UNIVERSIDADE FEDERAL DE SANTA CATARINA - UFSC
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PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA

SUMBAL SABA

Synthesis of unsymmetrical diorganyl chalcogenides by using arylboronic acids or C(sp^2)-H bond functionalization of arenes under greener conditions

Florianópolis
2016

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Thesis submitted to the Post-graduation Program of the Federal University of Santa Catarina in partial fulfillment of the requirements for degree of the Doctor of Philosophy in Chemistry
Area: Organic Chemistry

Supervisor: Prof. Dr. Antonio Luiz Braga

Florianópolis
2016

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Síntese de calcogenetos de diorganoíla via ácidos borônicos e funcionalização de ligação C(sp^2)-H de arenos sob condições ambientalmente mais adequadas

Tese apresentada ao Programa de Pós-Graduação em Química da Universidade Federal de Santa Catarina, como requisito parcial para obtenção grau de Doutor Química.
Área de concentração: Química Orgânica.

Orientador: Prof. Dr. Antonio Luiz Braga

Florianópolis
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Sumbal Saba

Synthesis of unsymmetrical diorganyl chalcogenides by using arylboronic acids or C(sp^2)-H bond functionalization of arenes under greener conditions

This thesis has been evaluated by the Post-graduation program of the **Department of Chemistry** at **Federal University of Santa Catarina** and approved for obtaining the degree of **Doctor of Philosophy in Chemistry**

Florianópolis, 3rd March 2016

Prof. Dr. Vanderlei Gageiro Machado
Coordinator of the Post-graduation Program in Chemistry
Federal University of Santa Catarina-UFSC

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Prof. Dr. Fábio Zazyki Galetto
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Prof. Dr. Maria da Graça Nascimento
(UFSC)
Member of the defense committee

Dedicated to my parents (Yasmin Ali Shakir and Shakirullah Khan), husband (Dr. Jamal Rafique), my sister (Sundus Ali) and brothers (Mudasar Ali and M. Adil Ali).

"Those who educate children well are more to be honored than they who produce them; for these only gave them life, those the art of living well."
— Aristotle

To my dear mentor, Professor Dr. Antonio Luiz Braga

I have no words to express my sincere thanks and gratitude to you. A special thanks for granted me the opportunity to be a part of your research group, for full support in difficult times and always helped me as a friend.

I'll always be grateful for your sincere academic teachings, research training and suggestions for improving my personality

I would like to dedicate this PhD thesis to late Dr. Syed Hamid Hussain, my husband's best friend and brother to me.

Dr. Hamid, embraced martyrdom on 20th Jan 2016 while protecting his students from the terrorist at Bacha Khan University, Charsadda-Pakistan.

ACKNOWLEDGMENTS

"In the name of God, most gracious, most compassionate. All respects for the Holy Prophet Muhammad (PBUH) for enlightening our souls with the essence of faith in Allah (SWT)."

This is a hard job to include names of all person, who were involved directly or indirectly in the accomplishment of this study. However, I am very grateful to all my teachers since my school days, I think without being trained enough, I would have not been able to venture in the area of higher studies.

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and hope the friendship established since 2012 will last in years to come.

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Last but not the least; I am indebted from the core of my heart to all the sacrifices made by my family. The more I say in honor of my parents (Yasmin Ali Shakir and Shakirullah), the lesser it would be. I just say that I am proud of them. I am proud that I could make their dreams come true. I am grateful to my life and research partner (Jamal Rafique), to be with me since 2012 in Brazil and helping me out in all difficult times. I wish to express my deepest gratitude to Sundus Ali (my sister) and Mudasar Ali, M Adil Ali (my brothers), my in-laws especially Aunty Asia, Baby, Saqib bhai, Samina and to my other family members. I am also thankful to Samira and Arif from Floripa to be like my elder sister and brother. Thank you all for the love, understanding, and support. It was not easy being so far away from you all, but knowing deep and down, you are very proud of me.

Sumbal Saba,
Florianópolis-Brazil.
3rd March 2016

RESUMO

Título: Síntese de calcogenetos de diorganoíla via ácidos borônicos e funcionalização de ligação C(sp^2)-H de arenos sob condições ambientalmente mais adequadas.

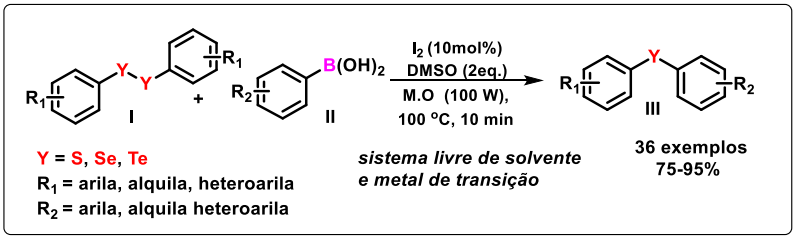
Autora: Sumbal Saba

Supervisor: Prof. Dr. Antonio Luiz Braga

No presente trabalho desenvolveram-se procedimentos robustos, econômicos e sustentável para a síntese de dicalcogentos de organoíla não simétricos usando uma variedade de ácidos borônicos arílicos substituídos e arenos [*O*- ou *N*-] subtituídos.

Na primeira parte, desenvolvemos um sistema catalítico oxidativo que combina iodo/DMSO para a síntese de uma grande variedade de dicalcogenetos de diorganoíla não simétricos (S, Se, Te), utilizando vários ácidos borônicos arílicos sob irradiação de micro-ondas. As reações foram realizadas pela mistura de ácidos boronicos com os dicalgenetos desejados, na presença de 10 mol% de iodo, um equiv. ácido borônicos arílicos **II**, 0,5 equiv. de vários dicalcogenetos de diorganoíla **I** e 2 equiv. de DMSO (como oxidante). Os produtos calcogenados desejados **III** foram obtidos em rendimentos de bons a excelentes.

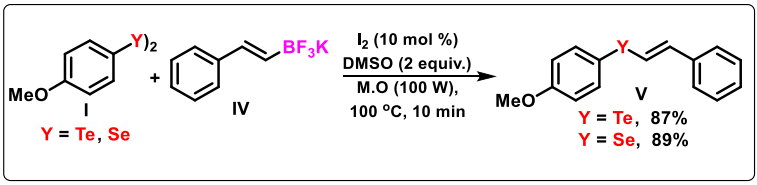
Todas as reações foram realizadas sem a exclusão de ar e umidade a 100 °C durante 10 minutos sob irradiação de microondas, como mostrado no Esquema 1. Vários substituintes com diferentes efeitos eletrônicos e estéricos foram tolerados nas condições ótimas de reação. A metodologia desenvolvida demonstrou ser robusta e pode ser facilmente efetuada na escala de 10 mmol, sem qualquer perda significativa de rendimento. A química aqui descrita representa um protocolo livre de solvente e de metal de transição para a preparação de calcogenetos de diorganoíla não simétricos (Esquema 1).



Esquema 1

O escopo da presente metodologia de acoplamento foi estendido usando trifluoroboratos de potássio vinilícos **IV** como uma alternativa para os ácidos borônicos, utilizando os parâmetros da condição otimizada. A reação de

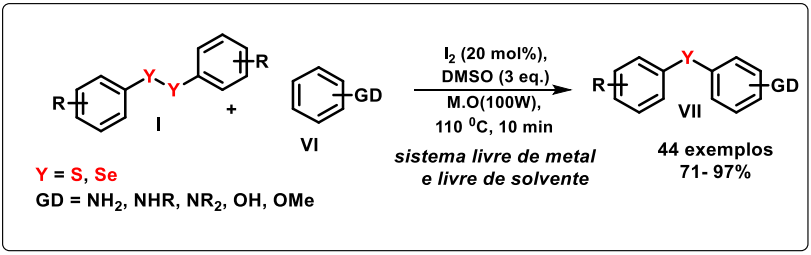
ditelureto e disseleneto de dirganoíla **I** ocorreu sem problemas e proporcionou a formação dos produtos acoplados correspondentes em rendimentos isolados de 87% e 89% (Esquema 2).



Esquema 2

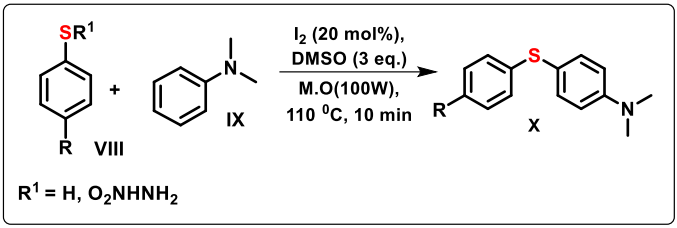
Considerando a importância dos compostos organocalcogênio, na segunda etapa deste trabalho, desenvolveu-se um método regiosseletivo, rápido e ambientalmente seguro, catalisado por iodo para a síntese de calcogentos de organoíla. Essa metodologia ocorre pela formação de ligações C-Se / C-S via clivagem oxidativa de ligação C (sp^2) -H utilizando arenos [*O*- ou *N*-] substituídos. Esse processo é realizado pela calcogenação direta de dicalcogenetos de organoíla **I** com vários arenos **VI**, catalisados por 20 mol% de iodo na presença de 3 equivalentes de DMSO (como oxidante). Essa metodologia regiosseletiva, sob irradiação de micro-ondas, permitiu obter os produtos desejados funcionalizados com um substituinte organocalcogenoíla, em 10 min, em bons rendimentos. Outras vantagens desse método são: condições livres de solvente e metal de transição; procedimento experimental sem a exclusão de ar e umidade.

A reação também foi efetuada em escala de 10 mmol (Esquema 3) sem perda significativa de rendimento. Além disso, por este protocolo, foi possível funcionalizar heteroarenos biologicamente importantes contendo S/Se, tais como: pirimidinas, piridinas e tiazóis.



Esquema 3

A versatilidade da metodologia desenvolvida permitiu ainda a utilização de tiofenol **VIII** e hidrazidas de sulfonila **VIII** como agentes de sulfenilação e *N*,*N*-dimetilanilina **IX**, levando-se ao produto tiolado **X** desejados, em bom rendimentos, em um tempo de reação curto usando irradiação de micro-ondas (Esquema 4).



Esquema 4

Palavras-chave: química verde; funcionalização da ligação C-H; acoplamento cruzado; disselenetos; diteluretos; dissulfetos; selenetos; teluretos; ácidos borônicos; arenos; iodo/DMSO.

ABSTRACT

Title: Synthesis of unsymmetrical diorganyl chalcogenides by using arylboronic acids or C(sp^2)-H bond functionalization of arenes under greener conditions

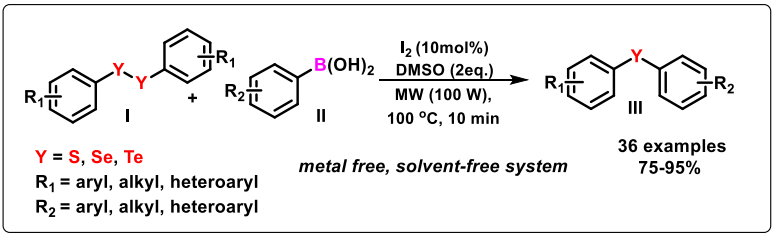
Author: Sumbal Saba

Supervisor: Prof. Dr. Antonio Luiz Braga

In the present work we developed robust, economical and greener procedures for the synthesis of unsymmetrical diorganyl chalcogenides by using various substituted arylboronic acids and [*O* or *N*]- containing arenes.

In the first part, we developed Iodine/DMSO catalyzed oxidative system for the synthesis of a variety of unsymmetrical diorganyl chalcogenides (S, Se, Te) using various arylboronic acids under microwave irradiations.

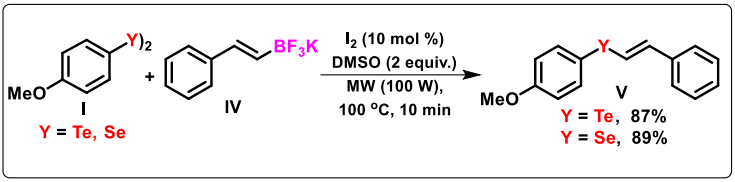
The desired chalcogenated products **III** (Scheme 1) were obtained in good to excellent yields in the presence of 10 mol% of iodine, one equiv. of arylboronic acids **II**, half equiv. of various diorganyl dichalcogenides **I** and 2 equiv. of DMSO (as an oxidant). All the reactions were performed without the exclusion of air and moisture at 100 ^{0}C for 10 min under microwave irradiation, as shown in Scheme 1. Various substituents with different electronic and steric effects tolerated in the optimized reaction conditions. The developed methodology was shown to be robust and could easily be scaled-up without any significant loss of yield. The chemistry described herein represents a transition metal and solvent free method for the preparation of unsymmetrical diorganyl chalcogenides (Scheme 1).



Scheme 1

We were also successful in scaling up the reaction in up to 10 mmol.

The scope of this coupling methodology was extended by using potassium vinyltrifluoroborate **IV** as an alternative to boronic acid in these tellurylation and selenylation reactions by applying the optimal reaction parameters. The reaction of ditelluride and diselenide **I** proceeded smoothly and afforded the corresponding coupled products **V,** in 87% and 89% isolated yields, respectively. (Scheme 2).

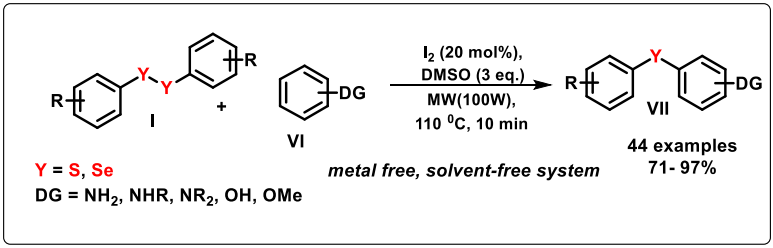


Scheme 2

Considering the importance of diorganyl chalcogenides, we developed a regioselective, rapid and greener iodine-catalyzed method for the synthesis of diorganyl chalcogenides through oxidative C–Se/C–S formation *via* direct C(sp^2)-H bond cleavage using [*O* or *N*]-containing arenes.

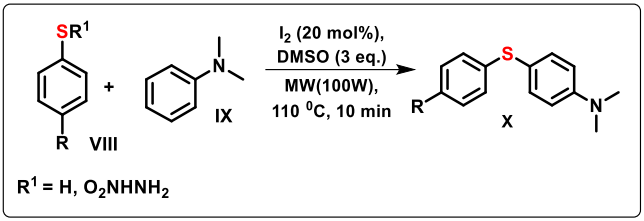
In this work, we reported the synthesis of unsymmetrical diorganyl chalcogenides **VII** (Scheme 3) *via* direct chalcogenation reactions between dichalcogenides **I** and various arenes **VI** catalyzed by 20 mol% of iodine in the presence of 3 equiv. of DMSO (as an oxidant). This regioselective methodology allowed us to obtain desired chalcogenated product in good to excellent yields under transition metal and solvent-free conditions, without the exclusion of air and moisture, applying microwave irradiations for 10 min. The reaction was also scaled-up to 10 mmol.

Additionally, by this protocol, we were able to access biologically important Se/S containing heteroarenes, such as, pyrimidines, pyridines, thiazole.



Scheme 3

The versatility of the developed methodology was observed by using thiophenol **VIII** and sulfonyl hydrazides **VIII** as another sulfenylating agents and *N*,*N*-dimethylaniline **IX**, affording the desired sulfonated product **X** in very good yield, in a short reaction time using MW irradiation (Scheme 4).



Scheme 4

Keywords: green chemistry; carbon-hydrogen bond functionalization; cross-coupling; diselenides; ditellurides; disulfides; selenides; tellurides; arylboronic acids; arenes; iodine/DMSO.

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SYMBOLS & ABBREVIATIONS

1,10 Phen	1,10-Phenanthroline
^{1}H NMR	Hydrogen – Nuclear Magnetic Resonance
^{13}C NMR	Carbon 13 – Nuclear Magnetic Resonance
^{77}Se NMR	Selenium 77 – Nuclear Magnetic Resonance
δ	Chemical shift
Ar	Aryl
$ArB(OH)_2$	Arylboronic acid
bpy	2,2'-Bipyridyl
CC	Column chromatography
CDC	Cross dehydrogenative coupling
Cu	Copper
CuI	Copper iodide
CuO nano	Copper (II) oxide nano particles
$CuSO_4.5H_2O$	Copper(II) Sulfate Pentahydrate
DMSO	Dimethyl sulfoxide
equiv.	Equivalent
ESI	Electrospray ionization
H_2O_2	Hydrogen peroxide
HI	Hydrogen iodide
HRMS	High resolution mass spectrometry

I_2	Iodine
IR	Infrared spectroscopy
J	Coupling constant
Me	Methyl
MW.	Microwave
$NaBH_4$	Sodium borohydride
NaI	Sodium iodide
NBS	*N*-Bromosuccinimide
NCS	*N*-Chlorosuccinimide
Pd	Palladium
Ph	Phenyl
PhH	Benzene
PIFA	Phenyliodinebis(trifluoroacetate)
R	Organic Group
rt	Room temperature
TBHP	*tert*-Butyl hydroperoxide
TLC	Thin layer chromatography
TM	Transition metal
TMS	tetramethylsilane
Y	Chalcogens

TABLE OF CONTENT

Chapter 1
Introduction

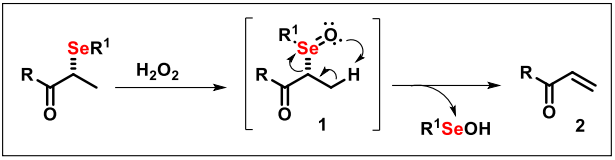
INTRODUCTION

This PhD Thesis Project involves the synthesis of unsymmetrical diorganyl chalcogenides from the coupling of diorganyl dichalcogenides with arylboronic acids and C(sp^2)-H bond functionalization of arenes using more sustainable and greener conditions. In the subsequent headings, there will be an introduction, which is related to the topics involved with our tentative goal. In this sequence, we are going to discuss our specific objectives, methodology, results & discussions and conclusions.

1.1. Organochalcogen chemistry

During the last three decades, the chemistry of organochalcogenides (S, Se, and Te) have attracted considerable attention among scientific community due to their importance as convenient reagents and intermediates in organic synthesis.[1] Synthetic usefulness and applicability of organochalcogenides in organic chemistry is extensively explored in a large number of scientific articles,[2] reviews,[3] and books.[4] In addition to their synthetic applications, organochalcogens present important properties like biological activities[5] and have their applications in material sciences.[6]

According to the synthetic point of view, organoselenium compounds have gained considerable attention after Walter and coworkers were able to demostrate the reaction of *β*-elimination of selenoxides **1** to the formation of alkenes **2** using milder reaction conditions (Scheme 1).[7] Various studies demonstrated the importance of organoselendie in the field of organic synthesis.[8]



Scheme 1. Elimination reaction of selenoxide.

There are many reports in literature, showing the utility of organotellurium compounds as an important intermediate in the reactions involving group transfer cyclization[9] and for controlled/living radical polymerization as novel initiators.[10]

Organochalcogenides, particularly selenium and tellurium, are attractive structural targets because of their selective reactions[11,12] their use in the form of ionic liquids[13], as catalysts[14], as an efficient chiral ligand in symmetric catalysis[15], as synthetic intermediates in total synthesis[16] and their remarkable properties of fluorescence.[17] Likewise, the use of organochalogen compounds in asymmetric synthesis directed to a novel developments in organometallic chemistry.[18]

From the biological aspect organoselenium compounds have been found to function as antioxidant, antimicrobial, antitumor, antidepressant, and chemopreventors in several organs and many of these compounds are also effective as competitive inhibitors for target proteins **3-10**[4a,19] as shown in Figure 1. Along with organoselenium, there are some organotellurium compounds **11-12**[20] that can be used as antioxidants and as efficient thiol peroxidase. In the literature there are some tellurium based drugs such as ammonium trichloro(dioxoethylene-*O*,*O*′)tellurite and 4,4′-dihydroxydiphenyltelluride **13-14**[21] which are reported to be used as enzyme inhibitors for cysteine proteases and as redox modulators for glutathione, respectively. Similarly, some biologically active organosulfur compounds i.e. a well-known antibiotic Amoxicilline (amox) and Bactrim **15-16**[22] are also shown in Figure 1.

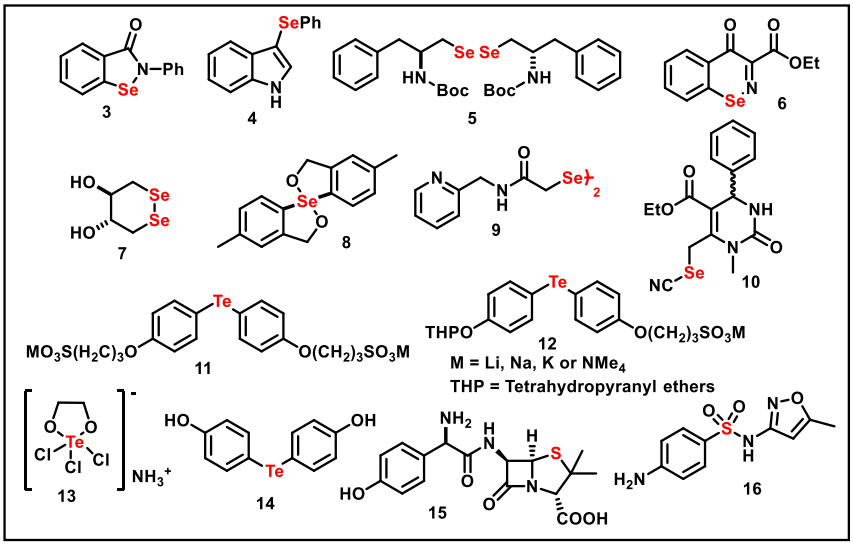


Figure 1. Biologically active organochalcogen compounds (Se, Te, S).

1.2. Organoboronic acids

Organoborons are an imporatant class of compounds. Some of the important examples of oxygenated organoboron compounds (**17**-**21**) are shown in Figure 2.[23] Among them organoboronic acids **19** are trivalent boron containing organic compounds with one alkyl substituent (C-B bond) and two hydroxyl groups to fill the remaining valences on the boron atoms[24] as shown in Figure 2. Organoboronic acids **19** has found comprehensive utility in the field of organic synthesis because of their commercially availability, stability, generally non-toxic nature, and compatibility with a variety of functional groups.[24] Moreover, because of their low toxicity and their degradation into environmentally friendly boric acid organoboronic acids **19** are known as "green" compounds. They are solids that have a tendency to exist as mixtures of oligomeric anhydrides, particularly in the form of the cyclic six-membered boroxines **21**.[25]

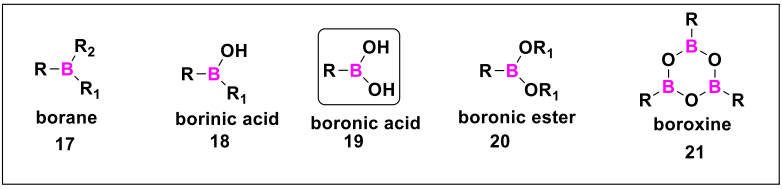
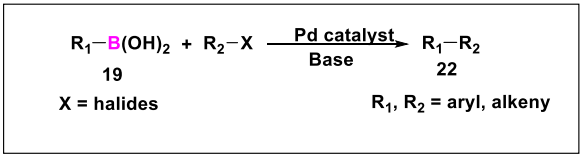


Figure 2. Organoboron compounds.

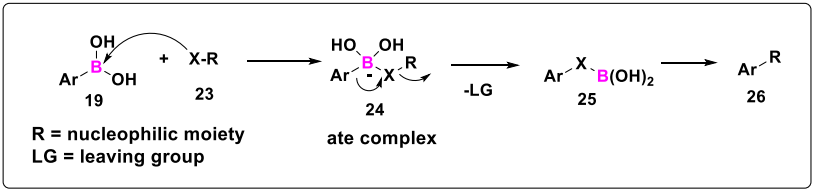
One of the most important application of organoboronic acids are their use as intermediates and chemical building blocks mainly in the famous Suzuki cross-coupling reaction (Scheme 2).[26] A crucial concept in this type of chemistry is transmetallation of organic residue of **19** to a transition metal (i.e. Palladium, Pd) forming **22** (C-C bond).[27]



Scheme 2. General scheme of palladium-catalyzed Suzuki cross-coupling reaction.

1.2.1. Transition metal-free functionalization of organoboronic aicds

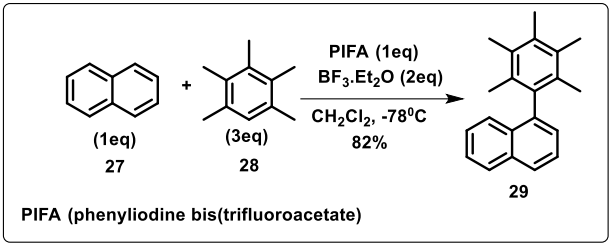
In organoboronic acids, the sp^2-hybridized boron act as a Lewis acid because of the available vacant p-orbital. Initially the addition of a nucleophile (R-LG) **23** or Lewis base creates a tetravalent boron "ate" complex **24** (Scheme 3), forming sp^3-boron. The subsequent dissociation of Ar-B bond due to high electron density on the boron and increased steric hindrance in the complex results the alkyl/aryl migration to the adjacent acceptor atom following the retention of configuration and forming the species **25**, which subsequently give the resultant compound **26** with the loss of boronic moiety. This overall process of ipso-substitution is accomplished without the assistance of transition metals (Scheme 3).[28]



Scheme 3. General pathway for transition metal-free functionalization of organoboronic acids.

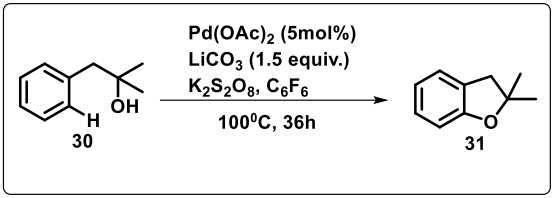
1.3. C-H functionalization of arenes

The direct functionalization of a C-H bond is a straightforward transformation in the area of organic synthesis.[29] Among these, much effort has been given to the construction of C-C[27] and C-hetero bonds.[30] Recently, reactions under metal-free and solvent-free conditions have been broadly used in the functionalization of the C-H bond, which is considered an important contribution to the development and progress of green chemistry.[31] Some examples regarding C-C and C-hetero bonds are represented in proceding discussion (Scheme 4-8).[32,33]



Scheme 4. Oxidative cross-coupling of naphthalene

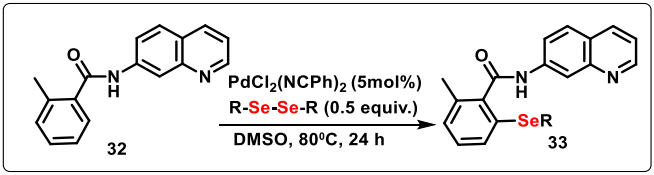
In the context of C-O bond formation, a alcohol derivative **30** in the presence of palladium catalyst and $K_2S_2O_8$ as an oxidant undergoes C-O cyclization and formed **31** as shown in Scheme (5).[33]



Scheme 5. Pd(II)-catalyzed C-O cyclization

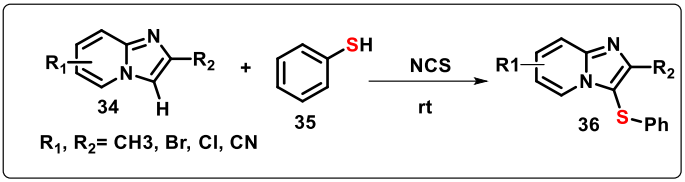
One of the important advantage for the use of direct arylation methods is to reduce the number of steps and waste generation in order to simplify the organic syntheses.[34]

In this regard, the formation of the aryl C−E (S/Se) bond through C-H bond functionalization is involved in the construction of a broad range of organic molecules, which are of supreme importance in drugs, functional materials, and metal complexes.[35] Few examples on the formation of a carbon–chalcogen bonds (e. g. C-S, C-Se) through C-H bond cleavage has been reported in the literature.[36] For example, in the case of C-Se bond formation starting from diaryl diselenides, Yasushi and co-workers described a direct selenation of inert C−H bonds of benzamide derivatives **32** with diselenides in the presence of palladium catalyst and DMSO as a solvent at 80 ^{0}C in order to form corresponding selenated products **33** as shown below in Scheme 6.[37]



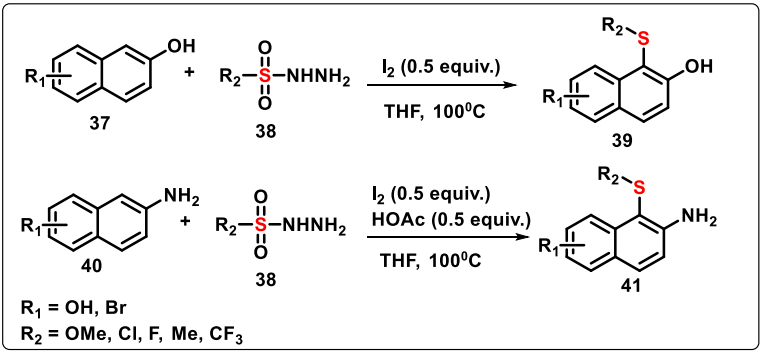
Scheme 6. Selenylation of aryl C-H bond.

In the case of C-S bond formation via direct C–H functionalization, different thiolating/sulfenylating regents had been used under metal-free conditions such as aryl sulfonyl hydrazides,[38a] arylsulfonyl chlorides,[38b] sodium sulfinates,[38c] diaryldisulfides[38d] and 1-(substituted phenylthio)- pyrrolidine-2,5-diones15p.[38e] Recently, a regioselective sulfenylation of imidazoheterocycles **34** with thiophenols **35** at room temperature is reported with the use of N-chlorosuccinimide under metal-free conditions to form corresponding sulfenylated products **36** as shown below in the Scheme 7.[39] The developed methodology works well with a broad range of substrates scopes.



Scheme 7. Regioselective sulfenylation of imidazoheterocycles.

Huang et al. reported a direct method for the iodine-mediated thiolation of naphthols **37** naphthylamines **40** and arylsulfonyl hydrazides **38** through the formation of C−S bond and cleavage of S−N/S−O bonds and form the corresponding sulfenylating products **39** and **41**, as represented in the Scheme 8.[40]



Scheme 8. Iodine-mediated thiolation of naphthols/naphthylamines.

In this transformation, a range of valuable thioethers **39** and **41** were easily achieved in a moderate to good yields employing iodine (0.5 equiv.) as a catalyst at 100 ^{0}C under reaction time of 5-10hr.

1.4. Green chemistry and it's principles

Green Chemistry is a set of concepts, which are designed for the improvement, and application of existing chemical processes and methodologies in order to decrease or eliminate the use or generation of lethal substances to the environment. Therefore, those reactions which avoid the use of any toxic solvents, reagents or catalysts are vital from the environmental aspect and are very suitable, as it diminishes the generation of waste as well as those problems which are associated to handling volatile, toxic and combustible substances.[41]

Keeping in view the importance of Green Chemistry Paul Anastas and John Warner developed its 12 basic principles, which highlights an early idea of what would make a greener chemical, process, or product.[42]

- **Atom Economy (atom efficiency):** Synthetic methods should be aimed to maximize the incorporation of all materials involved in the process into the final product.
- **Prevention:** It is advisable to avoid waste than to treat or clean up waste after it has been formed.
- **Less Harmful Chemical Syntheses:** All the synthetic methods should be designed to use and create substances that have little or no toxicity to human health and the surroundings.

- **Use of Safer Solvents and Auxiliaries:** The use of auxiliary materials (e.g., solvents, separation agents, etc.) should be made avoidable wherever possible and safe to use.
- **Designing Harmless Chemicals:** Chemical products should be designed in such a way that affect their desired function while reducing their toxicity.
- **Design for Energy Efficacy:** Energy requirements of chemical methods should be minimized and recognized for their environmental and cost-effective impacts. If possible, all the synthetic methods should be accomplished at ambient temperature and pressure.
- **Use of Renewable Feedstocks:** A raw material or feedstock should be renewable rather than diminishing whenever technically and economically feasible.
- **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- **To Reduce Derivatives:** Excessive and unnecessary derivatization (use of blocking groups, protecting/ deprotecting groups, temporary alteration of physical/chemical processes) should be reduced or avoidable if possible, because such steps involves the use of additional reagents and can create waste materials.
- **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not retain in the environment.
- **Real-time analysis for Pollution Prevention:** Such analytical procedures need to be further established that allow real-time, in-process monitoring and control before the formation of hazardous substances.
- **Inherently Safer Chemistry for Accident Prevention:** Substances and the form of a substance used in a chemical process should be selected to control chemical accidents, including releases, explosions, and fires.

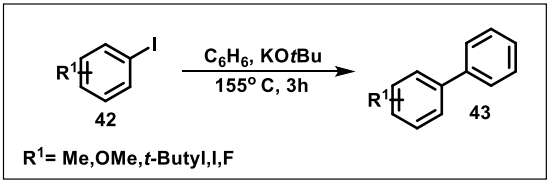
1.4.1. Reactions without the use of TM-catalyst and solvent

In organic synthesis, reactions without the use of solvents or TM-catalysts have been frequently employed, especially in methods involving one pot synthesis. These have been well established in the scientific community, because such methodologies applies the basic principles of green chemistry. [43]

In this view, several researchers have established new methods of synthesis in the absence of solvents or metal catalysts making them easier, energy efficient. Such methods preventing waste, hazardous materials, which are related to flammability, volatility and toxicity. These reactions are considered to be green because of their selective and high level of conversion of reactants to products.[44] Moreover, some of these chemical processes enhances the atom economy by avoiding the unnecessary derivatization processes and reduces waste generation.[45,46]

An interesting strategy for minimizing waste is to reduce the "factor E", for which a neat reaction is an effective approach in organic synthesis because it avoids the use of solid support and also the organic solvents.[47] This concept of "factor E" is used mainly in industry which was introduced firstly by Sheldon and is well-defined as the amount of waste produced for each kilogram of product formed. Therefore, by considering the above idea of green chemistry, the present study emphasized the expression "reactions without the use of transition metal catalyst" and "reactions without the use of solvent".

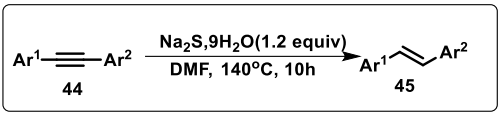
In the recent years, one of the most important achievements in organic chemistry has been the discovery that certain reactions which previously thought to preserve the use of transition metal catalysis (for example C–H activation,[48] biaryl couplings,[49,50] certain Heck[51] and Sonogashira[52] processes), can be also be achieved without the requirement for a transition metal. In this respect, Gray and Wilden established that transition metals or ligands are not important components in the synthesis of biaryl **43** (Scheme 9). Biaryl coupling **43** (often labelled 'C–H activation') of aromatic systems can be accomplished by potassium tert-butoxide as a base in the absence of transition metal and any amine or bipyridine catalyst.[53]



Scheme 9: Transition metal free synthesis of biaryl

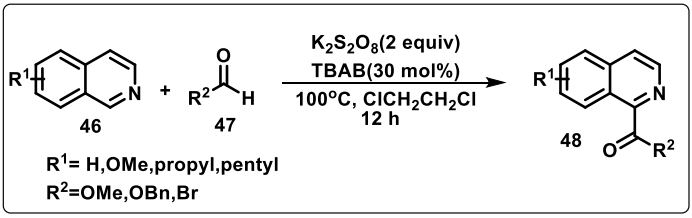
An important transformation in organic chemistry is the selective semihydrogenation of alkynes to alkenes with a defined *Z*- or *E*-configuration.[54] Among the several efficient means to access *Z*-alkenes, Lindlar's catalyst ($Pd/CaCO_3$) and its alternatives are the most

popular choices.[55] Lu and coworkers recently presented a highly stereoselective and efficient TM-free semihydrogenation of internal alkynes **44** to *E*-alkenes **45** using sodium sulfide nonahydrate (1.2equiv), an inexpensive and green water as hydrogen donor (Scheme 10).[56]



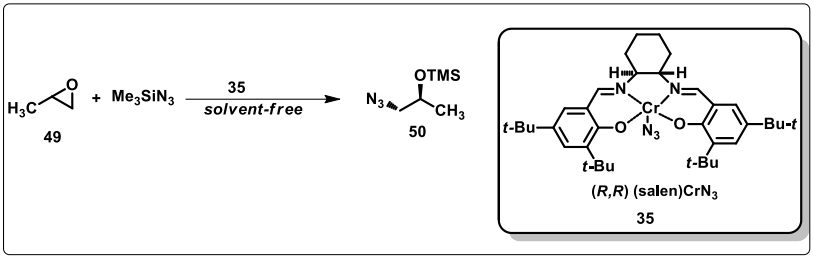
Scheme 10. Transition metal free synthesis of *E*-alkenes.

There are variety of drugs which comprises acyl derivatives of heterocyclic compounds and they are considered to be very essential in pharmacological studies.[57] Acylation of electron-rich arenes is easy[58]as compared to the acylation of electron deficient heteroarenes.[59] In this regard, Prabhu and coworkers established a TM-free acylation of isoquinoline, quinoline, and quinoxaline derivatives **46** employing a cross dehydrogenative coupling (CDC) reaction with aldehydes **47** using substoichiometric amount of TBAB (tetra-*n*-butylammonium bromide, 30 mol %) and $K_2S_2O_8$ (2 equiv) as an oxidant, forming acylated derivatives **48** (Scheme 11).[60]



Scheme 11. TM-free acylation of isoquinolines.

There are also various significant examples regarding the synthesis of different molecules under solvent free conditions. In 1995, Jacobsen and coworkers presented the synthesis of enantiomerically enriched azidoalcohols **50** from racemic epoxide **49** via chiral catalyst (R,R)(salen)CrN_3 **51** (Scheme 12) under solvent-free conditions forming the product **50** in quantitative yield and in 97% of enantiomeric excess.[61]



Scheme 12. Enantioselective synthesis of azidoalcohol.

1.4.2. Microwave irradiations and organic chemistry

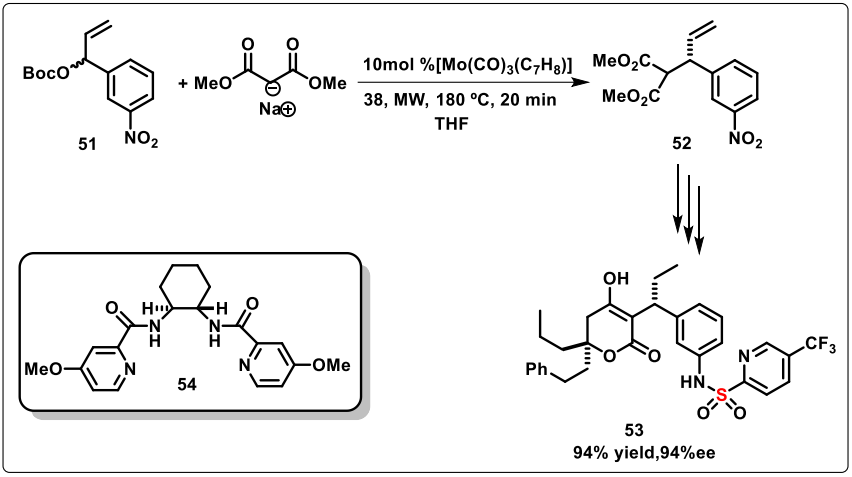
In organic synthesis, several studies under microwave irradiation have been led to establish the best reaction conditions in order to obtain the desired products in high yields, producing the least possible waste, and shorter reaction times. Thus, reactions carried out under microwave irradiation in solvent free condition, have proven to be effective reactive systems.

The use of this energy source to accelerate organic reactions is gaining more prominence by the academic community. This method is highly versatile since, compared to the reactions in conventional heating; it reduces the reaction time and can decrease the formation of by-products, making the reactions cleaner.[62]

In this perspective, several studies have been reported showing the use of microwave radiation instead of conventional heating, which follows the Green Chemistry Principles[63] e.g. reactions which require a lower reaction time and a decrease in the formation of byproducts.[64]

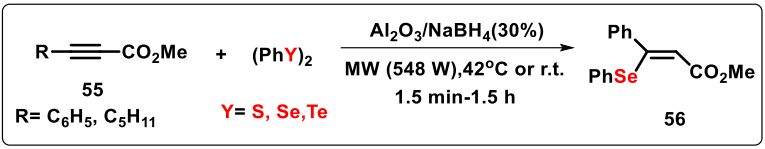
In the field of organic synthesis, several microwave-accelerated transformations are mentioned, for example, Heck reactions,[65] Suzuki[66] and Stille,[67]provided that its corresponding product in significant yields. Moreover, reactions of carbon-heteroatom bond[68] formation and asymmetric allylic alkylation reactions[69] have also been reported in the literature due to the use of the microwave.

One of the major advantage of MW-assisted heating is its use in the synthesis of the precursor drug molecule. In 2002, Trost and colleagues used this technique in one-step for the synthesis of anti-HIV drug Tipranavir **53** (Scheme 13).[70] The asymmetric allylic alkylation reaction in the formation of the intermediate **52** occurred in 20 minutes, using the chiral ligand **54** together with a molybdenum complex under microwave irradiation giving **53** with 94% yield and 94% enantiomeric excess.



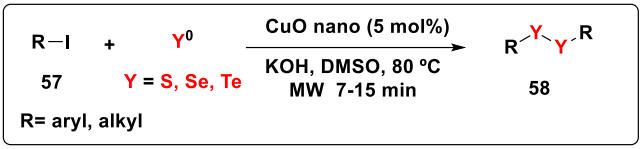
Scheme 13. Asymmetric allylic alkylation step in the synthesis of Tipranavir **53.**

Various organochlcogenides have also been synthesized using microwave, such as the vinyl chalcogenides **56**, as described by Perin and coworders.[71] These vinyl organochalcogen compounds were prepared by the addition of sodium chalcogenolates anion generated in situ by the cleavage of corresponding diorganyl dichalcogenides using $Al_2O_3/NaBH_4$ and acetylene ester **55**. The product **56** was obtained in good yields in a short reaction time (Scheme 14).



Scheme 14. Synthesis of vinyl chalcogenides using microwave energy.

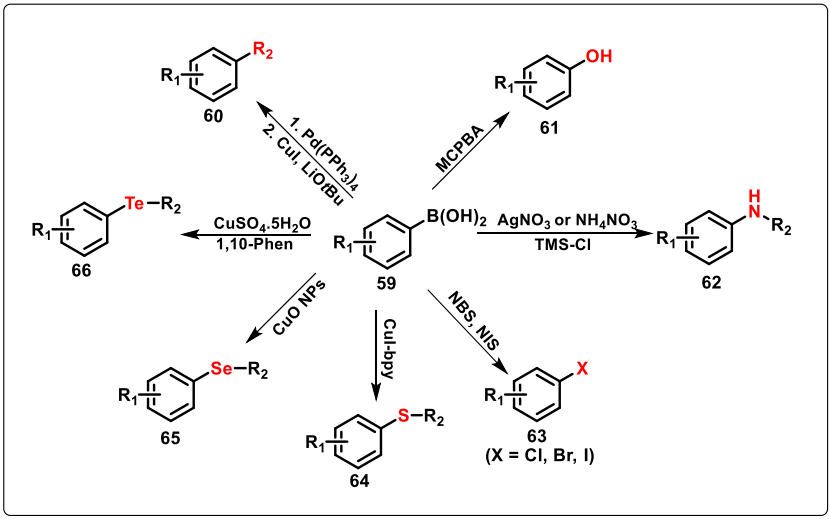
Reactions promoted by MW-irradiations are also a major focus of interest in our research group.[72]Recently, our group synthesized diorganodiselenides **58** by using arylhalides **57** and elemental selenium, catalyzed by copper nano-particules in the presene of MW irradiations (Scheme 15). This new protocol allowed the synthesis of various dichalcogenides **58** in good to excellent yields and in short reaction times.



Scheme 15. Synthesis of dichalcogenides catalyzed by CuO nanoparticles under MW irraditions.

1.5. Coupling reactions of organoboronic acids

Cross-coupling reactions of organoboronic acids are considered very important in organic synthesis. To date, the literature reports many methods for the coupling of organoboronic acids **59** with the formation of C-C **60**,[73] C-O **61**,[74] C-N **62**,[75] C-X **63** (X= F, Cl, Br, I),[76] C-S **64**,[77] C-Se **65**, [78] C-Te **66** bond formation,[79] (Scheme 16).

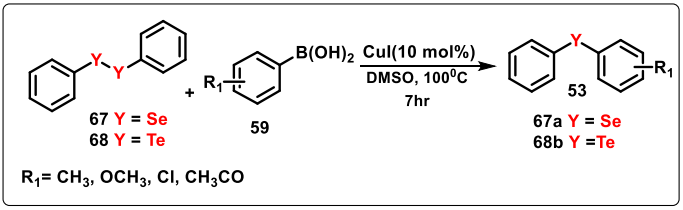


Scheme 16. Various methods of coupling of organoboronic acids.

Nevertheless, the drawbacks related with most of earlier described methodologies, owing to the consumption of transistion metal catalysts, lethal materials, costly or excessive reagents, severe reaction conditions, oxygen-free techniques or complicated multi-stepped processes, restricted their synthetic scope in organic synthesis.

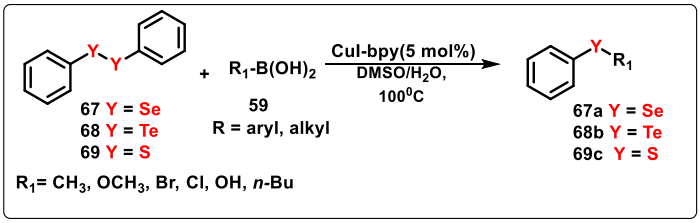
1.5.1. Coupling of arylboronic acids with diorganyl dichalcogenides

A number of methods have been developed for the synthesis of unsymmetrical aryl/alkyl chalcogenides. Among them transition metal-catalyzed, aryl carbon-chalcogen bond formation is one of the common methods for the preparation of unsymmetrical organochalcogenides.[80] In this regard, the first report was cited by Wang et al. in 2005. They reported the synthesis of unsymmetrical diaryl selenides **67a** and tellurides **67b** from the corresponding diselenides **67** and ditellurides 68 by using different substituted aryl boronic acids **59** using CuI (10 mol%) as a catalyst and DMSO as a solvent at 100 ^{0}C as shown in Scheme 17.[81]



Scheme 17. Synthesis of unsymmetrical diaryl selenides and tellurides.

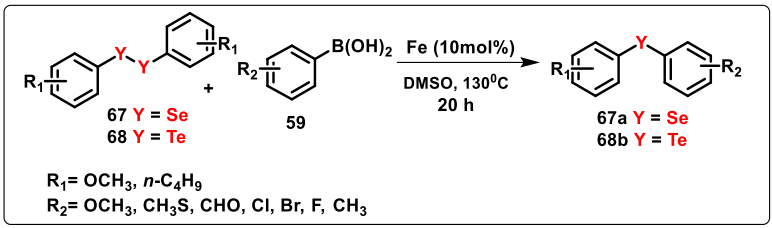
In 2007 Taniguchi described the copper catalyzed synthesis of unsymmetrical diorgano monoselenides **67a**, tellurides **68b** and sulfides **69c** by the coupling of aryl or alkylboronic boronic acids **59** using CuI-bpy (1:1, 5 mol %) and DMSO/H_2O at 100 ^{0}C (Scheme 18). [77]



Scheme 18. Copper-catalyzed synthesis of unsymmetrical diorganyl chalcogenides.

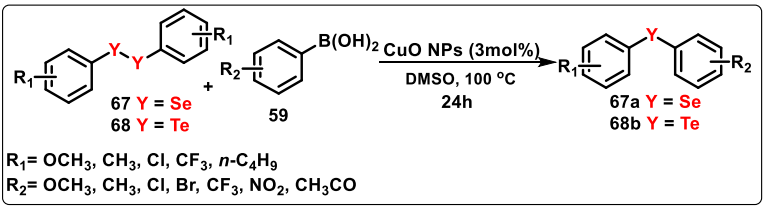
Wang et al. in 2009, developed the iron-catalyzed ligand-free direct C-Se and C-Te cross-couplings of several substituted arylboronic acids **59** with diselenides **67** and ditellurides **68**. The reactions were carried out in the presence of catalytic amounts of iron in DMSO without any ligand and additive. This method provides the desired

unsymmetrical diorgano monoselenides **67a** and monotellurides **68b** in good to excellent yields in most cases (Scheme 19).[82]



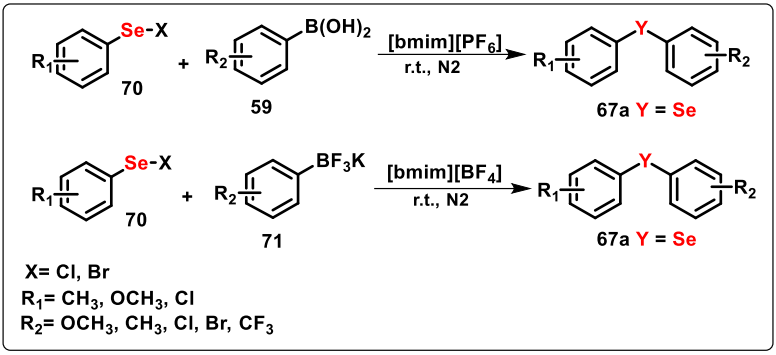
Scheme 19. Fe-catalyzed direct C-Se and C-Te cross-coupling reactions.

In the same year, Alves et al. also explored the synthesis of diorganyl monoselenides **67a** and tellurides **68b** using CuO nanoparticles (3mol%) in DMSO at 100 ^{0}C under air atmosphere (Scheme 20).[83]



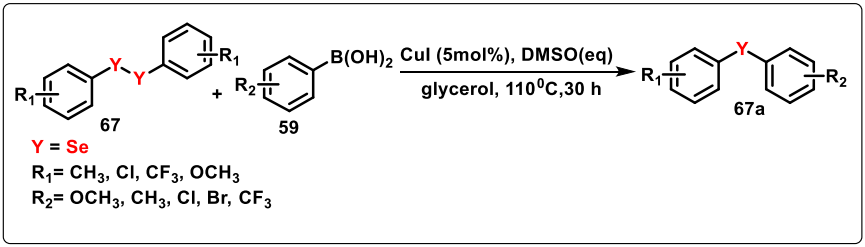
Scheme 20. CuO-NPs catalyzed coupling reactions of diselenides and ditellurides with aryl boronic.

Alves et al also described the synthesis of unsymmetrical diaryl selenides **67a** by using different arylboronic acids **59** and potassium aryltrifluoroborate **71** in the presence of imidazolium ionic liquids [bmim]BF_4 and [bmim]PF_6 at room temperature under nitrogen atmosphere. They used an electrophilic selenium species **70** instead of diselenides **67** (Scheme 16).[84]



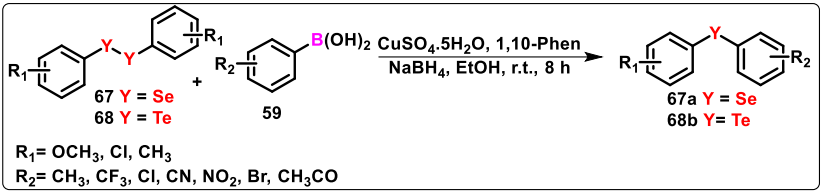
Scheme 21. Synthesis of diaryl selenides using ionic liquids.

In the continuation of same work in 2012, Alves et al described the synthesis of diaryl selenides **67a** by cross-coupling reactions of diaryl diselenides **67** with aryl boronic acids **59** using a catalytic amount of CuI (5mol%) and DMSO as additive, under open atmosphere at 110 °C. This cross-coupling reaction afforded the corresponding products in good to excellent yields and a range of diaryl diselenides and arylboronic acids were coupled (Scheme 22).[85]



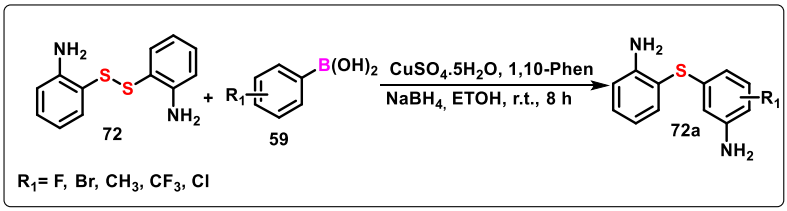
Scheme 22. Synthesis of diaryl selenides using glycerol as solvent.

Recently, Kumar et al. developed a cross-coupling reaction of organoboronic acids **59** with diaryl dichalcogenides **67-68** using $CuSO_4.5H_2O$, and the ligand 1,10 phenanthroline in the presence of $NaBH_4$, and ethanol at room temperature forming diaryl selenides **67a** and tellurides **68b** (Scheme 23).[79]



Scheme 23. $CuSO_4.5H_2O$ catalyzed synthesis of diorganyl chalcogenides.

In the same work, they stated that the reaction of organoboronic acids **59** with diaryldisulfides **69** provided low yield of corresponding product **72a** compared to diselenides **67** and ditellurides **68**. ortho-Aminosubstituted disulfide **72** has shown good compatibility with the arylboronic acids **59** under the optimized reaction condition (Scheme 24).[79]



Scheme 24. $CuSO_4.5H_2O$ catalyzed coupling of 2,2-disulfanediyldianiline with arylboronic acid.

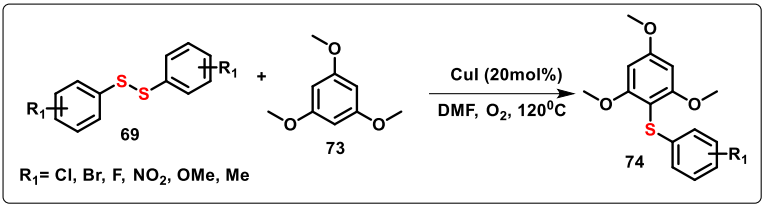
However, these kinds of transformations have their own specific drawbacks, such as the use of environmentally unfriendly solvents, costly ligands and catalysts, precious and rare metals, reducing agents, stoichiometric or greater amounts of reagents, long reaction times, harsh reaction conditions and oxygen-free techniques. Likewise, there are only a few general methods available, which are related to the synthesis of S, Se and Te-based unsymmetrical diarylchalcogenides as well as alkyl arylchalcogenides. Thus intende to develop an effective, fast, solvent free and sustainable new method for the synthesis of a range of unsymmetrical diorganyl chalcogenides**.**

1.6. C-Se/S bond formation through C-H functionalization of arenes

Unsymmetrical organochalcogenides with nitrogen-or oxygen-containing arenes and their derivatives are a very important class of

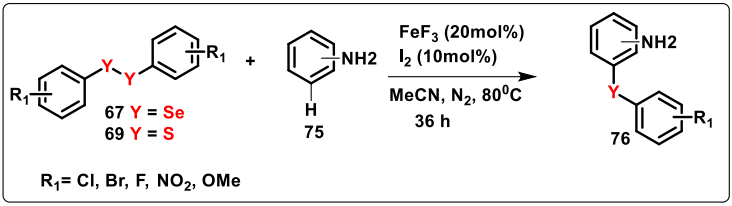
molecules, with different applications in biological sciences.[86] Aryl-sulfides containing these moieties are considered an important core structure in many important drugs.[87] However; studies on their counterpart in selenium compounds are limited.

In this regard, Cheng and co-workers described a thiolation of electron-rich arenes C-H bonds **73** with diphenyl disulfides **69** using 20 mol% copper iodide as a catalysts and DMF as a solvent under the reaction time of 24 hr at 120 ^{0}C, as shown in the Scheme 25 [88].



Scheme 25. Copper catalyzed thiolation of trimethoxy benzene.

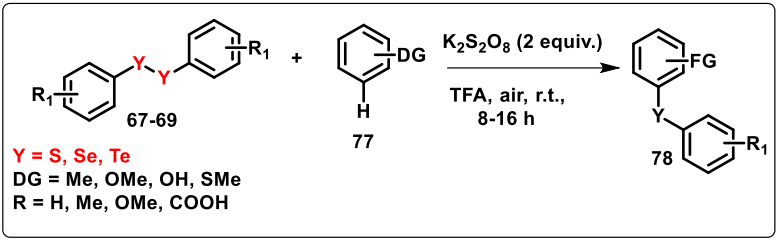
In another work, Zhang and Li developed a regioselective synthesis of chalcogen-substituted arylamines **75** by sulfenylation **69** and selenation **67** of arylamines **75** in the presence of FeF_3 and I_2 at 80 ^{0}C.The selenation and sulfenylation occur led at para position of the ring (Scheme 26). All the products were obtained in moderate to good yields.[89]



Scheme 26. Regioselective synthesis of 4-chalcogen-substituted-arylamines.

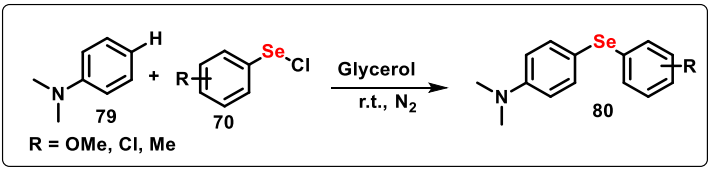
A transition-metal-free synthesis of unsymmetrical diaryl chalcogenides (S, Se, and Te) from diaryl dichalcogenides **67**-**69** and arenes **77** under oxidative conditions by using potassium persulfate (2 equiv.) at room temperature. This methodology were applied to various substituted arenes 77 such as anisole, thioanisole, diphenyl ether, phenol, naphthol, di- and trimethoxy benzenes, xylene, and mesitylene

to give unsymmetrical diaryl chalcogenides **78** in trifluoroacetic acid (Scheme 27).[90]



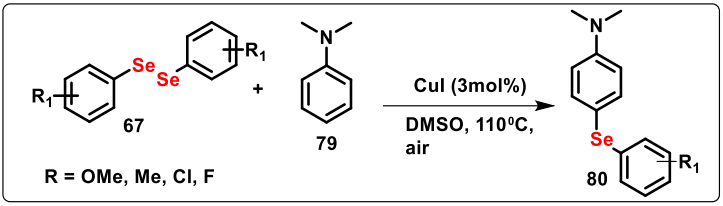
Scheme 27. Transition-metal-free synthesis of unsymmetrical diaryl chalcogenides.

Alves et al. described a metal and base-free method to access arylselanyl anilines from *N,N*-disubstituted anilines **79** and arylselanyl chloride **70** using glycerol as a solvent. The method was successfully applied to anilines with different substitution patterns in both the aromatic ring and the nitrogen atom (Scheme 28).[91]



Scheme 28. Transition-metal-free synthesis of arylselanyl aniline using glycerol as a solvent.

Similarly, the same group developed a regioselective copper-catalyzed direct arylselenation of arylamines by using a catalytic amount of CuI in DMSO at 110 ^{0}C under air atmosphere. All the selenated products were obtained in good yields *via* C-H bond cleavage of aryl amines (Scheme 29). [92]



Scheme 29. Aryl selenylation of aniline by C-H bond cleavage

Despite of their advantages, the previously reported methodologies have certain peculiars disadvantages such as, some of them suffer from limitations such as the use of non-greener solvents, prefunctionalized coupling partners, transition metal catalysts, stoichiometric or greater amounts of reagents, long reaction, times, harsh reaction conditions with non-regioselective protocols and oxygen-free techniques.

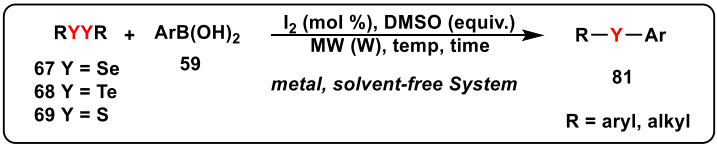
Chapter 2
Motivations and Objectives

MOTIVATIONS AND OBJECTIVES

In the view of the importance of organchalcogens compounds as well as the organoboroinc acids in the synthetic and medicinal chemisty, we decide to establish a new method including the iodine catalyzed cross-coupling of organoboroinc acids with organochalcogenides. These studies could be extended to all the three organochalcogens (S, Se, Te) involving a new greener methodology that could provide the desired products with high efficiency. We could try to avoid the use of transition metal catalyst and as well as the reaction carried out under solvent and ligand free condition.

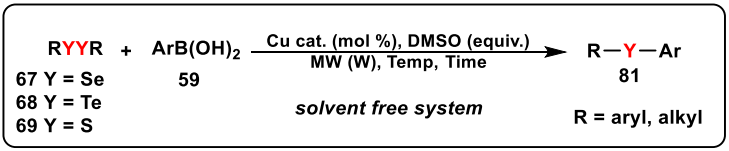
Moreover, different methods have been developed for the synthesis of unsymmetrical chalcogenides using direct C-H functionalization/activation.[93] For this reason and as part of our wider research program aimed at designing and developing eco-friendly processes,[94] this PhD work involves, for the first time, a greener iodine-catalyzed, metal, ligand and solvent-free method for the synthesis of a variety of unsymmetrical diorganyl chalcogenides **53** under microwave irradiation (Scheme 20).

The desire protocol could be performed under open atmosphere using one equiv. of organoboronic acids **59** and different dichalcogenides **67-69** in order to afford the desired unsymmetrical diorganyl chalcogenides **81** (Scheme 30).



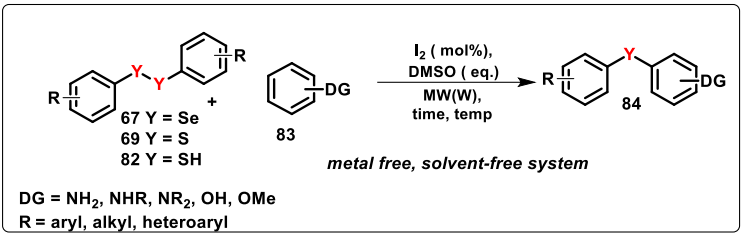
Scheme 30. I_2-catalyzed synthesis of unsymmetrical organochalcogenides under ligand, metal and solvent-free conditions.

In order to develop other green protocol associated to this transformation, the desired compounds could be also prepared by using ligand-free copper-catalyzed synthesis of unsymmetrical diorganyl chalcogenides **81** from different arylboronic acids **59** and dichalcogenides **67-69** under solvent-free condition and MW-irradiation as a source of energy (Scheme 31).



Scheme 31. Copper-catalyzed synthesis of unsymmetrical organochalcogenides under ligand, metal and solvent-free conditions.

In second part of this PhD work, we planned to develop a regioselective, metal and solvent free iodine-catalyzed method for the synthesis of diorganyl chalcogenides through oxidative C–Se/C–S formation via direct C(sp^2)-H bond cleavage from using [*O* or *N*]-containing arenes **83** (Scheme 32.), which could be applicable to analogous disulfides **82**. In fact, this protocol could be developed under open atmosphere using one equiv. of [*O* or *N*]-containing arenes **83**, half equiv. of various odorless diorganyl dichalcogenides (S/Se) **67-69**, iodine as the catalyst and DMSO as the oxidant, applying MW irradiation.



Scheme 32. I_2-catalyzed oxidative C–Se/C–S formation *via* direct C(sp^2)-H bond cleavage.

2.1. Specific Objectives

Based on our planning we decided to achieve following objectives in this PhD work:

Coupling of Arylboronic acids with diorganyl dochalcogenides

- To develop an ideal reaction condition for the synthesis of desired unsymmetrical diorganyl chalcogenides from different dichalcogenides and organoboronic acids under microwave irradiation.
- Search for the suitable transition metal free catalyst, oxidant and other reaction parameters to be used in this reaction system.
- Synthesis of a series of organoboronic acids under the best reaction conditions.
- Study some aspects of this methodology to support proposed mechanism.
- Expand the methodology for the synthesis all the three organochalcogens (S, Se, Te) involving a new greener approach.
- Search for an ecofriendly and ideal conditions utilizing microwave (MW) irradiation for the synthesis of unsymmetrical diorganyl chalcogenides, under solvent free conditions.
- Improve microwave parameters of various reaction conditions such as the time, temperature and power for the synthesis.
- Synthesis of a series of all three unsymmetrical organochalcogenides (S, Se, Te), under defined MW conditions.
- Expand the same methodology to the copper-catalysed synthesis of unsymmetrical diorganyl chalocogenides under solvent free condition and MW irradiation.
- Characterization of all the synthesized compounds by ^{1}H, ^{13}C NMR, ^{77}Se, IR, melting point and HRMS, when necessary.
- Present the developed methodology in various conferences.
- Publish the results in the form of patents and scientific articles in well-recognized journals among the scientific community.

Chalcogenation of [*O* or *N*]-containing arenes via C-H funcionalization

- Development of a regioselective synthesis of unsymmetrical chalcogenides with Nitrogen- or Oxygen-containing arenes under green conditions.
- Search for the appropriate oxidant, TM free catalyst and other reaction parameters to be used in this reaction system.

- Synthesis of a series of dicalcogenides (Se, S) and some of the unavailable [*O* or *N*]-containing arenes under the best reaction conditions.

- Study of reproducibility of the developed methodology.

-Study some aspects of this methodology to support proposed mechanism.

- Improve microwave parameters of various reaction conditions such as the time, temperature and power for the synthesis.

- Characterization of all the synthesized compounds by ^{1}H, ^{13}C, ^{77}Se-NMR, IR, melting point and HRMS, when necessary.

- Present the results in various conferences.

- Publish the results in the form of patents and scientific articles in well-recognized journals among the scientific community.

Chapter 3
Results and Discussions

RESULTS AND DISCUSSIONS

Considering the importance of organochalcogen compounds,[95] the direct chalcogenation using various aryl boronic acids and arenes through C-H bond functionalization, was investigated in the present work of PhD thesis. The chalcogenated compounds **81** and **84** (Figure 3) were prepared by coupling of different diorganyl dichalcogenides with aryl boronic acids and [*O or N*]-containing arenes.

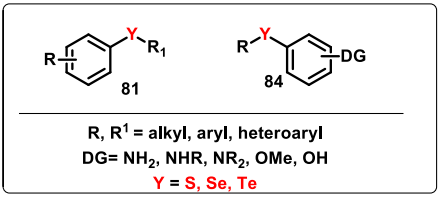
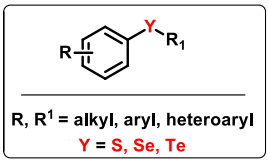


Figure 3. Unsymmetrical organochalcogenides (S, Se, Te).

In the following, we will present and discuss the results obtained during the course of this work. First, we will discuss the results obtained from the chalcogenation of various organoboronic acids. In the second part, we will discuss the different results achieved during the chalcogenation of electron rich arenes. Both of the developed methodologies were achieved under transition metal- and solvent-free conditions.



R, R^1 = alkyl, aryl, heteroaryl

Y = S, Se, Te

Chapter 3: Part A
Results and Discussions

3.1. Iodine/DMSO-catalyzed synthesis of unsymmetrical chalcogenides using arylboronic acids

In recent years, our research group has shown a great interest in the designing and developing eco-friendly processes, particularly in the area of new methods for the synthesis of organochalcogenides.[96,97]
From the last few years, the I_2/DMSO system has been applied in various greener organic transformations.[98] Moreover, the preparation of organochalcogen compounds through the reaction of organoboronic acids and diorganodichalcogenides under metal free conditions has emerged as an important and simple method for the synthesis of wide range of organochalcogenides.

The goal of the current work is mainly focused on the development of sustainable methodologies for the synthesis of unsymmetrical organosulfur **85**, organoselenium **86** and organotellurium **87** compounds (Figure 4), which could have potential applications in biological and/or in material sciences.

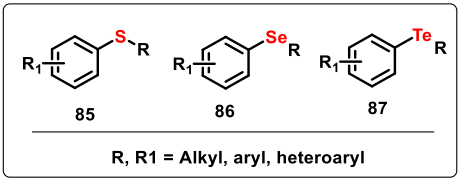


Figure 4. Unsymmetrical diorganyl chalcogenides.

Several methods have been developed in the literature regarding their synthesis.[99]Among them, transistion metal catalyzed aryl-chalcogen bond formation is one of the most commonly used protocol which generally involves the presence of ligands.[100] Despite their advantages, all the previous methodologies have their own peculiar disadvantages.

Based on this, and according to our interest in developing new methodologies for the synthesis of compounds containing sulfur and selenium, it was decided to design a straightforward, mild, and environmentally benign protocol for the synthesis of a variety of unsymmetrical diorganyl chalcogenides using various aryl boronic acids, which are also applicable to ditellurides, with a large structural diversity.

3.1.1. Synthesis of starting materials

As most of the starting materials were not commercially available, we synthesized various substituted arylboronic acids **59** and diorganyl dichalcogenides (S, Se, Te) **93-94**.

3.1.1.1. Syntheses of substituted arylboronic acids

Various substituted arylboronic acids **59a-m** were synthesized, with different electronic effects (Figure 5).

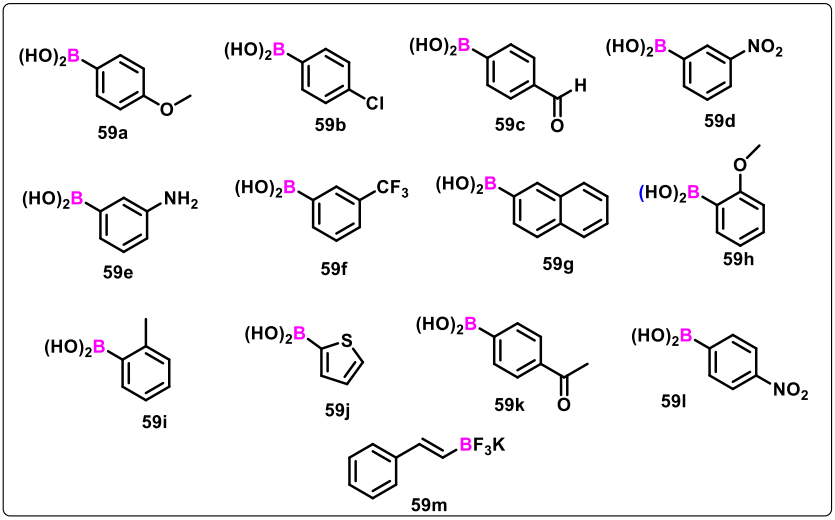
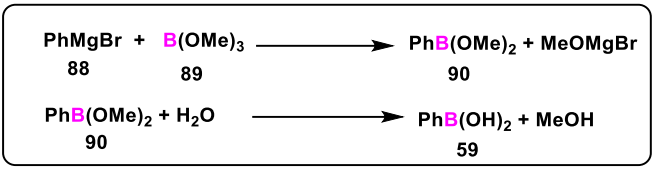


Figure 5. Different substituted arylboronic acids.

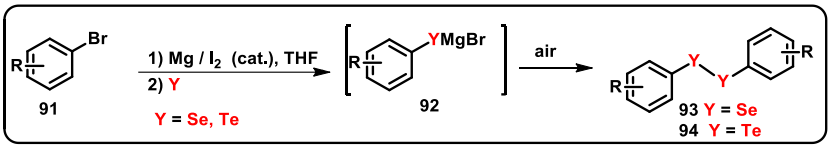
Arylboronic acids **59** were prepared through Grignard intermediate **88**, using organoyl bromides, pre-activated elemental magnesium followed by addition of trimethyl borate **89** to form an intermediate **90**. The resultant intermediate **90** finally undergoes acid hydrolysis to form the desired arylboronic acids **59**.[101] The general scheme of preparation is shown in Scheme 33.



Scheme 33. General scheme of preparation of arylboronic acids.

3.1.1.2. Synthesis of diorganyl chalcogenides (Se, Te)

Diorganyl dichalcogenides (Se, Te) were prepared through Grignard reagent starting from aryl and alkyl bromides **91**.[102] In first step Grignard reagent was regenerated in situ under inert atmosphere from the reaction of corresponding bromide **91**, which on subsequent reaction with elemental selenium form intermediate **92**. Oxidation of **92** resulted respected diselenide **93** and ditellurides **94**, with 40-65 % overall yield (Scheme 34).



Scheme 34. Synthetic route for accessing diorganyl dichalcogenides

Dibutyl diselenide **93k** and dibutyl ditellurides **94e** were prepared by the reaction of *n*-BuLi with elemental selenium and tellurium in dry THF.

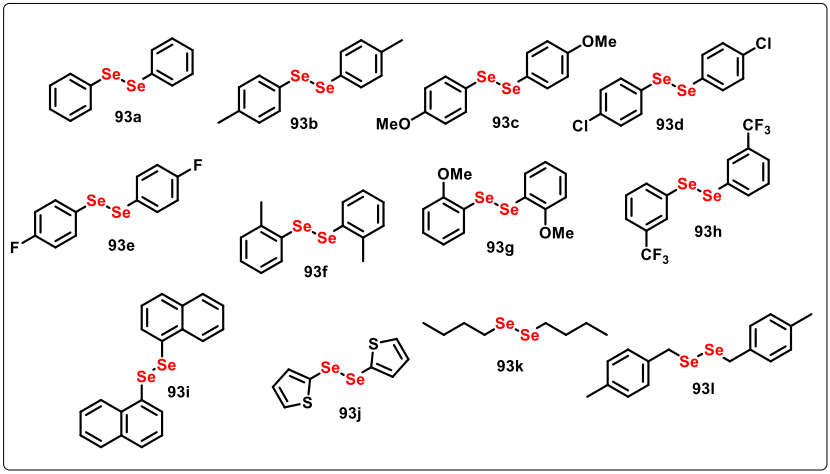


Figure 6. Synthesized library of diorganyl diselenides **93.**

Similarly, all the ditellurides **94a-e** (Figure 7) were prepared by the method of Grignard. While all the disulfides were purchased commercially.

