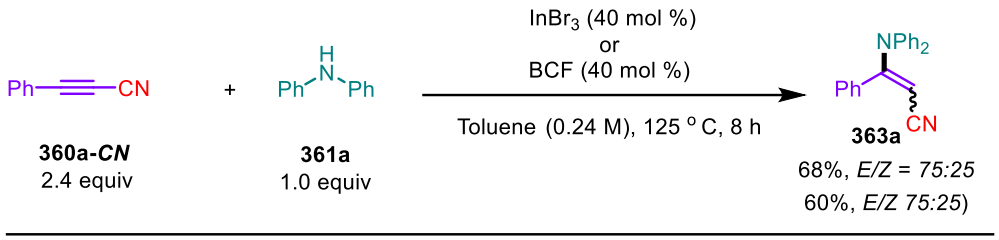
According to **GP-A**, using **360u** (23.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %).

According to **GP-B**, using **360u** (23.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (12.0 mg, 24 µmol, 40 mol %).



According to **GP-A**, using **360a-*d*$_1$** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (11.0 mg, 65%).

According to **GP-B**, using **360a-*d*$_1$** (16.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (12.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (10.0 mg, 60%).



According to **GP-B**, using **360a-*CN*** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (11.8 mg, 68%).

According to **GP-B**, using **360a-*CN*** (18.0 mg, 0.144 mmol, 2.4 equiv), **361a** (10.0 mg, 0.06 mmol, 1.0 equiv), **362a** (12.0 mg, 0.096 mmol, 1.6 equiv), and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (12.0 mg, 24 µmol, 40 mol %). Purification by column chromatography on silica gel using petroleum ether/EtOAc (9.3:0.7 v/v) as eluent afforded the product **363a** (10.0 mg, 60%).\

5.3 Detection of formation of succinimide 362 from crude reaction mixture by ^{1}H-NMR

Formation of **362** has been confirmed by ^{1}H-NMR of crude reaction mixture. Reaction performed by modified **GP-1**, using **360a** (16.0 mg, 0.144 mmol, 2.4 equiv), **361n** (17.0 mg, 0.06 mmol, 1.0 equiv), **362a** (8.0 mg, 0.06 mmol, 1.0 equiv), and indium tribromide ($InBr_3$) (8.0 mg, 24 µmol, 40 mol %). Stirred for eight hours in a preheated oil bath at 125 ^{o}C temperature. After 8 h, reaction mixture diluted with acetonitrile and passed through a silica-gel pad. After rota-evaporation, applied high vacuum for long time to avoid solvent peaks, then diluted in $CDCl_3$ and recorded ^{1}H-NMR.

***Note**: Why Acetonitrile? -Because of the high solubility of reaction mixture in acetonitrile.*

*Why **362a** used in 1.0 equiv? –To see clearly decreasing intensity of **362a** and increasing intensity of **362**.*

*Why **360a** is not visible or very low intensity in the region near 3 ppm, even it is taken in 2.4 equiv amount? –Because very high vacuum applied to evaporate all volatiles, as well as the decomposition in presence of Lewis acid during reaction time, might be possible reasons.*

6.0 X-Ray data of 363a, 363h, 363q, 363r and 363z:

For the determination of X-ray crystal structures of 363a, 363h, 363q, 363r and 363z a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[143] was used. Absorption correction was done

applying SADABS program.[144] The crystal structure was solved by SIR 92[145] and refined by full matrix least square method using SHELXL-97[146] WinGX system, Ver 1.70.01.[147] All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: **363a: CCDC 2104208, 363h: CCDC 2124438, 363q: CCDC 2158740, 363r: CCDC 2158723, 363z: CCDC 2158812**. [116, 117]

Crystal Data and Structure Refinement for Compound 363a (CCDC 2104208)

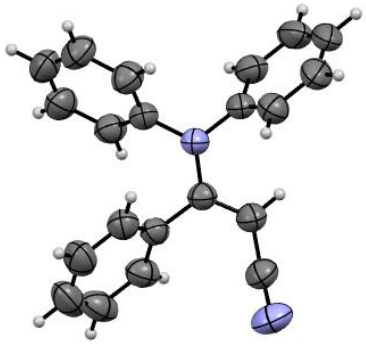


Figure 28: ORTEP drawing of compound (**363a**) showing thermal ellipsoids at the 50% probability.

Crystal data and structure refinement for Compound 363a (CCDC 2104208)	
Ccdc no.	2104208
Empirical formula	$C_{21}\ H_{16}\ N_2$
Formula weight	296.36
Temperature/K	298
Crystal system	monoclinic
Space group	P 21/c
a, b, c, (Å)	8.7088(18), 9.530(2), 20.145(4)
α, β, γ (°)	90, 91.662(7), 90
Volume ($Å^3$)	1671.2(6)
Z	4
ρ_{calc} (g/cm^3)	1.178
μ (mm^{-1})	0.070
F(000)	624.0
Crystal size/mm^3	0.356 × 0.278 × 0.256
Theta range for data collection:	2.3^o to 27.95^o
Data set	-11 : 11; -12 : 12; -26 : 26
R indices (all data)	R_1 = 0.0550, wR_2 = 0.1748
Reflection	4004
S	1.038
Npar	209

Crystal Data and Structure Refinement for Compound 363h (CCDC 2124438)

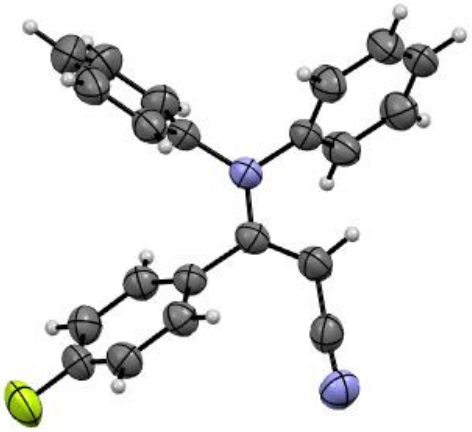


Figure 29: ORTEP drawing of compound (**363h**) showing thermal ellipsoids at the 50% probability.

Crystal data and structure refinement for Compound 363h (CCDC 2124438)	
Ccdc no.	2124438
Empirical formula	$C_{21}H_{15}FN_2$
Formula weight	314.35
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a, b, c (Å)	8.6527(8), 9.7189(8), 9.9280(8)
α, β, γ (°)	96.347(3), 91.670(3), 94.355(3)
Volume/Å^3	826.79(12)
Z	2
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.083
F(000)	328.0
Crystal size/mm^3	0.235 × 0.178 × 0.125
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	4.724° to 50.238°
Data set	-10 : 10, -11 : 11, -11 : 11
Reflections collected	12287
Final R indexes [all data]	R_1 = 0.0782, wR_2 = 0.1160
S	1.005
Npar	217

Crystal Data and Structure Refinement for Compound 363q (CCDC 2158740)

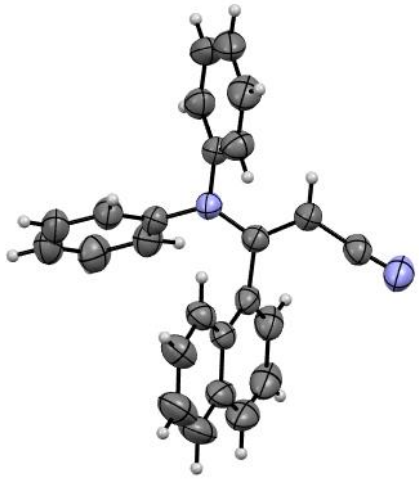


Figure 30: ORTEP drawing of compound (**363q**) showing thermal ellipsoids at the 50% probability.

Crystal data and structure refinement for Compound 363q (CCDC 2158740)	
Ccdc no.	2158740
Empirical formula	$C_{25}H_{18}N_2$
Formula weight	346.41
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a, b, c (Å)	9.3021(10), 11.0463(11), 18.531(2)
α, β, γ (°)	90, 96.290(4), 90
Volume/Å^3	1892.7(4)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.071
F(000)	728.0
Crystal size/mm^3	0.357 × 0.341 × 0.258
Theta range for data collection	5.746° to 52.918°
Data set	-11 : 11, -13 : 13, -23 : 23
Reflections collected	32280
Final R indexes [all data]	R_1 = 0.1207, wR_2 = 0.1441
S	1.023
Npar	245

Crystal Data and Structure Refinement for Compound 363r (CCDC 2158723)

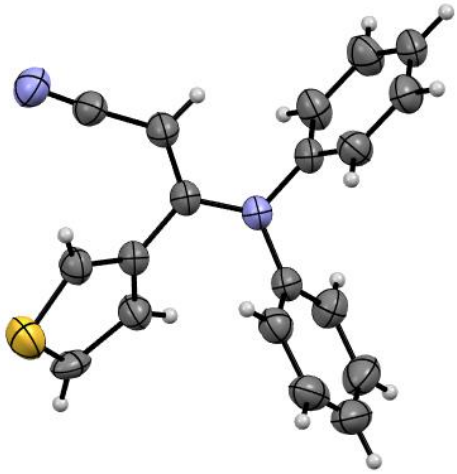


Figure 31: ORTEP drawing of compound (**363r**) showing thermal ellipsoids at the 50% probability.

Crystal data and structure refinement for Compound 363r (CCDC 2158723)	
Ccdc no.	2158723
Empirical formula	$C_{19}H_{14}N_2S$
Formula weight	302.38
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a, b, c (Å)	8.3877(7), 9.6991(7), 9.8944(7)
α, β, γ (°)	95.011(2), 93.842(3), 94.375(3)
Volume/Å^3	797.33(10)
Z	2
ρ_{calc}g/cm^3	1.260
μ/mm^{-1}	0.200
F(000)	316.0
Crystal size/mm^3	0.325 × 0.235 × 0.23
Theta range for data collection	4.144° to 55.952°
Data set	-11 : 11, -12 : 12, -13 : 13
Reflections collected	26329
Final R indexes [all data]	R_1 = 0.0908, wR_2 = 0.2396
S	1.087
Npar	199

Crystal Data and Structure Refinement for Compound 363z (CCDC 2158812)

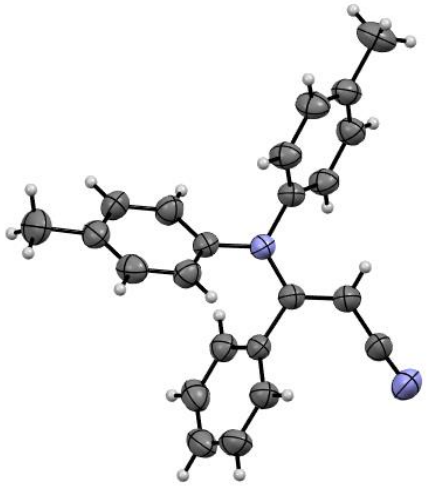


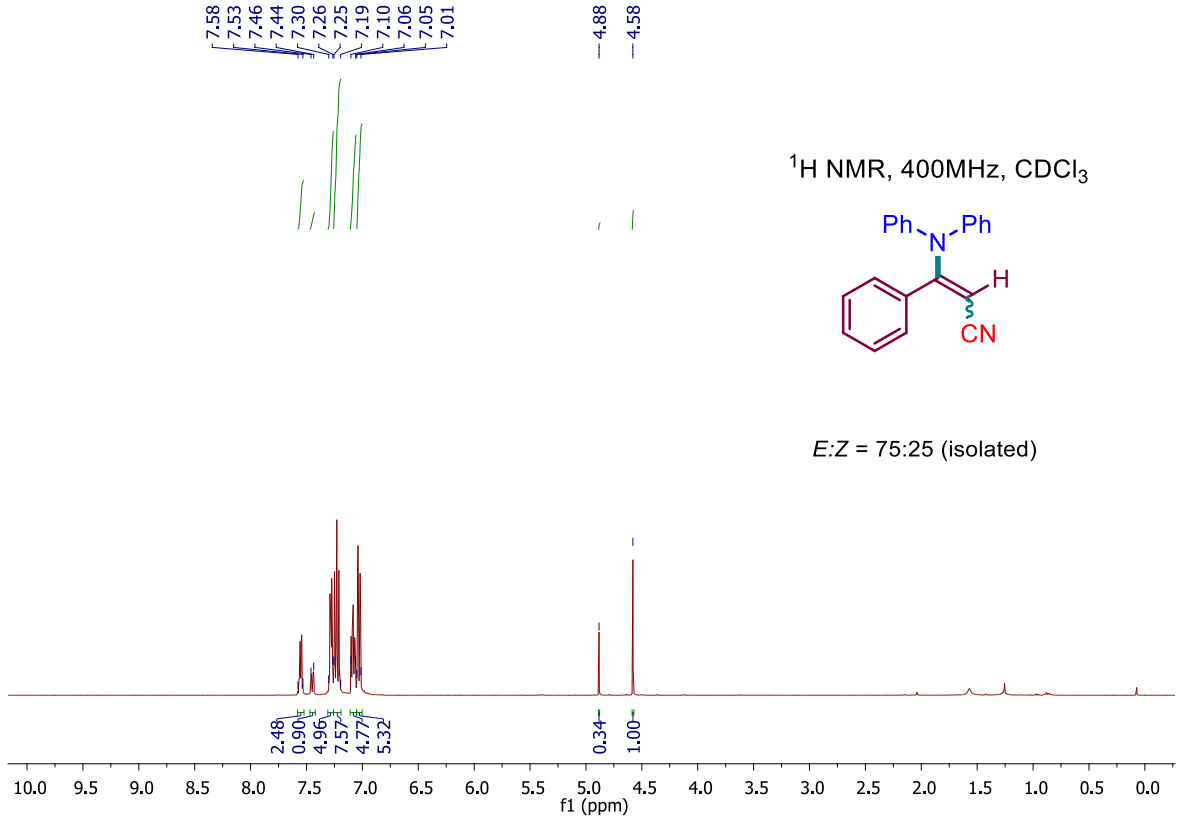
Figure 32: ORTEP drawing of compound (**363z**) showing thermal ellipsoids at the 50% probability.

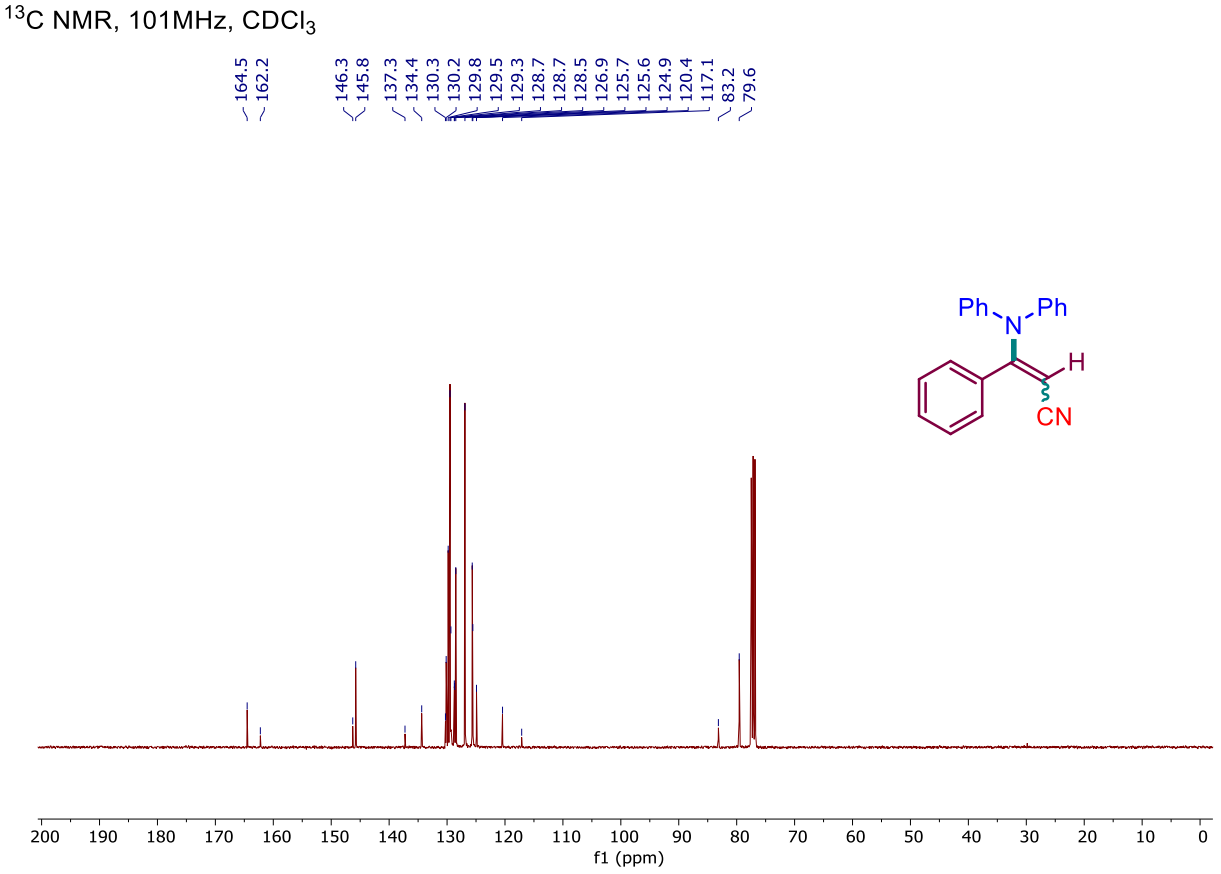
Crystal data and structure refinement for compound 363z (CCDC 2158812)	
Ccdc no.	2158812
Empirical formula	$C_{23}H_{20}N_2$
Formula weight	324.41
Temperature/K	298
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, b, c (Å)	9.0600(4), 14.1366(9), 14.6666(10)
α, β, γ (°)	90, 90, 90
Volume/Å^3	1878.46(19)
Z	4
ρ_{calc}g/cm^3	1.147
μ/mm^{-1}	0.067
F(000)	688.0
Crystal size/mm^3	0.456 × 0.389 × 0.256
Theta range for data collection	5.284° to 50.73°
Data set	-10 : 10, -17 :17, -17 : 17
Reflections collected	19099
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.1226
S	1.050
Npar	229

Atom color code: grey = carbon atom, white = hydrogen atom, blue = nitrogen atom, green = fluorine, and yellow = sulfur atom.

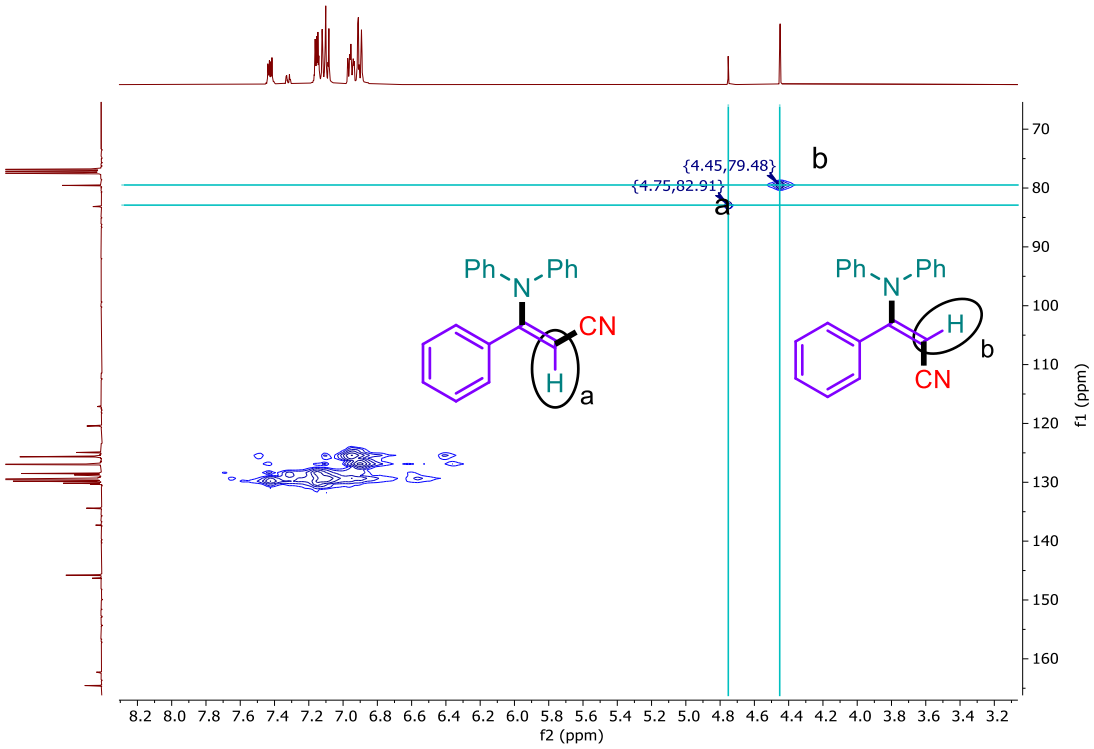
7. Experimental NMR Data

3-(diphenylamino)-3-phenylacrylonitrile (363a)



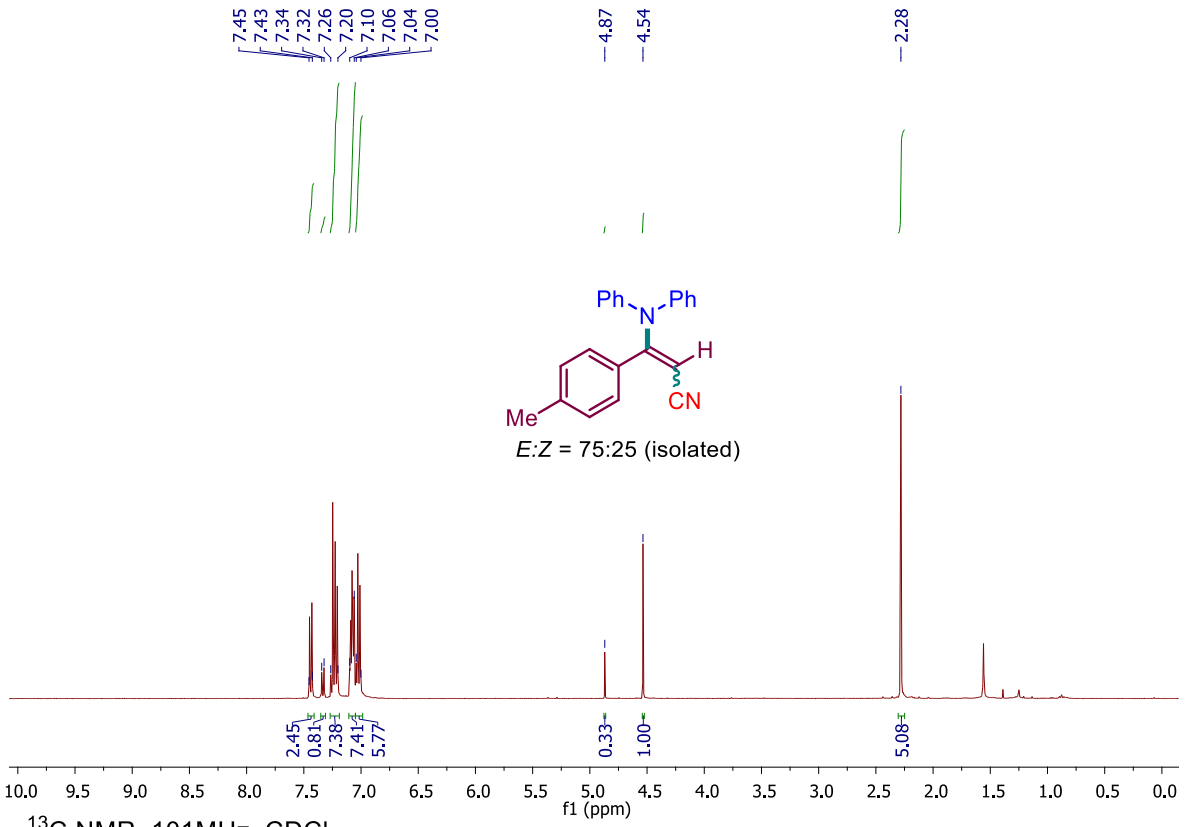


^{1}H-^{13}C HSQC NMR ($CDCl_3$)



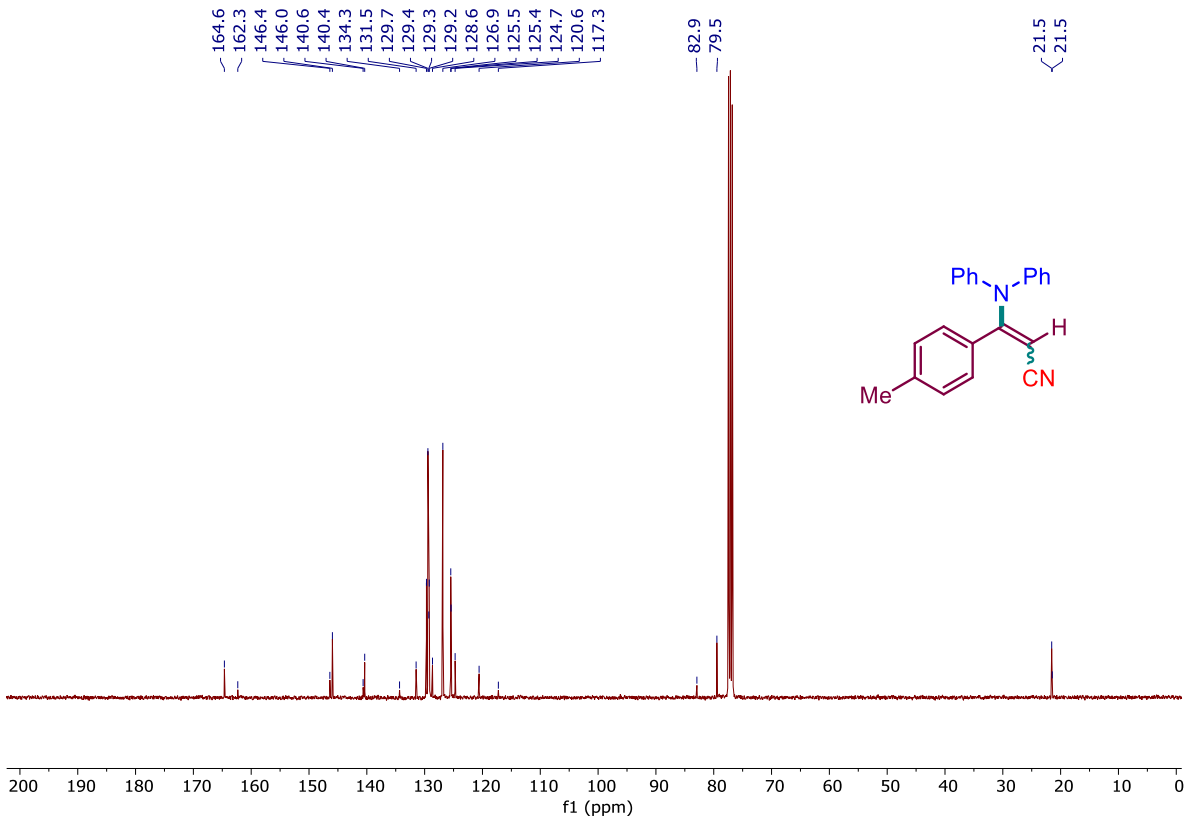
3-(diphenylamino)-3-(*p*-tolyl)acrylonitrile (363b)

^{1}H NMR, 400MHz, $CDCl_3$



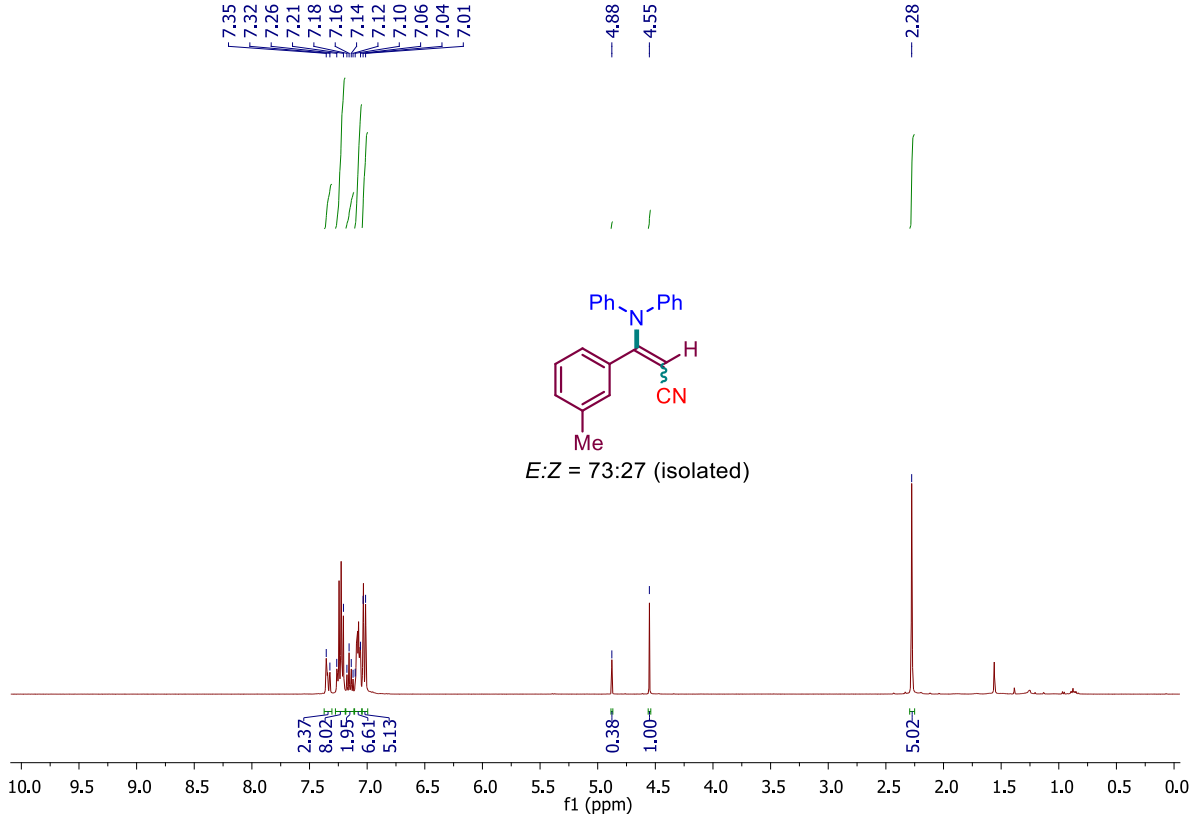
E:*Z* = 75:25 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



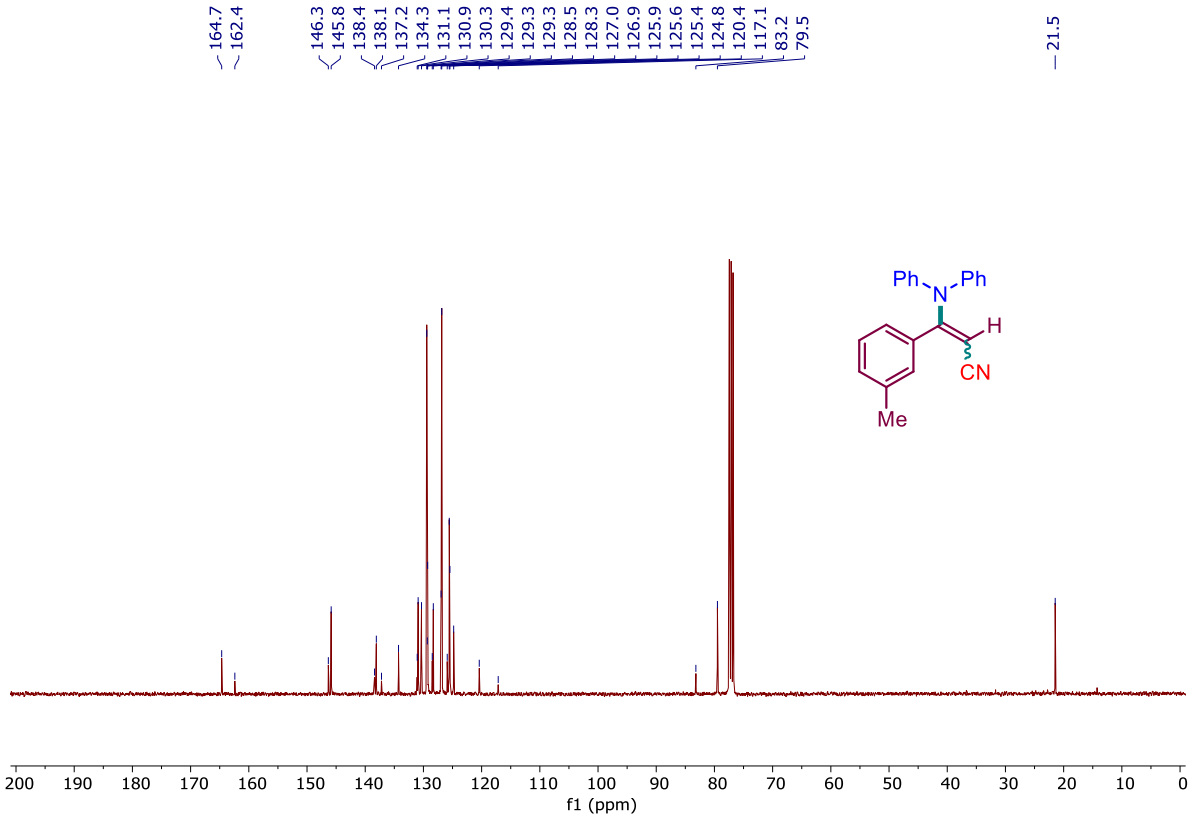
3-(diphenylamino)-3-(*m*-tolyl)acrylonitrile (363c)

^{1}H NMR, 400MHz, $CDCl_3$



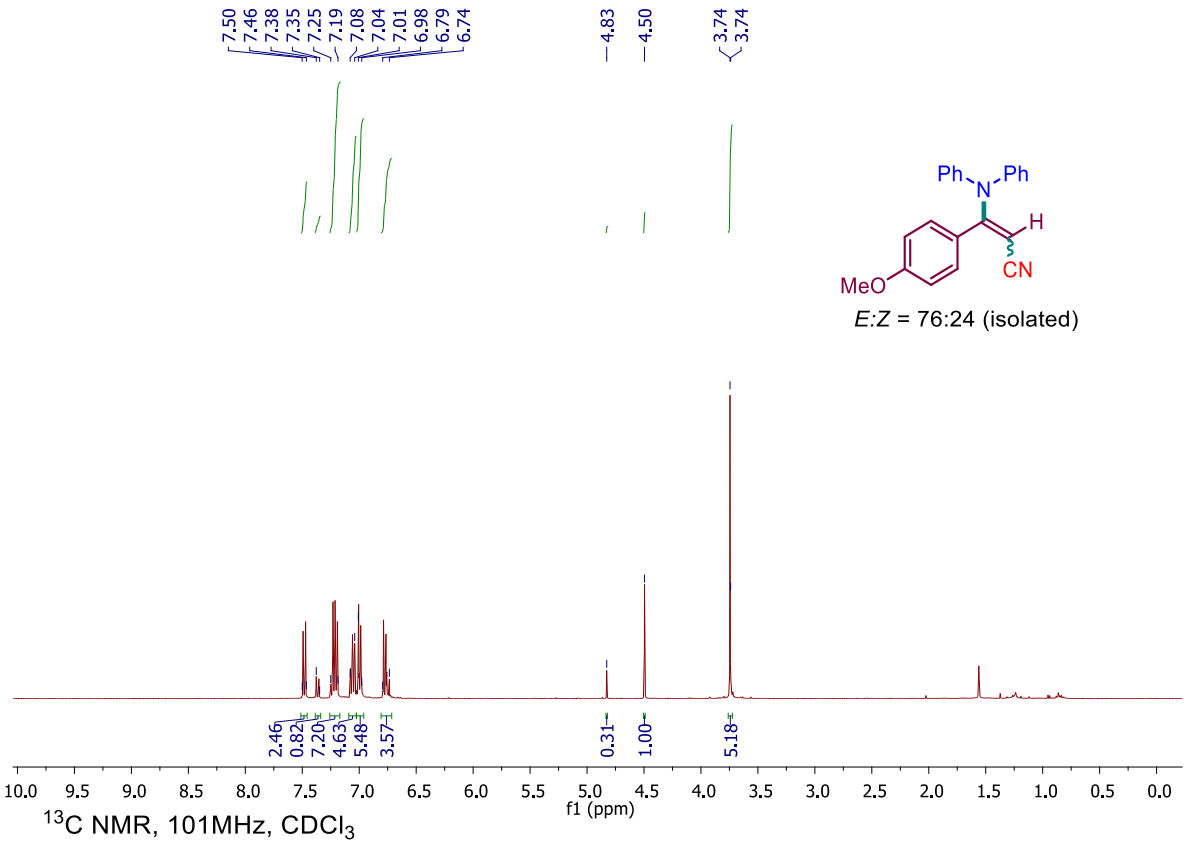
E:Z = 73:27 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



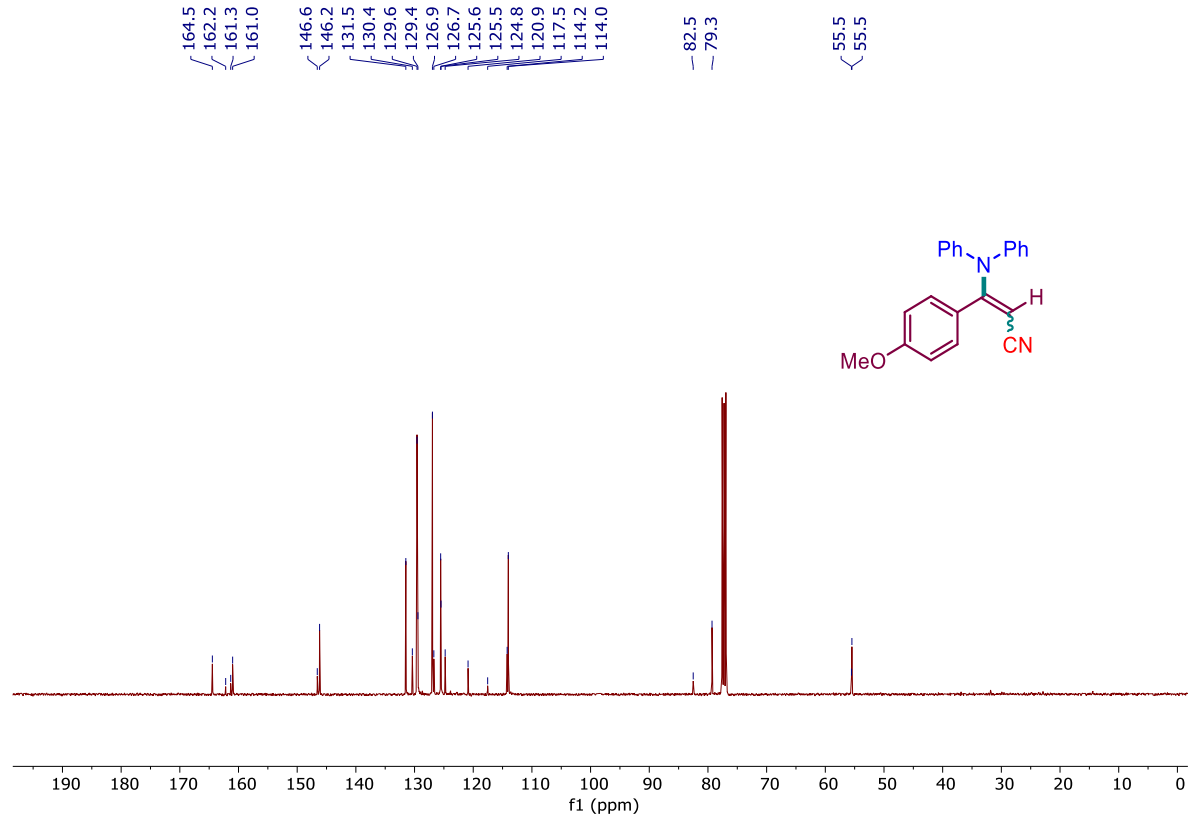
3-(diphenylamino)-3-(4-methoxyphenyl)acrylonitrile (363d)

^{1}H NMR, 400MHz, $CDCl_3$



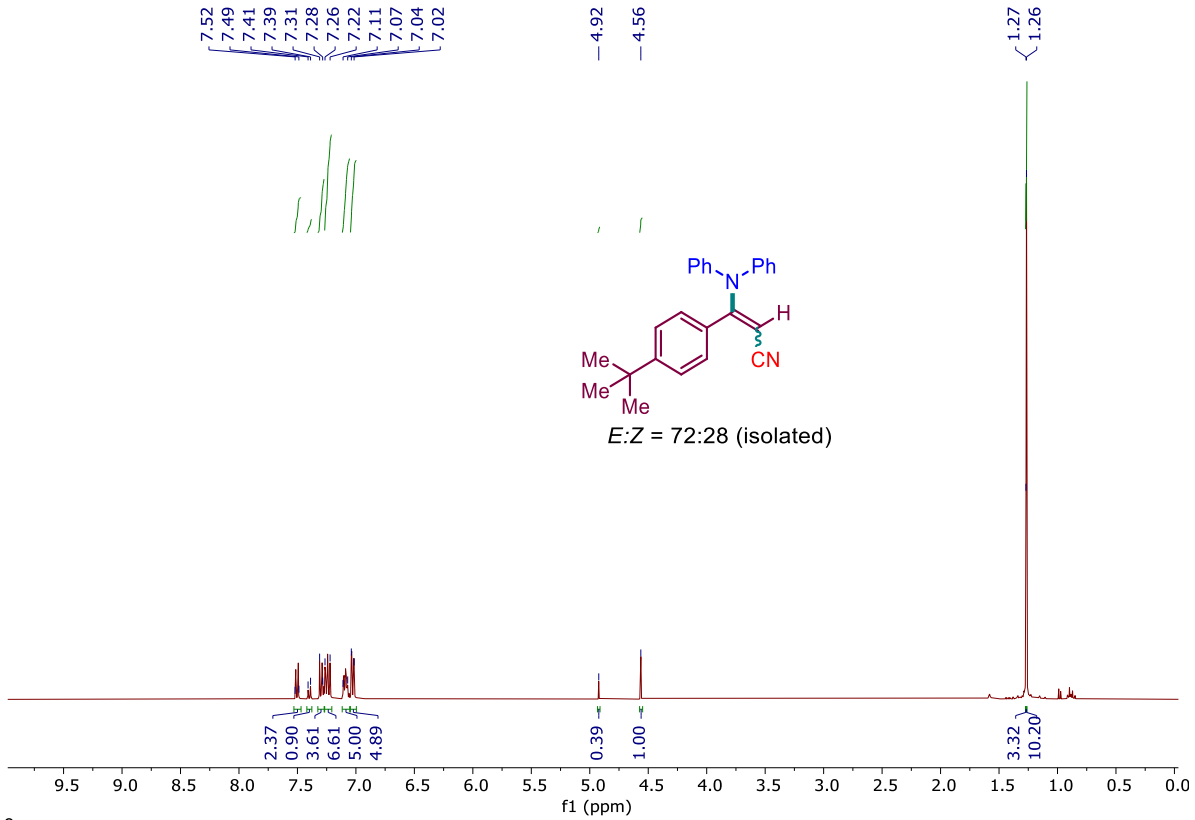
E:Z = 76:24 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



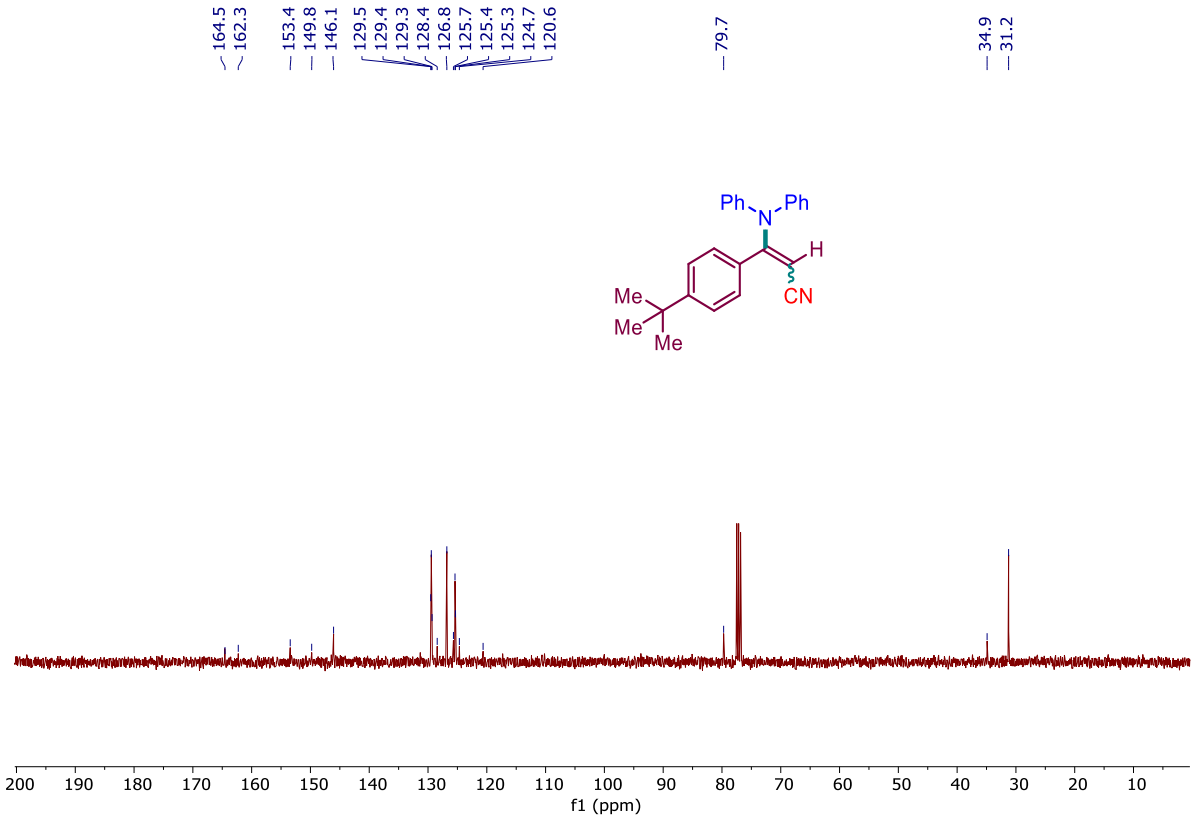
3-(4-(*tert*-butyl)phenyl)-3-(diphenylamino)acrylonitrile (363e)

^{1}H NMR, 400MHz, $CDCl_3$



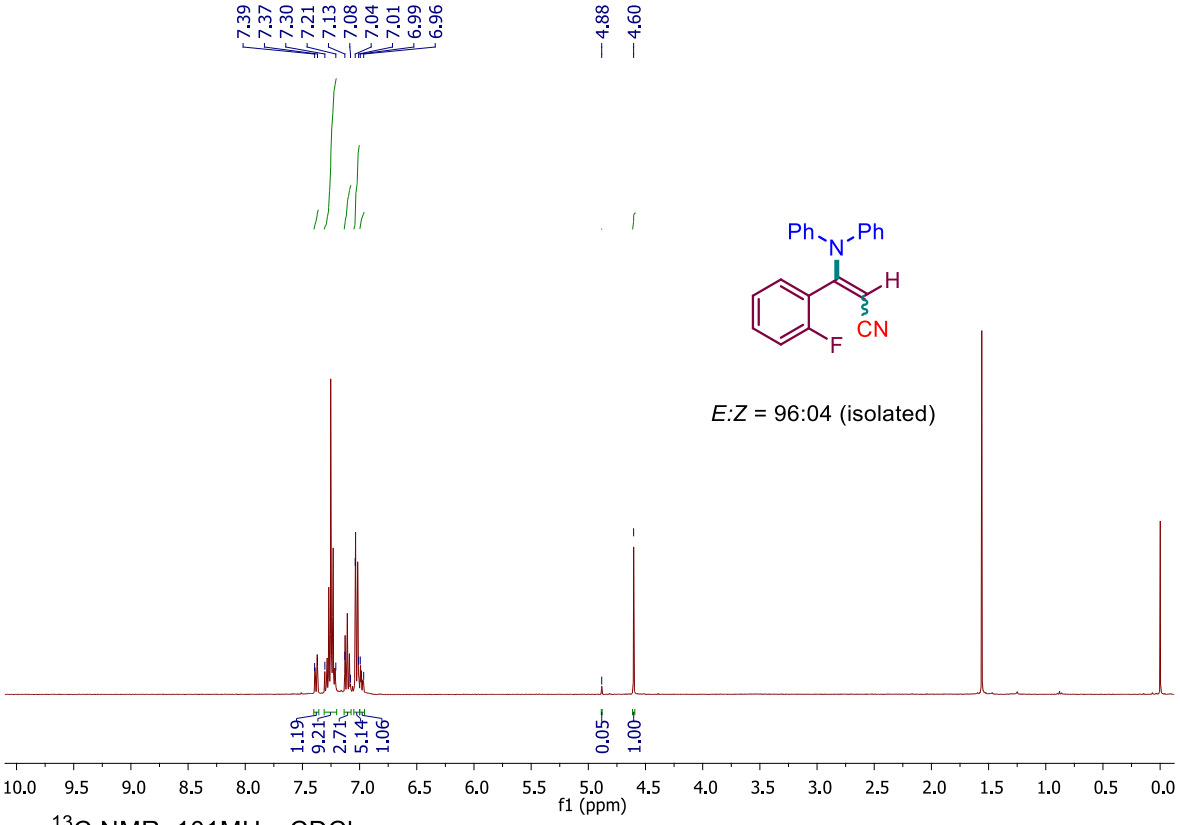
E:Z = 72:28 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



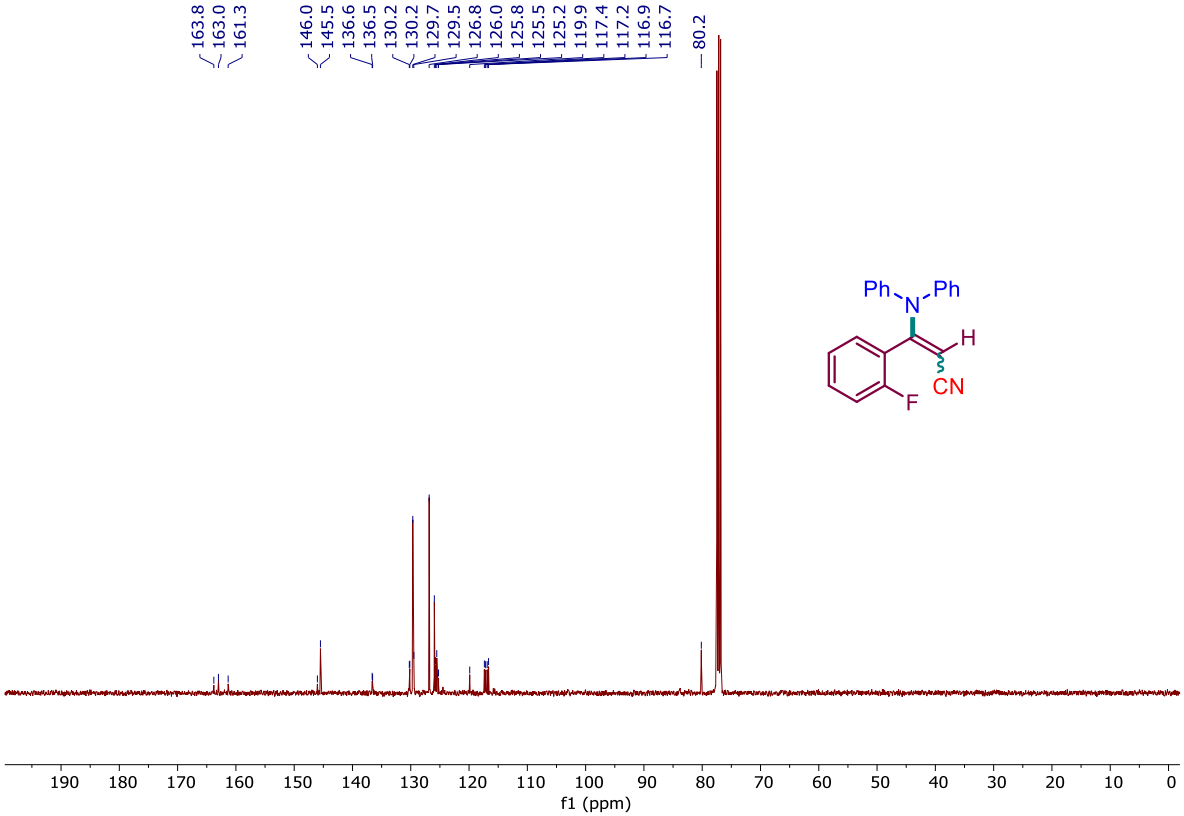
3-(diphenylamino)-3-(2-fluorophenyl)acrylonitrile (363f)

^{1}H NMR, 400MHz, $CDCl_3$

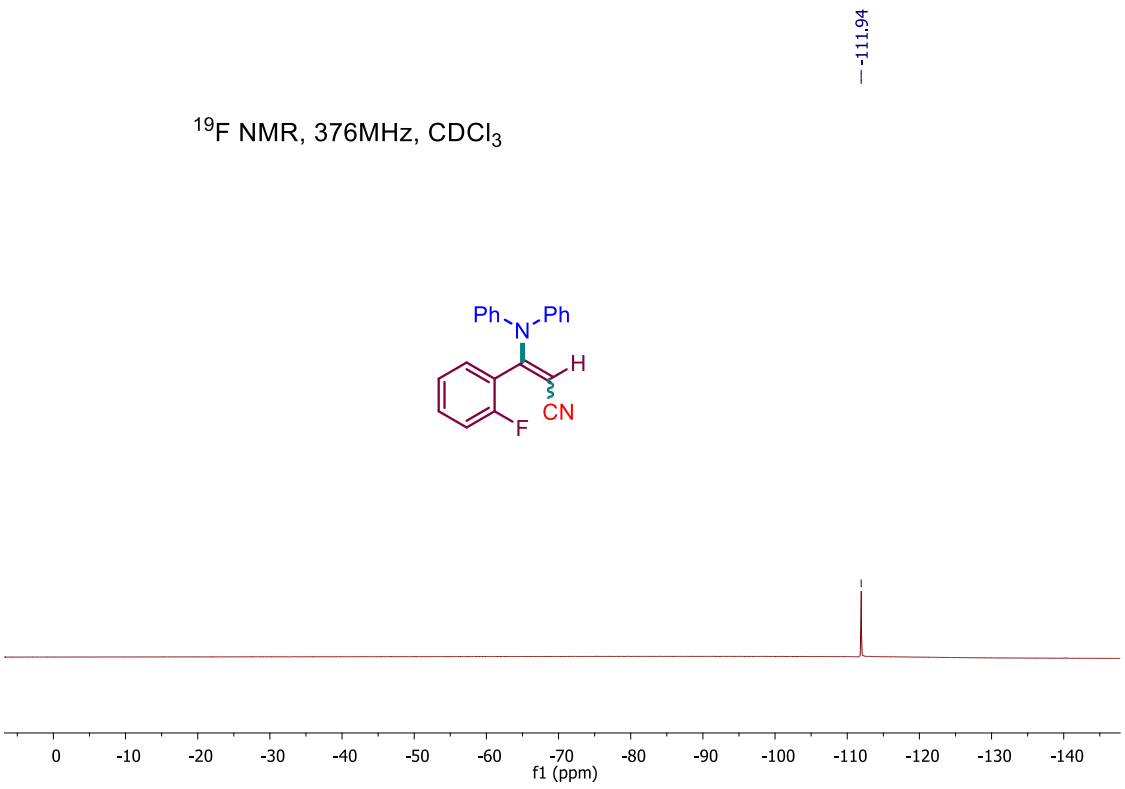


E:Z = 96:04 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

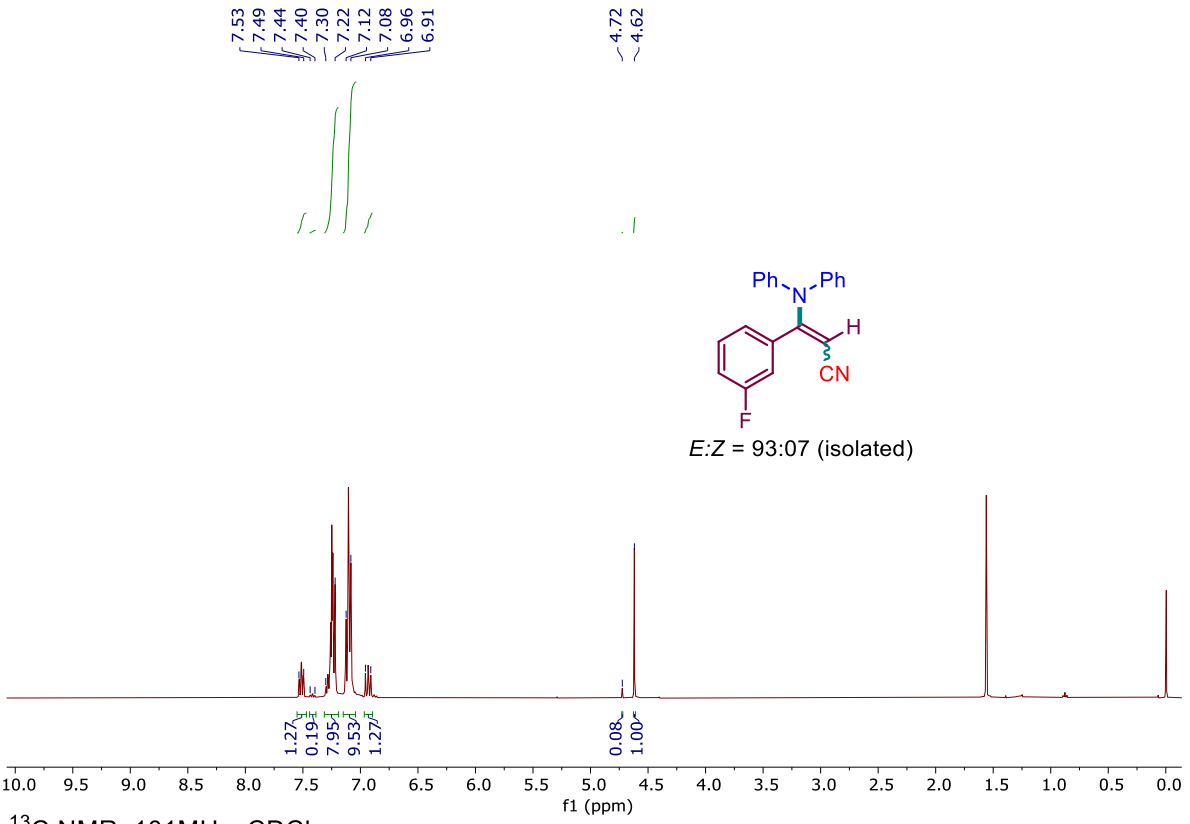


^{19}F NMR, 376MHz, $CDCl_3$



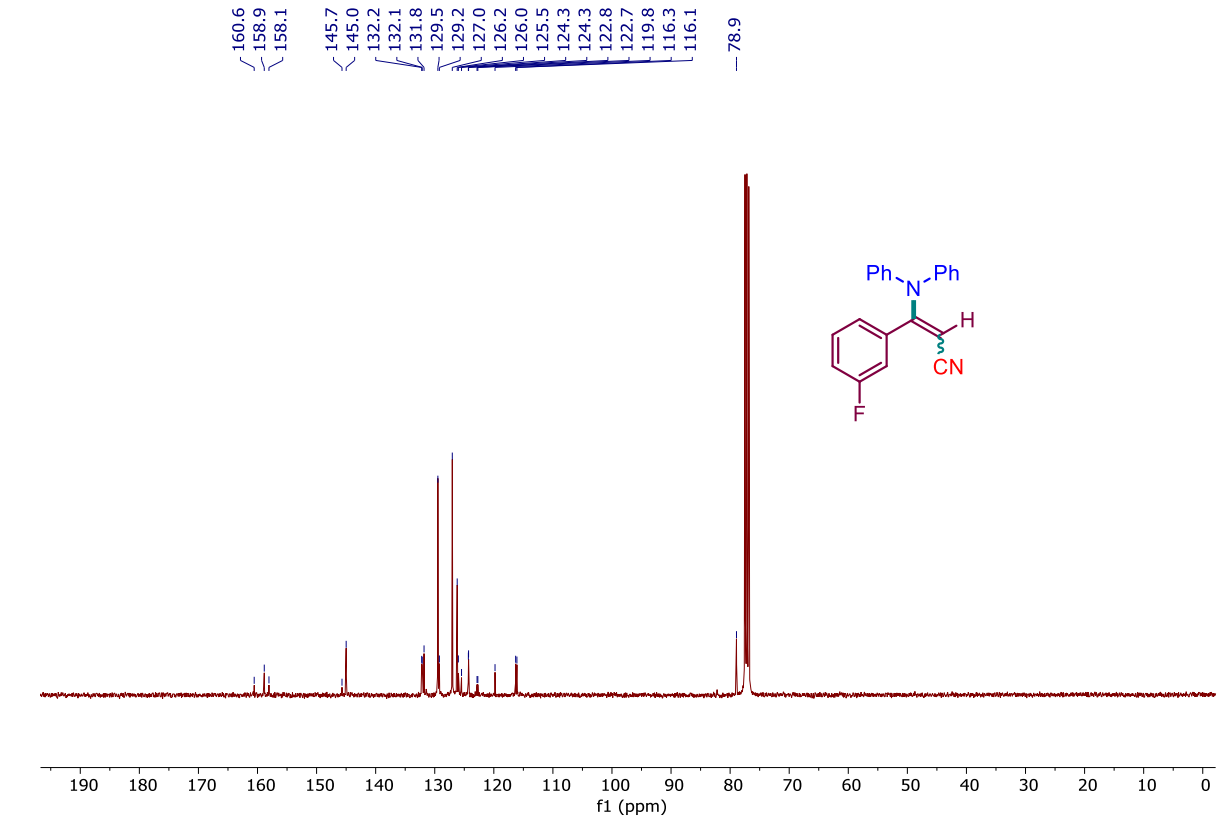
3-(diphenylamino)-3-(3-fluorophenyl)acrylonitrile (363g)

^{1}H NMR, 400MHz, $CDCl_3$

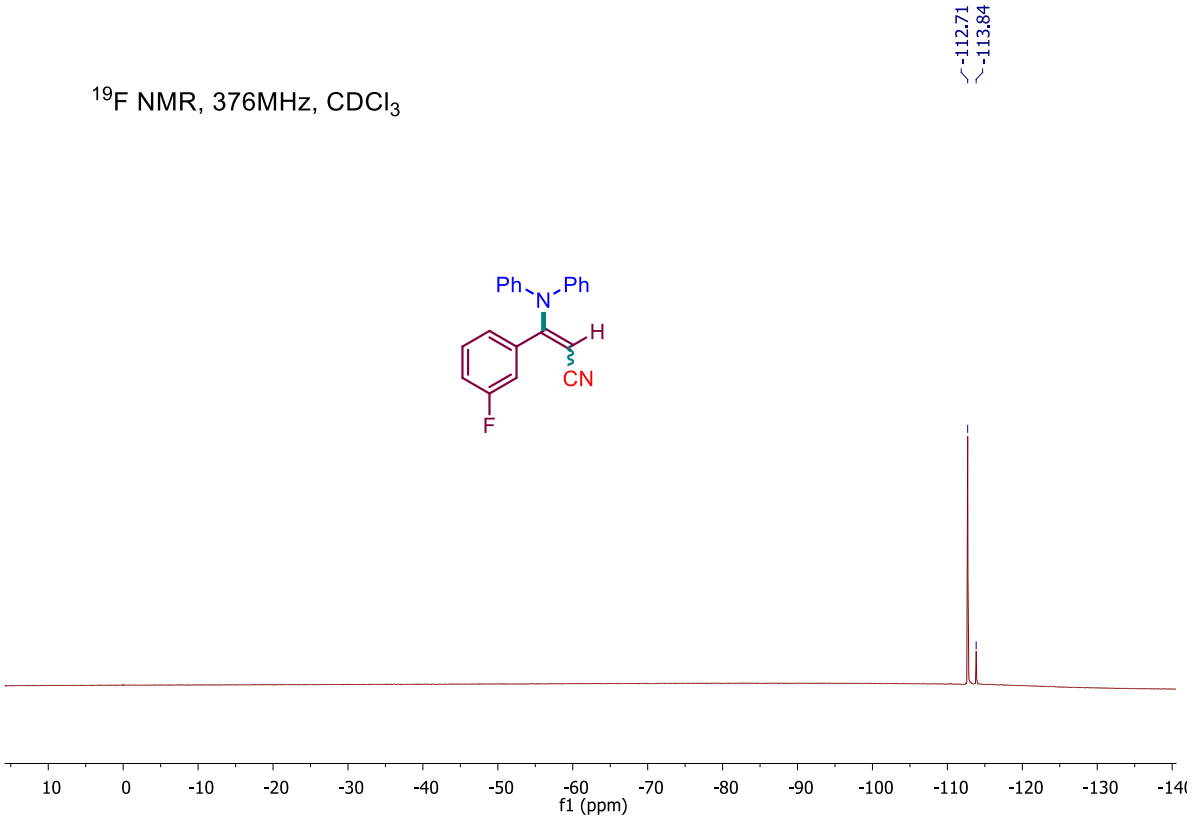


E:Z = 93:07 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

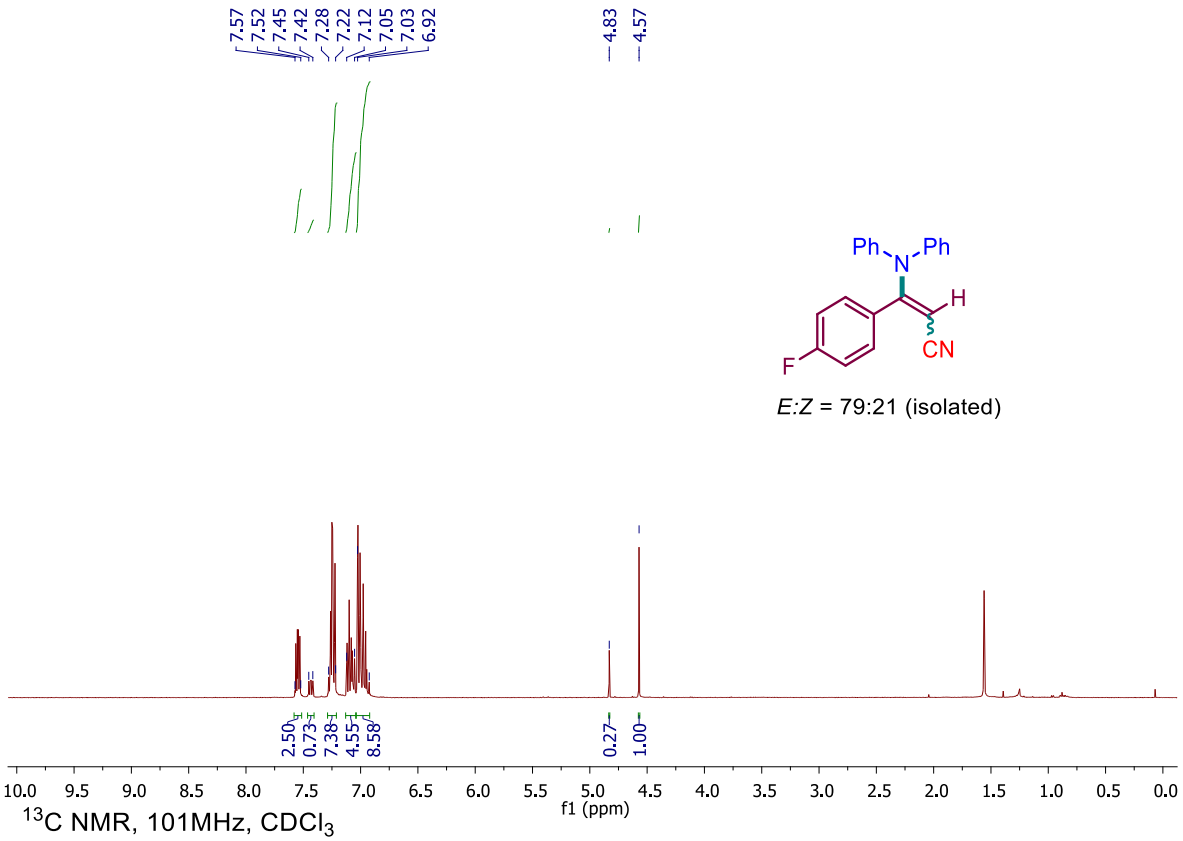


^{19}F NMR, 376MHz, $CDCl_3$



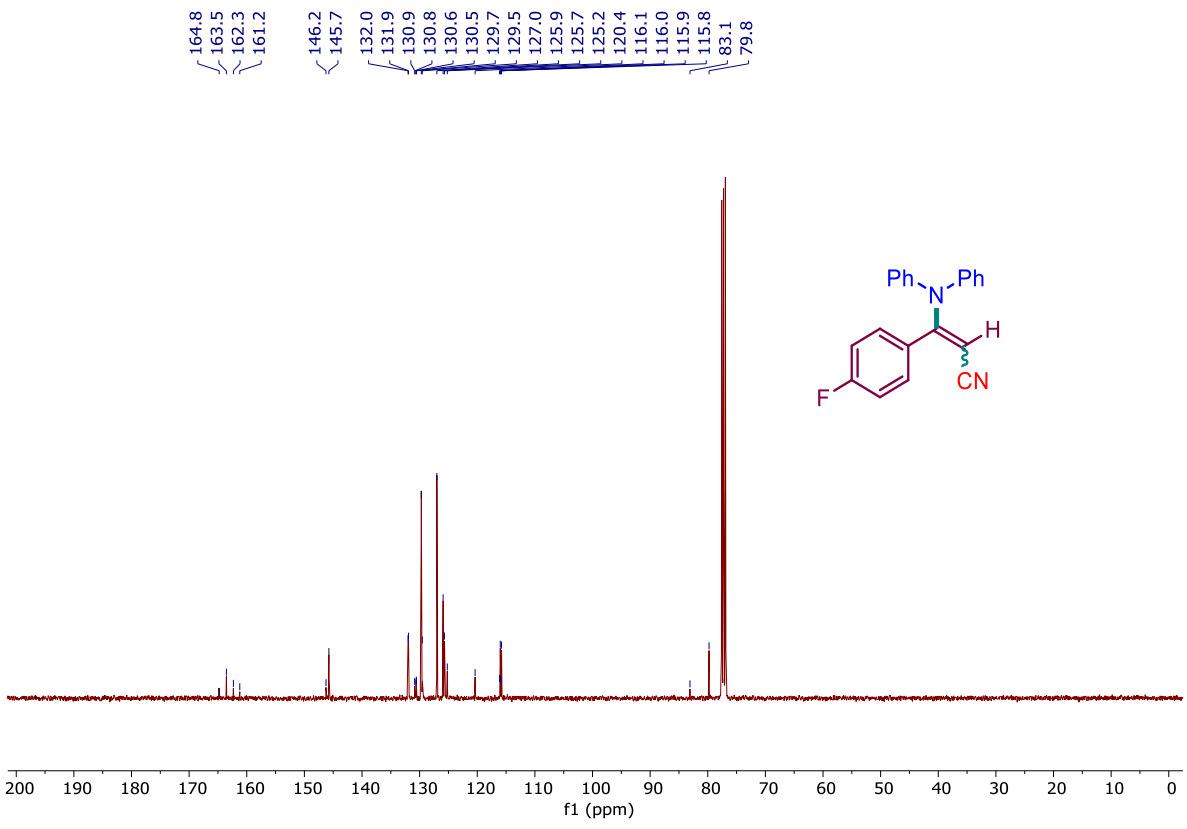
3-(diphenylamino)-3-(4-fluorophenyl)acrylonitrile (363h)

^{1}H NMR, 400MHz, $CDCl_3$

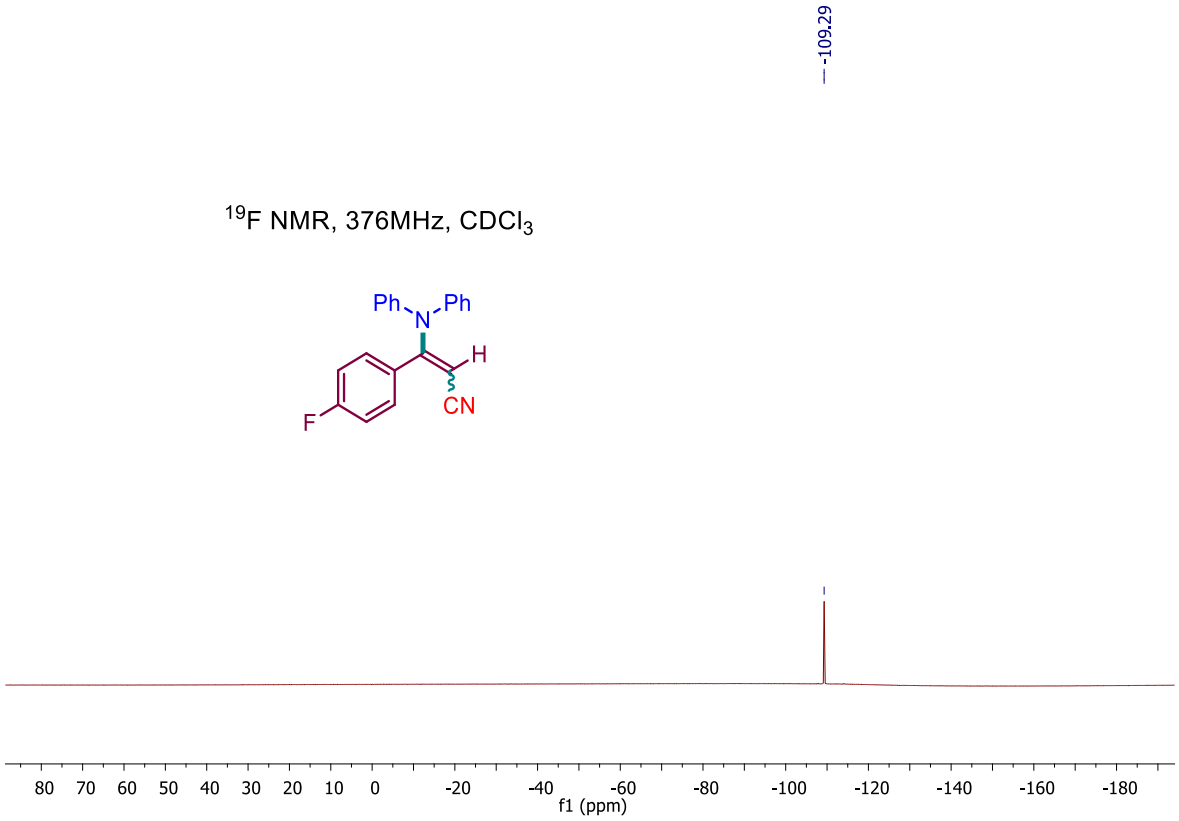


E:Z = 79:21 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

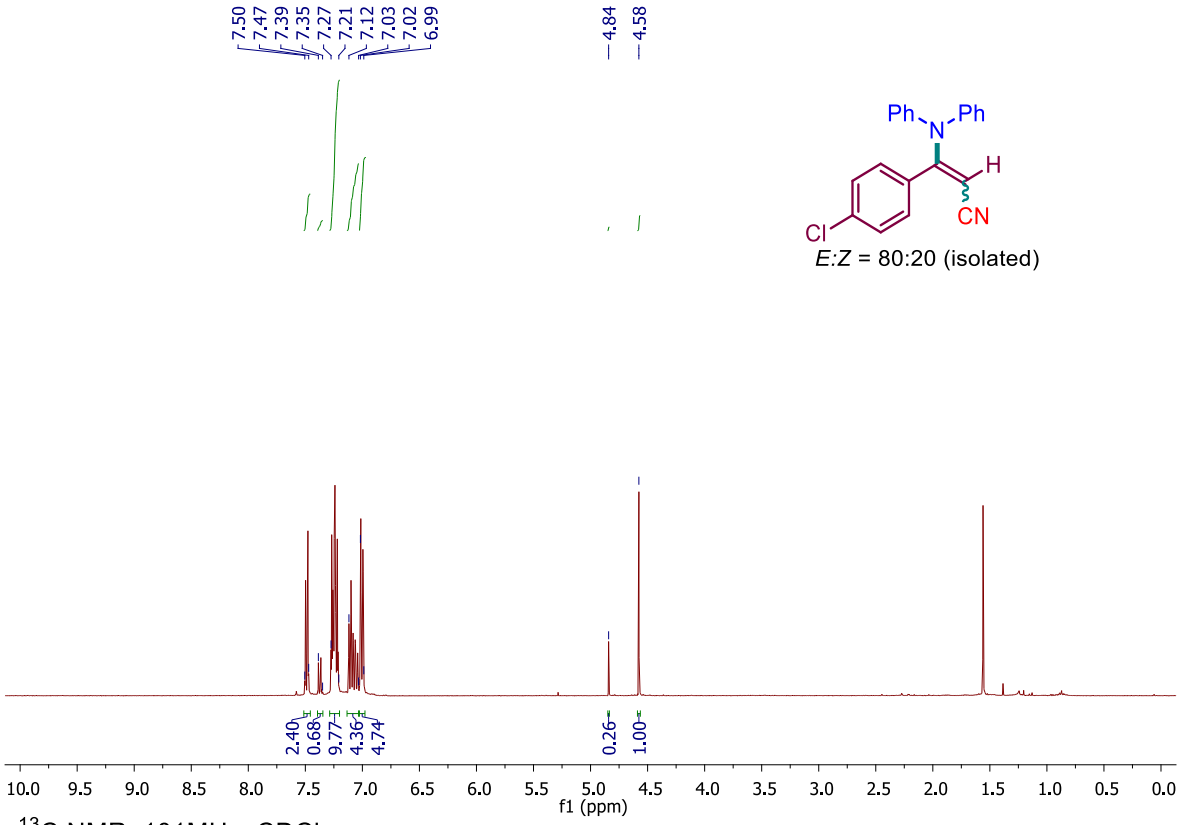


^{19}F NMR, 376MHz, $CDCl_3$



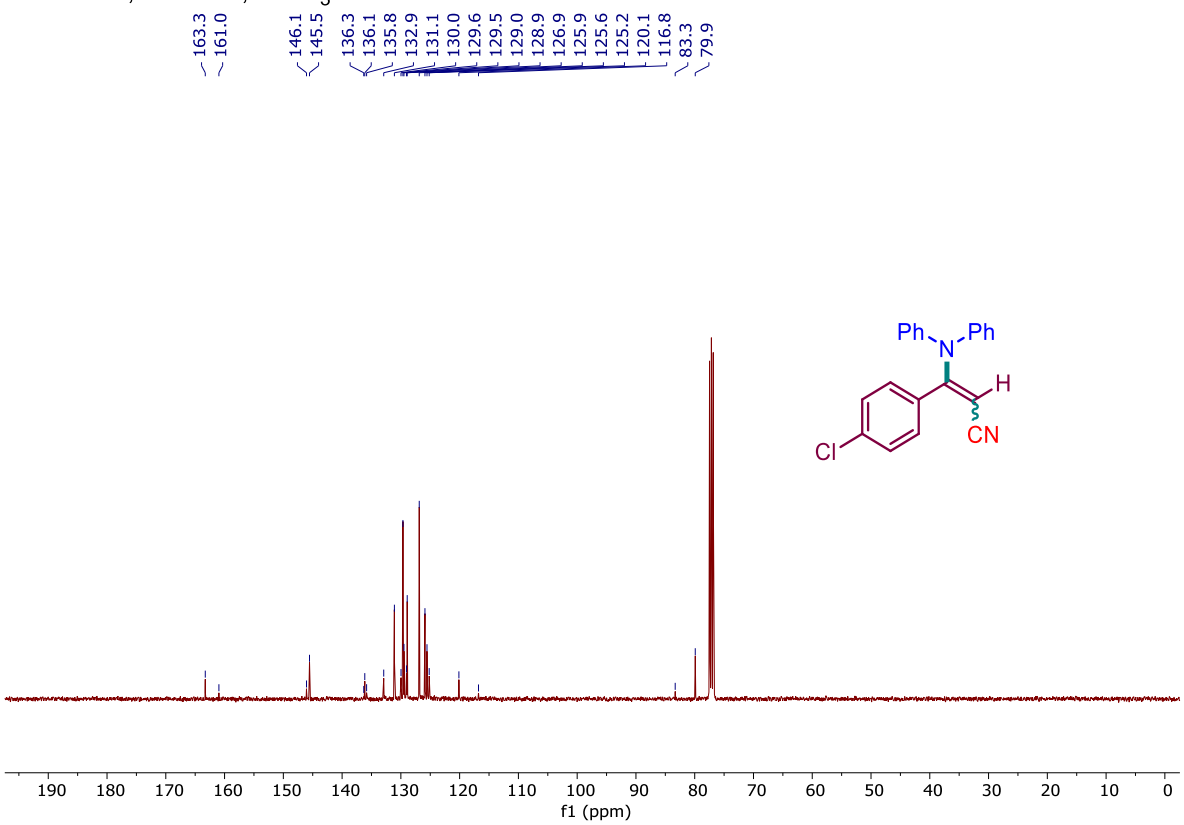
3-(4-chlorophenyl)-3-(diphenylamino)acrylonitrile (12)

^{1}H NMR, 400MHz, $CDCl_3$



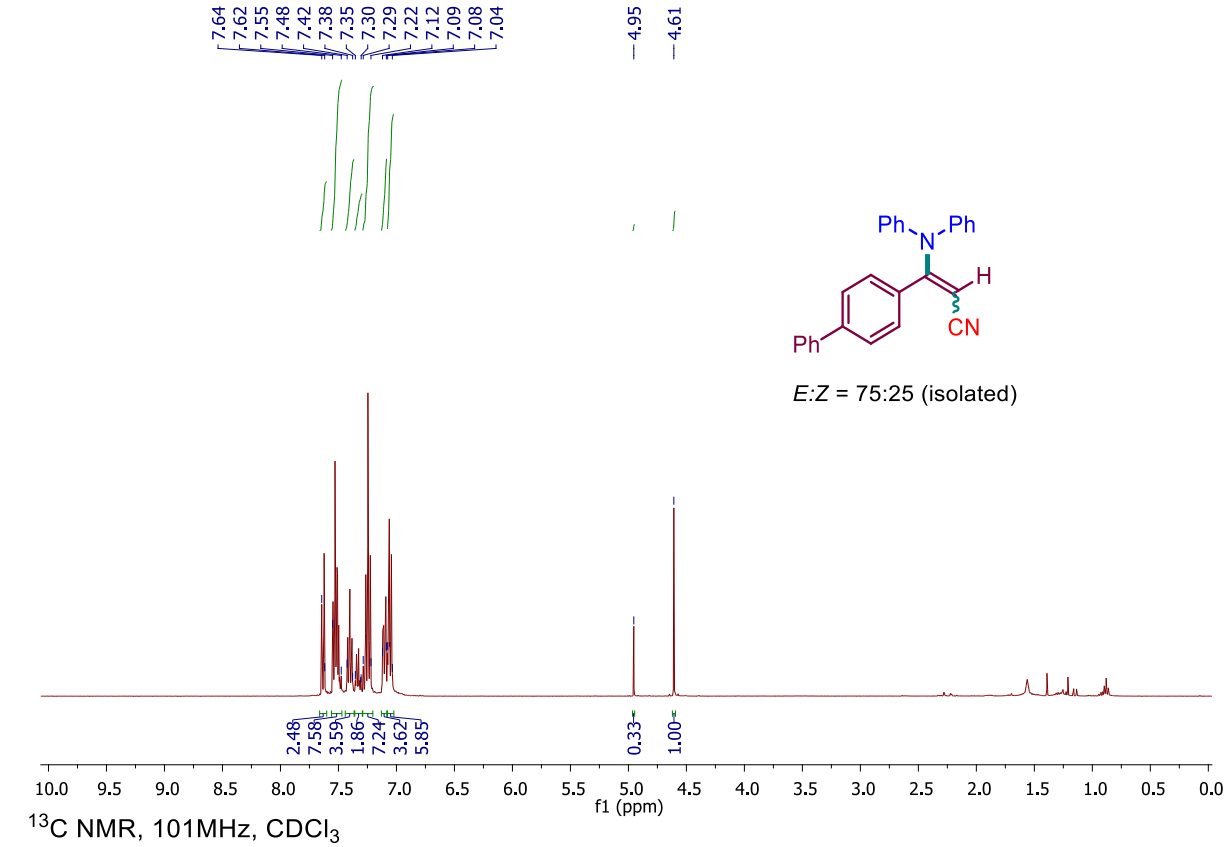
E:*Z* = 80:20 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



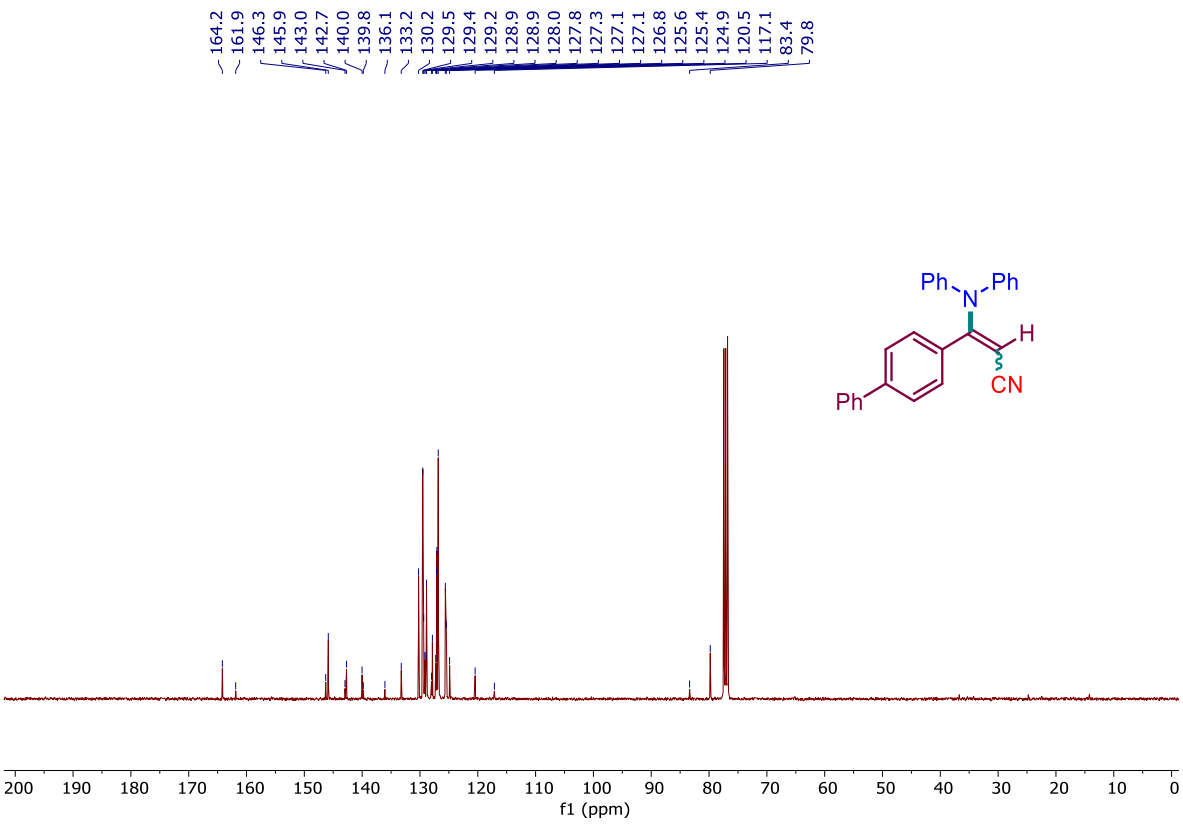
3-([1,1'-biphenyl]-4-yl)-3-(diphenylamino)acrylonitrile (363j)

^{1}H NMR, 400MHz, $CDCl_3$



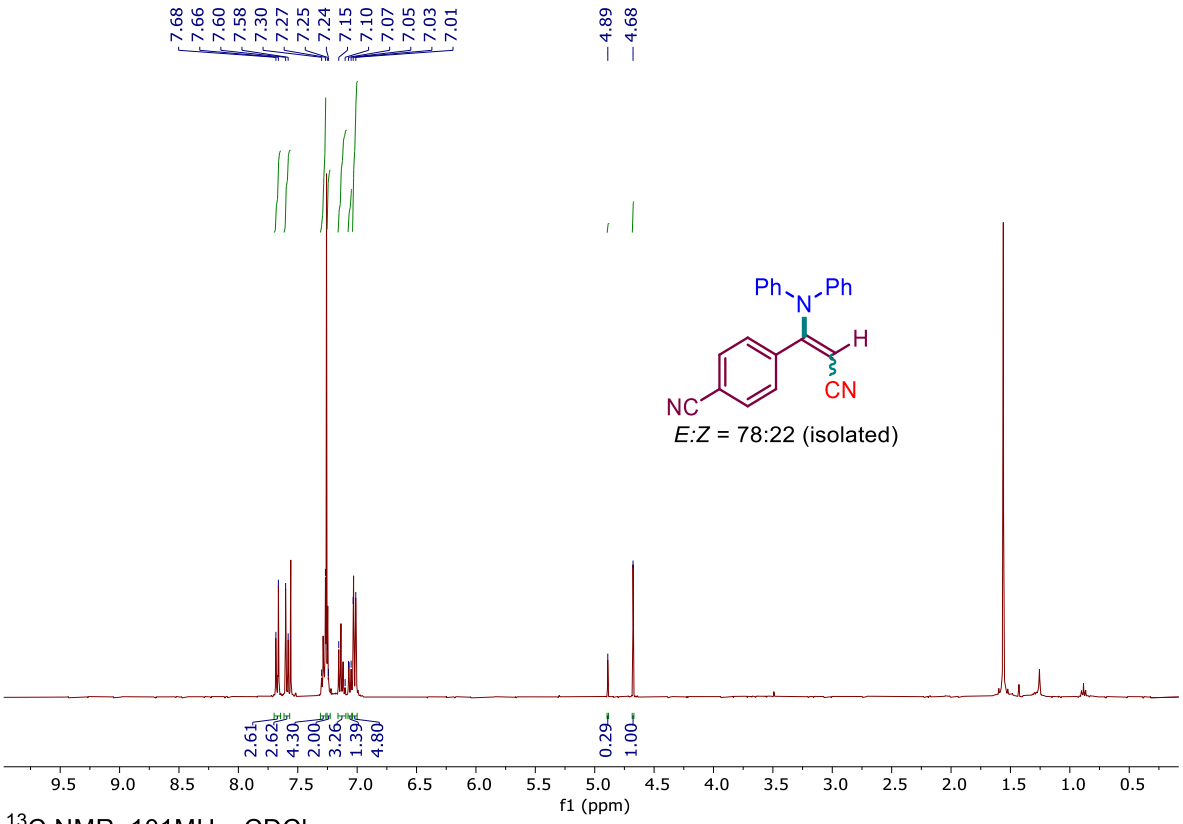
E:*Z* = 75:25 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

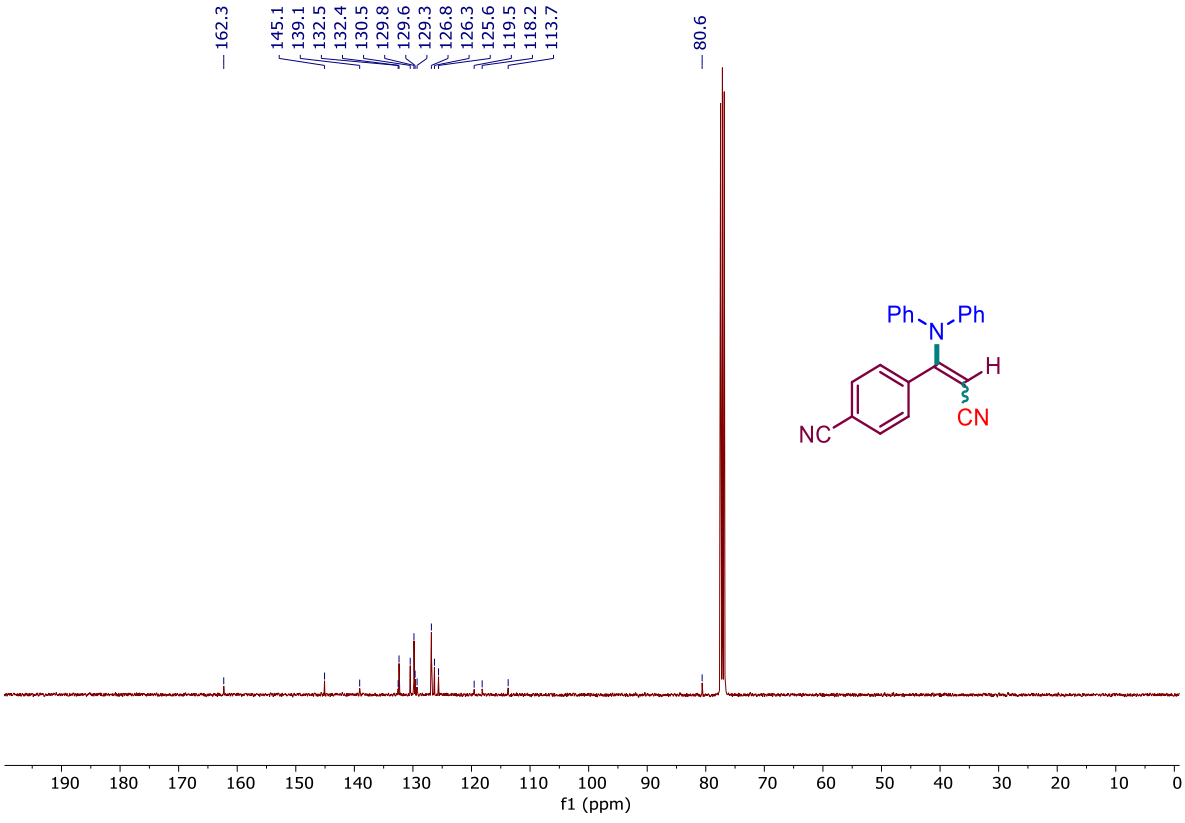


4-(2-cyano-1-(diphenylamino)vinyl)benzonitrile (363k)

^{1}H NMR, 400MHz, $CDCl_3$

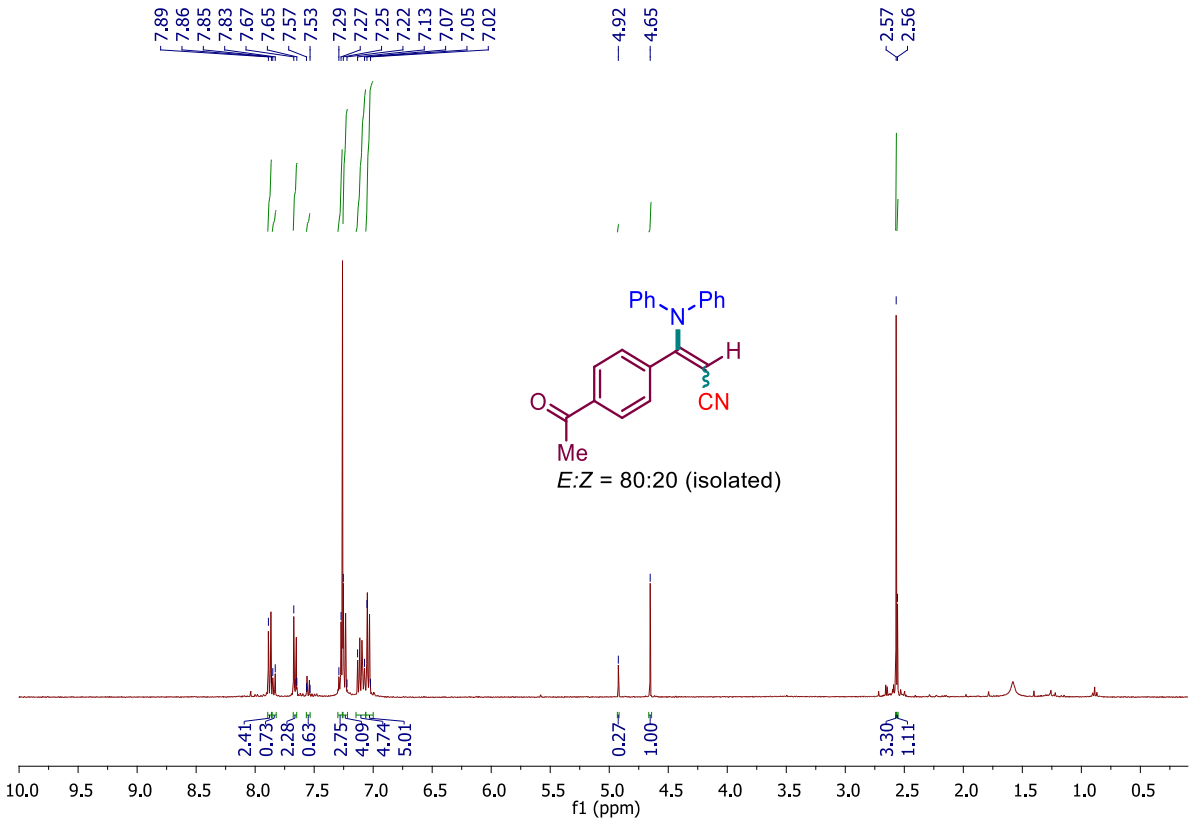


^{13}C NMR, 101MHz, $CDCl_3$

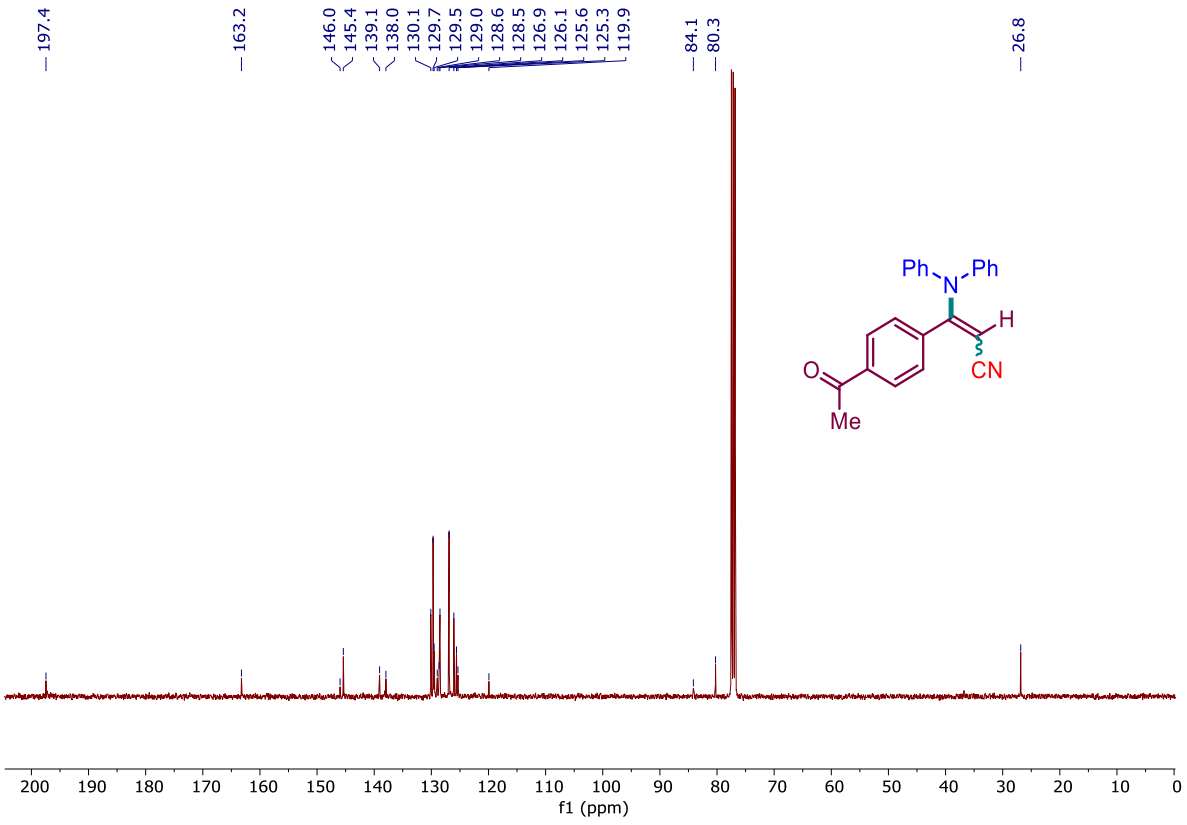


3-(4-acetylphenyl)-3-(diphenylamino)acrylonitrile (363l)

