

Supporting Information

**Photocatalytic Decarboxylative Selenocyanation of 2-Aryloxy and 2-Aryl Carboxylic Acids with *N*-Selenocyanatophthalimide**

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## 1. General Information

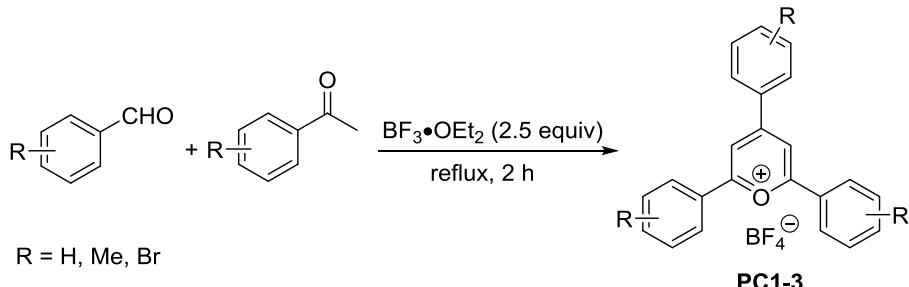
All chemicals were bought from commercial companies and used directly unless noted. The solvents were dried by standard methods when necessary. All reactions monitored by TLC.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker 400 or 700 instrument in  $\text{CDCl}_3$ . All the NMR spectra were referenced to residual  $\text{CHCl}_3$  (7.26 ppm,  $^1\text{H}$ ; 77.16 ppm,  $^{13}\text{C}\{^1\text{H}\}$ ). Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, septet; coupling constant(s) are in Hz, integration). Data for  $^{13}\text{C}\{^1\text{H}\}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). The high resolution mass spectrum (HRMS) were recorded on an Agilent (Q-TOF6520) unit with an ESI source. IR spectra were measured on a Shimadzu IRAffinity-1s spectrometer. Melting points were measured on a binocular microscope XT4A melting point apparatus (uncorrected).

## 2. Preparation of Reagents, Catalysts and Carboxylic Acids

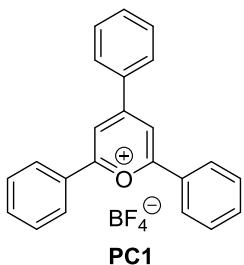
Reagents **2a–c** were prepared according to the literatures.<sup>[1]</sup>

The photocatalysts [Mes-Acr-Me][ClO<sub>4</sub>], [Mes-Acr-Ph][BF<sub>4</sub>], fac-Ir(ppy)<sub>3</sub> and 4CzIPN were bought from commercial companies and used directly.

The photocatalysts **PC1–4** were synthesized according to the literatures.<sup>[2]</sup>

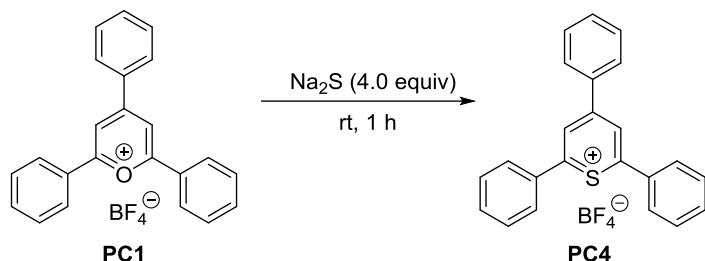


**Procedure for the Synthesis of PC1–3.** Boron trifluoride etherate (50 mmol, 2.5 equiv) was slowly added to a solution of aldehyde (20 mmol, 1.0 equiv) and ketone (40 mmol, 2.0 equiv) (if starting material are solids, they were dissolved in a small amount of toluene). The resulting mixture was refluxed for 2 h. After the completion of the reaction, it was cooled to room temperature and the formed diethyl ether was evaporated. The residue was dissolved in acetone and diethyl ether was added to precipitate the product. Filtration and purification was performed by multiple recrystallization from acetone.



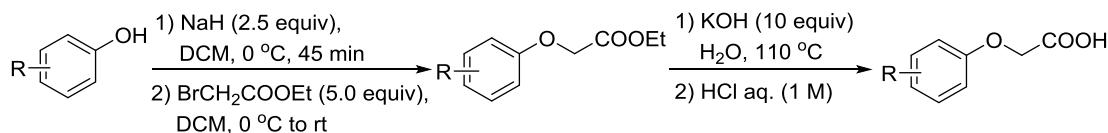
**PC1** was obtained as a yellow solid (2.37 g, 30% yield); mp: 228–230 °C (lit. 225–226 °C);<sup>[3a]</sup>  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.17 (s, 2H), 8.60 (d, *J* = 7.5 Hz, 6H), 7.88 (t, *J* = 7.3 Hz, 3H), 7.82–7.78 (m, 6H).

Analysis results are in accordance with the literature.<sup>[3b]</sup>



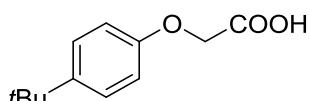
**Procedure for the Synthesis of PC4.** To a stirred solution of **PC1** (1.25 mmol, 1.0 equiv) in water (10 mL), an aqueous solution of disodium sulfide (5.0 mmol, 4.0 equiv) was added dropwise at room temperature. After being stirred for 1 h, the solution was added to an aqueous HBF<sub>4</sub> (0.25 M, 50 wt. %) and stirred for additional 1 h. The yellow precipitate was filtered and purified by multiple recrystallizations in acetone.

Carboxylic acids **1c–d**, **1j–l** were prepared according to the literature.<sup>[4]</sup>

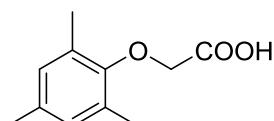


**Procedure for the Synthesis of **1c–d**, **1j–l**.** To an oven-dried flask was charged with NaH (300 mg, 7.5 mmol, 2.5 equiv) and THF (7.0 mL). The flask was degassed and filled with argon, then cooled to 0 °C. A solution of the phenol (3.0 mmol, 1.0 equiv) in THF (3.0 mL) was added dropwise to the suspension of NaH and stirred at 0 °C for 45 min. Bromoethyl acetate (2.5 g, 15 mmol, 5.0 equiv) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 12 h. After the completion of the reaction, the reaction was quenched with sat. NH<sub>4</sub>Cl and extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 20:1, v/v).

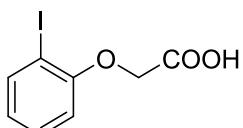
A solution of potassium hydroxide (10 equiv) in water (30 mL) was added to the ester, and the mixture was heated to 110 °C for 6 h. After consumption of starting material determined by TLC, the reaction was cooled to room temperature and acidified with aqueous HCl (1 M) to pH = 1–2. The aqueous phase was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo to afford the desired carboxylic acid.



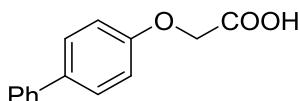
**2-(4-(tert-Butyl)phenoxy)acetic acid (1c).**<sup>[5]</sup> White solid; 324 mg, 52% yield; mp: 90–91 °C (lit. 87–88 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.10 (brs, 1H), 7.32 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.66 (s, 2H), 1.29 (s, 9H).



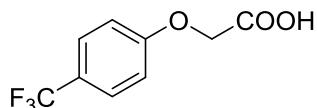
**2-(Mesityloxy)acetic acid (1d).**<sup>[4]</sup> White solid; 230 mg, 40% yield; mp: 144–145 °C (lit. 148–151 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.32 (brs, 1H), 6.83 (s, 2H), 4.45 (s, 2H), 2.26 (s, 6H), 2.24 (s, 3H).



**2-(2-Iodophenoxy)acetic acid (1j).**<sup>[5]</sup> White solid; 672 mg, 81% yield; mp: 132–134 °C (lit. 124–126 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.44 (brs, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.82–6.77 (m, 2H), 4.73 (s, 2H).



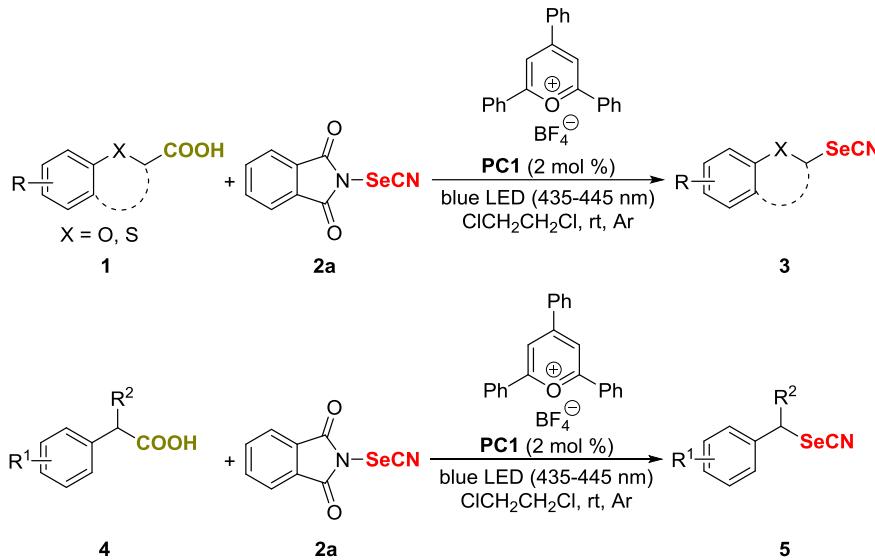
**2-([1,1'-Biphenyl]-4-yloxy)acetic acid (1k).**<sup>[4]</sup> White solid; 440 mg, 64% yield; mp: 191–192 °C (lit. 189–190 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.03 (brs, 1H), 7.60 (t, *J* = 6.8 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.73 (s, 2H).



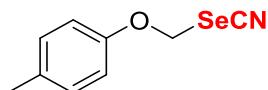
**2-(4-(Trifluoromethyl)phenoxy)acetic acid (1l).**<sup>[6]</sup> White solid; 565 mg, 86% yield; mp: 138–139 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.12 (brs, 1H), 7.65 (d, *J* = 8.3

Hz, 2H), 7.11 (d,  $J$  = 8.4 Hz, 2H), 4.80 (s, 2H).

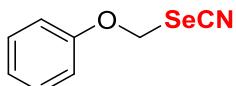
### 3. General Procedure for the Synthesis of 3 and 5



To a 25 mL Schlenk tube containing **1** or **4** (0.1 mmol, 1.0 equiv) was added **PC1** (0.8 mg, 0.002 mmol, 2 mol %) and 1,2-dichloroethane (1.0 mL) under an argon atmosphere. Then, **2a** (30.2 mg, 0.12 mmol, 1.2 equiv) was added. The reaction was irradiation with blue LED (435–445 nm, 5 W) for 5–24 h at room temperature. When the reaction was completed, the product was purified by column chromatography on silica gel with petroleum ether (PE)/ethyl acetate to afford the product **3** or **5**.

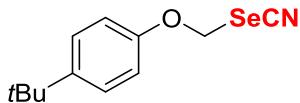


**1-Methyl-4-(selenocyanatomethoxy)benzene (**3a**).** White solid; 19.6 mg, 86% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.30; mp: 71–73 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (d,  $J$  = 8.3 Hz, 2H), 6.91 (d,  $J$  = 8.4 Hz, 2H), 5.91 (s, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 133.7, 130.5, 116.6, 100.8 (SeCN), 70.6, 20.7; IR (KBr,  $\text{cm}^{-1}$ ) 2920, 2151 (SeCN), 1589, 1506, 1449, 1300, 1234, 1196, 1177, 1059, 810; HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for  $\text{C}_9\text{H}_{10}\text{NOSe}$  227.9922, found 227.9929.

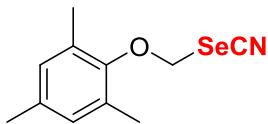


**(Selenocyanatomethoxy)benzene (**3b**).** White solid; 18.5 mg, 87% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.27; mp: 71–72 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (t,  $J$  = 8.0 Hz, 2H), 7.16 (t,  $J$  = 7.4 Hz, 1H), 7.02 (d,  $J$  = 8.0 Hz, 2H), 5.93 (s, 2H);

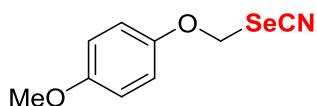
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.3, 130.0, 124.0, 116.6, 100.8 (SeCN), 70.0; IR (KBr, cm<sup>-1</sup>) 2926, 2156 (SeCN), 1589, 1487, 1456, 1302, 1234, 1192, 1169, 1051, 754; HRMS (ESI) *m/z*: [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>OSe 231.0031, found 231.0031.



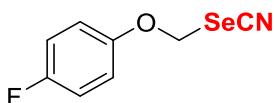
**1-(*tert*-Butyl)-4-(selenocyanatomethoxy)benzene (**3c**).** White solid; 20.5 mg, 76% yield; Eluent PE/EtOAc (10:1, v/v), TLC *R<sub>f</sub>* = 0.34; mp: 85–86 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.92 (s, 2H), 1.32 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.0, 147.0, 126.8, 116.0, 100.9 (SeCN), 70.4, 34.4, 31.4; IR (KBr, cm<sup>-1</sup>) 2965, 2151 (SeCN), 1609, 1512, 1462, 1368, 1308, 1236, 1209, 1184, 1059, 829; HRMS (ESI) *m/z*: [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>OSe 287.0657, found 287.0663.



