Supporting Information for

Visible-Light-Promted Cross-Coupling Reaction of Hypervalent Bis-Catecholato Silicon Compounds with Selenosulfonates or Thiosulfonates

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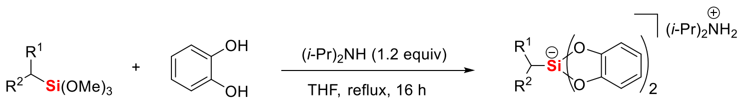
Contents

Ⅰ. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Anhydrous DMF, was purchased from Beijing InnoChem Science & Technology Co., Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 300-400 mesh silica gel was used. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI source. The starting materials were isolated by SepaBean machine Flash Chromatography, which purchased from Santai Technologies Inc.

II. Synthesis of Substrates

General procedure for the synthesis of alkylbis(catecholato)silicates.[1]



To an oven-dried, 100 mL round bottom flask equipped with a stir bar, reflux condenser, and gas inlet adapter was added catechol (3.01 g, 27.3 mmol, 1.95 equiv) followed by anhydrous THF (28 mL) and anhydrous *i*-Pr_2NH (1.70 g, 2.35 mL, 16.8 mmol, 1.2 equiv). The mixture was placed under an argon atmosphere and was allowed to stir at rt for 5 min until the solution became a pale red. After this time, organotrimethoxysilane derivatives (14 mmol, 1.0 equiv) was added. The solution immediately lightened to a golden yellow. The solution was then heated to reflux in an oil bath and allowed to stir overnight at this temperature. Once the reaction was judged to be complete by crude ^{1}H NMR analysis, the solvent was removed *in vacuo* by rotary evaporation. The resulting powder was collected *via* filtration through a medium porosity fritted funnel. The powder was washed with Et_2O (~100 mL) and pentane (~150 mL). The solid was collected and dried further *in vacuo* to give the desired silicate.

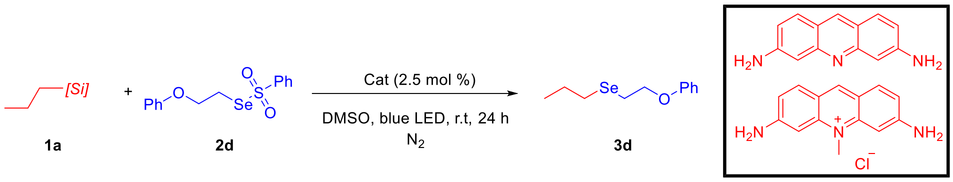
General Procedure for the synthesis of Selenium Sulfonate and Thiosulfonate[2].

Thiosulfonates and Selenium Sulfonates were prepared following the reported procedures[2].

III .General Procedure and Product Characterization

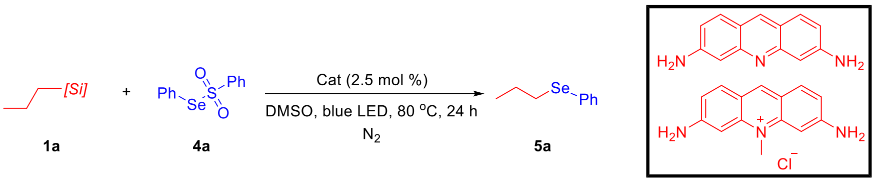
1. General Procedure A

A representative procedure synthesis of (2-phenoxyethyl)(propyl)selane (3d) is shown below.



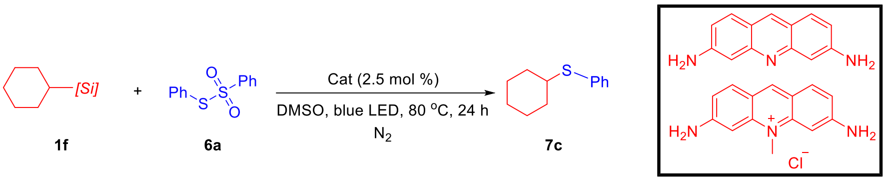
In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with diisopropylammonium bis(catecholato)propylsilicate **1a** (129.6 mg, 0.34 mmol) and *Se*-(2-phenoxyethyl) benzenesulfonoselenoate **2d** (68.4 mg 0.2 mmol), cat (1.4 mg, 2.5 mol %), DMSO (1.0 mL) was added via syringe. The reaction mixture was stirred at r.t for 24 h with a 40 W LED lamp (40 W; λ = 450- 460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass;). After 24h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product **3d**.

A representative procedure synthesis of phenyl(propyl)selane (5a) is shown below.



In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with diisopropylammonium bis(catecholato)propylsilicate **1a** (129.6 mg, 0.34 mmol) and *Se*-phenyl benzenesulfonoselenoate **4a** (59.6 mg 0.2 mmol), cat (1.4 mg, 2.5 mol %), DMSO (1.0 mL) was added via syringe. The reaction mixture was stirred at 80 °C for 24 h with a 40 W LED lamp (40 W; λ = 450- 460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass;). After 24h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product **5a**.

A representative procedure synthesis of cyclohexyl(phenyl)sulfane (7c) is shown below.

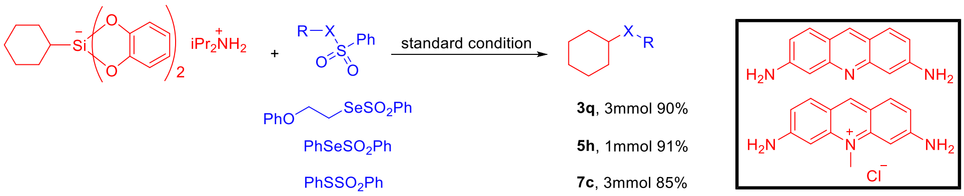


In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with bis(catechol)diisopropyl ammonium cyclohexyl silicate **1f** (129.6 mg, 0.34 mmol) and *S*-phenyl benzenesulfonothioate **6a** (50.0 mg 0.2 mmol), cat (1.4 mg, 2.5 mol %), DMSO (1.0 mL) was added via syringe. The reaction mixture was stirred at 80 °C for 24 h with a 40 W LED lamp (40 W; λ = 450- 460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass;). After 24h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product **7c**.

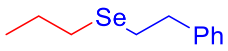
2. General Procedure B

The procedure scale-up synthesis of 3q, 5h and 7c is shown below.

In glovebox, An oven-dried screw-capped 50-mL vial equipped with a magnetic stir bar was charged with bis(catechol)diisopropyl ammonium cyclohexyl silicate **1f** and *Se*-(2-phenoxyethyl) benzenesulfonoselenoate **2d,** *Se*-phenyl benzenesulfonoselenoate **4a** and *S*-phenyl benzenesulfonothioate **6a**, respectively. Cat (2.5 mol %), DMSO was added via syringe. The reaction mixture was stirred for 24 h with a 40 W LED lamp (40 W; λ = 450- 460 nm; 5 cm away; made in TanLu. Ltd; borosilicate glass;). After 24h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product.

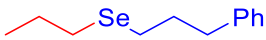


3. Product Characterization



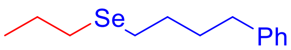
phenethyl(propyl)selane (3a)

Yield: 78% (35.5mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2924, 1495, 1453, 749, 697. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 2.97 (dd, J = 9.1, 6.9 Hz, 2H), 2.86 – 2.75 (m, 2H), 2.55 (t, J = 7.3 Hz, 2H), 1.68 (h, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.6, 128.6, 128.5, 126.4, 37.5, 26.5, 24.9, 24.0, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{11}H_{17}Se$ $(M+H)^+$: 229.0495, found 229.0496.



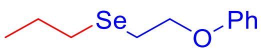
(3-phenylpropyl)(propyl)selane (3b)

Yield: 77% (68.0mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2926, 1495, 1453, 1208, 741, 697. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (m, J = 6.6, 5.6 Hz, 2H), 7.18 (m, J = 6.4, 1.6 Hz, 3H), 2.71 (t, J = 7.6 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.55 – 2.50 (m, 2H), 1.99 (q, J = 7.5 Hz, 2H), 1.67 (h, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 128.6, 128.5, 126.0, 36.1, 32.3, 26.3, 24.0, 23.3, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{19}Se$ $(M+H)^+$: 243.0652, found 243.0652.



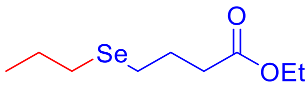
(4-phenylbutyl)(propyl)selane (3c)

Yield: 85% (43.4mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2958, 2926, 1496, 1453, 1206, 745, 697. **^{1}H NMR** δ 7.30 – 7.25 (m, 2H), 7.18 (m, J = 7.3, 2.8 Hz, 3H), 2.63 (dd, J = 8.1, 5.8 Hz, 2H), 2.57 (t, J = 6.9 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 1.71 (dt, J = 7.1, 3.5 Hz, 4H), 1.67 (s, 1H), 1.64 – 1.60 (m, 1H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 128.6, 128.5, 126.0, 36.1, 32.3, 29.8, 26.3, 24.0, 23.3, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{13}H_{21}Se$ $(M+H)^+$: 257.0808, found 257.0809.



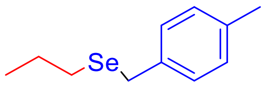
(2-phenoxyethyl)(propyl)selane (3d)

Yield: 99% (48.5mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2960, 2926, 1599, 1495, 1462, 1238, 1029, 750, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.94 (m, J = 7.4, 1.1 Hz, 1H), 6.91 – 6.86 (m, 2H), 4.23 – 4.14 (m, 2H), 2.94 – 2.86 (m, 2H), 2.64 (t, J = 7.3 Hz, 2H), 1.72 (q, J = 7.4 Hz, 2H), 1.00 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.6, 121.0, 114.7, 68.5, 27.0, 24.1, 22.0, 14.6. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{11}H_{16}OSe$ $(M+H)^+$: 245.0445, found 245.0445.



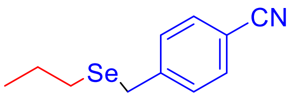
ethyl 4-(propylselanyl)butanoate (3e)

Yield: 93% (41.6mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2961, 2927, 1731, 1373, 1194, 1128, 1032. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.13 (q, *J* = 7.1 Hz, 2H), 2.56 (dt, *J* = 13.2, 7.3 Hz, 4H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.98 (p, *J* = 7.3 Hz, 2H), 1.69 (dt, *J* = 14.6, 7.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 60.5, 34.3, 26.3, 25.9, 24.0, 23.0, 14.7, 14.4. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_9H_{19}O_2Se$ $(M+H)^+$: 239.0550, found 239.0551.



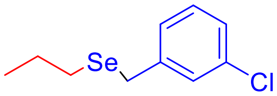
(4-methylbenzyl)(propyl)selane (3f)

Yield: 86% (39.3mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2922, 1512, 1453, 1181, 812, 714. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 3.74 (s, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.65 (h, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6, 136.3, 129.3, 128.8, 26.7, 26.3, 23.7, 21.2, 14.7. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{11}H_{17}Se$ $(M+H)^+$: 229.0495, found 229.0496.



4-((propylselanyl)methyl)benzonitrile (3g)

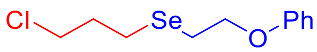
Yield: 99% (47.4mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2960, 2928, 2227, 1605, 1177, 837, 608. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.43 – 7.35 (m, 2H), 3.77 (s, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 1.69 – 1.59 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 132.4, 129.6, 119.0, 110.4, 26.7, 26.4, 23.5, 14.6. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{11}H_{14}NSe$ $(M+H)^+$: 240.0291, found 240.0292.



(3-chlorobenzyl)(propyl)selane (3h)

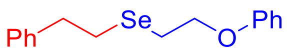
Yield: 94% (42.9mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2960, 2927, 1596, 1573, 1428, 1076, 870, 780, 692. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 1.9 Hz, 1H), 7.24 – 7.13 (m, 3H), 3.71 (s, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 1.65 (q, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.9, 134.3, 129.8, 129.0, 127.1, 126.9, 26.6, 26.3, 23.6, 14.7. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{10}H_{14}ClSe$ $(M+H)^+$:

248.9949, found 248.9947.



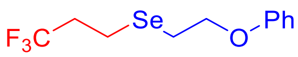
(3-chloropropyl)(2-phenoxyethyl)selane (3i)

Yield: 84% (46.6mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 2930, 1734, 1598, 1495, 1235, 1171, 751, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (m, *J* = 9.8, 7.0, 2.5 Hz, 2H), 6.95 (m, *J* = 7.3, 1.2 Hz, 1H), 6.90 – 6.87 (m, 2H), 4.20 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.12 (p, *J* = 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 129.6, 121.1, 121.1, 114.7, 114.6, 68.4 44.4, 33.2, 22.4, 21.3. **HRMS** (ESI^{+}, MeCN) m/z calcd for $C_{11}H_{16}ClOSe$ $(M+H)^{+}$: 270.0055, found 279.0052.



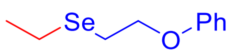
phenethyl(2-phenoxyethyl)selane (3j)

Yield: 81% (49.4mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 3026, 2927, 1598, 1494, 1237, 1171, 749, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.21 (m, *J* = 7.9, 1.3 Hz, 3H), 6.94 (m, *J* = 7.3, 1.1 Hz, 1H), 6.90 – 6.85 (m, 2H), 4.17 (t, *J* = 7.1 Hz, 2H), 3.05 – 2.97 (m, 2H), 2.94 – 2.86 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 141.1, 129.6, 128.6, 128.5, 126.5, 121.1, 114.7, 68.5, 37.4, 25.7, 22.4. **HRMS** (ESI^{+}, MeCN) m/z calcd for $C_{16}H_{19}OSe$ $(M+H)^{+}$: 307.0601, found 307.0602.



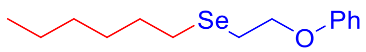
(2-phenoxyethyl)(3,3,3-trifluoropropyl)selane (3k)

Yield: 60%. Pale yellow oil. **IR** (neat, ν, cm^{-1}): 3041, 2937, 1599, 1496, 1362, 1262, 1209, 1128, 1072, 751, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 6.96 (m, *J* = 7.3, 1.1 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.24 (t, *J* = 6.5 Hz, 2H), 2.94 (t, *J* = 6.5 Hz, 2H), 2.85 – 2.77 (m, 2H), 2.58 – 2.44 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 129.5, 121.1, 114.4, 68.5, 36.3, 36.0, 35.7, 35.4, 22.7, 14.6, 14.5. **HRMS** (ESI^{+}, MeCN) m/z calcd for $C_{11}H_{14}F_3OSe$ $(M+H)^{+}$: 299.0162, found 299.0162.



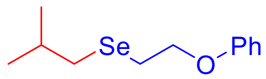
ethyl(2-phenoxyethyl)selane (3l)

Yield: 99%. Pale yellow oil. **IR** (neat, ν, cm^{-1}):2957, 2924, 1598, 1494, 1232, 1171, 749, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.94 (m, *J* = 7.4, 1.1 Hz, 1H), 6.91 – 6.86 (m, 2H), 4.19 (t, *J* = 7.3 Hz, 2H), 2.95 – 2.85 (m, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.43 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.6, 121.0, 114.7, 68.4, 21.6, 18.0, 16.0. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{10}H_{15}OSe$ (M+H)$^+$: 231.0288, found 231.0288.



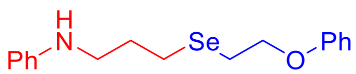
hexyl(2-phenoxyethyl)selane (3m)

Yield: 91% (52.3mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 2924, 1599, 1495, 1238, 1029, 750, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.94 (m, J = 7.9, 6.7 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.18 (t, J = 7.3 Hz, 2H), 2.88 (t, J = 7.3 Hz, 2H), 2.71 – 2.61 (m, 2H), 1.68 (p, J = 7.4 Hz, 2H), 1.42 – 1.35 (m, 2H), 1.28 (qd, J = 7.2, 5.6, 2.3 Hz, 4H), 0.89 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.6, 121.0, 114.7, 68.5, 31.4, 30.8, 29.7, 24.8, 22.6, 22.0, 14.1. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{14}H_{23}OSe$ (M+H)$^+$: 287.0914, found 287.0915.



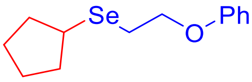
isobutyl(2-phenoxyethyl)selane (3n)

Yield: 86%. Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 2924, 1599, 1495, 1238, 1010, 750, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 6.94 (m, J = 7.4, 1.1 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.23 – 4.13 (m, 2H), 2.87 (dd, J = 7.6, 6.9 Hz, 2H), 2.58 (d, J = 6.8 Hz, 2H), 1.86 (dp, J = 13.3, 6.7 Hz, 1H), 1.01 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.6, 121.0, 114.7, 68.4, 34.9, 29.5, 22.7, 22.6. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{12}H_{19}OSe$ (M+H)$^+$: 259.0601, found 259.0602.



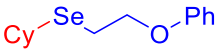
N-(3-((2-phenoxyethyl)selanyl)propyl)aniline (3o)

Yield: 61%. Yellow oil. **IR** (neat, ν, cm^{-1}):2926, 2857, 1599, 1494, 1237, 1028, 746, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.19 – 7.12 (m, 2H), 6.94 (m, J = 7.4, 1.1 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.69 (m, J = 7.4, 1.1 Hz, 1H), 6.62 – 6.55 (m, 2H), 4.19 (t, J = 7.0 Hz, 2H), 3.67 (s, 1H), 3.22 (t, J = 6.8 Hz, 2H), 2.89 (t, J = 7.0 Hz, 2H), 2.74 (t, J = 7.2 Hz, 2H), 1.97 (p, J = 7.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 148.2, 129.6, 129.4, 121.1, 117.5, 114.7, 112.9, 68.4, 43.7, 30.2, 22.4, 22.0. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{17}H_{22}NOSe$ (M+H)$^+$: 336.0867, found 336.0867.



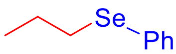
cyclopentyl(2-phenoxyethyl)selane (3p)

Yield: 99% (53.5mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2951, 2865, 1598, 1494, 1237, 749, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 6.93 (m, *J* = 7.4, 1.1 Hz, 1H), 6.91 – 6.86 (m, 2H), 4.24 – 4.17 (m, 2H), 3.34 (p, *J* = 7.0 Hz, 1H), 2.94 – 2.86 (m, 2H), 2.14 – 2.00 (m, 2H), 1.74 (tddd, *J* = 8.8, 6.9, 3.5, 2.0 Hz, 2H), 1.67 – 1.55 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.5, 120.9, 114.6, 68.4, 38.1, 34.7, 25.0, 22.1. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{13}H_{19}OSe$ $(M+H)^+$: 271.0601, found 271.0602.



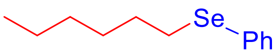
cyclohexyl(2-phenoxyethyl)selane (3q)

Yield: 97% (55.2mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2924, 2850.0, 1598, 1495, 1237, 1171, 991, 749, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.97 – 6.91 (m, 1H), 6.90 – 6.85 (m, 2H), 4.20 – 4.12 (m, 2H), 3.01 (tt, *J* = 10.8, 3.7 Hz, 1H), 2.94 – 2.86 (m, 2H), 2.05 (dq, *J* = 13.2, 3.4 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.62 (qd, *J* = 5.9, 4.5, 2.3 Hz, 1H), 1.57 – 1.45 (m, 2H), 1.38 – 1.25 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 129.5, 120.9, 114.6, 68.6, 39.3, 34.7, 34.7, 26.9, 25.8, 20.6. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{14}H_{21}OSe$ $(M+H)^+$: 285.0758, found 285.0758.



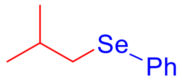
phenyl(propyl)selane (5a)

Yield: 92% (36.6mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 2852, 1464, 1079, 737, 688. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.27 – 7.21 (m, 3H), 2.89 (t, *J* = 7.3 Hz, 2H), 1.72 (h, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.6, 130.7, 129.1, 126.7, 30.2, 23.6, 14.6. **HRMS** (ESI^+, MeCN) m/z calcd for $C_9H_{13}Se$ $(M+H)^+$: 201.0182, found 201.0183.



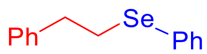
hexyl(phenyl)selane (5b)

Yield: 93% (44.8mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 2853, 1579, 1477, 1073, 1022, 732 **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.27 – 7.20 (m, 3H), 2.96 – 2.86 (m, 2H), 1.75 – 1.65 (m, 2H), 1.45 – 1.35 (m, 2H), 1.28 (tt, *J* = 5.6, 2.7 Hz, 4H), 0.90 – 0.85 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.5, 130.9, 129.1, 126.7, 31.4, 30.3, 29.7, 28.1, 22.7, 14.2. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{19}Se$ $(M+H)^+$: 243.0652 found 243.0652.



isobutyl(phenyl)selane (5c)

Yield: 58% (24.9mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2956, 2923, 1579, 1477, 1437, 1214, 1022, 732. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H), 7.23 (m, J = 8.5, 7.1, 5.2, 1.8 Hz, 3H), 2.84 (d, J = 6.8 Hz, 2H), 1.89 (dp, J = 13.3, 6.7 Hz, 1H), 1.02 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.4, 131.3, 129.1, 126.6, 37.9, 29.2, 22.8. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{10}H_{15}Se$ $(M+H)^+$: 215.0339 found 215.0336.

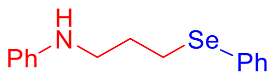


phenethyl(phenyl)selane (5d)

Yield: 88% (46.0mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 3025, 2929, 1578, 1436, 1022, 732, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 2H), 7.25 (m, J = 15.6, 7.4 Hz, 6H), 7.18 – 7.14 (m, 2H), 3.13 (dd, J = 9.2, 6.6 Hz, 2H), 3.04 – 2.92 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.1, 132.7, 130.3, 129.2, 128.6, 128.5, 127.0, 126.5, 36.7, 28.8. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{14}H_{15}Se$ $(M+H)^+$: 263.0339 found 263.0339.

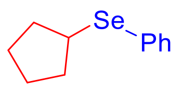
(3-chloropropyl)(phenyl)selane (5e)

Yield: 93% (43.5mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2955, 1578, 1477, 1436, 1262, 1022, 732, 654. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.30 – 7.24 (m, 3H), 3.64 (t, J = 6.3 Hz, 2H), 3.07 – 2.97 (m, 2H), 2.17 – 2.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.0, 129.6, 129.3, 127.2, 44.4, 32.7, 24.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_9H_{12}ClSe$ $(M+H)^+$: 234.9793, found 234.9790.



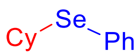
N-(3-(phenylselanyl)propyl)aniline (5f)

Yield: 58% (31.0mg). yellow oil. **IR** (neat, ν, cm^{-1}): 3050, 3018, 1600, 1504, 1435, 1251, 733, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.28 – 7.23 (m, 3H), 7.19 – 7.13 (m, 2H), 6.69 (m, J = 7.4, 1.2 Hz, 1H), 6.60 – 6.54 (m, 2H), 3.62 (s, 1H), 3.24 (t, J = 6.8 Hz, 2H), 2.99 (t, J = 7.1 Hz, 2H), 2.00 (p, J = 7.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 132.8, 130.2, 129.4, 129.3, 127.1, 117.5, 112.9, 43.6, 29.8, 25.4. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{15}H_{18}NSe$ $(M+H)^+$: 292.0604 found 292.0605.



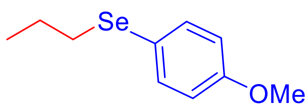
cyclopentyl(phenyl)selane (5g)

Yield: 69% (31.8mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2953, 2865, 1579, 1476, 1436, 1217, 1022, 732. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.27 – 7.21 (m, 3H), 3.62 (ddd, J = 13.1, 7.3, 6.0 Hz, 1H), 2.12 – 2.00 (m, 2H), 1.80 – 1.65 (m, 4H), 1.57 (tq, J = 6.9, 3.0, 2.2 Hz, 2H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 133.6, 131.2, 129.0, 126.9, 41.9, 34.2, 25.0. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{11}H_{15}Se$ $(M+H)^+$: 227.0339 found 227.0339.



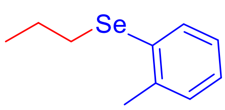
cyclohexyl(phenyl)selane (5h)

Yield: 77% (36.8mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2925, 2850, 1578, 1476, 1436, 1256, 992, 735. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.29 – 7.23 (m, 3H), 3.25 (tt, J = 10.8, 3.7 Hz, 1H), 2.08 – 1.97 (m, 2H), 1.79 – 1.70 (m, 2H), 1.62 – 1.57 (m, 1H), 1.56 – 1.46 (m, 2H), 1.35 (dt, J = 13.2, 3.2 Hz, 1H), 1.31 – 1.25 (m, 2H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 134.8, 129.5, 129.0, 127.3, 43.4, 34.4, 27.0, 25.9. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{17}Se$ $(M+H)^+$: 241.0495 found 241.0496.



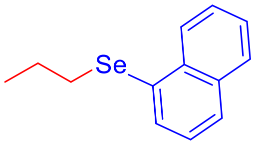
(4-methoxyphenyl)(propyl)selane (5i)

Yield: 94% (43.0mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2929, 1590, 1489, 1282, 1028, 819. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 6.85 – 6.76 (m, 2H), 3.79 (s, 3H), 2.79 (t, J = 7.3 Hz, 2H), 1.67 (h, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 159.3, 135.6, 120.3, 114.8, 55.4, 31.4, 23.6, 14.5. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{10}H_{15}OSe$ $(M+H)^+$: 231.0288 found 231.0288.



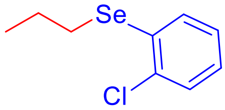
propyl(*o*-tolyl)selane (5j)

Yield: 73% (31.2mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2961, 2926, 1455, 1377, 1036, 739, 658. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.40 (m, J = 7.0, 2.1 Hz, 1H), 7.19 – 7.06 (m, 3H), 2.87 (t, J = 7.4 Hz, 2H), 2.39 (s, 3H), 1.73 (q, J = 7.3 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 139.3, 131.9, 131.1, 130.0, 126.5, 126.5, 29.0, 23.4, 22.4, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{10}H_{15}Se$ $(M+H)^+$: 215.0339 found 215.0336.



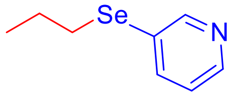
naphthalen-1-yl(propyl)selane (5k)

Yield: 94%. Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2926, 1560, 1453, 1197, 961, 787, 767, 650. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (m, *J* = 8.3, 1.3 Hz, 1H), 7.81 (m, *J* = 8.4, 1.2 Hz, 1H), 7.75 (m, *J* = 7.6 Hz, 2H), 7.58 – 7.46 (m, 2H), 7.36 – 7.30 (m, 1H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.69 (q, *J* = 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.5, 134.1, 132.0, 130.0, 128.7, 128.1, 127.7, 126.6, 126.2, 125.8, 30.5, 23.6, 14.6. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{13}H_{15}Se$ $(M+H)^+$: 251.0339 found 251.0339.



(2-chlorophenyl)(propyl)selane (5l)

Yield: 76% (35.4mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2961, 2928, 1573, 1448, 1024, 740. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (m, *J* = 7.5, 2.7, 1.9 Hz, 2H), 7.19 – 7.09 (m, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.78 (h, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.1, 131.9, 130.7, 129.6, 127.2, 127.1, 28.7, 23.0, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_9H_{12}ClSe$ $(M+H)^+$: 234.9793 found 234.9790.



3-(propylselanyl)pyridine (5m)

Yield: 58% (23.0mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2959, 2928, 1573, 1411, 1108, 750, 699. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (m, *J* = 5.0, 1.9, 0.9 Hz, 1H), 7.42 (m, *J* = 7.6, 1.9 Hz, 1H), 7.31 (m, *J* = 7.9, 1.1 Hz, 1H), 7.00 (m, *J* = 7.4, 4.9, 1.1 Hz, 1H), 3.16 (t, *J* = 7.3 Hz, 2H), 1.82 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 150.1, 135.9, 125.5, 120.2, 28.1, 23.7, 14.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_8H_{12}NSe$ $(M+H)^+$: 202.0135 found 202.0136.

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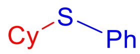
(3-chloropropyl)(phenyl)sulfane (7a)

Yield: 78% (40.3mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2958, 2924, 1583, 1480, 1438, 1267, 1025, 736. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.11 – 2.03

(m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.8, 129.6, 129.1, 126.4, 43.5, 31.8, 30.9. **HRMS** (ESI^+, MeCN) m/z calcd for $C_9H_{12}ClS$ $(M+H)^+$: 187.0348 found 187.0348.

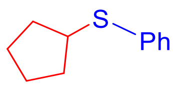
phenethyl(phenyl)sulfane (7b)

Yield: 41% (49.0mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 3026, 2923, 1730, 1583, 1479, 1438, 1025, 735, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.28 (m, *J* = 6.4, 5.6, 3.5 Hz, 4H), 7.23 – 7.16 (m, 4H), 3.20 – 3.11 (m, 2H), 2.91 (dd, *J* = 9.3, 6.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ140.3, 136.5, 132.6, 129.3, 129.0, 128.6, 126.6, 126.1, 35.7, 35.2. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{14}H_{15}S$ $(M+H)^+$: 215.0894 found 215.0894.



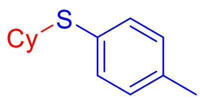
cyclohexyl(phenyl)sulfane (7c)

Yield: 77% (42.1mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2926, 2851, 1583, 1438, 997, 734, 690. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 3.10 (tt, *J* = 10.5, 3.6 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.77 (tdd, *J* = 7.1, 4.5, 2.4 Hz, 2H), 1.65 – 1.57 (m, 1H), 1.41 – 1.23 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.3, 132.0, 128.9, 126.7, 46.7, 33.5, 26.2, 25.9. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{17}S$ $(M+H)^+$: 193.1051 found 193.1051.



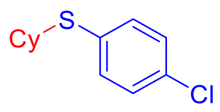
cyclopentyl(phenyl)sulfane (7d)

Yield: 74% (39.6mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2954, 2866, 1584, 1478, 1438, 1092, 1025, 735, 689. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 – 7.12 (m, 1H), 3.66 – 3.52 (m, 1H), 2.13 – 1.96 (m, 2H), 1.86 – 1.70 (m, 2H), 1.61 (tddd, *J* = 11.6, 6.1, 4.4, 2.0 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.36, 130.00, 128.82, 125.93, 33.64, 24.90. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{11}H_{15}S$ $(M+H)^+$: 179.0894 found 179.0894.



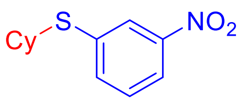
cyclohexyl(p-tolyl)sulfane (7e)

Yield: 98% (40.6mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2925, 2851, 1491, 1447, 1262, 997, 808, 738. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.01 (tt, J = 10.5, 3.7 Hz, 1H), 2.31 (s, 3H), 1.95 (ddt, J = 10.3, 3.8, 2.0 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.39 – 1.19 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.9, 132.9, 131.3, 129.6, 47.2, 33.5, 26.2, 25.9, 21.2. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{13}H_{19}S$ $(M+H)^+$: 207.1207 found 207.1207.



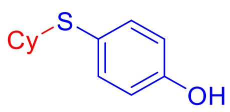
(4-chlorophenyl)(cyclohexyl)sulfane (7f)

Yield: 87% (39.4mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2927, 2852, 1474, 1447, 1389, 1094, 1012, 817, 745. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 3.05 (ddt, J = 10.5, 7.3, 3.6 Hz, 1H), 2.00 – 1.91 (m, 2H), 1.76 (ddt, J = 10.9, 5.4, 2.2 Hz, 2H), 1.42 – 1.18 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.8, 133.3, 132.8, 129.0, 47.0, 33.3, 26.1, 25.8. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{12}H_{16}ClS$ $(M+H)^+$: 227.0661 found 227.0661.



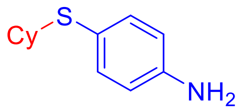
cyclohexyl(3-nitrophenyl)sulfane (7g)

Yield: 78% (36.8mg). Pale yellow oil. **IR** (neat, ν, cm^{-1}): 2928, 2852, 1522, 1344, 1265, 1127, 749, 670. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (m, J = 2.1 Hz, 1H), 8.02 (m, J = 8.2, 2.2 Hz, 1H), 7.65 (m, J = 7.8 Hz, 1H), 7.44 (m, J = 8.0 Hz, 1H), 3.26 (dp, J = 10.1, 3.8 Hz, 1H), 2.05 – 1.95 (m, 2H), 1.80 (dq, J = 7.7, 3.7 Hz, 2H), 1.69 – 1.60 (m, 1H), 1.42 (dd, J = 16.5, 6.6 Hz, 3H), 1.36 – 1.25 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 138.7, 136.4, 129.5, 124.9, 121.0, 46.4, 33.2, 26.0, 25.7. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{12}H_{16}NO_2S$ $(M+H)^+$: 238.0902 found 238.0902.



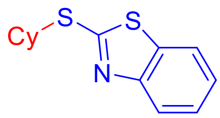
4-(cyclohexylthio)phenol (7h)

Yield: 49% (20.4mg). Yellow oil. **IR** (neat, ν, cm^{-1}): 2925, 2850, 1708, 1598, 1582, 1426, 1201, 1094, 827, 523. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 6.82 – 6.73 (m, 2H), 5.64 (s, 1H), 2.89 (ddt, J = 10.6, 7.3, 3.7 Hz, 1H), 1.97 – 1.87 (m, 2H), 1.74 (td, J = 6.0, 5.4, 3.0 Hz, 2H), 1.61 – 1.53 (m, 1H), 1.36 – 1.26 (m, 3H), 1.25 – 1.17 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 135.9, 125.0, 116.0, 48.1, 33.4, 26.2, 25.9. **HRMS** (ESI$^+$, MeCN) m/z calcd for $C_{12}H_{17}OS$ $(M+H)^+$: 209.1000 found 209.1003.



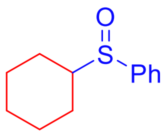
4-(cyclohexylthio)aniline (7i)

Yield: 52% (21.4mg). Yellow oil. **IR** (neat, ν, cm^{-1}): 2924, 2850, 1724, 1619, 1493, 1263, 1175, 996, 821, 520. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 6.64 – 6.56 (m, 2H), 3.39 (s, 2H), 2.82 (tt, J = 10.6, 3.8 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.77 – 1.71 (m, 2H), 1.60 – 1.53 (m, 1H), 1.36 – 1.27 (m, 2H), 1.26 – 1.20 (m, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ146.3, 136.1, 121.9, 115.4, 48.2, 33.5, 26.3, 25.9. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{18}NS$ $(M+H)^+$: 208.1160 found 208.1161.