^{1}H NMR, 400MHz, $CDCl_3$

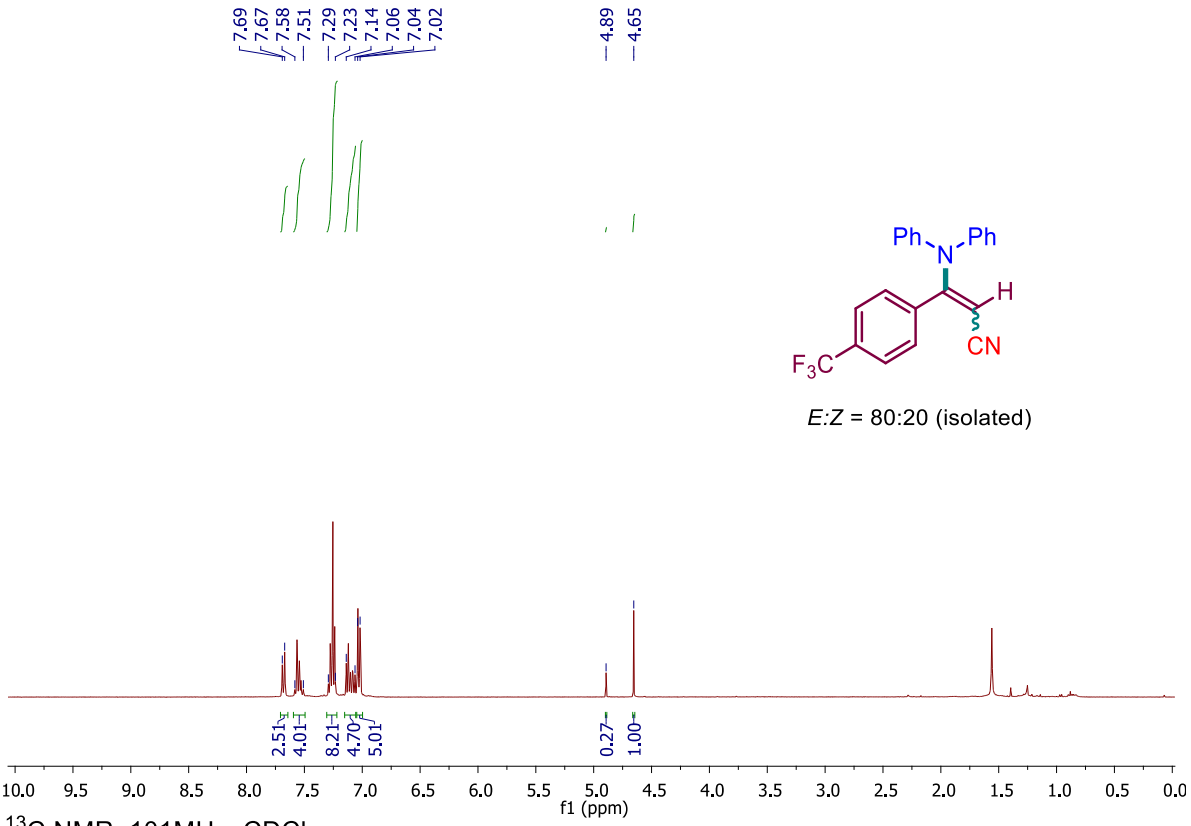


^{13}C NMR, 101MHz, $CDCl_3$



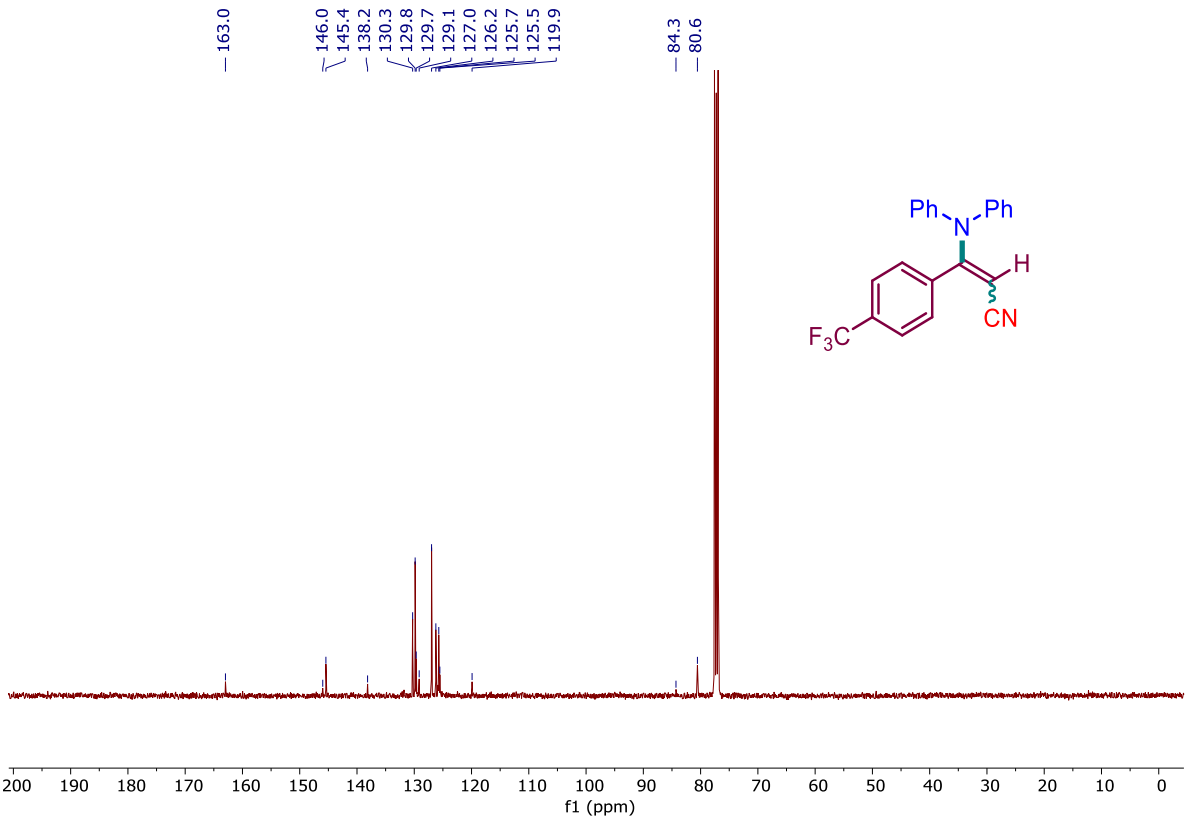
3-(diphenylamino)-3-(4-(trifluoromethyl)phenyl)acrylonitrile (363m)

^{1}H NMR, 400MHz, $CDCl_3$

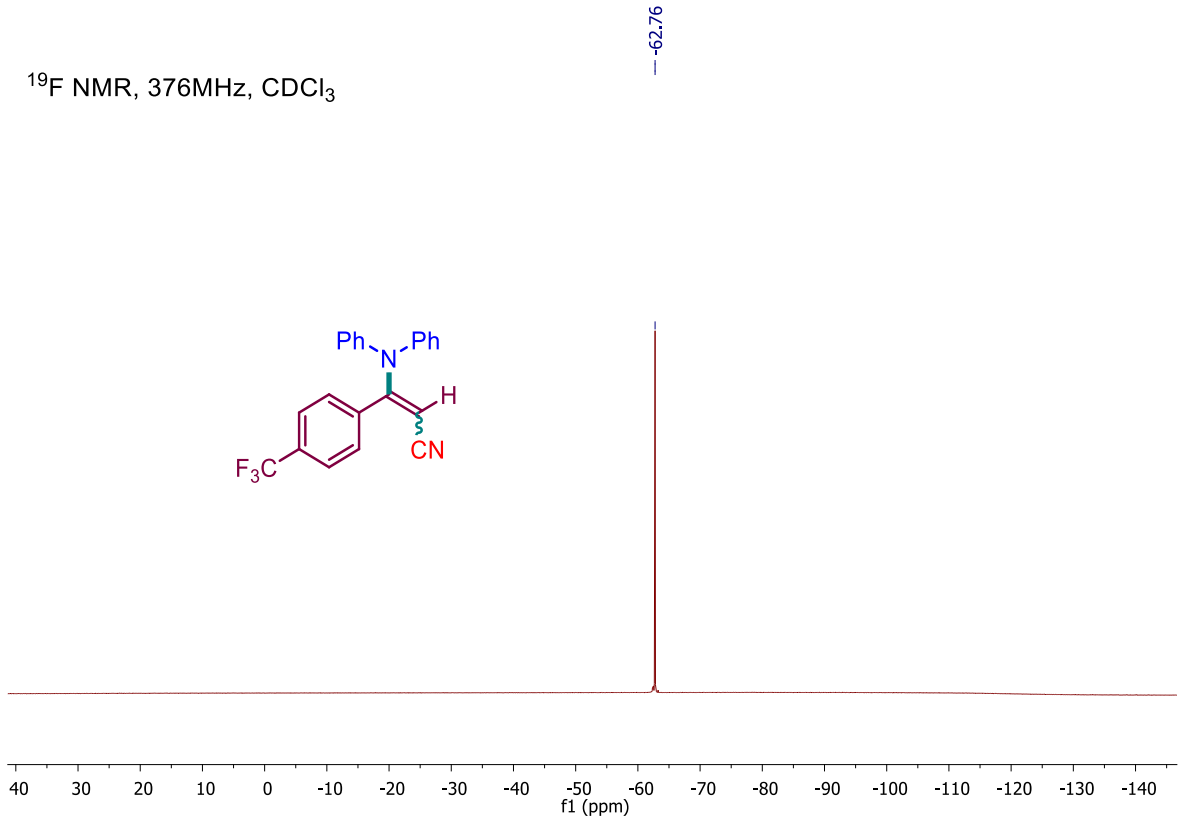


E:*Z* = 80:20 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

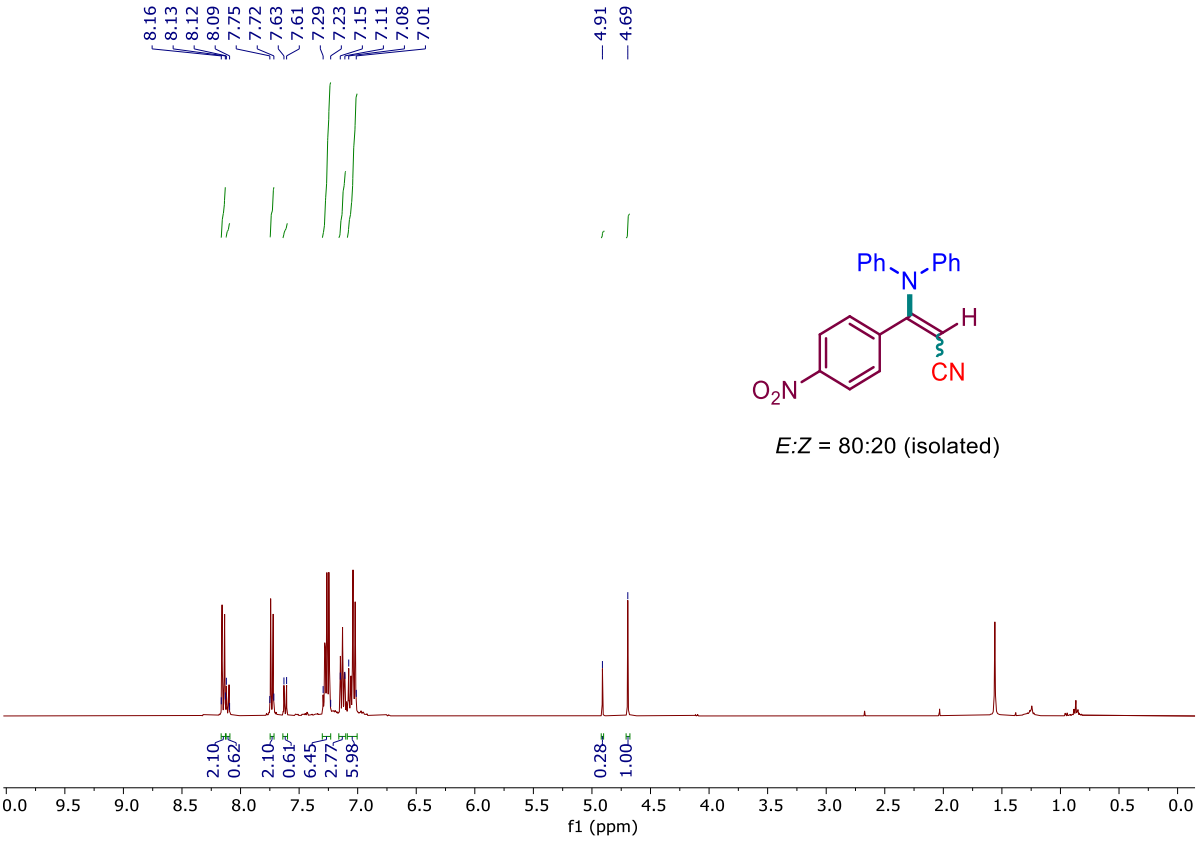


^{19}F NMR, 376MHz, $CDCl_3$



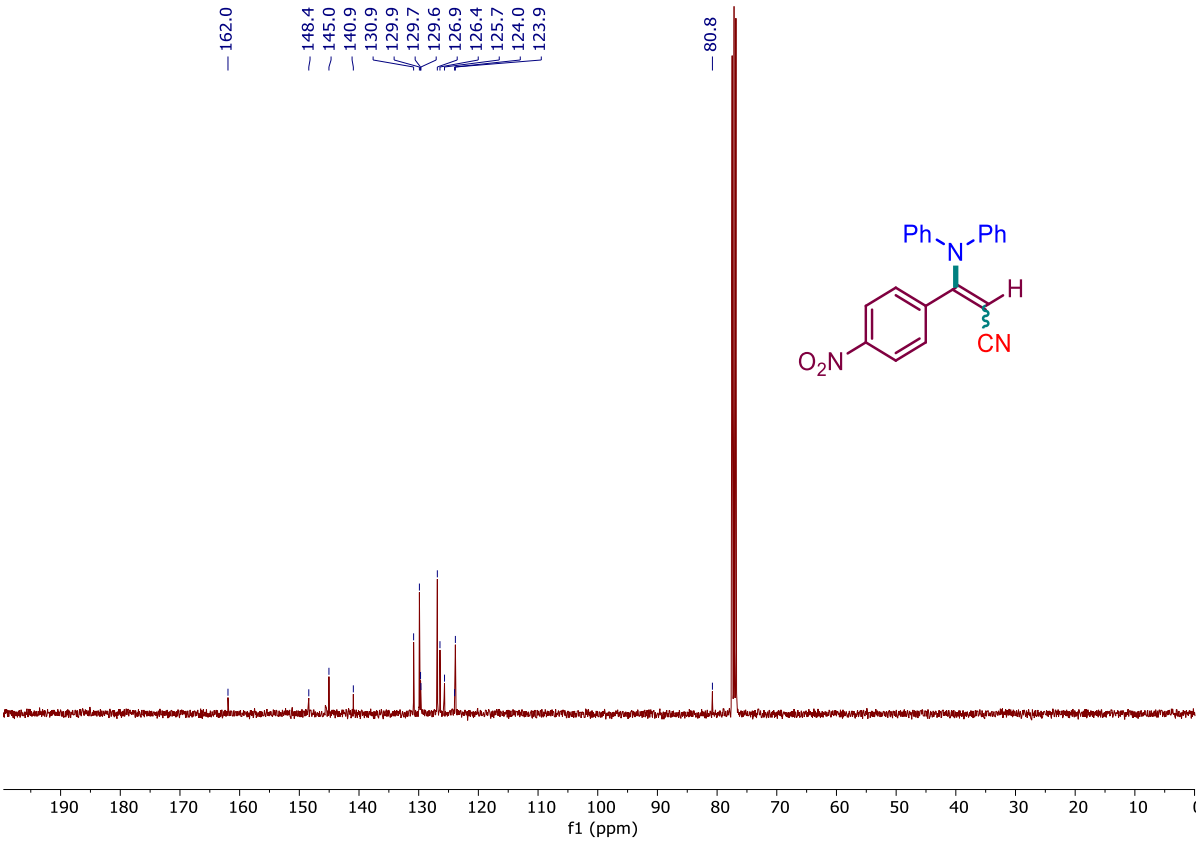
3-(diphenylamino)-3-(4-nitrophenyl)acrylonitrile (363n)

^{1}H NMR, 400MHz, $CDCl_3$



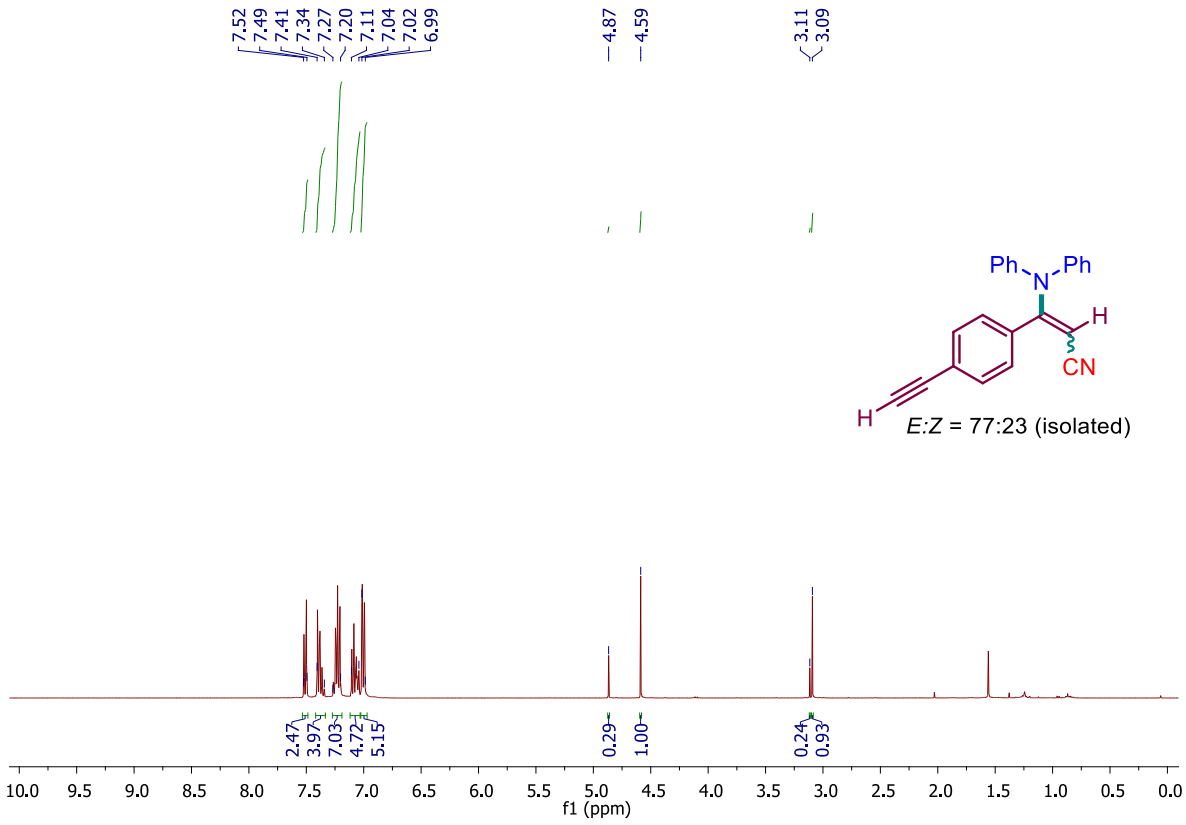
E:Z = 80:20 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

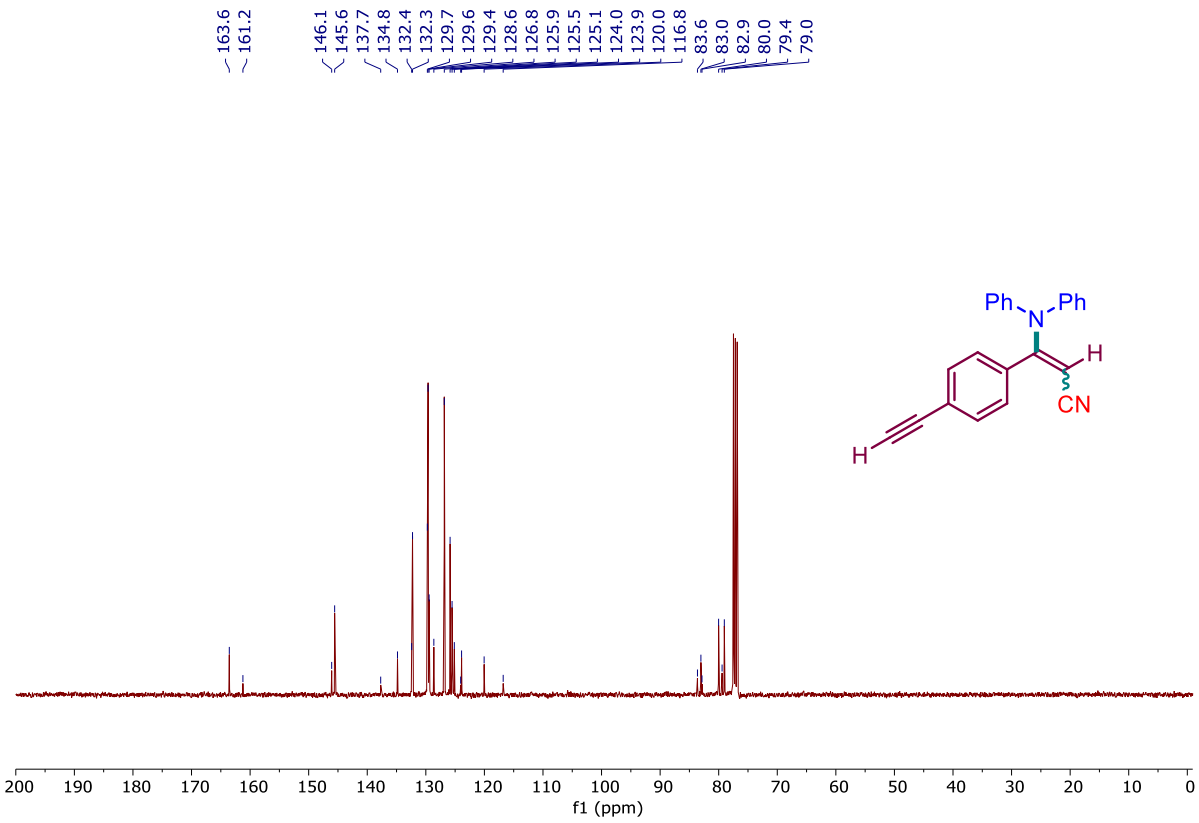


3-(diphenylamino)-3-(4-ethynylphenyl)acrylonitrile (363o)

^{1}H NMR, 400MHz, $CDCl_3$

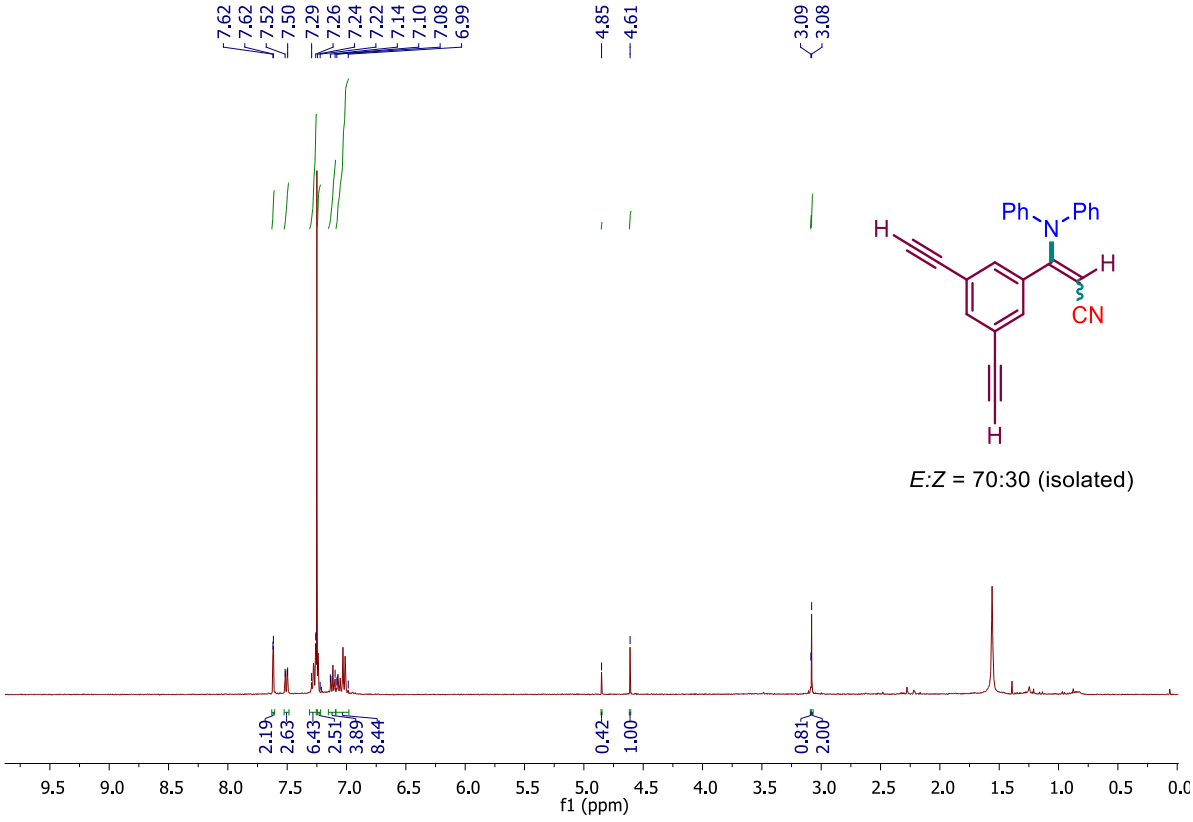


^{13}C NMR, 101MHz, $CDCl_3$



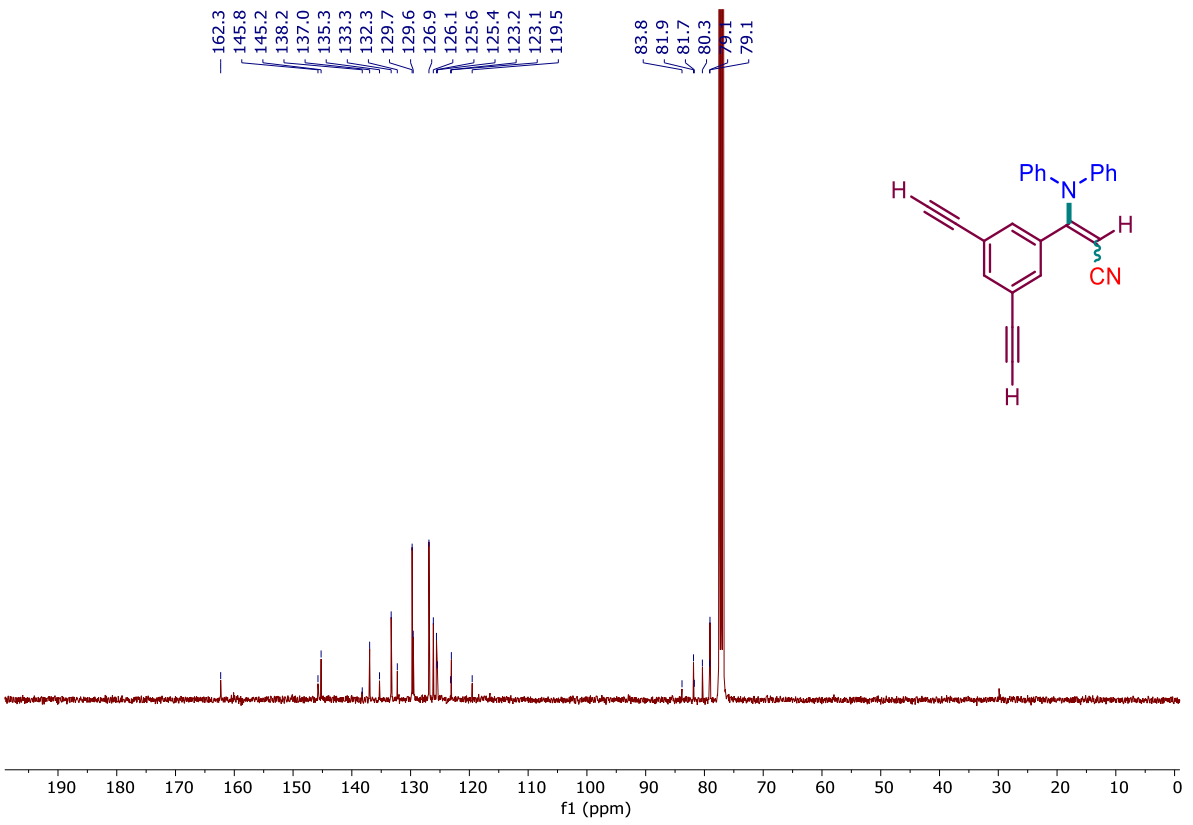
3-(3,5-diethynylphenyl)-3-(diphenylamino)acrylonitrile (363p)

^{1}H NMR, 400MHz, $CDCl_3$



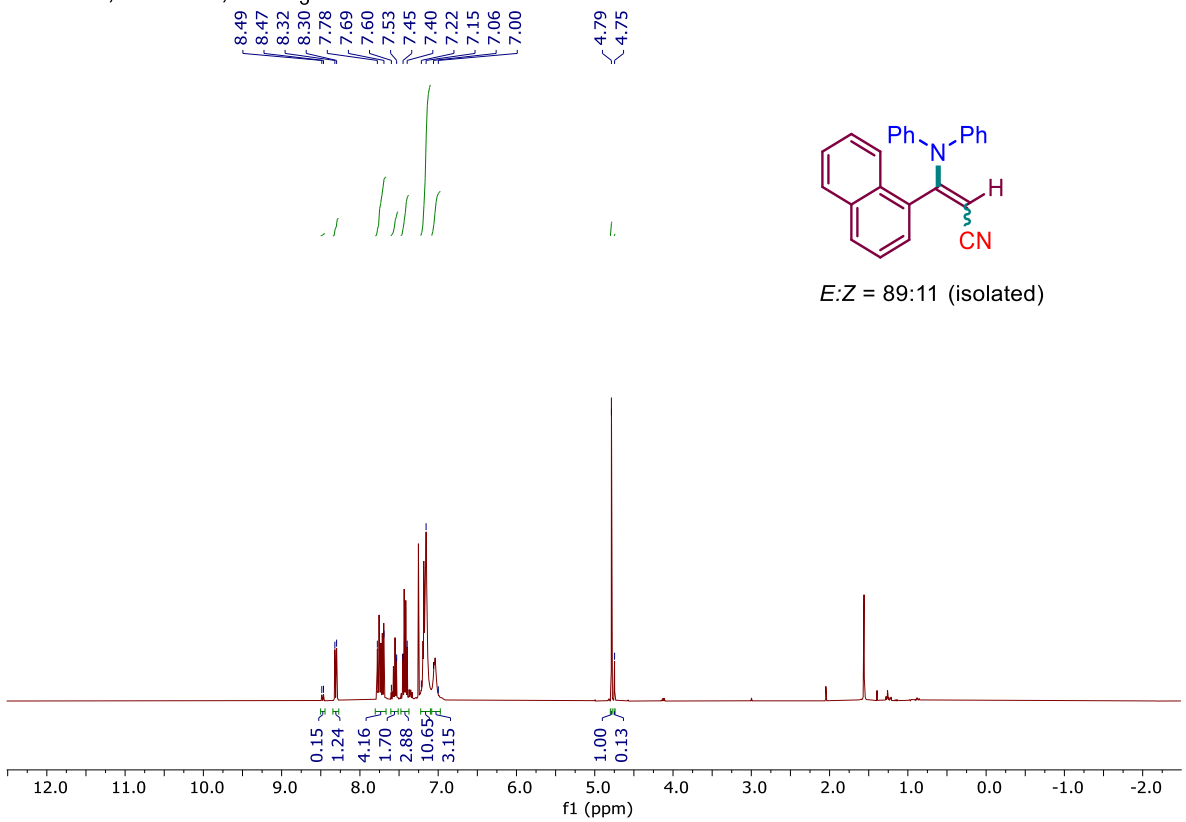
E:Z = 70:30 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



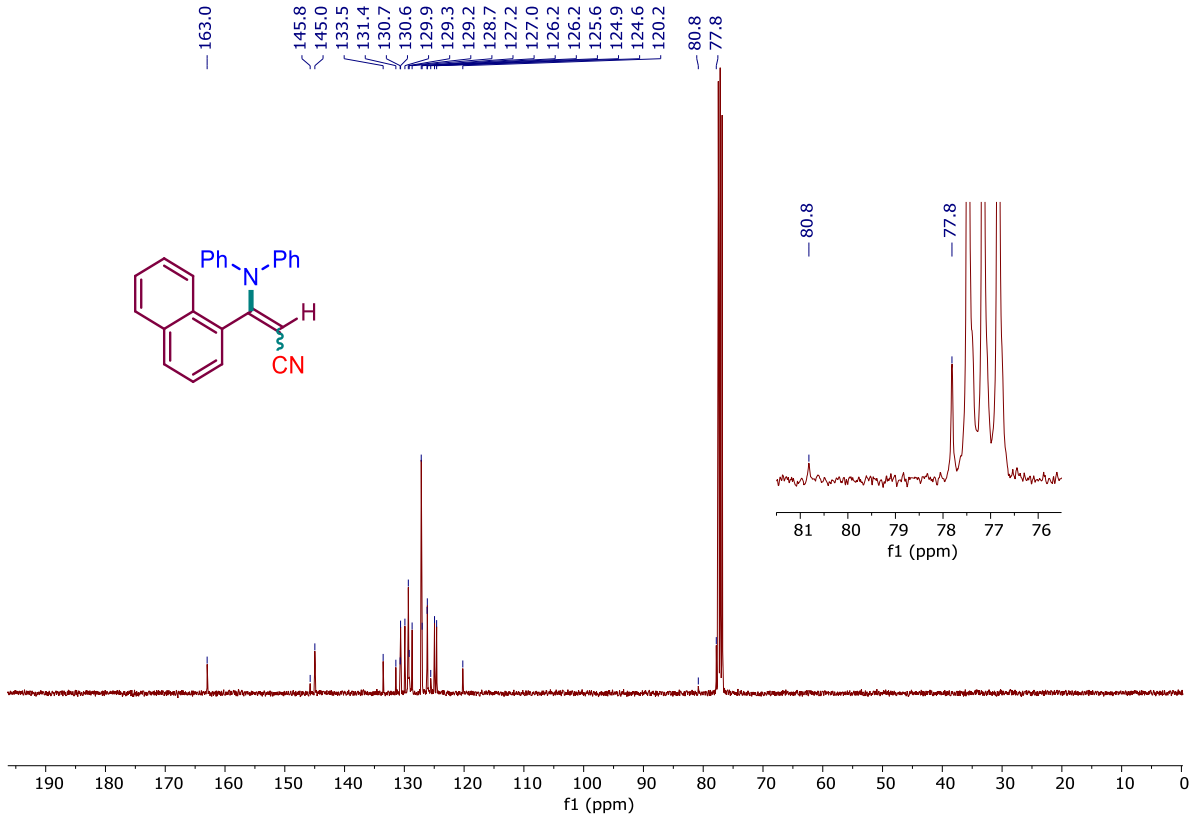
3-(diphenylamino)-3-(naphthalen-1-yl)acrylonitrile (363q)

^{1}H NMR, 400MHz, $CDCl_3$



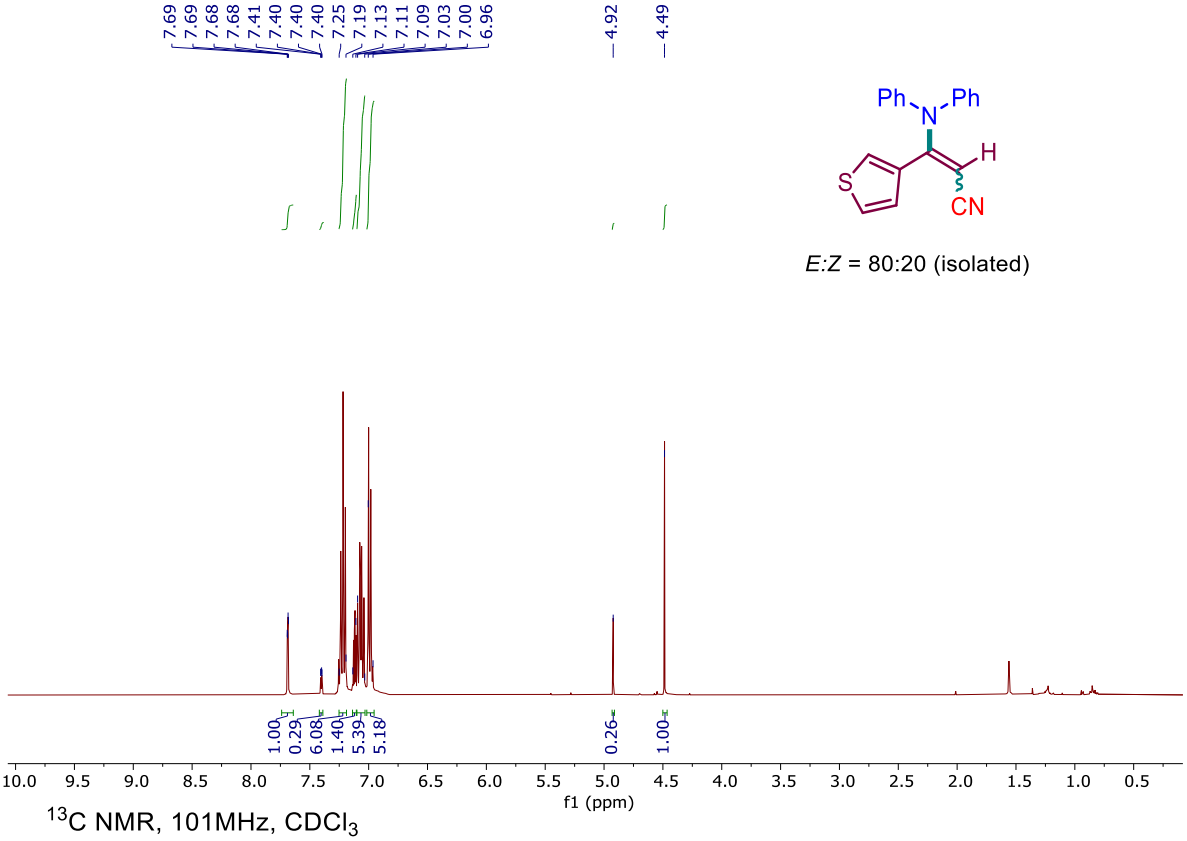
E:*Z* = 89:11 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



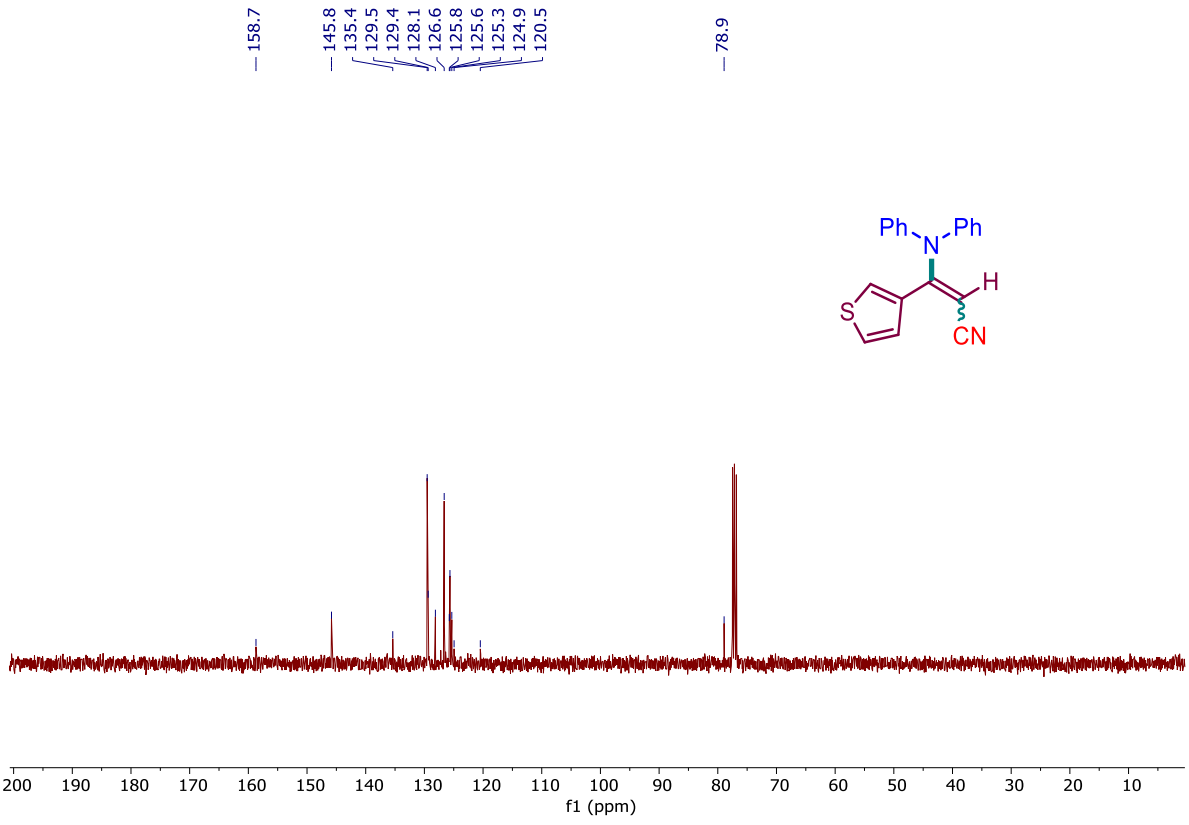
3-(diphenylamino)-3-(thiophen-3-yl)acrylonitrile (363r)

^{1}H NMR, 400MHz, $CDCl_3$



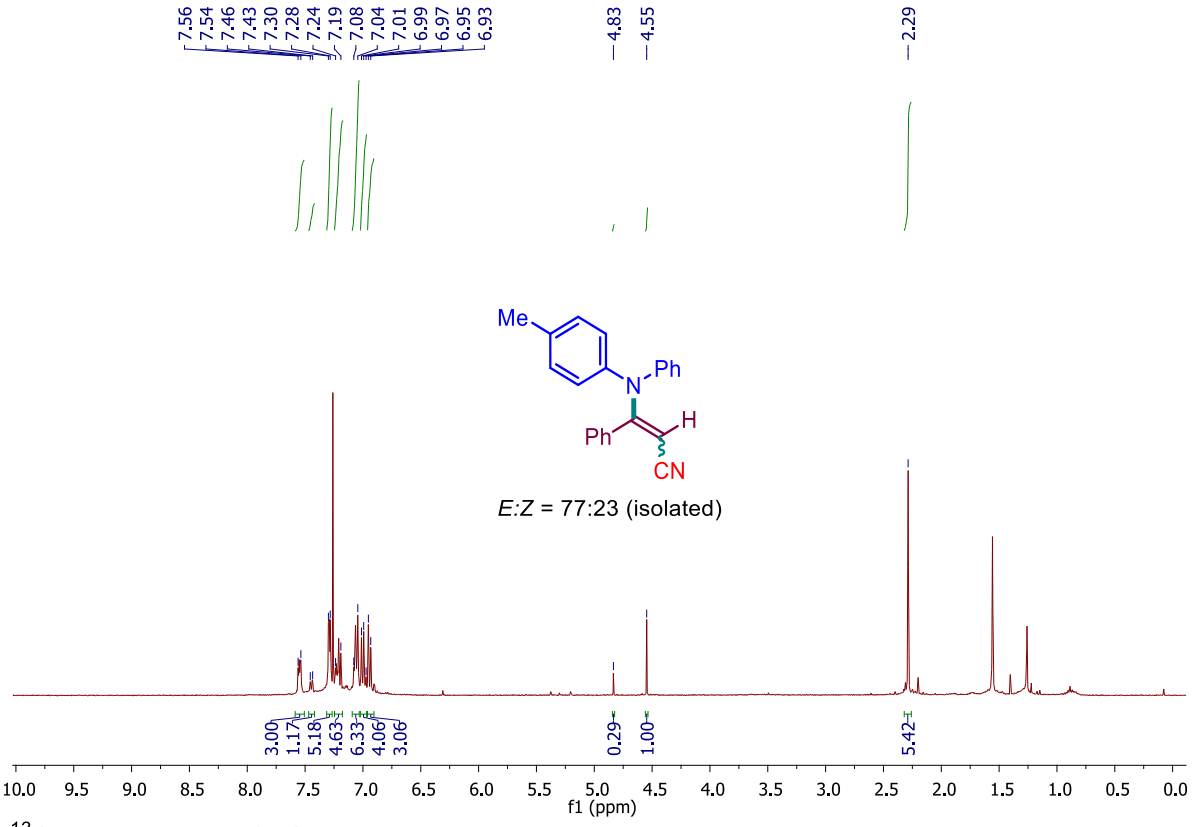
E:Z = 80:20 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



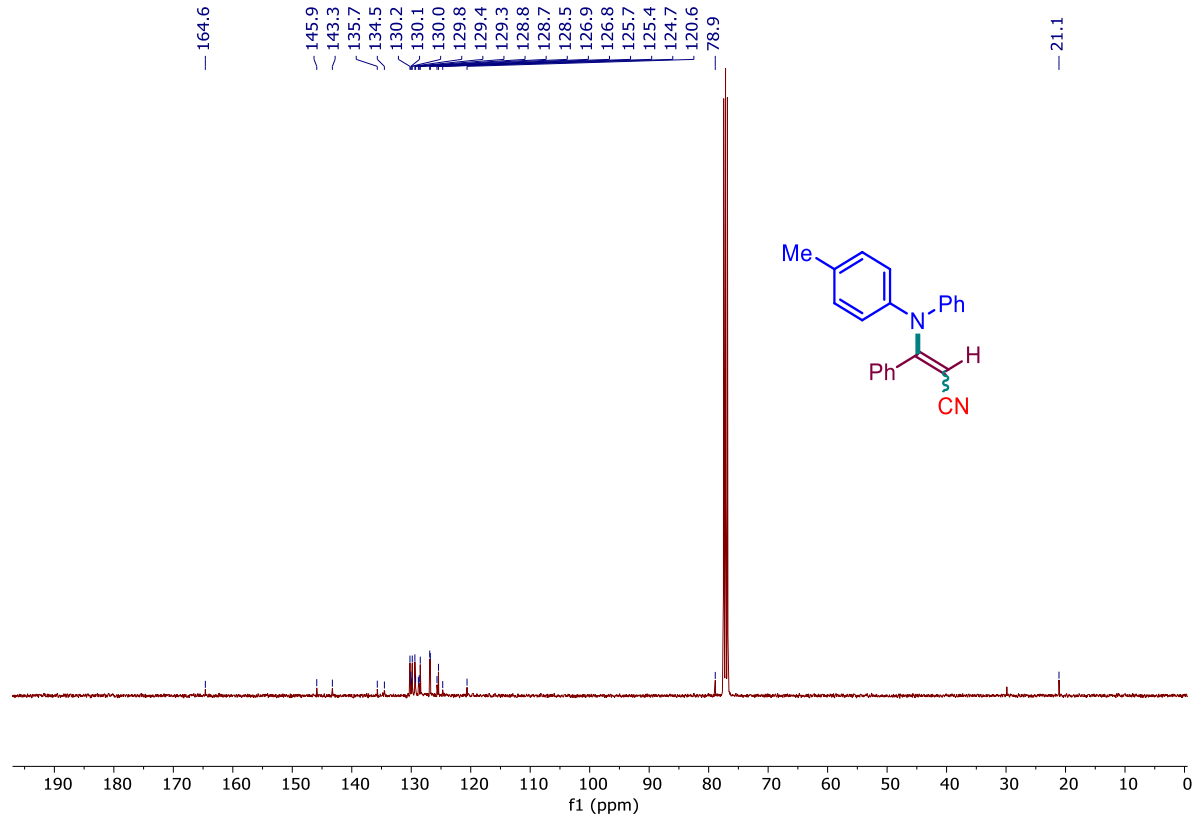
3-phenyl-3-(phenyl(*p*-tolyl)amino)acrylonitrile (363s)

^{1}H NMR, 400MHz, $CDCl_3$



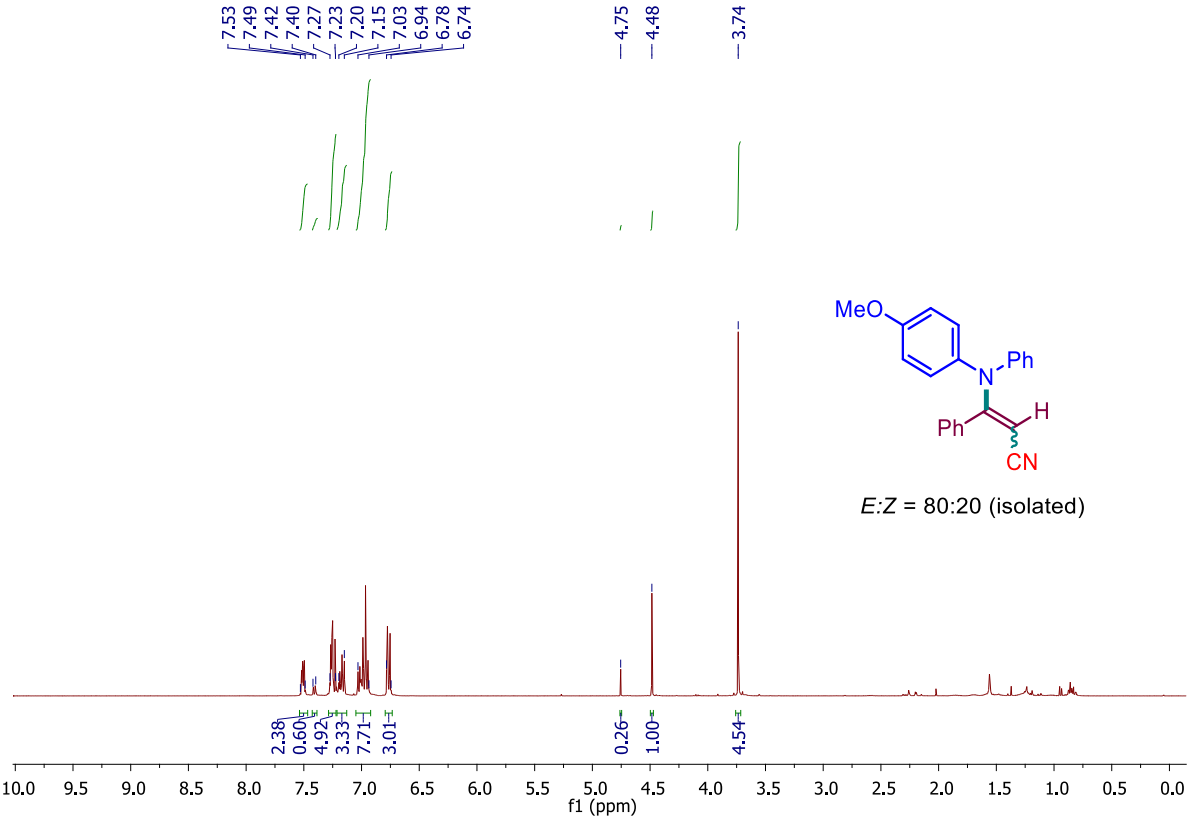
E:*Z* = 77:23 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

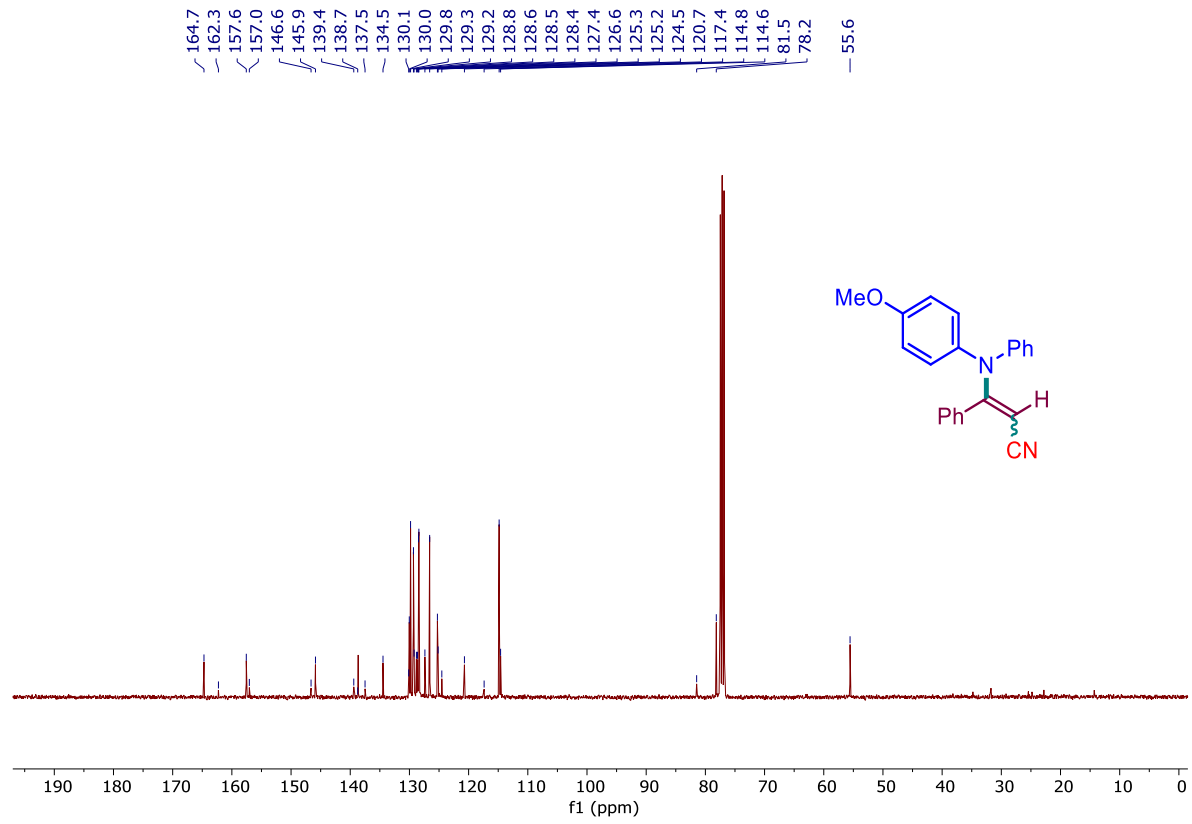


3-((4-methoxyphenyl)(phenyl)amino)-3-phenylacrylonitrile (363t)

^{1}H NMR, 400MHz, $CDCl_3$

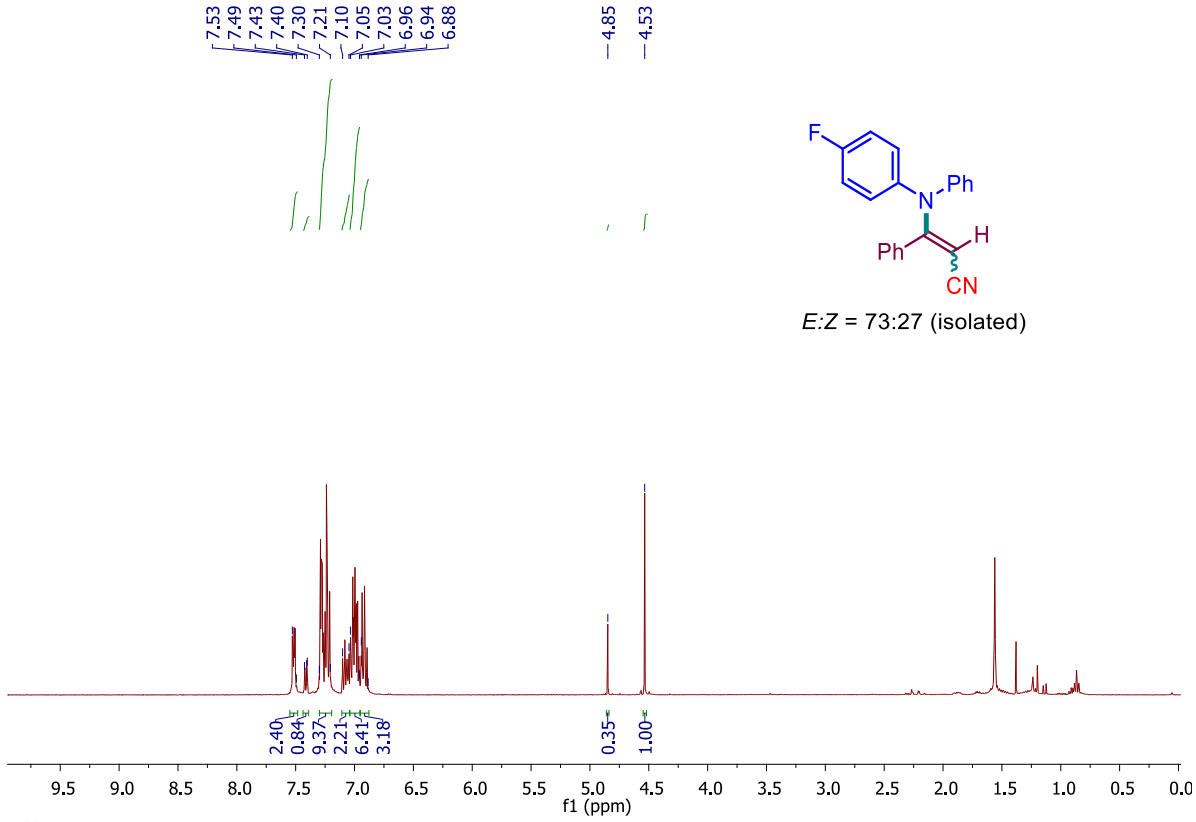


^{13}C NMR, 101MHz, $CDCl_3$



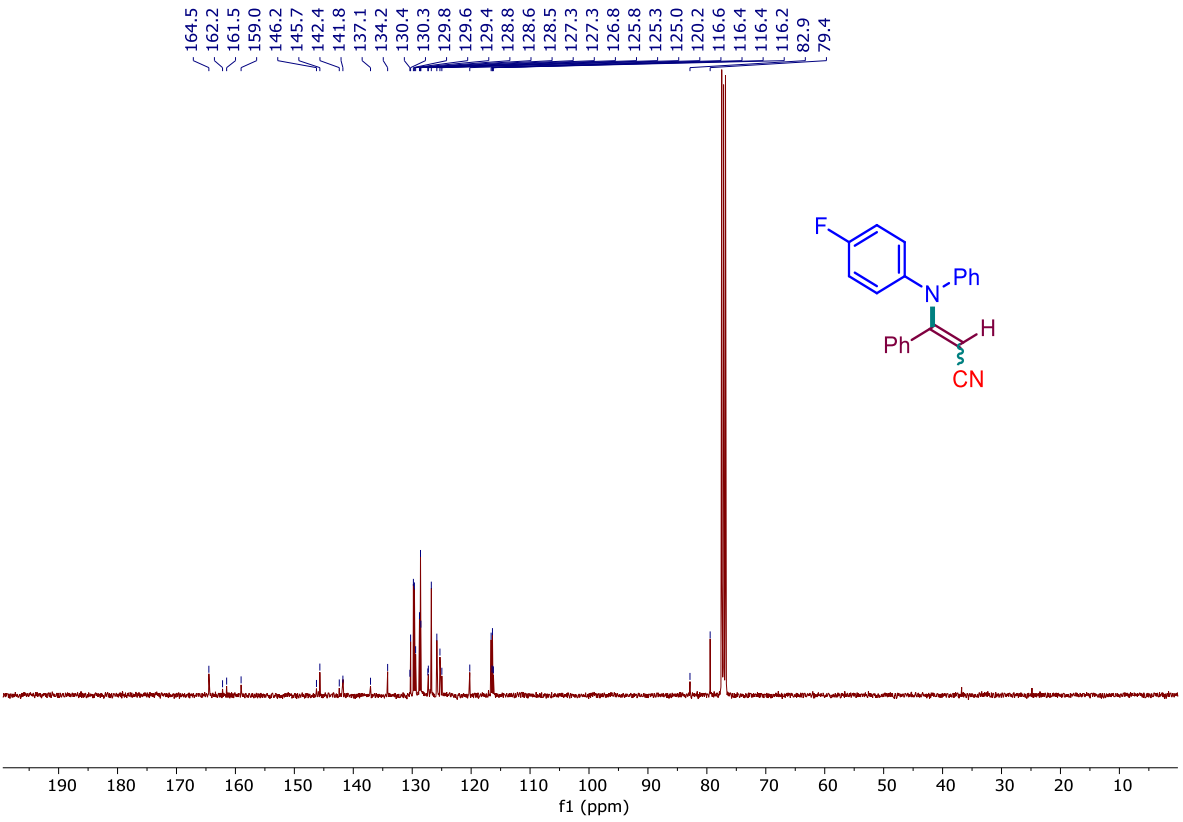
3-((4-fluorophenyl)(phenyl)amino)-3-phenylacrylonitrile (363u)

^{1}H NMR, 400MHz, $CDCl_3$

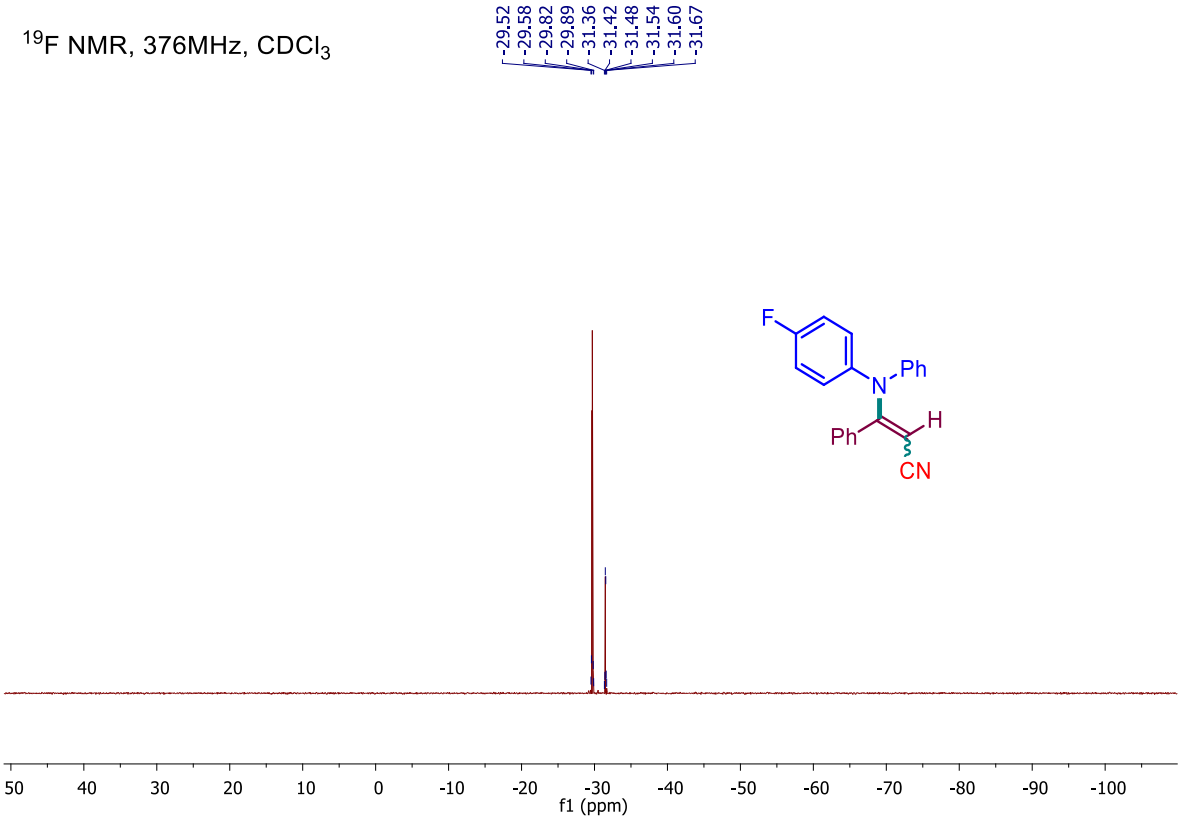


E:*Z* = 73:27 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

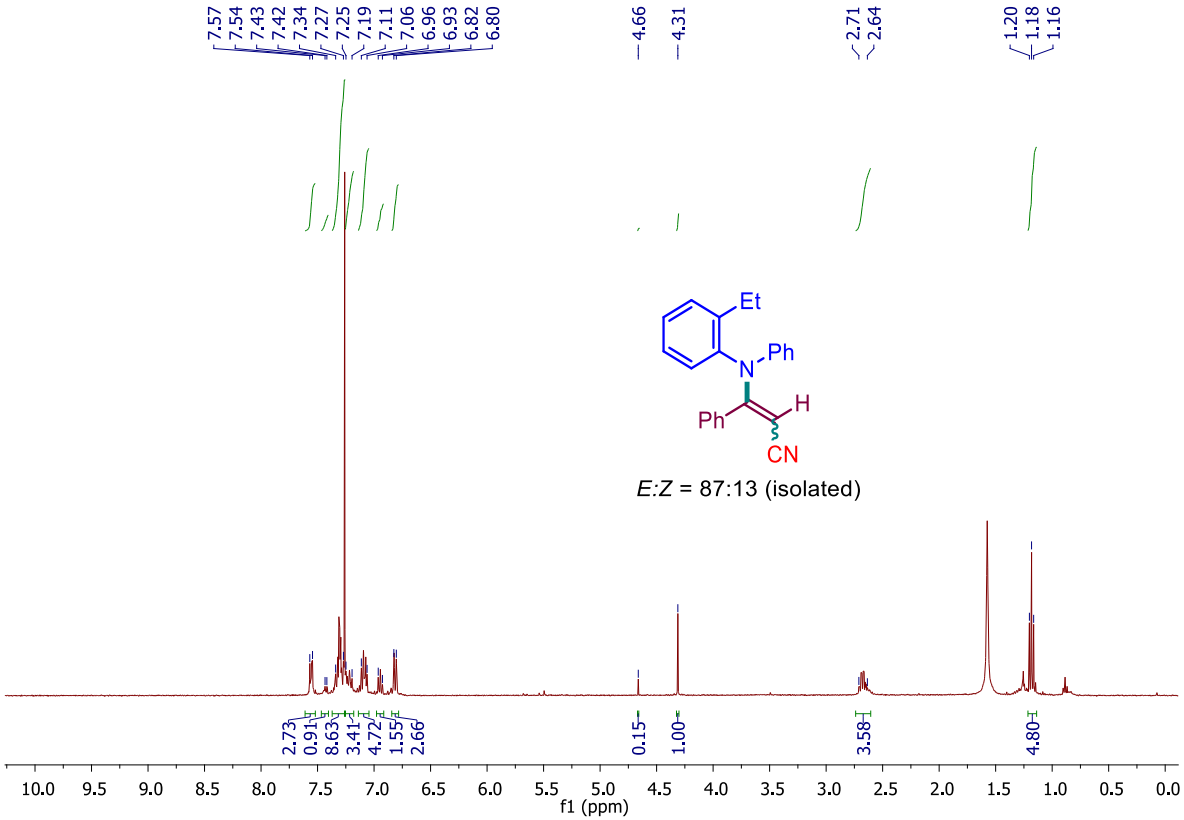


^{19}F NMR, 376MHz, $CDCl_3$



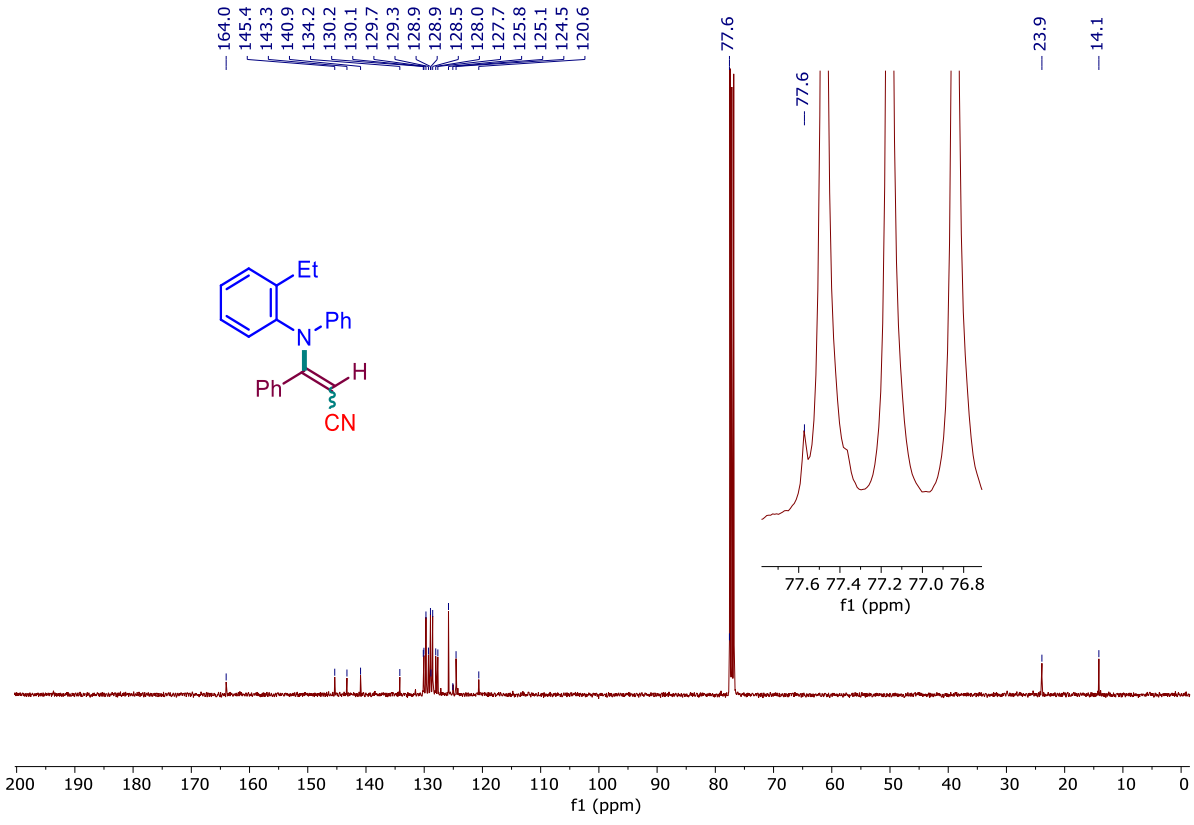
3-((2-ethylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363v)

^{1}H NMR, 400MHz, $CDCl_3$



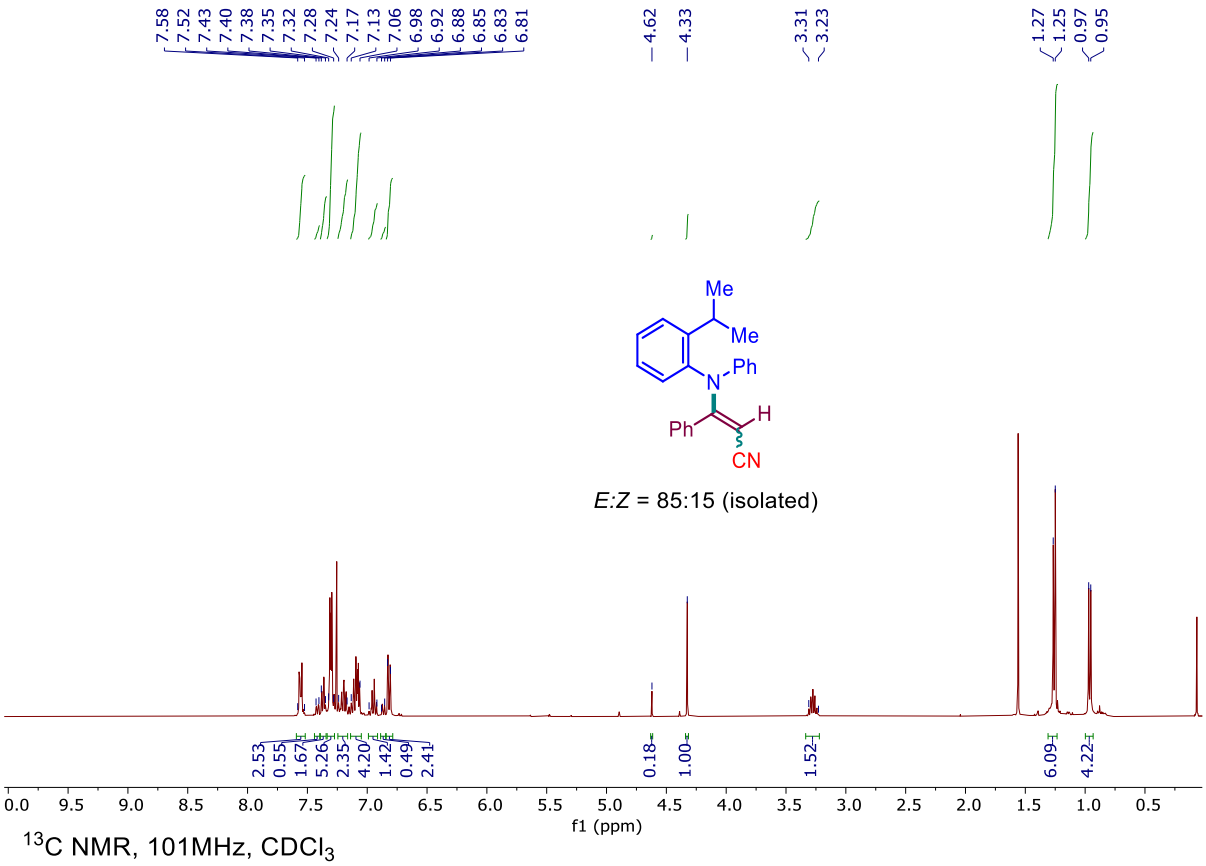
E:*Z* = 87:13 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



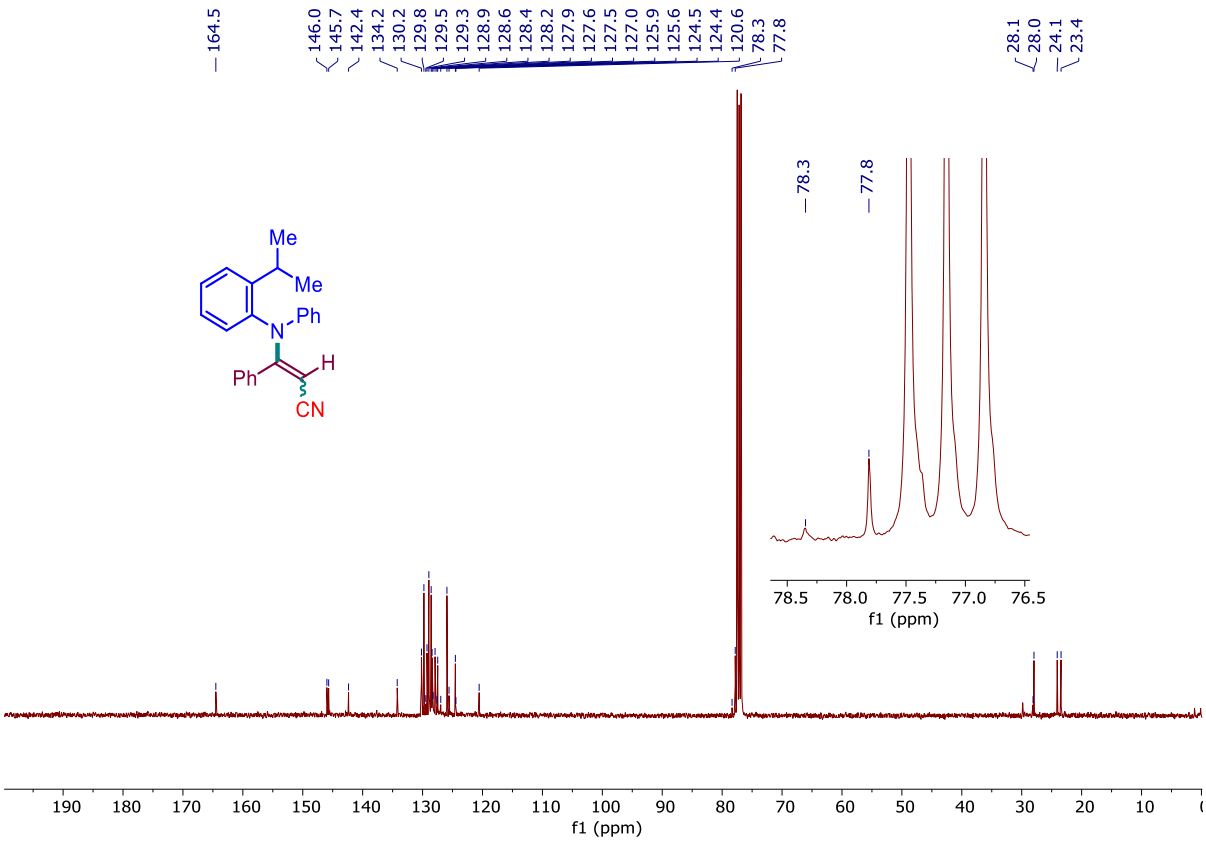
3-((2-isopropylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363w)

^{1}H NMR, 400MHz, $CDCl_3$



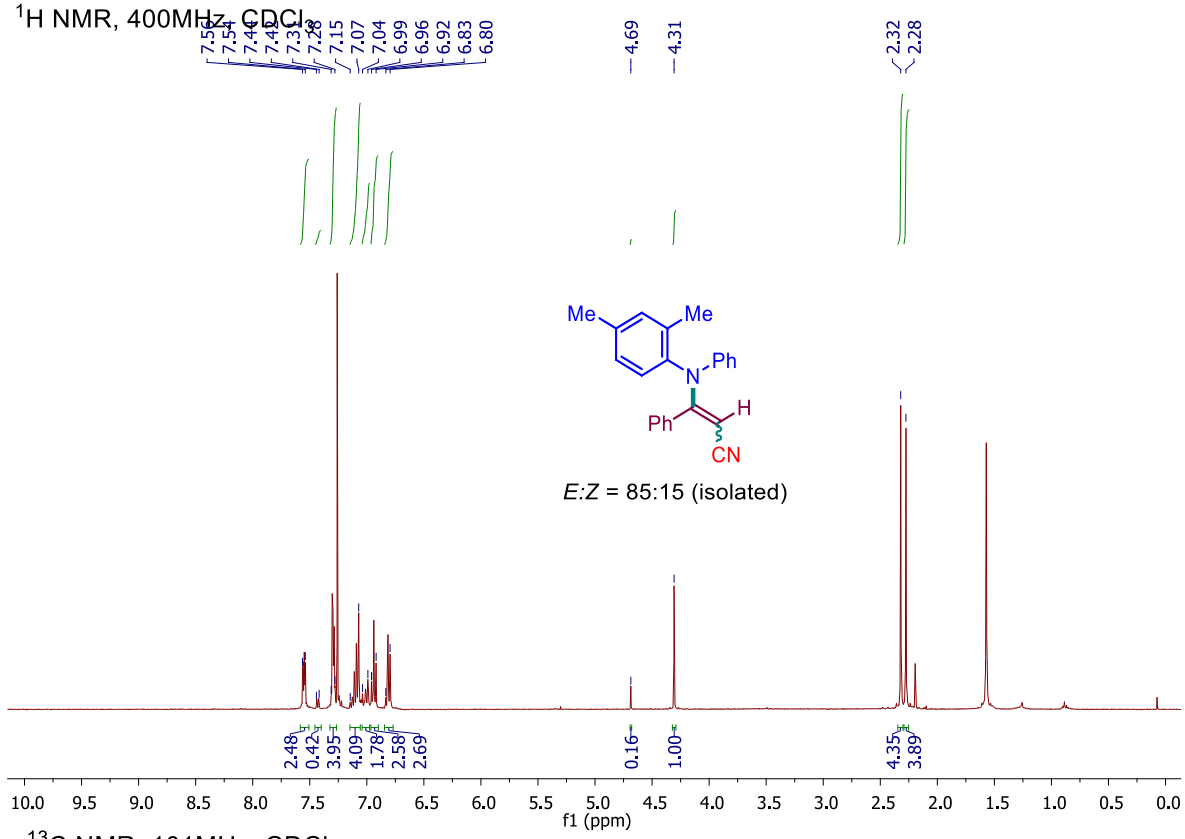
E:*Z* = 85:15 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

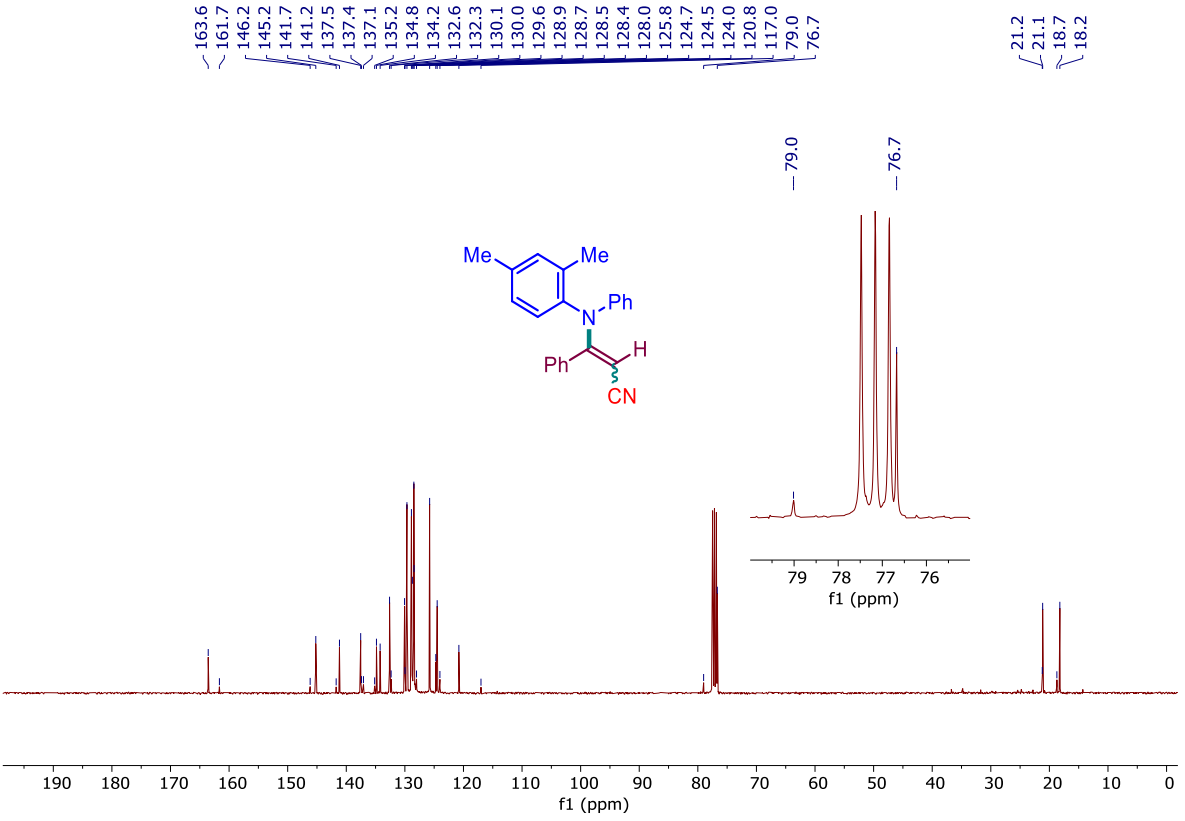


3-((2,4-dimethylphenyl)(phenyl)amino)-3-phenylacrylonitrile (363x)

^{1}H NMR, 400MHz, $CDCl_3$

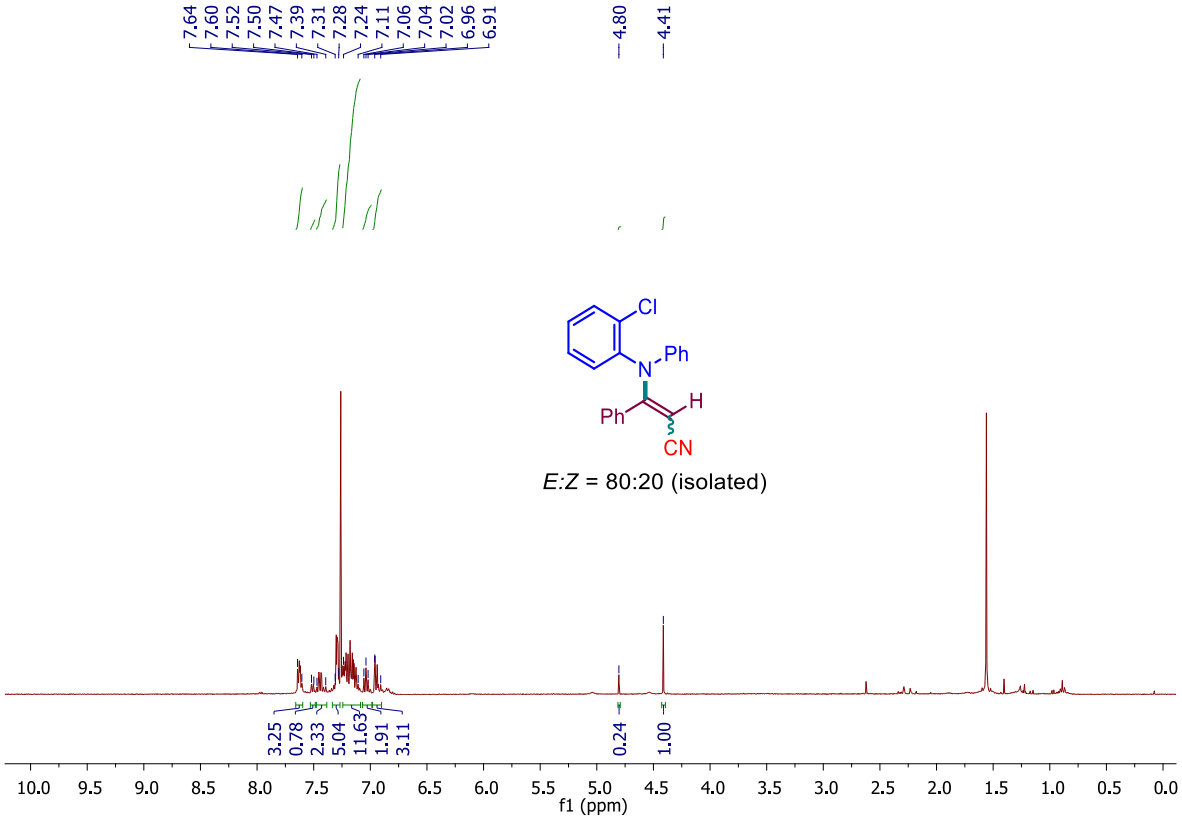


^{13}C NMR, 101MHz, $CDCl_3$



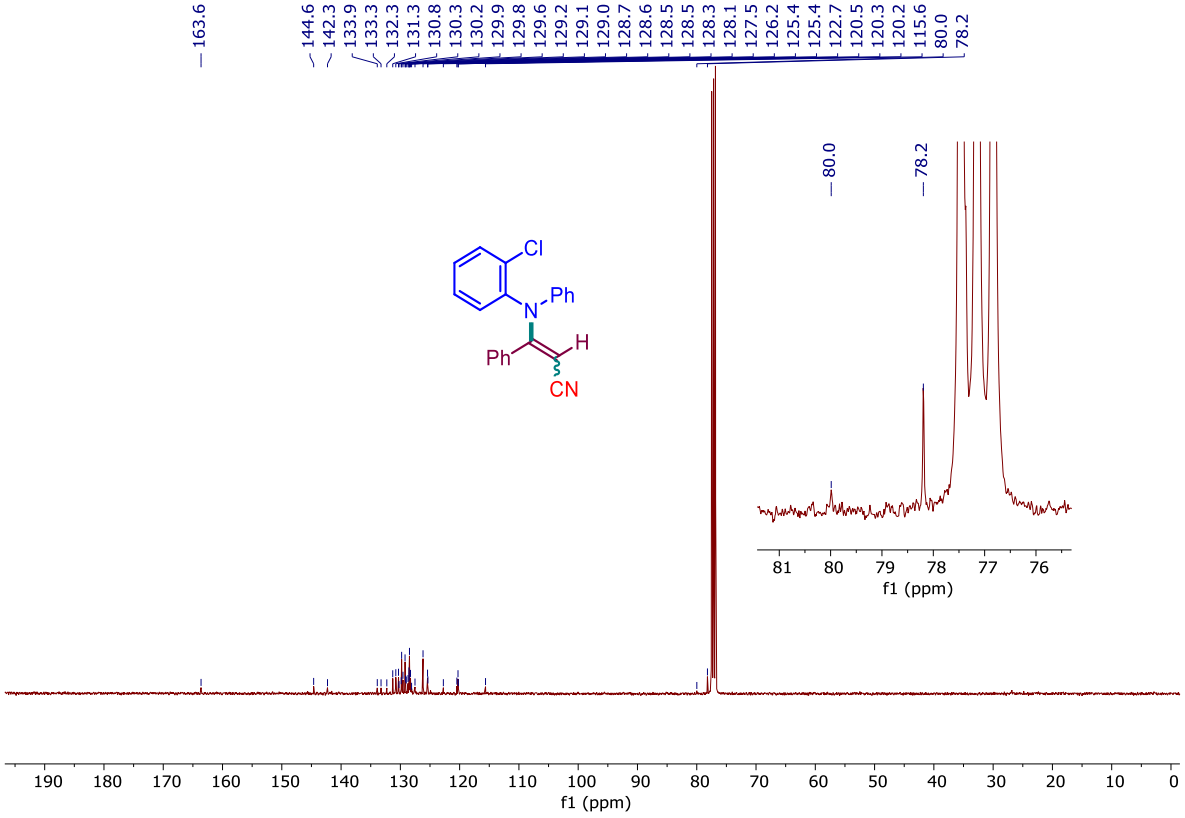
3-((2-chlorophenyl)(phenyl)amino)-3-phenylacrylonitrile (363y)

^{1}H NMR, 400MHz, $CDCl_3$



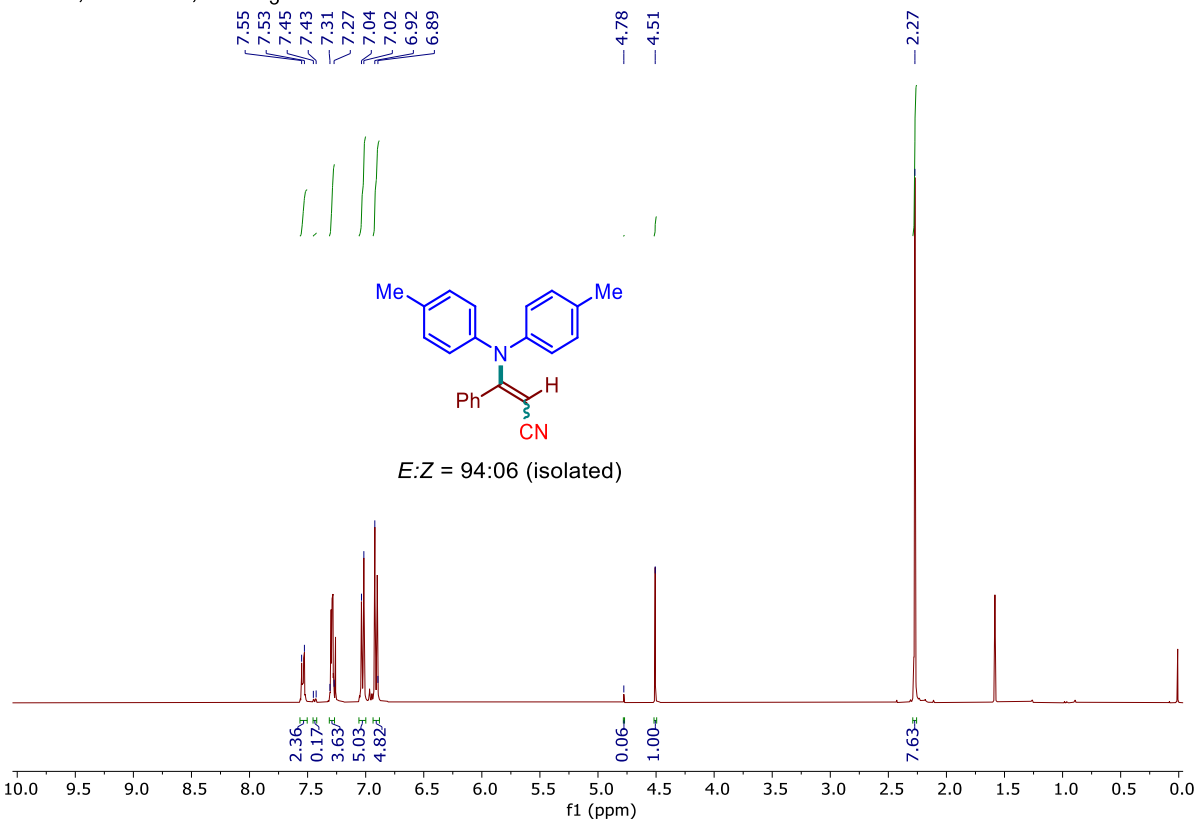
E:*Z* = 80:20 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



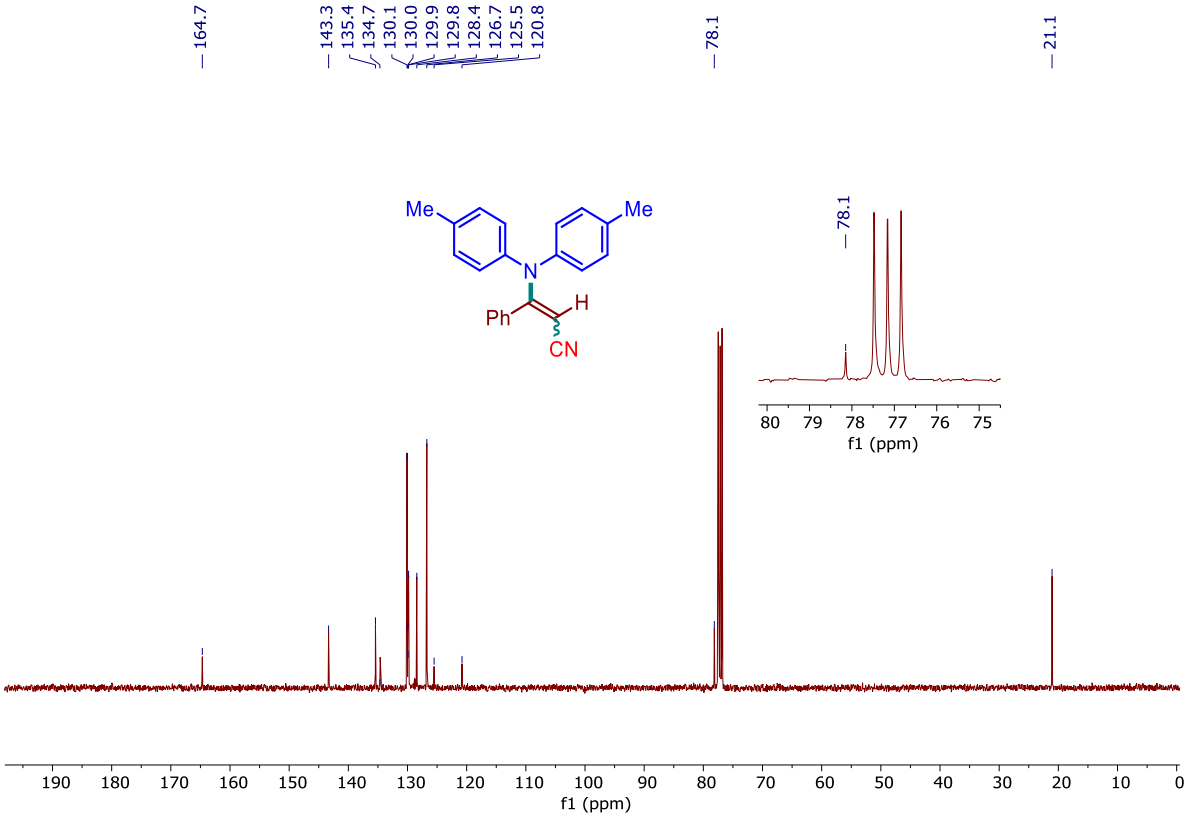
3-(di-*p*-tolylamino)-3-phenylacrylonitrile (363z)

^{1}H NMR, 400MHz, $CDCl_3$



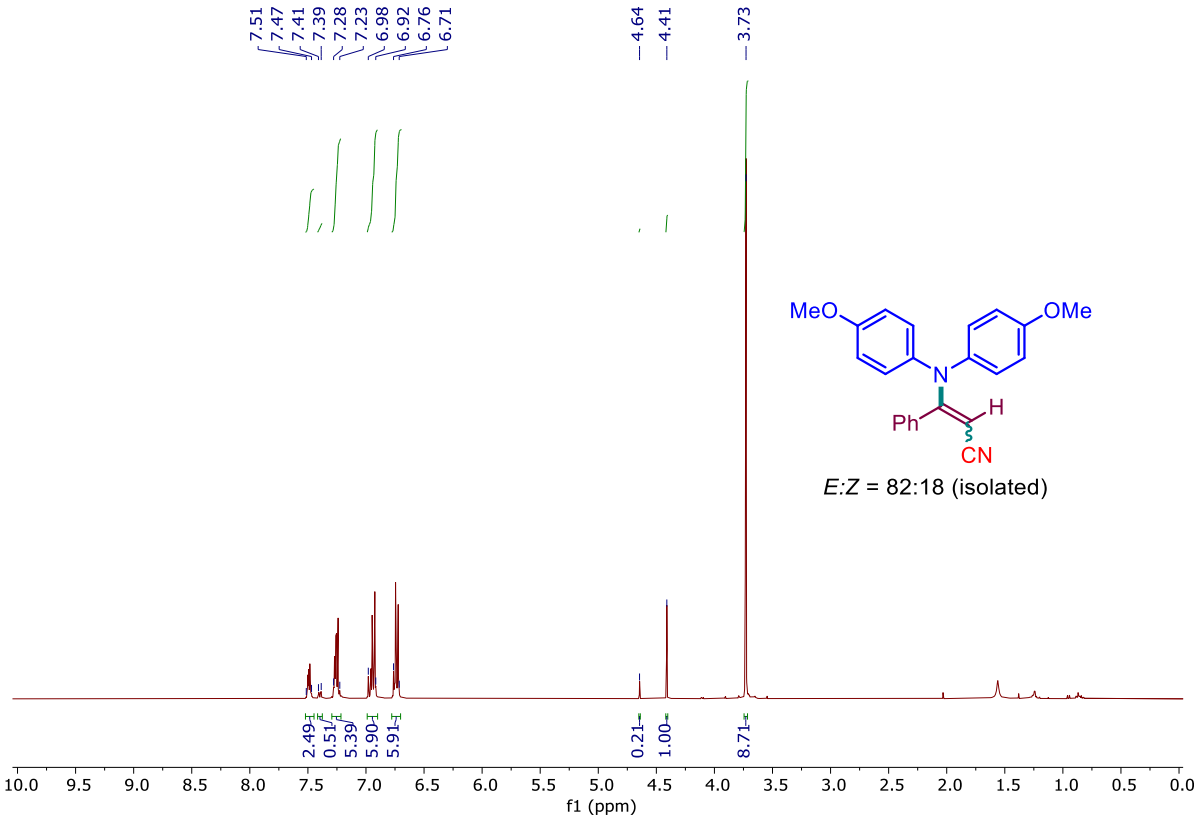
E:*Z* = 94:06 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



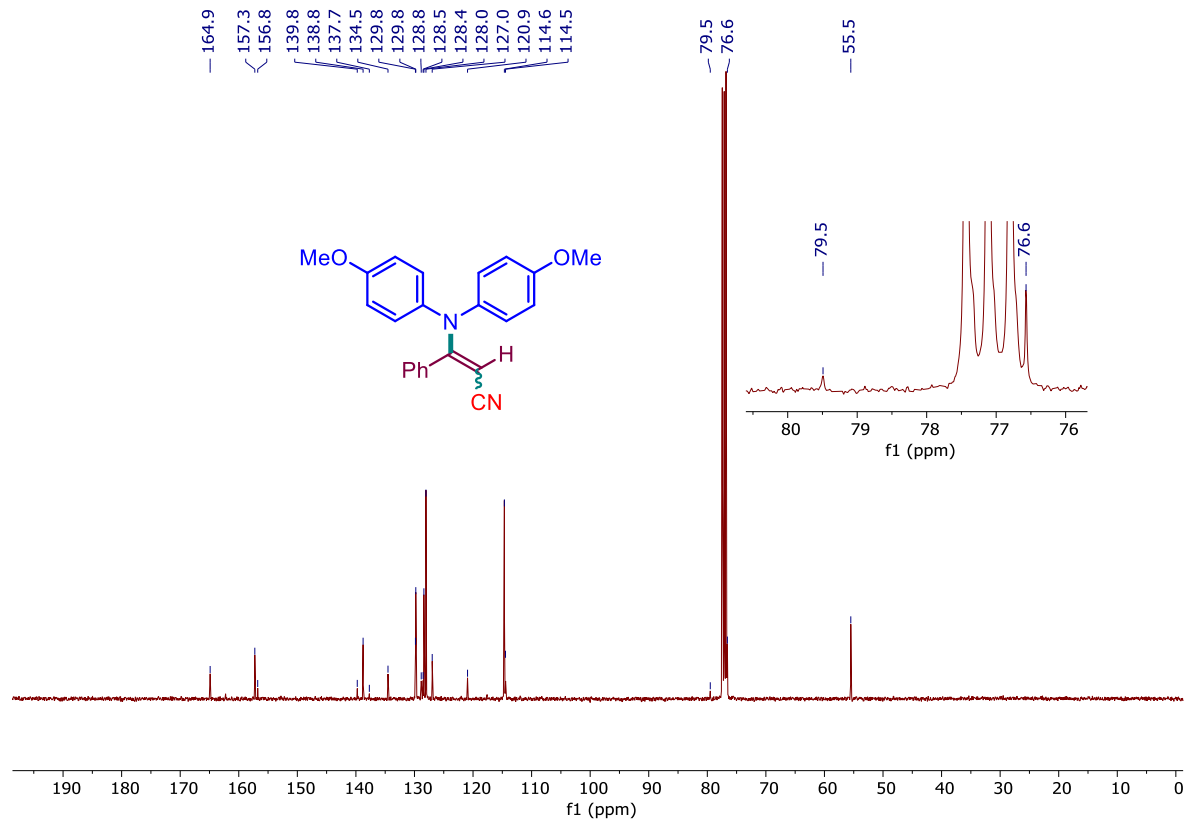
3-(bis(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363ja)

^{1}H NMR, 400MHz, $CDCl_3$



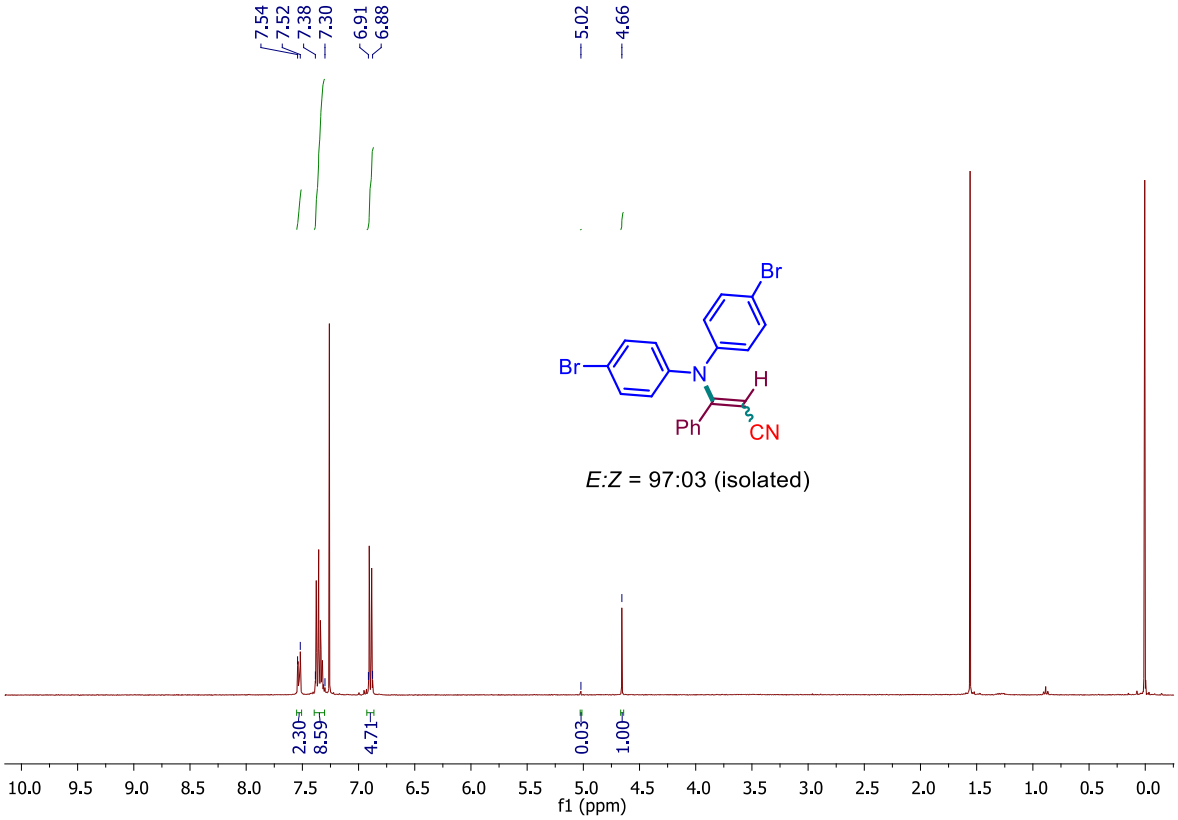
E:Z = 82:18 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$

