

# **Synthesis of Organochalcogen Propargyl Aryl Ethers and their Application in the Electrophilic Cyclization Reaction: An Efficient Preparation of 3-Halo-4-Chalcogen-2*H*-Benzopyrans**

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## Materials and Methods

Proton nuclear magnetic resonance spectra ( $^1\text{H}$  NMR) were obtained at 400 MHz. Spectra were recorded in  $\text{CDCl}_3$  solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of  $\text{CDCl}_3$  or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift ( $\delta$ ), multiplicity, coupling constant ( $J$ ) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra ( $^{13}\text{C}$  NMR) were obtained at 100 MHz. Spectra were recorded in  $\text{CDCl}_3$  solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of  $\text{CDCl}_3$ . Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still.<sup>1</sup> Thin layer chromatography (TLC) was performed using silica gel GF<sub>254</sub>, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

**General Procedure for the Preparation of the Organochalcogen Propargyl Aryl Ethers **2a-s**:** To a solution of the appropriate propargyl aryl ether (5 mmol) in dry THF (30 mL) at -78 °C, under argon atmosphere was added drop by drop, *n*-BuLi (2.2 mL of a 2.5 M solution in hexane, 5.5 mmol). After 1h at this temperature, the appropriate organochagen electrophile ( $\text{R}^2\text{SBr}$ ,  $\text{R}^2\text{SeBr}$ ,  $\text{R}^2\text{TeBr}$ ; 5.5 mmol) in THF (5mL) was added. The mixture was stirred at room temperature for 3h. After this time, the mixture was diluted with ethyl acetate (60 mL) and washed with saturated aq  $\text{NH}_4\text{Cl}$  (30 mL) and water (3 x 30 mL). The organic phase was separated, dried over  $\text{MgSO}_4$ , and concentrated under vacuum.

**2-*tert*-Butylphenyl 3-Phenylselenylprop-2-yn-1-yl Ether (2c):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.767 g (51%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 200 MHz,  $\delta$ (ppm): 7.49-7.43 (m, 2H), 7.33-7.07 (m, 5H), 6.98-6.86 (m, 2H), 4.91 (s, 2H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 155.8, 130.8, 129.5, 129.2, 128.1, 127.3, 127.2, 126.6. MS (EI, 70 eV)  $m/z$  (relative intensity): 340 (43), 260 (12), 185 (100), 170 (19), 156 (16), 114 (60), 102 (12), 77 (35). Anal. (%) Calcd for  $\text{C}_{19}\text{H}_{20}\text{OSe}$ : C 66.47, H 5.87. Found: C 66.27, H 5.62.

**4-Methoxyphenyl 3-Phenylselenylprop-2-yn-1-yl Ether (2d):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 1.125 g (71%).  $^1\text{H}$

<sup>1</sup> Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, 43, 2923-2925

NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.48-7.44 (m, 2H), 7.30-7.24 (m, 3H), 6.95-6.92 (m, 2H), 6.86-6.82 (m, 2H), 4.84 (s, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 154.4, 151.7, 129.5, 129.3, 128.1, 127.2, 116.4, 114.6, 98.9, 68.1, 57.8, 55.7. MS (EI, 70 eV) *m/z* (relative intensity): 314 (43), 234 (15), 192 (9), 159 (100), 145 (17), 117 (32), 102 (9), 76 (15). Anal. (%) Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Se: C 60.58, H 4.45. Found: C 60.42, H 4.29.

**3-Methoxyphenyl 3-Phenylselenylprop-2-yn-1-yl Ether (2e):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.982 g (62%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 7.51-7.46 (m, 2H), 7.34-7.16 (m, 4H), 6.62-6.54 (m, 3H), 4.88 (s, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 160.7, 158.7, 129.8, 129.4, 129.2, 128.0, 127.2, 107.1, 107.0, 101.4, 98.6, 68.8, 56.9, 55.2. MS (EI, 70 eV) *m/z* (relative intensity): 314 (24), 234 (22), 192 (25), 159 (45), 144 (5), 114 (100), 102 (19), 77 (32). Anal. (%) Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>Se: C 60.58, H 4.45. Found: C 60.33, H 4.29.

**3-Chlorinephenyl 3-Phenylselenylprop-2-yn-1-yl Ether (2f):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.804 g (50%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.49-7.46 (m, 2H), 7.32-7.19 (m, 4H), 7.01-6.97 (m, 2H), 6.89-6.86 (m, 1H), 4.88 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 158.2, 134.8, 130.2, 129.6, 129.3, 127.9, 127.3, 121.6, 115.4, 113.6, 98.0, 69.2, 57.1. MS (EI, 70 eV) *m/z* (relative intensity): 321 (1), 318 (6), 192 (41), 114 (100), 102 (15), 76 (13). Anal. (%) Calcd for C<sub>15</sub>H<sub>11</sub>ClOSe: C 56.01, H 3.45. Found: C 56.44, H 3.80.

**1-Naphthyl 3-Phenylselenylprop-2-yn-1-yl Ether (2g):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.011 g (60%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.78-7.71 (m, 3H), 7.46-7.43 (m, 3H), 7.38-7.36 (m, 1H), 7.28-7.27 (m, 1H), 7.23-7.18 (m, 4H), 5.01 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.4, 134.2, 129.5, 129.4, 129.3, 129.2, 128.0, 127.6, 127.2, 126.9, 126.4, 123.9, 118.8, 107.6, 98.6, 68.7, 56.9. MS (EI, 70 eV) *m/z* (relative intensity): 334 (45), 254 (25), 179 (97), 151 (100), 125 (17), 76 (11). Anal. (%) Calcd for C<sub>19</sub>H<sub>14</sub>OSe: C 67.66, H 4.18. Found: C 67.23, H 3.78.

**2-Naphthyl 3-Phenylselenylprop-2-yn-1-yl Ether (2h):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.263 g (75%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 8.31-8.26 (m, 1H), 7.82-7.77 (m, 1H), 7.50-7.24 (m, 9H), 6.96 (d, *J* = 7.4 Hz, 1H), 5.09 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 153.3, 134.5, 129.5, 129.3, 127.4, 127.3, 126.5, 125.5, 125.3, 122.1, 121.1, 105.7, 98.7, 68.5, 57.3. MS (EI, 70 eV) *m/z* (relative intensity): 338 (1), 334 (37), 254 (23), 179 (50), 151 (100), 125 (13), 76 (8). Anal. (%) Calcd for C<sub>16</sub>H<sub>14</sub>OSe: C 67.66, H 4.18. Found: C 67.44, H 3.79.

**4-Phenylphenyl 3-Phenylselenylprop-2-yn-1-yl Ether (2i):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.361 g (75%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 7.55-7.38 (m, 8H), 7.31-7.21 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.91 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 50 MHz, δ(ppm): 157.0, 140.5, 134.5, 129.4, 129.3, 128.7, 128.1, 127.2, 126.8, 126.7, 115.2, 98.5, 68.4, 56. MS (EI, 70 eV) *m/z* (relative intensity): 360 (50), 280 (24), 204 (100), 176 (40), 150 (29), 125 (7), 101 (4), 77 (11). HRMS calcd for C<sub>21</sub>H<sub>16</sub>OSe: 489.9333 . Found: 489.9329.

**3-(4-Methoxyl-Phenylselenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2j):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 1.075 g (65%).  
<sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.43-7.37 (m, 4H), 6.81-6.78 (m, 4H), 4.80 (s, 2H), 3.76 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 159.1, 134.5, 132.2, 130.6, 129.8, 122.0, 115.2, 114.9, 97.3, 69.3, 57.0, 55.2, 20.4. MS (EI, 70 eV) *m/z* (relative intensity): 331 (2), 328 (22), 248 (18), 222 (12), 144 (100), 114 (27), 106 (10), 76 (7). Anal. (%) Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>Se: C 61.44, H 4.59. Found: C 61.64, H 4.87.

**3-(3-Trifluoromethyl-Phenylselenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2k):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.160 g (65%).  
<sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.74 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.11-7.09 (m, 2H), 6.90-6.86 (m, 2H), 4.88 (s, 2H), 2.29 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.3, 132.2, 131.6, 130.9, 129.9, 129.7, 129.5, 125.6 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 3.7 Hz), 114.8, 100.3, 56.9, 55.8, 20.4. MS (EI, 70 eV) *m/z* (relative intensity): 367 (3), 260 (70), 181 (100), 144 (35), 132 (18), 116 (65), 76 (27). Anal. (%) Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>OSe: C 55.30, H 3.55. Found: C 55.61, H 3.84.

**3-(1-Naphthylselenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2l):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.053 g (60%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.98-7.95 (m, 1H), 7.90-7.88 (m, 1H), 7.79-7.77 (m, 1H), 7.53-7.50 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.07-7.05 (m, 2H), 6.88-6.84 (m, 2H), 4.83 (s, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.4, 133.9, 132.1, 130.7, 129.8, 129.6, 128.6, 128.5, 126.8, 126.5, 126.4, 126.1, 125.5, 114.9, 98.6, 68.1, 57.1, 20.5. MS (EI, 70 eV) *m/z* (relative intensity): 351 (3), 350 (10), 348 (42), 268 (41), 144 (100), 114 (65), 101 (8), 90 (20), 76 (7). Anal. (%) Calcd for C<sub>20</sub>H<sub>16</sub>OSe: C 68.38, H 4.59. Found: C 68.71, H 4.81.

**3-(Butylselenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2m):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.772 g (55%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.09-7.06 (m, 2H), 6.88-6.85 (m, 2H), 4.76 (s, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.74 (quint, *J* = 7.3 Hz, 2H), 1.40 (sext, *J* = 7.3, 2H), 0.9 (t, *J* = 7.3, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.5, 129.9, 129.8, 114.8, 114.7, 95.2, 57.1, 32.1, 28.9, 22.4, 20.4, 13.4. MS (EI, 70 eV) *m/z* (relative intensity): 281 (1), 279 (4), 223 (10), 172 (18), 144 (47), 131 (24), 116 (100), 106 (76), 92 (84), 76 (63), 56 (38). Anal. (%) Calcd for C<sub>18</sub>H<sub>14</sub>OSe: C 59.79, H 6.45. Found: C 60.00, H 6.19.

**3-(Propylselenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2n):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.667 g (50%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.08-7.05 (m, 2H), 6.86-6.84 (m, 2H), 4.75 (s, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.78 (sext, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 50 MHz, δ(ppm): 155.5, 130.5, 129.7, 114.7, 95.1, 75.2, 57.0, 31.2, 23.4, 20.4, 13.9. MS (EI, 70 eV) *m/z* (relative intensity): 265 (3), 204 (7), 159 (48), 144 (25), 116 (100), 106 (56), 76 (38), 43 (81). Anal. (%) Calcd for C<sub>13</sub>H<sub>16</sub>OSe: C 58.43, H 6.03. Found: C 58.76, H 6.31.

**3-(Ethylselenenyl)prop-2-yn-1-yl 4-Methylphenyl Ether (2o):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.695 g (55%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.10-7.06 (m, 2H), 6.88-6.84 (m, 2H), 4.77 (s, 2H), 2.77 (q, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.50 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.6, 129.8, 114.8, 114.7, 95.8, 68.7, 57.1, 22.7, 20.4, 15.6. MS (EI, 70 eV) *m/z* (relative intensity): 251 (3), 172 (14), 145 (60), 144 (36), 116 (100), 106 (34), 76 (29). Anal. (%) Calcd for C<sub>12</sub>H<sub>14</sub>OSe: C 56.92, H 5.57. Found: C 57.19, H 5.80.

**4-Methylphenyl 3-Phenylsulfurylprop-2-yn-1-yl Ether (2p):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.825 g (65%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.38-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.19 (m, 1H), 7.11-7.09 (m, 2H), 6.91-6.88 (m, 2H), 4.88 (s, 2H), 2.29 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.4, 132.1, 130.8, 129.9, 129.1, 126.7, 126.5, 114.9, 94.2, 74.7, 57.0, 20.5. MS (EI, 70 eV) *m/z* (relative intensity): 252 (2), 250 (10), 146 (86), 145 (44), 144 (12), 102 (100), 76 (27). HRMS calcd for C<sub>16</sub>H<sub>14</sub>OS: 254.0765. Found: 254.0769.

**4-Methylphenyl 3-Methylsulfonylprop-2-yn-1-yl Ether (2q):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.614 g (64%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.09-7.06 (m, 2H), 6.85-6.82 (m, 2H), 4.72 (s, 2H), 2.35 (s, 3H), 2.28 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.5, 129.8, 114.7, 99.9, 88.2, 79.8, 56.9, 20.4, 18.9. MS (EI, 70 eV) *m/z* (relative intensity): 190 (2), 175 (10), 144 (9), 116 (31), 106 (10), 84 (100), 76 (14), 69 (18). Anal. (%) Calcd for C<sub>11</sub>H<sub>12</sub>OS: C 68.71, H 6.29. Found: C 68.92, H 6.64.

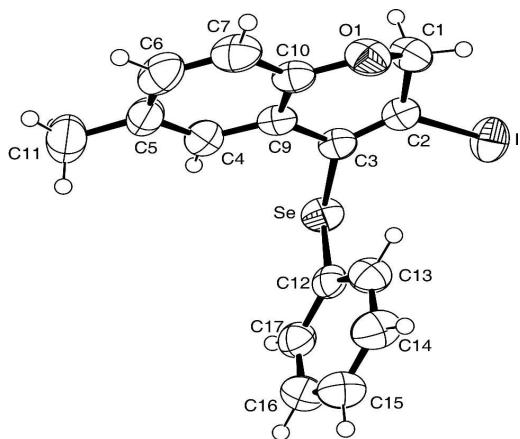
**4-Methylphenyl 3-Phenyltellurylprop-2-yn-1-yl Ether (2r):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.312 g (75%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.64-7.62 (m, 2H), 7.28-7.19 (m, 3H), 7.08-7.06 (m, 2H), 6.89-6.85 (m, 2H), 4.9 (s, 2H), 2.28 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 50 MHz, δ(ppm): 155.4, 135.4, 130.7, 129.8, 129.6, 127.9, 114.8, 110.0, 78.1, 68.7, 57.2, 20.5. MS (EI, 70 eV) *m/z* (relative intensity): 350 (1), 348 (7), 219 (4), 144 (30), 114 (100), 106 (15), 76 (19). HRMS calcd for C<sub>16</sub>H<sub>14</sub>OTe: 352.0107. Found: 352.0111.

**4-Methylphenyl 3-Buthyltellurylprop-2-yn-1-yl Ether (2s):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 1.072 g (65%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.10-7.05 (m, 2H), 6.88-6.85 (m, 2H), 4.86 (s, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.82 (quint, *J* = 7.5 Hz, 2H), 1.38 (sext, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.6, 130.6, 129.8, 114.8, 107.0, 57.3, 43.1, 33.6, 24.6, 20.4, 13.2, 9.55. MS (EI, 70 eV) *m/z* (relative intensity): 329 (5), 328 (16), 272 (11), 222 (28), 165 (69), 144 (64), 129 (11), 116 (63), 106 (94), 94 (67), 76 (55), 56 (37), 41 (100). HRMS calcd for C<sub>14</sub>H<sub>18</sub>OTe: 332.0420. Found: 332.0417.

**General Procedure for the I<sub>2</sub> Cyclization.** To a solution of the appropriate organochalcogen propargyl aryl ether (0.25 mmol) in 3 mL of THF, was added NaHCO<sub>3</sub> (0.5 mmol). After that, was added gradually I<sub>2</sub> (3 equiv) in 2 mL of THF. The reaction mixture was allowed to stir at room temperature for the time shown in the Table 4. Excess I<sub>2</sub> was removed by washing with saturated aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The product was then extracted by

ethyl acetate ( $3 \times 5$  mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$  and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel.

**3-Iodo-6-methyl-4-phenylselenenyl-2H-benzopyran (3a):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.088 g (83%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 400 MHz,  $\delta$ (ppm): 7.36-7.32 (m, 3H), 7.21-7.15 (m, 3H), 6.92-6.89 (m, 1H), 6.70 (d,  $J = 8.3$  Hz, 1H), 4.95 (s, 2H), 2.14 (s, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 151.1, 134.1, 131.4, 131.1, 130.3, 129.8, 129.3, 126.6, 123.2, 115.7, 105.3, 75.8, 20.6. MS (EI, 70 eV)  $m/z$  (relative intensity): 427 (15), 301 (21), 221 (71), 157 (18), 144 (15), 115 (100), 102 (3), 77 (94), 63 (44), 51 (71). Anal. (%) Calcd for  $\text{C}_{16}\text{H}_{13}\text{IOSe}$ : C 44.99, H 3.07. Found: C 45.21, H 3.23.



**Figura 1.** X-ray structure of compound **3a**.

**3-Iodo-5-methoxyl-4-phenylselenenyl-2H-benzopyran (3e):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.083 g (75%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 400 MHz,  $\delta$ (ppm): 7.44 (d,  $J = 8.4$  Hz, 1H), 7.33-7.30 (m, 2H), 7.22-7.15 (m, 3H), 6.38 (d,  $J = 2.6$  Hz, 1H), 6.32 (dd,  $J = 8.7$  Hz and  $J = 2.6$  Hz, 1H), 4.97 (s, 2H), 3.73 (s, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 160.9, 154.4, 133.7, 131.1, 130.6, 130.2, 129.3, 126.6, 116.9, 107.9, 101.6, 100.8, 75.8, 55.3. MS (EI, 70 eV)  $m/z$  (relative intensity): 443 (1), 439 (35), 313 (95), 283 (13), 234 (100), 192 (18), 153 (8), 131 (24), 116 (21), 101 (16), 76 (25). Anal. (%) Calcd for  $\text{C}_{16}\text{H}_{13}\text{IO}_2\text{Se}$ : C 43.37, H 2.96. Found: C 43.51, H 3.11.

**3-Iodo-7-chloro-4-phenylselenenyl-2H-benzopyran (3f):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.070 g (63%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 200 MHz,  $\delta$ (ppm): 7.62-7.57 (m, 2H), 7.42-7.39 (m, 2H), 7.30-7.16 (m, 3H), 6.87-6.80 (m, 1H), 4.82 (s, 2H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 158.2, 136.8, 130.9, 130.3, 129.8, 129.4, 129.1, 121.8, 116.1, 113.9, 99.4, 89.3, 80.9. MS (EI, 70 eV)  $m/z$  (relative intensity): 446 (2), 444 (17), 318 (5), 192 (35), 153 (3), 114 (100), 102 (14), 88 (7), 76 (11), 50 (15). Anal. (%) Calcd for  $\text{C}_{15}\text{H}_{10}\text{ClIOSe}$ : C 40.25, H 2.25. Found: C 40.42, H 2.39.

**3-Iodo-5-chloro-4-phenylselenyl-2H-benzopyran (3f')**: Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.029 g (26%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 7.45 (d, *J* = 8.3 Hz, 1H), 7.35-7.28 (m, 2H), 7.23-7.16 (m, 3H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.74 (dd, *J* = 8.3 Hz and *J* = 2.0 Hz, 1H), 5.00 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 50 MHz, δ(ppm): 153.7, 134.9, 133.4, 130.6, 130.4, 130.3, 129.5, 126.9, 122.3, 116.5, 105.0, 97.6, 75.9. MS (EI, 70 eV) *m/z* (relative intensity): 447 (4), 443 (24), 317 (68), 283 (61), 253 (9), 238 (100), 203 (34), 176 (49), 135 (48), 100 (48), 76 (36), 51 (36). Anal. (%) Calcd for C<sub>15</sub>H<sub>10</sub>ClIOSe: C 40.25, H 2.25. Found: C 40.35, H 2.39.

**3-Iodo-4-phenylselenyl-2H-benzo[*h*]chromene (3g)**: Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.089 g (77%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 8.16-8.13 (m, 1H), 7.69-7.65 (m, 2H), 7.47-7.42 (m, 2H), 7.36-7.32 (m, 2H), 7.24-7.21 (m, 1H), 7.18-7.12 (m, 3H), 5.17 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 149.4, 134.7, 134.2, 131.1, 130.3, 129.4, 127.5, 127.1, 126.7, 126.6, 125.8, 124.2, 121.9, 121.2, 118.3, 102.0, 76.1. MS (EI, 70 eV) *m/z* (relative intensity): 462 (3), 459 (29), 333 (50), 254 (63), 225 (24), 166 (12), 150 (100), 125 (21), 76 (18), 50 (12). HRMS calcd for C<sub>19</sub>H<sub>13</sub>IOSe: 463.9176. Found: 463.9189.

**2-Iodo-1-phenylselenyl-2H-benzo[*f*]chromene (3h)**: Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.095 g (82%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 8.60 (d, *J* = 8.3 Hz, 1H), 7.64-7.57 (m, 2H), 7.42-7.33 (m, 1H), 7.28-7.20 (m, 1H), 7.13-7.04 (m, 3H), 6.99-6.93 (m, 3H), 4.88 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 154.2, 132.4, 131.5, 131.0, 130.9, 129.9, 129.8, 128.7, 127.9, 126.6, 126.1, 125.5, 124.0, 118.9, 116.7, 99.2, 76.5. MS (EI, 70 eV) *m/z* (relative intensity): 461 (4), 459 (15), 333 (51), 254 (51), 223 (13), 150 (100), 125 (17), 101 (6), 76 (16), 44 (26). Anal. (%) Calcd for C<sub>19</sub>H<sub>13</sub>IOSe: C 49.27, H 2.83. Found: C 49.51, H 2.97.

**3-Iodo-6-phenyl-4-phenylselenyl-2H-benzopyran (3i)**: Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.078 g (64%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.74 (s, 1H), 7.40-7.16 (m, 11H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.01 (s, 2H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 152.8, 140.3, 135.2, 134.3, 131.1, 130.7, 129.4, 128.6, 128.4, 128.3, 126.9, 126.8, 126.6, 123.2, 116.4, 104.6, 75.9. MS (EI, 70 eV) *m/z* (relative intensity): 488 (1), 484 (70), 359 (47), 329 (18), 280 (100), 252 (19), 203 (17), 174 (61), 150 (65), 101 (10), 76 (26). HRMS calcd for C<sub>21</sub>H<sub>15</sub>IOSe: 489.9333. Found: 489.9329.

**3-Iodo-6-methyl-4-(4-methoxyphenylselenyl)-2H-benzopyran (3j)**: Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.085 g (75%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.39 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.91-6.88 (m, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.91 (s, 2H), 3.73 (s, 3H), 2.17 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 159.1, 135.0, 133.2, 131.3, 130.2, 129.9, 123.3, 121.0, 115.0, 103.8, 99.9, 75.8, 55.2, 20.6. MS (EI, 70 eV) *m/z* (relative intensity): 456 (4), 453 (56), 327 (53), 312 (11), 283 (6), 248 (92), 232 (26), 216 (18), 205 (59), 143 (31), 114 (100), 107 (7), 77 (9). HRMS calcd for C<sub>17</sub>H<sub>15</sub>IO<sub>2</sub>Se: 457.9282. Found: 457.9286.

**3-Iodo-6-methyl-4-(3-trifluorophenylselenyl)-2H-benzopyran (3k)**: Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.084 g (68%). <sup>1</sup>H

NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.63 (s, 1H), 7.45-7.41 (m, 2H), 7.31-7.25 (m, 2H), 6.95-6.92 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 2H), 2.15 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.2, 133.7, 133.4, 133.3, 132.3, 131.6, 131.3, 130.6, 129.6, 129.5, 126.9 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 3.7 Hz), 122.9, 115.9, 105.8, 75.8, 20.5. MS (EI, 70 eV) *m/z* (relative intensity): 493 (2), 489 (26), 365 (46), 286 (60), 243 (10), 216 (10), 155 (3), 143 (35), 114 (100), 101 (2), 76 (3). Anal. (%) Calcd for C<sub>17</sub>H<sub>12</sub>F<sub>3</sub>IOSe: C 41.24, H 2.44. Found: C 41.40, H 2.62.

**3-Iodo-6-methyl-4-(1-naphthylselenyl)-2*H*-benzopyran (3l):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.071 g (60%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 8.21 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.3, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60-7.44 (m, 3H), 7.30-7.23 (m, 2H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.98 (s, 2H), 2.00 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.1, 134.3, 134.0, 132.7, 131.4, 130.3, 130.1, 129.5, 128.8, 128.6, 127.5, 126.5, 126.2, 126.1, 126.0, 123.3, 115.7, 105.0, 75.9, 20.4. MS (EI, 70 eV) *m/z* (relative intensity): 474 (3), 472 (6), 347 (88), 332 (12), 266 (59), 143 (10), 126 (27), 114 (100), 101 (6), 76 (8). Anal. (%) Calcd for C<sub>20</sub>H<sub>15</sub>IOSe: C 50.34, H 3.17. Found: C 50.61, H 3.36.

**3-Iodo-6-methyl-4-(Butylselenyl)-2*H*-benzopyran (3m):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.071 g (70%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.47 (s, 1H), 6.98-6.96 (m, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.85 (s, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.62 (quint, *J* = 7.3 Hz, 2H), 1.40 (sext, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.1, 134.2, 131.5, 130.1, 129.5, 123.5, 115.9, 102.9, 75.7, 32.1, 28.9, 22.7, 20.7, 13.5. MS (EI, 70 eV) *m/z* (relative intensity): 406 (3), 403 (39), 347 (76), 221 (66), 143 (100), 114 (97), 101 (5), 76 (5), 57 (5). Anal. (%) Calcd for C<sub>14</sub>H<sub>17</sub>IOSe: C 41.30, H 4.21. Found: C 41.61, H 4.62.

**3-Iodo-6-methyl-4-(Propylselenyl)-2*H*-benzopyran (3n):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.075 g (77%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.47 (s, 1H), 6.98-6.95 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.84 (s, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.30 (s, 3H), 1.66 (sext, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.1, 134.2, 131.5, 130.1, 129.6, 116.0, 114.7, 103.0, 75.7, 31.3, 23.5, 20.7, 14.4. MS (EI, 70 eV) *m/z* (relative intensity): 392 (30), 389 (40), 347 (67), 221 (64), 143 (98), 114 (100), 101 (6), 77 (5), 41 (22). HRMS calcd for C<sub>13</sub>H<sub>15</sub>IOSe: 393.9333. Found: 393.9337.

**3-Iodo-6-methyl-4-(Ethylselenyl)-2*H*-benzopyran (3o):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.066 g (70%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.47 (s, 1H), 6.98-6.96 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.86 (s, 2H), 2.78 (quart, *J* = 7.3 Hz, 2H), 2.30 (s, 3H), 1.37 (t, *J* = 7.3, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.1, 133.8, 131.5, 130.1, 129.5, 123.5, 115.9, 103.3, 75.7, 22.7, 20.7, 15.4. MS (EI, 70 eV) *m/z* (relative intensity): 379 (3), 376 (55), 347 (76), 221 (60), 143 (77), 114 (100), 101 (6), 77 (6). HRMS calcd for C<sub>12</sub>H<sub>13</sub>IOSe: 379.9176. Found: 379.9179.

**3-Iodo-6-methyl-4-phenylsulfuryl-2*H*-benzopyran (3p):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.049 g (52%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.32 (s, 1H), 7.24-7.19 (m, 4H), 7.15-7.08 (m, 1H), 6.94-6.91 (m, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.97 (s, 2H), 2.14 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 148.0, 137.5, 134.5, 131.8, 130.7, 129.2, 129.1, 127.7, 127.6, 126.1, 117.5, 99.2, 20.7. MS (EI, 70 eV) *m/z* (relative intensity): 379 (2), 376 (61), 250 (100), 235 (38), 218 (27), 207 (14), 114 (57), 88 (14), 76 (11). Anal. (%) Calcd for C<sub>16</sub>H<sub>13</sub>IOS: C 50.54, H 3.45. Found: C 50.28, H 3.20.

**3-Iodo-6-methyl-4-Methylsulfuryl-2*H*-benzopyran (3q):** Purified by flash chromatography and eluted with hexane/ethyl acetate (95:5). Yield: 0.039 g (50%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 7.44 (s, 1H), 6.99-6.96 (m, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 4.84 (s, 2H), 2.30 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 151.6, 137.4, 131.3, 130.1, 126.9, 121.6, 116.1, 100.7, 75.5, 20.7, 17.8. MS (EI, 70 eV) *m/z* (relative intensity): 317 (2), 314 (100), 189 (77), 174 (42), 156 (15), 146 (37), 114 (51), 102 (8), 88 (21), 76 (5), 43 (17). Anal. (%) Calcd for C<sub>11</sub>H<sub>11</sub>IOS: C 41.52, H 3.48. Found: C 41.19, H 3.27.

**4-Methylphenyl 3-Iodoprop-2-yn-1-yl Ether (4):** Purified by flash chromatography and eluted with hexane. Yield: 0.048 g (71%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 400 MHz, δ(ppm): 7.09 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 2H), 2.29 (s, 3H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 155.4, 130.8, 129.9, 114.7, 89.4, 57.4, 20.5, 4.3. MS (EI, 70 eV) *m/z* (relative intensity): 271 (6), 269 (53), 254 (46), 163 (85), 144 (85), 116 (100), 106 (40), 90 (82), 76 (70), 64 (11), 52 (32).

**4-Hidroxyphenyl 3-Phenylselenylprop-2-yn-1-yl Ether (5):** Purified by flash chromatography and eluted with hexane/ethyl acetate (80:20). Yield: 0.034 g (45%). <sup>1</sup>H NMR: CDCl<sub>3</sub>, 200 MHz, δ(ppm): 7.45-7.19 (m, 5H), 6.49 (d, *J* = 10.0 Hz, 2H), 5.98 (d, *J* = 10.0 Hz, 2H), 4.84 (s, 2H), 1.65 (s, 1H). <sup>13</sup>C NMR: CDCl<sub>3</sub>, 100 MHz, δ(ppm): 184.9, 145.6, 135.2, 134.0, 129.3, 128.9, 128.5, 127.6, 104.7, 88.3, 82.0. MS (EI, 70 eV) *m/z* (relative intensity): 303 (6), 300 (55), 272 (12), 192 (41), 155 (19), 114 (100), 102 (15), 88 (17), 76 (22), 51 (12).

**General Procedure for the ICl cyclization.** To a solution of the appropriate organochalcogen propargyl aryl ether (0.25 mmol) in 3 mL of THF, was added gradually ICl (1.5 equiv) in 2 mL of THF at -25 °C. The reaction mixture was allowed to stir at this temperature for the time shown in the Table 4 and washed with saturated aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The product was extracted by ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel.

**General Procedure for the Palladium-catalyzed Coupling Reaction of 3m with Organozinc Reagents.** To a Schlenck tube, under argon, containing a solution of **3m** (0.25 mmol) in THF (3 mL) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), was added the organozinc compound (0.75 mmol) in THF (2 mL), previously prepared. The yellow mixture was stirred at room temperature for 24h. The reaction mixture was then quenched with aqueous NH<sub>4</sub>Cl (5 mL),

washed with  $\text{CH}_2\text{Cl}_2$  (3 x 5 mL), dried with  $\text{MgSO}_4$ , and the solvent removed under vacuum. The residue was purified by flash chromatography on silica gel.