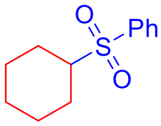
2-(cyclohexylthio)benzo[d]thiazole (7j)

Yield: 86% (43.0mg). Yellow oil. **IR** (neat, ν, cm^{-1}): 2926, 2851, 1455, 1424, 1236, 1076, 985, 752, 724. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.87 (m, J = 8.3, 1.1 Hz, 1H), 7.72 (m, J = 7.9, 1.2 Hz, 1H), 7.39 (m, J = 8.3, 7.2, 1.3 Hz, 1H), 7.29 – 7.24 (m, 1H), 3.89 (tt, J = 10.3, 3.8 Hz, 1H), 2.23 – 2.14 (m, 2H), 1.84 – 1.73 (m, 2H), 1.59 (dddd, J = 26.8, 13.1, 9.8, 4.0 Hz, 3H), 1.51 – 1.40 (m, 2H), 1.38 – 1.29 (m, 1H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 166.5, 153.5, 135.4, 126.0, 124.2, 121.6, 120.9, 47.4, 33.4, 25.9, 25.7. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{13}H_{16}NS_2$ $(M+H)^+$: 250.0724 found 250.0724.

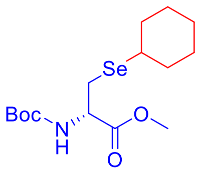


(cyclohexylsulfinyl)benzene (8a) According to Bahrami's method[3], in a round-bottomed flask (10 mL) equipped with a stir bar, a solution of **7c** (57.6 mg, 0.30 mmol) in CH_3CN (2 mL) was prepared. Aqueous 30% H_2O_2 (0.6 mmol, 0.8 mL) and Me_3SiCl (0.30 mmol, 38μL) were added and the mixture was stirred at 25 °C for 10 min. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (20 mL), extracted with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel (20→100% ethyl acetate/Petroleum ether).

Yield: 88% (54.9mg). Colorless oil. **IR** (neat, ν, cm^{-1}): 2929, 2854, 1443, 1083, 1036, 1022, 748, 691, 532. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.59 (m, J = 7.0, 2.7 Hz, 2H), 7.55 – 7.45 (m, 3H), 2.57 (tt, J = 11.7, 3.4 Hz, 1H), 1.90 – 1.78 (m, 4H), 1.64 (ddt, J = 9.7, 4.8, 1.6 Hz, 1H), 1.52 – 1.33 (m, 2H), 1.31 – 1.18 (m, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 141.8, 131.0, 128.9, 125.0, 63.2, 26.3, 25.6, 25.5, 25.4, 24.0. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{17}OS$ $(M+H)^+$: 209.1000 found 209.1000.



(cyclohexylsulfonyl)benzene (8b) According to Fang's method[4], in a round-bottomed flask (10 mL) equipped with a stir bar, a solution of **7c** (57.6 mg, 0.30 mmol) in CH_2Cl_2 (2.0 mL) was prepared. The solution was cooled to 0 °C. A solution of *m*-CPBA (purity: 85%, 207.1 mg, 1.2 mmol) in CH_2Cl_2 (10.0 mL) was added dropwise and the mixture was stirred at 25 °C. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (20 mL), extracted with EtOAc (3 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel (10→20% ethyl acetate/Petroleum ether).
Yield: 78% (52.4mg). Colorless oil. **IR** (neat, ν, cm^{-1}): 2932, 2856, 1446, 1302, 1142, 1084, 821, 689, 599. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.69 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 2.91 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.12 – 2.00 (m, 2H), 1.86 (dq, *J* = 12.7, 3.2 Hz, 2H), 1.67 (dddd, *J* = 10.9, 4.9, 2.9, 1.5 Hz, 1H), 1.41 (qd, *J* = 12.4, 3.2 Hz, 2H), 1.28 – 1.10 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ137.3, 133.6, 129.1, 129.0, 63.5, 25.5, 25.1, 25.1. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{12}H_{16}O_2SNa$ $(M+Na)^+$: 247.0769 found 247.0772.



methyl (*S*)-2-((tert-butoxycarbonyl)amino)-3-(cyclohexylselanyl)propanoate (3r)
Yield: 55% (40.2mg). Yellow oil. **IR** (neat, ν, cm^{-1}): 2926, 2851, 1745, 1713, 1495, 1347, 1209, 1160, 1007. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 8.0 Hz, 1H), 4.61 (dt, *J* = 9.4, 5.0 Hz, 1H), 3.76 (s, 3H), 2.99 (d, *J* = 5.1 Hz, 2H), 2.92 (ddd, *J* = 10.7, 7.0, 3.7 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.77 – 1.69 (m, 3H), 1.63 – 1.58 (m, 1H), 1.45 (s, 9H), 1.34 – 1.24 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 155.1, 80.0, 53.5, 52.5, 39.5, 34.5, 34.4 (*J*=3.5), 28.3, 26.8, 25.7, 24.3. **HRMS** (ESI^+, MeCN) m/z calcd for $C_{15}H_{27}NO_4S_e$ $(M+Na)^+$: 388.1003 found 388.0989.

IV. References

(1) (a) Jouffory, M.; Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc*. **2016**, *138*, 475. (b) Corcé, V.; Chamoreau, L. M.; Derat, E.; Goddard, J. P.; Ollivier, C.; Fensterbank, L. *Angew. Chem. Int. Ed*. **2015**, *54*, 11414.

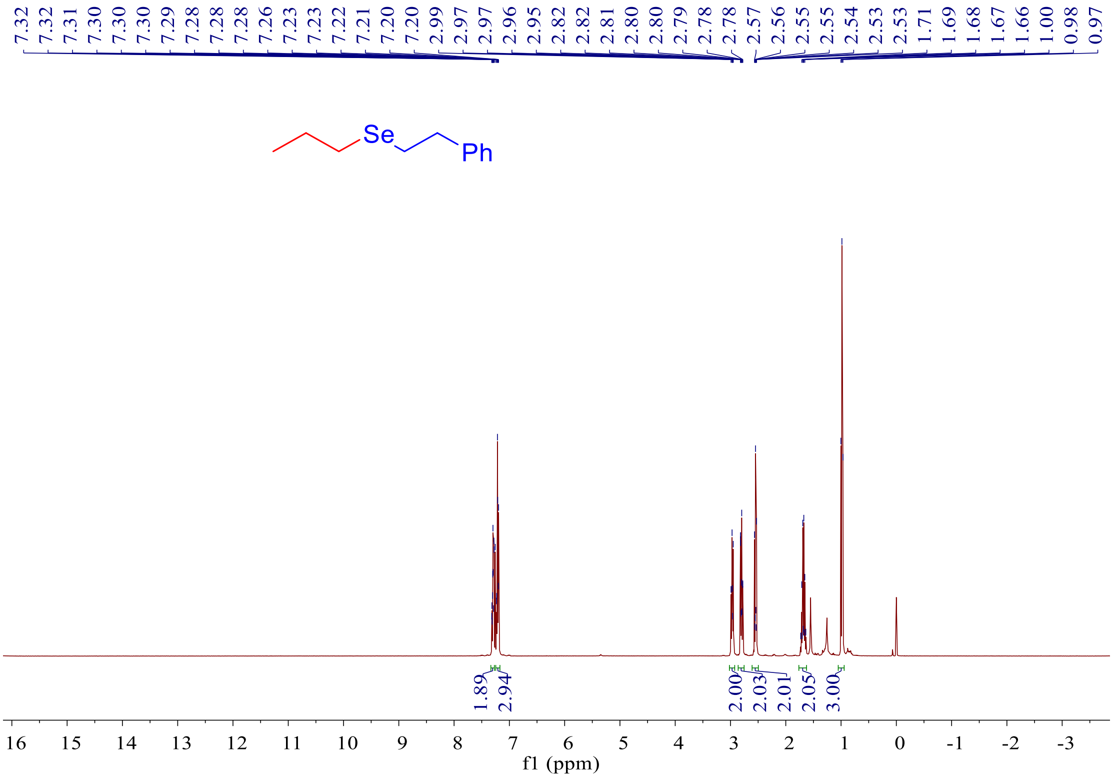
(2) (a) Li, J.; Rao, W.; Wang, S.-Y.; Ji, S.-J. *J. Org. Chem*. **2019**, *84*, 11542. (b) Fang, Y.; Rogge, T.; Ackermann, L.; Wang, S.-Y.; Ji, S.-J. *Nat. Commun*. **2018**, *9*, 2240.

(3) Bahrami, K., Khodaei, M. M., Yousefi, B. H., Arabi, M. S. *Tetrahedron Lett*. **2010**, *51*, 6939-6941.

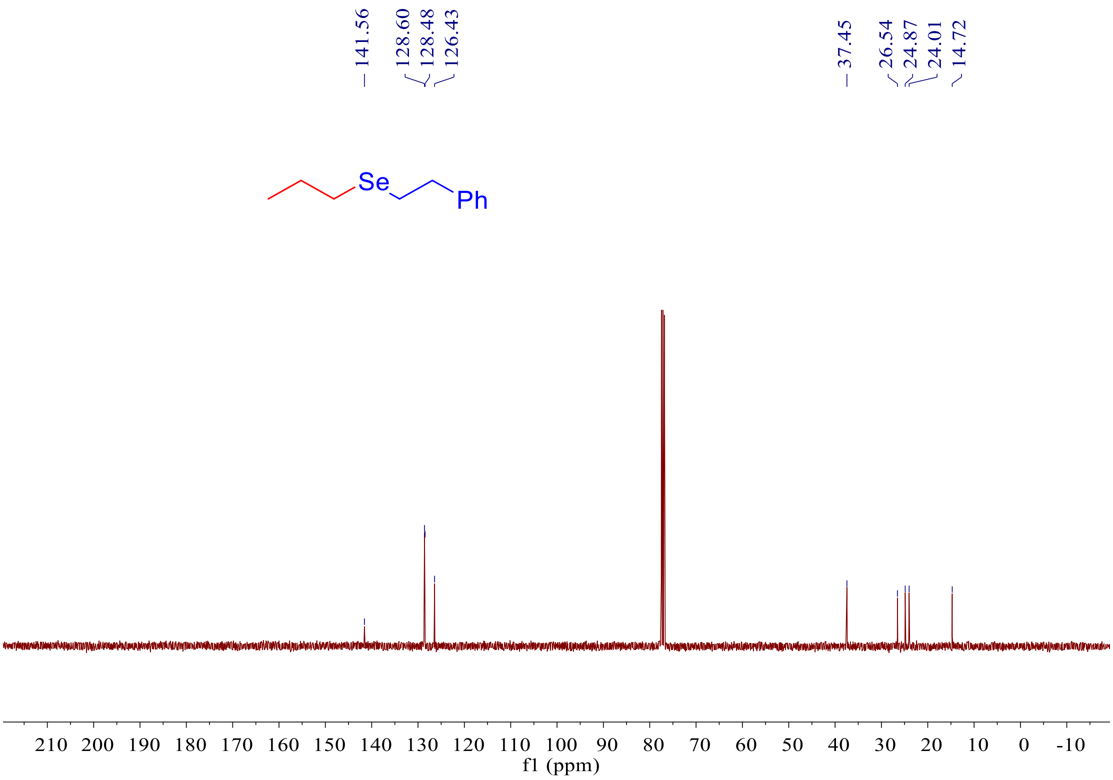
(4) Fang, Y.; Rogge, T.; Ackermann, L.; Wang, S.-Y.; Ji, S.-J. *Nat. Commun*. **2018**, *9*, 2240.

V. Copies of ^{1}H NMR and ^{13}C NMR Spectra

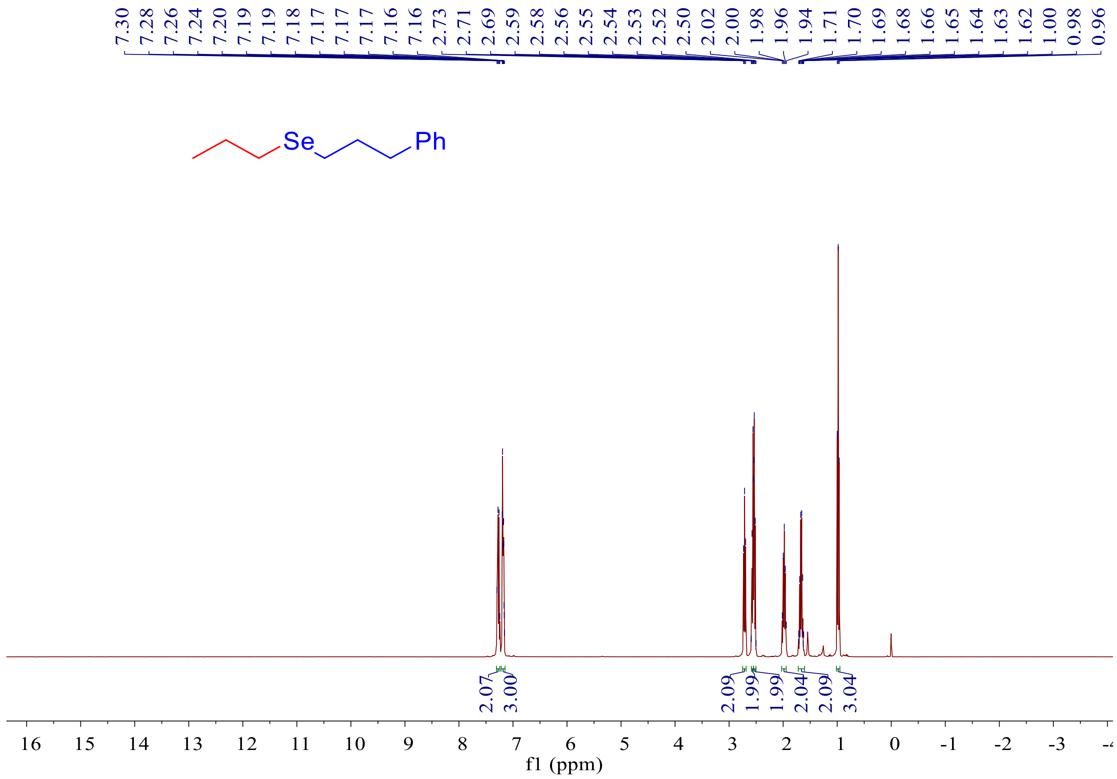
^{1}H NMR Spectra of **3a** (400 MHz, $CDCl_3$)



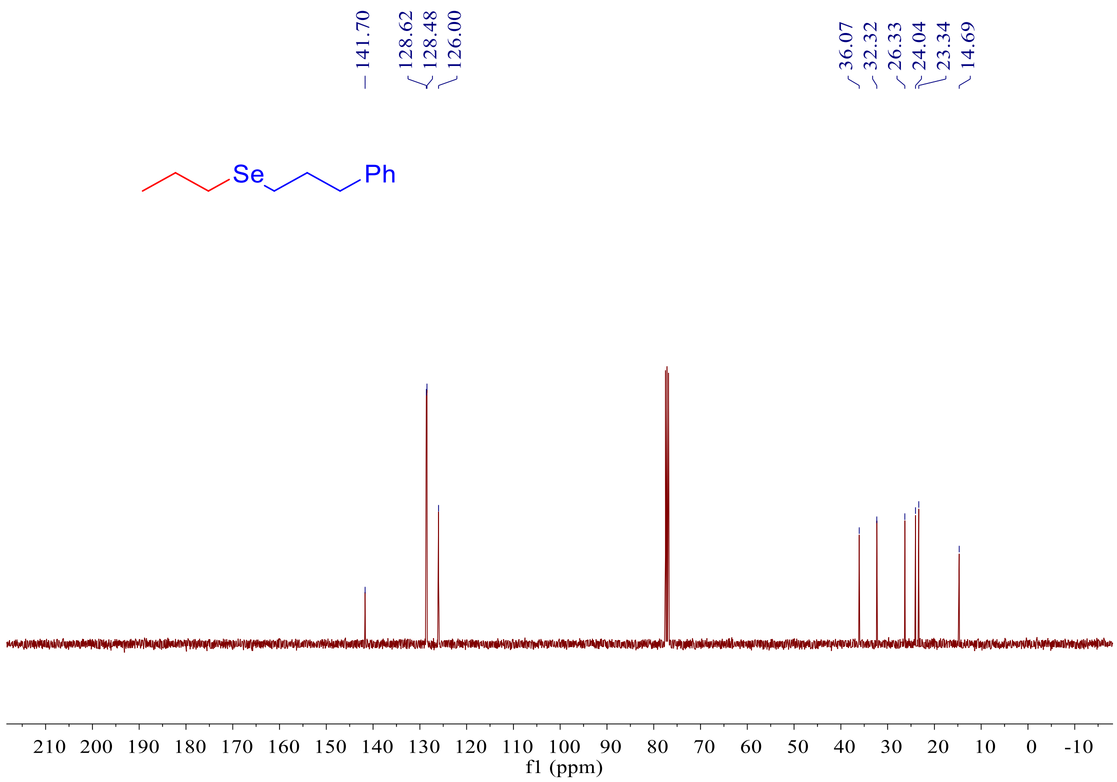
^{13}C NMR Spectra of **3a** (400 MHz, $CDCl_3$)



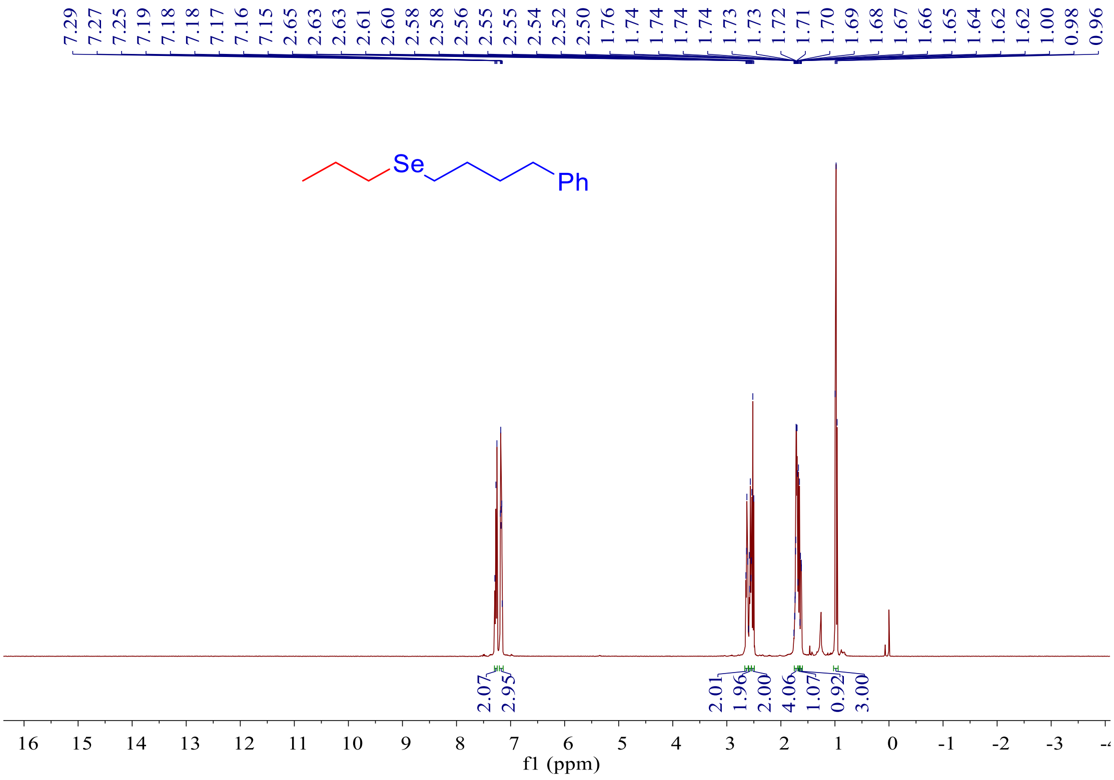
[1]H NMR Spectra of **3b** (400 MHz, $CDCl_3$)



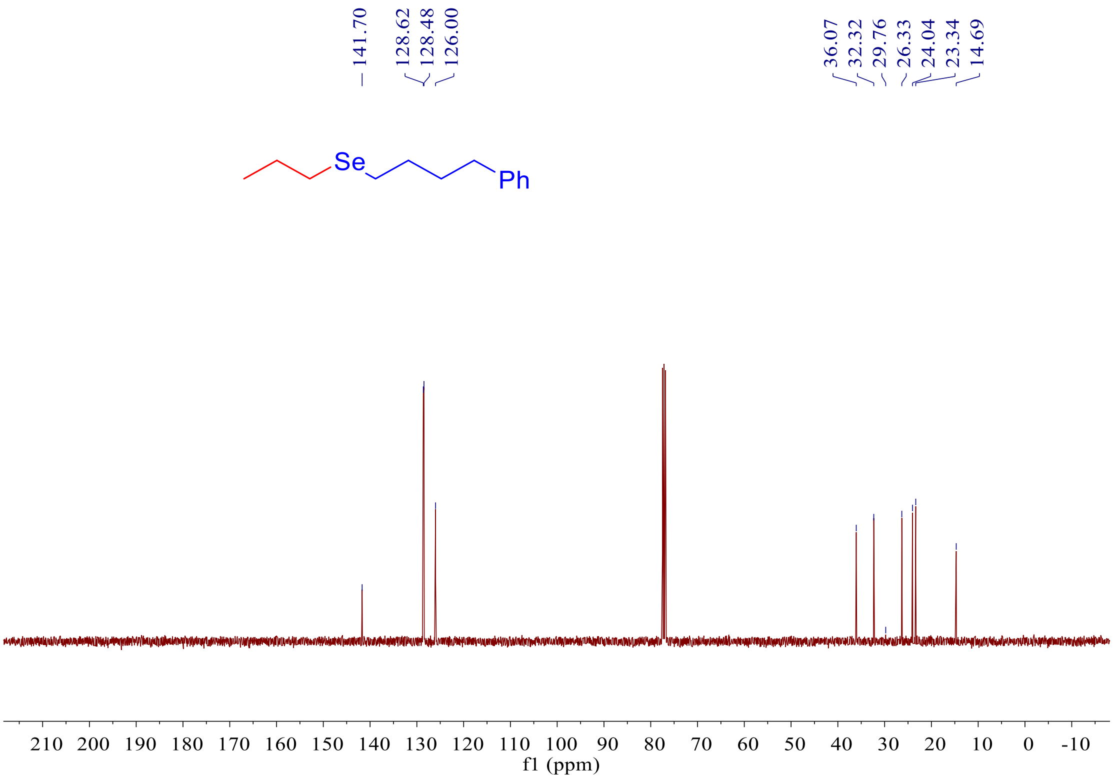
[13]C NMR Spectra of **3b** (400 MHz, $CDCl_3$)



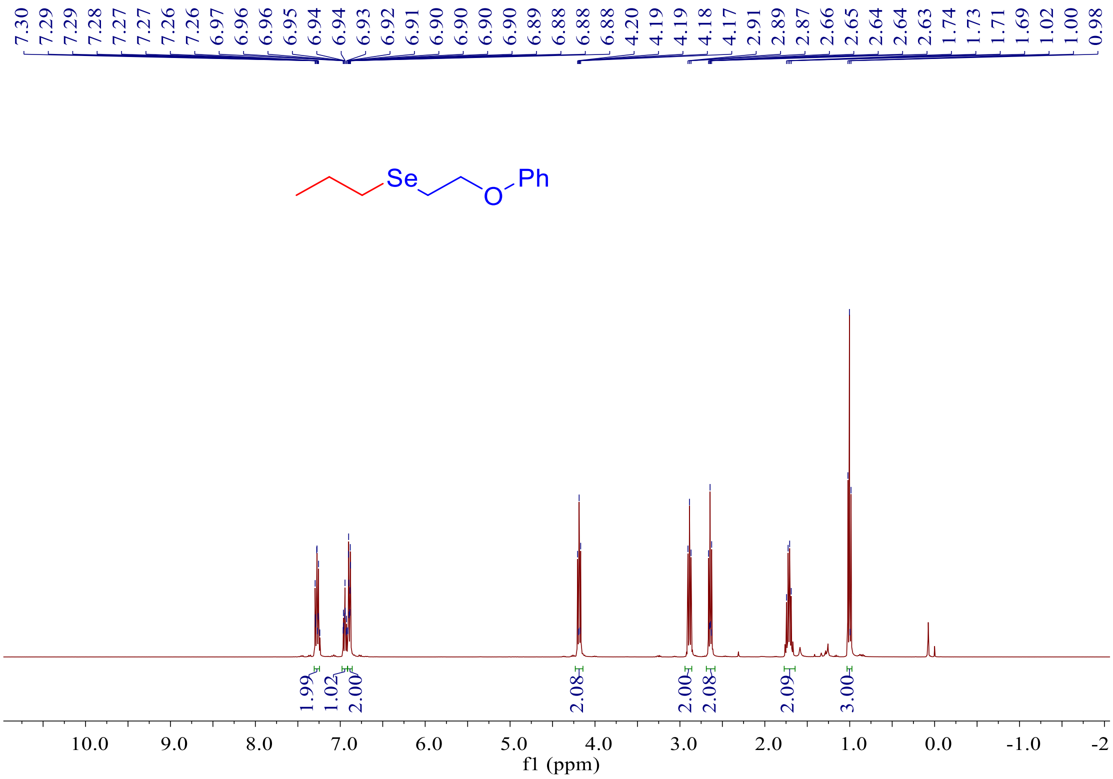
[1]H NMR Spectra of **3c** (400 MHz, $CDCl_3$)



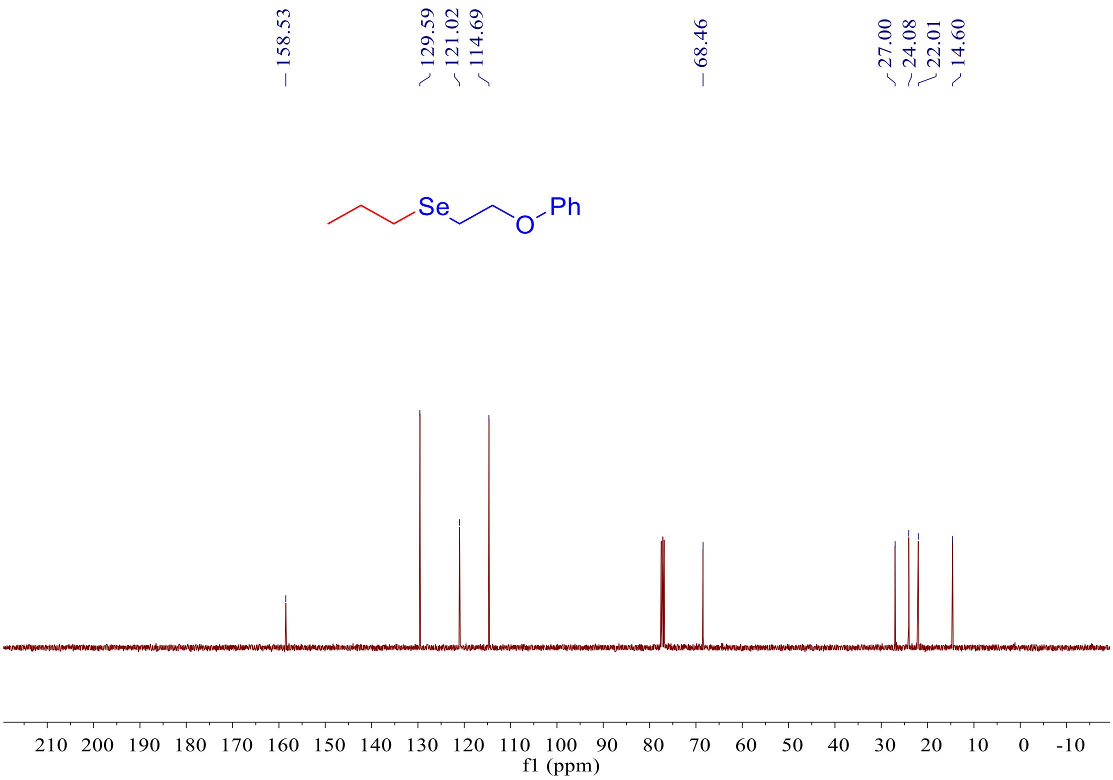
[13]C NMR Spectra of **3c** (400 MHz, $CDCl_3$)



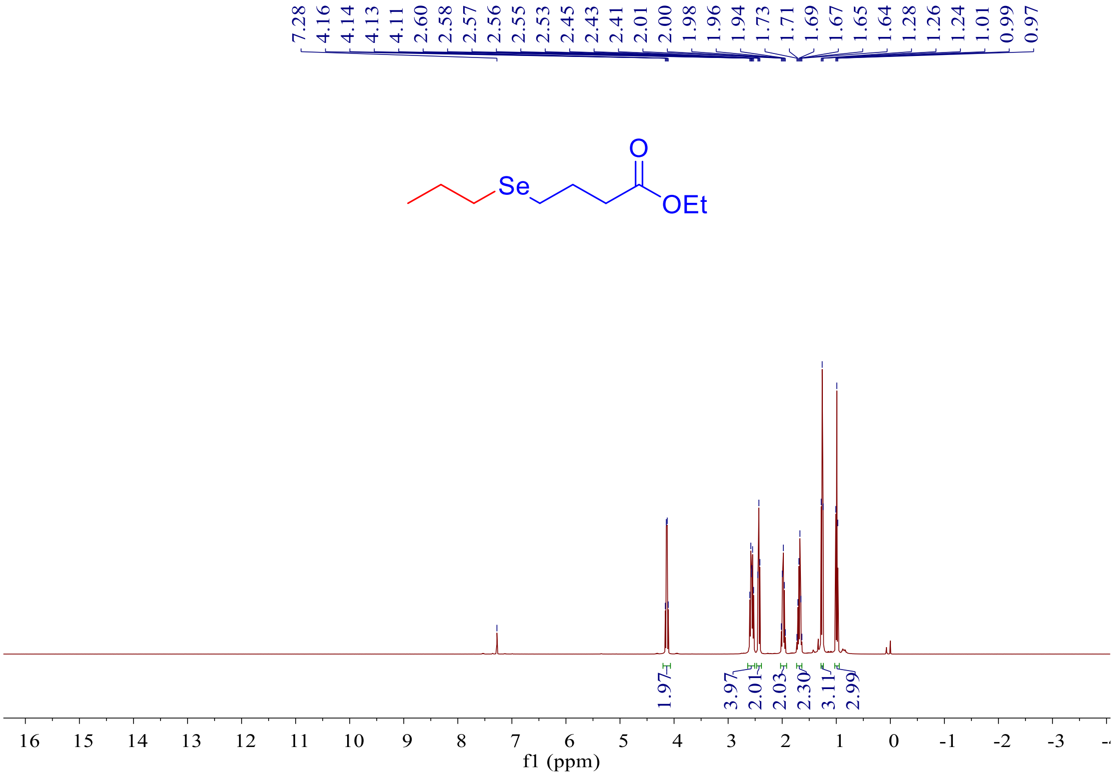
^{1}H NMR Spectra of **3d** (400 MHz, $CDCl_3$)



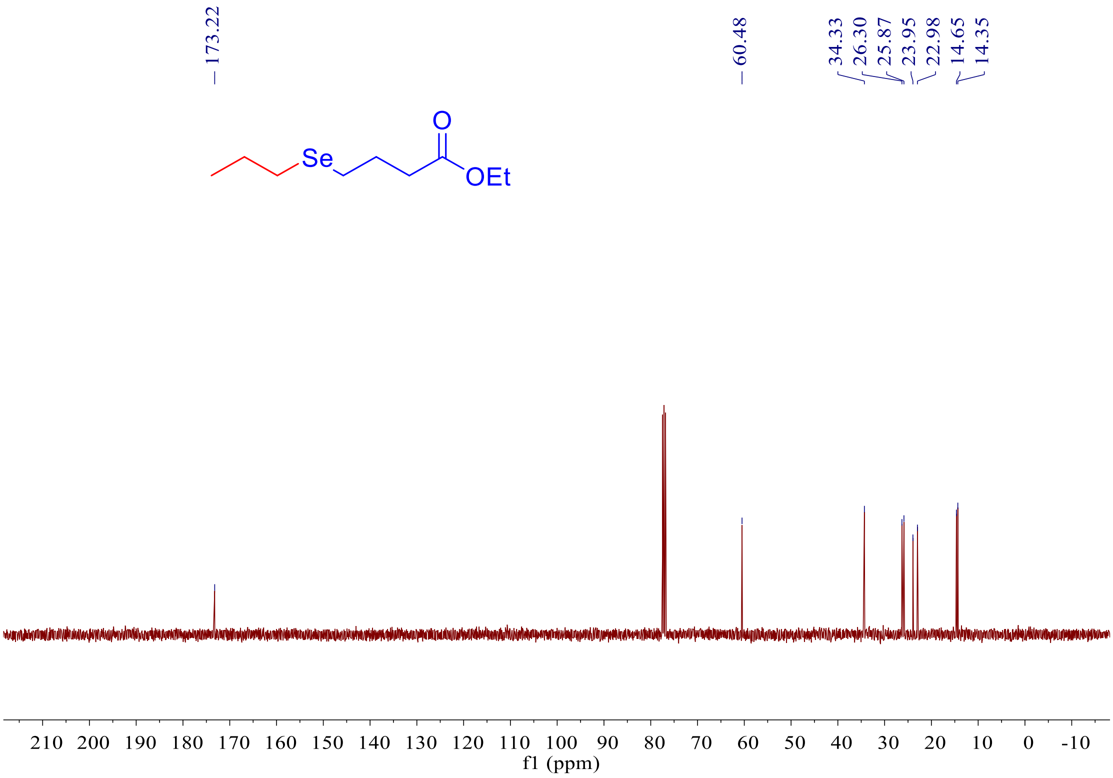
^{13}C NMR Spectra of **3d** (400 MHz, $CDCl_3$)