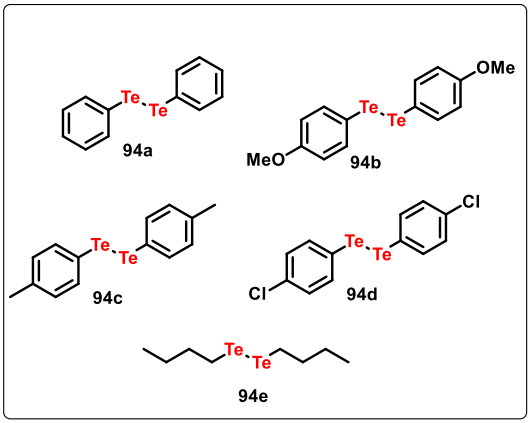
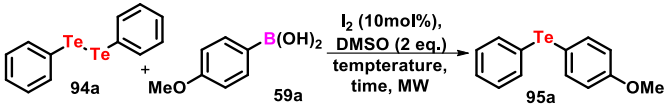


Figure 7. Synthesized library of diorganyl ditellurides **94.**

3.1.2. Optimization of reaction conditions

To identify the best reaction conditions, diphenyl ditelluride **94a** and 4-methoxyphenylboronic acid **59a** were used as standard substrates, a stoichiometric amount of oxidant (DMSO) was employed and I_2 was used as a catalyst under microwave irradiation forming corresponding unsymmetrical monotelluride **95a** (Table 1).

Table 1: Optimization of the reaction conditions for **95a.** [a]



Entry	MW [W]	T [°C]	T[min]	Yield [%][b]
1	100	100	1	49
2	100	100	3	77
3	100	100	5	84
4	100	100	10	94
5	100	100	15	96
6	100	80	10	84
7	100	120	10	95
8	80	100	10	80
9	120	100	10	85
10 [c]	--	100	18h	69

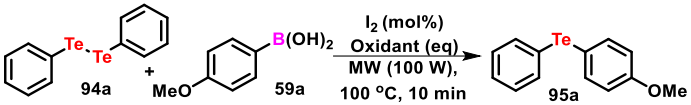
[a] Reaction conditions: **94a** (0.25 mmol), **59a** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100°C and 100 watts of MW irradiation.
[b] Isolated yields.
[c] Conventional heating.

At first, the reaction time and microwave parameters were evaluated for this coupling reaction (Table 1). We initiated our studies by varying the reaction time (entries 1-5). On performing the reaction for 1 min, we observed the formation of the desired product **95a** in only 49 % isolated yield (entry 1). Incremental increases in the reaction time resulted in a significant improvement in the yield. The best result was attained after 10 min at 100 °C with 100 W of power, where the product **95a** was accessed in 94% yield (entry 4). No substantial change in the yield was observed on applying a 15 min reaction time (entry 5).

In the next step, the temperature was screened and the ideal conditions were observed at 100 °C; lower temperatures afforded lower yield of 60 % (entry 6 *vs* 4) and higher temperature did not show a strong influence (entry 7 *vs* 4). The reaction was also carried out under different levels of MW irradiation power. Both, lower power (80 W; entry 8) and higher power (entry 9) had no effect on the isolated yield. In order to compare and evaluate the influence of the conventional heating, the reaction was also performed in an oil bath heating system (entry 10). A longer reaction time (18 h) gave the desired product in a lower yield, highlighting the superiority of the MW method.

In the next step, the effects of the catalyst loading and the stoichiometric oxidant on the reaction system were screened (Table 2). In the absence of iodine, the reaction afforded only trace amounts of (entry 1). With the use of 1 mol% of iodine (entry 2), the product was obtained in 48% yield. Increasing the catalyst loading to 5 mol% resulted an increase in the yield of **95a**, 86% (entry 3), which was further improved to 94% when 10 mol% of I_2 was used (entry 4). Further increase in the catalyst loading did not appear to have any effect on the isolated yield (entry 5). Subsequently, using NaI (entry 6) instead of I_2 resulted **95a** with 60% yield while using HI (entry 7) afforded coupled products with 84% yield, indicating that HI is probably one of the intermediate in this transformation. After ascertaining the best options for the catalyst and its loading, the effects of the oxidant quantity and type of oxidant used were evaluated. The product was obtained in poor yield when the reaction was performed in the absence of DMSO (entry 8), while 1 equiv. of DMSO afforded the desired product in 69% yield (entry 9). It should be noted that increasing the stoichiometric amount of DMSO to 3 equiv. did not affect the yield of **95a** (entry 10 *vs* 4). Other oxidants were also screened, but they failed to provide a more favorable outcome (entries 11-12).

Table 2. Optimization of Reaction Conditions for **95a.** [a]



Entry	I_2 [mol%]	Oxidant [equiv.]	Yield [%][b]
1	--	DMSO (2)	Traces
2	1	DMSO (2)	48
3	5	DMSO (2)	86
4	10	DMSO (2)	94
5	15	DMSO (2)	96
6 [c]	--	DMSO (2)	60
7 [d]	--	DMSO (2)	84
8	10	--	20
9	10	DMSO (1)	69
10	10	DMSO (3)	95
11	10	TBHP (2)	47
12	10	H_2O_2 (2)	70

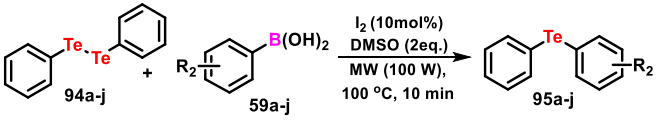
[a] Reaction conditions: **94a** (0.125 mmol), **59a** (0.5 mmol) in the presence of catalyst (10 mol%) and oxidant (2 equiv.) for 10 min at 100°C and 100 W of MW irradiation.
[b] Isolated yields.
[c] Reaction performed using 10 mol% of NaI.
[d] Reaction performed using 10 mol% of HI.

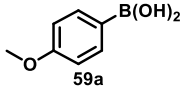
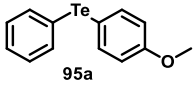
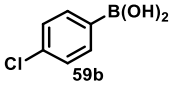
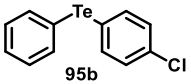
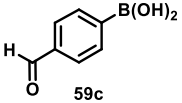
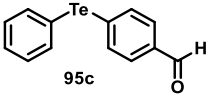
3.1.3. The reaction Scope

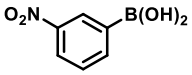
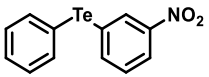
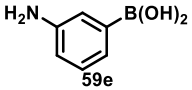
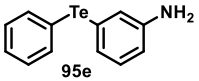
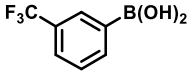
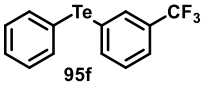
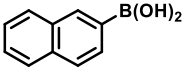
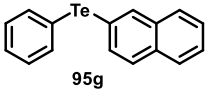
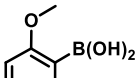
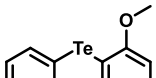
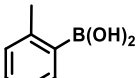
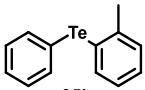
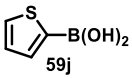
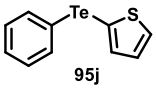
After determining the best reaction parameters, the efficiency and generality of our methodology was explored by applying it to various diorganyl ditellurides **94a-j** and arylboronic acids **59a-j** under the optimized conditions (Table 3-4).

The reaction worked well for structurally different organic moieties containing both electron withdrawing (R_1, R_2 = X, CF_3, NO_2, COR, etc.) and electron donating (R_1, R_2 = Me, OMe, NH_2, etc.) groups as well as bulky groups. Firstly, we used different arylboronic acids **59a-j** while keeping diphenyl ditelluride **94a** constant, resulting in **95a-j** in good to excellent yields (Table 3). In general, electron-donating groups at the aryl ring of **59** afforded good results. The steric hindrance of ortho-substituted aryl substrates did not appear to influence the yields of **95a-j**. Similarly, a bulky substrate (R = 2-naphthyl) resulted in the desired product **95g** in 93% yield. We were also delighted to find that heteroarylboronic acid afforded the desired product **95j** with 90% yield.

Table 3: Synthesis of unsymmetrical diorganyl tellurides **95a-j.** [a]



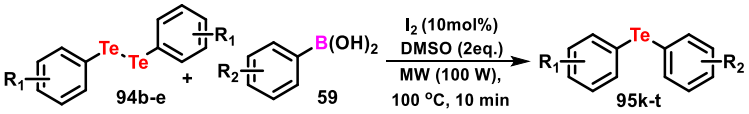
Entry	$R_2B(OH)_2$	Product	Yield[%][b]
1			94
2			86
3			89

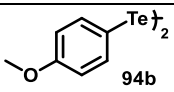
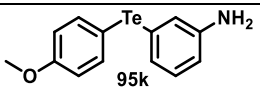
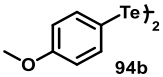
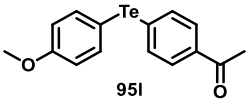
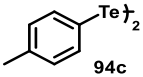
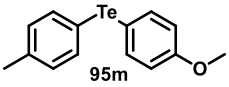
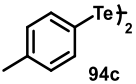
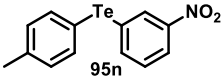
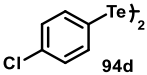
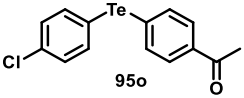
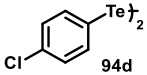
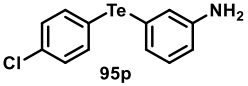
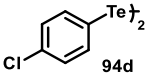
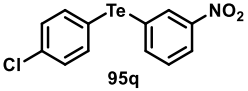
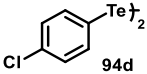
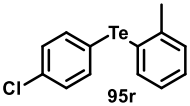
4	 59d	 95d	85
5	 59e	 95e	89
6	 59f	 95f	79
7	 59g	 95g	93
8	 59h	 95h	95
9	 59i	 95i	93
10	 59j	 95j	90

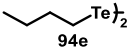
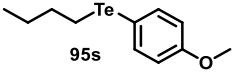
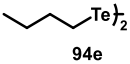
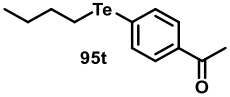
[a] Reaction conditions: **94a-j** (0.25 mmol), **59a-j** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 ^{0}C and 100W under MW irradiation.
[b] Isolated yields

We futher explored the efficiency of our optimized reaction by using various various diorganyl ditellurides **94b-e** (Table 4). All the desired product **95k-t** were obtained in good to excellent yield and the reaction tolerated electronic and steric effects.

Table 4: Synthesis of unsymmetrical diorganyl tellurides **95k-t.** [a]



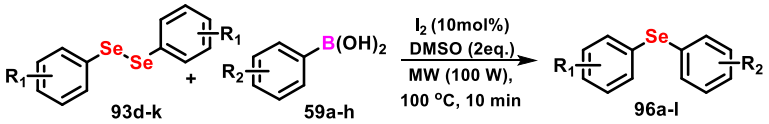
Entry	$(R_1Te)_2$	Product	Yield[%][b]
1	 94b	 95k	84
2	 94b	 95l	93
3	 94c	 95m	94
4	 94c	 95n	87
5	 94d	 95o	89
6	 94d	 95p	90
7	 94d	 95q	89
8	 94d	 95r	88

9			89
10			82

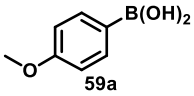
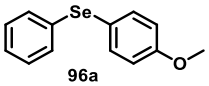
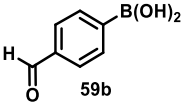
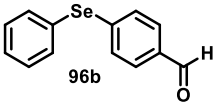
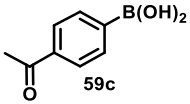
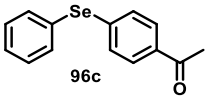
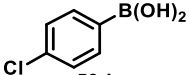
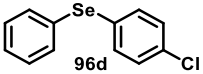
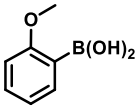
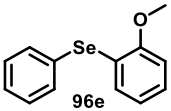
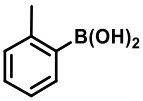
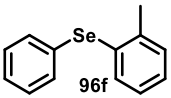
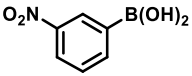
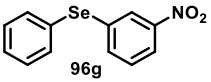
[a] Reaction conditions: **94b-e** (0.25 mmol), **59** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 ^{0}C and 100W under MW irradiation.
[b] Isolated yields

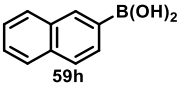
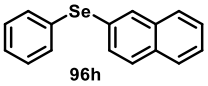
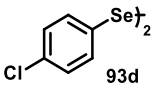
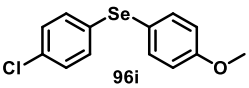
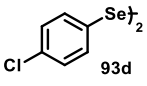
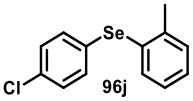
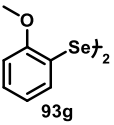
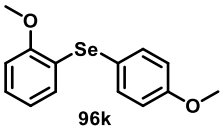
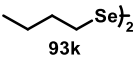
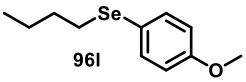
The success in the iodine-catalyzed synthesis of unsymmetrical diorganyl tellurides **95k-t** by intermolecular C-Te bond formation using diorganyl ditellurides **94b-e** and arylboronic acids **59**, prompted us to expand this methodology to diorganyl diselenides **93d-k** as a way to access unsymmetrical diorganyl selenides **96a-l** (Table 5). In order to evaluate the electronic and steric effects, initially, we varied the substituents at the aryl ring of boroic acid **59a-h**, furnishing the corresponding selenides **96a-h**, as shown in Table 5. Electron effects due to the *para* and *meta* substituents on **59a-g** exerted a limited influence, affording the corresponding product **96a-d** and **96g** in 86-93% yields The reaction seems not to be sensitive to steric effects at the ortho position (R = Me, OMe) or bulky groups (R = naphthyl) on the aryl ring of **59e-h**, furnishing the desired products **96e-f** and **96h** in 91-93% yields. Similarly, substituents at the aryl ring of diselenide **93d-k** afforded the corresponding products **96i-k** in 88-92% yields, showing no significant influence of the electronic or steric effects on the diselenides **93d-k**. Subsequently, we successfully carried out the reaction between aliphatic diselenide **93k** and **59a**, affording *n*-butyl(4-methoxyphenyl) selenide **96l** with 83% yield.

Table 5: Synthesis of unsymmetrical diorganyl selenides **96a-l.** [a]



93d-k 59a-h 96a-l

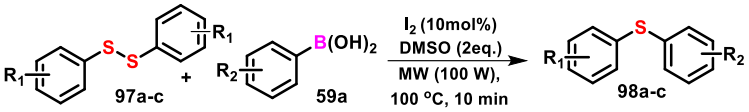
Entry	$R_2B(OH)_2$,$(RSe)_2$	Product	Yield[%][b]
1	 59a	 96a	93
2	 59b	 96b	90
3	 59c	 96c	89
4	 59d	 96d	87
5	 59e	 96e	93
6	 59f	 96f	92
7	 59g	 96g	86

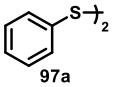
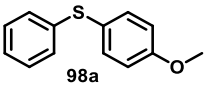
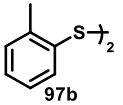
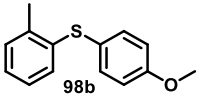
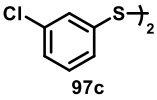
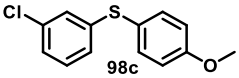
8	 59h	 96h	91
9	 93d	 96i	88
10	 93d	 96j	89
11	 93g	 96k	92
12	 93k	 96l	83

[a] Reaction conditions: **93d-k** (0.25 mmol), **59a-h** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 ^{0}C and 100W under MW irradiation.
[b] Isolated yields.

The scope of the reaction regarding the preparation of unsymmetrical diorganyl sulfides **98a-c** was then explored by using different disulfides **97a-c** under the optimal reaction conditions (Table 6). Interestingly, the reaction of different diaryl disulfides **97a-c** with 4-methoxyphenylboronic acid **59a** proceeded smoothly and afforded the corresponding products **98a-c** in 75-84% isolated yields (Table 6). The small decrease in the yields could be explained by the stronger S–S bond of the diaryl disulfides compared to the respective ditellurides **94** or diselendies **93**.

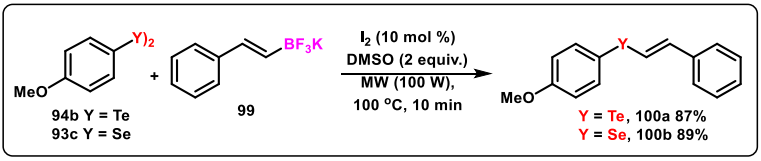
Table 6: Synthesis of unsymmetrical diorganyl sulphides **98a-c.** [a]



Entry	$(RS)_2$	Product	Yield[%][b]
1	 97a	 98a	79
2	 97b	 98b	84
3	 97c	 98c	75

[a] Reaction conditions: **97a-c** (0.25 mmol), **59a** (0.5 mmol) in the presence of I_2 (10 mol%) and DMSO (2 equiv.) for 10 min at 100 ^{0}C and 100W under MW irradiation.
[b] Isolated yields.

In order to further investigate the scope of this new coupling methodology we extended our study to potassium vinyltrifluoroborate **99** as an alternative to boronic acid in these tellurylation and selenylation reactions (Scheme 35), applying the optimal reaction conditions. Interestingly, the reaction of ditelluride **94b** and diselenide **93c** proceeded smoothly and afforded the corresponding coupled product **100a** and **100b** in 87% and 89% isolated yield (Scheme 35).



Scheme 35. Iodine-catalyzed reactions of potassium salt of vinyltrifluoroborate **99** with diorganyl dichalcogenides.

3.1.4. Reaction on large scale

One of major disadvantage of few methods of synthesis in organic chemistry is that generally synthetic reaction works well on small scale but on larger scale the reaction does not afford the desired product in the expected yields. This is an important factor, which restrict the applicability many methods in industry. Therefore, in order to demonstrate the synthetic utility of this new protocol, a series of reactions was carried out on different scales by increasing incrementally the scale up to 10 mmol. Ditelluride **94b** and boronic acid **59a** were selected as the test materials, affording **95a** with a slight decrease in the yield. Therefore, this method could be used as a practical way to synthesize unsymmetrical diorganyl chalcogenides on larger scale. Based on the experiments on different scale, as shown in Fig 8, we can say that this method could be used as a practical method to synthesize biologically relevant lead compounds.

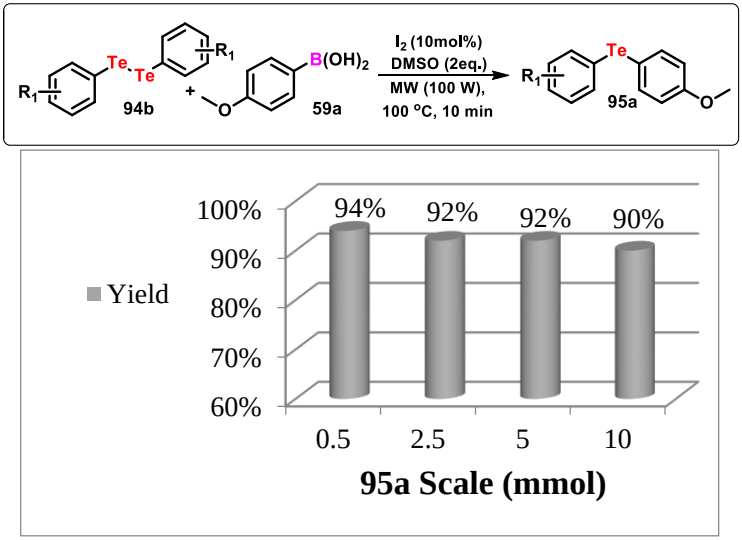


Figure 8. Results for the reaction at different scales.

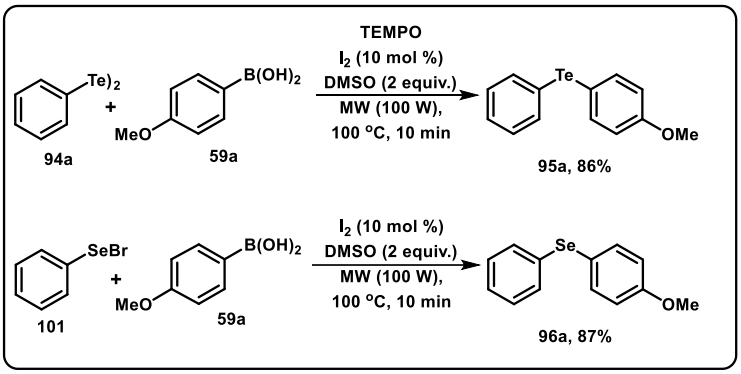
3.1.5. Investigation of the mechanism and proposed mechanism

Considering that little is known about the coupling reaction of diorganyl chalcogenides and organoboronic acids under metal-free conditions, it was proposed to run some experiments and taking help

from literature in order to develop a proposed mechanism for this transformation (Scheme 36).

Firstly, we evaluated the hypothesis of any possible radical mechanism for this coupling reaction using 2-methoxy boronic acid **59a** and diphenyl ditelluride **94a** in the presence of radical inhibitor (TEMPO) under standard conditions. The use of TEMPO did not hamper the reaction and the **95a** was obtained in 86% yield (Scheme 36). This result indicates that, most probably, a radical mechanism is not operating and the PhY radical species is not involved.

In the secondly step, when boronic acid **59a** was treated with PhSeBr **101** instead of diphenyl diselenide **93a**, the product **96a** was isolated with 87% yield (Scheme 36), indicating that the reaction passes through a phenylselenium cation species.

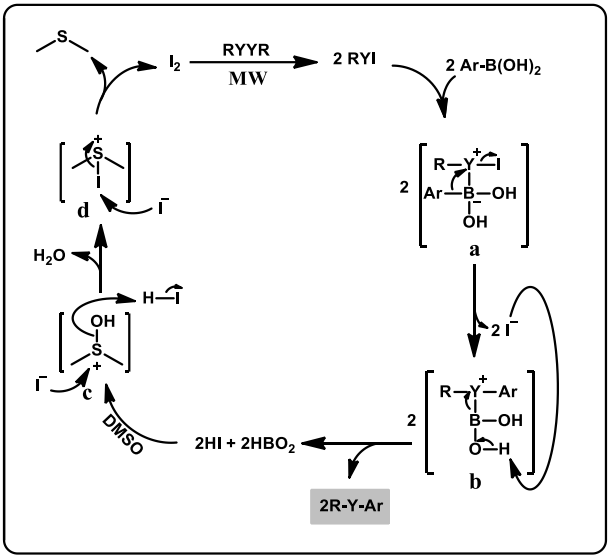


Scheme 36. Investigation of the mechanism.

Based on the experiments described above and in the literature data, the following ionic mechanism was proposed for this coupling reaction (Scheme 37).[105]

- Firstly, RYI (Y = Te, Se, S) would be generated through the reaction of diorganyl dichalcogenide RYYR with the catalyst (I_2).
- Subsequently, the reactive RYI intermediate on reaction with organoboronic acid would generate species **a** which on migration of the aryl moiety from boron to chalcogen and elimination of iodide could result in species **b**.
- The deboronation of species **b** would furnish the desired product RYAr with the simultaneous formation of HI.

- In the next step of the mechanism, two equivalents of HI on reaction with DMSO would then regenerate iodine,[24] through the protonated sulfur species **c**.
- This species would be rapidly converted to the iodine-dimethyl sulfide adduct **d** with the elimination of water.
- Finally, the cycle would be completed by the conversion of the iododimethylsulfonium iodide species **d** to dimethyl sulfide with the regeneration of the catalyst in the reaction medium.



Scheme 37. Proposed mechanism for the synthesis of Unsymmetrical Diorganyl Chalcogenides.

3.1.6. Characterization

The proposed structures of all synthesized unsymmetrical organochalcogenides were confirmed by nuclear magnetic resonance (NMR) spectroscopy and high resolution mass spectrometry (HRMS) and by other relevant techniques. In the following we will discuss the assignment of different signals from hydrogen and carbon-13 spectra of 1-(4-((4-chlorophenyl)tellanyl)phenyl)ethan-1-one **95o**, as a representative compound. The spectra were obtained in $CDCl_3$.

In the ^{1}H NMR spectrum (Figure 9), there is a singlet at 2.56 ppm with integral value of 3, referring to the methyl hydrogens of carbonyl group.

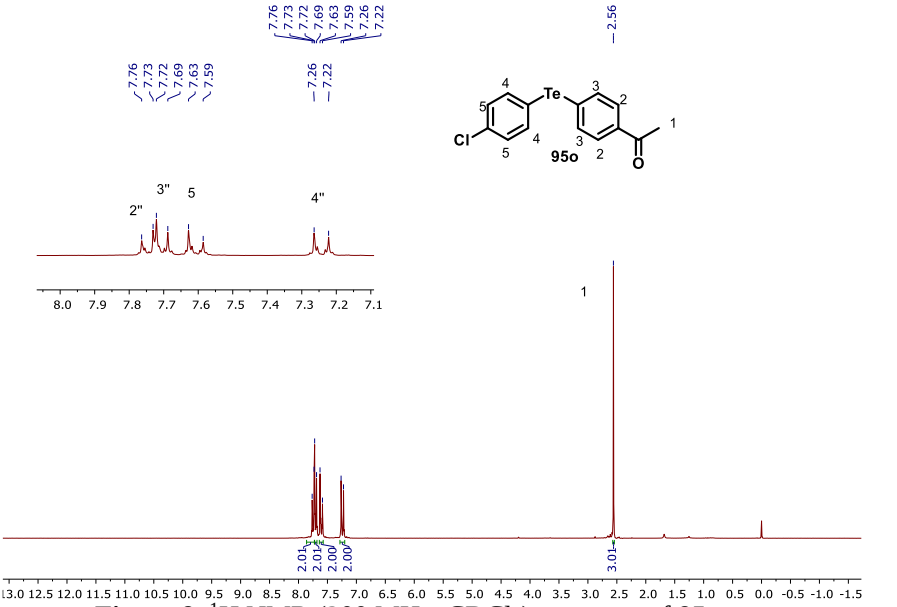


Figure 9. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95o.**

At 7.24 ppm, a doublet with integral value of 2 and with coupling constant J = 8.4 Hz, which can be attributed to two aromatic hydrogen bounded C-2 of the phenyl ring close to carbonyl group. Next a doublet at 7.61 ppm can be observed with integral value 2 and with coupling constant J = 8.4 Hz, referring to the aromatic hydrogens on C-3 of phenyl ring. On left hand side, there is a doublet at 7.70 ppm with integration value 2 and coupling constant J = 6.6 Hz, referring the 2 hydrogen at C-4 position on phenyl ring and lastly, at 7.75 ppm, a doublet with integral value of 2 and with coupling constant J = 6.6 Hz, which can be attributed to two aromatic hydrogen bounded C-5 of the phenyl ring close to chloro.

In the ^{13}C NMR spectrum (Fig. 10), all carbons for **95o** can be seem clearly; a total 10 signals are expected. A signal at 26.60 pm chemical shift (δ) is for C-1 for -Me group of carbonyl moiety. There are two peaks for quaternary carbon at 111.07 ppm and 123.55 ppm representing C-2, and C-3, respectively. While another three peaks for

quaternary carbon at 135.48, 136.29 and 197.66 ppm representing C-6, C-8, C-10 respectively. The remaining for signals at 129.05, 130.26, 136.19 and 140.91 representing aromatic carbons C-4, C-5, C-7 and C-9.

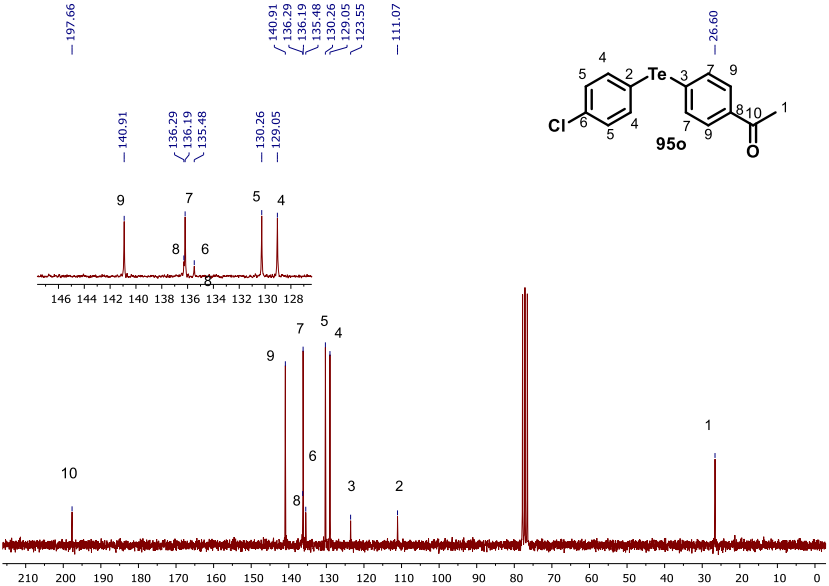


Figure 10. ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95o.**

For all new compounds we performed high-resolution mass spectrometry (HRMS) using electrospray ionization (ESI) or atmospheric pressure photoionization (APPI) technique for ionization. Compound **95o** was been analyzed by APPI-HRMS technique (Fig. 11). The molecular ion of the compound **95o** was obtained by adding a proton to the molecular weight i.e. $[M+H]^+$, and experimental value for $C_{14}H_{11}ClOTe$ $[M + H]^+$ found was to be 360.9621, and the calculated theoretical value for $[M+H]^+$ was 360.9623. In addition, the isotopic abundance of simulated and experimental spectrum matches with each other.

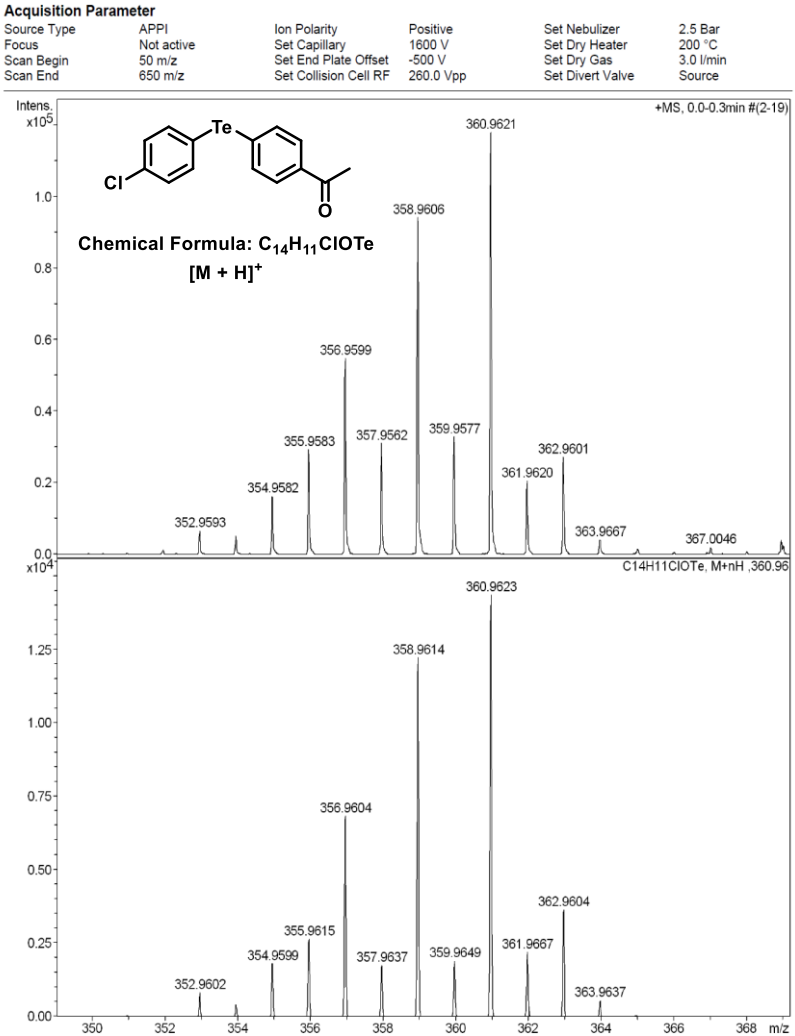
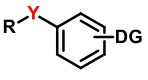


Figure 11. Spectrum of high resolution mass of the compound **95o** using APPI.



R = Alkyl, aryl, heteroaryl
DG= NH_2, NHR, OMe, OH
Y = S, Se

Chapter 3: Part B
Results and Discussions

3.2. DMSO/Iodine-catalyzed synthesis of unsymmetrical chalcogenides with nitrogen- or oxygen-containing arenes

After the successful studies on the synthesis of unsymmetrical chalcogenides using various aryl boronic acids, we extended our studies on the nitrogen and oxygen containing arenes as their alternative source of preparation. Moreover, unsymmetrical organochalcogenides with nitrogen-or oxygen-containing arenes and their derivatives are a very important class of molecules, with different applications in biological sciences. Functionalization of arenes via C(sp^2)–H bond activation has also emerged an important and simple method for the synthesis of wide range of unsymmetrical chalcogenides.

The goal of the current work is mainly focused on the development of sustainable methodologies for the synthesis of unsymmetrical chalcogenides containing organoselenium **102** and organosulfur **103** moieties (Fig. 12), which could have potential applications in biological and/or in material sciences.

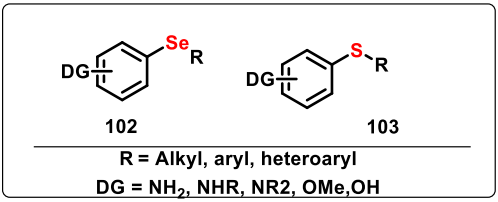


Figure 12. Selenated and thiolated [*O* or *N*]-containing arenes.

So far there are only few reports regarding oxidative C–Se/C–S bond formation through C(sp^2)–H bond functionalization of arenes,[89] but they have their own peculiar disadvantages. Based on this, and according to our interest in developing new ecofriendly methodologies for the synthesis of compounds containing sulfur and selenium, it was decided to design a straightforward, mild, and environmentally benign protocol for the chalcogenation of [*O* or *N*]-containing arenes, with a large structural diversity.

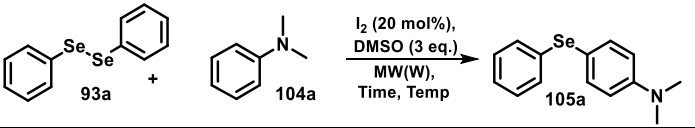
3.2.1. Synthesis of starting materials

As previously described in 3.1.2.2., a library of diorganyl diselenides (Fig. 6) was prepared through Scheme 34.

3.2.2. Optimization of reaction conditions

The initial screening and optimization of the reaction conditions were conducted with diphenyl diselenide **93a** and *N*,*N*-dimethylaniline **104a** as standard substrates, using a stoichiometric amount of oxidant and I_2 as a catalyst under microwave irradiation (Table 7).

Table 7: Optimization of catalyst for the synthesis of **105a.** [a]



Entry	MW [W]	T [°C]	t [min]	Yield [%][b]
1	100	110	3	47
2	100	110	5	69
3	**100**	**110**	**10**	**95**
4	100	110	15	96
5	100	80	10	53
6	100	120	10	96
7	80	110	10	79
8	120	110	10	91
9 [c]	-	110	8h	65

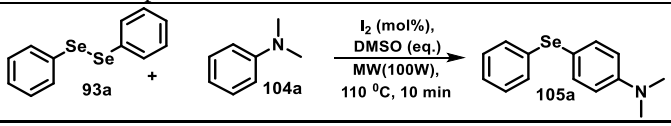
[a] Reaction conditions: **93a** (0.125 mmol), **104a** (0.25 mmol), I_2 (20 mol%), DMSO (3 equiv.) under MW irradiation.
[b] Isolated yield.
[c] Conventional heating in sealed tube.

Firstly, the influence of the reaction time and microwave parameters on the performance of the direct C(sp^2)–H bond selenation of

93a was investigated (Tables 7). Initially, the reaction time was varied (entries 1-4). Carrying out the reaction for 3 min afforded the desired product **105a** in only 47% yield (entry 1). An increase in the reaction time to 10 min resulted in a significant improvement and product **105a** was obtained in 95% yield (entry 3). However, no considerable alteration in the yield was noted on applying a 15-min reaction time (96%, entry 4). The influence of temperature on the reaction behavior was then screened (entries 5–8) and the ideal conditions were observed at 110 °C. We observed that by decreasing the temperature a lower yield of **105a** was obtained (entry 5) and a higher temperature did not show any significant influence (entry 6). We further investigated the reaction by investigating the effect of applying MW irradiations. The best result was obtained using 100 W (entries 7 and 8 *vs* 3). In order to evaluate the influence of the heating source, the reaction was also performed in a conventional oil bath heating system (entry 9). However, 8 h of heating was required to obtain **105a** in 65 % yield, highlighting the superiority of the MW method.

In the subsequent step, the influence of the catalyst loading and the stoichiometric quantity of oxidant on the reaction system was explored (Table 8). No product was observed in the absence of catalyst, I_2 (entry 1). By using 5 mol% of I_2, **105a** was obtained in 45% yield (entry 2). Increasing the catalyst loading to 10 mol% led to an improvement in the yield (87%, entry 3), which was further increased significantly to 95% when 20 mol% of I_2 was used (entry 4). Further increase in the catalyst loading was not effective, giving **105a** in 96% yield (entry 5).

Table 8: Optimization of reaction conditions for **105a.** [a]



Entry	I_2 (mol%)	Oxidant (equiv.)	Yield [%][b]
1	--	DMSO (3)	NR
2	5	DMSO (3)	45
3	10	DMSO (3)	87

4	**20**	**DMSO (3)**	**95**
5	30	DMSO (3)	96
6	20	--	32
7	20	DMSO (2)	75
8[c]	20	DMSO	93
9	20	DTBP (3)	45
10	20	H_2O_2	81

[a] Reaction conditions: **93a** (0.125 mmol), **104a** (0.25 mmol) in the presence of catalyst (20 mol%) and oxidant (3 equiv.) for 10 min at 110°C with 100 W of MW irradiation.
[b] Isolated yields.
[c] Reaction performed using 250μl DMSO.

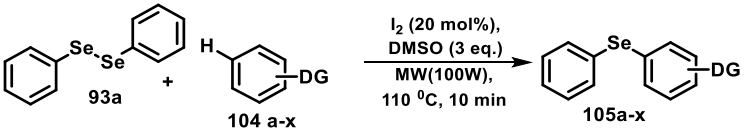
The influence of oxidant on the selenation of **104a** was then evaluated (entries 6-10). By decreasing the amount of DMSO from 3 to 2 eq., the yield of **105a** was reduced from 95 to 75%. In the absence of DMSO the yield dramatically decreased to 32% (entry 6). Using DMSO as solvent did not showed any further positive influence on the yield on 3a (entry 8 *vs* 4). The use of other oxidants i.e. H_2O_2 and DTBP instead of DMSO resulted in a less efficient transformation in 81 and 45% yields, respectively (entries 9-10).

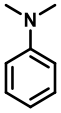
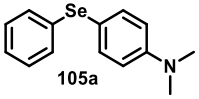
3.2.3. The Reaction Scope

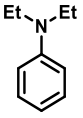
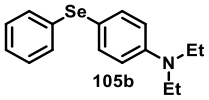
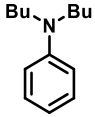
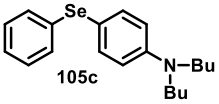
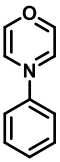
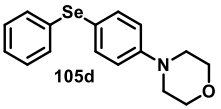
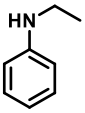
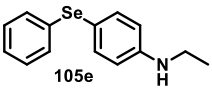
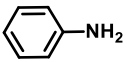
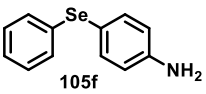
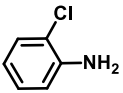
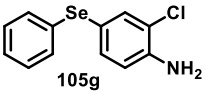
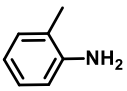
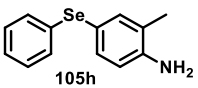
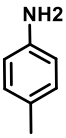
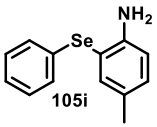
With the optimized conditions in hand, the applicability of other arenes, e.g. anilines, anisoles etc., and various diorganyl diselenides were screened (Tables 9 and 10). We first explored the scope of the reaction with respect to the different arenes **104a-x** while keeping diphenyl diselenide **93a** constant, which resulted the coupled product **105a-x** in good to excellent yields (Table 9). In general, *N*,*N*-disubstituted anilines afforded the selenated product selectively at the para position of the anilines **104a-d** in excellent yields.

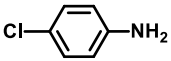
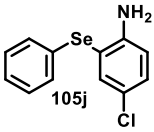
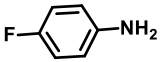
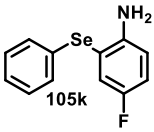
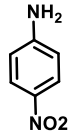
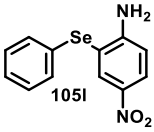
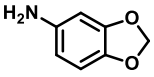
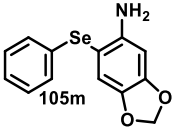
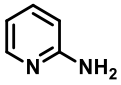
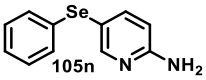
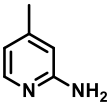
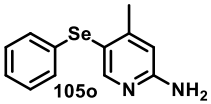
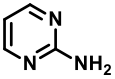
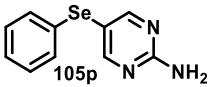
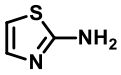
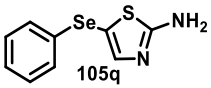
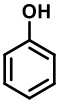
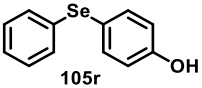
Furthermore, to our delight, when the reaction was carried out with a secondary-amine (*N*-ethyl aniline) and a primary-amine (aniline) only the coupled products **105e** and **105f** were observed at the para position, in 83% and 80% yields, respectively. In view of these results, ortho- and para-substituted aryl amines **104g-l** were reacted with **93a** under standard conditions. Ortho-substituted anilines resulted in selenation at the para-position, providing **105g-h** in good yields. Interestingly, an electron-withdrawing group at the ortho-position afforded better yields (entry **104g** *vs* **104h**). When the para position of the aniline was blocked by using 4-substituted anilines **104i-l**, the coupling took place at the ortho-position forming **105i-l** in 83-72% yields. The slight decrease in the yield of **104j-l** as compared to **104g-i** is most likely due to the steric effect. Similarly, on using 3,4-(methylenedioxy)aniline **104m**, the coupling took place at C6 instead of the C2 position, which is most probably due to the steric effect and the selenated product **105m** was obtained in 82% yield. Promising results from anilines **104a-m** motivated us to further extend this new protocol to different heteroaromatic amines **104n-p**. It is noteworthy that the compounds **104n-p** are well tolerated in this transformation and furnished exclusively the para selenated product **105n-p**, related to the amine, in 79-71% yields. Similarly, in the case of 2-aminothiazole **104q**, an electrophilic attachment took place at the C5 position resulting in **105q** in 75% yield. We further tested this method with the phenol and methoxy-arenes **104r-x** under the optimized conditions used for anilines. Encouragingly, the reactions proceeded cleanly and furnished the corresponding aryl selenides **105r-x** in 75-88% yields.

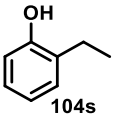
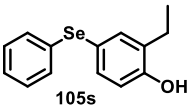
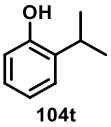
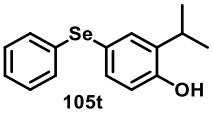
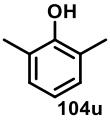
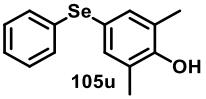
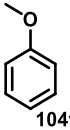
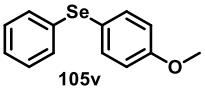
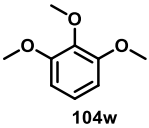
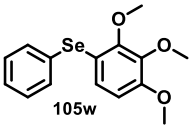
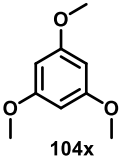
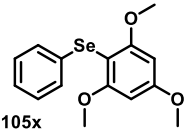
Table 9: Scope and generality of the reaction using arenes **104a-x.**[a]



Entry	Arenes	Product	Yield [%][b]
1	 104a	 105a	95

2	 104b	 105b	92
3	 104c	 105c	89
4	 104d	 105d	87
5	 104e	 105e	83
6	 104f	 105f	80
7	 104g	 105g	87
8	 104h	 105h	78
9	 104i	 105i	72

10	 104j	 105j	78
11	 104k	 105k	83
12	 104l	 105l	81
13	 104m	 105m	82
14	 104n	 105n	79
15	 104o	 105o	71
16	 104p	 105p	76
16	 104q	 105q	75
17	 104r	 105r	82

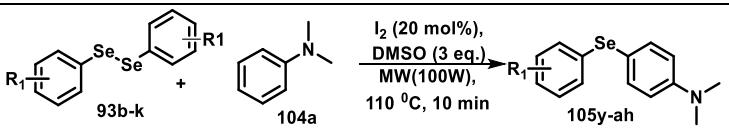
18	 104s	 105s	80
19	 104t	 105t	82
20	 104u	 105u	75
21	 104v	 105v	88
22	 104w	 105w	83
23	 104x	 105x	81

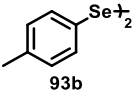
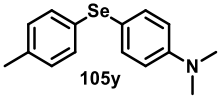
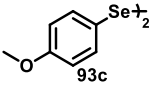
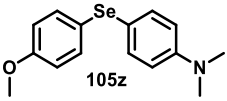
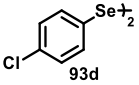
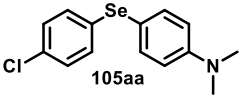
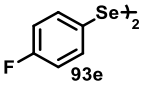
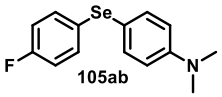
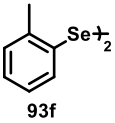
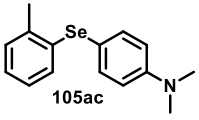
[a] Reaction conditions: **93a** (0.125 mmol), **104a-x** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation.
[b] Isolated yields.

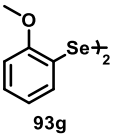
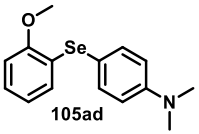
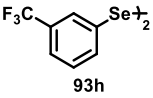
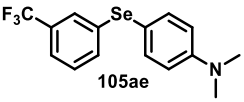
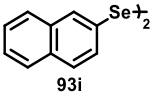
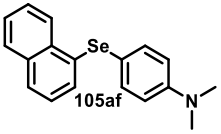
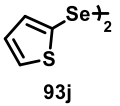
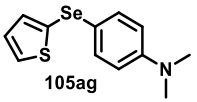
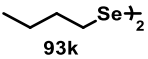
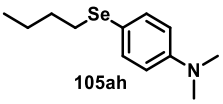
To extend the scope in terms of the substrate, the effects of other diorganyl diselenides **93b-k** were also investigated (Table 10). Interestingly, our protocol worked well for several diselenides containing both electron-donating and electron-withdrawing groups as well as bulky groups, verifying the sensitivity and tolerance to the electronic effects and steric effects of several different substituents. We observed that the desired products, **105y-105ah**, were obtained in good to excellent yields. The results revealed that electron-withdrawing

groups at the phenyl ring of **93** gave fairly good yields (**93b, 93c** vs **93f, 93h**). We also noted a weaker influence on the yields because of the steric hindrance of ortho-substituted aryl substrates as compared to the corresponding para derivatives (**93e** vs **93b and 93d** vs **93c**). In addition, we found that C-2 heteroaryl diselenide gave the desired selenide **105ag** with 82% yield. Interestingly, in the case of dibutyl diselenide, the reaction produced the corresponding product **105ah** in 78% yield (Table 10). This result is important since the alkyl group does not usually furnish the product in C(sp^2)-H bond activation.

Table 10: Scope and generality of the reaction using diorganyl diselenides **93b-k.** [a]



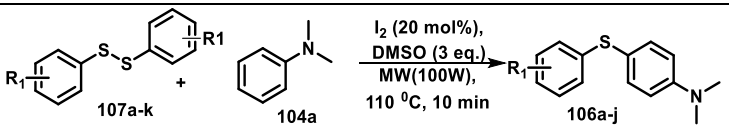
Entry	$(RSe)_2$	Product	Yield [%] [b]
1			86
2			85
3			92
4			90
5			83

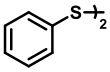
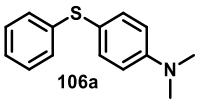
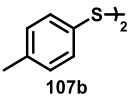
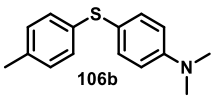
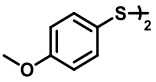
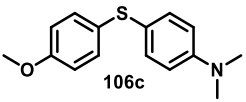
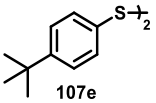
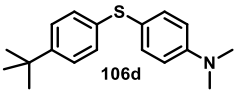
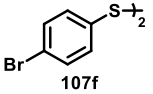
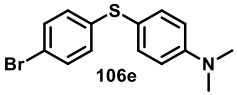
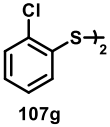
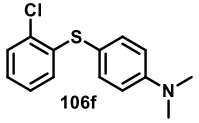
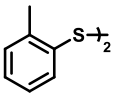
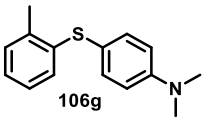
6	 93g	 105ad	81
7	 93h	 105ae	89
8	 93i	 105af	85
9	 93j	 105ag	82
10	 93k	 105ah	78

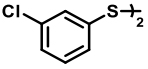
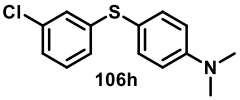
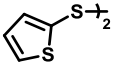
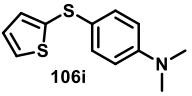
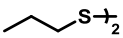
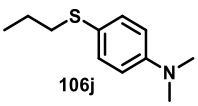
[a] Reaction conditions: **93b-k** (0.125 mmol), **104a** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation.
[b] Isolated yields.

The success in the iodine-catalyzed C-Se bond formation, through C(sp^2)–H bond activation, prompted us to expand this methodology to diorganyl disulfides **107a-k** as a way to access unsymmetrical sulfides. The desired products **106a-j** were obtained in 77% to 97% yields (Table 11). It was observed that the methodology used to prepared diorganyl sulfides **106a-j** presented similar electronic and steric effects as that used to obtain diorganyl selenides **105y-ah**. Furthermore, diorganyl disulfides **107a-k** afforded the coupling products in comparatively better yields compared to diorganyl diselenides **93b-k**.

Table 11: Scope and generality of the reaction using diorganyl disulfides **107a-k.** [a]

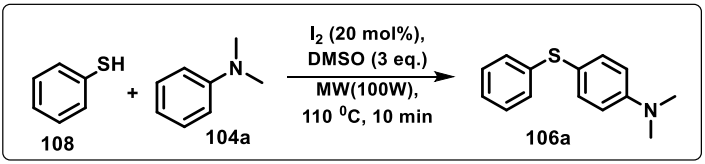


Entry	$(RS)_2$	Product	Yield [%][b]
1	 107a	 106a	97
2	 107b	 106b	90
3	 107d	 106c	87
4	 107e	 106d	93
5	 107f	 106e	95
6	 107g	 106f	93
7	 107h	 106g	90

8	 107i	 106h	90
9	 107j	 106i	86
10	 107k	 106j	77

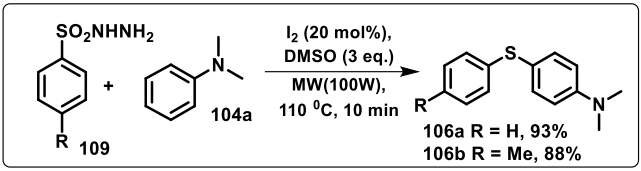
[a] Reaction conditions: **107a-k** (0.125 mmol), **104a** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation.
[b] Isolated yields.

To check the versatility of this protocol, we have observed that our methodology also worked efficiently by using thiophenol **108** as another sulfenylating agent and *N*,*N*-dimethylaniline **104a**, affording the desired product in very good yield, in a short reaction time using MW irradiation (Scheme 38).



Scheme 38. Synthesis of selenated product using thiol.

In order to further explore the scope of this new methodology we extended our study to sulfonyl hydrazides **109** (Scheme 39), applying the optimized reaction conditions. Interestingly, the reaction of different arylsulfonyl hydrazides **109** with *N*,*N*-dimethylaniline **104a** proceeded smoothly and afforded the corresponding coupled products **106a** and **106b** in 93% and 88% isolated yields, respectively (Scheme 39). This demonstrates that our protocol is versatile, being applicable to various kinds of organochalcogen sources.

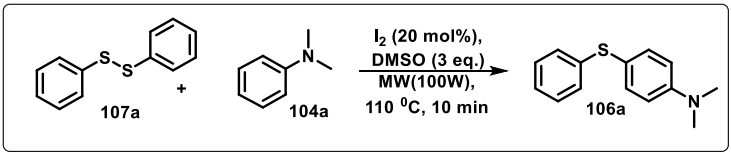


Scheme 39. Synthesis of selenated product using sulfonyl hydrazide.

3.2.4. Reaction on larger scale

One of major disadvantage of few methods of synthesis in organic chemistry is that generally synthetic reaction works well on small scale but on larger scale the reaction does not affords the desired product in expected yields.

In order to demonstrate the potential of this protocol, a series of reactions was carried out on different scales (Figure 13; up to 10 mmol). For this, *N*,*N*-dimethylaniline **104a**, diselenide **93a** and disulfide **107a** were selected as the reagents to be tested under optimized conditions, affording **105a** and **106a** with no major decrease in yield. Thus, this procedure could be used as a robust method for the synthesis of aryl chalcogenides on a larger scale.



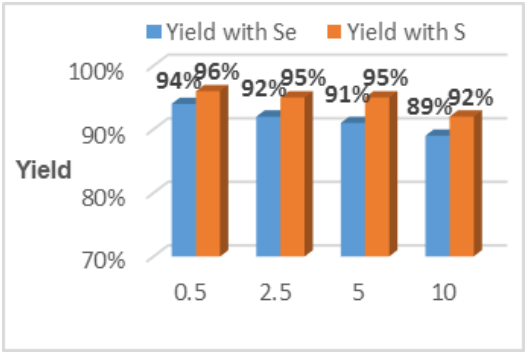


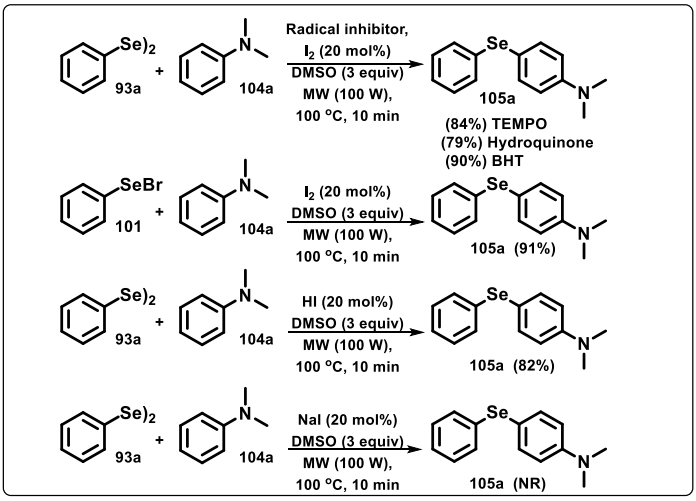
Figure 13. Results for the reaction on different scales.

Based on the reproducibility experiments as shown in Figure 13, we can say that this method could be used as practical method to

synthesize lead compounds with biological relevance and applications in material sciences.

3.2.5. Investigation of the mechanism

Bearing in mind that the coupling reaction of diorganyl chalcogenides and arenes under metal-free conditions is not well understood, some control experiments were performed in order to explain the mechanism (Scheme 40). Radical inhibitors, e.g. TEMPO, hydroquinone, BHT, did not hamper the reaction and the coupled product 105a was obtained in 84, 79 and 90% isolated yield, respectively. These experiments excluded any possibility of a radical pathway, which also indicates that the PhY radical species is not involved during the course of the reaction. Compound **105a** was obtained in 91% yield when **101** was treated with one equiv. of PhSeBr instead of diphenyl diselenide **93a,** indicating that the reaction proceeds through a phenylselenium cation species. Based on our previous experience, using a catalytic amount of HI instead of iodine, the reaction afforded **105a** with 82% yield, showing that HI is probably one of the intermediates of this transformation. It was observed that on using NaI instead of HI the reaction did not occur, demonstrating the importance of the presence of HI.

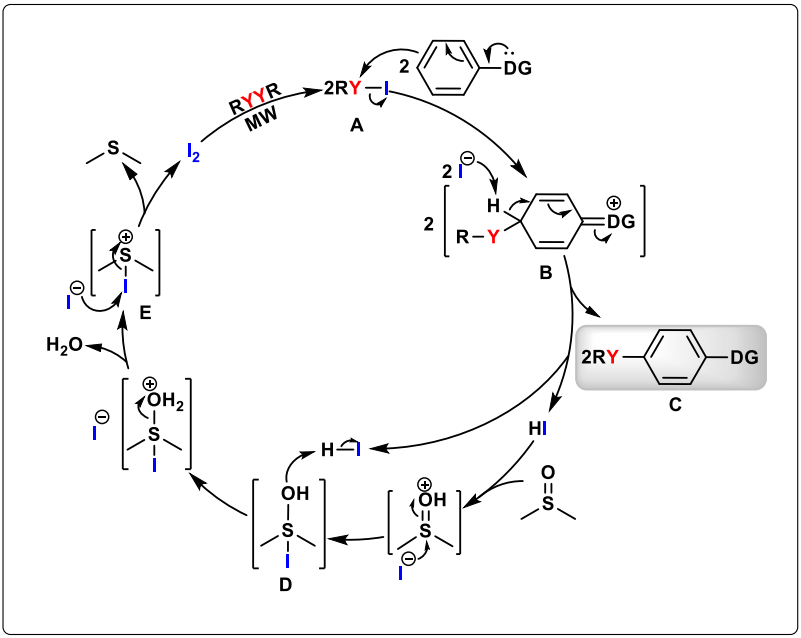


Scheme 40. Investigation of the mechanism.

3.2.6. Proposed Mechanism

Based on the above results and on previous reports,[106] a plausible mechanism for the direct C(sp^2)-H bond chalcogenation of arenes under metal-free conditions is illustrated in Scheme 40.

- Initially, the electrophilic chalcogen species **A** in the form an intermediate RYI (Y = Se, S) would be formed by the reaction of diorganyl dichalcogenide RYYR with the catalyst (I_2).
- Subsequently, the electron-rich arenes would attack the reactive RYI intermediates **A** at the para-position, to form the species **B**.
- This species would undergo proton elimination and would furnish the expected chalcogenides **C** with the simultaneous formation of HI.
- In the next step, the by-product HI would react with DMSO affording a protonated sulfur species **D**, which would be quickly converted to the iodine-dimethyl sulfide adduct E with the elimination of water.
- Lastly, the cycle would be completed by the transformation of the species **E** to dimethyl sulfide (DMS) with the regeneration of the catalyst (I_2).



Scheme 41. Proposed mechanism for the reaction.

An important feature of this process is that the concentration of iodide in the reaction medium is low, since it is continuously consumed by the mild oxidant, DMSO, avoiding the nucleophilic competition.

3.2.7. Characterization

The proposed structures of all synthesized unsymmetrical chalcogenides **105** and **106** were confirmed by nuclear magnetic resonance (NMR) spectroscopy and by other relevant techniques. In the following we will discuss the assignment of different signals from Hydrogen and Carbon-13 NMR spectra of N,N-dimethyl-4-(phenylselanyl)aniline **105a**, as a representative compound. The spectra were obtained in $CDCl_3$.

In the ^1H NMR spectrum (Figure 14), all signals corresponds to hydrogens of **105a.** There is a singlet at 2.97 ppm with integral value of 6, referring to the hydrogens of two methyl groups attached directly to the nitrogen atom. At 6.67 ppm there is a doublet with integral value of 2, and coupling constant J = 8.9 Hz referring to the hydrogens attached to C-2 of aromatic ring. At 7.31 – 7.05 ppm, a multiplet with 5 integral

value, representing C-4 protons of aromatic ring. At 7.48 ppm there is a doublet with integral value of 2, and coupling constant J = 8.9 Hz referring to the hydrogens of C-3 of the aromatic ring.

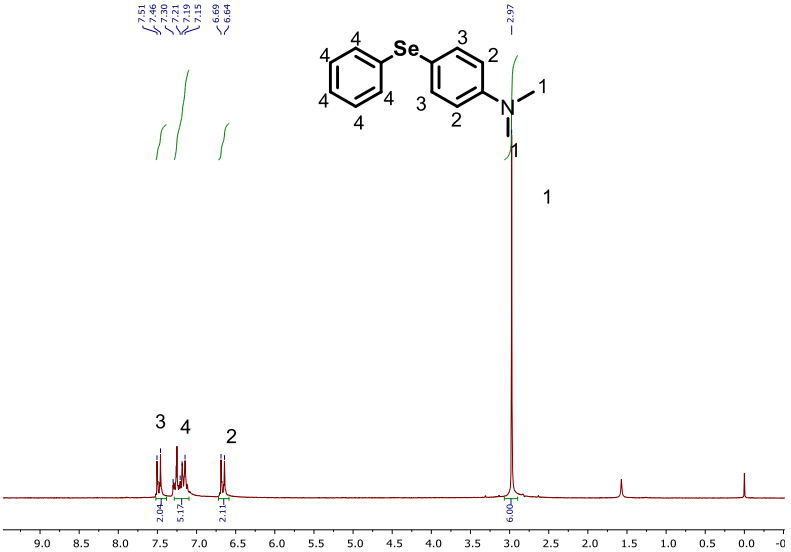


Figure 14. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105a.**

In the ^{13}C NMR spectrum (Fig. 15), all carbons for 105a can be seem clearly, a total 9 signals are expected. The one signal at 40.45 ppm represent C-1 of two Me groups attached to nitrogen. while 4 peaks at 113.31 ppm, 129.11 ppm, 129.994 ppm and 137.23 ppm signals represent the 4 aromatic carbons C-2, C-3, C-4 and C-5, respectively. There are 3 peaks for quaternary carbons of at 113.88 ppm, 134.72 ppm, and 150.66 ppm representing C-7, C-8, C9, respectively. A signal at 125.95 ppm correspond to C-6 of aromatic ring.

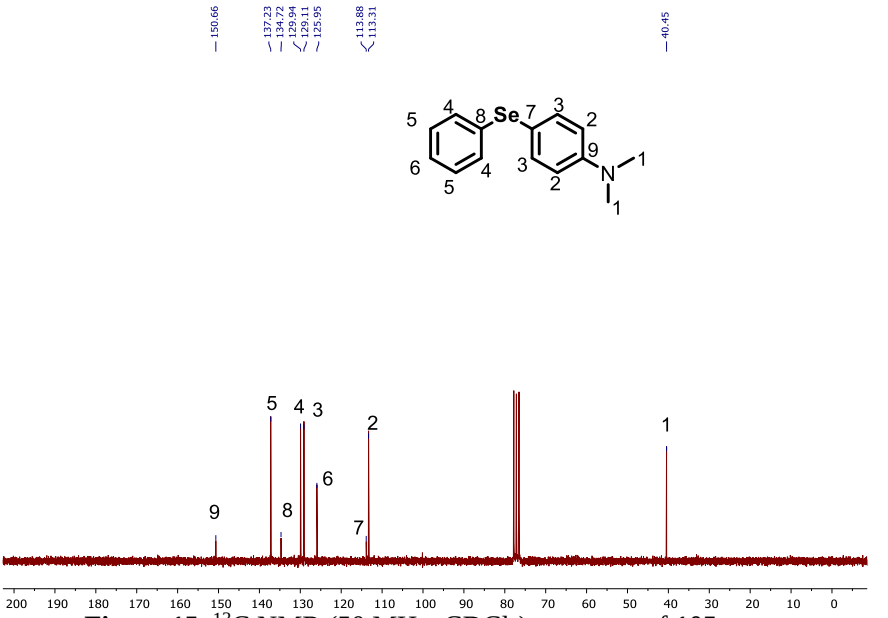


Figure 15. ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105a.**

In the ^{77}Se NMR spectrum (Fig. 16), there is one reference peak of diphenyl diselenides at 463.15 ppm, while the peak at 391.44 ppm represents the respective selenium compound.

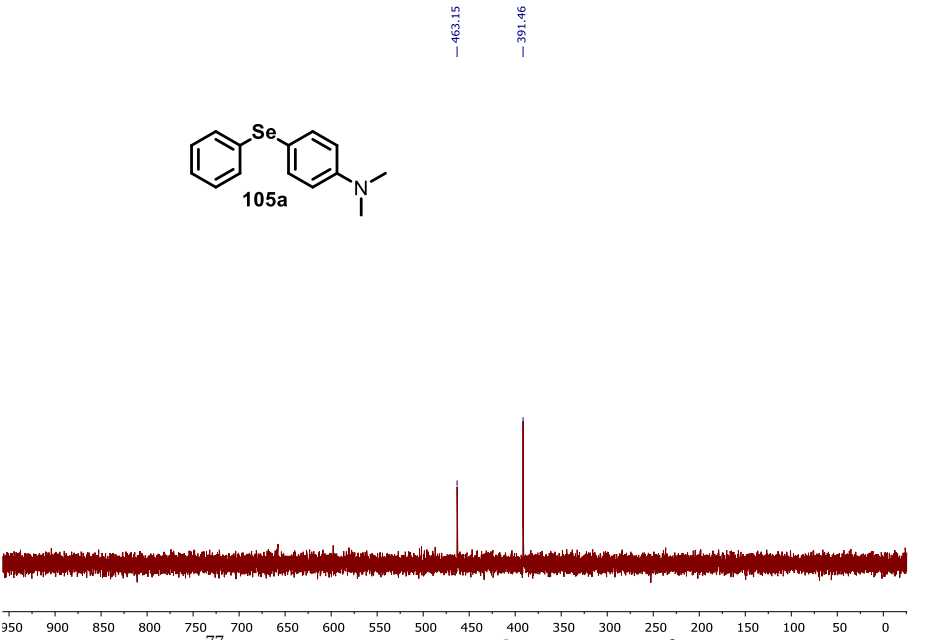


Figure 16. ^{77}Se NMR (50 MHz, CDCl3) spectrum of **105a.**

Chapter 4
Final Remarks, Conclusions and Perspectives

FINAL REMARKS, CONCLUSIONS AND PERSPECTIVES

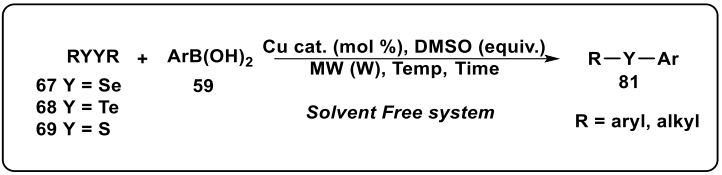
Considering the proposed objectives for this PhD study and analyzing the obtained results, it is possible to draw some observations relevant to the research we carried out.

In the first part of the work, we developed a new an efficient, economical and greener iodine/DMSO-catalyzed oxidative procedure for the synthesis of unsymmetrical organochalcogenides (S, Se, Te) through cross coupling reaction using various aryl boronic acids, under transition metal-free conditions and in the absence of solvent. We were successful in preparing various substituents with different electronic and steric effects. Under mild conditions, the reaction worked well in the presence of 10 mol% of iodine, one equiv. of arylboronic acids, half an equiv. of various diorganyl dichalcogenides and 2 equiv. of DMSO (as an oxidant)affording a wide range of chalcogenated products in good to excellent yields. The reaction was shown to be robust and could easily be scaled-up without any significant loss of yield. The chemistry described herein represents a feasible eco-friendly synthetic approach for the preparation of unsymmetrical chalcogenides through the C-S/Se/Te bond.

With the successful results from the cross coupling of aryl boronic acids, we extended our studies to different [*O* or *N*]-containing arenes. In this part of the work we developed a regioselective, rapid and greener iodine-catalyzed method for the synthesis of diorganyl chalcogenides through oxidative C–Se/C–S formation via direct C(sp^2)-H bond cleavage from using [*O* or *N*]-containing arenes This regioselective procedure resulted the desired products in good to excellent yields under metal and solvent-free conditions, without the exclusion of air and moisture, applying microwave irradiations for 10 min. The reaction worked very well with other sulfur sources e.g. thiols and sulfonyl hydrazides. The developed methodology is reproducible and we were able to access biologically important Se/S containing heteroarenes, such as, pyrimidines, pyridines, thiazoles.

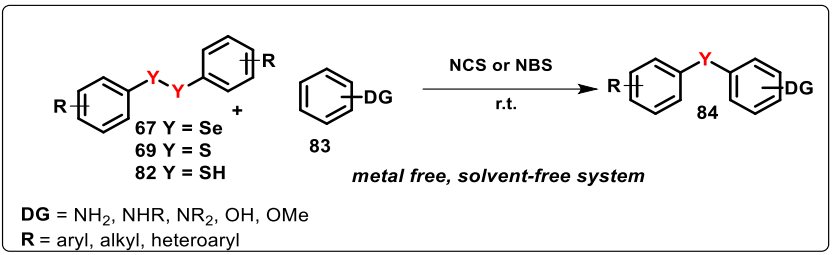
In order to explore different methodology for accessing diorganyl chalcogenides, it is planned to perform reactions between the substituted arylboronic acids **59** with diorganoyl dichalcogenides **67-69** by using different copper catalysts and a stoichiometric amount of oxidant in the absence of solvent under microwave irradiation (Scheme 42).

Unsymmetrical diorganyl chalcogenides **81** could conveniently synthesized via one-pot, one-step methodology under MW-irradiations through the synthetic route as described in Scheme 42.



Scheme 42. Copper-catalyzed synthesis of unsymmetrical organochalcogenides under ligand, metal and solvent-free conditions.

Another alternative and green method could be the use of different arenes **83** and dichalcogenides in the presence of *N*-halosuccinimides (NCS or NBS) as catalysts under metal and solvent free condition as shown in the Scheme 43.



Scheme 43. *N*-halo succinimide synthesis of unsymmetrical organochalcogenides.

The reaction parameters will be evaluated to develope the above two methodologies such as time, microwave power, temperature, catalyst, atmospheric condition and molar ratio. After that, systematic study will be performed by varying the different diorganyl dichalcogenides, substituted arylboronic acids and substituted arenes.

Chapter 5
Experimental Section

EXPERIMENTAL SECTION

5.1. MATERIALS & METHODS

5.1.1. Reagents and Solvents

The purified and dried solvents used in reactions were obtained according to procedures described in the literature. All solvents and reagents were purchased from commercial sources (Aldrich, Merck, Fluka, Synth, Brenttag) and in most cases were used without further purification. Potassium carbonate (99.997 %) for controlled reactions, was purchased from Sigma-Aldrich.

Dry DMF and DMSO were prepared by drying overnight over pre-activated 4 ºA molecular sieves, followed by decantation of the drying agent and vacuum distillation (~20 mmHg is a sufficient vacuum to lower the boiling point over DMF and DMSO to a reasonable value). Dry DMF and DMSO were stored over pre-activated 4ºA molecular sieves.

To dry THF, commercially available THF was distilled from sodium benzophenone ketyl by adding sodium wire and benzophenone to a volume of THF (pre-dried over calcium hydride or 4 ºA molecular sieves), heat at reflux under inter atmosphere for several hours until the solvent turns deep blue in color. This indicates the solvent was dry, and can be distill off freshly for the reaction.

Purification of reaction products were performed through column chromatography (CC), the material used was a glass column and flash silica gel (230-400 mesh) or gravity silica gel (70-230 mesh). For high performance flash chromatography, Super Flash SF25-40g Sepra Si 50 column coupled to a BSR (bottomless Solvent Reservoir) pump system was used. An elution solvent (hexane), or mixture of suitable solvents (hexane and ethyl acetate) were used.

Thin layer chromatography (TLC) was performed using commercially available TLC plates (Merck Silica Gel GF254, 0.25 mm thickness). For visualization different methods were used, TLC plates were placed under ultraviolet light, stained with iodine vapor and/or sprayed with acidified solution of vanillin, followed by heating at 110 ºC. The progress of all reactions were monitored by TLC for disappearance of starting materials. Solvents used in the synthesis, extraction, purification, CC and TLC are of analytical grade.

Reactions under inert atmosphere are conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents are handled

using standard syringe techniques. Temperatures above room temperature are maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac speed controller.

5.1.2. Microwave

The reactions in microwave were performed in special sealed tube (10mL) for microwave in a microwave reactor with focused field CEM Discover (CEM Corporation) connected with auto-sampler Explorer 24 (CEM Corporation), with pressure and temperature monitoring infrared controller and equipped with CEM's Synergy™ software for monitoring the reaction progress.

5.1.3. Solvent Evaporation

For removal of the organic solvent following rotary-evaporator and glass vacuum line were used:

- Büchi Rotavapor R 215 Digital Rotary Evaporators
- IKA Rotary Evaporators, RV 10 Digital, D (Diagonal) Condenser
- Glass vacuum line equipped with a high vacuum pump, vacuum pump model RD 4-4.3 m^3 / h.

5.2. Characterization

Proton Nuclear Magnetic Resonance (^{1}H-NMR) and Carbon Nuclear Magnetic Resonance (^{13}C-NMR), Gas chromatography coupled to mass spectrometry (GC-MS) and melting point when solid, characterized the synthesized compounds previously reported in literature. While for new synthesized compounds along with previously mentioned techniques other techniques such as high-resolution mass spectrometry (HRMS) and infrared spectroscopy (IR), are used. Where needed Selenium Nuclear Magnetic Resonance (^{77}Se-NMR) are applied.