**3-(4-Methylphenyl)-6-methyl-4-buthylselenyl-2H-benzopyran (6b):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.071 g (77%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 400 MHz,  $\delta$ (ppm): 7.56 (s, 1H), 7.20 (s, 4H), 6.99-6.95 (m, 1H), 6.80 (d,  $J$  = 8.2 Hz, 1H), 4.80 (s, 2H), 2.44 (t,  $J$  = 7.3 Hz, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 1.4 (quint,  $J$  = 7.3 Hz, 2H), 1.17 (sext,  $J$  = 7.3 Hz, 2H), 0.74 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 151.8, 140.9, 137.8, 136.3, 130.1, 129.3, 128.9, 128.8, 128.7, 124.3, 115.7, 99.9, 70.4, 31.7, 27.2, 22.5, 21.3, 20.8, 13.4. MS (EI, 70 eV)  $m/z$  (relative intensity): 371 (3), 368 (30), 311 (100), 294 (8), 232 (75), 216 (13), 190 (15), 176 (5), 163 (7), 151 (5), 127 (4), 114 (9), 76 (2), 55 (2). Anal. (%) Calcd for  $\text{C}_{21}\text{H}_{24}\text{OSe}$ : C 67.92, H 6.51. Found: C 68.12, H 6.75.

**3-(2-Thienyl)-6-methyl-4-buthylselenyl-2H-benzopyran (6c):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.063 g (70%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 400 MHz,  $\delta$ (ppm): 7.60 (s, 1H), 7.38 (dd,  $J$  = 5.3 Hz and  $J$  = 1.2 Hz, 1H), 7.21 (dd,  $J$  = 3.8 Hz and  $J$  = 1.2 Hz, 1H), 7.08-7.05 (m, 1H), 6.80 (d,  $J$  = 8.2 Hz, 1H), 4.96 (s, 2H), 2.60 (t,  $J$  = 7.3 Hz, 2H), 2.34 (s, 3H), 1.52 (quint,  $J$  = 7.6 Hz, 2H), 1.28 (sext,  $J$  = 7.6 Hz, 2H), 0.79 (t,  $J$  = 7.6 Hz, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 151.8, 140.3, 132.6, 131.1, 129.5, 129.4, 127.7, 127.0, 126.4, 124.6, 122.6, 115.6, 69.9, 31.9, 28.5, 22.6, 20.8, 13.4. MS (EI, 70 eV)  $m/z$  (relative intensity): 363 (4), 360 (43), 303 (79), 224 (100), 195 (7), 182 (18), 163 (9), 151 (11), 108 (4), 76 (2), 57 (2). Anal. (%) Calcd for  $\text{C}_{18}\text{H}_{20}\text{OSSe}$ : C 59.50, H 5.55. Found: C 59.72, H 5.81.

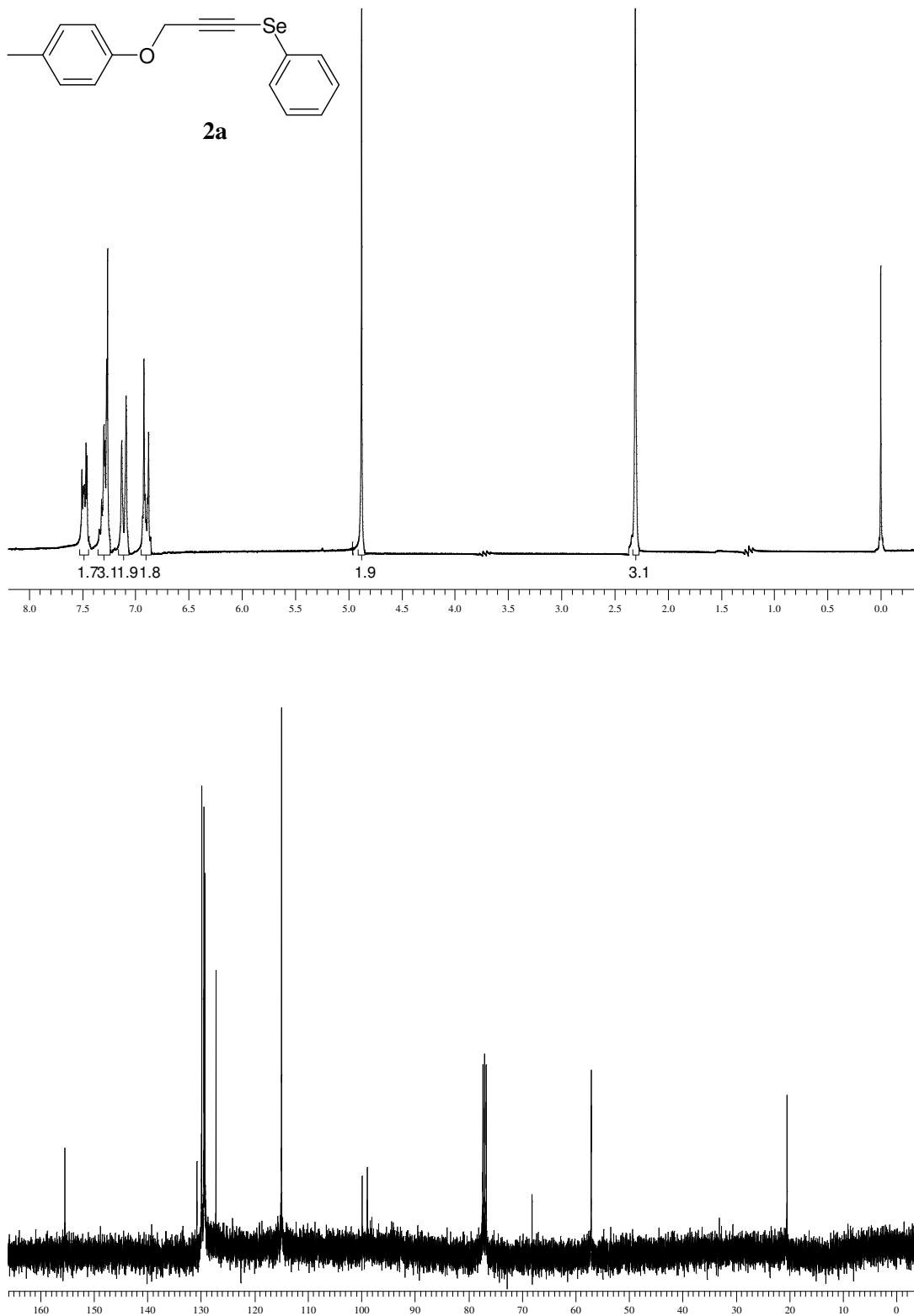
**General Procedure for the Copper-catalyzed Coupling Reaction of 3m with Aryl Thiols.** To a Schlenck tube, under argon, containing a solution of **3m** (0.25 mmol) in dioxane (2 mL) was added the appropriate aryl thiol (0.3 mmol) in 0.5 mL of dioxane. After that was added the CuI (10 mol%) and  $\text{Et}_3\text{N}$  in 0.5 mL of dioxane. The mixture was kept under reflux for 12h. After this time, the mixture was diluted with ethyl acetate (10 mL) and washed with saturated brine (3 x 20 mL). The organic phase was separated, dried over  $\text{MgSO}_4$ , and concentrated under vacuum. The residue was purified by flash chromatography on silica gel.

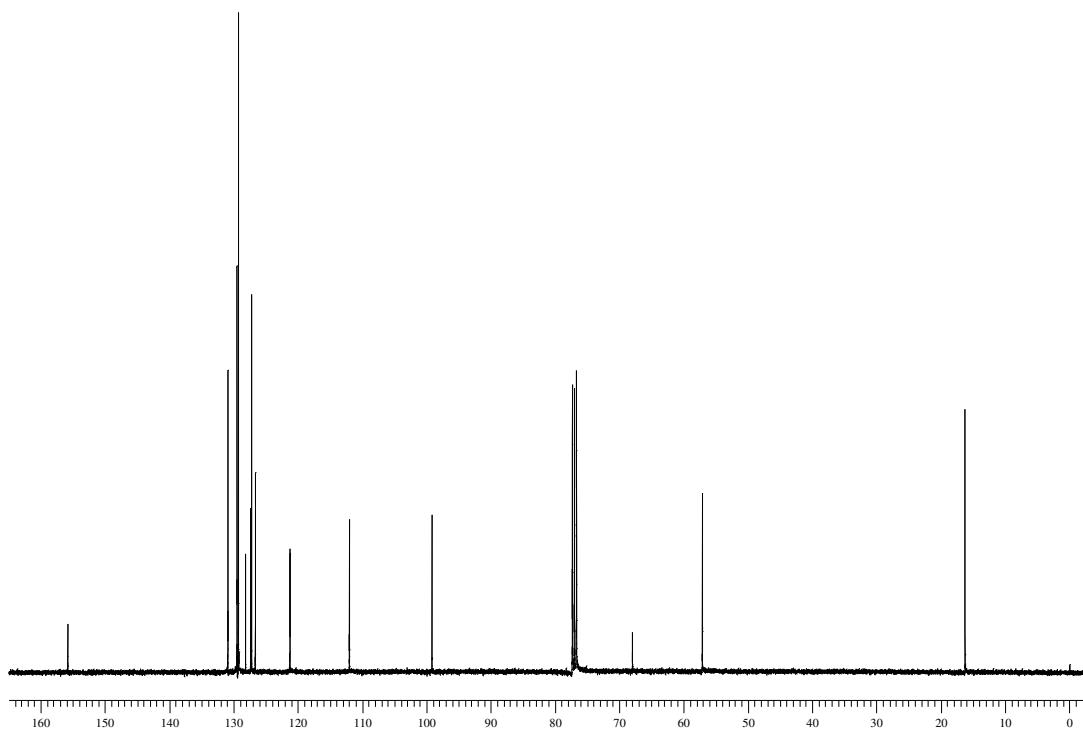
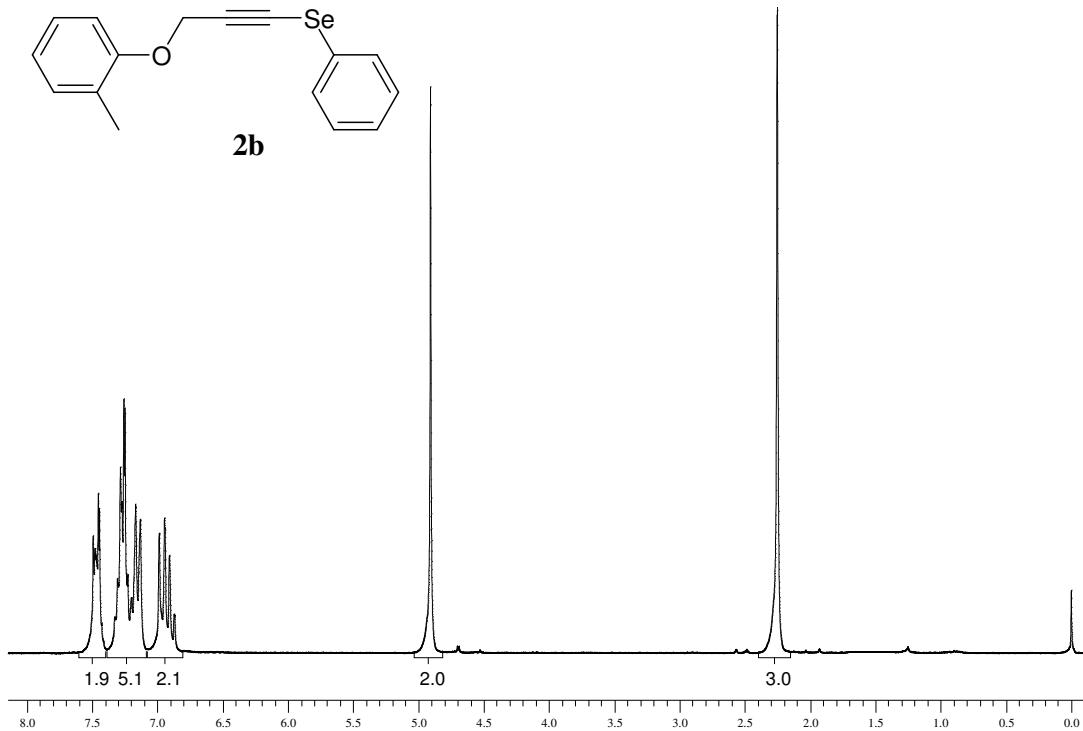
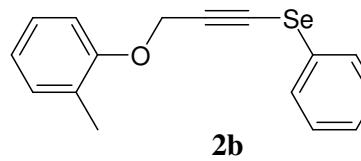
**3-(2-Chlorophenylsulfuryl)-6-methyl-4-buthylselenyl-2H-benzopyran (7b):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.069 g (65%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 200 MHz,  $\delta$ (ppm): 7.51-7.39 (m, 3H), 7.31-7.19 (m, 2H), 7.01-6.96 (m, 1H), 6.77 (d,  $J$  = 8.2 Hz, 1H), 4.49 (s, 2H), 2.80 (t,  $J$  = 7.3 Hz, 2H), 2.34 (s, 3H), 1.71-1.56 (m, 2H), 1.39 (sext,  $J$  = 7.2 Hz, 2H), 0.85 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 100 MHz,  $\delta$ (ppm): 151.6, 135.2, 133.3, 132.6, 131.9, 131.3, 130.1, 129.8, 128.8, 128.7, 128.6, 127.4, 124.1, 115.8, 68.4, 32.3, 28.2, 22.7, 20.8, 13.5. MS (EI, 70 eV)  $m/z$  (relative intensity): 424 (4), 419 (94), 363 (100), 284 (25), 248 (57), 222 (67), 143 (97), 114 (91), 107 (13), 88 (16), 76 (6), 56 (7). HRMS calcd for  $\text{C}_{20}\text{H}_{21}\text{ClOSSe}$ : 424.0167. Found: 424.0171.

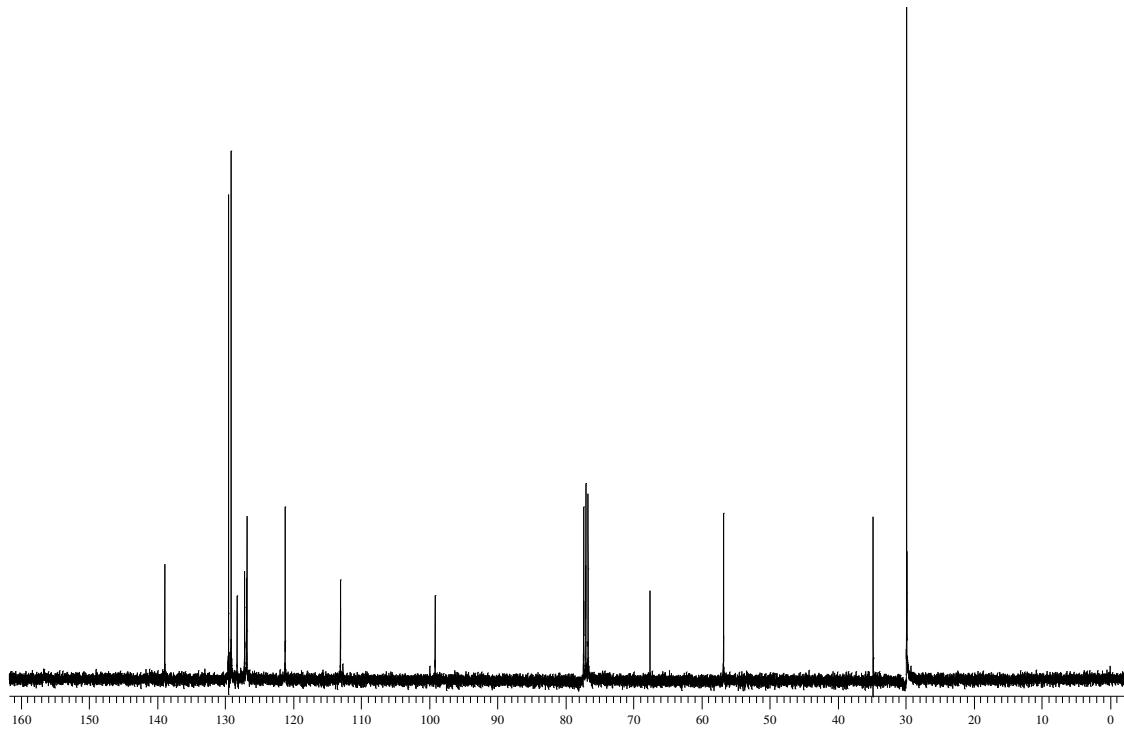
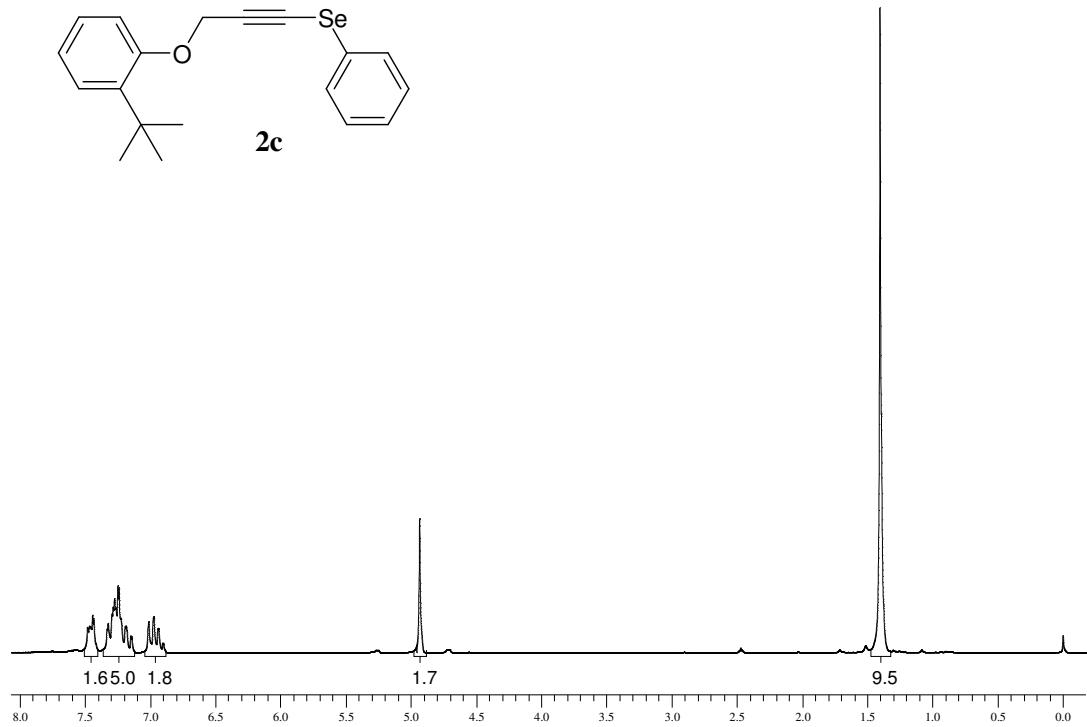
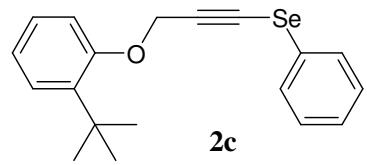
**3-(4-Methoxyphenylsulfuryl)-6-methyl-4-buthylselenyl-2H-benzopyran (7c):** Purified by flash chromatography and eluted with hexane/ethyl acetate (90:10). Yield: 0.095 g (91%).  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 200 MHz,  $\delta$ (ppm): 7.47-7.38 (m, 3H), 6.95-6.82 (m, 3H), 6.70 (d,

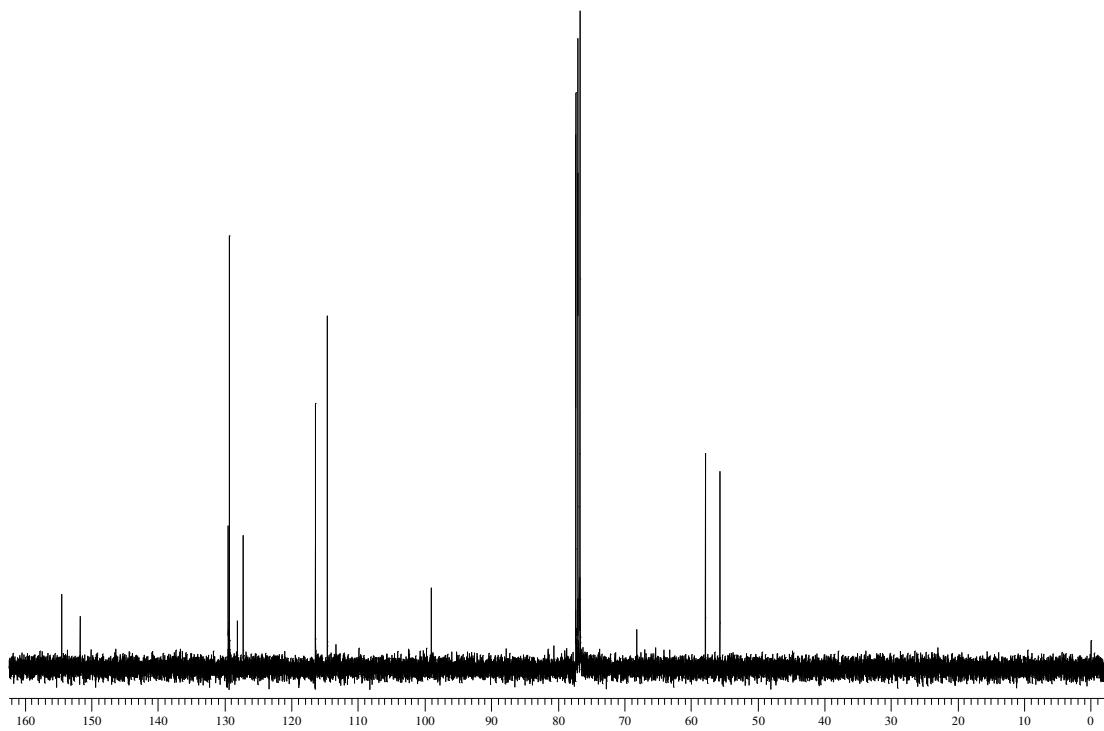
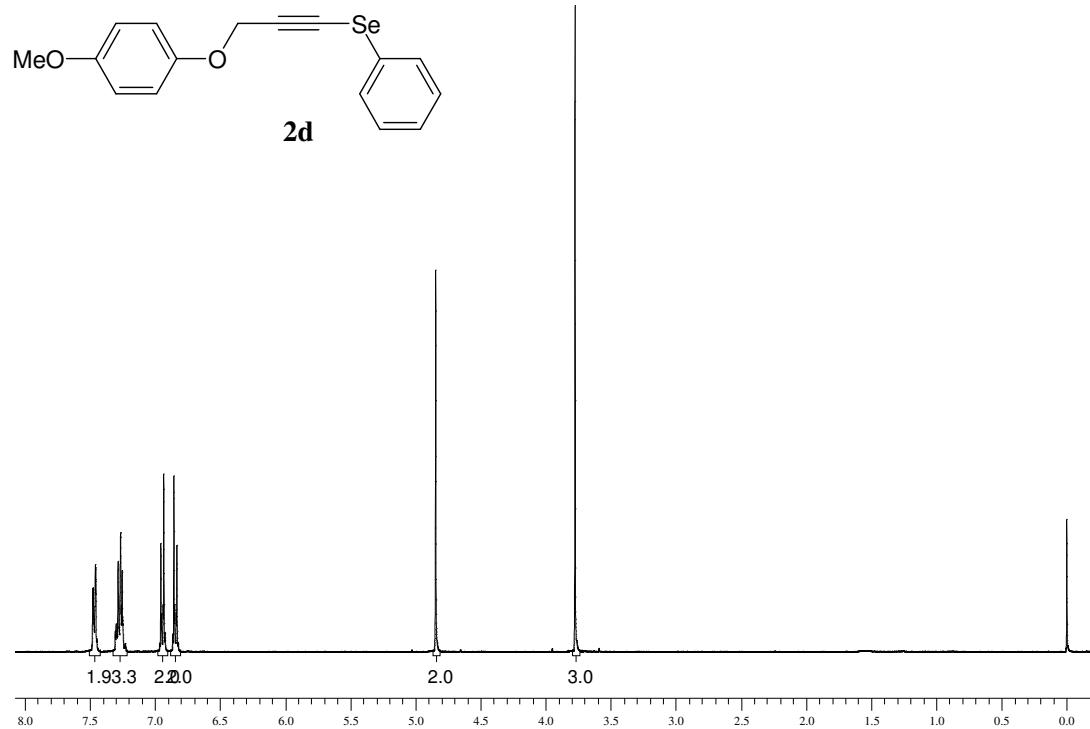
*J* = 8.0 Hz, 1H), 4.40 (s, 2H), 3.82 (s, 3H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.74-1.60 (m, 2H), 1.44 (sext, *J* = 7.8 Hz, 2H), 0.9 (t, *J* = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR: CDCl<sub>3</sub>, 100 MHz,  $\delta$ (ppm): 160.0, 151.0, 137.3, 134.8, 132.6, 131.2, 129.0, 128.0, 124.4, 122.1, 115.6, 114.8, 67.9, 55.3, 32.2, 27.8, 22.8, 20.8, 13.5. MS (EI, 70 eV) *m/z* (relative intensity): 419 (3), 415 (100), 359 (65), 280 (44), 248 (31), 222 (64), 143 (79), 114 (59), 94 (14), 76 (8). Anal. (%) Calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>SSe: C 60.13, H 5.77. Found: C 60.41, H 6.01.

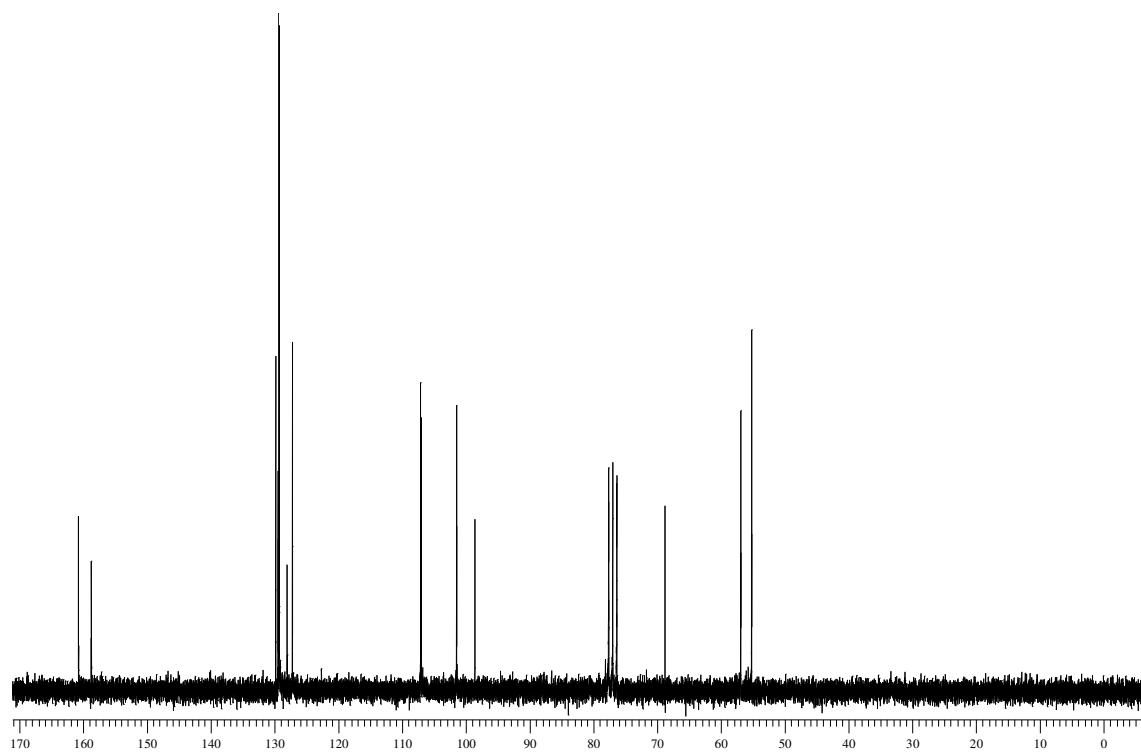
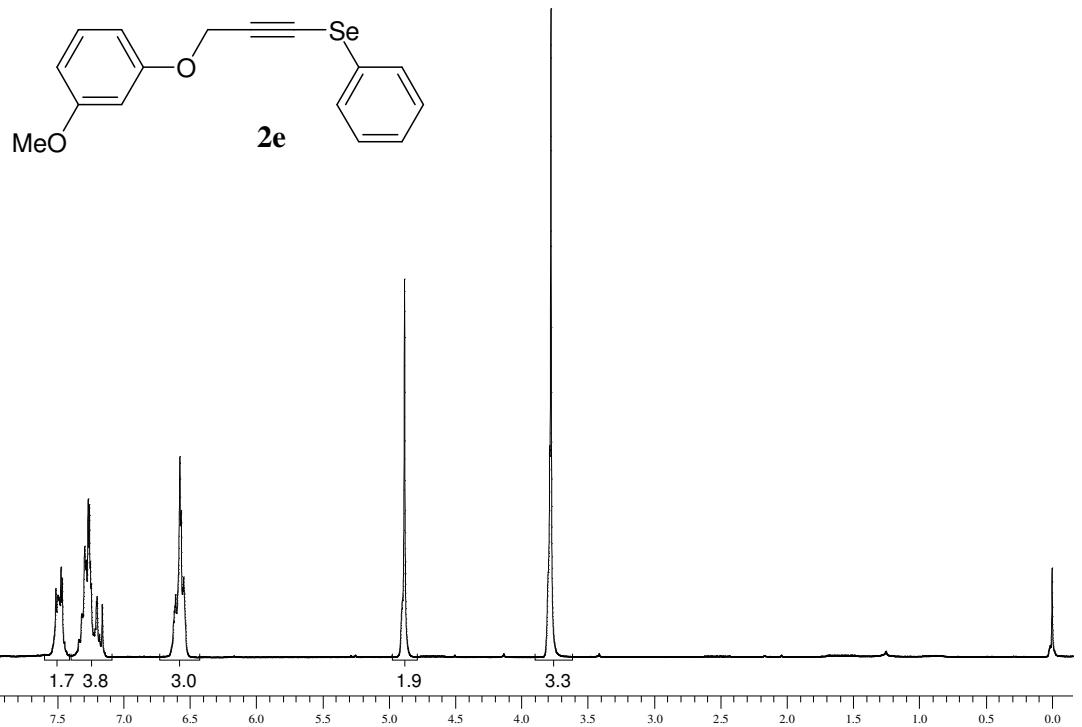
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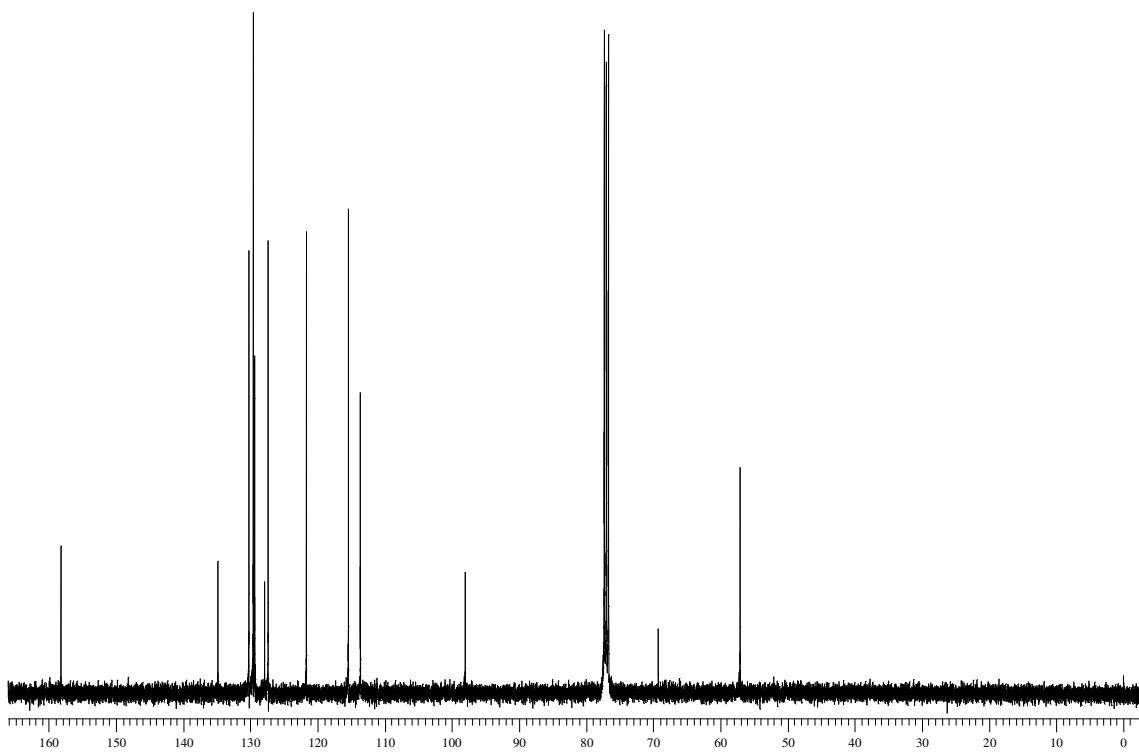
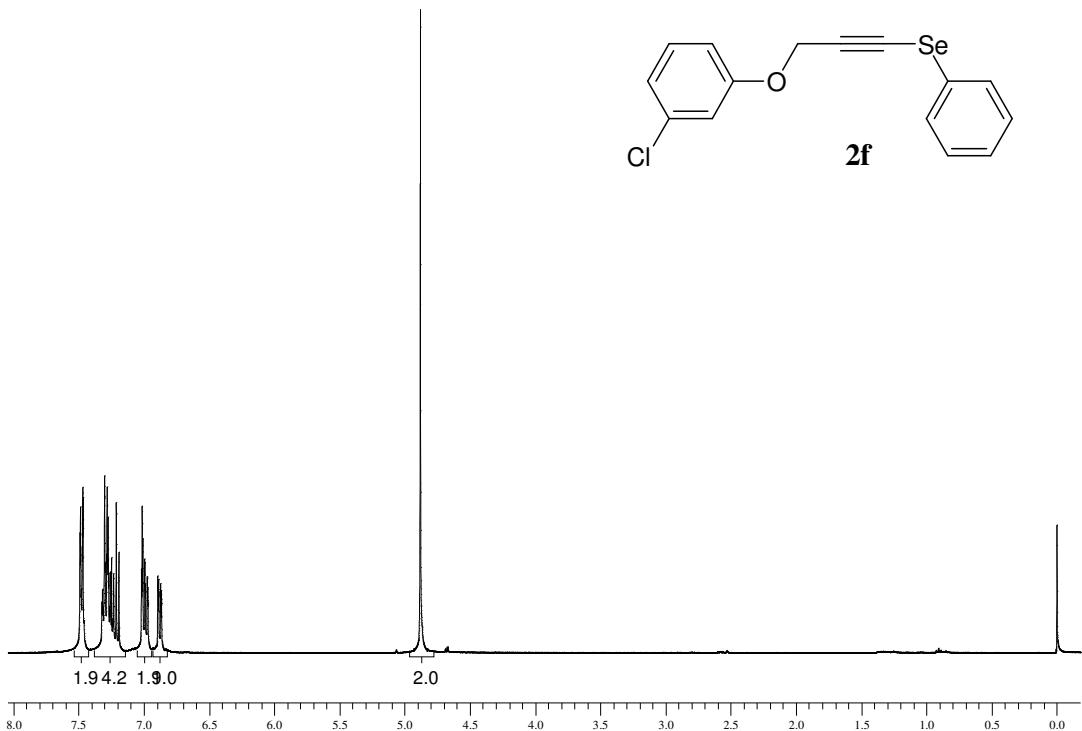