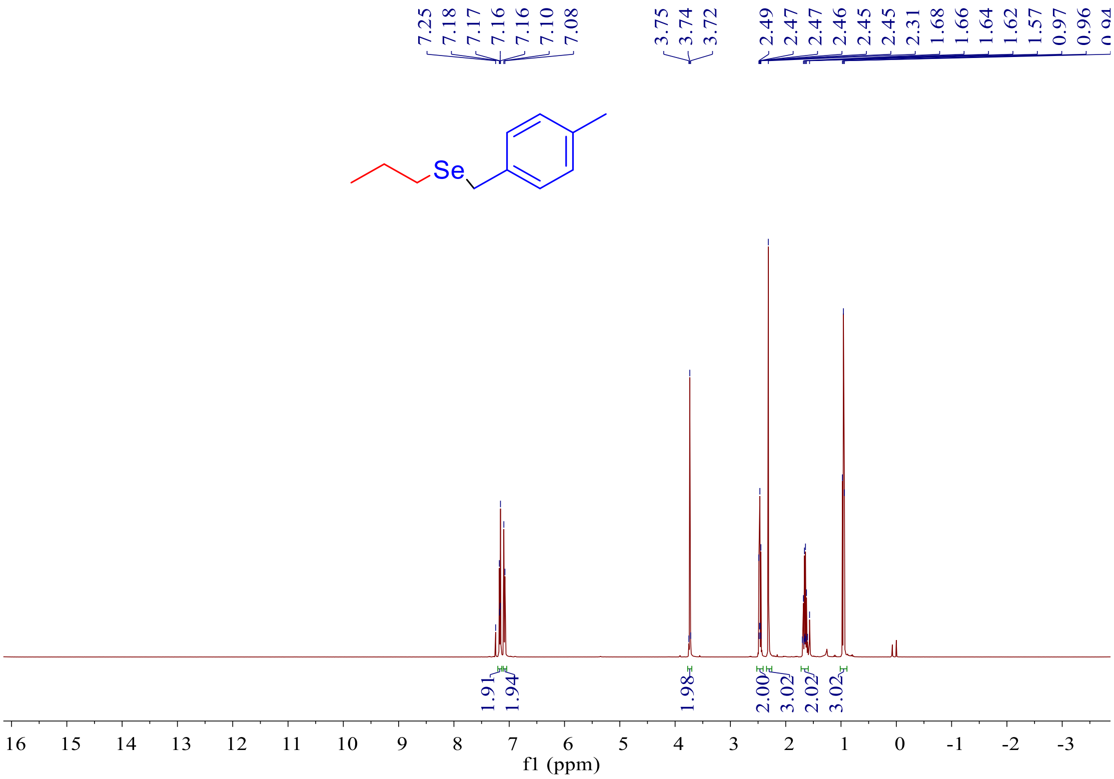
^{1}H NMR Spectra of **3e** (400 MHz, $CDCl_3$)



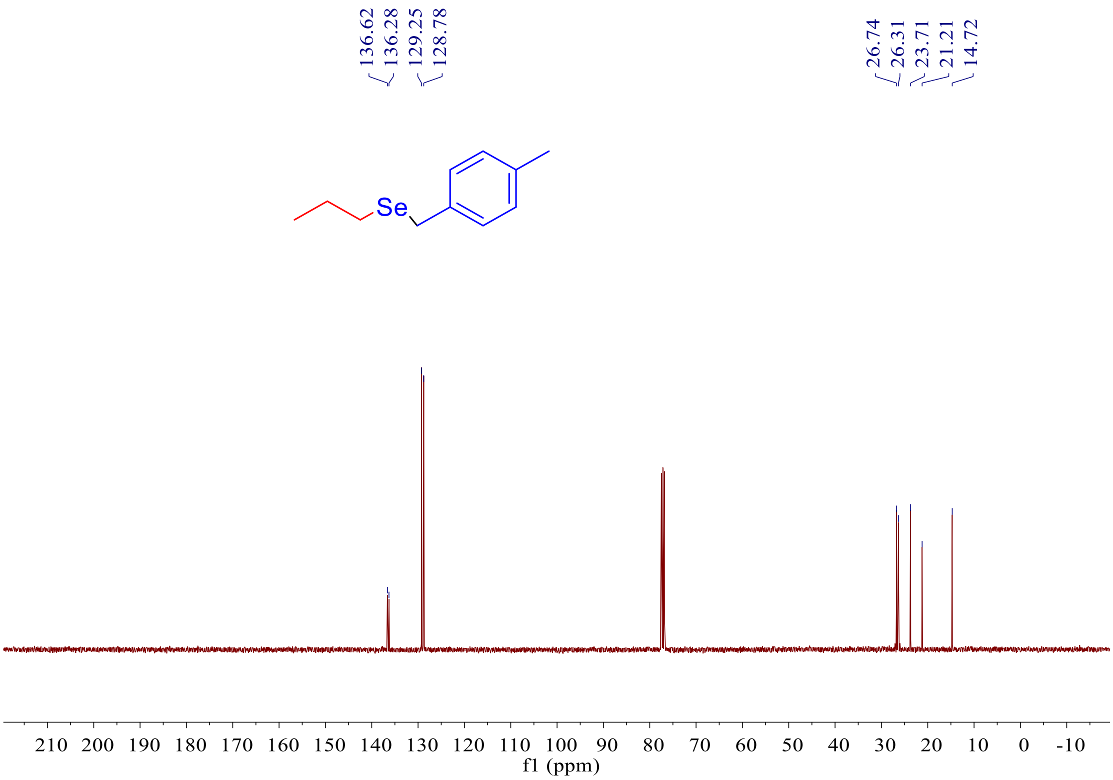
^{13}C NMR Spectra of **3e** (400 MHz, $CDCl_3$)



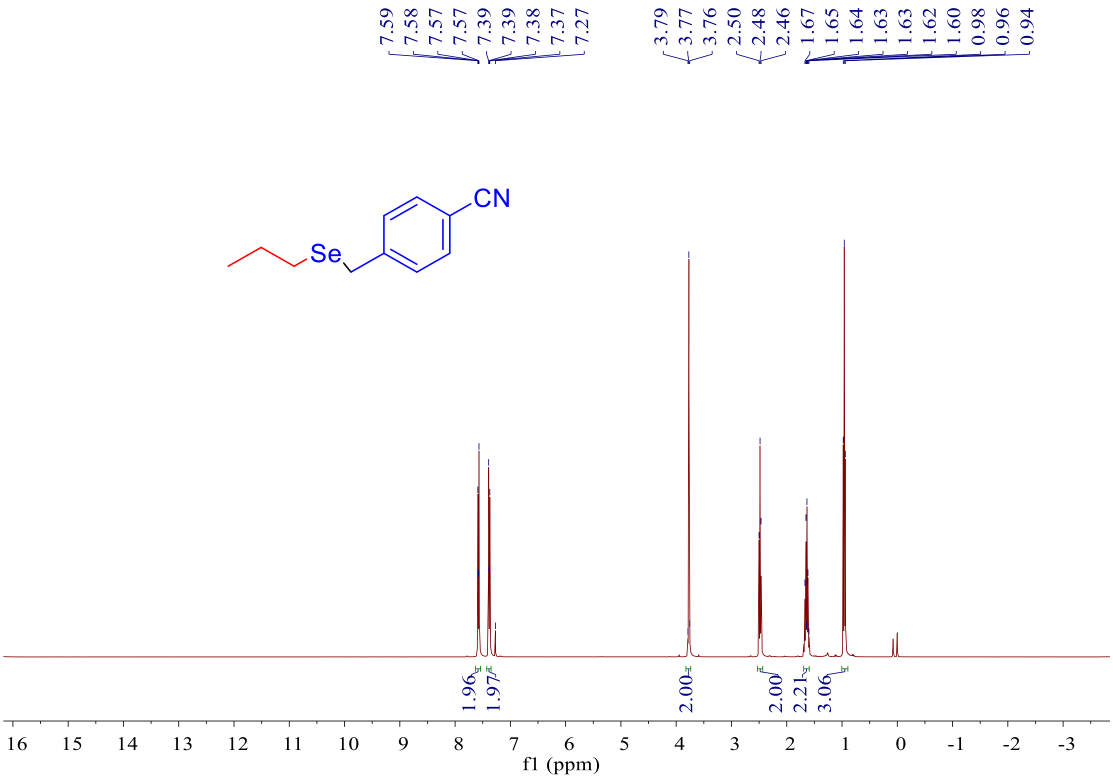
^{1}H NMR Spectra of **3f** (400 MHz, $CDCl_3$)



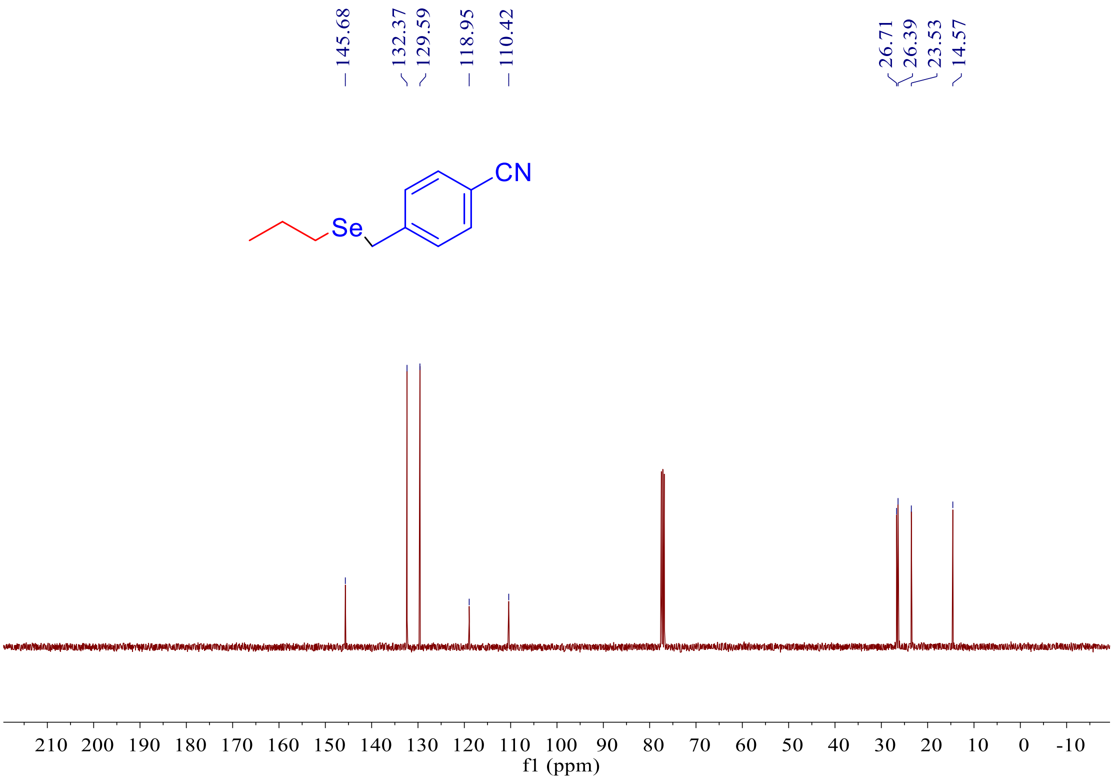
^{13}C NMR Spectra of **3f** (400 MHz, $CDCl_3$)



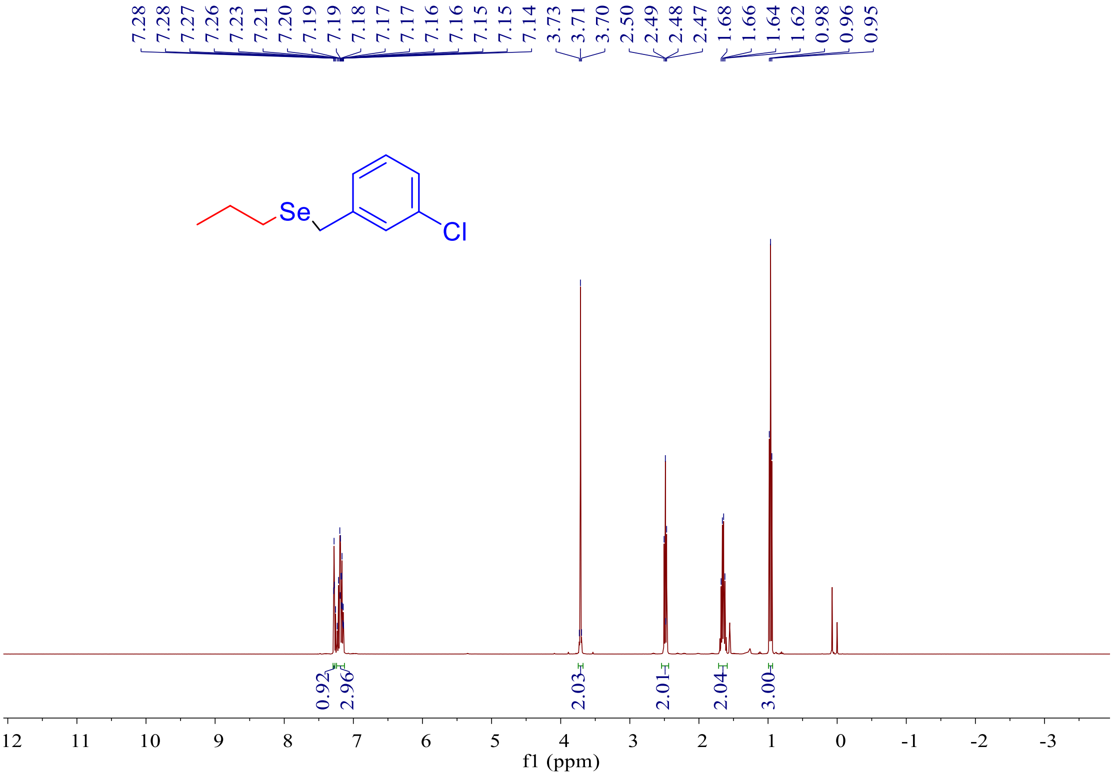
^{1}H NMR Spectra of **3g** (400 MHz, $CDCl_3$)



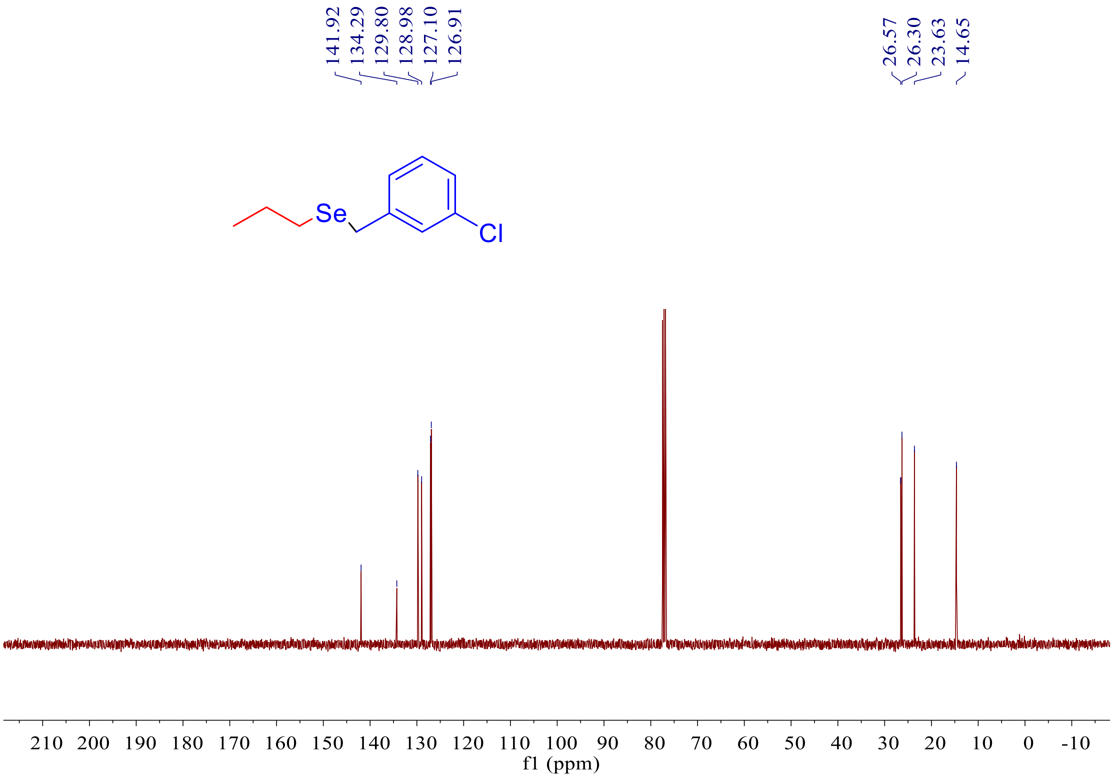
^{13}C NMR Spectra of **3g** (400 MHz, $CDCl_3$)



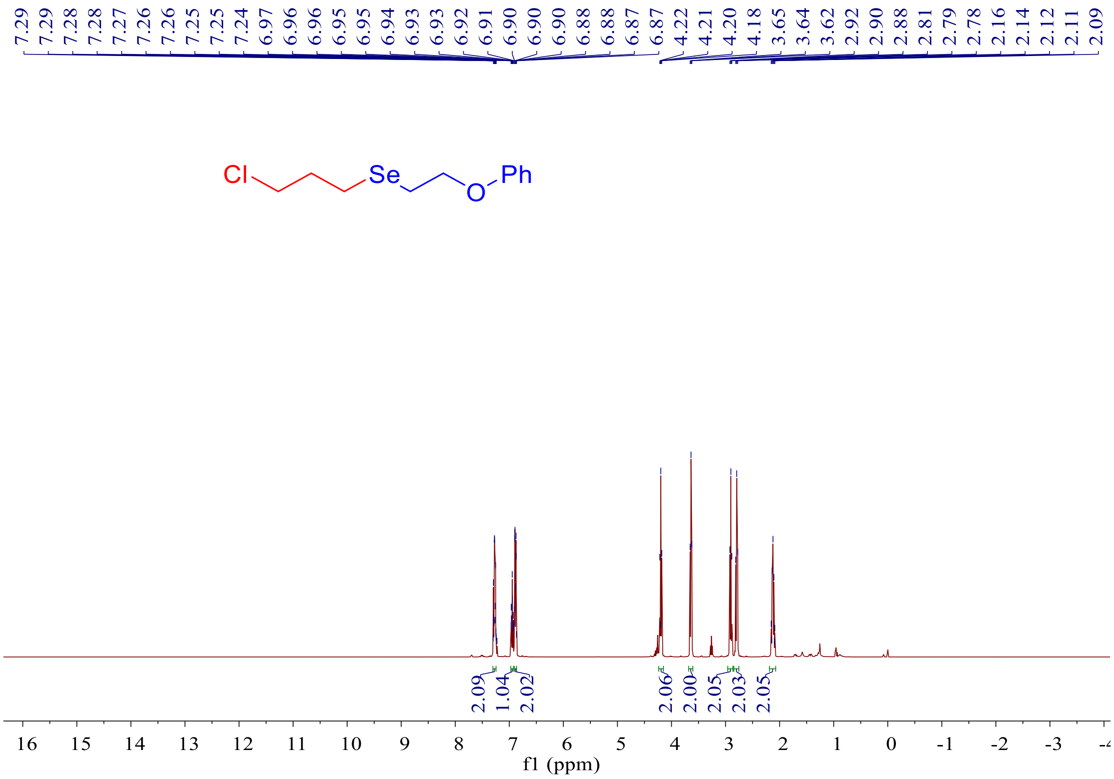
^{1}H NMR Spectra of **3h** (400 MHz, $CDCl_3$)



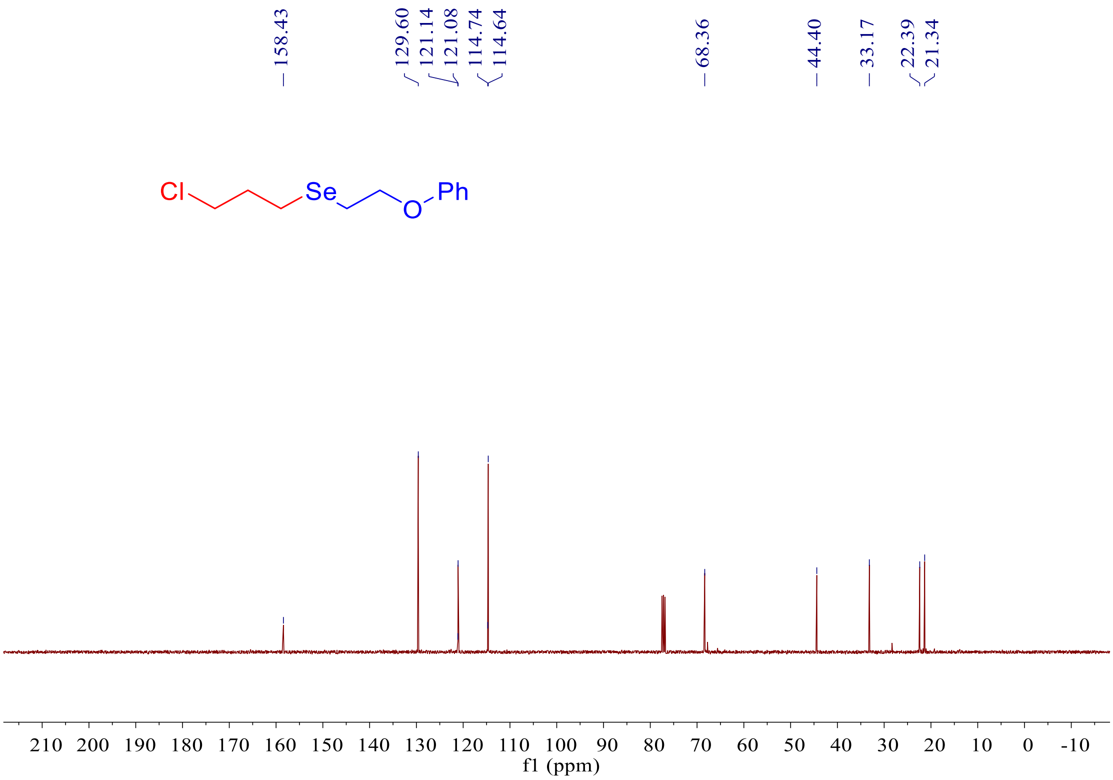
^{13}C NMR Spectra of **3h** (400 MHz, $CDCl_3$)



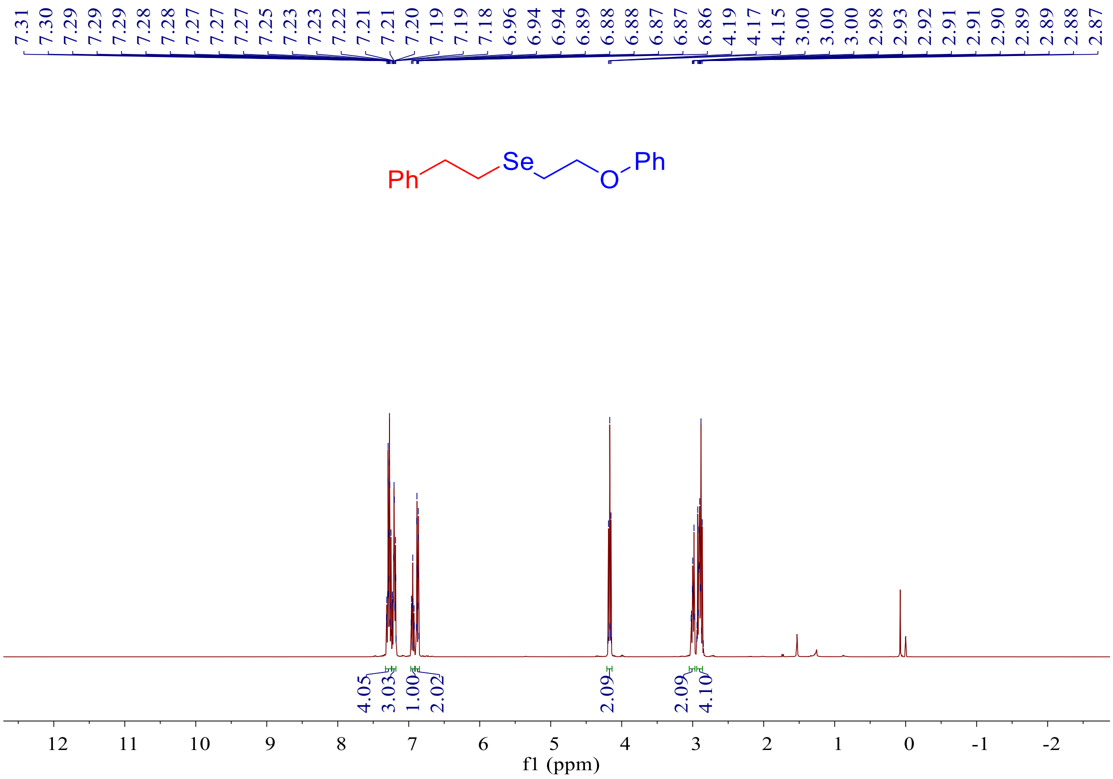
^{1}H NMR Spectra of **3i** (400 MHz, $CDCl_3$)



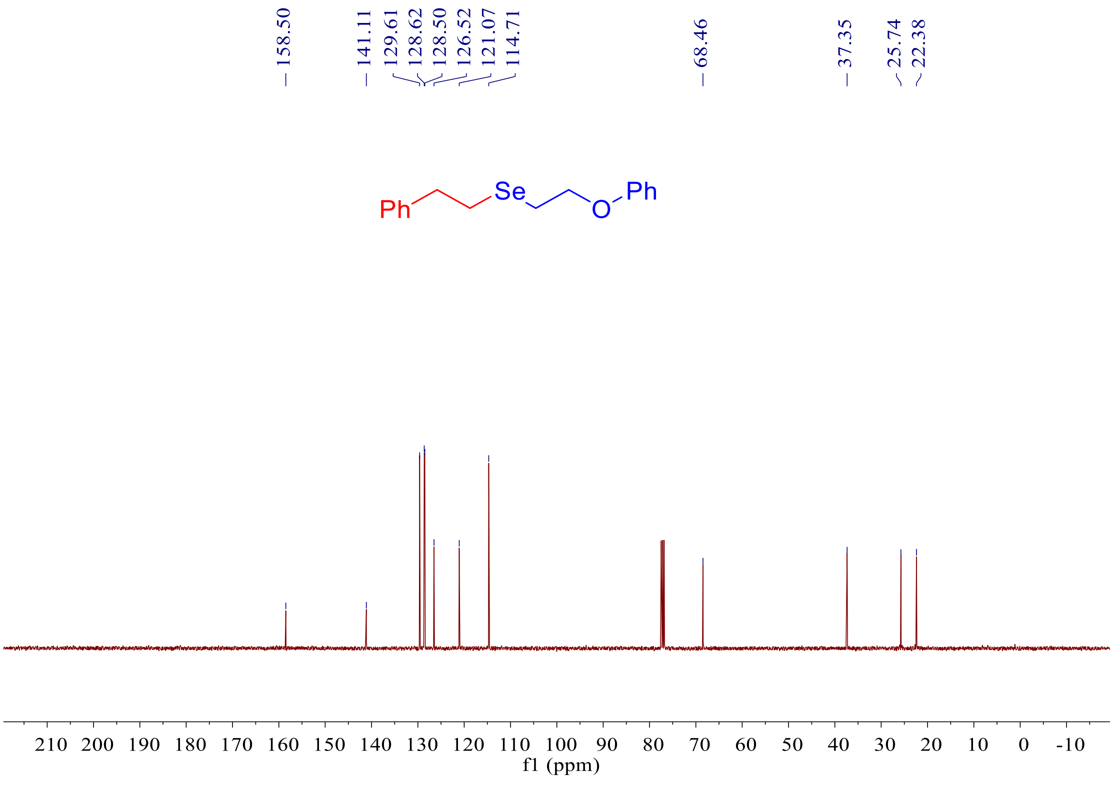
^{13}C NMR Spectra of **3i** (400 MHz, $CDCl_3$)



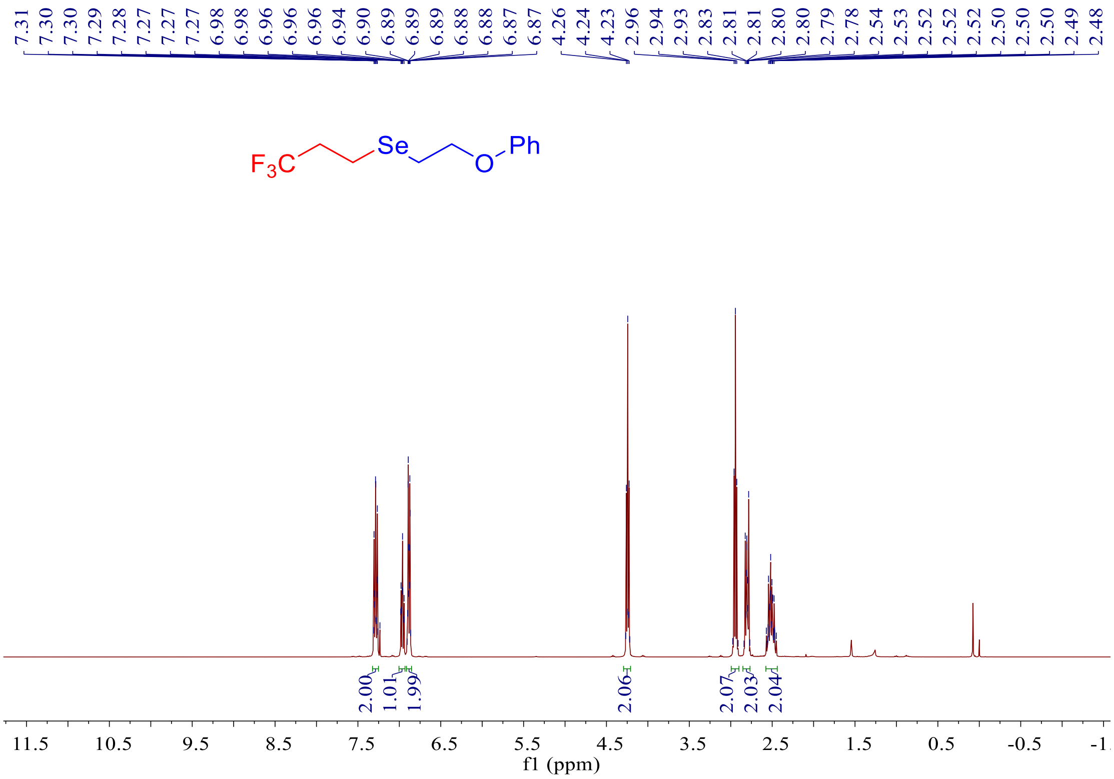
[1]H NMR Spectra of **3j** (400 MHz, $CDCl_3$)



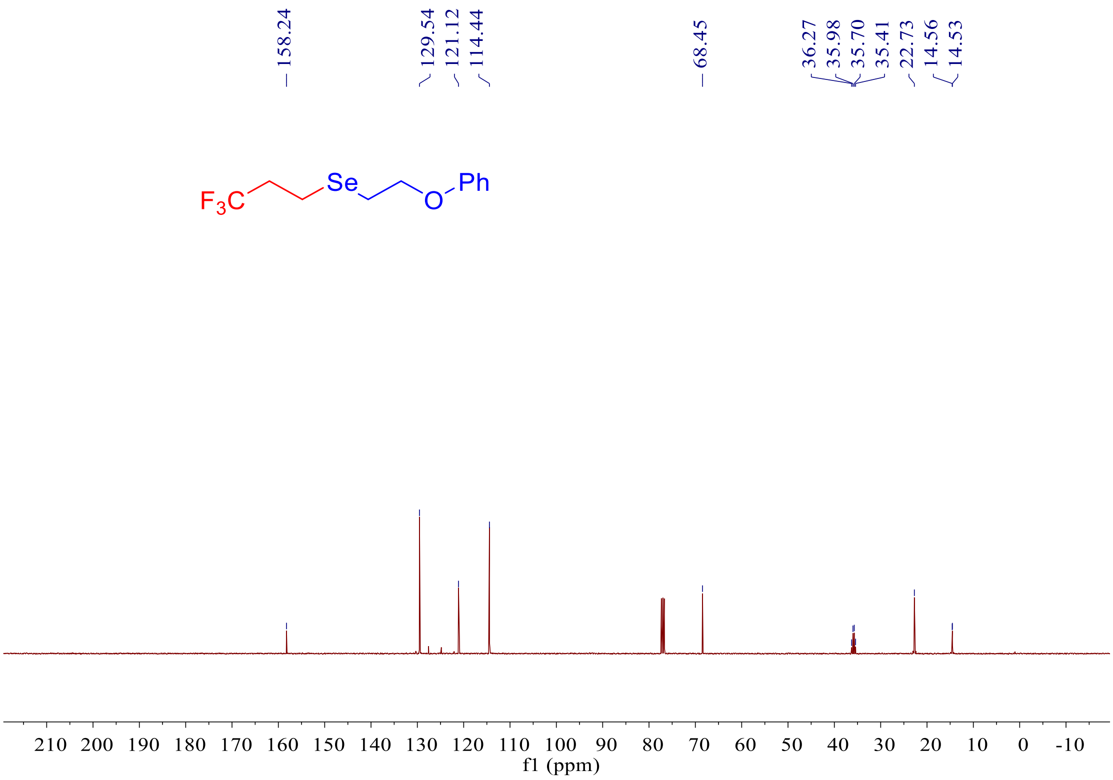
[13]C NMR Spectra of **3j** (400 MHz, $CDCl_3$)



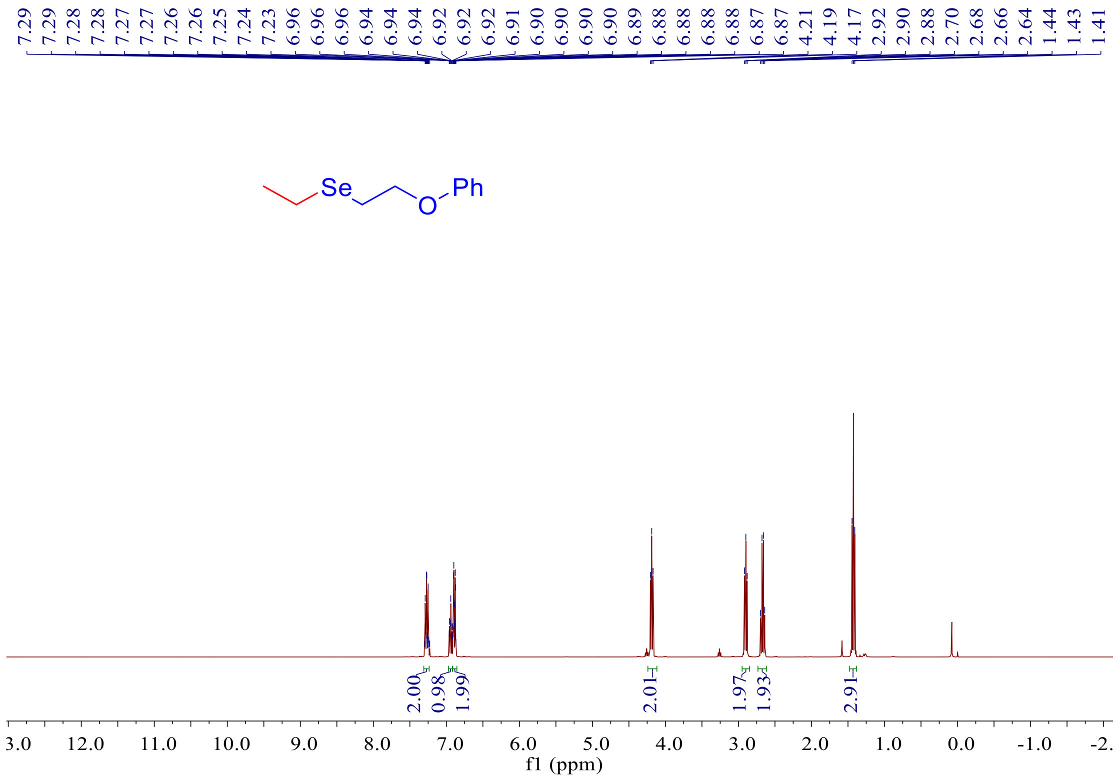
^{1}H NMR Spectra of **3k** (400 MHz, $CDCl_3$)



