Electronic Supplementary Information (ESI)

CuO Nano Particles and [bmim]BF_4: an Application Towards The Synthesis of Chiral β-seleno Amino Derivatives *via* Ring Opening Reaction of Aziridines With Diorganyl Diselenides

Syed M. Salman,[a,b] Senthil Narayanaperumal,[a,c] Ricardo S. Schwab,*[d] Caroline R. Bender,[a] Oscar E. D. Rodrigues*[a] and Luciano Dornelles*[a]

[a] *Departamento de Química, Universidade Federal de Santa Maria (UFSM), Santa Maria, RS, 97105-900, Brazil. Tel: +55 55 3220-8761; E-mail: ldornel@gmail.com*

[b] *Department of Chemistry, Abdul Wali Khan University (Palosa Campus), Mardan, Khyber Pakhtunkhwa, Pakistan*

[c] *Departamento de Química, Universidade Federal de São Carlos (UFSCar), São Carlos, SP, 13565-905, Brazil.*

[d] *Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, 91501-970, Brazil.*

Table of Contents

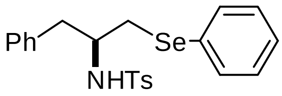
1 Experimental Section

1.1 Materials and Methods. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained, on 200 MHz on a Bruker DPX-200 NMR and 400 MHz on a Bruker DPX-400 spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of TMS. Data are reported as follows: chemical shift (δ), multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet), and coupling constant (*J*) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz and 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. High-resolution mass spectra (ESI) were measured at the Institut of Plant Biochemistry, Halle-Saale, Germany, with a Bruker BioApex 70e FT-ICR (Bruker Daltonics, Billerica, USA) instrument in ESI mode. Optical rotations were carried out on a Perkin Elmer Polarimeter 341. Column chromatography was performed using Merck Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, ninhidrin, or acidic vanillin. The yields of the products included in all tables refer to isolated yields. The ionic liquids were prepared according to the literature.[1] All other solvents were used as purchased unless otherwise noted.

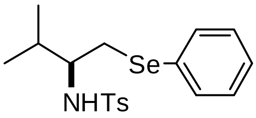
1.2 General procedure for the aziridine ring opening with diselenides: In a Schlenck tube under Argon atmosphere at room temperature CuO nanopowder (0.008 mmol, 5.0 mol%) followed by diorganyl diselenide (0.5 mmol) and KOH (1.0 mmol, 2.0 equiv) were added to a solution of aziridine (1.0 mmol) in [bmim]BF_4 (1.0 mL) and temperature of the reaction was raised up to 80 ^{o}C. After, completion of the reaction (monitored by TLC), the product was extracted by successive washing with diethyl ether (5 x 6 mL) and dried over $MgSO_4$. The solvents and volatiles were completely removed under rotary evaporator to give the crude product. The compound was purified by column chromatography over silica gel (hexane/ethyl acetate 80:20) furnished the pure β-seleno amines.

1.3 General procedure for recycle the [bmim]BF_4 and for recovering CuO catalyst: After completion of the reaction workup, the reaction mixture was treated with ethanol, and filtered through a Teflon membrane. The CuO nanopowder was recovered from the membrane by washing with water and collected by further centrifugation and drying under vacuum. It was reused for the next reaction, and no loss of activity was observed, providing the product in high yields. The ionic liquid was recovered from the ethanol (10 mL) after filtration, evaporation of the solvent and drying the [bmim]BF_4 (1 mL) under vacuum for reuse in subsequent reactions.

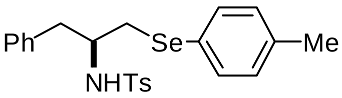
2 Characterization data for compounds 2a-p



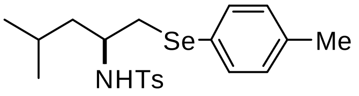
(S)-4-methyl-N-(1-phenyl-3-(phenylselanyl)propan-2-yl)benzenesulfonamide 2a. Yield: 91 % $[\alpha]_D{}^{20}$ = - 53 (*c* = 1, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.43-7.39 (m, 4H), 7.27-7.09 (m, 9H), 6.93-6.91 (m, 2H), 4,69 (d, *J* = 7.2 Hz, 1H), 3.55-3.48 (m, 1H), 3.12 (dd, J^1 = 12.6 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. **HRMS-ESI**: *m/z* calcd for $C_{22}H_{23}NO_2SSe$ $[M + Na]^+$ 468.0512; found 468.0510.



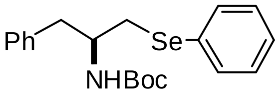
(S)-4-methyl-N-(3-methyl-1-(phenylselanyl)butan-2-yl)benzenesulfonamide 2b. Yield: 93 % $[\alpha]_D{}^{20}$ = - 18 (*c* = 1, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.37-7.35 (m, 2H), 7.26-7.17 (m, 5H), 4.82 (d, *J* = 6.4 Hz, 1H), 3.23-3.17 (m, 1H), 3.06 (dd, J^1 = 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. **HRMS-ESI**: *m/z* calcd for $C_{18}H_{23}NO_2SSe$ $[M + H]^+$ 398.0693; found 398.0694



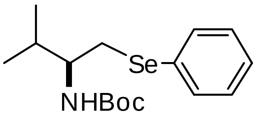
(S)-4-methyl-N-(1-phenyl-3-(p-tolylselanyl)propan-2-yl)benzenesulfonamide 2c. Yield: 75 % $[\alpha]_D{}^{20}$ = - 50 (*c* = 1, CH_2Cl_2); **^{1}H NMR** (200 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.3 Hz, 2H), 7.32-7.25 (m, 2H), 7.17-7.03 (m, 7H), 6.94-6.89 (m, 2H), 4.77 (d, *J* = 7.2 Hz, 1H), 3.54-3.42 (m, 1H), 3.11-2.89 (m, 2H), 2.82-2.68 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 143.02, 137.33, 136.73, 136.53, 133.32, 129.99, 129.42, 129.20, 128.50, 126.91, 126.60, 125.25, 54.52, 40.18, 33.09, 21.45, 21.06 ppm. **HRMS-ESI**: *m/z* calcd for $C_{23}H_{25}NO_2SSe$ $[M + Na]^+$ 482.0669; found 482.0661.



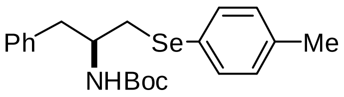
(S)-4-methyl-N-(4-methyl-1-(p-tolylselanyl)pentan-2-yl)benzenesulfonamide 2d. Yield: 72 % $[\alpha]_D^{20}$ = - 53 (c = 1, CH_2Cl_2); **^{1}H NMR** (200 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.3 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 4.77-4.73 (m, 1H), 3.49-3.33 (m, 1H), 3.05 (dd, J^1 = 12.6 Hz, J^2 = 3.6 Hz, 1H), 2.72-2.62 (m, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1,53-1,17 (m, 3H), 0.78 (d, J = 6.23 Hz, 3H), 0.61 (d, J = 6.11 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 143.16, 137.69, 137.36, 133.65, 129.90, 129.50, 127.00, 51.55, 43.85, 34.97, 24.32, 22.77, 21.59, 21.45, 21.08 ppm. **HRMS-ESI**: m/z calcd for $C_{20}H_{27}NO_2SSe$ $[M + Na]^+$ 448.0825; found 448.0819.



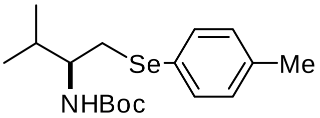
(S)-tert-butyl 1-phenyl-3-(phenylselanyl)propan-2-ylcarbamate 2e.[2] Yield: 93 % $[\alpha]_D^{20}$ = + 14 (c = 1, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51-7.48 (m, 2H), 7.29-7.12 (m, 8H), 4.70-4.66 (br s, 1H), 4.09-4.06 (m, 1H), 3.04-3.01 (m, 2H), 2.87-2.82 (m, 2H), 1.38 (s, 9H) ppm. **^{13}C 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 ppm.



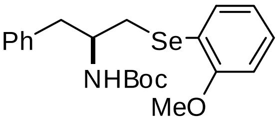
(S)-tert-butyl 3-methyl-1-(phenylselanyl)butan-2-ylcarbamate 2f.[2] Yield: 95 % $[\alpha]_D^{20}$ = + 35 (c = 1, CH_2Cl_2); **^{1}H NMR** (200 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 2H), 7.26-7.23 (m, 3H), 4.60-4.55 (br s, 1H), 3.69-3.59 (m, 1H), 3.07 (d, J = 5.6 Hz, 2H), 1.94-1.77 (m, 1H), 1.42 (s, 9H), 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.



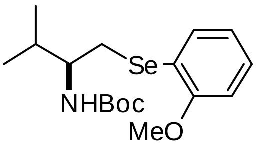
(S)-tert-butyl 1-phenyl-3-(p-tolylselanyl)propan-2-ylcarbamate 2g.[2] Yield: 85 % $[\alpha]_D^{20}$ = + 19 (c = 1, CH_2Cl_2); **^{1}H NMR** (200 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.1 Hz, 2H), 7.31-7.03 (m, 7H), 4.69-4.65 (br s, 1H), 4.09-4.00 (m, 1H), 2.98-2.84 (m, 4H), 2.31 (s, 3H), 1.37 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.99, 137.59, 133.34, 130.34, 129.95, 129.35, 128.72, 128.41, 126.43, 126.11, 79.20, 51.59, 40.33, 33.18, 28.27, 21.02 ppm.



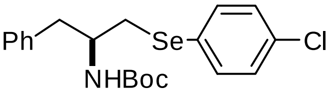
(S)-tert-butyl 3-methyl-1-(p-tolylselanyl)butan-2-ylcarbamate 2h. Yield: 80 % $[\alpha]_D^{20} = +29$ ($c = 1$, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.59-4.55 (m, 1H), 3.66-3.56 (m, 1H), 3.03-3.01 (m, 2H), 2.31 (s, 3H), 1.93-1.73 (m, 1H), 1.42 (s, 9H), 0.90-0.86 (m, 6H) ppm. ^{13}**C NMR** (50 MHz, $CDCl_3$): δ = 155.52, 137.02, 133.43, 129.83, 126.33, 78.99, 55.64, 32.71, 31.63, 28.29, 21.01, 19.40, 17.96 ppm. **HRMS-ESI**: *m/z* calcd for $C_{17}H_{27}NO_2Se$ $[M + Na]^+$ 380.1105; found 380.1099.



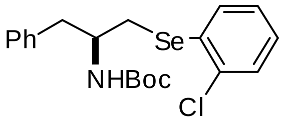
(S)-tert-butyl 1-(2-methoxyphenylselanyl)-3-phenylpropan-2-ylcarbamate 2i. Yield: 72 % $[\alpha]_D^{20} = +14$ ($c = 1$, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.41-7.14 (m, 8H), 6.89-6.79 (m, 2H), 5.03 (br s, 1H), 4.06-3.96 (m, 1H), 3.83 (s, 3H), 2.98-2.77 (m, 4H), 1.38 (s, 9H) ppm. ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 157.85, 154.95, 137.65, 132.76, 129.23, 128.26, 126.26, 121.34, 118.64, 110.38, 79.33, 55.57, 51.29, 40.25, 30.30, 28.17 ppm. **HRMS-ESI**: *m/z* calcd for $C_{21}H_{27}NO_3Se$ $[M + Na]^+$ 444.1054; found 444.1059.



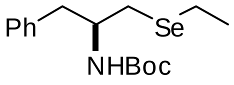
(S)-tert-butyl 1-(2-methoxyphenylselanyl)-3-methylbutan-2-ylcarbamate 2j. Yield: 74 % $[\alpha]_D^{20} = +22$ ($c = 1$, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.2 Hz, 2H), 7.27-7.18 (m, 1H), 6.92-6.81 (m, 2H), 4.47 (br s, 1H), 3.87 (s, 3H), 3.71-3.59 (m, 1H), 3.14-2.97 (m, 2H), 1.99-1.82 (m, 1H), 1.41 (s, 9H), 0.93-0.90 (m, 6H) ppm. ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 157.86, 155.47, 132.44, 128.03, 121.33, 119.10, 78.84, 55.66, 55.28, 31.61, 29.63, 28.24, 19.34, 18.04 ppm. **HRMS-ESI**: *m/z* calcd for $C_{17}H_{27}NO_3Se$ $[M + Na]^+$ 396.1054; found 396.1048.



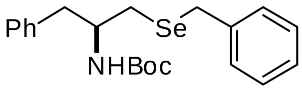
(S)-tert-butyl 1-(4-chlorophenylselanyl)-3-phenylpropan-2-ylcarbamate 2k.[2] Yield: >99 % $[\alpha]_D^{20} = +24$ ($c = 1$, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.43-7.11 (m, 9H), 4.65-4.61 (m, 1H), 4.13-3.99 (m, 1H), 3.00-2.84 (m, 4H), 1.38 (s, 9H) ppm. ^{13}**C NMR** (50 MHz, $CDCl_3$): δ = 154.96, 137.32, 134.12, 133.25, 129.31, 129.26, 128.50, 128.16, 126.58, 79.45, 51.52, 40.28, 33.09, 28.26 ppm.



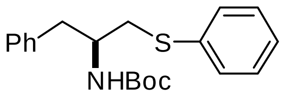
(S)-tert-butyl 1-(2-chlorophenylselanyl)-3-phenylpropan-2-ylcarbamate 2l. Yield: 76 % $[\alpha]_D^{20} = + 6.0$ (c = 1, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.39-7.05 (m, 10H), 4.74 (br s, 1H), 4.16-3.88 (m, 1H), 3.11-2.71 (m, 4H), 1.38 (s, 9H) ppm. ^{13}**C NMR** (50 MHz, $CDCl_3$): δ = 154.96, 137.28, 131.38, 129.43, 129.26, 128.44, 127.44, 127.25, 126.52, 126.28, 79.43, 51.30, 40.25, 31.10, 28.21 ppm. **HRMS-ESI**: *m/z* calcd for $C_{20}H_{24}ClNO_2Se$ $[M + H]^+$ 426.0739; found 426.0753.



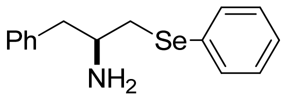
(S)-tert-butyl 1-(ethylselanyl)-3-phenylpropan-2-ylcarbamate 2m.[2] Yield: 82 % $[\alpha]_D^{20} = + 9.0$ (c = 1, CH_2Cl_2); ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 7.29-7.25 (m, 2H), 7.22-7.18 (m, 3H), 4.67 (br s, 1H), 3.99 (br s, 1H), 2.90-2.81 (m, 2H), 2.69-2.60 (m, 4H), 1.40 (s, 9H), 1.37 (t, J = 7.5 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 155.13, 137.78, 129.34, 128.42, 126.44, 79.31, 51.66, 40.44, 29.61, 28.34, 18.27, 15.78 ppm.



(S)-tert-butyl 1-(benzylselanyl)-3-phenylpropan-2-ylcarbamate 2n.[2] Yield: 75 % $[\alpha]_D^{20} = + 5.0$ (c = 1, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.31-7.12 (m, 10H), 4.61 (br s, 1H), 4.03-3.92 (m, 1H), 3.77 (s, 2H), 2.94-2.57 (m, 4H), 1.41 (s, 9H) ppm. ^{13}**C NMR** (50 MHz, $CDCl_3$): δ = 155.10, 139.06, 137.59, 129.33, 128.91, 128.80, 128.49, 128.41, 126.73, 126.44, 79.53, 51.27, 40.58, 28.57, 28.32, 27.73 ppm.