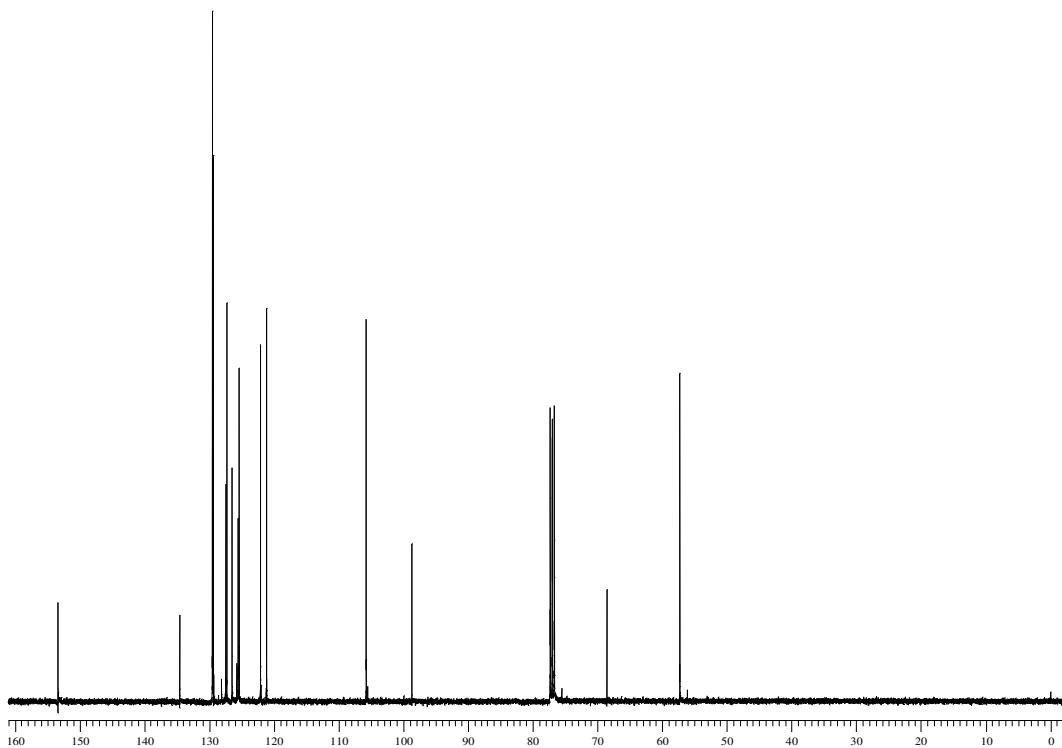
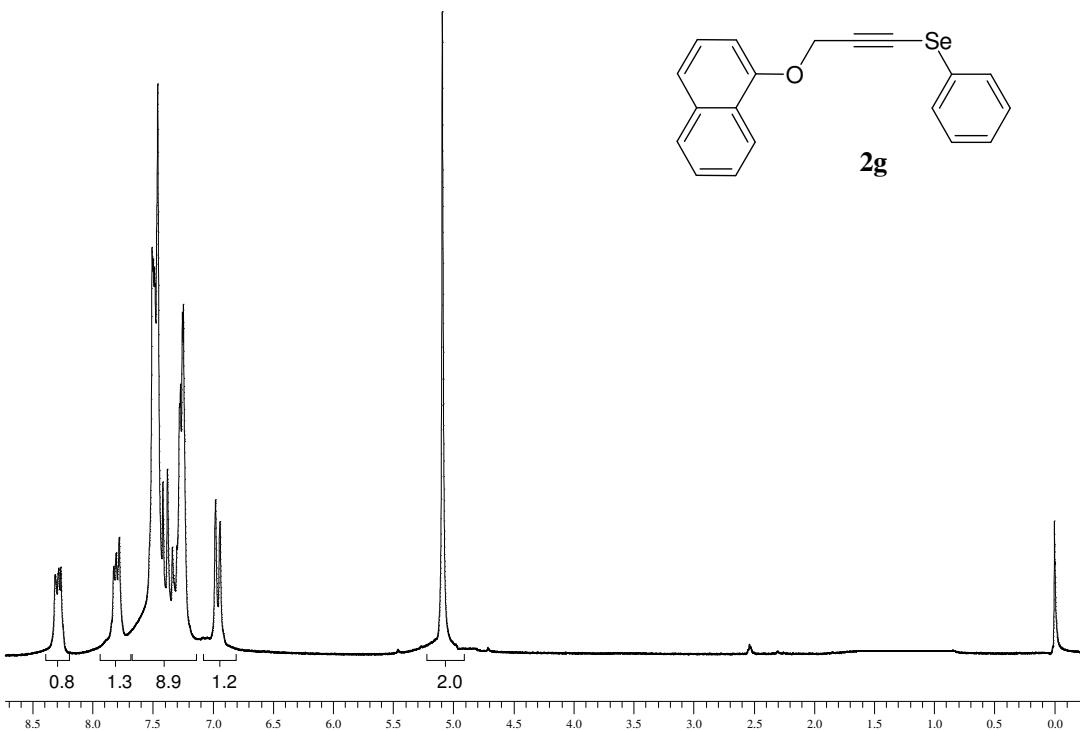


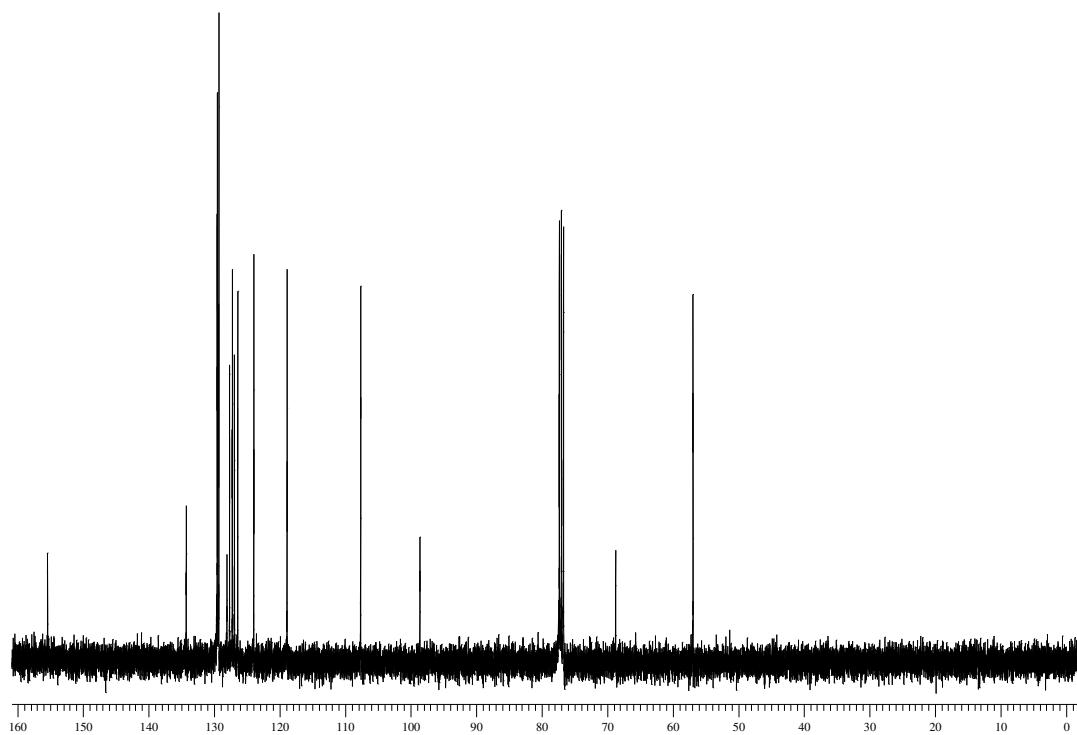
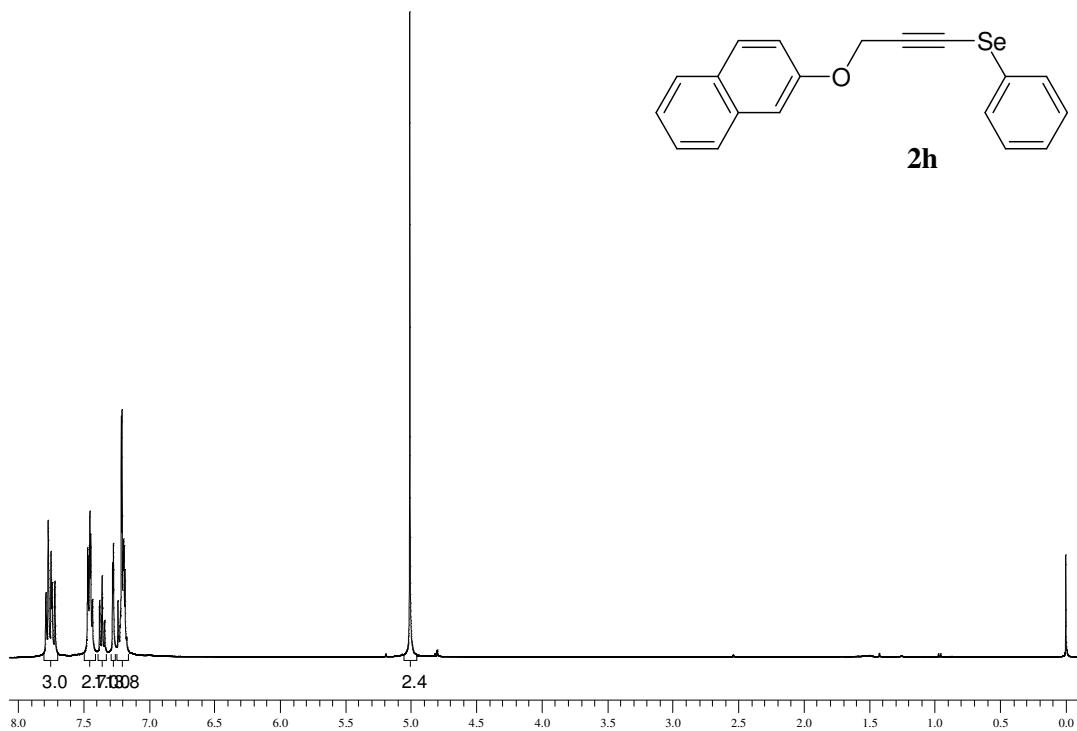
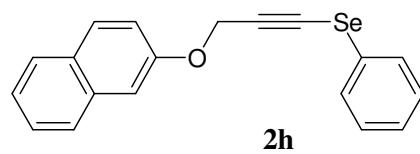


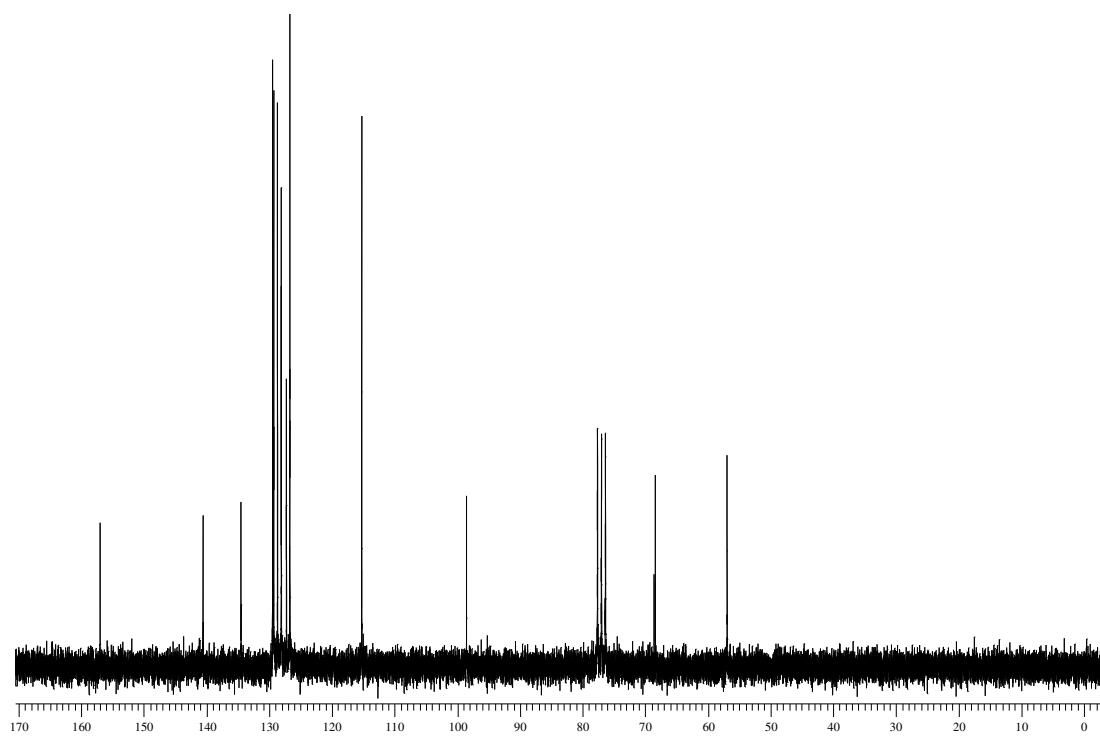
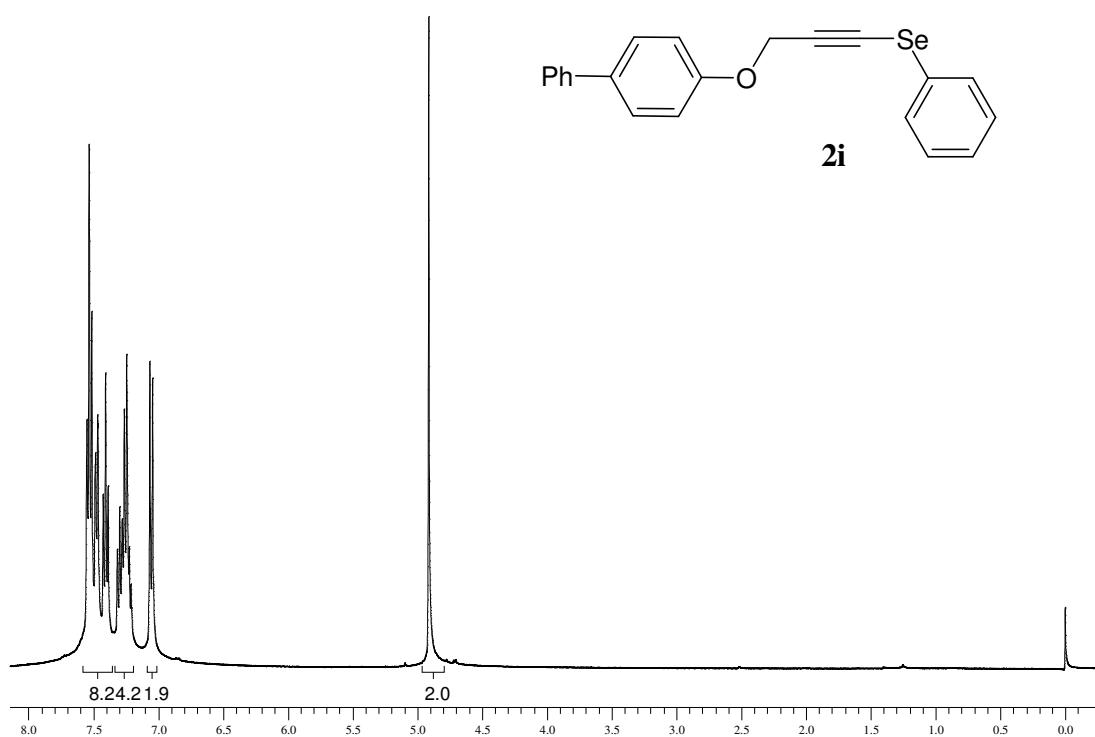
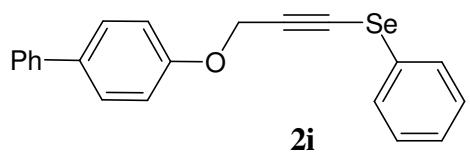


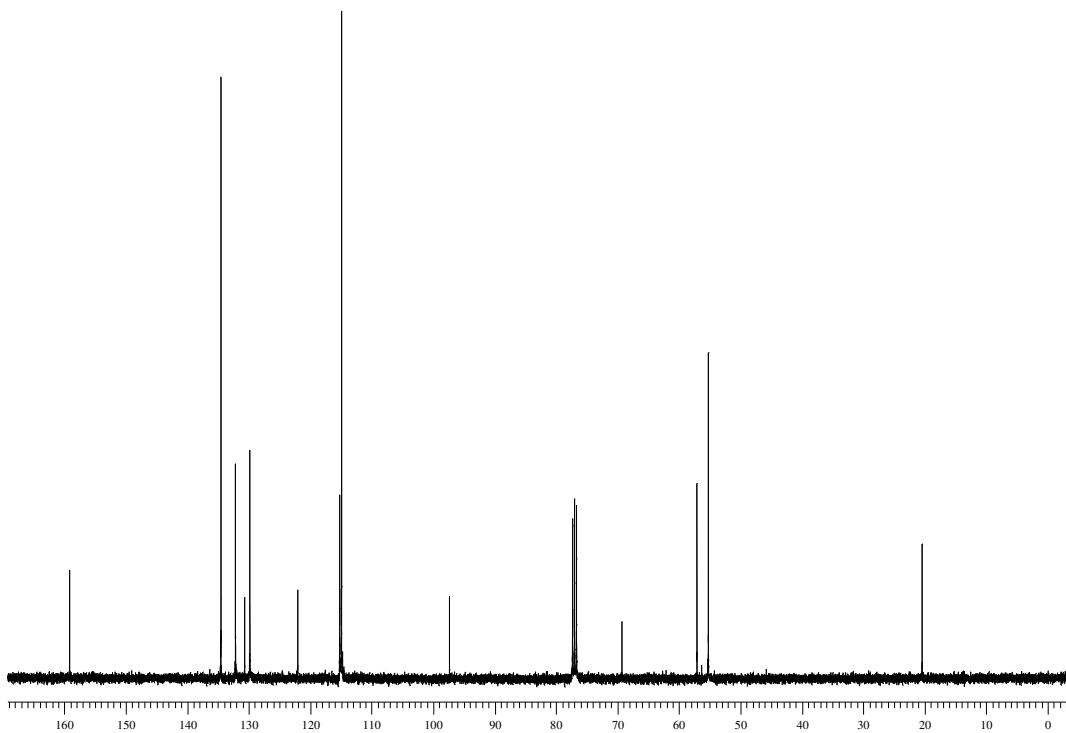
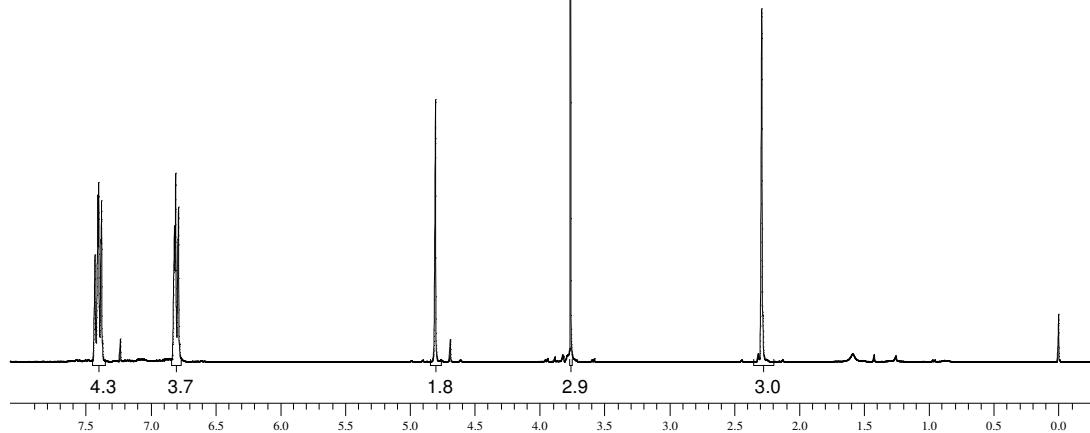
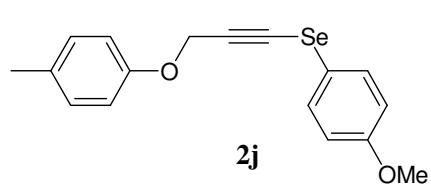


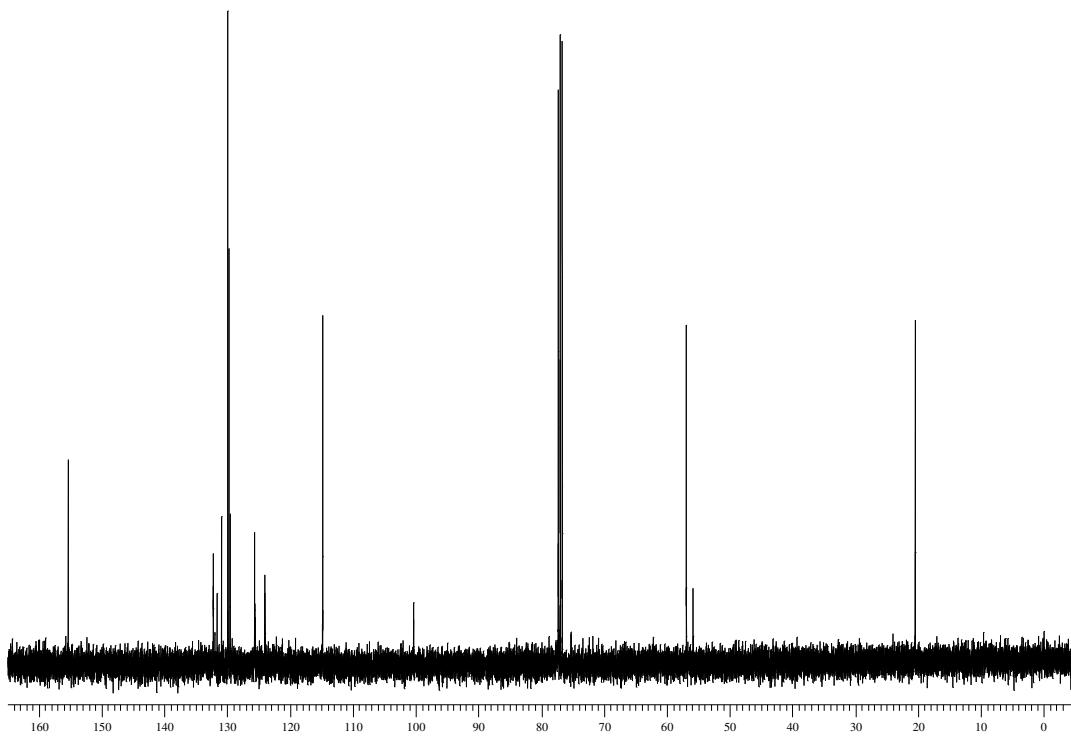
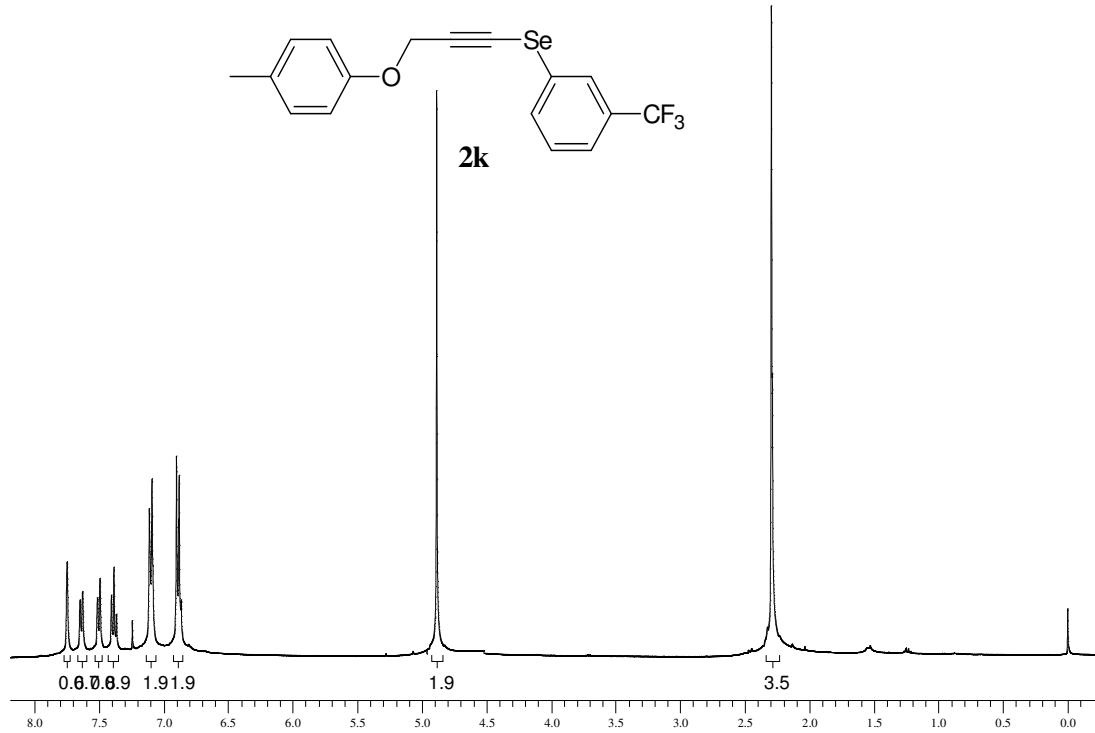


