

## SUPPORTING INFORMATION

### SYNTHESIS OF CHALCOGENYL-FUNCTIONALIZED 4*H*-CHROMEN-4-ONES VIA CYCLIZATION/CHALCOGENATION MEDIATED BY SELECTFLUOR®

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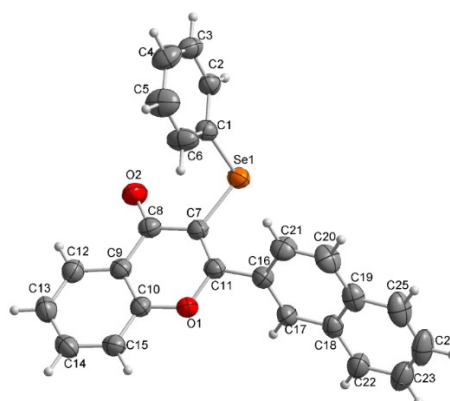
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## General Methods

Commercial reagents were used without further purification. All reactions were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm) followed by spraying with acidic vanillin solution. Hydrogen nuclear magnetic resonance spectra ( $^1\text{H}$  NMR) were obtained on Bruker Avance III HD 400 MHz employing a direct broadband probe at 400 MHz. The spectra were recorded in  $\text{CDCl}_3$  solutions. The chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference. Coupling constants ( $J$ ) are reported in Hertz. Carbon-13 nuclear magnetic resonance spectra ( $^{13}\text{C}$  NMR) were obtained on Bruker Avance III HD 400 MHz employing a direct broadband probe at 100 MHz. The chemical shifts are reported in ppm, referenced to the solvent peak of  $\text{CDCl}_3$  ( $\delta$  77.0 ppm). Fluor-19 nuclear magnetic resonance spectra ( $^{19}\text{F}$  NMR) were obtained on Bruker Avance III HD 400 MHz employing a direct broadband probe at 376 MHz. The chemical shifts are reported in ppm, referenced to 2-fluorobenzaldehyde ( $\delta$  -122.4 ppm) as the external reference. Selenium-77 nuclear magnetic resonance spectra ( $^{77}\text{Se}$  NMR) were obtained on Bruker Avance III HD 400 MHz employing a direct broadband probe at 76 MHz. The chemical shifts are reported in ppm, referenced to diphenyl diselenide ( $\delta$  463 ppm) as the external reference. The high-resolution electrospray ionization mass spectrometry (ESI-QTOF) analysis were performed on a Bruker Daltonics micrOTOF-Q II instrument in positive mode. The samples were solubilized in HPLC-grade acetonitrile and injected into the APCI source by means of a syringe pump at a flow rate of  $5.0\ \mu\text{L min}^{-1}$ . The follow instrument parameters were applied: capillary and cone voltages were set to +3500 V and -500 V, respectively, with a desolvation temperature of 180  $^\circ\text{C}$ . For data acquisition and processing, Compass 1.3 for micrOTOF-Q II software (Bruker Daltonics, USA) was used. The data were collected in the  $m/z$  range of 50-1200 at the speed of two scans per second. Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 mass spectrometer. Melting point (mp) values were measured in a Marte PFD III instrument with a 0.1  $^\circ\text{C}$  precision. A Bruker D8 Venture diffractometer operating with an Incoatec I $\mu$ S high brilliance Mo-K $\alpha$ ,  $\lambda = 0.71073\ \text{\AA}$ , X-ray tube with two-dimensional Montel micro-focusing optics and a Photon 100 detector was used to acquire the single-crystal data for compounds **3q**. The structure was solved by dual space methods with Bruker XT<sup>1</sup> and refined with Bruker XL<sup>2,3</sup> on  $F^2$  using anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms positions were calculated starting from the idealized positions. Diamond program was used for the crystal structure plots <sup>4</sup>. Table S1 contains the crystal data and further

details regarding to the data collection and refinement for the analyzed crystals. CCDC 2169580 contains the supplementary crystallographic data for **3q**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. The starting materials **1**<sup>5,6</sup> and **4**<sup>7</sup> were synthesized according to literature procedures.



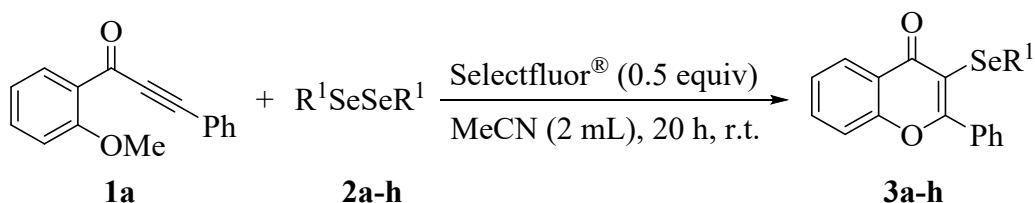
**Figure S1** Molecular structure of **3q**, non-hydrogen atoms are shown at the 50% probability level.

**Table S1.** Crystallographic and structure refinement data for **3q**.

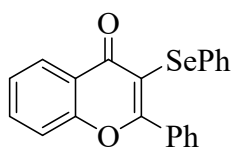
Formula	C <sub>25</sub> H <sub>16</sub> O <sub>2</sub> Se
Mw (g·mol <sup>-1</sup> )	427.34
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	13.835(3)
<i>b</i> (Å)	16.655(3)
<i>c</i> (Å)	8.5970(18)
$\alpha$ (°)	90
$\beta$ (°)	107.296(7)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	1891.4(6)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	1.501
$\mu$ (mm <sup>-1</sup> )	2.003
Collected	70153
Reflections	
Independent reflections [ <i>R</i> <sub>int</sub> ]	5798 [0.0426]
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.0326/0.0695
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0574/0.0785
GOOF	1.015

Compound **3q** single crystal was obtained by slowly evaporating ethyl acetate solution at room temperature for about 4-5 days.

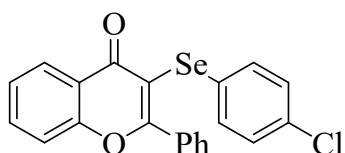
## Procedure for the synthesis of chromenones 3a-h



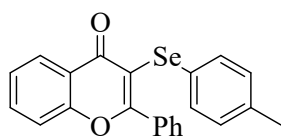
To a test tube, under ambient atmosphere, containing Selectfluor<sup>®</sup> (0.5 equiv) and MeCN (1.0 mL) were added diorganyl diselenide **2** (0.5 equiv), the reaction mixture was stirred for 5 min at room temperature. After this time, the appropriate alkynyl aryl ketone **1** (0.5 mmol) in MeCN (1.0 mL) was added and the reaction mixture was stirred at room temperature for 20 h. After this, the mixture was extracted with ethyl acetate (3 x 30 mL) and water (20 mL). the resulting organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/acetate (95:5).



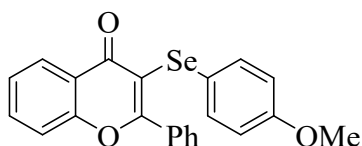
**2-phenyl-3-(phenylselanyl)-chromen-4-one 3a:** The product was isolated as a yellow solid. Yield: 0.169 g (90%). m.p. 127-128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.27 (dd,  $J$  = 7.9, 1.7 Hz, 1H), 7.74 – 7.64 (m, 3H), 7.54 – 7.40 (m, 5H), 7.36 – 7.28 (m, 2H), 7.18 – 7.11 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  176.0, 167.8, 156.0, 134.2, 134.0, 131.9, 131.0, 130.8, 129.2, 129.0, 128.4, 126.73, 126.70, 125.6, 122.4, 117.9, 114.0. <sup>77</sup>Se NMR (CDCl<sub>3</sub>, 76 MHz):  $\delta$  300.7. MS (EI, 70 eV;  $m/z$  (relative intensity)): 377 (47), 297 (69), 178 (79), 105 (100), 77 (51). HRMS: calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub>Se (ESI-TOF, [M+H]<sup>+</sup>), 379.0237, found 379.0220



**3-((4-chlorophenyl)selanyl)-2-phenyl-chromen-4-one 3b:** The product was isolated as a yellow solid. Yield: 0.136 g (66%). m.p. 178-179 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.25 (ddd,  $J$  = 8 Hz, 1H), 7.74 – 7.61 (m, 3H), 7.56 – 7.39 (m, 5H), 7.30 – 7.20 (m, 2H), 7.15 – 7.07 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  175.8, 167.8, 156.0, 134.0, 134.0, 133.0, 132.5, 130.9, 129.4, 129.2, 129.1, 128.0, 126.7, 125.7, 122.3, 118.0, 114.0. <sup>77</sup>Se NMR (CDCl<sub>3</sub>, 76 MHz):  $\delta$  298.0. MS (EI, 70 eV;  $m/z$  (relative intensity)): 414 (32), 412 (77), 331 (42), 212 (48), 165 (26), 105 (100), 77 (12). HRMS: calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub>Se (ESI-TOF, [M+H]<sup>+</sup>); 412.9847, found 412.9835.