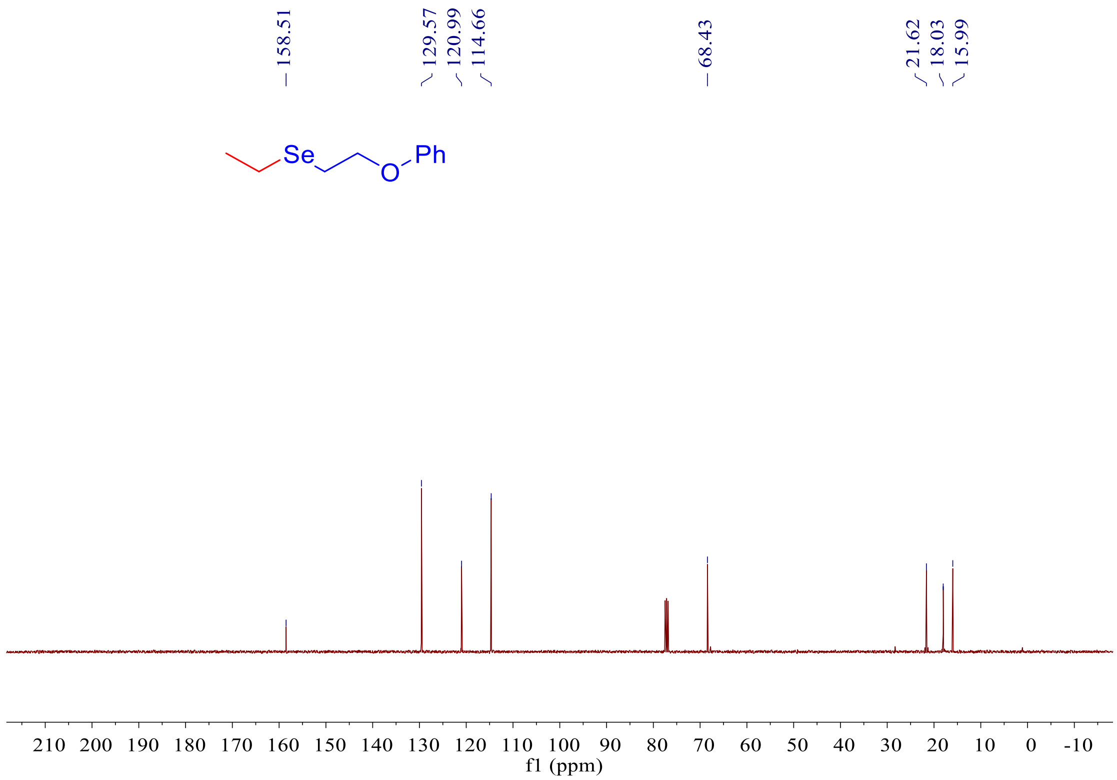
^{13}C NMR Spectra of **3k** (400 MHz, $CDCl_3$)



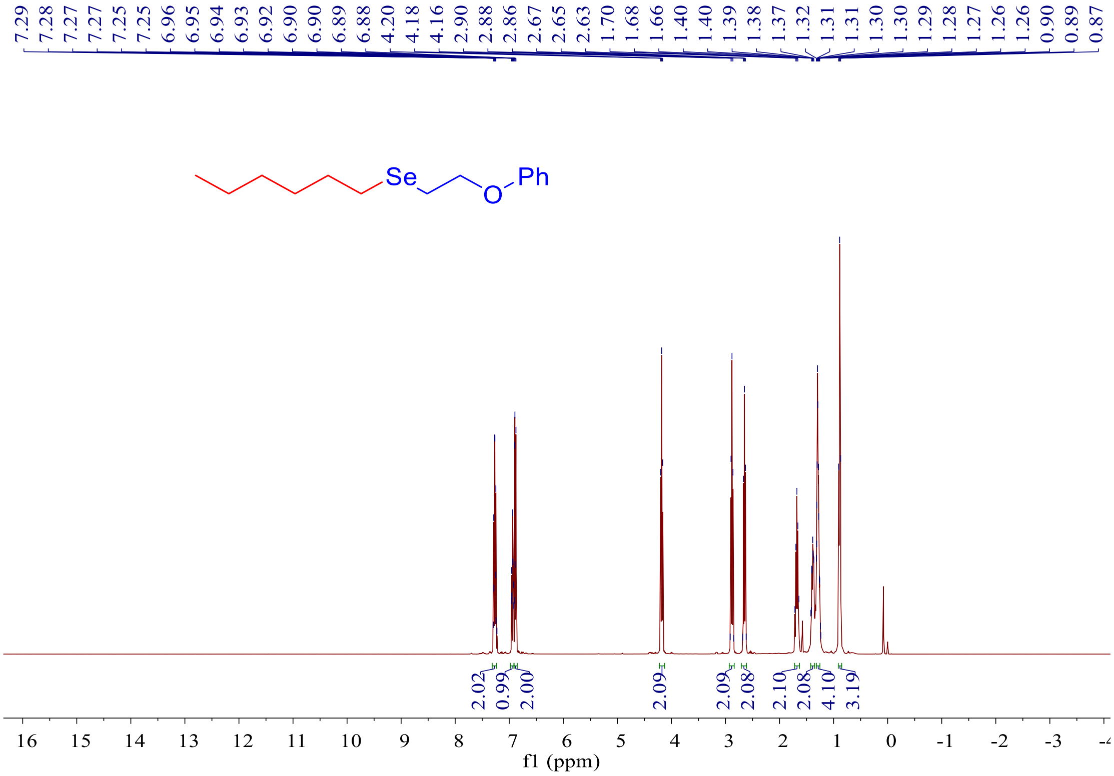
[1]H NMR Spectra of **3l** (400 MHz, $CDCl_3$)



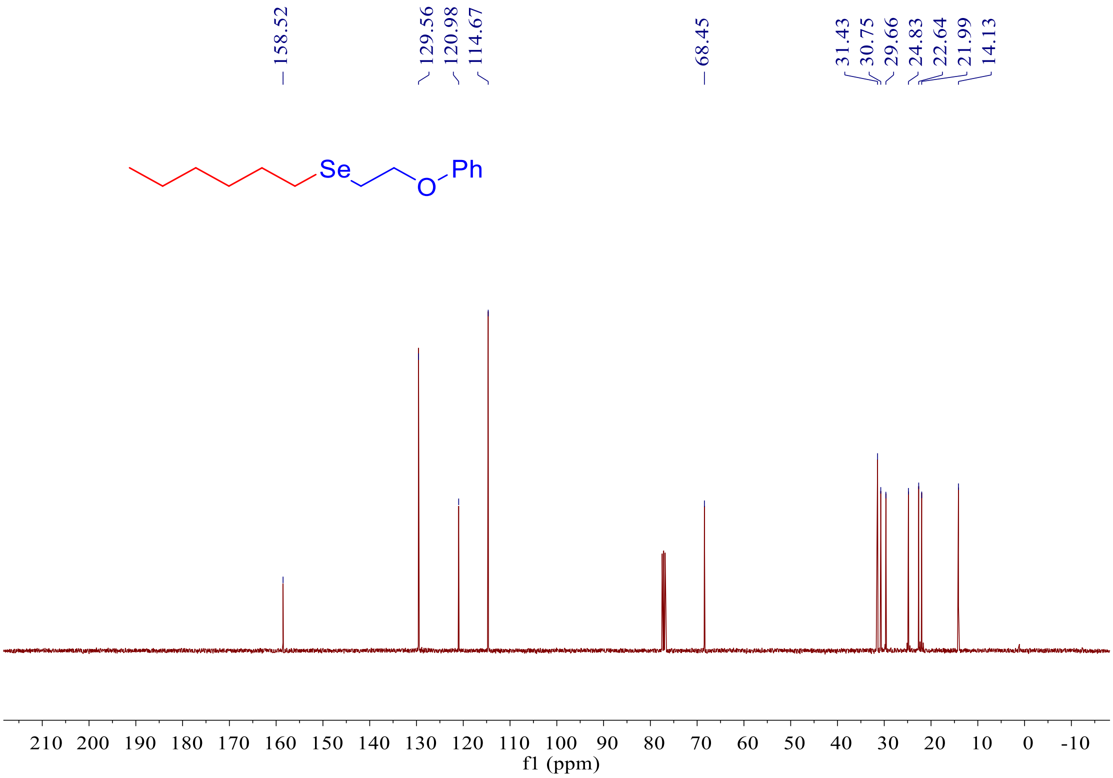
[13]C NMR Spectra of **3l** (400 MHz, $CDCl_3$)



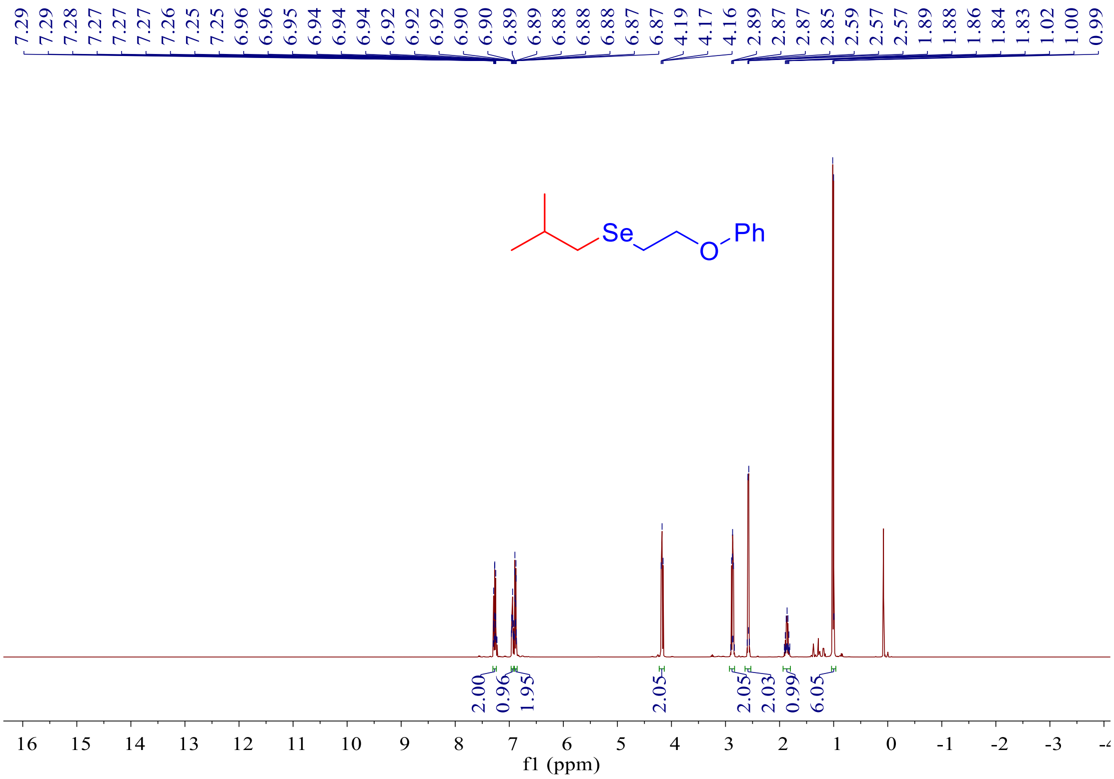
[1]H NMR Spectra of **3m** (400 MHz, $CDCl_3$)



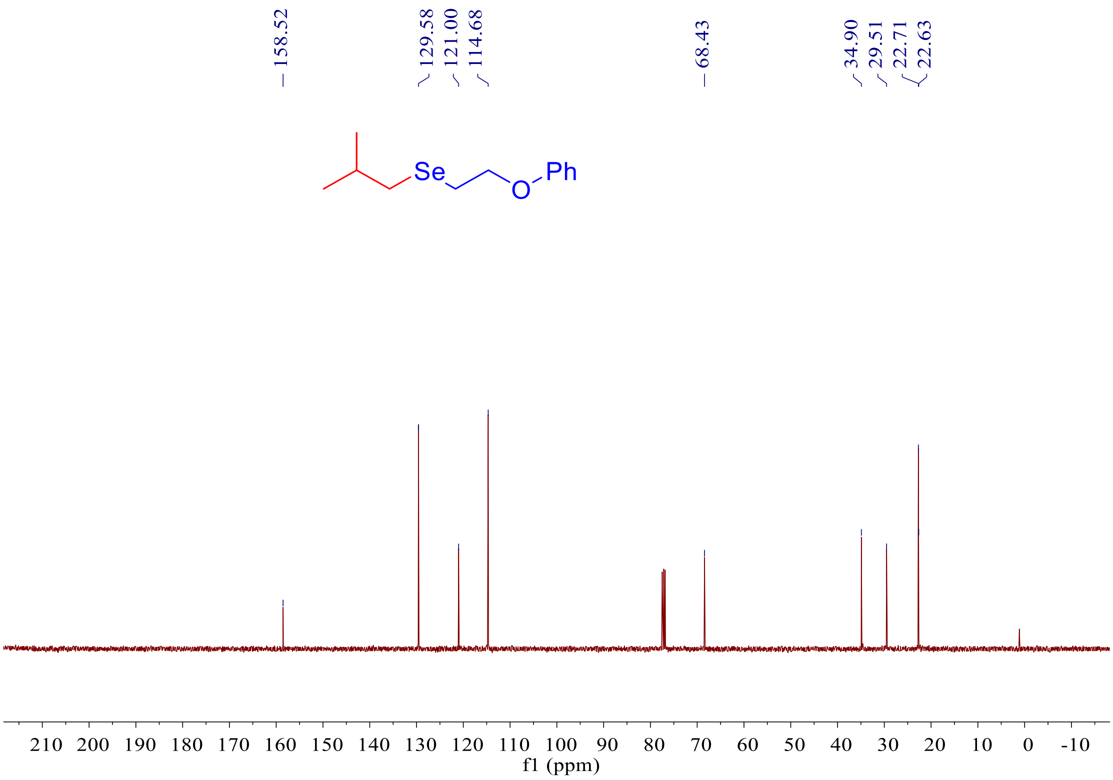
[13]C NMR Spectra of **3m** (400 MHz, $CDCl_3$)



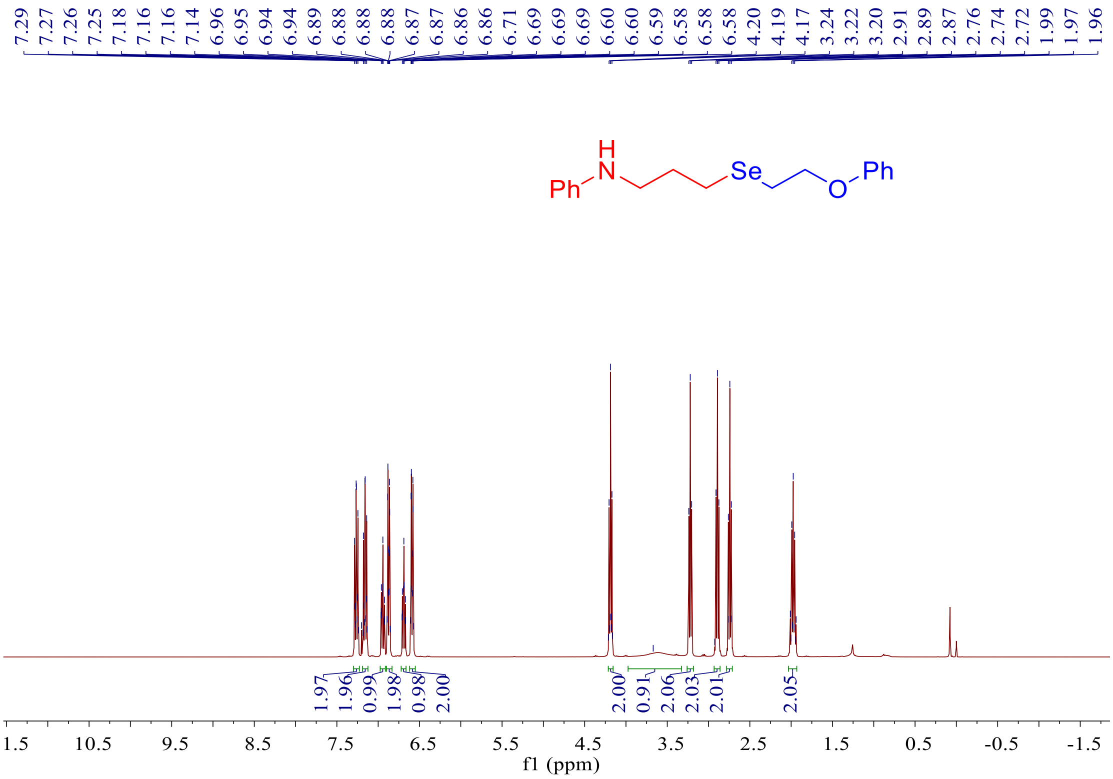
^{1}H NMR Spectra of **3n** (400 MHz, $CDCl_3$)



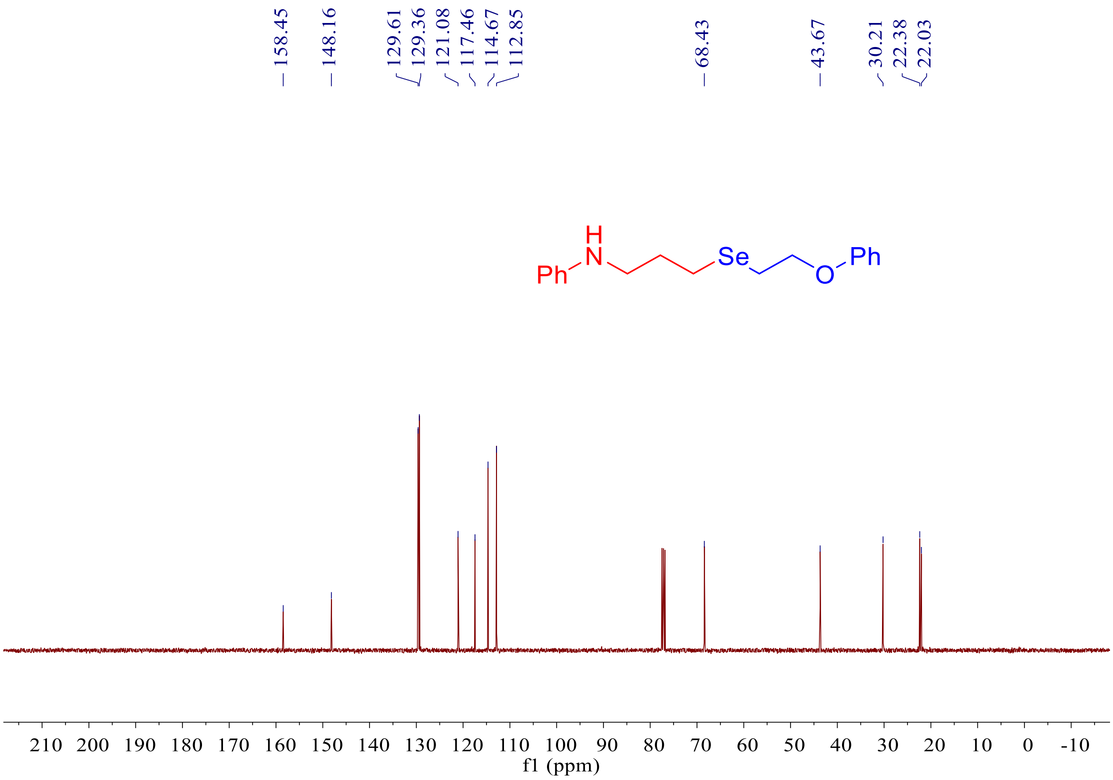
^{13}C NMR Spectra of **3n** (400 MHz, $CDCl_3$)



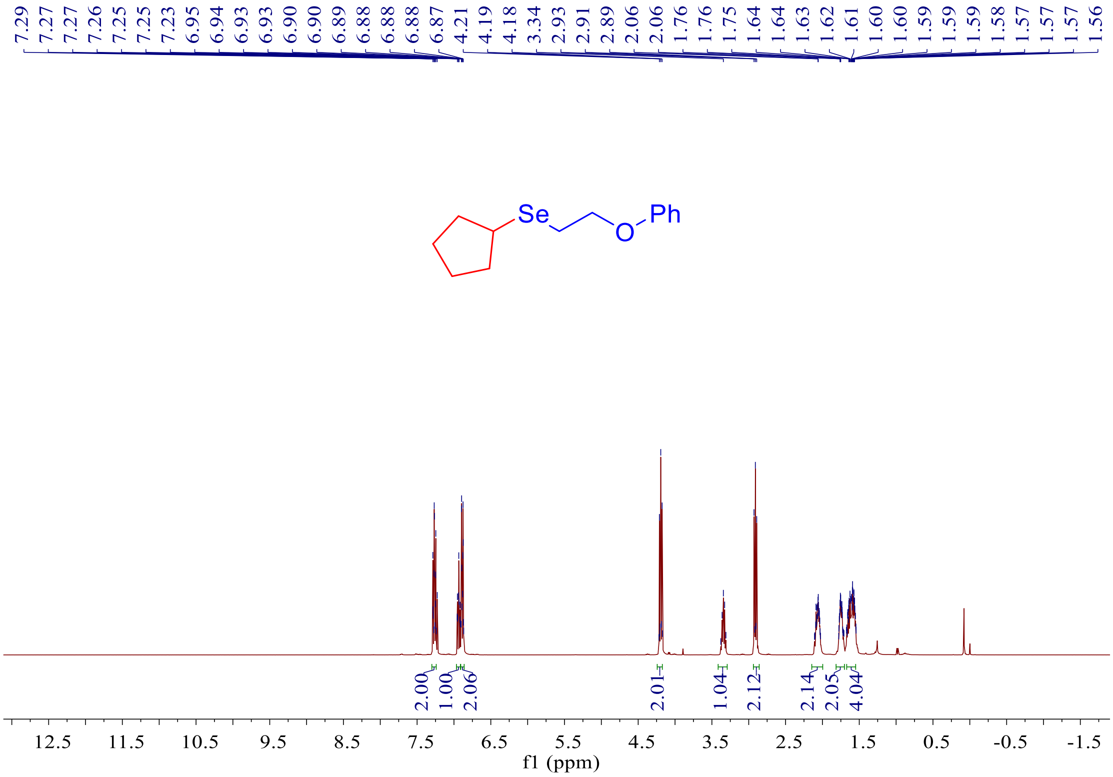
[1]H NMR Spectra of **3o** (400 MHz, $CDCl_3$)



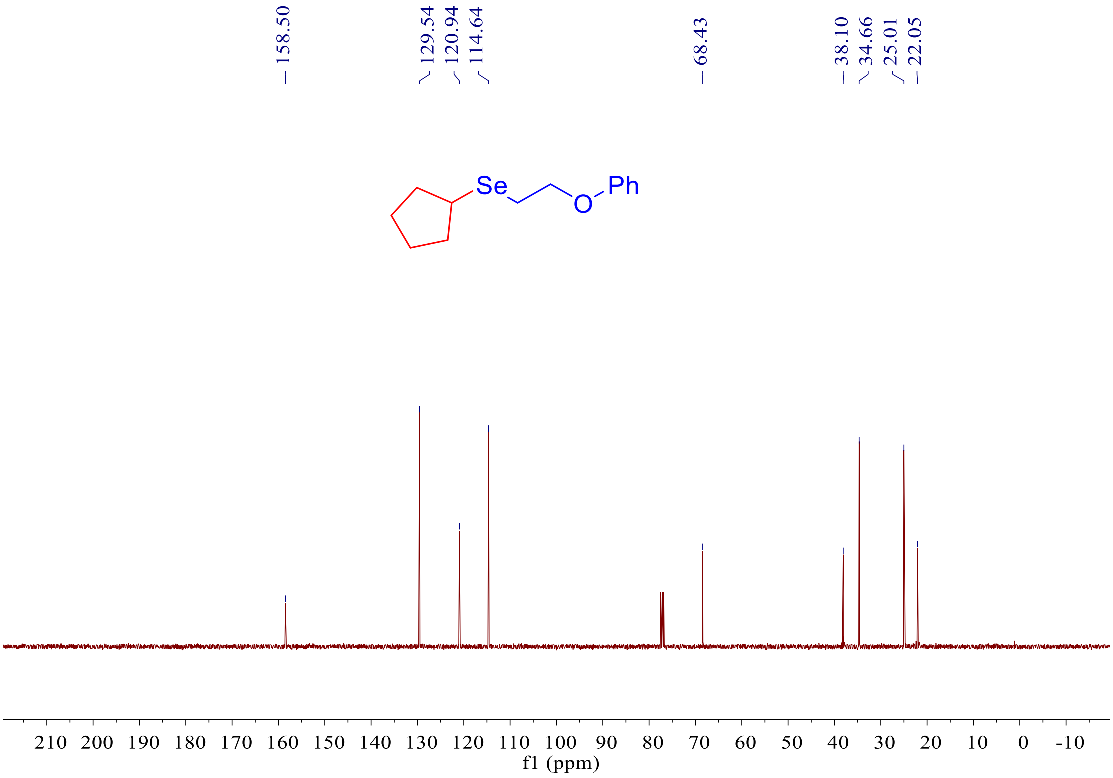
[13]C NMR Spectra of **3o** (400 MHz, $CDCl_3$)



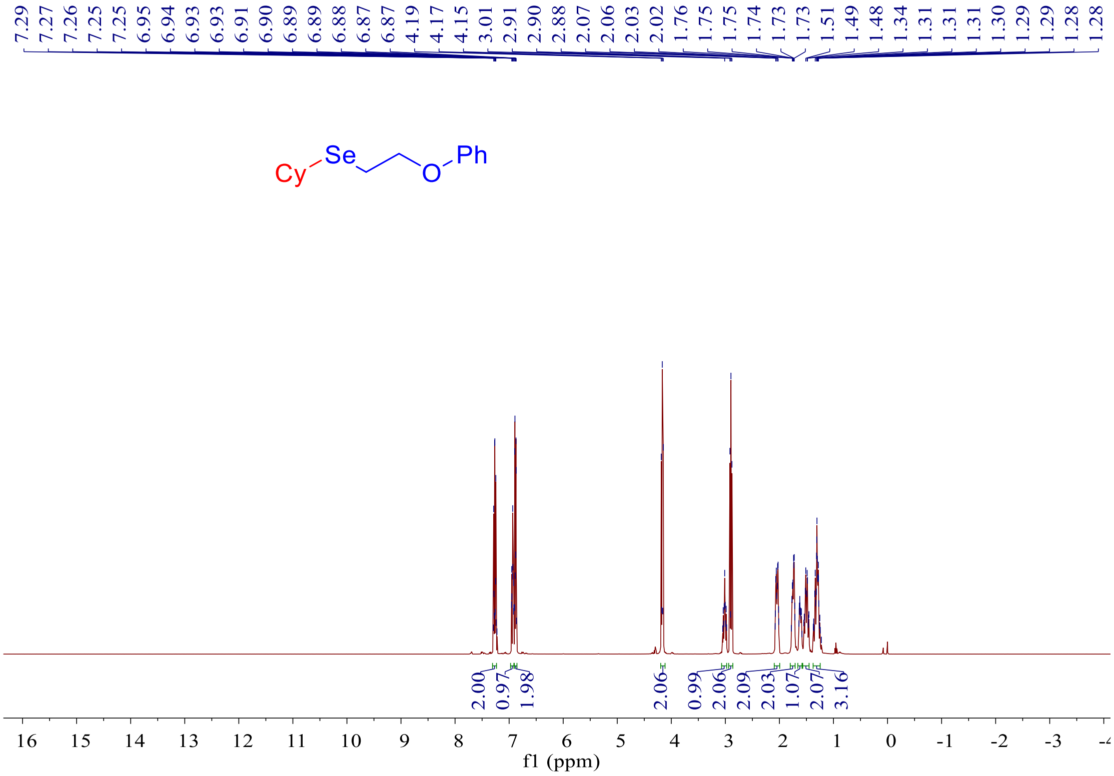
[1]H NMR Spectra of **3p** (400 MHz, $CDCl_3$)



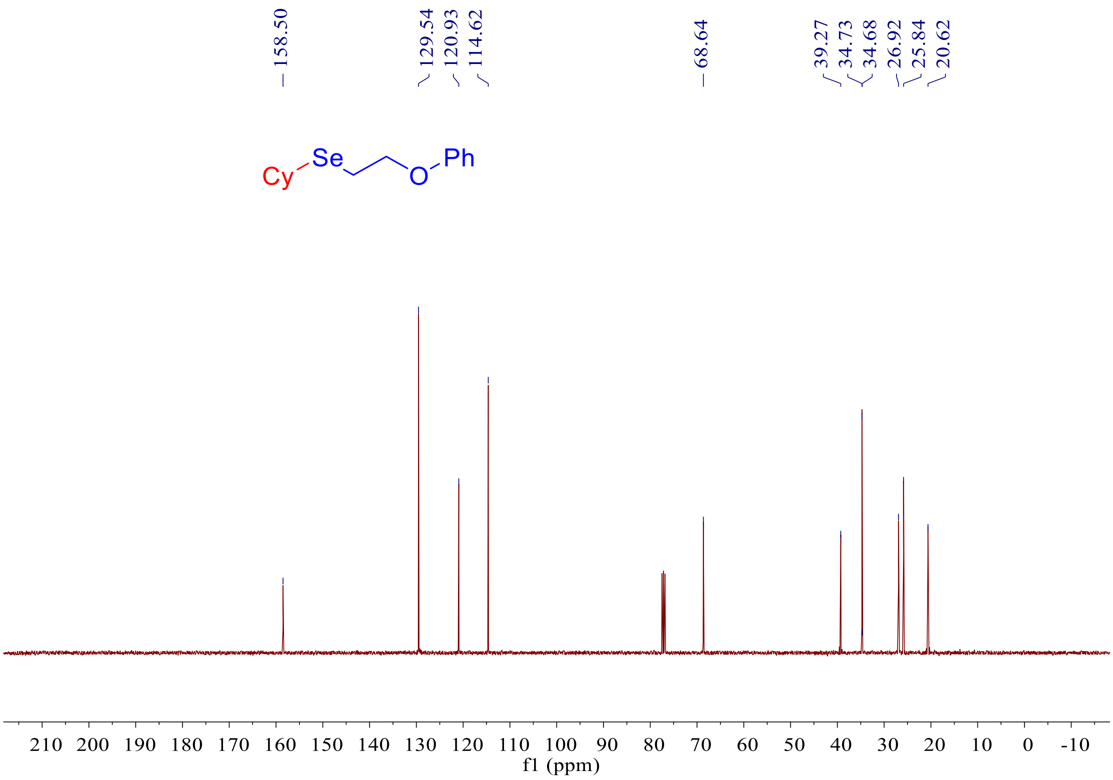
[13]C NMR Spectra of **3p** (400 MHz, $CDCl_3$)



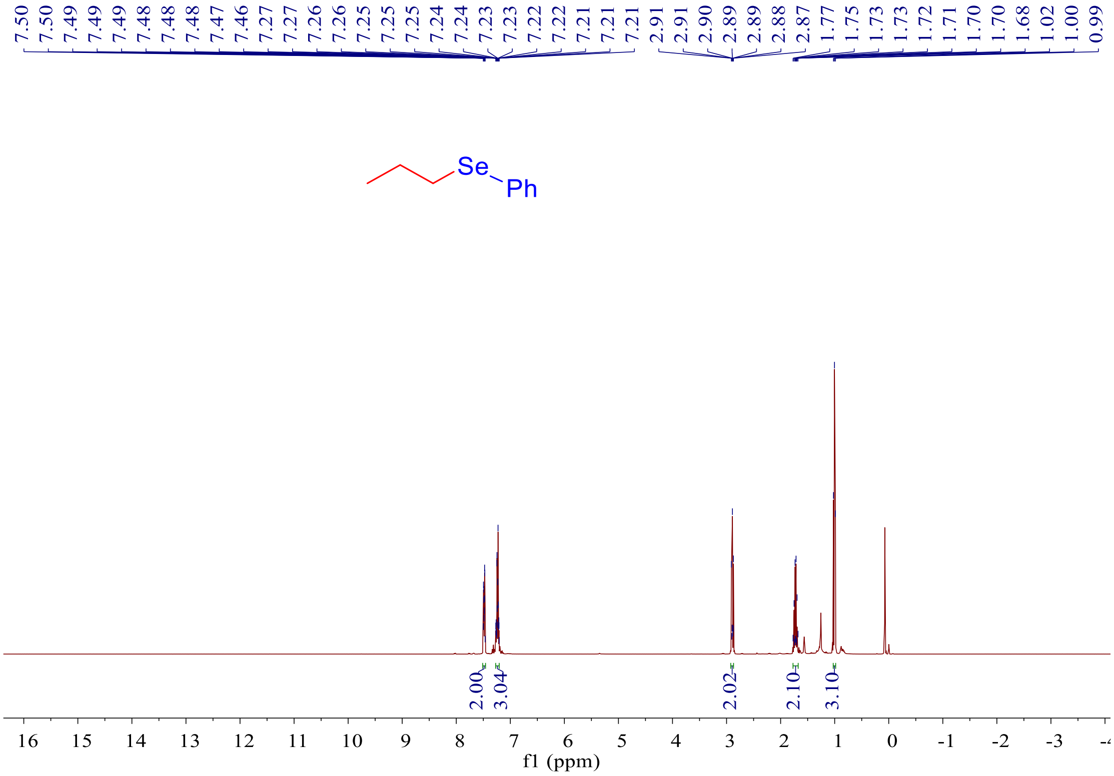
[1]H NMR Spectra of **3q** (400 MHz, $CDCl_3$)



