

Radical Selenation of C(sp^3)–H Bonds to Asymmetric Selenides and Mechanism Study

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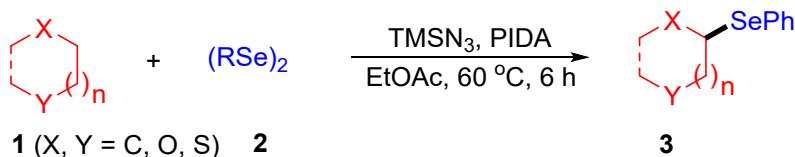
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I. General Conditions

All reagents were purchased from commercial sources and used without further purification. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AscendTM 400 or Bruker AscendTM 500 or a Bruker AscendTM 600 spectrometer in deuterated solvents containing TMS as an internal reference standard. All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization orthogonal acceleration time-of-flight (ESI-OA-TOF), and the purity of all samples used for HRMS (>95%) was confirmed by ^1H NMR and ^{13}C NMR spectroscopic analysis. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All the reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Purification by flash column chromatography was performed over SiO_2 (silica gel 200–300 mesh).

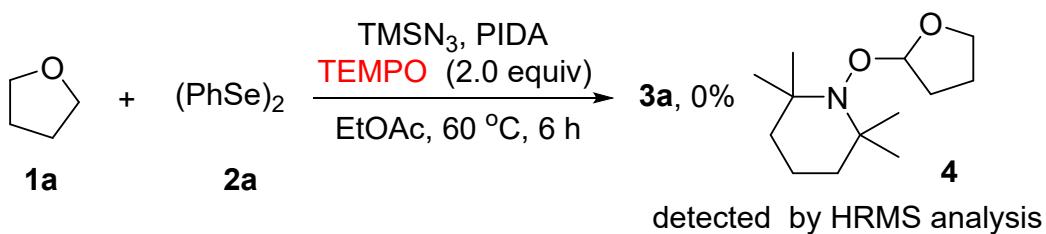
II. Typical Experimental Procedures



To a reaction tube, substrates **1** (5 equiv, 1.5 mmol), diphenyl diselenides **2** (1.0 equiv, 0.3 mmol), TMSN_3 (3.0 equiv, 0.9 mmol), PIDA (2.0 equiv, 0.4 mmol) were mixed in EtOAc (1 mL). The mixture was stirred at 60 °C for 6 h. After the completion of the reaction, the mixture was quenched with water, extracted with ethyl acetate (30×3 ml), and dried over anhydrous Na_2SO_4 . Then the organic solvent was concentrated in vacuo. The residue was purified by flash column chromatography with Petroleum ether as eluent to give **3**.

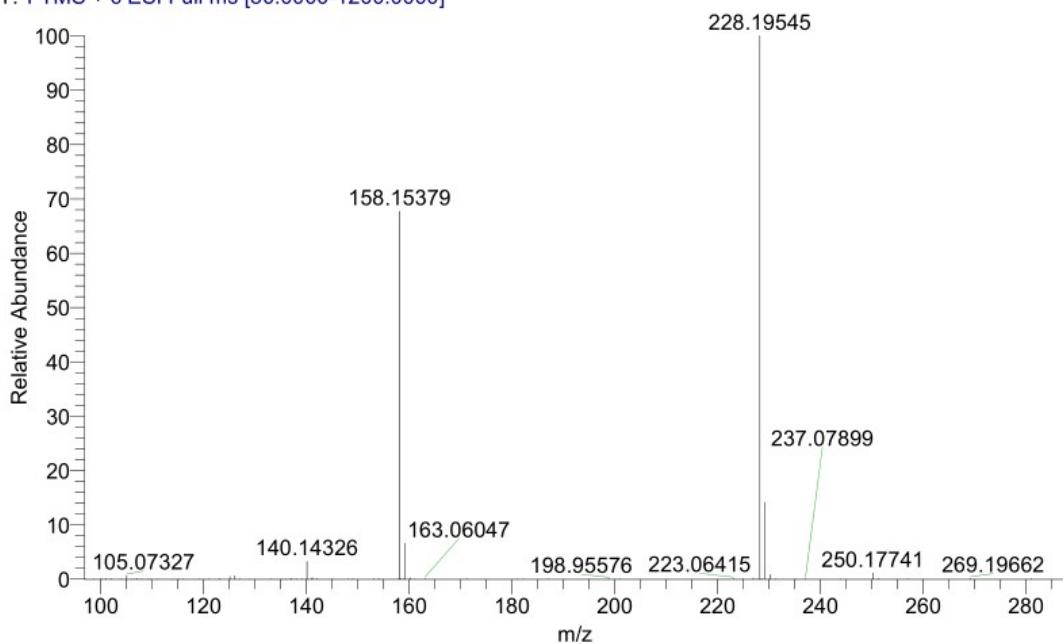
III. Control Experiments

3.1 Control experiment in the presence of TEMPO



To a reaction tube, tetrahydrofuran **1a** (5.0 equiv, 1 mmol), diphenyl diselenide **2a** (1.0 equiv, 0.2 mmol), TMSN_3 (3.0 equiv, 0.6 mmol), PIDA (2.0 equiv, 0.4 mmol), and the radical scavenger TEMPO (2.0 equiv, 0.4 mmol) were mixed in EtOAc (1 mL). Then the mixture was stirred at 60 °C for 6 h, and the adduct **4** was successfully detected by HRMS analysis. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{27}\text{NO} [\text{M}+\text{H}]^+$: 228.1958, found: 228.1954.

138a #858 RT: 4.63 AV: 1 NL: 4.34E9
T: FTMS + c ESI Full ms [80.0000-1200.0000]

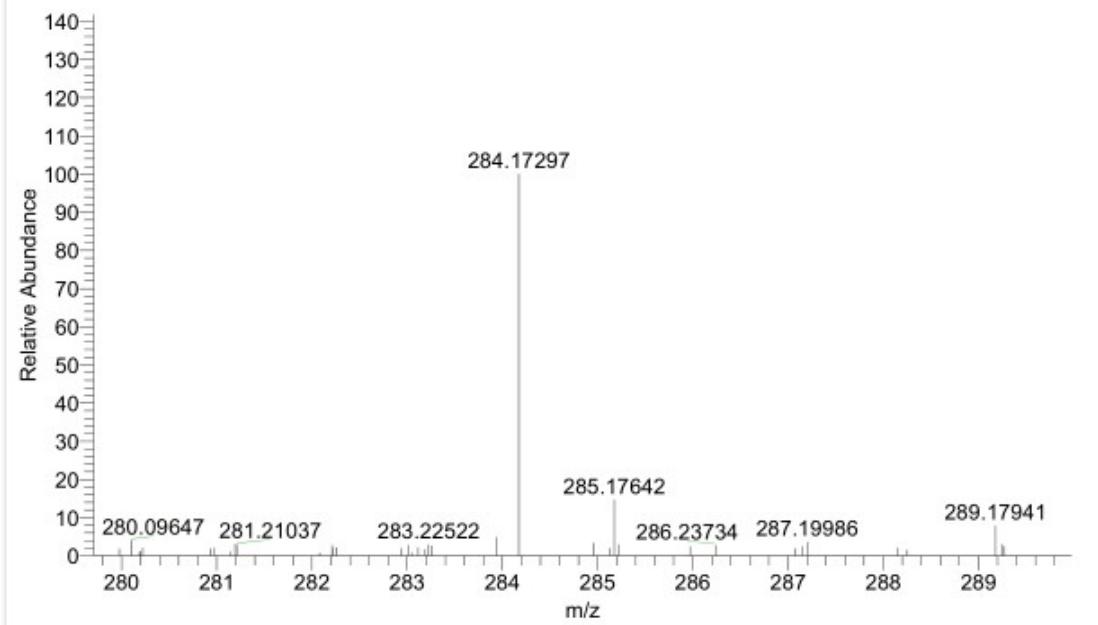


3.2 Control experiment in the presence of BHT



To a reaction tube, tetrahydrofuran **1a** (5.0 equiv, 1 mmol), diphenyl diselenide **2a** (1.0 equiv, 0.2 mmol), TMSN₃ (3.0 equiv, 0.6 mmol), PIDA (2.0 equiv, 0.4 mmol), and the radical scavenger BHT (2.0 equiv, 0.4 mmol) were mixed in EtOAc (1 mL). Then the mixture was stirred at 60 °C for 6 h, and the adduct **5** was successfully detected by HRMS analysis. HRMS (ESI) calcd for C₁₅H₂₃N₃O [M+Na]⁺: 284.1733, found: 284.1729.

138b_20210819121130 #1094 RT: 5.91 AV: 1 SB: 581 3.90-5.69 , 6.39-7.70 NL: 7.82E5
T: FTMS + c ESI Full ms [80.0000-1200.0000]

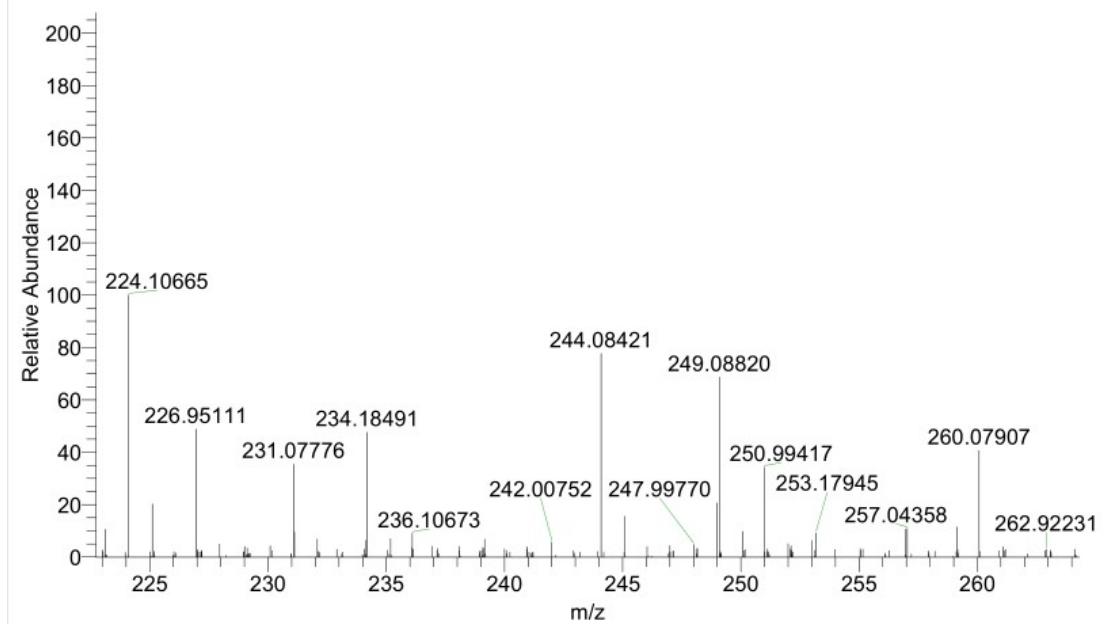


3.3 Control experiment in the presence of 1,1-diphenylethylene

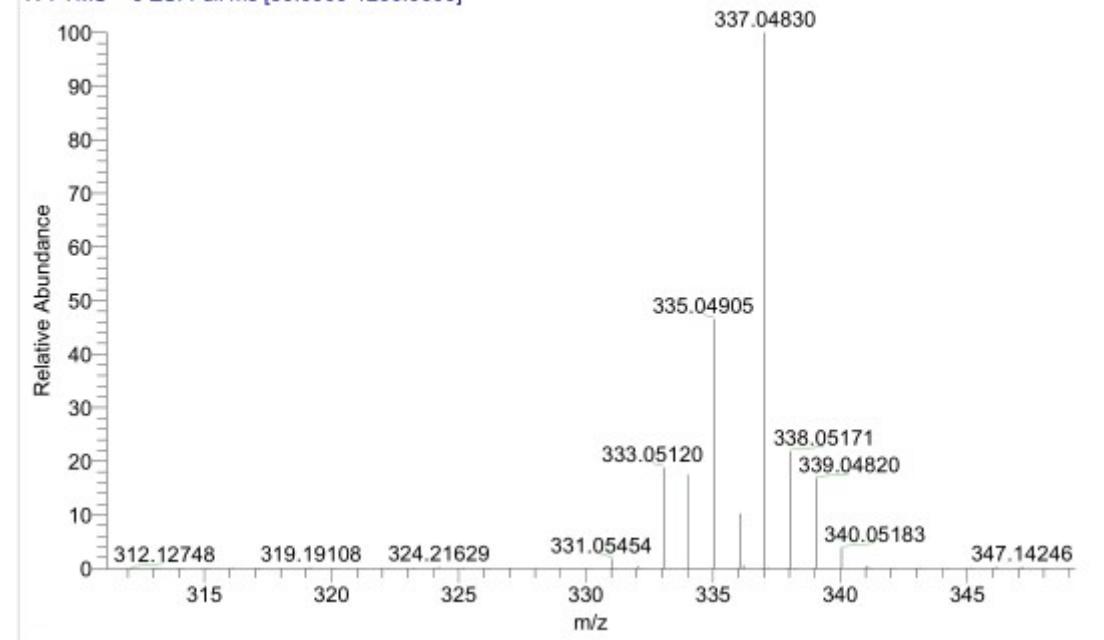


To a reaction tube, tetrahydrofuran **1a** (5.0 equiv, 1 mmol), diphenyl diselenide **2a** (1.0 equiv, 0.2 mmol), TMSN₃ (3.0 equiv, 0.6 mmol), PIDA (2.0 equiv, 0.4 mmol), and the radical scavenger 1,1-diphenylethylene (2.0 equiv, 0.4 mmol) were mixed in EtOAc (1 mL). Then the mixture was stirred at 60 °C for 6 h, we successfully detected the expected **6** and **7** by HRMS analysis. HRMS (ESI) calcd for **6** C₁₄H₁₁N₃ [M+Na]⁺: 224.0845, found: 224.0842. HRMS (ESI) calcd for **7** C₂₀H₁₆Se [M+H]⁺: 337.0490, found: 337.0483.

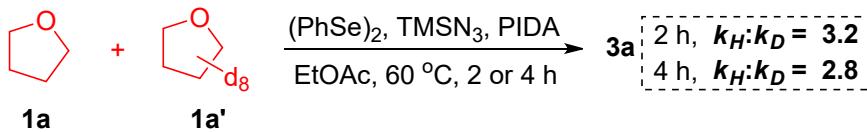
138c #491 RT: 2.65 AV: 1 SB: 347 1.77-2.49 , 2.94-4.03 NL: 1.96E6
T: FTMS + c ESI Full ms [80.0000-1200.0000]



138c #709-740 RT: 3.81-3.97 AV: 32 SB: 494 1.99-3.45 , 4.42-5.56 NL: 1.21E8
T: FTMS + c ESI Full ms [80.0000-1200.0000]

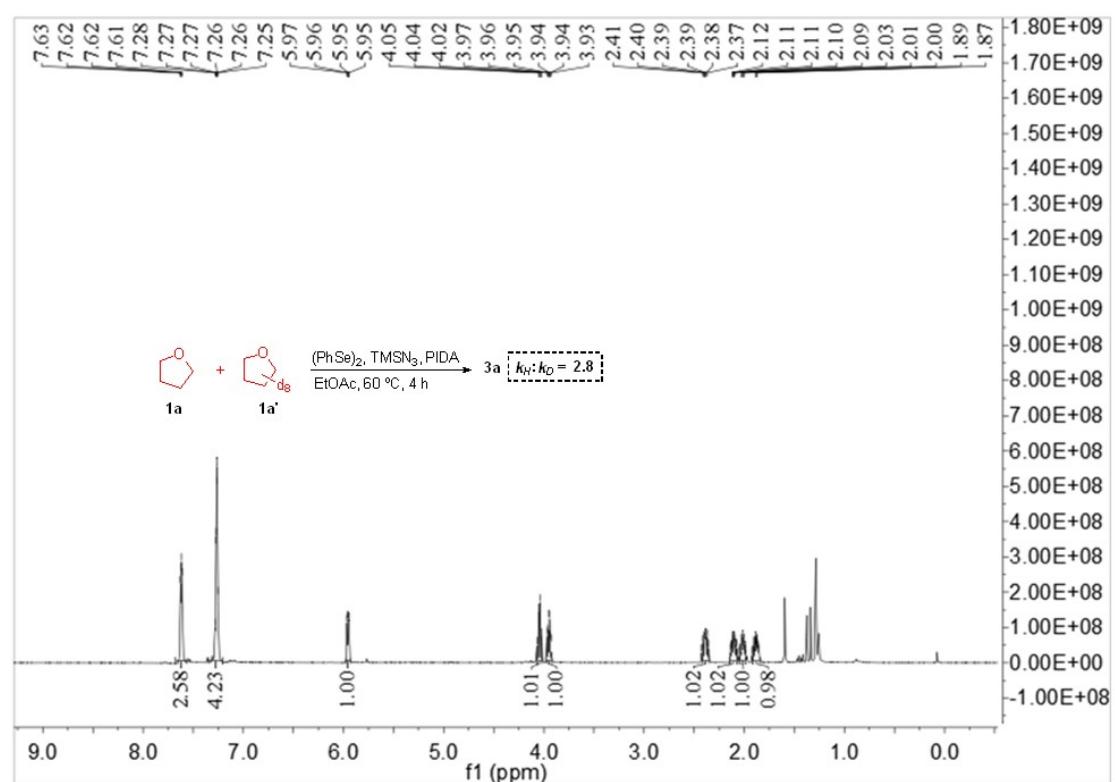
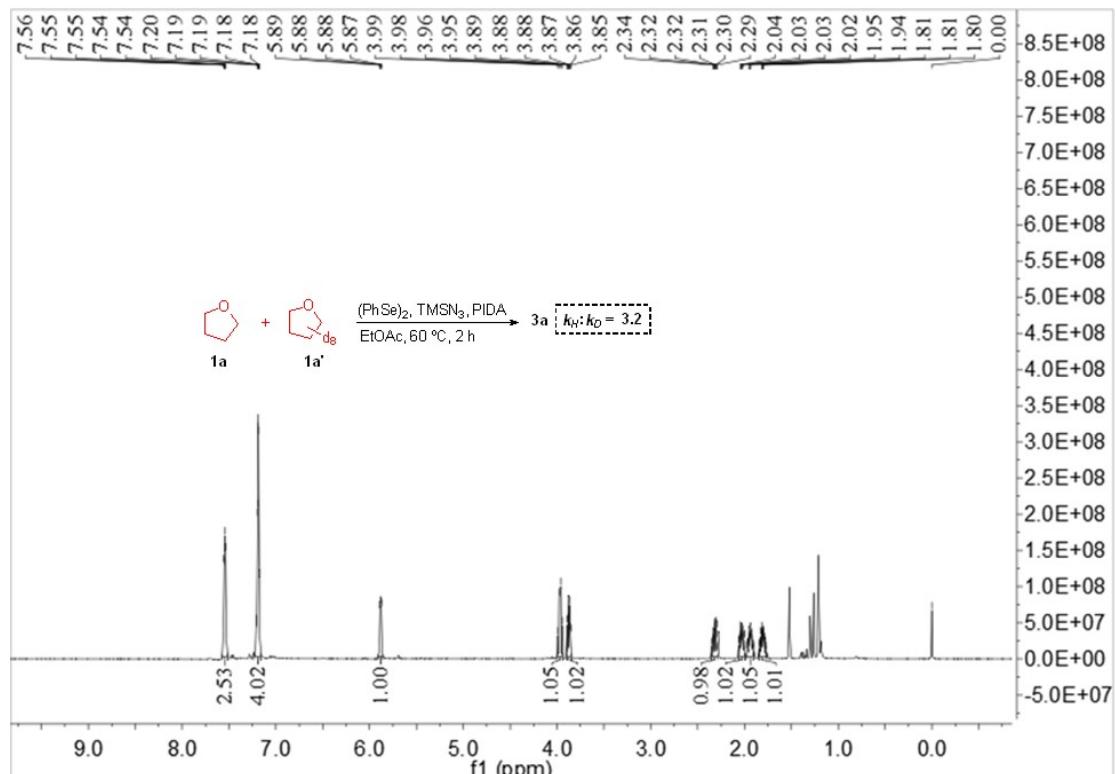


3.3 KIE Experiment between tetrahydrofuran and d₈-tetrahydrofuran

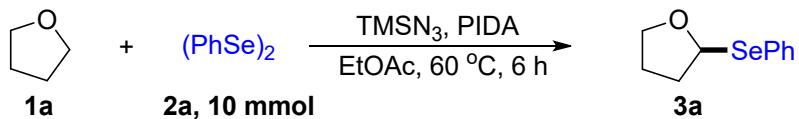


To a reaction tube, tetrahydrofuran **1a** (2.5 equiv, 0.5 mmol) and d₈-tetrahydrofuran **1a'** (2.5 equiv, 0.5 mmol), diphenyl diselenide **2a** (1.0 equiv, 0.2 mmol), TMSN₃ (3.0 equiv., 0.6 mmol), PIDA (2.0 equiv, 0.4 mmol) were mixed in EtOAc (1 mL). The mixture was stirred at 60 °C for 2 h or 4 h, quenched with water, extracted with ethyl acetate (5×3 mL), and

dried over anhydrous Na_2SO_4 . Then the organic solvent was concentrated in vacuo. The residue was purified by flash column chromatography with petroleum ether as eluent to give product **3a**, which was characterized by ^1H NMR spectra.



IV. Gram scale-up reactions



To a reaction tube, tetrahydrofuran **1a** (5 equiv, 50 mmol), diphenyl diselenide **2a** (1.0 equiv, 10 mmol), TMSN_3 (3.0 equiv, 30 mmol), PIDA (2.0 equiv, 20 mmol) were mixed in EtOAc (20 mL). The mixture was stirred at 60 °C for 6 h. After the completion of the reaction, the mixture was quenched with water, extracted with ethyl acetate (30×3 ml), and dried over anhydrous Na_2SO_4 . Then the organic solvent was concentrated in vacuo. The residue was purified by flash column chromatography with Petroleum ether as eluent to give **3a** (3.781 g, 83% yield).

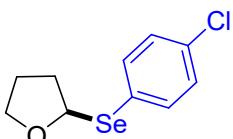
V. Products Characterization

2-(phenylselanyl)tetrahydrofuran (3a)



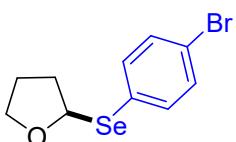
Colorless liquid (117.5 mg, 86% yield). R_f (Petroleum ether): 0.4. ^1H NMR (400 MHz, CDCl_3) δ 7.65–7.59 (m, 2H), 7.29–7.25 (m, 3H), 5.96 (m, 1H), 4.05 (m, 1H), 3.95 (m, 1H), 2.39 (m, 1H), 2.11 (m, 1H), 2.06–1.96 (m, 1H), 1.94–1.82 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 133.85, 130.60, 128.96, 127.26, 84.55, 67.56, 33.66, 24.59. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{OSe} [\text{M}+\text{Na}]^+$: 250.9946, found: 250.9942

2-((4-chlorophenyl)selanyl)tetrahydrofuran (3b)



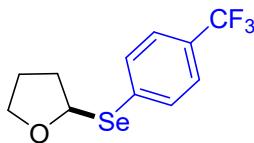
Colorless liquid (130.7 mg, 83% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.57–7.52 (m, 2H), 7.25–7.20 (m, 2H), 5.92 (m, 1H), 4.03 (m, 1H), 3.95 (m, 1H), 2.38 (m, 1H), 2.13–1.96 (m, 2H), 1.93–1.82 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.16, 133.54, 129.08, 128.88, 84.78, 67.56, 33.59, 24.56. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{ClOSe} [\text{M}+\text{Na}]^+$: 284.9556, found: 284.9552

2-((4-bromophenyl)selanyl)tetrahydrofuran (3c)



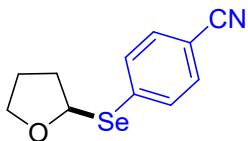
Colorless liquid (146.4 mg, 81% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.50–7.45 (m, 2H), 7.40–7.36 (m, 2H), 5.93 (m, 1H), 4.03 (m, 1H), 3.95 (m, 1H), 2.39 (m, 1H), 2.12–1.97 (m, 2H), 1.94–1.84 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.38, 132.01, 129.56, 121.66, 84.72, 67.58, 33.58, 24.54. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{BrOSe} [\text{M}+\text{Na}]^+$: 328.9051, found: 328.9047.

2-((4-(trifluoromethyl)phenyl)selanyl)tetrahydrofuran (3d)



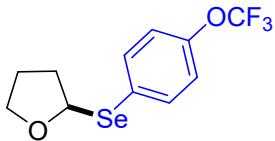
Colorless liquid (134.9 mg, 76% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 6.06 (m, 1H), 4.05 (m, 1H), 3.99 (m, 1H), 2.48–2.39 (m, 1H), 2.08 (m, 2H), 1.97–1.87 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 136.37, 132.83, 128.99 (q, $J = 32.6$ Hz), 125.58 (q, $J = 3.7$ Hz), 124.20 (q, $J = 271.8$ Hz) 84.51, 67.61, 33.52, 24.51. ^{19}F NMR (471 MHz, CDCl_3) δ -62.63. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 318.9819, found: 318.9815.

4-((tetrahydrofuran-2-yl)selanyl)benzonitrile (3e)



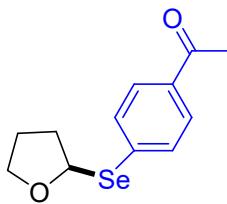
Colorless liquid (127.2 mg, 84% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H), 6.09 (m, 1H), 4.07–3.96 (m, 2H), 2.50–2.39 (m, 1H), 2.14–2.00 (m, 2H), 1.99–1.88 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 139.32, 132.32, 132.11, 118.91, 109.98, 84.47, 67.69, 33.43, 24.49. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{NOSe} [\text{M}+\text{Na}]^+$: 275.9898, found: 275.9893.

2-((4-(trifluoromethoxy)phenyl)selanyl)tetrahydrofuran (3f)



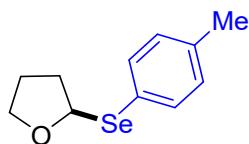
Colorless liquid (152.1 mg, 81% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.67–7.61 (m, 2H), 7.14–7.09 (m, 2H), 5.95 (m, 1H), 4.04 (m, 1H), 3.96 (m, 1H), 2.44–2.36 (m, 1H), 2.12–1.98 (m, 2H), 1.94–1.86 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 148.68, 135.19, 129.04, 121.45, 120.11 (t, $J = 386.0$ Hz), 119.43, 117.38, 84.79, 67.52, 33.54, 24.52. ^{19}F NMR (471 MHz, CDCl_3) δ -57.88. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 334.9769, found: 334.9765.

1-(4-((tetrahydrofuran-2-yl)selanyl)phenyl)ethan-1-one (3g)



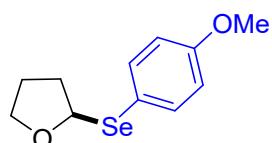
Colorless liquid (129.6 mg, 80% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 8.2$ Hz, 2H), 6.05 (m, 1H), 4.03–3.91 (m, 2H), 2.52 (s, 3H), 2.39 (m, 1H), 2.10–1.96 (m, 2H), 1.92–1.84 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.50, 139.03, 135.26, 131.96, 128.60, 84.26, 67.63, 33.50, 26.51, 24.53. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 293.0051, found: 293.0046.

2-(p-tolylselanyl)tetrahydrofuran (3h)



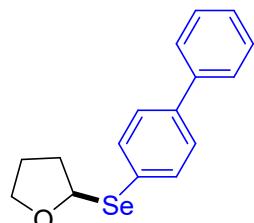
Colorless liquid (126.6 mg, 87% yield). R_f (Petroleum ether): 0.4. ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 7.9$ Hz, 2H), 5.90 (m, 1H), 4.04 (m, 1H), 3.94 (m, 1H), 2.40–2.35 (m, 1H), 2.33 (s, 3H), 2.14–2.07 (m, 1H), 2.06–1.97 (m, 1H), 1.87 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.35, 134.35, 129.80, 126.63, 84.61, 67.55, 33.64, 24.60, 21.18. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 265.0102, found: 265.0098.

2-((4-methoxyphenyl)selanyl)tetrahydrofuran (3i)



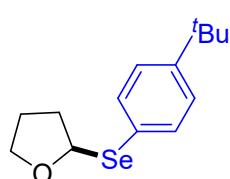
Colorless liquid (138 mg, 89% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.81 (m, 1H), 4.02 (q, $J = 7.8$ Hz, 1H), 3.92 (m, 1H), 3.79 (s, 3H), 2.39–2.30 (m, 1H), 2.12–2.04 (m, 1H), 1.98 (m, 1H), 1.91–1.81 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.53, 136.50, 120.28, 114.66, 84.76, 67.56, 55.27, 33.55, 24.59. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 281.0051, found: 281.0043.

2-([1,1'-biphenyl]-4-ylselanyl)tetrahydrofuran (3j)



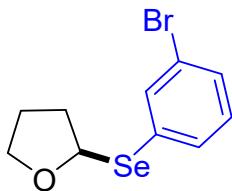
Colorless liquid (163.4 mg, 90% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 7.3$ Hz, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 1H), 6.01 (m, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 4.01–3.95 (m, 1H), 2.47–2.38 (m, 1H), 2.19–2.10 (m, 1H), 2.04 (m, 1H), 1.95–1.85 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 140.62, 140.23, 134.18, 129.68, 128.81, 127.67, 127.39, 127.02, 84.63, 67.59, 33.66, 24.60. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{OSe} [\text{M}+\text{Na}]^+$: 327.0259, found: 327.0263.

2-((4-(tert-butyl)phenyl)selanyl)tetrahydrofuran (3k)



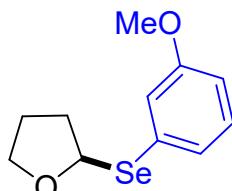
Colorless liquid (146.6 mg, 86% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.94 (m, 1H), 4.06 (m, 1H), 3.95 (m, 1H), 2.39 (m, 1H), 2.15–2.08 (m, 1H), 2.07–1.99 (m, 1H), 1.89 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 150.46, 133.89, 126.90, 126.09, 84.54, 67.51, 34.56, 33.66, 31.31, 24.61. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{OSe} [\text{M}+\text{Na}]^+$: 307.0572, found: 307.0564.

2-((3-bromophenyl)selanyl)tetrahydrofuran (3l)



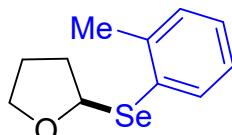
Colorless liquid (149.9 mg, 82% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (t, $J = 1.5$ Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.38 (m, 1H), 7.13 (t, $J = 7.9$ Hz, 1H), 5.99 (m, 1H), 4.04 (m, 1H), 3.97 (m, 1H), 2.40 (m, 1H), 2.12–2.05 (m, 1H), 2.05–1.98 (m, 1H), 1.94–1.86 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.83, 132.85, 131.96, 130.25, 130.18, 122.69, 84.80, 67.61, 33.60, 24.55. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{BrOSe} [\text{M}+\text{Na}]^+$: 328.9051, found: 328.9045.

2-((3-methoxyphenyl)selanyl)tetrahydrofuran (3m)



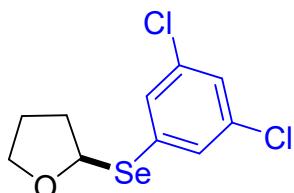
Colorless liquid (128.2 mg, 83% yield). R_f (Petroleum ether): 0.2. ^1H NMR (500 MHz, CDCl_3) δ 7.14–7.07 (m, 3H), 6.72 (m, 1H), 5.90 (m, 1H), 3.96 (q, $J = 7.8$ Hz, 1H), 3.86 (m, 1H), 3.71 (s, 3H), 2.31 (m, 1H), 2.02 (m, 1H), 1.98–1.88 (m, 1H), 1.85–1.74 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.64, 131.65, 129.70, 125.86, 118.88, 113.16, 84.56, 67.58, 55.28, 33.66, 24.60. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 281.0051, found: 281.0044

2-(o-tolylselanyl)tetrahydrofuran (3n)



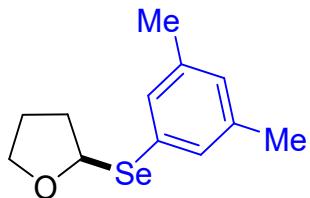
Colorless liquid (123.8 mg, 85% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.73–7.70 (m, 1H), 7.22–7.11 (m, 3H), 5.98 (m, 1H), 4.05 (m, 1H), 3.96 (m, 1H), 2.43 (s, 3H), 2.42–2.37 (m, 1H), 2.18–2.11 (m, 1H), 2.10–2.01 (m, 1H), 1.95–1.85 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 139.84, 133.47, 132.00, 129.87, 127.24, 126.52, 83.68, 67.58, 33.70, 24.65, 22.86. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 265.0102, found: 265.0097.