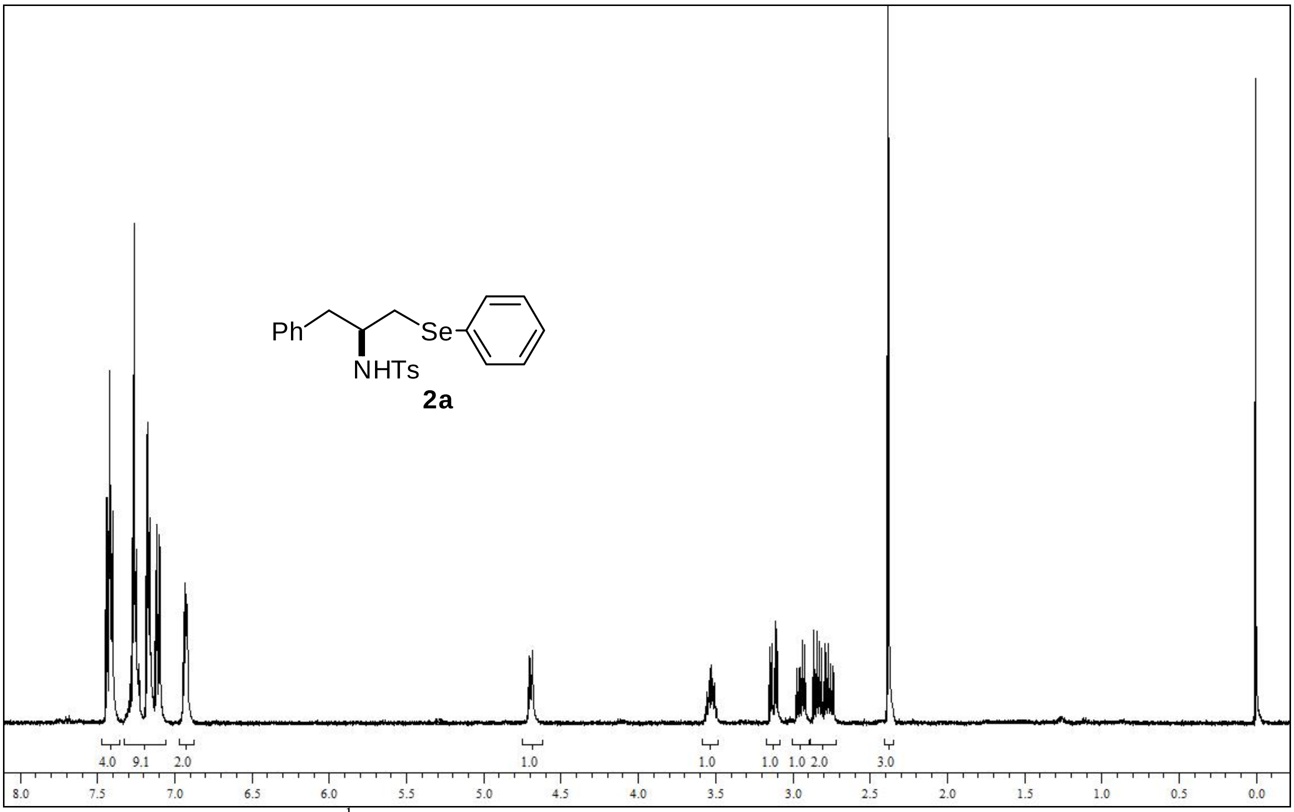


(S)-tert-butyl 1-phenyl-3-(phenylthio)propan-2-ylcarbamate 2o.[3] Yield: 73 % $[\alpha]_D^{20} = + 22$ (c = 1.05, CH_2Cl_2); ^{1}**H NMR** (200 MHz, $CDCl_3$): δ = 7.37-7.15 (m, 10H), 4.66 (br s, 1H), 4.10-3.99 (m, 1H), 3.04-2.89 (m, 4H), 1.38 (s, 9H) ppm. ^{13}**C NMR** (50 MHz, $CDCl_3$): δ = 155.04, 137.41, 135.95, 129.52, 129.36, 128.97, 128.46, 126.52, 126.22, 79.38, 51.21, 39.35, 37.64, 28.27 ppm.

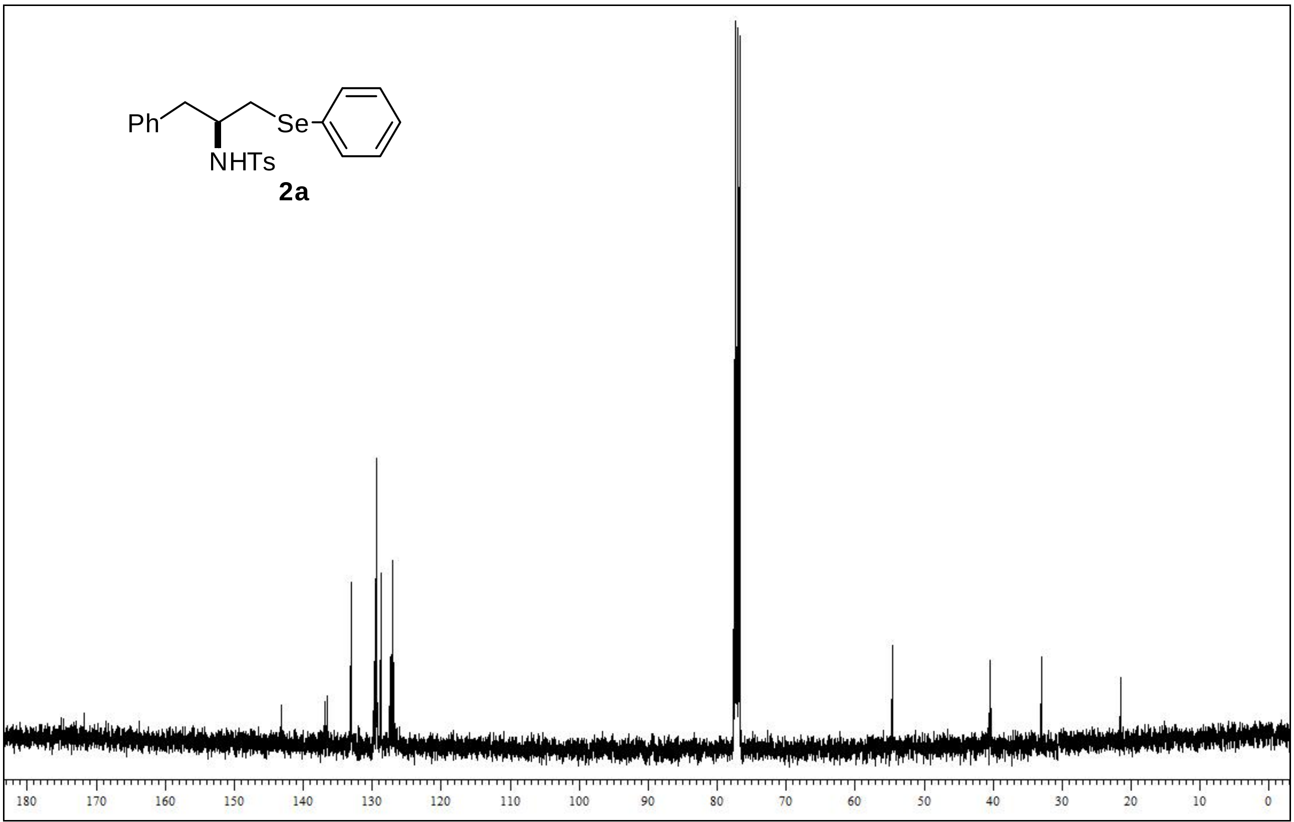


(S)-1-phenyl-3-(phenylselanyl)propan-2-amine 2p.[4] Yield: 62%, ^{1}**H NMR** (200 MHz, $CDCl_3$), δ = 7.48-7.01 (m, 10H), 3.8 (br s, 2H), 3.38-3.26 (m, 2H), 3.18-2.81 (m, 4H) ppm. ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ = 138.68, 132.62, 130.05, 129.22, 129.08, 128.48, 126.90, 126.41, 52.45, 43.87, 36.50 ppm.

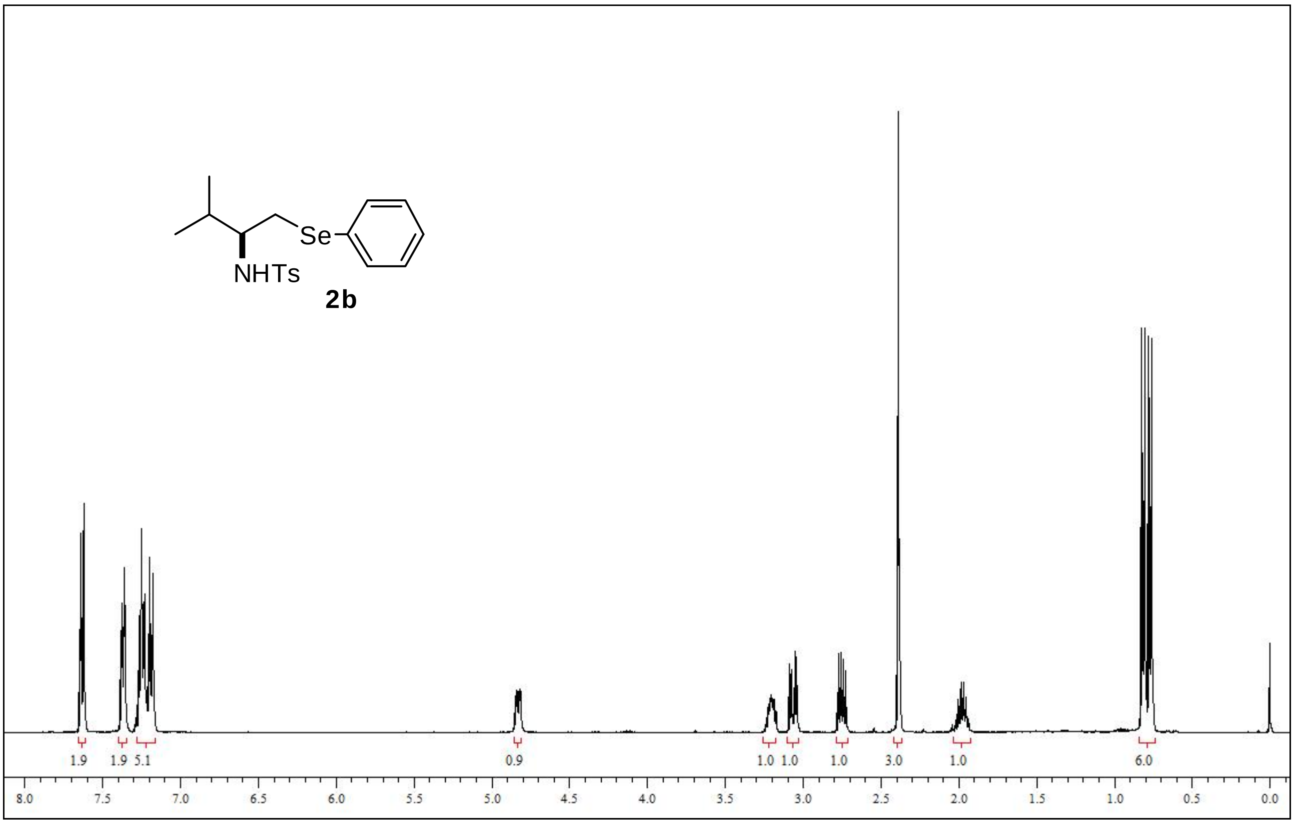
3 ^{1}H, ^{13}C-NMR spectra for compounds 2a-p



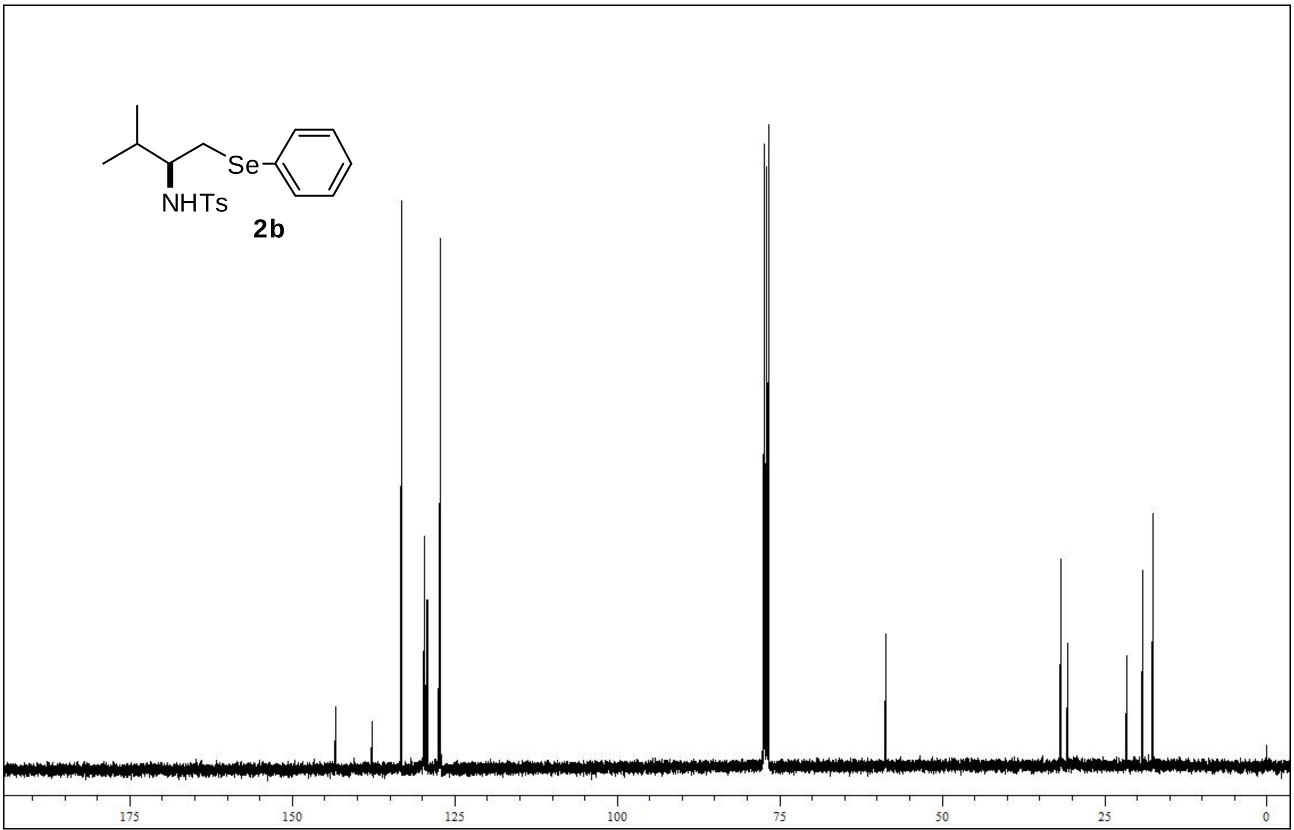
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2a**.



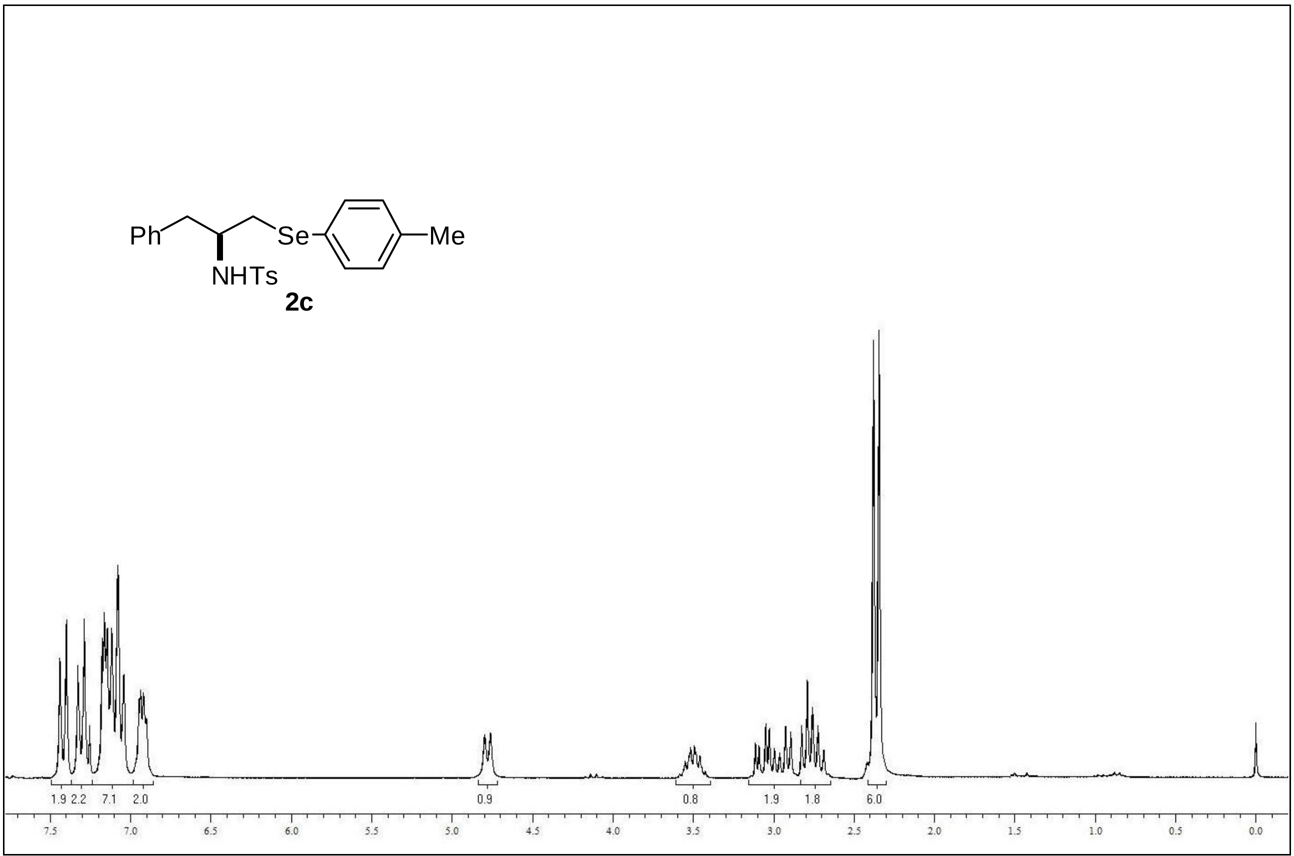
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum compound **2a**.



