

**An electrochemical method for deborylative selenylation of arylboronic acids  
under metal- and oxidant-free conditions**

Zhengjiang Fu,<sup>\*a,b</sup> Jian Yin,<sup>a</sup> Dongdong He,<sup>a</sup> Xuezheng Yi,<sup>a</sup> Shengmei Guo,<sup>a</sup> and Hu Cai<sup>\*a</sup>

<sup>a</sup> College of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, China

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China

\*E-mail: fuzhengjiang@ncu.edu.cn; caihu@ncu.edu.cn

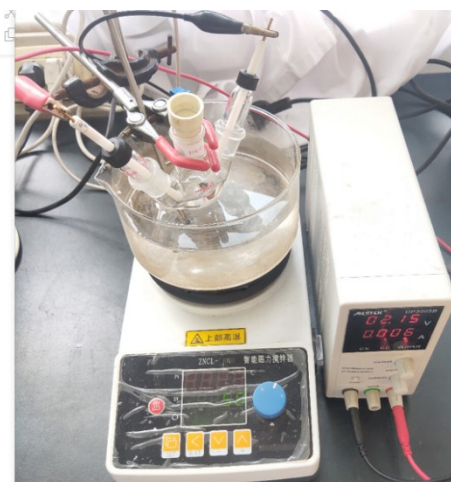
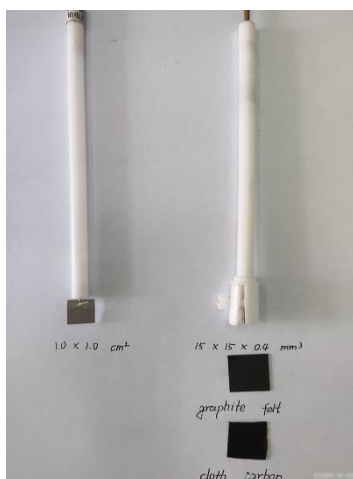
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## General considerations

The compounds of **2b-2j** and **2l-2s** were prepared following literature procedures,<sup>1,2</sup> all other reagents were commercially available and were used as received unless otherwise noted. The instrument for electrolysis is Adjustable DC Power Supply (DP3005B) (made in China). Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra of all compounds were recorded at 400, 100 and 377 MHz with CDCl<sub>3</sub> as solvent respectively. All coupling constants (J values) were reported in Hertz (Hz). HRMS (**3da-ea**, **3ga**, **3ac**, **3ae**, **3ai**, **3al**, **3aq-ar**) were performed by Analysis and Testing Center of Nanjing University. Cyclic voltammograms were obtained on a IVIUMSTAT potentiostat.

## Experimental procedures

**General procedure for electrochemical deborylative selenylation of arylboronic acids with diselenides:** arylboronic acid (0.2 mmol), diselenide compound (1.2 equiv., 0.24 mmol), tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg), CH<sub>3</sub>CN (10 mL) were combined and added into oven-dried three-necked flask with a stir bar. The flask was equipped with two platinum electrodes (1.0 × 1.0 × 0.3 cm<sup>3</sup>) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA at 50 °C under air conditions for 3 hours. Unless otherwise noted, after 3 h, the reaction was cooled to room temperature, washed with EtOAc and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.



**1-Methoxy-4-methylselenobenzene (3aa).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours. The reaction mixture was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 34.7 mg (86%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>3</sup> <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  7.41 (d,  $J$  = 8.8 Hz, 2 H), 6.82 (d,  $J$  = 8.8 Hz, 2 H), 3.79 (s, 3 H), 2.30 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 133.4, 121.5, 114.8, 55.3, 8.7.

**1-Methoxy-3-methylselanylbenzene (3ba).** Procedure was followed using 3-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 24.3 mg (60%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (t,  $J$  = 8.0 Hz, 1 H), 7.00 (d,  $J$  = 8.4 Hz, 1 H), 6.97 (s, 1 H), 6.74 (dd,  $J$  = 2.4, 8.4 Hz, 1 H), 3.80 (s, 3 H), 2.36 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.8, 133.0, 129.8, 122.4, 115.7, 111.7, 55.2, 7.1.

**1-Methoxy-2-methylselanylbenzene (3ca).** Procedure was followed using 2-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 27.5 mg (68%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>5</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (d,  $J$  = 7.6 Hz, 1 H), 7.19 (t,  $J$  = 8.0 Hz, 1 H), 6.94 (t,  $J$  = 7.6 Hz, 1 H), 6.82 (d,  $J$  = 8.0 Hz, 1 H), 3.89 (s, 3 H), 2.28 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.1, 128.4, 126.7, 121.5, 121.2, 110.0, 55.8, 4.8.

**2,4-Dimethoxy-1-methylselenybenzene (3da).** Procedure was followed using 2,4-methoxyphenylboronic acid (0.2 mmol, 36.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 36.7 mg (79%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (d,  $J$  = 8.4 Hz, 1 H), 6.47 (d,  $J$  = 8.4 Hz, 1 H), 6.45 (s, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 2.24 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.1, 158.6, 131.4, 110.9, 105.3, 98.7, 55.8, 55.4, 6.0. HRMS (ESI-Orbitrap MS)  $m/z$ : [M+H]<sup>+</sup> Calcd. for C<sub>9</sub>H<sub>13</sub>O<sub>2</sub>Se: 232.16576; found: 232.16581.

**2-Methoxy-5-(methylselanyl)benzaldehyde (3ea).** Procedure was followed using 3-formyl-4-methoxyphenylboronic acid (0.2 mmol, 36.0 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under N<sub>2</sub> conditions for 2 hours, then was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 26.3 mg (59%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.43 (s, 1 H), 7.90 (s, 1 H), 7.65 (dd,  $J$  = 1.6, 8.4 Hz, 1 H), 6.92 (d,  $J$  = 8.8 Hz, 1 H), 3.92 (s, 3 H), 2.34 (s, 3 H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  189.2, 160.8, 139.0, 131.2, 125.3, 122.5, 112.6, 55.8, 8.3. HRMS (ESI-Orbitrap MS)  $m/z$ : [M+H]<sup>+</sup> Calcd. for C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>Se: 230.99188; found: 230.99147.

**4-(Methylseleno)phenol (3fa).** Procedure was followed using 4-hydroxyphenylboronic acid (0.2 mmol, 27.6 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (85:15, petroleum ether: EtOAc) to afford 26.7 mg (71%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>6</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d,  $J$  = 8.4 Hz, 2 H), 6.76 (d,  $J$  = 8.8 Hz, 2 H), 2.30 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.7, 133.6, 121.6, 116.3, 8.8.

**4-*iso*Propyl-1-methylselanylbenzene (3ga).** Procedure was followed using 4-*isopropyl*benzeneboronic acid (0.2 mmol, 32.8 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was carried out at 60 °C for 3 hours in the mixed solvents of acetonitrile and acetic acid (9:1), then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 25.7 mg (60%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.37 (d,  $J$  = 8.0 Hz, 2 H), 7.14 (d,  $J$  = 8.0 Hz, 2 H), 2.91 - 2.84 (m, 1 H), 2.33 (s, 3 H), 1.24 (d,  $J$  = 6.8 Hz, 6 H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.1, 130.8, 128.2, 127.2, 33.7, 23.9, 7.5. HRMS (ESI-Orbitrap MS)  $m/z$ : [M] Calcd. for C<sub>10</sub>H<sub>15</sub>Se: 214.02552; found: 214.02501.

**4-(Methylseleno)-1,1'-biphenyl (3ha).** Procedure was followed using 4-biphenylboronic acid (0.2 mmol, 39.6 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 27.3 mg (55%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d,  $J$  = 8.0 Hz, 2 H), 7.50 (s, 4 H), 7.45 (t,  $J$  = 8.0 Hz, 2 H), 7.35 (t,  $J$  = 8.0 Hz, 1 H), 2.40 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.5, 139.1, 131.0, 130.7, 128.8, 127.7, 127.3, 126.9, 7.3.

**1-(Methylselanyl)naphthalene (3ia).** Procedure was followed using 1-naphthylboronic acid (0.2 mmol, 34.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 37.8 mg (85%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>8</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (d,  $J$  = 8.0 Hz, 1 H), 7.85 (d,  $J$  = 8.0 Hz, 1 H), 7.75 (d,  $J$  = 8.4 Hz, 1 H), 7.64 (d,  $J$  = 7.2 Hz, 1 H),

7.58 - 7.50 (m, 2 H), 7.39 (t,  $J = 7.6$  Hz, 1 H), 2.42 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.8, 133.3, 131.1, 128.6, 128.6, 127.2, 126.6, 126.4, 126.2, 125.9, 7.6.

**2-(Methylselanyl)naphthalene (3ja).** Procedure was followed using 2-naphthylboronic acid (0.2 mmol, 34.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu\text{L}$ ) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 60  $^\circ\text{C}$  under air conditions for 2 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 36.4 mg (82%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>9</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (s, 1 H), 7.80 (d,  $J = 7.6$  Hz, 1 H), 7.74 (t,  $J = 8.0$  Hz, 2 H), 7.54 - 7.43 (m, 3 H), 2.46 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.0, 131.8, 129.4, 128.4, 128.3, 128.2, 127.8, 126.9, 126.5, 125.6, 7.3.

**4-Bromoselenoanisole (3ka).** Procedure was followed using 4-bromophenylboronic acid (0.2 mmol, 40.2 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu\text{L}$ ) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). The reaction mixture was stirred in dichloromethane at room temperature under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (petroleum ether) to afford 20.0 mg (40%) of the product as a white solid. Exhibited spectral data in accordance with previous report.<sup>10</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 (d,  $J = 8.4$  Hz, 2 H), 7.26 (d,  $J = 8.4$  Hz, 2 H), 2.33 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.0, 131.9, 130.8, 120.1, 7.5.

**4-Chloroselenoanisole (3la).** Procedure was followed using 4-chlorophenylboronic acid (0.2 mmol, 31.3 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu\text{L}$ ) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was stirred in dichloromethane at room temperature for 3 hours, then was purified by flash column chromatography on silica gel (petroleum ether) to afford 7.1 mg (17%) of the product as a colorless oil. Exhibited spectral data in accordance with previous report.<sup>11</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34 (d,  $J = 8.8$  Hz, 2 H), 7.22 (d,  $J = 8.8$  Hz, 2 H), 2.34 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.2, 131.7, 130.0, 129.1, 7.6.

**3-(Methylseleno)benzo[*b*]thiophene (3ma).** Procedure was followed using benzothiophene-3-boronic acid (0.2 mmol, 35.6 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu\text{L}$ ) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50  $^\circ\text{C}$  under air conditions for 2 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 36.5 mg (80%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>12</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (d,  $J = 8.4$  Hz, 1 H), 7.89 (d,  $J = 8.4$  Hz, 1 H), 7.48 - 7.44 (m, 2 H), 7.40 (t,  $J = 8.0$  Hz, 1 H), 2.34 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.9, 127.1, 124.7, 124.5, 123.5, 122.8, 121.2, 8.1.

**2-(Methylseleno)benzofuran (3na).** Procedure was followed using benzofuran-2-boronic acid (0.2 mmol, 32.4 mg), dimethyl diselenide (1.2 equiv., 0.24 mmol, 23  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 1.5 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 25.5 mg (60%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>13</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d,  $J$  = 7.2 Hz, 1 H), 7.47 (d,  $J$  = 7.6 Hz, 1 H), 7.27 - 7.19 (m, 2 H), 6.82 (s, 1 H), 2.42 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.0, 145.0, 128.8, 123.9, 122.8, 120.0, 111.5, 110.8, 8.1.

**1-(Ethylseleno)-4-methoxybenzene (3ab).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), diethyl diselenide (1.2 equiv., 0.24 mmol, 43  $\mu$ L) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 30.3 mg (70%) of the product as a colorless oil. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d,  $J$  = 8.4 Hz, 2 H), 6.82 (d,  $J$  = 8.4 Hz, 2 H), 3.80 (s, 3 H), 2.82 (q,  $J$  = 7.6 Hz, 2 H), 1.39 (t,  $J$  = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 135.6, 119.7, 114.6, 55.2, 22.4, 15.6.

**1-Methoxy-4-propylselenyl-benzene (3ac).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), dipropyl diselenide (1.2 equiv., 0.24 mmol, 59 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 16.1 mg (35%) of the product as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (d,  $J$  = 8.8 Hz, 2 H), 6.81 (d,  $J$  = 8.8 Hz, 2 H), 3.79 (s, 3 H), 2.80 (t,  $J$  = 7.2 Hz, 2 H), 1.72 - 1.63 (m, 2 H), 0.98 (t,  $J$  = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.5, 132.9, 117.6, 112.1, 52.7, 28.7, 20.9, 11.8. HRMS (ESI-Orbitrap MS)  $m/z$ : [M+H]<sup>+</sup> Calcd. for C<sub>10</sub>H<sub>15</sub>OSe: 231.02826; found: 231.02747.

**1-(Butylseleno)-4-methoxybenzene (3ad).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), dibutyl diselenide (1.2 equiv., 0.24 mmol, 65.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 25.4 mg (52%) of the product as a colorless oil. Exhibited spectral data in accordance with previous report.<sup>15</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (d,  $J$  = 8.8 Hz, 2 H), 6.82 (d,  $J$  = 8.8 Hz, 2 H), 3.79 (s, 3 H), 2.82 (t,  $J$  = 7.6 Hz, 2 H), 1.68 - 1.60 (m, 2 H), 1.45 - 1.36 (m, 2 H), 0.89 (t,  $J$  = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.1, 135.4, 120.2, 114.7, 55.2, 32.3, 28.8, 22.9, 13.6.

**1-(*iso*Butylseleno)-4-methoxybenzene (3ae).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), di-2-butyl diselenide (1.2 equiv., 0.24 mmol, 65.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 30.3 mg (62%) of the product as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 (d, *J* = 7.2 Hz, 2 H), 6.81 (d, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.14 - 3.05 (m, 1 H), 1.69 - 1.60 (m, 1 H), 1.58 - 1.51 (m, 1 H), 1.35 (d, *J* = 6.8 Hz, 3 H), 0.99 (t, *J* = 7.6 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.5, 137.5, 119.1, 114.5, 55.2, 41.8, 30.3, 21.5, 12.3. HRMS (ESI-Orbitrap MS) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>17</sub>OSe: 245.04391; found: 245.04323.

**1-[(4-Methoxyphenyl)seleno]-2-methylbenzene (3af).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), di-*o*-tolyl diselenide (1.2 equiv., 0.24 mmol, 81.6 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 37.3 mg (65%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>16</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 (d, *J* = 8.8 Hz, 2 H), 7.18 (d, *J* = 6.8 Hz, 1 H), 7.13 (d, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 6.4 Hz, 1 H), 7.04 - 7.00 (m, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H), 2.40 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.8, 137.9, 136.7, 134.0, 130.8, 130.0, 126.6, 126.6, 119.3, 115.3, 55.3, 21.9.

**2-[(4-Methoxyphenyl)seleno]-1,3-dimethylbenzene (3ag).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(2,6-dimethylphenyl)diselenide (1.2 equiv., 0.24 mmol, 88.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 42.7 mg (73%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>17</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.21 - 7.13 (m, 3 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H), 2.50 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.2, 143.4, 131.5, 131.0, 128.9, 127.9, 123.0, 115.0, 55.3, 24.5.

**1-Methoxy-4-[(4-methylphenyl)seleno]benzene (3ah).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), di-*p*-tolyl diselenide (1.2 equiv., 0.24 mmol, 81.6 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 39.2 mg (75%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H),

6.84 (d,  $J = 8.4$  Hz, 2 H), 3.81 (s, 3 H), 2.31 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 136.7, 135.8, 131.8, 130.0, 128.93, 120.9, 115.1, 55.3, 21.1.

**1-Methoxy-4-[(4-isopropylphenyl)seleno]benzene (3ai).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(4-isopropylphenyl)diselenide (1.2 equiv., 0.24 mmol, 95.5 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 41.0 mg (67%) of the product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (d,  $J = 8.8$  Hz, 2 H), 7.30 (d,  $J = 8.4$  Hz, 2 H), 7.10 (d,  $J = 8.4$  Hz, 2 H), 6.85 (d,  $J = 8.8$  Hz, 2 H), 3.81 (s, 3 H), 2.91 - 2.80 (m, 1 H), 1.22 (d,  $J = 6.8$  Hz, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 147.6, 136.0, 131.5, 129.4, 127.4, 120.6, 115.0, 55.3, 33.7, 23.9. HRMS (ESI-Orbitrap MS)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{19}\text{OSe}$ : 307.05956; found: 307.05896.

**Di-4-anisyl selenide (3aj).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(*p*-methoxyphenyl)diselenide (1.2 equiv., 0.24 mmol, 89.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (petroleum ether) to afford 40.0 mg (68%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>16</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (d,  $J = 8.8$  Hz, 4 H), 6.82 (d,  $J = 8.8$  Hz, 4 H), 3.79 (s, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.2, 134.6, 122.1, 115.0, 55.3.

**4-(Phenylseleno)anisole (3ak).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), biphenyl diselenide (1.2 equiv., 0.24 mmol, 75.4 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 44.9 mg (85%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>3</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 (d,  $J = 8.8$  Hz, 2 H), 7.33 (d,  $J = 6.4$  Hz, 2 H), 7.24 - 7.19 (m, 3 H), 6.86 (d,  $J = 8.8$  Hz, 2 H), 3.82 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 136.5, 133.2, 130.8, 129.1, 126.4, 119.8, 115.1, 55.3.

**1-Bromo-2-[(4-methoxyphenyl)seleno]benzene (3al).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(*o*-bromophenyl)diselenide (1.2 equiv., 0.24 mmol, 112.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 21.9 mg (32%) of the product as a colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (d,  $J = 8.8$  Hz, 2 H), 7.47 (d,  $J = 8.0$  Hz, 1 H), 7.04 (t,  $J = 7.6$  Hz, 1 H), 7.00 (t,  $J = 8.0$  Hz, 1 H), 6.94



(d,  $J = 8.8$  Hz, 2 H), 6.74 (d,  $J = 8.0$  Hz, 1 H), 3.85 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.6, 138.6, 137.5, 132.6, 129.4, 126.8, 122.4, 118.3, 115.6, 55.4. HRMS (ESI-Orbitrap MS)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{13}\text{H}_{12}\text{BrOSe}$ : 342.92313; found: 342.92197.

**1-Bromo-4-[(4-methoxyphenyl)seleno]benzene (3am).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(*p*-bromophenyl)diselenide (1.2 equiv., 0.24 mmol, 112.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 55.4 mg (81%) of the product as a colorless oil. Exhibited spectral data in accordance with previous report.<sup>18</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 8.9$  Hz, 2 H), 7.32 (d,  $J = 8.5$  Hz, 2 H), 7.17 (d,  $J = 8.5$  Hz, 2 H), 6.87 (d,  $J = 8.8$  Hz, 2 H), 3.82 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 136.8, 132.4, 132.3, 132.2, 120.5, 119.4, 115.3, 55.3.

**4-Chlorophenyl 4-methoxyphenyl selenide (3an).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(4-chlorophenyl)diselenide (1.2 equiv., 0.24 mmol, 91.7 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 47.6 mg (80%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>14</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (d,  $J = 8.4$  Hz, 2 H), 7.25 (d,  $J = 8.4$  Hz, 2 H), 7.18 (d,  $J = 8.4$  Hz, 2 H), 6.87 (d,  $J = 8.8$  Hz, 2 H), 3.82 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 136.7, 132.5, 132.1, 131.6, 129.2, 119.6, 115.3, 55.3.

**4-Fluorophenyl-4-methoxyphenyl selenide (3ao).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(4-fluorophenyl)diselenide (1.2 equiv., 0.24 mmol, 84 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (97:3, petroleum ether: EtOAc) to afford 45.1 mg (80%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>18</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J = 8.8$  Hz, 2 H), 7.36 (t,  $J = 7.2$  Hz, 2 H), 6.94 (t,  $J = 8.8$  Hz, 2 H), 6.85 (d,  $J = 8.8$  Hz, 2 H), 3.81 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.1 (d,  $J = 244.5$  Hz), 159.7, 135.9, 133.5 (d,  $J = 7.7$  Hz), 127.3 (d,  $J = 3.7$  Hz), 120.6, 116.3 (d,  $J = 21.6$  Hz, 2 H), 115.2, 55.3.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -115.5 - -115.6 (m, 1 F).

**1-[(4-Methoxyphenyl)seleno]pyridine (3ap).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), 2,2'-dipyridyl diselenide (1.2 equiv., 0.24 mmol, 75.9 mg) and TBAB (1 equiv., 0.2 mmol, 65 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 53

mg (99%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>16</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.41 (d, *J* = 4 Hz, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.36 (td, *J* = 7.6, 2.0 Hz, 1 H), 7.00 - 6.96 (m, 1 H), 6.93 - 6.90 (m, 3 H), 3.83 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.4, 159.9, 149.7, 138.3, 136.5, 123.5, 120.0, 117.8, 115.4, 55.3.

**3-[(4-Methoxyphenyl)seleno]pyridine (3aq).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), 3,3'-dipyridyl diselenide (1.2 equiv., 0.24 mmol, 75.9 mg) and TBAB (1 equiv., 0.2 mmol, 65 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 50.8 mg (96%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.56 (d, *J* = 1.6 Hz, 1 H), 8.40 (dd, *J* = 4.8, 1.6 Hz, 1 H), 7.59 (dt, *J* = 8.0, 1.6 Hz, 1 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.13 (dd, *J* = 8.0, 4.8 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.81 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.1, 151.1, 147.5, 138.3, 136.8, 130.6, 124.1, 118.5, 115.4, 55.3. HRMS (ESI-Orbitrap MS) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>OSe: 266.00786; found: 266.00705.

**2-[(4-Methoxyphenyl)seleno]thiophene (3ar).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(2-thienyl)diselenide (1.2 equiv., 0.24 mmol, 78.3 mg) and TBAB (1 equiv., 0.2 mmol, 65 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 35.1 mg (65%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.42 - 7.39 (m, 3 H), 7.27 (dd, *J* = 3.2, 1.2 Hz, 1 H), 7.00 (dd, *J* = 5.2, 3.6 Hz, 1 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.3, 135.4, 133.4, 131.1, 128.2, 125.3, 122.8, 114.9, 55.3. HRMS (ESI-Orbitrap MS) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>11</sub>OSe: 270.96903; found: 270.96835.

**3-[(4-Methoxyphenyl)seleno]thiophene (3as).** Procedure was followed using 4-methoxyphenylboronic acid (0.2 mmol, 30.4 mg), bis(3-thienyl)diselenide (1.2 equiv., 0.24 mmol, 78.3 mg) and TBAB (1 equiv., 0.2 mmol, 65 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 40.5 mg (75%) of the product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43 (d, *J* = 8.8 Hz, 2 H), 7.31 - 7.29 (m, 1 H), 7.25 - 7.24 (m, 1 H), 7.03 (dd, *J* = 5.2, 1.2 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 3.79 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.3, 134.6, 131.6, 126.5, 126.5, 124.8, 121.1, 115.0, 55.3. HRMS (ESI-Orbitrap MS) *m/z*: [M+H]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>11</sub>OSe: 270.96903; found: 270.96835.