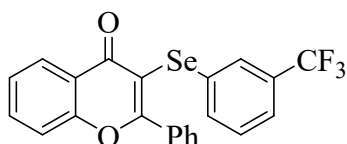


**2-phenyl-3-(p-tolylselanyl)-chromen-4-one 3c:** The product was isolated as a yellow solid. Yield: 0.125 g (64%). m.p. 107-108 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.24 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.70 – 7.58 (m, 3H), 7.51 – 7.34 (m, 5H), 7.27 – 7.21 (m, 2H), 6.97 – 6.92 (m, 2H), 2.23 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.9, 167.4, 155.8, 136.7, 134.2, 133.8, 131.5, 130.6, 129.7, 129.2, 127.8, 127.3, 126.1, 125.4, 122.4, 117.8, 114.4, 18.6.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  291.1. MS (EI, 70 eV;  $m/z$  (relative intensity)): 392 (100), 311 (97), 192 (47), 105 (80), 77 (20). HRMS: calcd for  $\text{C}_{22}\text{H}_{17}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 393.0394, found 393.0387.



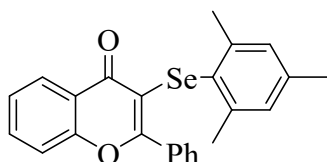
**3-((4-methoxyphenyl)selanyl)-2-phenyl-chromen-4-one 3d:**

The product was isolated as a yellow solid. Yield: 0.059 g (29%). m.p. 127-128 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 – 8.23 (m, 1H), 7.72 – 7.63 (m, 3H), 7.55 – 7.39 (m, 5H), 7.34 – 7.28 (m, 2H), 6.72 – 6.65 (m, 2H), 3.73 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  176.2, 167.1, 159.1, 156.0, 134.4, 134.3, 133.8, 130.6, 129.3, 128.0, 126.7, 125.4, 122.4, 121.0, 117.8, 115.3, 114.6, 55.2.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  283.6. MS (EI, 70 eV;  $m/z$  (relative intensity)): 407 (17), 327 (100), 165 (50), 105 (38), 77 (23). HRMS: calcd for  $\text{C}_{22}\text{H}_{17}\text{O}_3\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 409.0343, found 409.0332.



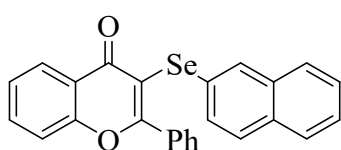
**2-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)-chromen-4-**

**one 3e:** The product was isolated as a yellow solid. Yield: 0.154 g (69%). m.p. 90-91 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.26 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.76 – 7.67 (m, 1H), 7.67 – 7.60 (m, 2H), 7.53 – 7.40 (m, 7H), 7.40 – 7.35 (m, 1H), 7.28 – 7.19 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.7, 167.8, 156.0, 134.3, 134.1, 133.8, 132.2, 131.1 (q,  $J = 32.4$  Hz), 131.0, 129.3, 129.0, 128.1, 127.6 (q,  $J = 3.9$  Hz), 126.6, 125.8, 123.6 (q,  $J = 273.0$  Hz), 123.5 (q,  $J = 3.8$  Hz), 122.2, 118.0, 113.7.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 375 MHz):  $\delta$  -63.1.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz)  $\delta$  309.0. MS (EI, 70 eV;  $m/z$  (relative intensity)): 446 (100), 365 (38), 246 (91), 165 (47), 105 (94), 89 (46), 77 (29). HRMS: calcd for  $\text{C}_{22}\text{H}_{14}\text{F}_3\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 447.0111, found 447.0105.

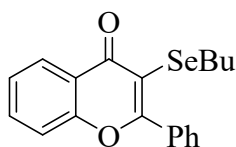


**3-(mesitylselanyl)-2-phenyl-chromen-4-one 3f:** The product was isolated as a yellow solid. Yield: 0.056 g (27%). m.p. 140-141 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.17 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 7.61 (ddd,  $J$  = 8.7, 7.1, 1.7 Hz, 1H), 7.52 (d,  $J$  = 1.6 Hz, 2H), 7.48 – 7.32 (m, 5H), 6.71 (q,  $J$  = 0.7 Hz, 2H), 2.29 (s, 6H), 2.15 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.9, 164.3, 155.8, 142.1, 137.7, 134.0, 133.5, 130.0, 128.8, 128.4, 127.8, 127.6, 125.9, 124.4, 120.8, 117.7, 115.5, 23.9, 20.8.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  201.5. MS (EI, 70 eV;  $m/z$  (relative intensity)): 420 (10), 339 (52), 119 (100), 91 (20), 77 (12). HRMS: calcd for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 421.0707, found 421.0679.

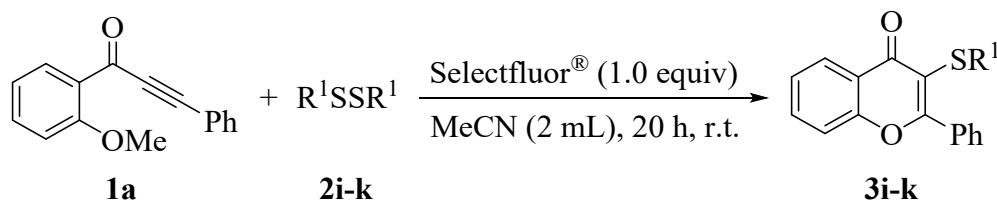


**3-(naphthalen-2-ylselanyl)-2-phenylchromen-4-one 3g:** The product was isolated as a yellow solid. Yield: 0.160 g (75%). m.p. 94–95 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.25 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 7.76 (d,  $J$  = 1.8 Hz, 1H), 7.72 – 7.56 (m, 6H), 7.49 – 7.33 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  176.0, 167.7, 156.0, 134.1, 133.9, 133.8, 132.1, 130.7, 129.8, 129.2, 128.8, 128.7, 128.4, 127.9, 127.6, 127.2, 126.7, 126.2, 125.7, 125.6, 122.4, 117.8, 114.1.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  301.8. MS (EI, 70 eV;  $m/z$  (relative intensity)): 427 (18), 347 (100), 228 (41), 105 (52), 77 (19). HRMS: calcd for  $\text{C}_{25}\text{H}_{17}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 429.0394, found 429.0384.



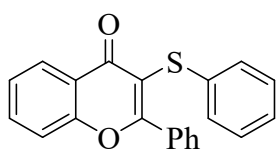
**3-(butylselanyl)-2-phenylchromen-4-one 3h:** The product was isolated as a yellow oil. Yield: 0.093 g (52%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.26 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.56 – 7.37 (m, 5H), 2.84 (t,  $J$  = 7.4 Hz, 2H), 1.49 (quint,  $J$  = 7.4 Hz, 2H), 1.26 (sex,  $J$  = 7.4 Hz, 2H), 0.79 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.1, 165.6, 154.0, 135.2, 133.6, 131.0, 129.3, 127.5, 125.2, 122.5, 117.2, 112.6, 31.5, 27.0, 22.6, 13.4.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  187.63. MS (EI, 70 eV;  $m/z$  (relative intensity)): 358 (16), 300 (100), 221 (32), 165 (35), 89 (38), 77 (18). HRMS: calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 359.0550, found 359.0548.

#### Procedure for the synthesis of chromenones 3i-k

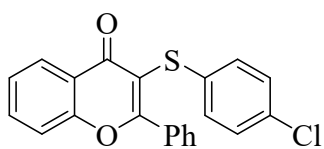


To a test tube, under ambient atmosphere, containing Selectfluor<sup>®</sup> (1.0 equiv) and

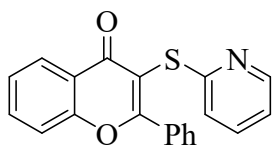
MeCN (1.0 mL) were added diorganyl disulfide (1.0 equiv), the reaction mixture was stirred for 5 min at room temperature. After this time, the appropriate alkynyl aryl ketone (0.5 mmol) in MeCN (1.0 mL) was added and the reaction mixture was stirred at room temperature for 20 h. After this, the mixture was extracted with ethyl acetate (3 x 30 mL) and water (20 mL). the resulting organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/acetate (95:5).