2-((3,5-dichlorophenyl)selanyl)tetrahydrofuran (3o)



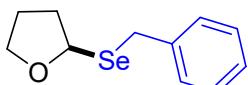
Colorless liquid (119.4 mg, 67% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 1.8$ Hz, 2H), 7.23 (t, $J = 1.8$ Hz, 1H), 6.02 (m, 1H), 4.07–3.96 (m, 2H), 2.47–2.36 (m, 1H), 2.12–1.98 (m, 2H), 1.96–1.86 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 134.91, 133.91, 130.87, 127.14, 84.92, 67.64, 33.50, 24.48. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{F}_2\text{NO}_3 [\text{M}+\text{Na}]^+$: 318.9166, found: 318.9162.

2-((3,5-dimethylphenyl)selanyl)tetrahydrofuran (3p)



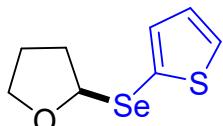
Colorless liquid (122.6 mg, 80% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.18 (d, $J = 6.1$ Hz, 2H), 6.81 (s, 1H), 5.88 (m, 1H), 3.97 (m, 1H), 3.87 (m, 1H), 2.31 (m, 1H), 2.21 (s, 6H), 2.09–1.99 (m, 1H), 1.99–1.90 (m, 1H), 1.86–1.75 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 138.50, 131.32, 130.12, 129.12, 84.46, 67.54, 33.70, 24.62, 21.20. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{OSe} [\text{M}+\text{Na}]^+$: 279.0259, found: 279.0254.

2-(benzylselanyl)tetrahydrofuran (3q)



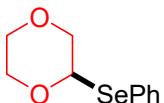
Colorless liquid (122.2 mg, 84% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.35 (t, $J = 7.0$ Hz, 2H), 7.31 (m, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 5.64 (m, 1H), 4.05–3.92 (m, 3H), 3.87–3.80 (m, 1H), 2.31–2.21 (m, 1H), 2.02 (m, 1H), 1.99–1.91 (m, 1H), 1.91–1.81 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 139.93, 128.92, 128.51, 126.54, 79.63, 67.10, 33.09, 27.20, 24.70. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 265.0102, found: 265.0096.

2-(thiophen-2-ylselanyl)tetrahydrofuran (3r)



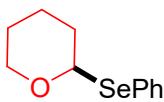
Colorless liquid (111 mg, 79% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.40 (m, 1H), 7.23 (m, 1H), 7.00 (m, 1H), 5.80 (m, 1H), 4.05 (m, 1H), 3.95 (m, 1H), 2.33 (m, 1H), 2.11 (m, 1H), 2.04–1.96 (m, 1H), 1.89 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.97, 131.05, 128.08, 123.45, 86.38, 68.00, 33.27, 24.34. HRMS (ESI) calcd for $\text{C}_8\text{H}_{10}\text{OSe} [\text{M}+\text{Na}]^+$: 256.9510, found: 256.9503.

2-(thiophen-2-ylselanyl)tetrahydrofuran (3s)



Colorless liquid (128.4 mg, 88% yield). R_f (Petroleum ether): 0.3. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 2H), 7.28–7.22 (m, 3H), 5.48–5.44 (m, 1H), 4.31–4.24 (m, 1H), 3.98 (m, 1H), 3.86 (m, 1H), 3.74–3.66 (m, 2H), 3.64–3.59 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 133.85, 129.51, 129.13, 127.56, 81.93, 71.15, 66.80, 63.56. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 266.9895, found: 266.9890.

2-(phenylselanyl)tetrahydro-2*H*-pyran (3t)



Colorless liquid (124.4 mg, 86% yield). R_f (Petroleum ether): 0.4. ^1H NMR (600 MHz, CDCl_3) δ 7.60–7.56 (m, 2H), 7.26–7.22 (m, 3H), 5.69 (t, $J = 4.1$ Hz, 1H), 4.18–4.13 (m, 1H), 3.69–3.64 (m,

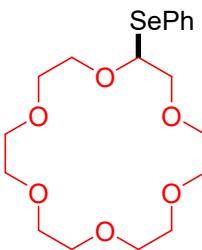
1H), 2.11 (m, 1H), 2.03–1.96 (m, 1H), 1.82–1.73 (m, 1H), 1.72–1.61 (m, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 133.55, 130.49, 128.96, 127.12, 84.77, 64.33, 32.79, 25.73, 21.49. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 265.0102, found: 265.0095.

2-(phenylselanyl)oxepane (3u)



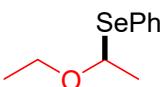
Colorless liquid (124.7 mg, 81% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 2H), 7.24 (m, 3H), 5.65 (m, 1H), 3.92–3.84 (m, 1H), 3.70–3.62 (m, 1H), 2.38 (m, 1H), 1.84 (m, 2H), 1.78–1.70 (m, 2H), 1.69–1.59 (m, 1H), 1.49 (m, 1H), 1.36–1.26 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 133.77, 130.74, 128.87, 127.13, 86.58, 64.20, 37.02, 29.94, 29.22, 25.77. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{OSe} [\text{M}+\text{Na}]^+$: 279.0259, found: 279.0254.

2-(phenylselanyl)-1,4,7,10,13,16-hexaoxacyclooctadecane (3v)



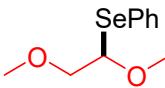
Colorless liquid (187.7 mg, 74% yield). R_f (Petroleum ether: ethyl acetate=10:3): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.53 (m, 2H), 7.26–7.18 (m, 3H), 5.21 (m, 1H), 4.02–3.94 (m, 1H), 3.86 (m, 1H), 3.69–3.59 (m, 20H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.50, 128.95, 127.85, 127.77, 90.71, 86.71, 74.62, 72.34, 70.91 (d, $J = 3.1$ Hz), 70.82 (d, $J = 3.0$ Hz), 70.72 (d, $J = 2.1$ Hz), 70.67 (d, $J = 2.8$ Hz), 70.53 (d, $J = 3.7$ Hz), 69.94, 69.50, 68.47. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Se} [\text{M}+\text{Na}]^+$: 443.0943, found: 443.0933.

(1-ethoxyethyl)(phenyl)selane (3w)



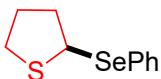
Colorless liquid (98.2 mg, 71% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 2H), 7.30–7.24 (m, 3H), 5.14 (q, $J = 6.2$ Hz, 1H), 3.98–3.90 (m, 1H), 3.49–3.41 (m, 1H), 1.68 (d, $J = 6.2$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.72, 128.86, 128.41, 127.63, 82.92, 64.96, 24.50, 14.75. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 253.0102, found: 253.0097

(1,2-dimethoxyethyl)(phenyl)selane (3x)



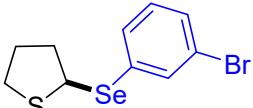
Colorless liquid (96.9 mg, 66% yield). R_f (Petroleum ether): 0.3. ^1H NMR (400 MHz, CDCl_3) δ 7.62–7.57 (m, 2H), 7.29 (m, 3H), 5.01 (m, 1H), 3.75 (m, 1H), 3.64 (m, 1H), 3.53 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 135.57, 129.04, 127.92, 87.78, 75.98, 59.07, 57.70. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Se} [\text{M}+\text{Na}]^+$: 269.0051, found: 269.0046.

2-(phenylselanyl)tetrahydrothiophene (3y)



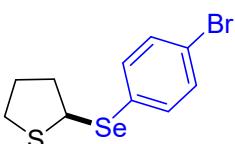
Colorless liquid (116.5 mg, 80% yield). R_f (Petroleum ether): 0.4. ^1H NMR (500 MHz, CDCl_3) δ 7.61–7.54 (m, 2H), 7.34–7.25 (m, 3H), 4.90–4.83 (m, 1H), 3.04 (m, 1H), 2.86 (m, 1H), 2.28–2.16 (m, 3H), 2.08 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 134.23, 131.61, 129.12, 127.75, 48.78, 39.30, 33.40, 28.67. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{SSe} [\text{M}+\text{Na}]^+$: 266.9717, found: 266.9713.

2-((3-bromophenyl)selanyl)tetrahydrothiophene (3z)



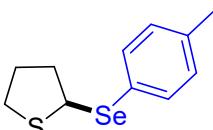
Colorless liquid (136.9 mg, 71% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.72 (s, 1H), 7.48 (d, $J = 7.7$ Hz, 1H), 7.44–7.39 (m, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 4.88 (t, $J = 3.9$ Hz, 1H), 3.05 (m, 1H), 2.90–2.83 (m, 1H), 2.26–2.20 (m, 3H), 2.14–2.06 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 136.30, 133.65, 132.38, 130.71, 130.47, 122.83, 49.11, 39.26, 33.37, 28.62. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{BrSSe} [\text{M}+\text{Na}]^+$: 344.8822, found: 344.8829.

2-((4-bromophenyl)selanyl)tetrahydrothiophene (3aa)



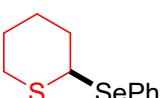
Colorless liquid (144.5 mg, 75% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.45–7.38 (m, 4H), 4.83 (t, $J = 4.0$ Hz, 1H), 3.03 (m, 1H), 2.86 (m, 1H), 2.23–2.17 (m, 3H), 2.12–2.03 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 135.87, 132.21, 130.35, 122.24, 49.10, 39.19, 33.41, 28.67. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{BrSSe} [\text{M}+\text{Na}]^+$: 344.8822, found: 344.8814.

2-(*p*-tolylselanyl)tetrahydrothiophene (3ab)



Colorless liquid (117.6 mg, 76% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 4.80 (m, 1H), 3.06–3.00 (m, 1H), 2.89–2.82 (m, 1H), 2.34 (s, 3H), 2.21 (m, 3H), 2.10–2.02 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.93, 134.76, 129.91, 127.78, 48.93, 39.22, 33.40, 28.62, 21.22. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{14}\text{SSe} [\text{M}+\text{Na}]^+$: 280.9874, found: 280.9881.

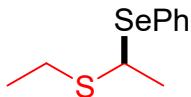
2-(phenylselanyl)tetrahydro-2*H*-thiopyran (3ac)



Colorless liquid (108.4 mg, 70% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (m, 2H), 7.32–7.24 (m, 3H), 4.36 (m, 1H), 2.88–2.80 (m, 1H), 2.60–2.52 (m, 1H), 2.26–2.18 (m, 1H), 1.96–1.83 (m, 2H), 1.83–1.76 (m, 2H), 1.56–1.46 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 134.89, 129.60, 129.05, 127.97, 44.02, 34.43, 29.03, 26.69, 24.59. HRMS (ESI) calcd for

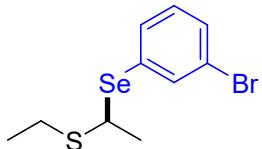
$C_{11}H_{14}SSe$ [M+Na]⁺: 280.9874, found: 280.9869.

ethyl(1-(phenylselanyl)ethyl)sulfane (3ad)



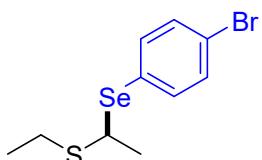
Colorless liquid (109.6 mg, 74% yield). R_f (Petroleum ether): 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.55–7.48 (m, 2H), 7.25–7.14 (m, 3H), 4.21 (q, J = 7.0 Hz, 1H), 2.70 (m, 1H), 2.66–2.57 (m, 1H), 1.65–1.60 (m, 3H), 1.20 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 135.42, 129.53, 128.98, 128.06, 42.89, 26.78, 24.02, 14.39. HRMS (ESI) calcd for C₁₀H₁₂SSe [M+Na]⁺: 268.9874, found: 268.9869.

(1-((3-bromophenyl)selanyl)ethyl)(ethyl)sulfane (3ae)



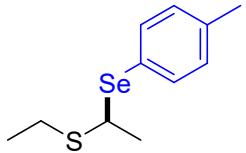
Colorless liquid (132.1 mg, 68% yield). R_f (Petroleum ether): 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.75 (s, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 4.32 (q, J = 6.9 Hz, 1H), 2.74 (m, 2H), 1.72 (d, J = 7.0 Hz, 3H), 1.29 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 137.42, 133.57, 131.55, 131.03, 130.32, 122.63, 43.37, 26.81, 24.03, 14.39. HRMS (ESI) calcd for C₁₀H₁₃BrSSe [M+Na]⁺: 346.8979, found: 346.8972.

(1-(4-bromophenyl)propan-2-yl)(ethyl)sulfane (3af)



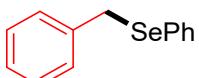
Colorless liquid (156.1 mg, 80% yield). R_f (Petroleum ether): 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 4.28 (d, J = 7.0 Hz, 1H), 2.73 (m, 2H), 1.70 (d, J = 7.0 Hz, 3H), 1.28 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 136.00, 131.04, 127.09, 121.66, 42.14, 25.71, 22.84, 13.27. HRMS (ESI) calcd for C₁₁H₁₃BrSSe [M+Na]⁺: 346.8979, found: 346.8983.

ethyl(1-(p-tolylselanyl)ethyl)sulfane (3ag)



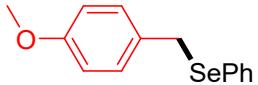
Colorless liquid (127.9 mg, 82% yield). R_f (Petroleum ether): 0.5. ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 4.24 (q, J = 6.9 Hz, 1H), 2.75 (m, 2H), 2.35 (s, 3H), 1.70 (d, J = 7.0 Hz, 3H), 1.29 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 138.23, 135.83, 129.78, 125.62, 42.83, 26.74, 23.91, 21.25, 14.36.. HRMS (ESI) calcd for C₁₁H₁₆SSe [M+Na]⁺: 283.0030, found: 283.0024.

benzyl(phenyl)selane (3ah)



Colorless liquid (96.8 mg, 65% yield). R_f (Petroleum ether): 0.7. ^1H NMR (500 MHz, CDCl_3) δ 7.39–7.35 (m, 2H), 7.19–7.14 (m, 5H), 7.14–7.09 (m, 3H), 4.03 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 138.66, 133.58, 130.46, 129.02, 128.89, 128.47, 127.34, 126.90, 32.27. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{12}\text{Se} [\text{M}+\text{Na}]^+$: 270.9996, found: 270.9991.

(4-methoxybenzyl)(phenyl)selane (3ai)



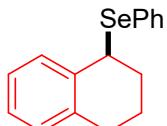
Colorless liquid (136.9 mg, 82% yield). R_f (Petroleum ether): 0.7. ^1H NMR (500 MHz, CDCl_3) δ 7.36 (m, 2H), 7.14 (m, 3H), 7.04 (d, $J = 8.6$ Hz, 2H), 6.69 (d, $J = 8.6$ Hz, 2H), 3.99 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 158.58, 133.49, 130.70, 130.60, 129.98, 129.01, 127.23, 113.90, 55.29, 31.76. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{OSe} [\text{M}+\text{Na}]^+$: 301.0102, found: 301.0097.

(2,3-dihydro-1*H*-inden-1-yl)(phenyl)selane (3aj)



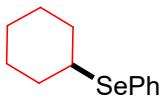
Colorless liquid (129.3 mg, 79% yield). R_f (Petroleum ether): 0.7. ^1H NMR (500 MHz, CDCl_3) δ 7.50–7.46 (m, 2H), 7.27–7.18 (m, 4H), 7.18–7.08 (m, 3H), 4.85 (m, 1H), 2.95 (m, 1H), 2.77 (m, 1H), 2.50 (m, 1H), 2.25 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.80, 143.70, 134.63, 130.50, 129.00, 127.56, 126.53, 124.93, 124.73, 47.32, 34.16, 31.04. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{Se} [\text{M}+\text{Na}]^+$: 297.0153, found: 297.0148.

phenyl(1,2,3,4-tetrahydronaphthalen-1-yl)selane (3ak)



Colorless liquid (143.5 mg, 83% yield). R_f (Petroleum ether): 0.5. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (m, 2H), 7.38–7.34 (m, 1H), 7.33–7.29 (m, 3H), 7.15–7.05 (m, 3H), 4.80 (t, $J = 3.2$ Hz, 1H), 2.83 (m, 2H), 2.33–2.22 (m, 1H), 2.11–2.01 (m, 2H), 1.80 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.16, 136.38, 134.76, 131.14, 130.51, 129.32, 129.09, 127.63, 126.85, 125.67, 44.59, 29.19, 29.05, 19.17.. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{Se} [\text{M}+\text{Na}]^+$: 311.0309, found: 311.0304.

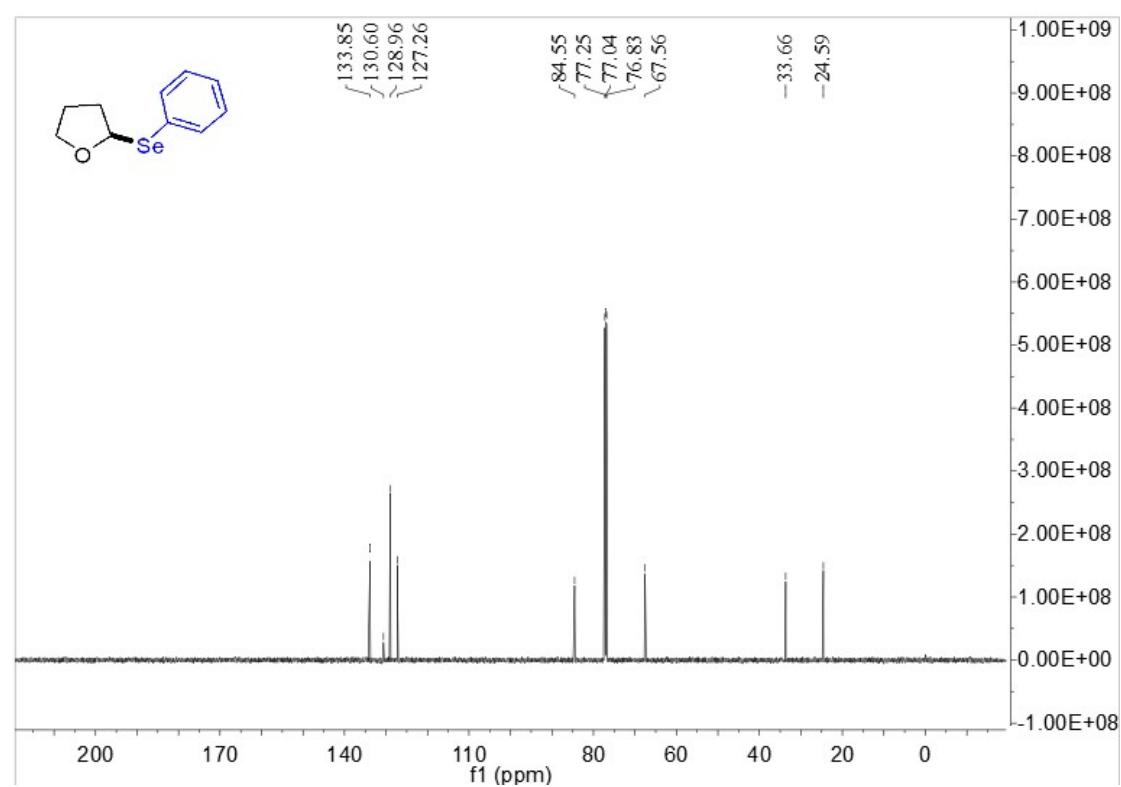
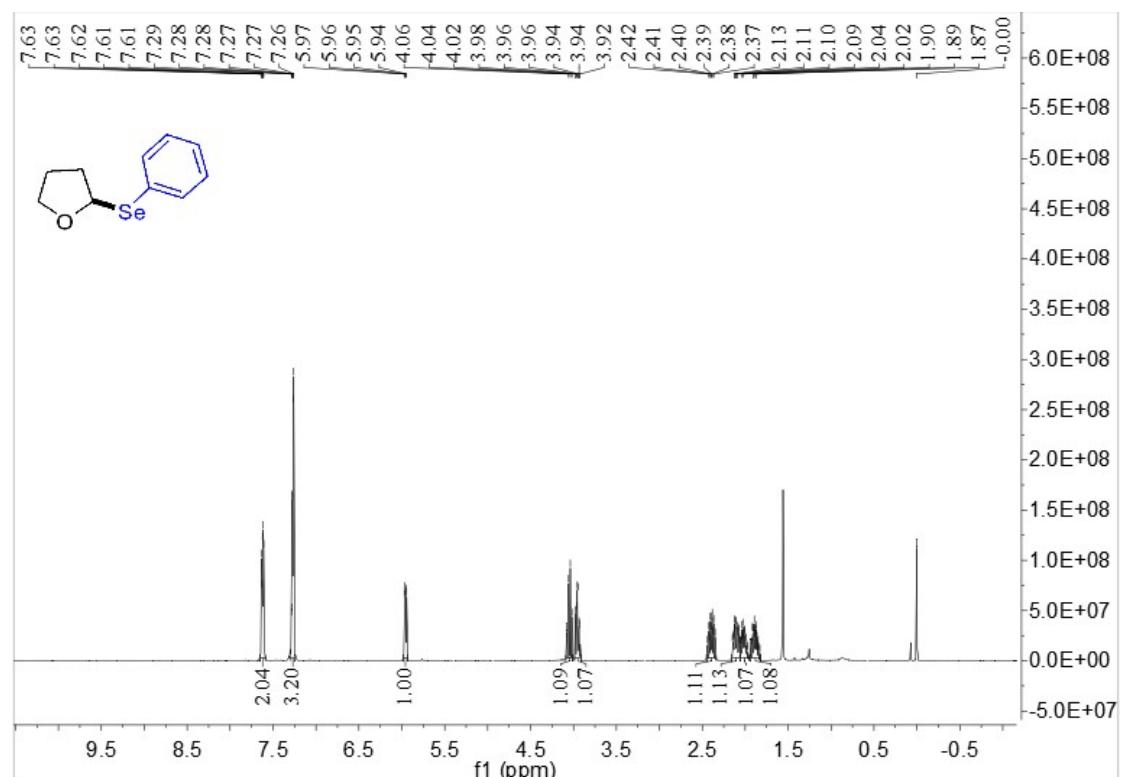
cyclohexyl(phenyl)selane (3al)



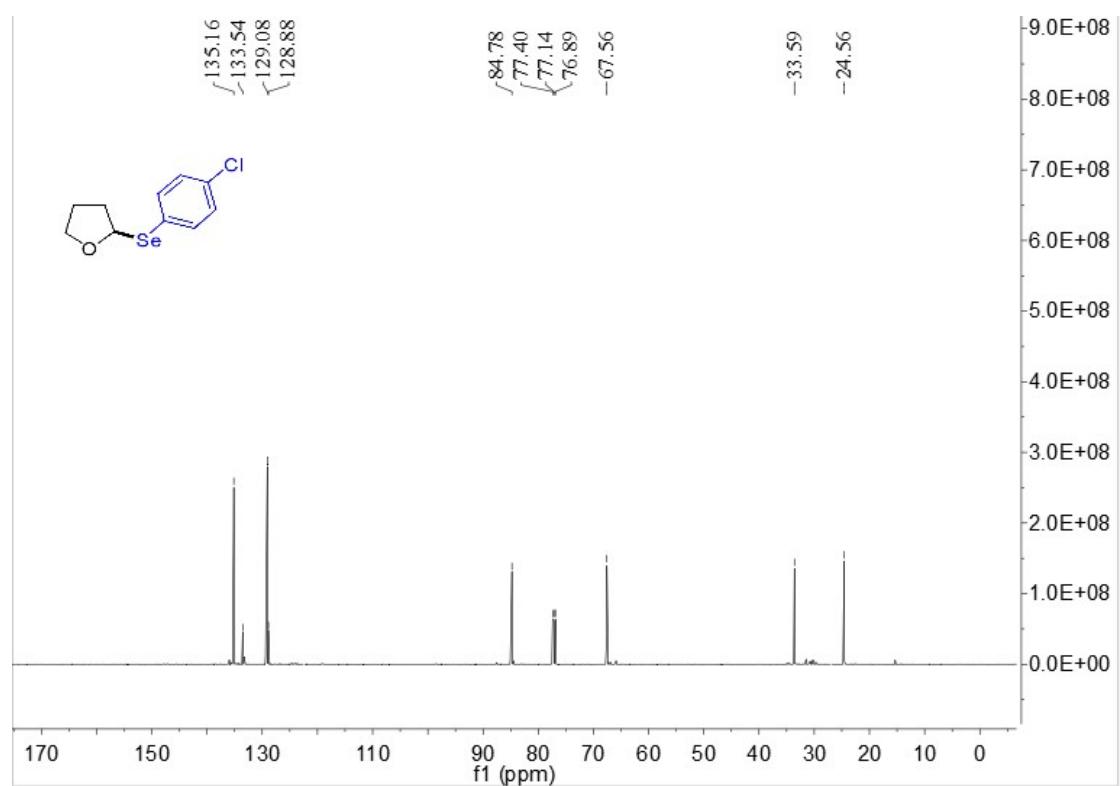
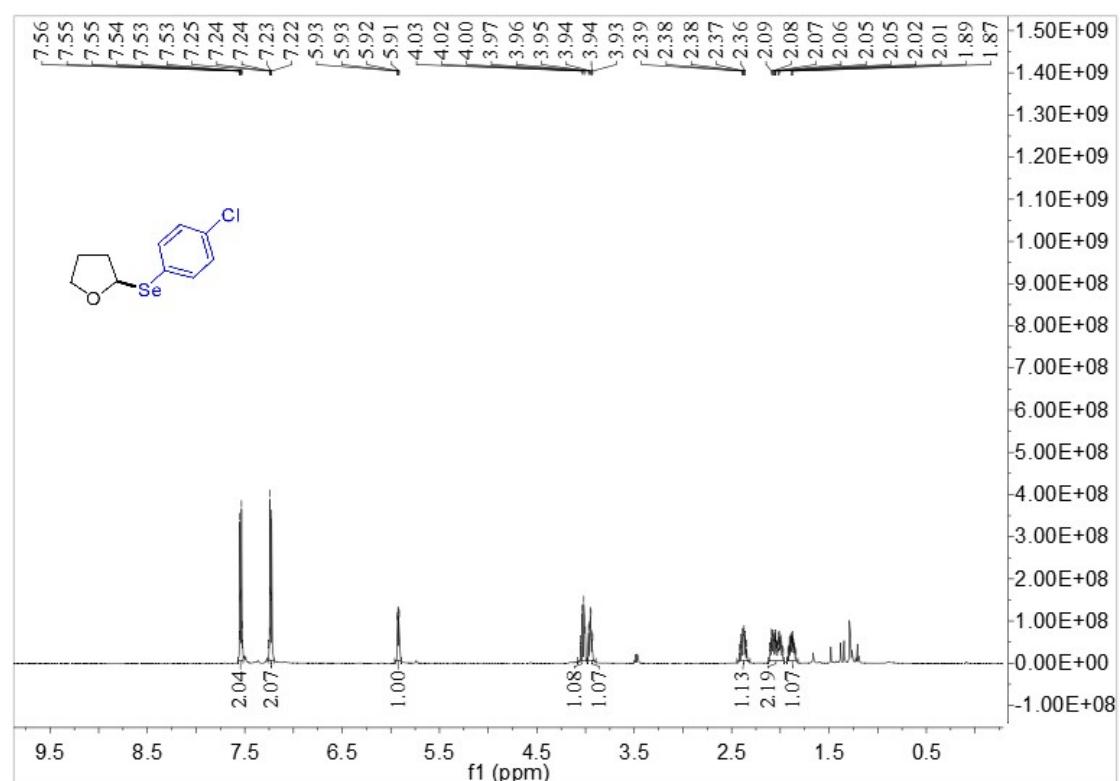
Colorless liquid (27.6 mg, 19% yield). R_f (Petroleum ether): 0.7. ^1H NMR (600 MHz, CDCl_3) δ 7.54 (m, 2H), 7.27–7.22 (m, 3H), 3.25 (m, 1H), 2.05–1.99 (m, 2H), 1.76–1.70 (m, 2H), 1.62–1.49 (m, 3H), 1.35–1.24 (m, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 134.74, 129.38, 128.87, 127.23, 43.28, 34.27, 26.91, 25.80. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{Se} [\text{M}+\text{Na}]^+$: 263.0309, found: 263.0305.