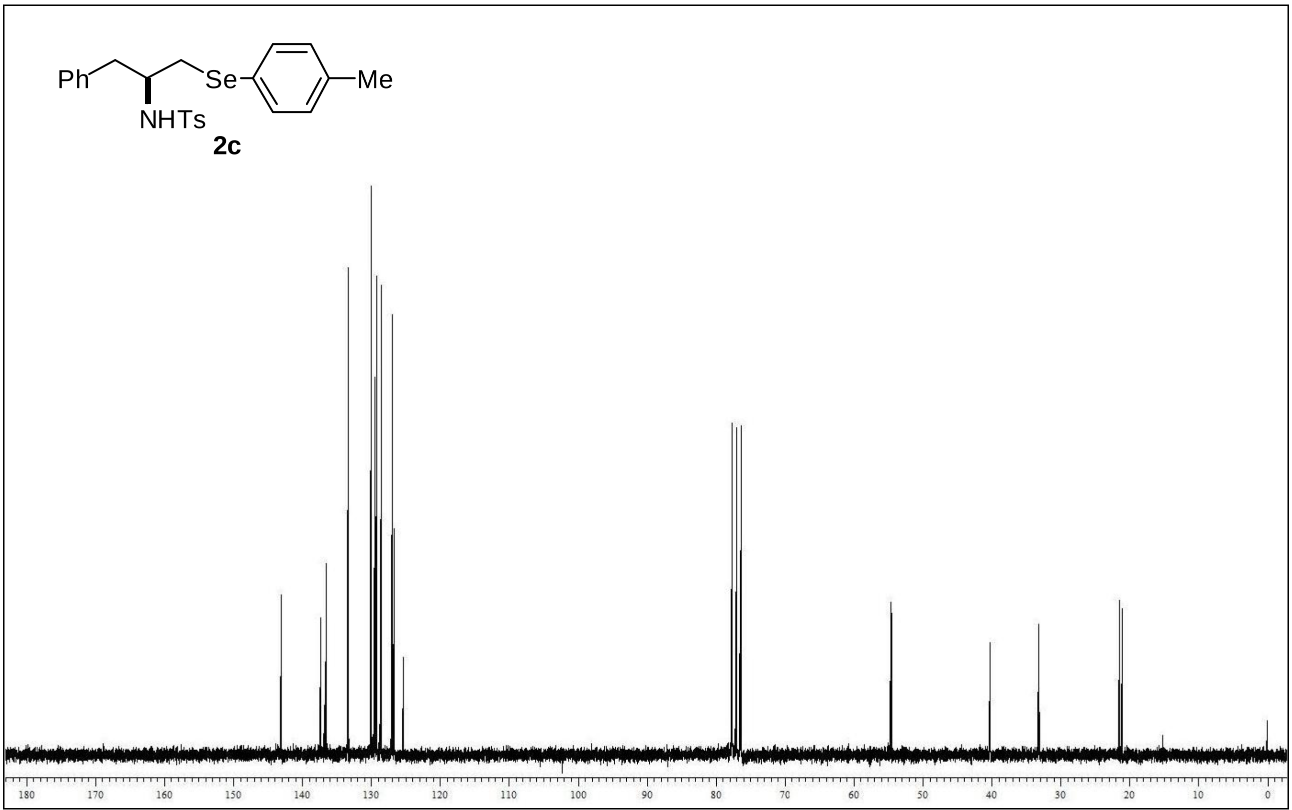
^{1}H NMR (400 MHz, CDCl$_3$) Spectrum of compound **2b**.



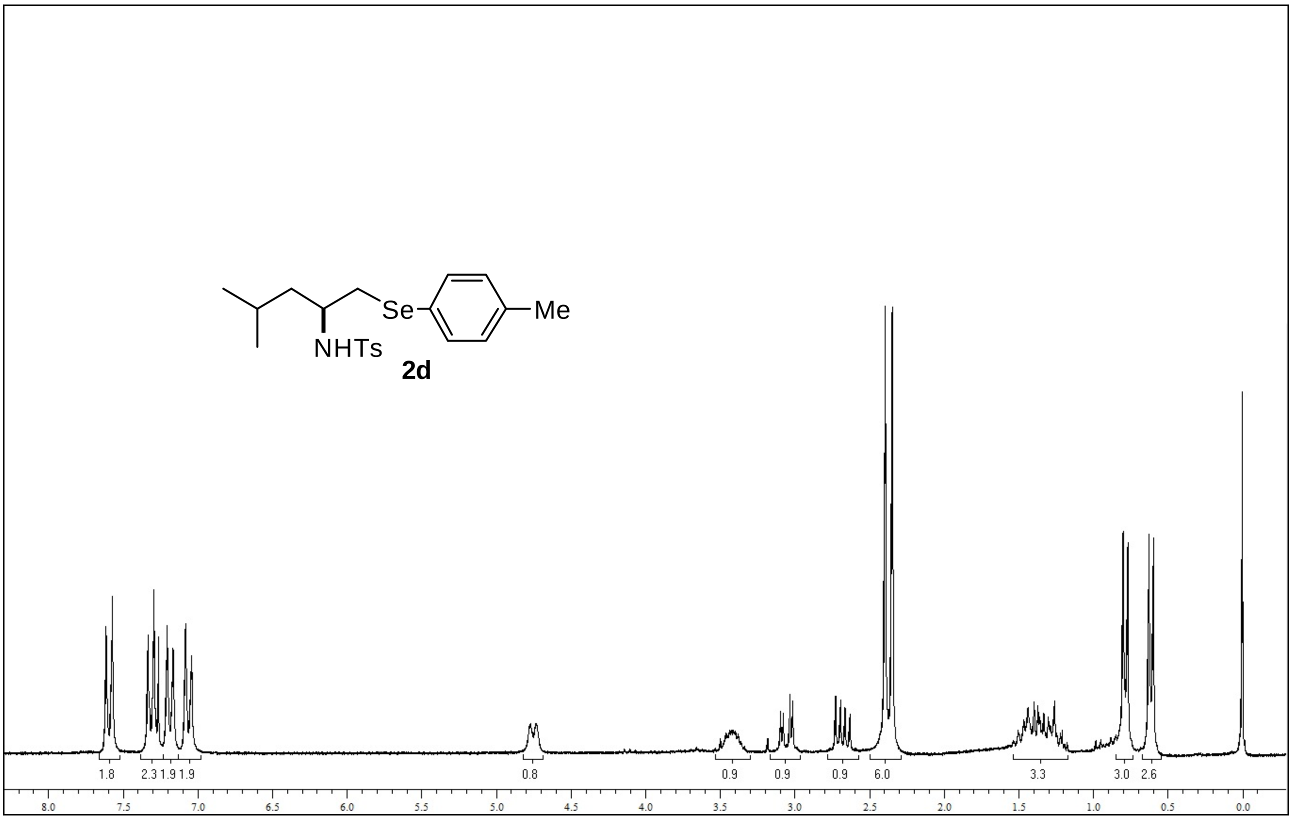
^{13}C NMR (100 MHz, CDCl$_3$) Spectrum of compound **2b**.



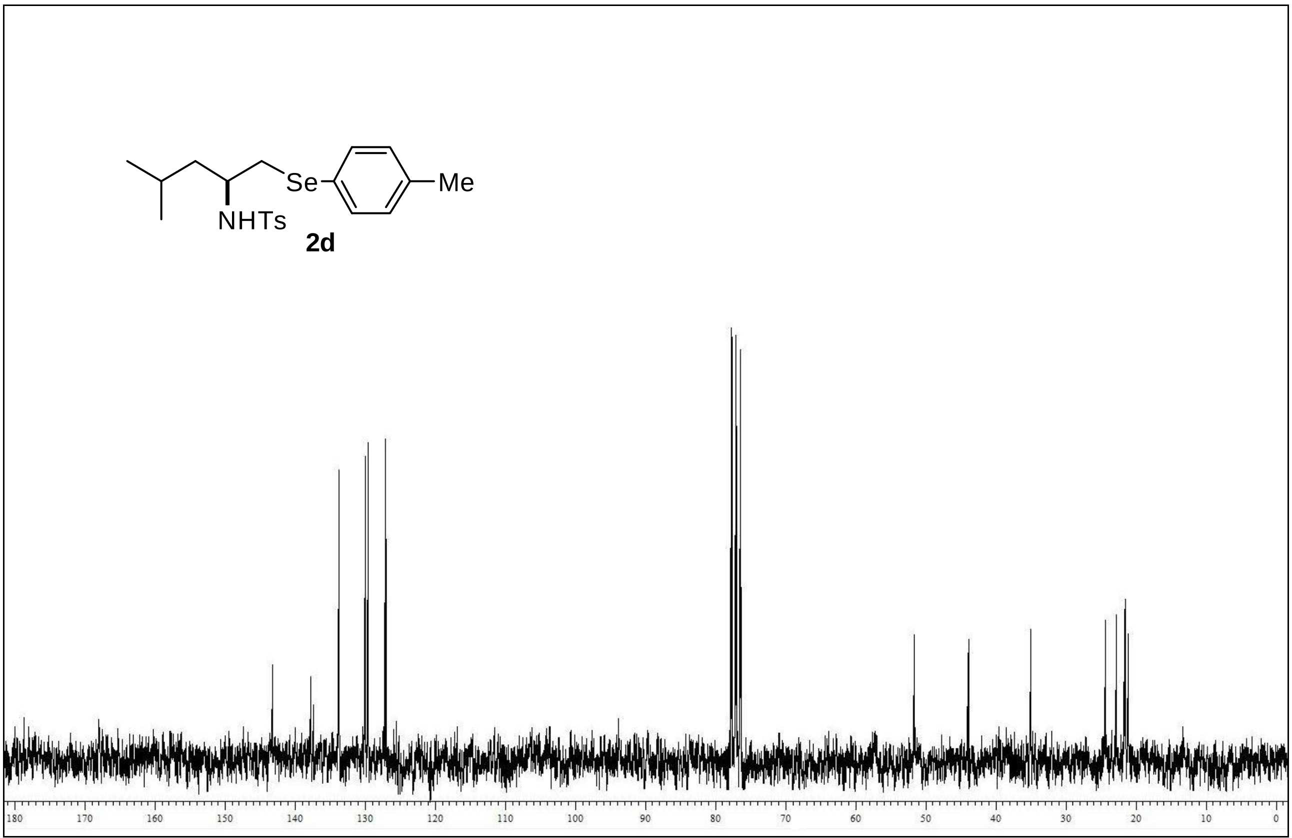
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2c**.



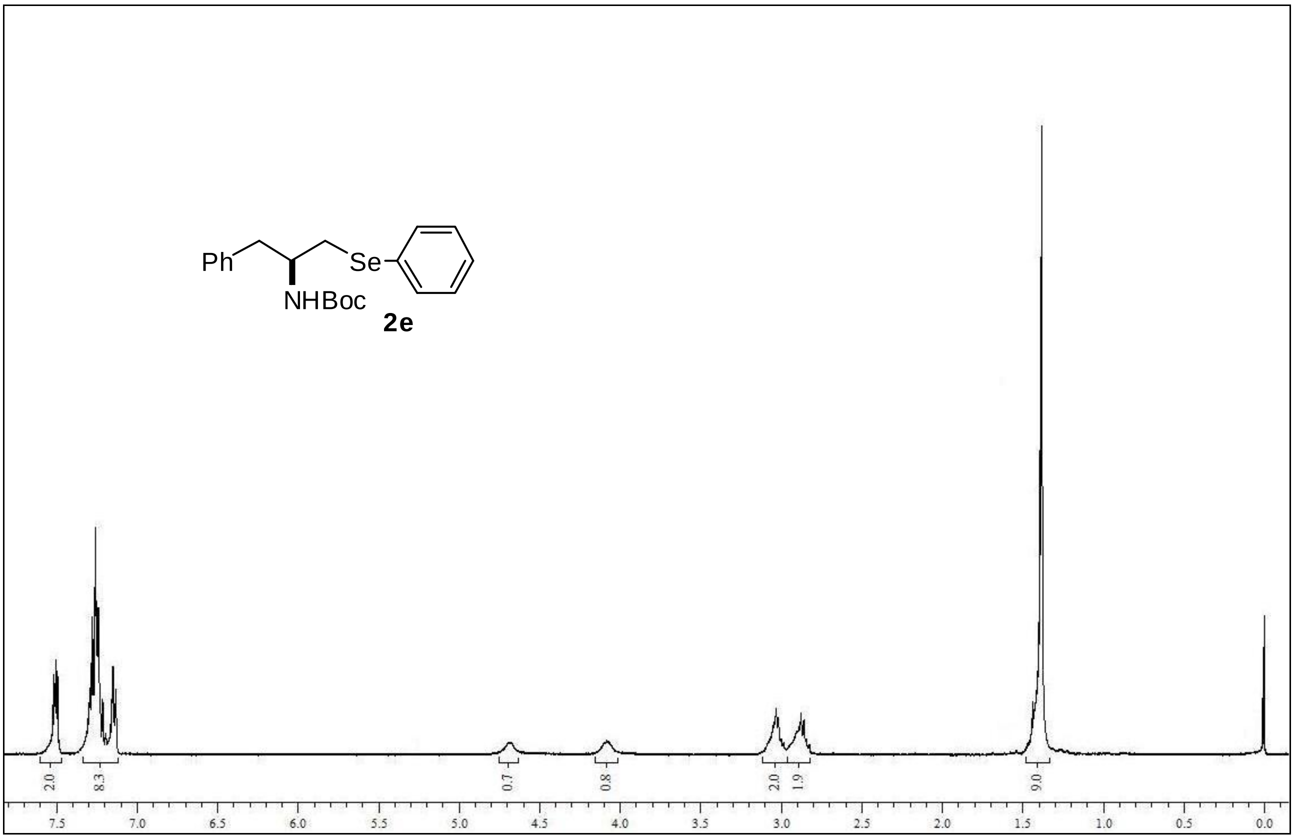
^{13}C NMR (50 MHz, CDCl$_3$) Spectrum of compound **2c**.