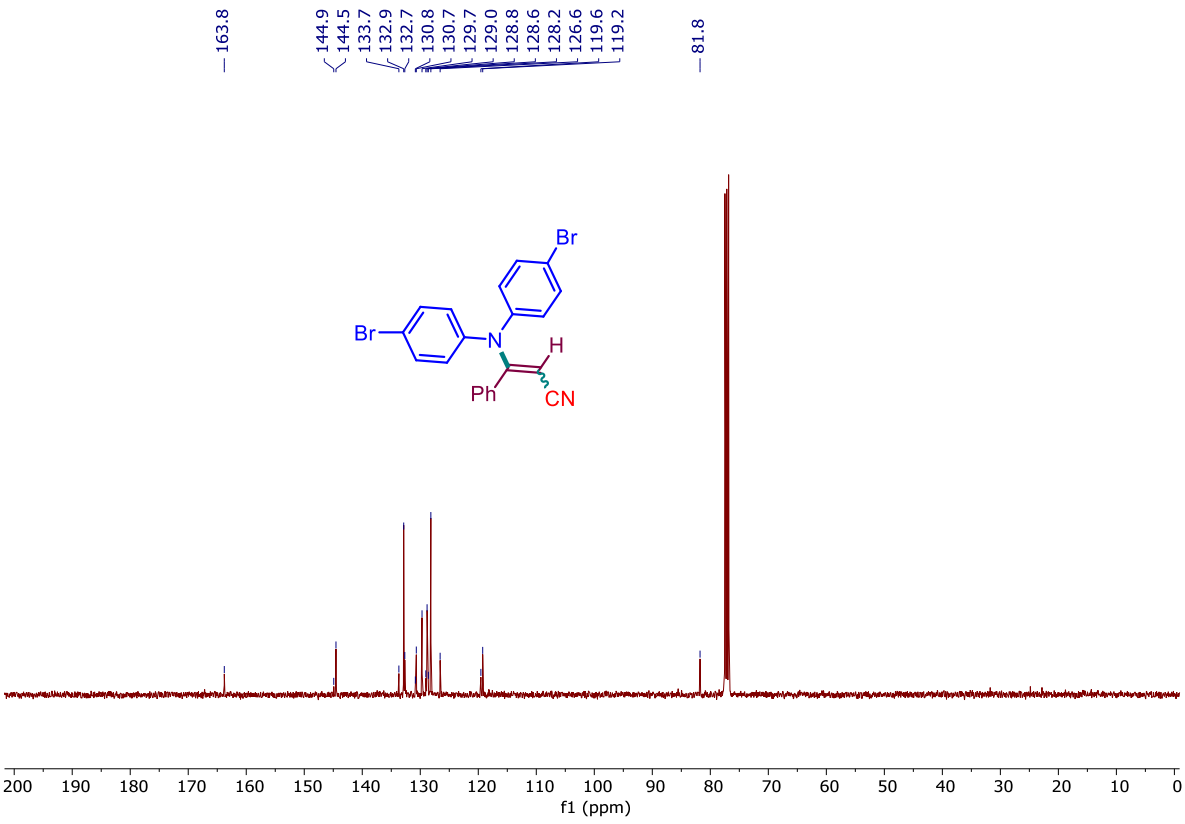


3-(bis(4-bromophenyl)amino)-3-phenylacrylonitrile (363ka)

^{1}H NMR, 400MHz, $CDCl_3$

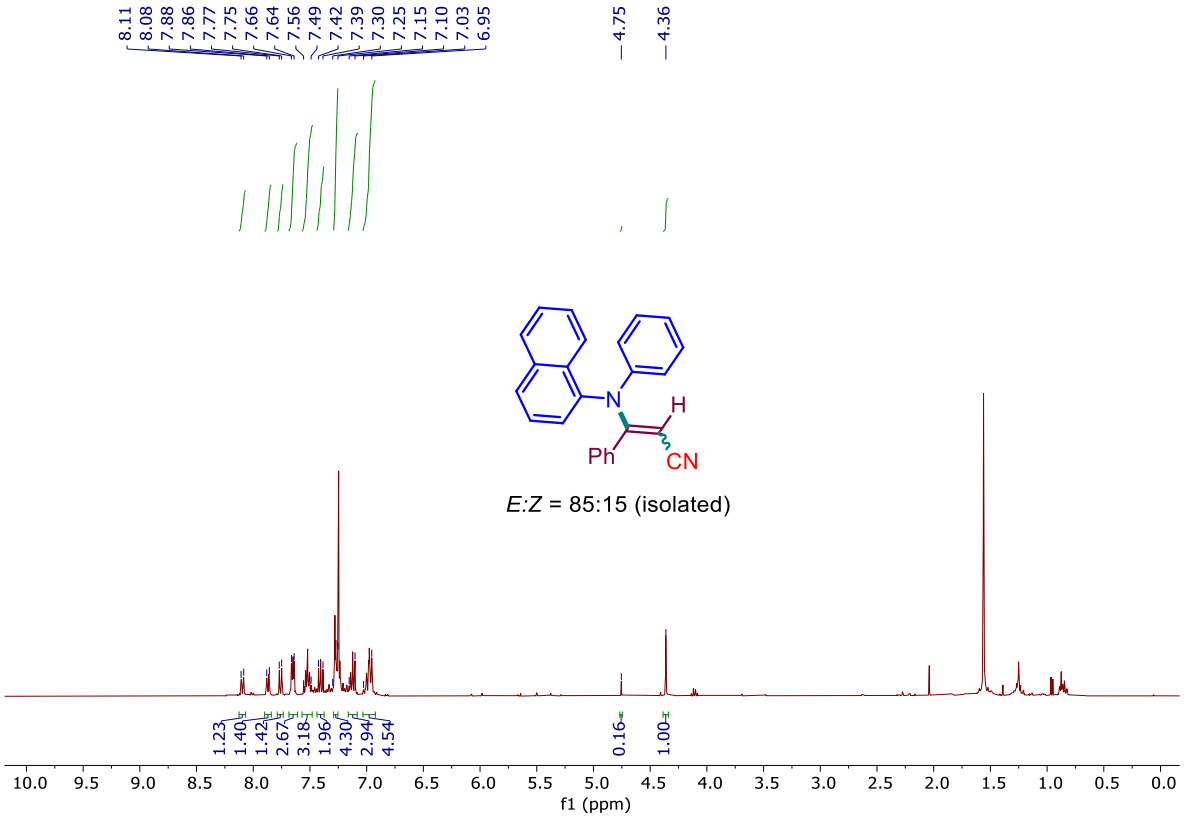


^{13}C NMR, 101MHz, $CDCl_3$

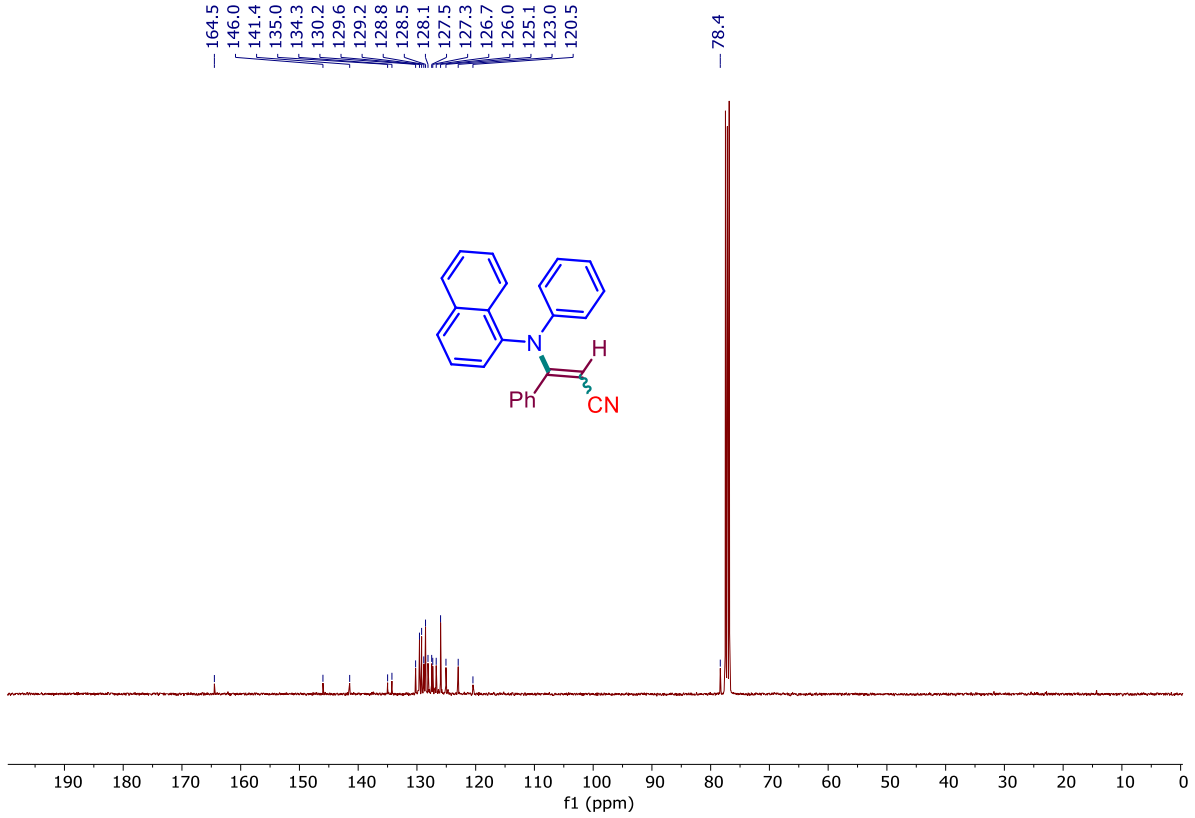


3-(naphthalen-1-yl(phenyl)amino)-3-phenylacrylonitrile (363la)

^{1}H NMR, 400MHz, $CDCl_3$

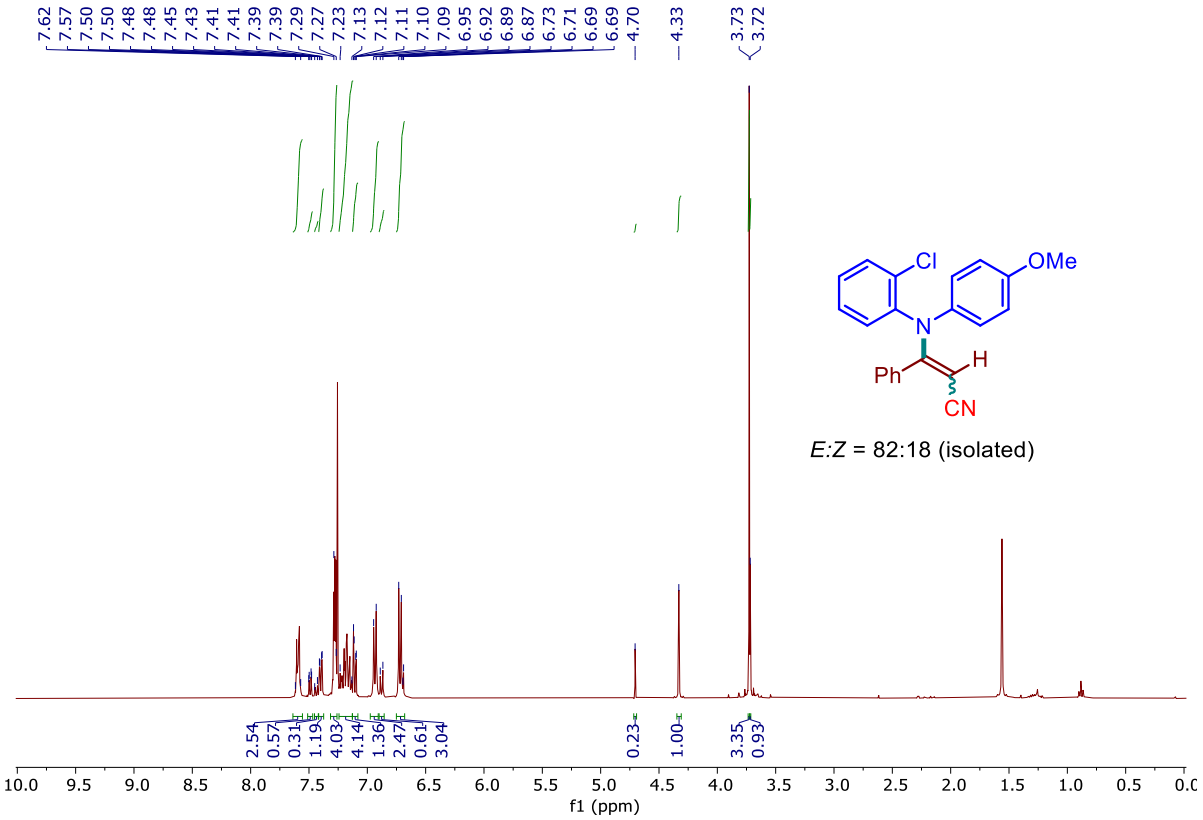


^{13}C NMR, 101MHz, $CDCl_3$



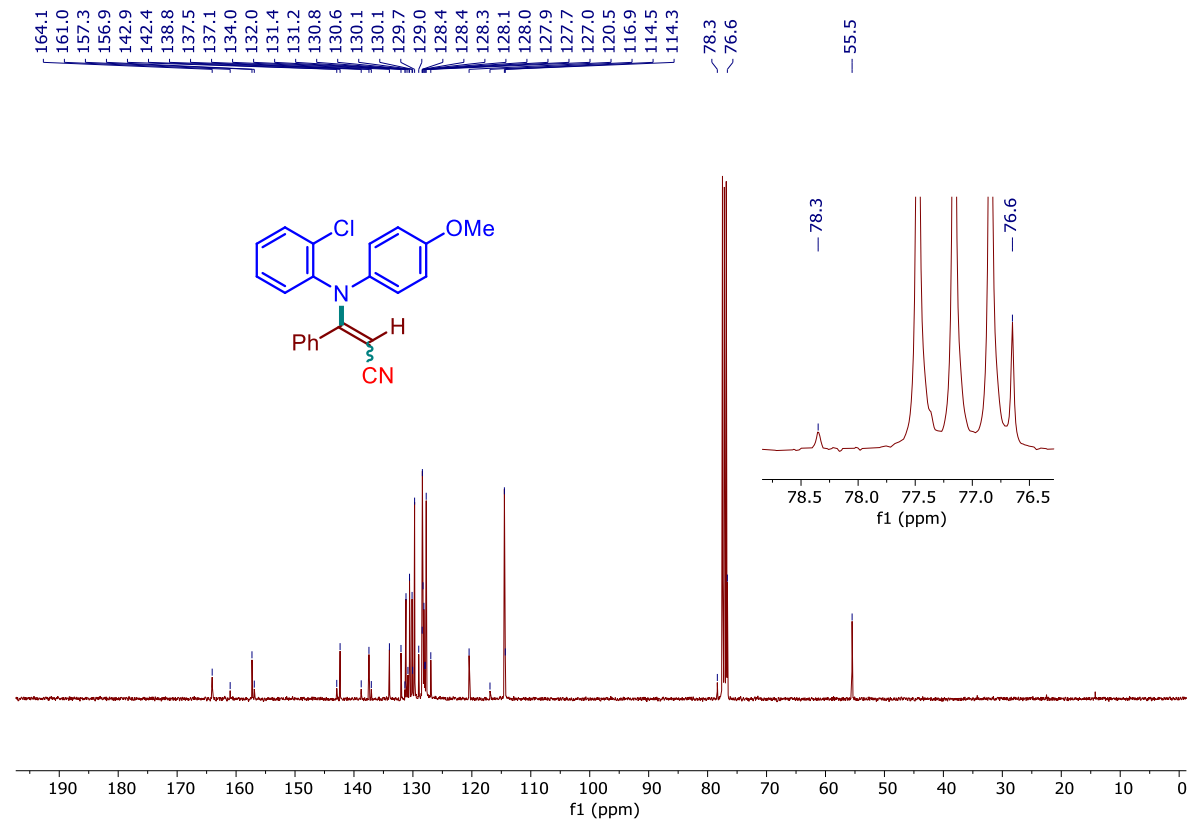
3-((2-chlorophenyl)(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363ma)

^{1}H NMR, 400MHz, $CDCl_3$

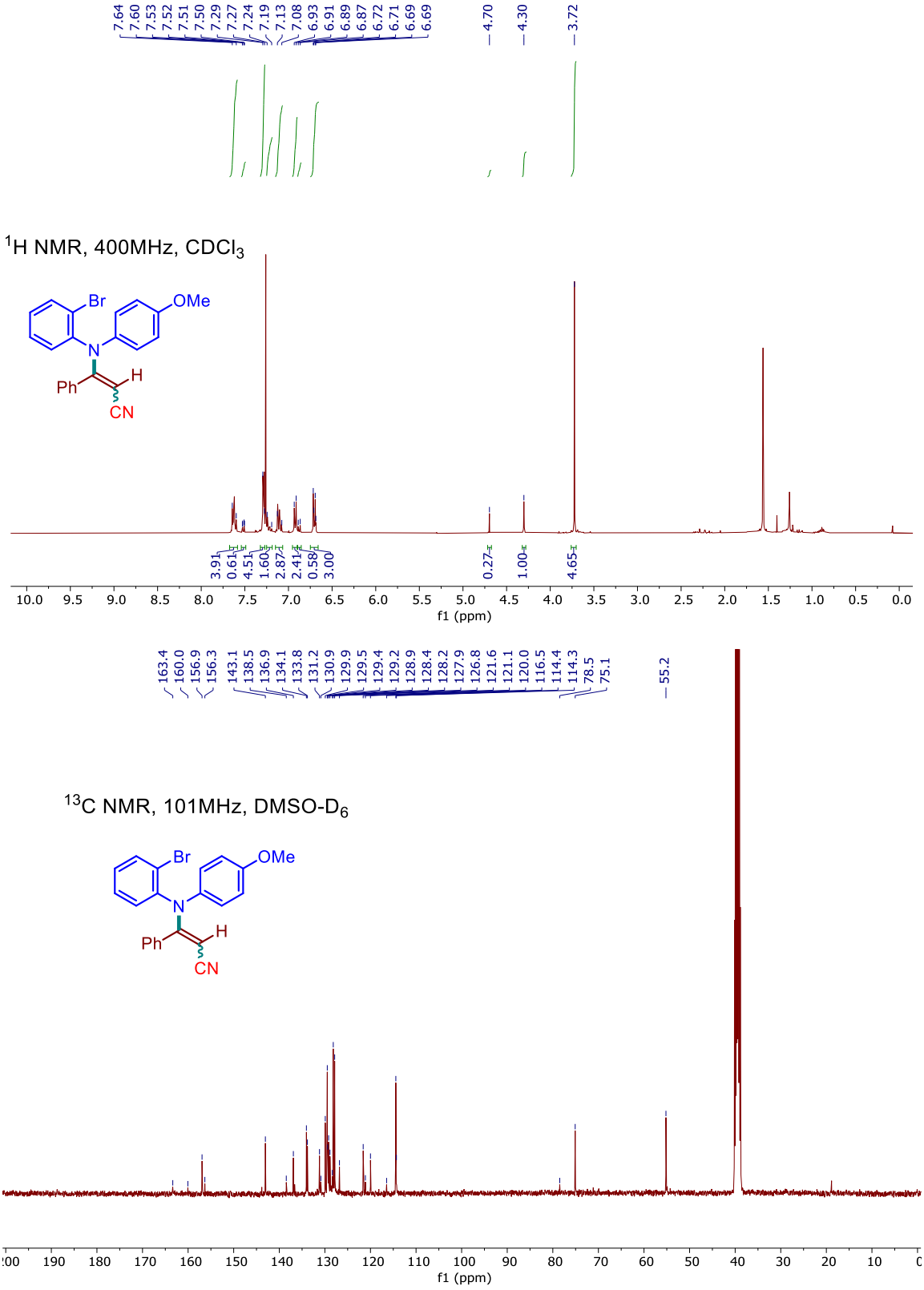


E:*Z* = 82:18 (isolated)

^{13}C NMR, 101MHz, $CDCl_3$



3-((2-bromophenyl)(4-methoxyphenyl)amino)-3-phenylacrylonitrile (363na)



Note- *In many ^{13}C-NMR the peaks for cis isomer are either invisible or have very low intensity due to the variation in E:Z ratio.*

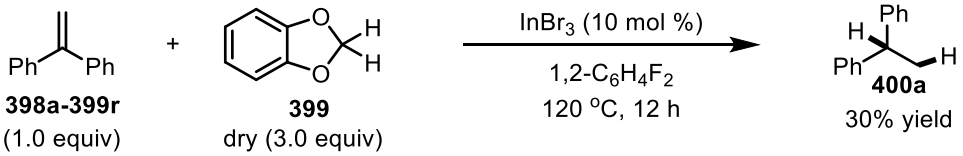
Annexure 4

Experimental part of Chapter 5: **Transition-metal-free Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins**

1. General Information

Reactions were performed in flame-dried glassware under aerobic condition unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled prior to use. $CDCl_3$ was stored over 4Å molecular sieves. Used chemicals were purchased from *Sigma-Aldrich*, *TCI*, *A*lfa-*A*esar and *Sisco Research Laboratories (SRL)* used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from *Merck* using the indicated solvents. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 unless otherwise stated on JEOL JNM ECS-400 FT-NMR instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for **^{1}H NMR** and $CDCl_3$: δ = 77.16 ppm for **^{13}C NMR**; DMSO-d_6: δ = 2.45 ppm for **^{1}H NMR** and DMSO-d_6: δ = 39.52 ppm for **^{13}C NMR**. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2-XS QTOF. Olefins **398a-398r**[122, 123, 131, 152, 153, 154] and deuterated 1,3-benzodioxole **399a-*d*$_2$**, [151] were synthesized according to the procedure in the literature

2. General Procedure for the Reaction of Hydrogenation (GP):



Procedure A: An oven-dried sealed tube is charged with indium tribromide ($InBr_3$) (10.0 mol %), 1,3-benzodioxole **399** (3.0 equiv), olefins **398a-398r** (1.0 equiv), and 1,2-difluorobenzene (0.25 ml, 0.4M) simultaneously added under aerobic conditions. The reaction mixture stirred for 12

hours in a preheated oil bath at 120 ^{o}C temperature. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and EtOAc as eluent.

Procedure B: An oven-dried sealed tube is charged with indium tribromide ($InBr_3$) (10.0 mol %), (dry) 1,3-benzodioxole **399** (3.0 equiv), olefins **398a-398r** (1.0 equiv), D_2O (3.0 equiv) and (dry) 1,2-difluorobenzene (0.25 ml, 0.4M) simultaneously added under argon. The reaction mixture stirred for 12 hours in a preheated oil bath at 120 ^{o}C temperature. The analytically pure product is obtained by column chromatography on silica gel using petroleum ether and EtOAc as eluent.

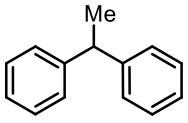
***Key Points**: **1**- Storage of $InBr_3$ was made in Ar filled glove box because it is highly hygroscopic in nature. The $InBr_3$ has bee taken from the glove box to set-up the reaction every time.*

***2**- Experiments with D_2O performed under dry conditions (dry **399** and dry 1,2-difluorobenzene) and substrates added inside glove box then sealed tube taken out and refluxed at 120 ^{o}C for 12 h.*

***3**- Reflux of the reaction mixture is necessary all the time otherwise yield will be low or sometimes reaction didn't work.*

3. Experimental Details for the Synthesized Compounds

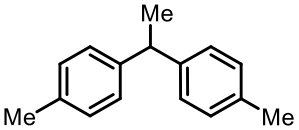
3.1 ethane-1,1-diyldibenzene (400a)



$C_{14}H_{14}$
M = 182.27 g/mol

Prepared according to the **GP-A**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a** (16.0 mg, 90% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 4H), 7.24–7.22 (m, 4H), 7.21–7.16 (m, 2H), 4.16 (q, *J* = 7.3 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 128.5, 127.8, 126.2, 44.9, 22.0. The analytical data are in accordance with the literature.[128]

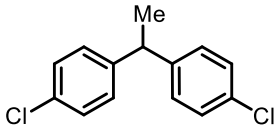
3.2 4,4'-(ethane-1,1-diyl)bis(methylbenzene) (400b)



$C_{16}H_{18}$
M = 210.32 g/mol

Prepared according to the **GP-A**, using **398b** (21.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400b** (17.0 mg, 80% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12–7.07 (m, 8H), 4.08 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 6H), 1.60 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 135.5, 129.2, 127.6, 44.1, 22.1, 21.1. The analytical data are in accordance with the literature.[128]

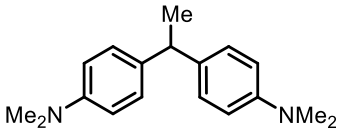
3.3 4,4'-(ethane-1,1-diyl)bis(chlorobenzene) (400c)



$C_{14}H_{12}Cl_2$
M = 251.15 g/mol

Prepared according to the **GP-A**, using **398c** (25.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400c** (24.0 mg, 95% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 4H), 7.13–7.10 (m, 4H), 4.10 (q, *J* = 7.3 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 132.1, 129.0, 128.7, 43.7, 21.9. The analytical data are in accordance with the literature.[132]

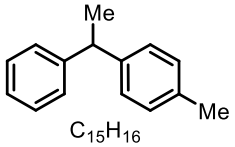
3.4 4,4'-(ethane-1,1-diyl)bis(*N*,*N*-dimethylaniline) (400d)



$C_{18}H_{24}N_2$
M = 268.40 g/mol

Prepared according to the **GP-A**, using **398d** (25.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether: EtOAc (9.7:0.3) as eluent afforded the product **400d** (20.0 mg, 75% yield, Brown liquid). **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{18}H_{25}N_2^+$ 269.2018; found 269.2018. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11–7.08 (m, 4H), 6.71–6.68 (m, 4H), 3.99 (q, *J* = 7.1 Hz, 1H), 2.90 (s, 12H), 1.57 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.9, 135.9, 128.3, 113.1, 42.9, 41.1, 22.4.

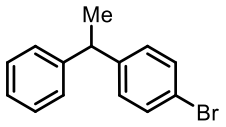
3.5 1-methyl-4-(1-phenylethyl)benzene (400e)



$C_{15}H_{16}$
M = 196.29 g/mol

Prepared according to the **GP-A**, using **398e** (20.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400e** (16.0 mg, 80% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.23–7.16 (m, 3H), 7.13–7.08 (m, 4H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.7, 143.5, 135.6, 129.2, 128.5, 127.7, 127.6, 126.1, 44.5, 22.1, 21.1. The analytical data are in accordance with the literature.[154]

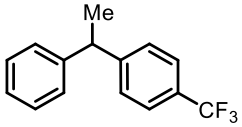
3.6. 1-bromo-4-(1-phenylethyl)benzene (400f)



$C_{14}H_{13}Br$
M = 261.16 g/mol

Prepared according to the **GP-A**, using **398f** (26.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400f** (23.0 mg, 90% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 2H), 7.31–7.27 (m, 2H), 7.22–7.18 (m, 3H), 7.11–7.07 (m, 2H), 4.11 (q, *J* = 7.3 Hz, 1H), 1.62 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 145.5, 131.5, 129.5, 128.6, 127.7, 126.4, 119.9, 44.3, 21.9. The analytical data are in accordance with the literature.[128]

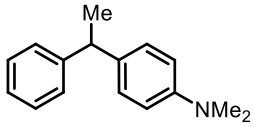
3.7 1-(1-phenylethyl)-4-(trifluoromethyl)benzene (400g)



$C_{15}H_{13}F_3$
M = 250.26 g/mol

Prepared according to the **GP-A**, using **398g** (25.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400g** (15.0 mg, 60% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.53 (d, *J* = 8.1 Hz, 2H), 7.34–7.29 (m, 4H), 7.23–7.19 (m, 3H), 4.21 (q, *J* = 7.3 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.6, 145.4, 128.7, 128.1, 127.7, 126.6, 125.5, (q, *J* = 3.8 Hz), 44.8, 21.8. The signal at 124.4 ppm for the CF_3 carbon was not detectable. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.24. The analytical data are in accordance with the literature.[132, 154]

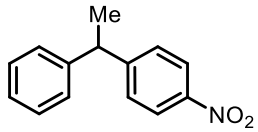
3.8 *N,N*-dimethyl-4-(1-phenylethyl)aniline (400h)



$C_{16}H_{19}N$
M = 225.33 g/mol

Prepared according to the **GP-A**, using **398h** (22.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether: EtOAc (9.8:0.2) as eluent afforded the product **400h** (18.0 mg, 80% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.24–7.21 (m, 2H), 7.18–7.14 (m, 1H), 7.12–7.09 (m, 2H), 6.72–6.68 (m, 2H), 4.08 (q, *J* = 7.3 Hz, 1H), 2.91 (s, 6H), 1.61 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 147.3, 134.9, 128.4, 128.3, 127.7, 125.9, 113.0, 43.9, 41.0, 22.2. The analytical data are in accordance with the literature.[155a]

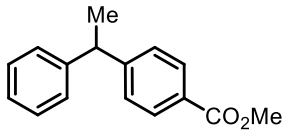
3.9 1-nitro-4-(1-phenylethyl)benzene (400i)



$C_{14}H_{13}NO_2$
M = 227.26 g/mol

Prepared according to the **GP-A**, using **398i** (22.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether : EtOAc (9.8:0.2) as eluent afforded the product **400i** (9.0 mg, 40% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16–8.12 (m, 2H), 7.39–7.35 (m, 2H), 7.34–7.29 (m, 2H), 7.25–7.18 (m, 3H), 4.26 (q, *J* = 7.3 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 146.5, 144.7, 128.9, 128.6, 127.7, 126.9, 123.8, 44.9, 21.6. The analytical data are in accordance with the literature.[155b]

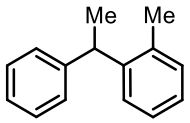
3.10 methyl 4-(1-phenylethyl)benzoate (400j)



$C_{16}H_{16}O_2$
M = 240.30 g/mol

Prepared according to the **GP-A**, using **398j** (24.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether : EtOAc (9.8:0.2) as eluent afforded the product **400j** (13.0 mg, 55% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.94 (m, 2H), 7.31–7.27 (m, 4H), 7.22–7.18 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 151.9, 145.6, 129.9, 128.6, 128.1, 127.8, 127.7, 126.5, 52.1, 45.0, 21.7. The analytical data are in accordance with the literature.[154]

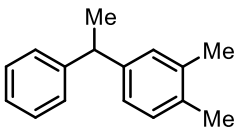
3.11 1-methyl-2-(1-phenylethyl)benzene (400k)



$C_{15}H_{16}$
M = 196.12 g/mol

Prepared according to the **GP-A**, using **398k** (19.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400k** (11.0 mg, 55% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.25 (m, 3H), 7.24–7.12 (m, 6H), 4.32 (q, *J* = 7.2 Hz, 1H), 2.24 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 144.0, 136.2, 130.5, 128.4, 127.8, 126.8, 126.2, 126.2, 126.0, 41.1, 22.2, 19.9. The analytical data are in accordance with the literature.[152]

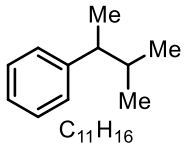
3.12 1,2-dimethyl-4-(1-phenylethyl)benzene (400l)



$C_{16}H_{18}$
M = 210.32 g/mol

Prepared according to the **GP-A**, using **398l** (19.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400l** (10.0 mg, 45% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.24–7.21 (m, 2H), 7.19–7.14 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.99–6.95 (m, 2H), 4.09 (q, *J* = 7.3 Hz, 1H), 2.22 (d, *J* = 1.4 Hz, 6H), 1.61 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 144.0, 136.6, 134.3, 129.7, 129.1, 128.5, 127.7, 126.0, 125.0, 44.5, 22.1, 19.5. The analytical data are in accordance with the literature.[152]

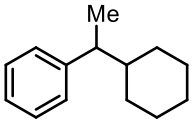
3.13 (3-methylbutan-2-yl)benzene (400m)



$C_{11}H_{16}$
M = 148.25 g/mol

Prepared according to the **GP-A**, using **398m** (15.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400m** (6.0 mg, 40% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.26–7.22 (m, 1H), 7.20–7.11 (m, 3H), 2.42 (p, *J* = 7.3 Hz, 1H), 1.81–1.72 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 128.2, 127.8, 125.8, 47.0, 34.6, 21.3, 20.3, 18.9. The analytical data are in accordance with the literature.[128]

3.14 (1-cyclohexylethyl)benzene (400n)

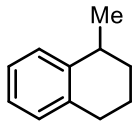


$C_{14}H_{20}$
M = 188.31 g/mol

Prepared according to the **GP-A**, using **398n** (19.0 mg, 0.10 mmol, 1.0 equiv), **399a** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400n** (13.0 mg, 70% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.19–7.12 (m, 3H), 2.43 (p, *J* = 7.1 Hz, 1H), 1.90–1.85 (m, 1H), 1.76–1.71 (m, 1H), 1.63–1.59 (m, 2H), 1.45–134 (m, 2H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.19–1.02 (m, 3H), 0.97–0.75 (m, 2H). **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 147.3, 128.1, 127.9, 125.8, 46.1, 44.3, 31.6, 30.7, 26.6, 19.0. The analytical data are in accordance with the literature.[128]

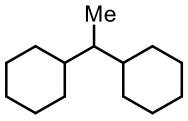
3.15 1-methyl-1,2,3,4-tetrahydronaphthalene (400o)



$C_{11}H_{14}$
M = 146.23 g/mol

Prepared according to the **GP-A**, using **398o** (14.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400o** (8.0 mg, 55% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.20 (m, 1H), 7.15–7.05 (m, 3H), 2.95–2.87 (m, 1H), 2.80–2.73 (m, 2H), 1.97–1.83 (m, 2H), 1.77–1.68 (m, 1H), 1.55–1.50 (m, 1H), 1.29 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 137.0, 129.1, 128.2, 125.7, 125.5, 32.6, 31.6, 30.1, 23.0, 20.5. The analytical data are in accordance with the literature.[132].

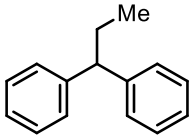
3.16 ethane-1,1-diyldicyclohexane (400p)



$C_{14}H_{26}$
M = 194.36 g/mol

Prepared according to the **GP-A**, using **389p** (19.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400p** (13.0 mg, 65% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.72–1.69. (m, 4H), 1.65–1.61 (m, 4H), 1.32–1.24 (m, 3H), 1.21–1.12 (m, 5H), 1.11–1.06 (m, 1H), 1.04–0.96 (m, 3H), 0.91–0.83 (m, 3H), 0.75 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 39.6, 32.0, 28.9, 26.9, 26.8, 12.2. The analytical data are in accordance with the literature.[128, 123]

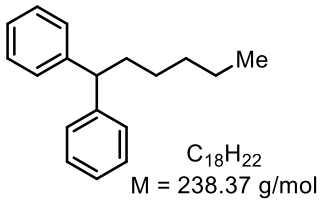
3.17 propane-1,1-diyldibenzene (400q)



$C_{15}H_{16}$
M = 196.29 g/mol

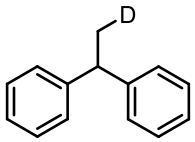
Prepared according to the **GP-A**, using **398q** (19.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400q** (15.0 mg, 75% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 8H), 7.19–7.15 (m, 2H), 3.79 (t, *J* = 7.8 Hz, 1H), 2.08 (p, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 128.5, 128.0, 126.1, 53.4, 28.7, 12.9. The analytical data are in accordance with the literature.[132]

3.18 hexane-1,1-diyldibenzene (400r)



Prepared according to the **GP-A**, using **398r** (24.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400r** (17.0 mg, 70% yield, colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 8H), 7.18–7.14 (m, 2H), 3.88 (t, *J* = 7.8 Hz, 1H), 2.03 (q, *J* = 7.7 Hz, 2H), 1.33–1.22 (m, 6H), 0.86–0.83 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 128.5, 128.0, 126.1, 51.5, 35.8, 32.0, 27.9, 22.7, 14.2. The analytical data are in accordance with the literature.[153]

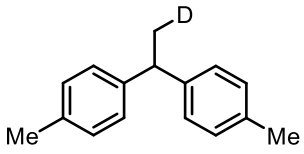
3.19 (ethane-1,1-diyl-2-*d*)dibenzene (398a-d_1)



Prepared according to the **GP-B**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a-d_1** (16.0 mg, 90% yield, Colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 7.25–7.17 (m, 6H), 4.17 (q, *J* = 6.9 Hz, 1H), 1.67–1.62 (m, 2.34H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 146.5, 128.5, 127.8, 126.2, 44.9, 44.8, 44.7, 22.0, 21.9, 21.7, 21.5. The analytical data are in accordance with the literature.[131]

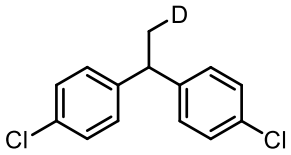
3.20 4,4'-(ethane-1,1-diyl-2-*d*)bis(methylbenzene) (400b-d_1)



$C_{16}H_{17}D$
M = 211.33 g/mol

Prepared according to the **GP-B**, using **398b** (21.0 mg, 0.10 mmol, 1.0 equiv), **299** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400b-d_1** (17.0 mg, 80% yield, Colorless liquid). **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.12–7.05 (m, 8H), 4.04 (q, *J* = 7.0 Hz, 1H), 2.23 (s, 6H), 1.50 (t, *J* = 7.3 Hz, 2.24H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 135.5, 129.2, 127.6, 44.1, 44.0, 43.9, 22.1, 22.0, 21.8, 21.6, 21.1. The analytical data are in accordance with the literature.[157]

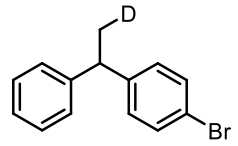
3.21 4,4'-(ethane-1,1-diyl-2-*d*)bis(chlorobenzene) (400c-d_1)



$C_{14}H_{11}DCl_2$
M = 252.15 g/mol

Prepared according to the **GP-B**, using **398c** (25.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400c-d_1** (23.0 mg, 90% yield, Colorless liquid). **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{14}H_{12}DCl_2^+$ 252.0452; found 252.0446. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.36–7.31 (m, 4H), 7.29–7.24 (m, 4H), 4.19 (q, *J* = 6.9 Hz, 1H), 1.53 (t, *J* = 7.3 Hz, 2.18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 132.1, 129.0, 128.7, 43.7, 43.6, 43.6, 21.9, 21.8, 21.6, 21.4.

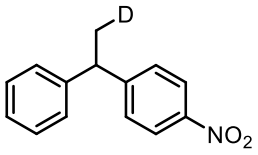
3.22 1-bromo-4-(1-phenylethyl-2-*d*)benzene (400f-d_1)



$C_{14}H_{12}DBr$
M = 262.16 g/mol

Prepared according to the **GP-B**, using **398f** (26.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400f-*d*$_1$** (24.0 mg, 90% yield, Colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.33–7.29 (m, 2H), 7.23–7.19 (m, 3H), 7.12–7.08 (m, 2H), 4.12 (t, *J* = 7.0 Hz, 1H), 1.62 (tt, *J* = 6.9, 1.9 Hz, 2.09H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 145.5, 131.5, 129.5, 128.6, 127.7, 126.4, 119.9, 44.3, 44.3, 44.2, 21.9, 21.8, 21.6, 21.4.

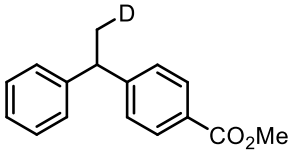
3.23 1-nitro-4-(1-phenylethyl-2-*d*)benzene (400i-*d*$_1$)



$C_{14}H_{12}DNO_2$
M = 228.27 g/mol

Prepared according to the **GP-B**, using **398i** (23.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400i-*d*$_1$** (6.0 mg, 25% yield, Colorless liquid). **HRMS** (ESI) *m/z*: [$(M+Na)^+$]: calcd for $C_{14}H_{12}DNO_2Na^+$ 251.0901; found 251.0900. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.18–8.13 (m, 2H), 7.57–7.53 (m, 2H), 7.34–7.27 (m, 4H), 7.23–7.18 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 1H), 1.61 (t, *J* = 7.3 Hz, 2.47H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 146.5, 144.7, 128.9, 128.6, 127.7, 126.8, 123.8, 44.9, 44.8, 44.7, 21.6, 21.5, 21.4, 21.2.

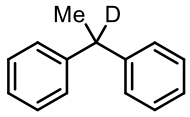
3.24 methyl 4-(1-phenylethyl-2-*d*)benzoate (400j-*d*$_1$)



$C_{16}H_{15}DO_2$
M. W: 241.30 g/mol

Prepared according to the **GP-B**, using **398j** (24.0 mg, 0.10 mmol, 1.0 equiv), **399** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400j-*d*$_1$** (13.0 mg, 55% yield, Colorless liquid). **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.89–7.86 (m, 2H), 7.42–7.40 (m, 2H), 7.31–7.25 (m, 4H), 7.20–7.16 (m, 1H), 4.25 (q, *J* = 6.7 Hz, 1H), 3.82 (s, 3H), 1.58 (t, *J* = 7.3 Hz, 2.20H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 151.9, 145.6, 129.9, 128.6, 128.1, 127.8, 127.7, 126.5, 52.2, 44.9, 44.9, 44.8, 21.7, 21.6, 21.4, 21.2. The analytical data are in accordance with the literature.[158]

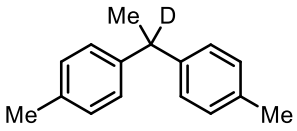
3.25 (ethane-1,1-diyl-1-*d*)dibenzene (400a-*d*$_1$′)



$C_{14}H_{13}D$
M. W: 183.27 g/mol

Prepared according to the **GP-A**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), **399-*d*$_2$** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a-*d*$_1$′** (16.0 mg, 90% yield, Colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 4H), 7.24–7.16 (m, 6H), 4.16 (q, *J* = 7.2 Hz, 0.20H), 1.64 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 146.4, 128.5, 127.7, 126.2, 44.9, 44.6, 44.5, 44.3, 22.0, 21.9. The analytical data are in accordance with the literature.[130]

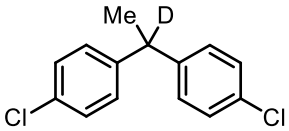
3.26 4,4'-(ethane-1,1-diyl-1-*d*)bis(methylbenzene) (400b-*d*$_1$′)



$C_{16}H_{17}D$
M = 211.32 g/mol

Prepared according to the **GP-A**, using **398b** (21.0 mg, 0.10 mmol, 1.0 equiv), **399-*d*$_2$** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400b-*d*$_1$′** (16.0 mg, 75% yield, Colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12–7.07 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 0.28H), 2.30 (s, 6H), 1.60 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 143.7, 135.5, 129.2, 127.5, 44.1, 43.8, 43.6, 43.4, 22.1, 22.0, 21.1. The analytical data are in accordance with the literature.[130]

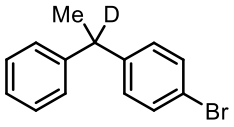
3.27 4,4'-(ethane-1,1-diyl-1-*d*)bis(chlorobenzene) (400c-*d*$_1$′)



$C_{14}H_{11}DCl_2$
M = 252.15 g/mol

Prepared according to the **GP-A**, using **398c** (25.0 mg, 0.10 mmol, 1.0 equiv), **399-*d*$_2$** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 μmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **3c-*d*$_1$′** (20.0 mg, 80% yield, Colorless liquid). **HRMS** (ESI) *m/z*: [$(M+H)^+$]: calcd for $C_{14}H_{12}DCl_2^+$ 252.0452; found 252.0446. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 4H), 7.12–7.09 (m, 4H), 4.09 (q, *J* = 7.1 Hz, 0.27H), 1.58 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 144.4, 132.1, 129.0, 128.7, 43.7, 43.5, 43.3, 43.1, 21.9, 21.8.

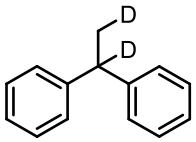
3.28 1-bromo-4-(1-phenylethyl-1-*d*)benzene (400f-*d*$_1$′)



$C_{14}H_{12}DBr$
M = 262.16 g/mol

Prepared according to the **GP-A**, using **398f** (26.0 mg, 0.10 mmol, 1.0 equiv), **399-*d*$_2$** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 μmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400f-*d*$_1$′** (23.0 mg, 88% yield, Colorless liquid). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.31–7.27 (m, 2H), 7.22–7.17 (m, 3H), 7.11–7.08 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 0.28H), 1.62 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 145.8, 145.5, 145.5, 131.5, 129.5, 128.6, 127.6, 126.4, 119.9, 44.4, 44.1, 43.9, 43.7, 21.9, 21.7. The analytical data are in accordance with the literature.[130].

3.29 (ethane-1,1-diyl-1,2-*d*$_2$)dibenzene (400a-*d*$_2$)



$C_{14}H_{12}D_2$
M = 184.27 g/mol

Prepared according to the **GP-B**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), **399-*d*$_2$** (36.0 mg, 0.30 mmol, 3.0 equiv), D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 μmol, 10 mol %). Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a-*d*$_2$** (16.0 mg, 85% yield, Colorless liquid). **^{1}H NMR** (400 MHz,

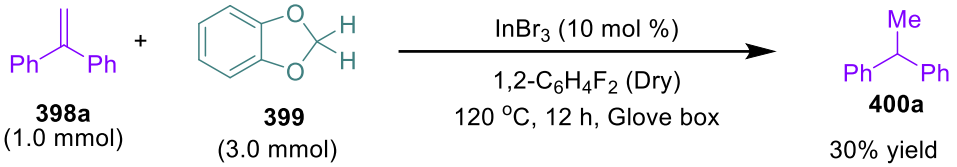
$CDCl_3$) δ 7.31–7.27 (m, 4H), 7.24–7.16 (m, 6H), 4.16 (q, *J* = 6.9 Hz, 0.27H), 1.65–1.60 (m, 2.10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 146.5, 128.5, 127.8, 126.2, 44.9, 44.8, 44.8, 44.7, 22.0, 21.9, 21.8, 21.7, 21.6, 21.5, 21.4. The analytical data are in accordance with the literature.[156]

***Note**: **1**- In ^{1}H NMR of deuterium labeled compounds we have taken values of no. of protons in decimals for ex. 0.28 to indicate the amount of deuterium labeling.*

***2**- The ^{1}H NMR for compounds **400b-d_1, 400c-d_1**, **400i-d_1**,* and ***400j-d_1** recorded in DMSO-d_6 because the peak for methyl protons was merging with water peak in $CDCl_3$ solvent, which creates problem in determining deuterium labeling %.*

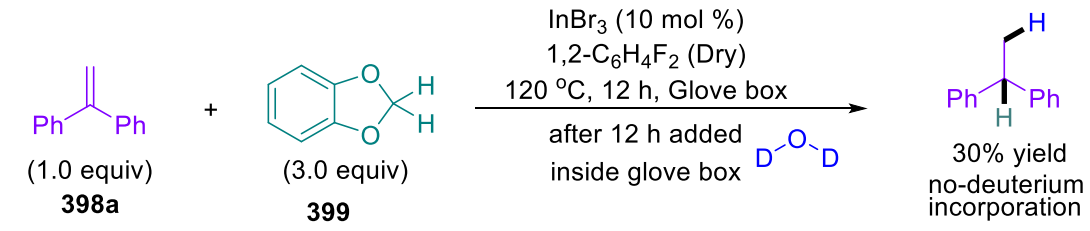
4. Control experiments

4.1. Reaction under completely dried system and glove box



According to **GP-B**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), dry **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %) added inside glove box. Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a** (5.0 mg, 30% yield, Colorless liquid).

4.2. Identification of π-bond activation by $InBr_3$



According to **GP-B**, using **398a** (18.0 mg, 0.10 mmol, 1.0 equiv), dry **399** (36.0 mg, 0.30 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). After 12 h of reflux the reaction tube was taken inside glove box and D_2O (6.0 mg, 0.30 mmol, 3.0 equiv), was added. Purification by column chromatography on silica gel using petroleum ether as eluent afforded the product **400a** (5.0 mg, 30% yield, Colorless liquid).

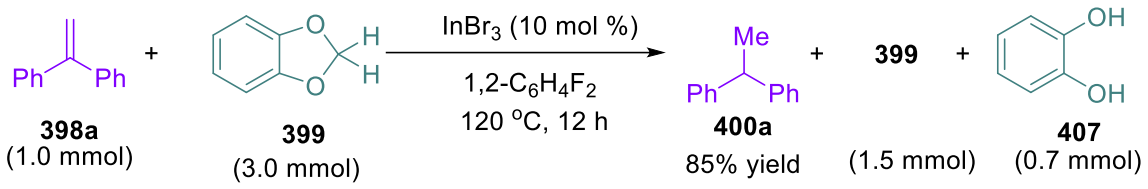
4.3. Identification of formic acid and other side products

According to **GP-A**, using **398a** (54.0 mg, 0.30 mmol, 3.0 equiv), **399** (12.0 mg, 0.10 mmol, 1.0 equiv), and indium tribromide ($InBr_3$) (4.0 mg, 10 µmol, 10 mol %). After 12 h reflux, the crude

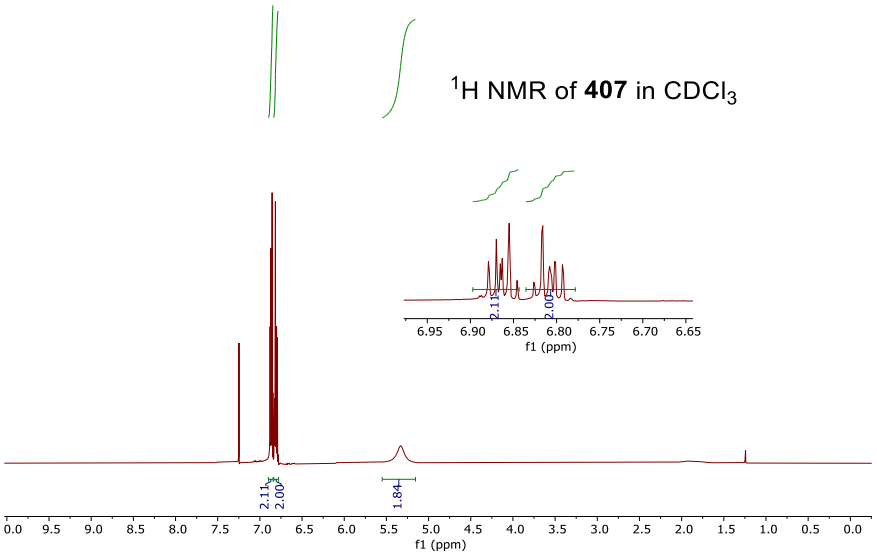
reaction mixture analyzed by ^{1}H-NMR. Also after isolation of product **400a** from column chromatography (in petroleum ether), 40%EtOAc+Petroleum ether was added and isolated the last part and recorded the ^{1}H-NMR. The formation of chatechol was found.

***Note**: **1**- Here we have used reverse equivalencies of **398a** and **399** because with standard reaction conditions the peak for formic acid and other intermediate was not visible in crude ^{1}H-NMR.*

5. Scale-up reaction setup

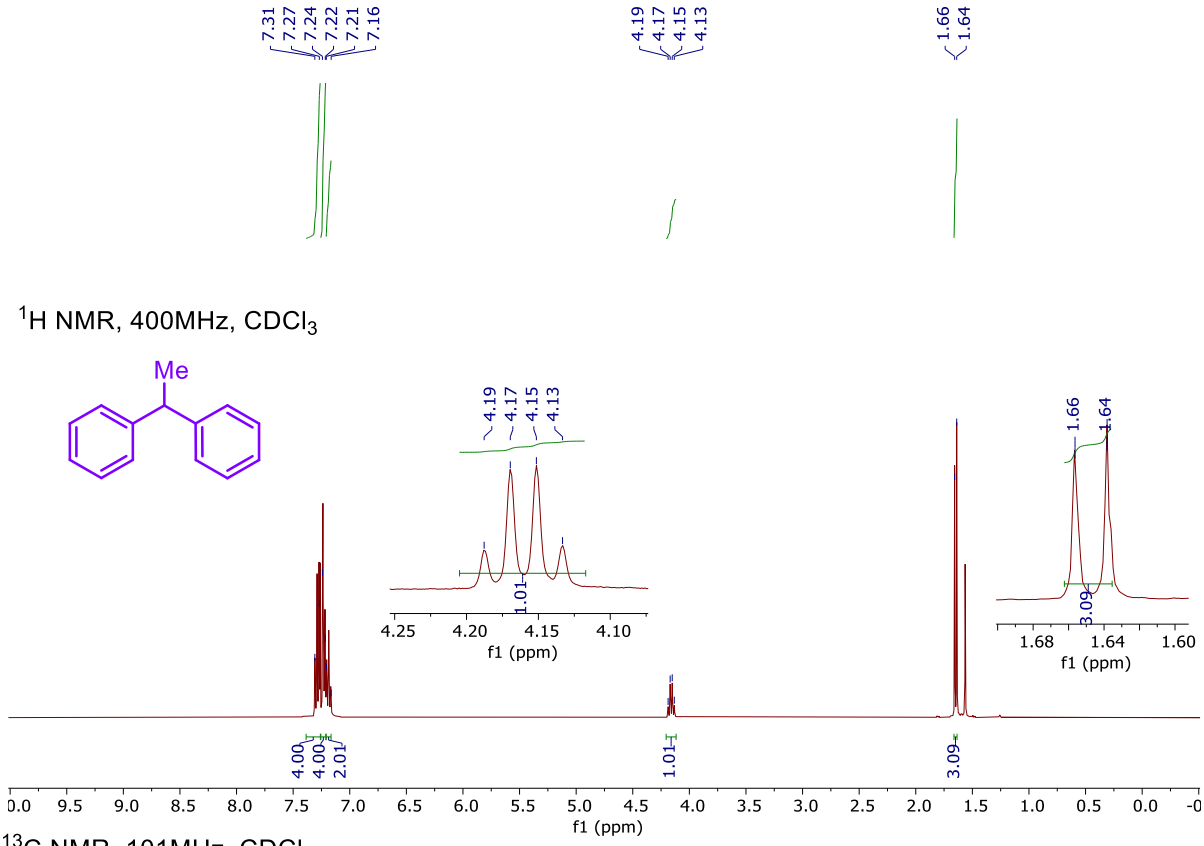


According to **GP-A**, using **398a** (180.0 mg, 1.0 mmol, 1.0 equiv), **399** (366.0 mg, 3.0 mmol, 3.0 equiv), and indium tribromide ($InBr_3$) (35.0 mg, 0.1 mmol, 10 mol %) added 2.5 ml of 1,2-difluorobenzene. After 12 h reflux at 120 ^{o}C reaction mixture quenched with DCM and washed with water. Organic layer was dried over anhydrous Na_2SO_4. The compound **400a** (155.0 mg, 85 % yield, colorless liquid) isolated by column chromatography (in petroleum ether), 1%EtOAc+Petroleum ether was added and recovered **399**(183.0 mg, 1.5 mmol). At last 30% EtOAc+Petroleum ether was added and isolated catechol **407** (77.0 mg, 0.7 mmol, brown solid).

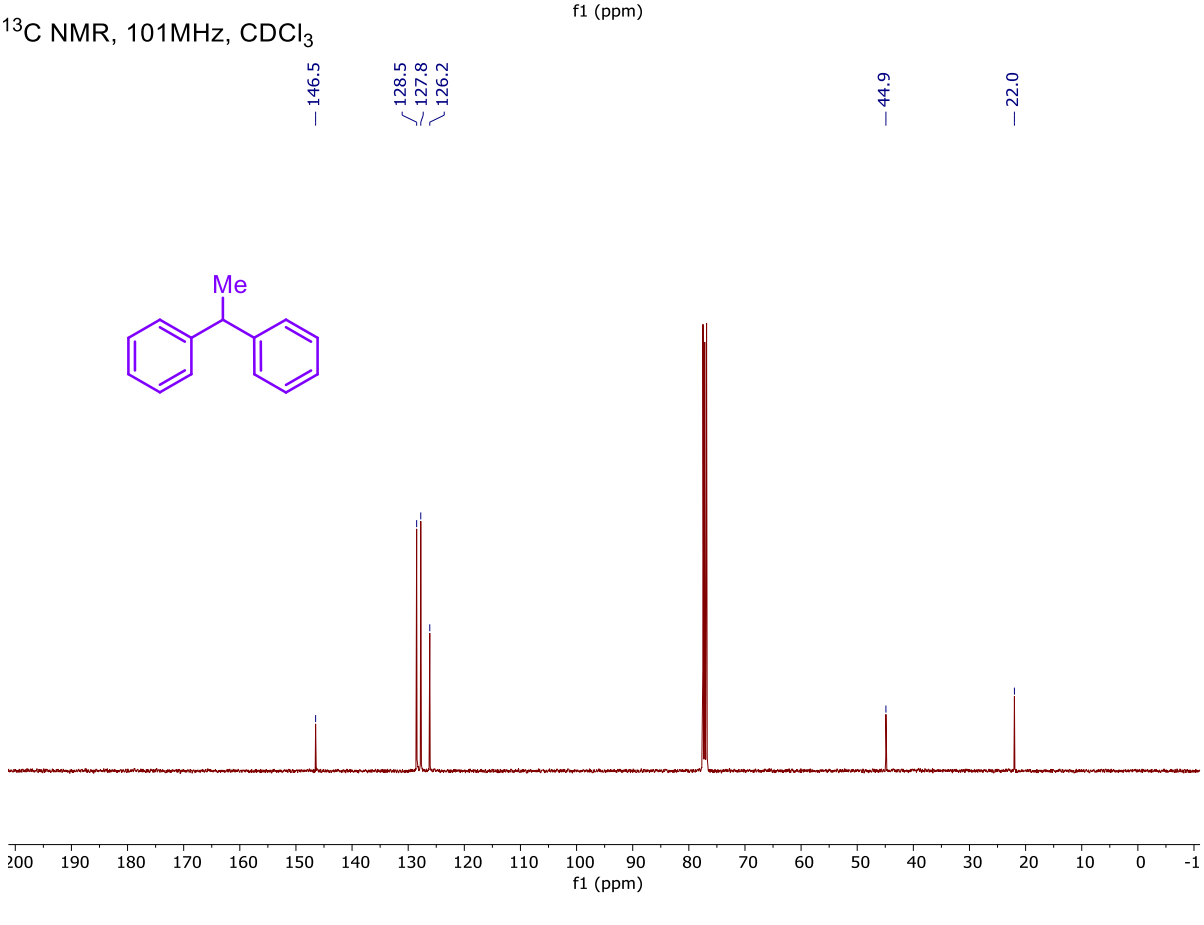


6. Experimental NMR Data

ethane-1,1-diyldibenzene (400a)



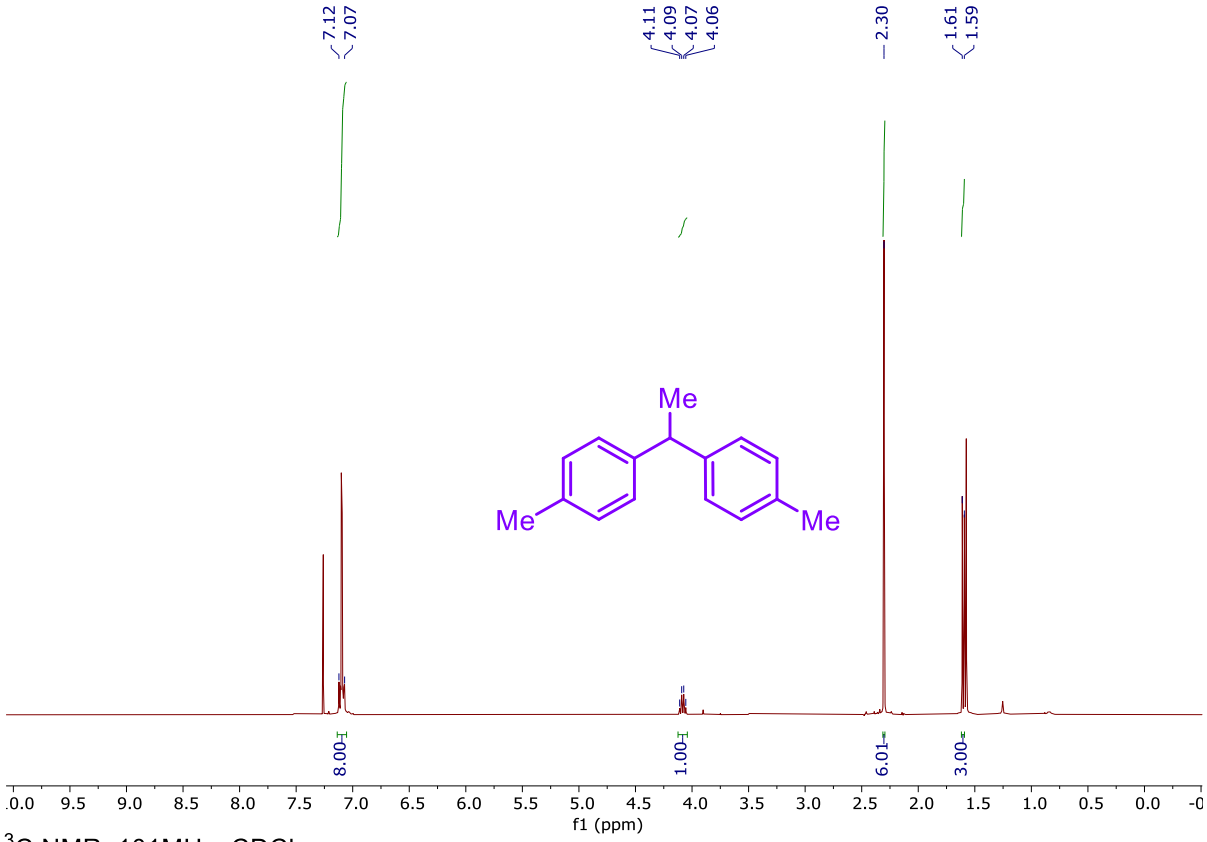
^{1}H NMR, 400MHz, $CDCl_3$



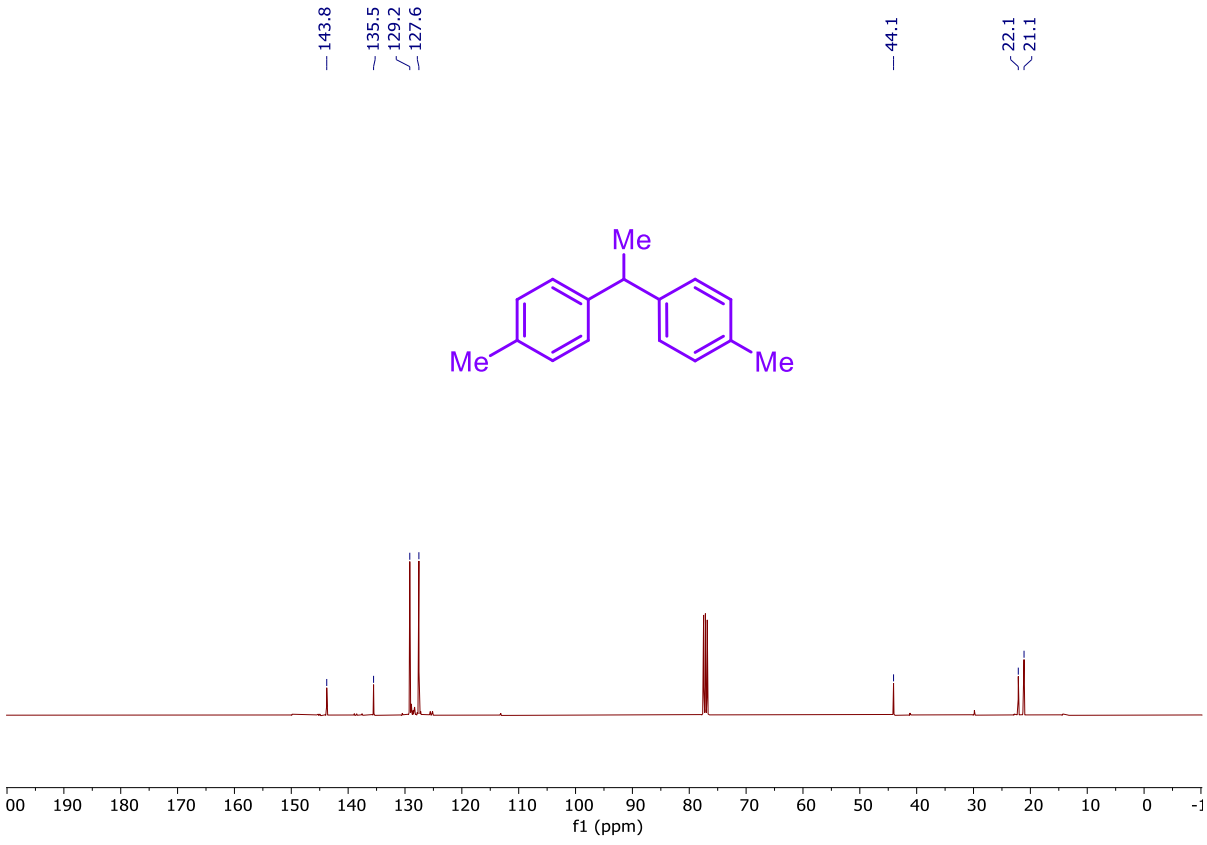
^{13}C NMR, 101MHz, $CDCl_3$

4,4'-(ethane-1,1-diyl)bis(methylbenzene) (400b)

^{1}H NMR, 400MHz, $CDCl_3$

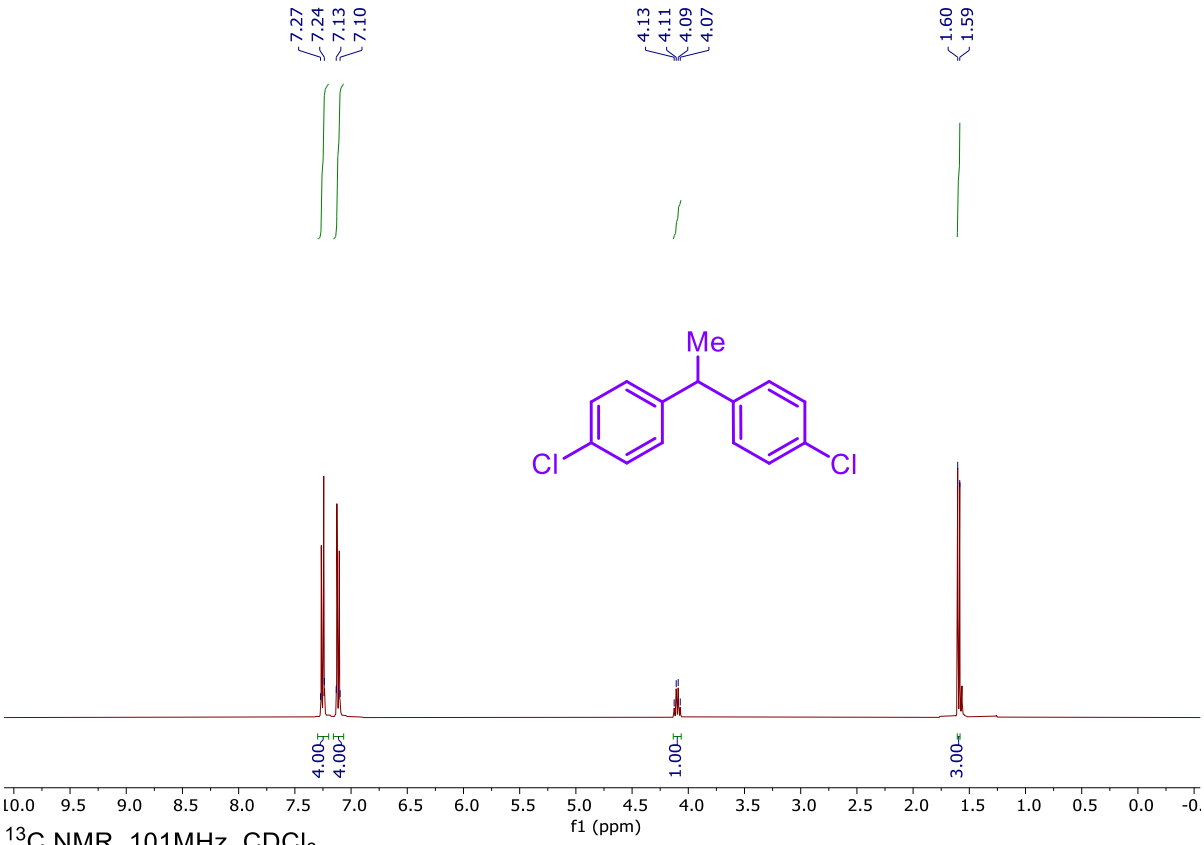


^{13}C NMR, 101MHz, $CDCl_3$

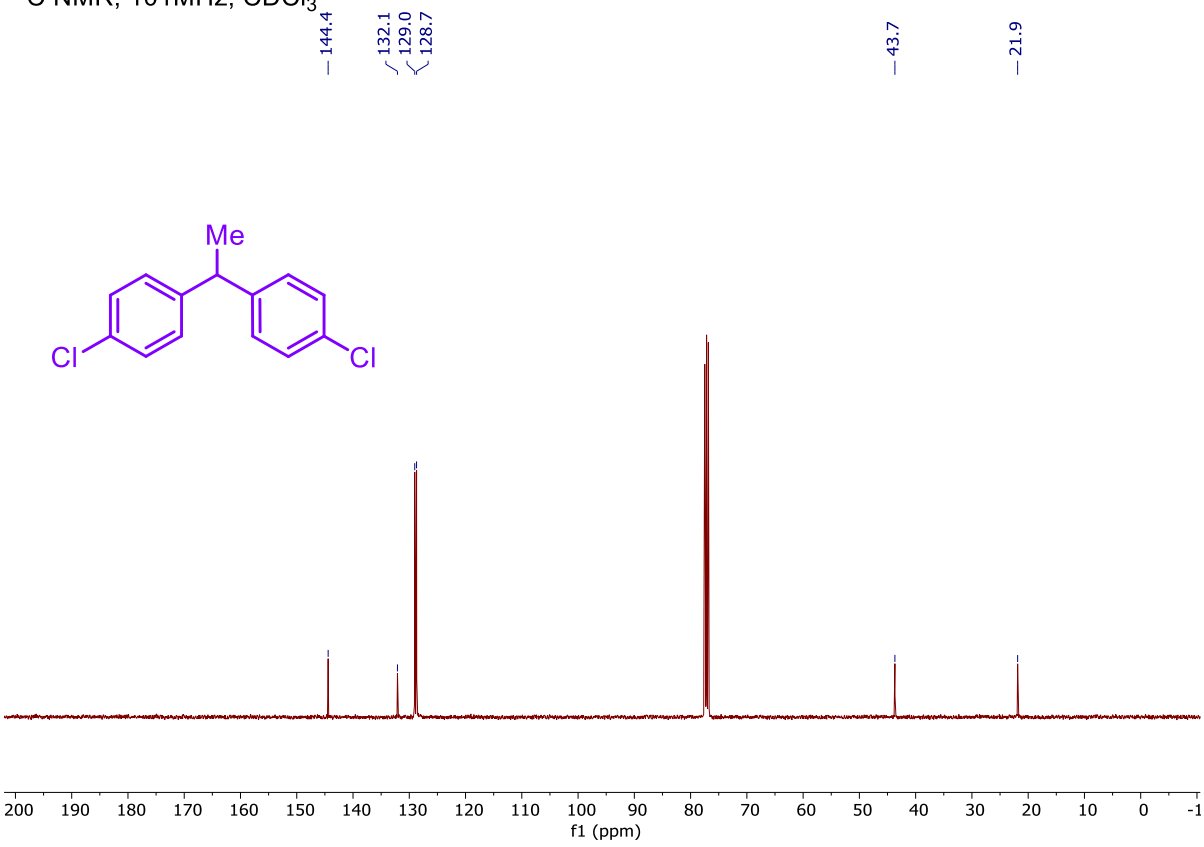


4,4'-(ethane-1,1-diyl)bis(chlorobenzene) (400c)

^{1}H NMR, 400MHz, $CDCl_3$

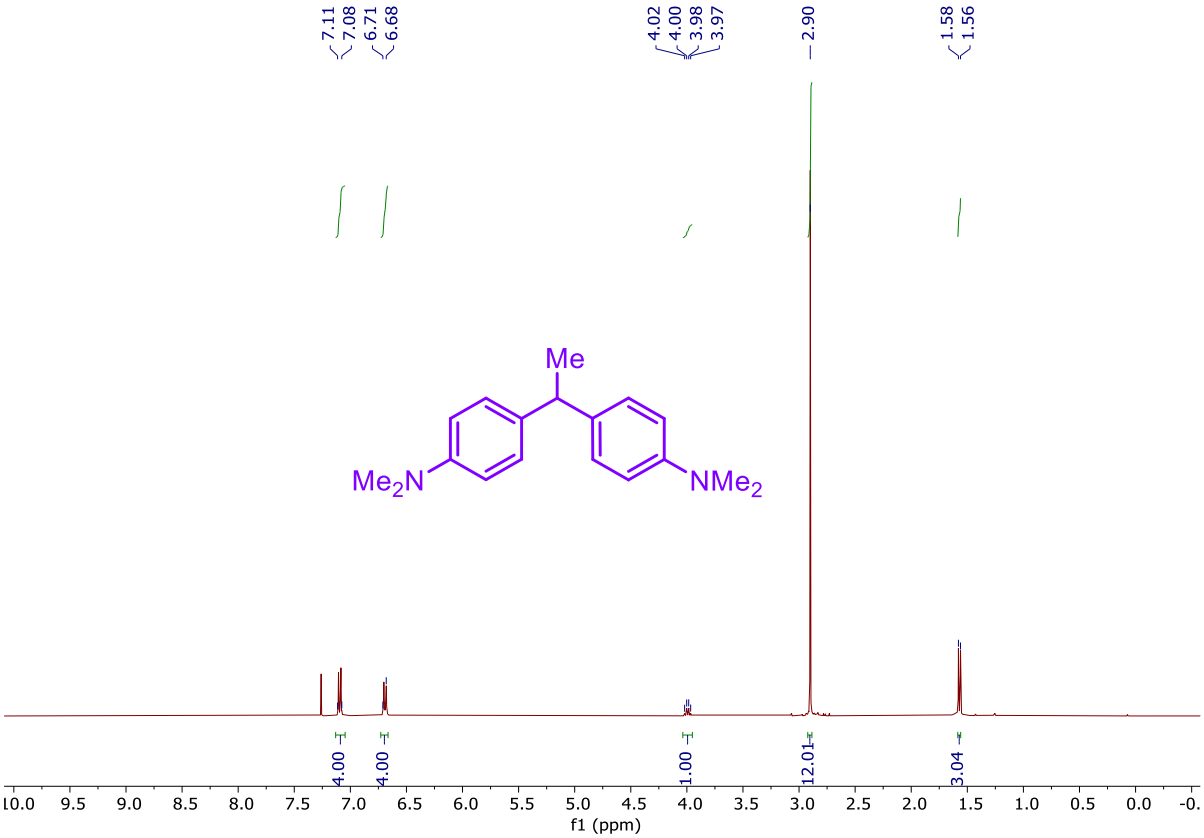


^{13}C NMR, 101MHz, $CDCl_3$

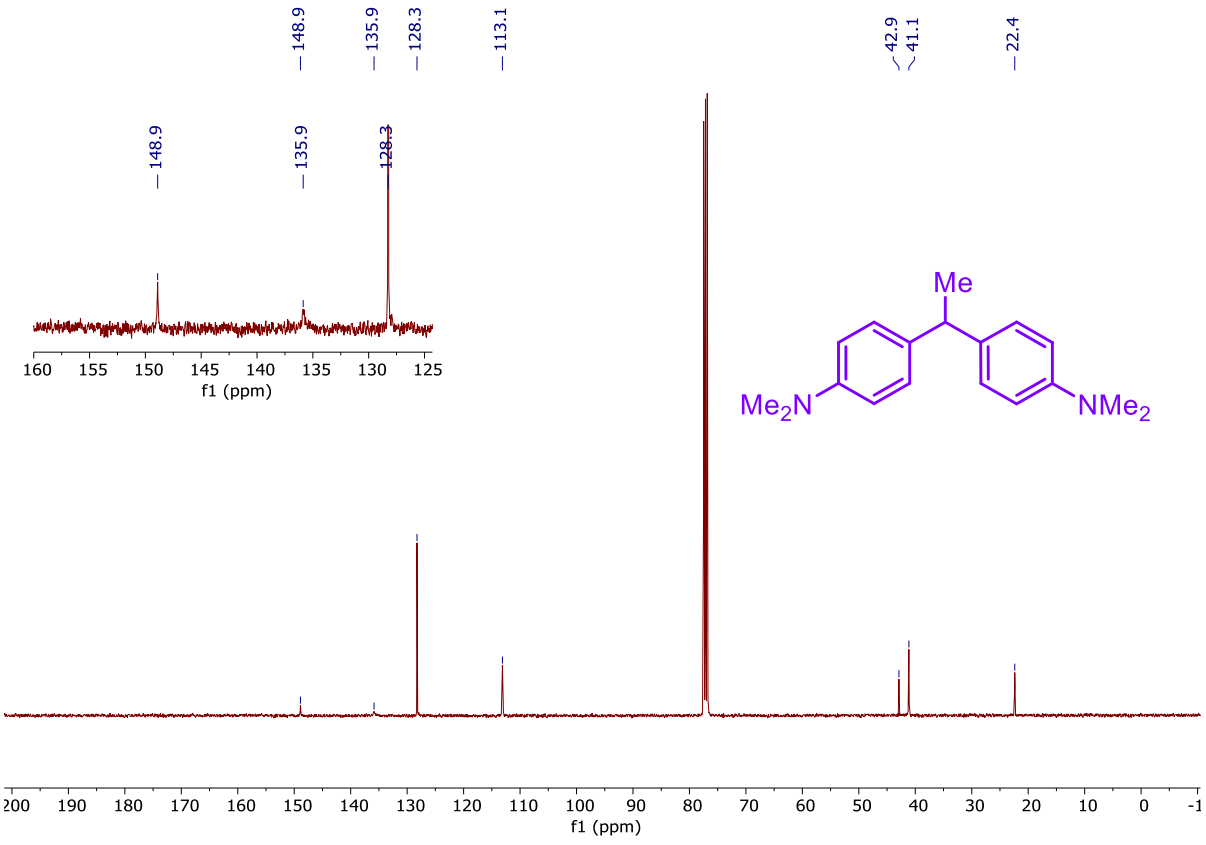


4,4'-(ethane-1,1-diyl)bis(*N*,*N*-dimethylaniline) (400d)

^{1}H NMR, 400MHz, $CDCl_3$

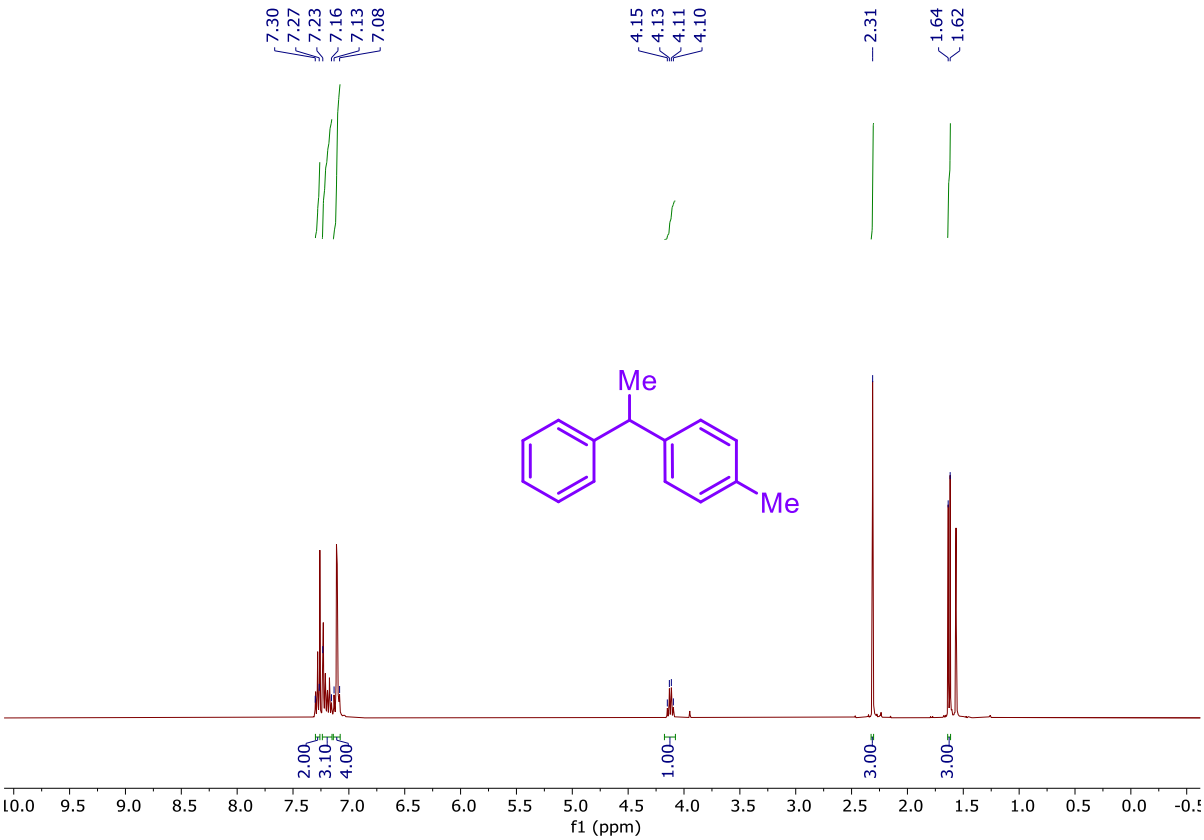


^{13}C NMR, 101MHz, $CDCl_3$

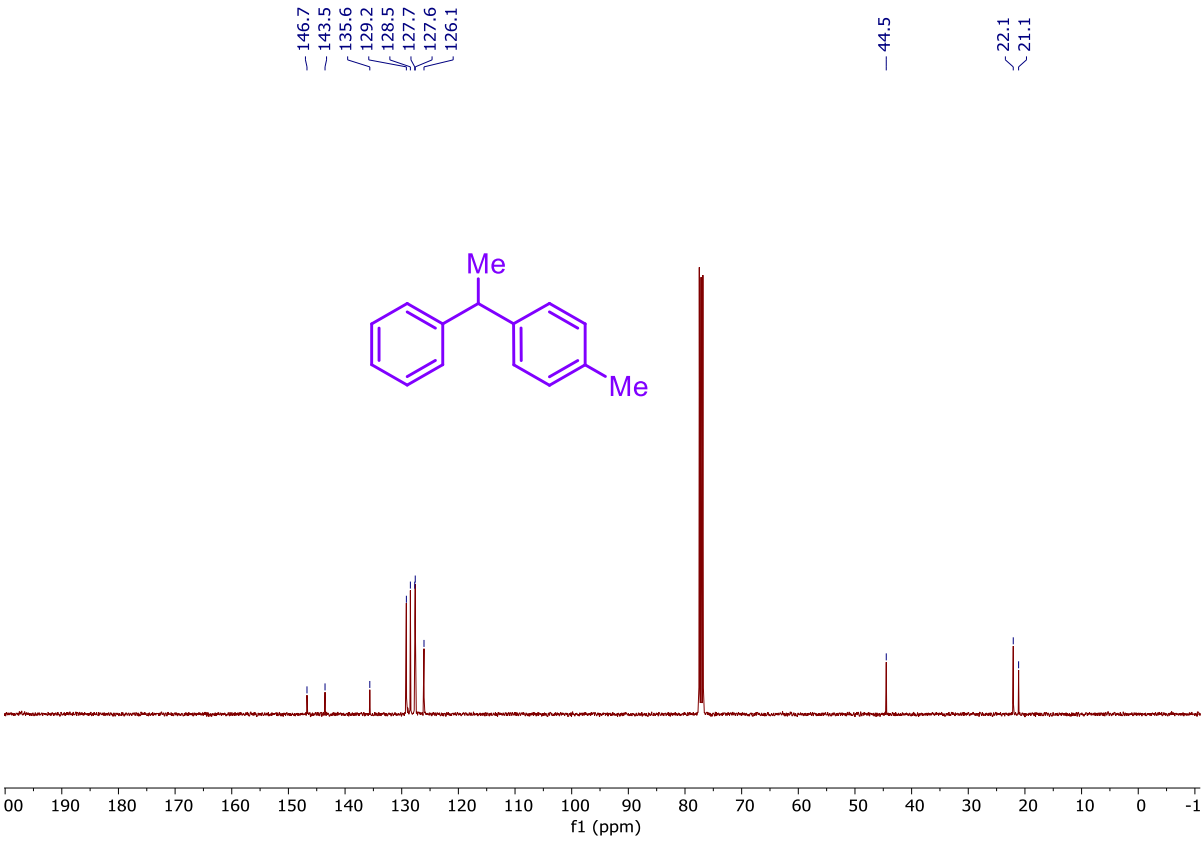


1-methyl-4-(1-phenylethyl)benzene (400e)

^{1}H NMR, 400MHz, $CDCl_3$

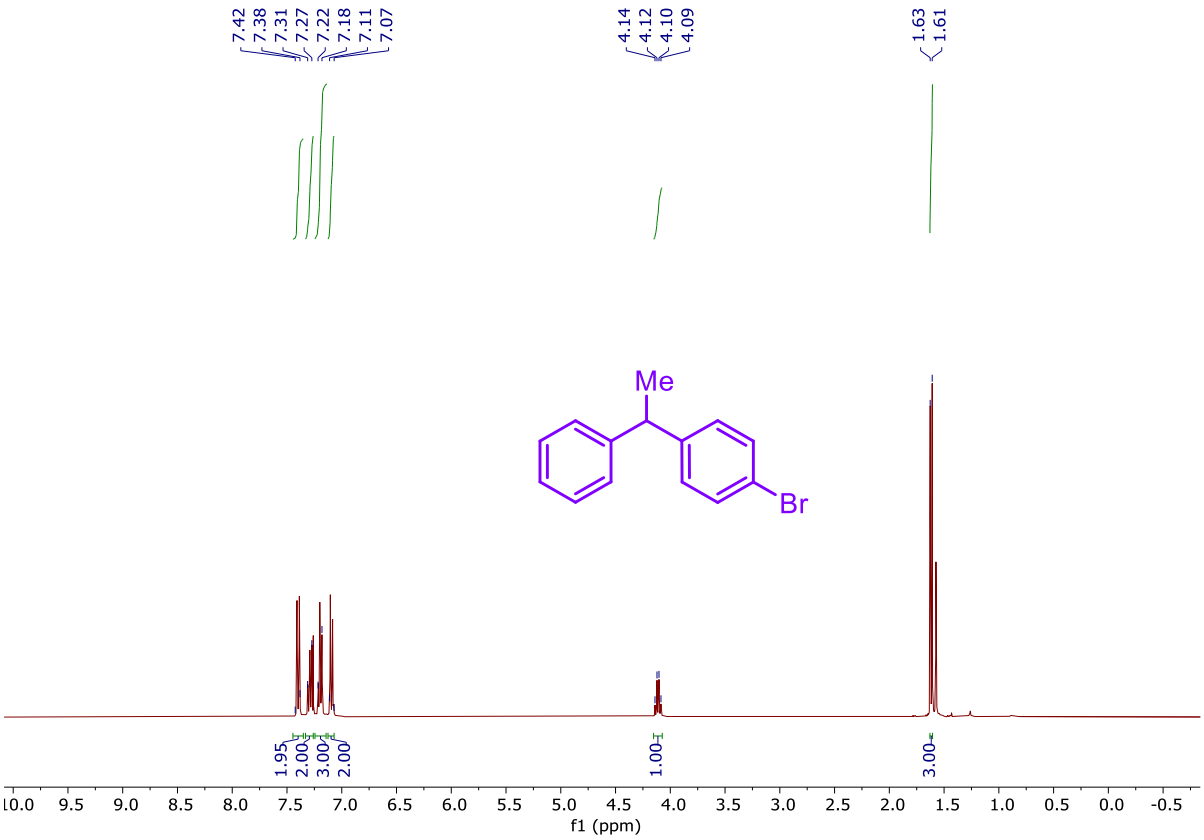


^{13}C NMR, 101MHz, $CDCl_3$

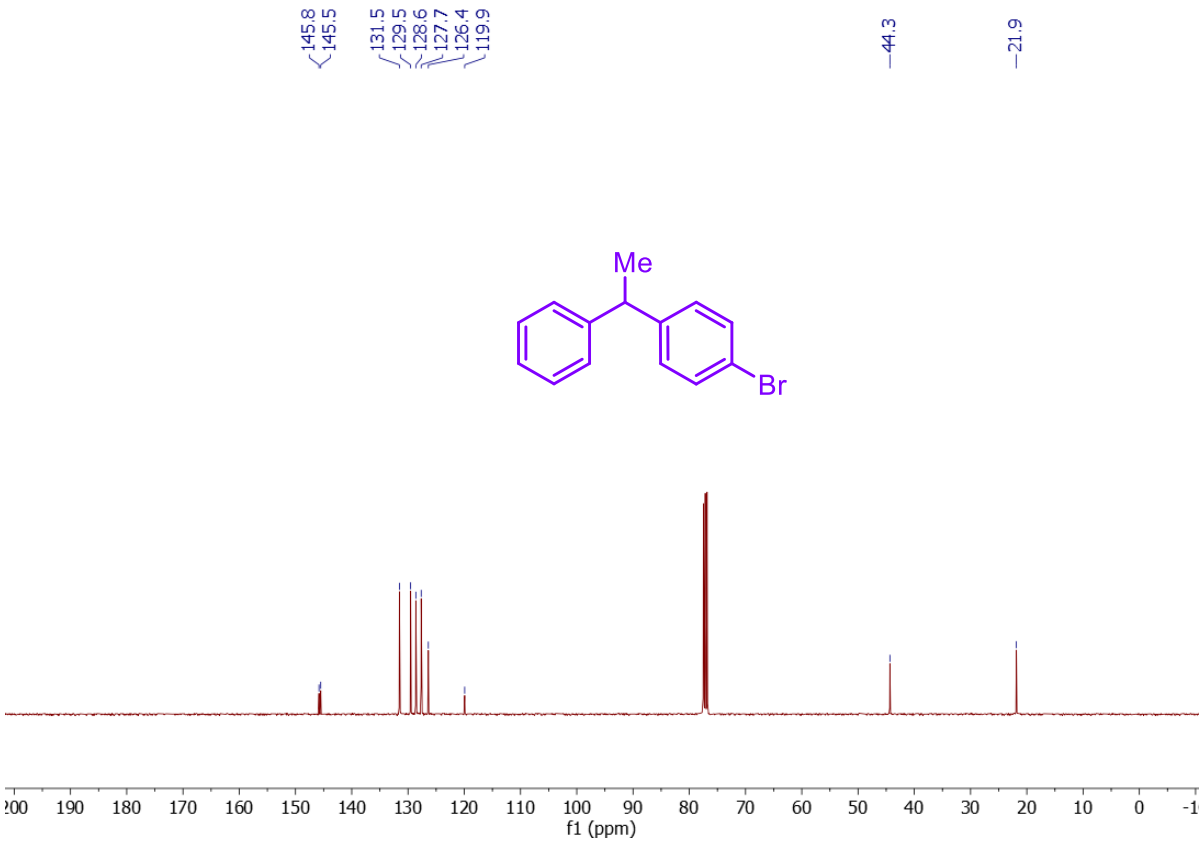


1-bromo-4-(1-phenylethyl)benzene (400f)

^{1}H NMR, 400MHz, $CDCl_3$

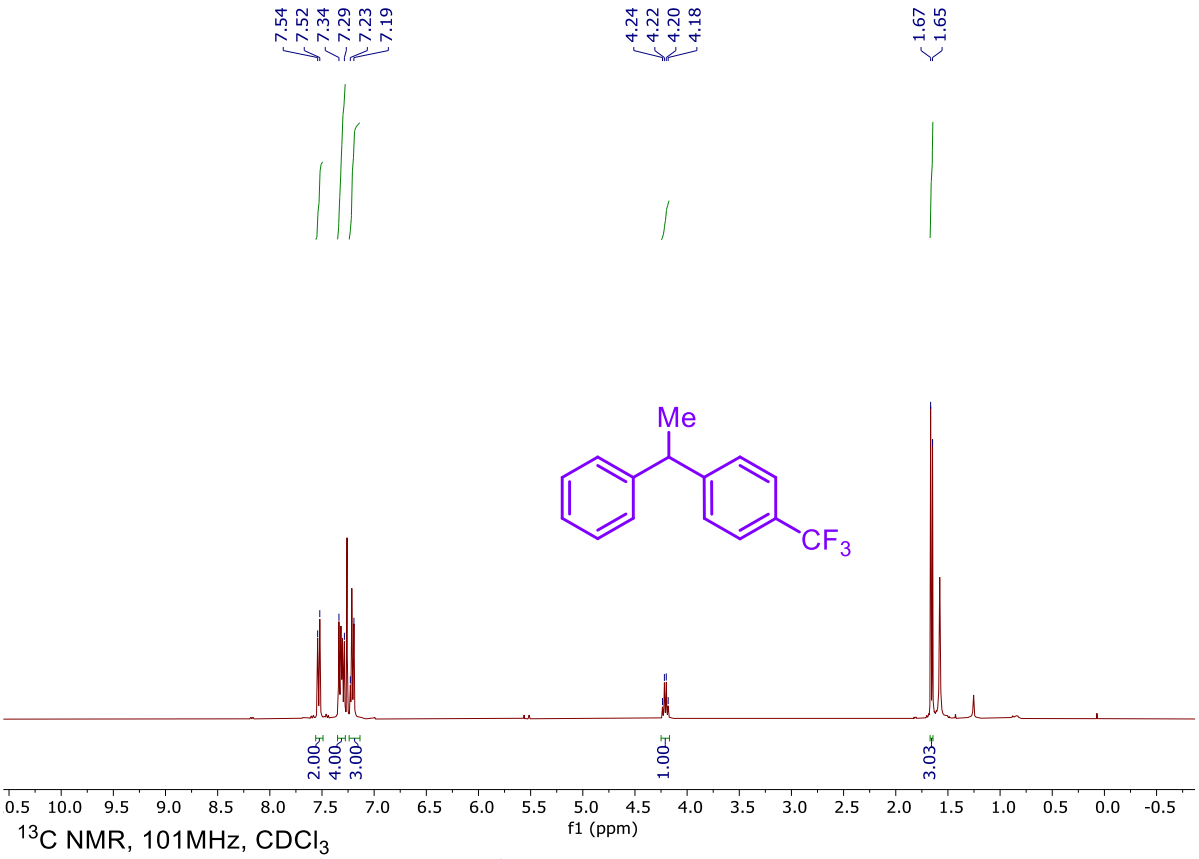


^{13}C NMR, 101MHz, $CDCl_3$

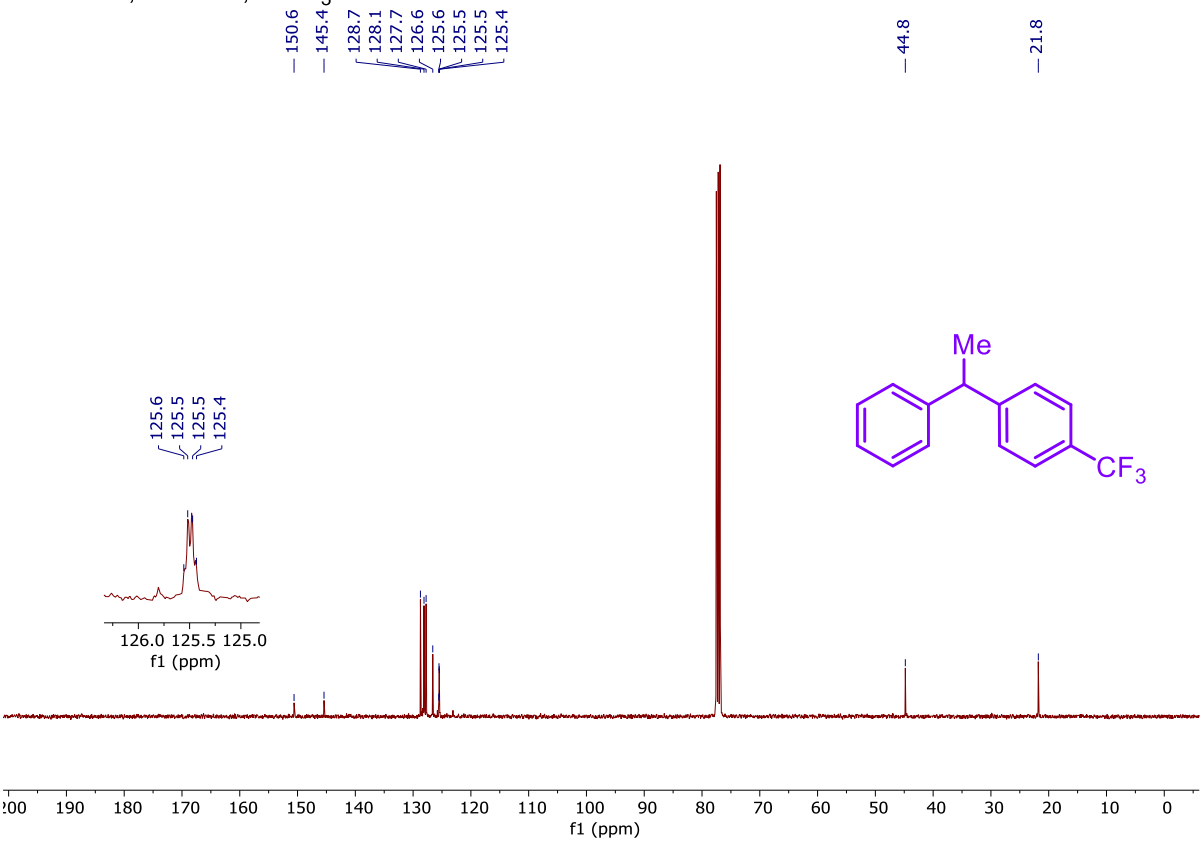


1-(1-phenylethyl)-4-(trifluoromethyl)benzene (400g)