VI. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra copies of compounds 3

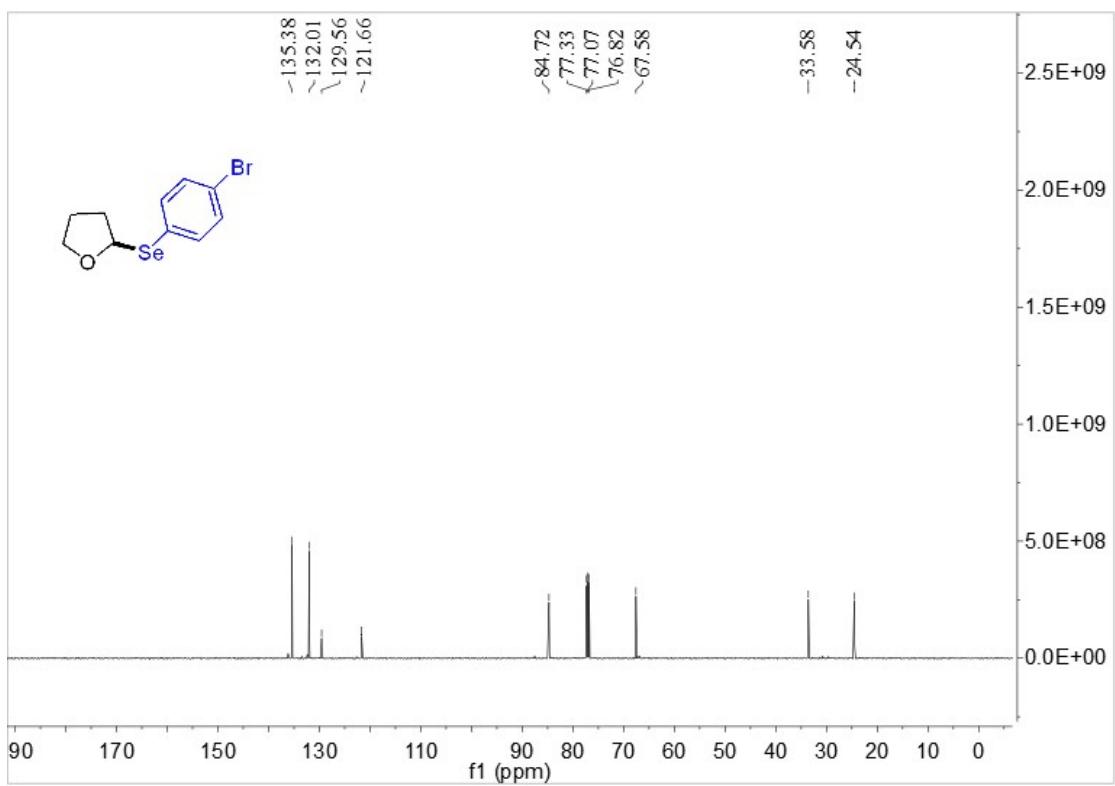
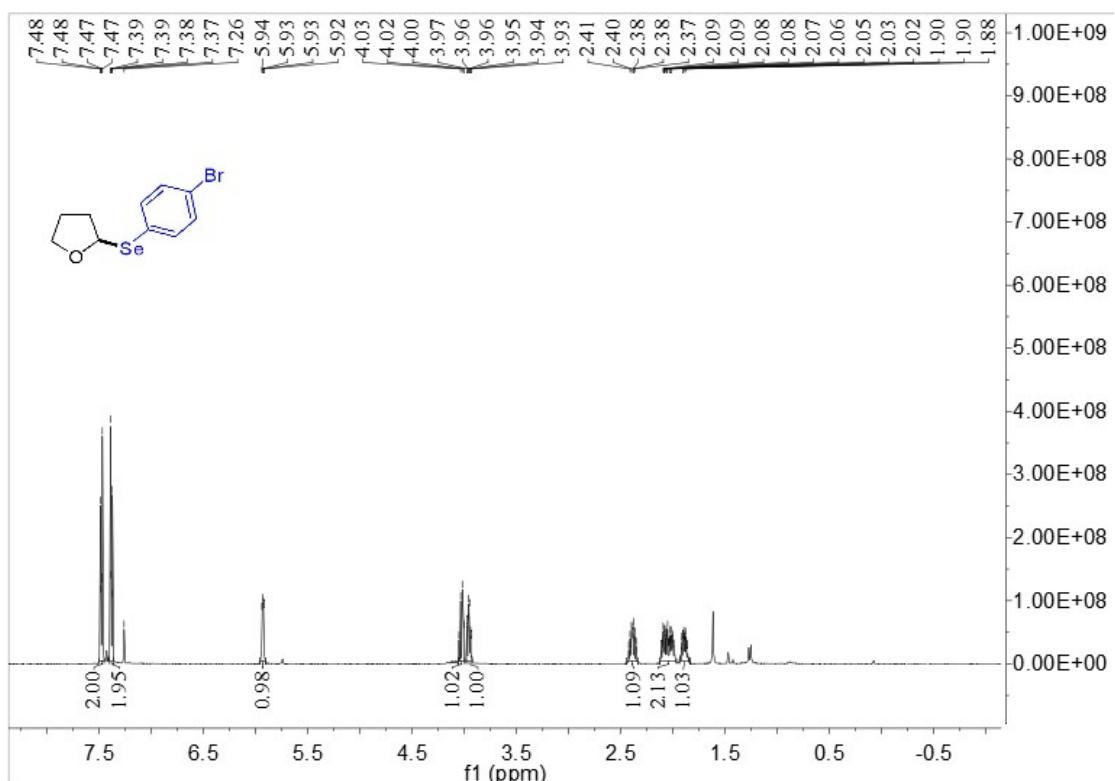
Compound 3a



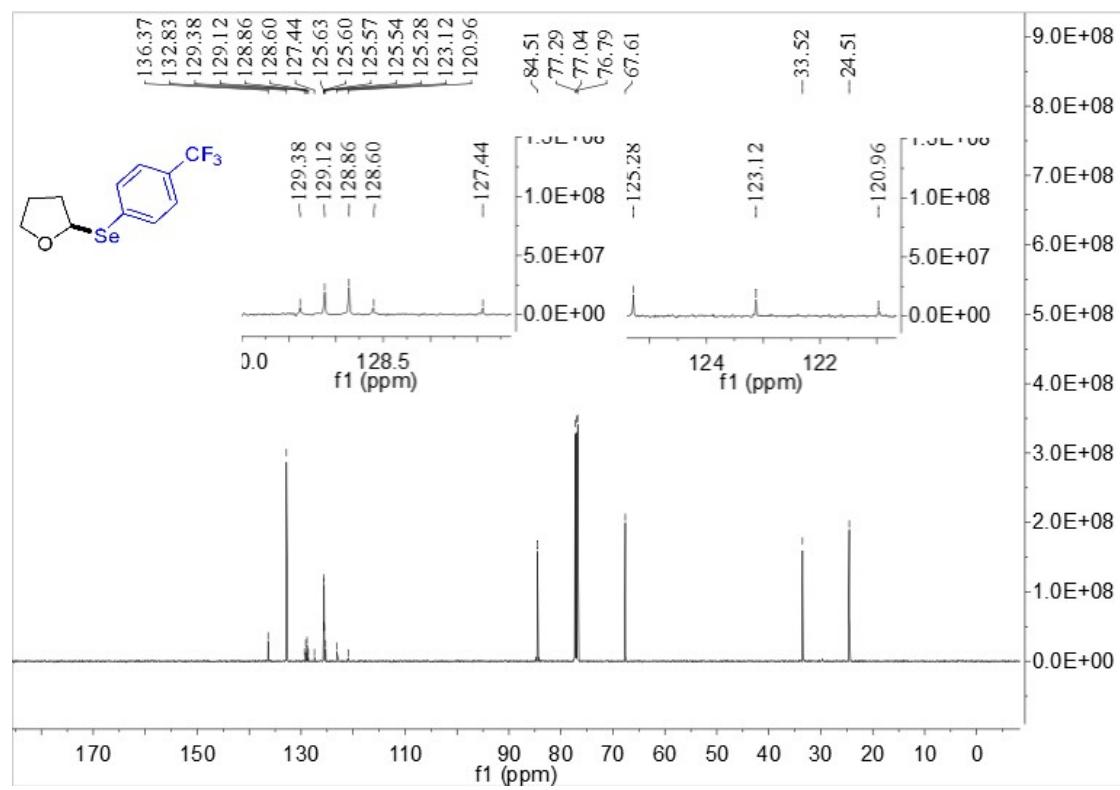
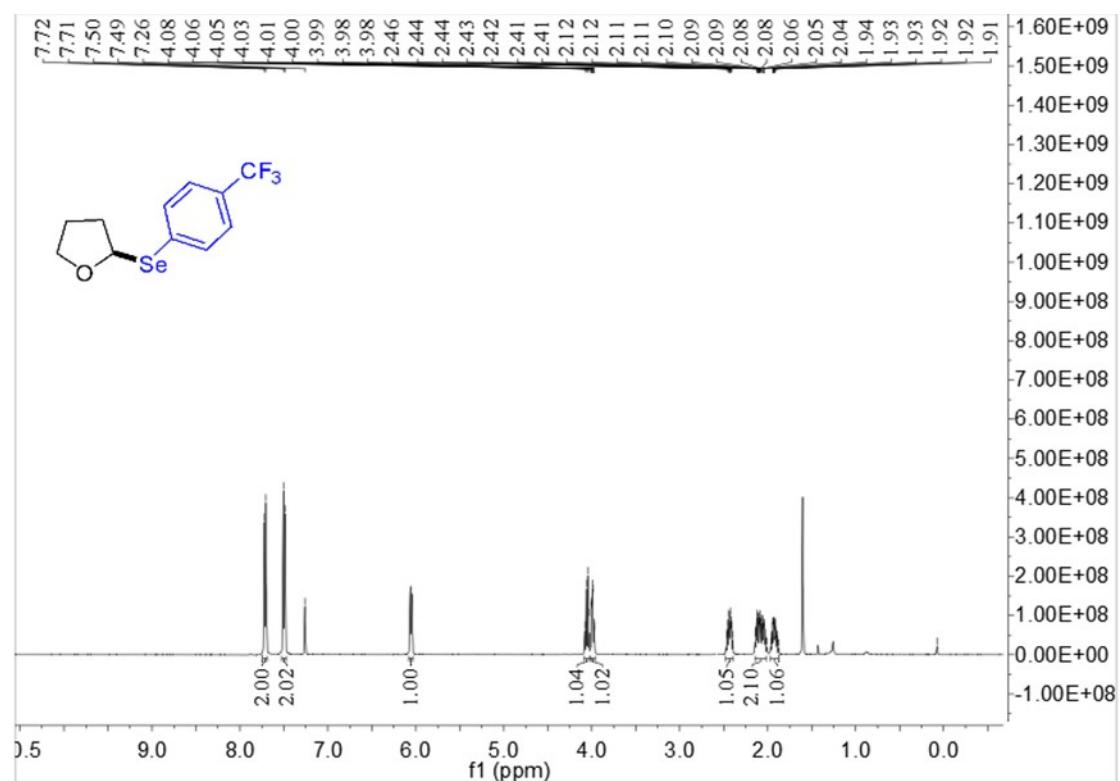
Compound 3b

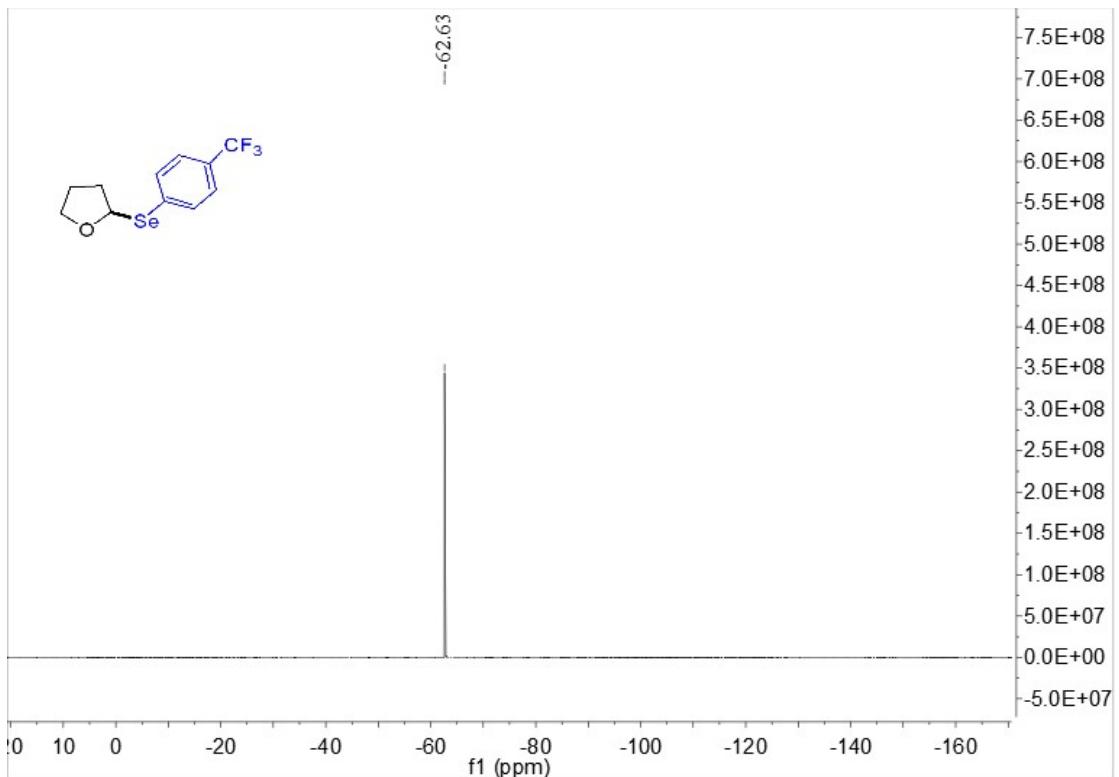


Compound 3c

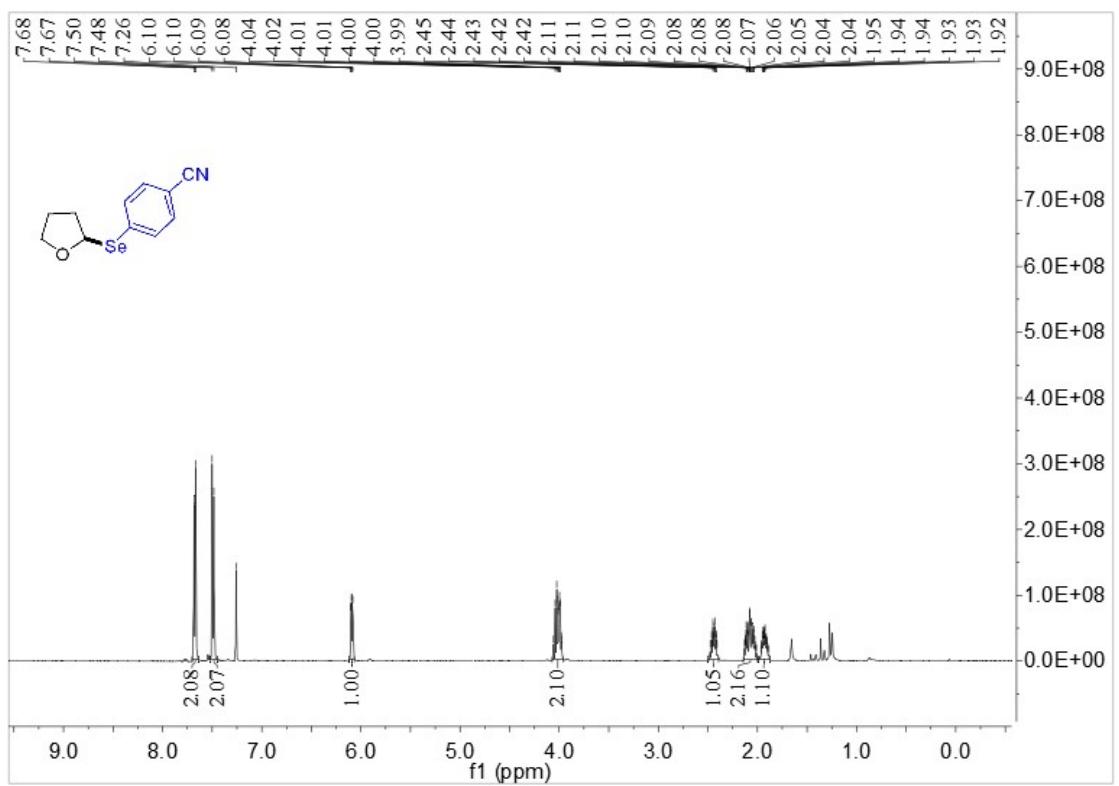


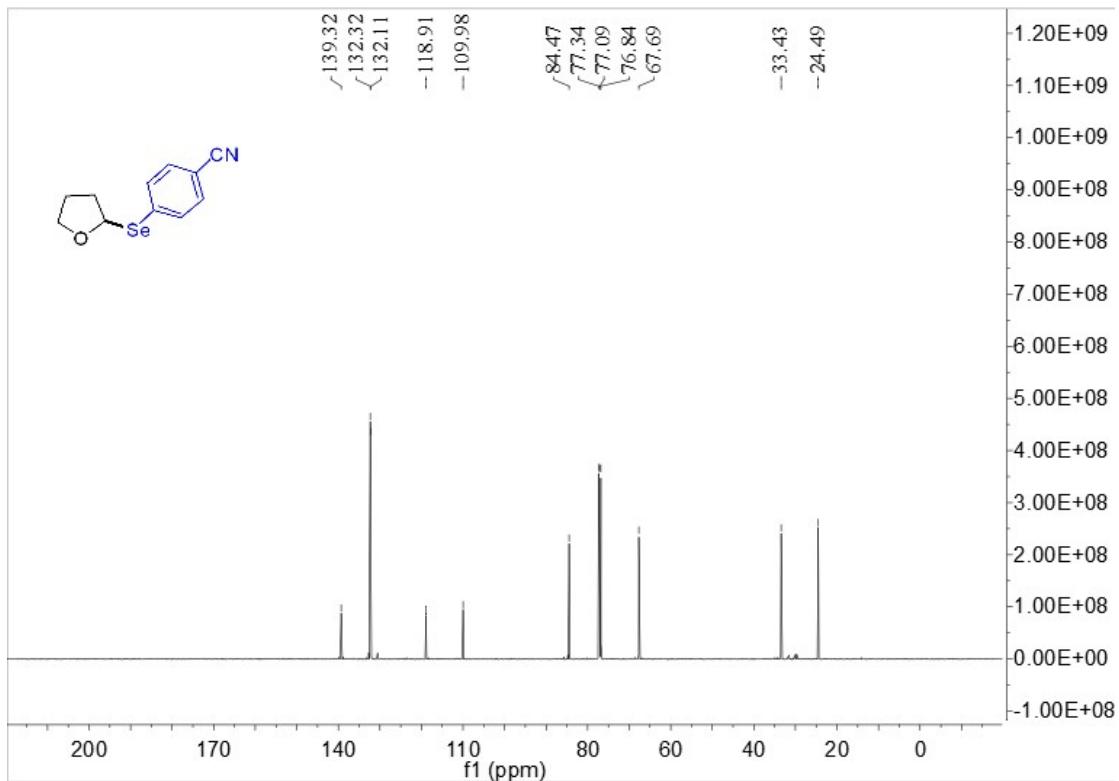
Compound 3d



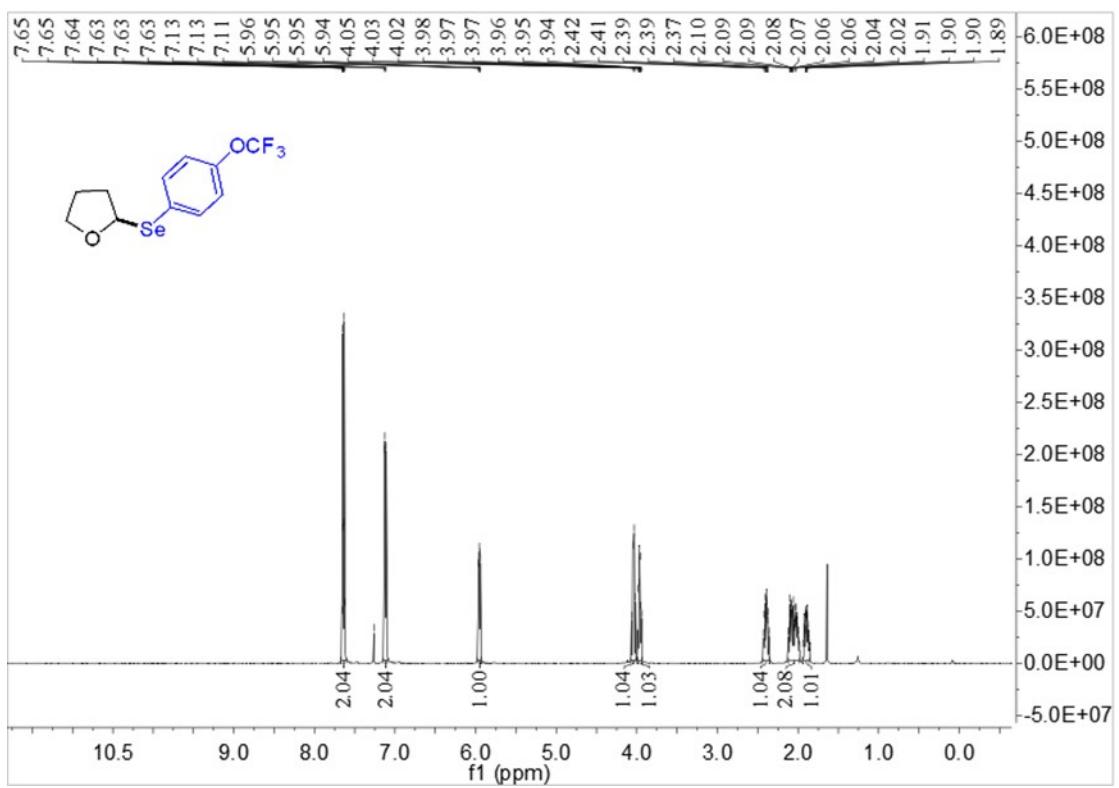


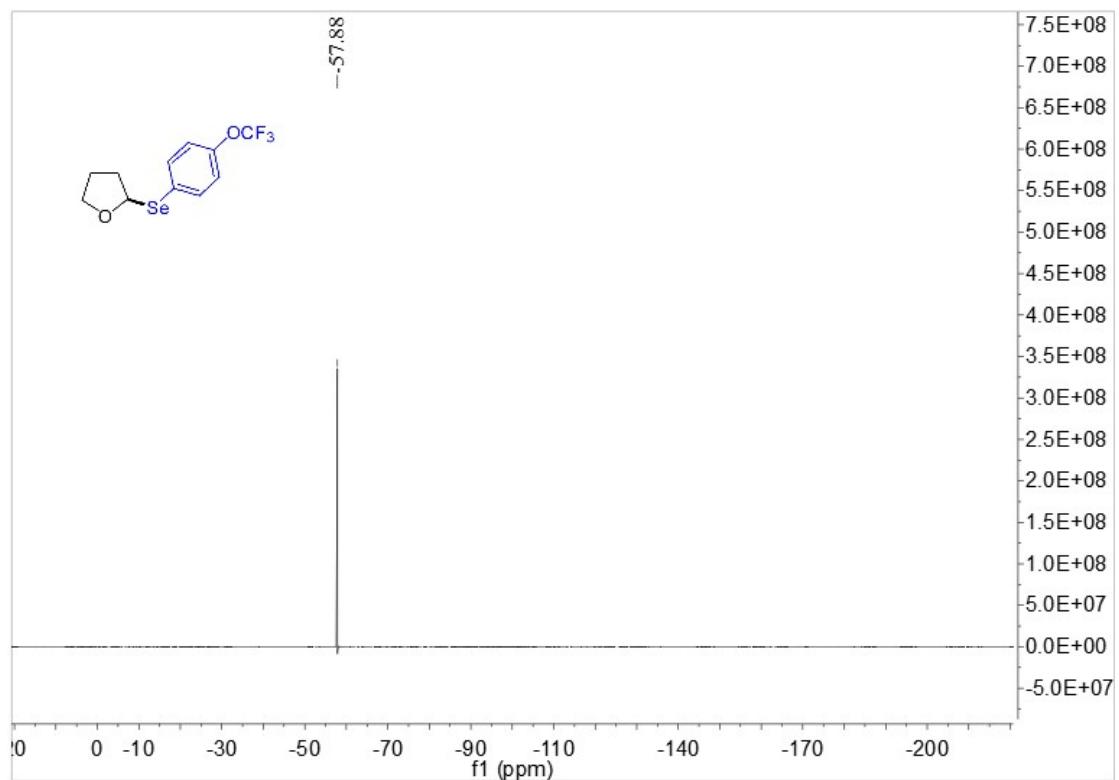
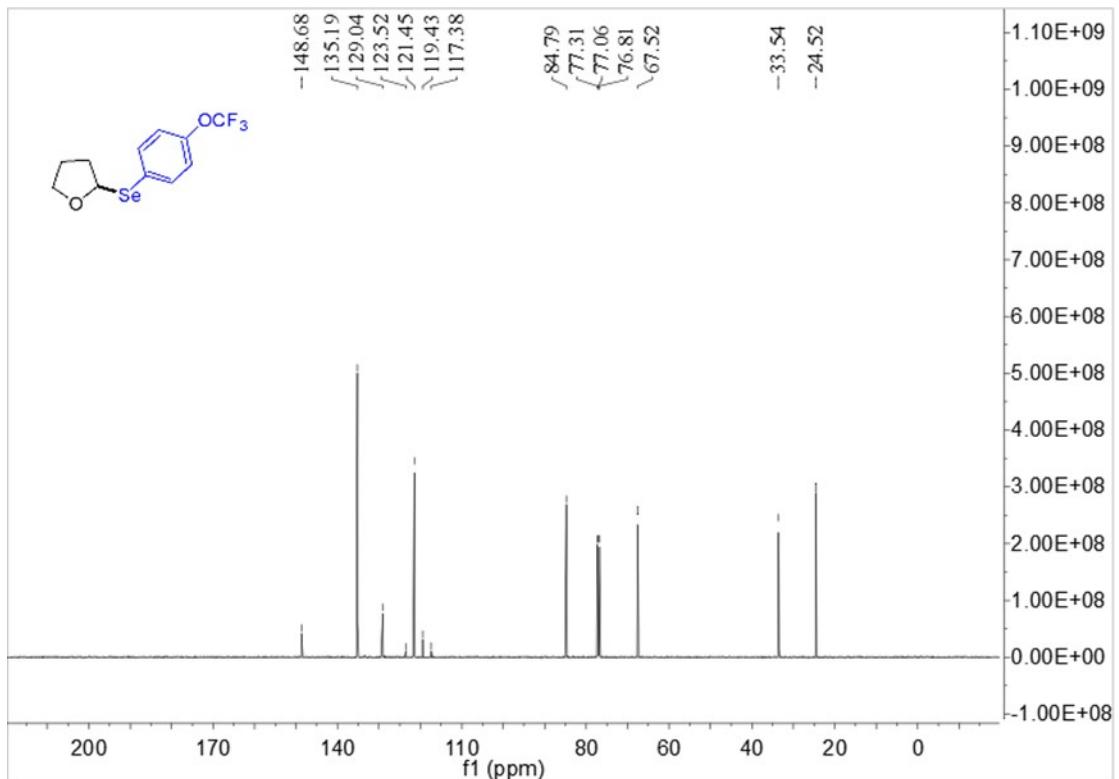
Compound 3e



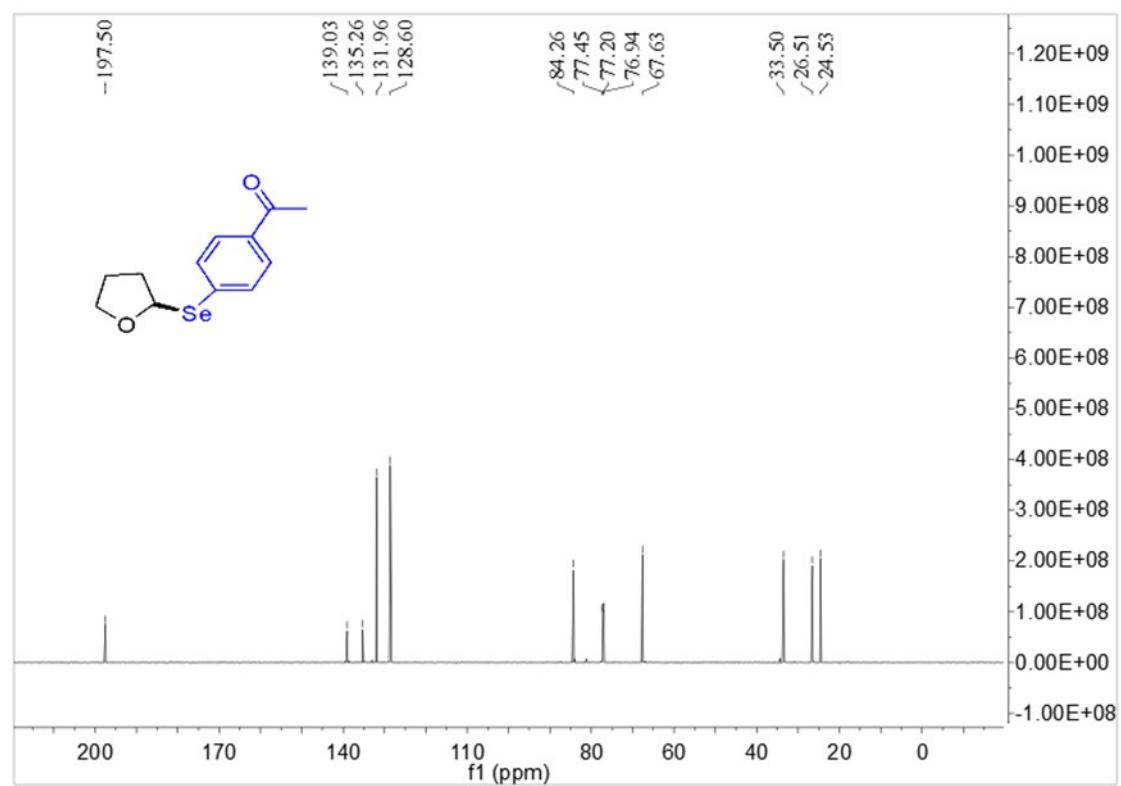
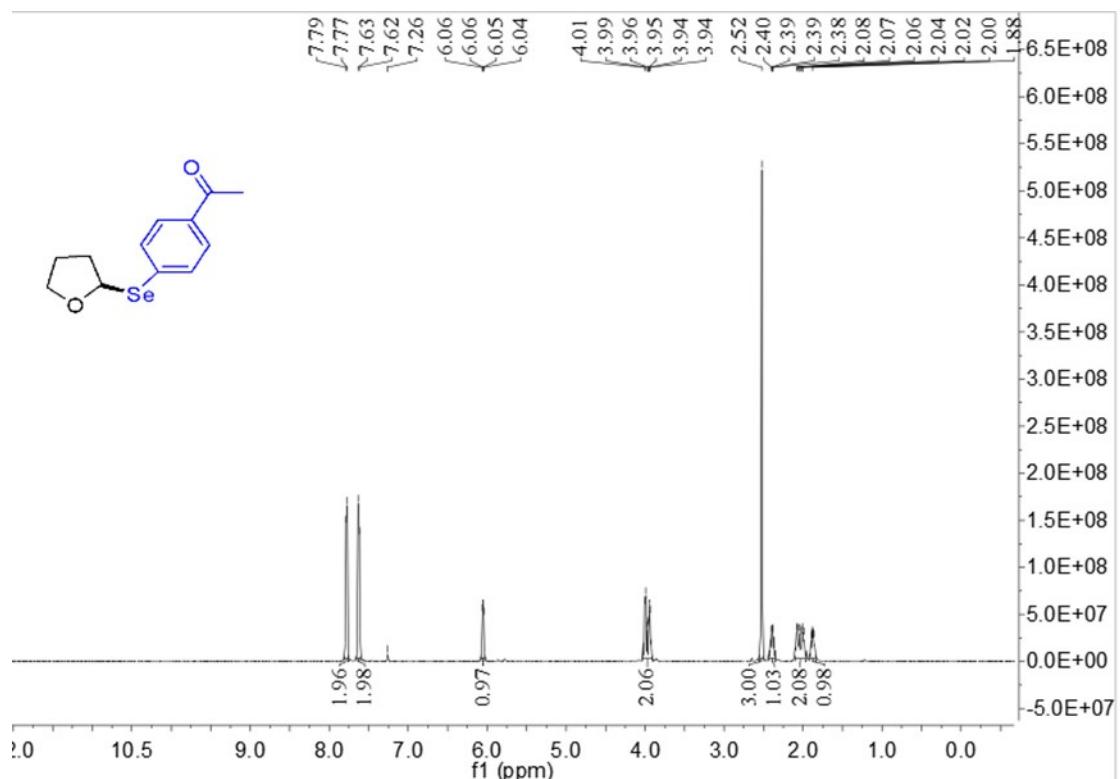


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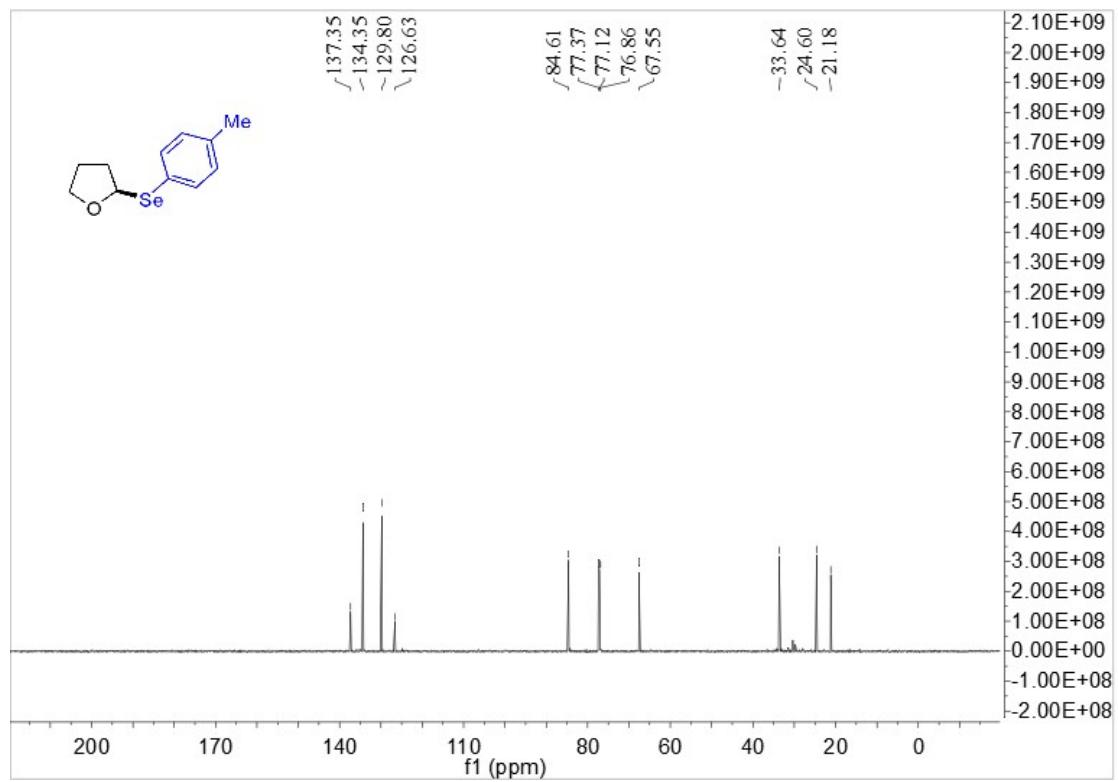
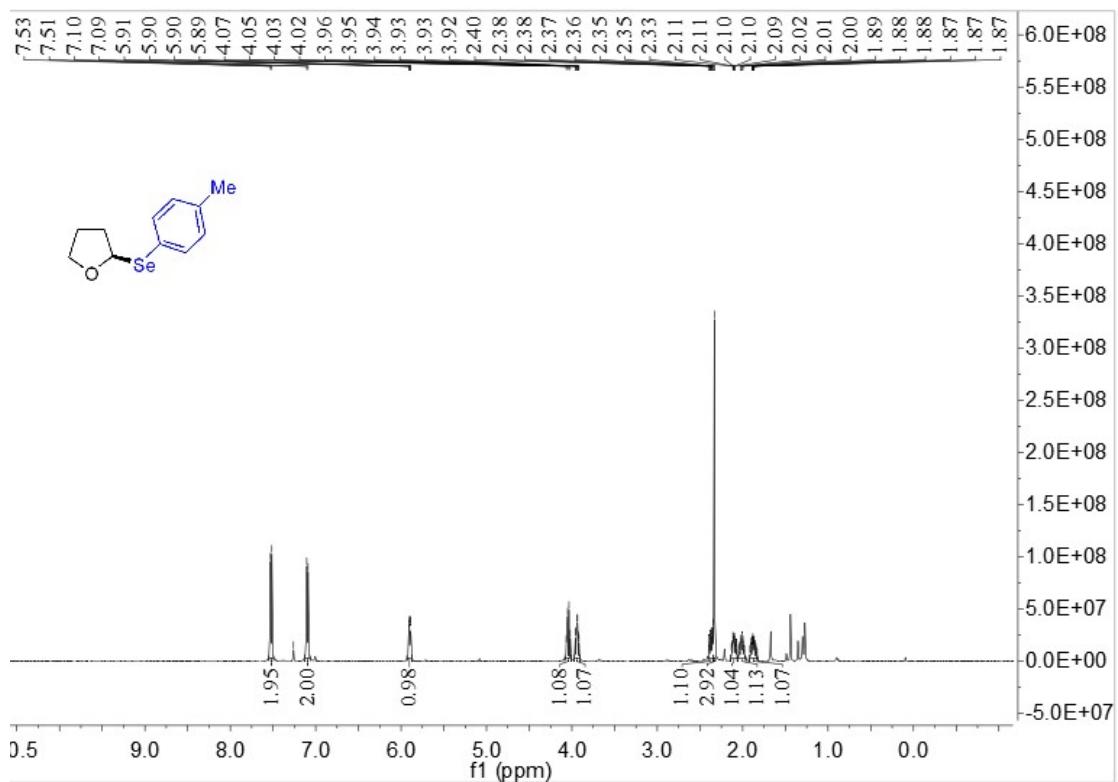




