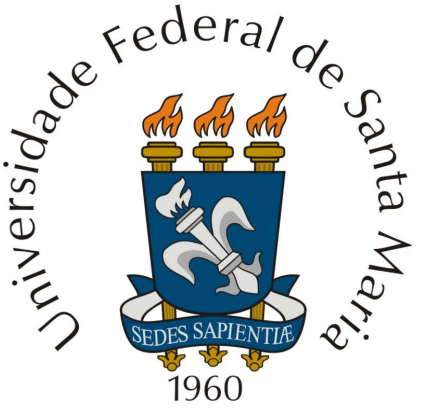

UFSM

PhD THESIS

IONIC LIQUID: AN EFFICIENT MEDIA TO SYNTHESIZE DIORGANYL SELENIDES, SULFIDES AND CHIRAL β-SELENO AMINE DERIVATIVES

KASHIF GUL

PPGQ

Santa Maria, RS, Brasil

2010

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2010

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Santa Maria, RS, Brazil

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Ionic Liquid: An Efficient Media to Synthesize Diorganyl Selenides, Sulfides and Chiral β-seleno Amine Derivatives

For the award of degree of Doctor of Philosophy (PhD) in Chemistry to

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RESUMO

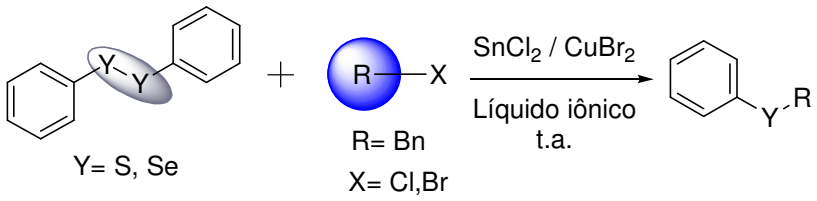
Título: Líquido Iônico: um Eficiente Meio para Sintetizar Selenetos e Sulfetos de Diorganoíla e quirais derivados de amina e β-Seleno

Author: Kashif Gul

Supervisor: Prof. Dr. Antonio Luiz Braga

No presente trabalho, descreveremos metodologias eficientes e simples para sintetizar selenetos e sulfetos de diorganoíla estruturalmente diversos, β-seleno aminas quirais e seleno- e tiol ésteres usando dois tipos de sistema, isto é, sistemas bimetálicos [Sn(II)/Cu(II)] e ZnO nanoestruturado usando Zn em líquido iônico o qual é reutilizável e exibiu alta performance quando comparado com solventes orgânicos.

Primeiro, o reagente bimetálico Sn(II)/Cu(II) em BMIM-BF_4 foi eficientemente usado para a quebra de disselenetos e dissulfetos de diarila e reage com uma variedade de substratos orgânicos, tais como, haletos orgânicos, cloretos ácidos e β-aminomesilatos fornecendo selenetos e sulfetos de diorganoíla em um curto tempo de reação, sob condições brandas e com excelentes rendimentos, usando BMIM-BF_4 como solvente reutilizável.



Como parte de nosso interesse na química de organocalcogênios, nós desenvolvemos uma síntese eficiente de selenetos de diorganoíla e β-seleno aminas usando uma quantidade catalítica de ZnO nanoestruturado como catalisador e líquido iônico como solvente reutilizável. Este sistema ZnO/líquido iônico apresenta alta eficiência para catalisar estas transformações com alto desempenho.

X = OMs, OTs
GP= Boc, Ts

R =Bn, *i*-Pro, *i*-Bu
R_1= Ph, *p*-Cl-Ph, *p*-Me-Ph

ABSTRACT

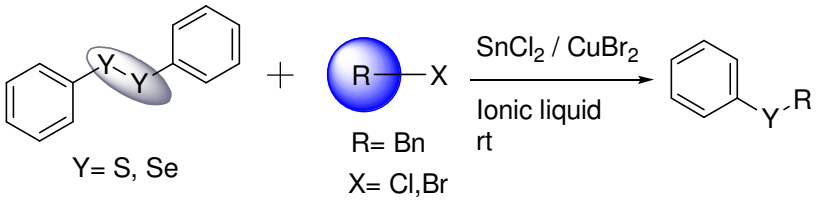
Title: Ionic Liquid: an Efficient Media to Synthesize Diorganyl Selenides, Sulfides and Chiral β-Seleno Amine Derivatives.

Author: Kashif Gul

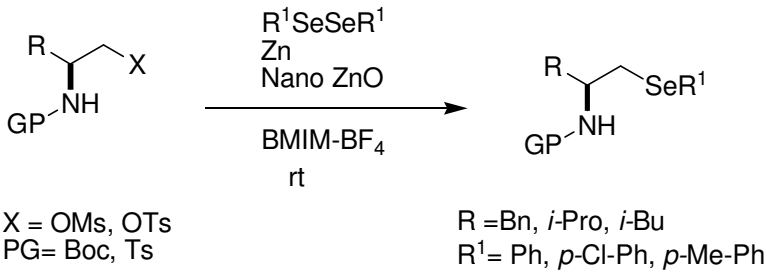
Supervisor: Prof. Dr. Antonio Luiz Braga

In the present work, a straightforward and efficient methodologies to synthesize structurally diverse diorganyl selenides and sulfides, chiral β-seleno amines, and seleno- and thioesters using two kind of systems i.e. bimetallic systems [Sn(II)/Cu(II)] and ZnO NPs using Zn in ionic liquid which is reusable and exhibited higher performance as compared with organic solvents..

Firstly, the bimetallic reagent Sn(II)/Cu(II) in BMIM-BF_4 was efficiently used for the cleavage of diaryl diselenides and disulfides and reacts with a variety of organic substrates, such as organic halides, acid chlorides and β-aminomesylates affording the diorganyl selenides and sulfides within very short reaction times, under mild conditions and with excellent yields, using BMIM-BF_4 as a reusable solvent.



On account of our interest in organochalochogens chemistry we have developed efficient synthesis of diorganyl selenides and β-seleno amines using Zn and a catalytic amount of ZnO NPs as a catalyst and an ionic liquid as a recyclable solvent. This ZnO/ionic liquid system shows high efficiency in catalyzing these transformations with high performance.



1. Introduction:

In synthetic organic reactions, the scope and application of organochalcogen chemistry have increased tremendously, since selenium and sulfur-containing groups serve an important auxiliary function in synthetic sequences.[1] Organochalcogenides are of considerable interest in academia as well as in industry because of their wide involvement as key intermediates in the transformation of a variety of functional groups and use as a food supplement[2] and the biological application of this class of compounds is well established.[3]

Organoselenium chemistry has continued to attract considerable attention due to its pivotal role in the synthesis of a large number of biological compounds (e.g., selenocarbohydrates, selenoamino acids, and selenopeptides). Additionally, organoselenium compounds have emerged as an exceptional class of structures that exemplify a role in biochemical processes, serving as important therapeutic compounds such as antiviral, anticancer agents and in a variety of situations where free radicals are involved.[3] Synthetic methods for the preparation of selenocysteine a natural amino acid, [4] selenium based peptides, [5] selenoglycosides [6] and other important natural compound derivatives[7] is nowadays an area of intensive research.

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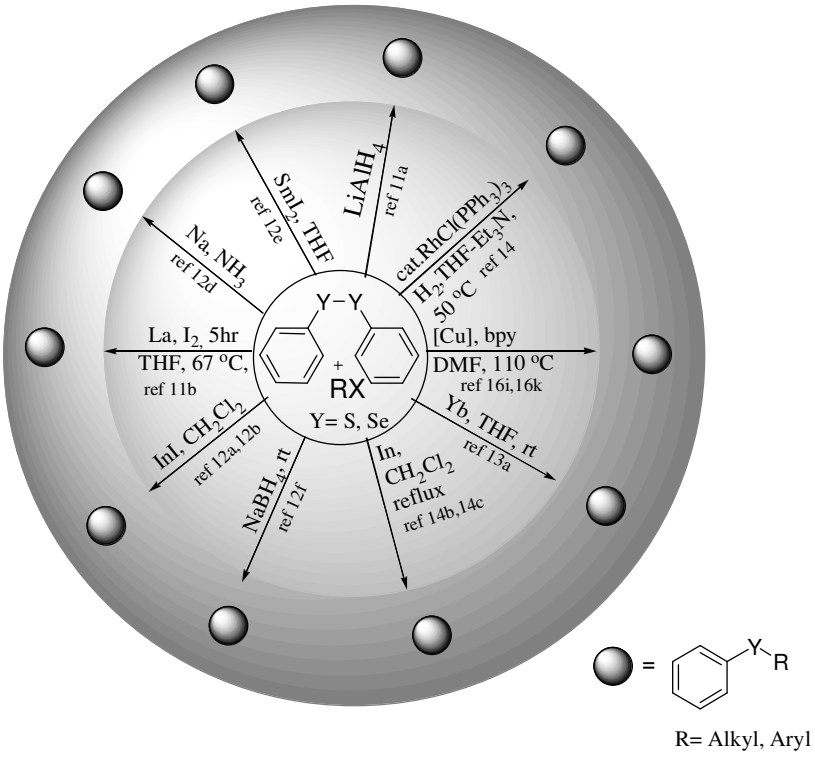
Scope and application of organosulfur chemistry have increased due to the synthetic versatility of this class of compounds.[8] Significant attention has also been focused on sulfur-containing groups as model compounds of both active sites of natural enzymes and catalytic metal surfaces.[9] Also, the carbon–sulfur bond plays an important role in many molecules of biological, pharmaceutical and materials interest.[10]

Organochalcogens are widely accepted as key intermediates in organic synthesis, and much effort is being devoted to accomplishing the synthesis of these compounds.



Scheme 1

[8] (a) For general reviews on sulfides, see: Jones, D. N. In *Comprehensive Organic Chemistry*, Vol. 3; D.H.R. Barton, W.D. Ollis, Eds.; Pergamon Press: Oxford, **1979**, pp 33–103. (b) *Organic Sulfur Chemistry: Structure and Mechanism*; Oae, S. Ed.; CRC Press: Boca Raton, FL, **1991**. (c) Cremlyn, R. J. *An Introduction to Organo-sulfur Chemistry*; Wiley & Sons: New York, **1996**.

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[10] Herradura, P. S.; Pendola, K. A.; Guy, R. K. *Org. Lett*. **2000**, *2*, 2019-2022 and references there in.

1.1 General methods of preparation of organochalcogenides.

These compounds are generally prepared by reductive cleavage of dichalcogenide bonds, employing common reducing agents and expensive metal sources, high yield selenide were obtained by treatment of diphenyldiselenide with $LiAlH_4$ in THF (Scheme 1).[11a]

1.1.1 Reaction with lanthanum metal.

Sonoda and coworkers have shown a convenient synthetic method to prepared unsymmetrical selenides. When diphenyl diselenide was allowed to react with two equimolar amounts of primary alkyl iodides and bromides in the presence of an equimolar amount of lanthanum metal, alkyl phenyl selenides (34-78%) were obtained in moderate to good yields (Scheme 1).[11b] A wide range of structurally diverse alkyl halides underwent reactions with diphenyl diselenides to produce the corresponding alkyl phenyl selenides.

1.1.2 Reaction with indium iodide

Diphenyl diselenides and disulfides undergo facile cleavages by indium (I) iodide and the corresponding generated selenolate and thiolate anions condense in situ with alkyl or acyl halides present in the reaction mixture. Thus unsymmetrical diorganyl selenides, sulfides (thioethers), selenoesters, and thioesters were prepared by this one pot reaction at room temperature (Scheme 1).[12a, b] This procedure demonstrates the synthetic potential of indium(I) iodide and provides great promise toward other useful applications.

1.1.3 Reaction with cesium hydroxide

In the presence of cesium hydroxide, molecular sieves, and DMF, benzeneselenol undergoes direct alkylation with various alkyl halides for the synthesis of alkyl phenyl selenides in moderate to excellent yields (Scheme 1).[12c] A wide spectrum of halides was screened in order to evaluate the scope, limitations, and practicality of the reaction procedure.

---

[11] (a) Yoshimatsu, M.; Sato, T.; Shimizu, H.; Hori, M.; Kataoka, T. *J. Org.Chem.* **1994**, *59*, 1011-1019. (b) Nishino, T.; Okada, M.; Kuroki, T.; Watanabe, T.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 8696-8698.

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1.1.4 Reaction with other metals

One-pot two-step selenylation reaction to form a C–Se bond was reported by Rossi *et. al.* Diphenyl Diselenide were allowed to react with Na metal in liquid ammonia yielding $PhSe^-$ ions (Scheme 1). [12d]

The development of new methods for the introduction of sulfur-, selenium-, and tellurium-containing groups into organic molecules, particularly in a stereocontrolled manner, remains a significant challenge. Convenient conditions were demonstrated by Procter *et. al.* for the preparation of ytterbium(III) chalcogenolate complexes by insertion of ytterbium metal into the chalcogen-chalcogen bond of disulfides and diselenides (Scheme 1). [13a]

In the phenylchalcogenation of aryl halide, to exploit two groups in diphenyl dichalcogenide, the requirement is an application of a metal catalyst with two abilities as follows. One is a cleavage of the chalcogen-chalcogen bond, and the other is an oxidative addition to aryl halide. To satisfy these qualifications, it seems that the employment of a transition-metal catalyst having a capability to insert into the dichalcogen bond is the most suitable. However, it is possible that production of complexes by the transition metal inserts into dichalcogenide prevents promoting the next step owing to the firmness of the metal-chalcogen bond. As a solution to this problem, Onami and coworker found that unsymmetrical diaryl sulfide or diaryl selenide can be synthesized from aryl iodide and PhYYPh (Y = S, Se) with a copper catalyst (CuI or Cu_2O) and magnesium metal in one pot (Scheme 1)[13b] under neutral condition.

A suitable and efficient method was developed by Jang and coworker for the synthesis of alkyl phenyl selenides, sulfides and selenoesters in one-pot reaction by using indium metal (Scheme 1). [13c]

[12(d)] Bonaterra, M.; Martín, S. E.; Rossi, R. A. *Tetrahedron Lett.* **2006**, *47*, 3511-3515.

[13] (a) Dowsland, J.; McKerlie, F.; Procter, D. J. *Tetrahedron Lett.* **2000**, *41*, 4923-4927. (b) Taniguchi, N.; Onami, T. *J. Org. Chem.* **2004**, *69*, 915-920. (c) Munbunjong, W.; Lee, E. H.; Ngernmaneerat, P.; Kim, S. J.; Singh, G.; Chavasiri, W.; Jang, D. O. *Tetrahedron.* **2009**, *65*, 2467–2471.

The reductive coupling of disulfides or diselenides with alkyl or aryl halides is an important reaction in the synthesis of various unsymmetrical sulfides and selenides, which can eliminate the use of unstable and odoriferous thiols and selenols. Tanaka *et. al.* established that $RhCl(PPh_3)_3$ catalyzes a reductive coupling of disulfides and diselenides with alkyl halides in the presence of triethylamine using hydrogen as a reducing agent. They prepared unsymmetrical sulfides and selenides from disulfides and diselenides (Scheme 1). [14a]

In addition, some other reagents have been reported in the literature for the reductive cleavage of S-S bonds including sodium hydrogen telluride (NaHTe), [15a] butyl lithium, [15b] $LiCl/NaBH_4$, [15c] $ZrCl_2/NaBH_4$, [15c] rongalite, [15d] benzyl triethyl ammonium tetrathiomolybdate $[BnEt_3N]_2MoS_4$ [15e] and transition metal complexes.[16] The synthesis of diorganyl sulfides has also been achieved from deoxygenation of the corresponding sulfoxides.[15f]

Symmetrical and unsymmetrical alkyl and aryl sulfides can be conveniently prepared by the transition metal-catalyzed reaction of a halide with a thiol under different reaction conditions. [17] The major drawback to the use of organothiol causes very unpleasant odor and its toxicity.

---

[14] (a) Ajiki, K.; Hirano, M.; Tanaka, K. *Org. Lett*. **2005**, *7*, 4193-4195. (b) de Andrade, F. M.; Massa, W.; Peppe, C.; Uhl, W. *J. Organomet. Chem.* **2005**, *690*, 1294–1299. (c) f) L. Wang, M. Wang, F. Huang, *Synlett* **2005**, 2007-2010. (d) W. Munbunjong, E. H. Lee, P. Ngernmaneerat, S. J. Kim ,G. Singh, W. Chavasiri, D. O. Jang, *Tetrahedron.* **2009**, *65*, 2467–2471.

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Moreover, most of the methods available to synthesize diorganyl selenides and sulfides are associated with serious disadvantages including: i) the use of expensive metal sources and reagents such as La, Yb, In, InI, SmI_2 and $[BnEt_3N]_2MoS_4$ etc.; ii) functional group incompatibility, iii) harsh reaction conditions, such as acidic or basic; and iv) high temperature or long reaction time. Thus, there is still considerable interest in the development of highly efficient methods for this transformation. [18,19]

On the other hand, chalcogenoesters are important intermediates in several organic transformations. For instance, selenoester compounds have been used as precursors of acyl radicals and anions [20] and have attracted attention for the synthesis of new molecular materials, especially superconducting materials and liquid crystals.[21]

Applications of selenoesters have been extended to the synthesis of proteins by chemical ligation of chalcogenol esters,[22] to the synthesis of substrates which undergo facile and efficient radical decarbonylation, as well as to the synthesis of the natural products *e.g.,* Crinipellin A, (+)-Geissoschizine, Ciguatoxins and (-)-Pseudolaric Acid B.[23]

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[18] Recently Santi *et al* described an elegant synthesis of stable PhSeZnX (X = Cl or Br) species prepared from PhSeX and Zn, which act as nucleophiles toward a series of electrophiles. However, we reasoned that for our purposes use of diselenides and elemental zinc would be more attractive since we would be able to prepare *in situ* a wide range of selenium species that act exactly in the same way than those mentioned above. (a) Santi, C.; Santoro, S.; Testaferri, L.; Tiecco, M. *Synlett* **2008**, 10, 1471-1474. (b) Santi, C.; Santoro, S.; Battistelli, B.; Testaferri, L.; Tiecco. M. *Eur. J. Org. Chem.* **2008**, 5387–5390. (c) Santoro, S.; Battistelli, B.; Testaferri, L.; Tiecco, M.; Santi, C. *Eur. J. Org. Chem.* **2009**, 4921–4925.

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1.2 Synthesis of seleno and thioester

Much effort has been devoted to the synthesis of seleno esters, and a number of reports have been published.[24] These compounds have been successfully prepared from aldehydes using *i*$Bu_2AlSePh$,[25] from chalcogeno acetylenes,[26] by coupling of aryl iodides with CO and $PhSeSnBu_3$ catalyzed by Pd,[27] and, most commonly, by the reaction of acyl chlorides with nucleophilic species of selenium, such as $Hg(SePh)_2$, [28] and $PhSeSnBu_3$/Pd,[29] from reductive cleavage of diselenides with InI,[12a,b] In[14,30] or SmI_2,[31] or by reductive coupling of $PhSe)_2$ and acyl chloride in a Rh/H_2 system.[12g]

Additionally, thioesters are considerably important class of compounds in the medicinal area because of their broad range of biological activities *e.g., in vivo* tumor suppression and anti-HIV agents.[32] Also, they have found application in native chemical ligation for peptide bond formation,[33] and natural product synthesis.[34]

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Thioesters have also emerged as crucial intermediates in a variety of organic transformations, such as C-C coupling, [35] synthesis of carbonyl compounds, [36] asymmetric aldol reactions [37] and asymmetric 1-4 additions.[38]

There are a number of methods reported in the literature to synthesize thioesters using the activation of carboxylic acids with diphosgene[39] or N-acyl benzotriazoles[40] followed by addition of thiol, or by reaction of acyl chlorides with zinc and thiols.[41] They have also been accomplished from thiols and carbon monoxide by carbonylation of organic substrates catalyzed by transition metals such as Pt[42], Pd[43] and etc.[44] Because of potential biological and pharmacological applications of these classes of compounds, it is considered worthwhile to develop a general and effective method.

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[40] Katritzky, A. R.; Shestopalov, A. A.; Suzuki, K. *Synthesis* **2004**, 1806-1813.

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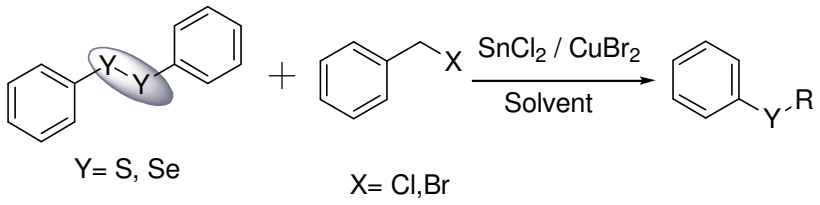
[44] Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem*. **2008**, *73*, 3530-3534.

1.3 Synthesis of organochalcogenides using bimetallic Cu(II)/Sn(II) system

Roy and coworker introduced a bimetallic Cu(II)/Sn(II) system for the reductive cleavage of the Se-Se and S-S bonds,[45] which was successfully used to synthesize the unsymmetrical diorganyl selenides and sulfides in good yield.[45d] Reactions of organic halides with diorganodiselenides in the presence of stannous chloride and catalytic cupric halide result in the formation of corresponding unsymmetrical selenides, whereas organic halides react with diorganodisulfides in the presence of stannous chloride and catalytic cupric halide, giving rise to corresponding unsymmetrical sulfides (scheme 2). [45c, d]



Scheme 2

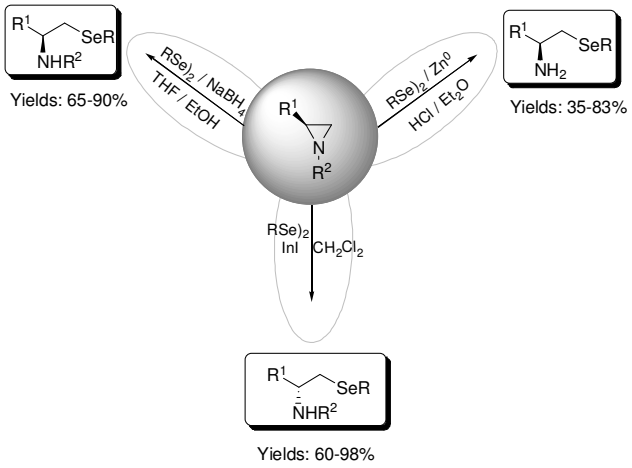
Although this methodology is effective, it is associated with some drawbacks, for example, organic solvents are used, there is a lack of generality and only the most reactive substrates give the desired products.

[45] (a) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics.,* **1997,** *16,* 4796-4799. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S.; *Organometallics.* **1999**, *18,* 2782-2785. (c) Kundu, A.; Roy, S. *Organometallics.* **2000,** *19,* 105-107. (d) Sinha, P.; Kundu, A.; Roy, S.; Prabhakar, S.; Vairamani, M.; Ravi Sankar, A.; Kunwar, A. C. *Organometallics.* **2001**, *20,* 157-162.

1.4 Synthesis of β-chalcogen amine derivatives

Development of methods for stereocontrolled synthesis of chiral β-chalcogen amine derivative continues to receive significant attention. Moreover, chiral selenide- and diselenides containing ligands offer attractive and practical options in the development of asymmetric transformations.[1] In particular, synthetic routes to sulfur and selenium-substituted unnatural amino acids and its derivatives, which are the building blocks for the synthesis of modified thio- and seleno-proteins.[46]

Generally, β-amino sulfides and selenides are prepared starting from an amino alcohol, followed by conversion of the hydroxy group into a good leaving group and subsequent nucleophilic substitution with thiolate or in situ generated selenolate.[5] Aziridines was also found to be the best starting materials to prepare these analogues in a stereo- and regiocontrolled manner.[47]



Scheme 3

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[1](a) Back, T. G. *Organoselenium Chemistry: A Practical Approach* Oxford University Press, USA, **1999**. (b) Devillanova, F. A. *Handbook of Chalcogen Chemistry: New Perspectives in S, Se and Te,* Royal Society of Chemistry, **2006.** (c) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri. R. B. *Chem. Rev.* **2009**, *109*, 3, 1277–1301. f) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T.; *Angew. Chem. Int. Ed.* **2009**, *48*, 8409–8411.

[5](a) Braga, A. L.; Lüdtke, D. S.; Paixão, M. W.; Alberto, E. E.; Stefani, H. A.; Juliano, L. *Eur. J. Org. Chem.* **2005**, *20*, 4260-4264. (b) Schwab, R. S.; Galetto, F. Z.; Azeredo, J. B.; Braga, A. L.; Lüdtke, D. S.; Paixão, M. W. *Tetrahedron Lett.* **2008**, *49*, 5094-5097. (c) Braga, A. L.; Schneider, P. H.; Paixão, M. W.; Deobald, A. M. *Tetrahedron Lett.,* **2006**, 47, 7195-7198.

[46] (a) Pegoraro, S.; Fiori, S.; Cramer, J.; Rudolph-Böhner, S.; Moroder, L. *Protein Sci.* **1999**, *8*, 1605. (b) Fiori, S.; Pegoraro, S.; Rudolph-Böhner, S.; Cramer, J.; Moroder, L. *Biopolymers* **2000**, ***53***, 550. (c) Moroder, R. J. *J. Pept. Sci.* **2005**, *11*, 187.

[47] (a) Wu, J.; Sun, X.; Li,V *Eur. J. Org. Chem.* **2005**, *20*, 4271-4275. (b) Sureshkumar, D.; Gunasundari, T.; Ganesh, V.; Chandrasekaran, S. *J. Org. Chem.* **2007**, *72*, 2106-2117. (c) Devan, N.; Sridhar, P. R.; Prabhu, K. R.; Chandrasekaran, S. *J. Org. Chem.* **2002,** *67*, 9417-9420.

However, these methods all possess one or more of the following disadvantages, including prolonged reaction time, suffered from the fact that a lewis acid or strong base was necessary to effect the reaction, or the requirement for costly, air-sensitive substances.[48]

Keeping in mind the wide range of applications of these analogues, general synthetic methodologies to prepare sulfur- and selenium-containing derivatives of amino acids in a simple, efficient, stereo-regulated manner is greatly appreciated and remains a highly challenging and desired endeavor. Due to the potential synthetic importance of chiral β-seleno amines, in particular the biological activity of selenocysteine and their derivatives, some successful recent and classical approaches aiming at their synthesis have been documented in recent years. [49]

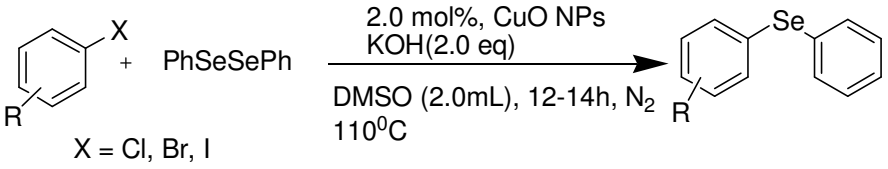
[48] (a) Stadman, T. C. *Annu. Rev. Biochem.* **1996**, *65*, 83-100. (b) Jacob, C.; Giles, G. I.; Giles, N. M.; Sies, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4742-4758.

[49] (a) Braga, A. L.; Paixão, M. W.; Marin, G. *Synlett*. **2005**, 1675-1678. (b) Ganesh, V.; Chandrasekaran, S. *Synthesis.* **2009**, *19*, 3267–3278.

1.5 Nanotechnology

Designing of new specific catalysts and exploring their catalytic activity has caused profound effects in optimizing the efficiency of a wide range of organic synthesis. In the last few years, literature has highlighted the importance of nanosized materials in several scientific and technological areas, and many research councils have intensified investments in nanotechnology for the coming years. Nano-catalysis can be considered as a bridge between homogeneous and heterogeneous catalysis. Because of the nano-size, *i.e*, high surface area, the contact between reactants and catalysts increases dramatically and the latter can operate in the same manner as homogeneous catalysts (close to homogeneous catalysis). At the same time, due to their insolubility in the reaction solvent, they can be separated out easily from the reaction mixture. Thus, nano-materials can combine the advantages of both systems and can offer unique activity with high selectivity. The recent availability of various high-purity metal oxides in nanoscale has allowed the improvement of cross-coupling reactions catalyzed by transition-metal nanoparticles in the presence of a base.

C-N and C-S cross coupling reaction can be accomplished in the presence of relatively inexpensive air-stable CuO nanoparticles. The reaction is simple and efficient and involves cheap air stable catalyst.[50] Rao and coworker developed a nanocrystalline CuO catalyzed coupling of aryl halides with diphenyl diselenide to form diaryl selenide under ligand-free conditions in excellent yields. This protocol has been utilized for the synthesis of a variety of aryl selenides in excellent yields from the readily available aryl halides and diaryl diselenides.[51]



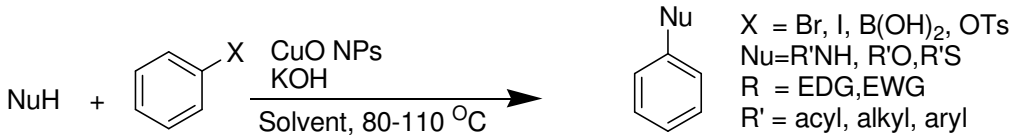
Scheme 4

[50] (a) Rout, L.; Jammi, S.; Punniyamurthy, T. *Org. Lett.* **2007**, *9*, 3397-3399. (b) Rout, L.; Sen, T. K.; Punniyamurthy, T.; *Angew. Chem. Int. Ed.* **2007**,*46*, 5583-5586. (c) Wang, M.; Jiang, H.; Wang, Z. C. *J. Therm. Anal. Cal.* 2006, 85, 751–754.

[51] (a) Reddy, V. P.; Kumar, A. V.; Swapna, K.; Rao, K. R. *Org. Lett.* **2009**, *11*, 951. (b) Reddy, V.P.; Kumar, A.V.; Swapna, K.; Rao, K. R. *Org. Lett.* **2009,** *11*, 1697-1700. (c) Reddy, V. P.; Swapna, K.; Kumar, A. V.; Rao, K. R. *J. Org. Chem.* **2009**, *74*, 3189-3191.

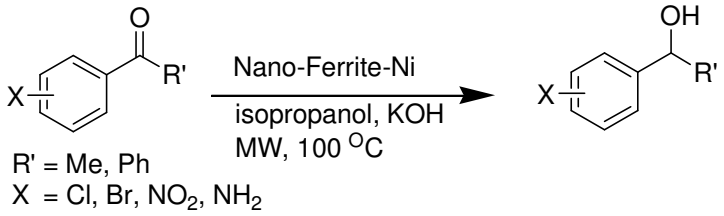
The same authors developed a novel indium-catalyzed C-S cross-coupling reaction. The cross-coupling of aliphatic and aromatic thiols with aryl iodides and aryl bromides generates the corresponding coupling products in good to excellent yields.[51c]

CuO NPs has been studied for the cross-coupling of nitrogen, oxygen, and sulfur nucleophiles with aryl iodides under ligand-free conditions. The catalyst is recyclable, and a variety of substrates undergo reaction in high yield (Scheme 5).[52]



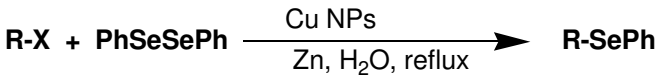
Scheme 5

Verma and coworker[53] developed a novel concept of nanoorganocatalyst, by supporting benign and naturally abundant glutathione on magnetic ferrite nanoparticles. The recyclable catalyst showed excellent activity for Paal–Knorr reaction of a variety of amines and crucially the entire process was carried out in aqueous medium, without using organic solvent in the reaction as well as during the workup (Scheme 6).



Scheme 6

Aryl and vinyl selenide can be conveniently synthesized by copper nanoparticle catalysed reaction of aryl iodide/vinyl bromide with diphenyl diselenide in the presence of zinc in water (Scheme 7). The catalyst was recycled.[54]



Scheme 7

[51](c) Reddy, V. P.; Swapna, K.; Kumar, A. V.; Rao, K. R. *J. Org. Chem.* **2009**, *74*, 3189-3191.

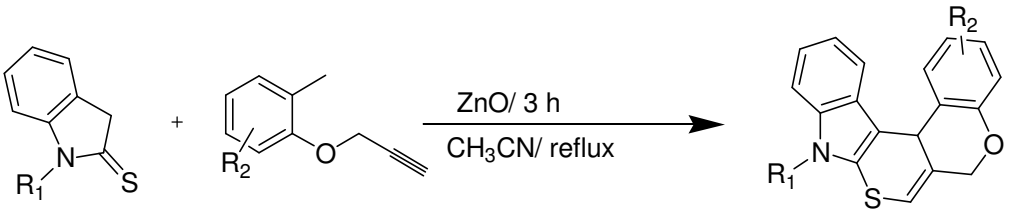
[52] (a) Jammi, S.; Sakthivel, S.; Rout, L.; Mukherjee, T.; Mandal, S.; Mitra, R.; Saha, P.; Punniyamurthy. T. *J. Org. Chem.* **2009**, *74*, 1971-1976.

[53] (a) Polshettiwar, V.; Baruwati, B.; Varma, R. S. *Chem. Commun*. **2009**, 1837-1839. (*b*) Polshettiwar, V. Varma, R. S.; *Org. Biomol. Chem.* **2009**, *7*, 37-40. (*c*) Polshettiwar, V.; Baruwati, B.; Varma, R. S. *Green Chem.* **2009**, *11*, 127. (d) Polshettiwar, V.; Varma, R. S. *Chem.–Eur. J.* **2009**, *15,* 1582-1586.

[54] Saha, A.; Saha, D.; Ranu, B. C. *Org. Biomol. Chem.* **2009**, *7*, 1652-1657.

ZnO NPs has been used for the synthesis of β-acetamido ketones/esters as a reusable, non-toxic and inexpensive heterogeneous nanocatalyst. The major advantage of this method is the ease of the work-up; i.e., the products can be isolated without chromatography. The method also offers some other advantages such as clean reaction, low loading of catalyst, high yields of products, short reaction times and use of various substrates, which make it a useful and attractive strategy for the synthesis of 2 β-acetamido ketones/esters.[55]

Sun and coworker developed ZnO-catalyzed domino Knoevenagel-intramolecular-hetero-Diels–Alder reaction, which provides an efficient route for the formation of polycyclic indole derivatives in a single step (Scheme 8). The major advantage of this reaction is the ease of the work-up during which the products can be isolated without chromatography. This method also offers other advantages such as clean reactions, low loading of catalyst, high yields of products, short reaction times, and the use of ZnO as a non-toxic, non-corrosive, commercially available, and inexpensive heterogeneous catalyst, which make it a useful and attractive strategy for the synthesis of pentacyclic indole derivatives.[56]



Scheme 8

[55] Mirjafary, Z.; Saeidian, H.; Sadeghi, A.; Moghaddam, F. M. *Catal Comm.,* **2008**, 9, 299-306.
[56] Kiamehr, M.; Moghaddam, F. M. *Tetrahedron Lett*., 50, **2009**, 6723-6727

1.6 Room temperature ionic liquids (RTILs)

One of the tasks in striving for sustainable chemistry is the development of new methods that are efficient, high yielding, responsive to mild reaction conditions, and byproduct-free. In this regard, ionic liquids have frequently been used in the last few years as alternative reaction media for a broad range of chemical transformations.

Ionic liquids (ILs) are low-melting organic salts composed solely of cations and anions, which makes them highly tunable for specific applications.[57] Some ILs are noted to have a number of unique properties, including negligible vapor pressures, good thermal stabilities, wide liquid temperature ranges, considerable ionic conductivities, wide electro-chemical windows, and enhanced solvation interactions with both polar and nonpolar compounds.[58] These properties have been shown to have a large number of applications. Moreover, ILs have received considerable attention due to their ability to serve as effective reaction media for a wide range of organic reactions and other applications in chemistry.[59] By modifying the structure of the cations or anions of ionic liquids, it has been shown that their properties can be altered in order to influence the outcome of the reaction.

In recent years, our group successfully employed ILs in the synthesis of diorganyl chalcogenides using different methods, demonstrating that ILs are much more appropriate than other common organic solvents. [60, 61]

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[57] Welton, T. *Chem. Rev*. **1999**, *99*, 2071–2083.

[58] Mallick, B.; Balke, B.; Felser, C.; Mudring, A. V. *Angew. Chem. Int. Ed.* **2008**, *47*, 7635–7638.

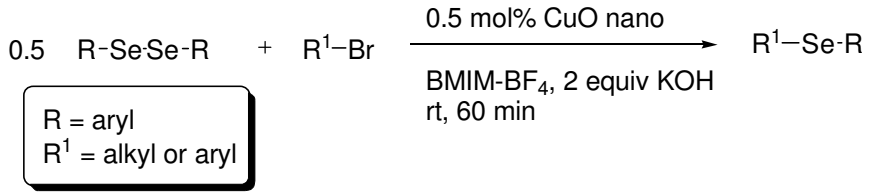
[59] (a) Wasserscheid, P.; Keim, W. *Angew.Chem. Int*. **2000**, *39,* 3772-3789. (b) Hagiwara, R.; Ito,V. *J. Fluorine Chem*. **2000**, *105*, 221-227. (c) Earle,V.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391-1398. (d) Rogers,V.; Seddon, K. R. Ionic Liquids Industrial Applications to Green Chemistry, **2001**, ACS, Symposium Series 818; (e) R. A. Sheldon, *Chem.Commun.* (*Cambridge)* **2001**, 2399-2407. (f) Dupont, J.; de Souza, V.; Suarez, P. A. Z. *Chem. Rev*. **2002**, *102*, 3667-3692. (g) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73-80. (h) Song, C. E. *Chem. Commun*. **2004**, *9*, 1033-1043. (i) Cassol, C. C.; Ebeling, G.; Ferrera, B.; Dupont, J. *Adv. Synth. Catal.* **2006**, *348*, 243-248. (j) Ranke, J.; Stolte, S.; Störmann, R.; Arning, J.; Jatropha, B. *Chem. Rev*. **2007**, *107*, 2183-2206. (k) Hapiot, P.; Lagrost, C. *Chem. Rev*. **2008**, *108*, 2238-2264. (l) Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis, 2nd ed., Wiley-VCH, Weinheim, **2008**. (m) Martins, M. A. P.; Frizzo, C. P.; Moreira, D. N.; Zanatta, N; Bonacorso, H. G. *Chem. Rev*. **2008**, *108*, 6, 2015–2050.