**2-phenyl-3-(phenylthio)-chromen-4-one 3i:** The product was isolated as a yellow solid. Yield: 0.127 g (77%). m.p. 127-128 °C. <sup>1</sup>H NRM (CDCl<sub>3</sub>, 400 MHz): δ 8.24 (ddd, *J* = 4.0 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.69 (ddd, *J* = 8.0 Hz, 1H), 7.53 – 7.39 (m, 5H), 7.23 – 7.16 (m, 4H), 7.13 – 7.07 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 175.8, 168.6, 155.8, 136.1, 134.0, 133.0, 131.0, 129.1, 128.9, 128.0, 127.3, 126.6, 125.8, 125.6, 122.7, 117.9, 115.2. MS (EI, 70 eV; *m/z* (relative intensity)): 330 (100), 210 (31), 165 (46), 121 (25), 77 (24). HRMS: calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub>S (ESI-TOF, [M+H]<sup>+</sup>); 331.0793, found 331.0790.



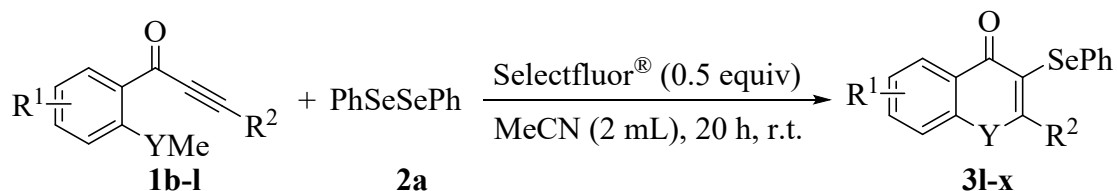
**3-((4-chlorophenyl)thio)-2-phenyl-chromen-4-one 3j:** The product was isolated as a yellow solid. Yield: 0.118 g (65%). m.p. 180-181 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.25 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.78 – 7.68 (m, 3H), 7.57 – 7.42 (m, 5H), 7.20 – 7.10 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 175.6, 168.7, 155.9, 134.7, 134.2, 132.9, 131.9, 131.1, 129.2, 129.0, 128.8, 128.2, 126.6, 125.8, 122.8, 118.0, 115.0. MS (EI, 70 eV; *m/z* (relative intensity)): 366 (39), 364 (100), 208 (27), 165 (53), 131 (16), 105 (18), 89 (30), 77 (21). HRMS: calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub>S (ESI-TOF, [M+H]<sup>+</sup>); 365.0398, found 365.0402



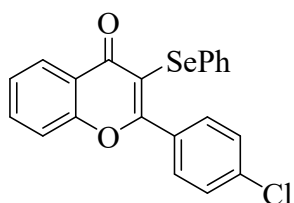
**2-phenyl-3-(pyridin-2-ylthio)-chromen-4-one 3k:** The product was isolated as a yellow oil. Yield: 0.050 (30%). <sup>1</sup>H NRM (CDCl<sub>3</sub>, 400 MHz): δ 8.33 (dd, *J* = 5.4, 1.5 Hz, 1H), 8.24 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.70 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.54 – 7.39 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 1H), 6.97 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 175.6, 168.6, 158.2, 155.9, 149.7, 136.3, 134.0, 133.1, 130.9, 129.1, 128.0, 126.5, 125.6, 122.7, 121.5, 120.0,

118.0, 113.6. MS (EI, 70 eV;  $m/z$  (relative intensity)): 344 (100), 311 (28), 224 (39), 165 (31), 135 (32), 91 (36), 77 (29). HRMS: calcd for  $C_{20}H_{14}NO_2S$  (ESI-TOF,  $[M+H]^+$ ); 332.0740, found 332.0758.

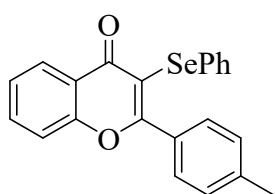
### Procedure for the synthesis of chromenones 3l-x



To a test tube, under ambient atmosphere, containing Selectfluor<sup>®</sup> (0.5 equiv) and MeCN (1.0 mL) were added diorganyl dichalcogenide (0.5 equiv), the reaction mixture was stirred for 5 min at room temperature. After this time, the appropriate alkynyl aryl ketone (0.5 mmol) in MeCN (1.0 mL) was added and the reaction mixture was stirred at room temperature for 20 h. After this, the mixture was extracted with ethyl acetate (3 x 30 mL) and water (20 mL). the resulting organic phase was separated, dried over  $MgSO_4$ , and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/acetate (95:5).



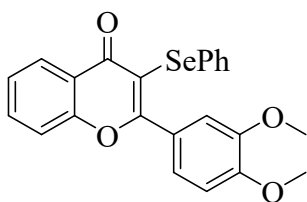
**2-(4-chlorophenyl)-3-(phenylselanyl)-chromen-4-one 3l:** The product was isolated as a yellow solid. Yield: 0.148 g (72%). m.p. 105-106 °C.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.24 (ddd,  $J = 8.0, 1.7, 0.5$  Hz, 1H), 7.67 (ddd,  $J = 8.4, 7.1, 1.7$  Hz, 1H), 7.63 – 7.58 (m, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.40 (m, 1H), 7.40 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 7.17 – 7.09 (m, 3H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  175.7, 166.3, 155.8, 136.8, 134.0, 132.4, 131.1, 131.0, 130.6, 129.0, 128.2, 126.8, 126.6, 125.6, 122.3, 117.8, 114.4.  $^{77}Se$  NMR ( $CDCl_3$ , 76 MHz):  $\delta$  299.4. MS (EI, 70 eV;  $m/z$  (relative intensity)): 412 (100), 331 (77), 214 (32), 163 (37), 139 (98), 92 (30), 77 (58). HRMS: calcd for  $C_{21}H_{14}ClO_2Se$  (ESI-TOF,  $[M+H]^+$ ); 412.9847, found 412.9843.



**3-(phenylselanyl)-2-(p-tolyl)-chromen-4-one 3m:** The product was isolated as a yellow solid. Yield: 0.149 g (76%). m.p. 108-109 °C.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.24 (dd,  $J = 8.0, 1.7$  Hz, 1H), 7.66 (ddd,  $J = 8.7, 7.1, 1.7$  Hz, 1H), 7.58 (d,  $J = 6.3$  Hz, 2H), 7.46 (dd,  $J = 8.5,$

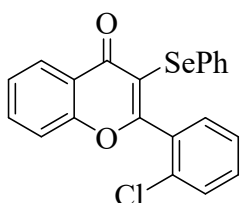


1.1 Hz, 1H), 7.40 (ddd,  $J = 8.1, 7.1, 1.1$  Hz, 1H), 7.33 (dd,  $J = 4.4, 3.2$  Hz, 2H), 7.27 – 7.21 (m, 2H), 7.13 (dd,  $J = 4.9, 2.0$  Hz, 3H), 2.41 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.9, 168.0, 156.0, 141.2, 133.8, 131.5, 131.4, 130.9, 129.2, 129.0, 128.6, 126.7, 126.6, 125.4, 122.4, 117.8, 113.6, 21.5.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  298.13. MS (EI, 70 eV;  $m/z$  (relative intensity)): 492 (100), 388 (24), 311 (63), 192 (45), 119 (83), 105 (22), 77 (16). HRMS: calcd for  $\text{C}_{22}\text{H}_{17}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 393.0394, found 393.0363.



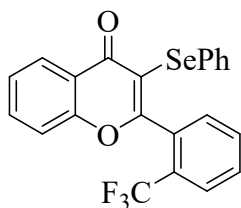
**2-(3,4-dimethoxyphenyl)-3-(phenylselanyl)-chromen-4-one 3n:**

The product was isolated as a yellow solid. Yield: 0.165 g (75%). m.p. 87-88 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.25 (dd,  $J = 8.0, 1.8$  Hz, 1H), 7.68 (ddd,  $J = 8.7, 7.1, 1.7$  Hz, 1H), 7.49 (dd,  $J = 8.2, 0.8$  Hz, 1H), 7.42 (ddd,  $J = 8.1, 7.1, 1.1$  Hz, 1H), 7.35 – 7.29 (m, 3H), 7.23 (d,  $J = 2.1$  Hz, 1H), 7.18 – 7.09 (m, 3H), 6.91 (d,  $J = 8.4$  Hz, 1H), 3.93 (s, 3H), 3.76 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  176.0, 167.6, 155.9, 151.2, 148.2, 133.8, 131.9, 130.4, 129.0, 127.1, 126.6, 126.4, 125.5, 123.1, 122.4, 116.8, 113.6, 112.6, 110.4, 56.0, 55.8.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  305.2. MS (EI, 70 eV;  $m/z$  (relative intensity)): 438 (100), 435 (28), 357 (56), 165 (93), 105 (36), 77 (13). HRMS: calcd for  $\text{C}_{23}\text{H}_{19}\text{O}_4\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 439.0448, found 439.0443.