**1,3,5-Trimethyl-2-(selenocyanatomethoxy)benzene (**3d**).** White solid; 18.0 mg, 71% yield; Eluent PE/EtOAc (10:1, v/v), TLC *R<sub>f</sub>* = 0.40; mp: 37–38 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.86 (s, 2H), 5.80 (s, 2H), 2.30 (s, 6H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 135.0, 130.1, 129.8, 101.2 (SeCN), 74.5, 20.7, 17.0; IR (KBr, cm<sup>-1</sup>) 2922, 2153 (SeCN), 1605, 1479, 1377, 1308, 1281, 1192, 1134, 1034, 854; HRMS (ESI) *m/z*: [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>11</sub>H<sub>17</sub>N<sub>2</sub>OSe 273.0501, found 273.0496.

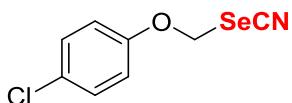


**1-Methoxy-4-(selenocyanatomethoxy)benzene (**3e**).** White solid; 20.0 mg, 82% yield; Eluent PE/EtOAc (10:1, v/v), TLC *R<sub>f</sub>* = 0.16; mp: 39–40 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.97 (d, *J* = 9.2 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 5.88 (s, 2H), 3.80 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.3, 149.1, 118.3, 115.0, 100.8 (SeCN), 72.0, 55.7; IR (KBr, cm<sup>-1</sup>) 2934, 2153 (SeCN), 1761, 1593, 1504, 1464, 1443, 1244, 1186, 1053, 827; HRMS (ESI) *m/z*: [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>Se 261.0137, found 261.0136.

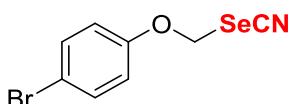


**1-Fluoro-4-(selenocyanatomethoxy)benzene (**3f**).** White solid; 16.2 mg, 70% yield; Eluent PE/EtOAc (10:1, v/v), TLC *R<sub>f</sub>* = 0.20; mp: 69–70 °C; <sup>1</sup>H NMR (400 MHz, S6

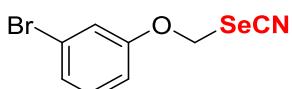
$\text{CDCl}_3$ )  $\delta$  7.10–7.05 (m, 2H), 7.02–6.98 (m, 2H), 5.88 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2 (d,  $J = 241.6$  Hz), 151.3 (d,  $J = 2.5$  Hz), 118.5 (d,  $J = 8.3$  Hz), 116.6 (d,  $J = 23.4$  Hz), 100.5 (SeCN), 71.0; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2153 (SeCN), 1634, 1504, 1454, 1310, 1227, 1188, 1059, 829; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_8\text{H}_{10}\text{FN}_2\text{OSe}$  248.9937, found 248.9937.



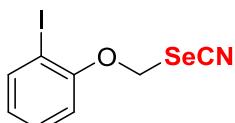
**1-Chloro-4-(selenocyanatomethoxy)benzene (3g).** White solid; 18.4 mg, 74% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f = 0.18$ ; mp: 106–107 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 9.0$  Hz, 2H), 6.96 (d,  $J = 9.0$  Hz, 2H), 5.89 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 130.0, 129.3, 118.1, 100.3 (SeCN), 69.8; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2151 (SeCN), 1585, 1489, 1447, 1377, 1306, 1246, 1198, 1055, 824; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_8\text{H}_{10}\text{ClN}_2\text{OSe}$  264.9641, found 264.9636.



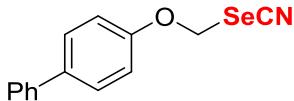
**1-Bromo-4-(selenocyanatomethoxy)benzene (3h).** White solid; 19.5 mg, 67% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f = 0.18$ ; mp: 116–117 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.9$  Hz, 2H), 6.91 (d,  $J = 8.9$  Hz, 2H), 5.89 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.3, 133.0, 118.4, 116.7, 100.3 (SeCN), 69.6; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2151 (SeCN), 1732, 1485, 1292, 1194, 1049, 820; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_8\text{H}_{10}\text{BrN}_2\text{OSe}$  308.9136, found 308.9132.



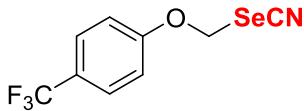
**1-Bromo-3-(selenocyanatomethoxy)benzene (3i).** White solid; 21.8 mg, 75% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f = 0.22$ ; mp: 102–103 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.28 (m, 2H), 7.21 (t,  $J = 1.8$  Hz, 1H), 7.00 (d,  $J = 8.0$  Hz, 1H), 5.92 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 131.1, 127.2, 123.2, 120.2, 115.2, 100.3 (SeCN), 69.3; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2154 (SeCN), 1576, 1472, 1429, 1296, 1227, 1196, 1053, 874, 775; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_8\text{H}_{10}\text{BrN}_2\text{OSe}$  308.9136, found 308.9134.



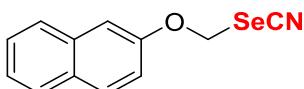
**1-Iodo-2-(selenocyanatomethoxy)benzene (3j).** Yellow oil; 27.8 mg, 82% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.20;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.39 (t,  $J$  = 8.5 Hz, 1H), 7.01 (d,  $J$  = 9.2 Hz, 1H), 6.92 (t,  $J$  = 8.2 Hz, 1H), 5.96 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 140.4, 129.7, 126.0, 115.9, 100.6 (SeCN), 88.3, 70.7; IR (KBr,  $\text{cm}^{-1}$ ) 2926, 2153 (SeCN), 1732, 1574, 1468, 1443, 1302, 1240, 1196, 1121, 1051, 1018, 748; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>8</sub>H<sub>10</sub>IN<sub>2</sub>OSe 356.8998, found 356.8994.



**4-(Selenocyanatomethoxy)-1,1'-biphenyl (3k).** White solid; 12.0 mg, 42% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.20; mp: 129–131 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J$  = 8.7 Hz, 2H), 7.56 (d,  $J$  = 7.3 Hz, 2H), 7.44 (t,  $J$  = 7.6 Hz, 2H), 7.34 (t,  $J$  = 7.3 Hz, 1H), 7.08 (d,  $J$  = 8.8 Hz, 2H), 5.96 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 140.1, 137.2, 128.9, 128.7, 127.3, 126.9, 116.8, 100.6 (SeCN), 69.9; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2147 (SeCN), 1717, 1516, 1485, 1447, 1310, 1233, 1206, 1175, 1063, 833; 760, 696; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>OSe 307.0344, found 307.0345.

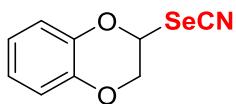


**1-(Selenocyanatomethoxy)-4-(trifluoromethyl)benzene (3l).** White solid; 17.0 mg, 60% yield; Eluent PE/EtOAc (5:1, v/v), TLC  $R_f$  = 0.30; mp: 74–75 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J$  = 8.6 Hz, 2H), 7.10 (d,  $J$  = 8.6 Hz, 2H), 5.94 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 127.5 (q,  $J$  = 3.7 Hz), 126.1 (d,  $J$  = 32.8 Hz), 123.9 (d,  $J$  = 270.0 Hz), 116.4, 100.1 (SeCN), 68.4; IR (KBr,  $\text{cm}^{-1}$ ) 2926, 2160 (SeCN), 1616, 1593, 1516, 1450, 1418, 1342, 1250, 1215, 1163, 1123, 1072, 1045, 839; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>9</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>OSe 298.9905, found 298.9905.

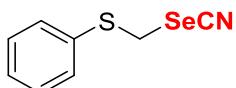


**2-(Selenocyanatomethoxy)naphthalene (3m).** White solid; 22.0 mg, 84% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.22; mp: 96–98 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85–7.79 (m, 3H), 7.50 (t,  $J$  = 7.4 Hz, 1H), 7.44 (t,  $J$  = 7.5 Hz, 1H), 7.27 (d,  $J$  = 2.4 Hz, 1H), 7.21 (dd,  $J$  = 8.9, 2.5 Hz, 1H), 6.02 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0, 133.9, 130.4, 130.3, 127.8, 127.3, 127.0, 125.2, 118.6, 110.2, 100.8

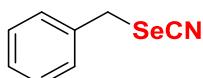
(SeCN), 69.4; IR (KBr,  $\text{cm}^{-1}$ ) 2961, 2153 (SeCN), 1630, 1595, 1510, 1468, 1283, 1234, 1209, 1161, 1123, 1057, 810, 748; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>OSe 281.0188, found 281.0182.



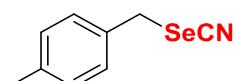
**2-Selenocyanato-2,3-dihydrobenzo[b][1,4]dioxine (3n).** White solid; 21.3 mg, 88% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.22; mp: 67–69 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02–6.93 (m, 4H), 6.59 (t,  $J$  = 1.7 Hz, 1H), 4.50 (d,  $J$  = 1.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.3, 139.5, 124.0, 123.1, 118.6, 117.8, 100.3 (SeCN), 80.4, 67.5; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2153 (SeCN), 1599, 1491, 1464, 1258, 1165, 1111, 1086, 1061, 897, 853, 748; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>Se 258.9980, found 258.9982.



**Phenyl(selenocyanatomethyl)sulfane (3o).** Yellow oil; 14.5 mg, 63% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.29; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d,  $J$  = 2.3 Hz, 1H), 7.49 (d,  $J$  = 1.6 Hz, 1H), 7.42–7.37 (m, 3H), 4.54 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  132.4, 131.9, 129.6, 128.8, 101.5 (SeCN), 35.1; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2149 (SeCN), 1682, 1506, 1456, 1362, 1339, 1171, 741, 689; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>SSe 246.9803, found 246.9805.

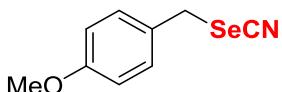


**(Selenocyanatomethyl)benzene (5a).** White solid; 15.4 mg, 78% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.22; mp: 70–71 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38–7.32 (m, 5H), 4.31 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.4, 129.2, 129.0, 128.7, 101.8 (SeCN), 32.8; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2145 (SeCN), 1491, 1454, 1423, 1217, 1192, 1069, 758, 694; HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>8</sub>H<sub>7</sub>NNaSe 219.9641, found 219.9646.

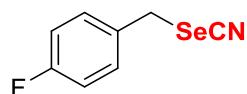


**1-Methyl-4-(selenocyanatomethyl)benzene (5b).** White solid; 17.0 mg, 80% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.27; mp: 55–56 °C; <sup>1</sup>H NMR (400 MHz,

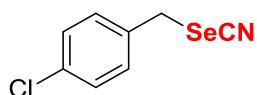
$\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J = 8.0$  Hz, 2H), 7.17 (d,  $J = 7.9$  Hz, 2H), 4.30 (s, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 132.3, 129.8, 128.9, 102.0 (SeCN), 32.9, 21.2; IR (KBr,  $\text{cm}^{-1}$ ) 2922, 2149 (SeCN), 1508, 1456, 1431, 1190, 1101, 820; HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_9\text{H}_9\text{NNaSe}$  233.9792, found 233.9796.



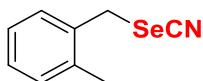
**1-Methoxy-4-(selenocyanatomethyl)benzene (5c).** White solid; 19.0 mg, 84% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f = 0.16$ ; mp: 56–57 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 8.6$  Hz, 2H), 6.89 (d,  $J = 8.6$  Hz, 2H), 4.31 (s, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 130.4, 127.2, 114.6, 102.1 (SeCN), 55.3, 32.9; IR (KBr,  $\text{cm}^{-1}$ ) 2934, 2147 (SeCN), 1609, 1510, 1456, 1423, 1302, 1250, 1175, 1099, 1032, 831; HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_9\text{H}_9\text{NNaOSe}$  249.9742, found 249.9746.



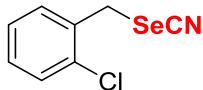
**1-Fluoro-4-(selenocyanatomethyl)benzene (5d).** White solid; 15.2 mg, 71% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f = 0.15$ ; mp: 63–64 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J = 8.6, 5.2$  Hz, 2H), 7.06 (t,  $J = 8.6$  Hz, 2H), 4.28 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $J = 247.2$  Hz), 131.4 (d,  $J = 3.3$  Hz), 130.8 (d,  $J = 8.4$  Hz), 116.2 (d,  $J = 21.8$  Hz), 101.6 (SeCN), 31.9; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2151 (SeCN), 1595, 1508, 1221, 1188, 1157, 1090, 835; HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_8\text{H}_6\text{FNNaOSe}$  237.9547, found 237.9556.



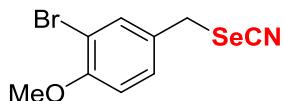
**1-Chloro-4-(selenocyanatomethyl)benzene (5e).** White solid; 17.6 mg, 76% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f = 0.18$ ; mp: 56–57 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.5$  Hz, 2H), 7.30 (d,  $J = 8.6$  Hz, 2H), 4.25 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.7, 134.1, 130.3, 129.4, 101.4 (SeCN), 31.9; IR (KBr,  $\text{cm}^{-1}$ ) 2926, 2149 (SeCN), 1595, 1489, 1406, 1219, 1190, 1094, 1015, 831; HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for  $\text{C}_8\text{H}_7\text{ClNSe}$  231.9432, found 231.9440.



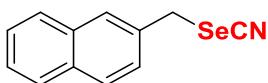
**1-Methyl-2-(selenocyanatomethyl)benzene (5f).** White solid; 15.9 mg, 75% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.27; mp: 47–48 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J$  = 7.1 Hz, 1H), 7.25–7.19 (m, 3H), 4.37 (s, 2H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 132.9, 131.1, 130.2, 129.2, 126.8, 101.8 (SeCN), 31.3, 19.2; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2147 (SeCN), 1684, 1653, 1491, 1456, 1379, 1204, 1180, 1088, 1032, 762, 719; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_9\text{H}_9\text{NNaSe}$  233.9792, found 233.9791.