5.2.1. Nuclear Magnetic Resonance Spectroscopy

The NMR technique provide information regarding the characterization of the synthesized compounds. ^{1}H NMR spectra are obtained at 200 MHz on a Bruker AC-200 NMR spectrometer or at 400 MHz on a Varian AS-400 NMR spectrometer. Spectra are recorded in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO *d*6) solutions. Chemical shifts are reported in ppm, referenced

to the solvent peak of deuterated solvent or tetramethylsilane (TMS) as internal reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. ^{13}C NMR are obtained either at 50 MHz on a Bruker AC-200 NMR spectrometer or at 100 MHz on a Varian AS-400 NMR spectrometer. Spectra are recorded in $CDCl_3$ or DMSO *d*6 solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or DMSO *d*6. ^{77}Se NMR at 38.14 MHz on a Bruker AC-200 NMR spectrometer. Spectra are recorded in CDCl3 solutions. Chemical shifts are reported in ppm, referenced to diphenyl diselenide as the external reference (463.15 ppm). Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet).

5.2.2. Low Resolution Mass Spectrometry

The mass spectra were obtained with low resolution from a Shimadzu MS-QP5050A apparatus equipped with a DB-5 capillary column (30 m) and ionization voltage of 70 eV.

5.2.3. High Resolution Mass Spectrometry

High resolution mass spectra were obtained from micrOTOF Q-II (Bruker Daltonics), at Centro de Biologia Molecular Estrutural (CEBIME), equipped with automatic syringe (KD Scientific) for injection of samples. The mass spectrometer with electro-spray ionization equipped with time of fight analyzer (ESI-QTOF MS) was operated in positive ion mode, where the samples were injected at a constant flow rate of 3 μL/min, using as solvent a mixture of acetonitrile and Liquid chromatography–mass spectrometry (LCMS) grade methanol. Data were processed on a Bruker Data Analysis software version 4.0.

5.2.4. Infrared Spectroscopy

The infrared analysis (IR) were recorded on a Bruker Optics Alpha bench top FT-IR spectrometer instrument using KBr pellets for sample preparation. Data were reported in frequency of absorption (cm^{-1}).

5.2.5. Melting Point

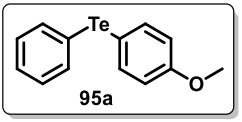
The melting points were determined in a Microquimica MQRPF-301 digital model equipment with heating plate. Data were reported in degree Celsius.

5.3. Experimental procedures for the synthesis of organochalcogenides from organoboronic acid

5.3.1. General procedure for the iodine-catalyzed synthesis of unsymmetric organochalcogenides

A mixture of the appropriate arylboronic acid (0.5 mmol), diorganyl dichalcogenide (0.25 mmol), iodine (10 mol%, 12 mg) and 2 equiv. of DMSO (1 mmol, 78 mg) were placed in a microwave glass tube, which was sealed and placed in a CEM Discover microwave device. A maximum irradiation power of 100 W and a temperature of 100 ºC were applied for 10 min. When the reaction was completed, the reaction mixture was dissolved in ethyl acetate (15 mL) and washed with 2 x 10 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent..

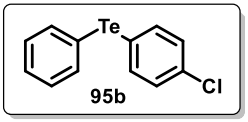
5.3.1.1. (4-methoxyphenyl)(phenyl)tellane (95a).



95a

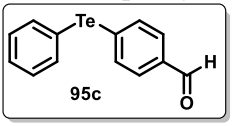
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl)boronic acid **59a** and diphenyl ditellurides **94a.** Yield: 94%; white solid; mp 59–61°C (lit. 60–62 °C); ^{1}H NMR (400 MHz, CDCl3) δ = 7.72 (d, J = 8.7 Hz, 2H), 7.57-7.54 (m, 2H), 7.23–7.13 (m, 3H), 6.79 (d, J = 8.7Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ = 160.1, 141.3, 136.4, 129.4, 127.3, 116.0, 115.6, 103.3, 55.2.

5.3.1.2. (4-chlorophenyl)(phenyl)tellane (95b).



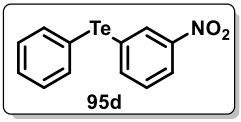
The experimental procedure similar to 5.3.1 was followed but using (4-chlorophenyl)boronic acid **59b** and diphenyl ditelluride **94a**. Yield: 86%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.69–7.36 (m, 4H), 7.25–6.98 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 139.3, 138.2, 134.4, 129.8, 129.7, 128.2, 114.5, 112.5.

5.3.1.3. 4-(phenyltellanyl)benzaldehyde (95c).



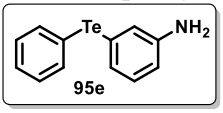
The experimental procedure similar to 5.3.1 was followed but using (4-formylphenyl)boronic acid **59c** and diphenyl ditelluride **94a**. Yield: 89%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 9.80 (s, 1H), 7.74 (d, J = 6.7Hz, 2H), 7.53(s, 4H), 7.35–7.17(m, 3H); 13C NMR (50 MHz, $CDCl_3$) δ = 191.7, 140.0, 135.7, 135.2, 130.0, 129.0, 128.2, 126.8, 113.1.

5.3.1.4. (3-nitrophenyl)(phenyl)tellane (95d).



The experimental procedure similar to 5.3.1 was followed but using (3-nitrophenyl)boronic acid **59h** and diphenyl ditelluride **94a**. Yield: 92%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.09–8.03 (m, 1H), 7.88–7.79(m, 3H), 7.43–7.25(m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.5, 142.3, 139.5, 131.0, 130.1, 129.9, 129.1, 122.5, 117.0, 113.2.

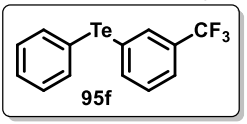
5.3.1.5. 3-(phenyltellanyl)aniline (95e).



The experimental procedure similar to 5.3.1 was followed but using (3-aminophenyl)boronic acid **59e** and diphenyl ditelluride **94a**. Yield: 85%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.57 (d, J = 8.2Hz, 2H), 7.15 (d, J = 8.2Hz, 2H), 7.07–6.94 (m, 4H), 6.60–6.55 (m, 1H), 3.61 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.3,

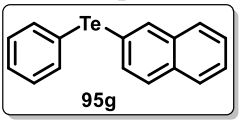
139.1, 134.2, 130.3, 129.7, 128.2, 124.4, 115.0, 112.5; IR (KBr); 3300, 3250, 3032, 2926, 1629, 1725, 1501, 1460,1097, 1013, 919, 821, 728; HRMS m/z Calcd. for $C_{12}H_{11}NTe$ $[M+H]^+$ 300.0027; found: 300.0027.

5.3.1.6. Phenyl(3-(trifluoromethyl)phenyl)tellane (95f) .



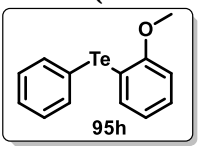
The experimental procedure similar to 5.3.1 was followed but using (3-(trifluoromethyl)phenyl)boronic acid **59f** and diphenyl ditelluride **94a.** Yield: 85%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.96–7.71 (m, 4H), 7.57–7.47 (m, 1H), 7.37–7.20 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5 (q, *Jc-f* = 1.5), 138.9, 138.1, 133.7 (q, *Jc-f* = 4), 131.6 (q, *Jc-f* = 32), 129.9,129.6, 128.6, 124.5 (q, *Jc-f* = 4), 123.7 (q, *Jc-f* = 271), 115.9, 113.8; IR (KBr); 3065, 3012, 2993, 2923, 1572, 1474, 1417, 1270, 1081, 1017, 997, 793, 695; HRMS m/z Calcd. for $C_{13}H_9F_3Te[M]^+$ 351.9714; found: 351.9716.

5.3.1.7. naphthalen-2-yl(phenyl)tellane (95g).



The experimental procedure similar to 5.3.1 was followed but using naphthalen-1-ylboronic acid **59g** and diphenyl ditelluride **94a**. Yield: 93%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18–8.13 (m, 1H), 7.98–7.96 (m, 1H), 7.80–7.75 (m, 2H), 7.61–7.58 (m, 2H), 7.49–7.43 (m, 2H), 7.26–7.17 (m, 2H), 7.15–7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 137.5, 135.9, 133.8, 131.8, 129.6, 128.9, 127.7, 127.1, 126.6, 126.4, 117.8, 114.8, 106.0.

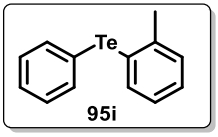
5.3.1.8. (2-methoxyphenyl)(phenyl)tellane (95h).



The experimental procedure similar to 5.3.1 was followed but using (2-methoxyphenyl)boronic acid **59h** and diphenyl ditelluride **94a.** Yield: 95%; white soild; mp 53-54°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.79 (m, 2H), 7.44–7.29 (m, 3H), 7.23–7.05 (m, 1H), 6.94 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.83–6.68 (m, 2H)), 3.86 (s, 3H);

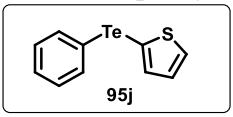
13C NMR (50 MHz, $CDCl_3$): δ = 158.2, 141.3, 133.7, 129.7, 128.7, 128.2, 122.5, 112.2, 109.8, 107.8, 56.0.

5.3.1.9. phenyl(o-tolyl)tellane (95i).



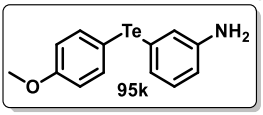
The experimental procedure similar to 5.3.1 was followed but using o-tolylboronic acid **59i** and diphenyl ditelluride **94a**. Yield: 95%; white oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.0Hz, 2H), 7.47 (d, J = 8.0Hz, 2H), 7.29–7.16 (m, 4H), 6.97–6.90 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 142.0, 138.7, 137.5, 129.7, 129.4, 128.2, 128.1, 126.8, 119.3, 114.1, 26.2.

5.3.1.10. 2-(phenyltellanyl)thiophene (95j).



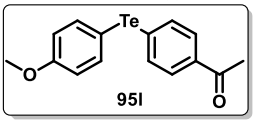
The experimental procedure similar to 5.3.1 was followed but using thiophen-2-ylboronic acid **59j** and diphenyl ditelluride **94a**. Yield: 90%; yellow solid; mp 36-38°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.58–7.48 (m, 4H), 7.25–7.14 (m, 3H), 7.04–6.95 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 142.2, 138.1, 135.8, 135.3, 129.5, 129.3, 127.8, 116.6; IR (KBr) 3112, 3069, 2996, 2926, 1876, 1796, 1658, 1564,1462, 1333, 1214, 1070, 1023, 921, 836, 719, 708; HRMS m/z Calcd. for $C_{10}H_8STe$ $[M]^+$ 289.9401; found 289.9403.

5.3.1.11. 3-((4-methoxyphenyl)tellanyl)aniline (95k).



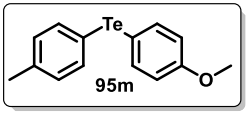
The experimental procedure similar to 5.3.1 was followed but using (3-aminophenyl) boronic acid **59e** and 1,2-bis(4-methoxyphenyl)ditellane **94b**. Yield: 84%; brown solid; mp 97–99 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.8Hz, 2H), 6.94 (d, J = 4.8Hz, 2H), 6.88–6.86 (m, 1H), 6.79 (d, J = 8.8Hz, 2H), 6.56–6.47 (m, 1H), 3.79 (s, 3H), 3.56 (s, 2H);^{13}C NMR (50 MHz, $CDCl_3$) δ = 160.0, 147.2, 141.2, 130.0, 126.5, 122.7, 116.7, 115.6, 114.3, 103.3, 55.2; IR (KBr) 3472, 3379, 3030, 2962, 2839, 1563, 1487, 1326, 1248, 1099, 987, 815, 774; HRMS m/z Calcd. for $C_{13}H_{13}NOTe$ $[M]^+$ 329.0054; found 329.0051.

5.3.1.12. 1-(4-((4-methoxyphenyl)tellanyl)phenyl)ethan-1-one (95l).



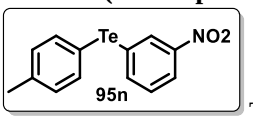
The experimental procedure similar to 5.3.1 was followed but using (4-acetylphenyl) boronic acid **59k** and 1,2-bis(4-methoxyphenyl)ditellane **94b**. Yield: 93%; yellow liquid; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.8Hz, 2H), 7.69 (d, J = 8.5Hz, 2H), 7.49 (d, J = 8.5Hz, 2H), 6.84 (d, J = 8.8Hz, 2H), 3.83 (s, 3H), 2.53 (s, 3H).13C NMR (50MHz, $CDCl_3$) δ = 197.7, 160.6, 142.4, 135.7, 134.6, 128.7, 125.6, 115.9, 102.2, 55.3, 26.5; IR (KBr) 3002, 2959, 2926, 2837, 1682, 1635, 1582, 1488, 1388, 1246, 1176, 1025, 954, 815, 742; HRMS m/z Calcd. for $C_{15}H_{14}O_2Te$ $[M]^+$ 356.0051; found 356.0057.

5.3.1.13. (4-methoxyphenyl)(p-tolyl)tellane (95m).



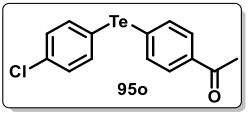
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl)boronic acid **59a** and 1,2-di-p-tolylditellane **94c**. Yield: 94%; white solid; mp 63–64°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.2Hz, 2H), 7.51 (d, J = 7.8Hz, 2H), 7.00 (d, J = 7.8Hz, 2H), 6.77 (d, J = 8.2Hz, 2H), 3.78 (s, 3H), 2.31(s, 3H). ^{13}C NMR (50MHz, $CDCl_3$) δ 159.9, 140.6, 137.5, 137.3, 130.4, 115.5, 111.5, 103.7, 55.2, 21.2.

5.3.1.14. (3-nitrophenyl)(p-tolyl)tellane (95n).



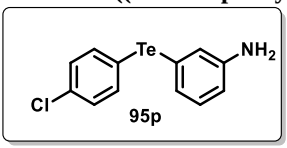
The experimental procedure similar to 5.3.1 was followed but using (3-nitrophenyl)boronic acid **59h** and 1,2-di-p-tolylditellane **94c**. Yield: 87%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 8.02 (dd, J = 8.7, 1.7 Hz, 1H), 7.81–7.68 (m, 3H), 7.28 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 148.4, 141.7, 140.0, 139.4, 131.0, 130.4, 129.8, 122.2, 117.6, 109.0, 21.4; IR (KBr) 3072, 2964, 2918, 2855, 1529, 1486, 1419, 1342, 1207,1103, 1011, 860, 801, 724; HRMS m/z Calcd. for $C_{13}H_{11}NO_2Te$ $[M]^+$ 342.9847; found 342.9849.

5.3.1.15. 1-(4-((4-chlorophenyl)tellanyl)phenyl)ethanone (95o).



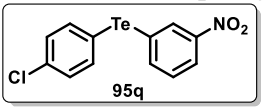
The experimental procedure similar to 5.3.1 was followed but using (4-acetylphenyl)boronic acid **59k** 1,2-bis(4-chlorophenyl)ditellane **94e.** Yield: 89%; yellow soild; mp 67–70 °C;^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.77–7.68 (m, 4H), 7.61 (d, J = 8.5Hz, 2H), 7.24 (d, J = 8.5Hz, 2H), 2.56 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 197.6, 140.9, 136.2, 136.1, 135.4, 130.2, 129.0, 123.5, 111.0, 26.6; IR (KBr) 3063, 3045, 3006, 1892, 1668, 1578, 1468, 1388, 1354, 1266, 956, 848, 742, 599; HRMS m/z Calcd. for $C_{14}H_{11}ClOTe$ $[M+H]^+$ 360.9623; found 360.9621.

5.3.1.16. 3-((4-chlorophenyl)tellanyl)aniline (95p).



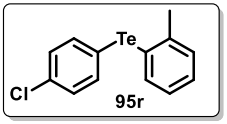
The experimental procedure similar to 5.3.1 was followed but using (3-aminophenyl)boronic acid **59e** and 1,2-bis(4-chlorophenyl)ditellane **94e**. Yield: 90%; brown solid; mp: 58–60°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.57 (d, J = 8.4Hz, 2H), 7.18–6.93 (m, 5H), 6.60–6.55 (m, 1H), 3.61(s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.3, 139.1, 134.2, 130.3, 129.7, 128.2, 124.4, 115.0, 112.5; IR (KBr); 3457, 3369, 3069, 3043, 2926, 2851, 1807, 1631, 1599, 1568, 1442, 1391, 1272, 1099, 1013, 993, 826, 791, 673; HRMS m/z Calcd. for $C_{12}H_{10}ClNTe$ [M]+ 332.9548; found 332.9551.

5.3.1.17(4-chlorophenyl)(3-nitrophenyl)tellane(95q).



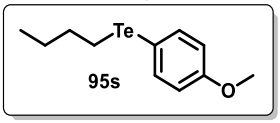
The experimental procedure similar to 5.3.1 was followed but using (3-nitrophenyl) boronic acid **59h** and 1,2-bis(4-chlorophenyl)ditellane **94e**. Yield: 89%; yellow solid; mp 90–92°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 8.09 (dd, J = 8.2, 1.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 8.2Hz, 2H), 7.40– 7.22 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.6, 142.5, 140.8, 135.7, 131.3, 130.4, 130.1, 122.8,116.5, 110.8; IR (KBr) 3096, 2924, 2849, 1597, 1562, 1468, 1415, 1342, 1268, 1056, 966, 874, 832, 726, 662; HRMS m/z Calcd. for $C_{12}H_8ClNO_2Te[M]^+$ 362.92900; found 362.92899.

5.3.1.18(4-chlorophenyl)(o-tolyl)tellan (95r).



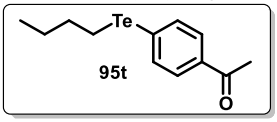
The experimental procedure similar to 5.3.1 was followed but using o-tolylboronic acid **59i** and 1,2-bis(4-chlorophenyl)ditellane **94e**. Yield: 89%; white oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.56 (d, J = 8.4Hz, 2H), 7.48 (d, J = 7.5Hz, 1H), 7.24–7.20 (m, 2H), 7.16 (d, J = 8.4Hz, 2H), 6.99–6.91(m, 1H), 2.39(s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 142.1, 139.8, 137.8, 134.6, 129.9, 129.6, 128.5, 127.0, 118.9, 111.8, 26.2; IR (KBr) 3055, 3002, 2967, 2922, 1652, 1558, 1470, 1458, 1378, 1089, 1007, 809, 744, 668; HRMS m/z Calcd. for $C_{13}H_{11}ClTe[M]^+$ 331.9596; found 331.9593.

5.3.1.19. butyl(4-methoxyphenyl)tellane (95s).



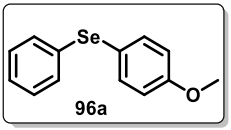
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl)boronic acid **59a** and 1,2-dibutylditellane **94e**. Yield: 89%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.84–2.80 (m, 2H),1.77–1.69 (m, 2H), 1.42–1.33 (m, 2H), 0.88 (t, J = 7.4Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 159.7, 140.9, 115.1, 100.6, 55.2, 33.9, 25.1, 13.5, 8.8.

5.3.1.20. 1-(4-(butyltellanyl)phenyl)ethan-1-one (95t).



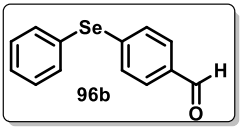
The experimental procedure similar to 5.3.1 was followed but using (4-acetylphenyl)boronic acid **59k** and 1,2-dibutylditellane **94e**. Yield: 82%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.73(s, 4H), 3.01–2.94 (m, 2H), 2.57 (s, 3H), 1.89–1.74 (m, 2H), 1.51-1.32 (m, 2H), 0.92 (t, J = 7.3Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 197.7, 136.6, 135.8, 128.5, 121.0, 33.8, 26.5, 25.1, 13.4, 8.7.

5.3.1.21. (4-methoxyphenyl)(phenyl)selane (96a).



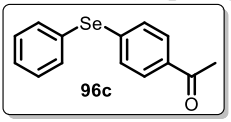
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl)boronic acid **59a** and 1,2-diphenyldiselane **93a**. Yield: 93%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51(d, J = 8.9Hz, 2H), 7.35–7.31 (m, 2H), 7.25-7.18(m, 3H), 6.86 (d, J = 8.9Hz, 2H), 3.81(s, 3H).^{13}C NMR (50MHz, $CDCl_3$) δ = 159.9, 136.6, 133.3, 131.0, 129.3, 126.6, 120.0, 115.3, 55.4.

5.3.1.22. 4-(phenylselanyl)benzaldehyde (96b).



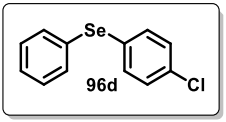
The experimental procedure similar to 5.3.1 was followed but using (4-formylphenyl) boronic acid **59c** and 1,2-diphenyldiselane **93a**. Yield: 90%; white oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 9.89 (s, 1H), 7.71–7.58 (m, 4H), 7.44–7.32 (m, 5H). ^{13}C NMR (50MHz, $CDCl_3$) δ = 191.4, 142.8, 135.6, 134.4, 130.2, 129.9, 128.9, 127.9.

5.3.1.23. 1-(4-(phenylselanyl)phenyl)ethanone (96c).



The experimental procedure similar to 5.3.1 was followed but using (4-acetylphenyl) boronic acid **59k** and 1,2-diphenyldiselane **93a.** Yield: 89%; white solid; mp 36–38°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.4Hz, 2H), 7.60–7.56 (m, 2H), 7.39–7.35 (m, 5H), 2.54 (s, 3H). ^{13}C NMR (50MHz, $CDCl_3$) δ = 197.4, 140.3, 135.2, 135.1, 130.3, 129.8, 129.0, 128.7, 128.5, 26.5.

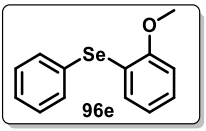
5.3.1.24. (4-chlorophenyl)(phenyl)selane (96d).



The experimental procedure similar to 5.3.1 was followed but using (4-chlorophenyl) boronic acid **59b** and 1,2-diphenyldiselane **93a**. Yield: 87%; colorless oil; ^{1}H NMR (200 MHz,

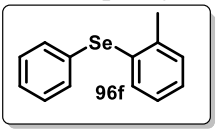
$CDCl_3$) δ = 7.47–7.42 (m, 2H), 7.35 (d, J = 8.3Hz, 2H), 7.27–7.22(m, 3H), 7.20(d, J = 8.3Hz, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 134.1, 133.5, 133.2, 130.7, 129.6, 129.5, 127.7.

5.3.1.25. (2-methoxyphenyl)(phenyl)selane (96e).



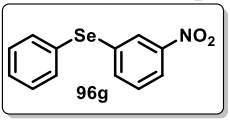
The experimental procedure similar to 5.3.1 was followed but using (2-methoxyphenyl) boronic acid **59h** and 1,2-diphenyldiselane **93a**. Yield: 93%; yellow oil; ^1H NMR (200MHz, $CDCl_3$) δ = 7.67–7.50 (m, 2H), 7.37–7.28 (m, 3H), 7.24–7.14 (m, 1H), 6.95 (dd, J = 7.7, 1.7 Hz, 1H), 6.87–6.74 (m, 2H).^{13}C NMR (50MHz, $CDCl_3$) δ = 156.7, 135.5, 130.9, 129.5, 128.4, 128.2, 127.8, 122.0, 121.7, 110.5, 55.9.

5.3.1.26. phenyl(o-tolyl)selane (96f).



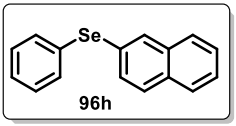
The experimental procedure similar to 5.3.1 was followed but using o-tolylboronic acid **59i** and 1,2-diphenyldiselane **93a**. Yield: 92%; colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ = 7.41–7.31 (m, 3H), 7.25–7.13 (m, 5H), 7.08–7.00 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 139.9, 133.7, 132.8, 131.8, 130.8, 130.3, 129.4, 127.8, 127.2, 126.8, 22.4.

5.3.1.27. (3-nitrophenyl)(phenyl)selane (96g).



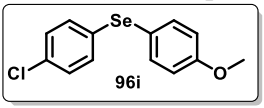
The experimental procedure similar to 5.3.1 was followed but using (3-nitrophenyl) boronic acid **59h** and 1,2-diphenyldiselane **93a**. Yield: 86%; yellow oil; ^1H NMR (200 MHz, $CDCl_3$) δ = 8.18 (s, 1H), 8.02 (dd, J = 8.1, 2.2 Hz, 1H), 7.69–7.55(m, 3H), 7.41–7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6, 136.9, 134.8, 129.9, 129.8, 128.8, 128.4, 125.7, 123.5, 121.6.

5.3.1.28. naphthalen-2-yl(phenyl)selane (96h).



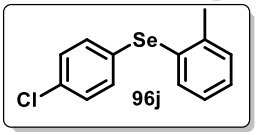
The experimental procedure similar to 5.3.1 was followed but using naphthalen-1-ylboronic acid **59g** and 1,2-diphenyldiselane **93a**. Yield: 91%; yellow solid; mp 69–71°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ= 8.35–8.30 (m, 1H), 7.85–7.73 (m, 3H), 7.53–7.44 (m, 2H), 7.38–7.29 (m, 3H), 7.20–7.14 (m, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 134.2, 133.9, 131.7, 129.4, 129.3, 128.6, 127.7, 127.0, 126.9, 126.4, 126.1.

5.3.1.29. (4-chlorophenyl)(4-methoxyphenyl)selane (96i).



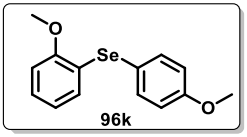
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1,2-bis(4-chlorophenyl)diselane **93f**. Yield: 88%; yellow solid; mp 58–59°C ;^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 160.0, 136.7, 132.5, 132.1, 131.7, 129.3, 119.5, 115.3, 55.4.

5.3.1.30. (4-chlorophenyl)(o-tolyl)selane (96j).



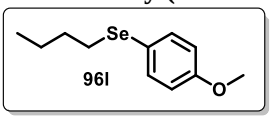
The experimental procedure similar to 5.3.1 was followed but using o-tolylboronic acid **59i** and 1,2-bis(4-chlorophenyl)diselane **93f**. Yield: 89%; white oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.35–7.01 (m, 8H), 2.37(s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 140.1,134.1, 133.8, 133.3, 131.2, 130.5, 129.6, 129.3, 128.2, 126.9, 22.4; IR (KBr) 3059, 3008, 2969, 1652, 1558, 1472, 1386, 1274, 1089, 1009, 811, 746, 668. HRMS m/z Calcd. for $C_{13}H_{11}ClSe$ $[M]^+$ 281.9707; found: 281.9707.

5.3.1.31. (2-methoxyphenyl)(4-methoxyphenyl)selane (96k).



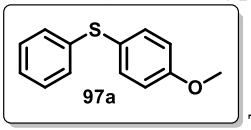
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1,2-bis(2-methoxyphenyl)diselane **93d**. Yield: 96%; white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, J = 8.7 Hz, 2H), 7.15–7.10 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.82–6.73 (m, 3H), 3.89 (s, 3H), 3.82(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.2, 155.9, 138.5, 129.0, 126.9, 123.6, 121.6, 117.3, 115.3, 110.1, 55.8, 55.3; IR (KBr) 3064, 2961, 2935, 1843, 1792, 1699, 1652, 1558, 1456, 1397, 1240, 1027, 824, 748, 668; ^{77}Se NMR (CDCl3, MHz): δ 349.09. HRMS m/z Calcd. for $C_{14}H_{14}O_2Se$ $[M]^+$ 294.0154; found 294.0150.

5.3.1.32. butyl(4-methoxyphenyl)selane (96l).



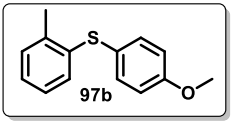
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1,2-dibutyldiselane **93k**. Yield: 83%; yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.85–2.78 (m, 2H), 1.71–1.58 (m, 2H), 1.48–1.25 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 159.2, 135.5, 120.4, 114.8, 55.4, 32.4, 28.9, 23.0, 13.7.

5.3.1.33. (4-methoxyphenyl)(phenyl)sulfane (97a).



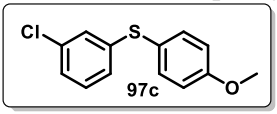
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1,2-diphenyldisulfane **98a**. Yield: 79%; white oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.41 (d, J = 8.9 Hz, 2H), 7.27–7.09 (m, 5H), 6.89 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 159.9, 138.7, 135.4, 129.0, 128.3, 125.8, 124.4, 115.1, 55.4.

5.3.1.34. (4-methoxyphenyl)(o-tolyl)sulfane (97b).



The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1-(m-tolyl)-2-(o-tolyl)disulfane **98b**. Yield: 84%; white solid; mp 61–62°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, J = 8.9 Hz, 2H), 7.17–6.95 (m, 4H), 6.88 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 159.6, 137.2, 137.0, 134.7, 130.3, 129.1, 126.5, 126.2, 124.5, 115.1, 55.4, 20.4.

5.3.1.35. (3-chlorophenyl)(4-methoxyphenyl)sulfane (97c).



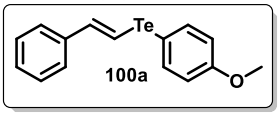
The experimental procedure similar to 5.3.1 was followed but using (4-methoxyphenyl) boronic acid **59a** and 1,2-bis(3-chlorophenyl)disulfane **98c**. Yield: 75%; white solid; mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, J = 8.8 Hz, 2H), 7.14–7.06 (m, 3H), 7.00–6.98 (m, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 160.4, 141.4, 136.2, 134.9, 129.9, 127.1, 125.7, 125.6, 122.8, 115.3, 55.5; IR (KBr) 3083, 3016, 2963, 2937, 2894, 2837, 2045, 1945, 1902, 1876, 1739, 1672, 1493, 1437, 1027, 872, 799, 642; HRMS m/z Calcd. for $C_{13}H_{11}ClOS[M]^+$ 250.0214; found 250.0213.

5.3.2. General Procedure for the Iodine-catalyzed reactions of potassium salt of vinyltrifluoroborate with diorganyl dichalcogenides

A mixture of aryl potassium salt of vinyltrifluoroborate **99** (0.5 mmol, 0.105 g), appropriate diorganyl dichalcogenides (0.25 mmol), iodine (10 mol%, 12 mg) and 2 equiv. of DMSO (1mmol, 78 mg) were charged in a microwave glass tube, which was sealed and placed in a CEM Discover microwave apparatus. A maximum irradiation power of 100 W and a temperature of 100 ºC were applied for 10 min. When the reaction was finished, the reaction mixture was dissolved in ethyl acetate (15 mL), and washed with 2 x 10 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over $MgSO_4$, and

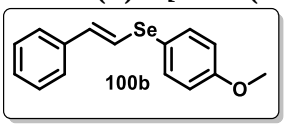
concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent.

5.3.2.1. (*E*)-1-[telluro(4-methoxy-phenyl)]-2-(phenyl) ethane (100a).



The experimental procedure similar to 5.3.1 was followed but using potassium vinyltrifluoroborate **99** and 1,2-bis(4-methoxyphenyl)ditellane **94b**. Yield: 87%; white solid; mp 62–64 ºC(lit. 61–63 ºC); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 16.6 Hz, 1H), 7.29–7.19 (m, 5H), 6.96 (d, J = 16.6Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 160.1, 141.4, 140.8, 138.3, 128.6, 127.7, 126.1, 115.6, 102.7, 101.9, 55.3.

5.3.2.2. (E)-1-[seleno(4-methoxy-phenyl)]-2-(phenyl) ethane (100b).



The experimental procedure similar to 5.3.1 was followed but using potassium vinyltrifluoroborate **99** and 1,2-bis(4-methoxyphenyl)diselane **93c**. Yield: 89%; white solid; mp 63–66 ºC(lit. 63–65 ºC); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.6 Hz, 2H), 7.39–7.37 (m, 1H), 7.28–7.20 (m, 4H), 7.12 (d, J = 15.8 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 15.8 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (50MHz, $CDCl_3$) δ = 159.8, 137.2, 135.6, 132.9, 128.7, 127.4, 126.0, 121.2, 119.2, 115.2, 55.4.

5.3.3. Control Experiments for the study of mechanism

5.3.4. Radical trapping study (TEMPO)

A mixture of diphenyl ditelluride **94a** (0.25 mmol, 0.102 g), 4-methoxyphenylboronic acid **59a** (0.5 mmol, 76 mg), iodine (10 mol%, 12 mg), TEMPO (0.5 mmol, 78 mg) and 2 equiv. of DMSO (1 mmol, 78 mg) were charged in a microwave glass tube, which was sealed and placed in a CEM Discover microwave apparatus. A maximum irradiation power of 100 W and a temperature of 100 ºC were applied

for 10 min. When the reaction was finished, the reaction mixture was dissolved in ethyl acetate (15 mL), and washed with 2 x 10 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over MgSO4, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent. Yield: 0.135 g (86%).

5.3.3.2. Reaction between phenylselenium bromide and 4-methoxyphenylboronic acid 2a

A mixture of phenylselenium bromide **101** (0.5 mmol, 0.118 g), 4-methoxyphenylboronic acid **59a** (0.5 mmol, 76 mg), iodine (10 mol%, 12 mg), and 2 equiv. of DMSO (1 mmol, 78 mg) were charged in a microwave glass tube, which was sealed and placed in a microwave apparatus (CEM Discover). A maximum irradiation power of 100 W and a temperature of 100 ºC were applied for 10 min. When the reaction was finished, the reaction mixture was dissolved in ethyl acetate (15 mL), and washed with 2 x 10 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over MgSO4, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent. Yield: 0.114 g (87%).

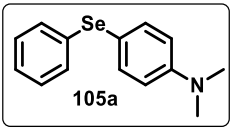
5.4. Experimental procedures for the synthesis of unsymmetrical diorganyl chalcogenides *via* c-h bond functionalization

5.4.1. General procedure for the iodine-catalyzed synthesis of unsymmetrical diorganyl chalocogenides

A mixture of appropriate arene **104a** (0.25 mmol), diorganyl dichalcogenides **93a** (0.125 mmol), iodine (20 mol %, 12 mg), and 3 equiv. of DMSO (0.75 mmol, 59 mg) were charged in a microwave glass tube, which was sealed and placed in a CEM Discover microwave apparatus. A maximum irradiation power of 100 W and a temperature of 110 ºC were applied for 10 min. When the reaction was finished, the homogenous reaction mixture was dissolved in ethyl acetate (10 mL), and washed with 2 x 5 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on

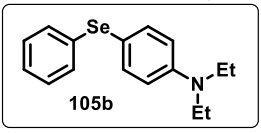
silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent.

5.4.1.1. N,N-dimethyl-4-(phenylselanyl)aniline (105a).



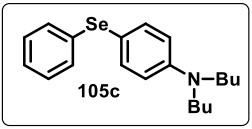
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 94% (65 mg); yellow solid; mp 36–38°C (lit.12b 35–38 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 (d, J = 9.0 Hz, 2H), 7.33–7.08 (m, 5H), 6.67 (d, J = 9.0 Hz, 2H), 2.97 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.6, 137.2, 134.7, 129.9, 129.1, 125.9, 113.8, 113.3, 40.4.^{77}Se NMR (38.14 MHz, $CDCl_3$): δ 391.4.

5.4.1.2. N,N-diethyl-4-(phenylselanyl)aniline (105b).



The experimental procedure similar to 5.4.1. was followed but diphenyl diselenide **93a** (0.125 mmol, 39 mg) and N,N-diethylaniline **104b** (0.25 mmol, 37mg) were used under standard conditions were used under standard conditions; Yield: 92% (70 mg); brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 (d, J = 9.0 Hz, 2H), 7.30–7.25 (m, 2H), 7.21–7.09 (m, 3H), 6.60 (d, J = 9.0 Hz, 2H), 3.34 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.0, 137.5, 134.9, 129.7, 129.0, 125.7, 112.5, 112.2, 44.4, 12.6.

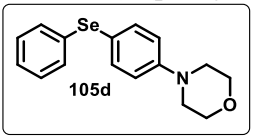
5.4.1.3. N,N-dibutyl-4-(phenylselanyl)aniline (105c)



The experimental procedure similar to 5.4.1. was followed but diphenyl diselenide **93a** (0.125 mmol, 39 mg) and N,N-dibutylaniline **104c** (0.25 mmol, 37mg) were used under standard conditions; Yield: 89% (80 mg); brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.43 (d, J = 9.0 Hz, 2H), 7.31–7.25 (m, 2H), 7.23–7.11 (m, 3H), 6.57 (d, J = 9.0 Hz, 2H), 3.34–3.16 (m, 4H), 1.67–1.46 (m, 4H), 1.44–1.26 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ =

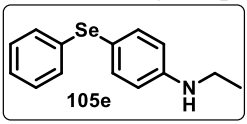
148.4, 137.5, 134.9, 129.8, 129.0, 125.8, 112.5, 112.0, 50.8, 29.4, 20.4, 14.1.

5.4.1.4. 4-(4-(phenylselanyl)phenyl)morpholine (105d)



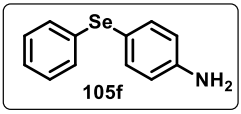
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-phenylmorpholine **104d** (0.25 mmol, 41mg) were used under standard conditions; Yield: 87% (69 mg); white solid; mp 69-71°C (lit.12b 69–71 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 (d, J = 7.5 Hz, 2H), 7.39–7.27 (m, 2H), 7.27–7.04 (m, 3H), 6.83 (d, J = 7.5 Hz, 2H), 3.92–3.73 (m, 4H), 3.26–3.03 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 151.2, 136.4, 133.6, 130.7, 129.2, 126.4, 118.6, 116.3, 66.9, 48.8. ^{77}Se NMR ($CDCl_3$,MHz): δ 397.7.

5.4.1.5. N-ethyl-4-(phenylselanyl)aniline (105e)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and N-ethylaniline **104e** (0.25 mmol, 30mg) were used under standard conditions; Yield: 83% (57 mg); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, J = 8.7 Hz, 2H), 7.36–7.23 (m, 2H), 7.23–7.11 (m, 3H), 6.56 (d, J = 8.7 Hz, 2H), 3.78 (s, 1H), 3.17 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.8, 137.4, 134.7, 129.9, 129.1, 125.9, 114.6, 113.7, 38.4, 14.9; IR (KBr); 3406, 3054, 2925, 2669, 1594, 1502, 1321, 1180, 1021, 814, 734; HRMS m/z Calcd. for $C_{14}H_{16}NSe$ $[M+H]^+$ 278.04427; found: 278.04429.

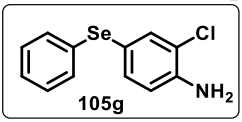
5.4.1.6. 4-(phenylselanyl)aniline (105f)



The experimental procedure similar to 5.4.1. was followed diphenyl diselenide **93a** (0.125 mmol, 39 mg) and aniline **104f** (0.25 mmol, 23mg) were used under standard conditions; Yield: 80% (50 mg); yellow solid; mp 86-89°C (lit.[107] 87–91 °C); ^{1}H NMR (200

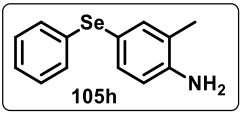
MHz, $CDCl_3$) δ = 7.39 (d, J = 8.5 Hz, 2H), 7.31–7.25 (m, 2H), 7.27–7.08 (m, 3H), 6.60 (d, J = 8.5 Hz, 2H), 3.72(s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.9, 137.1, 134.1, 130.2, 129.1, 126.1, 116.4, 116.1.

5.4.1.7. 2-chloro-4-(phenylselanyl)aniline (105g)



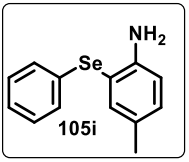
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 2-chloroaniline **104g** under standard conditions; Yield: 87% (62 mg); brown solid; mp 52-55°C (lit.[107] 51–54 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.54 (d, J = 2.4 Hz, 1H), 7.31–7.06 (m, 6H), 6.70 (d, J = 8.6 Hz, 1H), 4.27 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 143.2, 136.1, 135.1, 133.2, 130.8, 129.2, 126.6, 119.6, 117.1, 116.5.

5.4.1.8. 2-methyl-4-(phenylselanyl)aniline (105h)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 2-methylaniline **104h** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 78% (51 mg); brown soild; mp 55-57°C (lit.[107] 56–59 °C); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36–7.24 (m, 4H), 7.24–7.11 (m, 3H), 6.62 (d, J = 8.0 Hz, 1H), 3.71 (bs, 2H), 2.14 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.2, 138.1, 135.0, 134.4, 130.1, 129.1, 126.0, 123.5, 116.3, 115.8, 17.3.

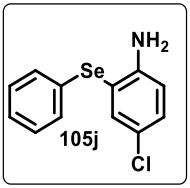
5.4.1.9. 4-methyl-2-(phenylselanyl)aniline (105i)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-methylaniline **104i** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 72% (47 mg); brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.39 (s, 1H), 7.27–7.09 (m, 5H), 7.09–6.95 (m, 1H), 6.69 (d, J = 8.1 Hz, 1H), 4.10 (bs, 2H), 2.22 (s, 3H); ^{13}C NMR (50 MHz, CDCl3) δ =

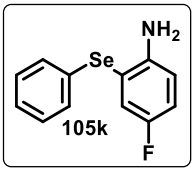
146.2, 138.7, 131.9, 131.8, 129.4, 129.3, 128.2, 126.1, 115.1, 112.7, 20.2.

5.4.1.10. 4-chloro-2-(phenylselanyl)aniline (105j)



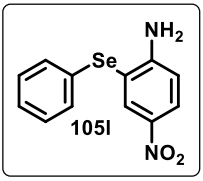
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-chloroaniline **104j** (0.25 mmol, 32 mg) were used under standard conditions; Yield: 78% (55 mg); brown solid; mp 58-60°C (lit.[107] 57–60 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.54 (d, J = 2.4 Hz, 1H), 7.33–7.06 (m, 6H), 6.70 (d, J = 8.6 Hz, 1H), 4.26 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.1, 137.3, 130.9, 130.8, 129.9, 129.5, 126.8, 122.6, 115.9, 114.1

5.4.1.11. 4-fluoro-2-(phenylselanyl)aniline (105k)



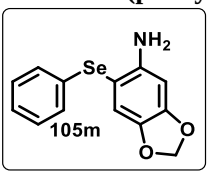
The experimental procedure similar to 5.4.1. was followed but using Diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-fluoroaniline **104k** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 83% (55 mg); yellow solid; mp 56–58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.31–7.19 (m, 6H), 7.03–6.86 (m, 1H), 6.75–6.68 (m, 1H), 4.09 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.4 (d, *Jc-f* = 239.4 Hz),, 144.7 (d, *Jc-f* = 2.2 Hz), 130.9, 130.2, 129.5, 126.8, 123.69 (d, *Jc-f* = 22.3 Hz), 117.71 (d, *Jc-f* = 22.4 Hz), 115.74 (d, *Jc-f* = 7.4 Hz), 113.85 (d, *Jc-f* = 7.1 Hz); IR (KBr) 3456, 3358, 3053, 1608, 1596, 1487, 1194, 1022, 877, 802, 740; HRMS m/z Calcd. for $C_{12}H_{11}FNSe$ $[M+H]^+$ 268.00355; found 268.00344.

5.4.1.12. 4-nitro-2-(phenylselanyl)aniline (105l)



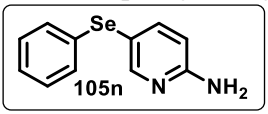
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-nitroaniline **104l** (0.25 mmol, 35 mg) were used under standard conditions; Yield: 81% (60 mg); yellow solid; mp 104–106 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.54 (d, J = 2.6 Hz, 1H), 8.10 (dd, J = 9.0, 2.6 Hz, 1H), 7.36–7.15 (m, 5H), 6.75 (d, J = 9.0 Hz, 1H), 5.07 (bs, 2H); ^{13}C NMR (50MHz, CDCl*3*) δ = 153.9, 138.8, 135.0, 130.2, 129.9, 129.7, 127.4, 127.3, 113.3, 112.0; IR (KBr) 3449, 3434, 3339, 1612, 1575, 1475, 1332, 1118, 1019, 907, 817, 740; HRMS m/z Calcd. for $C_{12}H_{11}N_2O_2Se$ $[M+H]^+$ 294.99806; found 294.99810.

5.4.1.13. 6-(phenylselanyl)benzo[d][1,3]dioxol-5-amine (105m)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and benzo[d][1,3]dioxol-5-amine **104m** (0.25 mmol, 34 mg) were used under standard conditions; Yield: 82% (59 mg); brown solid; mp 68–70°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.26–7.15 (m, 5H), 7.04 (s, 1H), 6.40 (s, 1H), 5.89 (s, 2H), 4.13 (s, 2H). ^{13}C NMR (50MHz, CDCl3) δ 150.4, 144.7, 140.5, 132.4, 129.3, 129.0, 126.2, 117.1, 102.5, 101.1, 97.0; IR (KBr) 3454, 3354, 3049, 2897, 1629, 1589, 1502, 1470, 1257, 1219, 1194, 1033, 934, 826; HRMS m/z Calcd. for $C_{13}H_{11}NO_2Se$ $[M]^+$ 292.9950; found 292.9955.

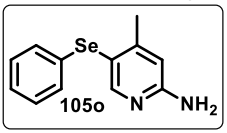
5.4.1.4. 5-(phenylselanyl)pyridin-2-amine (105n)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and pyridin-2-amine **104n** (0.25 mmol, 24 mg) were used under

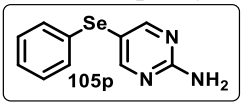
standard conditions; Yield: 79% (49 mg); yellow solid; mp 110-114°C (lit.[107] 111–114 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.95 (d, J = 1.8 Hz, 1H), 8.48–8.29 (m, 1H), 8.08–7.99 (m, 2H), 7.99–7.89 (m, 3H), 7.25 (d, J = 8.6 Hz, 1H), 5.27 (bs, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 157.9, 152.7, 145.6, 132.7, 130.7, 129.3, 126.8, 113.8, 110.2.

5.4.1.15. 4-methyl-5-(phenylselanyl)pyridin-2-amine (105o)



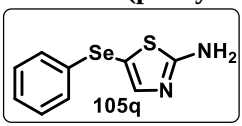
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 4-methylpyridin-2-amine **104o** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 71% (47 mg); yellow soild; mp 85–87 °C;^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 7.25–7.13 (m, 5H), 6.45 (s, 1H), 4.59 (bs, 2H), 2.27 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.4, 155.8, 153.3, 132.9, 129.5, 129.3, 126.2, 115.3, 109.9, 22.5; IR (KBr) 3467, 3293, 3135, 3057, 1640, 1592, 1477, 1437, 1412, 1021, 730, 668; HRMS m/z Calcd. for $C_{12}H_{13}N_2Se$ $[M+H]^+$ 265.0239; found 265.0240.

5.4.1.16. 5-(phenylselanyl)pyrimidin-2-amine (105p)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and pyrimidin-2-amine **104p** (0.25 mmol, 24 mg) were used under standard conditions; Yield: 76% (48 mg); white solid; mp: 146–148 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.41 (s, 2H), 7.62–7.18 (m, 5H), 7.08 (s, 2H); ^{13}C NMR (50 MHz, DMSO-d_6) δ = 164.1, 162.9, 132.6, 129.5, 129.4, 126.5, 109.3; IR (KBr); 3306, 3174, 3069, 1659, 1574, 1543, 1490, 1213, 1066, 1020, 936, 796, 689; HRMS m/z Calcd. for $C_{10}H_{10}N_3Se$ $[M+H]^+$ 252.0035; found 252.0038.

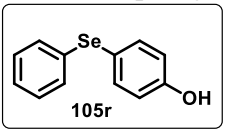
5.4.1.17. 5-(phenylselanyl)thiazol-2-amine (105q)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and thiazol-2-amine **104q** (0.25 mmol, 25 mg) were used under standard

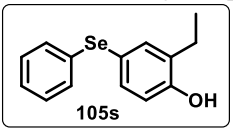
conditions; Yield: 75% (48 mg); brown solid; mp 120–122°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40–7.35 (m, 1H), 7.32–7.21 (m, 5H), 5.47 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 173.3, 148.2, 133.0, 129.5, 129.3, 126.8, 106.1; IR (KBr) 3378, 3272, 3163, 3087, 1625, 1513, 1483, 1067, 1052, 726, 516; HRMS m/z Calcd. for $C_9H_9N_2SSe$ $[M+H]^+$ 256.9646; found 256.9645.

5.4.1.18. 4-(phenylselanyl)phenol (105r)



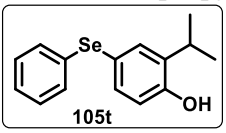
The experimental procedure similar to 5.4.1. was followed but using Diphenyl diselenide **93a** (0.125 mmol, 39 mg) and phenol **104r** (0.25 mmol, 25 mg) were used under standard conditions; Yield: 82% (51 mg); brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (d, J = 8.6 Hz, 2H), 7.39–7.29 (m, 2H), 7.28–7.15 (m, 3H), 6.78 (d, J = 8.6 Hz, 2H), 5.12 (bs, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 155.9, 136.8, 133.1, 131.1, 129.3, 126.6, 120.3, 116.7.

5.4.1.19. 2-ethyl-4-(phenylselanyl)phenol (105s)



The experimental procedure similar to 5.4.1. was followed but using Diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 2-ethylphenol **104s** (0.25 mmol, 31 mg) were used under standard conditions; Yield: 80% (55 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.53 – 7.09 (m, 7H), 6.71 (d, J = 8.2 Hz, 1H), 4.98 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.8, 136.4, 134.2, 133.5, 131.5, 130.9, 129.2, 126.5, 120.0, 116.4, 22.9, 13.9; IR (KBr) 3417, 2965, 2929, 1578, 1491, 1264, 1119, 1021, 891, 735; HRMS m/z Calcd. for $C_{14}H_{14}OSe$ $[M]^+$ 278.0205; found 278.0206.

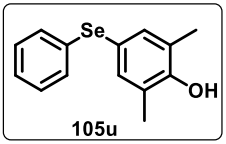
5.4.1.20. 2-isopropyl-4-(phenylselanyl)phenol (105t)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) 2-

isopropylphenol **104t** (0.25 mmol, 34 mg) were used under standard conditions; Yield: 82% (60 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 – 7.14 (m, 7H), 6.69 (d, J = 8.2 Hz, 1H), 4.89 (s, 1H), 3.25–3.11 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.2, 136.0, 133.9, 133.8, 133.5, 130.6, 129.2, 126.4, 119.9, 116.6, 27.2, 22.5; IR (KBr) 3441, 3070, 3056, 2961,1636, 1577, 1405, 1177, 1079, 813, 734; HRMS m/z Calcd. for $C_{15}H_{16}OSe$ $[M]^+$ 292.0361; found 292.0362.

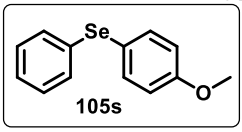
5.4.1.21. 2,6-dimethyl-4-(phenylselanyl)phenol (105u)



105u

The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) 2,6-dimethylphenol **104u** (0.25 mmol, 52 mg) were used under standard conditions; Yield: 75% (57 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.35–7.17 (m, 7H), 4.74 (s, 1H), 2.21 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 152.7, 135.7, 133.6, 130.8, 129.2, 126.4, 124.5, 119.1,15.8; IR (KBr) 3474, 3068, 3055, 2919, 2851, 1578, 1475, 1437, 1192, 1021, 869, 734; HRMS m/z Calcd. for $C_{14}H_{14}OSe$ $[M]^+$ 278.0205; found 278.0203.

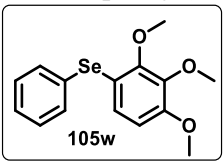
5.4.1.22. (4-methoxyphenyl)(phenyl)selane (105v)



105s

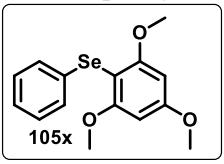
The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and anisole **104v** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 88% (58 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.8 Hz, 2H), 7.38–7.29 (m, 2H), 7.27–7.16 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 159.9, 136.6, 133.3, 131.0, 129.2, 126.5, 120.0, 115.2, 55.4.

5.4.1.23. phenyl(2,3,4-trimethoxyphenyl)selane (105w)



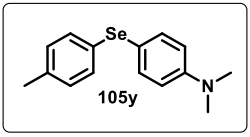
The experimental procedure similar to 5.4.1. was followed but using Diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 1,2,3-trimethoxybenzene **104w** (0.25 mmol, 42 mg) were used under standard conditions; Yield: 83% (67 mg); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51–7.46 (m, 2H), 7.28–7.25 (m, 3H), 6.87 (d, J = 8.7 Hz, 1H), 6.57 (d, J = 8.7 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.7, 152.5, 142.6, 133.5, 130.4, 129.3, 127.5, 127.4, 117.3, 108.5, 61.0, 60.9, 56.1; IR (KBr) 3069, 3055, 2996, 2835, 1577, 1478, 1456, 1292, 1092, 1012, 917, 847, 739; HRMS m/z Calcd. for $C_{15}H_{16}O_3Se$ $[M]^+$ 324.0260; found 324.0262.

5.4.1.24. phenyl(2,4,6-trimethoxyphenyl)selane (105x)



The experimental procedure similar to 5.4.1. was followed but using diphenyl diselenide **93a** (0.125 mmol, 39 mg) and 1,3,5-trimethoxybenzene **104x** (0.25 mmol, 42 mg) were used as substrates; Yield: 81% (66 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.31–7.01 (m, 5H), 6.21 (s, 2H), 3.86 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 163.0, 162.0, 133.6, 128.9, 128.7, 125.3, 97.2, 91.3, 56.4, 55.5.

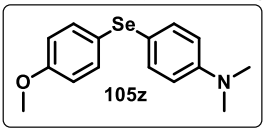
5.4.1.25. N,N-dimethyl-4-(p-tolylselanyl)aniline (105y)



The experimental procedure similar to 5.4.1. was followed but using Bis(4-methylphenyl) diselenide **93b** (0.125 mmol, 43 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 86% (63 mg); yellow solid; mp 67–69°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45 (d, J = 9.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H),

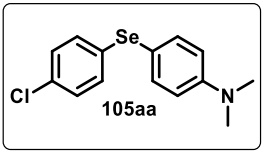
2.95 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$): δ = 150.4, 136.6, 135.9, 130.6, 130.4, 129.9, 114.7, 113.3, 40.4, 21.1; IR (KBr) 3068, 3016, 2915, 2884, 2810, 1597, 1504, 1442, 1224, 1064, 1014, 807, 799; HRMS m/z Calcd. for $C_{15}H_{18}NSe$ $[M+H]^+$ 292.0599; found 292.0597.

5.4.1.26. 4-((4-methoxyphenyl)selanyl)-N,N-dimethylaniline(105z)



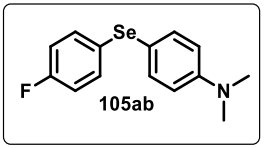
The experimental procedure similar to 5.4.1. was followed but using Bis(4-methoxyphenyl) diselenide **93c** (0.125 mmol, 47 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 85% (65 mg); yellow solid; mp 98-102°C; ^{1}H NMR (200MHz, $CDCl_3$) δ = 7.41 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 158.8, 150.3, 135.7, 133.3, 123.7, 116.0, 114.9, 113.3, 55.4, 40.5; IR (KBr) 3087, 3058, 2940, 2810, 1591, 1504, 1359, 1238, 1031, 808, 593; HRMS m/z Calcd. for $C_{15}H_{17}NOSe$ $[M+H]^+$ 308.0540; found 308.0550.

5.4.1.27. 4-((4-chlorophenyl)selanyl)-N,N-dimethylaniline (105aa)



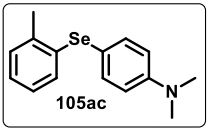
The experimental procedure similar to 5.4.1. was followed but using Bis(4-chlorophenyl) diselenide **93d** (0.125 mmol, 48 mg) and N,N-dimethylaniline 104a (0.25 mmol, 30 mg) were used under standard conditions; Yield: 92% (72 mg); white solid; mp 111-114°C (lit.[107] 111–116 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (d, J = 9.0 Hz, 2H), 7.28–7.05 (m, 5H), 6.66 (d, J = 9.0 Hz, 2H), 2.97 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.7, 137.2, 133.1, 131.9, 131.1, 129.1, 113.4, 113.3, 40.3.

5.4.1.28. 4-((4-fluorophenyl)selanyl)-N,N-dimethylaniline (105ab)



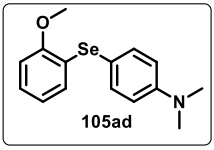
The experimental procedure similar to 5.4.1. was followed but using Bis(4-fluorophenyl) diselenide **93e** (0.125 mmol, 44 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 90% (66 mg); yellow solid; mp 47-50°C (lit.[107] 49–52 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ= 7.44 (d, J = 8.8 Hz, 2H), 7.30–7.23 (m, 2H), 6.88 (t, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 2.95 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 161.84 (d, *Jc-f* = 245.2 Hz), 150.6, 136.7, 132.31 (d, *Jc-f* = 7.7 Hz), 128.78 (d, *Jc-f* = 3.3 Hz), 116.19 (d, *Jc-f* = 21.6 Hz), 114.4, 113.3, 40.3.

5.4.1.29. N,N-dimethyl-4-(o-tolylselanyl)aniline (105ac)



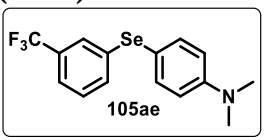
The experimental procedure similar to 5.4.1. was followed but using Bis(2-methylphenyl) diselenide **93f** (0.125 mmol, 43 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 83% (60 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 (d, J = 8.6 Hz, 2H), 7.29–6.90 (m, 5H), 6.69 (d, J = 8.6 Hz, 2H), 2.98 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.6, 137.4, 137.0, 135.4, 129.9, 129.4, 126.5, 125.9, 113.4, 113.0, 40.4, 21.7.

5.4.1.30. 4-((2-methoxyphenyl)selanyl)-N,N-dimethylaniline (105ad)



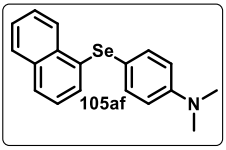
The experimental procedure similar to 5.4.1. was followed but using bis(2-methoxyphenyl) diselenide **93g** (0.125 mmol, 47 mg)and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 81% (62 mg); yellow solid; mp 85-88°C (lit. 85–90 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.3 Hz, 2H), 7.19–7.05 (m, 1H), 6.89–6.51 (m, 5H), 3.89 (s, 3H), 2.98 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 155.7, 150.8, 138.5, 128.5, 126.4, 124.7, 121.6, 113.3, 111.2, 110.0, 55.8, 40.3.

5.4.1.31. N,N-dimethyl-4-((3-(trifluoromethyl)phenyl)selanyl)aniline (105ae)



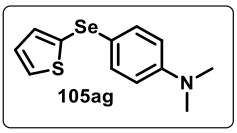
The experimental procedure similar to 5.4.1. was followed but using Bis(3-(trifluoromethyl)phenyl) diselenide **93h** (0.125 mmol, 56 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 89% (77 mg); brown solid; mp 47-50°C (lit.[107] 48–52 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48–7.43 (m, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.32–7.24 (m, 2H), 7.23–7.07 (m, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 2.90 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.7, 137.5, 136.3, 132.7, 131.3 (q, *Jc-f* = 32.2 Hz), 129.3, 126.0 (q, *Jc-f* = 3.9 Hz), 123.8 (q, *Jc-f* = 272.8 Hz), 122.6 (q, *Jc-f* = 3.8 Hz), 113.5, 112.8, 40.4.

5.4.1.32. N,N-dimethyl-4-(naphthalen-1-ylselanyl)aniline (105af)



The experimental procedure similar to 5.4.1. was followed but using Binaphthyl diselenide **93i** (0.125 mmol, 52 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 85% (69 mg); yellow soild; mp 122-124°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.57–7.40 (m, 4H), 7.39–7.18 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.5, 136.8, 134.0, 133.5, 132.9, 129.0, 128.5, 127.0, 126.5, 126.4, 126.2, 126.1, 113.7, 113.4, 40.4; IR (KBr) 3044, 2901, 2812, 1595, 1557, 1372, 1194, 1081, 807, 768; HRMS m/z Calcd. for $C_{18}H_{17}NSe$ $[M]^+$ 327.0521; found: 327.0521.

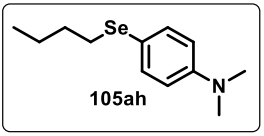
5.4.1.33. N,N-dimethyl-4-(thiophen-2-ylselanyl)aniline (105ag)



The experimental procedure similar to 5.4.1. was followed but using Di(thiophen-2-yl) diselenide **93j** (0.125 mmol, 41

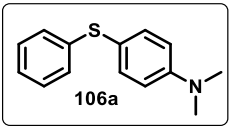
mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 82% (58 mg); yellow soild; mp 50-53°C;^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.42 (d, J = 9.0 Hz, 2H), 7.32 (dd, J = 5.3, 1.2 Hz, 1H), 7.20 (dd, J = 3.5, 1.2 Hz, 1H), 6.94 (dd, J = 5.3, 3.5 Hz, 1H), 6.61 (d, J = 9.0 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.1, 134.3, 133.9, 130.1, 127.8, 127.0, 117.0, 113.0, 40.3; IR (KBr) 3439, 3287, 3093, 2810, 1661, 1591, 1502, 1437, 1233, 1066, 846, 730; HRMS m/z Calcd. for C12H14NSSe $[M+H]^+$ 284.0006; found 284.0009.

5.4.1.33. 4-(butylselanyl)-N,N-dimethylaniline (105ah)



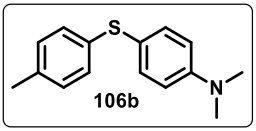
The experimental procedure similar to 5.4.1. was followed but using dibutyl diselenide **93k** (0.125 mmol, 34 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 78% (50 mg); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.42 (d, J = 8.9 Hz, 2H), 6.62 (d, J = 8.9 Hz, 2H), 2.93 (s, 6H), 2.87–2.64 (m, 2H), 1.79–1.55 (m, 2H), 1.48–1.30 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.0, 135.9, 115.0, 113.1, 40.5, 32.5, 29.1, 22.9, 13.7; IR (KBr) 3029, 2971, 2924, 2800, 1595, 1505, 1444, 1352, 1062, 945, 760; HRMS m/z Calcd. for $C_{12}H_{20}NSe$ $[M+H]^+$ 258.07558; found 258.07536.

5.4.1.34. N,N-dimethyl-4-(phenylthio)aniline (106a)



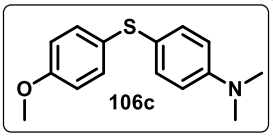
The experimental procedure similar to 5.4.1. was followed but using Diphenyl disulfide **107a** (0.125 mmol, 27 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 97% (56 mg); yellow solid; mp 67-69°C (lit.17 68–69 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.39 (d, J = 7.5 Hz, 2H), 7.25–7.01 (m, 5H), 6.70 (d, J = 7.5 Hz, 2H), 2.98 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.7, 140.3, 136.2, 128.8, 127.0, 125.1, 117.6, 113.1, 40.5.

5.4.1.35. N,N-dimethyl-4-(p-tolylthio)aniline (106b)



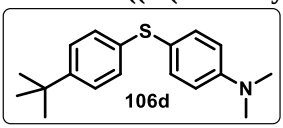
The experimental procedure similar to 5.4.1. was followed but using Bis(4-methylphenyl) disulfide **107b** (0.125 mmol, 31 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 90% (55 mg); yellow solid; mp 49-51°C (lit.[108] 51–52 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, J = 8.8 Hz, 2H), 7.20–6.99 (m, 5H), 6.74 (d, J = 8.8 Hz, 2H), 3.01 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.3, 136.2, 135.4, 135.1, 129.6, 127.9, 118.9, 113.1, 40.4, 21.0.

5.4.1.36. 4-((4-methoxyphenyl)thio)-N,N-dimethylaniline (106c)



The experimental procedure similar to 5.4.1. was followed but using Bis(4-methoxyphenyl) disulfide **107b** (0.125 mmol, 35 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 87% (56 mg); yellow solid; mp 91–93 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.30 (d, J = 9.0 Hz, 2H), 7.18 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 3.74 (s, 3H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 158.4, 150.2, 134.3, 130.9, 129.6, 120.6, 114.6, 113.1, 55.4, 40.4; IR (KBr) 3091, 3060, 2942, 2836, 1880, 1872, 1592, 1506, 1358, 1236, 1031, 827; HRMS m/z Calcd. for $C_{15}H_{18}NOS$ $[M+H]^+$ 260.1104; found 260.1102.

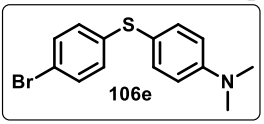
5.4.1.36. 4-((4-(tert-butyl)phenyl)thio)-N,N-dimethylaniline (106d)



The experimental procedure similar to 5.4.1. was followed but using Bis(4-(tert-butyl)phenyl) disulfide **107e** (0.125 mmol, 41 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 93% (53 mg); yellow solid; mp 86–88 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 2.98 (s, 6H), 1.27 (s, 9H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.5,

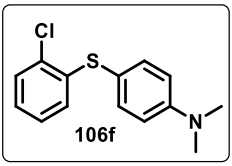
148.3, 136.5, 135.8, 127.1, 125.8, 118.3, 113.0, 40.4, 34.4, 31.3; IR (KBr) 3075, 2956, 2901, 2802, 1592, 1551, 1395, 1357, 1192, 1061, 1008, 812; HRMS m/z Calcd. for $C_{18}H_{23}NS$ $[M+H]^+$ 286.16240; found 286.16236.

5.4.1.36. 4-((4-bromophenyl)thio)-N,N-dimethylaniline (106e)



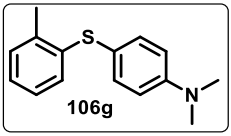
The experimental procedure similar to 5.4.1. was followed but using bis(4-bromophenyl) disulfide **107f** (0.125 mmol, 47 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 95% (73 mg); yellow solid; mp 126–128 °C(lit.[108] 127–128 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.35 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 2.96 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.8, 139.9, 136.3, 131.7, 128.3, 118.5, 116.5, 113.0, 40.3.

5.4.1.37. 4-((2-chlorophenyl)thio)-N,N-dimethylaniline (106f)



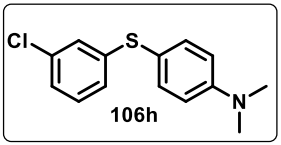
The experimental procedure similar to 5.4.1. was followed but using bis(4-chlorophenyl) disulfide **107g** (0.125 mmol, 36 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 93% (61 mg); white solid; mp 119–121°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (d, J = 8.9 Hz, 2H), 7.35–7.22 (m, 1H), 7.08–6.95 (m, 2H), 6.74 (d, J = 8.9 Hz, 2H), 6.71–6.60 (m, 1H), 3.01 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 151.2, 140.3, 137.3, 130.2, 129.3, 127.0, 126.8, 125.4, 115.0, 113.2, 40.3; IR (KBr) 3054, 2987, 2900, 2810, 1592, 1509, 1441, 1366, 1193, 1028, 945, 814, 746; HRMS m/z Calcd. for $C_{14}H_{15}ClNS$ $[M+H]^+$ 264.06082; found 264.06091.

5.4.1.38. N,N-dimethyl-4-(o-tolylthio)aniline (106g)



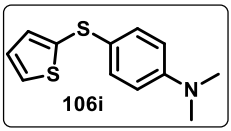
The experimental procedure similar to 5.4.1. was followed but using bis(4-methylphenyl) disulfide **107h** (0.125 mmol, 31 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield 90% (55 mg); white solid; mp 112–114 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.33 (d, J = 8.9 Hz, 2H), 7.14–7.10 (m, 1H), 7.03–6.98 (m, 2H), 6.85–6.80 (m, 1H), 6.70 (d, J = 8.9 Hz, 2H), 2.97 (s, 6H); 2.38 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.6, 139.2, 135.9, 135.5, 130.0, 127.0, 126.4, 125.1, 117.3, 113.2, 40.4, 20.2; IR (KBr) 3084, 3056, 2925, 2813, 1597, 1509, 1440, 1194, 1057, 946, 809, 797; HRMS m/z Calcd. for $C_{15}H_{18}NS$ $[M+H]^+$ 244.11545; found 244.11547.

5.4.1.39. 4-((3-chlorophenyl)thio)-N,N-dimethylaniline (106h)



The experimental procedure similar to 5.4.1. was followed but using bis(3-chlorophenyl) disulfide **107i** (0.125 mmol, 36 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions;Yield: 90% (59 mg); white solid; mp 58–60 °C; 1H NMR (200 MHz, $CDCl_3$) δ = 7.38 (d, J = 9.0 Hz, 2H), 7.20–6.89 (m, 4H), 6.70 (d, J = 9.0 Hz, 2H), 2.99 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 151.0, 143.0, 136.6, 134.8, 129.7, 126.1, 125.0, 124.5, 115.9, 113.1, 40.3; IR (KBr) 3396, 3043, 2889, 2811, 1592, 1574, 1505, 1358, 1193, 1097, 943, 884, 770; HRMS m/z Calcd. for $C_{14}H_{15}ClNS$ $[M+H]^+$ 264.06082; found 264.06069.

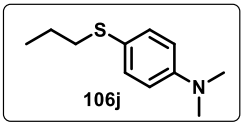
5.4.1.40. N,N-dimethyl-4-(thiophen-3-ylthio)aniline (106i)



The experimental procedure similar to 5.4.1. was followed but using Di(thiophen-2-yl) disulfide **107j** (0.125 mmol, 29 mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 86% (50 mg); yellow solid; mp 50–52

°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.33–7.25 (m, 3H), 7.12 (d, J = 3.5 Hz, 1H), 6.95–6.91 (m, 1H), 6.62 (d, J = 8.7 Hz, 2H), 2.91 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.2, 136.8, 132.6, 132.0, 128.8, 127.5, 122.2, 112.9, 40.9; IR (KBr) 3400, 3097, 3082, 2884, 2810, 1599, 1507, 1362, 1190, 1062, 843, 713; HRMS m/z Calcd. for $C_{12}H_{14}NS_2$ $[M+H]^+$ 236.05622; found 236.05625.

5.4.1.40. N,N-dimethyl-4-(propylthio)aniline (106j)



The experimental procedure similar to 5.4.1. was followed but using Dibutyl disulfide **107k** (0.125 mmol, 22mg) and N,N-dimethylaniline **104a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 77% (38 mg); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.32 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 2.94 (m, 6H), 2.83–2.64 (m, 2H), 1.73–1.43 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 149.9, 134.0, 121.3, 113.0, 40.6, 38.8, 22.9, 13.4; IR (KBr) 3444, 2959, 2929, 2870, 1596, 1504, 1443, 1352, 1061, 946, 812; HRMS m/z Calcd. for $C_{11}H_{18}NS$ $[M+H]^+$ 196.10081 found 196.10089.