***N,N*-dimethyl-4-(phenylseleno)benzenamine (3ok).** Procedure was followed using 4-(dimethylamino)phenylboronic acid (0.2 mmol, 33.0 mg), diphenyl diselenide (1.2 equiv., 0.24 mmol, 75.4 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air

conditions for 3 hours, then was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 39.4 mg (71%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>19</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (d,  $J$  = 9.2 Hz, 2 H), 7.31 (d,  $J$  = 7.8 Hz, 2 H), 7.22 (t,  $J$  = 7.6 Hz, 2 H), 7.18 - 7.14 (m, 1 H), 6.70 (d,  $J$  = 8.8 Hz, 2 H), 3.00 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.5, 137.2, 134.6, 129.7, 129.0, 125.8, 113.6, 113.2, 40.3.

**1,2,3-Trimethoxy-5-((4-methoxyphenyl)seleno)benzene (3pa).** Procedure was followed using 3,4,5-trimethoxyphenylboronic acid (0.2 mmol, 42.4 mg), bis(*p*-methoxyphenyl)diselenide (1.2 equiv., 0.24 mmol, 89.8 mg) and tetrabutylammonium tetrafluoroborate (1 equiv., 0.2 mmol, 66 mg). With stirring, the reaction mixture was performed at 50 °C under air conditions for 3 hours, then was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 53.1 mg (75%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.<sup>20</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (d,  $J$  = 8.8 Hz, 2 H), 6.86 (d,  $J$  = 8.4 Hz, 2 H), 6.61 (s, 2 H), 3.81 (s, 6 H), 3.76 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.6, 153.5, 137.2, 135.7, 126.7, 120.6, 115.0, 108.9, 60.8, 56.1, 55.3.

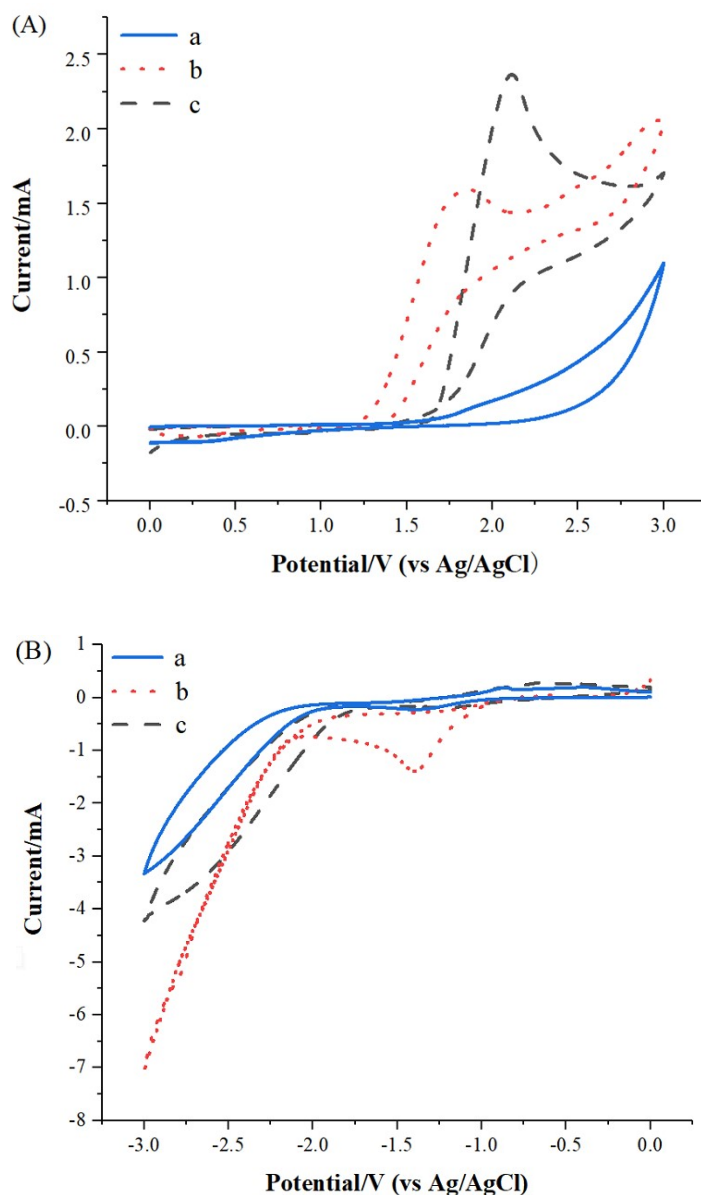
#### Scale-up synthesis of 4-(phenylseleno)anisole (3ak).

An undivided three-necked bottle (500 mL) equipped with 4-methoxyphenylboronic acid (5 mmol), diphenyl diselenide (1.2 equiv., 6 mmol), tetrabutylammonium tetrafluoroborate (1 equiv., 5 mmol), and a stir bar. The bottle was equipped with a platinum electrode (1.0×1.0 cm<sup>2</sup>) anode and cathode. Then, CH<sub>3</sub>CN (200 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA under 50 °C for 24 h. After 24 h, the reaction was cooled to room temperature, filtered and washed with EtOAc. The combined organic layers were concentrated with a rotary evaporator, and the pure product was obtained by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 0.99 g (75%) of the **3ak**.



## General procedure for cyclic voltammetry (CV).

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under room temperature. Platinum disk was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated KCl aqueous solution and separated from reaction by a salt bridge. The mixture of acetonitrile (10 mL) containing 0.02 M tetrabutylammonium tetrafluoroborate was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from 0 to 3.0 V and -3 V to 0 V.

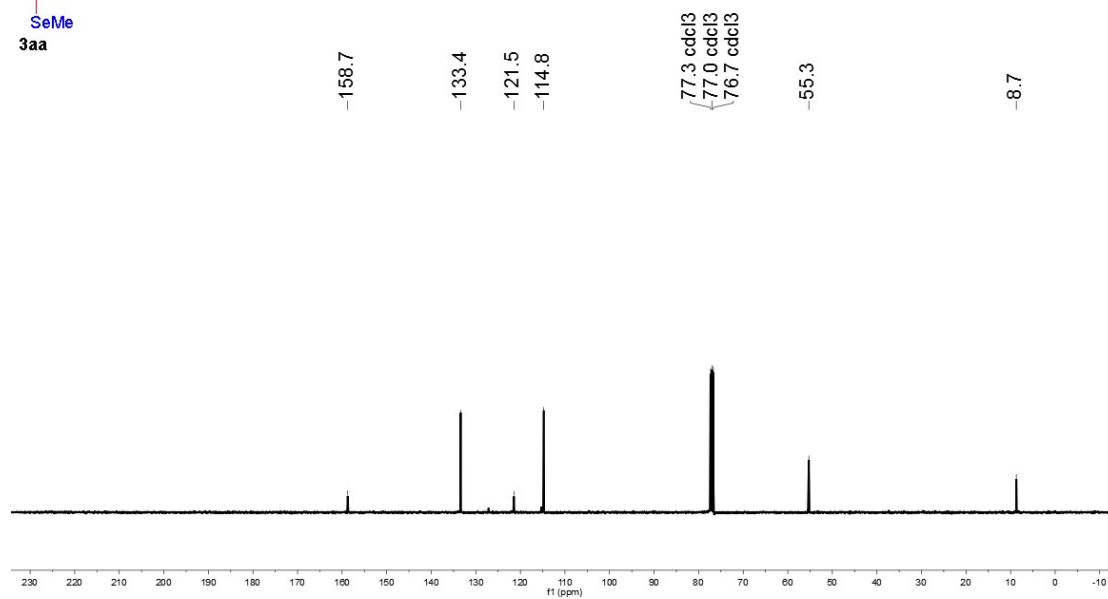
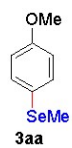
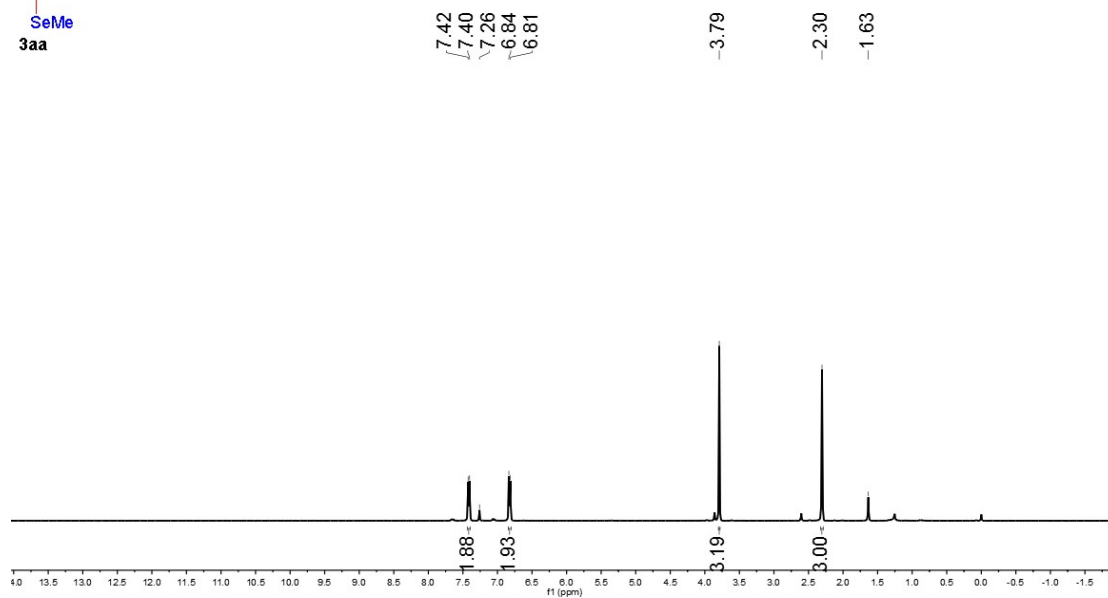
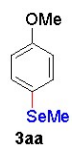


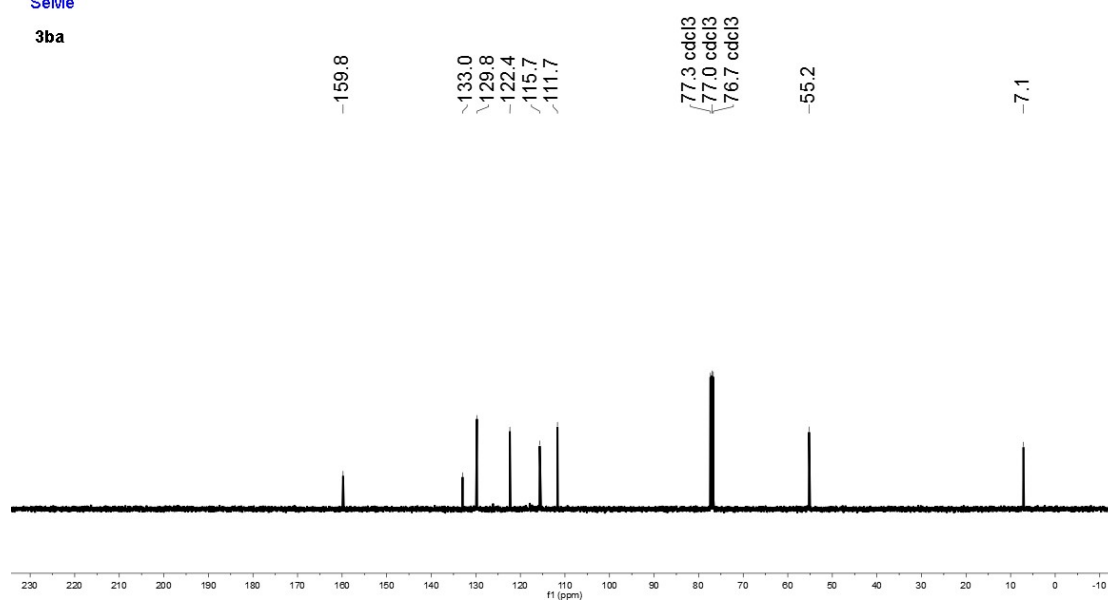
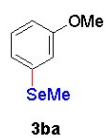
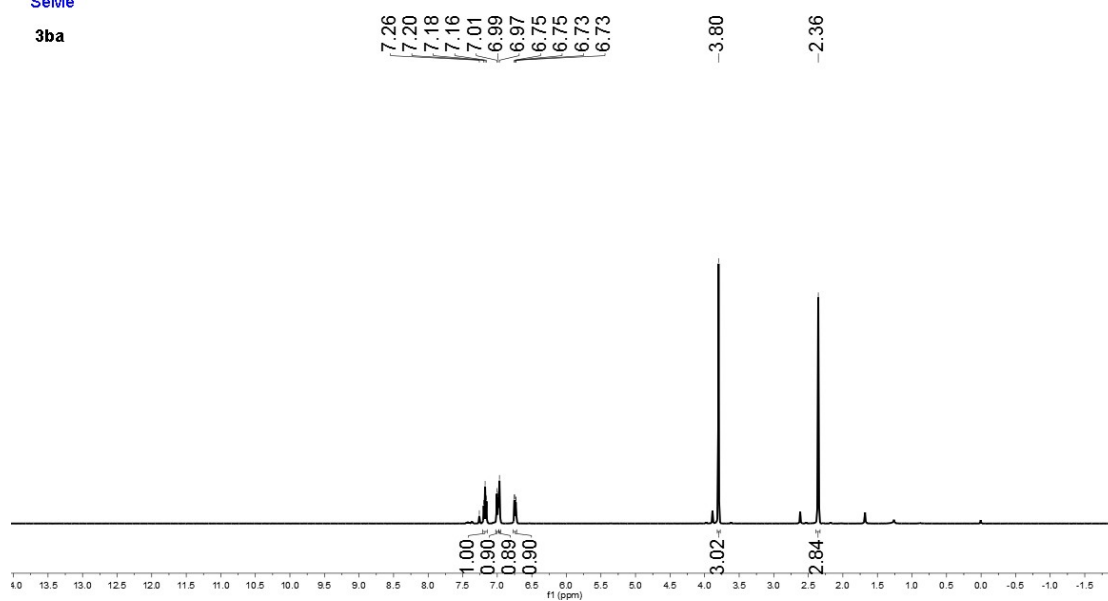
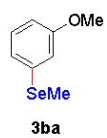
**Fig 1.** Cyclic voltammograms of substrates: (a) background ( $n\text{Bu}_4\text{NBF}_4$  0.02 mol/L<sup>-1</sup> in  $\text{CH}_3\text{CN}$ ); (b) diphenyl diselenide (0.02 mmol/L<sup>-1</sup>); (c) 4-methoxyphenylboronic acid (0.02 mol/L<sup>-1</sup>).

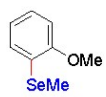
## References

- 1 D. Singh, A. M. Deobald, L. S. Camargo, G. Tabarelli, O. D. Rodrigues, A. Braga, *Org. Lett.*, 2010, **12**, 3288-3291.
- 2 A. Krief, M. Derock, *Synlett*, 2005, **6**, 1012-1028.
- 3 D. Kundu, N. Mukherjee, B. C. Ranu, *RSC Adv.*, 2013, **3**, 117-125.
- 4 V. I. Naddaka, V. P. Krasnov, V. I. Minkin, *Rus. J. Org. Chem.*, 1985, **21**, 477-482.
- 5 Hope, G. Eric, *J. Chem. Soc.*, 1987, **4**, 487-490.
- 6 S. M. Allin, W. R. S. Barton, W. R. Bowman, E. Bridge, M. R. J. Elsegood, T. McNally, V. McKee, *Tetrahedron*, 2008, **64**, 7745-7758.
- 7 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, M. Montanucci, *J. Org. Chem.*, 1983, **48**, 4291-4296.
- 8 S. Hayashi, W. Nakanishi, A. Furuta, J. Drabowicz, T. Sasamori, N. Tokitoh, *New J. Chem.*, 2009, **33**, 196-206.
- 9 L. Engman, J. S. E. Hellberg, *J. Organomet. Chem.*, 1985, **296**, 357-366.
- 10 Y. Pang, B. An, L. Lou, J. Zhang, J. Yan, L. Huang, X. Li, S. Yin, *J. Med. Chem.*, 2017, **60**, 7300-7352.
- 11 A. Krief, M. Trabelsi, W. Dumont, *Synthesis*, 1992, **6**, 933-935.
- 12 Y. L. Goldfarb, V. P. Lifvinov, V. Y. Mortikov, *Chem. Heterocycl. Comp.*, 1979, **7**, 898-904.
- 13 M. A. Abramov, W. Dehaen, B. D'hooge, M. L. Petrov, S. Smeets, S. Toppet, M. Voets, *Tetrahedron*, 2000, **56**, 3933-3940.
- 14 T. Taniguchi, A. Murata, M. Takeda, T. Mizuno, A. Nomoto, A. Ogawa, *Eur. J. Org. Chem.*, 2017, **33**, 4928-4934.
- 15 S. Saba, G. V. Botteselle, M. Godoi, T. E. A. Frizon, F. Z. Galetto1, J. Rafique, A. L. Braga, *Molecules*, 2017, **22**, 1367-1379.
- 16 C. S. Freitas, A. M. Barcellos, V. G. Ricordi, J. M. Pena, G. Perin, R. G. Jacob, E. J. Lenardao, D. Alves, *Green Chem.*, 2011, **13**, 2931-2938.
- 17 T. Chatterjee, B. C. Ranu, *J. Org. Chem.*, 2013, **78**, 7145-7153.
- 18 K. Ren, M. Wang, L. Wang, *Org. Biomol. Chem.*, 2009, **7**, 4858-4861.
- 19 L. Abenante, N. B. Padilha, J. M. Anghinoni, F. Penteado, O. Rosati, C. Santi, M. S. Silva, E. J. Lenardão, *Org. Biomol. Chem.*, 2020, **18**, 5210-5218.
- 20 E. A. Santosa, E. Hamelb, R. Baib, J. C. Burnette, C. S. S. Tozattia, D. Bogod, R. T. Perdomod, A. M. M. Antunese, M. M. Marquese, M. F. C. Matosd, D. P. Lima, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 4669-4673.

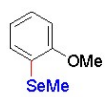
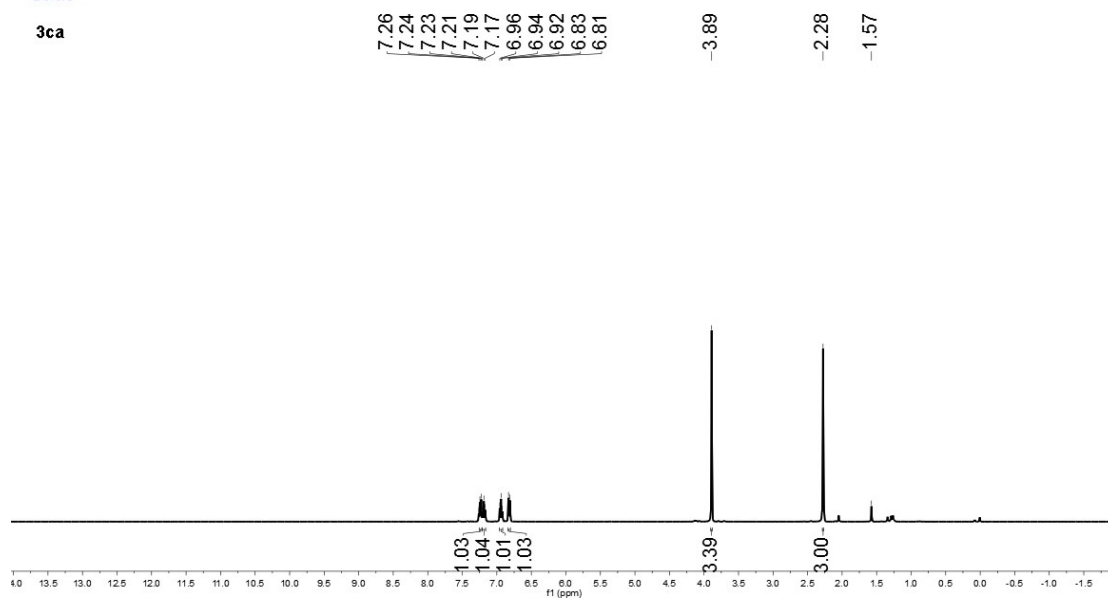
# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra



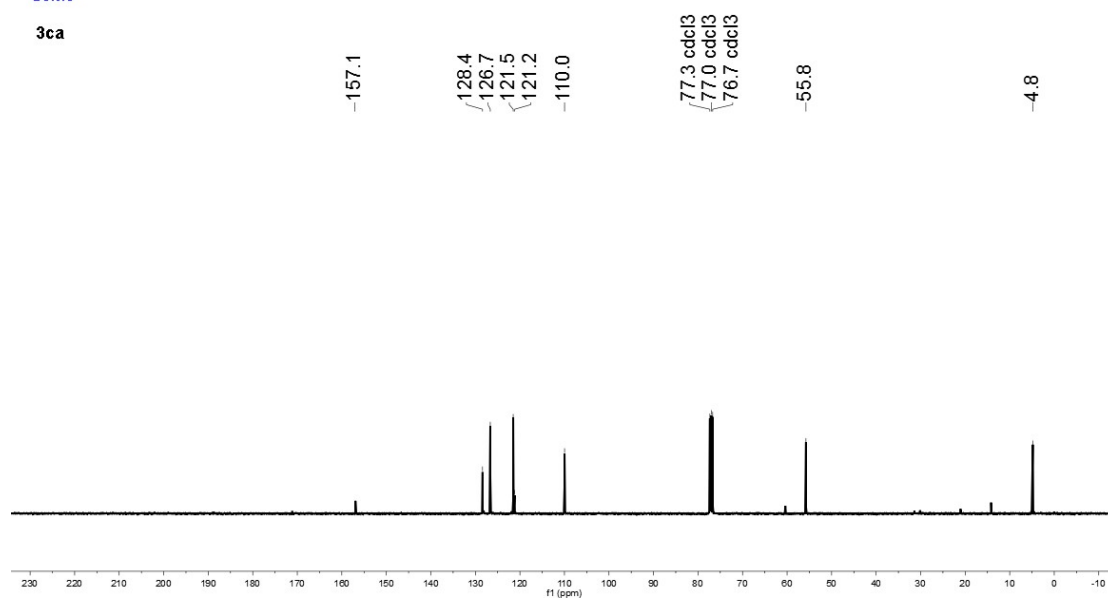




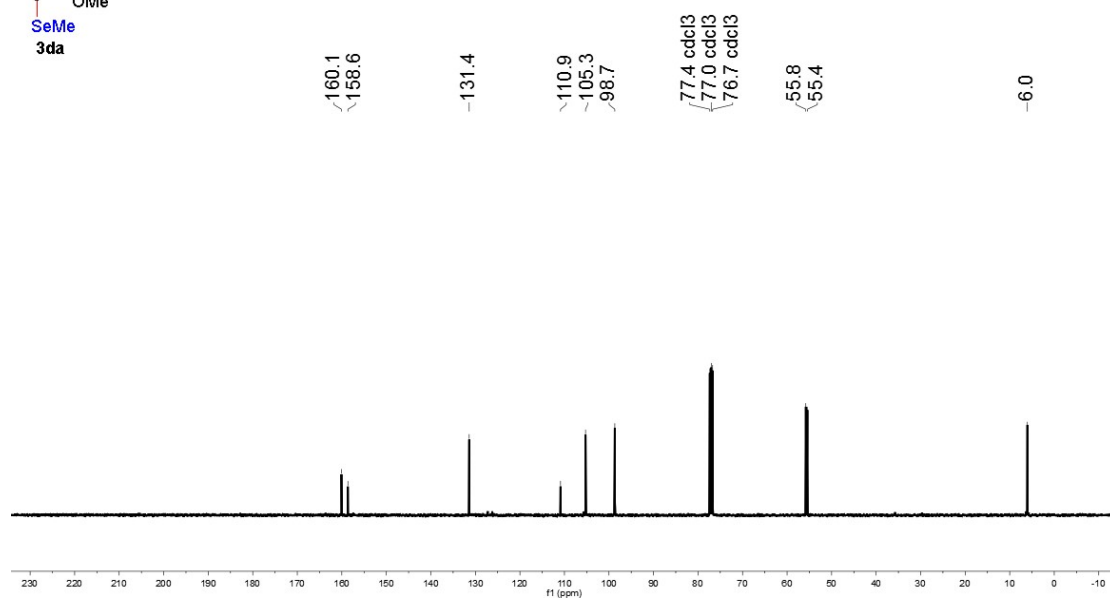
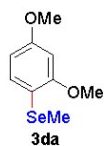
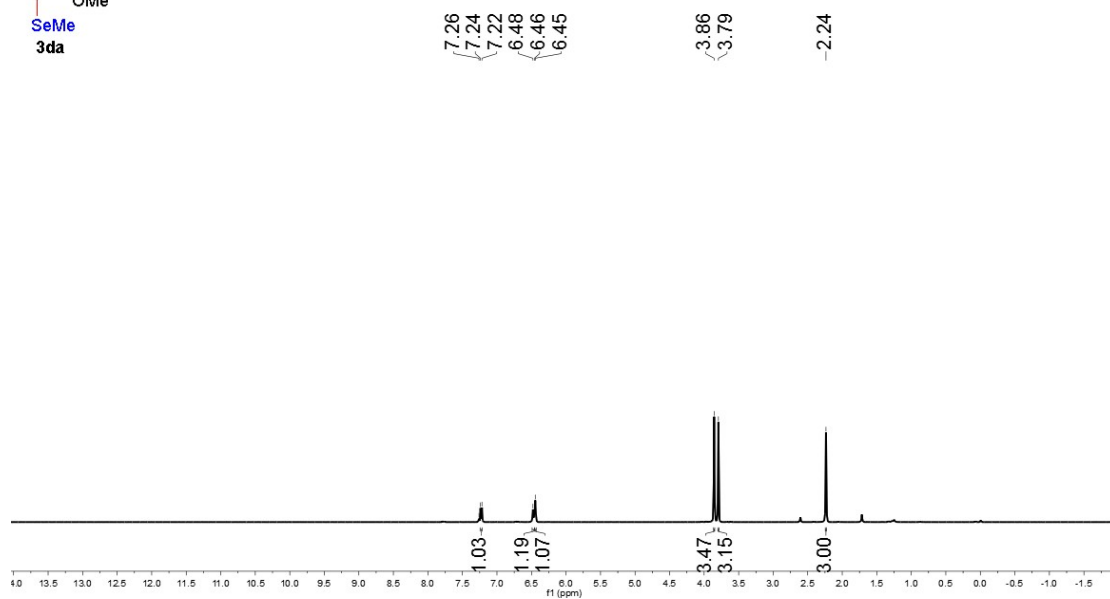
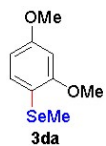
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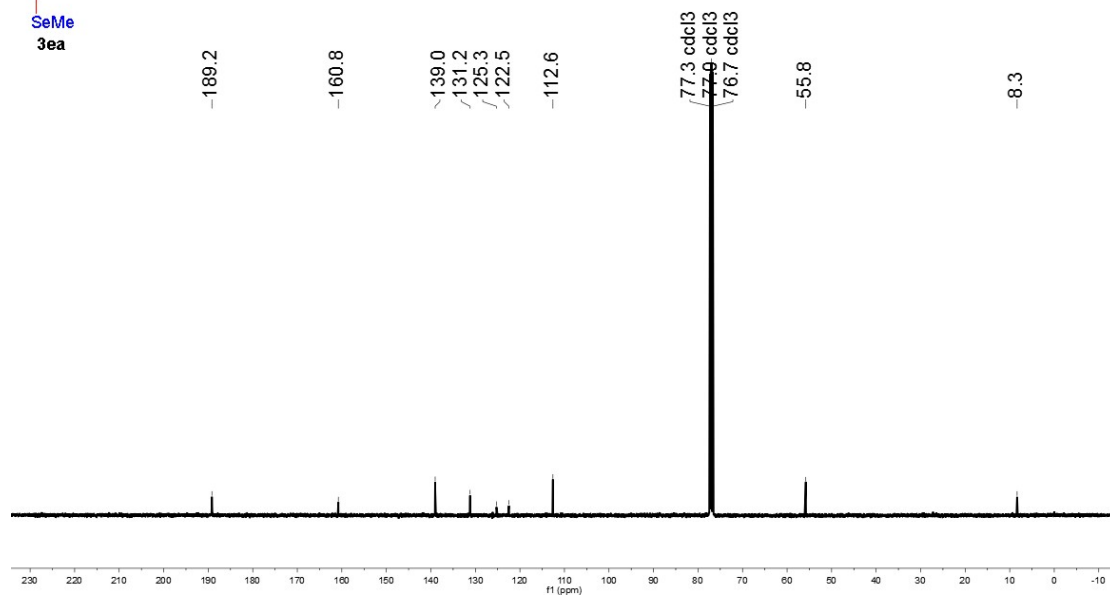
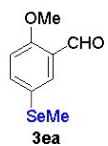
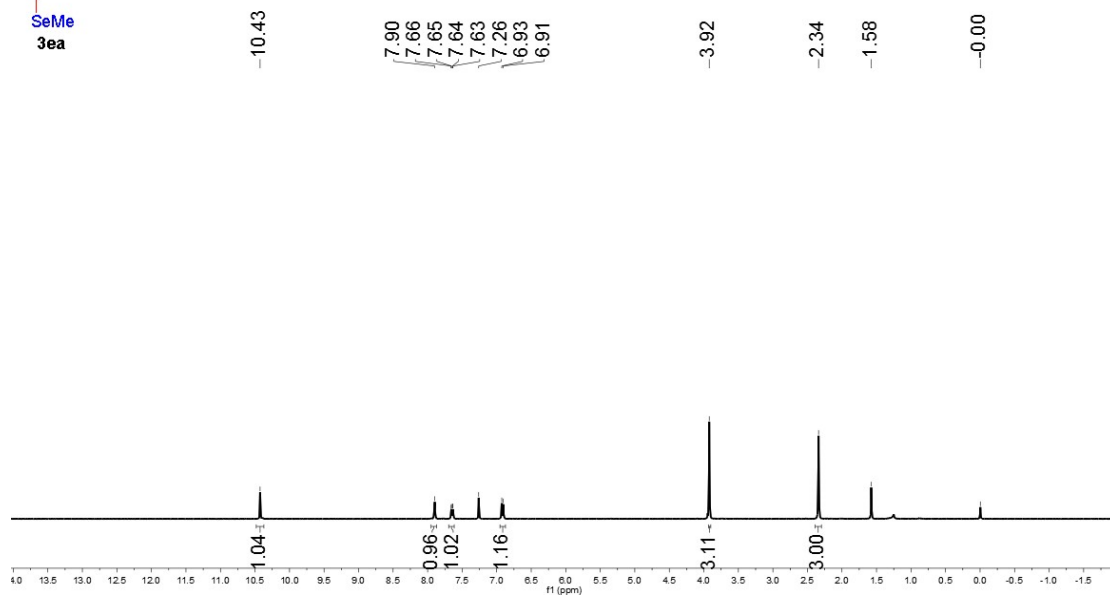
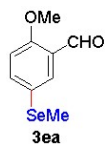


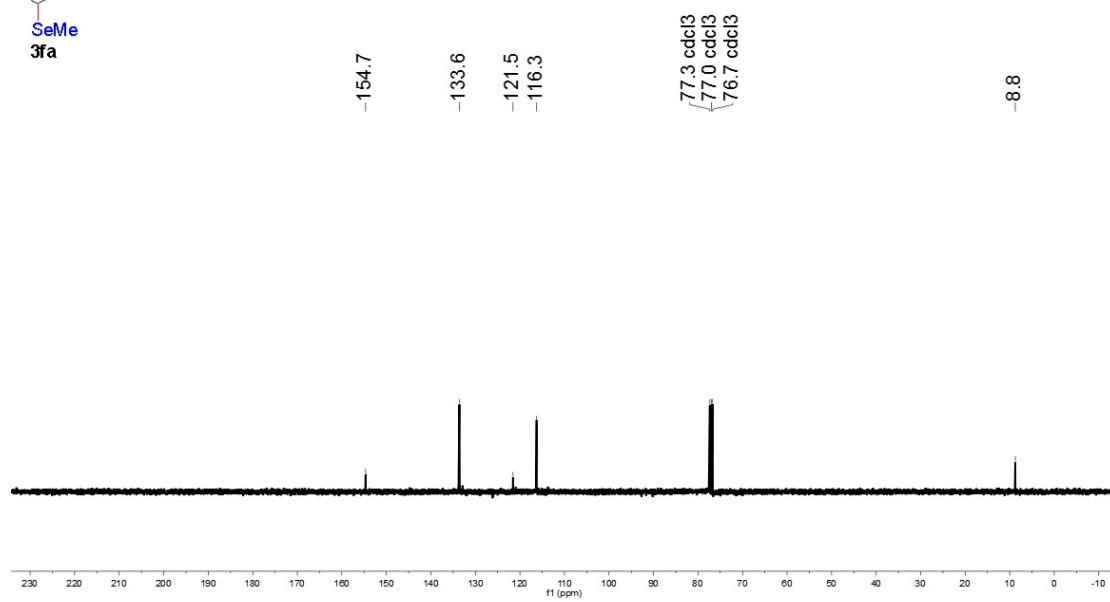
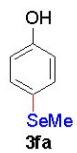
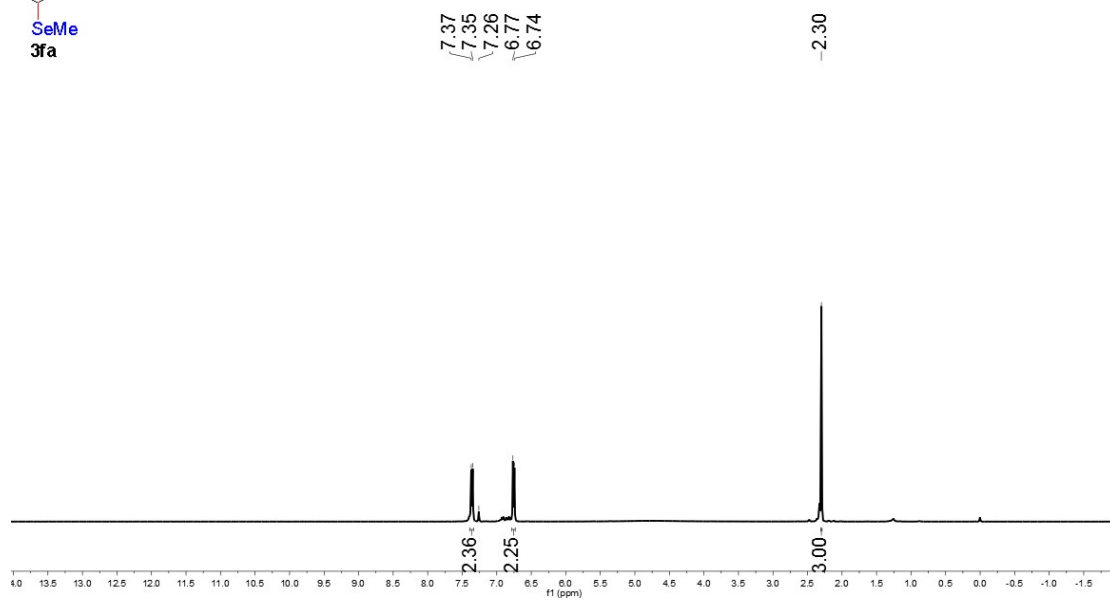
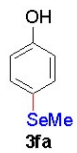
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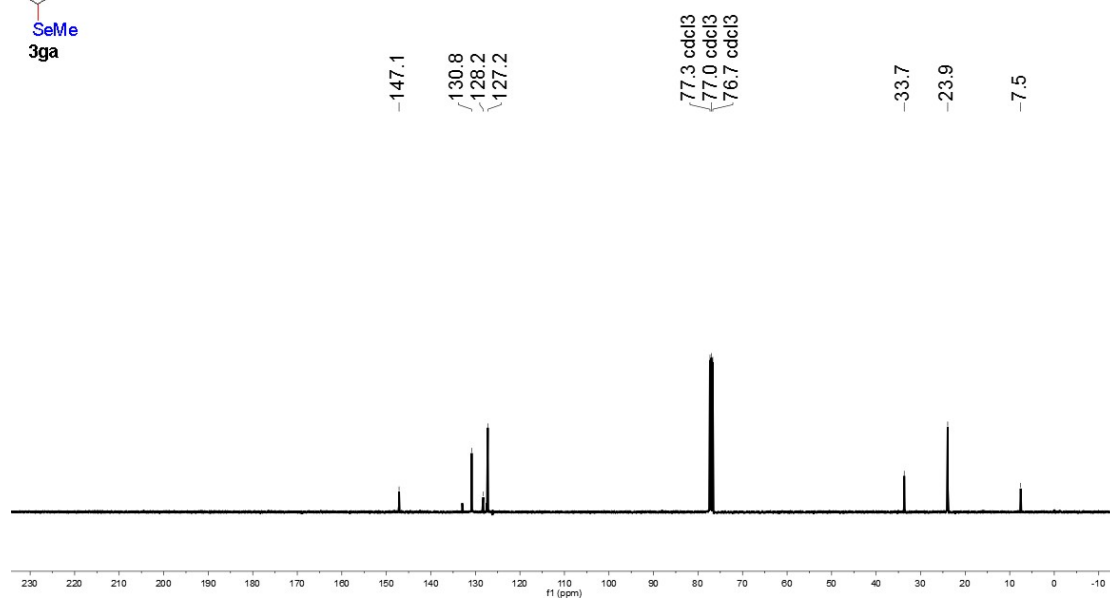
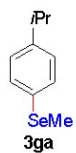
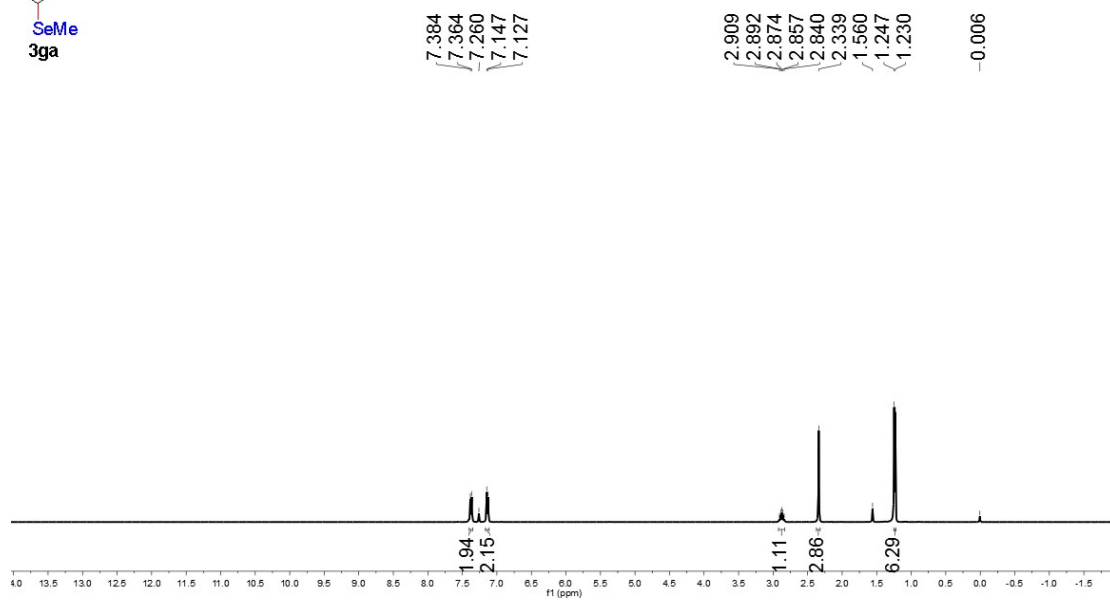
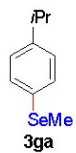


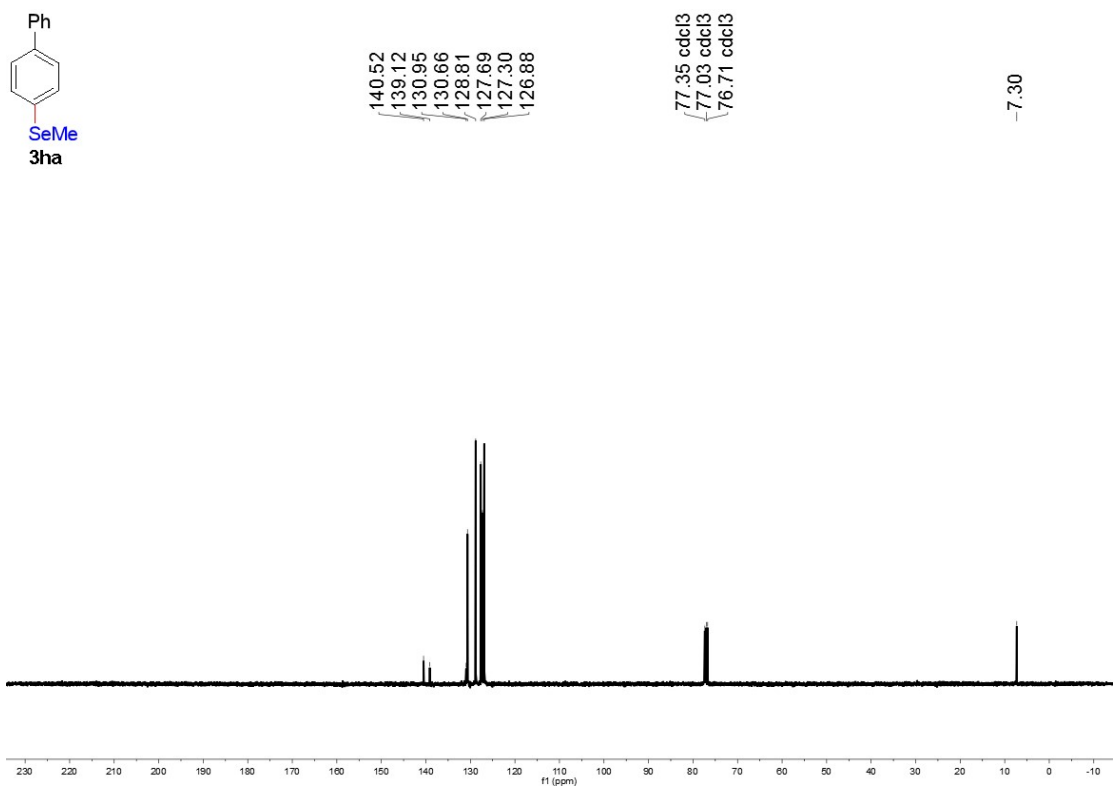
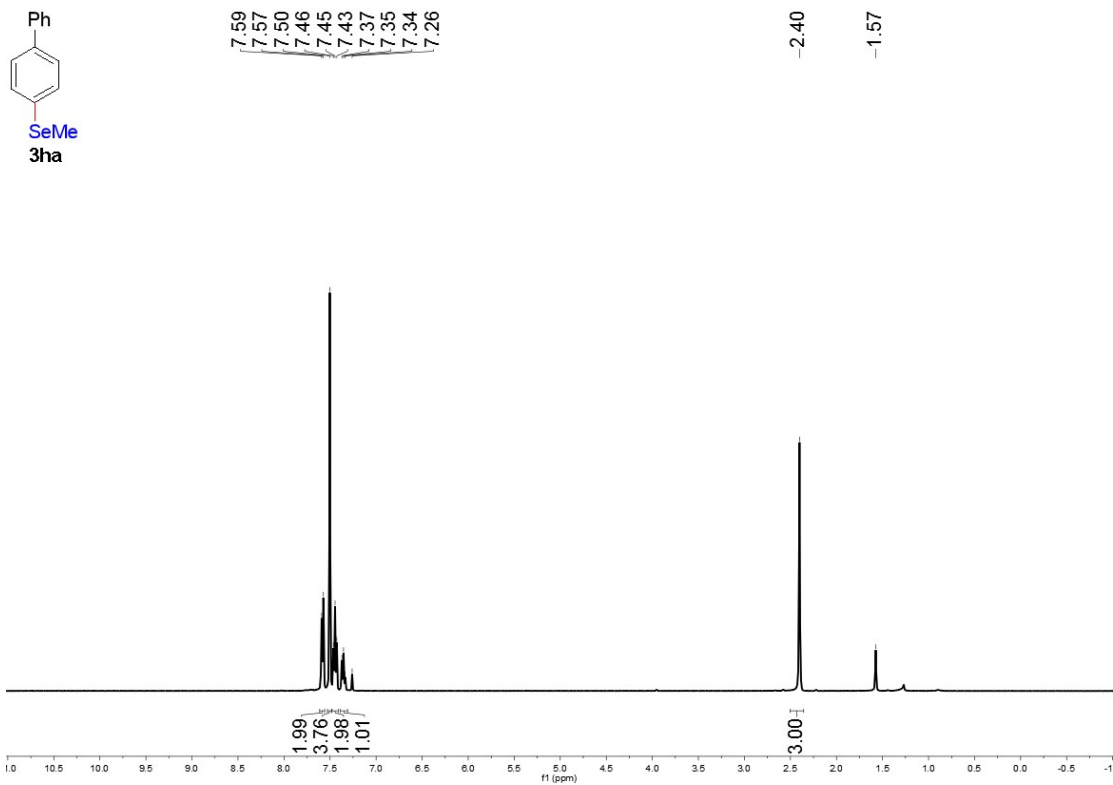