[60] Narayanaperumal, S.; Alberto, E. E.; Gul, K.; Rodrigues, O. E. D.; Braga, A. L. *J. Org. Chem.* **2010**, 75, 3886–3889.

[61] (a) Narayanaperumal, S.; Alberto, E. E.; de Andrade, F. M.; Lenardão, E. J.; Taube, P. S.; Braga, A. L.; *Org. Biomol. Chem*, **2009**, *7*, 4647-4650. (b) Singh, D.; Alberto, E. E.; Rodrigues, O. E. D.; Braga, A. L. *Green Chem.* **2009**, *11*, 1521–1524. (c) Singh, D.; Narayanaperumal, S.; Gul, K.; Godoi, M.; Rodrigues, O. E. D.; Braga, A. L. *Green Chem.,* **2010**, *12*, 957–960.

1.7 Use of IL on metal oxide nanoparticales

Next, we focused on the use of ionic liquids, which function as a mild and recyclable medium, and on effective metal oxide nanoparticles for the synthesis of unsymmetrical diorganyl selenides. In this regard, our group recently reported an eco-friendly cross-coupling of diaryl diselenides with aryl and alkyl bromides catalyzed by CuO NPs in ionic liquid (Scheme 9). [61b]



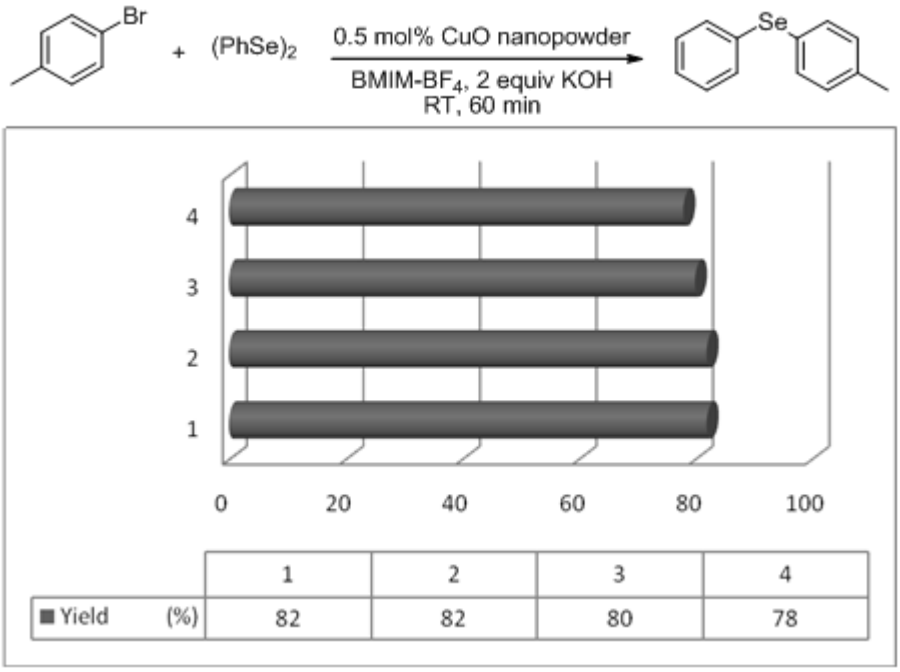
Scheme 9

Although, the synthesis of diaryl selenides using CuO NPs has appeared in the literature, [51] the reported protocol shows some shortcomings, such as long reaction times and high temperatures, limiting the scope of the reaction to substrates that can withstand these harsh reaction conditions. Moreover, the use of solvents such as DMSO is undesirable from an environmental point of view.

[61(b)] Singh, D.; Alberto, E. E.; Rodrigues, O. E. D.; Braga, A. L. *Green Chem.* **2009**, *11*, 1521–1524.

[51](a) Reddy, V. P.; Kumar, A. V.; Swapna, K.; Rao, K. R. *Org. Lett.* **2009**, *11*, 951. (b) Reddy, V.P.; Kumar, A.V.; Swapna, K.; Rao, K. R. *Org. Lett.* **2009,** *11*, 1697-1700. (c) Reddy, V. P.; Swapna, K.; Kumar, A. V.; Rao, K. R. *J. Org. Chem.* **2009**, *74*, 3189-3191.

By changing the solvent from DMSO to solvent/ionic liquid, the conversion rates were accelerated and higher yields were obtained. The developed methodology offers a clean, eco-friendly, inexpensive and efficient approach to obtaining diaryl or alkyl aryl selenides from alkyl or aryl halides with diaryl diselenides using CuO NPs in ionic liquid. In the search for a 'greener' protocol, the recyclability of ILs was studied and the respective solvent (BMIM-BF_4) was reused for four additional reaction runs without significant loss of efficiency, as shown in Figure 1.



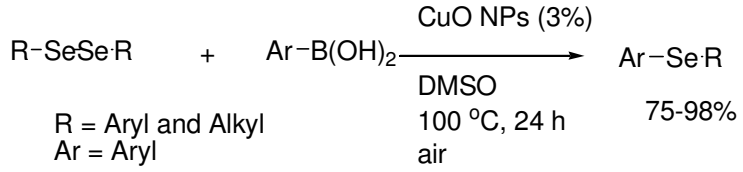
	1	2	3	4
Yield (%)	82	82	80	78

Figure 1: Reuse of BMIM-BF_4

The noteworthy features of this method include the following: (i) use of easily accessible alkylating agents; (ii) use of low-loading catalyst; and (iii) use of recyclable solvent.

Moreover, CuO NPs have been employed as a mediator, as an efficient and recyclable catalyst for cross-coupling reactions of organic diselenides with aryl boronic

acids (Scheme 10). [62] Generally, this kind of reaction involves particularly specific ligands, which may increase the cost and limit the scope of applications.



Scheme 10

These ligand-free cross-coupling reactions of organic diselenides with aryl boronic acids using a catalytic amount of CuO NPs in DMSO at 100 ^{0}C under air atmosphere afford the corresponding products in good to excellent yields. The catalyst can be easily recovered and utilized for further catalytic reactions, as depicted in the Figure 2.

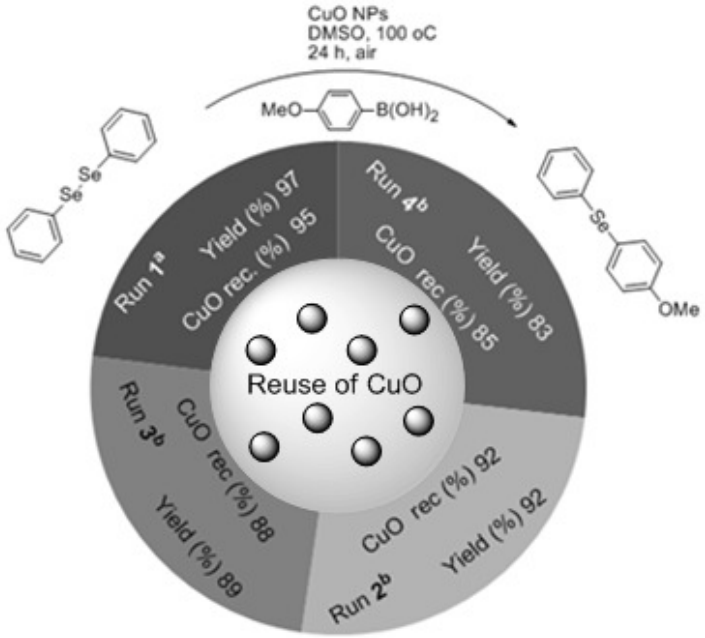


Figure 2: Reuse of CuO. [a] Reaction performed in the presence of diselenide (0.5 mmol), aryl boronic acid (1.5 equiv), 3 mol% of CuO NPs and DMSO (1 mL). [b] Recovered catalyst used. Yields are given for isolated products.

[62] Alves, D.; Santos, C.G.; Paixão, M. W.; Soares, L.C.; de Souza, D.; Rodrigues, O.E.D.; Braga, A.L. *Tetrahedron Lett*. **2009**, *50*, 6635–6638.

Objectives:

From the sustainable chemistry point of view, there is a need for new methods which are not only very efficient but high yielding under mild reaction conditions. In this context, ionic liquids have frequently been used in the last few years as alternative reaction media for a broad range of chemical transformations. Apart from direct replacement of organic solvents, ionic liquids have been shown to deliver improved yields in a number of chemical reactions and facilitate product recovery and have the potential for recyclability.

We planed herein a simple approach to prepare unsymmetrical diorganyl selenides and sulfides, using an ionic liquid as a reusable solvent. Besides, we planed to introduce the system Cu(II)/Sn(II) as a reducing agent for the Y-Y bond (Y= S, Se) to prepare unsymmetrical diorganyl selenides and sulfides.

Organic reactions catalyzed by metallic nanostructures gained enormous popularity and relevance in recent years. Generally, catalysts in nanoscale afford a more effective process and allow a genuine advance in relation to traditional methodologies. In this new intensive area one of the tasks in striving for sustainable chemistry is the development of new methods that are efficient, high yielding, responsive to mild reaction conditions, and byproduct-free. The search for efficient, convenient and recyclable reaction media based on ionic liquids remains a major challenge.

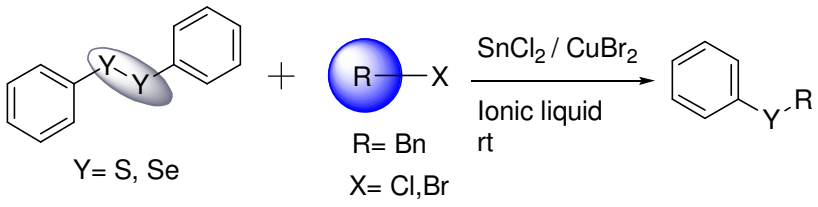
2. Results and Discussion:

In this chapter, results and discussion obtained during the synthesis of diorganyl selenides and sulfides, chiral β-seleno amines, and seleno- and thioesters using two kind of systems i.e bimetallic systems [Sn(II)/Cu(II)] and ZnO NPs using Zn in ionic liquid will be presented.

In our first attempt we used bimetallic system [Sn(II)/Cu(II)] to synthesize these class of compounds and secondly Transition-metal oxide nanopowder were used in ionic liquid.

2.1 Preparation of diorganyl selenides and sufides using bimetallic system [Sn(II)/Cu(II)]:

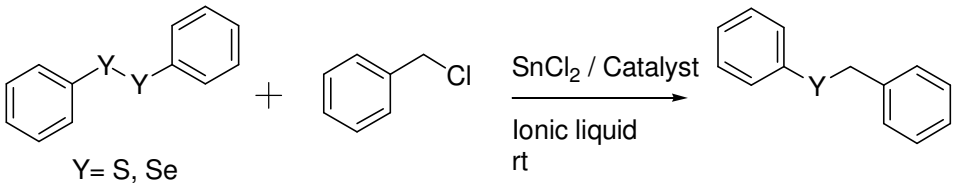
On account of our interest in organochalcogen chemistry it is evident that there is a need for reliable, reproducible and high yielding synthetic methods for the preparation of these classes of compounds (as described in chapter 1). In this context we turned our focused towards the synthesis of diorganyl selenide and sulfide using bimetallic system Cu (II)/Sn (II). Initially Cu(II)/Sn(II) is used as a reducing agent for the Y-Y bond (Y= S, Se) to prepare unsymmetrical diorganyl selenides and sulfides, looking to be having a short reaction times, under mild conditions, in a variety of substrates, at room temperature and with excellent yields, using an ionic liquid as a reusable solvent (Scheme 11).



Scheme 11

We began our investigation by employing bimetallic reagent Sn(II)/Cu(II) in ionic liquid for the cleavage of PhSeSePh and PhSSPh. Benzyl phenyl selenide and sulfide were afforded in a standard protocol using 0.5 equiv. of diphenyl diselenide and disulfide in the presence of 1.2 equiv. of $SnCl_2$, 0.2 equiv. of $CuBr_2$ and 1.1 equiv. of benzyl chloride as a halide, using different ionic liquids (Table 1).

Table 1. Optimization for the synthesis of diorganyl selenides and sulfides using Sn(II)/Cu(II) in ionic liquid.



Entry	$SnCl_2$ [mmols]	Catalyst[a] [mmols]	Ionic Liquid[b]	Time [min]		Yield[c] [%]	
				Y= Se	Y= S	Y=Se	Y= S
1	1.2	A	BMIM-BF_4	180	120	85	88
2	1.2	B	BMIM-BF_4	180	120	79	83
3	1.2	A	BMIM-PF_6	180	120	58	65
4	1.2	A	BMIM-NTf_2	180	120	28	37
5	1.2	A	BMMIM-BF_4	180	120	63	70
6	1.2	A	BPy-BF_4	180	120	34	38
7	1.2	-	BMIM-BF_4	180	120	Traces	

[a] Catalyst A= $CuBr_2$, B= $CuCl_2$; [b] Ionic liquids were prepared using a procedure available in the literature [ref. 59i] and were subjected to vacuum before use. [c] Yields refer to pure isolated products, characterized by ^1H and ^{13}C NMR spectroscopic data.

[59i]Cassol, C. C.; Ebeling, G.; Ferrera, B.; Dupont, J. *Adv. Synth. Catal.* **2006**, *348*, 243-248.

2.1.1 Influence of ionic liquid:

To understand the influence of different variables in this reaction, several components were studied to optimize our procedure. Initially, we investigated the effect of ionic liquids on the reaction course, using a standard model for the synthesis of diorganyl chalcogenides. To this aim, five different ionic liquids (Figure 3) were used for the synthesis of the desired products.

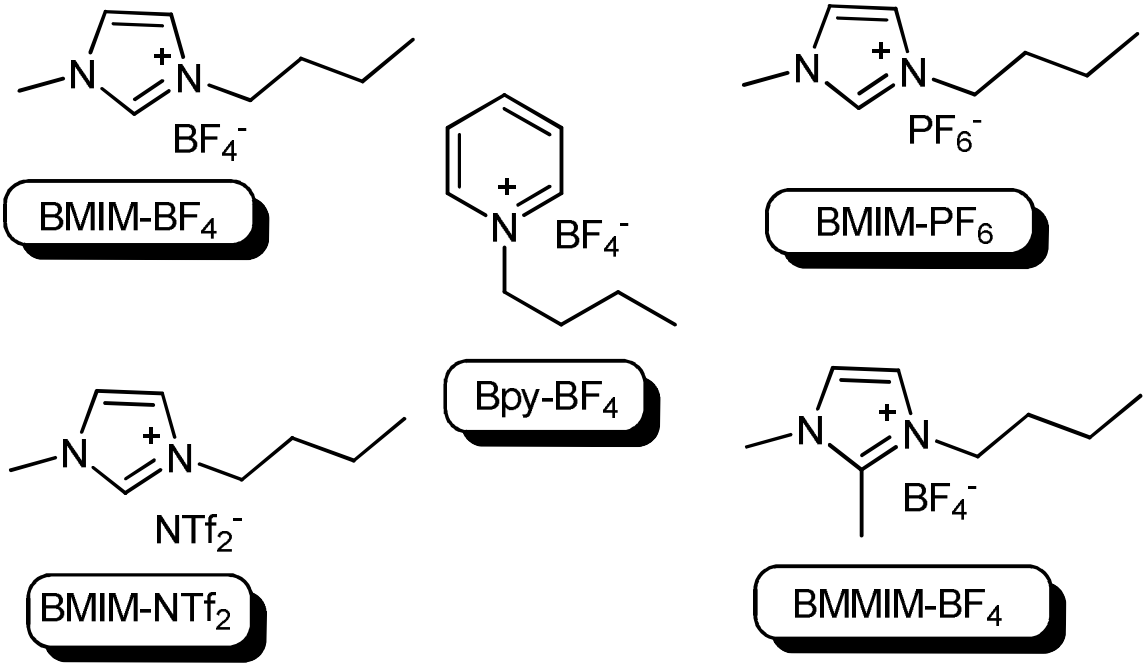


Figure 3. Room temperature ionic liquids.

According to the outcome of the methodology BMIM-BF_4 showed better result than other ionic liquids (Table 1, entry 5). The enhanced capability of ionic liquid to speed up many organic reactions compared to other organic solvents has been widely reported, the origin of its behavior is still an interesting option. Properties of ionic liquids such as strong dipolar and dispersion forces, hydrogen bond acidity (related to the cationic portion), and hydrogen bond basicity (related to the anionic portion) would

account for the complex solvent interactions exhibited by ILs.[63] In previous reports hydrogen bonds have been evoked as a key interaction in the formation of a given product in reactions performed in ILs.[63a-c] On the basis of our experimental results (Table 1) it is reasonable to visualize that perhaps the scale of hydrogen bond acidity of the tested ILs may be an eminent property for the product formation. For example If we consider that this characteristic would facilitate the reaction through the coordination of the acid hydrogen attached to C-2 in the imidazolium ring with the leaving group (chloride) in an S_N2 like reaction, the formation of products would be in the same range of yield for BMIM-BF_4, BMIM-PF_6, and BMIM-N- $(Tf)_2$ due to the similarity of their hydrogen bound donor (HBD) parameters.[63e-g] With the exception of BMIM-$N(Tf)_2$, which gives less yield (entry 4), BMIM-BF_4 and BMIM-PF_6 furnished the desired product in good to excellent yields, respectively (entries 1-3). Furthermore, if the extent of hydrogen bond interactions really accounts for an effective formation of products, reactions carried in Bpy-BF_4 and BMMIM-BF_4 which has a much lower (HBD) value compared to the above-mentioned ionic liquids would result in the formation of products in lower yields. Actually, these ILs exhibited poorer activity compared to BMIM-BF_4 and BMIM-PF_6 (entries 5 and 3).

The changes in the cationic and anionic moieties in the solvent/ionic liquid have a remarkable effect, as shown in Table 1. Using BMIM-BF_4 the desired products were achieved in good yield, followed by BMMIM-BF_4 and BMIM-PF_6. The use of BMIM-NTf_2 and BPy-BF_4 led to a significant decrease in the yield (Table 1, entries 4 and 6).

[63] (a) Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. *Tetrahedron Lett*. 1999, *40*, 793–796. (b) Chakraborti, A. K.; Roy, S. R. *J. Am. Chem. Soc*. **2009**, *131*, 6902–6903. (c) Baciocchi, E.; Chiappe, C.; Giacco, T. D.; Fasciani, C.; Lanzalunga, O.; Lapi, A.; Melai, B. *Org. Lett*. **2009**, *11*, 1413–1416. (d) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc*. **2002,** *124,* 14247–14254. (e) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B*. **2006**, *110*, 19593–19600. (f) Nockemann, P.; Thijs, B.; Hecke, K. V.; Meervelt, L. V.; Binnemans, K. *Cryst. Growth Des*. **2008**, *8,* 1353–1363.

2.1.2 Effect of Catalyst:

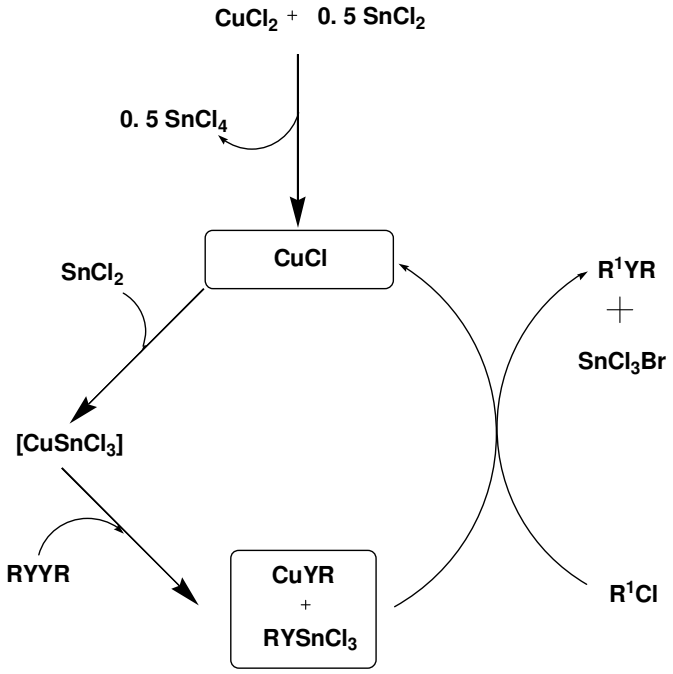
After the studying about the influence of ionic liquid we focused on the effect of catalyst. The investigation suggested a bimetallic reactivity toward the formation of unsymmetrical diorganyl selenides and sulfides under extremely mild conditions. There are two kind of catalyst used in this methodology. In this way the reaction proceeds very well with catalytic cupric bromide. But when $CuCl_2$ was used the yield was lower compared with the use of $CuBr_2$ (Table 1, entries 1 and 2). On the other hand, in the absence of $CuBr_2$ the reaction of benzyl chloride with diphenyl diselenide and disulfide gave only trace amounts of the corresponding product (Table 1; entry 7). Thus, a combination of $SnCl_2$ and $CuBr_2$ in ionic liquid is essential for this transformation.

2.1.3 Plausible Reaction Mechanism:

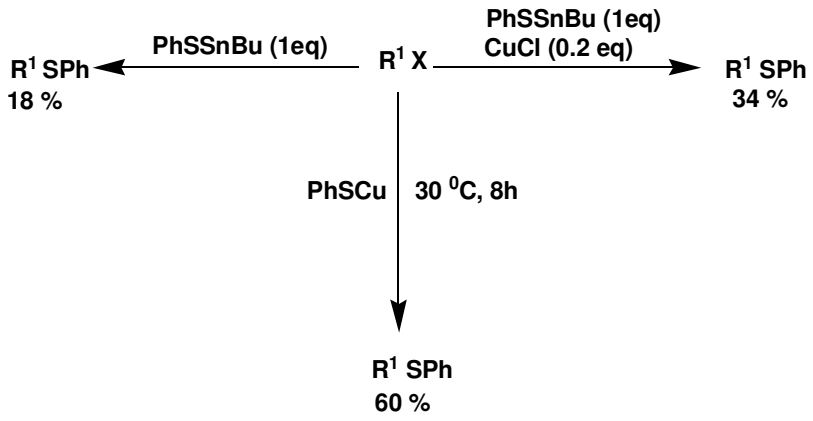
Based on the reported literature [45] we are going to propose the plausible reaction mechanism for this kind of reaction (Scheme 12). In the present study, as discussed before, is yet insufficient to postulate the actual pathway of PhSeSePh or PhSSPh cleavage reactions. The experimental evidence, however, suggests that bimetallic participation is mandatory during the cleavage of PhSeSePh or PhSSPh bond and subsequent C-Se or C-S bond formation. This observation could be observed during the optimization. A suggestion, pertaining to this hypothesis, for the activation of diphenyl diselenide or diphenyl disulfide is shown in Scheme 12, involving the earlier formation of intermediate $CuSnCl_3$ from the reaction of copper(I) chloride and stannous chloride. Further the formation of $PhYSnCl_3$ from the reaction of $CuCl_2$, $SnCl_2$, and PhYYPh is discrete proof of the bimetallic reactivity. [45c, d]

[45] (a)Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics.,* 1997, *16,* 4796-4799. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S.; *Organometallics.* 1999, *18,* 2782-2785. (c) Kundu, A.; Roy, S. *Organometallics.* 2000, *19,* 105-107. (d) Sinha, P.; Kundu, A.; Roy, S.; Prabhakar, S.; Vairamani, M.; Ravi Sankar, A.; Kunwar, A. C. *Organometallics.* 2001, *20,* 157-162.

Hence the plausible mechanisms for this kind of reaction are as follows:



Scheme 12



Scheme 13[45]

[45] (a)Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics.,* 1997, *16,* 4796-4799. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S.; *Organometallics.* 1999, *18,* 2782-2785. (c) Kundu, A.; Roy, S. *Organometallics.* 2000, *19,* 105-107. (d) Sinha, P.; Kundu, A.; Roy, S.; Prabhakar, S.; Vairamani, M.; Ravi Sankar, A.; Kunwar, A. C. *Organometallics.* 2001, *20,* 157-162.

However, in the present study there is a major question which is to be addressed which is between $PhYSnCl_3$ and $CuCl_2$ which one is principle reactive intermediate? To solve this problem here Roy and his coworker [45d] carried out a model study starting from the readlt available PhSSnBu (Scheme 13). On the basis of that observation it is prove that;

1. Reaction of PhSSnBu with organo halide under reflux and after 8 h affords the produt in 18% isolated yield along with unreacted starting material.

2. The above reaction, but in the presence of CuCl (0.2 equiv) and after 8 h, affords the product in 34% isolated yield along with n-Bu_3SnCl.

3. Reaction of authentic CuSPh and organo halide proceeds smoothly under ambient conditions and after 8 h affords the product in 60% isolated yield.

The above postulate clearly establishes "the catalytic role of copper" and demonstrates that the sulfur transfer reaction is proceeding majorly via in-situ generated copper thiolate.

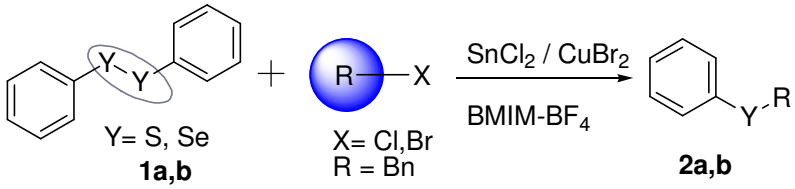
2.1.4 Optimization of Reaction time and Temprature:

Subsequently after the studying the influence of ionic liquids and the effect of catalyst we turned our attention to optimize the reaction time and temperature. The amount of $CuBr_2$, the reaction time and the temperature required to promote the transformation were also evaluated. The reaction was temperature-dependent both for diphenyl diselenides and disulfides, and at the higher temperature the product was formed in lower yields (Table 2, entry 1) when compared with room temperature.

[45] (a)Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics.,* 1997, *16,* 4796-4799. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S.; *Organometallics.* 1999, *18,* 2782-2785. (c) Kundu, A.; Roy, S. *Organometallics.* 2000, *19,* 105-107. (d) Sinha, P.; Kundu, A.; Roy, S.; Prabhakar, S.; Vairamani, M.; Ravi Sankar, A.; Kunwar, A. C. *Organometallics.* 2001, *20,* 157-162.

Afterwards, the reaction time was also monitored, ranging from 30 to 180 min. On analyzing Table 2, it is possible to verify that the sulfide **2a** afforded the desired compound in a shorter time than the selenide **2b** and with better yields (Table 2, entries 1-6). The best yield for the selenides was observed in 60 min whereas for sulfides **2a** the optimum reaction time was 30 min (Table 2, entries 4 and 6). The use of a longer reaction time in the synthesis of both chalcogenides did not afford considerable improvement in the yields (Table 2, entries 2-4) but with a shorter reaction time the desired chalcogenides were afforded in lower yield (Table 2, entry 5). By changing the substrate from benzyl chloride to bromide both disulfide **2a** and diselenide **2b** were obtained in better yields (Table 2, entry 6). This can be attributed to the greater leaving group ability of bromide compared with chloride.

Table 2. Optimization of reaction time and temperature.



	$SnCl_2$ [mmol]	$CuBr_2$ [mmol]	X	Ionic Liquid[a]	Time [min]		T [^{0}C]	Yield[b] [%]	
					Y= Se	Y= S		Y=Se	Y=S
1	1.2	0.2	Cl	$BMIM\text{-}BF_4$	180	120	90	73	75
2	1.2	0.1	Cl	$BMIM\text{-}BF_4$	180	120	rt	84	88
3	1.2	0.1	Cl	$BMIM\text{-}BF_4$	120	60	rt	83	85
4	1.2	0.1	Cl	$BMIM\text{-}BF_4$	60	30	rt	81	85
5	1.2	0.1	Cl	$BMIM\text{-}BF_4$	30	20	rt	75	78
6	1.2	0.1	Br	$BMIM\text{-}BF_4$	60	30	rt	88	92

[a] Ionic liquids were subjected to vacuum before use. [b] Yields refer to pure isolated products, characterized by ^1H and ^{13}C NMR spectroscopic data.

Therefore, the optimum combination for this transformation was found to be 0.5 equiv. of diaryl chalcogenide with 1.1 equiv. of organic halide, which requires 1.2 equiv. of $SnCl_2$, 0.1 equiv. of $CuBr_2$ and 0.5 mL of BMIM-BF_4 at room temperature, in 60 min of reaction time to afford the diorganyl selenide **2b** and in 30 minutes the diorganyl sulfides **2a**.

2.1.5 Comparison between Ionic liquid and Organic Solvent:

Some drawbacks to the synthesis of diorganyl selenides and sulfides using the bimetallic system Sn(II)/Cu(II) in organic solvents such as THF and benzene, is that it requires harsh reaction conditions such as longer reaction time, reactive halogenated systems and higher temperature.[64] In contrast, the use of solvent/BMIM-BF_4 yields the diorganyl selenide and sulfides in a short time, at room temperature and under neutral and very mild conditions with good to excellent yields (Table 3). Roy and his coworker [45] used bimetallic system Sn(II)/Cu(II) to the synthesis of diorganyl selenides and sulfides in organic solvents. By comparing the result with Roy *et.al,* our methodology is more efficient and pronounced the advantages of our methodology are:

1 Less reactive halide are also possible to convert into sulfides and selenides while in their methodology only the activated halide are possible to convert to sulfide and selenide.

2 Reaction time is very less (60 minutes to afford diorganyl selenide and 30 minutes to afford diorganyl sulfides) as compared with their reaction time.

3 In short reaction time better yield were obtained.

4 Eco-friendly nature of reaction.

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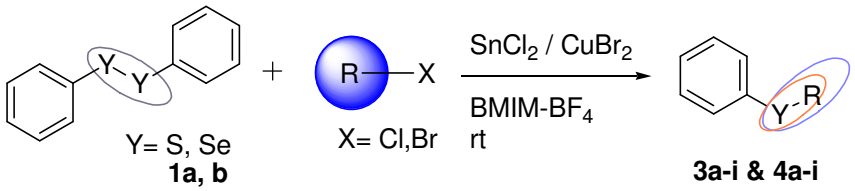
[64] J. Ranke, S. Stolte, R. Störmann, J. Arning, B. Jatropha, *Chem. Rev*. **2007**, *107,* 2183-2206

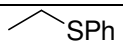
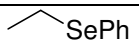
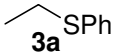
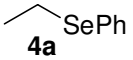
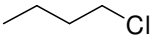
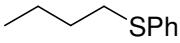
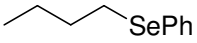
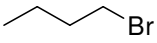
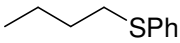
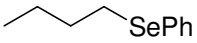
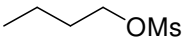
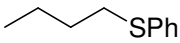
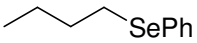
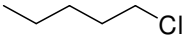
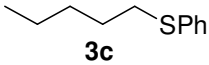
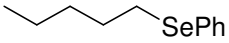
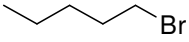
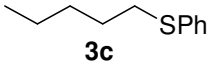
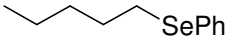
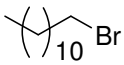
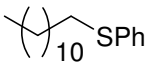
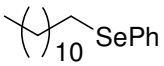
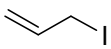
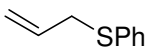
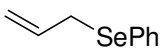
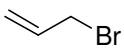
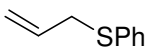
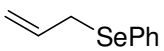
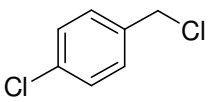
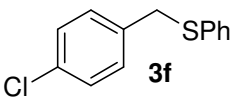
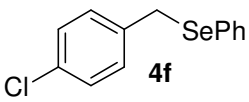
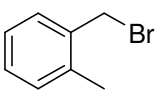
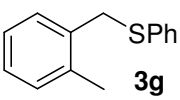
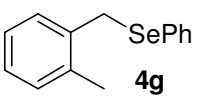
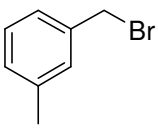
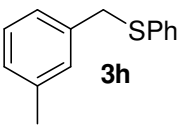
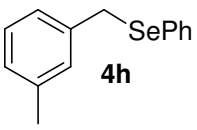
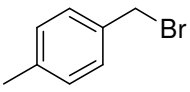
[45] (a)Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S. *Organometallics.,* 1997, *16,* 4796-4799. (b) Kundu, A.; Prabhakar, S.; Vairamani, M.; Roy, S.; *Organometallics.* 1999, *18,* 2782-2785. (c) Kundu, A.; Roy, S. *Organometallics.* 2000, *19,* 105-107. (d) Sinha, P.; Kundu, A.; Roy, S.; Prabhakar, S.; Vairamani, M.; Ravi Sankar, A.; Kunwar, A. C. *Organometallics.* 2001, *20,* 157-162.

With the optimized results in hand, we next turned to exploring the versatility of the substitution reaction for the synthesis of aryl alkylselenides and sulfides using diphenyl dichalcogenide and a variety of alkyl halides as starting materials. The results of this investigation are summarized in Table 3. From the Table 3, it is clear that this method is general, and all the reactions proceed smoothly under mild reaction conditions to afford the desired product.

In order to demonstrate further the scope of this methodology, we synthesized different diorganyl selenides and sulfides. In general, the diorganyl sulfides were obtained in better yield than the diorganyl selenides. Although the selenolate intermediate is more reactive than the respective thiolate, the lower stability of the selenium species can explain their lower efficiency in the selenide synthesis. A wide range of structurally diverse alkyl halides underwent reactions with diphenyl diselenides and disulfides by this procedure to produce the corresponding alkyl phenyl selenides and sulfides respectively, in good to excelent yields. Initially, the experiments were carried out with alkyl halides, with different chain lengths and halides. From Table 3 it is possible to verify that, in all cases, bromides furnished the respective selenides and sulfides in higher yields than the corresponding chlorides and mesylates (Table 3, entries 3 –7) and the best leaving group ability could be evidenced as an important factor in the reaction yield. This protocol shows high tolerance in terms of chain length and the corresponding chalocogenides could be prepared in good yield with 2 to 12 carbon atoms in the organic chain (Table 3, entries 1-8).

Table 3: Synthesis of diorganyl selenides and sulfides using Sn(II)/Cu(II) in BMIM-BF_4.



Entry[a]	RX	Products	Yield [%][b]	Products	Yield [%][b]
1		 **3a**	75	 **4a**	68
2		 **3a**	80	 **4a**	75
3		 **3b**	79	 **4b**	74
4		 **3b**	85	 **4b**	80
5		 **3b**	65	 **4b**	58
6		 **3c**	82	 **4c**	80
7		 **3c**	89	 **4c**	84
8		 **3d**	77	 **4d**	72
9		 **3e**	99	 **4e**	98
10		 **3e**	97	 **4e**	93
11		 **3f**	92	 **4f**	83
12		 **3g**	75	 **4g**	67
13		 **3h**	84	 **4h**	79
14		**3i**	98	**4i**	94

[a] Ionic liquids were subjected to vacuum before use. [b] Yields refer to pure isolated products. [c] Y= S reaction time 30 min. [d] Y= Se reaction time 60 min.

The use of more reactive allyl iodide allowed near quantitative conversion (Table 3; entry 9) with a similar result found for allyl bromide (Table 3; entry 10) showing the influence of the substrate on the reaction yield. Substituted benzylic systems were studied in the chalcogenide synthesis. A good result was obtained in the reaction of 4-chloro benzyl chloride, with diphenyl diselenide and disulfide (Table 3; entry 11). Notably, a steric effect by the aromatic substituents could be observed in the course of the reaction. For instance, with the more hindered *o*-methyl substituent the respective selenide and sulfide were obtained in lower yield than with the corresponding *m*- and *p*-methyl substituent (Table 3, entries 12 – 14).

2.2 Synthesis of Seleno- and thioester using Sn(II)/Cu(II) in BMIM-BF_4:

The versatility of this methodology was such that we were also able to synthesize seleno- and thioester. The distinct reactivity of Cu(II)/Sn(II) to cleave the PhSeSePh and PhSSPh bond, as illustrated above prompted us to check the applicability of our reaction to synthesize more diverse compounds. In order to improve the scope of our methodology, we attempted to synthesize interesting functionalities such as seleno- and thioesters.

Selenoesters have been extensively applied as mild acyl transfer agents, both as acyl radicals or anions, to promote the synthesis of carbonyl compounds.[20] On account of this, they have been the method of choice applied in the acylation step in the synthesis of many natural products.[65] This class of compounds has also found application as liquid crystals, [21] as precursors for the synthesis of N-aminoacyl sulfonamides, for lactonizations and as selenating agents.[66]

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There are a number of methods reported in the literature to synthesize selenoesters using different metals, including palladium complexes (such as $Pd(PPh_3)_4$), Sm, In, InI, $Hg(SePh)_2$, $PhSeSnBu_3$/Pd, and Rh/H_2 systems.[12,30] However, these procedures have limitations such as the air reactivity of metals, harsh conditions, and the difficulty involved in handling selenium or sulphur compounds, besides the use of toxic and carcinogenic solvents.