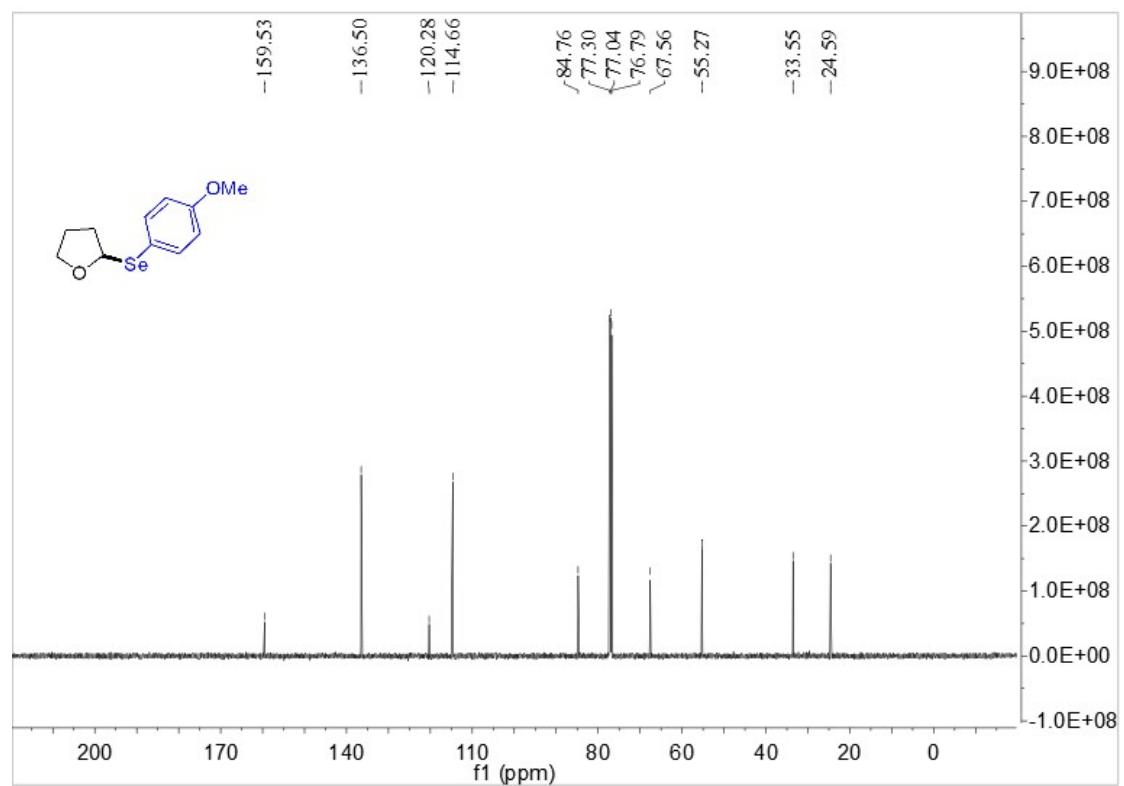
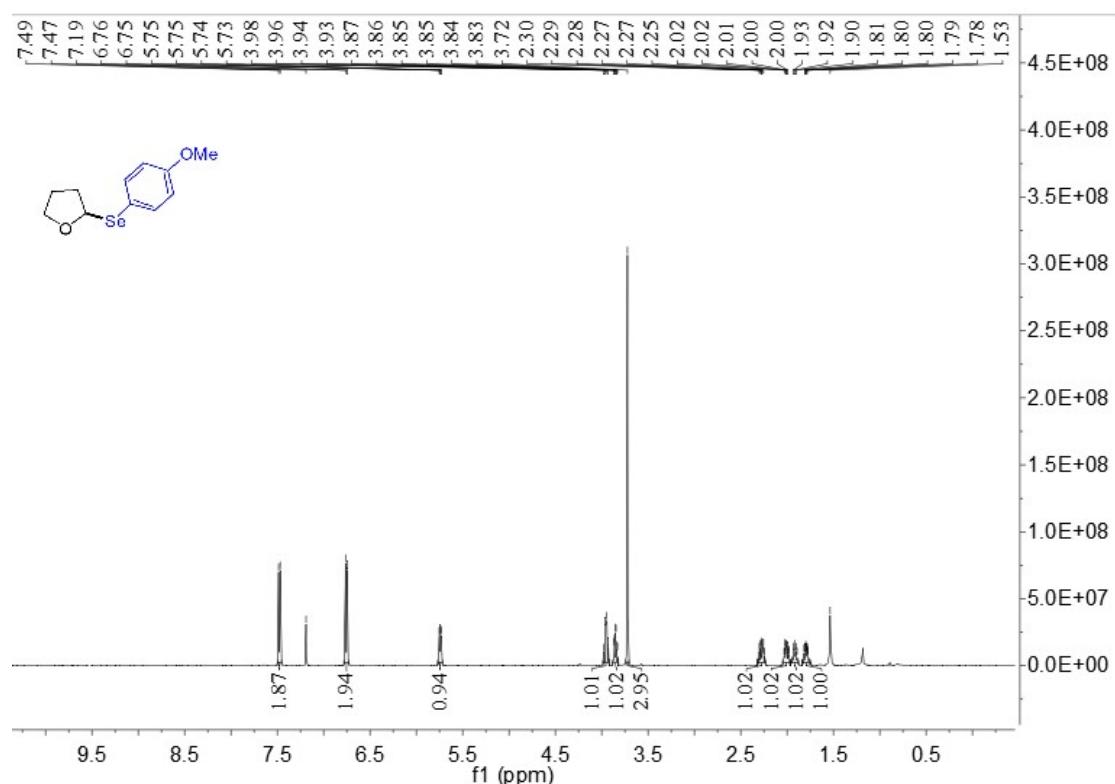
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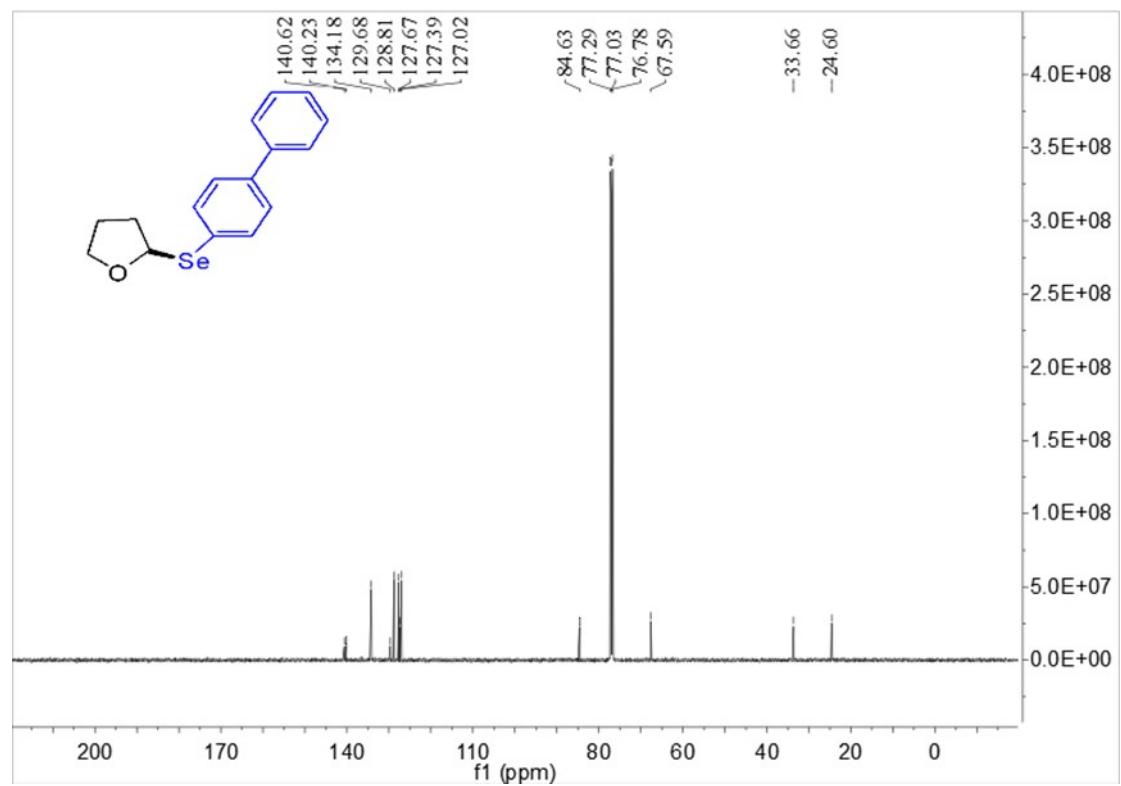
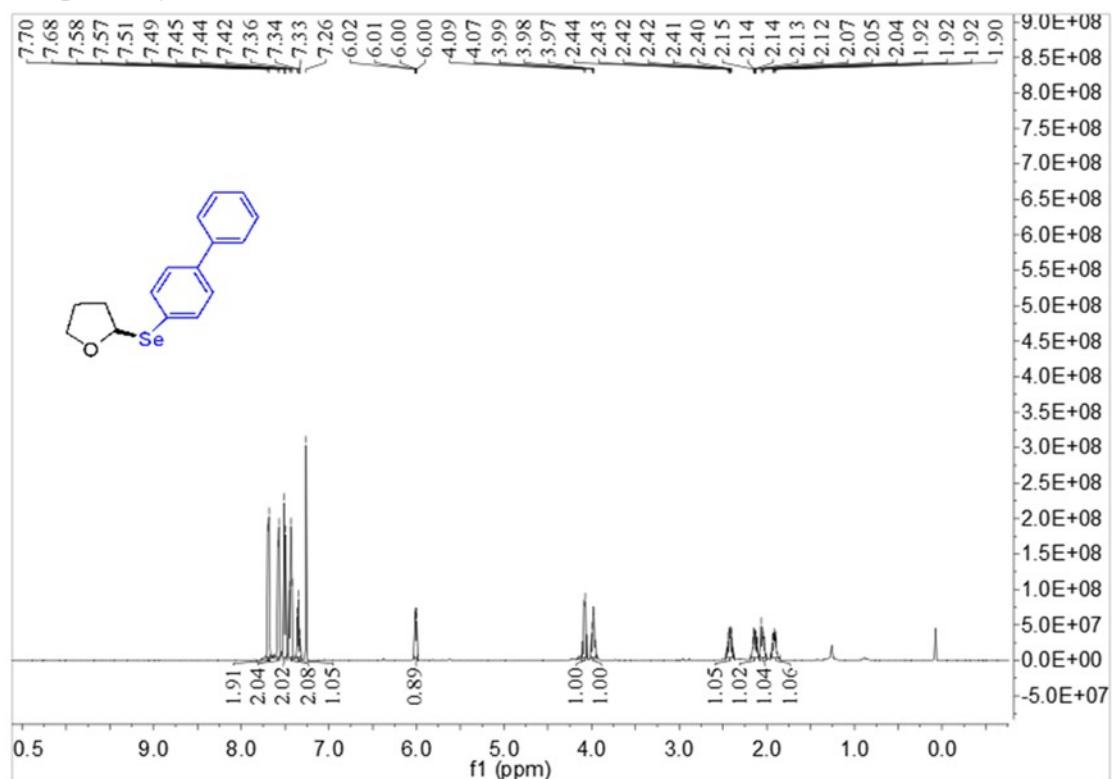
Compound 3h