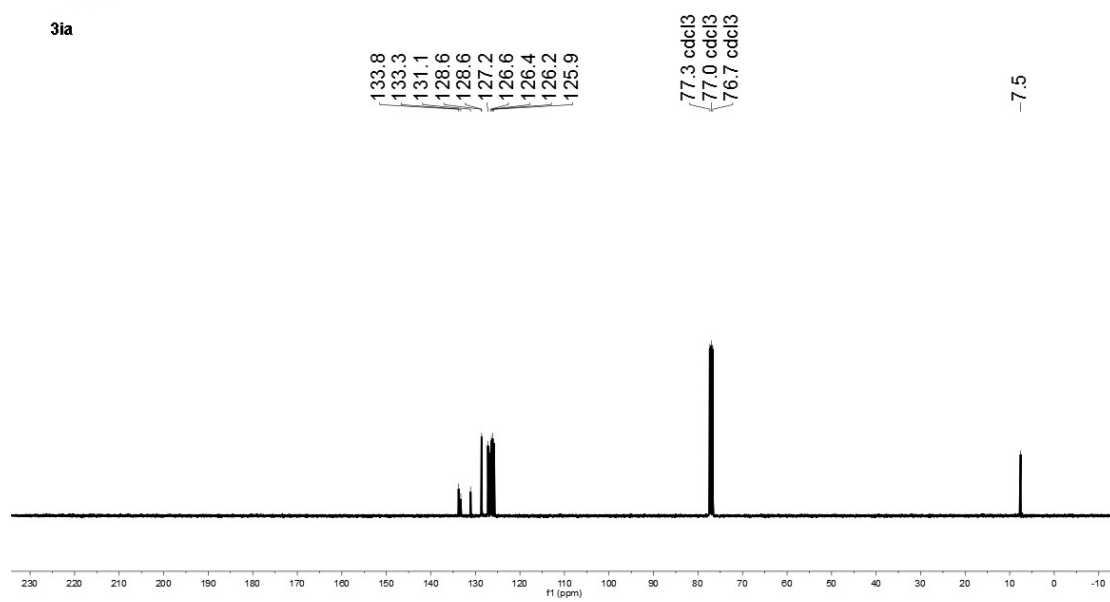
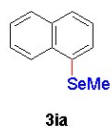
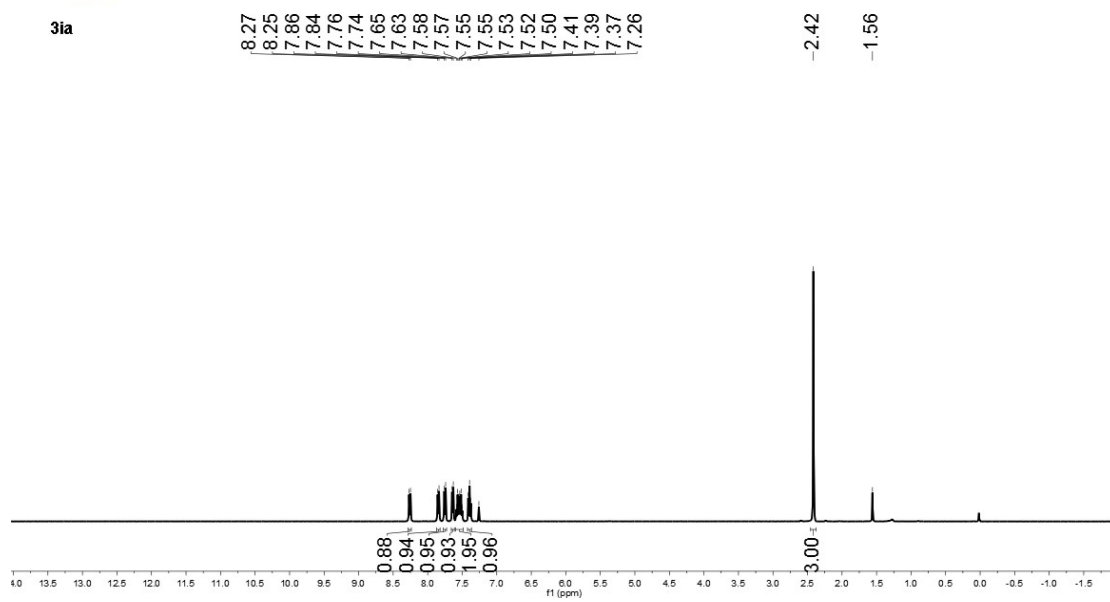


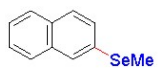




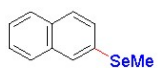
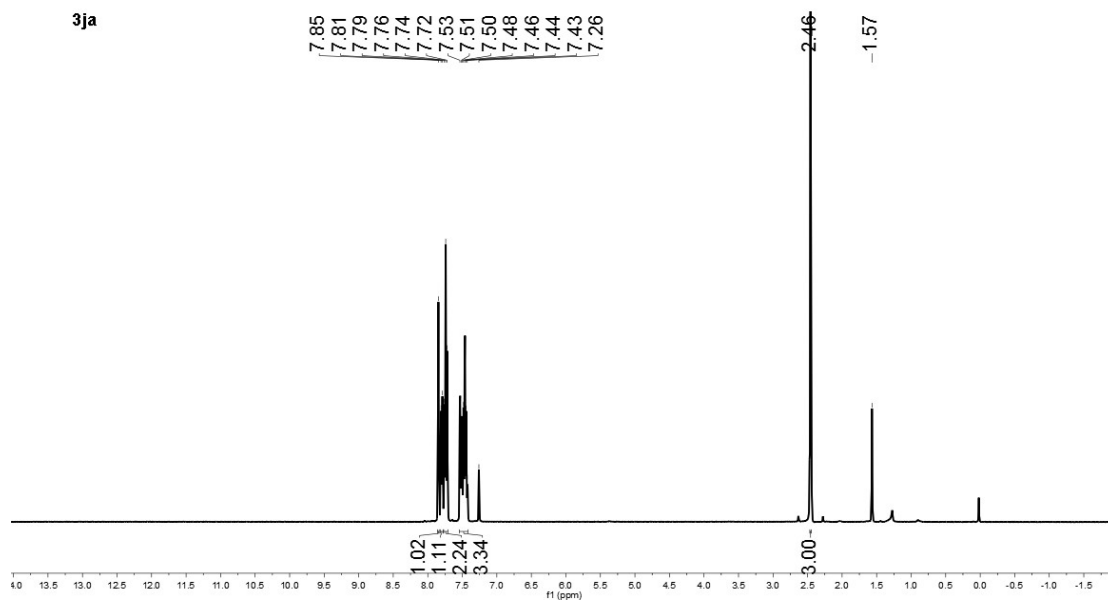




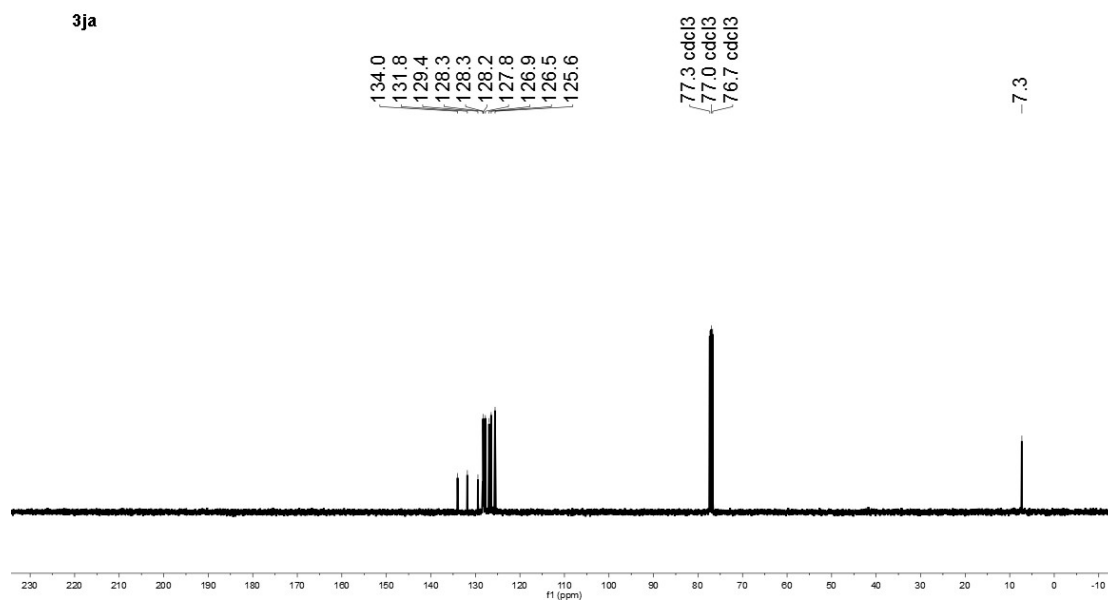


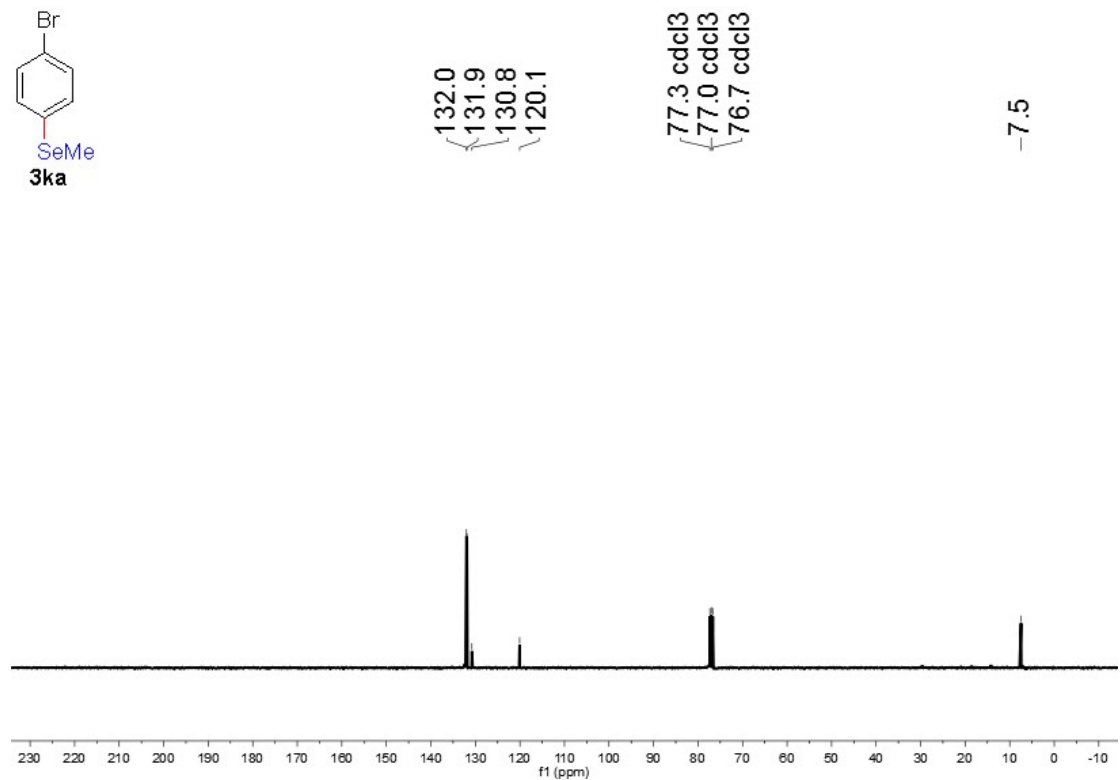
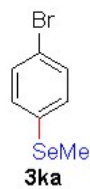
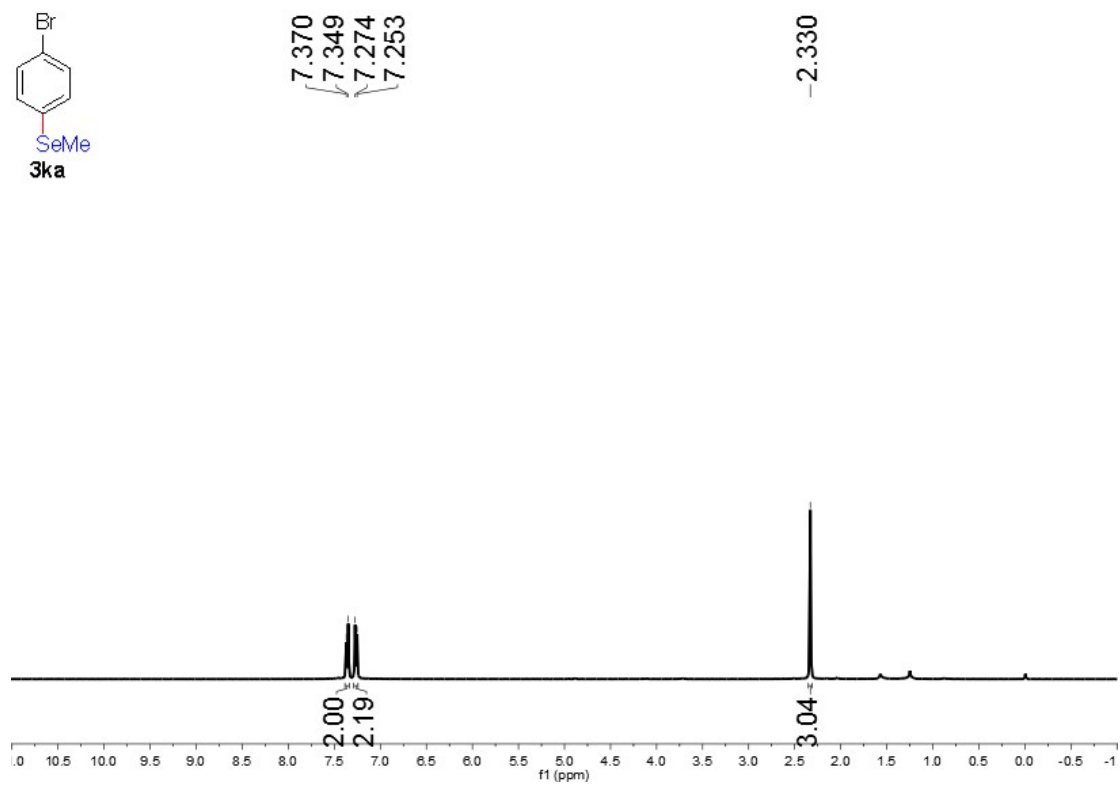
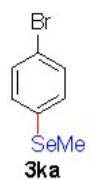


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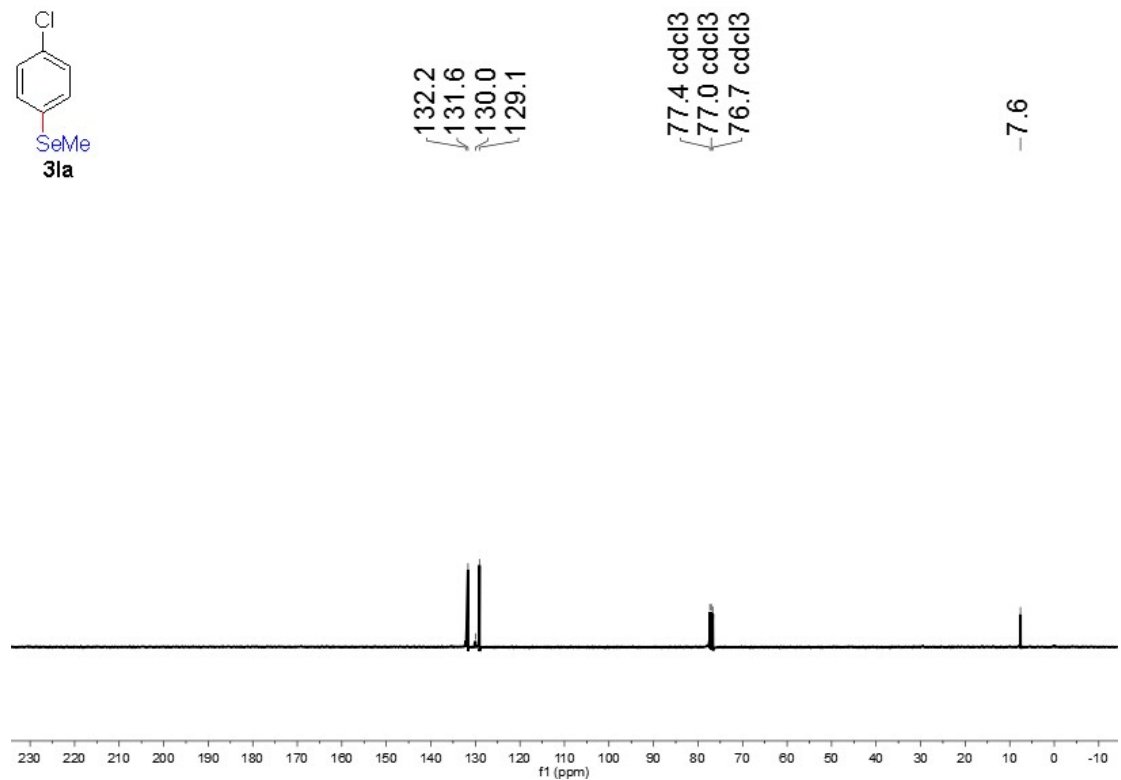
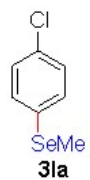
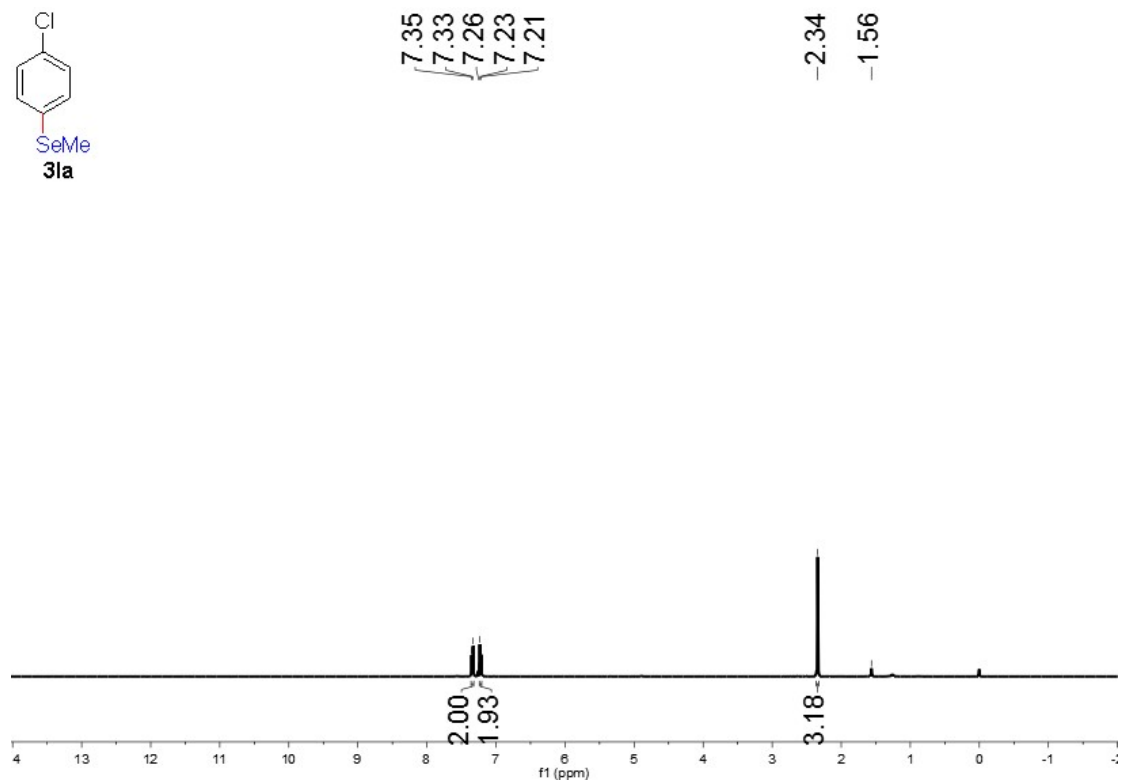
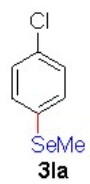


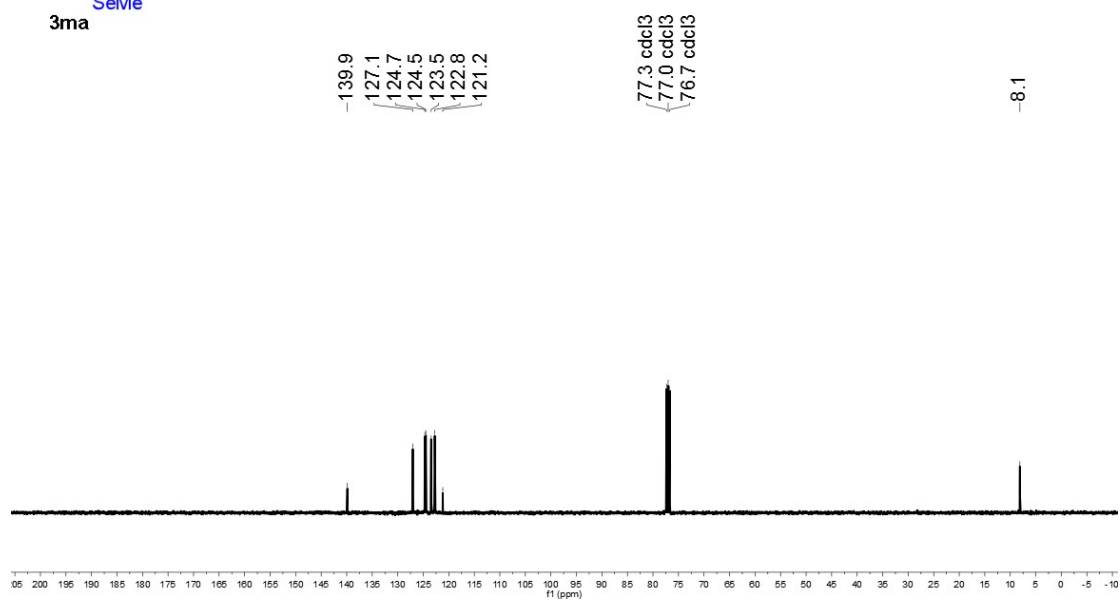
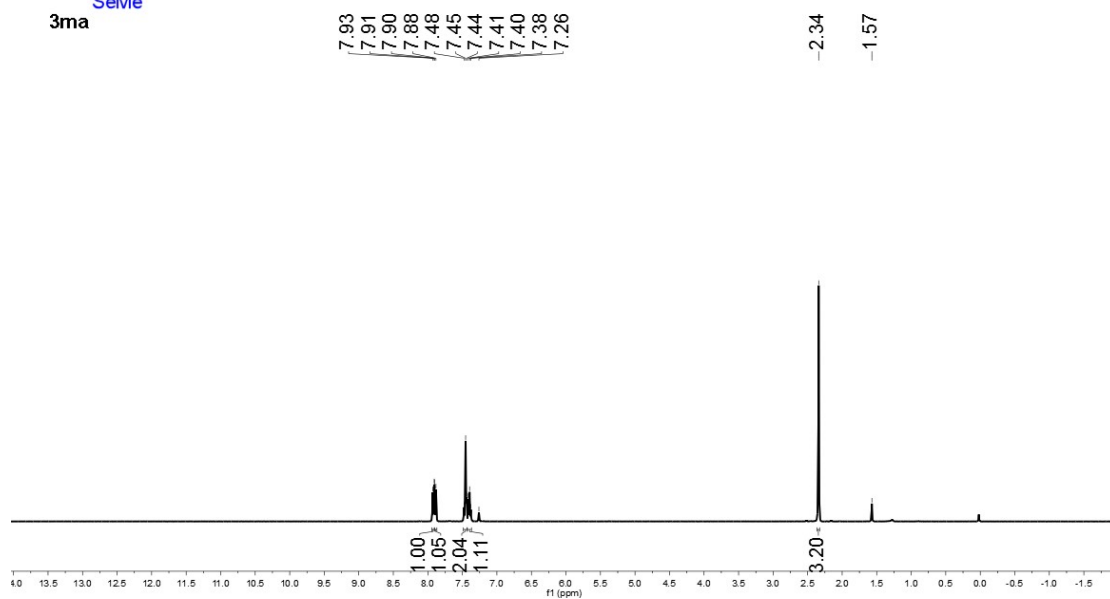
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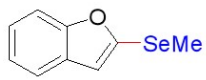