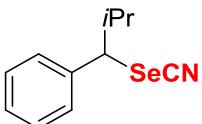
**1-Chloro-2-(selenocyanatomethyl)benzene (5g).** Colorless oil; 16.2 mg, 70% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.27;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.40 (m, 2H), 7.32–7.29 (m, 2H), 4.34 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.1, 133.7, 130.9, 130.2, 130.1, 127.5, 101.6 (SeCN), 30.6; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2149 (SeCN), 1717, 1653, 1558, 1506, 1456, 1418, 1339, 1204, 1032, 758; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_8\text{H}_6\text{ClNNaSe}$  253.9246, found 253.9247.



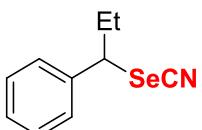
**2-Bromo-1-methoxy-4-(selenocyanatomethyl)benzene (5h).** White solid; 23.9 mg, 78% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.16; mp: 61–62 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 2.2 Hz, 1H), 7.29 (dd,  $J$  = 8.4, 2.2 Hz, 1H), 6.88 (d,  $J$  = 8.4 Hz, 1H), 4.24 (s, 2H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2, 133.8, 129.3, 128.8, 112.2, 112.1, 101.6 (SeCN), 56.3, 31.8; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2147 (SeCN), 1717, 1599, 1495, 1456, 1260, 1051, 1016, 810; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_9\text{H}_8\text{BrNNaOSe}$  327.8847, found 327.8852.



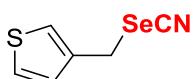
**2-(Selenocyanatomethyl)naphthalene (5i).** White solid; 20.0 mg, 81% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.16; mp: 120–121 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J$  = 12.4, 7.3 Hz, 4H), 7.53–7.50 (m, 2H), 7.46 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 4.47 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.2, 133.1, 132.7, 129.2, 128.2, 128.0, 127.8, 126.8, 126.8, 126.3, 101.9 (SeCN), 33.4; IR (KBr,  $\text{cm}^{-1}$ ) 2932, 2145 (SeCN), 1684, 1653, 1558, 1541, 1506, 1456, 1425, 1362, 1198, 827, 750; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{12}\text{H}_9\text{NNaSe}$  269.9792, found 269.9791.



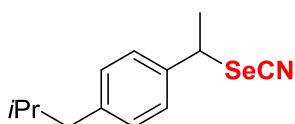
**(2-Methyl-1-selenocyanatopropyl)benzene (5j).** Yellow oil; 18.0 mg, 75% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.48;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 6.8 Hz, 2H), 7.31 (t,  $J$  = 5.9 Hz, 3H), 4.38 (d,  $J$  = 9.5 Hz, 1H), 2.52–2.43 (m, 1H), 1.22 (d,  $J$  = 6.6 Hz, 3H), 0.92 (d,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 129.0, 128.5, 127.8, 102.5 (SeCN), 60.4, 34.1, 22.3, 20.8; IR (KBr,  $\text{cm}^{-1}$ ) 2963, 2930, 2147 (SeCN), 1730, 1682, 1597, 1491, 1454, 1389, 1163, 1113, 766, 698; HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{11}\text{H}_{14}\text{NSe}$  240.0286, found 240.0294.



**(1-Selenocyanatopropyl)benzene (5k).** Yellow oil; 16.0 mg, 71% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.36;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.31 (m, 5H), 4.56 (dd,  $J$  = 8.8, 6.8 Hz, 1H), 2.39–2.27 (m, 2H), 0.99 (t,  $J$  = 7.3 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.5, 129.2, 128.8, 127.6, 102.5 (SeCN), 52.9, 29.8, 13.0; IR (KBr,  $\text{cm}^{-1}$ ) 2967, 2926, 2853, 2147 (SeCN), 1647, 1495, 1454, 1379, 1279, 1157, 1096, 758, 696; HRMS (ESI)  $m/z$ : [M + NH<sub>4</sub>] $^+$  calcd for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{Se}$  243.0395, found 243.0392.

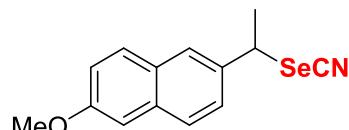


**3-(Selenocyanatomethyl)thiophene (5l).** White solid; 11.5 mg, 57% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.17; mp: 66–67 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J$  = 4.8, 3.0 Hz, 1H), 7.33 (s, 1H), 7.11 (d,  $J$  = 4.9 Hz, 1H), 4.35 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.4, 127.6, 127.3, 124.9, 101.9 (SeCN), 26.9; IR (KBr,  $\text{cm}^{-1}$ ) 2924, 2154 (SeCN), 1867, 1717, 1684, 1653, 1558, 1506, 1456, 1236, 1200, 1080, 874; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_6\text{H}_5\text{NNaSSe}$  225.9206, found 225.9212.

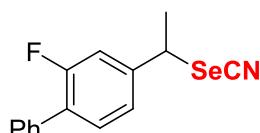


**1-Isobutyl-4-(1-selenocyanatoethyl)benzene (5m).** Colorless oil; 19.3 mg, 72% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.40;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J$

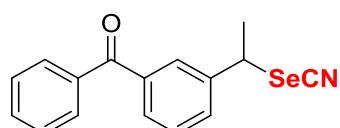
= 8.1 Hz, 2H), 7.14 (d,  $J$  = 8.1 Hz, 2H), 4.94 (q,  $J$  = 7.0 Hz, 1H), 2.47 (d,  $J$  = 7.2 Hz, 2H), 2.06 (d,  $J$  = 7.0 Hz, 3H), 1.86 (septet,  $J$  = 6.8 Hz, 1H), 0.90 (d,  $J$  = 6.6 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 136.5, 129.8, 126.9, 102.8 (SeCN), 45.7, 45.1, 30.1, 22.9, 22.4; IR (KBr,  $\text{cm}^{-1}$ ) 2955, 2926, 2868, 2147 (SeCN), 1732, 1510, 1456, 1381, 1202, 1165, 1059, 1020, 847, 800; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{13}\text{H}_{17}\text{NNaSe}$  290.0418, found 290.0420.



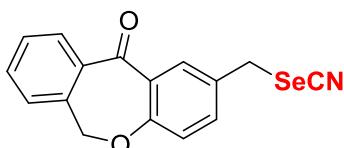
**2-Methoxy-6-(1-selenocyanatoethyl)naphthalene (5n).** White solid; 20.0 mg, 69% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.19; mp: 102–104 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (s, 1H), 7.73 (dd,  $J$  = 8.7, 4.7 Hz, 2H), 7.45 (dd,  $J$  = 8.5, 1.7 Hz, 1H), 7.17 (dd,  $J$  = 8.9, 2.5 Hz, 1H), 7.12 (d,  $J$  = 2.2 Hz, 1H), 5.08 (q,  $J$  = 7.0 Hz, 1H), 3.92 (s, 3H), 2.14 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 134.6, 134.3, 129.6, 128.6, 127.9, 126.1, 125.3, 119.7, 105.8, 102.7 (SeCN), 55.4, 46.3, 22.9; IR (KBr,  $\text{cm}^{-1}$ ) 2926, 2141 (SeCN), 1628, 1605, 1504, 1483, 1437, 1389, 1373, 1263, 1221, 1177, 1028, 856; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{14}\text{H}_{13}\text{NNaOSe}$  314.0055, found 314.0057.



**2-Fluoro-4-(1-selenocyanatoethyl)-1,1'-biphenyl (5o).** White solid; 16.3 mg, 53% yield; Eluent PE/EtOAc (20:1, v/v), TLC  $R_f$  = 0.20; mp: 70–71 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 7.4 Hz, 2H), 7.45 (t,  $J$  = 7.5 Hz, 3H), 7.39 (d,  $J$  = 7.0 Hz, 1H), 7.25–7.19 (m, 2H), 4.90 (q,  $J$  = 6.9 Hz, 1H), 2.06 (d,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7 (d,  $J$  = 248.4 Hz), 140.9 (d,  $J$  = 7.6 Hz), 134.9, 131.4 (d,  $J$  = 4.0 Hz), 129.7 (d,  $J$  = 13.5 Hz), 128.9 (d,  $J$  = 2.9 Hz), 128.6, 128.1, 123.2 (d,  $J$  = 3.3 Hz), 114.9 (d,  $J$  = 24.1 Hz), 102.0 (SeCN), 44.4, 22.6; IR (KBr,  $\text{cm}^{-1}$ ) 3059, 2970, 2926, 2149 (SeCN), 1686, 1582, 1560, 1485, 1416, 1277, 1186, 1069, 1011, 872, 768; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{15}\text{H}_{12}\text{FNNaSe}$  328.0011, found 328.0013.

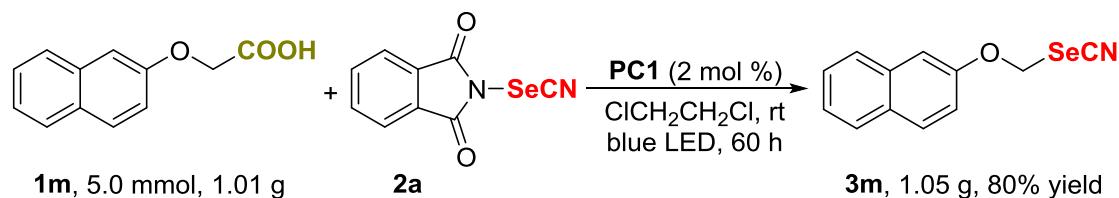


**Phenyl(3-(1-selenocyanatoethyl)phenyl)methanone (**5p**).** White solid; 10.0 mg, 32% yield; Eluent PE/EtOAc (10:1, v/v), TLC  $R_f$  = 0.18; mp: 96–98 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84–7.81 (m, 3H), 7.75 (d,  $J$  = 7.6 Hz, 1H), 7.65–7.60 (m, 2H), 7.51 (t,  $J$  = 7.5 Hz, 3H), 4.94 (q,  $J$  = 7.0 Hz, 1H), 2.06 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 140.4, 138.5, 137.1, 132.8, 130.9, 130.5, 130.1, 129.1, 128.5, 128.5, 101.9 (SeCN), 44.7, 22.5; IR (KBr,  $\text{cm}^{-1}$ ) 2926, 2147 (SeCN), 1653, 1558, 1506, 1456, 1317, 1285, 1206, 1179, 721; HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{16}\text{H}_{14}\text{NOSe}$  316.0235, found 316.0239.

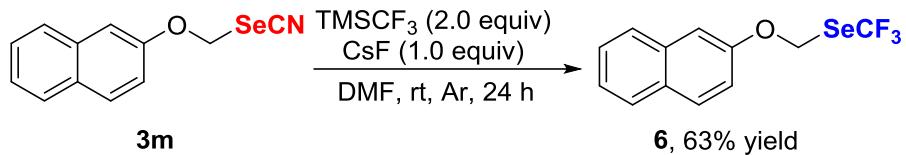


**2-(Selenocyanatomethyl)dibenzo[b,e]oxepin-11(6*H*)-one (**5q**).** White solid; 17.0 mg, 52% yield; Eluent PE/EtOAc (5:1, v/v), TLC  $R_f$  = 0.3; mp: 150–151 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d,  $J$  = 2.4 Hz, 1H), 7.90 (d,  $J$  = 6.7 Hz, 1H), 7.58 (td,  $J$  = 7.4, 1.2 Hz, 1H), 7.52–7.47 (m, 2H), 7.38 (d,  $J$  = 7.2 Hz, 1H), 7.08 (d,  $J$  = 8.5 Hz, 1H), 5.21 (s, 2H), 4.33 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 161.4, 140.2, 135.7, 135.3, 133.0, 132.6, 129.6, 129.4, 129.2, 128.0, 125.5, 121.9, 101.6 (SeCN), 73.7, 32.0; IR (KBr,  $\text{cm}^{-1}$ ) 2936, 2149 (SeCN), 1717, 1647, 1558, 1506, 1489, 1456, 1300, 1221, 1013, 831; HRMS (ESI)  $m/z$ : [M + H] $^+$  calcd for  $\text{C}_{16}\text{H}_{12}\text{NO}_2\text{Se}$  330.0028, found 330.0030.

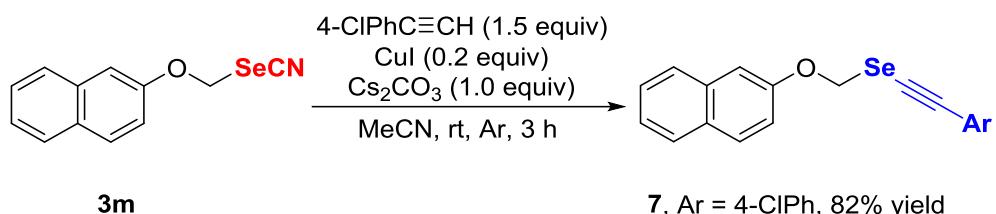
#### 4. Gram Scale Reaction and Derivatization of Products



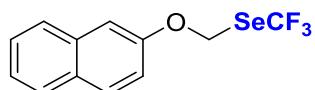
**Gram scale reaction.** To a 100 mL oven-dried flask containing **1m** (1.01 g, 5.0 mmol) was added **PC1** (39.6 mg, 0.1 mmol, 2 mol %) and 1,2-dichloroethane (50 mL) under an argon atmosphere. Then, reagent **2a** (1.51 g, 6.0 mmol, 1.2 equiv) was added. The reaction was irradiation with blue LED (435–445 nm, 5 W) for 60 h at room temperature. When the reaction was completed, the solution was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v/v) to afford the product **3m** (1.05 g, 80% yield).