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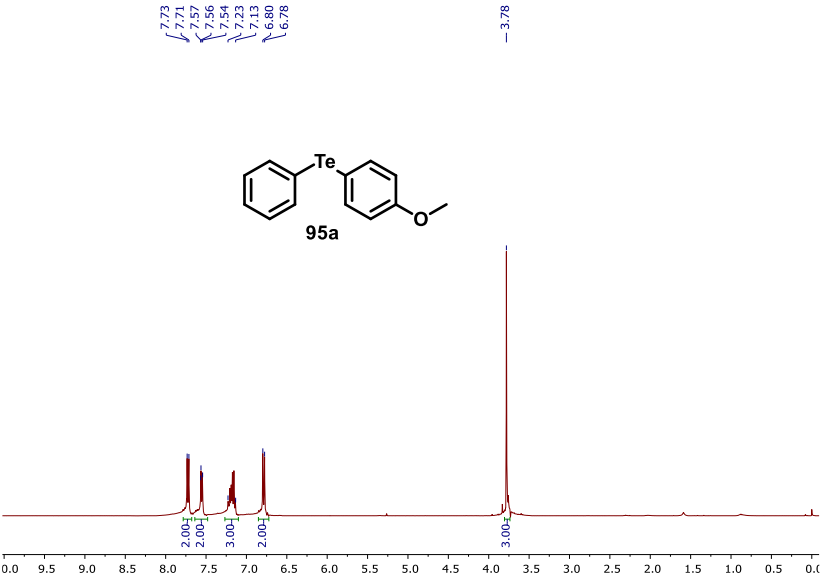
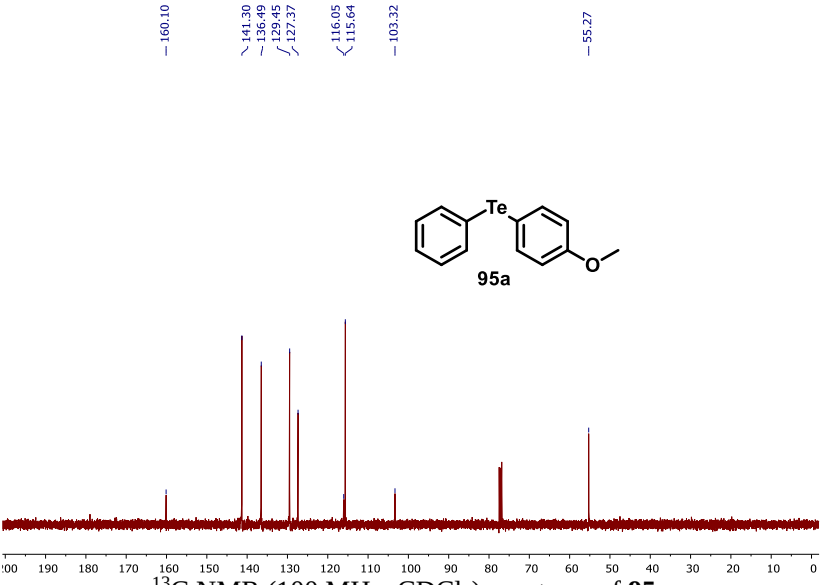
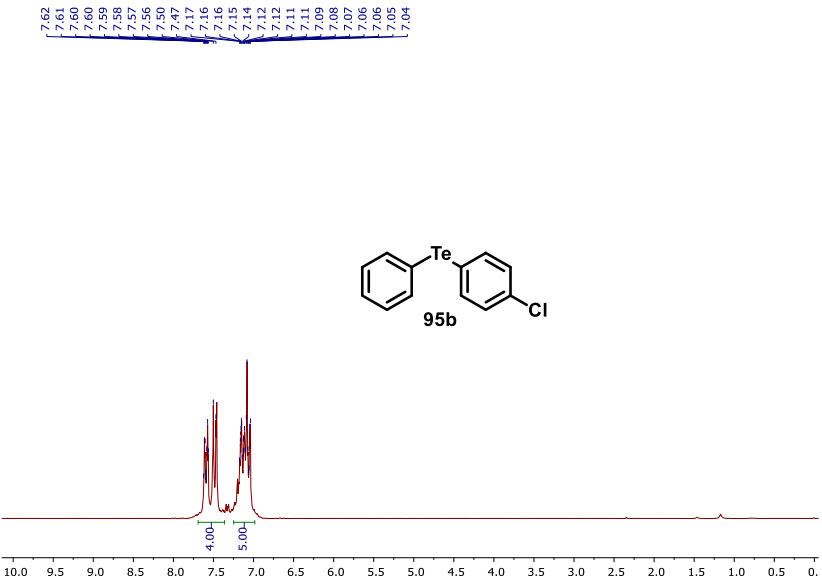
Spectroscopic Section



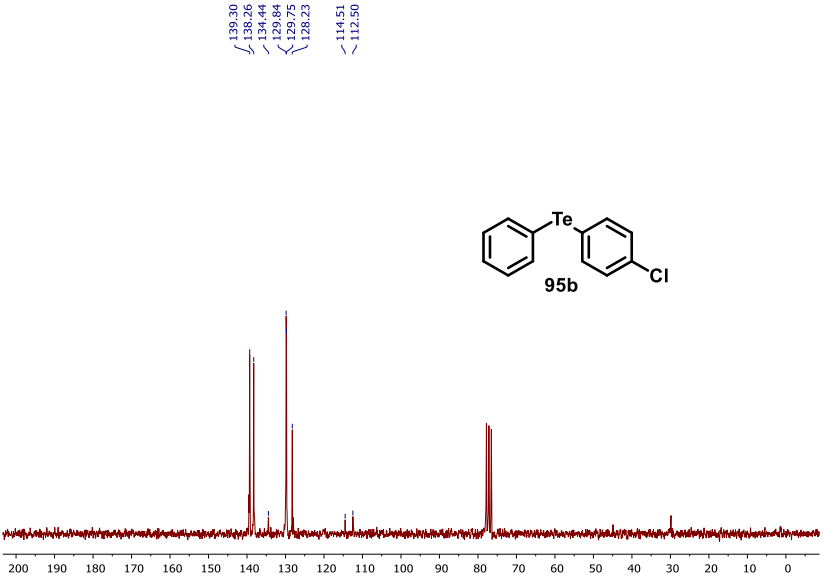
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **95a**



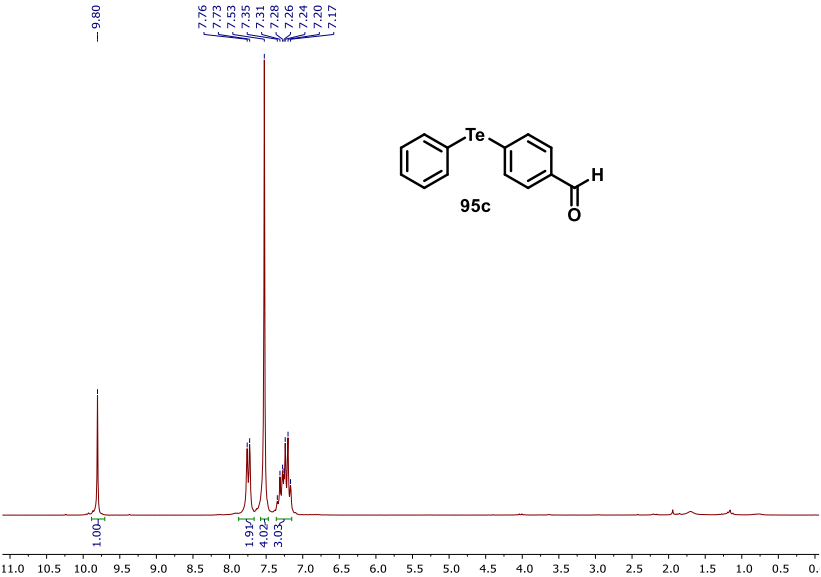
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **95a**



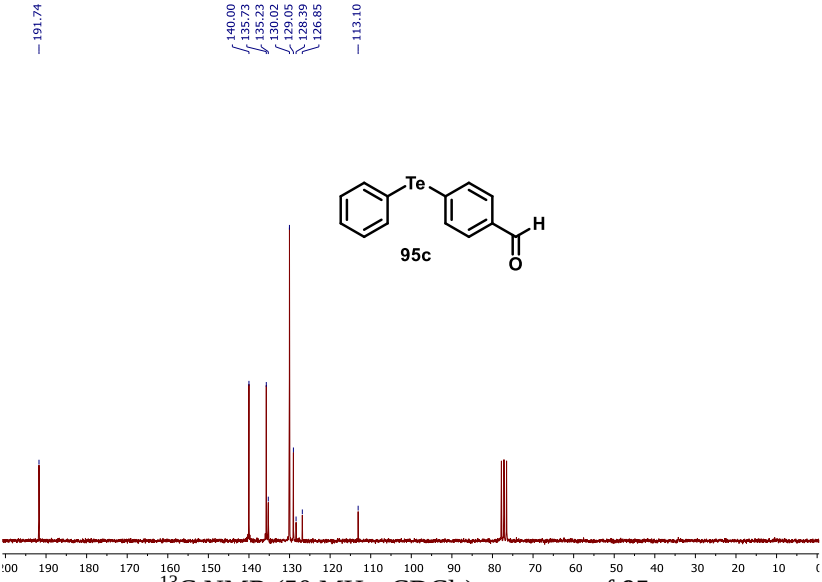
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95b**



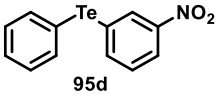
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95b**



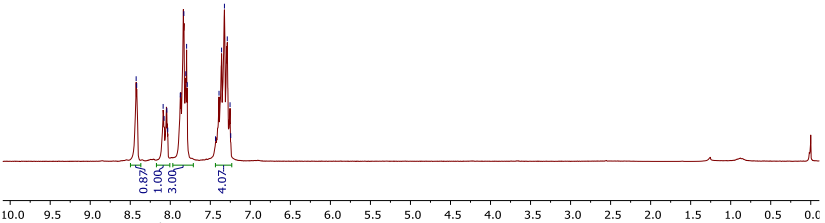
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95c**



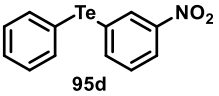
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95c**



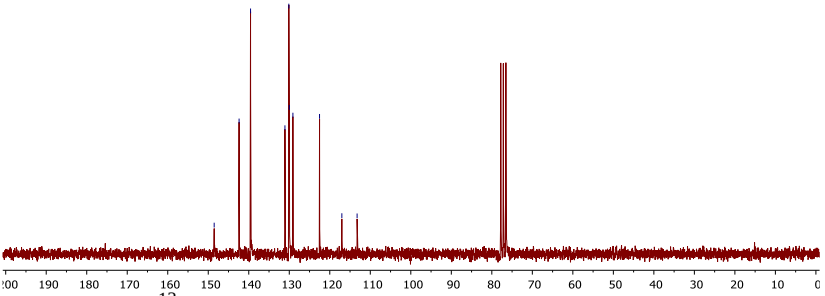
95d



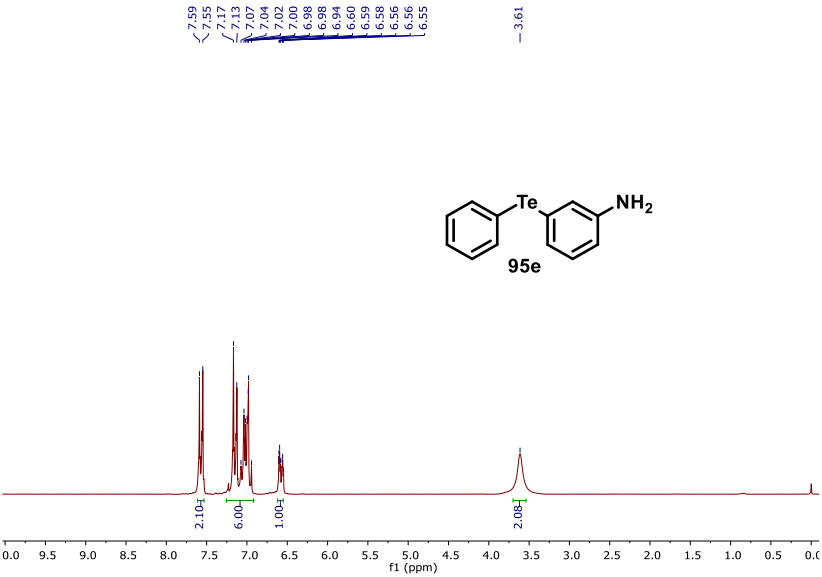
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95d**



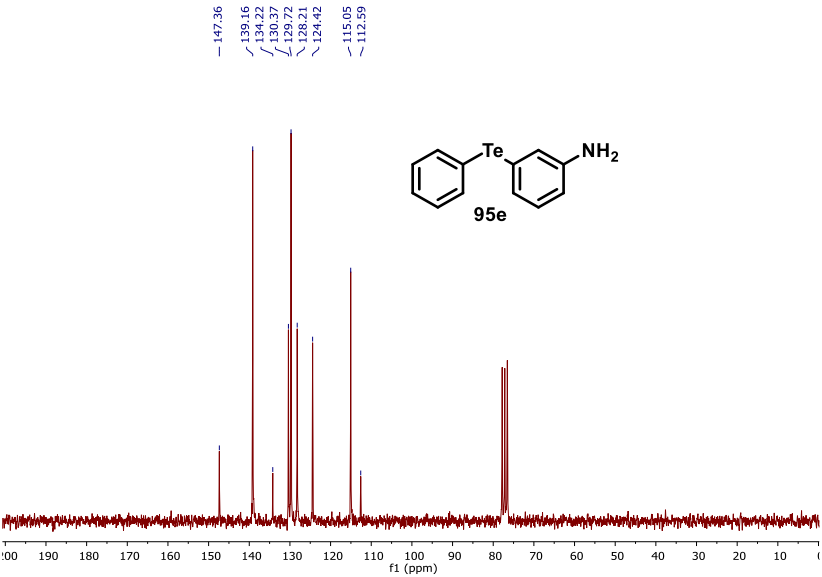
95d



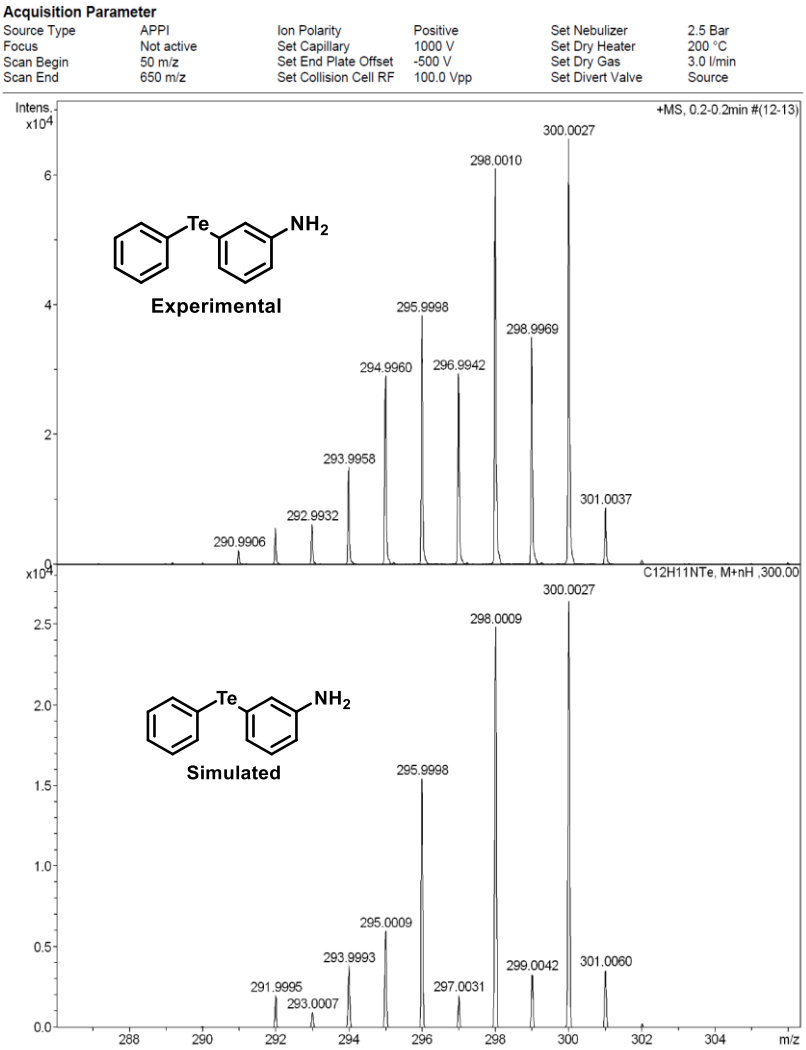
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95d**



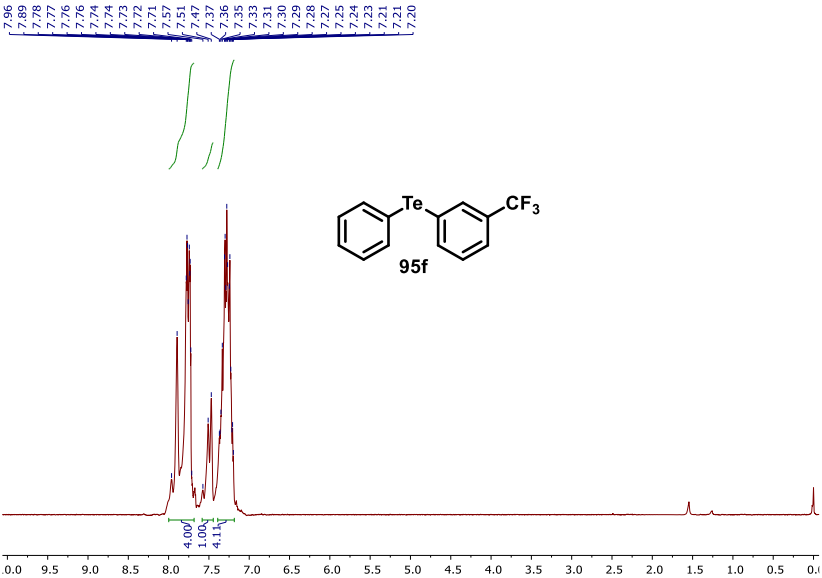
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95e**



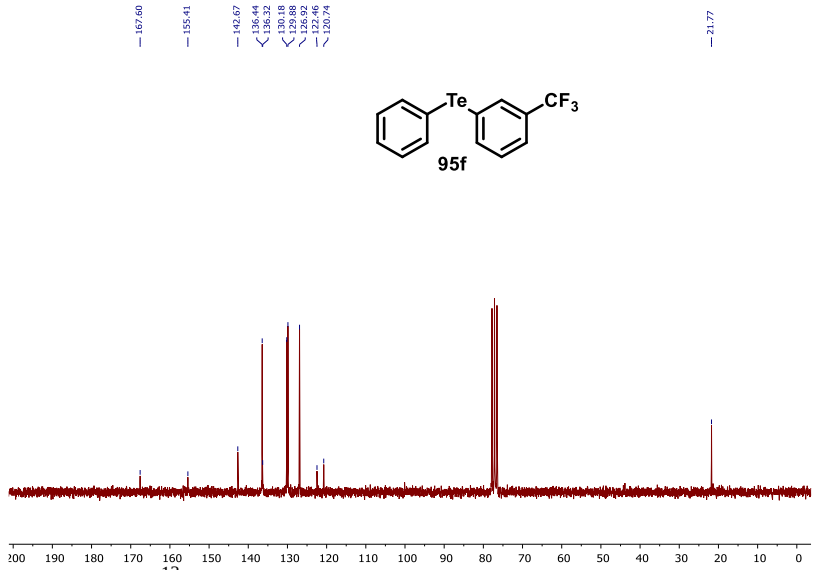
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95e**



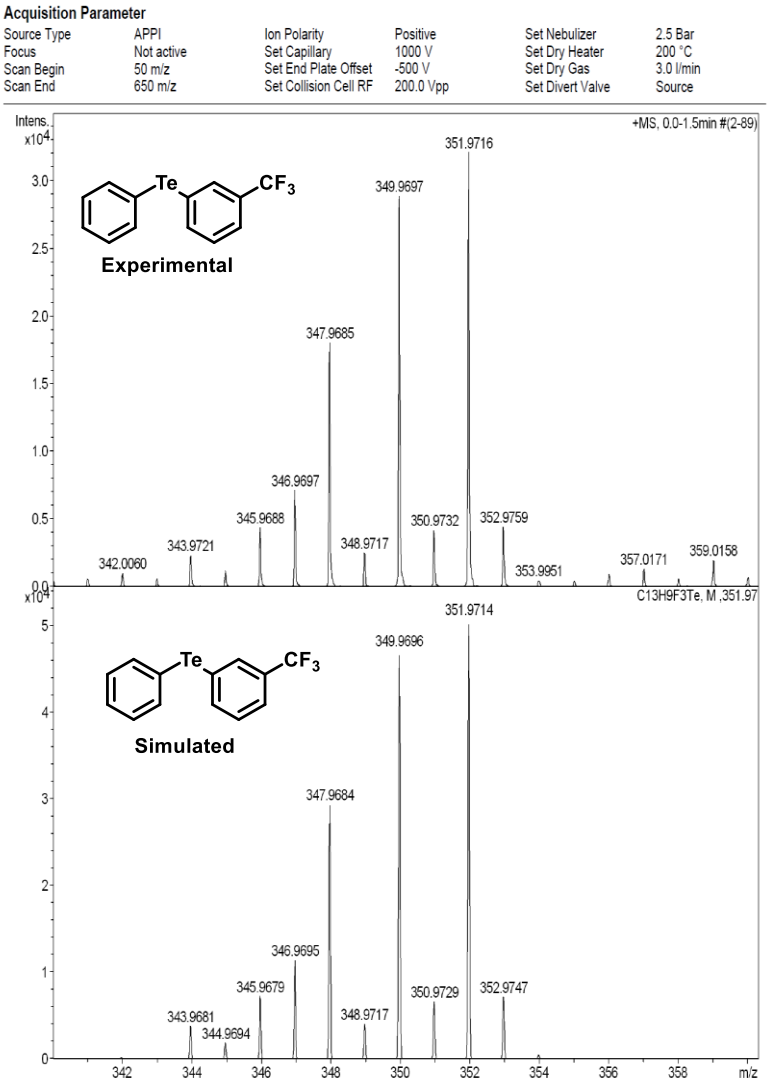
High-resolution mass spectrum of compound **95e**



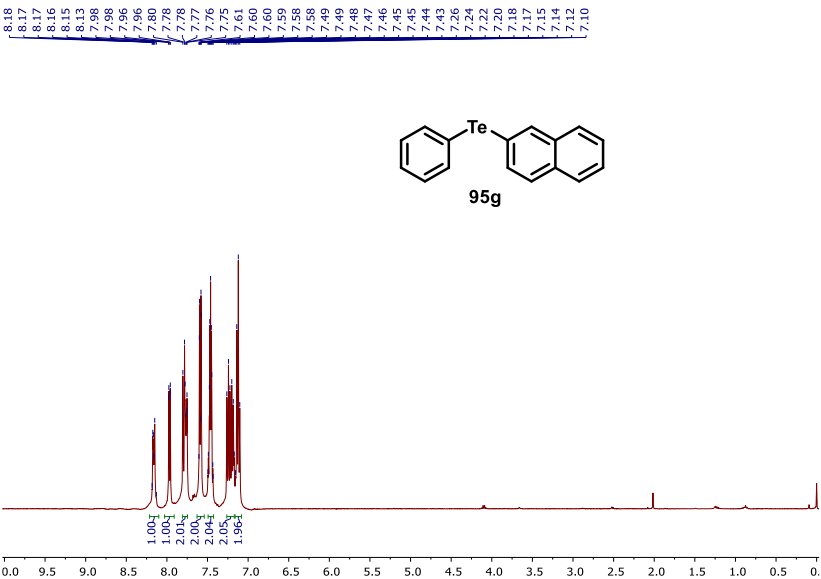
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95f**



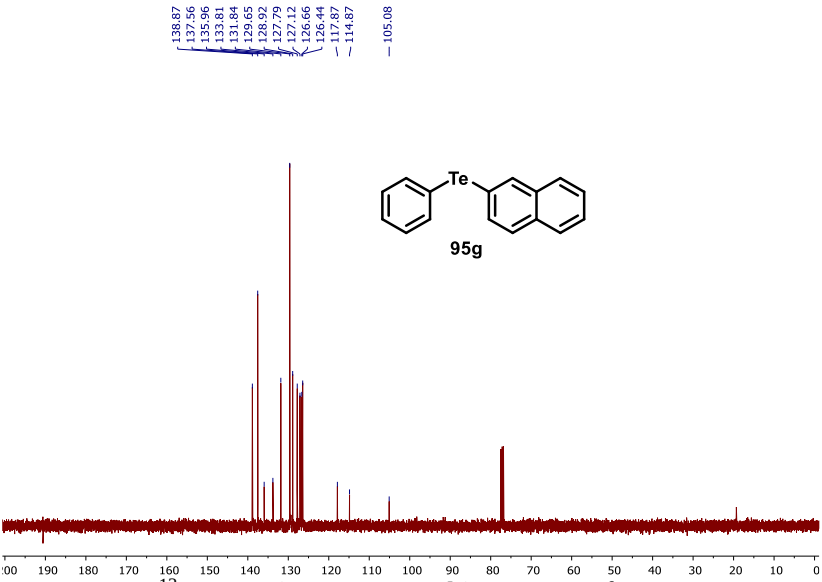
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95f**



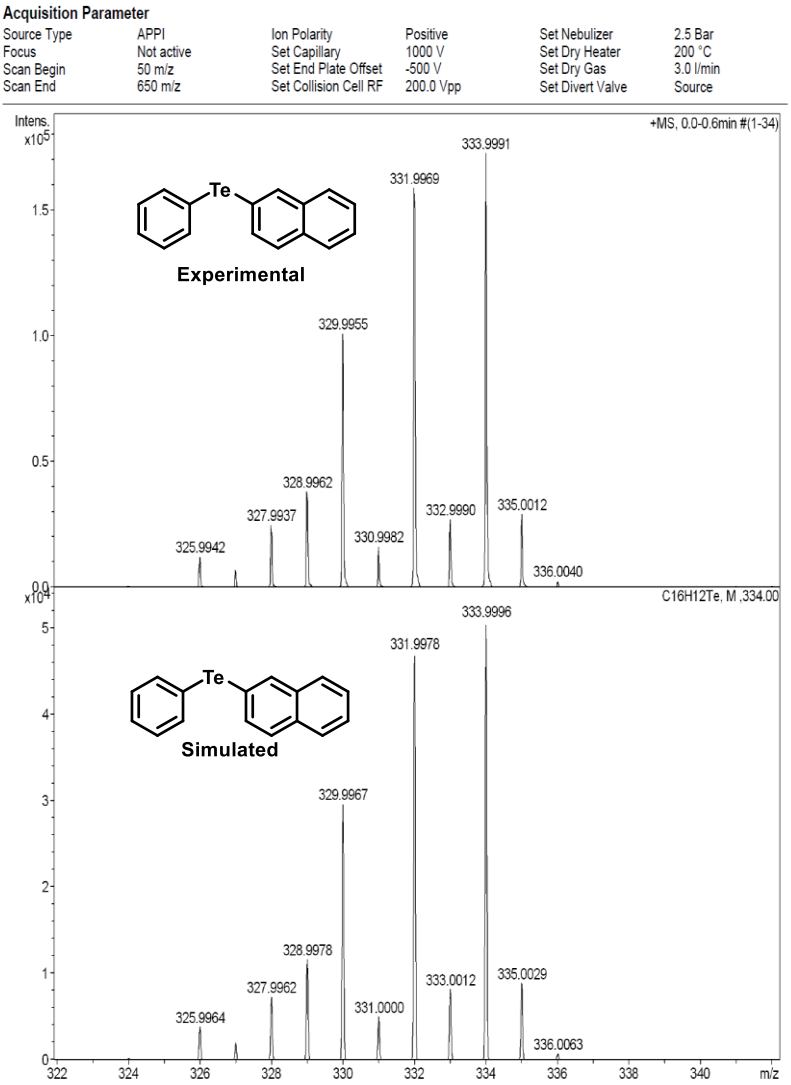
High-resolution mass spectrum of compound **95f**



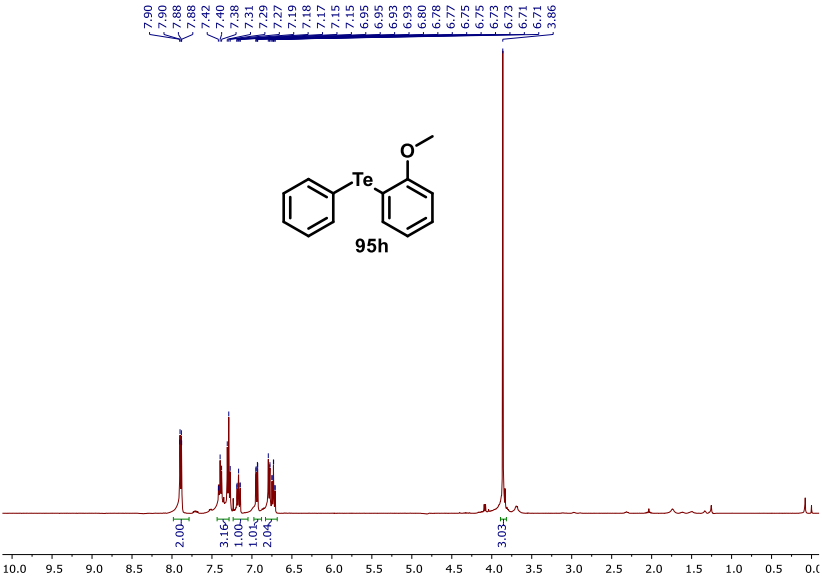
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95g**



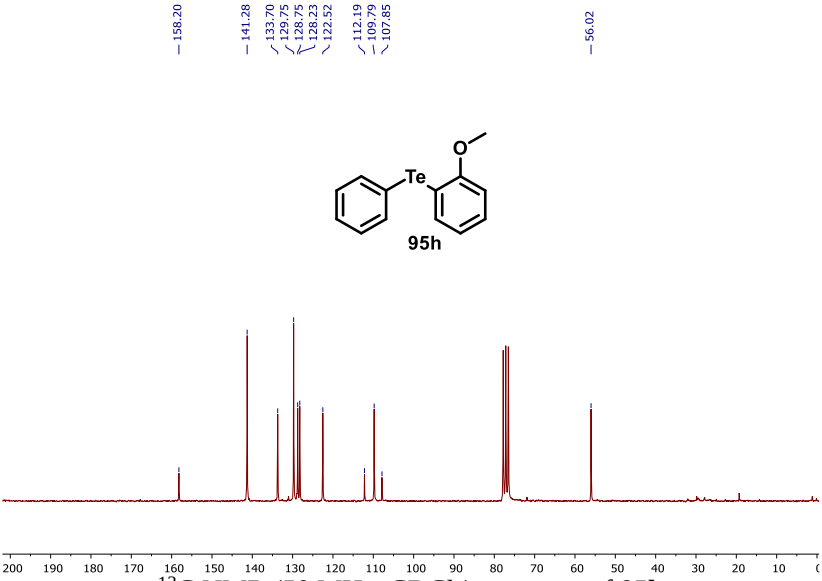
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95g**



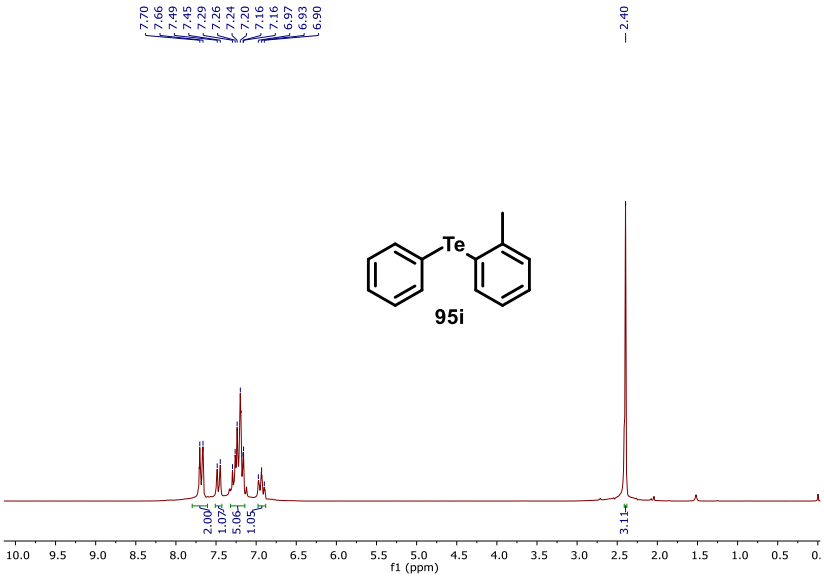
High-resolution mass spectrum of compound **95g**



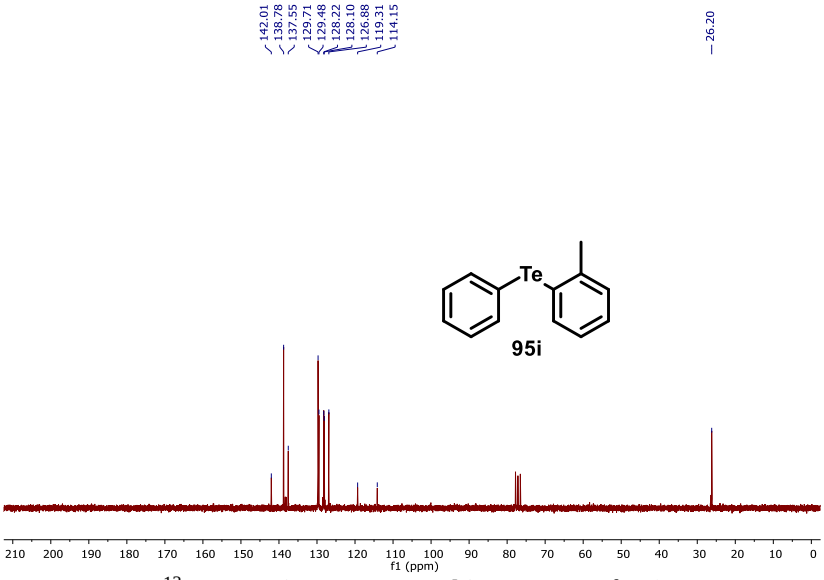
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95h**



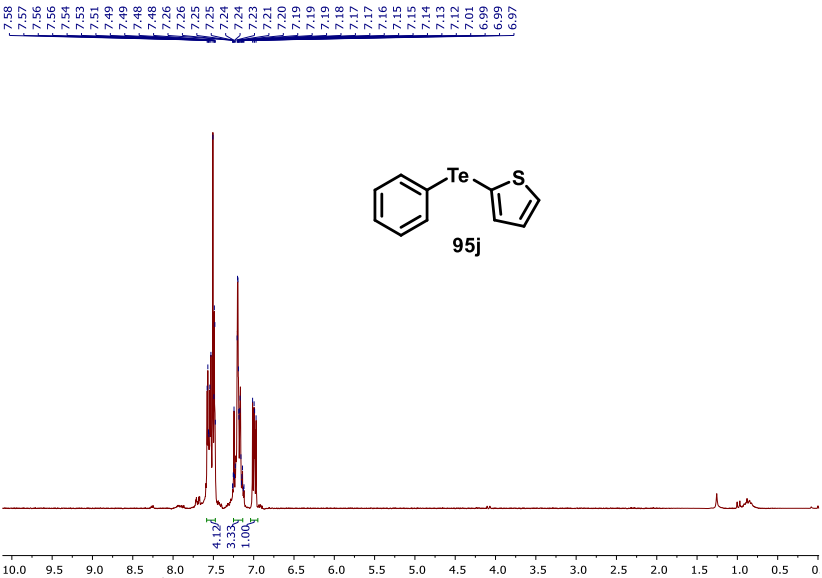
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95h**



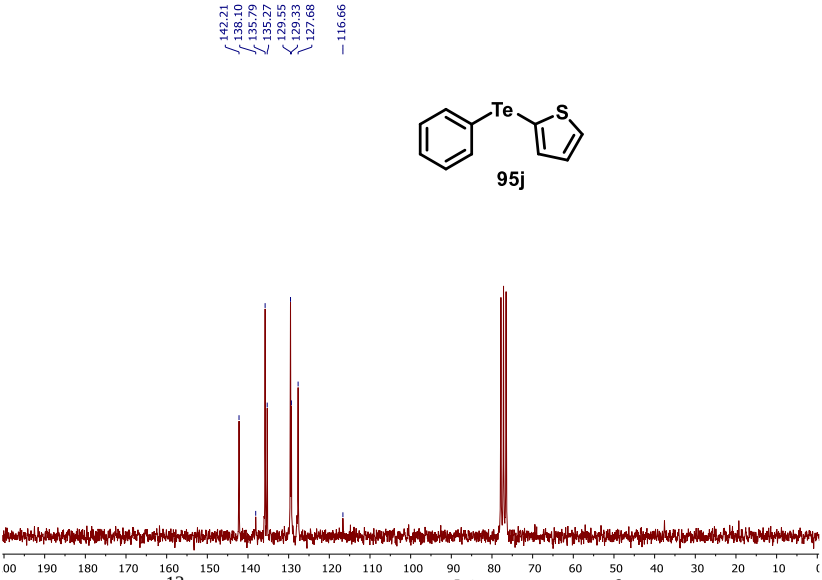
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95i**



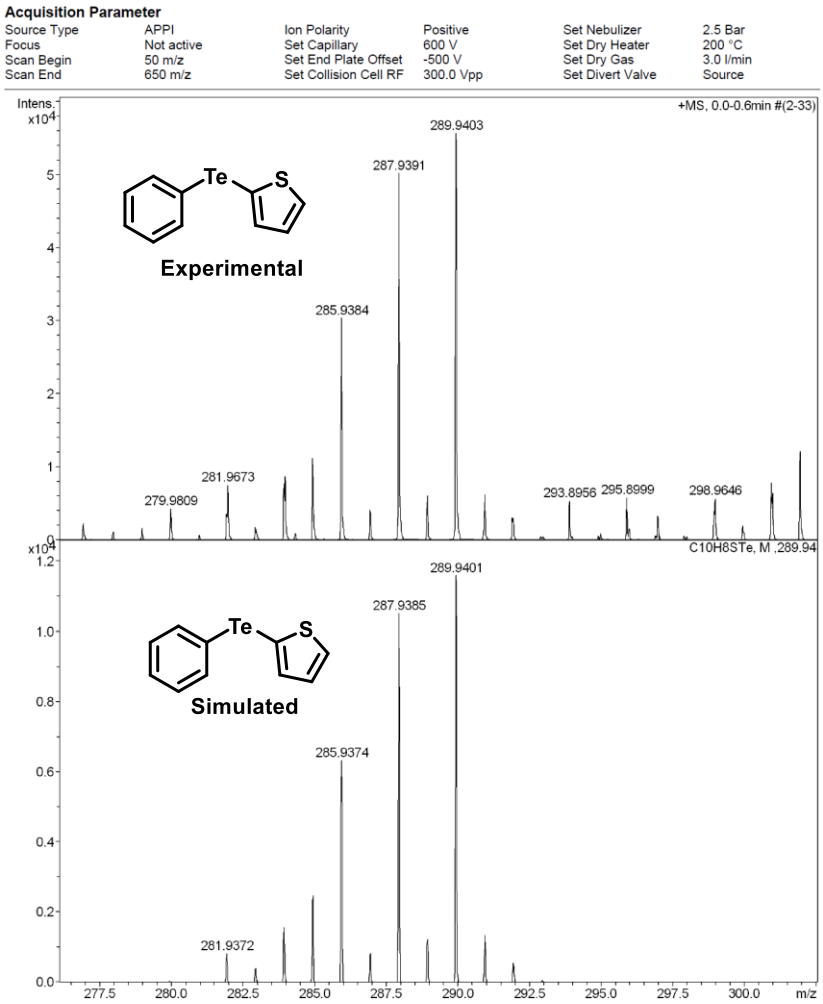
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95i**



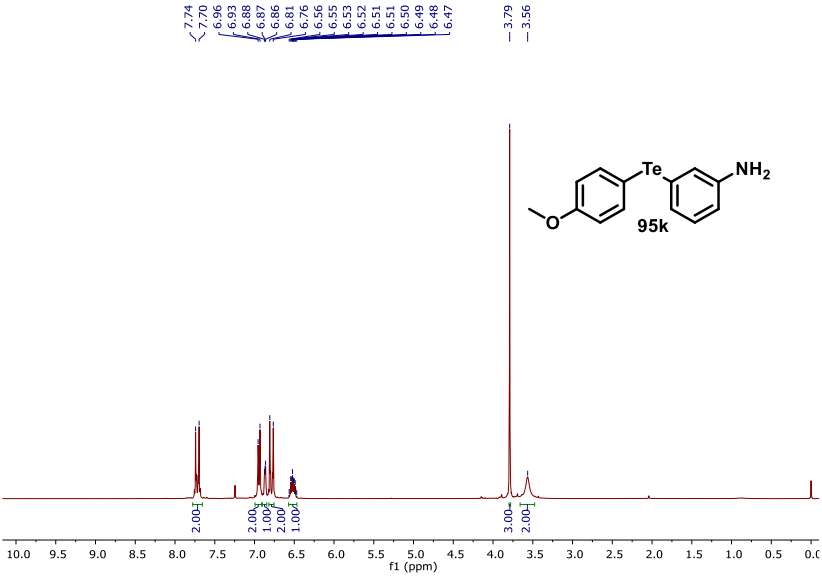
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95j**



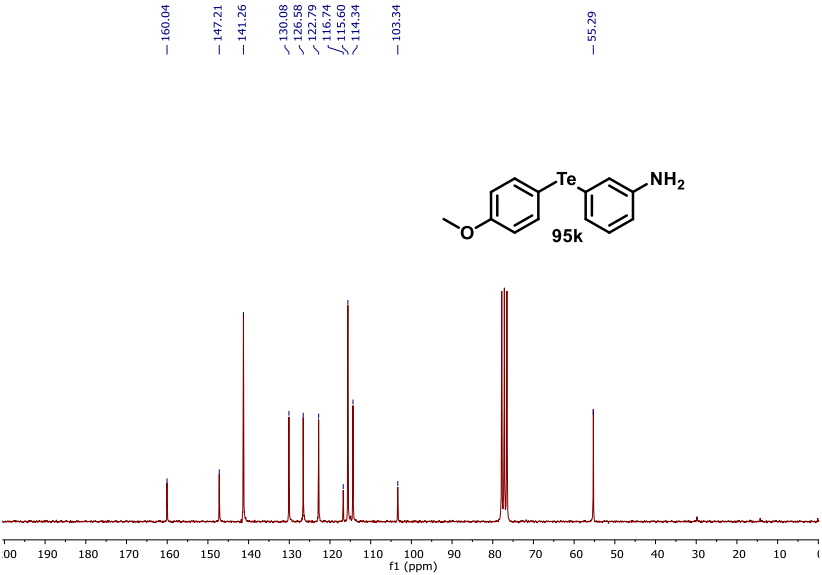
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95**



High-resolution mass spectrum of compound **95j**



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95k**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95k**

Acquisition Parameter

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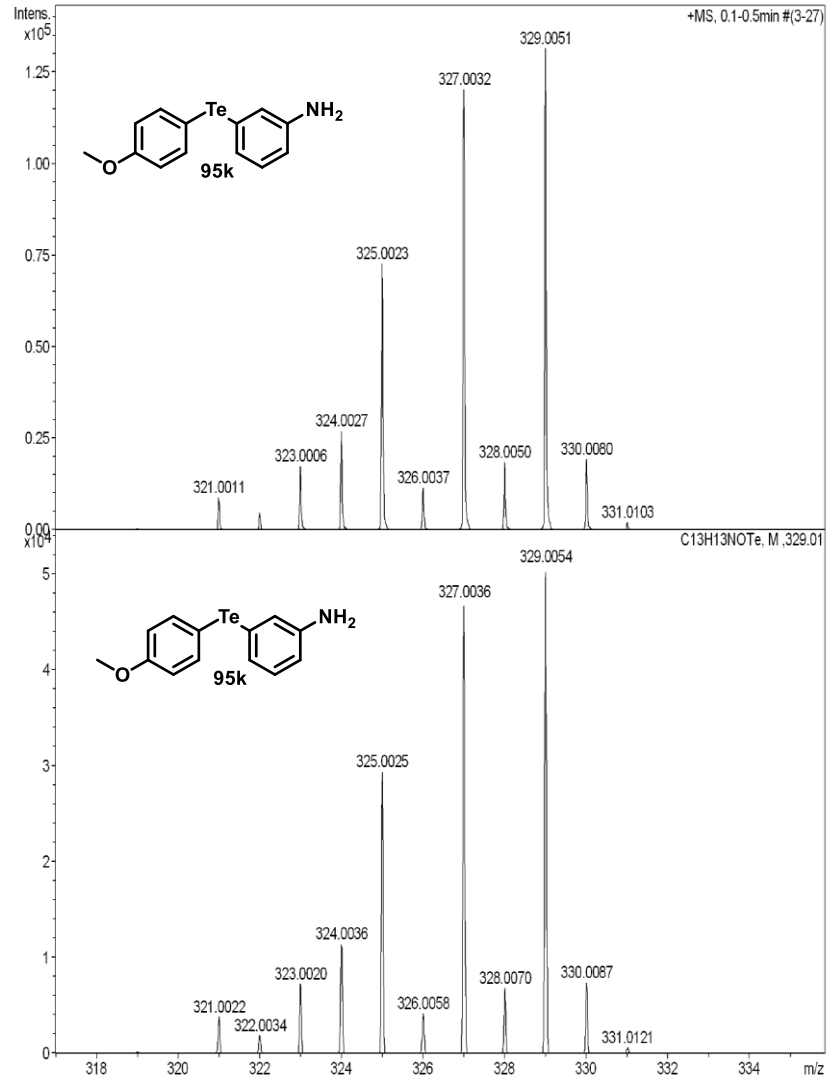
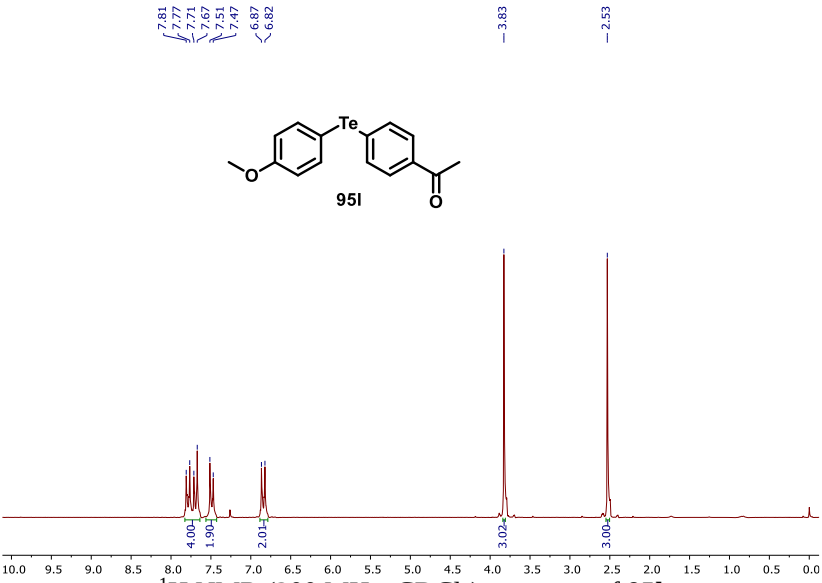
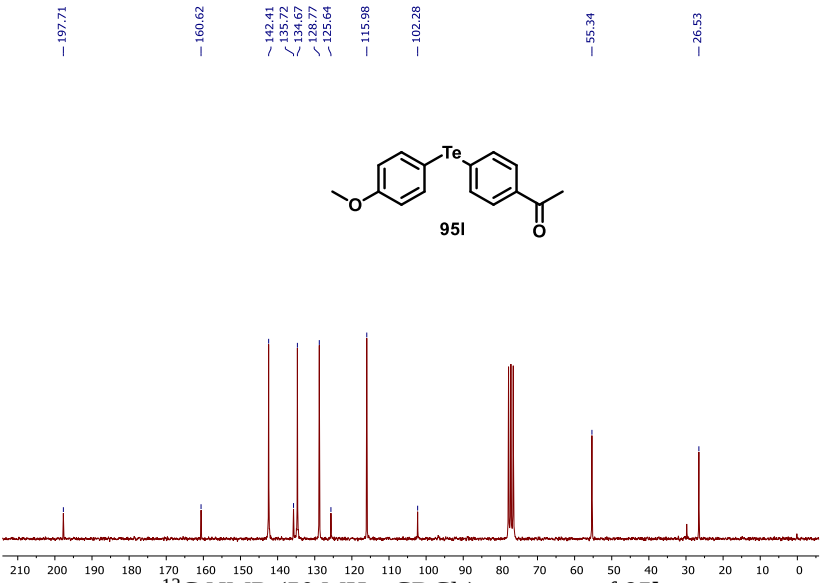
Focus	Not active	Set Capillary	1000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	650 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source



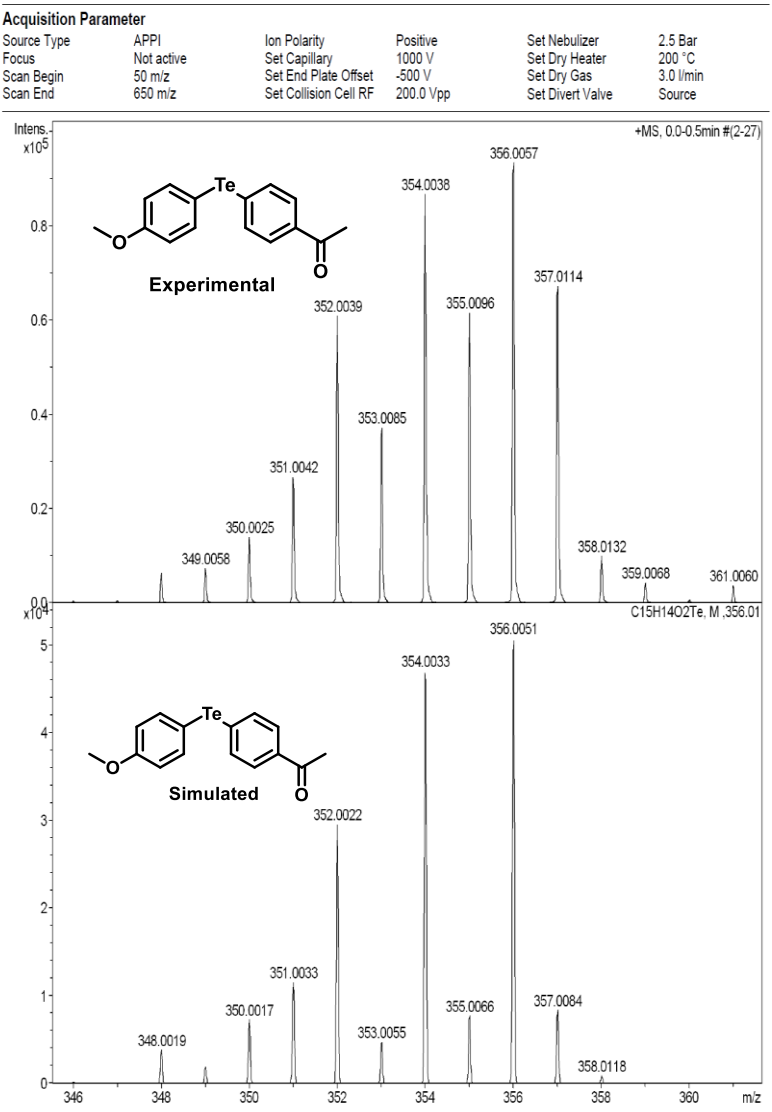
High-resolution mass spectrum of compound **95k**



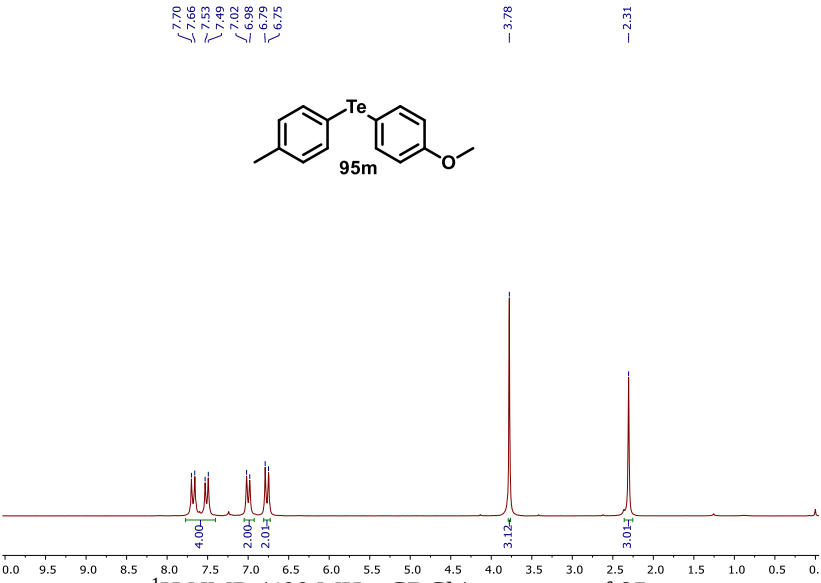
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95l**



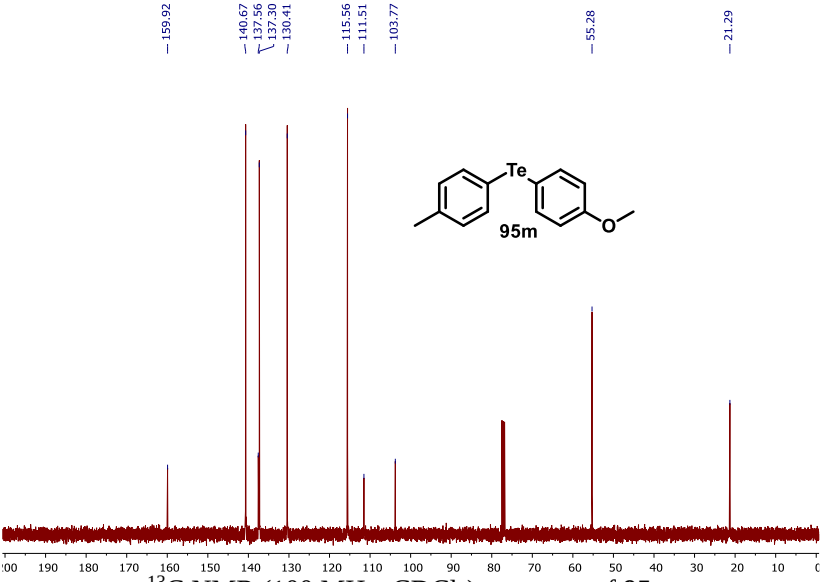
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95l**



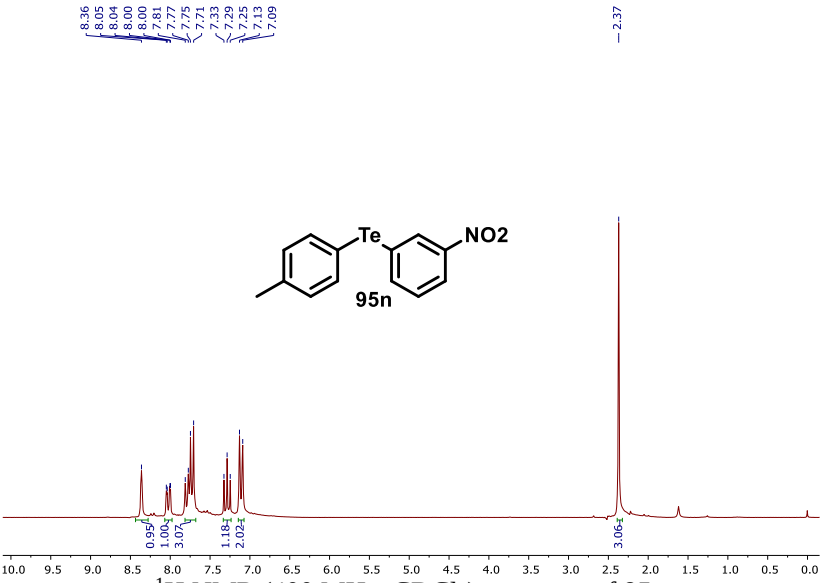
High-resolution mass spectrum of compound **95l**



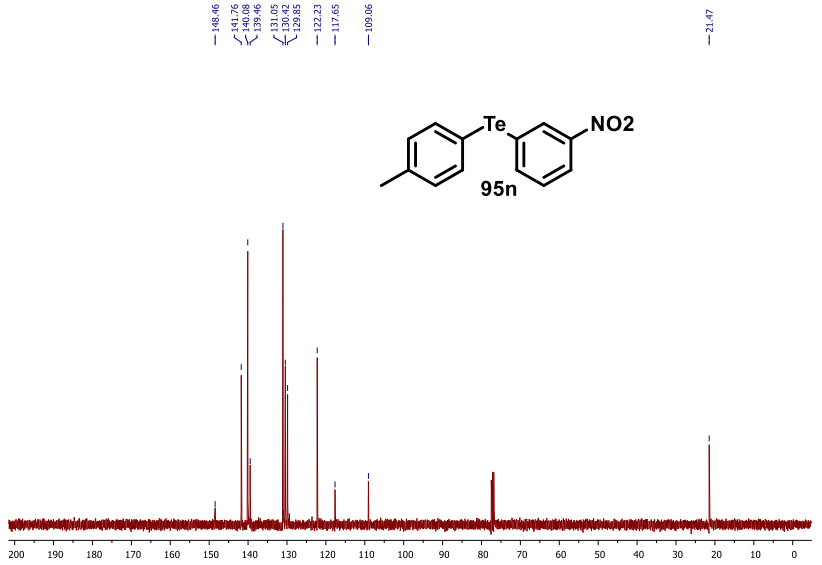
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **95m**



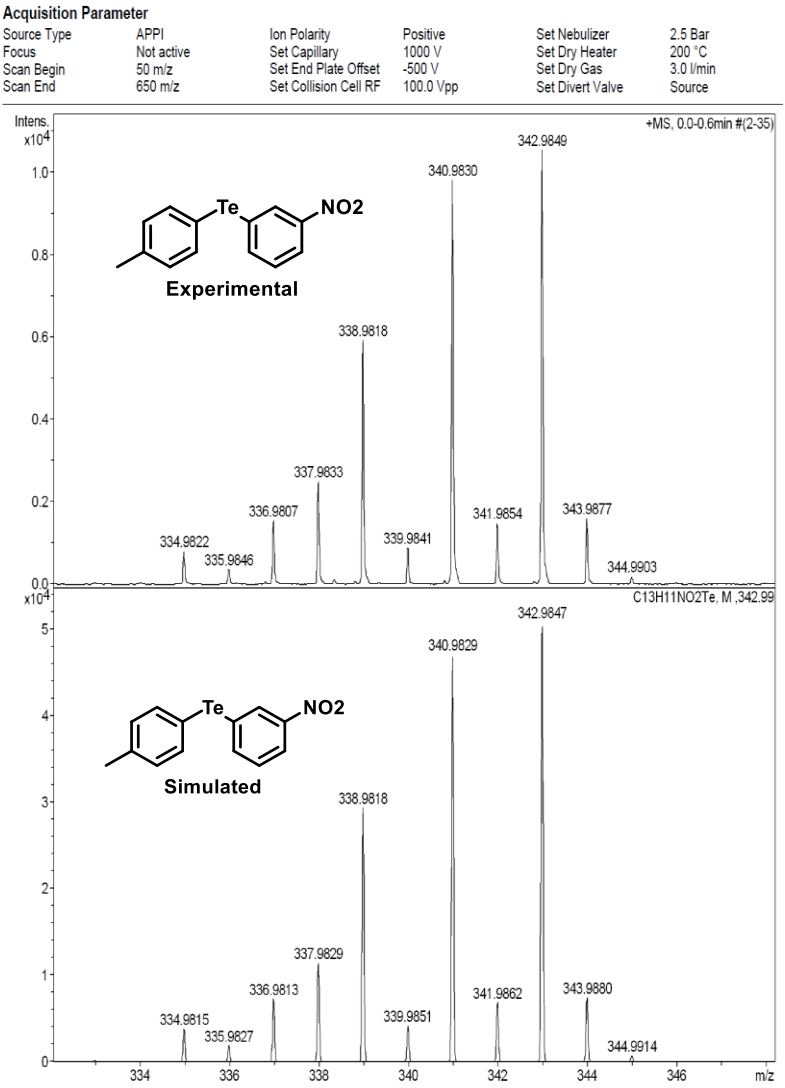
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **95m**



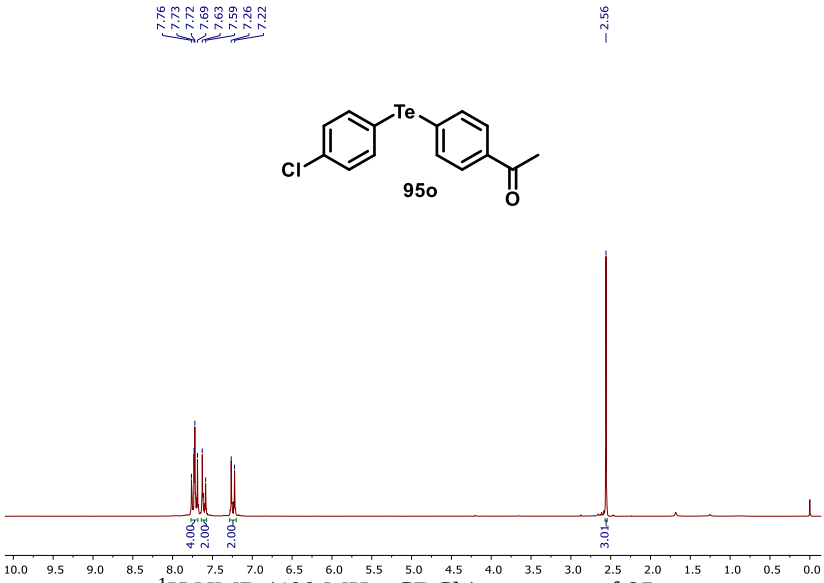
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **95n**



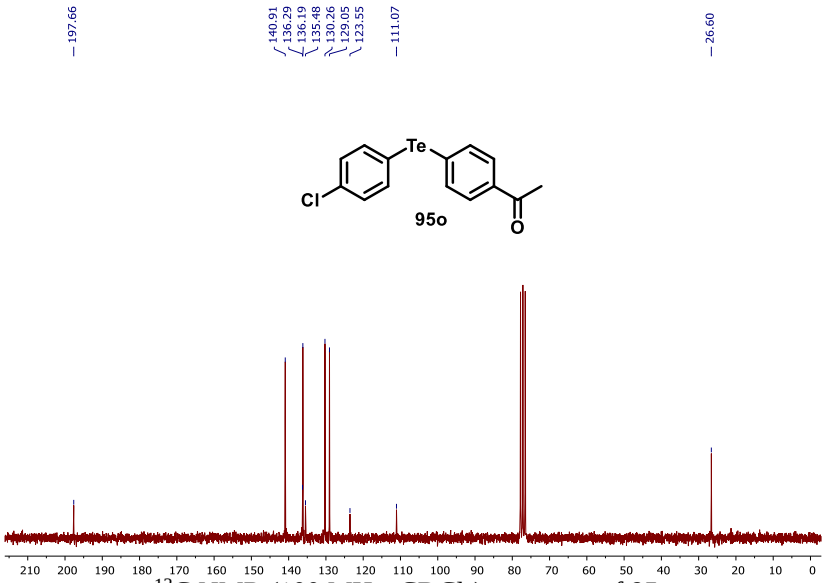
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **95n**



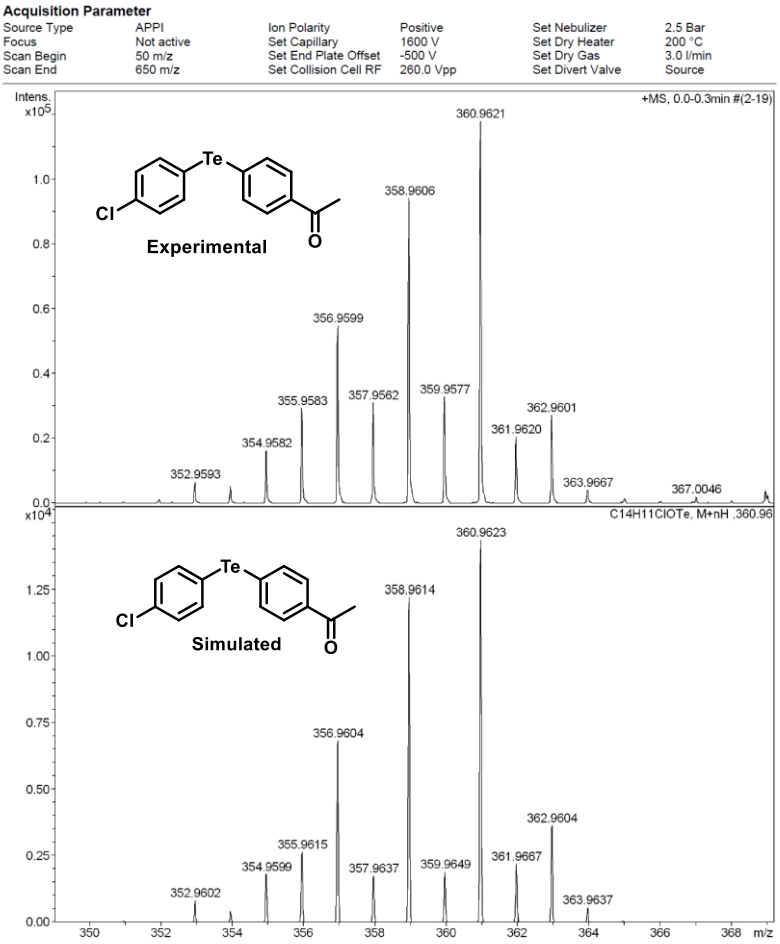
High-resolution mass spectrum of compound **95n**



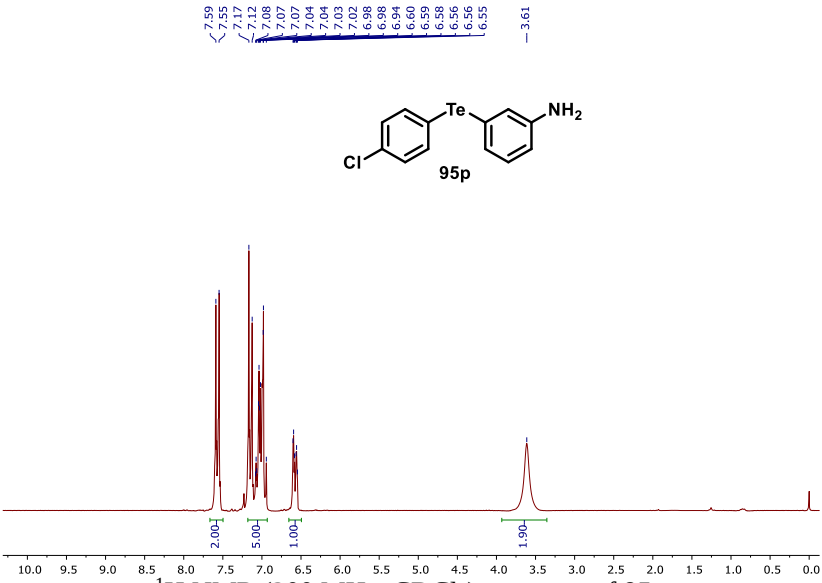
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **95o**



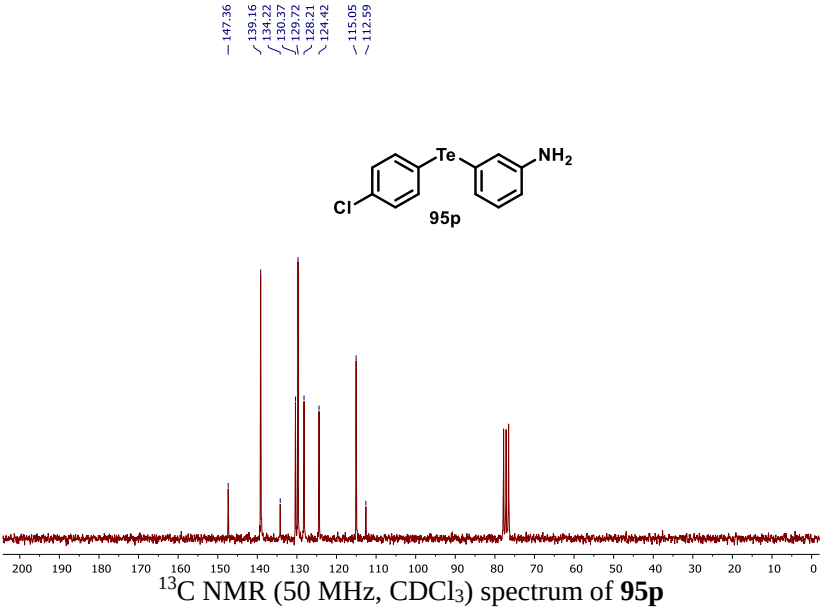
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **95o**



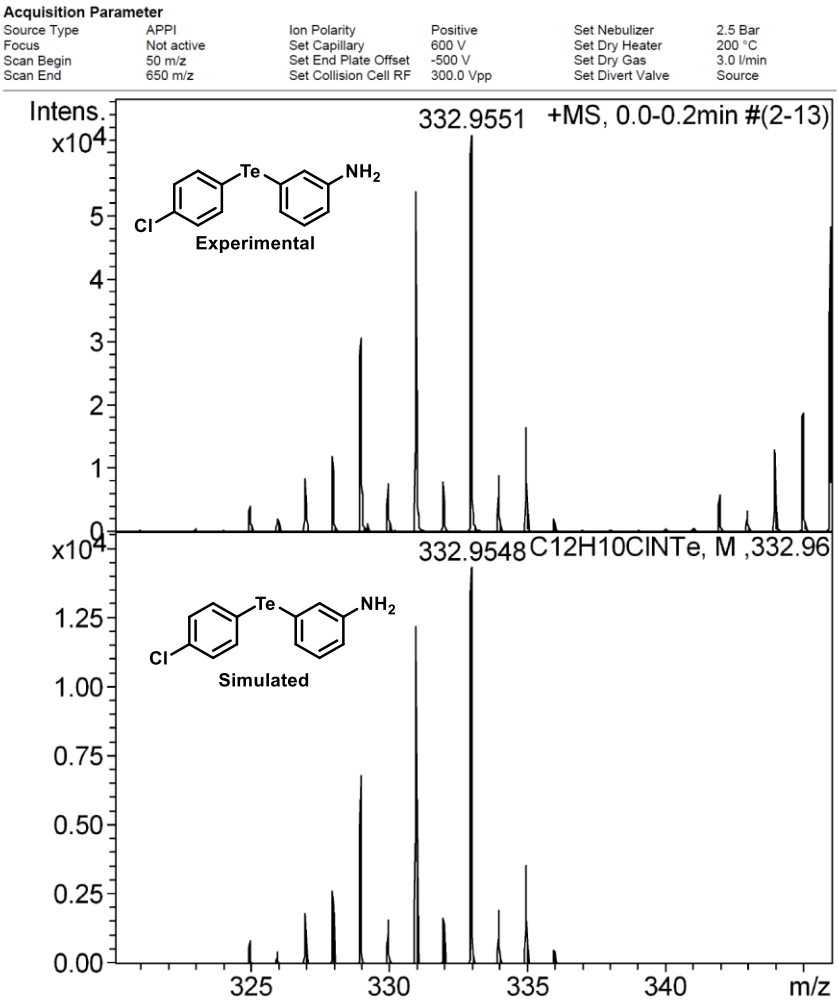
High-resolution mass spectrum of compound **95o**



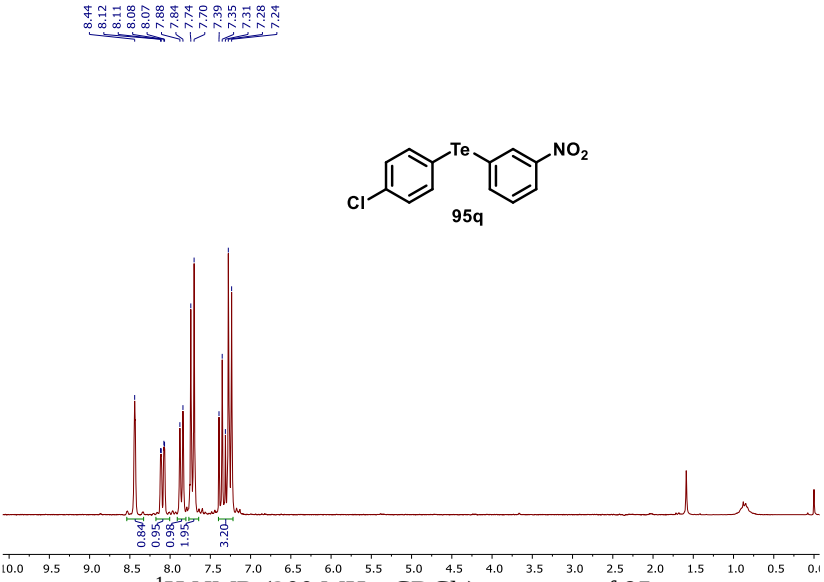
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95p**



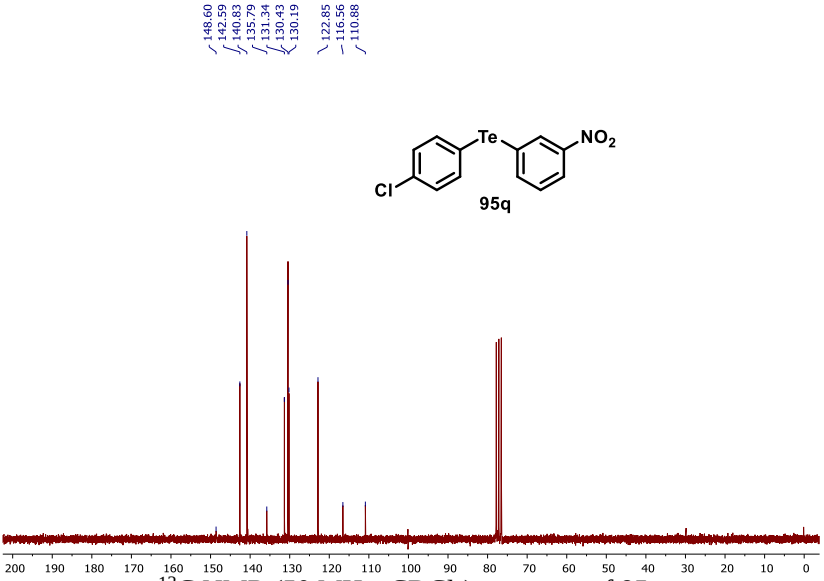
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95p**



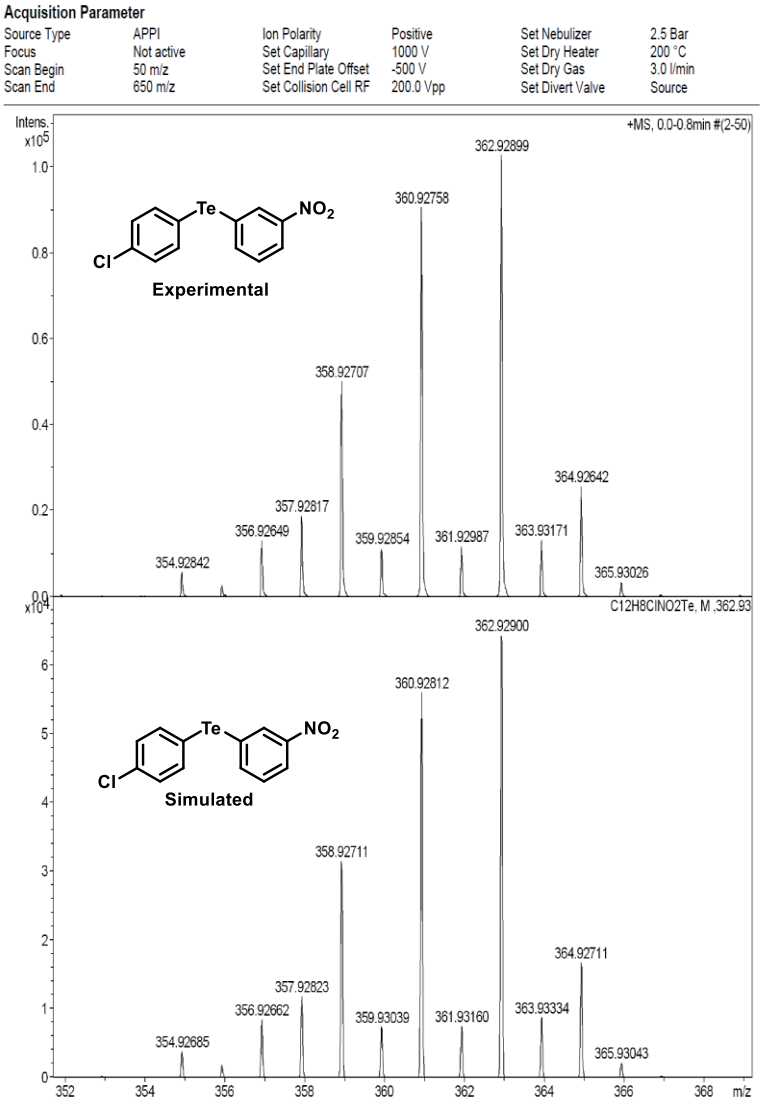
High-resolution mass spectrum of compound **95p**