Thioesters are one of the most useful building blocks for organic transformations. They have found application in C-C coupling, [35] for the synthesis of carbonyl compounds, [36] in asymmetric aldol reactions[37] and more recently, their α-β unsaturated analogs have been successfully applied for asymmetric 1-4 additions, which allow access to chiral intermediates for the synthesis of more complex compounds.[67] Furthermore, they have been applied in natural product synthesis and can act as biologically relevant substances for *in vivo* tumor suppression and as anti-HIV agents.[30] Many methods have been described in the literature for the synthesis of this valuable class of compounds.[39, 42]

In a fashion similar to the synthesis of diorganyl selenide and sulfide we turned our attention to employ our standard reaction conditions to synthesize the seleno- and thioesters and the results are presented in Table 4.

---

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[35](a) Choi, J.; Imai, E.; Mihara, M.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M. *J. Org. Chem.* **2003**, *68*, 6164- 6171. (b) Prokopcová, H.; Kappe, C. O. *Angew. Chem. Int. Ed.* **2008**, *47*, 3674-3676.

[37]McGarvey, G. J.; Williams, J. M.; Hiner, R. N.; Matsubara, Y.; Oh, T. *J. Am. Chem. Soc*. **1986**, *108*, 4943-4952.

[36](a) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763-4765. (b) Anderson, R. J.; Henrick, C. A.; Rosenblum, L. D. *J. Am. Chem. Soc.* **1974**, *96*, 3654-3655; (c) Liebeskind, L.S.; Srogl, J. *J. Am. Chem. Soc*. **2000**, *122*, 11260-11261.

[39]Ravi, D.; Rao, N.; Reddy, G. S. R.; Sucheta K.; Rao, V. J. *Synlett* **1994**, 856.

[42](a) Ogawa, A.; Kawakami, J.; Mihara, M.; Ikeda, T.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 12380-12381. (b) Kawakami, J.; Mihara, M.; Kamiya, I.; Takeba, M.; Ogawac, A.; Sonoda, N. *Tetrahedron* **2003**, *59*, 3521- 3526.

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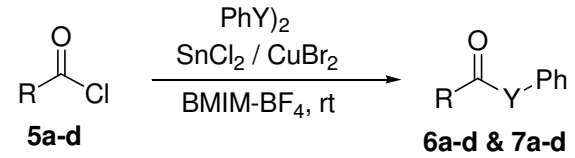
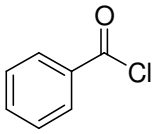
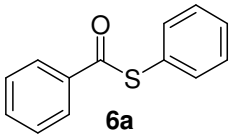
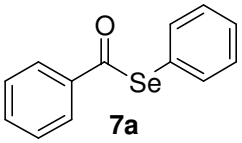
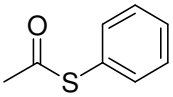
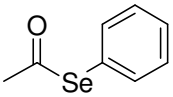
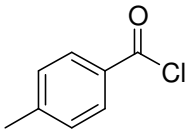
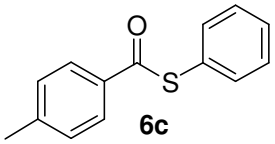
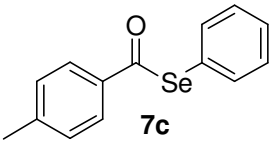
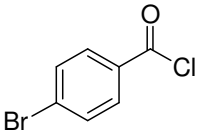
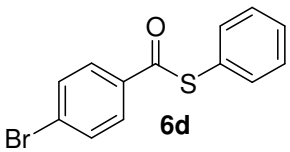
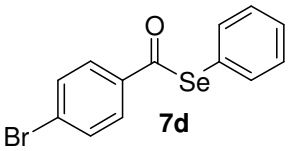
Table 4: Synthesis of seleno- and thioesters using Sn(II)/Cu(II) in BMIM-BF_4.



R = Ph, Me, *p*-Me-C_6H_4, *p*-Br-C_6H_4
Y = S,Se

Entry	Acyl Chloride	Products	Yield [%][a,b]	Products	Yield [%][a,b]
1		 **6a**	84	 **7a**	79
2		 **6b**	17	 **7a**	10
3		 **6c**	60	 **7c**	52
4		 **6d**	82	 **7d**	75

[a] Ionic liquids were subjected to vacuum before use. [b] Yields refer to pure isolated products. [c] Y= S reaction time 30 min. [d] Y= Se reaction time 60 min.

The use of benzoyl chloride, which reacts with diphenyl diselenide, gave the respective selenoester in 79% yield whereas with diphenyl disulfide afforded the thioester in 84% yield (Table 4, entry 1). A decrease in yield was obtained for reactions with aliphatic acyl chloride (Table 4, entry 2). Good yields were achieved by using electron donating or electron withdrawing groups attached to the acyl chloride moiety (Table 4, entries 3 and 4).

The purity of these compounds is assessed by NMR spectra. As an example the NMR spectra of one compound is given below,

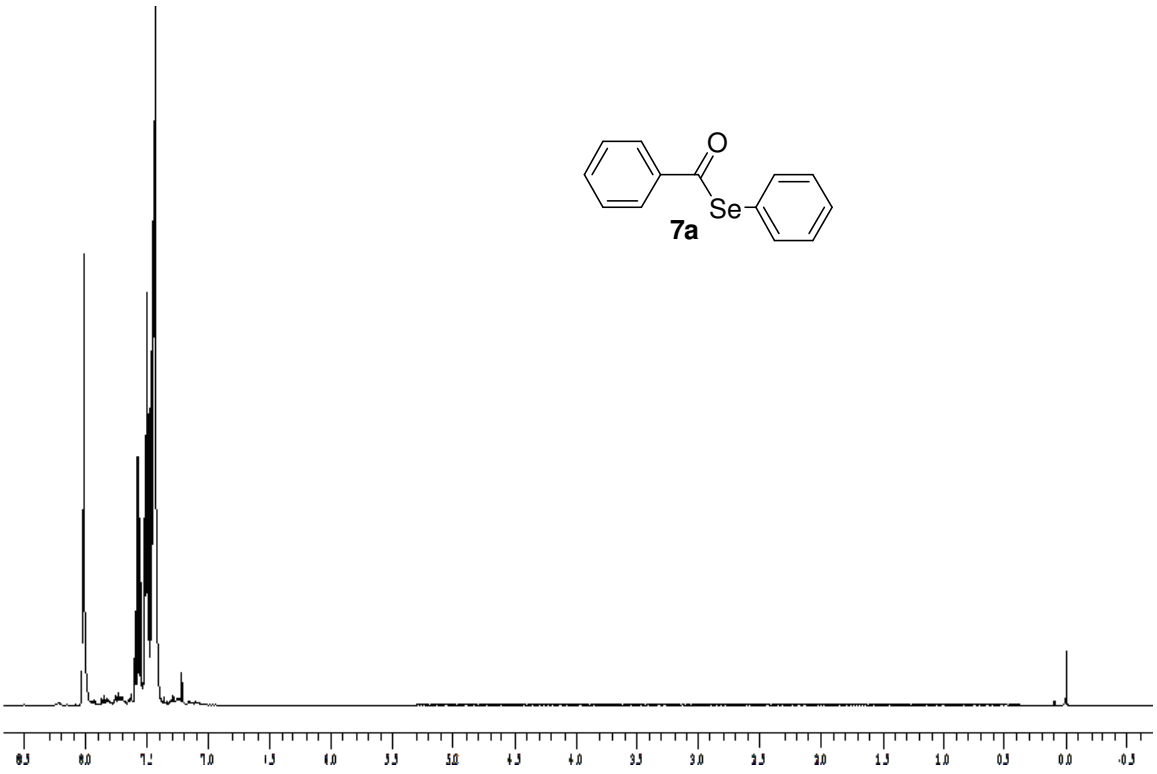


Figure 4: NMR spectra ^{1}H (200 MHz) in $CDCl_3$

In the ^{1}H NMR spectra (Figure 4) it is possible to observe one multiplet of signals in the region between 8.03 and 8.00 ppm relative to 2H, characteristic peak from the aromatic hydrogen of phenyl group. The second set of multiplet appeared between 7.59 and 7.41 ppm is relative to 8 H, characteristic of the aromatic hydrogen of phenyl group.

The ^{13}C NMR spectra (Figure 5) show one peak at 189.9 ppm of carbonyl carbon. Aromatic carbons appeared at 135.0, 133.5, 129.4, 129.1, 128.6, 127.3, 127.2 ppm. The ^{1}H and ^{13}C NMR spectral data of the compound confirmed that the formation of product was successfully accomplished.

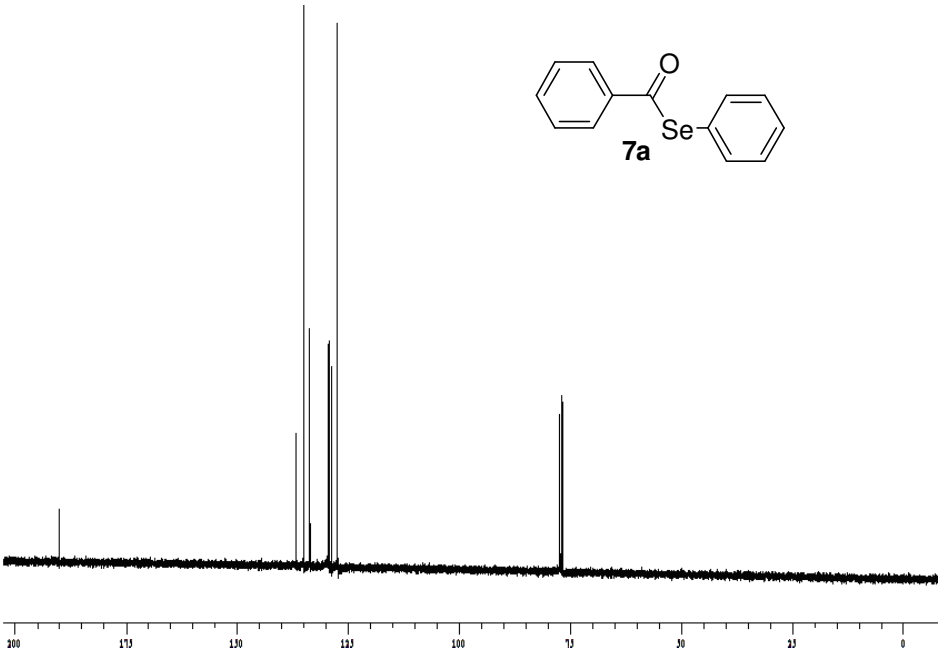


Figure 5: ^{13}C NMR spectra (100 MHz) in $CDCl_3$

2.3 Synthesis of chiral β-sulfur and seleno amines using Sn(II)/Cu(II) in BMIM-BF_4:

After the synthesis of seleno- and thioester, we decided to apply the similar strategy, to prepare chiral β-sulfur and seleno amines. A more complex challenge in organochalcogenium chemistry is the development of new methods for the introduction of selenium or sulfur-containing groups into organic molecules. Synthesis of chiral β-sulfur and seleno amines using bimetallic Sn(II)/Cu(II) reagents in ionic liquids is a highly versatile way to create C-Se and C-S bonds. [21, 68]

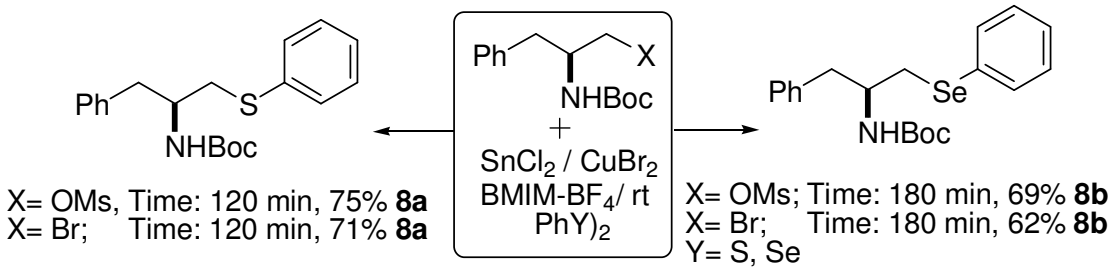
With this object in mind, we focused our attention on the synthesis of chiral β-sulfur and seleno amines which can be obtained from the reaction of β-amino mesylate and bromo

[21] (a) Heppke, G.; Martens, J.; Praefcke, K.; Simon, H. *Angew. Chem. Int. Ed* **1977**, *16*, 318-319. (b) Yamada, J.; Akutsu, H.; Nishikawa, H.; Kikuchi, K. *Chem. Rev*. 2004, *104,* 5057-5084. (c) Cristiano, R.; Vieira, A. A.; Ely, F.; Gallardo, H. *Liq. Cryst*. 2006, *33*, 381-390.

[68] For selected examples see: (a) Braga, A. L.; Silva, S. J. N.; Lüdtke, D. S.; Drekener, R. L.; Silveira, C. C.; Rocha, J. B. T.; Wessjohann, L. A. *Tetrahedron Lett.* **2002**, *43,* 7329-7331. (b) Braga, A. L.; Lüdtke, D. S.; Paixão, M. W.; Rodrigues, O. E. D. *Org. Lett*., **2003,** *5,* 2635-2638. (c) Braga, A. L.; Lüdtke, D. S.; Alberto, E. E.; Dornelles, L.; Filho, W. A. S.; Corbellini, V. A.; Rosa, D. M.; Schwab, R. S. *Synthesis* **2004**, 1589-1594. (d) Braga, A. L.; Lüdtke, D. S.; Alberto, E. E.; Sehnem, J. A. *Tetrahedron* **2005**, *61***,** 11664-11671 (e) Braga, A. L.; Sehnem, J. A.; Vargas, F.; Braga, R. C. *J. Org. Chem.* **2005,** *70,* 9021-9024. (f) Braga, A. L.; Lüdtke, D. S.; Alberto, E. E. *J. Braz. Chem. Soc*. **2006**, *17***,** 11-15. (g) Braga, A. L.; Schwab, R. S.; Alberto, E. E.; Salman, S. M.; Vargas, J.; Azeredo, J. B. *Tetrahedron Lett.* **2009**, *50,* 2309-2311.

derivative[69] with diphenyl diselenide/disulfide to give the corresponding β- amino sulfur and seleno derivatives, as depicted in scheme 14.

Scheme 14. Synthesis of chiral β-sulfur and seleno amines

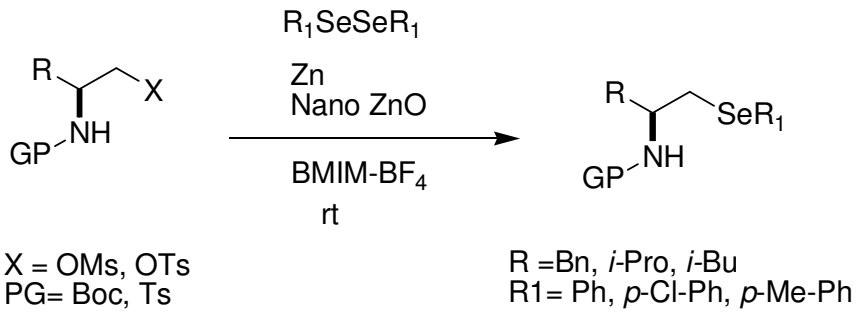


Using our standard reaction conditions it was possible to verify the versatility of the methodology, allowing the synthesis of diverse organochalcogenium compounds from different functionalities. The results revealed the same behavior, affording sulfide derivatives in higher yield as compared with selenides.

[69] Synthetic procedures for the bromo ester derivative see: Stocking, E. M.; Schwarz, J. N.; Senn, H.; Salzmann, M.; Silks, L. A. *J. Chem. Soc., Perkin Trans.* **1997**, *1*, 2443–2447.

2.4 Synthesis of chiral β-seleno amines catalyzed by ZnO nanopowder using Zn in ionic liquid:

Next we focused on the synthesis of chiral β-seleno amines by the reaction of amino sulfonates and selenolates anion btained by the reduction of diselenide with ZnO NPs using Zn in ionic liquid, which function as a mild and recyclable medium, and on effective metal oxide nanoparticles for the synthesis of unsymmetrical diorganyl selenides. In the search for an effective, mild and reusable reaction medium and in connection with our ongoing research, we combined here the introduction of a selenium-moiety in a stereoselective way with the use of a new and innovative ZnO[70] NPs in ionic liquid. A series of β-seleno amines were synthesized from N-protected β-amino mesylates mediated by Zn in ionic liquid catalyzed by ZnO NPs. To cleave the Se-Se bond in dibenzyl diselenide, the reaction of N-protected β-amino mesylates **9** was initially carried out in the presence of ZnO NPs using Zn in ionic liquid at room temperature to obtain the corresponding product.



Scheme 15

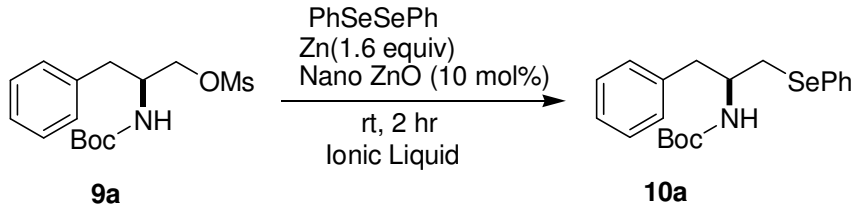
2.4.1 Optimization of Reaction Condition:

In an attempt to optimize the protocol and to understand the influence of different variables on this reaction, several components were studied to increase its efficiency. In a first set of experiments, we studied the influence of different ionic liquids (influence of

[70] ZnO nano powder (~30 nm) was purchased from Inframat® Advanced Materials and the Specifications are: average particle size ~30 nm (TEM & BET), BET multi-point specific surface area (SSA) ~35 m^2/g.

different ionic liquid discussed in section 2.1.1). For this, a standard condition was employed: β-amino mesylate **9a** (2.0 equiv) was treated with diphenyl diselenide (1.0 equiv) in the presence of 10 mol % of ZnO NPs and commercially available Zn dust (1.6 equiv) in ionic liquid (0.5 mL) for 2 hrs, under room temperature. The results are summarized in Table 5.

Table 5: Effect of ionic liquid for the synthesis of β-seleno amine



9a **10a**

Entry	[a]Ionic Liquid	[b]Yield (%)
1	BMIM-BF_4	87
2	BMMIM-BF_4	59
3	BMIM-PF_6	67
4	BMIM-NTf_2	26
5	BPy-BF_4	64

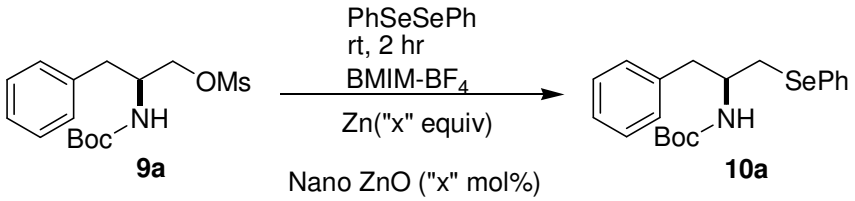
[a] Ionic liquids were prepared using a procedure available in the literature [55] and subjected to vacuum conditions before use. [b] Yields refer to pure isolated products and characterized by ^1H and ^{13}C NMR.

On analyzing Table 5, it is possible to verify that in all ionic liquids the desired product was obtained and as evident from the Table 5 that BMIM-BF_4 is the best ionic liquid for this reaction affording the correspoding compound **10a** with 87% yield (entry 1) as compared with other ionic liquids.

2.4.2 Optimization of Zn dust and nano ZnO catalyst:

The amount of Zn and catalyst ZnO NPs required to promote the reaction was also studied. Reactions with 1.6, 1.2 and 1.0 equiv of zinc showed similar results, leading to the product in excellent yields (Table 6, entries 1-3).

Table 6: Optimization of Zn dust and nano ZnO catalyst.



Entry	Amount of ZnO (% mol)	Amount of Zn (in eq)	[a]Yield (%)
1	10.0	1.6	87
2	10.0	1.2	87
3	10.0	1.0	85
4	5.0	1.0	84
5	3.0	1.0	84
6	2.0	1.0	71
7	--	1.0	69
8	3.0	--	--
9	--	1.3	72

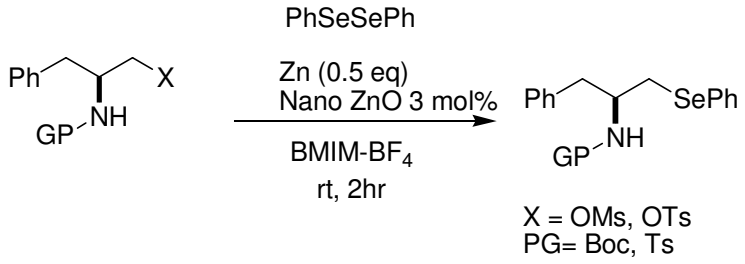
[a]Yields refer to pure isolated products as characterized by ^{1}H and ^{13}C NMR.

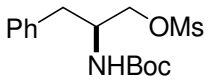
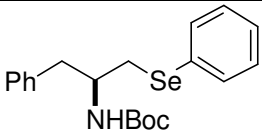
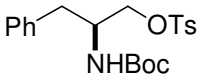
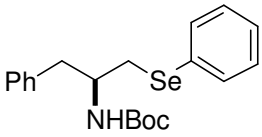
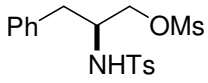
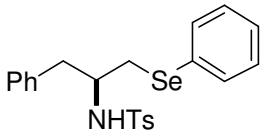
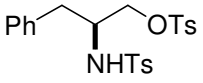
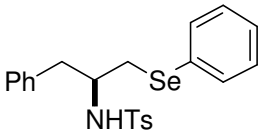
We found that varying the amount of ZnO NPs had an effective influence on the product formation and no significant alteration was verified on using 10.0 or 3 mol% of ZnO NPs, affording the respective compound in similar yields (87 and 84% respectively, entries 1–5). On decreasing the amount of ZnO NPs to 2 mol%, the desired product was obtained in lower efficiency, yielding 71% (table 6, entry 6). In the absence of ZnO NPs gave only 69 % of yield (table 6, entry 7). No product formation was observed in the absence of Zn (table 6, entry 8). By increasing the amount of Zn (1.3 mol%) 72 % product was accomplished (Table 6, entry 9). Thus, a combination of Zn dust and ZnO NPs is required for this reaction.

2.4.3 Effect of Protecting and Leaving groups:

Continuing our search for versatility in the scope of the reaction, the effects of the leaving group and the N-protecting group on the starting materials were investigated. The results of this investigation are presented in Table 7. Our investigation began with employing *L*-phenylalaninol derivatives (mesylate and tosylate) as standard amino alcohol derivatives and different protecting groups (Boc and Ts), in order to check their influence on the course of the reaction.

Table 7: Effects of protecting and leaving groups.



Entry	Reactant	Product	Time (h)	[a] Yield (%)
1	 **9a**	 **10a**	2	84
2	 **9b**	 **10a**	2	74
3	 **9c**	 **10b**	2	80
4	 **9d**	 **10b**	2	79

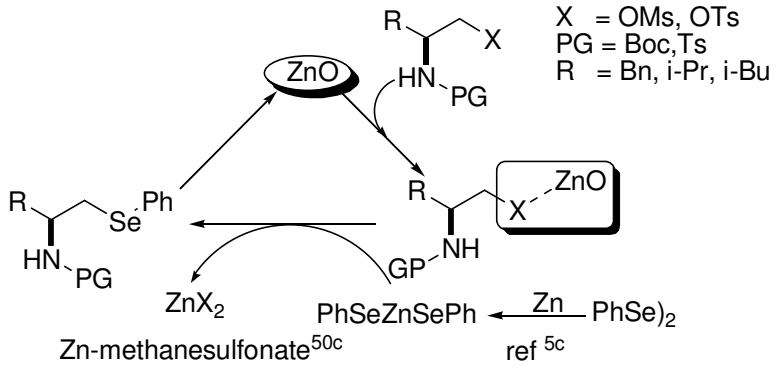
[a] Yields refer to pure isolated products as characterized by ^{1}H and ^{13}C NMR.

Analyzing table Table 7, it was evident that the reaction was not strongly affected by leaving and protecting group. For instance, when tosylate was used as the leaving group, the respective β-seleno amines were obtained in good yields, regardless of the N-protecting group (Table 7, entries 3 and 4). Although the effect of the leaving group was not so pronounced, it was observed that mesylates afforded slightly better yields than tosylates (Table 7, entries 1 and 3). These results show the versatility of the current methodology, affording an efficient conversion of different leaving groups (mesylates and tosylates) to chiral β-seleno amines with a mild and effective protocol.

After the optimization process, it was found that the best combination for the synthesis of chiral β-seleno amines involves 0.5 eq. of diaryl diselenide, 1 eq. of the mesylate **9,** 3 mol% of ZnO nanopowder, 0.5 eq. of Zn dust and 0.5 mL of BMIM-BF_4 at room temperature.

2.4.4 Proposed Mechanistic Pathway

Herein, the mechanistic pathway for these kinds of reactions is proposed. The Zn dust which make the zinc selenolate, PhSeZnSePh and this active species which would allow the formation of the preferred product.[5c] Although there are some improvement in the yield was observed by using ZnO catalyst and the origin of its behavior is still an intriguing subject of study. It may improve the leaving group ability by interact the catalyst ZnO with OMs/OTs or it may work as the oxidative addition and form the Zn-methanesulfonate.[50c] Hence, we speculate the mechanism for the synthesis of the desired product as shown in the Scheme 16.



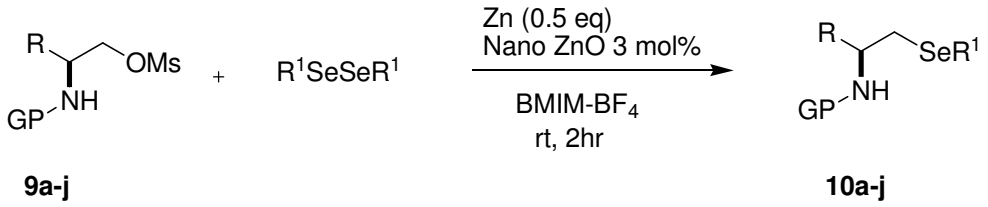
Scheme 16

With these results in hand, we extended the methodology to a variety of chiral β-seleno amines from β-amino mesylates derived from *L*-valine, *L*-leucine and *L*-isoleucine. The results are summarized in Table 9**.**

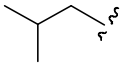
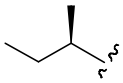
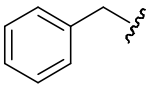
[5(c)] Braga, A. L.; Schneider, P. H.; Paixão, M. W.; Deobald, A. M. *Tetrahedron Lett.,* **2006**, 47, 7195-7198.

[50(c)] Wang, M.; Jiang, H.; Wang, Z. C. *J. Therm. Anal. Cal.* 2006, 85, 751–754.

Table 8: Synthesis of chiral β-seleno amines catalyzed by ZnO NPs using Zn in ionic liquid



9a-j **10a-j**

Entry	R	Reactant	PG	R^1	Product	[a]Yield (%)
1		**9e**	Boc	Ph	**10c**	72
2		**9f**	Ts	Ph	**10d**	85
3		**9g**	Boc	Ph	**10e**	79
4		**9h**	Ts	Ph	**10f**	82
5		**9i**	Boc	Ph	**10g**	68
6		**9j**	Ts	Ph	**10h**	77
7		**9a**	Boc	*p*-Cl-Ph	**10i**	91
8		**9a**	Boc	*p*-Me-Ph	**10j**	85

[a] Yields refer to pure isolated products as characterized by ^{1}H and ^{13}C NMR.

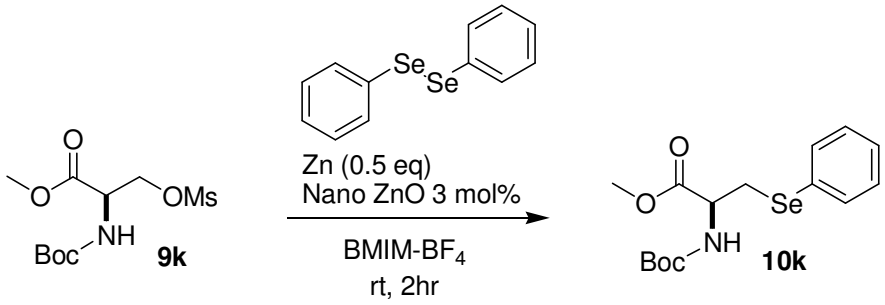
On analyzing Table 8, it was possible to verify that the "R" group derived from the corresponding amino acids had no significant effect on the course of the reaction, affording the desired chiral β-seleno amines in similar yields (Table 8, entries 1-6).

In the case of the R^1 group from diselenide, the presence of an electron donating or withdrawing group (methyl and chloro, respectively) attached to the aromatic ring shows an influence on the course of the reaction. For instance, the presence of the electron withdrawing atom chloro allowed the desired product **10i** to be obtained in high yield (91%). On the other hand, the electron donating group methyl afforded the product **10j** in more moderate yield (85%) (Table 8, entries 7 and 8). These results could be

rationalized due to the Se-Se cleavage in the *p*-chloro diselenide occurring more easily in the formation of the selenolate in the former case.

In order to elaborate this methodology for the synthesis of selenocysteine, we subjected the developed protocol to a more complex system. A biologically active selenocysteine[48] derivative was synthesized from the corresponding β-amino mesylate **9k**. The reaction afforded the product in 78% yield, showing the versatility of the methodology in the presence of more complex functionalities (Scheme 17).

Scheme 17. Synthesis of selenocysteine derivatives



According to the literature, the Zn dust which would make the zinc selenolate, PhSeZnSePh and this active species which would allow the formation of the desired product.[60] Although the improved yield was observed by using ZnO catalyst and the origin of its behavior is still an intriguing subject of study. The catalyst ZnO may enhance the leaving group ability by behaving as a lewis acid.[71] The interaction of Zn (from the catalyst of ZnO) with oxygen (from the leaving group OMs/OTs) may facilitate the leaving group ability.

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[48](a) Stadman, T. C. *Annu. Rev. Biochem.* **1996**, *65*, 83-100. (b) Jacob, C.; Giles, G. I.; Giles, N. M.; Sies, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4742-4758.

[60] Narayanaperumal, S.; Alberto, E. E.; Gul, K.; Rodrigues, O. E. D.; Braga, A. L. *J. Org. Chem.* **2010**, 75, 3886–3889.

[71] a) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev*. **2004**, *104*, 3079-3159. (b) Asao, N.; Sato, K.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70,* 3682-5685. (c) Asao, N.; Yudha, S.; Nogami, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 5526-5528. (d) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271-2296. (e) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180-3211. (f) Ermolat, D. S.; Mehta, V. P.; Eycken, E. V. V. *Synlett,* **2007**, 3117-3122. (g) Kiamehr, M.; Moghaddam, F. M. *Tetrahedron Letters*, **2009**, 50, 6723–6727.

The NMR spectra of the compound 10k are as follows:

The obtained product was characterized by NMR spectrum (Figure 6). In ^{1}H NMR one multiplet between 7.56 and 7.51 ppm shows the 2H of phenyl group. The other three aromatic protons (3H) of phenyl group are confirmed by another multiplet between 7.28 and 7.23, characteristic peak from the aromatic hydrogen denoted by **1**. Proton relative to CH_2 group appeared between 3.33 and 3.31 ppm denoted by **2**. The chiral single proton appeard between 4.67 and 4.61 ppm as a multiplet denoted by **3**. Around 5.42 ppm there is one broad singlet which shows the presence of NH group denoted by **4.** The singlet peak at 3.48 ppm shows the three hydrogen of methyl group denoted by **5**. At 1.41 ppm there is one singlet of 9H of Boc group denoted by **6.**

In ^{13}C spectrum **10k** (Figure 7) there is one peak at 170.90 ppm of ester carbonyl carbon and the ester carbonyl peak from boc is at 154.78**.** Peaks of aromatic carbons appeared at 135.67, 133.55, 128.97 and 127.37. The tertiary carbon peak appeared at 79.85 ppm. Rest of the carbons appeared at 53.06, 52.06, 30.48 and 28.07 ppm.

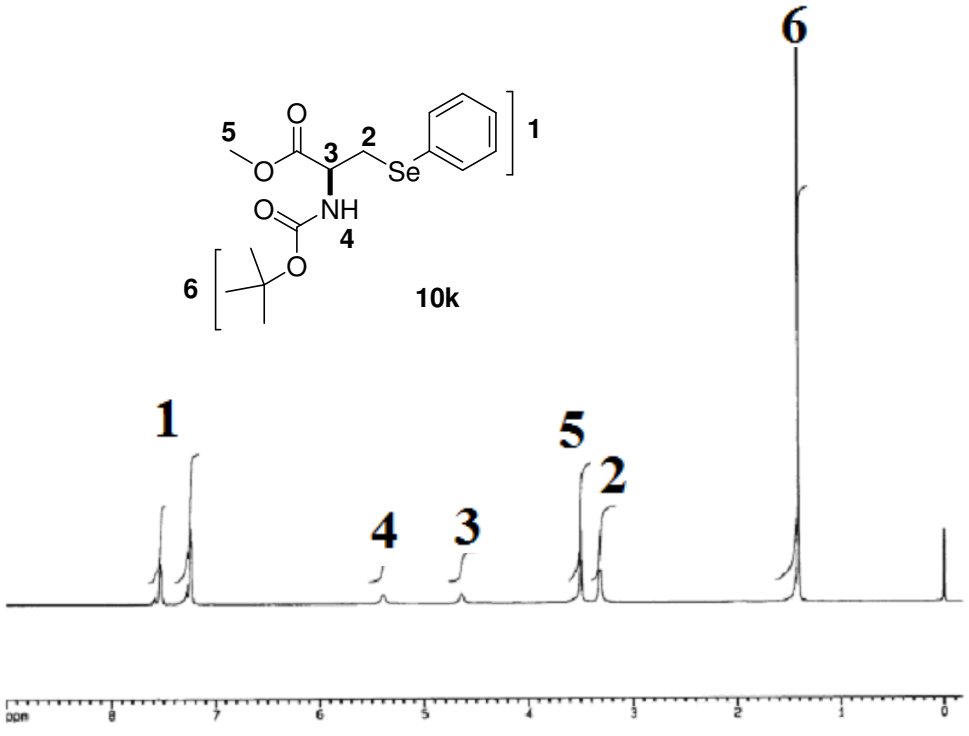

Figure 6: NMR spectra ^{1}H (200 MHz) in $CDCl_3$.

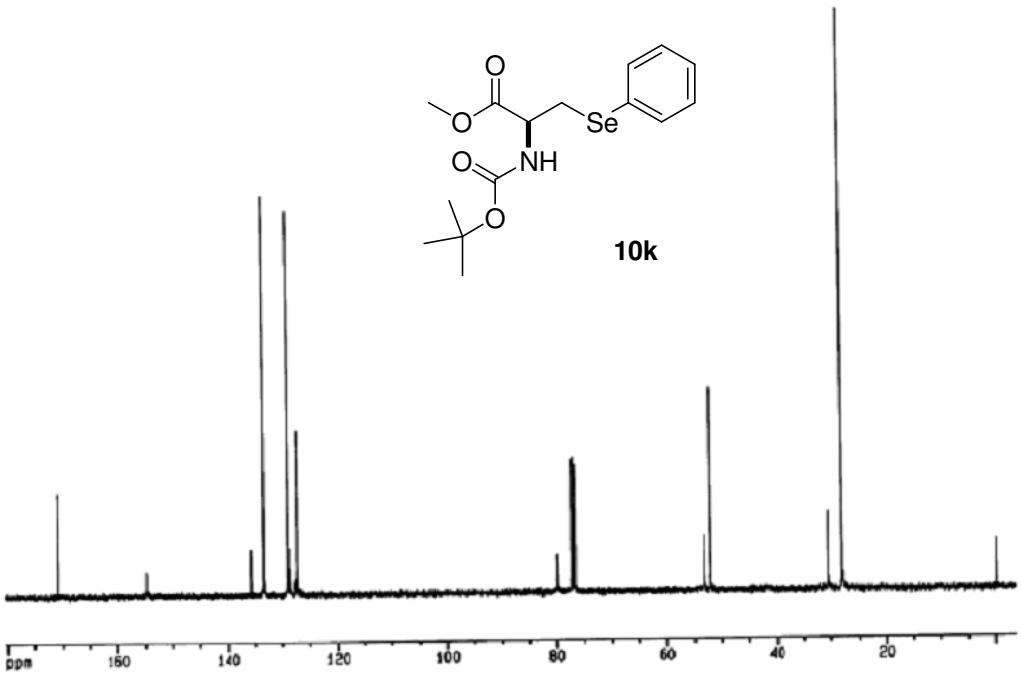

Figure 7: NMR spectra ^{13}C (100 MHz) in $CDCl_3$

2.5 Reusability of Ionic liquid:

To further explore the scope of our method, and in an effort to obtain an environmentally benign protocol, we examined the possibility of reusing the reaction media. Accordingly, after the work-up the ionic liquid was recovered and then used in another run.

