Supporting information

$F_5PhSeSePhF_5$ as a Novel and Verstile Photosensitive Reagent for the Low-Energy Green Light-Induced Seleno-Michael Addition Reaction

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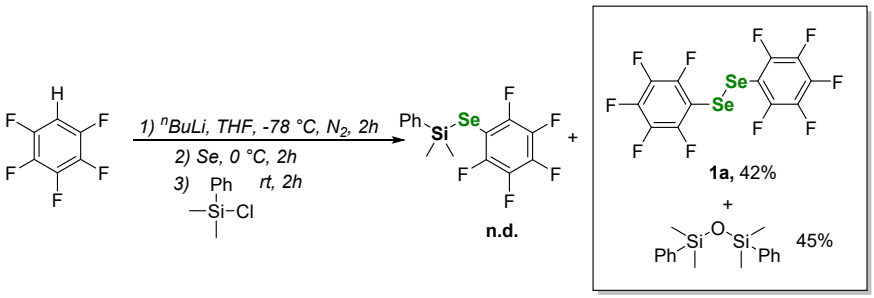
General Information

General information of experiments: Commercial reagents and solvents were used as received and without further purification, unless otherwise stated. Organic solution was concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates (Qingdao Haiyang Chemical China), and the compounds were visualized with a UV lamp at 254 nm. Flash chromatography was performed on silica gel 200 - 300 mesh (purchased from Qingdao Haiyang Chemical China) with commercial solvents (purchased from Adamas-beta®). The ^{1}H, ^{13}C, ^{19}F and ^{77}Se NMR spectra were recorded on a Bruker AM 400 or 600 Spectrometer (400 and 150 MHz for ^{1}H, ^{13}C, 564 MHz for ^{19}F and 114 MHz for ^{77}Se NMR, respectively) and are internally referenced to residual solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.16 ppm in ^{1}H and ^{13}C NMR, respectively). Data from the ^{1}H NMR spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (double of doublet), and m (multiplets). Coupling constants were reported in Hertz (Hz). Data for ^{13}C, ^{19}F and ^{77}Se NMR are reported in terms of chemical shift. High-resolution mass spectrometry (HRMS) was recorded on Waters LCT Premier XE spectrometer.

General information of photochemistry: The Green LED strip (2 meters, 24 W, Emission at 500 nm- 570 nm) was purchased from Epilight (China). LED strip wrapped on the inside of a 250 mL round bottom flask. A layer of aluminium foil was placed around the outside of the round bottom flask. 30V/5A DC Power Supply (MCH-K305D, MCH Instruments Co., Ltd) was used as power transformer. Tape the connector wires as well as the foil with duct tape to secure both in place. Schleck tube, which is made of pure borosilicate glass, was placed on top of the stirring place (the distance between the tube and the light source was about 5 cm). Position a fan about 20 cm above the reactor for cooling. Temperature should be monitored in real time using a temperature probe to determine the ambient temperature. No filter was used during the reaction in this research.

Synthesis of Selenosilane



Scheme S1. Synthesis of selenosilane

UV-Vis Absorption Spectroscopy

UV-Vis absorption spectra of **1a** and **1a′** in EtOH (3 mL) was recorded in 1 cm path quartz cuvettes using a Shimadzu UV-1800 UV/Vis spectromete.

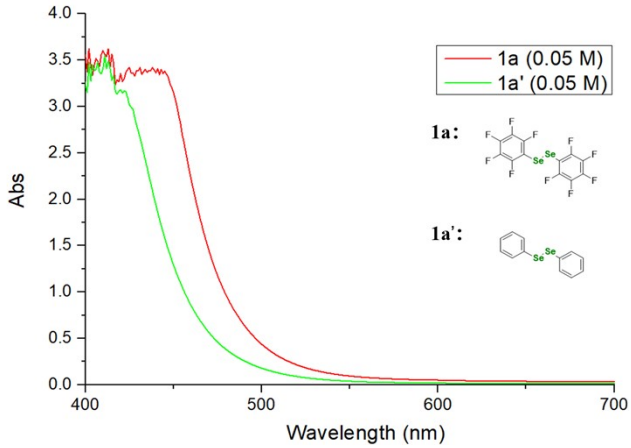


Figure S1. UV-Vis absorption spectra **1a** and **1a′**

UV-Vis absorption spectra of **1a**、HE and **1a** + HE in EtOH (3 mL) was recorded in 1 cm path quartz cuvettes using a Shimadzu UV-1800 UV/Vis spectromete.

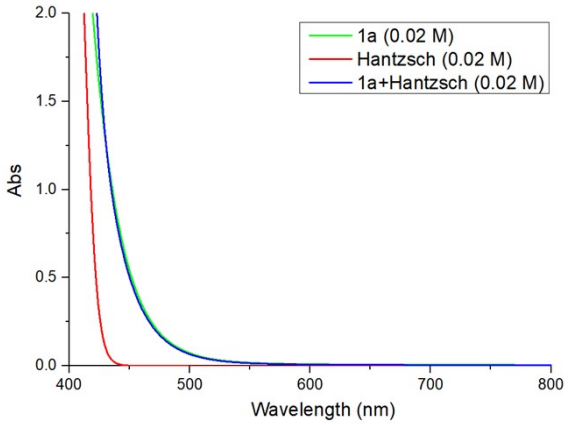


Figure S2. UV-Vis Absorption spectra of reaction components

Mechanism Study

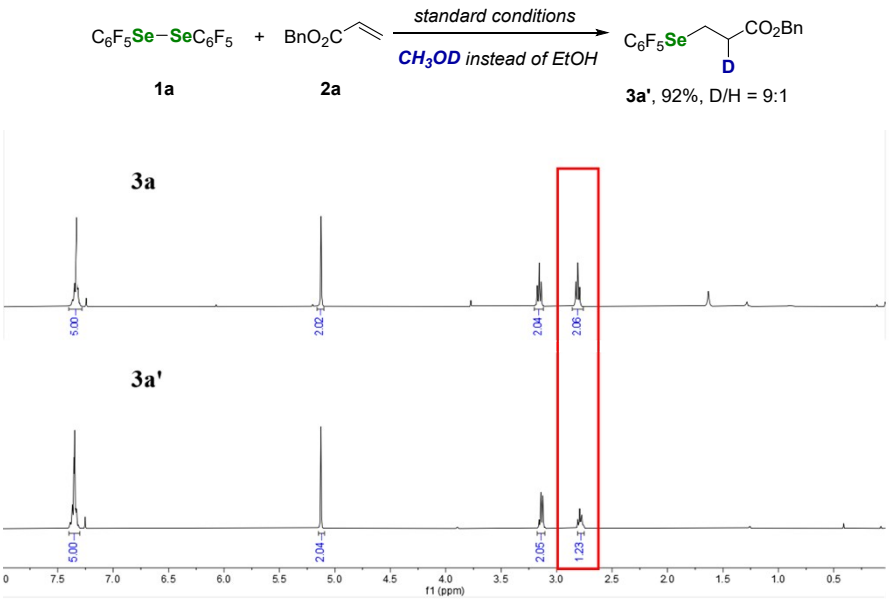
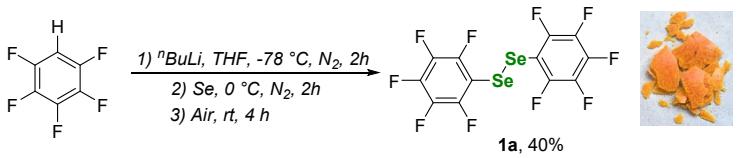


Figure S3. Deuteration experiment

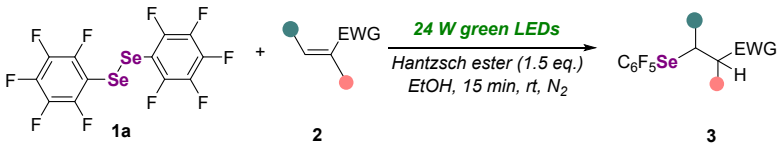
Experiment Procedures and Product Characterization

Synthesis of 1a [1]

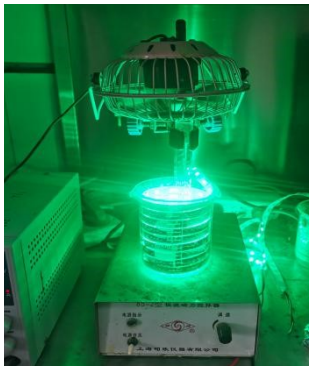


To a solution of pentafluorobenzene (1.2 mL, 10 mmol, 1.0 eq) in 50 mL of THF was slowly added 10 mmol of n-BuLi (2.5 M in hexanes, 4 mL, 10 mmol, 1.0 eq) at −78 °C during a period of 1 h under nitrogen protection. Then the resulting solution was stirred for an additional hour at the same temperature. A slight excess of selenium (0.87 g, 11 mmol, 1.1 eq) was added in one portion and the mixture was allowed to warm to 0 °C in 2 h. After that, it was stirred at room temperature under air for 4 h and filtered through diatomaceous earth. The filtrate was diluted with water and extracted with DCM three times. The combined organic phase was dried over Na_2SO_4. Filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE) to give **1a** as an orange solid (2.02 g, 40% yield). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 148.2-148.0 (m), 146.6-146.4 (m), 143.9-143.7 (m), 142.2-142.0 (m), 138.3-138.0 (m), 136.6-136.3 (m), 103.1 (t, J = 25.5 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -125.0 – -125.1 (m, 2F), -148.5 – -148.6 (m, 1F), -159.2 – -159.3 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 374.0. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}F_{10}Se_2$ 493.8171, Found 493.8170.

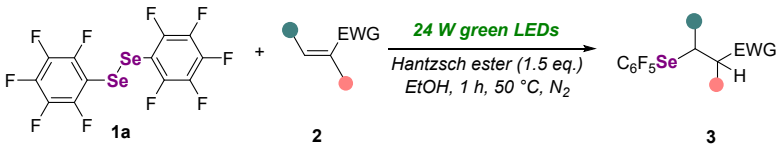
General procedure A



A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, $F_5PhSeSePhF_5$ **1a** (0.08 mmol, 0.8 eq), alkene (0.1 mmol, 1 eq), HE (0.15 mmol, 1.5 eq) and EtOH (1 mL) were added to the vial and bubbled with nitrogen for 15 minutes. Add a fan to maintain the temperature at 30 °C. Photoirradiation was carried out with stirring for 15 minutes. After the reaction, the solution diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired product.



General procedure B

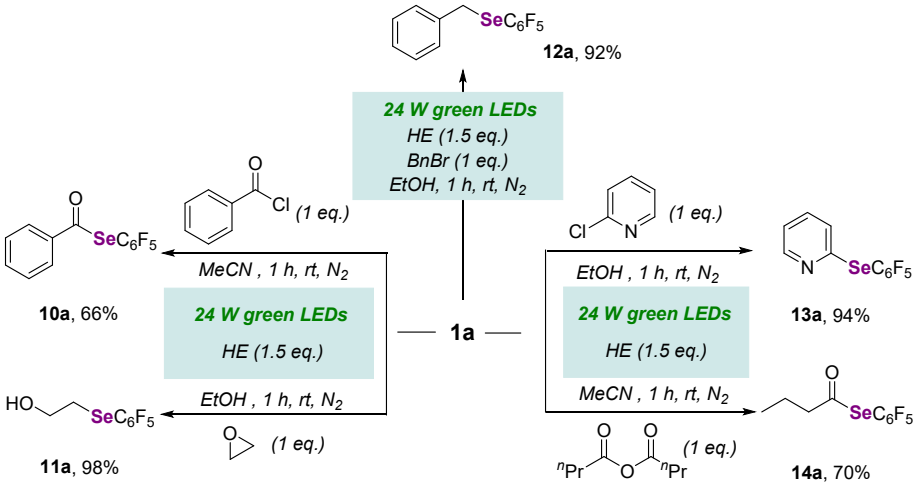


A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, $F_5PhSeSePhF_5$ **1a** (0.08 mmol, 0.8 eq), alkene (0.1 mmol, 1 eq), HE (0.15 mmol, 1.5 eq) and EtOH (1 mL) were added to the vial and bubbled with nitrogen for 15 minutes. Photoirradiation was carried out with stirring for 1 hours at 50 °C. After that, the solution was diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired product.

General procedure C

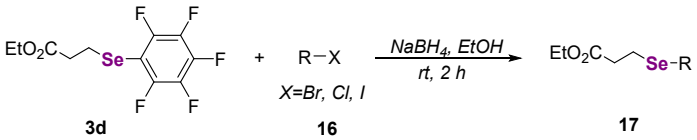
A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, $F_5PhSeSePhF_5$ **1a** (0.08 mmol, 0.8 eq), alkyne (0.1 mmol, 1 eq), HE (0.15 mmol, 1.5 eq) and EtOH (1 mL, 0.1 M) were added to the vial and bubbled with nitrogen for 15 minutes. Add a fan to maintain the temperature at room temperature. Photoirradiation was carried out with stirring for 30 minutes. After that, the solution was diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filterted and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired product.

General procedure D



A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, $F_5PhSeSePhF_5$ **1a** (0.08 mmol, 0.8 eq), electrophilic reagent (0.1 mmol, 1 eq), HE (0.15 mmol, 1.5 eq) and EtOH or MeCN (1 mL) were added to the vial and bubbled with nitrogen for 15 minutes. Add a fan to maintain the temperature at room temperature. Photoirradiation was carried out with stirring for 1 hour. After that, the solution was diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired product.

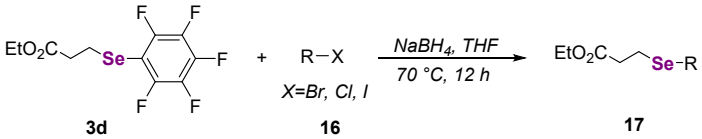
General procedure E



A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, ethyl 3-((perfluorophenyl)selenyl) propanoate **3d** (0.1 mmol, 1 eq), $NaBH_4$ (0.25 mmol, 2.5 eq) and EtOH (1 mL) were added to the vial under nitrogen protection. To this solution was added alkyl halide or aryl halide (0.15 mmol, 1.5 eq). The resulting solution was stirred at room temperature for 2 hours. After that, the solution was diluted and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filterted and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired

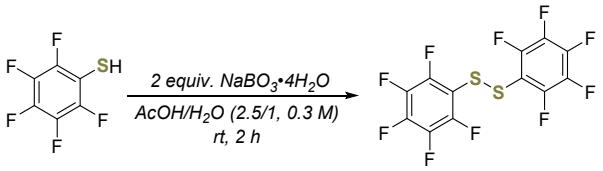
product.

General procedure F



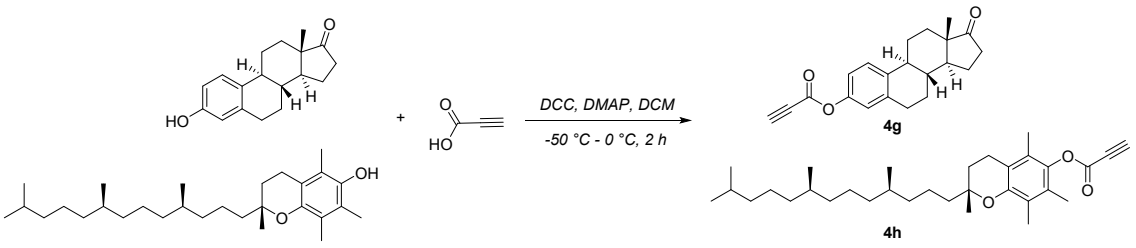
A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, ethyl 3-((perfluorophenyl)selenyl) propanoate **3d** (0.1 mmol, 1 eq), $NaBH_4$ (0.25 mmol, 2.5 eq) and THF (1 mL) were added to the vial under nitrogen protection. To this solution was added alkyl halide or aryl halide (0.15 mmol, 1.5 eq). The solution was stirred at 70℃ for 12 hours. After that, the solution was diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filterted and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give desired product.

Synthesis of 1b [2]



Pentafluorobenzenethiol (600 mg, 3.0 mmol, 1.0 eq) was added to a solution of sodium perborate monohydrate ($NaBO_3 \cdot 4H_2O$, 923 mg, 6.0 mmol, 2.0 eq) in a solvent mixture of acetic acid (AcOH, 7.5 mL) and water (3.0 mL) at room temperature. The reaction mixture was stirred for 2 hours. After that, the mixture was concentrated under reduced pressure and poured into saturated aqueous $NaHCO_3$ solution (10 mL). The resulting heterogeneous mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with pentane, to afford 595 mg of the title compound as a pale-yellow solid (yield: >99%).

Synthesis of 4g and 4h [3]



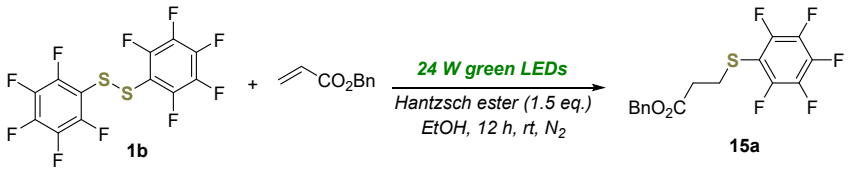
To the solution of phenol structure (5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (10.0 mL, 0.5 M) was added propiolic acid (5.1 mmol, 1.02 equiv.) and DCC (5.1 mmol, 1.02 equiv.), DMAP (2 mmol, 0.4 equiv.) at -50 ºC. The mixture was warmed up to 0 ºC and stirred at 0 ºC for 2 hours. Then the reaction mixture was filtered and the filtrate was concentrated under vacuum to give the crude product. It was purified

by flash column chromatography on silica gel to give the product.

Synthesis of 4g: According to the general procedure, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product **4g** as a yellow solid (193 mg, 12% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 8.5 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 3.07 (s, 1H), 2.91 (dd, *J* = 9.0, 4.3 Hz, 2H), 2.50 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.41 – 2.37 (m, 1H), 2.31 – 2.25 (m, 1H), 2.14 – 1.98 (m, 4H), 1.62 – 1.47 (m, 6H), 0.90 (s, 3H). The spectroscopic data is in agreement with that previously reported.[3]

Synthesis of 4h: According to the general procedure, crude product was purified by flash column chromatography on silica gel (PE/EA = 50 : 1) to give the product **4h** as a colorless oil (1.06 g, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.05 (s, 1H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.87 – 1.76 (m, 2H), 1.61 – 1.54 (m, 3H), 1.46 – 1.27 (m, 15H), 1.20 – 1.09 (m, 6H), 0.91 – 0.87 (m, 12H). The spectroscopic data is in agreement with that previously reported.[3]

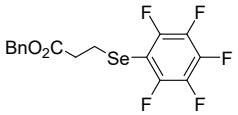
Synthesis of 15a



A 4 mL vial equipped with a magnetic stirring bar was dried in oven. After cooling the vial to room temperature, $F_5PhSSPhF_5$ **1b** (32 mg, 0.08 mmol, 0.8 eq), alkene (15 mg, 0.1 mmol, 1.0 eq), HE (38 mg, 0.15 mmol, 1.5 eq) and EtOH (1 mL) were added to the vial and bubbled with nitrogen for 15 minutes. Add a fan to maintain the temperature at room temperature. Photoirradiation was carried out with stirring for 12 hours. After that, the solution was diluted with water and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated under vacuum. The residue was purified by flash columnchromatography on silica gel to give the desired product as colorless oil (yield: 49%).

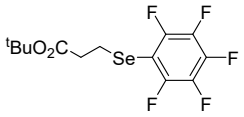
Product Characterization

Benzyl 3-((perfluorophenyl)selenyl) propanoate (3a)



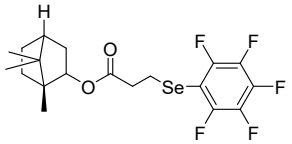
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (37 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 - 7.33 (m, 5H), 5.13 (s, 2H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 171.5, 148.2-148.0 (m), 146.6-146.4 (m), 142.6-142.4 (m), 140.9-140.7 (m), 138.5-138.3 (m), 136.9-136.6 (m), 135.6, 128.8, 128.6, 128.5, 102.0 (t, *J* = 25.6 Hz), 67.0, 35.7, 22.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.0 – -152.1 (m, 1F), -160.2 – -160.3 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 186.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{11}F_5O_2Se$ 409.9844, Found 409.9845.

tert-Butyl 3-((perfluorophenyl) selenyl) propanoate (3b)



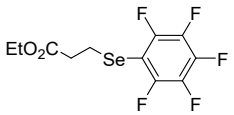
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (35 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.08 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H), 1.45 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 170.9, 148.2-148.1 (m), 146.6-146.5 (m), 142.5-142.3 (m), 140.8-140.6 (m), 138.5-138.3 (m), 136.9-136.6 (m), 102.2 (t, *J* = 25.4 Hz), 81.6, 36.7, 28.2, 23.1. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.5 – -152.6 (m, 1F), -160.5 – -160.6 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 184.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{13}F_5O_2Se$ 376.0001, Found 376.0003.

(1R)-1,7,7-Trimethylbicyclo [2.2.1] heptan-2-yl-3-((perfluorophenyl)selenyl) propanoate (3c)



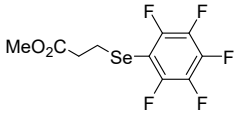
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (40 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.70 – 4.67 (m, 1H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.65 (m, 4H), 1.59 – 1.52 (m, 1H), 1.17 – 1.04 (m, 2H), 0.95 (s, 3H), 0.83 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 171.0, 148.2-148.0 (m), 146.6-146.4 (m), 142.6-142.4 (m), 140.9-140.7 (m), 138.6-138.3 (m), 136.9-136.6 (m), 102.0 (t, *J* = 25.0 Hz), 82.0, 48.9, 47.0, 45.1, 38.8, 36.0, 33.8, 27.1, 22.8, 20.2, 20.0, 11.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.4 – -126.5 (m, 2F), -152.3 – -152.4 (m, 1F), -160.3 – -160.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 187.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{21}F_5O_2Se$ 456.0627, Found 456.0629.

Ethyl 3-((perfluorophenyl)selanyl) propanoate (3d)



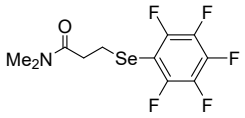
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (31 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.15 (q, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 171.7, 148.2-148.1 (m), 146.6-146.5 (m), 142.6-142.5 (m), 140.9-140.7 (m), 138.6-138.3 (m), 136.9-136.6 (m), 102.0 (t, *J* = 25.7 Hz), 61.1, 35.7, 22.7, 14.3. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.2 – -152.3 (m, 1F), -160.3 – -160.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 185.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_9F_5O_2Se$ 347.9688, Found 347.9689.

Methyl 3-((perfluorophenyl)selenyl) propanoate (3e)



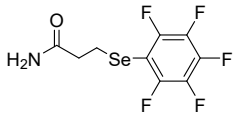
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (31 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.69 (s, 3H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.1, 148.2-148.0 (m), 146.6-146.5 (m), 142.6-142.4 (m), 140.9-140.7 (m), 138.6-138.3 (m), 136.9-136.6 (m), 102.1-101.7 (m), 52.1, 35.5, 22.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.1 – -152.2 (m, 1F), -160.3 – -160.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 186.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_7F_5O_2Se$ 333.9531, Found 333.9532.

N, N-Dimethyl-3-((perfluorophenyl) selenyl) propanamide (3f)



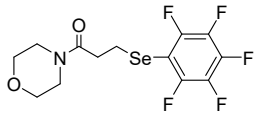
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 10: 1) to give the product as white solid (32 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.12 (t, *J* = 6.6 Hz, 2H), 2.98 (s, 3H), 2.95 (s, 3H), 2.83 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 171.0, 148.0-147.8 (m), 146.3-146.2 (m), 142.2-142.0 (m), 140.5-140.3 (m), 138.5-138.2 (m), 136.8-136.5 (m), 103.9 (t, *J* = 26.8 Hz), 37.0, 35.5, 34.7, 24.3. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.6 – -126.7 (m, 2F), -153.2 – -153.3 (m, 1F), -160.7 – -160.9 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 190.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_{10}F_5NOSe$ 346.9848, Found 346.9850.

3-((Perfluorophenyl) selenyl) propanamide (3g)



According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 1 : 1) to give the product as white solid (27 mg, 86% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 7.38 (s, 1H), 6.94 (s, 1H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d6) δ: 172.9, 148.0-147.9 (m), 146.4-146.3 (m), 142.0-141.8 (m), 140.3-140.1 (m), 138.3-138.1 (m), 136.6-136.4 (m), 103.3 (t, *J* = 26.6 Hz), 55.3, 36.3, 24.5. **^{19}F NMR** (564 MHz, DMSO-d6) δ: -127.0 – -127.1 (m, 2F), -154.0 – -154.1 (m, 1F), -161.3 – -161.4 (m, 2F). **^{77}Se NMR** (114 MHz, DMSO-d6) δ: 184.0. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_9H_6F_5NOSe$ 318.9535, Found 318.9537.

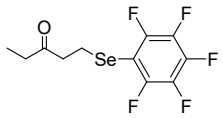
1-Morpholino-3-((perfluorophenyl)selenyl) propan-1-one (3h)



According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as white solid (33 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.70 – 3.69 (m, 2H), 3.69 – 3.68 (m, 2H), 3.64 – 3.61 (m, 2H), 3.45 – 3.42 (m, 2H), 3.15 (t, *J* = 6.6 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 169.6, 148.0-147.8 (m), 146.4-146.2 (m), 142.3-142.1 (m), 140.6-140.4 (m), 138.5-138.3 (m), 136.8-136.6 (m), 103.6 (t, *J* = 25.3 Hz), 66.9, 66.5, 45.8, 42.2, 34.4, 23.9. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.5 – -126.6 (m,

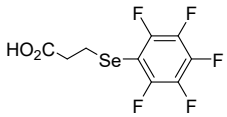
2F), -152.9 – -153.0 (m, 1F), -160.5 – -160.6 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 189.9. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{12}F_5NO_2Se$ 388.9953, Found 388.9955.

1-((Perfluorophenyl)selenyl) pentan-3-one (3i)



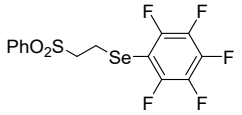
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (24 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.07 (t, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 209.2, 148.1-148.0 (m), 146.5-146.4 (m), 142.5-142.3 (m), 140.8-140.6 (m), 138.5-138.3 (m), 136.9-136.6 (m), 102.7 (t, *J* = 25.4 Hz), 43.1, 36.2, 22.0, 7.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.5 – -126.6 (m, 2F), -152.5 – -152.6 (m, 1F), -160.4 – -160.5 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 187.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_9F_5Ose$ 331.9739, Found 331.9740.

3-((Perfluorophenyl)selenyl) propanoic acid (3j)



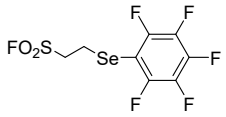
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (27 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 10.60 (s, 1H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.83 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d6) δ: 173.5, 148.1-148.0 (m), 146.5-146.4 (m), 142.0-141.9 (m), 140.5-140.3 (m), 138.3-138.1 (m), 136.7-136.4 (m), 102.6 (t, *J* = 26.1 Hz), 35.8, 23.9. **^{19}F NMR** (564 MHz, DMSO-d6) δ: -127.0 – -127.1 (m, 2F), -153.6 – -153.7 (m, 1F), -161.3 – -161.4 (m, 2F). **^{77}Se NMR** (114 MHz, DMSO-d6) δ: 183.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_9H_5F_5O_2Se$ 319.9375, Found 319.9379.

(Perfluorophenyl)(2-(phenylsulfonyl) ethyl) selane (3k)



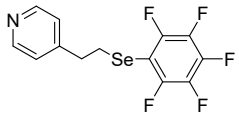
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (31 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.90-7.88 (m, 2H), 7.73 – 7.69 (m, 1H), 7.62 – 7.58 (m, 2H), 3.41 – 3.37 (m, 2H), 3.13 – 3.09 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 148.2-148.1 (m), 146.5-146.4 (m), 143.1-142.9 (m), 141.4-141.2 (m), 138.6-138.4 (m), 138.3, 136.9-136.7 (m), 134.4, 129.7, 128.3, 100.6 (t, *J* = 25.0 Hz), 57.4, 18.9. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.0 – -126.1 (m, 2F), -150.5 – -150.6 (m, 1F), -159.3 – -159.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 190.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_9F_5O_2SSe$ 415.9409, Found 415.9413.

2-((Perfluorophenyl)selenyl) ethane-1-sulfonyl fluoride (3l)



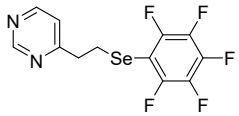
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (26 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.72 – 3.67 (m, 2H), 3.31 – 3.27 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 148.3-148.1 (m), 146.6-146.5 (m), 143.5-143.3 (m), 141.7-141.6 (m), 138.8-138.6 (m), 137.1-136.9 (m), 99.9 (t, *J* = 25.7 Hz), 52.2, 18.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: 53.7 (1F), -125.9 – -126.0 (m, 2F), -149.5 – -149.6 (m, 1F), -158.8 – -158.9 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 193.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_8H_4F_6O_2SSe$ 357.9001, Found 357.9003.

4-(2-((Perfluorophenyl)selenyl) ethyl) pyridine (3m)



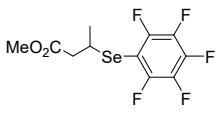
According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 2 : 1) to give the product as white solid (31 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 5.1 Hz, 2H), 7.11 (d, *J* = 5.0 Hz, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 149.8, 148.6, 148.0-147.9 (m), 146.3-146.2 (m), 142.4-142.2 (m), 140.6-140.5 (m), 138.4-138.2 (m), 136.7-136.5 (m), 123.9, 101.5 (t, *J* = 25.9 Hz), 36.2, 27.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: 53.7 (1F), -126.5 – -126.6 (m, 2F), -152.0 – -152.1 (m, 1F), -160.1 – -160.2 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 180.9. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_8F_5NSe$ 352.9742, Found 352.9742.

4-(2-((Perfluorophenyl)selenyl) ethyl) pyrimidine (3n)



According to the general procedure A, crude product was purified by flash column chromatography on silica gel (PE/EA = 2 : 1) to give the product as colorless oil (30 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.48 – 8.44 (m, 3H), 3.36 (t, *J* = 7.0 Hz, 2H), 3.23 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 154.9, 148.0-147.9 (m), 146.3-146.2 (m), 144.8, 144.1, 142.9, 142.3-142.2 (m), 140.6-140.5 (m), 138.3-138.1 (m), 136.6, 102.1 (t, *J* = 24.9 Hz), 36.0, 26.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.3 – -152.4 (m, 1F), -160.2 – -160.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 178.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_7F_5N_2Se$ 353.9695, Found 353.9698.

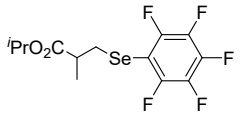
Methyl 3-((perfluorophenyl)selenyl) butanoate (3o)



According to the general procedure B, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (16 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.79 – 3.74 (m, 1H), 3.68 (s, 3H), 2.74 – 2.63 (m, 2H), 1.46 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR**

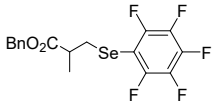
(150 MHz, $CDCl_3$) δ: 171.5, 148.5-148.4 (m), 146.9-146.8 (m), 142.8-142.7 (m), 141.2-141.0 (m), 138.5-138.3 (m), 136.8-136.7 (m), 101.3 (t, *J* = 26.0 Hz), 52.0, 42.9, 35.4, 22.2. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -124.9 – -125.0 (m, 2F), -151.2 – -151.3 (m, 1F), -160.0 – -160.2 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 270.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_9F_5O_2Se$ 347.9688, Found 347.9687.

Isopropyl 3-((perfluorophenyl)selenyl) butanoate (3p)



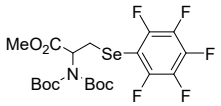
According to the general procedure B, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (20 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.03 – 4.97 (m, 1H), 3.17 (dd, *J* = 12.3, 8.1 Hz, 1H), 2.96 (dd, *J* = 12.3, 5.8 Hz, 1H), 2.69 – 2.60 (m, 1H), 1.26 – 1.22 (m, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 174.0, 148.1-147.9 (m), 146.4-146.3 (m), 142.3-142.2 (m), 140.7-140.6 (m), 138.4-138.2 (m), 136.7-136.5 (m), 102.3 (t, *J* = 24.6 Hz), 68.5, 41.0, 31.2, 21.7, 21.6, 17.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.4 – -126.5 (m, 2F), -152.5 – -152.6 (m, 1F), -160.4 – -160.6 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 160.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_{13}F_5O_2Se$ 376.0001, Found 376.0003.

Benzyl 2-methyl-3-((perfluorophenyl) selenyl) propanoate (3q)



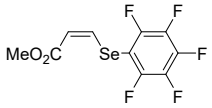
According to the general procedure B, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (22 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.31 (m, 5H), 5.16 – 5.08 (m, 2H), 3.21 (dd, *J* = 12.4, 7.8 Hz, 1H), 3.00 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.79 – 2.74 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 174.4, 148.1-148.0 (m), 146.5-146.4 (m), 142.5-142.3 (m), 140.8-140.7 (m), 138.5-138.3 (m), 136.8-136.6 (m), 135.7, 102.3 (t, *J* = 26.1 Hz), 66.9, 41.0, 31.2, 17.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.4 – -126.5 (m, 2F), -152.3 – -152.4 (m, 1F), -160.3 – -160.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 160.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{13}F_5O_2Se$ 424.0001, Found 424.0000.

Methyl-2-(bis(tert-butoxycarbonyl) amino)-3-((perfluorophenyl)selenyl) propanoate (3r)



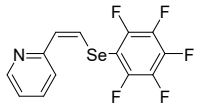
According to the general procedure B, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as white solid (24 mg, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.14 – 5.11 (m, 1H), 3.75 – 3.70 (m, 4H), 3.37 (dd, *J* = 13.1, 8.8 Hz, 1H), 1.47 (s, 18H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 170.1, 151.9, 148.1-148.0 (m), 146.5-146.4 (m), 142.4-142.3 (m), 140.8-140.6 (m), 138.5-138.3 (m), 136.8-136.7 (m), 102.3 (t, *J* = 25.3 Hz), 83.9, 58.9, 52.8, 28.0. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.2 – -126.3 (m, 2F), -152.8 – -152.9 (m, 1F), -160.5 – -160.7 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 160.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{24}F_5O_6Se$ 549.0689, Found 549.0692.

Methyl (Z)-3-((perfluorophenyl) selenyl) acrylate (5a)



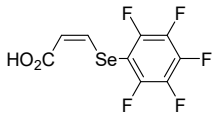
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (31 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 9.1 Hz, 1H), 6.48 (d, *J* = 9.0 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 168.5, 147.7-147.6 (m), 146.3, 146.0-145.9 (m), 143.1-143.0 (m), 141.4-141.2 (m), 138.7-138.4 (m), 137.0-136.8 (m), 117.9, 104.9 (t, *J* = 25.7 Hz), 52.3. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -127.0 – -127.1 (m, 2F), -151.1 – -151.2 (m, 1F), -159.7 – -159.8 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 357.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_5F_5O_2Se$ 331.9375, Found 331.9376.

(Z)-2-(2-((Perfluorophenyl)selenyl) vinyl) pyridine (5b)



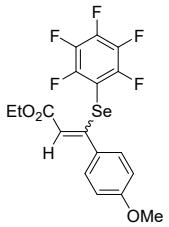
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (30 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.72 – 8.71 (m, 1H), 7.72 – 7.68 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.07 – 7.02 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 155.5, 147.7-147.6 (m), 147.3, 146.1-146.0 (m), 142.5-142.3 (m), 140.7-140.6 (m), 138.5-138.3 (m), 136.8-136.6 (m), 136.7, 130.8, 125.3, 123.6, 121.2, 108.7 (t, *J* = 26.6 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -127.6 – -127.7 (m, 2F), -153.0 – -153.1 (m, 1F), -160.4 – -160.5 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 336.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_6F_5NSe$ 350.9586, Found 350.9566.

3-((Perfluorophenyl)selenyl) acrylic acid (5c)



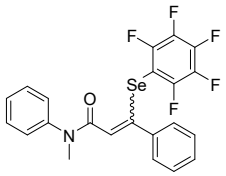
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (DCM/MeOH = 20 : 1) to give the product as white solid (23 mg, 72% yield). **^{1}H NMR** (400 MHz, DMSO-d6) δ: 7.98 (d, *J* = 15.5 Hz, 0.14H), 7.85 (d, *J* = 8.7 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 1H), 5.76 (d, *J* = 15.5 Hz, 0.14H), 3.51 (s, 1H). **^{13}C NMR** (150 MHz, DMSO-d6) δ: 169.3, 165.1, 147.2-147.1 (m), 146.3, 145.6-145.5 (m), 142.0-141.9 (m), 140.4, 140.3-140.2 (m), 137.9-137.6 (m), 136.2-136.0 (m), 121.8, 118.9, 105.2 (t, *J* = 26.8 Hz). **^{19}F NMR** (564 MHz, DMSO-d6) δ: -127.6 – -127.7 (m, 2F), -152.9 – -153.0 (m, 1F), -161.0 – -161.1 (m, 2F). **^{77}Se NMR** (114 MHz, DMSO-d6) δ: 348.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_9H_3F_5O_2Se$ 317.9218, Found 317.9221.

Ethyl -3-(4-methoxyphenyl)-3-((perfluorophenyl) selenyl) acrylate (5d)



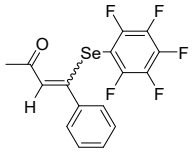
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as white solid (36 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.99 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.37 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 167.5, 160.1, 158.8, 147.6-147.5 (m), 146.0-145.9 (m), 143.0-142.9 (m), 141.2-141.1 (m), 138.0-137.7 (m), 136.3-136.1 (m), 131.2, 129.2, 118.1, 113.3, 104.2 (t, *J* = 27.2 Hz), 61.2, 55.4, 14.5. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -124.6 – -124.7 (m, 2F), -150.7 – -150.8 (m, 1F), -160.7 – -160.8 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 399.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{13}F_5O_3Se$ 451.9950, Found 451.9952.

N-Methyl-3-((perfluorophenyl)selenyl)-N,3-diphenylacrylamide (5e)



According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as white solid (28 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.06 – 7.04 (m, 3H), 6.92 – 6.90 (m, 2H), 6.26 (s, 1H), 3.44 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 166.9, 156.2, 147.7-147.5 (m), 146.1-145.9 (m), 143.3, 142.6-142.5 (m), 140.9-140.8 (m), 139.3, 137.8-137.5 (m), 136.1-135.8 (m), 130.0, 128.5, 128.1, 127.7, 127.6, 127.3, 118.3, 105.4 (t, *J* = 27.7 Hz), 37.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -124.4 – -124.5 (m, 2F), -151.6 – -151.7 (m, 1F), -161.3 – -161.4 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 403.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{14}F_5NOSe$ 483.0161, Found 483.0158.

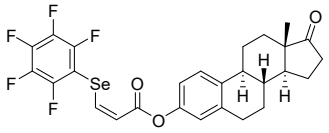
4-((Perfluorophenyl)selenyl)-4-phenylbut-3-en-2-one (5f)



According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE) to give the product as white solid (35 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.16 – 7.11 (m, 3H), 7.04 – 7.00 (m, 2H), 6.91 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 197.3, 161.0, 147.6-147.4 (m), 146.0-145.9 (m), 142.9-142.7 (m), 141.2-141.0 (m), 138.8, 137.8-137.6 (m), 136.2-135.9 (m), 129.0, 127.9, 127.6, 125.2, 104.6 (t, *J* = 26.7 Hz), 29.9. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -124.5 – -124.6 (m, 2F), -150.9 – -151.0 (m, 1F), -160.9 – -161.0 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 457.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_9F_5Ose$ 391.9739, Found 391.9741.

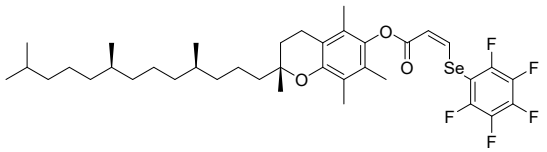
(13S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-

yl (Z)-3-((perfluorophenyl)selenyl)acrylate (5g)



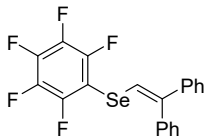
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as white solid (40 mg, 70% yield). It is noted that alkyne substrate **4g** was prepared according to a known procedure.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 9.0 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.91 (s, 1H), 6.70 (d, *J* = 9.1 Hz, 1H), 2.94 – 2.92 (m, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.44 – 2.40 (m, 1H), 2.34 – 2.27 (m, 1H), 2.17 – 2.01 (m, 4H), 1.66 – 1.44 (m, 7H), 0.92 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 220.9, 166.9, 148.9, 148.3, 147.7-147.6 (m), 146.1-146.0 (m), 143.1-143.0 (m), 141.4-141.3 (m), 138.7-138.6 (m), 138.3, 138.0, 137.0-136.8 (m), 126.7, 121.5, 118.7, 117.5, 104.8 (t, *J* = 25.5 Hz), 50.5, 48.1, 44.3, 38.1, 36.0, 31.7, 29.6, 26.4, 25.9, 21.7, 13.9. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.8 – -126.9 (m, 2F), -150.6 – -150.7 (m, 1F), -159.4 – -159.5 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 366.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{23}F_5O_3Se$ 570.0733, Found 570.0728.

2,5,7,8-Tetramethyl-2-((4,8,12-trimethyltridecyl)chroman-6-yl(Z)-3-((perfluorophenyl)selenyl)acrylate (5h)



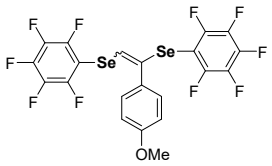
According to the general procedure C, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (60 mg, 82% yield). It is noted that alkyne substrate **4h** was prepared according to a known procedure.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 9.1 Hz, 1H), 6.79 (d, *J* = 9.1 Hz, 1H), 2.63 (t, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.85 – 1.77 (m, 2H), 1.61 – 1.54 (m, 3H), 1.47 – 1.37 (m, 5H), 1.32 – 1.27 (m, 10H), 1.18 – 1.07 (m, 6H), 0.89 – 0.86 (m, 12H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 166.9, 149.8, 148.6, 147.7-147.6 (m), 146.0-145.9 (m), 143.0-142.9 (m), 141.3-141.2 (m), 140.4, 138.7-137.5 (m), 137.0-136.9 (m), 126.7, 125.0, 123.4, 117.6, 117.3, 105.0 (t, *J* = 25.8 Hz), 75.3, 40.2, 39.5, 37.6, 37.4, 32.9, 32.8, 31.2, 28.1, 25.0, 24.6, 24.1, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.3, 12.0. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.9 – -127.0 (m, 2F), -150.9 – -151.0 (m, 1F), -159.5 – -159.6 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 367.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{38}H_{51}F_5O_3Se$ 730.2924, Found 730.2926.

(2,2-Diphenylvinyl)(perfluorophenyl)selane (7a)



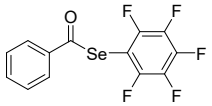
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 – 7.39 (m, 3H), 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 3H), 7.21 – 7.16 (m, 2H), 6.86 (s, 1H). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{11}F_5Se$ 426.0, Found 426.0.

(1-(4-Methoxyphenyl)ethene-1,2-diyl)bis((perfluorophenyl)selane) (9a)



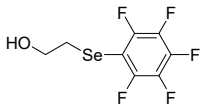
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{11}F_5Se$ 625.9, Found 625.9.

Benzyl 3-((perfluorophenyl) selenyl) propanoate (10a)



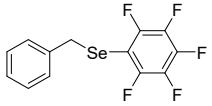
According to the general procedure D, crude product was purified by flash column chromatography on silica gel (100% PE) to give the product as colorless oil (24 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 187.8, 148.1-148.0 (m), 146.5-146.3 (m), 143.8-143.6, 142.1-141.8 (m), 138.7-138.5 (m), 137.1, 137.0-136.8 (m), 134.9, 129.5, 127.9, 100.0 (t, *J* = 26.6 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -125.2 – -125.3 (m, 2F), -149.6 – -149.7 (m, 1F), -160.0 – -160.1 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 506.6. HRMS (EI-TOF) m/z: $[M- C_6F_5Se]^+$ Calcd for C_7H_5O 105.0340; Found 105.0343, $[M- C_7H_5O]^+$ Calcd for C_6F_5Se 246.9085; Found 246.9090.

Benzyl 3-((perfluorophenyl) selenyl) propanoate (11a)



According to the general procedure D, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as colorless oil (27 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.78 (t, *J* = 6.0 Hz, 2H), 3.10 (t, *J* = 6.1 Hz, 2H), 2.18 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 148.4-148.3 (m), 146.8-146.7 (m), 142.7-142.6 (m), 141.0-140.8 (m), 138.6-138.3 (m), 136.9-136.7 (m), 101.2 (t, *J* = 26.2 Hz), 61.6, 32.2. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -151.9 – -152.0 (m, 1F), -160.1 – -160.2 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 119.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_8H_5F_5Ose$ 291.9426, Found 291.9427.

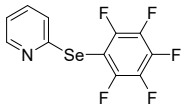
Benzyl 3-((perfluorophenyl) selenyl) propanoate (12a)



According to the general procedure D, crude product was purified by flash column chromatography on silica gel (100% PE) to give the product as colorless oil (32 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.19 – 7.11 (m, 5H), 4.08 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 148.2-148.0 (m), 146.5-146.4 (m), 142.5-142.3 (m), 140.8-140.6 (m), 138.4-138.2 (m), 137.1, 136.7-136.5 (m), 128.9, 128.8, 127.8, 102.2 (t, *J* = 25.5 Hz), 32.0. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -126.3 – -126.4 (m, 2F), -152.2 –

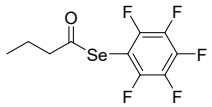
-152.3 (m, 1F), -160.7 – -160.8 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 243.6. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_7F_5Se$ 337.9633, Found 337.9637.

Benzyl 3-((perfluorophenyl) selenyl) propanoate (13a)



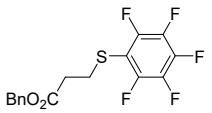
According to the general procedure D, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as colorless oil (29 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 4.1 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.06 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 153.6, 150.7, 148.3-148.2 (m), 146.7-146.6 (m), 143.4-143.3 (m), 141.7-141.6 (m), 138.8-138.5 (m), 137.2, 137.1-136.8 (m), 124.4, 121.8, 101.5 (t, *J* = 25.4 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -124.8 – -124.9 (m, 2F), -150.5 – -150.6 (m, 1F), -160.0 – -160.1 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 315.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_4F_5NSe$ 324.9429; Found 324.9425.

Benzyl 3-((perfluorophenyl) selenyl) propanoate (14a)



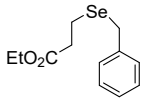
According to the general procedure D, crude product was purified by flash column chromatography on silica gel (100% PE) to give the product as colorless oil (20 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.74 (t, *J* = 7.3 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 194.5, 147.6-147.5 (m), 146.2-145.9 (m), 143.5-143.4 (m), 141.9-141.8 (m), 138.7-138.5 (m), 137.0-136.8 (m), 100.4 (t, *J* = 26.0 Hz), 49.2, 19.0, 13.4. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -125.6 – -125.7 (m, 2F), -150.1 – -150.2 (m, 1F), -160.1 – -160.2 (m, 2F). **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 521.8. HRMS (EI-TOF) m/z: $[M\text{-}C_6F_5Se]^+$ Calcd for C_4H_7O 71.0497; Found 71.0496, $[M\text{-}C_4H_7O]^+$ Calcd for C_6F_5Se 246.9085; Found 246.9091.

Benzyl 3-((perfluorophenyl)thio)propanoate (15a)



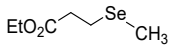
Crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (18 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 - 7.32 (m, 5H), 5.12 (s, 2H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 170.9, 148.7-148.6 (m), 147.0-146.9 (m), 142.7-142.5 (m), 140.9-140.8 (m), 138.8-138.6 (m), 137.1-136.9 (m), 135.6, 128.8, 128.6, 128.5, 108.5 (t, *J* = 22.5 Hz), 67.0, 35.1, 30.0. **^{19}F NMR** (564 MHz, $CDCl_3$) δ: -136.7 – -136.8 (m, 2F), -156.6 – -156.7 (m, 1F), -165.4 – -165.5 (m, 2F). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{11}F_5O_2S$ 362.0400, Found 362.0403.

Ethyl 3-(benzylselenyl) propanoate (17a)



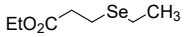
According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (25 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.66 – 7.14 (m, 5H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 2H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 6.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.2, 139.1, 128.8, 128.5, 126.8, 60.6, 35.5, 27.3, 17.6, 14.2. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 270.8. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{16}O_2Se$ 272.0316; Found 272.0317.

Ethyl 3-(methylselenyl) propanoate (17b)



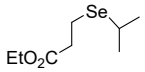
According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (10 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.14 (q, *J* = 7.1 Hz, 2H), 2.78 – 2.72 (m, 2H), 2.72 – 2.66 (m, 2H), 2.03 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.4, 60.8, 35.5, 19.1, 14.3, 4.4. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 98.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_6H_{12}O_2Se$ 196.0003, Found 195.9999.

Ethyl 3-(ethylselenyl) propanoate (17c)



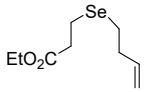
According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (16 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.14 (q, *J* = 7.1 Hz, 2H), 2.79 – 2.76 (m, 2H), 2.71 – 2.67 (m, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.5, 60.7, 35.9, 17.6, 17.1, 15.8, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 213.1. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_{14}O_2Se$ 210.0159, Found 210.0161.

Ethyl 3-(isopropylselenyl) propanoate (17d)



According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (18 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.15 (q, *J* = 7.1 Hz, 2H), 3.28 – 3.06 (m, 1H), 2.81 – 2.78 (m, 2H), 2.72 – 2.68 (m, 2H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.6, 60.8, 36.1, 29.4, 24.6, 16.7, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 307.3. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_8H_{16}O_2Se$ 224.0316, Found 224.0316.

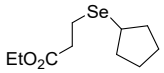
Ethyl 3-(isopropylselenyl) propanoate (17e)



According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (20 mg, 88% yield). **^{1}H NMR** (400 MHz,

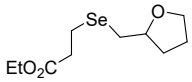
$CDCl_3$) δ: 5.86 – 5.76 (m, 1H), 5.09 – 5.01 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.45 – 2.39 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.4, 137.4, 116.0, 60.8, 35.9, 34.8, 23.3, 17.7, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 184.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_9H_{16}O_2Se$ 236.0316, Found 236.0319.

Ethyl 3-(cyclopentylselenyl) propanoate (17f)



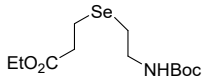
According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (20 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.15 (q, *J* = 7.1 Hz, 2H), 3.30 – 3.23 (m, 1H), 2.81 – 2.78 (m, 2H), 2.73 – 2.69 (m, 2H), 2.09 – 2.00 (m, 2H), 1.76 – 1.69 (m, 2H), 1.65 – 1.54 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.5, 60.6, 37.8, 36.0, 34.4, 24.9, 17.5, 14.2. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 266.8. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{18}O_2Se$ 250.0472, Found 250.0473.

Ethyl 3-(((tetrahydrofuran-2-yl) methyl) selenyl) propanoate (17g)



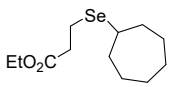
According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (19 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.14 (q, *J* = 7.1 Hz, 2H), 4.09 – 4.02 (m, 1H), 3.92 – 3.86 (m, 1H), 3.78 – 3.72 (m, 1H), 2.84 – 2.81 (m, 2H), 2.78 – 2.67 (m, 4H), 2.09 – 2.01 (m, 1H), 1.96 – 1.84 (m, 2H), 1.64 – 1.55 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.4, 79.2, 68.4, 60.8, 36.0, 31.8, 29.5, 26.1, 18.5, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 154.9. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{18}O_3Se$ 266.0421, Found 266.0422.

Ethyl 3-((2-((tert-butoxycarbonyl) amino) ethyl) selenyl) propanoate (17h)



According to the general procedure E, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as colorless oil (24 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.95 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.39 – 3.34 (m, 2H), 2.80 – 2.77 (m, 2H), 2.72 – 2.67 (m, 4H), 1.43 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.3, 155.9, 79.6, 60.9, 40.6, 35.8, 28.5, 24.6, 17.7, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 152.9. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{23}NO_4Se$ 325.0792, Found 325.0794.

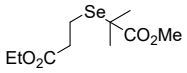
Ethyl 3-(cycloheptylselenyl) propanoate (17i)



According to the general procedure F, crude product was purified by flash column chromatography on silica gel (PE/EA = 20 : 1) to give the product as colorless oil (18 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.15 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 1H), 2.78 – 2.76 (m, 2H), 2.70 (t, *J* = 6.6 Hz, 2H), 2.09 –

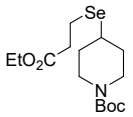
2.03 (m, 2H), 1.72 – 1.65 (m, 4H), 1.58 – 1.53 (m, 4H), 1.50 – 1.43 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.6, 60.8, 40.9, 36.1, 28.2, 26.8, 17.4, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 293.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{22}O_2Se$ 278.0785, Found 278.0787.

Methyl 2-((3-ethoxy-3-oxopropyl) selenyl)-2-methylpropanoate (17j)



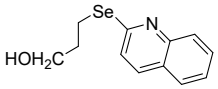
According to the general procedure F, crude product was purified by flash column chromatography on silica gel (PE/EA = 10 : 1) to give the product as colorless oil (18 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.14 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.61 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 175.5, 172.2, 60.7, 52.4, 40.7, 35.3, 26.1, 18.2, 14.2. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 441.8. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{18}O_4Se$ 282.0370, Found 282.0373.

tert-Butyl 4-((3-ethoxy-3-oxopropyl) selanyl) piperidine-1-carboxylate (17k)



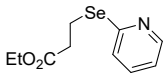
According to the general procedure F, crude product was purified by flash column chromatography on silica gel (PE/EA = 5: 1) to give the product as colorless oil (25 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 3.06 – 3.01 (m, 1H), 2.97 – 2.90 (m, 2H), 2.81 – 2.79 (m, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 1.99 – 1.94 (m, 2H), 1.65 – 1.61 (m, 2H), 1.45 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.4, 154.9, 79.7, 60.9, 36.1, 36.0, 33.5, 28.6, 16.5, 14.3. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 273.4. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{27}NO_4Se$ 365.1105, Found 365.1107.

tert-Butyl 4-((3-ethoxy-3-oxopropyl) selanyl) piperidine-1-carboxylate (17l)



According to the general procedure F, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (11 mg, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.49 – 7.45 (m, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 5.39 (s, 1H), 3.78 – 3.75 (m, 2H), 3.54 – 3.51 (m, 2H), 2.10 – 2.05 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 158.1, 148.7, 135.6, 130.4, 128.0, 127.1, 126.6, 126.1, 123.7, 59.4, 33.5, 22.9. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 347.2. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{13}NOSe$ 267.0162, Found 267.0163.

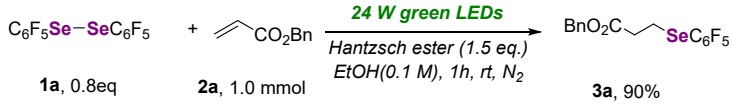
Ethyl 3-(pyridin-2-ylselanyl) propanoate (17m)



According to the general procedure F, crude product was purified by flash column chromatography on silica gel (PE/EA = 5 : 1) to give the product as colorless oil (19 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 3.9 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.03 – 7.00 (m, 1H),

4.16 (q, *J* = 7.1 Hz, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 172.5, 154.8, 150.1, 135.9, 125.5, 120.3, 60.7, 35.5, 19.5, 14.2. **^{77}Se NMR** (114 MHz, $CDCl_3$) δ: 355.7. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{13}NO_2Se$ 259.0112, Found 259.0113.

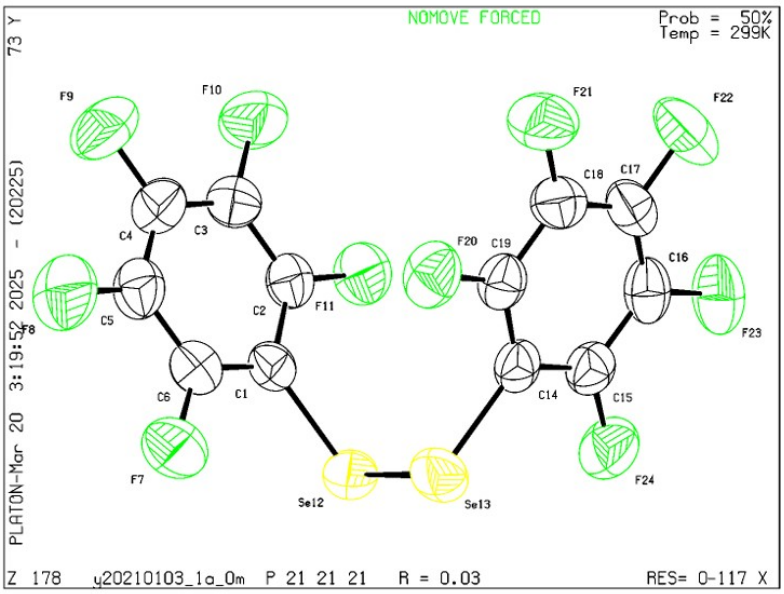
Scale-up experiment



A 25 ml Schlenk tube equipped with a magnetic stirring bar was dried in oven. After cooling the tube to room temperature, the tube was charged with $F_5PhSeSePhF_5$ **1a** (0.8 mmol, 0.8 eq), HE (1.5 mmol, 1.5 eq) and EtOH (10.0 mL). Then the resulting solution was degassed for 20 min by bubbling N_2. After that, **2a** (1.0 mmol, 1.0 equiv.) were added via a syringe. Add a fan to maintain the temperature at room temperature. The reaction mixture was then irradiated with 24 W green LEDs for 1 hours. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by flash silica-gel column chromatography to give the desired product **3a** as colorless oil (370mg, 90% yield).

Single crystal X-ray diffraction data for 1a

Preparation of the single crystals of **1a**: 100 mg of pure **1a** was dissolved in petroleum ether (0.5 mL) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing the slow solvent evaporation at 0 °C. After about three days, several small crystals were observed at the bottom of the bottle. The crystals were collected and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **1a**. The data set was collected by a Bruker proton III ((Bruker, Germany) 298.0 K equipped with Cu radiation source (Kα = 1.54178 Å). Applied with multi-scanabsorption correction, the structure solution was solved and refinement was processed by diamondprogram package.



Bond precision:	C-C = 0.0073 Å	Wavelength=1.54178	
Cell:	a=5.7599(3)	b=9.4957(5)	c=25.7505(13)
	alpha=90	beta=90	gamma=90
Temperature:	299 K		

	Calculated	Reported
Volume	1408.41(13)	1408.41(13)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C12 F10 Se2	C12 F10 Se2
Sum formula	C12 F10 Se2	C12 F10 Se2
Mr	492.04	492.04
Dx,g cm-3	2.320	2.321
Z	4	4
Mu (mm-1)	7.685	7.685
F000	920.0	920.0
F000’	917.34	
h,k,lmax	6,11,31	6,11,30
Nref	2565[1523]	2553
Tmin,Tmax	0.238,0.541	0.276,0.753
Tmin’	0.148	

Correction method= # Reported T Limits: Tmin=0.276 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 1.68/1.00 Theta(max)= 68.204

R(reflections)= 0.0288(2514) wR2(reflections)=0.0695(2553)

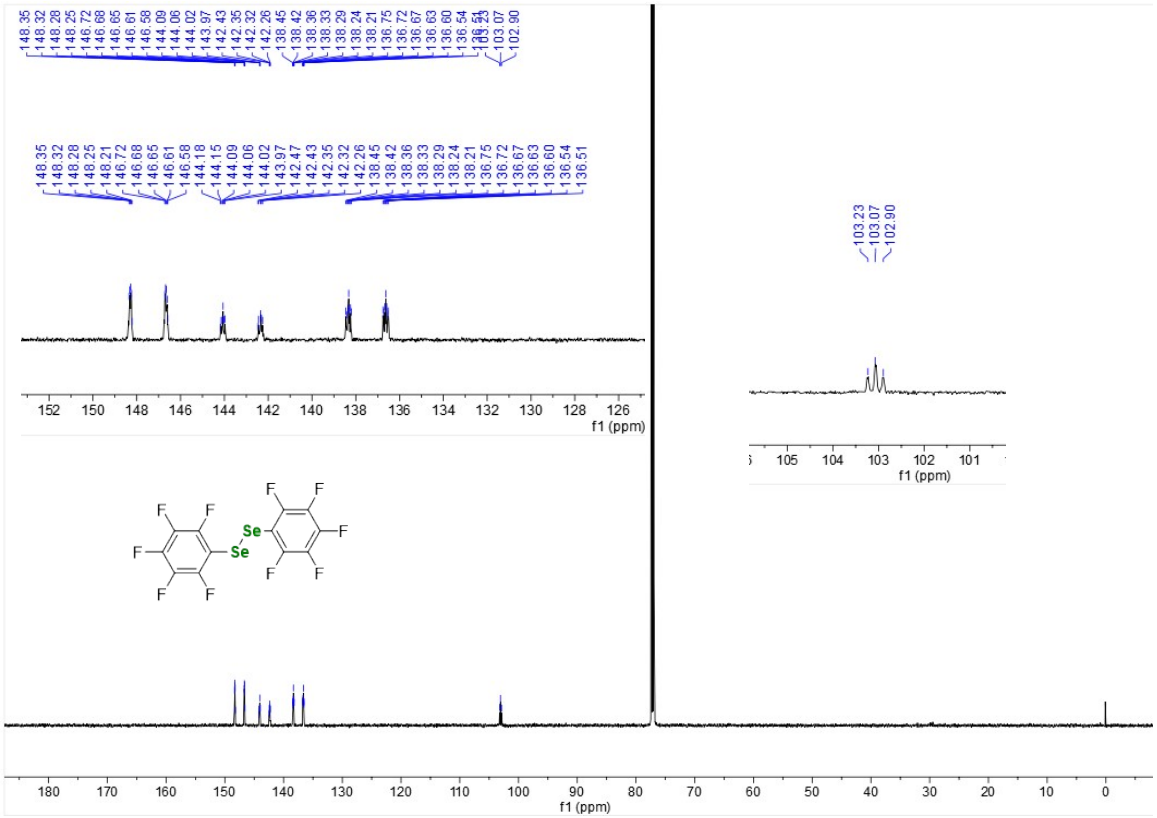
S = 1.116 Npar= 218

References:

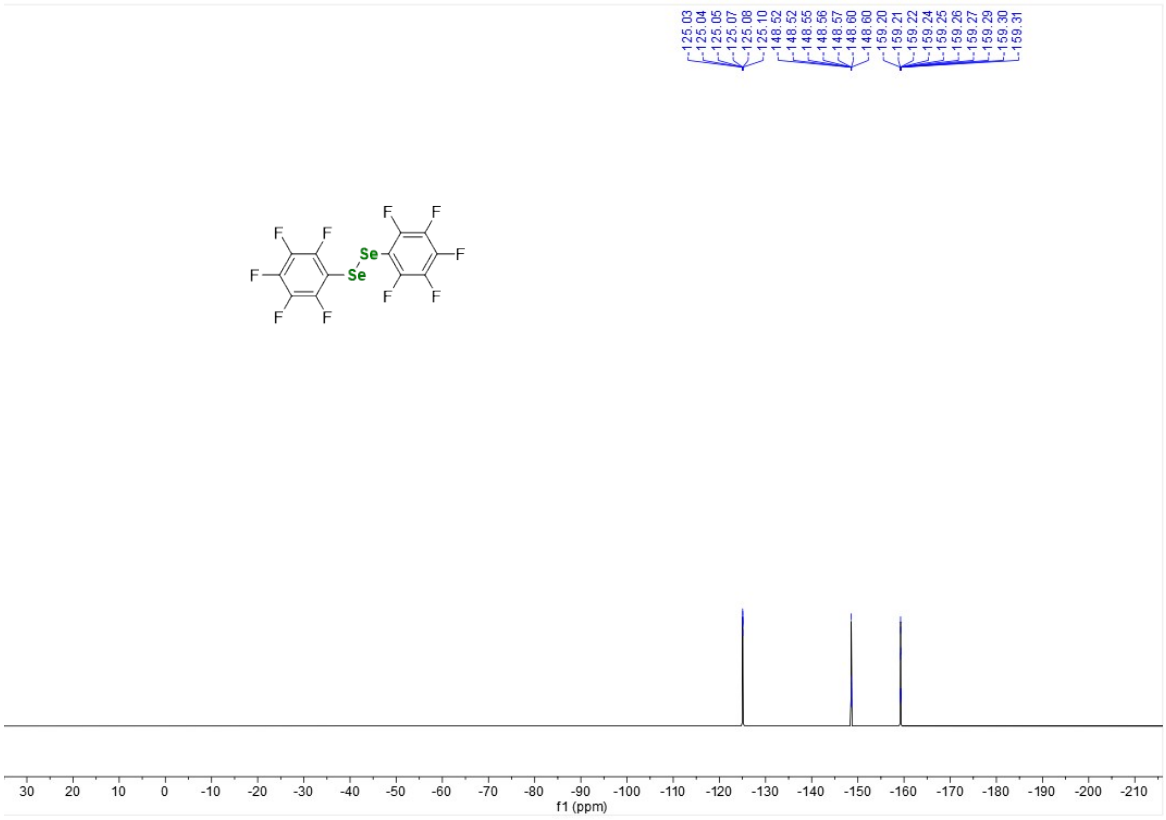
1. Thomas, M. K.; Burkhard, K.; Peter, M.; Holger, P.; Oliver, P. R.; Alexander, S. *Phosphorus Sulfur.* **2001**, *172*, 119-128.
2. Boris, A. V. D. W.; Tobias, R. *J. Am. Chem. Soc.* **2025**, 147, 4736-4742.
3. Wang, L.; Jeremy, M. L.; Sean, M. R.; Stacy, C. F.; David, A. N. *Science*. **2018**, 362, 225-229.