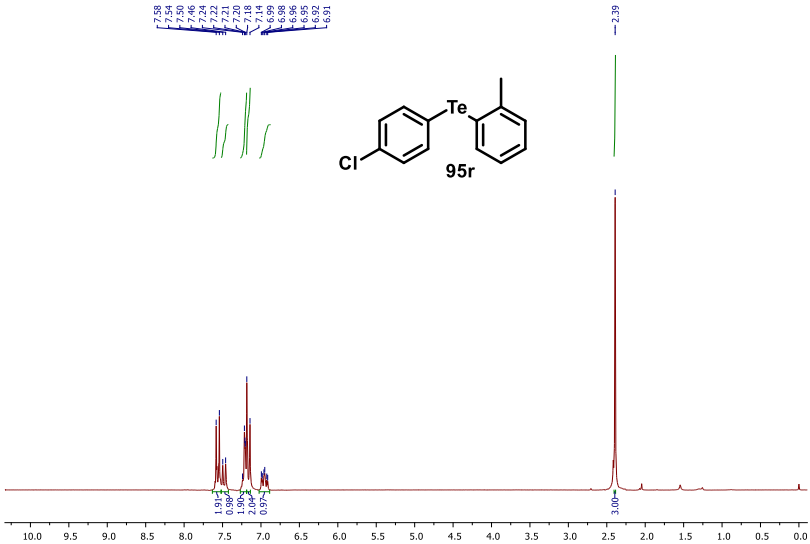
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95q**



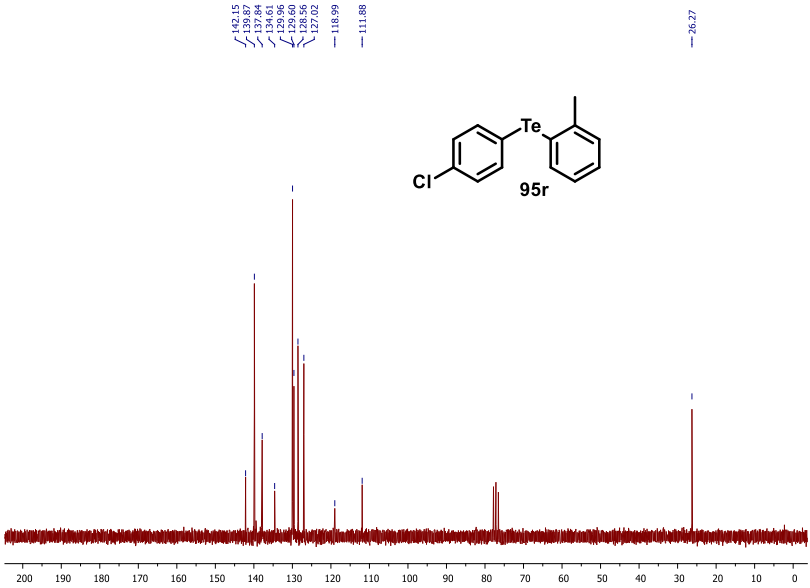
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95q**



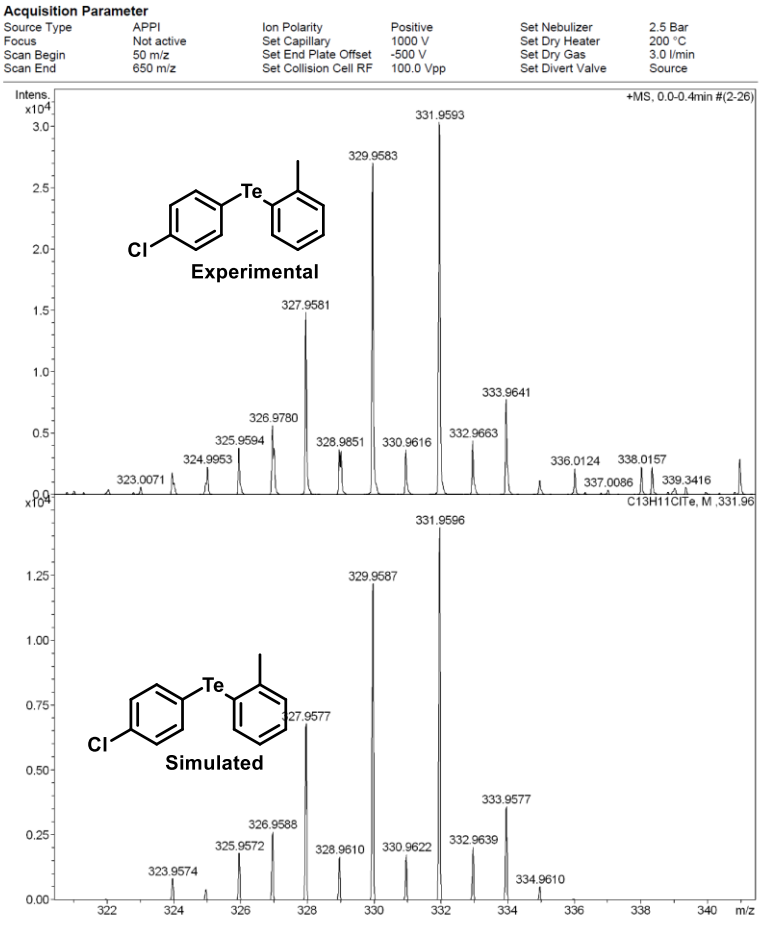
High-resolution mass spectrum of compound **95q**



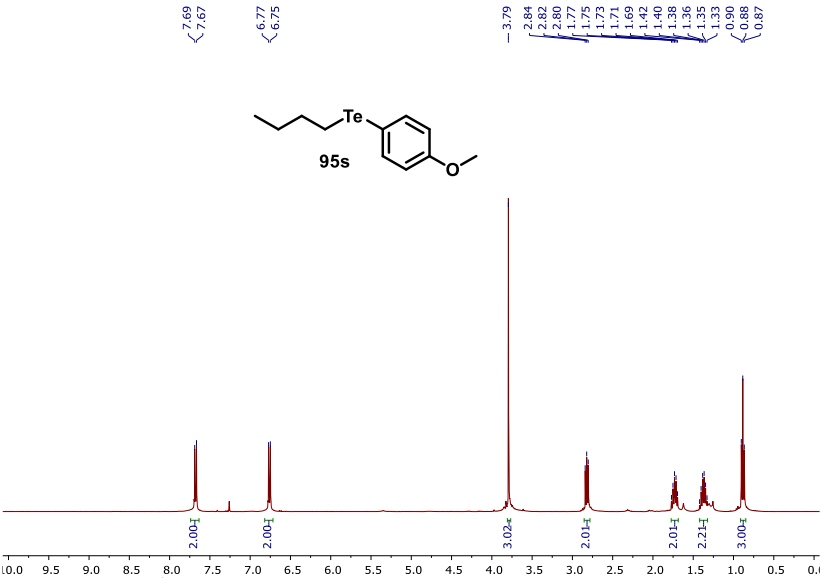
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95r**



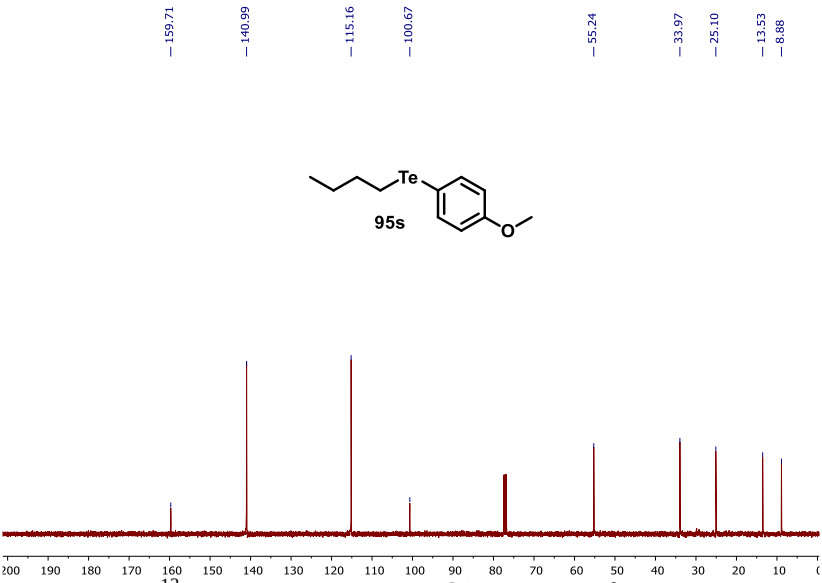
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95r**



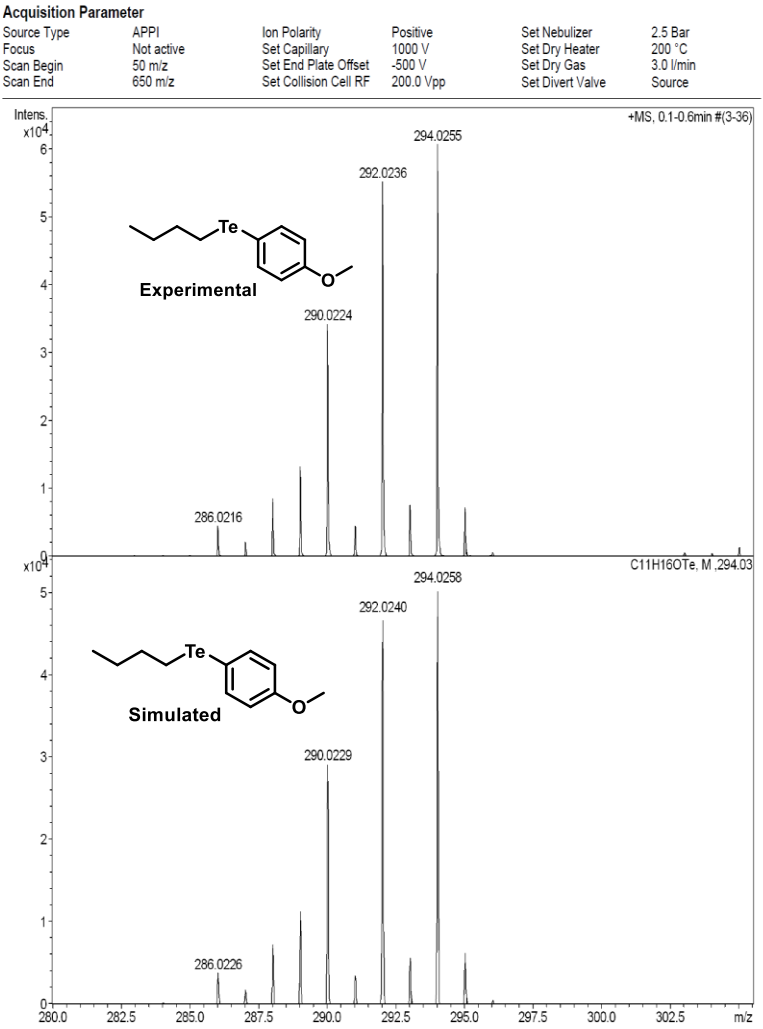
High-resolution mass spectrum of compound **95r**



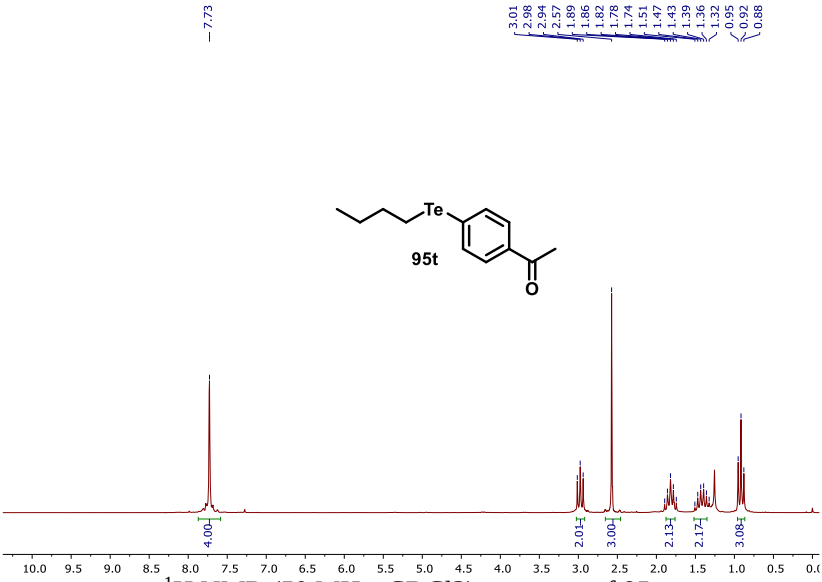
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **95s**



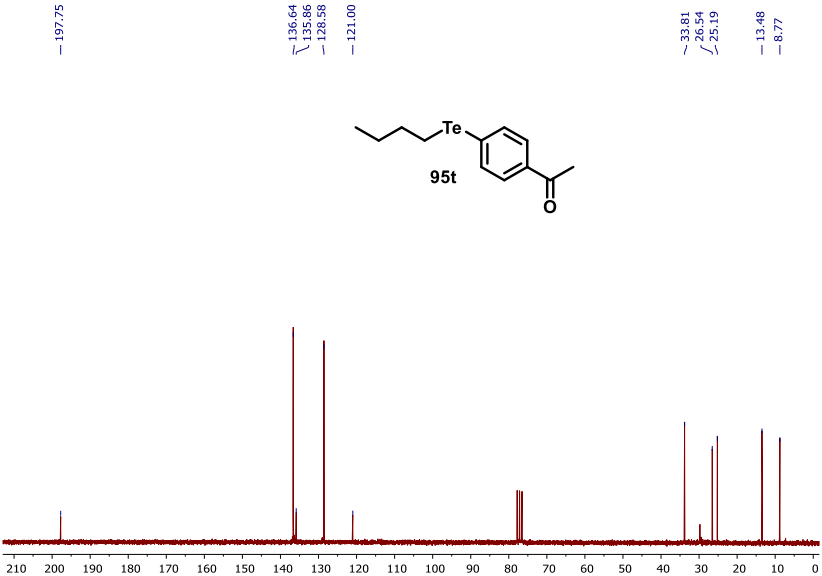
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95s**



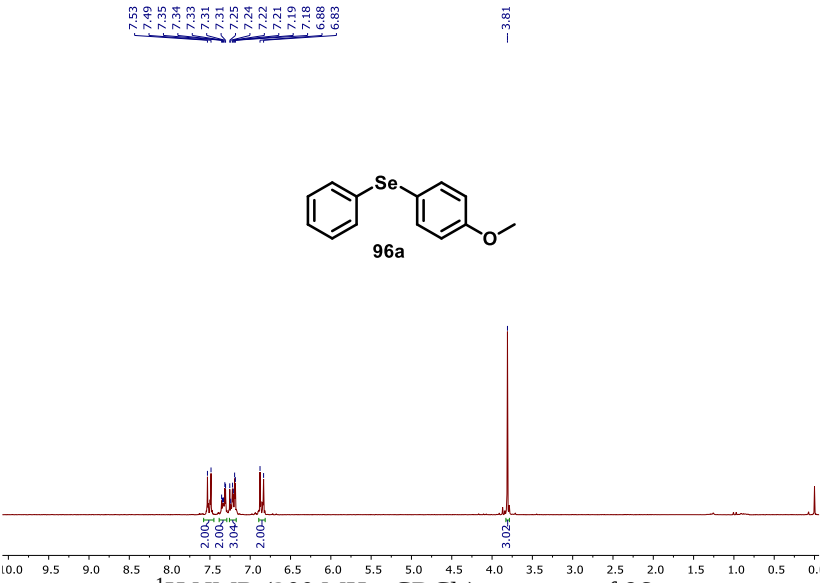
High-resolution mass spectrum of compound **95s**



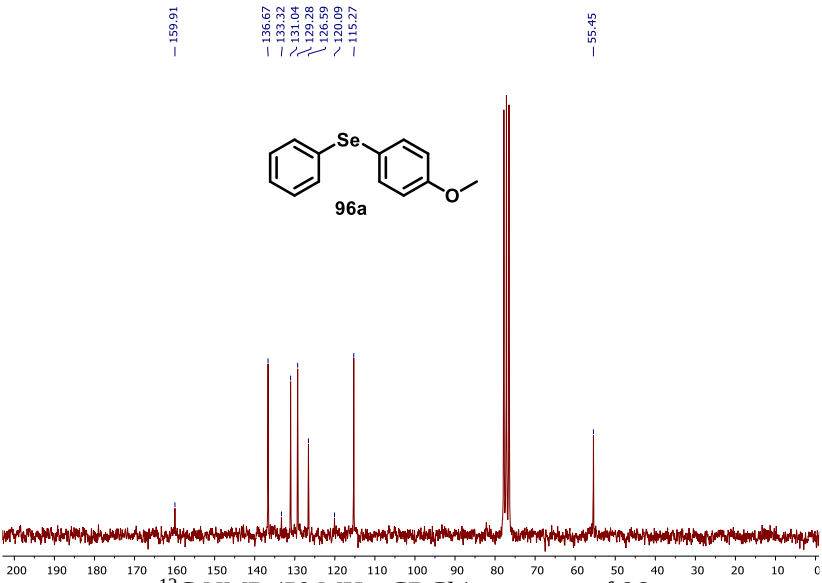
^{1}H NMR (50 MHz, CDCl3) spectrum of 95t



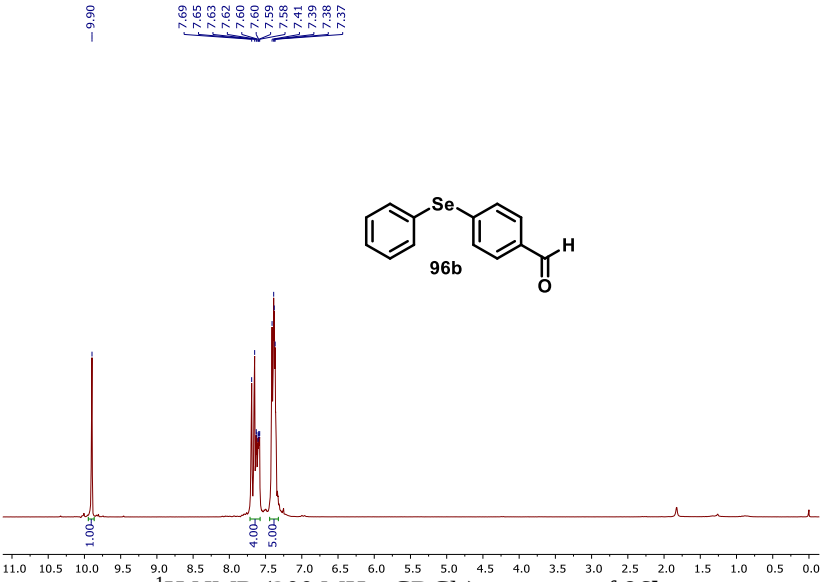
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **95t**



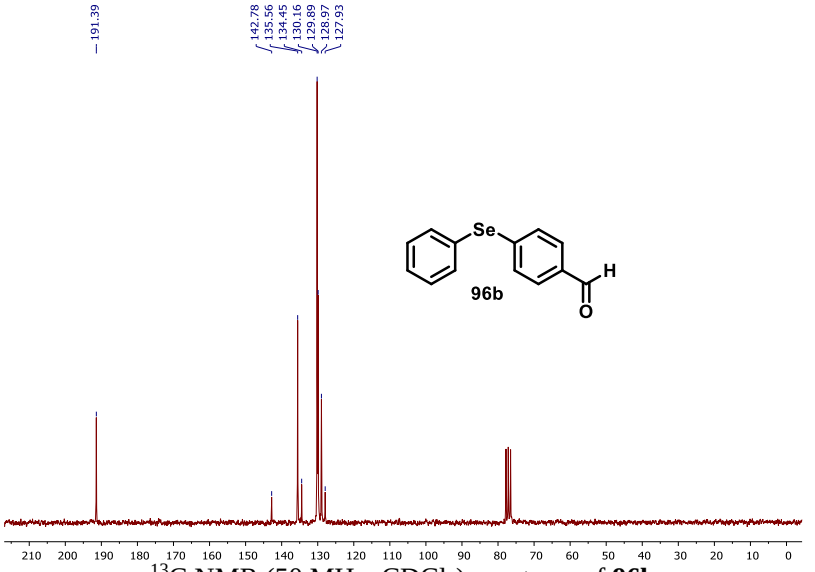
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96a**



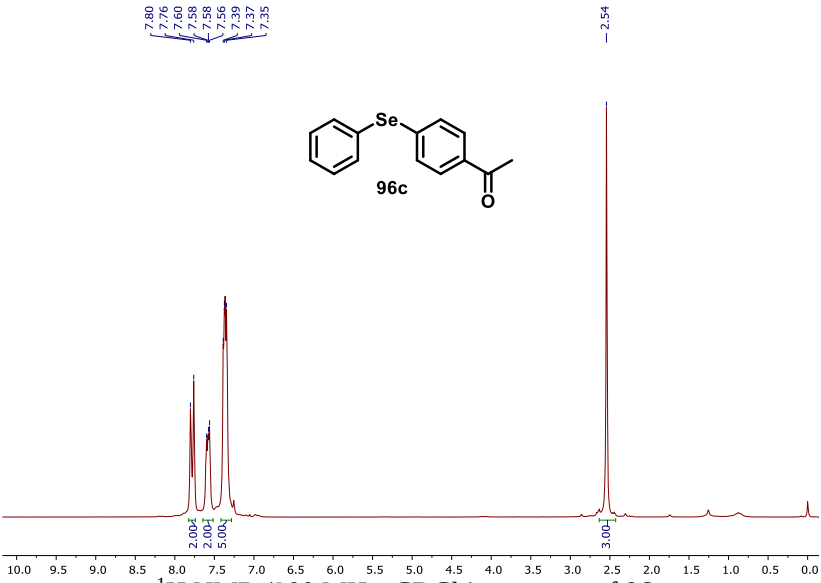
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96a**



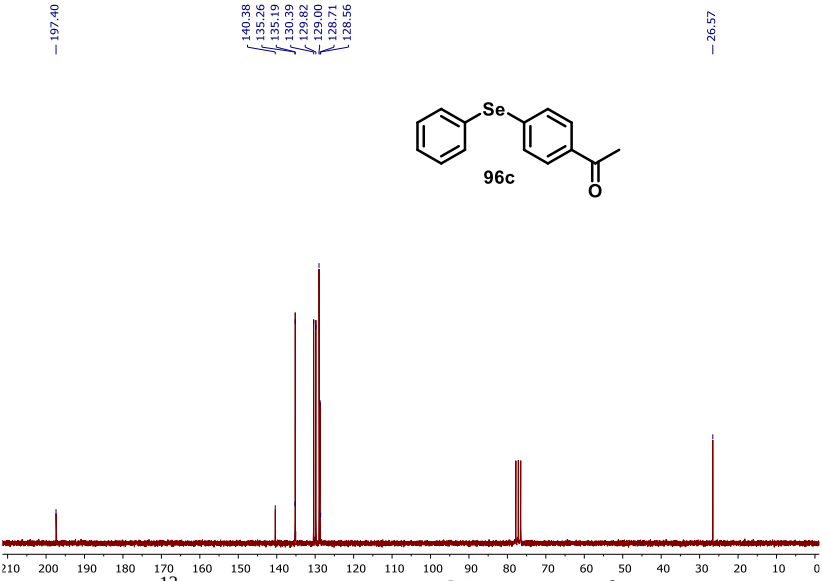
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96b**



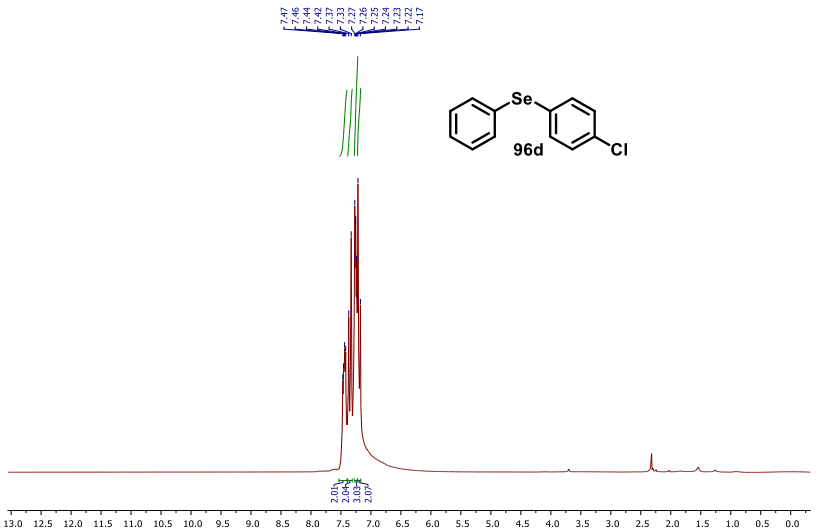
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96b**



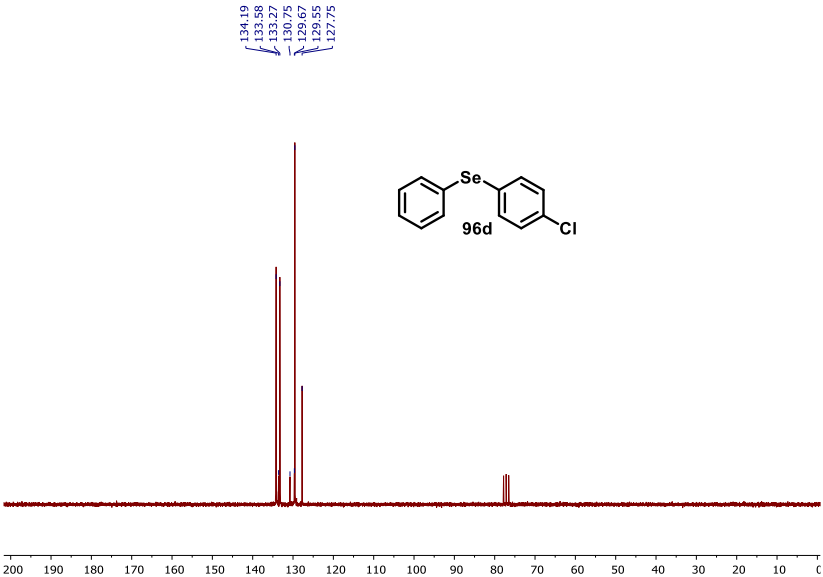
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96c**



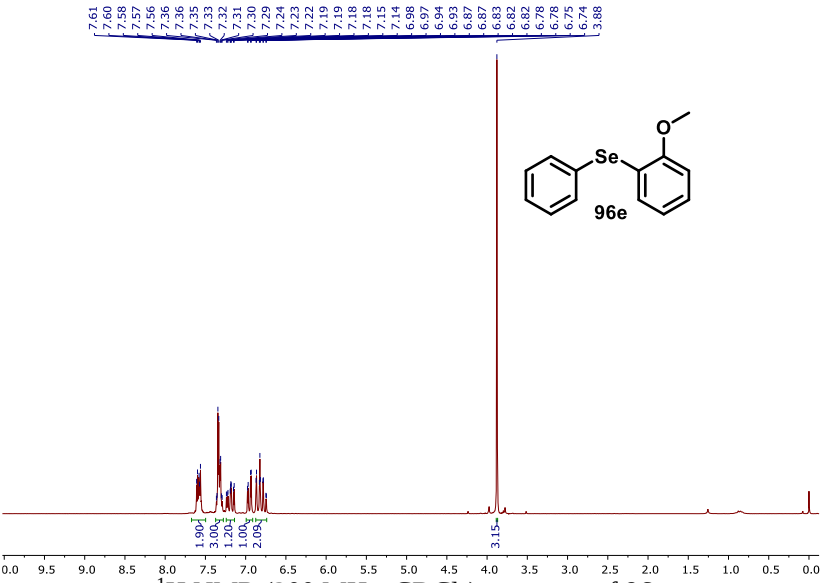
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96c**



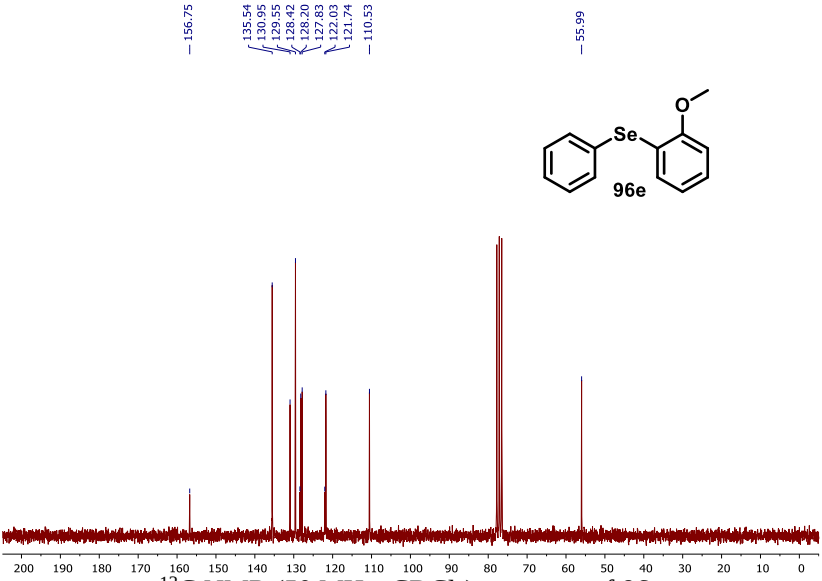
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96d**



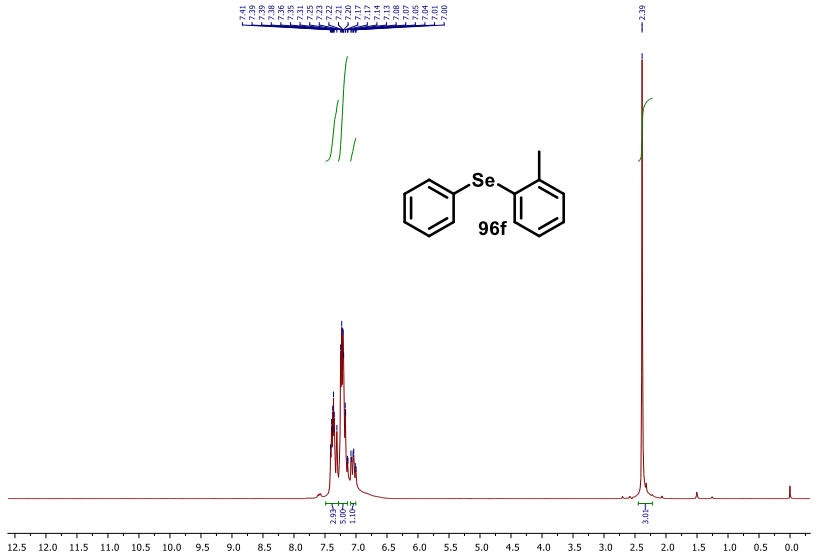
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96d**



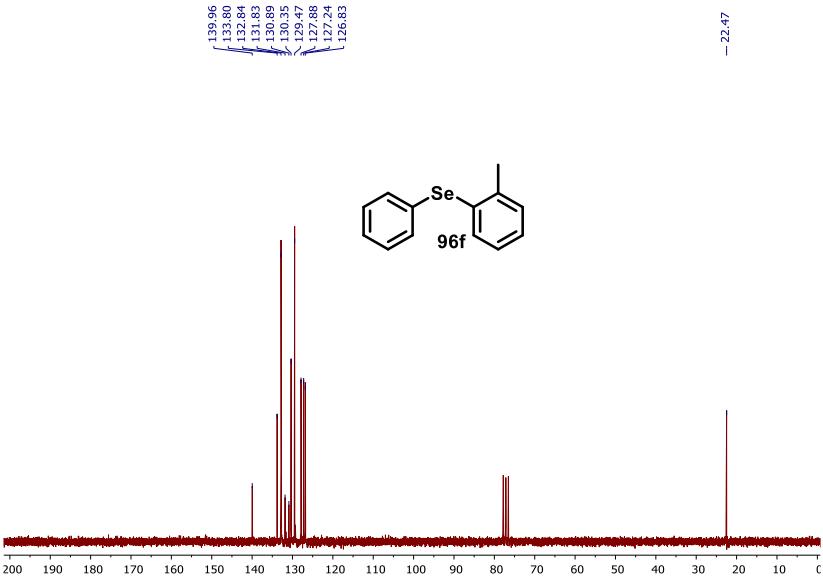
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96e**



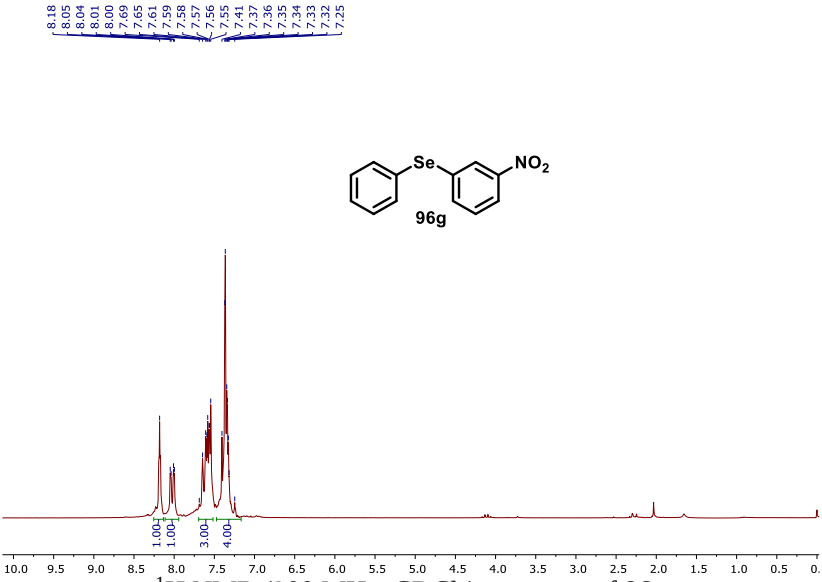
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96e**



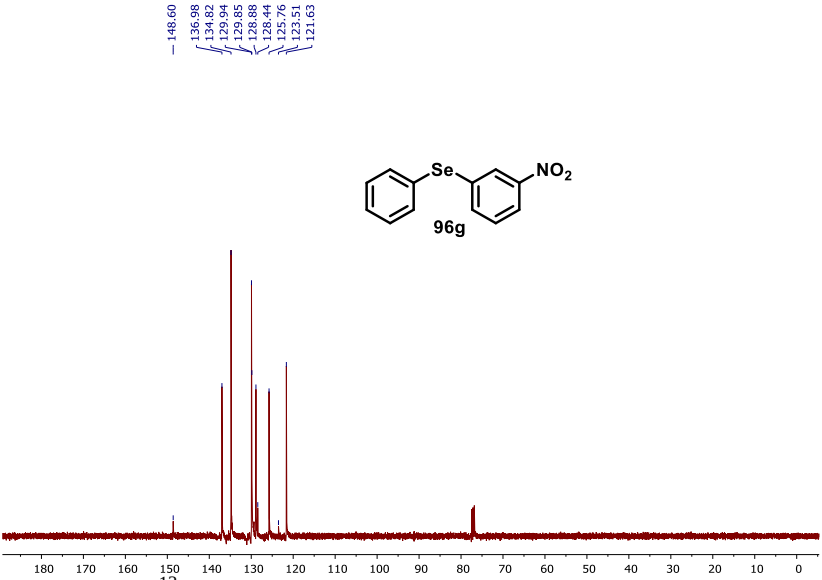
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96f**



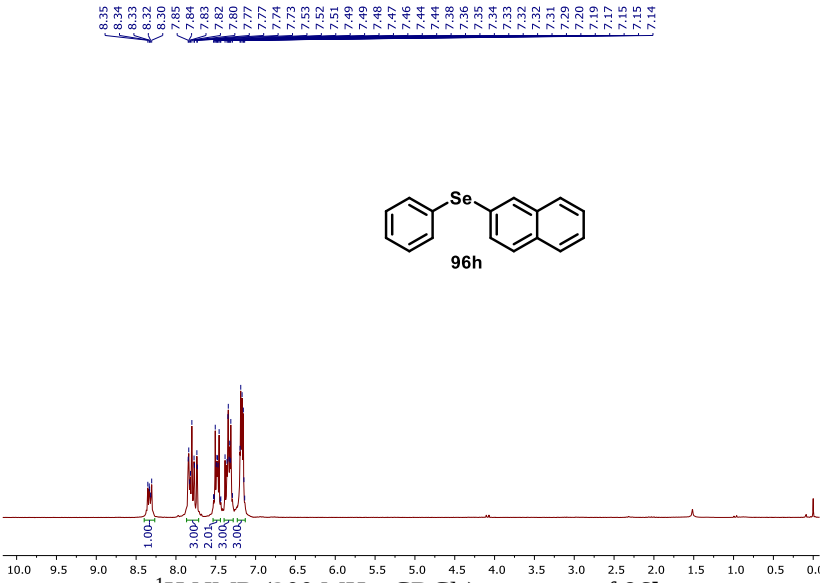
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96f**



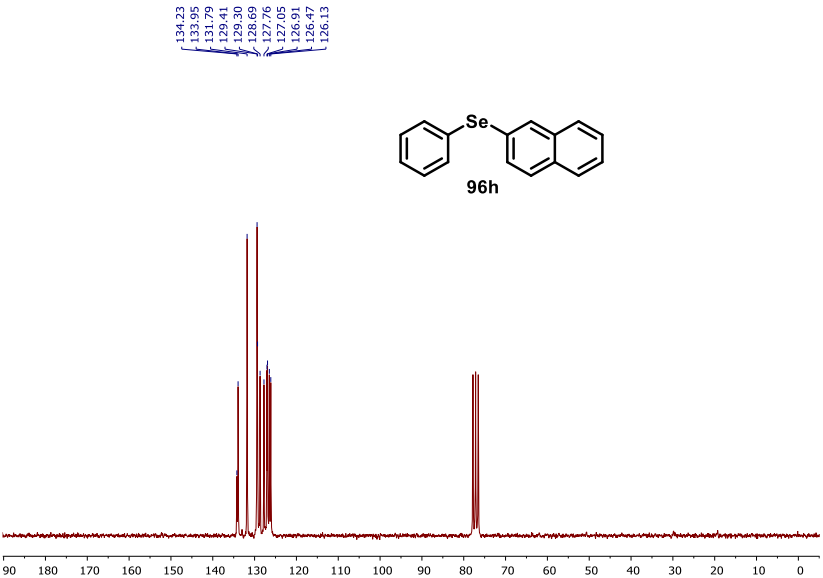
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96g**



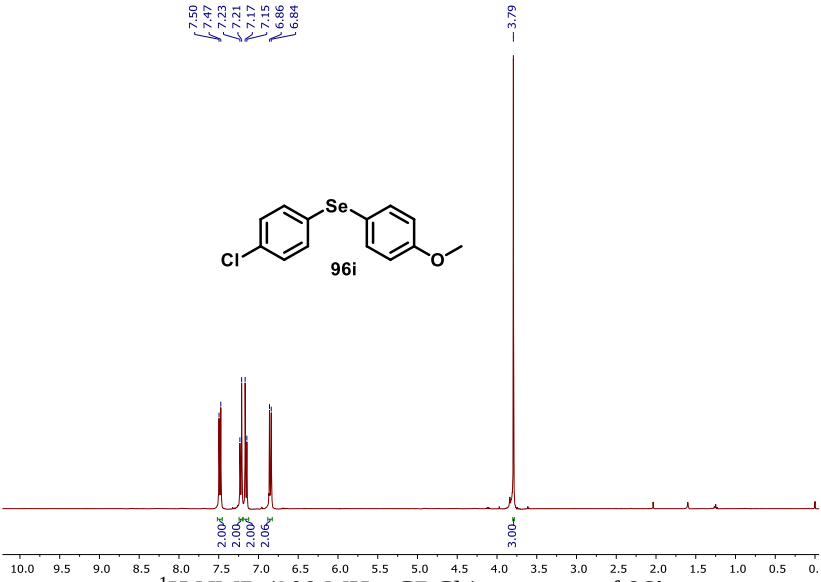
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96g**



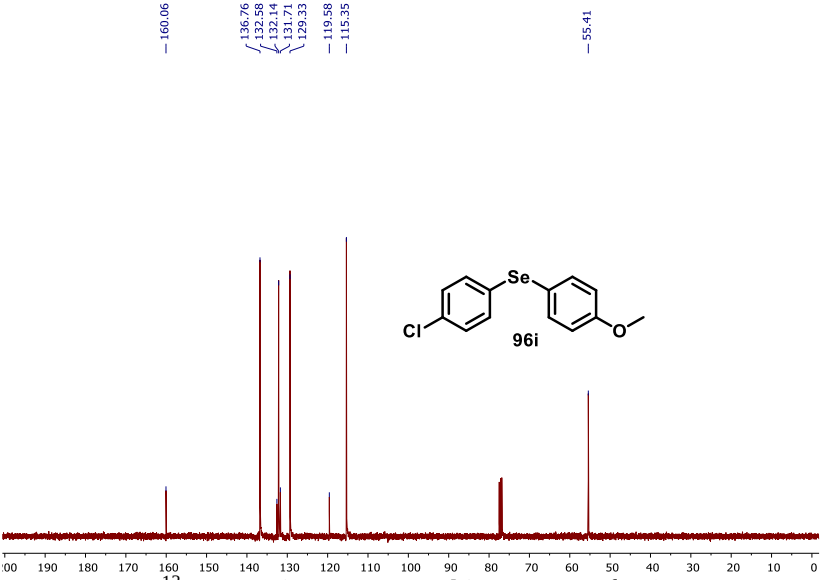
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96h**



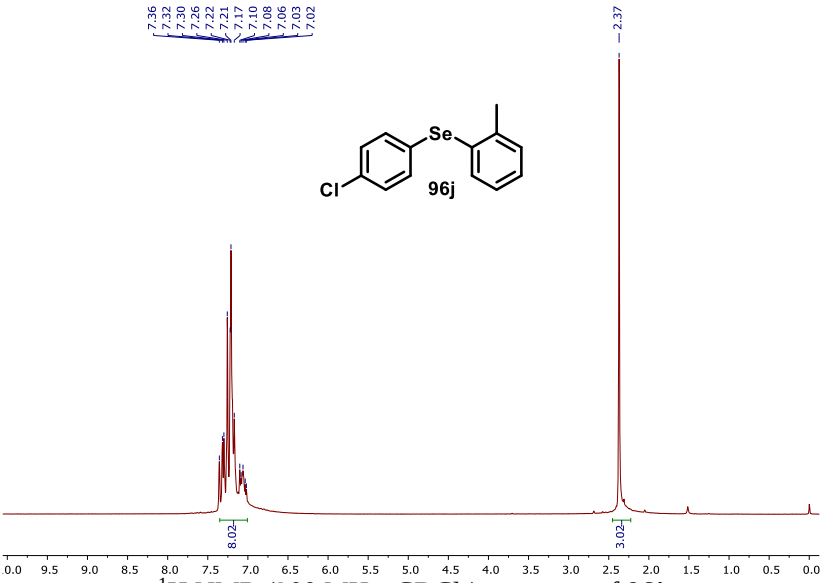
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96h**



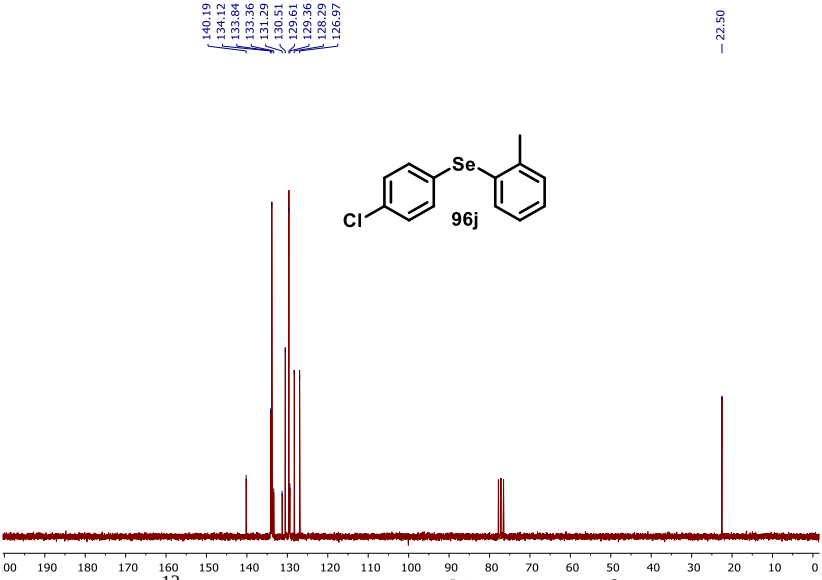
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96i**



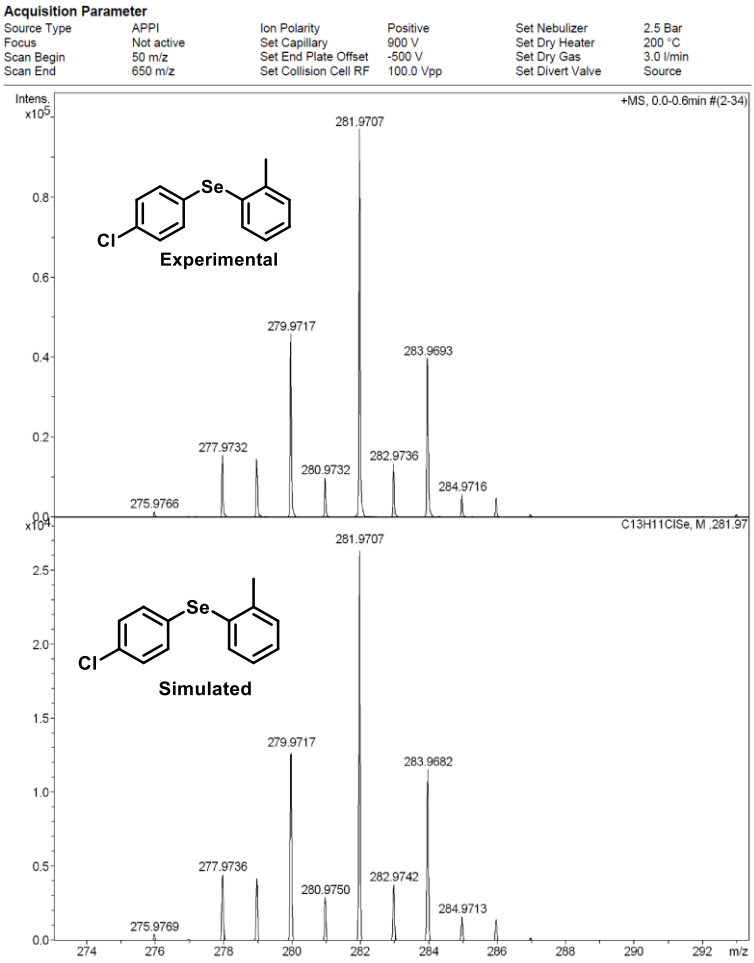
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96i**



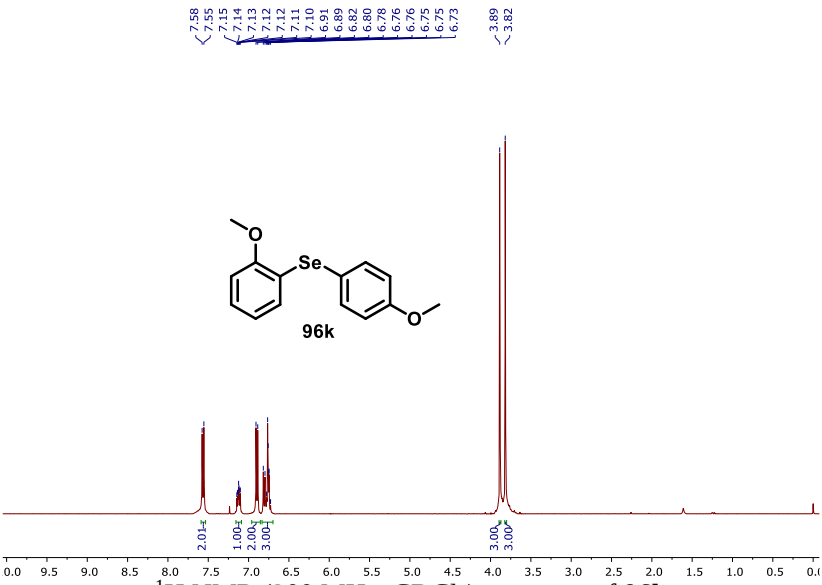
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96j**



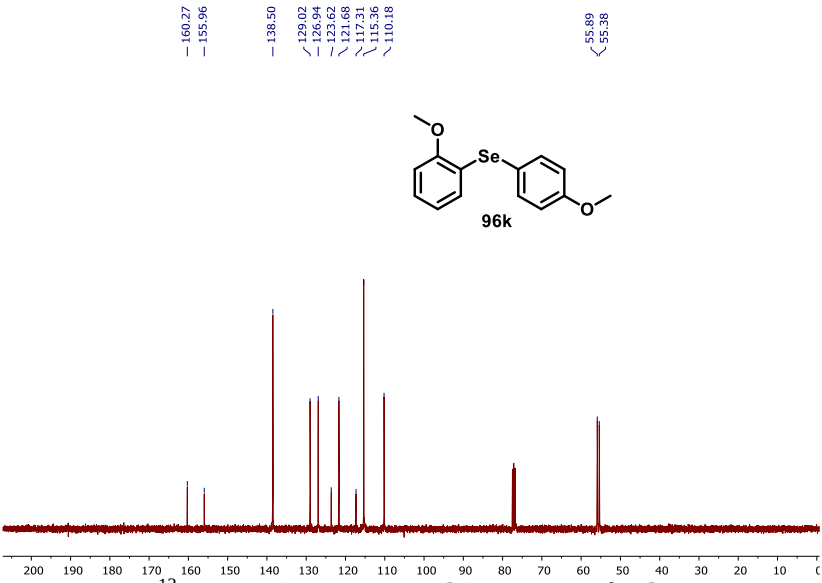
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96j**



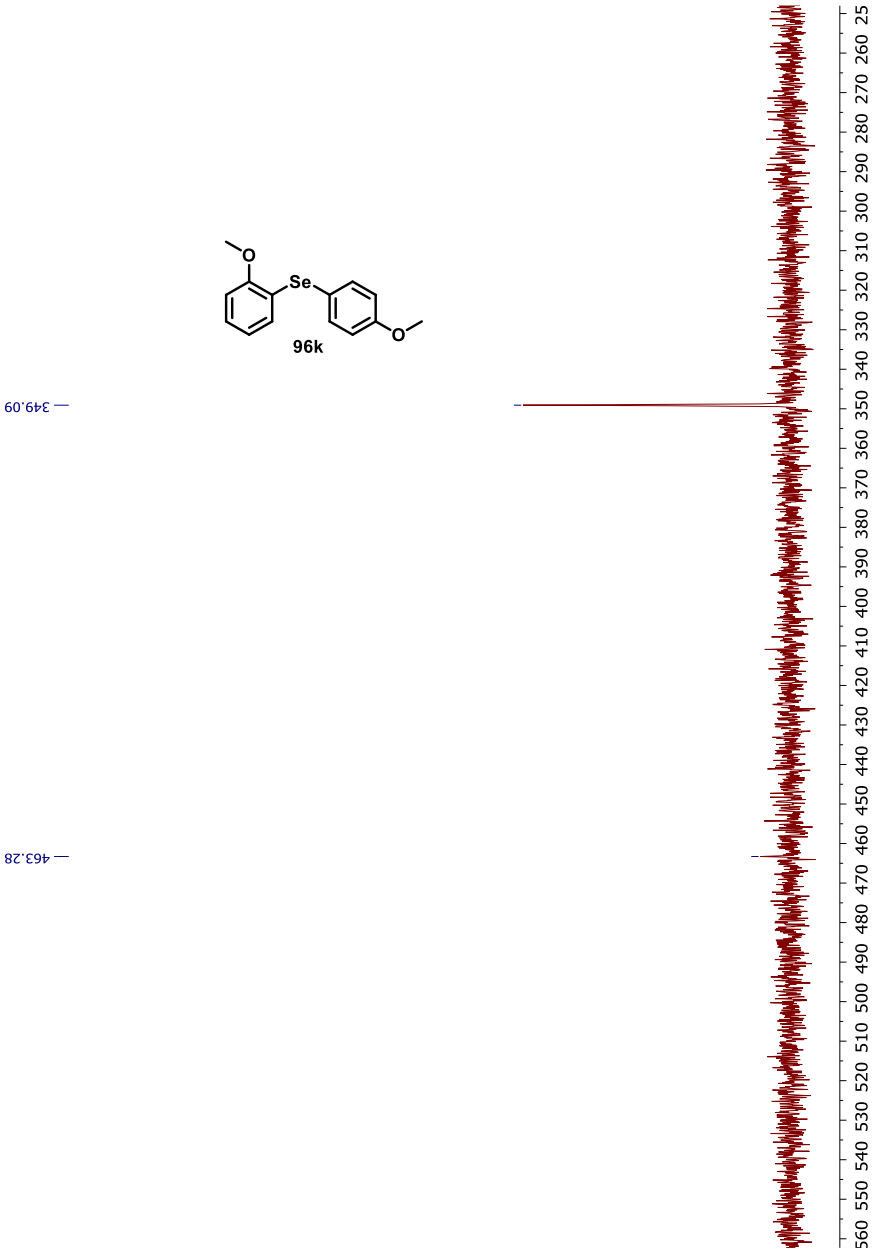
High-resolution mass spectrum of compound **96j**



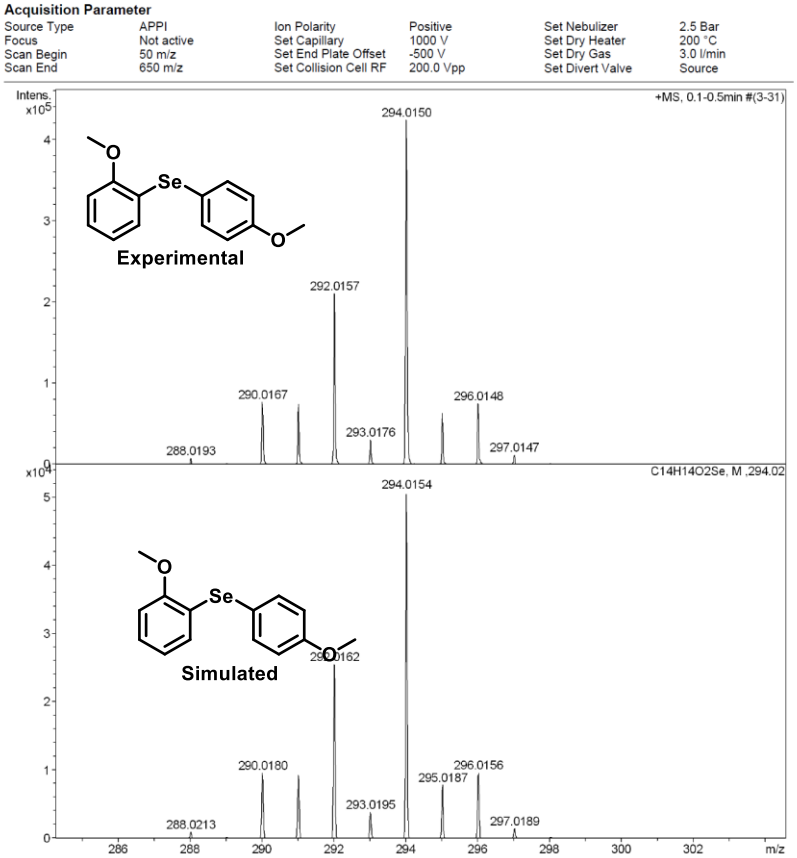
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96k**



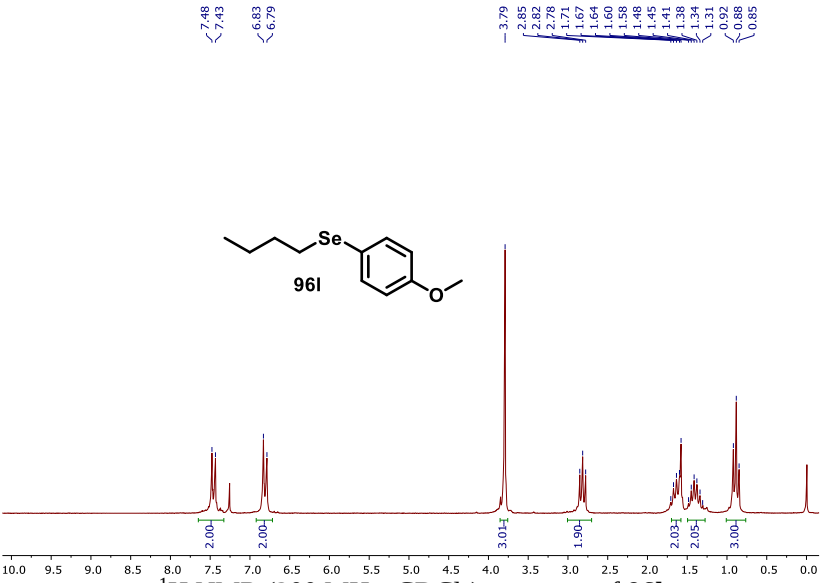
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96k**



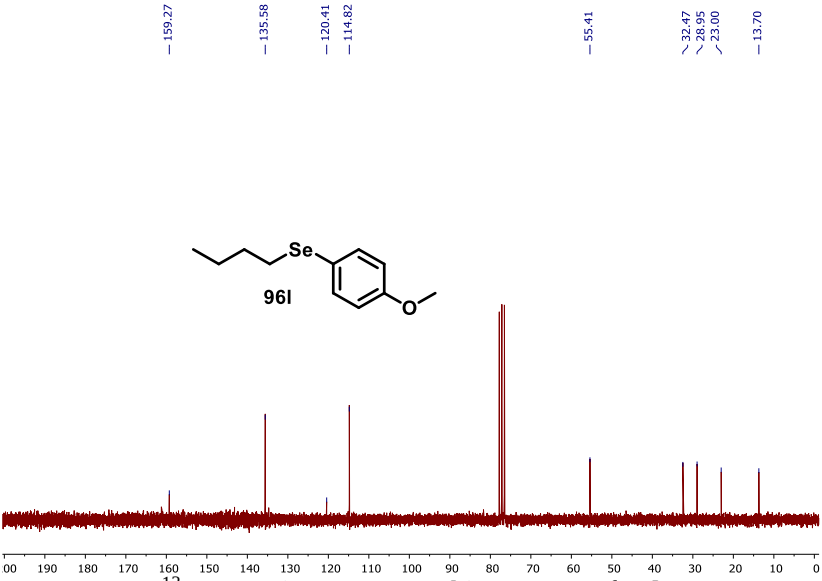
^{77}Se NMR (38.14 MHz, $CDCl_3$) spectrum of **96k**



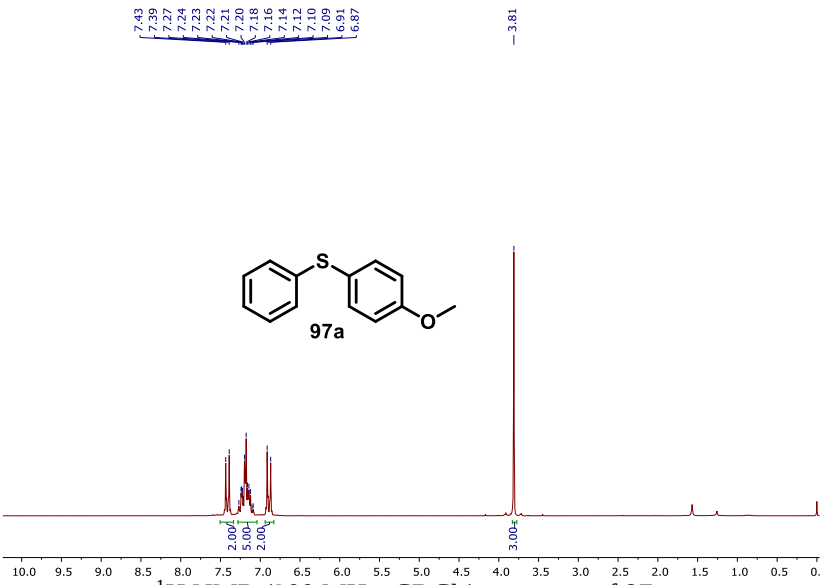
High-resolution mass spectrum of compound **96k**



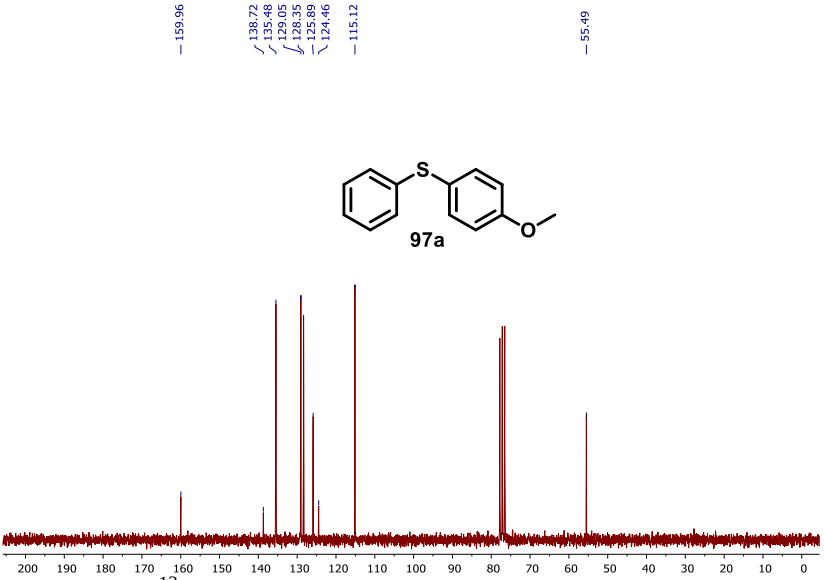
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **96l**



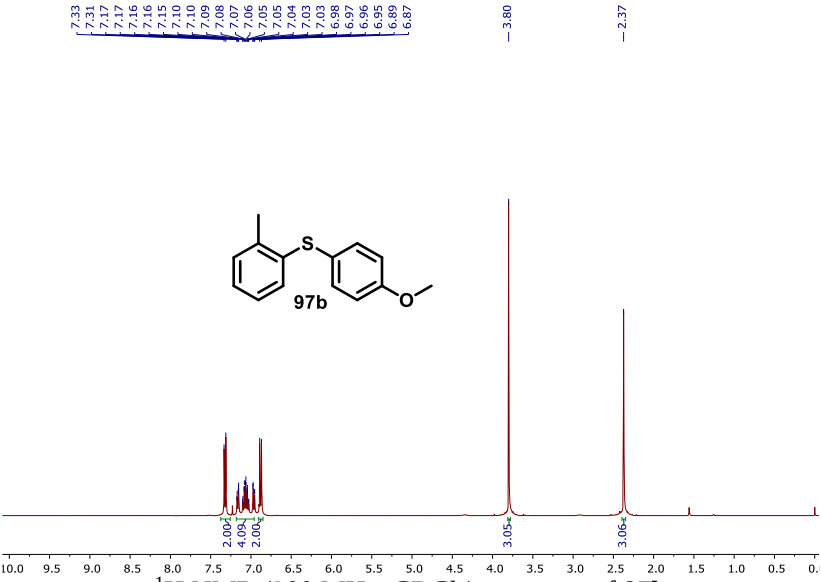
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **96l**



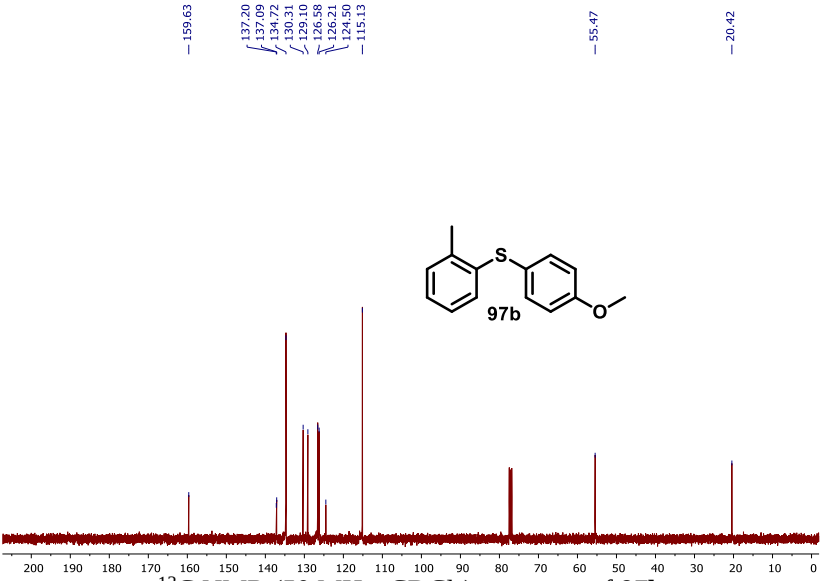
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **97a**



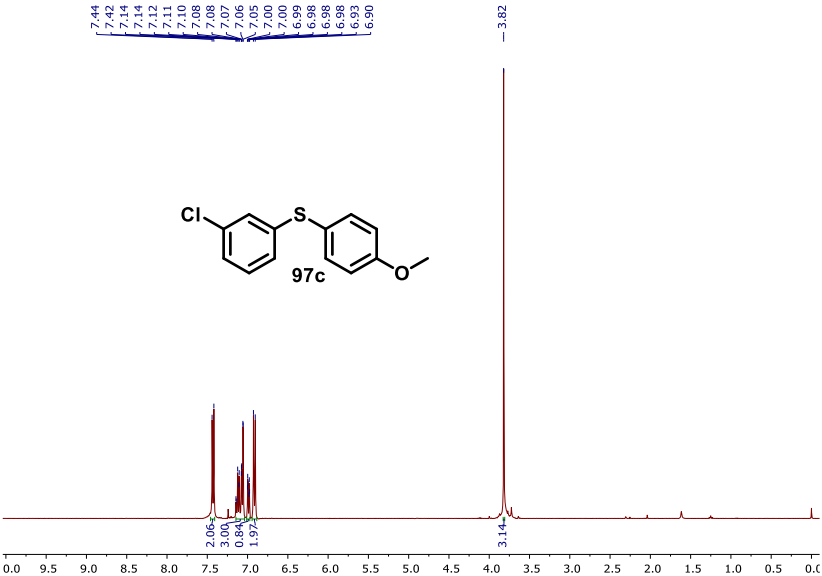
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **97a**



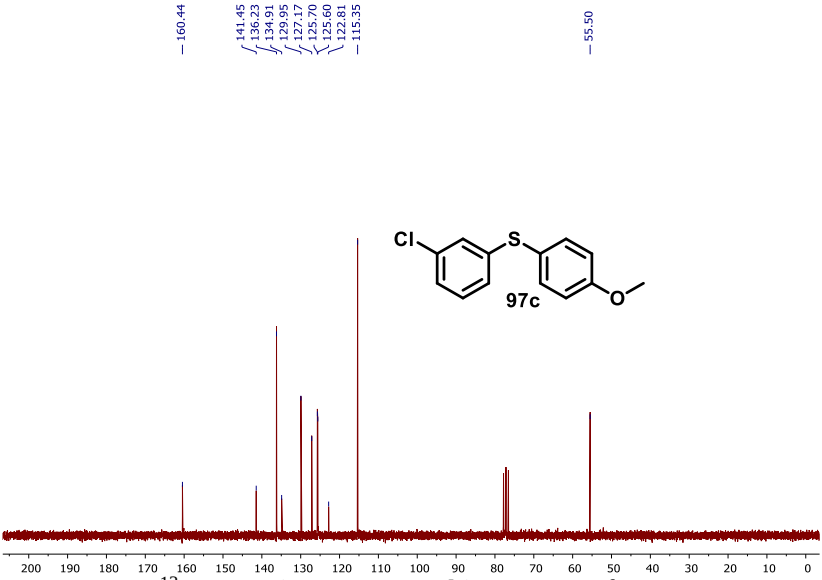
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **97b**



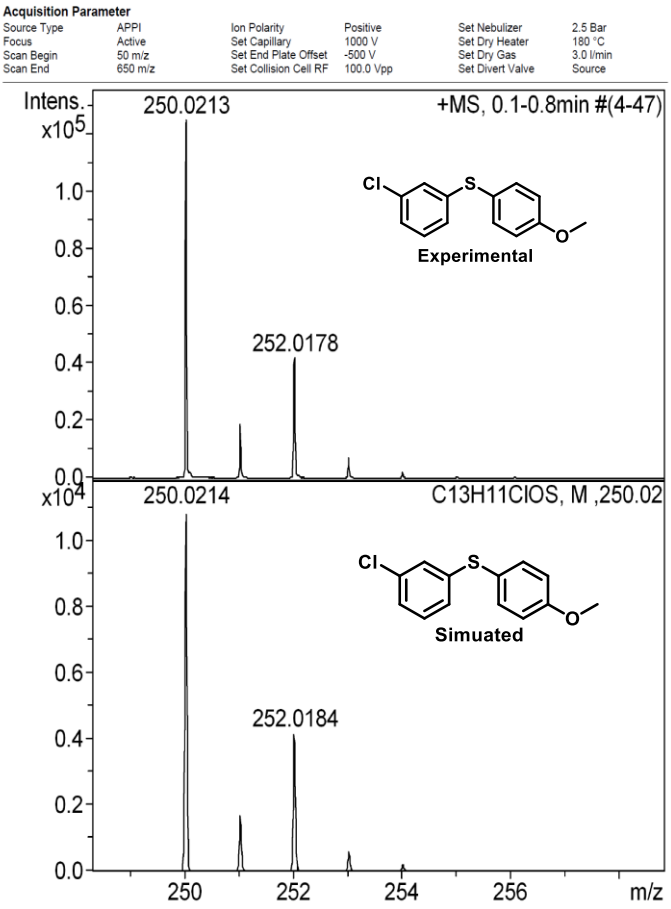
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **97b**



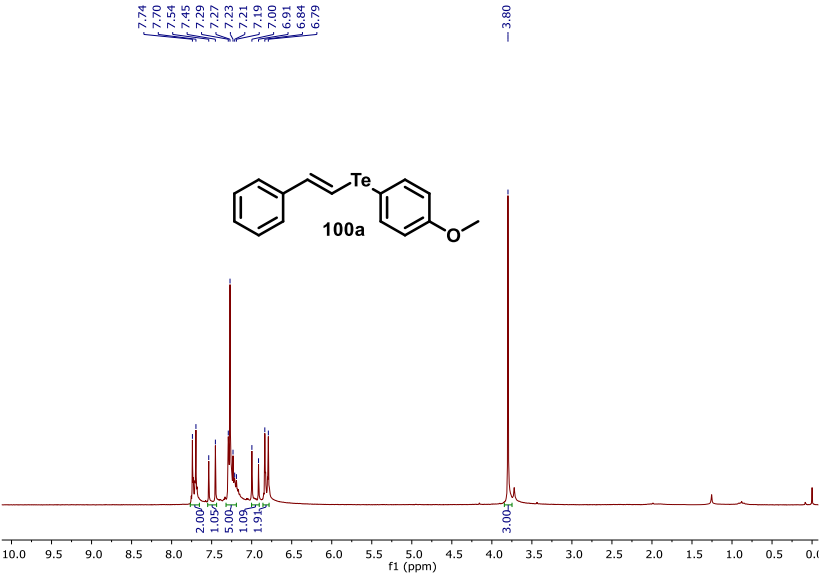
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **97c**



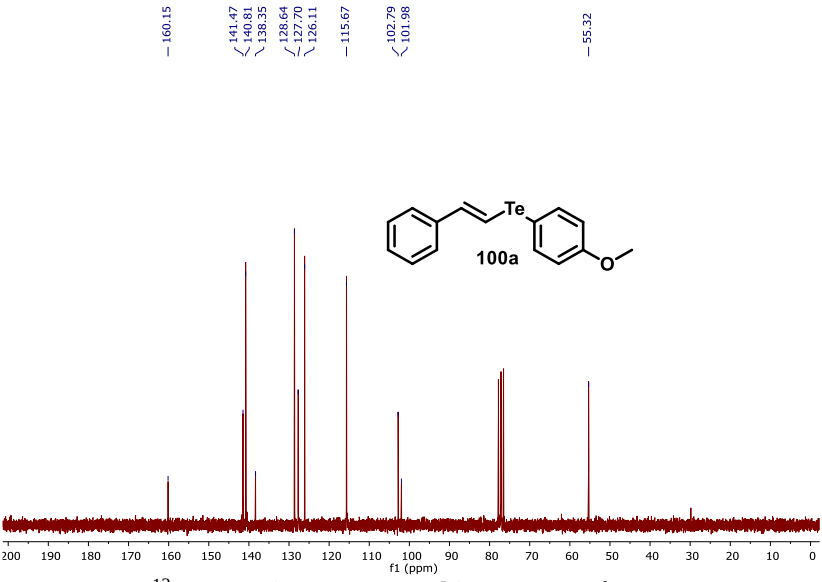
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **97c**