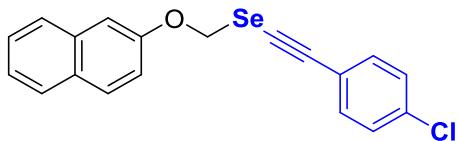
**Procedure for the synthesis of 6.** To a 25 mL Schlenk tube containing **3m** (52.6 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) was added CsF (30.4 mg, 0.2 mmol, 1.0 equiv) under an argon atmosphere. Subsequently, (trifluoromethyl)trimethylsilane (56.8 mg, 0.4 mmol, 2.0 equiv) was added to the solution. The reaction was stirred for 24 h at room temperature. When the reaction was completed, the mixture was extracted with dichloromethane, the combined organic phases were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate.



**Procedure for the synthesis of 7.** To a 25 mL Schlenk tube charged with CuI (7.6 mg, 0.04 mmol, 0.2 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 1.0 equiv) in acetonitrile (1.0 mL) under an argon atmosphere at room temperature was added **3m** (52.6 mg, 0.2 mmol, 1.0 equiv). Then, (4-chlorophenyl)acetylene (40.8 mg, 0.3 mmol, 1.5 equiv) was added. The reaction was stirred for 3 h. The solution was concentrated in vacuo to get the crude product, which was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate.

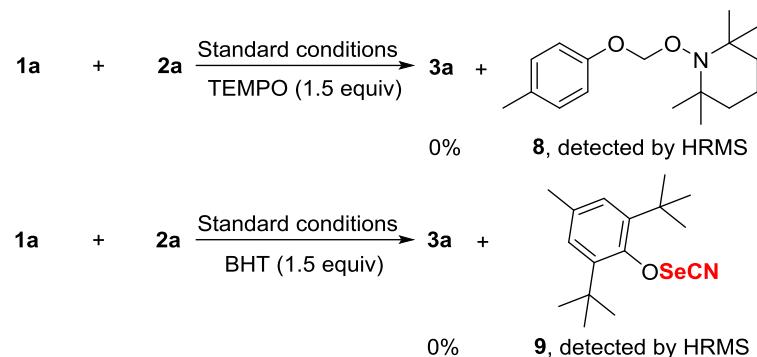


**(Naphthalen-2-yloxy)methyl(trifluoromethyl)selane (6).** Colorless oil; 38.5 mg, 63% yield; Eluent PE/EtOAc (50:1, v/v), TLC  $R_f$  = 0.27;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J$  = 8.6 Hz, 2H), 7.76 (d,  $J$  = 8.2 Hz, 1H), 7.48 (t,  $J$  = 7.5 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 1H), 7.18–7.14 (m, 2H), 5.91 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 134.0, 130.1, 130.0, 127.8, 127.1, 126.8, 124.7, 122.5 (q,  $J$  = 329.6 Hz), 119.0, 109.4, 64.9 (q,  $J$  = 2.2 Hz); IR (KBr,  $\text{cm}^{-1}$ ) 2928, 1632, 1601, 1510, 1468, 1294, 1252, 1209, 1126, 1098, 1036, 835, 739; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{12}\text{H}_9\text{F}_3\text{NaOSe}$  328.9663, found 328.9656.



**((4-Chlorophenyl)ethynyl)((naphthalen-2-yloxy)methyl)selane (7).** White solid; 61.0 mg, 82% yield; Eluent PE/EtOAc (50:1, v/v), TLC  $R_f$  = 0.18; mp: 88–90 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 8.7 Hz, 2H), 7.73 (d,  $J$  = 8.1 Hz, 1H), 7.45 (t,  $J$  = 7.0 Hz, 1H), 7.39 (t,  $J$  = 7.5 Hz, 1H), 7.35 (d,  $J$  = 2.3 Hz, 1H), 7.30 (d,  $J$  = 8.6 Hz, 2H), 7.26 (d,  $J$  = 8.5 Hz, 2H), 7.23 (dd,  $J$  = 9.0, 2.5 Hz, 1H), 5.86 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 134.4, 134.1, 132.9, 129.9, 128.6, 127.7, 127.2, 126.7, 124.6, 121.7, 119.1, 109.9, 100.1, 70.8, 69.6; IR (KBr,  $\text{cm}^{-1}$ ) 3057, 2947, 1632, 1508, 1487, 1466, 1287, 1206, 1167, 1119, 1084, 1028, 826; HRMS (ESI)  $m/z$ : [M + Na] $^+$  calcd for  $\text{C}_{19}\text{H}_{13}\text{ClNaOSe}$  394.9712, found 394.9718.

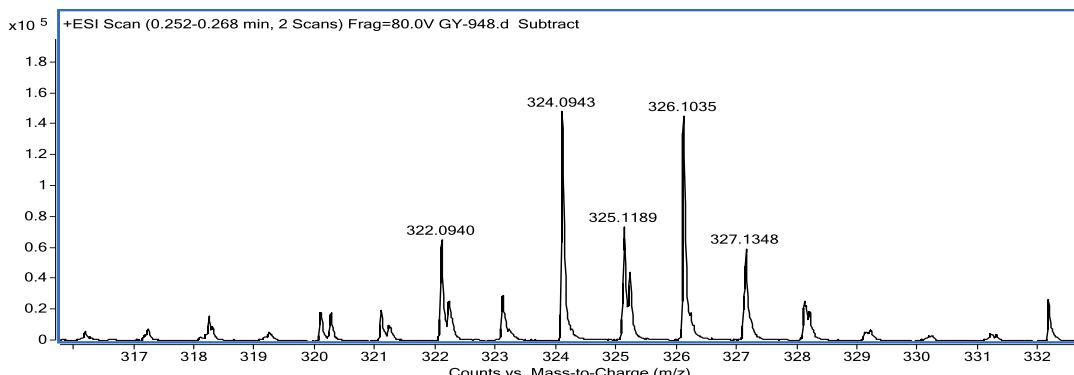
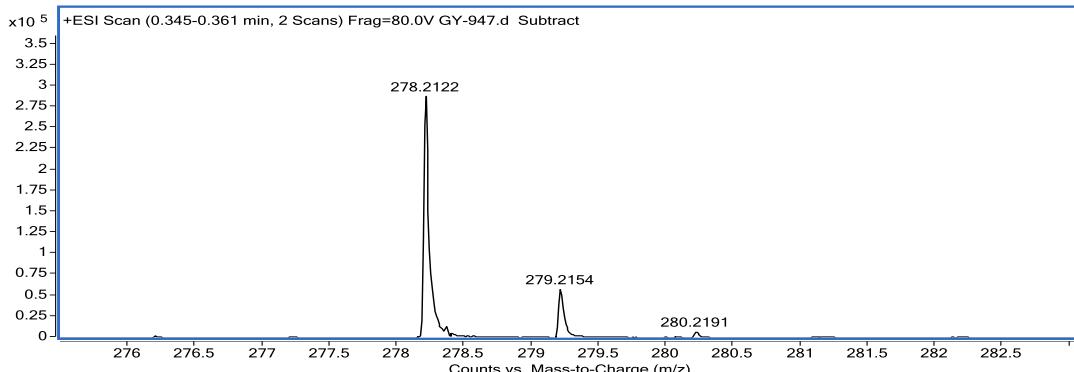
## 5. Radical Trapping Experiment



A 25 mL Schlenk tube equipped with a stirring bar was charged with **1a** (16.6 mg, 0.1 mmol, 1.0 equiv), **2a** (30.2 mg, 0.12 mmol, 1.2 equiv), **PC1** (0.8 mg, 0.002 mmol, 2 mol %) and 1,2-dichloroethane (1.0 mL) under an argon atmosphere. Then, TEMPO (23.4 mg, 0.15 mmol, 1.5 equiv) or BHT (33.0 mg, 0.15 mmol, 1.5 equiv) was added. The reaction was irradiation with blue LED (435–445 nm, 5 W) at room temperature. After 24 h, no product **3a** was detected, while the TEMPO-adduct **8** and BHT-adduct **9** were detected in the reaction mixture by ESI-HRMS analysis.

**8:** HRMS (ESI)  $m/z$ :  $[M + H]^+$  calcd for  $C_{17}H_{28}NO_2$  278.2115, found 278.2122.

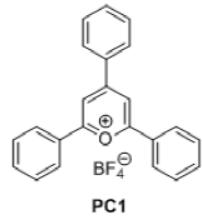
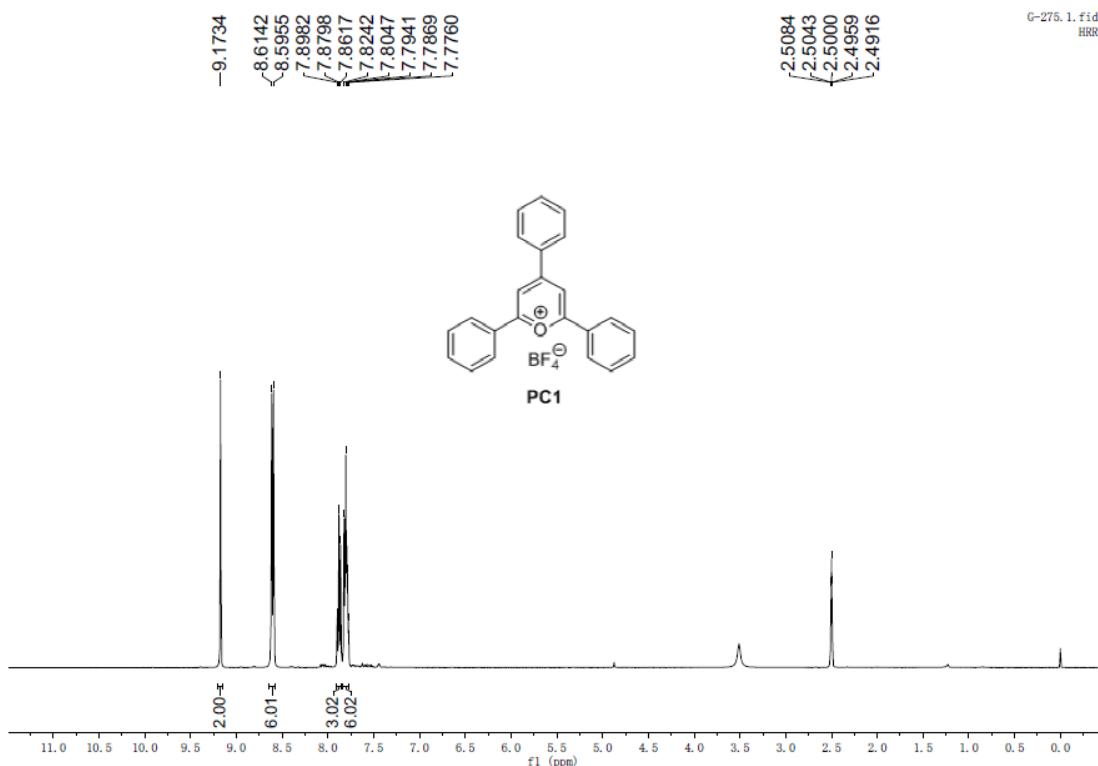
**9:** HRMS (ESI)  $m/z$ :  $[M + H]^+$  calcd for  $C_{16}H_{24}NOSe$  326.1018, found 326.1035.



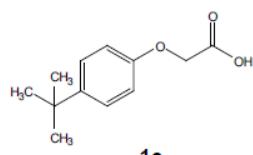
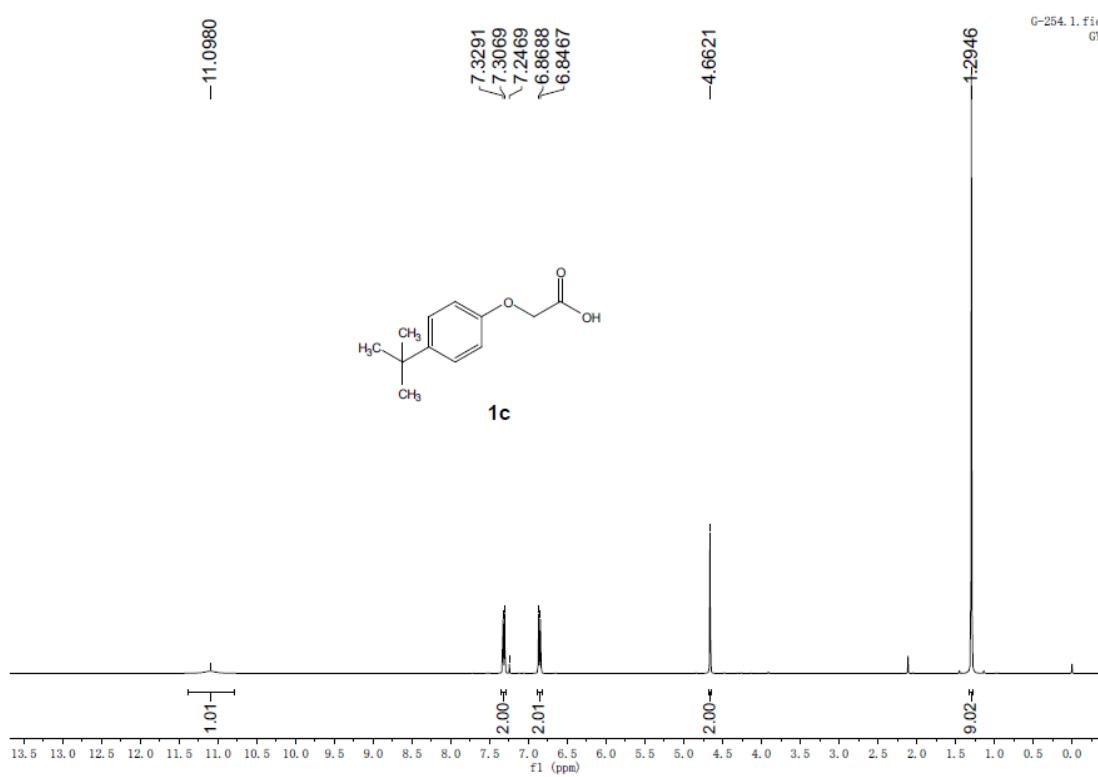
## 6. References