Spectral Data for Products

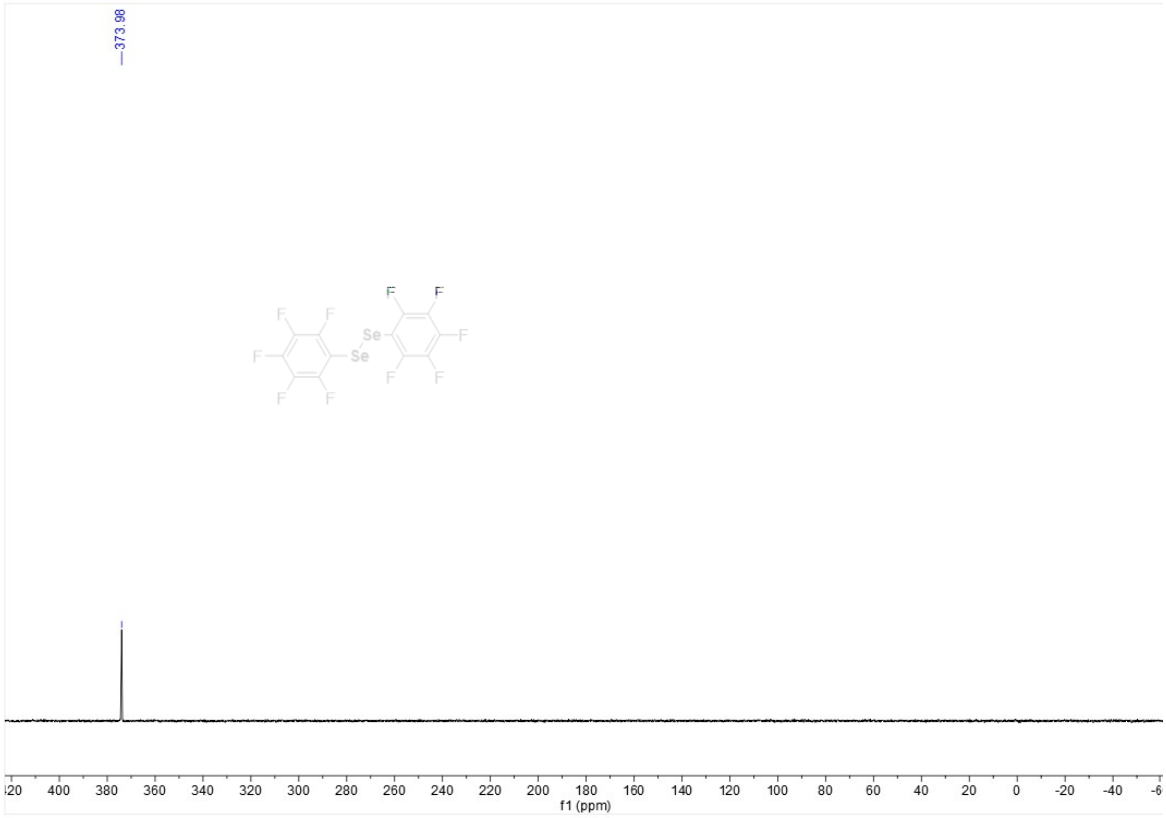
^{13}C NMR spectra of 1a ($CDCl_3$)



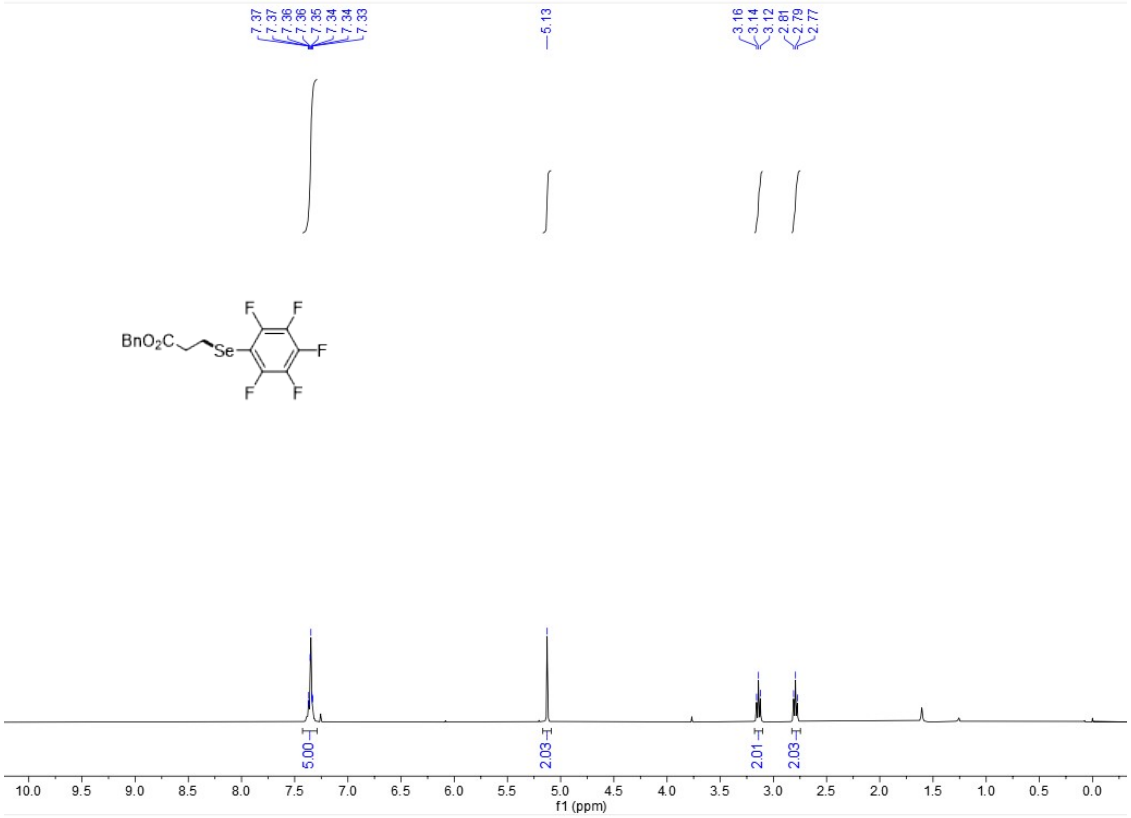
^{19}F NMR spectra of 1a ($CDCl_3$)



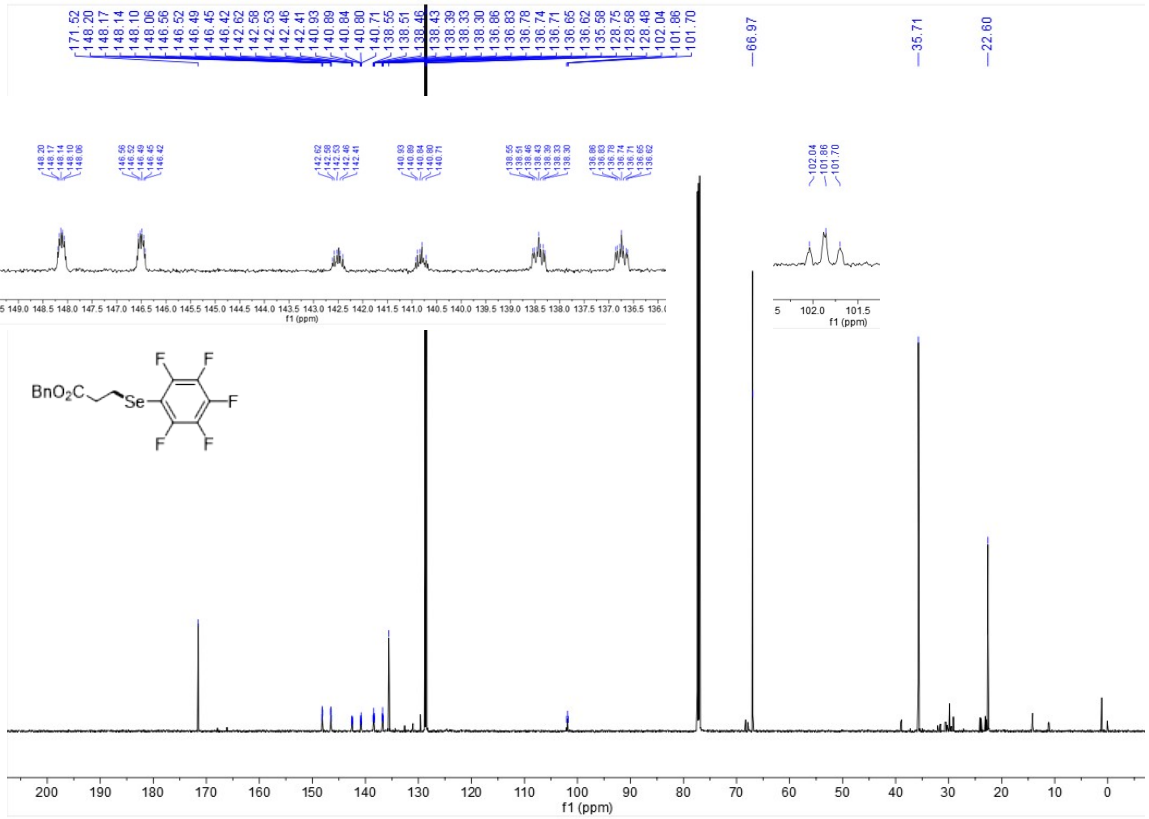
^{77}Se NMR spectra of 1a ($CDCl_3$)



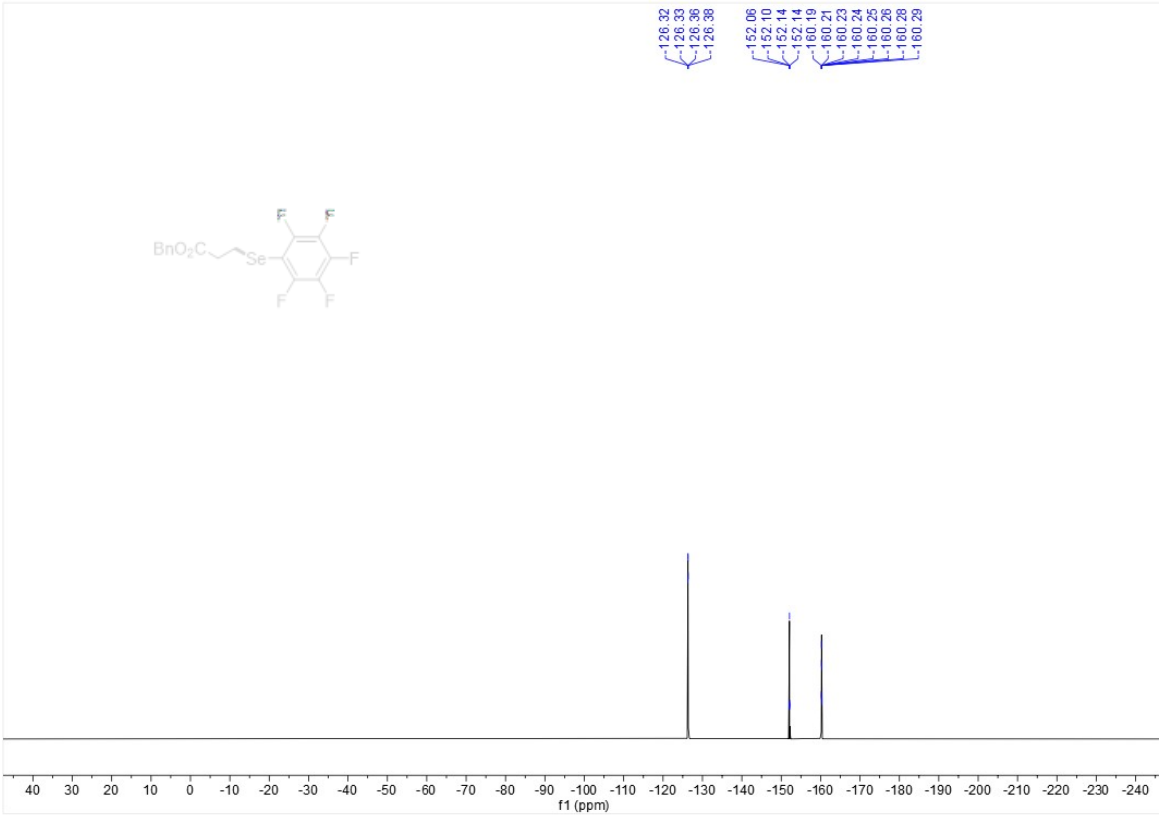
^{1}H NMR spectra of 3a ($CDCl_3$)



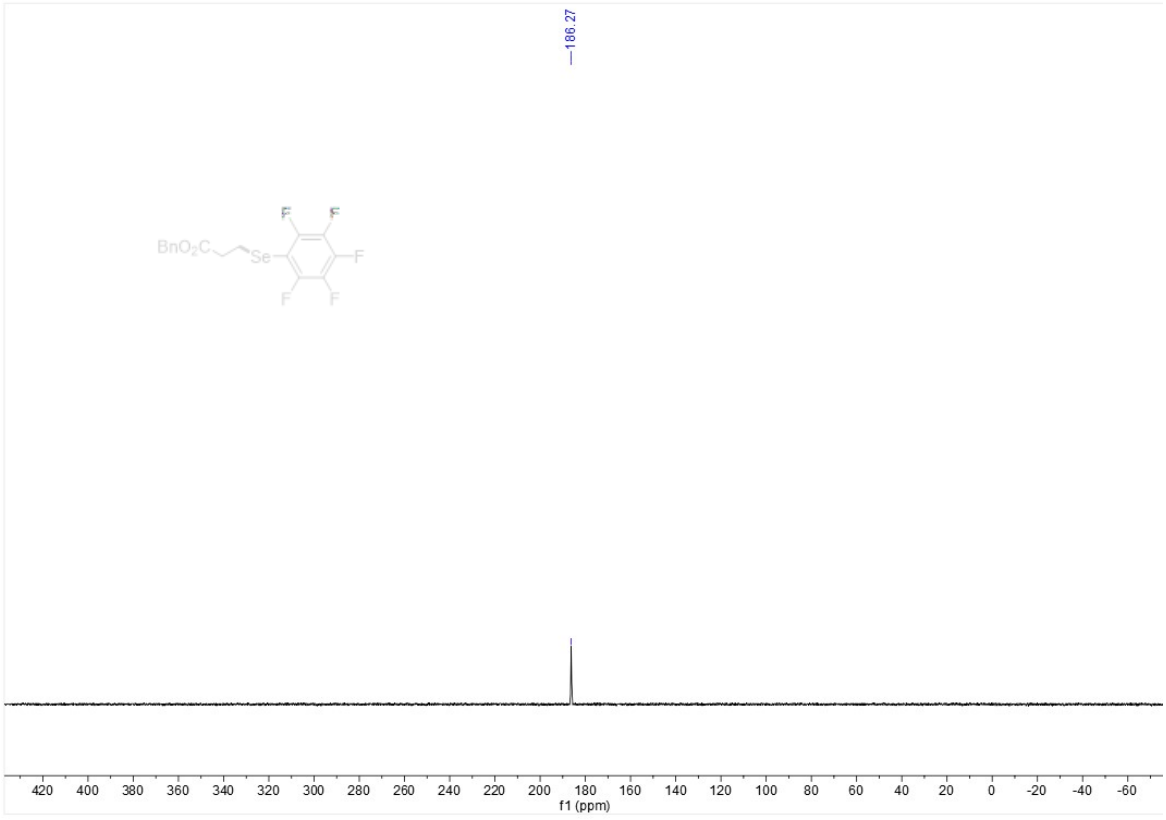
^{13}C NMR spectra of 3a ($CDCl_3$)



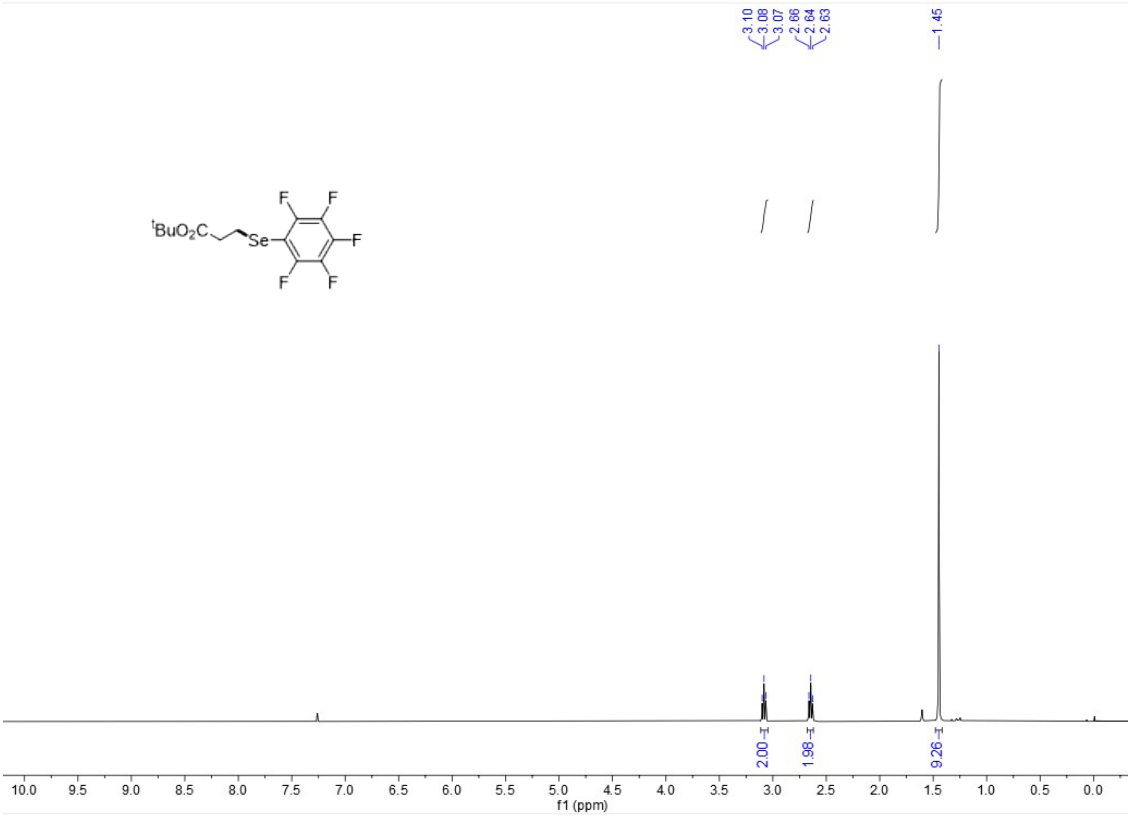
^{19}F NMR spectra of 3a ($CDCl_3$)



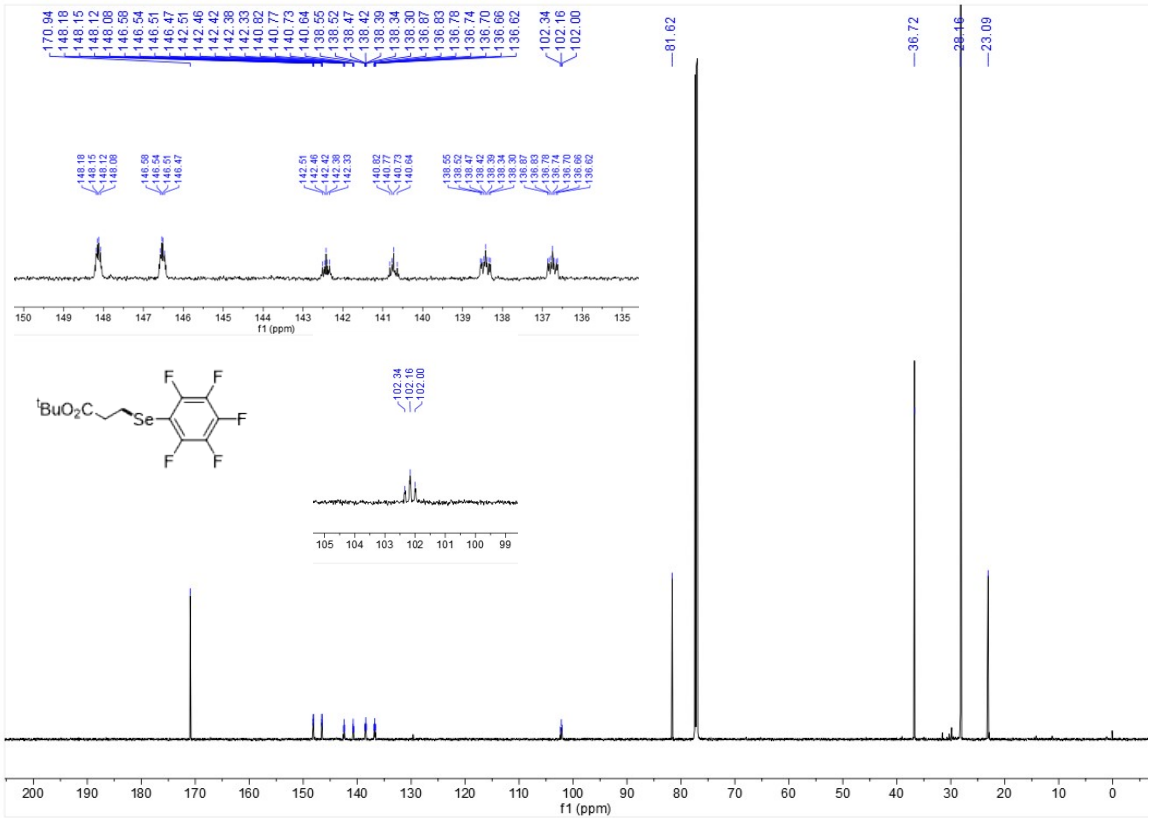
^{77}Se NMR spectra of 3a ($CDCl_3$)



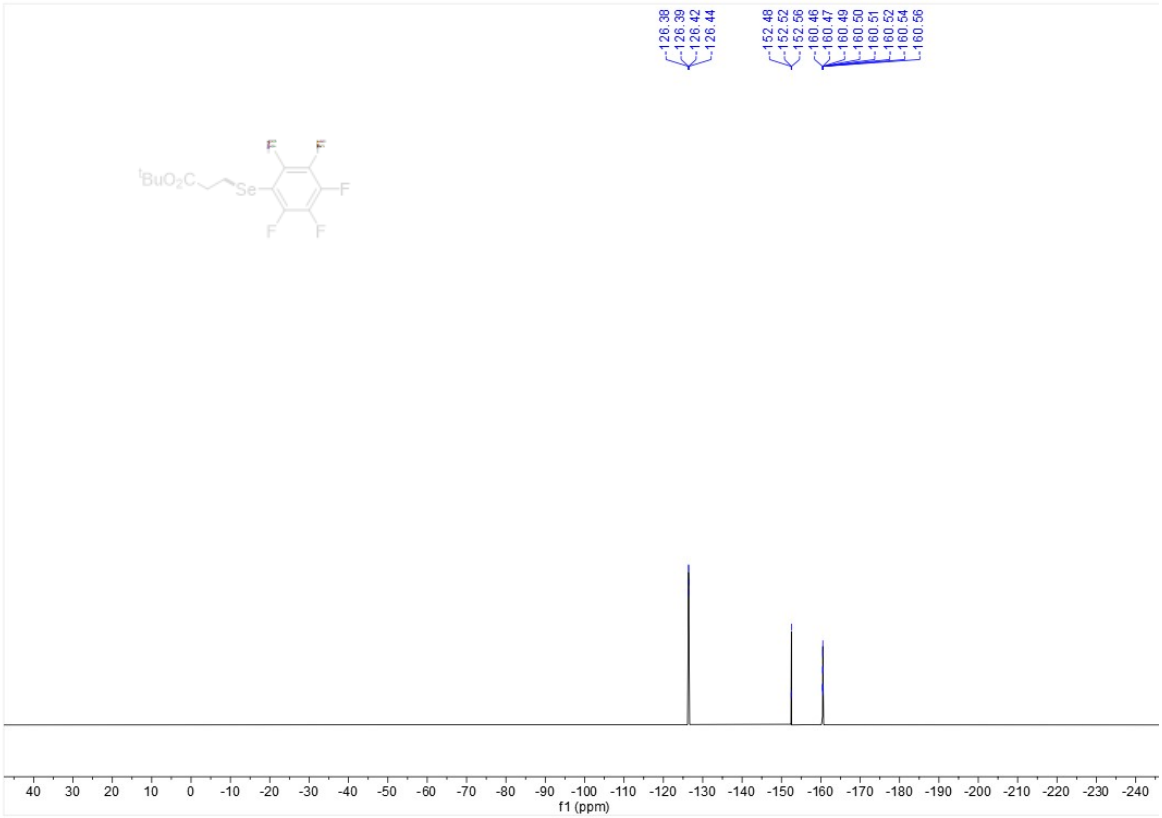
^{1}H NMR spectra of 3b ($CDCl_3$)



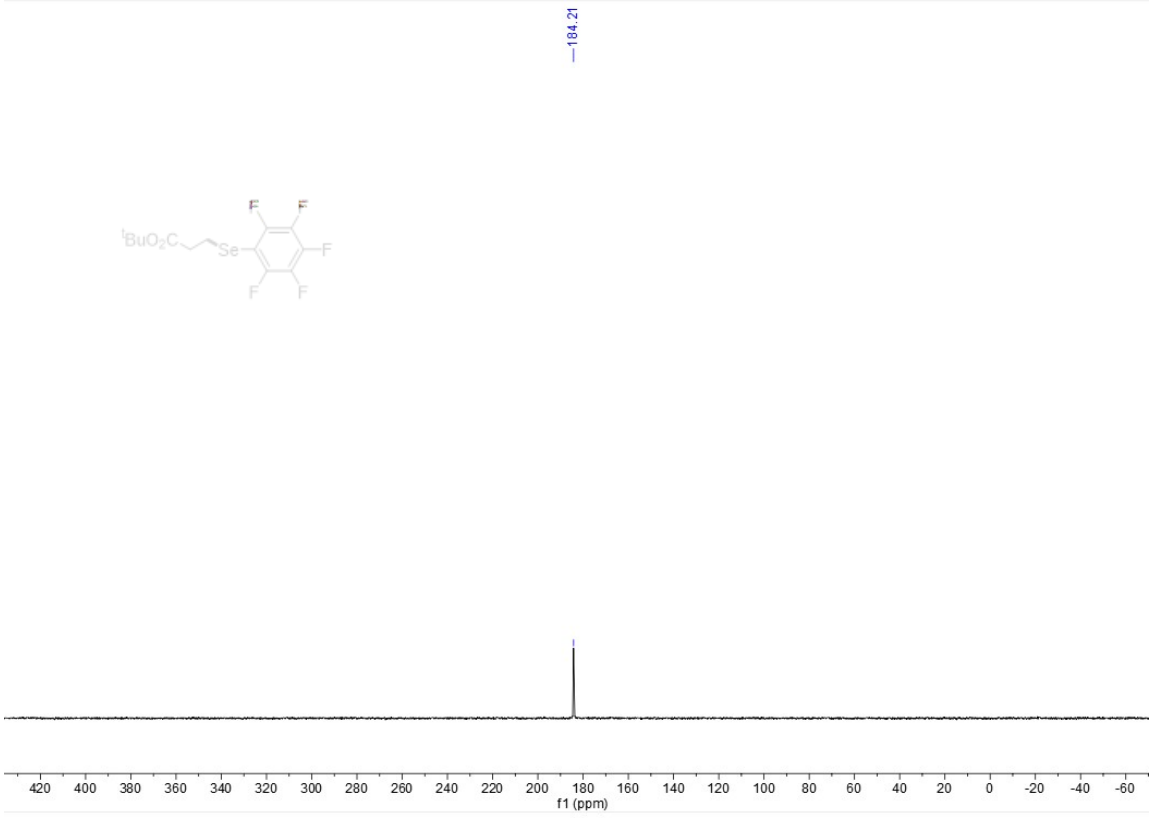
^{13}C NMR spectra of 3b ($CDCl_3$)



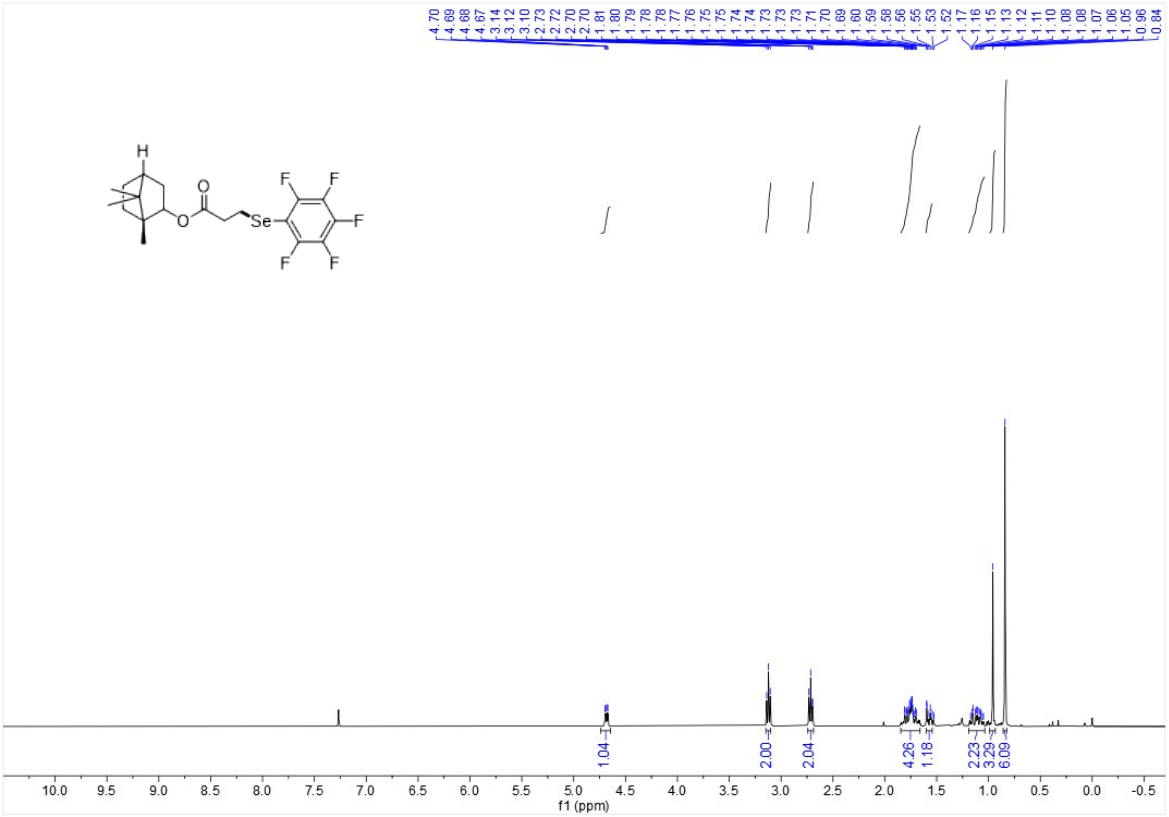
^{19}F NMR spectra of 3b ($CDCl_3$)



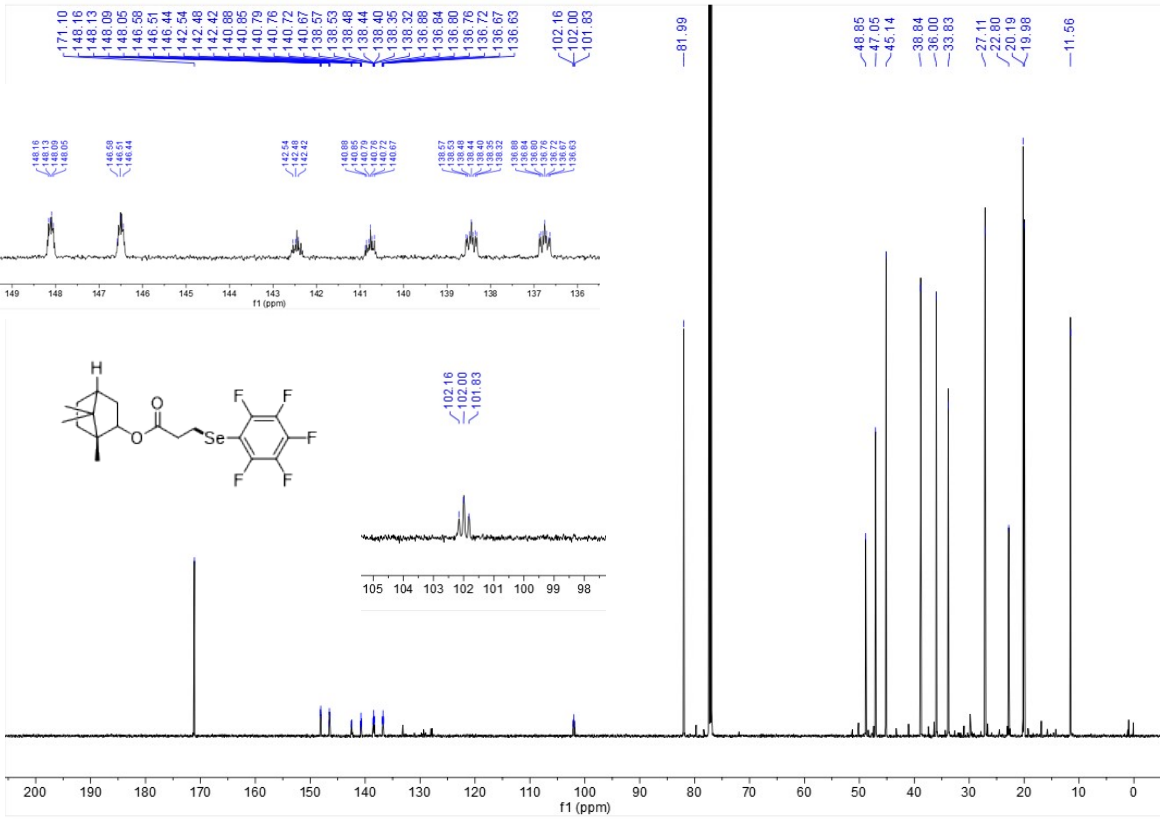
^{77}Se NMR spectra of 3b ($CDCl_3$)



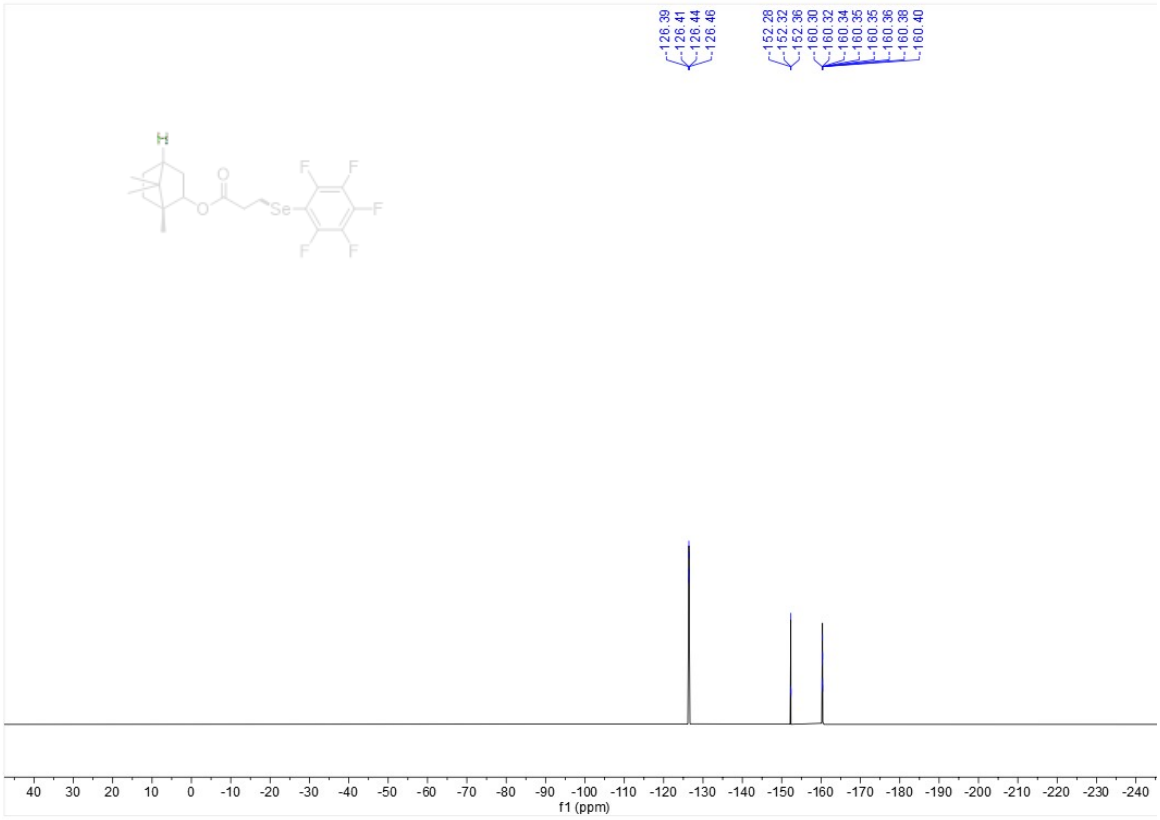
^{1}H NMR spectra of 3c ($CDCl_3$)



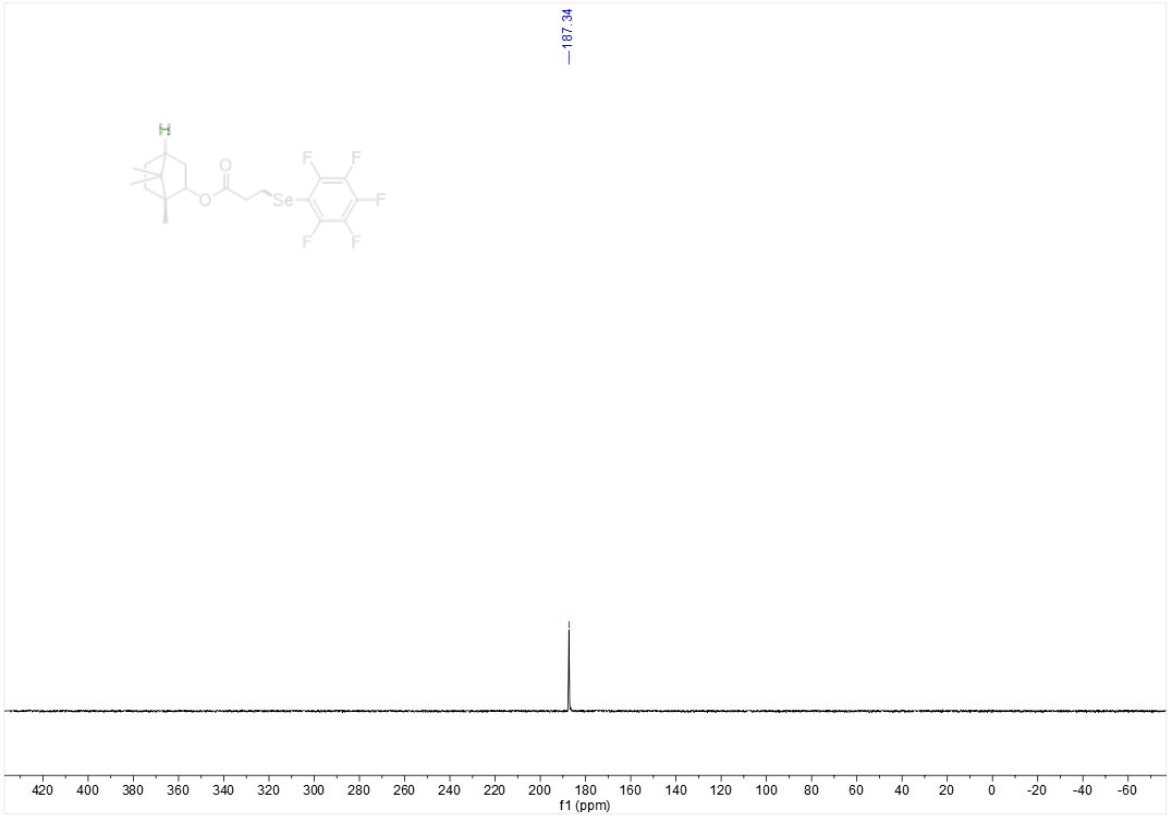
^{13}C NMR spectra of 3c ($CDCl_3$)



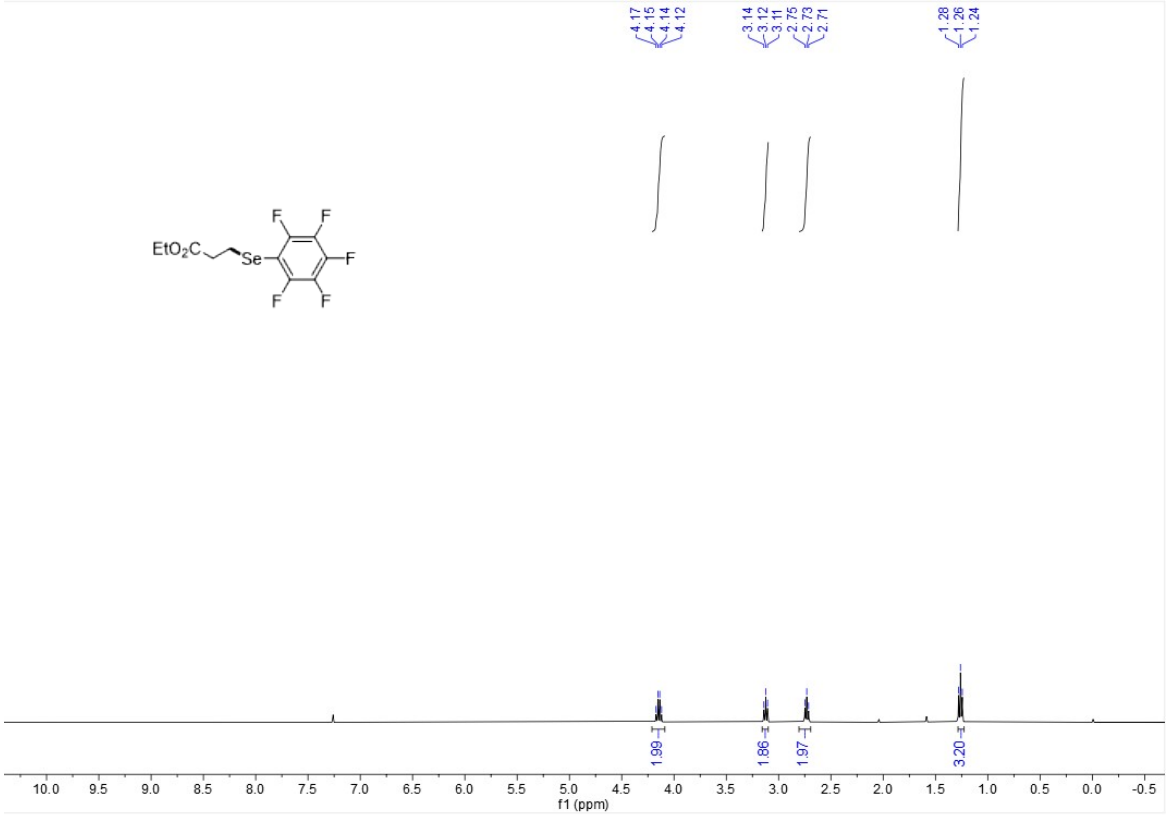
^{19}F NMR spectra of 3c ($CDCl_3$)



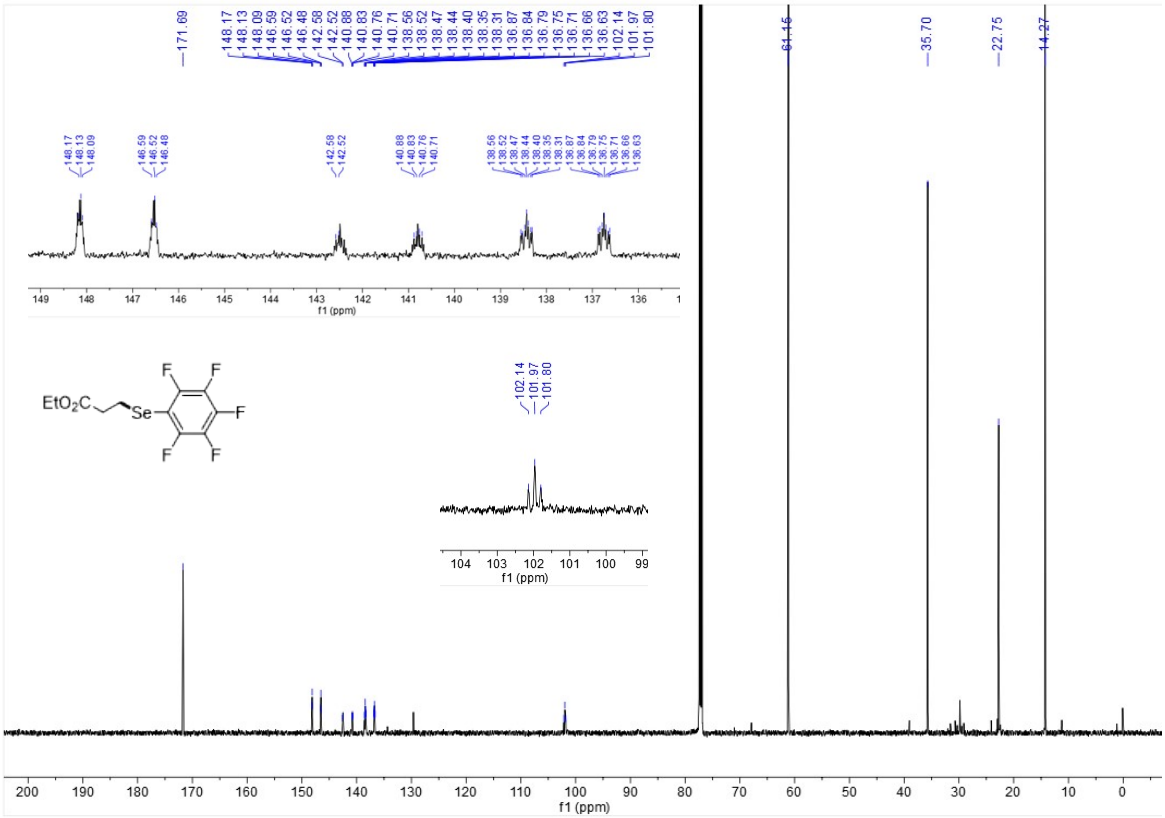
^{77}Se NMR spectra of 3c ($CDCl_3$)



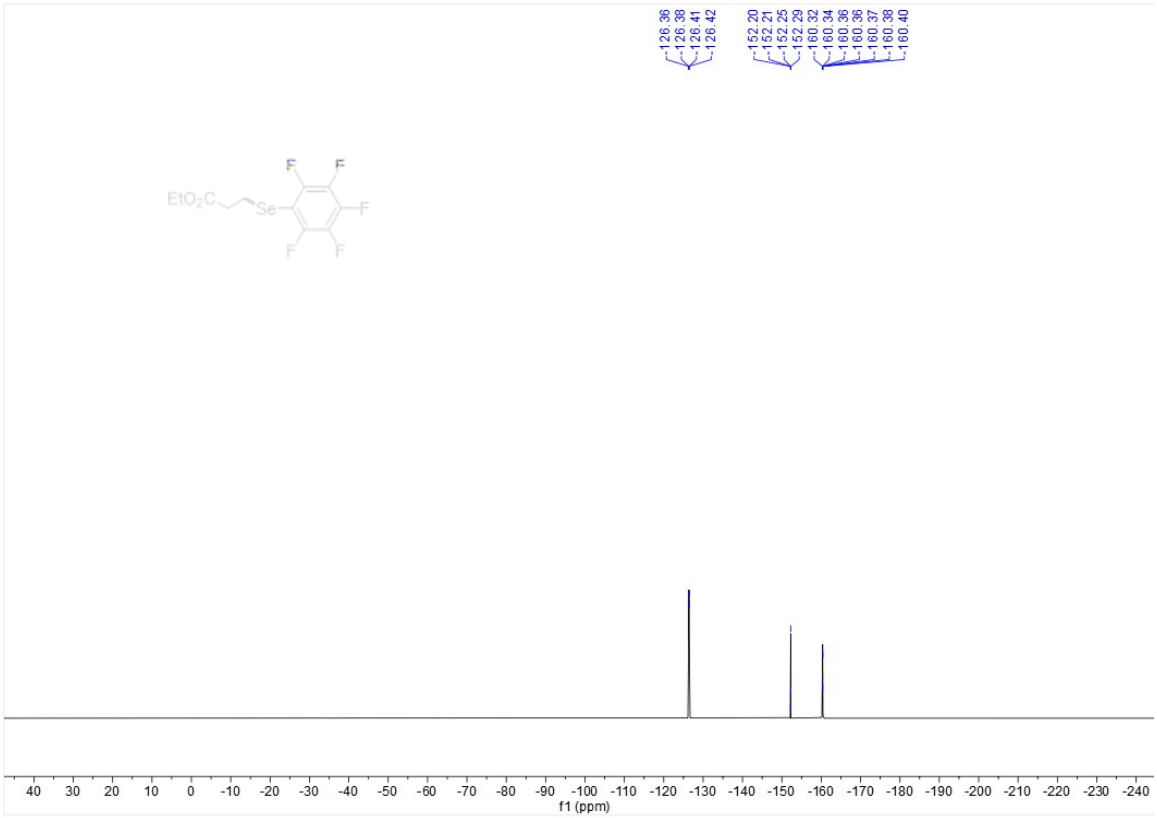
^{1}H NMR spectra of 3d ($CDCl_3$)



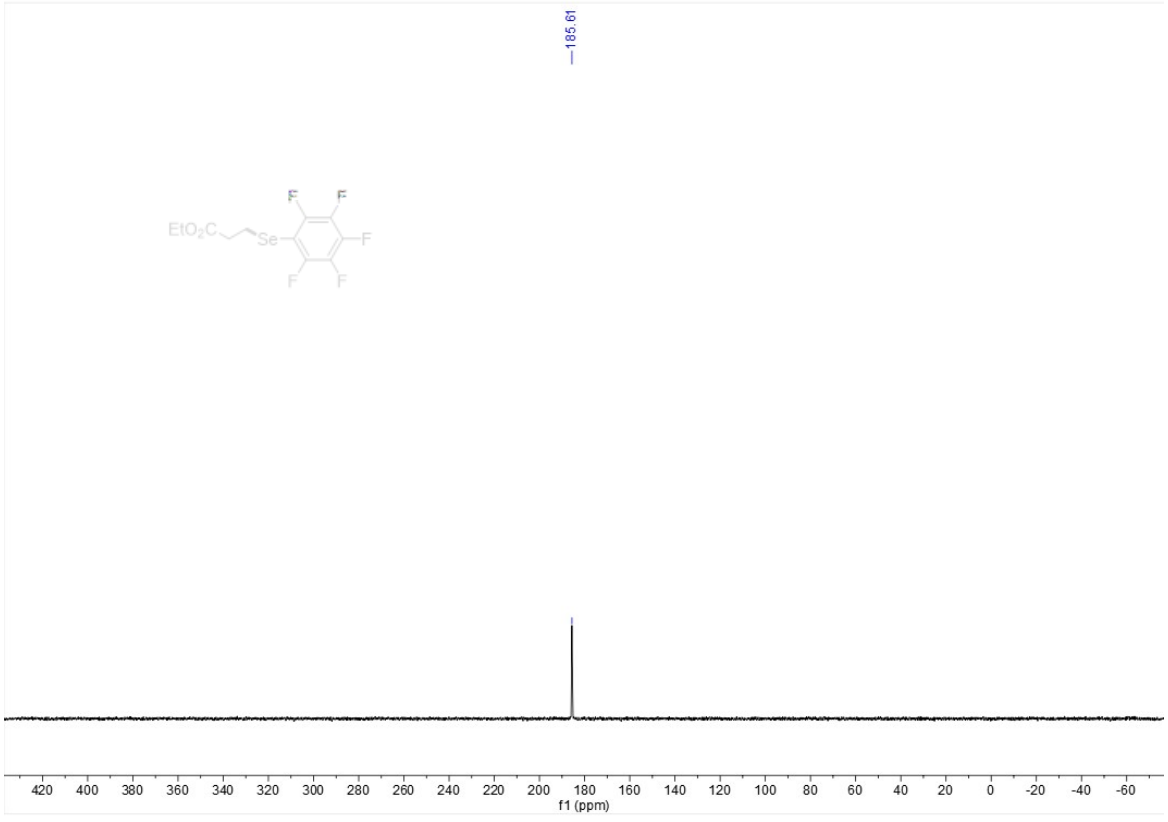
^{13}C NMR spectra of 3d ($CDCl_3$)



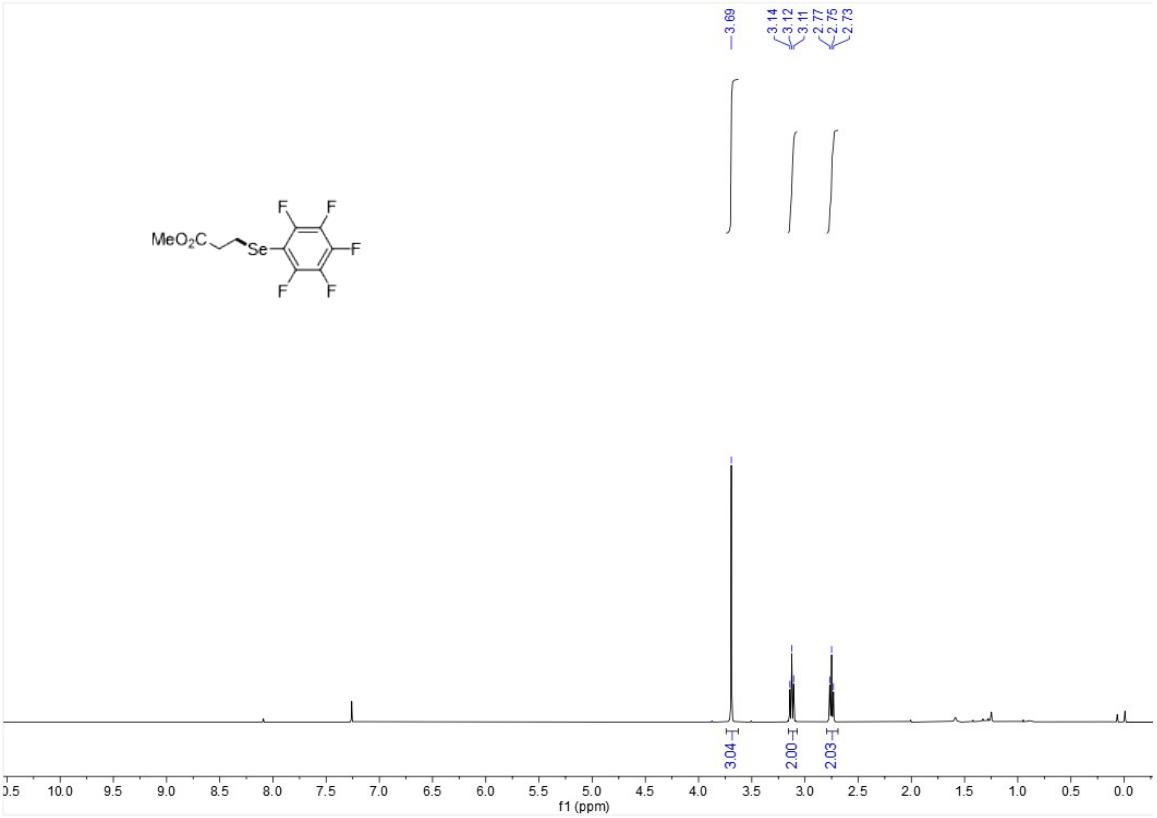
^{19}F NMR spectra of 3d ($CDCl_3$)



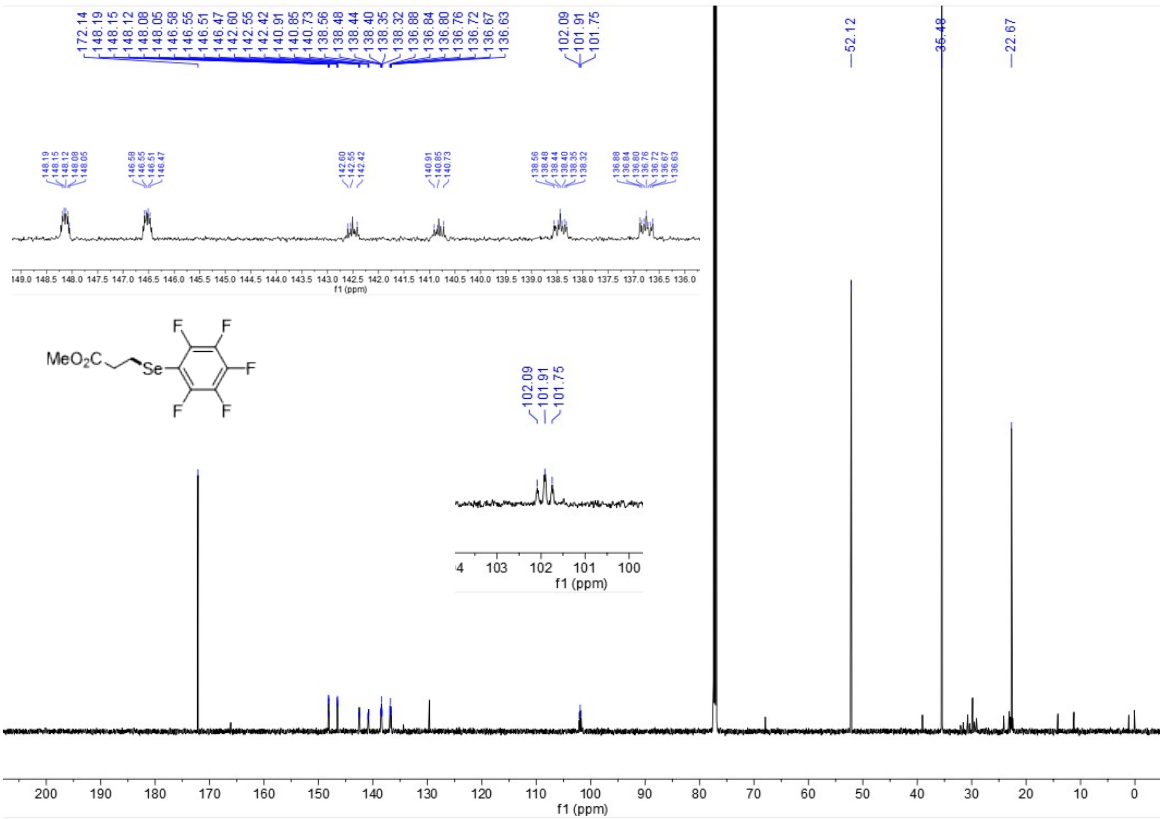
^{77}Se NMR spectra of 3d ($CDCl_3$)



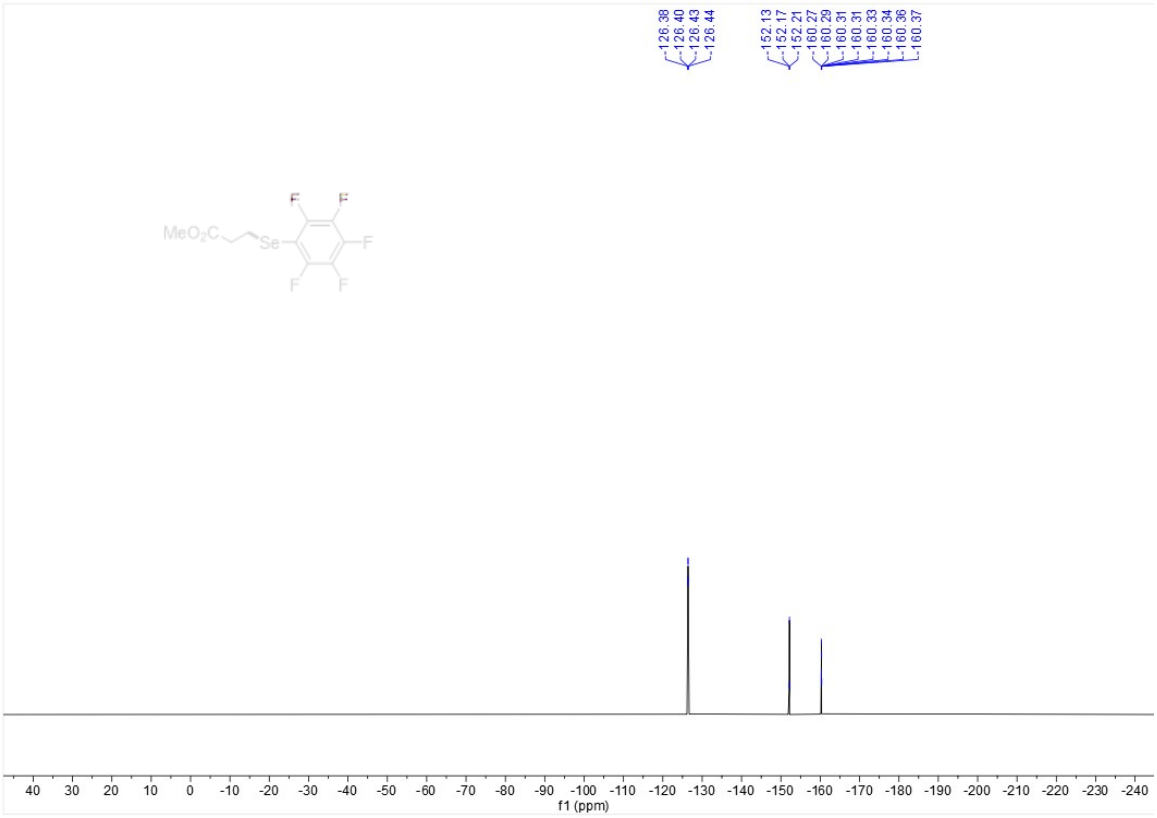
^{1}H NMR spectra of 3e ($CDCl_3$)



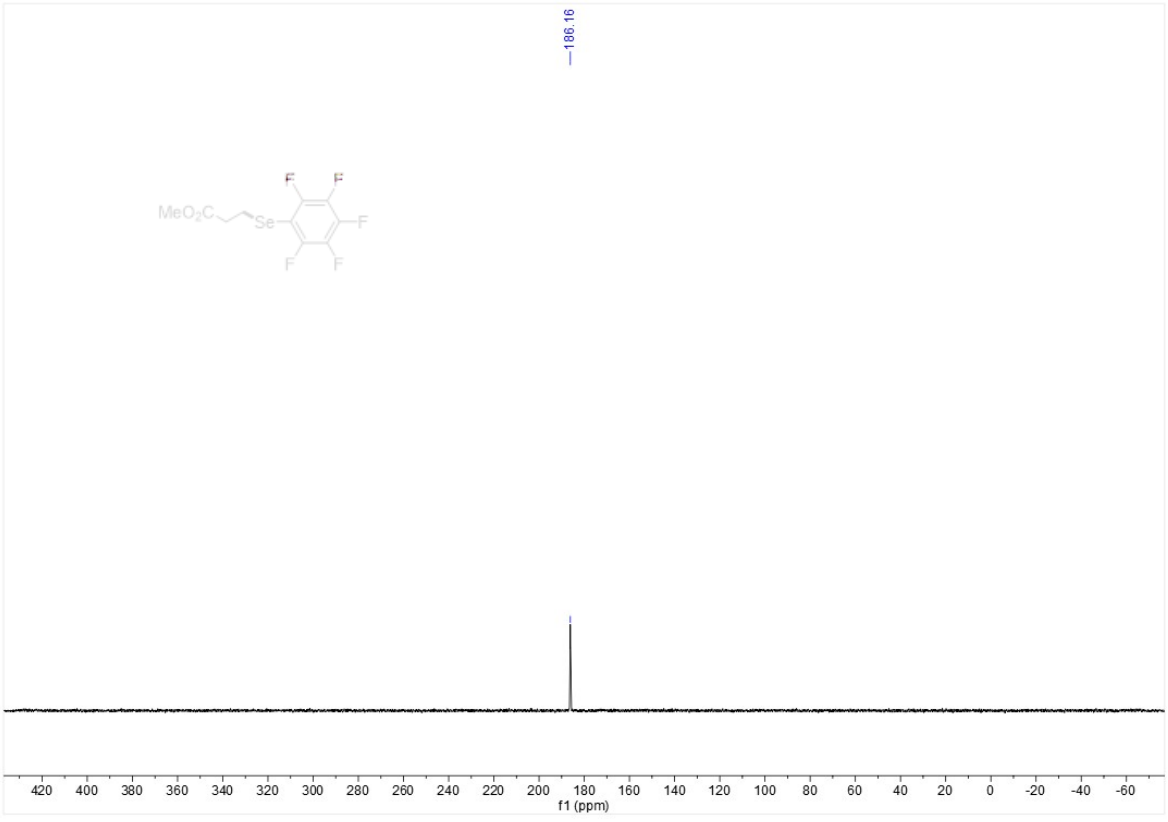
^{13}C NMR spectra of 3e ($CDCl_3$)



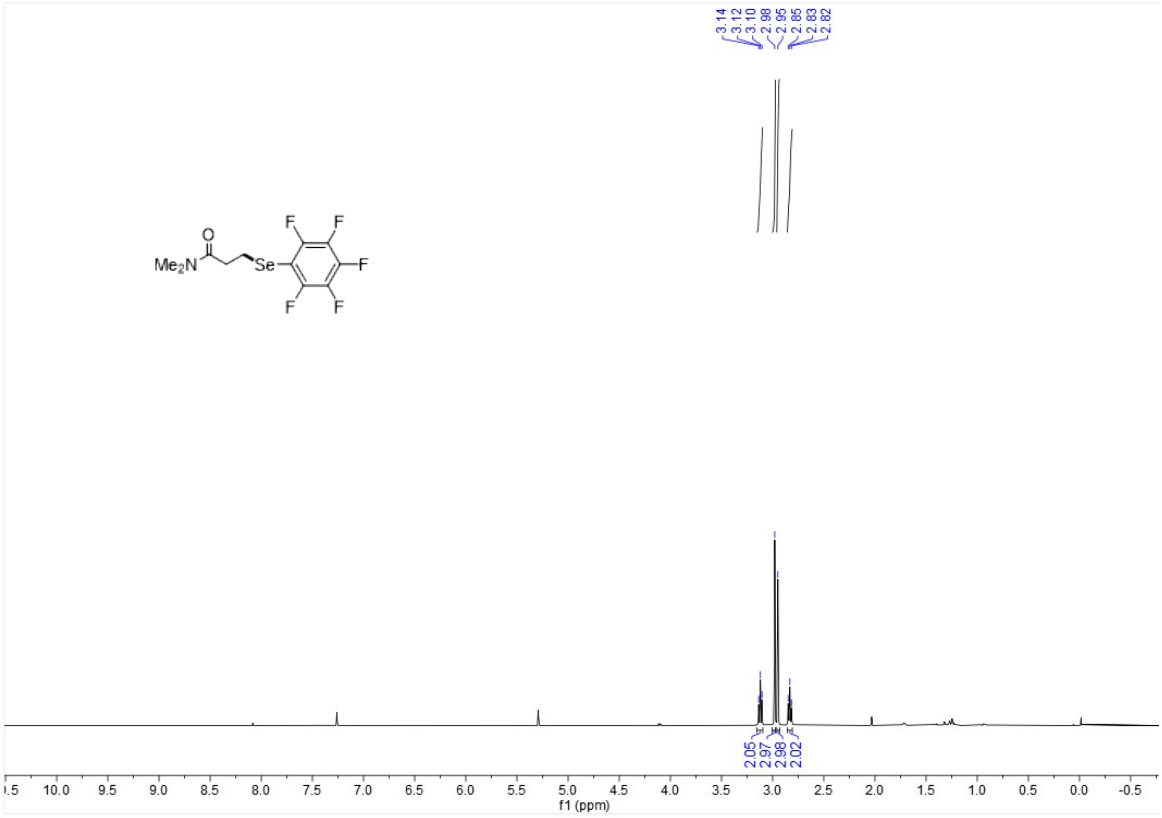
^{19}F NMR spectra of 3e ($CDCl_3$)



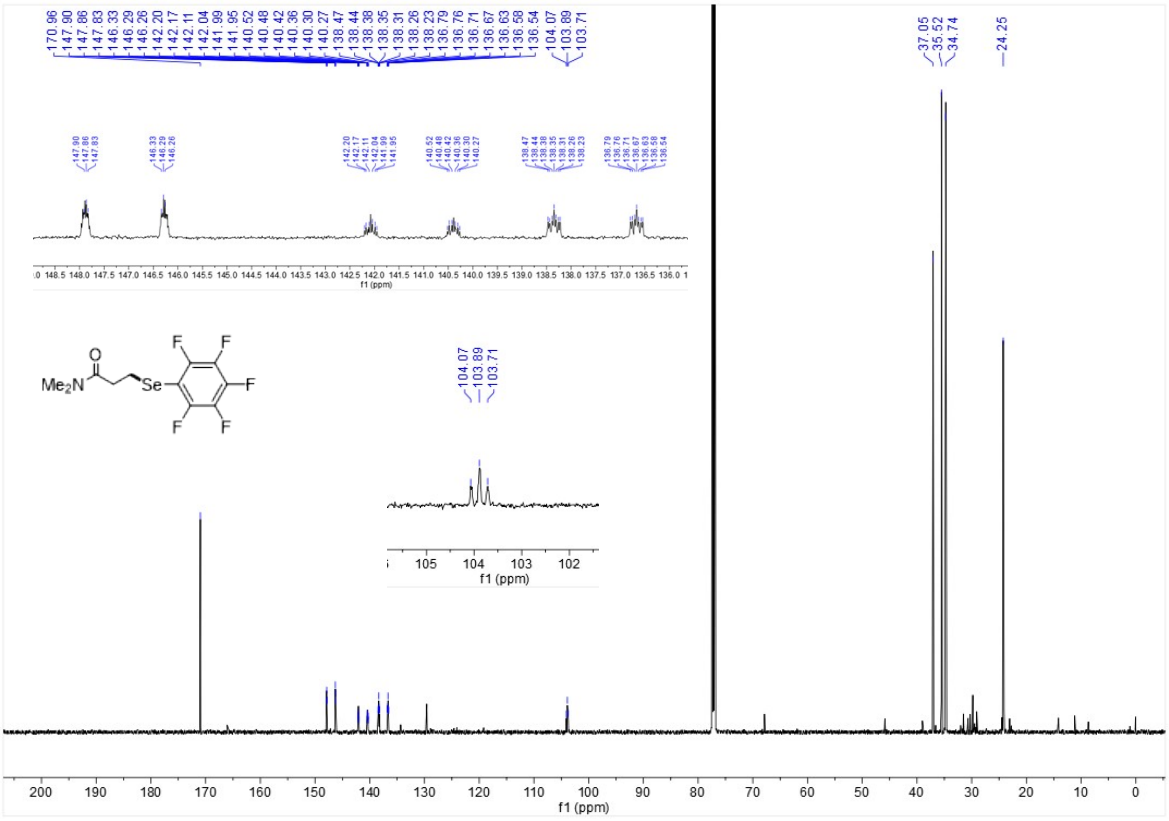
^{77}Se NMR spectra of 3e ($CDCl_3$)



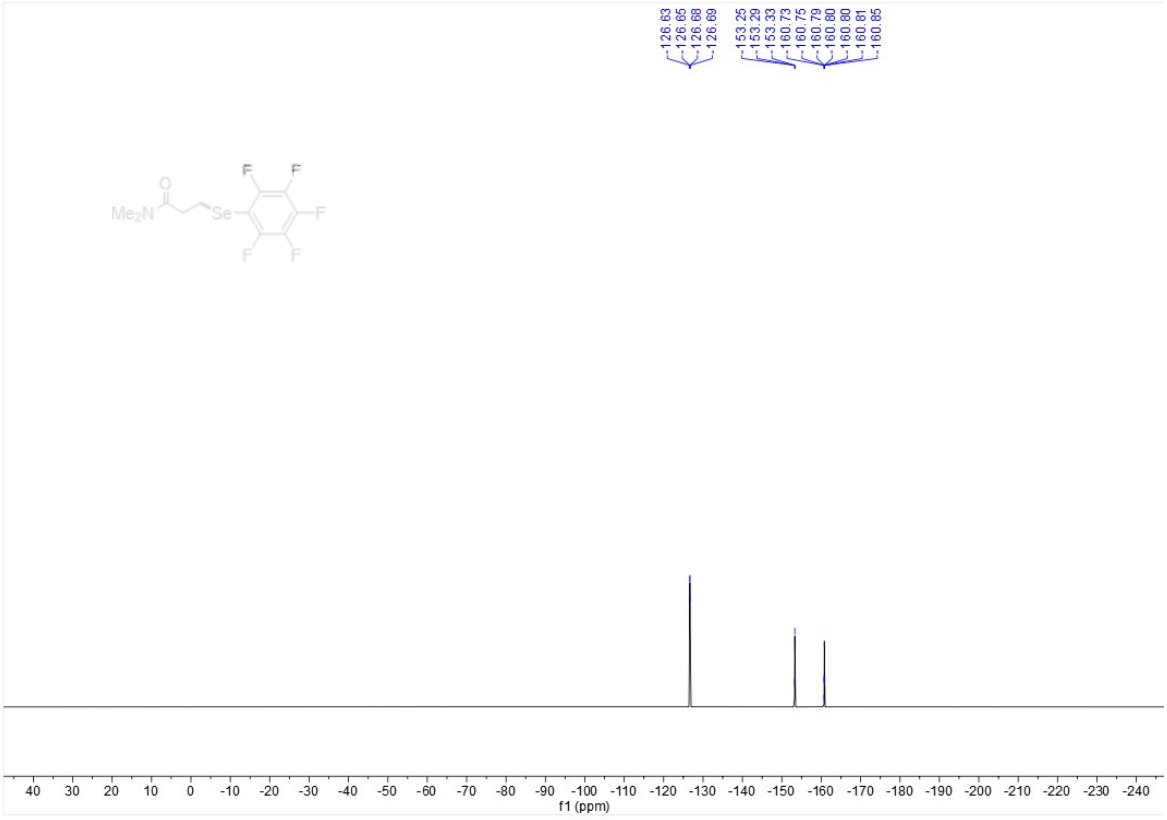
^{1}H NMR spectra of 3f ($CDCl_3$)



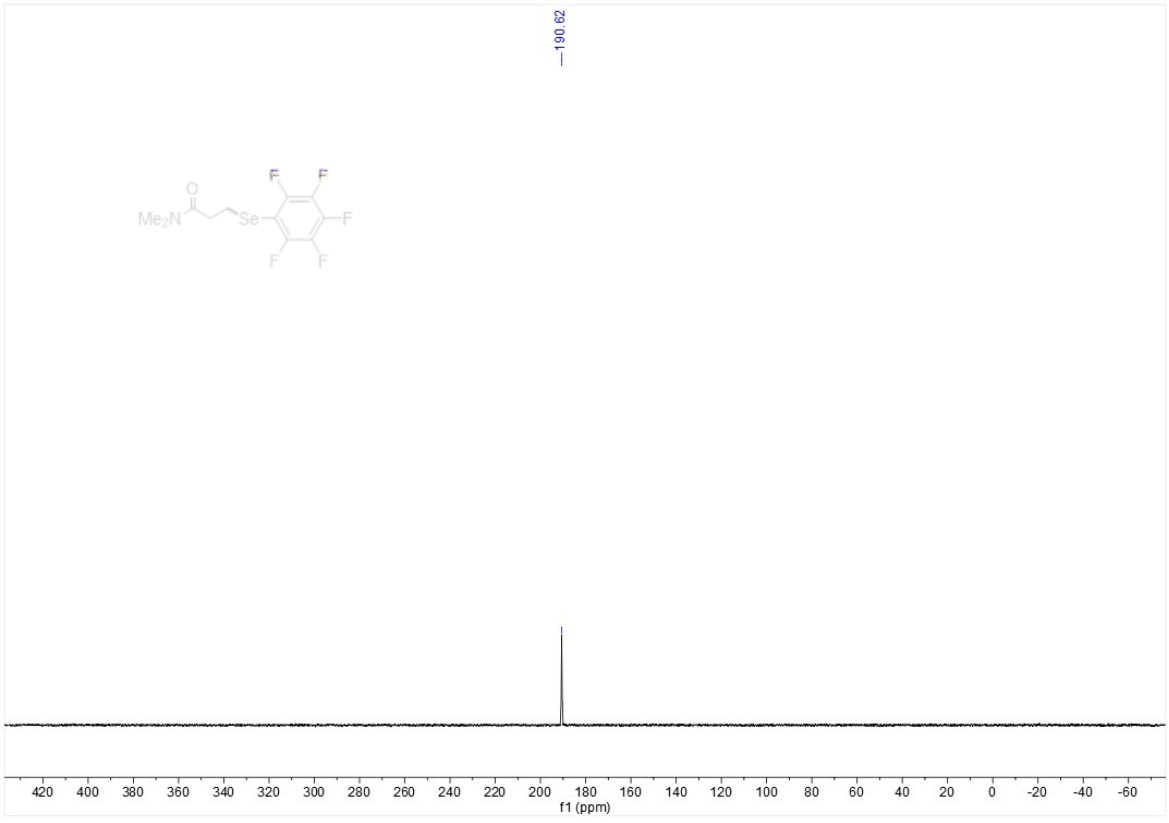
^{13}C NMR spectra of 3f ($CDCl_3$)



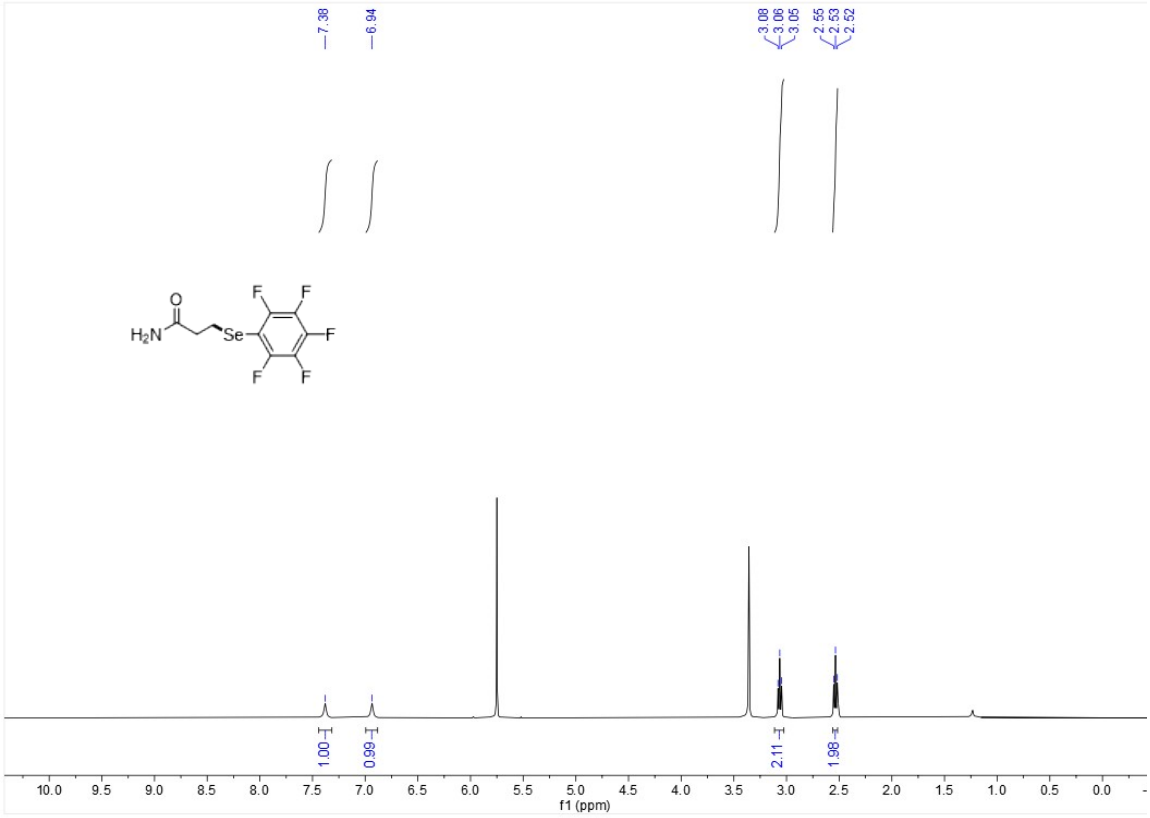
^{19}F NMR spectra of 3f ($CDCl_3$)