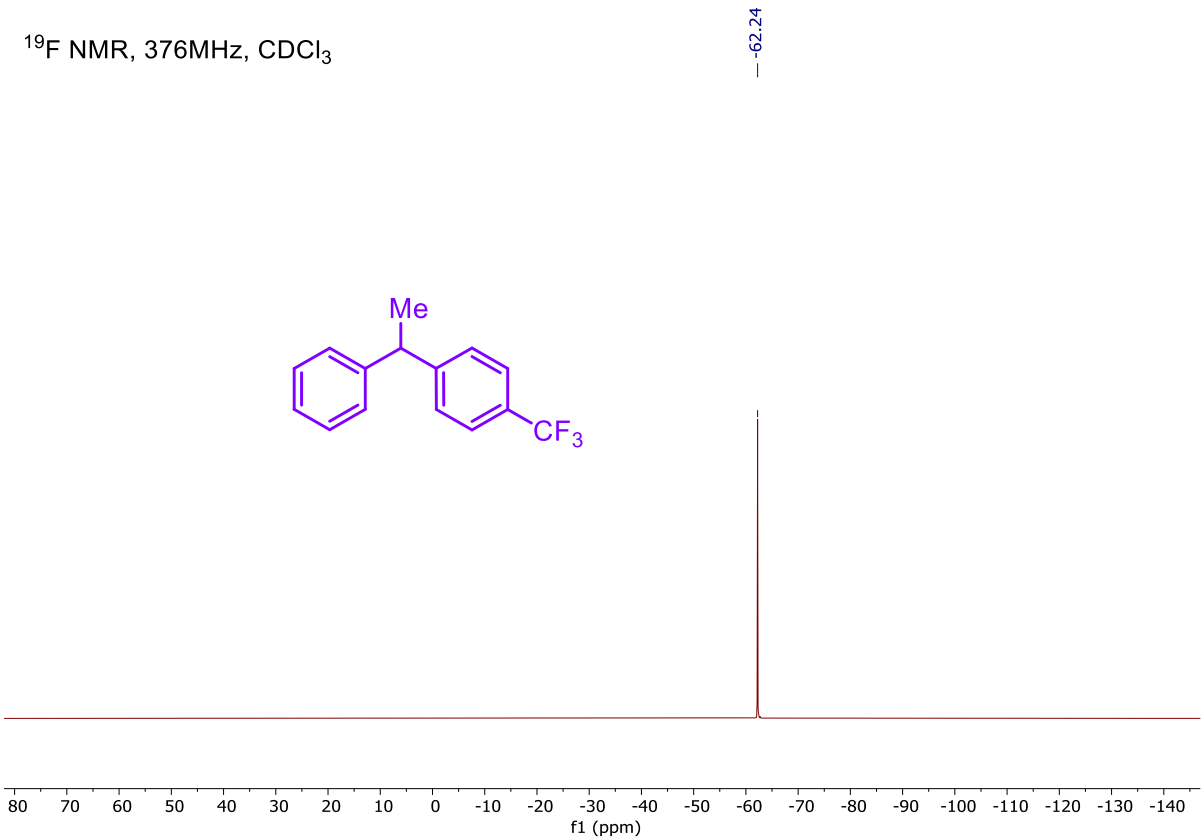
^{1}H NMR, 400MHz, $CDCl_3$



^{13}C NMR, 101MHz, $CDCl_3$

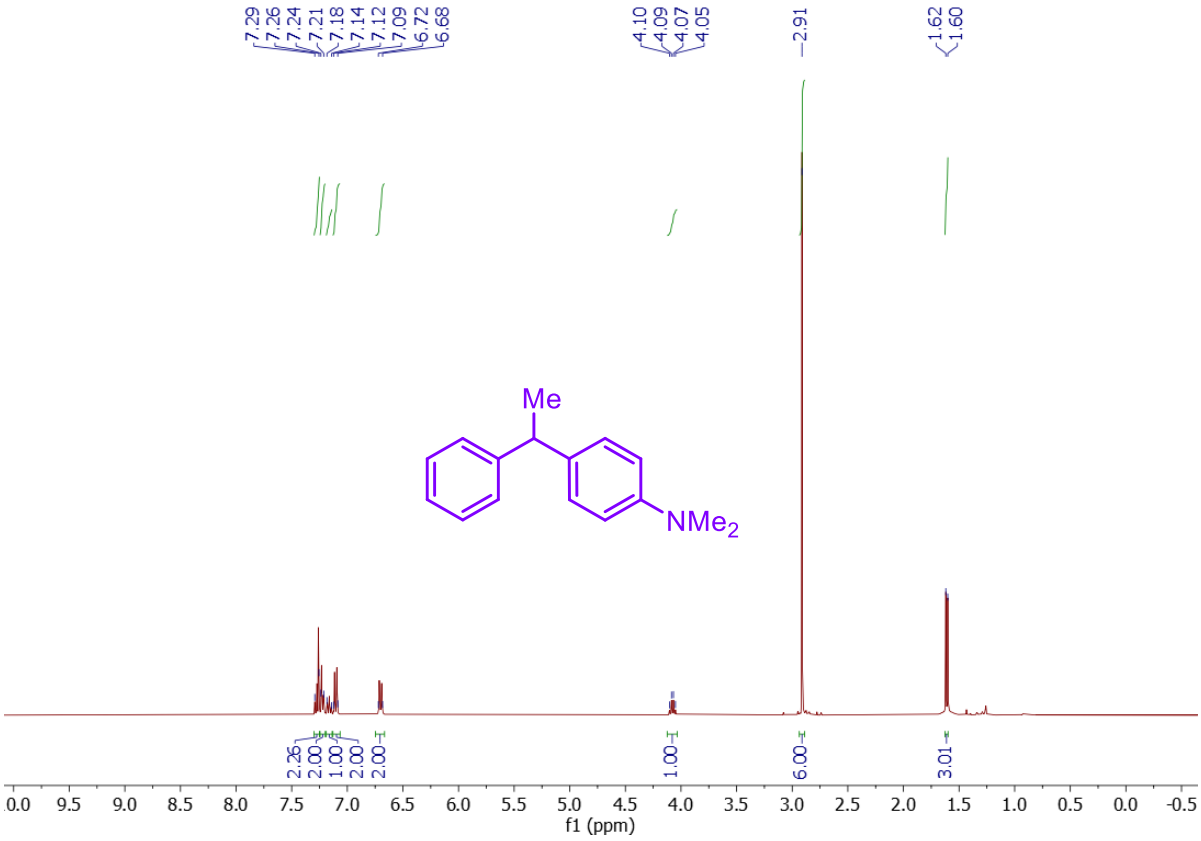


^{19}F NMR, 376MHz, $CDCl_3$

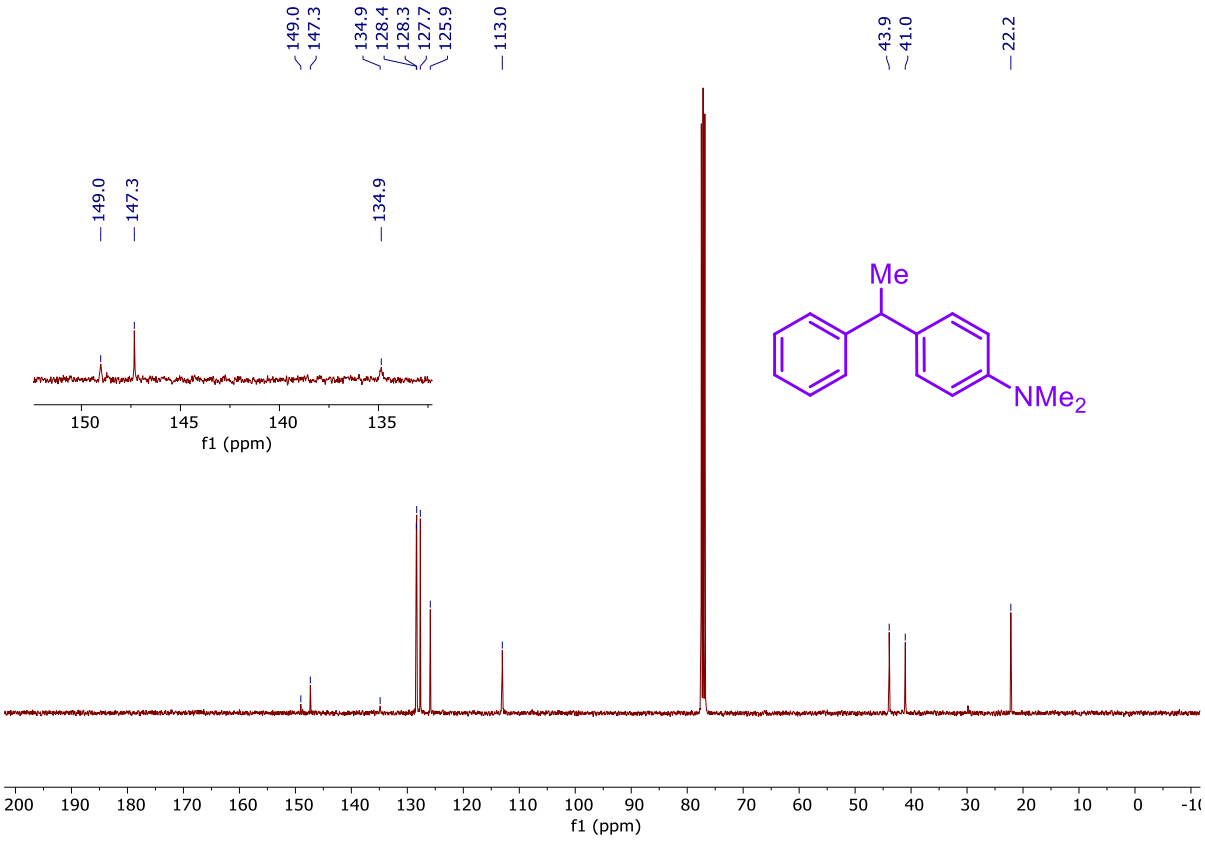


N,N-dimethyl-4-(1-phenylethyl)aniline (400h)

^{1}H NMR, 400MHz, $CDCl_3$

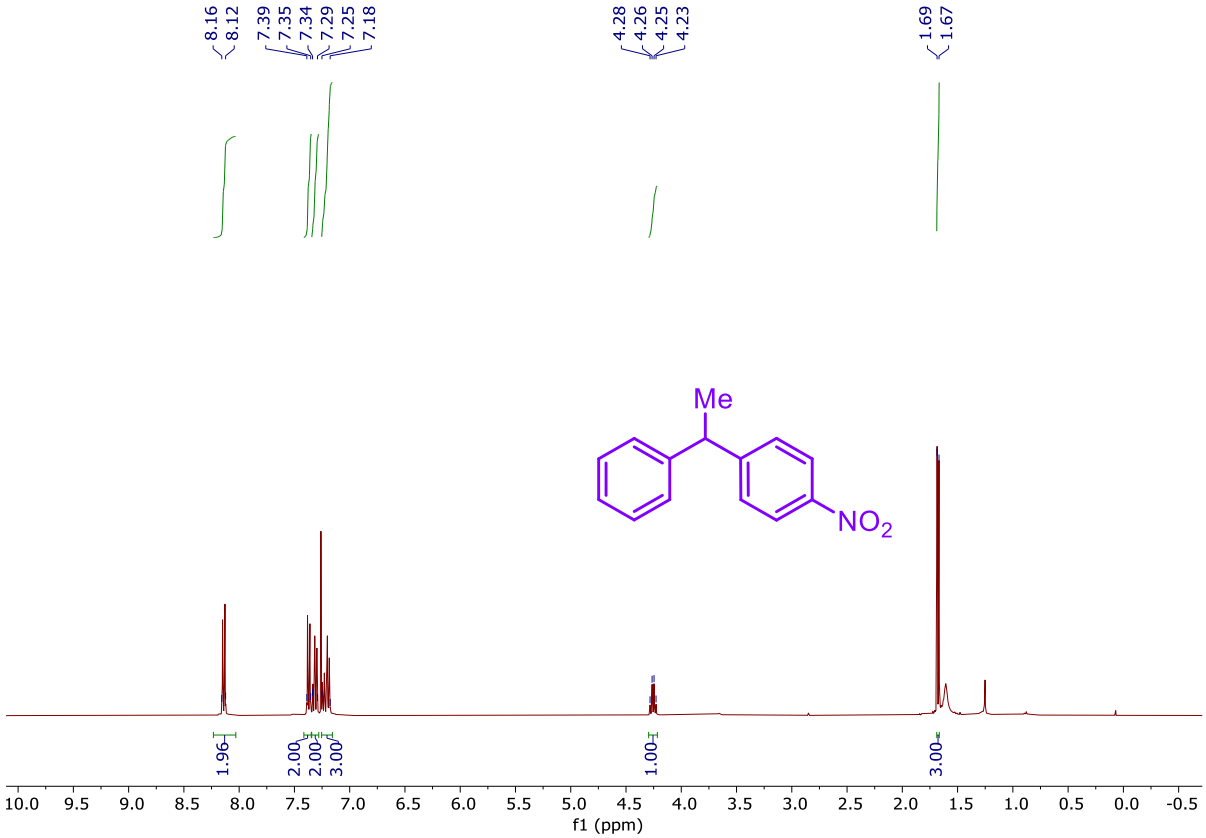


^{13}C NMR, 101MHz, $CDCl_3$

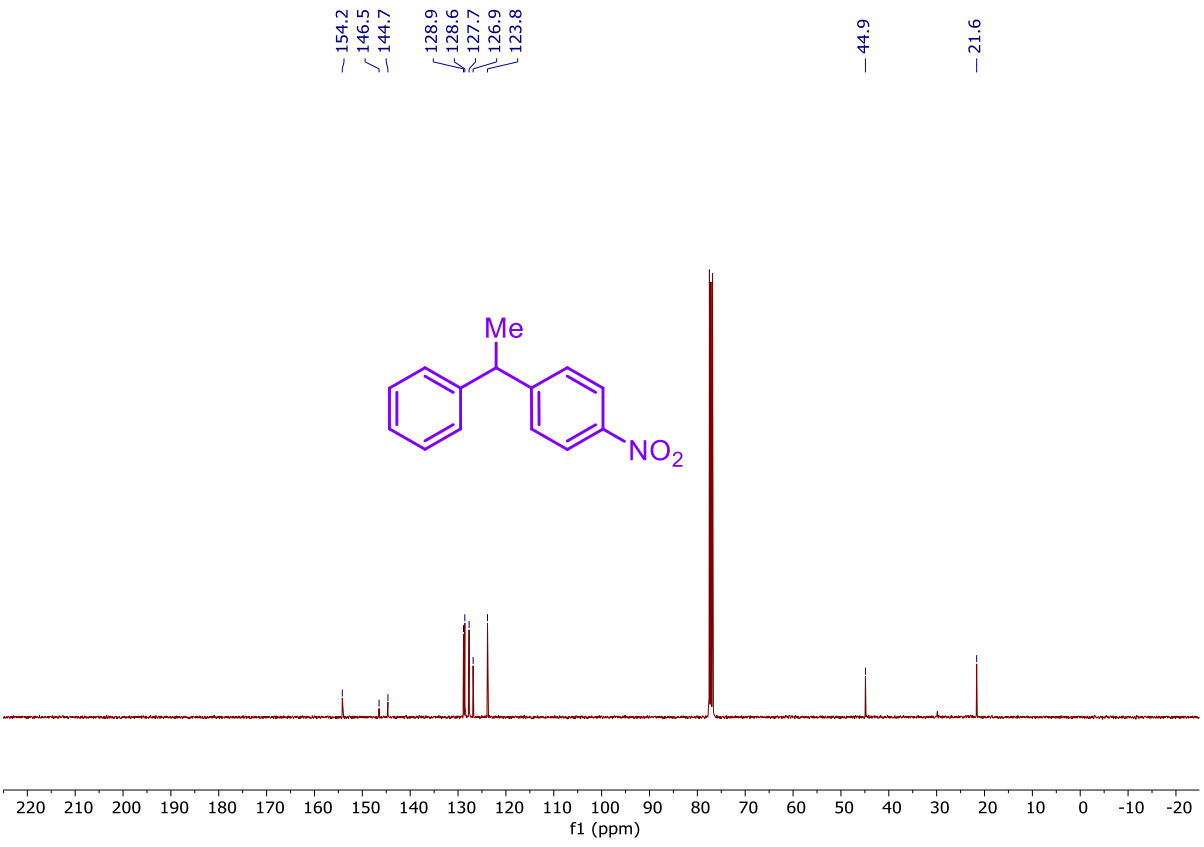


1-nitro-4-(1-phenylethyl)benzene (400i)

^{1}H NMR, 400MHz, $CDCl_3$

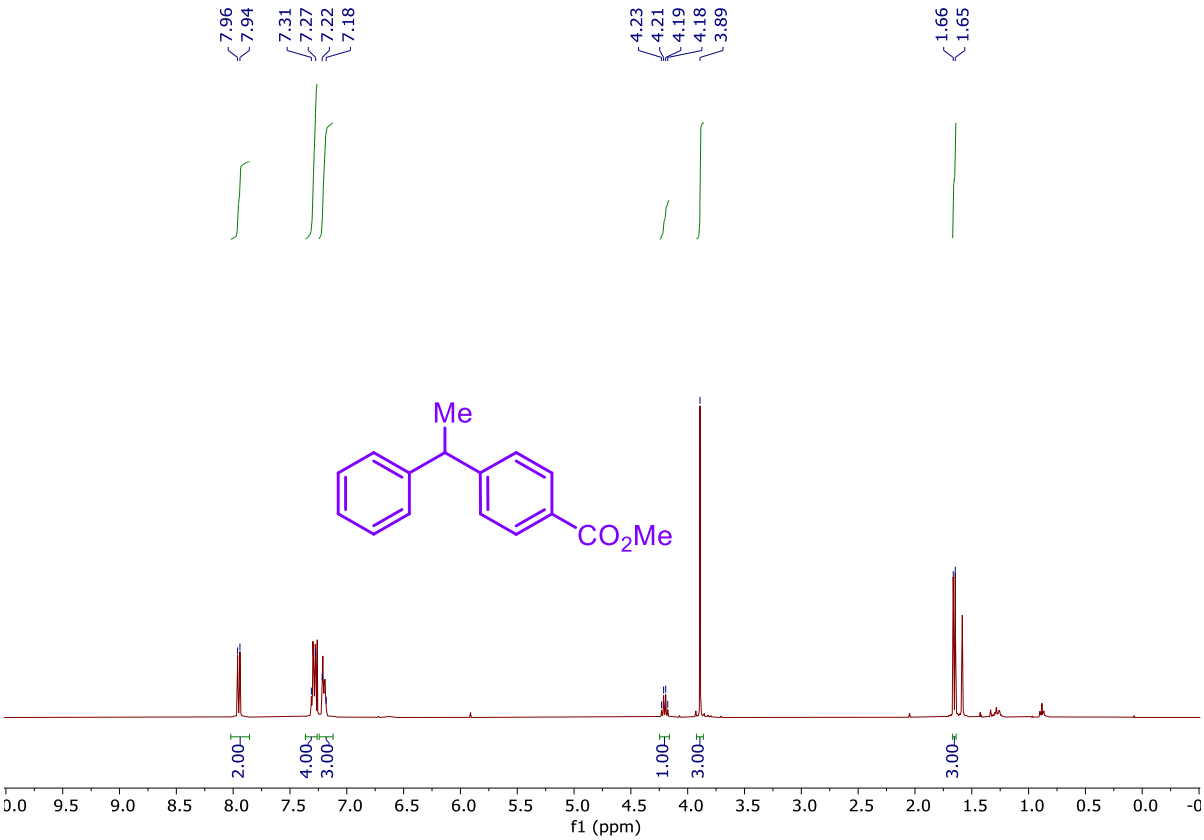


^{13}C NMR, 101MHz, $CDCl_3$

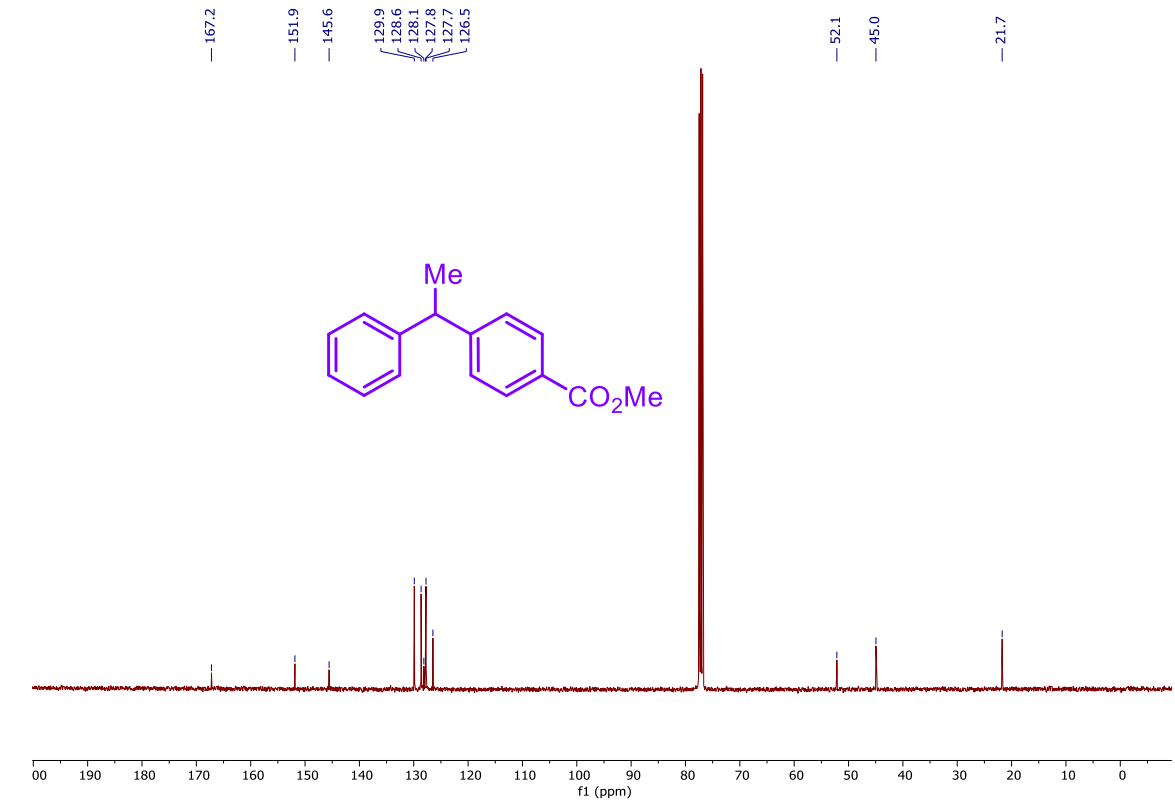


methyl 4-(1-phenylethyl)benzoate (400j)

^{1}H NMR, 400MHz, $CDCl_3$

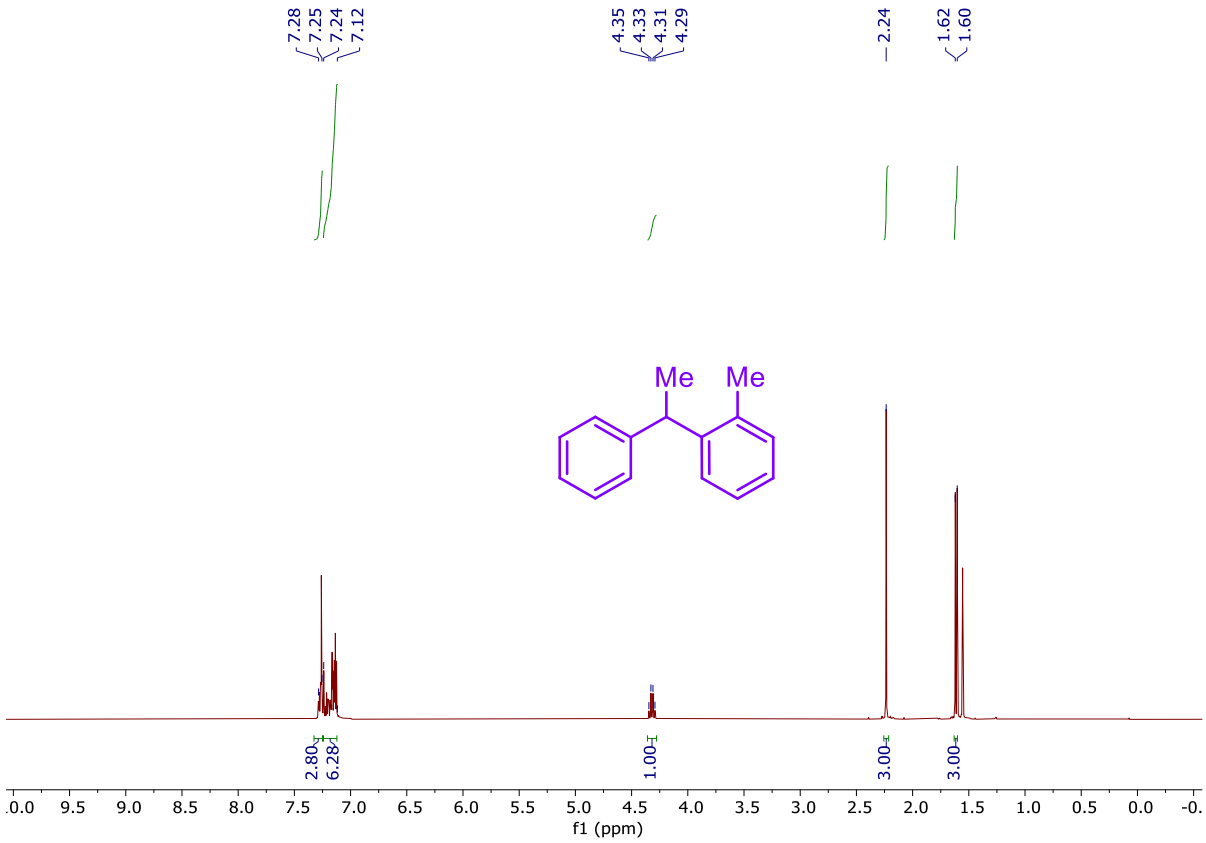


^{13}C NMR, 101MHz, $CDCl_3$

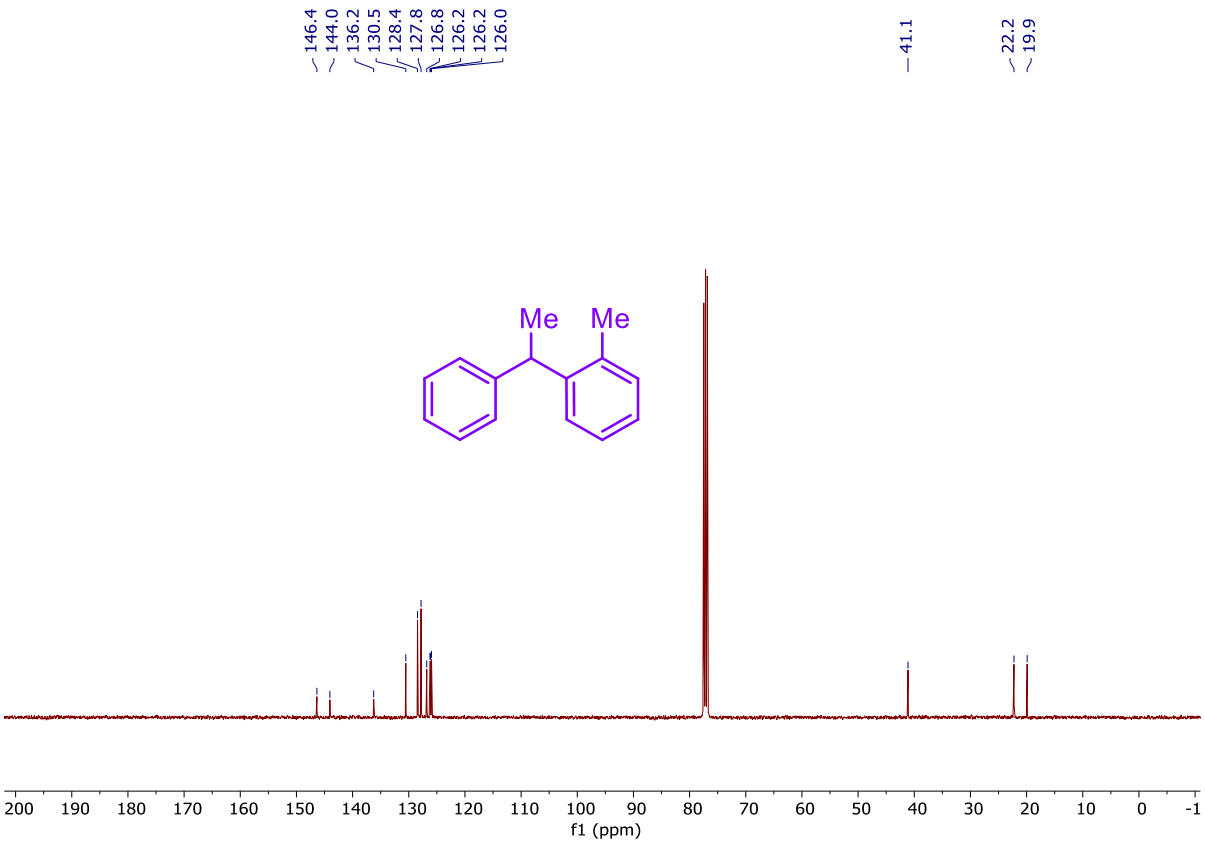


1-methyl-2-(1-phenylethyl)benzene (400k)

^{1}H NMR, 400MHz, $CDCl_3$

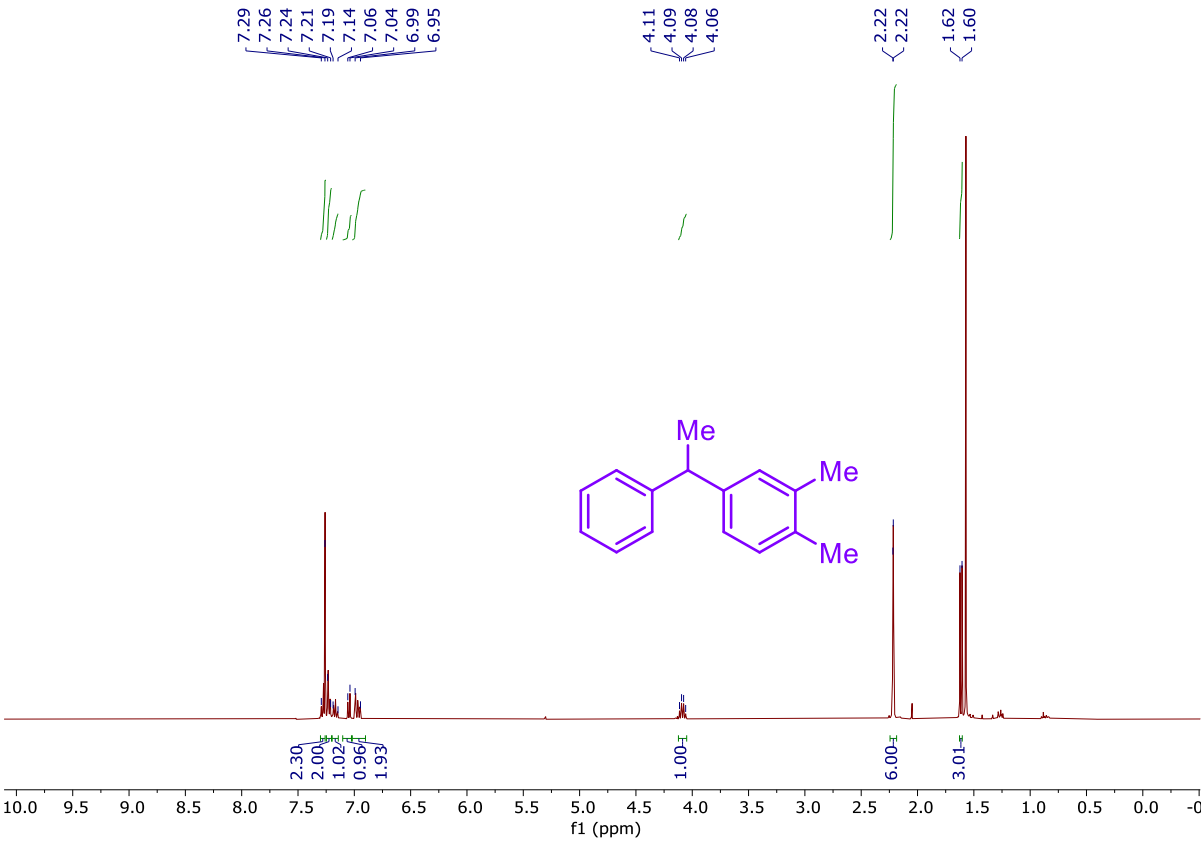


^{13}C NMR, 101MHz, $CDCl_3$

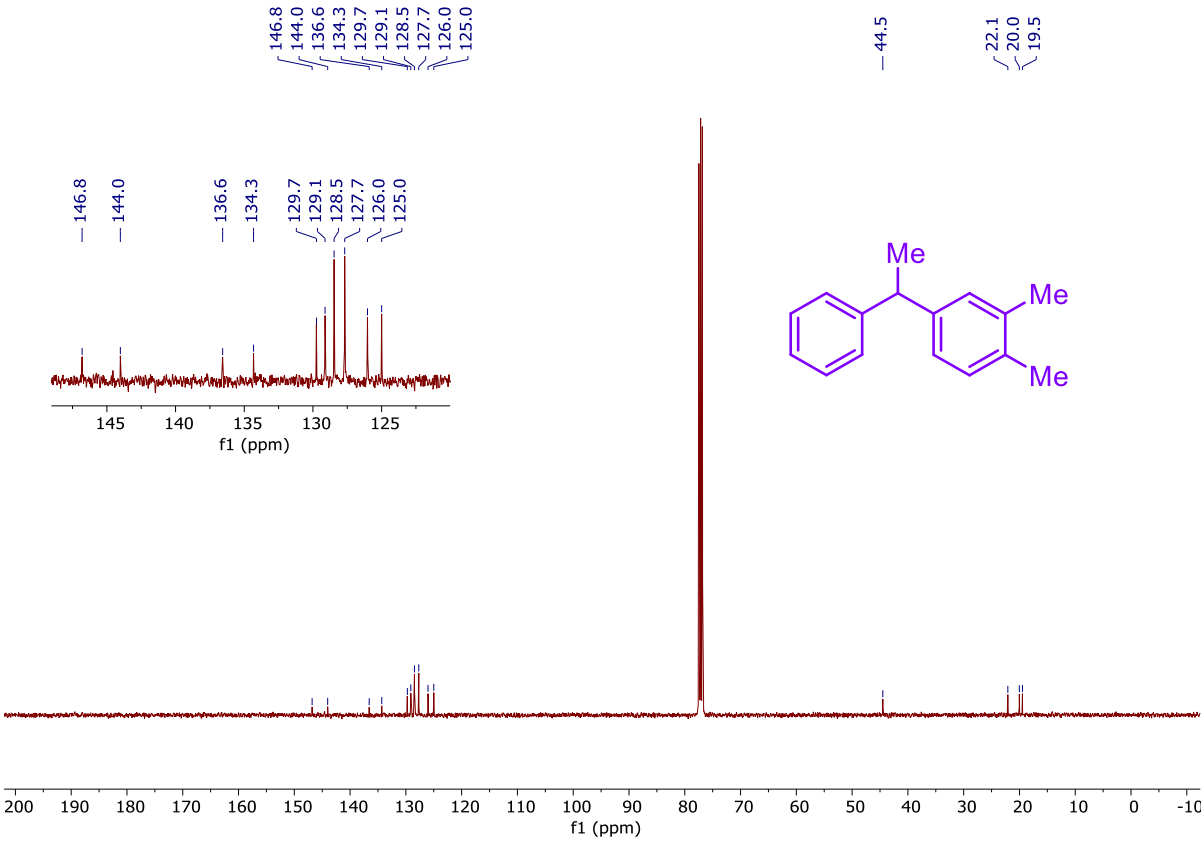


1,2-dimethyl-4-(1-phenylethyl)benzene (400l)

^{1}H NMR, 400MHz, $CDCl_3$

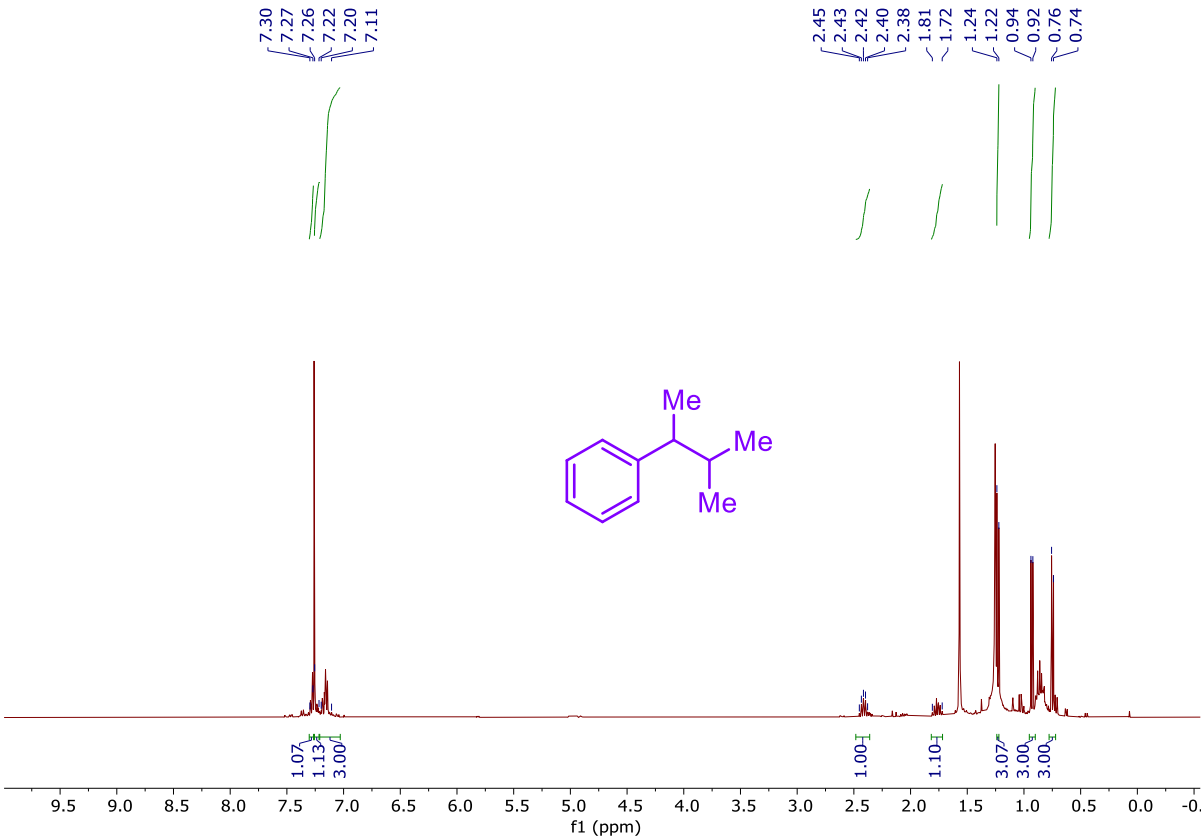


^{13}C NMR, 101MHz, $CDCl_3$

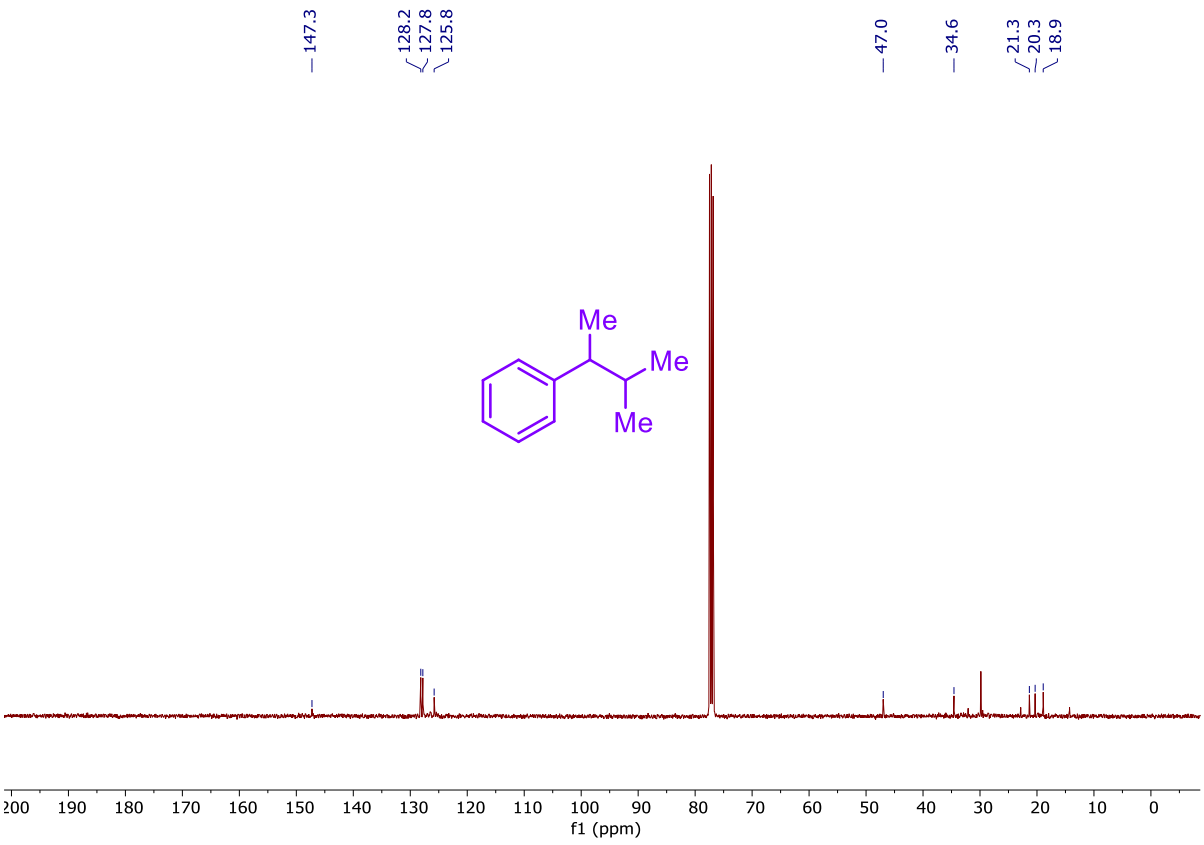


(3-methylbutan-2-yl)benzene (400m)

^{1}H NMR, 400MHz, $CDCl_3$

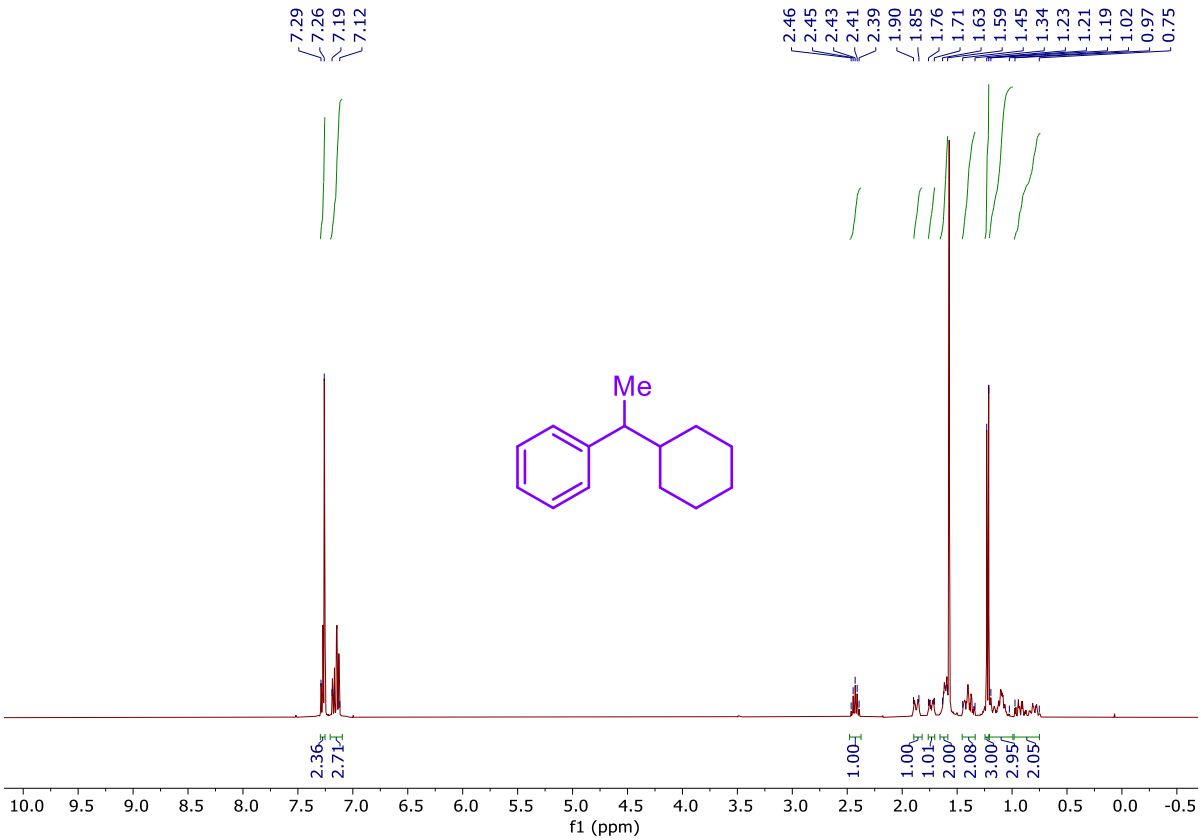


^{13}C NMR, 101MHz, $CDCl_3$

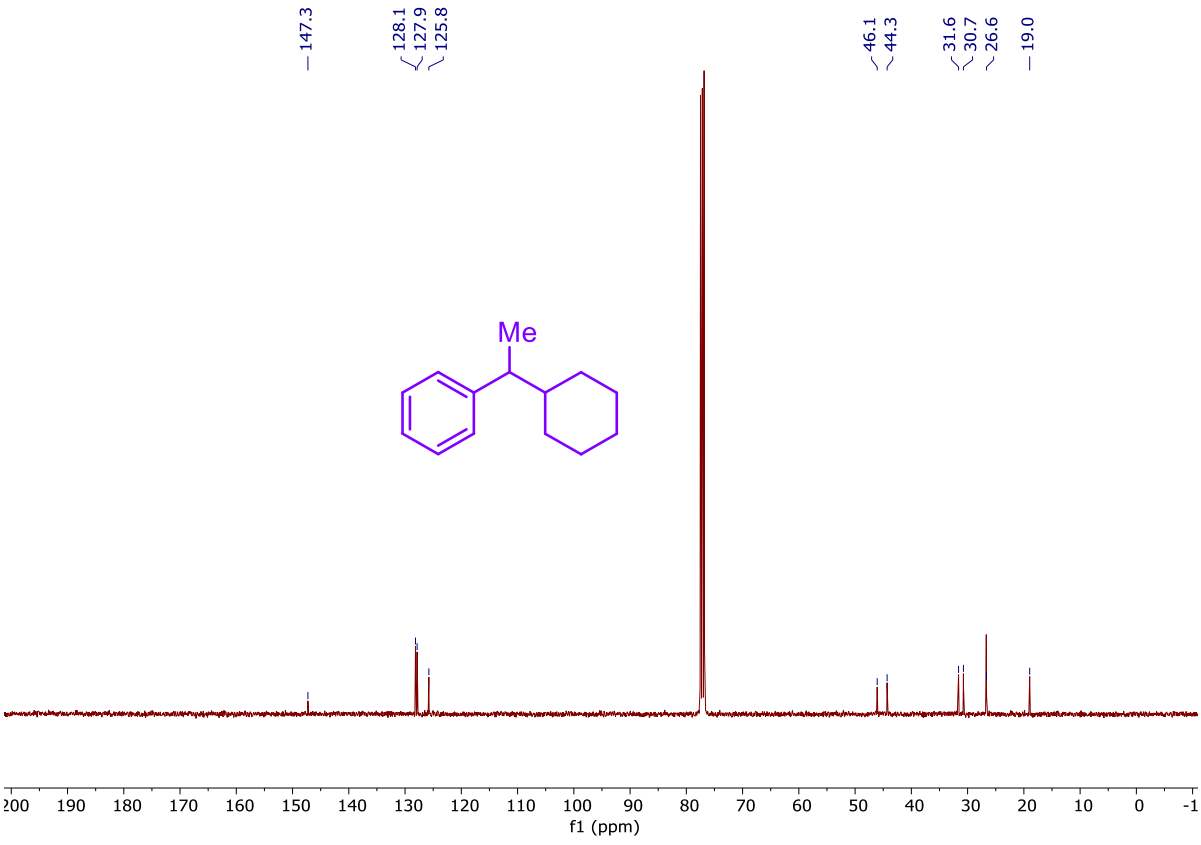


(1-cyclohexylethyl)benzene (400n)

^{1}H NMR, 400MHz, $CDCl_3$

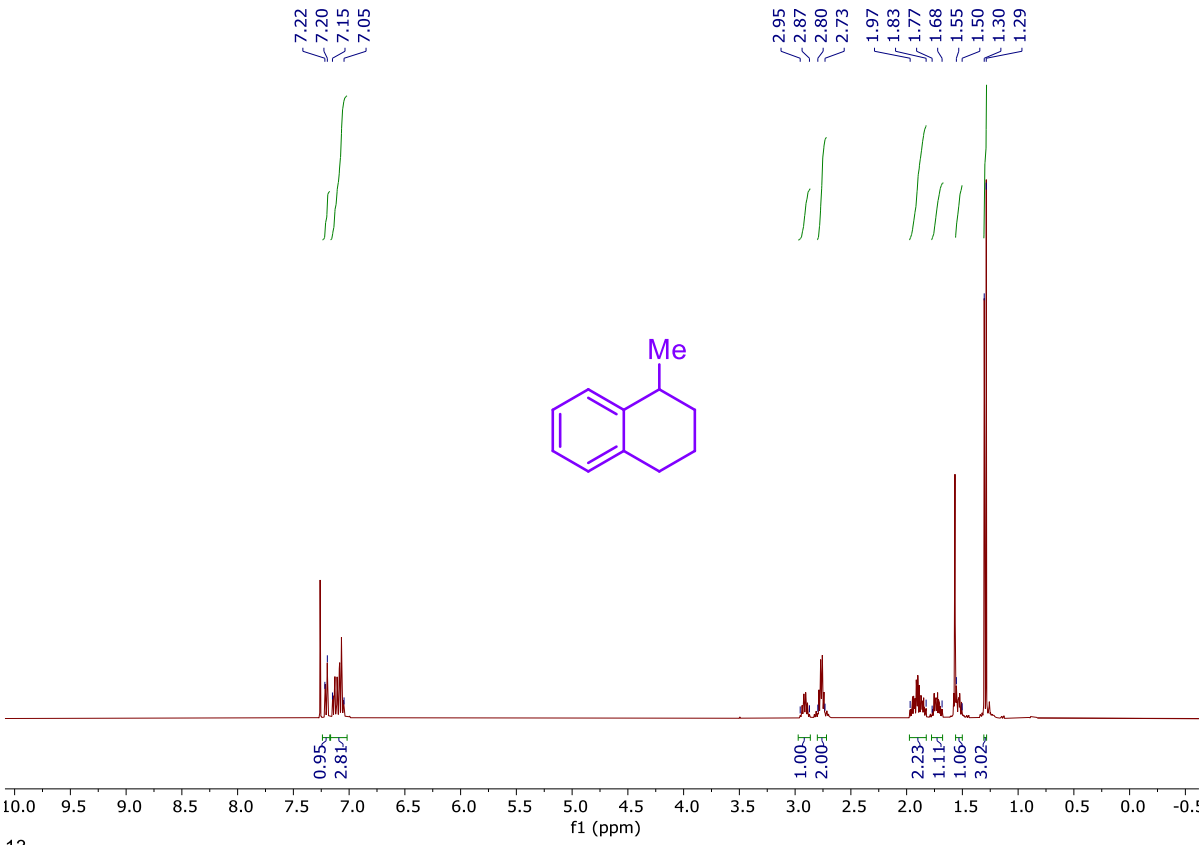


^{13}C NMR, 101MHz, $CDCl_3$

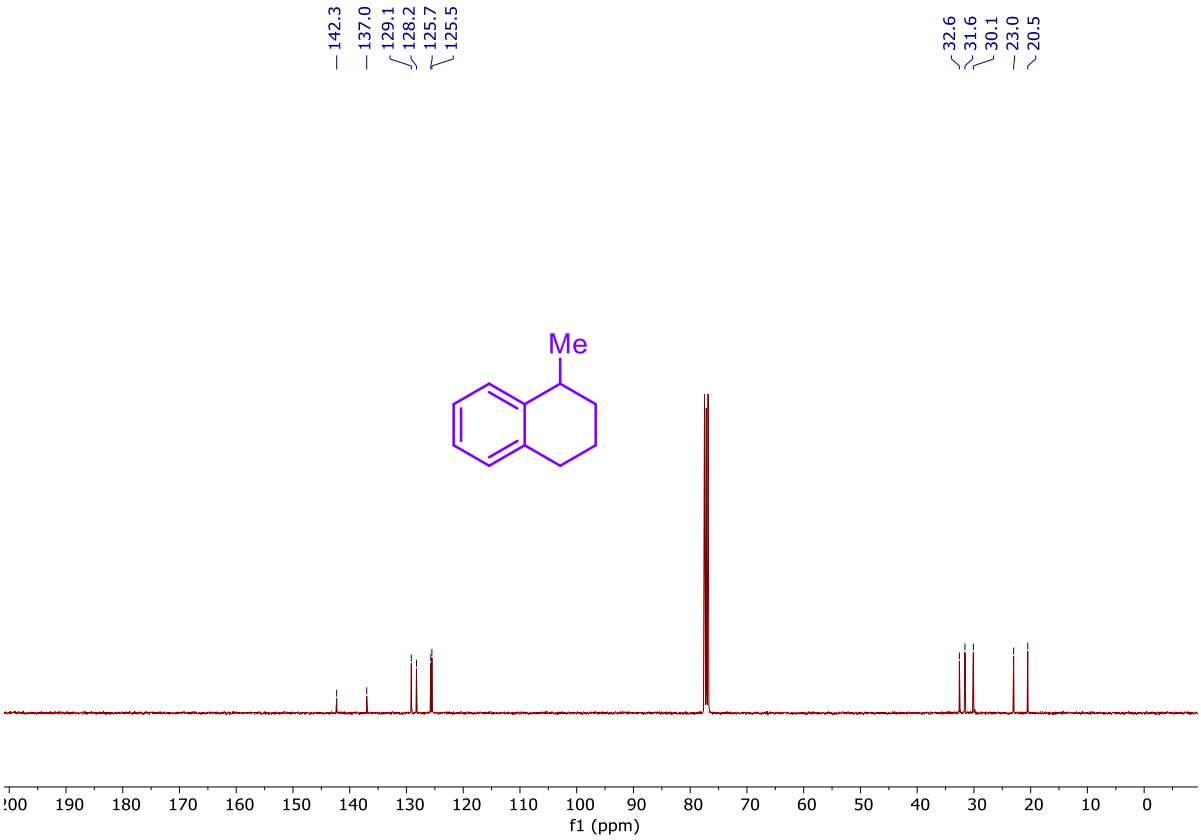


1-methyl-1,2,3,4-tetrahydronaphthalene (400o)

^{1}H NMR, 400MHz, $CDCl_3$

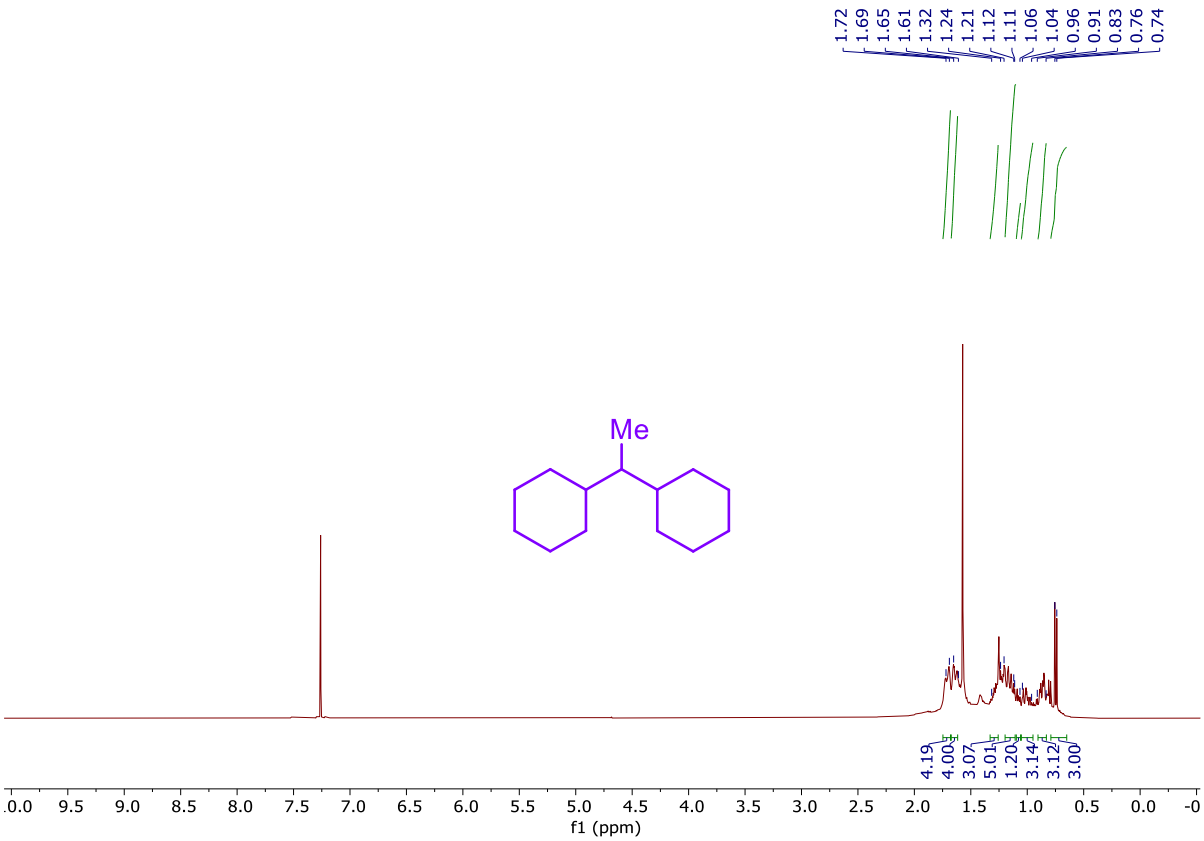


^{13}C NMR, 101MHz, $CDCl_3$

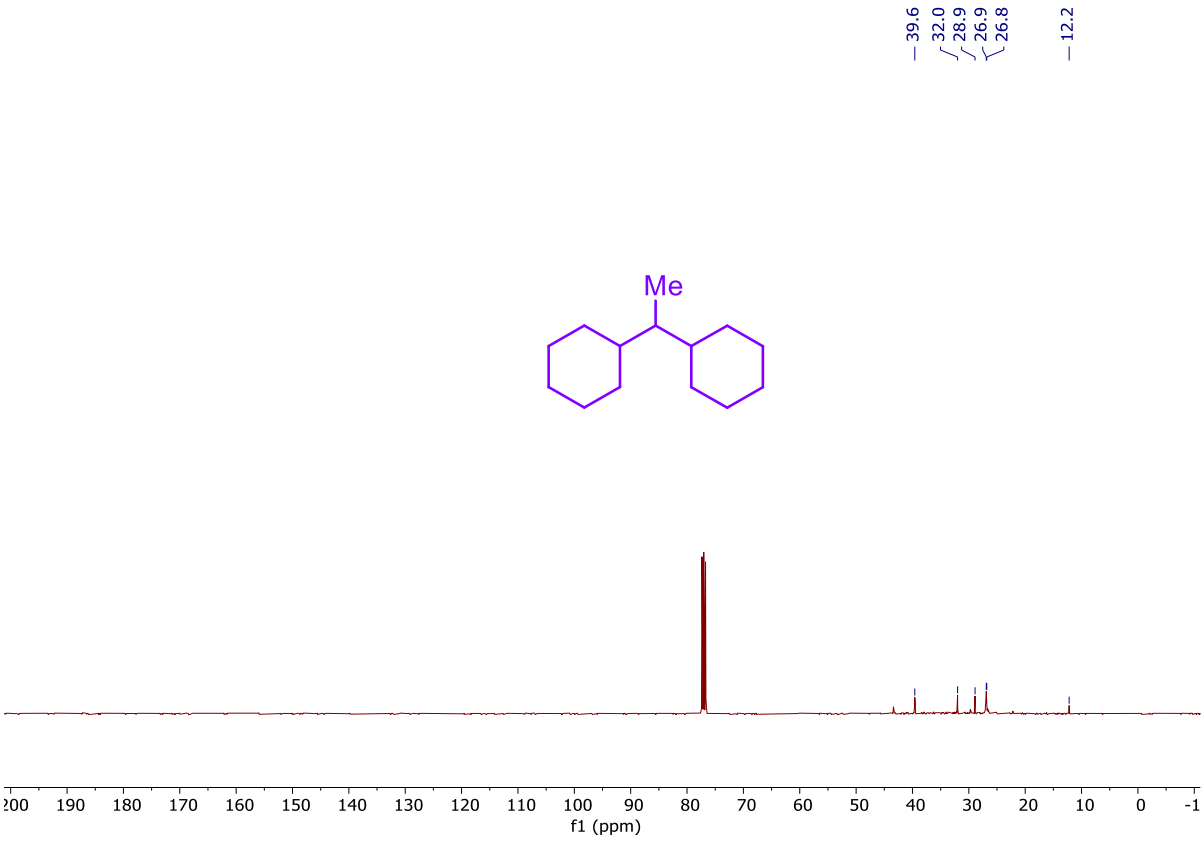


ethane-1,1-diyldicyclohexane (400p)

^{1}H NMR, 400MHz, $CDCl_3$

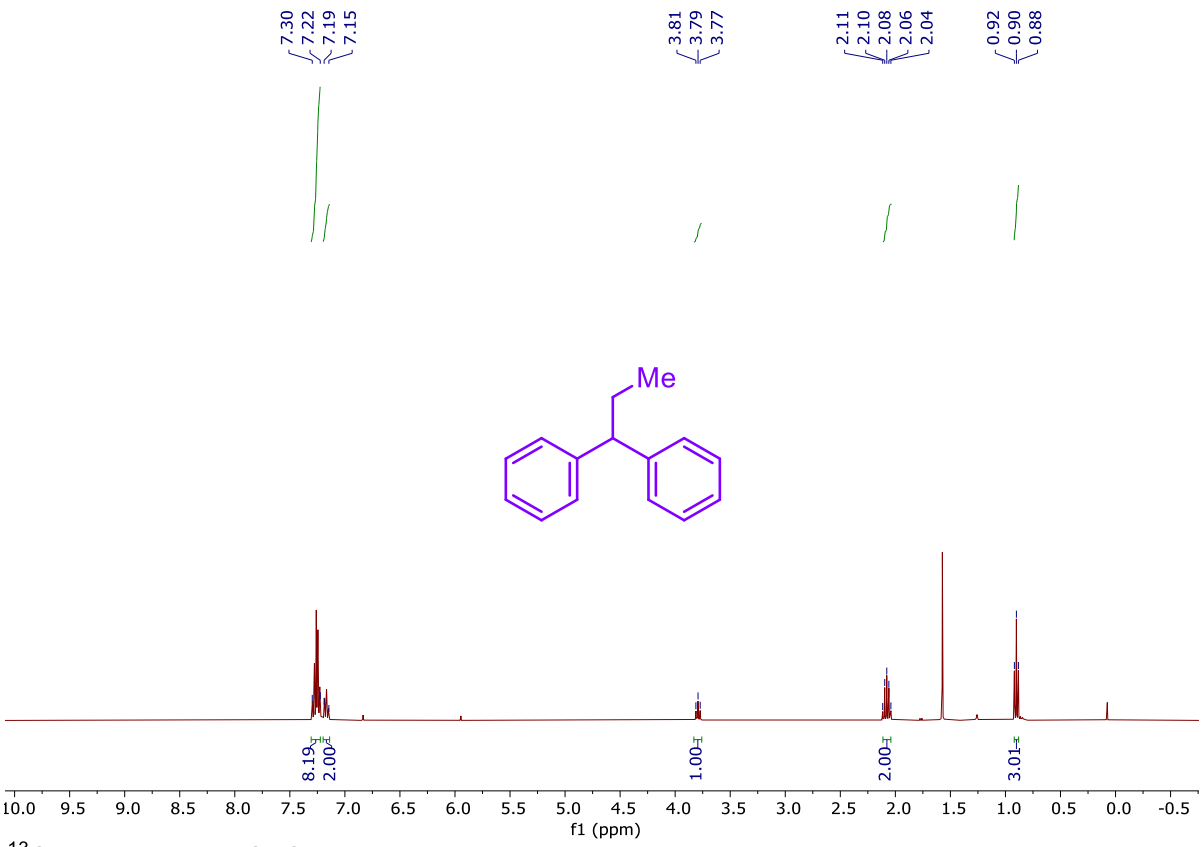


^{13}C NMR, 101MHz, $CDCl_3$

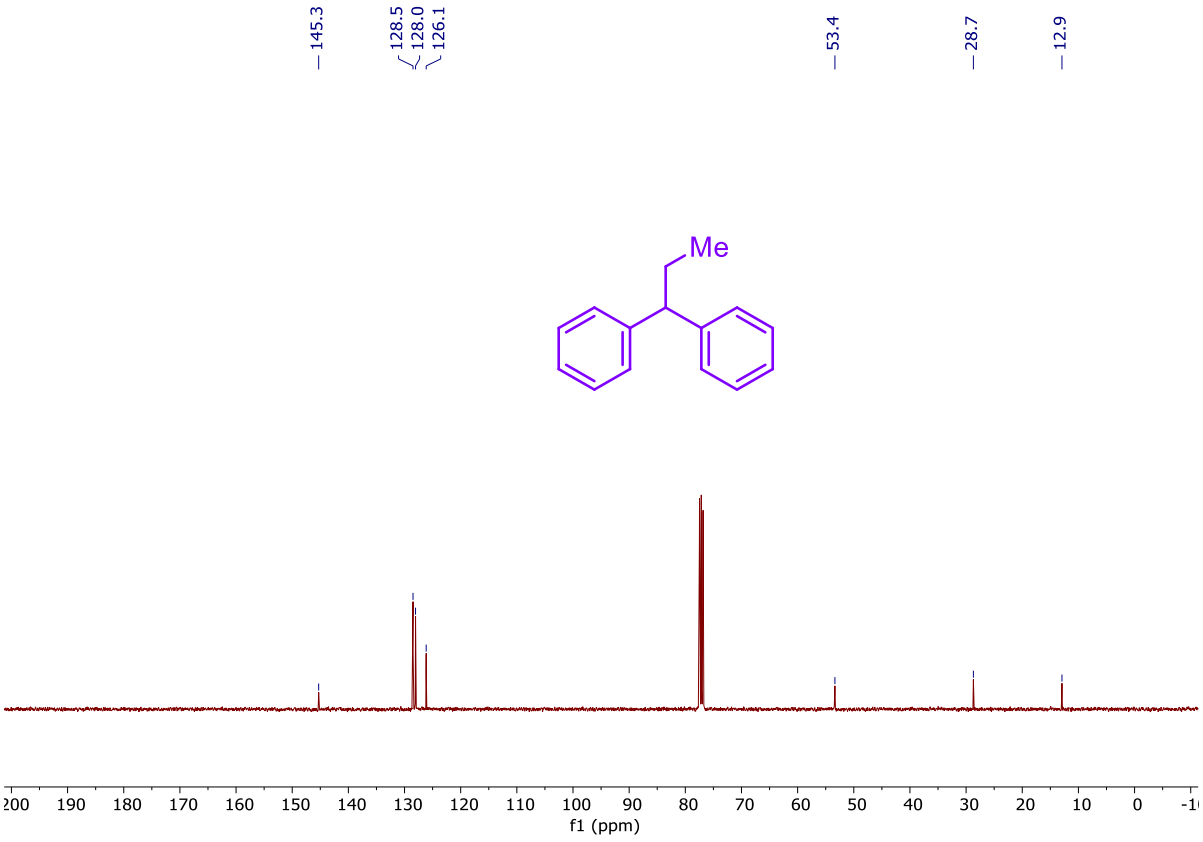


propane-1,1-diyldibenzene (400q)

^{1}H NMR, 400MHz, $CDCl_3$

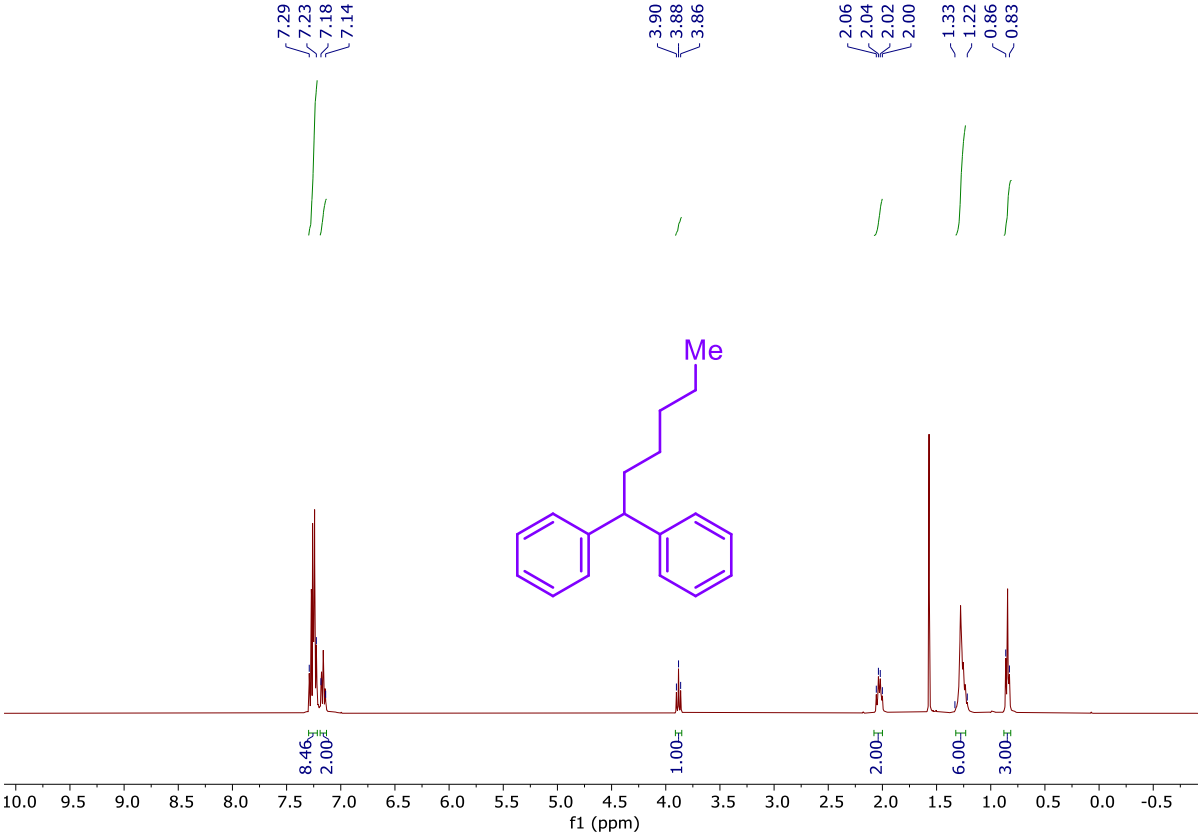


^{13}C NMR, 101MHz, $CDCl_3$

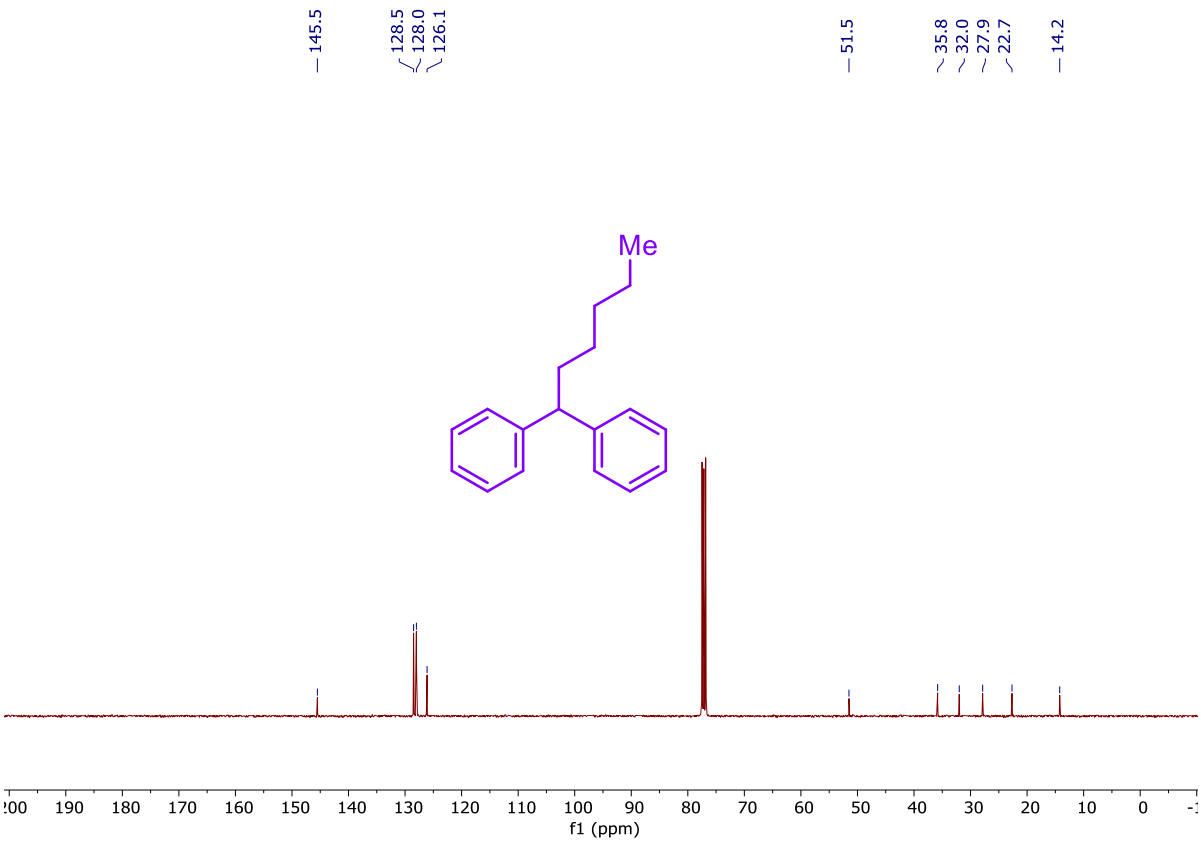


hexane-1,1-diyldibenzene (400r)

^{1}H NMR, 400MHz, $CDCl_3$

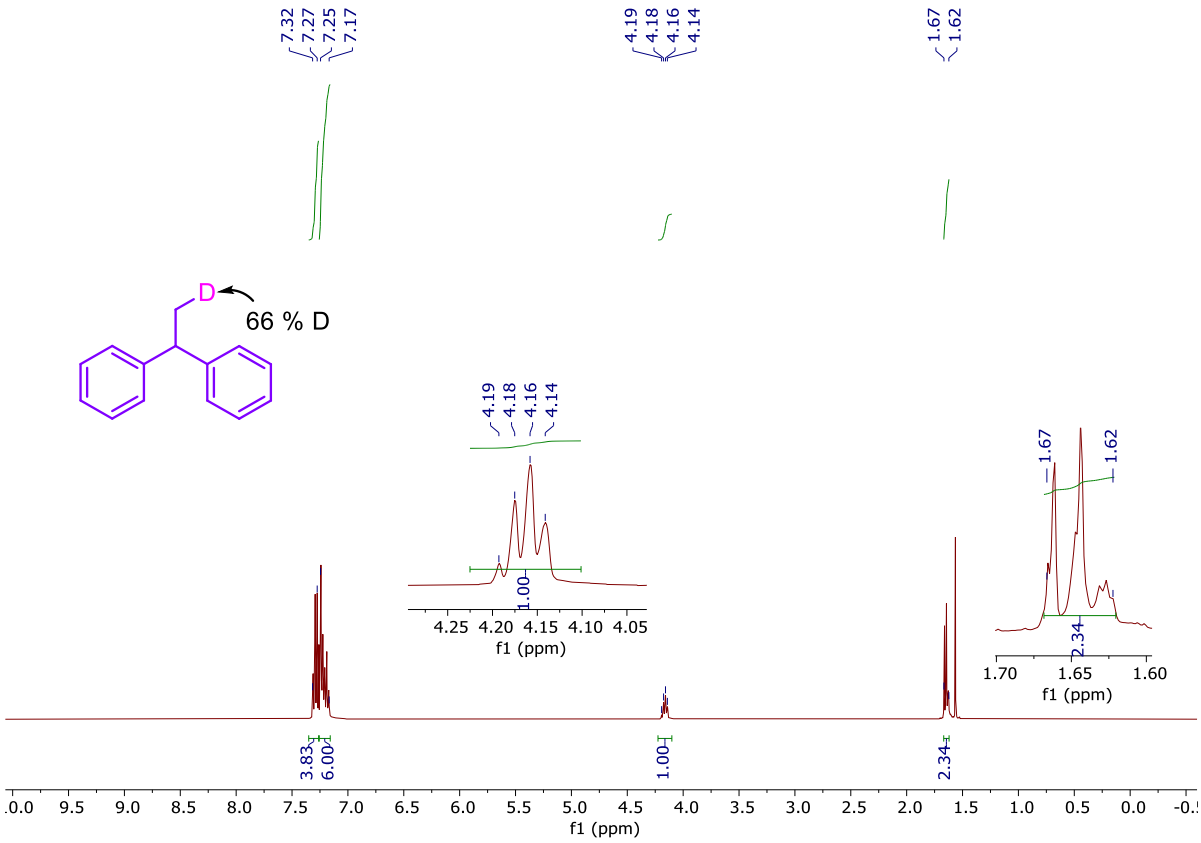


^{13}C NMR, 101MHz, $CDCl_3$

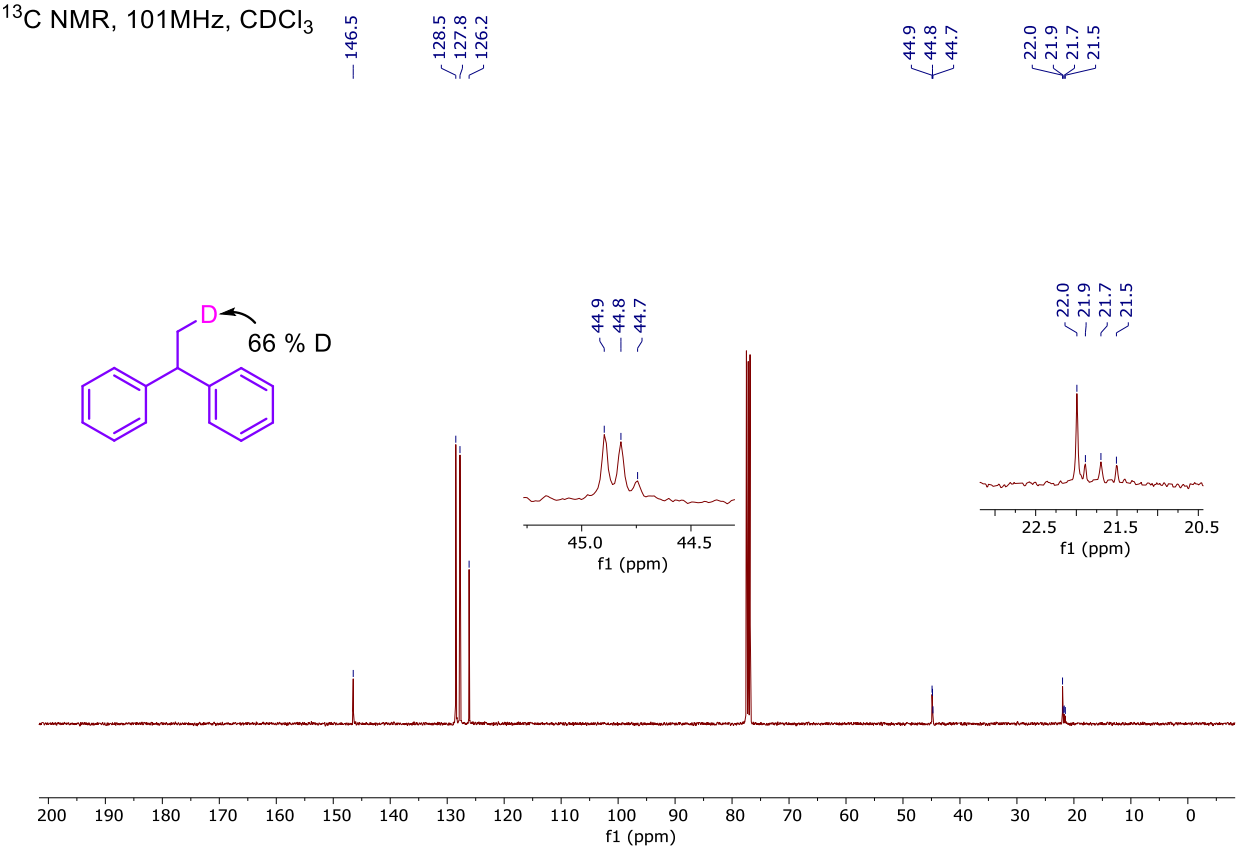


(ethane-1,1-diyl-2-*d*)dibenzene (400a-d_1)

^{1}H NMR, 400MHz, $CDCl_3$

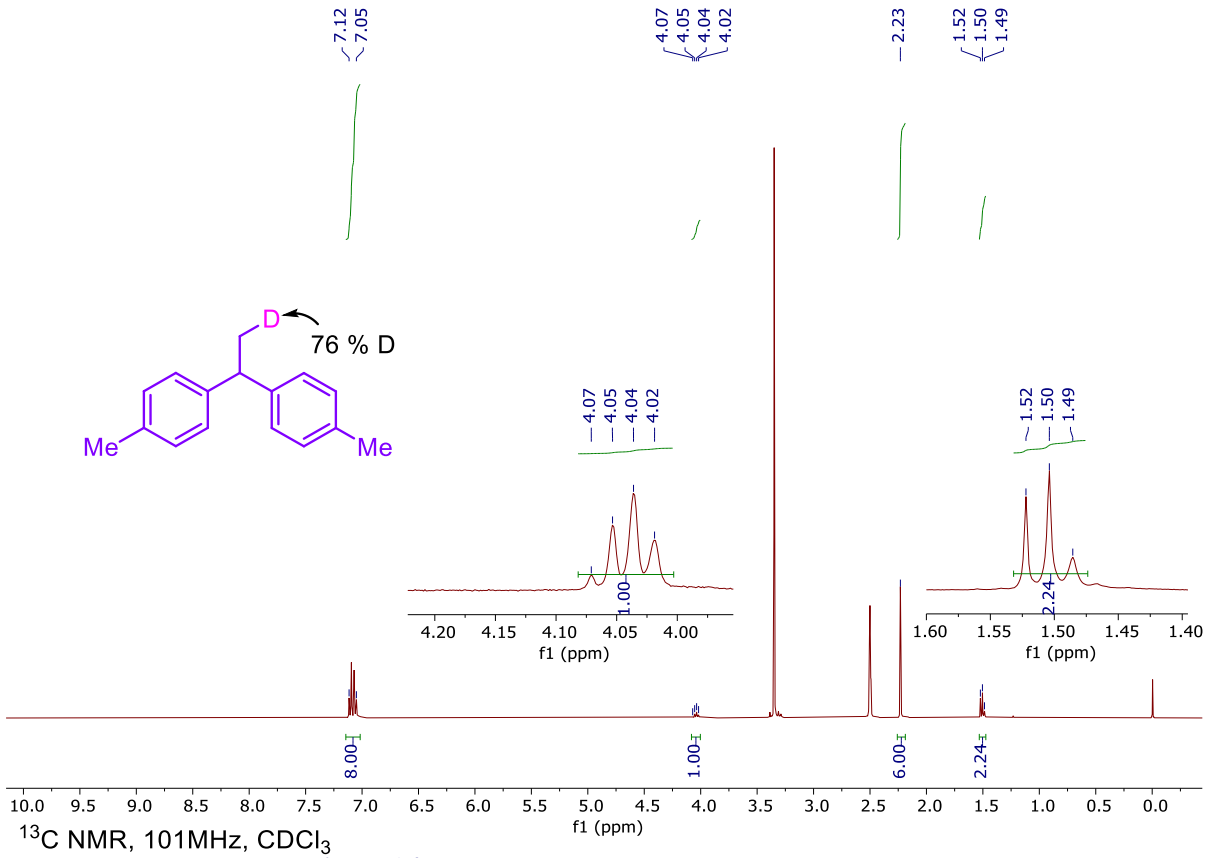


^{13}C NMR, 101MHz, $CDCl_3$

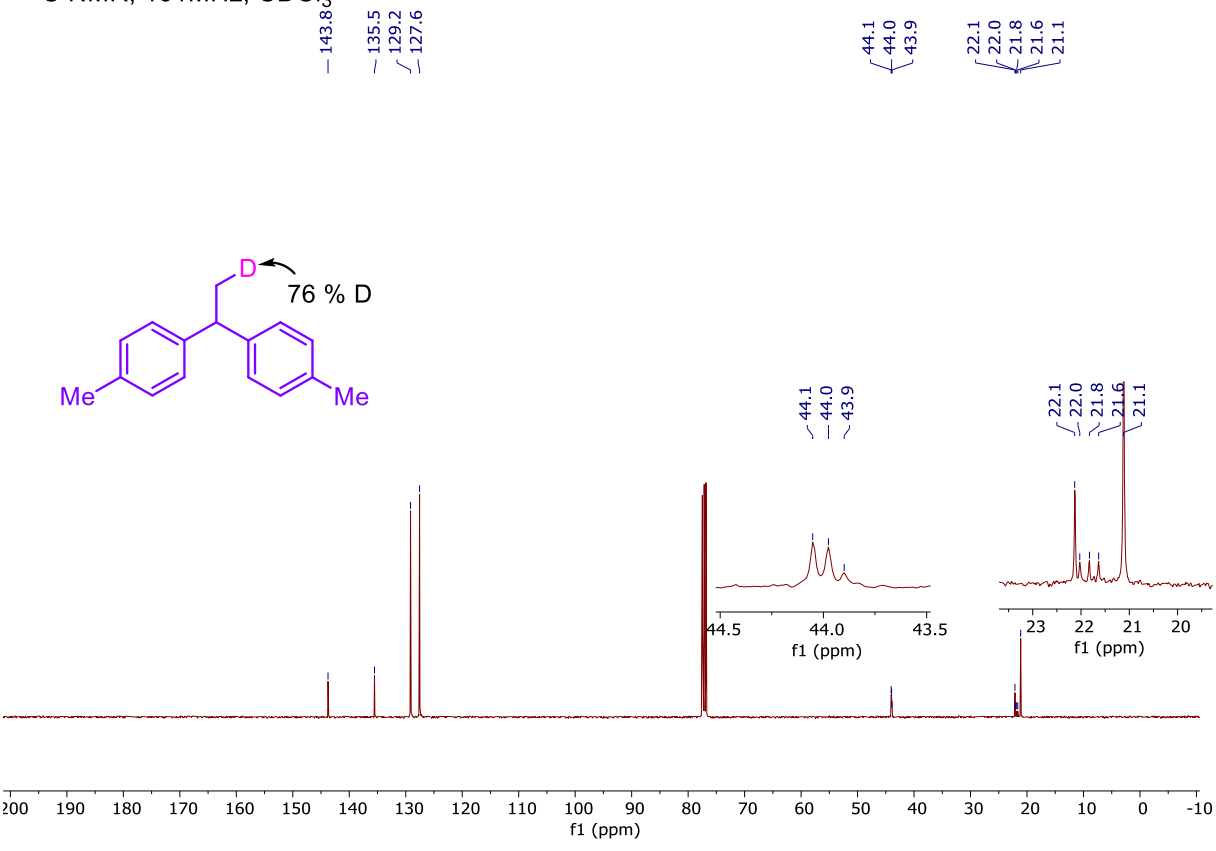


4,4'-(ethane-1,1-diyl-2-*d*)bis(methylbenzene) (400b-d_1)

^{1}H NMR, 400MHz, DMSO-D_6

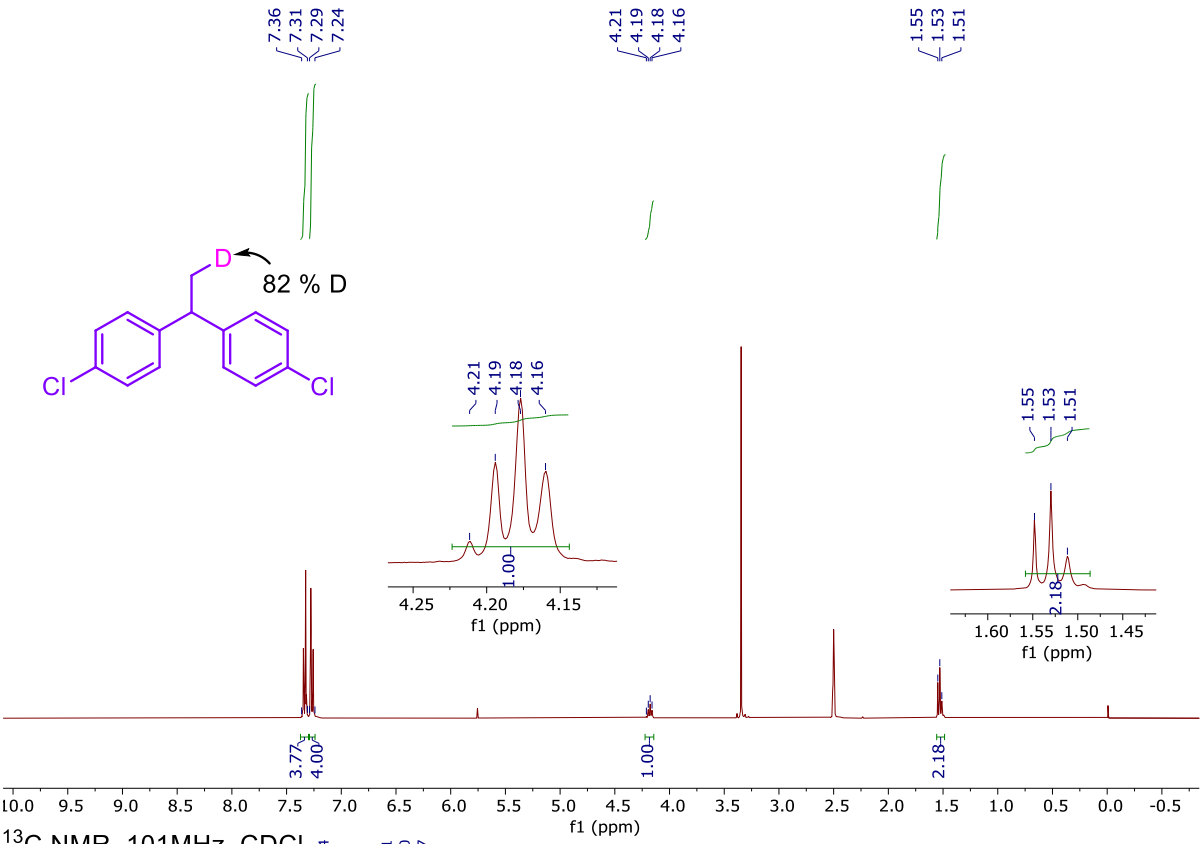


^{13}C NMR, 101MHz, $CDCl_3$

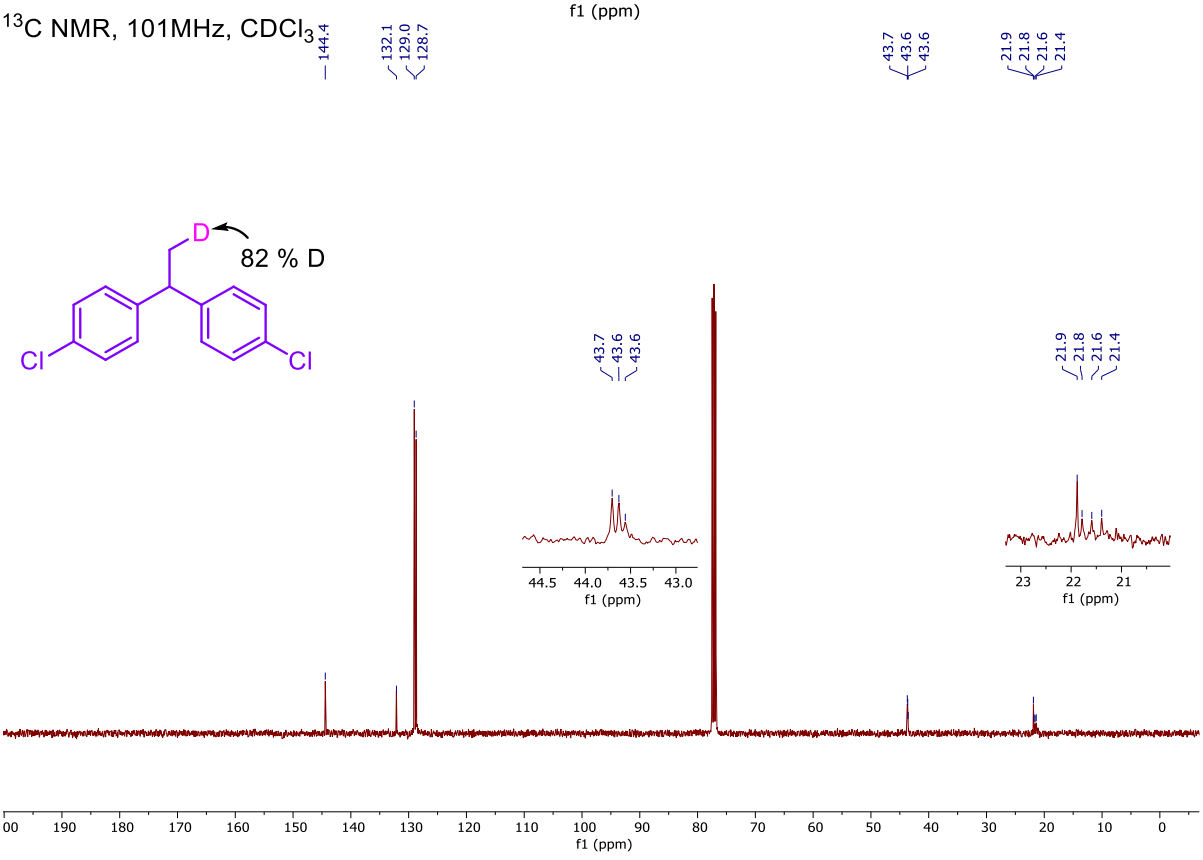


4,4'-(ethane-1,1-diyl-2-*d*)bis(chlorobenzene) (400c-d_1)

^{1}H NMR, 400MHz, DMSO-D_6

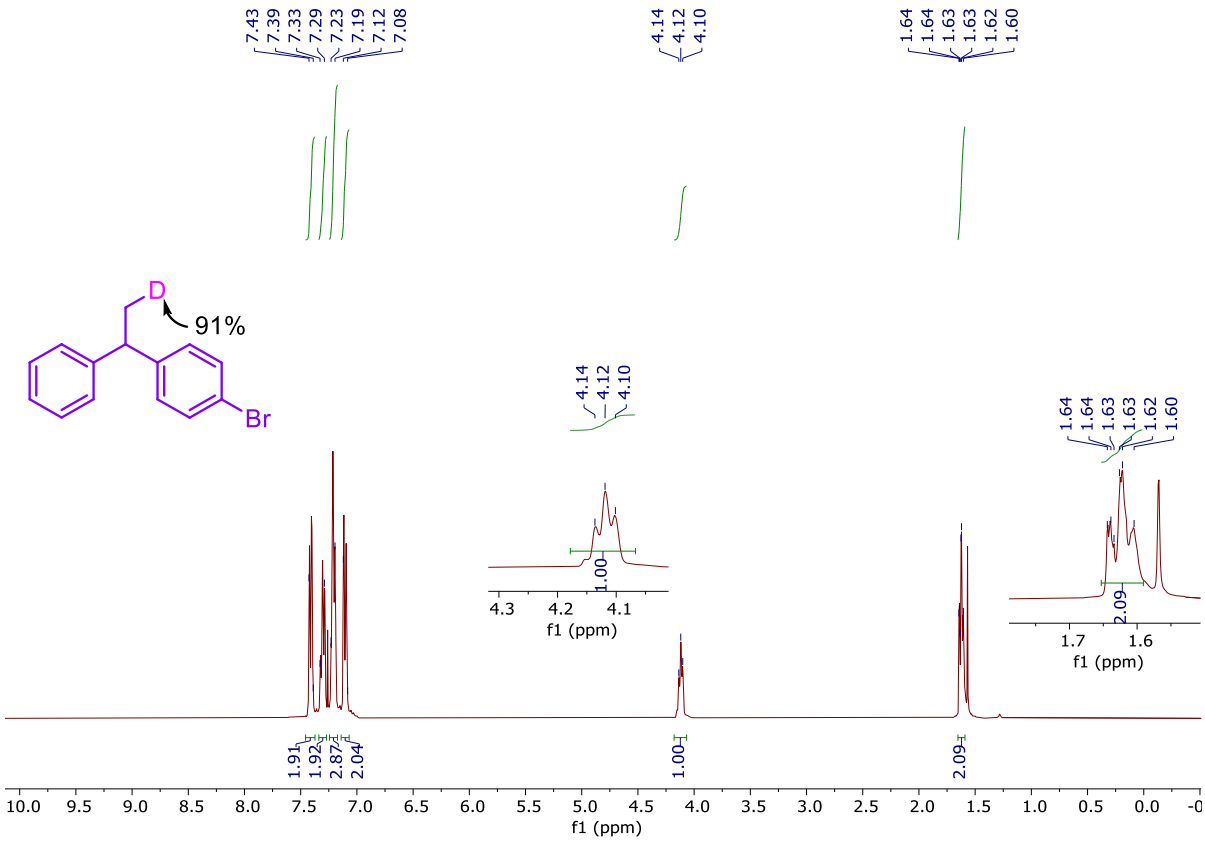


^{13}C NMR, 101MHz, $CDCl_3$

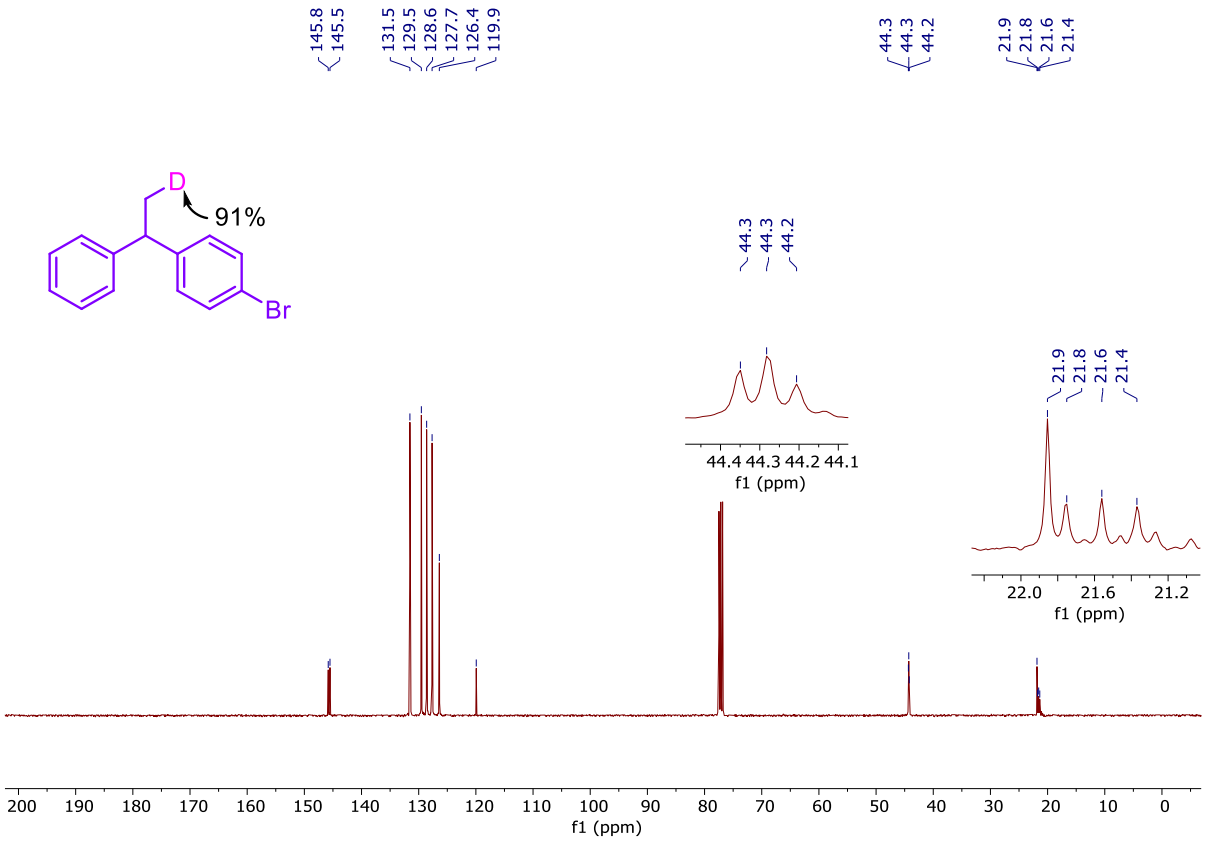


1-bromo-4-(1-phenylethyl-2-*d*)benzene (400f-d_1)

^{1}H NMR, 400MHz, $CDCl_3$

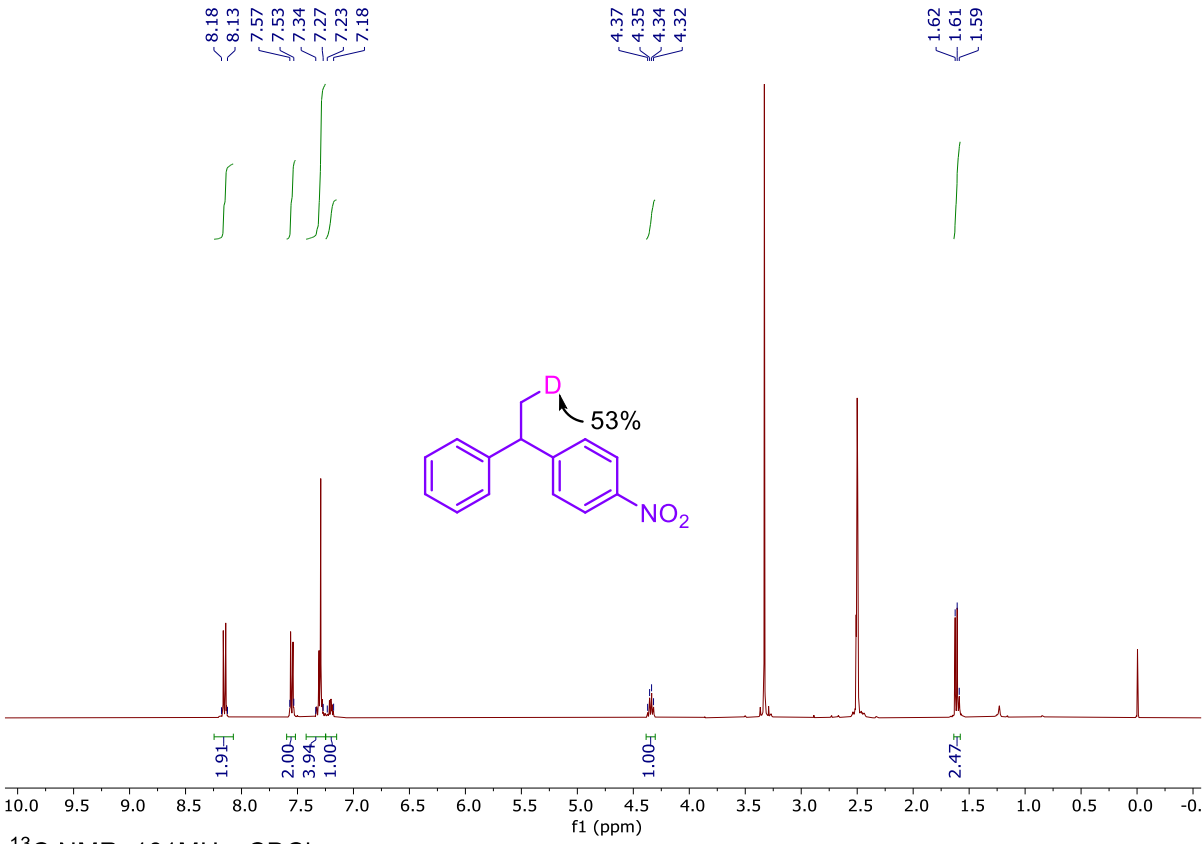


^{13}C NMR, 101MHz, $CDCl_3$

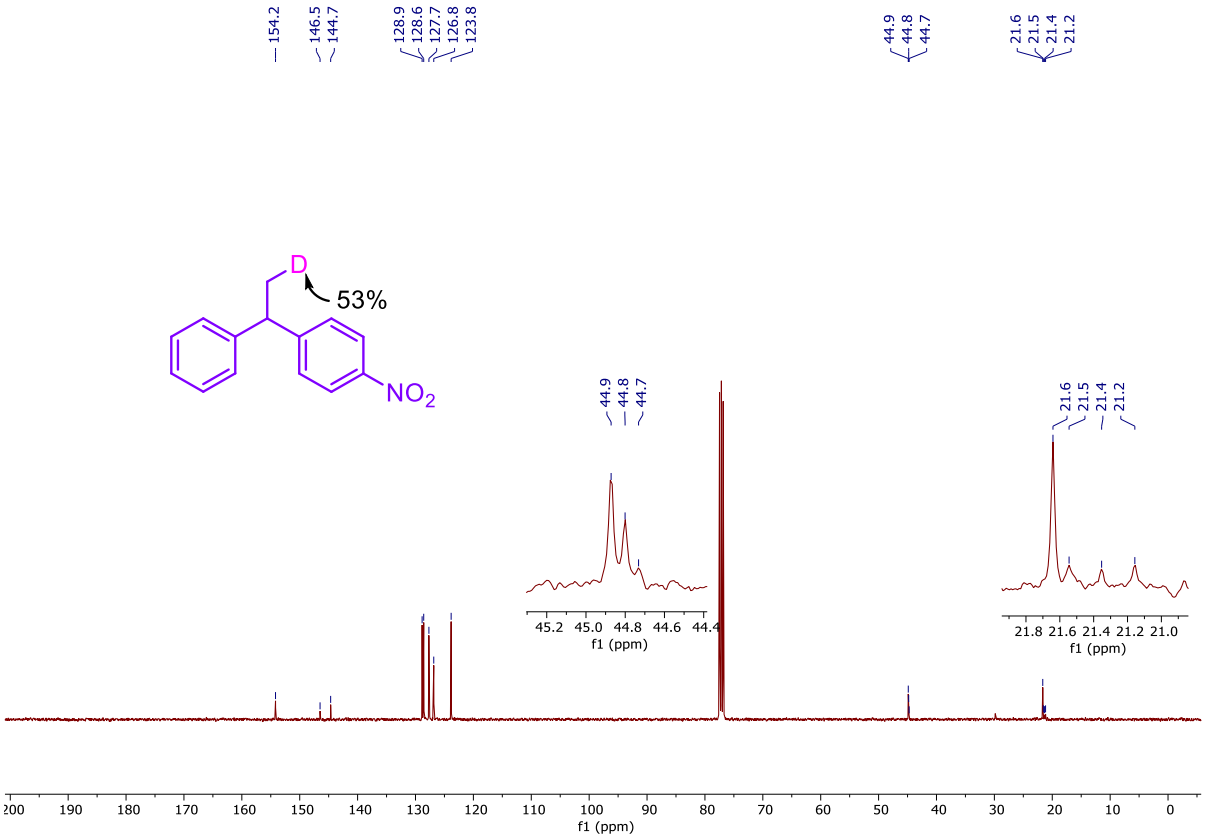


1-nitro-4-(1-phenylethyl-2-*d*)benzene (400i-d_1)