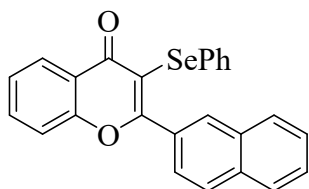
**2-(2-chlorophenyl)-3-(phenylselanyl)-chromen-4-one 3o:**

The product was isolated as a yellow solid. Yield: 0.124 g (60%). m.p. 127-128 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.27 (dd,  $J = 8.0, 1.7$  Hz, 1H), 7.67 (ddd,  $J = 8.7, 7.1, 1.7$  Hz, 1H), 7.48 – 7.29 (m, 8H), 7.13 (dd,  $J = 5.2, 2.0$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 165.5, 156.1, 134.0, 133.5, 133.0, 132.0, 131.3, 130.5, 130.2, 129.6, 128.8, 127.0, 126.6, 126.4, 125.6, 122.6, 117.9, 116.6.  $^{77}\text{Se}$  NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  301.0. MS (EI, 70 eV;  $m/z$  (relative intensity)): 412 (3), 414 (1), 377 (100), 297 (47), 163 (18), 77 (48), 51 (26). HRMS: calcd for  $\text{C}_{21}\text{H}_{14}\text{ClO}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 412.9847, found 412.9843.



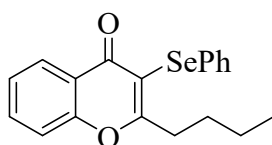
**3-(phenylselanyl)-2-(2-(trifluoromethyl)phenyl)-chromen-4-one 3p:**

The product was isolated as a yellow oil. Yield: 0.125 g (56%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 (dd,  $J = 8.0, 1.7$  Hz, 1H), 7.79 – 7.73 (m, 1H), 7.69 (ddd,  $J = 8.4, 7.2, 1.7$  Hz, 1H), 7.65 – 7.59 (m, 2H), 7.52 – 7.40 (m, 3H), 7.33 – 7.27 (m, 2H), 7.18 – 7.09 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.6, 165.9, 155.9, 134.1, 132.1 (d,  $J = 2.2$  Hz), 131.9, 131.5, 131.2, 130.5, 130.3, 129.0, 128.5 (q,  $J = 31.7$  Hz), 127.1, 126.7 (d,  $J = 3.7$  Hz), 126.6, 125.8, 123.5 (q,  $J = 274.4$  Hz), 122.6, 117.9, 115.8,  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 375 MHz):  $\delta$  -60.1.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  303.8. MS (EI, 70 eV;  $m/z$  (relative intensity)): 445 (12), 377 (100), 246 (25), 92 (23), 77 (38). HRMS: calcd for  $\text{C}_{22}\text{H}_{14}\text{F}_3\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 447.0111, found 447.0116.



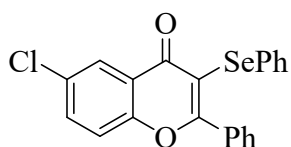
**2-(naphthalen-2-yl)-3-(phenylselanyl)-chromen-4-one 3q**

The product was isolated as a yellow solid. Yield: 0.190 g (89%). m.p. 169-170 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 (dd,  $J = 8.0, 1.7$  Hz, 1H), 8.13 (d,  $J = 1.9$  Hz, 1H), 7.89 – 7.81 (m, 3H), 7.73 (dd,  $J = 8.5, 1.8$  Hz, 1H), 7.67 (ddd,  $J = 8.7, 7.1, 1.7$  Hz, 1H), 7.60 – 7.46 (m, 3H), 7.42 (ddd,  $J = 8.1, 7.1, 1.2$  Hz, 1H), 7.38 – 7.28 (m, 2H), 7.10 (ddt,  $J = 5.1, 3.7, 2.0$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  176.0, 167.7, 156.0, 134.0, 133.9, 132.2, 131.4, 131.4, 131.1, 129.8, 129.0, 128.7, 127.7, 127.6, 126.7, 126.7, 126.7, 125.7, 125.5, 125.5, 122.4, 117.8, 114.3.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  300.2. MS (EI, 70 eV;  $m/z$  (relative intensity)): 428 (95), 347 (100), 228 (83), 2015 (49), 151 (30), 105 (39), 77 (48). HRMS: calcd for  $\text{C}_{25}\text{H}_{17}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 429.0394, found 429.0388.

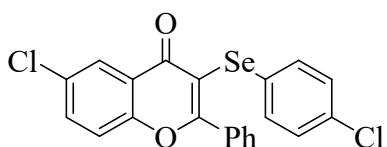


**2-butyl-3-(phenylselanyl)-chromen-4-one 3r:**

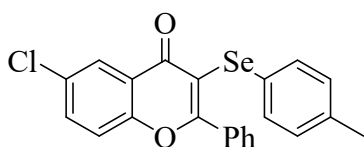
The product was isolated as a yellow oil. Yield: 0.071 g (40%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.27 (dd,  $J = 7.9, 1.8$  Hz, 1H), 7.76 – 7.59 (m, 3H), 7.55 – 7.38 (m, 5H), 2.84 (t,  $J = 7.4$  Hz, 2H), 1.50 (quint,  $J = 7.4$  Hz, 2H), 1.25 (sex,  $J = 7.4$  Hz, 2H), 0.80 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  176.6, 165.6, 155.6, 134.5, 133.6, 130.9, 129.4, 127.9, 126.4, 125.3, 122.0, 117.8, 112.8, 32.0, 27.0, 22.7, 13.4.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  187.3. MS (EI, 70 eV;  $m/z$  (relative intensity)): 358 (16), 301 (100), 298 (29), 221 (32), 89 (29), 77 (14). HRMS: calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 359.0550, found 359.0549.



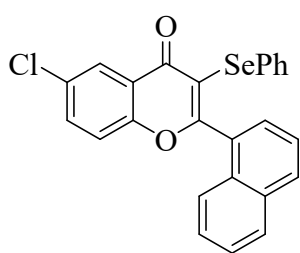
**6-chloro-2-phenyl-3-(phenylselanyl)-chromen-4-one 3s:** The product was isolated as a yellow solid. Yield: 0.169 g (82%). m.p. 104–105 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.20 (d,  $J$  = 2.6 Hz, 1H), 7.68 – 7.59 (m, 3H), 7.53 – 7.40 (m, 4H), 7.31 (dd,  $J$  = 6.6, 3.0 Hz, 2H), 7.18 – 7.09 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  174.9, 167.7, 154.3, 134.1, 133.8, 131.4, 131.3, 131.0, 130.9, 129.2, 129.0, 128.0, 127.0, 126.0, 123.3, 119.6, 114.3.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  301.7. MS (EI, 70 eV;  $m/z$  (relative intensity)): 414 (39), 412 (86), 331 (51), 257 (28), 178 (100), 105 (82), 77 (67). HRMS: calcd for  $\text{C}_{21}\text{H}_{14}\text{ClO}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 412.9847, found 412.9827.



**6-chloro-3-((4-chlorophenyl)selanyl)-2-phenyl-chromen-4-one 3t:** The product was isolated as a yellow solid. Yield: 0.158 g (71%). m.p. 155–156 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.20 (d,  $J$  = 2.5 Hz, 1H), 7.66 – 7.60 (m, 3H), 7.55 – 7.41 (m, 4H), 7.27 – 7.21 (m, 2H), 7.13 – 7.07 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  174.8, 167.8, 154.3, 134.3, 133.7, 133.3, 132.9, 131.6, 131.0, 129.2, 129.2, 129.0, 128.1, 126.0, 123.3, 119.7, 114.3.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  301.2. MS (EI, 70 eV;  $m/z$  (relative intensity)): 448 (66), 446 (100), 377 (30), 365 (43), 105 (95), 77 (14). HRMS: calcd for  $\text{C}_{21}\text{H}_{13}\text{Cl}_2\text{O}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 446.9458, found 446.9449.