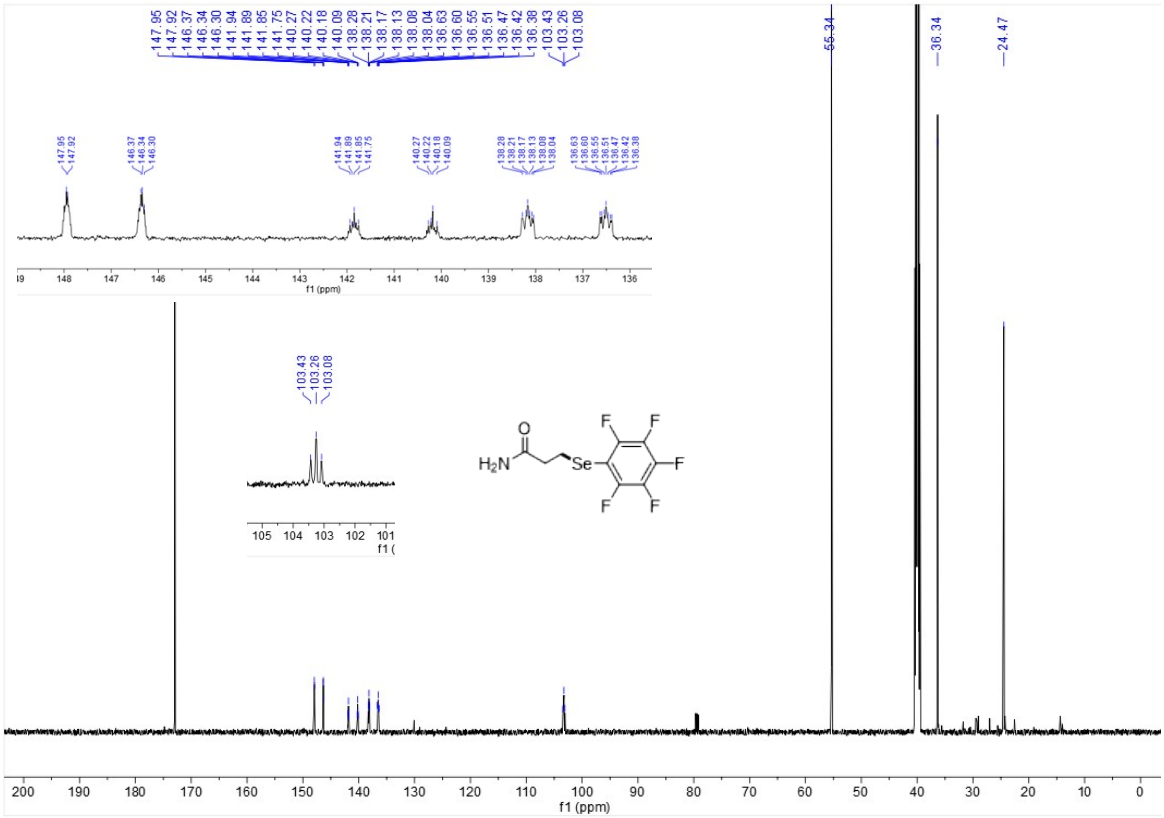
^{77}Se NMR spectra of 3f ($CDCl_3$)



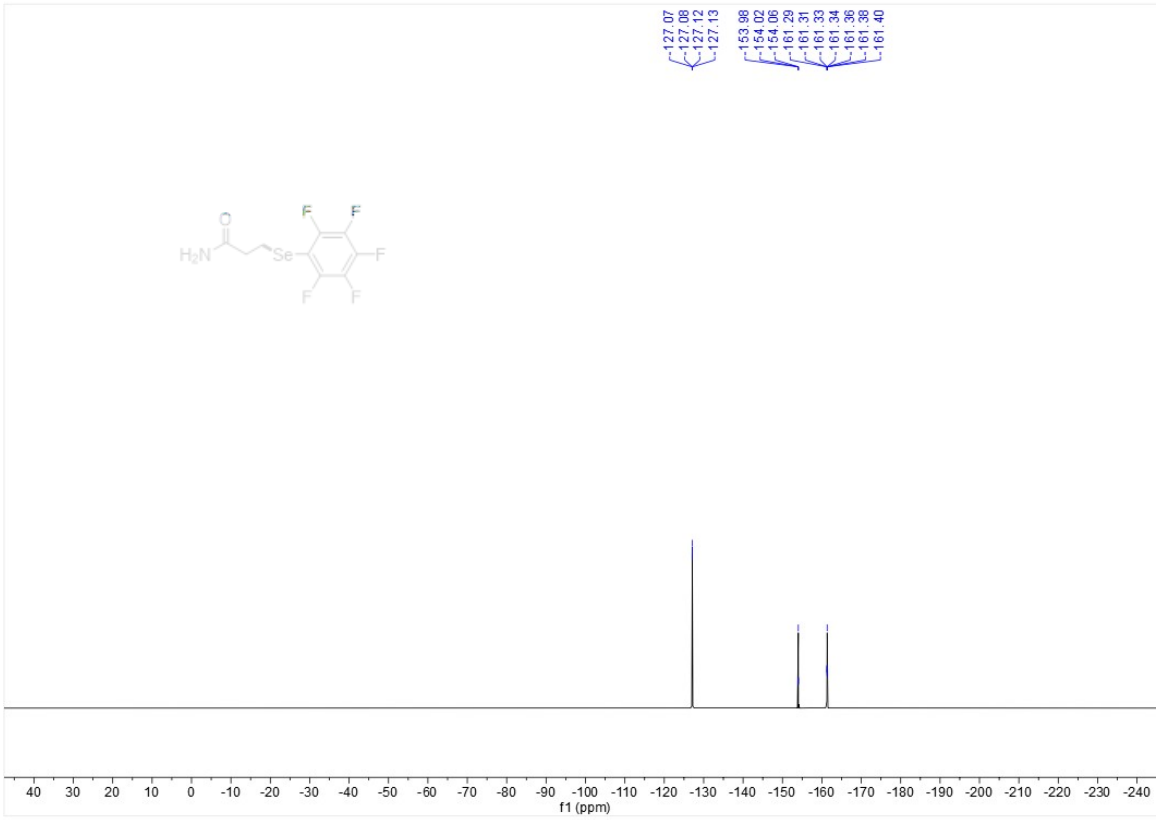
^{1}H NMR spectra of 3g (DMSO-d_6)



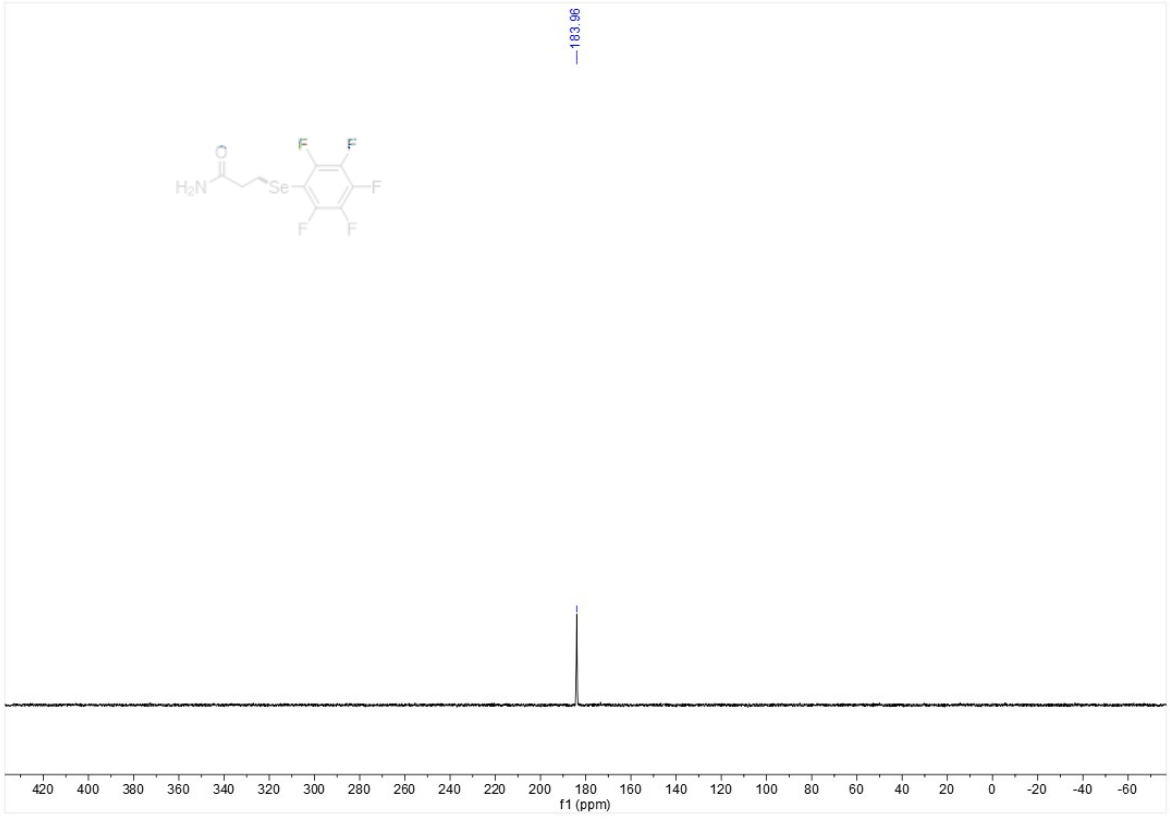
^{13}C NMR spectra of 3g (DMSO-d_6)



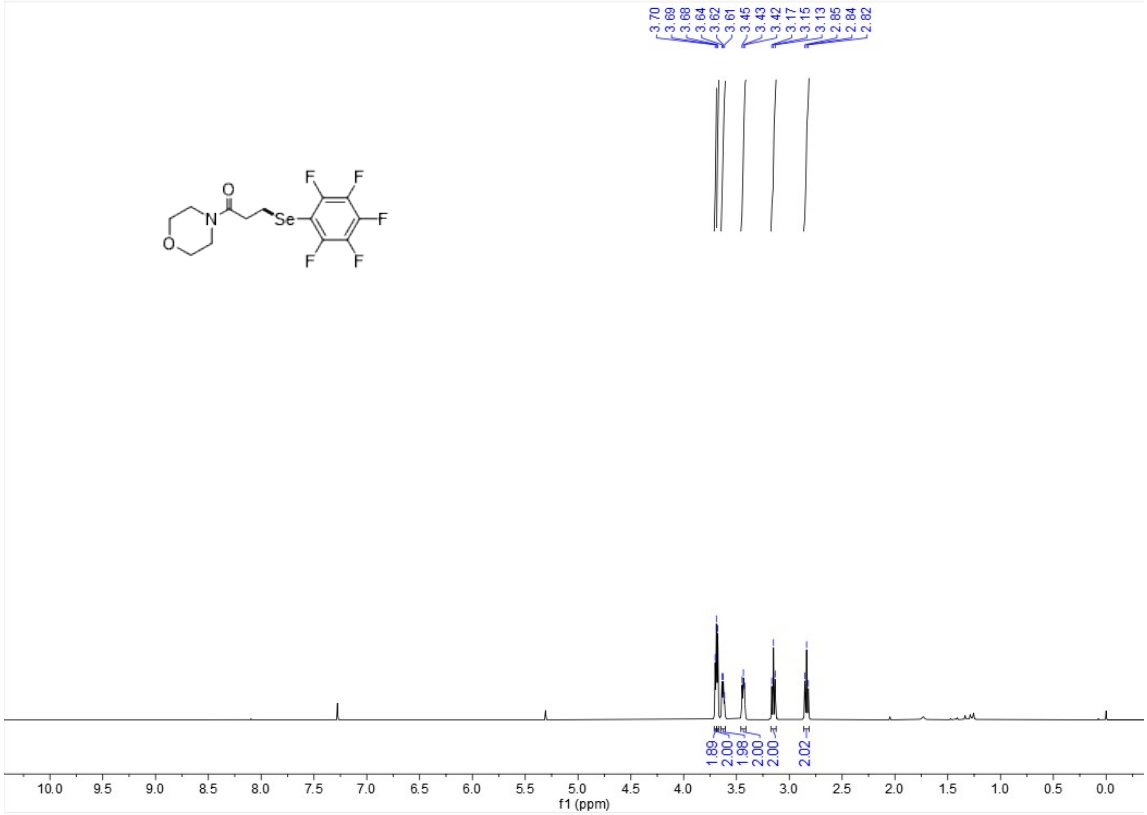
^{19}F NMR spectra of 3g (DMSO-d_6)



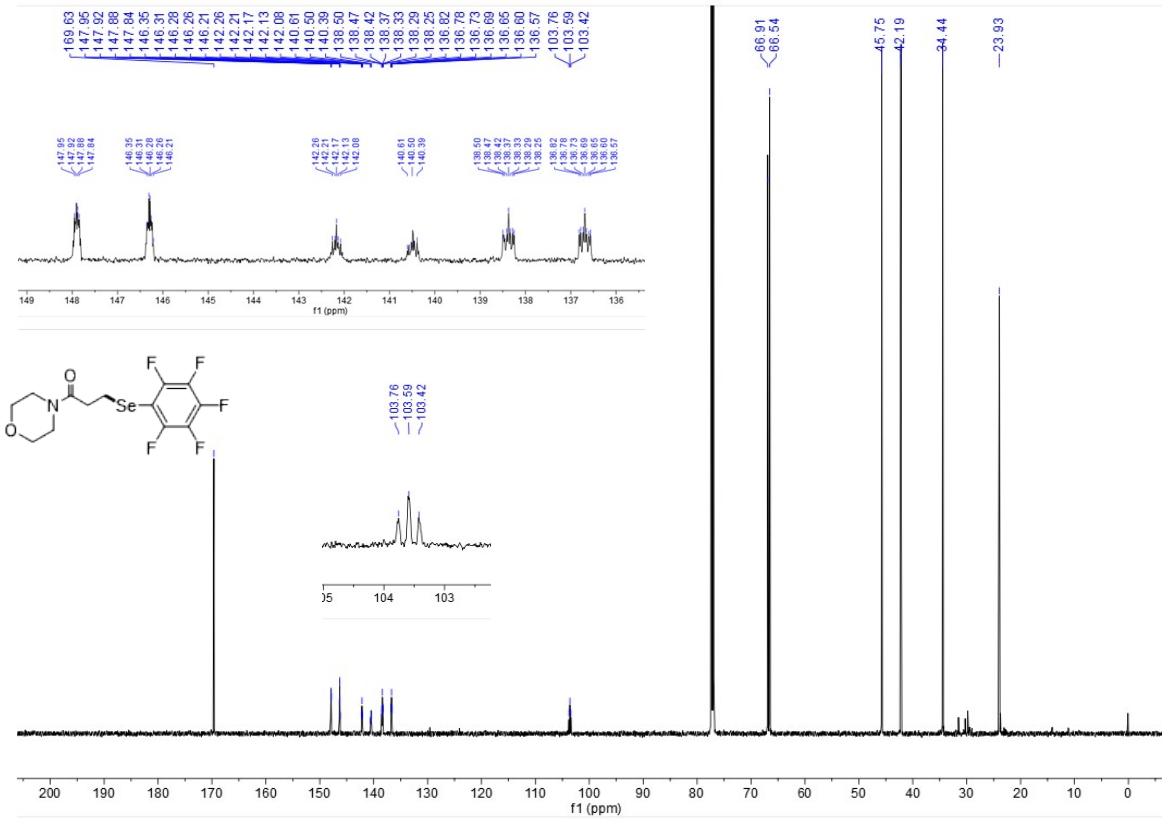
^{77}Se NMR spectra of 3g (DMSO-d_6)



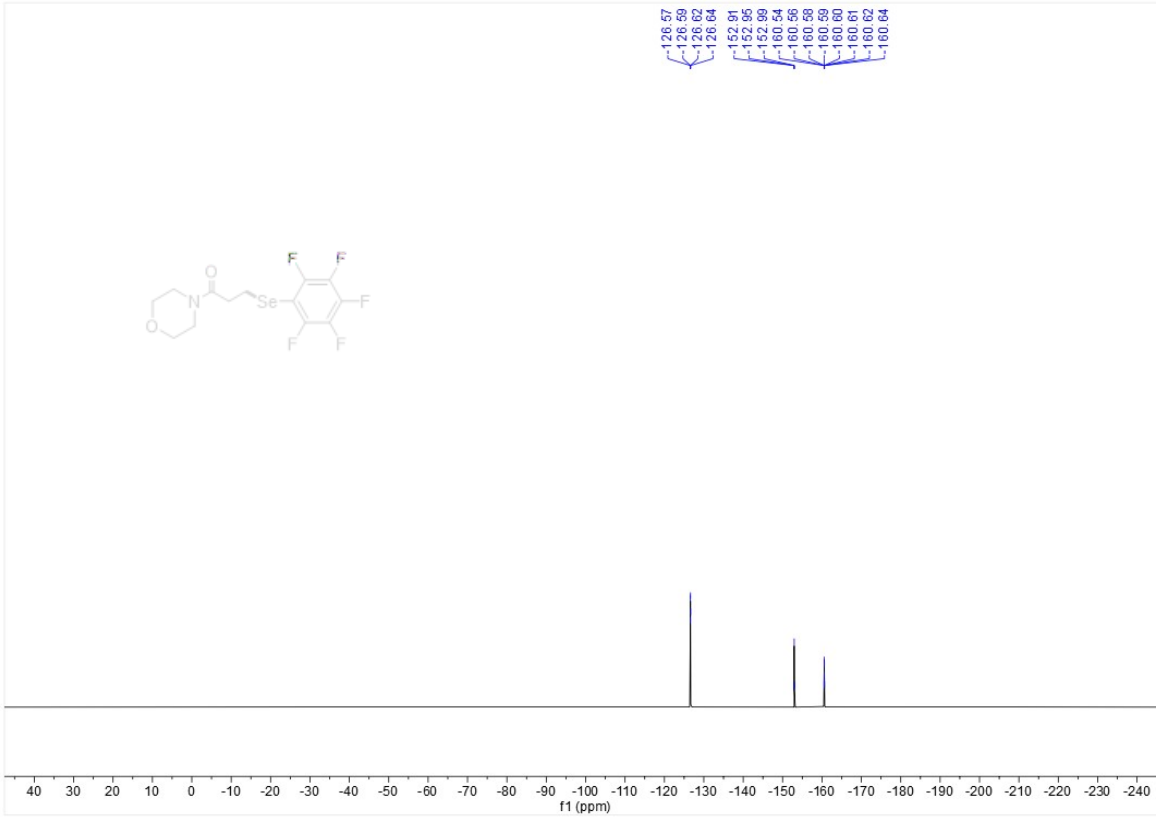
^{1}H NMR spectra of 3h ($CDCl_3$)



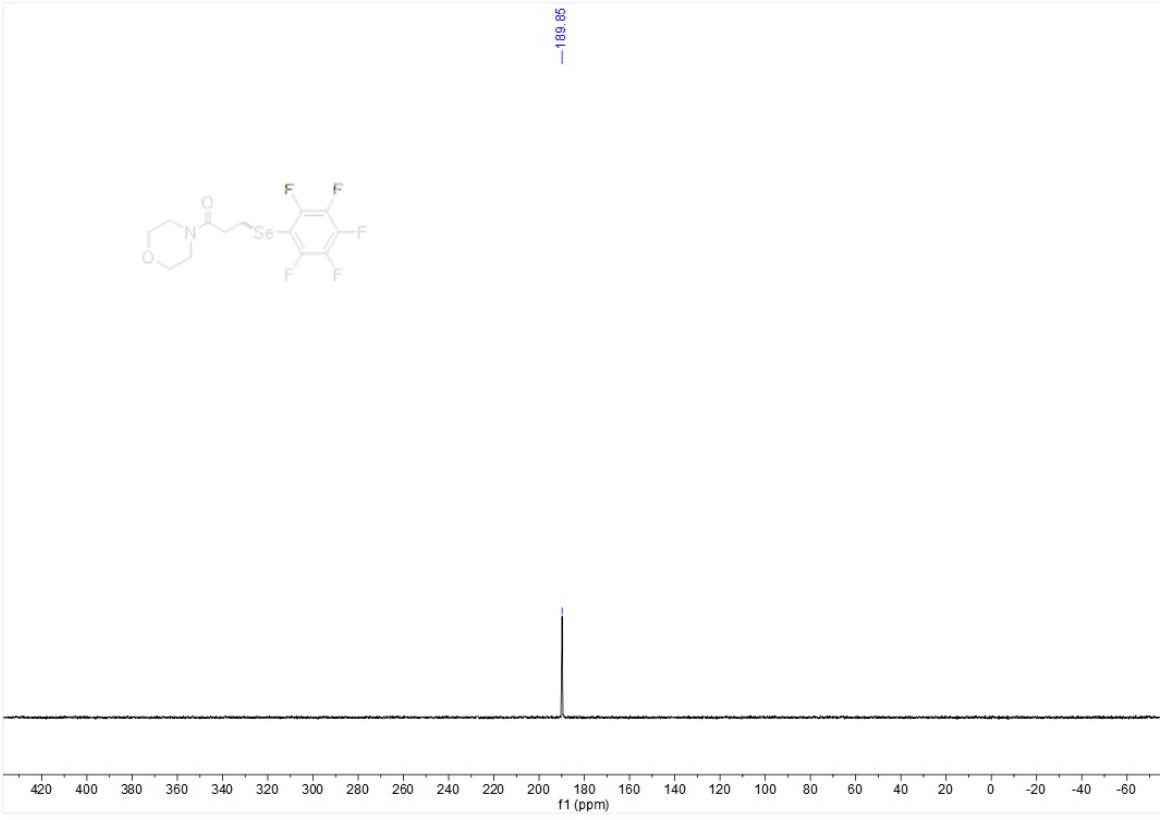
^{13}C NMR spectra of 3h ($CDCl_3$)



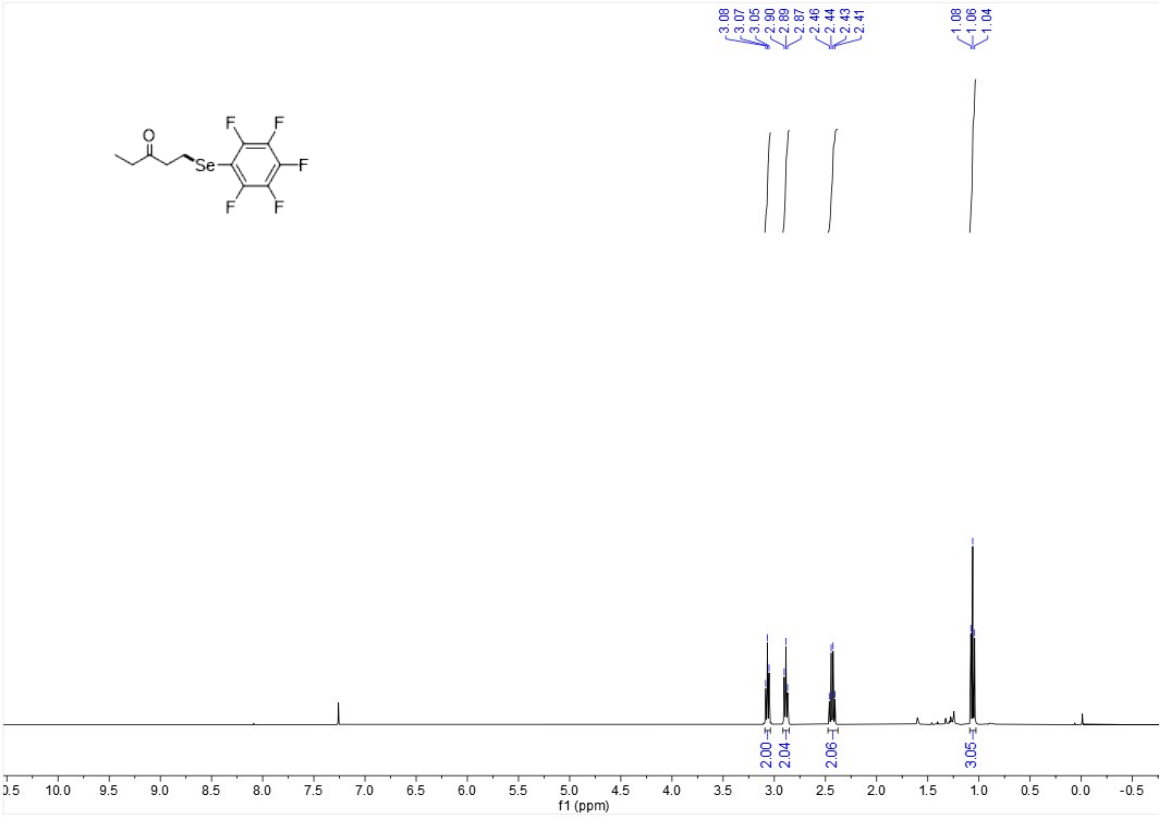
^{19}F NMR spectra of 3h ($CDCl_3$)



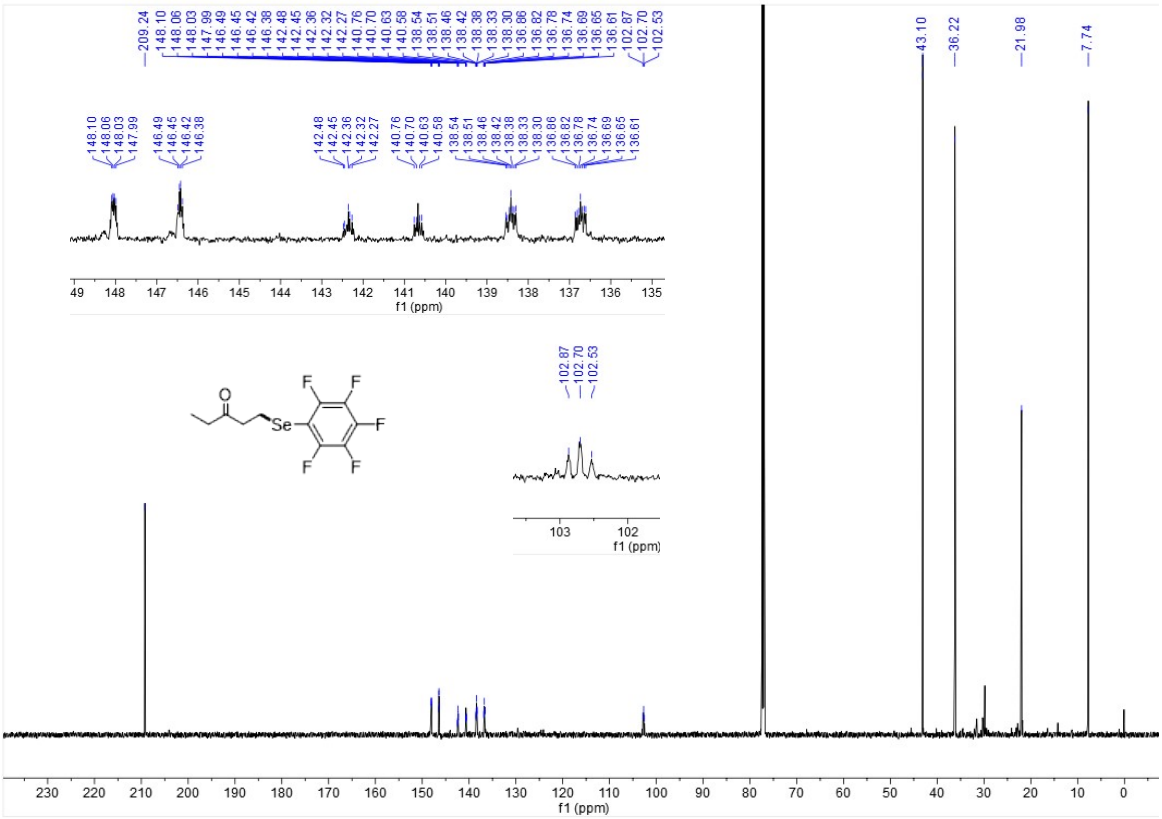
^{77}Se NMR spectra of 3h ($CDCl_3$)



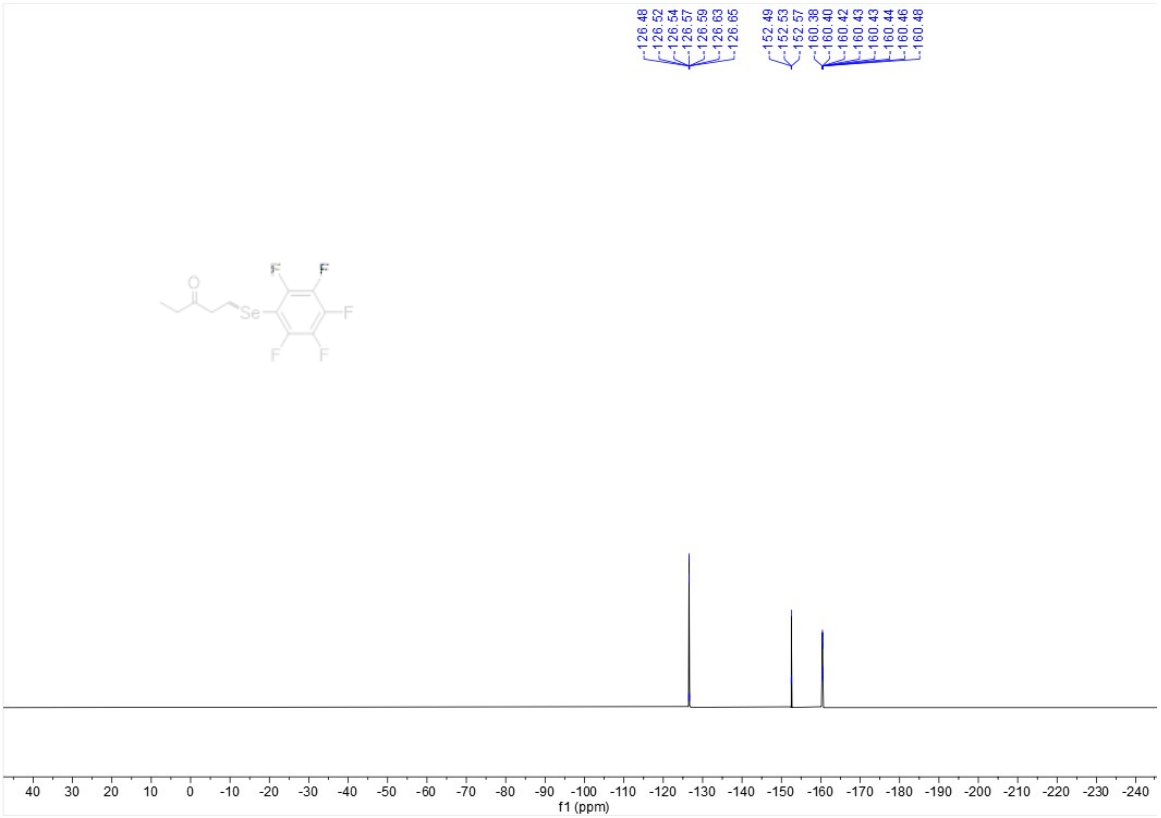
^{1}H NMR spectra of 3i ($CDCl_3$)



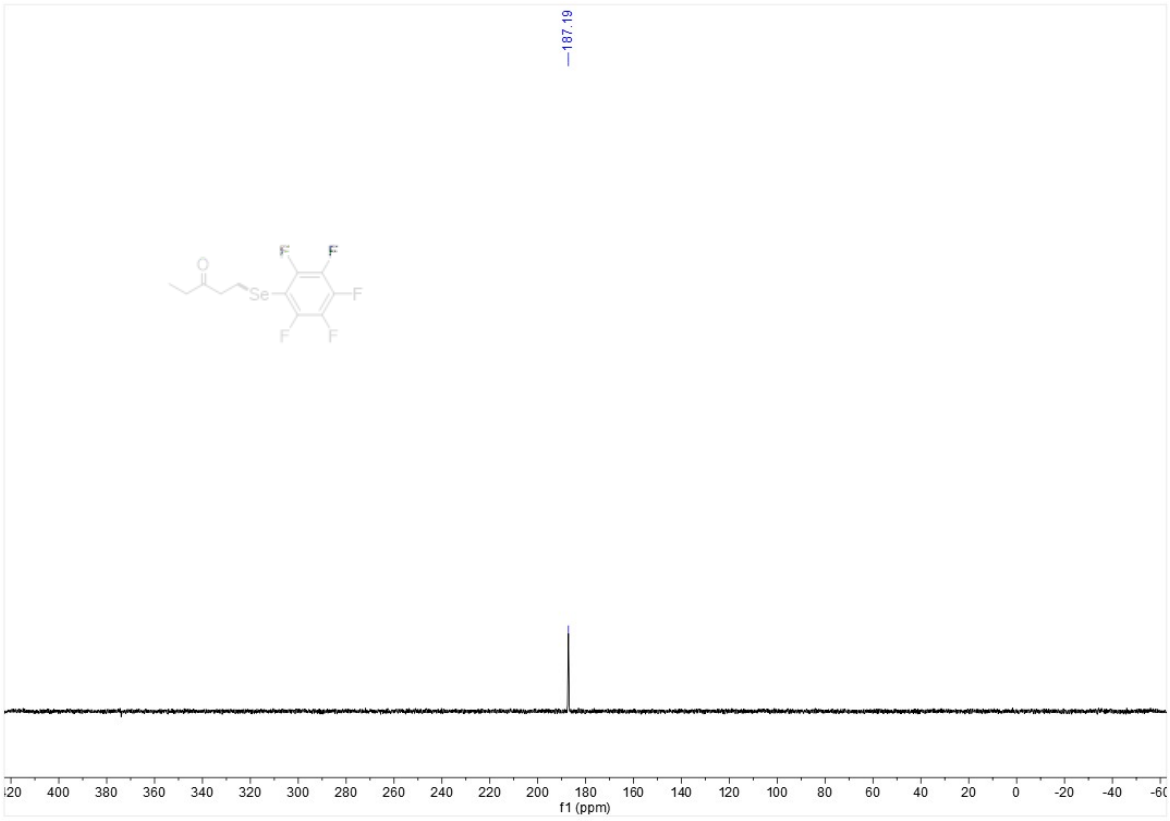
^{13}C NMR spectra of 3i ($CDCl_3$)



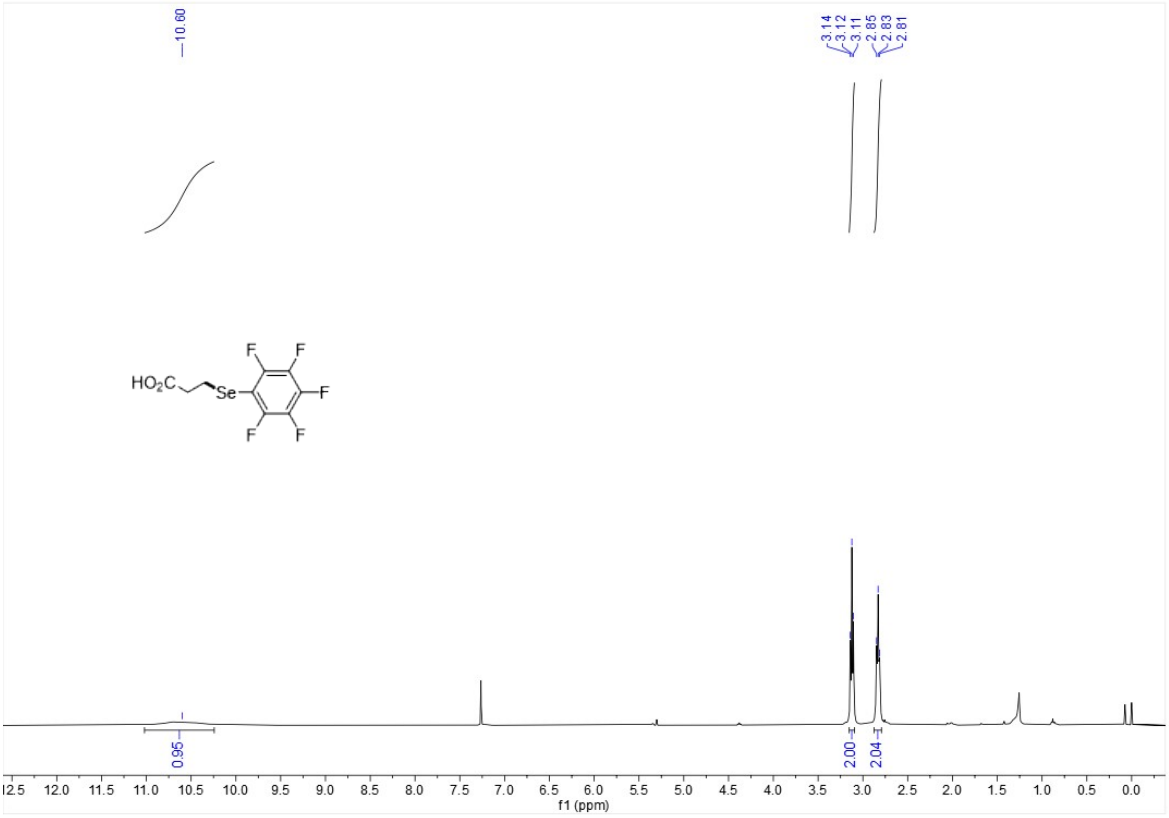
^{19}F NMR spectra of 3i ($CDCl_3$)



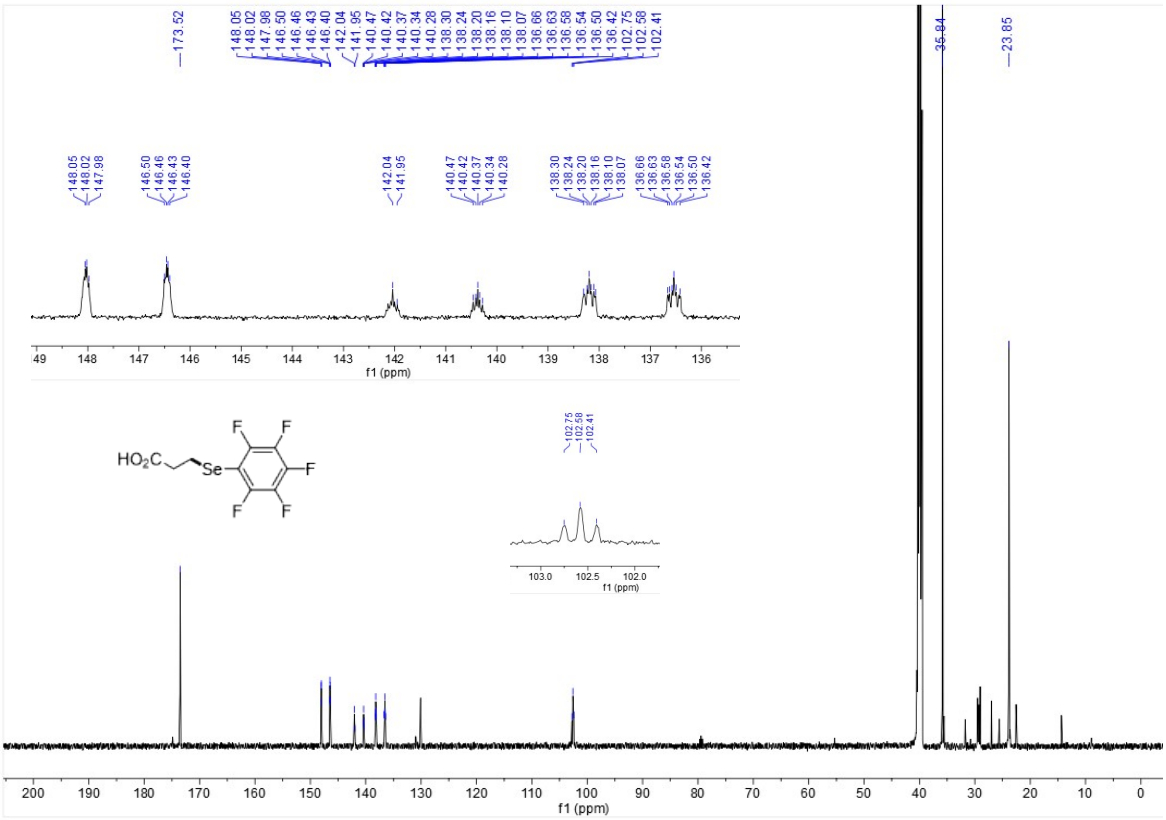
^{77}Se NMR spectra of 3i ($CDCl_3$)



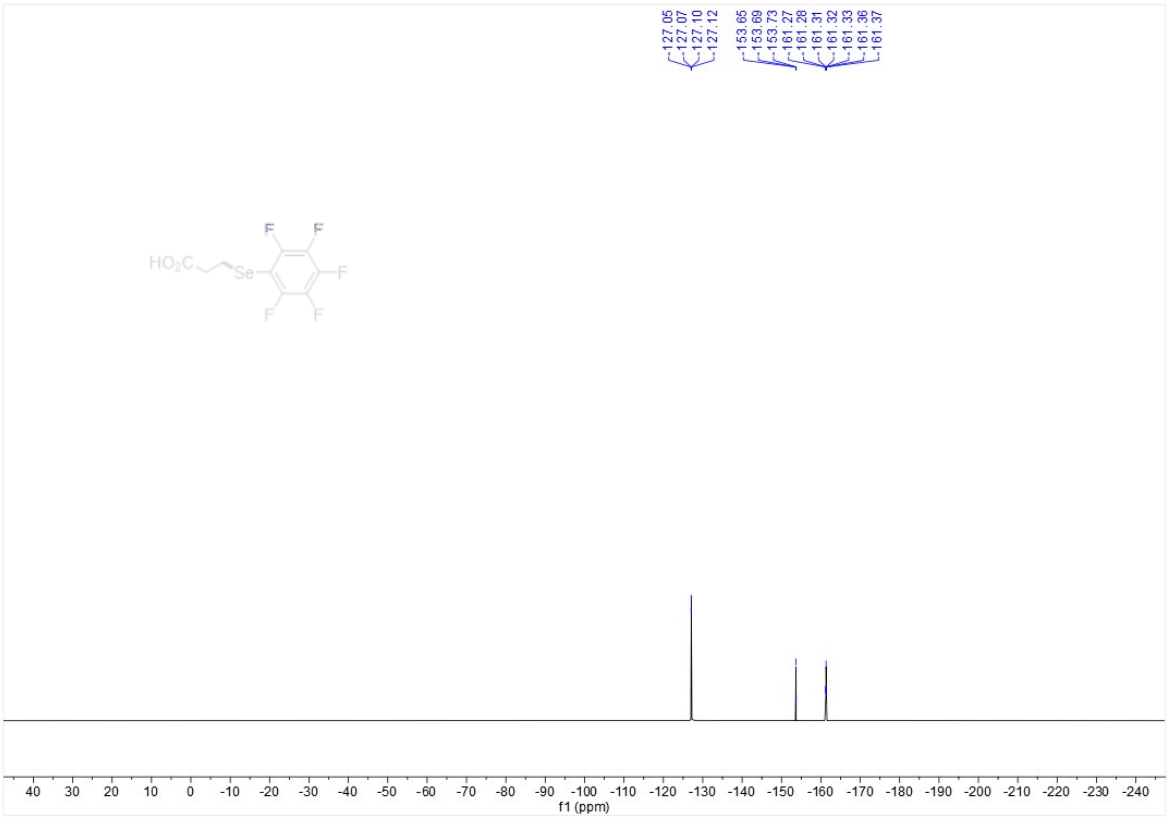
^{1}H NMR spectra of 3j ($CDCl_3$)



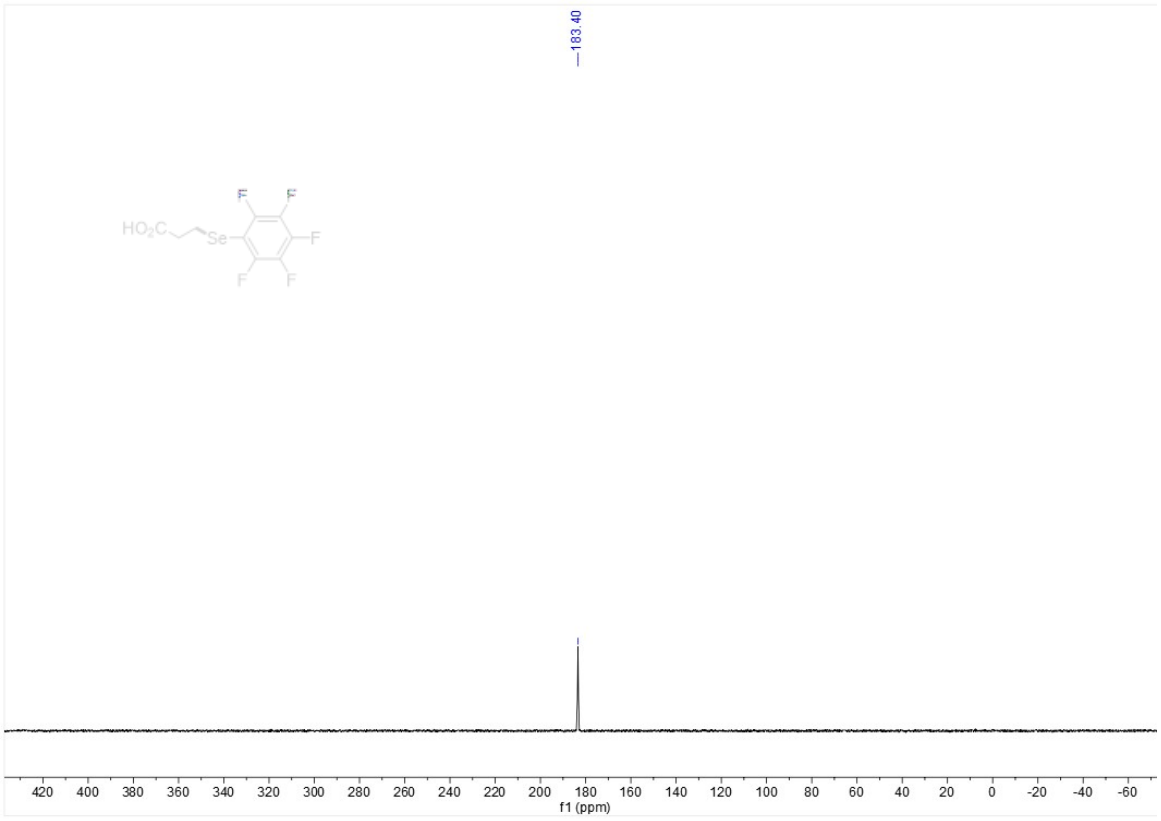
^{13}C NMR spectra of 3j (DMSO-d_6)



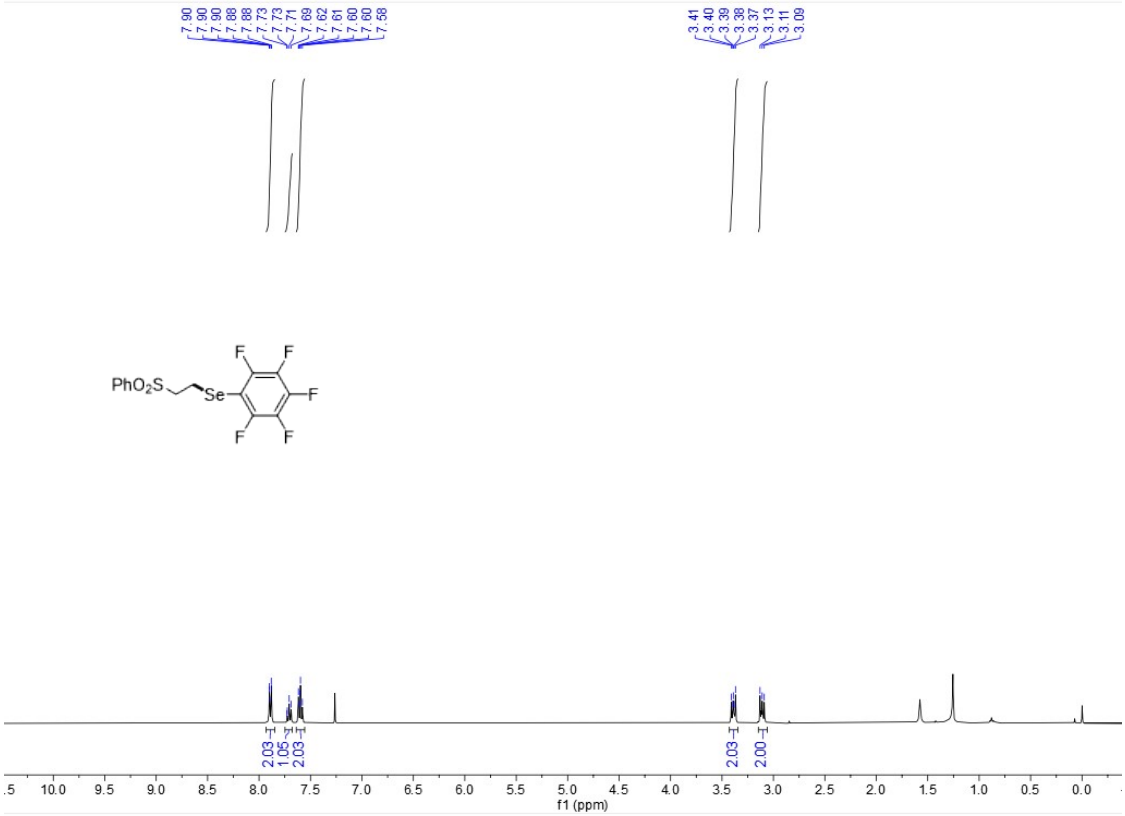
^{19}F NMR spectra of 3j (DMSO-d_6)



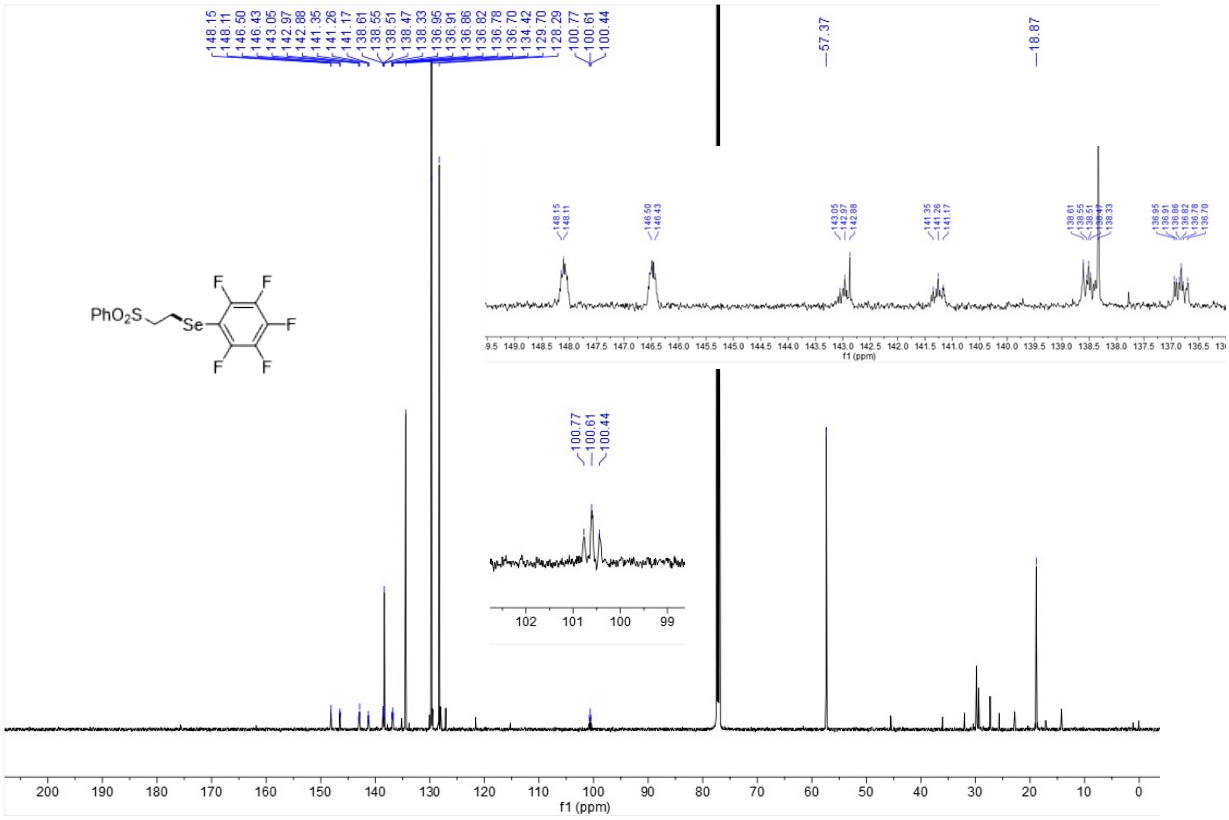
^{77}Se NMR spectra of 3j (DMSO-d_6)



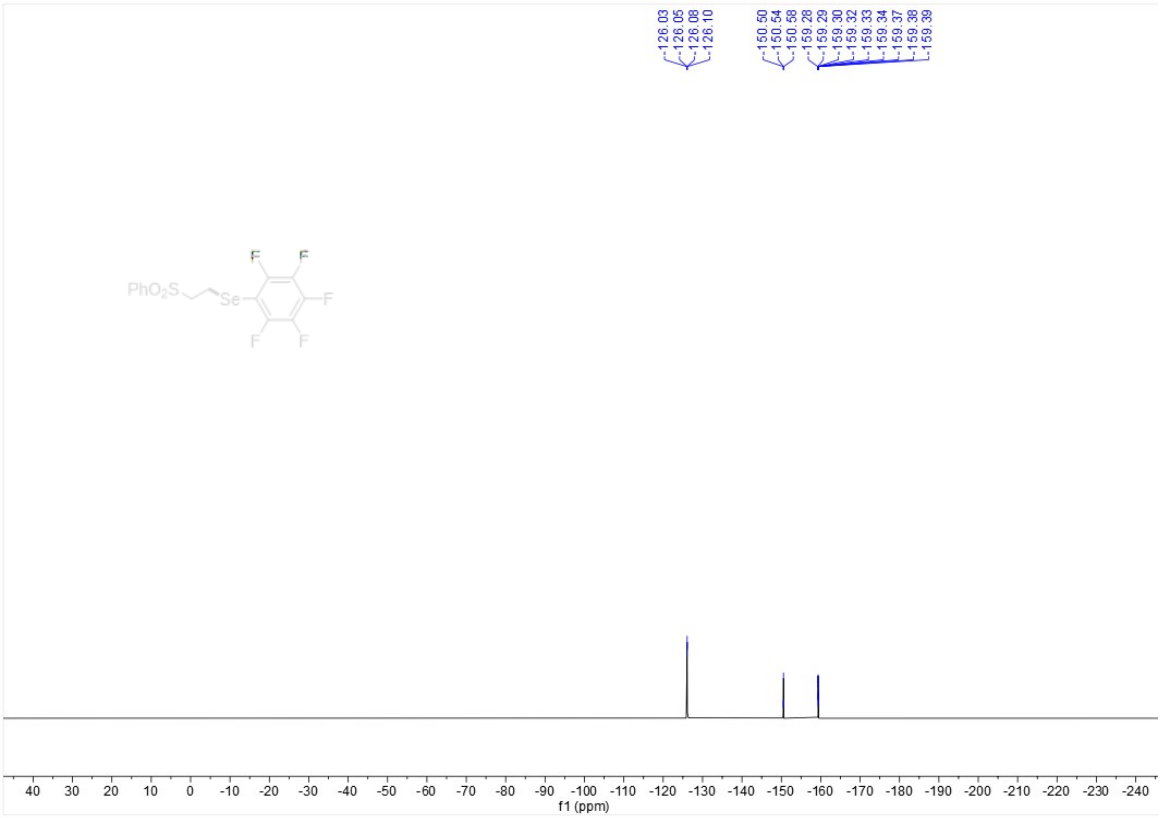
^{1}H NMR spectra of 3k ($CDCl_3$)



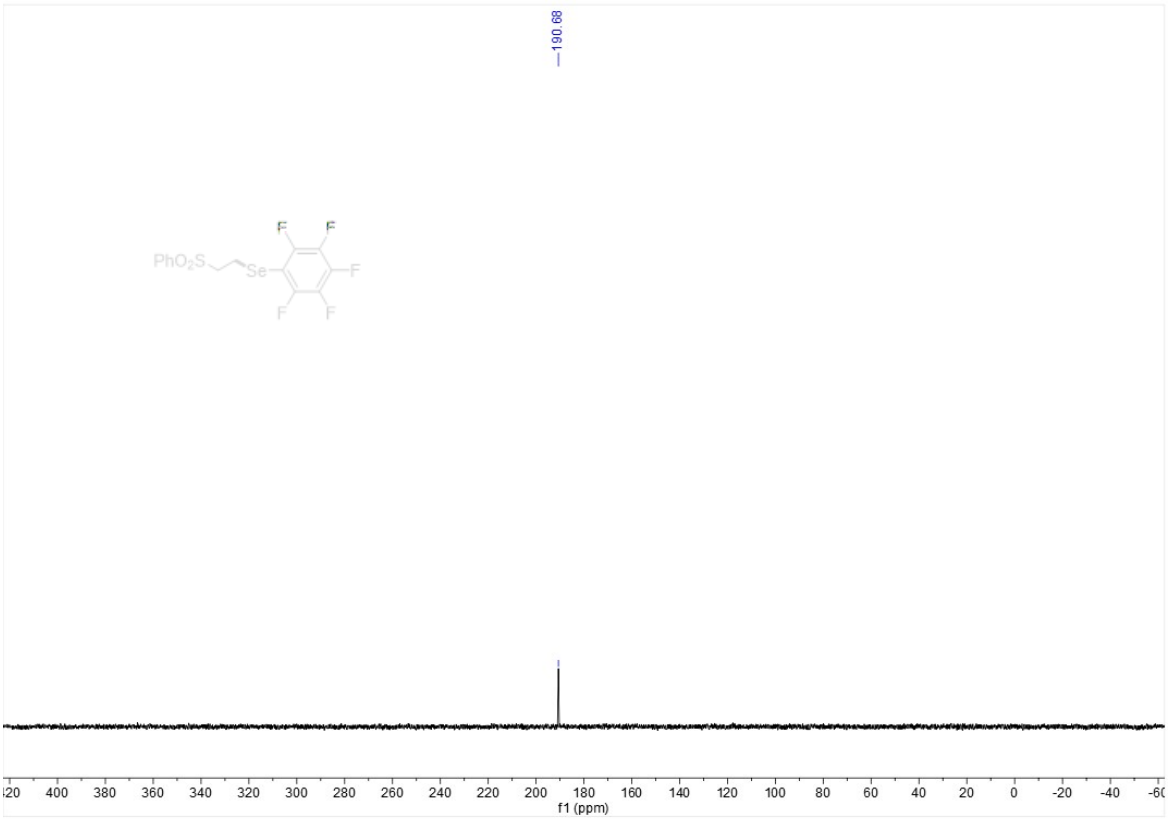
^{13}C NMR spectra of 3k ($CDCl_3$)



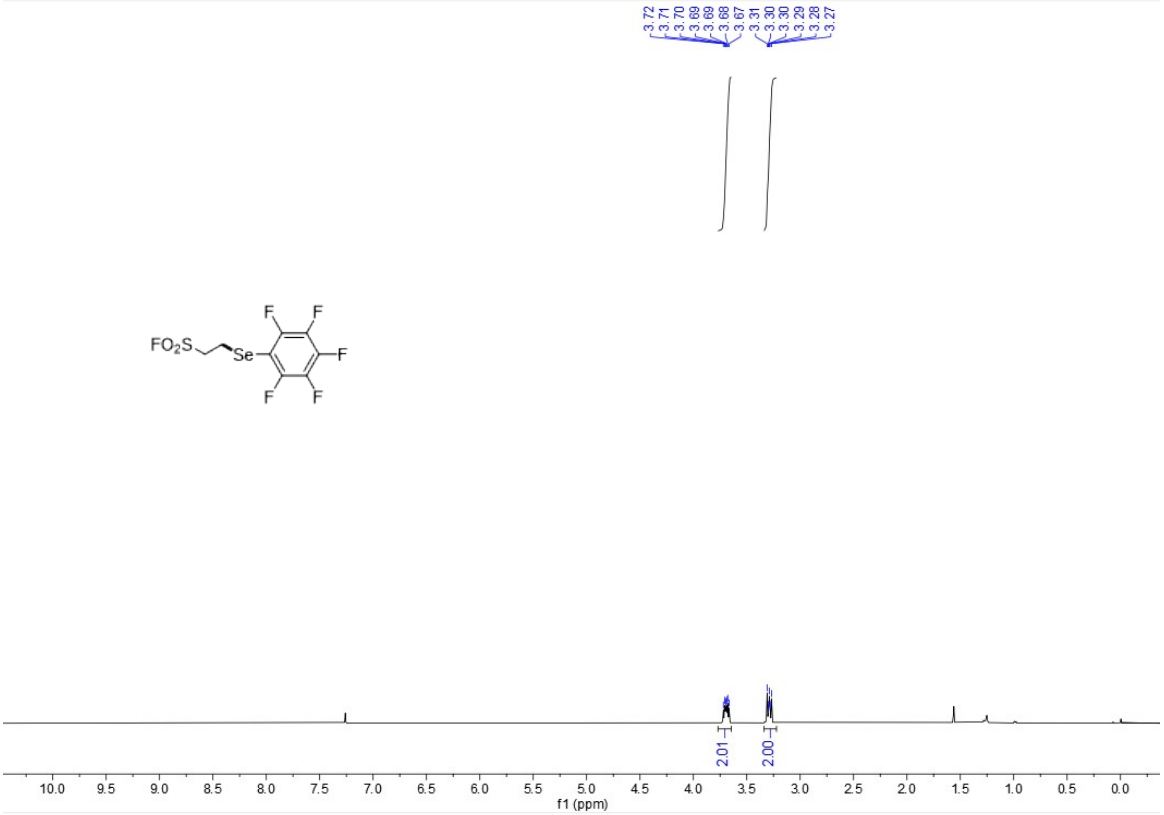
^{19}F NMR spectra of 3k ($CDCl_3$)



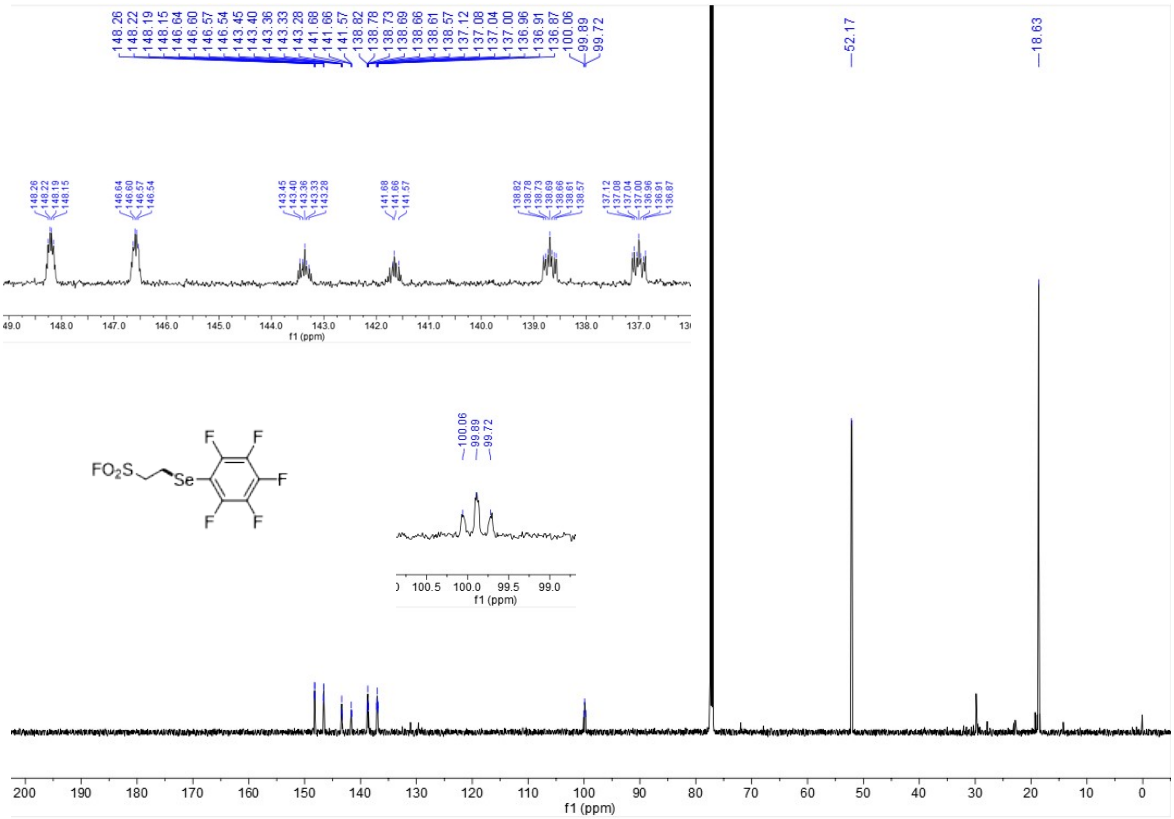
^{77}Se NMR spectra of 3k ($CDCl_3$)



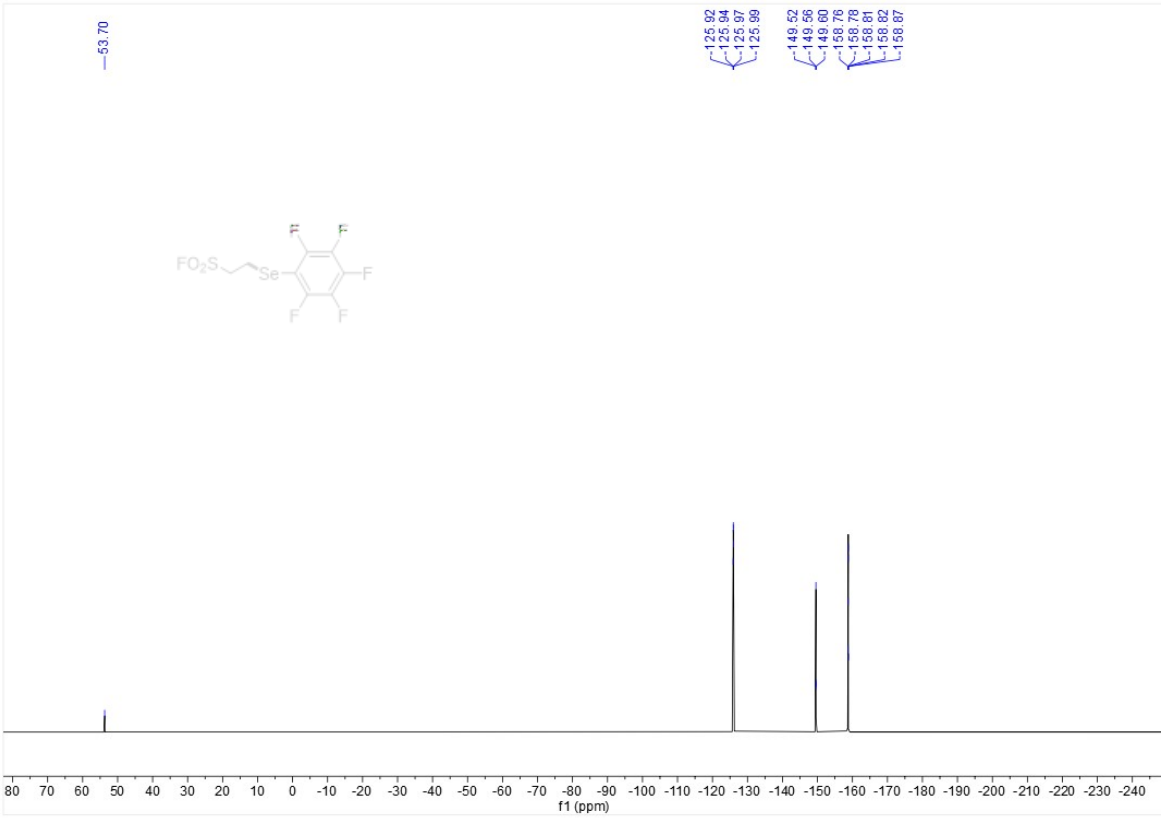
^{1}H NMR spectra of 3l ($CDCl_3$)



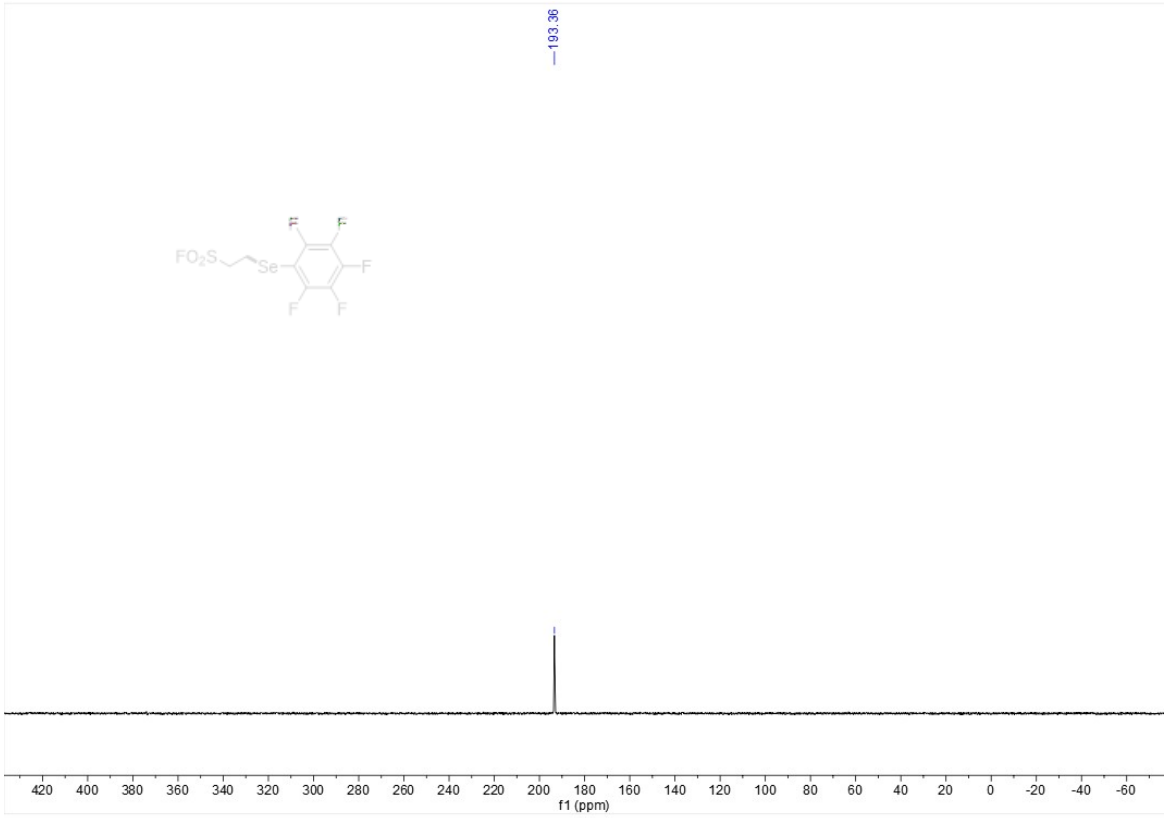
^{13}C NMR spectra of 3l ($CDCl_3$)



^{19}F NMR spectra of 3l ($CDCl_3$)

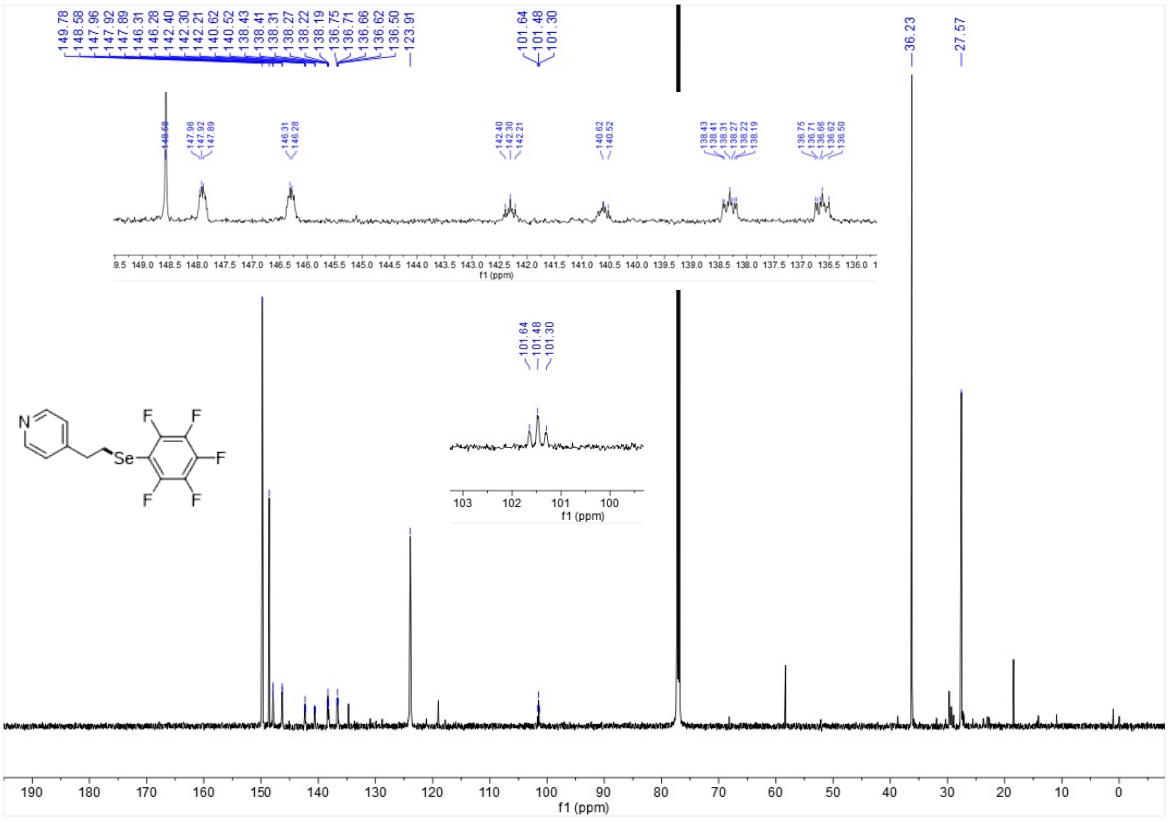


^{77}Se NMR spectra of 3l ($CDCl_3$)