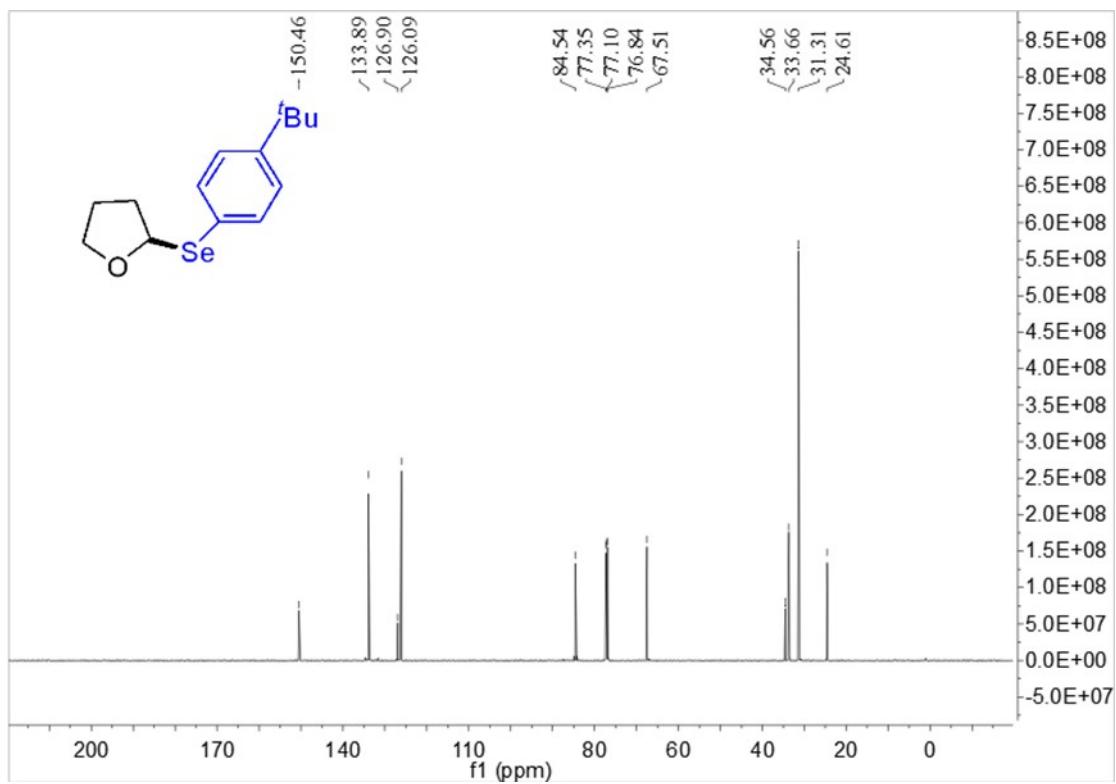
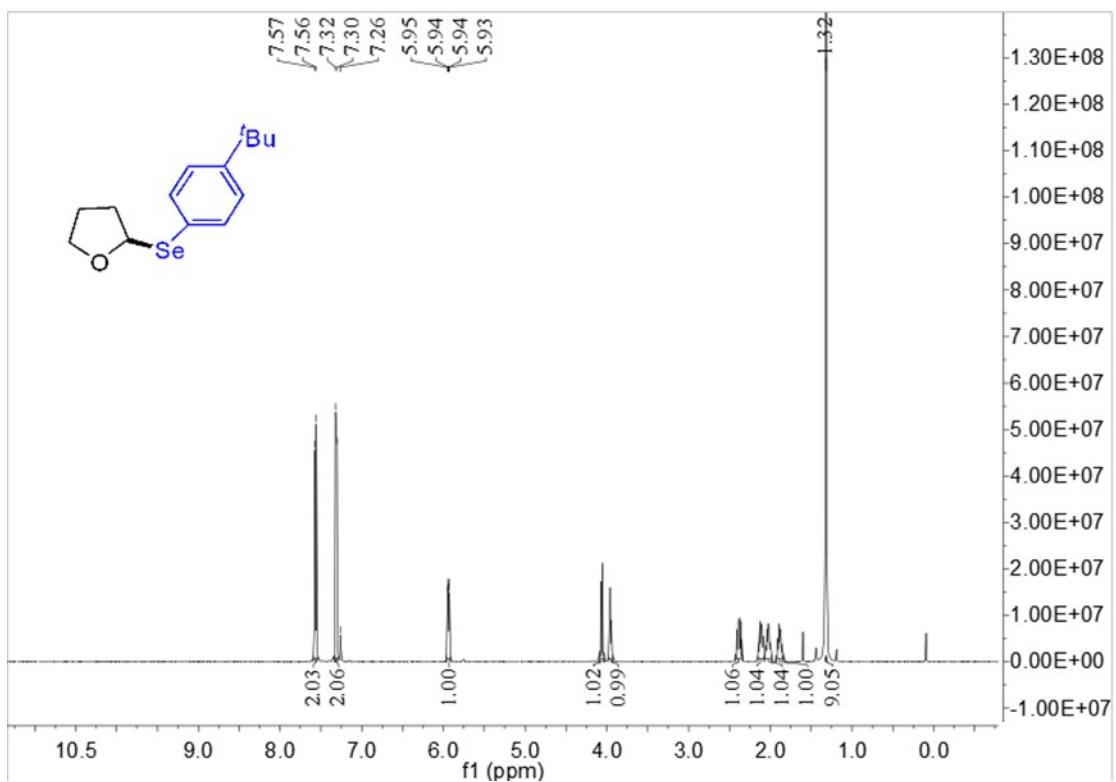
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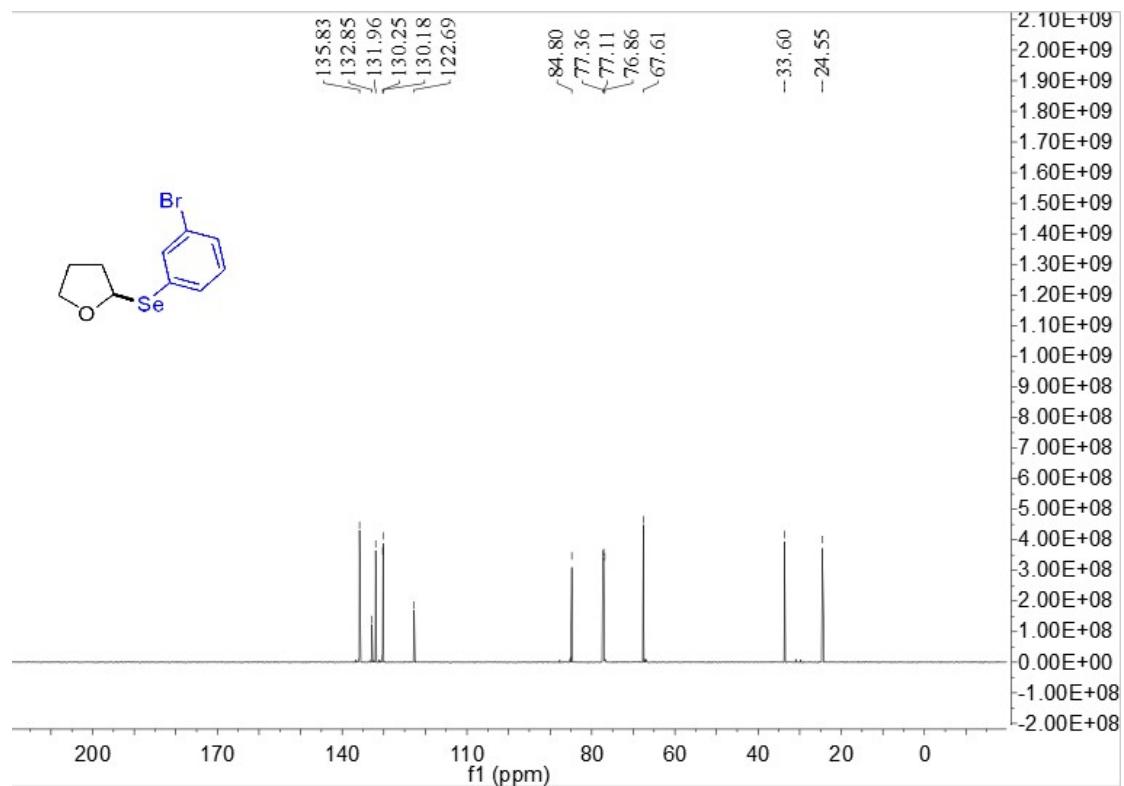
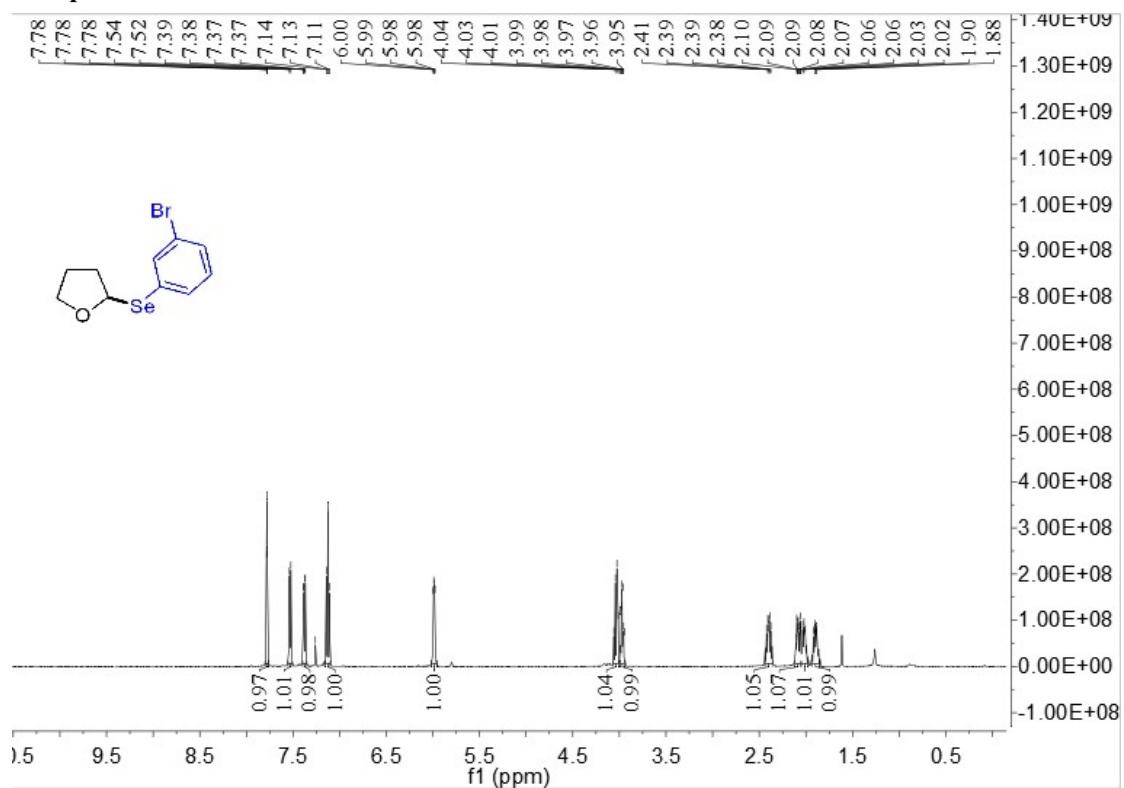
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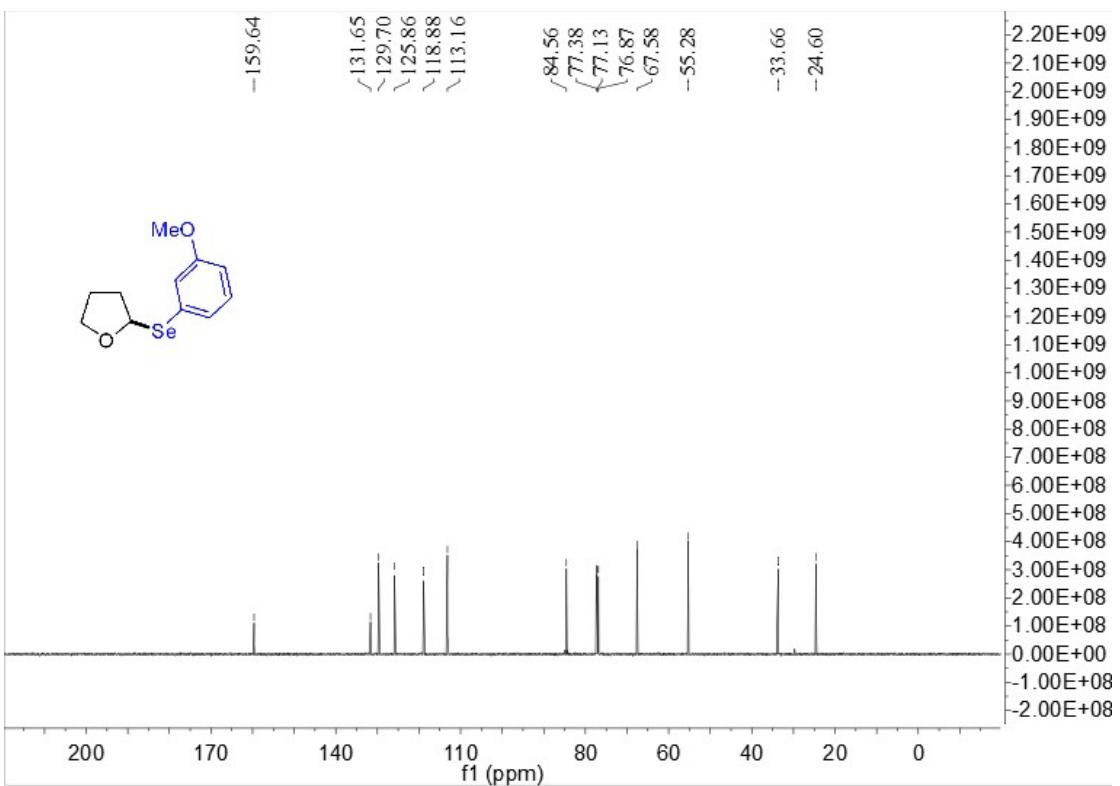
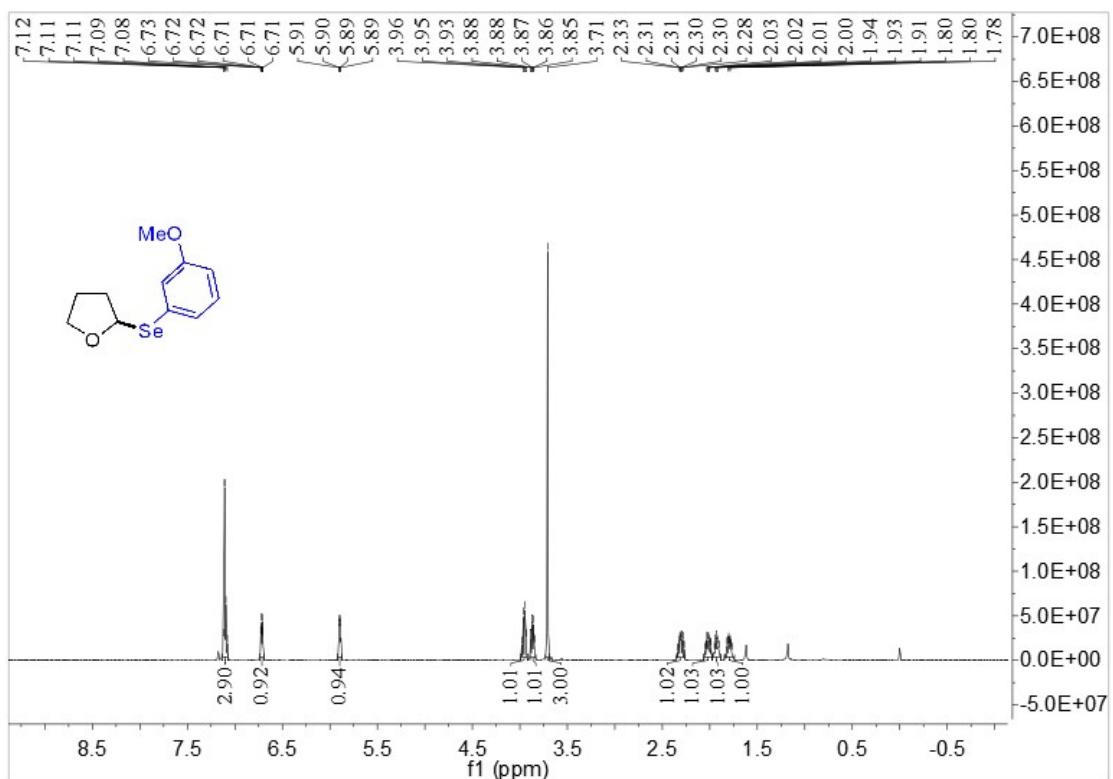
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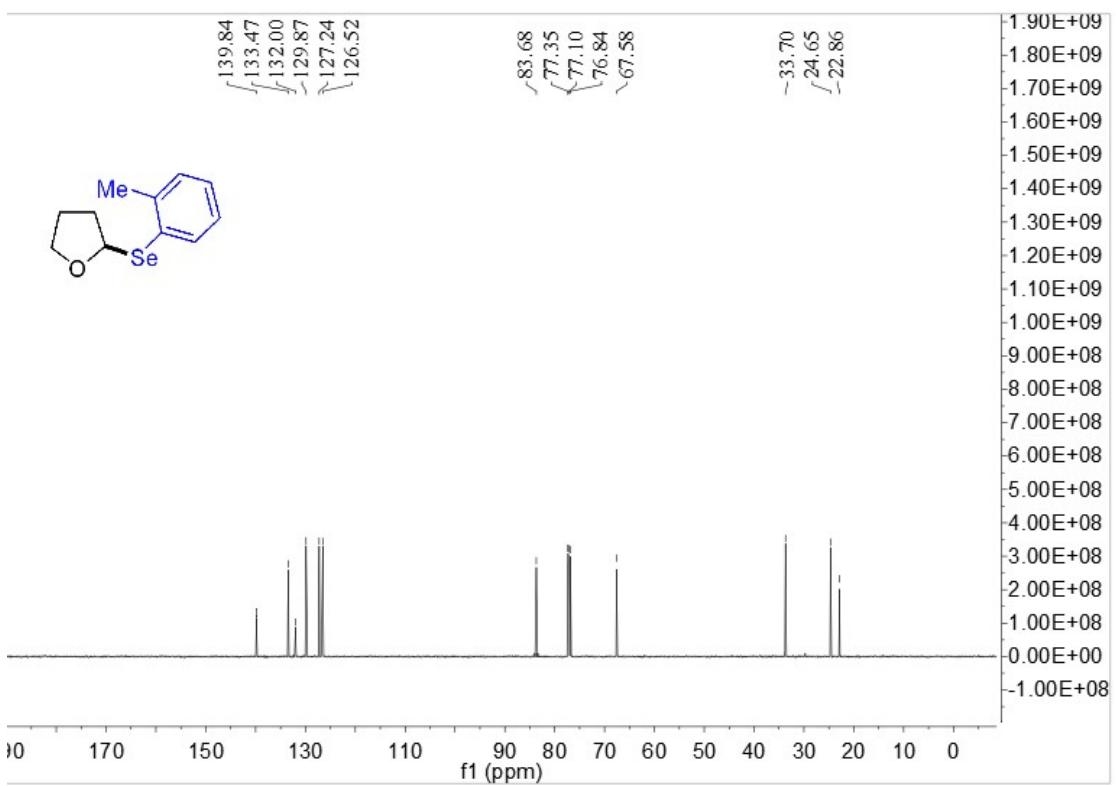
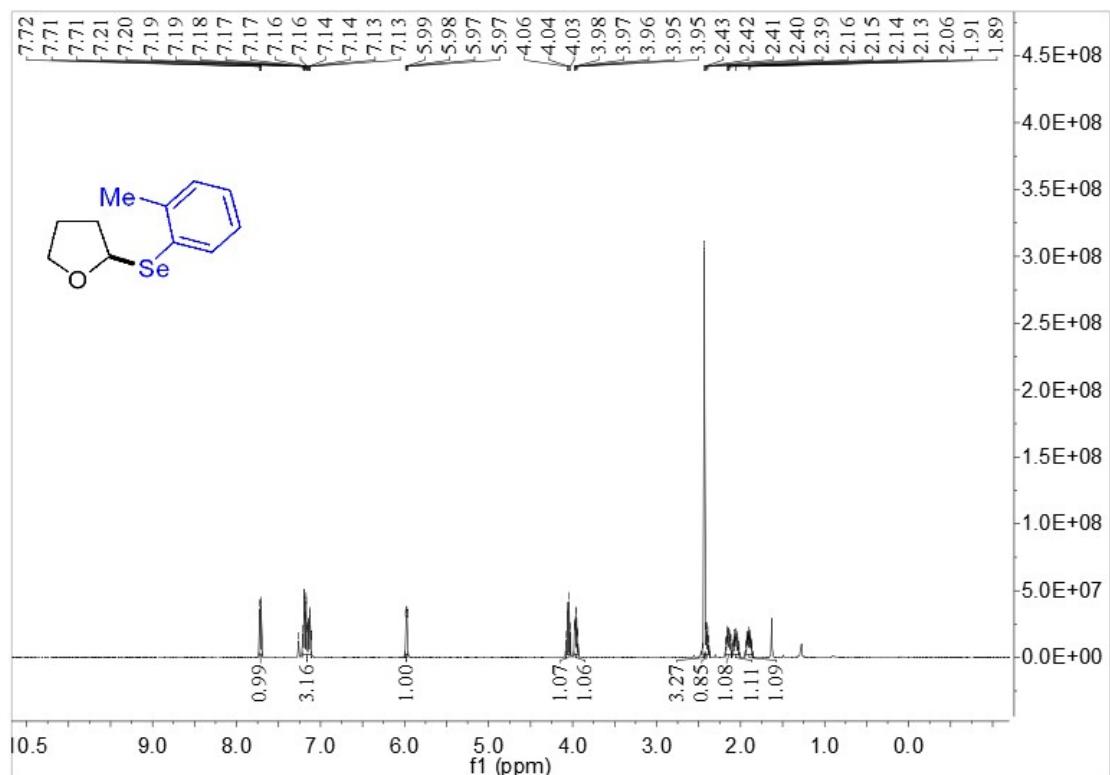
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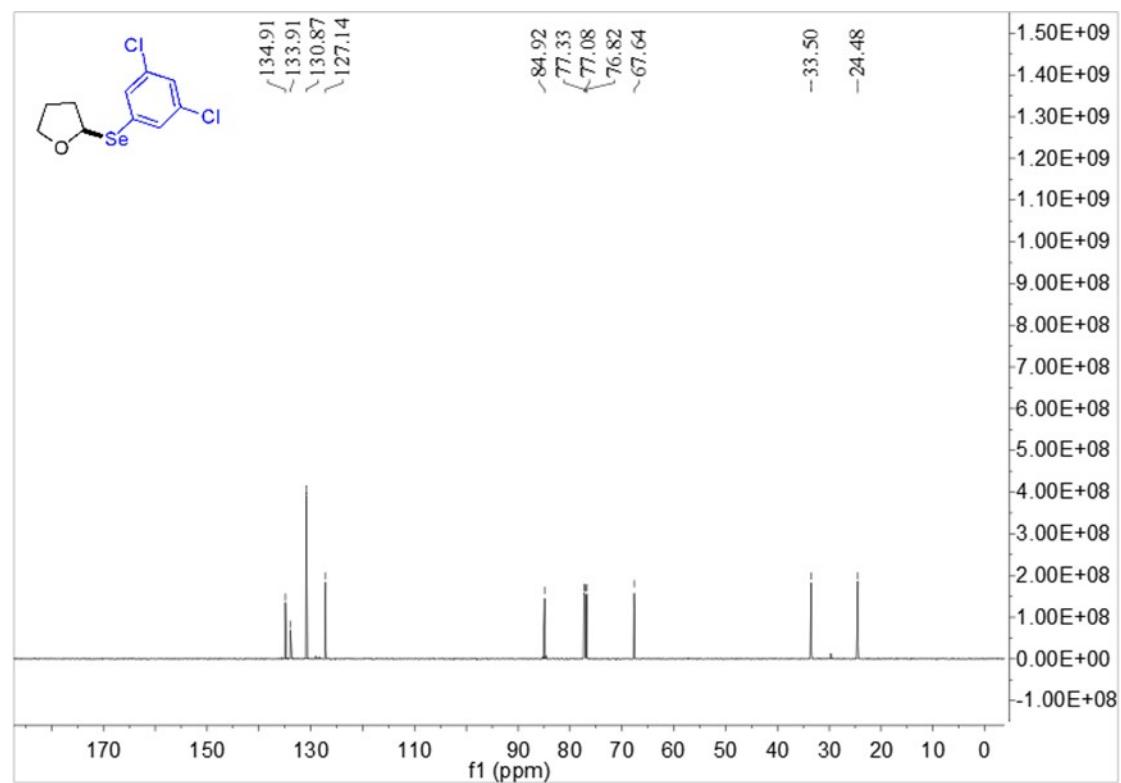
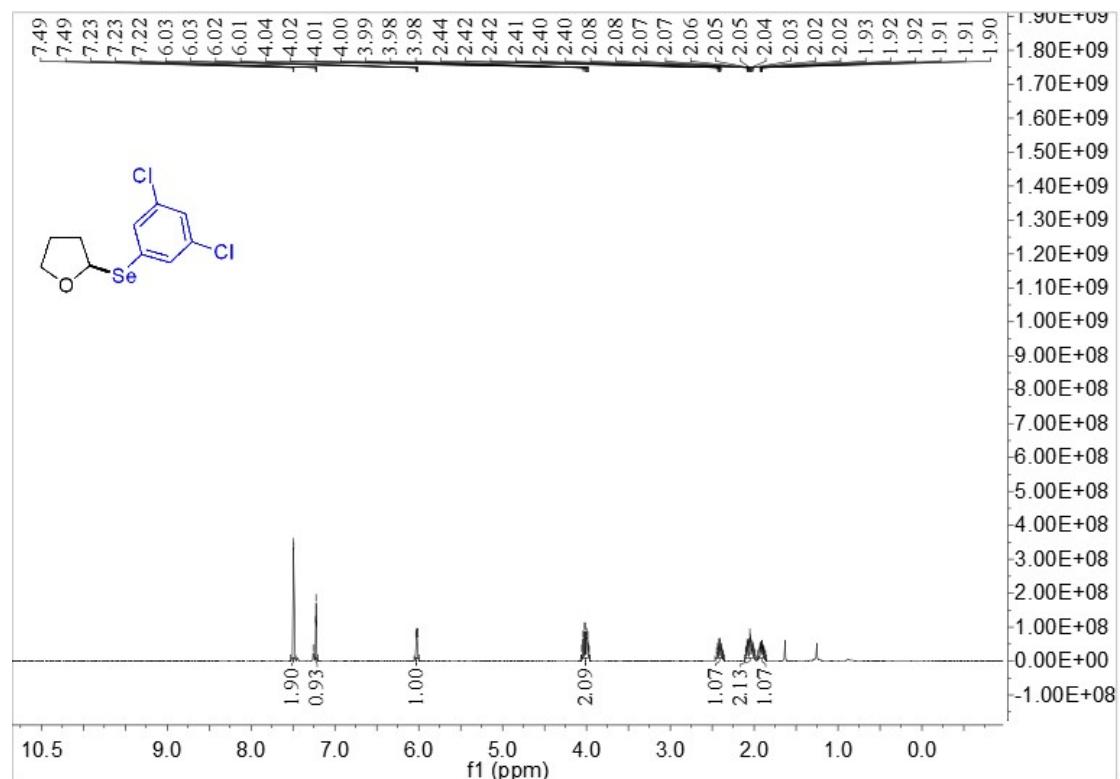
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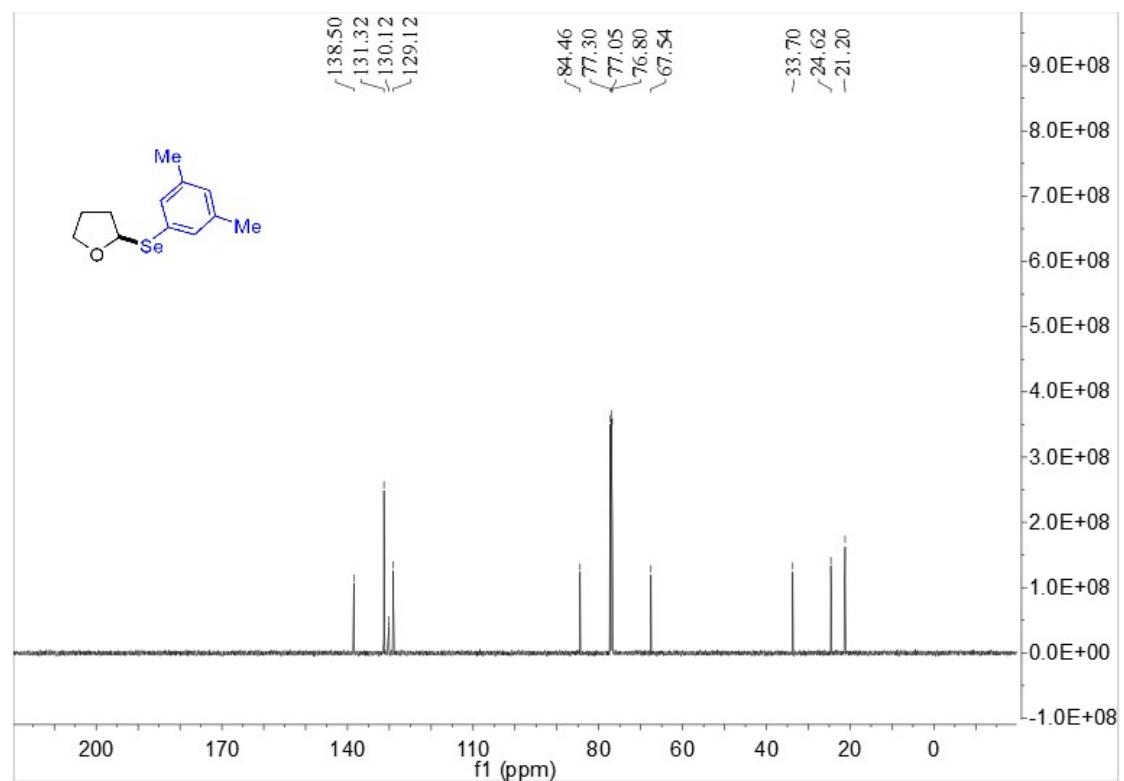
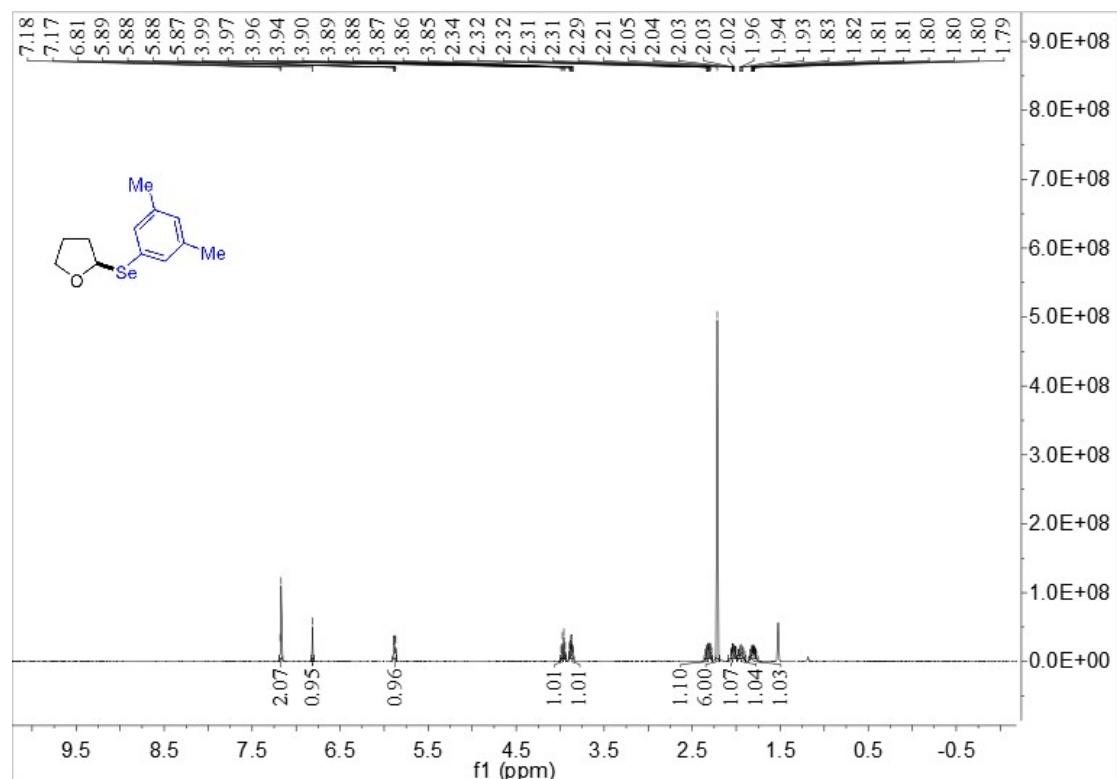
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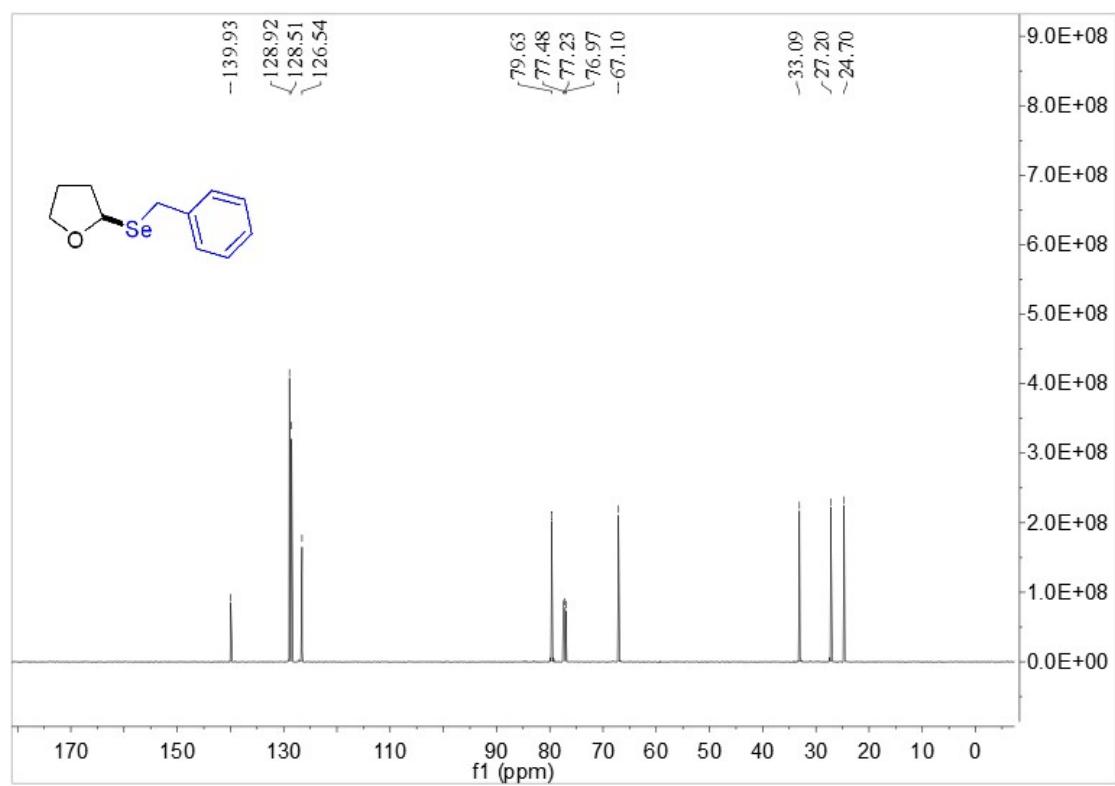
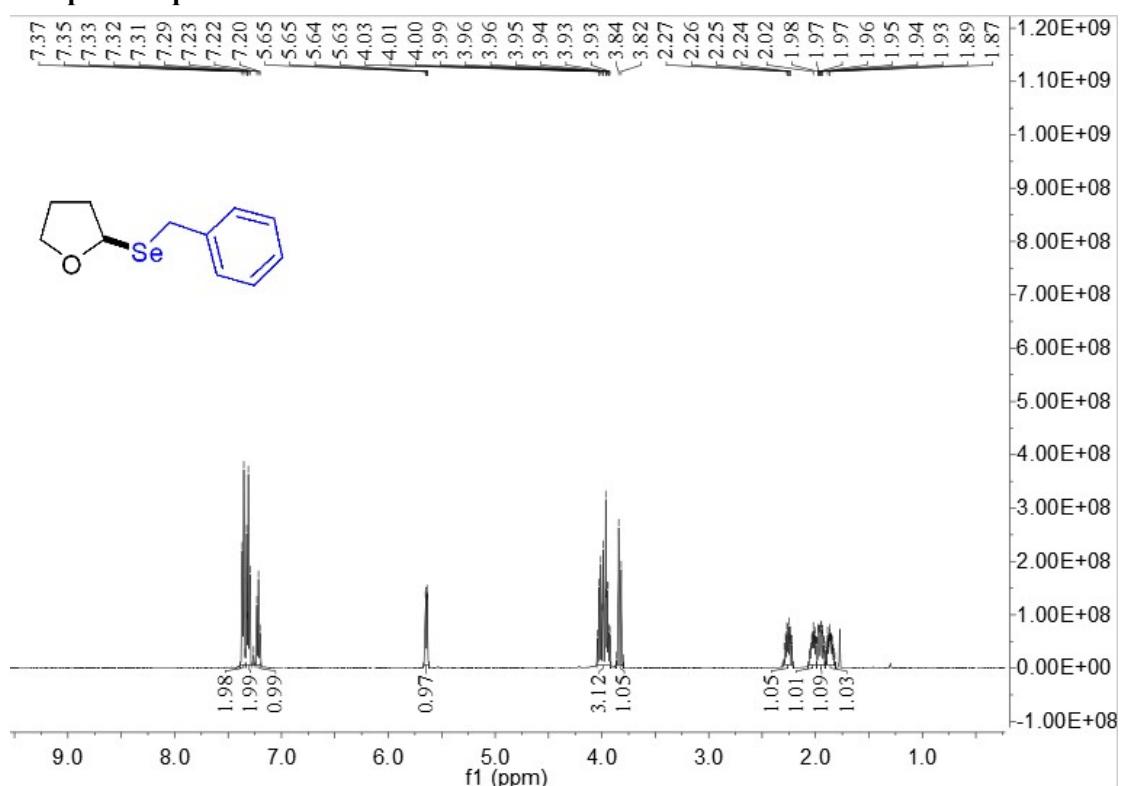
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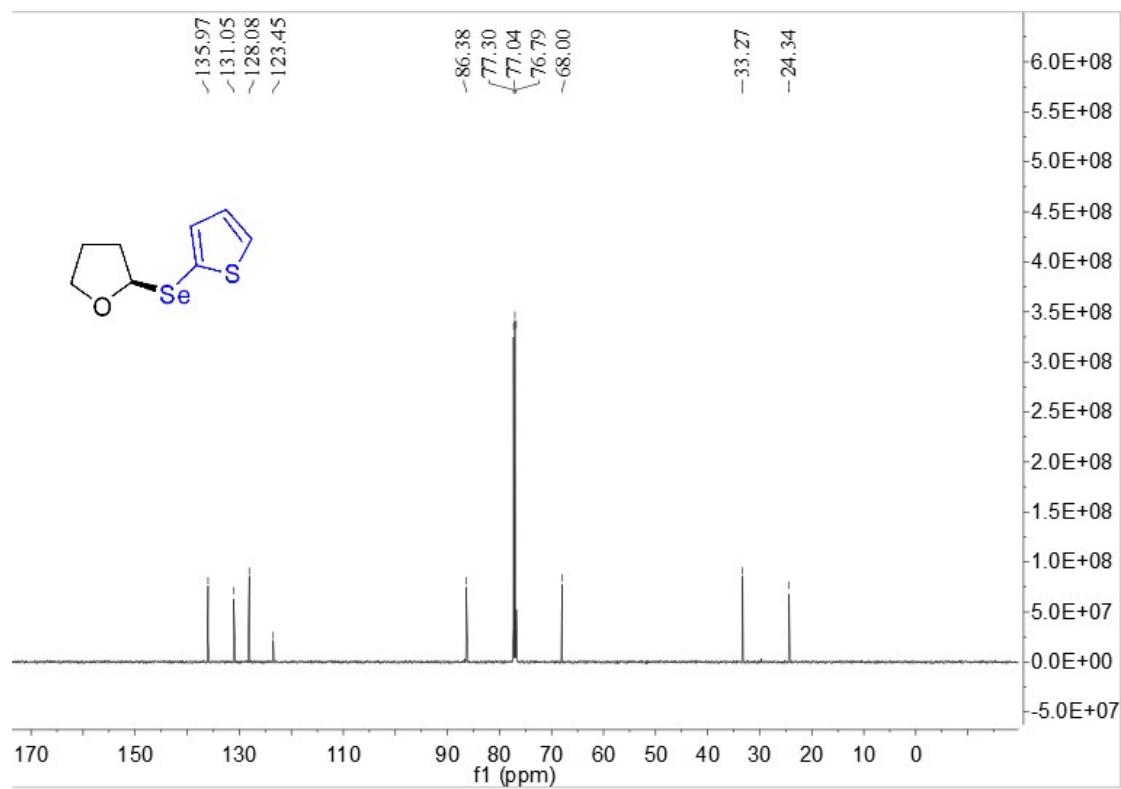
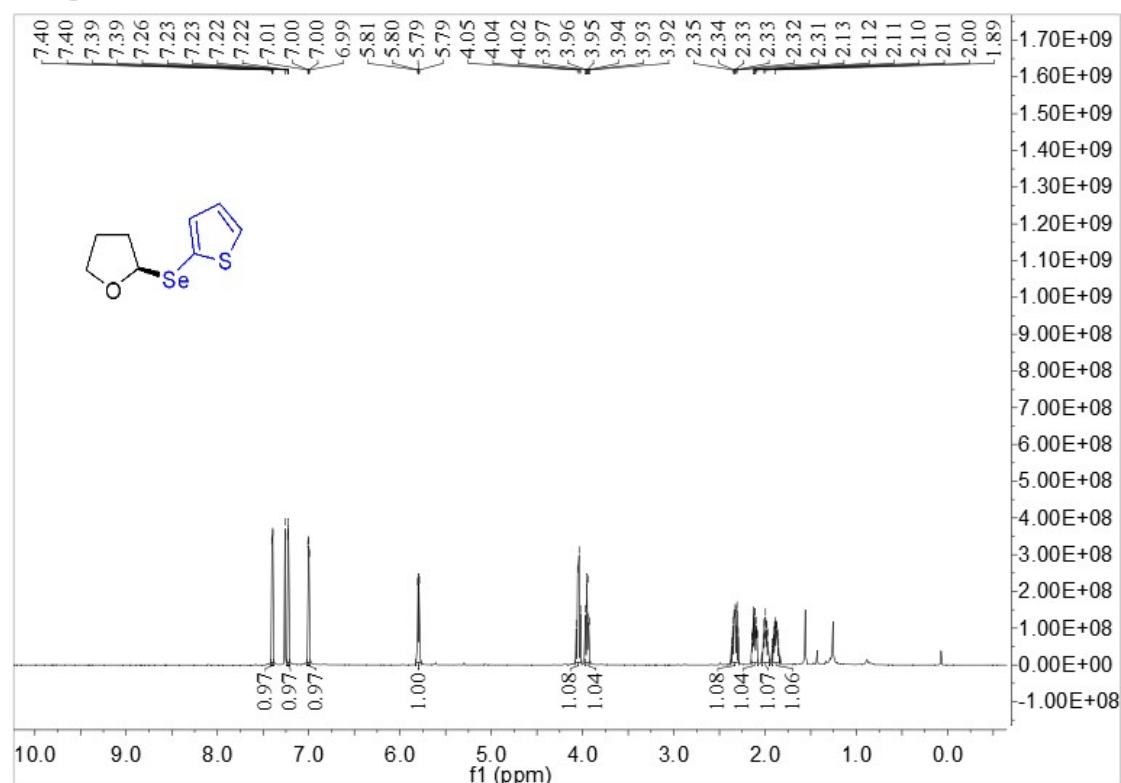
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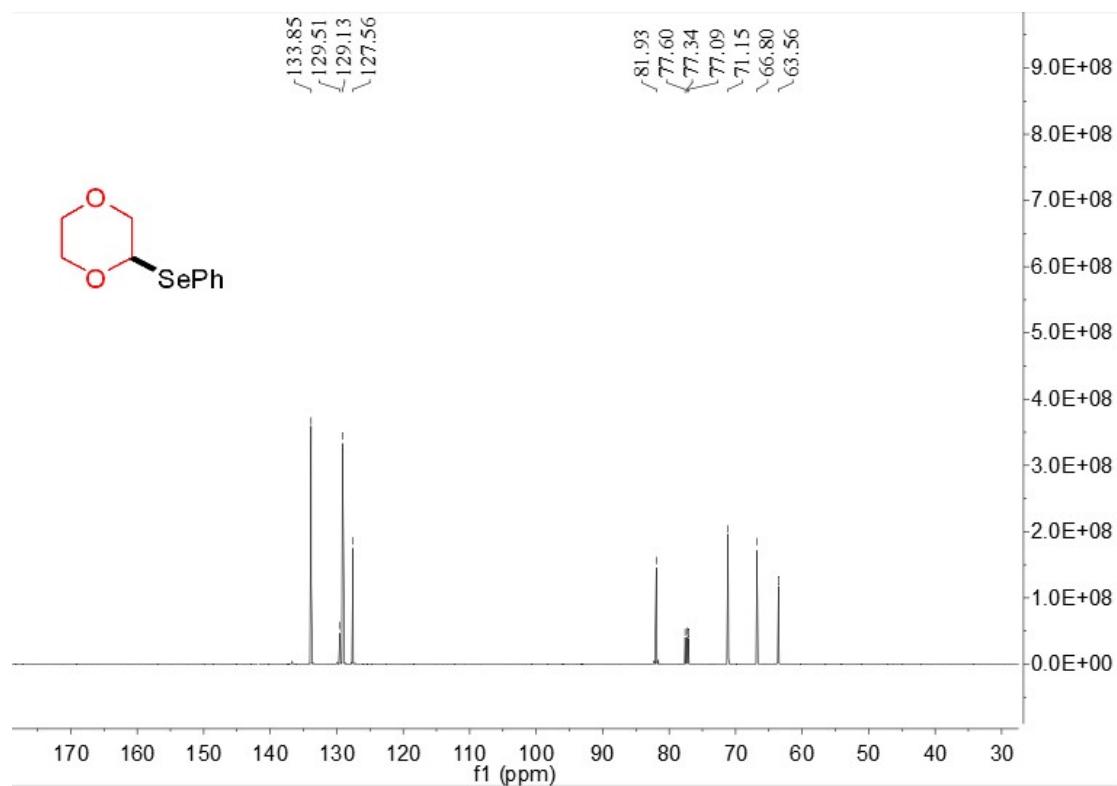
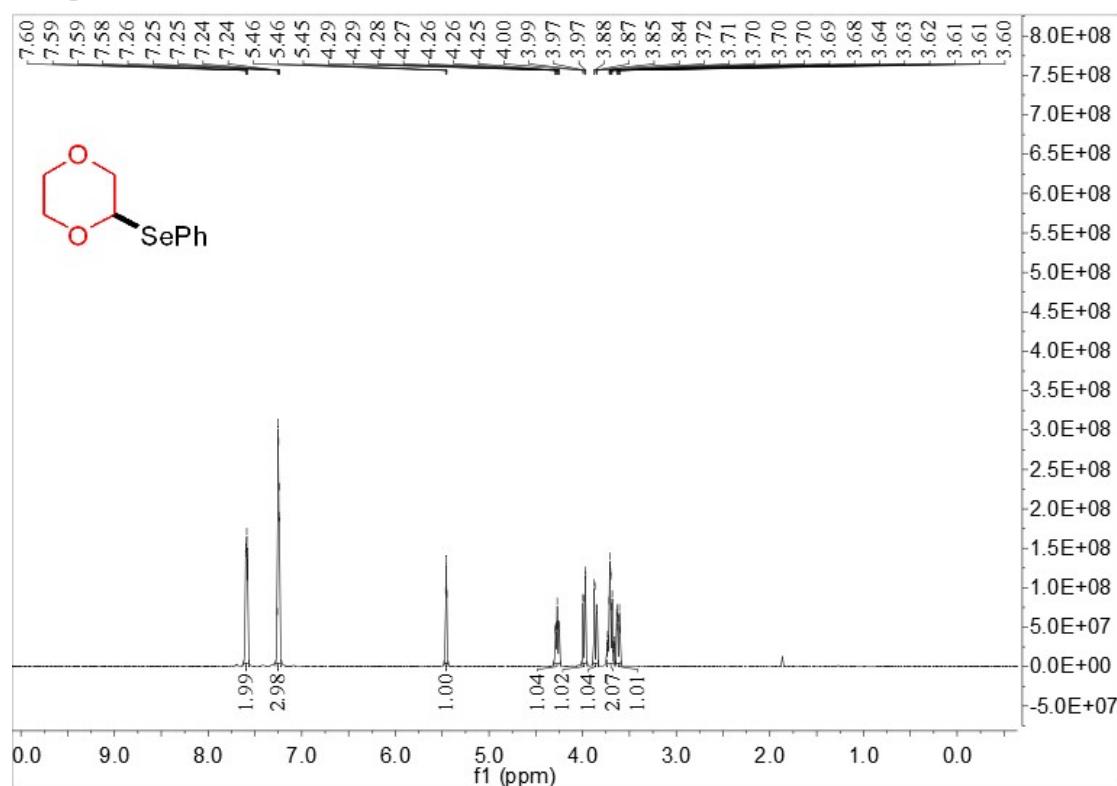
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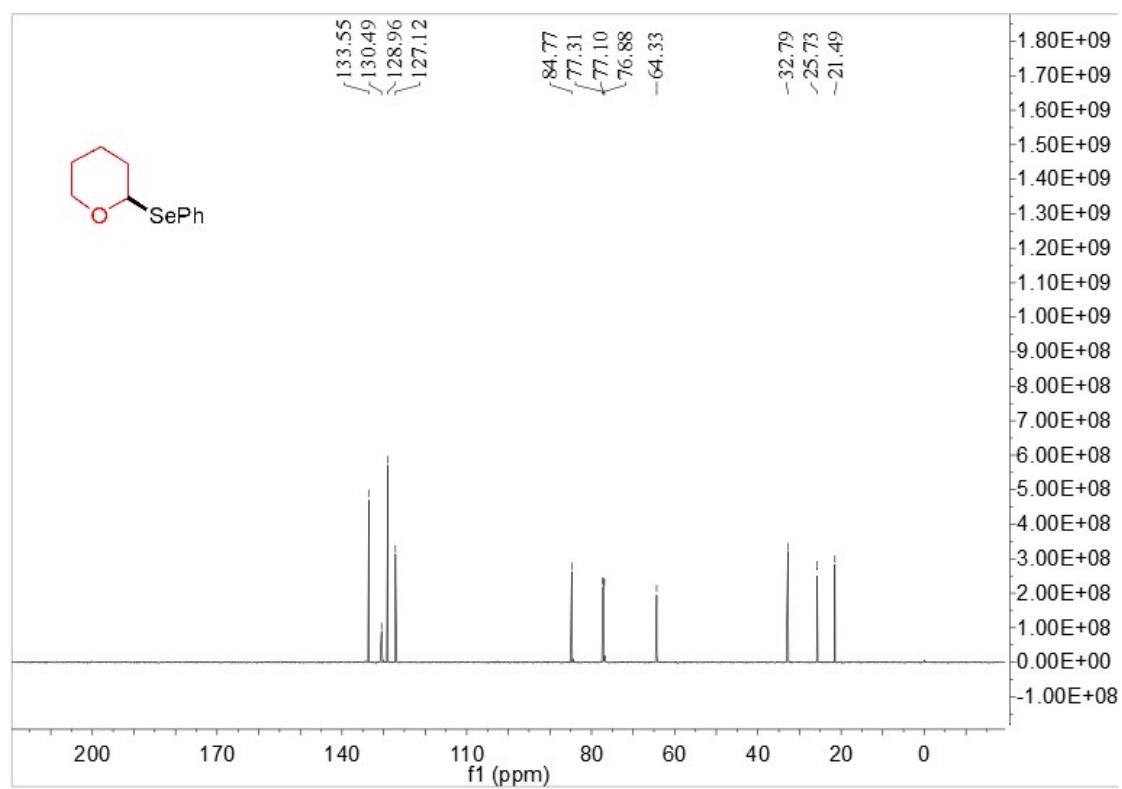
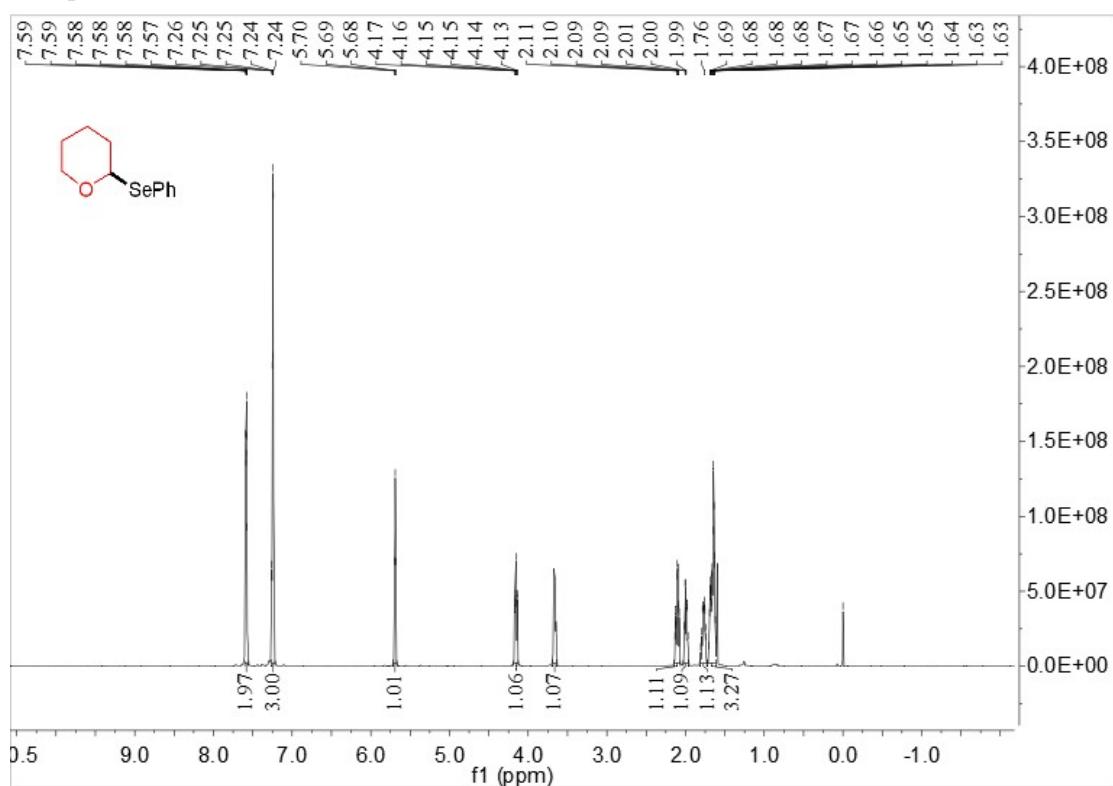
Compound 3r