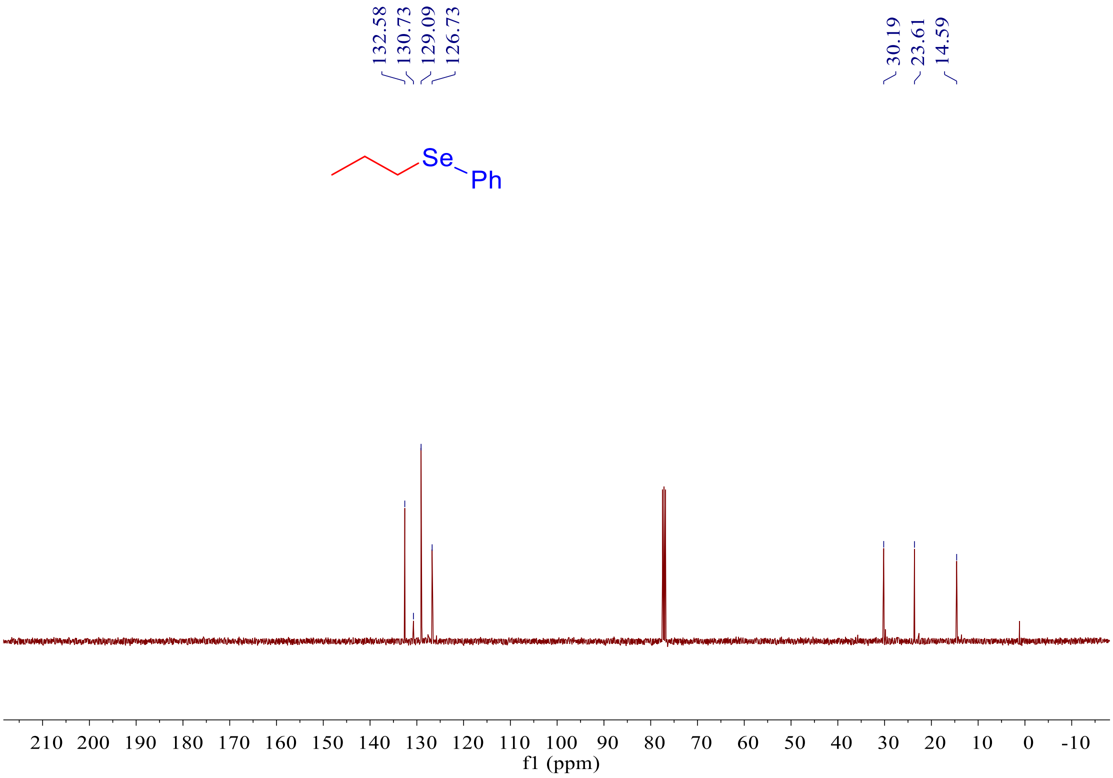
[13]C NMR Spectra of **3q** (400 MHz, $CDCl_3$)



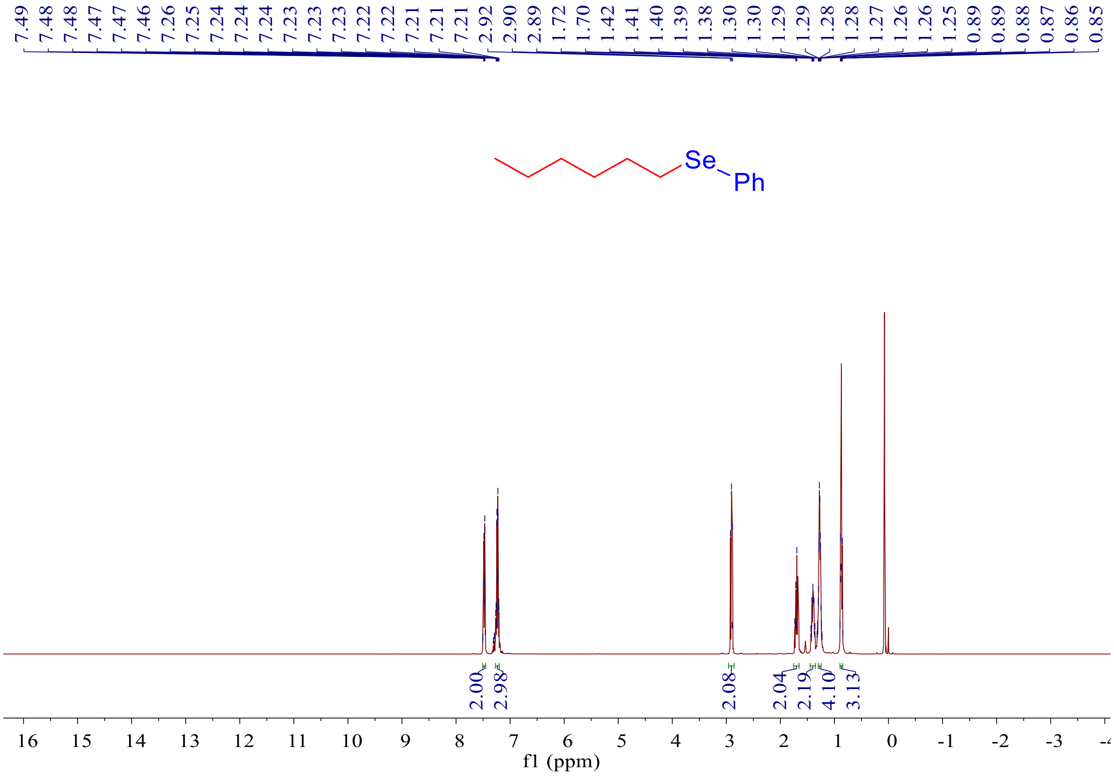
[1]H NMR Spectra of **5a** (400 MHz, $CDCl_3$)



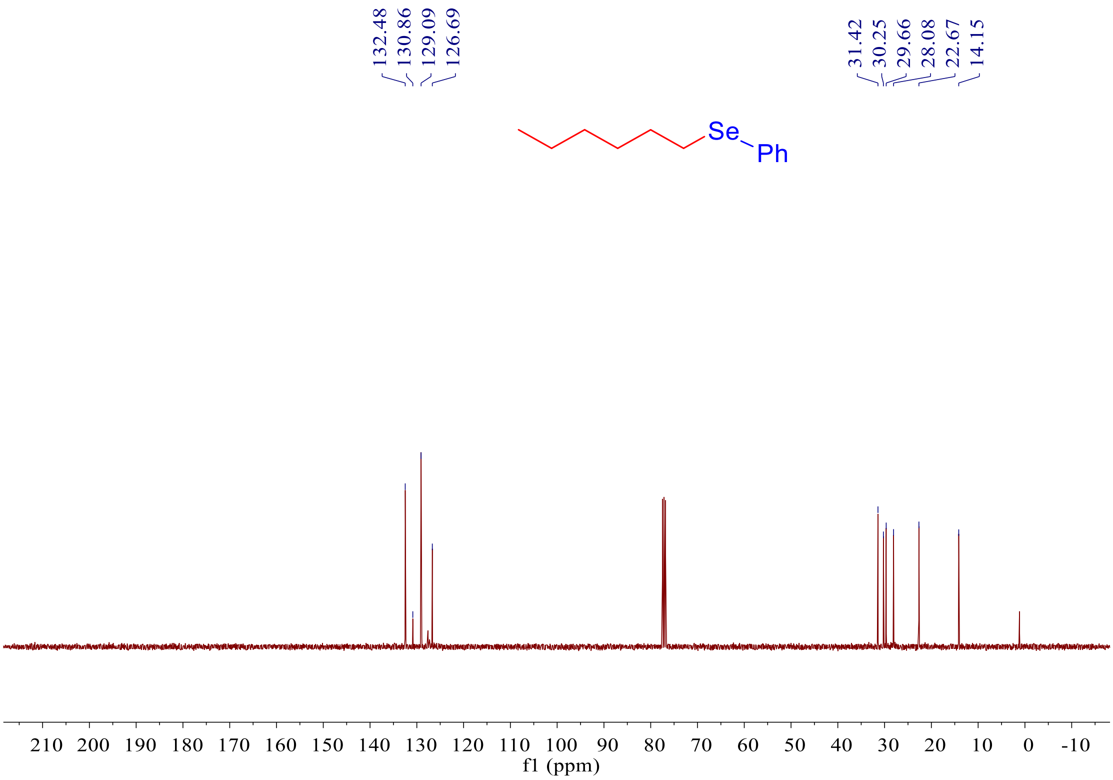
[13]C NMR Spectra of **5a** (400 MHz, $CDCl_3$)



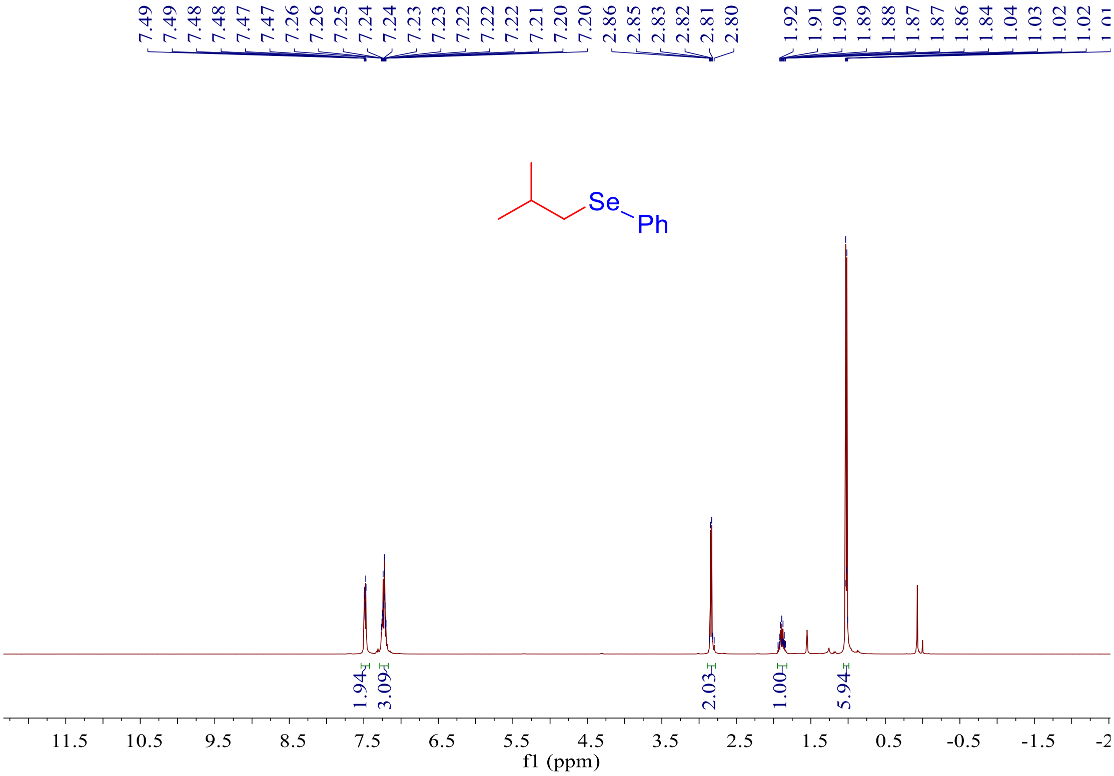
^{1}H NMR Spectra of **5b** (400 MHz, $CDCl_3$)



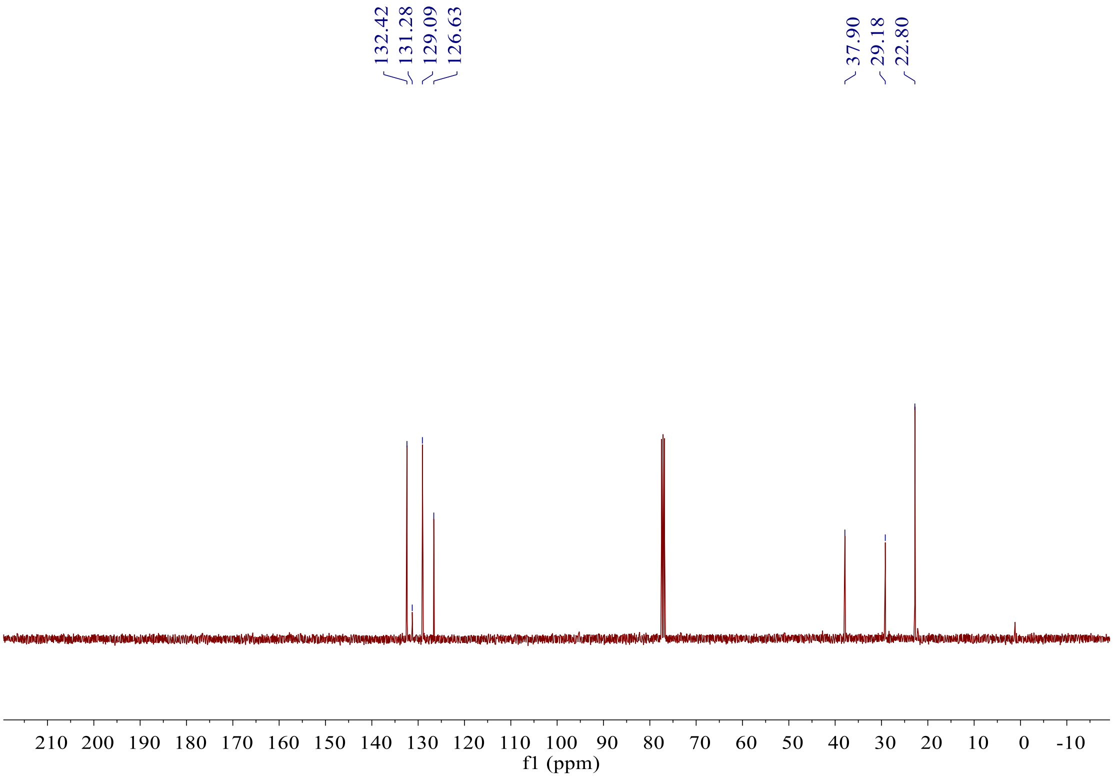
^{13}C NMR Spectra of **5b** (400 MHz, $CDCl_3$)

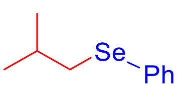


[1]H NMR Spectra of **5c** (400 MHz, $CDCl_3$)

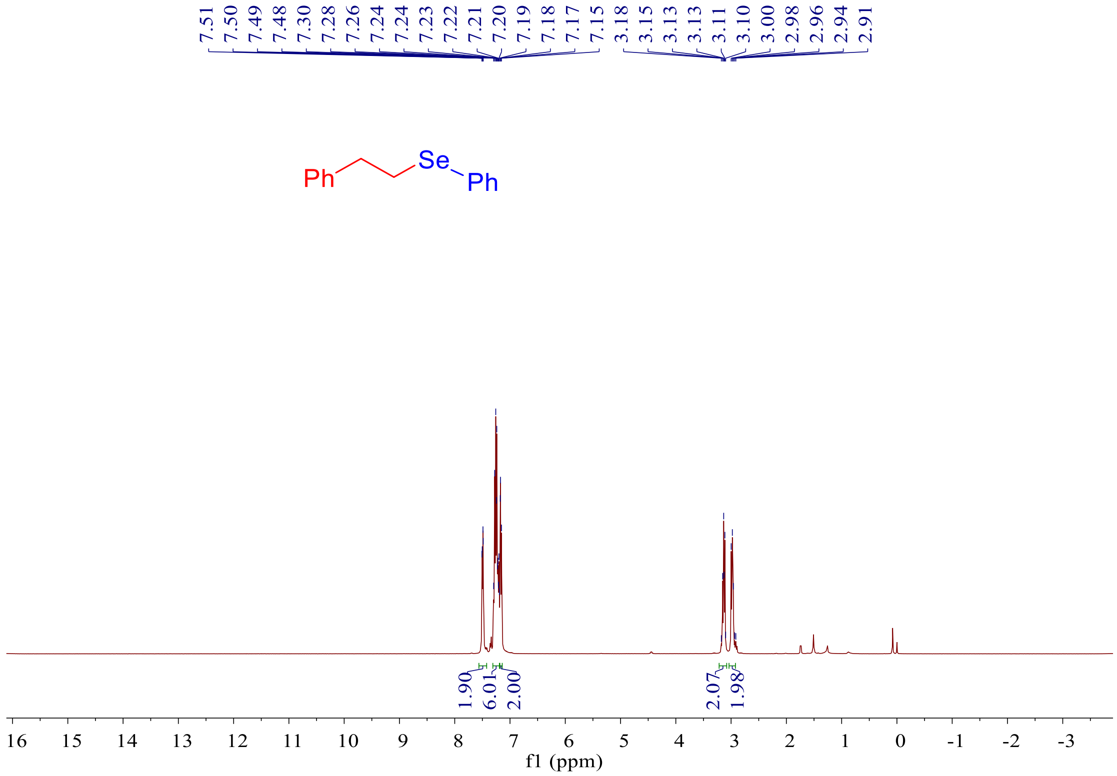


[13]C NMR Spectra of **5c** (400 MHz, $CDCl_3$)

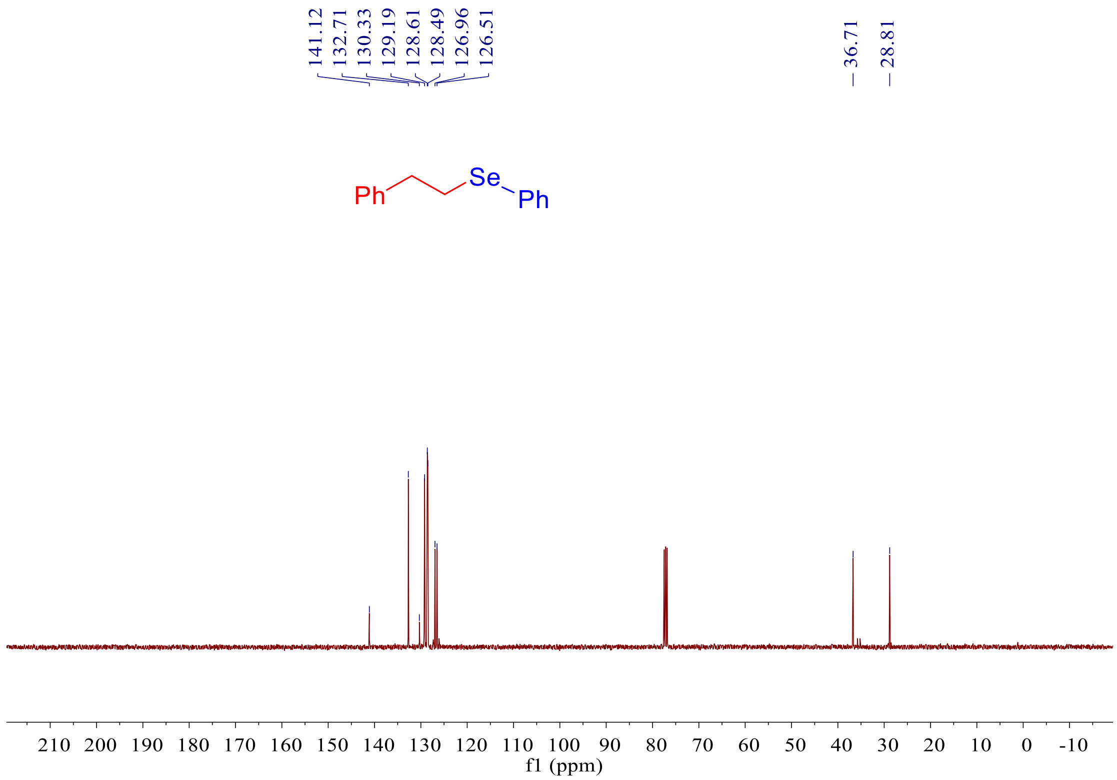




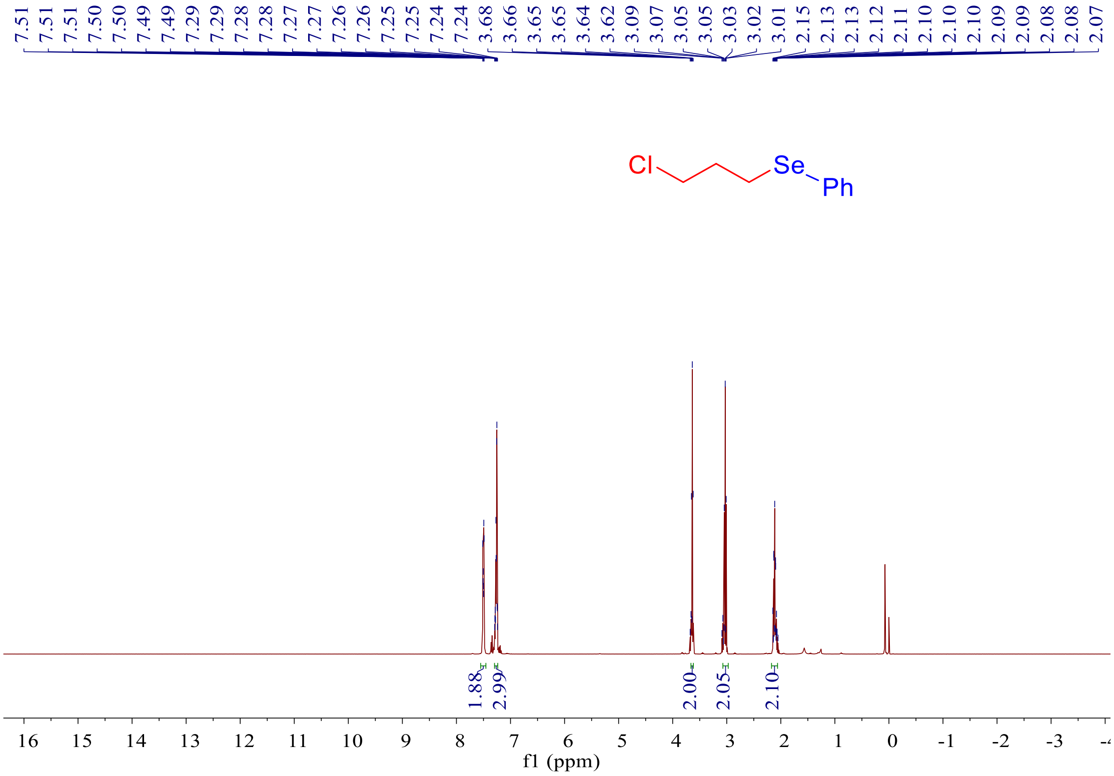
^{1}H NMR Spectra of **5d** (400 MHz, $CDCl_3$)



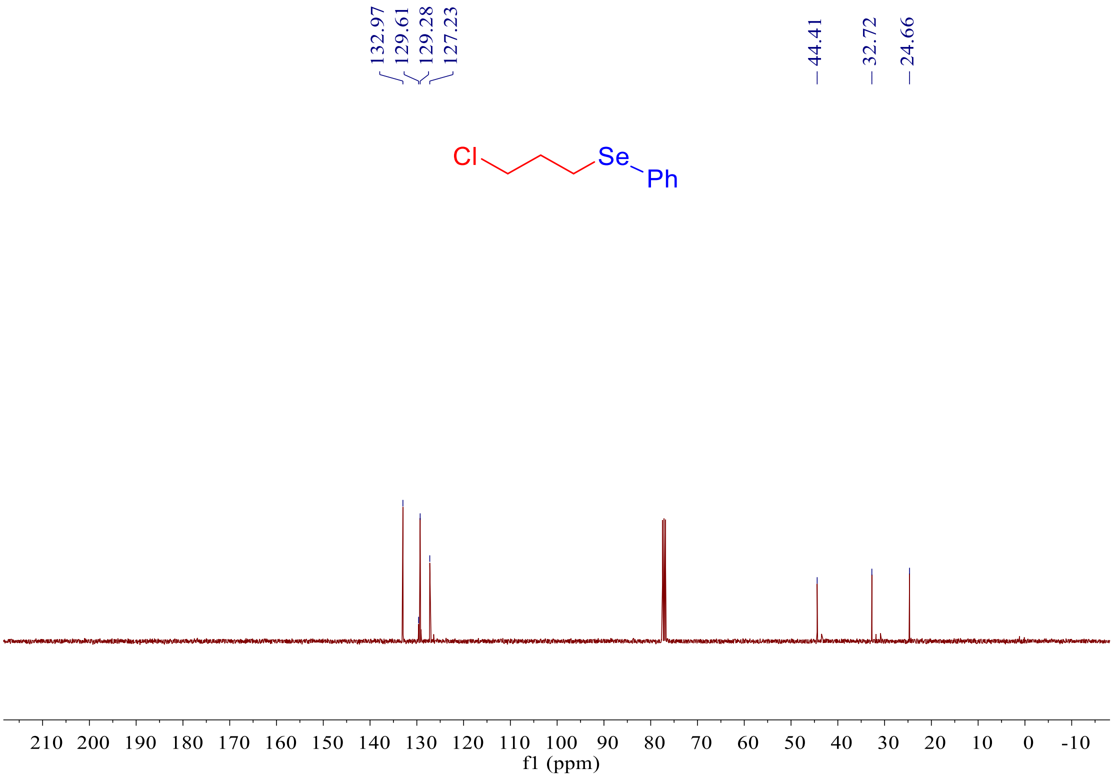
^{13}C NMR Spectra of **5d** (400 MHz, $CDCl_3$)



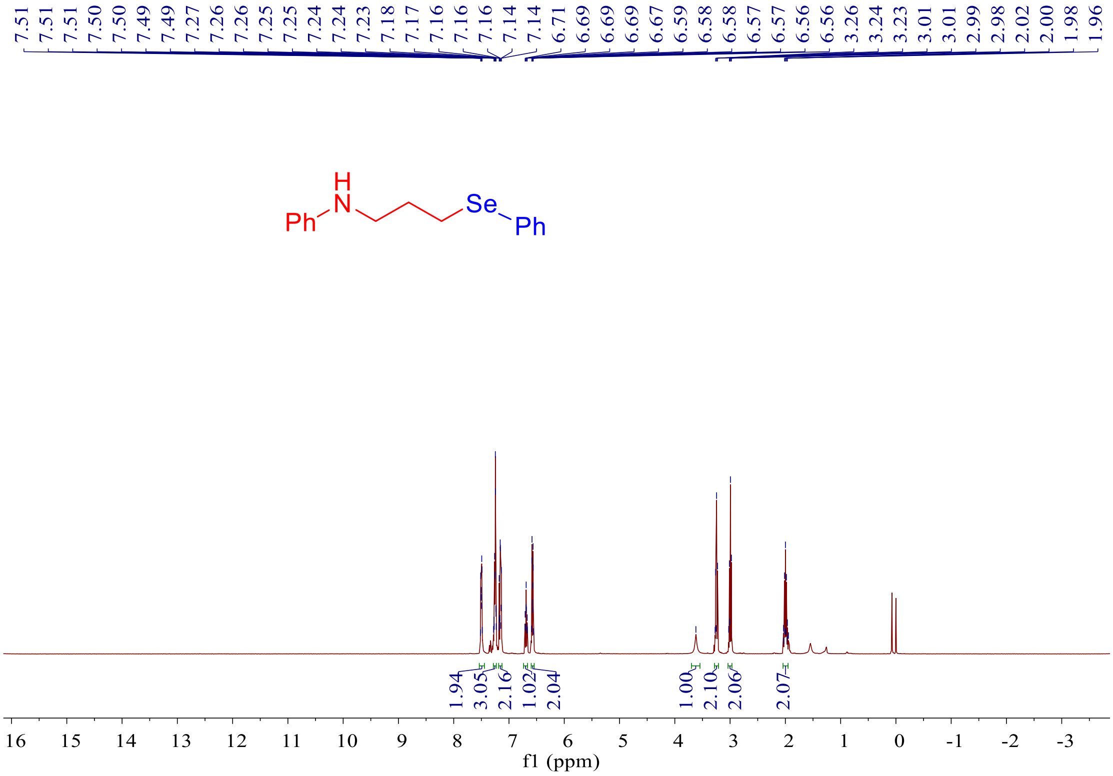
^{1}H NMR Spectra of **5e** (400 MHz, $CDCl_3$)



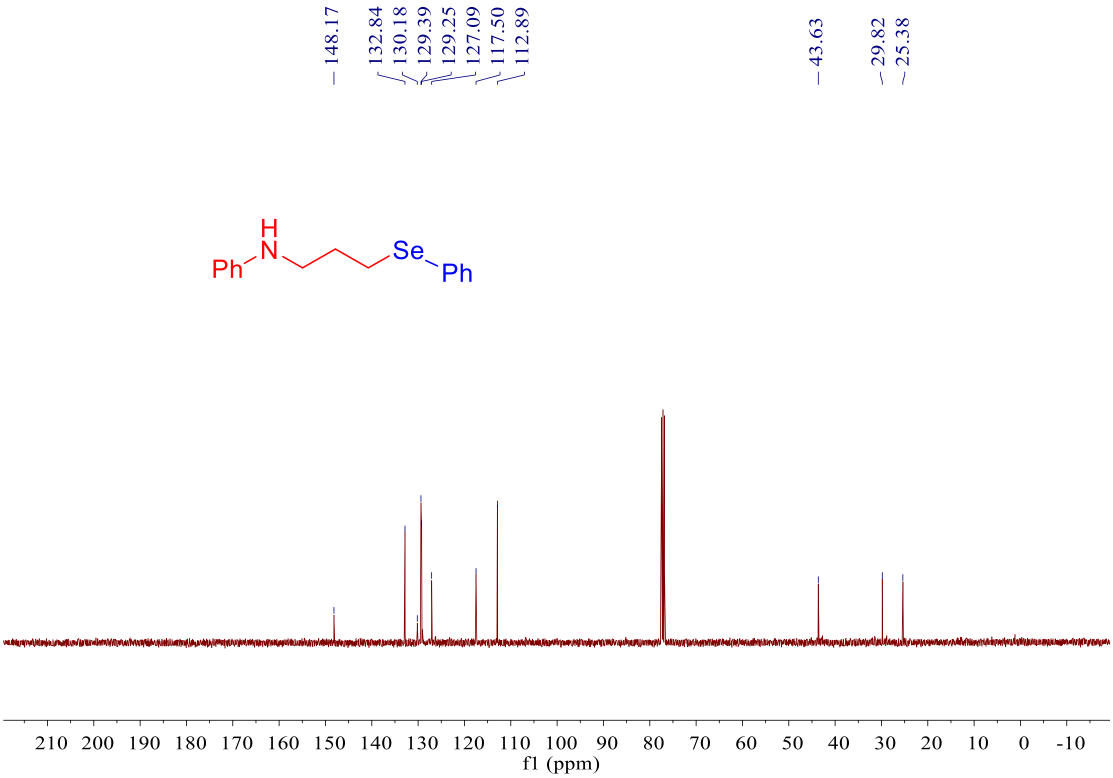
^{13}C NMR Spectra of **5e** (400 MHz, $CDCl_3$)



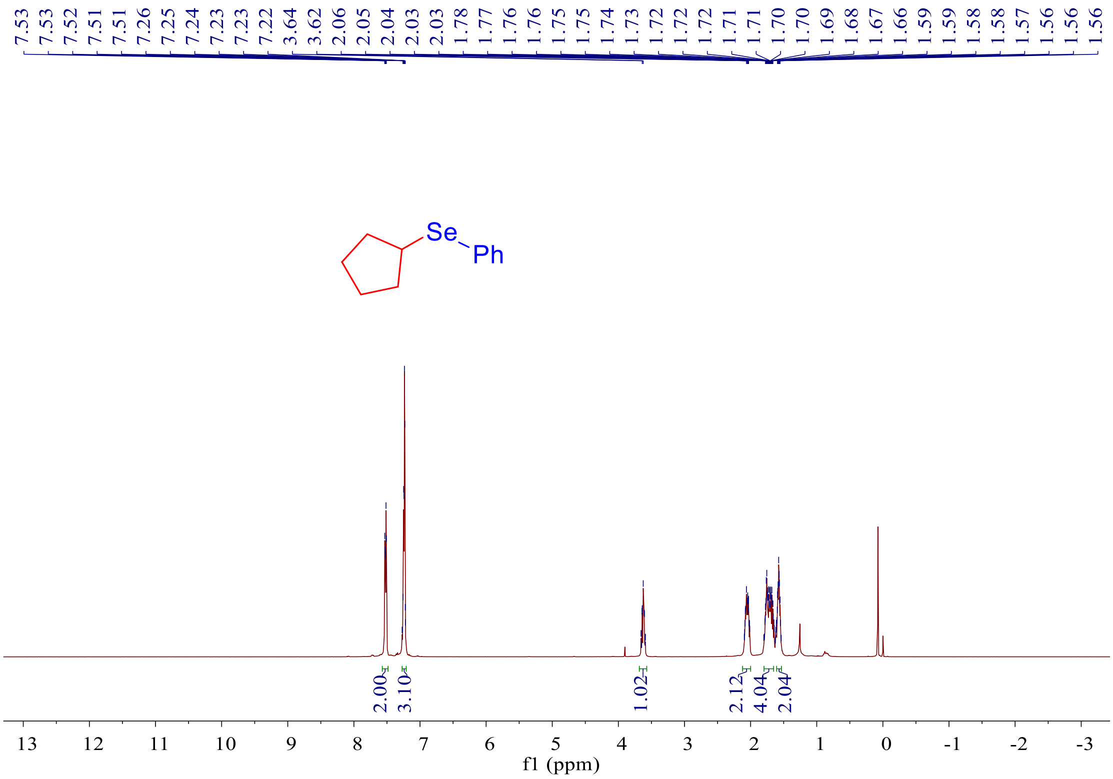
^{1}H NMR Spectra of **5f** (400 MHz, $CDCl_3$)



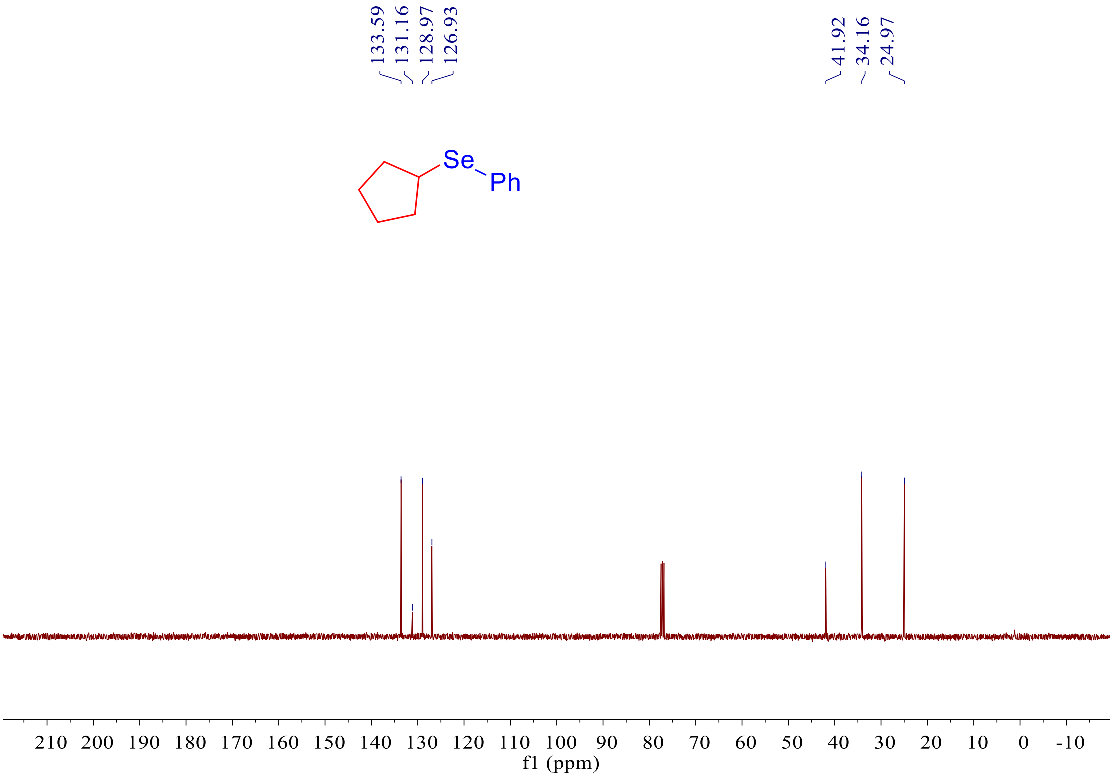
^{13}C NMR Spectra of **5f** (400 MHz, $CDCl_3$)