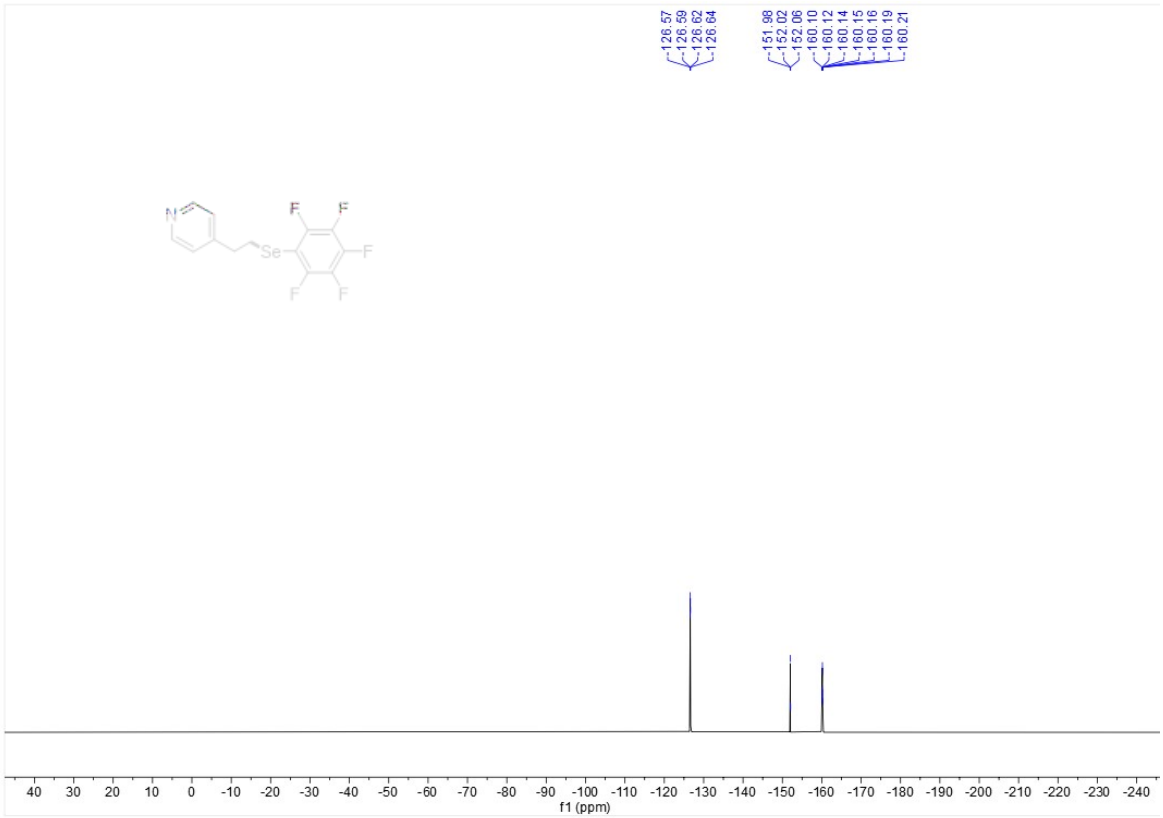


^{1}H NMR spectra of 3m ($CDCl_3$)

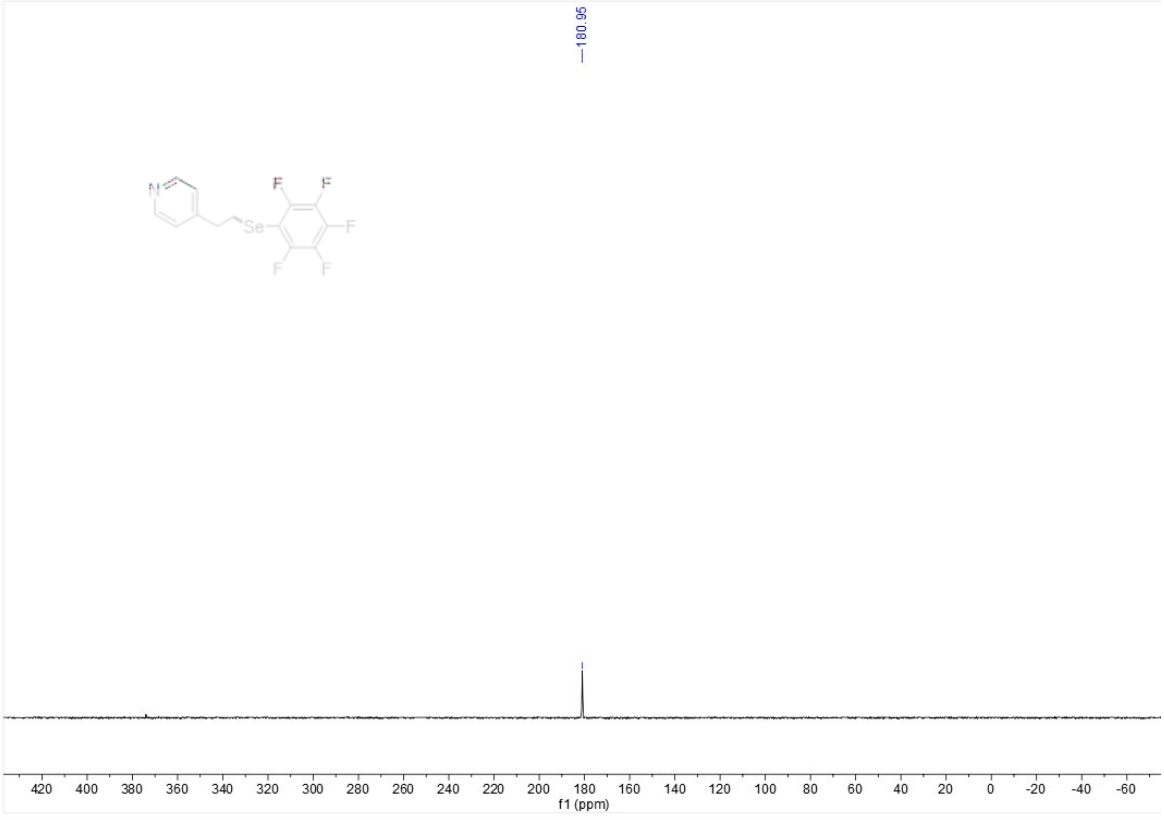
^{13}C NMR spectra of 3m ($CDCl_3$)



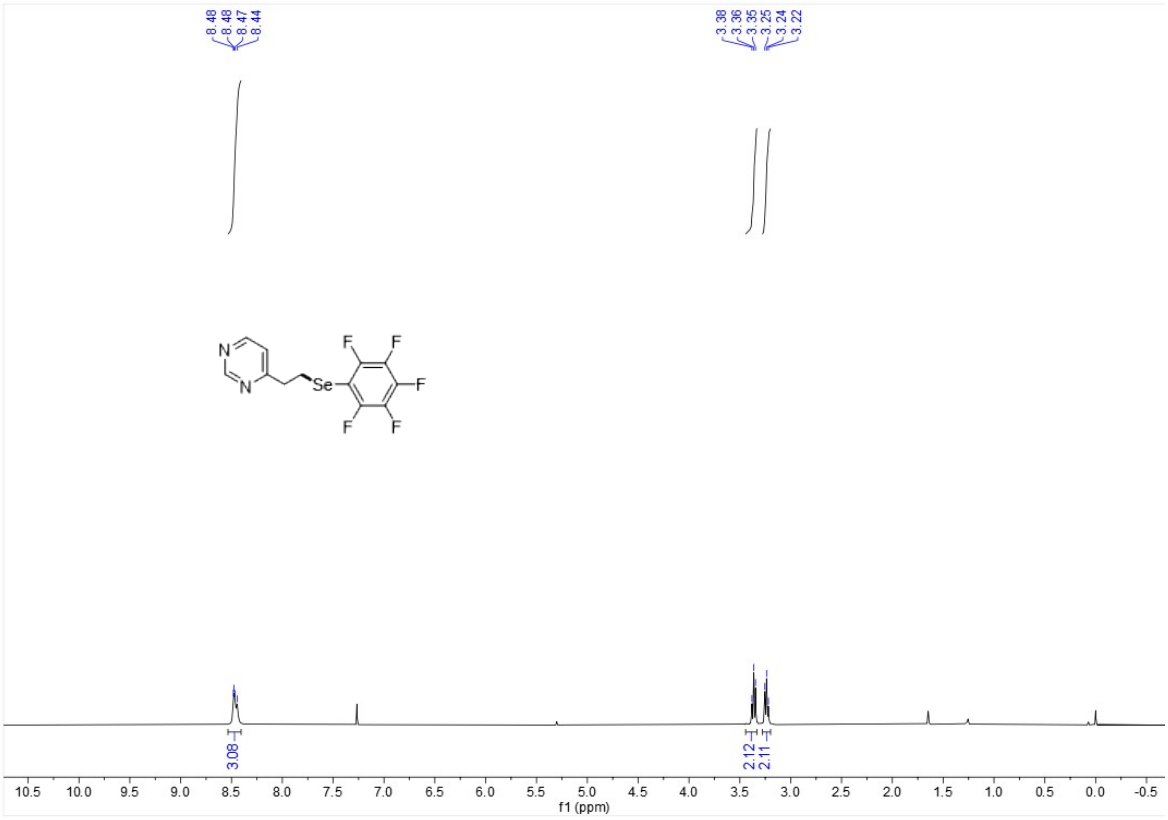
^{19}F NMR spectra of 3m ($CDCl_3$)



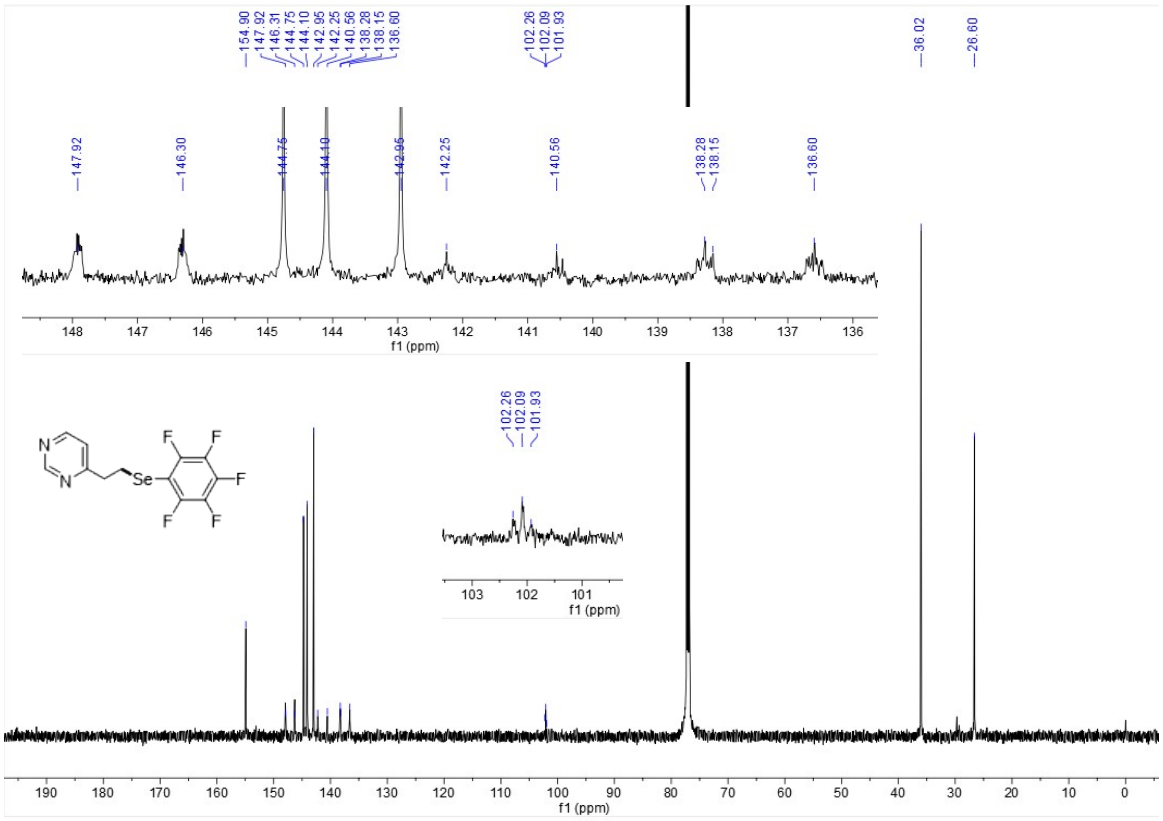
^{77}Se NMR spectra of 3m ($CDCl_3$)



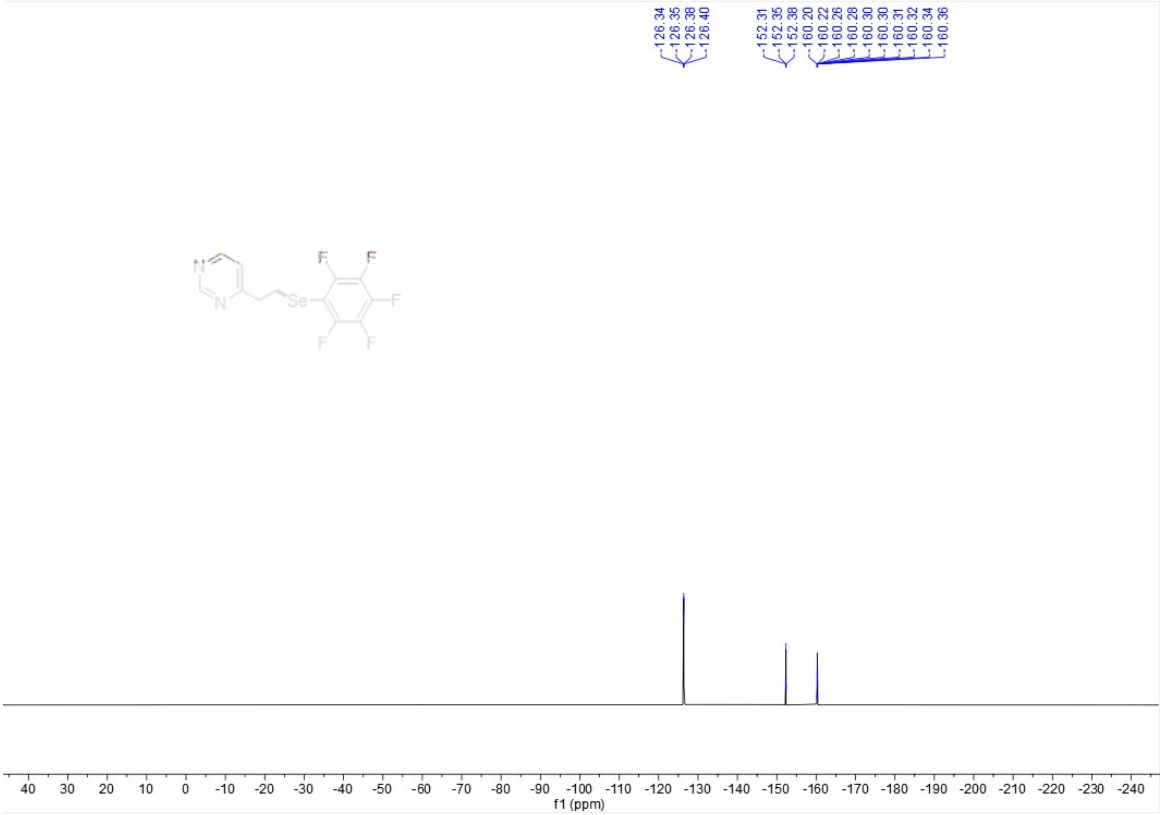
^{1}H NMR spectra of 3n ($CDCl_3$)



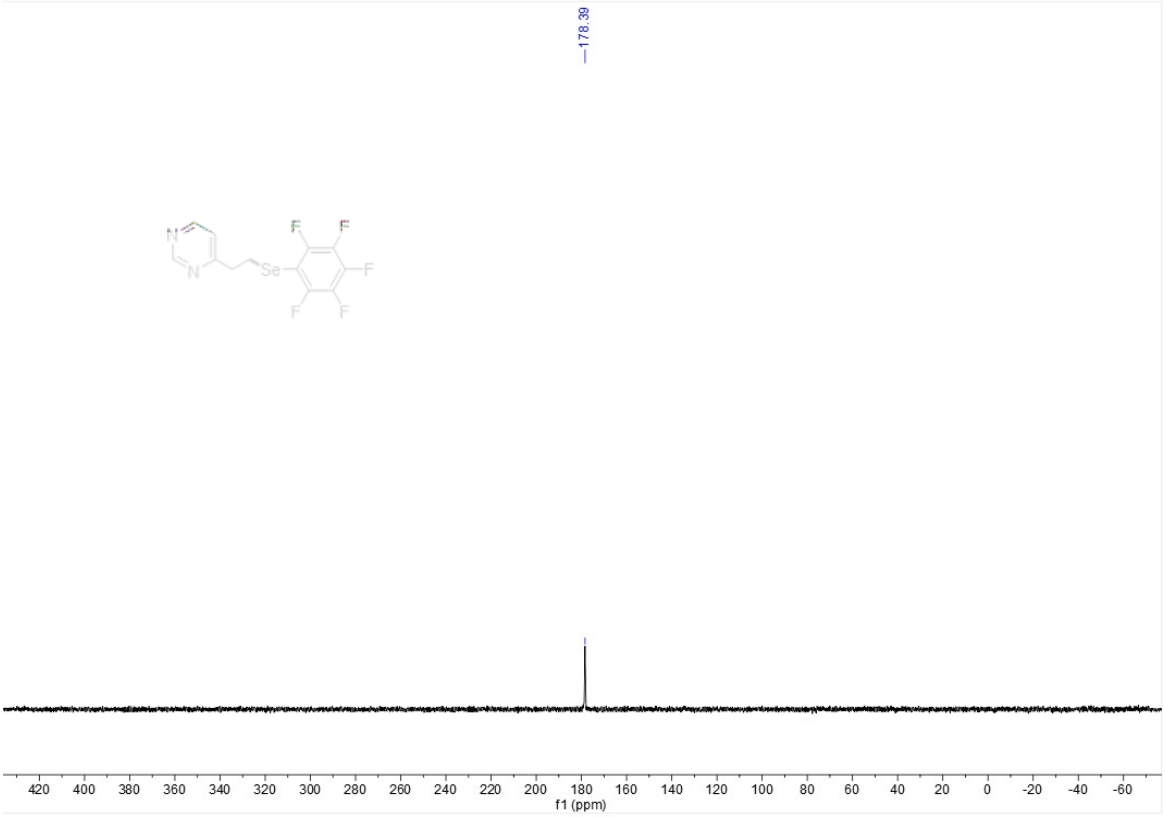
^{13}C NMR spectra of 3n ($CDCl_3$)



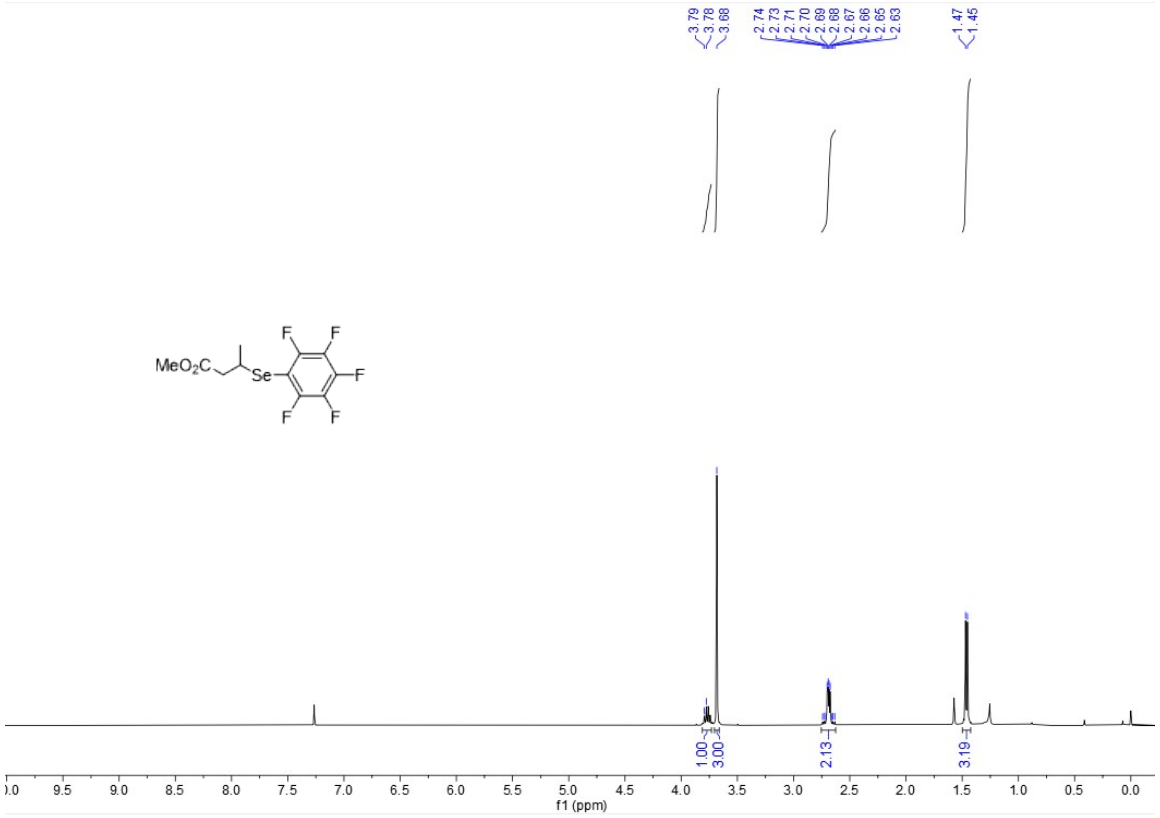
^{19}F NMR spectra of 3n ($CDCl_3$)



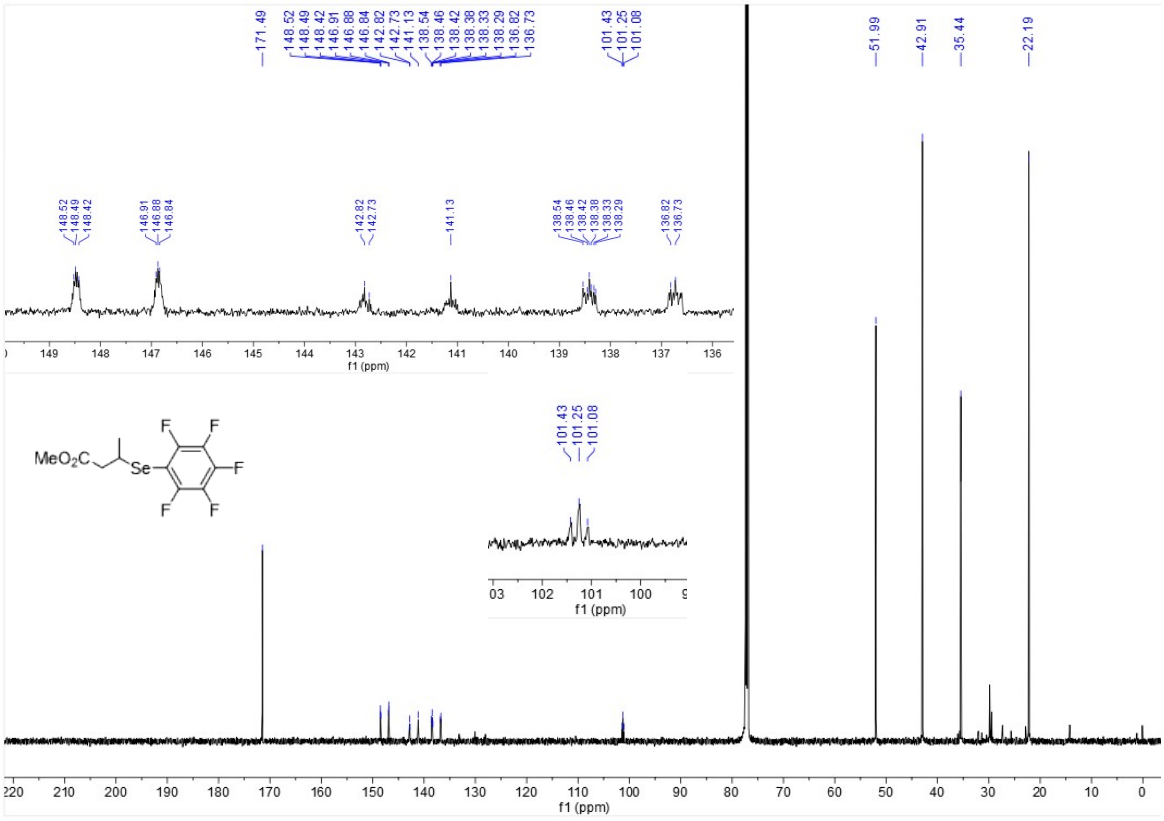
^{77}Se NMR spectra of 3n ($CDCl_3$)



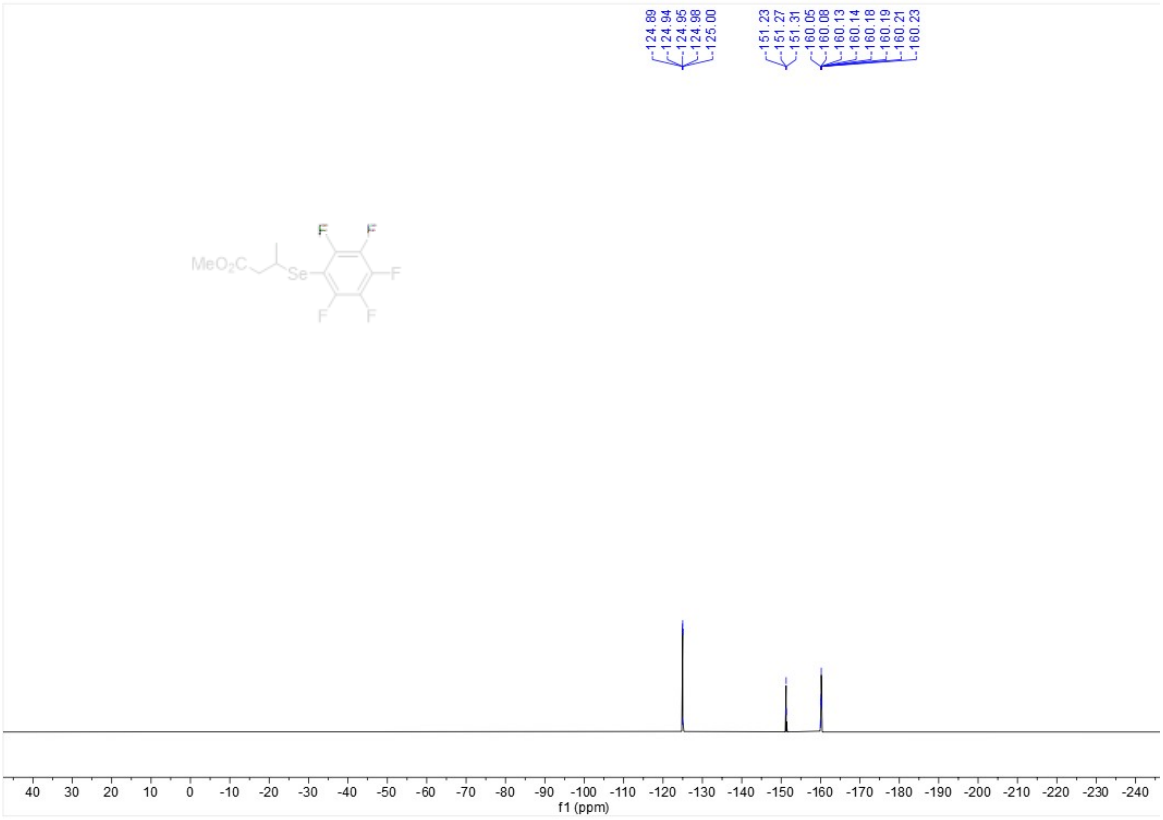
^{1}H NMR spectra of 3o ($CDCl_3$)



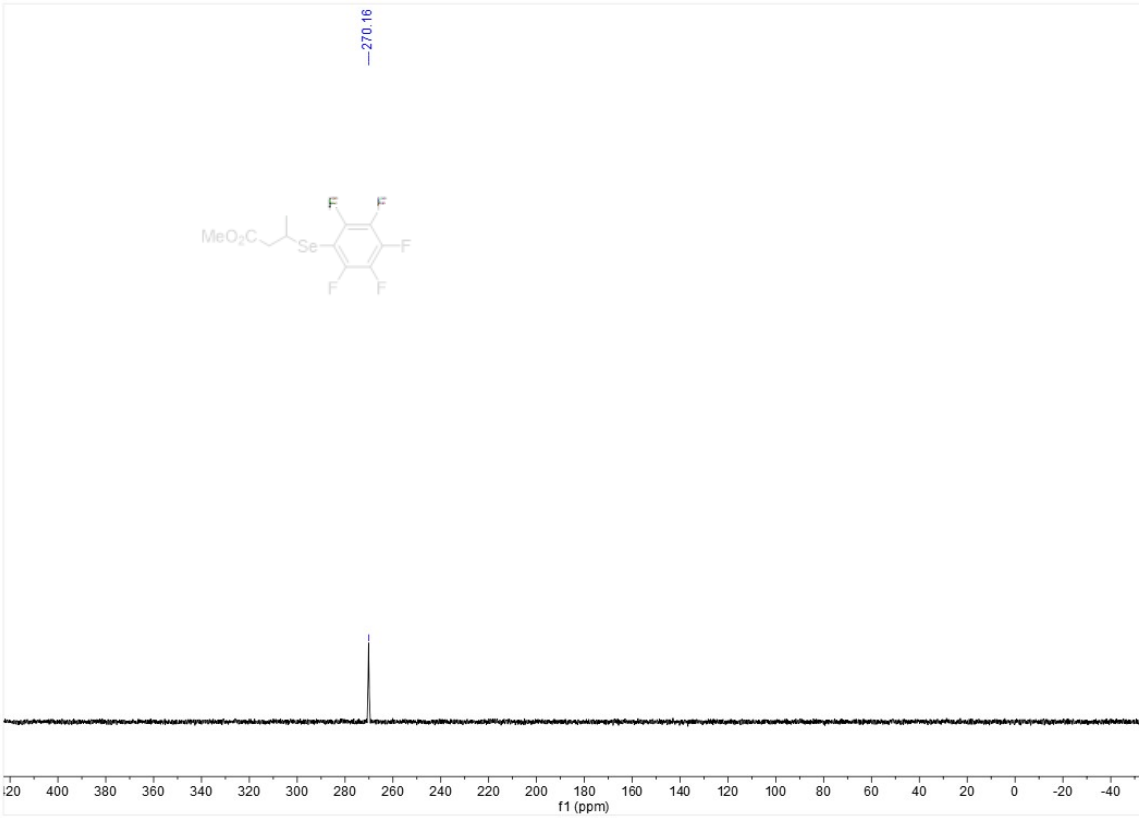
^{13}C NMR spectra of 3o ($CDCl_3$)



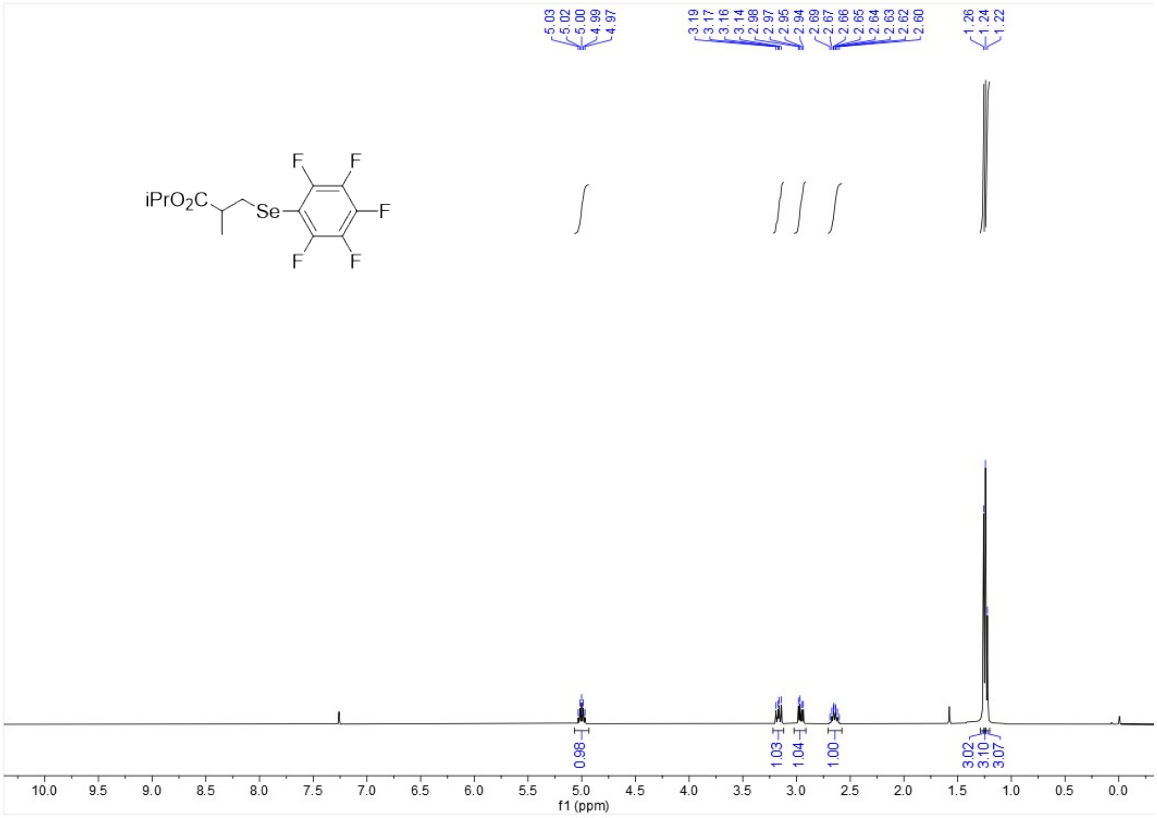
^{19}F NMR spectra of 3o ($CDCl_3$)



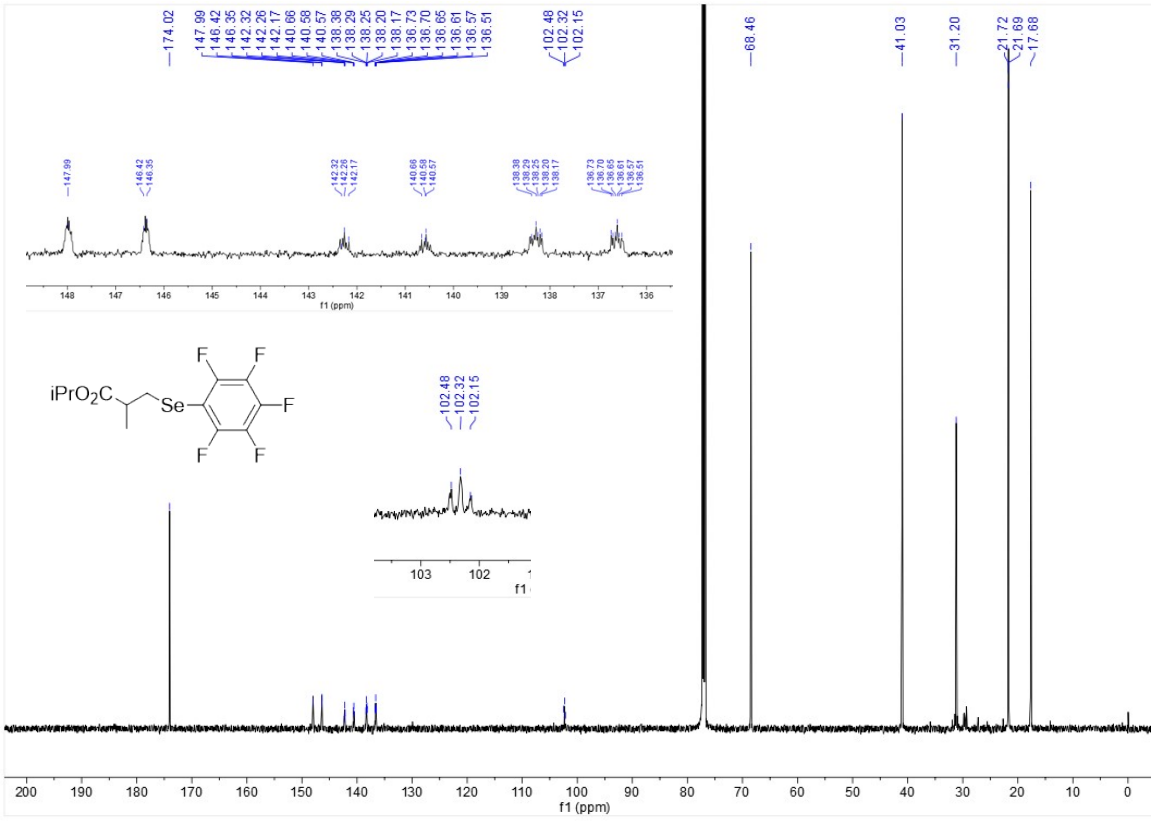
^{77}Se NMR spectra of 3o ($CDCl_3$)



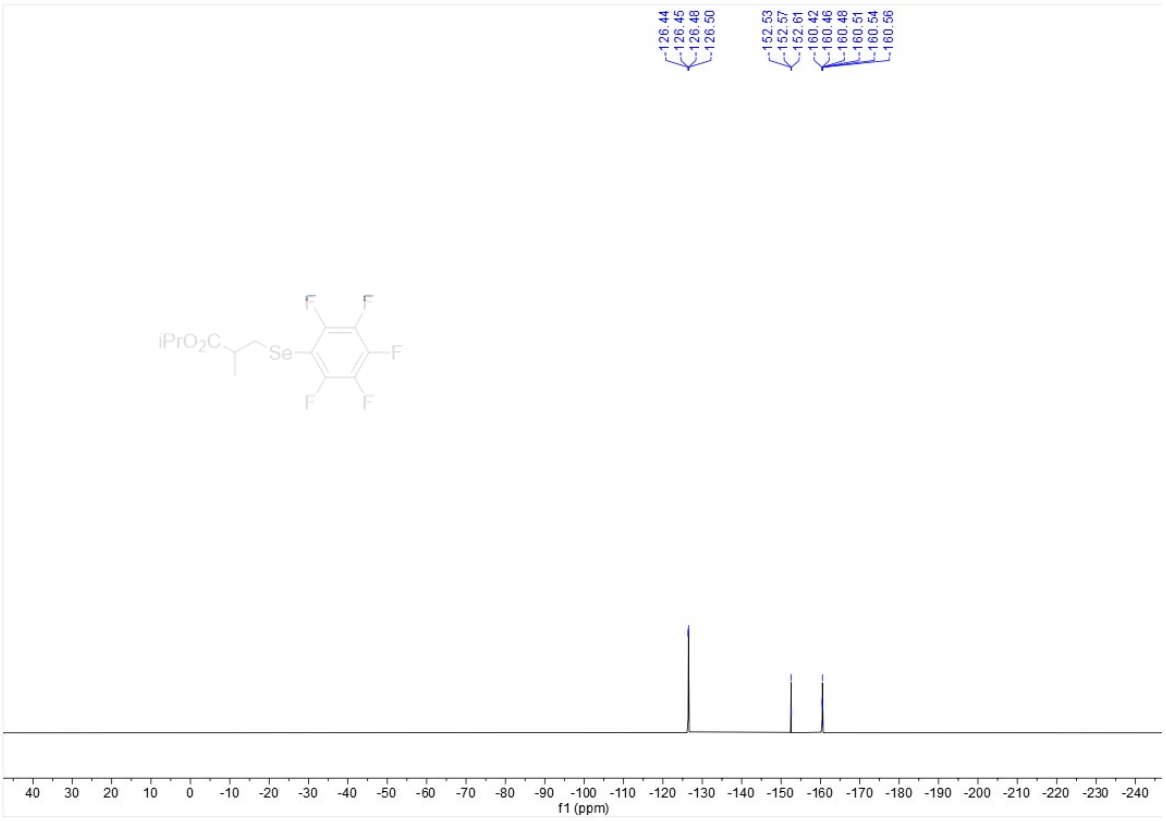
^{1}H NMR spectra of 3p ($CDCl_3$)



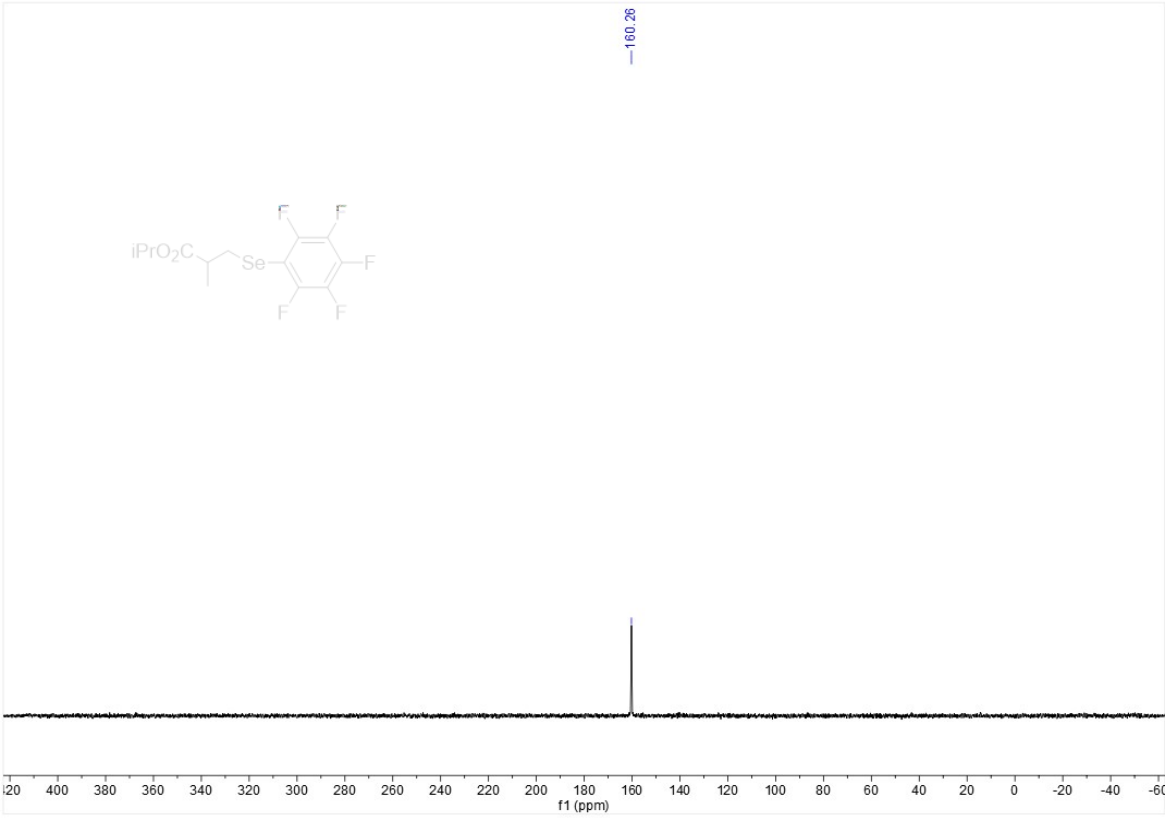
^{13}C NMR spectra of 3p ($CDCl_3$)



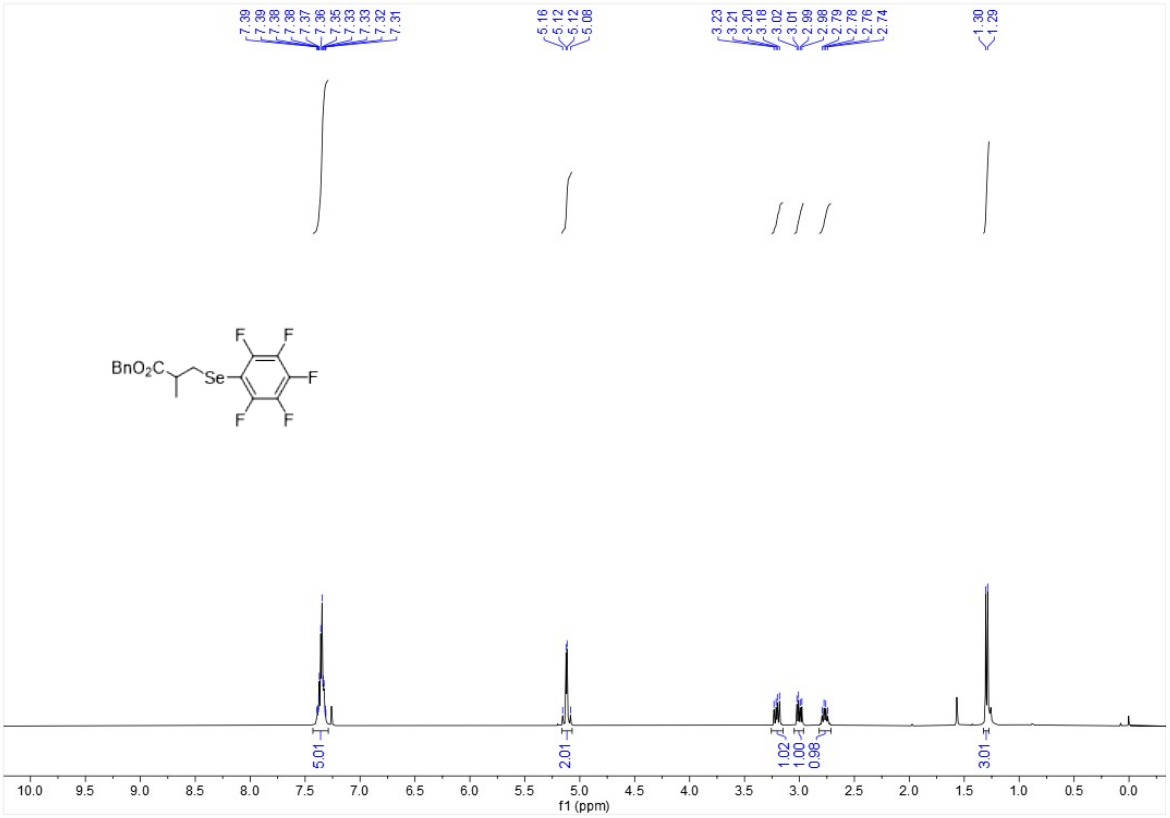
^{19}F NMR spectra of 3p ($CDCl_3$)



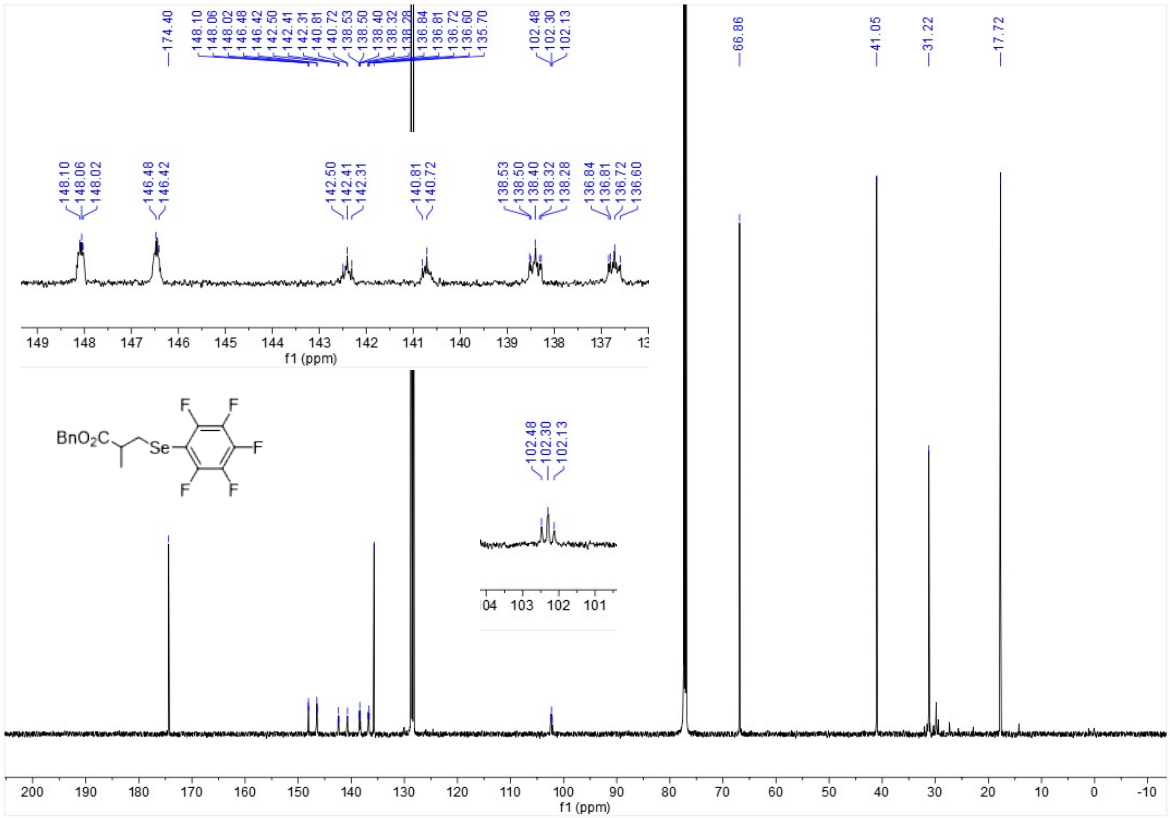
^{77}Se NMR spectra of 3p ($CDCl_3$)



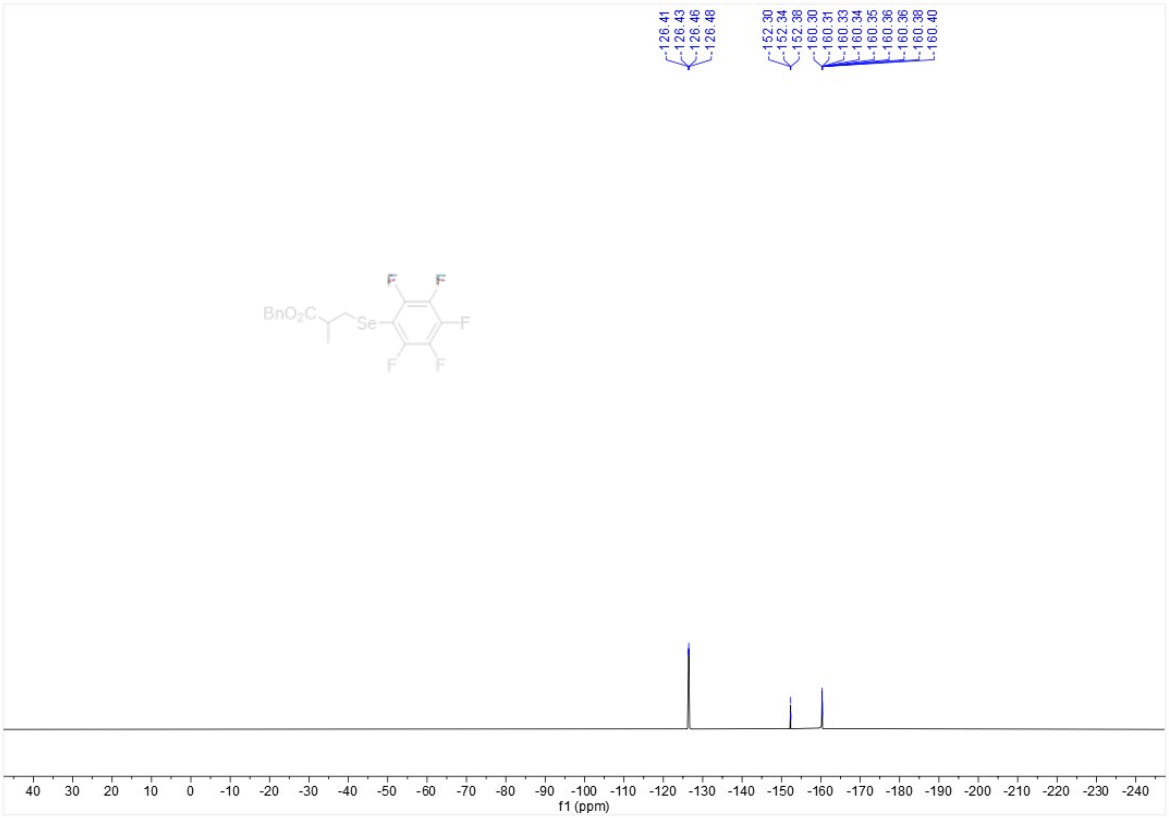
^{1}H NMR spectra of 3q ($CDCl_3$)



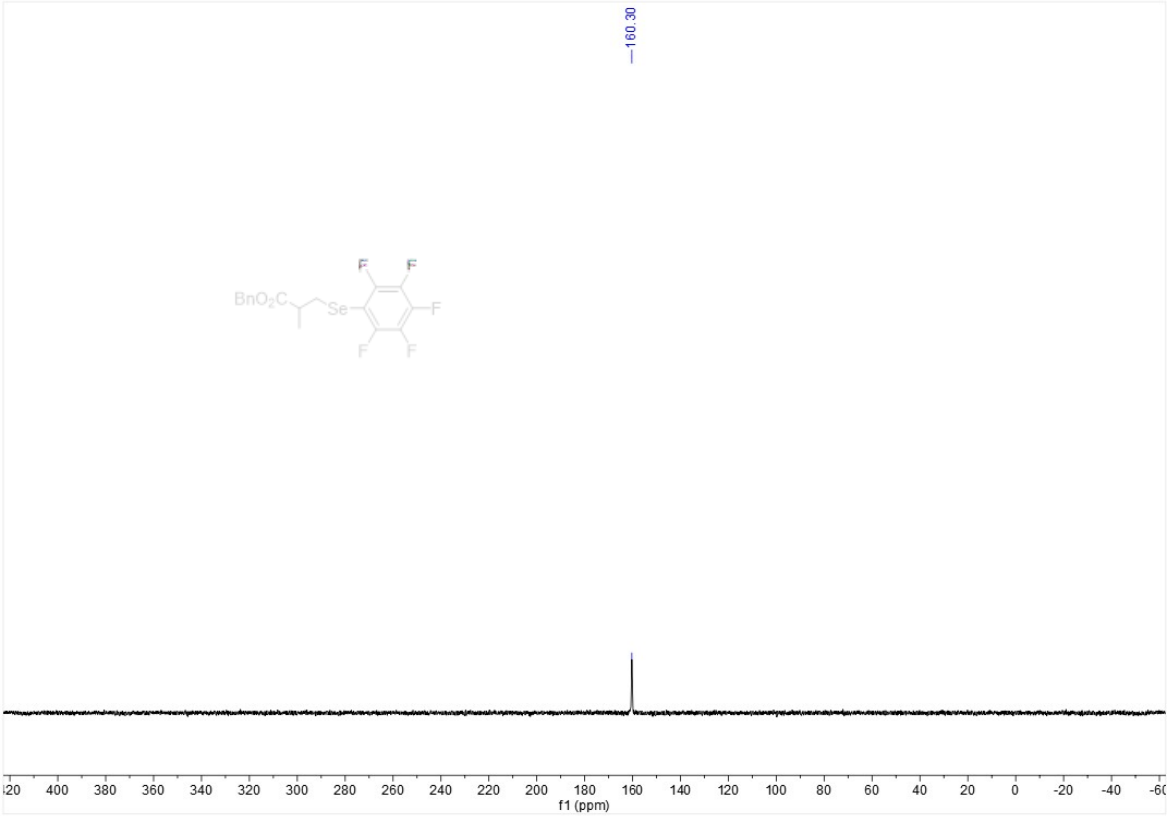
^{13}C NMR spectra of 3q ($CDCl_3$)



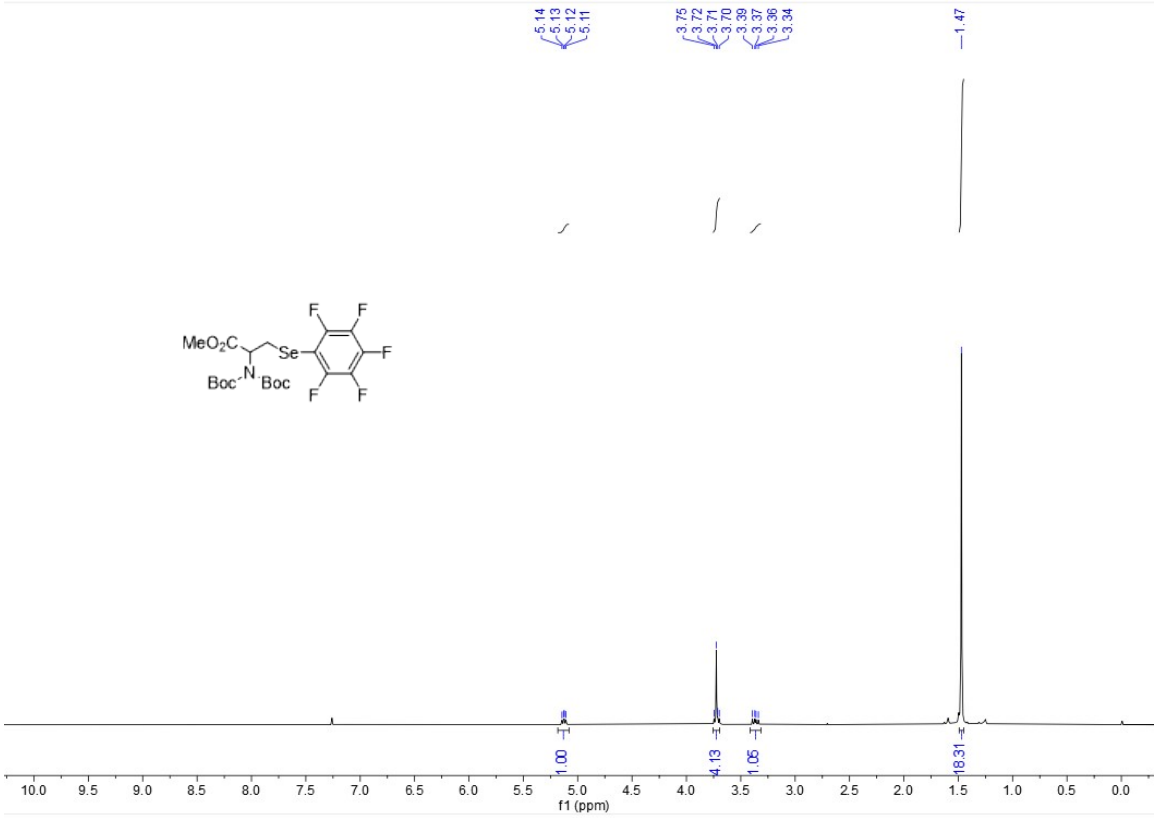
^{19}F NMR spectra of 3q ($CDCl_3$)



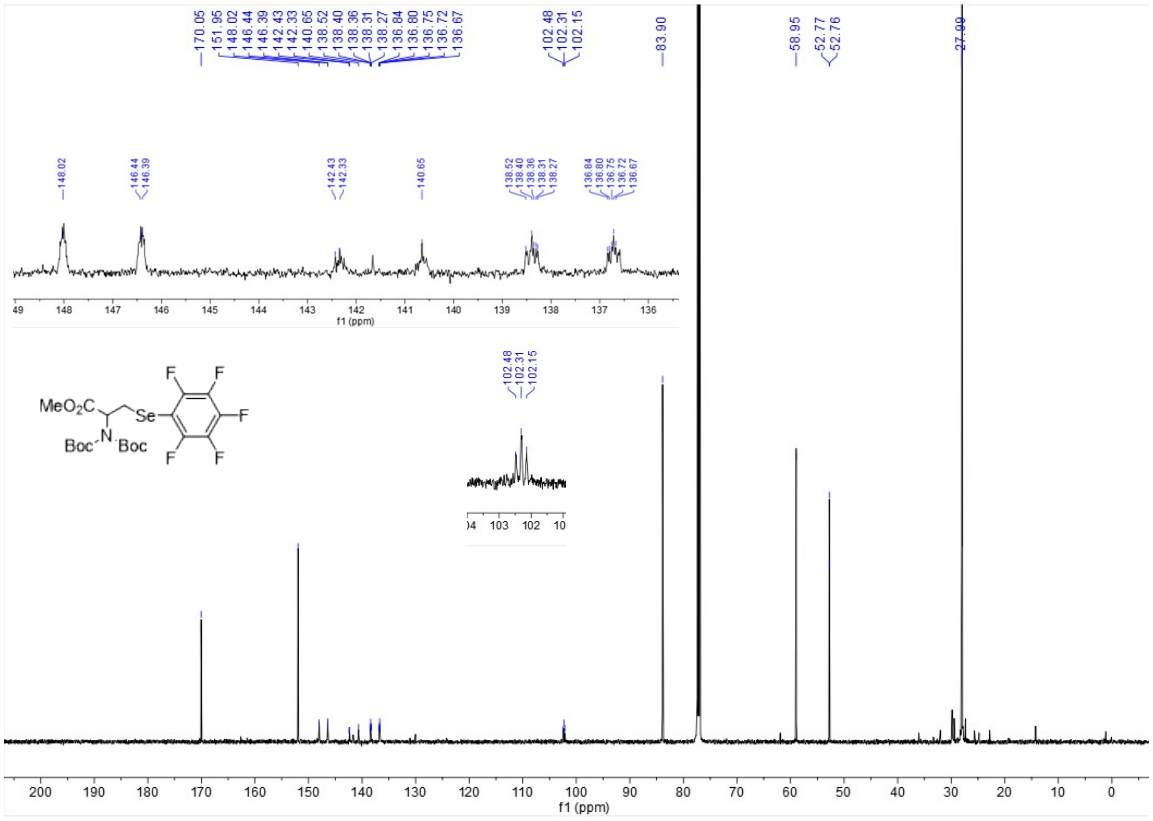
^{77}Se NMR spectra of 3q ($CDCl_3$)



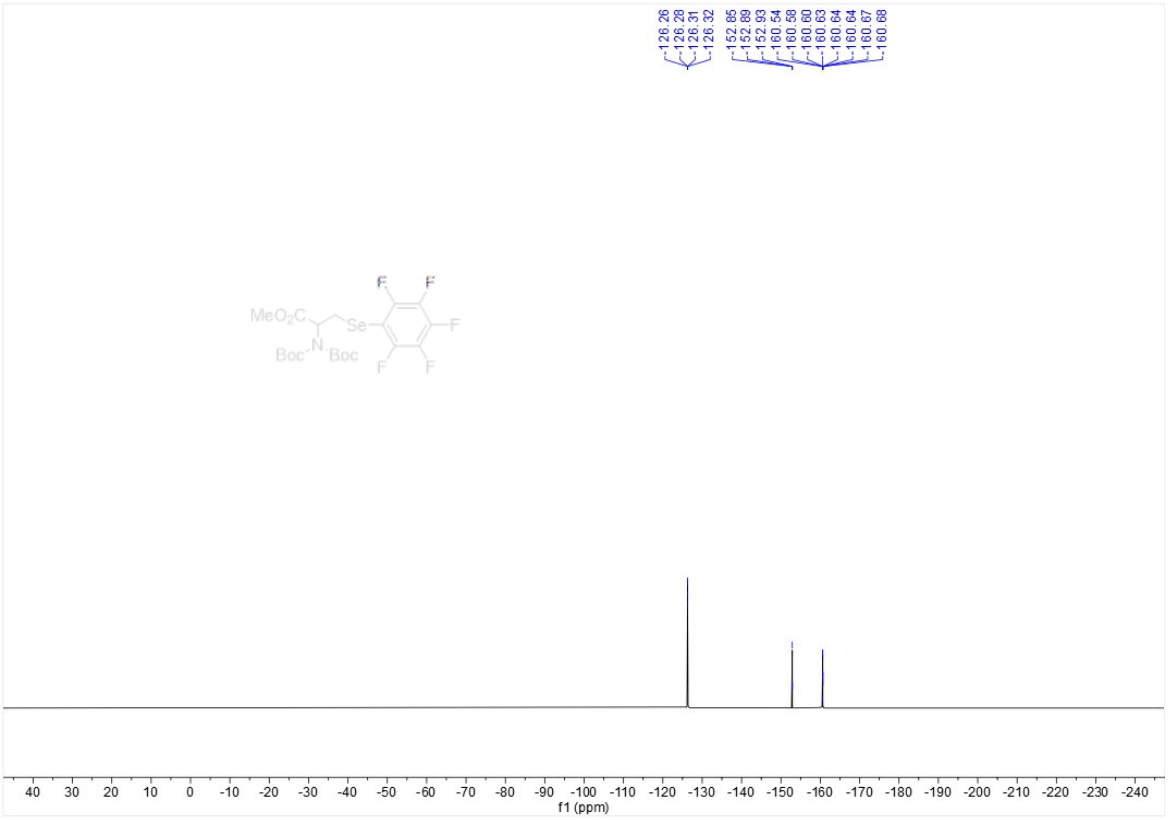
^{1}H NMR spectra of 3r ($CDCl_3$)



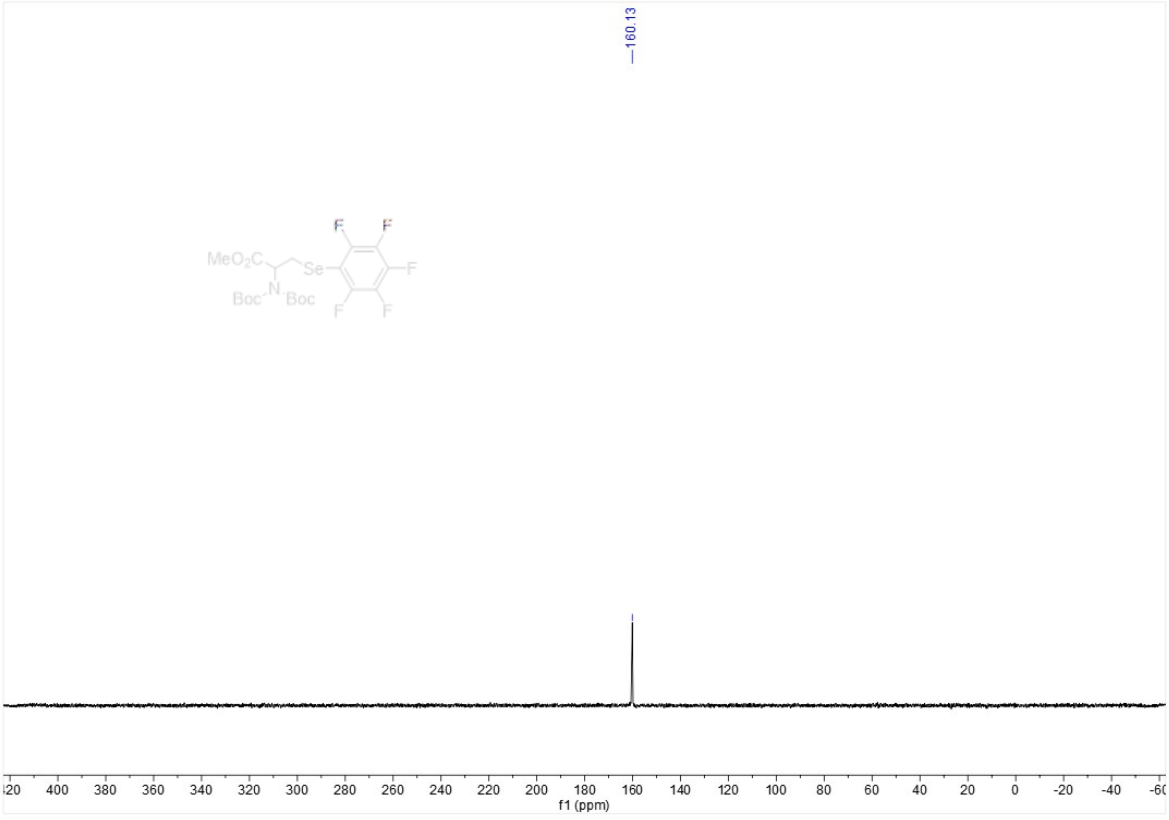
^{13}C NMR spectra of 3r ($CDCl_3$)



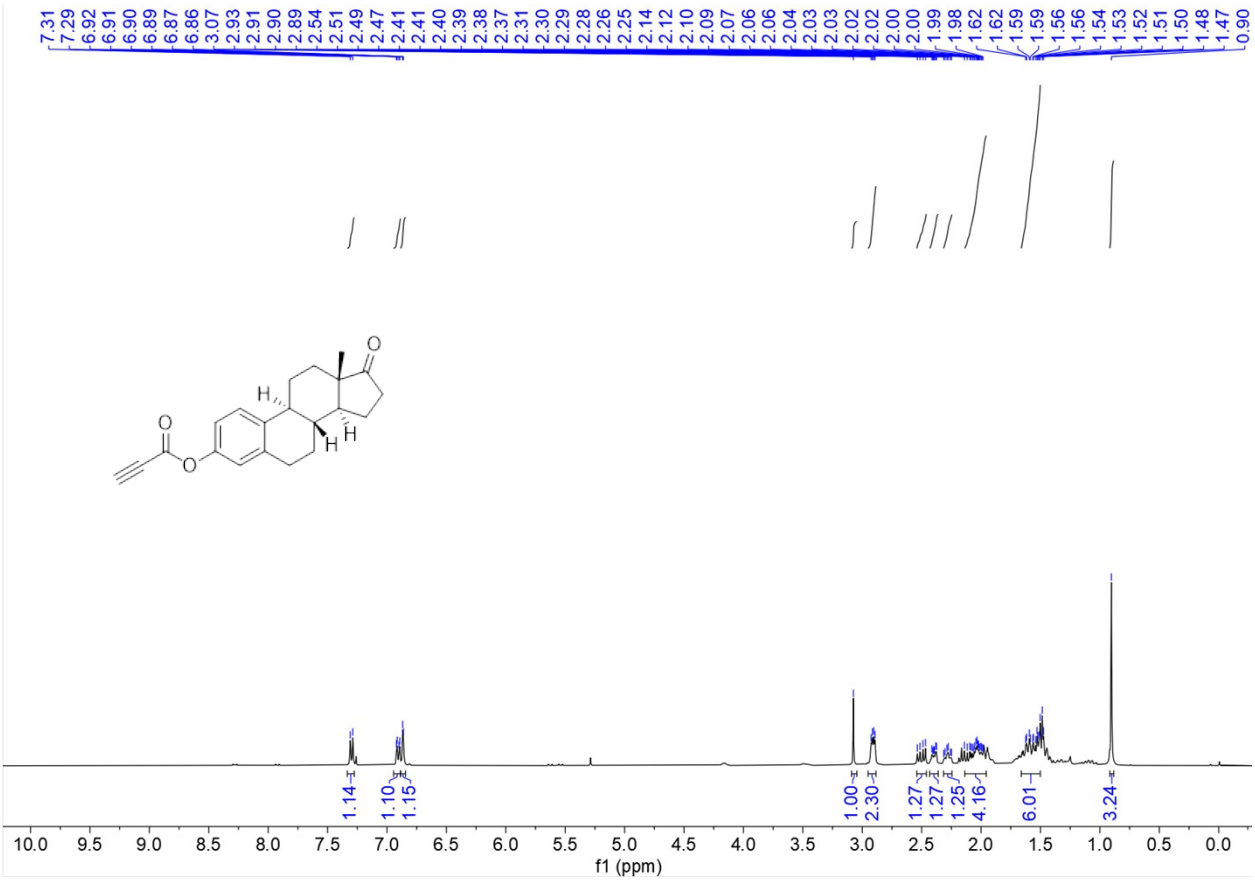
^{19}F NMR spectra of 3r ($CDCl_3$)



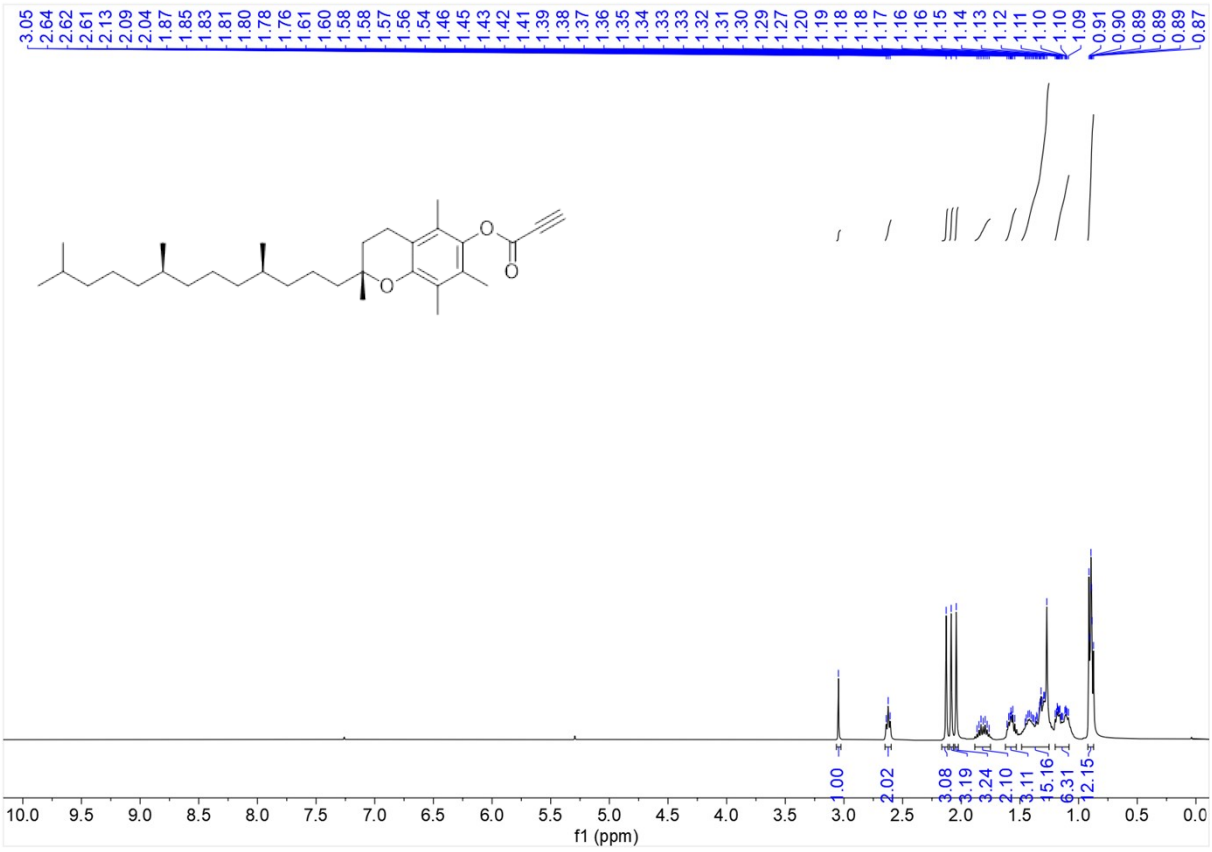
^{77}Se NMR spectra of 3r ($CDCl_3$)