- [1] (a) Xiao, J.-A.; Cheng, X.-L.; Meng, R.-F.; Qin, X.-S.; Peng, H.; Ren, J.-W.; Xie, Z.-Z.; Cui, J.-G.; Huang, Y.-M. *Synthesis* **2021**, *53*, 954–960; (b) Wu, D.; Qiu, J.; Li, C.; Yuan, L.; Yin, H.; Chen, F.-X. *J. Org. Chem.* **2020**, *85*, 934–941; (c) Zhu, D.; Ye, A.-H.; Chen, Z.-M. *Synthesis* **2021**, *53*, 3744–3750.
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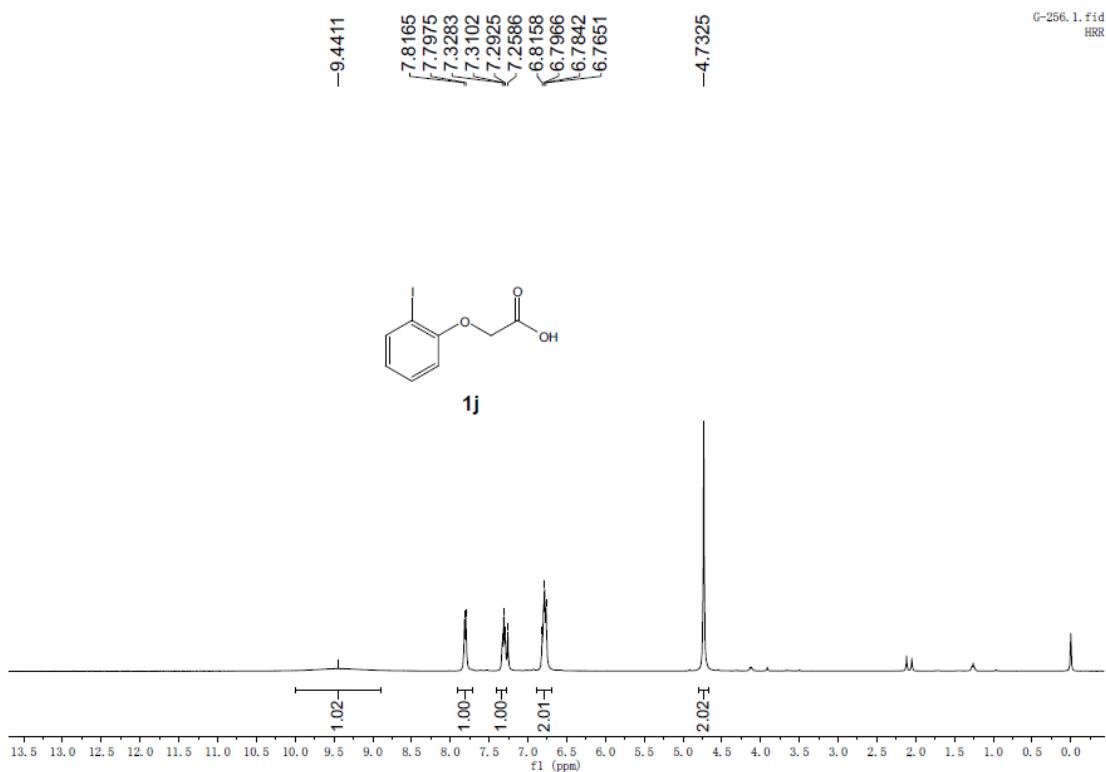
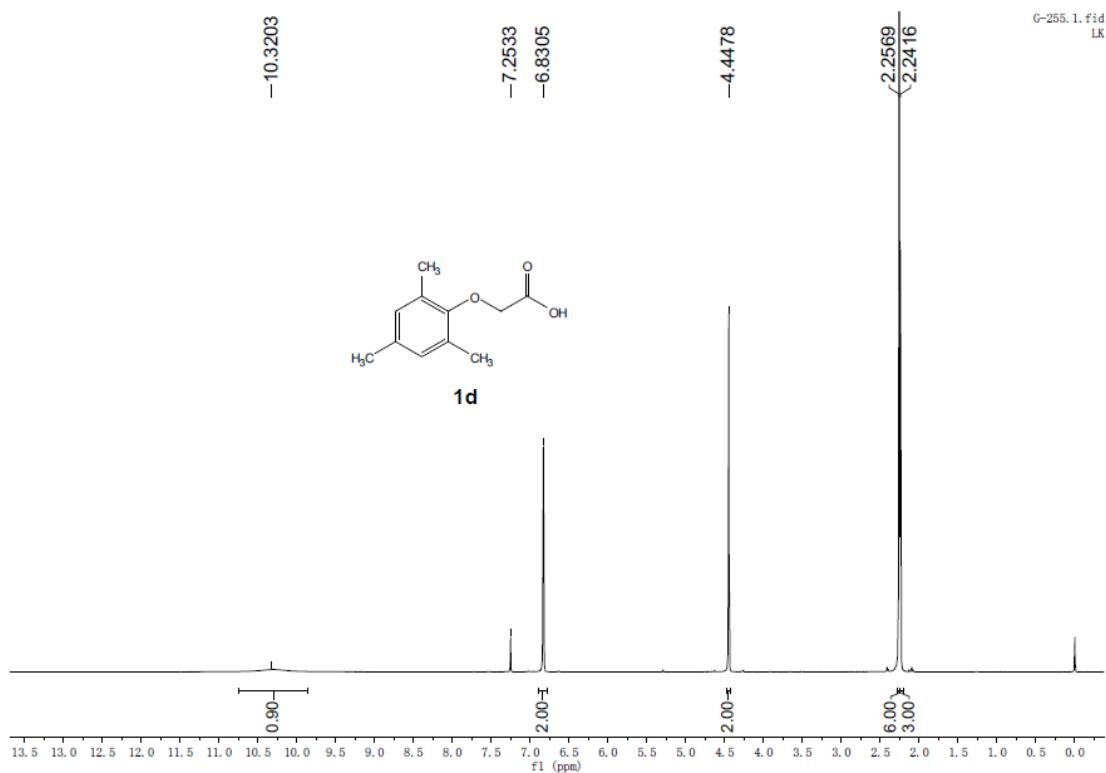
## 7. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

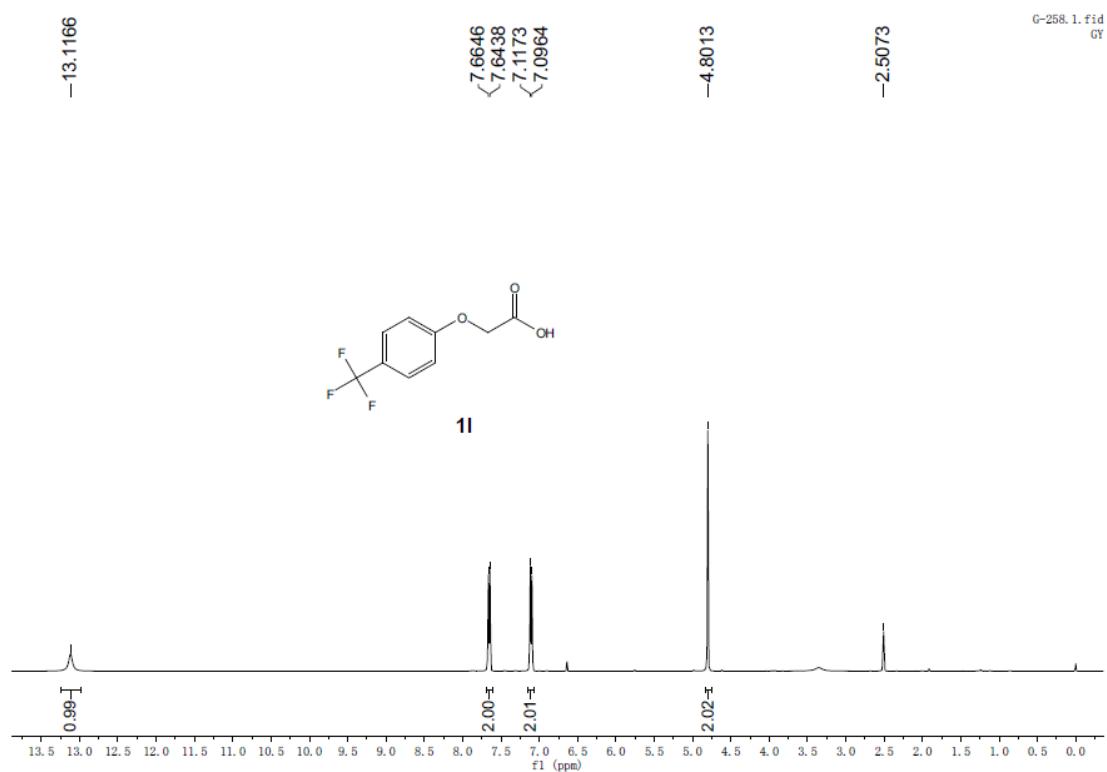
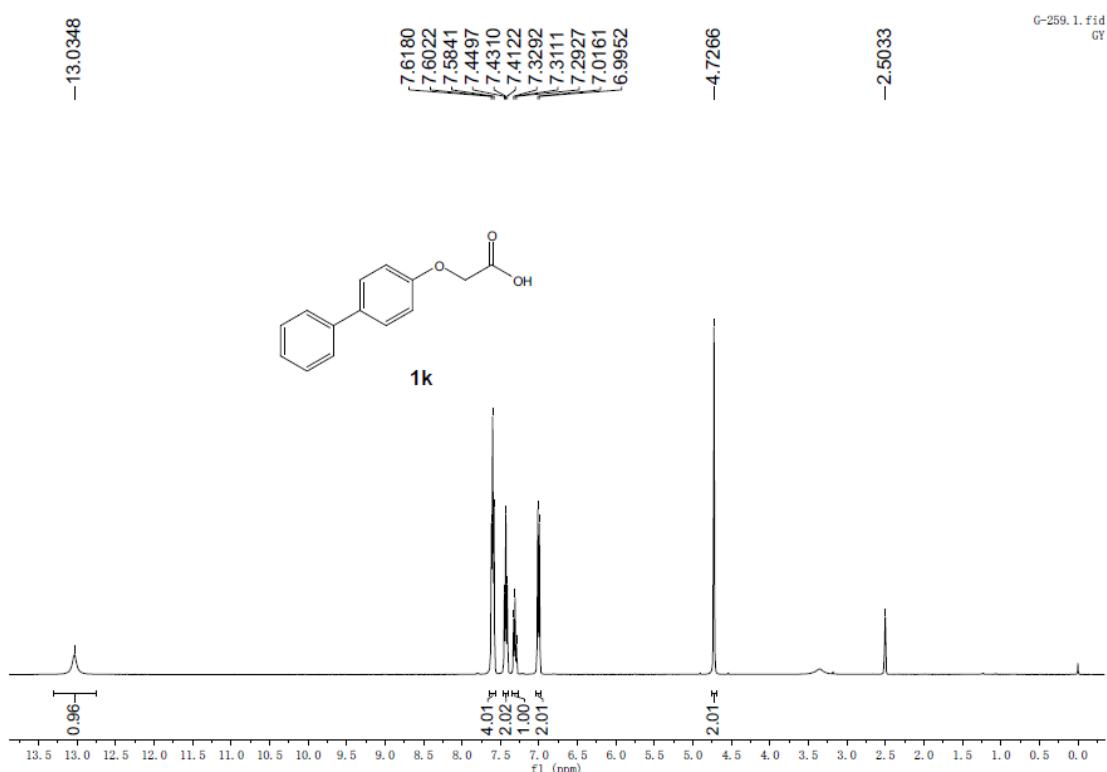