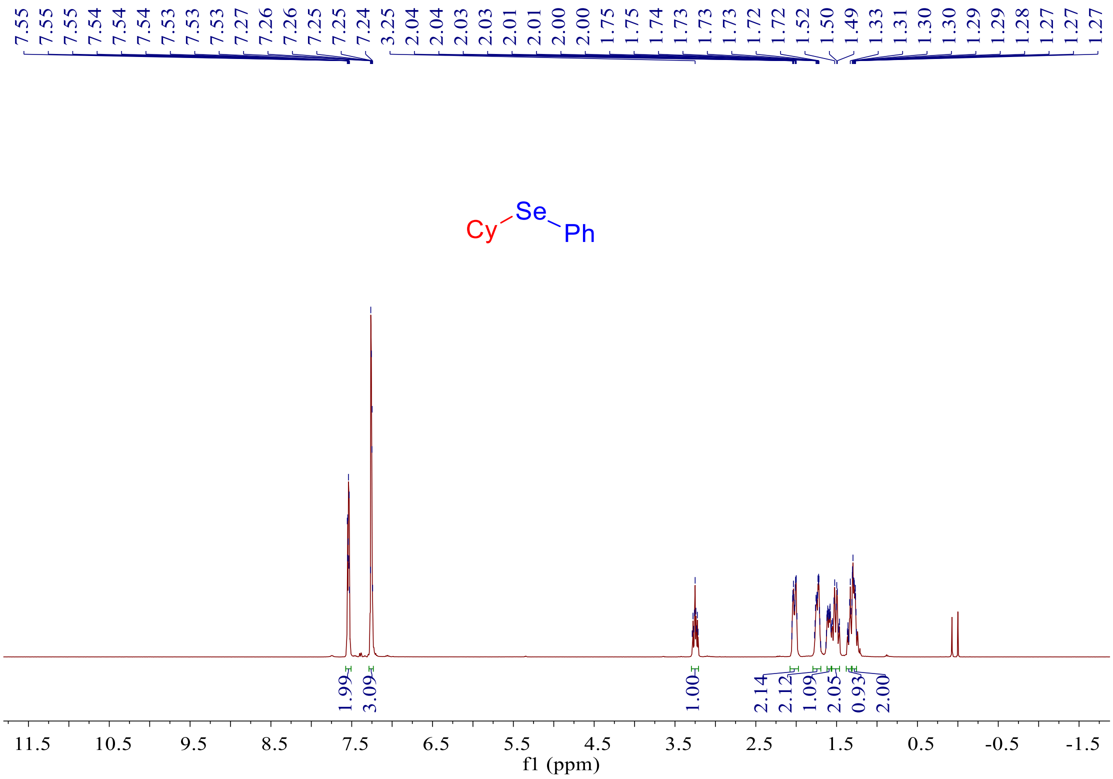
[1]H NMR Spectra of **5g** (400 MHz, $CDCl_3$)



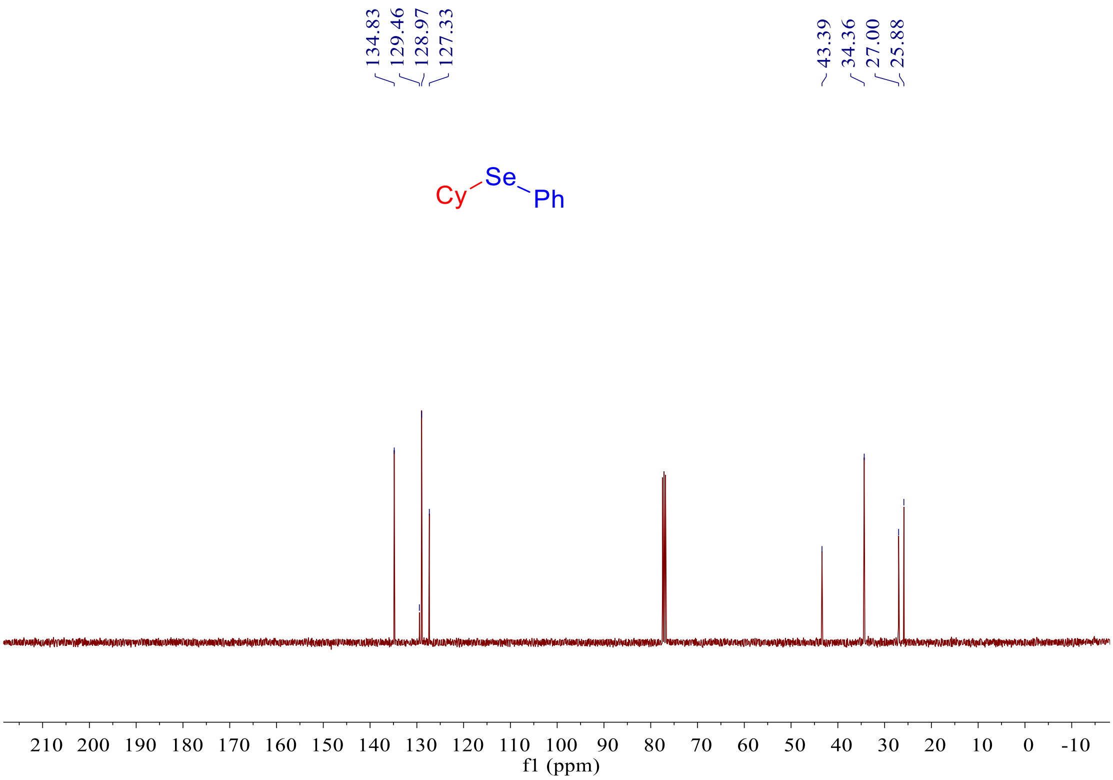
[13]C NMR Spectra of **5g** (400 MHz, $CDCl_3$)



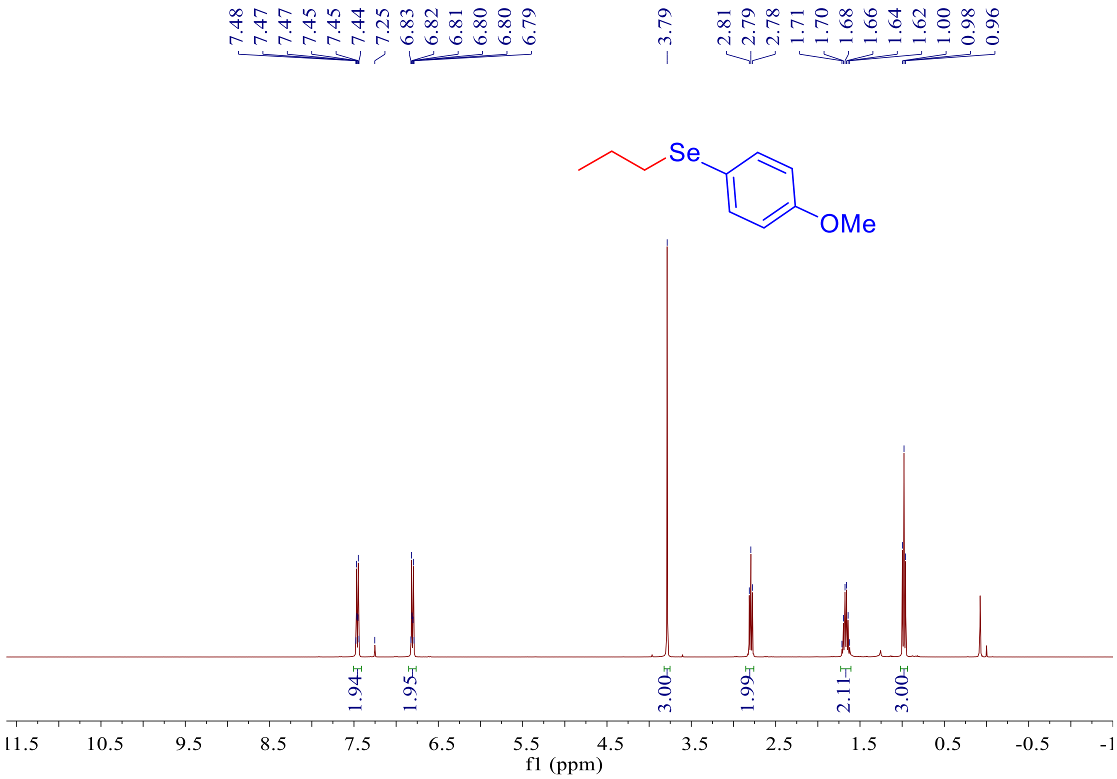
^1H NMR Spectra of **5h** (400 MHz, $CDCl_3$)



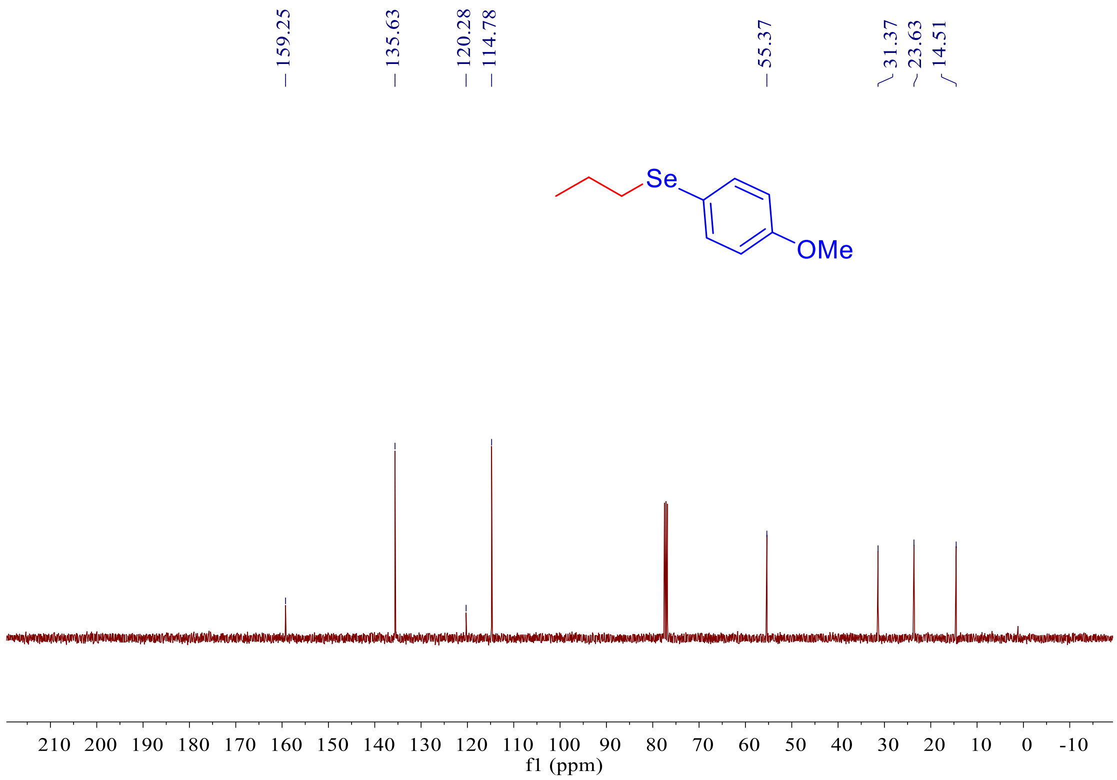
^{13}C NMR Spectra of **5h** (400 MHz, $CDCl_3$)



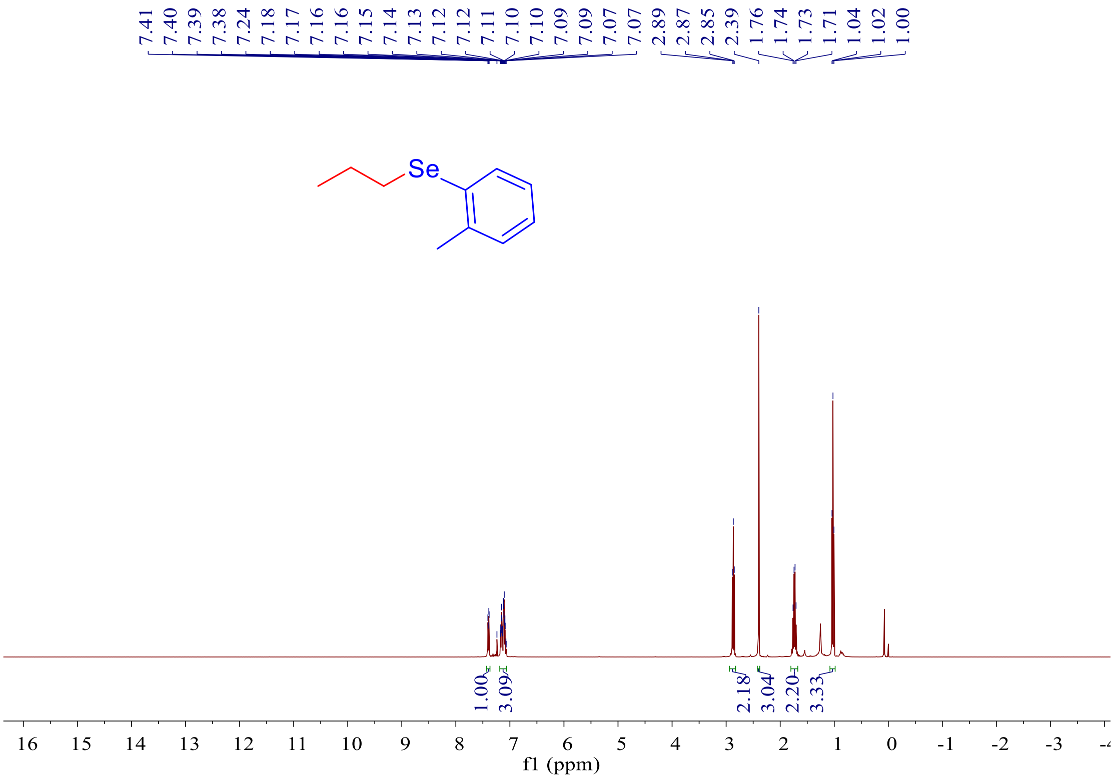
[1]H NMR Spectra of **5i** (400 MHz, $CDCl_3$)



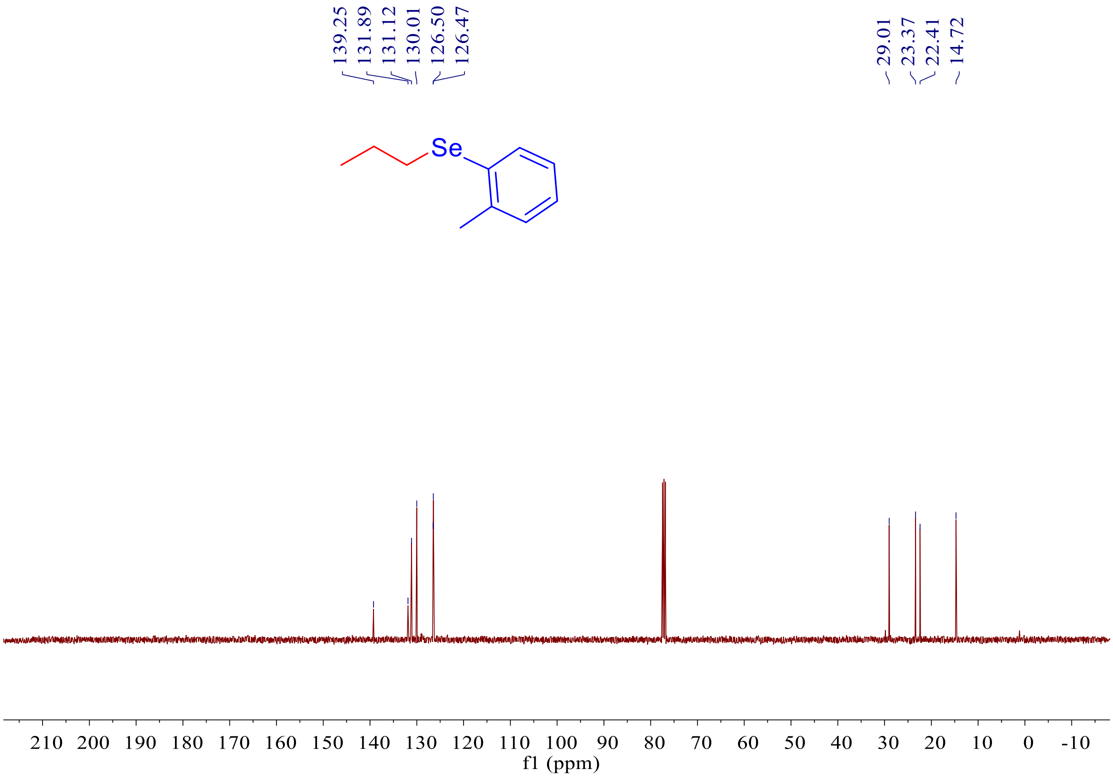
[13]C NMR Spectra of **5i** (400 MHz, $CDCl_3$)



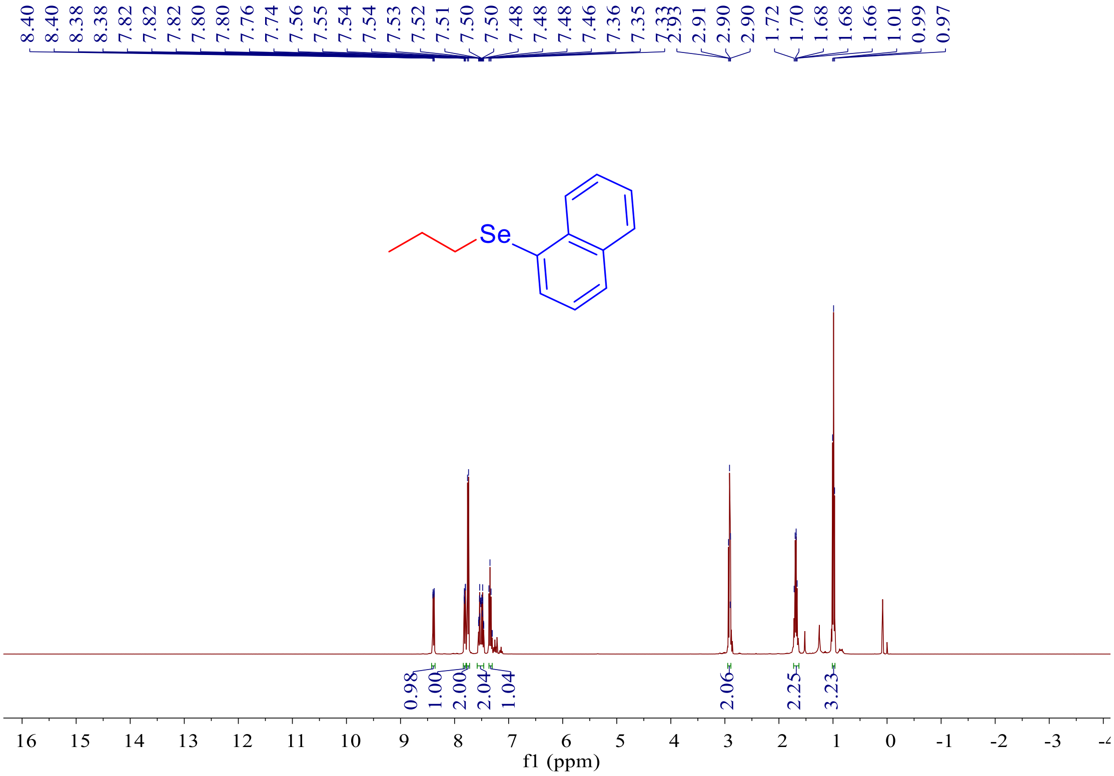
[1]H NMR Spectra of **5j** (400 MHz, $CDCl_3$)



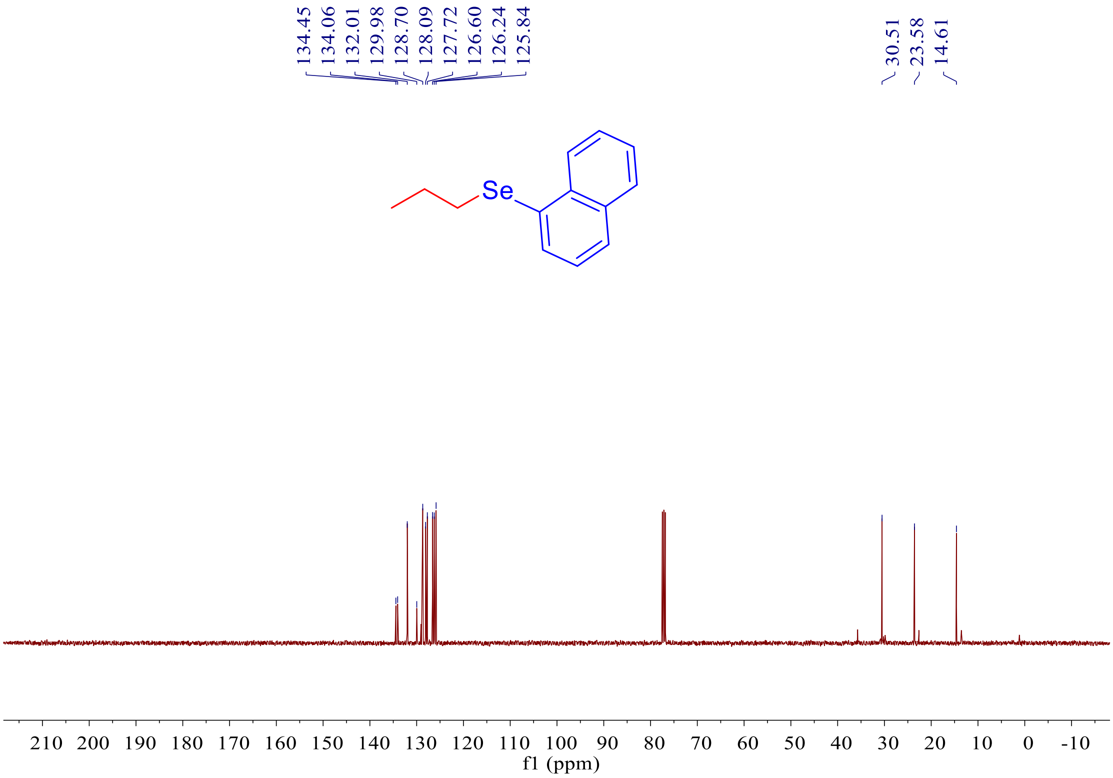
[13]C NMR Spectra of **5j** (400 MHz, $CDCl_3$)



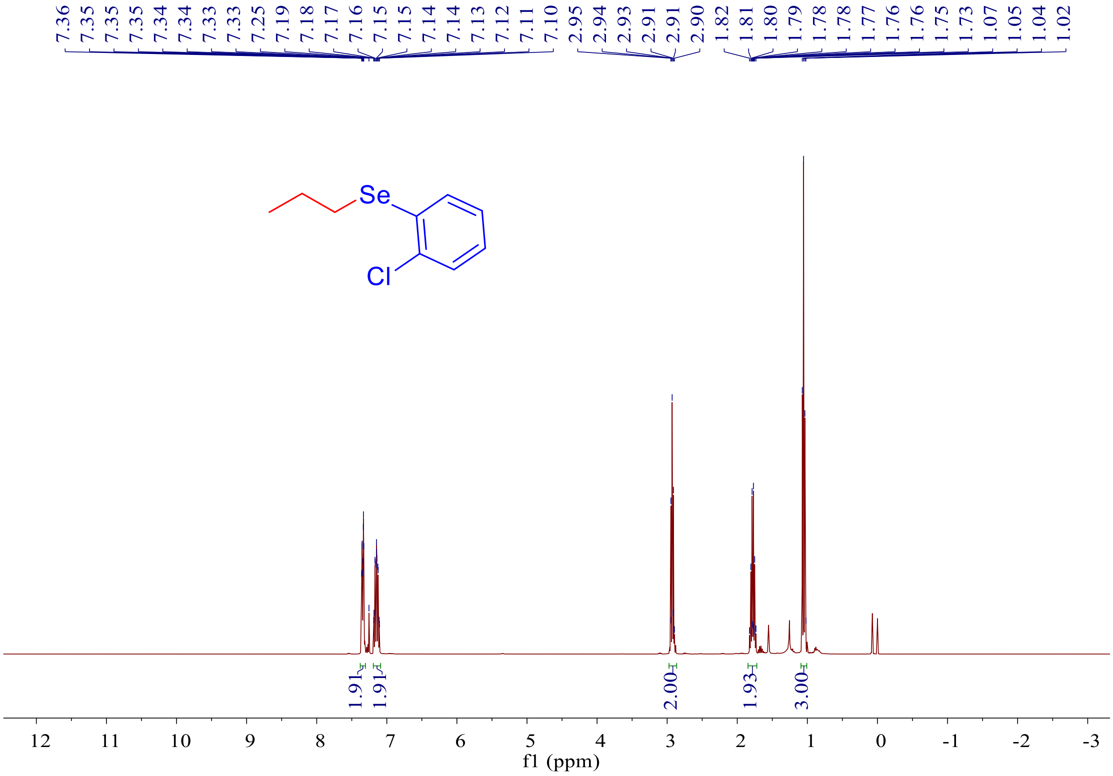
^{1}H NMR Spectra of **5k** (400 MHz, $CDCl_3$)



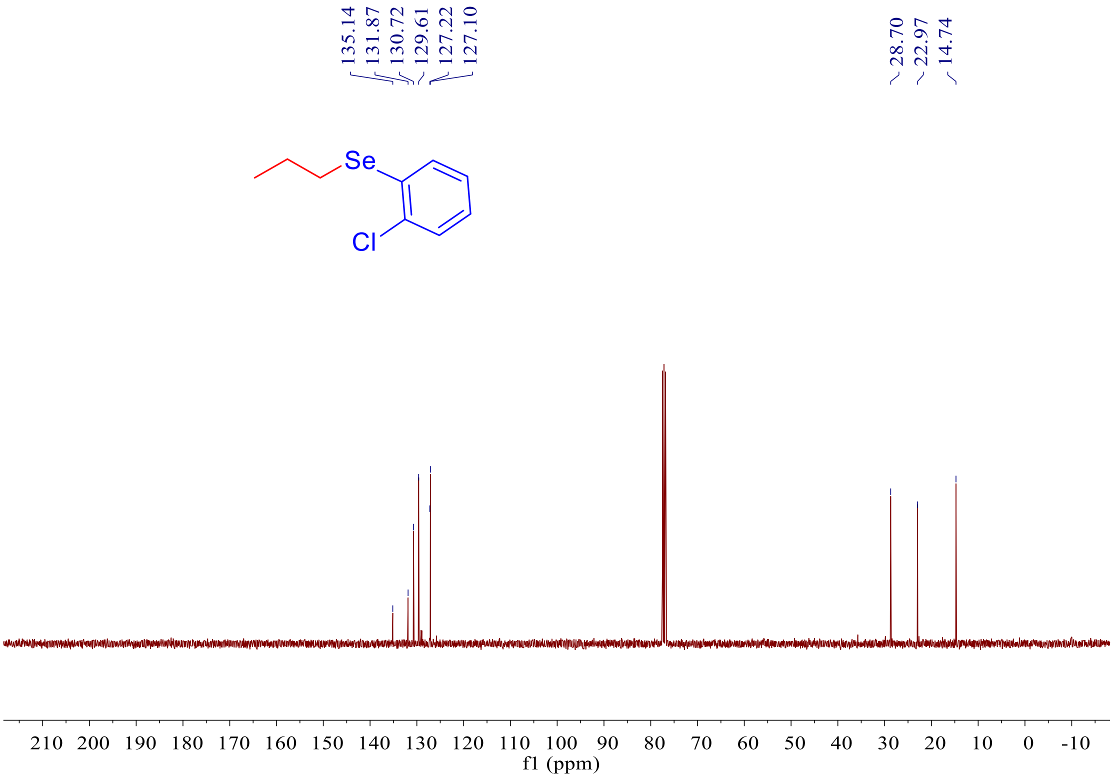
^{13}C NMR Spectra of **5k** (400 MHz, $CDCl_3$)



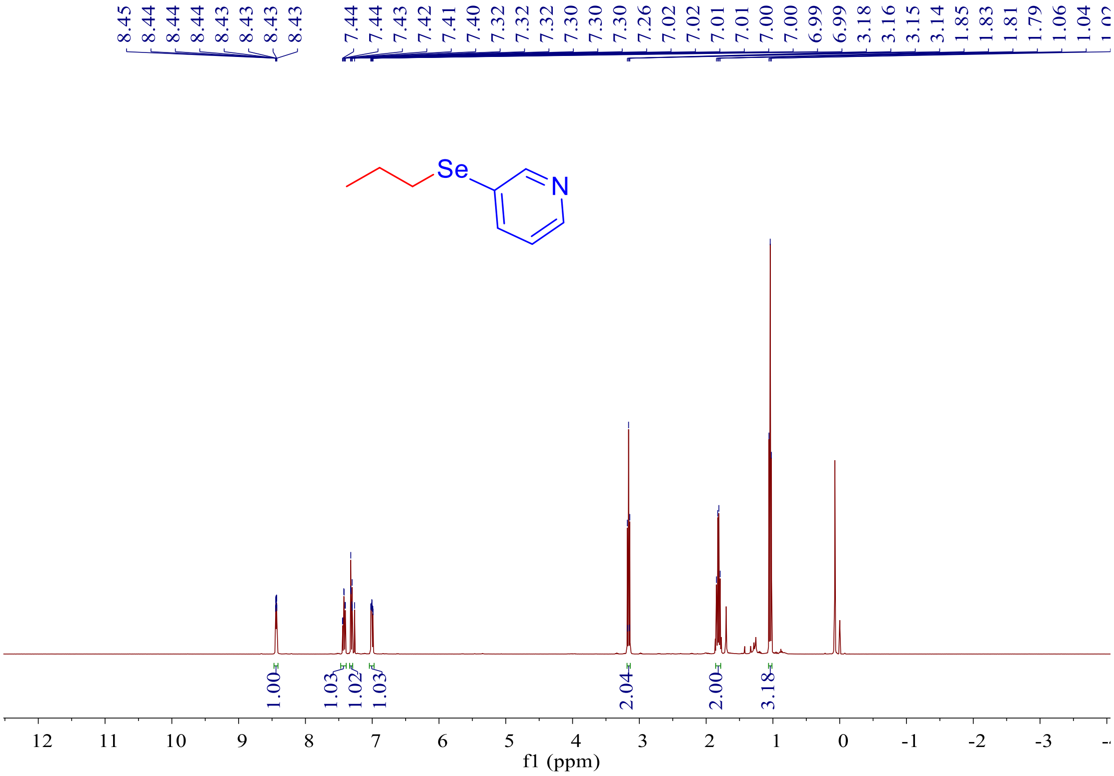
[1]H NMR Spectra of **5l** (400 MHz, $CDCl_3$)



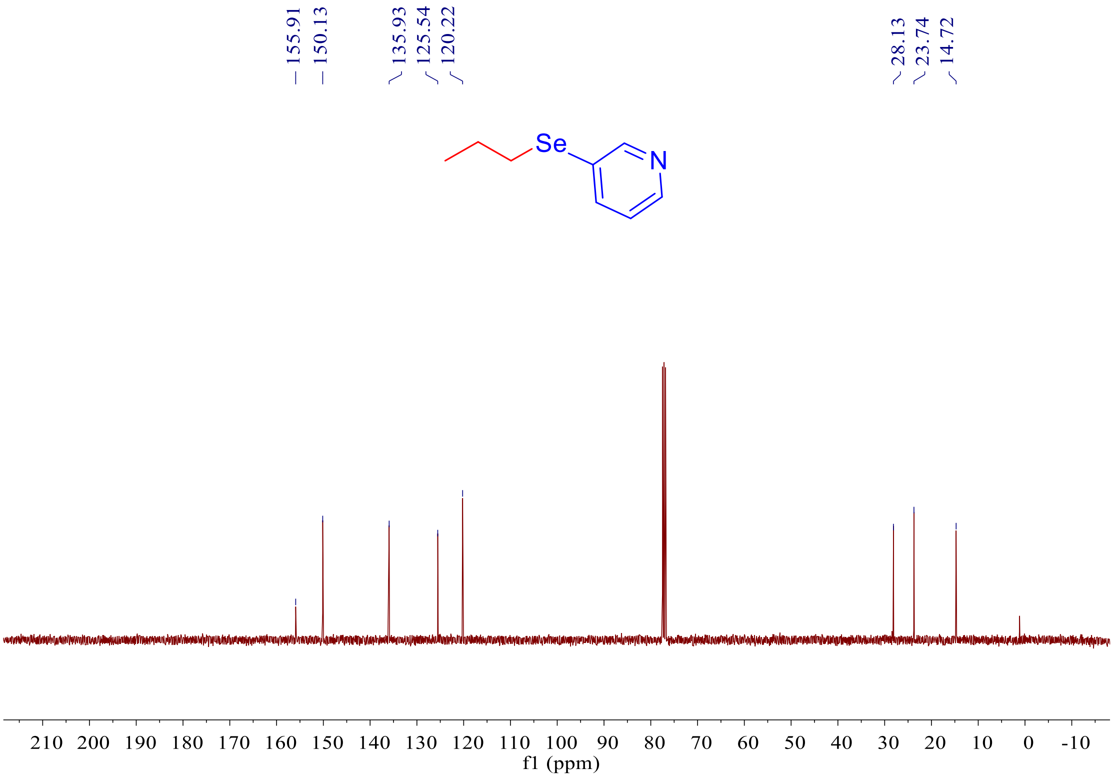
[13]C NMR Spectra of **5l** (400 MHz, $CDCl_3$)