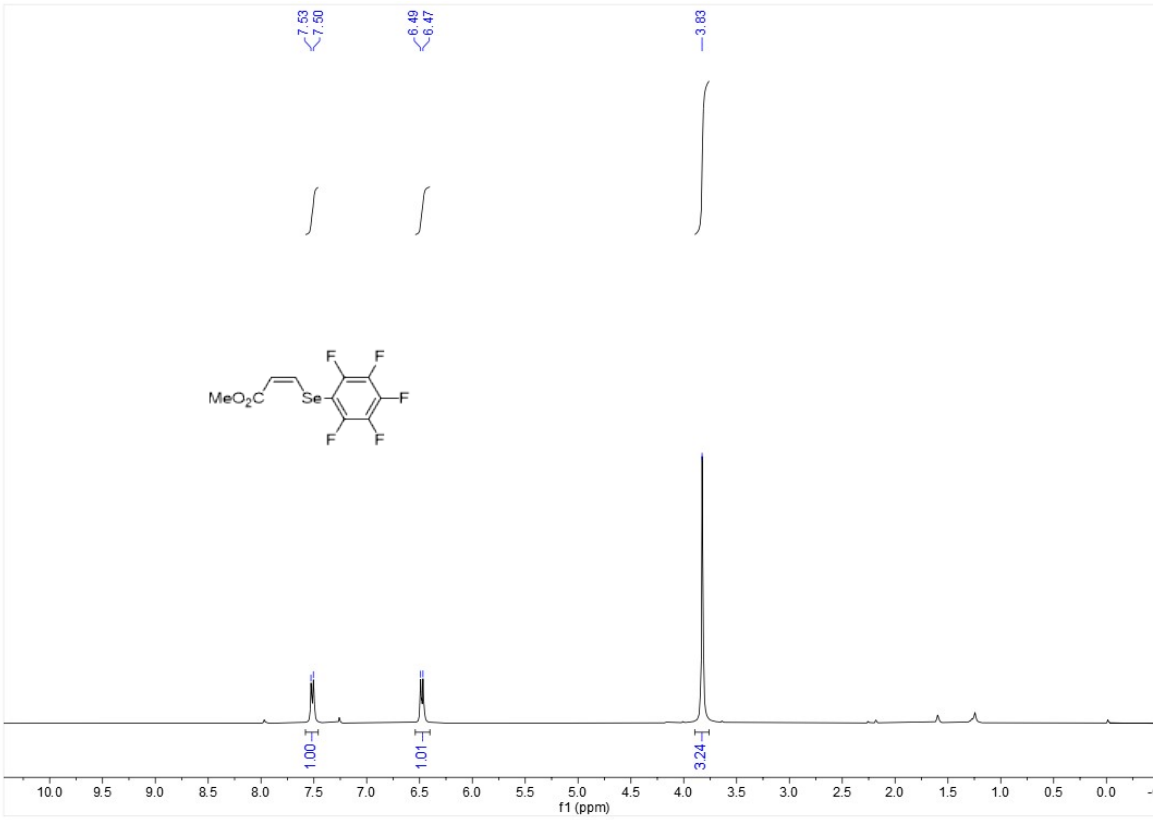
^{1}H NMR spectra of 4g ($CDCl_3$)



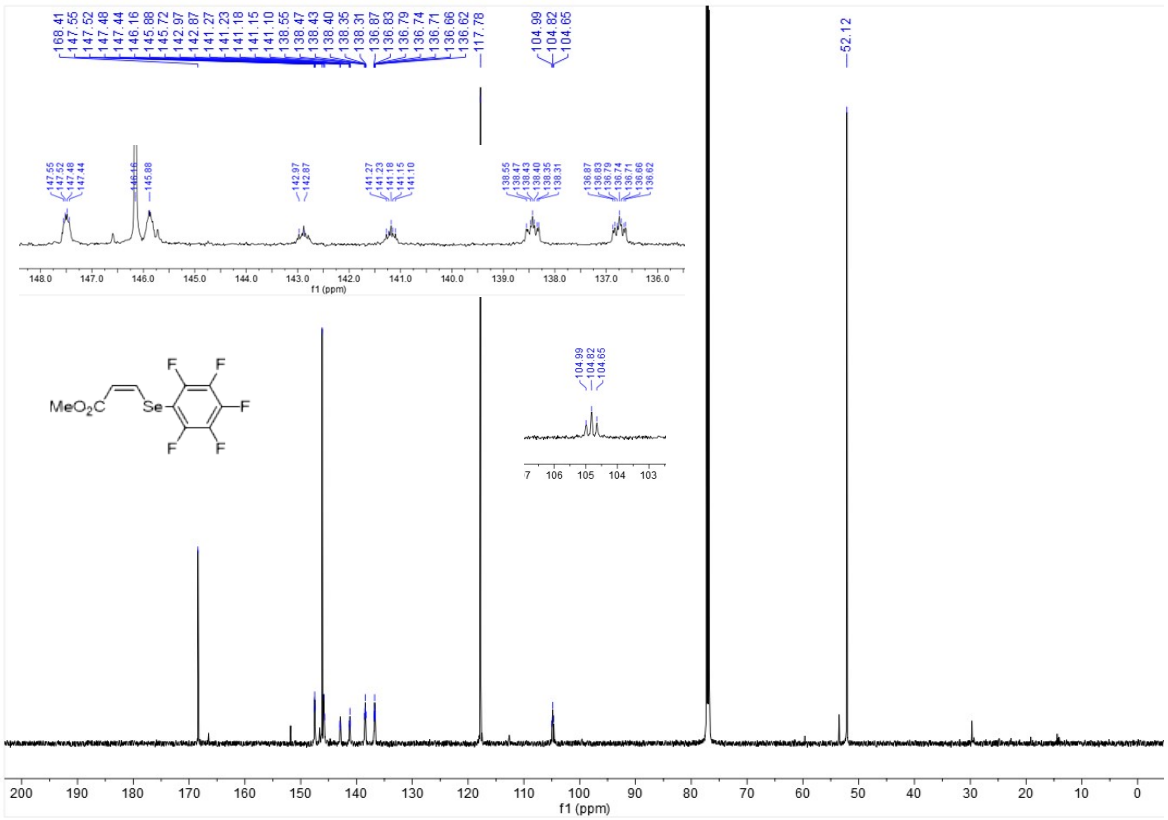
^{1}H NMR spectra of 4h ($CDCl_3$)



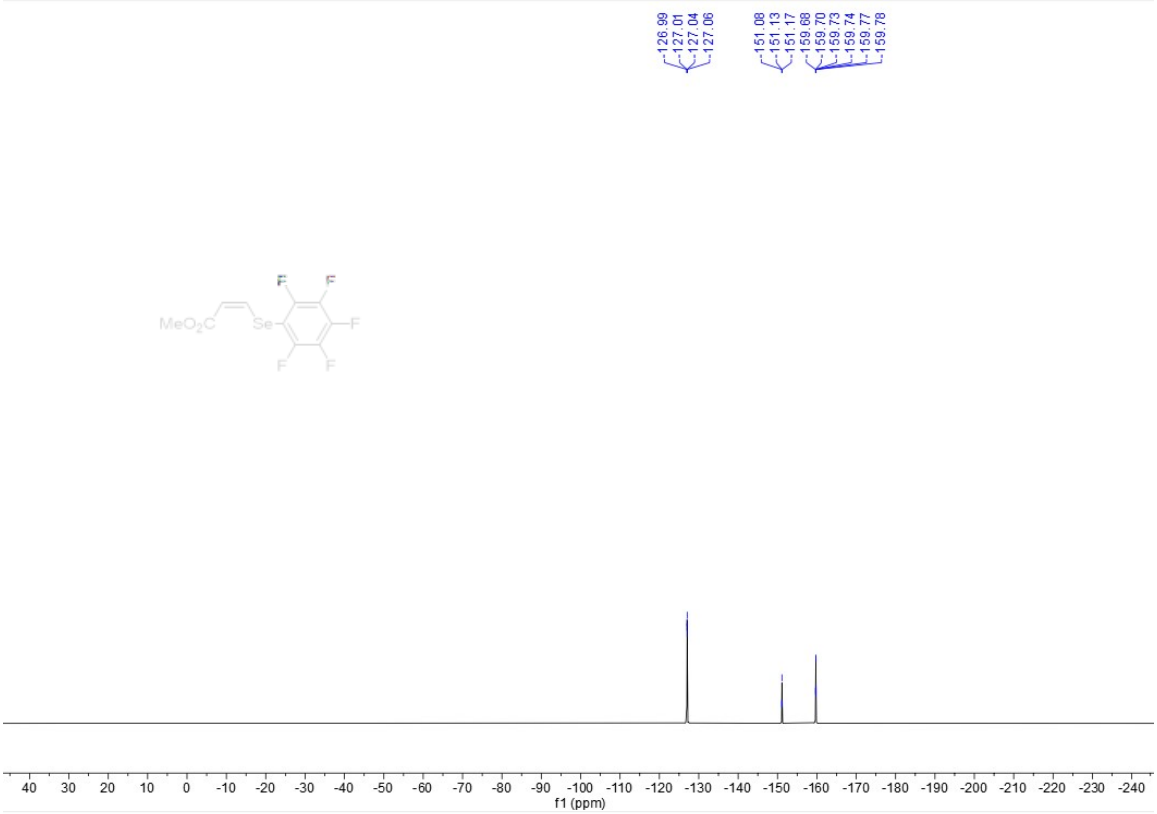
^{1}H NMR spectra of 5a ($CDCl_3$)



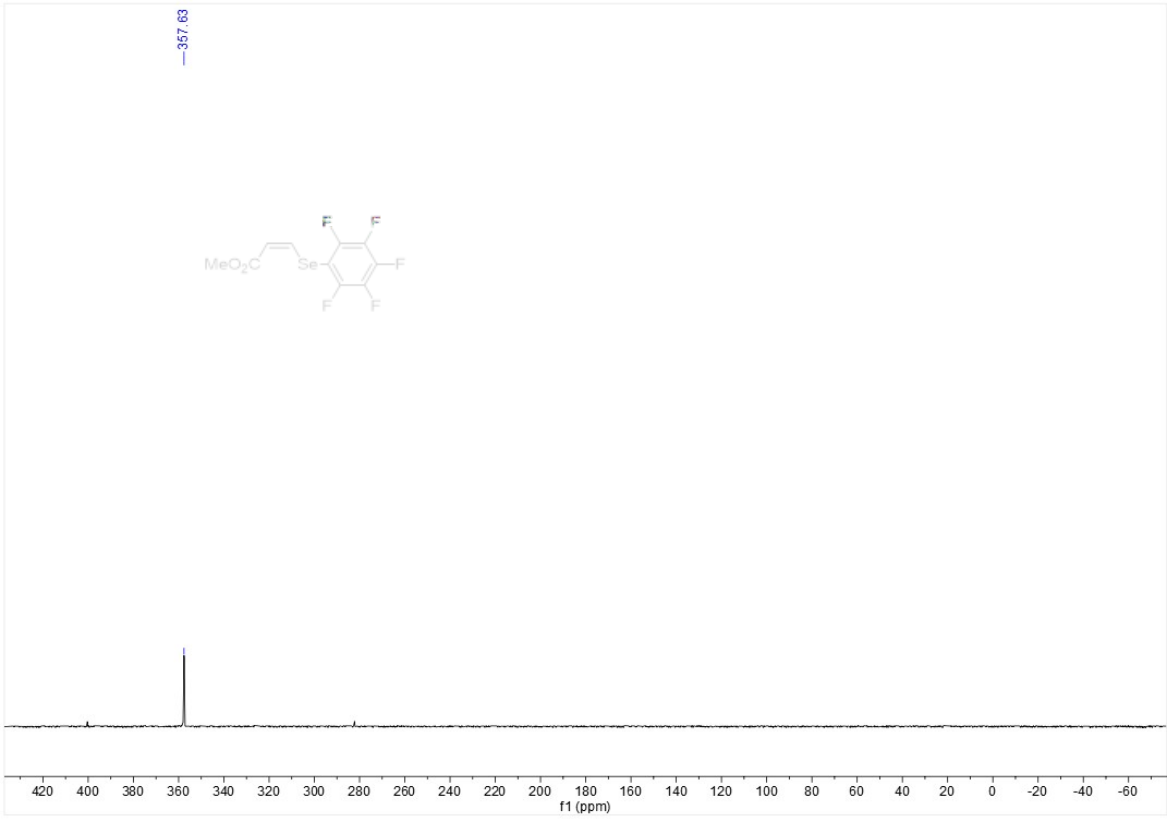
^{13}C NMR spectra of 5a ($CDCl_3$)



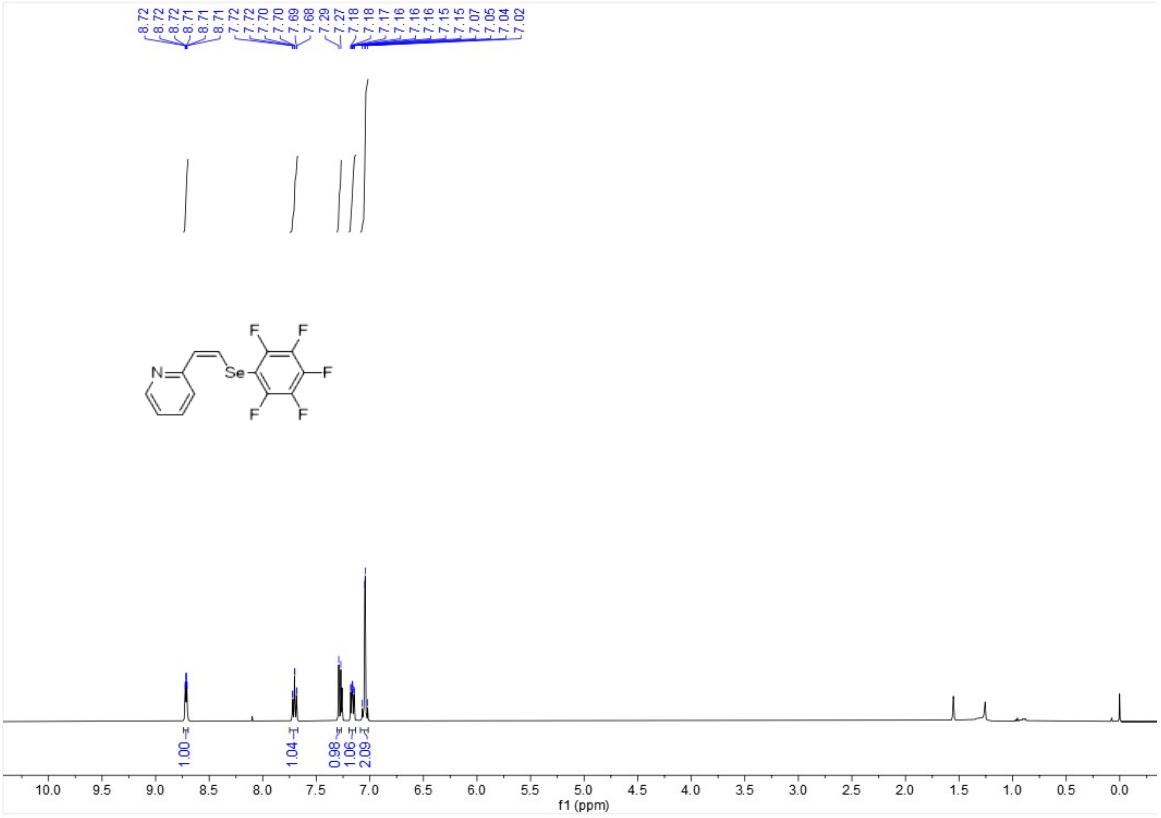
^{19}F NMR spectra of 5a ($CDCl_3$)



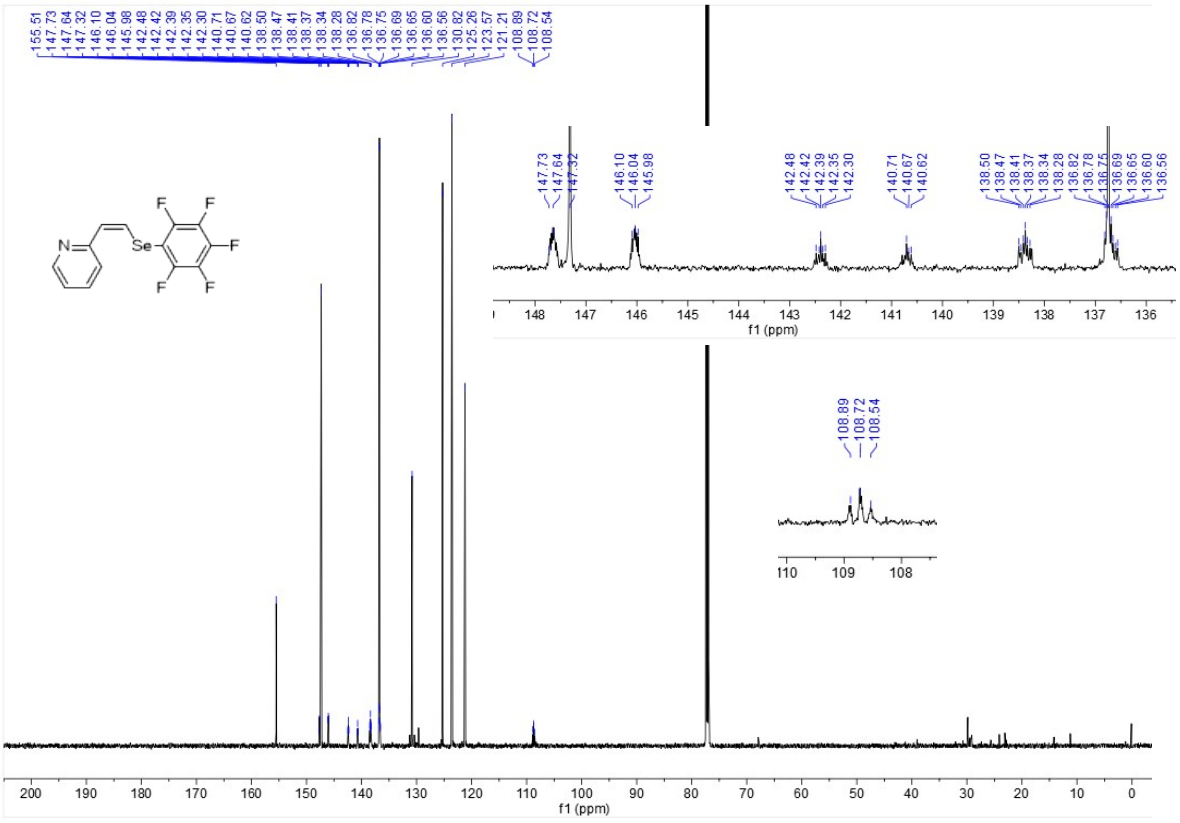
^{77}Se NMR spectra of 5a ($CDCl_3$)



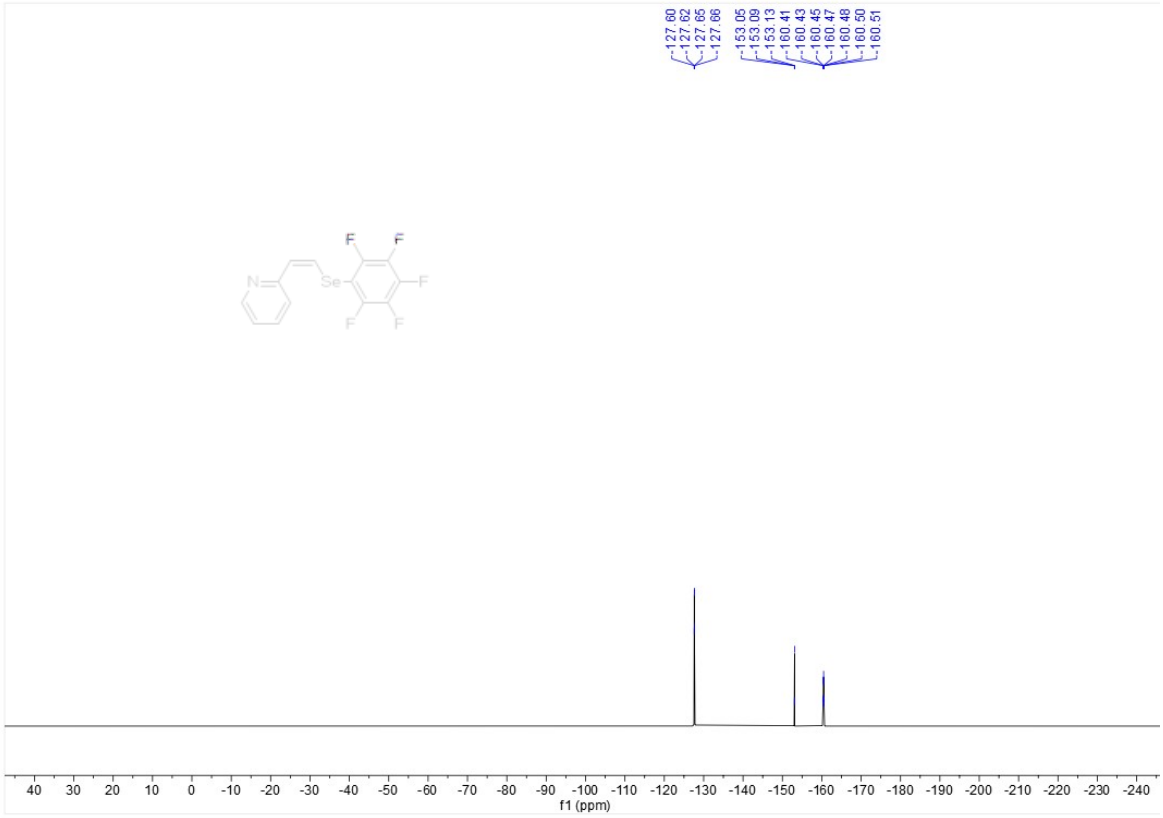
^{1}H NMR spectra of 5b ($CDCl_3$)



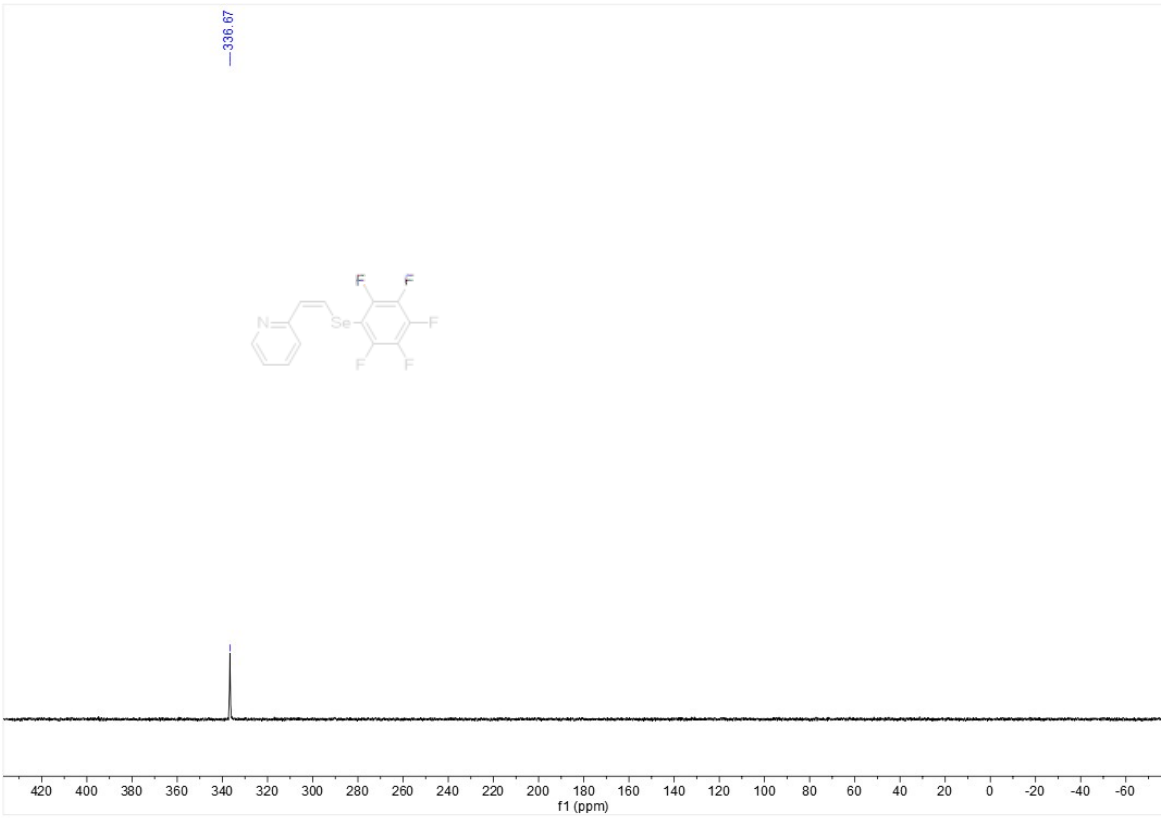
^{13}C NMR spectra of 5b ($CDCl_3$)



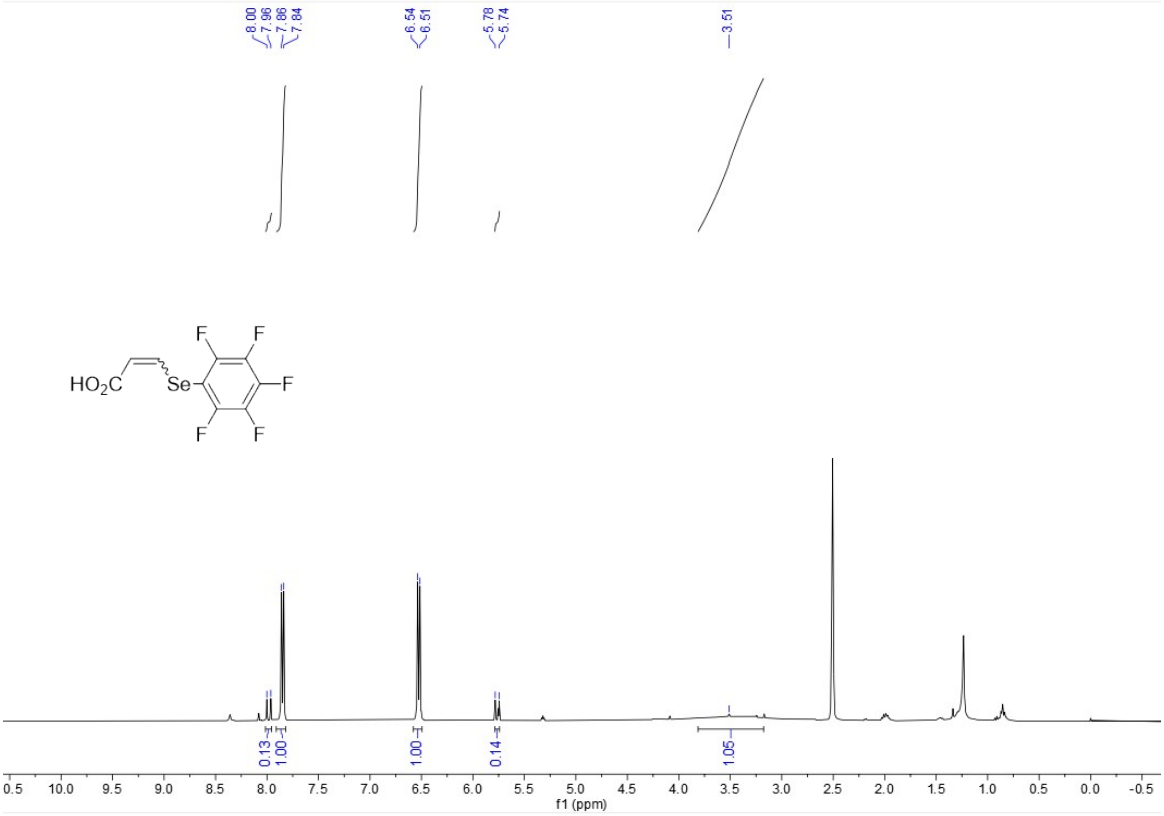
^{19}F NMR spectra of 5b ($CDCl_3$)



^{77}Se NMR spectra of 5b ($CDCl_3$)



^{1}H NMR spectra of 5c (DMSO-d_6)



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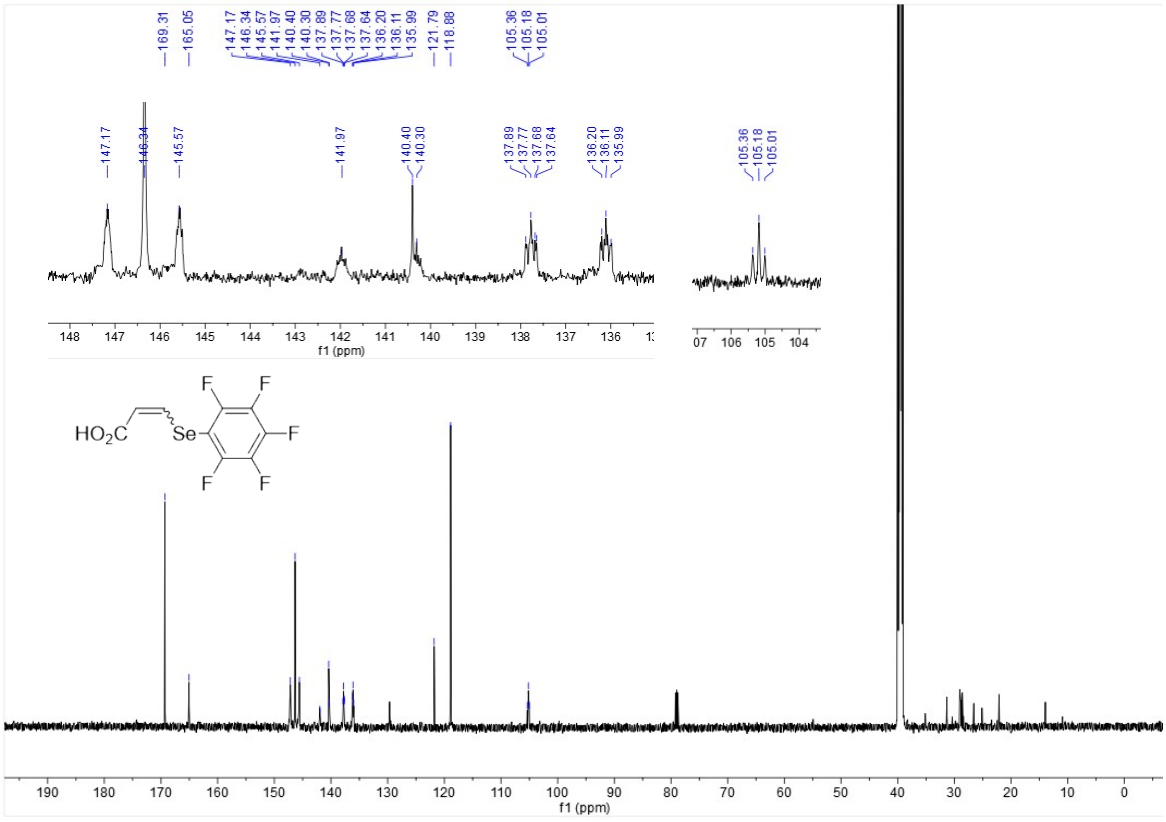
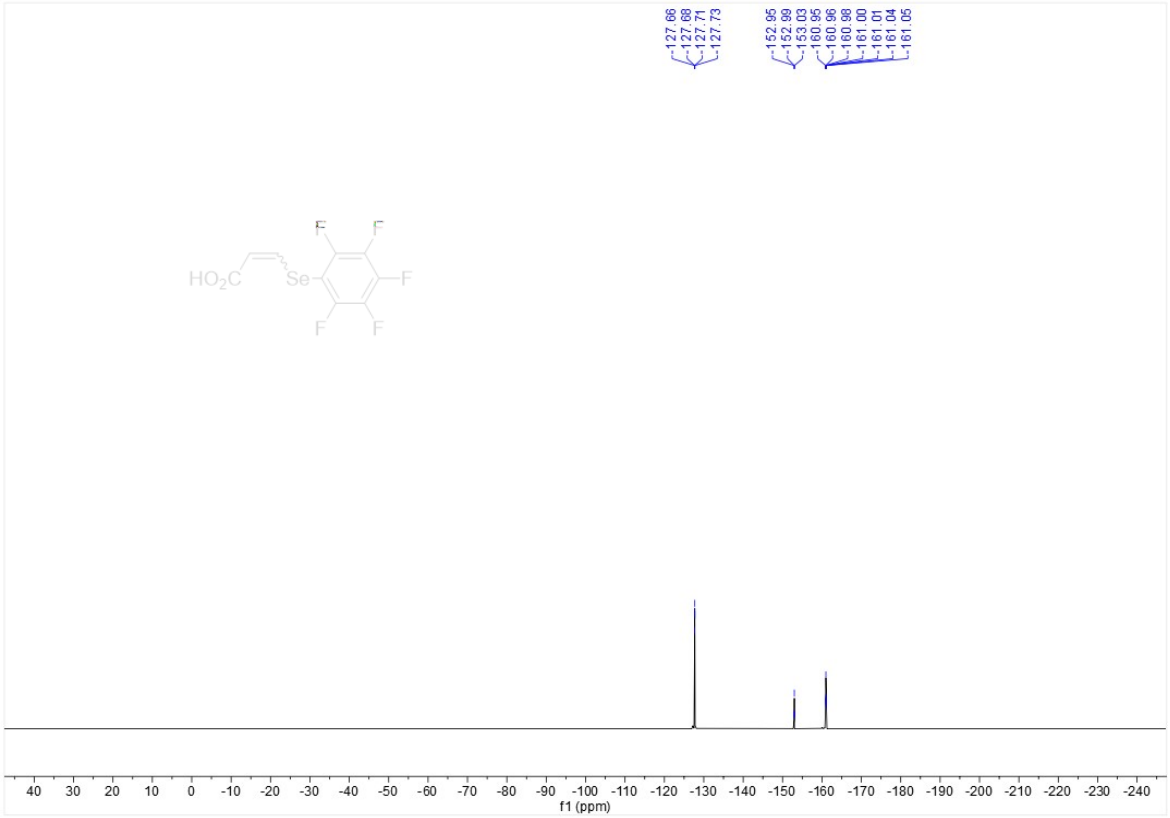
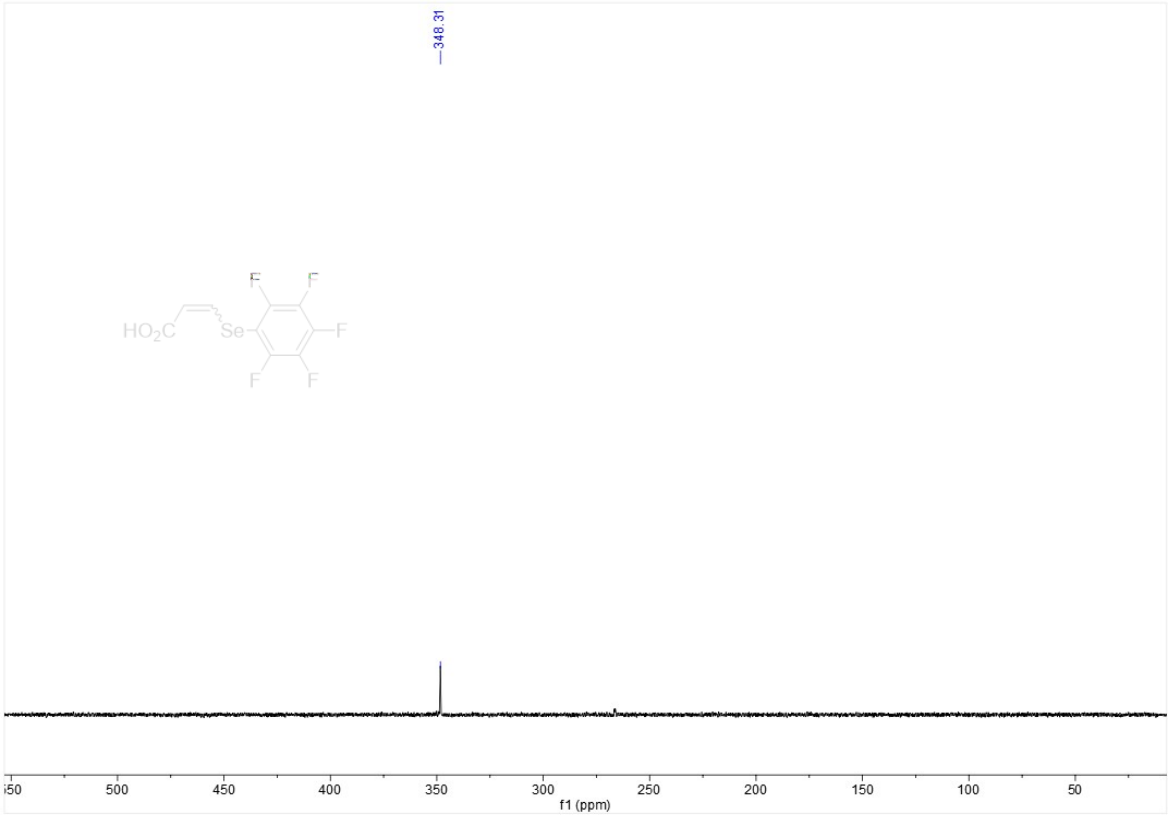


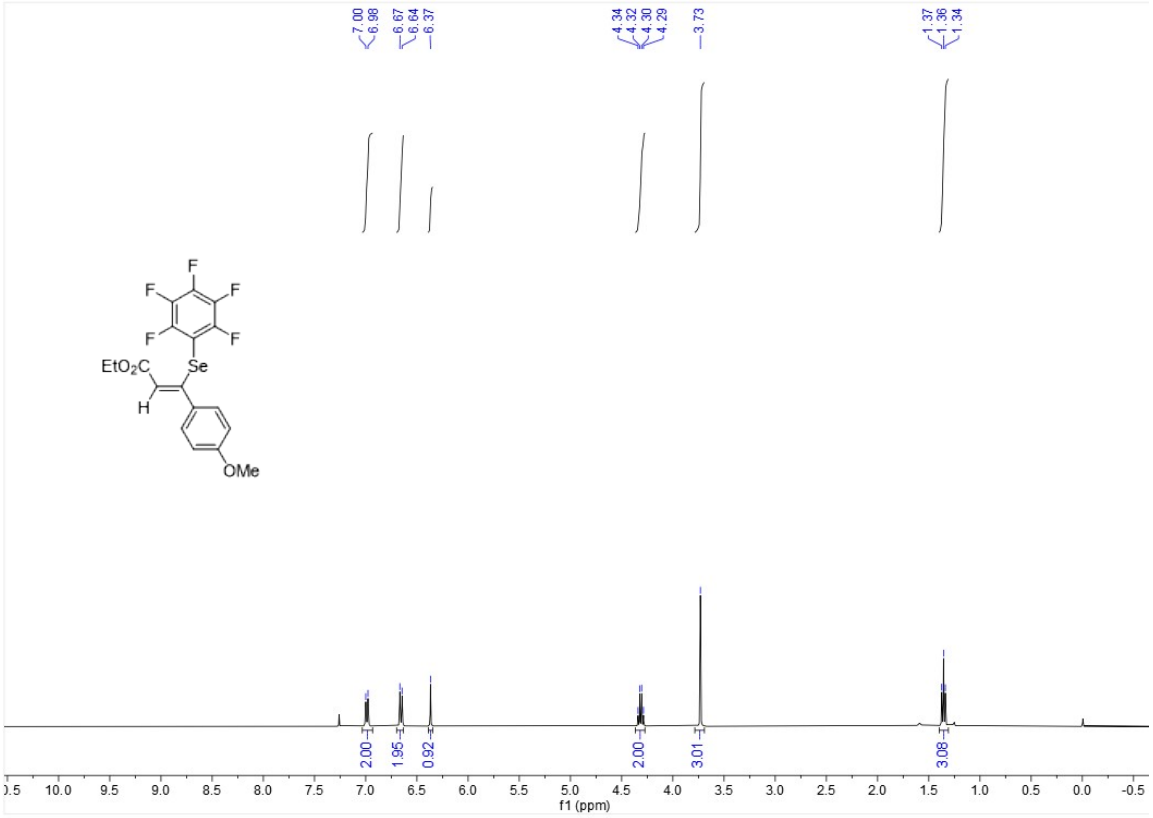
^{19}F NMR spectra of 5c (DMSO-d_6)



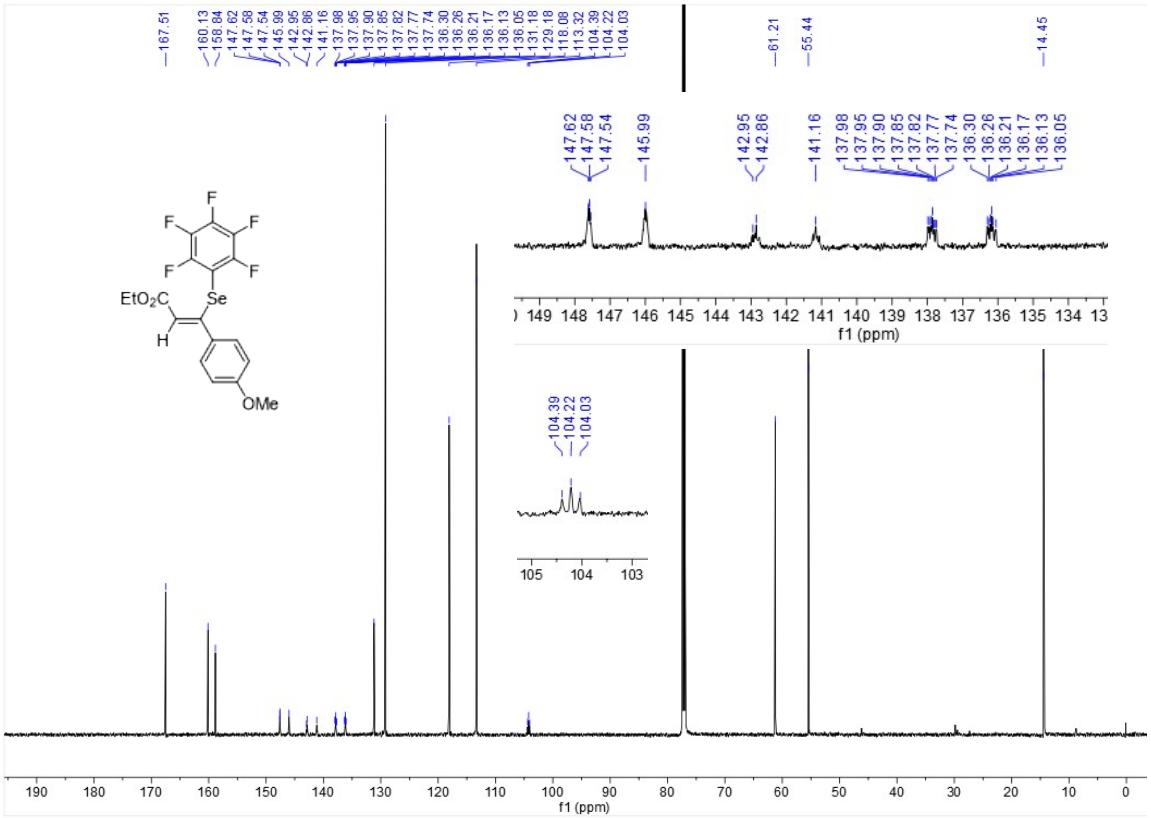
^{77}Se NMR spectra of 5b (DMSO-d_6)



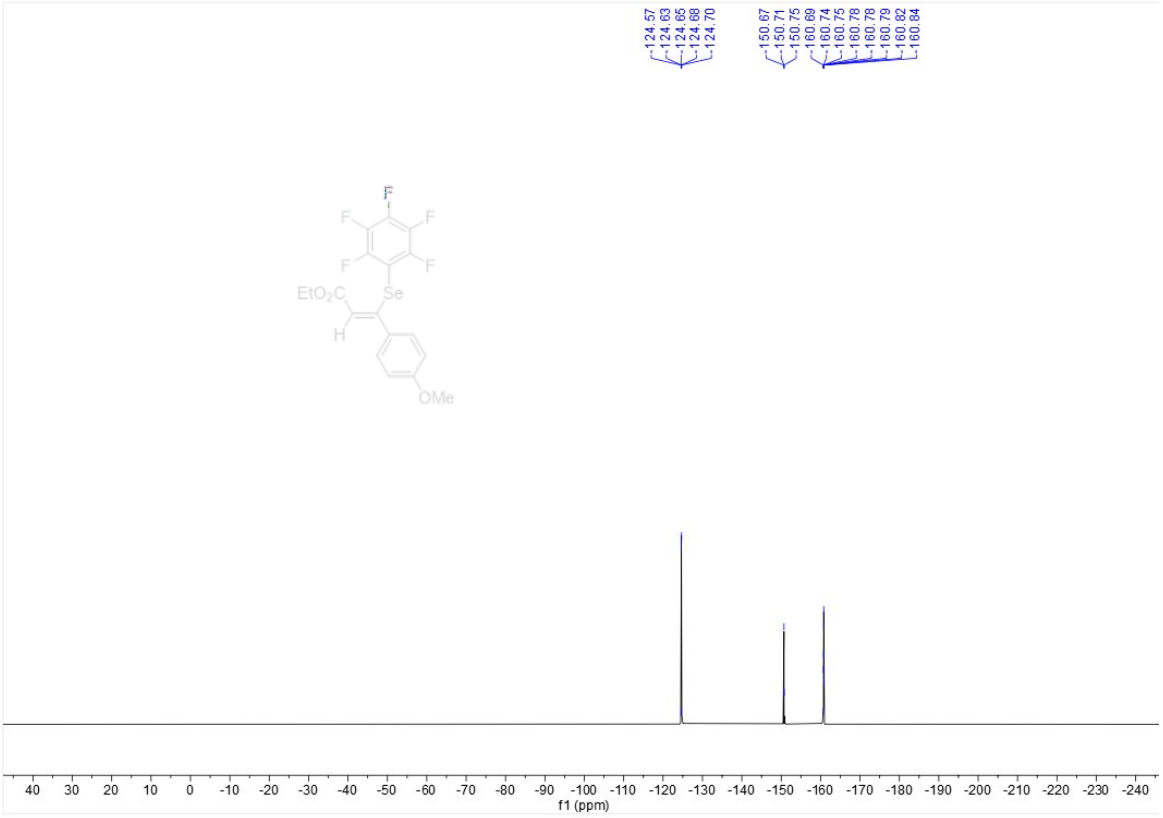
^{1}H NMR spectra of 5d ($CDCl_3$)



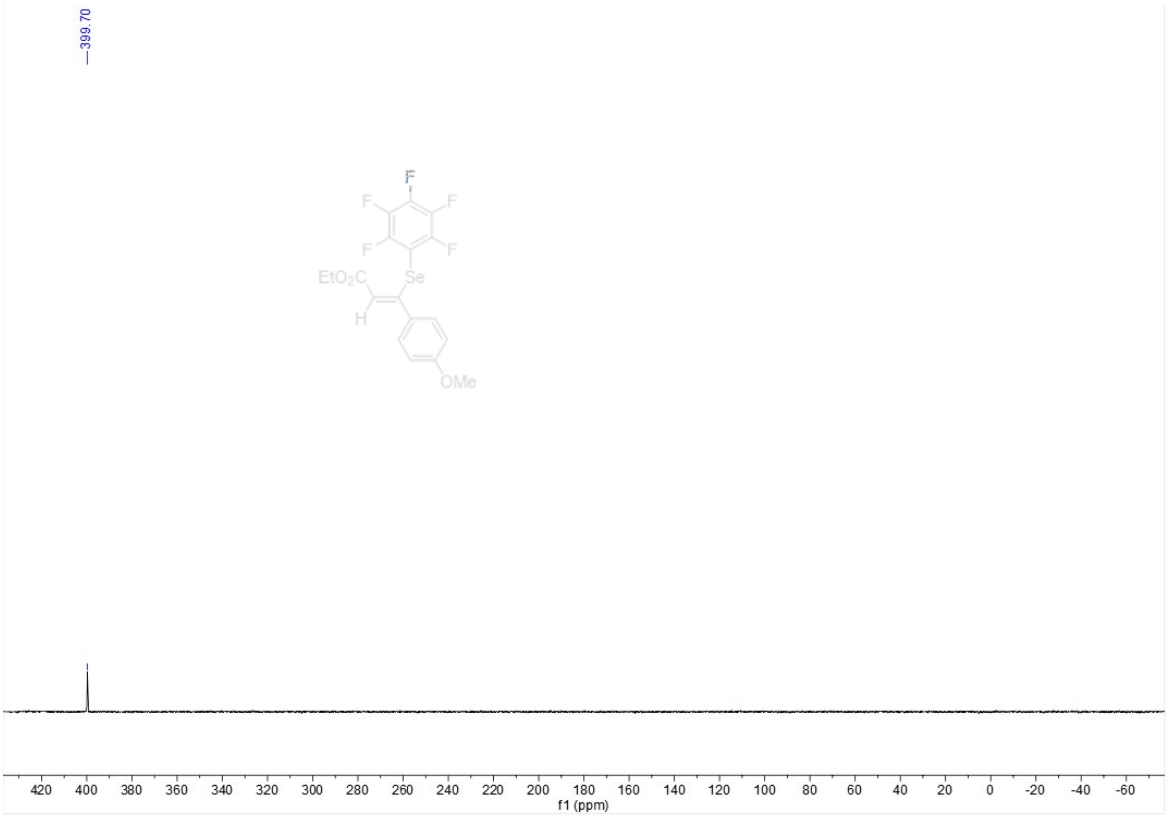
^{13}C NMR spectra of 5d ($CDCl_3$)



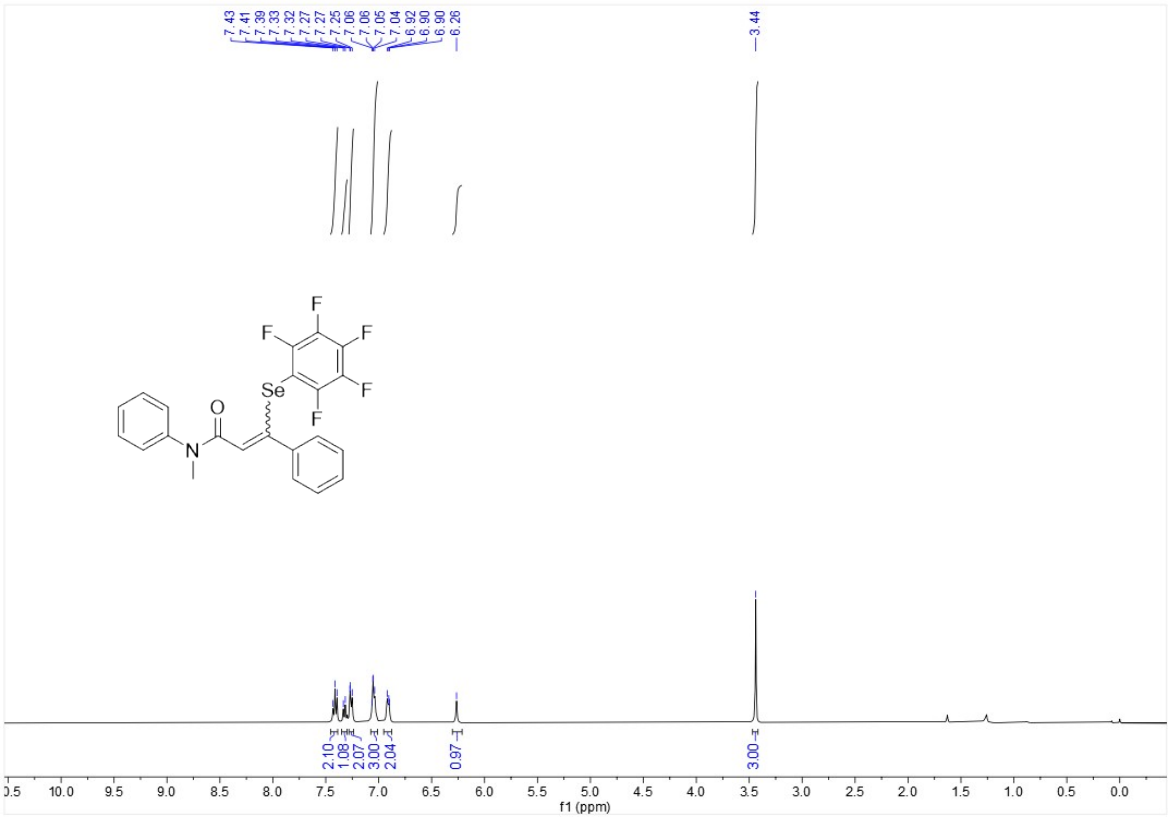
^{19}F NMR spectra of 5d ($CDCl_3$)



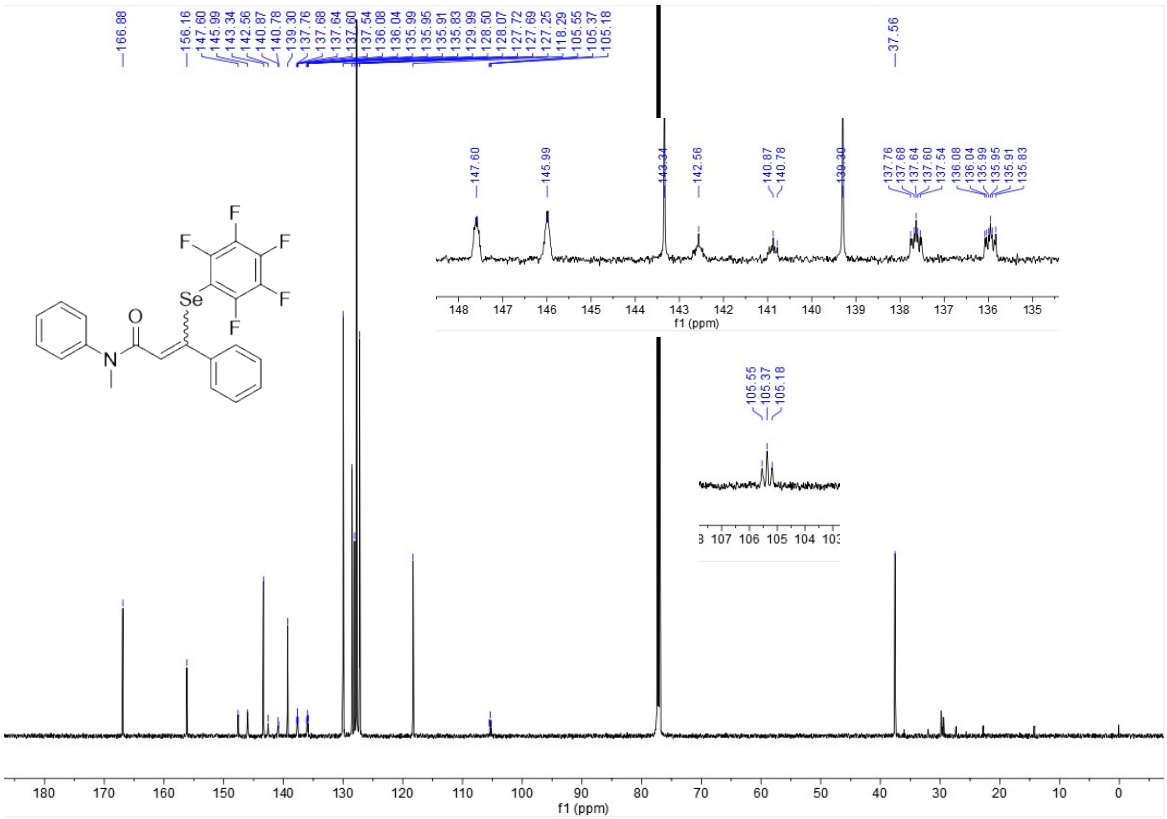
^{77}Se NMR spectra of 5d ($CDCl_3$)



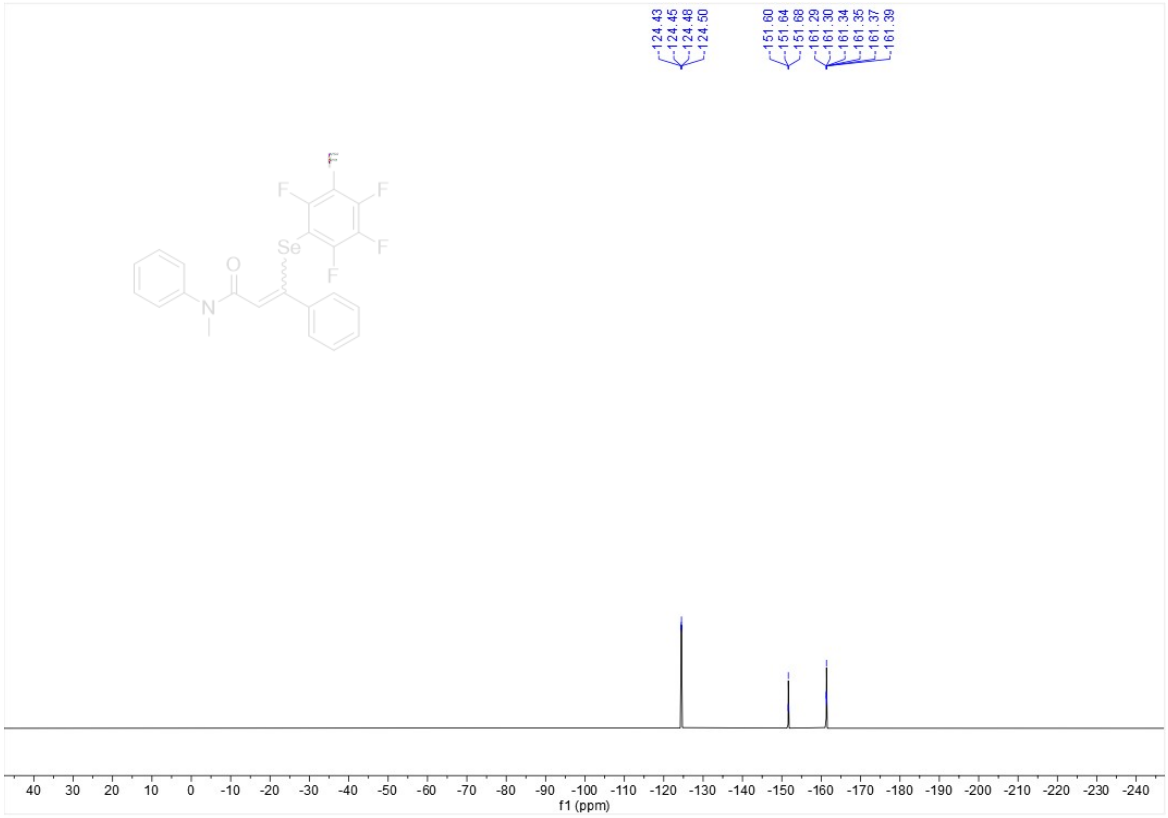
^{1}H NMR spectra of 5e ($CDCl_3$)



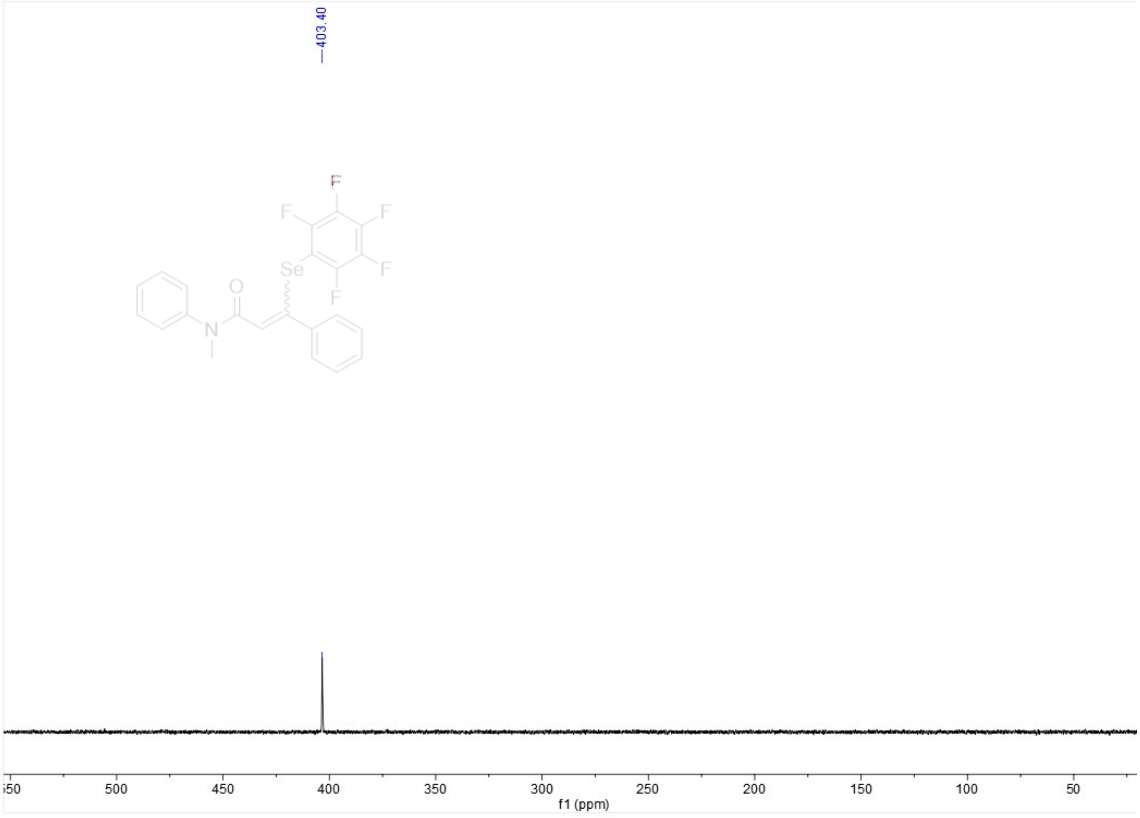
^{13}C NMR spectra of 5e ($CDCl_3$)



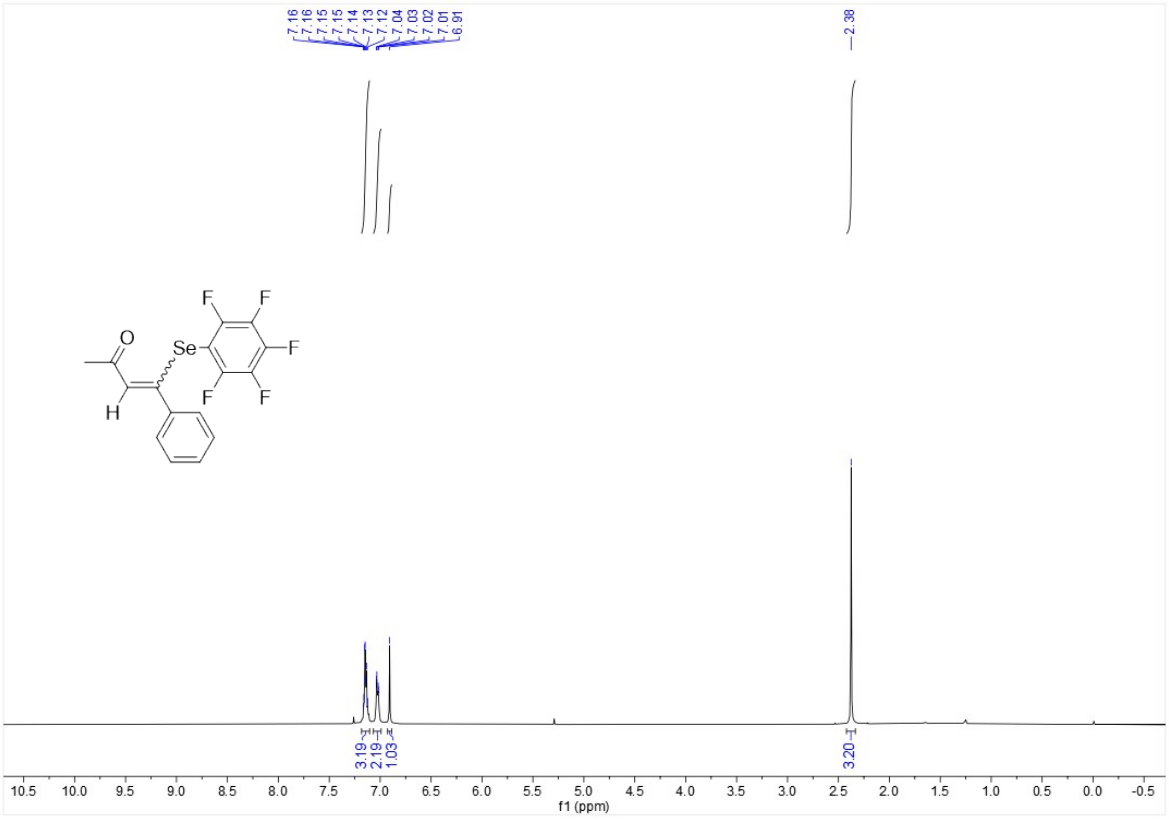
^{19}F NMR spectra of 5e ($CDCl_3$)



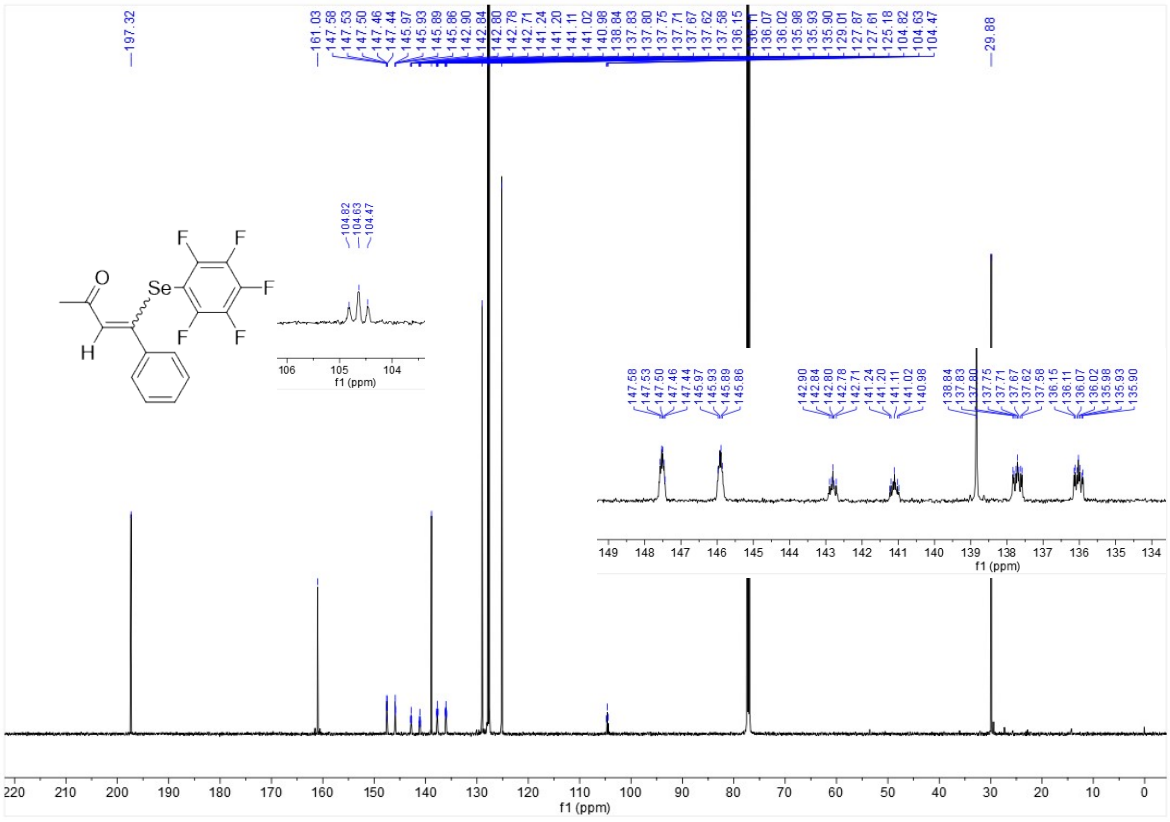
^{77}Se NMR spectra of 5e ($CDCl_3$)



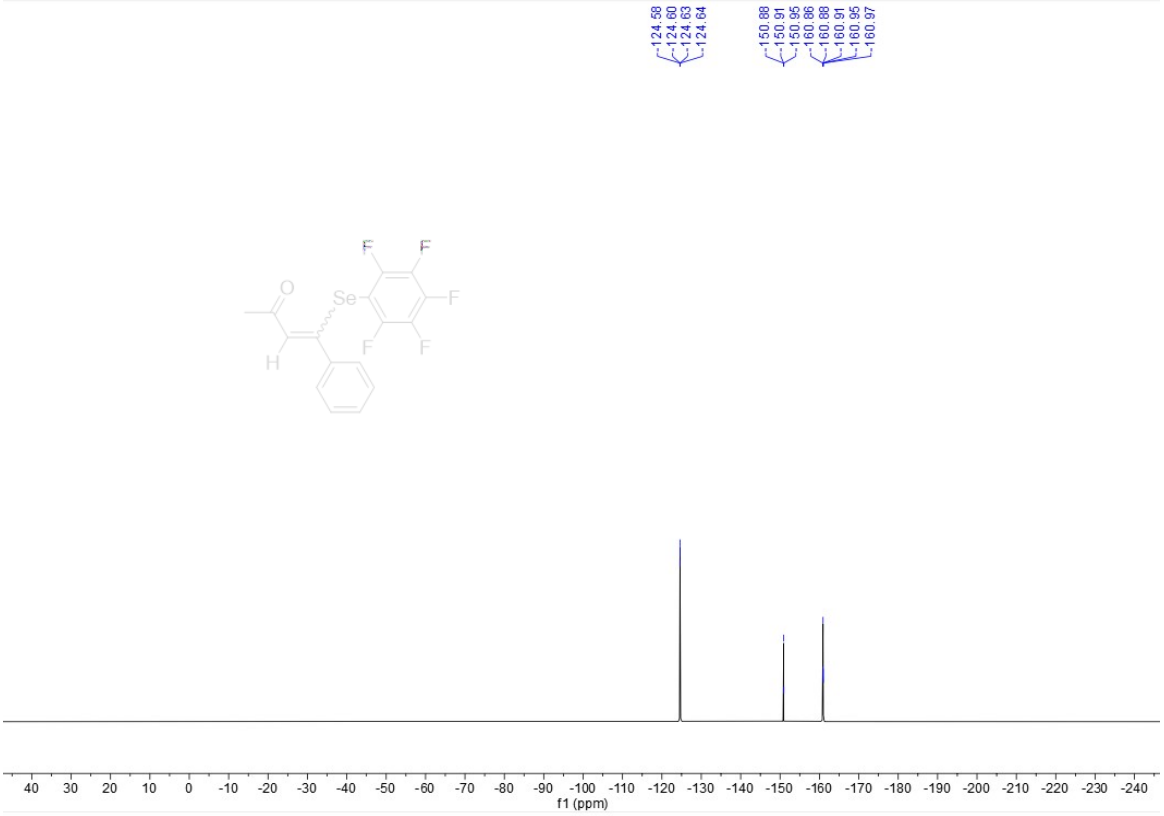
^{1}H NMR spectra of 5f ($CDCl_3$)



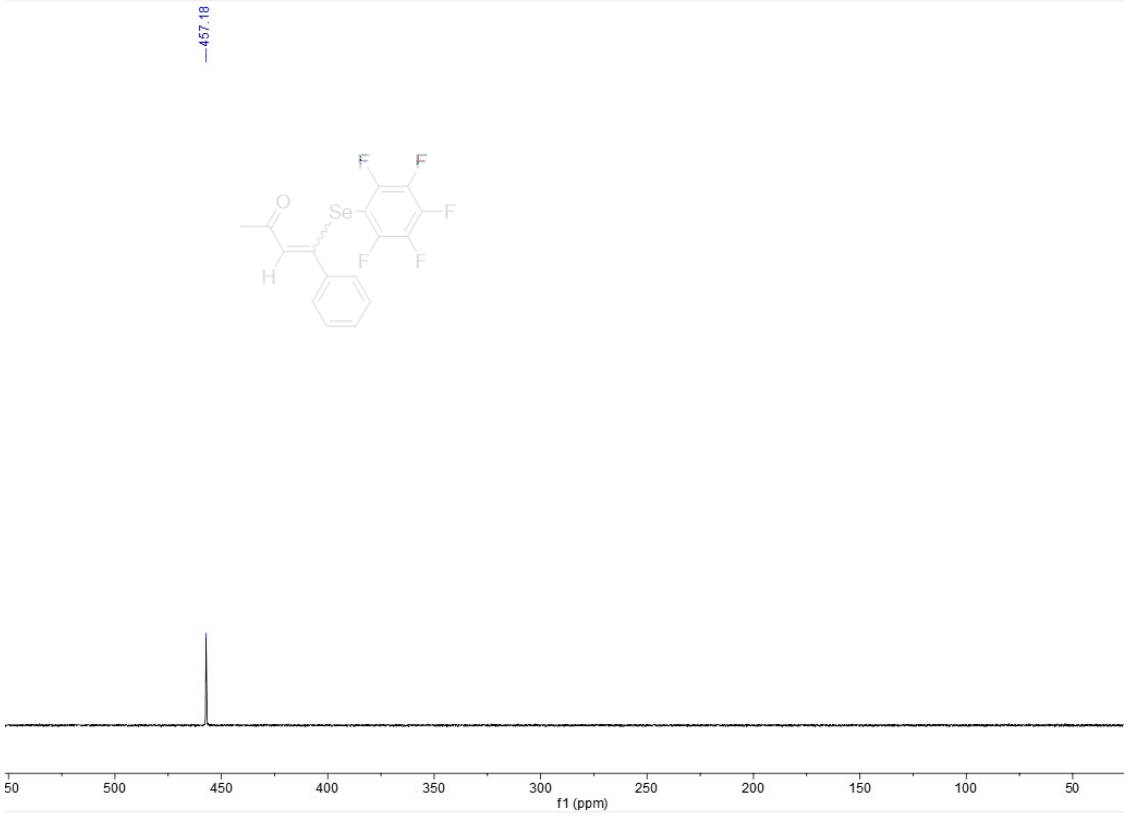
^{13}C NMR spectra of 5f ($CDCl_3$)