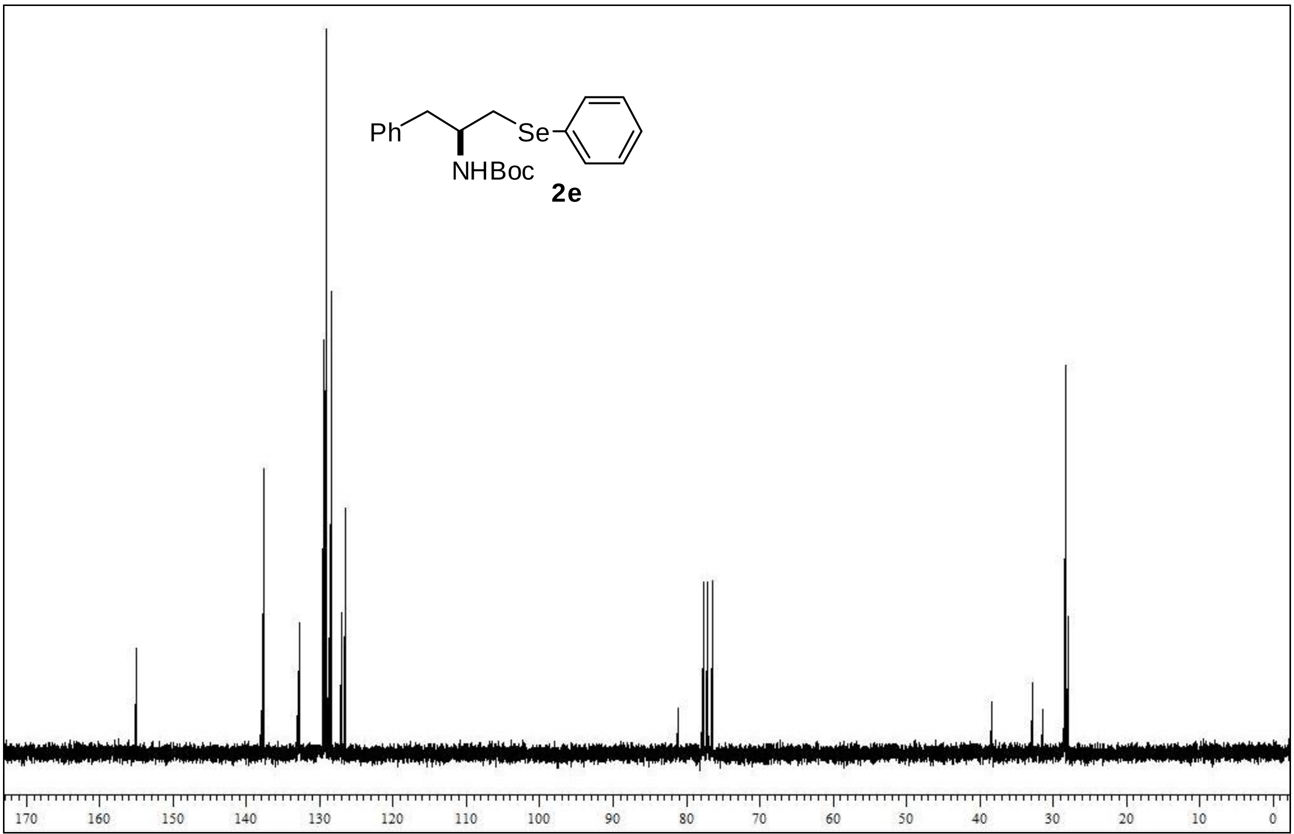
^{1}H NMR (200 MHz, $CDCl_3$) Spectrum of compound **2d**.



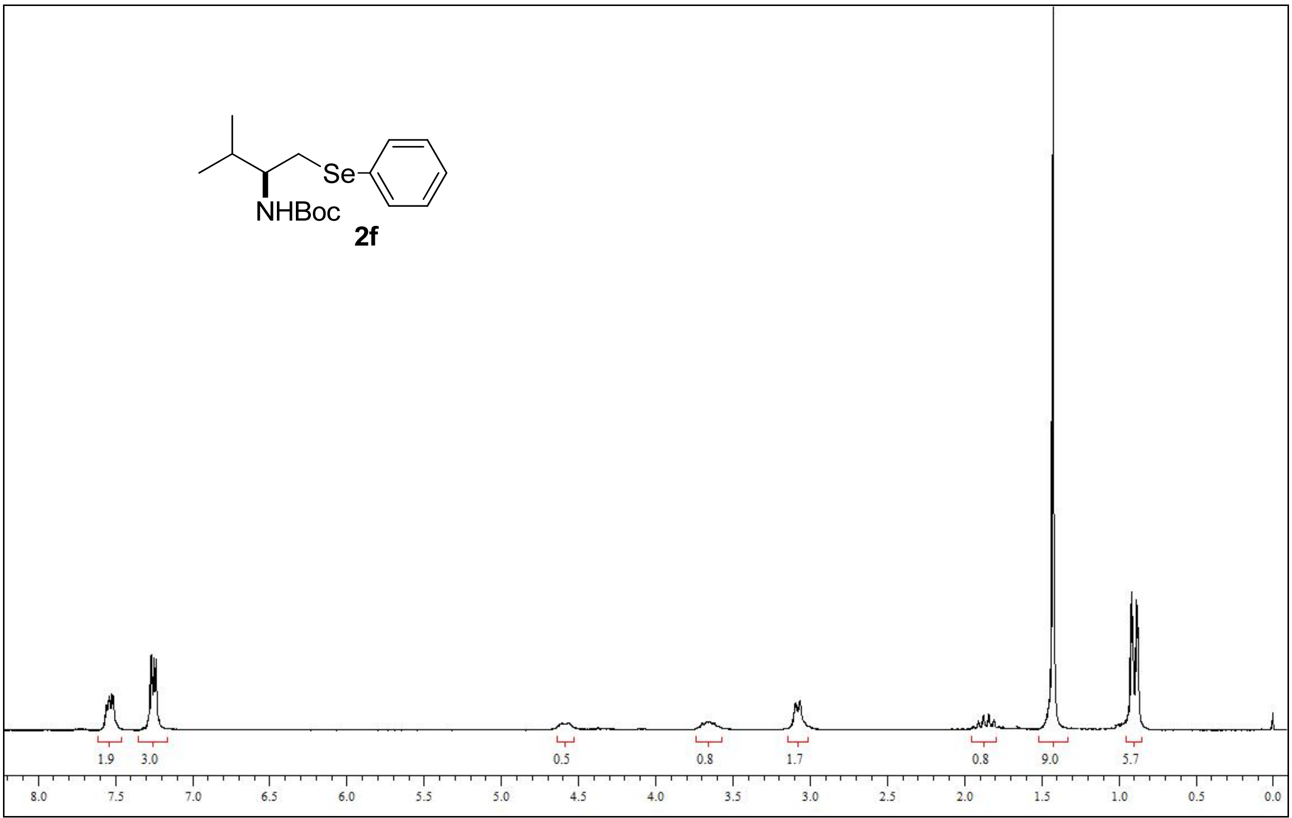
^{13}C NMR (50 MHz, $CDCl_3$) Spectrum of compound **2d**.



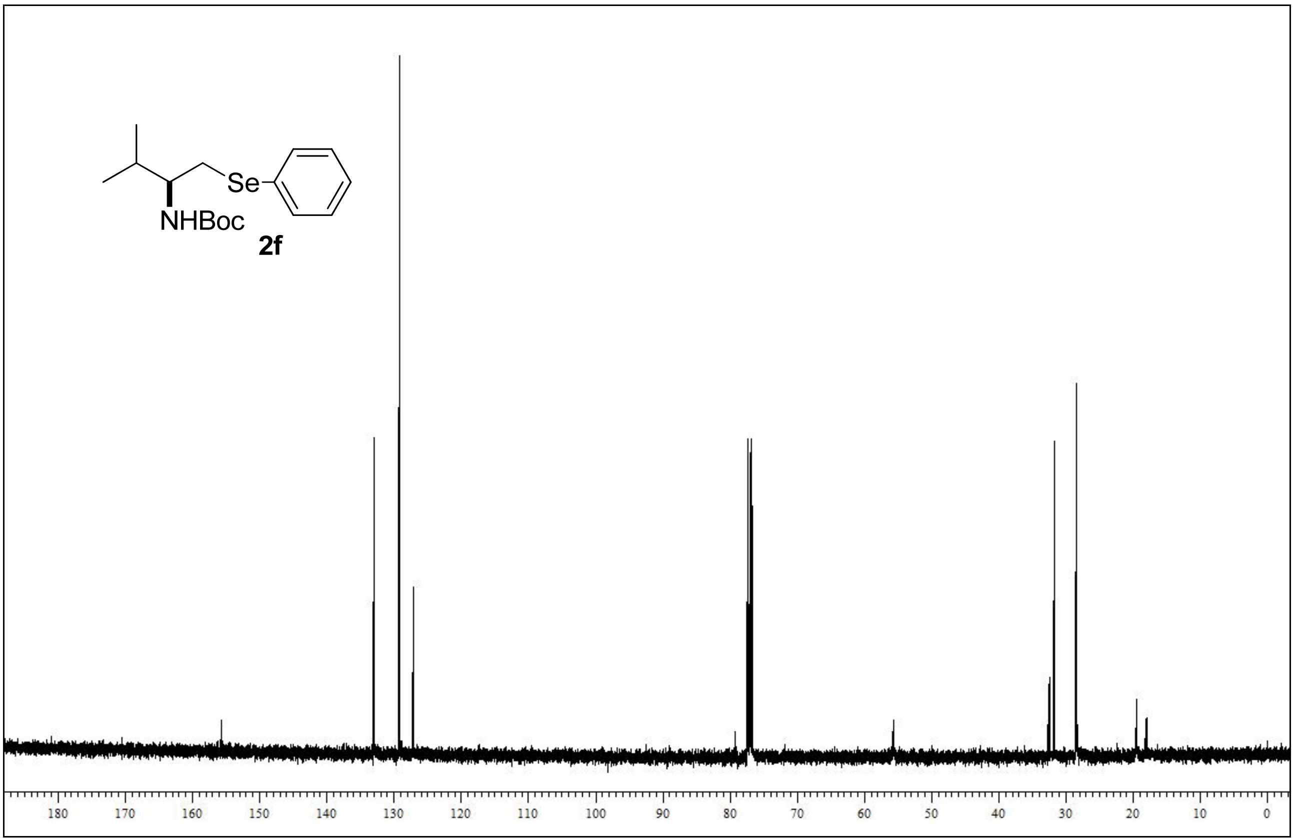
^{1}H NMR (400 MHz, CDCl$_3$) Spectrum of compound **2e**.



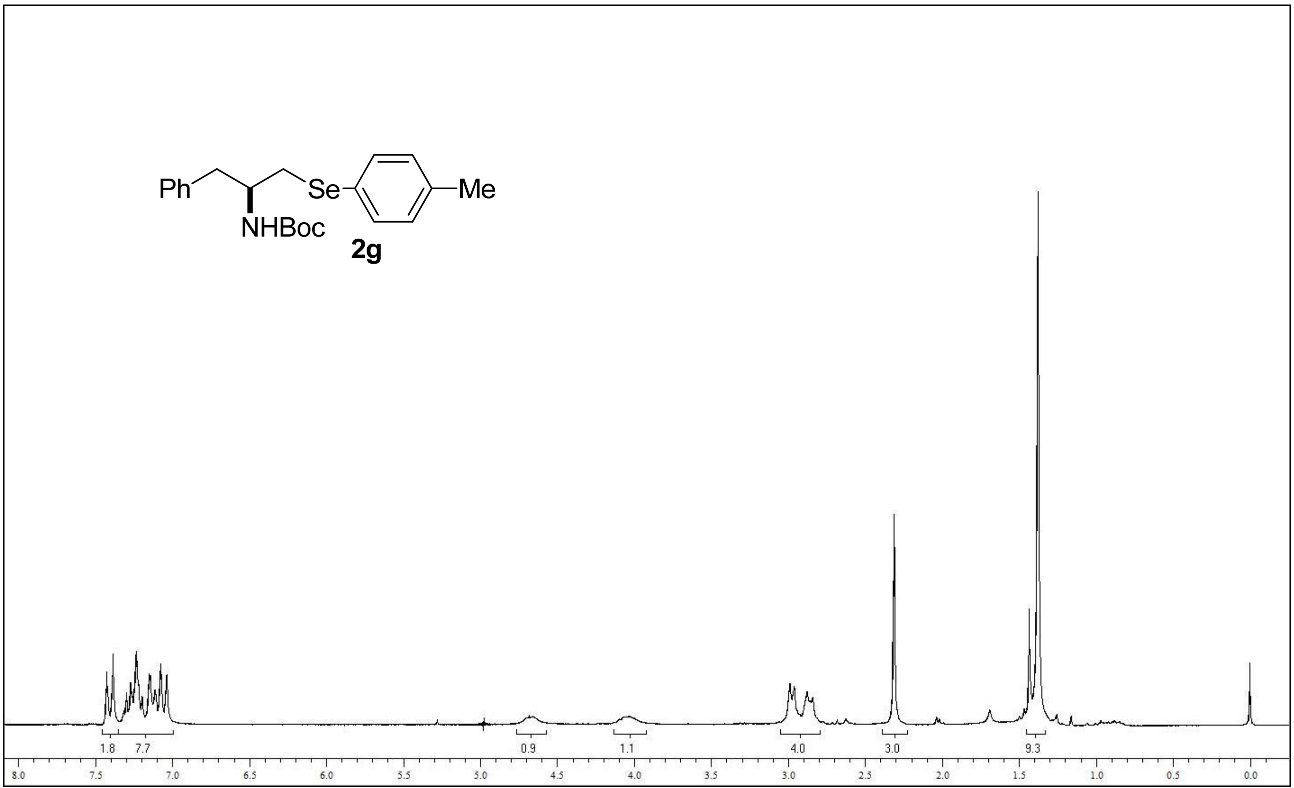
^{13}C NMR (50 MHz, CDCl$_3$) Spectrum of compound **2e**.



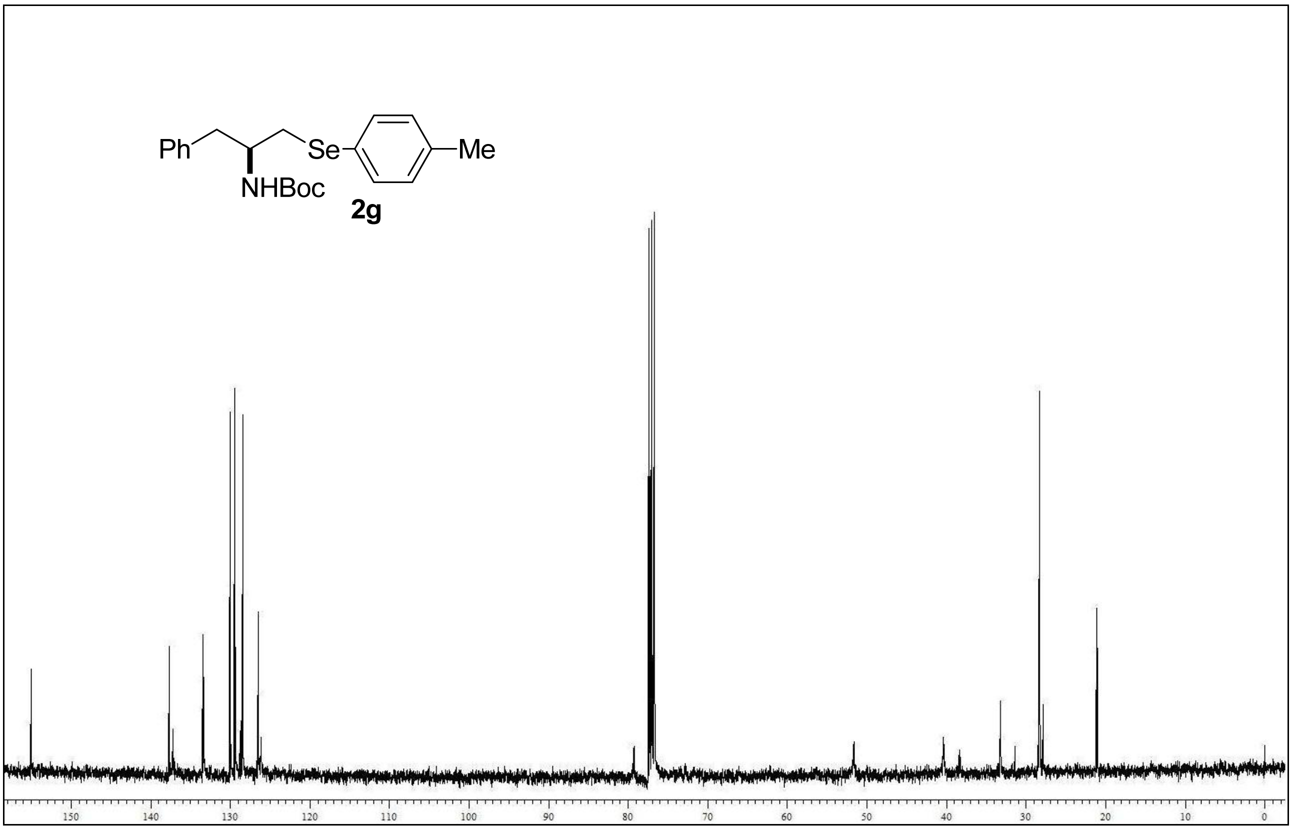
^{1}H NMR (200 MHz, $CDCl_3$) Spectrum of compound **2f**.