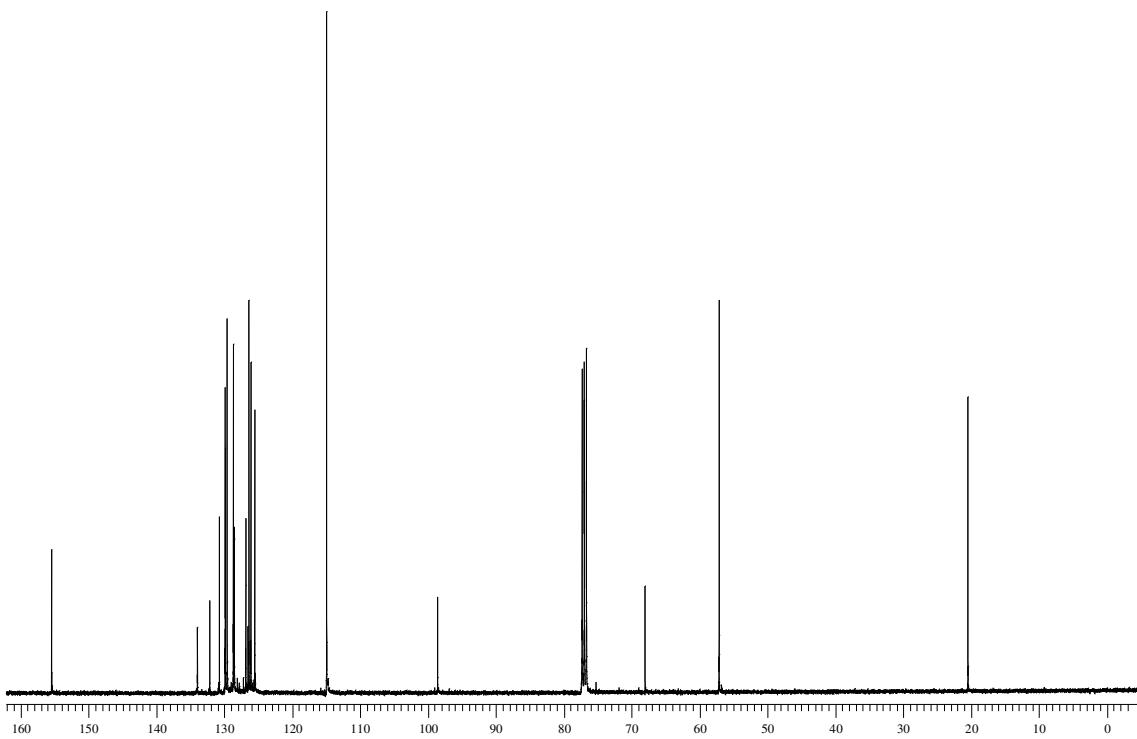
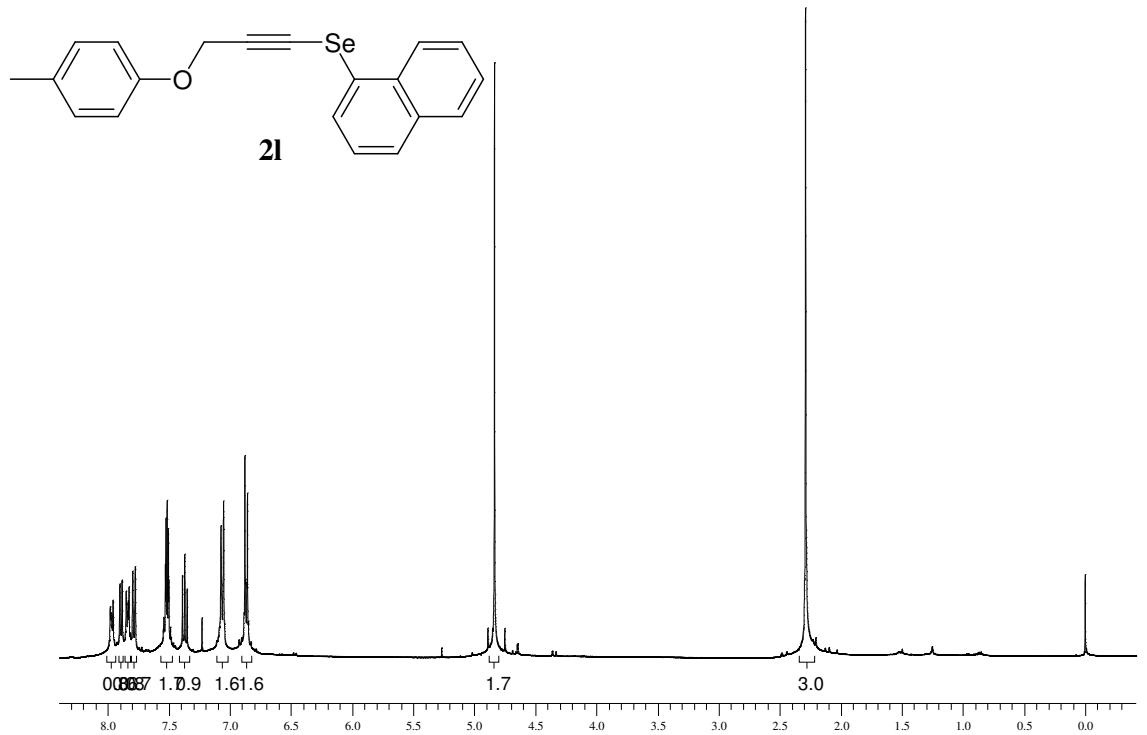


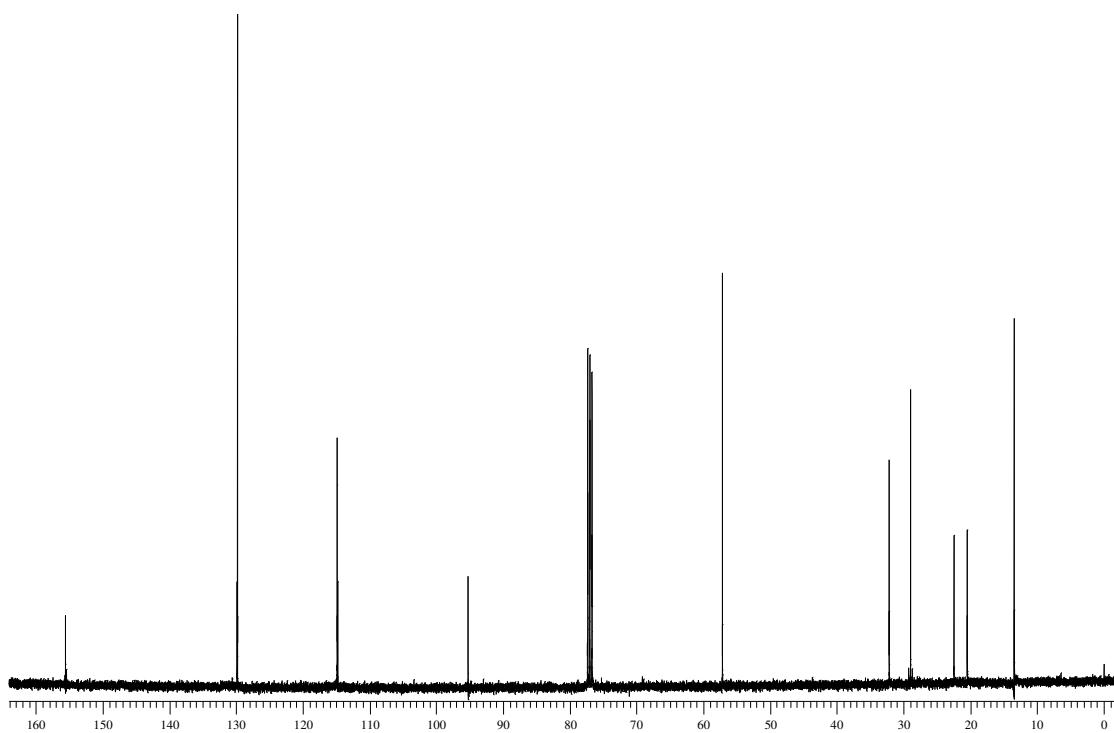
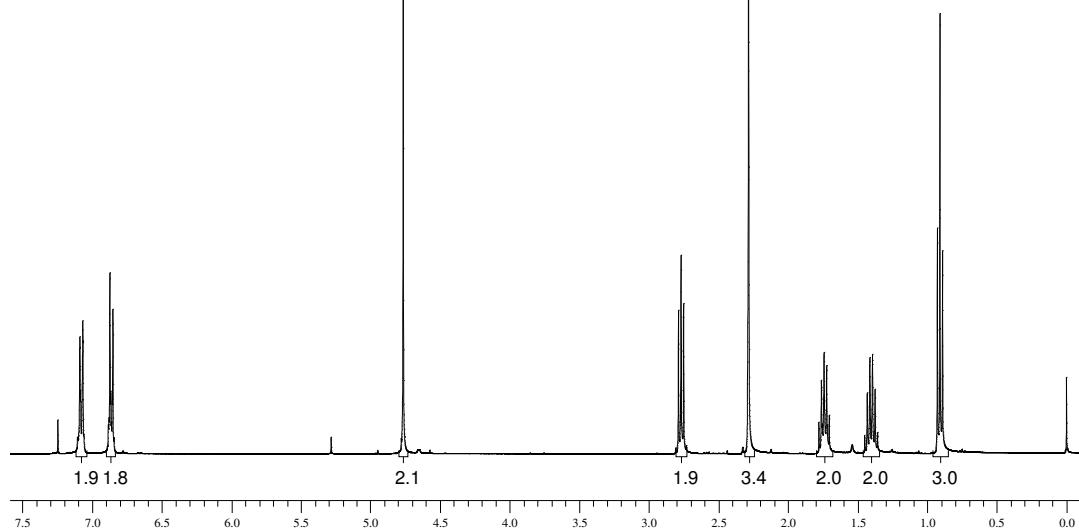
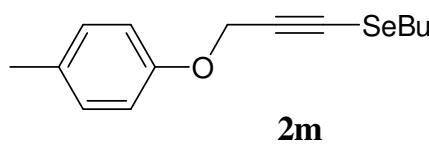


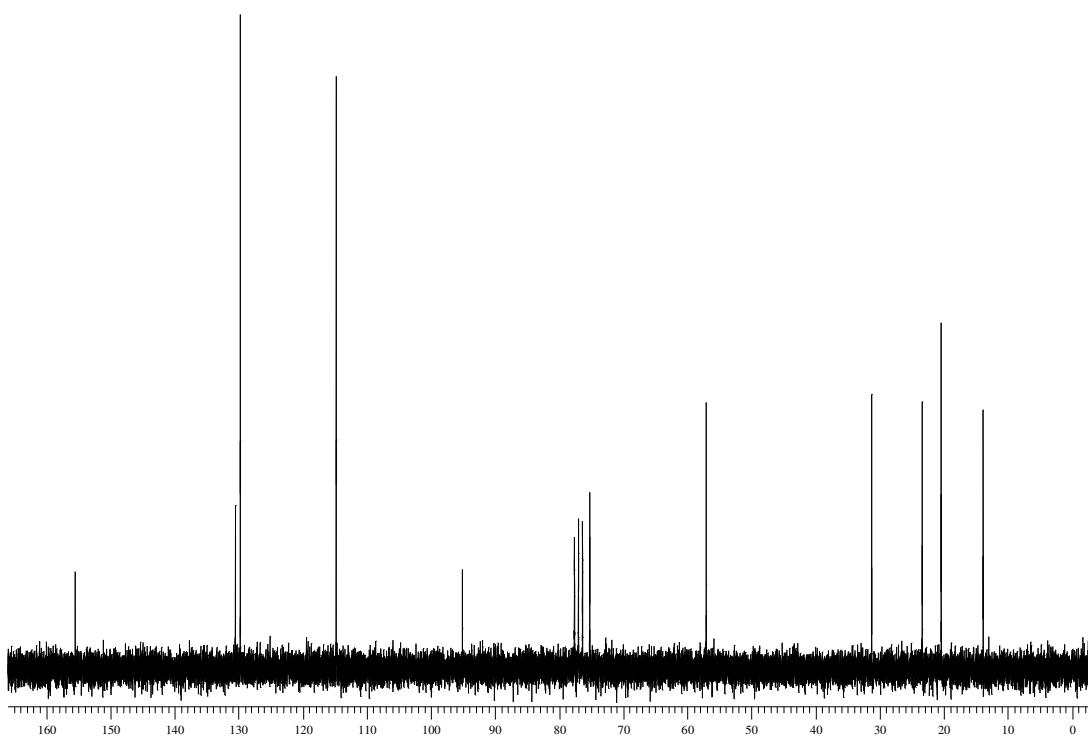
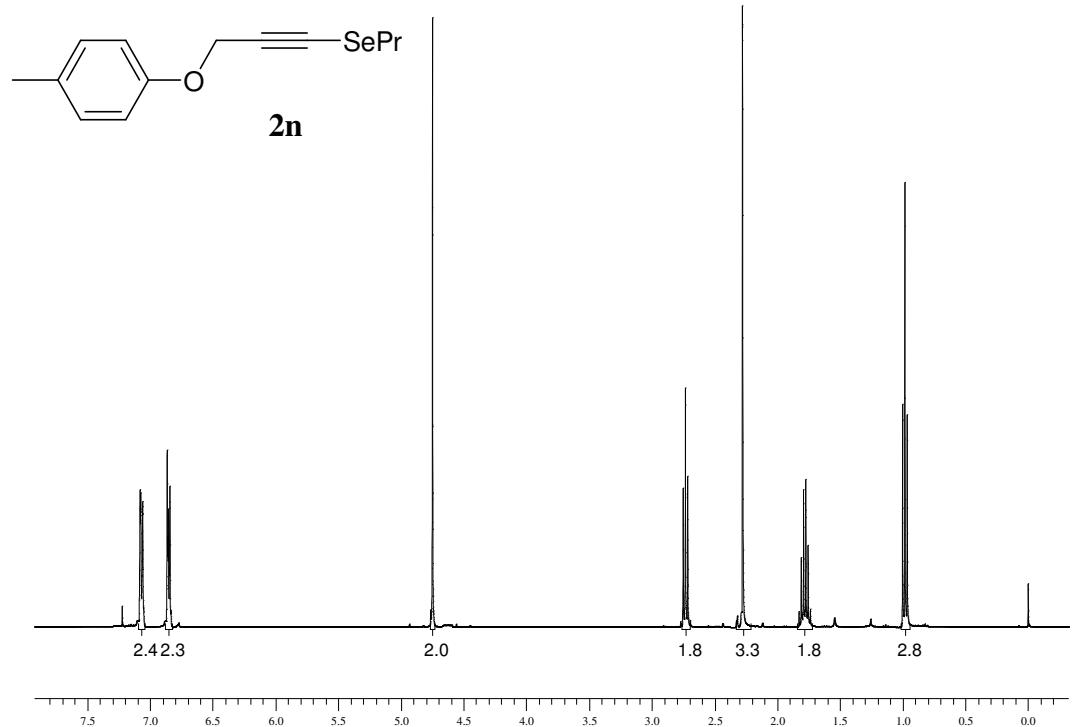


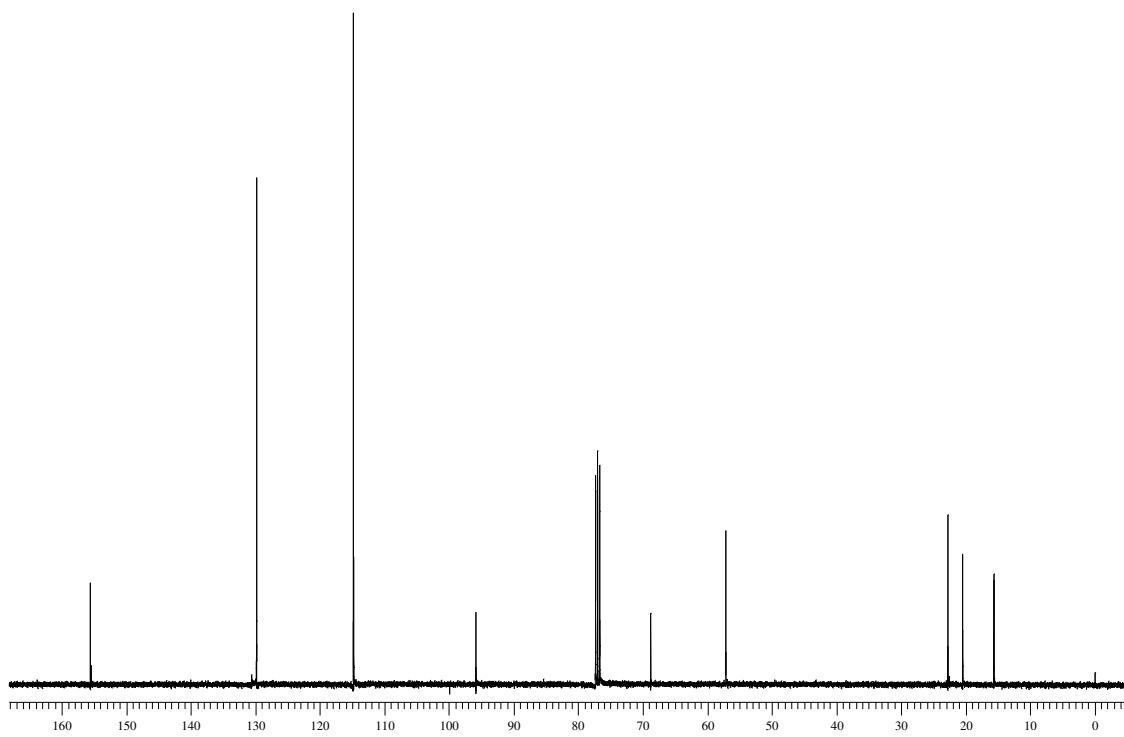
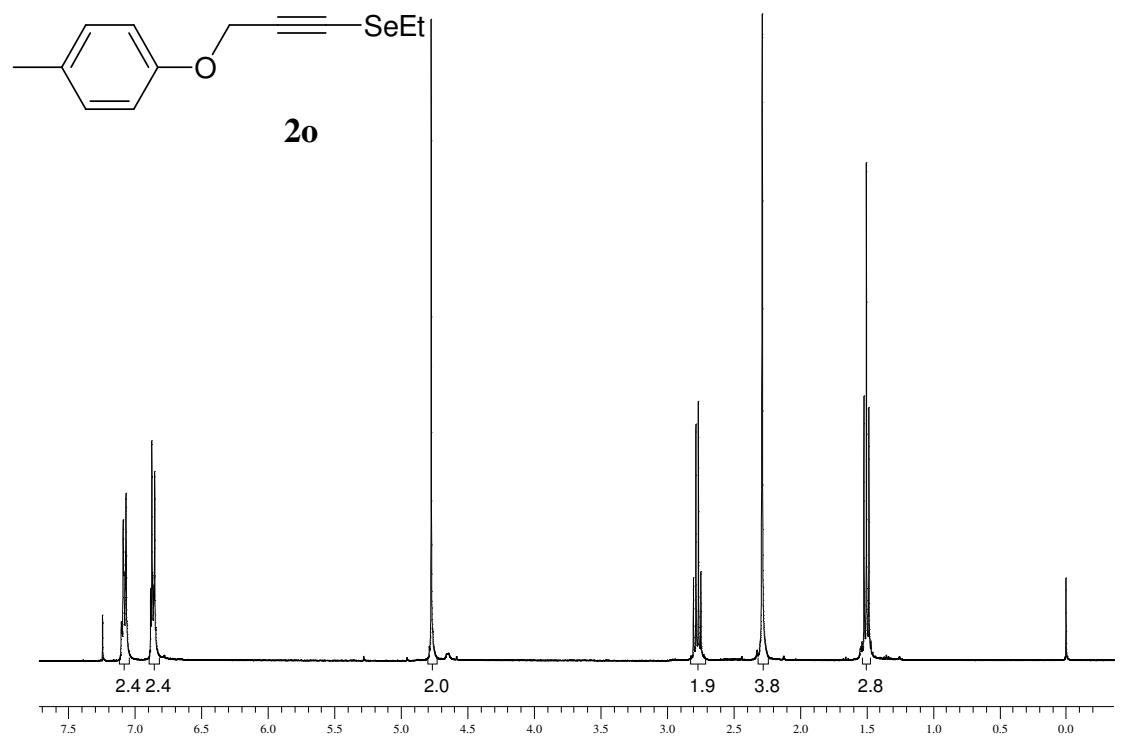


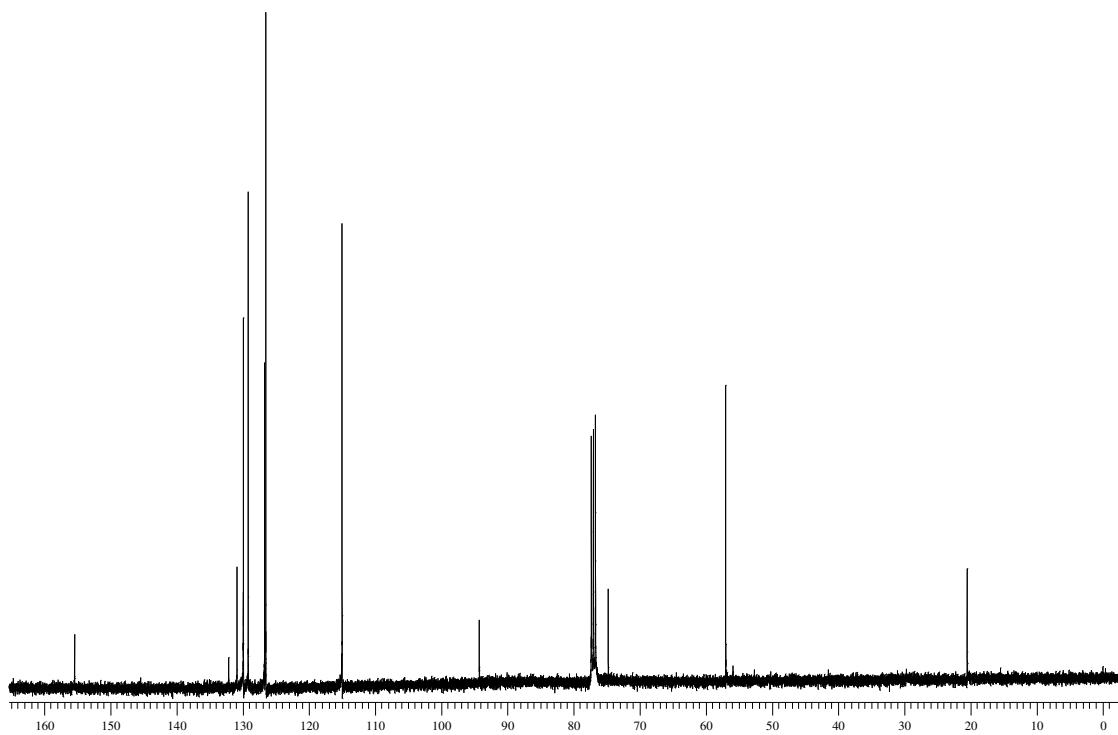
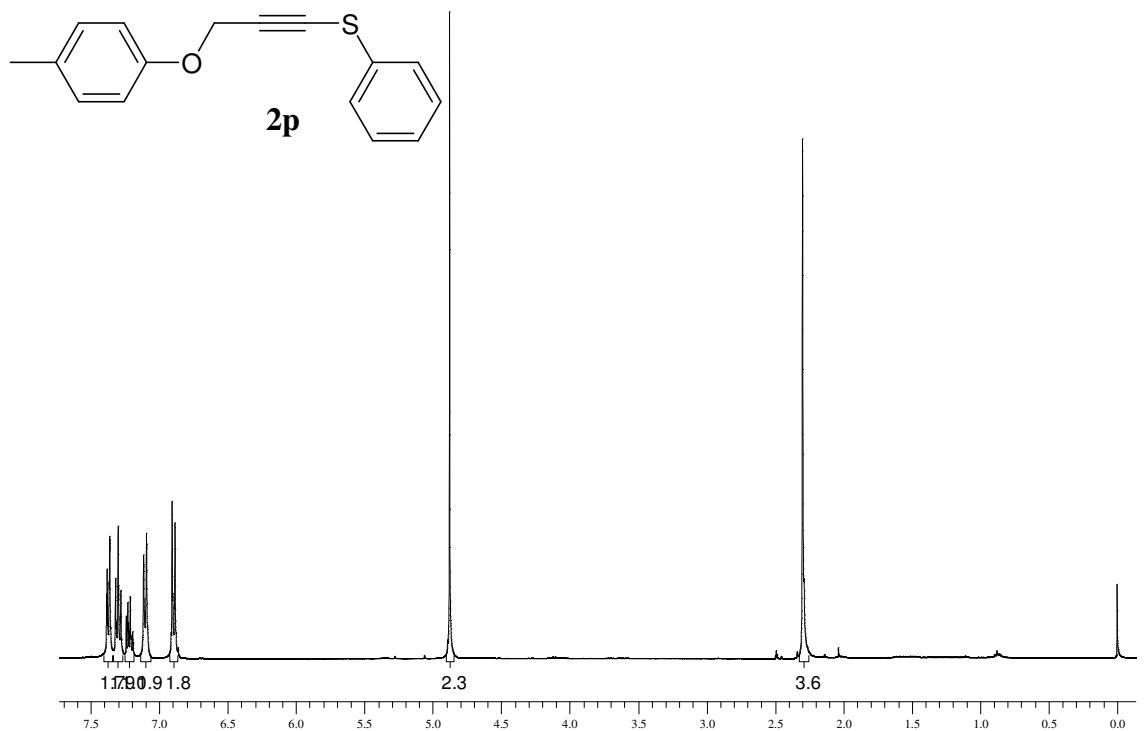


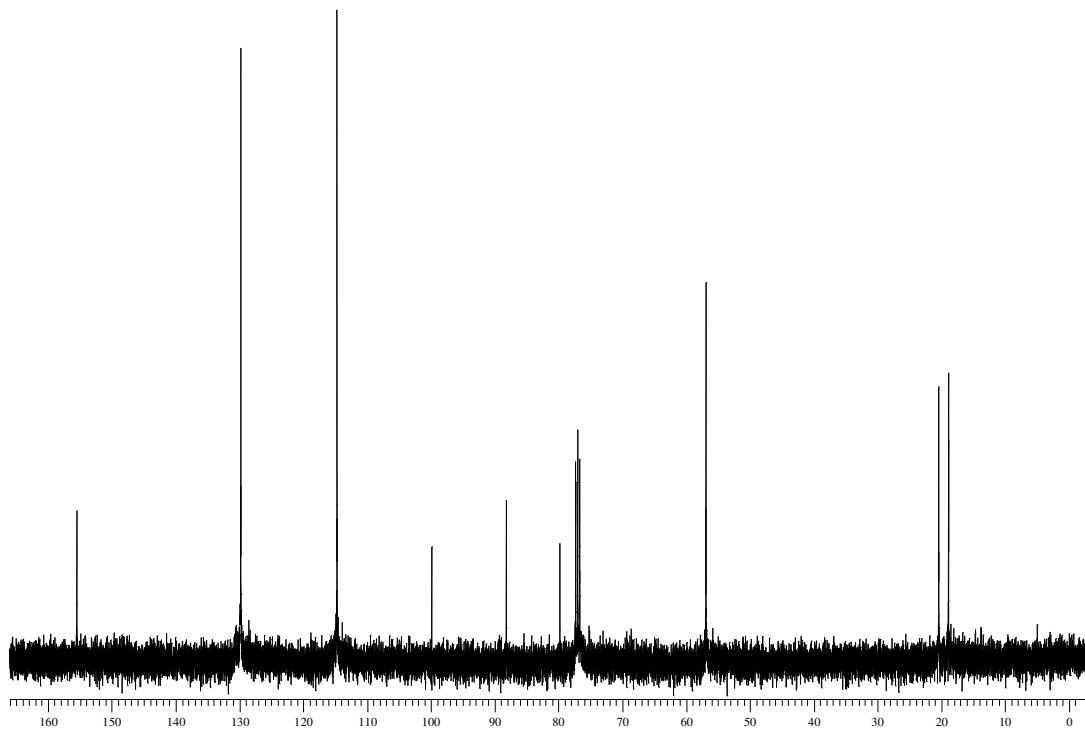
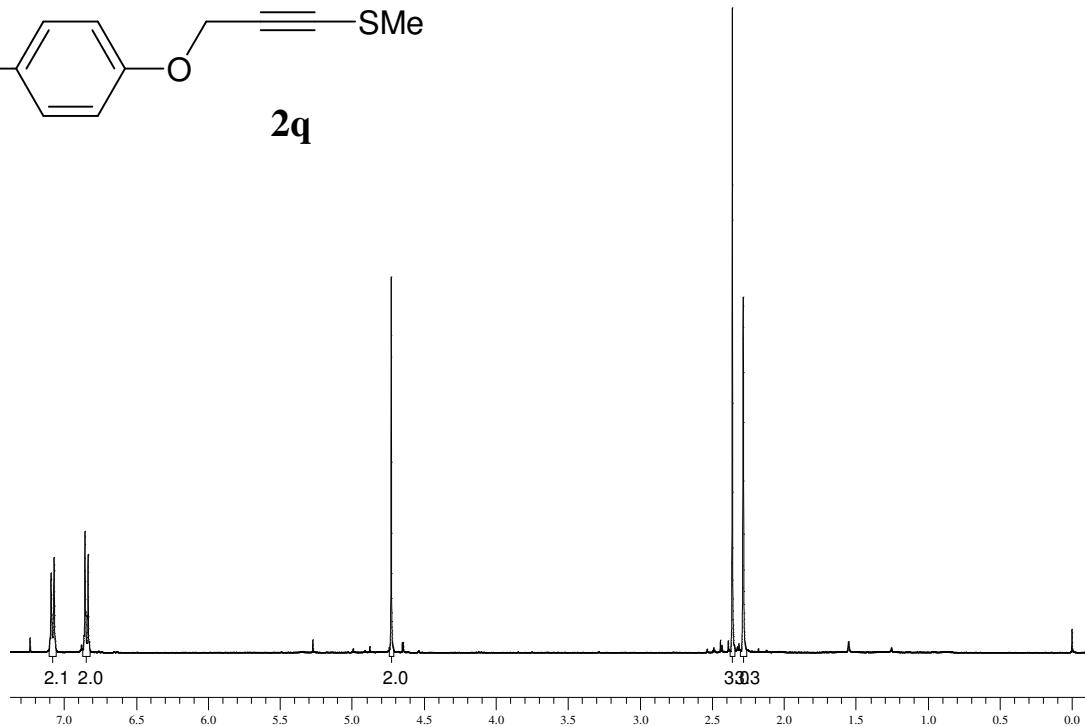
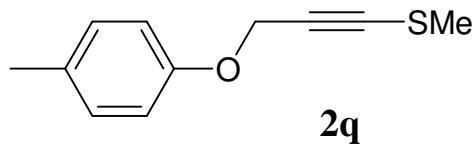