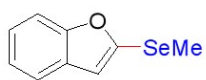
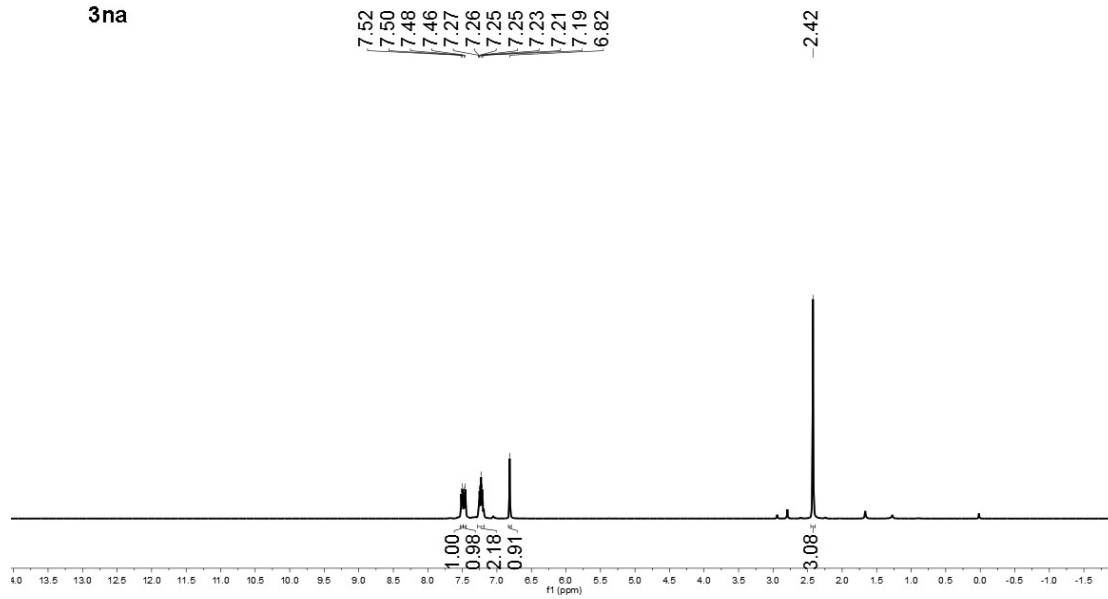




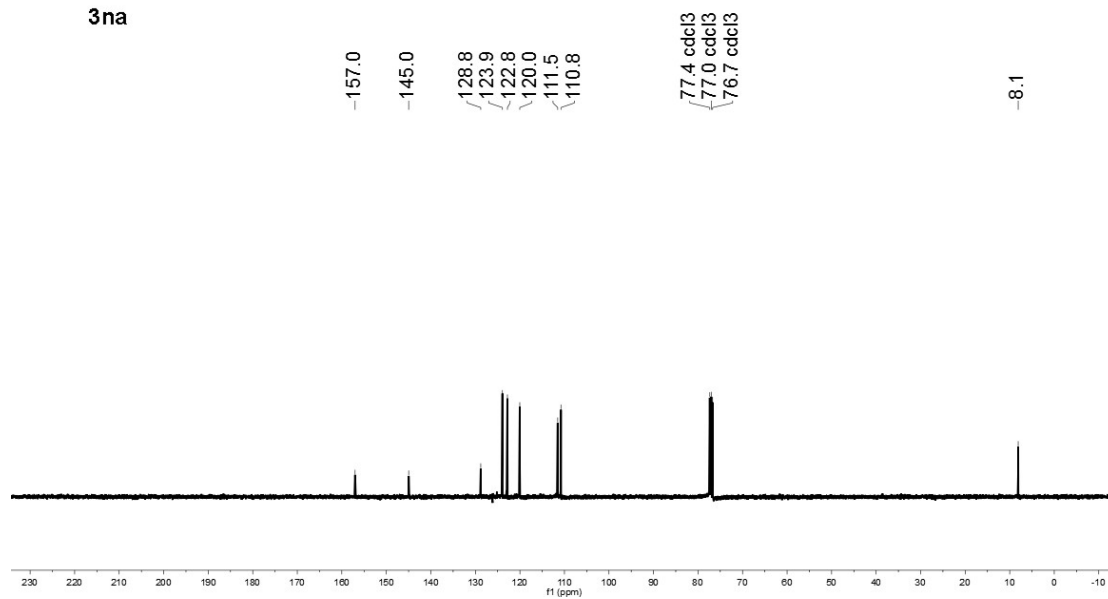


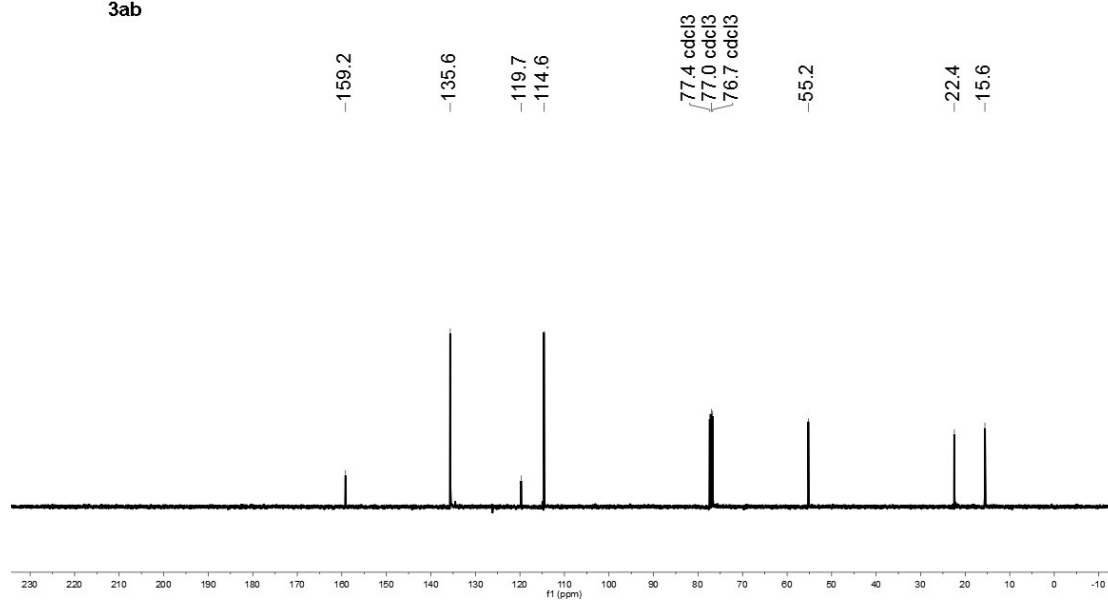
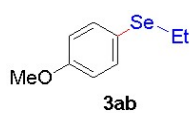
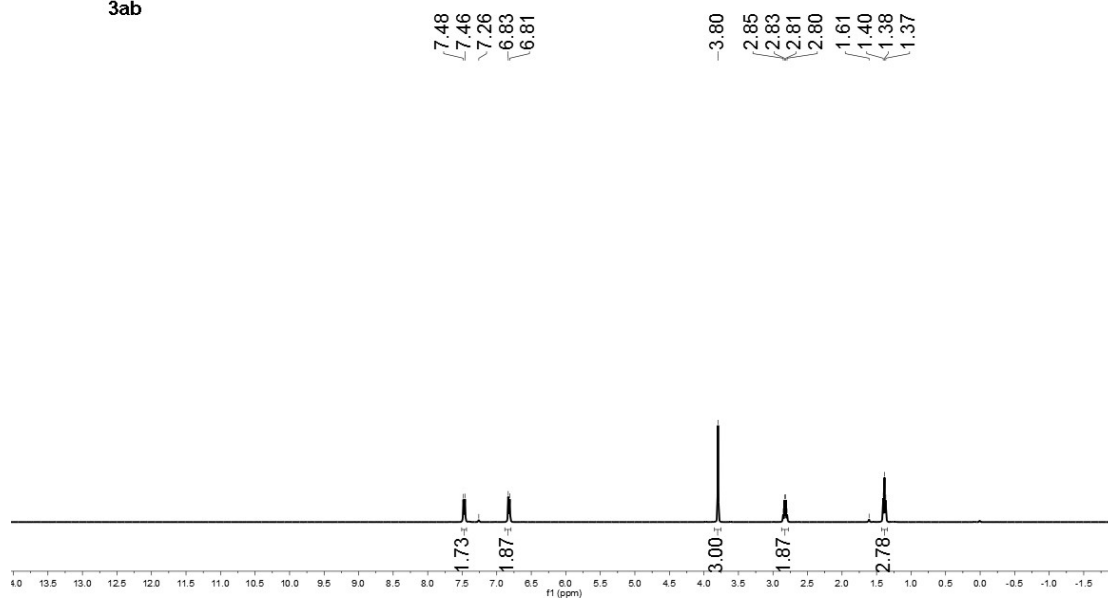


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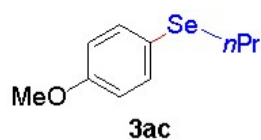
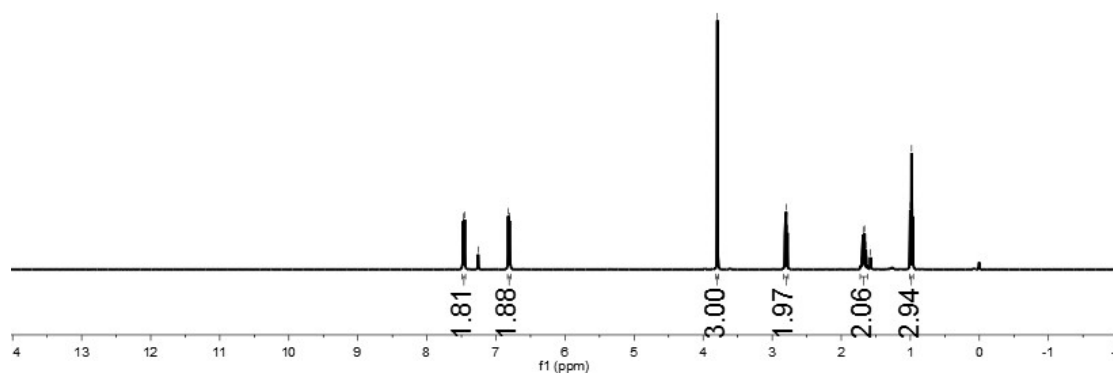
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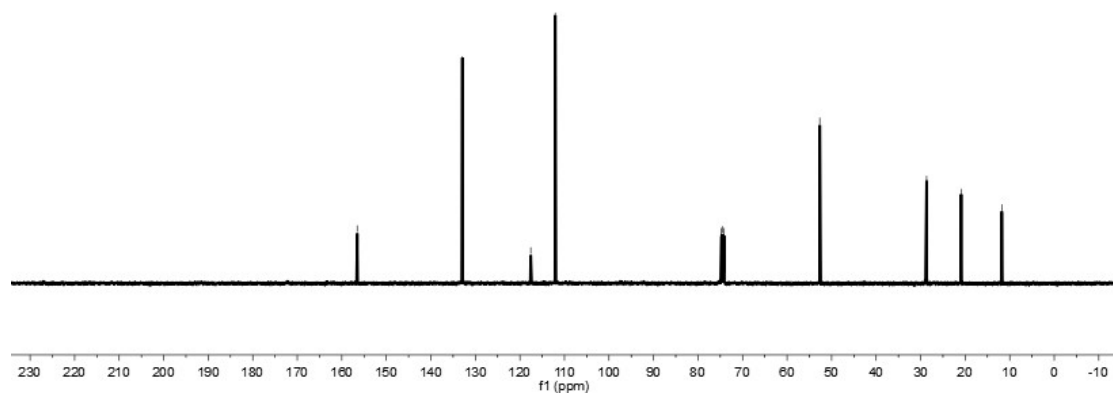


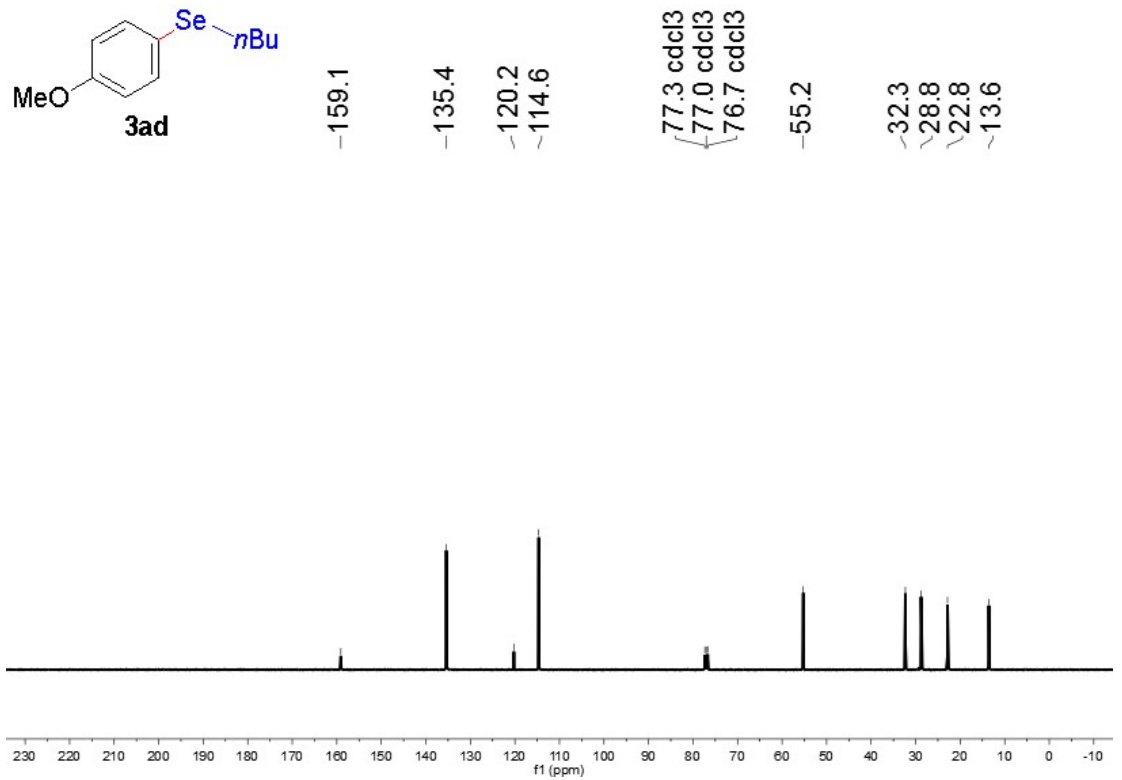
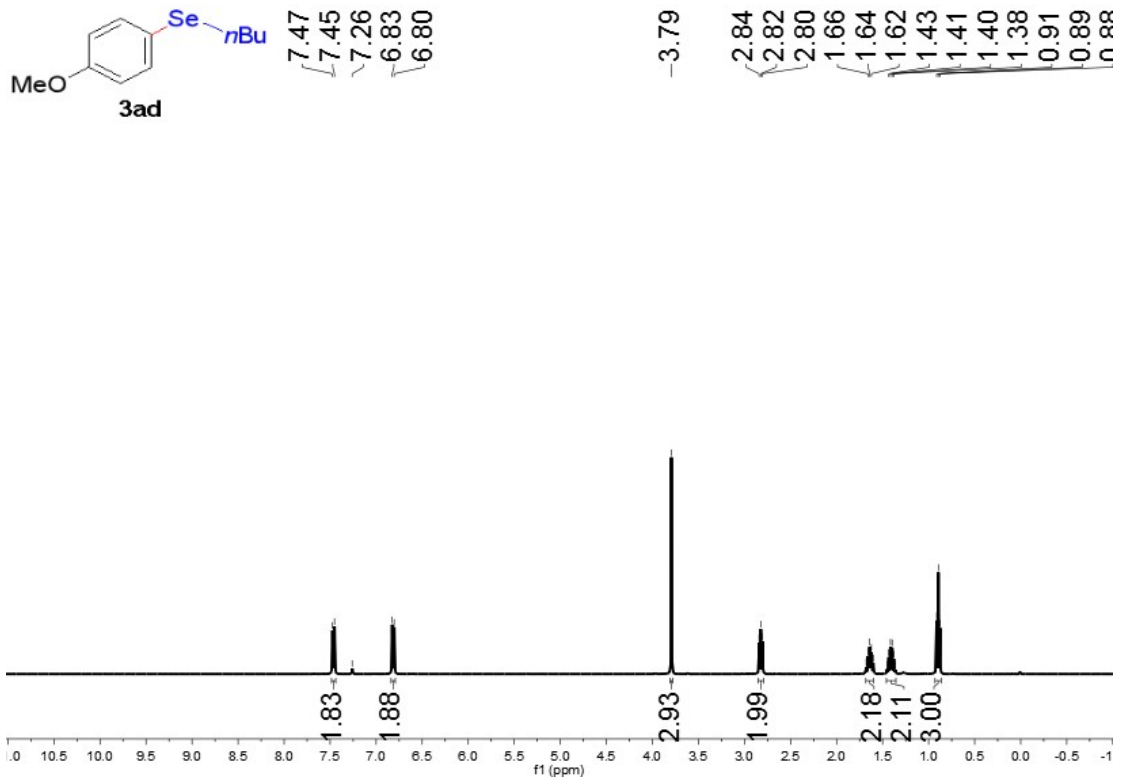


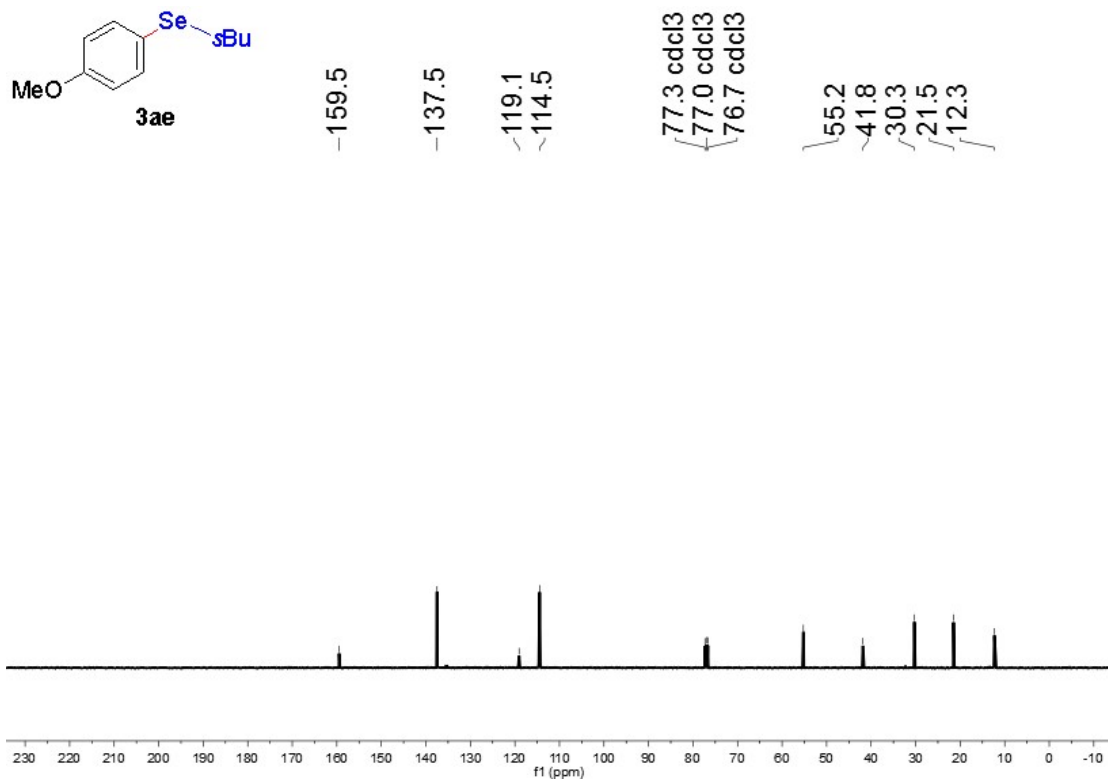
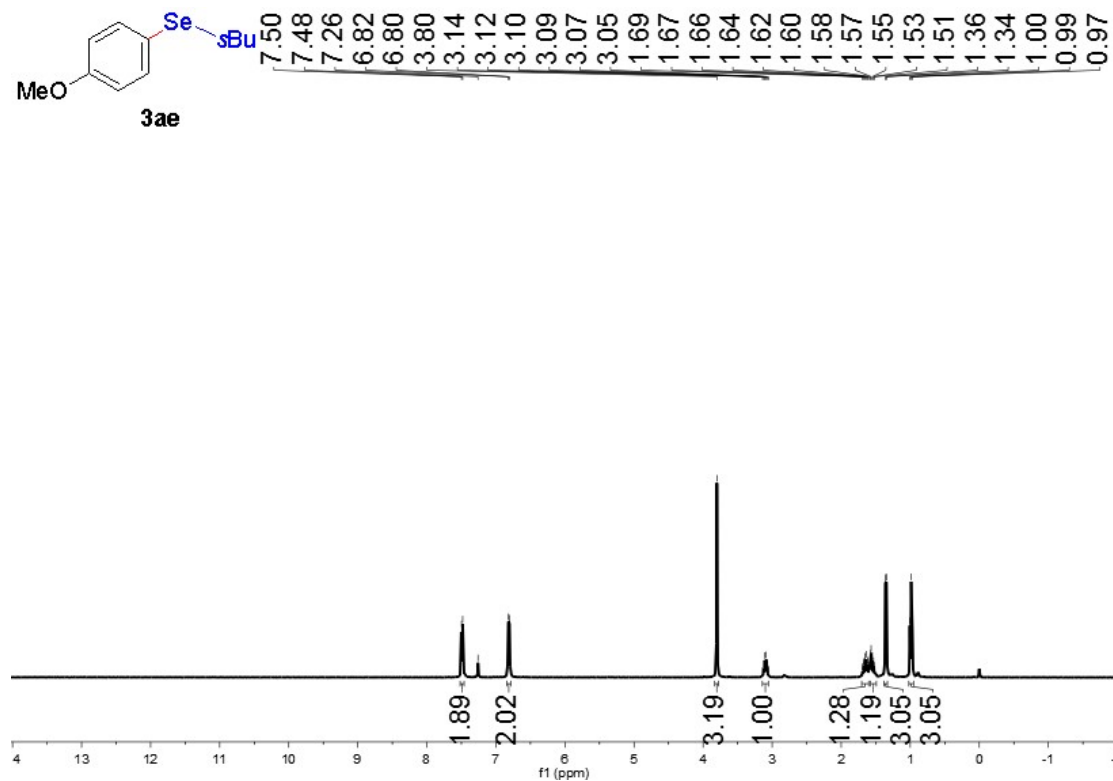
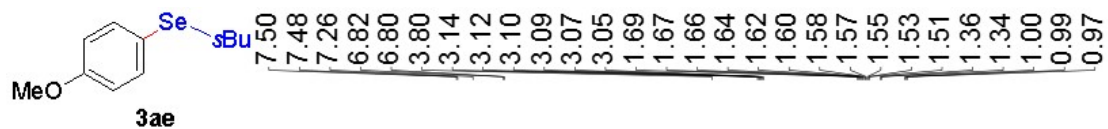
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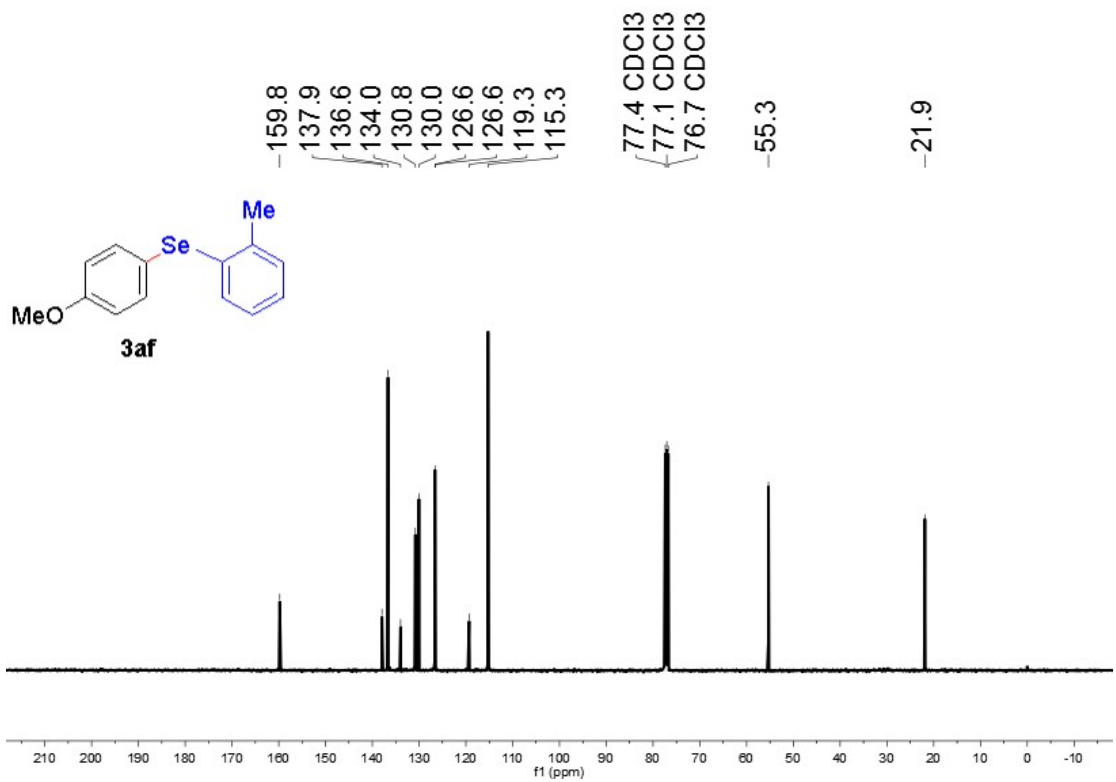
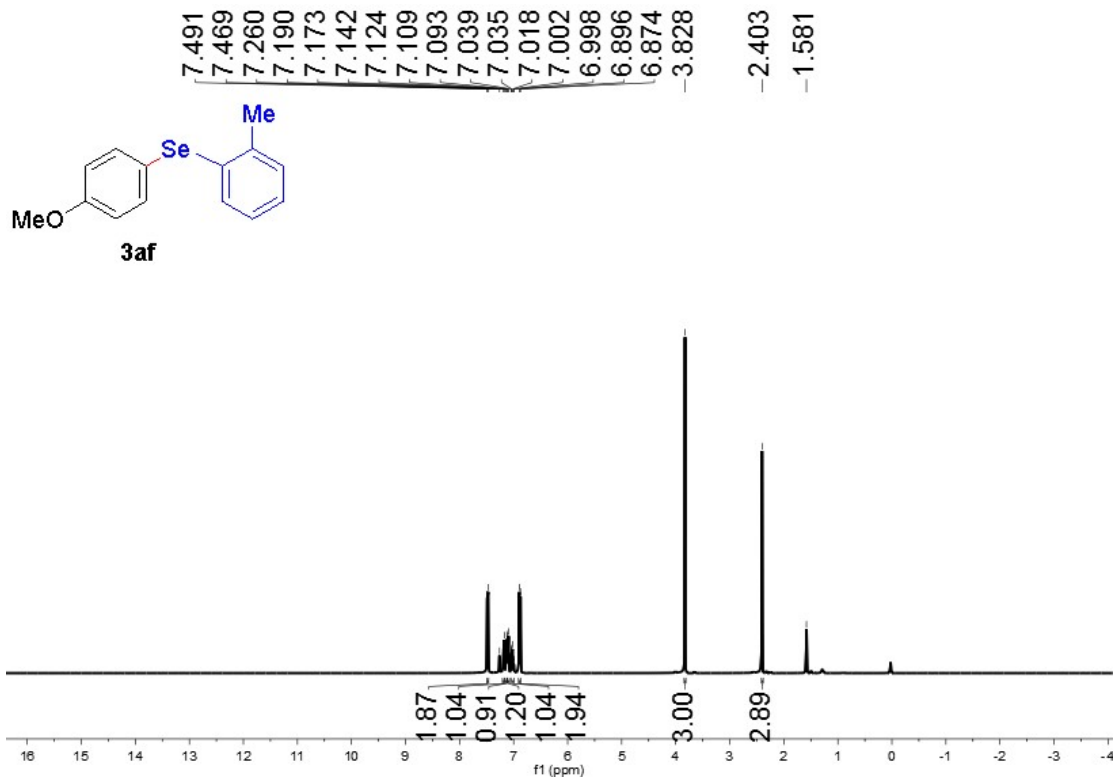