^{1}H NMR, 400MHz, DMSO-D_6

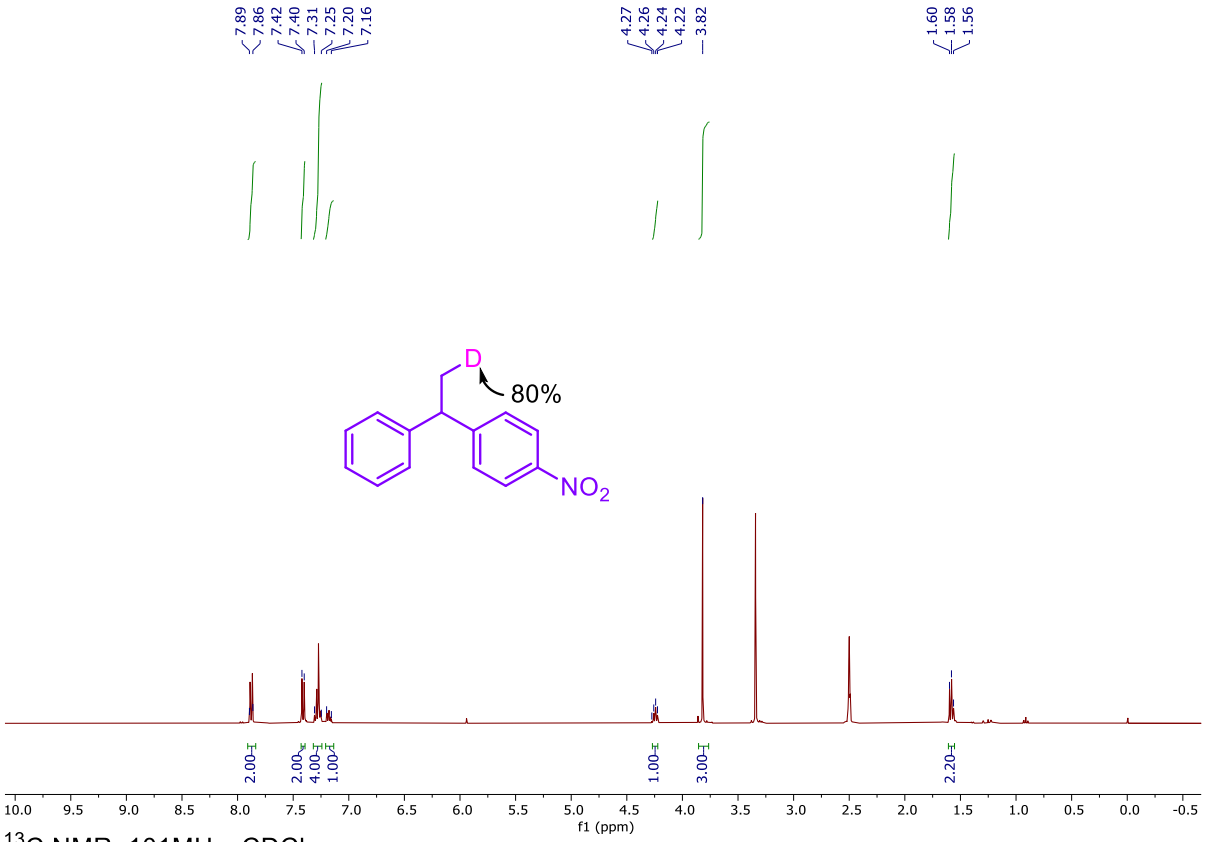


^{13}C NMR, 101MHz, $CDCl_3$

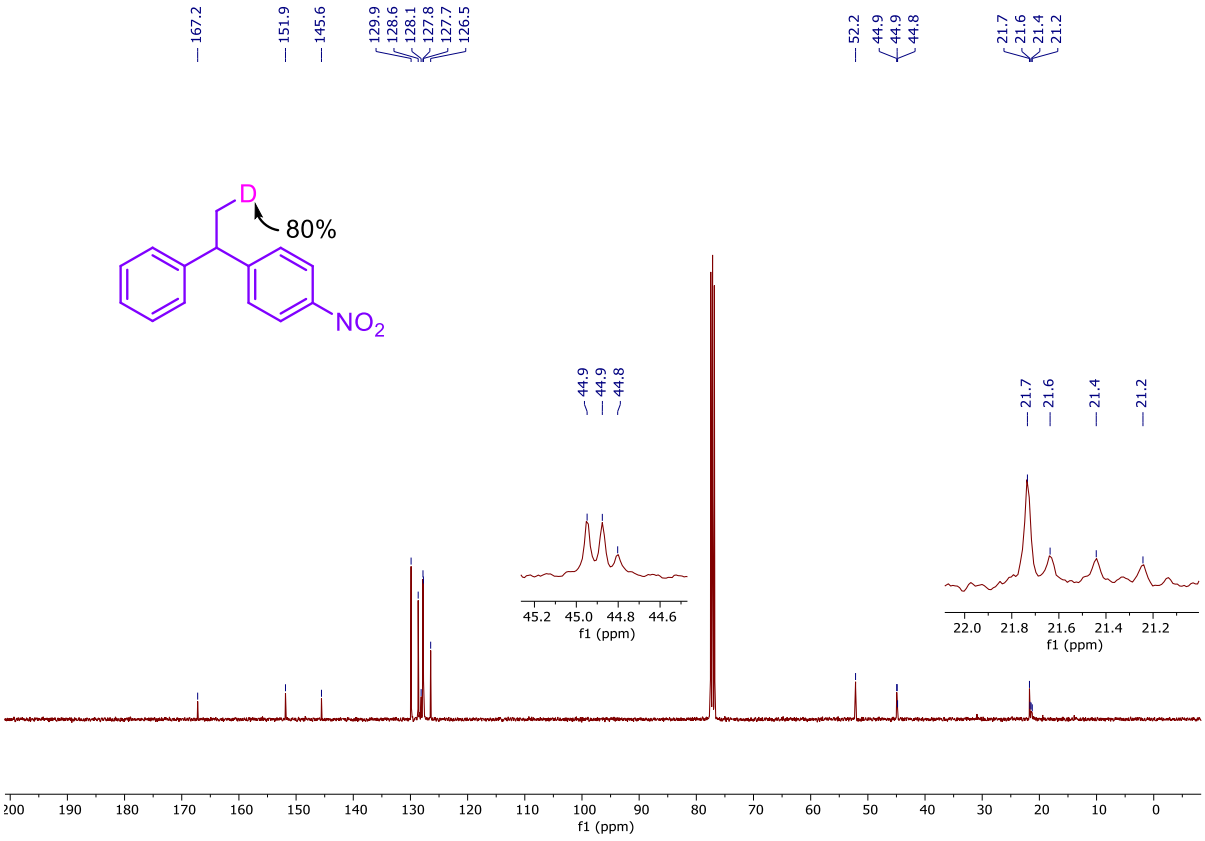


methyl 4-(1-phenylethyl-2-*d*)benzoate (400j-d_1)

^{1}H NMR, 400MHz, DMSO-D_6

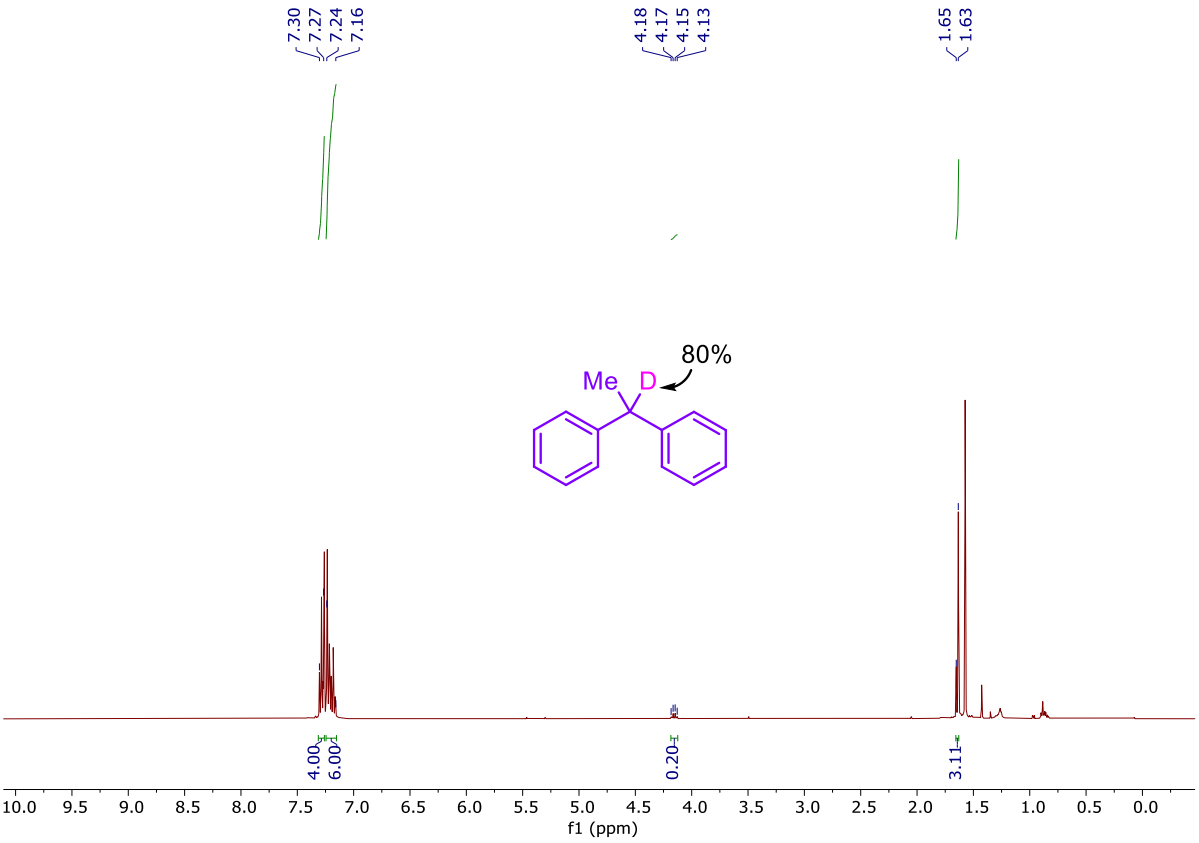


^{13}C NMR, 101MHz, CDCl$_3$

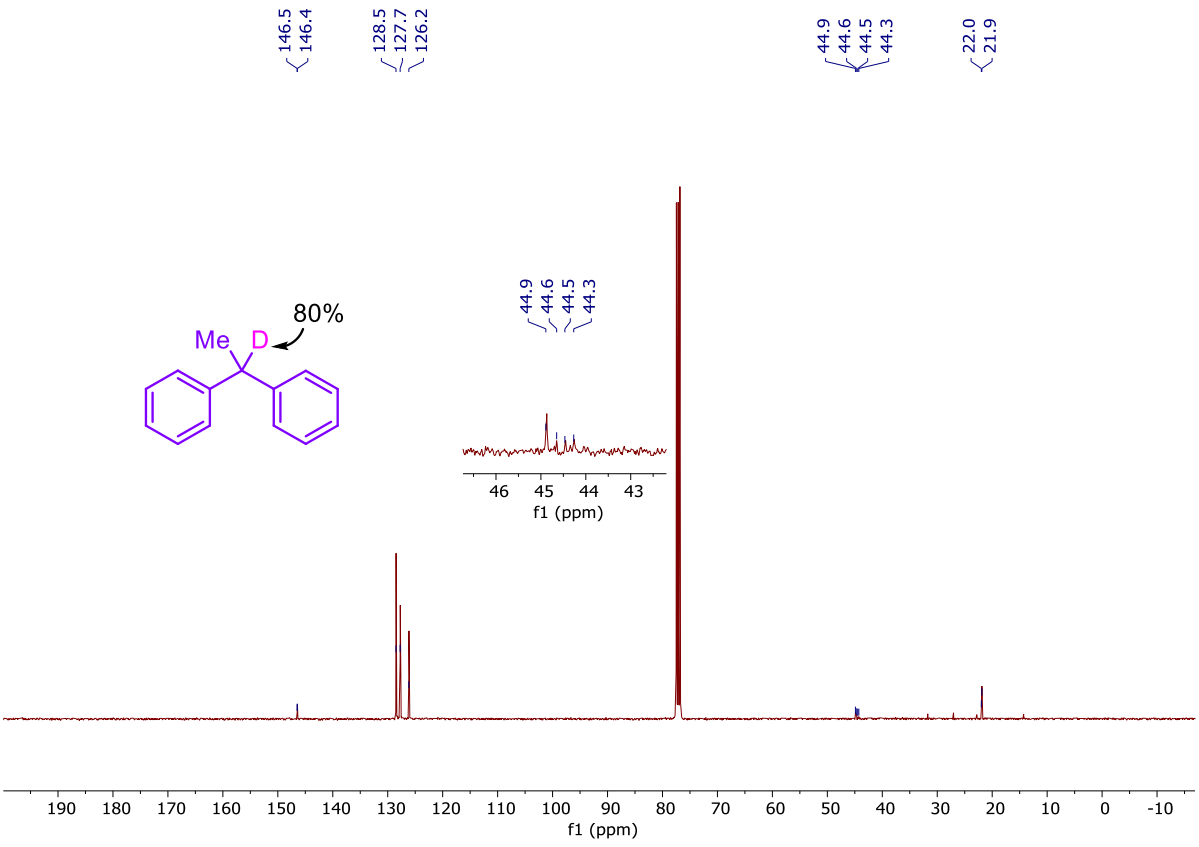


(ethane-1,1-diyl-1-*d*)dibenzene (400a-d_1′)

^{1}H NMR, 400MHz, $CDCl_3$

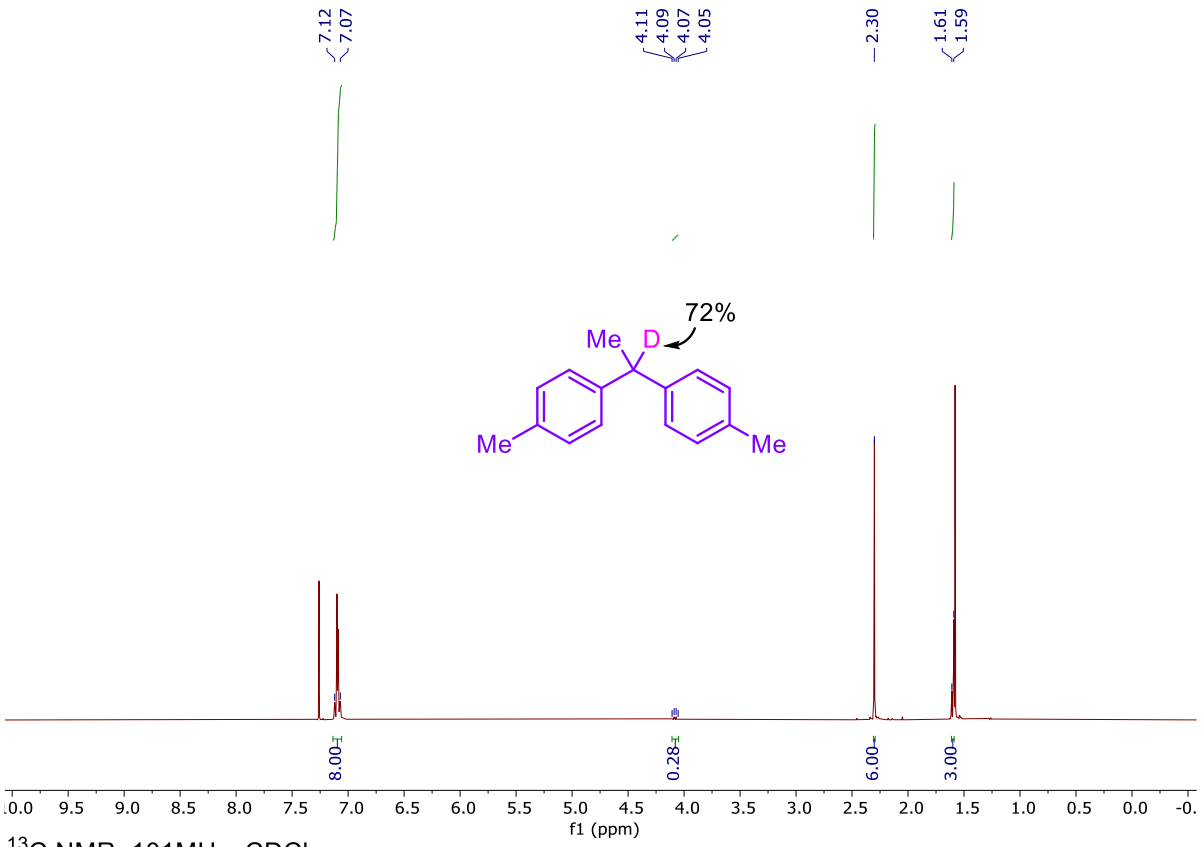


^{13}C NMR, 101MHz, $CDCl_3$

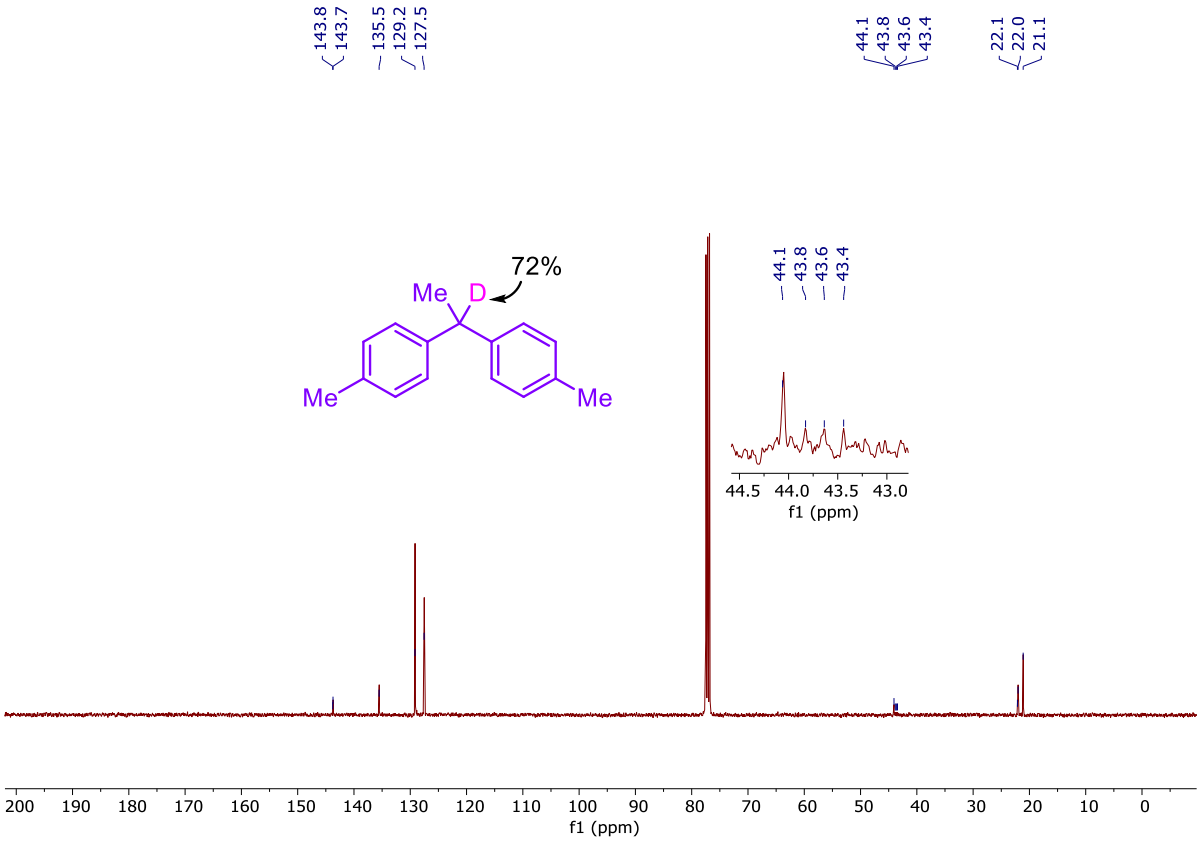


4,4'-(ethane-1,1-diyl-1-d)bis(methylbenzene) (400b-d_1')

^{1}H NMR, 400MHz, $CDCl_3$

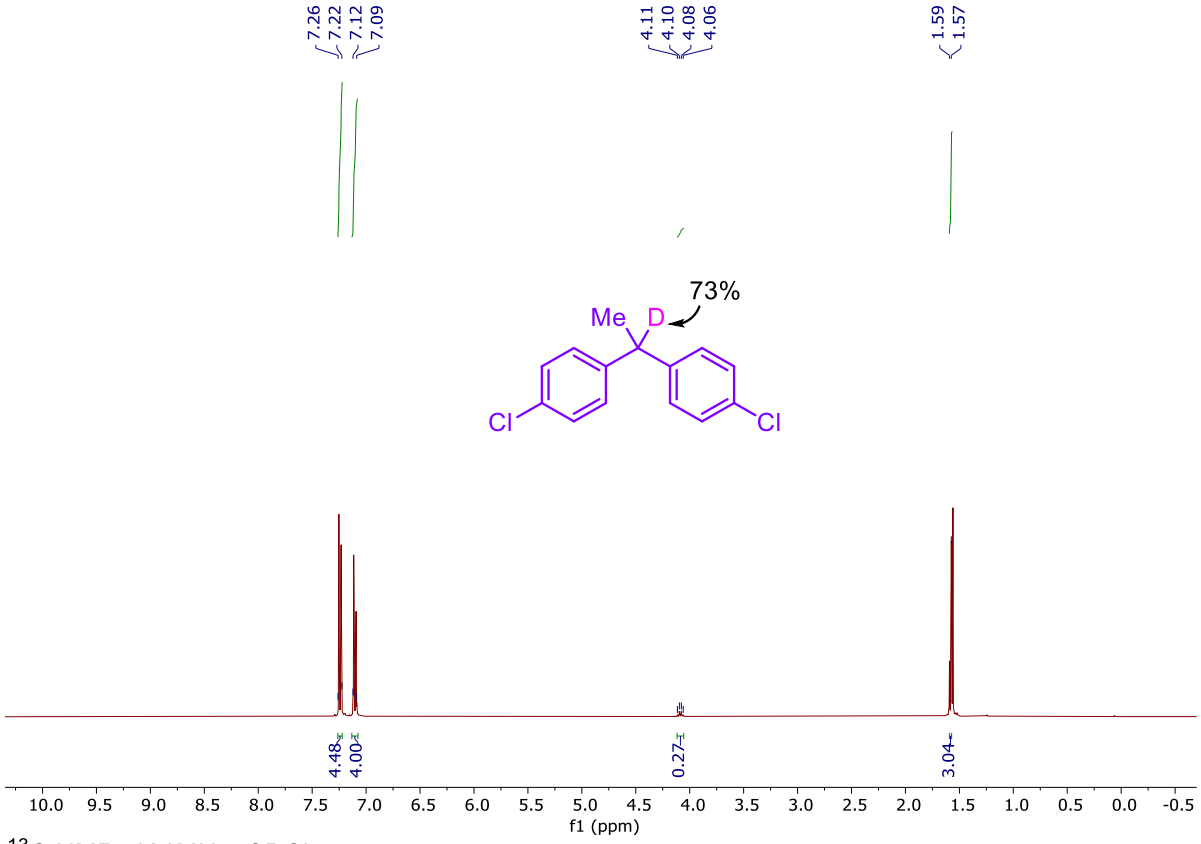


^{13}C NMR, 101MHz, $CDCl_3$

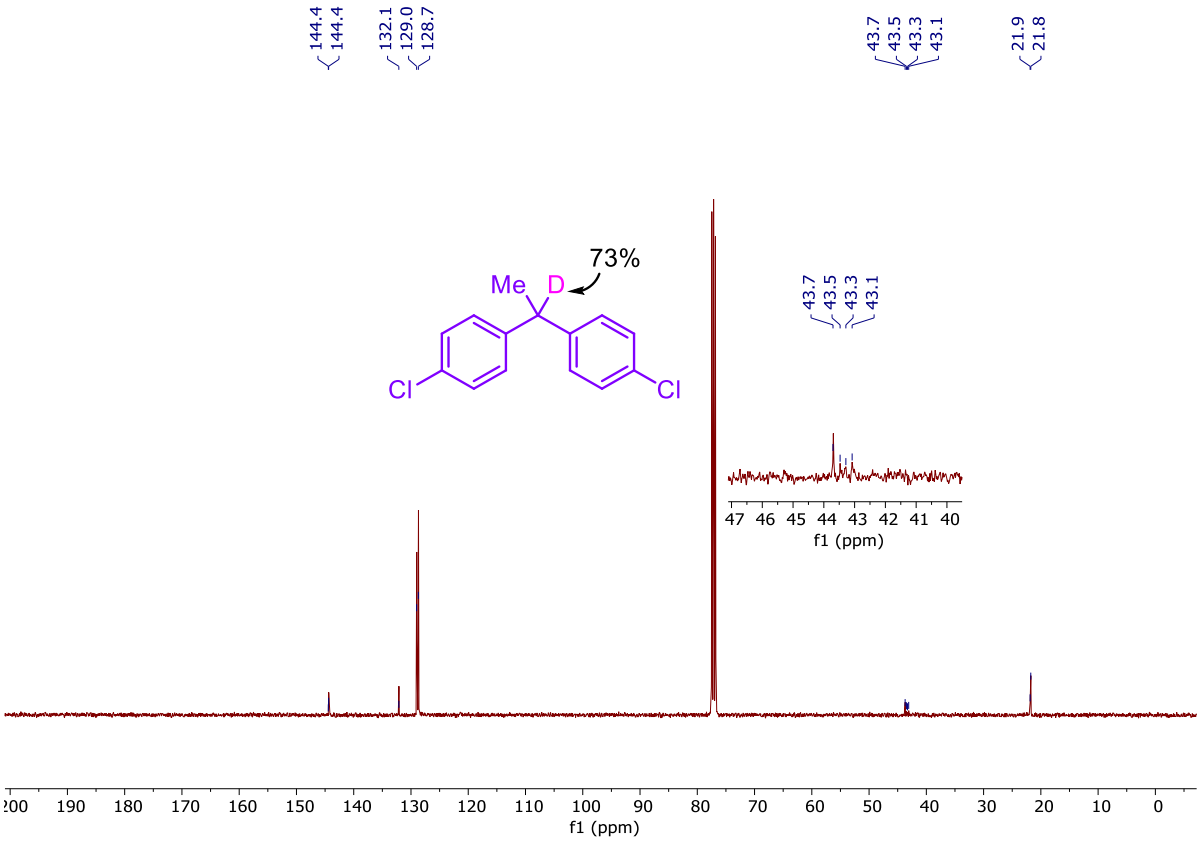


4,4'-(ethane-1,1-diyl-1-*d*)bis(chlorobenzene) (400c-d_1′)

^{1}H NMR, 400MHz, $CDCl_3$

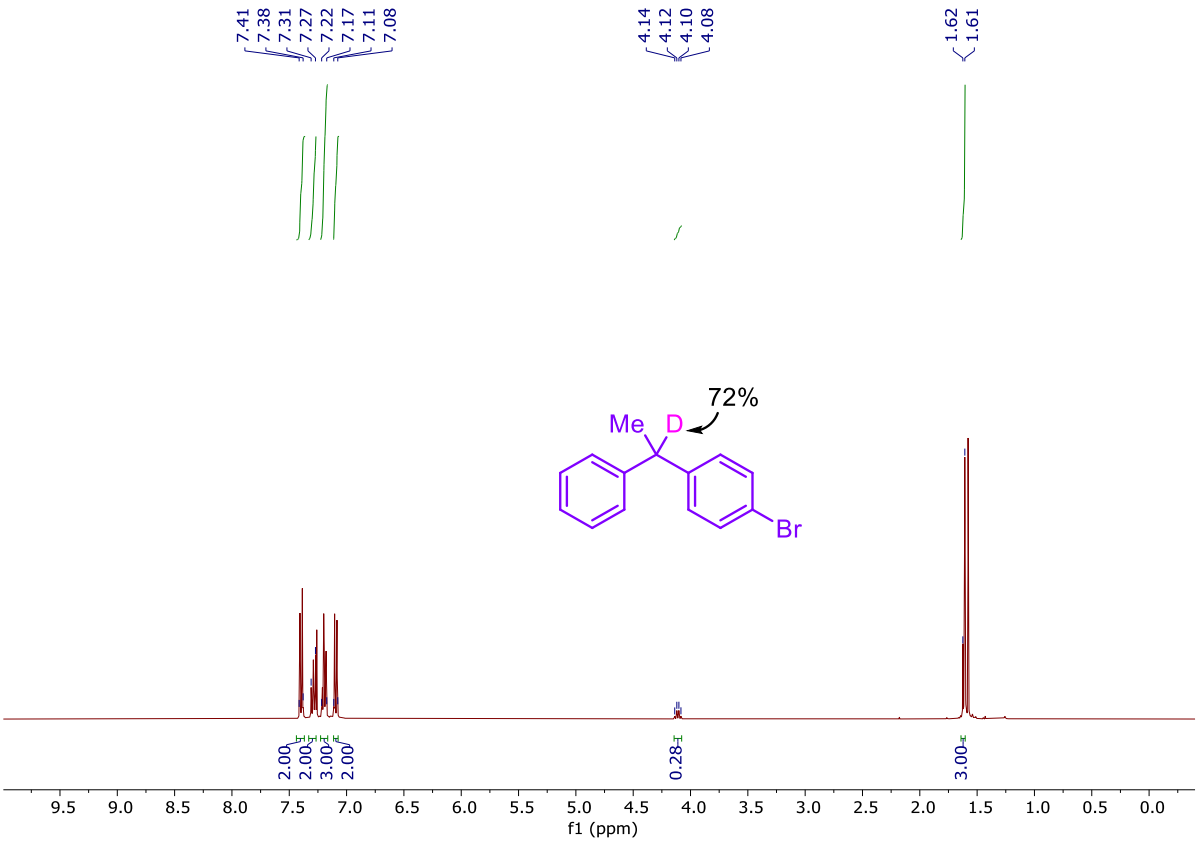


^{13}C NMR, 101MHz, $CDCl_3$

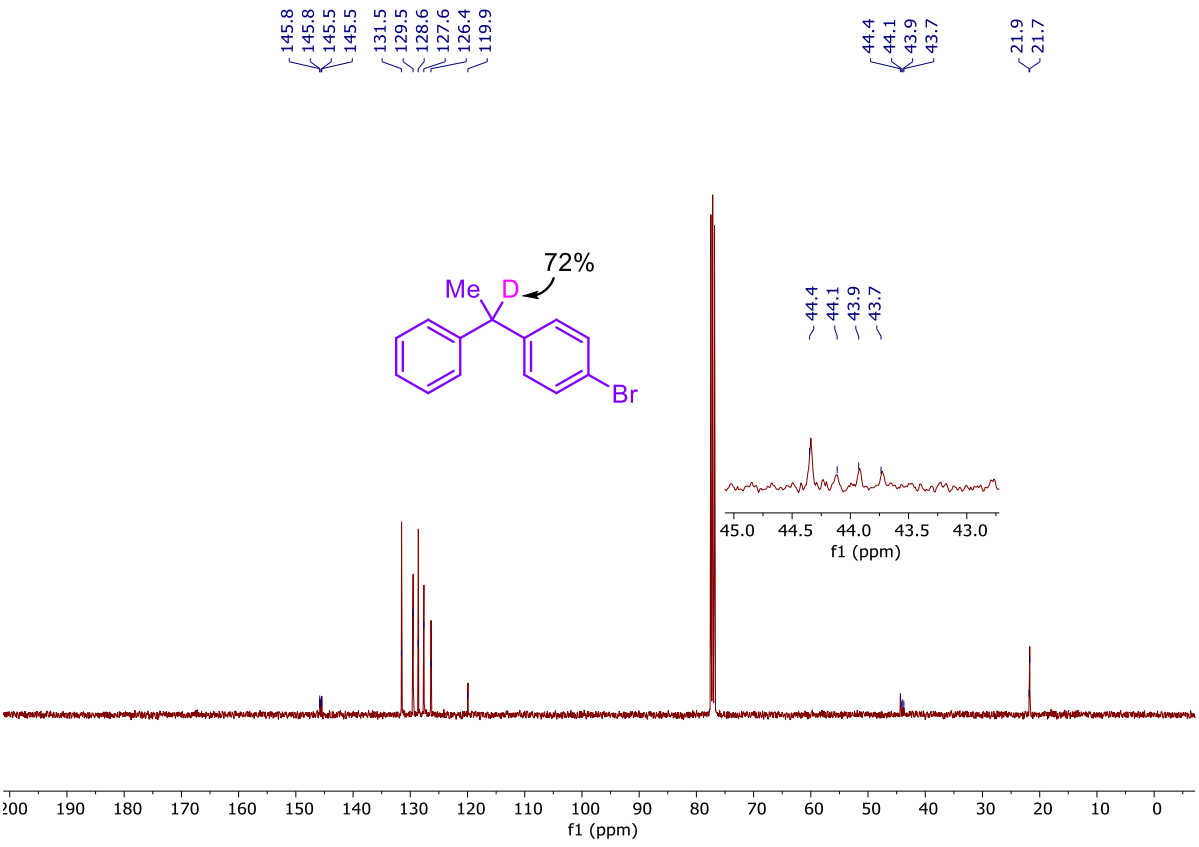


1-bromo-4-(1-phenylethyl-1-*d*)benzene (400f-d_1′)

^{1}H NMR, 400MHz, $CDCl_3$

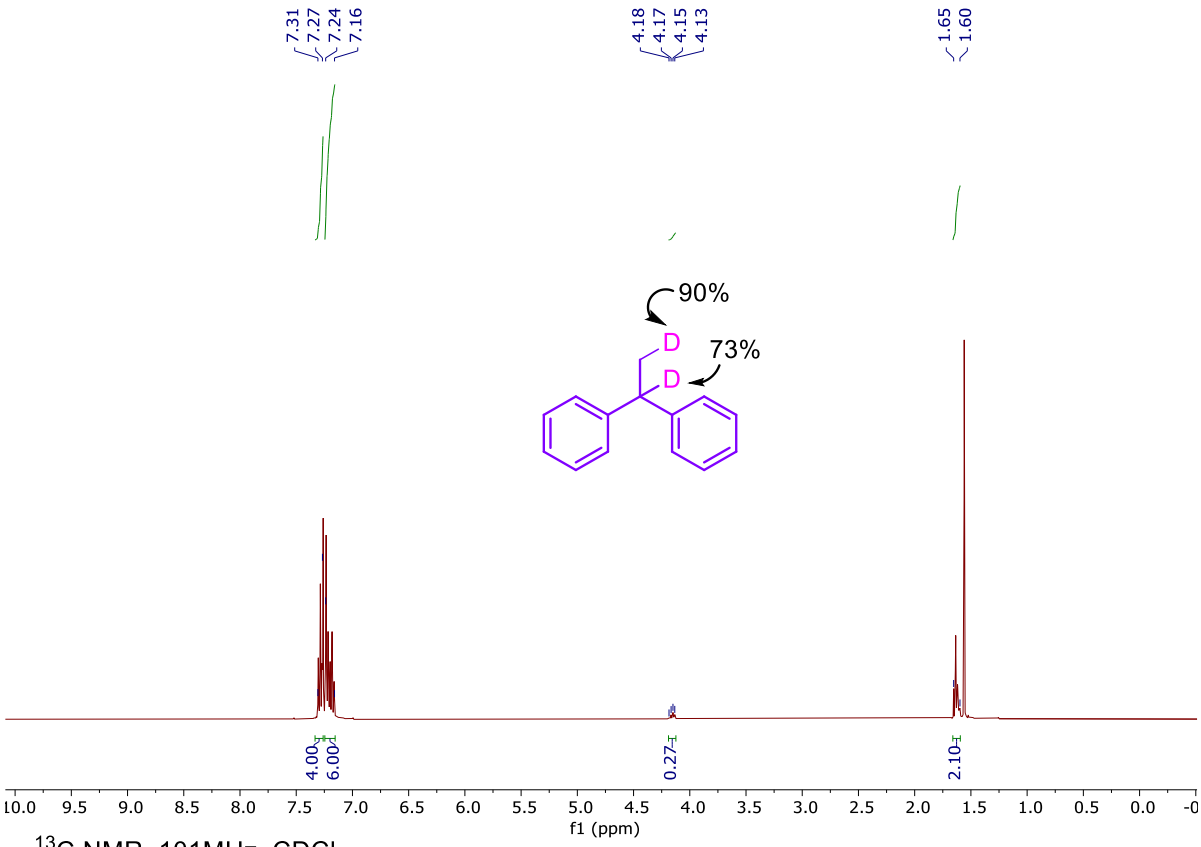


^{13}C NMR, 101MHz, $CDCl_3$

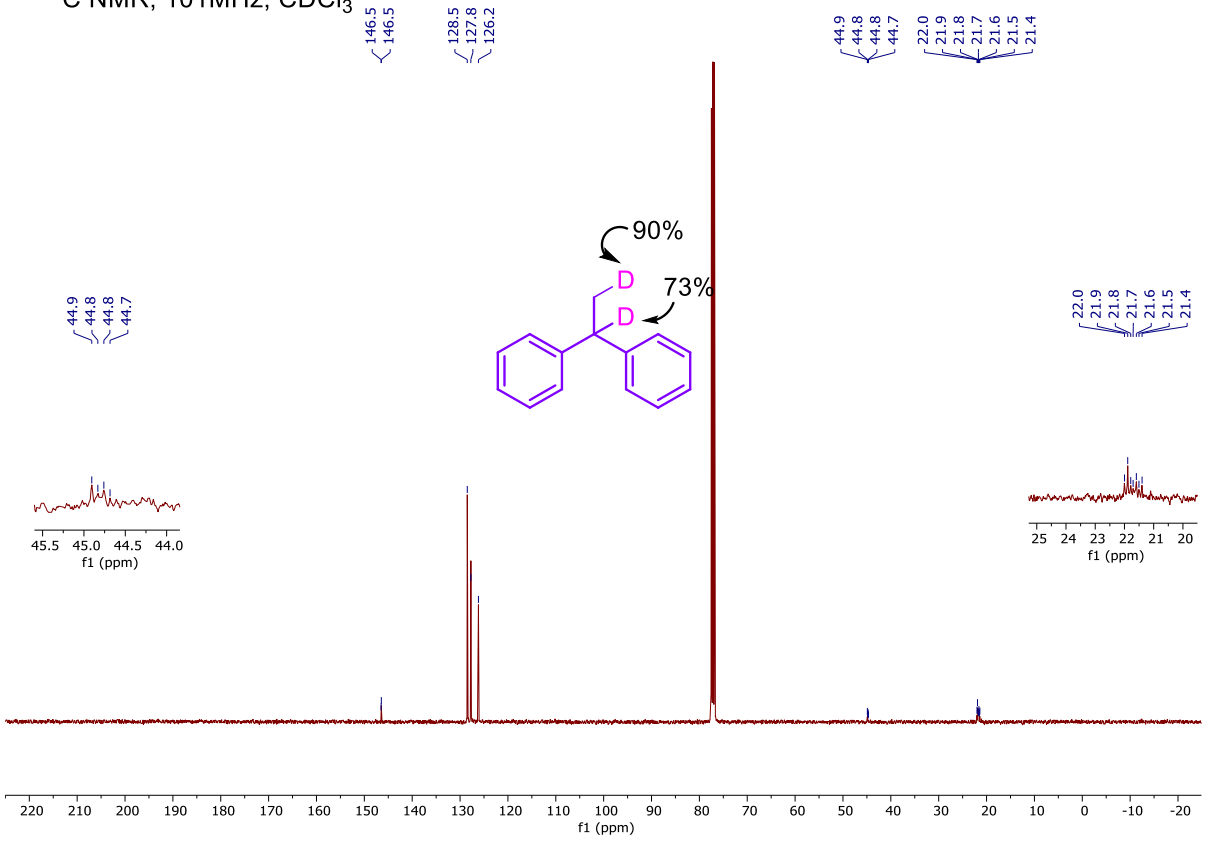


(ethane-1,1-diyl-1,2-d_2)dibenzene (400a-d_2)

^{1}H NMR, 400MHz, $CDCl_3$



^{13}C NMR, 101MHz, $CDCl_3$



Chapter 8

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Chapter 9

Appendix

Table 7. TPSS-D3/def2-TZVP + COSMO computed lowest imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in toluene solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the relative electronic energies (ΔET and ΔEP) and Gibbs free-energies (ΔGT and ΔGP) at the TPSS-D3 and PW6B95-D3 levels. Each structure is labeled either by its molecular formula or a specific name in bold. Transition structures (with only one imaginary frequency) are indicated by the "**TS**" prefix. See Figure 14, 15, 16 in chapter 2 for structural labellings.

Reactions	ImF	ZPE	Hc	Gc	Hsol	Gsol	TPSS-D3	PW6B95-D3	ΔET	ΔEP	ΔGP	ΔGT
	cm^{-1}	kcal/mol	kca/mol	kcal/mol	kcal/mol	kcal/mol	E_h	E_h	kcal/mol	kcal/mol	kcal/mol	kcal/mol
*Complexes of $B(C_6F_5)_3$ with thiophenol **274a** and 1-phenyl-1,3-diene **273a***												
274a + $B(C_6F_5)_3$	0	156.04	179.27	103.46	-27.69	-19.27	-2840.26808	-2843.07386	0.0	0.0	0.0	0.0
A	0	156.78	180.31	117.58	-24.41	-18.32	-2840.28704	-2843.09158	-11.9	-11.1	2.1	1.3
273a + $B(C_6F_5)_3$	0	197.97	222.79	143.42	-28.62	-19.98	-2596.93450	-2599.60900	0.0	0.0	0.0	0.0
TSAa	-20	198.28	223.03	158.06	-26.91	-20.33	-2596.93574	-2599.60635	-0.8	1.7	14.1	11.6
Aa	0	198.89	223.85	158.66	-29.09	-22.06	-2596.93382	-2599.60588	0.4	2.0	13.2	11.7
*Hydrothiolation via protonation of 1,3-diene **273a** and sulfide anion transfer*												
273a + **274a** + $B(C_6F_5)_3$	0	259.75	288.97	186.29	-39.38	-26.90	-3227.58037	-3230.80853	0.0	0.0	0.0	0.0
273a + **A**	0	260.49	290.02	200.40	-36.10	-25.95	-3227.59933	-3230.82624	-11.9	-11.1	2.1	1.3
TSAB (at site 4)	-1131	258.14	288.19	212.38	-34.73	-26.58	-3227.59606	-3230.81554	-9.9	-4.4	18.2	12.8
$\mathbf{B}^+ + \mathbf{C}^-$	0	261.26	290.93	200.89	-101.75	-89.60	-3227.48393	-3230.71014	60.5	61.8	11.8	10.5
D	0	263.27	292.95	218.42	-30.57	-23.08	-3227.63118	-3230.85833	-31.9	-31.3	0.9	0.3
275a + $B(C_6F_5)_3$	0	262.43	291.76	202.58	-36.10	-25.76	-3227.61186	-3230.83993	-19.8	-19.7	-4.2	-4.2
TSABa (at site 1)	-3	259.19	288.90	214.38	-33.53	-25.70	-3227.58342	-3230.80199	-1.9	4.1	29.6	23.6

Ba$^+$**.C**$^-$	0	262.13	292.33	216.85	-30.95	-23.86	-3227.62028	-3230.84152	-25.1	-20.7	9.1	4.8
Da	0	262.66	292.55	217.46	-30.55	-23.11	-3227.62569	-3230.85296	-28.4	-27.9	3.3	2.8
275a' + $B(C_6F_5)_3$	0	262.02	291.49	201.98	-36.08	-25.75	-3227.60432	-3230.83273	-15.0	-15.2	-0.2	-0.1
G (via unstable **Aa**)	0	261.09	291.21	215.73	-33.59	-25.53	-3227.59587	-3230.81961	-9.7	-7.0	20.1	17.3
TS3G	-1183	258.56	287.98	213.86	-31.80	-24.11	-3227.53489	-3230.75842	28.6	31.5	58.0	55.1
275a + $B(C_6F_5)_3$	0	262.43	291.76	202.58	-36.10	-25.76	-3227.61186	-3230.83993	-19.8	-19.7	-4.2	-4.2
Competing 1,3-diene addition to intermediate ***B***$^+$*and sulfide anion transfer from* ***C***$^-$												
273a + **B**$^+$	0	214.93	227.25	172.80	-62.37	-52.69	-774.98846	-775.82730	0.0	0.0	11.8	0.0
TSBE$^+$ (at site 3)	-193	215.47	227.66	187.96	-51.48	-45.01	-775.01934	-775.85015	-19.4	-14.3	18.4	1.6
E$^+$	0	217.88	229.81	190.57	-52.51	-45.71	-775.02683	-775.86451	-24.1	-23.4	11.3	-1.2
TSBEa$^+$ (at site 1)	-289	215.40	227.73	187.39	-52.14	-44.91	-775.01314	-775.84465	-15.5	-10.9	21.4	5.0
Ea$^+$	0	217.45	229.57	189.72	-53.91	-46.39	-775.01627	-775.85408	-17.5	-16.8	16.3	3.9
E$^+$ **+ C**$^-$	0	367.93	403.20	301.49	-103.58	-90.25	-3614.83460	-3618.48201	0.0	0.0	0.0	0.0
F + $B(C_6F_5)_3$	0	368.13	403.45	302.04	-43.50	-31.47	-3614.95295	-3618.60463	-74.3	-77.0	-17.6	-14.9
Potential E-to-Z conversion via ***B***$^+$ *rotation (high overall barrier of 11.8 + 18.7 = 30.5 kcal/mol)*												
B$^+$ (*E*-allyl cation)	0	111.22	117.54	89.97	-50.67	-45.06	-387.67617	-388.09264	0.0	0.0	0.0	0.0
TSBz$^+$	-383	109.98	116.13	88.92	-51.61	-45.98	-387.64216	-388.05972	21.3	20.7	18.7	19.4
Bz$^+$ (*Z*-allyl cation)	0	111.34	117.52	90.31	-50.92	-45.40	-387.66675	-388.08287	5.9	6.1	6.1	5.9

*Hydrothiolation via protonation of 1-methyl 1,3-diene **m1** and sulfide anion transfer*												
m1 + **274a** + $B(C_6F_5)_3$	0	226.24	253.80	155.78	-33.95	-22.70	-3035.71112	-3038.72469	0.0	0.0	0.0	0.0
mTSAB	-1000	225.01	253.21	181.19	-30.69	-23.54	-3035.72288	-3038.72795	-7.4	-2.1	18.8	13.4
mTSABa	-952	225.63	253.47	182.63	-28.56	-21.71	-3035.72410	-3038.73019	-8.2	-3.5	20.6	15.9
$mB^+.C^-$	0	228.97	256.88	186.08	-32.32	-25.07	-3035.73348	-3038.73763	-14.0	-8.1	16.0	10.1
$mB^+ + C^-$	0	227.40	255.30	170.12	-104.52	-93.01	-3035.59175	-3038.60491	74.9	75.2	17.3	17.1
mD	0	229.99	257.95	186.85	-26.42	-19.89	-3035.76545	-3038.77898	-34.1	-34.1	-4.0	-4.0
m3 + $B(C_6F_5)_3$	0	229.34	256.83	171.66	-31.12	-21.85	-3035.74252	-3038.75599	-19.7	-19.6	-4.8	-4.9
*Protonated 1-phenethyl 1,3-diene **p1** : 1-phenethyl-directed protonation at site 1 & unfavorable at site 3*												
pB^+ (at site 4: missing)	0	146.00	154.00	122.77	-53.13	-47.05	-466.33783	-466.83718	0.0	0.0	0.0	0.0
pBa^+ (at site 1)	0	146.84	154.24	124.76	-50.35	-45.24	-466.34360	-466.83975	**-3.6**	**-1.6**	2.2	**0.2**
pBh^+ (at site 3)	0	147.74	154.72	126.04	-52.17	-46.85	-466.30347	-466.80171	21.6	22.3	25.7	25.0

Table 8. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in toluene. Each structure is labeled by the specific name (See also **Figure 14, 15, 16** (chapter 2) and **Table 7**), followed by the number of atoms, the total energy, and the detailed atomic coordinate

273a PhCH=CHCH=CH_2
20
Energy = -387.2948935894
C -7.8843669 -0.4276773 0.0617659
C -6.5420996 -0.5383881 0.0613318
H -8.3747102 0.5408702 0.0616884
H -8.5247133 -1.3072277 0.0620084
H -5.9315868 0.3654308 0.0610112
C -5.8312878 -1.7970003 0.0612815
C -4.4802946 -1.8885303 0.0609842
H -6.4420800 -2.6995718 0.0614978
H -3.9065735 -0.9606912 0.0607235
C -3.6821344 -3.1106027 0.0609795
C -2.2775327 -3.0028957 0.0609938
C -4.2461457 -4.4031878 0.0610740
C -1.4659870 -4.1359021 0.0611142
H -1.8263798 -2.0133134 0.0608928
C -3.4357703 -5.5333747 0.0612260
H -5.3256650 -4.5239722 0.0610329
C -2.0415543 -5.4078451 0.0612756
H -0.3849701 -4.0260352 0.0611220
H -3.8900594 -6.5203427 0.0613070
H -1.4133125 -6.2939245 0.0614190

274a PhSH
13
Energy = -630.6254585196
S -4.6158371 -1.6524170 0.0602695
H -3.6283100 -0.7388677 0.0611306
C -3.5759938 -3.0917279 0.0606331
C -2.1770811 -3.0078258 0.0604751
C -4.1977888 -4.3487146 0.0608990
C -1.4124140 -4.1746561 0.0606909
H -1.6877788 -2.0379614 0.0602183
C -3.4223702 -5.5074179 0.0610726
H -5.2821238 -4.4198058 0.0610048
C -2.0278136 -5.4282431 0.0608984
H -0.3285876 -4.0981524 0.0604787
H -3.9147166 -6.4758292 0.0612943
H -1.4281371 -6.3333898 0.0611083

275a' PhCH=CHCH_2CH_2SPh (3,4-hydrothiolation)
33
Energy = -1017.941235813
S 0.6665961 0.3959312 -0.7903999
C 0.9787413 -1.1014329 -1.6972344
C 1.9969407 -1.9741628 -1.2866879
C 0.2049023 -1.4174642 -2.8224979
C 2.2439378 -3.1453504 -2.0031016
H 2.5865421 -1.7283145 -0.4088515
C 0.4527860 -2.5925161 -3.5327688
H -0.5798435 -0.7373970 -3.1375045
C 1.4730188 -3.4552003 -3.1268269
H 3.0357413 -3.8169496 -1.6831918
H -0.1493184 -2.8318492 -4.4048063
H 1.6654039 -4.3696711 -3.6809945
C 1.8495602 1.6064808 -1.6516063
H 1.6308622 2.5239725 -1.0968394
C 3.2683260 1.2019304 -1.4245231
C 4.1145256 1.8802482 -0.6419835
H 3.6101460 0.2961750 -1.9236980
H 3.7597704 2.7841617 -0.1429918
C 1.4362196 1.7769380 -3.0906329
C 0.4986305 2.7649534 -3.4240510
C 1.9389034 0.9563918 -4.1088737
C 0.0715026 2.9295639 -4.7399803
H 0.1016932 3.4067072 -2.6406906
C 1.5083016 1.1160695 -5.4271470
H 2.6637977 0.1832504 -3.8763041
C 0.5742243 2.1014067 -5.7480688
H -0.6518948 3.7039241 -4.9804484
H 1.9039557 0.4668689 -6.2034627
H 0.2414068 2.2263213 -6.7746685
C 5.5373327 1.4871517 -0.3824321
H 5.8069232 0.5802228 -0.9327473
H 6.2272094 2.2896169 -0.6740803
H 5.7019270 1.3057742 0.6881014

275a PhCH=CHCH(SPh)CH_3 (4,3-hydrothiolation)
33
Energy = -1017.948696586
C -0.7268294 2.7190632 -2.6793240
C -0.8121445 1.7609962 -1.4925774
H -0.3904375 2.1958688 -3.5807522
H -1.6983431 3.1795419 -2.8819753
H -1.2005412 2.2701572 -0.6065721
C 0.4585178 1.0536630 -1.1901255
C 0.8518411 0.7424902 0.0585407
H 1.0280543 0.7153425 -2.0552526
H 0.2206297 1.0585289 0.8895132
C 2.0362951 -0.0305086 0.4355430
C 2.1630373 -0.4775522 1.7633062
C 3.0601022 -0.3588516 -0.4739450
C 3.2640793 -1.2309687 2.1687330
H 1.3795466 -0.2355357 2.4777240
C 4.1605362 -1.1082298 -0.0696248

H	2.9994496	-0.0148715	-1.5026088
C	4.2694947	-1.5498939	1.2539743
H	3.3382744	-1.5673382	3.1994171
H	4.9414504	-1.3460949	-0.7869711
H	5.1322504	-2.1309049	1.5668590
S	-2.1131770	0.4591933	-1.9170895
H	-0.0044458	3.5108403	-2.4540816
C	-2.1731234	-0.3845817	-0.3517747
C	-2.9116723	0.1588875	0.7077376
C	-1.4398557	-1.5615478	-0.1559055
C	-2.9139356	-0.4703333	1.9521794
H	-3.4746417	1.0749273	0.5534949
C	-1.4522024	-2.1926117	1.0888448
H	-0.8539880	-1.9674847	-0.9744487
C	-2.1853660	-1.6475075	2.1442324
H	-3.4838702	-0.0414683	2.7715311
H	-0.8762244	-3.1015564	1.2358915
H	-2.1886720	-2.1363093	3.1141678

A.273a

$B(C_6F_5)_3$.PhSH.PhCH=CHCH=CH_2 complex

67

Energy = -3227.467223860

B	-0.5632335	-0.1083382	0.5280473
C	0.2584632	-0.3921328	1.8979153
C	-1.8336910	0.9074999	0.6221316
C	-1.0643648	-1.4107315	-0.3156260
C	0.8667972	-1.6122457	2.2087697
C	0.5804596	0.6505088	2.7750625
C	-2.2979641	1.5581888	-0.5231678
C	-2.6219400	1.1070164	1.7592734
C	-0.8254140	-1.7660357	-1.6422457
C	-1.9717335	-2.2529975	0.3404819
C	1.7068176	-1.7967962	3.3040558
C	1.4066607	0.5090509	3.8832795
C	-3.4283392	2.3650024	-0.5646564
C	-3.7671456	1.9006890	1.7641250
C	-1.4135489	-2.8624298	-2.2716761
C	-2.5813314	-3.3562573	-0.2416316
C	1.9781731	-0.7300327	4.1517487
C	-4.1739581	2.5375112	0.5968273
C	-2.3001965	-3.6668031	-1.5688013
F	0.6857807	-2.7012388	1.4259290
F	0.1153512	1.9028875	2.5365858
F	-1.6197554	1.4061961	-1.6927552
F	-2.3101830	0.5175038	2.9356616
F	0.0288170	-1.0540887	-2.4257777
F	-2.2881899	-2.0020547	1.6340033
F	2.2687007	-2.9968474	3.5408406
F	1.6771158	1.5592148	4.6814336
F	-3.8072159	2.9698205	-1.7058855
F	-4.4873380	2.0565189	2.8917326
F	-1.1281303	-3.1427398	-3.5576110
F	-3.4361832	-4.1236652	0.4602120
F	2.7910501	-0.8893014	5.2075034
F	-5.2739352	3.3071381	0.5902422
F	-2.8779383	-4.7253123	-2.1586423
S	0.9211976	1.0164926	-0.3901055
C	2.4405256	0.1326554	-0.0772020
C	3.3407047	0.7540430	0.7893324
C	2.6928704	-1.1397504	-0.5952358
C	4.5069528	0.0831966	1.1544300
H	3.1326010	1.7487144	1.1688818
C	3.8667605	-1.7937047	-0.2312067
H	1.9879296	-1.6135671	-1.2663305
C	4.7690409	-1.1887059	0.6469676
H	5.2108573	0.5614612	1.8280950
H	4.0728909	-2.7817414	-0.6307955
H	5.6787274	-1.7088321	0.9305321
C	-1.0891219	0.5025224	-5.4467456
C	-0.3939714	1.4598332	-4.8063575
H	-0.6623246	-0.4821064	-5.6231648
H	-2.1007416	0.6747068	-5.8004640
H	-0.8537924	2.4328190	-4.6318472
C	0.9472493	1.2787534	-4.2991455
C	1.6168640	2.2339113	-3.6079161
H	1.4106649	0.3103643	-4.4853828
H	1.1102564	3.1848340	-3.4375881
C	2.9481637	2.1279798	-3.0188195
C	3.4240513	3.1916351	-2.2274536
C	3.7732703	0.9960956	-3.1740617
C	4.6719690	3.1285233	-1.6116531
H	2.7979148	4.0708713	-2.0962994
C	5.0174111	0.9337917	-2.5579581
H	3.4346432	0.1573614	-3.7753412
C	5.4733395	1.9973942	-1.7725989
H	5.0170786	3.9593384	-1.0026447
H	5.6340389	0.0485797	-2.6815754
H	6.4425018	1.9398471	-1.2862752
H	0.8008417	0.8293916	-1.7219650

Aa $B(C_6F_5)_3$.CH_2=CHCH=CHPh

54

Energy = -2596.815955899

B	0.8295841	0.0756573	-0.5090584
C	1.2637525	1.6131657	-0.1754663
C	-0.3132764	-0.5935601	0.4641835
C	2.0871685	-0.9854494	-0.5098591
C	2.5729334	2.0982043	-0.2801303
C	0.3259917	2.6054162	0.1344456
C	-0.9675627	-1.7710307	0.0833963
C	-0.6814785	-0.1421335	1.7369047
C	2.6238336	-1.7334411	-1.5588600
C	2.6985299	-1.2323084	0.7259187
C	2.9318796	3.4261777	-0.0555132
C	0.6339166	3.9402604	0.3644078
C	-1.9578601	-2.4033868	0.8278303
C	-1.6604346	-0.7467656	2.5239406
C	3.6572020	-2.6572931	-1.4031733

C	3.7345456	-2.1351693	0.9284950
C	1.9570784	4.3584026	0.2748264
C	-2.3177397	-1.8808691	2.0638390
C	4.2199292	-2.8643007	-0.1514877
F	3.5971462	1.2813552	-0.6319030
F	-0.9946721	2.2893779	0.2095058
F	-0.6501944	-2.3825406	-1.0918182
F	-0.0733204	0.9248170	2.3054091
F	2.1763947	-1.5963897	-2.8352516
F	2.2952273	-0.5364767	1.8194784
F	4.2172782	3.8166129	-0.1680565
F	-0.3321167	4.8305291	0.6666095
F	-2.5651265	-3.5154386	0.3636742
F	-1.9691942	-0.2451642	3.7369336
F	4.1183398	-3.3507101	-2.4647147
F	4.2754852	-2.3054986	2.1520057
F	2.2831998	5.6437326	0.4905126
F	-3.2683494	-2.4728719	2.8066696
F	5.2197707	-3.7481821	0.0128443
C	0.1861355	0.1934391	-2.2087264
C	-1.0439657	0.8897285	-2.1790686
H	0.9976671	0.7239897	-2.7048267
H	0.0916739	-0.8448045	-2.5103374
H	-1.0351579	1.9775457	-2.2106683
C	-2.2913956	0.2747883	-2.0089895
C	-3.4114489	1.0260286	-1.7404357
H	-2.3425569	-0.8090156	-2.0385168
H	-3.2986505	2.1099819	-1.7484198
C	-4.7159325	0.5325274	-1.4012111
C	-5.7402117	1.4699559	-1.1361144
C	-5.0069029	-0.8479376	-1.2902011
C	-7.0121324	1.0451472	-0.7754291
H	-5.5177840	2.5302801	-1.2181565
C	-6.2774077	-1.2661621	-0.9289139
H	-4.2350235	-1.5851877	-1.4850350
C	-7.2820439	-0.3226459	-0.671351
H	-7.7921244	1.7720302	-0.5728028
H	-6.4960681	-2.3259192	-0.8442024
H	-8.2750874	-0.6577626	-0.3875289

A $B(C_6F_5)_3$.PhSH complex

47

Energy = -2840.161921022

B	-0.2642178	0.0216776	0.1455389
C	1.1383117	-0.1539895	-0.6191080
C	-1.2662930	-1.2549143	0.1945664
C	-1.1096348	1.3715294	-0.1742246
C	1.7202969	0.8131448	-1.4440810
C	1.9509410	-1.2682919	-0.3769328
C	-2.3038588	-1.3155419	1.1287401
C	-1.2611672	-2.3026027	-0.7313774
C	-1.0942092	2.5785881	0.5229944
C	-1.9699144	1.3601464	-1.2783347
C	3.0004052	0.6939120	-1.9820686
C	3.2339946	-1.4233160	-0.8800981
C	-3.2464137	-2.3353600	1.1870072
C	-2.1859499	-3.3429818	-0.7143579
C	-1.8846608	3.6764360	0.1944776
C	-2.7749769	2.4312798	-1.6485344
C	3.7672895	-0.4276582	-1.6938143
C	-3.1843576	-3.3646490	0.2537445
C	-2.7382756	3.6027428	-0.8994824
F	1.0645543	1.9563384	-1.7530092
F	1.4980428	-2.2614855	0.4299938
F	-2.4246675	-0.3258650	2.0551941
F	-0.3600840	-2.3313466	-1.7388288
F	-0.2567810	2.7586852	1.5810632
F	-2.0217768	0.2677893	-2.0799901
F	3.5055029	1.6644948	-2.7662645
F	3.9679483	-2.5102187	-0.5814558
F	-4.2098908	-2.3345861	2.1260654
F	-2.1295047	-4.3241893	-1.6340822
F	-1.8223302	4.8077392	0.9210833
F	-3.5786338	2.3490593	-2.7248956
F	5.0072771	-0.5503364	-2.1898740
F	-4.0810312	-4.3618867	0.2824256
F	-3.5053980	4.6507938	-1.2367746
S	0.3601141	0.1457902	2.2103940
H	0.3505124	-1.1821963	2.4316094
C	2.1386793	0.3127119	2.2010281
C	2.9351697	-0.7218046	2.6991824
C	2.7066491	1.4818661	1.6880404
C	4.3220160	-0.5850781	2.6663566
H	2.4833714	-1.6266489	3.0924633
C	4.0951345	1.5996886	1.6562023
H	2.0821841	2.2829813	1.3101882
C	4.9034689	0.5691928	2.1396895
H	4.9446546	-1.3902073	3.0434716
H	4.5420566	2.5016502	1.2501647
H	5.9840321	0.6673488	2.1095250

Ba$^+$ $PhCH_2CH{=}CHCH_2^+$ (1-protonated **273a**)

21

Energy = -387.6892217846

C	-3.2354169	0.7190180	0.9602954
C	-2.5011000	0.2638101	-0.0842109
H	-3.1205325	0.2930068	1.9534394
H	-3.9736483	1.5043696	0.8342715
H	-2.6163062	0.6899997	-1.0768219
C	-1.6418544	-0.8503937	0.0949693
C	-0.8373457	-1.4670903	-0.9550514
H	-1.5515672	-1.2595745	1.0991416
H	-0.6229468	-2.5235162	-0.8109105
C	0.3312982	-0.5754943	-0.4802902
C	1.1553427	-1.0041990	0.5801615
C	0.5631211	0.6689025	-1.1015790
C	2.2409283	-0.2271464	0.9636417
H	0.9526974	-1.9509422	1.0720425
C	1.6536573	1.4336317	-0.7153119

H	-0.0922408	1.0072702	-1.8981153
C	2.4897144	0.9888067	0.3178283
H	2.8924388	-0.5638697	1.7631498
H	1.8559982	2.3769543	-1.2117425
H	3.3347671	1.5974676	0.6241923
H	-1.1419157	-1.2304290	-1.9723159

B^{+} *E*-PhCH=CHCHCH$_3^{+}$ (4-protonated **273a**)

21

Energy = -387.7195204942

C	-4.4324162	0.3244797	0.0074940
C	-3.1658724	-0.4197076	0.0817744
H	-5.0473286	-0.0844466	-0.8075771
H	-4.2899264	1.3971636	-0.1312331
H	-3.2305404	-1.5011482	0.2033221
C	-1.9159178	0.1439271	0.0116548
C	-0.7843921	-0.6776666	0.0938199
H	-1.8178416	1.2190641	-0.1076920
H	-0.9649849	-1.7457966	0.2096703
C	0.5705534	-0.2727407	0.0397252
C	1.5717373	-1.2784708	0.1304008
C	0.9617747	1.0875597	-0.1009307
C	2.9119996	-0.9378108	0.0800780
H	1.2663814	-2.3151218	0.2377110
C	2.3026709	1.4166455	-0.1458065
H	0.2110717	1.8669738	-0.1729380
C	3.2762636	0.4080069	-0.0566451
H	3.6765503	-1.7043174	0.1463634
H	2.6070743	2.4524129	-0.2509125
H	4.3273366	0.6774995	-0.0948505
H	-5.0147818	0.1382538	0.9225349

Bz^{+} *Z*-PhCH=CHCHCH$_3^{+}$

21

Energy = -387.7103449718

C	-3.1187825	2.3265034	0.5630154
C	-1.9268701	1.4647104	0.4886324
H	-3.3148239	2.6090241	1.6064236
H	-4.0040609	1.8688414	0.1193704
H	-1.0248973	1.8334835	0.9732168
C	-1.9109782	0.2126018	-0.0729511
C	-0.7772381	-0.6189156	-0.1278408
H	-2.8549910	-0.2197720	-0.3974717
H	-0.9713294	-1.6876480	-0.2128268
C	0.5867789	-0.2430453	-0.0863924
C	1.5384234	-1.2495778	0.2413447
C	1.0414905	1.0786481	-0.3537044
C	2.8746337	-0.9233841	0.3871418
H	1.1928302	-2.2648959	0.4117074
C	2.3816957	1.3892715	-0.2187274
H	0.3469590	1.8213766	-0.7299677
C	3.2950645	0.3951604	0.1643300
H	3.5970893	-1.6843528	0.6616741
H	2.7319711	2.3925400	-0.4367653
H	4.3477726	0.6438644	0.2574992
H	-2.8980599	3.2736476	0.0461489

C^{-} $(C_6F_5)_3BSPh^{-}$ anion

46

Energy = -2839.719473233

B	-0.1523078	-0.0817498	0.3527194
C	1.1526646	-0.3325463	-0.5983205
C	-1.3003594	-1.2658255	0.2983905
C	-0.9679762	1.3130528	0.0156916
C	1.7380402	0.6262410	-1.4275627
C	1.8964915	-1.5157983	-0.4981771
C	-2.3380196	-1.2693081	1.2367585
C	-1.4059023	-2.2735472	-0.6627915
C	-1.1025528	2.4512132	0.8124300
C	-1.6788727	1.3813126	-1.1880313
C	2.9456733	0.4466817	-2.1000965
C	3.1054334	-1.7365668	-1.1442769
C	-3.3682386	-2.2032796	1.2651387
C	-2.4164368	-3.2329011	-0.6719888
C	-1.8868559	3.5512691	0.4604809
C	-2.4690095	2.4534506	-1.5815556
C	3.6413485	-0.7437272	-1.9577087
C	-3.4055258	-3.2047584	0.3023206
C	-2.5786235	3.5566999	-0.7423438
F	1.1695336	1.8494581	-1.6052463
F	1.4542894	-2.5357190	0.2759839
F	-2.3927915	-0.3019310	2.1901475
F	-0.5258806	-2.3596938	-1.6913437
F	-0.4543708	2.5761310	1.9956877
F	-1.5877160	0.3560782	-2.0767954
F	3.4553723	1.4323435	-2.8733669
F	3.7678543	-2.9055874	-0.9944832
F	-4.3328882	-2.1455309	2.2098695
F	-2.4521669	-4.1850584	-1.6311264
F	-1.9761804	4.6204899	1.2837195
F	-3.1180235	2.4449075	-2.7674317
F	4.8145612	-0.9365611	-2.5929712
F	-4.3885200	-4.1263718	0.3095737
F	-3.3365147	4.6138839	-1.0951922
S	0.5412117	-0.2459026	2.2080286
C	2.2220599	0.2991823	2.1611364
C	3.1860828	-0.4503899	2.8571634
C	2.6338167	1.4592505	1.4835357
C	4.5216995	-0.0497986	2.8757878
H	2.8806660	-1.3578334	3.3713708
C	3.9745732	1.8416392	1.4846993
H	1.9006136	2.0621027	0.9588949
C	4.9264888	1.0936782	2.1824460
H	5.2512375	-0.6452893	3.4191269
H	4.2755693	2.7350533	0.9430463
H	5.9698112	1.3966602	2.1836576

Da $CH_3CH=CHCHPhSPh.B(C_6F_5)_3$ complex

67
Energy = -3227.479507112

B	-0.9836267	0.0934695	-0.0992046
C	0.0943876	-0.3016043	1.0448774
C	-1.5287048	1.6355749	-0.1176686
C	-2.3205608	-0.8557208	-0.1567369
C	0.2000810	-1.5973976	1.5651032
C	1.0881171	0.5721284	1.5016427
C	-2.1066362	2.1915411	-1.2653650
C	-1.6250715	2.4520296	1.0175738
C	-2.8938880	-1.5194273	-1.2427912
C	-3.0740465	-0.9470415	1.0207779
C	1.1762361	-1.9921035	2.4771057
C	2.0874911	0.2196358	2.4011065
C	-2.6610440	3.4656191	-1.3274941
C	-2.1784076	3.7303339	1.0017683
C	-4.0956544	-2.2241185	-1.1738732
C	-4.2728885	-1.6385243	1.1373178
C	2.1323603	-1.0786030	2.9004799
C	-2.6914566	4.2500714	-0.1805619
C	-4.7945351	-2.2874390	0.0235374
F	-0.6437430	-2.5766256	1.1662574
F	1.1424879	1.8531465	1.0530114
F	-2.1640601	1.4669683	-2.4101160
F	-1.1999975	2.0267295	2.2281822
F	-2.3011997	-1.5289439	-2.4630008
F	-2.6264604	-0.3393347	2.1471029
F	1.2232673	-3.2616211	2.9209122
F	3.0125378	1.1186674	2.7873449
F	-3.1754995	3.9370637	-2.4785177
F	-2.2284591	4.4654439	2.1291681
F	-4.5844466	-2.8427228	-2.2670894
F	-4.9301042	-1.6856600	2.3121132
F	3.0926879	-1.4437786	3.7635136
F	-3.2244264	5.4812767	-0.2102299
F	-5.9540081	-2.9604226	0.1057544
S	0.0758829	-0.1760126	-1.8679739
C	1.0349399	-1.6687119	-1.7030437
C	2.0768457	-1.8469758	-0.7855722
C	0.6815635	-2.6964834	-2.5872679
C	2.7531150	-3.0647621	-0.7499555
H	2.3692147	-1.0434580	-0.1245720
C	1.3579745	-3.9134878	-2.5335702
H	-0.1180238	-2.5416931	-3.3031364
C	2.3928942	-4.0990514	-1.6153481
H	3.5631835	-3.2042563	-0.0402318
H	1.0798794	-4.7113107	-3.2148426
H	2.9214077	-5.0466162	-1.5771959
C	1.3017730	1.2975930	-2.0112179
H	1.0443582	1.9348703	-1.1668517
C	2.7272029	0.8667660	-1.9437360
C	3.5835537	1.3124747	-1.0172202
H	3.0756271	0.2022692	-2.7326649
H	3.2206318	1.9887989	-0.2446150
C	0.9527136	1.9819272	-3.3111946
C	0.4943489	3.3020763	-3.2880395
C	1.1115571	1.3296642	-4.5404378
C	0.1975195	3.9660392	-4.4791906
H	0.3722631	3.8112545	-2.3354455
C	0.8194969	1.9926860	-5.7291961
H	1.4559128	0.2988282	-4.5690648
C	0.3613094	3.3135230	-5.7015189
H	-0.1619058	4.9903969	-4.4509945
H	0.9477825	1.4804486	-6.6782245
H	0.1305876	3.8281998	-6.6296972
C	5.0321927	0.9448234	-0.9577641
H	5.3105737	0.2632574	-1.7666094
H	5.6629581	1.8403406	-1.0179045
H	5.2652482	0.4644693	0.0017485

D PhCH=CHCHMeSPh.B(C_6F_5)$_3$ complex
67
Energy = -3227.484977325

B	-1.0025066	0.1150844	-0.0757829
C	0.0873825	-0.2856189	1.0537421
C	-1.5875572	1.6431313	-0.0459570
C	-2.3194867	-0.8619451	-0.1513455
C	0.2214030	-1.5880606	1.5498888
C	1.0665786	0.5999728	1.5182473
C	-2.1934692	2.2167152	-1.1698870
C	-1.7022071	2.4214155	1.1144092
C	-2.8803587	-1.5191654	-1.2477384
C	-3.0707412	-0.9890289	1.0247598
C	1.2161988	-1.9800711	2.4430861
C	2.0802778	0.2521667	2.4033471
C	-2.7962979	3.4694440	-1.1881882
C	-2.3063532	3.6764751	1.1442394
C	-4.0655339	-2.2524317	-1.1893218
C	-4.2549603	-1.7068329	1.1300988
C	2.1588500	-1.0555649	2.8731956
C	-2.8508454	4.2135923	-0.0157957
C	-4.7627585	-2.3501361	0.0065098
F	-0.6088800	-2.5755832	1.1428262
F	1.0859492	1.8891283	1.0921225
F	-2.2319561	1.5294388	-2.3415131
F	-1.2443568	1.9795851	2.3067948
F	-2.2920406	-1.4918035	-2.4698493
F	-2.6362782	-0.3898161	2.1606472
F	1.2934767	-3.2566371	2.8623460
F	2.9832572	1.1645110	2.8079987
F	-3.3359830	3.9565610	-2.3213723
F	-2.3723493	4.3729347	2.2949144
F	-4.5404269	-2.8644430	-2.2921975
F	-4.9111995	-1.7854413	2.3039323
F	3.1358297	-1.4174834	3.7183225
F	-3.4319664	5.4228008	-0.0012704
F	-5.9069295	-3.0498223	0.0774186
S	0.0537332	-0.0899469	-1.8589615
C	1.0240729	-1.5823687	-1.7362352

C	2.0651631	-1.7758830	-0.8200767
C	0.6860009	-2.5881982	-2.6500449
C	2.7605223	-2.9832816	-0.8216963
H	2.3471839	-0.9914607	-0.1329537
C	1.3788856	-3.7978617	-2.6306259
H	-0.1117102	-2.4222550	-3.3652300
C	2.4162978	-3.9962088	-1.7182579
H	3.5738120	-3.1291280	-0.1173397
H	1.1120071	-4.5788273	-3.3358648
H	2.9589806	-4.9366369	-1.7088652
C	0.9849587	2.0002443	-3.3724971
C	1.2845031	1.3757555	-2.0073932
H	-0.0695780	2.2689775	-3.4689247
H	1.2464558	1.3107858	-4.1805333
H	0.9957210	2.0387466	-1.1917800
C	2.6900622	0.9202283	-1.8702730
C	3.5140011	1.3313424	-0.8901301
H	3.0401837	0.2293828	-2.6342800
H	3.1383681	2.0516497	-0.1658928
C	4.8872855	0.8817897	-0.6666779
C	5.6351383	1.4826450	0.3620290
C	5.4827378	-0.1580544	-1.4066851
C	6.9375532	1.0706129	0.6370812
H	5.1815999	2.2776437	0.9486785
C	6.7821940	-0.5695625	-1.1311874
H	4.9227806	-0.6546942	-2.1935262
C	7.5167354	0.0433872	-0.1098209
H	7.4987950	1.5482952	1.4350780
H	7.2258860	-1.3750115	-1.7097125
H	8.5302461	-0.2836790	0.1038653
H	1.5910395	2.9059097	-3.4784198

Ea^{+} (site 4-to-1 adduct of **273a** and **B**$^{+}$)

41

Energy = -775.0315457612

H	0.4171335	1.1903832	-0.4481290
C	0.5305664	0.1867034	-0.8765686
C	1.6700993	-0.5473694	-0.2381606
H	-0.4158457	-0.3391471	-0.6929979
H	0.6714888	0.2811669	-1.9572675
H	1.6055284	-0.7041289	0.8406655
C	2.7352736	-1.0195199	-0.8945714
C	3.8422430	-1.7938206	-0.2454660
H	2.8066834	-0.8722856	-1.9727218
H	3.7307084	-1.7533498	0.8421459
C	5.2258337	-1.3027526	-0.6164371
C	6.1780242	-1.0818100	0.3860454
C	5.5825957	-1.0748612	-1.9529082
C	7.4573966	-0.6269443	0.0628471
H	5.9123354	-1.2607620	1.4250037
C	6.8594125	-0.6198317	-2.2773155
H	4.8624259	-1.2490242	-2.7478513
C	7.8011969	-0.3940707	-1.2697611
H	8.1843545	-0.4539928	0.8512576
H	7.1194734	-0.4403997	-3.3165074
H	8.7963792	-0.0401023	-1.5225789
C	3.7680386	-3.3612232	-0.6645222
C	2.5100994	-3.9047698	-0.1587715
H	4.6382195	-3.8478505	-0.2223456
H	3.8222382	-3.3971648	-1.7556763
H	2.4815620	-4.2908987	0.8592324
C	1.3261755	-3.7948039	-0.8533846
C	0.1100449	-4.0948701	-0.2395072
H	1.3486866	-3.4100798	-1.8681749
H	0.1483371	-4.4934593	0.7735708
C	-1.1818221	-3.8885089	-0.7905222
C	-2.3123334	-4.1949983	0.0128349
C	-1.3819984	-3.3658028	-2.0971806
C	-3.5932563	-3.9843842	-0.4693825
H	-2.1553281	-4.5925656	1.0109097
C	-2.6642160	-3.1631129	-2.5714960
H	-0.5308037	-3.1285046	-2.7254973
C	-3.7689473	-3.4701532	-1.7603002
H	-4.4550298	-4.2150863	0.1481460
H	-2.8208192	-2.7674695	-3.5693242
H	-4.7723345	-3.3046370	-2.1407404

E^{+} (site 4-to-3 adduct of **273a** and **B**$^{+}$)

41

Energy = -775.0416175950

H	4.8017481	0.9785107	-2.2933098
C	4.6535555	-0.0774494	-2.0465957
C	3.1544279	-0.3617942	-1.8757724
H	5.0756512	-0.6867365	-2.8511942
H	5.1970237	-0.2957908	-1.1211820
H	2.6289115	-0.1593358	-2.8145766
C	2.5364387	0.4225555	-0.7691415
C	1.3312199	1.0154346	-0.8604013
H	3.0852924	0.4278193	0.1732035
H	0.8184586	0.9807145	-1.8226901
C	0.5819126	1.6790709	0.2067494
C	-0.6753983	2.2325620	-0.0982866
C	1.0352442	1.7513952	1.5391805
C	-1.4534246	2.8381214	0.8859120
H	-1.0400370	2.1788110	-1.1212838
C	0.2579076	2.3553955	2.5215028
H	1.9989399	1.3285095	1.8083878
C	-0.9903037	2.9016763	2.2007766
H	-2.4216965	3.2568694	0.6274911
H	0.6235244	2.4010620	3.5435137
H	-1.5947903	3.3697361	2.9721286
C	2.9962957	-1.9439093	-1.5749199
C	1.5794255	-2.2926959	-1.6712649
H	3.3959451	-2.1141242	-0.5708469
H	3.5993591	-2.4692446	-2.3178284
H	1.1843125	-2.6006007	-2.6383143
C	0.6906044	-2.0537060	-0.6470188
C	-0.6839035	-2.0575417	-0.8901666
H	1.0724835	-1.7456062	0.3206414
H	-1.0150018	-2.4225838	-1.8618334

C -1.6888577 -1.5593453 -0.0227717
C -3.0346373 -1.5716147 -0.4782923
C -1.3934790 -1.0059385 1.2526093
C -4.0447298 -1.0493231 0.3108072
H -3.2546653 -1.9935703 -1.4546155
C -2.4088196 -0.4843902 2.0312166
H -0.3726742 -0.9836634 1.6150548
C -3.7309721 -0.5035750 1.5627425
H -5.0725523 -1.0590604 -0.0358955
H -2.1838446 -0.0530792 3.0001385
H -4.5232773 -0.0897074 2.1791291

$(C_6F_5)_3BH^-$ borate anion
35
Energy = -2210.269512126
B 0.0039517 -0.0012074 0.8299942
C 0.0323310 1.5729667 0.3769834
C 1.3518479 -0.8138841 0.3750220
C -1.3740181 -0.7611967 0.3761258
C -0.7718453 2.4967224 1.0480314
C 0.8091067 2.1274895 -0.6384579
C 2.5542498 -0.5799041 1.0453490
C 1.4416923 -1.7655477 -0.6394940
C -1.7748694 -1.9179326 1.0473262
C -2.2416993 -0.3633701 -0.6394694
C -0.8111480 3.8566203 0.7571428
C 0.8132818 3.4821159 -0.9624445
C 3.7504716 -1.2284722 0.7558107
C 2.6119559 -2.4488777 -0.9622039
C -2.9353282 -2.6284704 0.7575489
C -3.4195618 -1.0331020 -0.9618690
C -0.0042242 4.3574723 -0.2587247
C 3.7790281 -2.1792153 -0.2588996
C -3.7720923 -2.1772762 -0.2575912
F -1.5978539 2.0745369 2.0436516
F 1.6099347 1.3418713 -1.4090238
F 2.6008715 0.3478969 2.0395066
F 0.3596667 -2.0664962 -1.4085126
F -0.9973215 -2.4235809 2.0431338
F -1.9593878 0.7220591 -1.4104031
F -1.6193761 4.6974638 1.4442150
F 1.5938876 3.9551432 -1.9619885
F 4.8837831 -0.9514561 1.4421411
F 2.6301914 -3.3632686 -1.9600641
F -3.2623993 -3.7479004 1.4448890
F -4.2190207 -0.5915035 -1.9608010
F -0.0196461 5.6728175 -0.5601285
F 4.9245628 -2.8263391 -0.5595707
F -4.9057720 -2.8448108 -0.5582398
H 0.0047455 -0.0024110 2.0428209

$(C_6F_5)_3B$ borane Lewis acid catalyst
34
Energy = -2209.516817574
B 0.0000063 0.0013582 -0.0000364
C -0.0000080 1.5641699 0.0000084
C 1.3524692 -0.7816899 -0.0032858
C -1.3524661 -0.7816992 0.0032394
C -0.9452615 2.3155953 0.7154288
C 0.9452759 2.3156120 -0.7154525
C 2.4758647 -0.3418505 0.7132955
C 1.5275707 -1.9754051 -0.7207647
C -1.5275554 -1.9754073 0.7207174
C -2.4758614 -0.3418566 -0.7133362
C -0.9562446 3.7039037 0.7342548
C 0.9562510 3.7039211 -0.7342273
C 3.6819192 -1.0290931 0.7317163
C 2.7228622 -2.6815690 -0.7395612
C -2.7228583 -2.6815666 0.7395622
C -3.6819281 -1.0290909 -0.7317160
C 0.0000206 4.4026124 0.0000136
C 3.8063244 -2.2056925 -0.0038381
C -3.8063324 -2.2056614 0.0038698
F -1.8839380 1.6924057 1.4580106
F 1.8839388 1.6924283 -1.4580410
F 2.4074305 0.7825997 1.4563558
F 0.5175645 -2.4725503 -1.4653357
F -0.5175297 -2.4725474 1.4652710
F -2.4074366 0.7825973 -1.4563808
F -1.8730037 4.3777899 1.4470797
F 1.8730240 4.3778120 -1.4470408
F 4.7247843 -0.5749585 1.4445503
F 2.8477128 -3.8114417 -1.4540374
F -2.8476957 -3.8114119 1.4540684
F -4.7248183 -0.5749393 -1.4445004
F 0.0000033 5.7388820 0.0000348
F 4.9624211 -2.8755343 -0.0045252
F -4.9624367 -2.8755118 0.0045761

F PhCH=CHCHMe-CH_2CH(CH=CHPh)SPh
53
Energy = -1405.269064077
C -0.6895942 2.7160669 -2.5902705
C -0.7799476 1.7428176 -1.4098825
H -0.4550764 2.1601779 -3.5076610
H -1.6730923 3.1787257 -2.7349560
H -1.0905961 2.2714098 -0.5036296
C 0.4335263 0.9288832 -1.1580068
C 0.8594504 0.6104729 0.0766247
H 0.9407774 0.5420181 -2.0397031
H 0.2914203 0.9899011 0.9262570
C 2.0251874 -0.2010683 0.4196568
C 2.2216524 -0.5745110 1.7613110
C 2.9805469 -0.6122479 -0.5288685
C 3.3245906 -1.3360824 2.1440798
H 1.4920474 -0.2629919 2.5055060
C 4.0834617 -1.3672863 -0.1473390
H 2.8755096 -0.3104869 -1.5664127
C 4.2619850 -1.7363683 1.1903137

H	3.4545640	-1.6132550	3.1870527
H	4.8190810	-1.6564619	-0.8927922
H	5.1277663	-2.3227813	1.4853723
S	-2.2111819	0.5722211	-1.8127102
C	-2.2873730	-0.3339275	-0.2838249
C	-3.0367061	0.1636731	0.7906449
C	-1.5668683	-1.5259692	-0.1345265
C	-3.0625657	-0.5259836	2.0029828
H	-3.5917074	1.0898066	0.6721697
C	-1.5979738	-2.2142749	1.0789306
H	-0.9784256	-1.8999061	-0.9658718
C	-2.3429028	-1.7151196	2.1485758
H	-3.6447950	-0.1349191	2.8328096
H	-1.0326829	-3.1350680	1.1900826
H	-2.3637358	-2.2502525	3.0938223
C	0.3620147	3.8384190	-2.3914667
C	0.1124150	4.9602898	-3.4179816
H	0.2360182	4.2518035	-1.3820312
H	0.8328553	5.7736415	-3.2857019
H	0.2142550	4.5763793	-4.4399127
H	-0.8982351	5.3680242	-3.3053700
C	1.7594060	3.3036184	-2.5201345
C	2.6592266	3.2714534	-1.5255387
H	2.0105326	2.8876547	-3.4977640
H	2.3597291	3.6598561	-0.5513212
C	3.9992882	2.6805012	-1.5670937
C	4.7056800	2.5201839	-0.3620380
C	4.6036492	2.2215955	-2.7528637
C	5.9577841	1.9099342	-0.3342064
H	4.2475841	2.8569615	0.5648671
C	5.8551392	1.6141975	-2.7269016
H	4.0894053	2.3415211	-3.7025174
C	6.5388061	1.4514814	-1.5169332
H	6.4758167	1.7834638	0.6124196
H	6.3029334	1.2664501	-3.6543160
H	7.5144771	0.9740360	-1.5001867

G $(C_6F_5)_3B.CH_2=CHCH=CHPh.PhSH$ complex

67

Energy = -3227.453223505

B	0.5485046	-0.3325075	-0.1000840
C	1.2851712	0.6639156	0.9676359
C	-0.8419445	-1.0458467	0.4142338
C	1.5193884	-1.5485116	-0.6373557
C	2.6717342	0.7291354	1.1492553
C	0.5831998	1.6161955	1.7160049
C	-1.6957149	-1.6699591	-0.5017082
C	-1.2795855	-1.1487786	1.7387696
C	2.1063952	-1.7199013	-1.8925822
C	1.7971567	-2.5884166	0.2581850
C	3.3027684	1.6164827	2.0180438
C	1.1680541	2.5303445	2.5831282
C	-2.9150858	-2.2547538	-0.1752967
C	-2.4904471	-1.7262763	2.1159681
C	2.8713452	-2.8306464	-2.2462936
C	2.5559840	-3.7119459	-0.0467772
C	2.5483520	2.5275407	2.7436516
C	-3.3275468	-2.2726208	1.1511124
C	3.0967908	-3.8405716	-1.3209381
F	3.5107375	-0.0789055	0.4553281
F	-0.7720586	1.6962223	1.6157087
F	-1.3569829	-1.7353651	-1.8199880
F	-0.5155017	-0.7045056	2.7645580
F	1.9895783	-0.7809016	-2.8694120
F	1.3412345	-2.5125222	1.5350078
F	4.6463132	1.6210351	2.1353640
F	0.4152988	3.4221397	3.2589764
F	-3.6960332	-2.8020177	-1.1306533
F	-2.8521405	-1.7727972	3.4146399
F	3.4033564	-2.9281284	-3.4827492
F	2.7805437	-4.6680373	0.8779785
F	3.1436228	3.4127095	3.5619961
F	-4.5032516	-2.8261703	1.4952824
F	3.8336563	-4.9172897	-1.6473417
C	0.1794967	0.7336013	-1.4979720
C	-0.8759993	1.6161020	-1.1553840
H	1.1404041	1.2279086	-1.6374729
H	-0.0770549	0.0531323	-2.3047015
H	-0.6457574	2.5055697	-0.5764995
C	-2.2348000	1.3247504	-1.3634232
C	-3.2153917	2.0363882	-0.7202704
H	-2.4861590	0.4712861	-1.9851334
H	-2.9013130	2.8933229	-0.1240372
C	-4.6217767	1.7399015	-0.6981822
C	-5.4752310	2.5797686	0.0516697
C	-5.1780874	0.6250907	-1.3679653
C	-6.8377135	2.3198043	0.1274550
H	-5.0504968	3.4339334	0.5721782
C	-6.5372646	0.3672249	-1.2850554
H	-4.5422661	-0.0364324	-1.9468766
C	-7.3702294	1.2124298	-0.5388732
H	-7.4850849	2.9724456	0.7044655
H	-6.9578171	-0.4918967	-1.7980892
H	-8.4339788	1.0033613	-0.4771457
S	-0.0348958	3.9825126	-3.0416911
H	0.2952193	3.1233904	-4.0227388
C	1.4809790	3.8673418	-2.1333154
C	2.5673987	3.1012796	-2.5791276
C	1.5639403	4.5546255	-0.9138719
C	3.7270578	3.0315745	-1.8075117
H	2.5073890	2.5644807	-3.5212108
C	2.7315981	4.4822971	-0.1569223
H	0.7244055	5.1495019	-0.5642606
C	3.8168002	3.7226781	-0.5985581
H	4.5623368	2.4324839	-2.1577470
H	2.7897241	5.0231317	0.7830399
H	4.7221588	3.6644623	-0.0028349

TSAa (TS for **273a** addition to $B(C_6F_5)_3$ into unstable **Aa**)

54

Energy = -2596.815584045

B	0.8920580	0.0199105	-0.2809017
C	1.2924314	1.5516643	0.0531900
C	-0.3289118	-0.6464419	0.5616667
C	2.1378984	-1.0363826	-0.3534962
C	2.6108392	2.0127829	0.1752450
C	0.3320482	2.5641391	0.1912688
C	-0.8963974	-1.8576941	0.1510556
C	-0.8772705	-0.1445737	1.7462897
C	2.9608065	-1.3119738	-1.4502977
C	2.4711294	-1.7688255	0.7941237
C	2.9496730	3.3434450	0.4139633
C	0.6229452	3.9019012	0.4226660
C	-1.9633584	-2.4831520	0.7870010
C	-1.9498237	-0.7309342	2.4143187
C	3.9762304	-2.2640337	-1.4430870
C	3.4806364	-2.7248977	0.8494459
C	1.9506364	4.3000777	0.5369894
C	-2.5105431	-1.9052474	1.9258977
C	4.2371897	-2.9866850	-0.2856646
F	3.6647053	1.1680999	0.0729458
F	-0.9884393	2.2617309	0.1042437
F	-0.4109502	-2.5024760	-0.9450865
F	-0.3440115	0.9421874	2.3531426
F	2.8349408	-0.6212682	-2.6122622
F	1.8277005	-1.5391641	1.9673957
F	4.2411479	3.7102293	0.5253677
F	-0.3630690	4.8115791	0.5442243
F	-2.4718698	-3.6359641	0.3060541
F	-2.4353325	-0.1817846	3.5453075
F	4.7208622	-2.4787388	-2.5462523
F	3.7378433	-3.3878020	1.9944088
F	2.2596054	5.5862270	0.7638358
F	-3.5479109	-2.4822640	2.5539341
F	5.2160846	-3.9061459	-0.2593944
C	0.2550847	0.1492283	-2.1397067
C	-1.0439590	0.6688396	-2.1315336
H	1.0254237	0.8032584	-2.5328846
H	0.3512209	-0.8987227	-2.4104932
H	-1.1714254	1.7481862	-2.1568639
C	-2.2199326	-0.0949346	-1.9922641
C	-3.4132429	0.5127563	-1.6983933
H	-2.1474665	-1.1757253	-2.0577836
H	-3.4228460	1.6020639	-1.6636801
C	-4.6556212	-0.1355897	-1.3676313
C	-5.7642765	0.6700408	-1.0261388
C	-4.7994228	-1.5414191	-1.3313102
C	-6.9734100	0.0933405	-0.6566986
H	-5.6585853	1.7513162	-1.0524671
C	-6.0069758	-2.1124531	-0.9597895
H	-3.9640594	-2.1817749	-1.5937014
C	-7.0960317	-1.2984459	-0.6203531
H	-7.8182812	0.7223232	-0.3943777
H	-6.1086227	-3.1928290	-0.9310483
H	-8.0381590	-1.7520757	-0.3274936

TSABa (TS for 1-protonation of **273a**)

67

Energy = -3227.441130435

B	-0.5440680	0.0477167	0.4580340
C	0.0732449	-0.2300726	1.9396017
C	-1.7425738	1.1649401	0.3627582
C	-1.1326714	-1.2700948	-0.3196330
C	0.4807879	-1.4842038	2.4017754
C	0.4304495	0.8306534	2.7831680
C	-2.0832441	1.7225791	-0.8730943
C	-2.5758294	1.5585870	1.4141010
C	-0.7890049	-1.7665649	-1.5744966
C	-2.2084175	-1.9390680	0.2769692
C	1.1708154	-1.6844470	3.5951593
C	1.1131276	0.6762301	3.9827360
C	-3.1208626	2.6265296	-1.0693491
C	-3.6288374	2.4593578	1.2648628
C	-1.4437946	-2.8279416	-2.1988381
C	-2.8876124	-3.0046137	-0.2990298
C	1.4911623	-0.5968897	4.3960172
C	-3.9032499	3.0040274	0.0161185
C	-2.5032563	-3.4555367	-1.5586062
F	0.2363563	-2.6101932	1.6847117
F	0.1397033	2.1075111	2.4328814
F	-1.3859964	1.3687203	-1.9870824
F	-2.4111328	1.0622454	2.6623356
F	0.2521323	-1.2494986	-2.2773633
F	-2.6367248	-1.5458898	1.5021165
F	1.5408091	-2.9253298	3.9726059
F	1.4257101	1.7462051	4.7430485
F	-3.3793208	3.1297051	-2.2936412
F	-4.3905251	2.8049266	2.3229841
F	-1.0500884	-3.2512656	-3.4184348
F	-3.9114774	-3.6029699	0.3428555
F	2.1601251	-0.7694978	5.5496806
F	-4.9150629	3.8750245	-0.1419312
F	-3.1462051	-4.4818538	-2.1426641
S	1.0335257	0.9971690	-0.3609803
C	2.4688890	0.0630198	0.0938014
C	3.5429112	0.7677758	0.6537747
C	2.5584082	-1.3253182	-0.0794445
C	4.6952721	0.0869491	1.0366171
H	3.4676342	1.8431171	0.7846772
C	3.7095159	-1.9999343	0.3171474
H	1.7309587	-1.8741211	-0.5097440
C	4.7805383	-1.2976839	0.8741562
H	5.5248243	0.6401701	1.4671882
H	3.7689863	-3.0780661	0.1903071
H	5.6767378	-1.8284837	1.1796170
C	-0.6008551	-0.3033079	-5.6697166
C	-0.0648322	0.6499663	-4.8676370

H	-0.0731274	-1.2338526	-5.8611936
H	-1.5644264	-0.1680946	-6.1499124
H	-0.6053919	1.5743444	-4.6774936
C	1.2019948	0.4734868	-4.2579152
C	1.7571406	1.3833678	-3.3287042
H	1.7207632	-0.4618088	-4.4607382
H	1.3320017	2.3895376	-3.3866594
C	3.2074446	1.3724548	-2.9540445
C	3.7862643	2.5666312	-2.5066592
C	3.9771778	0.2018203	-2.9610976
C	5.1204934	2.5989624	-2.1015684
H	3.1872514	3.4738173	-2.4781049
C	5.3076942	0.2331748	-2.5526562
H	3.5380683	-0.7433571	-3.2674448
C	5.8839080	1.4315111	-2.1229833
H	5.5573240	3.5331555	-1.7603209
H	5.8913857	-0.6826563	-2.5543056
H	6.9189906	1.4504641	-1.7951968
H	1.2247873	1.0123544	-2.2824108

TSAB (TS for 4-protonation of **273a**)

67

Energy = -3227.453824217

B	-1.2578677	0.1937563	0.5416003
C	-0.6952050	-1.1118143	1.3297214
C	-1.8018163	1.4329267	1.4583542
C	-2.4270651	-0.0901730	-0.5638101
C	-0.8181535	-2.4212944	0.8549834
C	0.1402085	-0.9865549	2.4475130
C	-1.8991161	2.7163434	0.9131911
C	-2.3111063	1.3198890	2.7551131
C	-2.4585159	0.2429888	-1.9162233
C	-3.6198572	-0.6514361	-0.0912901
C	-0.1906031	-3.5190266	1.4390816
C	0.7792321	-2.0542121	3.0650390
C	-2.4165524	3.8170177	1.5860830
C	-2.8432610	2.3936837	3.4659198
C	-3.5608280	0.0272576	-2.7432667
C	-4.7427860	-0.8848634	-0.8740525
C	0.6139952	-3.3378781	2.5559087
C	-2.8935787	3.6539599	2.8820198
C	-4.7147716	-0.5408359	-2.2219049
F	-1.5546757	-2.6983639	-0.2488535
F	0.4049930	0.2377918	2.9668999
F	-1.4764922	2.9366969	-0.3609353
F	-2.3250107	0.1304029	3.4001184
F	-1.3872863	0.8068961	-2.5289826
F	-3.7120053	-1.0120890	1.2128623
F	-0.3470157	-4.7536372	0.9209965
F	1.5744525	-1.8572830	4.1361838
F	-2.4665555	5.0287053	0.9977436
F	-3.3135269	2.2210963	4.7177376
F	-3.5136357	0.3708980	-4.0465937
F	-5.8522126	-1.4394954	-0.3461584
F	1.2334120	-4.3837563	3.1292224
F	-3.4015101	4.6987325	3.5578051
F	-5.7872645	-0.7530077	-3.0038773
S	0.5466272	0.8688770	-0.1488222
C	1.4368719	-0.5864404	-0.6638407
C	2.5866775	-0.9413453	0.0507141
C	1.0120168	-1.3613583	-1.7483346
C	3.3016705	-2.0816271	-0.3121294
H	2.9109248	-0.3279175	0.8852390
C	1.7344998	-2.4994370	-2.1054002
H	0.1232441	-1.0825631	-2.3018765
C	2.8747816	-2.8636732	-1.3867988
H	4.1922814	-2.3567466	0.2444983
H	1.4020912	-3.1034965	-2.9443563
H	3.4318923	-3.7526492	-1.6669572
C	1.2228625	2.1526870	-2.8135581
C	2.5768223	2.3678585	-2.5789996
H	0.9359994	1.2829197	-3.4023347
H	0.5591361	3.0116066	-2.8825633
H	2.8940376	3.3359273	-2.1914449
C	3.5669569	1.3617660	-2.6790335
C	4.8594428	1.5856694	-2.2938725
H	3.2593764	0.3861208	-3.0486354
H	5.1106724	2.5823568	-1.9309848
C	5.9407470	0.6268305	-2.2913725
C	7.2130335	1.0448859	-1.8459379
C	5.7758781	-0.7162592	-2.6954844
C	8.2822423	0.1560779	-1.8049753
H	7.3478566	2.0766758	-1.5315877
C	6.8443038	-1.6005851	-2.6520303
H	4.8067813	-1.0666152	-3.0348374
C	8.1008050	-1.1696310	-2.2073334
H	9.2549794	0.4928263	-1.4593193
H	6.7047287	-2.6318164	-2.9627230
H	8.9327532	-1.8669696	-2.1745832
H	0.7919132	1.6496375	-1.5774681

TSBEa^{+} (TS for 4-to-1 addition of **273a** and **B**$^{+}$)

41

Energy = -775.0251638862

H	-1.1624445	2.6280971	2.2376048
C	-1.0826228	2.1873020	1.2358188
C	-0.1204642	1.0497472	1.2417778
H	-2.0898918	1.8309981	0.9780173
H	-0.7909265	2.9650791	0.5254373
H	-0.3310843	0.2341208	1.9333071
C	1.0001922	0.9821678	0.4884843
C	1.9051936	-0.1445984	0.5466000
H	1.2291757	1.7953468	-0.1969581
H	1.7125107	-0.8390259	1.3613439
C	3.3344960	0.0056368	0.2281865
C	4.2609398	-0.8386800	0.8681322
C	3.8058593	0.9641491	-0.6878087
C	5.6237852	-0.7130136	0.6186964
H	3.9016313	-1.5854785	1.5715102

C	5.1682843	1.0835286	-0.9397914
H	3.1084595	1.6146193	-1.2065771
C	6.0811045	0.2478518	-0.2874751
H	6.3292046	-1.3622857	1.1282824
H	5.5222395	1.8286254	-1.6458057
H	7.1440955	0.3445972	-0.4871732
C	1.3728956	-1.3755934	-0.9880049
C	0.1134122	-1.8012909	-0.5572420
H	2.2062937	-2.0663172	-0.9267907
H	1.4319940	-0.6352203	-1.7810067
H	0.0479004	-2.6777071	0.0855820
C	-1.0525671	-1.0482353	-0.7588657
C	-2.2268836	-1.3610220	-0.1070137
H	-1.0006615	-0.1867668	-1.4184931
H	-2.2193737	-2.2401316	0.5369059
C	-3.4614323	-0.6339731	-0.1604125
C	-4.5395591	-1.0829355	0.6384844
C	-3.6400011	0.5195737	-0.9629617
C	-5.7501466	-0.4038582	0.6390773
H	-4.4053680	-1.9684390	1.2535321
C	-4.8524134	1.1910050	-0.9601435
H	-2.8303944	0.8769669	-1.5906395
C	-5.9082830	0.7334461	-0.1596691
H	-6.5711168	-0.7546250	1.2560916
H	-4.9853233	2.0722155	-1.5796085
H	-6.8549021	1.2653421	-0.1616303