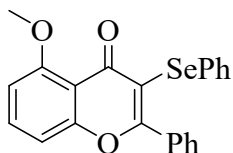


**6-chloro-2-phenyl-3-(p-tolylselanyl)-chromen-4-one 3u:** The product was isolated as a yellow solid. Yield: 0.107 g (50%). m.p. 125–126 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.19 (d,  $J$  = 2.6 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.59 (dd,  $J$  = 8.9, 2.6 Hz, 1H), 7.52 – 7.37 (m, 4H), 7.26 – 7.19 (m, 2H), 6.95 (d,  $J$  = 7.9 Hz, 2H), 2.24 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  174.9, 167.4, 154.2, 137.0, 134.0, 133.9, 131.9, 131.3, 130.8, 129.8, 129.3, 128.0, 127.0, 126.0, 123.3, 119.6, 114.7, 21.0.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  294.0. MS (EI, 70 eV;  $m/z$  (relative intensity)): 428 (37), 426 (100), 345 (67), 192 (47), 105 (76), 77 (10). HRMS: calcd for  $\text{C}_{22}\text{H}_{16}\text{ClO}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 427.0004, found 426.9994.

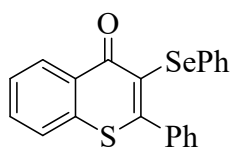


**6-chloro-2-(naphthalen-1-yl)-3-(phenylselanyl)-chromen-4-one**

**3v:** The product was isolated as a yellow solid. Yield: 0.074 g (32%). m.p. 164-165 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.28 (d,  $J = 2.6$  Hz, 1H), 7.97 (ddd,  $J = 6.2, 3.0, 0.9$  Hz, 1H), 7.90 (dd,  $J = 7.8; 1.3$  Hz, 1H), 7.63 – 7.57 (m, 2H), 7.55 – 7.40 (m, 4H), 7.36 (d,  $J = 8.9$  Hz, 1H), 7.21 – 7.16 (m, 2H), 7.08 – 6.96 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  174.7, 167.3, 154.6, 134.2, 133.3, 132.5, 131.5, 131.4, 130.8, 130.4, 130.0, 128.8, 128.6, 127.6, 127.2, 127.1, 126.4, 126.0, 124.7, 124.6, 123.6, 119.8, 117.6.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  307.5. MS (EI, 70 eV;  $m/z$  (relative intensity)): 464 (40), 462 (89), 305 (100), 228 (72), 213 (49), 77 (41). HRMS: calcd for  $\text{C}_{25}\text{H}_{16}\text{ClO}_2\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ); 463.0004, found 462.9998.

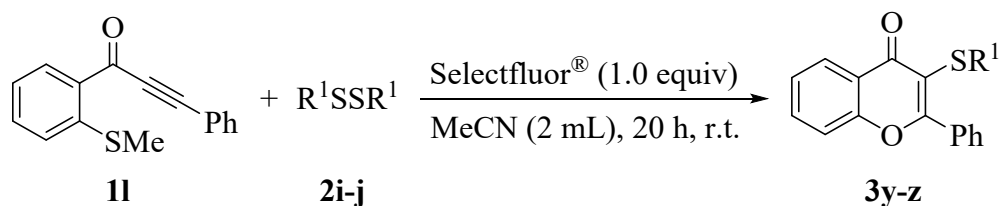


**5-methoxy-2-phenyl-3-(phenylselanyl)-chromen-4-one 3w:** The product was isolated as a yellow solid. Yield: 0.051 g (25%). m.p. 166-167 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68 – 7.61 (m, 2H), 7.54 (t,  $J = 8.4$  Hz, 1H), 7.49 – 7.36 (m, 3H), 7.34 – 7.27 (m, 2H), 7.10 (dd,  $J = 6.2, 3.2$  Hz, 3H), 7.02 (dd,  $J = 8.5, 1.0$  Hz, 1H), 6.83 (dd,  $J = 8.4, 1.0$  Hz, 1H), 3.96 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  175.1, 165.7, 160.0, 158.0, 134.0, 133.9, 131.7, 131.1, 130.4, 129.2, 128.9, 127.8, 126.4, 115.5, 113.2, 109.8, 106.9, 56.5.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  299.7. MS (EI, 70 eV;  $m/z$  (relative intensity)): 408 (38), 251 (78), 250 (100), 178 (68), 107 (37), 77 (75). HRMS: calcd for  $\text{C}_{22}\text{H}_{17}\text{O}_3\text{Se}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ), 409.0343, found 409.0323.

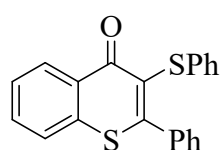


**2-phenyl-3-(phenylselanyl)-thiochromen-4-one 3x:** The product was isolated as a yellow solid. Yield: 0.123 g (63%). m.p. 112-113 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.55 (dd,  $J = 8.3, 1.3$  Hz, 1H), 7.67 – 7.50 (m, 3H), 7.44 – 7.28 (m, 5H), 7.24 – 7.16 (m, 2H), 7.14 – 7.00 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  178.1, 155.9, 138.2, 137.2, 132.1, 132.0, 131.6, 129.9, 129.8, 129.6, 128.8, 128.5, 128.3, 128.2, 128.0, 126.6, 125.5.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 76 MHz):  $\delta$  351.3. MS (EI, 70 eV;  $m/z$  (relative intensity)): 394 (100), 313 (41), 208 (88), 178 (65), 165 (63), 89 (27). HRMS: calcd for  $\text{C}_{21}\text{H}_{15}\text{OSse}$  (ESI-TOF,  $[\text{M}+\text{H}]^+$ ), 395.0009, found 395.0020.

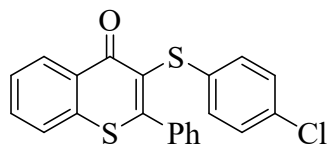
## Procedure for the synthesis of chromenones 3y-z



To a test tube, under ambient atmosphere, containing Selectfluor<sup>®</sup> (1.0 equiv) and MeCN (1.0 mL) were added diorganyl disulfide (1.0 equiv), the reaction mixture was stirred for 5 min at room temperature. After this time, the appropriate alkynyl aryl ketone (0.5 mmol) in MeCN (1.0 mL) was added and the reaction mixture was stirred at room temperature for 20 h. After this, the mixture was extracted with ethyl acetate (3 x 30 mL) and water (20 mL). the resulting organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/acetate (95:5).

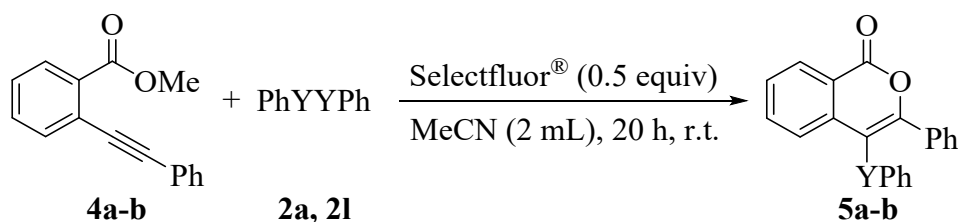


**2-phenyl-3-(phenylthio)-thiochromen-4-one 3y:** The product was isolated as a yellow solid. Yield: 0.108 g (63%). m.p. 142-143 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  8.52 (dd,  $J$  = 7.6, 1.4 Hz, 1H), 7.71 – 7.52 (m, 3H), 7.47 – 7.31 (m, 5H), 7.20 – 6.97 (m, 5H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  177.4, 158.2, 136.74, 136.69, 136.4, 131.7, 130.3, 129.8, 129.7, 128.7, 128.4, 128.30, 128.27, 128.0, 127.7, 125.64, 125.57. EM (EI, 70 eV;  $m/z$  (relative intensity)): 345 (100), 207 (23), 164 (44), 121 (17), 108 (16), 77 (16). HRMS: calcd for C<sub>21</sub>H<sub>15</sub>OS<sub>2</sub> (ESI-TOF, [M+H]<sup>+</sup>); 347.0564, found 347.0559.