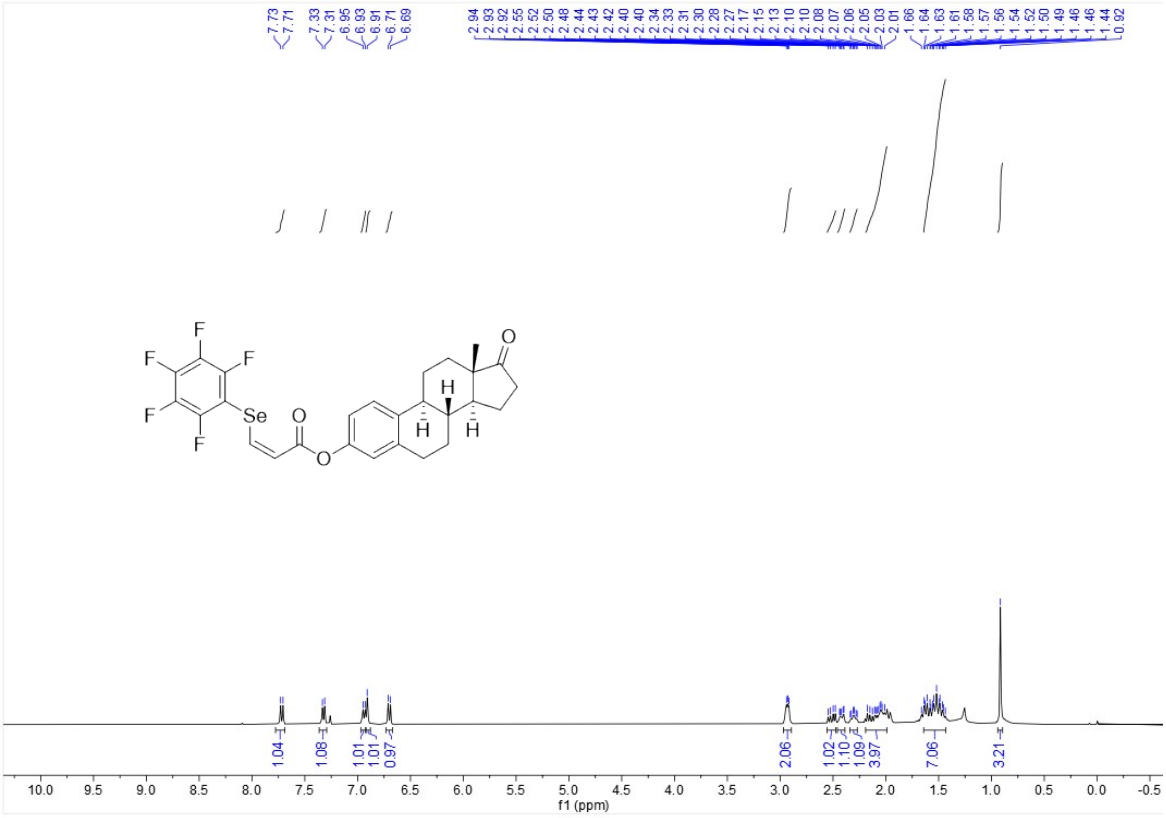
^{19}F NMR spectra of 5f ($CDCl_3$)



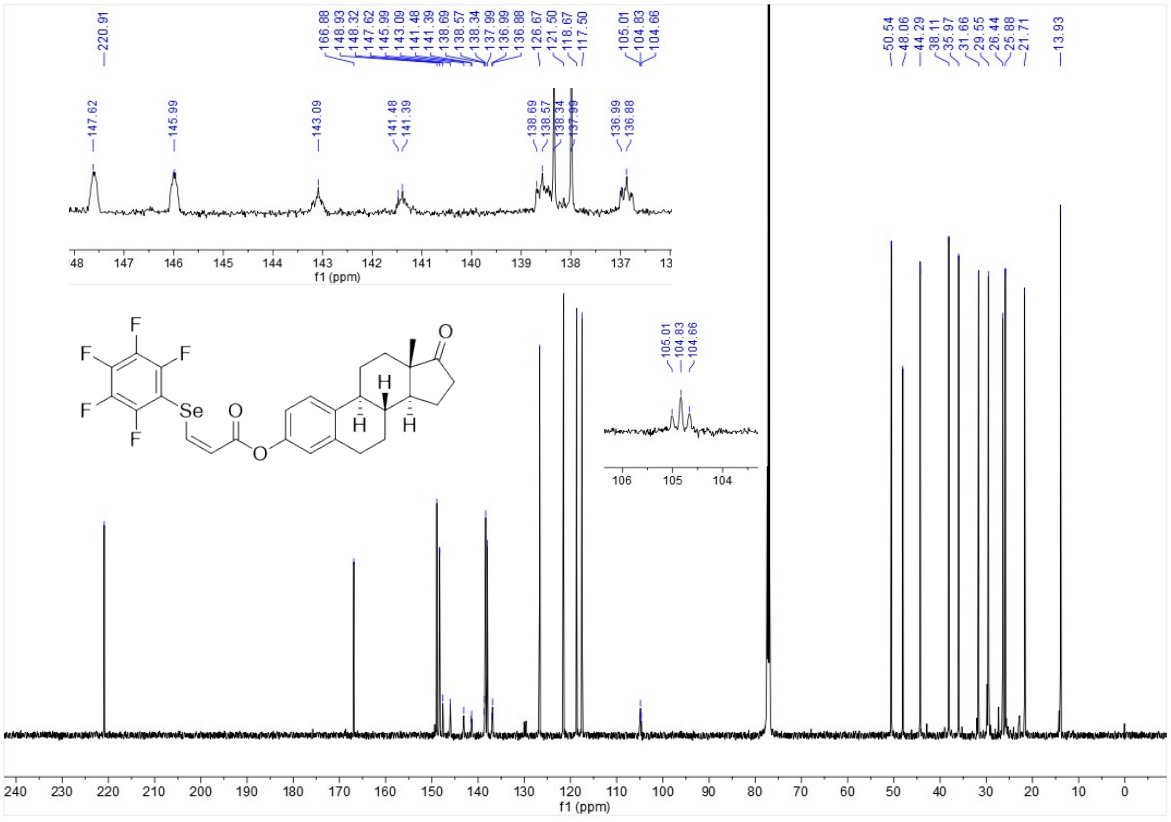
^{77}Se NMR spectra of 5f ($CDCl_3$)



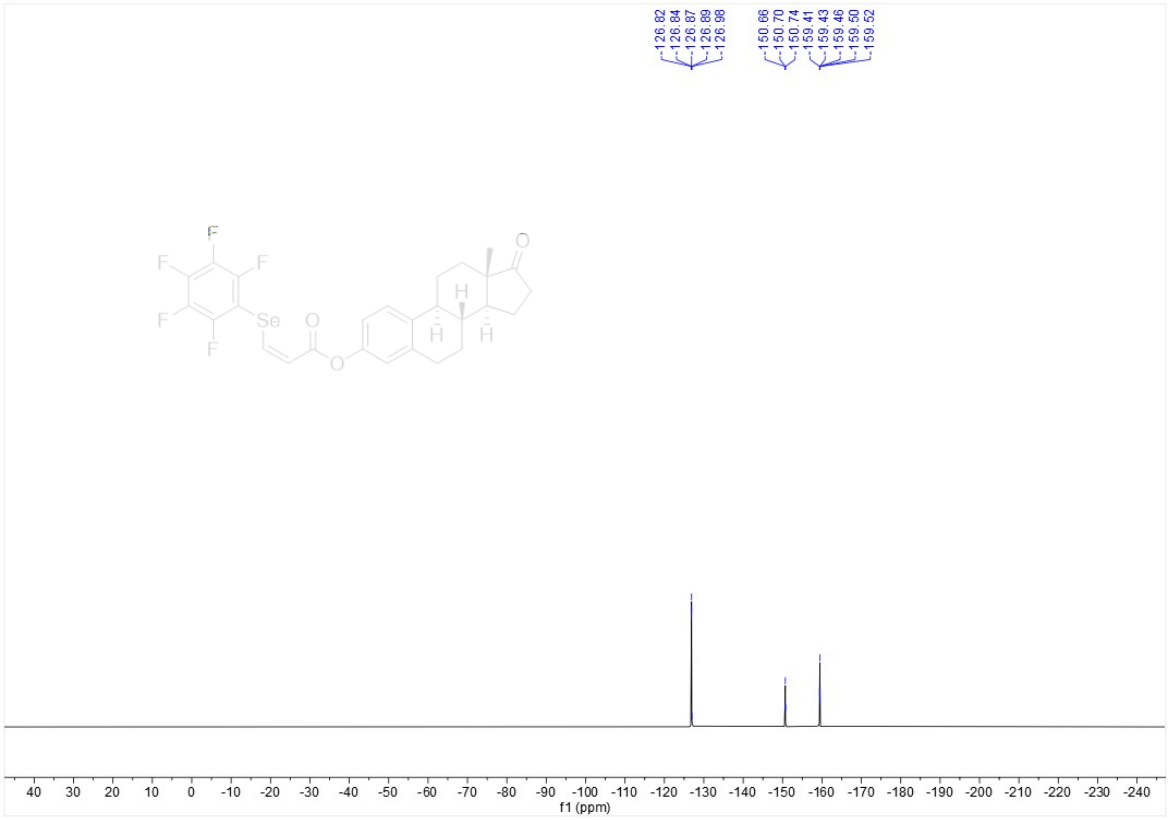
^{1}H NMR spectra of 5g ($CDCl_3$)



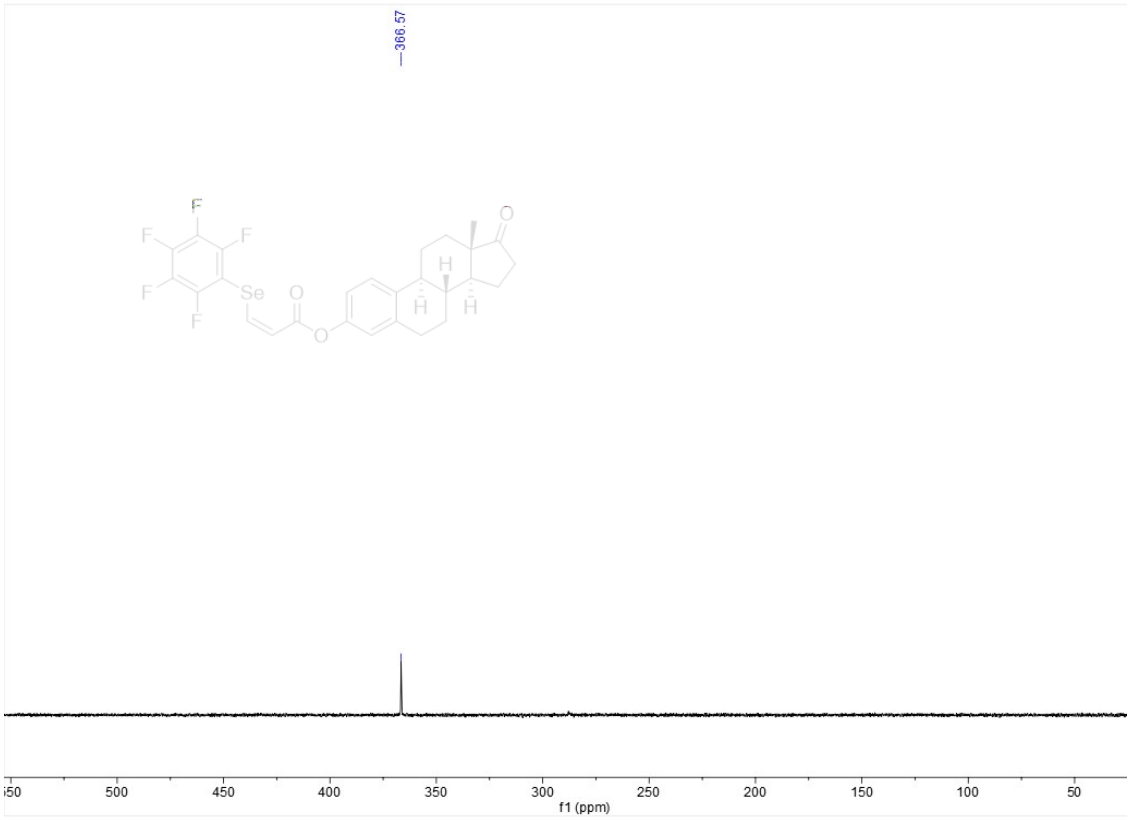
^{13}C NMR spectra of 5g ($CDCl_3$)



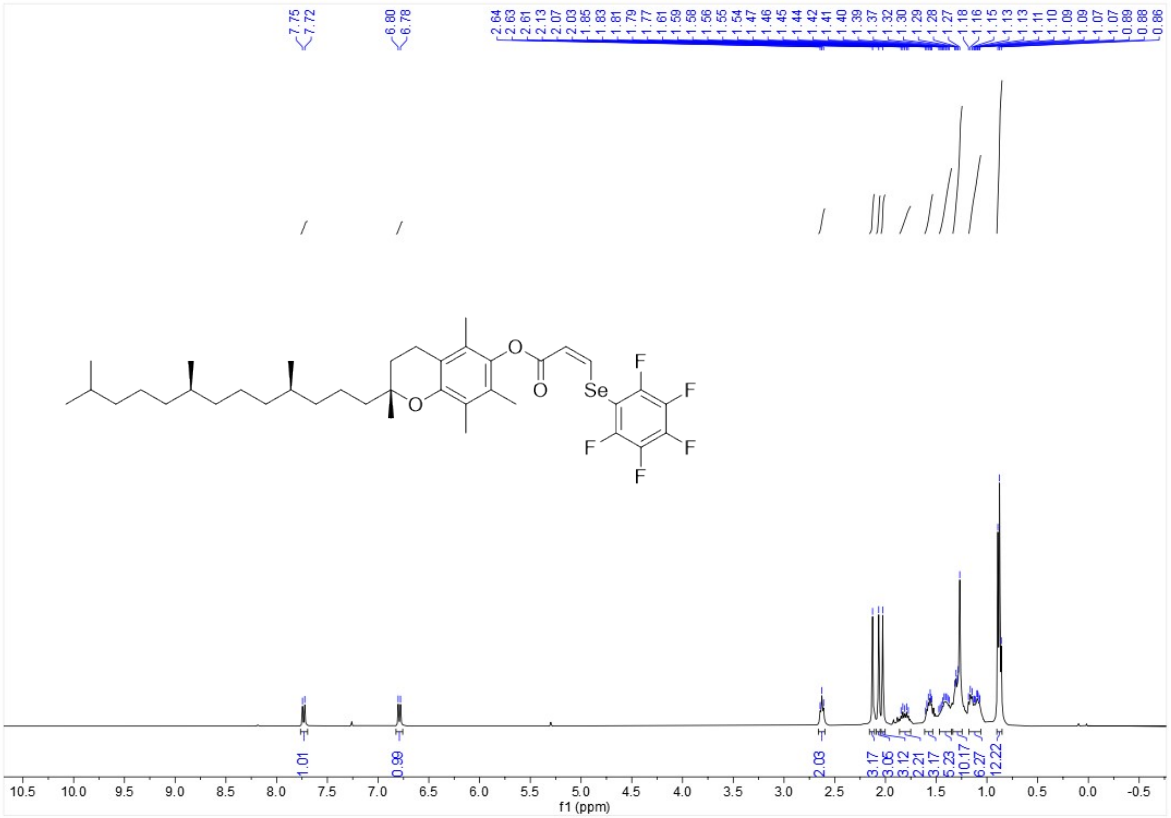
^{19}F NMR spectra of 5g ($CDCl_3$)



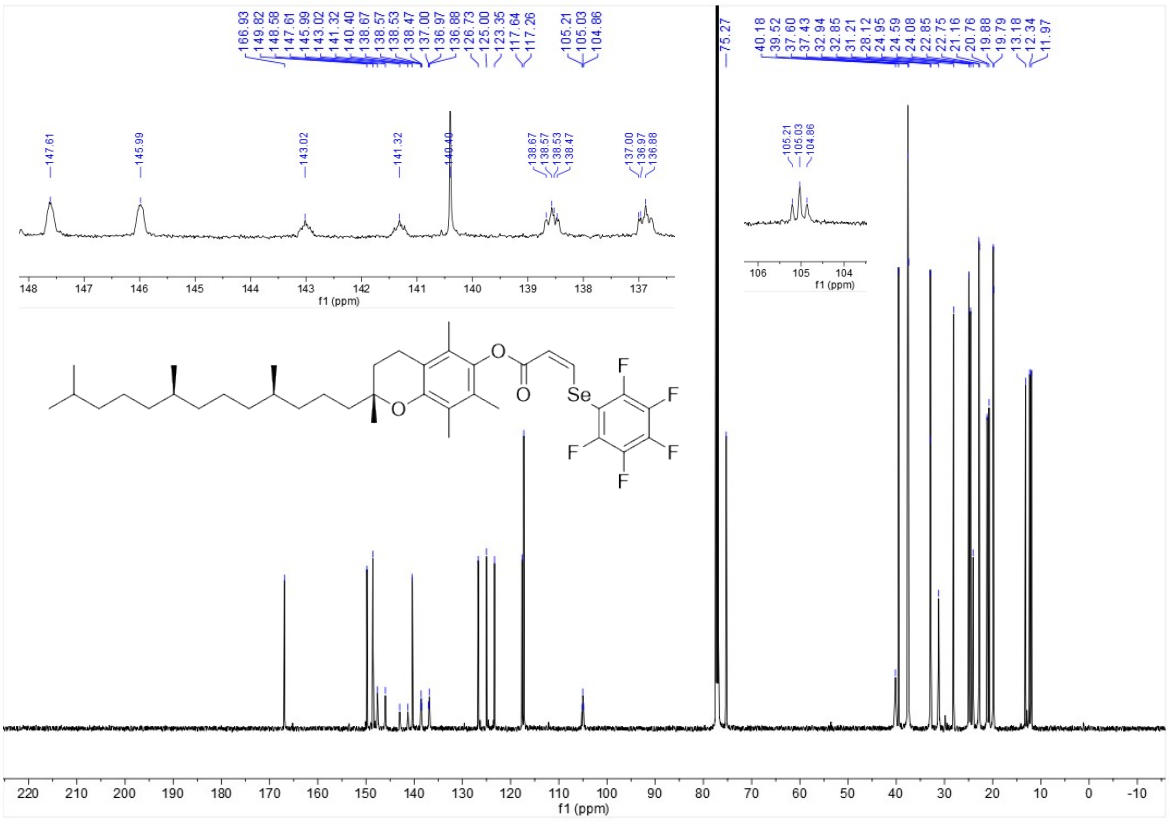
^{77}Se NMR spectra of 5g ($CDCl_3$)



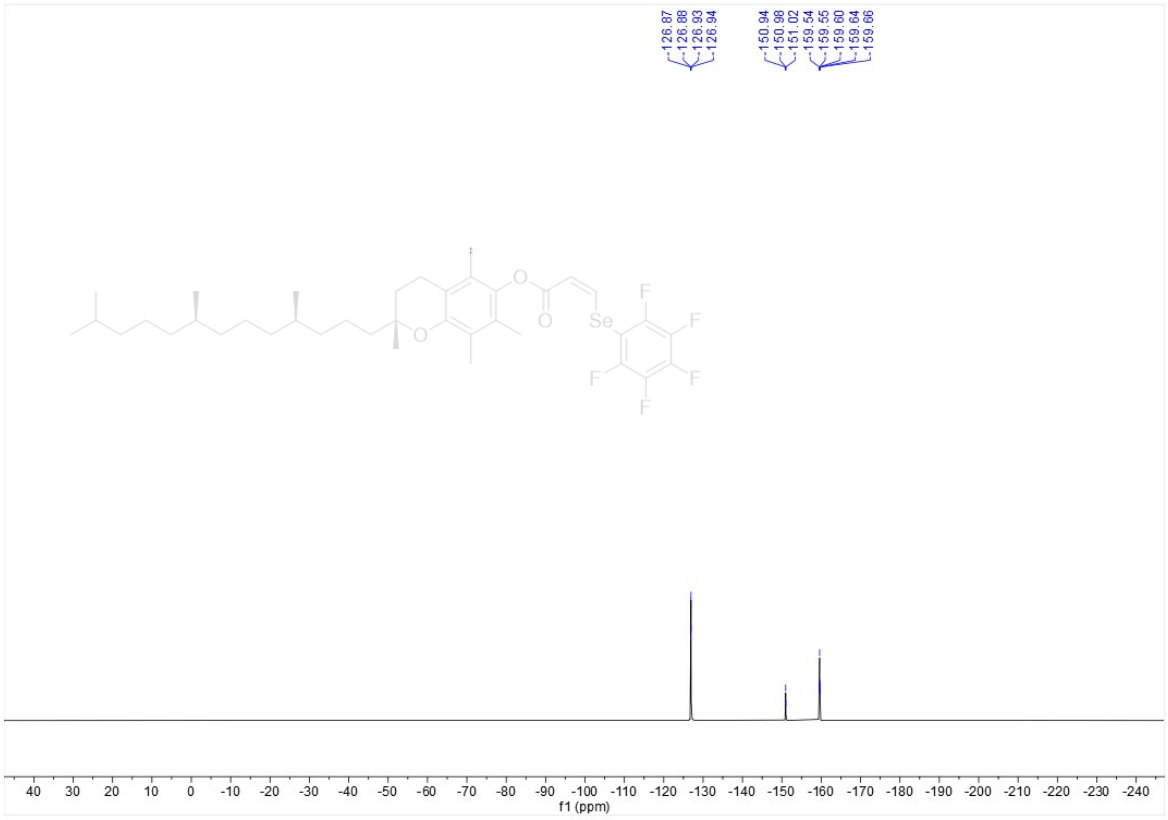
^{1}H NMR spectra of 5h ($CDCl_3$)



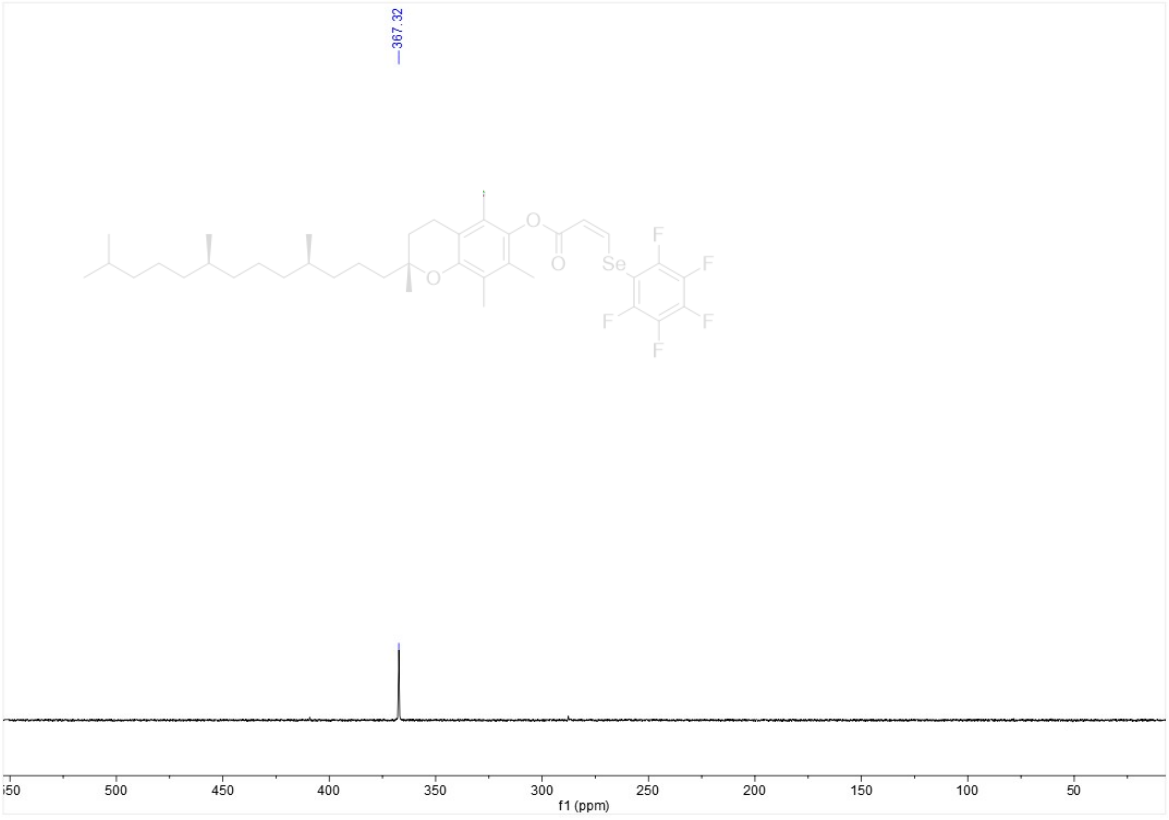
^{13}C NMR spectra of 5h ($CDCl_3$)



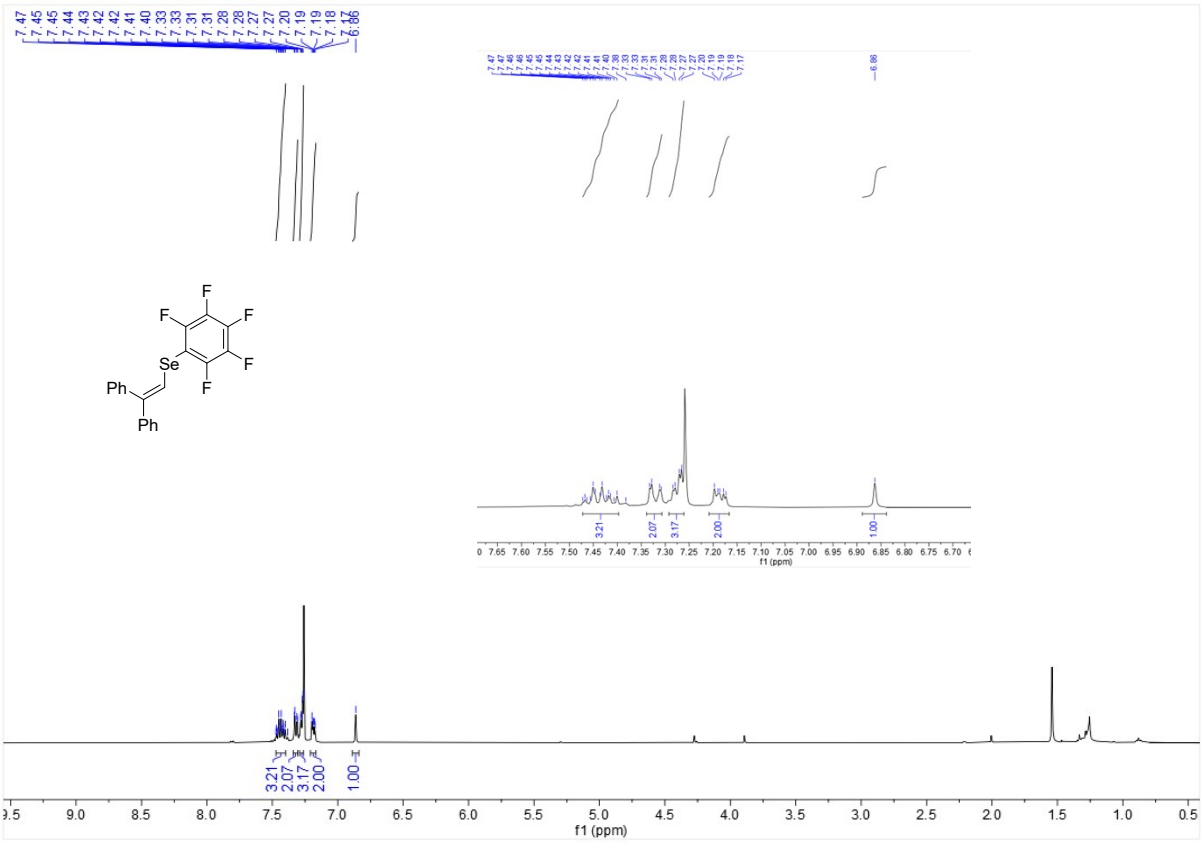
^{19}F NMR spectra of 5h ($CDCl_3$)



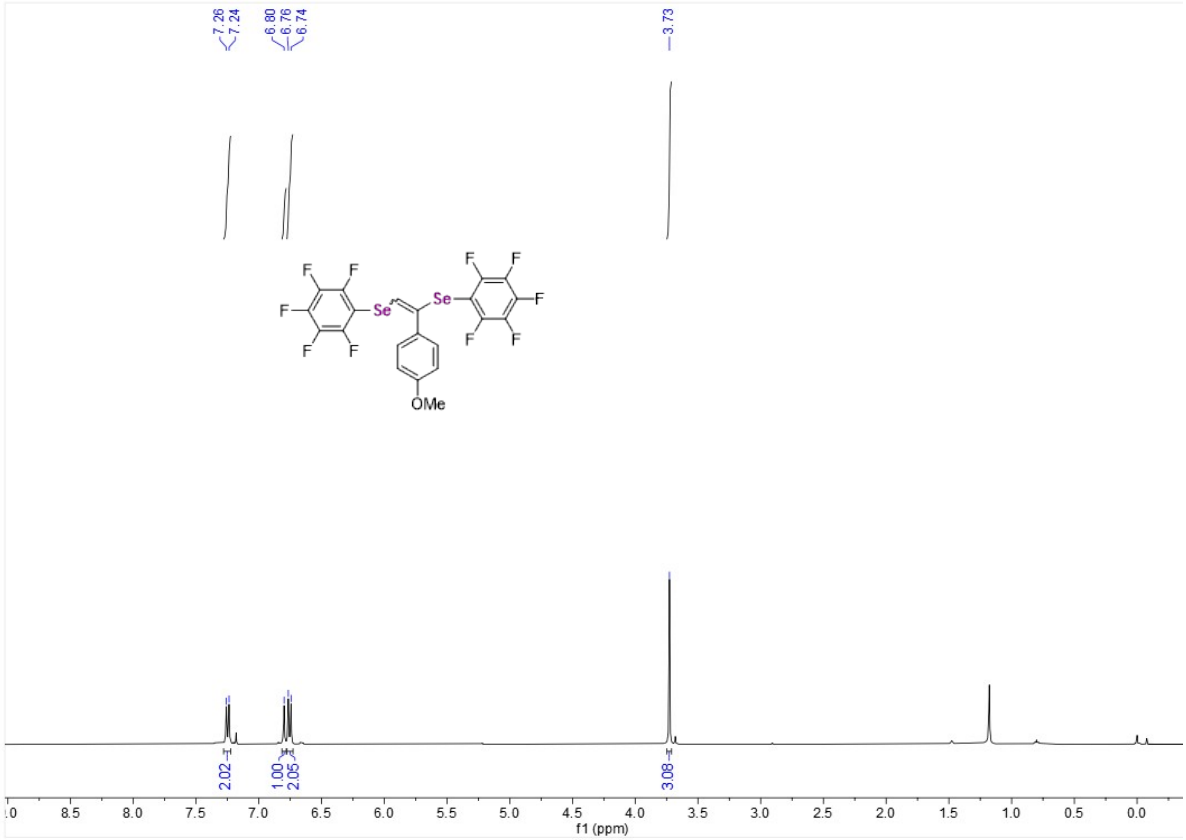
^{77}Se NMR spectra of 5h ($CDCl_3$)



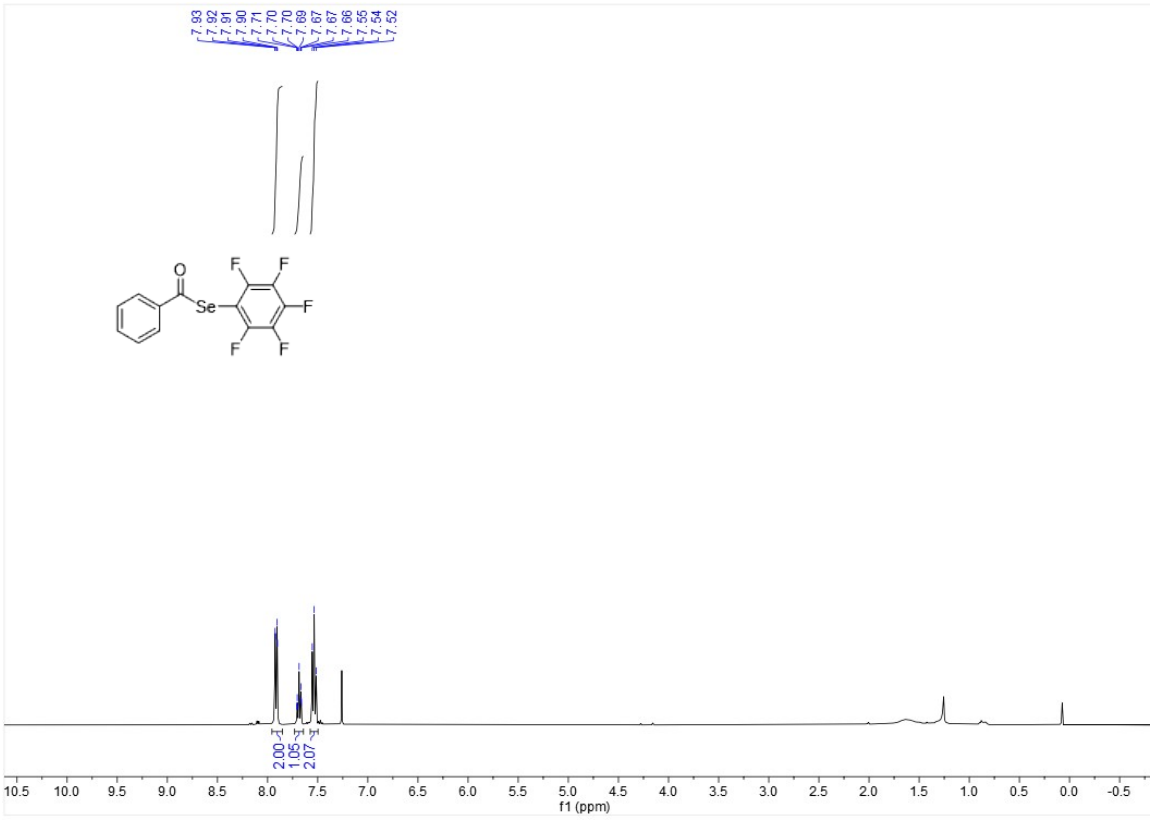
^{1}H NMR spectra of 7a ($CDCl_3$)



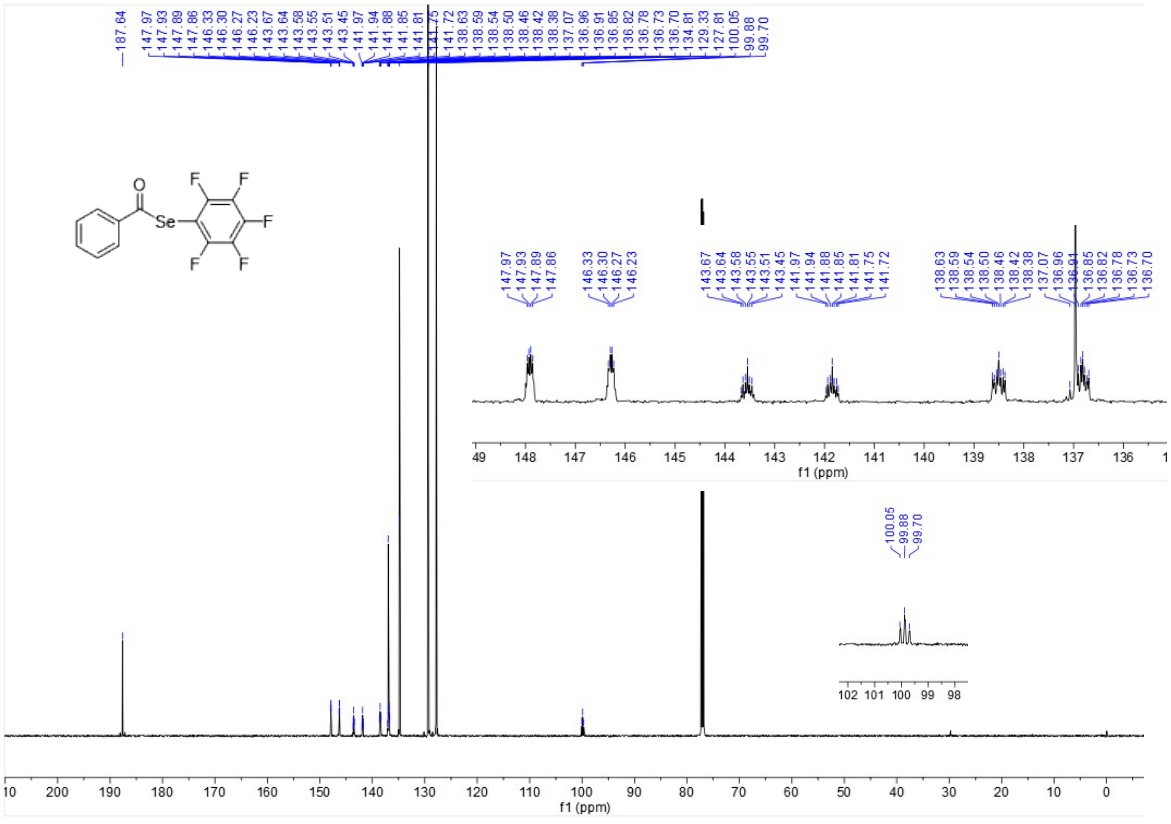
^{1}H NMR spectra of 9a ($CDCl_3$)



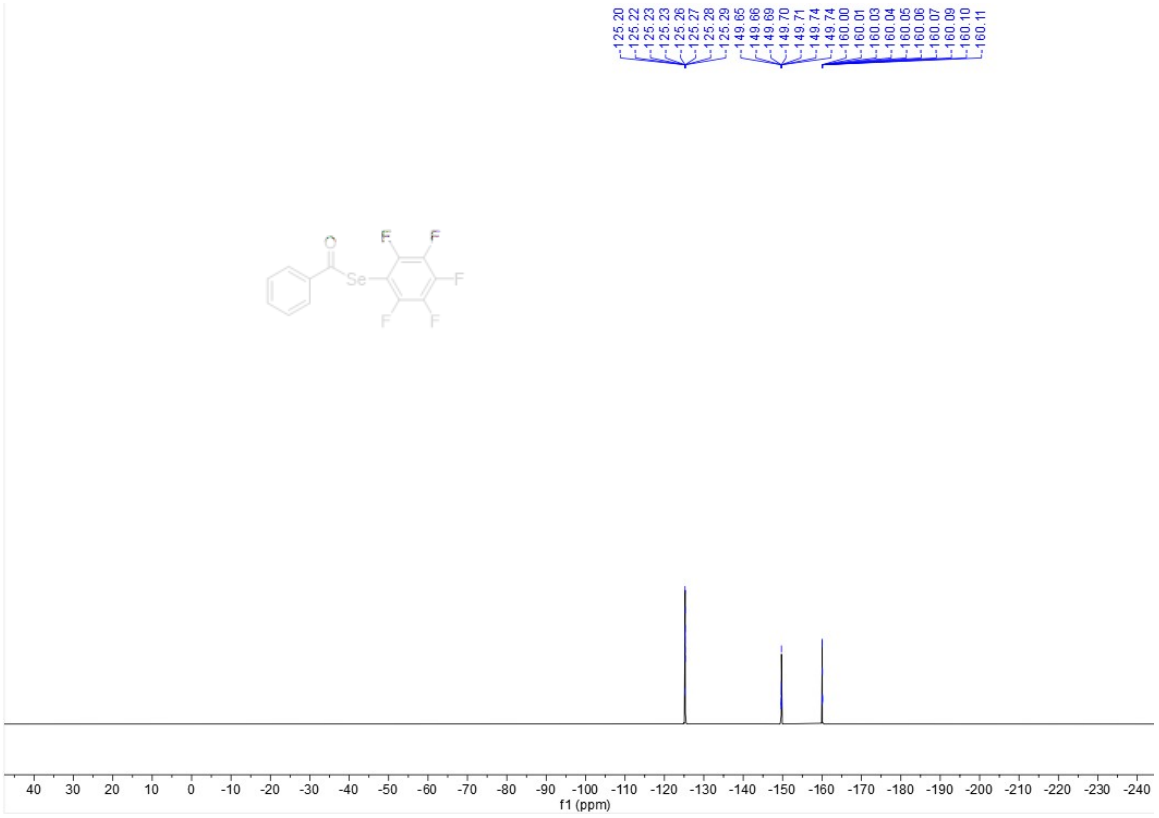
^{1}H NMR spectra of 10a ($CDCl_3$)



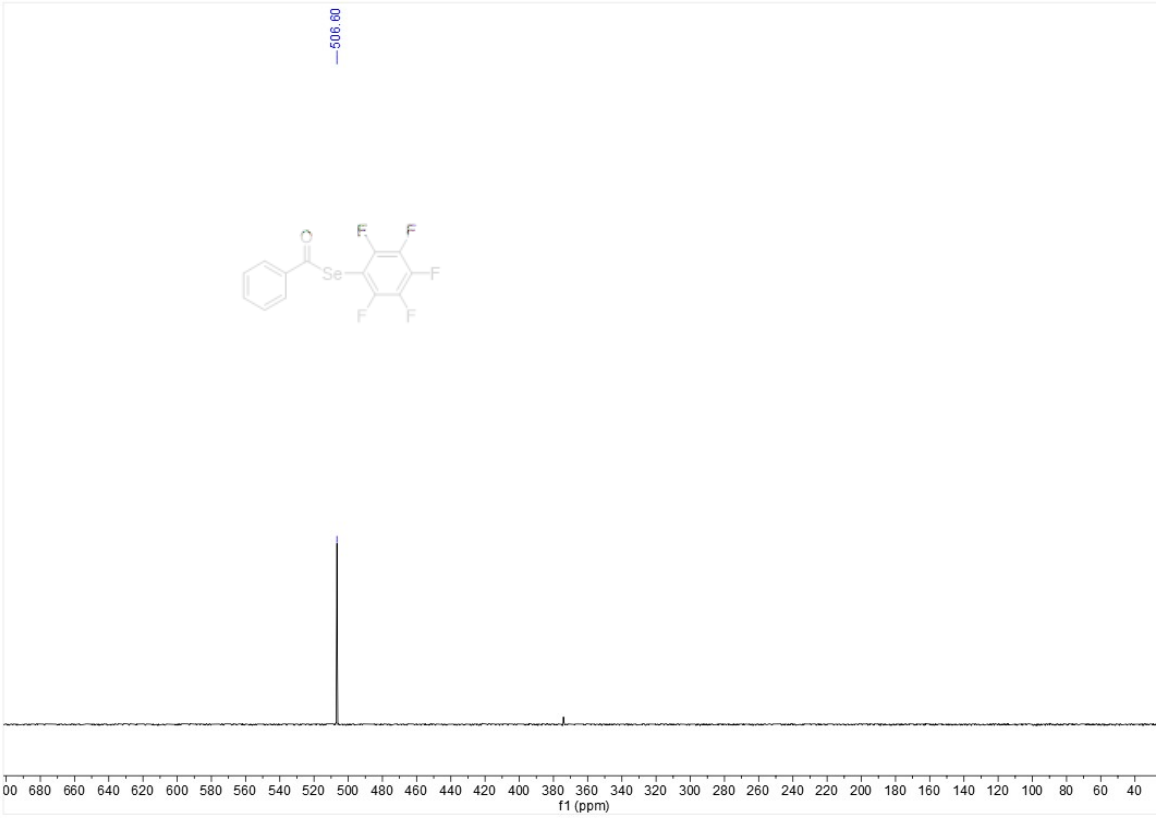
^{13}C NMR spectra of 10a ($CDCl_3$)



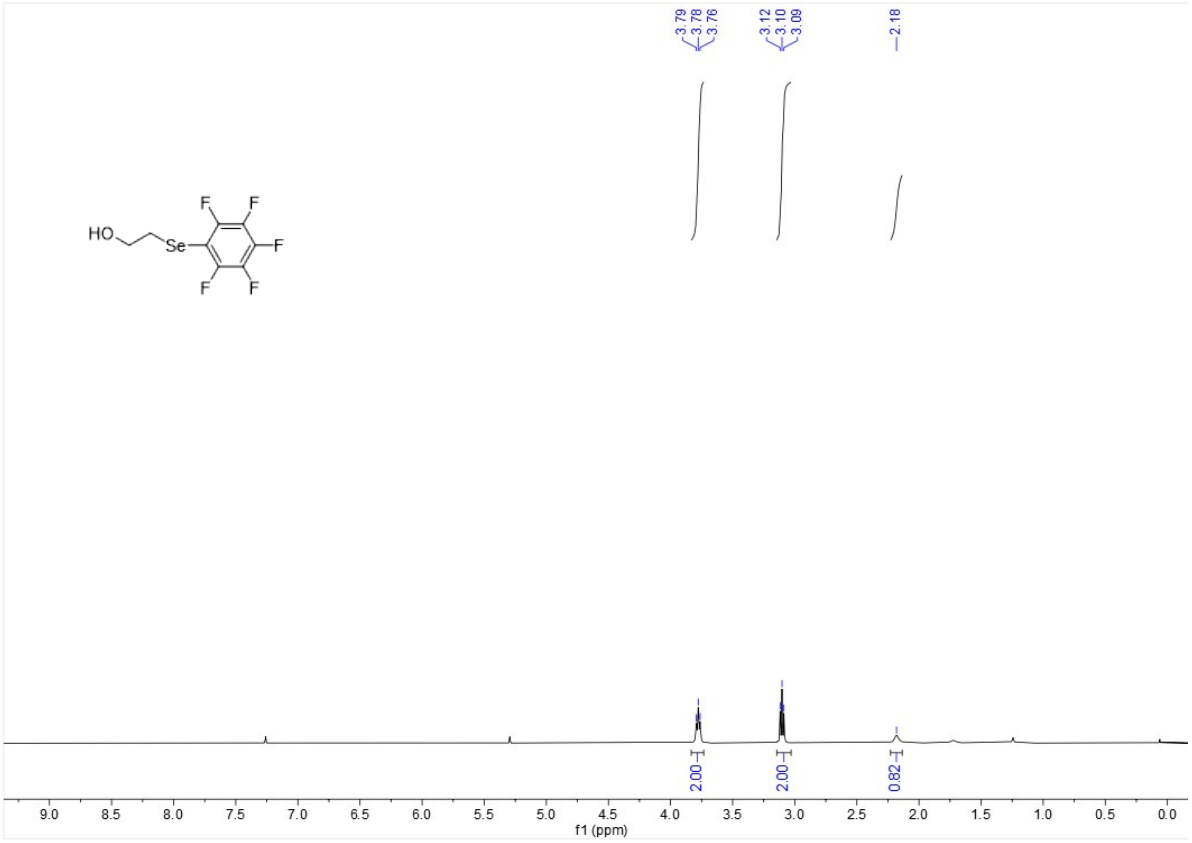
^{19}F NMR spectra of 10a ($CDCl_3$)



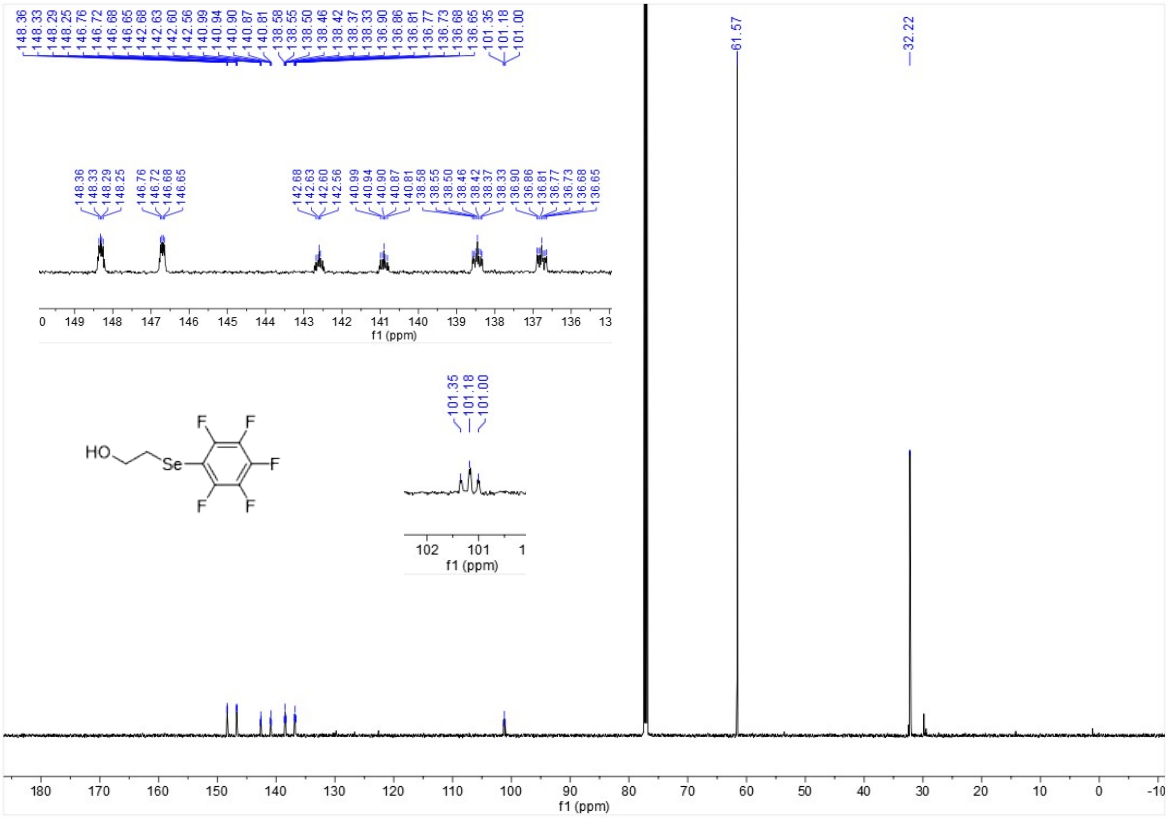
^{77}Se NMR spectra of 10a ($CDCl_3$)



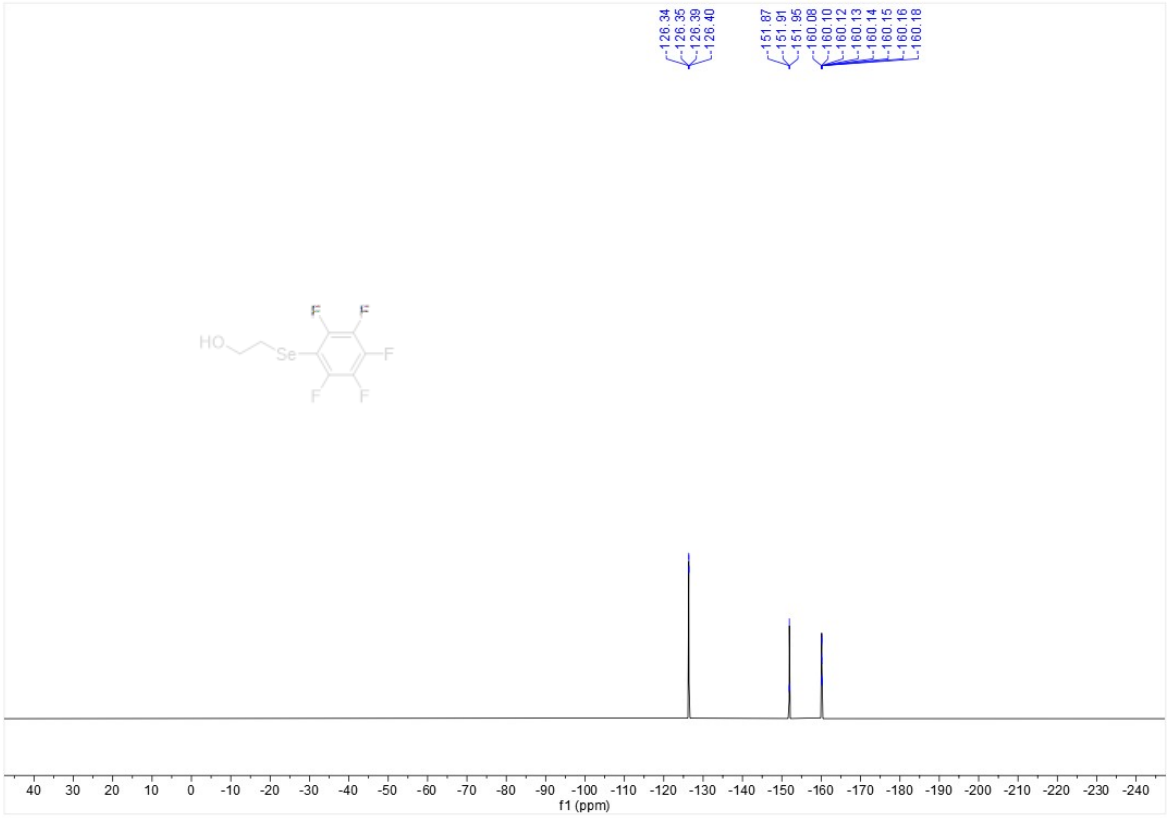
^{1}H NMR spectra of 11a ($CDCl_3$)



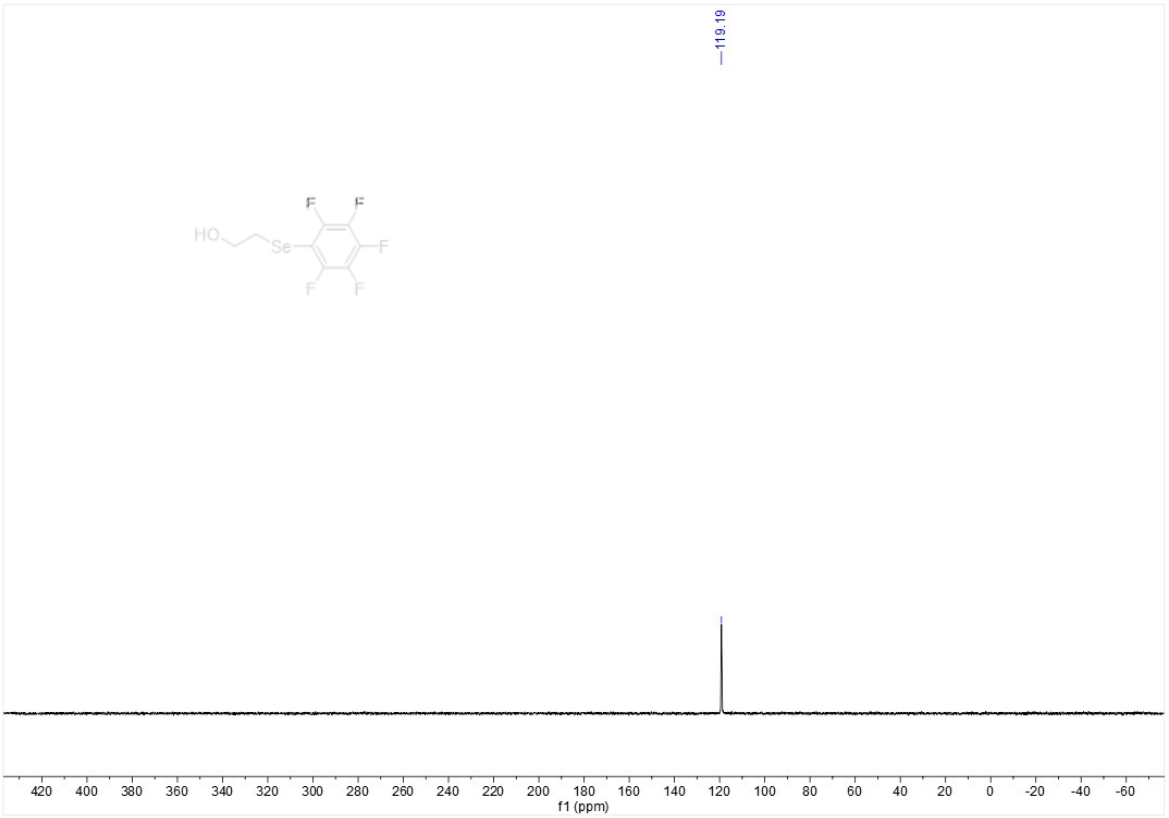
^{13}C NMR spectra of 11a ($CDCl_3$)



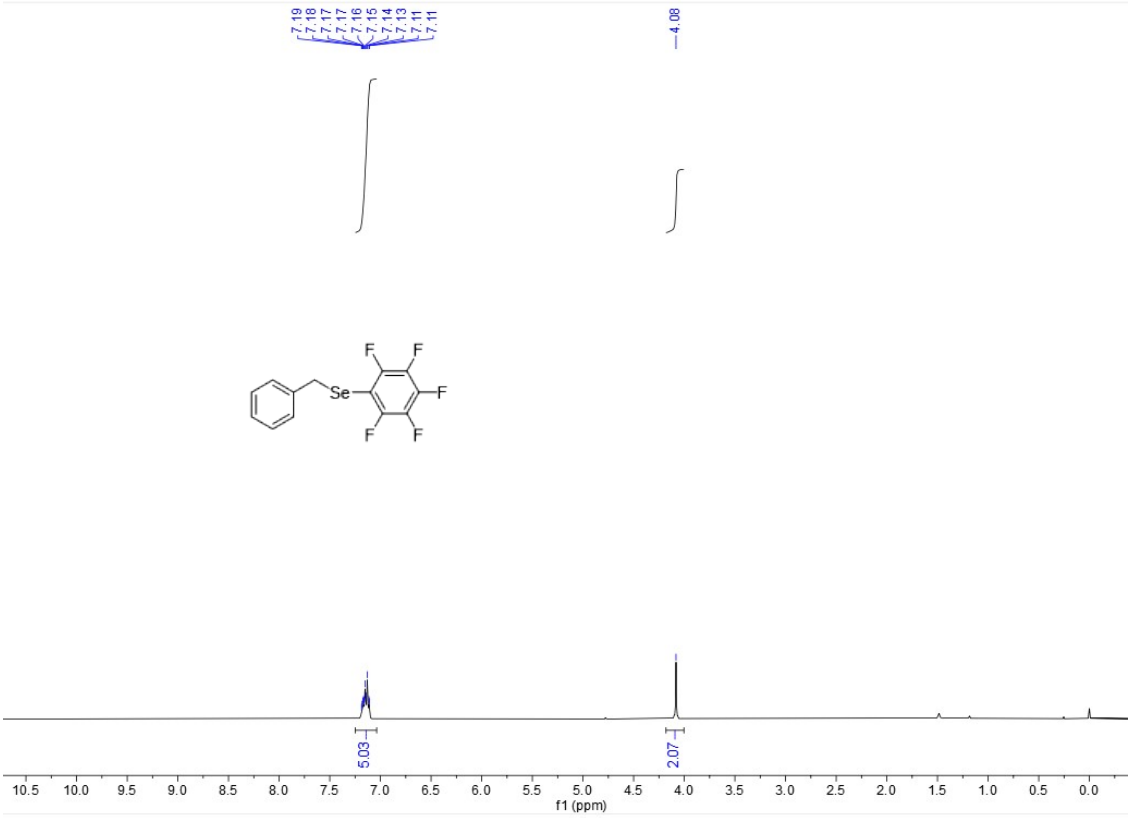
^{19}F NMR spectra of 11a ($CDCl_3$)



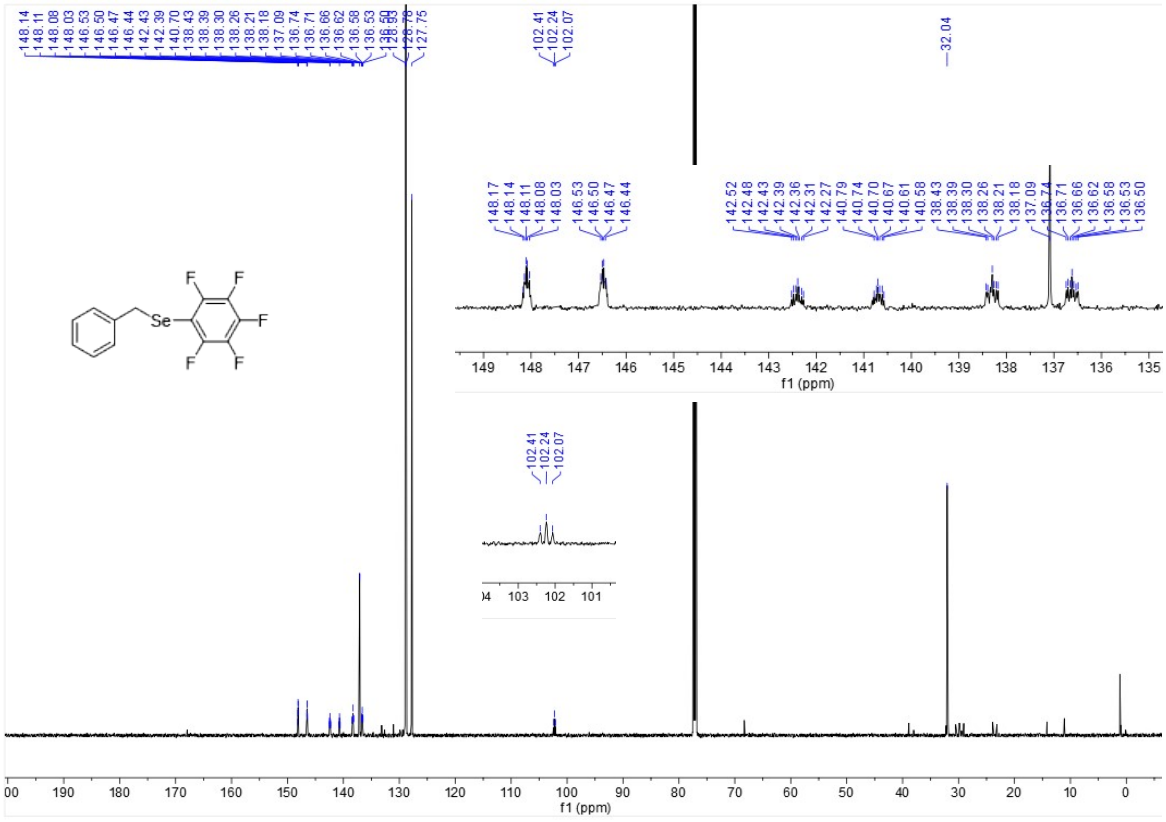
^{77}Se NMR spectra of 11a ($CDCl_3$)



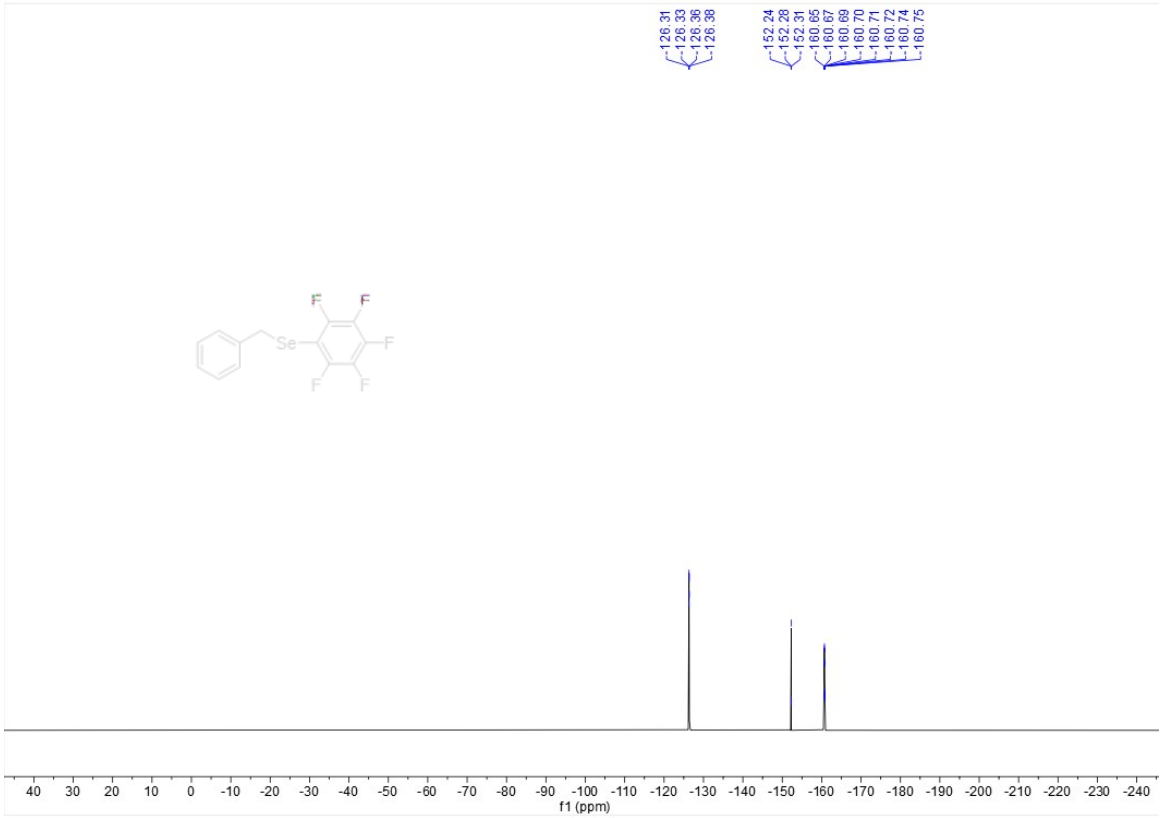
^{1}H NMR spectra of 12a ($CDCl_3$)



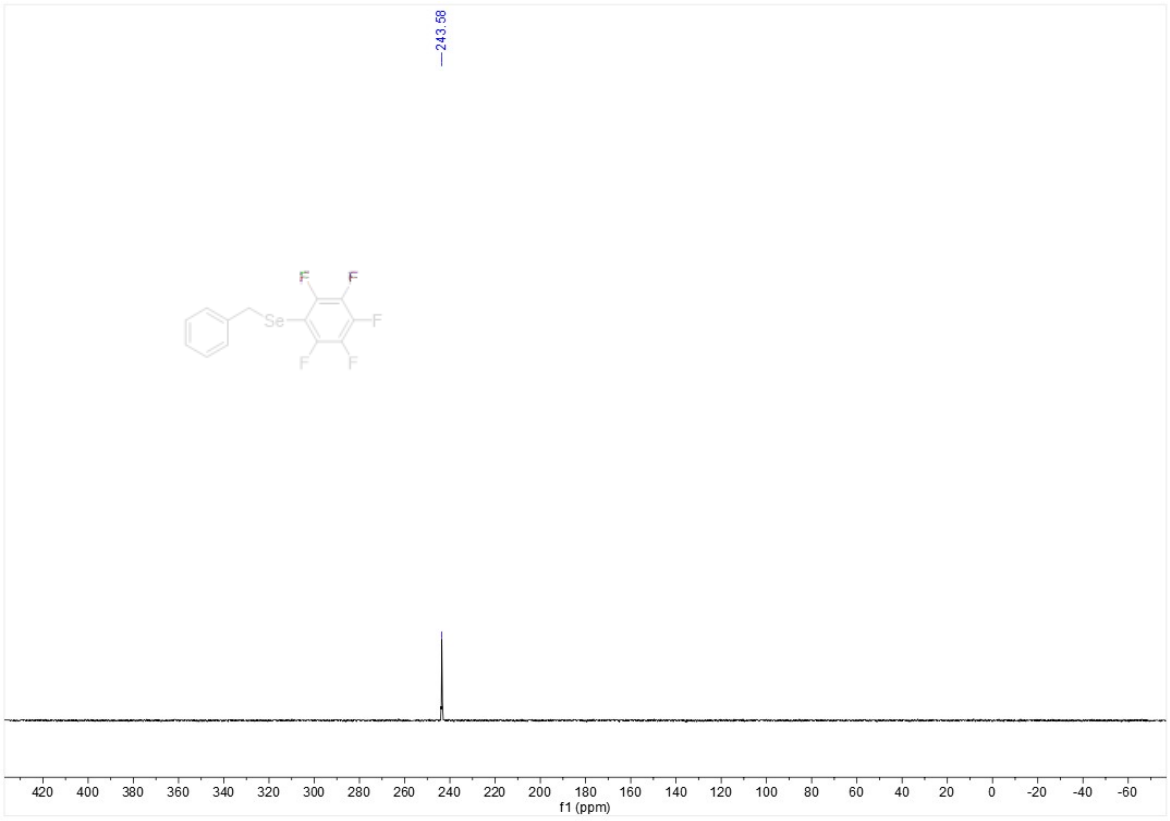
^{13}C NMR spectra of 12a ($CDCl_3$)



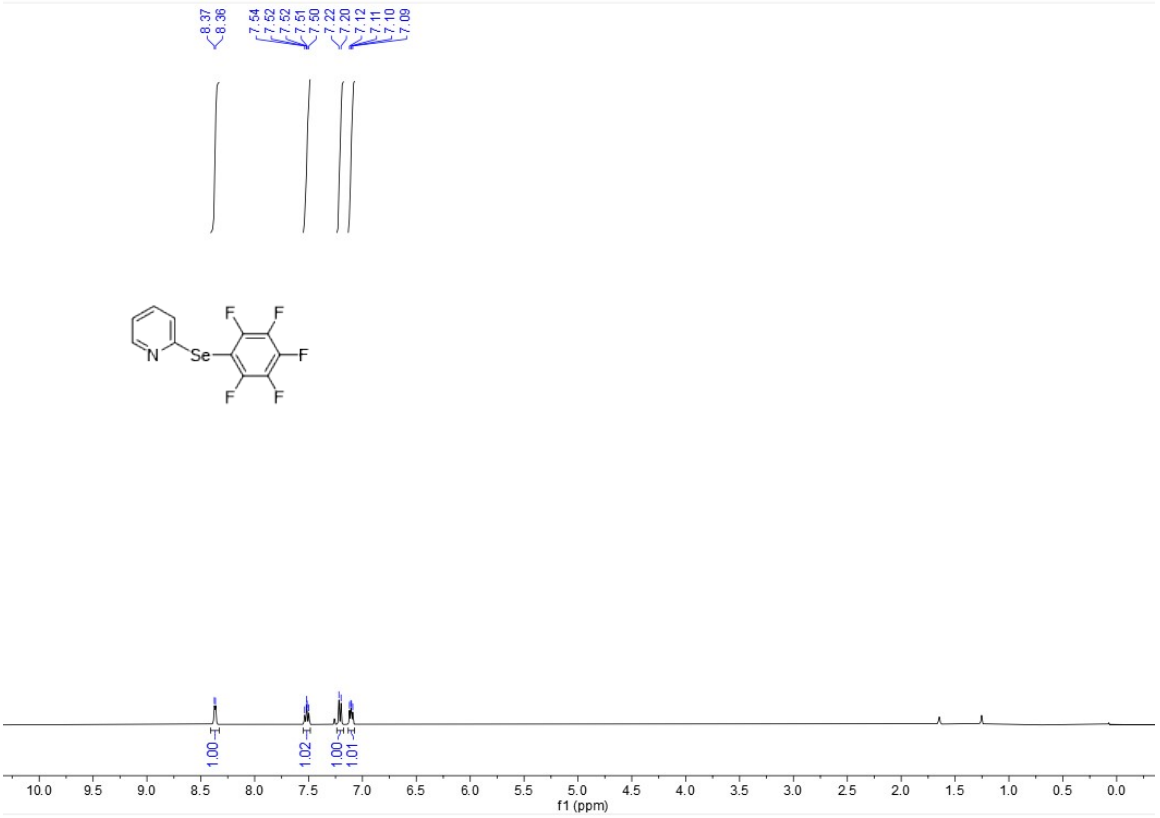
^{19}F NMR spectra of 12a ($CDCl_3$)



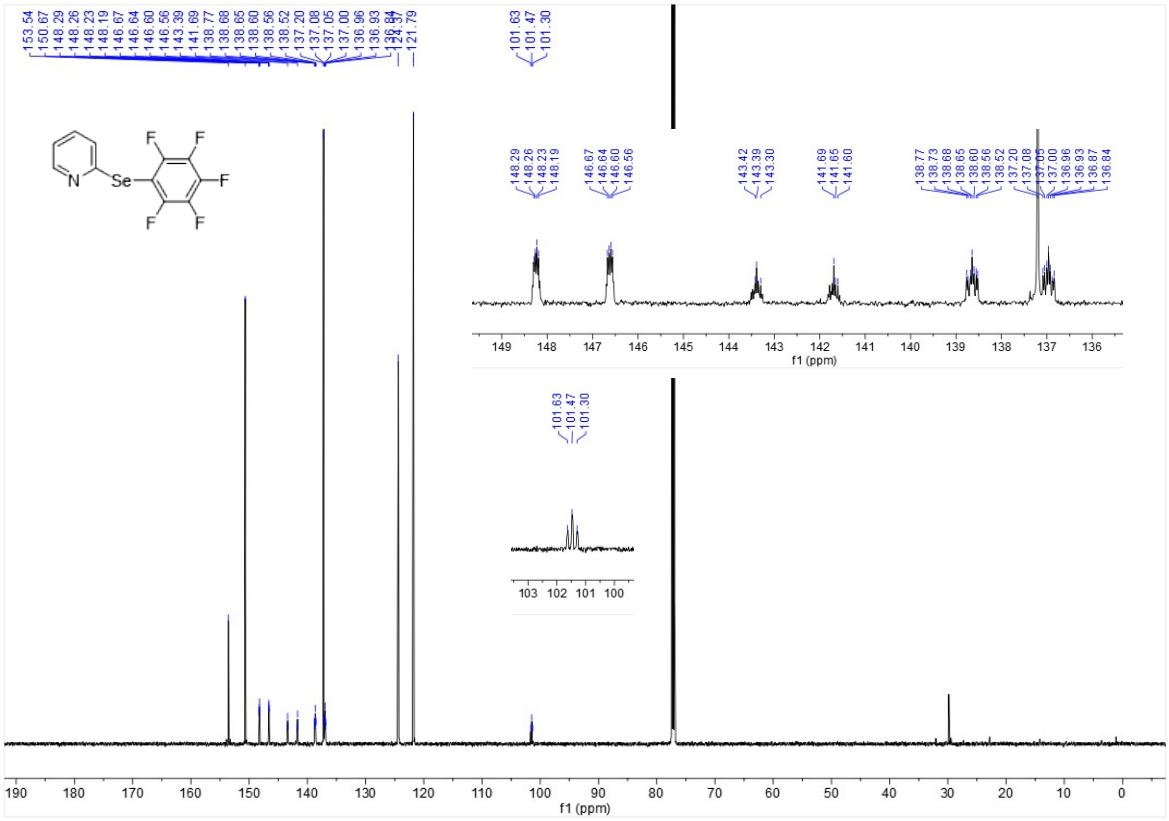
^{77}Se NMR spectra of 12a ($CDCl_3$)