TSBE$^+$ (TS for 4-to-3 addition of **273a** and **B**$^+$)

41

Energy = -775.0325863372

H	5.4906758	1.2359429	-0.4894667
C	5.1440479	0.3480937	0.0590830
C	3.7745258	0.0065197	-0.4527964
H	5.8667931	-0.4498323	-0.1214565
H	5.1295721	0.5983356	1.1232474
H	3.7295958	-0.4328253	-1.4462686
C	2.6490249	0.7618490	-0.0452975
C	1.4708294	0.7535338	-0.7509336
H	2.7297556	1.3272557	0.8809277
H	1.4500006	0.1882176	-1.6815355
C	0.2554899	1.4643261	-0.4317385
C	-0.8234021	1.3906081	-1.3398927
C	0.0914681	2.2210282	0.7504560
C	-2.0148684	2.0590551	-1.0877292
H	-0.7071648	0.8055027	-2.2479080
C	-1.1010118	2.8851422	0.9994755
H	0.9008323	2.2859795	1.4708960
C	-2.1569779	2.8082284	0.0823702
H	-2.8349507	1.9919659	-1.7953360
H	-1.2163875	3.4635054	1.9110403
H	-3.0881582	3.3288759	0.2845756
C	3.5642060	-1.9028235	0.5676650
C	2.3887475	-2.3672073	0.0053137
H	3.5450252	-1.4479652	1.5536500
H	4.5167445	-2.2999581	0.2357070
H	2.4330823	-2.9624464	-0.9052534
C	1.1259390	-1.9297910	0.4498180
C	-0.0210244	-2.1386550	-0.2810036
H	1.0870859	-1.3513329	1.3691221
H	0.0644774	-2.7282311	-1.1935186
C	-1.3201205	-1.6018918	0.0049313
C	-2.3589995	-1.8160135	-0.9312462
C	-1.5930028	-0.8300141	1.1594813
C	-3.6202254	-1.2745863	-0.7258894
H	-2.1523312	-2.4065720	-1.8196556
C	-2.8548856	-0.2962135	1.3610769
H	-0.8150991	-0.6559109	1.8947199
C	-3.8692982	-0.5115793	0.4192772
H	-4.4091485	-1.4402969	-1.4526355
H	-3.0560585	0.2972269	2.2468603
H	-4.8546610	-0.0850168	0.5810488

TSBz$^+$ (TS for *E*-to-*Z* rotation of **B**$^+$)

21

Energy = -387.6866499990

C	4.1372421	0.5821867	-0.1509478
C	2.8256610	-0.0736775	-0.4455237
H	4.9585060	-0.0149915	-0.5661097
H	4.2954320	0.7049843	0.9237070
H	2.5793926	-0.2316337	-1.4948252
C	1.9521702	-0.4617094	0.4913225
C	0.6748023	-1.1152418	0.2259773
H	2.1760199	-0.3203085	1.5533237
H	0.6663228	-2.2040826	0.1345232
C	-0.5502758	-0.4730442	0.1160692
C	-1.7258006	-1.2620695	-0.1072182
C	-0.6580006	0.9518143	0.2160268
C	-2.9529644	-0.6464643	-0.2230883
H	-1.6257797	-2.3405529	-0.1815259
C	-1.8916563	1.5500695	0.0991500
H	0.2410704	1.5364282	0.3802457
C	-3.0324537	0.7530552	-0.1191711
H	-3.8516934	-1.2285467	-0.3927645
H	-1.9936287	2.6269741	0.1725904
H	-4.0013362	1.2348419	-0.2107235
H	4.1878871	1.5657543	-0.6336060

TSG3 (TS for 4,3-thiolation of **Aa**)

67

Energy = -3227.390446945

B	0.3924880	-0.4815132	0.0247428
C	1.2780711	0.5777020	0.9100007
C	-1.1197158	-0.8250133	0.5519877
C	1.1403397	-1.9201169	-0.2245332
C	2.6756340	0.5033961	0.9846778
C	0.7519887	1.7127438	1.5390280
C	-2.0553653	-1.4186245	-0.3032083
C	-1.5907901	-0.6553990	1.8588491
C	1.6534827	-2.4301875	-1.4167457

C	1.2676749	-2.7911315	0.8625631
C	3.4753321	1.4247169	1.6559573
C	1.5095342	2.6575508	2.2227611
C	-3.3648805	-1.7262581	0.0457321
C	-2.8964460	-0.9391010	2.2539059
C	2.2231567	-3.6950558	-1.5422603
C	1.8314703	-4.0597663	0.7903543
C	2.8890381	2.5115552	2.2894575
C	-3.7995916	-1.4659183	1.3392013
C	2.3120310	-4.5222292	-0.4298781
F	3.3547304	-0.4899942	0.3574216
F	-0.5813769	1.9787152	1.4883748
F	-1.7068139	-1.7411443	-1.5818543
F	-0.7734100	-0.2250783	2.8482126
F	1.6421280	-1.6869269	-2.5597155
F	0.8476169	-2.3933792	2.0894973
F	4.8151702	1.2858029	1.6705910
F	0.9214756	3.7281051	2.7923694
F	-4.2070628	-2.2748761	-0.8507576
F	-3.2874141	-0.7252914	3.5268383
F	2.6935423	-4.1207460	-2.7319919
F	1.9230567	-4.8394616	1.8859466
F	3.6444704	3.4266046	2.9193827
F	-5.0615502	-1.7423298	1.7052925
F	2.8590155	-5.7457946	-0.5297107
C	0.2332752	0.4063744	-1.5456642
C	-0.6015049	1.6964130	-1.5097648
H	1.3231552	0.5491902	-1.5939604
H	-0.2254240	-0.4009950	-2.1228326
H	-0.4091504	2.3416995	-0.6577144
C	-2.0474774	1.4538694	-1.7049870
C	-2.9731483	1.9367990	-0.8575822
H	-2.3231905	0.7883791	-2.5209032
H	-2.6366546	2.5684843	-0.0363276
C	-4.4004862	1.6252279	-0.8589285
C	-5.1721014	2.0155838	0.2503091
C	-5.0299573	0.9107781	-1.8954160
C	-6.5240184	1.6895916	0.3329628
H	-4.6958470	2.5676010	1.0569402
C	-6.3802150	0.5898668	-1.8146564
H	-4.4609133	0.6041207	-2.7681722
C	-7.1325872	0.9736215	-0.6991445
H	-7.1014691	1.9926187	1.2015333
H	-6.8507352	0.0360913	-2.6220077
H	-8.1860198	0.7162081	-0.6383586
S	0.1571375	2.5880993	-3.0387711
H	0.5113707	0.8424891	-2.7844504
C	1.7338472	2.9871844	-2.3092472
C	2.8861830	2.3041064	-2.7181274
C	1.8008644	3.9615667	-1.3056294
C	4.1091331	2.5982301	-2.1133485
H	2.8266424	1.5561380	-3.5031686
C	3.0265466	4.2418898	-0.7061219
H	0.9055763	4.4945090	-1.0004583
C	4.1794930	3.5617024	-1.1069902
H	5.0028360	2.0684445	-2.4278651
H	3.0804925	4.9949175	0.0741463
H	5.1311898	3.7835022	-0.6343145

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m1 MeCH=CHCH=CH_2 (1-methyl 1,3-diene)

13

Energy = -195.4327803876

C	-7.8901650	-0.4331866	0.0617317
C	-6.5500536	-0.5434523	0.0613923
H	-8.3793600	0.5364438	0.0615904
H	-8.5322367	-1.3116830	0.0621566
H	-5.9430812	0.3632104	0.0610091
C	-5.8210674	-1.7994883	0.0614577
C	-4.4773469	-1.8824196	0.0610424
H	-6.4136915	-2.7165538	0.0618022
H	-3.9002015	-0.9558554	0.0607181
C	-3.6939915	-3.1571587	0.0609515
H	-3.0379522	-3.2136364	0.9400038
H	-4.3514764	-4.0317267	0.0612887
H	-3.0386154	-3.2138583	-0.8185895

m3 *E*-MeCH=CHCHSPhCH_3 (**m1** 4,3-hydrothiolation)

26

Energy = -826.0869596923

S	0.0509867	-0.2466451	-1.4770721
C	1.2035225	-1.5969676	-1.5951084
C	1.7758397	-2.1478291	-0.4408898
C	1.5484779	-2.1092127	-2.8512007
C	2.6948673	-3.1910808	-0.5463433
H	1.5035059	-1.7559524	0.5348784
C	2.4543326	-3.1664868	-2.9510986
H	1.1147770	-1.6692680	-3.7439194
C	3.0345118	-3.7043368	-1.8010037
H	3.1387366	-3.6097271	0.3527250
H	2.7154331	-3.5603352	-3.9294575
H	3.7480426	-4.5195620	-1.8804842
C	0.3127834	2.3446711	-0.6355288
C	1.1879834	1.1073097	-0.8438615
H	0.9198137	3.1513014	-0.2112789
H	-0.5134740	2.1316624	0.0498197
H	1.5792534	0.7501065	0.1128514
C	2.2959242	1.3062065	-1.8203958
C	3.5484348	0.8805031	-1.6214035
H	2.0239140	1.7841254	-2.7631472
H	3.7849618	0.3818059	-0.6801428
H	-0.1025101	2.6918512	-1.5874965
C	4.6683881	1.0100133	-2.6084829
H	5.0486272	0.0189946	-2.8903523
H	4.3424870	1.5253964	-3.5173623
H	5.5151717	1.5610116	-2.1792055

m3z *Z*-MeCH=CHCHSPhCH$_3$ (**m1** 4,3-hydrothiolation)

26

Energy = -826.0865657824

C	3.0267004	-3.7126079	-1.6124224
C	2.3467325	-3.4367284	-0.4232467
C	1.4242825	-2.3920346	-0.3719157
C	1.1806094	-1.6136380	-1.5113925
C	1.8588875	-1.8958884	-2.7038733
C	2.7787067	-2.9445152	-2.7519986
S	0.0318744	-0.2561910	-1.4333101
C	1.1756943	1.1083355	-0.8273551
C	2.2233358	1.3673434	-1.8555809
C	3.4963557	0.9457585	-1.8232336
C	4.1638276	0.1359450	-0.7523107
C	0.2891807	2.3246276	-0.5524367
H	0.8929319	-2.1711042	0.5492220
H	1.6684066	-1.2873747	-3.5816901
H	2.5348426	-4.0343281	0.4643753
H	3.3037894	-3.1585371	-3.6787797
H	3.7451526	-4.5265460	-1.6512319
H	0.9026939	3.1383812	-0.1513785
H	-0.4925761	2.0848207	0.1746172
H	1.6031895	0.7333671	0.1047159
H	1.8810599	1.9272098	-2.7262520
H	4.1296104	1.2072401	-2.6714858
H	-0.1850784	2.6765939	-1.4748682
H	5.0746946	0.6364844	-0.4001447
H	3.5145284	-0.0479477	0.1064025
H	4.4698432	-0.8390005	-1.1533628

mBa$^+$ *E*-MeCH$_2$CHCH=CH$_2^+$ (**m1** protonation at site 1)

14

Energy = -195.8276371601

C	-4.4568185	-0.6563369	-0.7110923
C	-3.2236237	-1.0438668	-0.2648745
H	-5.1933344	-1.3776164	-1.0535066
H	-4.7330508	0.3949433	-0.7360829
H	-2.9355989	-2.0904771	-0.2399995
C	-2.3287546	-0.0565697	0.1631955
C	-0.9982283	-0.2962571	0.6938217
H	-2.6676402	0.9795163	0.1126876
H	-0.7047580	-1.3454097	0.6161700
H	-1.1098713	-0.0612393	1.7741195
C	0.0758636	0.6764457	0.1430302
H	-0.2378944	1.7159315	0.2667501
H	1.0049536	0.5179814	0.6934880
H	0.2498031	0.4783889	-0.9169865

mB$^+$.C$^-$ (loose complex of **mB$^+$** and **C$^-$**)

60

Energy = -3035.604530402

B	-0.9650161	0.3673876	0.4183923
C	-1.1313697	-1.1401828	1.032043
C	-2.0954304	1.4593182	0.9053750
C	-0.9694645	0.4575602	-1.2201191
C	-1.0338265	-2.3297255	0.3066097
C	-1.2766985	-1.3336530	2.4129314
C	-1.8957723	2.8231243	0.6607318
C	-3.3388439	1.1581079	1.4686002
C	0.0221873	0.9452935	-2.0695807
C	-2.1489505	0.0895586	-1.8787142
C	-1.0794933	-3.5998237	0.8795463
C	-1.3309409	-2.5779562	3.0268527
C	-2.8122708	3.8186855	0.9819842
C	-4.2878625	2.1220109	1.8029514
C	-0.1245175	1.0492847	-3.4530669
C	-2.3438201	0.1777224	-3.2505904
C	-1.2305912	-3.7296485	2.2523913
C	-4.0232914	3.4649987	1.5651365
C	-1.3156317	0.6645172	-4.0523307
F	-0.8628001	-2.3209150	-1.0425267
F	-1.3798161	-0.2657915	3.2411280
F	-0.7556976	3.2424626	0.0527589
F	-3.7119754	-0.1225808	1.7030247
F	1.2235079	1.3525927	-1.5913792
F	-3.1842345	-0.4081815	-1.1564212
F	-0.9663872	-4.7025435	0.1098040
F	-1.4832061	-2.6830664	4.3634375
F	-2.5444651	5.1154693	0.7246046
F	-5.4681772	1.7622567	2.3488246
F	0.8850224	1.5247542	-4.2127424
F	-3.5074391	-0.2078205	-3.8134437
F	-1.2778111	-4.9452286	2.8260322
F	-4.9291482	4.4065844	1.8829596
F	-1.4745106	0.7594271	-5.3845147
S	0.6764269	1.0221162	1.3581511
C	1.9352778	-0.1511692	1.1361008
C	3.0145071	-0.1222738	2.0550730
C	1.9573973	-1.0993515	0.0926465
C	4.0565742	-1.0358839	1.9522715
H	2.9904714	0.5918350	2.8730502
C	3.0154070	-1.9836812	-0.0192976
H	1.1560219	-1.1214920	-0.6342229
C	4.0826191	-1.9506665	0.8984429
H	4.8626536	-1.0155261	2.6796008
H	3.0275342	-2.7035110	-0.8325943
H	4.8907149	-2.6706536	0.8180063
C	3.2778424	2.8030487	0.1341523
C	4.2439692	1.7021611	0.1751031
H	3.0508229	3.1181066	-0.8871002
H	3.5933147	3.6479560	0.7506177
H	4.8854956	1.6172167	1.0492631
C	4.4483276	0.7939374	-0.8557469
C	5.4260105	-0.1777687	-0.7754622
H	3.8236440	0.8521599	-1.7445868
H	6.0655223	-0.1856942	0.1041909
H	2.3020958	2.4450164	0.5557250
C	5.7853788	-1.0905851	-1.8879828

H 6.0144596 -2.0968687 -1.5242630
H 5.0064371 -1.1374527 -2.6523679
H 6.7098281 -0.7193841 -2.3576525

mB$^+$ *E*-MeCH=CHCHCH$_3^+$ (**m1** protonation at site 4)
14
Energy = -195.8480527241
C -4.3999222 0.3313530 0.0112043
C -3.1467201 -0.4153195 0.0828504
H -5.0138047 -0.0864826 -0.8025625
H -4.2648614 1.4049009 -0.1181350
H -3.2171074 -1.4965874 0.2028185
C -1.8802907 0.1392374 0.0113152
C -0.7777236 -0.6936511 0.0950157
H -1.7536266 1.2120677 -0.1084421
H -0.9604090 -1.7619259 0.2140501
H -4.9862750 0.1204130 0.9201524
C 0.6146681 -0.2561729 0.0366055
H 0.7313145 0.8207749 -0.0813638
H 1.1329389 -0.6071506 0.9432474
H 1.1192129 -0.7941222 -0.7819502

mBz$^+$ *Z*-MeCH=CHCHCH$_3^+$
14
Energy = -195.8438888362
C -4.4807069 0.2161533 0.0197075
C -3.1635558 -0.4181760 0.0806611
H -5.0449361 -0.2528640 -0.8016039
H -4.4780544 1.2984309 -0.0963945
H -3.1736823 -1.5009979 0.2008085
C -1.9120293 0.1803057 0.0045057
C -1.7523290 1.5462279 -0.1465175
H -1.0310494 -0.4519722 0.0667658
H -2.6393934 2.1740444 -0.2081172
H -5.0384434 -0.0685349 0.9253540
C -0.4628998 2.2264263 -0.2302226
H 0.3933119 1.5558420 -0.1620242
H -0.4303979 2.8067346 -1.1665518
H -0.4195909 2.9961060 0.5573481

mD MeCH=CHCHMeSPh.B(C_6F_5)$_3$ complex
60
Energy = -3035.626140120
B -0.9230239 0.3868983 0.4817514
C 0.1464606 0.5777184 1.6712203
C -1.6272832 1.7396844 -0.0543849
C -1.8856087 -0.8993330 0.4973618
C 1.0309434 -0.4347638 2.0636967
C 0.2896542 1.7633096 2.4067463
C -0.9161653 2.7834070 -0.6534278
C -2.9981010 1.9868783 0.0778134
C -2.6724327 -1.2101825 -0.6211329
C -2.0434593 -1.7835623 1.5692721
C 2.0039747 -0.2974938 3.0437329
C 1.2471991 1.9450447 3.4035076
C -1.4971999 3.9446033 -1.1464032
C -3.6235102 3.1391468 -0.3911533
C -3.4808636 -2.3329314 -0.7200289
C -2.8429137 -2.9232909 1.5143139
C 2.1195111 0.9121319 3.7217762
C -2.8706438 4.1239983 -1.0191092
C -3.5572457 -3.2098885 0.3572681
F 0.9661630 -1.6537345 1.4725281
F -0.5292410 2.8204014 2.2050160
F 0.4347595 2.7099782 -0.7434731
F -3.8066220 1.1028008 0.7115410
F -2.6707505 -0.3806321 -1.6932758
F -1.4411866 -1.5532606 2.7596713
F 2.8243462 -1.3198204 3.3479952
F 1.3242906 3.1115907 4.0690015
F -0.7449648 4.9033443 -1.7200740
F -4.9505980 3.3097156 -0.2362163
F -4.1872759 -2.5808588 -1.8383350
F -2.9436698 -3.7402472 2.5803962
F 3.0445094 1.0699973 4.6785188
F -3.4566174 5.2403391 -1.4793707
F -4.3286750 -4.3057147 0.2876342
S 0.3790613 -0.0909793 -1.3829862
C -0.0617231 -1.6967285 -2.0170945
C 0.0610518 -2.8704645 -1.2672961
C -0.5377335 -1.7412596 -3.3309143
C -0.2983266 -4.0892801 -1.8384053
H 0.4261694 -2.8359176 -0.2505422
C -0.9011082 -2.9646215 -3.8922943
H -0.6265503 -0.8231710 -3.9022065
C -0.7838012 -4.1385244 -3.1470010
H -0.2027988 -5.0010017 -1.2563360
H -1.2732087 -2.9976347 -4.9117478
H -1.0687332 -5.0905780 -3.5846770
C 2.8457613 0.9641163 -0.5676762
C 2.2378627 -0.3471816 -1.0598719
H 2.3483043 1.3395546 0.3275699
H 2.7983933 1.7315670 -1.3443846
H 2.2964857 -1.1288003 -0.3023973
C 2.8221304 -0.8158519 -2.3483428
C 3.2161187 -2.0765119 -2.5610594
H 2.9063428 -0.0705391 -3.1395711
H 3.1053177 -2.8010167 -1.7532536
H 3.8982681 0.7779056 -0.3308613
C 3.7923709 -2.5901825 -3.8422192
H 4.7855823 -3.0270559 -3.6793213
H 3.1595151 -3.3911575 -4.2468164
H 3.8743679 -1.7984461 -4.5925155

mE$^+$ (site 4-to-3 adduct of **m1** and **mB**$^+$)
27
Energy = -391.3069110904
H 0.5702748 1.3653392 -0.5763151

C	0.6480501	0.3852157	-1.0632844
C	1.6651306	-0.4705715	-0.3737856
H	-0.3486764	-0.0715125	-1.0010289
H	0.8978298	0.5364051	-2.1173289
H	1.4834735	-0.6859630	0.6808236
C	2.7671684	-0.9696534	-0.9479830
C	3.7761106	-1.8101964	-0.2396684
H	2.9653591	-0.7691371	-2.0025227
H	3.5564028	-1.8405718	0.8316025
C	3.7278584	-3.3450279	-0.7946652
C	2.5136373	-3.9229437	-0.2635556
H	4.6216665	-3.8404401	-0.4138573
H	3.7372277	-3.2815348	-1.8850281
H	2.5509991	-4.3789411	0.7248441
C	1.2670120	-3.7957938	-0.8684701
C	0.1365170	-4.1847481	-0.1827557
H	1.1836844	-3.3592230	-1.8597254
H	0.2691415	-4.6285133	0.8040371
C	5.2157707	-1.3206796	-0.4600542
H	5.3018569	-0.2937037	-0.0908089
H	5.9306578	-1.9490756	0.0782672
H	5.4703532	-1.3287991	-1.5248654
C	-1.2369262	-4.0350764	-0.6719021
H	-1.7308287	-5.0187997	-0.6609324
H	-1.8117522	-3.4346170	0.0498534
H	-1.2957498	-3.5921556	-1.6664277

mTSABa (TS for 1-protination of **m1**)
60
Energy = -3035.588479006

B	-0.2145533	-0.3973862	0.0762630
C	1.1031830	-1.3570308	0.0985439
C	-1.5598757	-1.0008631	0.7911708
C	-0.6922955	0.1236181	-1.3959315
C	1.9753200	-1.5455197	-0.9775436
C	1.5091872	-1.9981490	1.2775485
C	-2.6189079	-0.1458919	1.1115550
C	-1.8262804	-2.3531244	1.0247379
C	-0.8169766	1.4277225	-1.8684086
C	-1.1401728	-0.8521912	-2.2949509
C	3.1384985	-2.3098053	-0.9095716
C	2.6572845	-2.7714806	1.3894119
C	-3.8241545	-0.5614342	1.6651358
C	-3.0212110	-2.8165514	1.5714483
C	-1.3295488	1.7528639	-3.1240572
C	-1.6558128	-0.5793825	-3.5547972
C	3.4850087	-2.9312452	0.2825289
C	-4.0279903	-1.9165528	1.9003948
C	-1.7542894	0.7434040	-3.9769079
F	1.7382353	-0.9695645	-2.1838143
F	0.7656018	-1.8804946	2.4044086
F	-2.5022874	1.1879773	0.8698277
F	-0.9236322	-3.3097765	0.7075538
F	-0.4326116	2.4860228	-1.1124647
F	-1.0606012	-2.1602042	-1.9459577
F	3.9323171	-2.4447424	-1.9902856
F	2.9770767	-3.3666164	2.5554416
F	-4.7918752	0.3278495	1.9625897
F	-3.2137094	-4.1344876	1.7774505
F	-1.4181965	3.0409459	-3.5122560
F	-2.0563660	-1.5749032	-4.3697180
F	4.6007973	-3.6740746	0.3672052
F	-5.1836314	-2.3503869	2.4301318
F	-2.2511103	1.0368837	-5.1903508
S	0.3929230	0.9935967	1.4294825
C	1.9621029	1.6376245	0.9629485
C	2.7241212	2.2168816	1.9908864
C	2.4177017	1.6800140	-0.3621335
C	3.9180784	2.8654556	1.6857125
H	2.3797802	2.1505130	3.0184163
C	3.6127616	2.3234716	-0.6545498
H	1.8320807	1.2334835	-1.1555546
C	4.3546079	2.9376142	0.3622522
H	4.5013482	3.3201428	2.4805958
H	3.9615823	2.3656839	-1.6819396
H	5.2826601	3.4475528	0.1227489
C	2.4561514	5.5010223	0.2680659
C	1.2435377	4.9028170	0.2910980
H	3.0061818	5.6898225	1.1852929
H	2.9081957	5.8357404	-0.6596416
H	0.7054133	4.7283903	-0.6377990
C	0.6268042	4.4836176	1.5088825
C	-0.6074155	3.8420670	1.6060531
H	1.1941065	4.6528152	2.4245846
H	-1.2433039	3.8910280	0.7203562
H	-0.2144524	2.5441037	1.4153268
C	-1.3290429	3.7409908	2.9380728
H	-1.8893257	4.6619862	3.1341454
H	-2.0397016	2.9101622	2.9346379
H	-0.6208442	3.5898579	3.7586082

mTSAB (TS for 4-protination of **m1**)
60
Energy = -3035.589463794

B	-1.2751175	0.2323802	0.6032033
C	-0.7048538	-1.0666306	1.3973336
C	-1.9169037	1.4288451	1.5132113
C	-2.3726776	-0.0725390	-0.5685750
C	-0.7406843	-2.3685476	0.8884219
C	0.0562670	-0.9319054	2.5658809
C	-2.0253354	2.7238563	0.9985348
C	-2.5083506	1.2588018	2.7684193
C	-2.3554003	0.3165910	-1.9063418
C	-3.5548697	-0.7163908	-0.1825731
C	-0.1020979	-3.4520487	1.4866301
C	0.7034097	-1.9857978	3.1987604
C	-2.6303442	3.7838105	1.6639642
C	-3.1301903	2.2899384	3.4693123
C	-3.3998961	0.0759657	-2.7988872
C	-4.6212982	-0.9778037	-1.0327119

C	0.6250057	-3.2631565	2.6542474
C	-3.1898881	3.5642685	2.9177770
C	-4.5445632	-0.5764341	-2.3627063
F	-1.3963524	-2.6500386	-0.2641845
F	0.2351956	0.2898518	3.1263183
F	-1.5263514	2.9983578	-0.2366577
F	-2.5175171	0.0514374	3.3798424
F	-1.2891448	0.9657901	-2.4384472
F	-3.6948490	-1.1344414	1.0998133
F	-0.1729165	-4.6797292	0.9342141
F	1.4231749	-1.7802116	4.3206281
F	-2.6875565	5.0099867	1.1070316
F	-3.6784427	2.0622640	4.6800191
F	-3.3056341	0.4776537	-4.0830158
F	-5.7227958	-1.6140593	-0.5863259
F	1.2536985	-4.2950875	3.2428682
F	-3.7851426	4.5684231	3.5839334
F	-5.5620135	-0.8141381	-3.2083463
S	0.5402935	0.9747726	0.0199671
C	1.4913642	-0.4402841	-0.4936339
C	2.6135276	-0.7929310	0.2639420
C	1.1499813	-1.1745973	-1.6346963
C	3.3916574	-1.8838955	-0.1198859
H	2.8693017	-0.2144662	1.1459752
C	1.9335590	-2.2638981	-2.0114518
H	0.2817980	-0.8966084	-2.2204822
C	3.0536027	-2.6195590	-1.2571386
H	4.2605154	-2.1587314	0.4706878
H	1.6675652	-2.8352216	-2.8958566
H	3.6607590	-3.4690895	-1.5550674
C	1.3424672	2.4035746	-2.5358990
C	2.7242881	2.3331096	-2.4029612
H	0.8645843	1.7423646	-3.2562257
H	0.8572082	3.3658597	-2.3820547
H	3.2356247	3.1187470	-1.8466572
C	3.5212537	1.2420795	-2.8472115
C	4.8506126	1.1700527	-2.5832124
H	3.0349240	0.4419062	-3.4026511
H	5.3078323	1.9822178	-2.0170734
H	0.8866145	1.8010636	-1.3881157
C	5.7399810	0.0531469	-2.9937331
H	6.5848730	0.4332131	-3.5833514
H	6.1797692	-0.4195895	-2.1048538
H	5.2065874	-0.7051815	-3.5717448

mTSBE$^+$ (TS for 4-to-3 addition of **m1** and **mB**$^+$)

27

Energy = -391.2972724698

H	-1.0314420	3.4804213	0.4844023
C	-1.0821901	2.5680624	-0.1280176
C	-0.1292644	1.5728444	0.4169699
H	-2.1158329	2.2139899	-0.0406109
H	-0.8641340	2.8261096	-1.1662909
H	-0.3220818	1.1951584	1.4196497
C	1.0300480	1.1927629	-0.2053144
C	1.9590659	0.3374453	0.4148807
H	1.2543874	1.5709798	-1.2010731
H	1.7545097	0.0337480	1.4379039
C	1.3484012	-1.8458026	-0.3943857
C	0.1311028	-1.8081054	0.2206283
H	2.1906497	-2.3482455	0.0668693
H	1.4589668	-1.5378582	-1.4300841
H	0.0363195	-2.1856047	1.2376269
C	-1.0144290	-1.1831172	-0.3570806
C	-2.1600096	-0.9791705	0.3462768
H	-0.9517708	-0.8505279	-1.3919953
H	-2.1961848	-1.3260960	1.3793691
C	3.3675189	0.2313439	-0.0547484
H	3.9150989	1.0627638	0.4191491
H	3.8533695	-0.6899463	0.2702315
H	3.4551762	0.3505546	-1.1369511
C	-3.3861715	-0.3376840	-0.1875881
H	-4.2218184	-1.0504201	-0.1497225
H	-3.6893231	0.5033119	0.4510281
H	-3.2604927	0.0090825	-1.2157943

mTSBz$^+$ (TS for *E*-to-*Z* conversion of **mB**$^+$)

14

Energy = -195.7991417307

C	-2.3210938	0.4810868	-0.1911368
C	-1.3143738	-0.4618479	0.1877117
H	-3.1730276	-0.0789752	-0.6264721
H	-1.9905972	1.3115529	-0.8088011
H	-1.6467949	-1.3091011	0.7965645
C	0.0584934	-0.4146499	-0.2273971
C	1.1026936	0.1594200	0.3815377
H	0.1816169	-0.9479423	-1.1849991
H	0.9389026	0.6720849	1.3271033
H	-2.7930843	0.8150392	0.7588766
C	2.4959642	0.1448180	-0.1572571
H	2.5579994	-0.3806217	-1.1131259
H	2.8571259	1.1719390	-0.2873278
H	3.1675975	-0.3384337	0.5626372

p1 $PhCH_2CH_2CH=CHCH=CH_2$ (1-phenethyl 1,3-diene)

26

Energy = -465.9629856669

C	-4.2835044	-0.1555600	-0.1411148
C	-2.9804882	0.1763468	-0.1379549
H	-4.6169160	-1.1431776	0.1712499
H	-5.0485506	0.5491920	-0.4526421
H	-2.6826617	1.1759080	-0.4577301
C	-1.9100247	-0.7144578	0.2730509
C	-0.6063464	-0.3789063	0.2671635
H	-2.2017986	-1.7129087	0.6044775
H	-0.3241319	0.6229092	-0.0631977
C	0.5066747	-1.2731761	0.7153621

C 1.2540026 -0.7032576 1.9514682
H 1.2400841 -1.3963648 -0.0939363
H 0.1170307 -2.2690452 0.9565054
H 1.6469259 0.2895527 1.7034755
H 0.5351372 -0.5783093 2.7690256
C 2.3767327 -1.6127537 2.3869534
C 2.1417426 -2.6461524 3.3038881
C 3.6623101 -1.4805836 1.8455248
C 3.1611332 -3.5264756 3.6695158
H 1.1498345 -2.7590420 3.7360436
C 4.6859868 -2.3578450 2.2078312
H 3.8625699 -0.6807519 1.1356871
C 4.4378987 -3.3858898 3.1204011
H 2.9592815 -4.3202999 4.3836818
H 5.6774884 -2.2377541 1.7792562
H 5.2333978 -4.0690673 3.4043370

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pBa^{+} (1-protonated **p1** with strong Ph...allyl cation interaction)

27

Energy = -466.3810971459

C 0.6090953 0.2210353 -0.3441734
C -0.0619882 -0.9237032 -0.0013841
H 0.6014287 1.0863063 0.3099756
H 1.0909303 0.3301849 -1.3101916
H -0.0701259 -1.7763953 -0.6747244
C -0.6426188 -1.0526825 1.2617363
C -1.3673461 -2.2400881 1.7490911
H -0.6581491 -0.1704509 1.8995499
H -2.4173415 -1.9377920 1.8907505
H -1.3377846 -3.0498613 1.0140959
C -0.8410995 -2.7164957 3.1264283
C 0.5980522 -3.2546542 2.9902236
H -1.5007030 -3.4951405 3.5179372
H -0.8685475 -1.8777513 3.8300930
H 0.9888080 -3.4583082 3.9957464
H 0.5940196 -4.2008239 2.4406992
C 1.4883314 -2.2681994 2.2904636
C 2.1799095 -2.6206314 1.1139212
C 1.6471222 -0.9585133 2.8066101
C 2.9135028 -1.6740674 0.4206330
H 2.0997629 -3.6360928 0.7369357
C 2.3980578 -0.0132317 2.1227220
H 1.1749767 -0.6964232 3.7491881
C 2.9883279 -0.3494573 0.8985231
H 3.4175816 -1.9413940 -0.5026505
H 2.5033591 0.9906812 2.5209221
H 3.5699157 0.3883250 0.3545340

pBh^{+} (high-lying 3-protonated **p1**)

27

Energy = -466.3419872627

C -2.4595021 -0.1076187 0.1642647
C -1.9599975 0.7575548 -0.7254468
H -2.7166323 0.2410548 1.1660190
H -1.6834091 0.4069355 -1.7213954
C -1.3599318 2.0395999 -0.2748872
C 0.1590032 1.7896989 -0.1571202
H -1.7677362 2.3633583 0.6867418
H 0.5963128 1.5663448 -1.1322986
H -1.4571006 2.8606430 -0.9972817
C -2.2369229 -1.5798805 0.0008908
H -2.9777728 -2.2123687 0.4978080
H -2.1792964 -1.8581719 -1.0562290
H 0.6520552 2.6680249 0.2628091
C -0.8523129 -1.7721414 0.6754314
H -0.5014331 -2.8004446 0.5354029
H -0.9653112 -1.6017007 1.7533301
C 0.2419648 -0.8304612 0.1885817
C 1.1689993 -1.3170160 -0.7209839
C 0.5357401 0.4874585 0.8138718
C 2.4523241 -0.7618091 -0.8146015
H 0.9561415 -2.2303366 -1.2689339
C 1.9669079 0.8430686 0.8876156
H -0.0182728 0.6564199 1.7395201
C 2.8818308 0.2673692 0.0460541
H 3.1628206 -1.2004933 -1.5094675
H 2.2372482 1.6811437 1.5220545
H 3.9148083 0.5954923 0.0335554

pB^{+} (4-protonated **p1**, missing channel in experiment)

27

Energy = -466.3781843259

C -1.3872657 1.2199494 0.1088612
C -1.4400442 0.2150040 1.1699980
H -0.9059944 0.8676641 -0.8033493
H -0.8824630 2.1207310 0.4923519
H -1.9222293 0.5016143 2.1045533
C -0.9399106 -1.0700481 1.0776650
C -1.0833666 -1.9302716 2.1566296
H -0.4569905 -1.4103509 0.1651745
H -1.5694906 -1.5412513 3.0511458
H -2.4124645 1.5610734 -0.1044728
C -0.5564666 -3.2844023 2.2093784
C 0.8238456 -3.2621320 3.0217157
H -0.3626069 -3.6958266 1.2172418
H -1.2267762 -3.9349977 2.7784520
H 0.6473264 -2.8079154 3.9995323
H 1.0591977 -4.3192940 3.1707509
C 1.9255616 -2.5593349 2.2824121
C 2.6369144 -3.2190387 1.2701151
C 2.2493092 -1.2288227 2.5797332
C 3.6554259 -2.5649761 0.5770013
H 2.3979930 -4.2527277 1.0303841
C 3.2679516 -0.5726067 1.8888955
H 1.7097565 -0.7092178 3.3683111
C 3.9729508 -1.2398031 0.8845595
H 4.2047883 -3.0909677 -0.1984147
H 3.5142528 0.4554248 2.1382401
H 4.7681713 -0.7312719 0.3475205

Table 9. TPSS-D3/def2-TZVP + COSMO computed imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in dichloroethane (DCE); TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the total PW6B95-D3 free energies G_P; the relative electronic energies (ΔE_T and ΔE_P) and Gibbs free-energies (ΔG_T and ΔG_P) at the TPSS-D3 and PW6B95-D3 levels. See also Figure **20, 21, 22 (**chapter-3) for most labellings of structures.

Reactions	ImF	ZPE	Hc	Gc	Hsol	Gsol	TPSS-D3	PW6B95-D3	G_P	ΔE_T	ΔE_p	ΔG_p	ΔG_T
in DCE solution	cm^{-1}	kcal /mol	kcal /mol	kcal /mol	kcal /mol	kcal /mol	Eh	Eh	Eh	kcal /mol	kcal /mol	*kcal /mol*	kcal /mol
Hw^+ (H_2O + Bf_3 – $HOBf_3^-$)	0	5.59	6.72	-3.36	27.09	27.94	-0.45807	-0.45365	-0.41148				
273a ($PhCH=CHCH=CH_2$)	0	103.34	109.48	82.26	-11.28	-7.29	-387.31229	-387.73467	-387.61220				
315a (Ph_2NH)	0	122.93	129.81	101.30	-15.27	-10.65	-518.99784	-519.56654	-519.41907				
H_2O	0	13.00	15.38	1.92	-4.57	-2.82	-76.47338	-76.54983	-76.54826				
Bf_3 ($B(C_6F_5)_3$)	0	94.50	113.21	61.07	-12.06	-9.31	-2209.62232	-2211.87404	-2211.78854				
$HOBf_3^-$ anion	0	101.91	121.87	66.35	-43.72	-40.06	-2285.63764	-2287.97023	-2287.92532				
Proton affinity of 1-phenyl-1,3-diene 273a is 6.8, 3.2 and 5.6 kcal/mol higher than the product 316a, tertiary amine Ph_3N (315g), and cyclohexa-1,3-diene 273u													
316aH^+ + 273**a**	0	341.64	360.25	292.50	-71.35	-57.82	-1294.01362	-1295.42234	-1295.04234	0.00	0.00	*0.00*	0.00
316a + 273**a**H^+	0	341.66	360.30	292.47	-77.92	-64.07	-1294.01352	-1295.42322	-1295.05323	0.06	-0.56	*-6.84*	-6.21
315gH^+ + 273**a**	0	283.07	299.23	236.50	-65.81	-53.77	-1137.87784	-1139.11694	-1138.81972	0.00	0.00	*0.00*	0.00
315g + 273**a**H^+	0	284.17	300.12	238.49	-71.34	-59.35	-1137.87644	-1139.11625	-1138.82474	0.88	0.44	*-3.15*	-2.71

273uH^+ + 273**a**	0	18 7.03	19 6.97	14 8.31	- 69.35	- 59.14	- 621.22473	- 621.89594	- 621.74782	0. 00	0. 00	*0.* *00*	0. 00
273u + 273aH^+	0	18 8.02	19 7.89	14 9.46	- 59.85	- 50.38	- 621.25064	- 621.92058	- 621.75667	- 16.26	- 15.47	- *5.55*	- 6.34
In contrast, Bf_3-induced proton transfer from secondary amine 315a is difficult, especially from the para-position C-H bond.													
Bf_3 + 2*315**a**	0	34 0.36	37 2.84	26 3.67	- 42.60	- 30.61	- 3247.61800	- 3251.00713	- 3250.6266 8	0. 00	0. 00	*0.* *00*	0. 00
315a.Bf_3 + **315a**	0	34 1.67	37 4.20	27 9.50	- 38.72	- 29.11	- 3247.63978	- 3251.03017	- 3250.6251 2	- 13.66	- 14.46	*0.* *98*	1. 77
TS0a	1 262i	33 8.90	37 1.66	29 2.09	- 33.47	- 26.94	- 3247.62272	- 3251.00809	- 3250.5825 5	- 2.96	- 0.61	*27* *.69*	25 .34
315aH^+ + $Ph_2NBf_3^-$	0	34 1.33	37 3.91	27 9.21	- 106.80	- 94.98	- 3247.50150	- 3250.89174	- 3250.5921 3	73 .11	72 .41	*21* *.68*	22 .38
315a.Bf_{3c} + **315a**	0	34 0.79	37 3.67	27 8.20	- 42.00	- 32.13	- 3247.61881	- 3251.00718	- 3250.6090 1	- 0.51	- 0.03	*11* *.09*	10 .61
TS0b	1 495i	33 7.50	37 0.95	28 8.99	- 40.10	- 32.28	- 3247.60026	- 3250.98380	- 3250.5717 0	11 .14	14 .63	*34* *.50*	31 .00
315aH^+ + $PhNHC_6H_4Bf_3^-$	0	34 0.92	37 4.07	27 7.52	- 109.38	- 96.78	- 3247.49670	- 3250.88818	- 3250.5941 4	76 .12	74 .64	*20* *.42*	21 .90
Protonation of amine 315a Ph_2NH with the help of residual water H_2O													
315a + Bf_3 + H_2O	0	23 0.43	25 8.40	16 4.29	- 31.90	- 22.78	- 2805.09355	- 2807.99042	- 2807.7558 7	0. 00	0. 00	*0.* *00*	0. 00
315a + $H_2O.Bf_3$	0	23 3.68	26 0.48	17 6.46	- 32.92	- 25.21	- 2805.11433	- 2808.01085	- 2807.7637 9	- 13.04	- 12.82	- *4.97*	- 5.19
TS0	1 021i	23 6.02	26 2.81	19 3.86	- 28.39	- 22.86	- 2805.14031	- 2808.03376	- 2807.7582	- 29.35	- 27.20	- *1.48*	- 3.63

									3				
315aH^+HOBf_3	0	23 3.80	26 1.04	19 1.37	- 29.45	- 23.87	- 2805.14163	- 2808.03643	- 2807.76650	- 30.17	- 28.87	- *6.67*	- 7.97
315aH^+ + $HOBf_3^-$	0	23 3.90	26 0.81	17 6.58	- 102.13	- 91.34	- 2804.99572	- 2807.89399	- 2807.75214	61 .39	60 .51	*2.* *34*	3. 22
..followed by facile but 1.2 kcal/mol endergonic protonation of diene 273a with ammonium 315aH^+													
273a + **315a** + Hw^+	0	23 1.85	24 6.01	18 0.20	0.5 4	9.9 9	- 906.76820	- 907.75487	- 907.44275	0. 00	0. 00	*0.* *00*	0. 00
315aH^+ + **273a**	0	23 5.33	24 8.42	19 2.48	- 69.68	- 58.57	- 906.67037	- 907.65844	- 907.43902	61 .39	60 .51	*2.* *34*	3. 22
TS1$^+$	1 349i	23 1.82	24 5.12	20 2.79	- 57.21	- 48.30	- 906.68884	- 907.66727	- 907.41807	49 .80	54 .97	*15* *.49*	10 .32
315a + 273aH^+	0	23 4.99	24 7.97	19 2.41	- 68.34	- 56.86	- 906.67402	- 907.65922	- 907.43718	59 .10	60 .02	*3.* *49*	2. 57
..selective electrophilic aromatic substitution of allyl cation 273aH^+ via 3-position on para-position of 315a													
273a + **315a** + Hw^+	0	23 1.85	24 6.01	18 0.20	0.5 4	9.9 9	- 906.76820	- 907.75487	- 907.44275	0. 00	0. 00	*0.* *00*	0. 00
315a.273aH^+ (loose π-adduct)	0	23 6.54	24 9.68	20 8.15	- 56.74	- 48.09	- 906.71123	- 907.68883	- 907.43074	35 .75	41 .44	*7.* *53*	1. 85
TS2$^+$	1 69i	23 4.38	24 7.74	20 5.00	- 56.86	- 47.60	- 906.69758	- 907.67519	- 907.42135	44 .32	50 .00	*13* *.43*	7. 75
316aaH^+ (tight σ-adduct)	0	23 8.30	25 0.77	21 0.12	- 60.10	- 50.58	- 906.70160	- 907.68774	- 907.43049	41 .79	42 .12	*7.* *69*	7. 36
TS2a$^+$ (via 1-position)	3 02i	23 3.85	24 6.79	20 5.10	- 56.41	- 47.40	- 906.69361	- 907.67235	- 907.41802	46 .81	51 .78	*15* *.52*	10 .55
316aaH^+1	0	23 7.22	24 9.96	20 8.84	- 58.66	- 49.40	- 906.69917	- 907.68614	- 907.42904	43 .32	43 .13	*8.* *60*	8. 79
TS2$^+$m (on meta-position)	0	23 4.37	24 8.06	20 4.95	- 59.17	- 49.57	- 906.66836	- 907.64788	- 907.39726	62 .65	67 .13	*28* *.54*	24 .06
..and facile deprotonation with 315a													
273a + 2***315a** + Hw^+	0	35	37	28	-	-	-	-	-	0.	0.	*0.*	0.

		4.78	5.83	1.50	14.72	0.66	1425.76604	1427.32141	1426.86182	00	00	*00*	00
316aaH^+ + **315a**	0	36 1.23	38 0.58	31 1.42	-75.37	-61.23	-1425.69944	-1427.25429	-1426.84956	41 .79	42 .12	*7. 69*	7. 36
TS3$^+$	1 159i	35 5.89	37 6.53	31 9.14	-66.57	-55.11	-1425.71275	-1427.26218	-1426.83840	33 .44	37 .17	*14 .69*	10 .97
316a + **315a**H^+	0	36 1.59	38 1.08	31 1.58	-83.25	-69.14	-1425.69542	-1427.25431	-1426.86194	44 .32	42 .10	*-0.08*	2. 14
316a + **315a** + Hw^+	0	35 8.12	37 8.67	29 9.29	-13.02	-0.58	-1425.79325	-1427.35074	-1426.86567	-17.07	-18.41	*-2.42*	-1.08
Deprotonation with $HOBf_3^-$ anion is kinetically similarly favorable but limited by low concentration													
273a + **315a** + Bf_3 + H_2O	0	33 3.77	36 7.88	24 6.55	-43.18	-30.07	-3192.40584	-3195.72509	-3195.36807	0. 00	0. 00	*0. 00*	0. 00
316aaH^+ + $HOBf_3^-$	0	34 0.21	37 2.63	27 6.47	-103.83	-90.64	-3192.33924	-3195.65797	-3195.35581	41 .79	42 .12	*7. 69*	7. 36
316aaH^+HOBf_3	0	33 9.61	37 2.87	29 1.76	-41.89	-33.57	-3192.44250	-3195.75857	-3195.34411	-23.01	-21.00	*15 .03*	13 .03
TS3a	3 67i	33 8.74	37 2.22	28 9.25	-42.04	-33.71	-3192.44163	-3195.75660	-3195.34636	-22.46	-19.77	*13 .62*	10 .93
316a + Bf_3 + H_2O	0	33 7.10	37 0.73	26 4.34	-41.48	-29.99	-3192.43305	-3195.75442	-3195.37192	-17.07	-18.41	*-2.42*	-1.08
Deprotonation with 315a is kinetically 5.6 kcal/mol less efficient													
2***273a** + **315a** + Hw^+	0	33 5.19	35 5.50	26 2.46	-10.74	2.70	-1294.08049	-1295.48954	-1295.05495	0. 00	0. 00	*0. 00*	0. 00
316aaH^+ + **273a**	0	34	36	29	-	-	-	-	-	41	42	*7.*	7.

		1.64	0.25	2.38	71.38	57.87	1294.01389	1295.42242	1295.04269	.79	.12	*69*	36
TS3a^{+}	1142i	33 6.48	35 6.10	30 0.88	-63.93	-52.82	-1294.02152	-1295.42096	-1295.02264	37 .01	43 .04	*20 .27*	14 .24
TS3b^{+}	1101i	35 5.42	37 6.25	31 8.45	-65.11	-54.06	-1425.71082	-1427.26091	-1426.83658	34 .66	37 .96	*15 .84*	12 .53
316a + **273a**H^{+}	0	34 1.66	36 0.30	29 2.47	-77.92	-64.07	-1294.01352	-1295.42322	-1295.05323	42 .03	41 .62	*1. 08*	1. 49
Effects of N-methylation of Ph_2NH: more electron-rich phenyl within 315h Ph_2NMe													
The proton affinity of 315h is 3.8 kcal/mol higher than 315a													
315hH^{+} + **315a**	0	27 1.81	28 6.62	22 7.05	-71.90	-59.85	-1077.69563	-1078.86924	-1078.59677	0. 00	0. 00	*0. 00*	0. 00
315h + **315a**H^{+}	0	27 1.85	28 6.63	22 7.08	-73.39	-61.65	-1077.68647	-1078.86027	-1078.59063	5. 75	5. 63	*3. 85*	3. 97
*Preferred protonation of **2h** at first with $H_2O.Bf_3$*													
315h + Bf_3 + H_2O	0	24 7.36	27 6.27	17 9.84	-31.62	-22.50	-2844.42410	-2847.36038	-2847.10061	0. 00	0. 00	*0. 00*	0. 00
3152h + $H_2O.Bf_3$	0	25 0.61	27 8.36	19 2.01	-32.64	-24.93	-2844.44488	-2847.38081	-2847.10853	-13.04	-12.82	*-4.97*	-5.19
2hH^{+}HOBf$_3$	0	25 1.44	27 9.74	20 7.94	-29.77	-24.03	-2844.47449	-2847.40957	-2847.11347	-31.62	-30.87	*-8.07*	-8.82
315hH^{+} + $HOBf_3^{-}$	0	25 0.79	27 8.67	19 2.10	-100.36	-89.26	-2844.33543	-2847.27292	-2847.10301	55 .64	54 .88	*-1.51*	-0.75
.. elading to kinetically more favorable electrophilic attack of allyl cation 273aH^{+} via 1-position of than on 3-position on phenyl para-position of 315h													

273a + **315h** + Hw^+	0	24 8.79	26 3.89	19 5.75	0.8 3	10. 27	- 946.09875	- 947.12483	- 946.78749	0. 00	0. 00	*0.* *00*	0. 00
315hH^+ + **273a**	0	25 2.21	26 6.29	20 8.01	- 67.91	- 56.49	- 946.01008	- 947.03737	- 946.78989	55 .64	54 .88	- *1.51*	- 0.75
TS1h$^+$	1 381i	24 9.03	26 3.23	21 9.24	- 56.26	- 47.28	- 946.02611	- 947.04337	- 946.76632	45 .58	51 .12	*13* *.28*	7. 75
315h + **273a**H^+	0	25 1.92	26 5.84	20 7.97	- 68.06	- 56.59	- 946.00457	- 947.02917	- 946.78192	59 .10	60 .02	*3.* *49*	2. 57
TS2h$^+$	1 64i	25 1.29	26 5.70	22 0.82	- 55.52	- 46.26	- 946.03041	- 947.04619	- 946.76499	42 .89	49 .34	*14* *.11*	7. 66
316hH^+	0	25 5.46	26 8.83	22 6.52	- 59.02	- 49.36	- 946.03794	- 947.06340	- 946.77807	38 .16	38 .54	*5.* *91*	5. 52
TS2ha$^+$	2 86i	25 1.01	26 5.55	22 0.44	- 55.52	- 46.42	- 946.02885	- 947.04669	- 946.76637	43 .86	49 .03	*13* *.25*	8. 09
316hHa^+	0	25 4.46	26 8.10	22 5.38	- 57.64	- 48.24	- 946.03545	- 947.06153	- 946.77624	39 .72	39 .72	*7.* *06*	7. 06
...315h Ph_2NMe is less efficient for deprotonation due to higher steric hindrance at N-center													
273a + 2***315h** + Hw^+	0	38 8.65	41 1.58	31 2.60	- 14.16	- 0.11	- 1504.42714	- 1506.06133	- 1505.5512 9	0. 00	0. 00	*0.* *00*	0. 00
TS3h$^+$	1 432i	39 0.75	41 3.07	35 3.06	- 61.48	- 50.57	- 1504.38221	- 1506.00997	- 1505.5248 9	28 .20	32 .23	*16* *.57*	12 .53
TS3ha$^+$	1 441i	39 0.23	41 2.76	35 2.33	- 61.03	- 50.27	- 1504.37686	- 1506.00372	- 1505.5193 4	31 .56	36 .15	*20* *.05*	15 .46
..facile deprotonation with $HOBf_3^-$ instead to form the product 316h and kinetically more favorable but less stable 316ha													
273a + **315h** + Bf_3	0	35 0.70	38 5.76	26 2.10	- 42.90	- 29.79	- 3231.73639	- 3235.09505	- 3234.7128 0	0. 00	0. 00	*0.* *00*	0. 00
316hH^+ + $HOBf_3^-$	0	35 7.37	39 0.70	29 2.87	- 102.75	- 89.43	- 3231.67558	- 3235.03363	- 3234.7033 9	38 .16	38 .54	*5.* *91*	5. 52
316hH^+HOBf_3	0	35 6.05	39 0.45	30 7.51	- 39.24	- 31.26	- 3231.78253	- 3235.13974	- 3234.6965	- 28.95	- 28.04	*10* *.22*	9. 31

									1				
316h + $H_2O.Bf_3$	0	35 7.17	39 0.62	29 2.36	- 42.16	- 32.10	- 3231.78452	- 3235.14493	- 3234.7241 7	- 30.20	- 31.30	- *7.13*	- 6.03
316hHa^+ + $HOBf_3^-$	0	35 6.38	38 9.96	29 1.73	- 101.36	- 88.30	- 3231.67308	- 3235.03176	- 3234.7015 6	39 .72	39 .72	*7.* *06*	7. 06
316hHa^+HOBf_3	0	35 7.23	39 1.26	30 8.96	- 39.95	- 31.77	- 3231.78450	- 3235.14047	- 3234.6957 4	- 30.19	- 28.50	*10* *.71*	9. 02
316ha + $H_2O.Bf_3$	0	35 6.27	38 9.98	29 1.39	- 41.37	- 31.59	- 3231.77993	- 3235.14065	- 3234.7206 1	- 27.32	- 28.61	- *4.90*	- 3.61
Effects of H/Ph replacement of 315a Ph_2NH : less electron-rich phenyl ring within 315g Ph_3N with preferred phenyl para-position as H^+ acceptor													
Tertiary amine 315g cannot transfer proton to diene 273a and another Ph_3N with the help of Bf_3 only.													
315g + Bf_3 + **273a**	0	36 9.95	40 4.66	29 0.71	- 41.61	- 29.73	- 3347.13487	- 3350.63229	- 3350.2073 7	0. 00	0. 00	*0.* *00*	0. 00
TS0g	1 456i	36 7.19	40 2.62	31 7.28	- 39.79	- 32.28	- 3347.11208	- 3350.59782	- 3350.1406 3	14 .31	21 .63	*41* *.88*	34 .55
273aH^+ + **315gc**Bf_3^-	0	37 1.24	40 6.21	30 6.34	- 105.48	- 92.82	- 3347.01973	- 3350.51651	- 3350.1702 3	72 .26	72 .65	*23* *.31*	22 .91
2***315g** + Bf_3	0	43 8.73	47 7.14	35 5.83	- 48.60	- 35.58	- 3710.02285	- 3713.92118	- 3713.4018 0	0. 00	0. 00	*0.* *00*	0. 00
315gHc^+ + **315gc**Bf_3^-	0	43 8.91	47 7.80	36 9.47	- 106.94	- 93.08	- 3709.90910	- 3713.80610	- 3713.3596 3	71 .37	72 .22	*26* *.46*	25 .62
Proton affinity of tertiary amine Ph_3N (315g) is 3.2 and 4.3 kcal/mol smaller than 273a and 315a, respectively													
315gHc^+ + **273a**	0	28 3.07	29 9.23	23 6.50	- 65.81	- 53.77	- 1137.87784	- 1139.11694	- 1138.8197 2	0. 00	0. 00	*0.* *00*	0. 00

315g + **273a**H^+	0	28 4.17	30 0.12	23 8.49	-71.34	-59.35	-1137.87644	-1139.11625	-1138.8247 4	0. 88	0. 44	*-3.15*	-2.71
315g Hc+ + **315a**	0	30 2.66	31 9.56	25 5.54	-69.80	-57.12	-1269.56339	-1270.94881	-1270.6265 9	0. 00	0. 00	*0. 00*	0. 00
315g + **315a**H^+	0	30 4.10	32 0.90	25 7.60	-76.67	-64.41	-1269.55834	-1270.94734	-1270.6334 5	3. 17	0. 92	*-4.30*	-2.06
315g + Bf_3	0	26 6.61	29 5.17	20 8.45	-30.33	-22.44	-2959.82258	-2962.89761	-2962.5951 7	0. 00	0. 00	*0. 00*	0. 00
315g.Bf_3 (unstable π-adduct)	0	26 7.95	29 7.04	22 4.22	-25.18	-19.92	-2959.84085	-2962.91594	-2962.5873 4	-11.46	-11.50	*4. 91*	4. 95
315g.Bf_3c	0	26 7.66	29 6.47	22 4.30	-29.34	-23.55	-2959.82259	-2962.89618	-2962.5732 6	0. 00	0. 90	*13 .75*	12 .84
..leading to selective protonation of 273a at first													
273a + Bf_3 + H_2O	0	21 0.84	23 8.07	14 5.25	-27.91	-19.42	-2673.40800	-2676.15855	-2675.9490 0	0. 00	0. 00	*0. 00*	0. 00
273a + H_2O.Bf_3	0	21 4.09	24 0.15	15 7.41	-28.94	-21.85	-2673.42878	-2676.17898	-2675.9569 2	-13.04	-12.82	*-4.97*	-5.19
TS1g	8 89i	21 0.86	23 7.23	16 8.84	-26.07	-20.67	-2673.43042	-2676.17255	-2675.9334 1	-14.07	-8.78	*9. 78*	4. 49
273a$H^+$$HOBf_3$	0	21 6.17	24 2.08	17 5.30	-22.77	-17.72	-2673.45609	-2676.20698	-2675.9528 4	-30.18	-30.39	*-2.41*	-2.20
$HOBf_3^-$ + **273a**H^+	0	21 3.97	24 0.02	15 7.46	-96.79	-86.27	-2673.31381	-2676.06290	-2675.9434 3	59 .10	60 .02	*3. 49*	2. 57
***..followed by facile electrophilic aromatic substitution with allyl action 273a**H^+*													

273a + **315g** + Hw^+	0	28 1.04	29 8.16	22 6.27	- 2.46	7.5 1	- 1137.97062	- 1139.21190	- 1138.8303 1	0. 00	0. 00	*0.* *00*	0. 00
315g + **273a**H^+	0	28 4.17	30 0.12	23 8.49	- 71.34	- 59.35	- 1137.87644	- 1139.11625	- 1138.8247 4	59 .10	60 .02	*3.* *49*	2. 57
TS2g+	3 37i	28 3.56	29 9.93	25 0.98	- 57.98	- 47.96	- 1137.90077	- 1139.13291	- 1138.8063 7	43 .84	49 .57	*15* *.02*	9. 29
316gH^+	0	28 7.51	30 2.94	25 6.53	- 59.88	- 49.63	- 1137.90875	- 1139.14848	- 1138.8157 6	38 .83	39 .80	*9.* *13*	8. 16
..and deprotonation with $HOBf_3^-$ anion to form product 316g													
273a + **315g** + Bf_3 + H_2O	0	38 2.95	42 0.03	29 2.62	- 46.18	- 32.55	- 3423.60826	- 3427.18212	- 3426.7556 3	0. 00	0. 00	*0.* *00*	0. 00
$HOBf_3^-$ + **316g**H^+	0	38 9.43	42 4.81	32 2.88	- 103.60	- 89.69	- 3423.54639	- 3427.11870	- 3426.7410 8	38 .83	39 .80	*9.* *13*	8. 16
316gH^+HOBf_3	0	38 9.13	42 5.36	33 8.76	- 42.78	- 34.10	- 3423.65085	- 3427.21960	- 3426.7310 8	- 26.73	- 23.52	*15* *.40*	12 .19
316g + H_2O.Bf_3	0	38 9.23	42 4.79	32 2.27	- 45.66	- 35.06	- 3423.65649	- 3427.23207	- 3426.7683 6	- 30.27	- 31.35	- *7.99*	- 6.91
Primary amine $PhNH_2$ may quench Bf_3 into stabel acid/base adduct; further H^+ transfer to 273a is not feasible													
$PhNH_2$ + Bf_3	0	16 7.45	19 0.29	11 6.24	- 23.30	- 16.70	- 2497.41858	- 2499.98387	- 2499.8192 1	0. 00	0. 00	*0.* *00*	0. 00
$PhNH_2$.Bf_3	0	16 9.71	19 2.45	13 1.60	- 21.58	- 17.12	- 2497.45674	- 2500.02350	- 2499.8380 6	- 23.95	- 24.86	- *11.83*	- 10.91
$2PhNH_2$ + Bf_3	0	24 0.41	26 7.36	17 1.42	- 34.53	- 24.09	- 2785.21484	- 2788.09370	- 2787.8498	0. 00	0. 00	*0.* *00*	0. 00

									9				
$PhNH_3^+ + PhNHBf_3^-$	0	24 2.43	26 9.55	18 6.02	- 108.78	- 98.63	- 2785.09849	- 2787.97784	- 2787.83256	73 .01	72 .71	*10* *.88*	11 .18
$PhNH_2.Bf_3$ + **273a**	0	27 3.05	30 1.93	21 3.85	- 32.86	- 24.41	- 2884.76903	- 2887.75817	- 2887.45026	0. 00	0. 00	*0.* *00*	0. 00
273a$H^+ + PhNHBf_3^-$	0	27 1.48	30 0.58	21 1.98	- 98.42	- 87.42	- 2884.62683	- 2887.61167	- 2887.40716	89 .23	91 .93	*27* *.05*	24 .35
***Ph to Cy replacement of 273a leads to 1,3-diene 273q with 2.9 kcal/mol smaller proton affinity but more reactive 1-position within allyl cation 273q**H^+*													
273aH^+ + **273q**	0	25 9.05	27 1.84	21 6.64	- 62.83	- 52.51	- 778.61431	- 779.45039	- 779.18281	0. 00	0. 00	*0.* *00*	0. 00
273qH^+ + **273a**	0	25 7.74	27 0.98	21 4.76	- 65.74	- 54.88	- 778.60406	- 779.43903	- 779.17822	6. 43	7. 13	*2.* *88*	2. 19
…and highly selective electrophilic aromatic substitution via 1-position (TS2n**$^+$**)													
315a + **273u**H^+	0	27 7.33	29 1.31	23 3.81	- 69.73	- 58.24	- 910.28961	- 911.27090	- 910.98509	0. 00	0. 00	*0.* *00*	0. 00
TS2n$^+$ (via 1-position)	243i	27 7.31	29 1.42	24 7.69	- 56.09	- 47.61	- 910.32649	- 911.30268	- 910.98081	- 23.14	- 19.94	*2.* *68*	- 0.51
TS2na$^+$ (via 3-position)	139i	27 6.71	29 1.08	24 6.62	- 56.39	- 47.55	- 910.31913	- 911.29273	- 910.97248	- 18.52	- 13.70	*7.* *91*	3. 09
Effects of multiple alkylation:													
Tertiary amine 315l: 10.4 and 11.5 kcal/mol higher proton affinity than amine 315a and 1,3-diene 273a, respectively													
315lH^+ + **315a**	0	26 3.00	27 6.09	22 0.47	- 72.81	- 61.27	- 963.31546	- 964.36020	- 964.10047	0. 00	0. 00	*0.* *00*	0. 00
315aH^+ + **315l**	0	26 2.22	27 5.52	21 9.33	- 70.81	- 59.69	- 963.29983	- 964.34441	- 964.08397	9. 81	9. 91	*10* *.35*	10 .24
..leading to protonation of 315l at first, followed by proton transfer to 273a and further electrophilic aromatic substitution via 3 or 1 position on phenyl para-position													
273a + **315l** + Hw^+	0	23 9.15	25 2.78	18 8.00	3.4 1	12. 23	- 831.71211	- 832.60897	- 832.28084	0. 00	0. 00	*0.* *00*	0. 00

315lH^+ + **273a**	0	24 3.41	25 5.76	20 1.43	- 68.82	- 57.91	- 831.62991	- 832.52834	- 832.29359	51 .58	50 .60	- *8.01*	- 7.02
273aH^+ + **315l**	0	24 2.29	25 4.74	20 0.22	- 65.48	- 54.62	- 831.61793	- 832.51332	- 832.27527	59 .10	60 .02	*3.* *49*	2. 57
273aH^{+315}**l** (N-C adduct)	0	24 4.86	25 7.05	21 7.55	- 57.39	- 48.64	- 831.65687	- 832.55261	- 832.28041	34 .66	35 .37	*0.* *26*	- 0.44
TS2l$^+$**o** (on *ortho*-position)	3 79i	24 1.75	25 4.61	21 3.50	- 55.10	- 46.80	- 831.64572	- 832.53646	- 832.26780	41 .66	45 .50	*8.* *18*	4. 34
TS2l$^+$ (on *para*-position)	3 51i	24 1.82	25 4.68	21 3.69	- 54.37	- 46.20	- 831.65365	- 832.54460	- 832.27468	36 .69	40 .39	*3.* *86*	0. 16
316lH^+ (via 3-position)	0	24 6.35	25 8.07	21 9.40	- 59.26	- 50.09	- 831.65600	- 832.55263	- 832.27983	35 .21	35 .35	*0.* *63*	0. 50
TS2la$^+$	1 63i	24 2.38	25 5.03	21 4.55	- 53.87	- 45.86	- 831.65814	- 832.54728	- 832.27544	33 .87	38 .71	*3.* *39*	- 1.46
316lHa^+ (via 1-position)	0	24 6.77	25 8.34	21 9.96	- 58.77	- 49.67	- 831.65621	- 832.55310	- 832.27871	35 .08	35 .06	*1.* *34*	1. 36
..facile deprotonation with amine 315l													
273a +2***315l** + Hw^+	0	36 9.38	38 9.37	29 7.11	- 9.00	3.8 2	- 1275.65386	- 1277.02961	- 1276.5379 9	0. 00	0. 00	*0.* *00*	0. 00
273a + **315l** + **315l**H^+	0	37 3.63	39 2.34	31 0.54	- 81.22	- 66.32	- 1275.57166	- 1276.94898	- 1276.5507 5	51 .58	50 .60	- *8.01*	- 7.02
TS3l$^+$	1 085i	37 0.31	38 9.68	33 5.66	- 60.12	- 50.00	- 1275.61244	- 1276.98229	- 1276.5240 6	25 .99	29 .69	*8.* *74*	5. 04
315lH^+ + **316l**	0	37 5.62	39 4.23	32 7.01	- 78.50	- 65.50	- 1275.59450	- 1276.97416	- 1276.5514 0	37 .25	34 .79	- *8.41*	- 5.96
TS3la$^+$	1 127i	37 0.94	38 9.64	33 7.00	- 61.50	- 51.13	- 1275.61416	- 1276.98393	- 1276.5253 5	24 .91	28 .66	*7.* *93*	4. 18
315lH^+ + **316la**	0	37 6.94	39 5.15	32 8.61	- 79.26	- 66.03	- 1275.59908	- 1276.97863	- 1276.5541 7	34 .37	31 .99	- *10.15*	- 7.76

The use of cyclo-1,3-hexadiene (273u) instead: 2.2 kcal/mol higher overall barrier (TS1w$^+$) due to lower proton affinity than 315a												
273u	0	75.96	79.73	58.35	-6.78	-4.17	-233.57446	-233.82791	-233.73856			
273u + **315a** + Hw$^+$	0	20 4.48	21 6.26	15 6.28	5.05	13.12	-753.03037	-753.84810	-753.56911	0.00	0.00	*0.00*	0.00
315aH+ + **273u**	0	20 7.95	21 8.67	16 8.57	-65.18	-55.45	-752.93254	-753.75168	-753.56538	61.39	60.51	*2.34*	3.22
TS1w$^+$	1 208i	20 4.18	21 5.27	17 7.48	-56.03	-47.98	-752.94057	-753.75021	-753.54084	56.35	61.43	*17.74*	12.66
315a.273uH$^+$ (loose π-complex)	0	20 8.98	21 9.71	18 2.90	-56.83	-48.59	-752.95307	-753.76235	-753.54530	48.51	53.81	*14.94*	9.64
273uH$^+$ + **315a**	0	20 6.62	21 7.30	16 7.35	-73.33	-62.50	-752.91028	-753.72781	-753.55470	75.36	75.49	*9.05*	8.92
..forming stable N-C adduct of reactive allyl cation 273uH$^+$ that may favor electrophilic aromatic substitution on ortho-position and deprotonation with 315a												
273uH$^+$**315a**	0	20 9.76	22 0.21	18 3.89	-55.22	-47.27	-752.97535	-753.79261	-753.57187	34.52	34.82	*-1.73*	-2.03
TS2w$^+$ (on ortho-position)	-122	20 7.05	21 7.78	18 0.93	-55.41	-47.58	-752.95635	-753.76639	-753.55087	46.45	51.27	*11.44*	6.62
316uaH$^+$	0	20 9.37	21 9.82	18 3.64	-55.08	-47.27	-752.96769	-753.78328	-753.56294	39.33	40.68	*3.87*	2.53
273u + 2***315a** + Hw$^+$	0	32 7.41	34 6.08	25 7.59	-10.22	2.47	-1272.02821	-1273.41464	-1272.98818	0.00	0.00	*0.00*	0.00
TS3w$^+$	-1188	32 9.06	34 6.54	29 5.87	-59.37	-49.70	-1271.98004	-1273.35873	-1272.96342	30.23	35.09	*15.53*	10.67
316ua + **315a**H$^+$	0	33 2.79	35 0.30	28 5.00	-78.11	-65.51	-1271.96184	-1273.35116	-1272.99535	41.65	39.84	*-4.50*	-2.69

Table 10. TPSS-D3/def2-TZVP + COSMO optimized Cartesian coordinates (in Å) in DCE solution. Each structure is labeled by the specific name (See **Figure 20, 21, 22** (chapter-3), **Table 9**), followed by the number of atoms, the total energy (in hartrees), and the atomic coordinates (in double-column text list).

316ha : 4,1-hydroarylation of **273a** with **315h** Ph_2NMe

47

Energy = -945.6166594500

N	-2.9407068	1.1690881	-0.1578752
C	-3.8763359	0.1101345	-0.0593025
C	-1.5899614	0.9915468	0.1615401
C	-4.9188243	0.0024204	-0.9941632
C	-3.8005670	-0.8327812	0.9793068
C	-0.7915826	2.0715652	0.5790854
C	-0.9644071	-0.2648700	0.0089383
C	-5.8606646	-1.0198539	-0.8881046
H	-4.9823041	0.7130074	-1.8131508
C	-4.7359180	-1.8611811	1.0693378
H	-3.0069850	-0.7512657	1.7154405
C	0.5665784	1.8906706	0.8504554
H	-1.2238433	3.0582072	0.7029269
C	0.3830727	-0.4270374	0.2940118
H	-1.5436629	-1.1134428	-0.3399389
C	-5.7744327	-1.9618884	0.1395736
H	-6.6570741	-1.0874359	-1.6243669
H	-4.6616541	-2.5784906	1.8824299
C	1.1817469	0.6446641	0.7252102
H	1.1549759	2.7467176	1.1705614
H	0.8282529	-1.4117055	0.1750958
H	-6.5052015	-2.7615836	0.2156661
C	4.2392278	2.3881822	1.3511782
C	4.8620936	3.4956286	2.1489182
H	4.6095951	2.2541269	0.3327817
C	3.2795004	1.5725513	1.7947397
H	5.9455593	3.3474736	2.2482141
H	4.4285479	3.5556449	3.1522696
H	4.7225579	4.4648278	1.6523264
C	2.6745289	0.4459510	0.9899511
H	2.8959290	1.6914380	2.8097911
H	3.1929751	0.4186995	0.0213166
C	2.9596768	-0.8784826	1.6911632
C	3.9455778	-1.7419349	1.2038119
C	2.2652094	-1.2381941	2.8536439
C	4.2336644	-2.9415850	1.8589567
H	4.4900080	-1.4730866	0.3011243
C	2.5524936	-2.4316412	3.5143914
H	1.4845184	-0.5834981	3.2330791
C	3.5382948	-3.2896815	3.0181205
H	4.9985821	-3.6039703	1.4621307
H	2.0042542	-2.6965527	4.4147282
H	3.7583260	-4.2231090	3.5289310
C	-3.4525441	2.5338412	-0.2906731
H	-3.4634531	3.0550684	0.6775547
H	-2.8358616	3.1047008	-0.9919101
H	-4.4733832	2.4925012	-0.6671824

316h : 4,3-hydroarylation of **273a** with **315h** Ph_2NMe

47

Energy = -945.6218235385

N	-3.5964665	0.6716927	-0.1124197
C	-3.9489274	-0.6951209	0.0015918
C	-2.2826270	1.1153835	0.0698602
C	-4.9153280	-1.2476243	-0.8545143
C	-3.3663558	-1.5157776	0.9817154
C	-2.0091797	2.4427438	0.4451343
C	-1.1821654	0.2679159	-0.1867848
C	-5.2884853	-2.5850198	-0.7294741
H	-5.3654966	-0.6308841	-1.6269096
C	-3.7328292	-2.8552333	1.0902930
H	-2.6300716	-1.0946539	1.6590537
C	-0.6925540	2.8929242	0.5760971
H	-2.8197993	3.1354120	0.6414298
C	0.1159755	0.7306260	-0.0415746
H	-1.3544155	-0.7540206	-0.5075224
C	-4.6978839	-3.4000587	0.2387980
H	-6.0343428	-2.9942449	-1.4055362
H	-3.2726556	-3.4724057	1.8573501
C	0.3967452	2.0525978	0.3428095
H	-0.5324424	3.9263653	0.8691224
H	0.9410639	0.0495787	-0.2387599
H	-4.9854841	-4.4432499	0.3295635
C	1.8515231	2.4871788	0.5070278
C	2.0288131	4.0069905	0.6579565
H	2.3973067	2.1665067	-0.3908357
C	2.4482645	1.7624013	1.6863282
H	3.0940322	4.2541370	0.6909589
H	1.5701405	4.3704707	1.5842527
H	1.5730669	4.5402143	-0.1834918
C	3.4566954	0.8801312	1.6008490
H	1.9880355	1.9861737	2.6493498
H	3.8885286	0.6890332	0.6169660
C	4.0654649	0.1227520	2.6991454
C	5.1709176	-0.7030900	2.4237255
C	3.5976305	0.1752234	4.0266586
C	5.7908104	-1.4433679	3.4301579
H	5.5442320	-0.7590646	1.4034962
C	4.2153742	-0.5625954	5.0317187
H	2.7403635	0.7950400	4.2733401
C	5.3165683	-1.3761867	4.7412019
H	6.6433259	-2.0729523	3.1897999
H	3.8357915	-0.5073318	6.0485772

H 5.7951882 -1.9512781 5.5287359
C -4.6708249 1.6645982 -0.1514404
H -4.8028997 2.1498072 0.8260895
H -4.4548323 2.433606 -0.9001945
H -5.6023877 1.1649813 -0.4122101

316la : 4,3-hydroarylation of **273a** with **315l**

44

Energy = -831.2393569533

N -.6205138 0.1026684 1.2866072
C -.5445858 -0.7216172 0.9792072
C -07354266 -1.2751932 1.9926902
C -12430276 -1.0558153 -0.3693420
C 0.3073824 -2.1521539 1.6901707
H -0.9174848 -1.0221189 3.0312702
C -0.2001842 -1.9370815 -0.6317930
C 0.5991649 -2.5048594 0.3714690
H 08970035 -2.5518464 2.5100110
H 0.0002915 -2.1972121 -1.6706055
C 1.7113927 -3.4763670 -0.0220383
C 2.5881508 -3.9182172 1.1611285
H 2.3574767 -2.9707725 -0.7533531
C 1.1026403 -4.6734566 -0.7048295
H 3.3962038 -4.5632375 0.8035993
H 2.0049053 -4.4826483 1.8973866
H 3.0322046 -3.0532034 1.6654942
C 1.3208594 -5.0038664 -1.9879026
H 0.4334572 -.2713231 -0.0850989
H 2.0021968 -4.3792326 -2.5682047
C 0.7427580 -6.1332851 -2.723008
C 1.1583510 -6.3660609 -4.0467954
C -0.2164490 -7.0047712 -2.1717669
C 0.6452618 -7.4277139 -4.7913387
H 1.8962192 -5.7013306 -4.4906716
C -0.7285924 -8.0649158 -2.9131742
H -0.5675877 -6.8482719 -1.1557942
C -0.3010306 -8.2847840 -4.2275221
H 0.9844457 -7.5848938 -5.8117257
H -1.4681750 -8.7242560 -2.4665730
H -0.7040619 -9.1132109 -4.8030729
C -2.7494667 0.6299531 2.6370657
H -2.8465135 -0.1823707 3.3651237
H -1.8906238 1.2553575 2.9296758
H -3.6550139 1.2380965 2.6827454
C -3.2411471 0.8863888 0.2179199
H -2.6400588 1.7820144 -0.0189450
H -4.2130524 1.2294280 0.5849535
C -3.4095728 0.0303129 -1.0333310
H -3.9064623 0.6155071 -1.8139007
H -4.0512848 -0.8260329 -0.7941215
C -2.0385529 -0.4541211 -1.5081784
H -1.4862279 0.3968851 -1.9316458
H -2.1420888 -1.1892959 -2.3141197

316l : 4,1-hydroarylation of **273a** with **315l**

44

Energy = -831.2342998280

N -3.3647445 -0.9682875 0.5798172
C -1.9823074 -0.9221257 0.7285480
C -1.3916420 -0.4960046 1.9368774
C -1.1206444 -1.3331356 -0.3238188
C -0.0083295 -0.5113985 2.1094815
H -2.0156976 -0.1532672 2.7548560
C 0.2555861 -1.3406806 -0.1131022
C 0.8470709 -0.9389844 1.0920258
H 0.4084628 -0.1778923 3.0565552
H 0.8929478 -1.6818771 -0.9272413
C 3.4721571 0.0374126 3.3092258
C 3.9147975 0.0167453 4.7427985
H 3.7312630 0.9277980 2.7325649
C 2.7932826 -0.9405509 2.7043357
H 5.0064735 0.1076282 4.8194275
H 3.6102222 -0.9100408 5.2395152
H 3.4900897 0.8631673 5.2984472
C 2.3681387 -0.9185581 1.2541730
H 2.5214124 -1.8366484 3.2653927
H 2.7501713 0.0143804 0.8157344
C 3.0450078 -2.0695571 0.5178855
C 4.1091700 -1.8258535 -0.3557201
C 2.6361934 -3.3937518 0.7254903
C 4.7542267 -2.8781162 -1.0104375
H 4.4331549 -0.8014217 -0.5267536
C 3.2786681 -4.4478723 0.0779650
H 1.7983499 -3.5950329 1.3883825
C 4.3413138 -4.1937227 -0.7944047
H 5.5763653 -2.6690093 -1.6900280
H 2.9481034 -5.4691241 0.2490480
H 4.8387989 -5.0144080 -1.3040516
C -4.2059933 -0.2913561 1.5564426
H -4.0513635 -0.7069729 2.5576934
H -4.0152824 0.7933847 1.5984338
H -5.2497641 -0.4519449 1.2788315
C -3.9230933 -1.1170931 -0.7649616
H -3.8971349 -0.1594588 -1.3148935
H -4.9728556 -1.4052246 -0.6539891
C -3.1513373 -2.1806886 -1.5393379
H -3.6012107 -2.3142206 -2.5286315
H -3.2271556 -3.1344806 -1.0033643
C -1.6860826 -1.7588688 -1.6625368
H -1.6132168 -0.9229910 -2.3730829
H -1.0796127 -2.5722067 -2.0770363

273aH^+**315l** : N-C adduct of allyl cation **273a**H^+ and **315l**

45

Energy = -831.6673760664

N -1.9562828 -1.0914094 -0.0754723
C -1.5015465 -1.0604665 1.3562286

C	-0.5956133	-0.0653613	1.7354052
C	-1.9582160	-2.0061073	2.2840640
C	0.0801711	-0.0438699	3.0272411
H	0.2766005	0.6968857	1.0386755
C	-1.4180899	-1.9653992	3.5771481
C	-0.4759669	-1.0129260	3.9484538
H	0.6265909	0.7310642	3.3050440
H	-1.7771170	-2.6882978	4.3047320
H	-0.0767531	-1.0065406	4.9579859
C	-0.7412951	-1.6010058	-1.0078166
C	-1.1774558	-1.6552128	-2.4707044
H	-0.5787802	-2.6040063	-0.6069178
C	0.4895674	-0.7831003	-0.8496840
H	-0.3772354	-2.1581556	-3.0204461
H	-1.2881990	-0.6528326	-2.8922422
H	-2.0967761	-2.2206663	-2.6313619
C	1.5799135	-1.2560129	-0.2207467
H	0.4960081	0.1936856	-1.3300651
H	1.5199775	-2.2506608	0.2220684
C	2.8569892	-0.5738845	-0.0324724
C	3.8759124	-1.2409033	0.6710066
C	3.1082567	0.7290383	-0.5031574
C	5.1078485	-0.6304813	0.8979024
H	3.6916449	-2.2469596	1.0398966
C	4.3372695	1.3379705	-0.2763041
H	2.3400202	1.2684528	-1.0494755
C	5.3424901	0.6612408	0.4243576
H	5.8827631	-1.1614939	1.4430014
H	4.5164426	2.3436921	-0.6454432
H	6.3013067	1.1408795	0.5981781
C	-2.4188127	0.2818189	-0.4972416
H	-3.2278958	0.5804214	0.1686737
H	-1.5941176	0.9857419	-0.4244001
H	-2.7728242	0.2247225	-1.5245029
C	-3.1129380	-2.0773982	-0.3216869
H	-2.6520862	-3.0184150	-0.6281930
H	-3.6793933	-1.6714453	-1.1578518
C	-3.9680237	-2.3190365	0.9027154
H	-4.7834395	-2.9840901	0.6035759
H	-4.4150028	-1.3888557	1.2709715
C	-3.0843110	-2.9567507	1.9694910
H	-2.7001230	-3.9170461	1.5998313
H	-3.6421355	-3.1655691	2.8861798

273a$H^+HOBf_3^-$: contact ion pair of **315a**H^+

57

Energy = -2673.329303618

B	-0.2794197	0.1325010	0.8266418
C	-1.4625917	0.2473192	1.9541171
C	-0.0930393	-1.3105042	0.1166874
C	1.0623242	0.7622897	1.5322630
O	-0.5519384	1.1120348	-0.4138369
C	-1.3836133	-0.5838384	3.0764119
C	-2.4990244	1.1761776	2.0087627
C	0.9981181	-1.5307389	-0.7303945
C	-1.0099478	-2.3600213	0.1618188
C	1.1535355	2.1321050	1.7767363
C	2.1308681	0.0207929	2.0426710
H	-0.6055705	2.0363396	-0.0932145
C	-2.2618157	-0.5315112	4.1506893
F	-0.3982756	-1.5121622	3.1431776
C	-3.4060314	1.2704785	3.0627310
F	-2.6825391	2.0800328	1.0028981
C	1.1962772	-2.6990221	-1.4548150
F	1.9259427	-0.5574227	-0.9026898
C	-0.8551641	-3.5469670	-0.5505480
F	-2.1582426	-2.2560370	0.8756909
C	2.2010691	2.7540158	2.4422732
F	0.1422812	2.9593195	1.3465536
C	3.2034929	0.5937720	2.7234669
F	2.1783766	-1.3227748	1.8995356
C	-3.2897128	0.4075378	4.1443879
F	-2.1303292	-1.3729489	5.1933624
F	-4.3860885	2.1939899	3.0426339
C	0.2590056	-3.7220960	-1.3618132
F	2.2684892	-2.8432835	-2.2562242
F	-1.7901062	-4.5141943	-0.4845648
C	3.2435491	1.9690370	2.9244115
F	2.2163579	4.0863775	2.6270211
F	4.2068653	-0.1742954	3.1870092
F	-4.1513390	0.4807589	5.1714041
F	0.4144523	-4.8507496	-2.0671026
F	4.2734518	2.5326753	3.5740526
C	-1.9159801	2.2764480	-2.0484907
H	-2.2281485	2.9867310	-1.2765210
H	-1.0269419	2.6554091	-2.5611793
H	-2.7256117	2.1917806	-2.7777403
C	-1.6489774	0.8983738	-1.4646573
C	-1.1509819	-0.0756365	-2.4703763
H	-2.5117869	0.5113972	-0.9197982
H	-0.2160484	0.1836033	-2.9625572
C	-1.8574408	-1.1648544	-2.8128815
H	-2.7886981	-1.3590005	-2.2796808
C	-1.5025222	-2.1624805	-3.8215113
C	-2.3401674	-3.2795752	-3.9866734
C	-0.3371371	-2.0774753	-4.6060643
C	-2.0226991	-4.2852121	-4.8974045
H	-3.2413702	-3.3576795	-3.3833319
C	-0.0196438	-3.0821395	-5.5130652
H	0.3274949	-1.2247440	-4.5022797
C	-0.8596785	-4.1910617	-5.6627348
H	-2.6797316	-5.1433268	-5.0060434
H	0.8869495	-3.0042685	-6.1063238
H	-0.6064526	-4.9743460	-6.3712447

273aH^+ : allyl cation after 4-protonation of **273a**

21

Energy = -387.7179768055

C -4.4343469 0.3217941 0.0129677
C -3.1651782 -0.4180413 0.0798339
H -5.0429685 -0.0754083 -0.8127290
H -4.2973900 1.3973513 -0.1058789
H -3.2266043 -1.5003586 0.1932232
C -1.9162712 0.1480963 0.0112690
C -0.7844968 -0.6735384 0.0889095
H -1.8189900 1.2238878 -0.1018817
H -0.9652364 -1.7420795 0.2011061
C 0.5708759 -0.2704190 0.0366461
C 1.5701885 -1.2772621 0.1331572
C 0.9644024 1.0887072 -0.1073198
C 2.9109430 -0.9384678 0.0868449
H 1.2632743 -2.3130782 0.2432585
C 2.3057466 1.4158458 -0.1522950
H 0.2145070 1.8684872 -0.1816052
C 3.2775949 0.4061413 -0.0556133
H 3.6739453 -1.7057105 0.1603191
H 2.6113942 2.4506481 -0.262653
H 4.3292415 0.6733784 -0.0918886
H -5.0212198 0.1147857 0.9202928

273a : $PhCH=CHCH=CH_2$
20
Energy = -387.2947304513
C -7.8837161 -0.4239420 0.0619242
C -6.5418411 -0.5388658 0.0610881
H -8.3708224 0.5462907 0.0614759
H -8.5262022 -1.3019043 0.0630590
H -5.9287485 0.3632065 0.0597450
C -5.8340171 -1.7989711 0.0616168
C -4.4829807 -1.8912061 0.0606557
H -6.4456457 -2.7009946 0.0630071
H -3.9100348 -0.9629009 0.0600698
C -3.6833892 -3.1120144 0.0607895
C -2.2788810 -3.0025799 0.0612043
C -4.2453079 -4.4054777 0.0606274
C -1.4660657 -4.1345898 0.0614533
H -1.8286291 -2.0125744 0.0615666
C -3.4336798 -5.5347570 0.0608842
H -5.3246389 -4.5276365 0.0603911
C -2.0396368 -5.4074457 0.0612901
H -0.3852543 -4.0232008 0.0618495
H -3.8876099 -6.5219937 0.0607705
H -1.4101229 -6.2926244 0.0612616

273uH^+ : allyl cation after 4-protonation of **273a**
27
Energy = -391.3313268072
C -0.7435798 -1.1215169 -1.0322830
C 0.6954299 -1.3171830 -1.2112287
H -1.1208329 -0.4936179 -1.8548298
H -1.3064040 -2.0531345 -0.9743617
H 1.3156212 -0.4228248 -1.2742462
C 1.3281475 -2.5410472 -1.3112381
C 2.7034435 -2.5809819 -1.4951390
H 0.7558317 -3.4636795 -1.2559003
H 3.2324186 -1.6274211 -1.5457648
C 3.5099109 -3.7858935 -1.5931192
C 4.4265473 -3.7545687 -2.8531860
C 4.4158869 -3.8420757 -0.3025507
H 2.8758196 -4.6785130 -1.6099142
C 5.3320675 -4.9889595 -2.8843259
H 5.0313325 -2.8395058 -2.8270467
H 3.7977254 -3.7133325 -3.7475164
C 5.3180830 -5.0794904 -0.3627899
H 5.0204088 -2.9287514 -0.2576866
H 3.7752799 -3.8691918 0.5831024
C 6.1929326 -5.0916559 -1.6203027
H 5.9674549 -4.9334648 -3.7756149
H 4.7132302 -5.8902035 -2.9856477
H 5.9421523 -5.0853743 0.5388056
H 4.6956016 -5.9828244 -0.3321147
H 6.7960448 -6.0054287 -1.6478431
H 6.8909392 -4.2442520 -1.5854582
H -0.9099713 -0.5122210 -0.1301954

273q : $CyCH=CHCH=CH_2$
26
Energy = -390.9149327081
C -0.7571927 -1.2300277 -1.313178
C 0.5863874 -1.2698611 -1.3489314
H -1.2974045 -0.2894633 -1.2655096
H -1.3506733 -2.1417449 -1.3311473
H 1.1476615 -0.3347240 -1.3299170
C 1.3724588 -2.4884895 -1.4130653
C 2.7176650 -2.5145250 -1.4491555
H 0.8211457 -3.4303939 -1.4333876
H 3.2612167 -1.5665592 -1.4310336
C 3.5580897 -3.7513940 -1.5142392
C 4.4072805 -3.7762942 -2.805744
C 4.4809875 -3.8601688 -0.2790283
H 2.8938755 -4.6276346 -1.5238574
C 5.3017794 -5.0212056 -2.8720629
H 5.0337455 -2.8730171 -2.8323930
H 3.7449097 -3.7331625 -3.6782347
C 5.3776890 -5.1034008 -0.3477765
H 5.1083562 -2.9585675 -0.2280316
H 3.8705379 -3.8777914 0.6314397
C 6.2073433 -5.1228622 -1.6380221
H 5.9050409 -4.9974195 -3.7876539
H 4.6680008 -5.9174676 -2.9300434
H 6.0351577 -5.1364402 0.5293553
H 4.7483191 -6.0038284 -0.3093809
H 6.8140760 -6.0351217 -1.6858946
H 6.9050399 -4.2733278 -1.6313073

273uH^+**315a** : N-C adduct of allyl cation **273u**H^+

39
Energy = -752.9887510798
N 0.0893856 -0.0997787 0.1298821
H 0.4271285 -0.4279015 1.043399
C 0.4041060 1.3525131 0.0658410
C 0.1766033 2.0651460 -1.1058688
C 0.9227347 1.9489488 1.2087201
C 0.4843586 3.4247806 -1.1237389
H -0.2271089 1.5862993 -1.9905418
C 1.2242602 3.3110720 1.1781159
H 1.0902620 1.3674413 2.1114734
C -1.3778814 -0.3626616 0.1240970
C 1.0048499 4.0470158 0.0136439
H 0.3151407 3.9958541 -2.0306503
H 1.6298303 3.7889739 2.0636903
C -1.9903088 -0.5710741 1.3531721
C -2.0898778 -0.3726375 -1.0695304
H 1.2396266 5.1063283 -0.0096231
C -3.3660101 -0.7979948 1.3909783
H -1.4075883 -0.5553878 2.2697522
C -3.4652228 -0.5991403 -1.0184314
H -1.6018305 -0.2221909 -2.0255923
C -4.1025158 -0.8096942 0.2060409
H -3.8545122 -0.9657170 2.3451060
H -4.0349040 -0.6137680 -1.9417456
H -5.1727849 -0.9871968 0.2351241
C 1.3807099 -3.2664735 -0.0828049
C 0.5321230 -2.4133992 -0.6716906
C 0.8902853 -0.9776512 -0.9107913
C 2.3810546 -0.6983997 -0.7493094
C 2.9404438 -1.3767915 0.5048914
C 2.7396900 -2.8939444 0.4316390
H 0.5272288 -0.6275390 -1.8782741
H -0.4352463 -2.7557157 -1.0263851
H 1.0857585 -4.3094326 0.0157309
H 2.5719694 0.3784486 -0.7455055
H 3.9998102 -1.1327490 0.6201034
H 2.4400215 -0.9859012 1.4035335
H 3.4940155 -3.3455153 -0.2303393
H 2.8961682 -3.3540874 1.4143223
H 2.8697811 -1.1043008 -1.6421049

273uH^+ allyl cation *c*-$CH_2CH_2CH_2CHCHCH^+$
15
Energy = -233.9737835884
C -0.0735373 0.7759935 1.1901215
C 0.0248231 1.4819601 0.0000069
C -0.0738920 0.7759736 -1.1900894
C -0.0915173 -0.6911753 -1.2605965
C 0.4525003 -1.3657440 -0.0000061
C -0.0913648 -0.6911690 1.2606425
H -0.2145354 1.3320345 -2.1152520
H 0.0257388 2.5658584 -0.0000254
H -0.2149931 1.3320916 2.1151285
H 0.4227480 -1.0189760 -2.1724295
H 0.2081119 -2.4293442 0.0000132
H 1.5445175 -1.2780971 -0.0000294
H -1.1526952 -0.9531228 1.4516239
H 0.4228528 -1.0190061 2.1724872
H -1.1528437 -0.9531251 -1.4515955

273u : cyclo-1,3-hexadiene
14
Energy = -233.5621699697
C 0.0998143 -1.4211403 -0.0989276
C 1.2486710 -0.7206182 -0.1288628
C 1.2486982 0.7206699 0.1285079
C 0.0997902 1.4211304 0.0991199
C -1.2018200 0.7321016 -0.2339441
C -1.2018503 -0.7320754 0.2338300
H 2.1977638 1.2167211 0.3188296
H 2.1977599 -1.2167395 -0.3189304
H 0.1000910 -2.4985325 -0.2488219
H 0.0999575 2.4984348 0.2497209
H -2.0495667 1.2681112 0.2053917
H -1.3451702 0.7707633 -1.3275669
H -1.3454715 -0.7707800 1.3274137
H -2.0495033 -1.2680936 -0.2056752

315a.273aH^+ : loose π-complex of **315a** and **273a**H^+
45
Energy = -906.7171755430
N 1.5942672 -0.1943372 0.1921418
C 1.7697510 -1.5708333 -0.0145284
C 1.0775801 0.8070835 -0.5926042
H 1.9516278 0.1262458 1.0860469
C 2.0638558 -2.3405302 1.1256813
C 1.7234303 -2.1974847 -1.2694803
C 1.2667577 2.1377243 -0.1368043
C 0.3463893 0.6035375 -1.7863974
C 2.2627273 -3.7124050 1.0200767
H 2.1357363 -1.8501139 2.0920737
C 1.9180374 -3.5746945 -1.3593658
H 1.5820870 -1.6249963 -2.1761383
C 0.8363070 3.2172513 -0.8913701
H 1.8055396 2.3010135 0.7932236
C -0.0920853 1.6928223 -2.5199641
H 0.1023791 -0.3949072 -2.1212399
C 2.1750047 -4.3434385 -0.2224529
H 2.4859415 -4.2884662 1.9132095
H 1.8824477 -4.0456098 -2.3373967
C 0.1458488 3.0087797 -2.0884815
H 1.0241997 4.2253138 -0.5351511
H -0.6503791 1.5191697 -3.4348418
H 2.3236199 -5.4153662 -0.3067726
H -0.1723156 3.8503062 -2.6940403
C -2.3533889 3.1134625 -0.7359928
C -3.2003698 3.4735022 -1.8989968

H	-1.8980113	3.9292822	-0.1775349
C	-2.2132209	1.8364702	-0.2435265
H	-4.1087558	3.9741608	-1.5294436
H	-3.4991996	2.5980852	-2.4799270
H	-2.7008777	4.2001223	-2.5478920
C	-1.4765677	1.5842940	0.9146778
H	-2.6681336	1.0138269	-0.7885342
H	-1.0785364	2.4458387	1.4467752
C	-1.2626441	0.3090472	1.5232864
C	-0.5649515	0.2540556	2.7535450
C	-1.6951848	-0.9035263	0.9333838
C	-0.3292589	-0.9615391	3.3809555
H	-0.2250907	1.1810699	3.2075339
C	-1.4485047	-2.1131923	1.5581435
H	-2.2142241	-0.8886581	-0.0189564
C	-0.7669861	-2.1472777	2.7828175
H	0.1990381	-0.9916732	4.3285630
H	-1.7751721	-3.0388531	1.0956523
H	-0.5760487	-3.0999224	3.2668337

315a.273uH^+ : loose π-complex of **315a** and **273u**H^+

39

Energy = -752.9691214331

H	2.0836637	-0.9561679	-0.3983160
N	1.0699910	-0.9568762	-0.4551201
H	0.4830838	0.0596422	1.4523857
C	0.5450202	0.1646184	-1.0670600
C	0.4900299	-2.2257009	-0.2375088
C	-0.7900435	0.2634292	-1.5280871
C	1.4054354	1.2713388	-1.2366194
C	-0.8384243	-2.3978084	0.1763502
C	1.3203524	-3.3487048	-0.3764894
C	-1.2218350	1.4261146	-2.1712885
H	-1.4511355	-0.5921233	-1.4720925
C	0.9446396	2.4315730	-1.8309856
H	2.4371725	1.1958568	-0.9028129
C	-1.3302395	-3.6804267	0.4134688
H	-1.4818357	-1.5435937	0.3437711
C	0.8218875	-4.6236578	-0.1277309
H	2.3536793	-3.2135448	-0.6853530
C	-0.3785634	2.5220278	-2.3023217
H	-2.2392214	1.4686990	-2.5471284
H	1.6196182	3.2736820	-1.9508191
C	-0.5093625	-4.7982551	0.2595131
H	-2.3610122	-3.8002814	0.733079
H	1.4751603	-5.4832154	-0.2436088
H	-0.7249890	3.4311186	-2.7825107
H	-0.8993616	-5.7935592	0.4475811
C	-0.1616973	0.7338319	2.0535443
C	-1.2449238	1.2306014	1.1809460
H	-0.5977589	0.0689416	2.8103845
H	-2.0647459	0.5592274	0.9431281
C	-1.3235431	2.5521884	0.7435571
C	-0.2648626	3.4094434	0.9479328
H	-2.1828153	2.8767999	0.1685571
H	-0.3019138	4.4094188	0.5233967
C	0.9371264	3.0098450	1.7213884
H	1.3523118	3.8826370	2.2364910
H	1.7067576	2.7112425	0.9893061
C	0.6445487	1.8669497	2.7034522
H	1.5775669	1.4785943	3.1184989
H	0.0594326	2.2707127	3.5375438

315a.Bf_3 : B-N adduct of amine **315a** and Bf_3

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Energy = -2728.513210611

B	0.0958400	0.0327574	0.0489781
C	-1.1848352	-0.2060811	-0.9493813
C	0.7459629	1.5544213	-0.0610837
C	1.3995220	-0.9463785	-0.1752222
C	-1.4685542	-1.3822852	-1.6524352
C	-2.1473187	0.7973913	-1.1450385
C	1.5060543	2.1430906	0.9535036
C	0.7485865	2.3033576	-1.2471784
C	2.2330724	-1.4639705	0.8209407
C	1.8735141	-1.1797298	-1.4730929
C	-2.5969731	-1.5737861	-2.4462378
F	-0.6299332	-2.4523363	-1.6083713
C	-3.2872243	0.6529657	-1.9273529
F	-2.0006396	2.0156636	-0.5753356
C	2.1617058	3.3653434	0.8608821
F	1.6591075	1.5079162	2.1608168
C	1.3966669	3.5275646	-1.3951148
F	0.1065738	1.8678268	-2.3545381
C	3.3830727	-2.2094704	0.5712338
F	1.9724641	-1.2467028	2.1379093
C	3.0143411	-1.9156040	-1.7718028
F	1.2163613	-0.6620887	-2.5378159
C	-3.5220056	-0.5480115	-2.5848863
F	-2.7931724	-2.7438462	-3.0833040
F	-4.1650940	1.6665040	-2.0499358
C	2.1073634	4.0727436	-0.3331944
F	2.8525134	3.8557146	1.9067044
F	1.3393303	4.1889493	-2.5656913
C	3.7786922	-2.4455695	-0.7383259
F	4.1210637	-2.6868905	1.5917785
F	3.3899818	-2.1098632	-3.0502583
F	-4.6161955	-0.7108727	-3.3438160
F	2.7346662	5.2514386	-0.4601700
F	4.8871075	-3.1554432	-1.0016726
N	-0.5022305	-0.1439022	1.6363764
H	0.2512480	0.2697409	2.1956764
C	-1.7064905	0.6790952	1.9145191
C	-0.7088955	-1.4964593	2.2363919
C	-2.9666101	0.1557224	1.6363992
C	-1.5546683	1.9470498	2.4642399
C	-0.8075520	-2.6450764	1.4704235
C	-0.8153468	-1.5431029	3.6263972

C	-4.0929410	0.9389757	1.8784793
H	-3.0668301	-0.8500690	1.2437228
C	-2.6894536	2.7217825	2.7085582
H	-0.5706058	2.3305424	2.710433
C	-1.0175785	-3.8711444	2.1100029
H	-0.6993632	-2.6111471	0.3985019
C	-1.0184399	-2.7669326	4.2562784
H	-0.7442413	-0.6299772	4.2108684
C	-3.9568115	2.2241630	2.4075694
H	-5.0777245	0.5397301	1.6570756
H	-2.5769884	3.7120853	3.1383923
C	-1.1240452	-3.9360142	3.4969953
H	-1.0930695	-4.7742126	1.5121482
H	-1.0943981	-2.8060225	5.3384216
H	-4.8375103	2.8300701	2.5965240
H	-1.2856765	-4.8908514	3.9876478