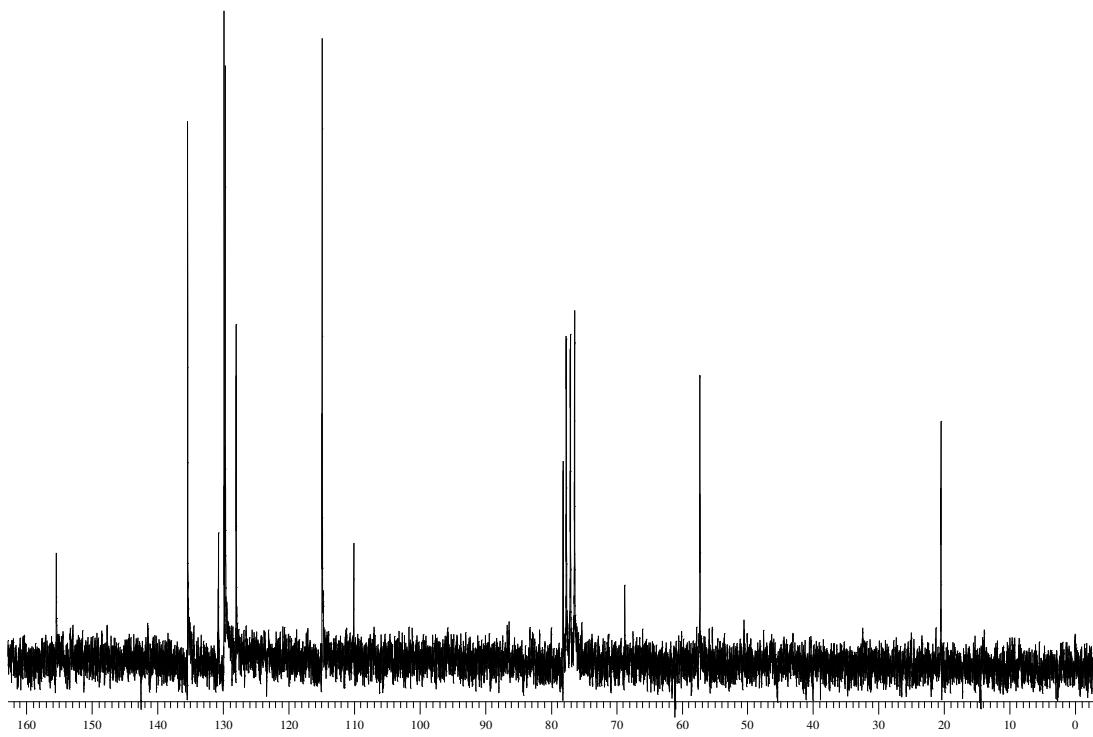
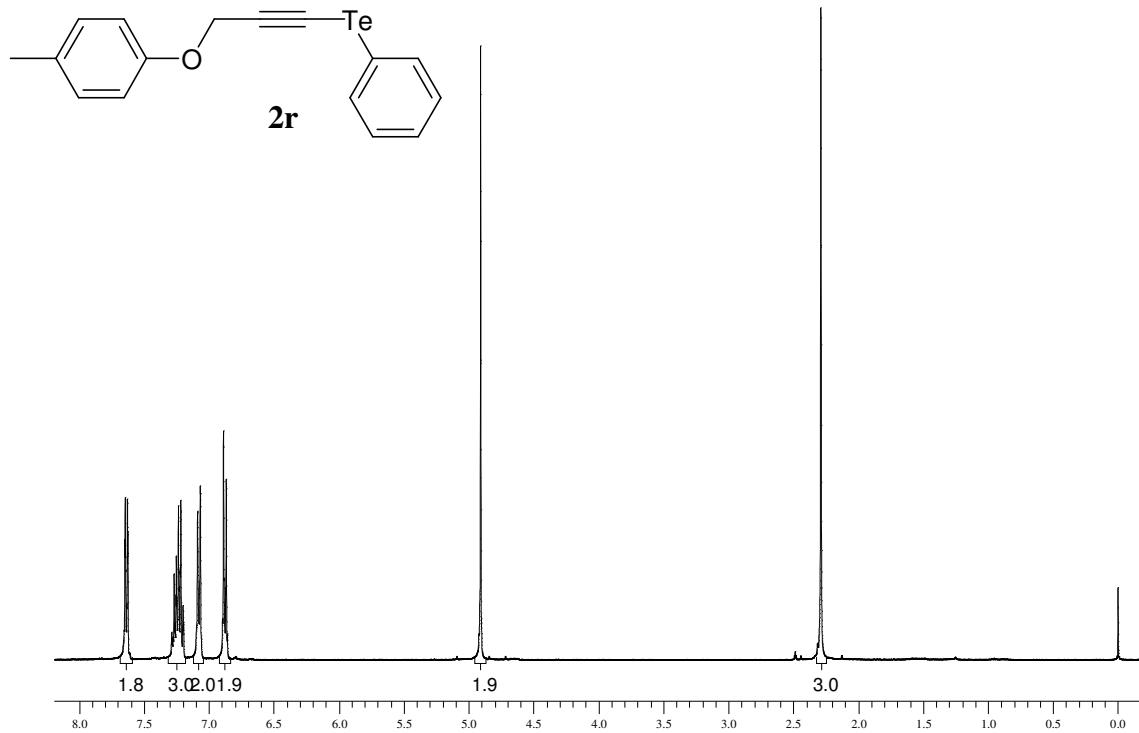


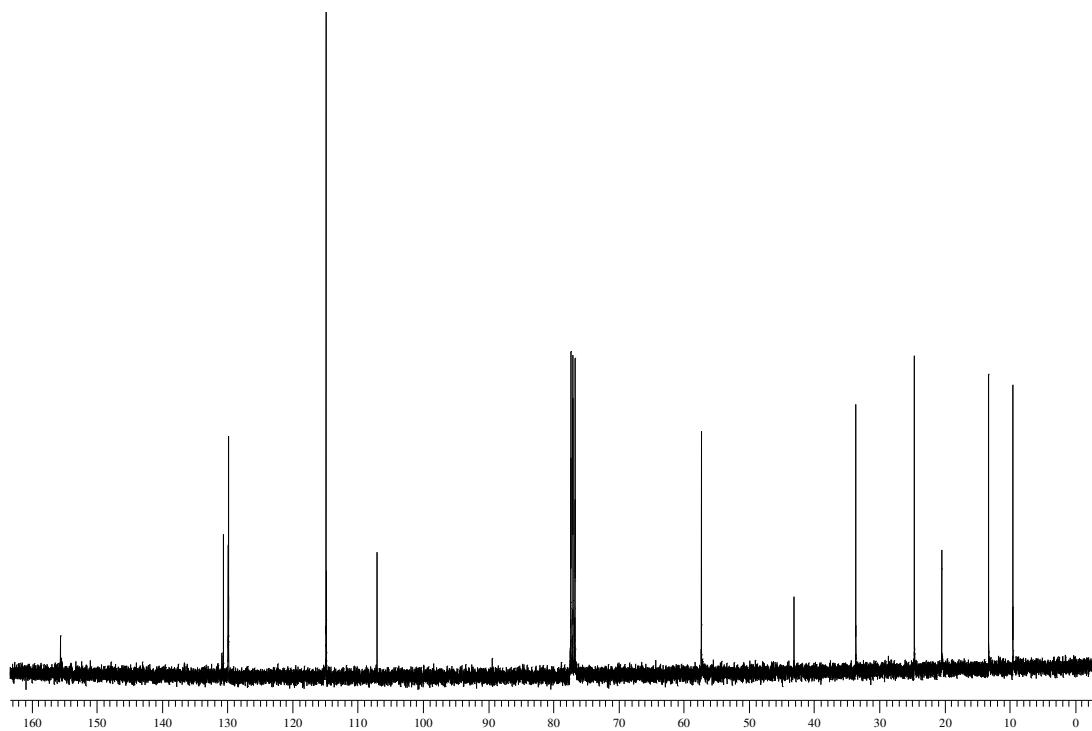
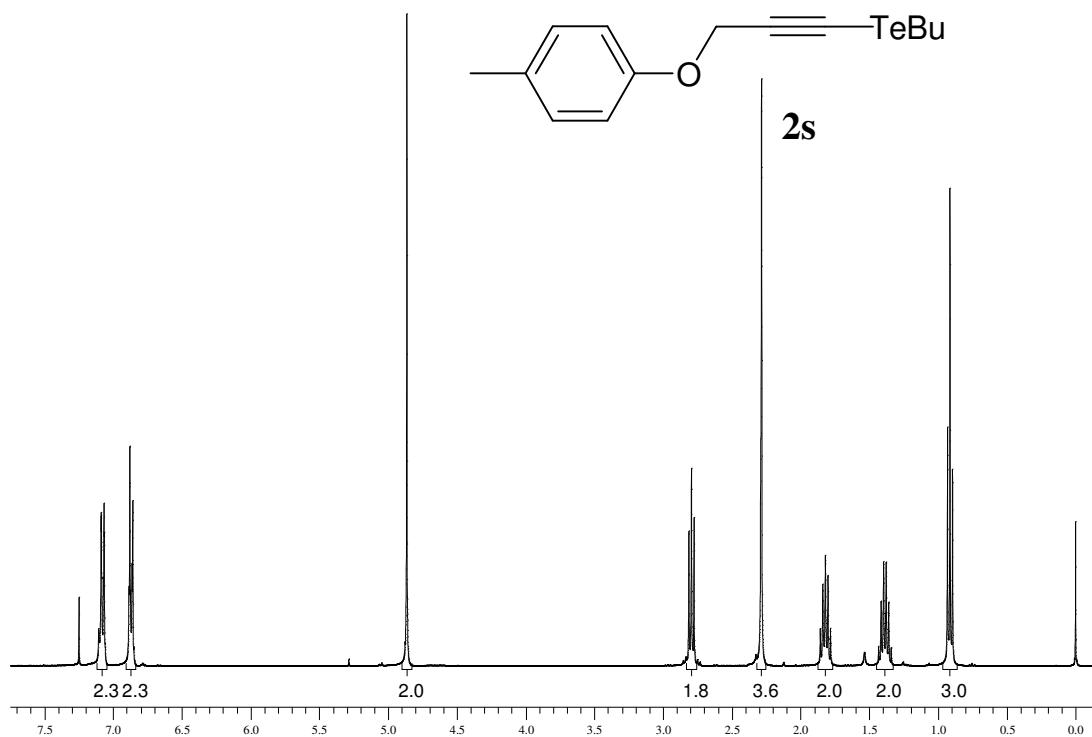


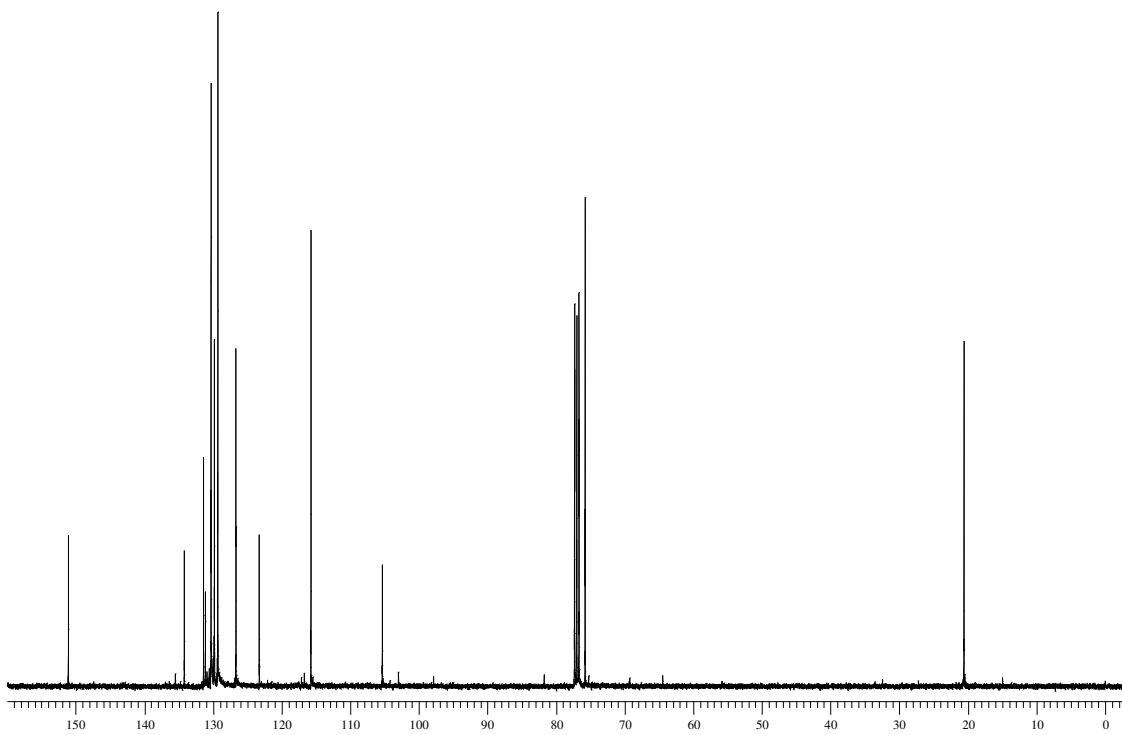
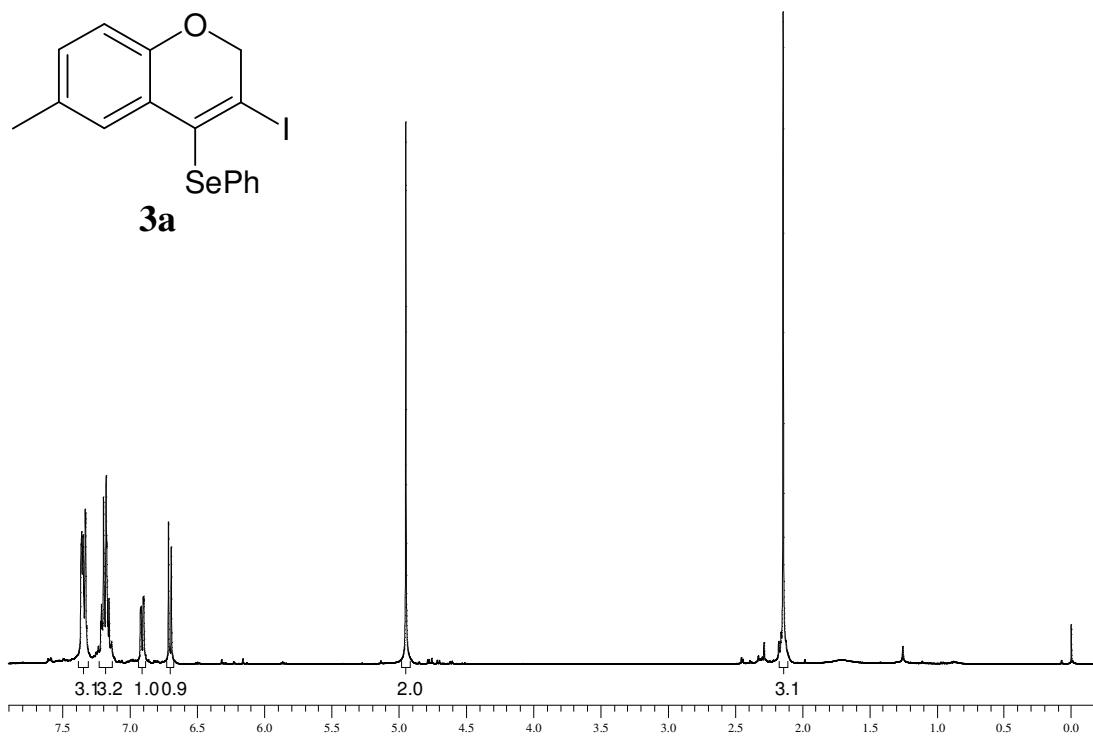
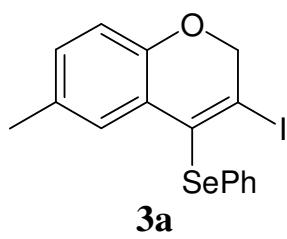


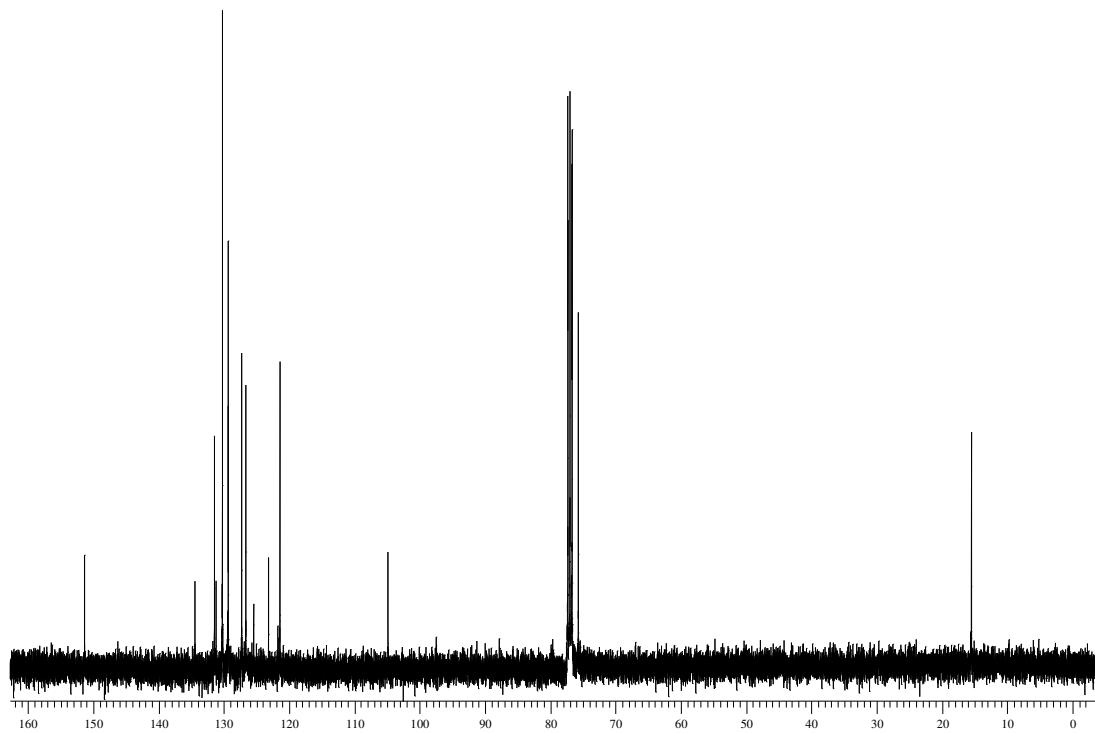
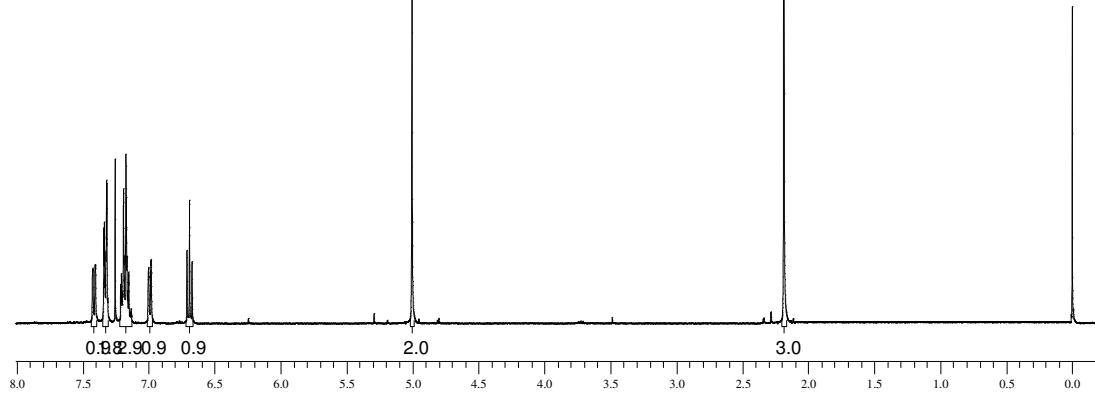
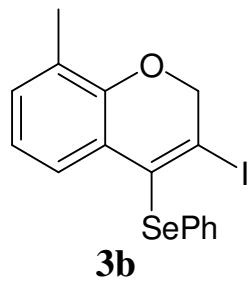


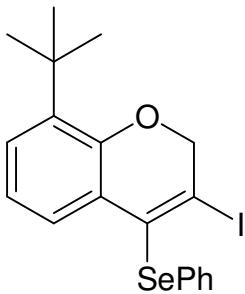




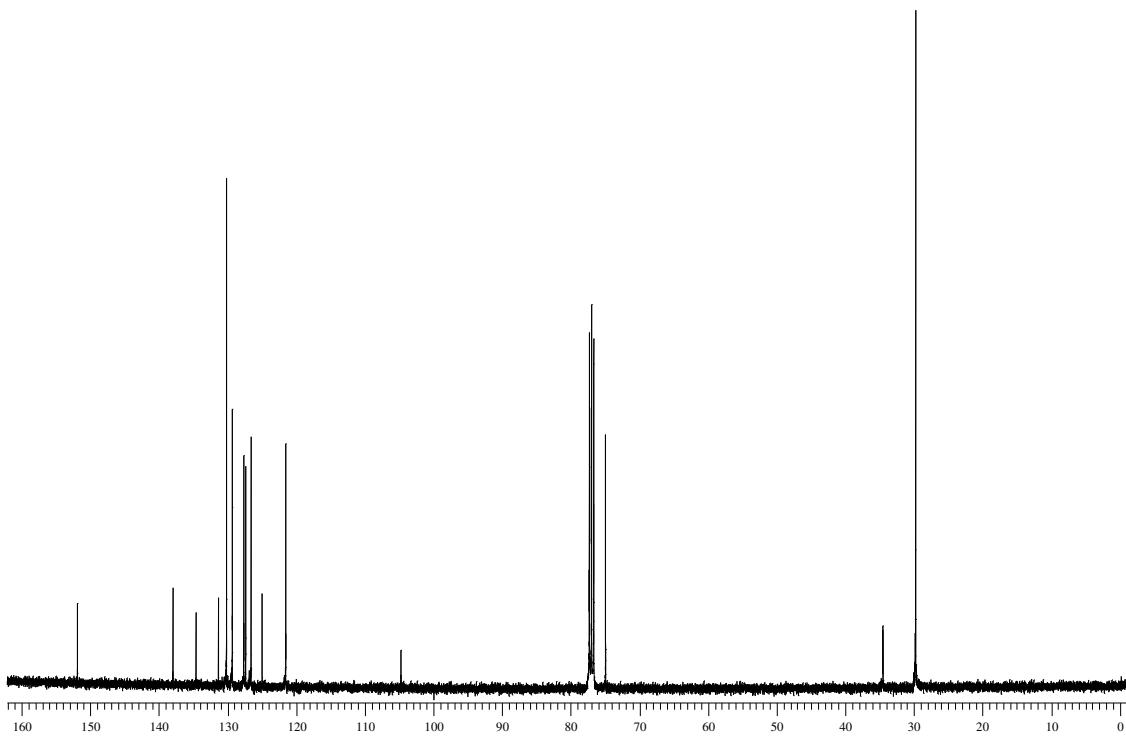
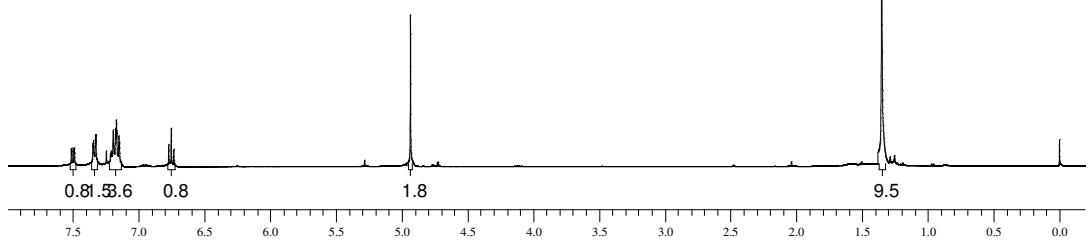


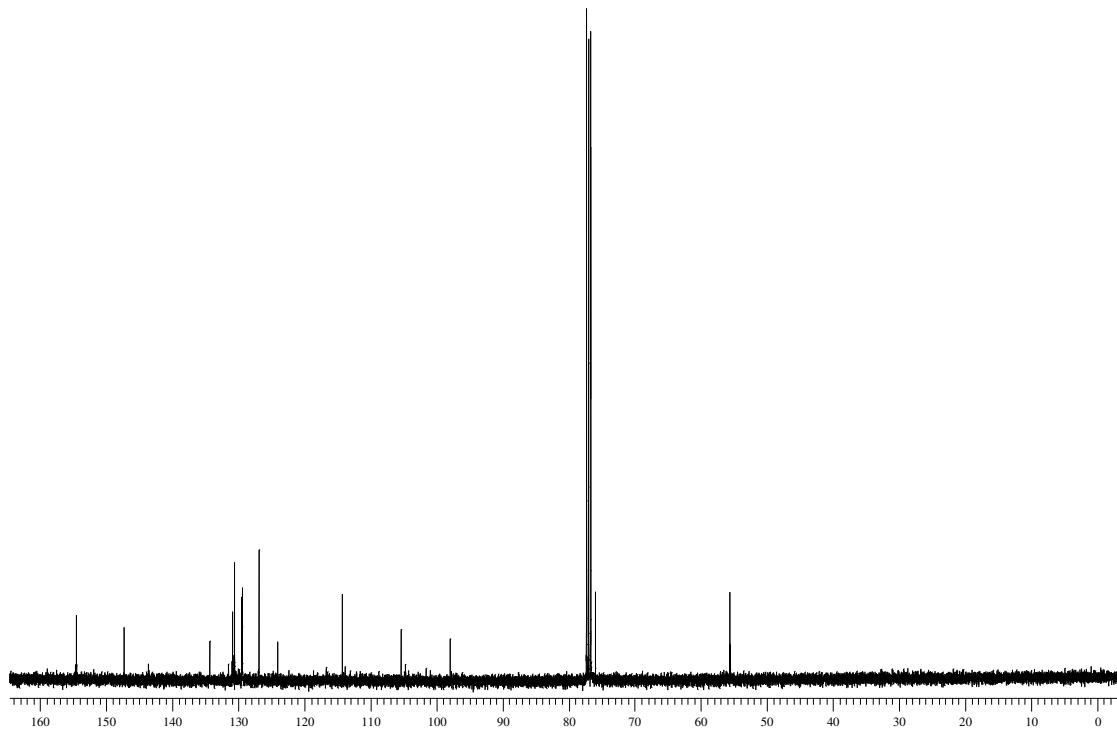
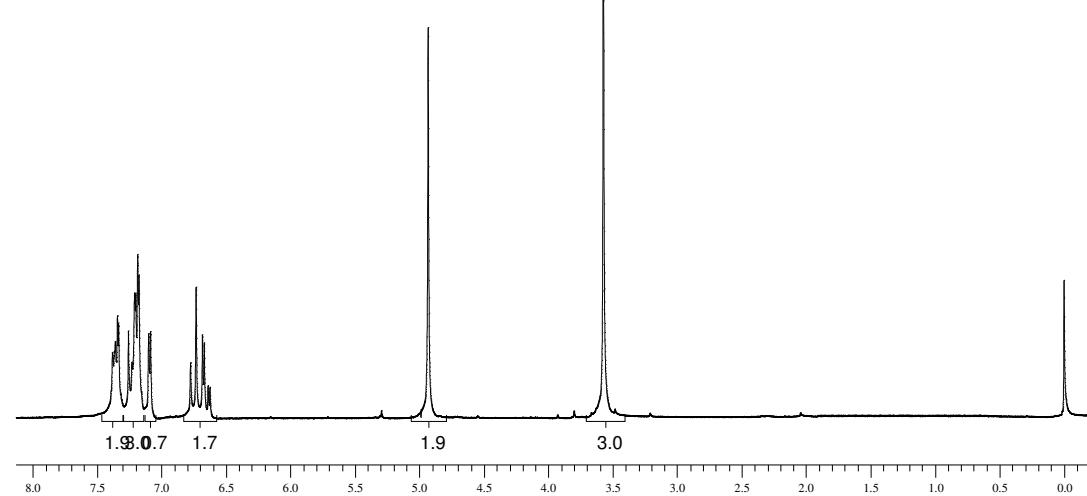
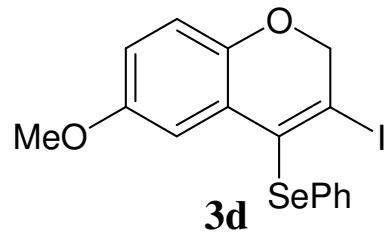