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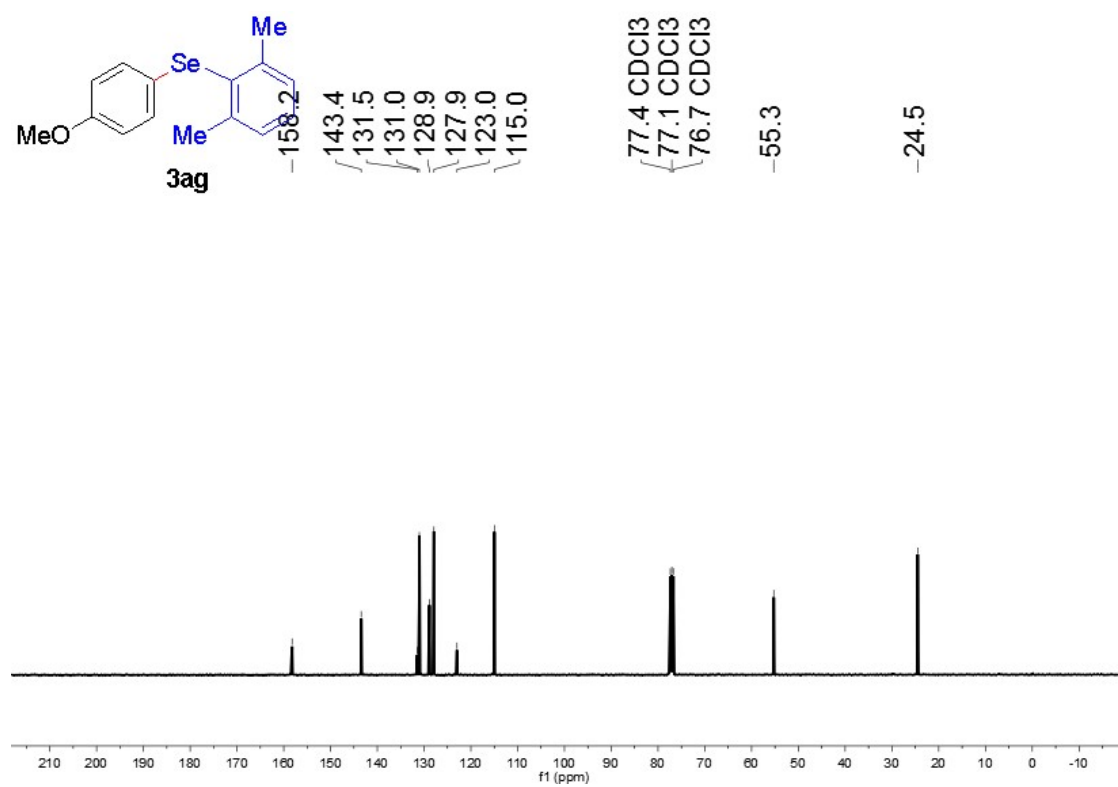
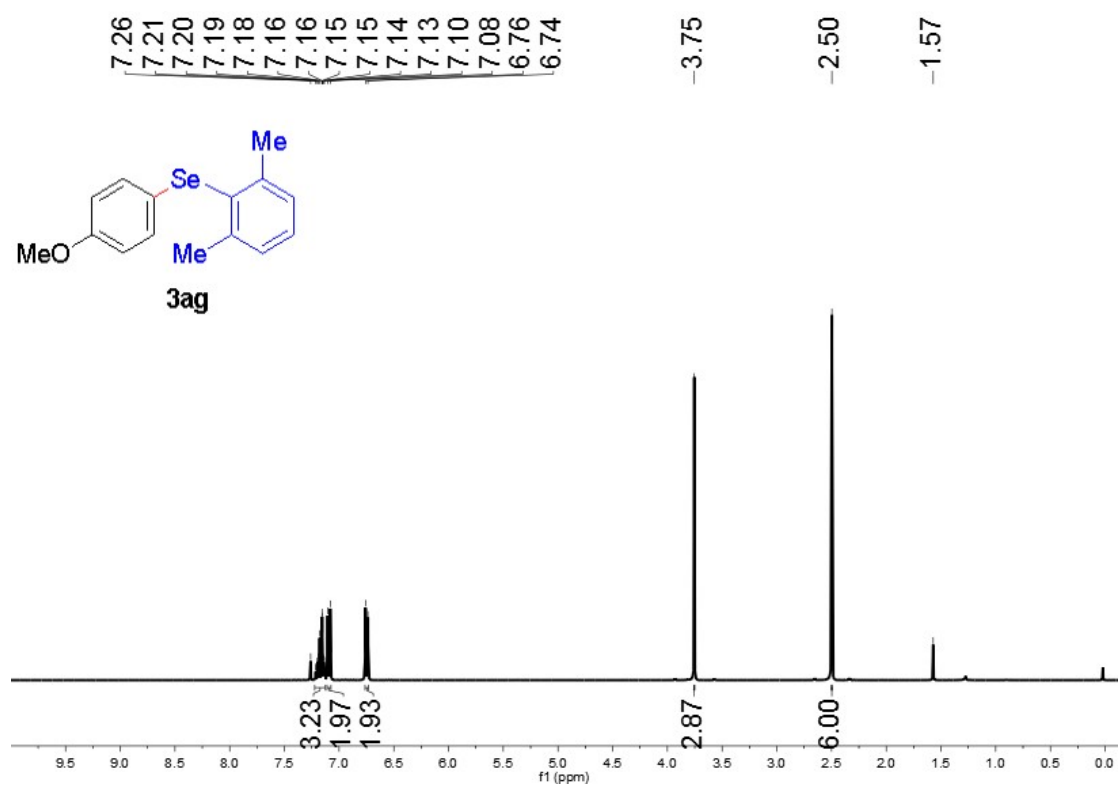


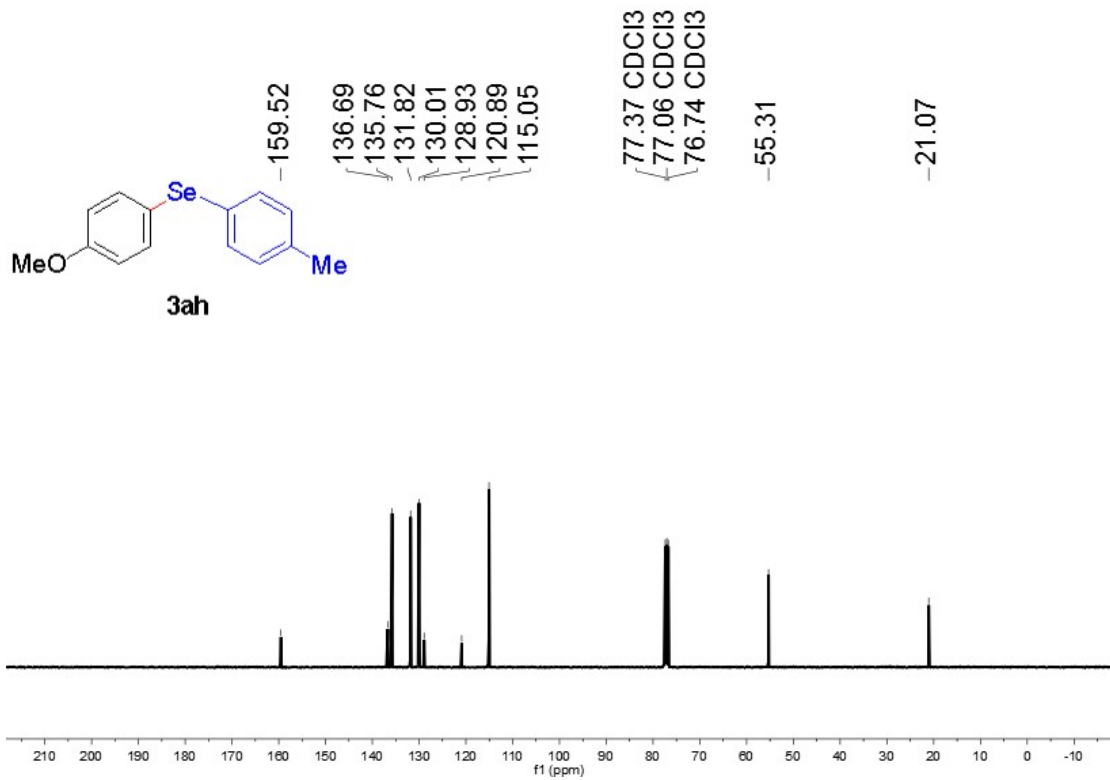
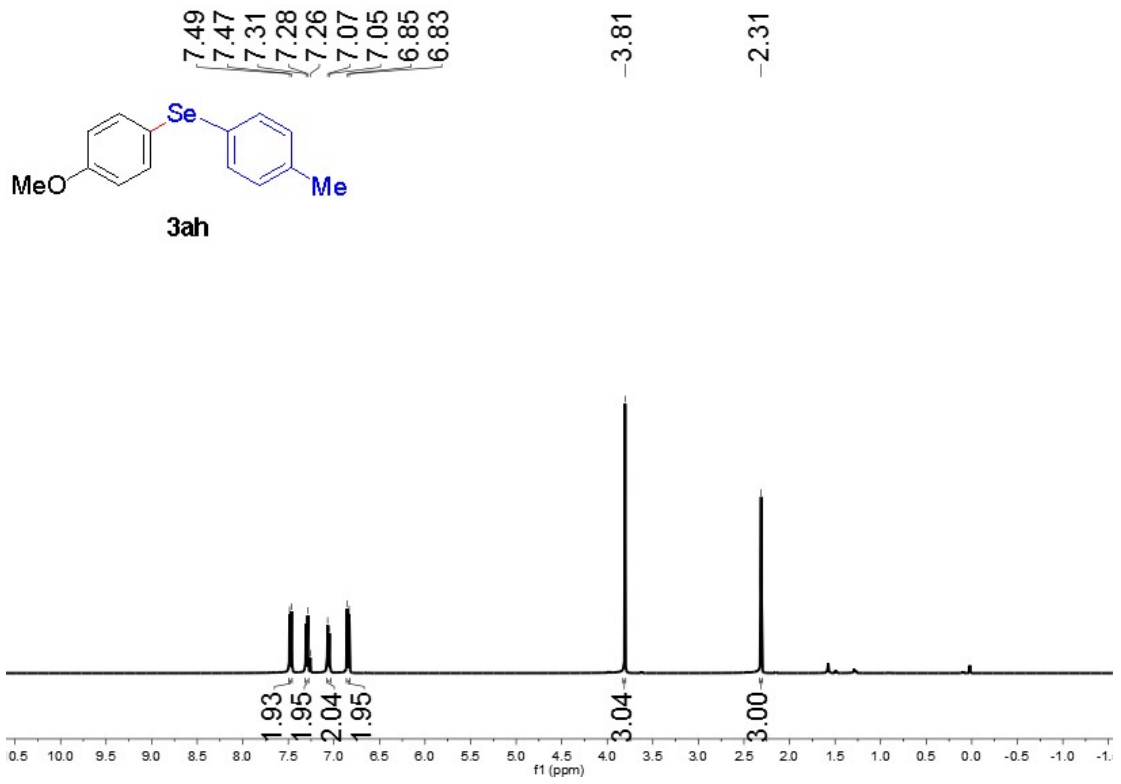


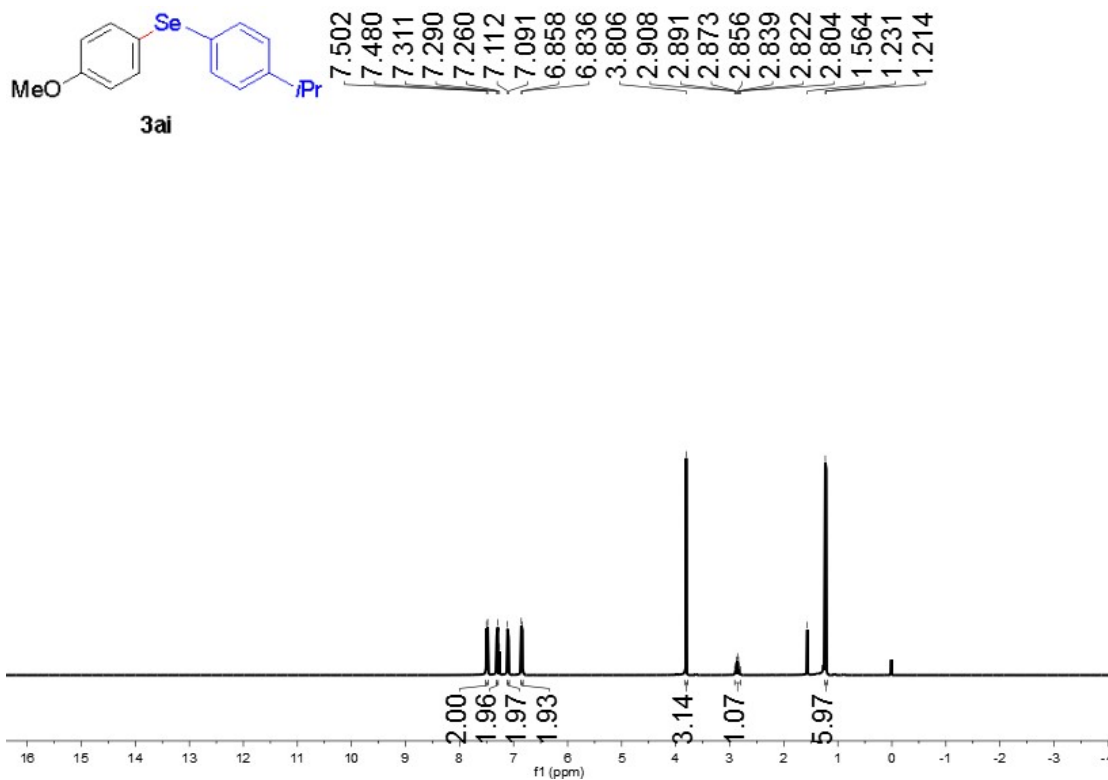
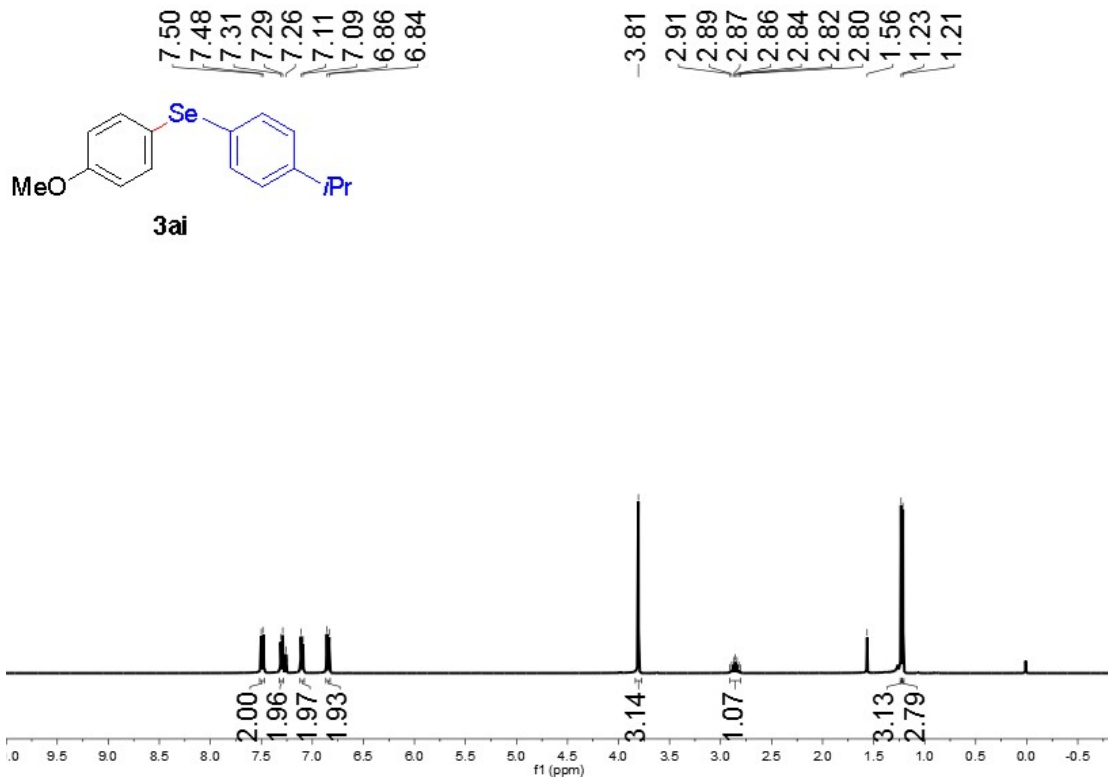