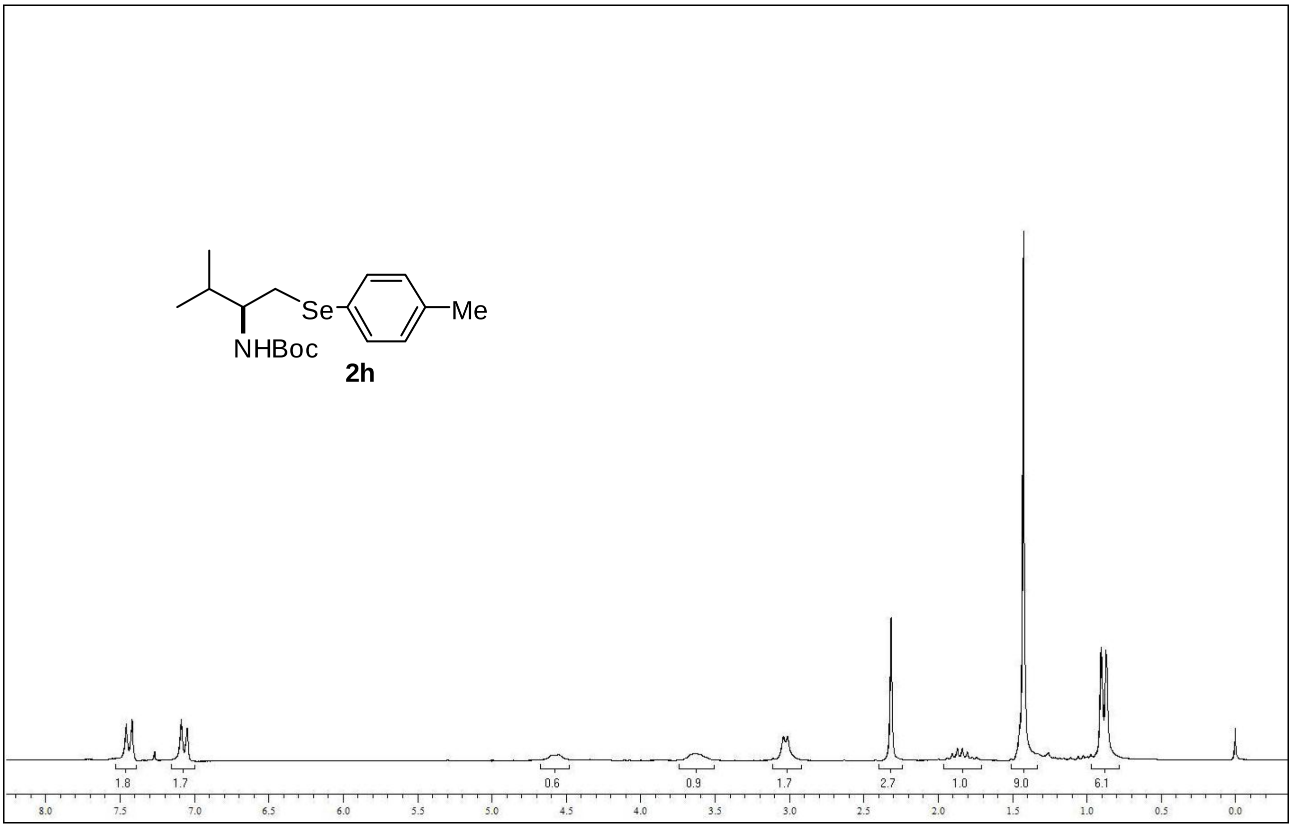
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of compound **2f**.



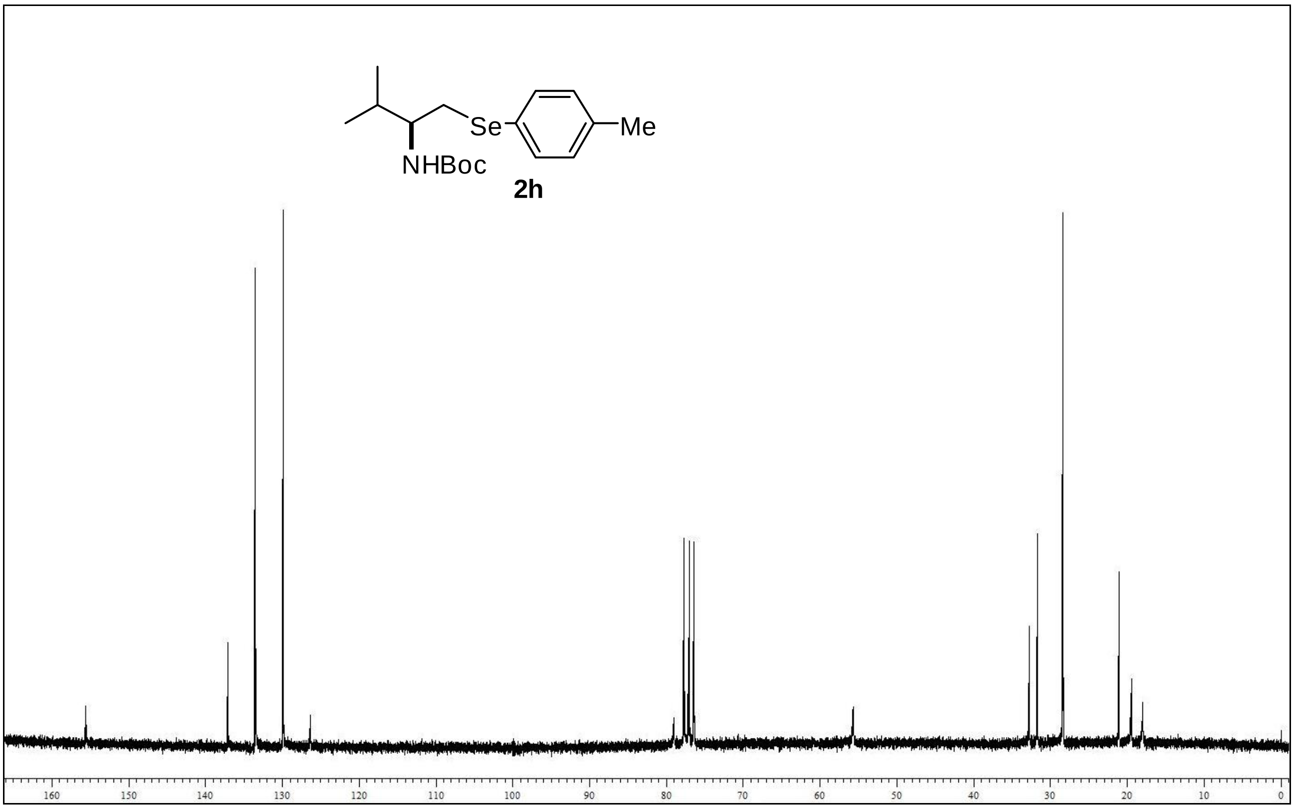
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2g**.



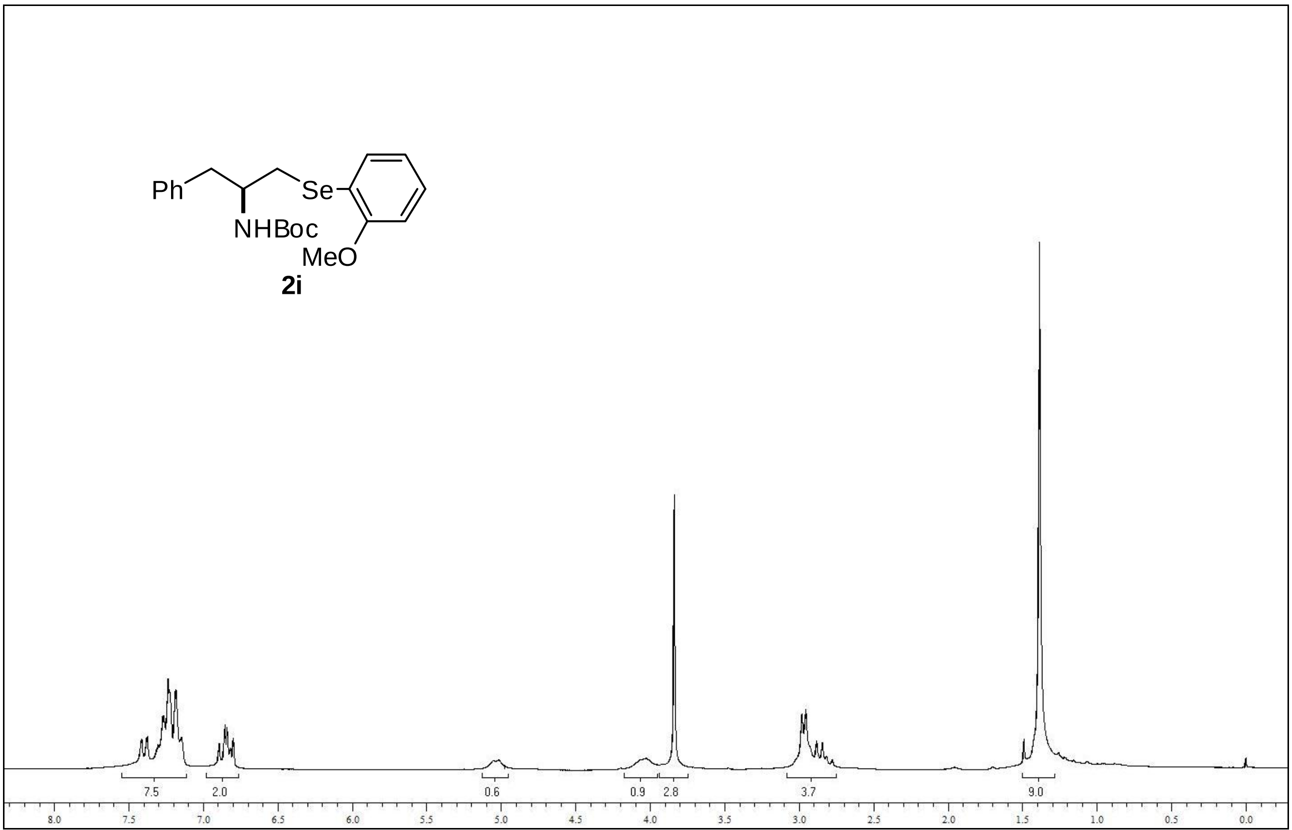
^{13}C NMR (100 MHz, CDCl$_3$) Spectrum of compound **2g**.



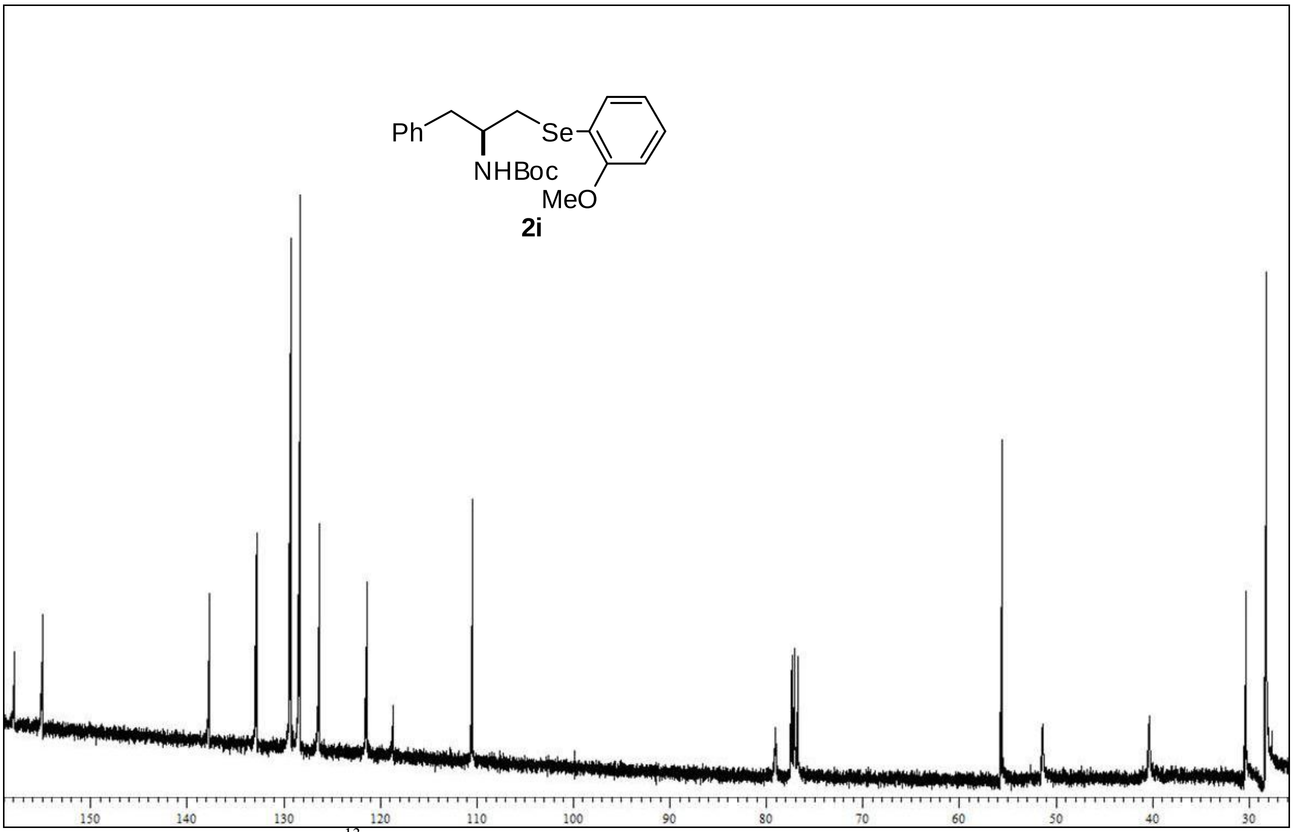
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2h**.