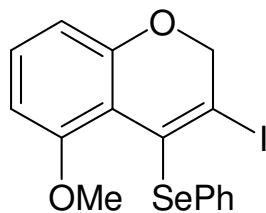




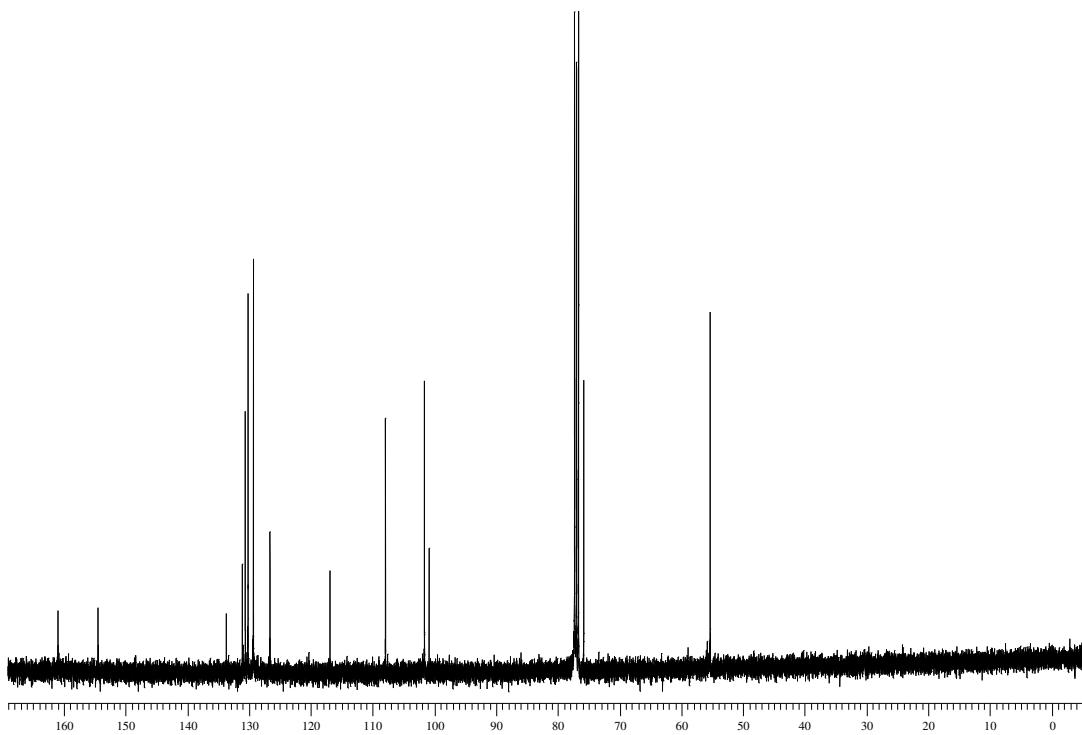
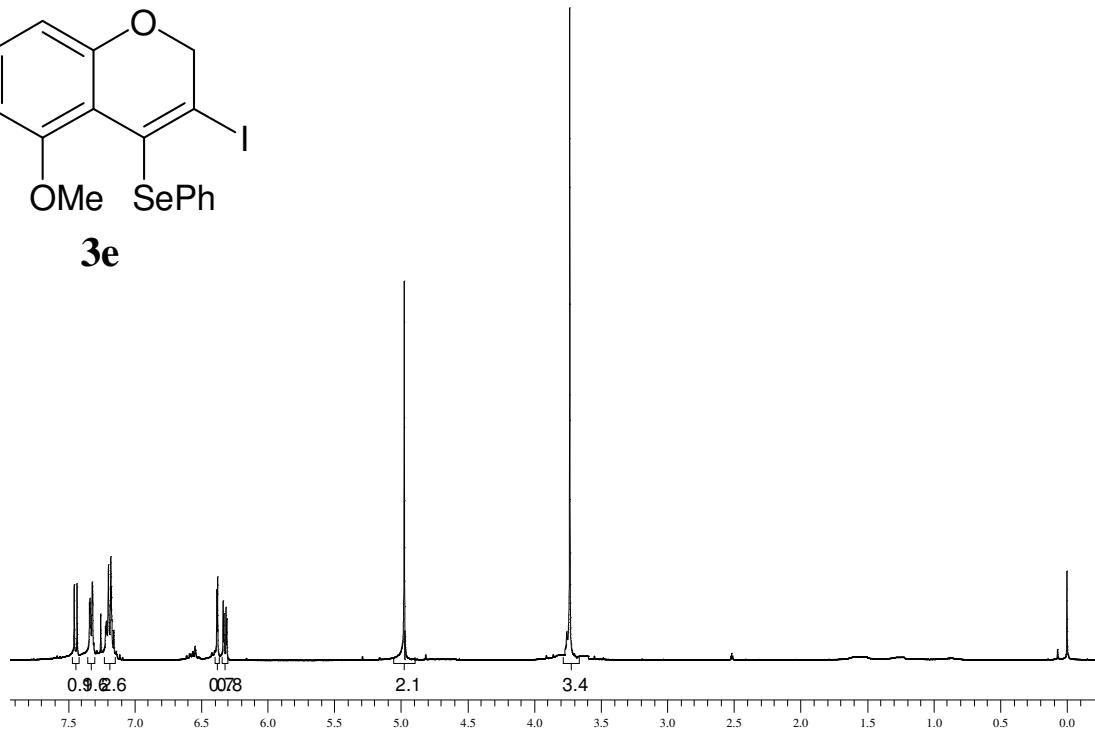
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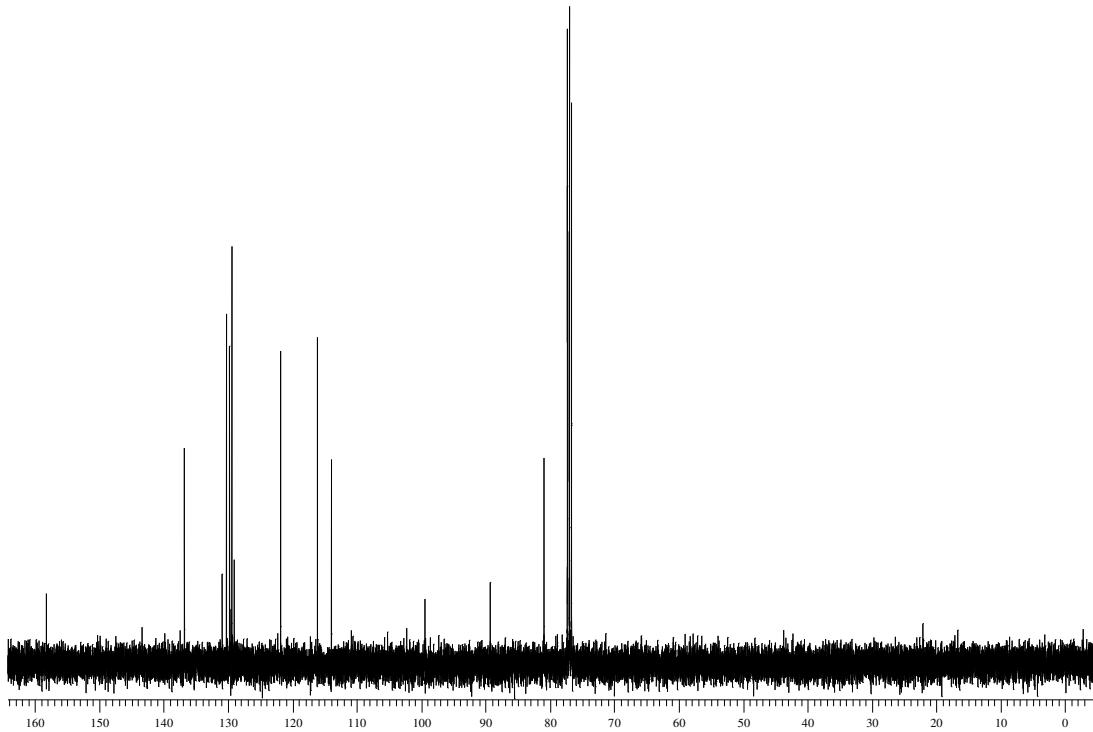
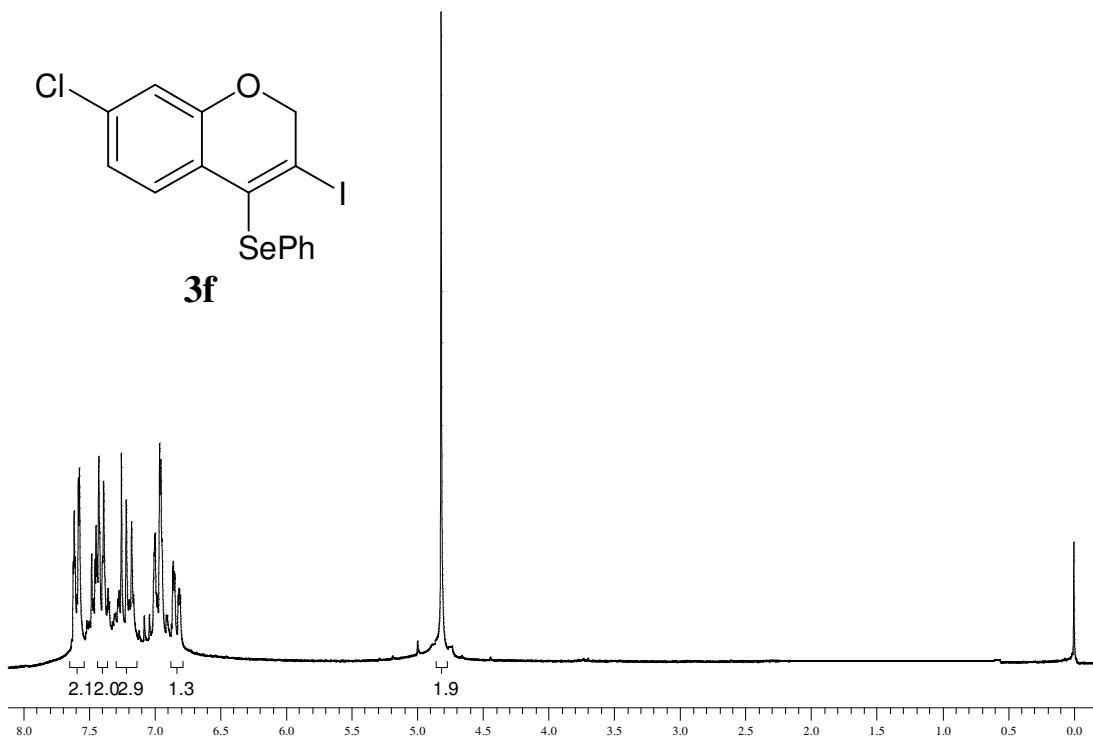
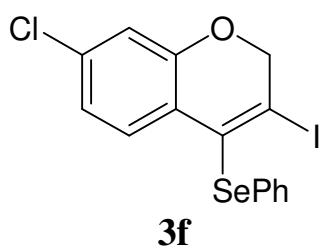


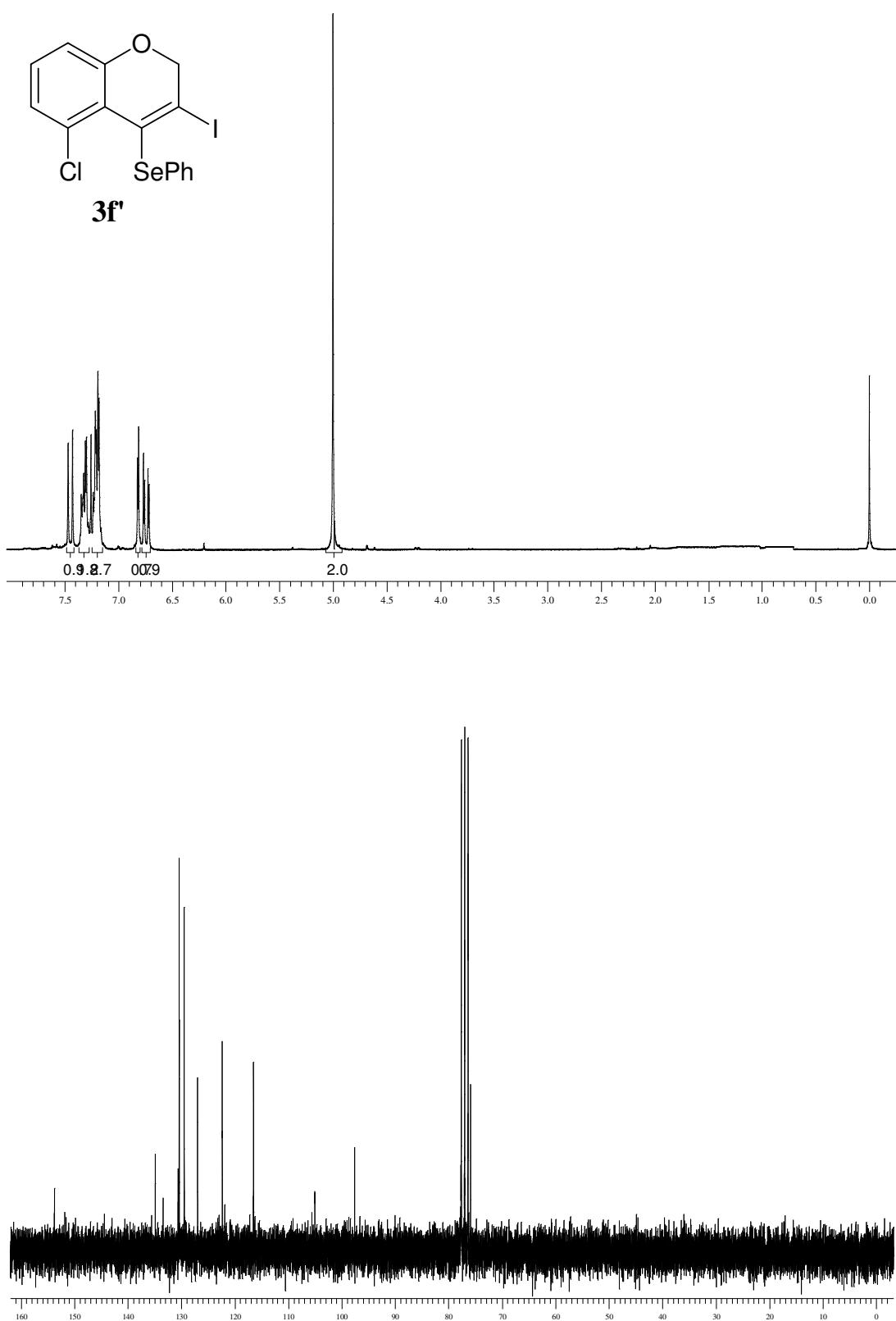
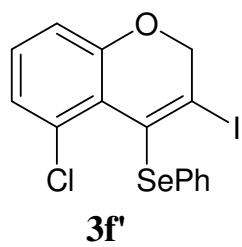


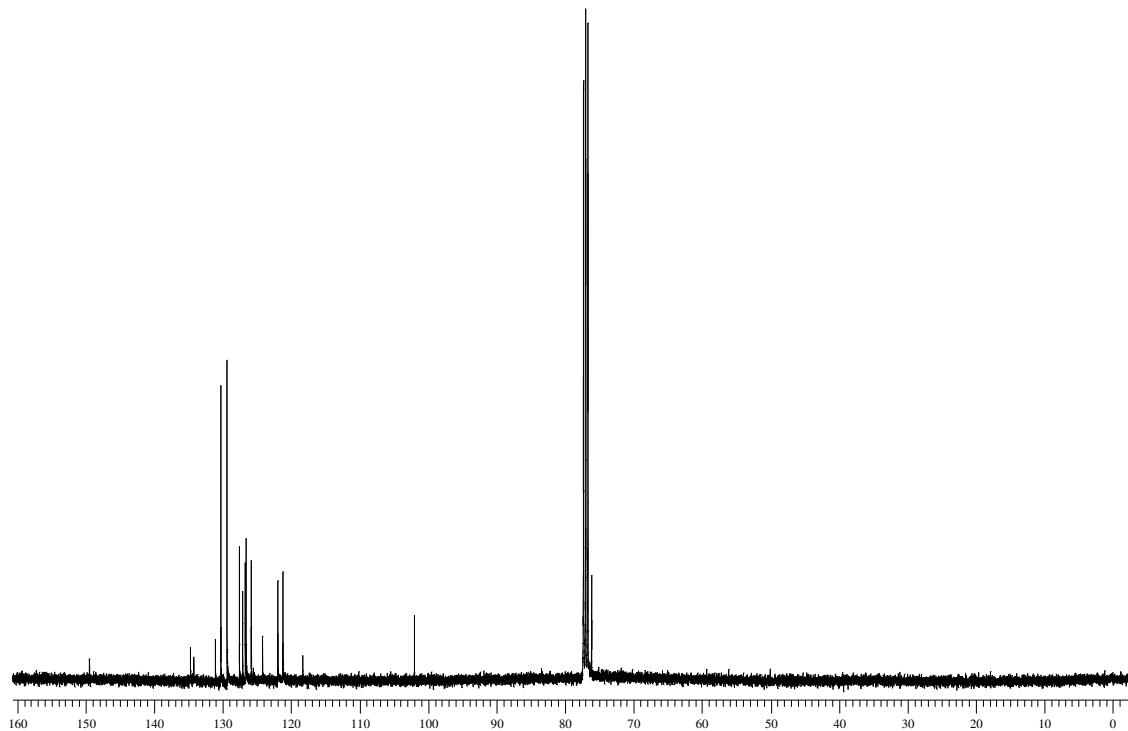
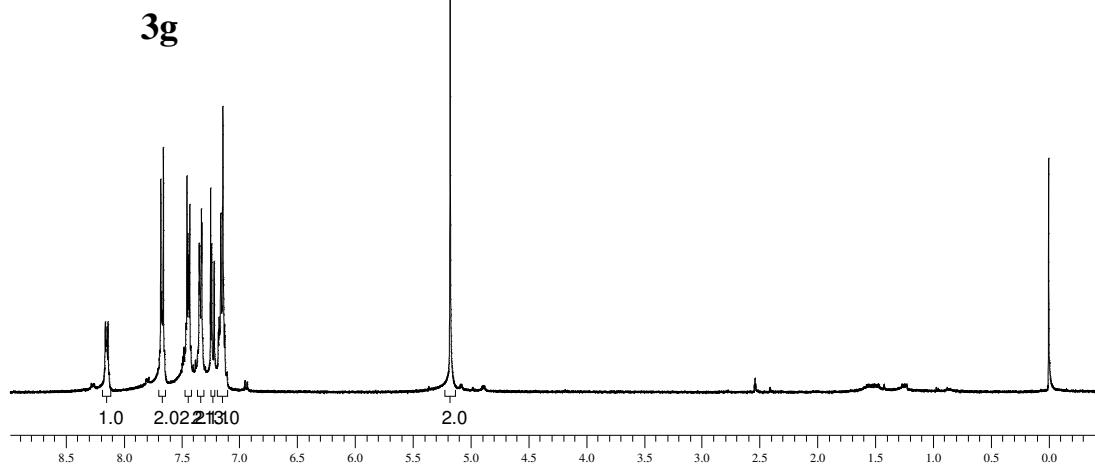
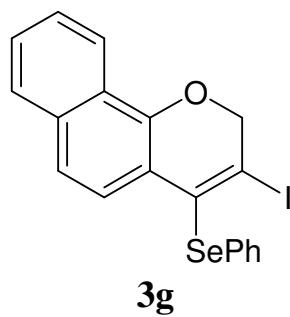


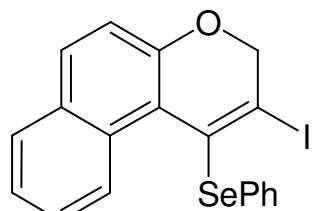
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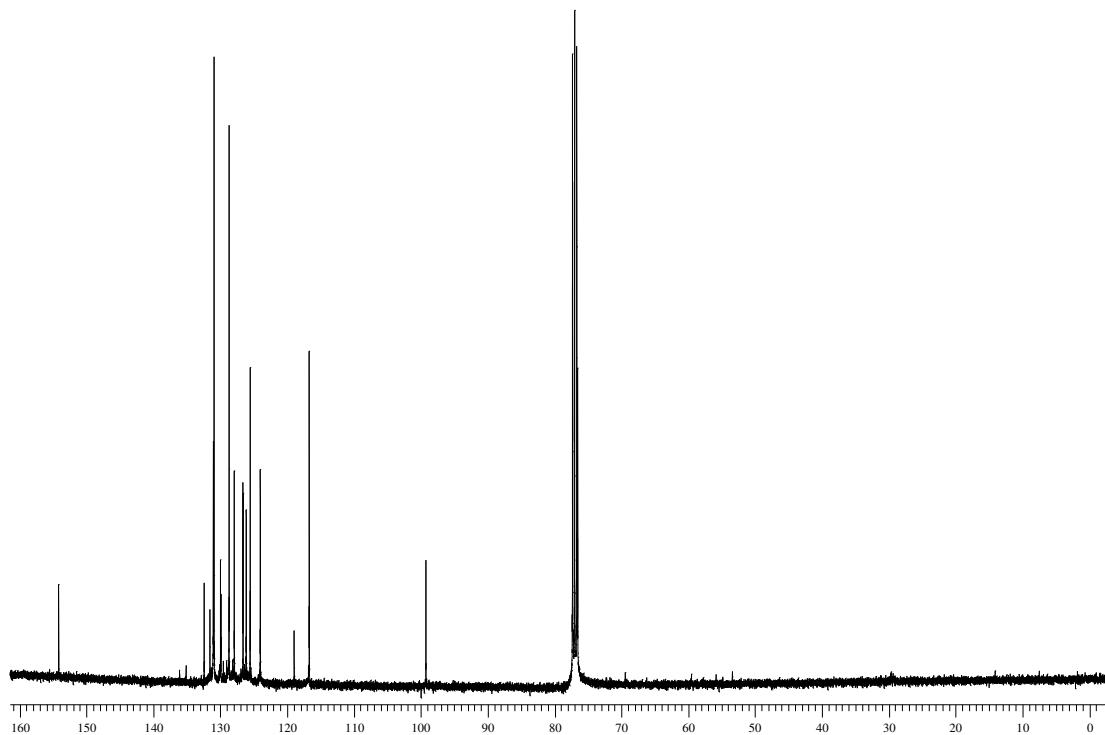
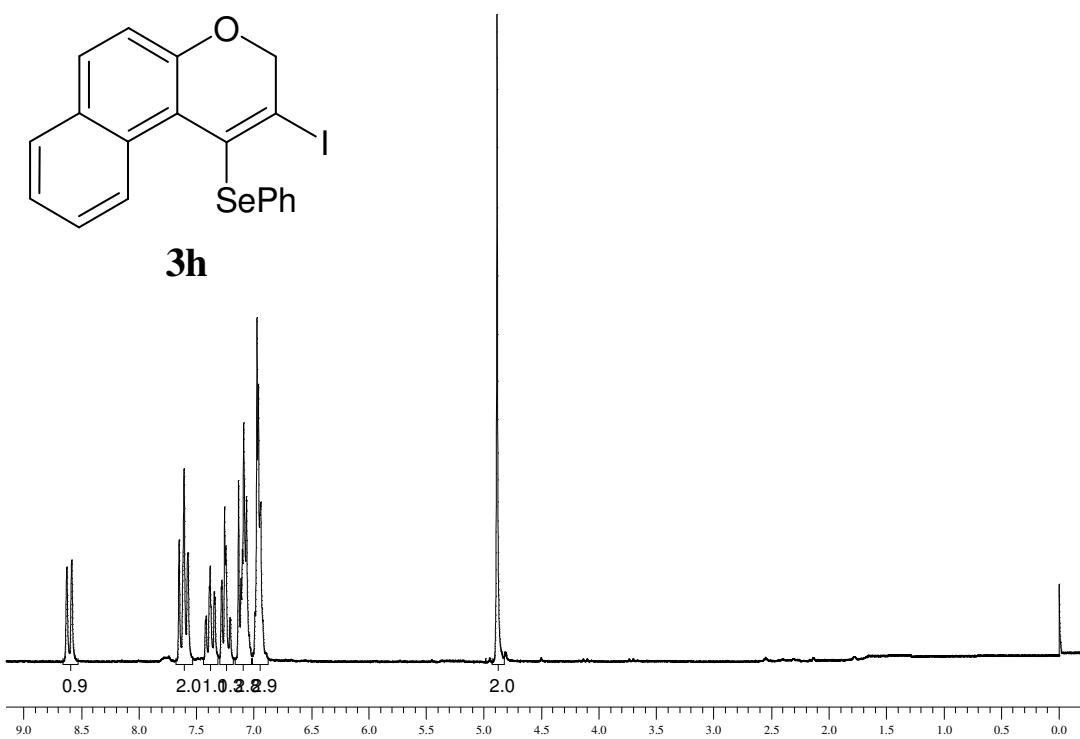


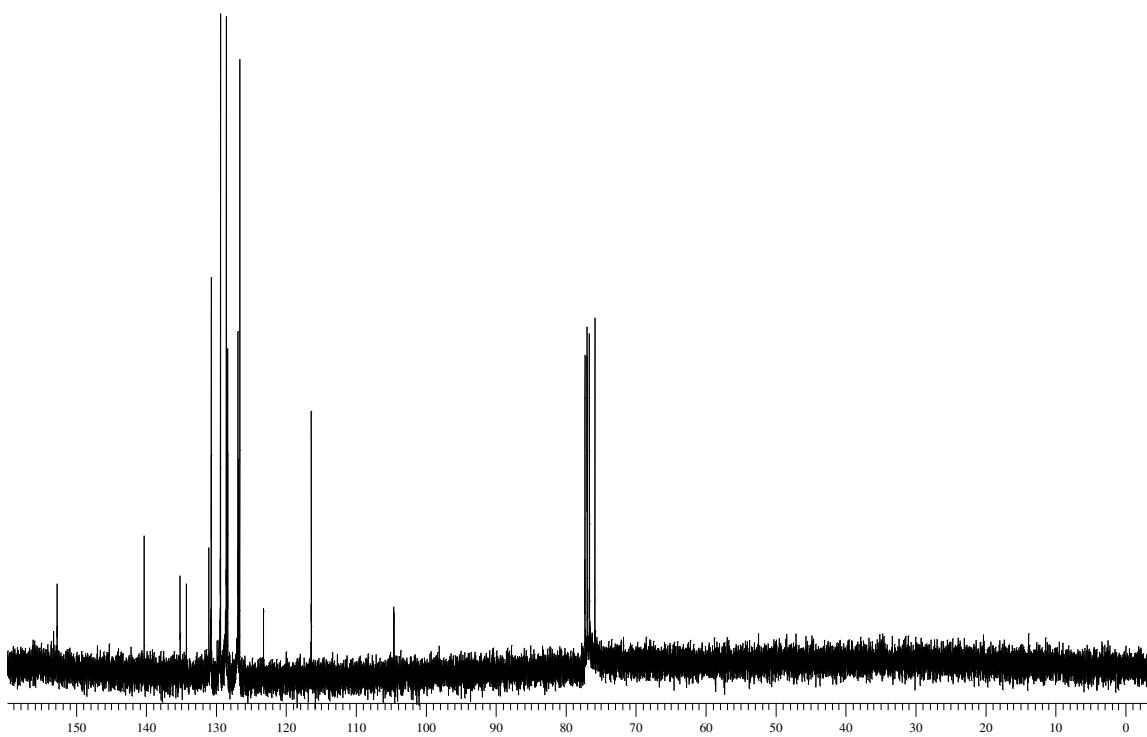
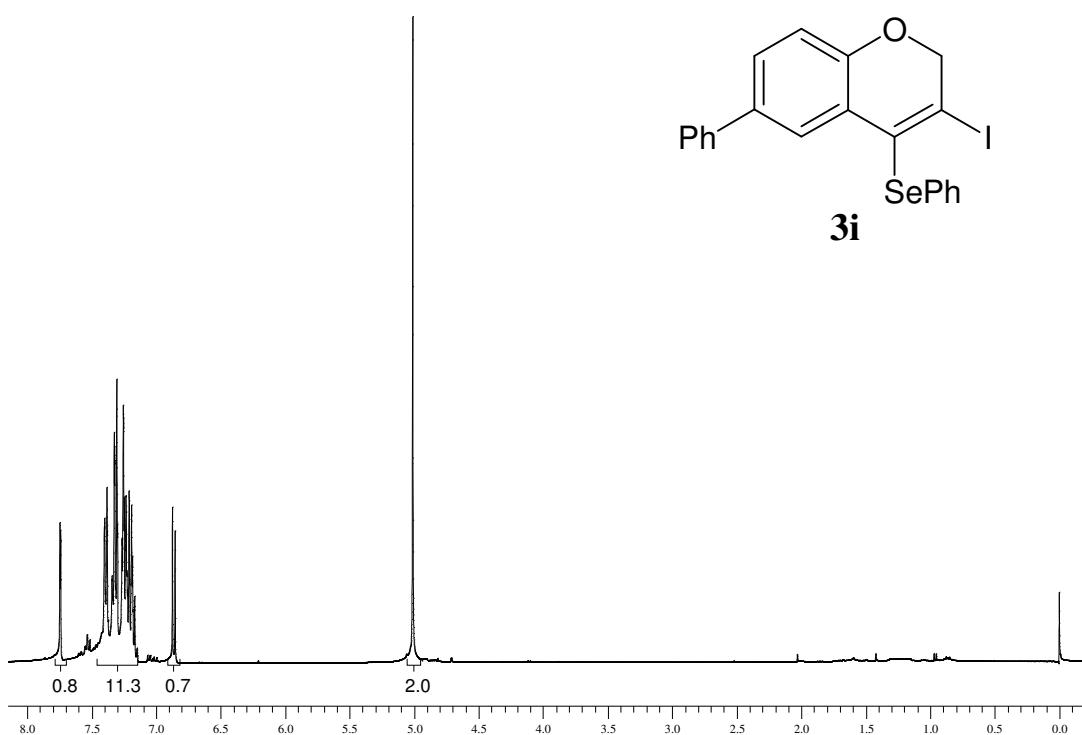
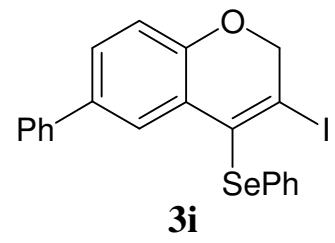


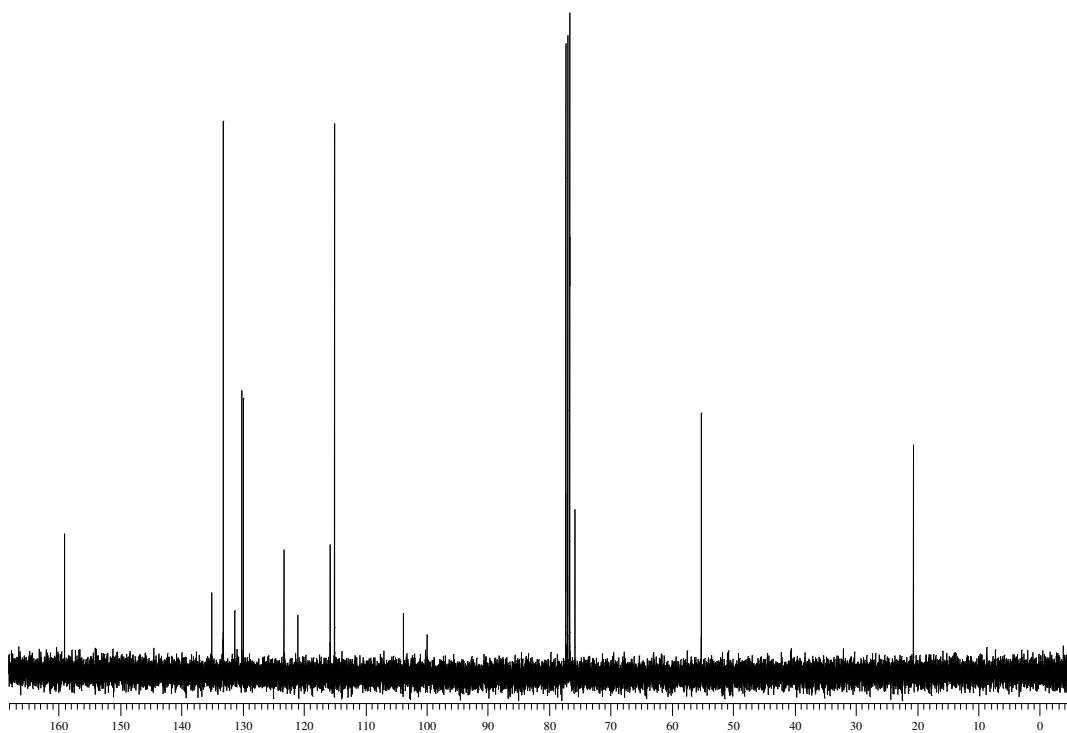
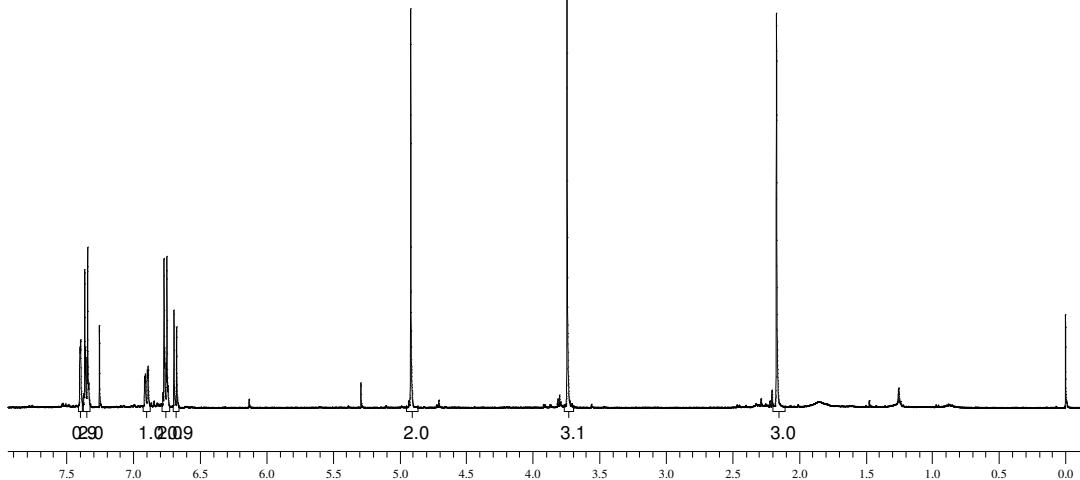
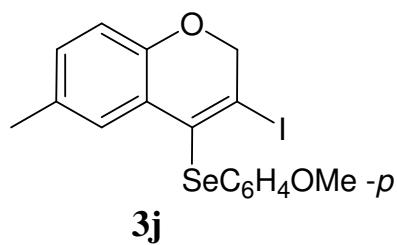