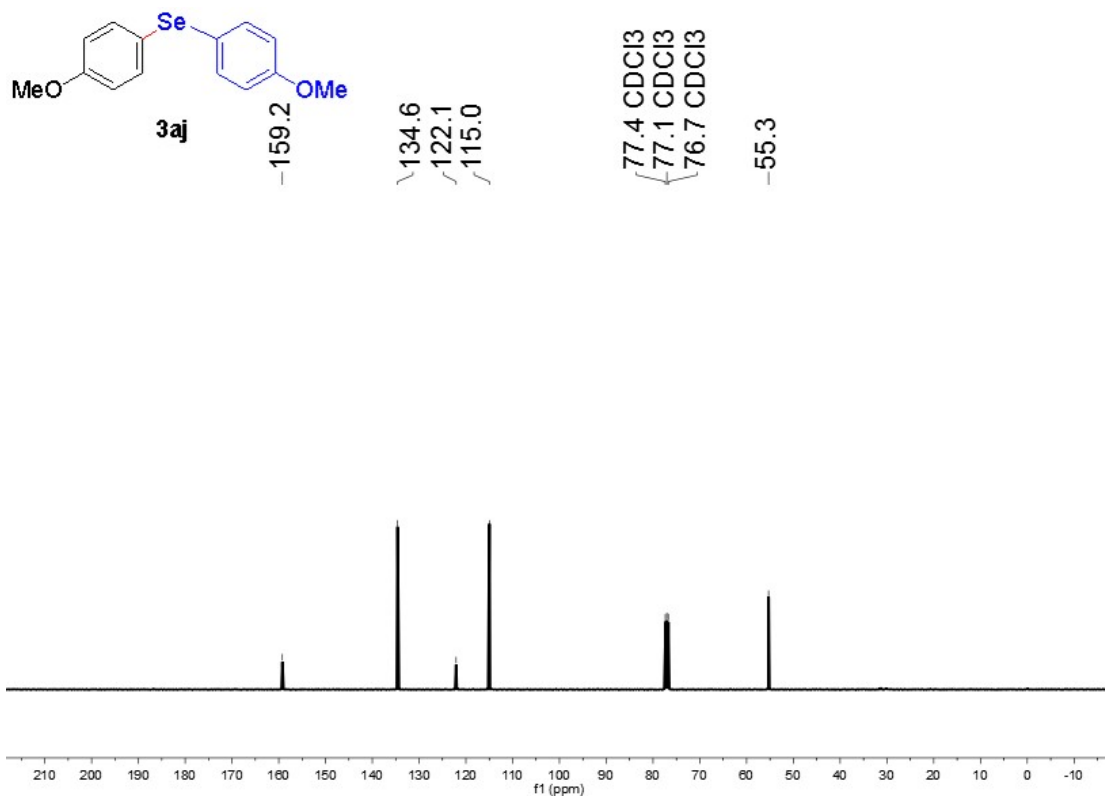
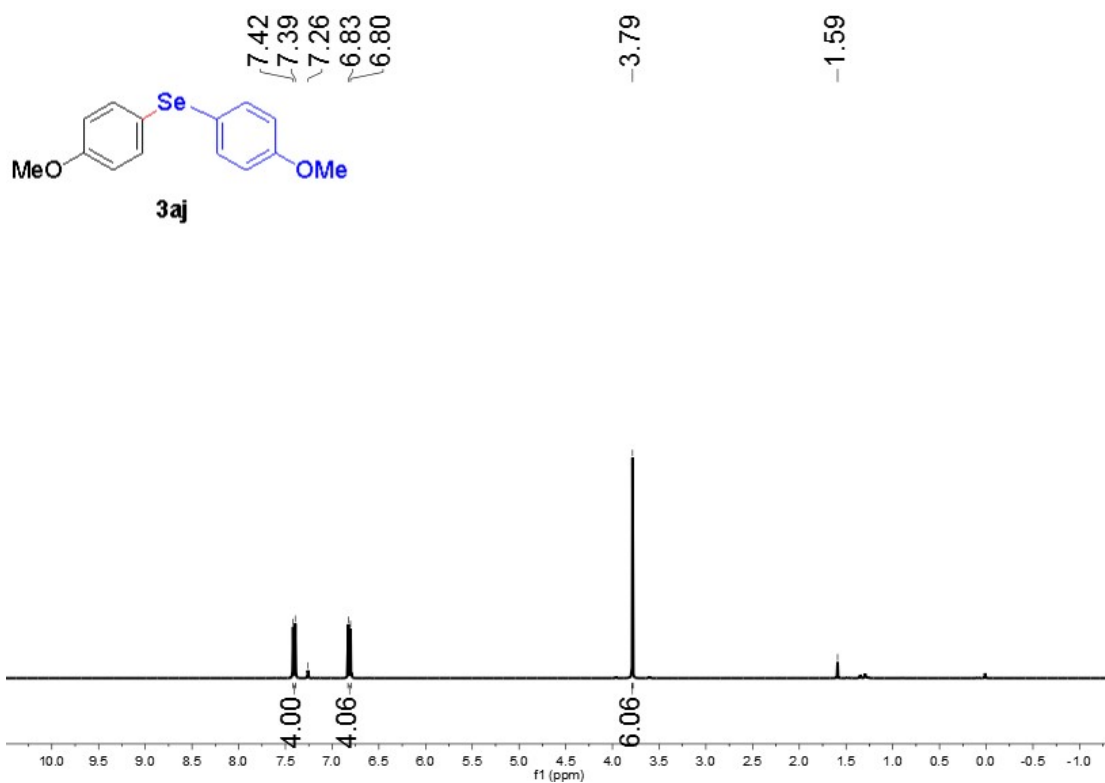


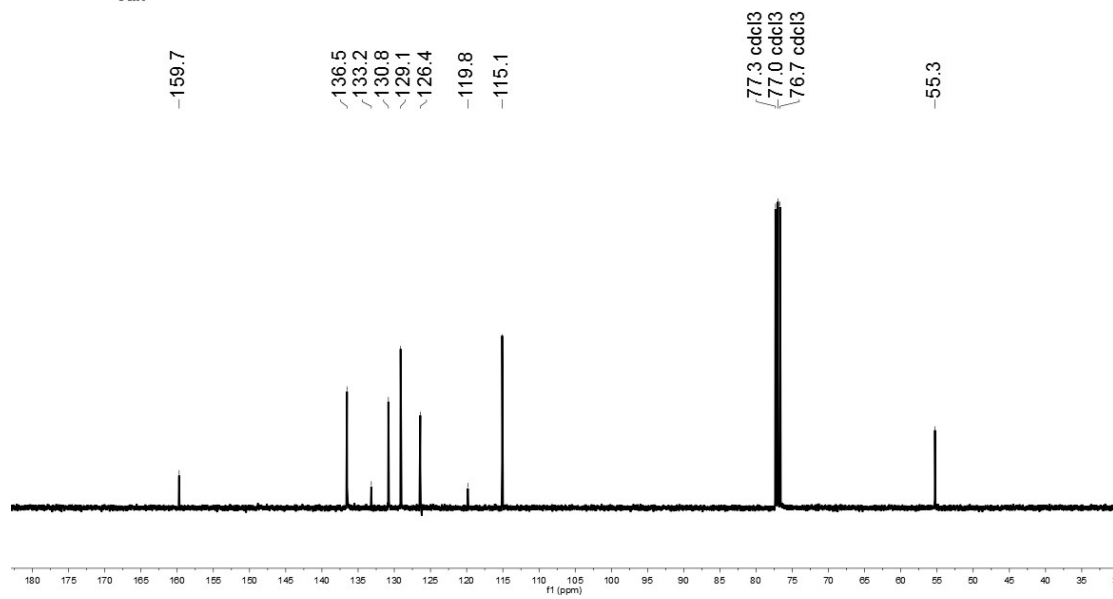
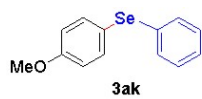
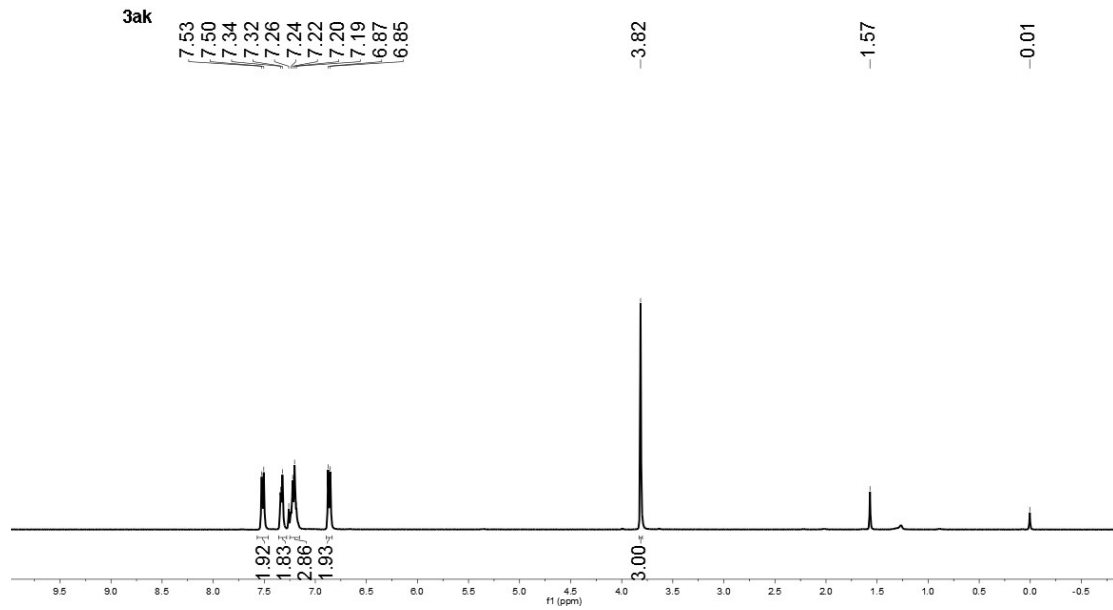
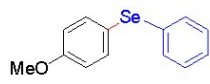


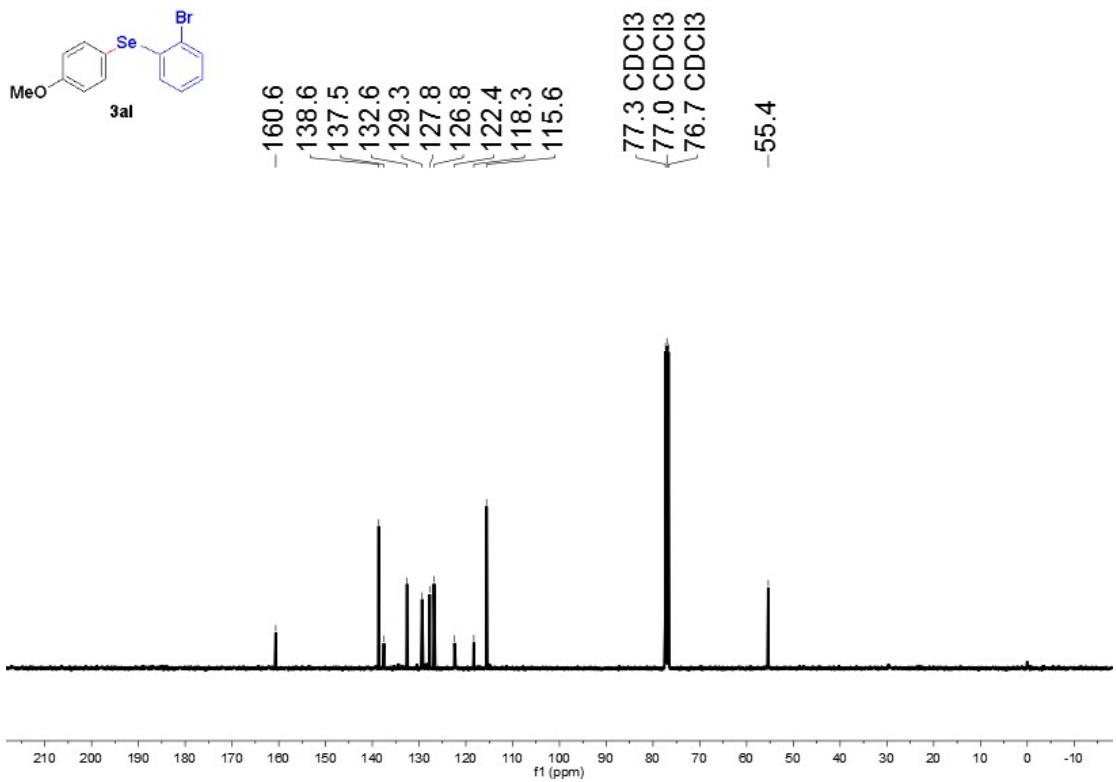
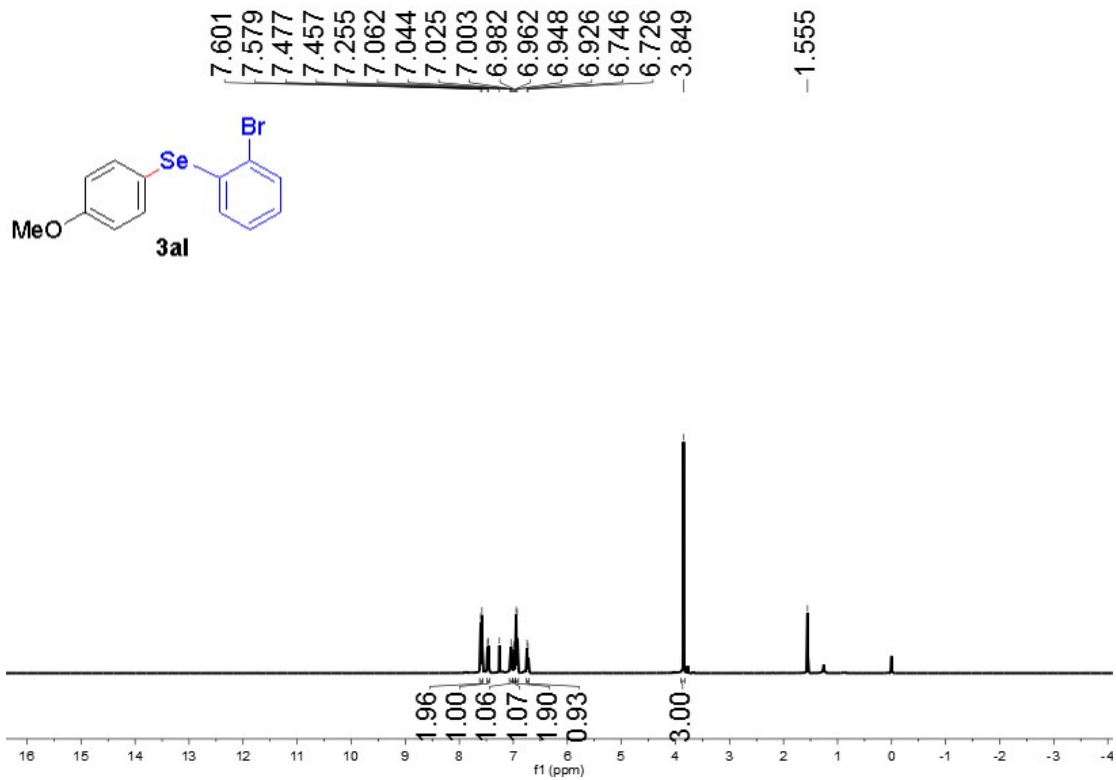


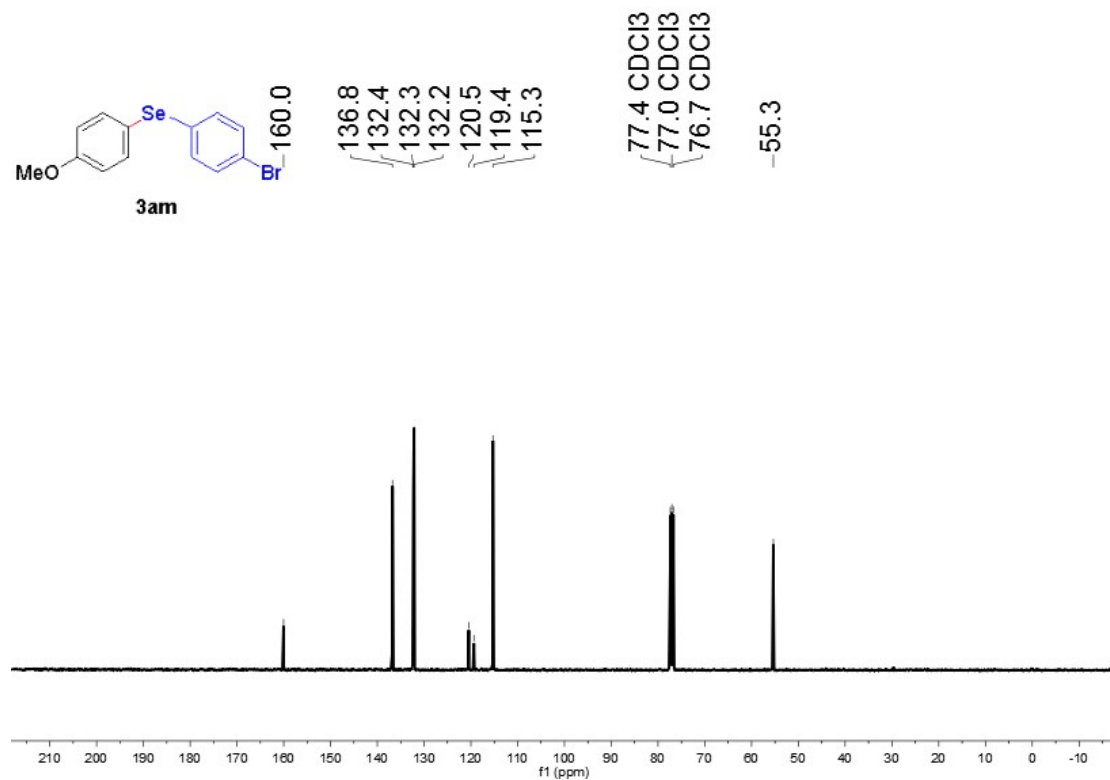
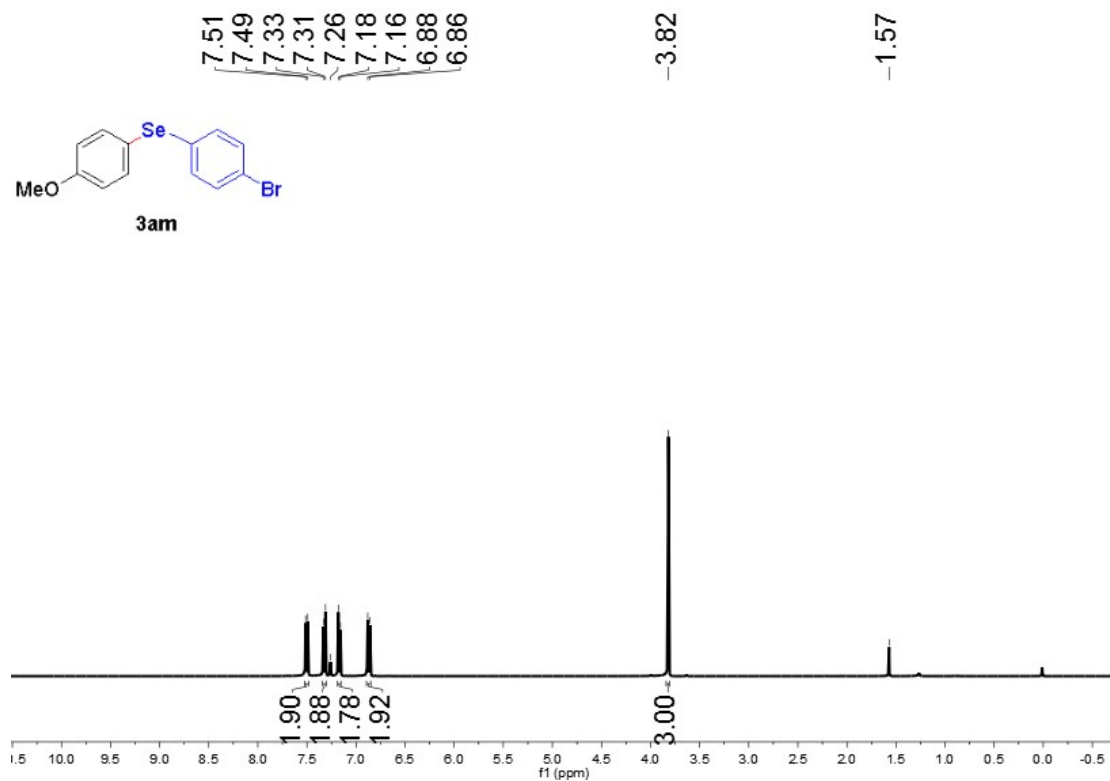


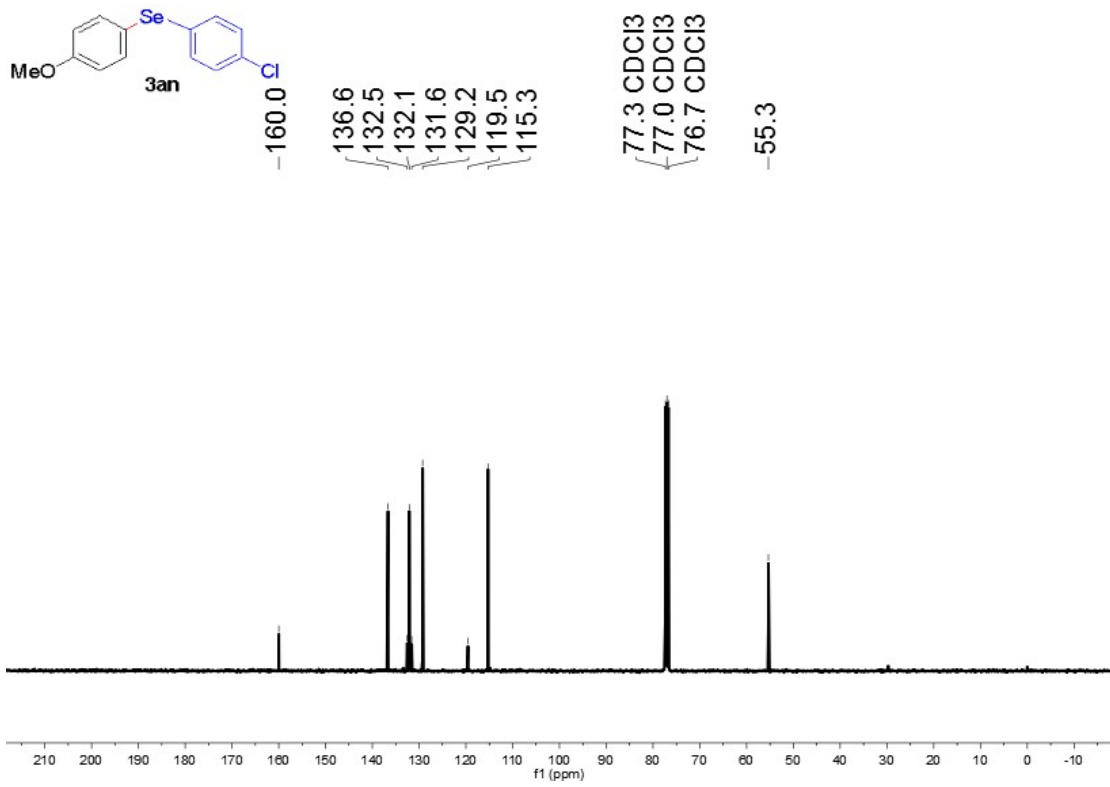
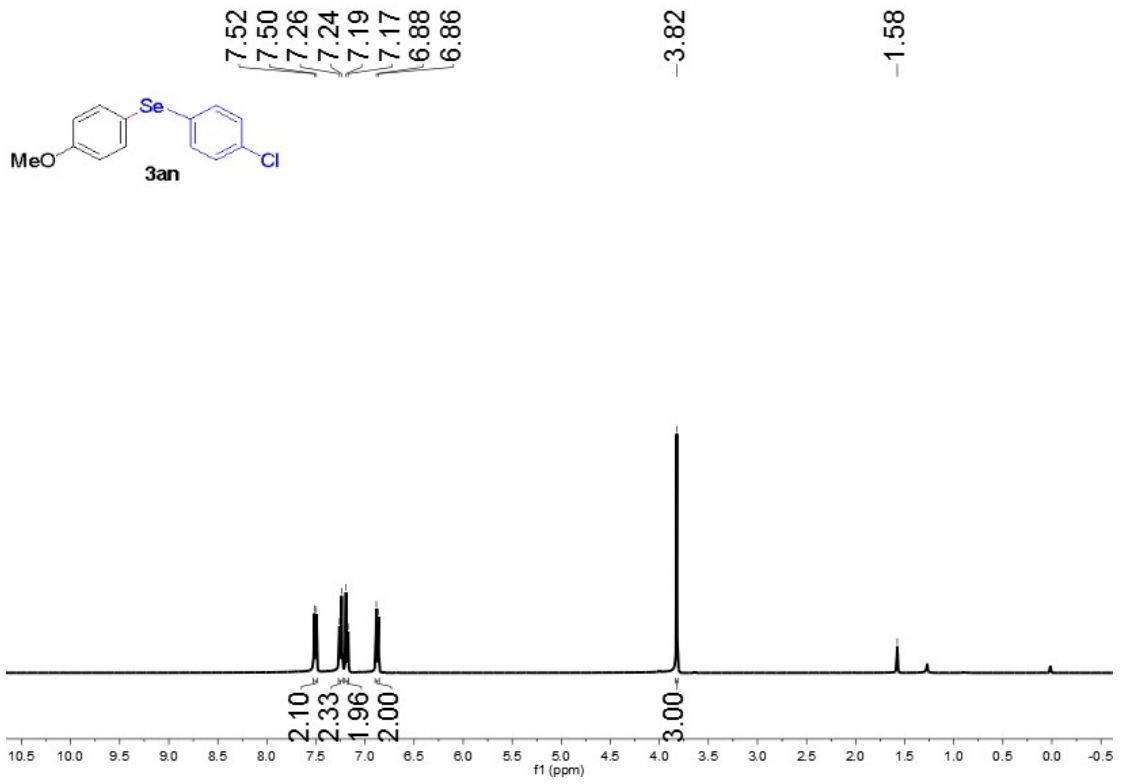