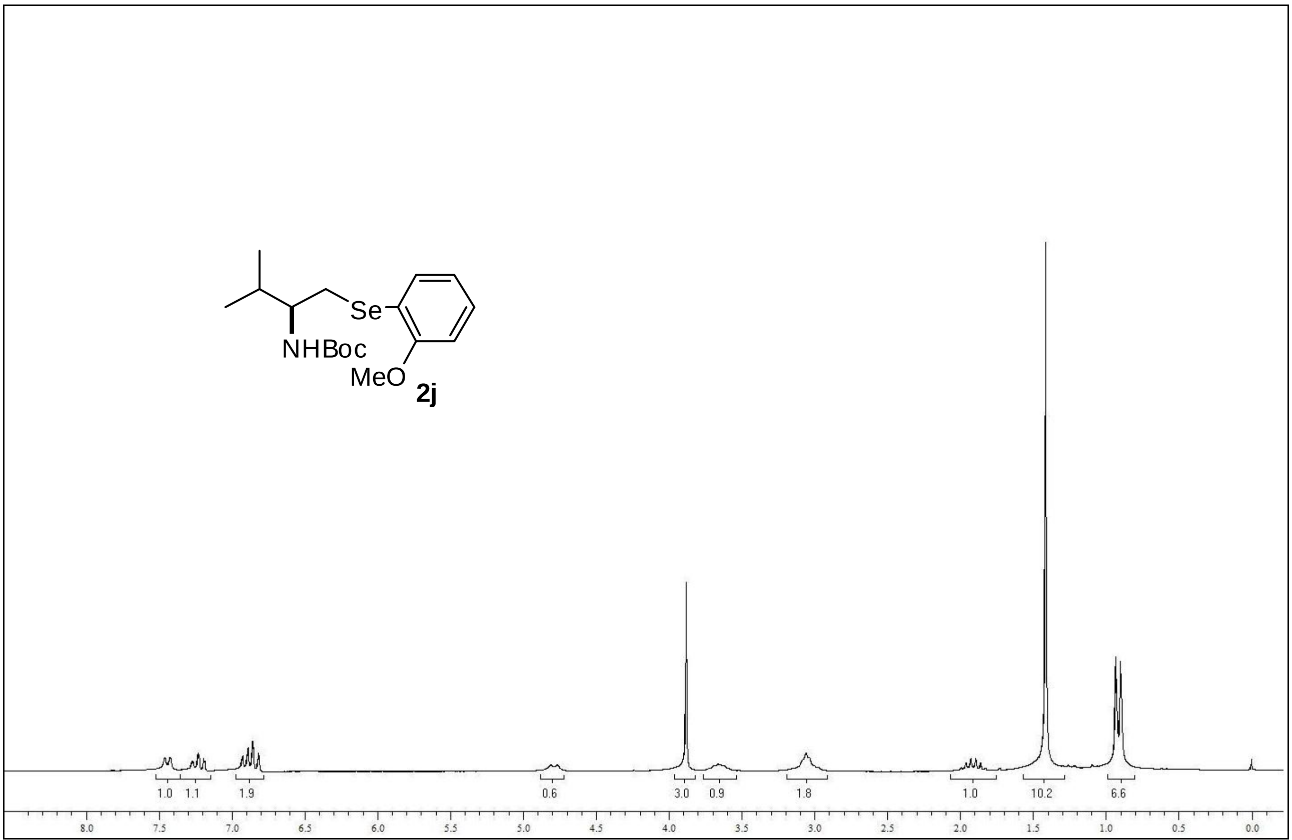
^{13}C NMR (50 MHz, CDCl$_3$) Spectrum of compound **2h**.



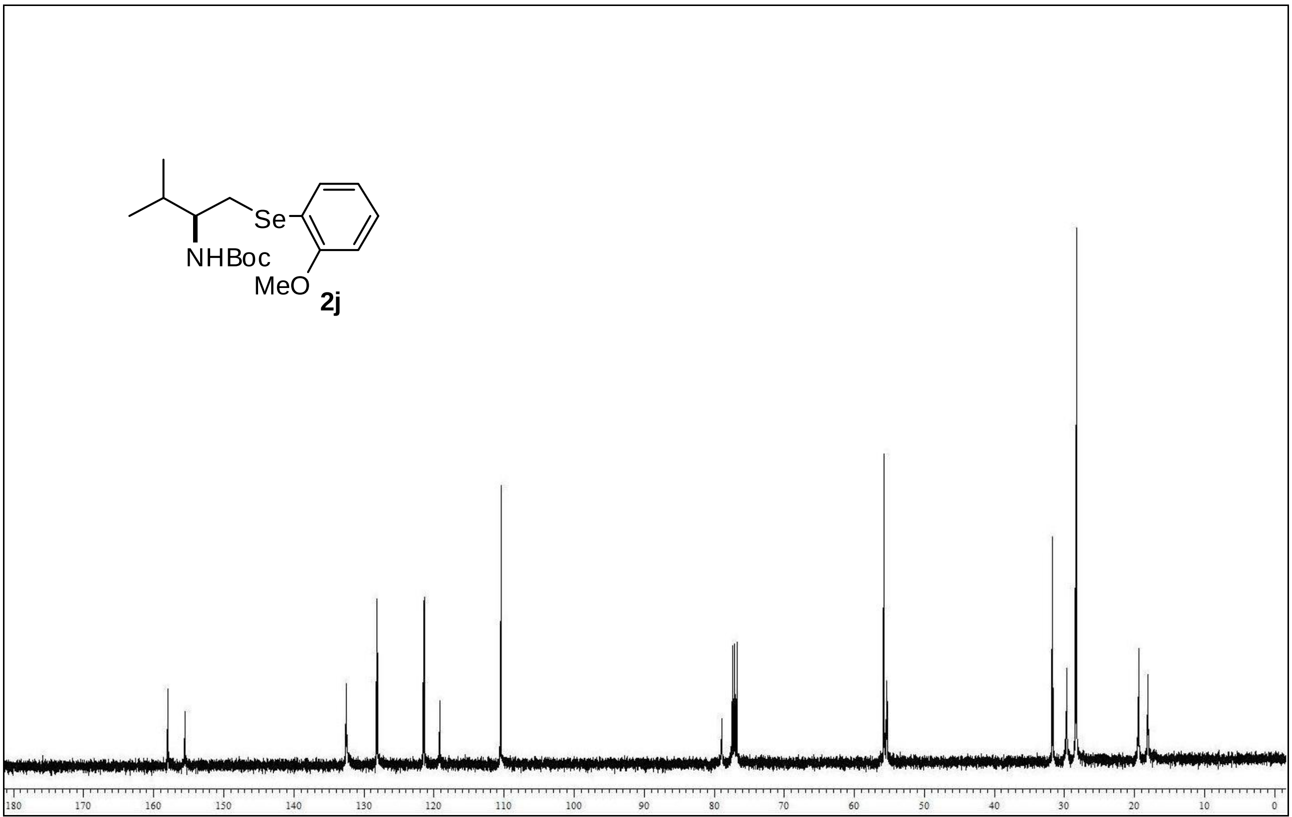
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2i**.



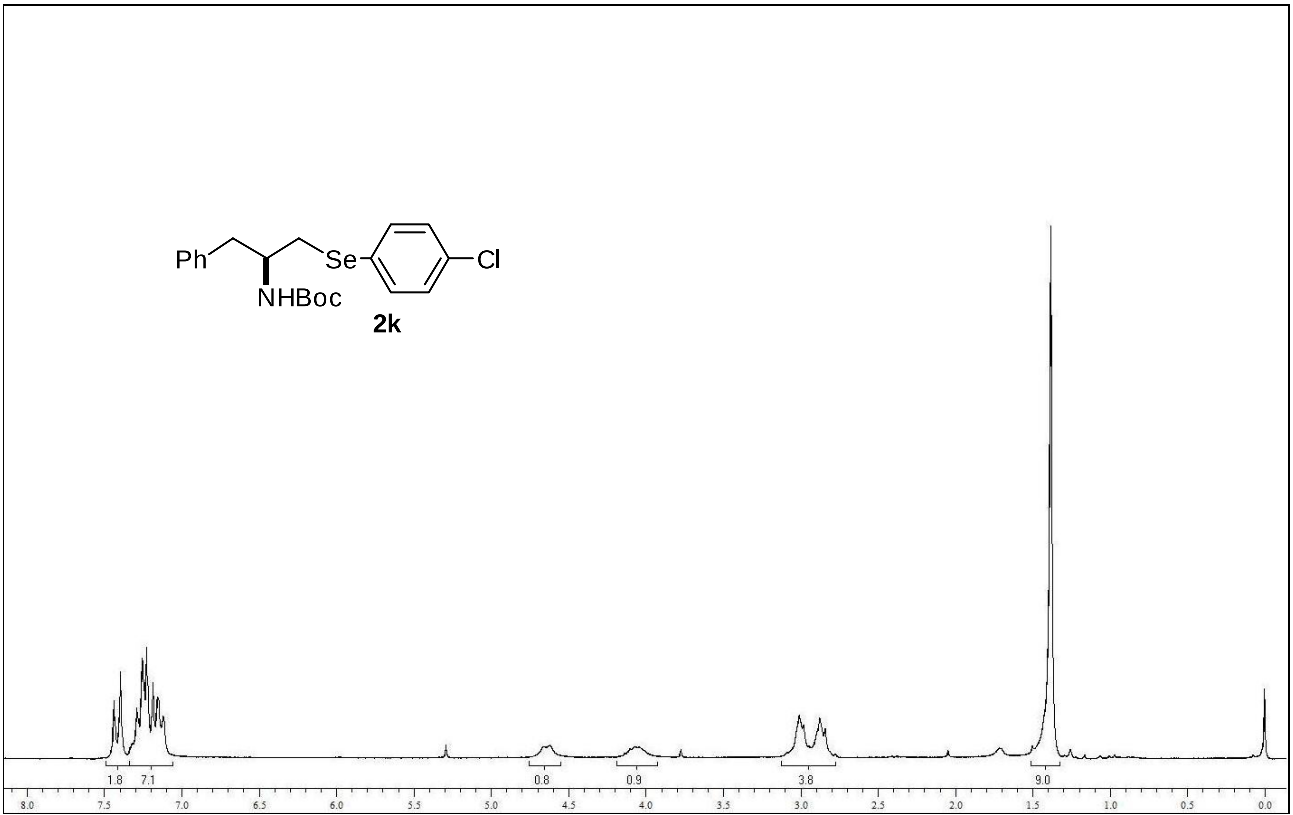
^{13}C NMR (100 MHz, CDCl$_3$) Spectrum of compound **2i**.



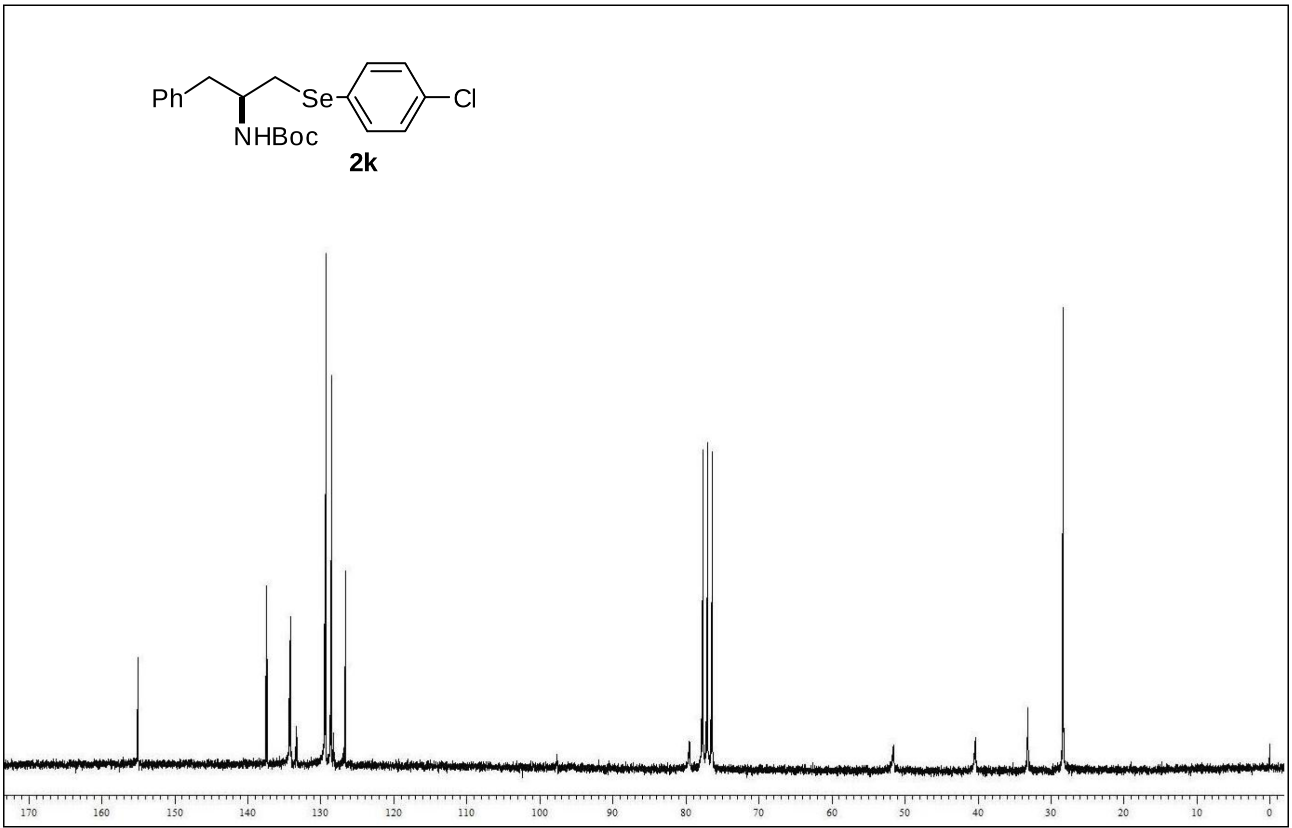
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2j**.



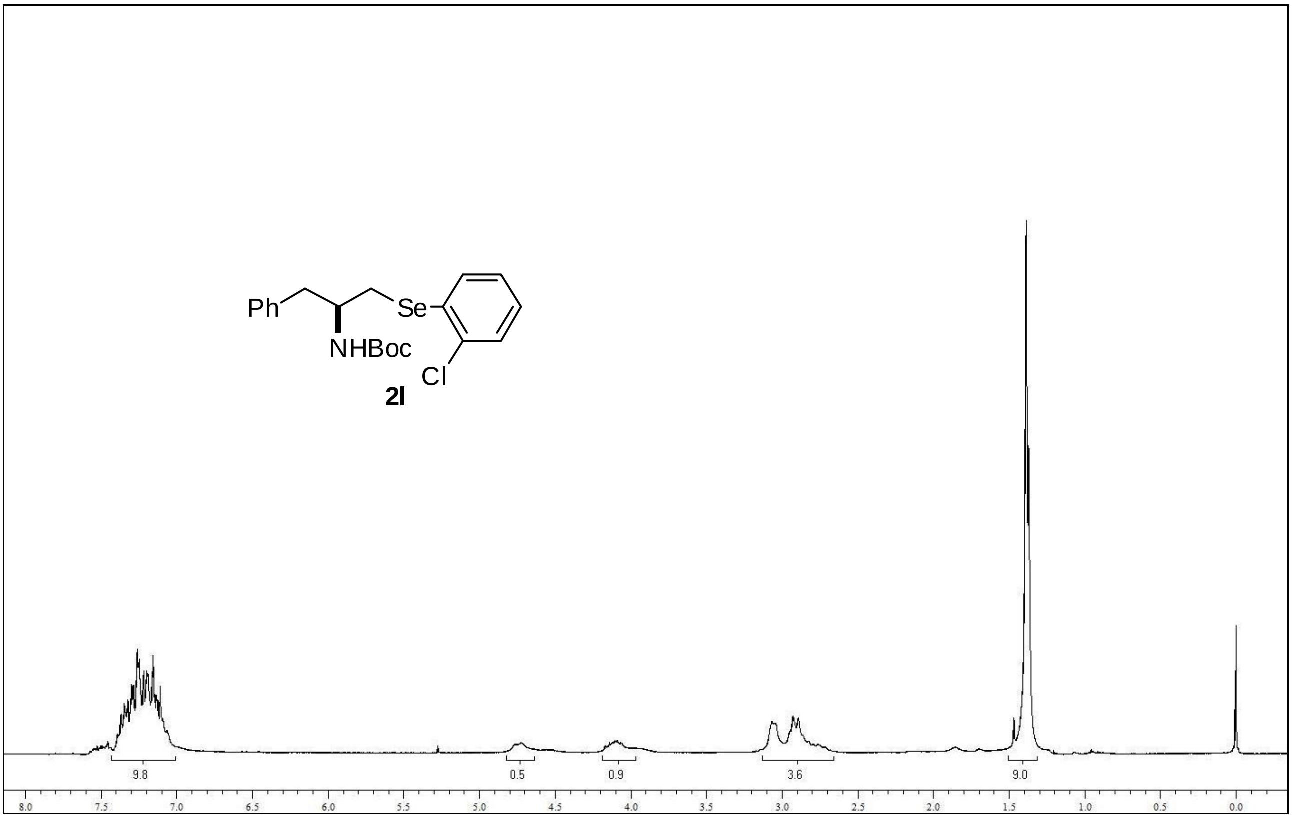
^{13}C NMR (100 MHz, CDCl$_3$) Spectrum of compound **2j**.