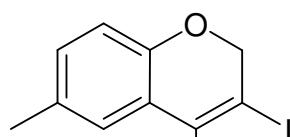


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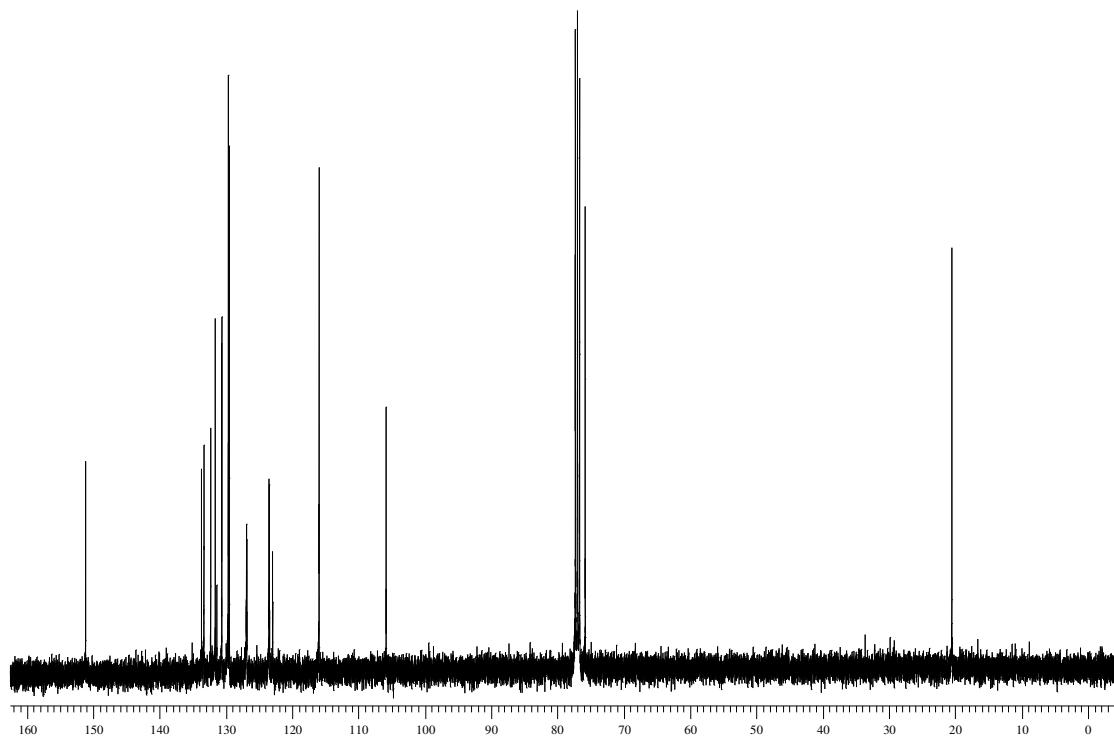
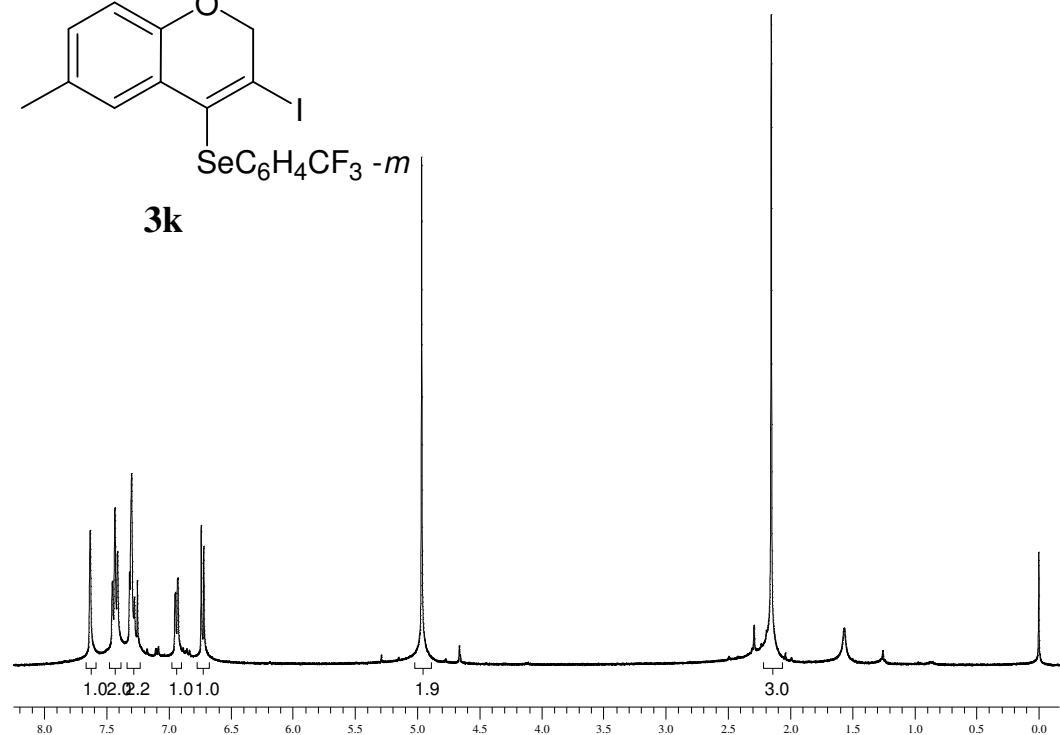


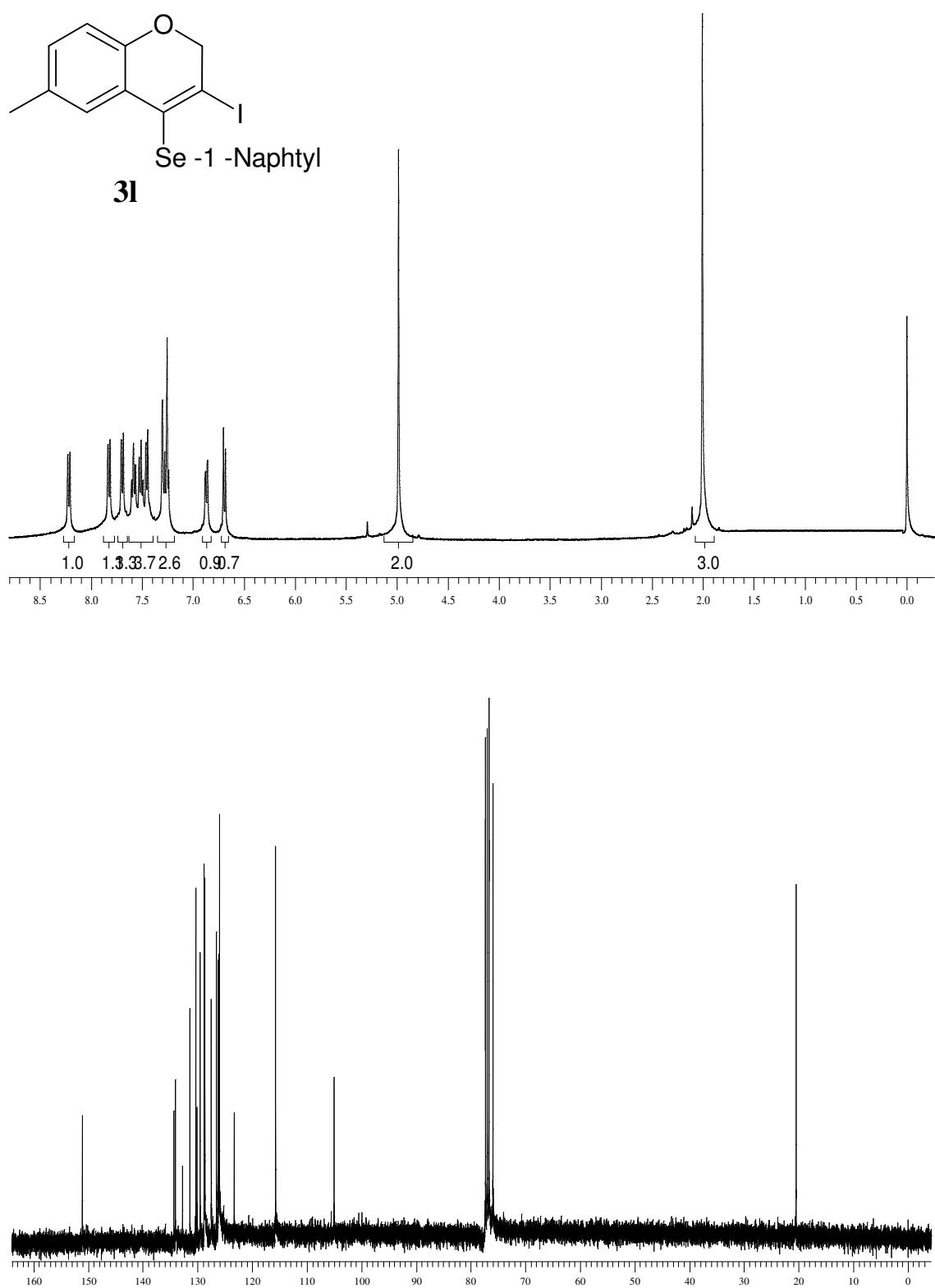


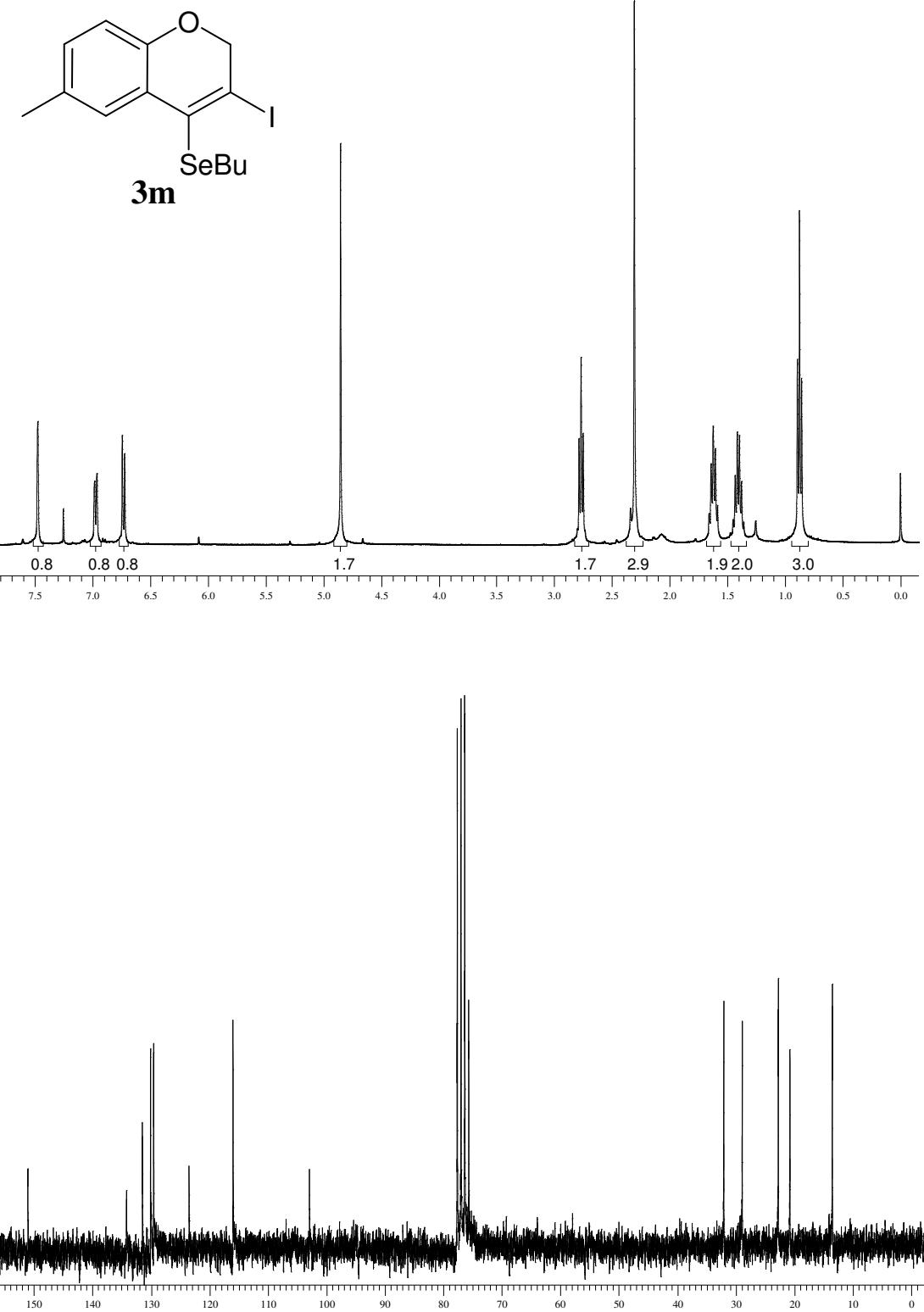


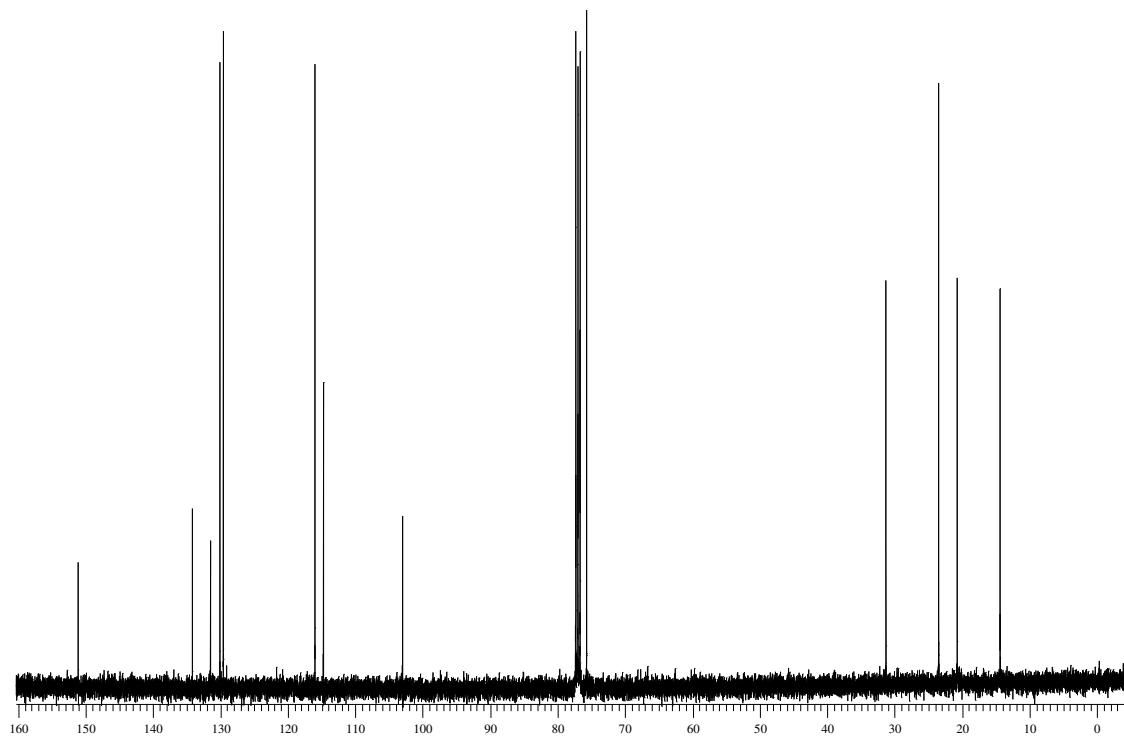
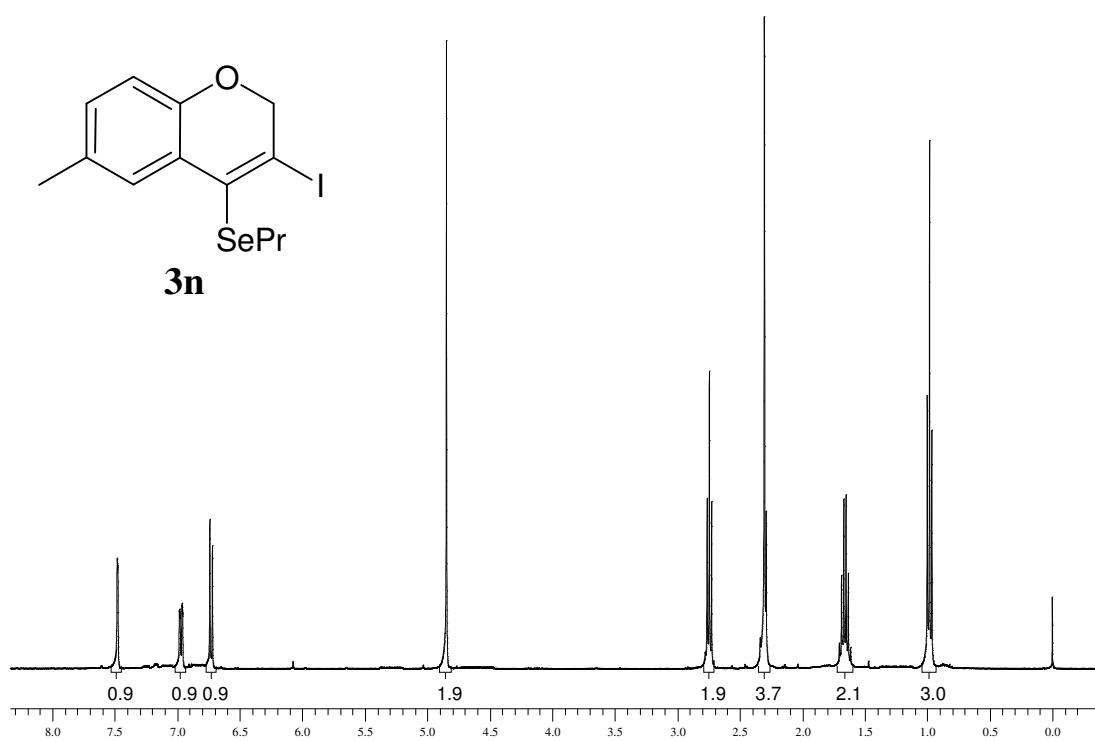
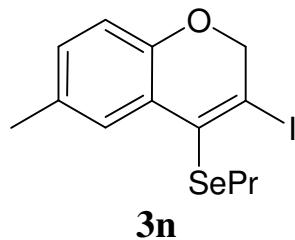


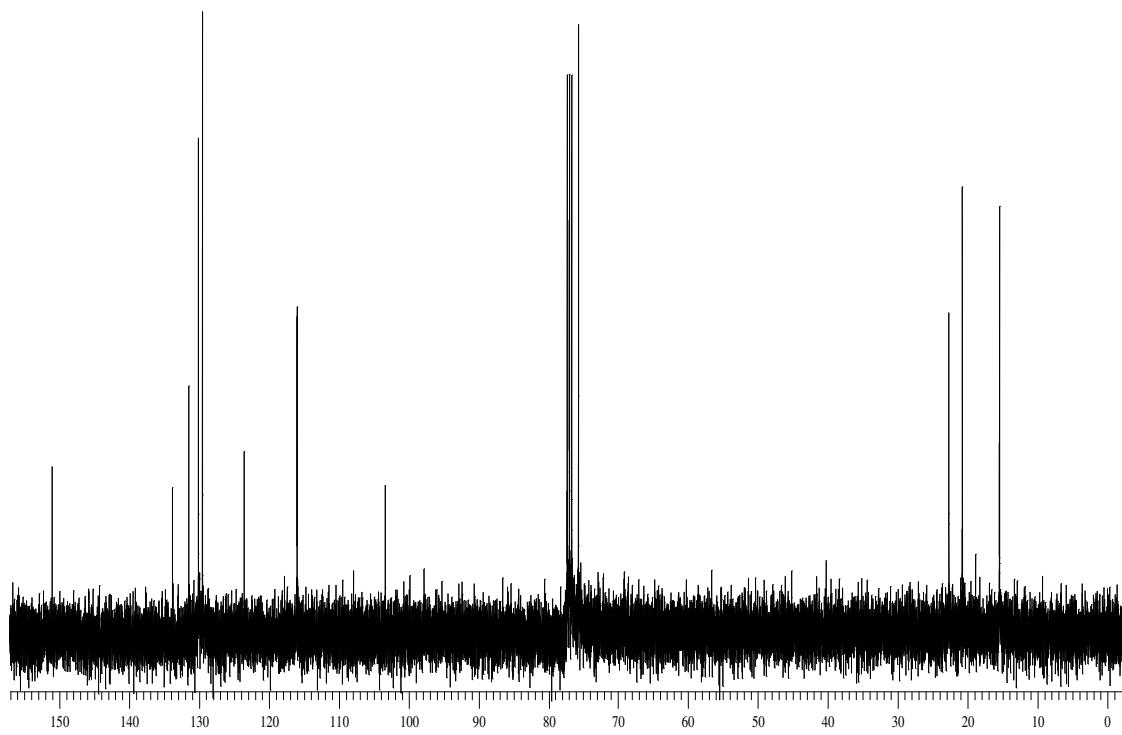
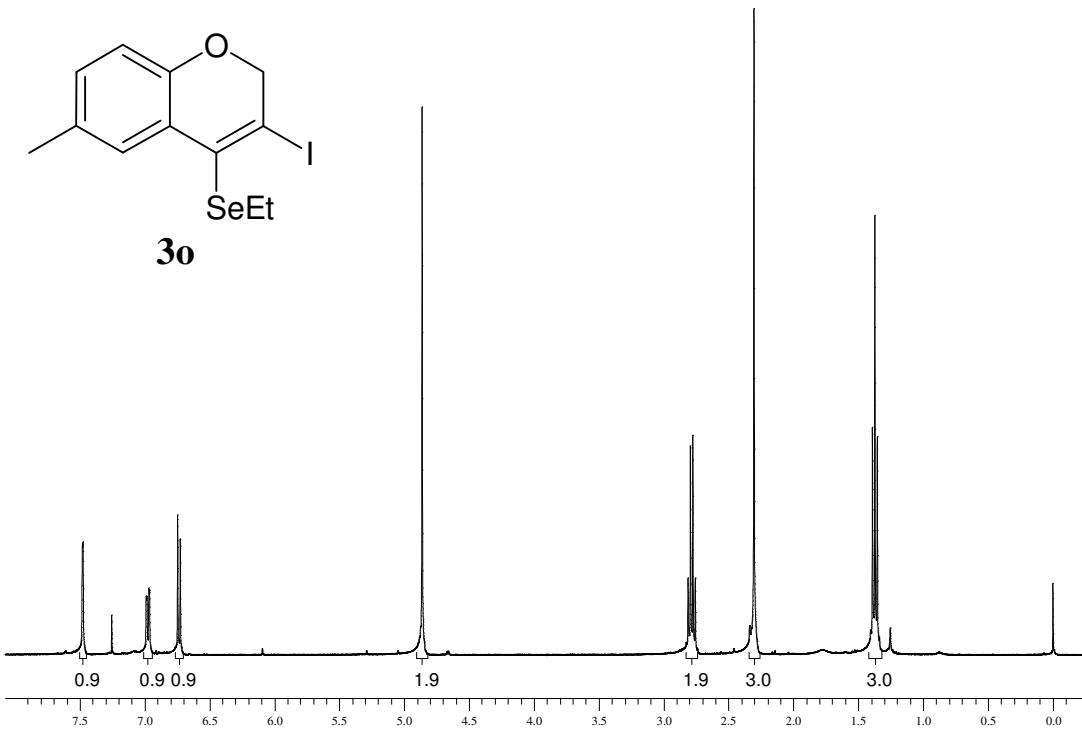
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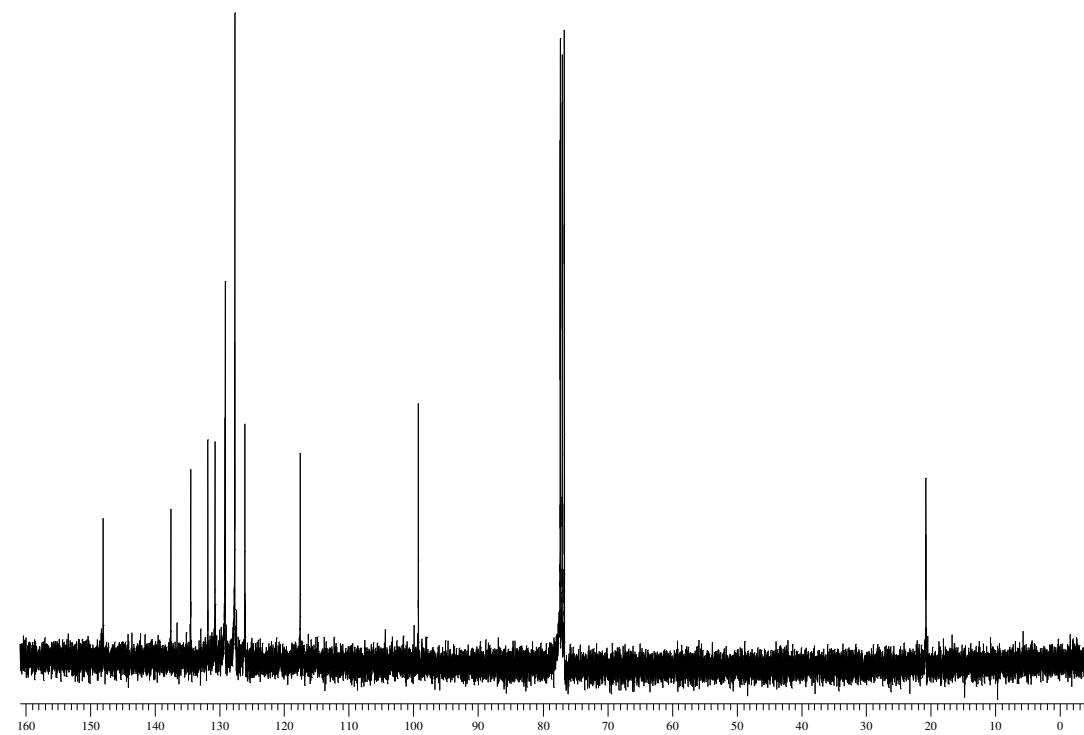
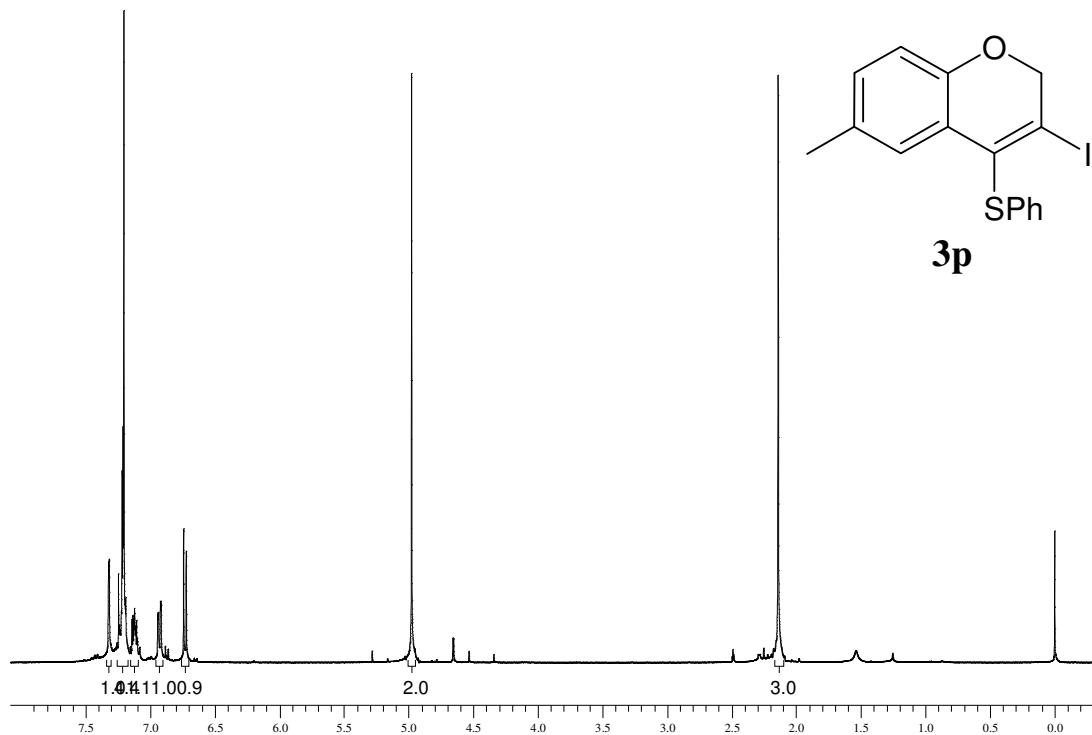


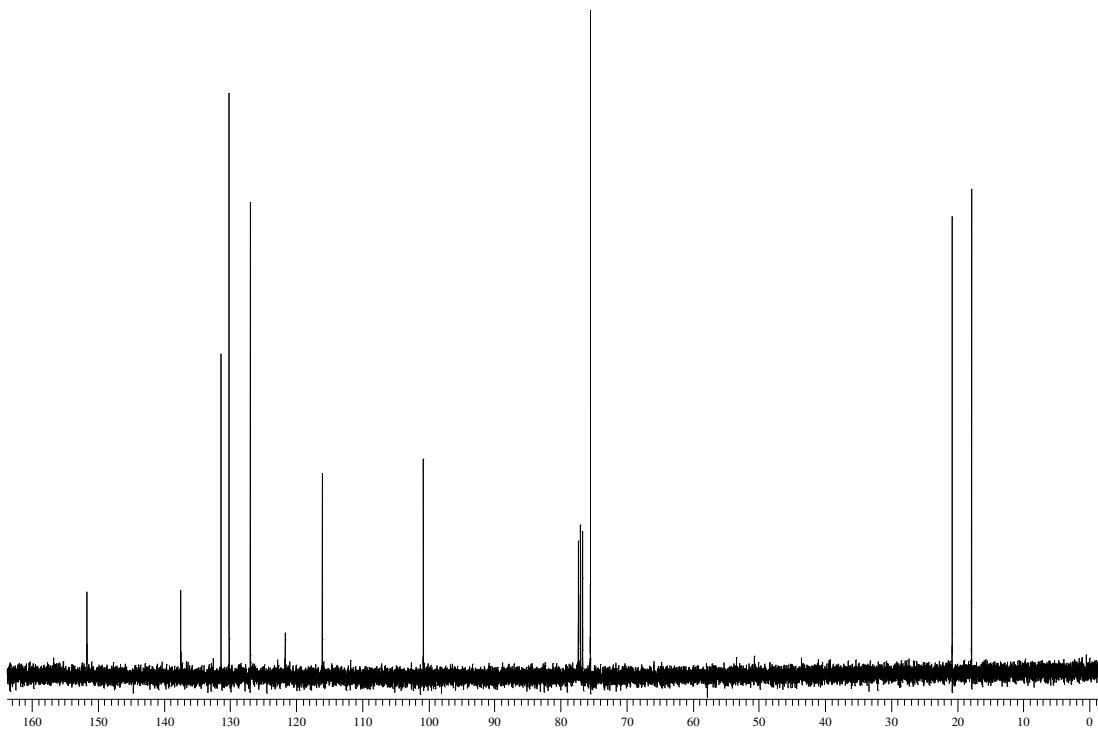
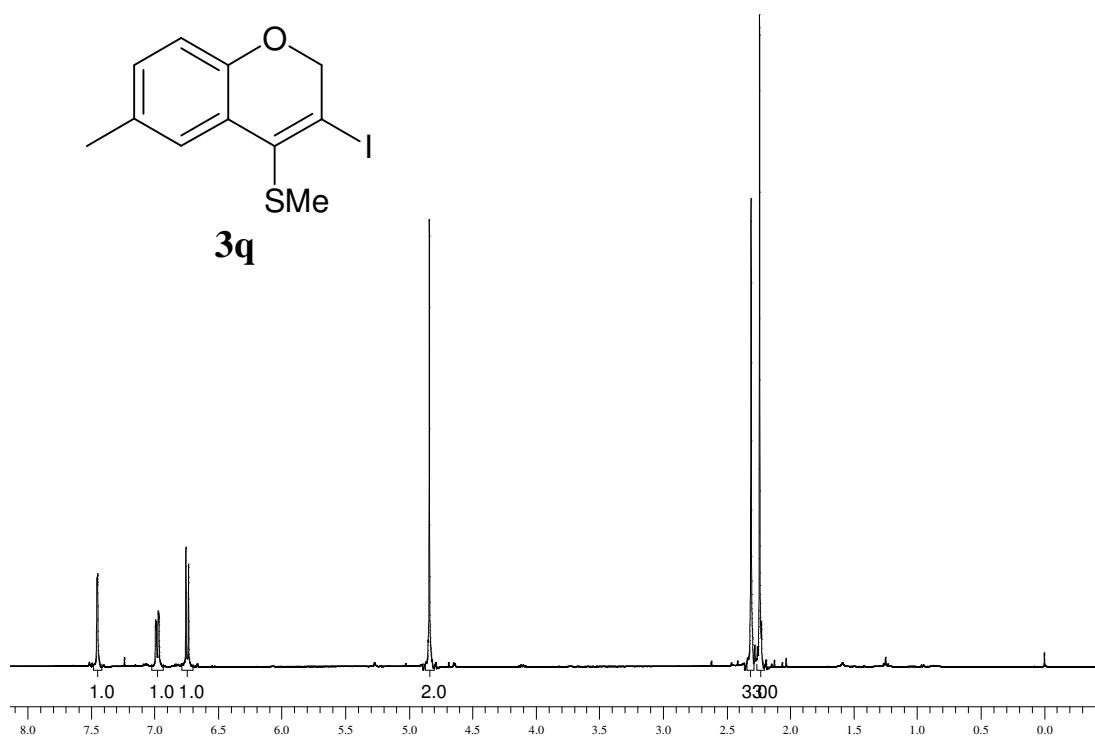
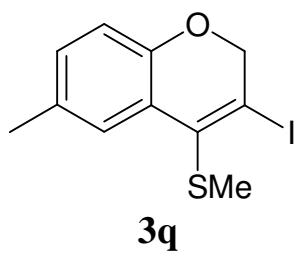