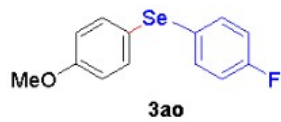




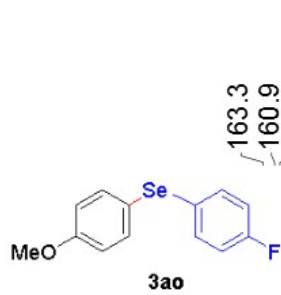
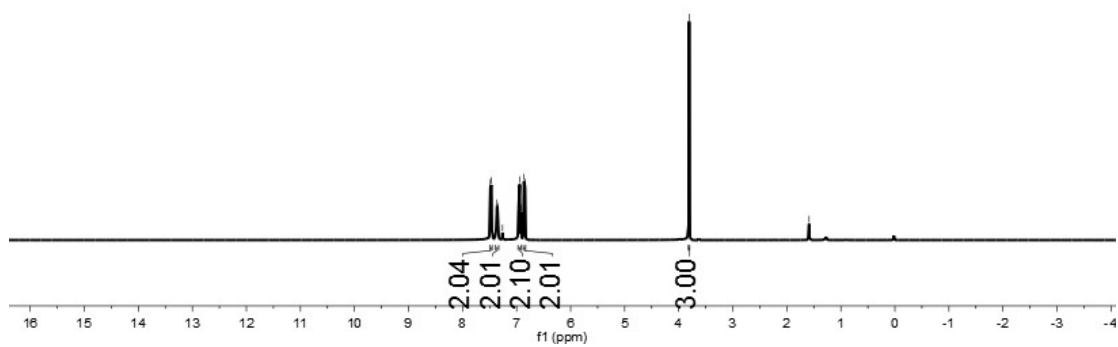




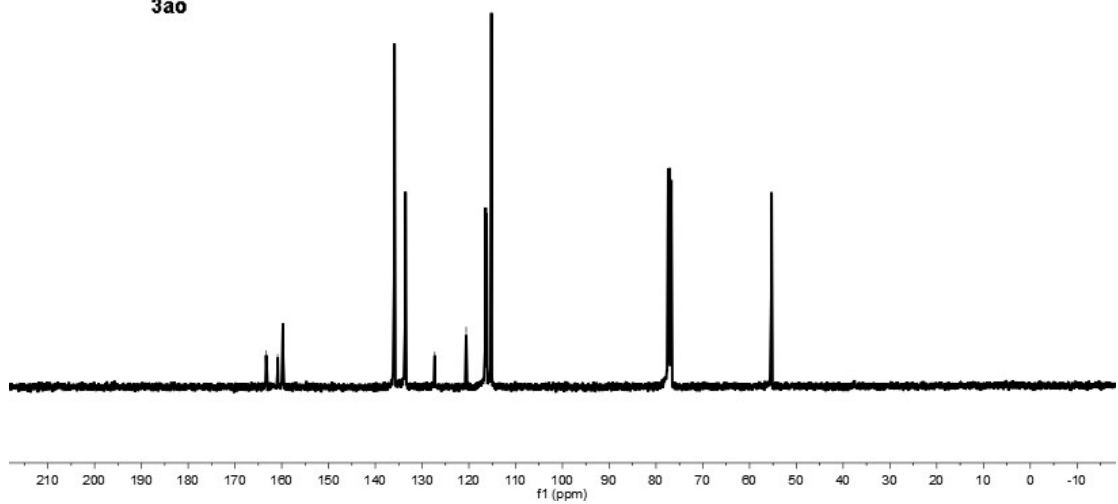




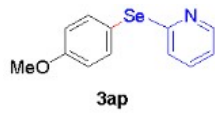
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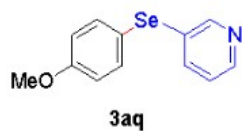
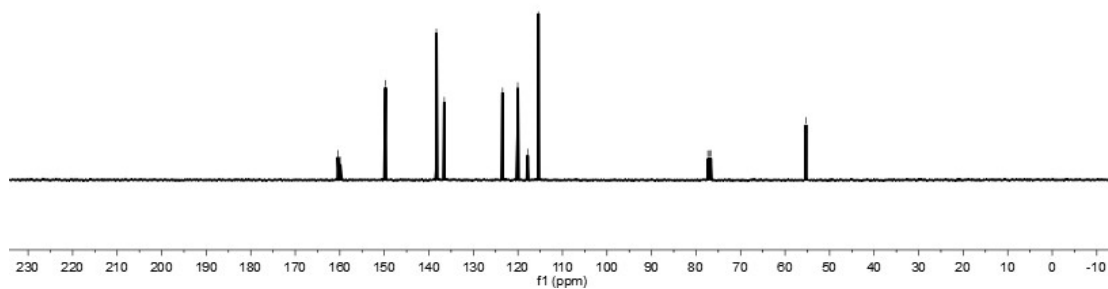




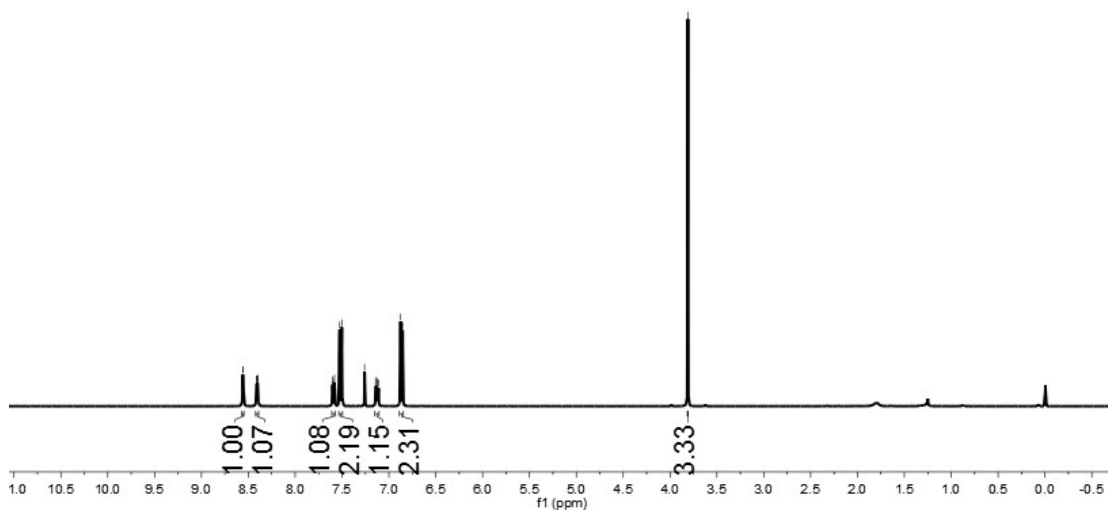


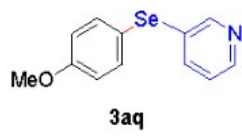
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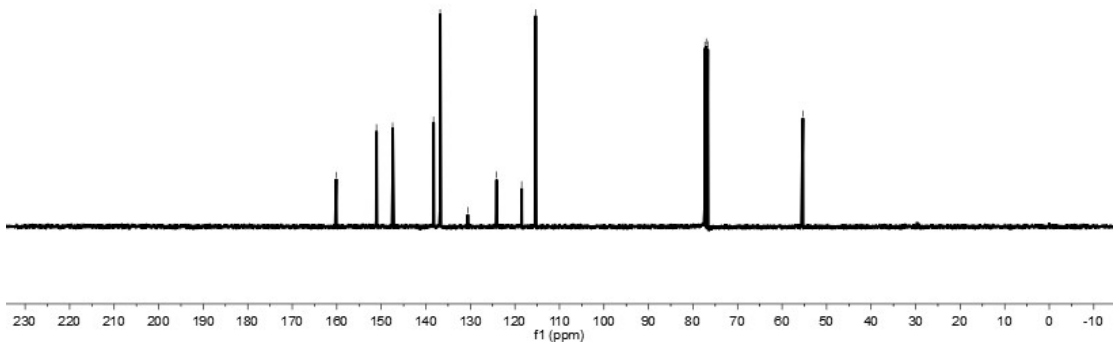




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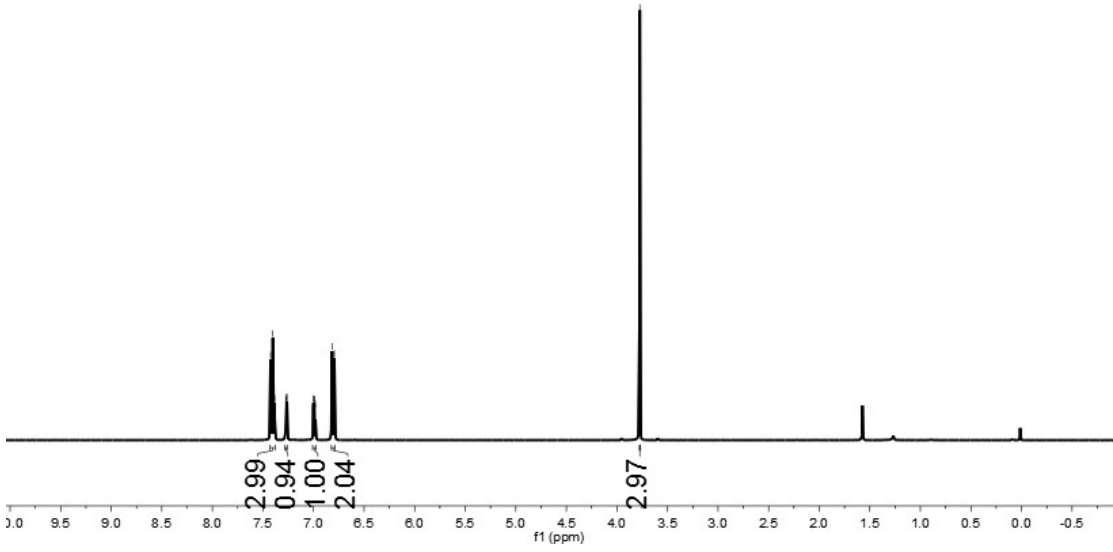
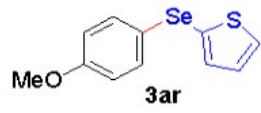
77.3 cdcl3  
 77.0 cdcl3  
 76.7 cdcl3

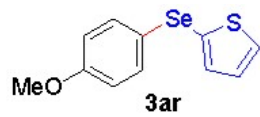
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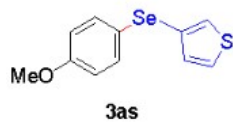
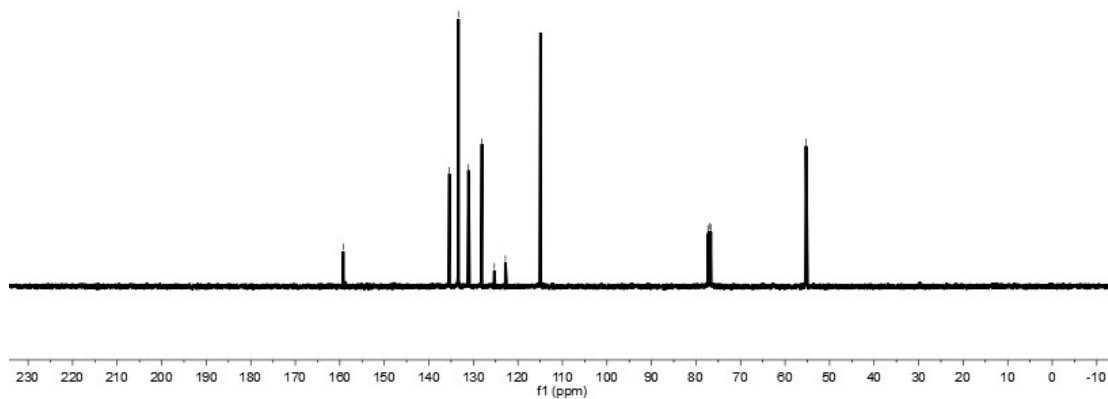
7.42  
 7.40  
 7.39  
 7.38  
 7.27  
 7.27  
 7.27  
 7.26  
 7.26  
 7.00  
 7.00  
 6.99  
 6.98  
 6.82  
 6.79

-3.77

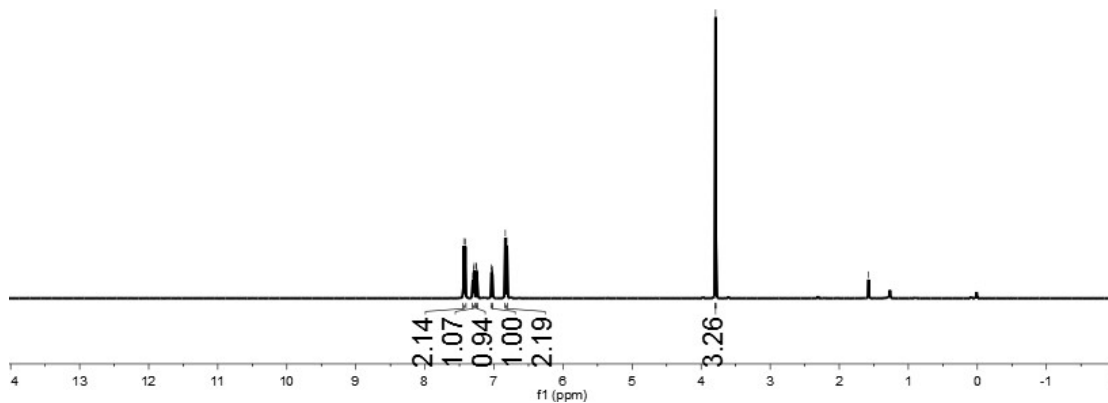


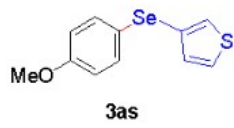


-159.3  
 135.4  
 133.4  
 131.1  
 128.1  
 125.3  
 122.8  
 114.9  
 77.3 cdcl3  
 77.0 cdcl3  
 76.7 cdcl3  
 -55.3

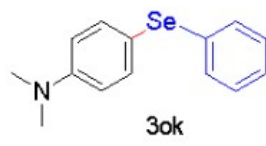
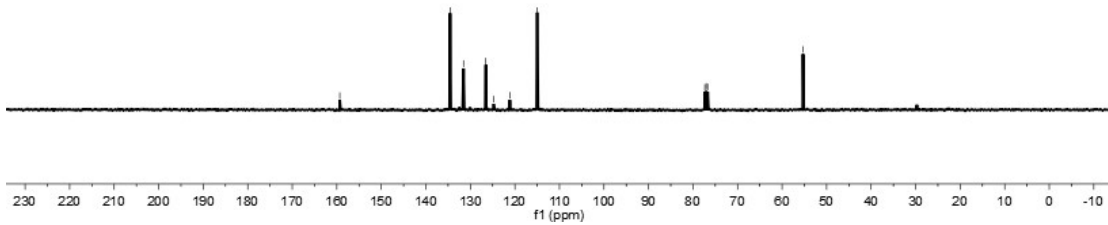


7.44  
 7.42  
 7.31  
 7.30  
 7.29  
 7.29  
 7.26  
 7.25  
 7.25  
 7.25  
 7.24  
 7.04  
 7.03  
 7.02  
 7.02  
 6.84  
 6.81  
 -3.79  
 -1.57

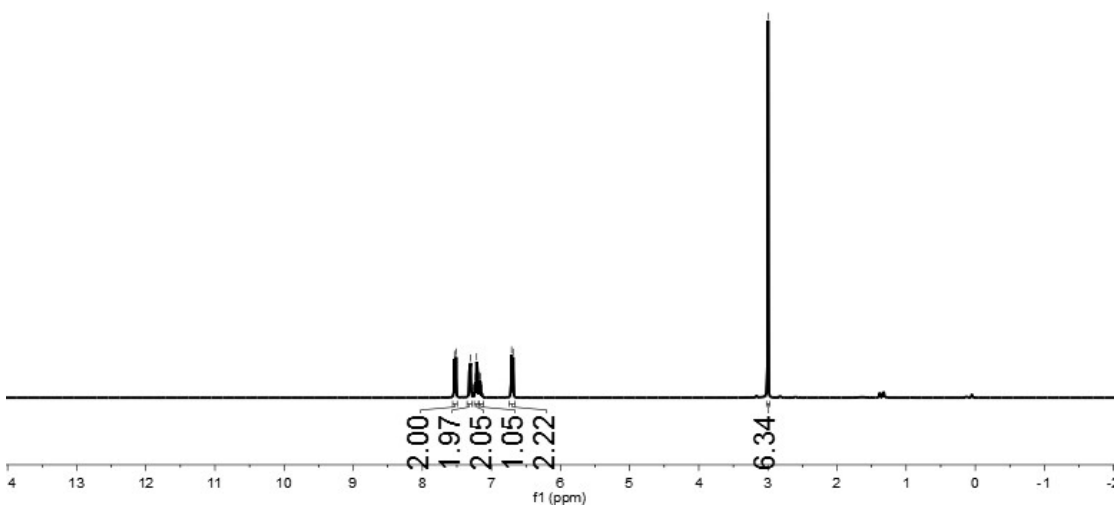


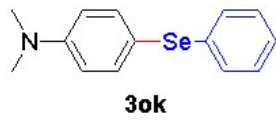


-159.3  
 134.6  
 131.5  
 126.5  
 126.5  
 124.8  
 121.1  
 115.0  
 77.4 cdcl3  
 77.0 cdcl3  
 76.7 cdcl3  
 -55.3

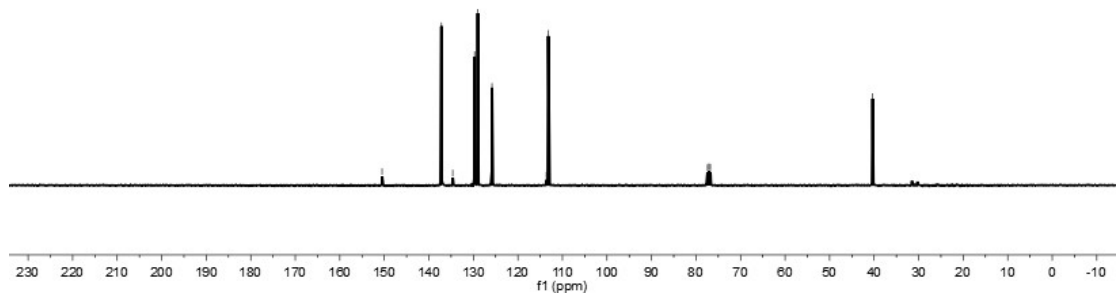


7.536  
 7.513  
 7.323  
 7.302  
 7.260  
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 7.215  
 7.196  
 7.177  
 7.160  
 7.141  
 6.709  
 6.687  
 -2.999

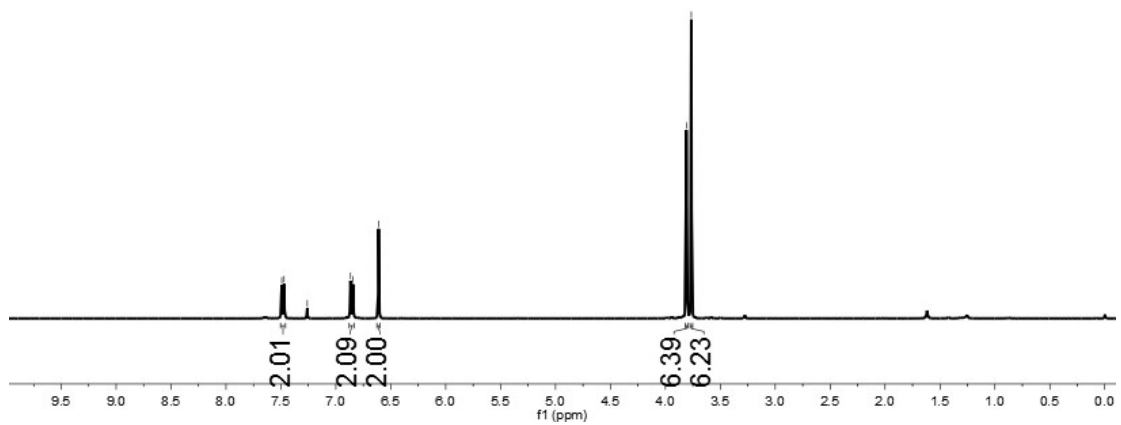


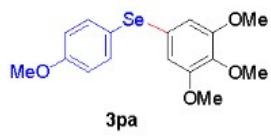


150.50  
 137.17  
 134.64  
 129.74  
 129.02  
 125.82  
 113.62  
 113.18  
 77.41 cdcl3  
 77.10 cdcl3  
 76.78 cdcl3  
 -40.34



7.49  
 7.47  
 7.26  
 6.87  
 6.84  
 6.61  
 3.81  
 3.81  
 3.76





~159.6  
~153.5

~137.2  
~135.7  
~126.7  
~120.6  
~115.0  
~108.9

77.3 cdcl3  
77.0 cdcl3  
76.7 cdcl3  
60.8  
56.1  
55.3