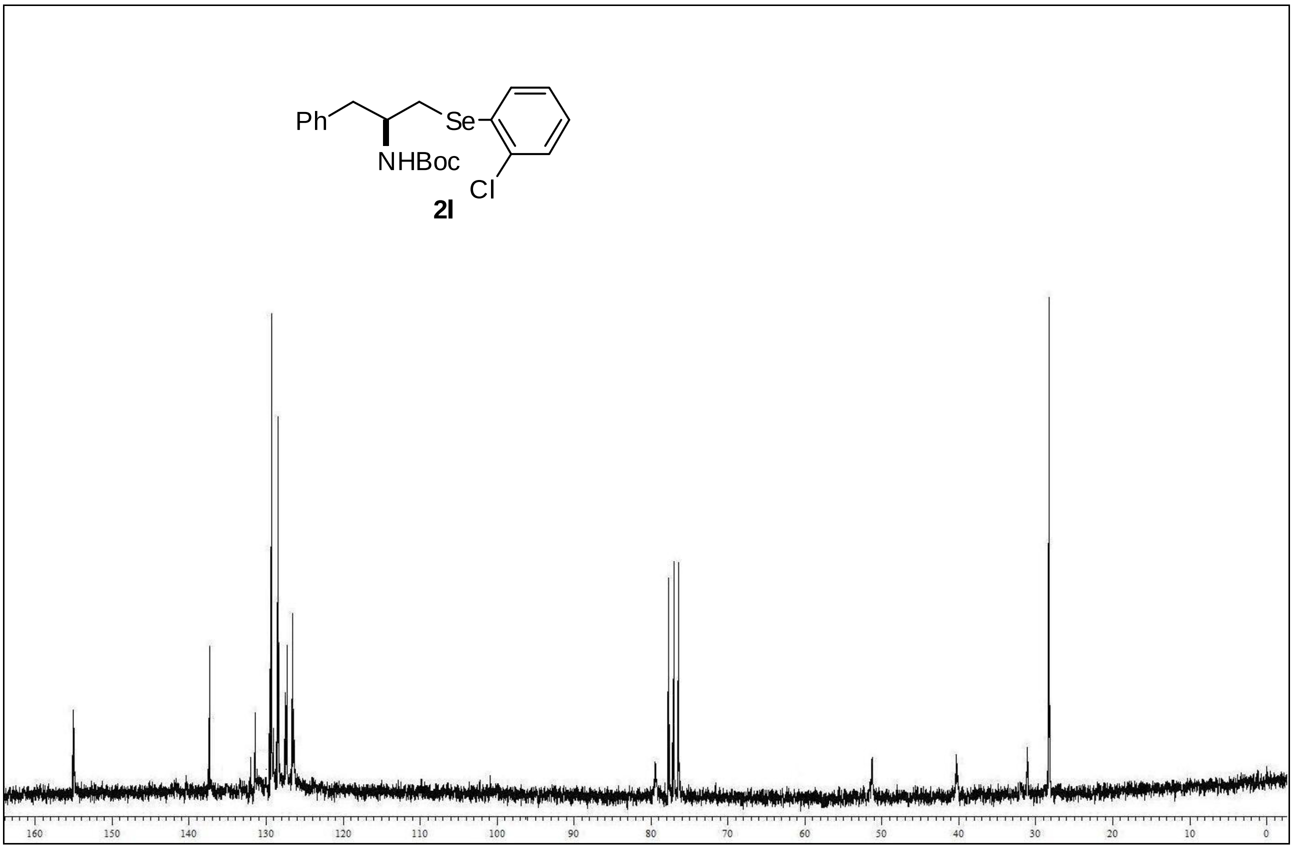
^{1}H NMR (200 MHz, $CDCl_3$) Spectrum of compound **2k**.



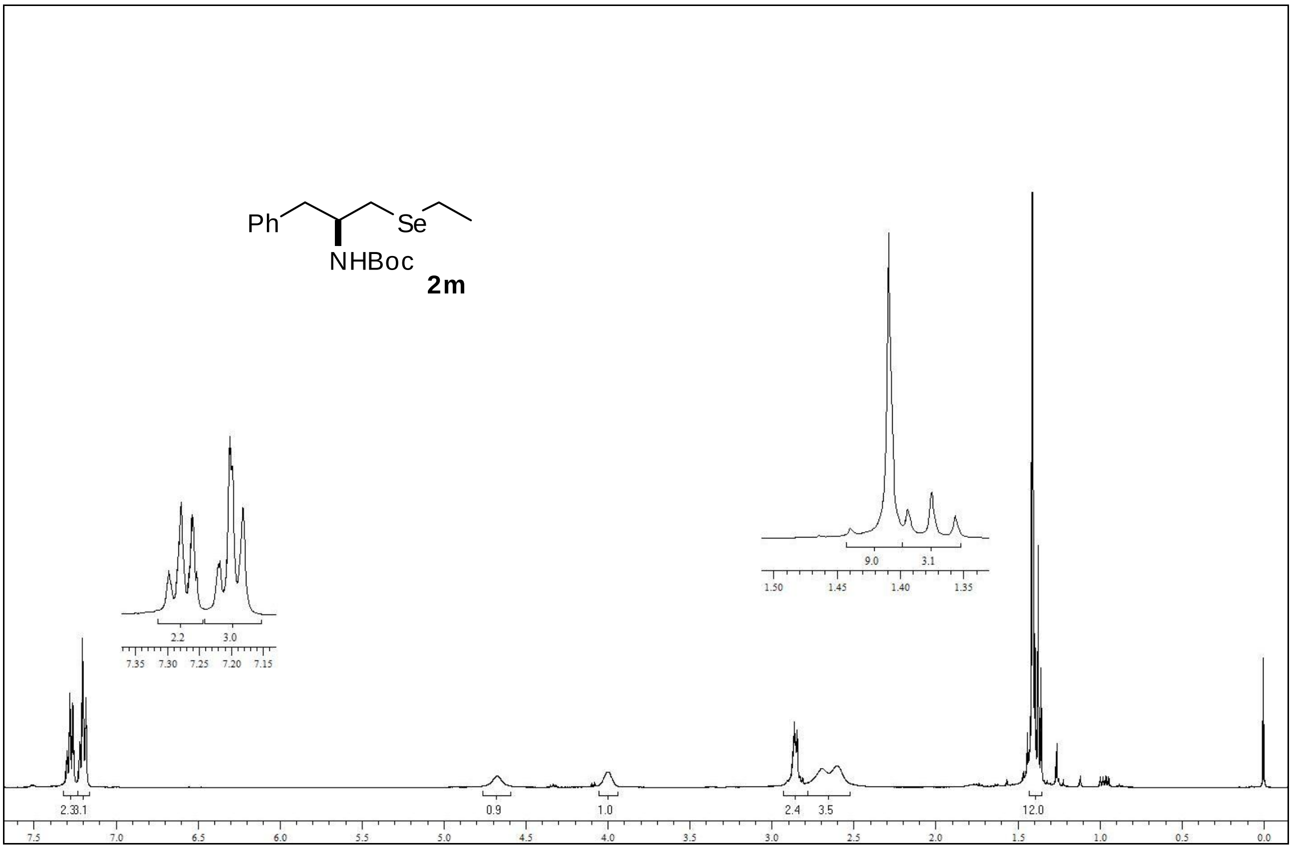
^{13}C NMR (50 MHz, $CDCl_3$) Spectrum of compound **2k**.



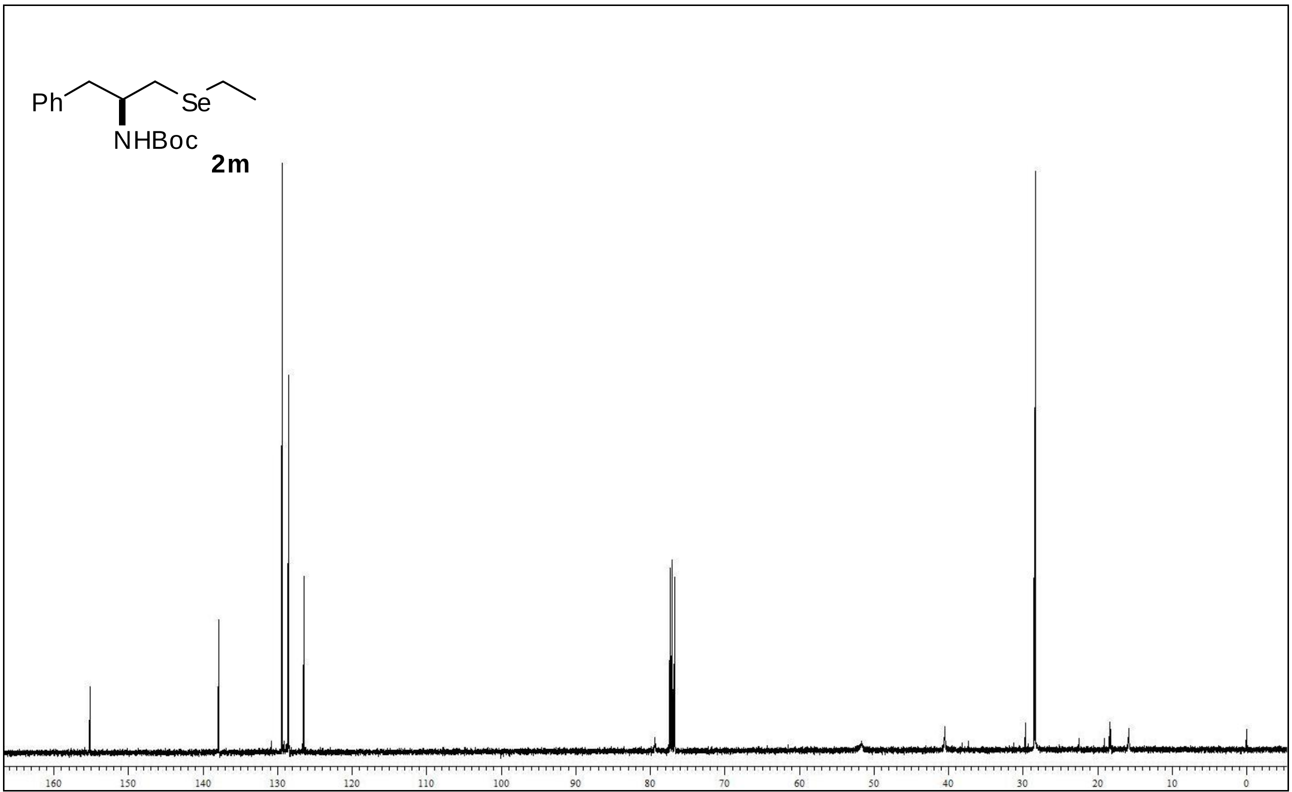
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2l**.



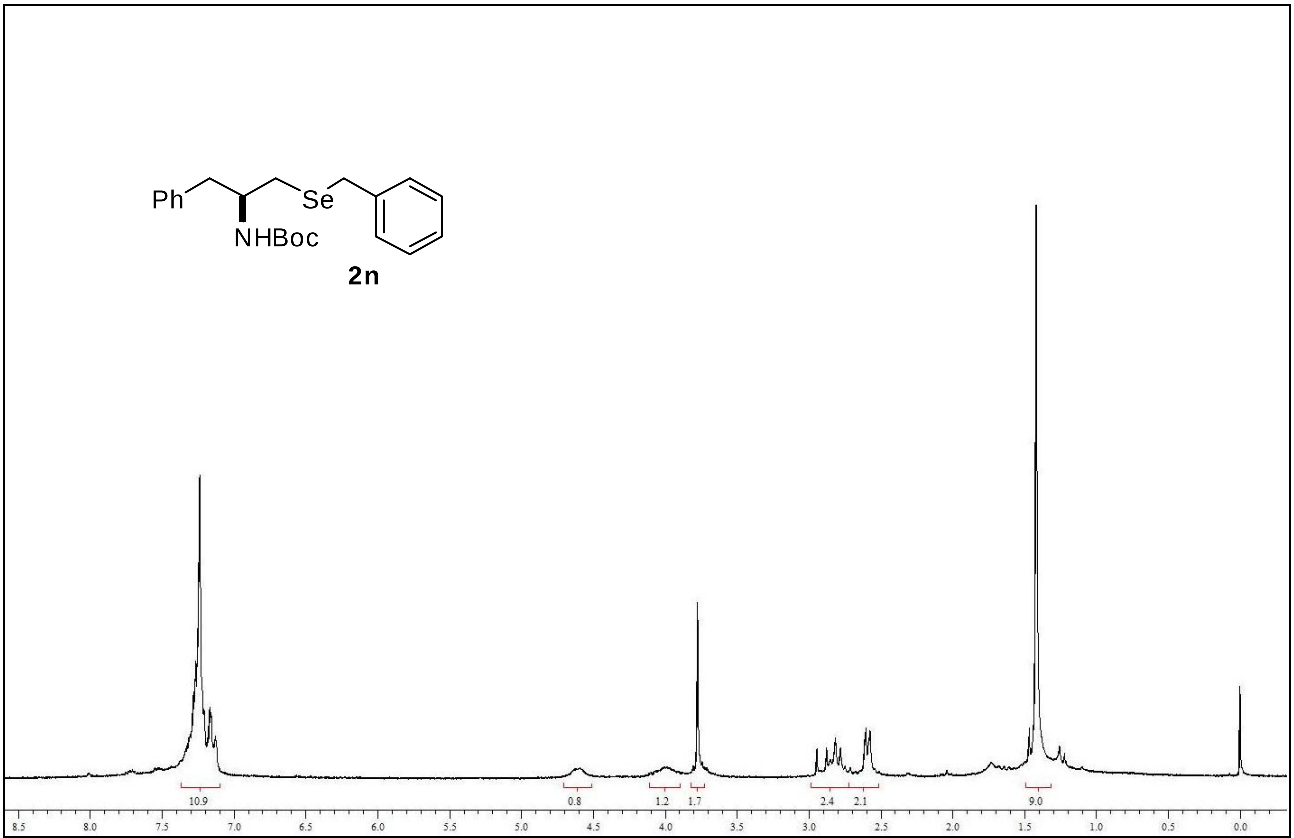
^{13}C NMR (50 MHz, CDCl$_3$) Spectrum of compound **2l**.



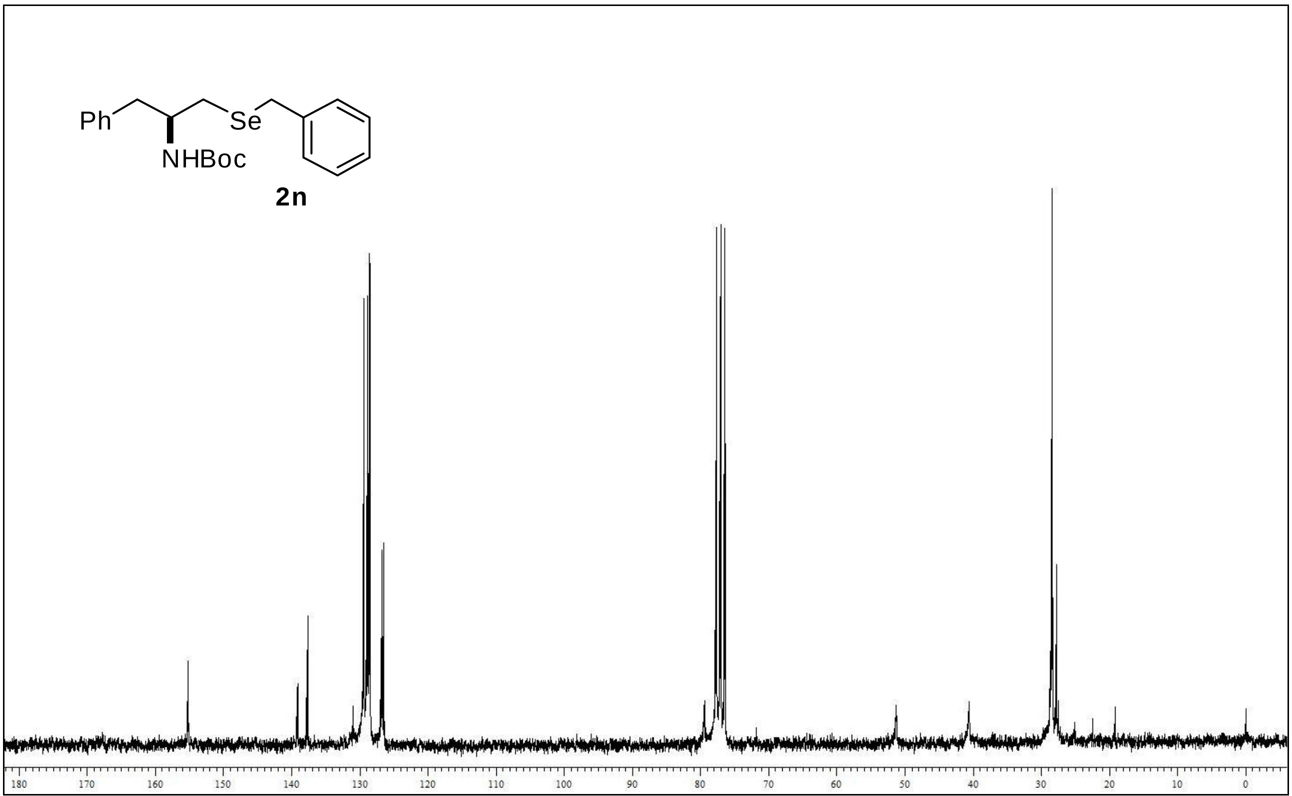
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of compound **2m**.