2.5.1 Reusability of ionic liquid in syntheis of diorganyl chalcogenides using bimetallic system Sn(II)/Cu(II):

In a general protocol, 0.5 equiv. of diphenyl diselenide or diphenyl disulfide and 1.1 equiv. of benzyl bromide were added to the recovered IL, followed by 1.2 equiv. of $SnCl_2$ and 0.1 equiv. of $CuBr_2$. In a positive response, the yield was found to be similar to that obtained in the first run (Figure 8; run 2). This operation was repeated three more times without appreciable loss of efficiency (Figure 8).

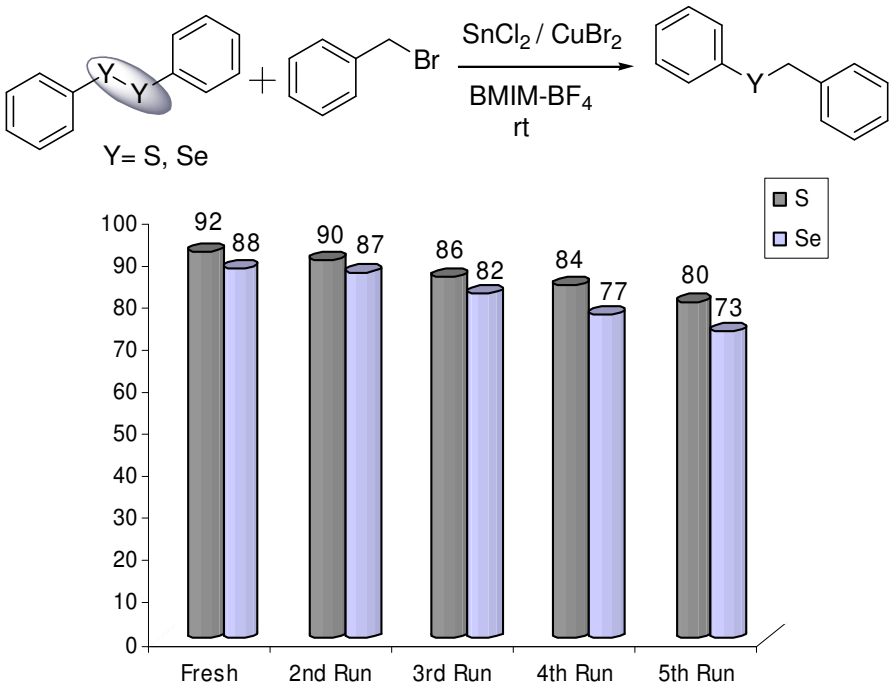

Figure 8. Recyclability of BMIM-BF_4.

2.5.2 Reusability of ionic liquid in synthesis of chiral β-seleno amines catalyzed by ZnO nanopowder using Zn:

An important feature of ionic liquids is their immediate reusability. Thus, as a further extension to our work, we checked the reusability potential of the ionic liquid. The data shown in Figure 9 illustrate that the medium could be reused at least three times without appreciable loss of efficiency in the synthesis of chiral β-seleno amines. Unfortunately, all attempts fail to recover the ZnO catalyst.

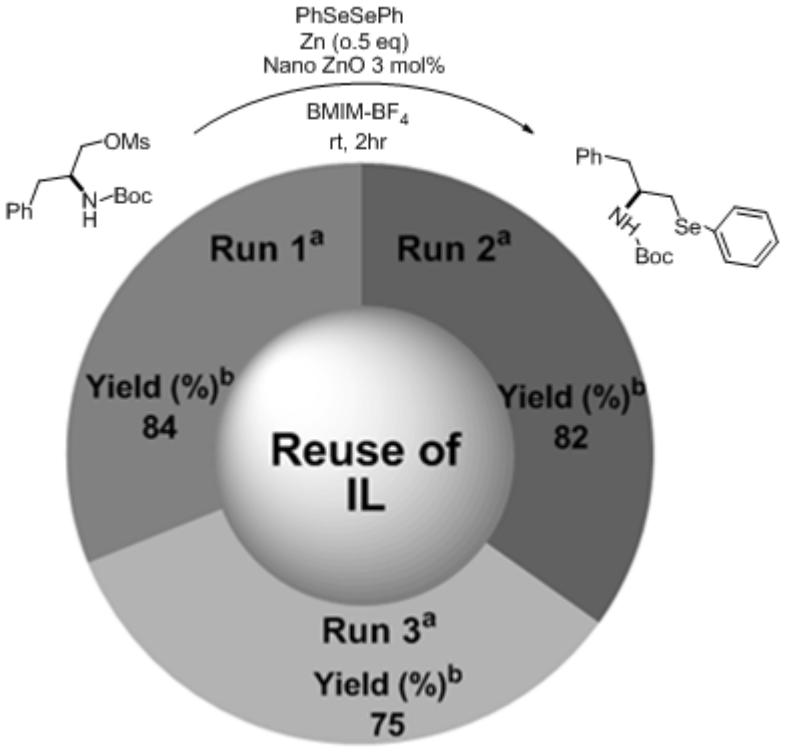

Figure 9: Reuse of BMIM-BF_4. [a] Ionic liquids were subjected to vacuum conditions before use; [b] Yields refer to pure isolated products and characterized by ^1H and ^{13}C NMR.

CONCLUSIONS:

In summary, herein we describe an efficient methodology for the preparation diorganyl selenides and sulfides from the corresponding alkyl and aryl halides using bimetallic system [Sn(II)/Cu(II)]. Some important aspects of this methodology are the high reactivity in the preparation of the different organochalcogen compounds, with very short reaction times, mild reaction conditions, room temperature and excellent yields using an ionic liquid as a reusable solvent. The methodology shows a wide versatility, allowing the synthesis of different classes of organochalcogen compounds.

Furthermore, we described an efficient, mild, and high yielding methodology for the preparation of chiral β-amino selenides from the corresponding β-amino mesylates and tosylates. To check the scope of our methodology, a biologically active selenocysteine derivative was also synthesized from the corresponding β-amino mesylate. The products were obtained by employing different amino acid moieties and protecting groups. Compared to the commonly employed organic solvents, BMIM-BF_4 exhibited higher performance, with the advantage that it can be reused in up to three successive runs.

The combinatorial design and synthesis of organoselenium compounds using ionic liquids and metal oxide nanoparticles offers great potential for rapid and easily accessible developments in this area, due to the efficient, economical and convenient operations.

3. Material and Methods:

^{1}H and ^{13}C NMR spectra were recorded at 400 and 200 MHz respectively with tetramethylsilane as internal standard. Column chromatography was performed using Merck Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. All solvents were used as purchased unless otherwise noted. The diselenides, disulfides and halides were used as purchased. ^{1}H and ^{13}C NMR spectral data of the compounds are identical to those reported.

3.1 General Procedure for the synthesis of diorganyl sulfides(3a-i) and selenide(4a-i) using Sn(II)/Cu(II):

In a Schlenk tube, under argon atmosphere, diaryl dichalcogenide (0.5 mmol) $SnCl_2$ (1.2 mmol) and $CuBr_2$ (0.1 mmol) were added to BMIM-BF_4 (0.5 mL) at room temperature. Then organic halide (1.1 mmol) was slowly added. The reaction mixture was stirred 60 min to afford the corresponding diorganyl selenide whereas 30 minute reaction time was used for the synthesis of diorganyl sulfide. After completion of the reaction, (monitored by TLC) the mixture was then extracted with diethylether (5x 10 mL), and the combined ether extract was washed with brine, dried ($MgSO_4$) and evaporated to leave the crude products which were purified by column chromatography.

3.2 General Procedure for the Synthesis of Seleno- and Thioester using Sn(II)/Cu(II) 6a-d & 7a-d:

Under an argon atmosphere, a mixture of $SnCl_2$ (1.2 mmol) and $CuBr_2$ (0.1 mmol) diaryl dichalcogenide (0.5 mmol) and acyl chloride (1 mmol) in BMIM-BF_4 (0.5 mL) was stirred at room temperature for 60 minute to obtain the selenoester whereas thioester required 30 minute reaction time. After this time, the product was extracted with diethylether (60 mL). The organic layer was dried over $MgSO_4$, filtered and the solvents

evaporated. The crude product was purified by column chromatography, over silica gel, eluting with hexanes. The same procedure was used for the synthesis of chiral β-sulfur and seleno amines.

3.3 General Procedure for the preparation of N-Protected amino mesylate:[72]

To a stirred solution of N-Protected amino alcohol (5 mmol) dissolved in CH_2Cl_2 (15 mL), followed by the addition of Et_3N (1.2 equiv) the reaction mixture kept under 0 ºC. Then mesyl chloride (1.2 equiv) dissolved in 15 mL of CH_2Cl_2 was added drop wise over 30 min duration at 0 ºC and allowed to stirred for 2 hours. After completion of the reaction, the solvent was evaporated and extracted with 5% $NaHCO_3$ and ethyl acetate, Sat. NaCl and dried over $MgSO_4$ afforded the crude product. By recrystallization using EtOAc/hexane afforded the white fluffy crystals.

3.4 General procedure for the synthesis of 10a-k:

Under argon atmosphere, diselenide (0.5 mmol) and Zn (0.5 mmol) were stirred in BMIM-BF_4 (0.5 mL) at room temperature for 1-2 min. The mesylate **9** (1 mmol) and 3 mol% of ZnO NPs were then added and stirred for 2 hrs at room temperature. After completion of the reaction (monitored by TLC) the β-seleno amines were extracted from BMIM-BF_4 using Et_2O (3x 10 mL) and dried over $MgSO_4$. The solvent was then removed, yielding the crude products **10a-k**, which were purified by column chromatography.

3.5 Representative Experimental Procedure to Reuse BMIM-BF_4:

After the work-up of the first run, BMIM-BF_4 is diluted in ethanol and filtered through celite pad to remove the inorganic materials followed by concentrated to remove the organic solvents and subjected to the vacuum for 1 hour to eliminate the moisture and trace organic solvents.

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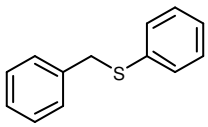
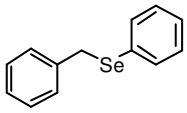
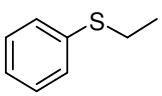
[72] (a) Argouarch, G.; Gibson, C.L.; Stones, G.; Sherrington, D.C. *Tetrahedron Lett.* **2002**, *43*, 3795–3798. (b) Arwin, J. B.; Bunschoten, A.; Liskamp, R. M. *J. Bioorg. Med. Chem.* **2007**, *15*, 6985–6993 and references there in. (c) Kawamura, K.; Fukuzawa, H.; Hayashi, M. *Org. Lett.,* **2008**, *10,* 3509-3512. (d) Shang, L.; Fang, H.; Zhu, H.; Wang, X.; Wang, Q.; Mu, J.; Wang, B.; Kishioka, S.; Xu, W. *Bioorg. Med. Chem.* **2009**,*17*, 2775–2784.



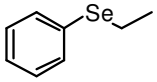
Benzyl phenyl sulfide (2a) 184 mg, 92% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.34-7.15 (m, 10H), 4.12 (s, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 137.49, 136.32, 129.83, 129.79, 128.79, 128.45, 127.13, 126.32, 39.65 ppm.



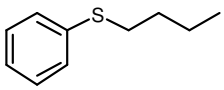
Benzyl phenyl selenide (2b) 217 mg, 88 % Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.50-7.42 (m, 2H), 7.28-7.14 (m, 8H), 4.10 (s, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 138.6, 133.5, 130.4, 128.9, 128.8, 128.4, 127.3, 126.8, 32.2 ppm.



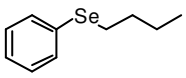
Ethyl phenyl sulfide (3a) 110 mg, 80% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.34-7.25 (m, 5H), 2.94 (q, *J*= 7.6 Hz, 2H), 1.31 (t, *J*= 7.2 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.65, 129.02, 128.79, 125.74, 27.67, 14.42 ppm.



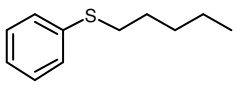
Ethyl phenyl selenide (4a) 144 mg,78% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.50-7.45 (m, 2H), 7.27-7.20 (m, 3H), 2.91 (q, *J*= 7.6 Hz, 2H), 1.43 (t, *J*= 7.2 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 132.6, 130.3, 129.0, 126.7, 21.3, 15.5 ppm.



***n*-Butyl phenyl sulfide (3b)** 141 mg, 85% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.33-7.25 (m, 4H), 7.17-7.13 (m, 1H), 2.92 (t, *J*= 7.2 Hz, 2H), 1.67-1.60 (m, 2H), 1.49-1.40 (m, 2H), 0.92 (t, *J*= 7.6 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 137.03, 128.83, 128.77, 125.59, 33.25, 31.21, 21.94, 13.60 ppm.

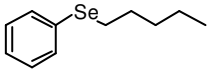


***n*-Butyl phenyl selenide (4b)** 170 mg, 80% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 7.49-7.45(m, 2H), 7.26-7.18(m, 3H), 2.90 (t, *J*= 7.6 Hz, 2H), 1.71-1.64 (m, 2H), 1.46-1.37 (m, 2H), 0.90 (t, *J*= 7.2Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 132.4, 130.8, 129.0, 126.6, 32.3, 27.7, 23.0, 13.6 ppm.

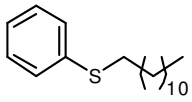


Pentyl phenyl sulfide (3c) 160 mg, 89% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.35-7.23 (m, 4H), 7.19-7.11 (m, 1H), 2.91 (t, *J*= 7.2

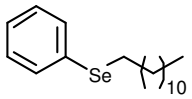
Hz, 2H), 1.72-1.58 (m, 2H), 1.48-1.23 (m, 4H), 0.89 (t, *J*= 6.6 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.98, 128.73, 127.98, 125.51, 36.71, 30.72, 29.98, 22.17, 13.90 ppm.



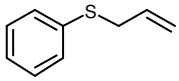
Pentyl phenyl selenide (4c) 190 mg, 84% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.47-7.44 (m, 2H), 7.22-7.14 (m, 3H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.68 (m, 2H), 1.39-1.24 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 132.4, 130.9, 129.0, 126.6, 32.1, 30.5, 28.3, 22.3, 14.1 ppm.



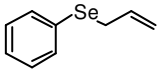
Dodecyl phenyl sulfide (3d) 214 mg, 77% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.33-7.25 (m, 4H), 7.17-7.14 (m, 1H), 2.91 (t, *J*= 7.2 Hz, 2H), 1.64 (m, 2H), 1.43-1.25 (m, 18H), 0.88 (t, *J*= 6.8 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ= 137.08, 128.82, 128.73, 125.56, 33.58, 31.89, 29.62, 29.60, 29.55, 29.48, 29.32, 29.16, 29.13, 28.81, 22.66, 14.07 ppm.



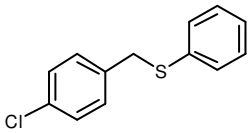
Dodecyl phenyl selenide (4d) 234 mg, 72% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ= 7.50-7.46 (m, 2H), 7.26-7.22 (m, 3H), 2.90 (t, *J*= 7.2 Hz, 2H), 1.69 (m, 2H), 1.38-1.25 (m, 18H), 0.87 (t, *J*= 6.0 Hz, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ= 132.35, 130.73, 128.92, 126.52, 31.90, 30.14, 29.81, 29.60, 29.56, 29.47, 29.32, 29.06, 28.21, 27.93, 22.67, 14.08 ppm.



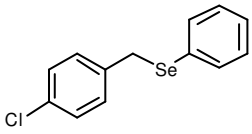
Allyl phenyl sulfide (3e) 148 mg, 99% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.51-7.16 (m, 5H), 5.93-5.82 (m, 1H), 5.19-5.06 (m, 2H), 3.55 (d, *J*= 6.8 Hz, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.08, 133.09, 129.10, 126.8, 125.2, 117.20, 37.10 ppm.



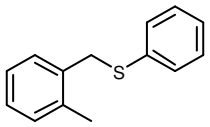
Allyl phenyl selenide (4e) 193 mg, 98% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.63-7.58 (m, 2H), 7.27-7.23 (m, 3H), 6.05-5.84 (m, 1H), 5.02-4.92 (m, 2H), 3.52 (d, J= 7.6 Hz, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 134.4, 133.3, 131.5, 128.9, 127.1, 116.8, 30.6 ppm.



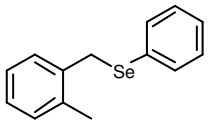
4-Chlorobenzyl phenyl sulfide (3f) 215 mg, 92% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ= 7.28-7.21 (m, 9H), 4.06 (s, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.60, 135.74, 133.29, 130.57, 130.22, 128.87, 128.58, 126.98, 42.39 ppm.



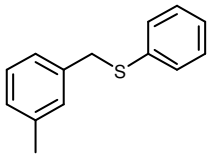
4-Chlorobenzyl phenyl selenide (4f) 233 mg, 83% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ= 7.45-7.41 (m, 2H), 7.25-7.11 (m, 5H), 7.09-7.07 (m, 2H), 4.03 (s, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 137.32, 133.38, 132.5, 130.08, 129.80, 129.04, 128.48, 127.54, 31.45.



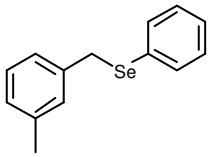
2-Methylbenzyl phenyl sulfide (3g) 160 mg, 75% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.33-7.09 (m, 9H), 4.09 (s, 2H), 2.38 (s, 3H); ^{13}C ($CDCl_3$, 50 MHz) δ = 136.66, 136.59, 134.99, 130.41, 130.14, 129.72, 128.77, 127.45, 126.38, 125.95, 37.34, 19.12 ppm.



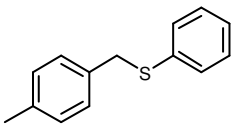
2-Methylbenzyl phenyl selenide (4g) 175 mg, 67% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.47-7.45 (m, 2H), 7.26-7.20 (m, 3H), 7.13-7.11 (m, 2H), 7.06-7.01 (m, 2H), 4.10 (s, 2H), 2.35 (s, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 133.8, 130.5, 129.7, 128.9, 127.4, 127.2, 125.9, 30.5, 19.2 ppm.



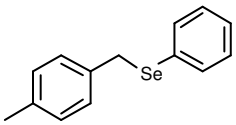
3-Methylbenzyl phenyl sulfide (3h) 180 mg, 84% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.33-7.02 (m, 9H), 4.08 (s, 2H), 2.30 (s, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 138.09, 137.21, 136.58, 129.62, 129.52, 128.76, 128.32, 127.91, 126.19, 125.81, 38.94, 21.29 ppm.



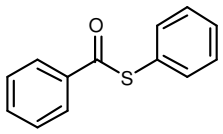
3-Methylbenzyl phenyl selenide (4h) 206 mg, 79% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.46-7.43 (m, 2H), 7.26-7.21 (m, 3H), 7.15-7.11 (m, 1H), 7.01-6.99 (m,3H), 4.07 (s, 2H), 2.28 (s, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 138.38, 138.02, 133.45, 130.61, 129.59, 128.92, 128.30, 127.63, 127.21, 125.84, 32.23, 21.29.



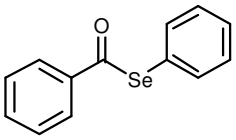
4-Methylbenzyl phenyl sulfide (3i) 210 mg, 98% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ= 7.33-7.06 (m, 9H), 4.08 (s, 2H), 2.31 (s, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.78, 136.61, 134.27, 129.58, 129.15, 128.76, 128.66, 126.15, 38.65, 21.06 ppm.



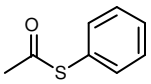
4-methylbenzyl phenyl selenide (4i) 244 mg, 94% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.47-7.44 (m, 2H), 7.25-7.23 (m, 3H), 7.11 (d, *J*= 8 Hz, 2H), 7.05 (d, *J*= 8.4 Hz, 2H), 4.09 (s, 2H), 2.30 (s, 3H); ^{13}C ($CDCl_3$, 100 MHz) δ = 136.3, 135.4, 133.2, 130.7, 129.0, 128.8, 128.6, 127.0, 31.8, 21.0 ppm.



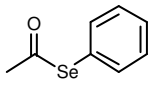
***S*-Phenyl benzothioate (6a)** 180 mg, 84% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.03 – 8.00 (m, 2H), 7.59 - 7.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 189.9, 136.5, 135.0, 133.5, 129.4, 129.1, 128.6, 127.3, 127.2 ppm.



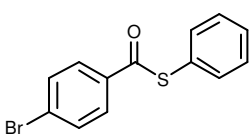
***Se*-Phenyl selenobenzoate (7a)** 206 mg, 79% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.94 - 7.92 (m, 2H), 7.63 - 7.58 (m, 3H) 7.50 - 7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 193.7, 138.9, 138.4, 136.7, 134.2, 129.7, 129.4 , 129.3, 127.7, 126.1 ppm.



***S*-Phenyl etanethioate (6b)** 25 mg, 17% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 – 7.37 (m, 5H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 193.8, 134.3, 129.3, 129.0, 127.8, 30.0 ppm.

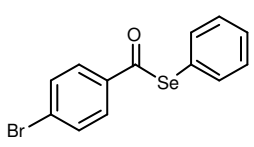


***Se*-Phenyl etaneselenoate (7b)** 19 mg, Yield: 10%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 – 7.25 (m, 5H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 196.4, 135.7, 131.4, 129.1, 127.7, 68.8 ppm.

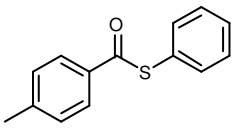


***S*-Phenyl 4-bromobenzothioate (6c)** 240 mg, 82% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (d, *J*= 8.8 Hz, 2H), 7.60 (d, *J*= 8 Hz, 1H), 7.48 (d, *J*= 8.4, 2H), 7.29 - 7.17 (m, 4H); ^{13}C NMR ($CDCl_3$,

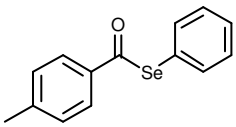
100 MHz) δ = 167.5, 136.9, 132.4, 132.2, 131.9, 131.0, 128.9, 127.4, 127.0 ppm.



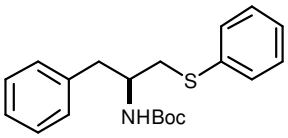
***Se*-Phenyl 4-bromoselenobenzoate (7c)** 255 mg,75% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.85 (d, *J*= 6.8 Hz, 2H), 7.57 (d, *J*= 6.0 Hz, 2H), 7.44 - 7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 193.4, 140.2, 136.2, 129.4, 129.2, 129.1, 128.5, 125.4, 121.5 ppm.



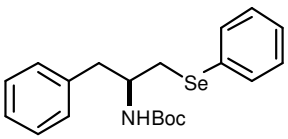
***S*-Phenyl 4-methylbenzothioate (6d)** 136 mg, 60% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, *J*= 8.8 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 - 7.40 (m, 3H), 7.24 (d, *J*= 8.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 189.5, 144.4, 135.0, 134.0, 129.3, 129.1, 127.5, 127.4, 21.6 ppm.



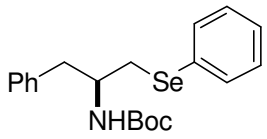
***Se*-Phenyl 4-methylselenobenzoate (7d)** 143 mg, 52% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.96 - 7.80 (m, 2H), 7.54 - 7.38 (m, 5H), 7.18 (d, *J*= 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.7, 142.5, 138.6, 137.7, 133.7, 130.4, 129.8, 128.8, 127.2, 127.2, 126.5, 22.9 ppm.



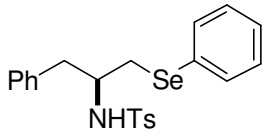
(*S*)-*tert*-Butyl 1-phenyl-3-(phenylthio)propan-2-ylcarbamate (8a) 257 mg, 75% Yield; ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.35-7.15 (m, 10H), 4.68-4.66 (m,1H), 4.10-4.04 (m, 1H), 3.09-3.01 (m, 2H), 2.91-2.86 (m, 2H), 1.39 (s, 9H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.16, 138.0, 136.35, 129.26, 128.79, 128.81, 128.16, 126.62, 125.19, 79.5, 57.2, 40.08, 39.61, 28.40.



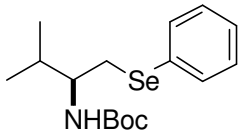
(*S*)-*tert*-Butyl 1-phenyl-3-(phenylselanyl)propan-2-ylcarbamate (8b) 269 mg, 69% Yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 2H), 7.29-7.12 (m, 8H), 4.70-4.66 (m, 1H), 4.09-4.06 (m, 1H), 3.04-3.01 (m, 2H), 2.87-2.82 (m, 2H), 1.38 (s, 9H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.96, 137.48, 132.74, 129.29, 129.09, 128.68, 128.40, 126.99, 126.44, 80.98, 38.21, 32.77, 28.24, 27.81.



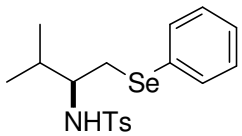
(*S*)-*tert*-butyl-1-phenyl-3-(phenylselanyl)propan-2-yl carbamate (10a). 339 mg, 87% Yield; ^{1}H NMR (CDCl3, 400 MHz) δ = 7.50 –7.40 (m, 2H), 7.39 – 7.12 (m, 8H), 4.68 (br s, 1H), 4.09 – 4.07 (m, 1H), 3.02–2.98 (m, 2H), 2.87 – 2.82 (m, 2H), 1.38 (s, 9H) ppm. ^{13}C NMR (CDCl3, 100 MHz) δ= 154.80, 137.40, 132.43, 129.89, 129.10, 128.90, 128.16, 126.71, 126.20, 78.90, 51.42, 40.10, 32.50, 28.07 ppm.



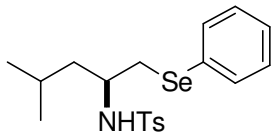
(S)-4-methyl-N-(1-phenyl-3-(phenylselanyl)propan-2-yl)benzenesulfonamide (10b). 355 mg, 80% Yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.39 (m, 4H), 7.27-7.09 (m, 9H), 6.93-6.91 (m, 2H), 4,69 (d, J = 7.2 Hz, 1H), 3.55-3.48 (m, 1H), 3.12 (dd, J^1 = 12.6 Hz, J^2 = 4.4 Hz, 1H), 2.94 (dd, J^1 = 13.8 Hz, J^2 = 6.4 Hz, 1H), 2.83 (dd, J^1 = 12.6 Hz, J^2 = 6.8 Hz, 1H), 2.76 (dd, J^1 = 14.0 Hz, J^2 = 6.8 Hz, 1H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.13, 136.79, 136.45, 132.92, 129.51, 129.24, 128.61, 127.29, 126.96, 126.72, 54.49, 40.29, 32.87, 21.47 ppm.



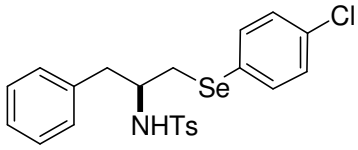
(S)-tert-butyl-3-methyl-1-(phenylselanyl)butan-2-ylcarbamate (10c). 246 mg,72% Yield; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 2H), 7.26-7.23 (m, 3H), 4.60-4.55 (m, 1H), 3.69-3.59 (m, 1H), 3.07 (d, J = 5.6 Hz, 2H), 1.94-1.77 (m, 1H), 1.42 (s, 9H), 0.91-0.87 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.54, 132.93, 129.05, 126.99, 79.10, 55.64, 32.41, 31.69, 28.33, 19.43, 17.97 ppm.



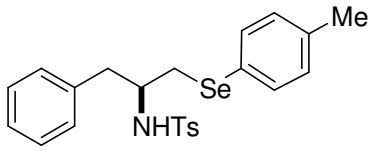
(S)-4-methyl-N-(3-methyl-1-(phenylselanyl)butan-2-yl)benzenesulfonamide (10d). 336 mg, 85% Yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.4 Hz, 2H), 7.37-7.35 (m, 2H), 7.26-7.17 (m, 5H), 4.82 (d, J = 6.4 Hz, 1H), 3.23-3.17 (m, 1H), 3.06 (dd, J^1 = 12.8 Hz, J^2 = 4.8 Hz, 1H), 2.74 (dd, J^1 = 12.6 Hz, J^2 = 6.6 Hz, 1H), 2.38 (s, 3H), 2.01-1.93 (m, 1H), 0.81 (d, J = 6.8 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.19, 137.65, 133.07, 129.54, 129.15, 127.29, 127.05, 58.57, 31.64, 30.68, 21.49, 19.01, 17.44 ppm.



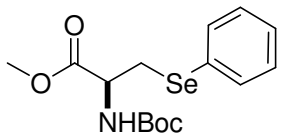
(S)-4-methyl-N-(4-methyl-1-(phenylselanyl)pentan-2-yl)benzenesulfonamide (10f). 324 mg, 79% Yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 2H), 7.42-7.40 (m, 2H), 7.29-7.21 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.86 (d, *J* = 8.4 Hz, 1H), 3.46-3.38 (m, 1H), 3.10 (dd, J^1 = 12.4 Hz, J^2 = 3.6 Hz, 1H), 2.73 (dd, J^1 = 12.8 Hz, J^2 = 6.8 Hz, 1H), 2.38 (s, 3H), 1.48-1.36 (m, 2H), 1.29-1.23 (m, 1H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.59 (d, *J* = 6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.19, 137.65, 133.19, 129.52, 129.08, 127.23, 126.98, 51.54, 43.82, 34.65, 24.30, 22.76, 21.52, 21.43 ppm.



(*S*)-*tert*-butyl 1-(4-chlorophenylselanyl)-3-phenylpropan-2-ylcarbamate (10i). 435 mg, 91% Yield; ^{1}H NMR (CDCl3, 400 MHz) δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.11 (m, 7H), 4.61 (br s, 1H), 4.13 – 3.39 (m, 1H), 3.10 – 2.95 (m, 2H), 2.94 – 2.79 (m, 2H), 1.38 (s, 9H) ppm. ^{13}C NMR (CDCl3, 100 MHz) δ = 154.98, 137.38, 134.19, 133.34, 129.31, 129.30, 128.53, 128.22, 126.61, 79.49, 51.63, 40.39, 33.18, 28.29 ppm.



(*S*)-*tert*-butyl 1-phenyl-3-(p-tolylselanyl)propan-2-ylcarbamate (10j). 389 mg, 85% Yield ^{1}H NMR (CDCl3, 400 MHz) δ = 7.40 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.19 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 4.67 (br s, 1H), 4.11 – 3.96 (m, 1H), 3.05 – 2.92 (m, 2H), 2.91 – 2.80 (m, 2H), 2.31 (s, 3H), 1.38 (s, 9H) ppm. ^{13}C NMR (CDCl3, 100 MHz) δ =155.03, 137.64, 137.18, 133.40, 129.98, 129.38, 128.44, 126.47, 126.17, 79.33, 51.67, 40.48, 33.24, 28.31, 21.03 ppm.



(*S*)-methyl-2-(*tert*butoxycarbonylamino)-3-(phenylselanyl) propanoate (10k). 279 mg, 78% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.56-7.51 (m, 2H), 7.28-7.23 (m, 3H), 5.42 (br s, 1H), 4.67-4.61 (m, 1H), 3.48 (s, 3H), 3.33-3.31 (m, 2H), 1.41 (s,9H); ^{13}C ($CDCl_3$, 100 MHz) δ = 170.90, 154.78, 133.52, 128.94, 127.35, 79.81, 53.07, 52.06, 30.48, 28.07.

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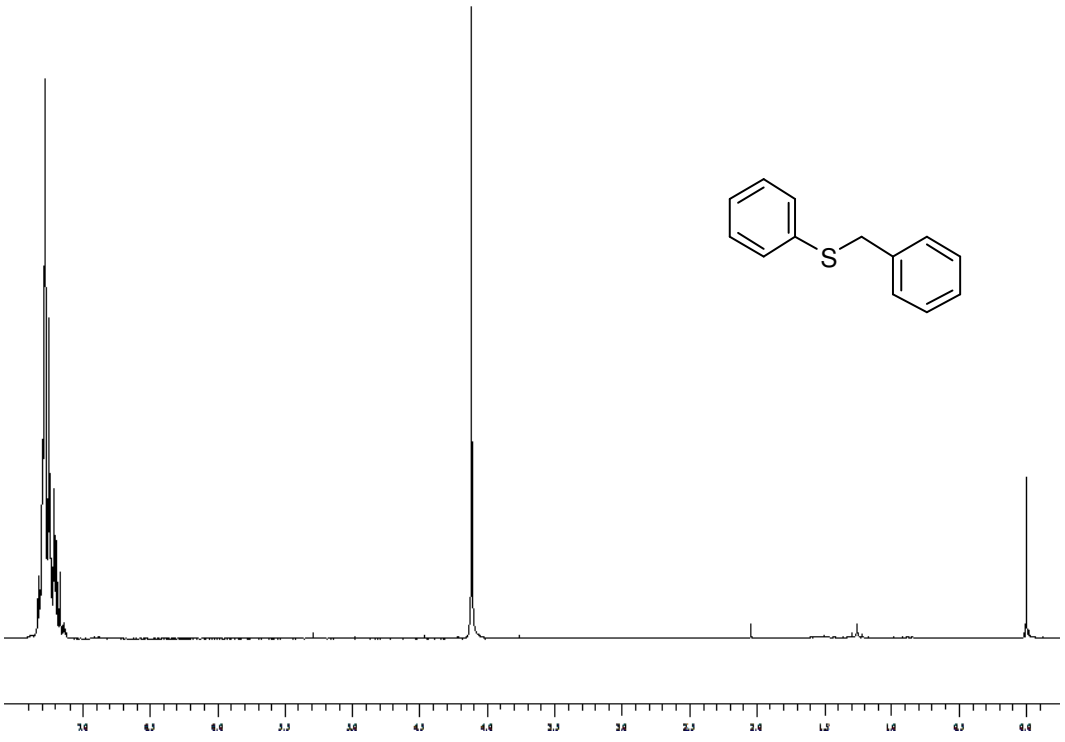
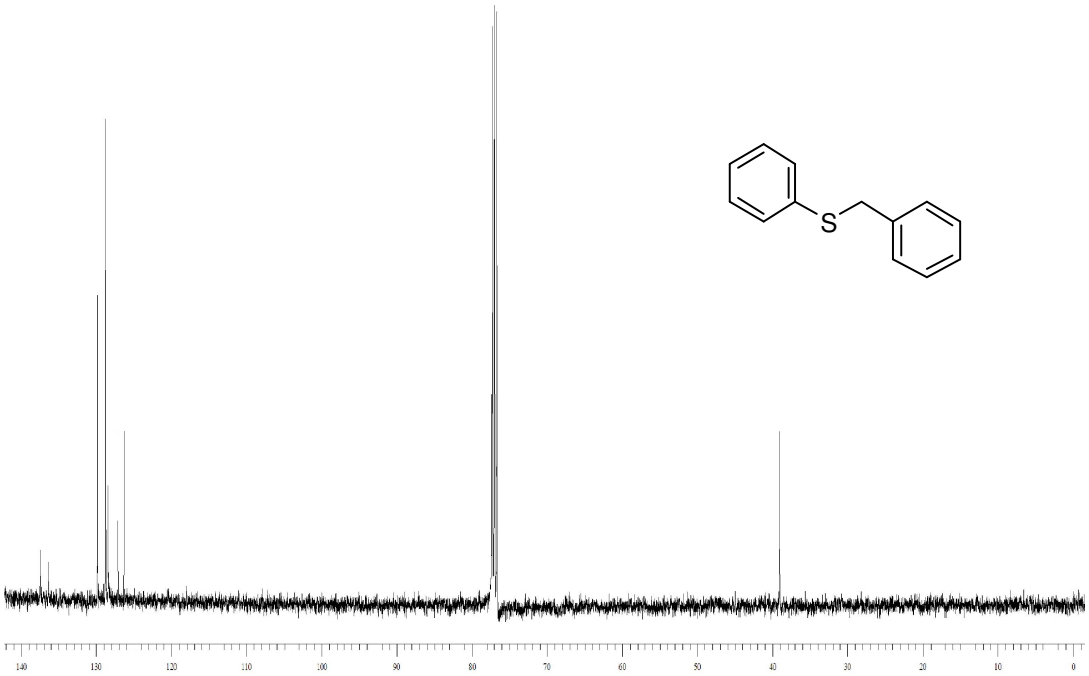
4. NMR SPECTRA