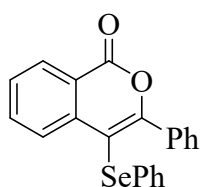


**3-((4-chlorophenyl)thio)-2-phenyl-thiochromen-4-one 3z:** The product was isolated as an orange solid. Yield: 0.076 g (40%). m.p. 122-123 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  8.58 – 8.50 (m, 1H), 7.73 – 7.52 (m, 3H), 7.51 – 7.37 (m, 5H), 7.18 – 7.09 (m, 2H), 7.08 – 7.00 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  177.4, 158.5, 136.7, 136.5, 135.3, 131.9, 131.7, 130.4, 130.0, 129.8, 129.3, 128.9, 128.6, 128.4, 128.2, 127.5, 125.7. EM (EI, 70 eV;  $m/z$  (relative intensity)): 380 (100), 253 (21), 208 (43), 165 (64), 108 (45), 75 (18). HRMS: calcd for C<sub>21</sub>H<sub>14</sub>ClOS<sub>2</sub> (ESI-TOF, [M+H]<sup>+</sup>); 381.0175, found 381.0169.

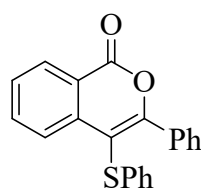
## Procedure for the synthesis of isochromenones **5a** and **5b**



To a test tube, under ambient atmosphere, containing Selectfluor<sup>®</sup> (0.5 equiv) and MeCN (1.0 mL) were added diorganyl dichalcogenide **2** (0.5 equiv), and the reaction mixture was stirred for 5 min at room temperature. After this time, the appropriate methyl 2-(organoethynyl)benzoate **4** (0.5 mmol) in MeCN (1 mL) was added and the reaction mixture was stirred at room temperature for 20 h. After this, the mixture was extracted with ethyl acetate (3 X 30 mL) and water (20 mL). The resulting organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane/acetate (95:5).



**3-phenyl-4-(phenylselanyl)-1H-isochromen-1-one 5a:** The product was isolated as a white solid. Yield: 0.143 g (76%). m.p. 122-123 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.62 (m, 3H), 7.54 – 7.46 (m, 1H), 7.45 – 7.33 (m, 3H), 7.22 – 7.08 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ 161.6, 159.6, 138.4, 135.3, 134.0, 131.8, 130.0, 129.6, 129.4, 128.9, 128.8, 128.6, 128.2, 127.7, 126.4, 120.8, 104.8. <sup>77</sup>Se NMR (CDCl<sub>3</sub>, 76 MHz): δ 293.25. MS (EI, 70 eV, *m/z* (relative intensity)): 378 (11), 193 (12), 165 (20), 105 (100), 77 (22). HRMS: calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub>Se (ESI-TOF, [M+H]<sup>+</sup>), 379.0237, found 379.0250.



**3-phenyl-4-(phenylthio)-1H-isochromen-1-one 5b:** The product was isolated as a yellow solid. Yield: 0.132 g (80%). m.p. 103-104 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.35 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.76 – 7.65 (m, 3H), 7.52 (td, *J* = 7.6, 1.2 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.24 – 7.17 (m, 2H), 7.11 (dt, *J* = 6.2, 1.4 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 161.2, 160.1, 137.9, 136.5, 135.2, 132.8, 130.2, 129.7, 129.4, 129.2, 128.6, 127.9, 125.99, 125.95, 125.7, 120.9, 106.5. MS (EI, 70 eV, *m/z* (relative intensity)): 330 (47), 225 (23), 197 (20), 165 (18), 105 (100), 77 (29). HRMS: calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub>S (ESI-TOF, [M+H]<sup>+</sup>); 331.0793, found 331.0792.

### Procedure for control experiments:

**Radical trapping study:** A mixture of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (0.25 mmol, 59 mg), diphenyl diselenide **2a** (0.125 mmol, 39 mg), Selectfluor® (0.125 mmol, 44 mg) and TEMPO (0.5 mmol, 78 mg), were used under standard conditions. Yield for **3a**: 70 % (66 mg).

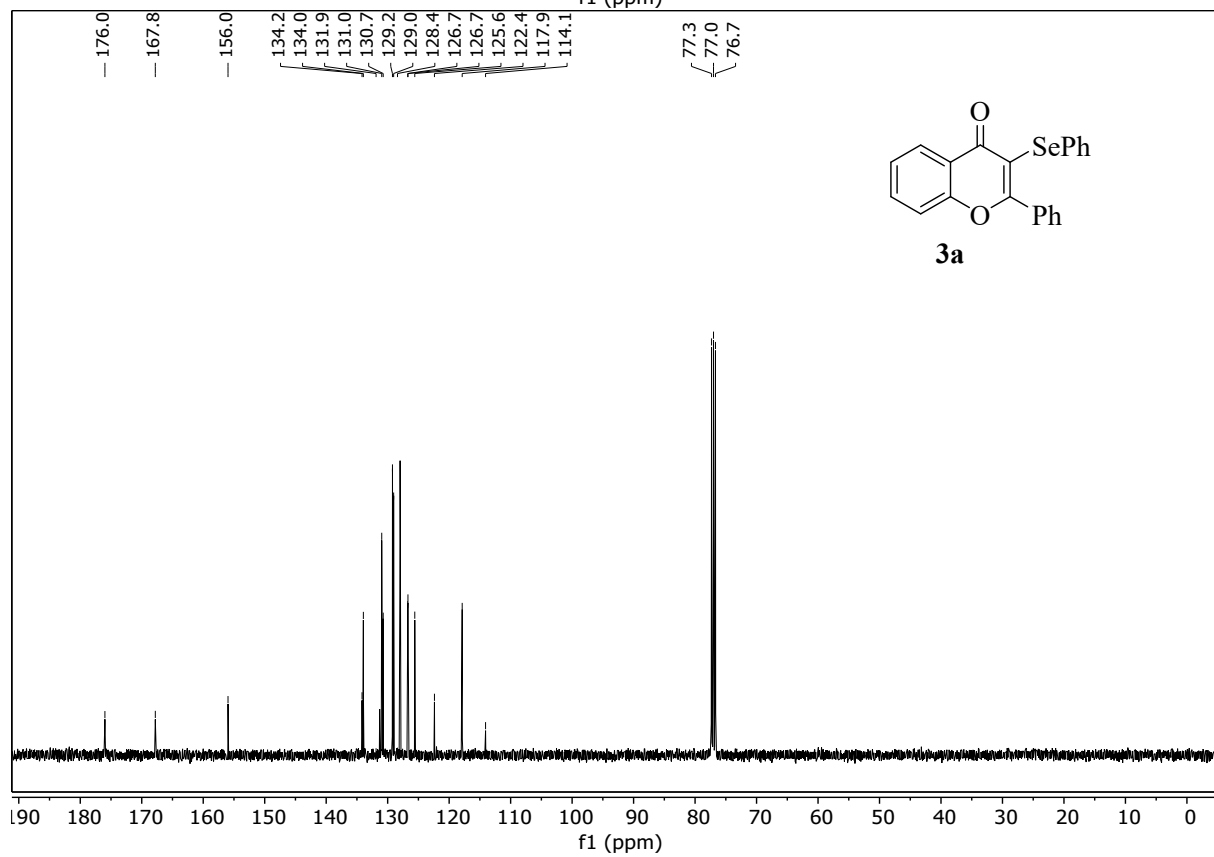
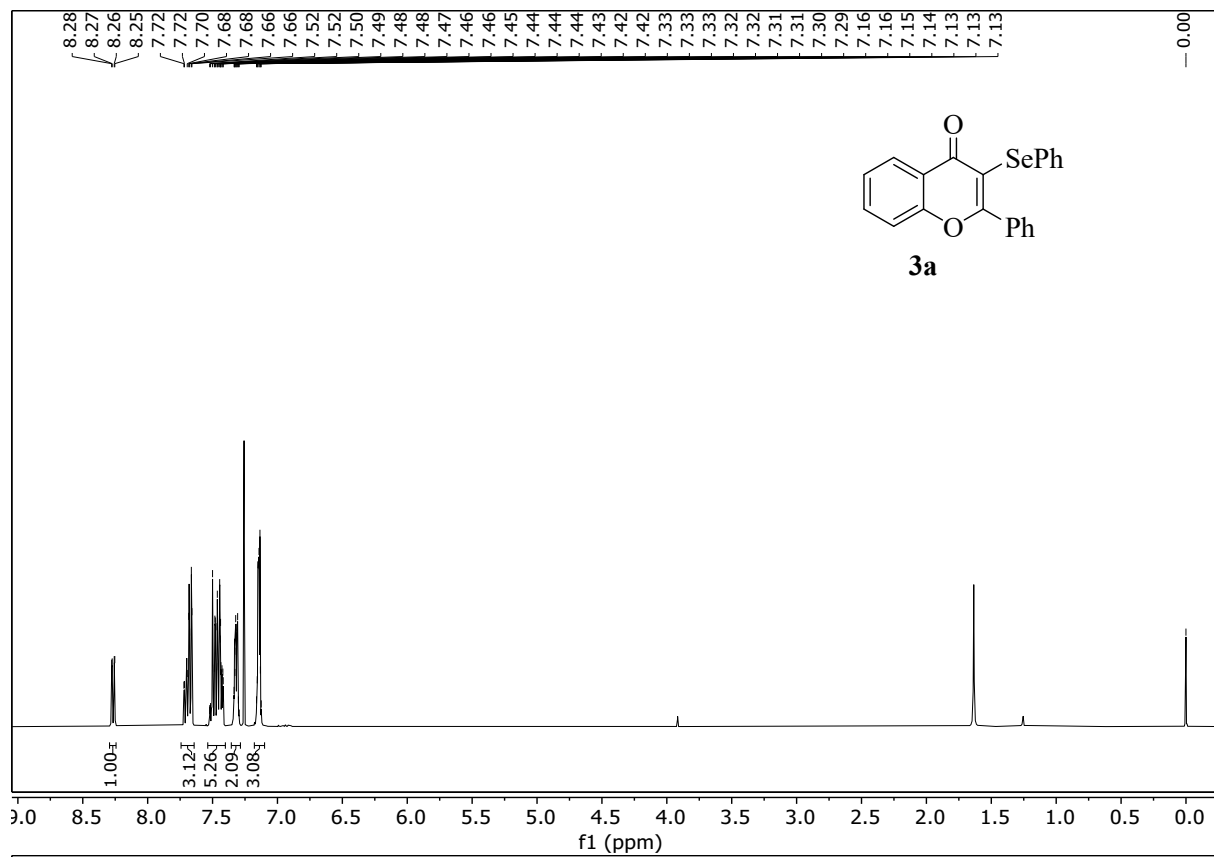
**Reaction in the absence of diphenyl diselenide:** A mixture of 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (0.25 mmol, 59 mg) and Selectfluor® (0.125 mmol, 44 mg) was used under standard conditions. No product was detected and the starting material **1a** was recovered untouched.