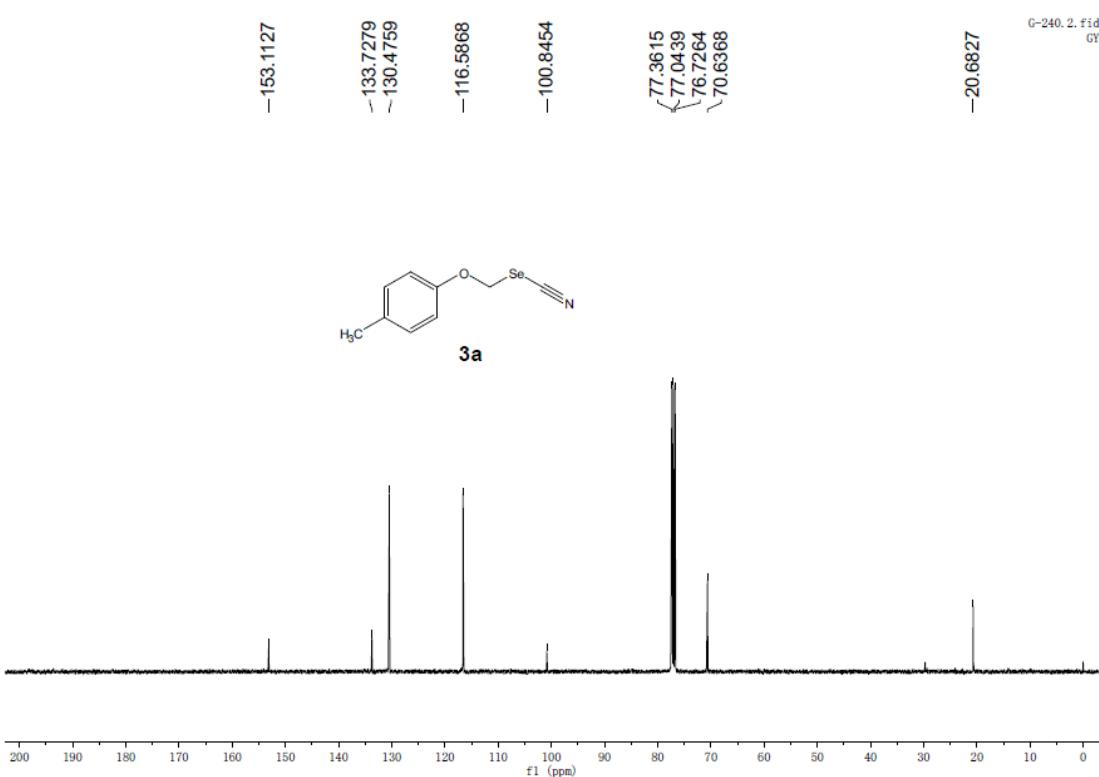
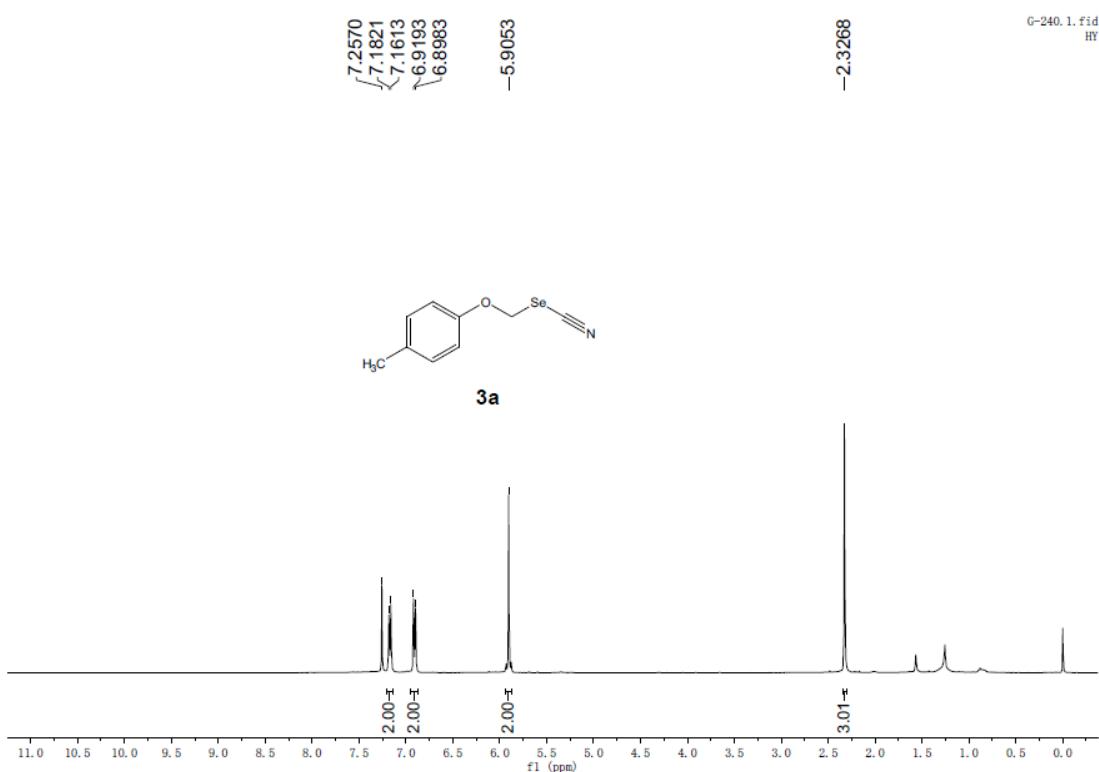
PC1

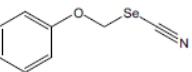


1c

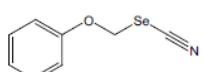
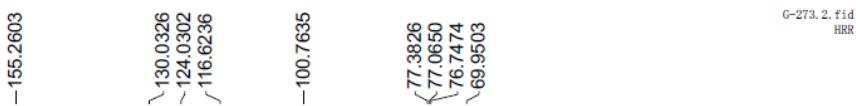
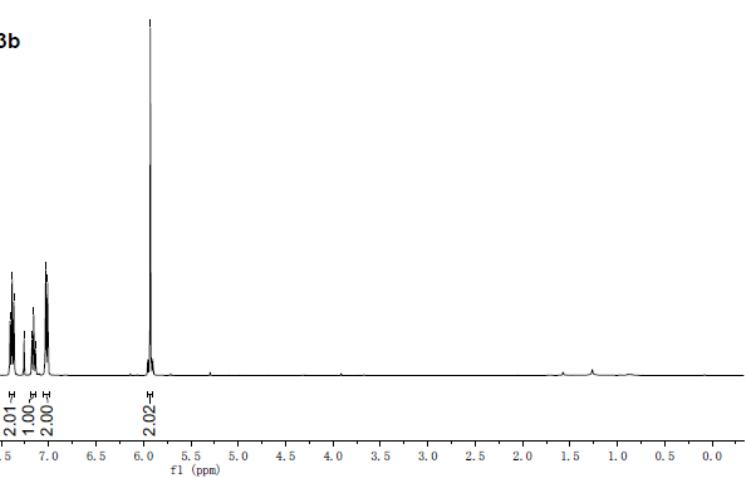




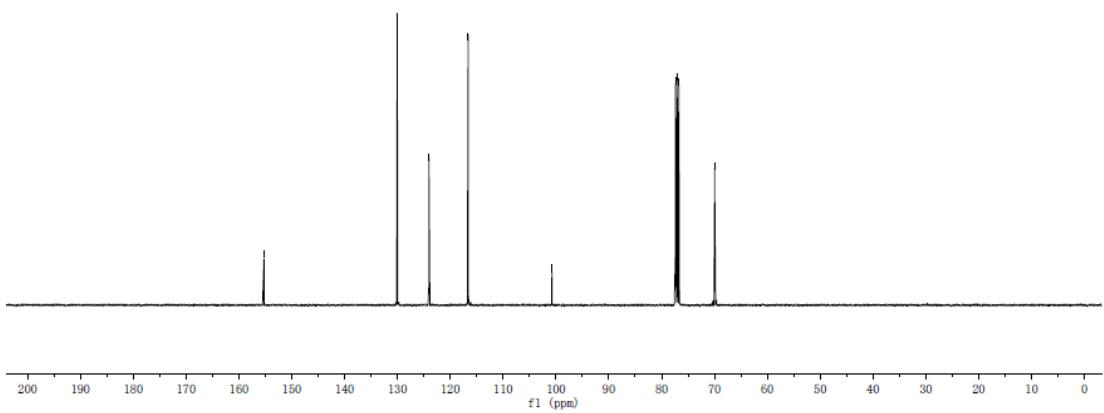


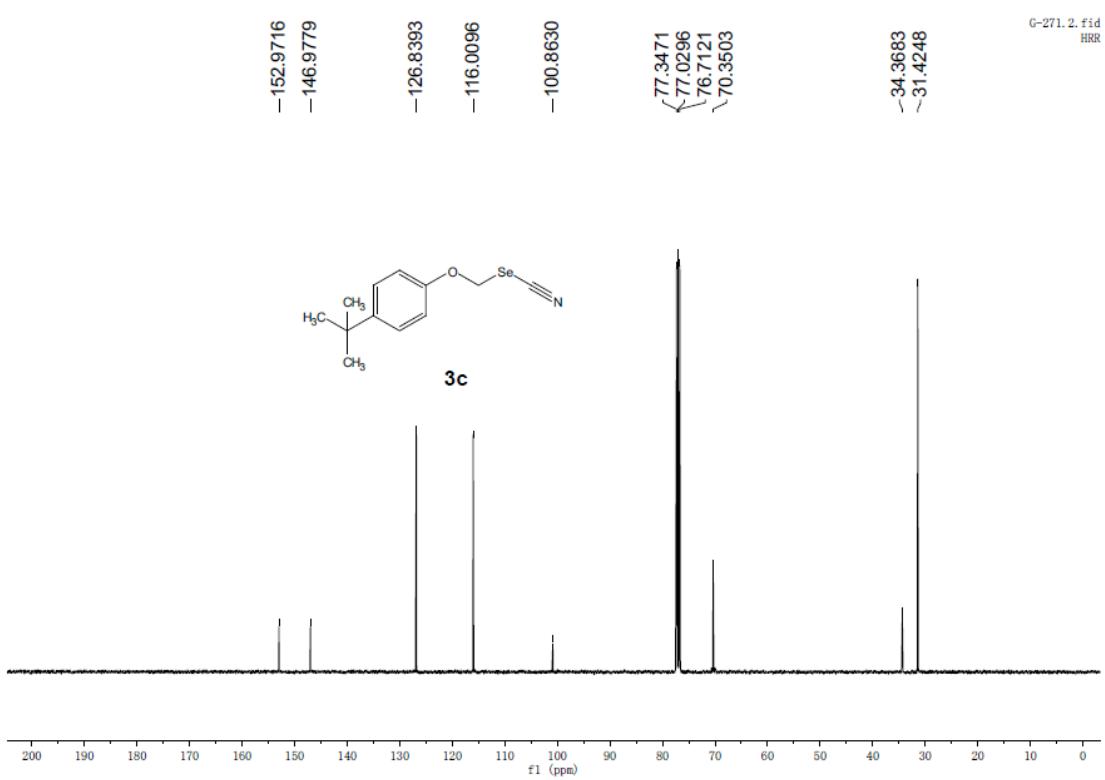
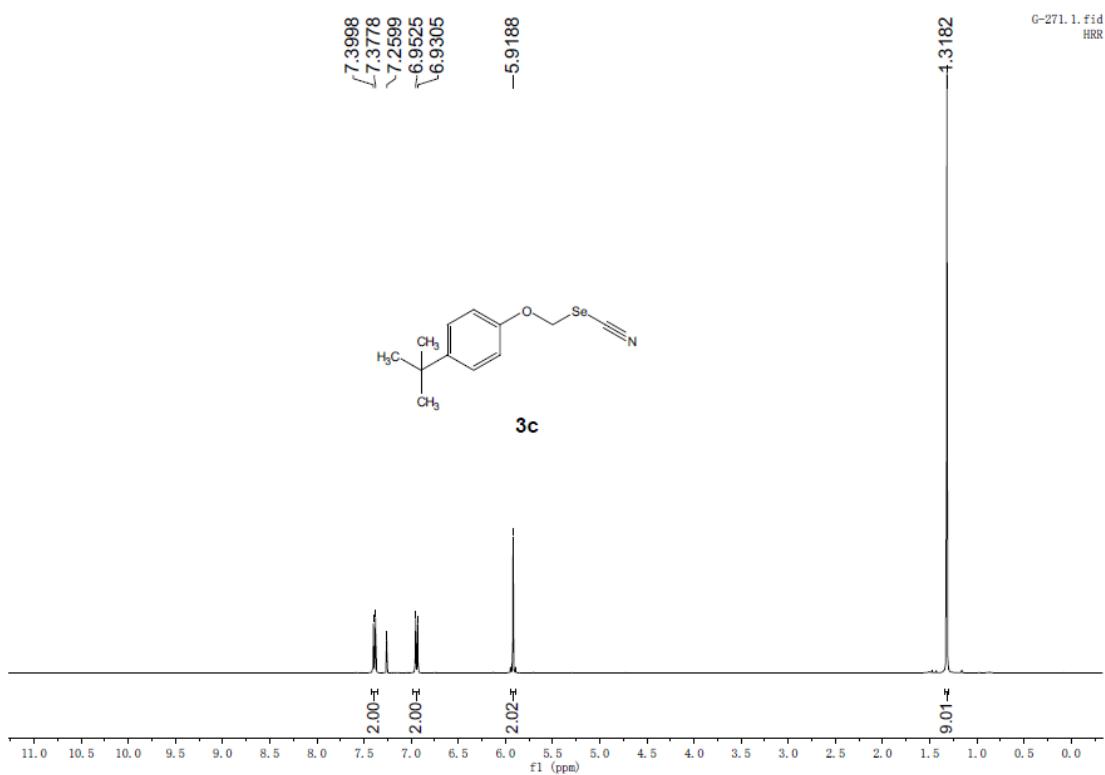