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of benzyl phenyl sulfide



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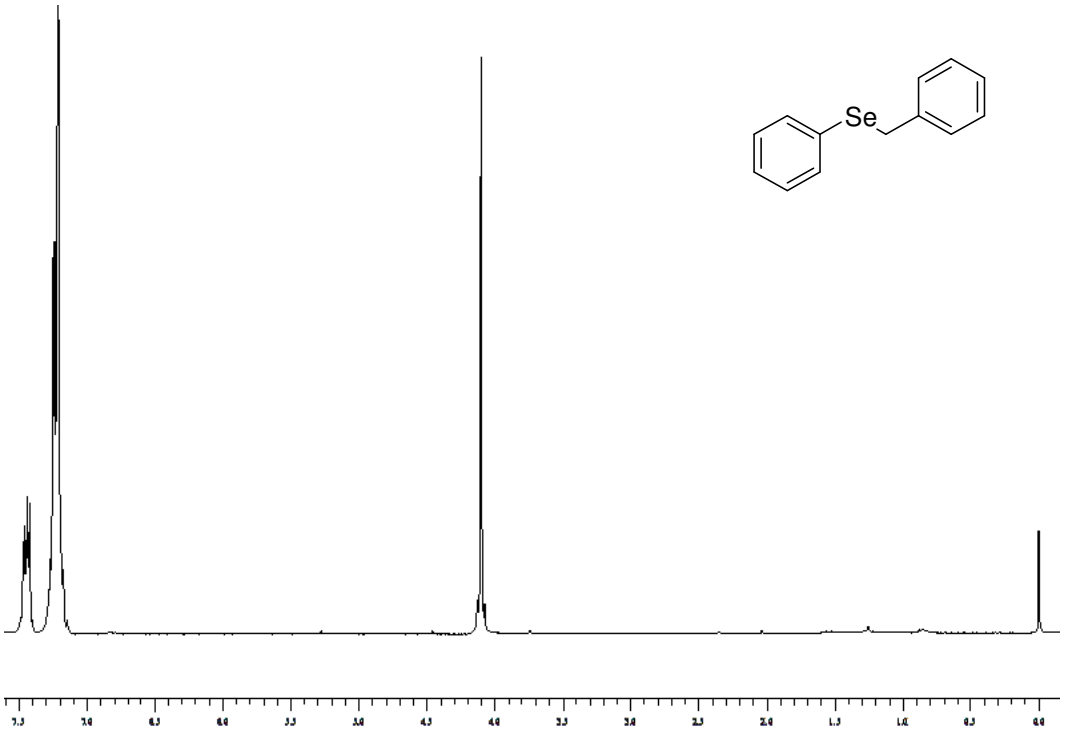

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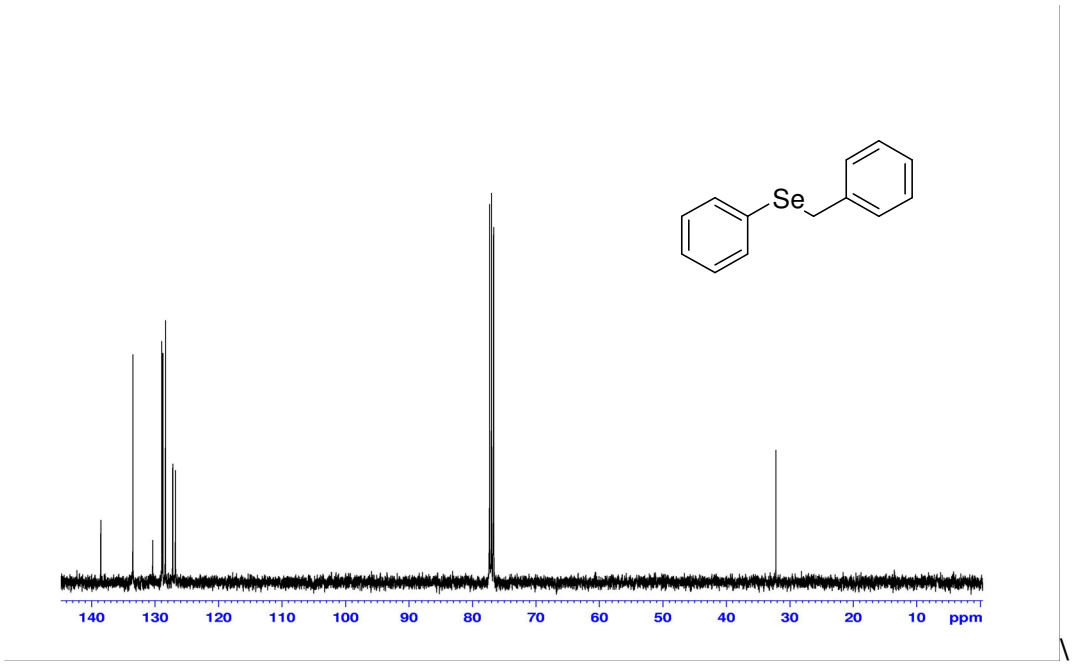

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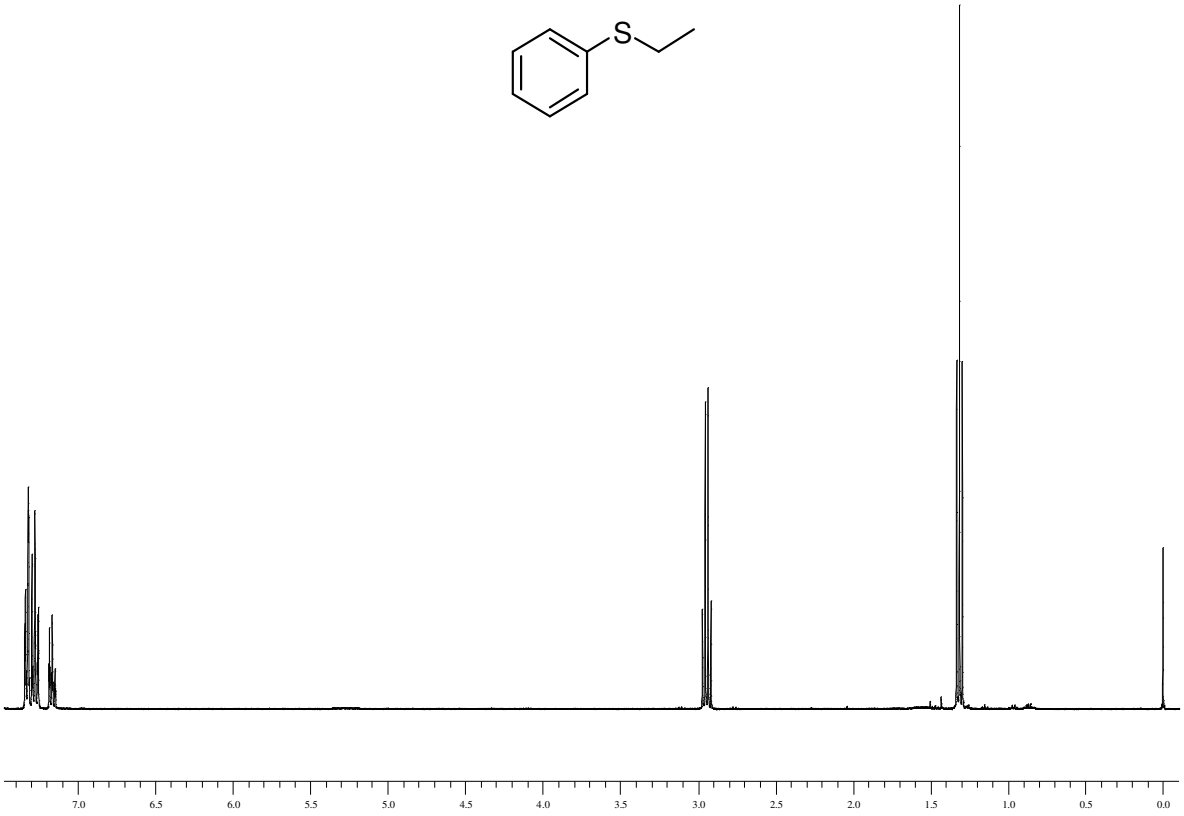

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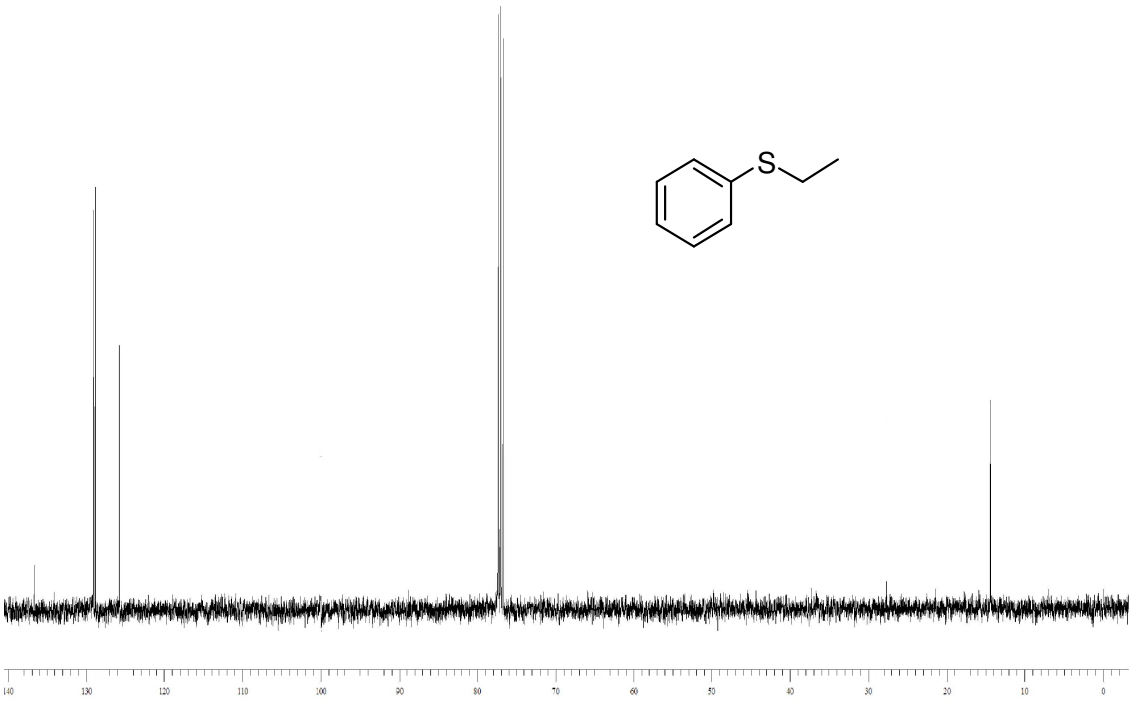

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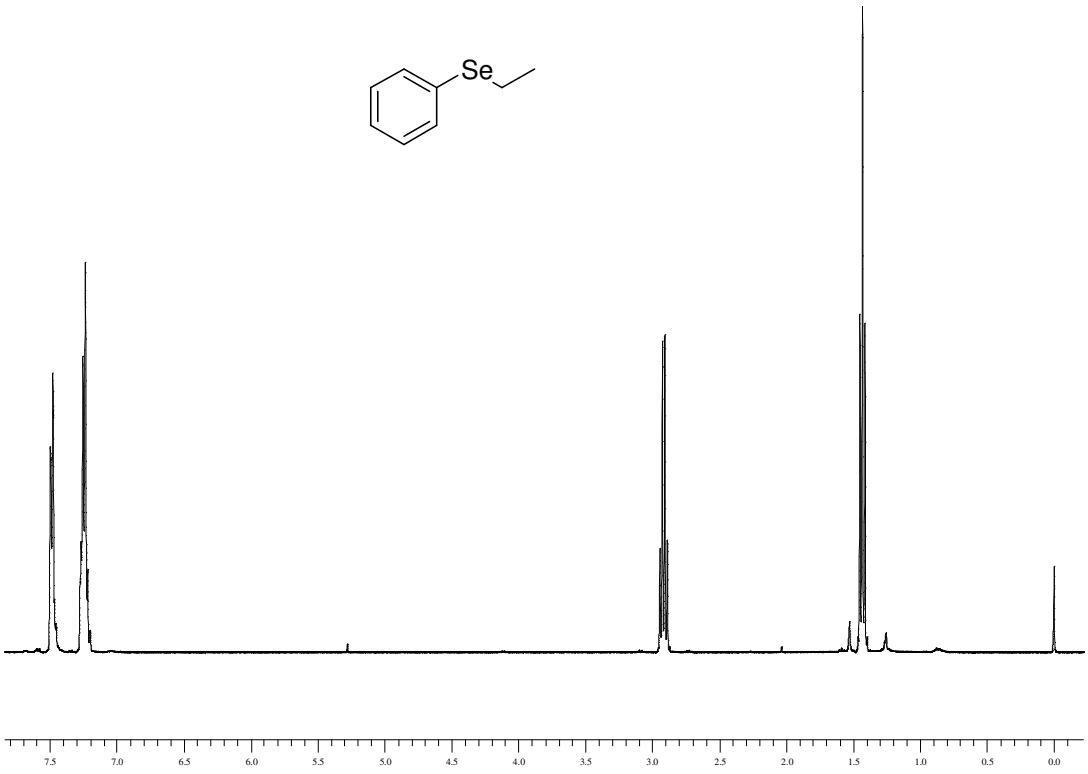

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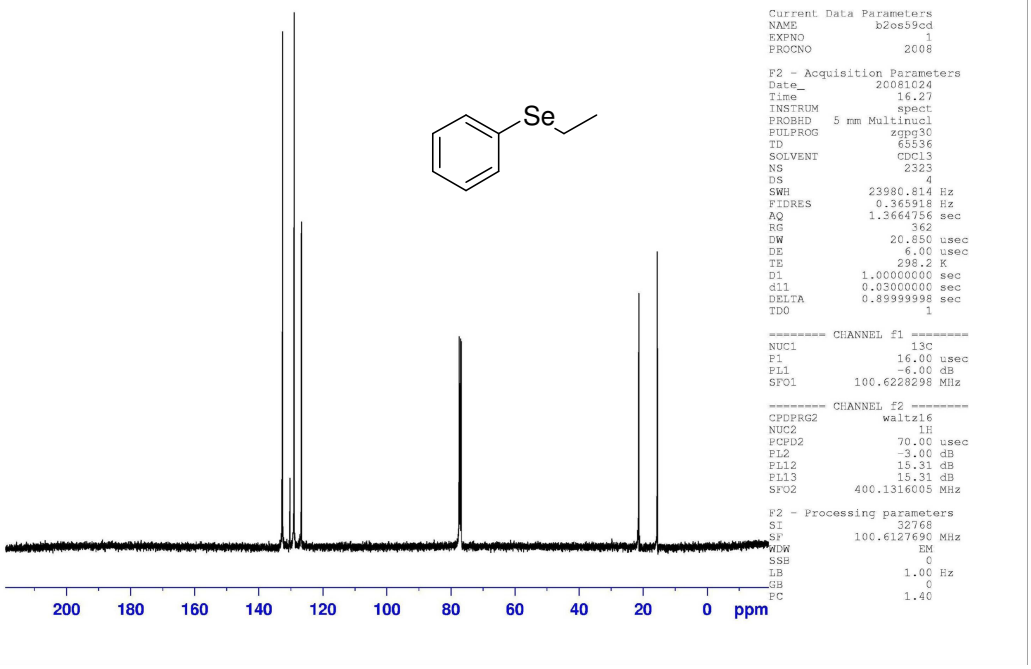

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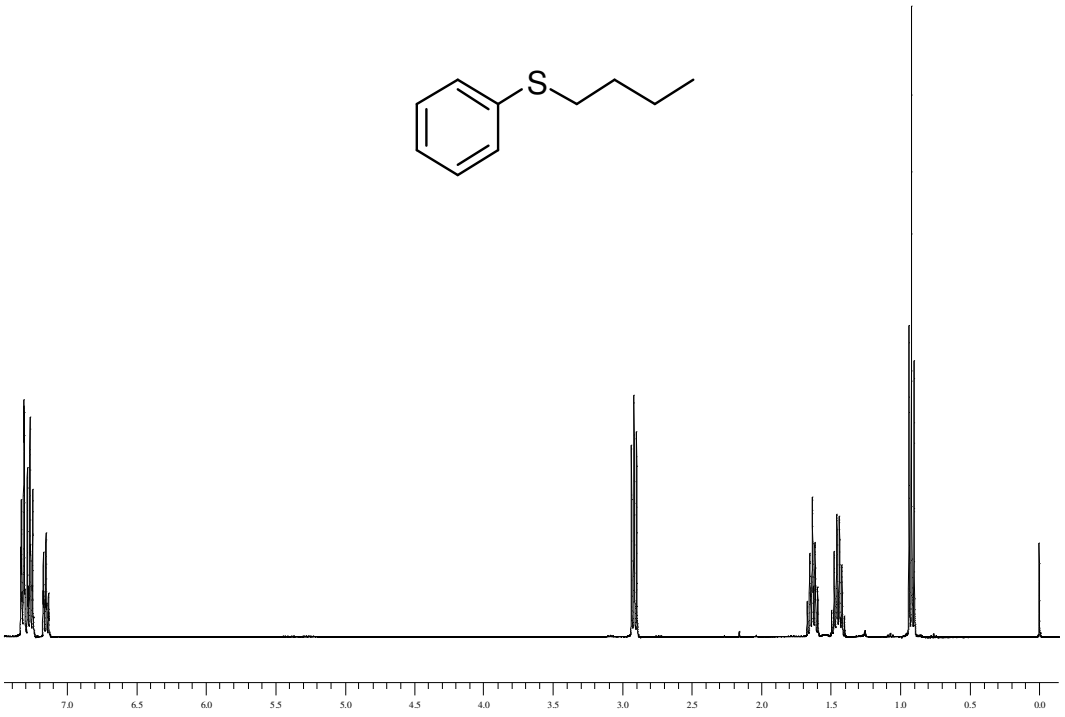

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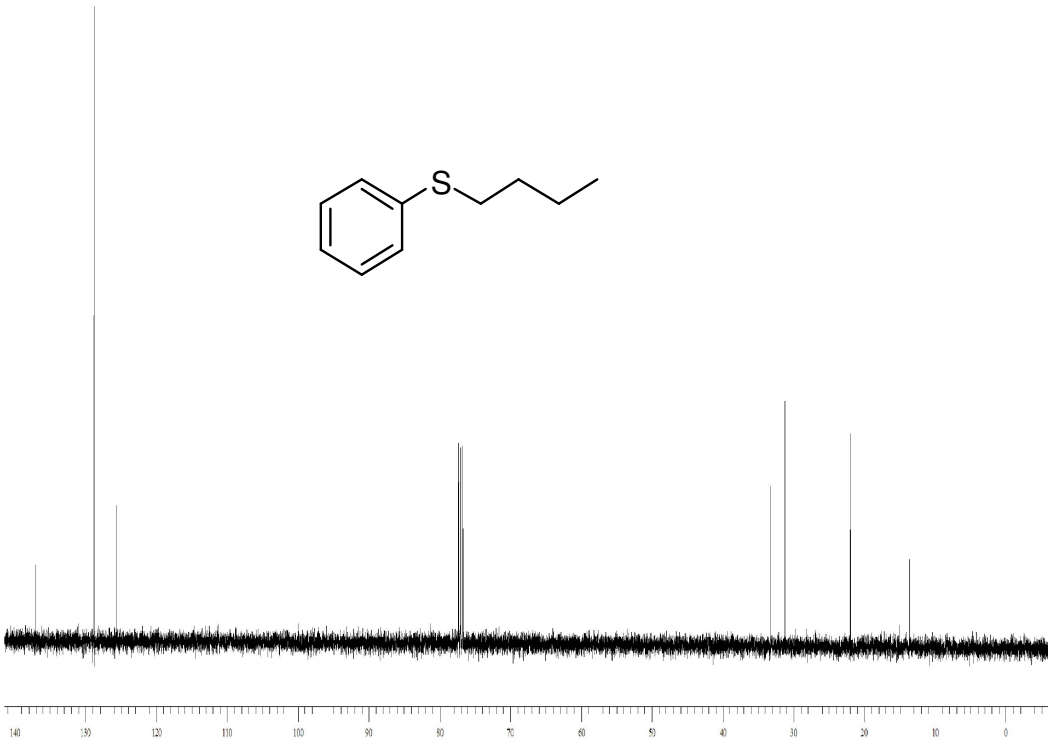

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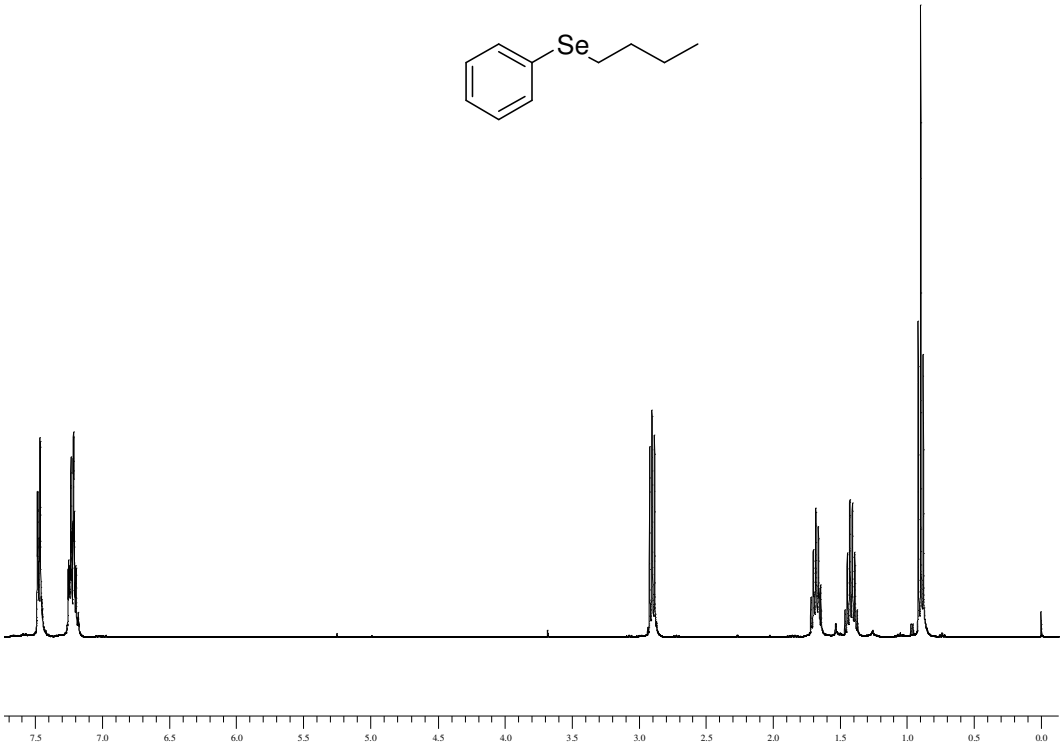

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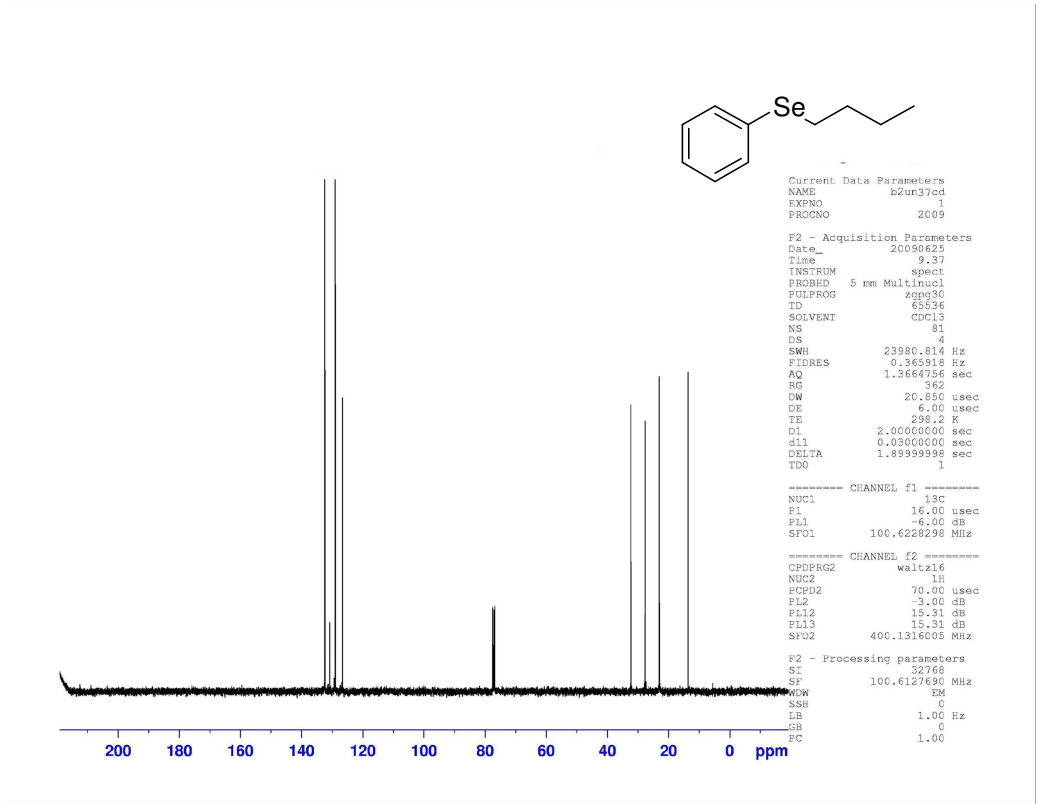

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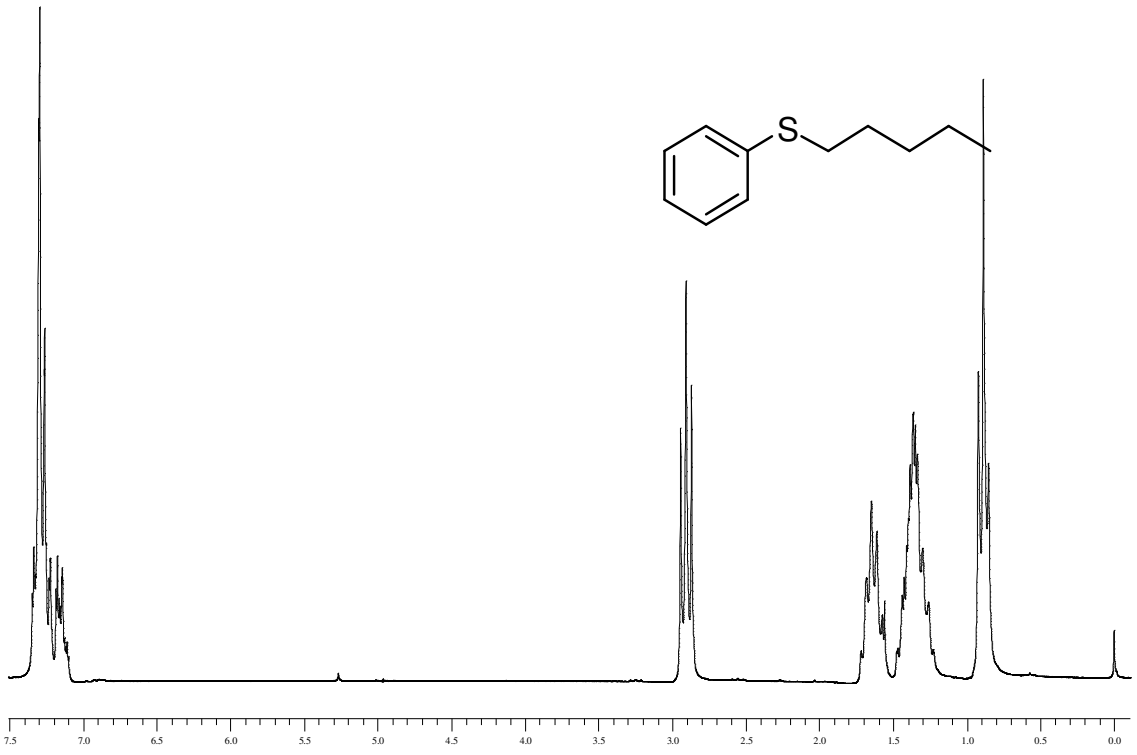

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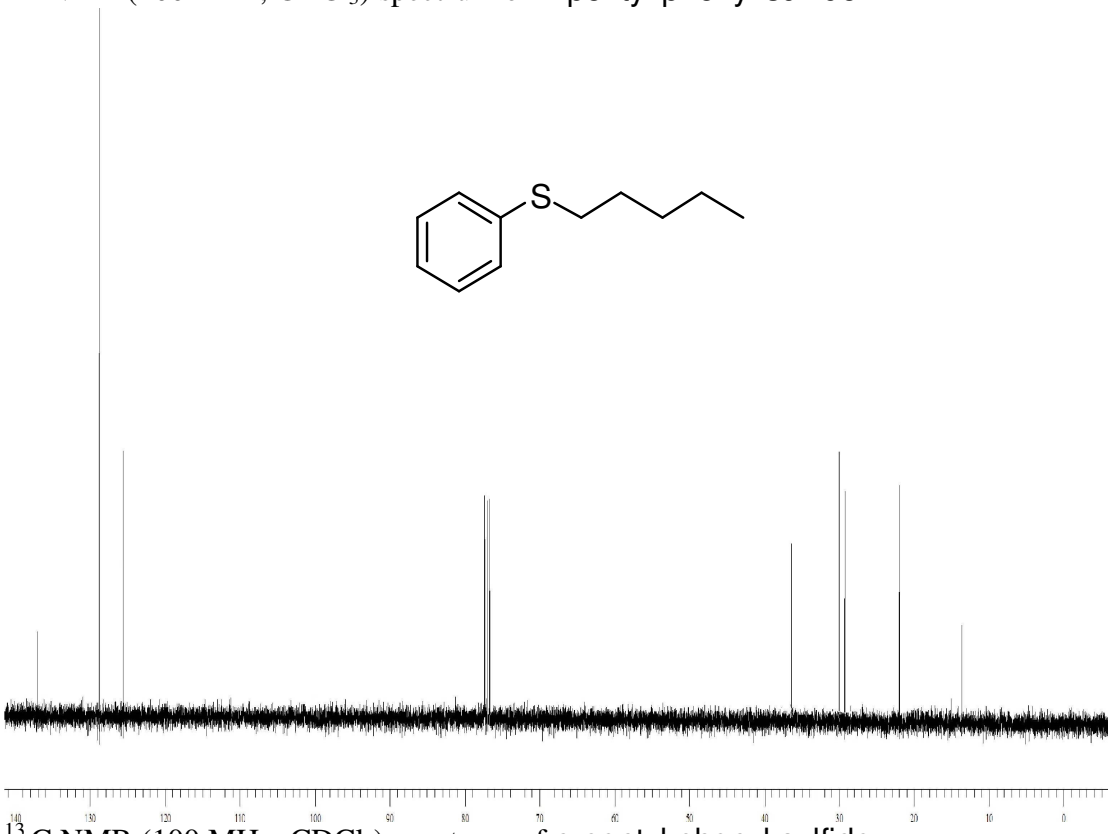

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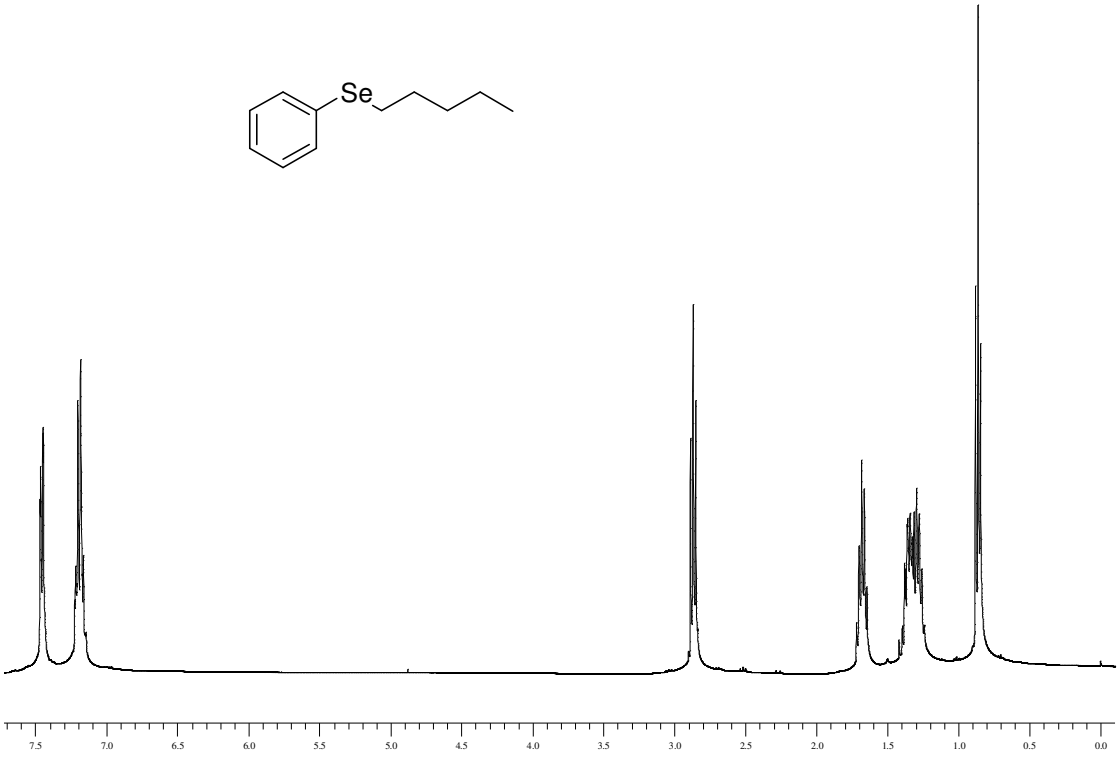

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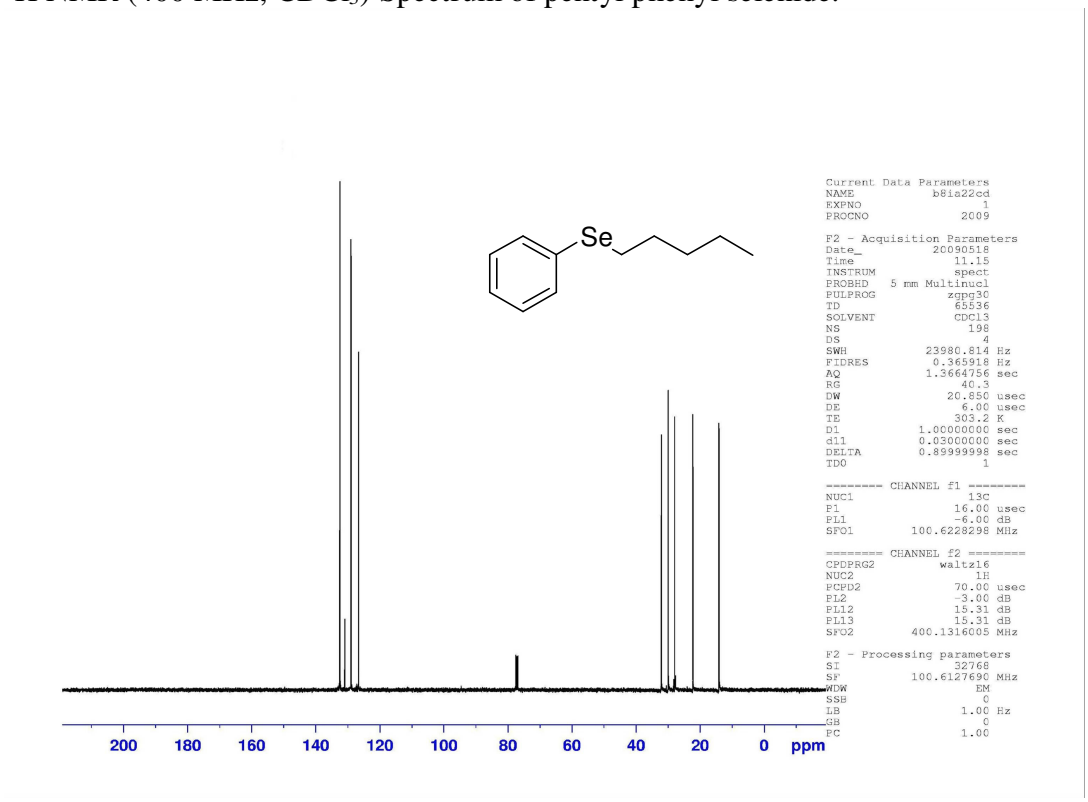

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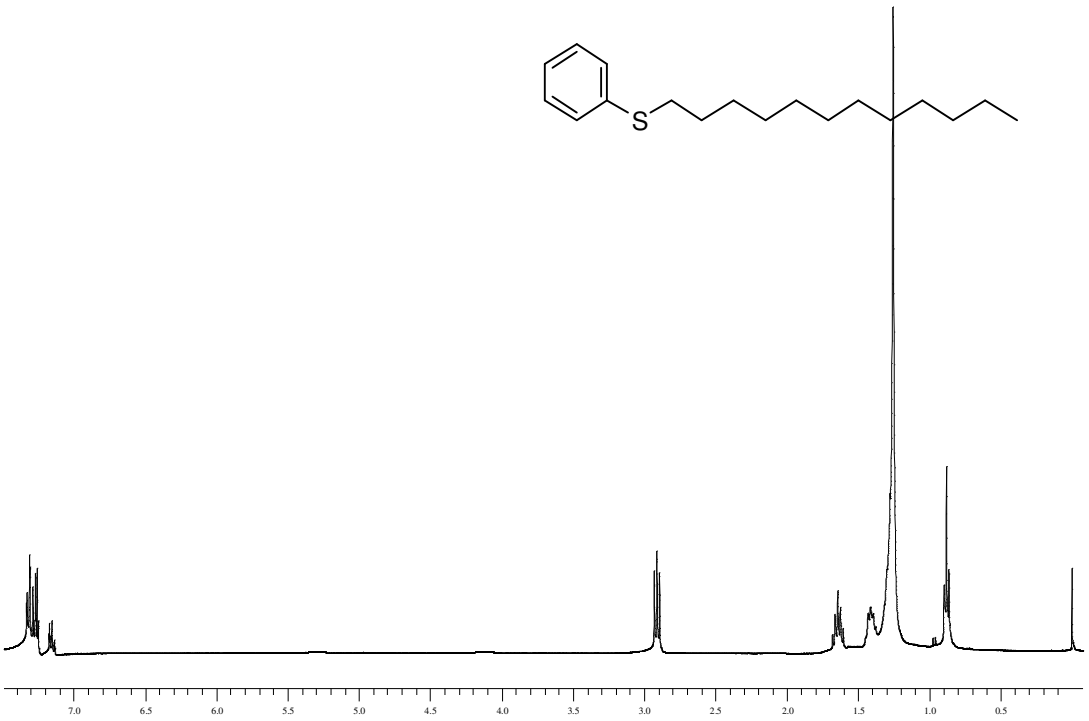