315$H^+HOBf_3^-$: contact ion pair of **315a**H^+

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Energy = -2805.014475965

B	0.1413923	0.3472974	0.5838982
C	-1.3113004	-0.1141700	1.2263462
C	0.8116965	-0.7613528	-0.4246899
C	1.1116118	0.7373076	1.8709821
O	0.0107038	1.5822536	-0.2770400
C	-1.3629569	-1.1042326	2.2107941
C	-2.5519376	0.4381815	0.9169300
C	2.0275395	-0.4583919	-1.0462278
C	0.2811033	-2.0010130	-0.7813719
C	0.8205464	1.8835863	2.6092478
C	2.2081863	0.0194040	2.3462532
H	-0.2937628	2.3401050	0.2469259
H	-0.6125949	1.5675093	-1.6004691
C	-2.5263622	-1.5180847	2.8472174
F	-0.2226260	-1.7485151	2.5683732
C	-3.7487191	0.0590448	1.5227667
F	-2.6774751	1.4125120	-0.0360858
C	2.6781869	-1.2989343	-1.941795
F	2.6625616	0.7084116	-0.7619617
C	0.9066803	-2.8851674	-1.6589253
F	-0.9056024	-2.4298492	-0.2850679
C	1.5439420	2.3214993	3.7119137
F	-0.2561899	2.6555029	2.2554345
C	2.9683054	0.4123071	3.4460736
F	2.5928990	-1.1388473	1.7544455
N	-1.0607694	1.6196975	-2.6266167
C	-3.7378524	-0.9271253	2.5004169
F	-2.5002178	-2.4881675	3.7838754
F	-4.9151651	0.6394043	1.1688940
C	2.1123511	-2.5316362	-2.2484220
F	3.8483656	-0.9387449	-2.5099101
F	0.3405110	-4.0714282	-1.9598892
C	2.6377305	1.5737653	4.1345969
F	1.2020420	3.4475161	4.3710883
F	4.0223092	-0.3246858	3.8540391
H	-2.0074353	1.9877171	-2.4904398
C	-1.1817090	0.2541345	-3.1917117
C	-0.2863864	2.5713555	-3.4463931
F	-4.8803468	-1.3082447	3.0996312
F	2.7132353	-3.3597850	-3.1220205
F	3.3633043	1.9679081	5.1963500
C	-2.3121240	-0.4893199	-2.8696187
C	-0.1667475	-0.2585344	-3.9900485
C	-0.8682175	3.1020290	-4.5935057
C	1.0114360	2.8869974	-3.0596658
C	-2.4270014	-1.7875284	-3.3655811
H	-3.0912638	-0.0647540	-2.2435197
C	-0.2956934	-1.5574106	-4.4821118
H	0.7031179	0.3417466	-4.2321640
C	-0.1242516	3.9849517	-5.3744409
H	-1.8815513	2.8294073	-4.8738032
C	1.7477849	3.7687405	-3.8540336
H	1.4321731	2.4579145	-2.1562386
C	-1.4216240	-2.3214107	-4.1725229
H	-3.3043960	-2.3774113	-3.1213025
H	0.4896096	-1.9699278	-5.1076149
C	1.1828622	4.3153802	-5.0066803
H	-0.5658018	4.4119244	-6.2692450
H	2.7619281	4.0279788	-3.5668885
H	-1.5143634	-3.3315705	-4.5578373
H	1.7597986	5.0008836	-5.6196965

315aH^+ : ammonium $Ph_2NH_2^+$

25

Energy = -519.4015153536

N	0.0539200	0.0000027	-1.4525163
H	-0.7421779	-0.0905123	-2.0950566
C	-0.0886451	1.2443639	-0.6433376
C	-1.1994571	1.3756181	0.1805508
C	0.9055360	2.2073884	-0.7314685
C	-1.3157634	2.5354671	0.9445339
H	-1.9528792	0.5955779	0.2312835
C	0.7767096	3.3622540	0.0435453
H	1.7591089	2.0690244	-1.3888922
C	0.1528611	-1.2450591	-0.6377964
C	-0.3299816	3.5242343	0.8770969
H	-2.1760331	2.6634868	1.5931997
H	1.5425029	4.1290250	-0.0087657
C	-0.8359167	-2.2073609	-0.7789231
C	1.2183492	-1.3774177	0.2436791
H	-0.4264860	4.4232035	1.4775124
C	-0.7495237	-3.3621803	0.0020041
H	-1.6532163	-2.0685528	-1.4808985
C	1.2930558	-2.5373607	1.0126302
H	1.9685003	-0.5978695	0.3347065
C	0.3108757	-3.5248050	0.8935892
H	-1.5118269	-4.1285540	-0.0912746
H	2.1178848	-2.6663258	1.7056199
H	0.3739814	-4.4233209	1.4990936

H 0.8833742 0.0910895 -2.0513208

315a : amine Ph_2NH
24
Energy = -518.9759278348
N 0.0000340 0.0000127 -1.0237770
H 0.0001905 0.0000575 -2.0363386
C -0.0209054 1.2630260 -0.4307484
C -0.4783854 1.4920706 0.8794629
C 0.3849002 2.3662198 -1.2066866
C -0.5037328 2.7874983 1.3945917
H -0.8411223 0.6680879 1.4828992
C 0.3430965 3.6550316 -0.6840935
H 0.7340993 2.1991411 -2.2231015
C 0.0211741 -1.2630576 -0.4308486
C -0.0915982 3.8781787 0.6259839
H -0.8634217 2.9418878 2.4084762
H 0.6611839 4.4892954 -1.3035695
C -0.3847337 -2.3662180 -1.2067807
C 0.4786762 -1.4921438 0.8793296
H -0.1140564 4.8829834 1.0366429
C -0.3435526 -3.6549707 -0.6839909
H -0.7332347 -2.1991913 -2.2234436
C 0.5035746 -2.7875040 1.3946079
H 0.8418684 -0.6682586 1.4826080
C 0.0914895 -3.8781753 0.6259634
H -0.6627433 -4.4890949 -1.3030870
H 0.8626131 -2.9418227 2.4087314
H 0.1145864 -4.8830538 1.0364089

315g.Bf_3c : B-C adduct of Bf_3 on *para*-position
68
Energy = -2959.685177997
B -1.3180066 0.2428645 -0.2972539
C -2.1656909 1.5741343 0.1665385
C -2.4661614 -0.8206808 -0.8116141
C -0.2671187 -0.3436148 0.8002173
C -2.4828224 1.8744720 1.4990036
C -2.7722146 2.4381642 -0.7536987
C -2.8811025 -1.0964063 -2.1166417
C -3.2367799 -1.4689976 0.1631486
C 0.5193639 0.4806308 1.6140632
C 0.0344505 -1.7041089 0.9243285
C -3.2736254 2.9532633 1.8878224
F -2.0386412 1.1036023 2.5191327
-3.5619963 3.5314562 -0.4116189
F -2.6292207 2.2340911 -2.0924798
C -3.9388539 -1.9475123 -2.4372053
F -2.2623962 -0.5434794 -3.1964792
C -4.2960903 -2.3262471 -0.1060918
F -2.9526981 -1.2793078 1.4753905
C 1.4868901 0.0146115 2.4998312
F 0.3652433 1.8274667 1.5853377
C 0.9738208 -2.2181787 1.8138050
F -0.5828514 -2.6238468 0.1414345
C -3.8148186 3.7981521 0.9277715
F -3.5223310 3.1824532 3.1928872
F -4.0920033 4.3223947 -1.3658273
C -4.6556617 -2.5717942 -1.4266672
F -4.2718952 -2.1645425 -3.7258903
F -4.9740761 -2.9217378 0.8953811
C 1.7114423 -1.3514426 2.6124118
F 2.2120764 0.8756388 3.2421839
F 1.2046974 -3.5462856 1.8803184
F -4.5782077 4.8437897 1.2866192
F -5.6785358 -3.3936859 -1.7171070
F 2.6478844 -1.8257968 3.4520805
H 2.5437099 2.4323106 -0.5736459
C 1.9649972 1.6130275 -0.9813658
C 2.5965097 0.3513265 -1.2059903
C 0.6379559 1.7742607 -1.2527244
C 1.8369072 -0.6968106 -1.8127826
N 3.9039690 0.1689894 -0.8764955
C -0.1950580 0.6870754 -1.7060621
H 0.1743568 2.7368763 -1.0608052
C 0.5144698 -0.5120824 -2.0897160
H 2.3304122 -1.6224355 -2.0830650
C 4.7423705 1.2794959 -0.4917828
C 4.5362361 -1.1231300 -0.8605960
H -0.9874396 0.9807804 -2.3875466
H -0.0337600 -1.3057935 -2.5852345
C 5.0182230 2.2950603 -1.4084430
C 5.2918133 1.2986279 0.7907457
C 3.9482825 -2.1858146 -0.1716636
C 5.7710408 -1.2843763 -1.4937119
C 5.8458256 3.3508707 -1.0273753
H 4.5901880 2.2534578 -2.4053047
C 6.1197408 2.3565198 1.1621580
H 5.0693331 0.4948139 1.4857171
C 4.5871573 -3.4228179 -0.1343478
H 3.0008967 -2.0332432 0.3315677
C 6.4071984 -2.5237920 -1.4470105
H 6.2255347 -0.4475162 -2.0143089
C 6.3969008 3.3825716 0.2554352
H 6.0648891 4.1431942 -1.7365445
H 6.5442946 2.3811596 2.1609711
C 5.8176102 -3.5953761 -0.7720815
H 4.1279893 -4.2462707 0.4041159
H 7.3649168 -2.6513032 -1.9422131
H 7.0437461 4.2041609 0.5476936
H 6.3173173 -4.5585337 -0.7382233

315g.Bf_3 : loose π-complex of Ph_3N and Bf_3
68
Energy = -2959.697545601
B 0.0026773 -0.0036215 -1.5692086
C 1.5410338 -0.2976551 -1.5707261
C -1.0194600 -1.1903812 -1.5668547

C	-0.5127130	1.4749252	-1.5652114
C	2.4578515	0.5098692	-2.2640142
C	2.1095689	-1.3802635	-0.8805510
C	-2.2413389	-1.1427150	-0.8764426
C	-0.7754702	-2.3899542	-2.2562211
C	0.1478834	2.5098819	-0.8834259
C	-1.6823667	1.8633232	-2.2399713
C	3.8264423	0.2771263	-2.2713675
F	2.0214088	1.5545061	-2.9983899
C	3.4731160	-1.6390464	-0.8530514
F	1.3288363	-2.2235140	-0.1757406
C	-3.1450381	-2.1959915	-0.8465185
F	-2.5845073	-0.0433900	-0.1758486
C	-1.6585833	-3.4611963	-2.2598790
F	0.3473110	-2.5339888	-2.9909379
C	-0.3138231	3.8184742	-0.8458627
F	1.2805948	2.2587658	-0.1970810
C	-2.1702023	3.1629804	-2.2357203
F	-2.3773117	0.9629751	-2.9661522
C	4.3381367	-0.8012070	-1.5520535
F	4.6583730	1.0709898	-2.9646674
F	3.9641461	-2.6807396	-0.1663051
C	-2.8488973	-3.3655955	-1.5416304
F	-4.2936344	-2.1010709	-0.1612892
F	-1.3836817	-4.5807613	-2.9483442
C	-1.4845313	4.1460205	-1.5246288
F	0.3500562	4.7652346	-0.1672731
F	-3.2864287	3.4840774	-2.9093093
F	5.6541999	-1.0339634	-1.5378626
F	-3.7064374	-4.3906641	-1.5250683
F	-1.9459890	5.4000196	-1.4987246
H	-0.0933794	-2.3448614	1.7052979
C	-0.9868129	-2.1284267	2.2784613
C	-1.0741871	-0.9227394	2.9905501
C	-2.0365901	-3.0426308	2.3132324
C	-2.2342379	-0.6522928	3.7320847
N	-0.0006896	0.0056930	2.9613650
C	-3.1976619	-2.7659323	3.0381112
H	-1.9492598	-3.9724040	1.7573406
C	-3.2876951	-1.5639014	3.7437461
H	-2.3076593	0.2735112	4.2936627
C	1.3404413	-0.4592871	2.9871337
C	-0.2678622	1.3998177	2.9911438
H	-4.0194840	-3.4751457	3.0524816
H	-4.1795261	-1.3368577	4.3213851
C	1.6887218	-1.5997184	3.7265673
C	2.3386283	0.2206581	2.2733088
C	-1.3543153	1.9276819	2.2775761
C	0.5459385	2.2682972	3.7341512
C	3.0052538	-2.0553078	3.7346466
H	0.9253611	-2.1272072	4.2894964
C	3.6555864	-0.2307625	2.3039457
H	2.0771237	1.1033641	1.7023075
C	-1.6199016	3.2942723	2.3120851
H	-1.9886139	1.2625796	1.7040170
C	0.2843699	3.6366025	3.7458518
H	1.3831660	1.8678449	4.2967992
C	3.9990331	-1.3750078	3.0271187
H	3.2564654	-2.9416806	4.3106747
H	4.4152170	0.3107547	1.7465071
C	-0.8000366	4.1605682	3.0383529
H	-2.4675442	3.6843970	1.7549907
H	0.9262741	4.2947323	4.3249916
H	5.0244329	-1.7313941	3.0388035
H	-1.0025431	5.2270505	3.0528312

31gcBf_3^- : anion of deprotonated adduct **315g.**Bf_3c

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Energy = -2959.235489022

B	-1.3809968	0.3982049	-0.7620152
C	-1.9638485	1.4291974	-1.9216546
C	-2.6659439	-0.6226972	-0.5282117
C	-0.8868484	1.1776975	0.6145826
C	-3.0112343	2.3003387	-1.6068250
C	-1.6014537	1.4500912	-3.2697389
C	-3.0252958	-1.5068227	-1.5521885
C	-3.5393014	-0.6453496	0.5616681
C	-0.5804707	0.4341930	1.7594157
C	-0.5277595	2.5218332	0.7113111
C	-3.6351320	3.1470147	-2.5138926
F	-3.4752440	2.3543659	-0.3300823
C	-2.1978871	2.2828431	-4.2182589
F	-0.6313609	0.6379085	-3.7571684
C	-4.1105659	-2.3760849	-1.4978097
F	-2.3103571	-1.5337264	-2.7055722
C	-4.6401466	-1.4949071	0.6601990
F	-3.3746057	0.1945720	1.6158277
C	-0.0161470	0.9629057	2.9133129
F	-0.8233507	-0.9023151	1.7827611
C	0.0424578	3.0999974	1.8449902
F	-0.6928867	3.3718800	-0.3409957
C	-3.2207624	3.1414363	-3.8416189
F	-4.6341035	3.9737743	-2.1269732
F	-1.7933833	2.2555112	-5.5099390
C	-4.9281695	-2.3751597	-0.3741847
F	-4.3862835	-3.2107250	-2.5258853
F	-5.4386441	-1.4667572	1.7523376
C	0.2977573	2.3171363	2.9619246
F	0.2365921	0.1793467	3.9875019
F	0.3569341	4.4165500	1.8654211
F	-3.8082796	3.9510436	-4.7469822
F	-5.9888163	-3.2047469	-0.2951702
F	0.8473958	2.8559810	4.0707559
N	3.7802322	-2.2437493	-1.8561772
C	2.5121338	-1.6228975	-1.6283065
C	4.9286459	-1.7083711	-1.2336973
C	2.3717653	-0.2350059	-1.7492532
C	1.4000631	-2.3886566	-1.2722759
C	4.8290654	-1.1071527	0.0328945

C	6.1810879	-1.7410600	-1.8710620
C	1.1390172	0.3590289	-1.5057586
H	3.2345267	0.3687009	-2.0183254
C	0.1681088	-1.7714137	-1.0545686
H	1.5028818	-3.4659080	-1.1705043
C	5.9539899	-0.5566419	0.6417181
H	3.8633492	-1.0681723	0.5265817
C	7.3023525	-1.1991378	-1.2476700
H	6.2687024	-2.1889701	-2.8558100
C	-0.0068379	-0.3853882	-1.1681698
H	1.0622812	1.4416947	-1.5920899
H	-0.6732794	-2.3953178	-0.7631787
C	7.2007708	-0.6012458	0.0117890
H	5.8562445	-0.0977787	1.6221370
H	8.2606657	-1.2315112	-1.7595798
H	8.0766042	-0.1745282	0.4916462
C	3.8511768	-3.3854131	-2.6835440
C	4.7681831	-4.4171420	-2.4186908
C	2.9804515	-3.5173498	-3.7788755
C	4.8201826	-5.5405145	-3.2402522
H	5.4348042	-4.3347775	-1.5661357
C	3.0317491	-4.6508498	-4.5860562
H	2.2613823	-2.7304456	-3.9830655
C	3.9536664	-5.6695893	-4.3293075
H	5.5344828	-6.3284968	-3.0158128
H	2.3506804	-4.7329562	-5.4291213
H	3.9934754	-6.5500058	-4.9639820

315gHc^+ : para-protonated Ph_2NPhH^+

35

Energy = -750.5809335832

N	0.0636162	0.0000336	-0.0003960
C	-0.7038026	-1.2223264	0.0335315
C	1.4080713	-0.0003064	0.0000317
C	-1.6986198	-1.4239734	-0.9246728
C	-0.4746646	-2.1514357	1.0503675
C	2.1359760	1.2053979	0.3044800
C	2.1354420	-1.2063103	-0.3048873
C	-2.4596476	-2.5894536	-0.8733278
H	-1.8660606	-0.6816855	-1.6983717
C	-1.2435048	-3.3130264	1.0918407
H	0.2831062	-1.9576380	1.8029125
C	3.4869514	1.2007736	0.3258453
H	1.5825723	2.0998742	0.5633243
C	3.4863606	-1.2026183	-0.3262703
H	1.5811212	-2.1002914	-0.5634992
C	-2.2327944	-3.5339600	0.1312761
H	-3.2287699	-2.7597158	-1.6199216
H	-1.0760537	-4.0375567	1.8824009
C	4.2871210	-0.0009773	-0.0005536
H	4.0218969	2.1021261	0.6097509
H	4.0209294	-2.1040991	-0.6104293
H	-2.8317660	-4.4384634	0.1691920
C	-0.7034398	1.2224778	-0.0337970
C	-0.4729531	2.1528633	-1.0491485
C	-1.6990717	1.4234491	0.9237590
C	-1.2412905	3.3148033	-1.0899265
H	0.2855651	1.9598647	-1.8011482
C	-2.4596733	2.5892083	0.8730794
H	-1.8671715	0.6805664	1.6967364
C	-2.2315048	3.5348878	-0.1301375
H	-1.0727284	4.0402532	-1.8794055
H	-3.2295285	2.7587559	1.6190788
H	-2.8303760	4.4394695	-0.1677347
H	4.9802167	-0.2193231	0.8305633
H	4.9762596	0.2179517	-0.8351408

315gH^+ : N-protonated ammonium Ph_3NH^+

35

Energy = -750.5822054832

N	-1.2093291	-0.2255446	1.3466192
C	-1.2857724	1.0390964	2.1535716
C	-1.7478191	-1.4247617	2.0733126
C	-1.4160945	2.2283217	1.4467279
C	-1.1959068	0.9920469	3.5370277
C	-0.8811963	-2.3196421	2.6834788
C	-3.1298061	-1.5610801	2.1224185
C	-1.4612681	3.4235032	2.1626911
H	-1.4782640	2.2265222	0.3623261
C	-1.2352551	2.1985645	4.2393201
H	-1.1024261	0.0478450	4.0613173
C	-1.4327723	-3.3984450	3.3779472
H	0.1933986	-2.1909253	2.6213348
C	-3.6646017	-2.6471191	2.8135109
H	-3.7774291	-0.8366487	1.6370333
C	-1.3679218	3.4079438	3.5563340
H	-1.5699539	4.3620853	1.6294359
H	-1.1654433	2.1848537	5.3219339
C	-2.8168874	-3.5619323	3.4425497
H	-0.7731824	-4.1102273	3.8631682
H	-4.7410976	-2.7749725	2.8574525
H	-1.4030873	4.3404977	4.1103642
C	0.1448018	-0.4596323	0.7401278
C	0.1848139	-1.1785625	-0.4482742
C	1.2859465	0.0058479	1.3766944
C	1.4272505	-1.4384110	-1.0243514
H	-0.7299071	-1.5327038	-0.9146899
C	2.5234658	-0.2689346	0.7907557
H	1.2223763	0.5708264	2.2996702
C	2.5941925	-0.9866254	-0.4036344
H	1.4791046	-1.9920663	-1.9559576
H	3.4288918	0.0851906	1.2723126
H	3.5598085	-1.1915946	-0.8546575
H	-3.2369391	-4.4056213	3.9806763
H	-1.8433372	-0.0808841	0.5513093

315g : amine Ph_3N

34

Energy = -750.1646787371

N	0.0042349	0.0023798	2.8574619
C	-1.0459399	-0.9509810	2.8602243
C	1.3542360	-0.4314608	2.8568478
C	-0.2964069	1.3879813	2.8577365
C	-0.9387045	-2.1261102	2.1010862
C	-2.2034224	-0.7303809	3.6218784
C	1.7409480	-1.5494340	3.6115553
C	2.3191734	0.2516208	2.1010560
C	-1.3738870	1.8802824	2.1056004
C	0.4794666	2.2831638	3.6098613
H	-0.0470308	-2.2983073	1.5064469
C	-1.9681050	-3.0645960	2.1137881
C	-3.2346952	-1.6669850	3.6157475
H	-2.2894701	0.1755884	4.2136300
C	3.0665967	-1.9773291	3.6009104
H	0.9991884	-2.0785310	4.2016003
C	3.6456008	-0.1740164	2.1092415
H	2.0243669	1.1143667	1.5119695
C	-1.6707519	3.2413044	2.1147630
H	-1.9742890	1.1924957	1.5184050
C	0.1849739	3.6446760	3.5999896
H	1.3109265	1.9068703	4.1975466
C	-3.1240804	-2.8415313	2.8667136
H	-1.8708534	-3.9689453	1.5193290
H	-4.1239665	-1.4827223	4.2123611
C	4.0290643	-1.2922581	2.8544223
H	3.3504122	-2.8436716	4.1921830
H	4.3804348	0.3645694	1.5170666
C	-0.8929008	4.1338163	2.8571609
H	-2.5072046	3.6069957	1.5254141
H	0.7944461	4.3247086	4.1889076
H	-3.9270574	-3.5725784	2.8700279
H	5.0627661	-1.6249187	2.8534344
H	-1.1231992	5.1950285	2.8568310

315h$H^+HOBf_3^-$: contact ion pair of **315h**H^+

64

Energy = -2844.344295869

B	0.0067481	0.3677563	0.5900421
C	-1.3409607	-0.2715635	1.3087400
C	0.7476589	-0.6420888	-0.4738748
C	0.9840088	0.8246378	1.8543702
O	-0.3014855	1.5851656	-0.2418918
C	-1.2184789	-1.3566202	2.1804420
C	-2.6402481	0.2174066	1.1978828
C	1.9320002	-0.2201172	-1.0853406
C	0.2923257	-1.8858987	-0.9104962
C	0.6052267	1.9171385	2.6332654
C	2.1557743	0.2020083	2.2831891
H	-0.6800716	2.2933297	0.3015692
H	-0.7607283	1.6576330	-1.7099794
C	-2.2756033	-1.9281455	2.8768016
F	-0.0010208	-1.9302627	2.3607622
C	-3.7365977	-0.3191620	1.8718837
F	-2.9291757	1.2879012	0.3982282
C	2.6131496	-0.9438066	-2.0566286
F	2.5064428	0.9533557	-0.7115356
C	0.9561618	-2.6615484	-1.8602968
F	-0.8522900	-2.4274105	-0.4258982
C	1.3134754	2.3924502	3.7303671
F	-0.5527272	2.5863790	2.3338753
C	2.9045967	0.6363084	3.3752213
F	2.6385969	-0.8940740	1.6459335
N	-1.1286925	1.7454901	-2.7363824
C	-3.5549086	-1.4024723	2.7211055
F	-2.0825365	-2.9861682	3.6918158
F	-4.9698490	0.2068194	1.7107382
C	2.1198424	-2.1840307	-2.4472277
F	3.7475366	-0.4674782	-2.6117884
F	0.4681106	-3.8629150	-2.2318667
C	2.4842630	1.7420449	4.1048984
F	0.8830821	3.4616739	4.4321263
F	4.0360004	-0.0062175	3.7349991
C	-1.3676924	0.3494036	-3.2114941
C	-0.1122238	2.4848805	-3.5227372
F	-4.5977089	-1.9344465	3.3848528
F	2.7546287	-2.9049154	-3.3899142
F	3.1974765	2.1751258	5.1605420
C	-2.4409164	-0.3634320	-2.6806466
C	-0.4924640	-0.2402786	-4.1181942
C	-0.3808444	2.8242712	-4.846859
C	1.0818235	2.8292428	-2.9029711
C	-2.6549290	-1.6774358	-3.0932198
H	-3.1021658	0.0797544	-1.9462744
C	-0.7193586	-1.5556350	-4.5248766
H	0.3554839	0.3097923	-4.5067702
C	0.5849043	3.5229414	-5.5684249
H	-1.3158008	2.5370570	-5.3170349
C	2.0425440	3.5282641	-3.6377270
H	1.2557225	2.5563851	-1.8682344
C	-1.8018495	-2.2742324	-4.0209043
H	-3.4893839	-2.2338422	-2.6790047
H	-0.0387325	-2.0158128	-5.2342449
C	1.7967327	3.8728546	-4.9661474
H	0.3902451	3.7896743	-6.6022953
H	2.9812067	3.8008830	-3.1657810
H	-1.9722690	-3.2976868	-4.3383542
H	2.5467718	4.4139654	-5.5346054
C	-2.3987421	2.5630919	-2.6435453
H	-3.0514755	2.1192565	-1.8965982
H	-2.1118071	3.5680910	-2.3370591
H	-2.8832564	2.5803740	-3.6180733

315hH^+ : ammonium Ph_2MeNH^+

28

Energy = -558.7322384590

N	-2.7761487	1.1915912	-0.6458884
C	-3.8255391	0.2195124	-0.2054062
C	-1.4477979	0.8937038	-0.0220519

C	-4.5295058	-0.4685414	-1.1832752
C	-4.0638426	0.0518983	1.1528143
C	-0.9568009	1.6712736	1.0168853
C	-0.7651705	-0.2148816	-0.5118317
C	-5.5199127	-1.3665776	-0.7799016
H	-4.3161539	-0.3119673	-2.2369602
C	-5.0576078	-0.8454346	1.5400893
H	-3.4861287	0.5935801	1.8946469
C	0.2713635	1.3186756	1.5828427
H	-1.4953268	2.5342776	1.3892003
C	0.4599436	-0.5511019	0.0591320
H	-1.1813020	-0.8094046	-1.3201238
C	-5.7836246	-1.5516271	0.5772340
H	-6.0782033	-1.9181386	-1.5289778
H	-5.2576262	-0.9957710	2.5957964
C	0.9761841	0.2135661	1.1083828
H	0.6715463	1.9180354	2.3938509
H	1.0078327	-1.4086027	-0.3171654
H	-6.5542202	-2.2499182	0.8875820
H	1.9295888	-0.0522833	1.5534433
C	-3.2514789	2.6191003	-0.4821581
H	-3.4934044	2.7848209	0.5651842
H	-2.4581036	3.2842108	-0.8193817
H	-4.1443362	2.7274962	-1.0956497
H	-2.6552441	1.0435833	-1.6539537

315h : amine Ph_2NMe

27

Energy = -558.3022197299

N	-2.8112990	1.1478501	-0.1493348
C	-3.8494865	0.1888795	-0.0324290
C	-1.5159817	0.8964430	0.3089526
C	-4.7723144	0.0216932	-1.0765931
C	-3.9917681	-0.5870417	1.1291492
C	-0.6403648	1.9577711	0.6170584
C	-1.0209433	-0.4223678	0.4105685
C	-5.8132943	-0.8983255	-0.9580456
H	-4.6646739	0.6038252	-1.9872524
C	-5.0243529	-1.5164022	1.2338668
H	-3.2919980	-0.4538496	1.9482404
C	0.6709179	1.7024247	1.0210152
H	-0.9804732	2.9847614	0.5482470
C	0.2855947	-0.6605068	0.8200173
H	-1.6646237	-1.2570744	0.1544262
C	-5.9442155	-1.6768903	0.1939634
H	-6.5149757	-1.0168953	-1.7792029
H	-5.1200070	-2.1057713	2.1418257
C	1.1477272	0.3968117	1.1330553
H	1.3207457	2.5420704	1.2540713
H	0.6379245	-1.6868777	0.8836721
H	-6.7523337	-2.3970189	0.2815447
H	2.1680440	0.2039055	1.4503379
C	-3.1739228	2.5161412	-0.5223192
H	-3.1987176	3.1777341	0.3551946
H	-2.4591800	2.9183337	-1.2474478
H	-4.1666983	2.5052980	-0.9695870

315l$H^+HOBf_3^-$: contact ion pair of **315l**H^+

61

Energy = -2729.970804236

B	-0.0368299	0.2817866	0.5954215
C	-1.3996059	0.2700137	1.5372596
C	0.1831642	-1.0790705	-0.3011426
C	1.1957890	0.5820404	1.6677705
O	-0.0637459	1.3607359	-0.4501196
C	-1.5453177	-0.6872116	2.5439851
C	-2.4288713	1.2079090	1.4966415
C	1.3775717	-1.2377435	-1.0105319
C	-0.7506227	-2.0890543	-0.5280134
C	1.3195496	1.8621054	2.2076901
C	2.1226755	-0.3344987	2.1639252
H	-0.2111498	2.2323360	-0.0524457
H	-0.8170390	1.0984710	-1.7901384
C	-2.6133305	-0.7379865	3.4304412
F	-0.6052722	-1.6579729	2.6772525
C	-3.5226570	1.2032012	2.3614879
F	-2.4244524	2.2239183	0.5812148
C	1.6567353	-2.3174896	-1.8397442
F	2.3596080	-0.3084219	-0.8990665
C	-0.5180209	-3.1905049	-1.3498629
F	-1.9889481	-2.0418394	0.0350322
C	2.2793154	2.2388094	3.1397232
F	0.4411583	2.8424446	1.8289820
C	3.1027978	-0.0109187	3.1004909
F	2.1183011	-1.6264208	1.7491204
N	-1.3665774	0.9927279	-2.7227535
C	-3.6179965	0.2212154	3.3387865
F	-2.6930613	-1.7022176	4.3708922
F	-4.4849561	2.1450463	2.2620703
C	0.6977513	-3.3096004	-2.0090628
F	2.8369376	-2.4104609	-2.4846364
F	-1.4767554	-4.1206975	-1.5444124
C	3.1862076	1.2864172	3.5921104
F	2.3375341	3.5016002	3.6123383
F	3.9751739	-0.9441949	3.5367645
C	-0.6629324	0.0368136	-3.6011382
F	-4.6636935	0.1977087	4.1852394
F	0.9341746	-4.3559933	-2.8193213
F	4.1285352	1.6159907	4.4943728
C	-1.2359228	-1.1577994	-4.0189426
C	0.6156973	0.4354948	-4.0075291
C	-0.5028596	-1.9915313	-4.8670597
H	-2.2287307	-1.4528691	-3.7015539
C	1.3266093	-0.4102667	-4.8601345
C	0.7740107	-1.6197219	-5.2846712
H	-0.9363870	-2.9307749	-5.1948871
H	2.3201083	-0.1171363	-5.1874830
H	1.3411351	-2.2721341	-5.9413973
C	-2.7576754	0.5989468	-2.3470121

H	-2.7280908	-0.3505843	-1.8138427
H	-3.1515320	1.3759149	-1.6937025
H	-3.3682117	0.5171121	-3.2464740
C	-1.3662249	2.3752090	-3.3650946
H	-1.8654401	3.0336525	-2.6523930
H	-1.9892392	2.2847191	-4.2561814
C	0.0591912	2.8575539	-3.6978902
H	0.0704444	3.1944627	-4.7373930
H	0.3127523	3.7159770	-3.0712694
C	1.1271862	1.7556780	-3.5074745
H	1.3583224	1.6667455	-2.4391309
H	2.0496446	2.0325081	-4.0227431

315lH^+ : tertiary ammonium

25

Energy = -444.3617204927

H	1.1486216	-1.6669754	-1.1184335
N	1.1630431	-0.9968271	-0.3436577
C	-0.2243913	-0.4667484	-0.2050840
C	-1.2605579	-1.3904043	-0.3272674
C	-0.4391279	0.8860257	0.0551394
C	-2.5738691	-0.9596767	-0.1749868
H	-1.0433515	-2.4328378	-0.5447663
C	-1.7746922	1.2901753	0.2083236
C	-2.8273300	0.3873872	0.0997489
H	-3.3893296	-1.6690633	-0.2683970
H	-1.9782190	2.3374679	0.4147853
H	-3.8486916	0.7327665	0.2260494
C	1.5841579	-1.7662562	0.8893174
H	1.5832369	-1.0823258	1.7351471
H	0.8633212	-2.5660851	1.0497151
H	2.5797648	-2.1711482	0.7097166
C	2.1733878	0.0784904	-0.7166227
H	1.9355210	0.3707777	-1.7415849
H	3.1515111	-0.4026940	-0.6937253
C	2.0604400	1.2521107	0.2398088
H	2.8450525	1.9700725	-0.0124441
H	2.2505491	0.9253241	1.2672741
C	0.6801031	1.9000401	0.1199084
H	0.6404076	2.5075904	-0.7938181
H	0.5035874	2.5839258	0.9554196

315l : tertiary amine with only one aryl

24

Energy = -443.9199259592

C	2.4839571	0.9806320	-0.1334334
C	1.1496540	1.3827963	-0.1491460
C	0.1008724	0.4383880	-0.0681385
C	0.4405193	-0.9362916	0.0612895
C	1.7850292	-1.3061166	0.0680227
C	2.8182561	-0.3696356	-0.0280235
H	3.2633393	1.7355562	-0.2022368
H	0.9207709	2.4396005	-0.2286217
H	2.0247920	-2.3644908	0.1575983
H	3.8562999	-0.6886563	-0.0158011
N	-1.2267583	0.8403538	-0.1386884
C	-1.5533030	2.2538089	-0.0106802
H	-1.2407379	2.6719579	0.9595608
H	-1.0785836	2.8370871	-0.8067802
H	-2.6352414	2.3643679	-0.1061378
C	-0.6402815	-1.9879206	0.1963095
H	-0.3289910	-2.9046965	-0.3170161
H	-0.7642341	-2.2509070	1.2566369
C	-1.9776800	-1.4854496	-0.3502001
H	-2.7865295	-2.1768539	-0.0923378
H	-1.9350464	-1.4092144	-1.4433402
C	-2.2795861	-0.1077781	0.2302245
H	-3.2224782	0.2801647	-0.1666873
H	-2.3834029	-0.1772191	1.3272798

316uap : 4,3-hydroarylation of **273u** and **315a** on para

38

Energy = -752.5679684578

N	-2.0087555	-0.9780400	-0.6672487
H	-2.1263498	-1.6956298	-1.3717866
C	-0.7448247	-0.9338076	-0.0704455
C	-0.5122120	-0.4232084	1.2169128
C	0.3420403	-1.4815696	-0.7782209
C	0.7734025	-0.4472497	1.7572055
H	-1.3336609	-0.0390116	1.8106868
C	1.6132772	-1.5089461	-0.2175361
H	0.1762954	-1.8881570	-1.7734737
C	-3.1571451	-0.2467580	-0.3676712
C	1.8598743	-0.9822150	1.0583963
H	0.9281229	-0.0491920	2.7581263
H	2.4335712	-1.9441299	-0.7841285
C	-3.1243398	1.0159046	0.2521761
C	-4.4036577	-0.7729642	-0.7599829
C	-4.3096247	1.7117266	0.4856045
H	-2.1760788	1.4649232	0.5239283
C	-5.5778697	-0.0623756	-0.5313599
H	-4.4390423	-1.7462405	-1.2442845
C	-5.5446248	1.1827026	0.1040792
H	-4.2601720	2.6873650	0.9619756
H	-6.5263314	-0.4900013	-0.8452563
H	-6.4623982	1.7312518	0.2925989
C	3.2594419	-0.9624133	1.6438094
C	3.9708372	-2.2846761	1.4532400
C	5.2550581	-2.3999407	1.0963280
C	6.1720436	-1.2236313	0.8844524
C	5.5677556	0.0714431	1.4437775
C	4.0940551	0.1912017	1.0435208
H	5.6814290	-3.3932795	0.9579903
H	3.3731716	-3.1819850	1.6113778
H	3.1529112	-0.7798468	2.7244482
H	6.3791244	-1.1102782	-0.1909873
H	5.6444730	0.0636336	2.5393179
H	6.1334089	0.9393253	1.0860995
H	3.6733799	1.1501613	1.3662161

H 4.0078155 0.1509113 -0.0506826
H 7.1431795 -1.4279055 1.3540480

3l6ua : 4,3-hydroarylation of **273** and **315a** on ortho
38
Energy = -752.5660269961
H -0.4337029 -1.0544854 -0.7028747
N -0.9629601 -0.2750737 -0.3358673
H 2.8816889 -0.2344233 -1.5431672
C -0.2733120 0.9431856 -0.2301077
C -2.3179937 -0.5253867 -0.1254501
C -0.9185639 2.1668746 -0.4725238
C 1.1053051 0.9284706 0.0860638
C -3.1234547 0.2887170 0.6912174
C -2.8880256 -1.6735371 -0.7072340
C -0.2152843 3.3660755 -0.3993023
H -1.9691742 2.1711864 -0.7433145
C 1.7916660 2.1456588 0.1279247
C -4.4625363 -0.0369394 0.8983395
H -2.6974018 1.1594631 1.1774019
C -4.2238718 -1.9934671 -0.4828363
H -2.2723006 -2.3115644 -1.3375980
C 1.1490296 3.3624201 -0.1020324
H -0.7340034 4.3013409 -0.5915887
H 2.8533751 2.1323440 0.3629442
C -5.0275845 -1.1738592 0.3149351
H -5.0665536 0.6040911 1.5351688
H -4.6401213 -2.8857713 -0.9427553
H 1.7056850 4.2936298 -0.0500464
H -6.0720764 -1.4188750 0.4817854
C 2.3315258 -1.0045060 -0.9873327
C 1.8303590 -0.3817205 0.3377951
H 1.4823290 -1.2988639 -1.6171353
H 1.1002558 -1.0726834 0.7898803
C 2.9737555 -0.2301367 1.3149710
C 4.1607089 -0.8308749 1.1774244
H 2.7898785 0.4090227 2.1777013
H 4.9326967 -0.6572646 1.9265102
C 4.5013685 -1.7617769 0.0434552
H 5.0361129 -2.6359658 0.4368686
H 5.2062798 -1.2638158 -0.6401520
C 3.2474149 -2.2032336 -0.7224766
H 3.5278993 -2.6840311 -1.6662544
H 2.7026382 -2.9487231 -0.1279412

316aH^+1 : adduct of **273a**H^+ C1 on **315a** para
45
Energy = -906.7066857594
N -3.1813948 1.2489558 0.2080011
C -4.2381211 0.2975190 0.1077846
C -1.8881775 1.0374492 0.4474597
H -3.4559085 2.2188726 0.0661897
C -5.1897643 0.4810703 -0.9000747
C -4.3542641 -0.7512782 1.0255244
C -1.0395680 2.1867112 0.6225078
C -1.3168243 -0.2801784 0.5060543
C -6.2489076 -0.4166076 -1.0084836
H -5.0906552 1.3100416 -1.5944380
C -5.4158688 -1.6449524 0.9022692
H -3.6476508 -0.8462333 1.8429778
C 0.2761203 2.0329201 0.8797491
H -1.4895924 3.1737440 0.5615302
C 0.0048343 -0.4290940 0.7463726
H -1.9466263 -1.1424083 0.3253150
C -6.3594753 -1.4844677 -0.1146811
H -6.9857578 -0.2820898 -1.7939423
H -5.5128024 -2.4579753 1.6147705
C 0.9314451 0.7071098 0.9526073
H 0.9047886 2.9063284 1.0226002
H 0.4337212 -1.4266311 0.7622087
H -7.1864877 -2.1820689 -0.2020664
H 1.4077883 0.6022863 1.9422517
C 3.4288076 2.7073968 -0.6673947
C 4.4342037 3.7939135 -0.4366902
H 2.8983759 2.7301915 -1.6212541
C 3.1486564 1.7280518 0.1971998
H 5.2127141 3.7722372 -1.2100007
H 4.9127289 3.6957907 0.5422457
H 3.9600111 4.7819058 -0.4974898
C 2.1604240 0.6274040 -0.0763753
H 3.6673787 1.6842610 1.1558927
H 1.7386902 0.7631938 -1.0771845
C 2.8134942 -0.7408296 -0.0037663
C 2.8355018 -1.5628635 -1.1354396
C 3.4059635 -1.2008118 1.1794773
C 3.4399804 -2.8204287 -1.0898378
H 2.3766832 -1.2149425 -2.0578546
C 4.0082769 -2.4575406 1.2287113
H 3.4001369 -0.5786182 2.0715642
C 4.0269875 -3.2715340 0.0933311
H 3.4499166 -3.4466036 -1.9774939
H 4.4636395 -2.8010639 2.1531601
H 4.4955633 -4.2506185 0.1320831

316aH.OHBf_3 : H-bonded **316a**H^+ and $HOBf_3^-$
81
Energy = -3192.299955693
N -3.4656108 2.7341401 1.1578297
H -3.5236174 3.1696678 2.0745491
C -3.1870411 1.4288761 1.1210631
C -3.5606281 3.6042732 0.0215714
C -2.9702219 0.7450337 -0.1205540
C -3.0765930 0.7060209 2.3550997
C -4.5627815 3.4094798 -0.9305150
C -2.6357225 4.6416171 -0.1056824
C -2.5118976 -0.5270530 -0.1059597
H -3.1446379 1.2690869 -1.0520936

C	-2.5941599	-0.5590770	2.3580701
H	-3.3434575	1.2109423	3.2789795
C	-4.6257393	4.2592131	-2.0341255
H	-5.2866225	2.6109897	-0.8008767
C	-2.7137826	5.4907638	-1.2082668
H	-1.8586149	4.7685778	0.6419883
C	-2.1430035	-1.2344428	1.1302711
H	-2.3302936	-1.0435412	-1.0441768
H	-2.4730966	-1.0791830	3.3032233
C	-3.7049195	5.2993995	-2.1725370
H	-5.3992856	4.1099112	-2.7808441
H	-1.9907577	6.2925161	-1.3184481
C	-2.3674805	-2.7810760	1.0593430
H	-3.7617273	5.9626081	-3.0300547
C	-1.7056748	-3.4996051	2.2460988
H	-1.8722637	-3.1083209	0.1369275
C	-3.8331747	-3.0901460	0.9508126
H	-0.6574228	-3.1974957	2.3421000
H	-2.2202208	-3.2807335	3.1875692
H	-1.7475052	-4.5813304	2.0902437
C	-4.4000381	-3.6557615	-0.1258538
H	-4.4388971	-2.8149281	1.8153390
H	-3.7534445	-3.9192896	-0.9648541
C	-5.8176527	-3.9789406	-0.3166035
C	-6.2098713	-4.6274810	-1.5010878
C	-6.8126751	-3.6709066	0.6303600
C	-7.5435739	-4.9617033	-1.7337254
H	-5.4534088	-4.8728085	-2.2432288
C	-8.1432385	-4.0049310	0.4000348
H	-6.5444105	-3.1640568	1.5529504
C	-8.5171146	-4.6528358	-0.7827837
H	-7.8215439	-5.4627367	-2.6569342
H	-8.8955969	-3.7589578	1.1445681
H	-9.5573761	-4.9114024	-0.9587759
H	-1.0044039	-1.1330599	1.1349857
H	0.7254768	-2.0278051	0.0985173
O	0.7991939	-1.3193434	0.7554398
B	1.7821636	-0.2988307	0.2679742
C	3.0957733	-1.0912733	-0.3509888
C	3.6274844	-2.1979137	0.3218601
C	3.7455498	-0.7911928	-1.5485390
C	4.6862930	-2.9642888	-0.1532442
C	4.8108605	-1.5282049	-2.0638105
C	5.2843878	-2.6292942	-1.3631017
C	1.0437498	0.6371226	-0.9002825
C	1.1017505	2.0268639	-0.9981357
C	0.2178730	0.0434411	-1.8526151
C	0.3618475	2.7774160	-1.9091351
C	-0.5408275	0.7426765	-2.7854723
C	-0.4793281	2.1312453	-2.8076413
C	2.1358733	0.6109976	1.5992318
C	3.3862554	0.7998038	2.1846177
C	1.0966352	1.2620931	2.2644137
C	3.5943051	1.5496528	3.3425297
C	1.2493122	2.0194800	3.4189332
C	2.5178212	2.1627091	3.9703203
F	3.1418128	-2.5588862	1.5358788
F	5.1522923	-4.0187955	0.5519310
F	6.3115333	-3.3565077	-1.8423999
F	5.3893873	-1.1822728	-3.2350612
F	3.3770699	0.2844880	-2.2950418
F	0.1188986	-1.3199476	-1.9211789
F	-1.3474506	0.0924969	-3.6553216
F	-1.2132094	2.8349631	-3.6904081
F	0.4573915	4.1243097	-1.9354975
F	1.9252937	2.7458950	-0.1890077
F	-0.1625723	1.2148927	1.7541325
F	0.1896551	2.6275932	3.9990358
F	2.6998616	2.8905641	5.0892017
F	4.8343433	1.6870729	3.8613701
F	4.5099961	0.2665620	1.6375545

316aH^+ : adduct of **273a**H^+ C3 on **315a** *para*-position

45

Energy = -906.7109398510

N	-3.7537563	0.7359561	-0.3573989
C	-4.3569761	-0.5343618	-0.1245444
C	-2.5068569	1.1261281	-0.0962064
H	-4.3593491	1.4324433	-0.7867375
C	-5.2038865	-1.0482465	-1.1114082
C	-4.1562289	-1.2175983	1.0791707
C	-2.1784741	2.5126334	-0.2936739
C	-1.4881717	0.2153016	0.3497033
C	-5.8281445	-2.2754470	-0.9017387
H	-5.3588522	-0.4962502	-2.0335843
C	-4.7828429	-2.4466327	1.2736319
H	-3.5494011	-0.7794338	1.8642783
C	-0.9331403	2.9661423	-0.0349356
H	-2.9651138	3.1877166	-0.6192732
C	-0.2370204	0.6696656	0.5811765
H	-1.7247629	-0.8358723	0.4592913
C	-5.6131013	-2.9799134	0.2853245
H	-6.4802728	-2.6816609	-1.6683691
H	-4.6333745	-2.9785617	2.2078346
C	0.1742712	2.0807337	0.3955396
H	-0.7246019	4.0255843	-0.1392880
H	0.5375164	-0.0320227	0.8768140
H	-6.1019479	-3.9357437	0.4454449
H	0.5806435	2.4663187	1.3464175
C	1.4269292	2.1483424	-0.6055946
C	1.8525786	3.6046071	-0.8518539
H	1.1003995	1.6968182	-1.5484835
C	2.5640376	1.3536142	-0.0390523
H	2.7534932	3.6134667	-1.4719443
H	2.0828844	4.1107053	0.0922657
H	1.0782092	4.1722173	-1.3748575
C	3.0563958	0.2431968	-0.6117644
H	2.9990920	1.7439378	0.8817803
H	2.5839933	-0.1119378	-1.5291871

C	4.1809325	-0.5718862	-0.1439501
C	4.5330820	-1.7186153	-0.8783507
C	4.9285860	-0.2652595	1.0092418
C	5.5907916	-2.5342021	-0.4778740
H	3.9663562	-1.9665277	-1.7728768
C	5.9840565	-1.0783988	1.4089473
H	4.6848049	0.6155585	1.5962387
C	6.3210734	-2.2173442	0.6684176
H	5.8446175	-3.4150798	-1.0608206
H	6.5498728	-0.8249030	2.3011429
H	7.1466805	-2.8486288	0.9839557

316gH.OHBf$_3$: H-bonded **316g**H$^+$ and HOBf$_3^-$

91

Energy = -3423.491354426

N	-3.5193202	2.6844420	0.9821808
C	-3.1681498	1.3788504	0.9952738
C	-4.0302303	3.3210917	-0.2047858
C	-3.3324991	3.5252386	2.1369563
C	-2.9525763	0.6657441	-0.2320183
C	-2.9979750	0.6863210	2.2378632
C	-5.1435474	2.7803254	-0.8521920
C	-3.4210078	4.4875183	-0.6698602
C	-4.3757496	4.3516060	2.5581375
C	-2.0937056	3.5375957	2.7837511
C	-2.4282449	-0.5813961	-0.2005110
H	-3.1540839	1.1612298	-1.1735529
C	-2.5151171	-0.5802388	2.2572237
H	-3.2697394	1.1892384	3.1582977
C	-5.6351017	3.4046668	-1.9969255
H	-5.6208328	1.8899903	-0.4538012
C	-3.9215593	5.1042466	-1.8139507
H	-2.5623440	4.8955162	-0.1476735
C	-4.1784320	5.1856541	3.6568175
H	-5.3261601	4.3350485	2.0343855
C	-1.9102028	4.3715110	3.8840826
H	-1.2882031	2.9050521	2.4260007
C	-2.0582597	-1.2748123	1.0449481
H	-2.2116038	-1.0926098	-1.1347533
H	-2.4088367	-1.0876816	3.2108199
C	-5.0240146	4.5638599	-2.4800089
H	-6.5022457	2.9923269	-2.5032261
H	-3.4450195	6.0046723	-2.1881226
C	-2.9499724	5.1946777	4.3225506
H	-4.9875134	5.8254632	3.9948449
H	-0.9506787	4.3836238	4.3914007
C	-2.3416507	-2.8181672	0.9918427
H	-5.4103593	5.0486512	-3.3711073
H	-2.8013008	5.8466700	5.1776829
C	-1.7172675	-3.5449708	2.1926843
H	-1.8580507	-3.1765324	0.0746613
C	-3.8195138	-3.0618489	0.8810191
H	-0.6596744	-3.2817365	2.2964855
H	-2.2322307	-3.2927376	3.1255330
H	-1.8010815	-4.6263644	2.0512799
C	-4.4155682	-3.5666229	-0.2099259
H	-4.4097108	-2.7788705	1.7537608
H	-3.7841438	-3.8407915	-1.0569335
C	-5.8491980	-3.8021066	-0.4091352
C	-6.2773265	-4.3889839	-1.6131125
C	-6.8258321	-3.4639221	0.5466887
C	-7.6282408	-4.6346610	-1.8561576
H	-5.5354902	-4.6548602	-2.3628982
C	-8.1737088	-3.7087356	0.3054144
H	-6.5293052	-3.0036674	1.4849542
C	-8.5834024	-4.2961690	-0.8968561
H	-7.9339700	-5.0901660	-2.7940974
H	-8.9114591	-3.4396484	1.0565445
H	-9.6371032	-4.4851565	-1.0813731
H	-0.9179006	-1.2186392	1.0800456
O	0.9155824	-1.4542801	0.9914375
H	0.9324754	-2.1480969	0.3166664
B	1.8753444	-0.3671986	0.6152281
C	3.1662786	-1.0026979	-0.2049846
C	1.0608640	0.6878100	-0.3902889
C	2.3307413	0.3338969	2.0384483
C	3.6689175	-2.2764532	0.0759111
C	3.8503897	-0.3391186	-1.2256470
C	0.8890532	2.0613715	-0.2326780
C	0.4320830	0.1683962	-1.5221188
C	3.6325975	0.5101410	2.5054670
C	1.3498678	0.7827389	2.9231280
C	4.7274844	-2.8667720	-0.6096467
F	3.1455514	-3.0194121	1.0874334
C	4.9126723	-0.8864625	-1.9395822
F	3.5261645	0.9392190	-1.5600683
C	0.1415368	2.8570300	-1.1000688
F	1.4821863	2.7287960	0.7928567
C	-0.3132113	0.9177161	-2.4251546
F	0.5305518	-1.1651343	-1.8023826
C	3.9424706	1.0713174	3.7452553
F	4.7081267	0.1487600	1.7576857
C	1.6038426	1.3508845	4.1644963
F	0.0414104	0.7244017	2.5586989
C	5.3545136	-2.1679976	-1.6338084
F	5.1572607	-4.1057302	-0.2851778
F	5.5248522	-0.1849828	-2.9182615
C	-0.4671334	2.2825328	-2.2094568
F	0.0138285	4.1845462	-0.8812980
F	-0.9182139	0.3347231	-3.4839194
C	2.9215843	1.4952928	4.5852552
F	5.2278661	1.2074503	4.1376621
F	0.5941304	1.7822263	4.9536895
F	6.3787138	-2.7190375	-2.3120345
F	-1.2010076	3.0291362	-3.0554323
F	3.2012940	2.0423795	5.7834430

316gH$^+$: adduct of **273a**H$^+$ C3 on **215g** Ph$_3$N para

55
Energy = -1137.898392186
N -2.6717915 0.1452930 -0.1784049
C -2.9288041 1.5632030 -0.2527054
C -1.4826440 -0.3833360 -0.5188740
C -3.4505779 2.2167078 0.8651871
C -2.6987783 2.2429257 -1.4507754
C -1.3577954 -1.7931010 -0.7775142
C -0.3162723 0.4522682 -0.6392803
C -3.7233739 3.5801834 0.7842899
H -3.6314292 1.6647192 1.7818354
C -2.9766264 3.6068012 -1.5194445
H -2.3228979 1.7063579 -2.3162059
C -0.1613235 -2.3256445 -1.1139221
H -2.2493795 -2.4086276 -0.7601207
C 0.8855575 -0.0938508 -0.9254938
H -0.4078740 1.5137631 -0.4437861
C -3.4856279 4.2758096 -0.4042439
H -4.1198598 4.0990856 1.6511525
H -2.8063088 4.1414790 -2.4484301
C 1.0950441 -1.5428725 -1.1511312
H -0.1129879 -3.3748478 -1.3857765
H 1.7675481 0.5397916 -0.9415626
H -3.7038369 5.3375370 -0.4629656
H 1.5692648 -1.6947567 -2.1354736
C 2.1889281 -2.0971071 -0.1146403
C 2.3891167 -3.6104211 -0.2926150
H 1.7999938 -1.8939706 0.8892618
C 3.4802107 -1.3631855 -0.3077373
H 3.1867439 -3.9480328 0.3752235
H 2.6811026 -3.8483871 -1.3214731
H 1.4826388 -4.1706485 -0.0472150
C 4.0241264 -0.5536616 0.6155846
H 3.9823232 -1.5361939 -1.2603257
H 3.4817501 -0.4069422 1.5511189
C 5.2916686 0.1753734 0.5190458
C 5.6824560 0.9932167 1.5945631
C 6.1408287 0.1000014 -0.6016936
C 6.8755520 1.7137491 1.5554766
H 5.0379126 1.0595770 2.4680908
C 7.3312689 0.8183893 -0.6410037
H 5.8698229 -0.5256704 -1.4472603
C 7.7054192 1.6294549 0.4366185
H 7.1568121 2.3393499 2.3979202
H 7.9736906 0.7468280 -1.5142881
H 8.6362816 2.1880110 0.4016107
C -3.7658797 -0.6725286 0.2845848
C -5.0193224 -0.5301390 -0.3136312
C -3.5657544 -1.5520440 1.3509451
C -6.0816396 -1.3013904 0.1517293
H -5.1536638 0.1680412 -1.1334454
C -4.6366096 -2.3171386 1.8085871
H -2.5905295 -1.6201101 1.8225566
C -5.8921534 -2.1949917 1.2093348
H -7.0571928 -1.2049280 -0.3139647
H -4.4912543 -2.9977756 2.6413888
H -6.7247323 -2.7901849 1.5710436

316h Ha**.**$OHBf_3$: H-bonded **316h**Ha^+ and $HOBf_3^-$
84
Energy = -3231.635424669
N -3.4507013 2.6445950 1.3447438
C -3.0386835 1.3714531 1.3670444
C -3.6114875 3.3590416 0.0997986
C -2.9314716 0.6152507 0.1483146
C -2.7121185 0.7272885 2.6090641
C -4.8838429 3.7735464 -0.2937806
C -2.4841945 3.6514381 -0.6699860
C -2.3976099 -0.6273479 0.1675722
H -3.2972040 1.0519854 -0.7733745
C -2.1606330 -0.5118201 2.6095082
H -2.8695298 1.2507723 3.5436501
C -5.0276162 4.4867845 -1.4838221
H -5.7478665 3.5333584 0.3182849
C -2.6397730 4.3631043 -1.8589669
H -1.5047597 3.3256112 -0.3352812
C -1.8257756 -1.2368678 1.3767138
H -2.3615979 -1.2063998 -0.7503783
H -1.8802285 -0.9605199 3.5574268
C -3.9085000 4.7801940 -2.2660369
H -6.0153182 4.8071564 -1.8004898
H -1.7684177 4.5926212 -2.4629716
C -1.9678110 -2.7965544 1.4092836
H -4.0253171 5.3356149 -3.1915152
C -1.2872051 -3.4081262 2.6441566
H -1.4542677 -3.1584277 0.5106974
C -3.4163949 -3.1838133 1.3223048
H -0.2729407 -3.0159059 2.7736234
H -1.8534419 -3.1986529 3.5574707
H -1.2293409 -4.4943560 2.5319754
C -3.9586798 -3.8242850 0.2751331
H -4.0328110 -2.8946477 2.1746300
H -3.3021455 -4.1010677 -0.5519103
C -5.3623373 -4.2119910 0.1028962
C -5.7290772 -4.9335116 -1.0470169
C -6.3690882 -3.8940899 1.0341314
C -7.0489955 -5.3294831 -1.2607112
H -4.9637762 -5.1856086 -1.7776767
C -7.6859751 -4.2890445 0.8225151
H -6.1209452 -3.3309527 1.9292526
C -8.0342986 -5.0096455 -0.3255517
H -7.3069470 -5.8875239 -2.1566011
H -8.4476543 -4.0334232 1.5541966
H -9.0639559 -5.3156738 -0.4871289
H -0.6862639 -1.0792058 1.2869109
H 1.2834407 -2.0227866 1.1509512
O 1.0693748 -1.0882810 1.2853901
B 1.8558812 -0.2336659 0.3475030
C 3.2163839 -0.9790022 -0.2291487

C	3.5695541	-2.3109248	-0.0308822
C	4.0855887	-0.2856850	-1.0747118
C	4.6867772	-2.9192126	-0.5997209
C	5.2140028	-0.8400491	-1.6652615
C	5.5199734	-2.1765967	-1.4260623
C	0.9651932	0.0709215	-1.0350367
C	0.7788475	1.2944205	-1.6785121
C	0.3508912	-1.0036912	-1.6803665
C	0.0193755	1.4552531	-2.8358167
C	-0.4320285	-0.8941277	-2.8251755
C	-0.6037762	0.3546495	-3.4115866
C	2.1636705	1.1178832	1.2436719
C	3.3793827	1.4543493	1.8355769
C	1.1100670	1.9562275	1.6051607
C	3.5541001	2.5525948	2.6782940
C	1.2280601	3.0605042	2.4386286
C	2.4706544	3.3664927	2.9832455
F	2.8085993	-3.1310177	0.7621612
F	4.9642278	-4.2182542	-0.3600692
F	6.6055628	-2.7401056	-1.9876115
F	6.0166952	-0.1025294	-2.4612194
F	3.8474986	1.0237137	-1.3438760
F	0.4962603	-2.2676042	-1.1886346
F	-1.0304735	-1.9788455	-3.3652384
F	-1.3528343	0.4935549	-4.5211660
F	-0.1159288	2.6708190	-3.4097264
F	1.3391215	2.4333332	-1.1960411
F	-0.1379960	1.7140459	1.1192384
F	0.1563005	3.8355742	2.7248449
F	2.6179432	4.4274613	3.7991845
F	4.7634463	2.8249698	3.2146973
F	4.4924261	0.7021953	1.6302558
C	-3.6375646	3.4239212	2.5860127
H	-2.6705326	3.5945383	3.0686085
H	-4.0776796	4.3807006	2.3125211
H	-4.3066028	2.8981852	3.2699730

316hHa^+ : adduct of **273a**H^+ C1 on **315h** Ph_2NMe para

48

Energy = -946.0361831182

N	-2.9372847	1.2070754	0.0454022
C	-3.8642728	0.0976402	0.0258473
C	-1.6381133	1.0325739	0.2897278
C	-4.5133582	-0.2272270	-1.1655012
C	-4.1197142	-0.5997238	1.2071588
C	-0.7659926	2.1707235	0.4415104
C	-1.0747787	-0.2924932	0.3853192
C	-5.4256284	-1.2816051	-1.1719529
H	-4.2990949	0.3280164	-2.0734186
C	-5.0348776	-1.6517571	1.1882649
H	-3.6133762	-0.3161437	2.1244850
C	0.5533430	1.9955350	0.6742904
H	-1.1771881	3.1709320	0.3891390
C	0.2473777	-0.4599936	0.6007925
H	-1.7255008	-1.1492674	0.2611215
C	-5.6861393	-1.9931990	0.0014688
H	-5.9282870	-1.5482446	-2.0962160
H	-5.2411543	-2.1981064	2.1031420
C	1.1972422	0.6662509	0.7479285
H	1.1934894	2.8637823	0.7978391
H	0.6563887	-1.4648371	0.6456018
H	-6.3988215	-2.8119222	-0.0089828
H	1.7030628	0.5777129	1.7247350
C	3.6682022	2.6116175	-0.9705371
C	4.6963470	3.6846316	-0.7835861
H	3.1047719	2.6348861	-1.9053313
C	3.4039670	1.6426320	-0.0893605
H	5.4473716	3.6462383	-1.5830925
H	5.2075646	3.5880129	0.1788607
H	4.2347542	4.6791018	-0.8364699
C	2.3892316	0.5560703	-0.3183430
H	3.9561270	1.5981359	0.8504566
H	1.9371419	0.6892214	-1.3064039
C	3.0200157	-0.8229638	-0.2535636
C	2.9840067	-1.6588648	-1.3745476
C	3.6478162	-1.2798746	0.9124786
C	3.5659193	-2.9271966	-1.3355519
H	2.4982011	-1.3132374	-2.2839442
C	4.2278862	-2.5472175	0.9551883
H	3.6869891	-0.6470758	1.7962084
C	4.1884367	-3.3751771	-0.1695263
H	3.5306914	-3.5639916	-2.2149474
H	4.7111835	-2.8881244	1.8663095
H	4.6394130	-4.3626523	-0.1357578
C	-3.5157714	2.5516734	-0.1760094
H	-3.5032748	3.1210992	0.7573061
H	-2.9537346	3.0827045	-0.9461457
H	-4.5454495	2.4175412	-0.4998848

316h$H^+HOBf_3^-$: contact ion pair of **315h**H^+

84

Energy = -3231.633306900

N	0.9930800	4.5047881	1.2160941
C	0.0017493	3.6051219	1.2489543
C	1.5872861	4.9209098	-0.0308219
C	-0.6722416	3.2145054	0.0394570
C	-0.4173086	3.0179312	2.4919584
C	1.5970902	6.2739703	-0.3717939
C	2.1755574	3.9632271	-0.8605268
C	-1.5620819	2.1983768	0.0576980
H	-0.4556880	3.7478771	-0.8780926
C	-1.3032617	1.9918434	2.4944469
H	0.0215124	3.3567562	3.4218644
C	2.1961416	6.6687914	-1.5676838
H	1.1306575	7.0049336	0.2816443
C	2.7673002	4.3684846	-2.0554146
H	2.1676116	2.9189425	-0.5669500
C	-1.8542218	1.4064131	1.2630707

H	-2.0774618	1.9286877	-0.8588733
H	-1.5520746	1.5129278	3.4368342
C	2.7789346	5.7190822	-2.4098391
H	2.1995988	7.7188476	-1.8430095
H	3.2232526	3.6277457	-2.7043356
C	-3.8737178	-1.2953002	2.3306191
H	3.2440245	6.0320875	-3.3395280
C	-4.1489067	-2.2466612	3.4550795
H	-3.8820333	-1.7190679	1.3245610
C	-3.6254670	0.0104268	2.4711555
H	-3.4093358	-3.0577377	3.4658660
H	-4.1222747	-1.7395811	4.4243432
H	-5.1318238	-2.7198917	3.3346451
C	-3.3546018	0.9314936	1.3122315
H	-3.6311578	0.4519295	3.4681565
H	-3.5039607	0.3607354	0.3897238
C	-4.2927104	2.1270515	1.2765274
C	-5.1152357	2.3298094	0.1630773
C	-4.3422124	3.0515025	2.3271488
C	-5.9667320	3.4341216	0.0945724
H	-5.0876895	1.6162518	-0.6576676
C	-5.1908521	4.1562180	2.2629164
H	-3.7150727	2.9133861	3.2043569
C	-6.0056159	4.3518753	1.1449699
H	-6.5977521	3.5761424	-0.7784580
H	-5.2167260	4.8649179	3.0860852
H	-6.6656094	5.2132507	1.0944849
H	-1.2744247	0.4290017	1.1687638
H	-1.2397587	-1.7935649	1.3470422
O	-0.4689521	-1.2111823	1.2915129
B	0.4554951	-1.6145378	0.1970481
C	0.2733077	-3.1828719	-0.2929521
C	-0.6562177	-4.0955096	0.1974411
C	1.0414021	-3.6706015	-1.3524091
C	-0.8212494	-5.3869062	-0.2998874
C	0.9207474	-4.9476149	-1.8851440
C	-0.0245314	-5.8192022	-1.3521135
C	0.0927462	-0.7216648	-1.1736176
C	0.9496791	0.0517418	-1.9549519
C	-1.2270903	-0.7368225	-1.6289576
C	0.5365773	0.7906059	-3.0624567
C	-1.6904922	-0.0230822	-2.7295377
C	-0.7967851	0.7591037	-3.4536321
C	1.9521772	-1.2902612	0.8195601
C	2.9299608	-2.2145790	1.1825155
C	2.2625013	0.0228983	1.1723038
C	4.1279937	-1.8701455	1.8105203
C	3.4360753	0.4197669	1.7987798
C	4.3873197	-0.5420528	2.1223748
F	-1.4953217	-3.7601975	1.2257625
F	-1.7458255	-6.2183942	0.2256738
F	-0.1650225	-7.0620532	-1.8502775
F	1.7083302	-5.3565368	-2.9027120
F	1.9930212	-2.8738634	-1.9060697
F	-2.1623743	-1.4840472	-0.9755896
F	-2.9910975	-0.0696217	-3.0941638
F	-1.2159155	1.4705709	-4.5167142
F	1.4178560	1.5342053	-3.7661565
F	2.2762964	0.1288531	-1.6733930
F	1.3831752	1.0194547	0.8817723
F	3.6643020	1.7212206	2.0917318
F	5.5355431	-0.1918468	2.7327288
F	5.0347223	-2.8185178	2.1315547
F	2.7648202	-3.5436942	0.9530707
C	1.6259913	5.0027866	2.4550206
H	0.8681893	5.3713332	3.1484094
H	2.2045823	4.2018440	2.9254388
H	2.2955058	5.8158432	2.1825049

316hH^+ : adduct of **271a**H^+ C3 on **315h** Ph_2NMe para

48

Energy = -946.0405126156

N	-3.6091575	0.6966957	-0.2381513
C	-4.0089522	-0.6693038	0.0143335
C	-2.3799049	1.1310301	0.0423733
C	-4.3682738	-1.4848583	-1.0591013
C	-4.0618092	-1.1330753	1.3294383
C	-2.0611537	2.5332369	-0.0537459
C	-1.3409194	0.2092653	0.4341909
C	-4.7721214	-2.7951728	-0.8065672
H	-4.3202743	-1.1042538	-2.0746790
C	-4.4680829	-2.4452775	1.5694599
H	-3.7959585	-0.4720675	2.1484299
C	-0.8085550	2.9713301	0.2047814
H	-2.8418028	3.2435235	-0.2957541
C	-0.0867611	0.6513807	0.6633721
H	-1.5770559	-0.8449324	0.5121973
C	-4.8208785	-3.2758271	0.5041217
H	-5.0444107	-3.4401668	-1.6359447
H	-4.5135274	-2.8133846	2.5895170
C	0.3185682	2.0708162	0.5353910
H	-0.6117718	4.0379337	0.1735078
H	0.6916899	-0.0631677	0.9140087
H	-5.1350556	-4.2972712	0.6946797
H	0.7621281	2.4066584	1.4884852
C	1.5226099	2.2035365	-0.5144500
C	1.9485214	3.6714248	-0.6757329
H	1.1485654	1.8228529	-1.4711118
C	2.6781609	1.3629919	-0.0627317
H	2.8145759	3.7220514	-1.3417209
H	2.2341479	4.1047311	0.2892283
H	1.1522315	4.2808545	-1.1117272
C	3.1337015	0.2978677	-0.7417612
H	3.1588978	1.6791852	0.8638262
H	2.6195123	0.0223274	-1.6640589
C	4.2682600	-0.5604368	-0.3901972
C	4.5735989	-1.6495290	-1.2263451
C	5.0703005	-0.3509431	0.7481609
C	5.6381167	-2.5029171	-0.9385330

H	3.9647993	-1.8227065	-2.1108293
C	6.1322444	-1.2021929	1.0358465
H	4.8640981	0.4842091	1.4114747
C	6.4219951	-2.2830898	0.1950347
H	5.8554993	-3.3373949	-1.5992620
H	6.7399345	-1.0239888	1.9186520
H	7.2522295	-2.9449743	0.4236992
C	-4.6535580	1.5998600	-0.7719535
H	-4.9997206	2.2753060	0.0152818
H	-4.2619310	2.1731073	-1.6134263
H	-5.4847583	0.9813731	-1.1037012

316aH^+ : adduct of **273a**H^+ C3 on **315a** Ph_2NH para

45

Energy = -906.7106998180

N	-3.2130111	-1.2453017	-0.4358844
H	1.4043853	3.6710875	0.3927455
C	-4.5850936	-0.9638500	-0.1666295
C	-2.1755400	-0.4098266	-0.4307957
C	-5.2132081	0.1526619	-0.7272247
C	-5.2977414	-1.8701023	0.6240506
C	-2.2829859	0.9561183	0.0017265
C	-0.8994035	-0.9177360	-0.8603257
C	-6.5612767	0.3784832	-0.4573744
H	-4.6662809	0.8136945	-1.3910086
C	-6.6464741	-1.6355546	0.8808363
H	-4.7958433	-2.7391050	1.0387464
C	-1.1904048	1.7530580	-0.0057343
H	-3.2372541	1.3314743	0.3499612
C	0.1842222	-0.1145196	-0.8785035
H	-0.8393685	-1.9524893	-1.1861218
C	-7.2775500	-0.5082120	0.3495607
H	-7.0546146	1.2412008	-0.8936985
H	-7.2022699	-2.3329544	1.4994795
C	0.1553622	1.2951528	-0.4206184
H	-1.2929507	2.7815492	0.3240787
H	1.1390110	-0.5067172	-1.2150212
H	-8.3286258	-0.3285063	0.5525190
H	0.5103875	1.9434123	-1.2404571
C	1.2335767	2.9785250	1.2244307
C	1.2434900	1.5210224	0.7364156
H	0.2907350	3.2408081	1.7118703
H	2.0376508	3.1159673	1.9529768
H	0.9685951	0.8545274	1.5609118
C	2.6013756	1.1456505	0.2242794
C	3.3278481	0.1286193	0.7149020
H	2.9911762	1.7705055	-0.5802893
H	2.8922478	-0.4720283	1.5151480
C	4.6691198	-0.2866163	0.2946450
C	5.2570129	-1.4001902	0.9212996
C	5.4012076	0.3737191	-0.7107367
C	6.5282874	-1.8435543	0.5584189
H	4.7042916	-1.9194259	1.7009153
C	6.6693304	-0.0683563	-1.0733382
H	4.9768495	1.2389342	-1.2120520
C	7.2403457	-1.1788735	-0.4410178
H	6.9621055	-2.7063256	1.0560495
H	7.2187430	0.4543883	-1.8513479
H	8.2316645	-1.5190886	-0.7260367
H	-3.0023484	-2.2175555	-0.6516576

316lHa^+ : adduct of **273a**H^+ C1 on amine **315l** para

45

Energy = -831.6666734673

N	-2.2691053	0.4854583	1.1688061
C	-1.4046219	-0.4935636	0.9406628
C	-0.3977742	-0.8199969	1.9237077
C	-1.4598653	-1.2564758	-0.2969053
C	0.5021398	-1.7988752	1.6952093
H	-0.3948363	-0.2985587	2.8727956
C	-0.5480269	-2.2330747	-0.4999804
C	0.5529954	-2.5706012	0.4333232
H	1.2196537	-2.0446523	2.4713513
H	-0.5795368	-2.7903178	-1.4332958
H	0.4948529	-3.6439454	0.6826585
C	1.9642199	-2.4210495	-0.3042438
C	3.1203678	-2.7746839	0.6456894
H	2.0491760	-1.3731895	-0.6126336
C	1.9931306	-3.2999266	-1.5185207
H	4.0645569	-2.7322895	0.0952765
H	3.0025307	-3.7887096	1.0439429
H	3.1863157	-2.0749816	1.4834095
C	2.0712818	-2.8340705	-2.7752241
H	1.9666665	-4.3730939	-1.3243023
H	2.1032956	-1.7526483	-2.9186580
C	2.1254081	-3.6200329	-4.0114722
C	2.1974622	-2.9395620	-5.2401499
C	2.1074529	-5.0277714	-4.0319867
C	2.2498865	-3.6348953	-6.4477079
H	2.2136581	-1.8519713	-5.2404636
C	2.1615136	-5.7221686	-5.2361223
H	2.0510624	-5.5836515	-3.1003438
C	2.2336667	-5.0303455	-6.4507566
H	2.3035038	-3.0874150	-7.3846274
H	2.1492464	-6.8086635	-5.2310522
H	2.2793233	-5.5769852	-7.3882923
C	-2.1726456	1.3733503	2.3402431
H	-2.6330779	0.8994113	3.2122691
H	-1.1318615	1.6174938	2.5495935
H	-2.7128765	2.2895453	2.1023243
C	-3.4298230	0.7622294	0.2870304
H	-3.1837456	1.6474123	-0.3114325
H	-4.2579293	1.0247258	0.9503794
C	-3.7769253	-0.4261932	-0.5926283
H	-4.5463422	-0.1186438	-1.3051891
H	-4.1908695	-1.2331104	0.0225514
C	-2.5173047	-0.9078925	-1.3125803
H	-2.1454676	-0.1064425	-1.9649393

H -2.7214275 -1.7757298 -1.9447581

316lH^+ : adduct of **273a**H^+ C3 on amine **315l** para

45

Energy = -831.6670543264

N -4.4461868 1.0167163 0.2704901
C -3.2273669 0.4919688 0.2635333
C -2.0809029 1.3213156 0.5578226
C -3.0300894 -0.9190857 -0.0305659
C -0.8355834 0.8032815 0.5558548
H -2.2312723 2.3620589 0.8163345
C -1.7718433 -1.4149617 -0.0139354
C -0.5529539 -0.6120604 0.2348770
H 0.0060160 1.4440067 0.8030436
H -1.6241026 -2.4716156 -0.2290302
H -0.0049649 -1.0559912 1.0812792
C 0.4682385 -0.7617708 -0.9894968
C -0.1475424 -0.2123863 -2.2830965
H 0.6309232 -1.8408478 -1.0879952
C 1.7755410 -0.1011461 -0.6728278
H 0.5309048 -0.3906255 -3.1222002
H -0.3199049 0.8666497 -2.2076596
H -1.1033202 -0.6987542 -2.5031406
C 2.8846466 -0.7785395 -0.3333235
H 1.7964662 0.9861151 -0.7448126
H 2.8246783 -1.8671047 -0.2830830
C 4.2032109 -0.2201612 -0.0199947
C 5.2482753 -1.1025204 0.3083117
C 4.4787041 1.1608815 -0.0297132
C 6.5229723 -0.6279411 0.6155441
H 5.0509114 -2.1719933 0.3213849
C 5.7502258 1.6348807 0.2760742
H 3.6940380 1.8696693 -0.2788767
C 6.7796616 0.7437260 0.6005100
H 7.3144922 -1.3287303 0.8658167
H 5.9429476 2.7040684 0.2621194
H 7.7710097 1.1183657 0.8384198
C -4.6802933 2.4604785 0.4507287
H -4.5862775 2.7316237 1.5064836
H -3.9759802 3.0381675 -0.1480878
H -5.6938422 2.6745838 0.1139529
C -5.6789032 0.2036613 0.1282694
H -6.0457502 0.3384907 -0.8961610
H -6.4131542 0.6436102 0.8077529
C -5.4376153 -1.2619818 0.4450032
H -6.3409109 -1.8247145 0.1963973
H -5.2518327 -1.3824922 1.5183063
C -4.2355372 -1.7626535 -0.3554605
H -4.4555009 -1.6825037 -1.4287316
H -4.0188688 -2.8129639 -0.1453269

316uaH^+p : adduct of **273u**H^+ C3 on **315a** Ph_2NH para

39

Energy = -752.9840861855

N -1.9667134 -0.9168022 -0.7922877
H -2.0462693 -1.4862920 -1.6322856
C -0.7839283 -0.9394062 -0.1799134
C -0.5676158 -0.3256472 1.102079
C 0.2971714 -1.6334085 -0.8301694
C 0.6612351 -0.3641606 1.6633679
H -1.4026134 0.1286084 1.6214998
C 1.5285969 -1.6427061 -0.2789519
H 0.1005303 -2.1183467 -1.7824345
C -3.1448673 -0.2033706 -0.4257299
C 1.8381565 -0.9812380 1.0107914
H 0.8139341 0.0753966 2.6455254
H 2.3485635 -2.1334938 -0.7958813
C -3.0792108 1.1309905 -0.0122298
C -4.3736910 -0.8586041 -0.5504780
H 2.2319811 -1.7503647 1.6989847
C -4.2573133 1.7984625 0.3150632
H -2.1268095 1.6494411 0.0190754
C -5.5443548 -0.1780546 -0.2248856
H -4.4058769 -1.8905168 -0.8869284
C -5.4883838 1.1464555 0.2156648
H -4.2116038 2.8354870 0.6320182
H -6.4999028 -0.6850053 -0.3136891
H -6.4030664 1.6735867 0.4680336
C 3.0338431 0.0539526 0.8788601
C 4.2768397 -0.6566121 0.4097848
C 5.1033174 -0.1611018 -0.5178329
C 4.9161303 1.1837193 -1.1668121
C 3.9054472 2.0462141 -0.4000050
C 2.6615379 1.2282052 -0.0375015
H 5.9750429 -0.7425082 -0.8148447
H 4.4926567 -1.6216544 0.8683266
H 3.1959007 0.4235723 1.9012354
H 4.5851216 1.0434907 -2.2073033
H 4.3731254 2.4194657 0.5203490
H 3.6211853 2.9203757 -0.9953490
H 1.9104920 1.8588941 0.4504849
H 2.2079998 0.8370780 -0.9584205
H 5.8851070 1.6944872 -1.2300700

316uaH^+ : adduct of **273u**H^+ C3 on **315a** Ph_2NH ortho

39

Energy = -752.9822644727

N 0.8369762 -0.5233523 0.1951717
H 1.4913477 -0.2911356 -0.5527421
C 0.3850763 0.5045368 0.9110639
C -0.6905287 0.3927508 1.8285445
C 1.0074519 1.8371421 0.6532215
C -1.0276778 1.4664780 2.6102522
H -1.2397481 -0.5373821 1.9068810
C 0.6647741 2.8826542 1.6502607
H 2.0961667 1.7310090 0.5909180
C 0.4011334 -1.8796922 0.2227770

C	-0.3131573	2.7112584	2.5656787
H	-1.8653488	1.3704839	3.2946228
H	1.1979422	3.8246180	1.5626672
C	0.1935171	-2.5269145	-0.9992944
C	0.2414272	-2.5615779	1.4327460
H	-0.5826636	3.5025622	3.2565030
C	-0.2039920	-3.8615853	-1.0064932
H	0.3388435	-1.9868342	-1.9298198
C	-0.1622640	-3.8949881	1.4116812
H	0.4614720	-2.0674706	2.3728446
C	-0.3907078	-4.5452573	0.1971033
H	-0.3710610	-4.3650949	-1.9533312
H	-0.2825204	-4.4293333	2.3487132
H	-0.7016099	-5.5851226	0.1882680
C	0.5937000	2.4055523	-0.8148322
C	1.2577568	1.6012445	-1.8907191
C	0.5846051	0.9298833	-2.8376099
C	-0.9131893	0.8543449	-2.9052676
C	-1.5740452	1.2781990	-1.5881897
C	-0.9225347	2.5460557	-1.0213409
H	1.1458456	0.4308377	-3.6262958
H	2.3471956	1.6208746	-1.9108653
H	1.0502413	3.4012918	-0.8062283
H	-1.2188783	-0.1630286	-3.1798216
H	-2.6432705	1.4533612	-1.7423225
H	-1.4975989	0.4585481	-0.8652682
H	-1.0786067	3.3699263	-1.7282534
H	-1.4059883	2.8430663	-0.0848171
H	-1.2561788	1.4953559	-3.7313761

316a : 4,3-hydroarylation of **273a** and **315a**

44

Energy = -906.2956332458

N	-0.9012472	-0.2879282	2.0720746
C	-1.1261846	1.0355158	2.4487395
C	-1.5467798	-1.4532003	2.4935588
C	-0.6455053	2.0576508	1.6068348
C	-1.7617972	1.3965673	3.6508067
C	-0.8741853	-2.6787668	2.3558590
C	-2.8610004	-1.4682557	2.9953288
C	-0.8034909	3.3956984	1.9536655
H	-0.1493858	1.7886452	0.6770689
C	-1.9256362	2.7415676	3.9790719
H	-2.1007253	0.6311046	4.3391514
C	-1.4893241	-3.8761242	2.7153401
H	0.1398918	-2.6875966	1.9625972
C	-3.4509951	-2.6705678	3.3680141
H	-3.4292816	-0.5480556	3.0685571
C	-1.4546263	3.7524518	3.1385314
H	-0.4198205	4.1647639	1.2886493
H	-2.4197048	2.9971383	4.9127321
C	-2.7866107	-3.8982966	3.2391160
H	-0.9357754	-4.8009965	2.5849276
H	-4.4636150	-2.6557609	3.7647567
H	-1.5842978	4.7970137	3.4044788
C	-2.7914162	-6.4647452	3.2304161
C	-3.4883837	-5.1758090	3.6964856
H	-3.3895185	-7.3338118	3.5196140
H	-1.8018580	-6.5698982	3.6887975
H	-4.5026427	-5.1641850	3.2754982
C	-3.6182524	-5.1540889	5.1981795
C	-4.7886873	-5.1254934	5.8553825
H	-2.6750886	-5.1447320	5.7456335
H	-5.7074545	-5.1357182	5.2665238
C	-4.9873140	-5.0836935	7.3078342
C	-6.2983828	-5.1386072	7.8155268
C	-3.9273667	-4.9878374	8.2304123
C	-6.5455699	-5.1067082	9.1877375
H	-7.1300454	-5.2084455	7.1179054
C	-4.1726632	-4.9569813	9.5997106
H	-2.9030955	-4.9315116	7.8730426
C	-5.4828357	-5.0181529	10.0881538
H	-7.5681400	-5.1494518	9.5529272
H	-3.3389160	-4.8815634	10.2926574
H	-5.6696676	-4.9952498	11.1579538
H	-2.6690168	-6.4729854	2.1418928
H	-0.1569079	-0.4252225	1.3996673

316g : 4,3-hydroarylation of **273a** and **315g** Ph_3N

54

Energy = -1137.484559148

N	-2.6564207	0.1710346	-0.1317787
C	-2.8102765	1.5779993	-0.2002217
C	-1.3862934	-0.4130266	-0.3750604
C	-3.6555296	2.2462530	0.6992084
C	-2.1145714	2.3215040	-1.1661180
C	-1.2737971	-1.5991295	-1.1095933
C	-0.2190227	0.1898246	0.1192951
C	-3.8055006	3.6290260	0.6243609
H	-4.1912240	1.6770594	1.4523971
C	-2.2590471	3.7057839	-1.2232967
H	-1.4620359	1.8084631	-1.8656346
C	-0.0230809	-2.1722419	-1.3375024
H	-2.1683865	-2.0764043	-1.4977797
C	1.0218662	-0.3802657	-0.1340457
H	-0.2922730	1.1066095	0.6962078
C	-3.1071146	4.3698451	-0.3330576
H	-4.4616627	4.1314647	1.3298866
H	-1.7157834	4.2668500	-1.9788423
C	1.1476651	-1.5748682	-0.8590423
H	0.0279565	-3.0940173	-1.9087988
H	1.9167976	0.1062913	0.2469290
H	-3.2216573	5.4484770	-0.3842292
C	2.5429341	-2.1385916	-1.1199794
C	2.5389736	-3.5908721	-1.6250039
H	3.0932126	-2.1064340	-0.1701522
C	3.2588836	-1.2370450	-2.0936364
H	3.5665693	-3.9578693	-1.7026534

H	2.0797245	-3.6666100	-2.6167554
H	1.9867487	-4.2429825	-0.9396217
C	4.3661256	-0.5367897	-1.8005924
H	2.8046286	-1.1678791	-3.0825570
H	4.7868279	-0.6389466	-0.7988786
C	5.0995752	0.3713208	-2.6882753
C	6.2876419	0.9633710	-2.2218303
C	4.6740113	0.6878064	-3.9930545
C	7.0272662	1.8320674	-3.0240051
H	6.6300575	0.7334504	-1.2152531
C	5.4113152	1.5537982	-4.745389
H	3.7561708	0.2562557	-4.3818469
C	6.5930633	2.1314359	-4.3162989
H	7.9419404	2.2750195	-2.6392786
H	5.0630357	1.7838399	-5.7979460
H	7.1647534	2.8082799	-4.9448339
C	-3.7690632	-0.6548113	0.1665108
C	-5.0397206	-0.3498763	-0.3452597
C	-3.6117258	-1.7909003	0.9752343
C	-6.1300987	-1.1628101	-0.0438186
H	-5.1658864	0.5242157	-0.9764054
C	-4.7048374	-2.6063679	1.2587276
H	-2.6312324	-2.0289319	.3756468
C	-5.9717909	-2.2976677	0.560943
H	-7.1067805	-0.9145309	-04502758
H	-4.5668017	-3.4807194	1.8889632
H	-6.8229281	-2.9323393	.9840490

Bf_3 : Lewis-acidic borane $B(C_6F_5)_3$
34
Energy = -2209.516675314

B	-0.0001016	0.0008045	-0.0006333
C	-0.0001801	1.5634586	-0.0005958
C	1.3522102	-0.7827958	-0.0035299
C	-1.3524183	-0.7827862	0.0028896
C	-0.9416191	2.3140682	0.728581
C	0.9415179	2.3142697	-.7215026
C	2.4664577	-0.3605799	0.768735
C	1.5346001	-1.9571833	-0.490138
C	-1.5346709	-1.9567415	07490302
C	-2.4667663	-0.3608365	-.7374543
C	-0.9500339	3.7022183	0.7427237
C	0.9504412	3.7024303	-0.7423427
C	3.6716043	-1.0495868	0.7533276
C	2.7325470	-2.6585408	-0.7787205
C	-2.7325318	-2.6582390	0.7790745
C	-3.6719237	-1.0498484	-0.7533881
C	0.0003325	4.4001814	0.0004627
C	3.8062504	-2.2031571	-0.0164994
C	-3.8062656	-2.2033966	0.0165463
F	-1.8755305	1.6897508	1.4685544
F	1.8753412	1.6901384	-1.4694782
F	2.3860451	0.7441975	1.5080182
F	0.5303473	-2.4351907	-1.5136696
F	-0.5305536	-2.4337952	1.5144791
F	-2.3865259	0.7438964	-1.5087074
F	-1.8577099	4.3770968	1.4659196
F	1.8586958	4.3775254	-1.4646227
F	4.7044422	-0.6196228	1.4954508
F	2.8684764	-3.7639754	-1.5283882
F	-2.8682402	-3.7634966	1.5290634
F	-4.7048145	-0.6203316	-1.4957030
F	0.0004853	5.7363190	0.0008567
F	4.9632735	-2.8717301	-0.0230722
F	-4.9631129	-2.8723109	0.0231667

$H_2O.Bf_3$: B-O adduct of H_2O and Bf_3
37
Energy = -2286.012914771

B	-1.6172784	-0.7060328	-0.1462413
C	-0.9173596	-1.5570544	1.0420188
C	-1.8141680	0.8750476	0.1739063
C	-2.9269879	-1.3980410	-0.8231156
C	-1.4842717	-2.6539986	1.6941333
C	0.3517823	-1.1926735	1.5066408
C	-1.8912928	1.8202892	-0.8466792
C	-1.9733683	1.4005965	1.4574594
C	-2.8082909	-2.5358727	-1.6210361
C	-4.2386147	-0.9518064	-0.6507208
C	-0.8448007	-3.3532093	2.7155601
F	-2.7245771	-3.0930350	1.3703438
C	1.0279177	-1.8654902	2.5172675
F	0.9777417	-0.1111134	0.9817147
C	-2.0859763	3.1811159	-0.6522509
F	-1.7766555	1.4069941	-2.1536029
C	-2.1756929	2.7553418	1.7088169
F	-1.9706093	0.5889461	2.5401416
C	-3.8709128	-3.1890166	-2.2292208
F	-1.5655391	-3.0849288	-1.8208266
C	-5.3413787	-1.5728629	-1.2338400
F	-4.5085974	0.1169954	0.1352838
C	0.4230863	-2.9601350	3.1273511
F	-1.4425991	-4.4051050	3.3062170
F	2.2502369	-1.4671199	2.9170743
C	-2.2294724	3.6543019	0.6484618
F	-2.1392171	4.0329695	-1.6908254
F	-2.3262597	3.2033345	2.9678879
C	-5.1581905	-2.6968039	-2.0317245
F	-3.6758541	-4.2788415	-2.9917953
F	-6.5825976	-1.0964928	-1.0306994
F	1.0554677	-3.6250290	4.1062052
F	-2.4195864	4.9618503	0.8761896
F	-6.2088947	-3.3012253	-2.6047085
O	-0.4608841	-0.7126387	-1.3073893
H	-0.3830005	-1.5921714	-1.7330475
H	-0.6482255	-0.0512800	-2.0077371

H_2O : water
3
Energy = -76.47484731353

O 0.0517792 0.0517783 0.0000000
H 1.0151520 -0.0669314 0.0000000
H -0.0669312 1.0151531 0.0000000

HOBf3- : aa
36
Energy = -2285.569322315
B -1.3200437 -0.8934790 -0.1957754
C -0.8453076 -1.6556602 1.1900766
C -1.6820072 0.7321554 0.0417515
C -2.7472592 -1.4840927 -0.8286467
C -1.3109711 -2.8785959 1.6670986
C 0.2218933 -1.1286546 1.9215017
C -1.7860952 1.5586707 -1.0775312
C -1.9537939 1.3806931 1.2457789
C -2.9166332 -1.9633039 -2.1261313
C -3.9291956 -1.4332747 -0.0873963
C -0.8021143 -3.5167440 2.7984199
F -2.3084840 -3.5499206 1.0301194
C 0.7636318 -1.7250250 3.0545570
F 0.7859036 0.0494545 1.5489250
C -2.1028347 2.9120578 -1.0362370
F -1.5914790 1.0381748 -2.3274186
C -2.2757110 2.7331939 1.3442772
F -1.9236731 0.7089705 2.4271327
C -4.1431495 -2.3704105 -2.6514540
F -1.8638562 -2.0604514 -2.9876459
C -5.1739819 -1.8283502 -0.5604679
F -3.8928079 -0.9872875 1.1969489
C 0.2432499 -2.9346496 3.5019686
F -1.3050231 -4.7037906 3.2092575
F 1.7863998 -1.1484600 3.7266846
C -2.3489264 3.5096209 0.1945686
F -2.1825273 3.6489994 -2.1676750
F -2.5198667 3.3029588 2.5471181
C -5.2839339 -2.3044130 -1.8631580
F -4.2362351 -2.8241583 -3.9227554
F -6.2748012 -1.7629112 0.2230522
F 0.7526230 -3.5360533 4.5964626
F -2.6579808 4.8202692 0.2701961
F -6.4793131 -2.6938561 -2.3516188
O -0.1557257 -1.0572090 -1.0761168
H -0.3480607 -0.7334348 -1.9670718

$Ph_2NBf_3^-$: borate anion
57
Energy = -2728.048857568
B 0.0118233 -0.0057852 0.0886463
C -1.1939334 -0.3175461 -1.0290301
C 0.6636956 1.5202966 -0.0845165
C 1.3924422 -0.9119105 -0.1091214
C -1.3878400 -1.5118972 -1.7259583
C -2.2571128 0.5840303 -1.1827860
C 1.5258387 2.0300465 0.8937036
C 0.6023559 2.3176777 -1.2328499
C 2.1915890 -1.4632618 0.9001117
C 1.9585938 -1.0173421 -1.3850701
C -2.5317014 -1.8240046 -2.4584899
F -0.4277663 -2.4824444 -1.7536137
C -3.4165388 0.3205587 -1.9027902
F -2.1906706 1.8288998 -0.6458913
C 2.2060203 3.2392783 0.7997810
F 1.7554632 1.3289120 2.0333535
C 1.2694175 3.5342207 -1.3746776
F -0.1146541 1.9474749 -2.3227734
C 3.4011652 -2.1157497 0.6583746
F 1.8482626 -1.3969994 2.2064459
C 3.1576630 -1.6584285 -1.6713276
F 1.3330754 -0.4540511 -2.4508543
C -3.5655209 -0.9032274 -2.5436915
F -2.6406058 -3.0135254 -3.0953541
F -4.3983735 1.2465488 -1.9966238
C 2.0748726 4.0086935 -0.3493525
F 2.9991630 3.6675672 1.8077449
F 1.1460015 4.2554167 -2.5119792
C 3.8911533 -2.2226503 -0.6350521
F 4.1109943 -2.6413109 1.6831768
F 3.6219281 -1.7298455 -2.9396123
F -4.6861791 -1.1850637 -3.2407677
F 2.7268583 5.1818879 -0.4709804
F 5.0606456 -2.8473051 -0.8805038
N -0.6939046 -0.2212235 1.4793923
C -1.6703043 0.7342487 1.9045763
C -0.8906693 -1.4929658 2.0468980
C -3.0351344 0.3989852 1.8325764
C -1.3243629 2.0023517 2.3862260
C -0.6634003 -2.6969603 1.3555403
C -1.3048459 -1.5927291 3.3956837
C -4.0191993 1.3102105 2.2000700
H -3.3099382 -0.5889085 1.4752039
C -2.3131791 2.9190193 2.7485585
H -0.2826154 2.2663394 2.5039673
C -0.8263462 -3.9314831 1.9840564
H -0.3409260 -2.6772408 0.3260346
C -1.4786227 -2.8260347 4.0110043
H -1.4795231 -0.6820853 3.960015
C -3.6641325 2.5841344 2.6541432
H -5.0670058 1.0314165 2.1198532
H -2.0206204 3.8980035 3.1204110
C -1.2407339 -4.0161988 3.3129804
H -0.6372380 -4.8384746 1.4139826
H -1.7916164 -2.8584119 5.0523618
H -4.4300097 3.3012594 2.9368084
H -1.3737621 -4.9804197 3.7956388

$PhNH_2.Bf_3$: B-N adduct of $PhNH_2$ and Bf_3
48
Energy = -2497.342003392
B 0.1249196 0.1655055 -0.0170172

C	-1.1596569	-0.1488880	-0.9752135
C	0.7842978	1.6638623	-0.1359677
C	1.3881553	-0.8708378	-0.2087672
C	-1.4329649	-1.4207415	-1.4876630
C	-2.1520723	0.8008617	-1.2476892
C	1.5986298	2.1668165	0.8823317
C	0.7455559	2.4771599	-1.2745779
C	2.0197112	-1.6323048	0.7728517
C	1.9861030	-0.9661090	-1.4697212
C	-2.5602485	-1.7285851	-2.2459861
F	-0.5955066	-2.4611975	-1.2453545
C	-3.2933362	0.5382239	-1.9971472
F	-2.0525547	2.0581857	-0.7586407
C	2.2693407	3.3828028	0.8386077
F	1.7884695	1.4349281	2.0247047
C	1.4057661	3.7008003	-1.3707207
F	0.0619218	2.1062888	-2.3794798
C	3.1401468	-2.4283708	0.5456554
F	1.5486777	-1.6453448	2.0560535
C	3.1011396	-1.7462668	-1.7495236
F	1.4597346	-0.2743592	-2.5089462
C	-3.4992365	-0.7385164	-2.5077541
F	-2.7523495	-2.9756717	-2.7167523
F	-4.2090606	1.5012924	-2.2159799
C	2.1682446	4.1656011	-0.3058686
F	3.0159586	3.7991415	1.8782900
F	1.3141305	4.4375453	-2.4934646
C	3.6889998	-2.4873833	-0.7287156
F	3.6919389	-3.1383347	1.5481828
F	3.6149800	-1.7945547	-2.9930215
F	-4.5955289	-1.0136105	-3.2316934
F	2.8061656	5.3433523	-0.3842335
F	4.7689024	-3.2469516	-0.9723097
N	-0.4846484	-0.0408545	1.5201475
C	-1.6815510	0.7293025	1.8769694
C	-2.9340089	0.1566882	1.6774118
C	-1.5440911	2.0180632	2.3821535
C	-4.0755162	0.9024391	1.9701208
H	-3.0187199	-0.8573502	1.2979252
C	-2.6912713	2.7553131	2.6734925
H	-0.5610570	2.4426744	2.5547487
C	-3.9555166	2.2033543	2.4607266
H	-5.0558137	0.4628519	1.8160073
H	-2.5934157	3.7615993	3.0683090
H	-4.8453924	2.7831182	2.6851590
H	-0.6986451	-1.0355239	1.6262867
H	0.2549825	0.1541971	2.1996115

$PhNH_2$: aniline
14
Energy = -287.7864448520

C	0.9414573	0.0000537	-0.0143627
C	0.2221069	-1.2095604	-0.0082362
C	-1.1710645	-1.2034256	0.0001770
C	-1.8824289	-0.0001084	0.0030053
C	-1.1711977	1.2032897	-0.0002259
C	0.2219670	1.2095751	-0.0079320
H	0.7643080	-2.1524756	-0.0106488
H	-1.7044152	-2.1505216	0.0078158
H	-2.9680853	-0.0001624	0.0103187
H	-1.7046740	2.1503227	0.0063269
H	0.7640424	2.1525568	-0.0092717
N	2.3343817	0.0001235	-0.0937716
H	2.7871490	0.8385342	0.2532204
H	2.7872352	-0.8381556	0.2534239

$PhNH_3^+$: ammonium
15
Energy = -288.2213701460

N	2.3127260	0.0013032	-0.0002915
C	0.8292196	-0.0010073	0.0007324
C	0.1666789	-1.2222446	-0.0001169
C	0.1643686	1.2168601	0.0015244
C	-1.2279944	-1.2142765	-0.0005750
H	0.7191518	-2.1570239	-0.0014410
C	-1.2318335	1.2083389	0.0005935
H	0.7160916	2.1525602	0.0028463
C	-1.9242418	-0.0030490	-0.0007020
H	-1.7671812	-2.1558754	-0.0004486
H	-1.7716112	2.1495519	0.0008376
H	-3.0096122	-0.0046842	-0.0012429
H	2.6974834	-0.4656970	0.8290388
H	2.6817226	0.9581374	-0.0059651
H	2.6963309	-0.4750937	-0.8247821

$PhNHBf_3^-$: B-N borate anion
47
Energy = -2496.867237478

B	-0.1559690	0.1520630	-0.2209311
C	-1.2018822	-0.1172278	-1.4947114
C	0.6009296	1.6295718	-0.2226012
C	1.1501157	-0.8848353	-0.2694372
C	-1.3756606	-1.3755636	-2.0763431
C	-2.1374425	0.8252121	-1.9283729
C	1.2522832	2.0612133	0.9402888
C	0.7826228	2.4797142	-1.3166956
C	1.6397475	-1.6635198	0.7813717
C	1.9432332	-0.9421487	-1.4197526
C	-2.3430217	-1.6751746	-3.0327976
F	-0.5884896	-2.4285632	-1.7145165
C	-3.1223907	0.5767300	-2.8790031
F	-2.1390469	2.0849725	-1.4171253
C	1.9652464	3.2510911	1.0433348
F	1.2354119	1.2972556	2.0594772
C	1.4913988	3.6790722	-1.2595582
F	0.2734348	2.1816757	-2.5381132
C	2.8015987	-2.4327236	0.7052655
F	0.9938711	-1.7435084	1.9777967
C	3.1052372	-1.6929769	-1.5454296
F	1.5800061	-0.2337686	-2.5202027

C	-3.2274158	-0.6878311	-3.4450594
F	-2.4389279	-2.9200716	-3.5556149
F	-3.9815946	1.5510125	-3.2587579
C	2.0840329	4.0757897	-0.0687104
F	2.5544487	3.6079552	2.2069071
F	1.6164868	4.4584337	-2.3579517
C	3.5448074	-2.4510364	-0.4660950
F	3.2110384	-3.1657326	1.7655260
F	3.8091307	-1.6982150	-2.6997171
F	-4.1785054	-0.9546872	-4.3642054
F	2.7750365	5.2311658	0.0033176
F	4.6696771	-3.1884371	-0.5565554
N	-0.9880248	-0.1042603	1.0417106
C	-1.7801698	0.6879450	1.8288174
C	-2.4600210	0.1045905	2.9302591
C	-1.9595295	2.0781380	1.6325309
C	-3.2579388	0.8603952	3.7796471
H	-2.3397188	-0.9631207	3.1069330
C	-2.7602368	2.8241737	2.4930683
H	-1.4761678	2.5682470	0.7987005
C	-3.4214650	2.2362777	3.5754399
H	-3.7590555	0.3692230	4.6113628
H	-2.8708798	3.8908225	2.3078091
H	-4.0449365	2.8288978	4.2388327
H	-0.9991084	-1.0674796	1.3516304

$PhNHC_6H_4Bf_3^-$: B-C borate anion

57

Energy = -2728.045730602

B	-1.5602249	0.4796043	-2.2032602
C	-2.0183581	1.8506448	-3.0168754
C	-2.5199839	-0.6735748	-2.9095257
C	-1.7559041	0.6015420	-0.5620768
C	-3.3138738	2.3501528	-2.8512333
C	-1.2760771	2.5268724	-3.9865719
C	-2.2874232	-1.0227544	-4.2446931
C	-3.6431178	-1.2944335	-2.3579796
C	-1.6260069	-0.5392826	0.2375456
C	-1.8289355	1.7873451	0.1684508
C	-3.8391060	3.4325919	-3.5450646
F	-4.1471609	1.7625017	-1.9518248
C	-1.7590103	3.6194374	-4.7089975
F	-0.0124028	2.1510483	-4.3040140
C	-3.0489877	-1.9375633	-4.9650024
F	-1.2759855	-0.4330041	-4.9335239
C	-4.4381271	-2.2145149	-3.0400072
F	-4.0518724	-1.0191445	-1.0927603
C	-1.6131143	-0.5293025	1.6264596
F	-1.4863104	-1.7594452	-0.3432275
C	-1.8152695	1.8510246	1.5615034
F	-1.8911182	2.9968113	-0.4568888
C	-3.0489918	4.0804522	-4.4887092
F	-5.1013701	3.8645125	-3.3178310
F	-0.9823647	4.2314303	-5.6337580
C	-4.1374709	-2.5478505	-4.3539156
F	-2.7508342	-2.2317696	-6.251403
F	-5.5087876	-2.7820322	-2.4377997
C	-1.7122061	0.6823840	2.3024028
F	-1.5004282	-1.6796713	2.3309913
F	-1.8923274	3.0425792	2.1999163
F	-3.5312083	5.1332640	-5.1812547
F	-4.8944996	-3.4375658	-5.0282361
F	-1.6990553	0.7200778	3.6519565
N	4.1824539	-0.8297008	-2.0898987
H	4.4627796	-1.5555762	-2.7374510
C	2.8165755	-0.4933944	-2.1162926
C	5.1638194	-0.4177743	-1.1982694
C	2.3389182	0.7759118	-1.7517434
C	1.8940661	-1.4426500	-2.5765488
C	4.8795653	0.2463037	0.0113105
C	6.5108777	-0.7103156	-1.5003947
C	0.9778250	1.0524394	-1.8266875
H	3.0314915	1.5470174	-1.4294084
C	0.5375912	-1.1298923	-2.6617987
H	2.2468469	-2.4328297	-2.8603816
C	5.9140927	0.6153228	0.8694392
H	3.8509394	0.4503522	0.2856729
C	7.5317218	-0.3427017	-0.6303165
H	6.7436922	-1.2298563	-2.4274793
C	0.0302239	0.1225588	-2.2909093
H	0.6427781	2.0426691	-1.5214575
H	-0.1435730	-1.9038785	-3.0078344
C	7.2470646	0.3326031	0.5614171
H	5.6686959	1.1241592	1.7983523
H	8.5600643	-0.5811839	-0.8897757
H	8.0457357	0.6268173	1.2355852