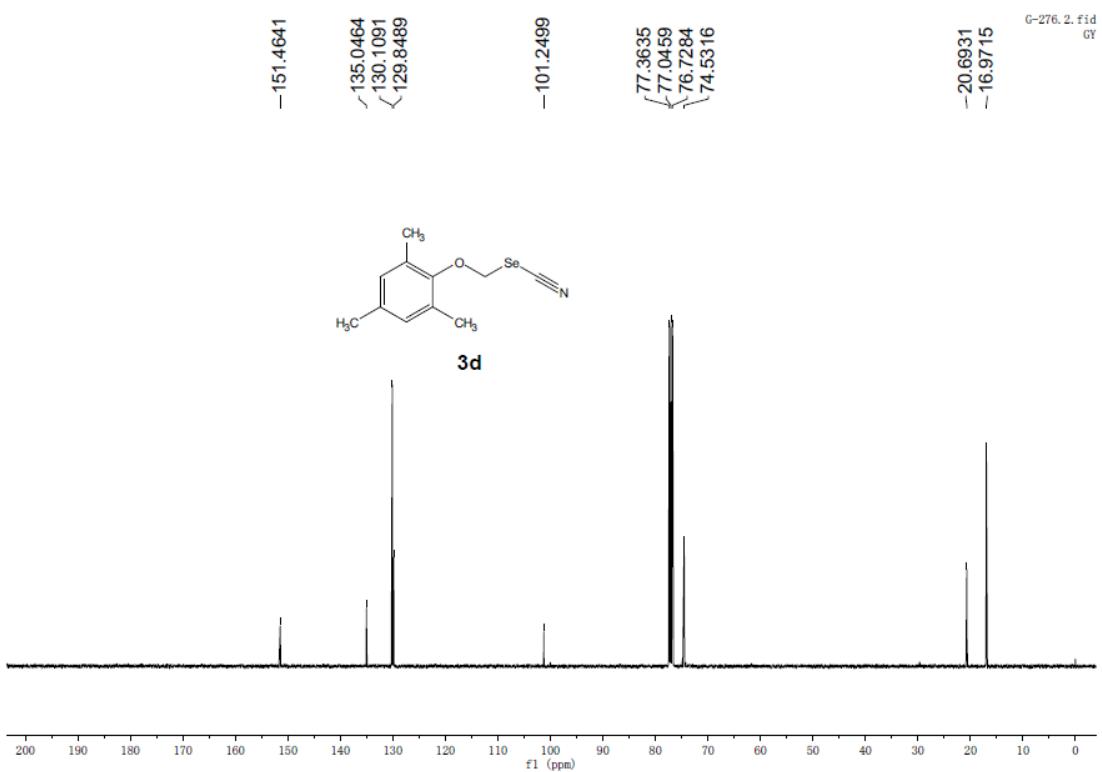
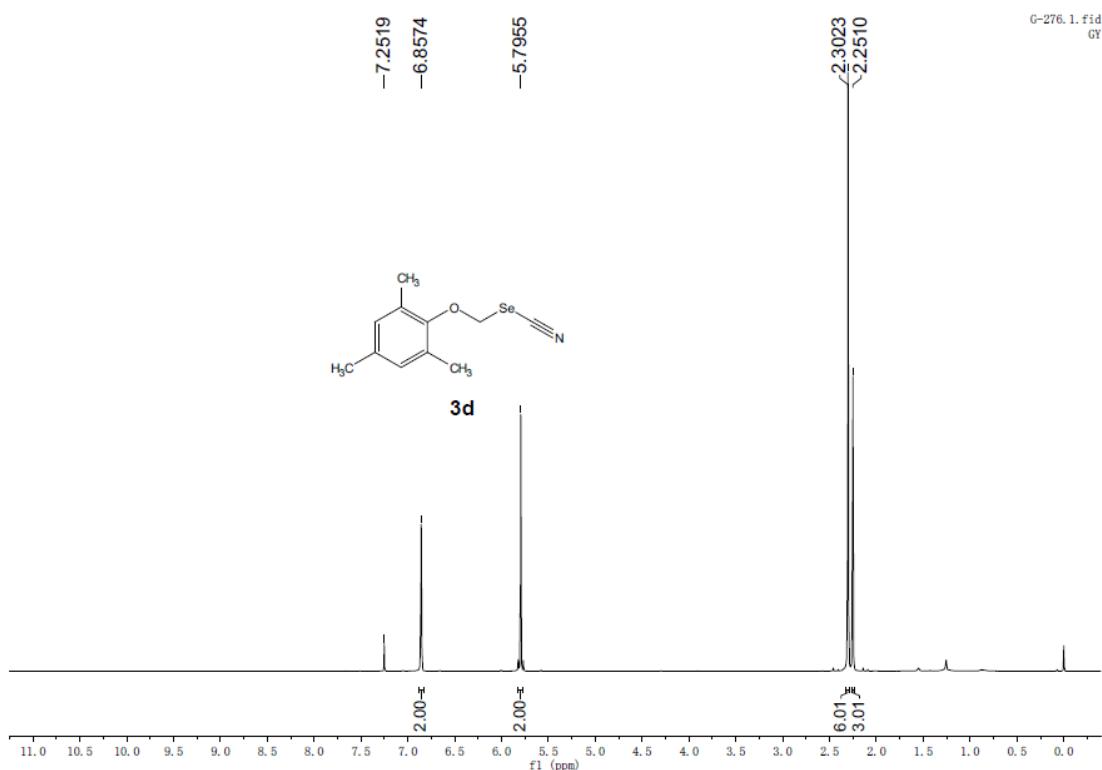
**3b**

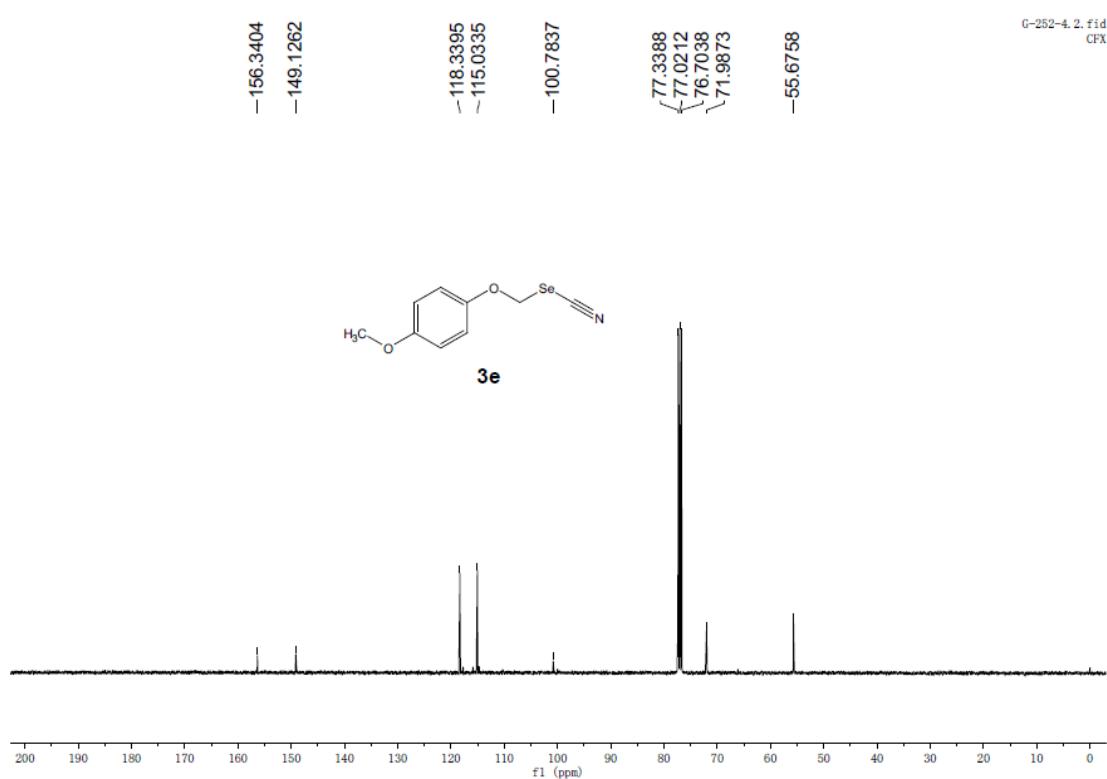
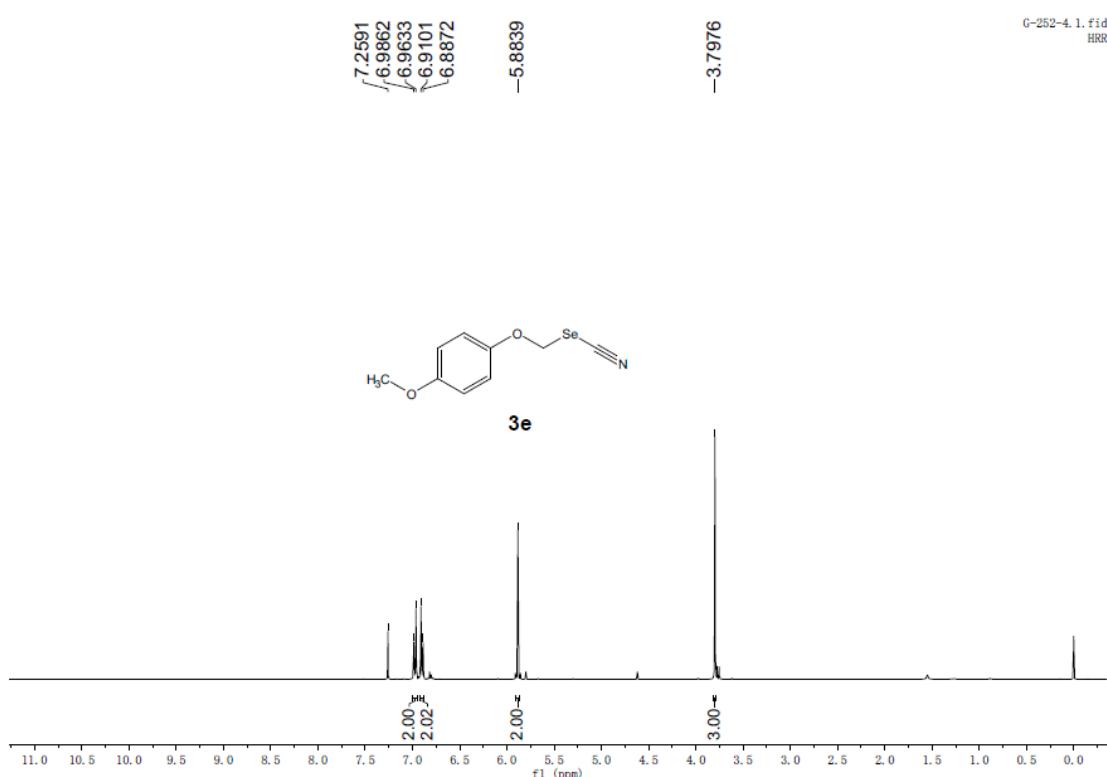