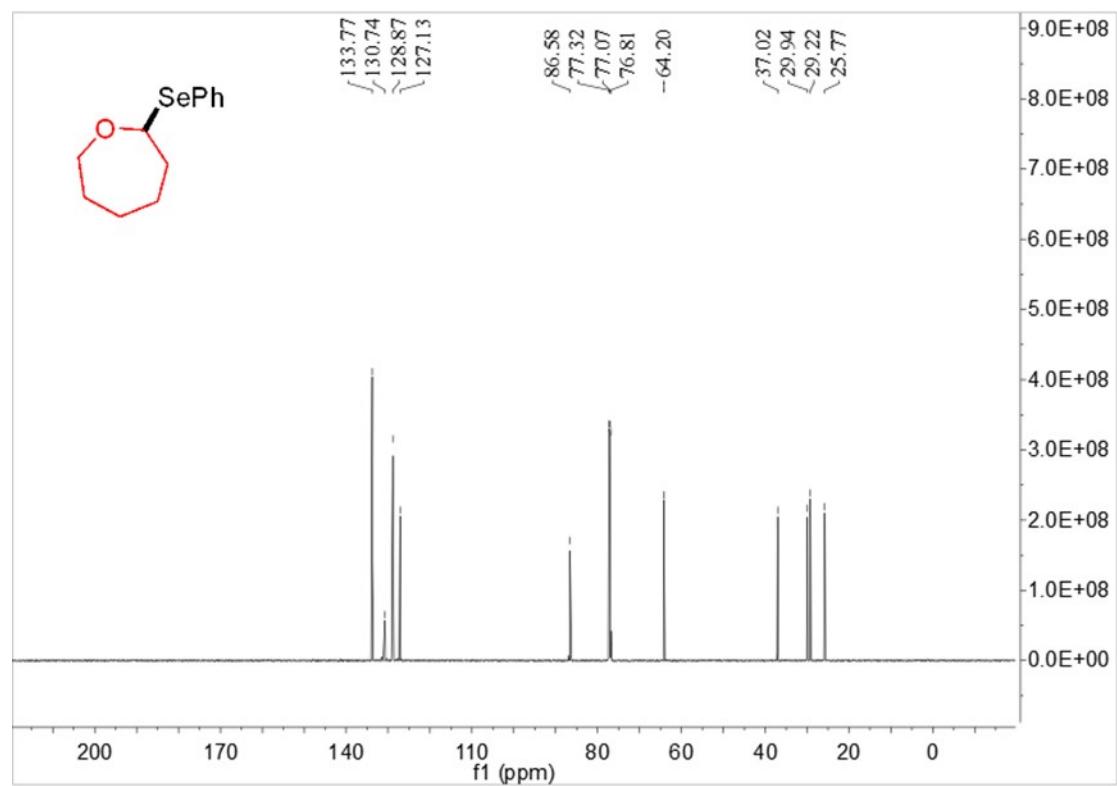
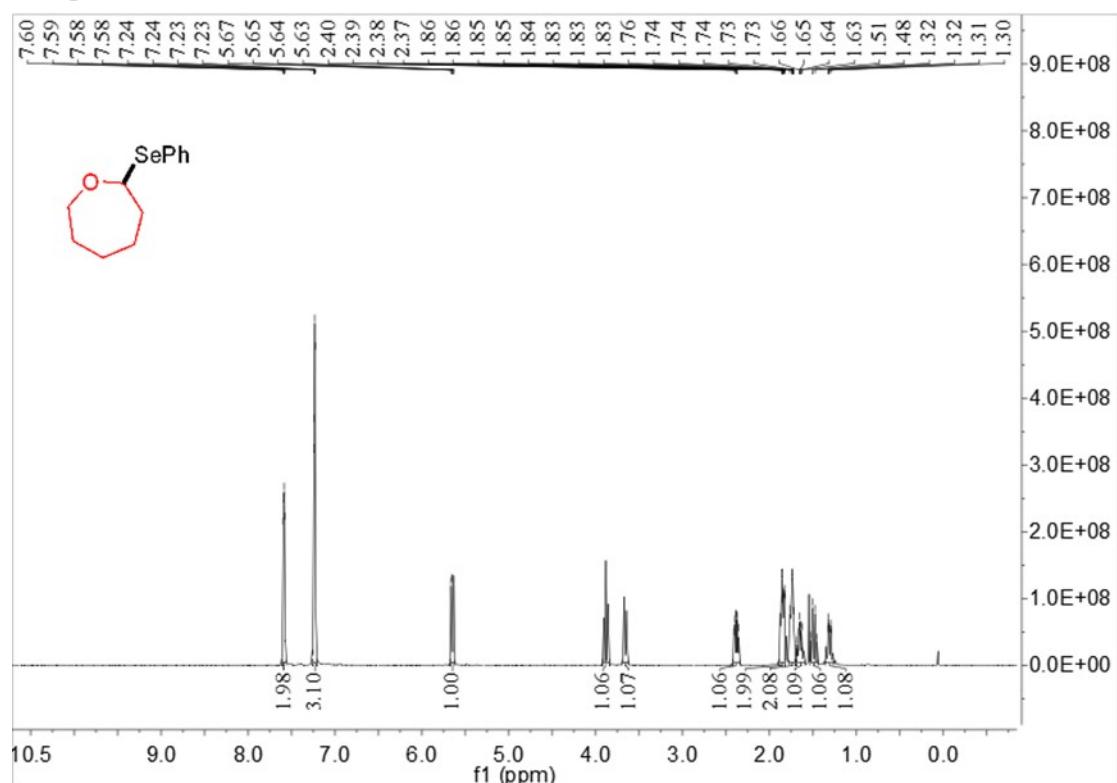
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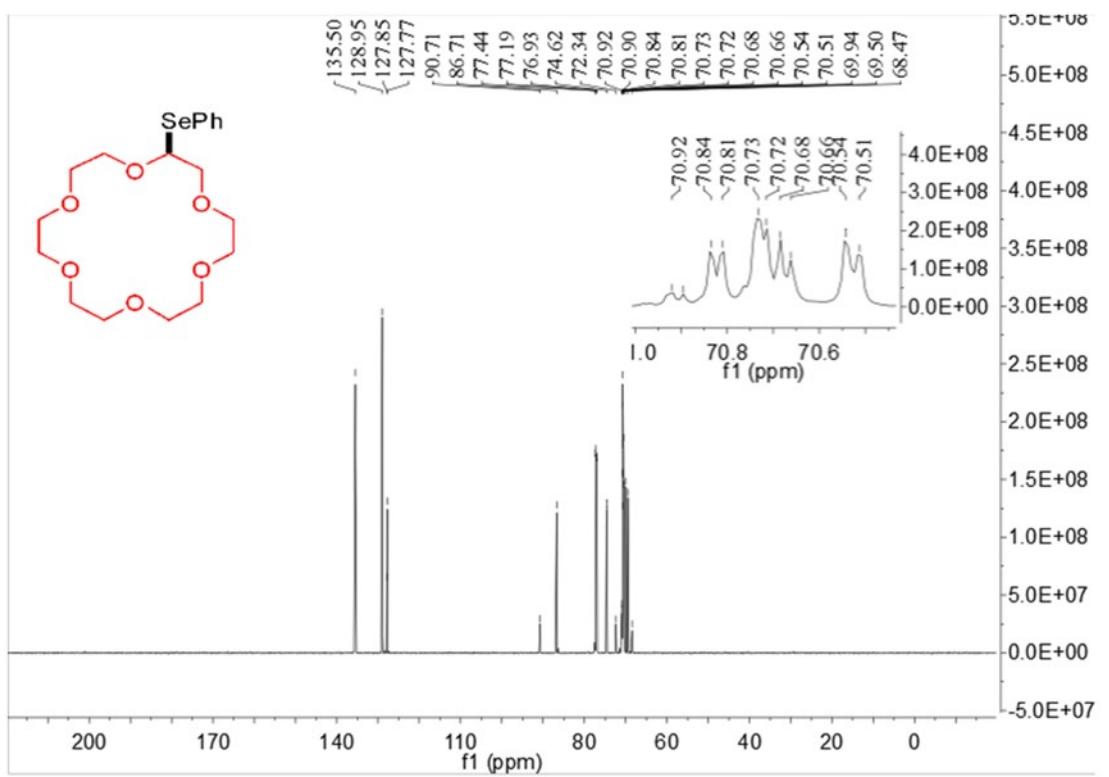
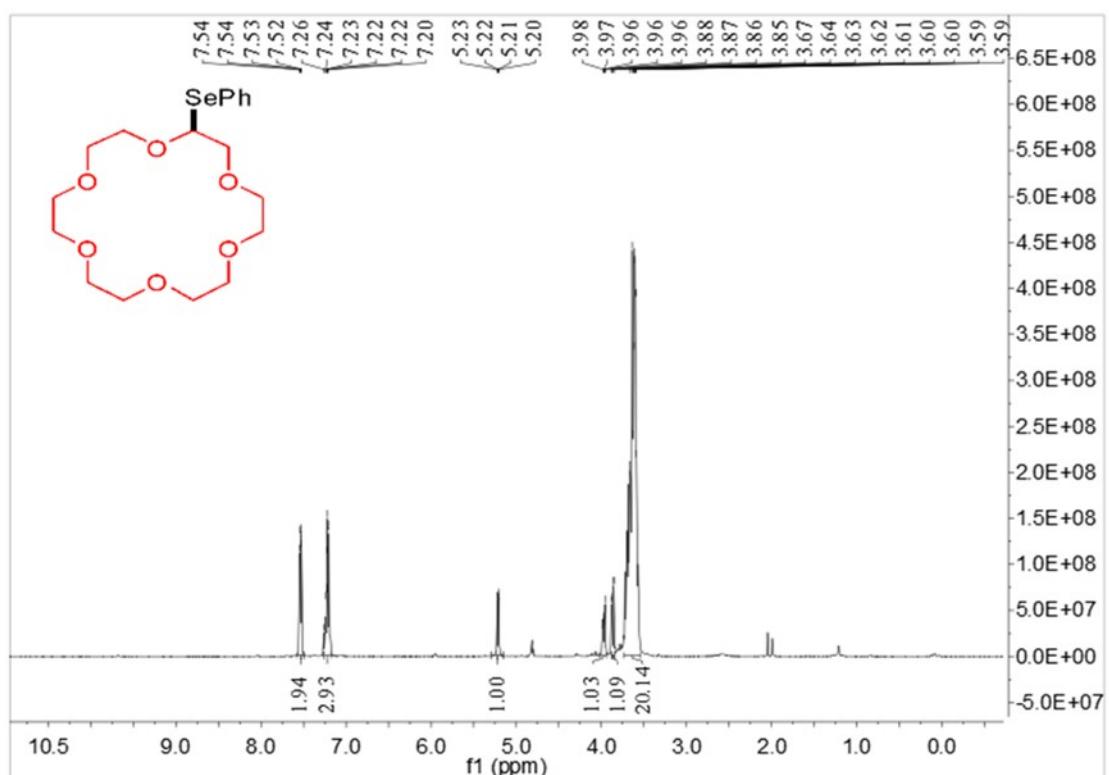
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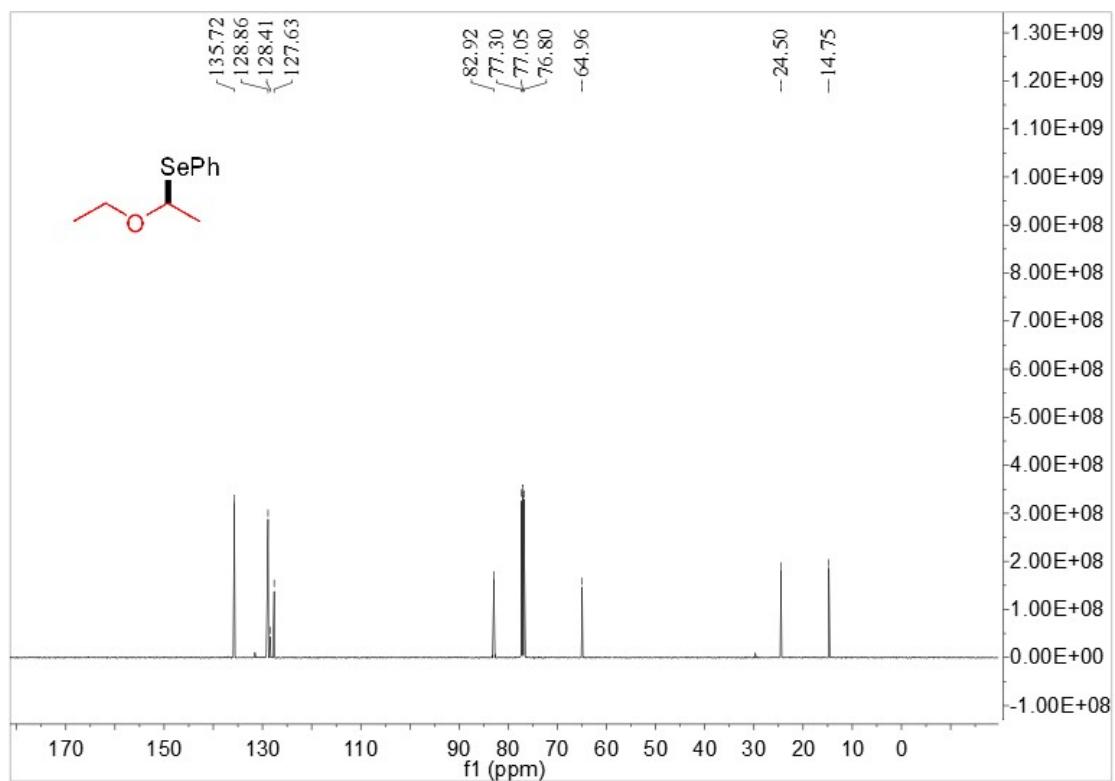
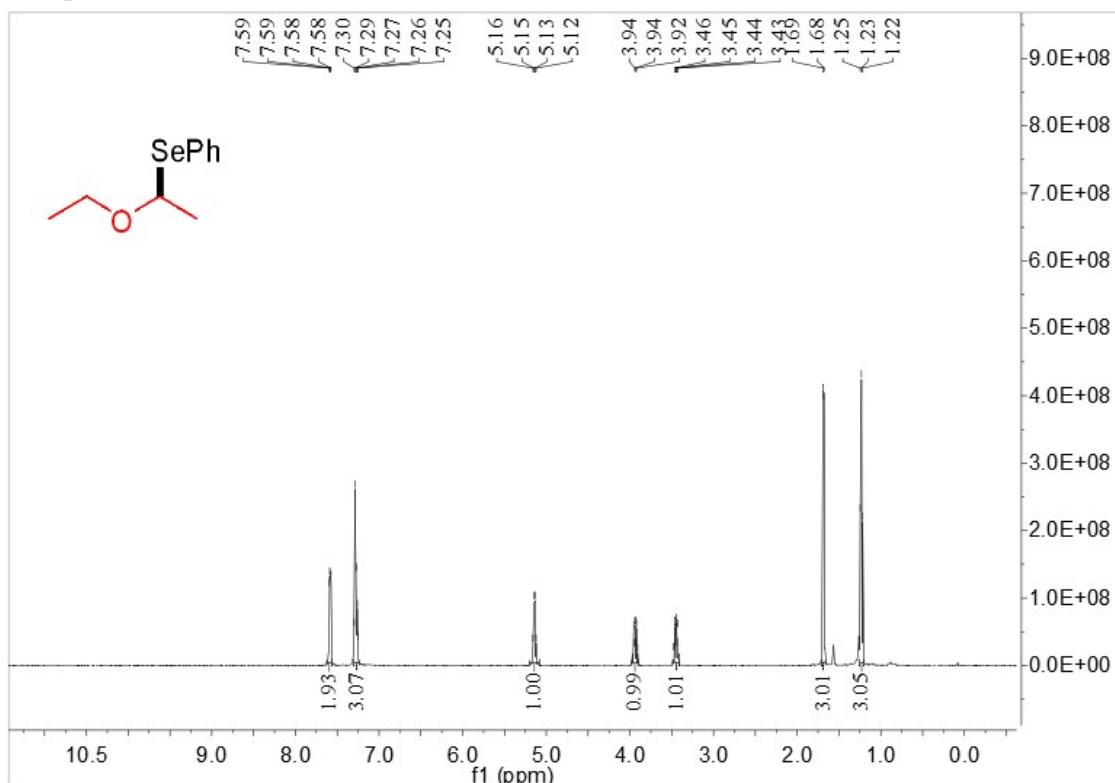
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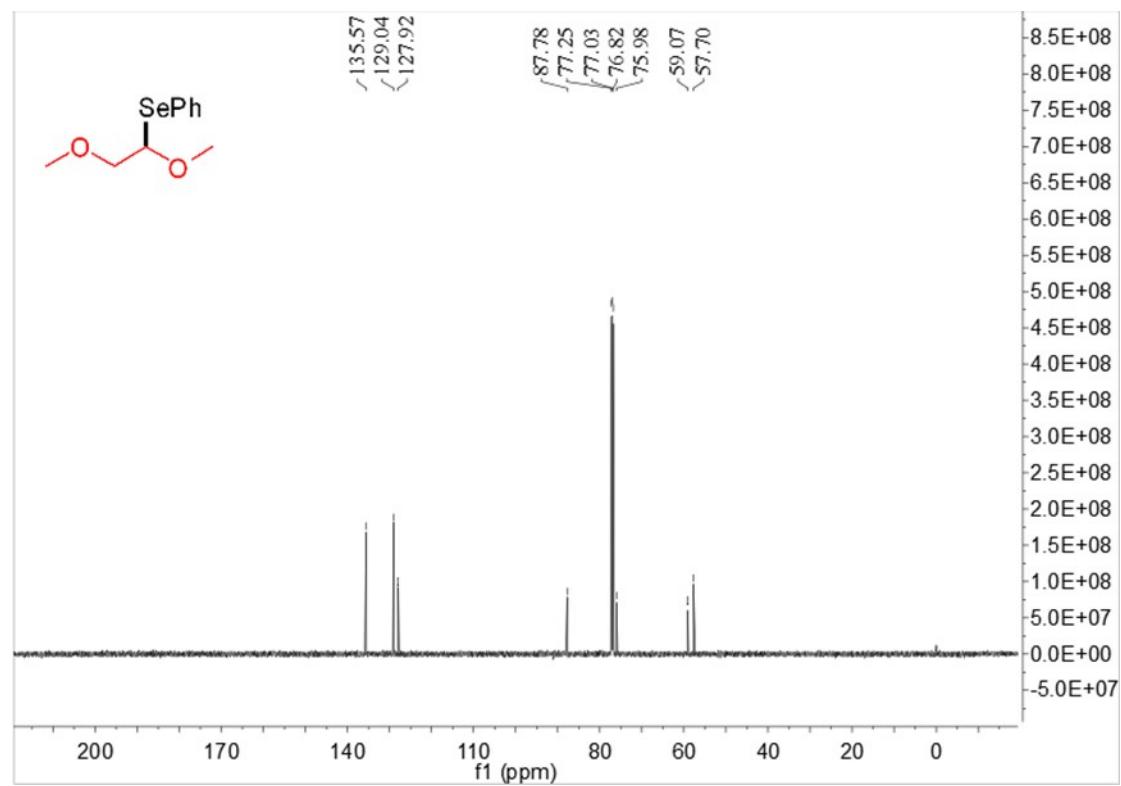
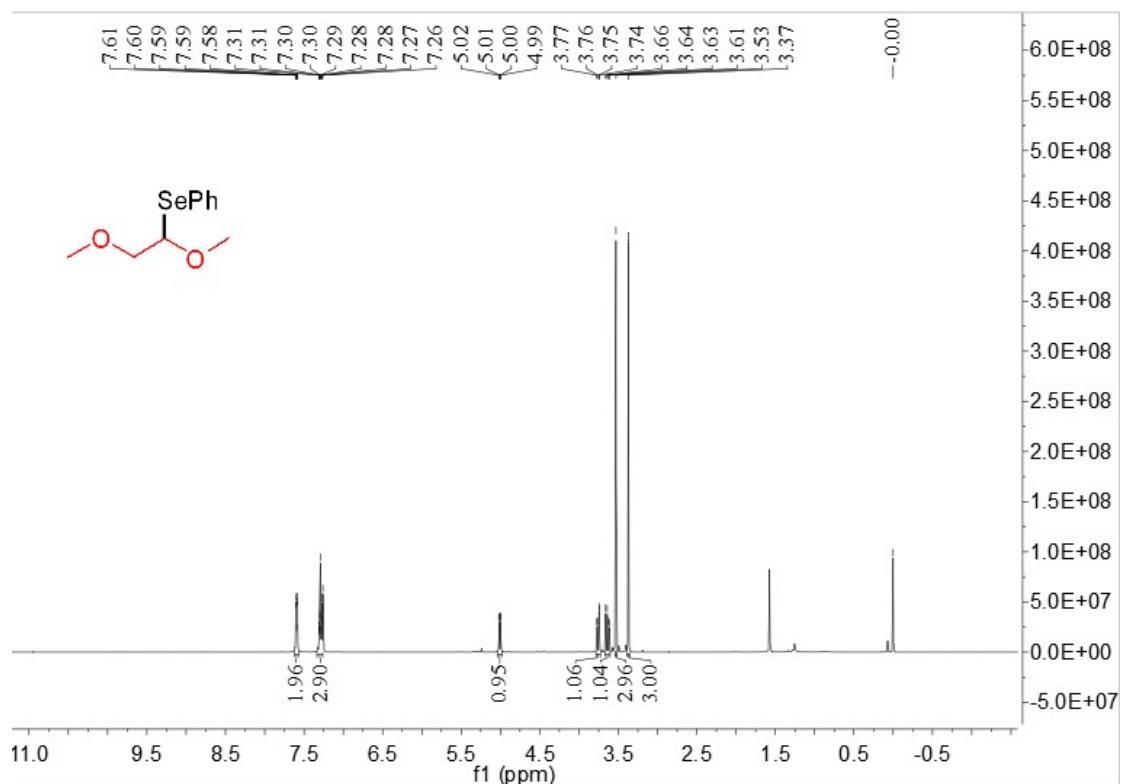
Compound 3v



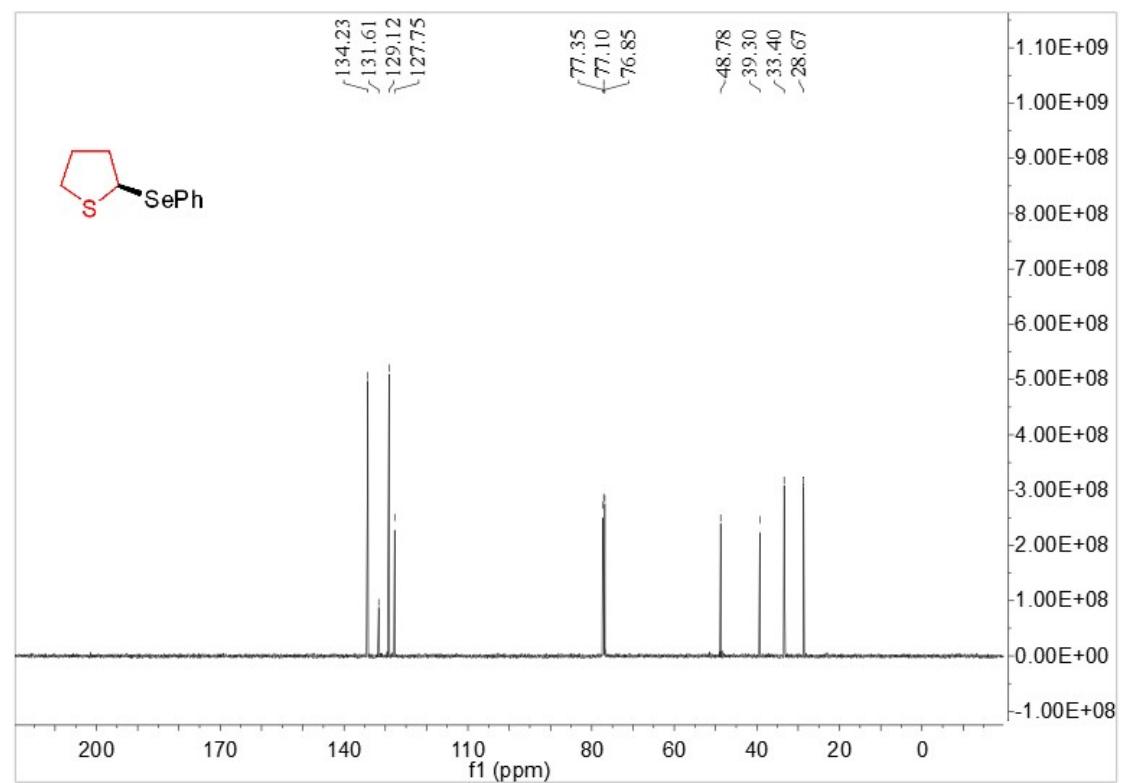
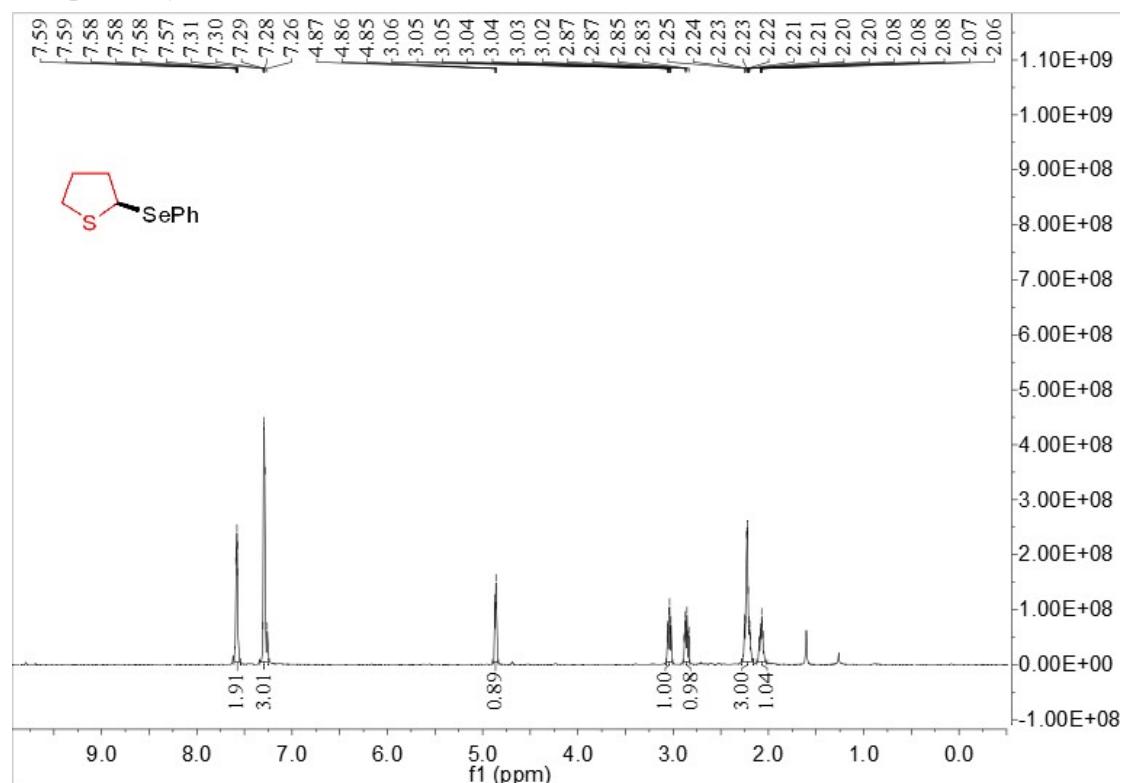
Compound 3w