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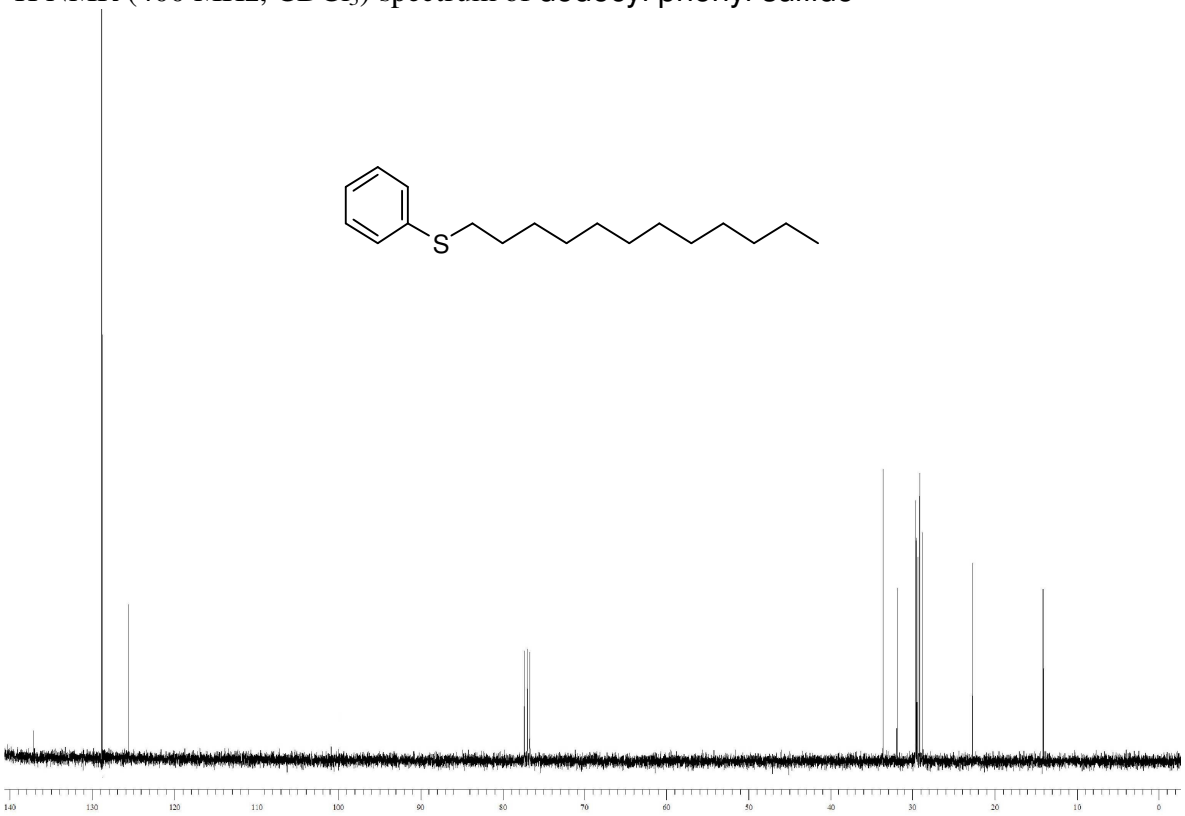

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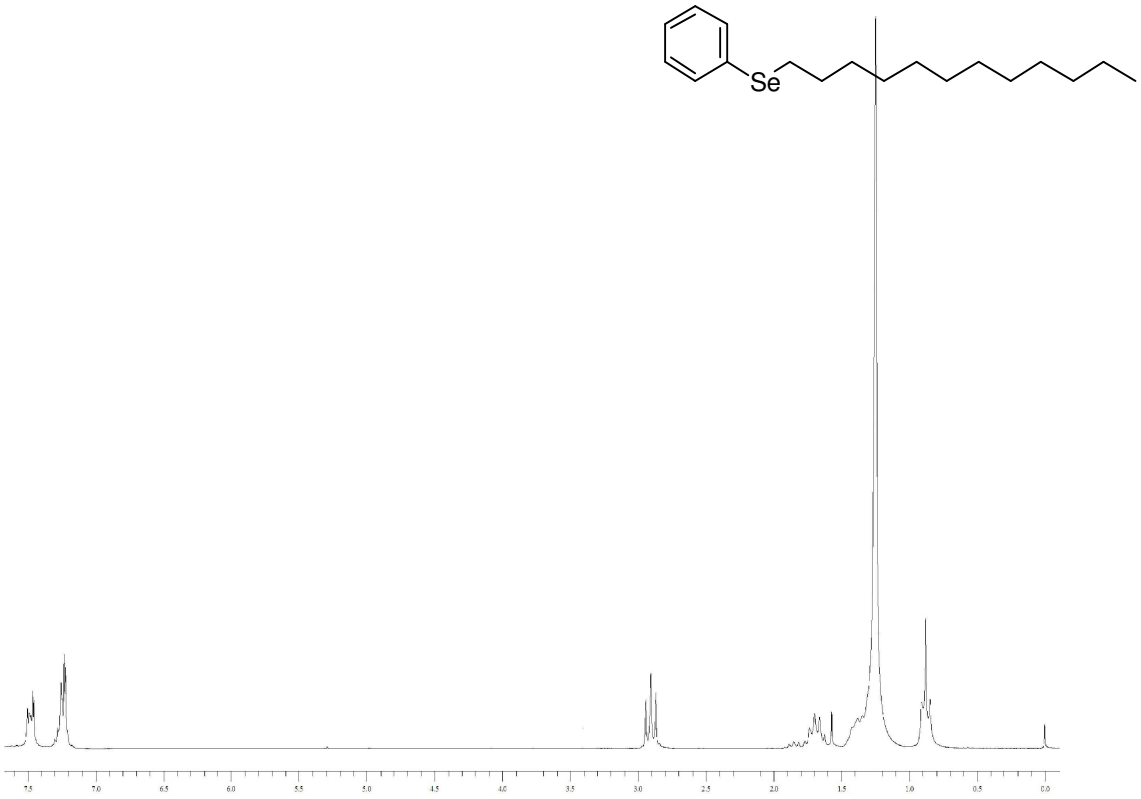

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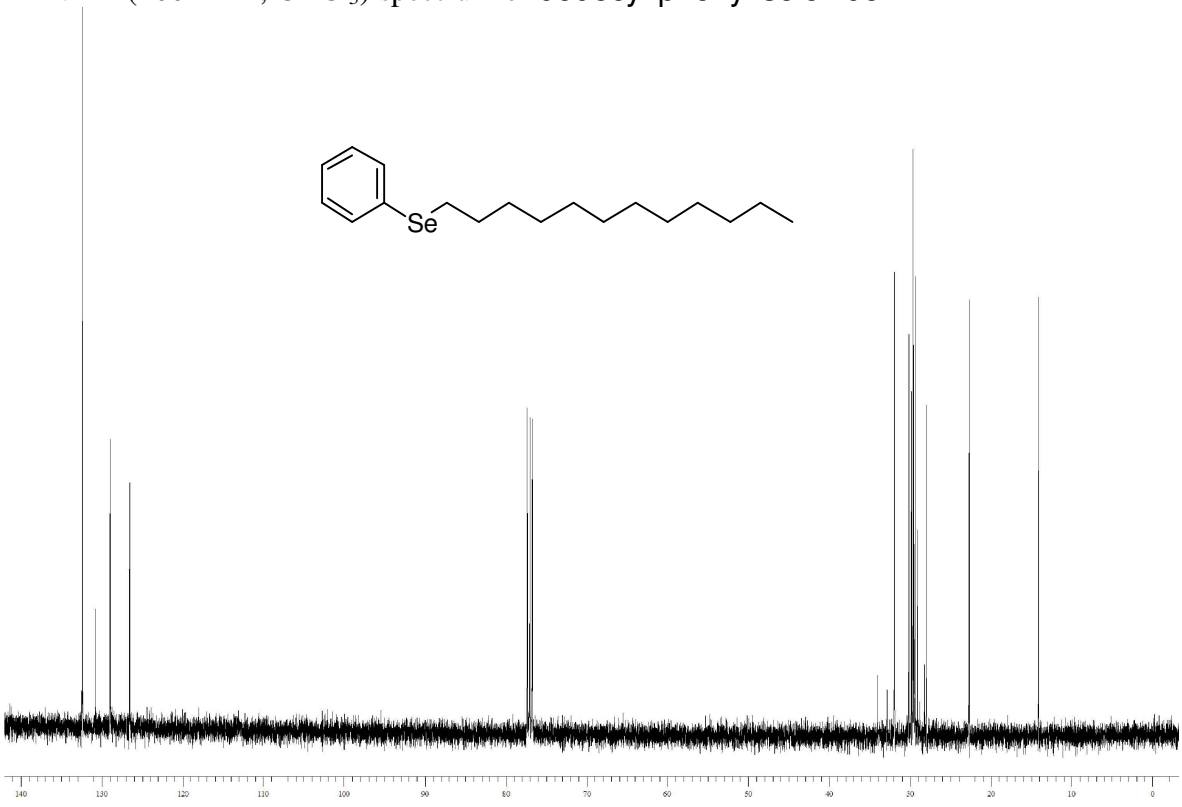

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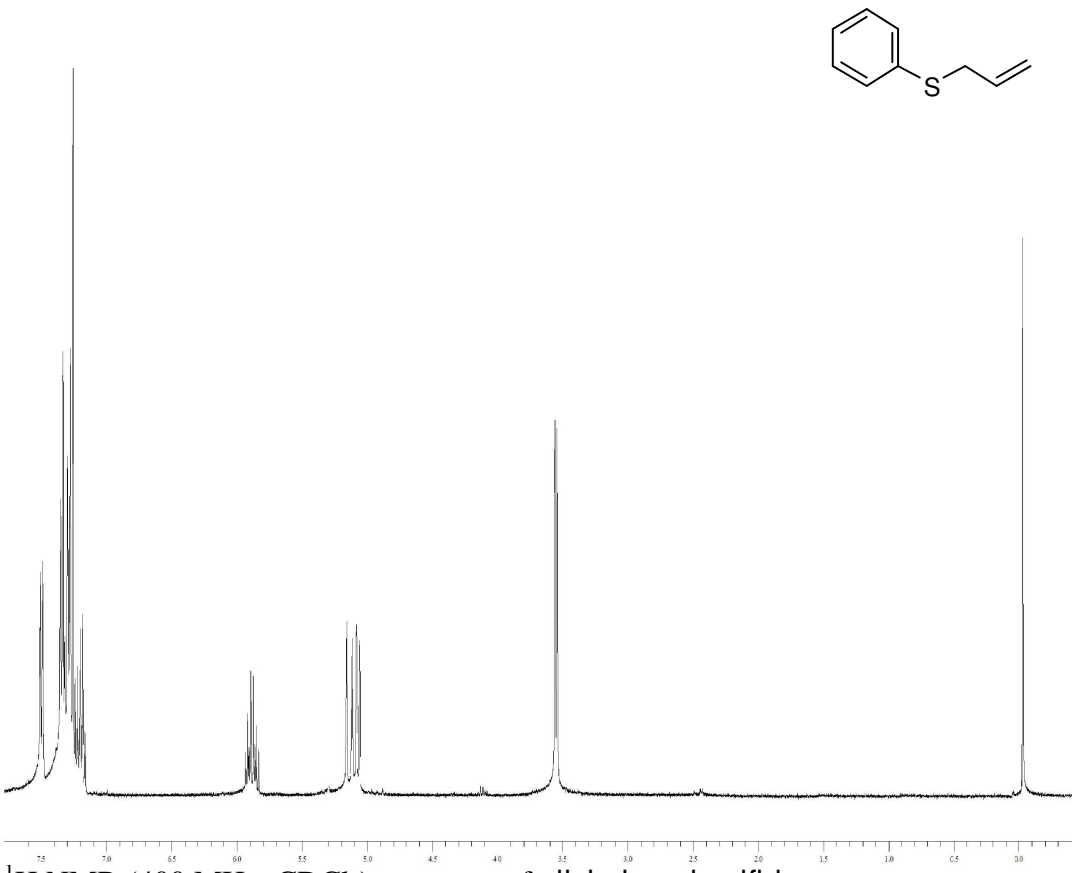

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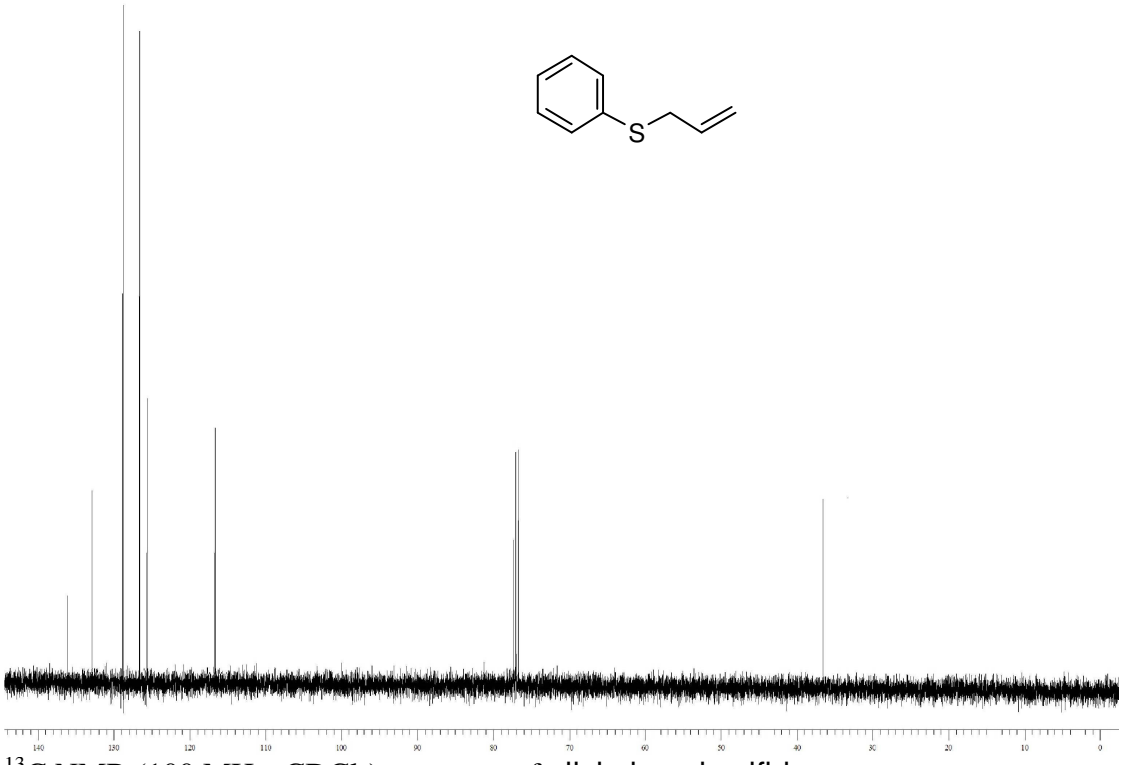

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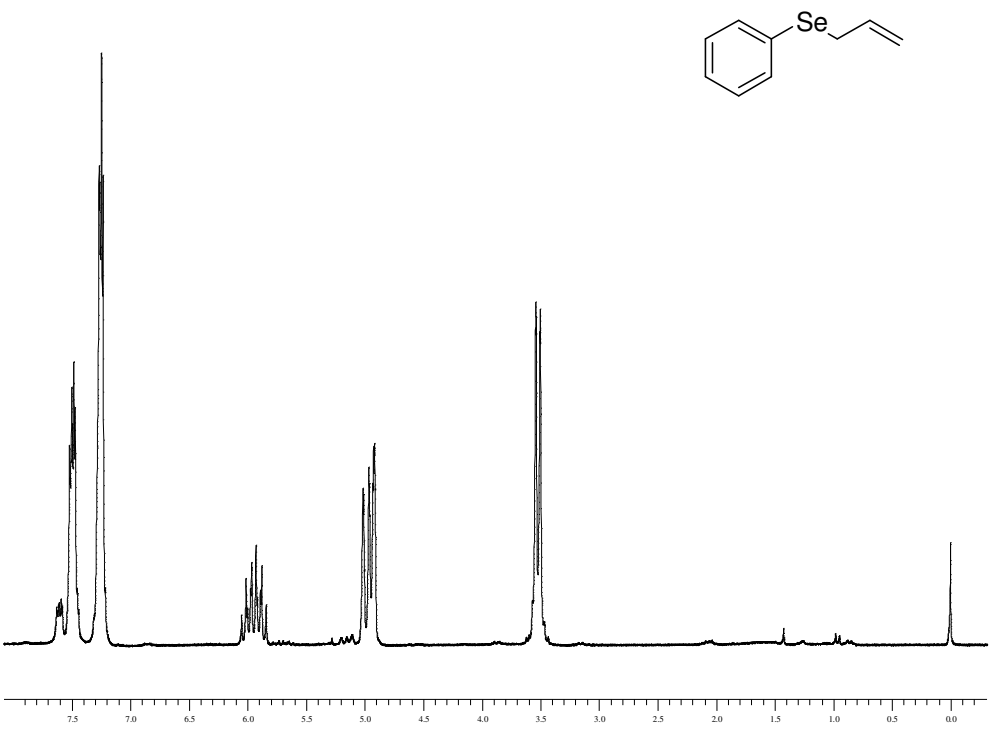

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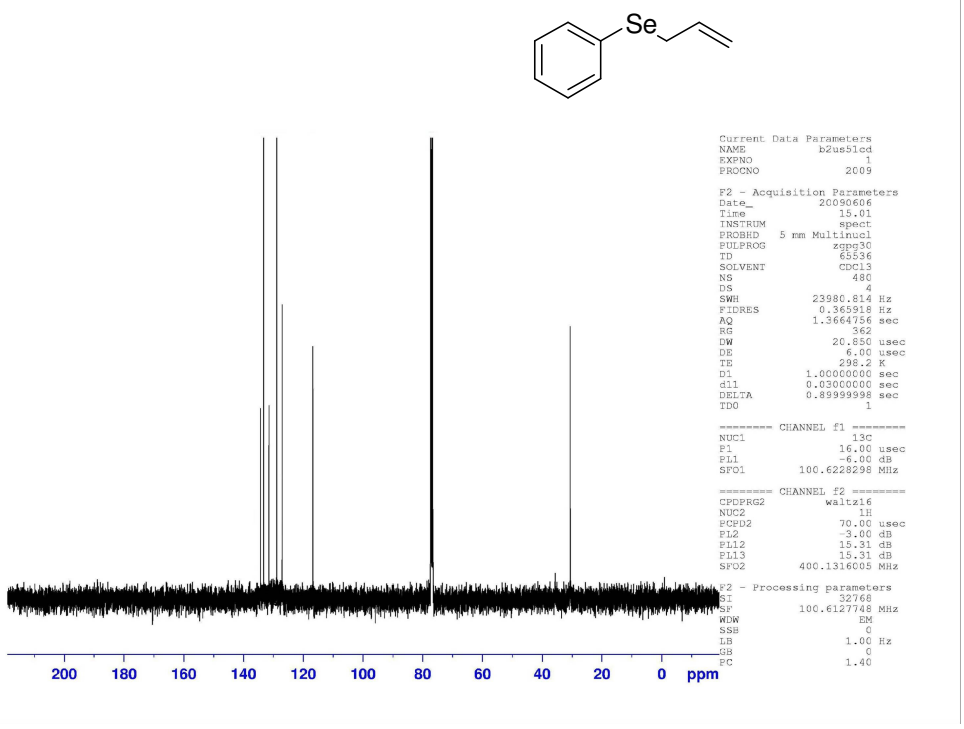

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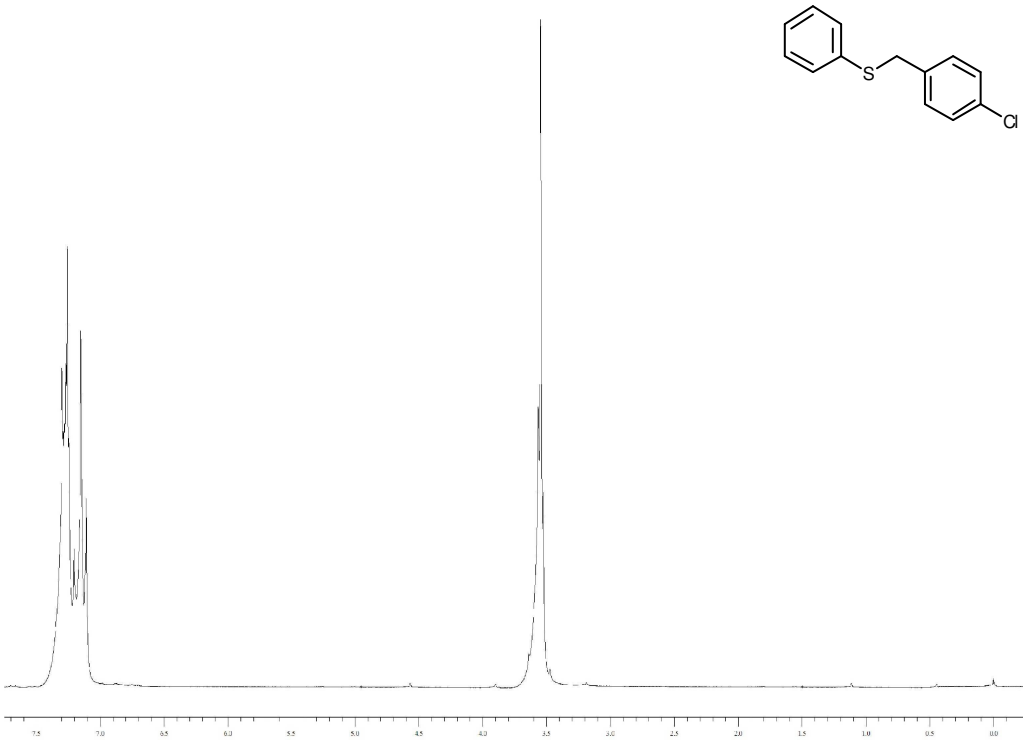

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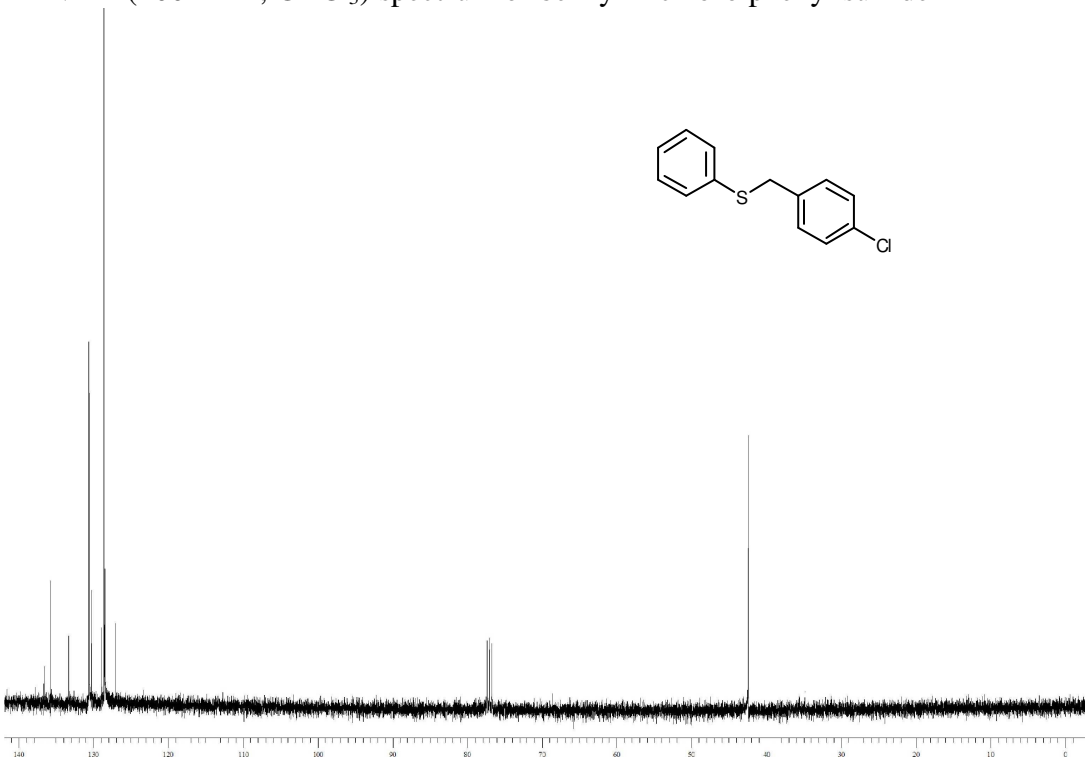

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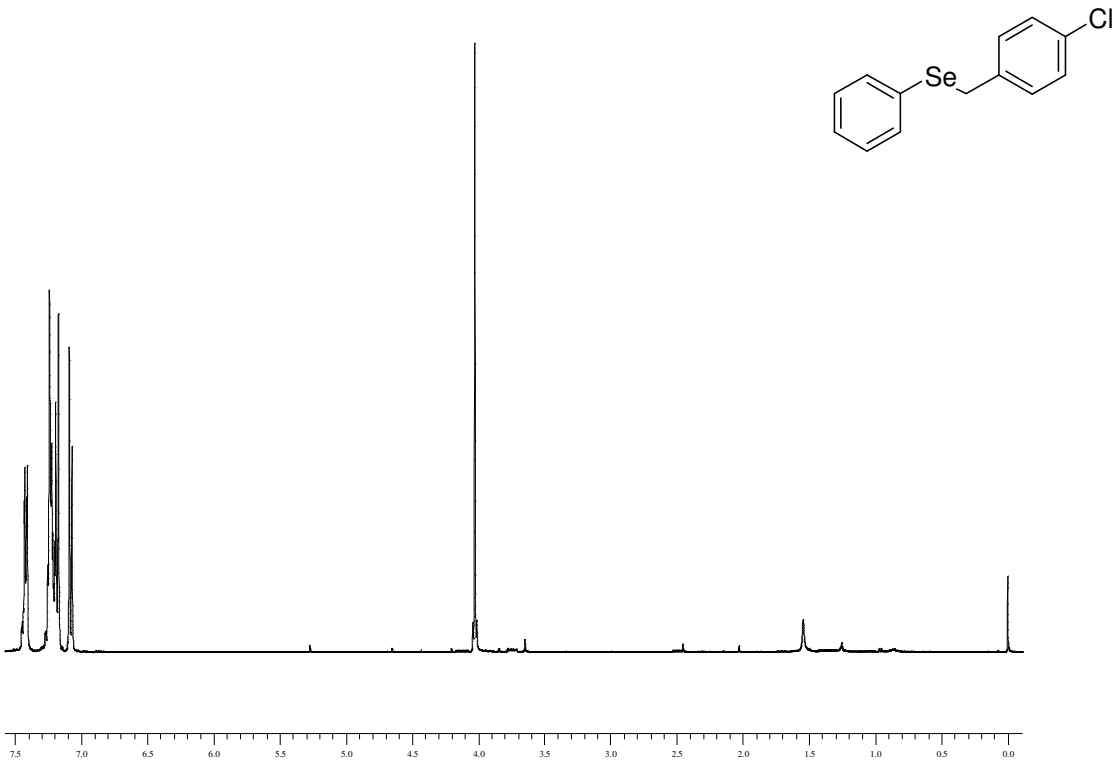

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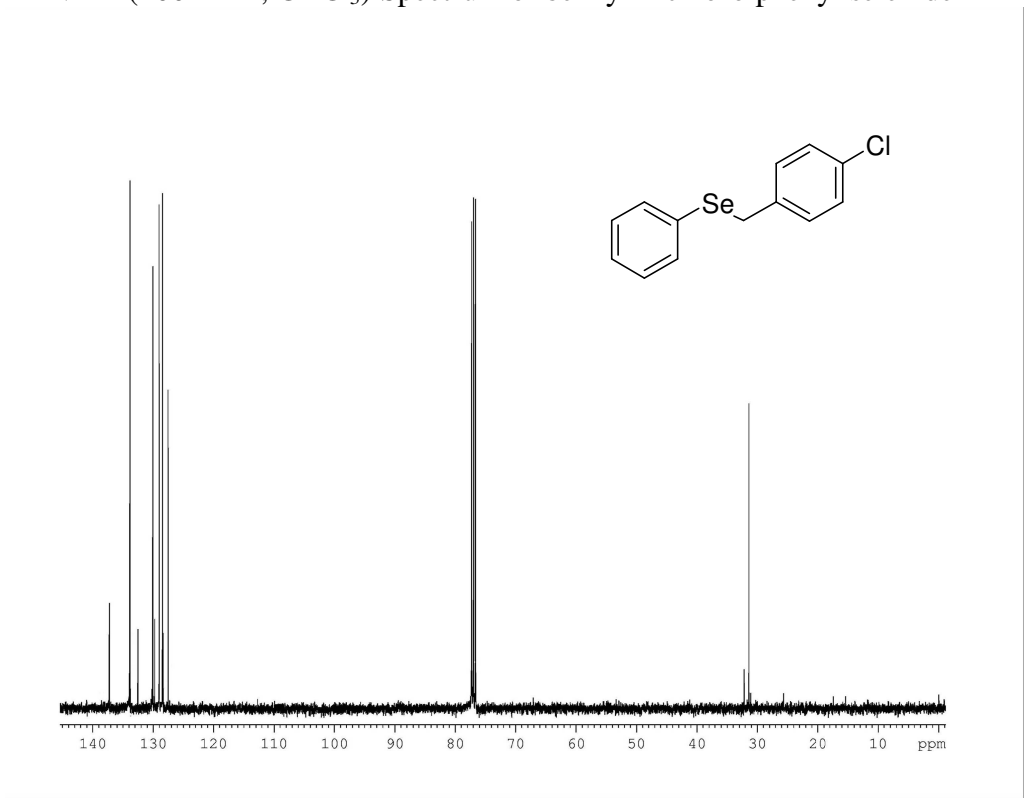

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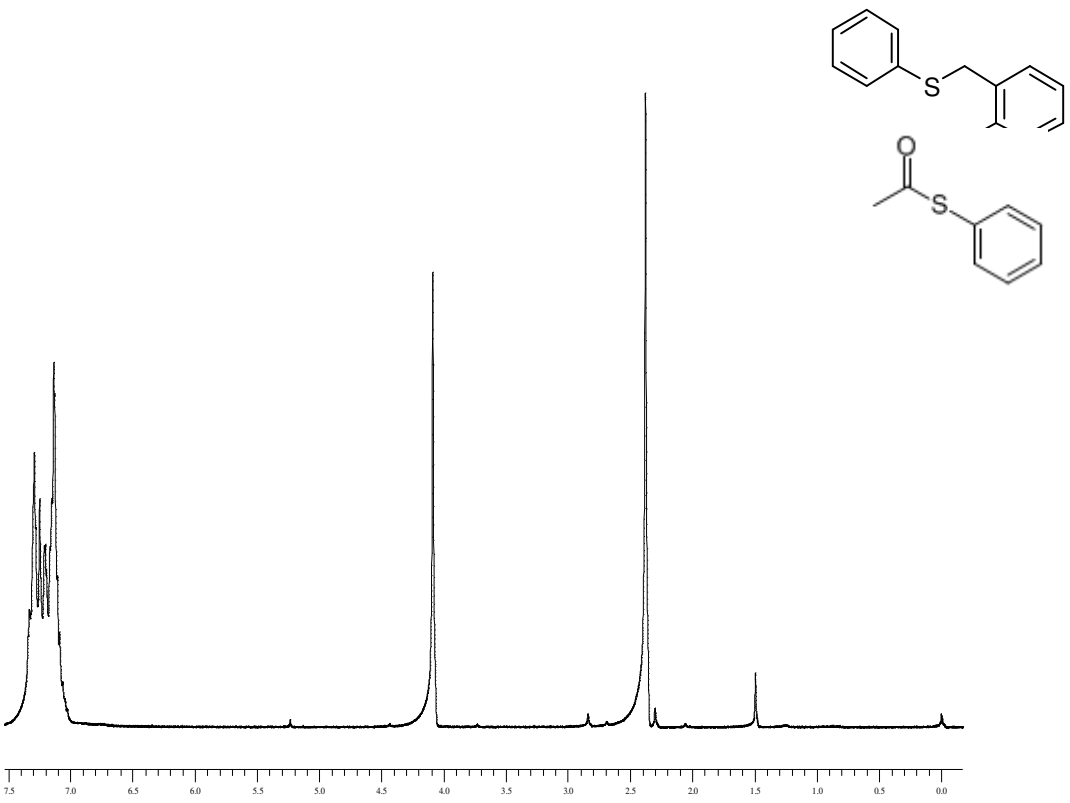

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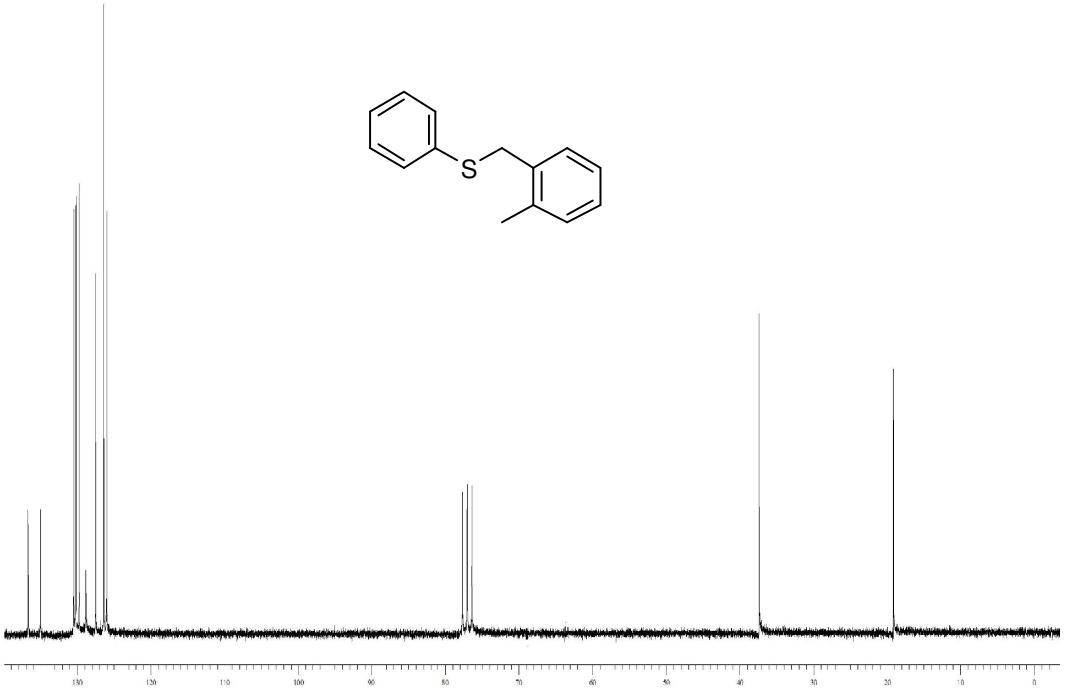

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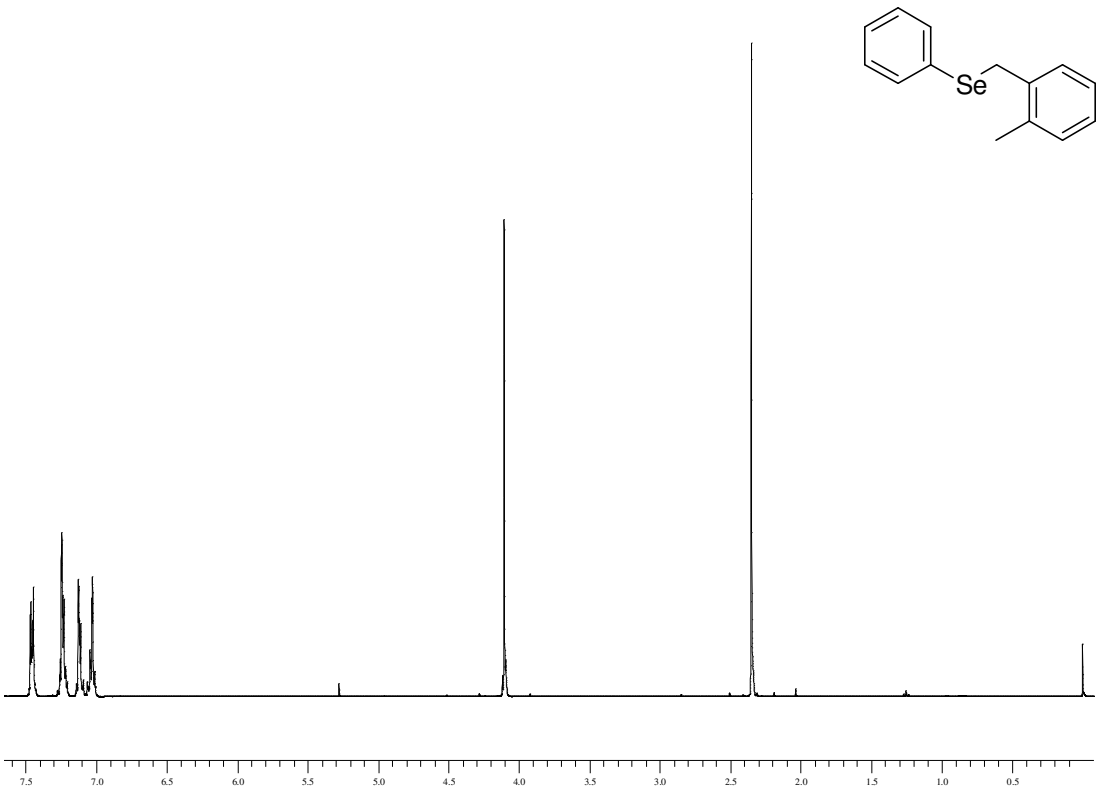