TS0a : Bf_3-induced N-site H^+ transfer of two **315a**

82

Energy = -3247.469095316

B	0.1425372	-0.0590434	-0.8134978
C	-0.8282873	-0.5155199	-2.0753857
C	0.6487049	1.5216403	-0.9117872
C	1.6294916	-0.8031637	-0.8286687
C	-0.7565973	-1.7482573	-2.7367426
C	-1.8793146	0.2913804	-2.5424955
C	1.3196412	2.1025614	0.1680077
C	0.6875692	2.3194888	-2.0644755
C	2.3473267	-1.3049536	0.2532732
C	2.3745083	-0.7969778	-2.0174390
C	-1.6625760	-2.1825314	-3.7018615
F	0.2587905	-2.6234736	-2.5053040
C	-2.8057663	-0.0998842	-3.5038381
F	-2.0400081	1.5595205	-2.0996918
C	1.8774597	3.3740187	0.1869597
F	1.4745270	1.3878333	1.3166349
C	1.2407975	3.6002507	-2.1015993
F	0.2150015	1.8904623	-3.2561662
C	3.6517909	-1.7895769	0.1941923

F	1.7759484	-1.3746574	1.4881961
C	3.6757704	-1.2709645	-2.1351128
F	1.8314932	-0.3029341	-3.1546778
C	-2.7093472	-1.3566870	-4.0853079
F	-1.5201199	-3.3946682	-4.2779754
F	-3.7955291	0.7364256	-3.8798149
C	1.8298768	4.1444428	-0.9687240
F	2.4742273	3.8524875	1.2967286
F	1.2201652	4.3136901	-3.2455037
C	4.3297182	-1.7757233	-1.0161873
F	4.2539115	-2.2682288	1.3016619
F	4.3115354	-1.2416624	-3.3229671
F	-3.5958197	-1.7549601	-5.0145048
F	2.3642586	5.3768456	-0.9947990
F	5.5887058	-2.2357583	-1.1060448
N	-0.8116563	-0.3300530	0.5661771
H	-0.3738106	-0.0824811	1.9116392
C	-1.9842651	0.5559343	0.4963011
C	-1.2101991	-1.7199980	0.8351656
C	-3.2273498	0.1082758	0.0313246
C	-1.8452836	1.8914778	0.8723548
C	-2.2458305	-1.9693624	1.7514618
C	-0.5214867	-2.8108107	0.3112387
C	-4.3069684	0.9842331	-0.0446163
H	-3.3512064	-0.9237653	-0.2745641
C	-2.9255860	2.7694405	0.7897537
H	-0.8963907	2.2523489	1.2445912
C	-2.5864108	-3.2674077	2.1124794
H	-2.7906230	-1.1425276	2.1914122
C	-0.8611558	-4.1151581	0.6767490
H	0.2931635	-2.6631568	-0.3781405
C	-4.1628578	2.3205504	0.3330855
H	-5.2618318	0.6195616	-0.4118731
H	-2.7949427	3.8034405	1.0953708
C	-1.8956887	-4.3549113	1.5755233
H	-3.3840057	-3.4235026	2.8320332
H	-0.3029926	-4.9427054	0.2482429
H	-5.0060526	3.0021396	0.2719486
H	-2.1574584	-5.3695189	1.8601546
H	0.9930447	-0.1740976	2.9845615
N	-0.0070843	-0.0289596	3.1419557
C	-0.4534118	-1.1582970	3.9932877
C	0.2684859	-2.3497535	3.9352574
C	-1.5589631	-1.0426355	4.8322692
C	-0.1443633	-3.4428196	4.6934856
H	1.1329979	-2.4396671	3.2894215
C	-1.9626617	-2.1426590	5.5887979
H	-2.1091316	-0.1141393	4.9072742
C	-1.2644229	-3.3473436	5.5191100
H	0.4153784	-4.3709593	4.6334626
H	-2.8297777	-2.0483691	6.2353932
H	-1.5861262	-4.2015245	6.1067369
C	-0.1403777	1.2934477	3.7685556
C	1.0079528	1.9046936	4.2653820
C	-1.3804708	1.9199455	3.8639610
C	0.9180825	3.1640418	4.8563824
H	1.9701939	1.4069271	4.1813479
C	-1.4655772	3.1746276	4.4664079
H	-2.2666974	1.4560737	3.4483068
C	-0.3199804	3.7993721	4.9611758
H	1.8157151	3.6441094	5.2329358
H	-2.4309522	3.6659364	4.5371910
H	-0.3912712	4.7798752	5.4217230

TS0b : Bf_3-induced para H^+ transfer of two **315a**

82

Energy = -3247.452071286

B	-0.9852057	0.0472129	0.6342715
C	-1.7426458	1.4975820	0.3937057
C	-2.1474894	-1.0511508	0.2078660
C	-0.4468056	-0.1007450	2.2011210
C	0.4800502	-0.2146125	-0.1783774
C	-2.8834758	1.7841293	1.1536773
C	-1.4506762	2.4772601	-0.5496093
C	-2.5563458	-1.1026844	-1.1266112
C	-2.8947195	-1.8860266	1.0456532
C	-0.0268190	-1.3279053	2.7272832
C	-0.1569177	0.9829069	3.0354307
C	0.9066437	-1.5820054	-0.3071474
C	1.5372551	0.6868879	0.2095768
C	-3.6652845	2.9227821	1.0049671
F	-3.2745191	0.9207116	2.1254285
C	-2.2003565	3.6363359	-0.7440521
F	-0.3670570	2.3578511	-1.3713608
C	-3.5363896	-1.9471864	-1.6344802
F	-2.0100553	-0.2347803	-2.0230768
C	-3.8873102	-2.7526843	0.5889539
F	-2.7273619	-1.8766289	2.3893085
C	0.5919776	-1.4881521	3.9618738
F	-0.2002498	-2.4752320	2.0191453
C	0.4563761	0.8736761	4.2821777
F	-0.4351212	2.2596251	2.6533539
C	2.2143143	-1.9812559	-0.1567172
H	0.1612091	-2.3296570	-0.5625617
C	2.8435209	0.3075040	0.3936871
H	1.2813339	1.7267770	0.3928471
C	-3.3221528	3.8651178	0.0403548
F	-4.7472384	3.1283260	1.7852773
F	-1.8473249	4.5328271	-1.6906212
C	-4.2052656	-2.7980440	-0.7625615
F	-3.8575930	-1.9338040	-2.9447496
F	-4.5574307	-3.5425496	1.4549599
C	0.8349006	-0.3744606	4.7566561
F	0.9613926	-2.7130674	4.3952017
F	0.6961044	1.9735251	5.0292045
C	3.2179741	-1.0467597	0.2011448
H	2.4925510	-3.0237647	-0.2942880
H	3.5785068	1.0351912	0.7137932
F	-4.0640698	4.9754895	-0.1277702

F	-5.1615303	-3.6294904	-1.2151844
F	1.4319582	-0.5030905	5.9571558
N	4.4961625	-1.5044219	0.3606992
H	4.5934667	-2.5136567	0.3882777
C	5.6958283	-0.7884063	0.5575351
C	5.9334287	0.4635325	-0.0270291
C	6.7051242	-1.3994601	1.3159506
C	7.1559334	1.1013136	0.1752952
H	5.1828781	0.9253137	-0.6572176
C	7.9277566	-0.7591707	1.4997412
H	6.5235155	-2.3744625	1.7607057
C	8.1575158	0.4996415	0.9394240
H	7.3289146	2.0710946	-0.2825617
H	8.6995931	-1.2442100	2.0900655
H	9.1084353	1.0014825	1.0890798
H	0.4373894	0.0229769	-1.5652811
N	0.5420474	0.2418548	-2.9465767
H	-0.2759877	0.8355861	-3.0854626
C	1.7219226	1.0343411	-3.2658907
C	0.3423317	-0.9821003	-3.7123868
C	1.5386132	2.2991903	-3.8254319
C	3.0056101	0.5569055	-3.0064364
C	-0.7333306	-1.0393580	-4.5998756
C	1.1774177	-2.0862954	-3.5447663
C	2.6461314	3.0882617	-4.1343375
H	0.5345656	2.6667403	-4.0196378
C	4.1086242	1.3430642	-3.3351396
H	3.1502315	-0.4095474	-2.5407180
C	-0.9761033	-2.2054957	-5.3220685
H	-1.3831618	-0.1773226	-4.7203073
C	0.9332542	-3.2480979	-4.2778687
H	1.9974352	-2.0576803	-2.8398844
C	3.9348984	2.6094624	-3.8963630
H	2.4979118	4.0720204	-4.5688432
H	5.1081908	0.9629484	-3.1470730
C	-0.1416904	-3.3136630	-5.1645145
H	-1.8165541	-2.2441536	-6.0081042
H	1.5842136	-4.1068541	-4.1443361
H	4.7980215	3.2193481	-4.1444262
H	-0.3303886	-4.2231284	-5.7266670

TS0g : Bf_3-induced para H^+ of **315g** to **273a** C4

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Energy = -3346.956917129

B	-2.0492900	-0.0411248	0.1210950
C	-2.8475261	0.8767848	-1.0152232
C	-2.6676759	-1.5731355	0.0324940
C	-2.1928643	0.6295314	1.6311473
C	-4.1710612	0.6135962	-1.3932955
C	-2.3146053	1.9906502	-1.6665136
C	-2.5506772	-2.2859356	-1.1639551
C	-3.3465817	-2.2720508	1.0320111
C	-1.4908954	0.0752343	2.7093063
C	-2.8881700	1.7942869	1.9613863
C	-4.8704992	1.3231362	-2.3663550
F	-4.8961650	-0.3564976	-0.7777279
C	-2.9680694	2.7331197	-2.6461273
F	-1.0775820	2.4590558	-1.3384268
C	-3.0213187	-3.5776944	-1.3694895
F	-1.9425773	-1.7031704	-2.2357369
C	-3.8340072	-3.5692281	0.8789014
F	-3.6187743	-1.7003180	2.2324551
C	-1.4456784	0.6179389	3.9861557
F	-0.8072682	-1.0863688	2.5422337
C	-2.8755577	2.3778179	3.2297900
F	-3.6439844	2.4544898	1.0450455
C	-4.2624032	2.3910374	-3.0130434
F	-6.1419138	0.9928575	-2.6765165
F	-2.3579923	3.7861872	-3.2322565
C	-3.6682420	-4.2341679	-0.3291096
F	-2.8567742	-4.1970231	-2.5576688
F	-4.4809369	-4.1837142	1.8921739
C	-2.1458078	1.7904211	4.2529167
F	-0.7414669	0.0188202	4.9709525
F	-3.5678020	3.5124081	3.4697789
F	-4.9184700	3.0886710	-3.9577616
F	-4.1324433	-5.4868580	-0.4920809
F	-2.1202302	2.3390656	5.4820478
N	3.7749468	-0.6472346	0.7675889
C	2.4248172	-0.5115848	0.5408809
C	4.4949748	0.3495709	1.5127883
C	1.7933966	0.7562643	0.6816026
C	1.6176407	-1.6155948	0.1715584
C	4.0506092	0.7299983	2.7822497
C	5.6534971	0.9066110	0.9666847
C	0.4618857	0.9051406	0.4036849
H	2.3782761	1.6109446	1.0001863
C	0.2836119	-1.4396982	-0.1014182
H	2.0486914	-2.6095638	0.1450446
C	4.7621273	1.6909449	3.4982156
H	3.1595483	0.2715459	3.2005260
C	6.3607697	1.8628384	1.6918710
H	5.9910687	0.5913943	-0.0146709
C	-0.3720608	-0.1556950	-0.1104978
H	0.0303779	1.8922273	0.5195491
H	-0.2947997	-2.3244517	-0.3459476
C	5.9169886	2.2600006	2.9553461
H	4.4211716	1.9860019	4.4860059
H	7.2562205	2.3026894	1.2636770
H	-0.1120452	0.1134581	-1.4941352
H	6.4705397	3.0061726	3.5172192
C	0.2472566	0.2266962	-2.8792677
C	1.2915886	1.1436540	-2.8865693
H	-0.7395541	0.5519425	-3.1996707
H	0.4739538	-0.8217159	-3.0637373
H	1.0463622	2.2040929	-2.8445124
C	2.6662482	0.8055474	-2.8472181
C	3.6464065	1.7461193	-2.6991542
H	2.9247123	-0.2486042	-2.9198513

H	3.3343026	2.7856307	-2.5996365
C	5.0671506	1.5045321	-2.5838283
C	5.9048807	2.5696071	-2.1881947
C	5.6538069	0.2390109	-2.8054125
C	7.2680384	2.3728820	-1.9939350
H	5.4659679	3.5493566	-2.0190048
C	7.0137318	0.0440579	-2.6039683
H	5.0423093	-0.5899768	-3.1436097
C	7.8267409	1.1075178	-2.1926008
H	7.8953426	3.2023654	-1.6814995
H	7.4461777	-0.9386311	-2.7667046
H	8.8894820	0.9496683	-2.0352220
C	4.5323657	-1.7681089	0.3034485
C	5.5358693	-2.2989993	1.1228825
C	4.3211508	-2.3031041	-0.9724247
C	6.3176139	-3.3563828	0.6649079
H	5.7004997	-1.8812957	2.1105538
C	5.1010203	-3.3664751	-1.4192114
H	3.5503684	-1.8861858	-1.6095073
C	6.1046858	-3.8955292	-0.6059938
H	7.0917743	-3.7637782	1.3081142
H	4.9316503	-3.7713688	-2.4123671
H	6.7159873	-4.7200095	-0.9596703

TS0 : H^+ from $H_2O.Bf_3$ to **315a** Ph_2NH N-site

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Energy = -2805.009863155

B	-0.0340765	0.1675685	0.6474181
C	-1.4959483	0.0545976	1.4000651
C	0.3588749	-1.1393087	-0.2522107
C	1.1508812	0.5473890	1.7333010
O	-0.0668419	1.3380035	-0.3557995
C	-1.6498508	-0.3480296	2.7298708
C	-2.7018139	0.3513850	0.7627397
C	1.4935637	-1.1007948	-1.0690453
C	-0.3205301	-2.3573249	-0.2690687
C	1.2179881	1.8305508	2.2713825
C	2.1459817	-0.3136951	2.1970304
H	-0.3632481	2.1601304	0.0723480
H	-0.5160263	1.2698788	-1.5495172
C	-2.8757117	-0.4170584	3.3865666
F	-0.5761252	-0.7377074	3.4620869
C	-3.9510079	0.3004278	1.3724472
F	-2.7216024	0.6839312	-0.5632952
C	1.9340449	-2.1688681	-1.8402870
F	2.2576129	0.0208123	-1.1171353
C	0.0829047	-3.4540975	-1.0272967
F	-1.4375498	-2.5480108	0.4778729
C	2.1848878	2.2639894	3.1709100
F	0.2736013	2.7569362	1.9212864
C	3.1387631	0.0675369	3.0966800
F	2.1761728	-1.6147123	1.8123896
N	-0.9037220	1.3310066	-2.7270149
C	-4.0401302	-0.0826879	2.7052649
F	-2.9467464	-0.8107198	4.6737973
F	-5.0698334	0.6060142	0.6851895
C	1.2184295	-3.3605045	-1.8205575
F	3.0414345	-2.0657114	-2.6014029
F	-0.6308185	-4.5988859	-1.0172862
C	3.1634860	1.3683139	3.5868942
F	2.1837192	3.5278058	3.6411374
F	4.0733279	-0.8148448	3.5053735
H	-1.9232912	1.3397854	-2.6488103
C	-0.5281445	0.1336535	-3.4975879
C	-0.4649581	2.6123144	-3.2923237
F	-5.2331327	-0.1398143	3.3210586
F	1.6110998	-4.4015133	-2.5743163
F	4.1153423	1.7529569	4.4548468
C	-1.3462891	-0.9893485	-3.3941251
C	0.6226344	0.1214163	-4.2786192
C	-1.2552331	3.2440664	-4.2482753
C	0.7421304	3.1601356	-2.8653171
C	-1.0058797	-2.1448839	-4.0949157
H	-2.2390811	-0.9633031	-2.7752150
C	0.9535261	-1.0417987	-4.9751598
H	1.2495403	1.0027376	-4.3526036
C	-0.8302637	4.4601971	-4.7821630
H	-2.1890883	2.7933629	-4.5733643
C	1.1629522	4.3735045	-3.4121996
H	1.3414553	2.6432607	-2.1224594
C	0.1429518	-2.1732812	-4.8879196
H	-1.6418535	-3.0213347	-4.0195754
H	1.8504818	-1.0574913	-5.5858559
C	0.3785800	5.0232053	-4.3662589
H	-1.4425293	4.9635852	-5.5235399
H	2.1028620	4.8098168	-3.0887152
H	0.4054254	-3.0750189	-5.4318551
H	0.7081413	5.9686056	-4.7859328

TS1g : H^+ from $H_2O.Bf_3$ to **273a** C4-site

57

Energy = -2673.308662006

B	-0.9755340	0.0353333	0.6625380
C	-1.7486178	1.4020738	0.1575285
C	0.4849846	-0.2290830	-0.0402776
C	-2.0620952	-1.1919474	0.4142222
O	-0.6648652	0.0430545	2.1543940
C	-2.1818076	1.4977184	-1.1675530
C	-2.1105287	2.4877029	0.9518973
C	1.1729262	-1.4128235	0.2501868
C	1.1466868	0.6089553	-0.9370753
C	-3.1962947	-1.2586830	1.2245541
C	-2.0143052	-2.1717108	-0.5778294
H	-1.4520835	0.2490817	2.6871928
C	-2.8984602	2.5701432	-1.6823012
F	-1.8781111	0.5018149	-2.0389596
C	-2.8292652	3.5877620	0.4856054
F	-1.7797973	2.5305664	2.2751421
C	2.3802133	-1.7781202	-0.3345087

F	0.6368040	-2.3083950	1.1143273
C	2.3514406	0.2802058	-1.5579159
F	0.6510469	1.8321943	-1.2549538
C	-4.2001954	-2.2119682	1.1037556
F	-3.3756494	-0.3257533	2.2107143
C	-2.9953210	-3.1479250	-0.7442752
F	-0.9879266	-2.2205044	-1.4628689
C	-3.2271923	3.6317877	-0.8441445
F	-3.2705667	2.6002291	-2.9783306
F	-3.1464342	4.6048892	1.3138233
C	2.9677310	-0.9307624	-1.2679747
F	2.9774154	-2.9467459	-0.0239191
F	2.9364307	1.1363742	-2.4214250
C	-4.0962738	-3.1730933	0.1037733
F	-5.2647936	-2.2137389	1.9312367
F	-2.8885692	-4.0710433	-1.7220863
F	-3.9199966	4.6836186	-1.3154688
F	4.1222710	-1.2686138	-1.8633400
F	-5.0490599	-4.1109225	-0.0418470
C	1.1940576	1.5846080	3.2336577
H	0.5795975	2.4383555	3.5152057
H	1.4529379	0.9058169	4.0473489
H	0.3100882	0.8628383	2.5983185
C	2.1635690	1.7989005	2.2474516
C	3.2685237	0.9608060	2.0031115
H	2.0295466	2.6399979	1.5661234
H	3.4185760	0.1014935	2.6517333
C	4.1489137	1.2476187	0.9918672
H	3.9477179	2.1373355	0.3954967
C	5.3286428	0.5069069	0.6263160
C	6.1294003	0.9977168	-0.4277334
C	5.7008717	-0.6997942	1.2603115
C	7.2653788	0.3090334	-0.8346534
H	5.8424553	1.9225291	-0.9206932
C	6.8320408	-1.3863830	0.8468538
H	5.0970408	-1.0987824	2.0690486
C	7.6174529	-0.8845428	-0.1995226
H	7.8742769	0.6950861	-1.6461391
H	7.1095666	-2.3155774	1.3346886
H	8.5020914	-1.4276584	-0.5183243

TS1h$^+$: H^+ from ammonium **315h**H^+ to diene **273a**

48

Energy = -946.0264375808

N	0.8149519	-2.0592764	0.3569420
H	0.2014401	-1.5900625	1.4608703
C	0.4318741	-1.0187923	-0.5714681
C	0.2786926	-3.3962190	0.0680732
C	-0.9251281	-0.9237997	-0.9077059
C	1.3393135	-0.0453009	-0.9973755
C	-0.0952993	-4.2088774	1.1360138
C	0.1993492	-3.8488236	-1.2479240
C	-1.3713354	0.1530725	-1.6668786
H	-1.6204372	-1.6872929	-0.5746874
C	0.8790534	1.0291541	-1.7546709
H	2.3911731	-0.1122826	-0.7483135
C	-0.5691832	-5.4955281	0.8787327
H	-0.0155690	-3.8478449	2.1565567
C	-0.2763837	-5.1363220	-1.4946589
H	0.5013208	-3.2046545	-2.0673300
C	-0.4741983	1.1405204	-2.0781220
H	-2.4233643	0.2270846	-1.9230013
H	1.5828435	1.7868566	-2.0838018
C	-0.6629498	-5.9590606	-0.4346742
H	-0.8675595	-6.1309985	1.7065511
H	-0.3406111	-5.4946998	-2.5173552
H	-0.8259035	1.9888941	-2.6563995
H	-1.0351538	-6.9596082	-0.6318694
C	-0.3367695	-0.9301940	2.5562227
C	-0.9439700	0.1636627	1.9355100
H	0.5921003	-0.7564884	3.1017704
H	-0.9853932	-1.6999440	2.9692023
H	-1.9837375	0.0687739	1.6254153
C	-0.2971536	1.3806342	1.6122124
C	-0.9482465	2.3705151	0.9299258
H	0.7408457	1.5028058	1.9134682
H	-1.9887168	2.1910042	0.6615490
C	-0.4096791	3.6496187	0.5219020
C	-1.2552847	4.5490318	-0.1598160
C	0.9298112	4.0273360	0.7546645
C	-0.7822645	5.7821068	-0.5958391
H	-2.2878998	4.2642764	-0.3442355
C	1.4000040	5.2582554	0.3172427
H	1.6026433	3.3529300	1.2751542
C	0.5474674	6.1397769	-0.3594398
H	-1.4456161	6.4637057	-1.1197652
H	2.4332686	5.5373411	0.5002132
H	0.9211016	7.1008813	-0.6999500
C	2.2573858	-2.1138288	0.7375871
H	2.3686669	-2.9019215	1.4809293
H	2.8686019	-2.3420051	-0.1383669
H	2.5503566	-1.1560909	1.1694853

TS1w$^+$: H^+ from ammonium **315a**H^+ to diene **273u**

39

Energy = -752.9558033030

H	1.8117389	-0.5104309	0.2706994
N	0.7993545	-0.5869706	0.1538883
H	0.2428073	0.1782957	1.1629509
C	0.3834198	0.1541696	-1.0133815
C	0.3842638	-1.9767762	0.3025446
C	-0.9369959	0.0837430	-1.4629450
C	1.2923076	1.0467328	-1.5859576
C	-0.8773851	-2.2799581	0.8121593
C	1.2795371	-2.9836487	-0.0554819
C	-1.3455338	0.9251696	-2.4991639
H	-1.6308568	-0.6291108	-1.0325742
C	0.8701971	1.8858691	-2.6120729

H	2.3201673	1.0773316	-1.2349318
C	-1.2506462	-3.6174863	0.9486780
H	-1.5630095	-1.4932870	1.1076388
C	0.9002188	-4.3168980	0.0925552
H	2.2599289	-2.7277311	-0.4475296
C	-0.4518861	1.8325248	-3.0653544
H	-2.3687915	0.8696731	-2.8563741
H	1.5753123	2.5766341	-3.0632469
C	-0.3655206	-4.6347614	0.5897524
H	-2.2326130	-3.8596699	1.3425394
H	1.5942155	-5.1044289	-0.1833207
H	-0.7776764	2.4891229	-3.8660051
H	-0.6593609	-5.6736148	0.7016034
C	-0.3103950	1.0066648	2.0849205
C	-1.3167889	1.5774080	1.3068574
H	-0.6192423	0.2152896	2.7717330
H	-2.2325546	1.0186516	1.1269057
C	-1.1905712	2.8759221	0.7163835
C	-0.0243059	3.5600105	0.8192937
H	-2.0277979	3.2813913	0.1579428
H	0.0800444	4.5267007	0.3328010
C	1.1750128	2.9793265	1.5006928
H	1.7849576	3.7731910	1.9419742
H	1.8043897	2.5319207	0.7122484
C	0.8066951	1.9281772	2.5623159
H	1.6940640	1.3544573	2.8443911
H	0.4557005	2.4335936	3.4723879

TS1^{+} : H^{+} from ammonium **315a**H^{+} to diene **273a**

45

Energy = -906.6947198096

H	2.0509869	-2.3114064	-0.0408756
N	1.0429356	-2.2198046	0.0988461
H	0.8964628	-1.6722054	1.3301454
C	0.5259916	-1.1504889	-0.7258686
C	0.4077011	-3.5303643	0.0598483
C	-0.8439177	-1.0177133	-0.9510806
C	1.4273628	-0.1696795	-1.1526595
C	-0.7507688	-3.7629591	0.7993747
C	0.9911583	-4.5384306	-0.7055689
C	-1.3136965	0.1257916	-1.5962798
H	-1.5343103	-1.7902571	-0.6328061
C	0.9465388	0.9630831	-1.7985552
H	2.4908803	-0.2914963	-0.9653065
C	-1.3407710	-5.0265240	0.7564678
H	-1.1881984	-2.9777369	1.4061914
C	0.3980202	-5.8001023	-0.7353790
H	1.8961906	-4.3392402	-1.2721899
C	-0.4268960	1.1220404	-2.0048906
H	-2.3789092	0.2381163	-1.7715520
H	1.6409290	1.7293384	-2.1274579
C	-0.7694402	-6.0436929	-0.0093670
H	-2.2440015	-5.2128674	1.3284013
H	0.8488697	-6.5891916	-1.3287144
H	-0.8020406	2.0161720	-2.4925812
H	-1.2302258	-7.0261258	-0.0364953
C	0.7258300	-0.9771163	2.5085300
C	-0.1297725	0.0395687	2.0753945
H	1.7618203	-0.7148983	2.7249792
H	0.3046383	-1.7723626	3.1213827
H	-1.2014771	-0.1605879	2.0584330
C	0.2816004	1.3022249	1.5893999
C	-0.6228805	2.2059109	1.1028952
H	1.3438212	1.5341611	1.6105819
H	-1.6727253	1.9140713	1.1060272
C	-0.3429493	3.5284237	0.5889118
C	-1.4229173	4.3223100	0.1499813
C	0.9643900	4.0511881	0.4896895
C	-1.2074092	5.5929452	-0.3727236
H	-2.4323104	3.9253165	0.2219114
C	1.1766211	5.3195821	-0.0330219
H	1.8134463	3.4603175	0.8191594
C	0.0932842	6.0950518	-0.4658237
H	-2.0488075	6.1923463	-0.7072000
H	2.1867554	5.7115605	-0.1058273
H	0.2657754	7.0863230	-0.8743193

TS2a^{+} : addition of **273a**H^{+} C1 to amine **315a** para

45

Energy = -906.6973814946

N	-2.8068634	1.1952793	0.0274894
C	-3.8434734	0.2359415	-0.1002668
C	-1.5444700	1.0275558	0.4760574
H	-3.0436979	2.1331051	-0.2836063
C	-4.6920079	0.3307815	-1.2102472
C	-4.0623146	-0.7424179	0.8773146
C	-0.7351464	2.1931080	0.6480973
C	-0.9820538	-0.2544953	0.7536508
C	-5.7417872	-0.5725203	-1.3539500
H	-4.5199915	1.1023618	-1.9553285
C	-5.1101806	-1.6466382	0.7167188
H	-3.4465002	-0.7733914	1.7694371
C	0.5554665	2.0810095	1.0760057
H	-1.1748957	3.1671603	0.4527978
C	0.3154067	-0.3507444	1.1720848
H	-1.5787996	-1.1472324	0.6153670
C	-5.9483710	-1.5696292	-0.3975312
H	-6.3956150	-0.4992670	-2.2175061
H	-5.2810342	-2.4022342	1.4773571
C	1.1665926	0.7989400	1.2868388
H	1.1518328	2.9758478	1.2202403
H	0.7342949	-1.3311637	1.3743842
H	-6.7659052	-2.2743690	-0.5132204
H	2.0034618	0.7406654	1.9771943
C	3.2640846	2.8725579	-0.8349825
C	4.2692548	3.9718620	-0.7730072
H	2.3892343	3.0439570	-1.4640821
C	3.3701827	1.6944112	-0.1900027

H	4.6502774	4.2003229	-1.7767582
H	5.1105448	3.7177986	-0.1229240
H	3.8007450	4.8947428	-0.4055130
C	2.3912430	0.6286145	-0.3429063
H	4.2373357	1.5045389	0.4391414
H	1.6200527	0.8254186	-1.0854799
C	2.8382018	-0.7741384	-0.3064579
C	2.2177016	-1.7054164	-1.1580564
C	3.8624757	-1.2133921	0.5503246
C	2.6208700	-3.0373160	-1.1659036
H	1.4224771	-1.3722475	-1.8197077
C	4.2559398	-2.5485099	0.5497873
H	4.3448522	-0.5155012	1.2283583
C	3.6394253	-3.4632957	-0.3089657
H	2.1420136	-3.7436386	-1.8373945
H	5.0451649	-2.8775185	1.2190024
H	3.9507787	-4.5035884	-0.3089181

TS2g^{+} : addition of **273a**H^{+} C3 to **315g** Ph_3N para

55

Energy = -1137.887562409

N	-2.5093437	-0.1639171	0.2346291
C	-2.7114670	-1.5869299	0.2406685
C	-1.3705839	0.4001027	0.7280339
C	-3.1162391	-2.2237816	-0.9353505
C	-2.5433655	-2.3081599	1.4261573
C	-1.3414802	1.7797685	1.0906821
C	-0.1856657	-0.3829311	0.9035947
C	-3.3375193	-3.5991275	-0.9243911
H	-3.2510739	-1.6454459	-1.8437829
C	-2.7628165	-3.6844268	1.4247648
H	-2.2563558	-1.7919617	2.3370072
C	-0.1923202	2.3430705	1.5729584
H	-2.2542097	2.3610547	1.0347204
C	0.9628475	0.2019244	1.3485594
H	-0.2030152	-1.4359811	0.6490456
C	-3.1591176	-4.3315962	0.2521339
H	-3.6461475	-4.0992872	-1.8371500
H	-2.6375517	-4.2471745	2.3445464
C	1.0433320	1.6124021	1.6245724
H	-0.2132372	3.3714975	1.9177008
H	1.8651369	-0.3956815	1.4339742
H	-3.3342253	-5.4031927	0.2560736
H	1.7908003	1.9447697	2.3402726
C	2.0926000	2.2806518	0.0332990
C	2.0486592	3.7829563	0.1709530
H	1.4338566	1.8693590	-0.7305273
C	3.3903211	1.6508322	0.1232898
H	2.6230471	4.2151112	-0.6602901
H	2.5150242	4.1178062	1.1026794
H	1.0307427	4.1727793	0.1154076
C	3.7067901	0.5260720	-0.5671879
H	4.1247410	2.1278547	0.7695875
H	2.9320710	0.0896621	-1.1989089
C	4.9797675	-0.1723642	-0.5786749
C	5.1115416	-1.3148088	-1.3940951
C	6.0900672	0.2365855	0.1900722
C	6.3065597	-2.0267875	-1.4411617
H	4.2632524	-1.6353054	-1.9939590
C	7.2811762	-0.4758717	0.1422362
H	6.0180105	1.1136783	0.8262435
C	7.3957556	-1.6090158	-0.6733780
H	6.3901332	-2.9043111	-2.0752452
H	8.1279333	-0.1512502	0.7397902
H	8.3304076	-2.1608896	-0.7071509
C	-3.5688467	0.6352315	-0.3157420
C	-4.8828794	0.4088977	0.1014406
C	-3.2819112	1.5956063	-1.2900183
C	-5.9137956	1.1649038	-0.4517346
H	-5.0888451	-0.3473809	0.8519977
C	-4.3195593	2.3491006	-1.8337355
H	-2.2588572	1.7368985	-1.6239005
C	-5.6354008	2.1368414	-1.4158896
H	-6.9352040	0.9967515	-0.1248938
H	-4.1006488	3.0915064	-2.5948292
H	-6.4422624	2.7224131	-1.8451274

TS2ha^{+} : addition of **273a**H^{+} C1 to amine **315h** para

48

Energy = -946.0265943000

N	-2.7124473	1.1539728	-0.0756293
C	-3.6246175	0.0422190	-0.1068220
C	-1.4597505	1.0343145	0.4140632
C	-4.1436919	-0.3869408	-1.3303590
C	-4.0083902	-0.5717798	1.0881928
C	-0.6386923	2.1930351	0.5968884
C	-0.9101446	-0.2493201	0.7382528
C	-5.0480385	-1.4478688	-1.3547367
H	-3.8353976	0.0980041	-2.2515960
C	-4.9095825	-1.6349966	1.0530433
H	-3.6089923	-0.2125108	2.0316226
C	0.6421220	2.0657324	1.0559389
H	-1.0415567	3.1776478	0.3960621
C	0.3742339	-0.3577560	1.1840639
H	-1.5222733	-1.1344023	0.6166699
C	-5.4299195	-2.0741349	-0.1661033
H	-5.4484434	-1.7880930	-2.3047129
H	-5.2112400	-2.1120410	1.9804767
C	1.2388066	0.7839731	1.2917903
H	1.2423727	2.9572905	1.2061646
H	0.7733591	-1.3394702	1.4172656
H	-6.1341364	-2.9001196	-0.1898663
H	2.0686253	0.7283075	1.9906176
C	3.4023697	2.8192966	-0.8223815
C	4.4281321	3.8991314	-0.7524615
H	2.5387527	3.0055803	-1.4626067
C	3.4766776	1.6423592	-0.1709863
H	4.8236902	4.1181520	-1.7526898

H	5.2577560	3.6299477	-0.0934880
H	3.9743473	4.8317543	-0.3910999
C	2.4796590	0.5950468	-0.3320142
H	4.3334751	1.4374684	0.4675066
H	1.7167841	0.8058182	-1.0792794
C	2.8955955	-0.8164224	-0.2887018
C	2.2557529	-1.7372799	-1.1375838
C	3.9068001	-1.2756924	0.5731268
C	2.6267725	-3.0785158	-1.1372179
H	1.4701776	-1.3881831	-1.8025433
C	4.2682756	-2.6197064	0.5804268
H	4.4036810	-0.5861398	1.2491621
C	3.6324219	-3.5241860	-0.2752409
H	2.1330978	-3.7767659	-1.8064131
H	5.0473239	-2.9641325	1.2538711
H	3.9188724	-4.5716193	-0.2687447
C	-3.2243884	2.4530822	-0.5507854
H	-3.3789249	3.1324414	0.2935043
H	-2.5251757	2.9001123	-1.2610253
H	-4.1790023	2.2763031	-1.0421140

TS2h^{+} : addition of **273a**H^{+} C3 to amine **315h** para

48

Energy = -946.0278922285

N	-3.2801737	0.6203006	-0.3356353
C	-3.5914823	-0.7639612	-0.1232306
C	-2.1687042	1.1944717	0.1928189
C	-3.7872626	-1.6045448	-1.2225783
C	-3.7291533	-1.2545220	1.1790693
C	-2.0009565	2.6097394	0.1687963
C	-1.1251760	0.3972857	0.7626268
C	-4.1132399	-2.9438835	-1.0135107
H	-3.6741148	-1.2153740	-2.2299243
C	-4.0485609	-2.5966455	1.378561
H	-3.5947237	-0.5851252	2.0232226
C	-0.8576631	3.1826549	0.6724447
H	-2.7930832	3.2428454	-0.2109594
C	0.0133869	0.9848451	1.2403261
H	-1.2397387	-0.6794881	0.7961016
C	-4.2412595	-3.4430699	0.2846187
H	-4.2590557	-3.5986074	-1.8672453
H	-4.1581903	-2.9761460	2.3899240
C	0.2237147	2.3918908	1.1503392
H	-0.7775552	4.2645799	0.6949638
H	0.8017102	0.3599806	1.6482287
H	-4.4938713	-4.4870454	0.4429566
H	0.9879702	2.8560777	1.7644519
C	1.5690426	2.4709747	-0.5909350
C	1.7989469	3.9459329	-0.7228490
H	0.8037730	2.0355657	-1.2298329
C	2.6651981	1.6271524	-0.2518886
H	2.4480878	4.1019057	-1.5970094
H	2.3227722	4.3562566	0.1455049
H	0.8745794	4.4982715	-0.8929316
C	2.6975262	0.3084107	-0.6053320
H	3.4957287	2.0765724	0.2883846
H	1.8353388	-0.0843674	-1.1453630
C	3.7574547	-0.6411354	-0.3557842
C	3.5999899	-1.9628613	-0.8259131
C	4.9402209	-0.3093082	0.3422156
C	4.5834895	-2.9207935	-0.6055920
H	2.6953513	-2.2252836	-1.3685422
C	5.9198619	-1.2678043	0.5597998
H	5.0882964	0.7002885	0.7124119
C	5.7463476	-2.5757208	0.0879446
H	4.4472556	-3.9333853	-0.9726985
H	6.8246993	-1.0021403	1.0980017
H	6.5171975	-3.3206527	0.2614256
C	-4.2589764	1.4264094	-1.0844548
H	-4.8058149	2.0915235	-0.4073576
H	-3.7552585	2.0185984	-1.8521843
H	-4.9659333	0.7459494	-1.5553805

TS2la^{+} : addition of **273a**H^{+} C3 to amine **315l** para

45

Energy = -831.6645133299

N	0.7580244	0.3553798	1.8173308
C	0.7458907	-0.7645826	1.0770976
C	1.8773730	-1.1229798	0.2693517
C	-0.3996937	-1.6446409	1.1009013
C	1.8434219	-2.2363705	-0.5230091
H	2.7830597	-0.5315422	0.3260543
C	-0.4006364	-2.7464141	0.2923778
C	0.6479213	-3.0002025	-0.6541788
H	2.7145708	-2.5036357	-1.1127071
H	-1.2623265	-3.4095423	0.3103116
H	0.7070592	-3.9846761	-1.1072924
C	-0.1483856	-2.1073632	-2.3811158
C	-1.1414142	-3.1391090	-2.8419124
H	0.7992262	-2.1017213	-2.9160033
C	-0.6094375	-0.8348719	-1.9233762
H	-1.4996892	-2.8480446	-3.8393912
H	-2.0086193	-3.1914981	-2.1777690
H	-0.6914605	-4.1307970	-2.9289606
C	0.1997473	0.2593299	-1.8563771
H	-1.6298911	-0.7820382	-1.5500525
H	1.2046813	0.1725513	-2.2671081
C	-0.1419211	1.5618754	-1.3098008
C	0.7782447	2.6187033	-1.4522189
C	-1.3381664	1.8044687	-0.6041364
C	0.5174972	3.8725038	-0.9071206
H	1.7047374	2.4415006	-1.9931398
C	-1.5970945	3.0560119	-0.0585833
H	-2.0629299	1.0063710	-0.4756309
C	-0.6694083	4.0942055	-0.2040045
H	1.2392285	4.6750977	-1.0250163
H	-2.5215550	3.2276410	0.4853721
H	-0.8734413	5.0691410	0.2286634

C	1.8494313	1.3318412	1.7478054
H	2.6618957	1.0564766	2.4293256
H	2.2292909	1.4087948	0.7303779
H	1.4478019	2.3020123	2.0440284
C	-0.2796386	0.6632021	2.8237811
H	-0.9469783	1.4253908	2.4021279
H	0.2373528	1.1105621	3.6775645
C	-1.0526218	-0.5770278	3.2449482
H	-1.8814246	-0.2729103	3.8894860
H	-0.4001019	-1.2378451	3.8270677
C	-1.5588655	-1.3090683	2.0019609
H	-2.2652815	-0.6603124	1.4646979
H	-2.1006552	-2.2223303	2.2646502

TS2l^{+}o : addition of **273a**H^{+} C1 to amine **315l** ortho

45

Energy = -831.6525481960

N	-2.1915167	0.9310888	-0.5494825
C	-1.4510608	0.5873902	0.5145884
C	-0.0519461	0.9698747	0.6019770
C	-1.9877985	-0.2653480	1.5376038
C	0.5972211	0.8618165	1.8905596
H	0.2810731	1.7895007	-0.0247165
C	-1.2494452	-0.4600880	2.6809198
C	0.0288208	0.1360451	2.8910970
H	1.5811577	1.3032438	2.0009894
H	-1.6748810	-1.0775171	3.4681543
H	0.5331951	0.0002449	3.8417251
C	-0.9042187	-1.3597904	-1.9222514
C	-1.5216712	-1.5401475	-3.2669485
H	-1.3737838	-1.8896532	-1.0924327
C	0.2057431	-0.6354986	-1.6744541
H	-1.5140115	-2.5999721	-3.5521190
H	-0.9995731	-0.9627356	-4.0343434
H	-2.5783278	-1.2383570	-3.2525746
C	0.8047513	-0.5341500	-0.3524039
H	0.6952776	-0.1143227	-2.4949211
H	0.4761124	-1.3049087	0.3439591
C	2.2546937	-0.2428396	-0.2632284
C	3.0327755	-0.9340157	0.6784406
C	2.8729442	0.7083516	-1.0899069
C	4.4010423	-0.6922642	0.7811912
H	2.5581617	-1.6671471	1.3248351
C	4.2386800	0.9566067	-0.9804001
H	2.2864228	1.2663595	-1.8149254
C	5.0070445	0.2554355	-0.0465359
H	4.9935336	-1.2410676	1.5071544
H	4.7052101	1.6969453	-1.6232051
H	6.0723814	0.4491849	0.0359642
C	-1.7295626	1.8835456	-1.5682055
H	-1.9265980	2.9083156	-1.2339360
H	-0.6702418	1.7592753	-1.7776224
H	-2.2880095	1.6925575	-2.4851326
C	-3.6281391	0.5789237	-0.6718257
H	-3.7135483	-0.2317592	-1.4048850
H	-4.1254915	1.4567814	-1.0917730
C	-4.2510084	0.1843215	0.6575789
H	-5.2504665	-0.2155337	0.4672163
H	-4.3579300	1.0703945	1.2927611
C	-3.3629878	-0.8476786	1.3554528
H	-3.3061958	-1.7552298	0.7380127
H	-3.7759597	-1.1419195	2.3236293

TS2l^{+} : addition of **273a**H^{+} C1 to amine **215l** para

45

Energy = -831.6598342943

N	-2.7077412	-0.2898564	0.3850293
C	-1.4800376	-0.7127983	0.7065945
C	-0.9093121	-0.3827596	1.9842982
C	-0.7139501	-1.5223418	-0.2180419
C	0.3899723	-0.6826632	2.2556823
H	-1.5261115	0.0912975	2.7373522
C	0.5848708	-1.8031007	0.0886444
C	1.2409894	-1.2412160	1.2408528
H	0.8139832	-0.4289918	3.2224621
H	1.1749252	-2.3929061	-0.6084425
H	2.1651193	-1.7078900	1.5660807
C	4.4495911	-0.2729428	0.0618468
C	5.5764597	-0.7688921	-0.7831858
H	4.6914951	-0.0075977	1.0923447
C	3.1809231	-0.1252907	-0.3584496
H	6.3777954	-0.0207075	-0.8363470
H	5.2472229	-1.0056795	-1.7988176
H	6.0221031	-1.6679956	-0.3372991
C	2.1197139	0.3927585	0.5050598
H	2.9251119	-0.3907308	-1.3822467
H	2.4867896	0.7625975	1.4613193
C	1.0334702	1.2089828	-0.0545488
C	0.4033192	2.1668314	0.7613797
C	0.5616197	1.0382289	-1.3692868
C	-0.6497393	2.9391238	0.2776564
H	0.7546424	2.3073824	1.7798390
C	-0.4962967	1.8039241	-1.8508937
H	1.0226654	0.3029255	-2.0206342
C	-1.1093136	2.7520048	-1.0276893
H	-1.1141995	3.6819856	0.9192261
H	-0.8441420	1.6610107	-2.8696623
H	-1.9357161	3.3472731	-1.4049240
C	-3.4591990	0.6343091	1.2430329
H	-3.9386715	0.0966628	2.0680542
H	-2.7950485	1.4034915	1.6388256
H	-4.2275701	1.1080586	0.6320778
C	-3.4104744	-0.7476157	-0.8329720
H	-3.2988873	0.0236418	-1.6051211
H	-4.4704624	-0.8135098	-0.5751126
C	-2.8765447	-2.0877388	-1.3140165
H	-3.3690060	-2.3461118	-2.2551343
H	-3.1238196	-2.8637392	-0.5806719

C -1.3621819 -1.9957381 -1.4944996
H -1.1393052 -1.2827681 -2.2997274
H -0.9336220 -2.9577905 -1.7895355

TS2^{+}m : addition of **273a**H^{+} C3 to amine **315a** meta

45

Energy = -906.6751465456

N 3.4622968 0.9067919 -0.0841772
C 4.6700935 0.1947435 0.0772021
C 2.2162711 0.4013054 -0.3818634
H 3.5016241 1.8966040 0.1262811
C 5.5925927 0.6462567 1.0311911
C 4.9914726 -0.9055444 -0.7302124
C 1.1844535 1.2652126 -0.7458985
C 1.9153632 -0.9839616 -0.3133632
C 6.8186681 0.0003882 1.1772897
H 5.3453294 1.5039410 1.6511043
C 6.2118937 -1.5574135 -0.5608604
H 4.3088867 -1.2325393 -1.5084547
C -0.1568230 0.7928617 -0.9824415
H 1.3828984 2.3291651 -0.8285322
C 0.6586308 -1.4895779 -0.6705416
H 2.6779964 -1.6731849 0.0325734
C 7.1304475 -1.1119635 0.3922472
H 7.5265509 0.3625187 1.9170883
H 6.4503305 -2.4081234 -1.1925538
C -0.3600066 -0.6384032 -1.0307268
H -0.6781459 1.3590151 -1.7589346
H 0.4956952 -2.5612546 -0.6312329
H 8.0819987 -1.6200123 0.5144377
H -1.3509615 -1.0150066 -1.2589862
C -1.1758762 1.3253780 0.3776002
C -0.8790700 2.8020832 0.6119897
H -0.8286862 0.6980230 1.1991579
C -2.5788210 1.0642836 0.0245901
H -1.5788257 3.1670214 1.3715348
H -1.0287604 3.3937768 -0.2961697
H 0.1373026 2.9552061 0.9797000
C -3.3055380 0.0837570 0.6031323
H -3.0270140 1.7396090 -0.7027828
H -2.7975407 -0.5769677 1.3074801
C -4.7155135 -0.2105764 0.3889962
C -5.2721763 -1.3319334 1.0350253
C -5.5475837 0.5711025 -0.4386502
C -6.6101413 -1.6713916 0.8522788
H -4.6408327 -1.9361786 1.6817505
C -6.8821518 0.2308016 -0.6198743
H -5.1478099 1.4473915 -0.9400193
C -7.4192556 -0.8912376 0.0236220
H -7.0220309 -2.5410331 1.3555164
H -7.5118880 0.8412069 -1.2604393
H -8.4639701 -1.1508531 -0.1196372

TS2na^{+} : addition of **273q**H^{+} C3 to amine **315a** para

51

Energy = -910.3186513868

C 0.9426936 3.6714744 0.9426548
C 1.1877718 2.2319046 0.6258614
H 1.4850653 3.8959123 1.8739828
H 1.3476214 4.3340968 0.1720901
H 0.5485666 1.4995984 1.1133218
C 2.5095051 1.8035894 0.2948569
C 2.9308827 0.5306141 0.5046841
H 3.2034288 2.5451173 -0.0988302
H 2.2122800 -0.1938890 0.8941169
C 4.2985407 0.0205514 0.2409369
C 4.9146736 -0.6065751 1.5155063
C 4.2458373 -1.0397034 -0.8940203
H 4.9374243 0.8493949 -0.0913568
C 6.3043956 -1.1889812 1.2305807
H 4.2466436 -1.4016151 1.8750709
H 4.9702625 0.1521893 2.3040266
C 5.6396924 -1.6186354 -1.1690723
H 3.5619502 -1.8454834 -0.5936059
H 3.8351764 -0.5826635 -1.8013465
C 6.2568090 -2.2224929 0.0982622
H 6.7041014 -1.6422369 2.1451935
H 6.9868247 -0.3740843 0.9518019
H 5.5672031 -2.3758354 -1.9586451
H 6.2919774 -0.8200043 -1.5482717
H 7.2644790 -2.5974586 -0.1147233
H 5.6541991 -3.0840140 0.4192721
H -0.1110924 3.8929419 1.1102871
N -2.7173745 -1.0641220 -0.4033792
H -2.3152549 -1.9930409 -0.4779622
C -4.0622736 -1.0246223 0.0337549
C -4.9796874 -0.0975023 -0.4780522
C -4.4811712 -1.9903086 0.9591491
C -6.3000148 -0.1209559 -0.0328608
H -4.6758952 0.6090196 -1.2423757
C -5.8058590 -2.0107611 1.3876196
H -3.7659581 -2.7130842 1.3422422
C -1.8797609 -0.0351798 -0.6991811
C -6.7180078 -1.0704175 0.9020831
H -7.0082897 0.5969525 -0.4353197
H -6.1231575 -2.7595151 2.1070206
C -0.6111060 -0.3539452 -1.2685795
C -2.1966360 1.3257754 -0.4458185
H -7.7493504 -1.0851378 1.2405548
C 0.2831917 0.6378109 -1.5711633
H -0.3758081 -1.3948365 -1.4742585
C -1.2852205 2.3092185 -0.7541686
H -3.1464422 1.5884164 0.0023112
C 0.0012078 1.9991874 -1.2713570
H 1.2377577 0.3783201 -2.0169644
H -1.5503752 3.3455459 -0.5723522
H 0.6001082 2.7815195 -1.7247298

TS2n$^+$: addition of **273q**H$^+$ C1 to amine **315a** para

51

Energy = -910.3275346240

C	-0.5875094	2.2614823	2.0346140
C	0.4541449	1.1981379	1.9521899
H	-0.3180696	3.0081345	2.7923045
H	-0.7322466	2.7638492	1.0745618
H	0.6598653	0.6409374	2.8656874
C	1.1679426	0.9068101	0.8436075
C	2.1596508	-0.1417693	0.7786474
H	0.9665792	1.4548550	-0.0762086
H	2.4952789	-0.5225129	1.7433040
C	3.2613709	0.0023513	-0.2491557
C	4.0983550	1.2407190	0.1895023
C	4.1855841	-1.2162559	-0.3961901
H	2.8116894	0.2387918	-1.2234376
C	5.2538516	1.5104511	-0.7829177
H	4.4981712	1.0545335	1.1958152
H	3.4438178	2.1158585	0.2589229
C	5.3523640	-0.9383081	-1.3544109
H	4.5770379	-1.4856153	0.5950760
H	3.6260050	-2.0812156	-0.7679054
C	6.1640447	0.2865056	-0.9201369
H	5.8232483	2.3782716	-0.429875
H	4.8426479	1.7730349	-1.7673939
H	5.9941356	-1.8247638	-1.4116058
H	4.9526542	-0.7679622	-2.3640547
H	6.9644134	0.4862603	-1.6419497
H	6.6452666	0.0813702	0.0465013
H	-1.5455806	1.8328580	2.3583290
N	-2.7855809	-0.4385961	0.8459987
H	-3.0948592	-0.4537817	1.8131893
C	-3.6993394	0.1339663	-0.0824276
C	-3.9697088	-0.4842882	-1.3078670
C	-4.3686525	1.3068401	0.2828628
C	-4.8875340	0.0978457	-2.1805759
H	-3.4917131	-1.4243672	-1.5621347
C	-5.2939811	1.8726253	-0.5914546
H	-4.1584275	1.7721015	1.2415635
C	-1.5557203	-0.9411442	0.6091015
C	-5.5486201	1.2762968	-1.8286244
H	-5.0977393	-0.3836513	-3.1306669
H	-5.8104817	2.7842085	-0.3071396
C	-0.8707913	-1.5768836	1.6929582
C	-0.9241752	-0.8679837	-0.6693423
H	-6.2665867	1.7218136	-2.5101606
C	0.3952023	-2.0555632	1.5210306
H	-1.3913748	-1.6961890	2.6390209
C	0.3487576	-1.3393914	-0.8211648
H	-1.4468734	-0.4202596	-1.5049949
C	1.1026727	-1.8287668	0.2982131
H	0.9022934	-2.5534677	2.3416027
H	0.8316088	-1.2686145	-1.7909876
H	1.9753170	-2.4416440	0.1024517

TS2w$^+$p : addition of **273u**H$^+$ to amine **315a** para

39

Energy = -752.9721195171

N	1.0137024	-1.6765718	-0.3446186
H	1.7601059	-1.5925856	-1.0281301
C	0.7432725	-0.5628904	0.3713353
C	-0.3927103	-0.4456586	1.2294399
C	1.6294455	0.5477423	0.2352291
C	-0.6051073	0.7180697	1.9168174
H	-1.0791936	-1.2770767	1.3335701
C	1.4003238	1.7068026	0.9214180
H	2.5011266	0.4448799	-0.4055134
C	0.3757087	-2.9434649	-0.2980730
C	0.2299845	1.8678105	1.7298264
H	-1.4654848	0.7962671	2.5756326
H	2.0919654	2.5382799	0.8238169
C	0.1770481	-3.6245491	-1.5050324
C	0.0123084	-3.5362653	0.9168309
H	0.2379345	2.6256243	2.5065746
C	-0.4052536	-4.8897313	-1.4954140
H	0.4733091	-3.1601024	-2.4412153
C	-0.5812914	-4.7972244	0.9125635
H	0.2231890	-3.0345366	1.8548861
C	-0.7961221	-5.4754037	-0.2891394
H	-0.5600808	-5.4147634	-2.4328160
H	-0.8585911	-5.2569662	1.8560311
H	-1.2513705	-6.4607621	-0.2844420
C	-1.0087073	3.0284969	0.5273207
C	-0.4709638	4.3705644	0.6257536
C	-0.0624044	5.0490338	-0.4695041
C	-0.0622989	4.4665053	-1.8478837
C	-0.0651724	2.9352114	-1.8211382
C	-1.0976114	2.3890392	-0.8286044
H	0.2205893	6.0944795	-0.3615496
H	-0.4791893	4.8567293	1.5976813
H	-1.8428486	2.8235962	1.1931296
H	0.8046150	4.8408458	-2.4043541
H	-0.2635893	2.5331903	-2.8196777
H	0.9306679	2.5899928	-1.5283458
H	-2.1189544	2.5784758	-1.1926437
H	-1.0196987	1.2979207	-0.7415489
H	-0.9428860	4.8533094	-2.3831001

TS2w$^+$: addition of **273u**H$^+$ to amine **315a** ortho

39

Energy = -752.9719281582

N	0.5529356	0.3790700	-1.1883063
H	0.5392738	-0.0082042	-2.1270273
C	-0.6087840	0.9291472	-0.7614495
C	-0.8496874	1.2508494	0.6225744
C	-1.6661977	1.1106422	-1.6863771

C	-2.0230549	2.0003027	0.9582840
H	-0.0040565	1.3135061	1.2949104
C	-2.8336432	1.7253206	-1.2923742
H	-1.5242511	0.8052539	-2.7190868
C	1.8358386	0.4330777	-0.5756203
C	-3.0140839	2.2018397	0.0348871
H	-2.1309406	2.3518065	1.9794825
H	-3.6222468	1.8763288	-2.0232962
C	2.7070156	-0.6448803	-0.7650294
C	2.2550645	1.5577655	0.1427314
H	-3.9244670	2.7284204	0.2995022
C	3.9842533	-0.6084732	-0.2125708
H	2.3748739	-1.5100178	-1.3314975
C	3.5298849	1.5769586	0.7070467
H	1.6061916	2.4218578	0.2373965
C	4.3966867	0.4962248	0.5371449
H	4.6547798	-1.4494896	-0.3607861
H	3.8498237	2.4517099	1.2649806
H	5.3894382	0.5186379	0.9755542
C	-0.0865348	-2.5345092	0.5263011
C	-0.1495739	-1.3876242	1.2436649
C	-1.3780443	-0.6439703	1.3639615
C	-2.6076823	-1.1705580	0.6868098
C	-2.3061370	-2.0441942	-0.5359538
C	-1.2420725	-3.1021402	-0.2304856
H	-1.5440786	-0.1729487	2.3287680
H	0.7151261	-1.0500575	1.8074998
H	0.8302514	-3.1197822	0.5587507
H	-3.2861802	-0.3487309	0.4288929
H	-3.2276084	-2.5184410	-0.8850866
H	-1.9488045	-1.4086186	-1.3517090
H	-1.6631514	-3.9242094	0.3709272
H	-0.8846787	-3.5726374	-1.1537352
H	-3.1413487	-1.7559011	1.4529165

TS2^{+} : addition of **273a**H^{+} C3 to amine **315a** para

45

Energy = -906.7023018157

N	-3.5026222	0.9082647	-0.2396499
C	-4.0777565	-0.3815177	-0.1227744
C	-2.2857114	1.3400879	0.1670893
H	-4.0745615	1.5948529	-0.7221635
C	-4.8650489	-0.8477792	-1.1834574
C	-3.9253022	-1.1539804	1.0354102
C	-2.0036205	2.7359939	0.0609360
C	-1.2787253	0.4647834	0.6688820
C	-5.4754663	-2.0961623	-1.0940682
H	-4.9874833	-0.2352108	-2.0722957
C	-4.5321793	-2.4064130	1.1083576
H	-3.3707822	-0.7667744	1.8830907
C	-0.7859291	3.2266746	0.4397940
H	-2.7825156	3.4006082	-0.3026281
C	-0.0597413	0.9701831	1.0389052
H	-1.4732351	-0.5978050	0.7418666
C	-5.3031347	-2.8842681	0.0465652
H	-6.0817185	-2.4549788	-1.9201697
H	-4.4149770	-3.0015373	2.0088709
C	0.2623462	2.3521173	0.8694202
H	-0.5934582	4.2935167	0.3790797
H	0.7004504	0.2967075	1.4233169
H	-5.7769365	-3.8587132	0.1126332
H	1.0793797	2.7650815	1.4494099
C	1.4870120	2.2761434	-0.8442123
C	0.6146119	1.7318232	-1.9317916
H	2.1649705	1.5620840	-0.3806094
C	1.9970039	3.6132891	-0.9645131
H	1.2476345	1.5617243	-2.8135895
H	-0.1684242	2.4388428	-2.2181837
H	0.1644310	0.7752199	-1.6589704
C	3.1559098	4.0065513	-0.3693704
H	1.4180694	4.3113717	-1.5660973
H	3.6907281	3.2691025	0.2304041
C	3.7831052	5.3108656	-0.4506705
C	5.0020227	5.5139227	0.2293674
C	3.2300619	6.3874801	-1.1774886
C	5.6454248	6.7471326	0.1896464
H	5.4364303	4.6899441	0.7897549
C	3.8749233	7.6164942	-1.2161247
H	2.2947696	6.2589613	-1.7135402
C	5.0839453	7.8021465	-0.5333916
H	6.5825832	6.8870868	0.7199013
H	3.4391448	8.4366927	-1.7788490
H	5.5834923	8.7657819	-0.5675251

TS3a : H^{+} from adduct **316a**H^{+} to $HOBf_3^-$

81

Energy = -3192.297704247

N	-3.5252109	2.7776842	1.4821982
H	-3.4043397	3.1384516	2.4246016
C	-3.0977257	1.5253403	1.2673004
C	-4.0704805	3.6899627	0.5327839
C	-3.0389240	0.9508737	-0.0435508
C	-2.6517035	0.7601437	2.3921931
C	-5.1002389	3.2976399	-0.3278982
C	-3.5819795	4.9993500	0.5112853
C	-2.5208454	-0.2918008	-0.2063092
H	-3.3737548	1.5315021	-0.8944530
C	-2.1419158	-0.4845278	2.2162759
H	-2.7297317	1.1994033	3.3824953
C	-5.6166909	4.2164886	-1.2394217
H	-5.5100516	2.2949310	-0.2616709
C	-4.1139742	5.9132300	-0.3960252
H	-2.7867345	5.2914734	1.1908323
C	-1.9572609	-1.0797550	0.8920542
H	-2.4519971	-0.7138496	-1.2063165
H	-1.8081787	-1.0466516	3.0832019
C	-5.1230295	5.5220838	-1.2789897
H	-6.4159864	3.9133681	-1.9082133

H	-3.7315409	6.9289686	-0.4179002
C	-2.2218309	-2.6227124	0.7724757
H	-5.5311704	6.2353015	-1.9882979
C	-1.4477746	-3.4147759	1.8389772
H	-1.8502319	-2.9145760	-0.2178197
C	-3.6967725	-2.8987020	0.8251950
H	-0.3932720	-3.1214932	1.8493922
H	-1.8674348	-3.2567682	2.8378745
H	-1.5150301	-4.4838805	1.6174821
C	-4.3904510	-3.4480546	-0.1835398
H	-4.1945148	-2.6269701	1.7571313
H	-3.8460039	-3.7242023	-1.0884978
C	-5.8238049	-3.7559522	-0.2076636
C	-6.3392089	-4.4939869	-1.2879880
C	-6.7155477	-3.3495235	0.8027928
C	-7.6912685	-4.8284492	-1.3536616
H	-5.6639533	-4.8114890	-2.0794260
C	-8.0649585	-3.6814998	0.7375610
H	-6.3516556	-2.7642549	1.6424657
C	-8.5608048	-4.4248754	-0.3393859
H	-8.0647948	-5.4034129	-2.1964166
H	-8.7370532	-3.3571015	1.5274595
H	-9.6152028	-4.6819021	-0.3864118
H	-0.8083819	-1.0269507	0.6946759
H	0.6688031	-2.0122181	-0.4126513
O	0.7740547	-1.3542204	0.2909572
B	1.9301565	-0.4532292	-0.0433509
C	3.2401012	-1.4249361	-0.3157777
C	3.4913908	-2.5118026	0.5310826
C	4.1310085	-1.3236034	-1.3853007
C	4.5083944	-3.4383357	0.3293795
C	5.1650274	-2.2270831	-1.6273188
C	5.3541870	-3.2989715	-0.7659333
C	1.5571169	0.4548462	-1.3850243
C	1.9892136	1.7659758	-1.5839450
C	0.7175856	-0.0192368	-2.3903457
C	1.5918367	2.5659147	-2.6505355
C	0.2838917	0.7380009	-3.4751410
C	0.7217024	2.0503408	-3.6050653
C	2.0682532	0.5339484	1.2728180
C	3.1307138	0.6007861	2.1723985
C	1.0092128	1.3907450	1.5816721
C	3.1393876	1.4219600	3.3002704
C	0.9686890	2.2260168	2.6917744
C	2.0478900	2.2389083	3.5683255
F	2.7472166	-2.6951013	1.6500752
F	4.6950342	-4.4631897	1.1896615
F	6.3441206	-4.1856257	-0.9825372
F	5.9838203	-2.0712343	-2.6904578
F	4.0464154	-0.2995989	-2.2756199
F	0.2630808	-1.3114217	-2.3683947
F	-0.5495534	0.2132156	-4.4001060
F	0.3209946	2.8057043	-4.6450767
F	2.0438268	3.8327198	-2.7759066
F	2.8691728	2.3349789	-0.7169763
F	-0.0620767	1.4669032	0.7486901
F	-0.0954252	3.0287077	2.9215898
F	2.0391929	3.0360748	4.6533397
F	4.1994483	1.4322413	4.1370460
F	4.2550846	-0.1371631	1.9895925

TS3a^{+} : H^{+} from adduct **316a**H^{+} to neutral diene **273a**

65

Energy = -1294.003657597

N	1.6983981	0.9734194	0.6585108
H	2.2180132	0.6906235	1.4847339
C	0.5582871	0.2742751	0.4480124
C	2.2609345	2.0893374	-0.0034721
C	-0.2373389	0.3708022	-0.7318656
C	0.1763646	-0.6555062	1.4588573
C	1.5147785	2.9972324	-0.7666103
C	3.6330817	2.3029240	0.1916829
C	-1.3125548	-0.4591662	-0.8943760
H	0.0168326	1.0784515	-1.5086017
C	-0.8891903	-1.4898124	1.2781777
H	0.7430918	-0.6809367	2.3854670
C	2.1599589	4.0748853	-1.3715704
H	0.4402980	2.9038029	-0.8550298
C	4.2637414	3.3833894	-0.4154206
H	4.1992642	1.6161190	0.8138716
C	-1.5861494	-1.5408431	0.0157280
H	-1.9030954	-0.3937529	-1.8036928
H	-1.1521419	-2.1964462	2.0582052
C	3.5332019	4.2673955	-1.2129852
H	1.5750882	4.7767344	-1.9586014
H	5.3281791	3.5331037	-0.2645220
C	-2.9449332	-2.2527140	-0.1086503
H	4.0254137	5.1093492	-1.6896452
C	-2.9948722	-3.5833594	0.6604490
H	-3.0965092	-2.4587941	-1.1754429
C	-4.0311805	-1.3134996	0.3462355
H	-2.1681774	-4.2412341	0.3726283
H	-2.9489222	-3.4236516	1.7425392
H	-3.9348239	-4.0962357	0.4409497
C	-4.9970238	-0.8404795	-0.4563556
H	-3.9909584	-1.0268459	1.3975941
H	-5.0013426	-1.1619279	-1.4992053
C	-6.0852048	0.0703603	-0.0874553
C	-7.0436730	0.4082572	-1.0600272
C	-6.2214739	0.6268607	1.1986020
C	-8.1017289	1.2667686	-0.7631363
H	-6.9527524	-0.0122006	-2.0587829
C	-7.2766936	1.4831551	1.4957858
H	-5.4961732	0.3895227	1.9720233
C	-8.2232872	1.8083926	0.5171940
H	-8.8303428	1.5124559	-1.5310362
H	-7.3631011	1.9014368	2.4947175
H	-9.0455316	2.4776589	0.7529221
H	-0.6945425	-2.3894702	-0.5731265

C	0.2802477	-3.3135224	-1.1686764
C	1.3510936	-2.4680880	-1.4329700
H	-0.3692616	-3.6056892	-1.9916038
H	0.3570605	-4.0191782	-0.3435294
H	1.3349241	-1.8899673	-2.3562395
C	2.4661858	-2.2651776	-0.5792236
C	3.4590750	-1.3860793	-0.9056934
H	2.5099555	-2.8411161	0.3430148
H	3.3659592	-0.8573940	-1.8544350
C	4.6474395	-1.0768266	-0.1400365
C	5.6212269	-0.2369400	-0.7188275
C	4.8611012	-1.5478726	1.1733326
C	6.7679284	0.1186534	-0.0153834
H	5.4625163	0.1357454	-1.7269454
C	6.0023661	-1.1840673	1.8759016
H	4.1258304	-2.1921176	1.6455295
C	6.9604673	-0.3500848	1.2856660
H	7.5081331	0.7646288	-0.4771587
H	6.1509877	-1.5475990	2.8880553
H	7.8505903	-0.0689234	1.8402504

TS3b^{+} : deprotonation of C1 adduct with **273a**

69

Energy = -1425.686147266

N	1.6864135	2.4480378	1.7198574
H	2.1716659	2.2721670	2.5932576
C	0.8883338	1.4441740	1.2745862
C	2.0541057	3.6392324	1.0458901
C	0.3076878	1.4323207	-0.0208441
C	0.6630685	0.3326178	2.1349282
C	1.1107770	4.4277187	0.3772333
C	3.3952911	4.0387800	1.0944766
C	-0.3935824	0.3352438	-0.4460550
H	0.4631764	2.2669520	-0.6918937
C	-0.0503348	-0.7537122	1.7030791
H	1.0676581	0.3595456	3.1431092
C	1.5221133	5.5911647	-0.2715051
H	0.0616429	4.1525522	0.3892331
C	3.7931269	5.2107333	0.4557276
H	4.1190453	3.4254494	1.6239504
C	-0.5250853	-0.8613797	0.3470654
H	-0.8200538	0.3370266	-1.4460221
H	-0.2068638	-1.5889951	2.3783567
C	2.8611609	5.9849668	-0.2392986
H	0.7864018	6.1996174	-0.7887858
H	4.8350109	5.5141198	0.4949499
C	-1.2445387	-4.2927286	0.1664416
H	3.1742950	6.8944740	-0.7426558
C	-1.1031285	-5.5999399	0.8836025
H	-1.0520932	-4.3072502	-0.9084333
C	-1.5752174	-3.1346161	0.7429953
H	-0.0806663	-5.9837773	0.7807136
H	-1.3284483	-5.4960048	1.9491157
H	-1.7723332	-6.3571306	0.4558692
C	-1.6871899	-1.8242959	0.0016604
H	-1.7907982	-3.1084822	1.8114820
H	-1.6137719	-2.0404235	-1.0722375
C	-3.0472814	-1.1764323	0.2393772
C	-4.0718455	-1.3672992	-0.6946138
C	-3.3132150	-0.4230234	1.3879232
C	-5.3375110	-0.8174532	-0.4870013
H	-3.8759160	-1.9519778	-1.5906741
C	-4.5783739	0.1252336	1.6011923
H	-2.5277263	-0.2526826	2.1200917
C	-5.5950780	-0.0701034	0.6640672
H	-6.1203172	-0.9708519	-1.2247065
H	-4.7685925	0.7088773	2.4976469
H	-6.5787932	0.3605978	0.8275607
H	0.4958573	-1.5547626	-0.1778926
H	1.1693306	-2.5319768	-1.7144821
N	1.5906421	-2.1812373	-0.8521296
C	2.4328345	-1.0441377	-1.1736972
C	3.4115516	-0.5804965	-0.2955653
C	2.1375292	-0.3446520	-2.3458106
C	4.0662466	0.6157809	-0.5823212
H	3.6569576	-1.1326454	0.6035296
C	2.8017582	0.8481783	-2.6246256
H	1.3821606	-0.7245349	-3.0286071
C	3.7552301	1.3419988	-1.7340905
H	4.8227510	0.9821269	0.1046370
H	2.5649017	1.3918664	-3.5337574
H	4.2614773	2.2796655	-1.9396444
C	2.1183401	-3.3002815	-0.0955127
C	2.3451366	-4.5061903	-0.7587673
C	2.3392098	-3.1880608	1.2769903
C	2.8041168	-5.6101482	-0.0418578
H	2.1639542	-4.5804644	-1.8277030
C	2.8031725	-4.2962641	1.9854250
H	2.1423376	-2.2547027	1.7913636
C	3.0367810	-5.5063720	1.3308027
H	2.9801230	-6.5485180	-0.5584484
H	2.9760007	-4.2117818	3.0538408
H	3.3936969	-6.3664276	1.8887182

TS3ha^{+} : H^{+} from adduct **316h**Ha^{+} to amine **315h**

75

Energy = -1504.345507374

N	-4.2122348	0.0434525	0.9954226
C	-4.8802262	0.9620830	0.1157784
C	-2.8746715	0.1037904	1.2133428
C	-5.8840565	1.7928227	0.6185158
C	-4.5504109	0.9934647	-1.2419964
C	-2.2147898	-0.9042546	1.9742691
C	-2.0866346	1.1807505	0.7020533
C	-6.5546342	2.6608795	-0.2434237
H	-6.1309660	1.7636296	1.6754697
C	-5.2175511	1.8702381	-2.0958436
H	-3.7794063	0.3317271	-1.6245809

C	-0.8592626	-0.8536565	2.1775594
H	-2.7830195	-1.7242912	2.3951278
C	-0.7347329	1.2086665	0.9095867
H	-2.5735664	1.9938684	0.1765688
C	-6.2211535	2.7045258	-1.5985855
H	-7.3327768	3.3088661	0.1483270
H	-4.9611844	1.8922566	-3.1506546
C	-0.0187683	0.1579752	1.5918967
H	-0.3980634	-1.6367795	2.7710371
H	-0.1637052	2.0624735	0.5527526
H	-6.7433656	3.3834864	-2.2656434
H	0.4799180	-0.5690406	0.5038868
C	1.2512166	0.6526843	2.3731944
C	1.7774177	-0.3575758	3.4017908
H	0.9102068	1.5386837	2.9227050
C	2.3433135	1.0809699	1.4358983
H	2.6421858	0.0725933	3.9154527
H	2.0993322	-1.2873436	2.9235889
H	1.0196556	-0.5926705	4.1548816
C	2.5789460	2.3496947	1.0643824
H	2.9608607	0.2776225	1.0357628
H	1.9460668	3.1396762	1.4718815
C	3.6013793	2.7950260	0.1117436
C	3.5456084	4.1093823	-0.3845014
C	4.6338268	1.9550193	-0.3472236
C	4.4730672	4.5646575	-1.3208920
H	2.7602153	4.7741676	-0.0325051
C	5.5590780	2.4084440	-1.2820170
H	4.7223456	0.9457626	0.0439997
C	5.4819204	3.7146657	-1.7770923
H	4.4089020	5.5833600	-1.6928347
H	6.3511160	1.7462499	-1.6208931
H	6.2076290	4.0667201	-2.5043894
C	-5.0333577	-0.9949987	1.6412908
H	-4.7378241	-1.9887585	1.2876674
H	-4.9292463	-0.9501286	2.7288050
H	-6.0721929	-0.8189286	1.3688164
N	0.9934459	-1.2016891	-0.6579026
C	-0.0246380	-2.1515983	-1.1282612
C	-1.3517241	-1.7267806	-1.1684368
C	0.3170984	-3.4341286	-1.5567521
C	-2.3461169	-2.5944932	-1.6111890
H	-1.6034560	-0.7228173	-0.8464720
C	-0.6848662	-4.2980976	-2.0026061
H	1.3501051	-3.7618648	-1.5471226
C	-2.0171191	-3.8865599	-2.0258255
H	-3.3802474	-2.2635232	-1.6295110
H	-0.4148387	-5.2955873	-2.3352721
H	-2.7925717	-4.5642846	-2.3686134
C	2.2474681	-1.8249066	-0.2633236
C	3.4584851	-1.4989539	-0.8718320
C	2.2094871	-2.7485747	0.7858643
C	4.6386375	-2.0894288	-0.4111249
H	3.4996947	-0.7959868	-1.6950395
C	3.3884271	-3.3364911	1.2331728
H	1.2585670	-3.0117167	1.2384007
C	4.6095376	-3.0038699	0.6396476
H	5.5803866	-1.8318349	-0.8858977
H	3.3534985	-4.0511655	2.0494496
H	5.5291769	-3.4592968	0.9929263
C	1.1286071	-0.0517848	-1.5982061
H	0.1473845	0.4119426	-1.6977778
H	1.8284338	0.6687506	-1.1736799
H	1.4675031	-0.3958477	-2.5779613

TS3h^{+} : H^{+} from adduct **316h**H^{+} to **315h**

75

Energy = -1504.339718223

N	-3.6442244	1.2084465	0.2537462
C	-4.7321038	0.4352946	-0.2752644
C	-2.3750121	1.0618439	-0.2012977
C	-5.0441341	0.5079133	-1.6356274
C	-5.4901235	-0.3650825	0.5833474
C	-1.3500170	1.9643728	0.2076690
C	-2.0114111	-0.0181665	-1.0638330
C	-6.1088117	-0.2385653	-2.1390231
H	-4.4591868	1.1494134	-2.2877661
C	-6.5592487	-1.1013677	0.0741976
H	-5.2433584	-0.4126405	1.6397825
C	-0.0573145	1.7827971	-0.2075932
H	-1.5981280	2.8240572	0.8182716
C	-0.7081785	-0.2061342	-1.4353481
H	-2.7746262	-0.7087001	-1.4026093
C	-6.8677658	-1.0434293	-1.2866214
H	-6.3511826	-0.1810686	-3.1958607
H	-7.1455563	-1.7258969	0.7412593
C	0.3680557	0.6328903	-0.9638387
H	0.6959532	2.5192234	0.0585486
H	-0.4633684	-1.0482362	-2.0756195
H	-7.6990924	-1.6200628	-1.6805726
H	0.8161257	-0.1462022	0.1053957
C	2.9869254	2.9115730	-1.6065677
C	4.1255043	3.6910969	-1.0213306
H	2.3502437	3.4406466	-2.3183401
C	2.7101895	1.6358019	-1.3231895
H	4.7912618	4.0600561	-1.8117590
H	4.7106274	3.0798574	-0.3287095
H	3.7599128	4.5747284	-0.4824436
C	1.5723022	0.8768135	-1.9514266
H	3.3372666	1.1067943	-0.6098577
H	1.1422323	1.5289995	-2.7225568
C	2.0287502	-0.3866576	-2.6698427
C	3.1322374	-1.1355925	-2.2448832
C	1.3480878	-0.8063621	-3.8210862
C	3.5235453	-2.2883926	-2.9281077
H	3.7061119	-0.8123326	-1.3826278
C	1.7326529	-1.9584841	-4.5068866
H	0.5128760	-0.2155253	-4.1905224
C	2.8199163	-2.7099039	-4.0567312
H	4.3850368	-2.8523050	-2.5813944

H	1.1885951	-2.2640454	-5.3960641
H	3.1251650	-3.6051689	-4.5905070
C	-3.9639047	2.2184407	1.2775327
H	-3.2879054	2.1203093	2.1315786
H	-3.8852250	3.2287967	0.8621354
H	-4.9883572	2.0518450	1.6053158
N	1.3093793	-0.9487735	1.1769244
C	0.3622953	-0.9326987	2.3033378
C	-0.9999905	-1.0390079	2.0301728
C	0.8124488	-0.8753046	3.6228207
C	-1.9189706	-1.0495808	3.0762201
H	-1.3416936	-1.1101155	1.0046874
C	-0.1141317	-0.8877233	4.6665280
H	1.8728035	-0.8194314	3.8408885
C	-1.4808393	-0.9666338	4.3991172
H	-2.9789928	-1.1283781	2.8548267
H	0.2409110	-0.8404079	5.6914540
H	-2.1974802	-0.9732235	5.2142620
C	2.5948369	-0.3443356	1.4821205
C	3.7993359	-1.0041837	1.2453516
C	2.5927829	0.9686655	1.9681276
C	5.0054882	-0.3375049	1.4814667
H	3.8159512	-2.0260405	0.8857121
C	3.7971452	1.6188594	2.2119600
H	1.6502916	1.4698391	2.1617884
C	5.0098675	0.9703894	1.9622015
H	5.9416309	-0.8537419	1.2927733
H	3.7880146	2.6368940	2.5883740
H	5.9500384	1.4806197	2.1462195
C	1.3586629	-2.3061262	0.5602414
H	0.3396888	-2.5788928	0.2863794
H	1.9759495	-2.2681538	-0.3374022
H	1.7513708	-3.0359115	1.2725040

TS3la^{+} : H^{+} from adduct **316l**Ha^{+} to **315l**

69

Energy = -1275.592174913

N	-3.2312652	-1.1889847	0.8772199
C	-2.1055553	-0.6787077	0.3362406
C	-0.9771573	-0.3796756	1.1585417
C	-2.0121423	-0.4298970	-1.0767223
C	0.1882602	0.0719343	0.6056509
H	-1.0429162	-0.5098072	2.2316071
C	-0.8170805	-0.0156600	-1.6034329
C	0.3821580	0.1739916	-0.8203175
H	1.0189778	0.3270066	1.2598275
H	-0.7621360	0.1441912	-2.6779433
H	1.0326810	-0.9814212	-1.0209726
C	1.4198669	1.2294782	-1.2950729
C	1.7638356	1.1108933	-2.7882196
H	2.3358415	1.0710121	-0.7133383
C	0.8977940	2.6029602	-0.9704468
H	2.5687876	1.8081132	-3.0365305
H	0.9039042	1.3587626	-3.4180276
H	2.0942607	0.1001303	-3.0479413
C	1.4811274	3.4427713	-0.1020815
H	-0.0234070	2.8832209	-1.4821823
H	2.4036531	3.1191487	0.3822932
C	1.0186404	4.7796974	0.2842909
C	1.8119942	5.5445756	1.1572566
C	-0.1886711	5.3404105	-0.1733119
C	1.4216903	6.8227889	1.5557674
H	2.7464961	5.1253907	1.5222301
C	-0.5789295	6.6155648	0.2232536
H	-0.8292852	4.7730566	-0.8412904
C	0.2238609	7.3653387	1.0894534
H	2.0525855	7.3942118	2.2298848
H	-1.5148694	7.0291681	-0.1410658
H	-0.0851206	8.3600881	1.3973147
C	-3.3359073	-1.4078152	2.3216929
H	-2.5841243	-2.1333537	2.6551644
H	-3.2009186	-0.4717397	2.8722552
H	-4.3292727	-1.8003131	2.5361078
C	-4.4102132	-1.5528574	0.0676752
H	-5.1494865	-0.7429200	0.1351665
H	-4.8506268	-2.4417052	0.5277887
C	-4.0440871	-1.8230344	-1.3850256
H	-4.9647234	-1.9681861	-1.9572702
H	-3.4594562	-2.7476361	-1.4534764
C	-3.2299243	-0.6519266	-1.9383189
H	-3.8547110	0.2522072	-1.9363344
H	-2.9264002	-0.8304781	-2.9739498
N	1.7868678	-2.2091483	-1.0057243
C	0.9866111	-3.0324057	-0.1151316
C	-0.3102919	-3.3704407	-0.5238285
C	1.4582931	-3.4223231	1.1481005
C	-1.1637467	-4.0481946	0.3358938
H	-0.6642344	-3.0723556	-1.5043630
C	0.5744026	-4.0971181	2.0018723
C	-0.7268565	-4.3996543	1.6164622
H	-2.1687592	-4.2986033	0.0115805
H	0.9328766	-4.4005478	2.9825461
H	-1.3884350	-4.9276697	2.2964239
C	1.9183397	-2.7610769	-2.3786779
H	2.4566125	-3.7139624	-2.3587591
H	0.9297412	-2.9142772	-2.8101478
H	2.4669010	-2.0427348	-2.9889881
C	3.0985303	-1.7749650	-0.4382436
H	2.8963067	-0.9186035	0.2161488
H	3.7092591	-1.4294704	-1.2738206
C	3.7715496	-2.8728733	0.3729736
H	4.7627783	-2.5342411	0.6873861
H	3.9066733	-3.7705971	-0.2418899
C	2.8848593	-3.1717291	1.5800483
H	2.9173943	-2.3198162	2.2736359
H	3.2496309	-4.0418554	2.1356976

TS3l^{+} : H^{+} from adduct **316l**H^{+} to **315l**

69

Energy = -1275.588054082

N	-3.3852967	-1.4653354	0.3478147
C	-2.3030071	-0.6680853	0.2331658
C	-1.4358208	-0.4581448	1.3481768
C	-1.9887844	-0.0237951	-1.0123450
C	-0.2982861	0.2884537	1.2182077
H	-1.6822463	-0.8891025	2.3105043
C	-0.8188403	0.6816384	-1.1210042
C	0.1432872	0.8081834	-0.0518056
H	0.3247169	0.4595227	2.0933076
H	-0.5836139	1.1332278	-2.0820357
H	1.0185334	-0.1420259	-0.3788912
C	2.9679762	2.5233058	-1.5613791
C	3.5867178	2.9213862	-2.8671604
H	3.6589342	2.3100724	-0.7432644
C	1.6548357	2.4257912	-1.3331920
H	4.1990470	3.8244938	-2.7483725
H	2.8245210	3.1157912	-3.6279964
H	4.2581187	2.1361004	-3.2391060
C	1.0552881	2.0632192	0.0024341
H	0.9568698	2.6723412	-2.1338169
H	1.8824126	1.8351108	0.6842893
C	0.3136273	3.2592141	0.5955121
C	0.9225137	4.0111372	1.6063420
C	-0.9512984	3.6458142	0.1382757
C	0.2826912	5.1246018	2.1529079
H	1.9060751	3.7209111	1.9690077
C	-1.5928515	4.7600855	0.6791015
H	-1.4460874	3.0698624	-0.6392813
C	-0.9783973	5.5036506	1.6892898
H	0.7682336	5.6934408	2.9410965
H	-2.5753643	5.0463868	0.3140107
H	-1.4800393	6.3688035	2.1134396
C	-3.7131975	-2.1037637	1.6250722
H	-2.8986128	-2.7652929	1.9424928
H	-3.8946929	-1.3569712	2.4048410
H	-4.6176447	-2.6949739	1.4881669
C	-4.3048353	-1.7211320	-0.7774047
H	-5.1719193	-1.0535538	-0.6852426
H	-4.6642788	-2.7474734	-0.6690599
C	-3.6228552	-1.5299763	-2.1244688
H	-4.3726031	-1.6247952	-2.9147914
H	-2.8781509	-2.3193413	-2.2762345
C	-2.9457253	-0.1592897	-2.1699528
H	-3.7141495	0.6233999	-2.1060007
H	-2.4138289	-0.0089929	-3.1137143
N	1.9842840	-1.1874742	-0.5653154
C	1.2536261	-2.3725238	-0.1509505
C	0.1149325	-2.7320106	-0.8843615
C	1.6196639	-3.0994750	0.9929215
C	-0.6952221	-3.7759565	-0.4595918
H	-0.1564808	-2.1717739	-1.7721220
C	0.7820806	-4.1453033	1.4054847
C	-0.3712310	-4.4792528	0.7042914
H	-1.5792895	-4.0395810	-1.0316258
H	1.0607071	-4.7122100	2.2905216
H	-0.9999322	-5.2959632	1.0456321
C	2.4091929	-1.1925067	-1.9887697
H	3.1765681	-1.9545900	-2.1571692
H	1.5506765	-1.3999233	-2.6260672
H	2.7989994	-0.2021094	-2.2262481
C	3.0917347	-0.7896165	0.3530524
H	2.6364248	-0.2498257	1.1919358
H	3.7256394	-0.0943079	-0.1987114
C	3.8573628	-1.9901919	0.8892224
H	4.7110349	-1.6422852	1.4776337
H	4.2483067	-2.5907205	0.0592116
C	2.8978431	-2.8115823	1.7468777
H	2.6692358	-2.2571551	2.6679076
H	3.3527206	-3.7582730	2.0559062

TS3w^{+}p : H^{+} from adduct **316ua**H^{+}p to **315a**

63

Energy = -1271.958011495

N	-3.2287678	-1.6471673	-0.7024712
H	-3.1780436	-2.6401691	-0.9041165
C	-2.0955023	-0.9356770	-0.9308969
C	-1.9388277	0.4198882	-0.5276419
C	-1.0082613	-1.5890168	-1.5814484
C	-0.7525087	1.0707292	-0.7534744
H	-2.7548404	0.9348185	-0.0359810
C	0.1708483	-0.9281700	-1.8027259
H	-1.1428762	-2.6104825	-1.9273385
C	-4.4764074	-1.1873219	-0.2067956
C	0.4016260	0.3975629	-1.2893259
H	-0.6433600	2.1035870	-0.4326549
H	0.9839079	-1.4299815	-2.3207504
C	-5.0358477	0.0228895	-0.6336560
C	-5.1732710	-2.0065903	0.6895659
H	0.8517230	0.0157852	-0.0714679
C	-6.2734850	0.4228760	-0.1321845
H	-4.5263558	0.6298914	-1.3741721
C	-6.4162400	-1.6039789	1.1726157
H	-4.7364170	-2.9494372	1.0070848
C	-6.9658163	-0.3837065	0.7728401
H	-6.7041263	1.3617682	-0.4669871
H	-6.9512635	-2.2424640	1.8689993
H	-7.9316818	-0.0688327	1.1555566
C	1.5310460	1.2450968	-1.8958144
C	2.8288796	0.4767056	-1.9893341
C	3.6451734	0.5280782	-3.0475045
C	3.3977063	1.3896133	-4.2559603
C	2.2948619	2.4252596	-3.9995193
C	1.1080694	1.7799346	-3.2791959
H	4.5532353	-0.0735081	-3.0433071
H	3.0969333	-0.1528597	-1.1423873
H	1.6730949	2.1069104	-1.2257337
H	3.1264088	0.7482259	-5.1082742
H	2.6963285	3.2364808	-3.3779417
H	1.9677208	2.8741704	-4.9434520

H	0.2835348	2.4915774	-3.1599764
H	0.7285875	0.9398989	-3.8769367
H	4.3321544	1.8872906	-4.5445357
N	1.1567537	-0.4309823	1.2417044
H	0.3926522	-1.0923886	1.3905748
C	0.9693911	0.7202549	2.0966227
C	0.0503710	0.6494113	3.1423232
C	1.6405606	1.9102319	1.8111067
C	-0.1913626	1.7808022	3.9206128
H	-0.4702808	-0.2827492	3.3469530
C	1.4014024	3.0335385	2.6012128
H	2.3412502	1.9589457	0.9840979
C	0.4861154	2.9719738	3.6539677
H	-0.9061813	1.7285529	4.7357600
H	1.9252282	3.9595487	2.3861632
H	0.2980422	3.8513881	4.2618320
C	2.4125533	-1.1583104	1.2223167
C	2.4088951	-2.4022137	0.5853847
C	3.5895326	-0.6259586	1.7440683
C	3.5992596	-3.1149119	0.4625807
H	1.4818468	-2.8089299	0.1897979
C	4.7762733	-1.3488831	1.6127509
H	3.5874649	0.3304003	2.2537959
C	4.7884396	-2.5872004	0.9701242
H	3.5947990	-4.0822823	-0.0298220
H	5.6938397	-0.9371146	2.0214146
H	5.7167395	-3.1408401	0.8709170

TS3w^{+} : H^{+} from adduct **316ua**H^{+} to **315a** to ortho-**35**

63

Energy = -1271.956688941

N	-0.1020485	-1.8587474	0.2127095
H	0.2088795	-1.9488383	-0.7559703
C	-1.0905991	-0.9416421	0.4088448
C	-1.8232970	-0.8678967	1.6139681
C	-1.3552356	0.0367351	-0.6420438
C	-2.7879632	0.1012408	1.8032698
H	-1.6592489	-1.6150567	2.3800592
C	-2.4330100	0.9624265	-0.4013303
H	-0.2887679	0.8382421	-0.3849020
C	0.4462283	-2.8155266	1.0973870
C	-3.0893597	1.0463943	0.8002123
H	-3.3400330	0.1144892	2.7380909
H	-2.6992092	1.6293130	-1.2172216
C	0.8797091	-4.0263513	0.5367592
C	0.6364473	-2.5804569	2.4660277
H	-3.8586030	1.7933789	0.9627776
C	1.4822104	-4.9934756	1.3361591
H	0.7368990	-4.2061742	-0.5255755
C	1.2317503	-3.5605659	3.2591735
H	0.3482487	-1.6344073	2.9073859
C	1.6540374	-4.7694834	2.7041743
H	1.8104611	-5.9268082	0.8888894
H	1.3739652	-3.3688431	4.3186261
H	2.1170933	-5.5265861	3.3291615
C	-1.1223436	-0.2504928	-2.1590495
C	0.2164859	-0.8374298	-2.5440154
C	0.3669759	-2.0658213	-3.0626129
C	-0.7579213	-3.0462447	-3.2421593
C	-2.0486819	-2.5962637	-2.5439265
C	-2.2732464	-1.0962871	-2.7523835
H	1.3571622	-2.3839537	-3.3845190
H	1.0888318	-0.1884718	-2.4702501
H	-1.1700608	0.7446149	-2.6213044
H	-0.4434614	-4.0345286	-2.8819450
H	-2.9006180	-3.1623687	-2.9325719
H	-1.9912900	-2.8162803	-1.4708534
H	-2.3214898	-0.8870428	-3.8281906
H	-3.2243701	-0.7780789	-2.3140750
H	-0.9329681	-3.1737572	-4.3207980
N	0.8589269	1.5757064	-0.1870392
H	1.6157948	0.9167247	-0.3776402
C	0.8822332	1.8875921	1.2344935
C	0.3717806	3.0761645	1.7504497
C	1.3815819	0.8940494	2.0783445
C	0.3549986	3.2583585	3.1336652
H	0.0058183	3.8581339	1.0967361
C	1.3629073	1.0883628	3.4569554
H	1.7895322	-0.0212459	1.6569062
C	0.8406937	2.2685185	3.9894467
H	-0.0383894	4.1853115	3.5394198
H	1.7612004	0.3201030	4.1126965
H	0.8222726	2.4198265	5.0640449
C	0.8804219	2.6183848	-1.1955007
C	1.9879250	2.7018130	-2.0381714
C	-0.2230631	3.4539538	-1.3747926
C	1.9988438	3.6423337	-3.0669682
H	2.8353393	2.0378835	-1.8889987
C	-0.1985781	4.3974736	-2.4017213
H	-1.0915341	3.3689172	-0.7322259
C	0.9076927	4.4938994	-3.2470884
H	2.8608187	3.7081681	-3.7227761
H	-1.0518321	5.0530413	-2.5425162
H	0.9175599	5.2279896	-4.0465603

TS3^{+} : H^{+} from adduct **316aa**H^{+} to **315a** to form **316**

69

Energy = -1425.689634525

N	1.5669447	2.3063436	1.7727125
H	2.0108051	2.0871128	2.6582987
C	0.7493888	1.3449383	1.2693248
C	2.0315626	3.4834517	1.1344859
C	0.2175855	1.3884185	-0.0453903
C	0.4463725	0.2226046	2.0913790
C	1.1678776	4.3311658	0.4316546
C	3.3886375	3.8075745	1.2543203
C	-0.5023010	0.3258008	-0.5254918
H	0.4240631	2.2344765	-0.6875097
C	-0.2790585	-0.8314027	1.6009315

H	0.8039840	0.2136650	3.1177588
C	1.6753205	5.4758620	-0.1818775
H	0.1054175	4.1168506	0.3907820
C	3.8826467	4.9610160	0.6500785
H	4.0500431	3.1500627	1.8116350
C	-0.6949744	-0.8901571	0.2234814
H	-0.8932543	0.3687978	-1.5388780
H	-0.4943804	-1.6720466	2.2528951
C	3.0311180	5.7929325	-0.0806222
H	1.0009063	6.1298993	-0.7263757
H	4.9367002	5.2046073	0.7440250
C	-1.8634835	-1.8138264	-0.1994622
H	3.4192569	6.6879381	-0.5571665
C	-1.7665241	-3.2141987	0.4302083
H	-1.8073440	-1.9165737	-1.2910692
C	-3.1713362	-1.1519656	0.1404124
H	-0.7885551	-3.6718245	0.2457915
H	-1.9261560	-3.1768106	1.5125023
H	-2.5361733	-3.8626894	0.0036842
C	-4.0743664	-0.7609517	-0.7715062
H	-3.3490031	-0.9909879	1.2042599
H	-3.8561300	-0.9498392	-1.8238872
C	-5.3586754	-0.1006508	-0.5166751
C	-6.2197315	0.1462926	-1.6008438
C	-5.7766549	0.3023231	0.7659877
C	-7.4554715	0.7654247	-1.4148198
H	-5.9106412	-0.1560758	-2.5989429
C	-7.0091702	0.9200667	0.9526501
H	-5.1313370	0.1355560	1.6236428
C	-7.8567755	1.1544569	-0.1359798
H	-8.1038512	0.9437928	-2.2680912
H	-7.3123028	1.2238130	1.9509616
H	-8.8180168	1.6375576	0.0142011
H	0.3541008	-1.5660354	-0.3036061
H	1.0334946	-2.5389034	-1.8252057
N	1.4491151	-2.1705916	-0.9670308
C	2.2853906	-1.0321897	-1.3059213
C	3.2688717	-0.5568782	-0.4397654
C	1.9789291	-0.3469769	-2.4832254
C	3.9200797	0.6365598	-0.7450321
H	3.5233071	-1.0985464	0.4631386
C	2.6386634	0.8445580	-2.7794739
H	1.2199188	-0.7362337	-3.1567943
C	3.5984622	1.3494978	-1.9020539
H	4.6813478	1.0119149	-0.0685437
H	2.3940507	1.3778025	-3.6926702
H	4.1021707	2.2854192	-2.1220094
C	1.9807378	-3.2725195	-0.1876977
C	2.1997935	-4.4952002	-0.8226672
C	2.2044971	-3.1279971	1.1821426
C	2.6546354	-5.5836065	-0.0798354
H	2.0182435	-4.5925925	-1.8894294
C	2.6675928	-4.2205408	1.9154925
H	2.0104366	-2.1817658	1.6737224
C	2.8924112	-5.4472371	1.2892746
H	2.8250332	-6.5351354	-0.5737197
H	2.8448778	-4.1110560	2.9808543
H	3.2478953	-6.2951220	1.8664243

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Department of Chemistry, Indian Institute of Technology (IIT) Ropar, India

July 2018 to Feb 2023 (Anticipated) (CGPA= 8.0): Doctor of Philosophy (PhD) in Synthetic Organic Chemistry with Specialization in organic synthesis, purifications and characterization techniques.

Department of Applied Chemistry, DIAT-DRDO, Pune, India

Aug 2016 to May 2018 (CGPA= 8.1): Master of Technology (M.Tech.): in Chemical Science and Technology

HNBGU, Garhwal University, Srinagar (Garhwal),, India

Aug 2013 to Jun 2015 (CGPA= 7.3): Master of Science (M.Sc.): in Chemistry

Department of Science, Gurukula Kangri Vishwavidyalaya, Haridwar, India

July 2010 to Jun 2013 (67.3%): Bachelor of Science (B.Sc.): in Chemistry

Research Experience:

Department of Chemistry, Indian Institute of Technology (IIT) Ropar, India

July 2018 to Present: PhD Research Fellow

Title of Thesis: Main Group Lewis Acid Catalyzed Functionalization of 1,3-dienes and Other Unsaturated Compounds

Supervisor: Prof. Dr. Indranil Chatterjee, IIT Ropar, Punjab, India

Year Awarded: 2023

- Development of transition-Metal free 1,3-conjugated dienes functionalization techniques for the formation of C-heteroatom (C–S, C–N) and C–C bonds.
- Explored the Lewis Acid assisted bifunctionalization of alkynes to synthesize series of β-aminoacrylonirile derivatives.
- Use of $InBr_3$ in transfer hydrogenation of alkenes by a novel hydride donor moiety.

Department of Applied Chemistry, DIAT-DRDO, Pune, India

July 2017 to May 2018: M.Tech. Research Details

Title of Thesis: Synthesis of Novel Adamantyl Triazoles and Their Exploration in the Field of Energetic and Biological Applications

Supervisor: Prof. Dr. Shaibal Banerjee

Year Awarded: 2018

- Worked on the synthesis and development of novel adamantly triazoles (Click reactions).
- Characterized the synthesized molecules via NMR, Mass spectroscopy and FT-IR.

Teaching Experience:

Department of Chemistry, Indian Institute of Technology (IIT) Ropar, India

Aug 2021 to March 2022: Trained one Master Student during his M.Sc. thesis work in research laboratory.

Jan 2021 to Mar 2021: Teaching Assistant for Undergraduate Student, Laboratory instructor.

Aug 2019 to Nov 2019: Trained one Master Student during her M.Sc. thesis work in research laboratory.

Experimental & Technical Skills:

Synthetic Chemistry:

- Synthesis of organic molecules such as, 1,3-dienes, alkenes, amines, sulfides, sulfoxides, ketones, esters, alcohols etc.
- Expertise in multistep synthesis as well as multicomponent reactions.
- Handling Lewis acids, metal-catalysts, and air sensitive chemicals.
- Running catalytic reactions.

Compound Characterization:

- Structural characterization of organic molecules by NMR, Mass Spectrometry (D-Mass & HRMS), SC-XRD.
- Spectroscopic analysis of organic molecules using FT-IR, UV-Vis, Fluorescence spectroscopy.

Hands-on Experience:

- Instrument: NMR, HRMS, SC-XRD, UV-Vis spectrometer, Fluorescence spectrometer, Glove Box, HPLC.
- Computational Softwares: Microsoft Office, ChemDraw Ultra, PowerPoint, WinGx.

Publications:

- Ghosh, S.; **Kumar, G**.; Naveen, N.; Pradhan. S.; Chatterjee, I. EDA Complex Directed N-centred Radical Generation from Nitrosoarene: A Divergent Synthetic Approach. *Chem. Commun*. **2019**, *55*, 13590-13593.

- **Kumar, G.;** Qu, Z-W.; Ghosh, S.; Grimme, S.; Chatterjee, I. Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated Dienes with Thiols. *ACS Catal.* **2019**, *9*, 11627−11633.

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- **Kumar, G.;** Qu, Z-W.; Grimme, S.; Chatterjee, I. Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines. *Org. Lett.* **2021**, *23*, 8952−8957.

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- **Kumar, G.;** Bhattacharya, D.; Chatterjee, I. Lewis Acid-Assisted Transition Metal-Free Aminocyanation of Alkynes with Arylamines and *N*-Cyanosuccinimide. *Adv. Synth. Catal*. **2022**, *364*, 2416–2421.

- **Kumar, G.;** Bhattacharya, D.; Mistry, P.; Chatterjee, I. In-Catalyzed Transfer Hydrogenation and Regioselective Hydrogen-Deuterium Addition to the Olefins. *J. Org. Chem.* **2023**, DOI:10.1021/acs.joc.3c00272.

🎓 Conference Attended and Poster Presentation

- **CRIKC-2019:** Department of Chemistry, Indian Institute of Science Education and Research (IISER) Mohali, Punjab, India

Activity: Poster Presentation: Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated Dienes with Thiols.

- **JNOST-2020:** Indian Institute of Science (IISc) Banalore, India

Activity: Oral Presentation: Boron Lewis Acid-Catalyzed Regioselective Hydrothiolation of Conjugated Dienes with Thiols.

- **ICRTGC-2021:** Akal University, Punjab, India

Activity: Poster Presentation: Nitrosoarene Catalyzed HFIP Assisted C–heteroatom bond Forming Reactions.

- **29-CRSI-NSC-2022:** Department of Chemistry, Indian Institute of Science Education and Research (IISER) Mohali, Punjab, India

Activity: Poster Presentation: Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines. (Best Poster award).

- **CRIKC-2022:** National Institute of Pharmaceutical Education and Research (NIPER) Mohali, Punjab, India

Activity: Poster Presentation: Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and *N*-cyanosuccinimide.

- **FICS-2022:** Indian Institute of Technology Guwahati, Guwahati, Assam, India

Activity: Poster Presentation: Lewis Acid-assisted Transition-metal-free Aminocyanation of Alkynes with Arylamines and *N*-cyanosuccinimide.

Summary

Highly motivated and aspired researcher with five years of laboratory research experience at IIT Ropar, India. Research Expertise includes organic synthesis, catalytic reactions, photoredox reactions, handling fine chemicals. Highly skilled in organic research and solid understanding in analytical as well as compound characterization techniques. Have a leadership quality and also accustomed to work within multidisciplinary groups. Demonstrated strong verbal/communication and interpersonal skills.