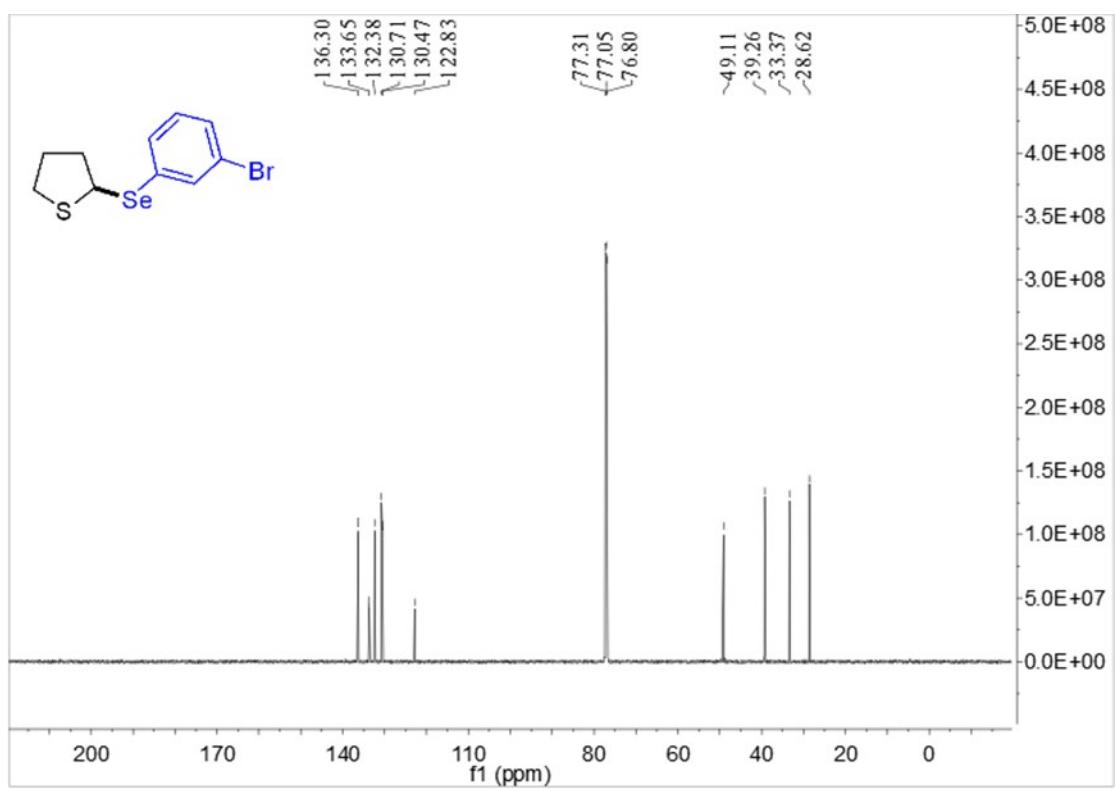
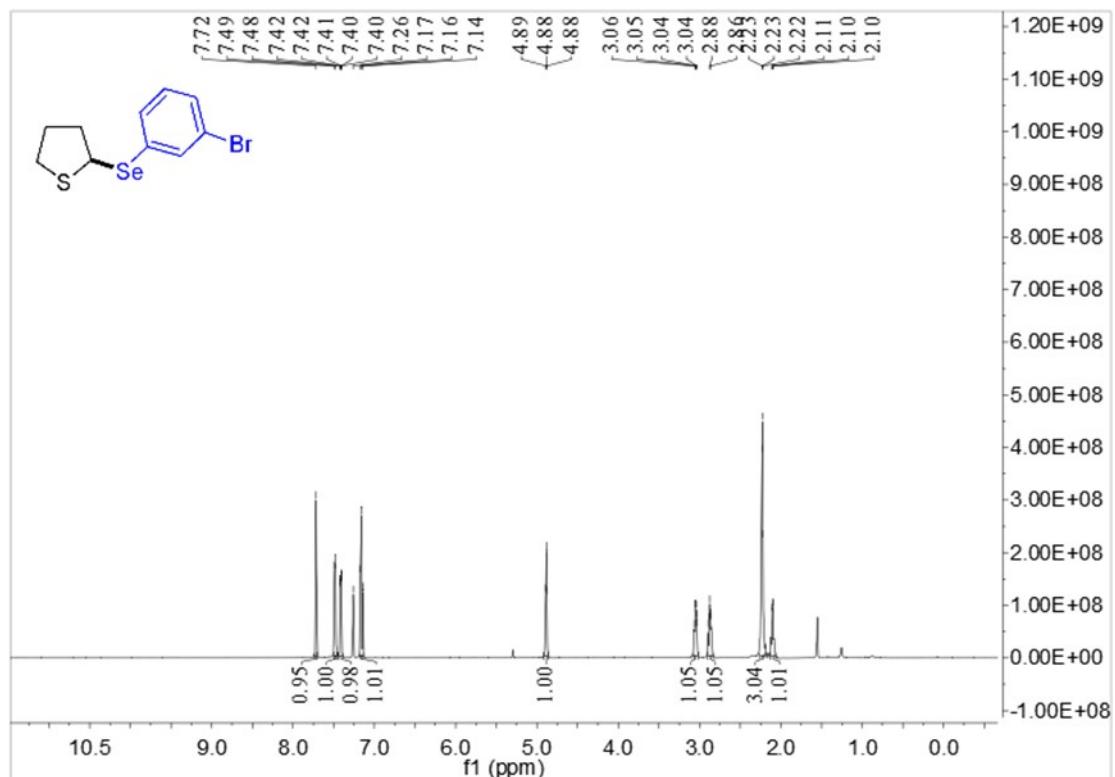
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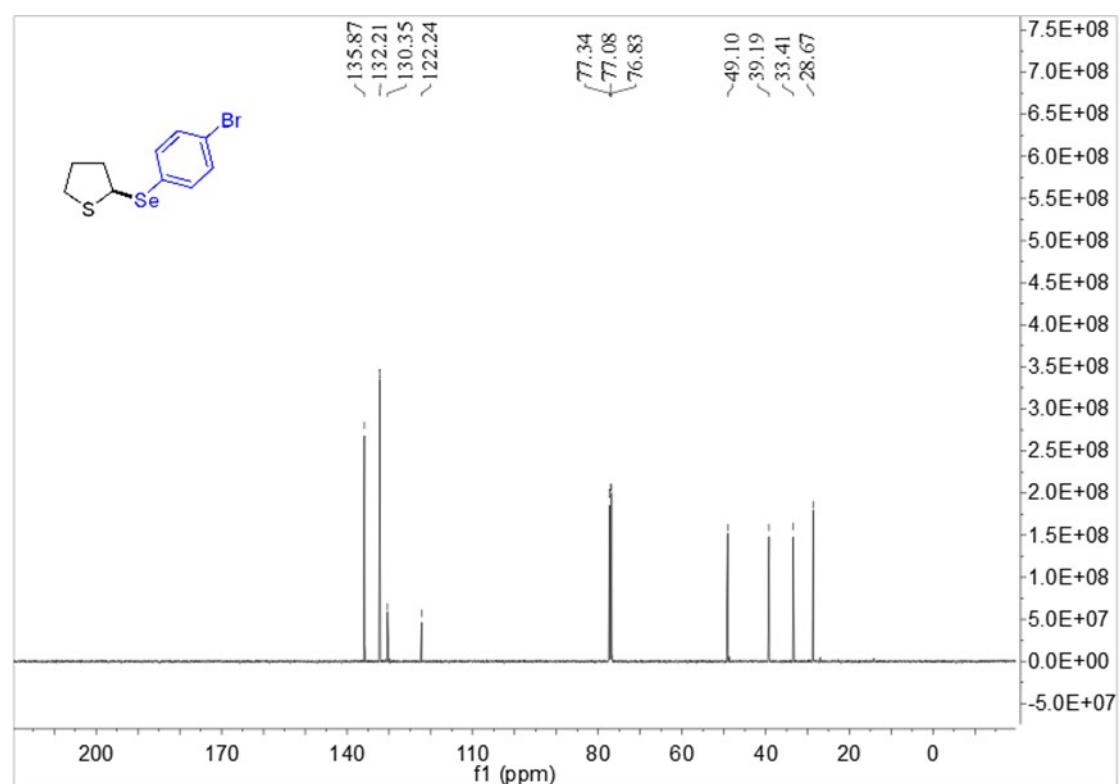
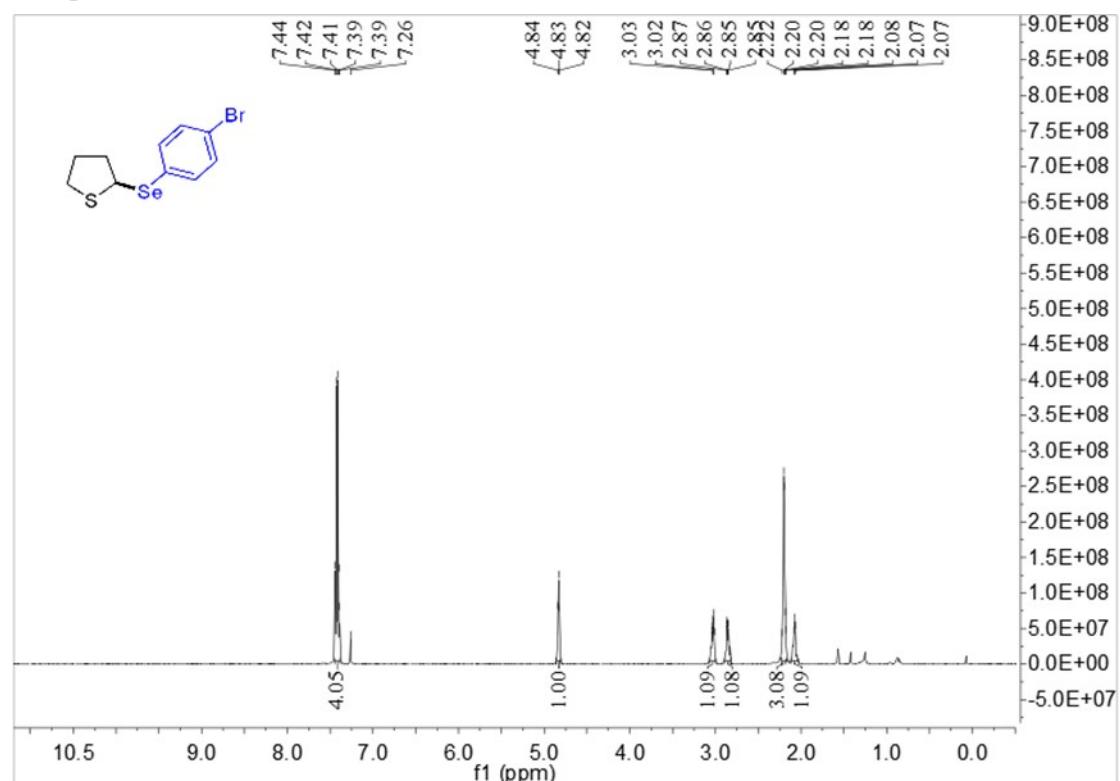
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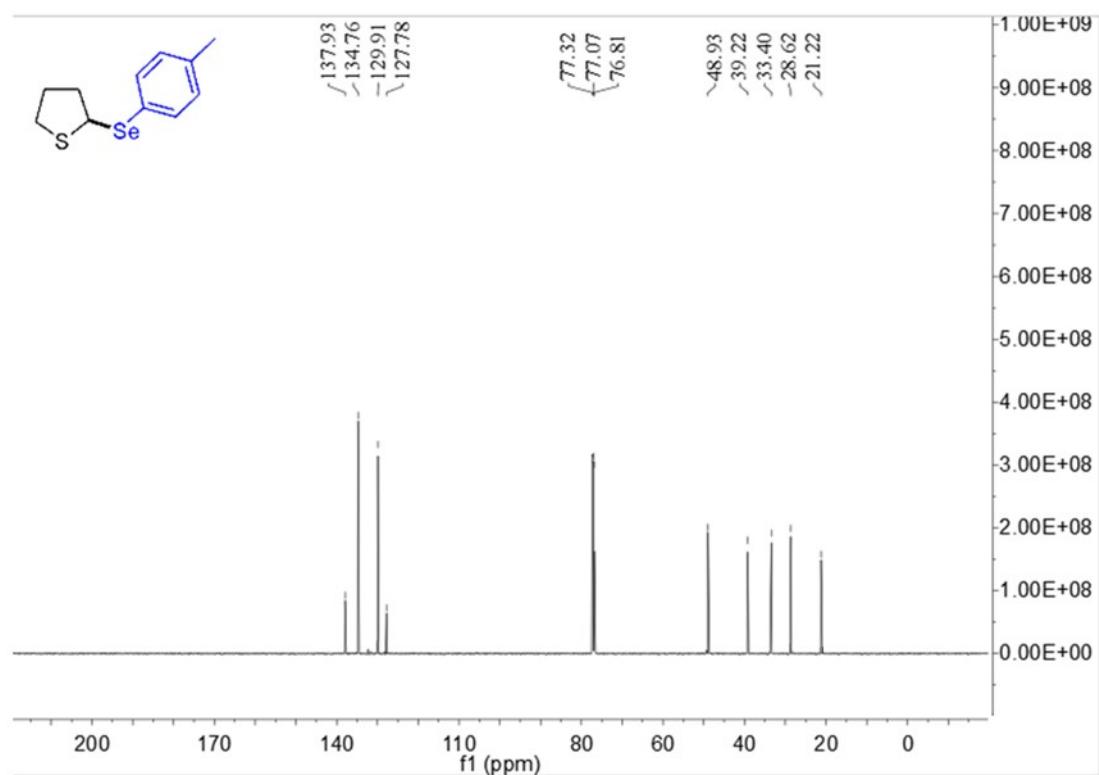
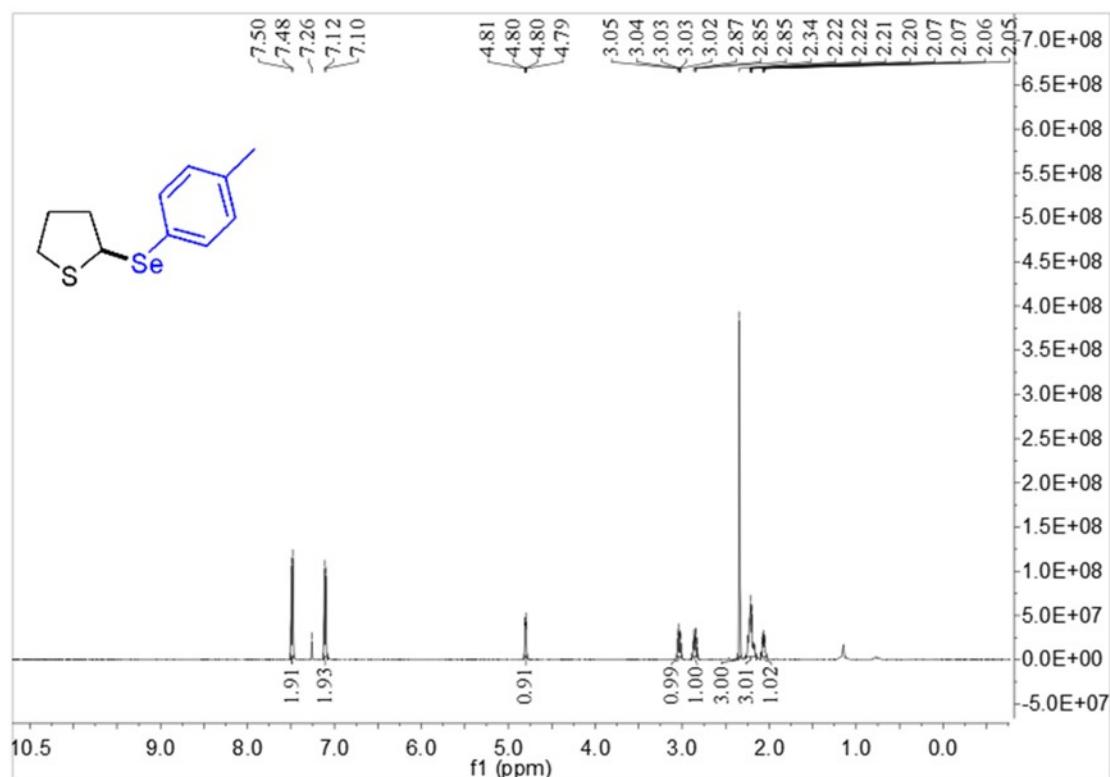
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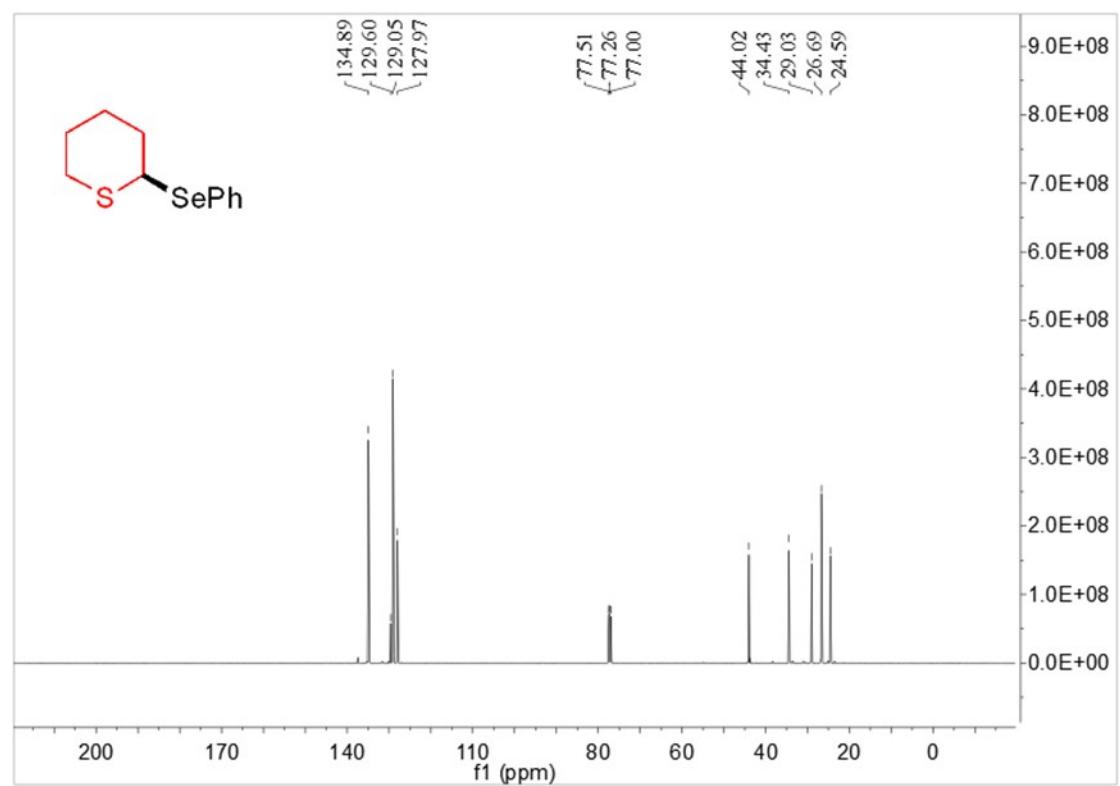
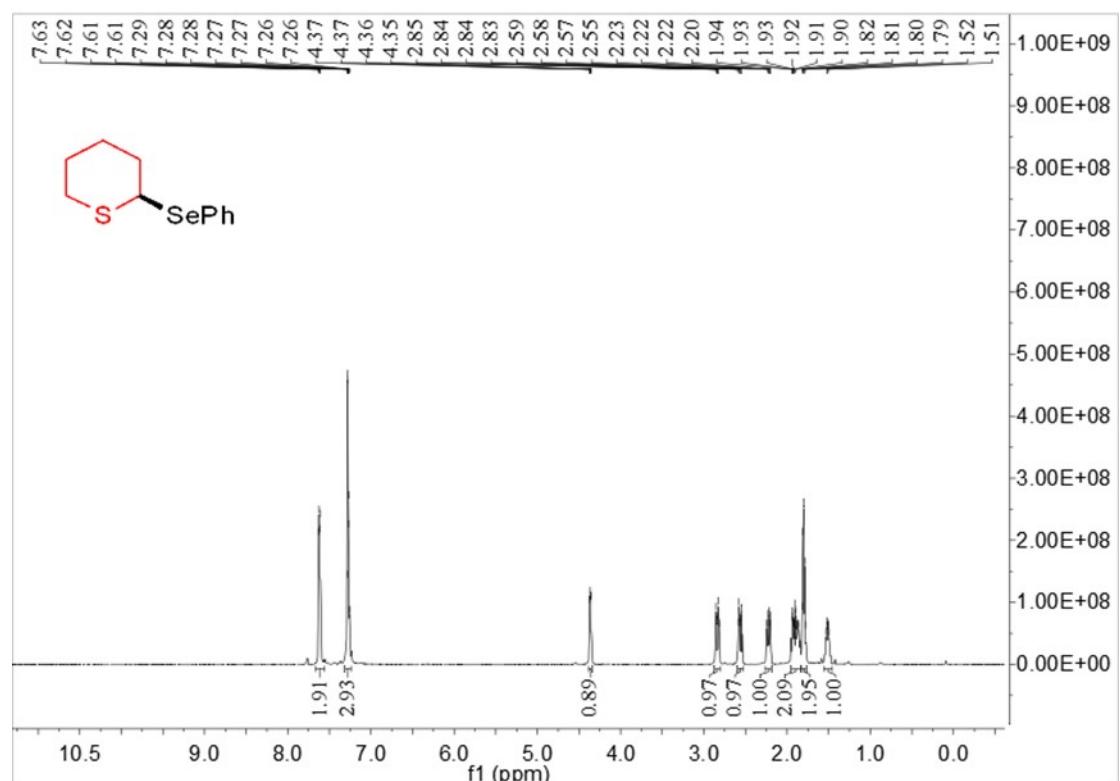
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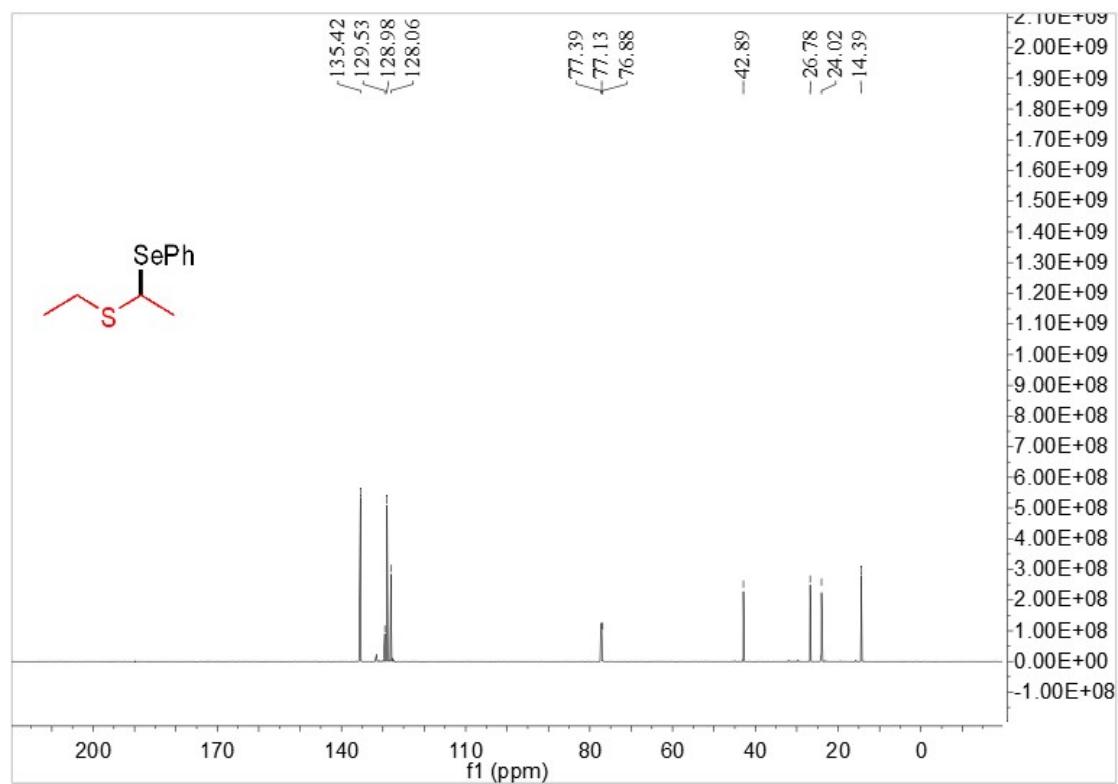
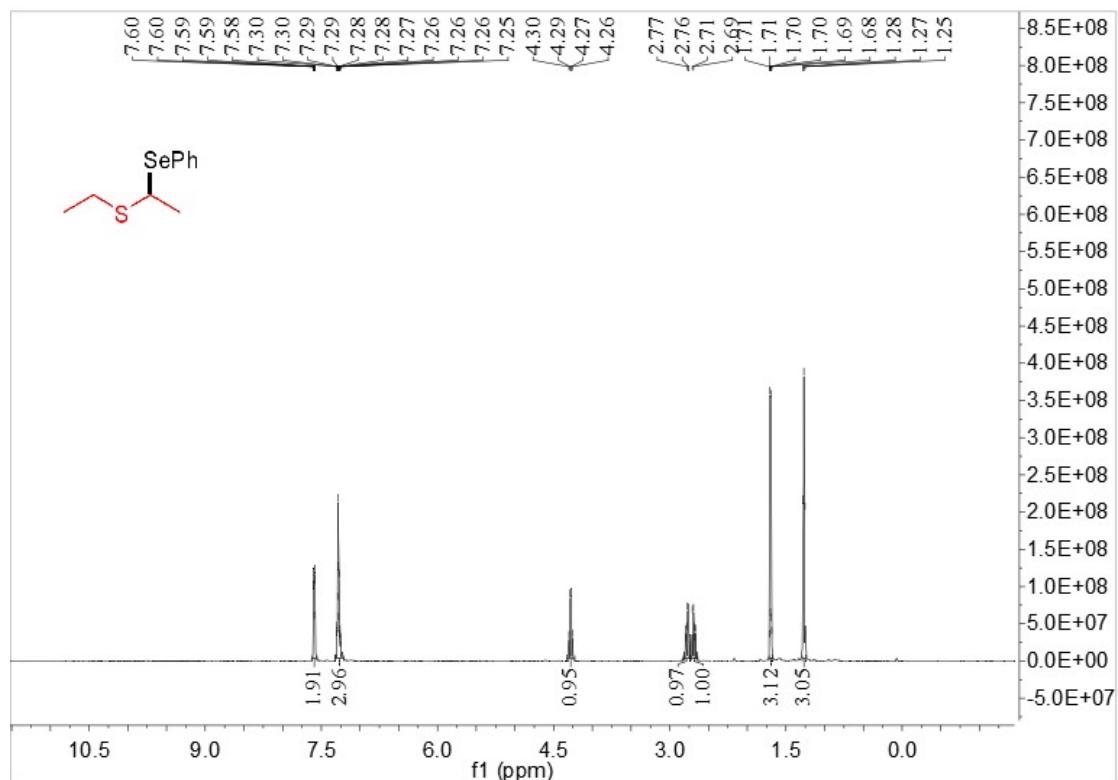
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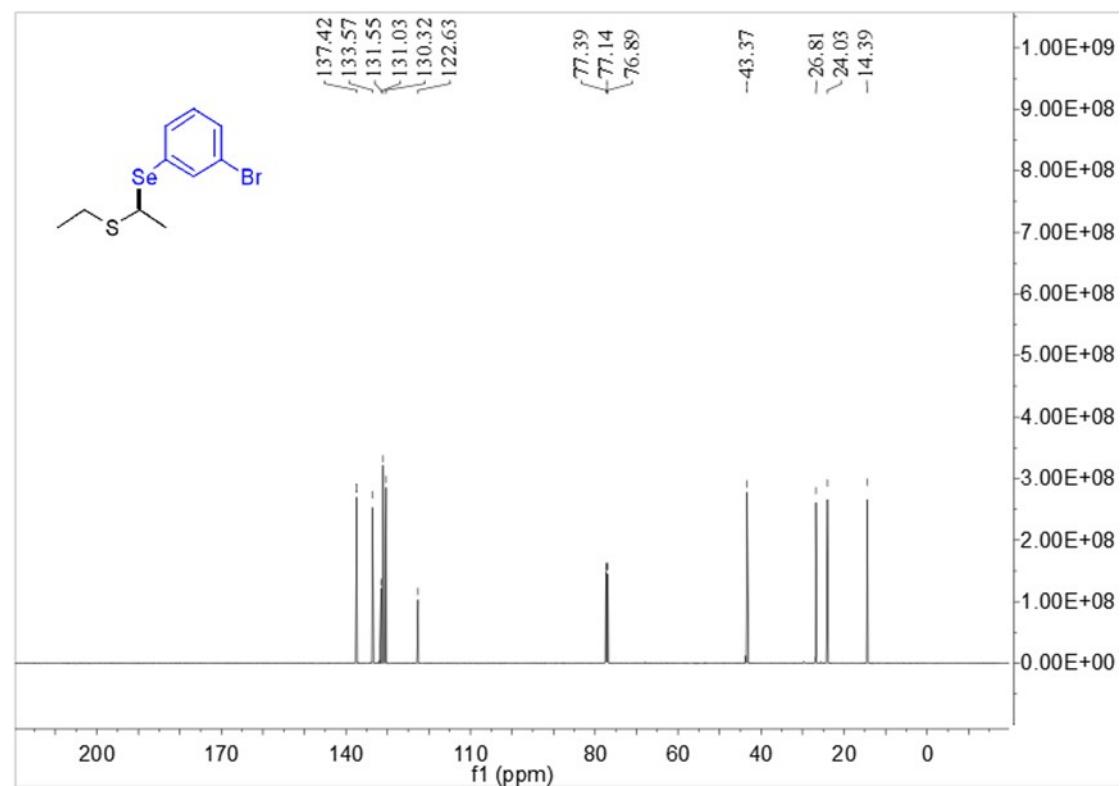
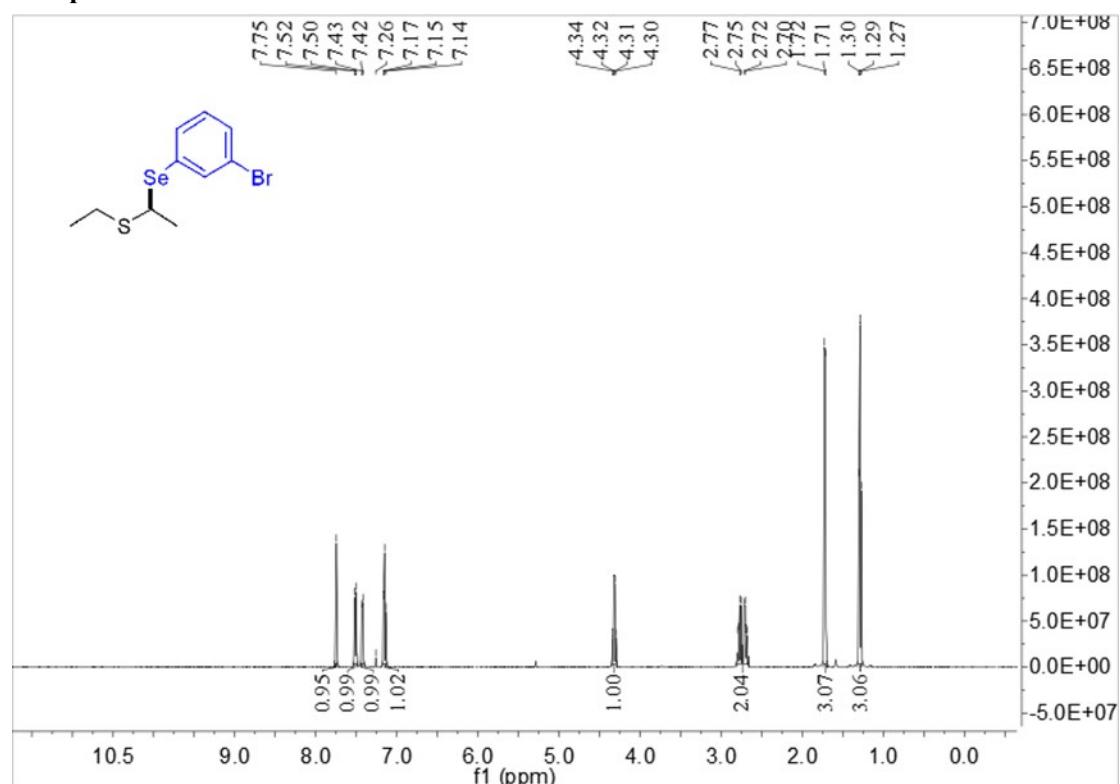
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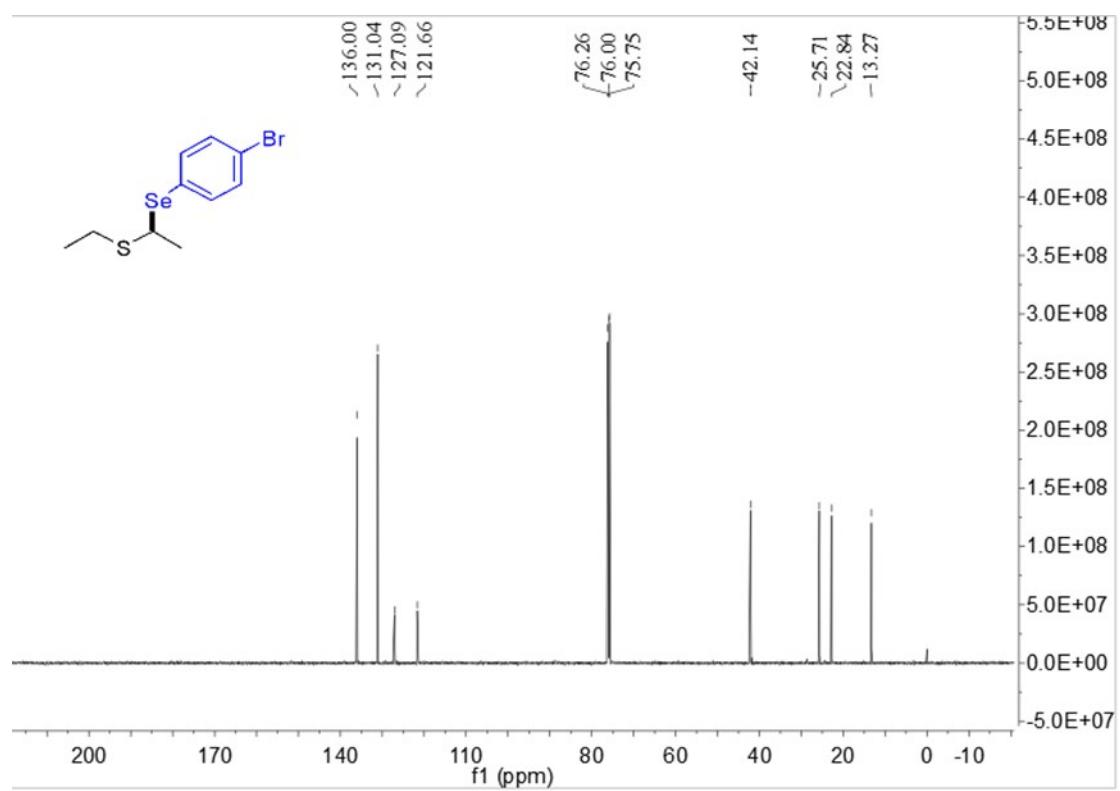