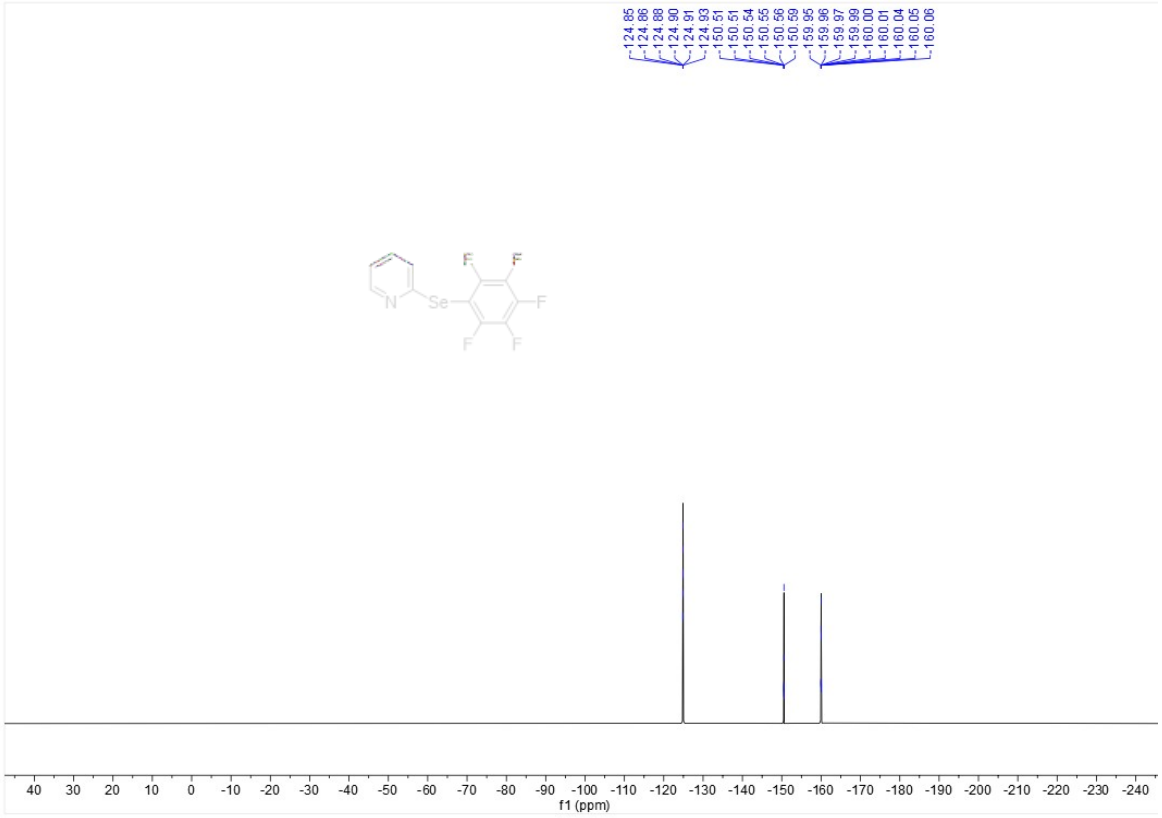
^{1}H NMR spectra of 13a ($CDCl_3$)



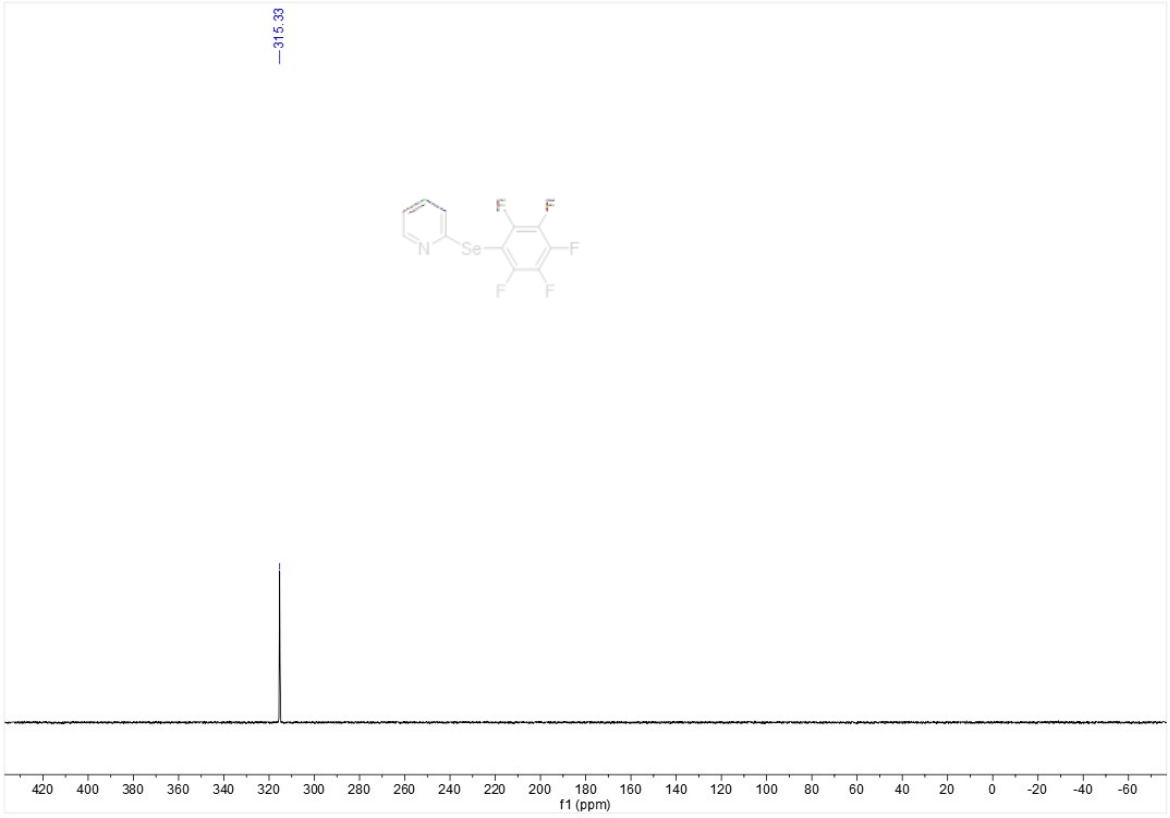
^{13}C NMR spectra of 13a ($CDCl_3$)



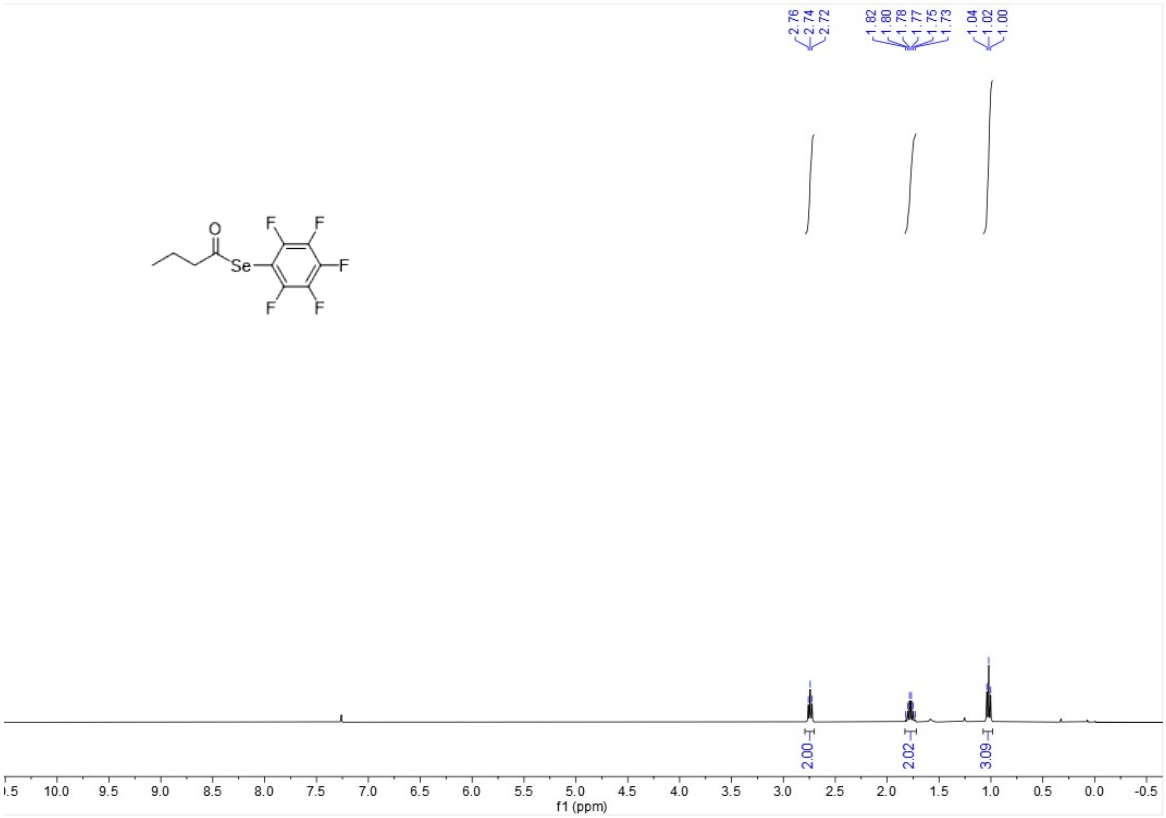
^{19}F NMR spectra of 13a ($CDCl_3$)



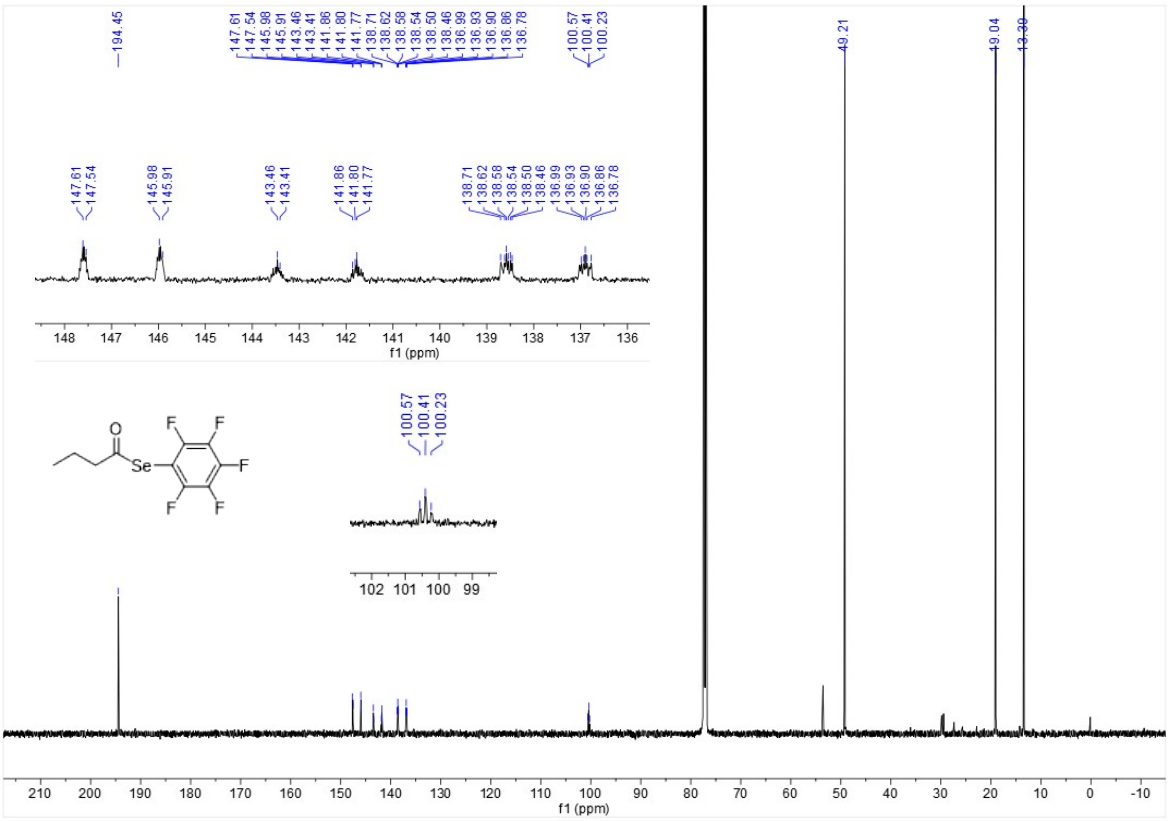
^{77}Se NMR spectra of 13a ($CDCl_3$)



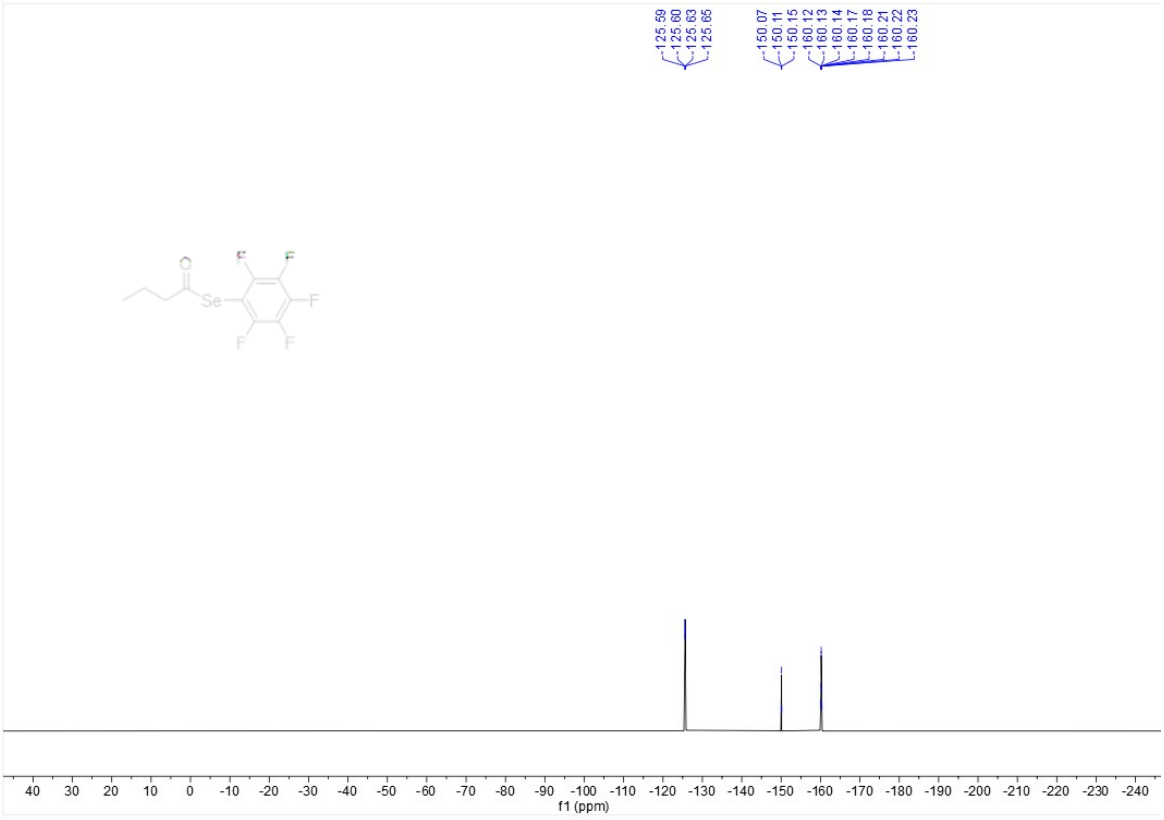
^{1}H NMR spectra of 14a ($CDCl_3$)



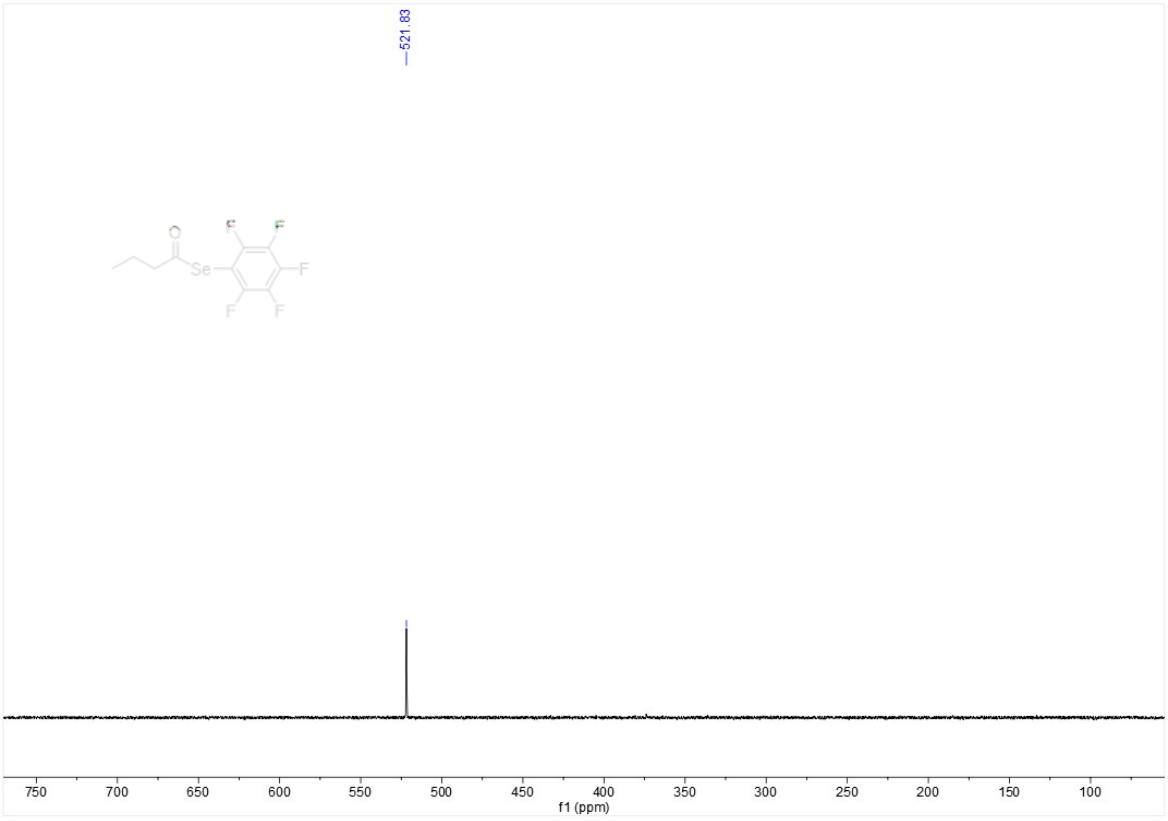
^{13}C NMR spectra of 14a ($CDCl_3$)



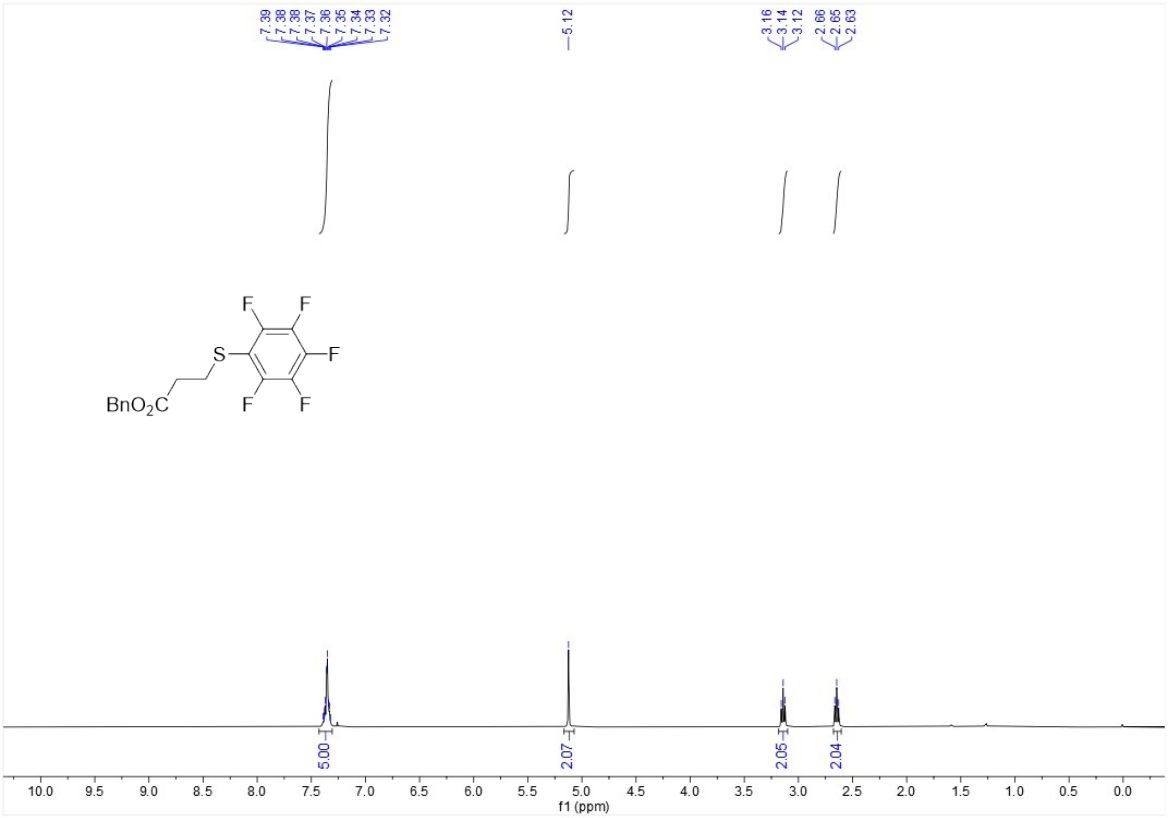
^{19}F NMR spectra of 14a ($CDCl_3$)



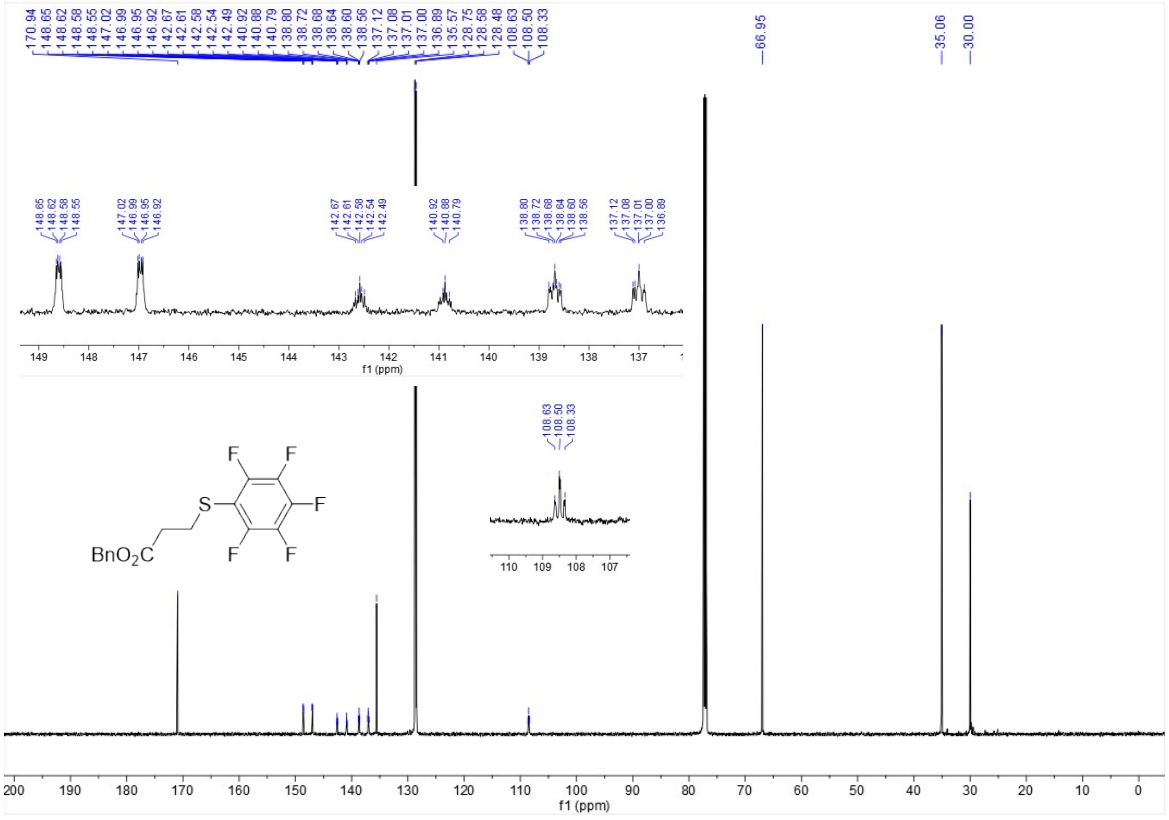
^{77}Se NMR spectra of 14a ($CDCl_3$)



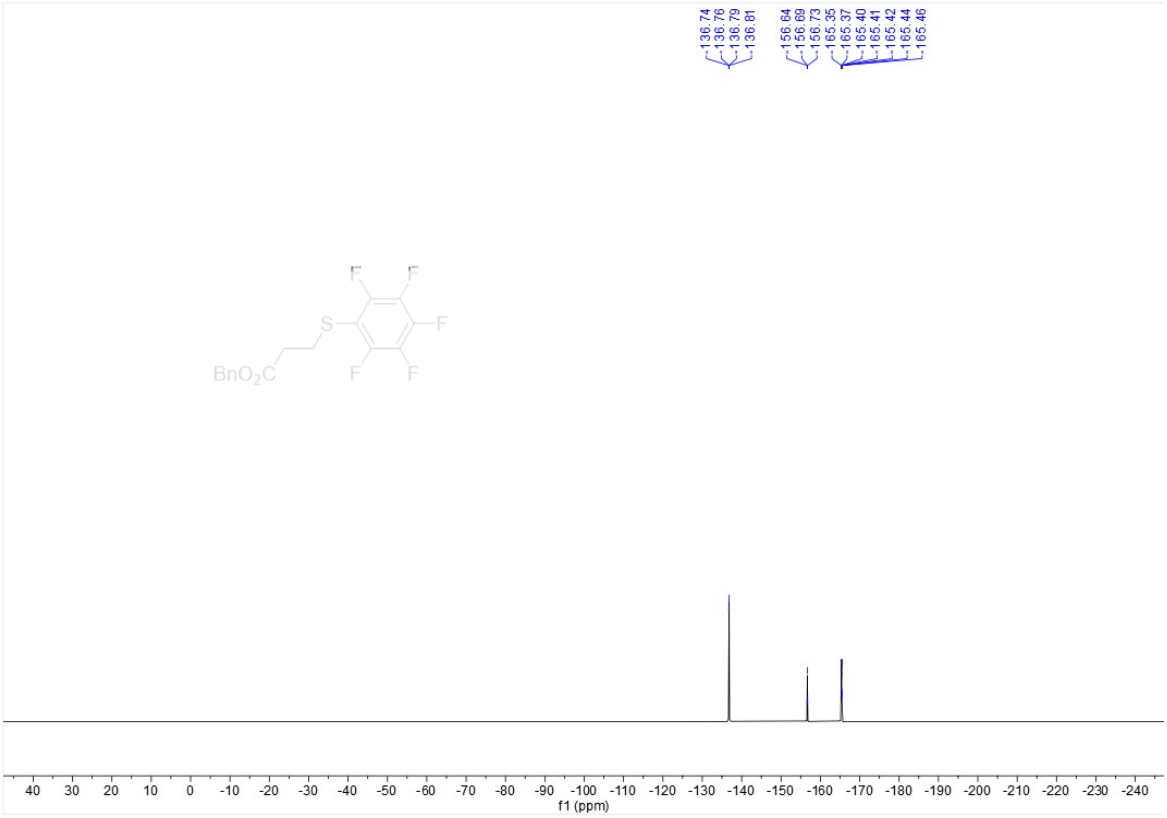
^{1}H NMR spectra of 15a ($CDCl_3$)



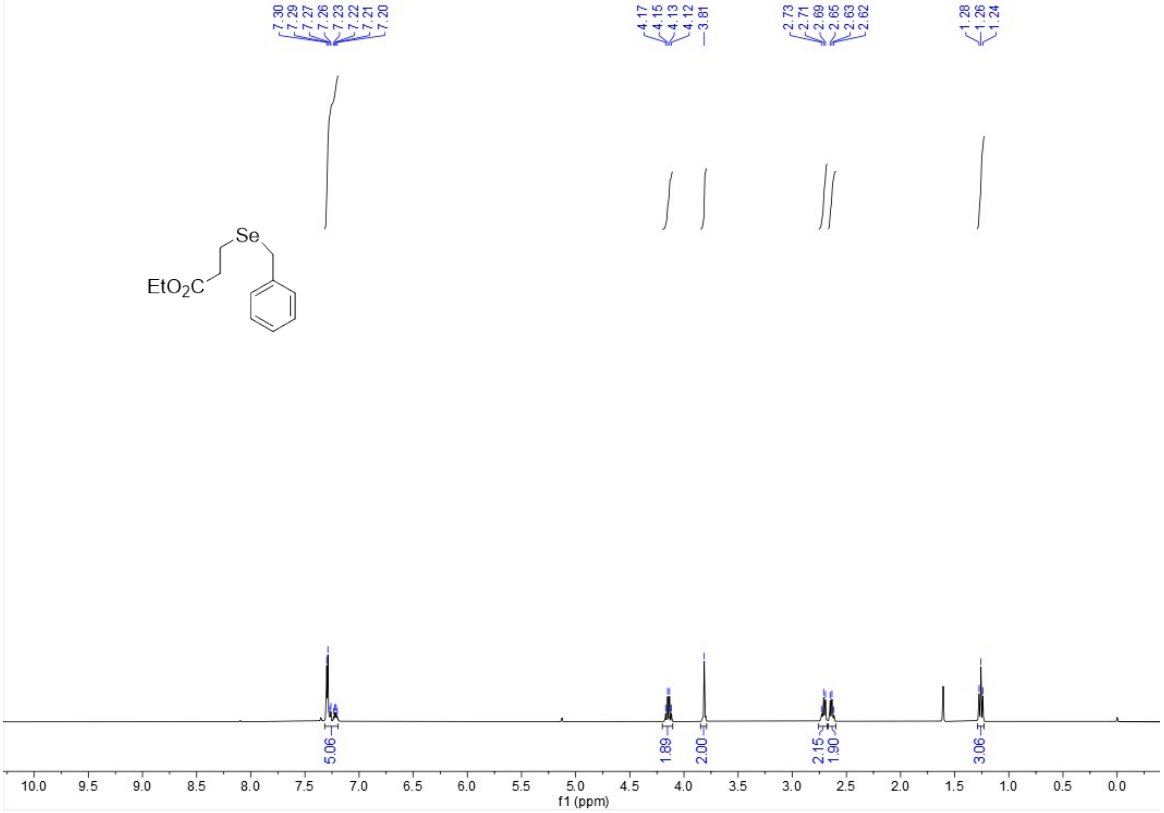
^{13}C NMR spectra of 15a ($CDCl_3$)



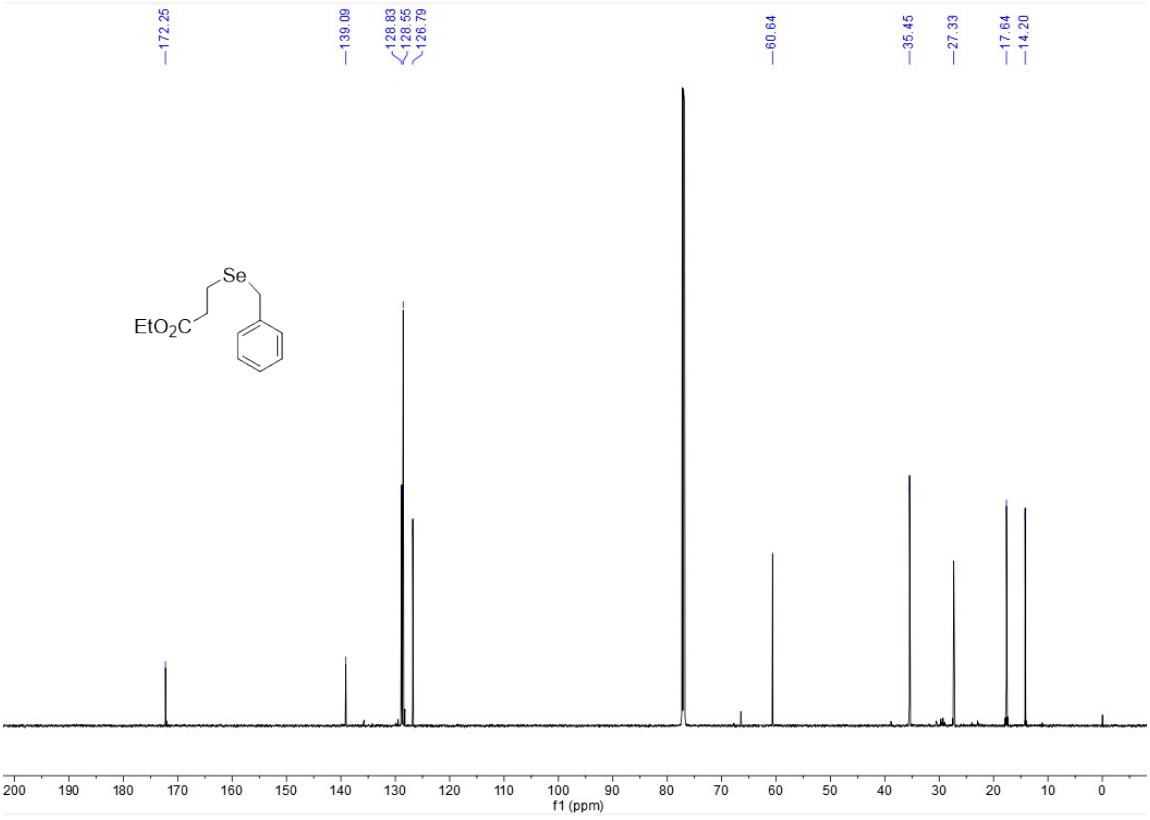
^{19}F NMR spectra of 15a ($CDCl_3$)



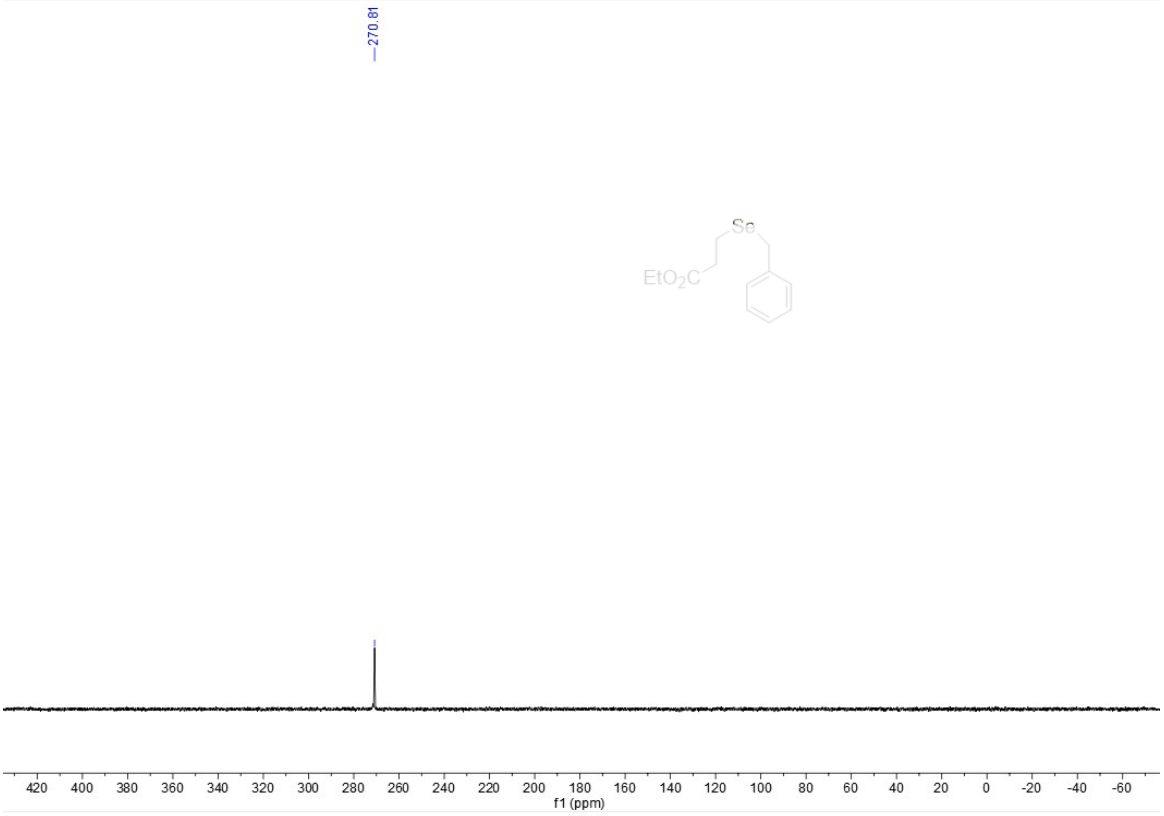
^{1}H NMR spectra of 17a ($CDCl_3$)



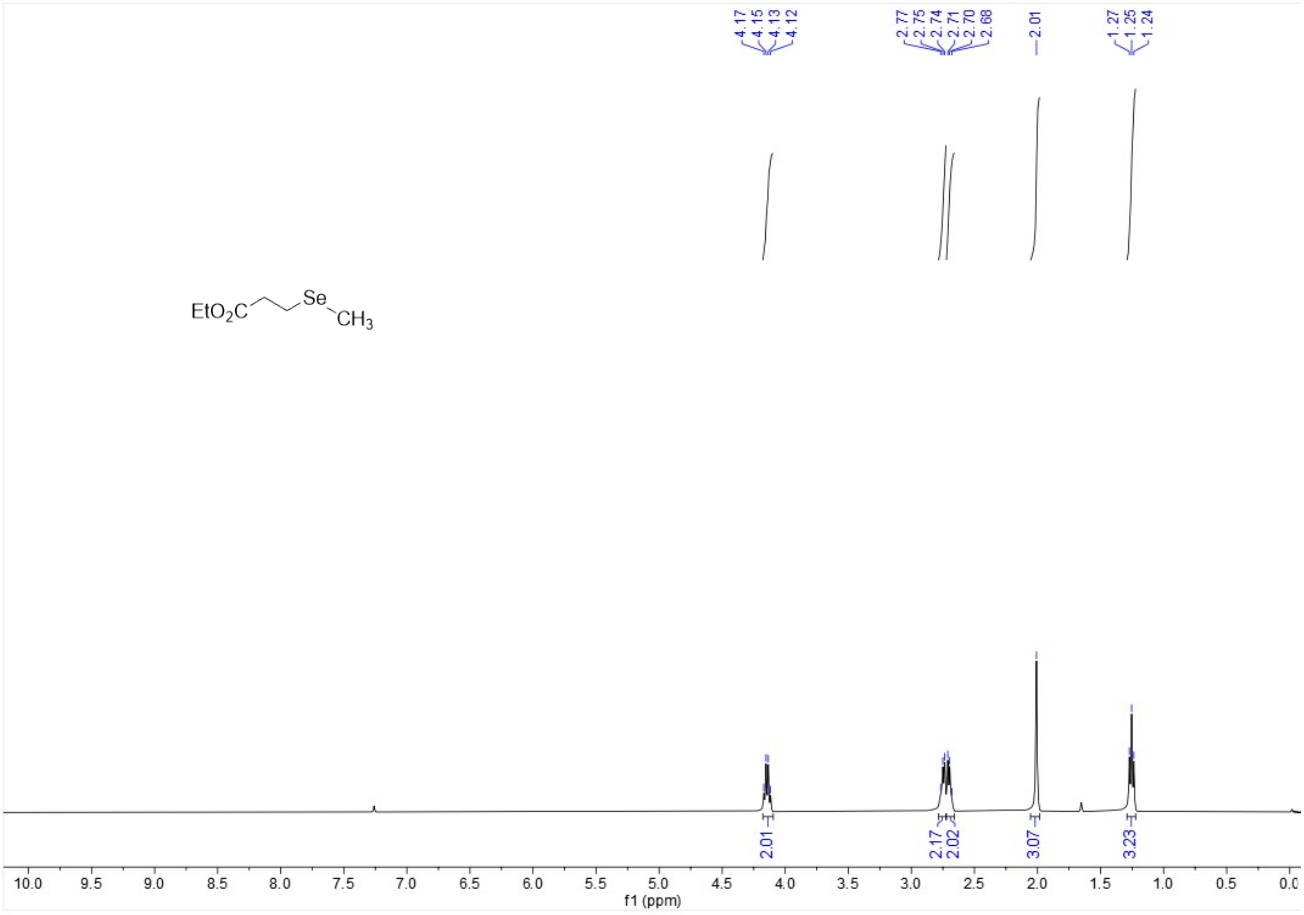
^{13}C NMR spectra of 17a ($CDCl_3$)



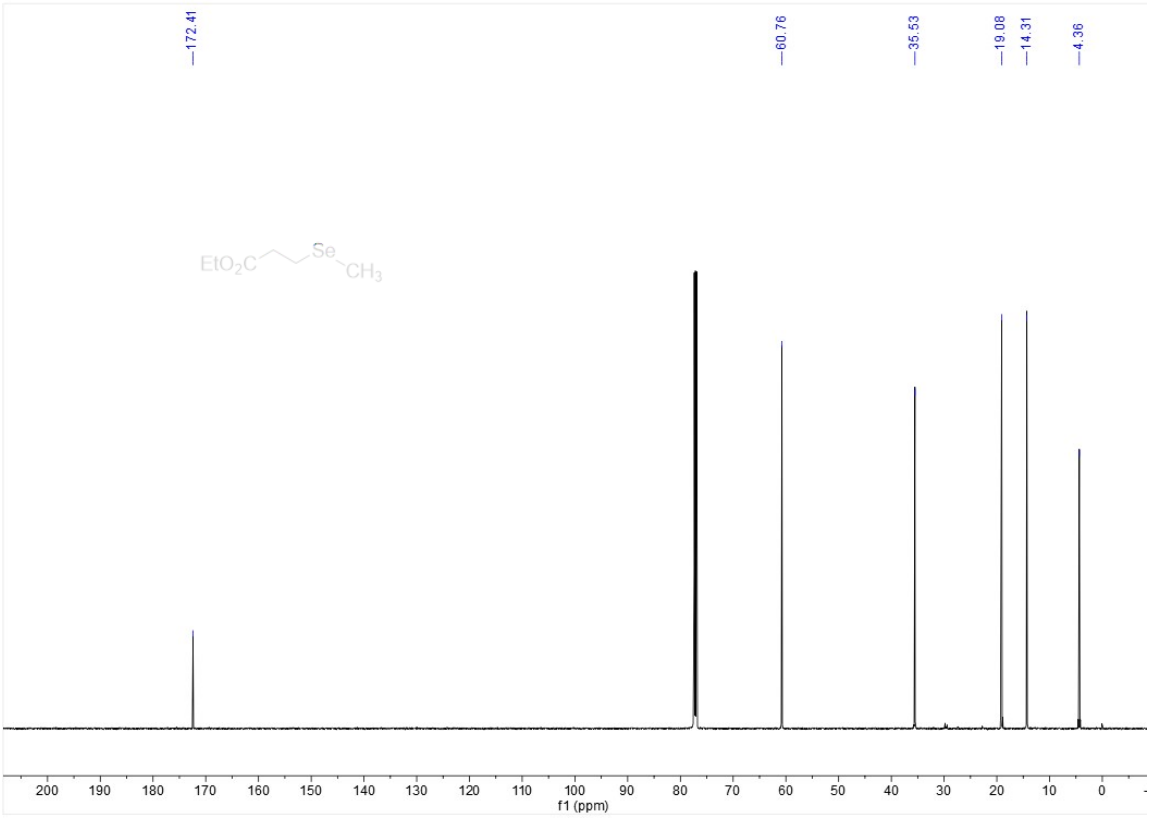
^{77}Se NMR spectra of 17a ($CDCl_3$)



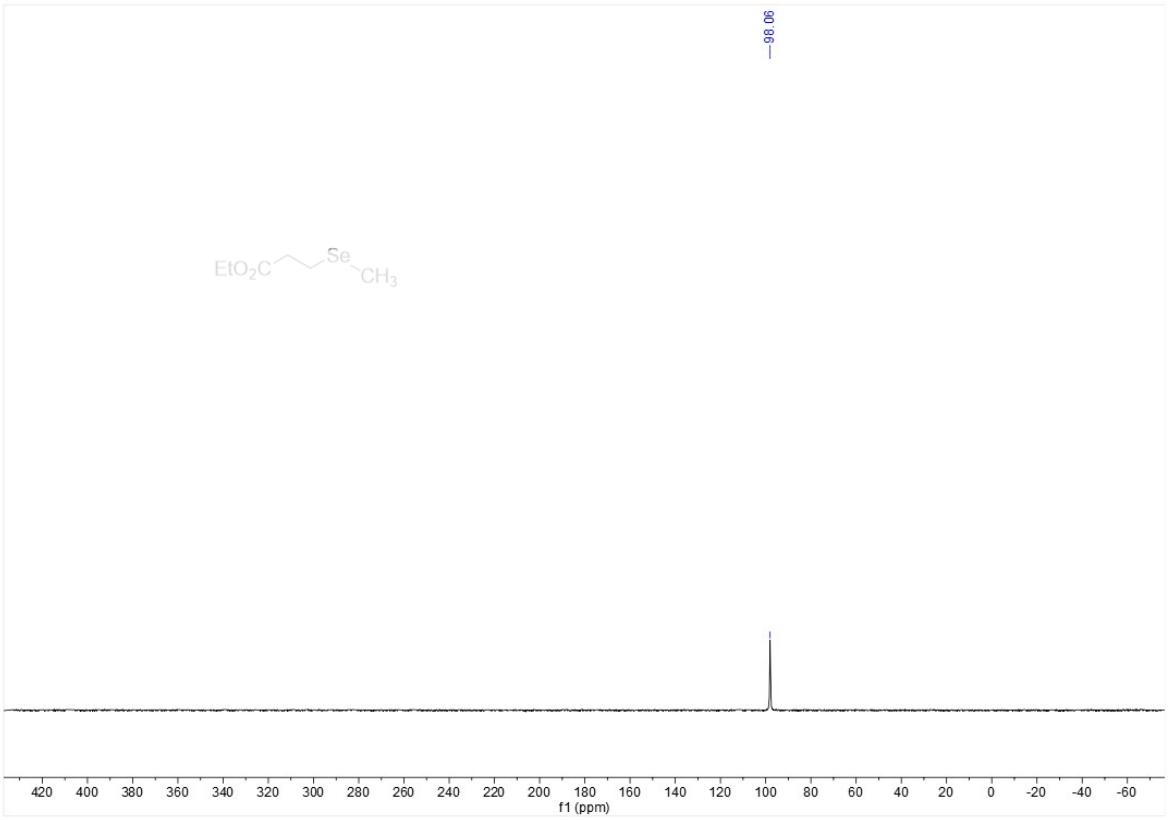
^{1}H NMR spectra of 17b ($CDCl_3$)



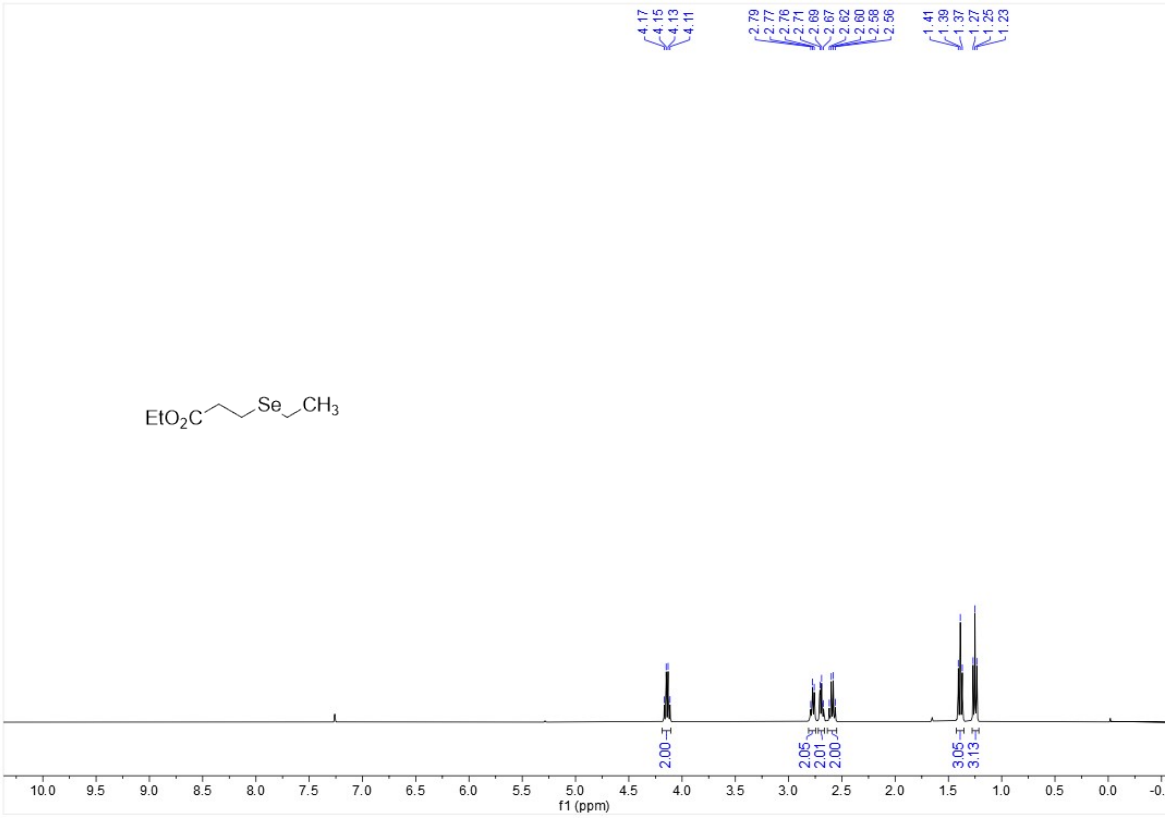
^{13}C NMR spectra of 17b ($CDCl_3$)



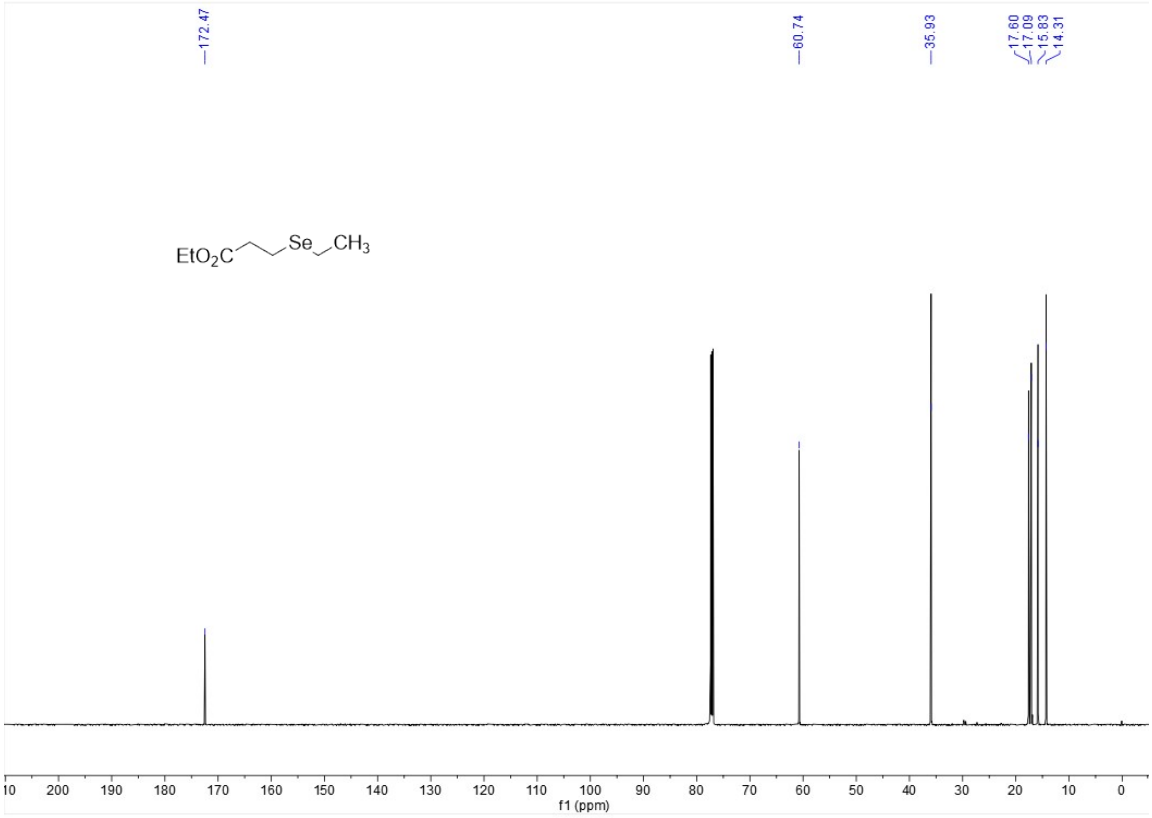
^{77}Se NMR spectra of 17b ($CDCl_3$)



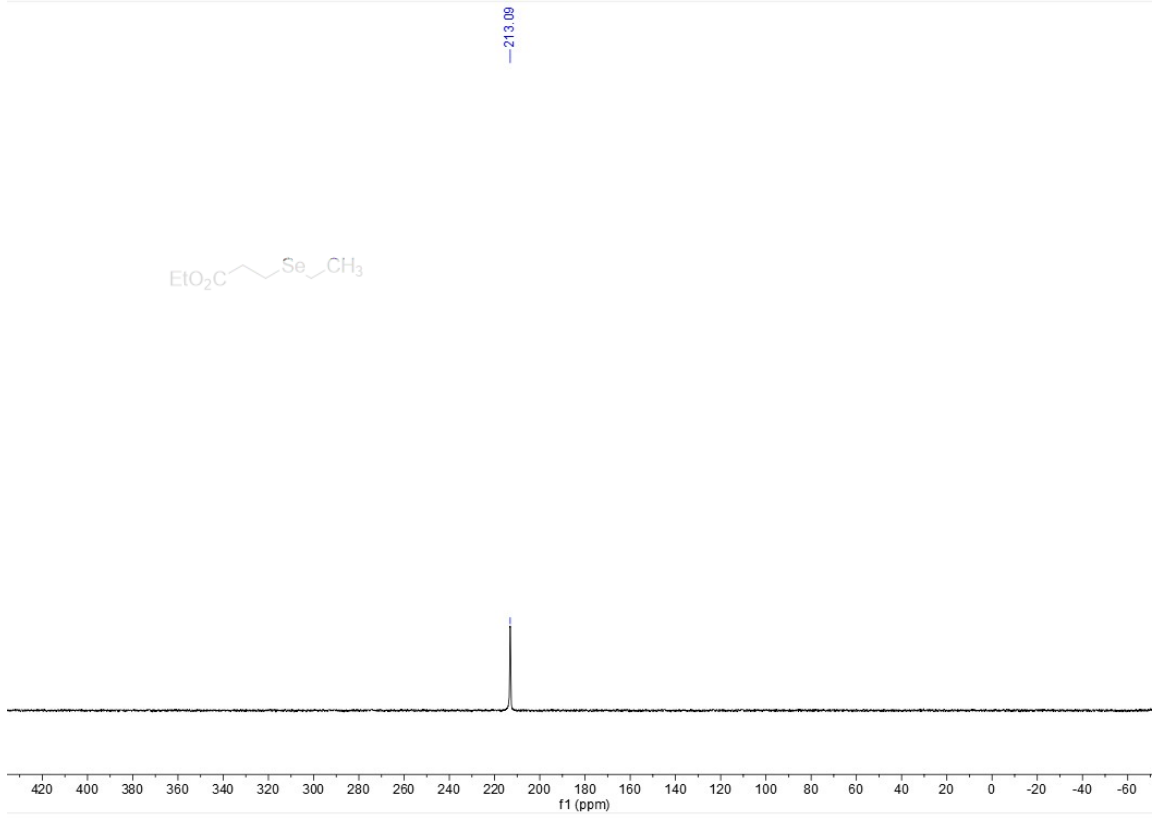
^{1}H NMR spectra of 17c ($CDCl_3$)



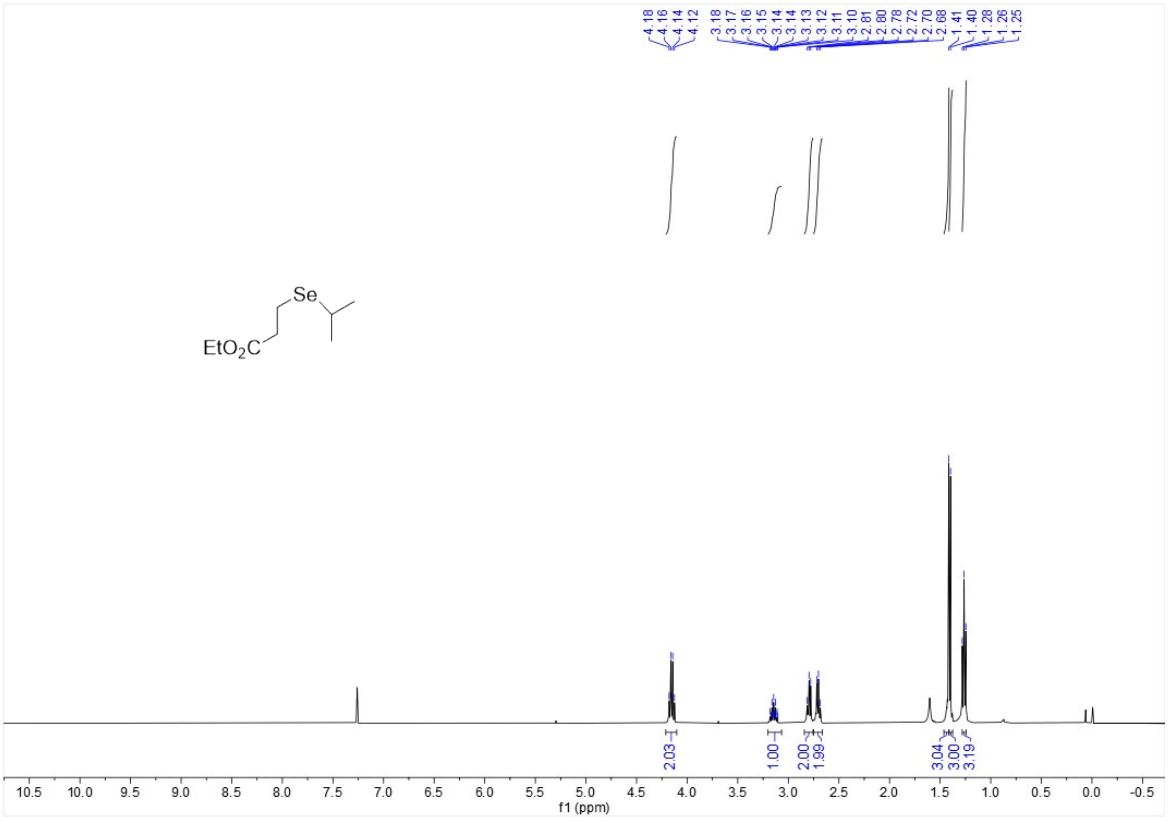
^{13}C NMR spectra of 17c ($CDCl_3$)



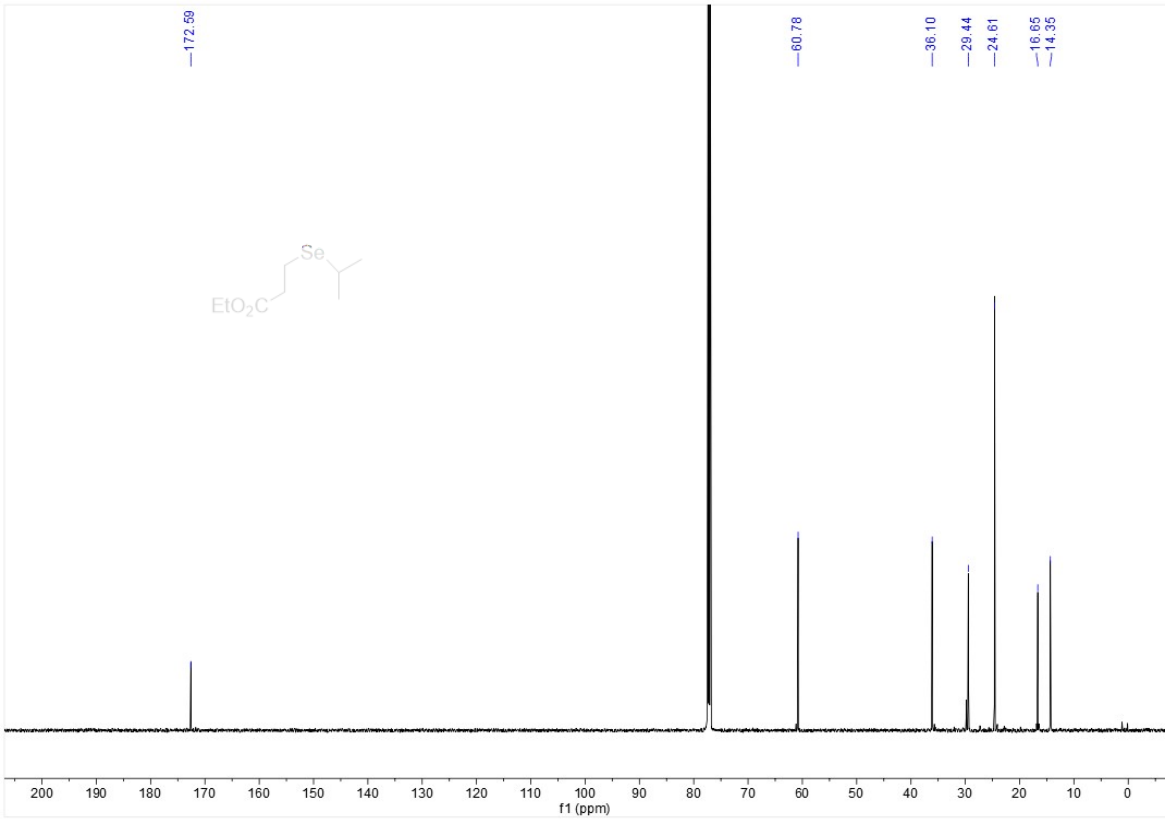
^{77}Se NMR spectra of 17c ($CDCl_3$)



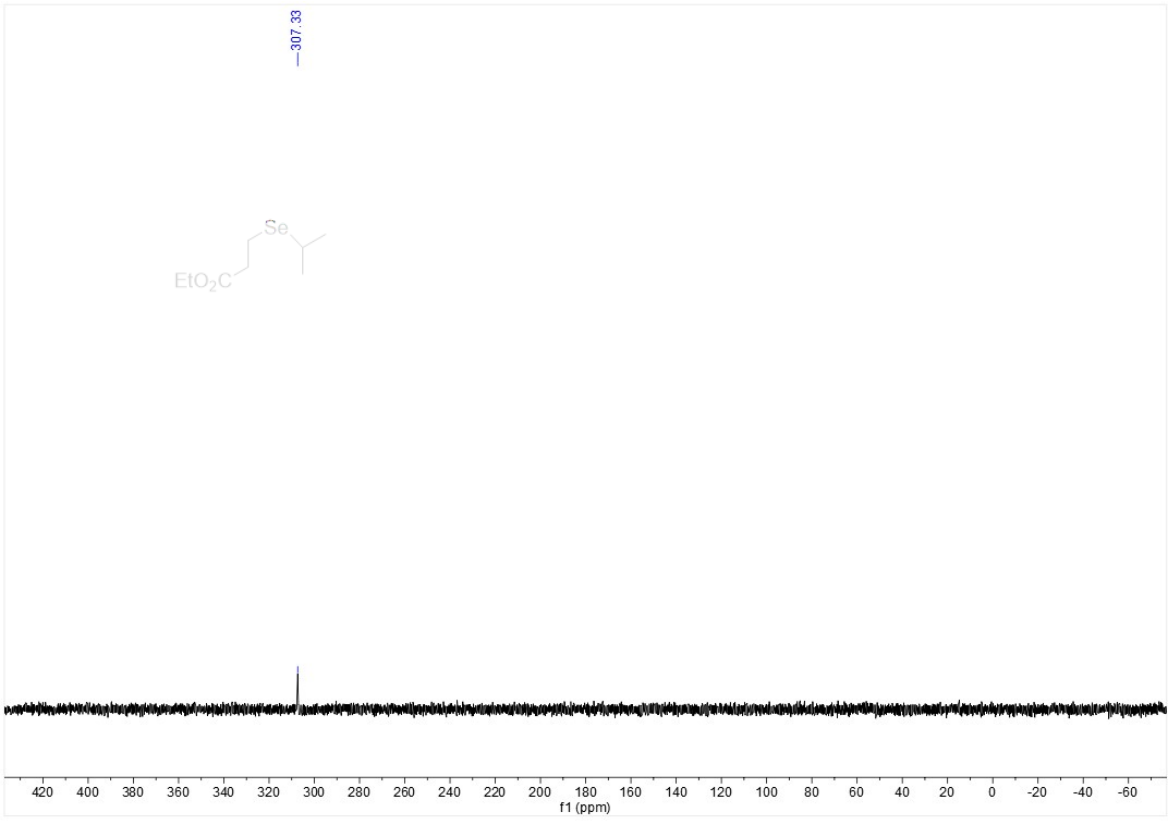
^{1}H NMR spectra of 17d ($CDCl_3$)



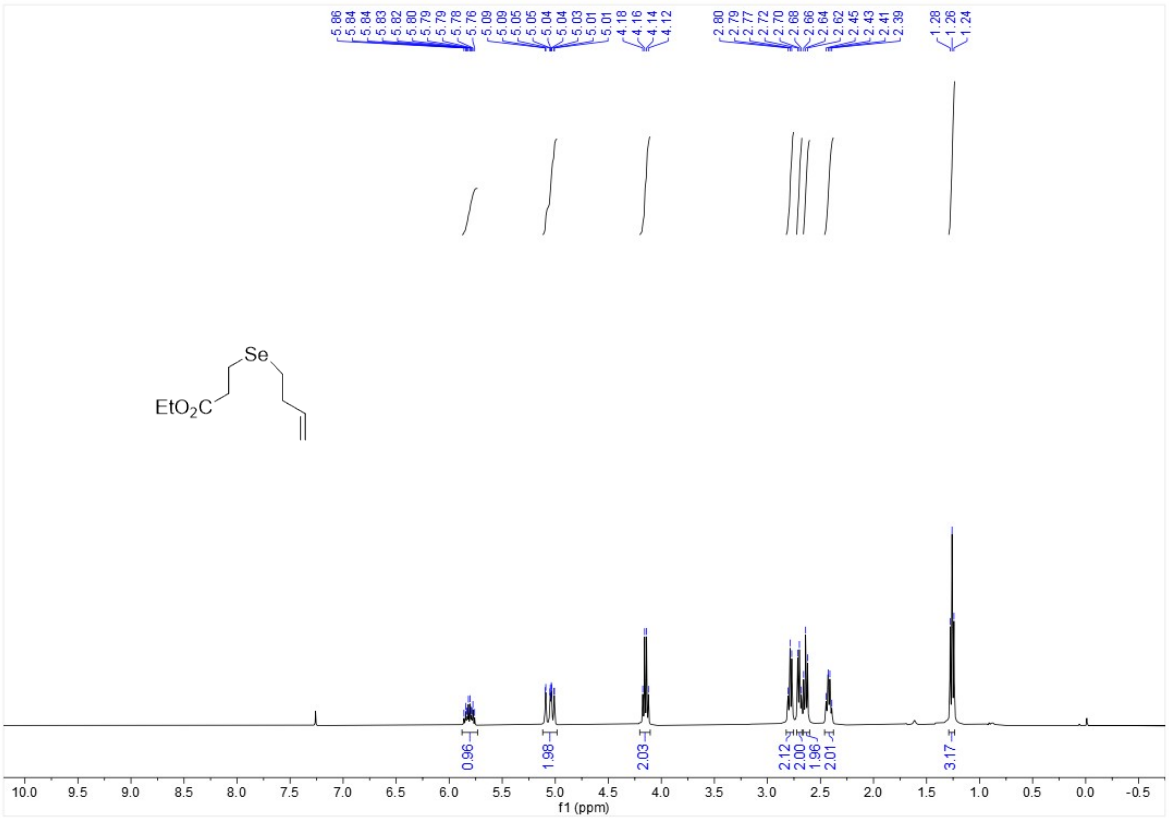
^{13}C NMR spectra of 17d ($CDCl_3$)



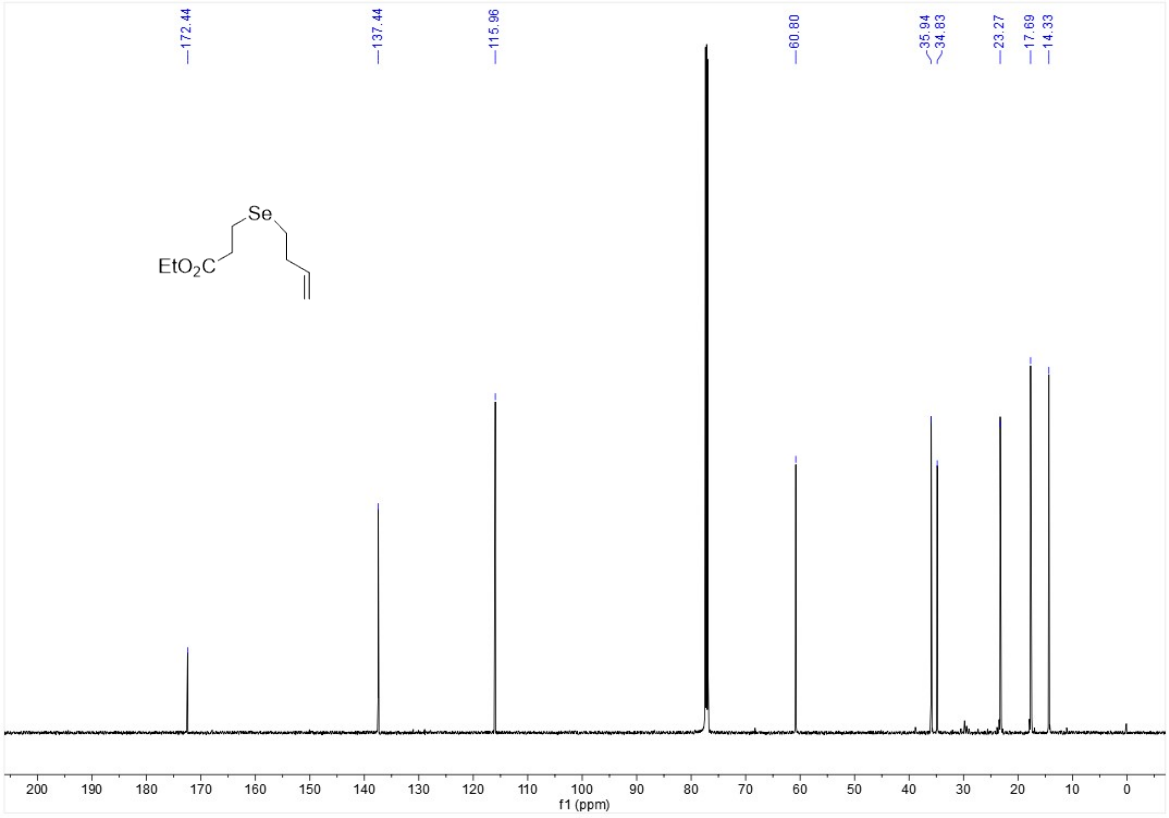
^{77}Se NMR spectra of 17d ($CDCl_3$)