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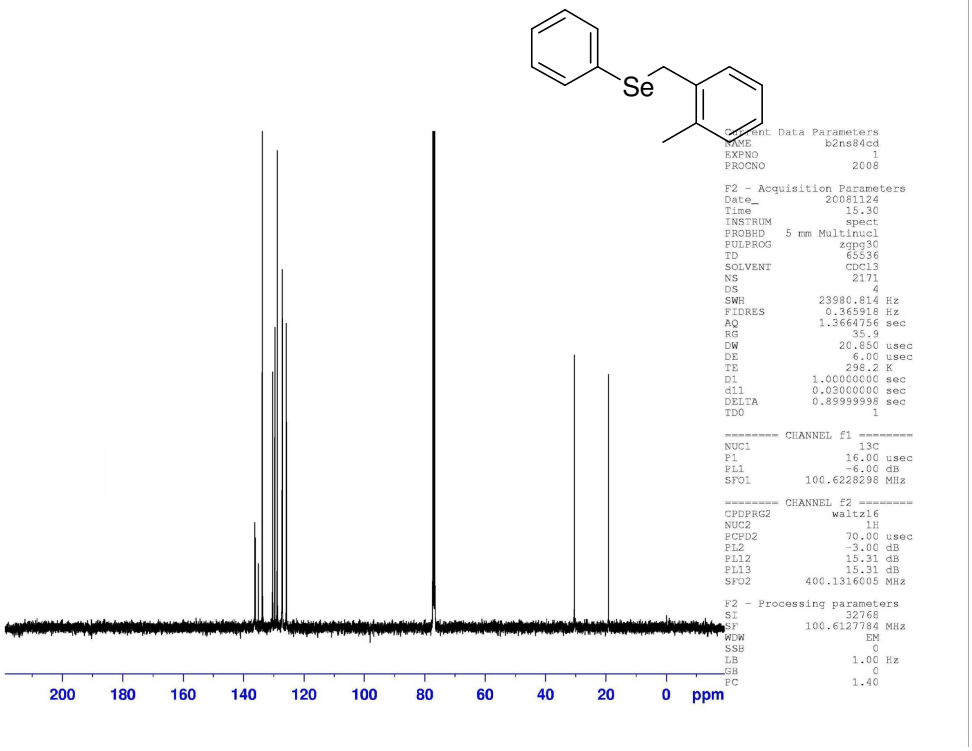

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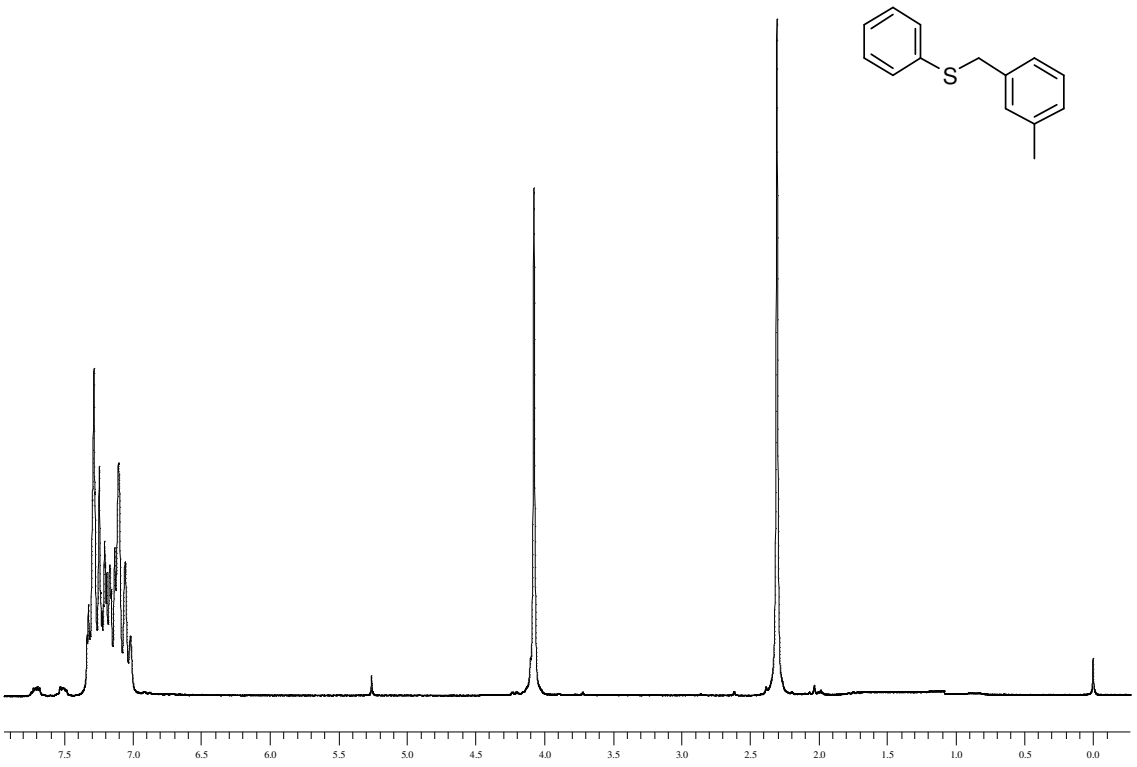

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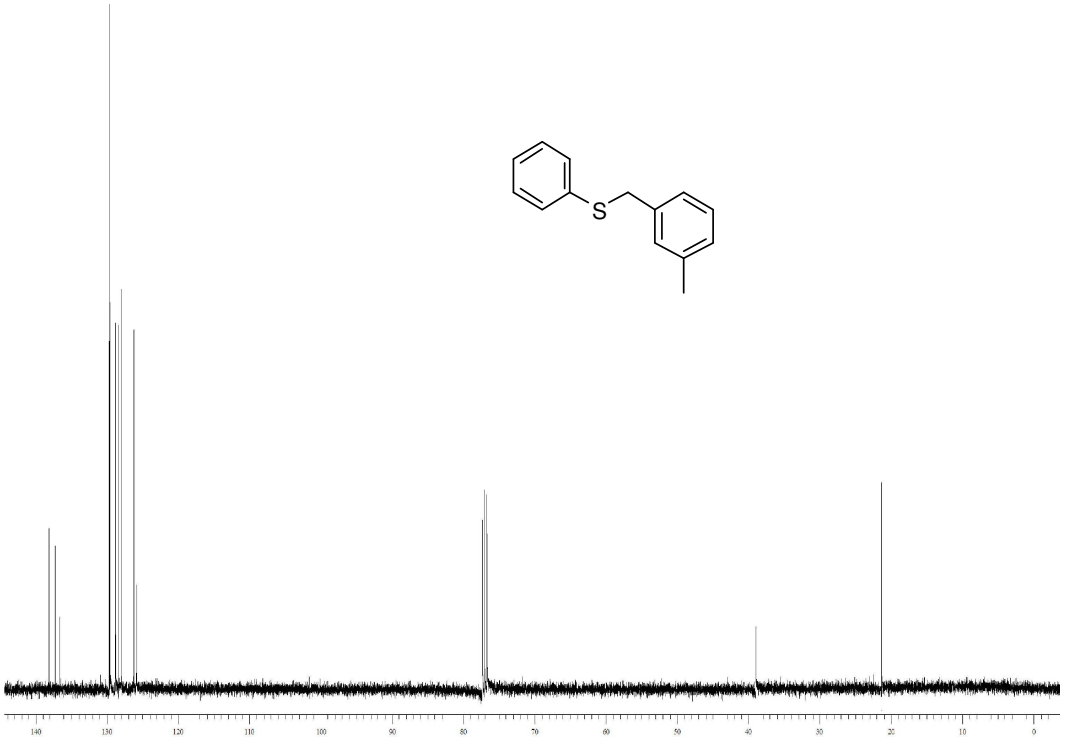

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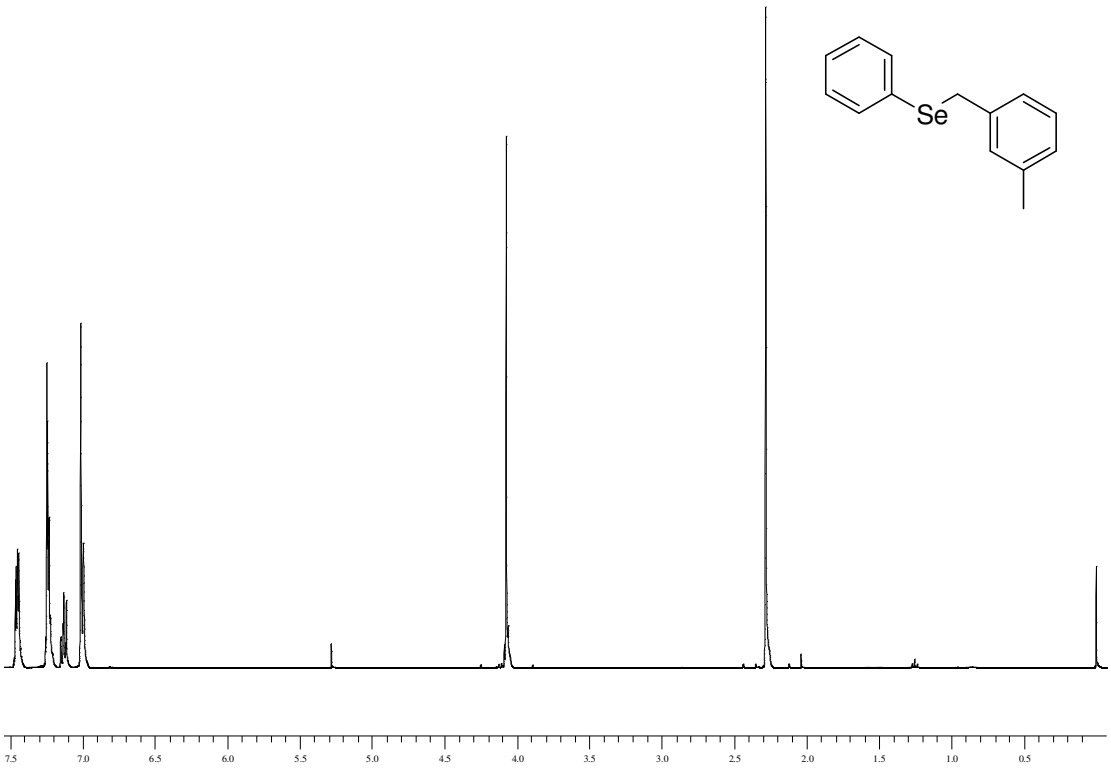
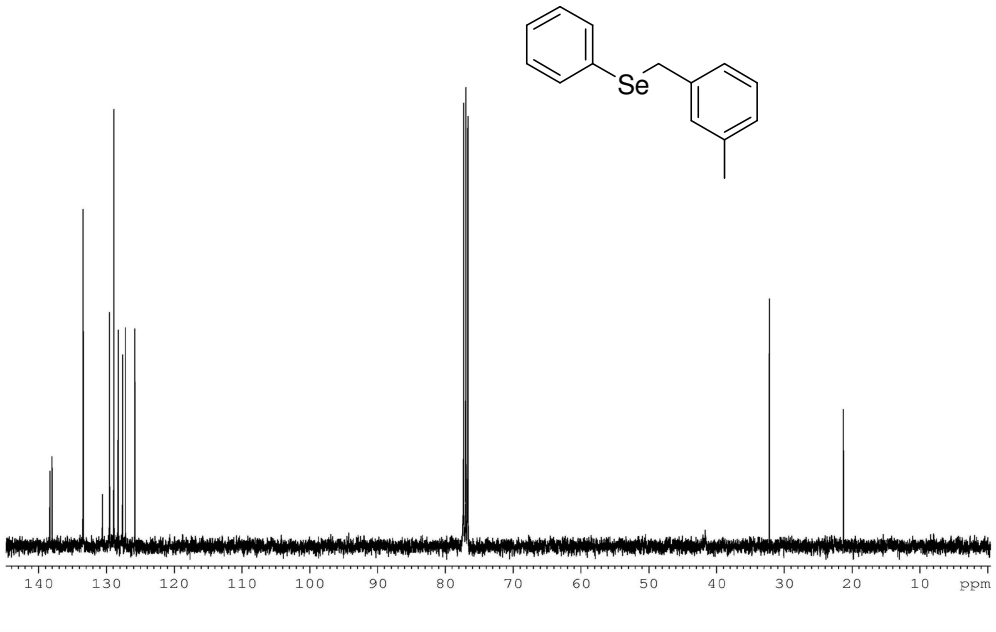
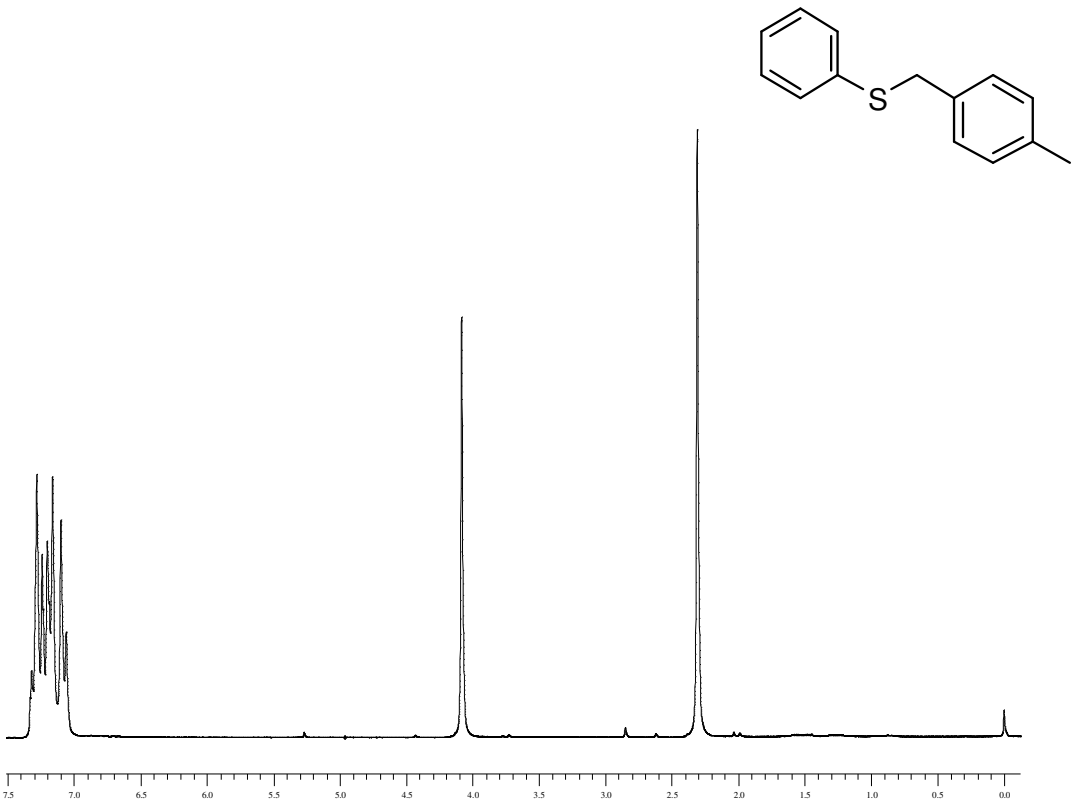


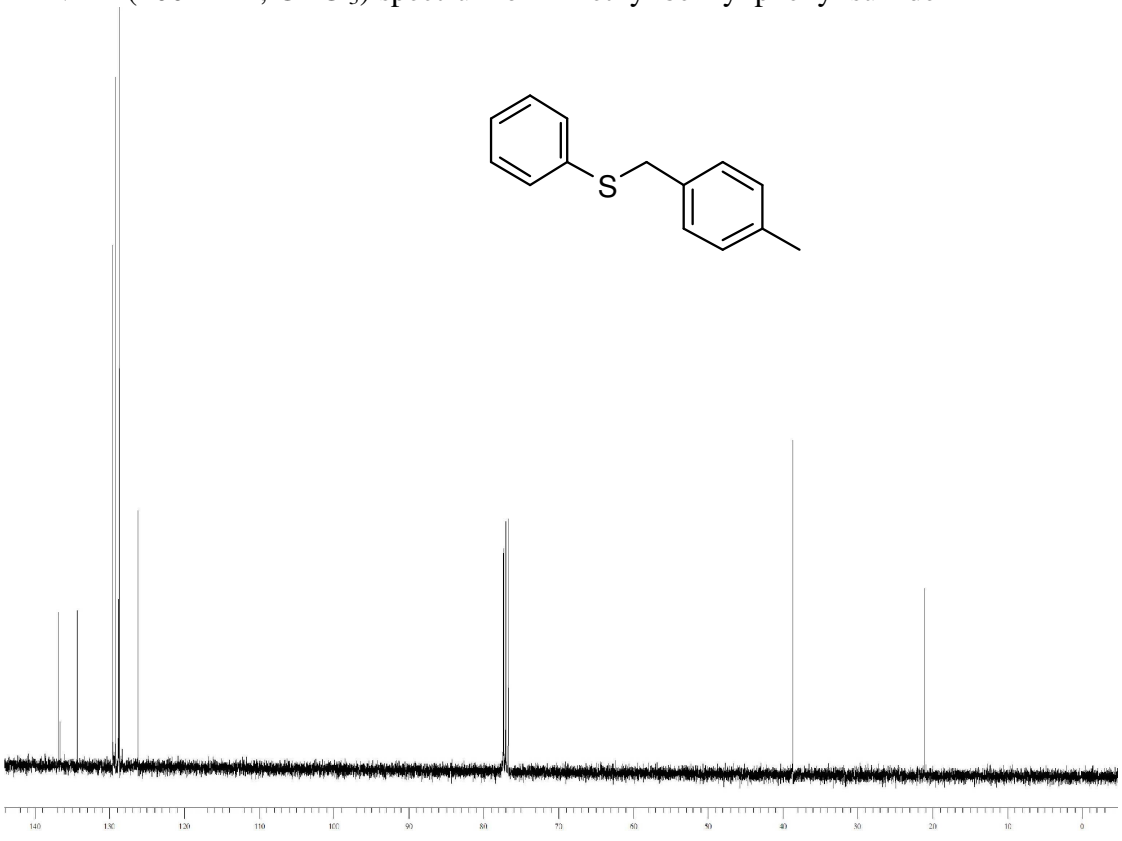
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3-methyl benzyl phenyl selenide



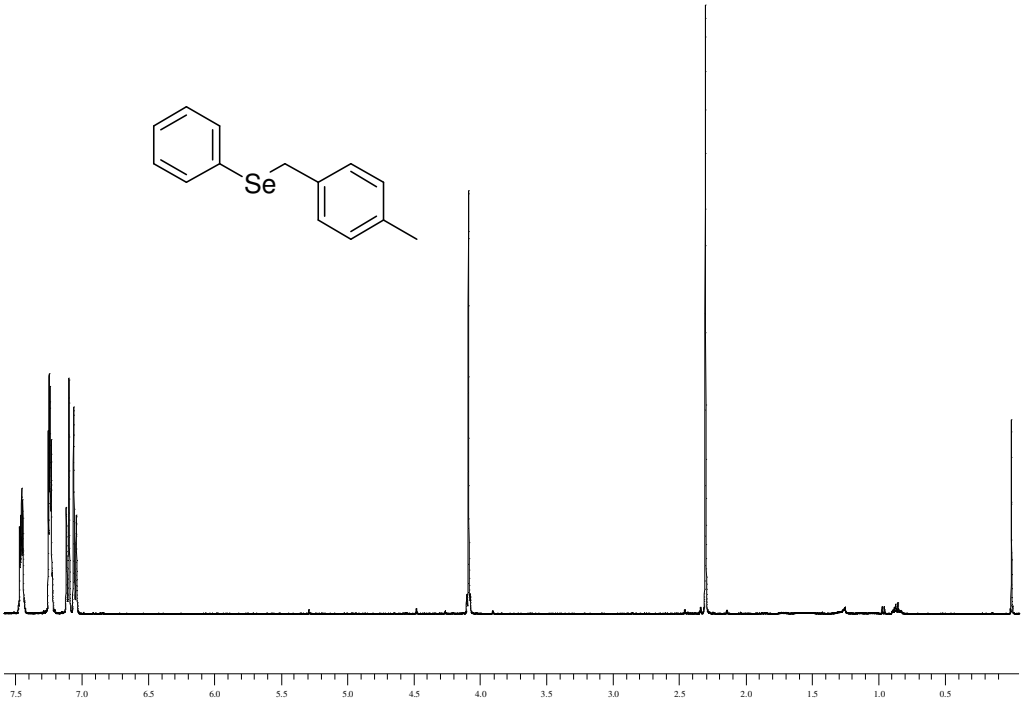
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 3-methyl benzyl phenyl selenide



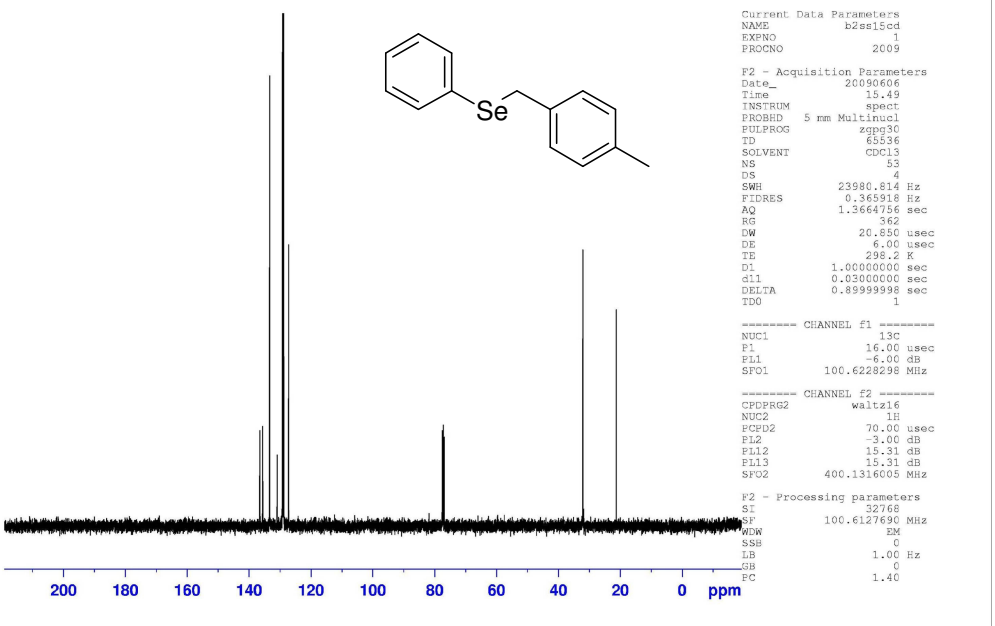
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of 4-methyl benzyl phenyl sulfide



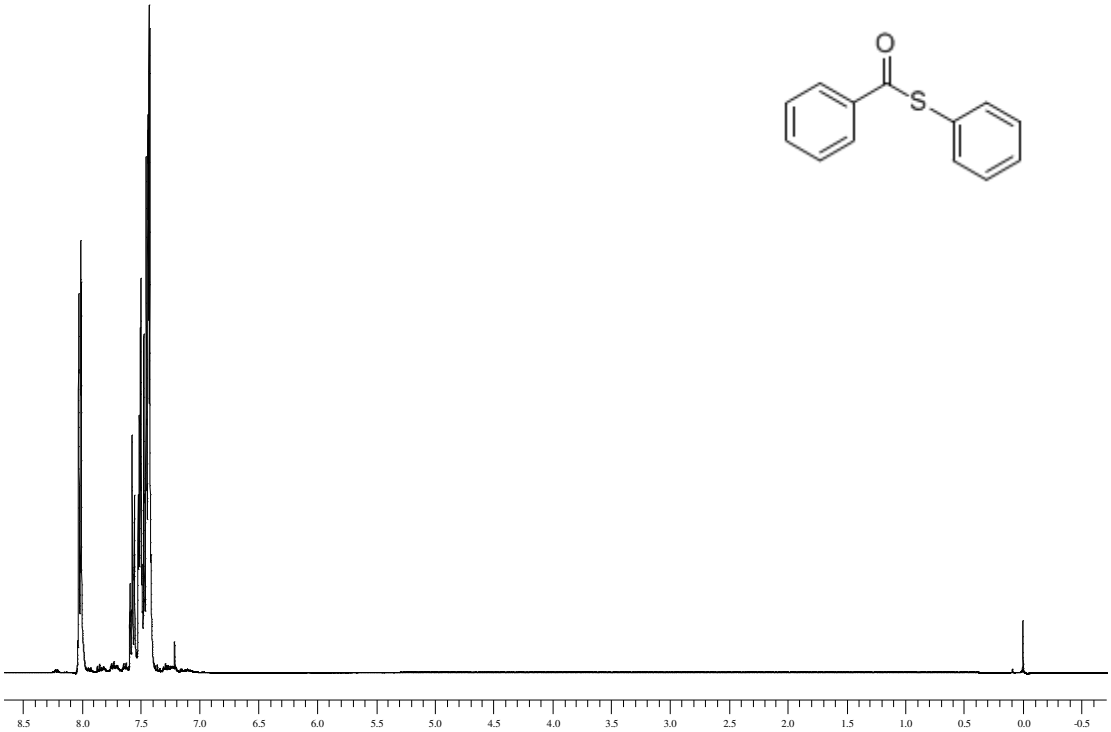
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4-methyl benzyl phenyl sulfide



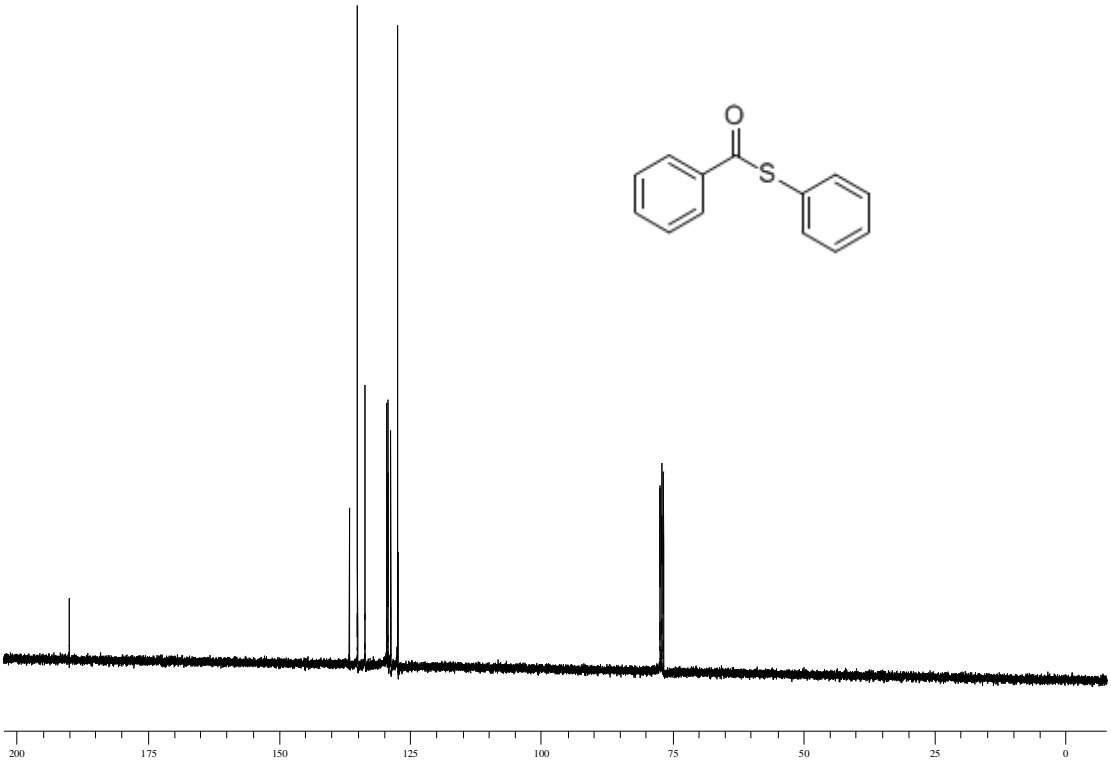
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 4-methyl benzyl phenyl selenide



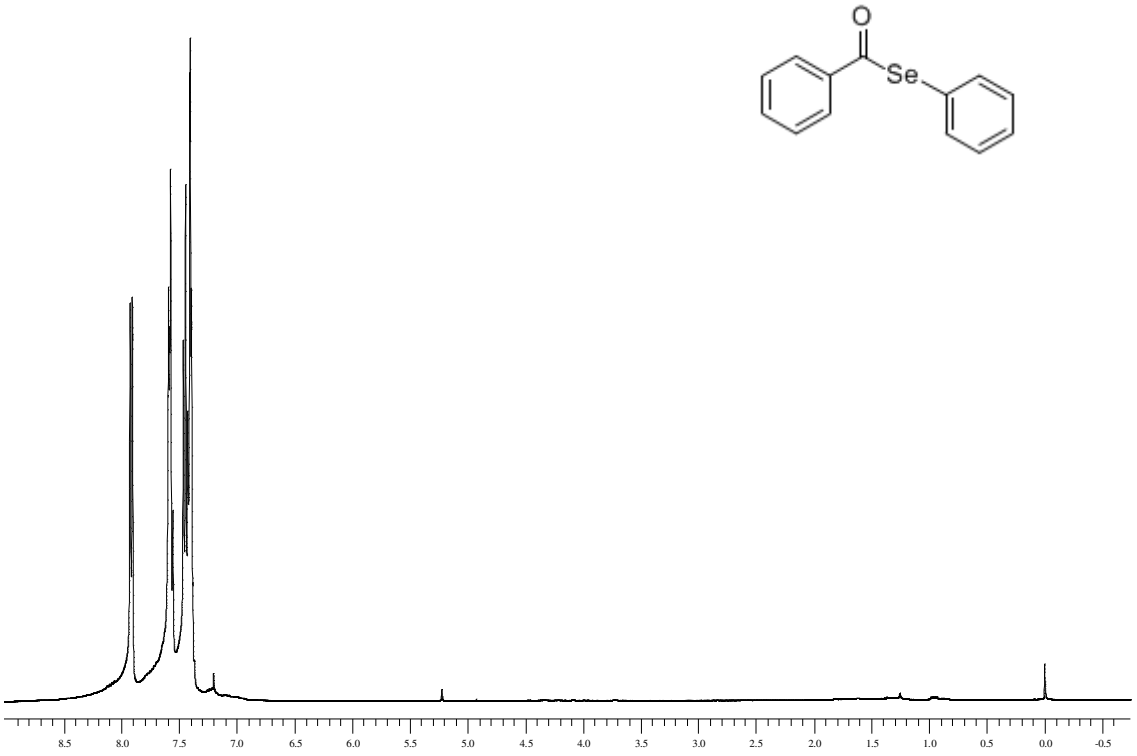
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of 4-methyl benzyl phenyl selenide



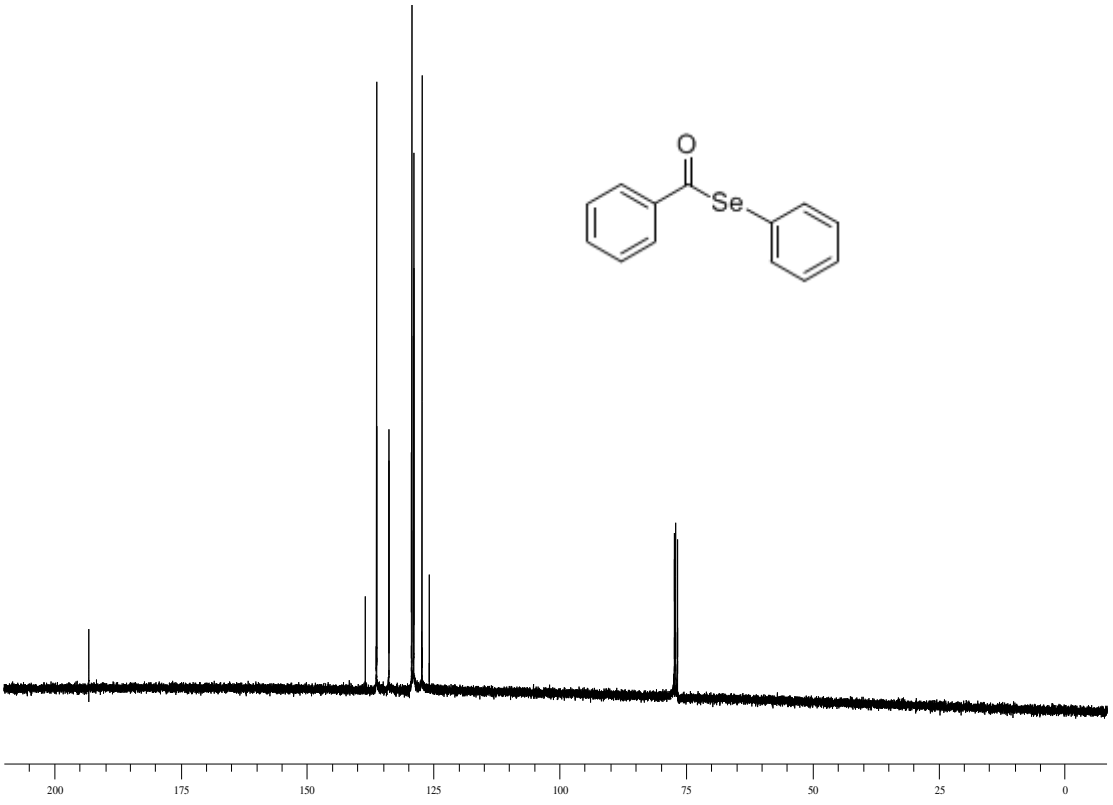
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *S*-phenyl benzothioate.



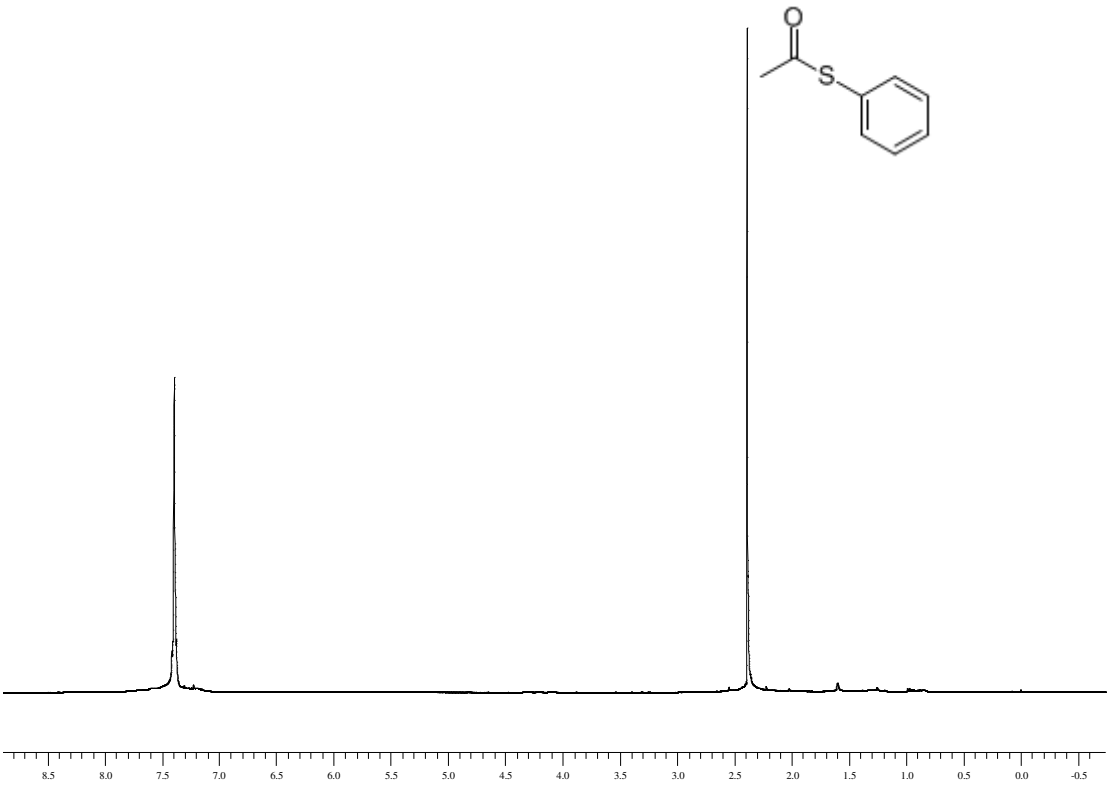
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *S*-phenyl benzothioate



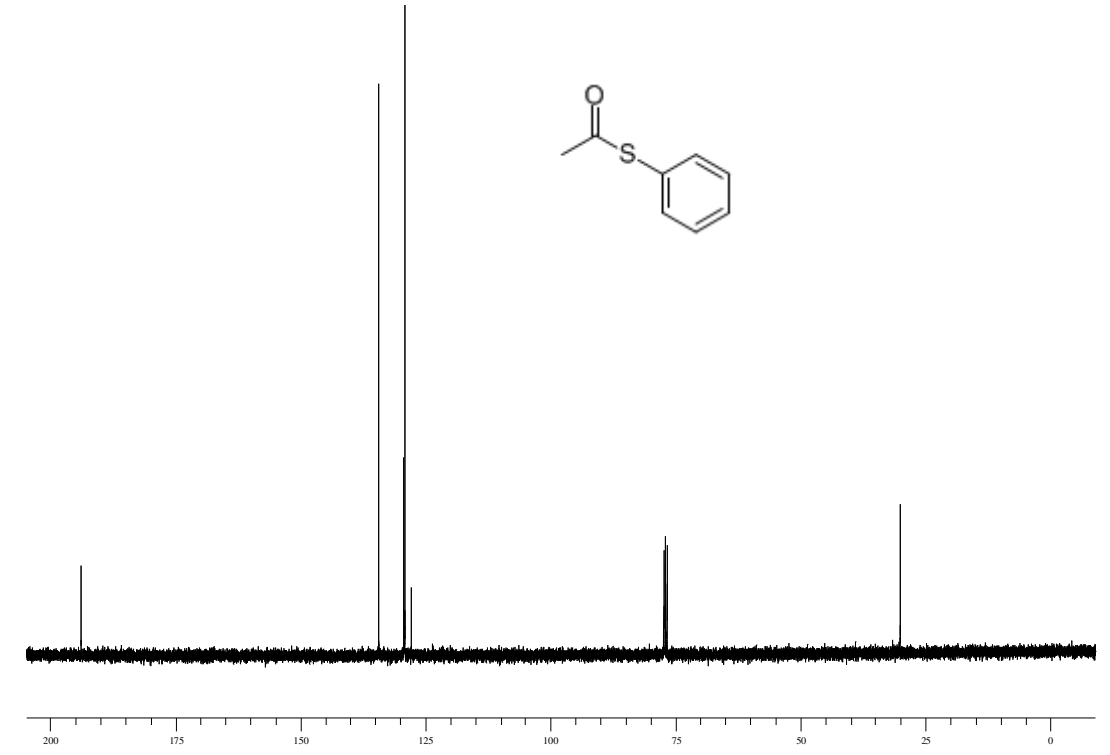
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-phenyl selenobenzoate.