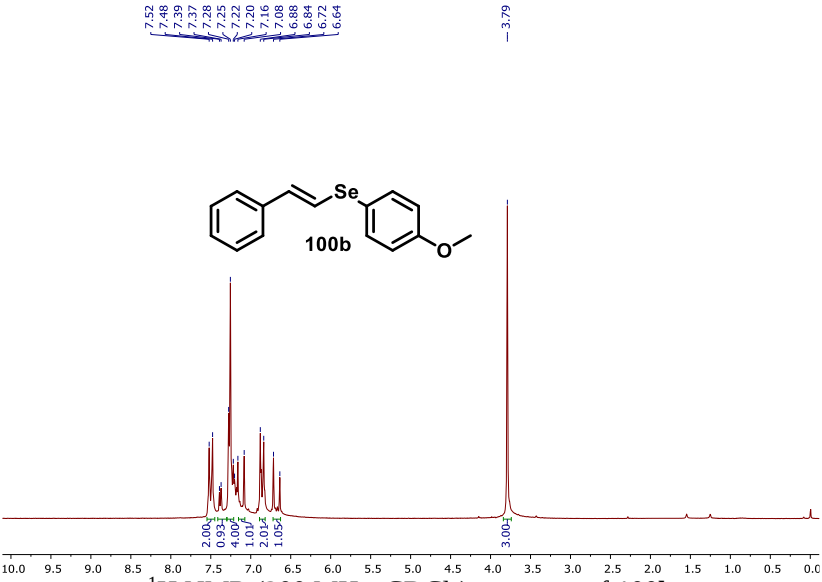
High-resolution mass spectrum of compound 97t



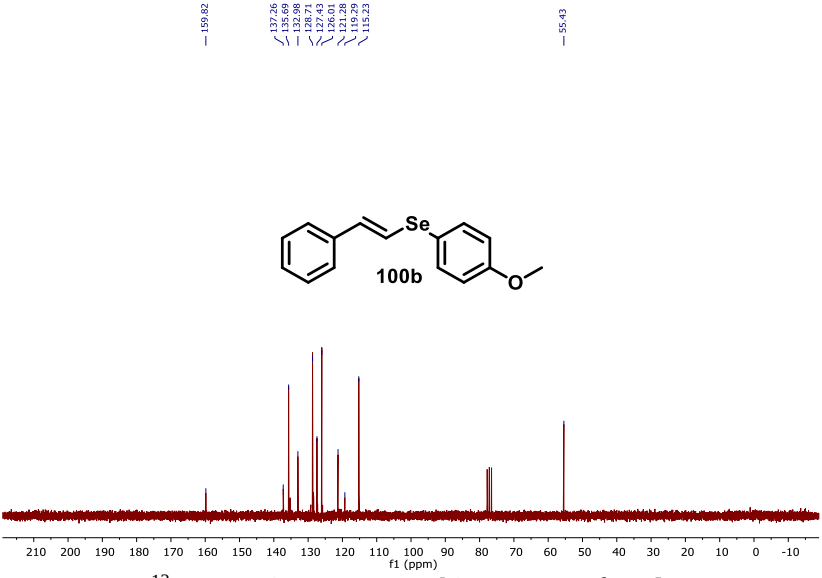
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **100a**



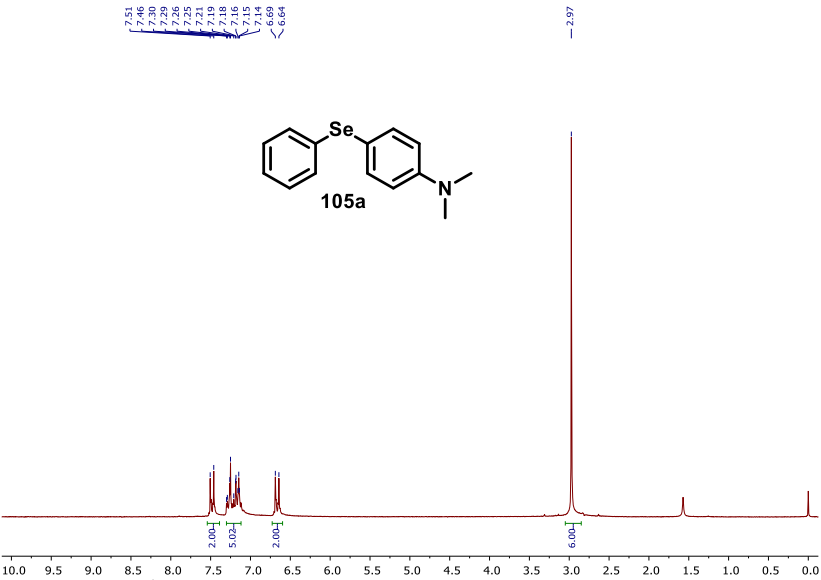
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **100a**



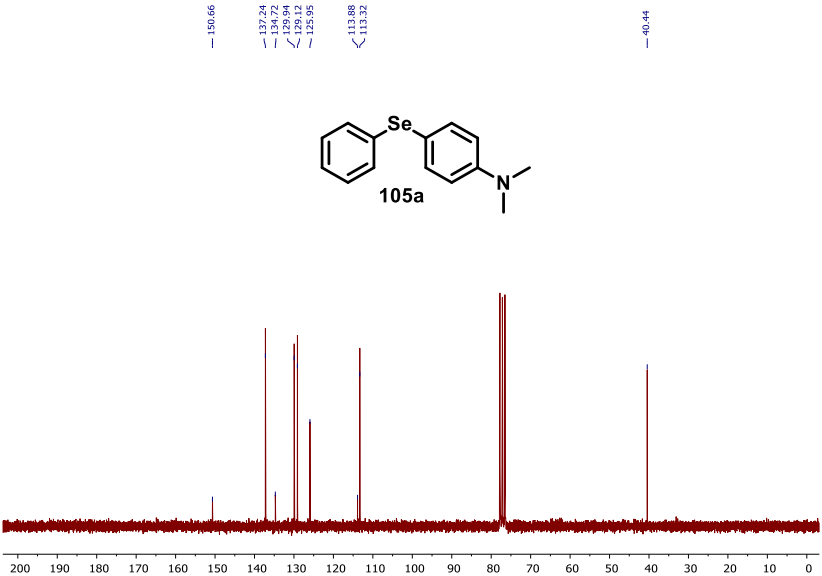
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **100b**



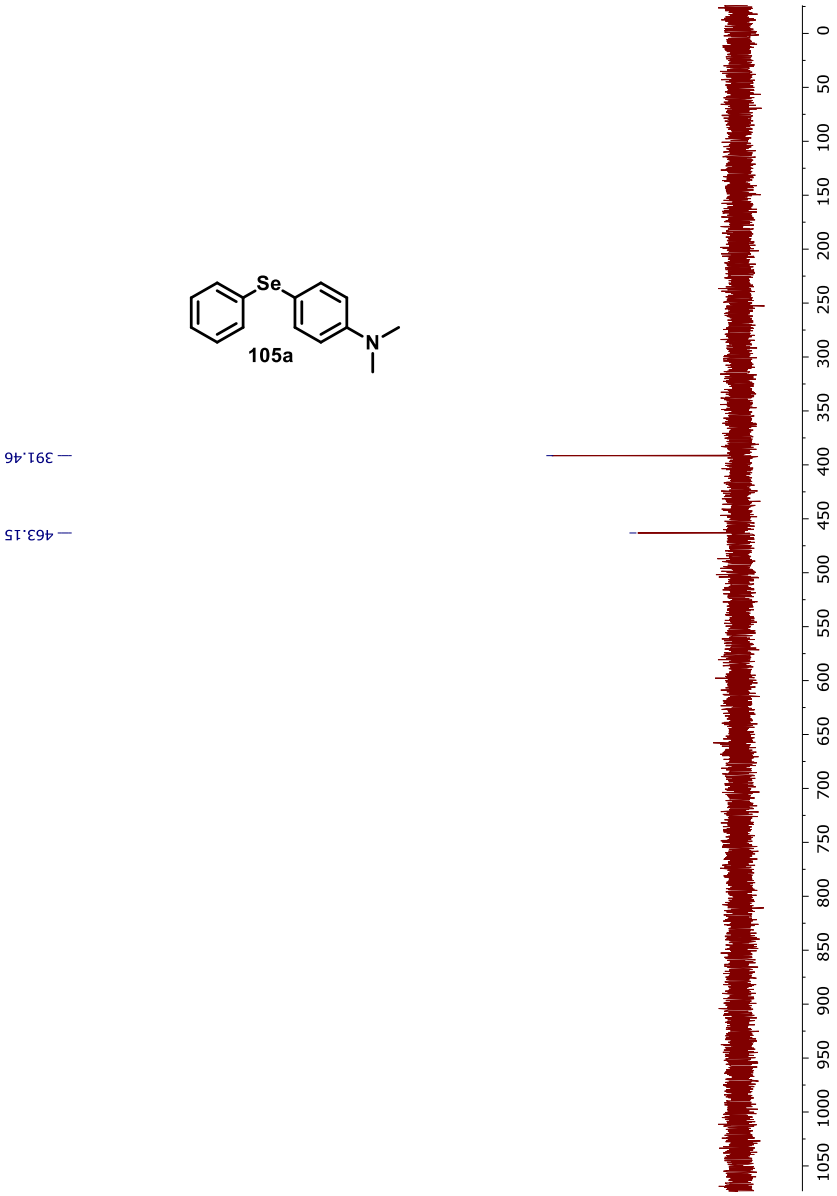
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **100b**



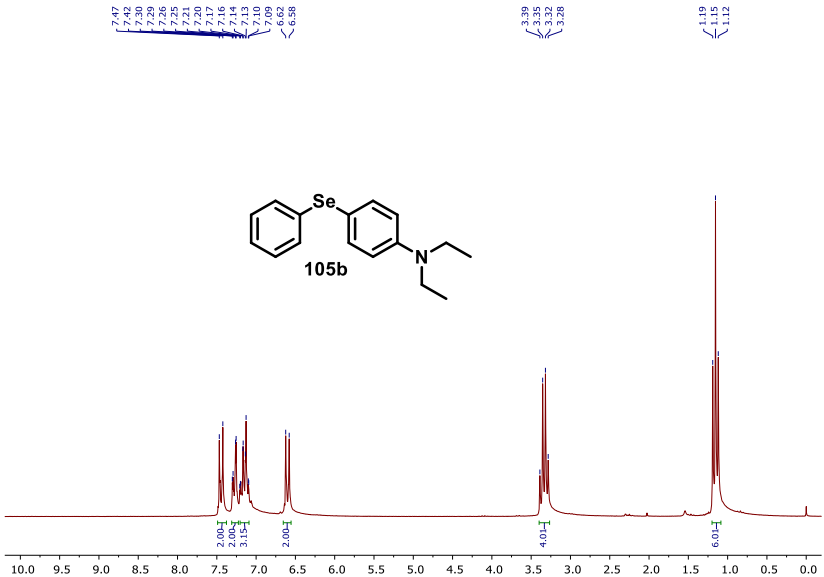
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105a**



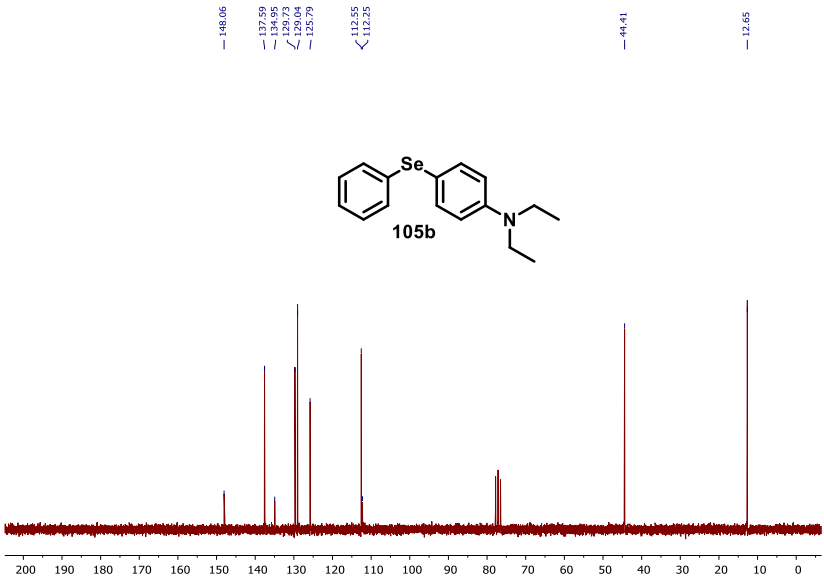
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105a**



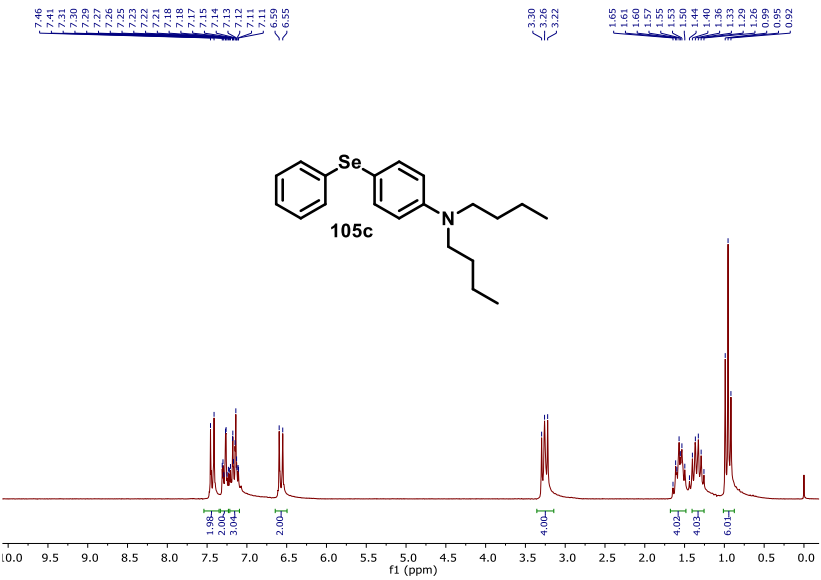
^{77}Se NMR (38.14 MHz, $CDCl_3$) spectrum of **105a**



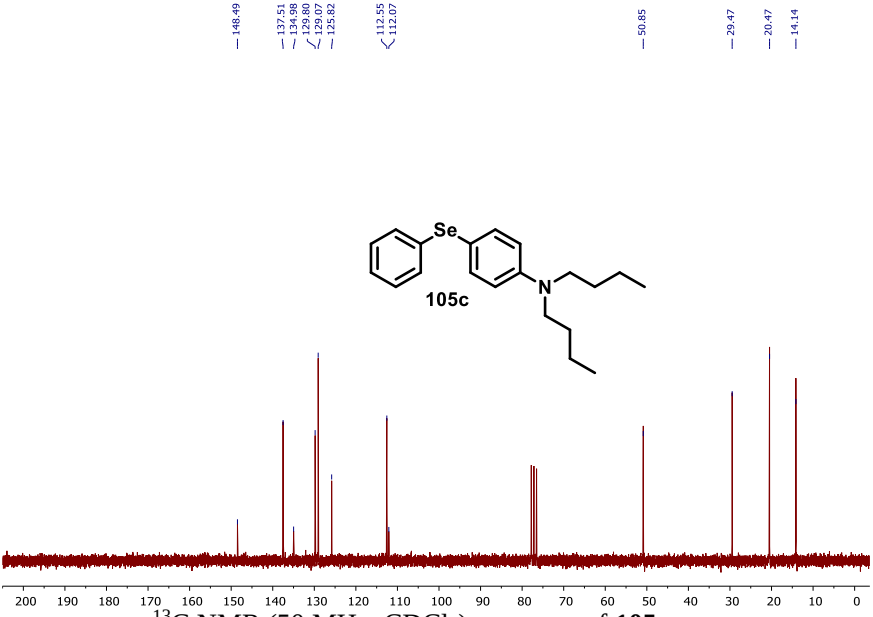
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105b**



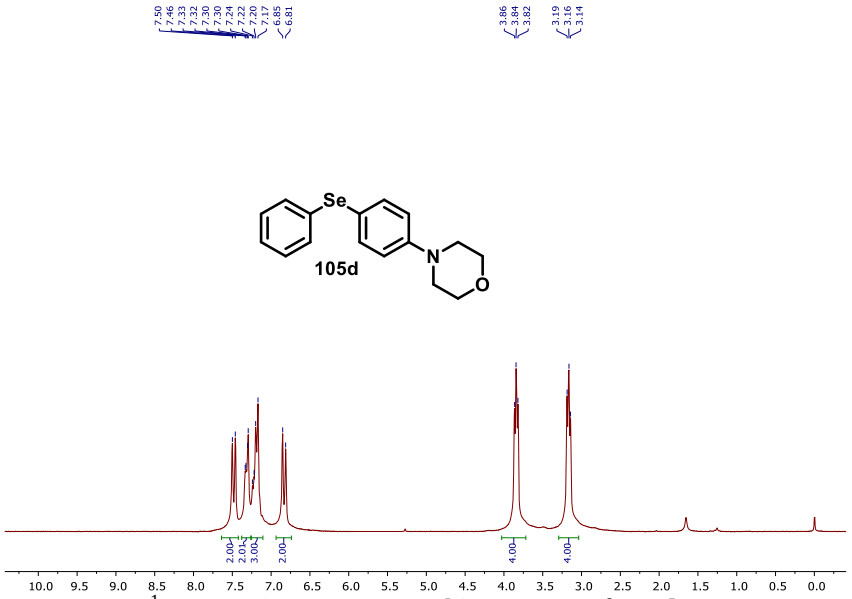
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105b**



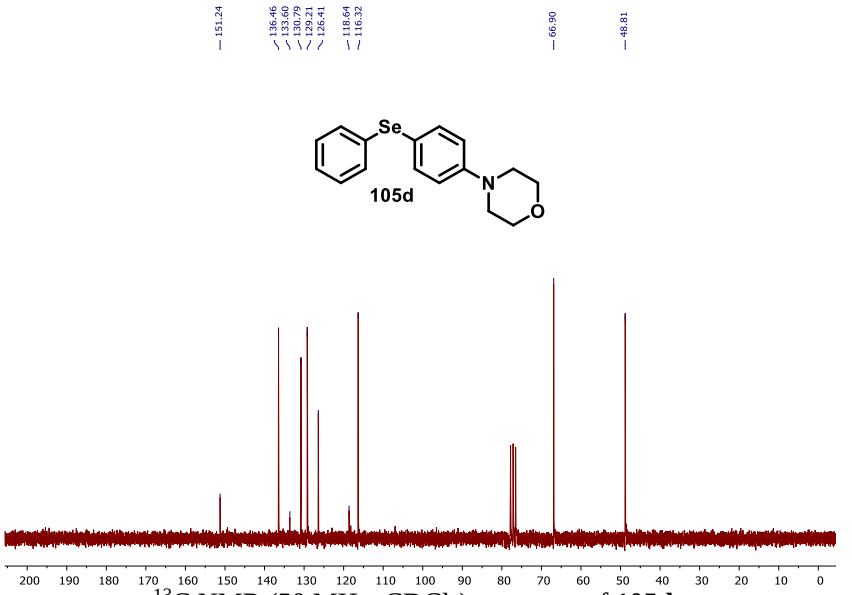
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105c**



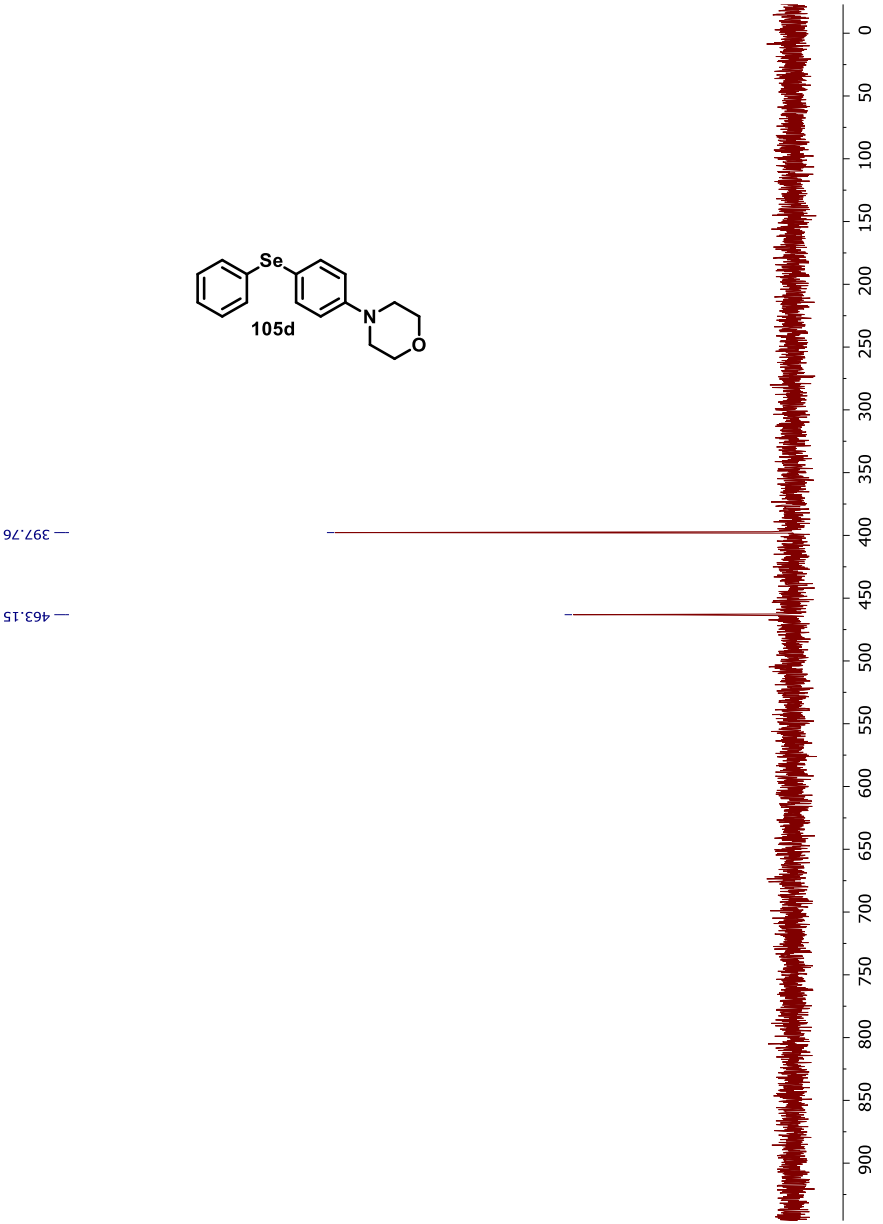
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105c**



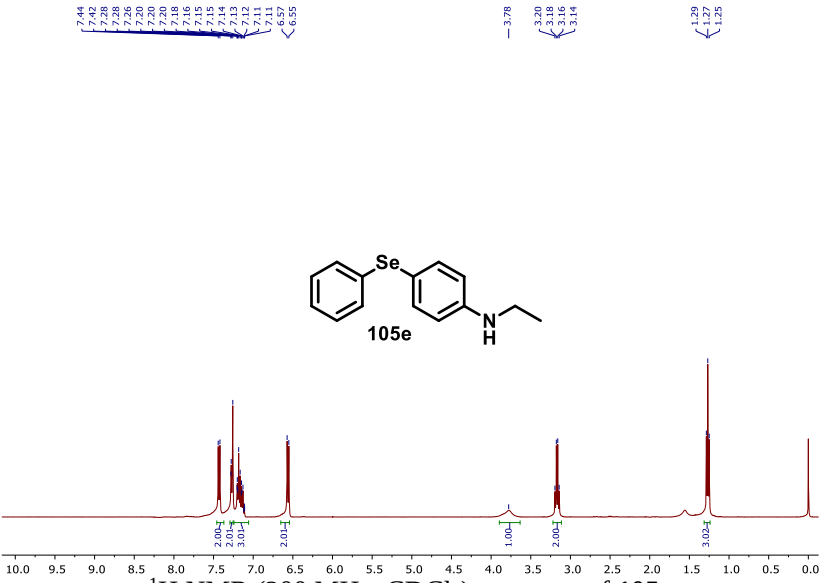
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105d**



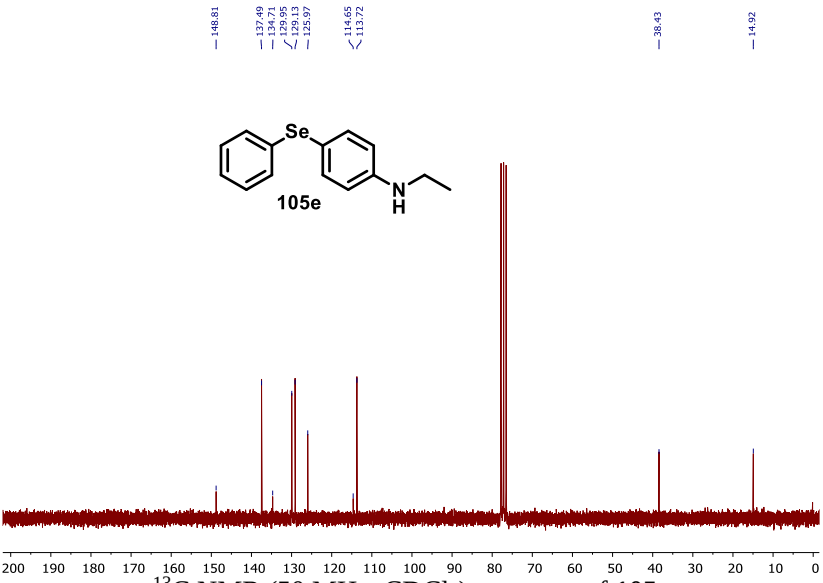
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105d**



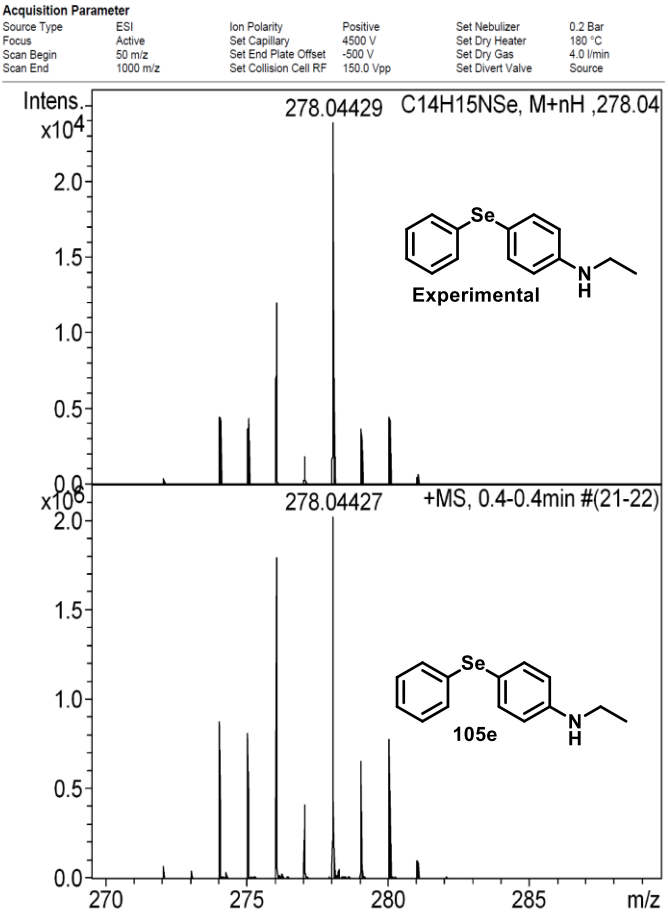
^{77}Se NMR (38.14 MHz, $CDCl_3$) spectrum of **105d**



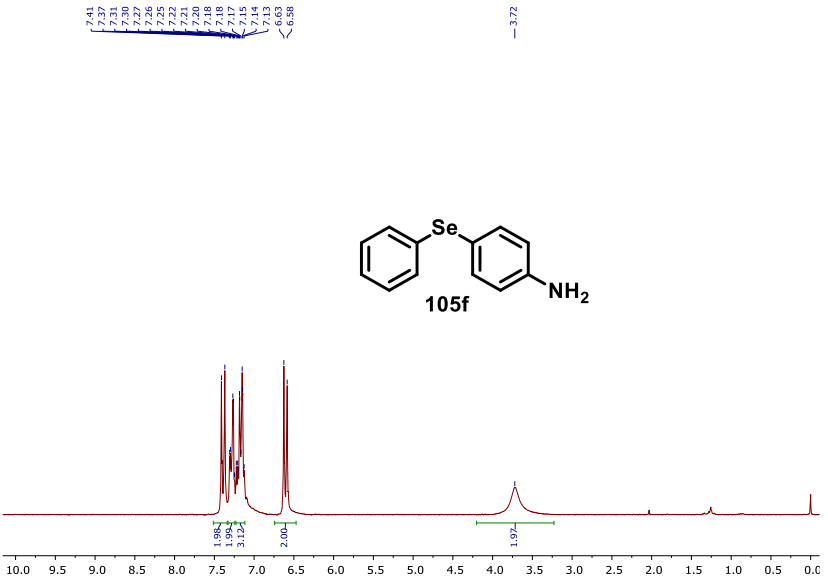
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105e**



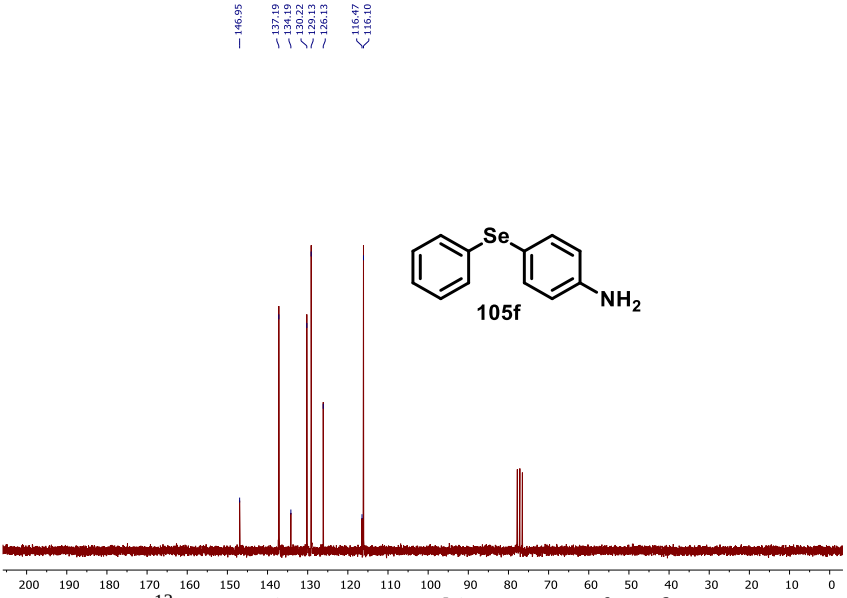
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105e**



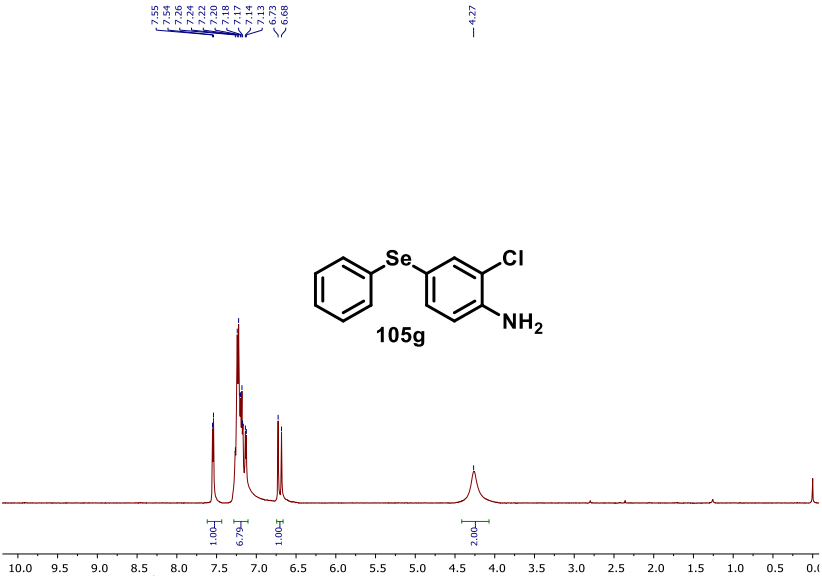
High-resolution mass spectrum of compound **105e**



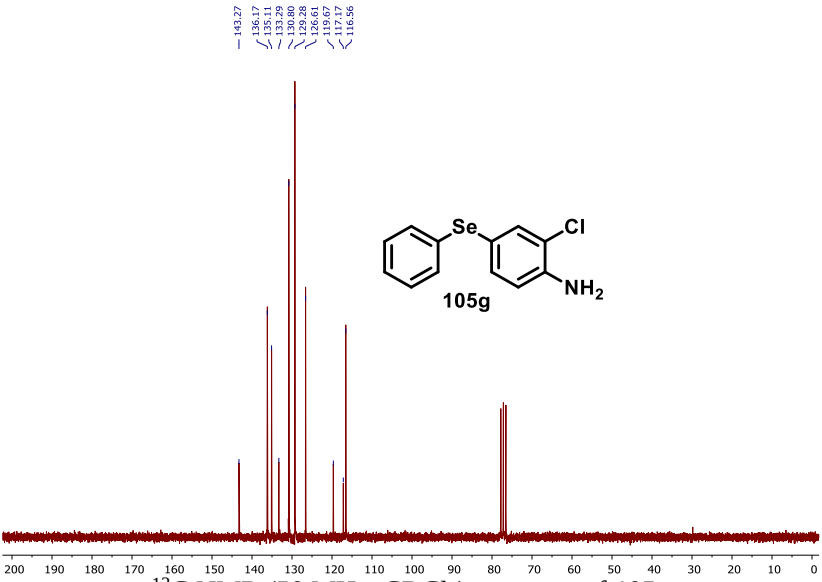
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105f**



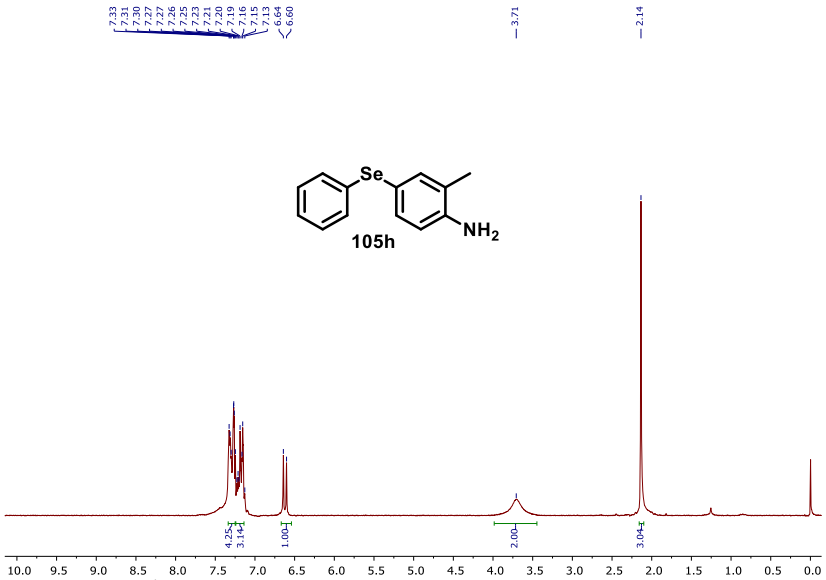
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105f**



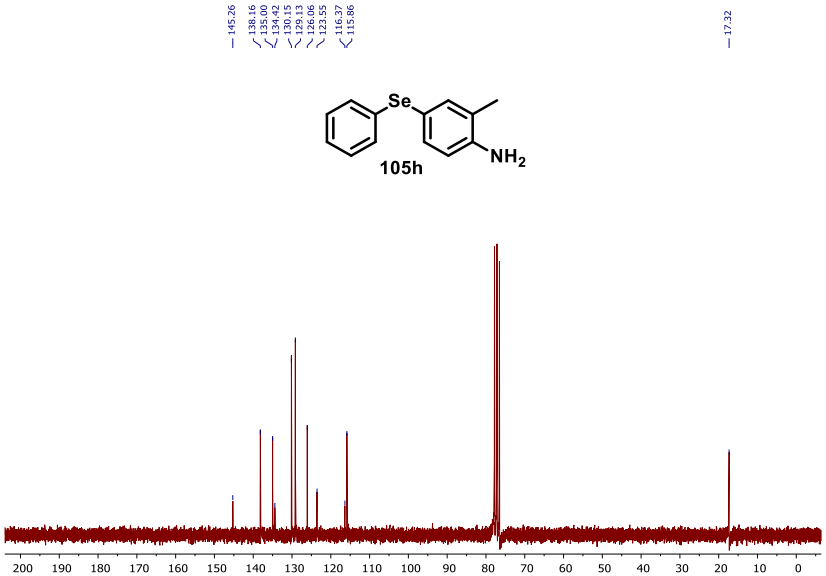
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105g**



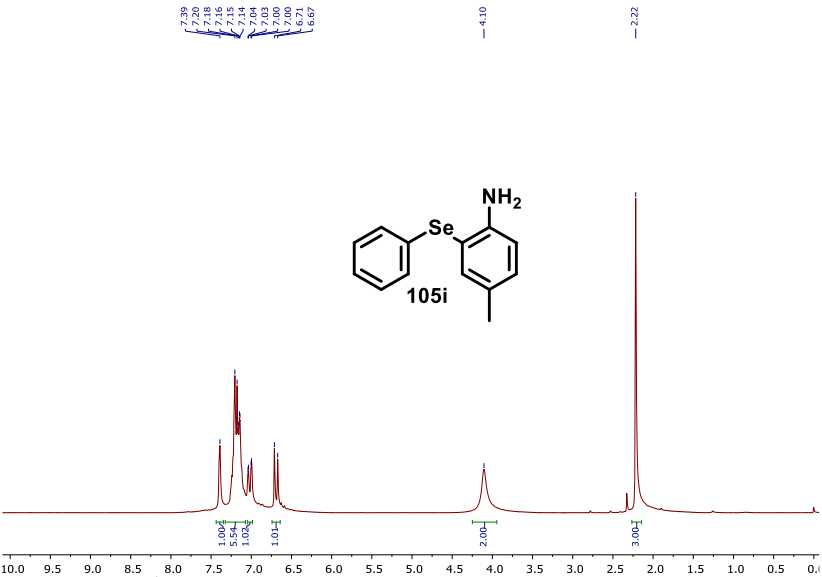
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105g**



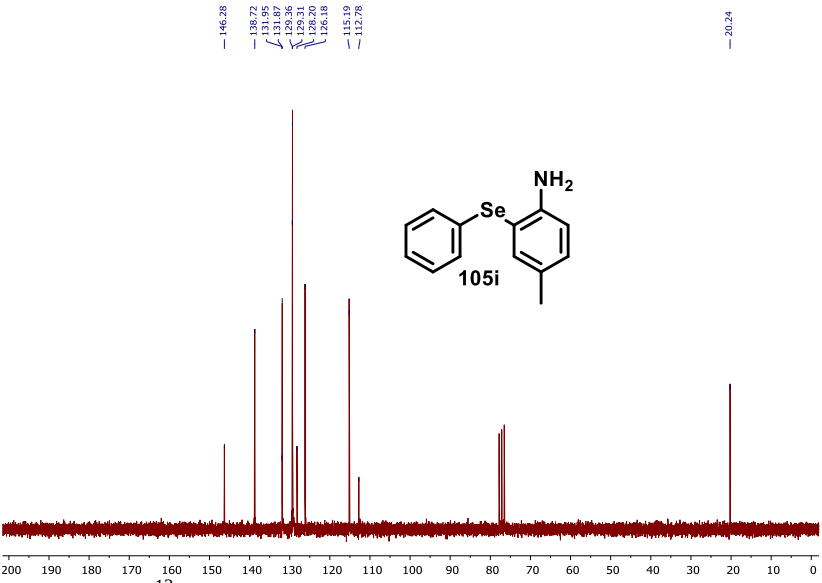
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105h**



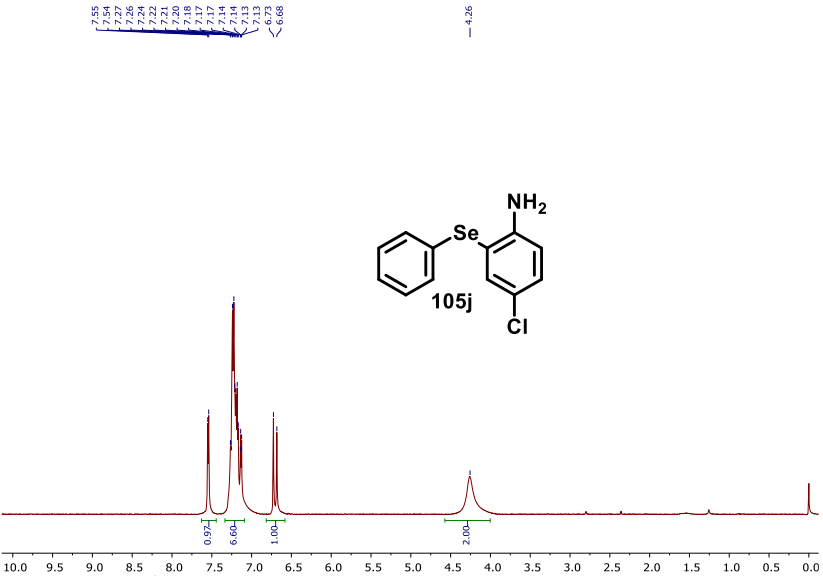
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105h**



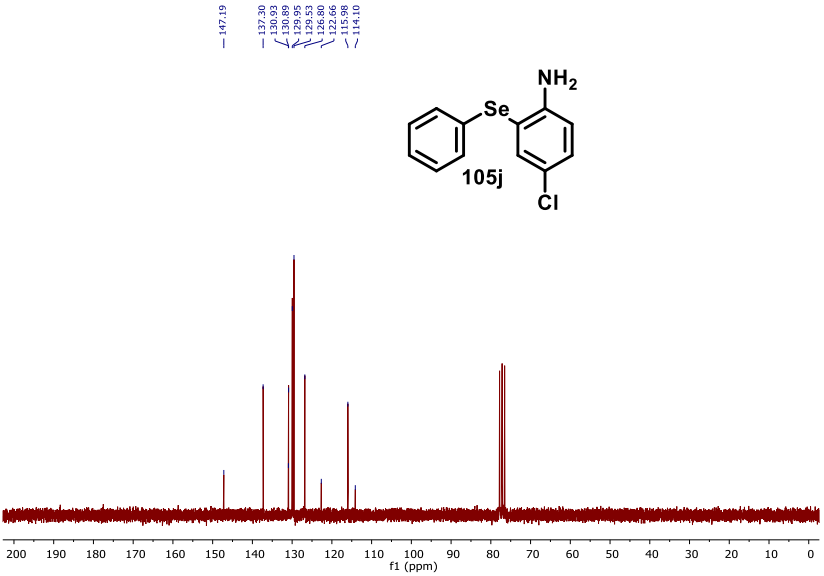
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105i**



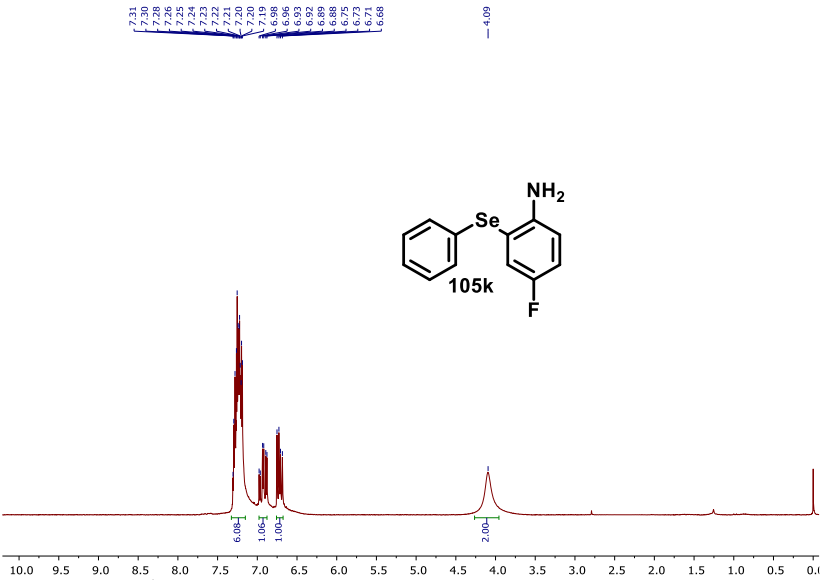
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105i**



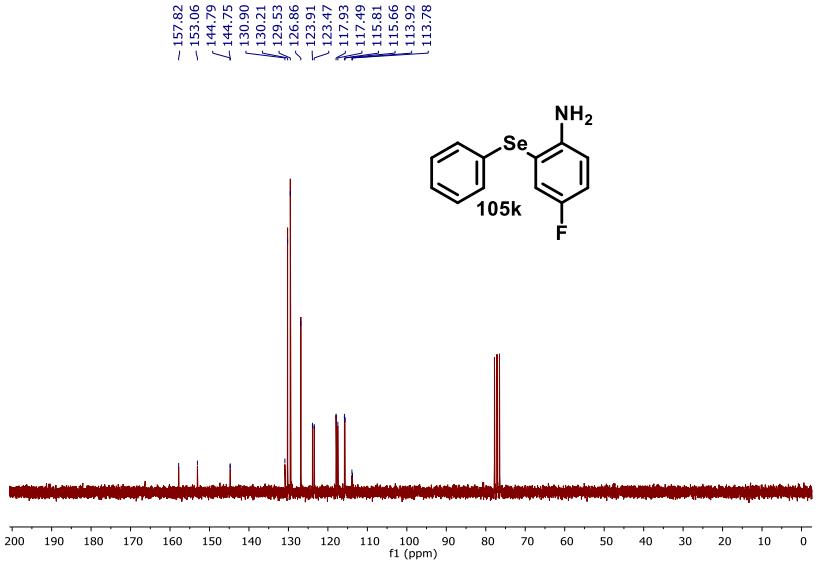
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105j**



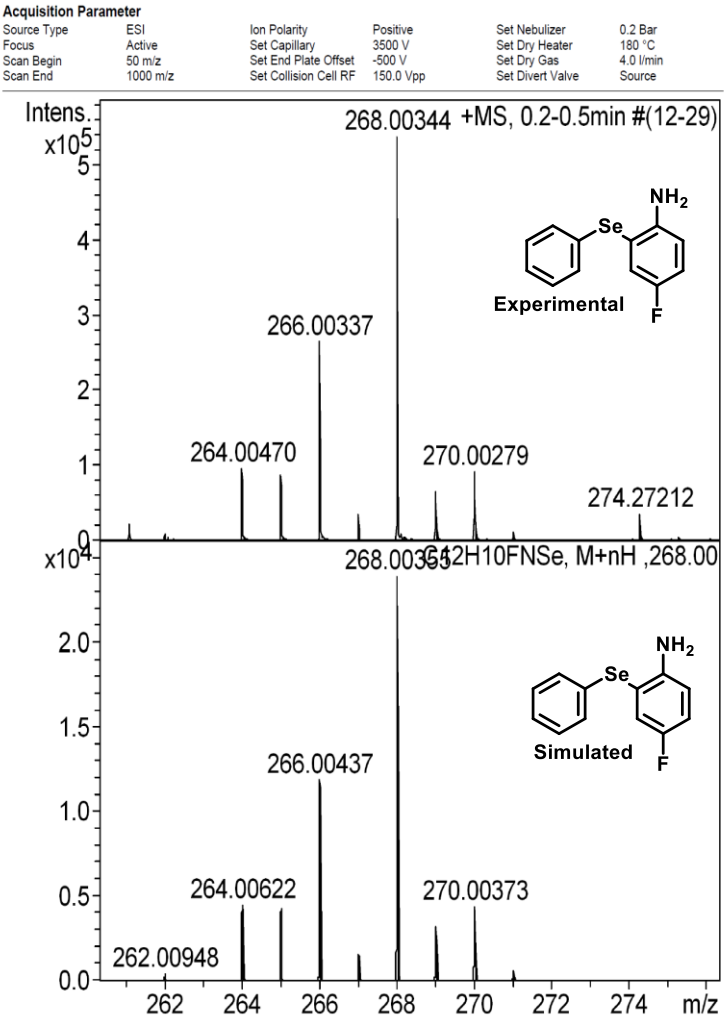
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105j**



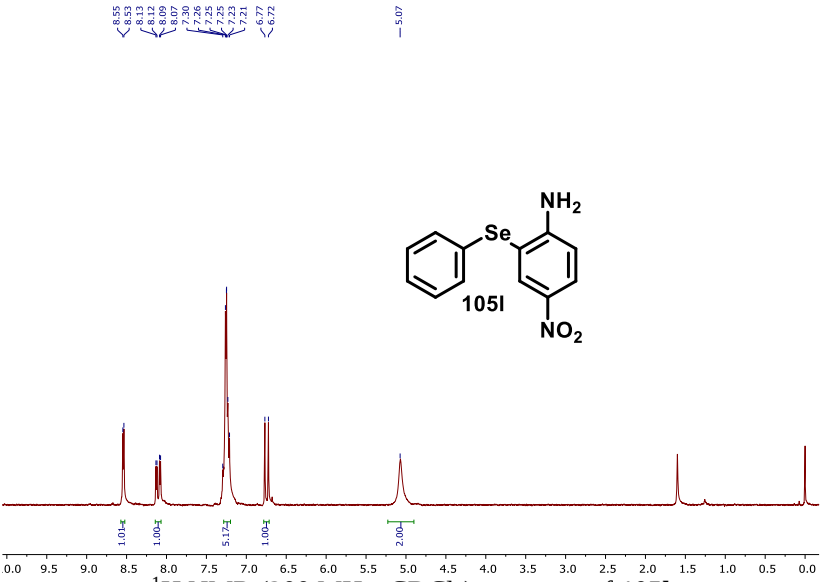
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105k**



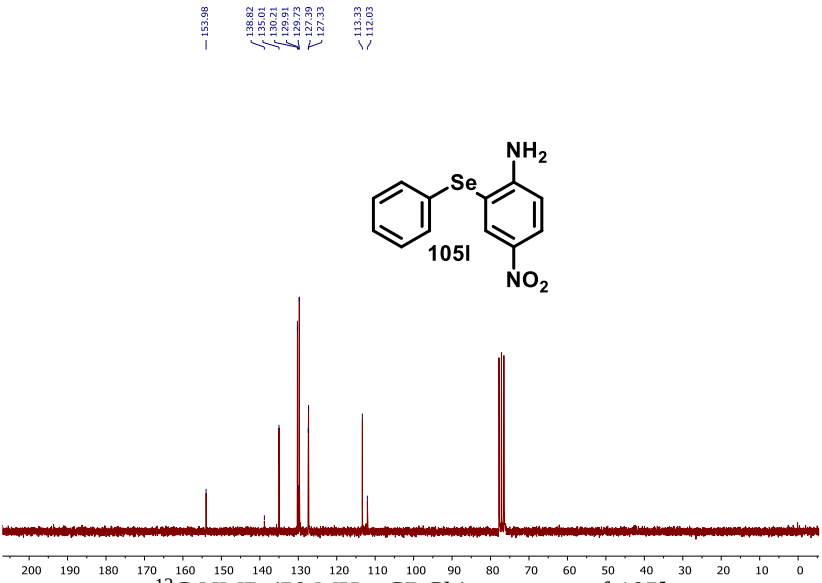
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105k**



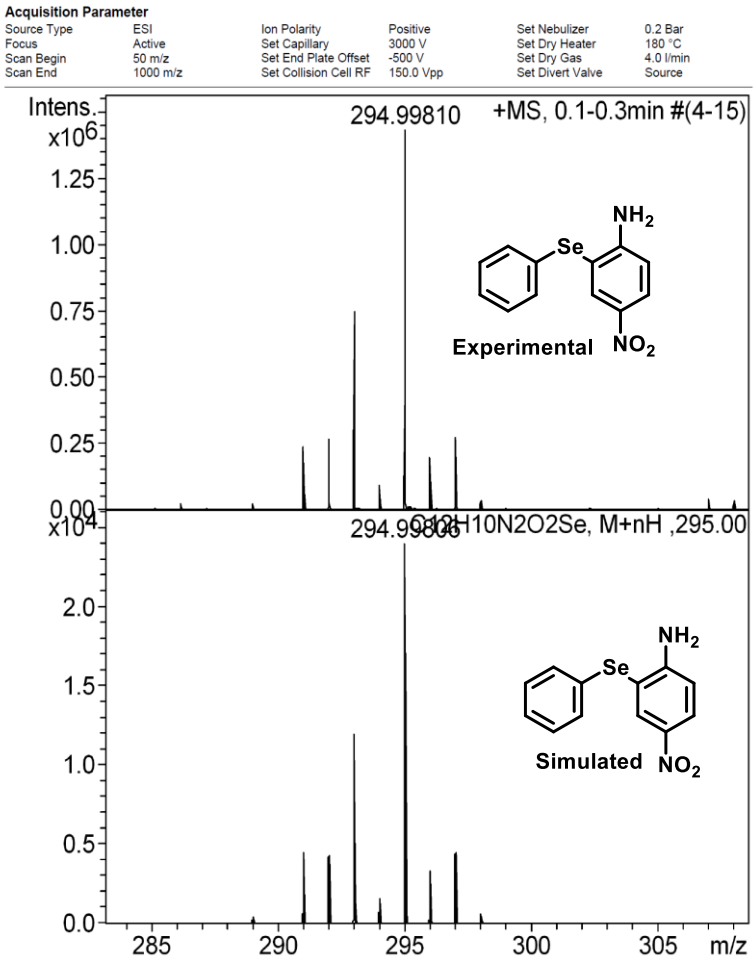
High-resolution mass spectrum of compound **105k**



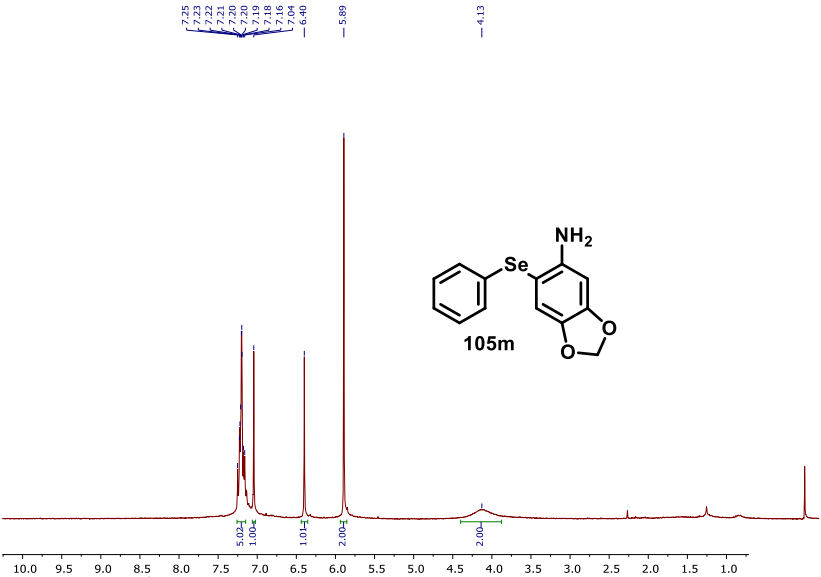
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105l**



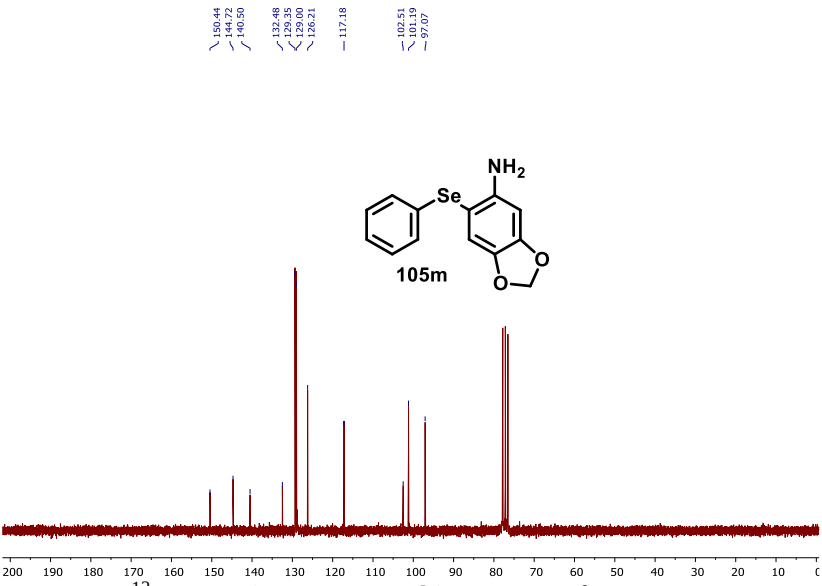
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105l**



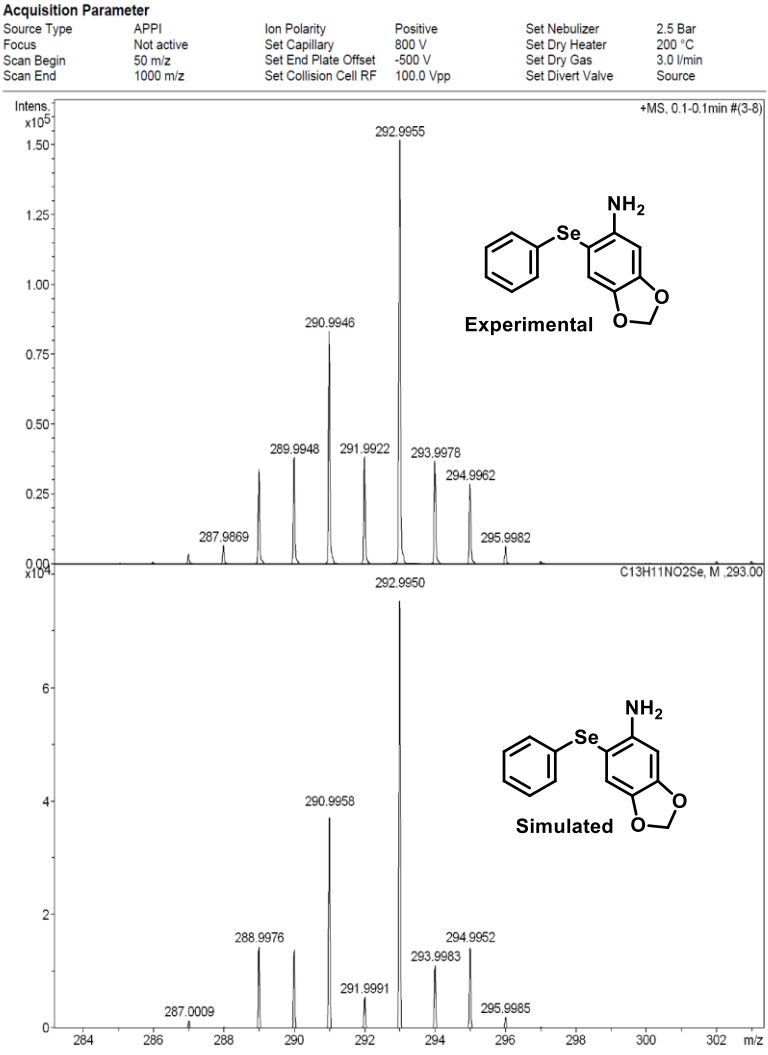
High-resolution mass spectrum of compound **105l**



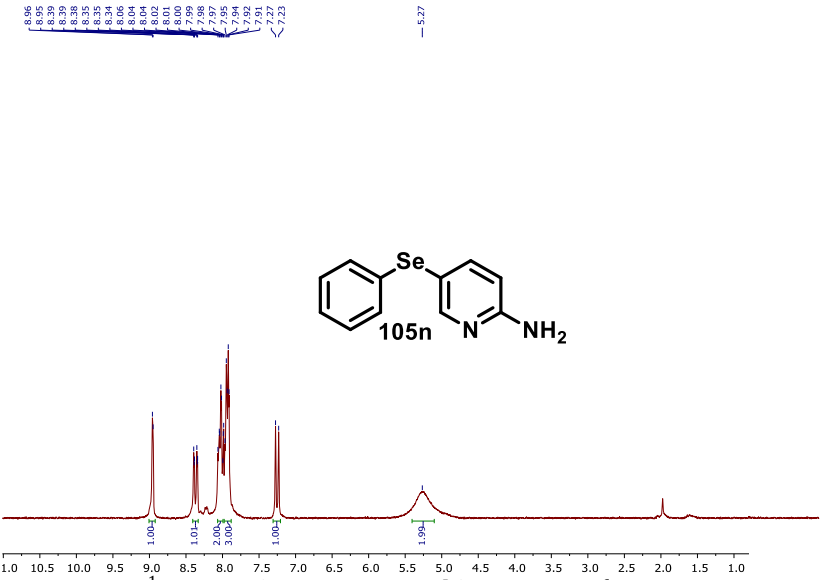
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105m**



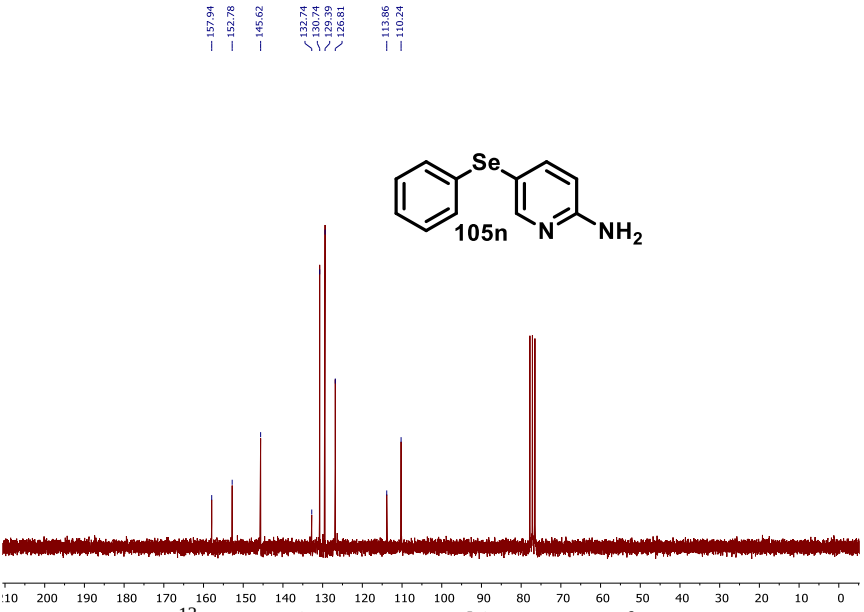
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105m**



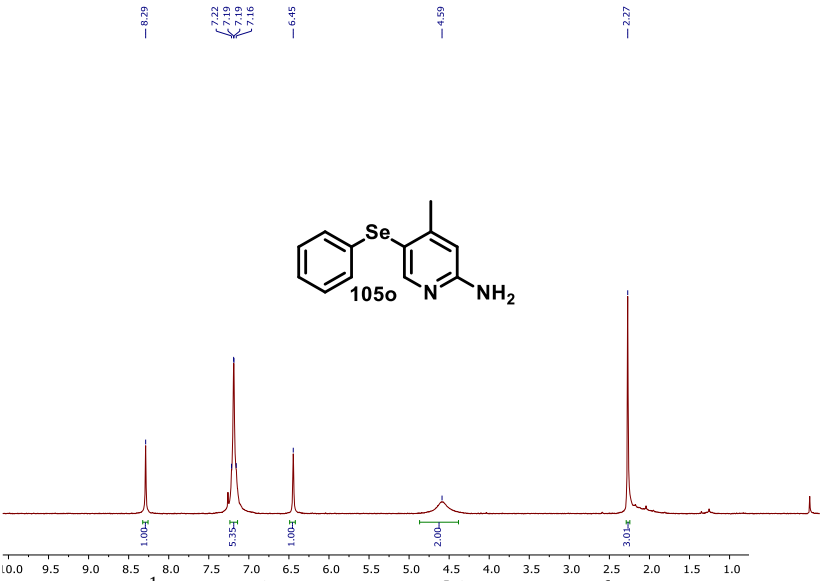
High-resolution mass spectrum of compound **105m**



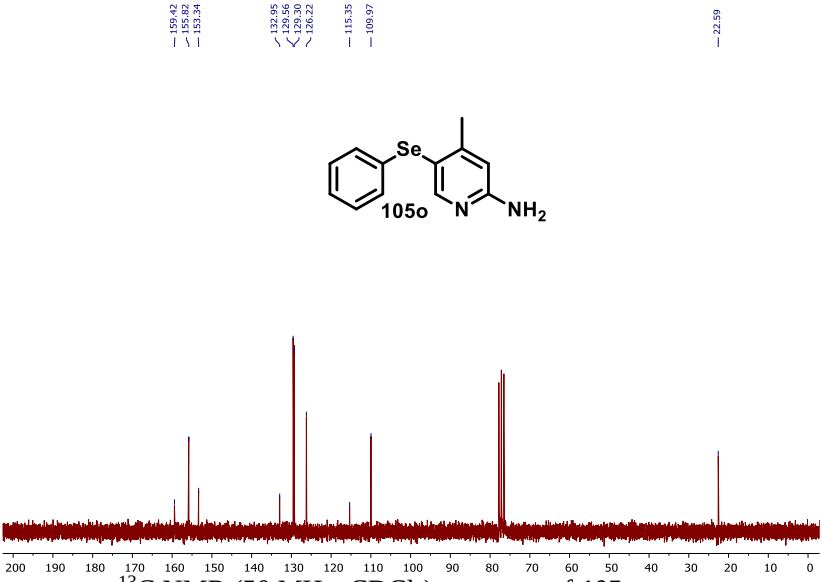
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105n**



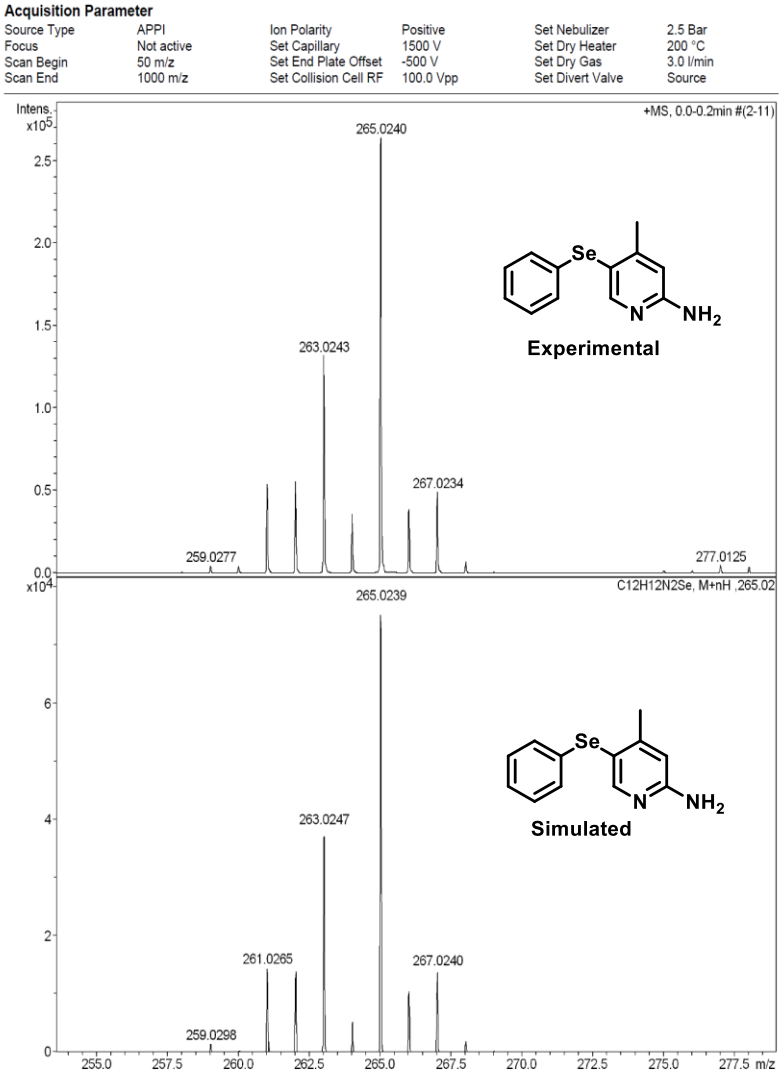
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105n**



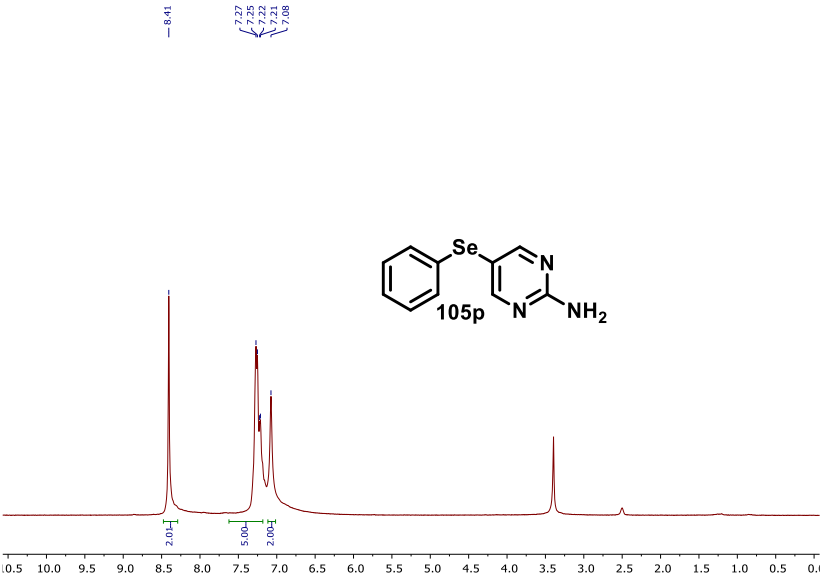
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105o**



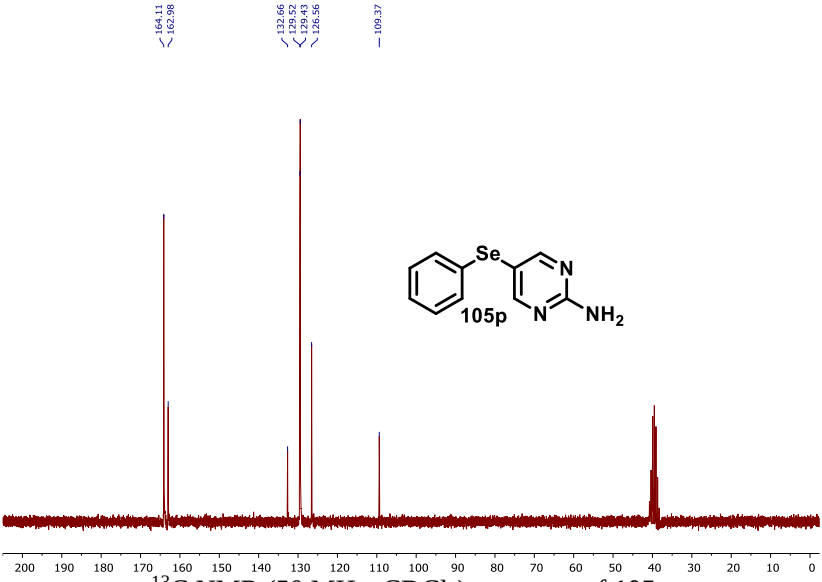
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105o**



High-resolution mass spectrum of compound **105o**



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105p**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105p**