### References:

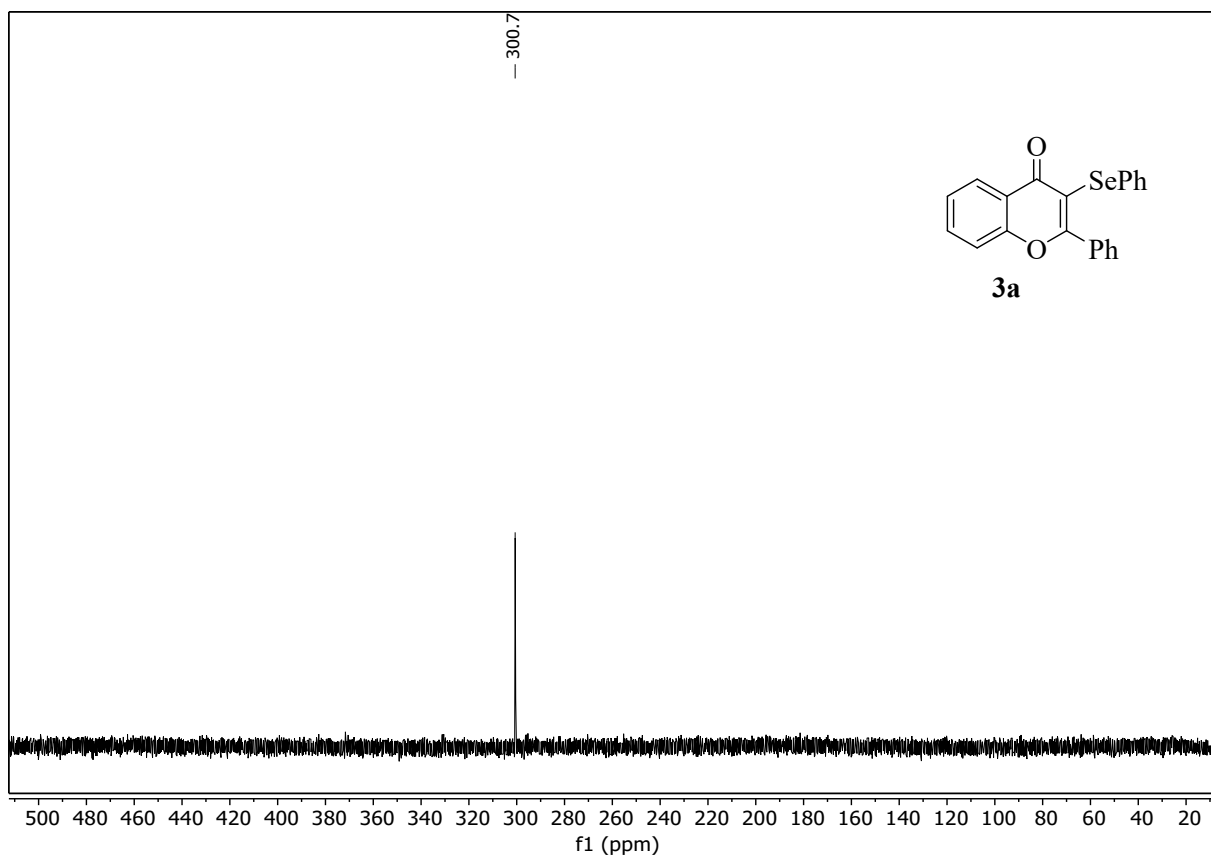
- [1] Bruker AXS Inc., SHELXTL XT, Version 2014/5 - Crystal Structure Solution, Madison, Wisconsin, USA, 2014.
- [2] Bruker AXS Inc., SHELXTL XT, Version 2017/1 - Crystal Structure Solution, Madison, Wisconsin, USA, 2017.
- [3] Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
- [4] Brandenburg, K.; Putz, H. *Diamond - Crystal and Molecular Structure Visualization*, 1997-2019, Crystal Impact GbR, Bonn, Germany.
- [5] C. Zhou, A. V. Dubrovsky, R. C. Larock, *J. Org. Chem.*, 2006, **71**, 1626–1632.
- [6] L. Wang, H. Wang, W. Meng, X.-H. Xu, Y. Huang, *Chin. Chem. Lett.*, 2021, **32**, 389-392.
- [7] T. Yao, R. C. Larock, *J. Org. Chem.*, 2003, **68**, 5936-5942.

# Copies of $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ , $^{77}\text{Se}$ and $^{19}\text{F}$ NMR spectra

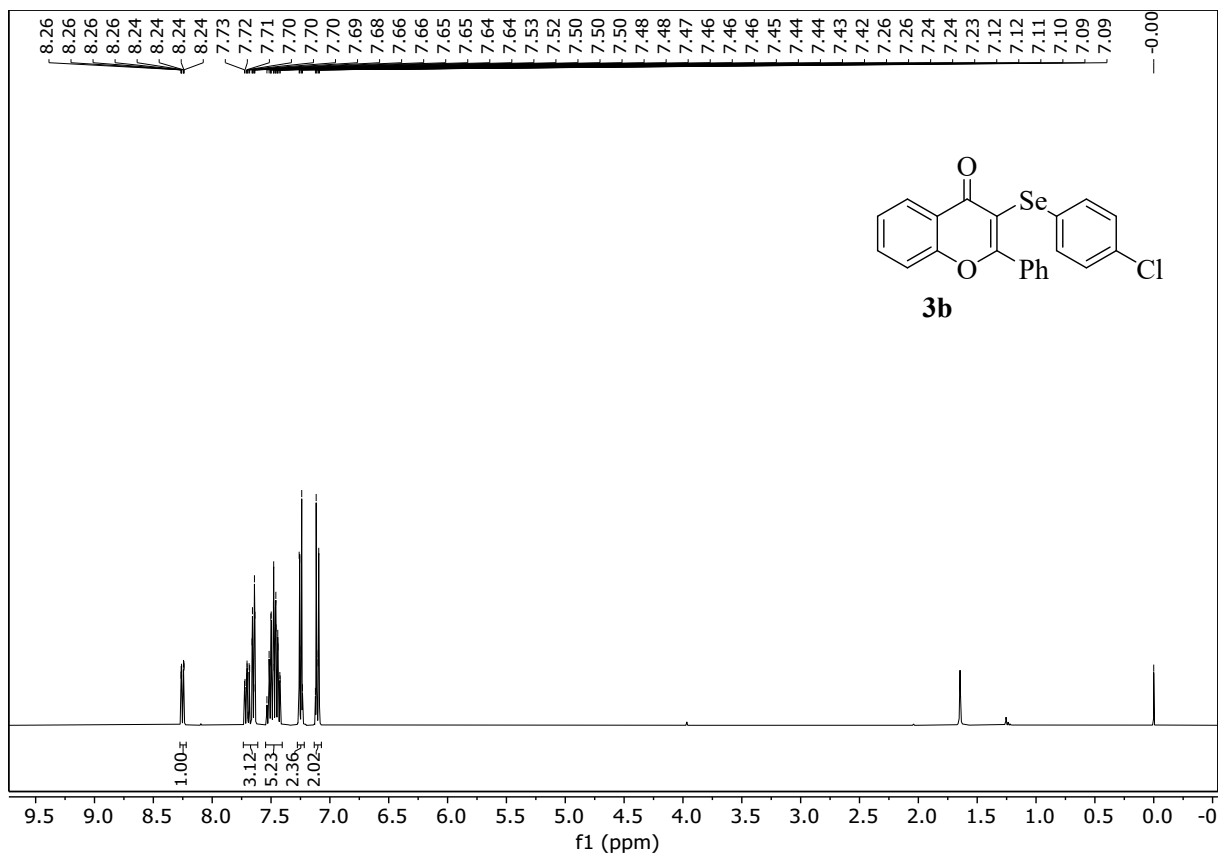
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3a** in  $\text{CDCl}_3$ .