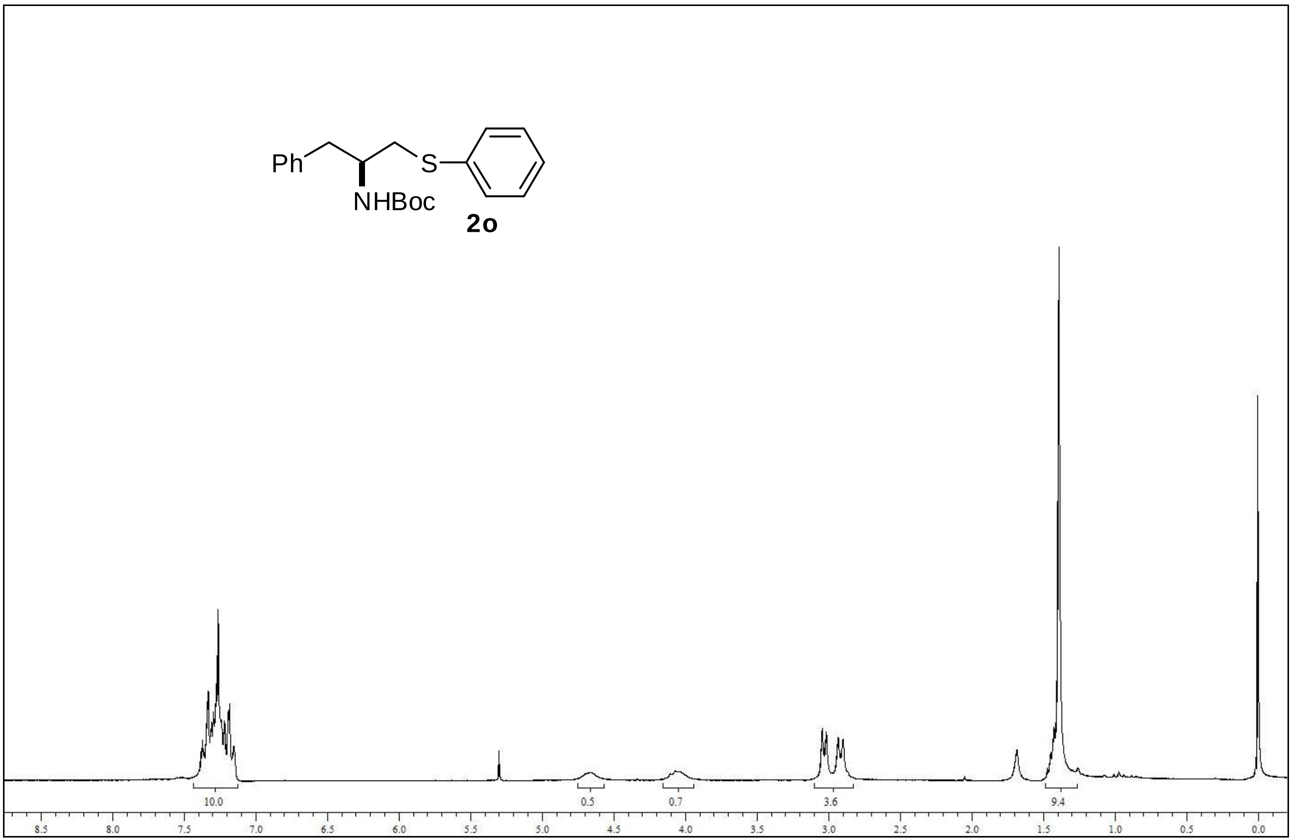
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of compound **2m**.



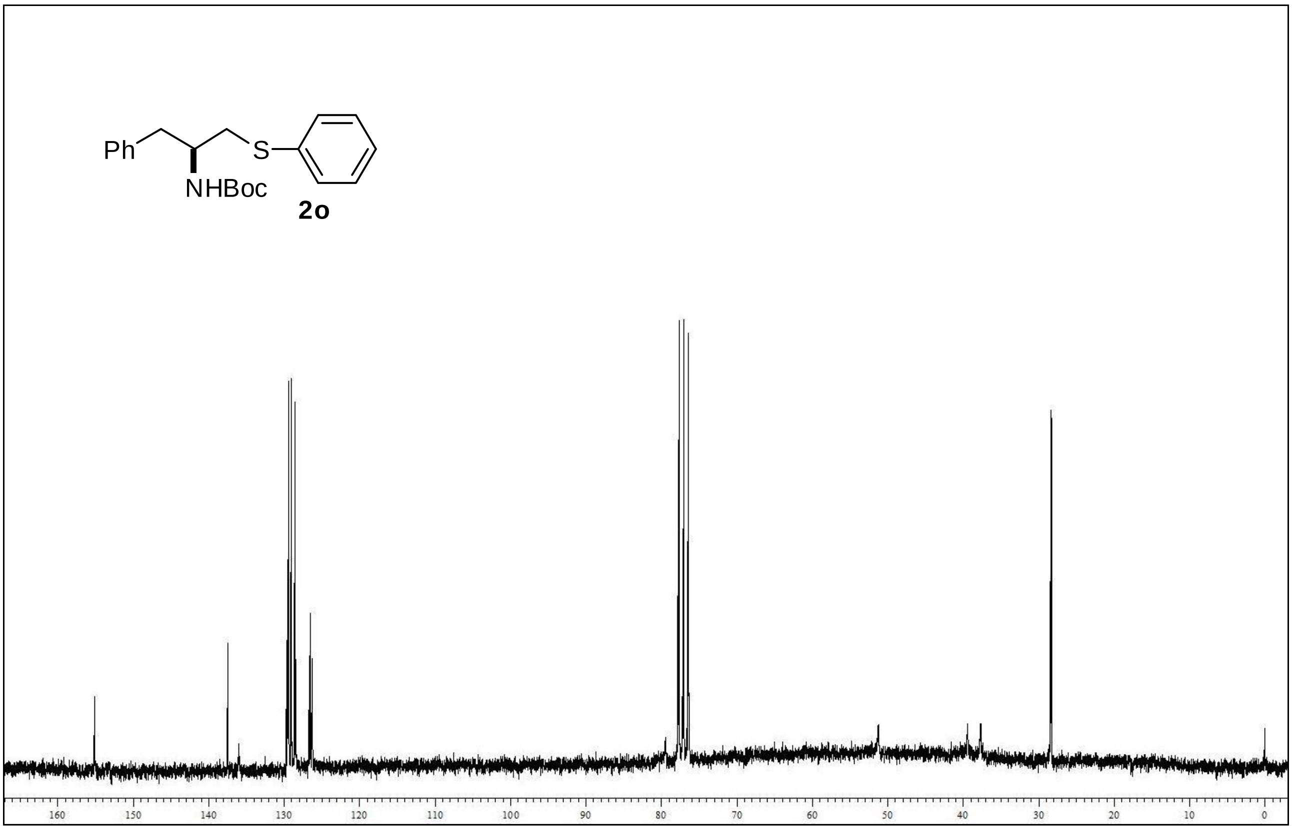
^{1}H NMR (200 MHz, $CDCl_3$) Spectrum of compound **2n**.



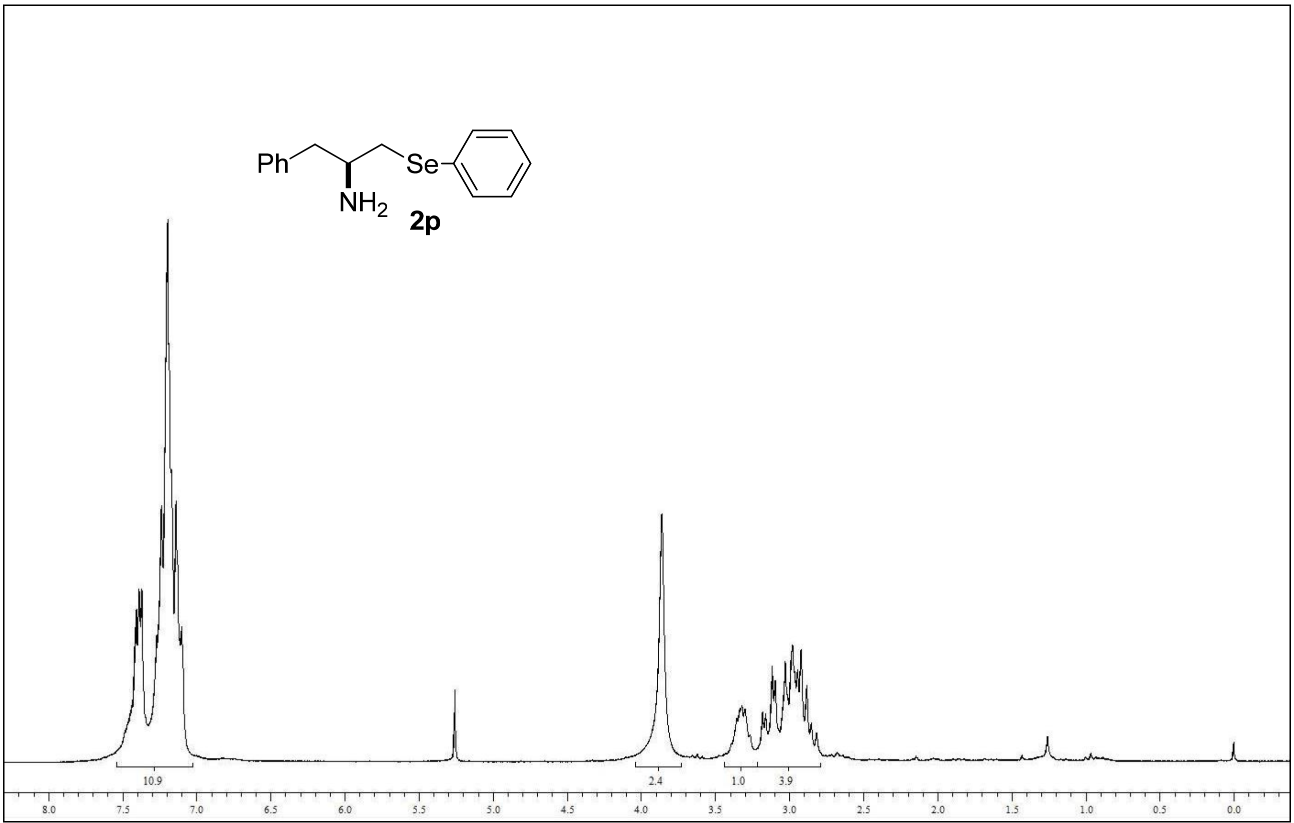
^{13}C NMR (50 MHz, $CDCl_3$) Spectrum of compound **2n**.



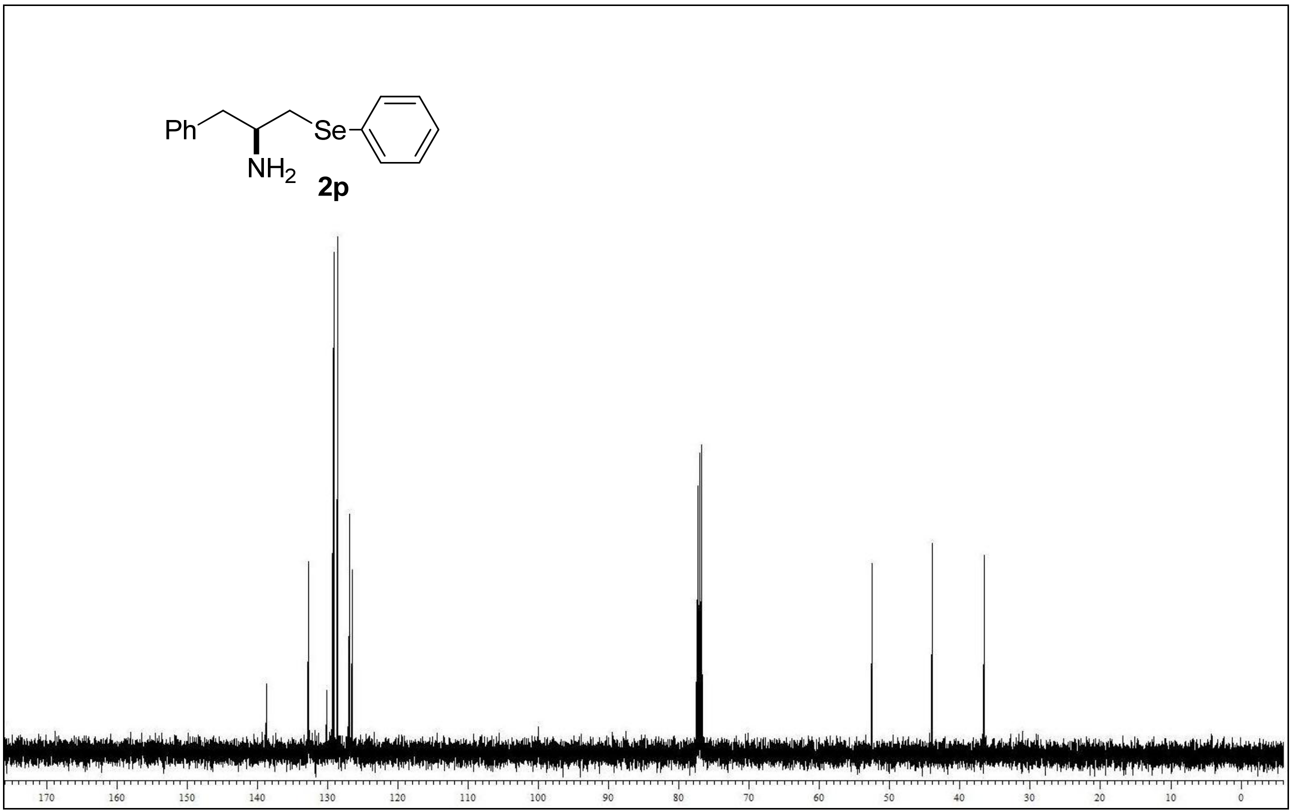
^{1}H NMR (200 MHz, CDCl$_3$) Spectrum of compound **2o**.



^{13}C NMR (50 MHz, CDCl$_3$) Spectrum of compound **2o**.



^{1}H NMR (200 MHz, $CDCl_3$) Spectrum of compound **2p**.



^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of compound **2p**.

4 References

[1] C. C. Cassol, G. Ebeling, B. Ferrera and J. Dupont, *Adv. Synth. Catal.* 2006, **348**, 243.

[2] A. L. Braga, P. H. Schneider, M. W. Paixão, A. M. Deobald, C. Peppe and D. P. Bottega, *J. Org. Chem.* 2006, **71**, 4305.

[3] A. L. Braga, D. S. Lüdtke, M. W. Paixão, E. E. Alberto, H. A. Stefani, L. Juliano, *Eur. J. Org. Chem.* 2005, 4260.

[4] S. Berlin, C. Ericsson and L. Engman, *J. Org. Chem.* 2003, **68**, 8386.