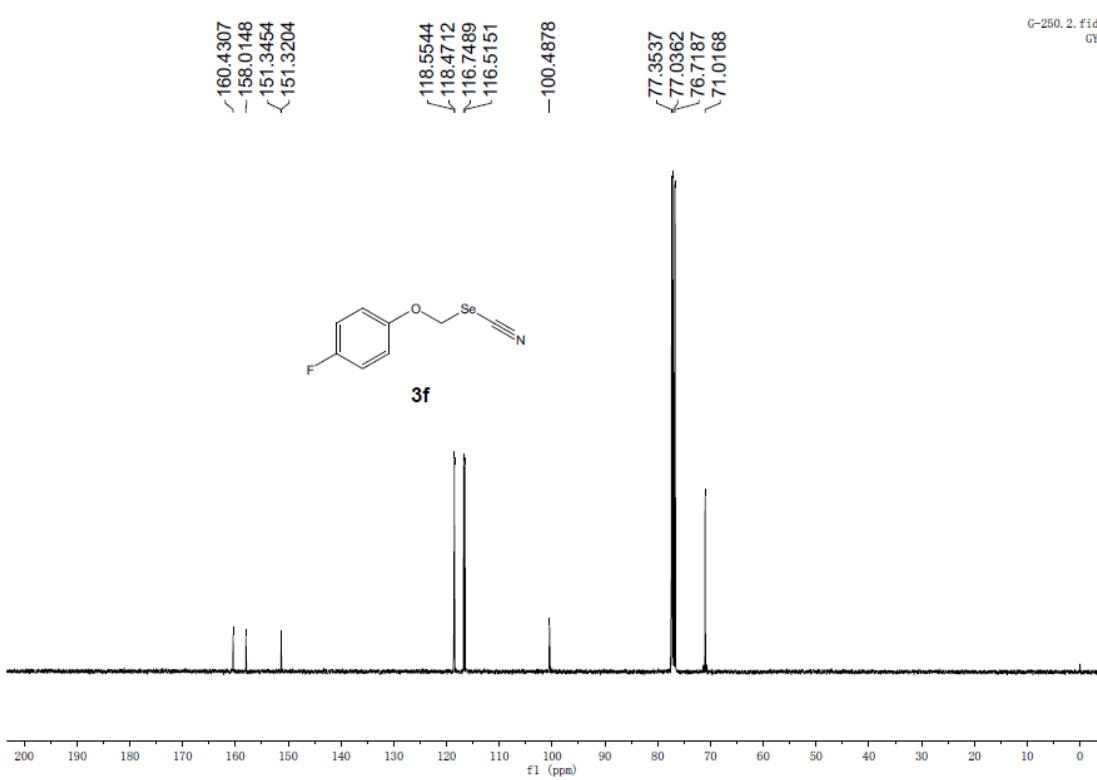
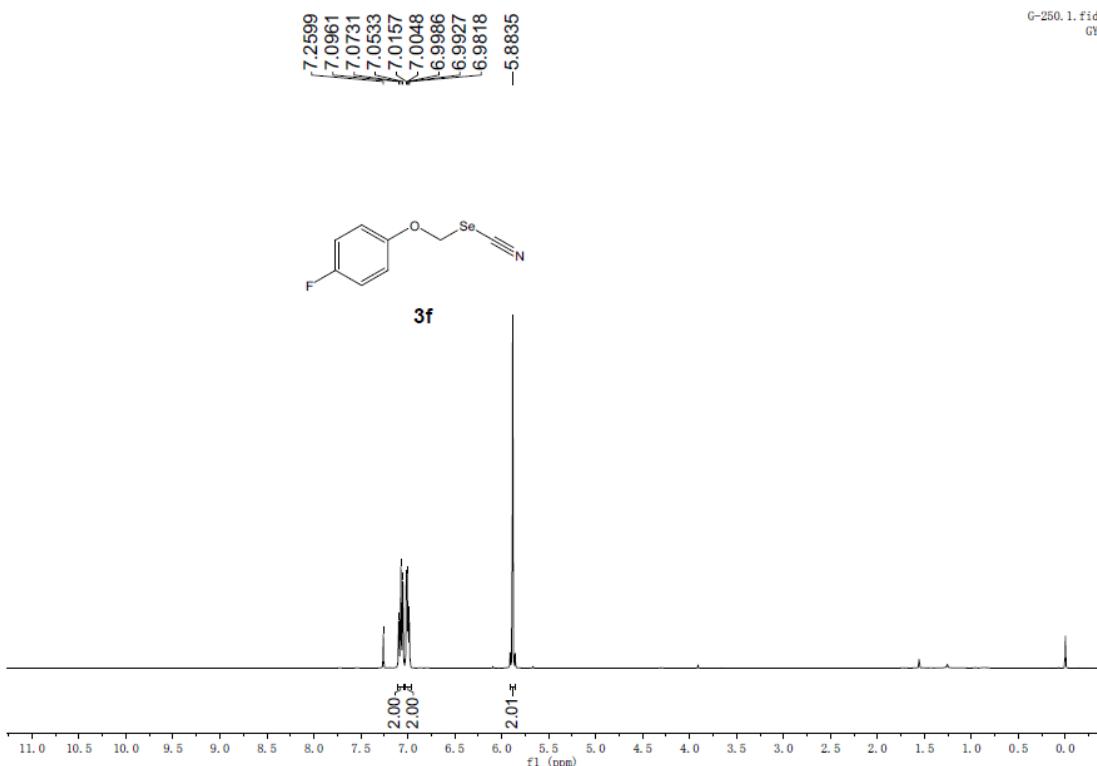
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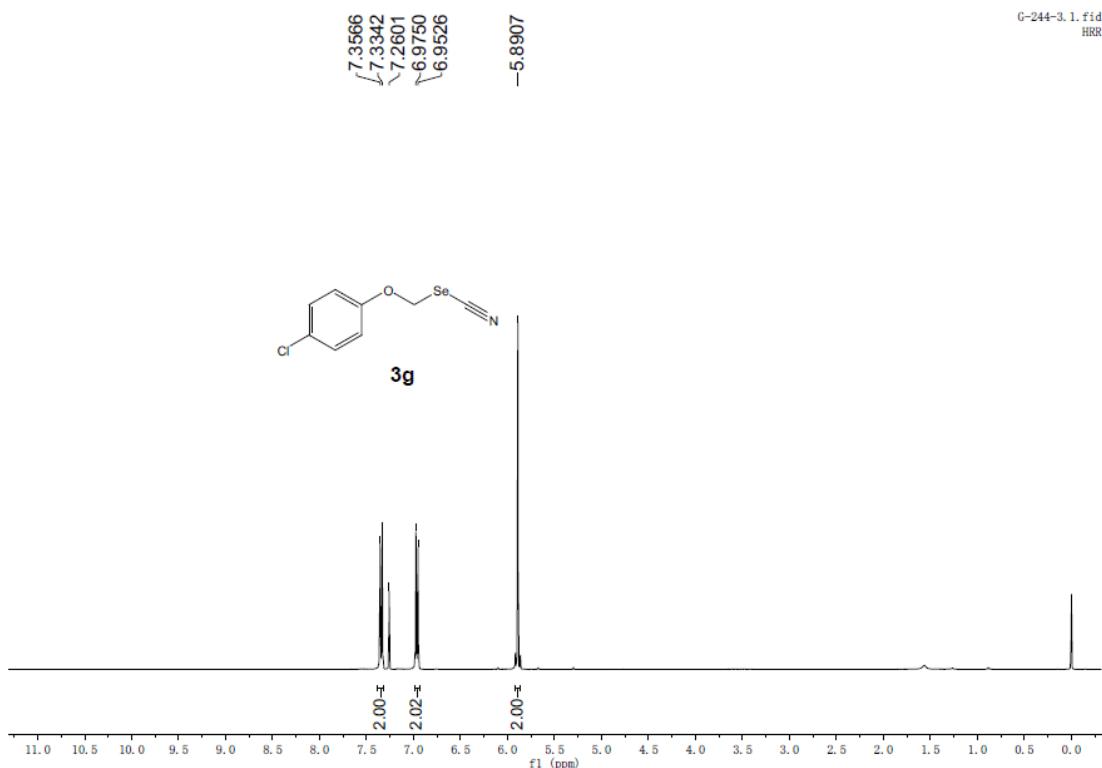




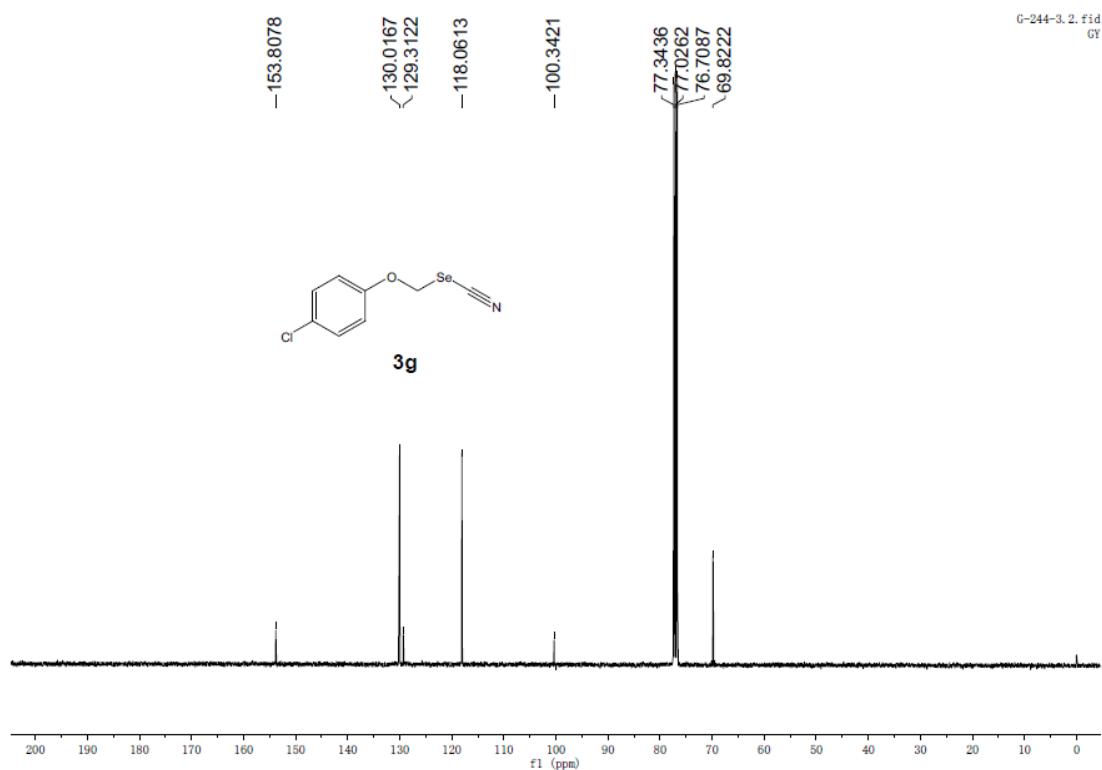


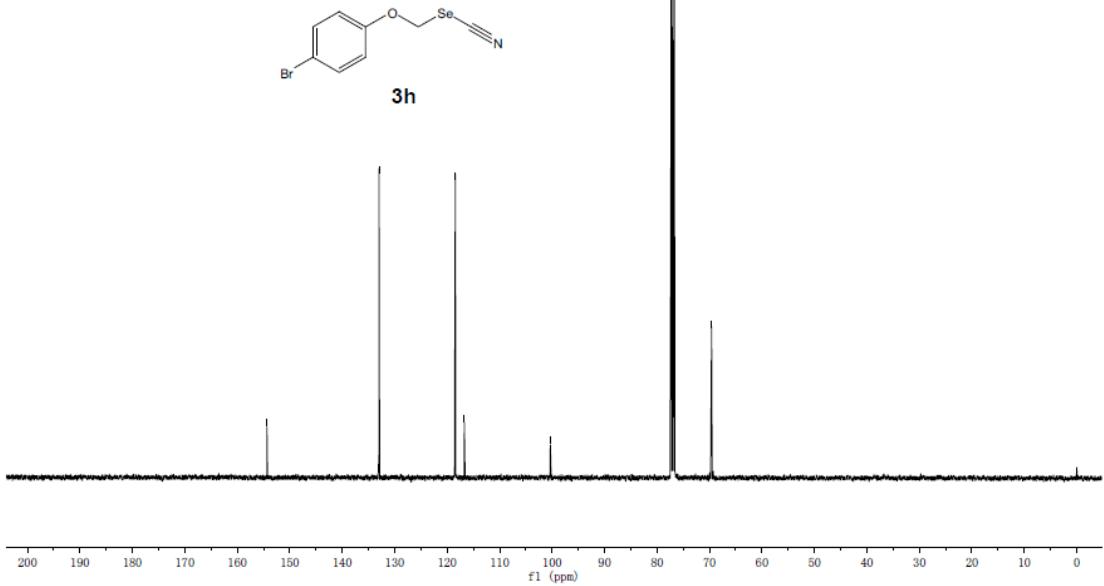
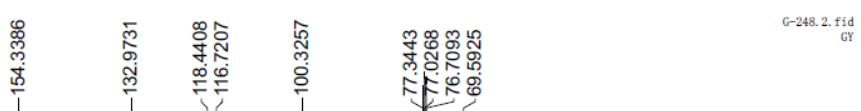
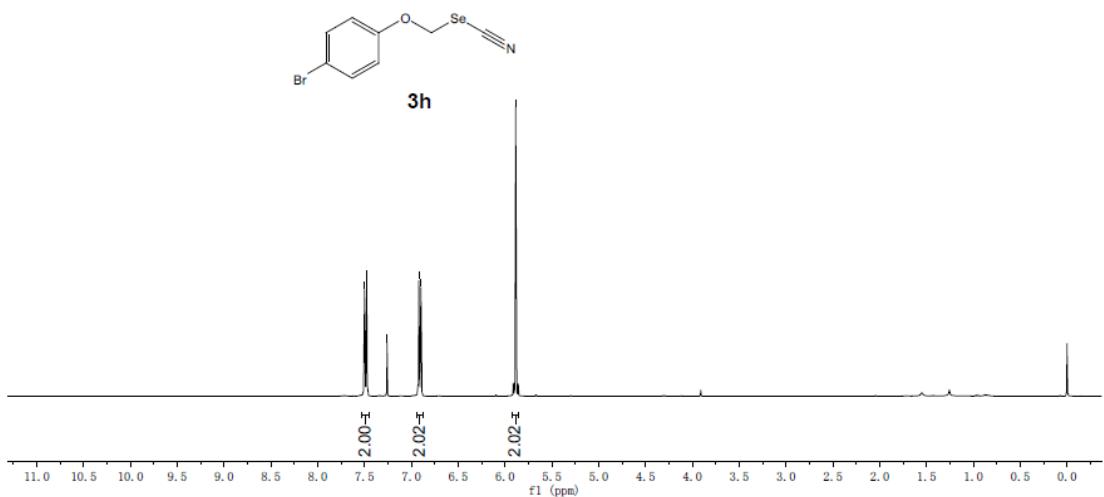


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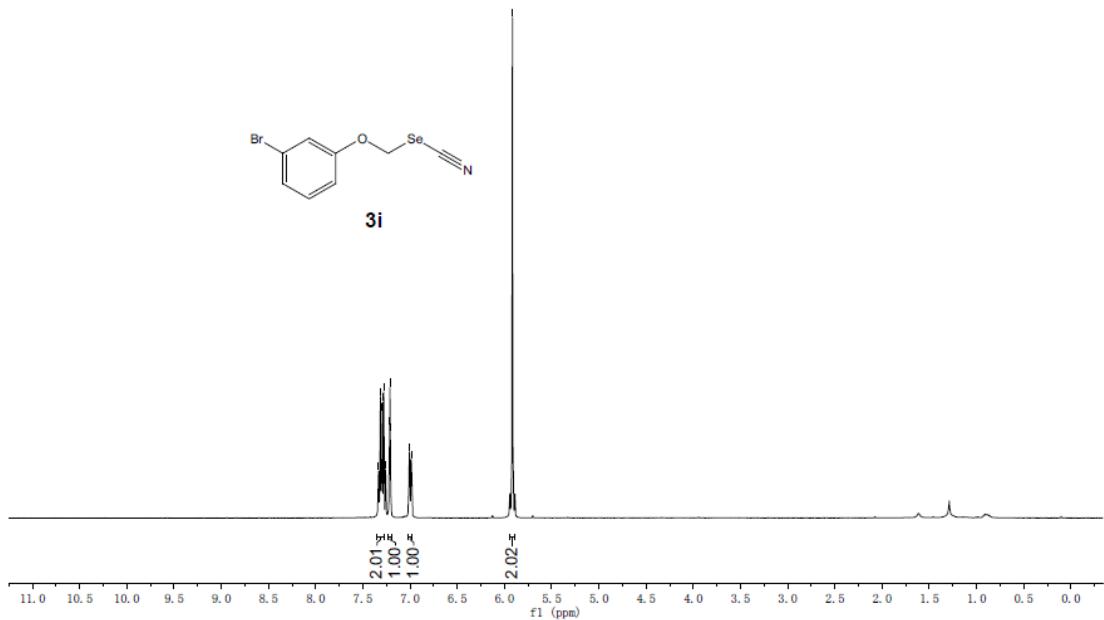


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G-272.1.fid  
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G-272.2.fid  
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