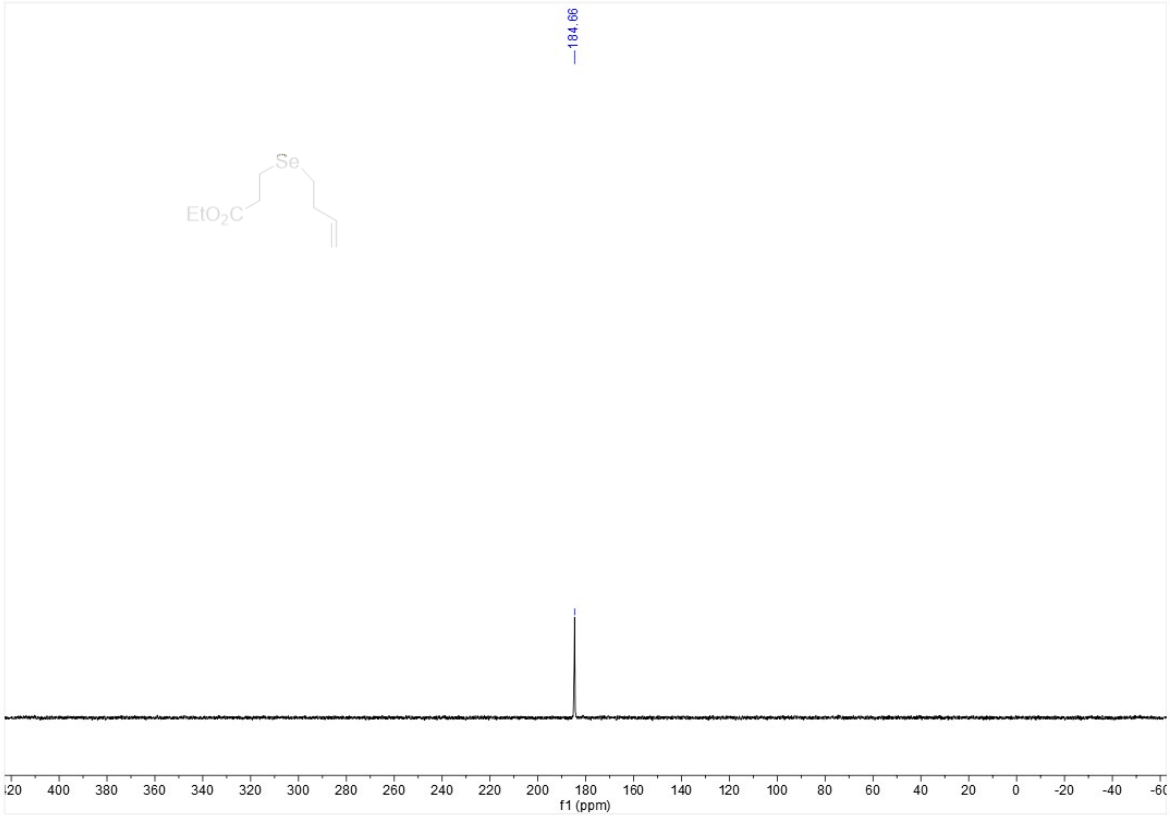
^{1}H NMR spectra of 17e ($CDCl_3$)



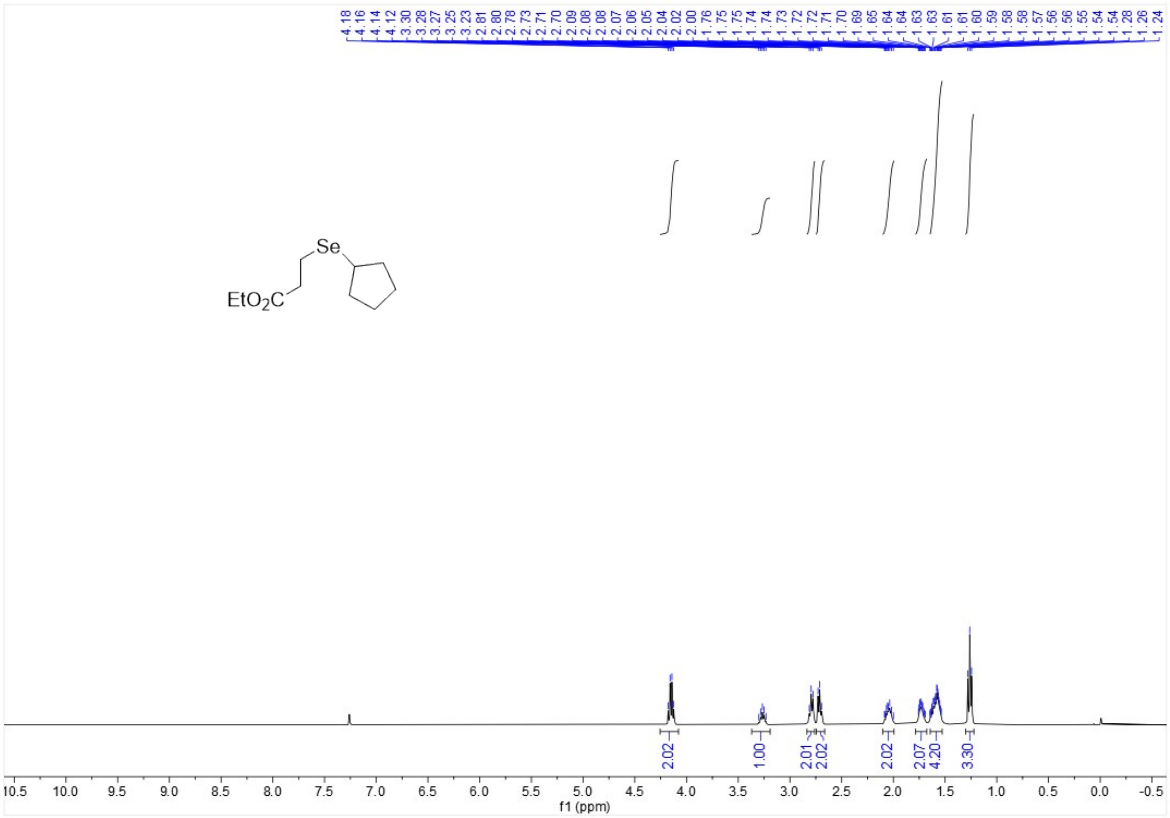
^{13}C NMR spectra of 17e ($CDCl_3$)



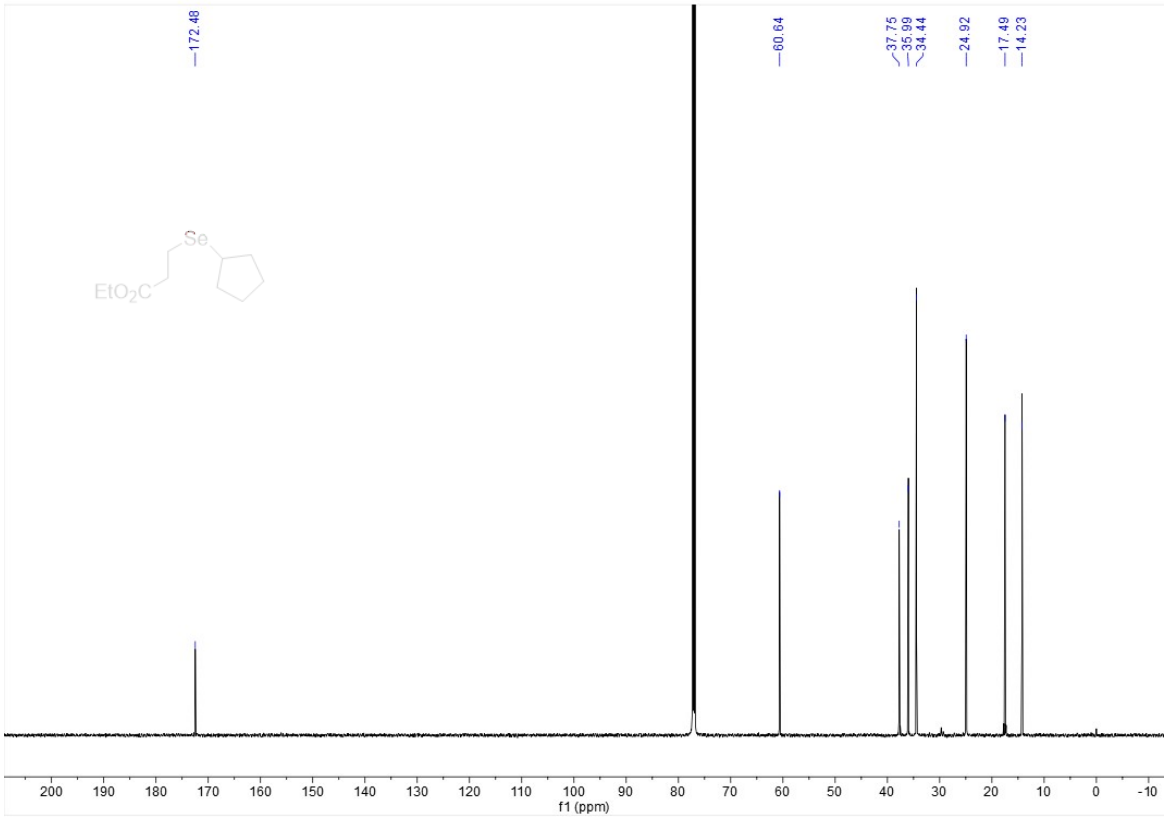
^{77}Se NMR spectra of 17e ($CDCl_3$)



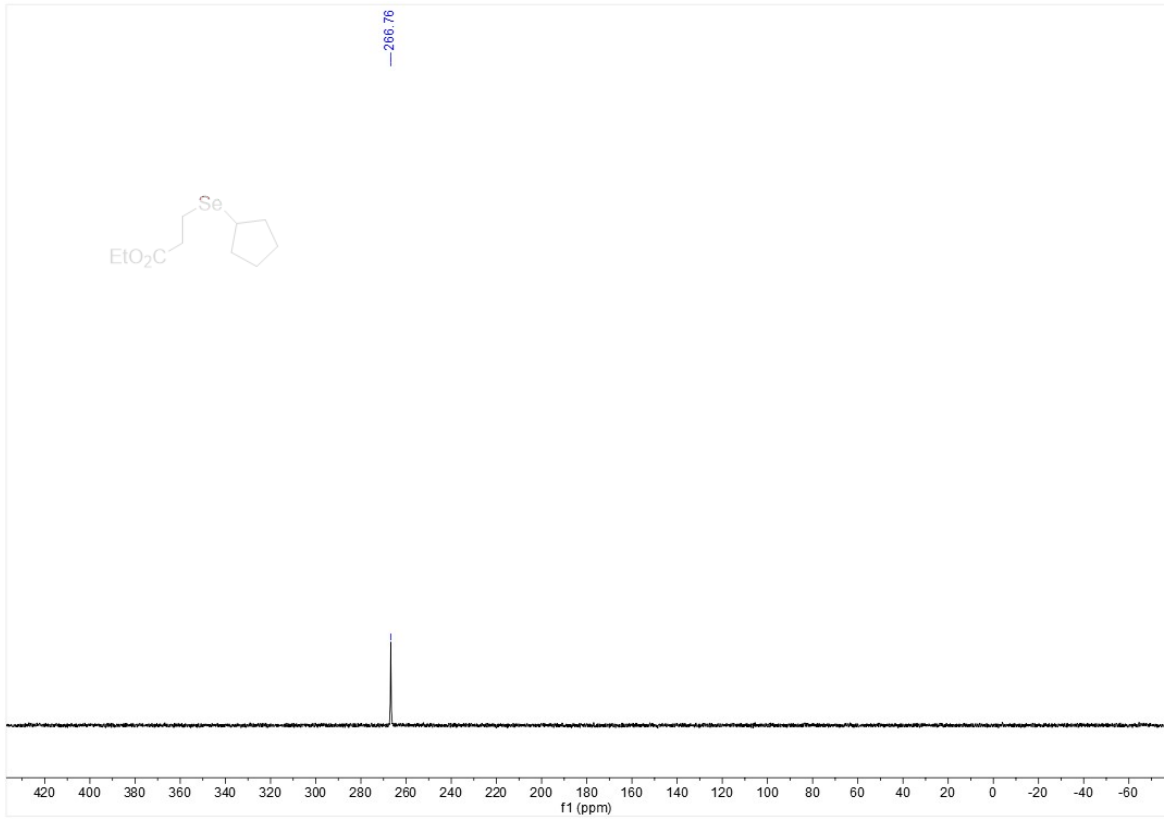
^{1}H NMR spectra of 17f ($CDCl_3$)



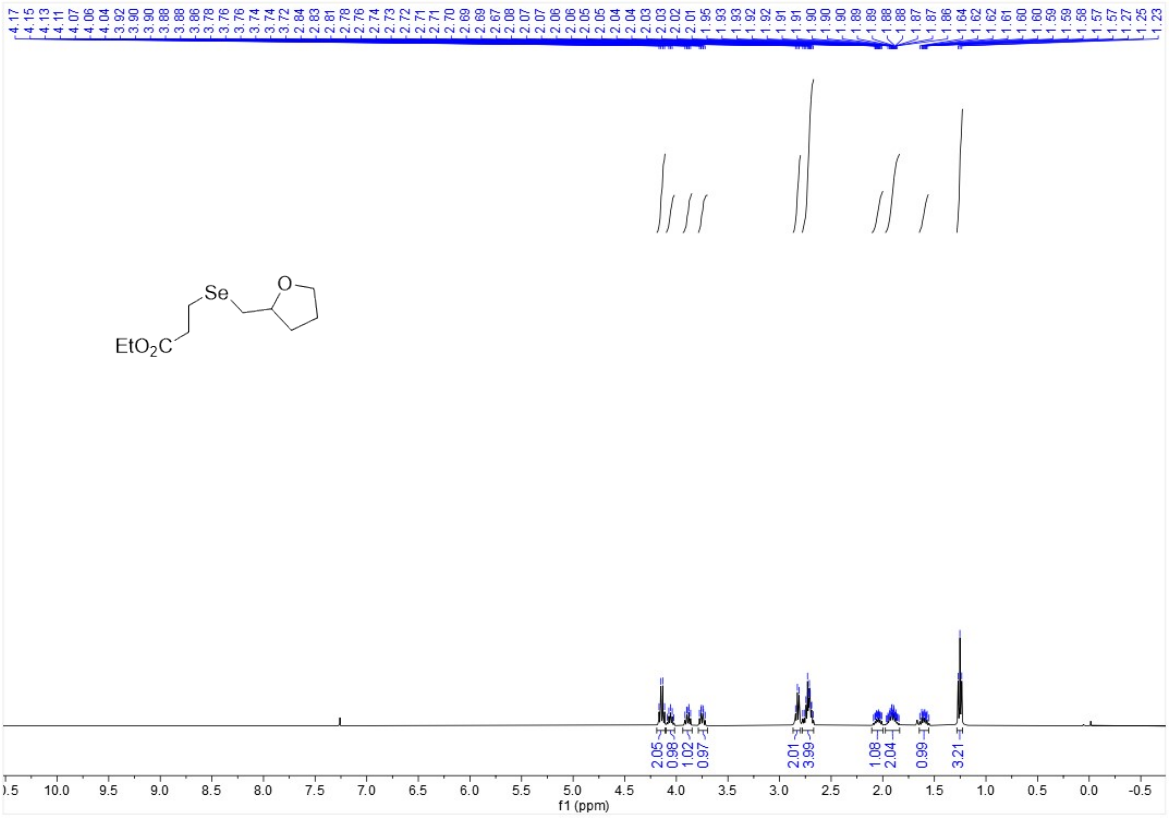
^{13}C NMR spectra of 17f ($CDCl_3$)



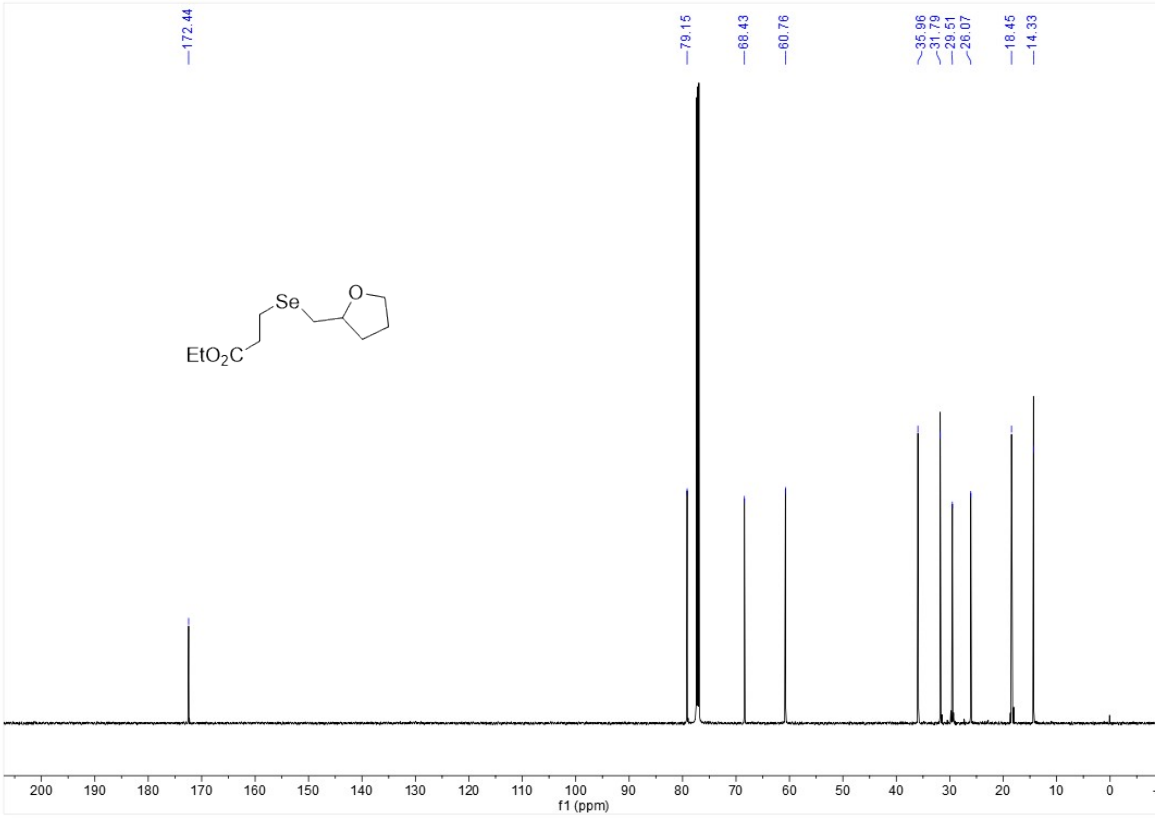
^{77}Se NMR spectra of 17f ($CDCl_3$)



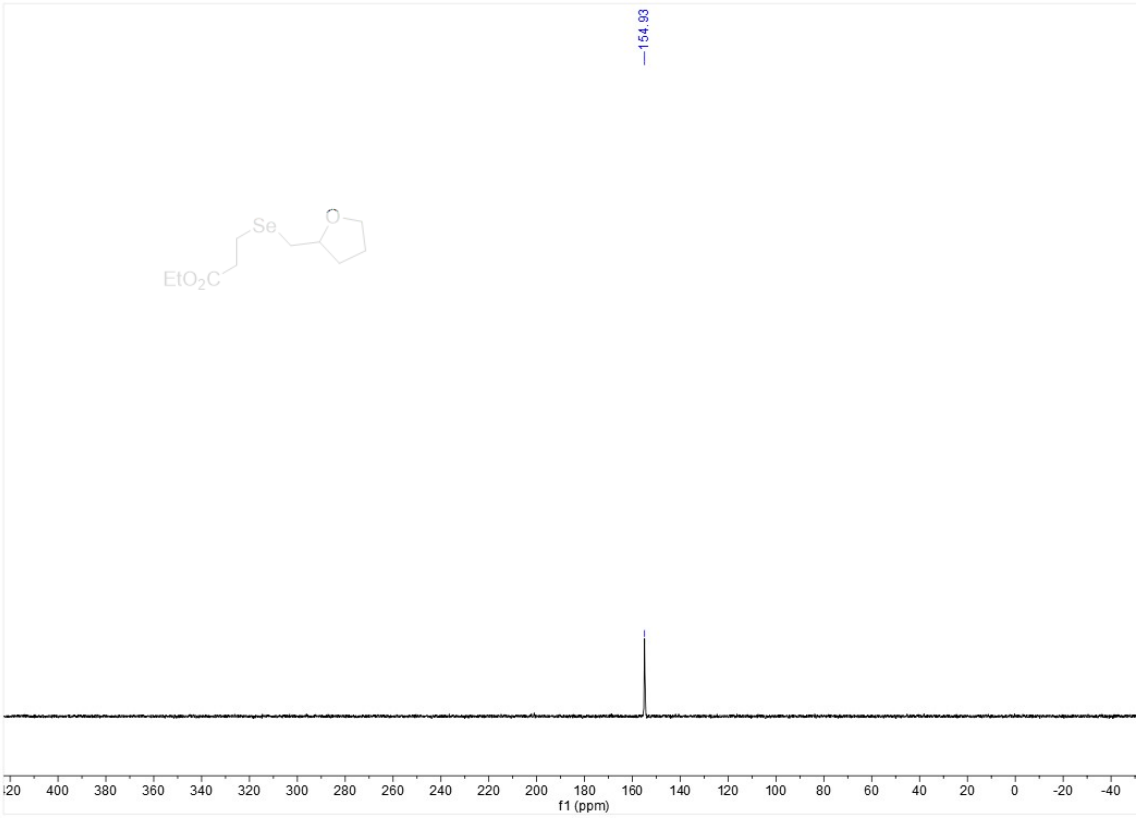
^{1}H NMR spectra of 17g ($CDCl_3$)



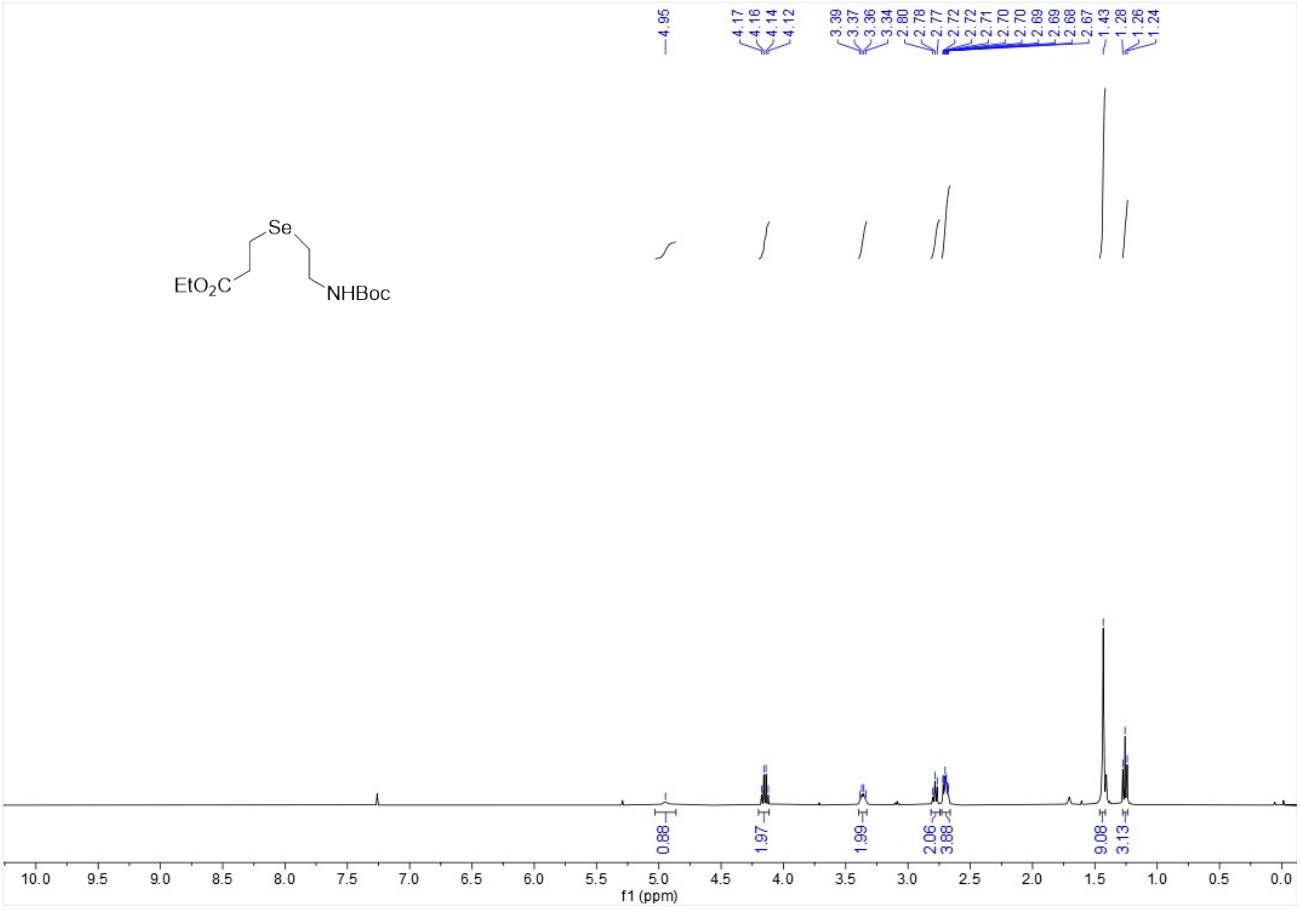
^{13}C NMR spectra of 17g ($CDCl_3$)



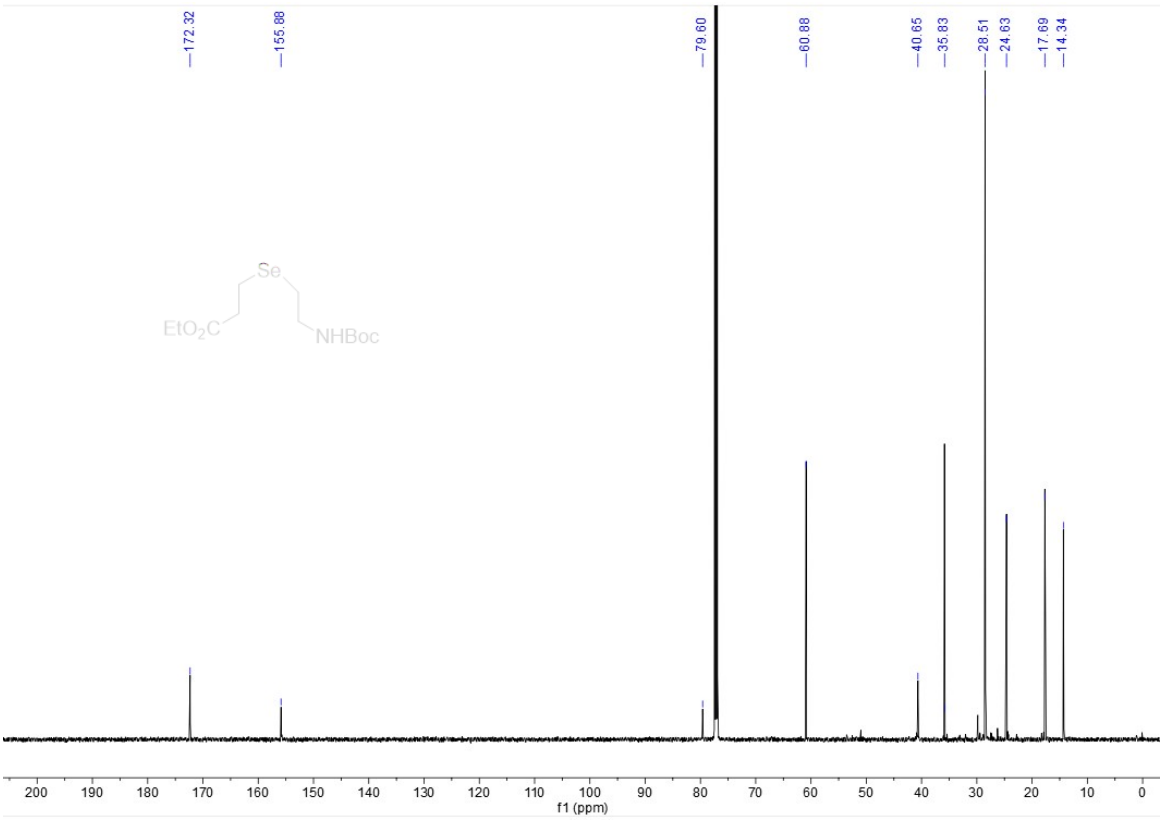
^{77}Se NMR spectra of 17g ($CDCl_3$)



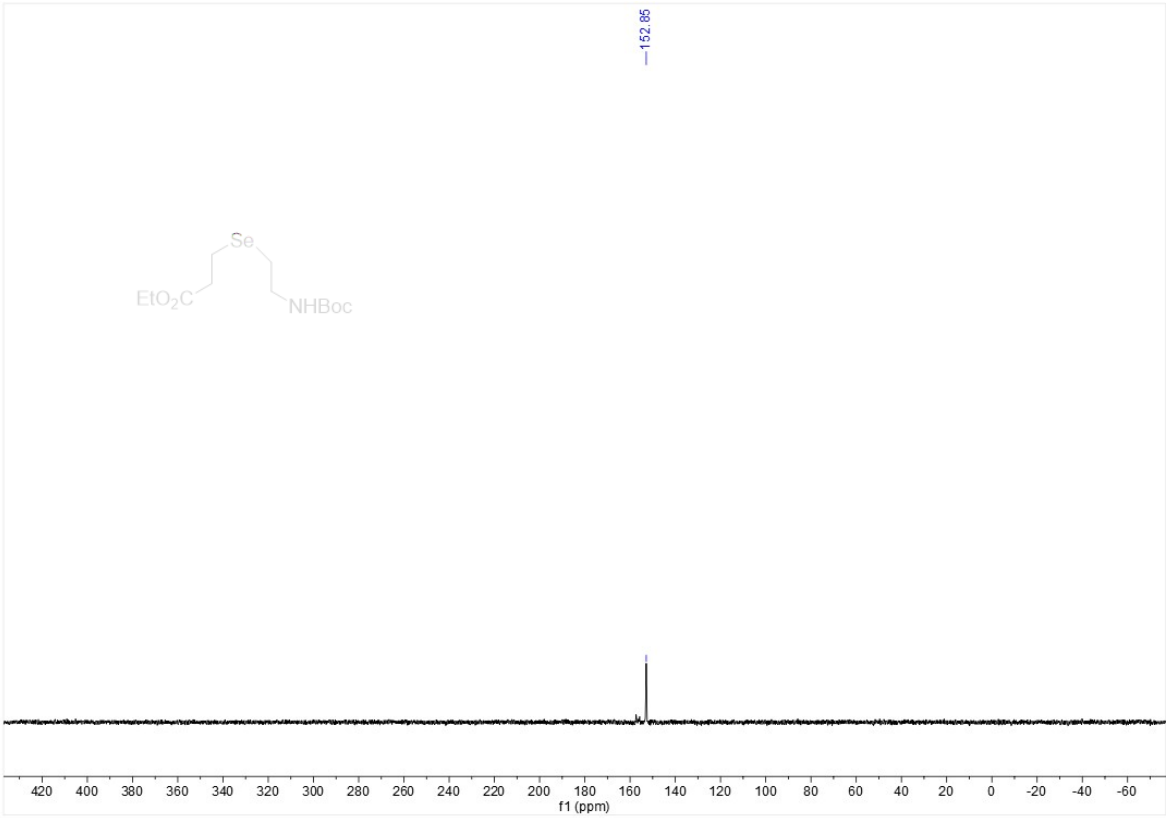
^{1}H NMR spectra of 17h ($CDCl_3$)



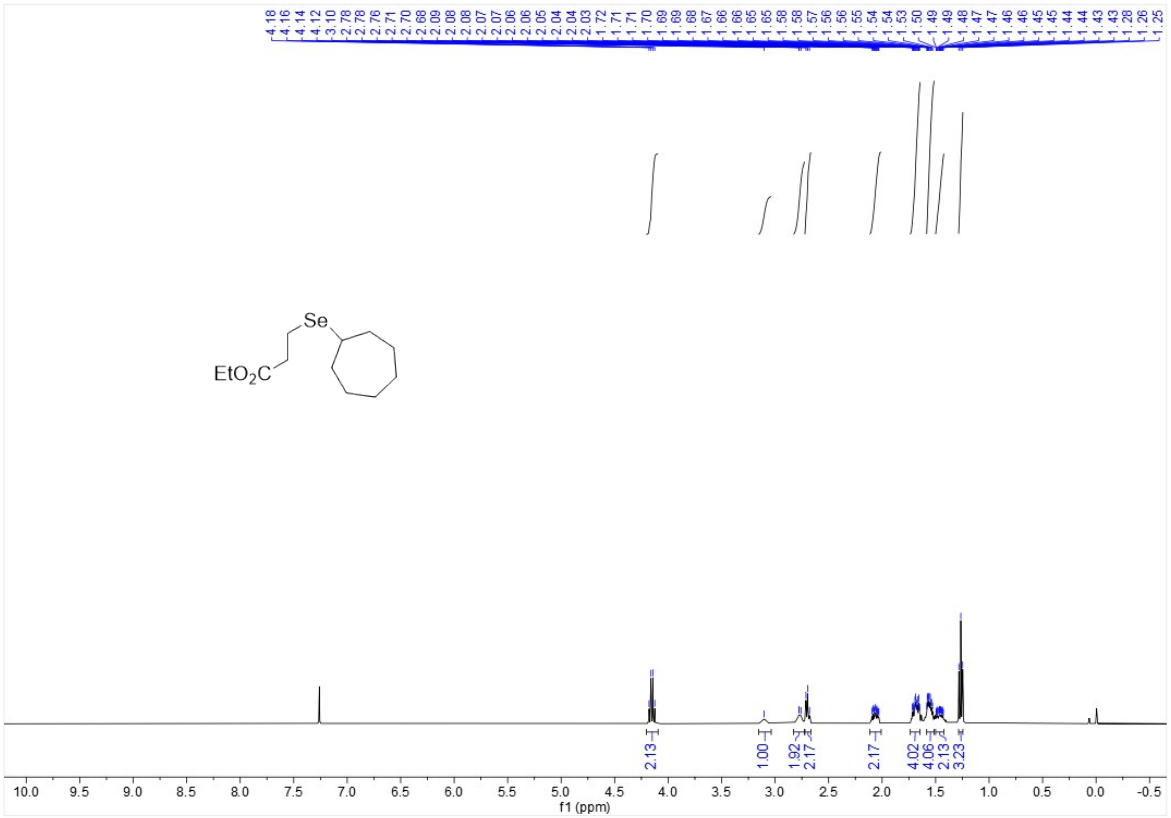
^{13}C NMR spectra of 17h ($CDCl_3$)



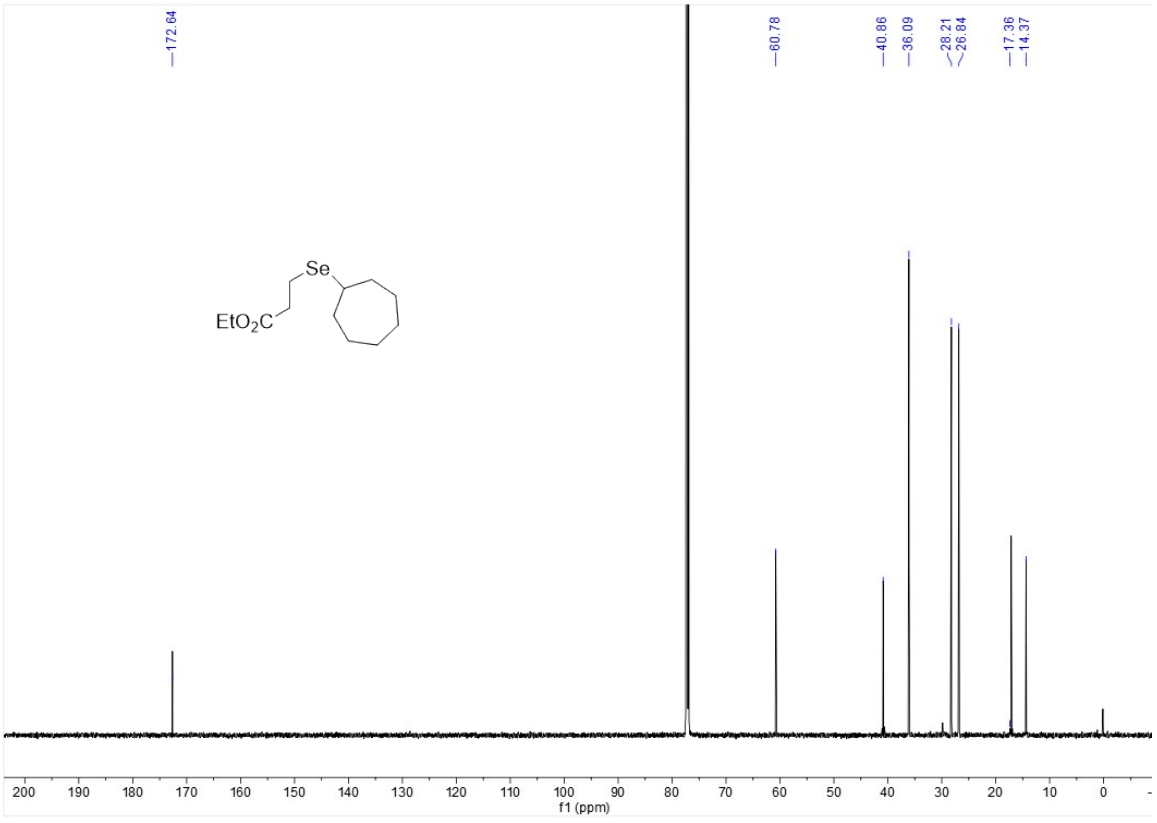
^{77}Se NMR spectra of 17h ($CDCl_3$)



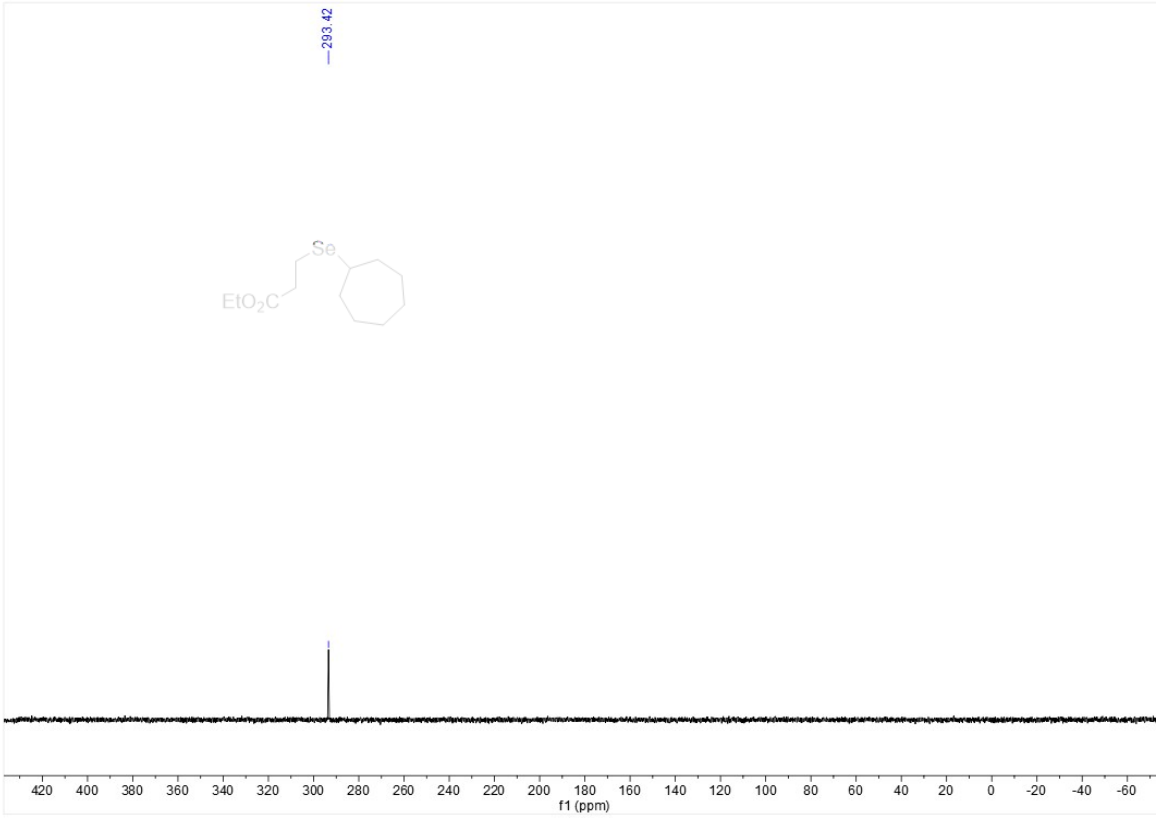
^{1}H NMR spectra of 17i ($CDCl_3$)



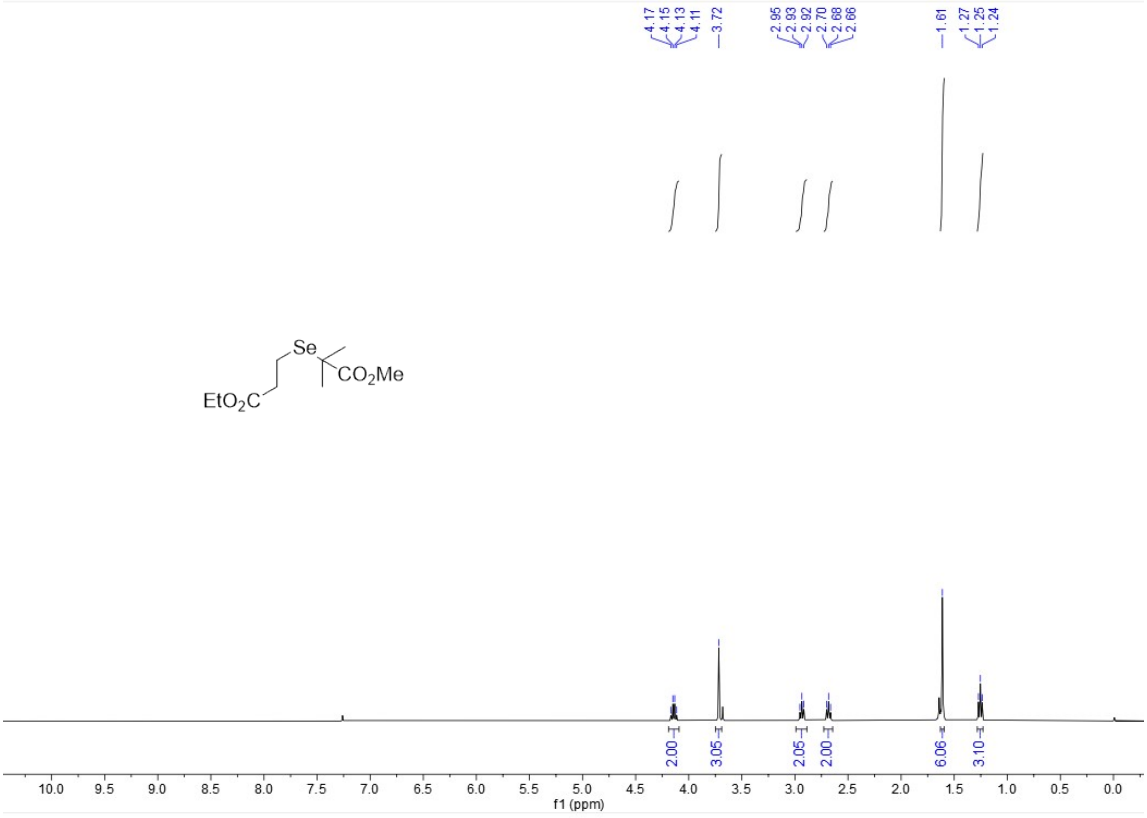
^{13}C NMR spectra of 17i ($CDCl_3$)



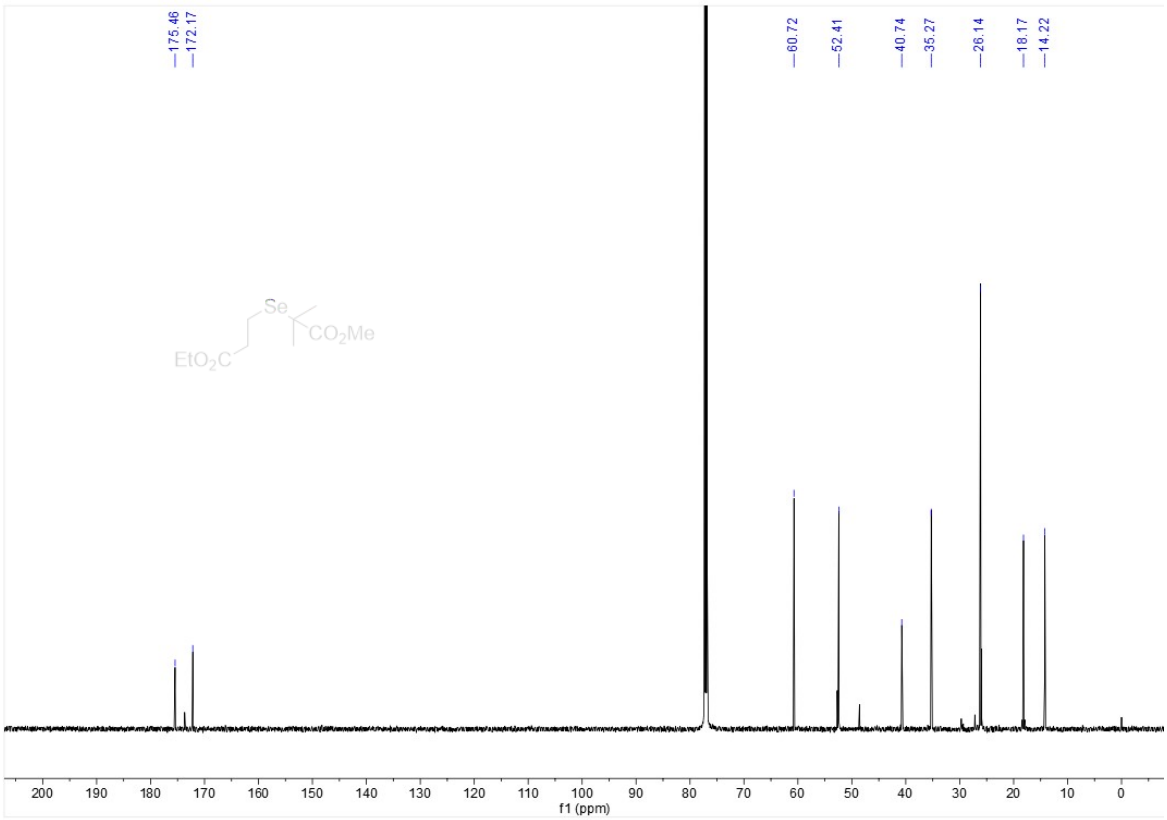
^{77}Se NMR spectra of 17i ($CDCl_3$)



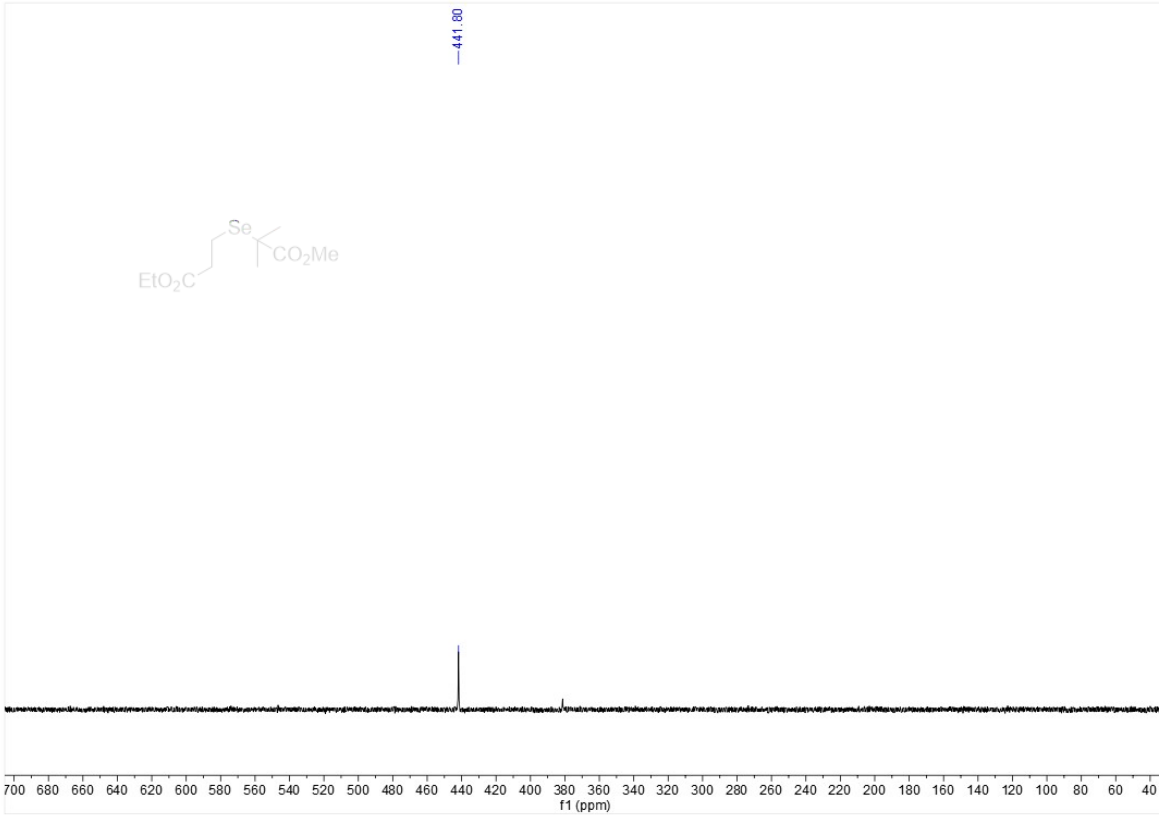
^{1}H NMR spectra of 17j ($CDCl_3$)



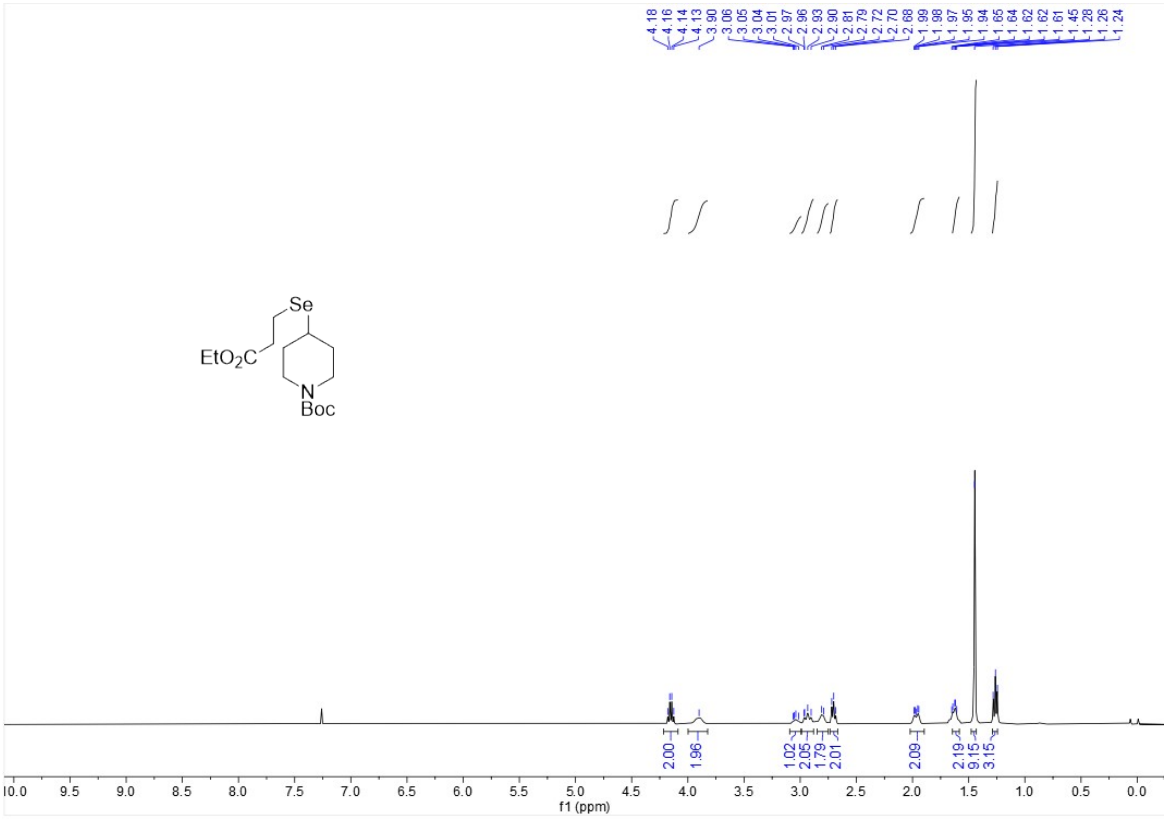
^{13}C NMR spectra of 17j ($CDCl_3$)



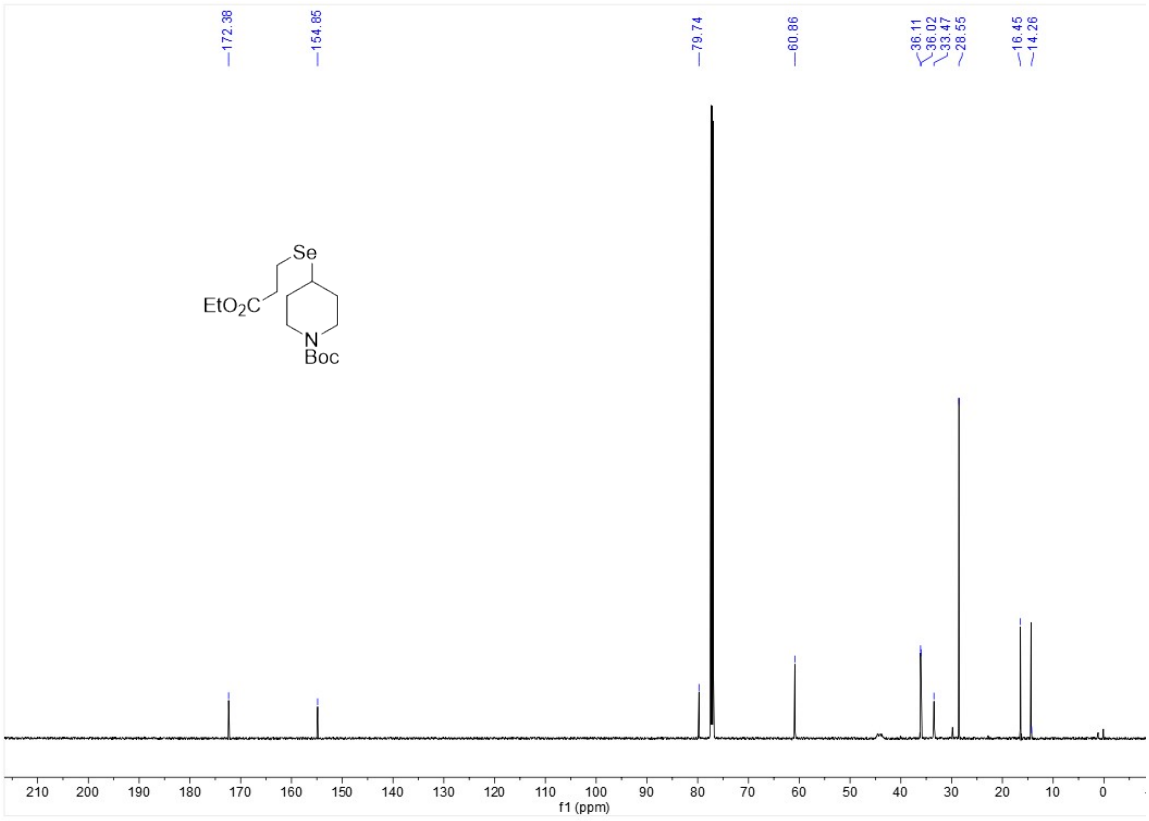
^{77}Se NMR spectra of 17j ($CDCl_3$)



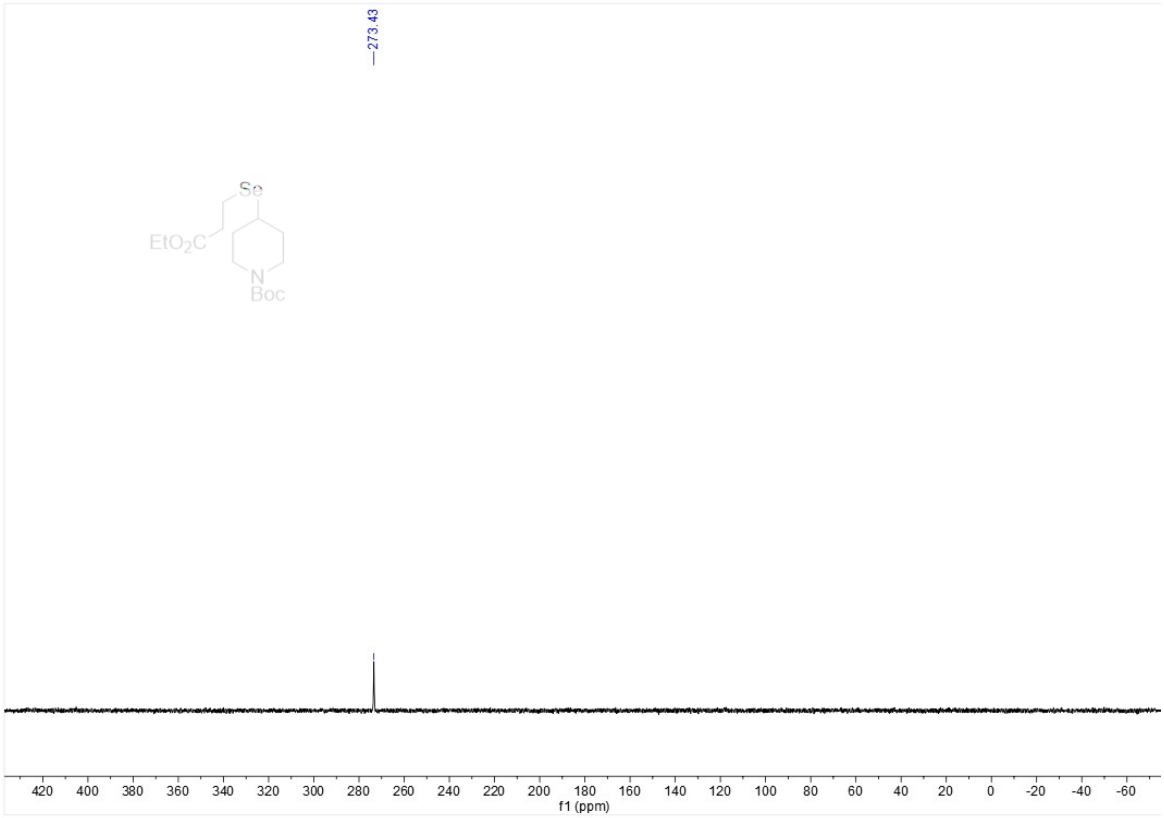
^{1}H NMR spectra of 17k ($CDCl_3$)



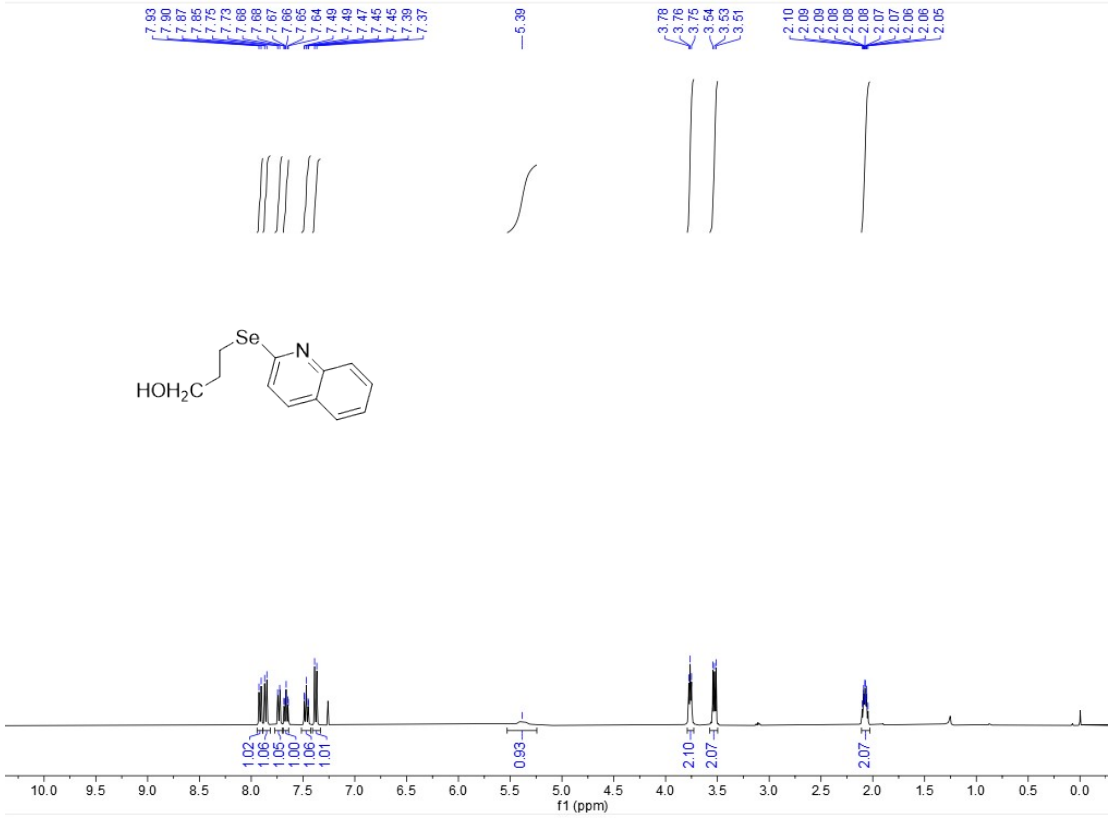
^{13}C NMR spectra of 17k ($CDCl_3$)



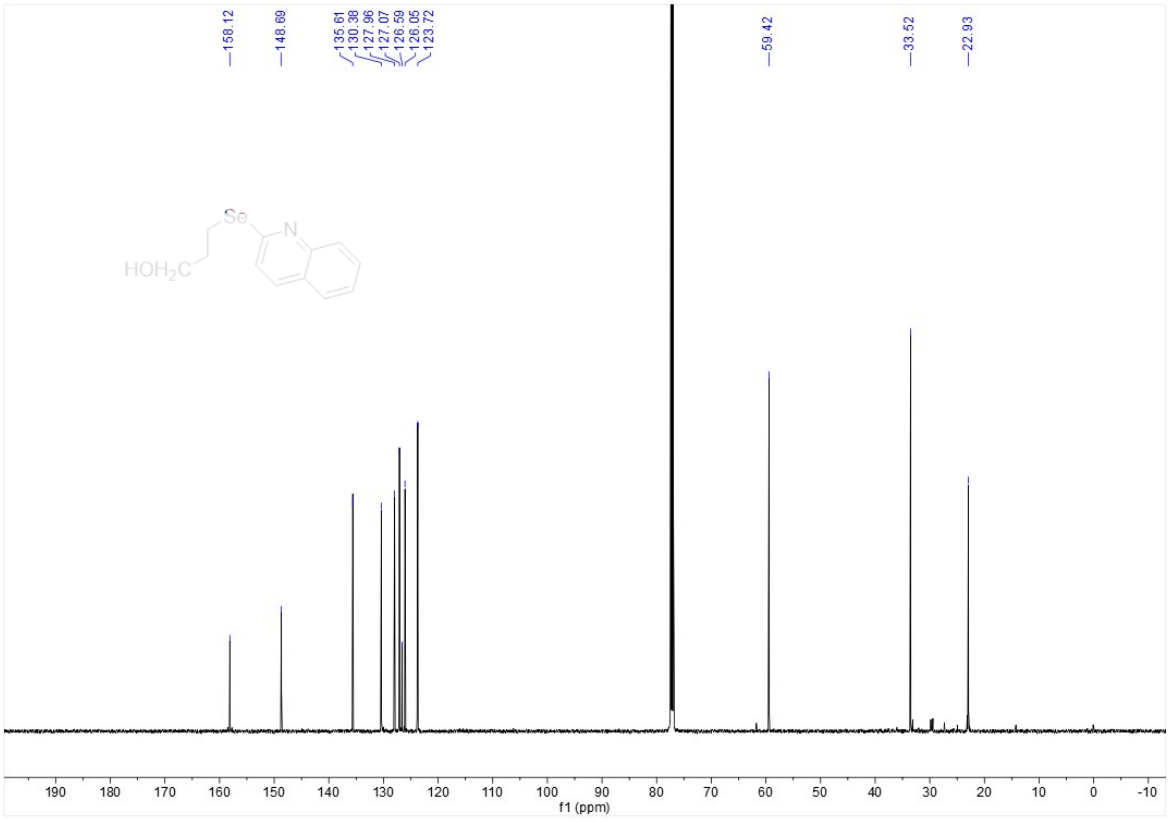
^{77}Se NMR spectra of 17k ($CDCl_3$)



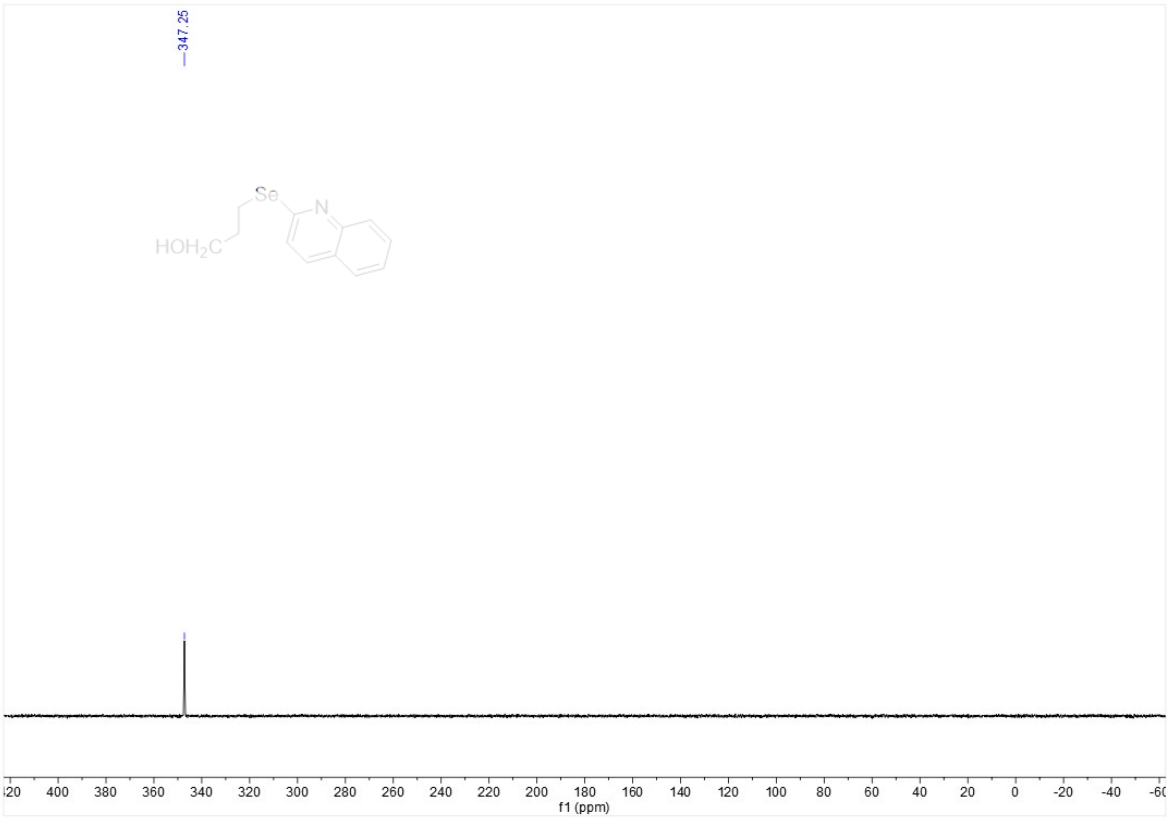
^{1}H NMR spectra of 17l ($CDCl_3$)



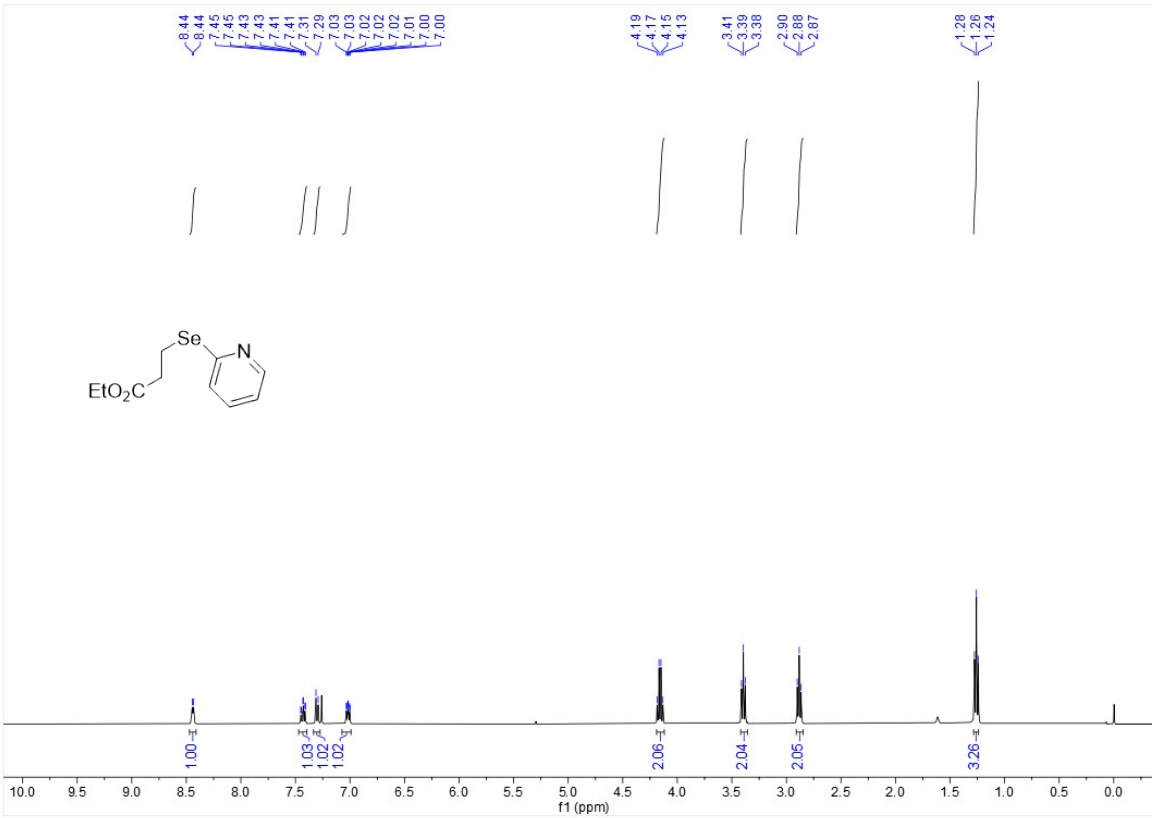
^{13}C NMR spectra of 17l ($CDCl_3$)



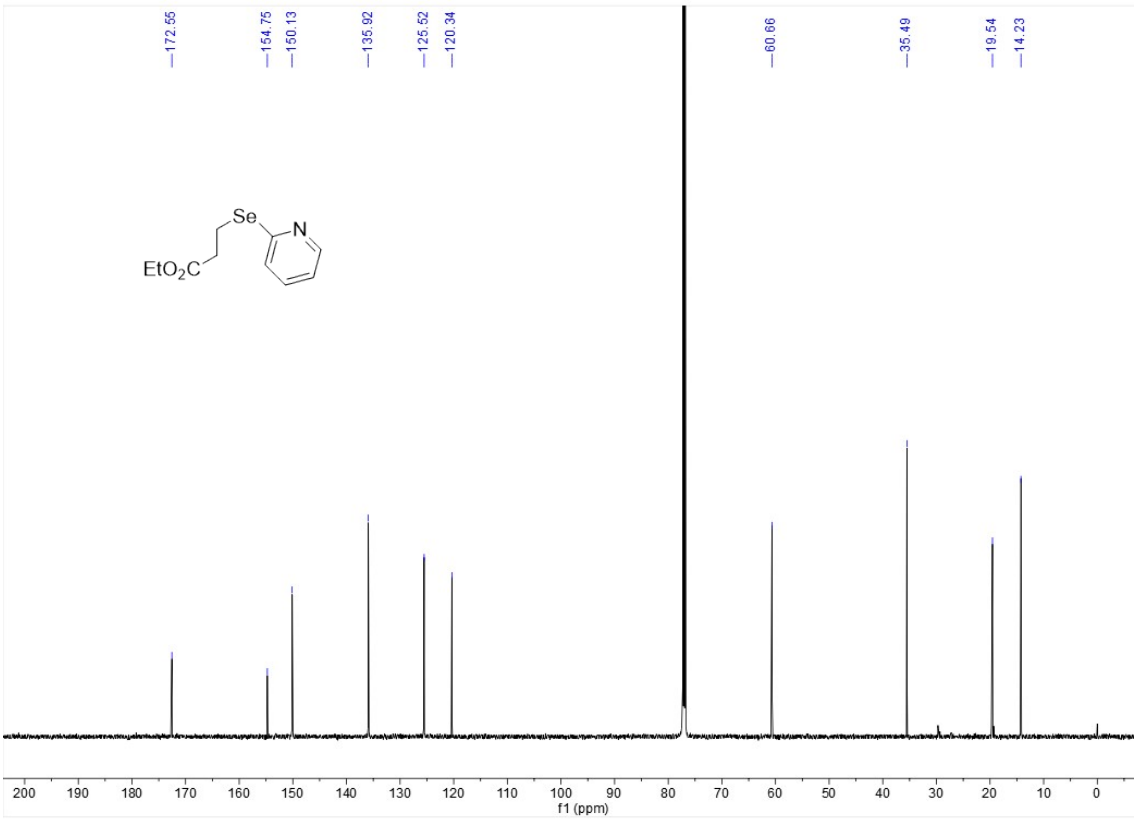
^{77}Se NMR spectra of 17l ($CDCl_3$)



^{1}H NMR spectra of 17m ($CDCl_3$)



^{13}C NMR spectra of 17m ($CDCl_3$)



^{77}Se NMR spectra of 17m ($CDCl_3$)