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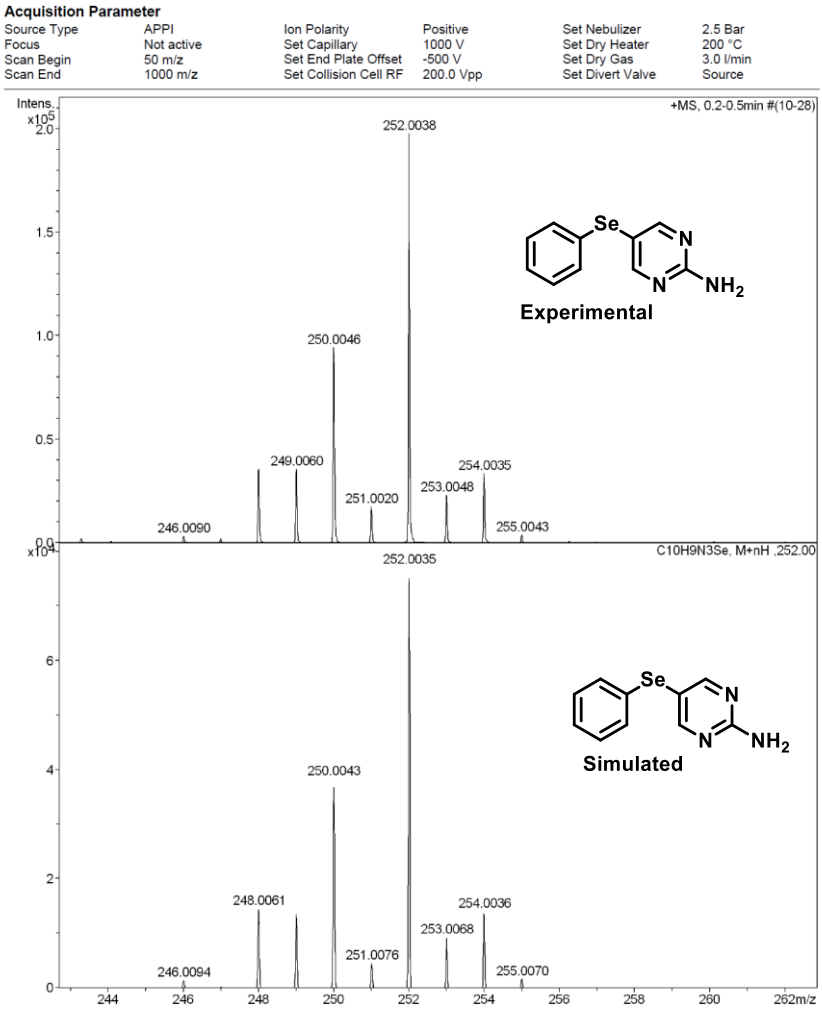
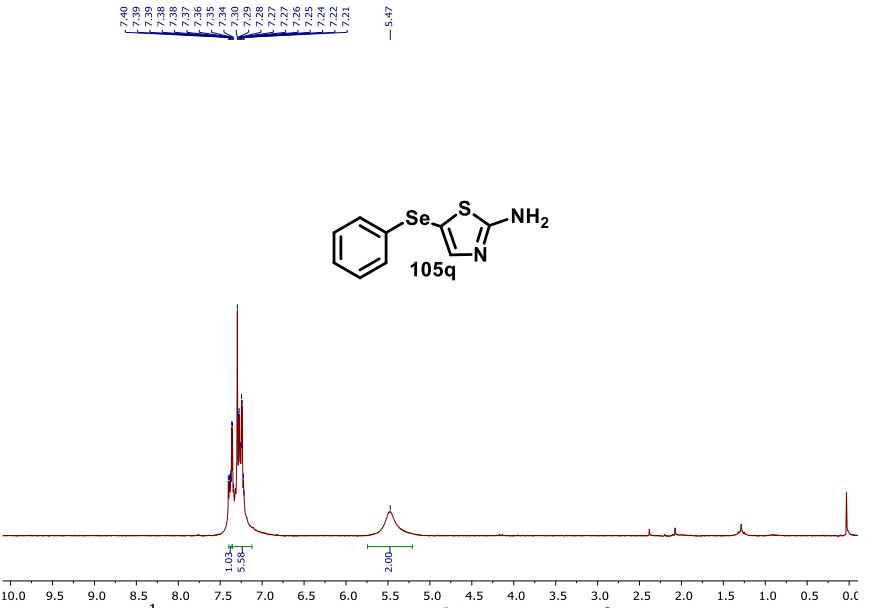
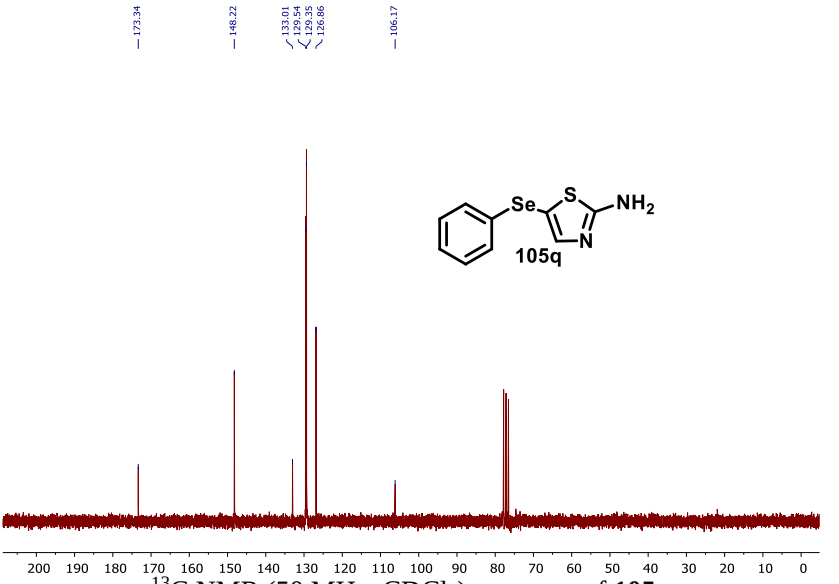


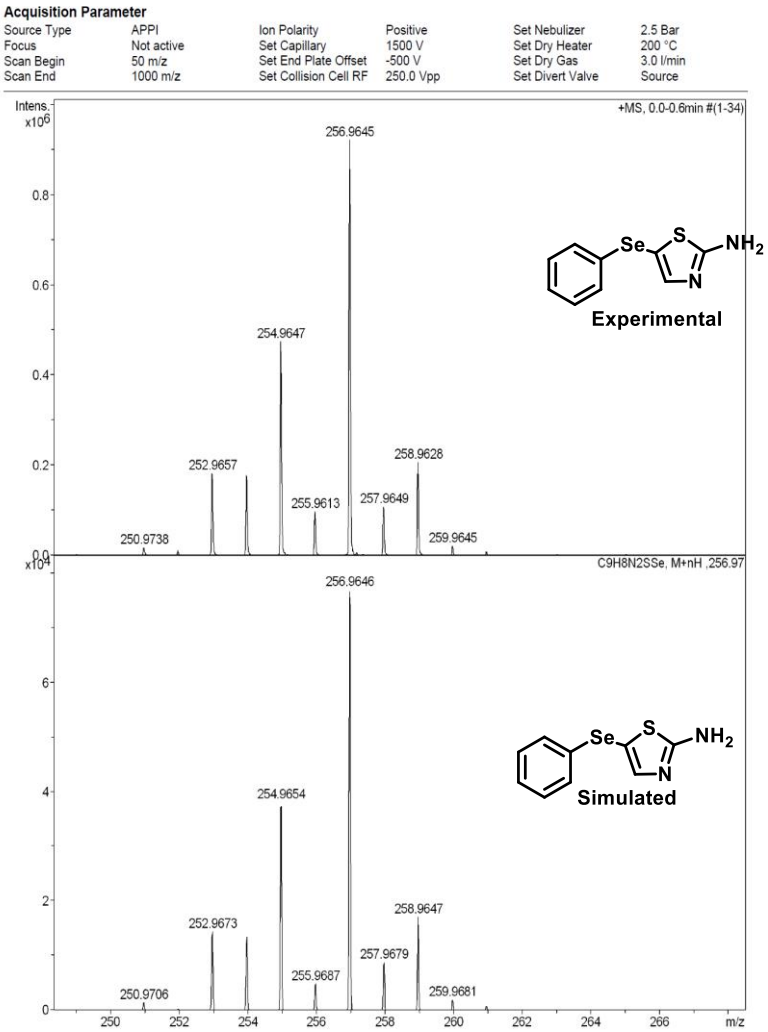
High-resolution mass spectrum of compound **105p**



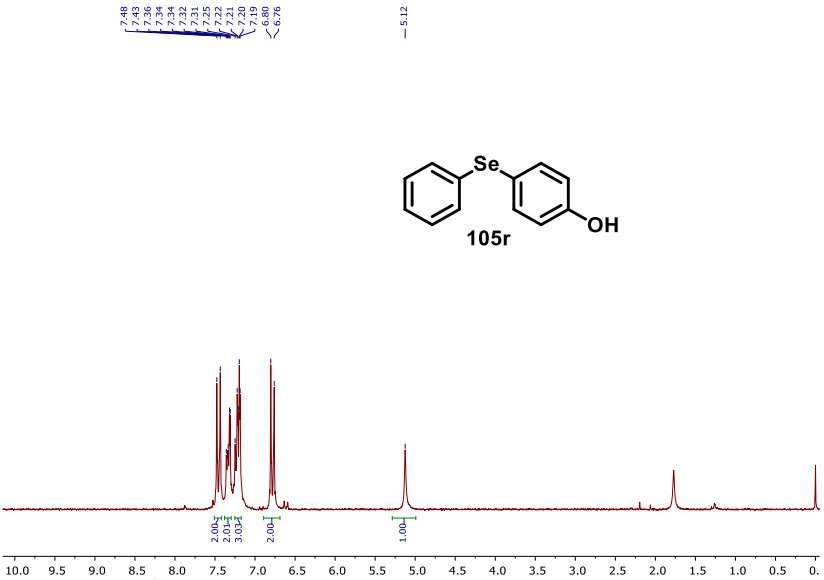
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105q**



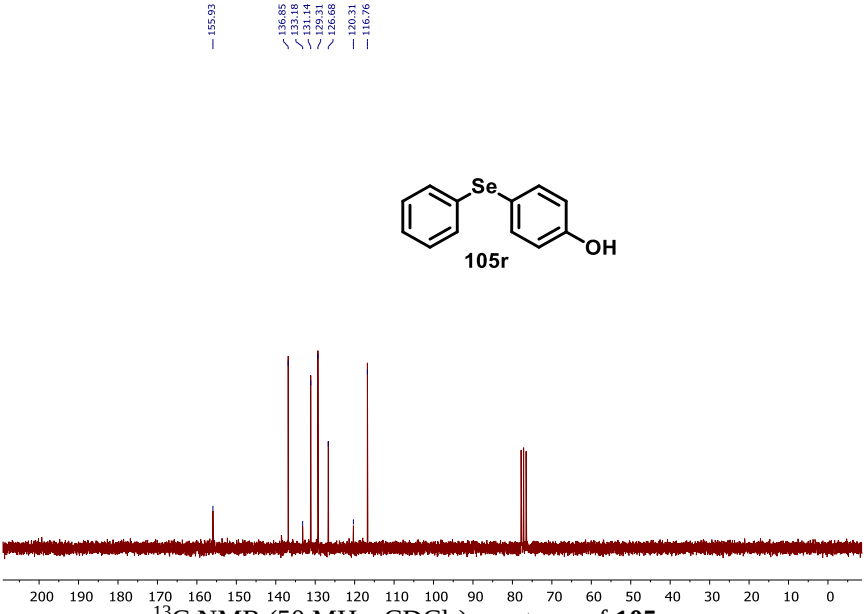
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105q**



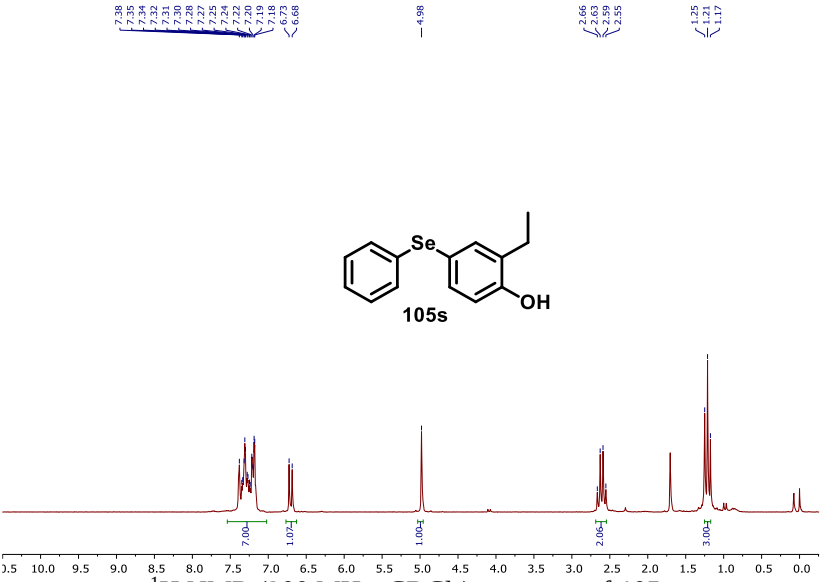
High-resolution mass spectrum of compound **105q**



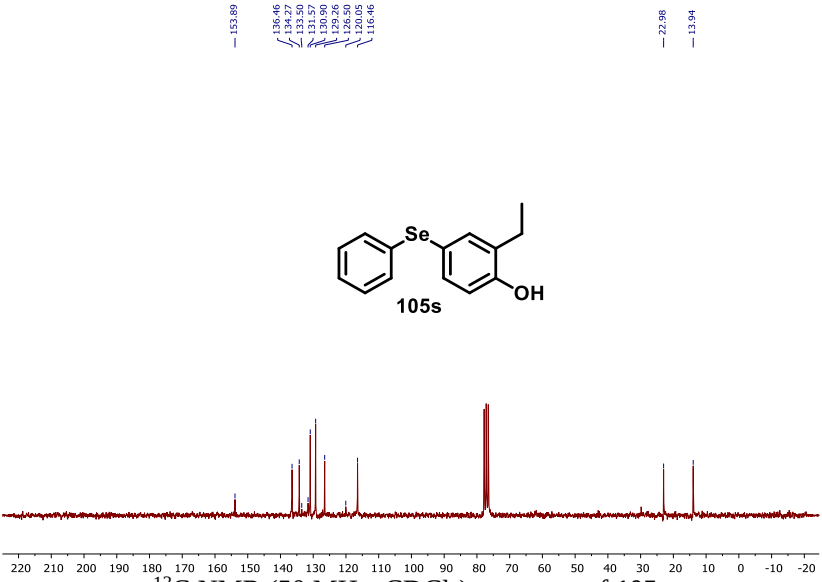
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105r**



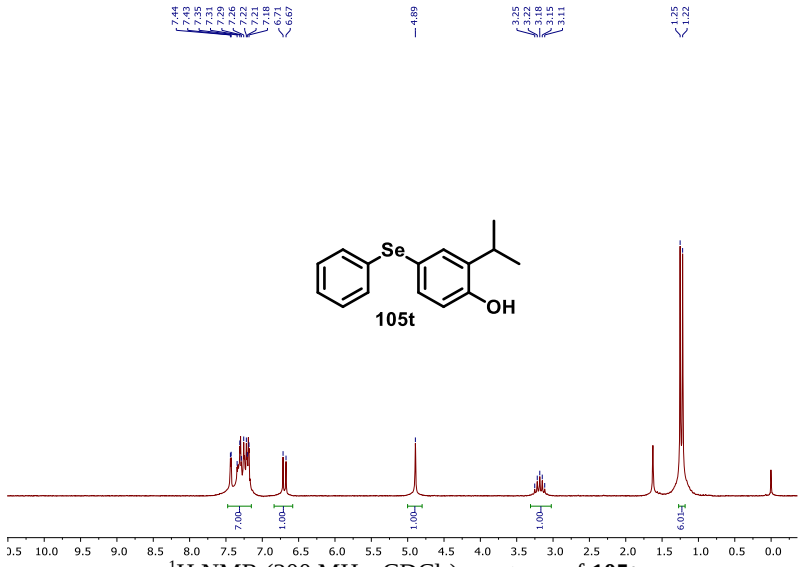
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105r**



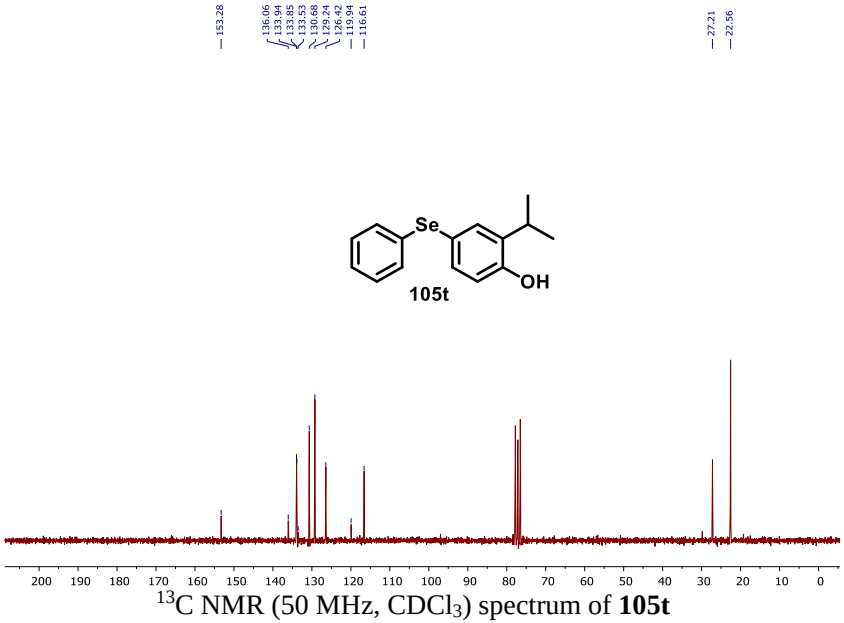
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105s**



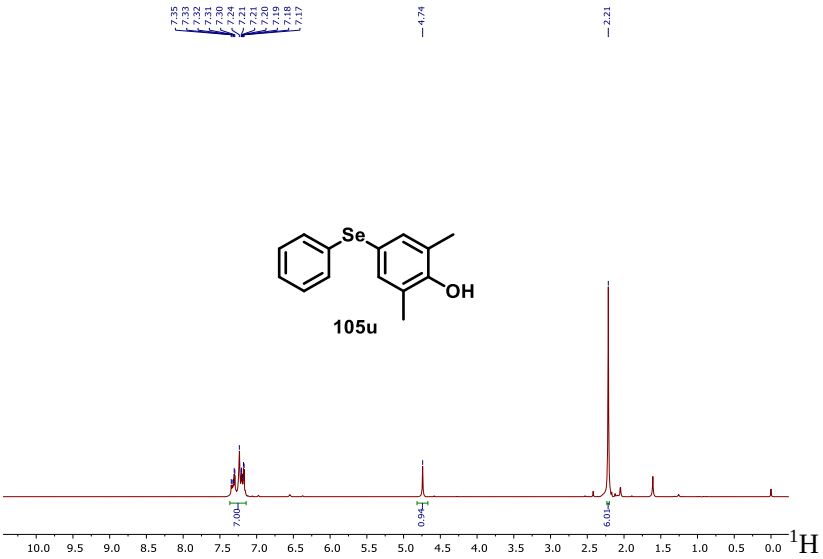
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105s**



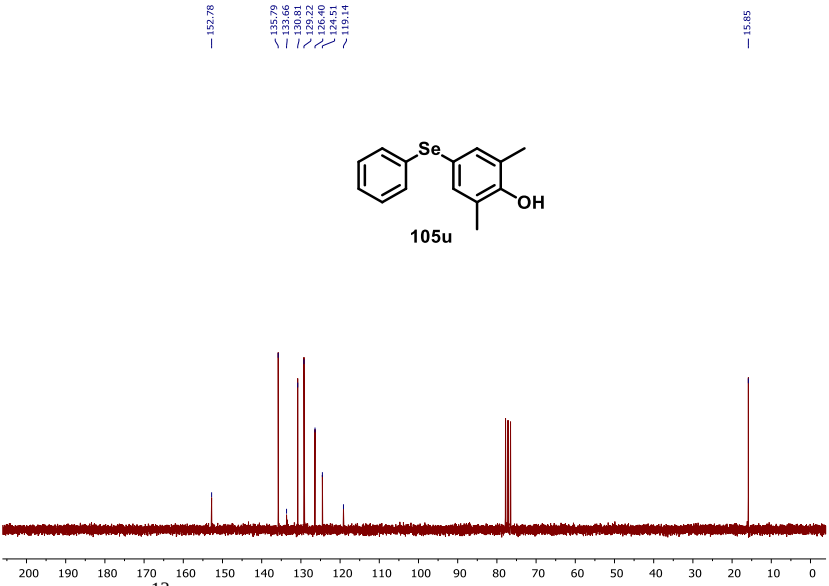
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105t**



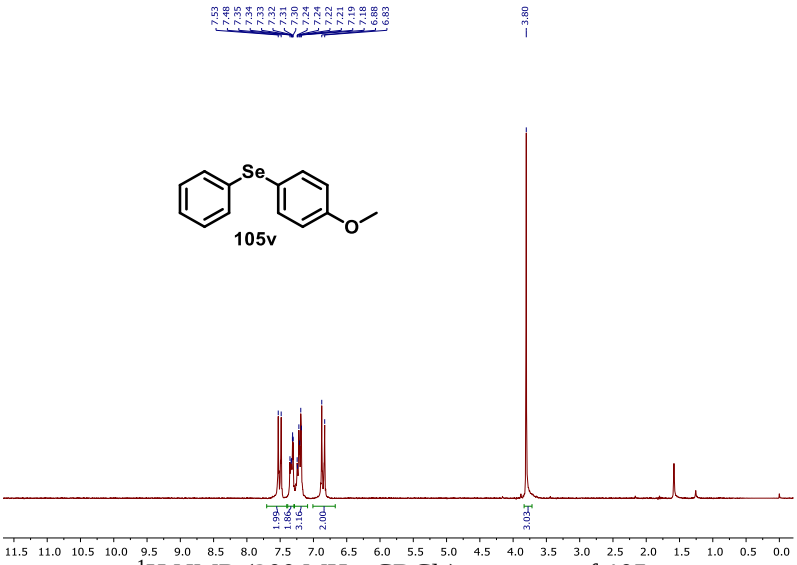
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105t**



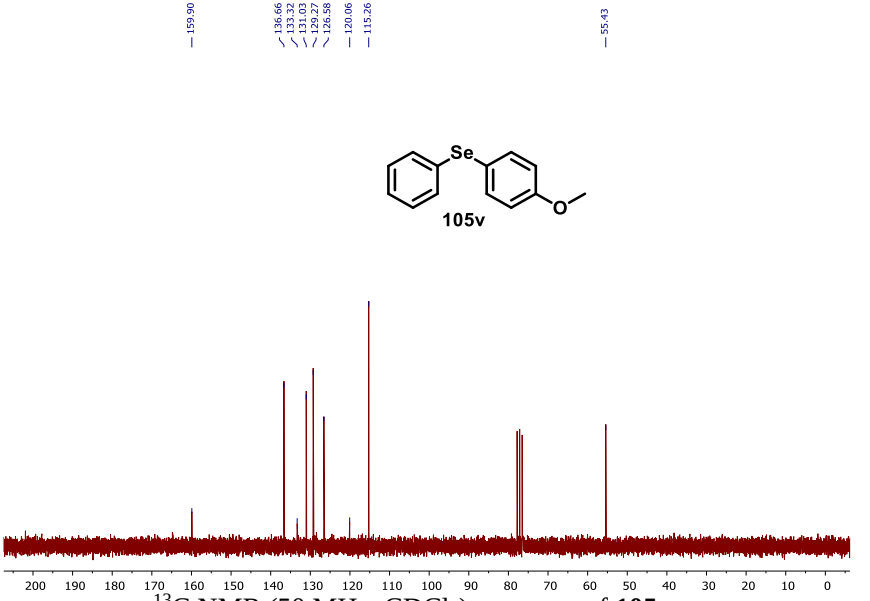
NMR (200 MHz, $CDCl_3$) spectrum of **105u**



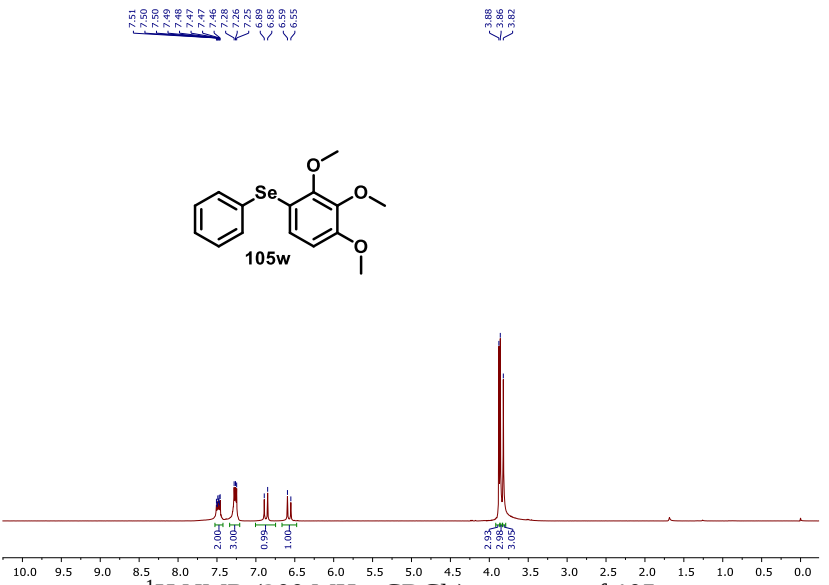
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105u**



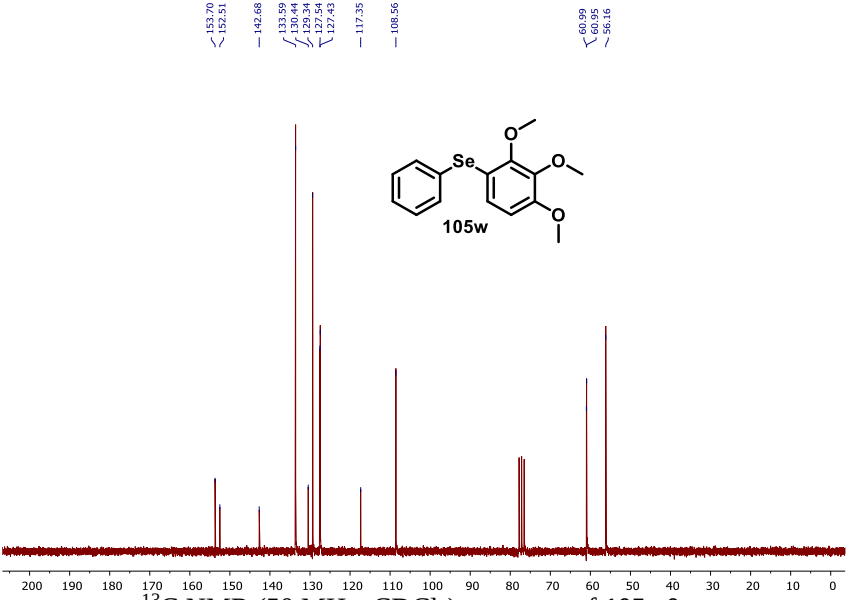
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105v**



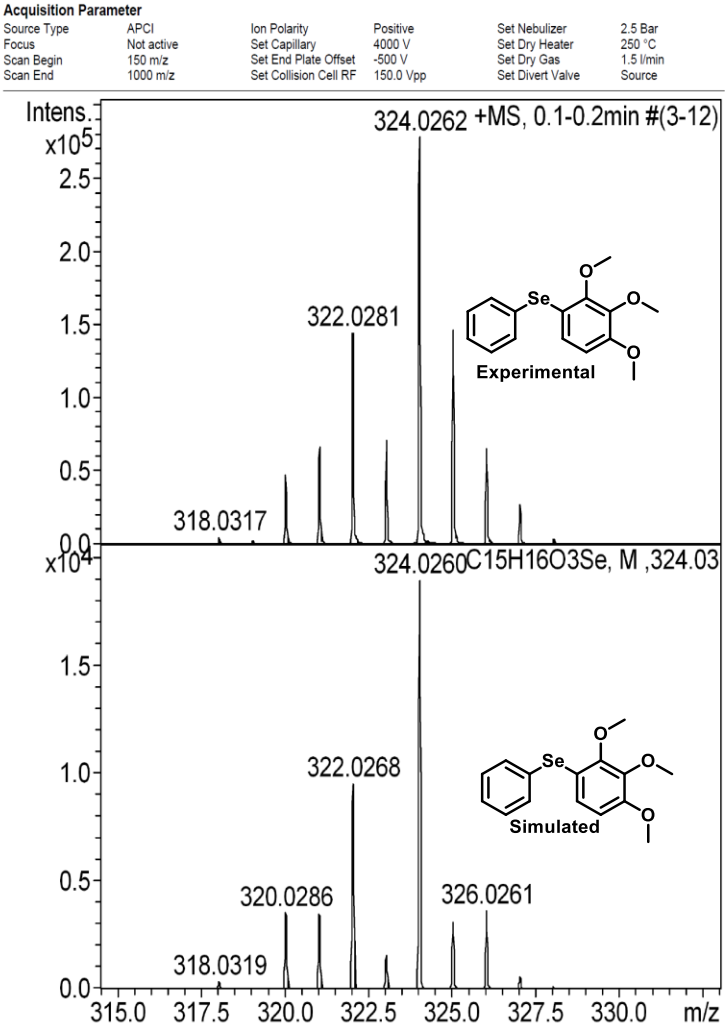
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105v**



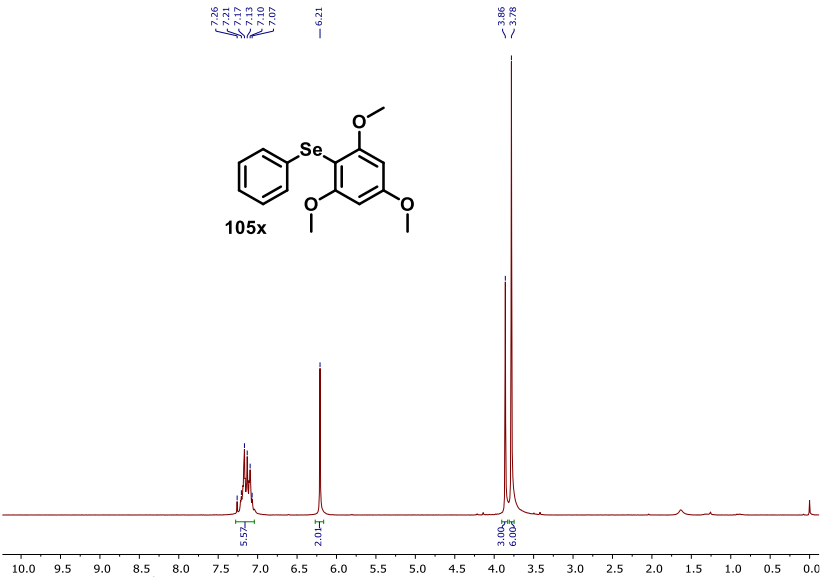
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105w**



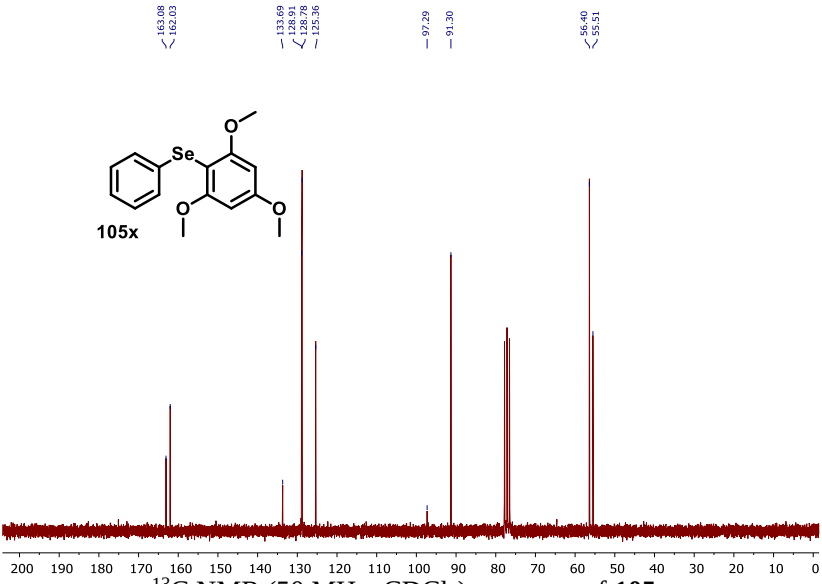
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105w0**



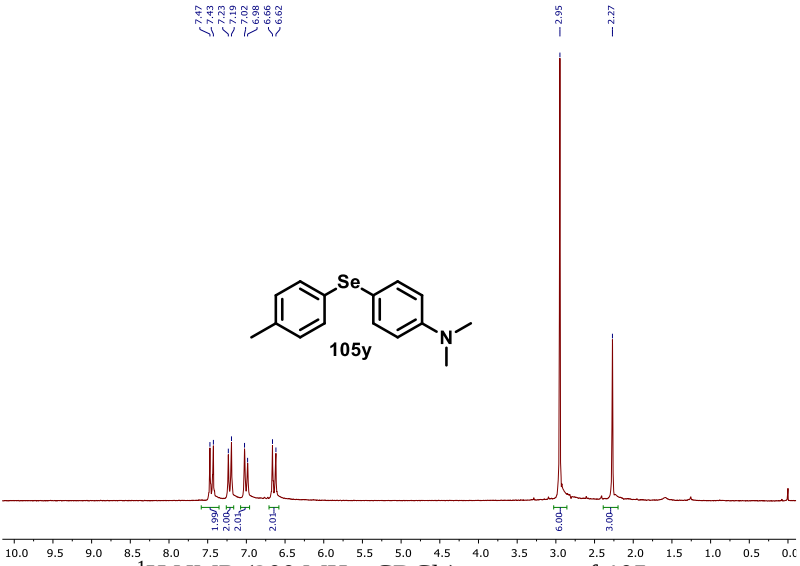
High-resolution mass spectrum of compound **105w**



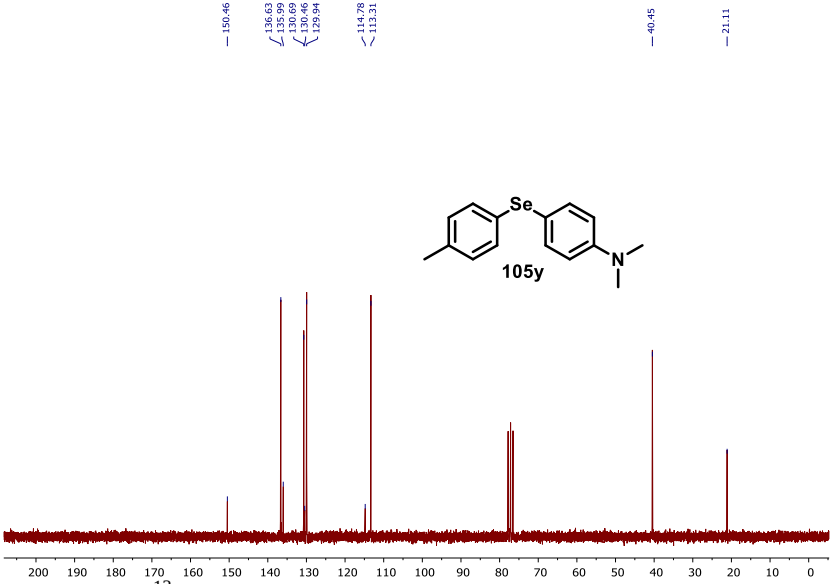
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105x**



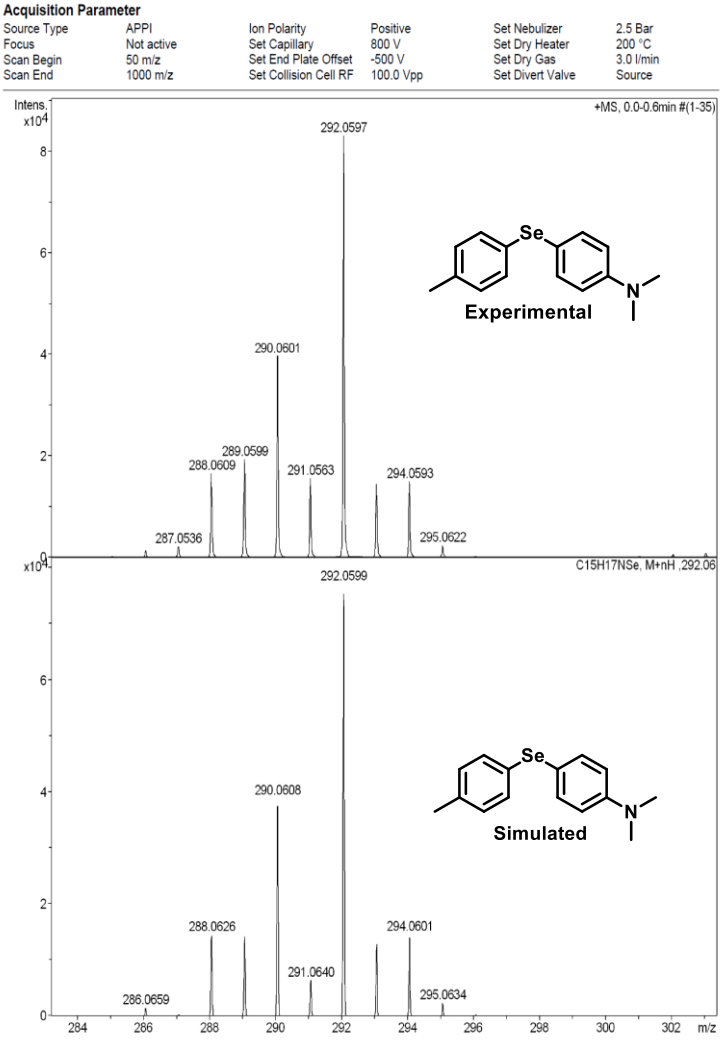
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105x**



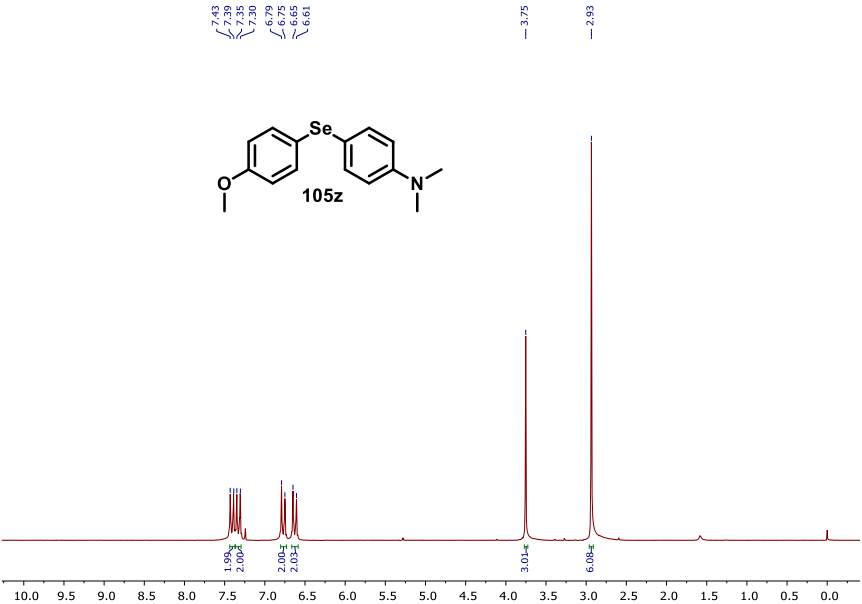
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105y**



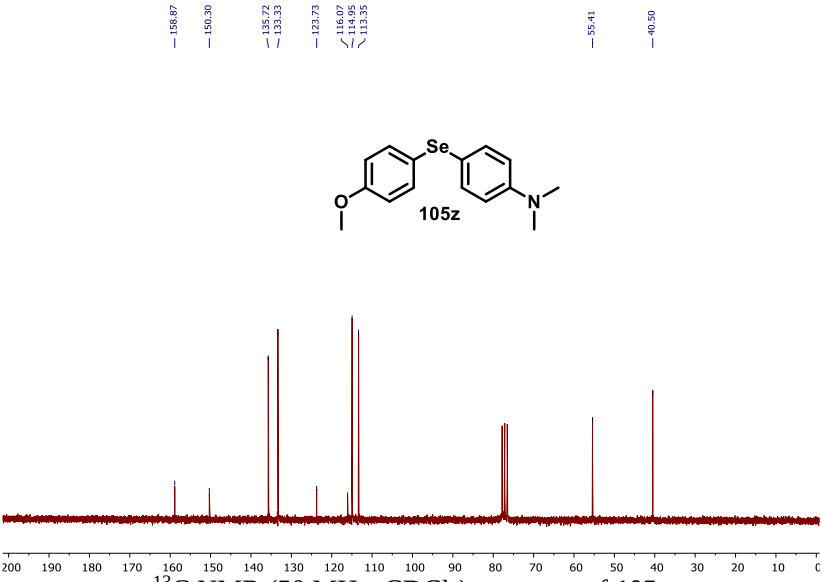
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105y**



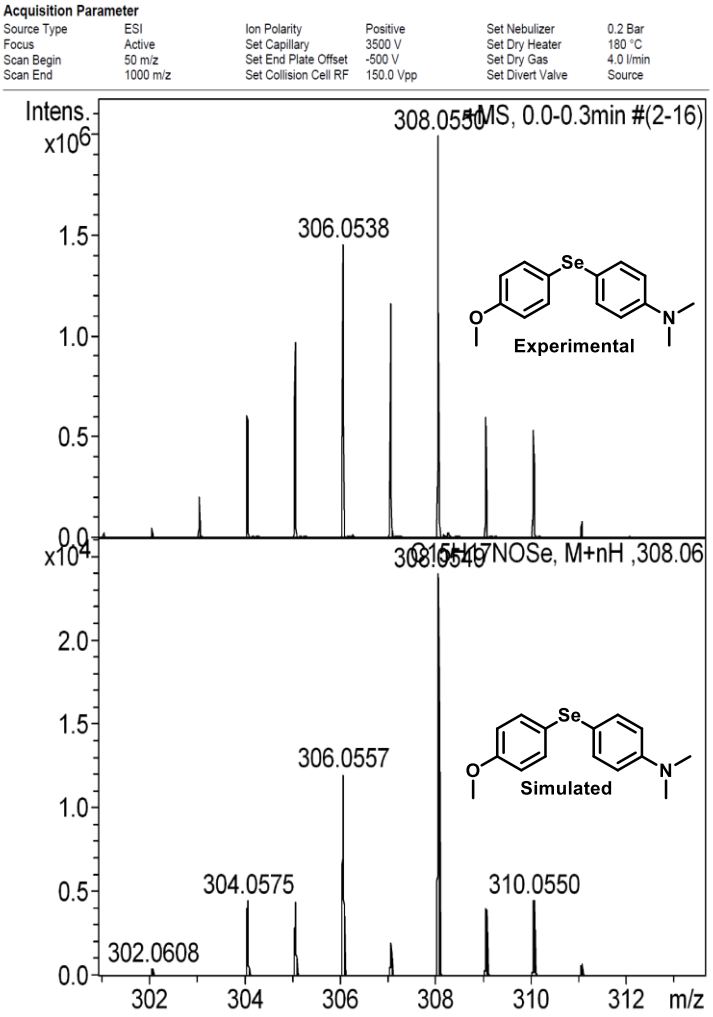
High-resolution mass spectrum of compound **105y**



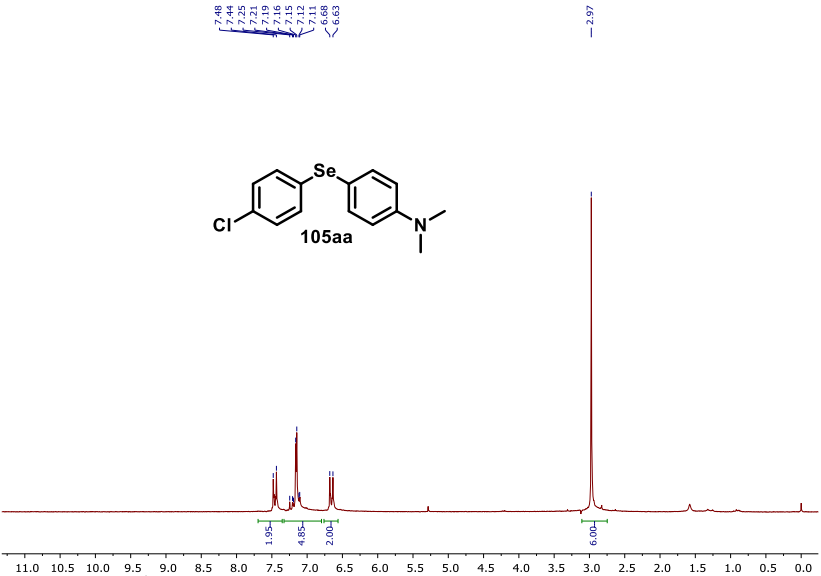
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105z**



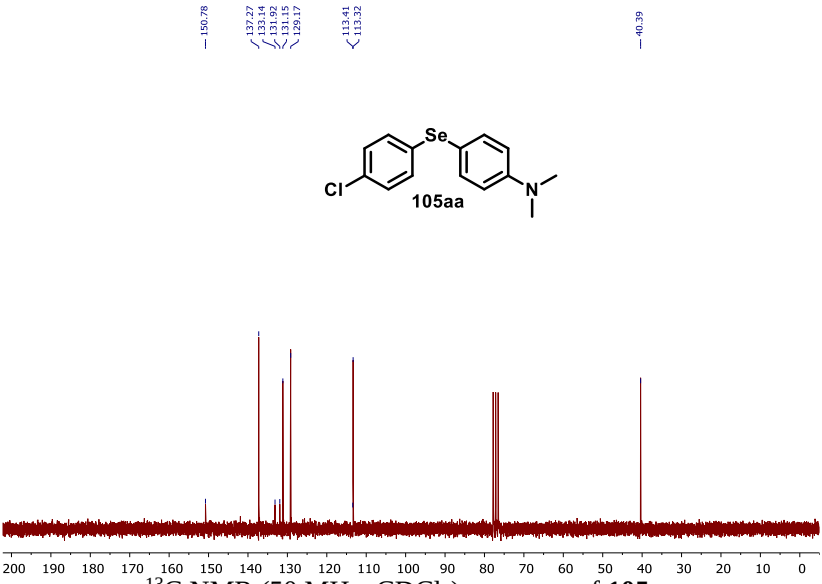
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105z**



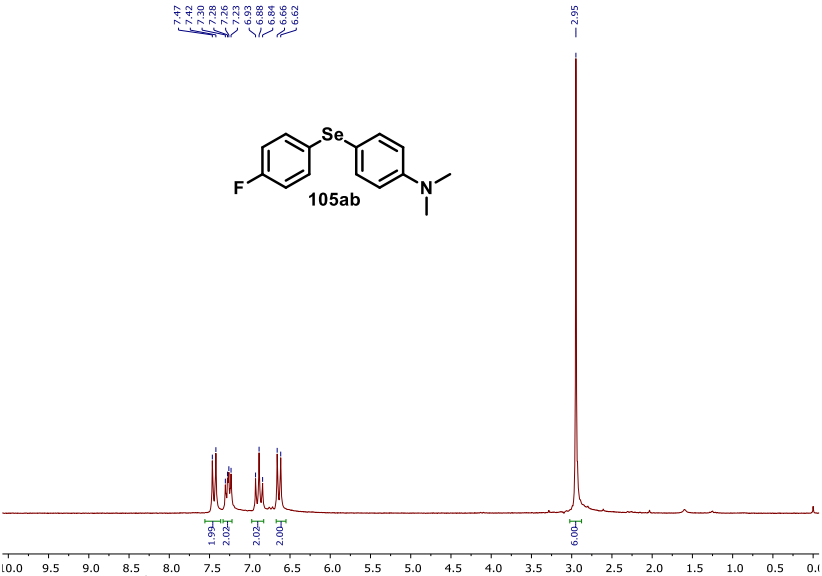
High-resolution mass spectrum of compound **105z**



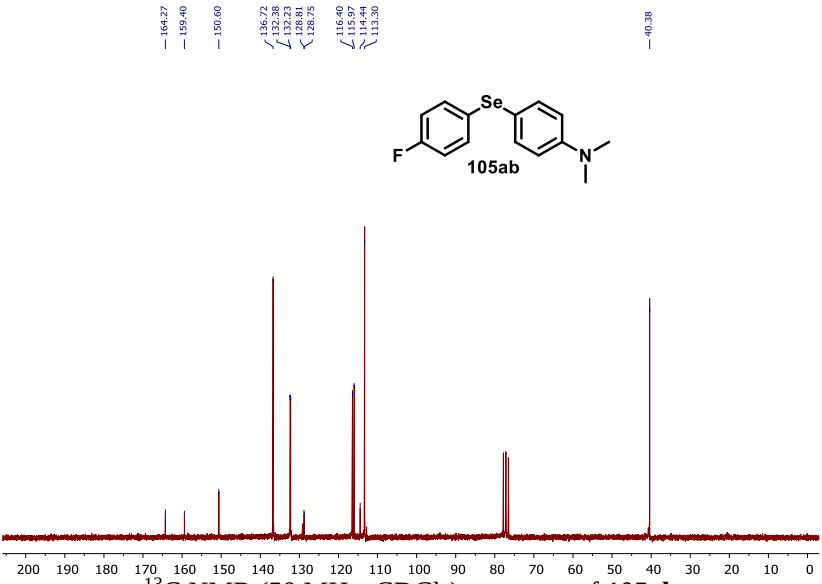
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105aa**



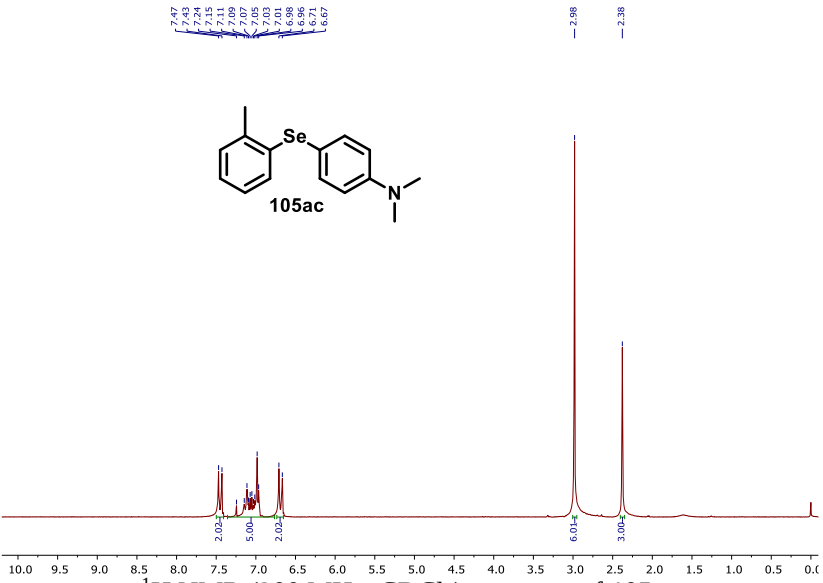
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105aa**



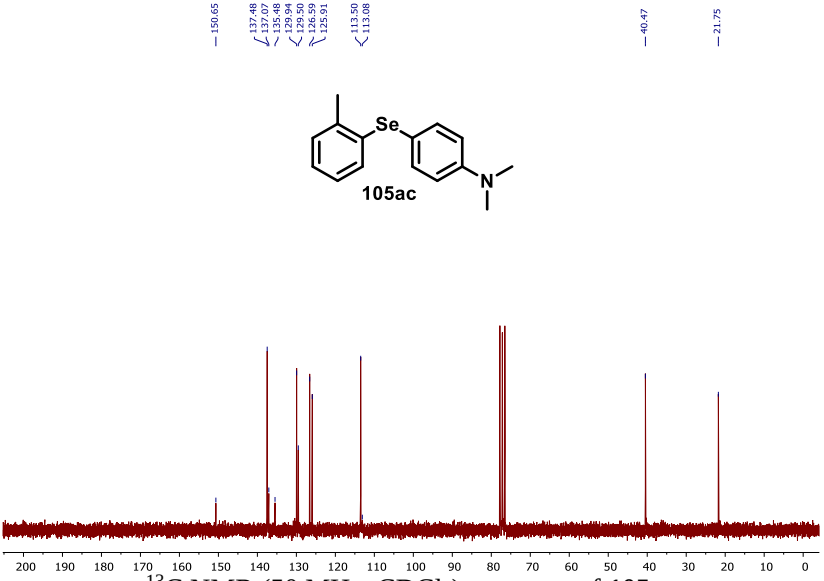
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ab**



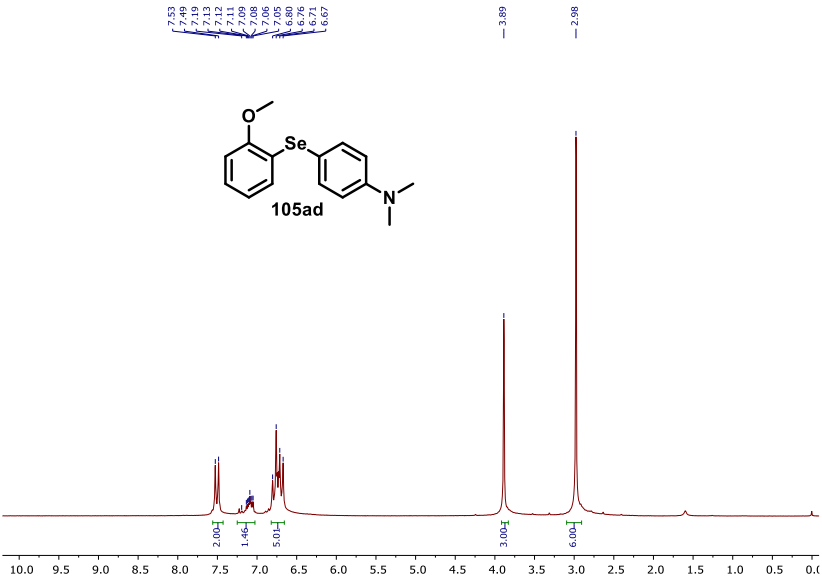
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ab**



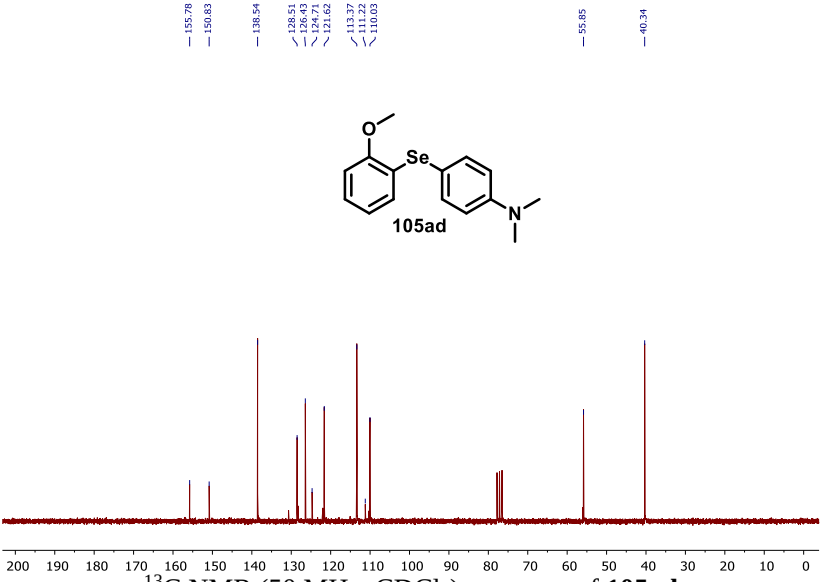
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ac**



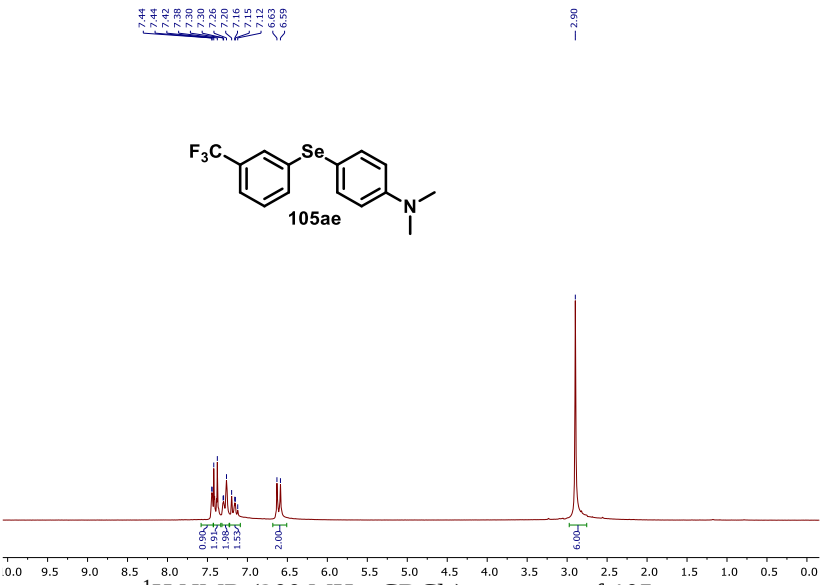
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ac**



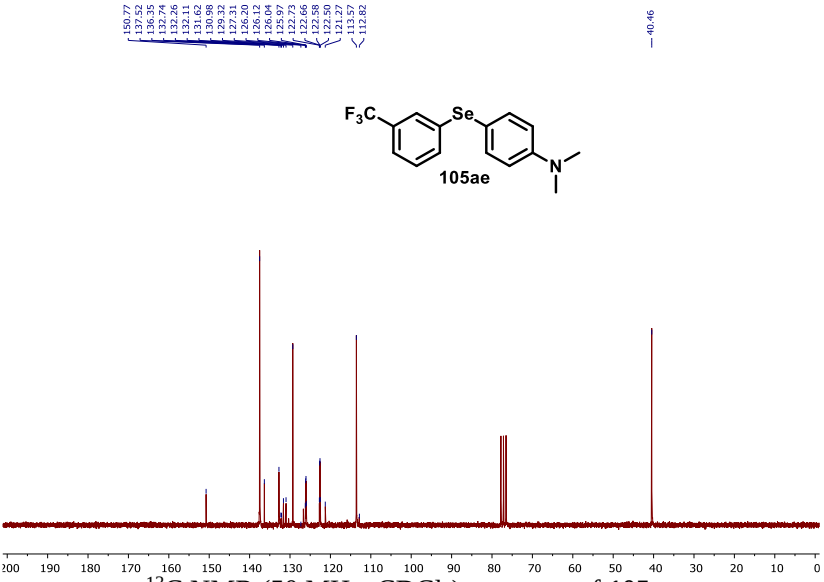
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ad**



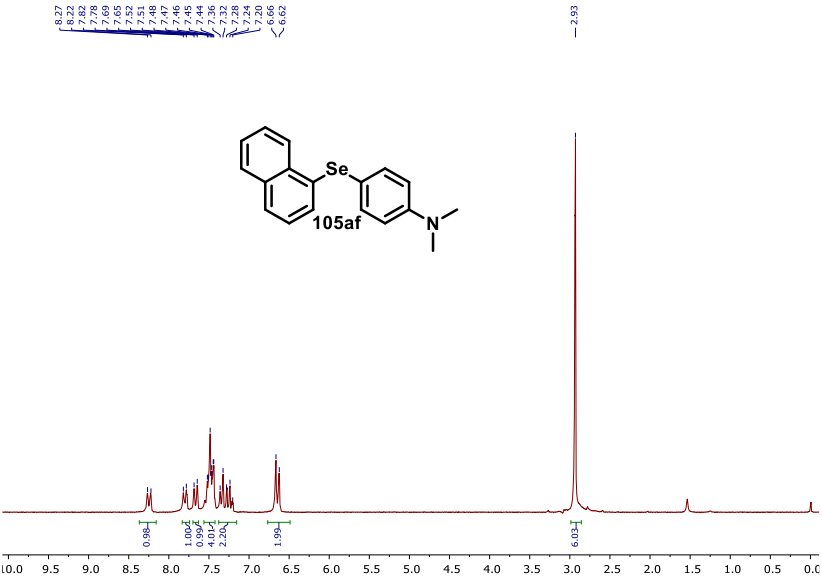
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ad**



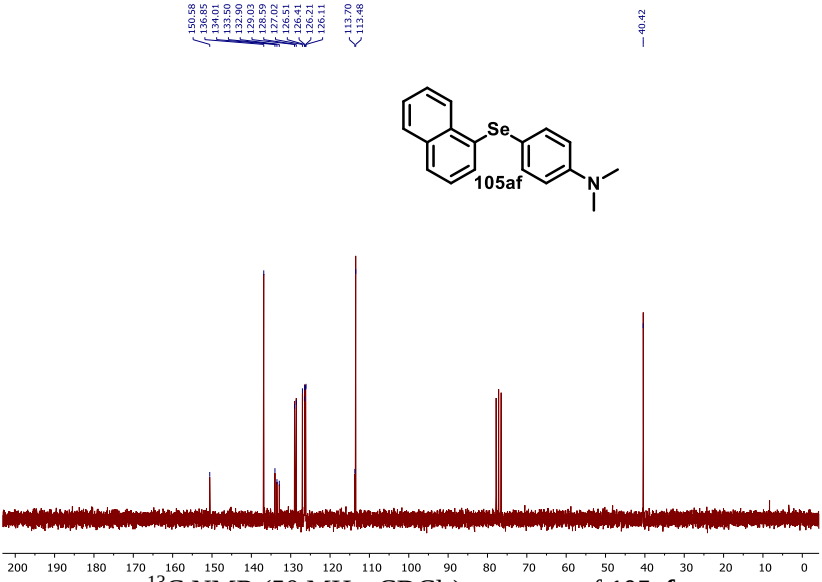
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ae**



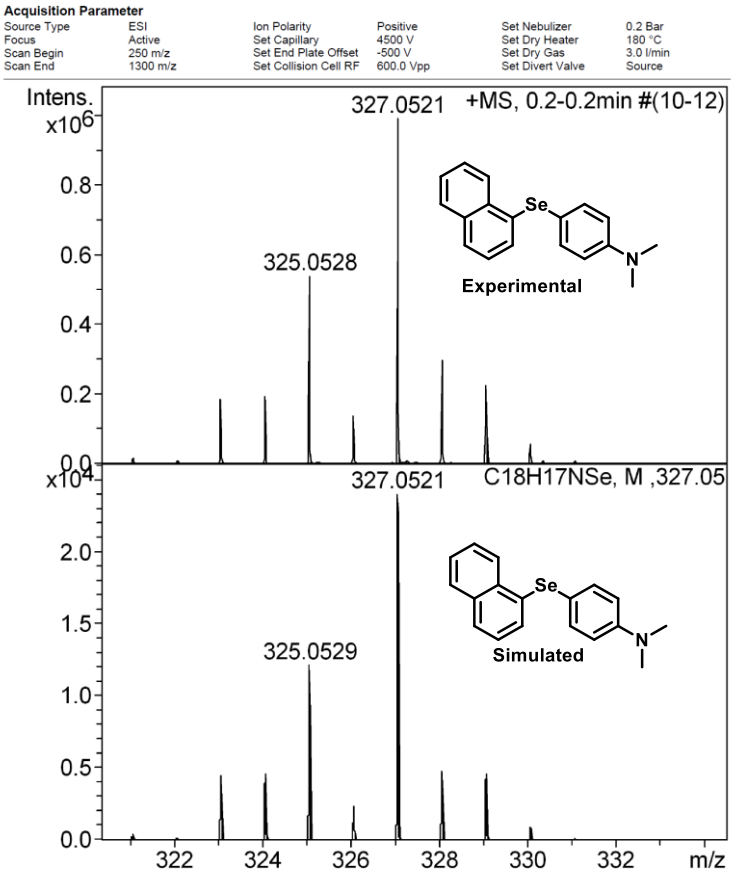
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ae**



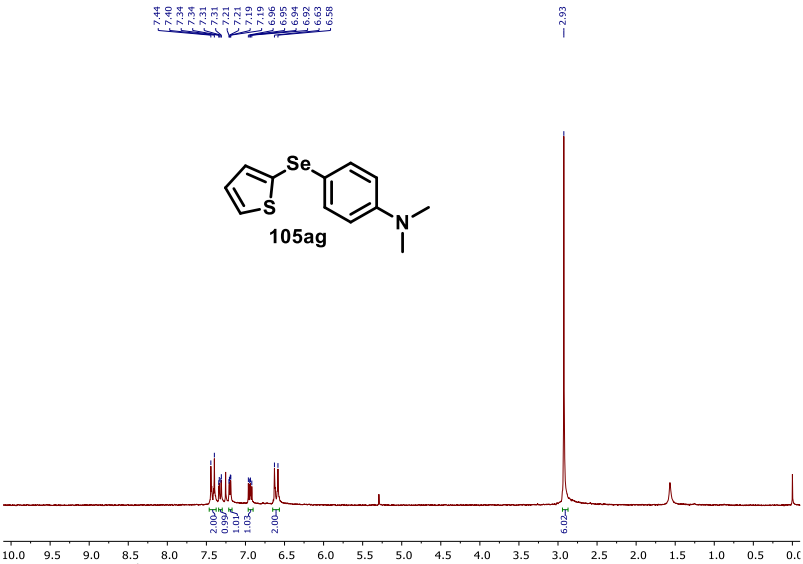
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105af**



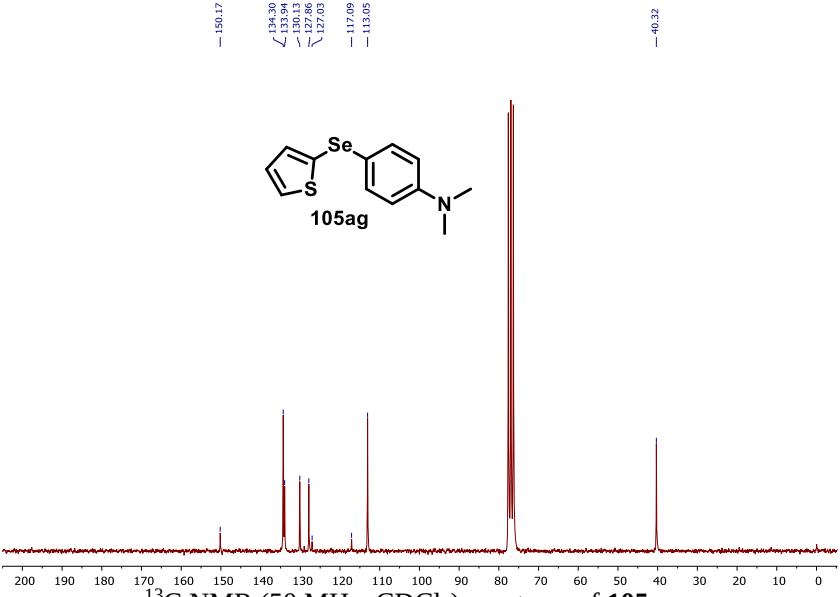
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105af**



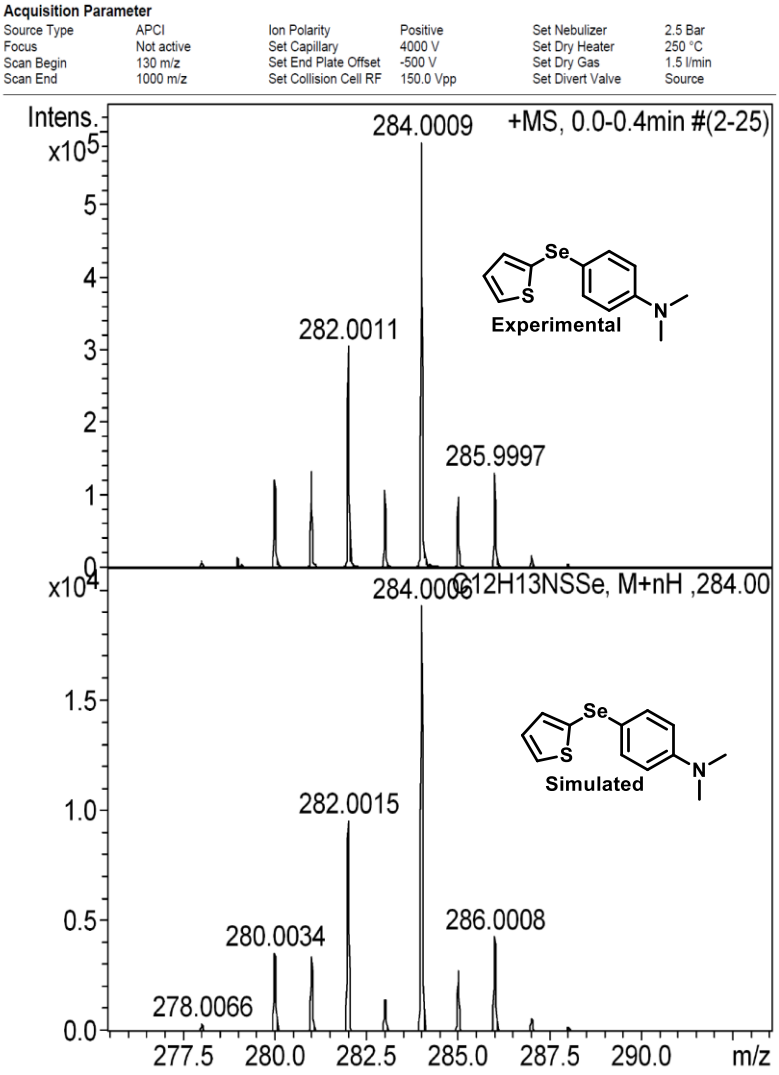
High-resolution mass spectrum of compound **105af**



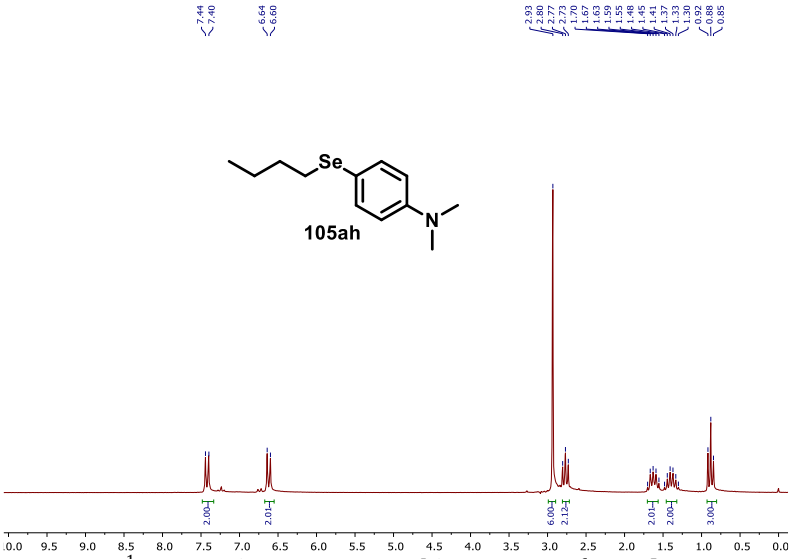
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ag**



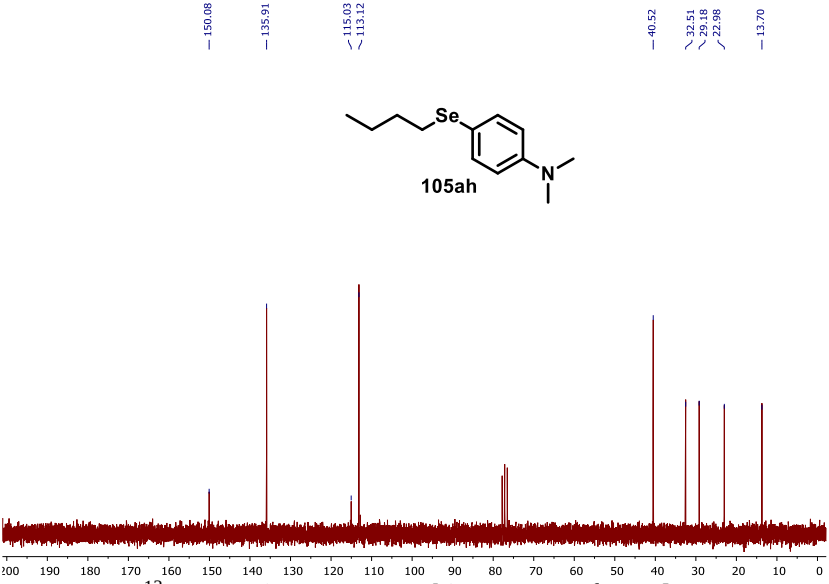
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ag**



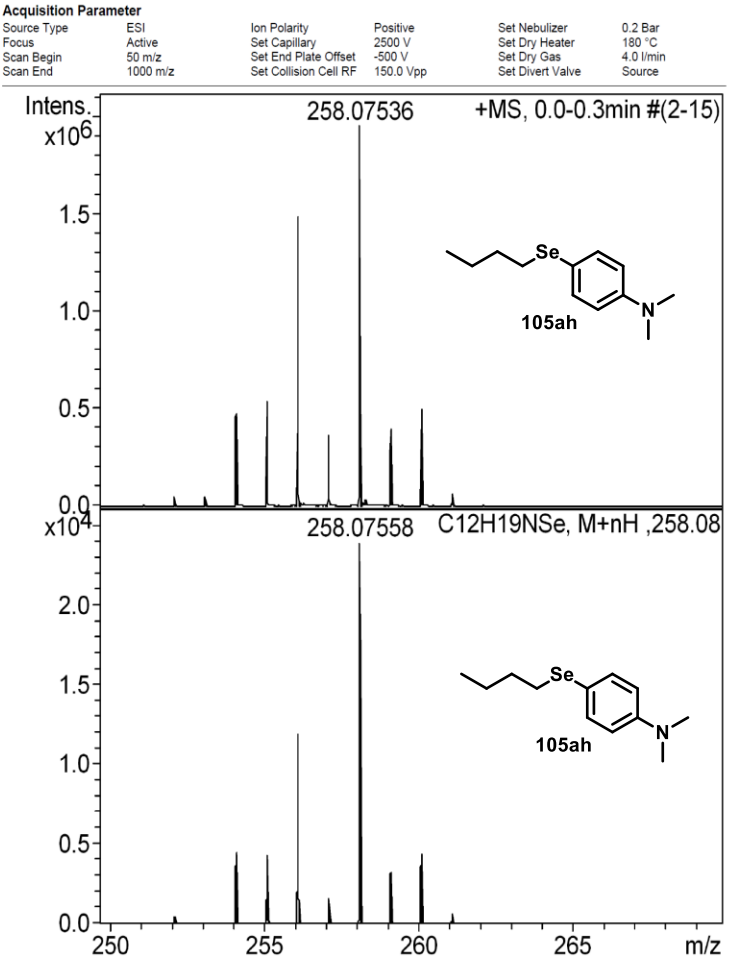
High-resolution mass spectrum of compound **105ag**