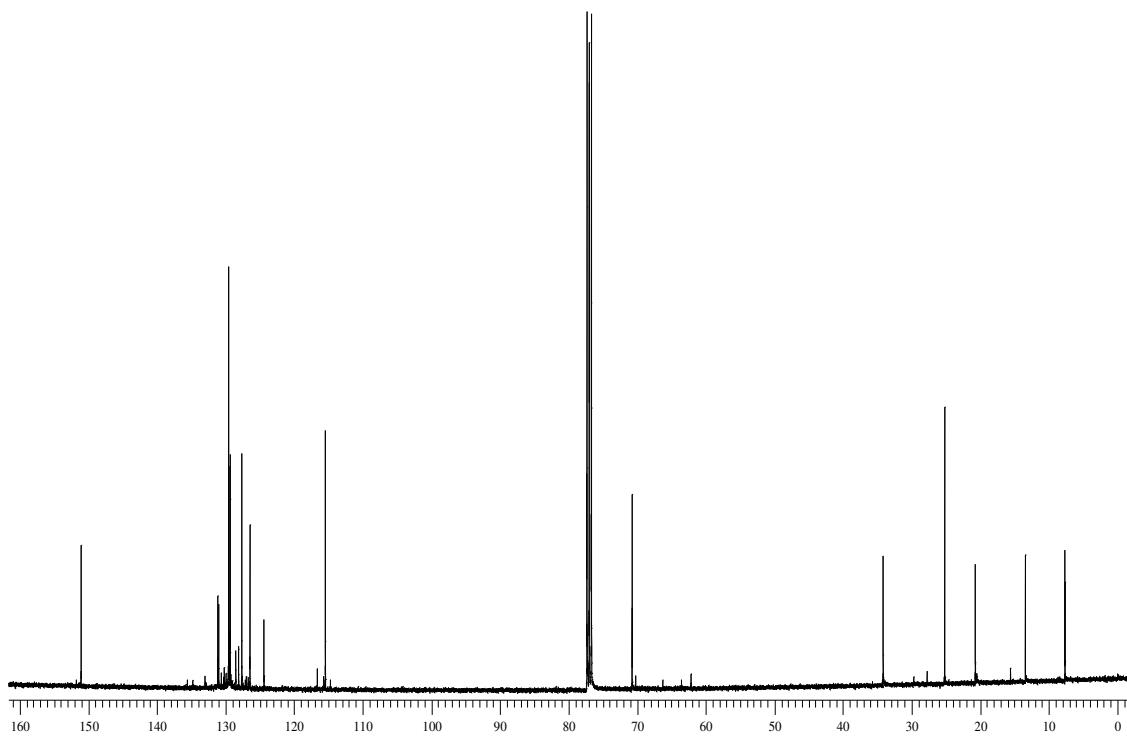
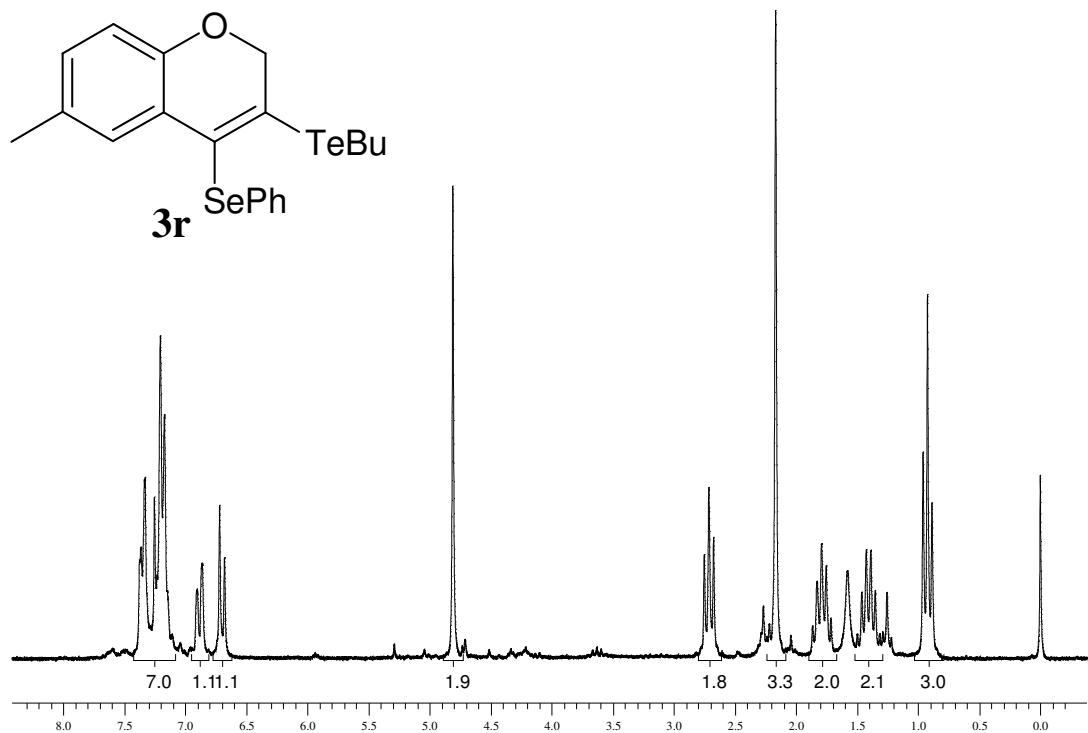


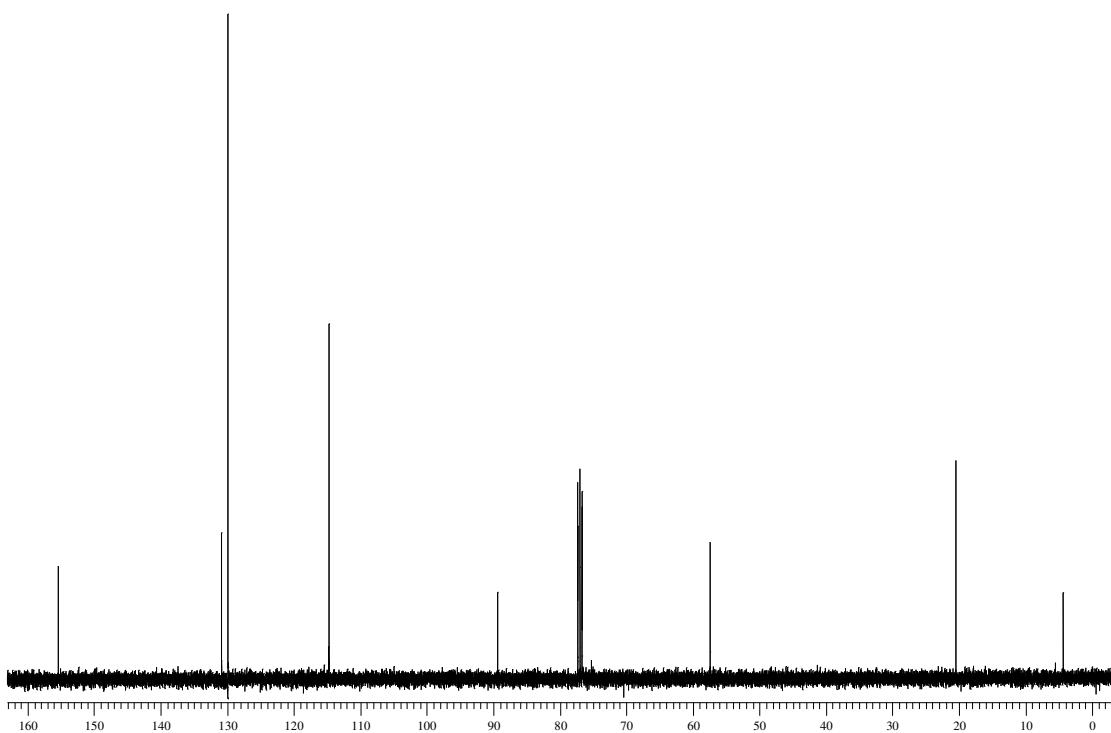
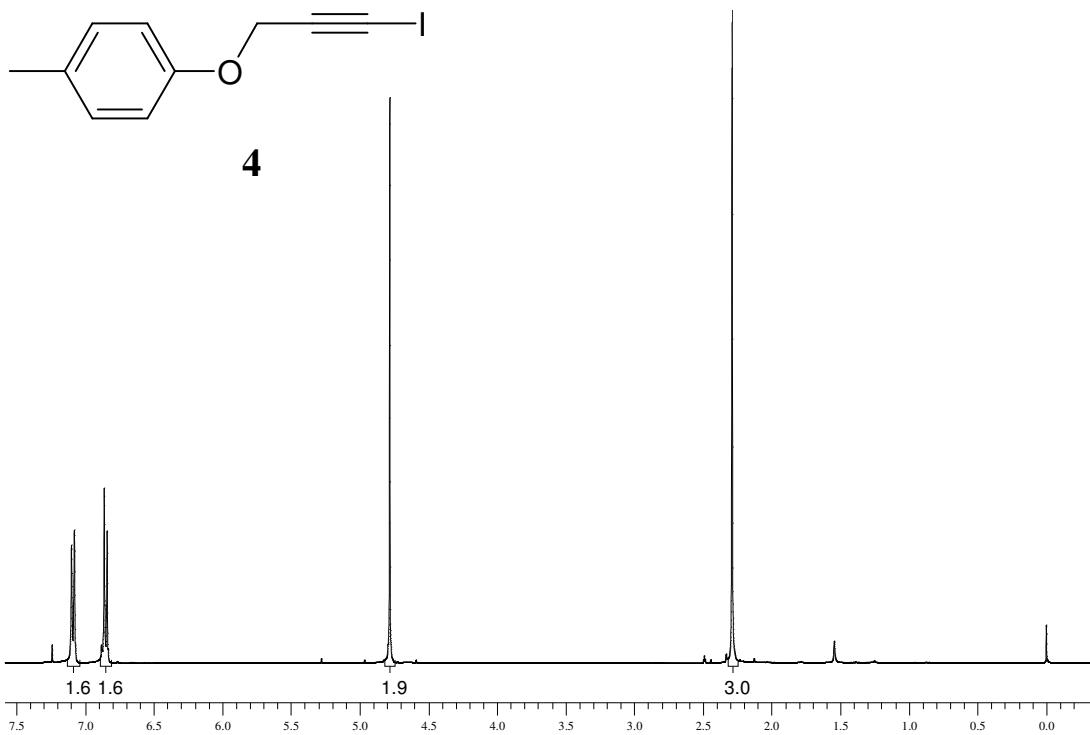


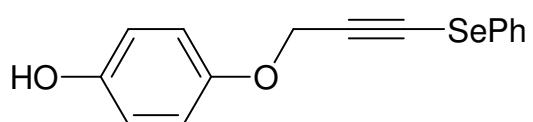




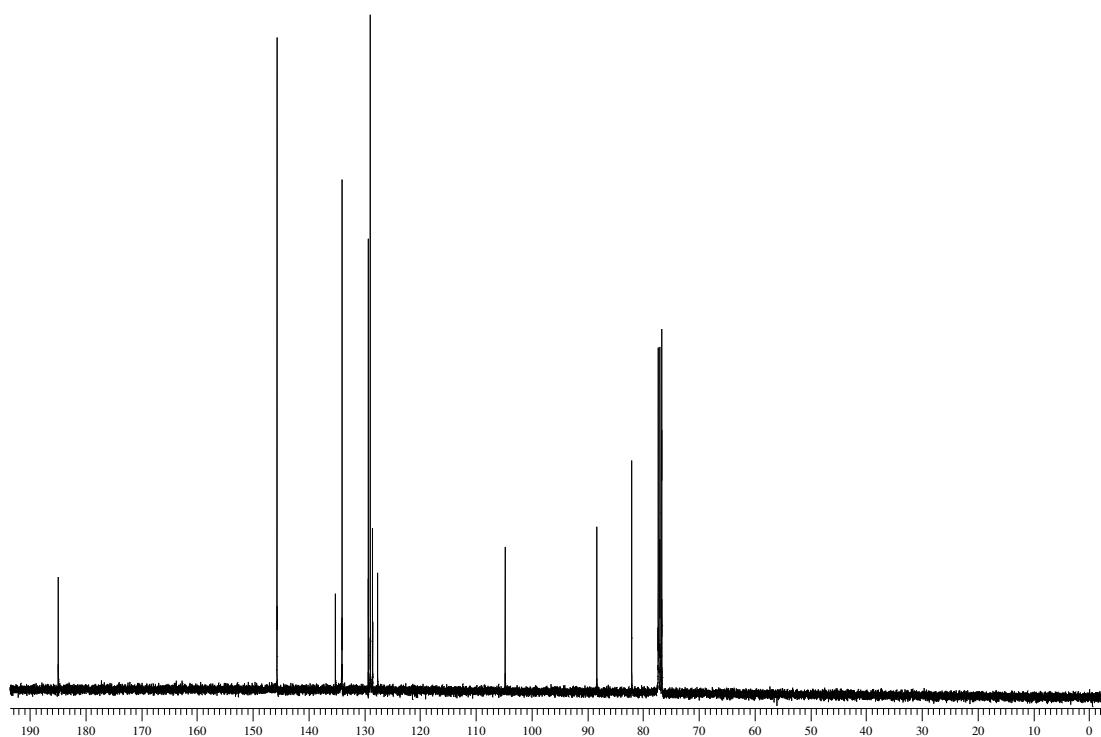
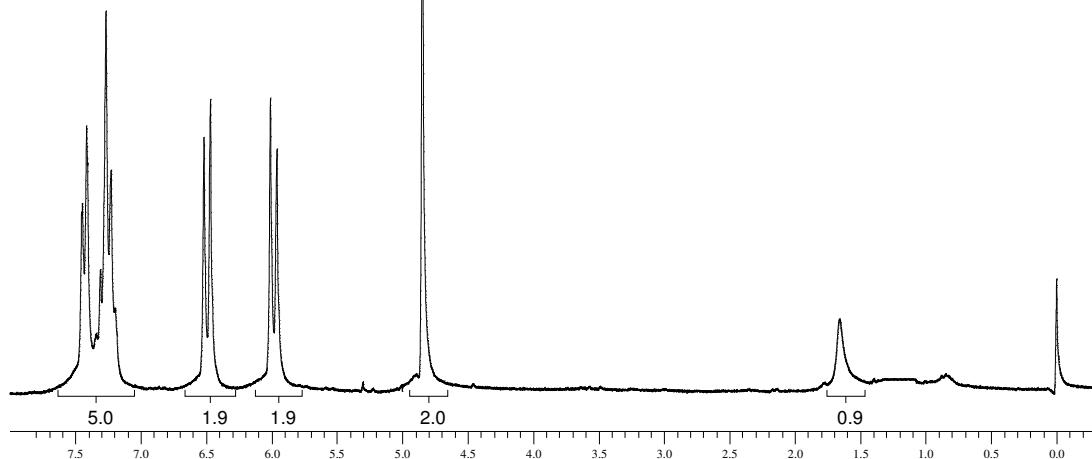


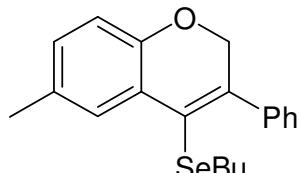




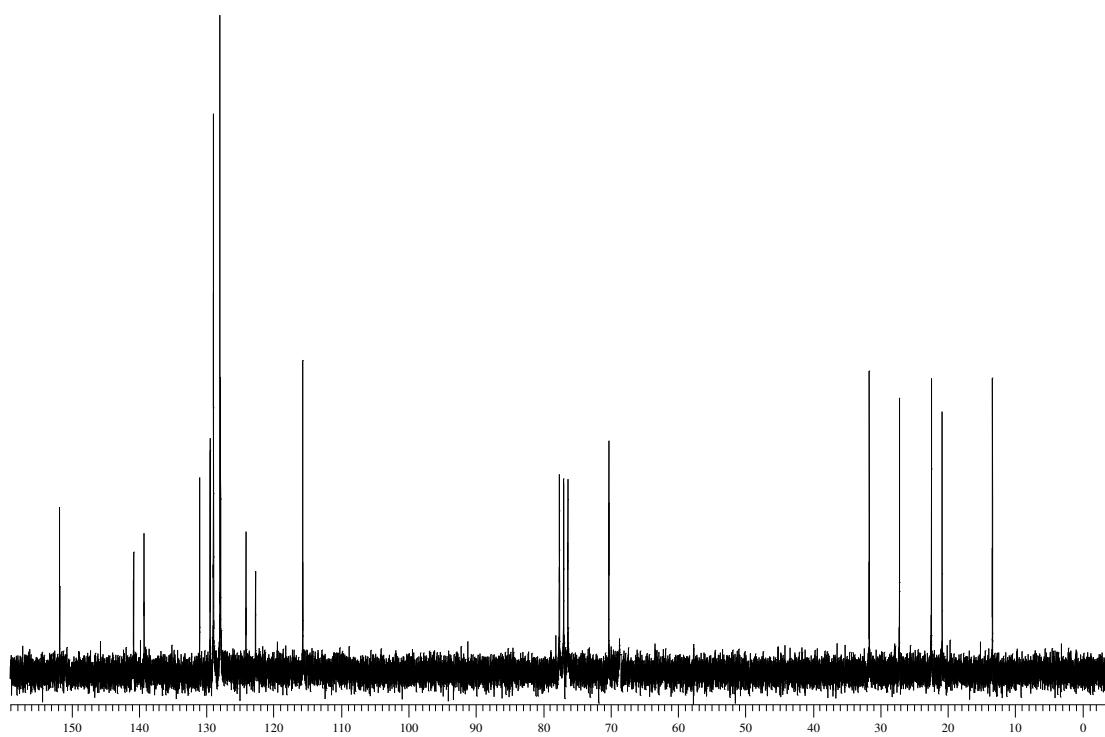
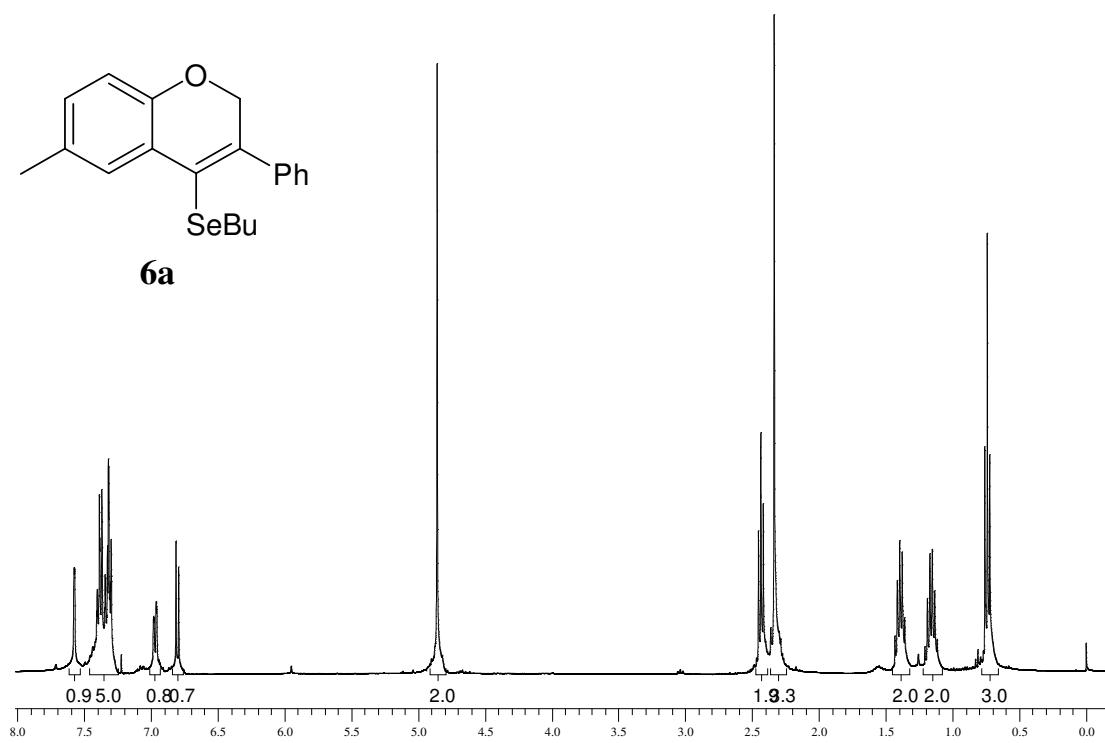


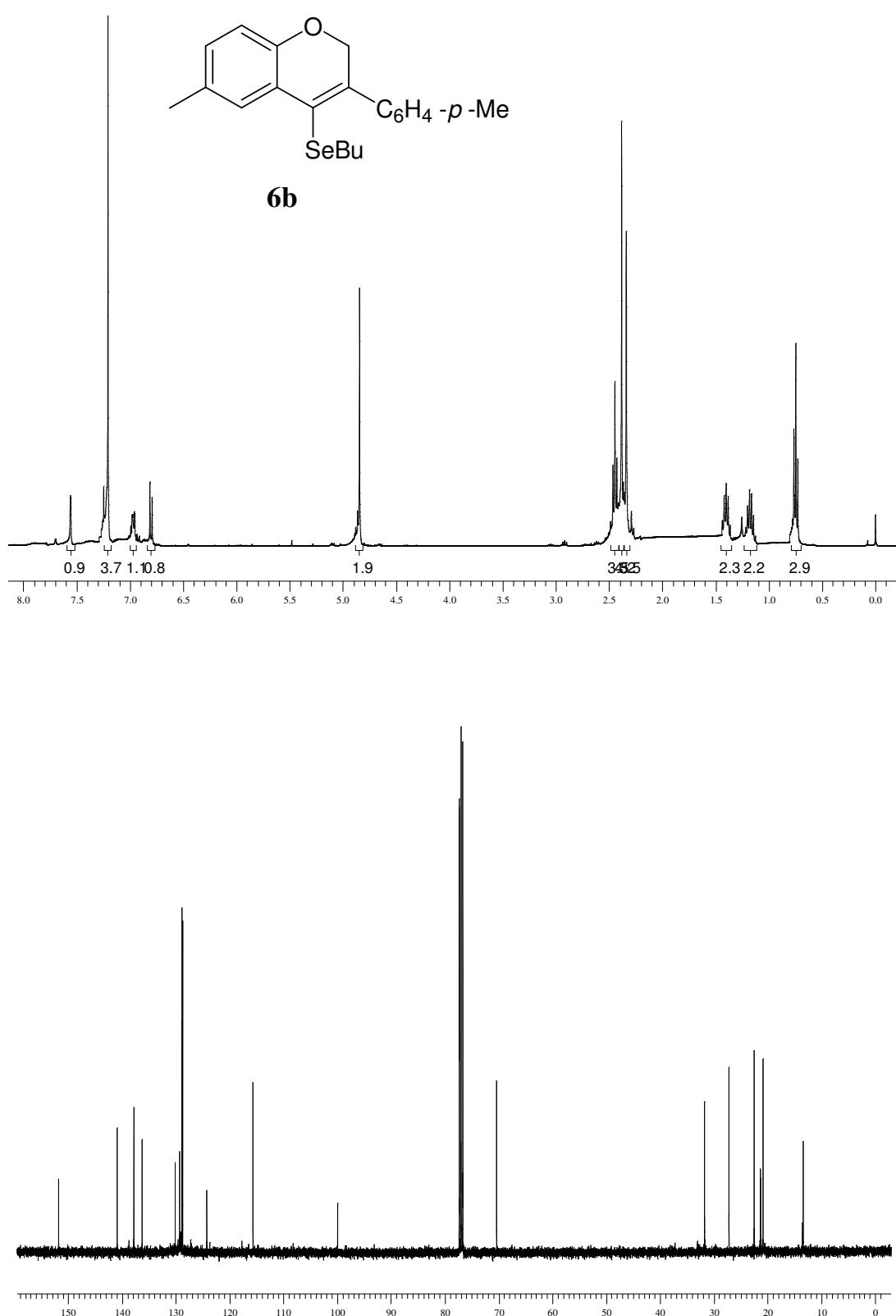
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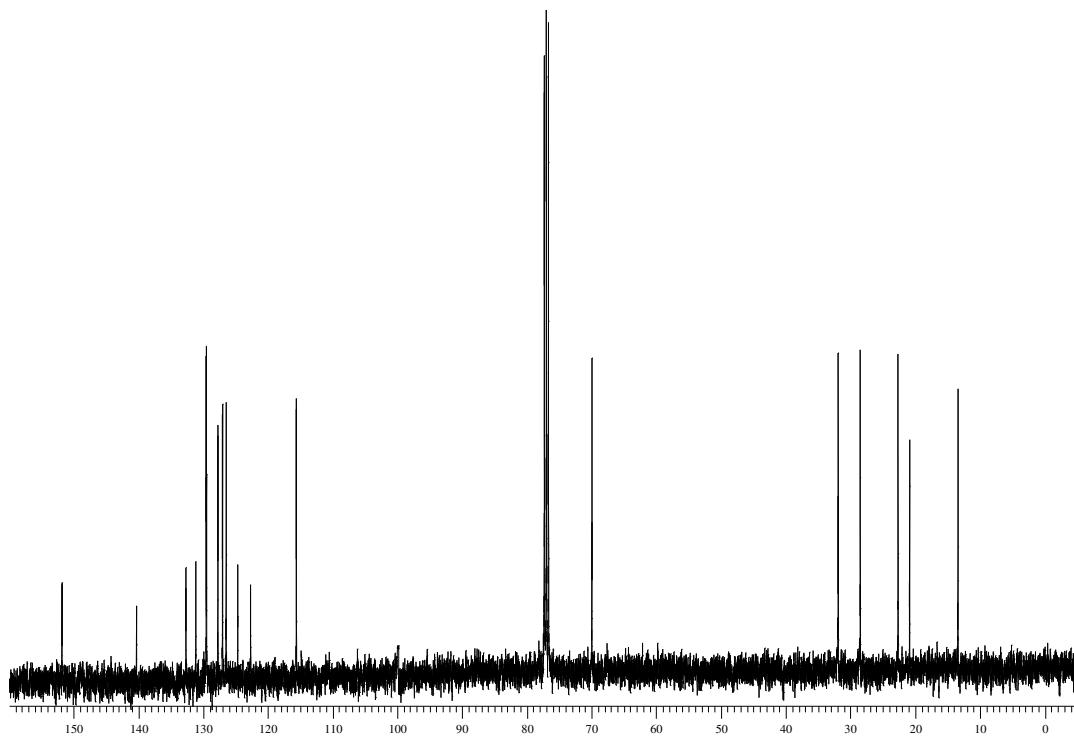
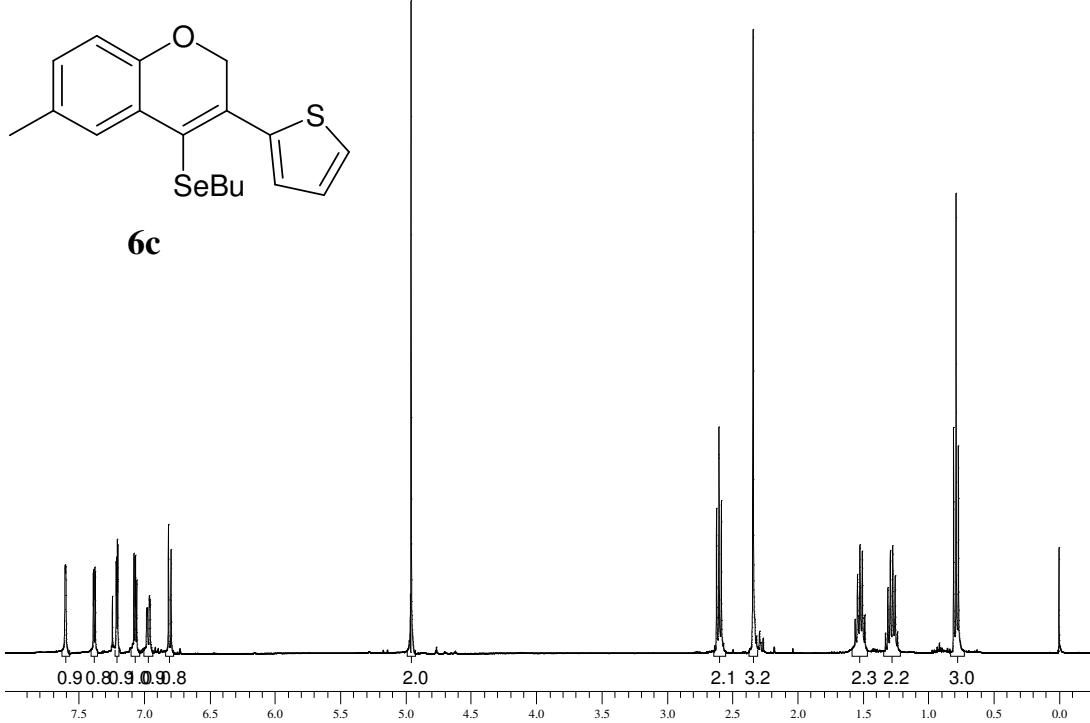


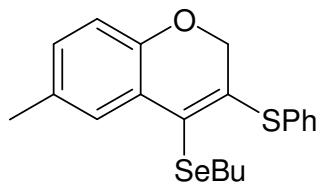


**6a**









**7a**