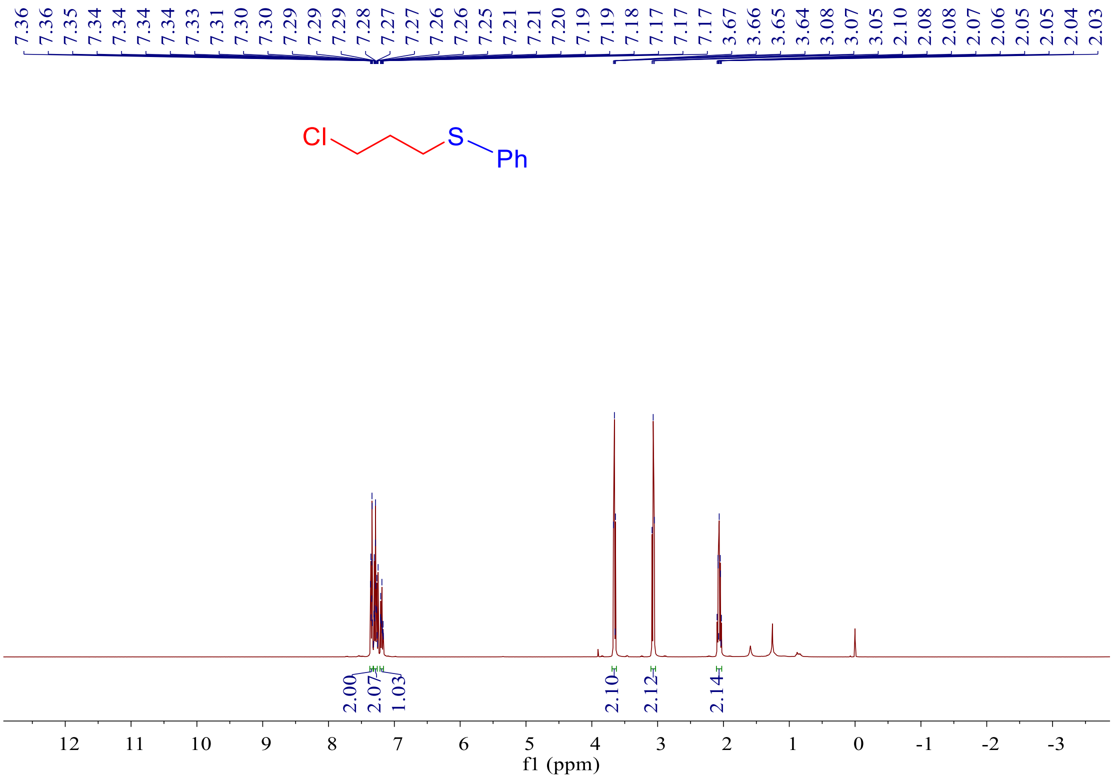
[1]H NMR Spectra of **5m** (400 MHz, $CDCl_3$)



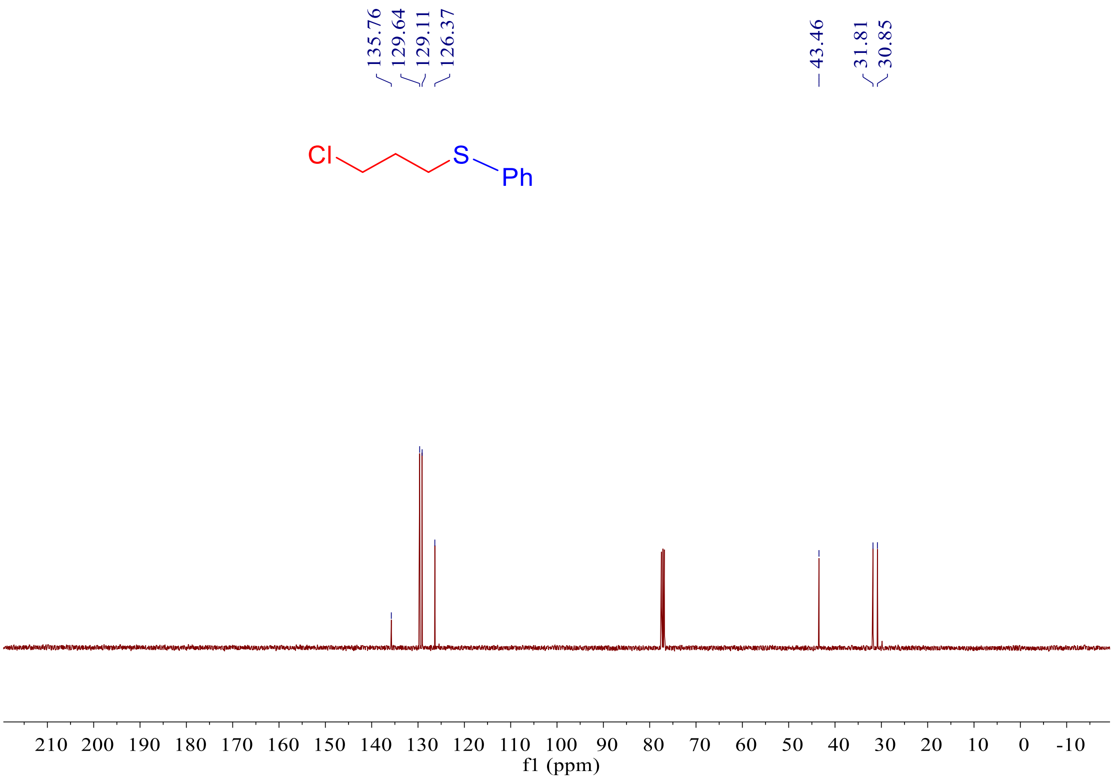
[13]C NMR Spectra of **5m** (400 MHz, $CDCl_3$)



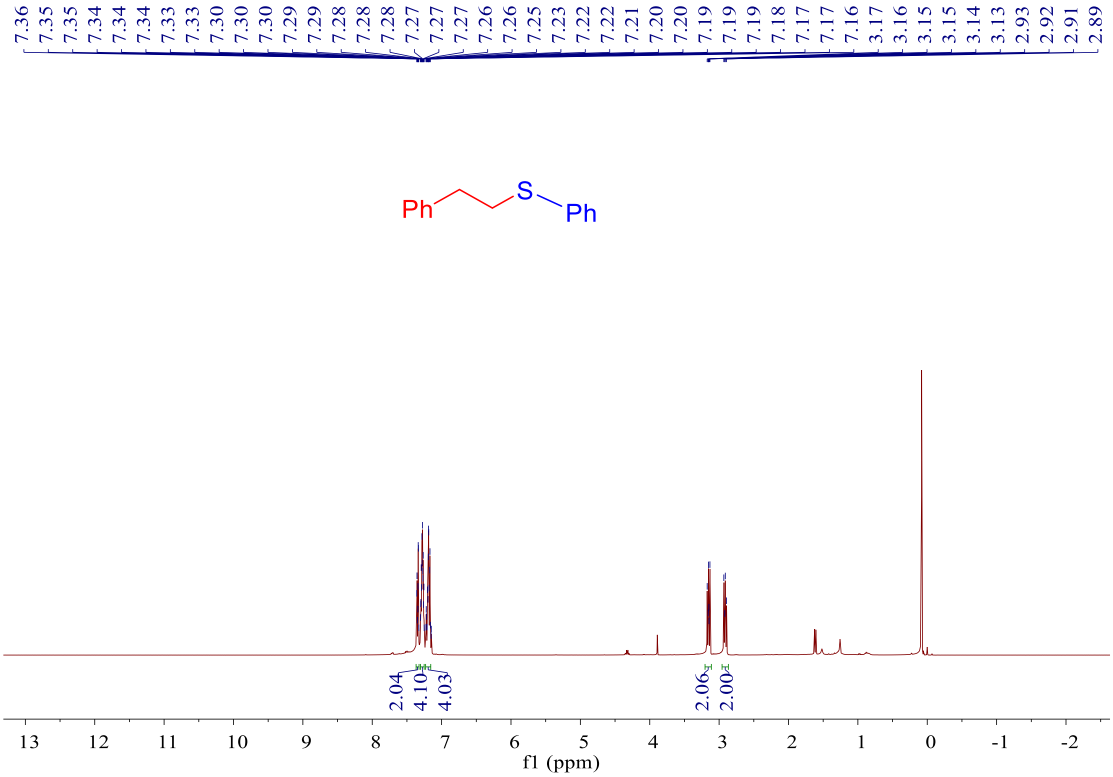
[1]H NMR Spectra of **7a** (400 MHz, $CDCl_3$)



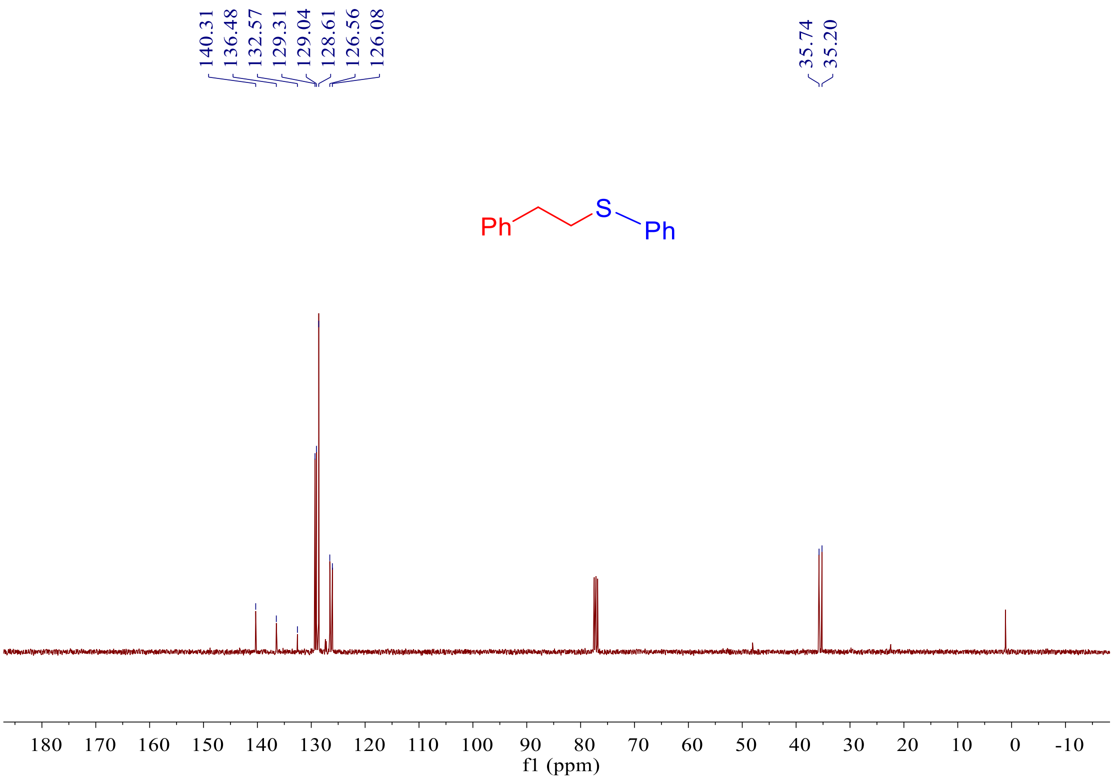
[13]C NMR Spectra of **7a** (400 MHz, $CDCl_3$)



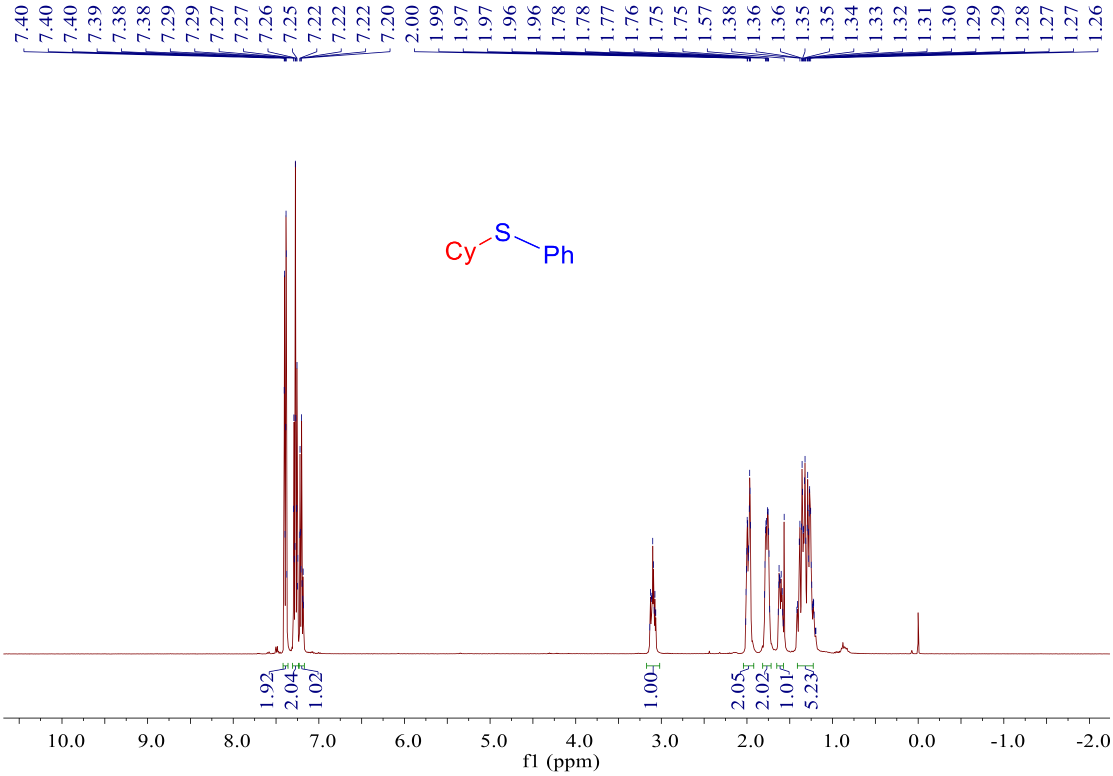
[1]H NMR Spectra of **7b** (400 MHz, $CDCl_3$)



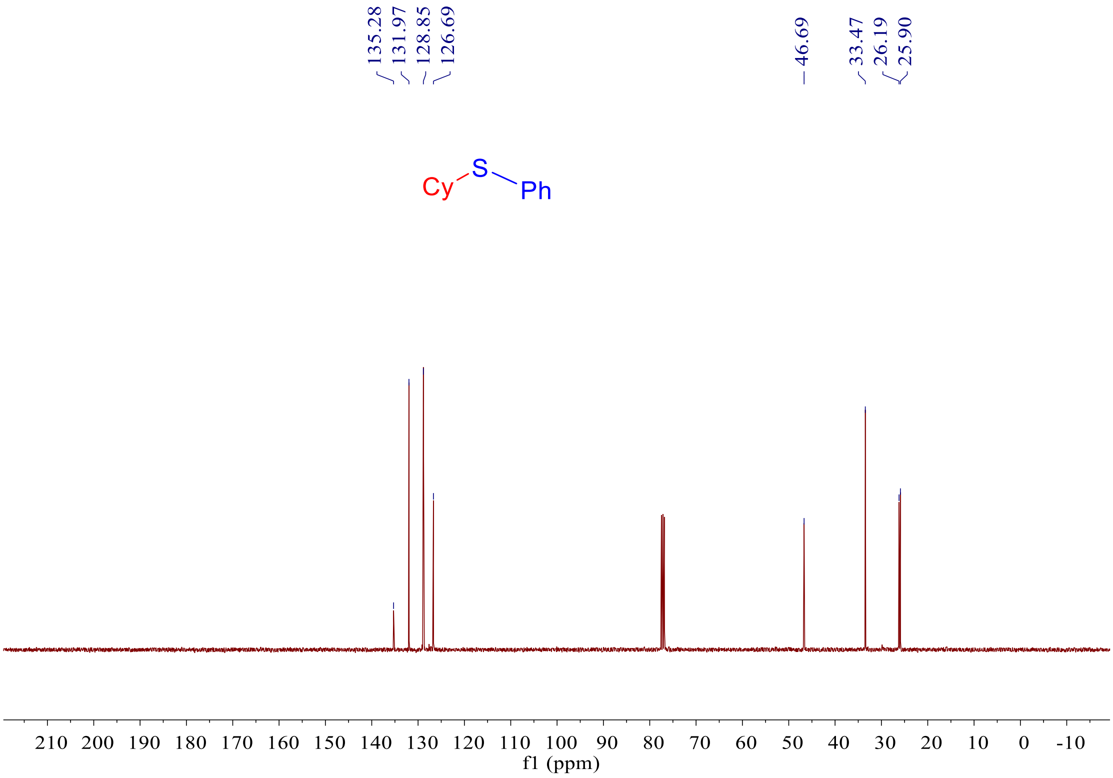
[13]C NMR Spectra of **7b** (400 MHz, $CDCl_3$)



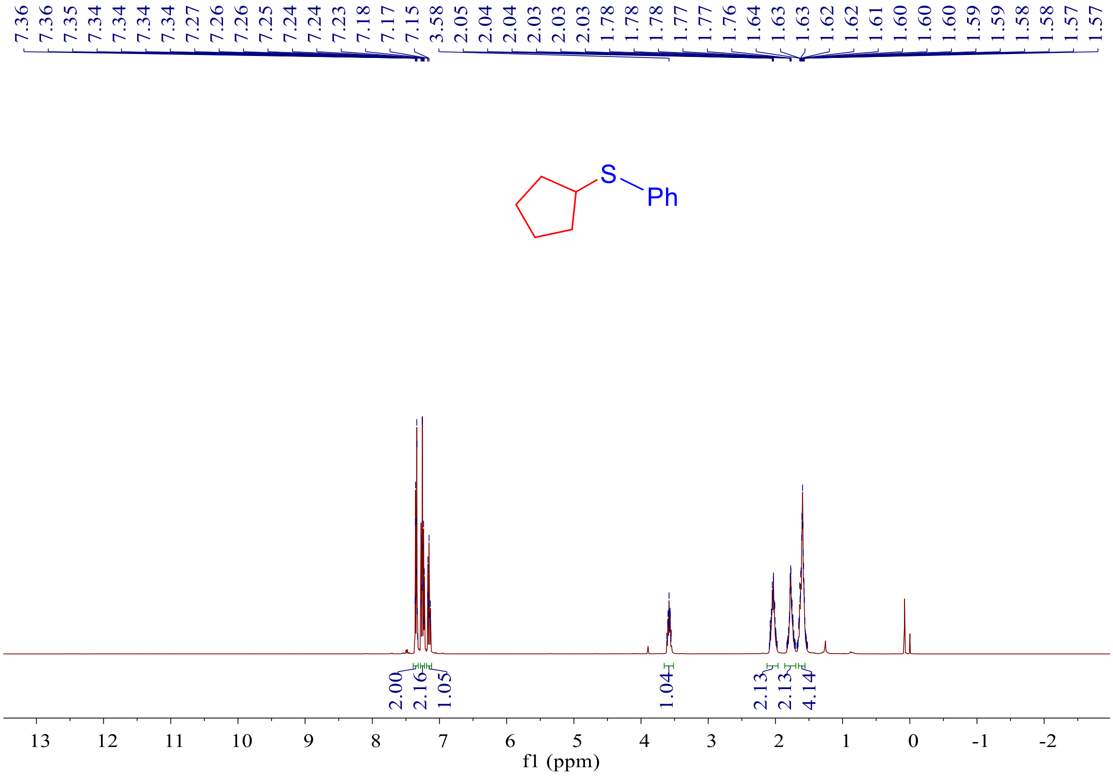
[1]H NMR Spectra of **7c** (400 MHz, $CDCl_3$)



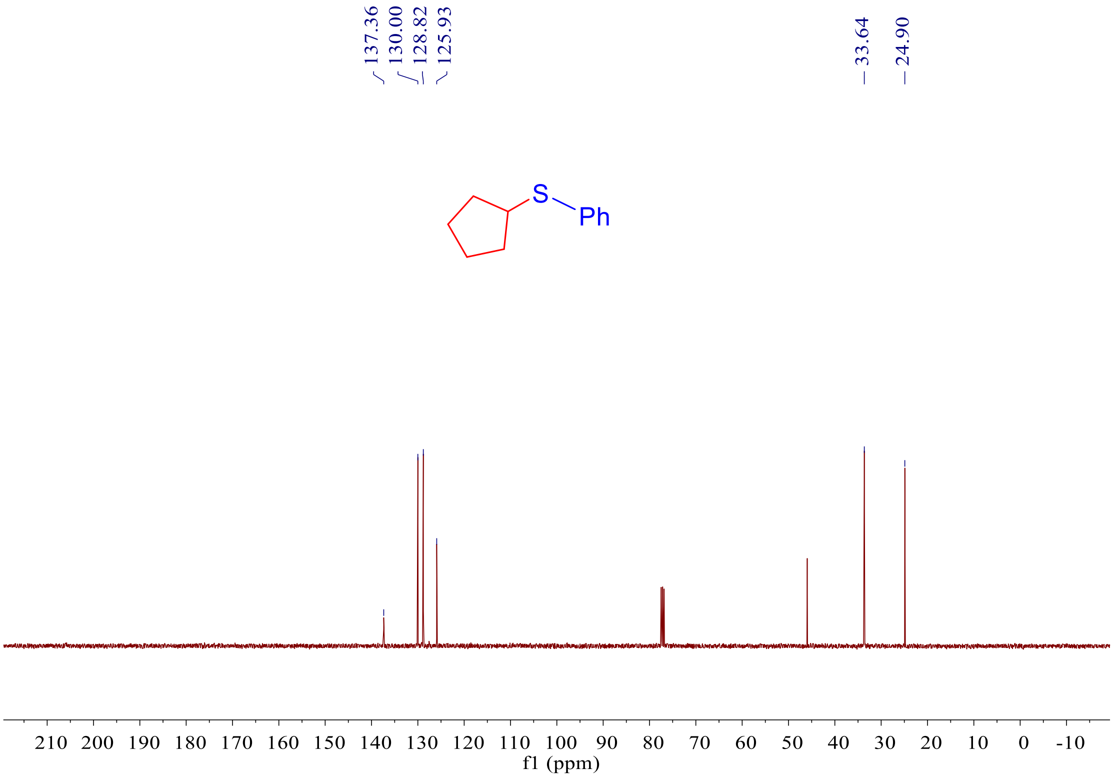
[13]C NMR Spectra of **7c** (400 MHz, $CDCl_3$)



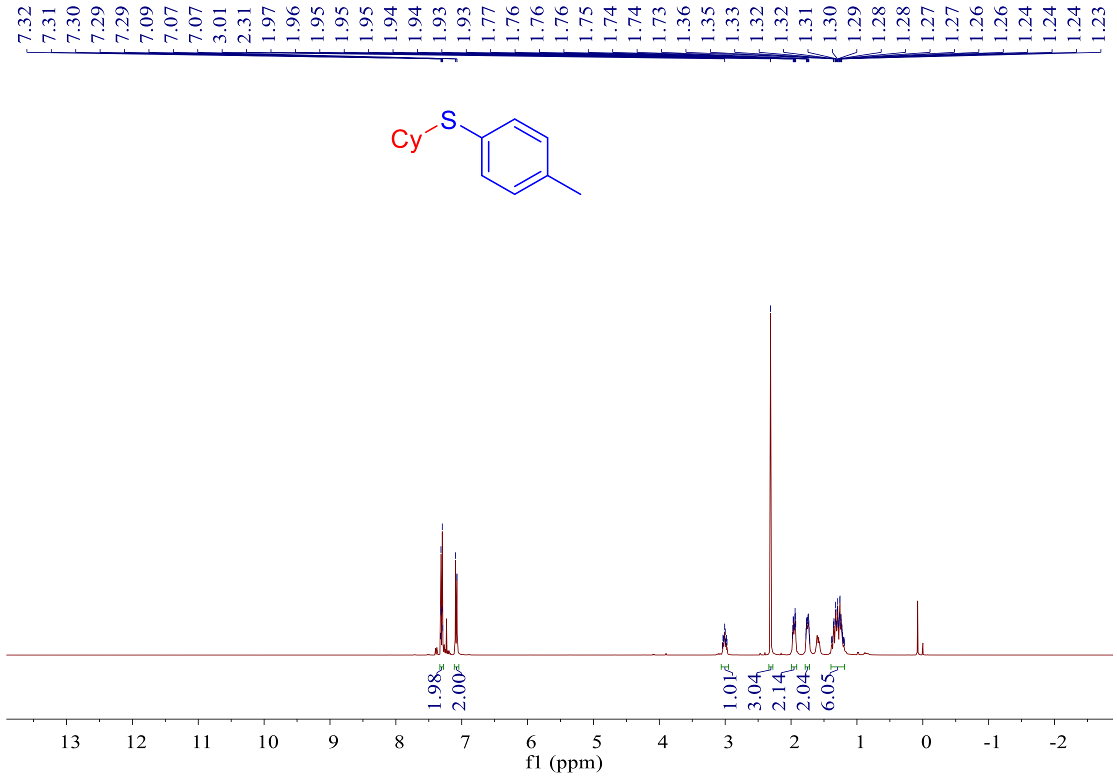
[1]H NMR Spectra of **7d** (400 MHz, $CDCl_3$)



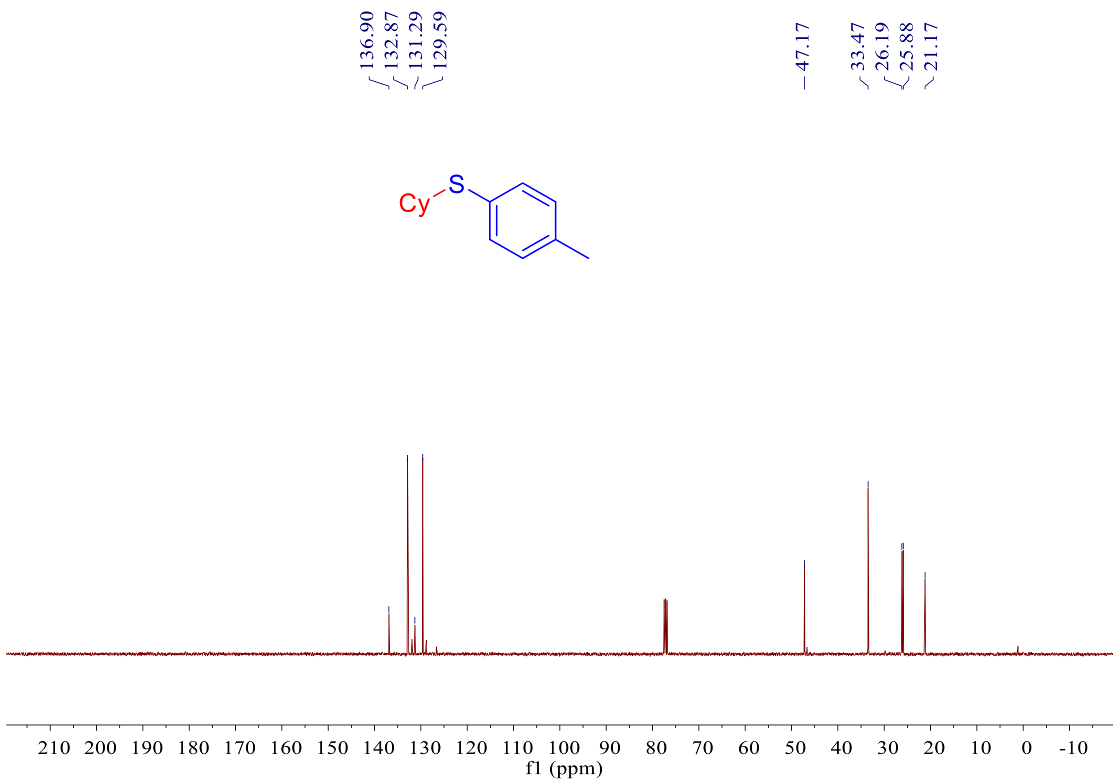
[13]C NMR Spectra of **7d** (400 MHz, $CDCl_3$)



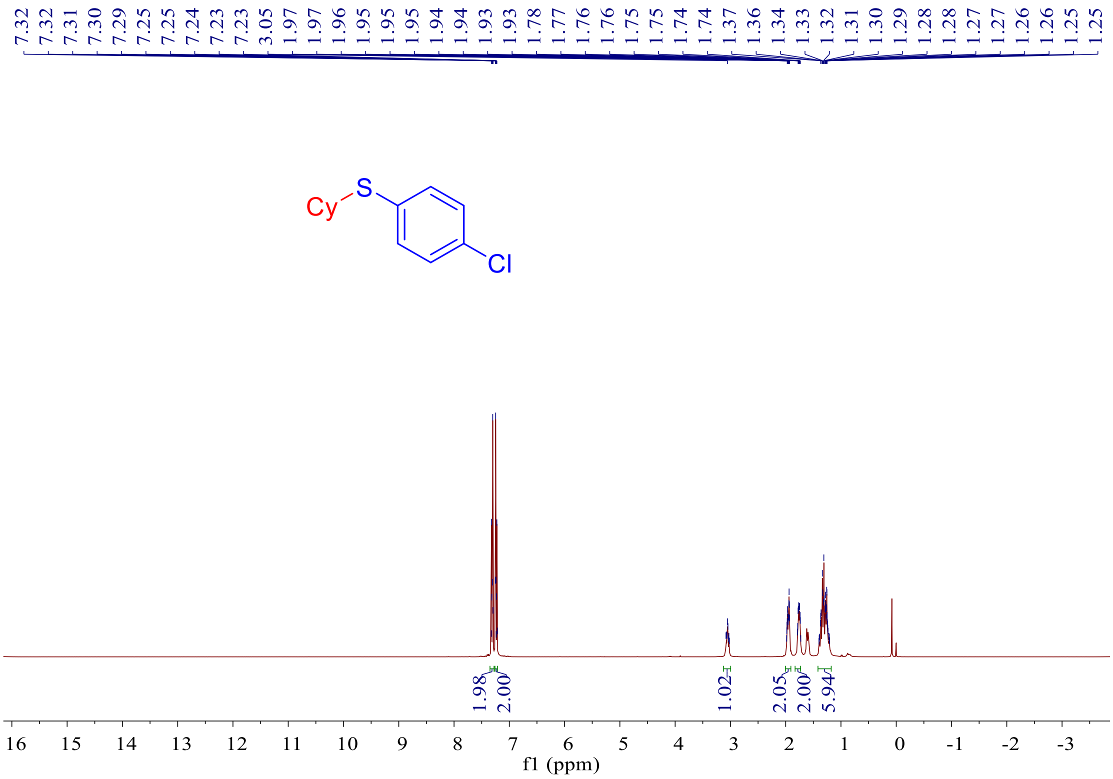
[1]H NMR Spectra of **7e** (400 MHz, $CDCl_3$)



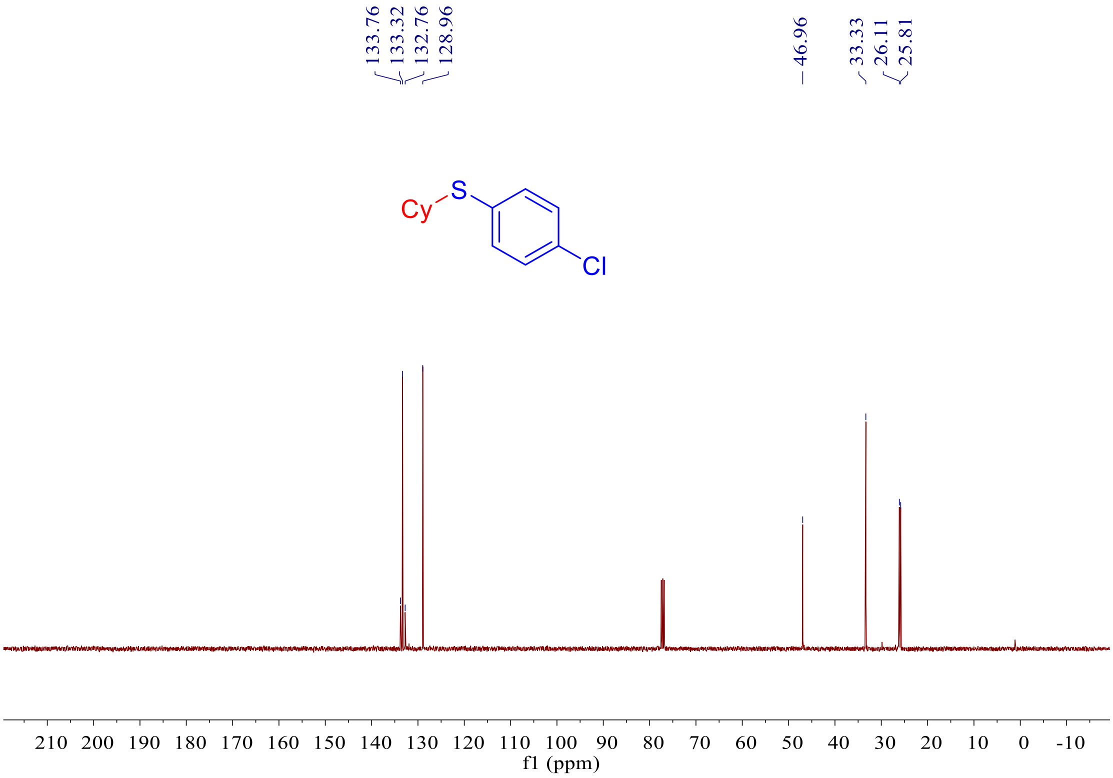
[13]C NMR Spectra of **7e** (400 MHz, $CDCl_3$)



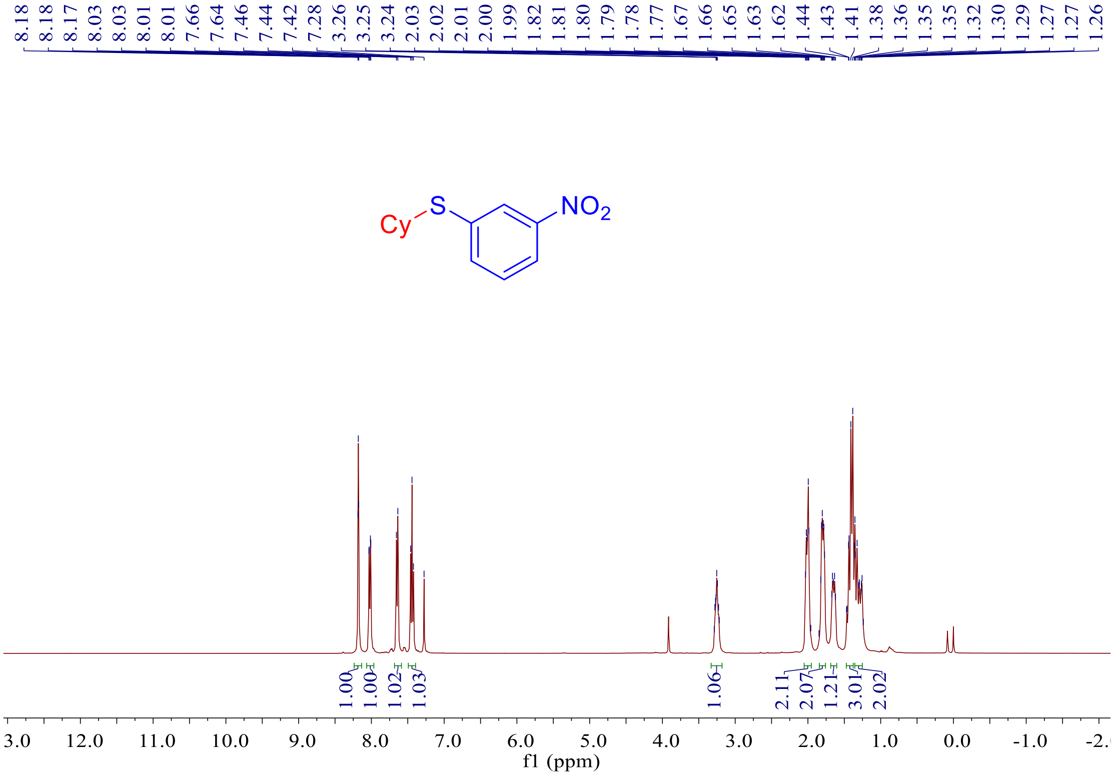
^{1}H NMR Spectra of **7f** (400 MHz, $CDCl_3$)