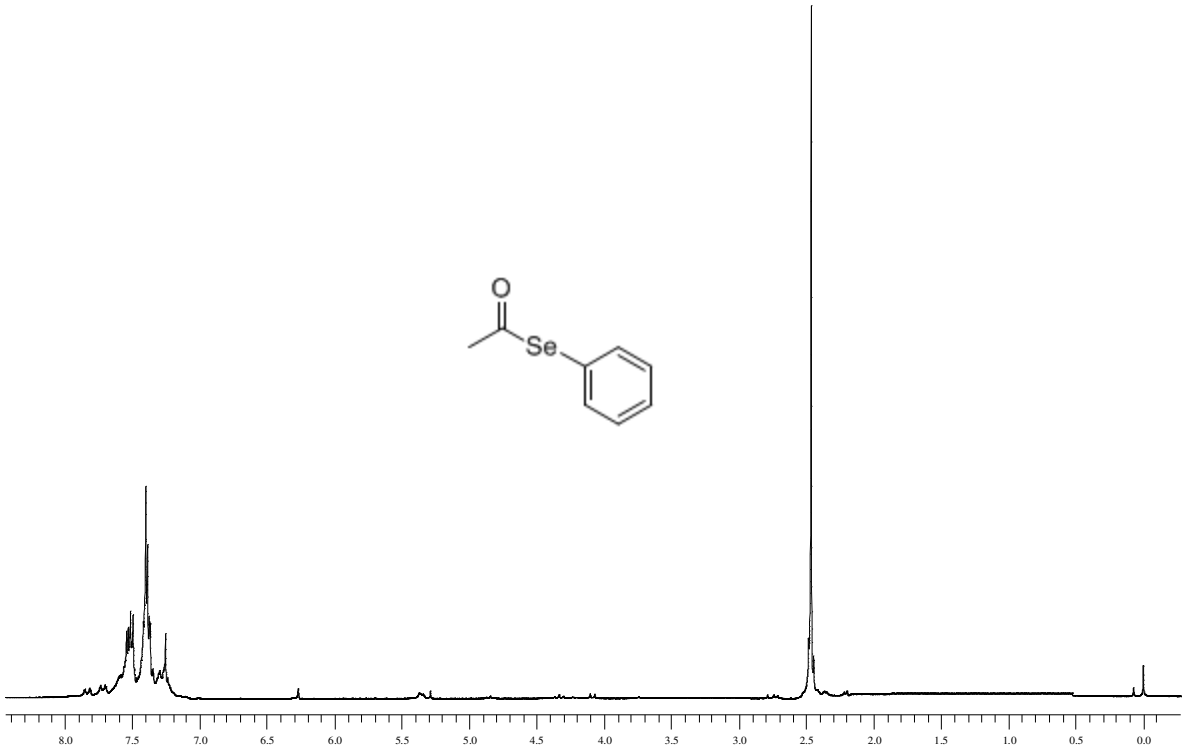
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-phenyl selenobenzoate



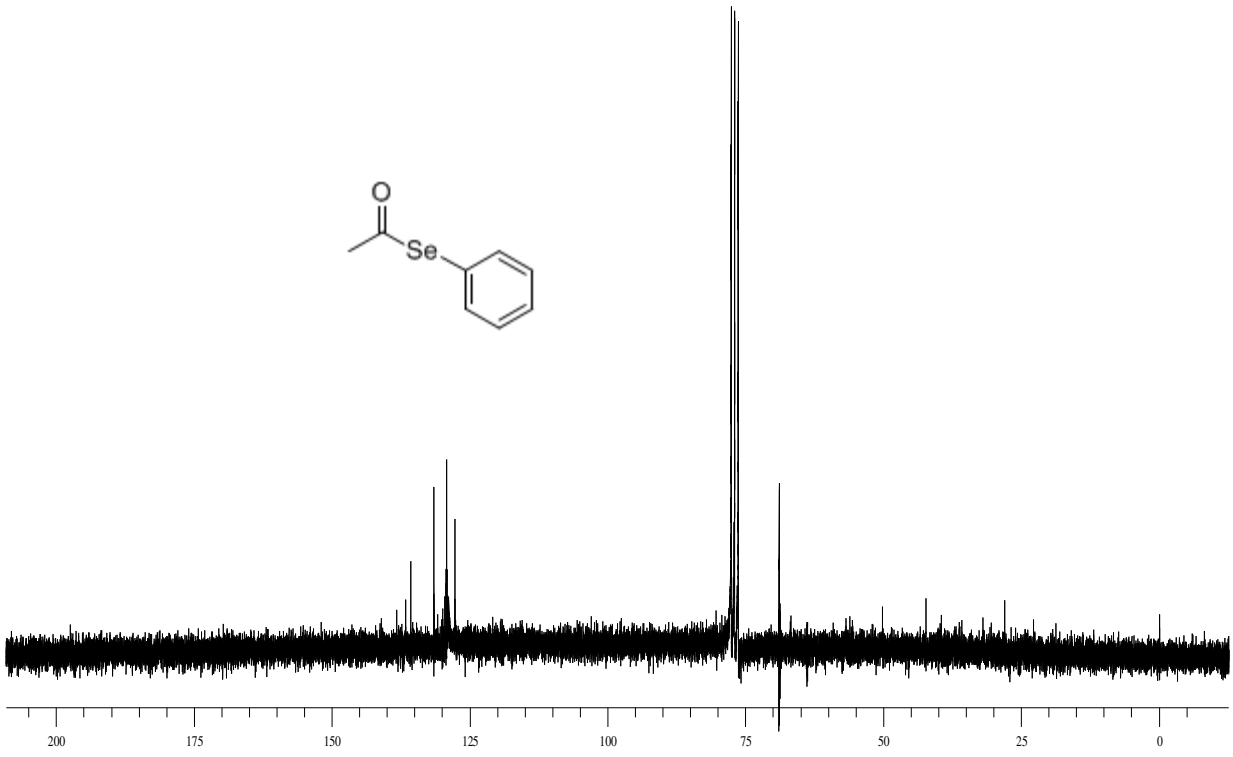
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-phenyl etanethioate



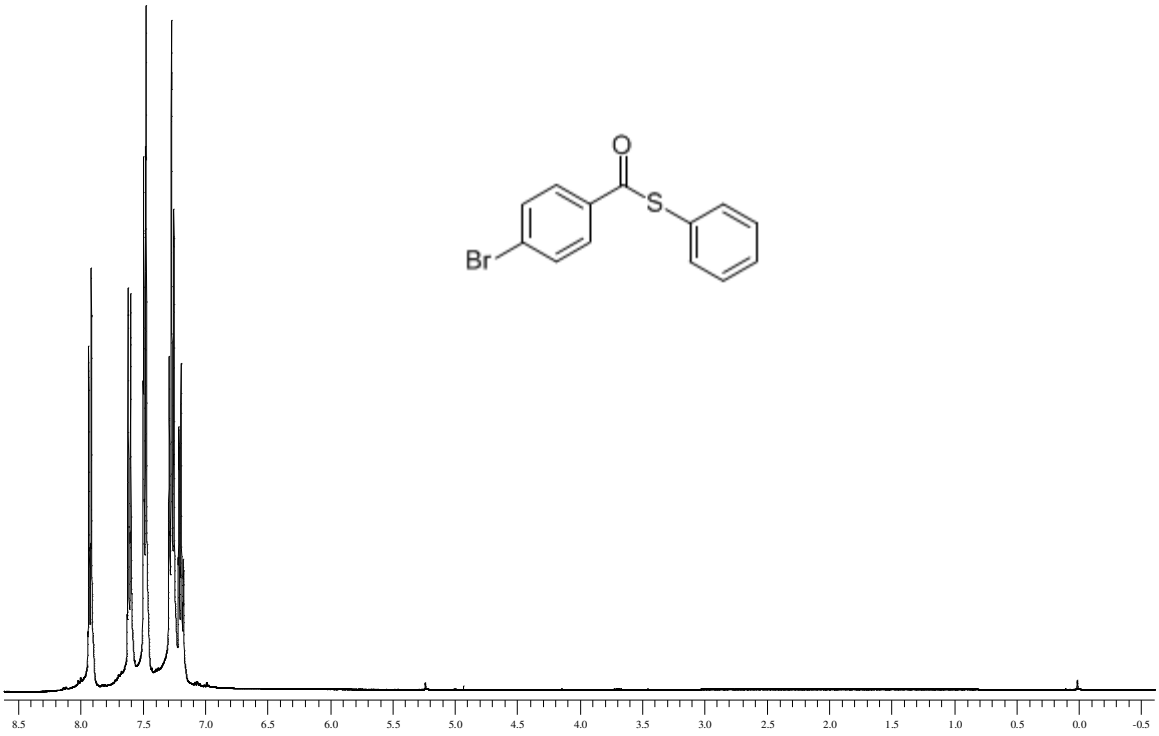
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-phenyl etanethioate



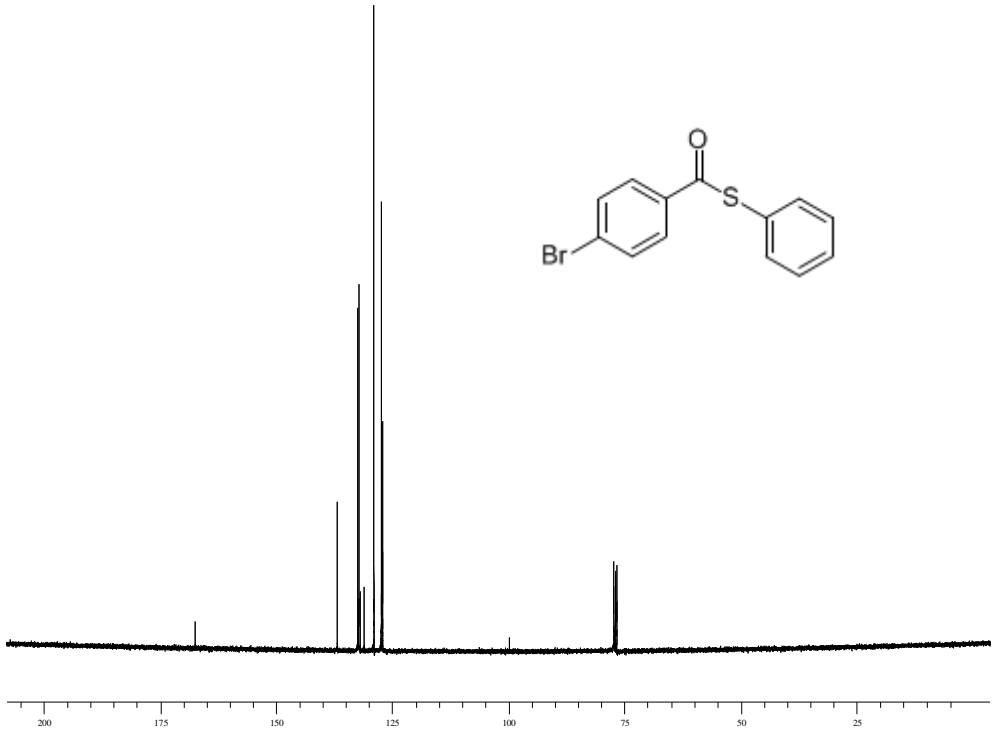
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-phenyl etaneselenoate.



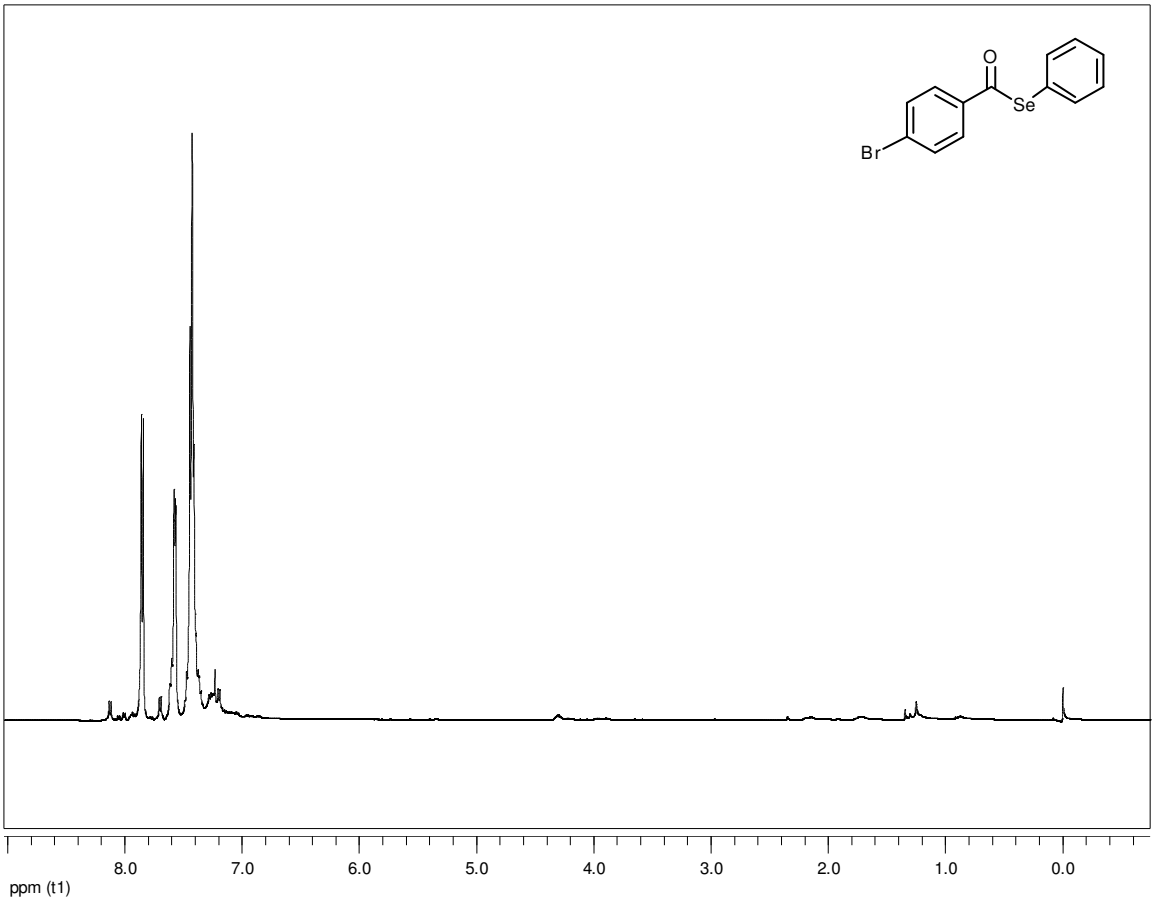
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *Se*-phenyl etaneselenoate



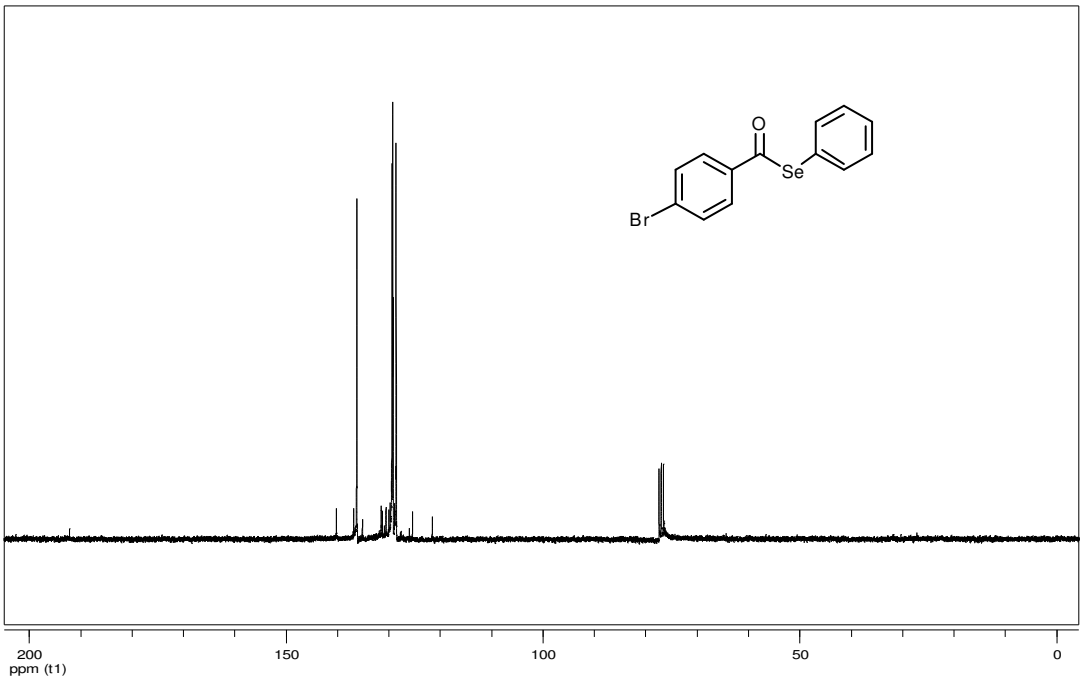
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *S*-phenyl 4-bromobenzothioate.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *S*-phenyl 4-bromobenzothioate.

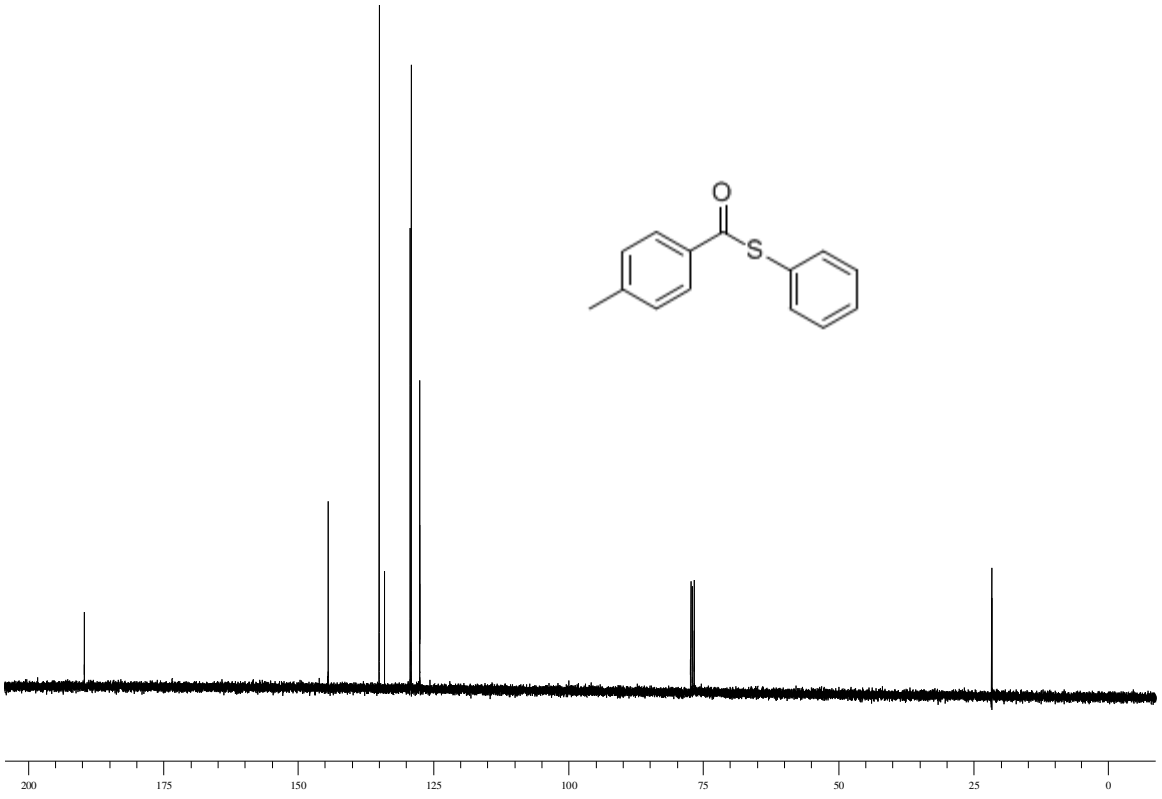


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se*-phenyl 4-bromoselenobenzoate.

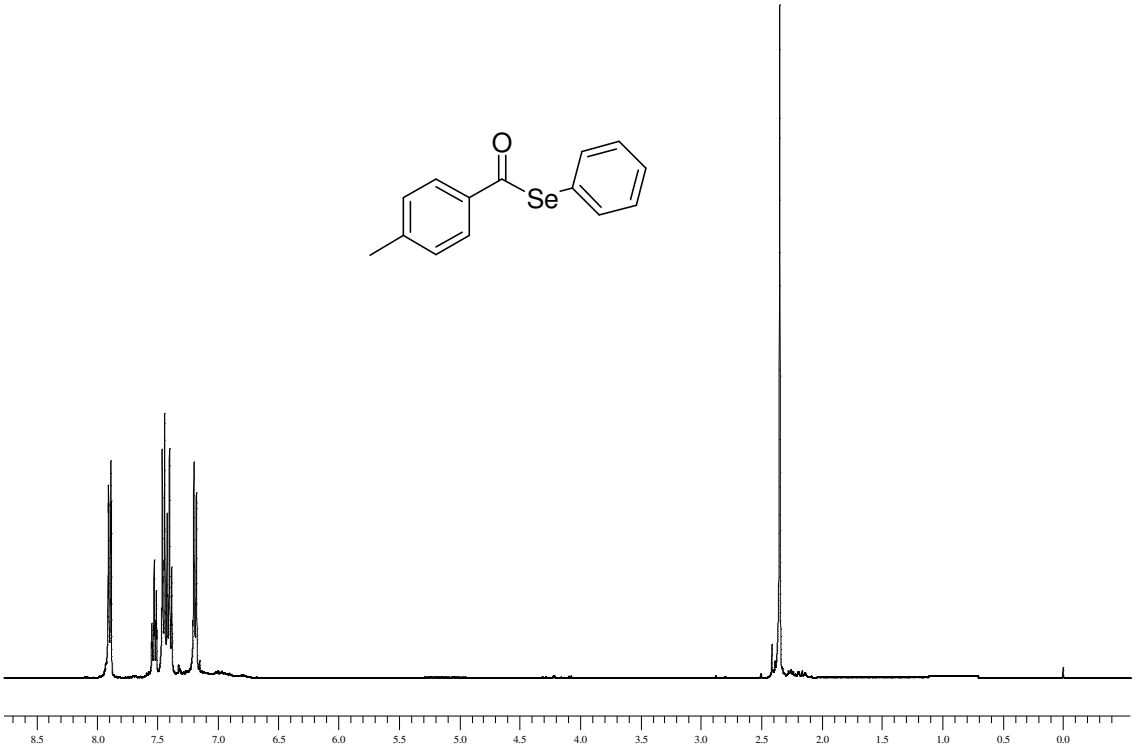


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se*-phenyl 4-bromoselenobenzoate

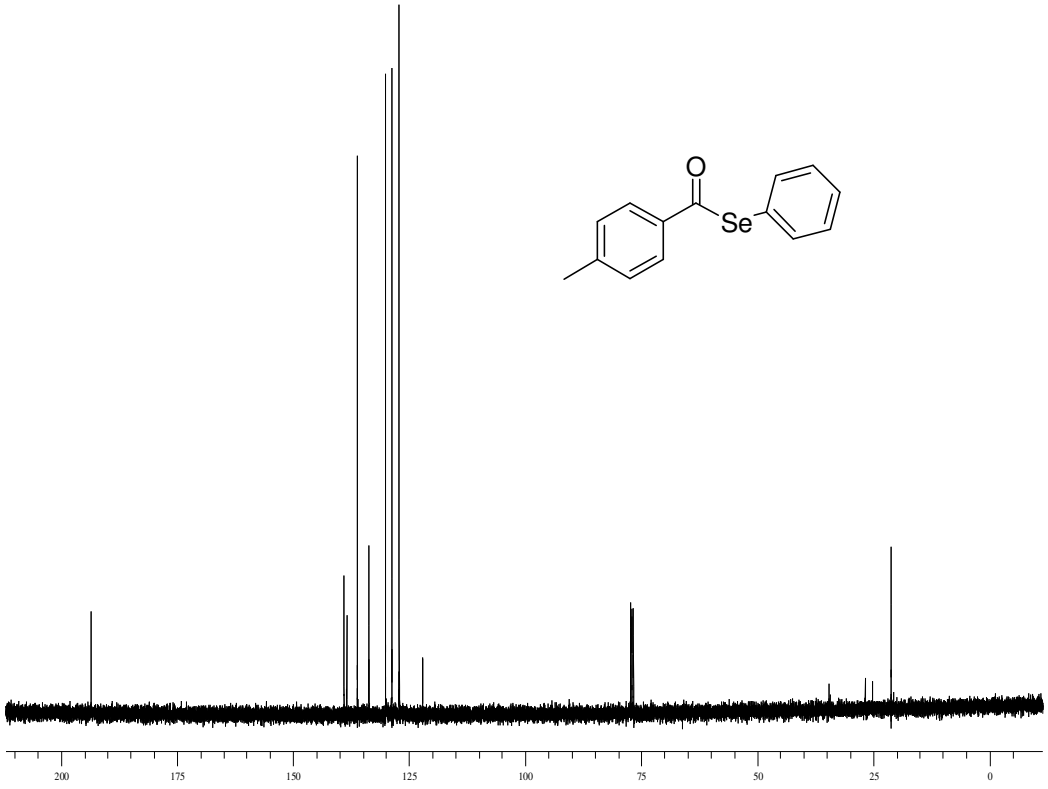
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *S*-phenyl 4-methylbenzothioate



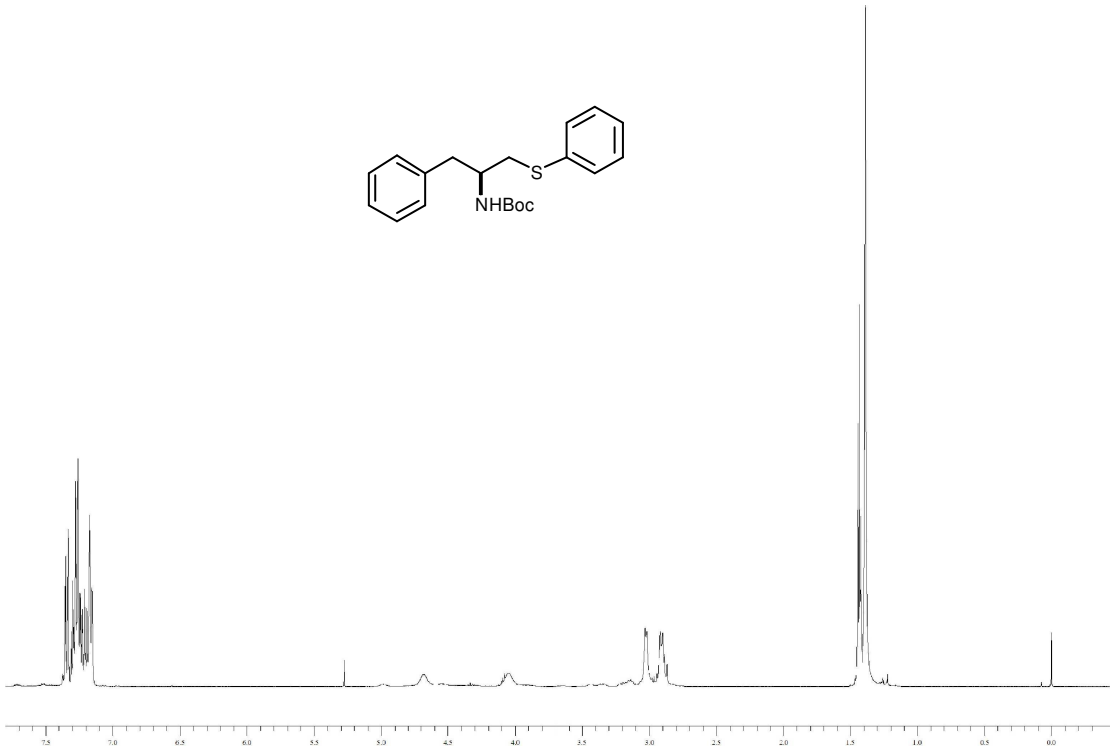
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *S*-phenyl 4-methylbenzothioate



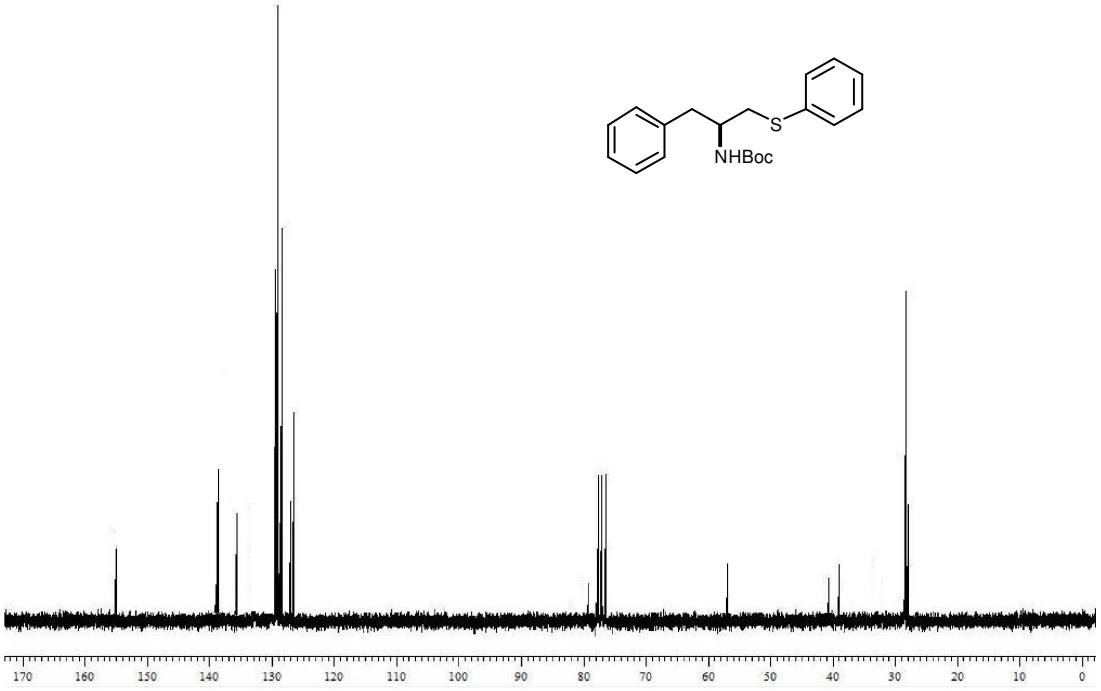
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Se-4*-tolyl selenobenzoate.



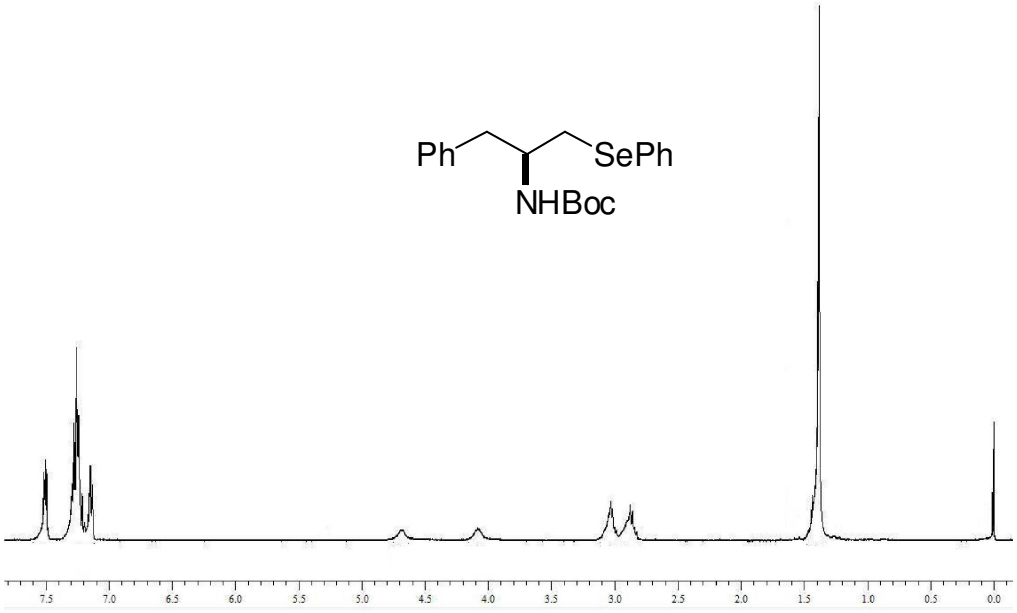
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Se-4*-tolyl selenobenzoate.



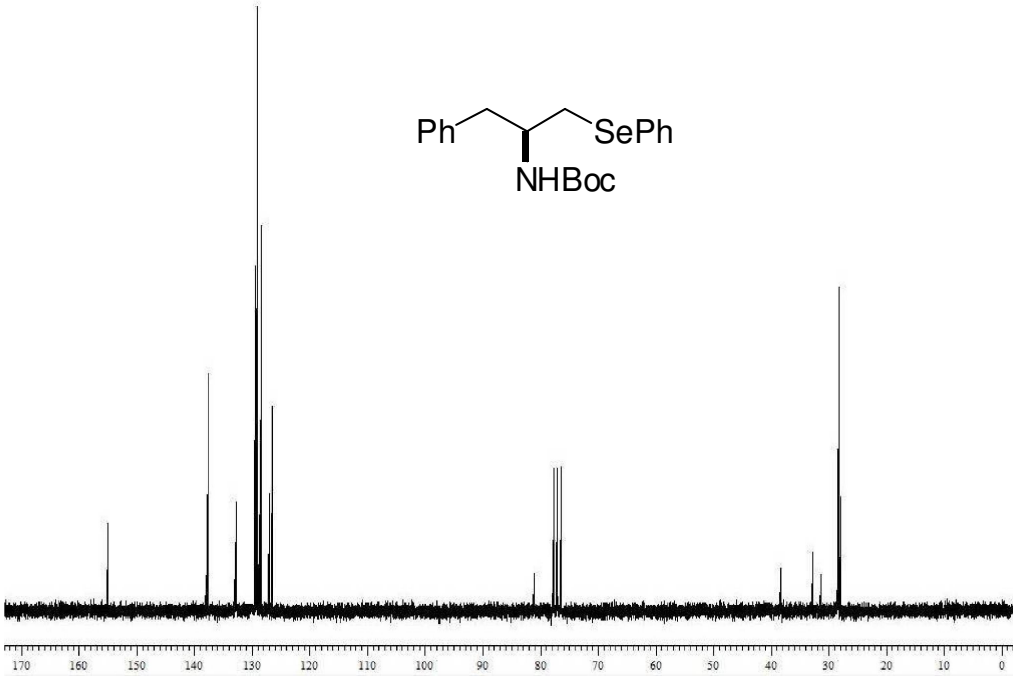
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of β- amino sulfur.



^{13}C NMR (50MHz, $CDCl_3$) Spectrum of of β- amino sulfur.



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of β- amino selenium.



^{13}C NMR (50MHz, $CDCl_3$) Spectrum of β- amino selenium.

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