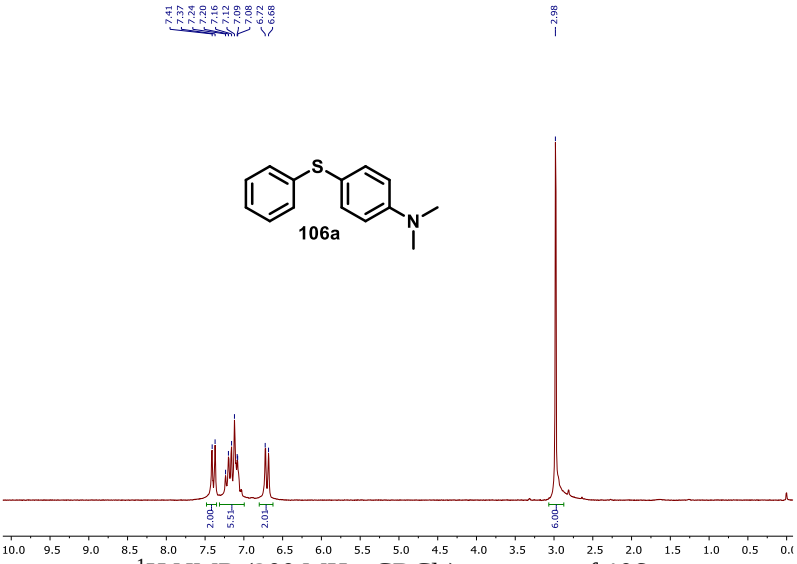
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **105ah**



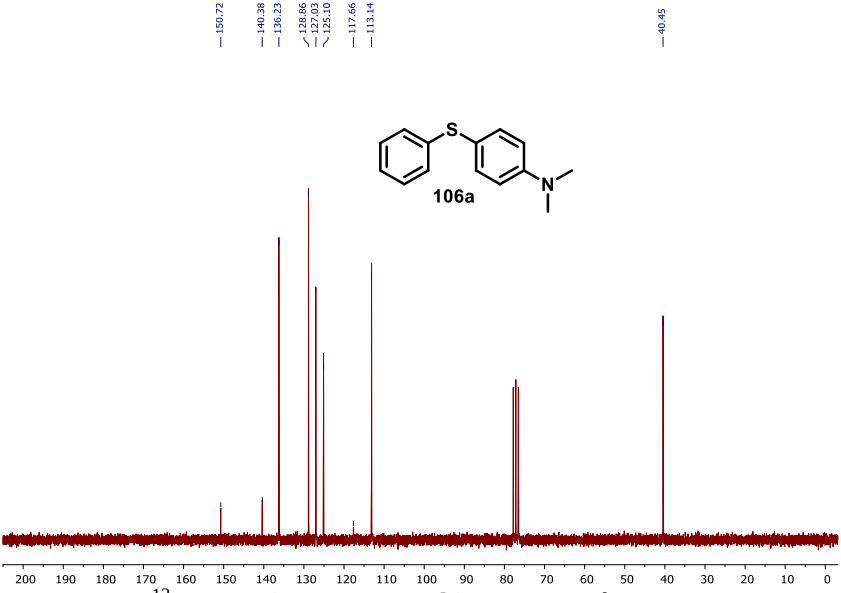
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **105ah**



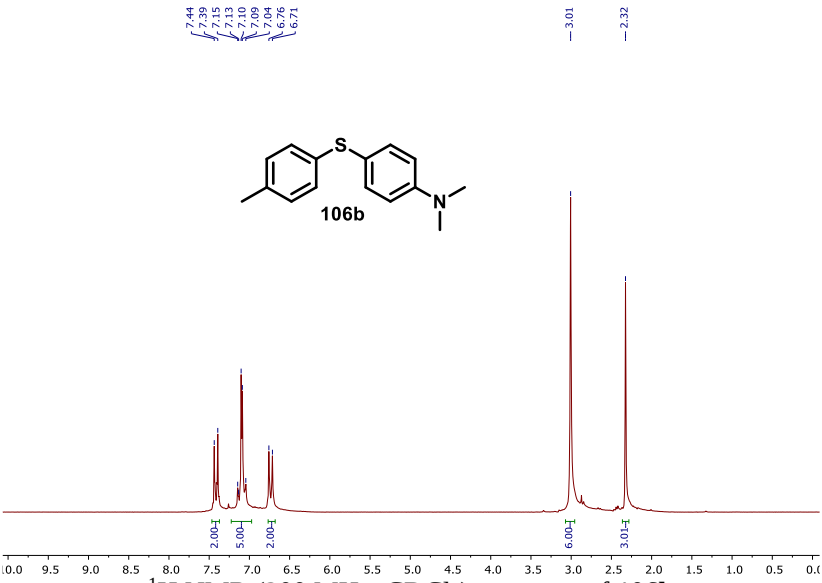
High-resolution mass spectrum of compound **105ah**



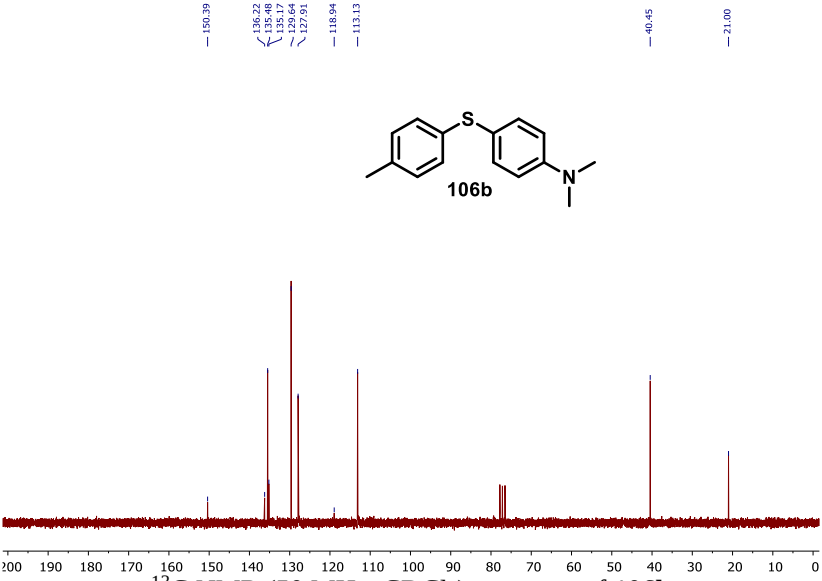
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106a**



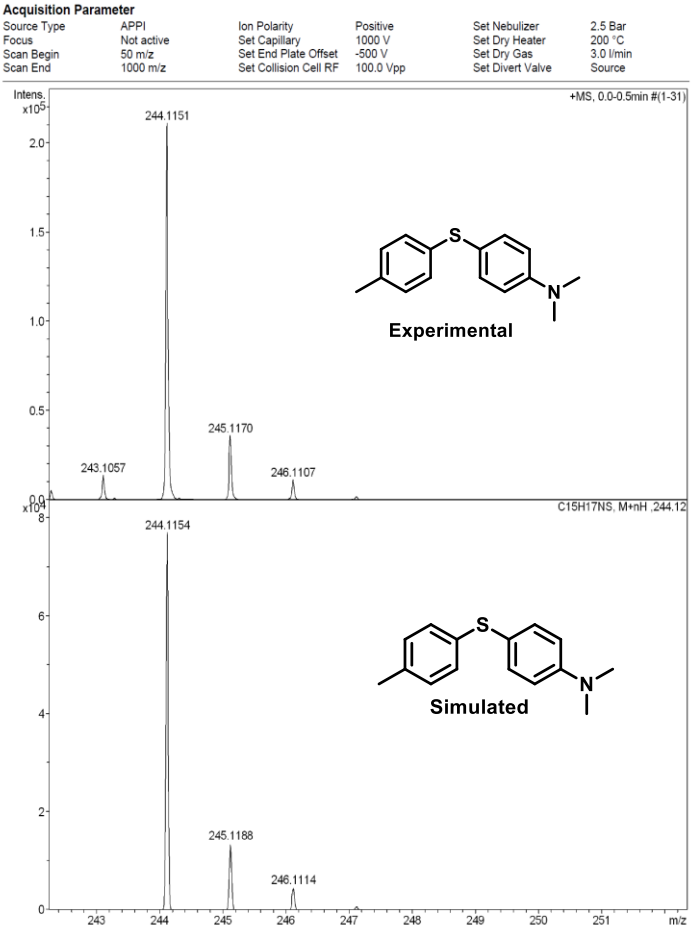
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106a**



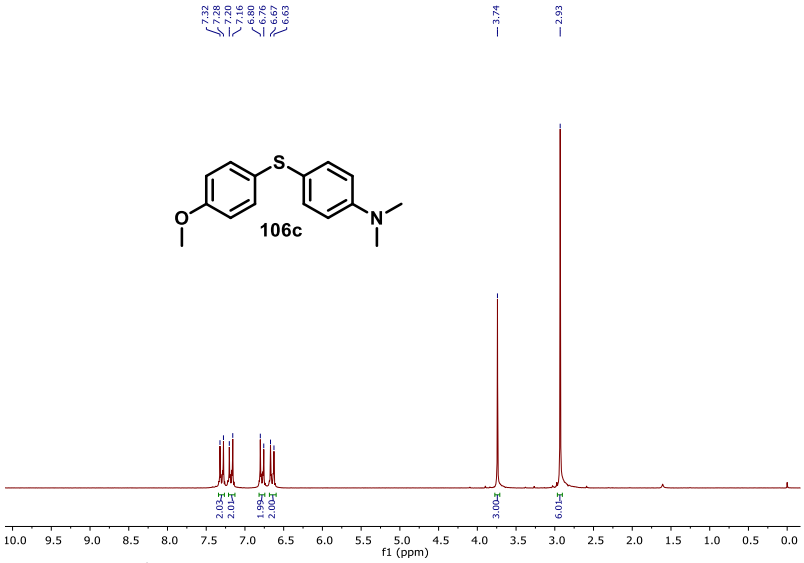
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106b**



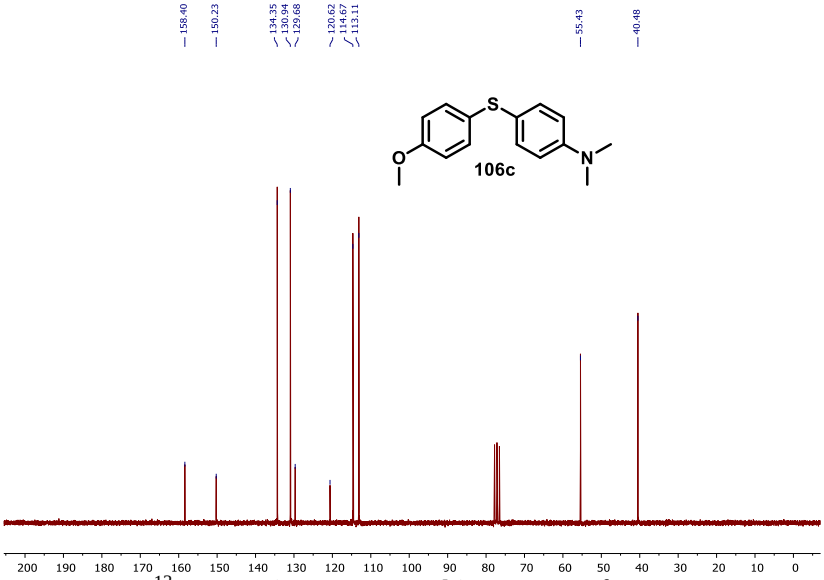
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106b**



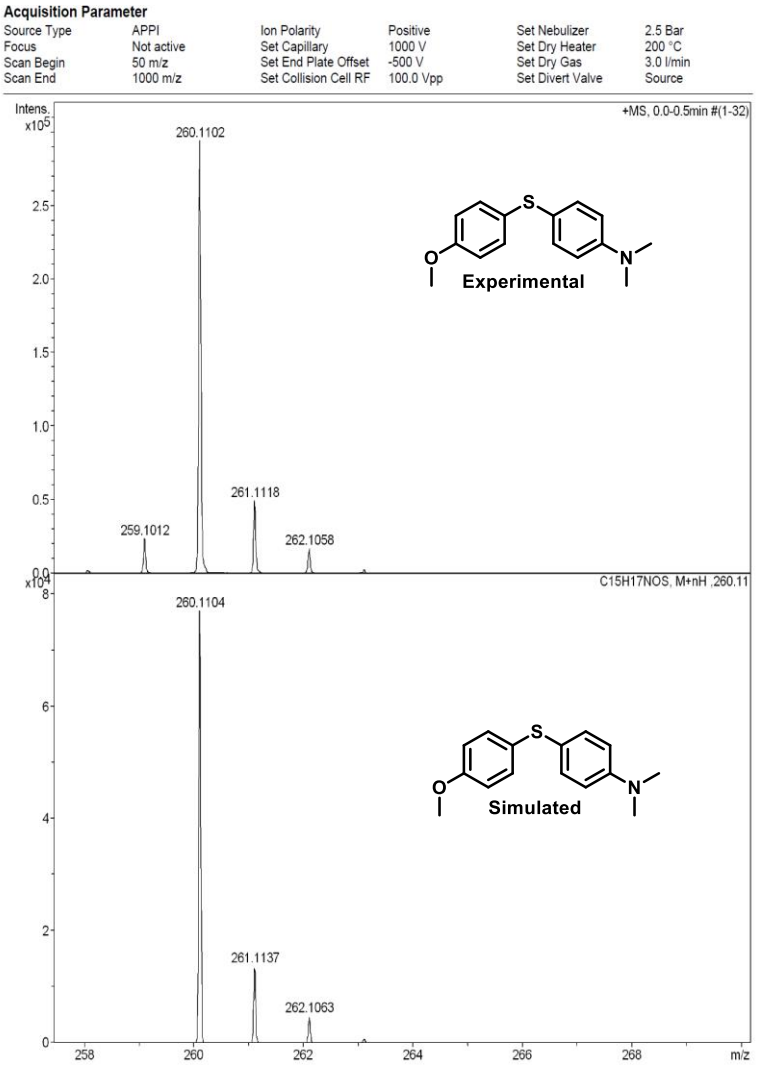
High-resolution mass spectrum of compound **106b**



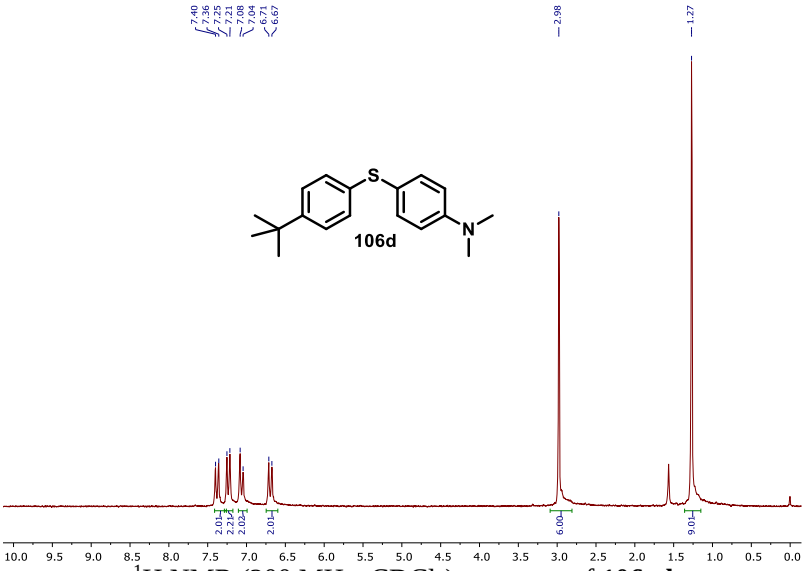
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106c**



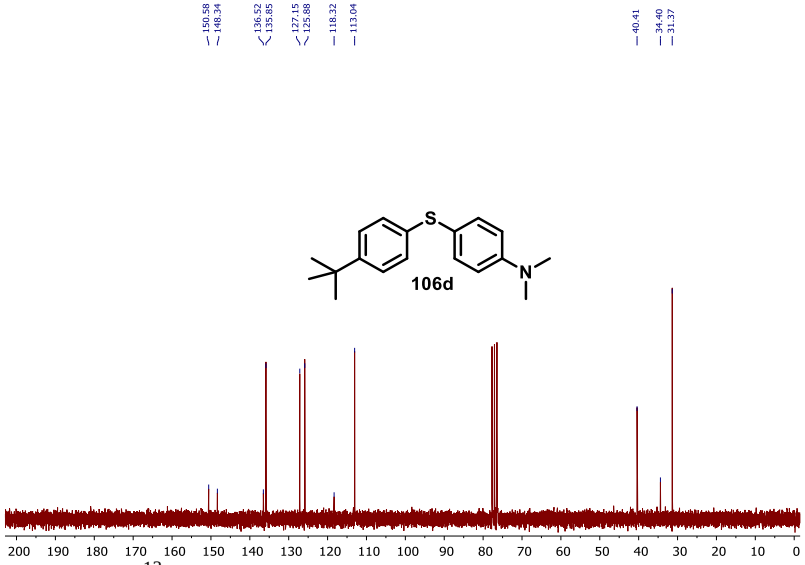
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106c**



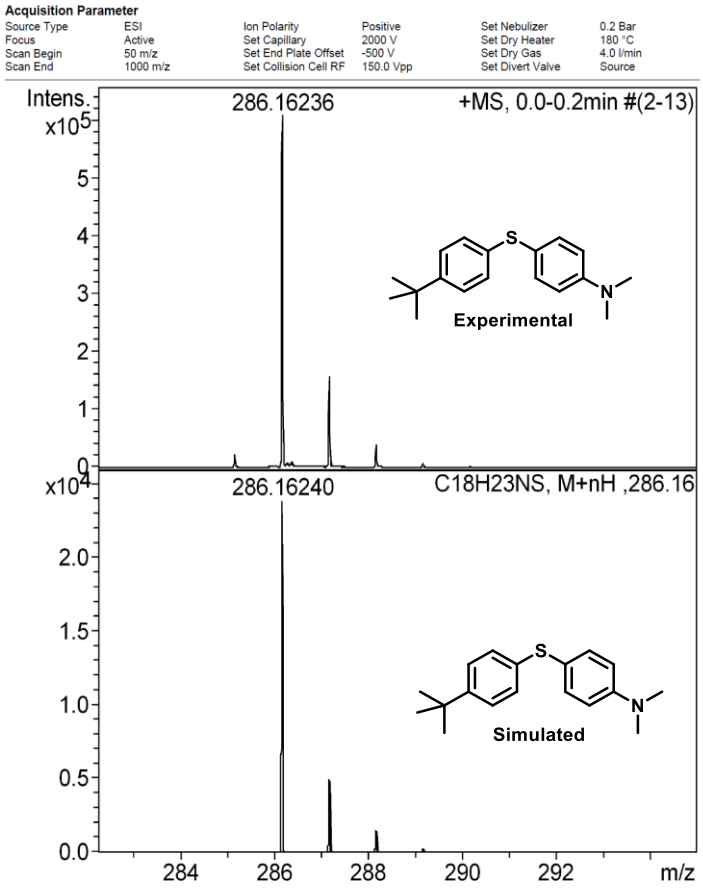
High-resolution mass spectrum of compound **106c**



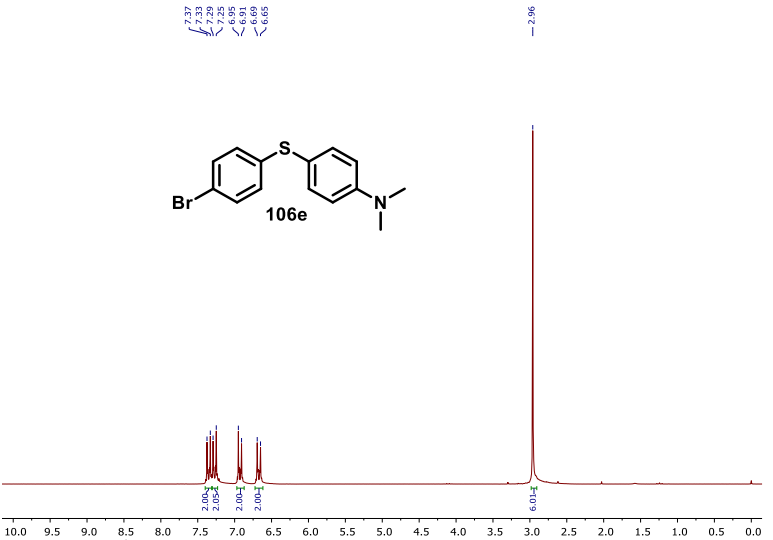
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106ad**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106d**



High-resolution mass spectrum of compound **106d**



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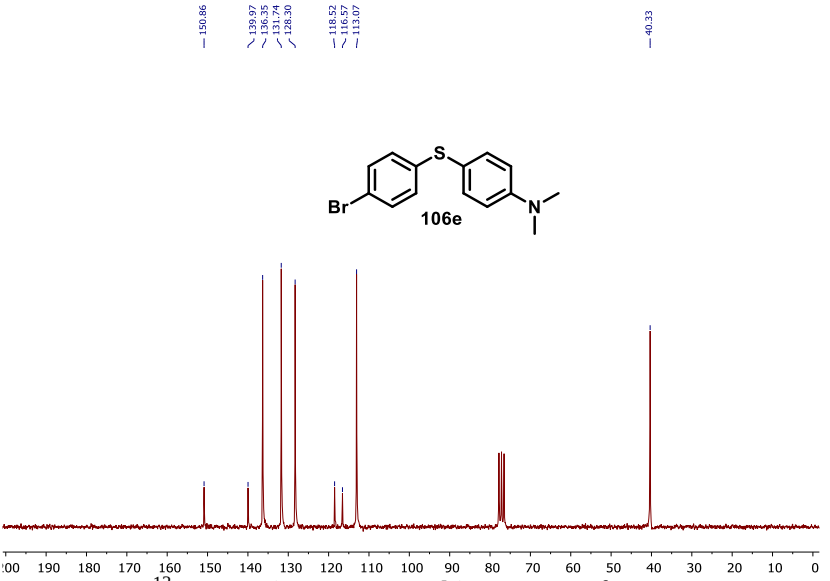
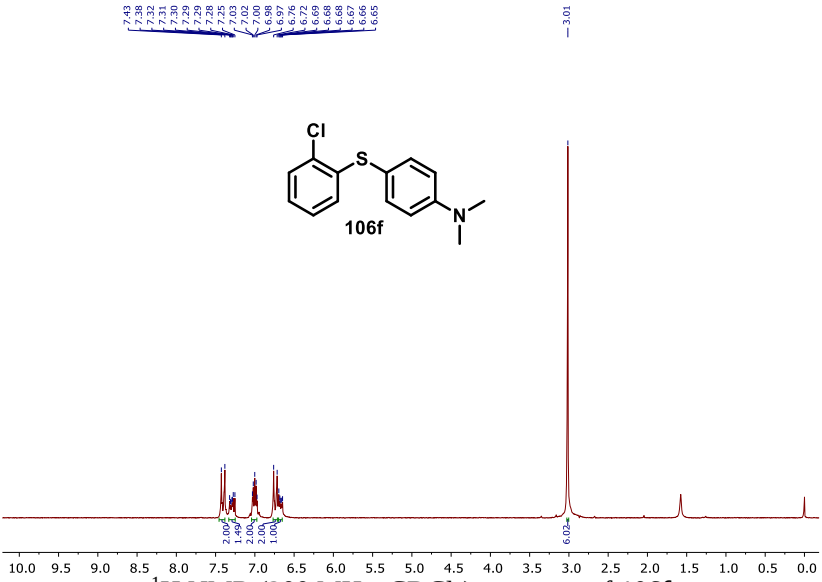
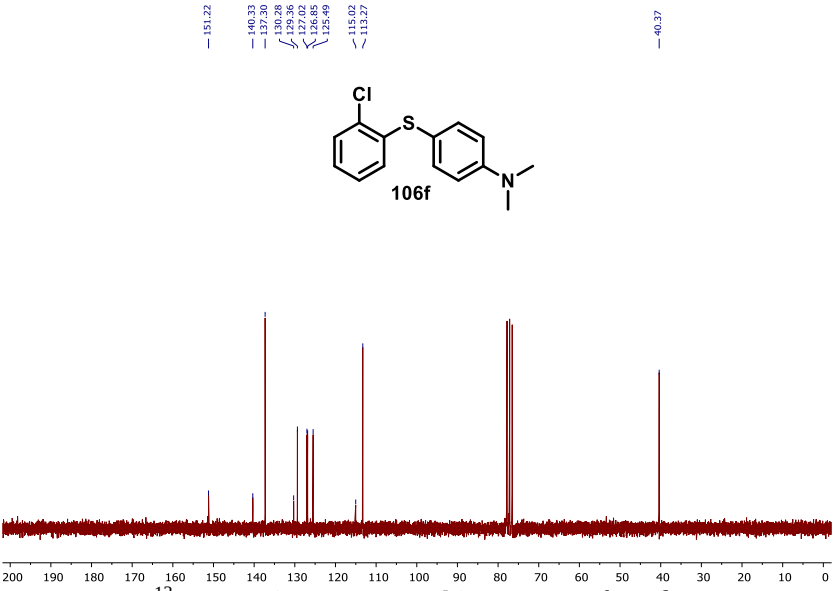


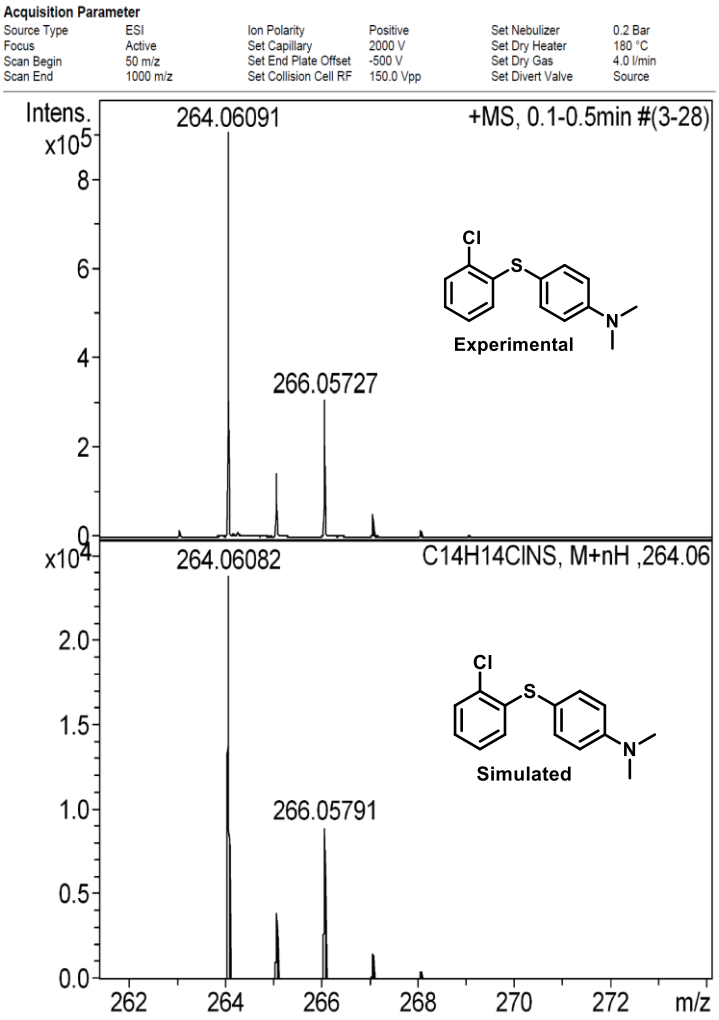
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106e**



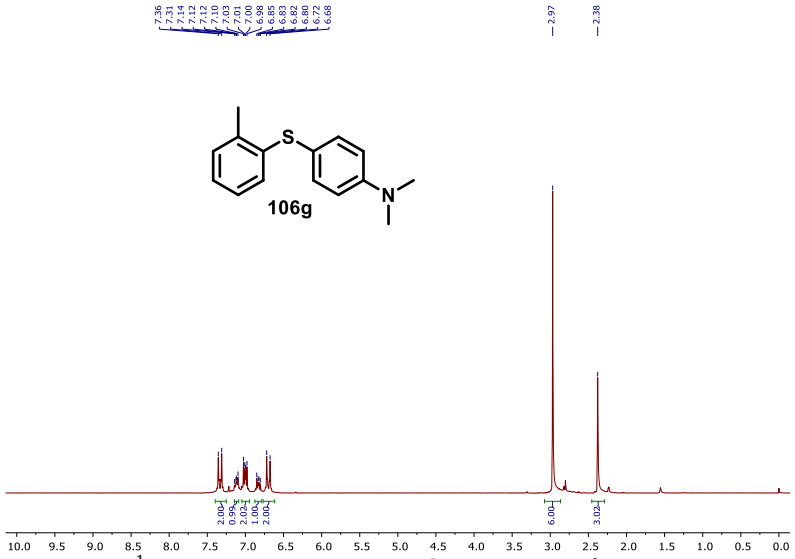
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106f**



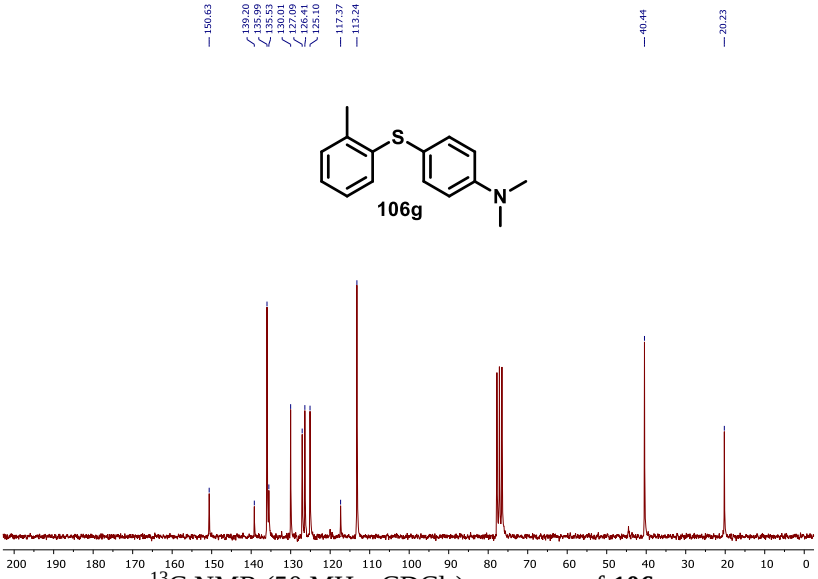
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106f**



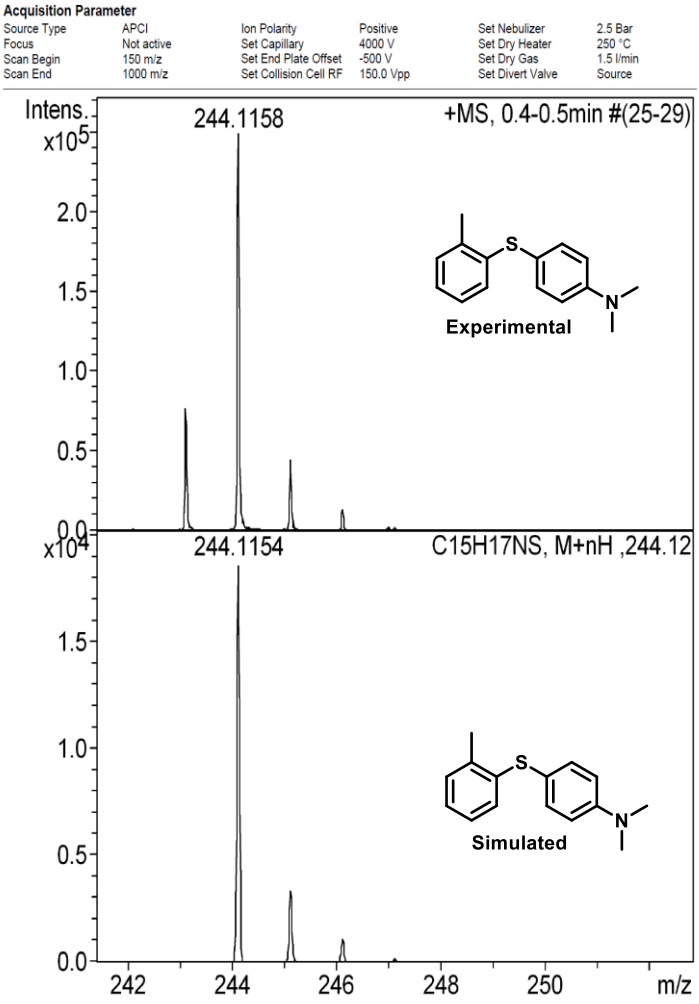
High-resolution mass spectrum of compound **106f**



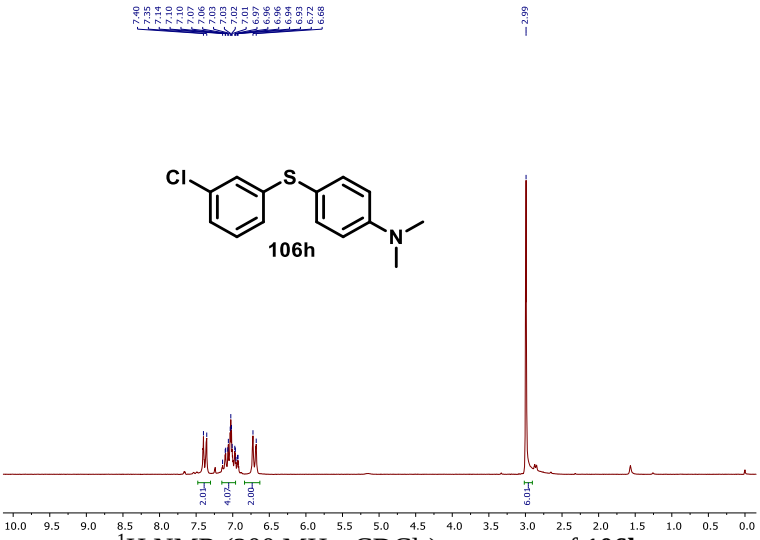
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106g**



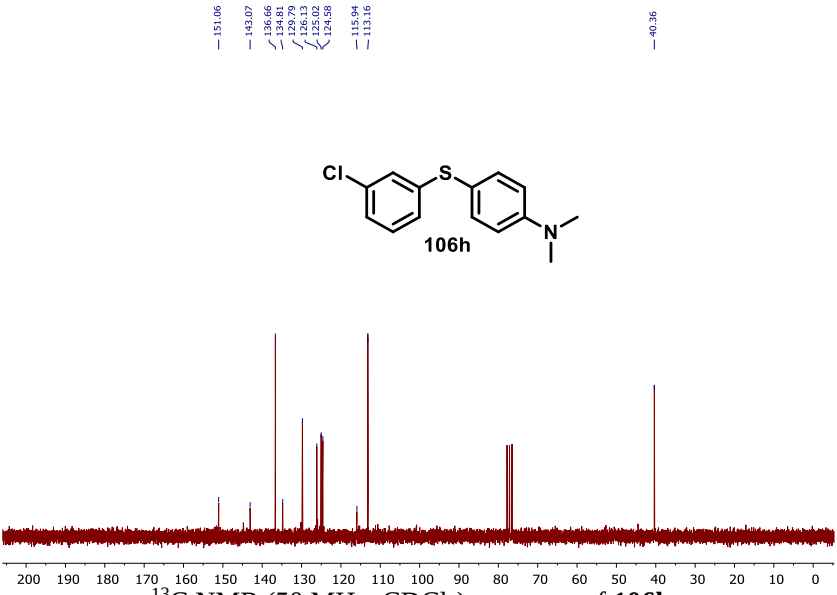
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106g**



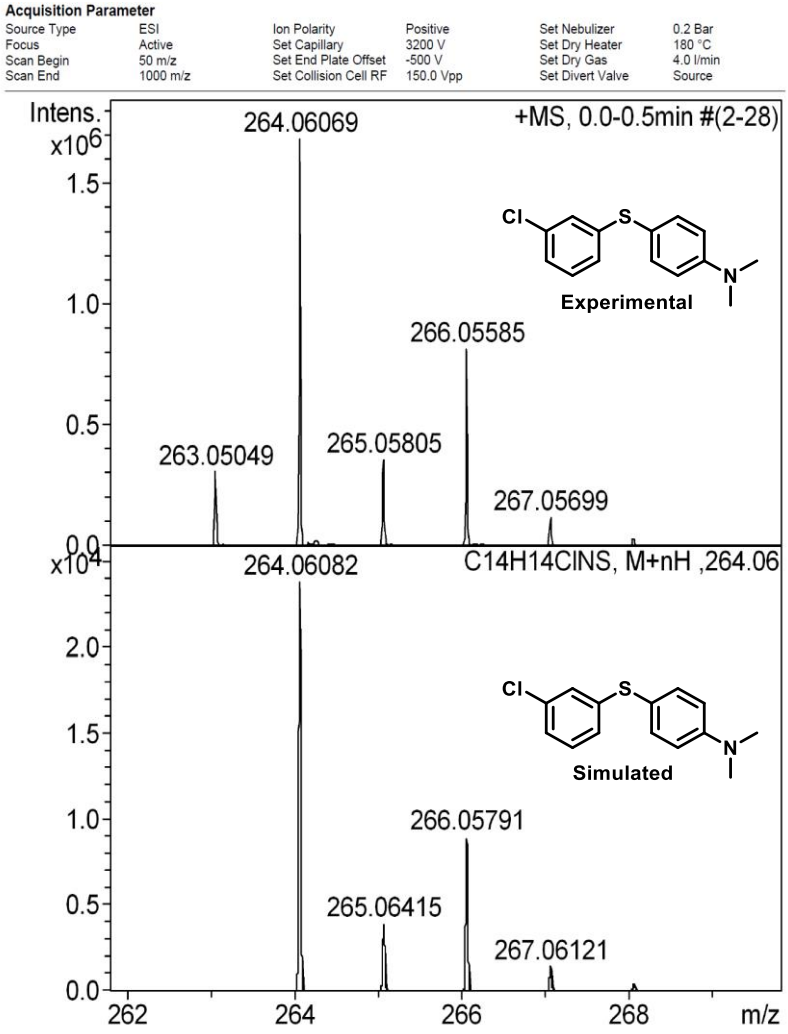
High-resolution mass spectrum of compound **106g**



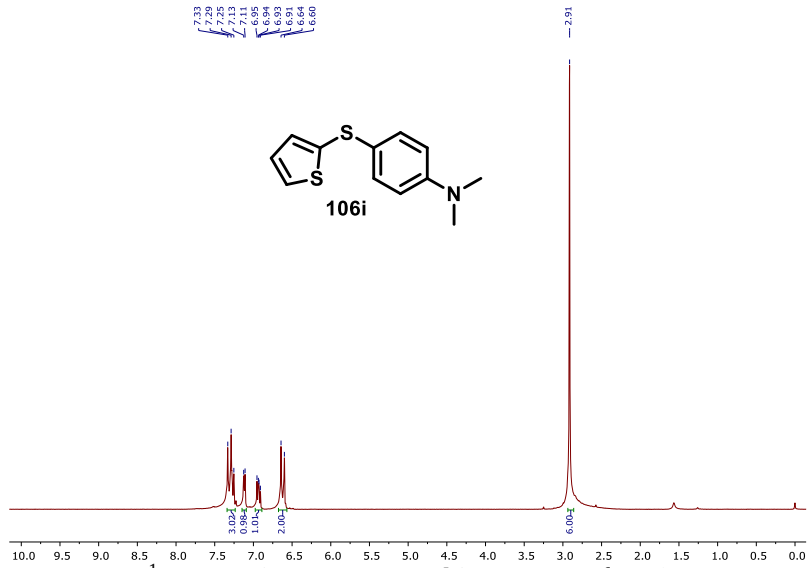
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106h**



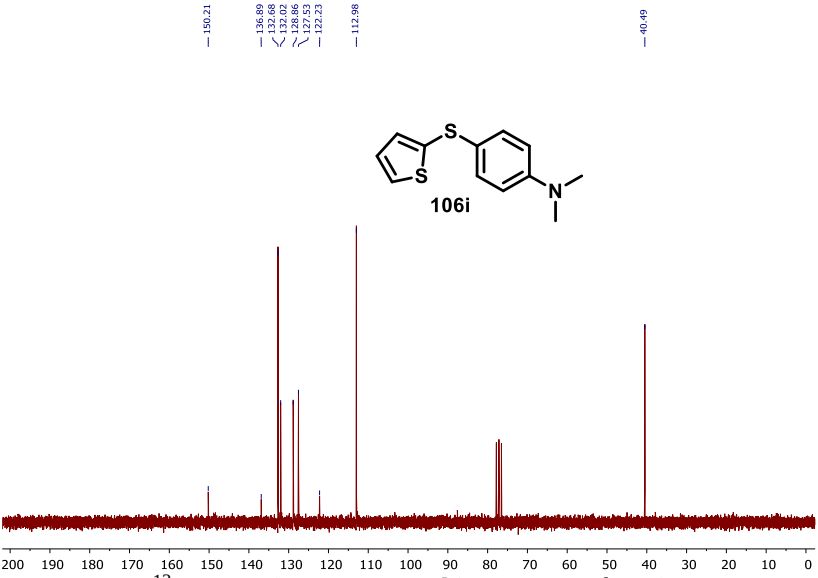
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106h**



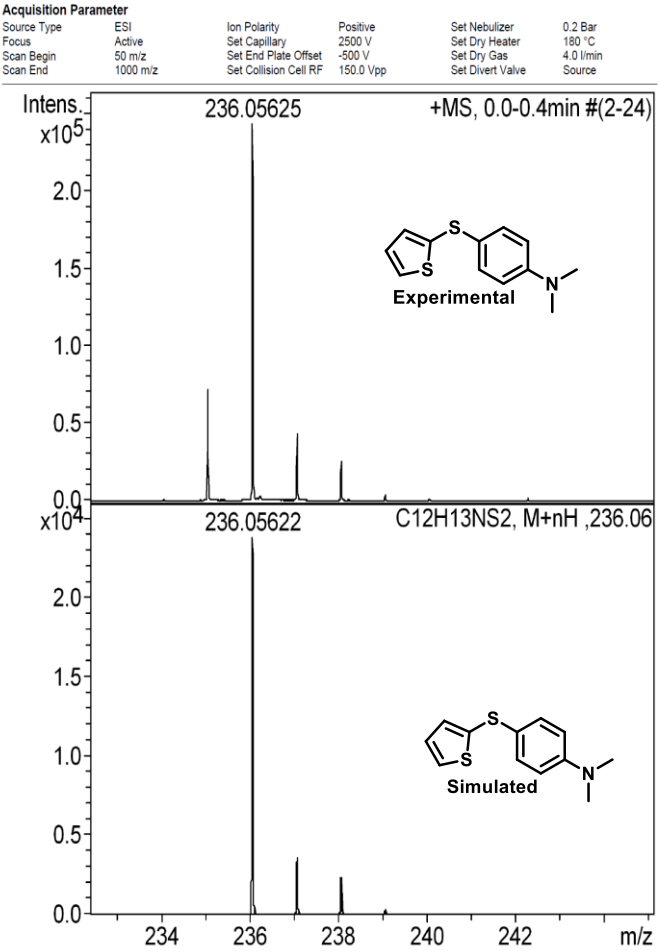
High-resolution mass spectrum of compound **106h**



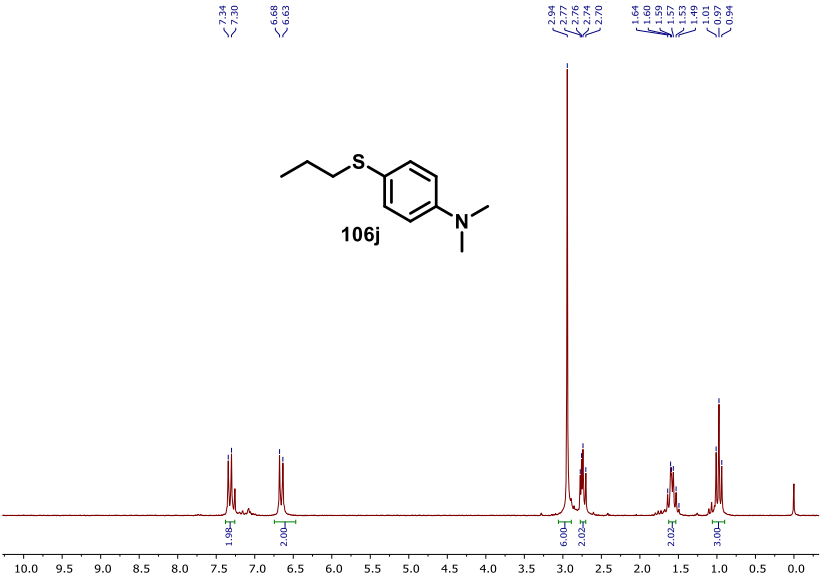
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106i**



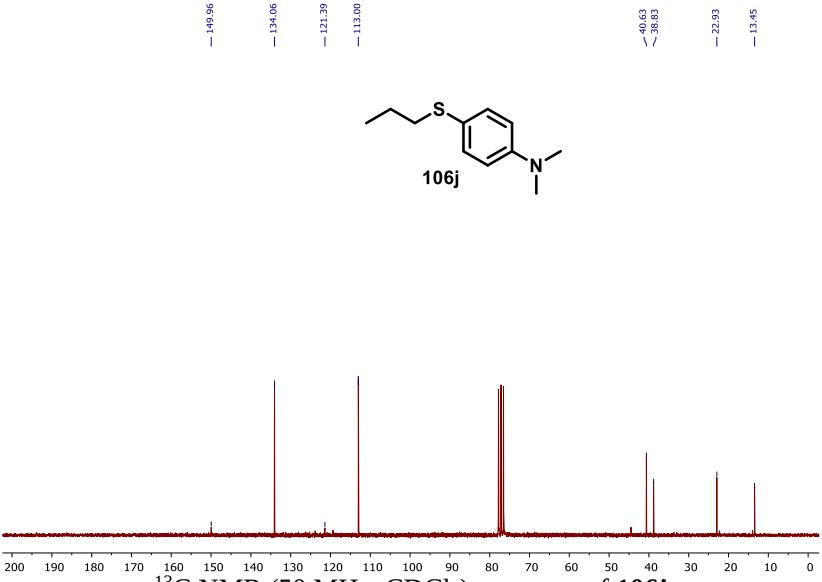
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106i**



High-resolution mass spectrum of compound **106i**



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **106j**



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **106j**

Annexes

1. Published/Accepted Article

Catalysis Science & Technology

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cy01503k

DMSO/iodine-catalyzed oxidative C–Se/C–S bond formation: a regioselective synthesis of unsymmetrical chalcogenides with nitrogen- or oxygen-containing arenes†

Sumbal Saba, Jamal Rafique and Antonio L. Braga*

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www.rsc.org/catalysis

A convenient metal-free and solvent-free iodine-catalyzed regioselective greener protocol to access different types of unsymmetrical chalcogenides with nitrogen- or oxygen-containing arenes through oxidative C–Se/C–S formation *via* direct C(sp^2)–H bond activation was developed. The products were obtained in good to excellent yields using [O or N]-containing arenes, half equiv. of various odorless diorganyl dichalcogenides (S/Se), iodine (20 mol%) as the catalyst and 3 equiv. of DMSO as the oxidant, applying MW irradiation for 10 min.

Introduction

In recent years, reactions under metal-free and solvent-free conditions have been widely used in the functionalization of the C–H bond,[1,2] which is considered an important contribution to the development and progress of green chemistry.[3] Additionally, the use of microwave (MW) irradiation may open new horizons in the field of modern sustainable organic synthesis,[4] since it significantly reduces the reaction time and saves energy.[5]

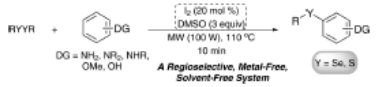
The biological and medicinal properties of organochalcogenides (S, Se) are becoming increasingly appreciated,[6] mainly the antioxidant, antitumor, anti-inflammatory and antiviral activities.[7] Moreover, researchers in the area of modern organic synthesis[8,9] and catalysis[10] have been motivated by the potential applications of chalcogen compounds in this field.[6,9] Unsymmetrical organochalcogenides with nitrogen-or oxygen-containing arenes and their derivatives are a very important class of molecules, with different applications in biological sciences.[6,9,11] Aryl-sulfides containing these moieties are considered to be an important core structure in many important drugs.[6] However, studies on their counterpart in selenium compounds are limited.

In relation to preparing this class of compounds, particularly unsymmetrical diaryl chalcogenides containing OH and NH_2 functionalities,[12] few research articles are available on the oxidative C–Se/C–S bond formation through C(sp^2)–H bond activation of arenes.[12a–f] However, some of them suffer from limitations such as the use of non-greener solvents, prefunctionalized coupling partners, transition metal catalysts, stoichiometric or greater amounts of reagents, long reaction times, harsh reaction conditions with non-regioselective protocols and oxygen-free techniques.

Recently, the I_2/DMSO oxidative system has been successfully applied in different types of greener organic reactions.[13]

Considering the significance of unsymmetrical diorganyl chalcogenides, it would be advantageous and highly desirable to develop a regioselective, ligand-free and metal-free protocol in a solvent-free system for their preparation. In addition, this new protocol should operate with a shorter reaction time and be applicable to a broad range of selenylating and sulfenylating species.[14] To the best of our knowledge, no studies in which this attractive strategy was applied to the synthesis of diorganyl chalcogenides using arenes and diorganyl dichalcogenides have been reported.

As part of our wider research program aimed at designing and developing eco-friendly processes,[15,16] as well as using iodine/DMSO as a mild oxidizing agent, herein we report, for the first time, C–Se/C–S coupling by C(sp^2)–H bond activation, under MW irradiation (Scheme 1). A less extensive study using aryl thiols as sulfenylating agent under conventional



Scheme 1

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cy01503k

2 Published Article

Advanced Synthesis & Catalysis

FULL PAPERS

DOI: 10.1002/adsc.201500024

Synthesis of Unsymmetrical Diorganyl Chalcogenides under Greener Conditions: Use of an Iodine/DMSO System, Solvent- and Metal-Free Approach

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Abstract: Herein, we report a greener iodine-catalyzed protocol to access different types of unsymmetrical diorganyl chalcogenides. This new approach works in the absence of solvent and metal. The desired products were obtained in good to excellent yields using one equivalent of arylboronic acids, half an equivalent of various diorganyl dichalcogenides, iodine (10 mol%) as a catalyst and 2 equivalents of dimethyl sulfoxide (DMSO; as oxidant), with a reaction time of 10 min under microwave irradiation.

Keywords: boronic acids; iodine; metal-free conditions; microwave irradiation; selenides; sulfides; tellurides

Introduction

Unsymmetrical organochalcogenides (S, Se, and Te) have become an attractive synthetic target in the past few decades and they have been extensively reported in various research articles,[1] reviews[2] and books.[3] In recent years these compounds have been employed in certain reactions[4] as catalysts,[5a,b] ligands,[5c] ionic liquids[6] and synthetic intermediates in total synthesis[2,3,7] besides being applied in asymmetric catalysis.[4a] Moreover, synthetic organochalcogen compounds have been found to function as antioxidant, anticancer, antihypertensive and antiviral agents.[2d,e,3,8] They also have important applications in materials science.[9]

Similarly, organoboronic acids and their derivatives are easily accessible, stable and are compatible with several functional groups. Due to these properties they have been used as coupling partners in different organic transformations.[10]

Considering the importance of unsymmetrical organochalcogenides, several methods have been developed for their synthesis.[11] Among them, metal-catalyzed aryl-chalcogen bond formation is one of the most commonly used protocols,[2a–c,11] which generally involves the presence of a ligand. Several metal sources, such as Pd,[12] Ni,[13] Cu,[14] Zn,[15] Fe[16] and In,[17] have been used. However, these types of transformations have their own particular drawbacks, such as the use of environmentally unfriendly solvents, expensive ligands and catalysts, precious and rare metals, reducing agents, stoichiometric or greater amounts of reagents, long reaction times, harsh reaction conditions and oxygen-free techniques. Also, there are only a few general methods available which are applicable to the synthesis of S-, Se- and Te-based unsymmetrical diaryl chalcogenides as well as alkyl aryl chalcogenides.[18]

Similarly, different methods have been developed for the synthesis of unsymmetrical chalcogenides using direct C–H functionalization/activation.[19] This strategy is important, since it eliminates an unnecessary step, directly accessing the desired product. However, in most cases the use of a solvent, a transition metal catalyst and additives is required.

In the last few years, the I_2/DMSO system has been applied in various greener organic transformations.[20] However, to date, to the best of our knowledge, there have been no reports involving the application of this catalytic oxidant system to the preparation of organotellurim compounds. In addition, the preparation of organochalcogen compounds through the reaction of organoboronic acids and diorganodichalcogenides using this system has not been explored. Recently, we successfully explored the selenylation and thiolation of indoles catalyzed by the iodine/DMSO system, avoiding the use of solvents and metals, in an open atmosphere.[21]

In this context, it would be advantageous and highly desirable to develop a ligand-free and metal-

3 Published Article

FULL PAPER

DOI: 10.1002/ejoc.201500124

Synthesis of Functionalized Organoselenium Materials: Selenides and Diselenides Containing Cholesterol

Tiago E. Frizon,[a,b] Jamal Rafique,[a] Sumbal Saba,[a] Ivan H. Bechtold,[c] Hugo Gallardo,[a] and Antonio L. Braga*[a]

Keywords: Liquid crystals / Mesophases / Selenium / Steroids

A simple and efficient procedure for the synthesis of three new series of chalcogen liquid crystals, based on selenides and diselenides, containing cholesterol in their structure, is described. Thermal and liquid crystalline properties were investigated by POM, DSC, TGA and XRD scattering. Six of the nine molecules synthesized showed liquid crystal properties, with smectic mesomorphism. All the compounds presented good thermal stability. The smectic mesomorphism was confirmed through XRD analysis. The morphology of the surface of the films was investigated by using atomic force microscopy (AFM). All prepared diselenides showed good glutathione peroxidase like activity and one of the diselenides was 3.3 times more active than the standard Ebselen.

Introduction

In recent years, interest in organochalcogen compounds has been driven by their potential applications in modern organic synthesis of materials and in catalysis.[1,2] Additionally, diorganodiselenides, the selenium counterpart of organic peroxides, play an important role in organochalcogen chemistry, because they are stable, easy to handle, and sufficiently reactive to produce electrophilic, nucleophilic, and radical species.[3,4] The design of new organoselenium compounds, along with other developments, is attracting considerable attention, particularly because of their ability to mimic natural compounds with important biological properties, such as antioxidant, antitumor, antimicrobial, and antiviral activity.[5–8] In addition, it has been shown that the presence of different chalcogen atoms in organic compounds can induce changes in their photophysical properties.[9,10] Moreover, the photophysical properties allied with their liquid crystalline character mean that such materials are promising for optical device applications, such as emissive LC displays, polarized organic lasers, and anisotropic OLEDs. However, examples of the use of selenium compounds as liquid crystalline materials are rare.[9] Organo selenium derivatives have been studied in relation to the architecture of organic materials of technological interest; such compounds exhibit behavior that may be suitable for use in electroconductive polymers, organic semiconductors, and liquid crystals.[9–15] Despite the potentially beneficial properties of applying diorganodiselenide compounds as constituent units in organic functionalized materials, to our knowledge, only the disulfide structures have been investigated.[16,17]

In this context, the aim of this study was to associate the remarkable properties of selenium with the structure of cholesterol, to generate an important class of biological and synthetic materials in which the molecules are macroscopically arranged in a periodic helicoidal structure.[18,19]

Cholesterol is a well-known natural product that appears as a building block in molecular associations. Its versatility comes from its unique structural features, which are not found in other compounds. Cholesterol is extensively incorporated in molecular systems for a number of reasons: (i) it is commercial availability; (ii) it has a rigid structure with eight chiral centers; and (iii) the structure can be easily derivatized.[18–20] Derivatives of cholesterol are present in several unique aggregates, including liquid crystals, organic gels, and monolayers, making it a versatile building block in organic synthesis.[21,22] The self-assembly of cholesterol-derived compounds into thermotropic liquid crystalline (LC) phases is well known. In fact, the first observation of LC phases was reported for cholesteryl benzoates and cholesteryl acetates.[23] According to their chemical nature, cholesteric liquid crystals can be divided into: (a) steroidal, mainly cholesterol esters; (b) nonsteroidal, better known as chiral nematics; and (c) induced cholesteric systems, comprised of a nematic matrix and an optically active

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4 Published Article

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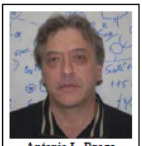
Current Organic Chemistry, 2016, *20*, 000-000 1

Recent Advances in the Synthesis of Biologically Relevant Selenium-containing 5-Membered Heterocycles

Jamal Rafique, Rômulo F. S. Canto, Sumbal Saba, Flavio A. R. Barbosa and Antonio L. Braga*

Departamento de Química, Universidade Federal de Santa Catarina, Florianopolis, 88040-900, SC-Brazil



Antonio L. Braga

Abstract: Organoselenium compounds are molecules with important potential therapeutic applications. Selenium-containing 5-membered heterocycles have emerged as an important class of biological compounds. In the past five years, several articles related to the design, synthesis and biological evaluation of these compounds have been published. These heterocycles have been applied as antioxidants, cytotoxic agents, apoptosis inducers and chemopreventors, and they possess antidepressant activity, among others. This review describes the methodologies involved in the synthesis of biologically significant selenium-containing 5-membered heterocycles from 2010 to the present.

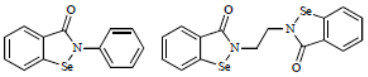
Keywords: Anticancer, Antioxidant, Diselenide, Ebselen, Heterocycle, Selenium, Selenazole, Selenide.

1. INTRODUCTION

Synthetic organoselenium compounds have attracted increasing attention since the 1970s, when many reports described the identification of several selenoproteins involved in a wide variety of physiological process in mammals, such as antioxidant defense and thyroid hormone production [1-5]. Furthermore, they have been found to function as antioxidants, apoptosis inducers and chemopreventors in several organs including the brain, liver, stomach, skin, colon, lung, prostate and kidney [6-9]. Therefore, areas related to the synthesis, reactivity and biological study of organoselenium compounds have achieved a new dimension in chemistry/biochemistry. The design and synthesis of biologically relevant small molecules containing selenium constitute a significant research theme in both chemical/pharmaceutical companies and academic laboratories [10-17]. In this context, selenium-containing heterocycles are considered as privileged structures, since they present high biological activity and are usually more stable molecules compared with their aliphatic counterparts [15-19]. Their structural modification can have a profound effect on their chemical, and therefore biological, activity. For this reason, several methods for their preparation have appeared in the literature. Excellent books, chapters and reviews have been published on this class of compounds [4-8,17,20-27]. The latest review on selenium-containing heterocycles was published in 2011 [28]. Accordingly, the review presented herein covers the scientific literature (excluding the patent literature) from 2010 to the present.

2. EBSELEN AND ETHASELEN DERIVATIVES

Ebselen [2-phenyl-1,2-benzisoselenazol-3(2*H*)-one]; PZ-51, DR-3305; **1** (Fig. **1**) and its analogs continue to attract the attention of scientific communities because of their versatile activities, e.g., antioxidant and anti-inflammatory, and low toxicity profile [7,815,29-31]. Ebselen **1** was subjected to phase III clinical trials to treat ischemic stroke [32, 33]. Even though ebselen **1** has not been used as a commercial/marketed drug until now, the investigations has been focused on the treatment of neurological disorders [34]. This compound is a cyclic selenamide and is established as a glutathione peroxidase mimetic [26]. The dimeric form of this structure bearing a saturated two-carbon spacer is known as ethaselen; [1,2-(bis-1,2-benzisoselenazol-3(2*H*)-one) ethane] **2** (Fig. **1**) and it inhibit thioredoxin reductase (TrxR) instead of being substrate of it. Because of this action, this compound exhibits a broad spectrum of antitumor effects with slight toxicity and its testing has entered the phase II clinical trials phase [35-37].



1 **2**

Fig. (1). Ebselen **1** and ethaselen **2**.

The synthesis of cyclic selenamides (ebselen nucleus) is based on four main approaches (Schemes **1** and **2**). The most commonly and extensively used method is the diazotization of the anthranilic acid **3** and reaction with alkali metals diselenide species (generated *in situ*) to form the *ortho*-diselenide of benzoic acid **4**. The diselenide intermediate **5** on reaction with thionyl chloride forms the acyl and selenyl chlorides **5**, which on reaction with aniline form Ebselen **1**. This method often gives moderate yields [38].

Another route for accessing ebselen **1** is the *ortho*-lithiation of *N*-substituted benzamides **6** with *n*-butyllithium (Scheme **2**), which on further reaction with elemental selenium and copper bromide as an oxidant afforded **1** [39]. Recently, two new methods have been presented where *N*-substituted *o*-iodobenzamide **7** is used as the starting material (Scheme **2**) [40-42]. One of them is based on the coupling of the inorganic selenium species (formed *in situ* through the reaction of selenium with a base) with the aryl iodide catalyzed by copper iodide with 1,10-phenantroline as a ligand and finally the Se-N bond is formed in an oxidation step resulting in **1** [40,41]. Another method for the synthesis of **1** involves the direct reaction of aryl iodide **7** with elemental selenium and potassium *tert*-butoxide [42].

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Article

Synthesis and Biological Evaluation of 2-Picolylamide-Based Diselenides with Non-Bonded Interactions

Jamal Rafique [1,†], Sumbal Saba [1,†], Rômulo Faria Santos Canto [1], Tiago Elias Allievi Frizon [1], Waseem Hassan [2,3], Emily Pansera Waczuk [2], Maryam Jan [3], Davi Fernando Back [4], João Batista Teixeira Da Rocha [2] and Antonio Luiz Braga [1,*]

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Abstract: In this paper, we report the synthesis and biological evaluation of picolylamide-based diselenides with the aim of developing a new series of diselenides with O···Se non-bonded interactions. The synthesis of diselenides was performed by a simple and efficient synthetic route. All the products were obtained in good yields and their structures were determined by ^{1}H-NMR, ^{13}C-NMR and HRMS. All these new compounds showed promising activities when tested in different antioxidant assays. These amides exhibited strong thiol peroxidase-like (TPx) activity. In fact one of the compounds showed 4.66 times higher potential than the classical standard *i.e.*, diphenyl diselenide. The same compound significantly inhibited iron (Fe)-induced thiobarbituric acid reactive species (TBARS) production in rat's brain homogenate. In addition, the X-ray structure of the most active

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K_2CO_3-mediated, direct C–H bond selenation and thiolation of 1,3,4-oxadiazoles in the absence of metal catalyst: an eco-friendly approach†

Jamal Rafique,[a] Sumbal Saba,[a] Alisson R. Rosário,[a] Gilson Zeni[b] and Antonio L. Braga*[a]

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An eco-friendly, straightforward and high-yielding methodology for the synthesis of chalcogenyl oxadiazoles *via* the K_2CO_3-promoted direct C–H bond chalcogenation of 2-substituted-1,3,4-oxadiazoles is described herein. The reaction was performed in the absence of metal catalyst and inert atmosphere using only half an equiv. of dichalcogenide and a low-cost base.

Metal-free reactions can be applied in the functionalization of C–H bonds to access C–C and C–heteroatom bonds and this has become a rapidly developing area.[1] In this regard, one of the most important discoveries made in organic synthesis in recent years is that certain reactions which were thought to involve transition metal (TM) catalysis can, in fact, proceed without the requirement for a TM.[2] Reactions carried out under metal-free conditions are particularly attractive in the synthesis of pharmaceuticals.[3] Therefore, from the economic and environmental viewpoints, it would be advantageous and desirable to develop TM-free systems in the area of organic synthesis.

The synthetic versatility of organochalcogenides has been explored extensively in research articles,[4] reviews[5] and books.[6] This group includes the organoselenium compounds, which can be employed in certain reactions[7] as catalysts,[8] ionic liquids,[9] and synthetic intermediates in total synthesis.[5,6,10] Another important advancement in this context is the formation of C–Se bonds, which has contributed to the synthesis of a wide range of biologically active molecules[11] and functional materials.[12] A large number of organoselenides have been found to function as antioxidants, antinociceptive agents, antidepressant apoptosis inducers and chemopreventors in several organs, *etc.*[5d–f,11]

Functionalization of the 1,3-4-oxadiazoles scaffold is an important synthetic task, since oxadiazoles are well established as "privileged scaffolds" and are widely used for pharmaceutical, biological and material applications.[13] They show a very broad spectrum of biological activity, being used, for instance, as inhibitors of various enzymes and as antimicrobial, analgesic, antiviral and antitumor agents.[14] Interestingly, few of the active compounds have a sulphur linkage at C-5.[14b] 1,3,4-Oxadiazole motifs are also of interest in material science and have been widely used to create novel materials.[15]

Many methods for the C–H functionalization of 1,3,4-oxadiazoles have been reported in the literature with the formation of C-alkyl,[16a] C-allyl,[16b] C-alkynyl,[16c] C-aryl,[16d] C-benzyl,[16e] C–N,[16f] C–S,[16g–k] *etc.* However, the disadvantages associated with many of these methodologies, owing to the use of TM catalysts, expensive reagents, harsh reaction conditions, hazardous materials, oxygen-free techniques or elaborate multi-stepped processes, have limited their synthetic scope.

Considering the significance of these compounds, the challenging task of developing new green routes for the syntheses of chalcogenides which provide high efficiency, through direct substitution with heteroaromatics and other organic moieties, is an important research area.[17] As part of our wider research program aimed at designing and developing eco-friendly processes,[18] herein we report for the first time a straightforward, mild, and environmentally benign protocol for the direct selenation of 1,3,4-oxadiazole, which is also applicable to disulphides. The functionalization of C_{sp^2}–H bonds proceeded smoothly with half equiv. of different dichalcogenides and a low-cost base in the absence of a metal catalyst and in an inert atmosphere.

To identify the best reaction conditions, 2-(4-methylphenayl)-1,3,4-oxadiazole (**1a**) and diphenyl diselenide (**2a**) were initially used as standard substrates under different conditions, Table 1. Considering the need for a metal catalyst and base under inert atmosphere for C_{sp^2}–H bond funtionalization,[17b] a preliminary experiment was performed using 1 equiv. of K_2CO_3 and 20 mol% of CuO-nanopowder under an inert atmosphere in

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† Electronic supplementary information (ESI) available: Details on the experimental procedure and characterization, as well as the spectral data for all synthesized compound. See DOI: 10.1039/c4ra10490k

1. Deposited Patent

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PhD Academic Record

Universidade Federal de Santa Catarina
Pró-Reitoria de Pós-Graduação

HISTÓRICO ESCOLAR

Nome: **Sumbal Saba** Matrícula: 201201668

Data de nascimento: 6 de Maio de 1986 Identificação: 5093181

Naturalidade: não informada Nacionalidade: paquistanesa

Filiação:

Yasmeen Ali Shakir

Programa de Pós-Graduação em Química

Portaria nº 1077/MEC/2012 de 31/08/2012 DOU de 13/09/2012

Pólo: Universidade Federal de Santa Catarina

Nível: Doutorado

Área de Concentração: Química Orgânica

Linha de Pesquisa: Não definida

Orientador: Dr. ANTONIO LUIZ BRAGA

Data de Início no Curso: 05/03/2012 Previsão de Término: 05/03/2016 Regimento: 2010

Situação: Regularmente Matriculado

Modalidade: Presencial

DISCIPLINAS

Periodo Letivo: 2012/1

Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
QMC510018	Metodologia da Pesquisa 1	A	FS	4				Dr. ALMIR SPINELLI

Periodo Letivo: 2012/2

Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
QMC3209000	Síntese Orgânica	A	FS	4				Dr. ANTONIO LUIZ BRAGA
QMC510019	Metodologia da Pesquisa 2	A	FS	4				Drª. IOLANDA DA CRUZ VIEIRA

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Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
EST510006	Estágio de Docência 2 Semestre: 20132 Disciplina: QMC5222 Química Orgânica Teórica A 03205 Fase: 03 Créditos: 4 Curso: QUÍMICA - Licenciatura Prof(a): ANTONIO LUIZ BRAGA	A	FS	4				Dr. ANTONIO LUIZ BRAGA
QMC510026	QMC 3206 TEQO: Química Supramolecular	A	FS	4				Dr. VANDERLEI GAGEIRO MACHADO
QMC510030	TEQ: Bioquimica Estrutural	A	FS	4				HERNAN FRANCISCO TERENZI, Phd.

Periodo Letivo: 2014/2

Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
QMC510035	QMC3120 Tópicos Especiais em Química: Element Analysis for Speciaton, Bioanalysis and Metallomics	A	FS	1				Dr. BERNHARD WELZ Dr. JÖRG FELDMANN

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Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
FAR410061	T.E - Introduction to Strategies for the Synthesis of Complex Molecules	A	FS	1				Drª. MAIQUE WEBER BIAVATTI

Periodo Letivo: 2015/2

Disciplina		Conc.	Freq.	- Créd. - T	TP	P	Val.	Professor
EST510005	Estágio de Docência 1 Semestre: 20152 Disciplina: QMC5230 Química Orgânica Experimental I 04216B Fase: 04 Créditos: 4 Curso: ENGENHARIA QUÍMICA Prof(a): ANTONIO LUIZ BRAGA			4				Dr. ANTONIO LUIZ BRAGA

QMC510041	QMC 3120 - Técnicas Avançadas de Ressonância Magnetica Nuclear	A	FS	2	Dr. GIANLUCA CIANCALEONI

Índice de aproveitamento:	**4,00**	**Créditos completados em disciplinas:**	**28**
Carga horária:	**780 horas/aula**	**Créditos externos à UFSC em Disciplinas:**	**24**
Créditos exigidos em Disciplinas:	**48**		
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		Total de créditos completados:	**52**

Escala de Equivalência dos Conceitos:	**Conceito**	**Descrição**	**Valor**
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	B	BOM, com direito a créditos	3
	C	REGULAR, com direito a créditos	2
	E	INSUFICIENTE, sem direito a créditos	0
	I	INCOMPLETO, sem direito a créditos	0
	T	TRANSFERIDO, sem direito a conceito e com direito a créditos	0

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P = Prático (1 = 45 Horas Aula)
Val. Validação

BOLSAS

Descrição	**Data de Início**	**Data de Término**
CNPq	01/03/2012	29/02/2016

EVENTOS

Descrição	**Data da Avaliação**	**Avaliação**	**Data de Início**	**Data de Término**	**Crédito/Carga Horária**
Seminários	30/11/2012	Aprovado	17/08/2012	30/11/2012	
Seminários oferecidos pelo Programa de Pós-Graduação em Química da UFSC.					
Seminários	04/12/2012	Aprovado	06/08/2012	07/12/2012	
Seminários oferecidos pelo Programa de Pós-Graduação em Química da UFSC.					
Qualificação do Projeto de Tese	10/08/2015	Não Avaliado	03/03/2012	10/08/2015	
Exame de Qualificação defendido no Programa de Pósd-Graduação em Química da UFSC. Portaria Nº 069/PPGQ/2015.					
Proficiência em Língua - Inglês	15/08/2012	Aprovado			
Exame de Proficiência em Língua Inglesa, realizado no Mestrado na University of Peshawar e validado para do Programa de Pós-Graduação em Química da UFSC.					
Proficiência em Língua - Português	08/09/2012	Aprovado			
Exame de Proficiência de Língua Estrangeira (Português), elaborado e aplicado no Programa de Pós-Graduação em Qu'mica da UFSC.					

OBSERVAÇÕES

A aluna Sumbal Saba, solicita validação dos créditos obtidos no Curso de mestrado da University of Peschawar e os crédits obtidos em nível de M.Phil na University of Karachi para integralização dos 48 créditos do PPGQ-UFSC, área de Química Orgânica. Considerando que as ementas e os programas das disciplinas cursadas no curso de Mestrado da University of Peshawar e os créditos obtidos em nível de M.Phil na University of Karachi:
1. Organica Chemistry;
2. MSC01 Physical Chemistry;
3. MSC03 Inorgânica Chemistry;
4. MSCF1 Environmental Chemistry
5. Spectral Analysis of Organic Compounds;
6. Oxidation/Reduction;

são similares com ao menos 75% do conteúdo coincidentes, das seguintes disciplinas respectivamente:
1. QMC 3207 Química Orgânica Avançada I - 04 créditos;
2. QMC 3426 Físico-Química - 04 créditos;
3. QMC 3111 Química Inorgânica Avançada - 04 créditos;
4. QMC 3208 Análise Orgânica - 04 créditos;
5. QMC 4209 Química Orgânica Avançada II - 04 créditos;
6. QMC 3443 TEQA: Química Ambiental.

Assim sendo sugiro que sejam validados 24 créditos pela equivalência dessas disciplinas. Alem da validação da proficiência em Inglês, conforme ayestam os documentos anexos a solicitação Relator do pedido: Prof. Dr. Hugo Alejandro Gallardo Olmedo
Aprovado em Reunião do Colegiado po unanimidade, realizada em 19/09/2012.

Florianópolis, 31 de janeiro de 2016

Dr. VANDERLEI GAGEIRO MACHADO
Coordenador(a)