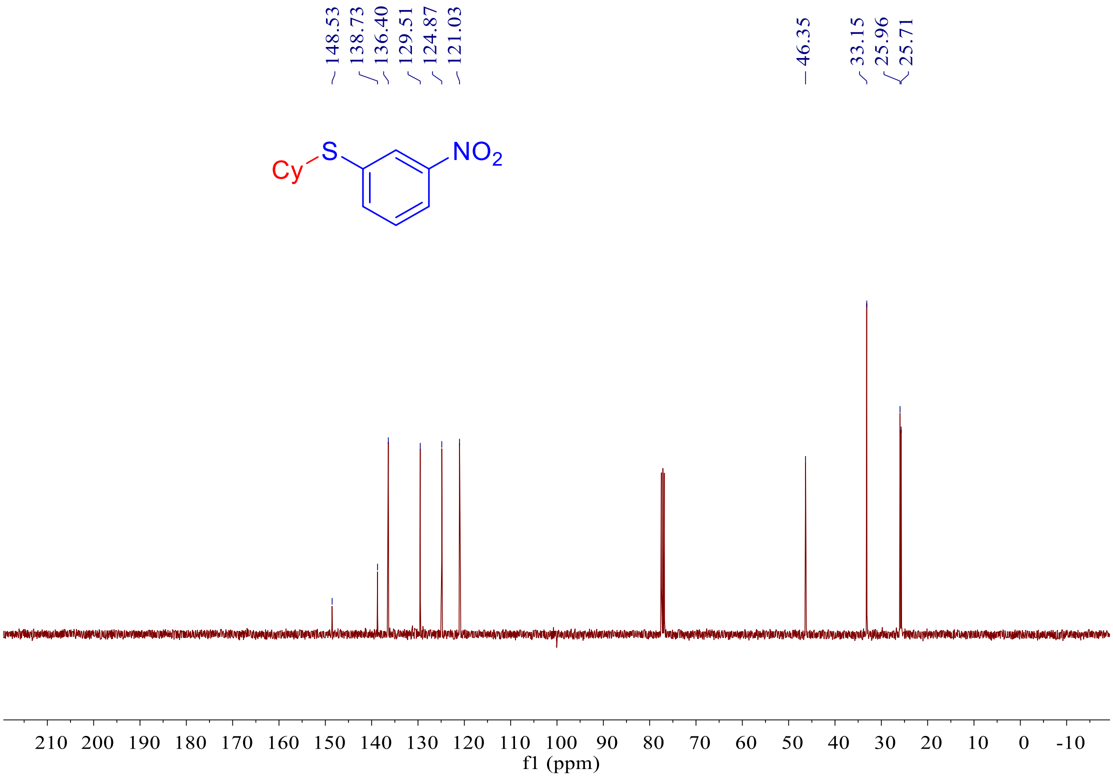
^{13}C NMR Spectra of **7f** (400 MHz, $CDCl_3$)



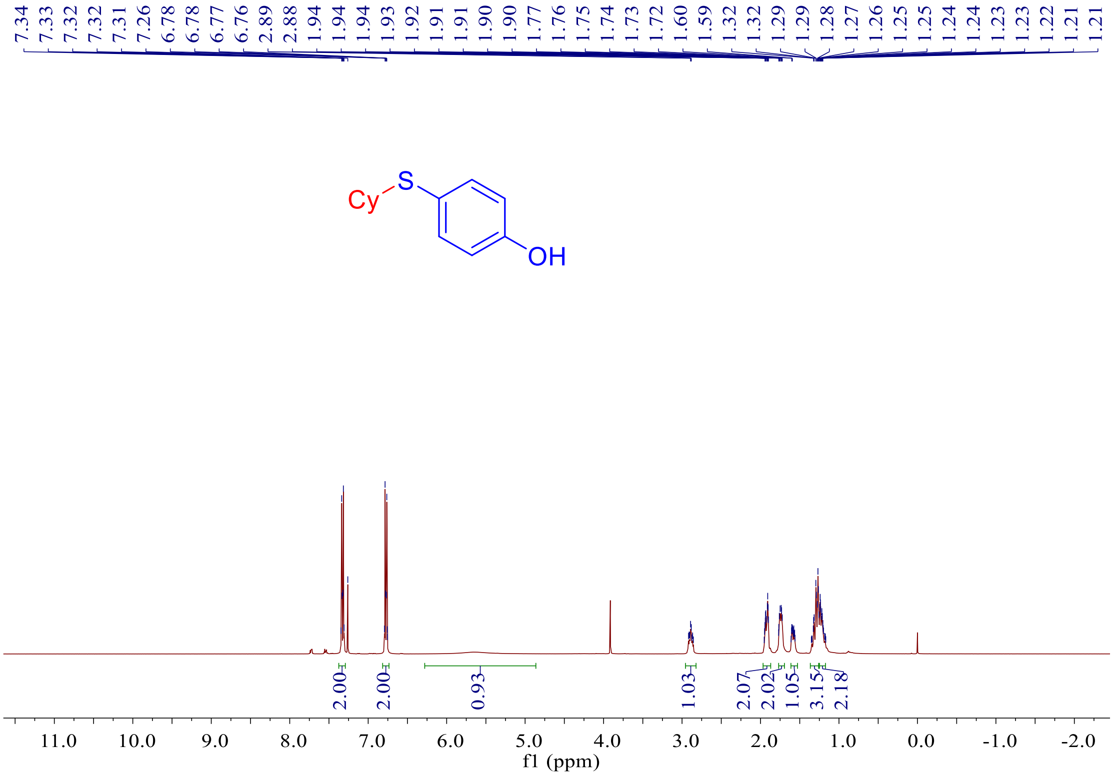
[1]H NMR Spectra of **7g** (400 MHz, $CDCl_3$)



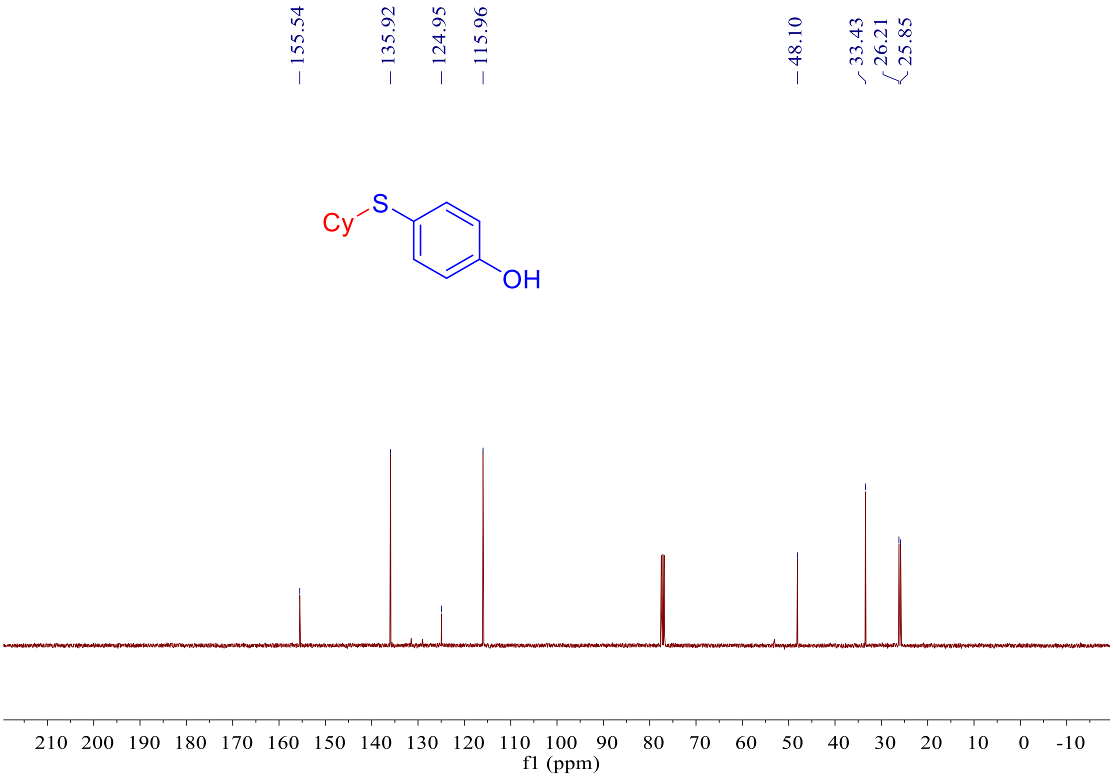
[13]C NMR Spectra of **7g** (400 MHz, $CDCl_3$)



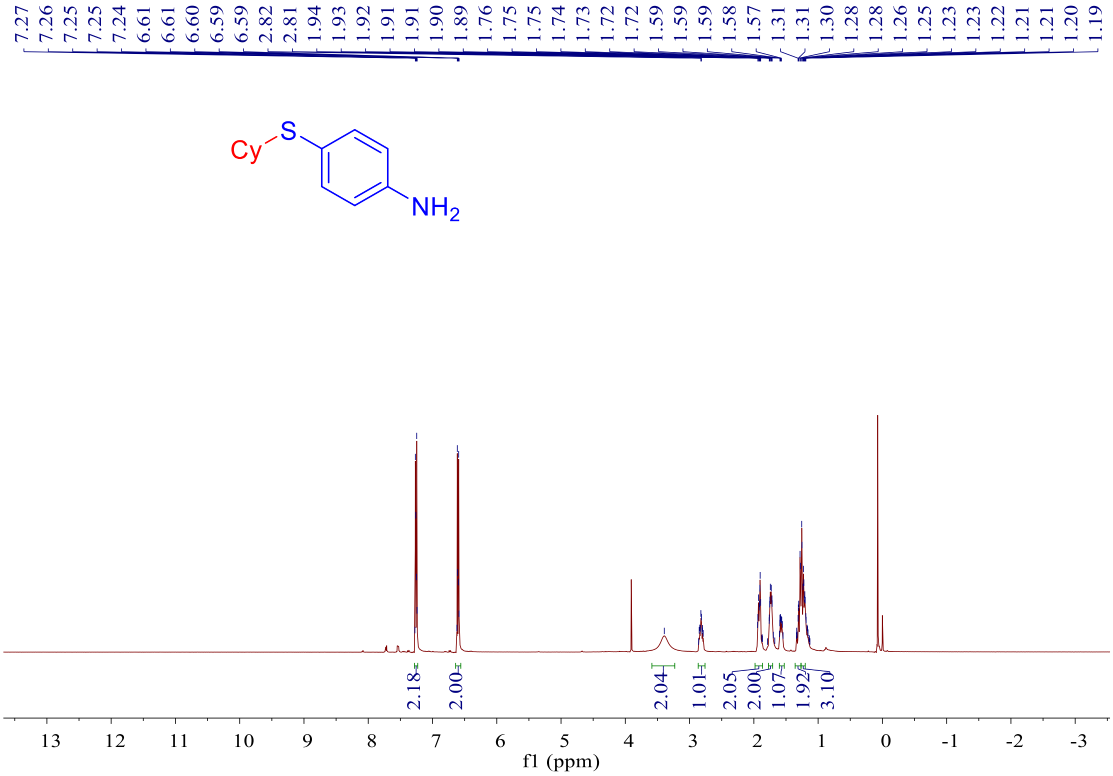
^{1}H NMR Spectra of **7h** (400 MHz, $CDCl_3$)



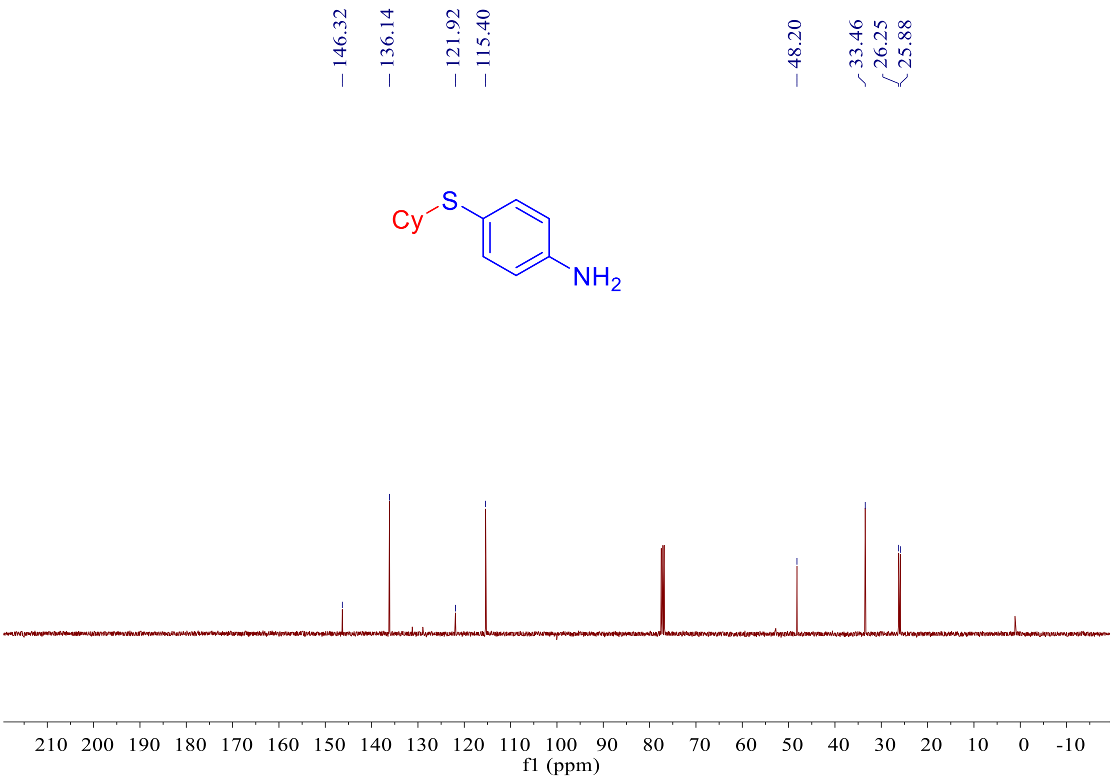
^{13}C NMR Spectra of **7h** (400 MHz, $CDCl_3$)



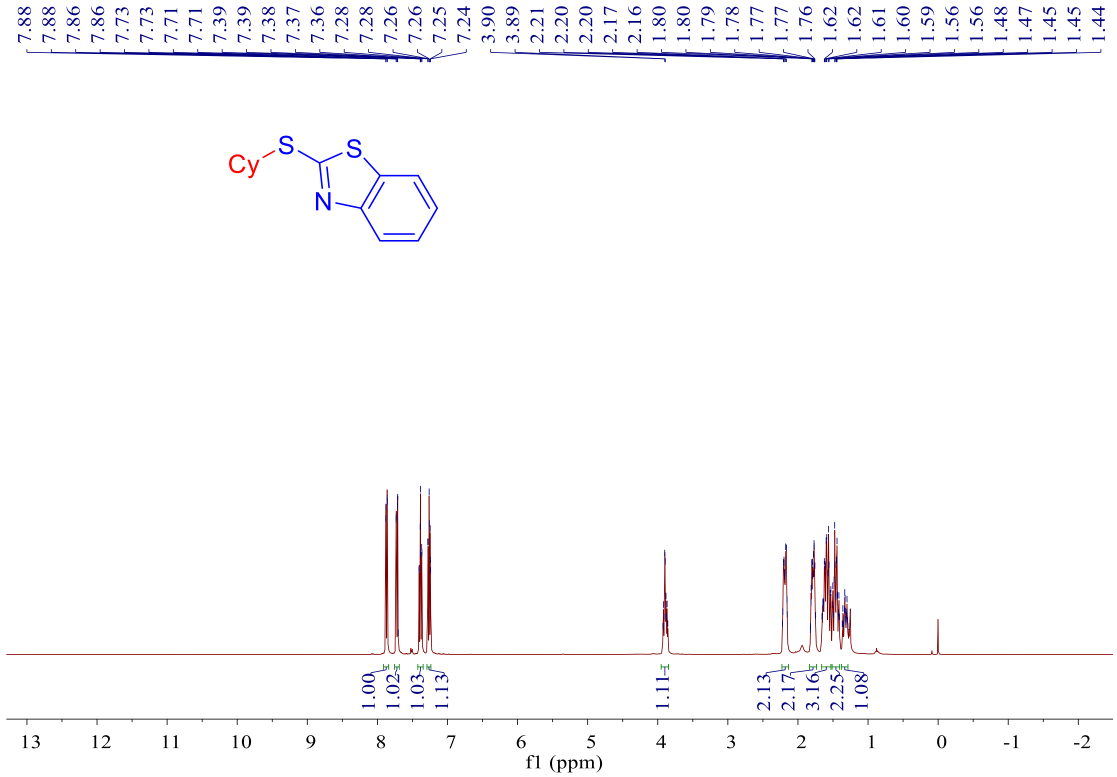
[1]H NMR Spectra of **7i** (400 MHz, $CDCl_3$)



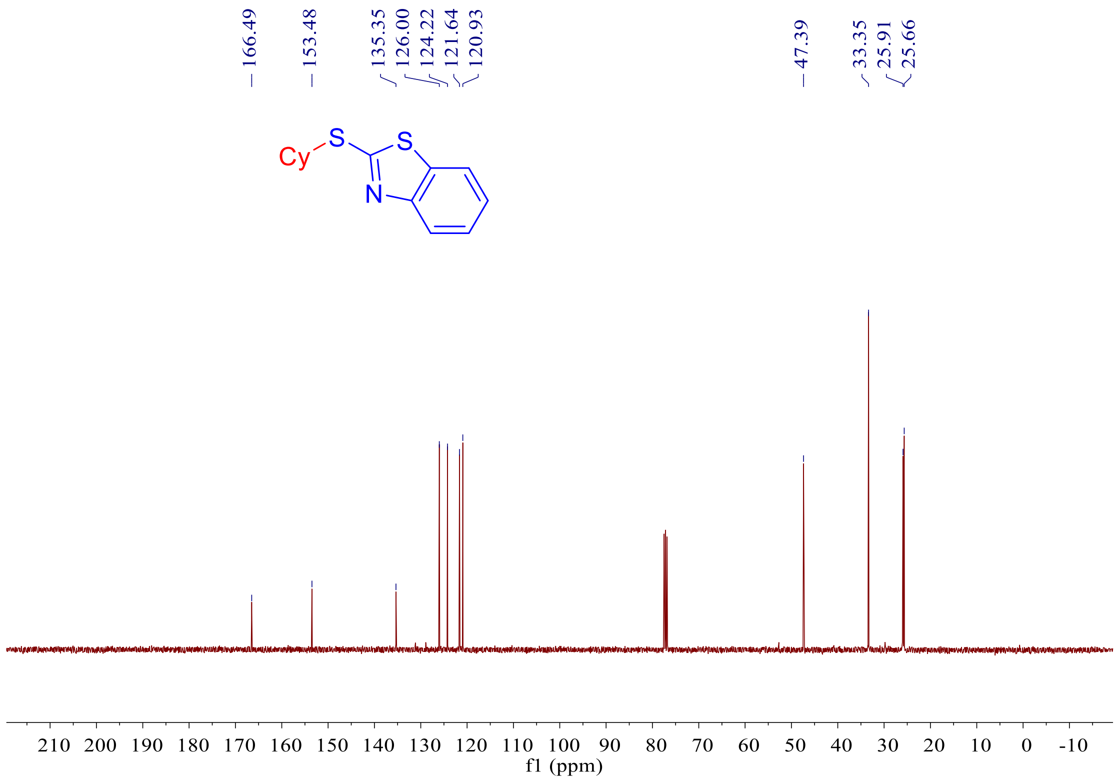
[13]C NMR Spectra of **7i** (400 MHz, $CDCl_3$)



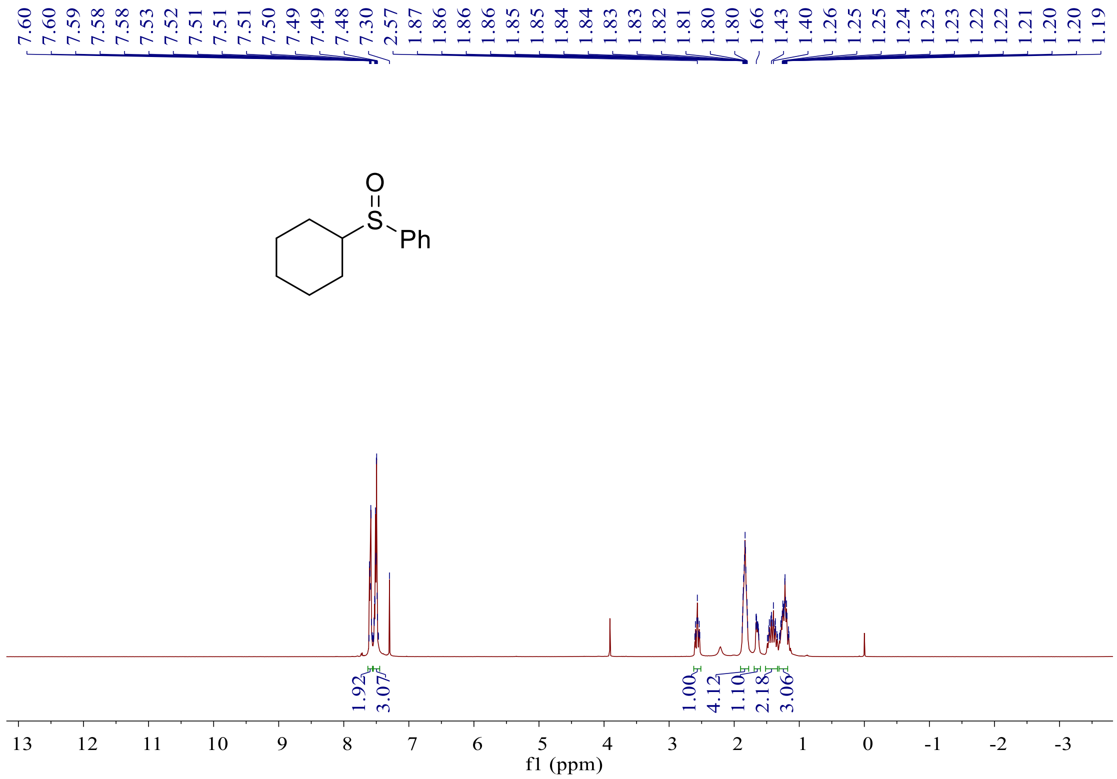
[1]H NMR Spectra of **7j** (400 MHz, $CDCl_3$)



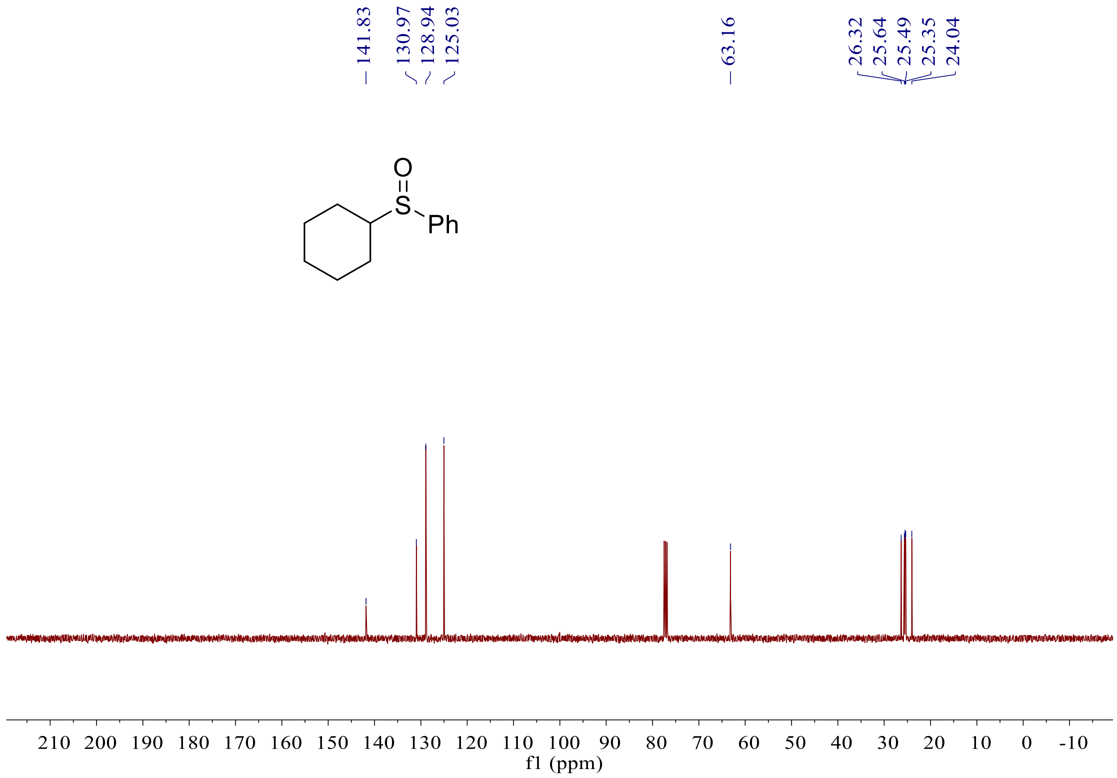
[13]C NMR Spectra of **7i** (400 MHz, $CDCl_3$)



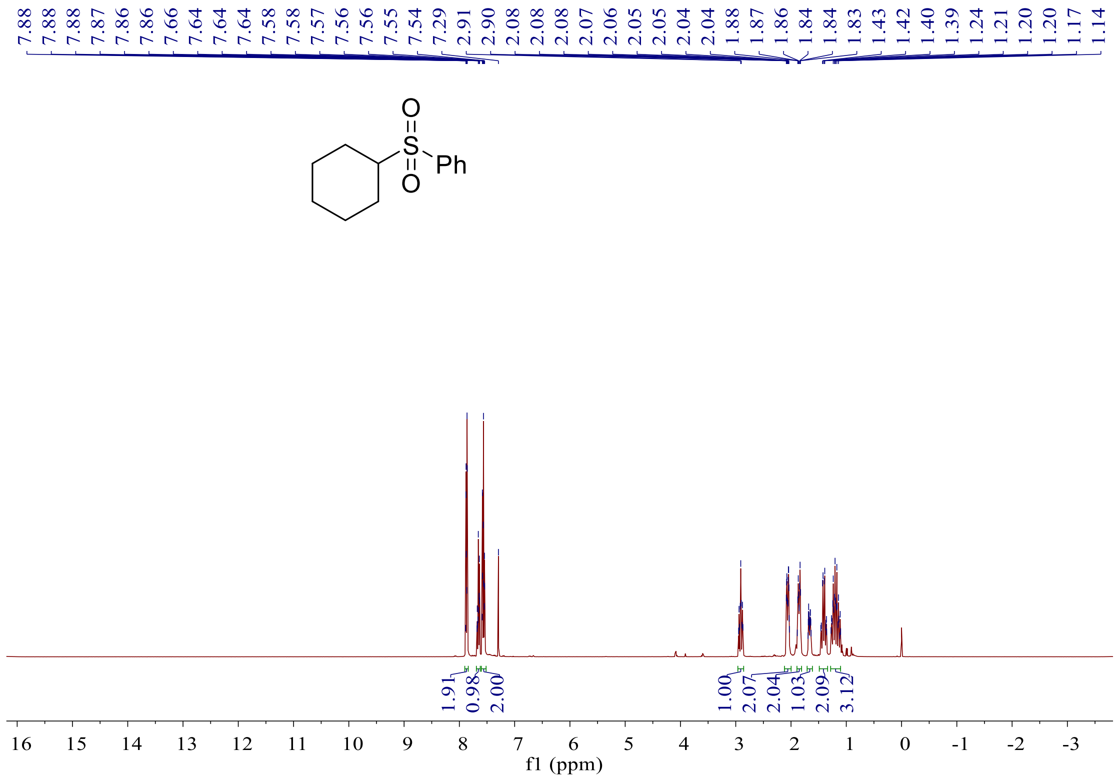
[1]H NMR Spectra of **8a** (400 MHz, $CDCl_3$)



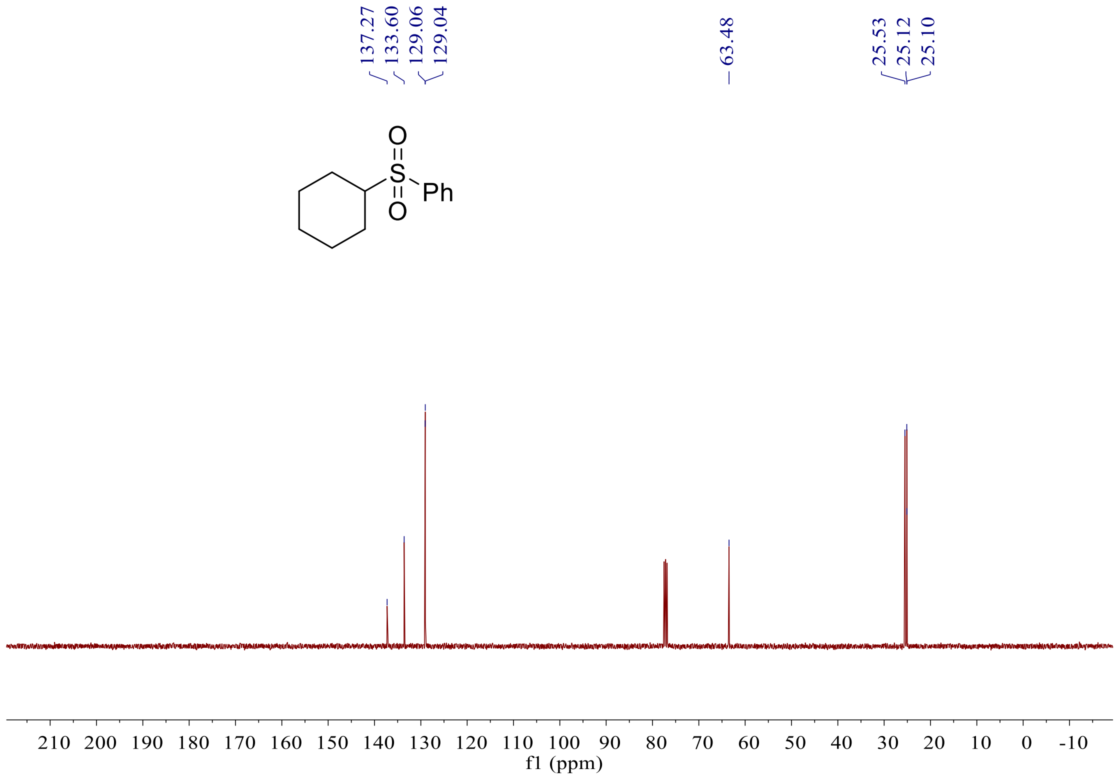
[13]C NMR Spectra of **8a** (400 MHz, $CDCl_3$)



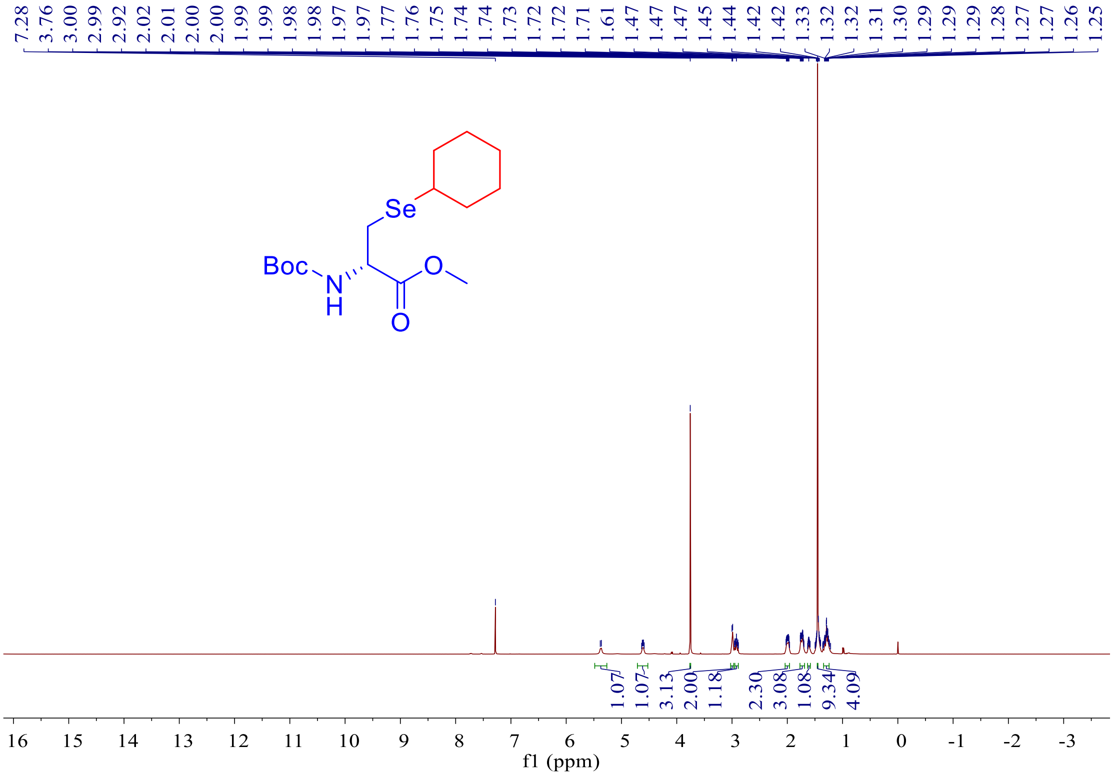
^{1}H NMR Spectra of **8b** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of **8b** (400 MHz, $CDCl_3$)



[1]H NMR Spectra of **3r** (400 MHz, $CDCl_3$)



[13]C NMR Spectra of **3r** (400 MHz, $CDCl_3$)