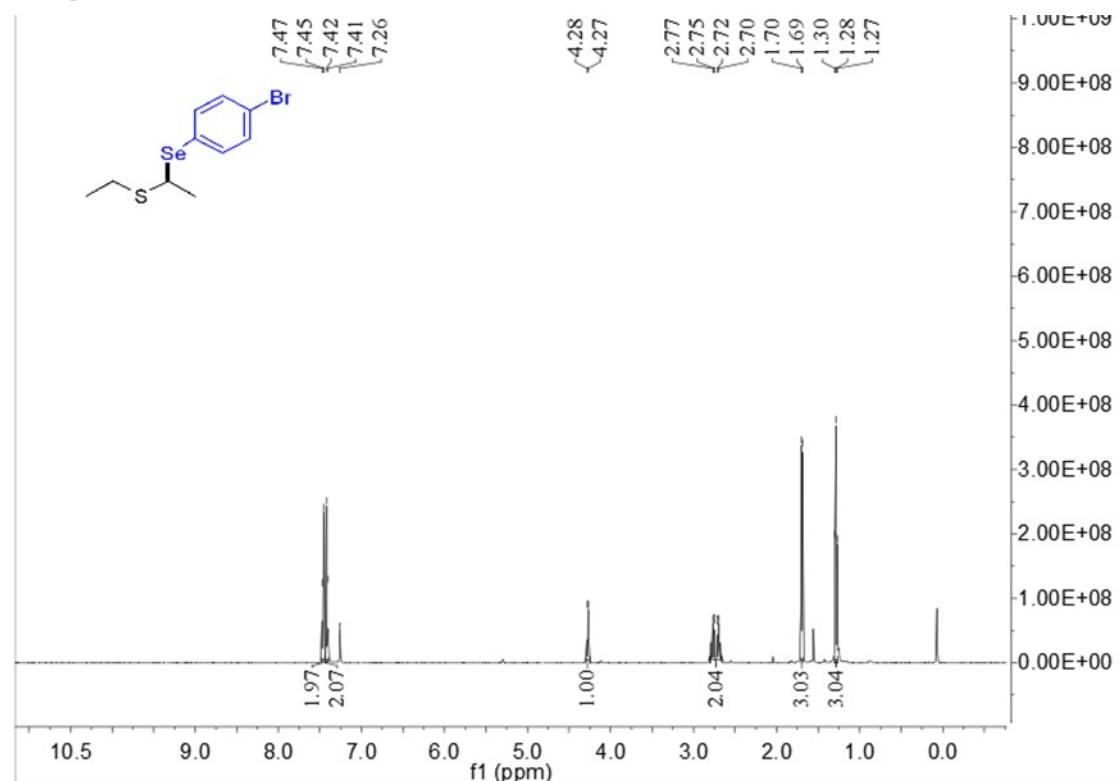
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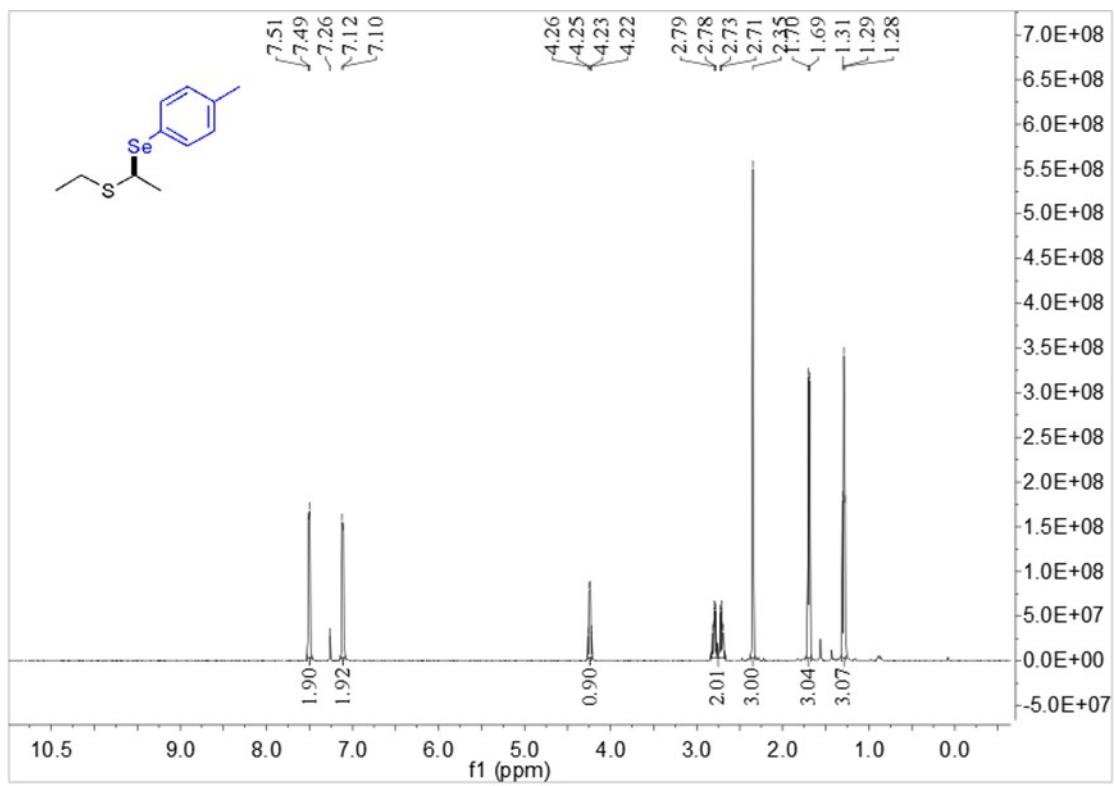
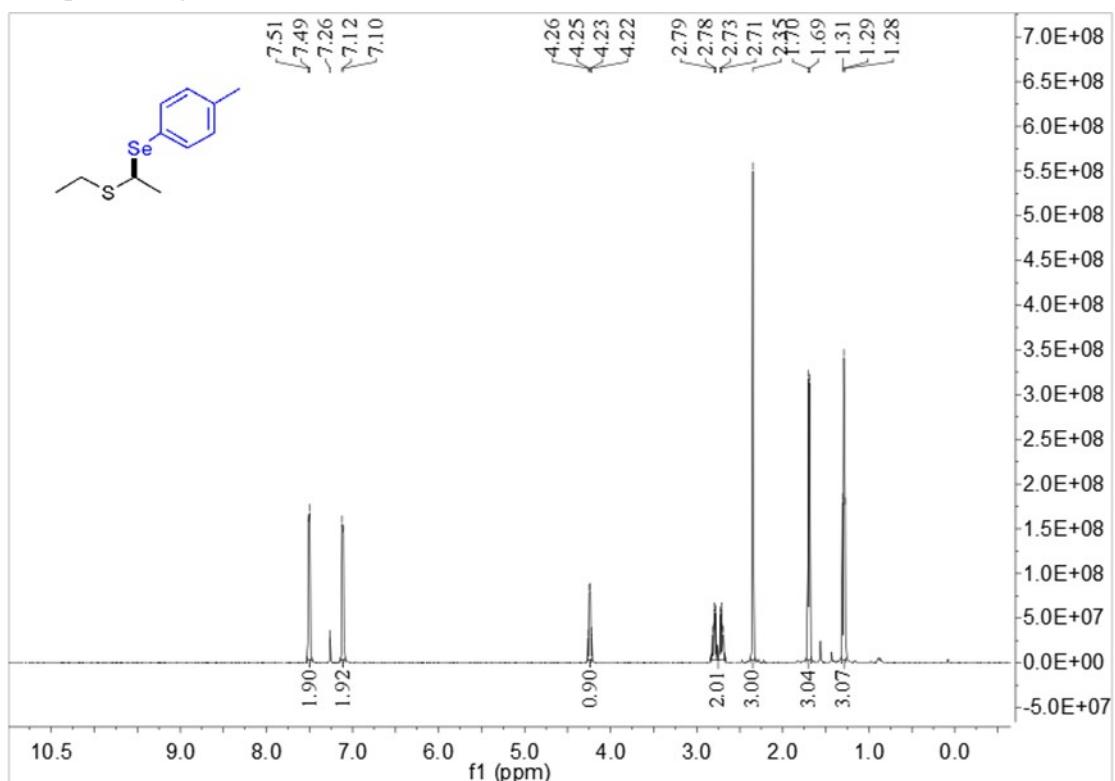
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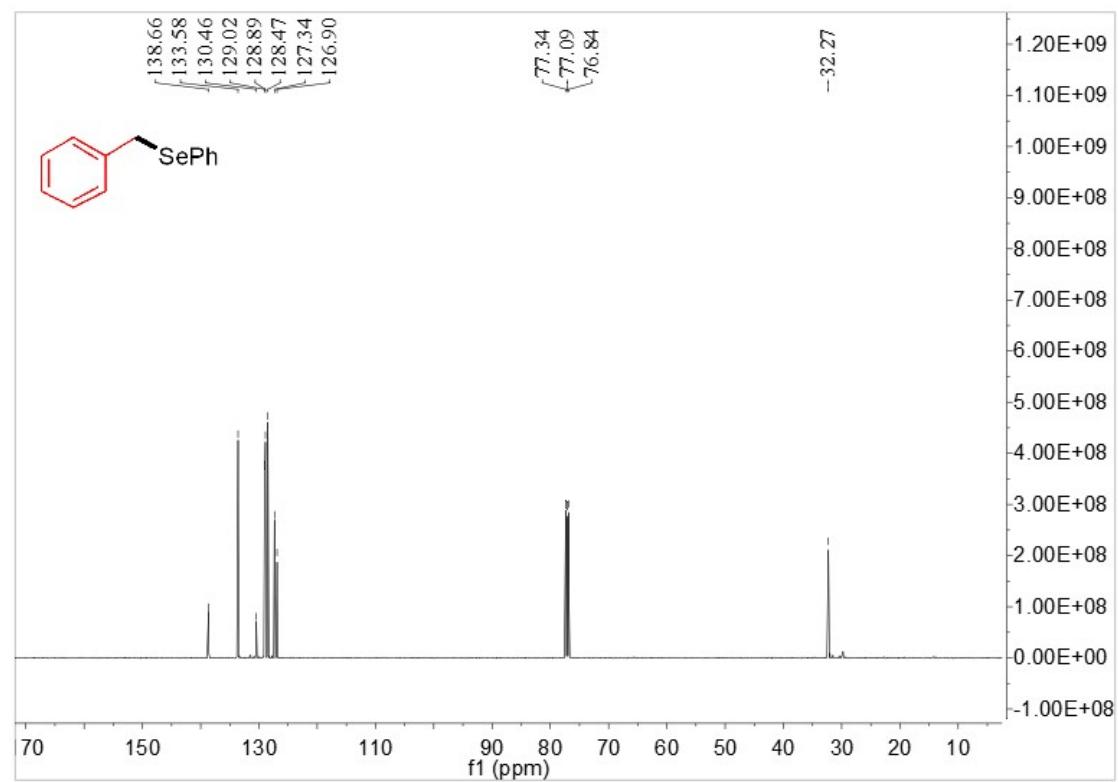
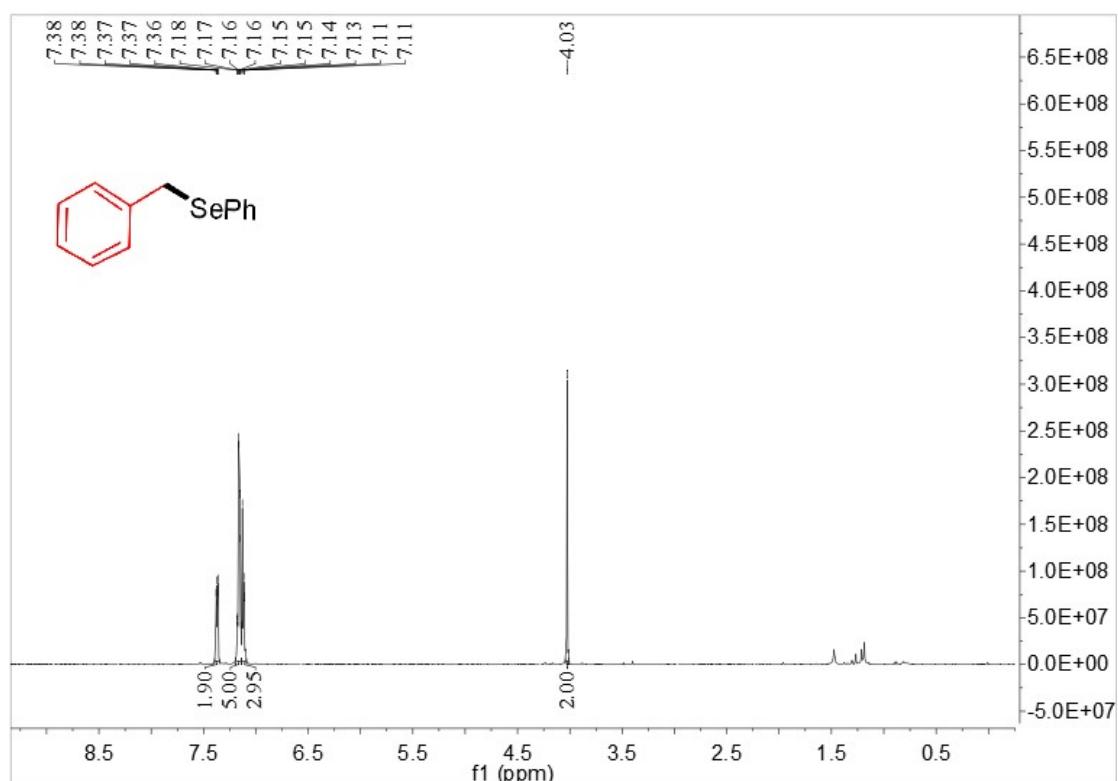
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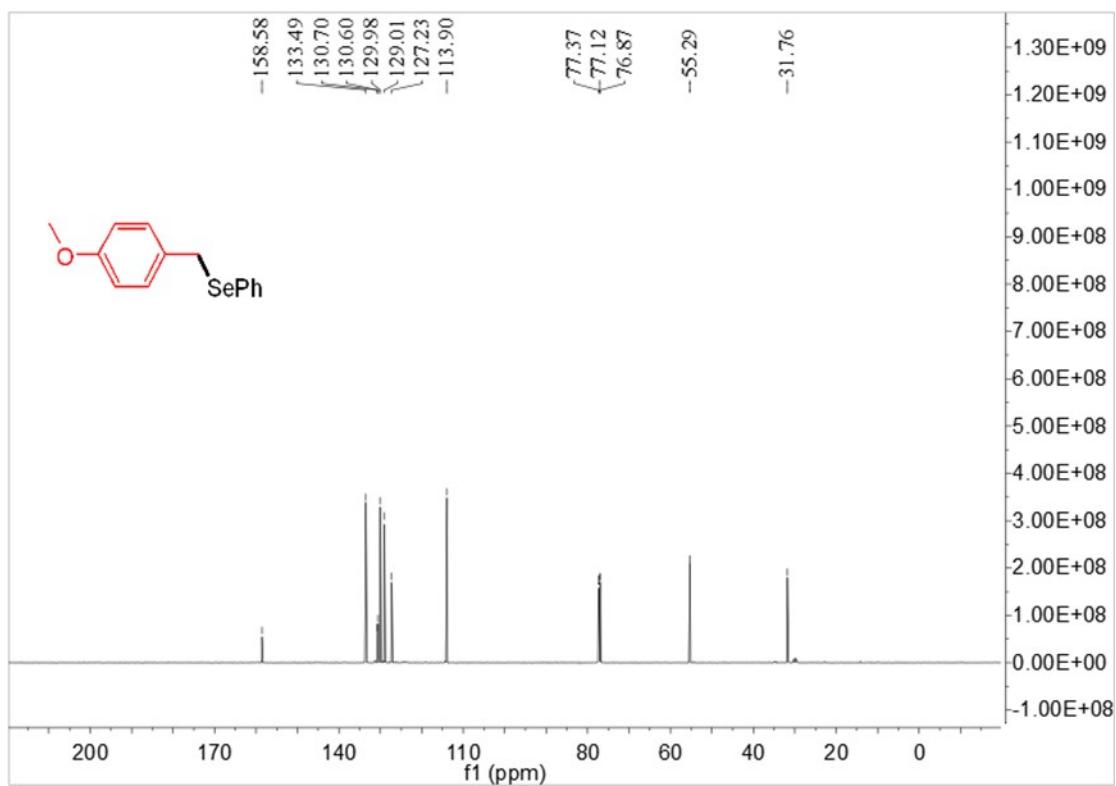
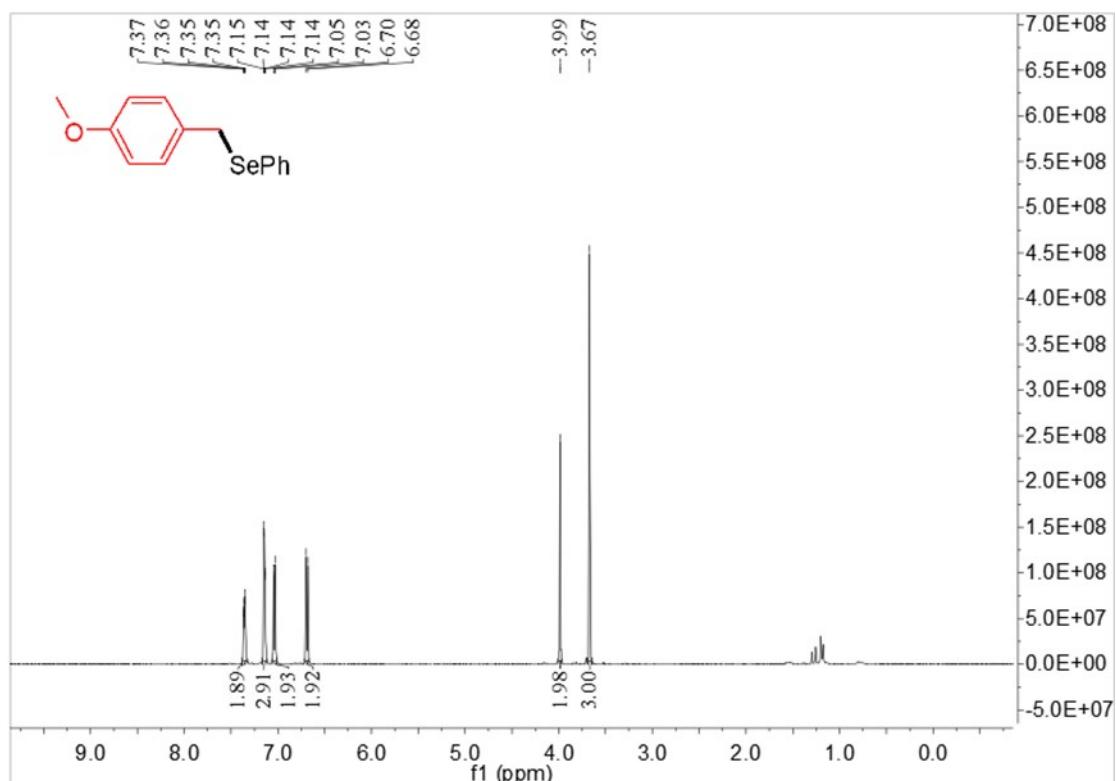
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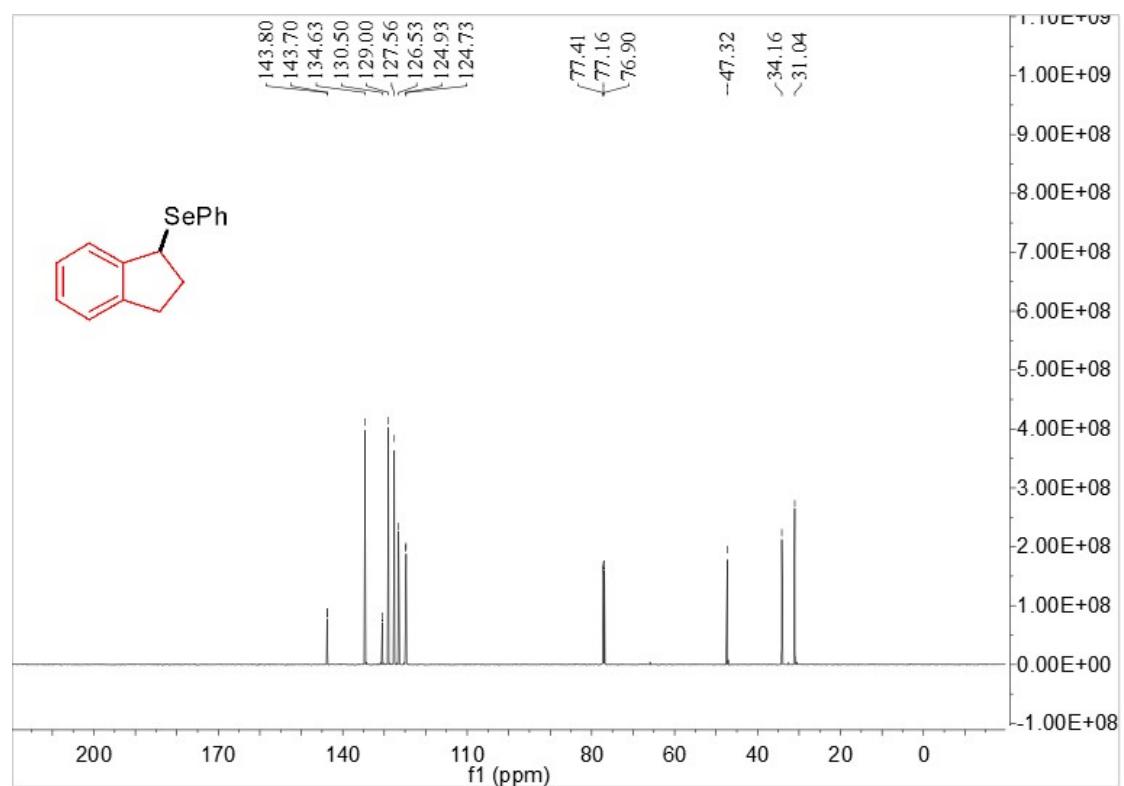
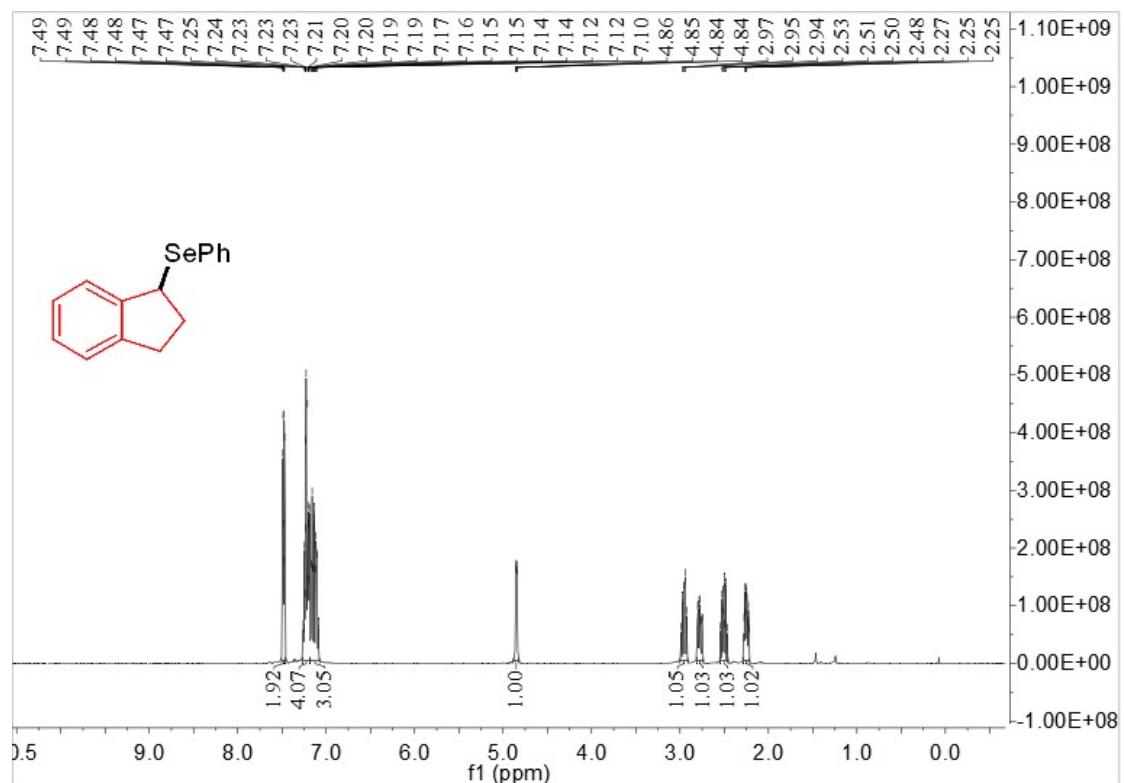
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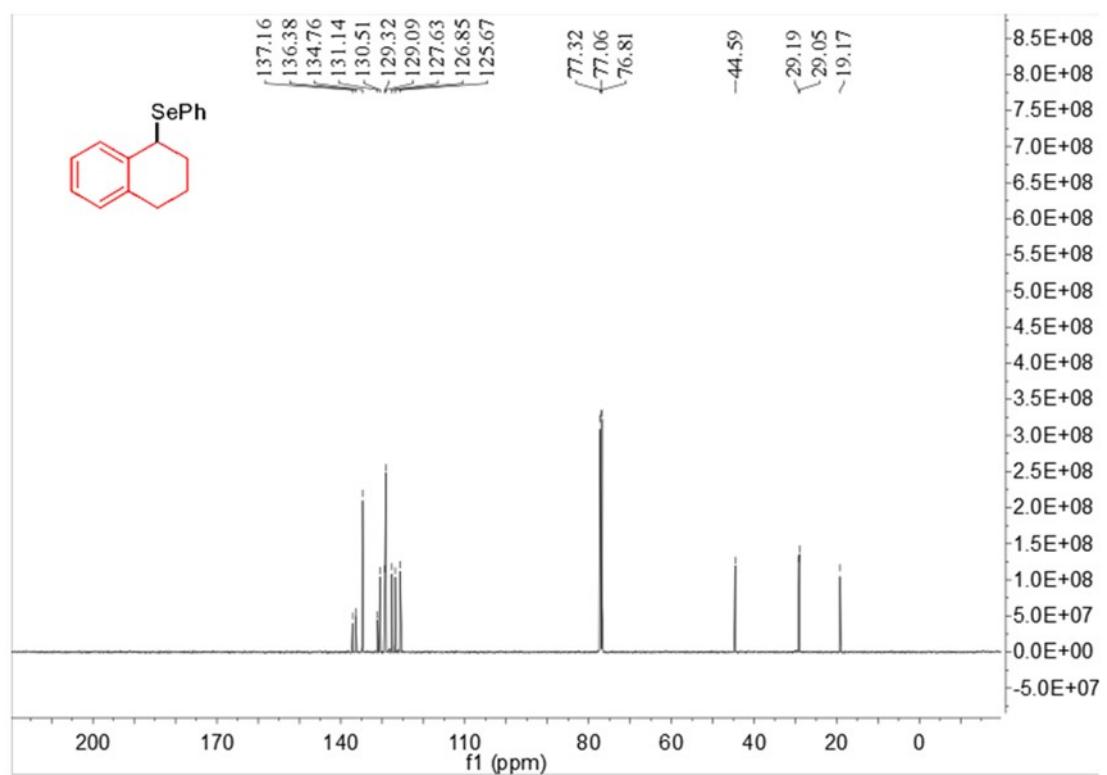
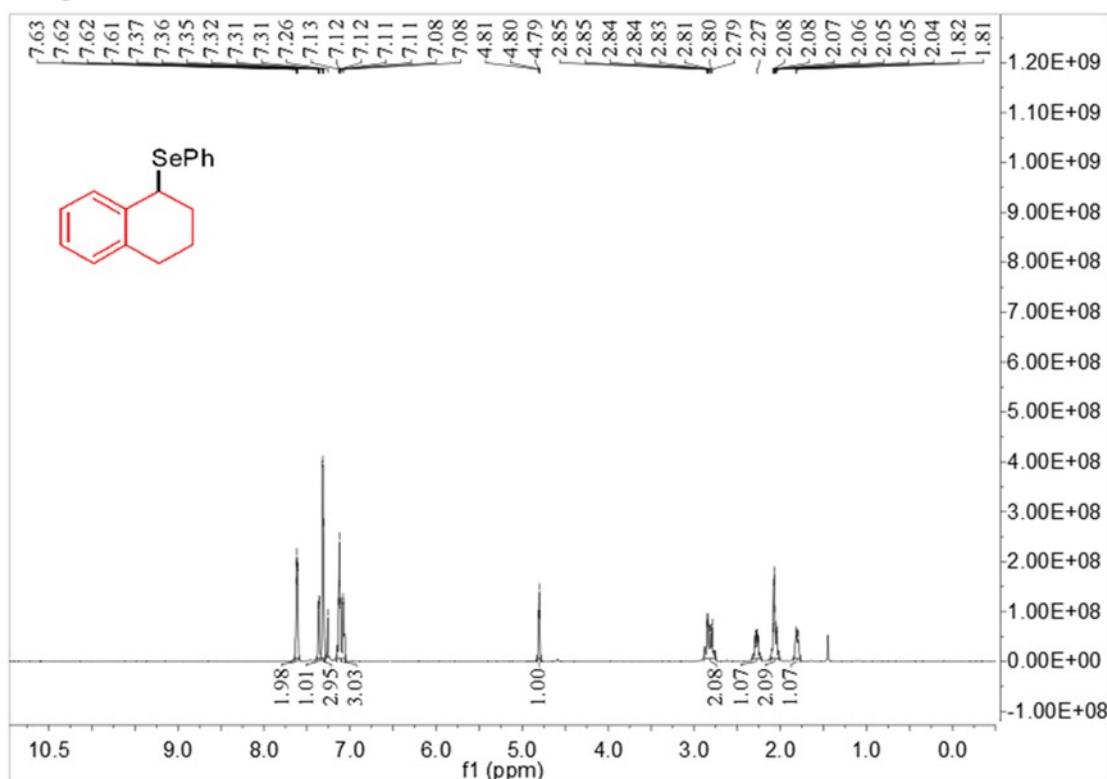
Compound 3ai



Compound 3aj



Compound 3ak



Compound 3al