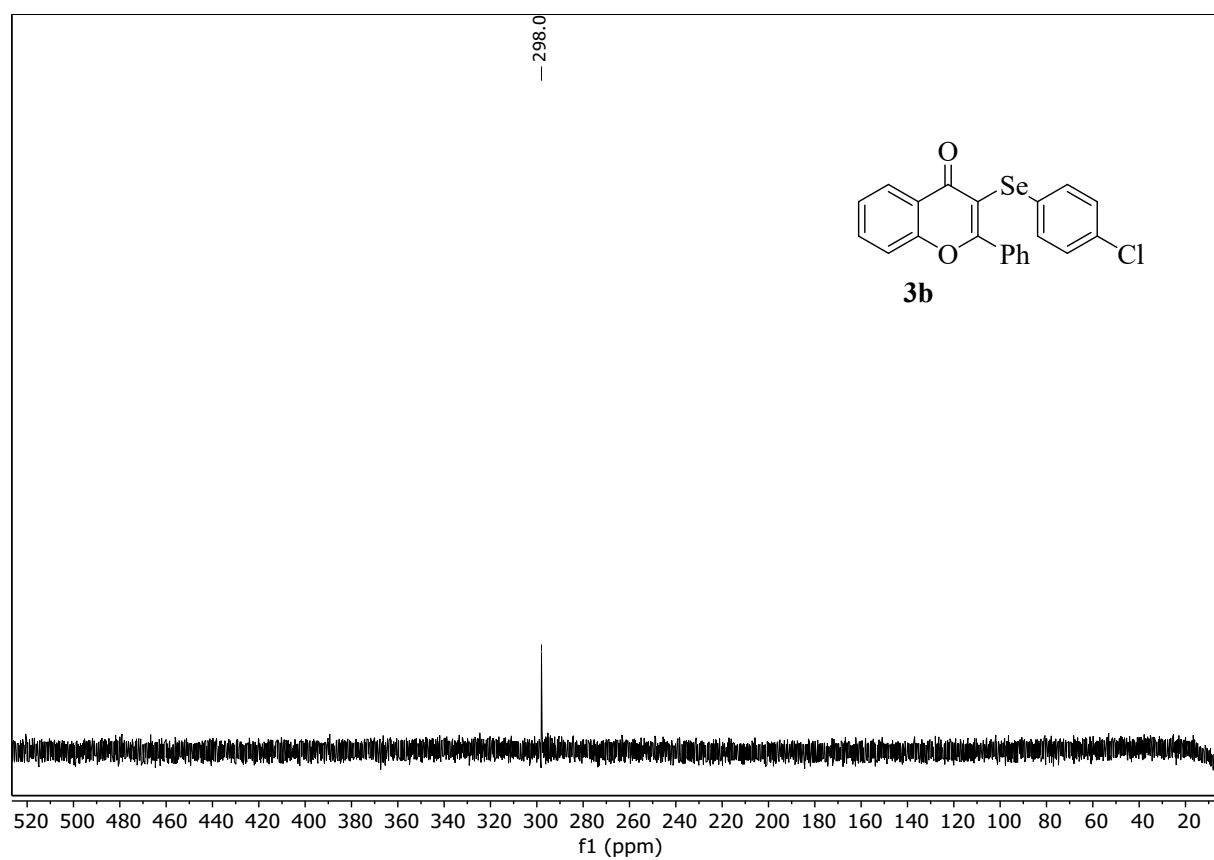
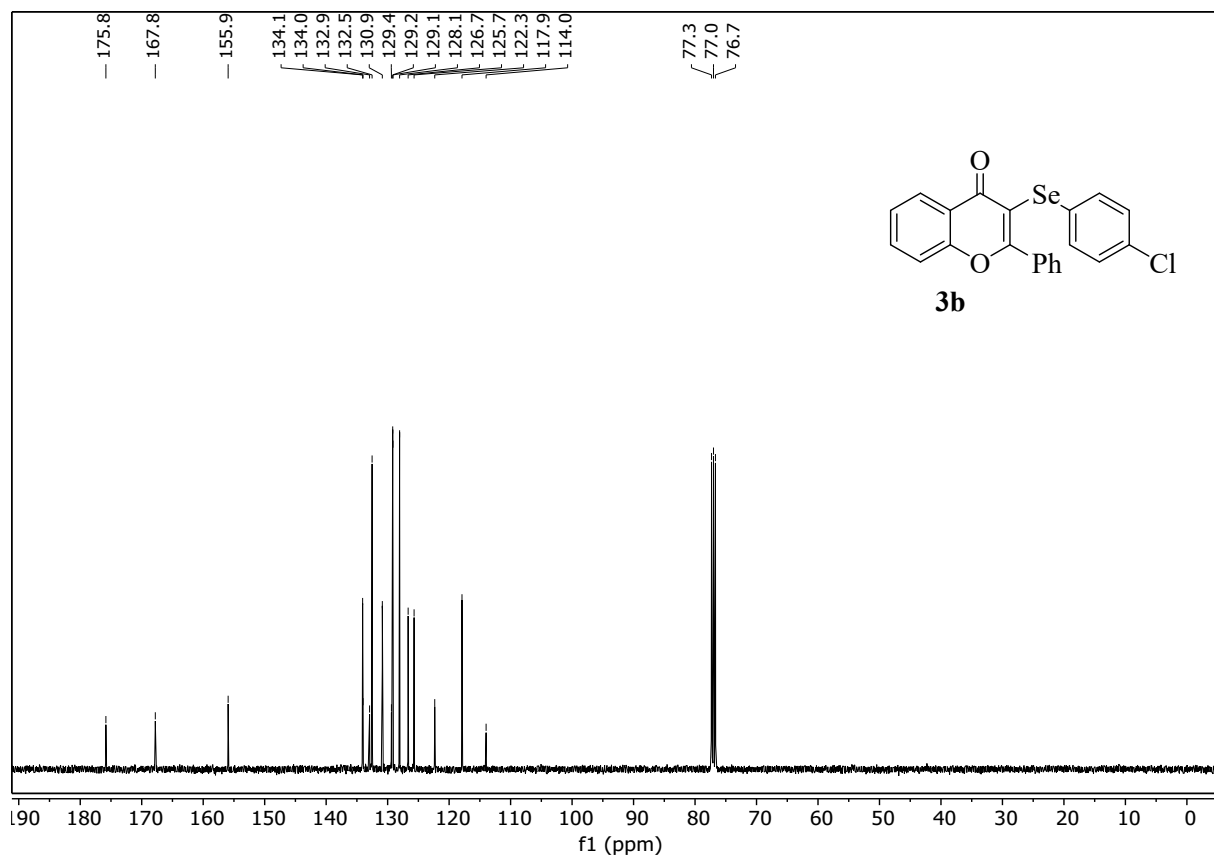




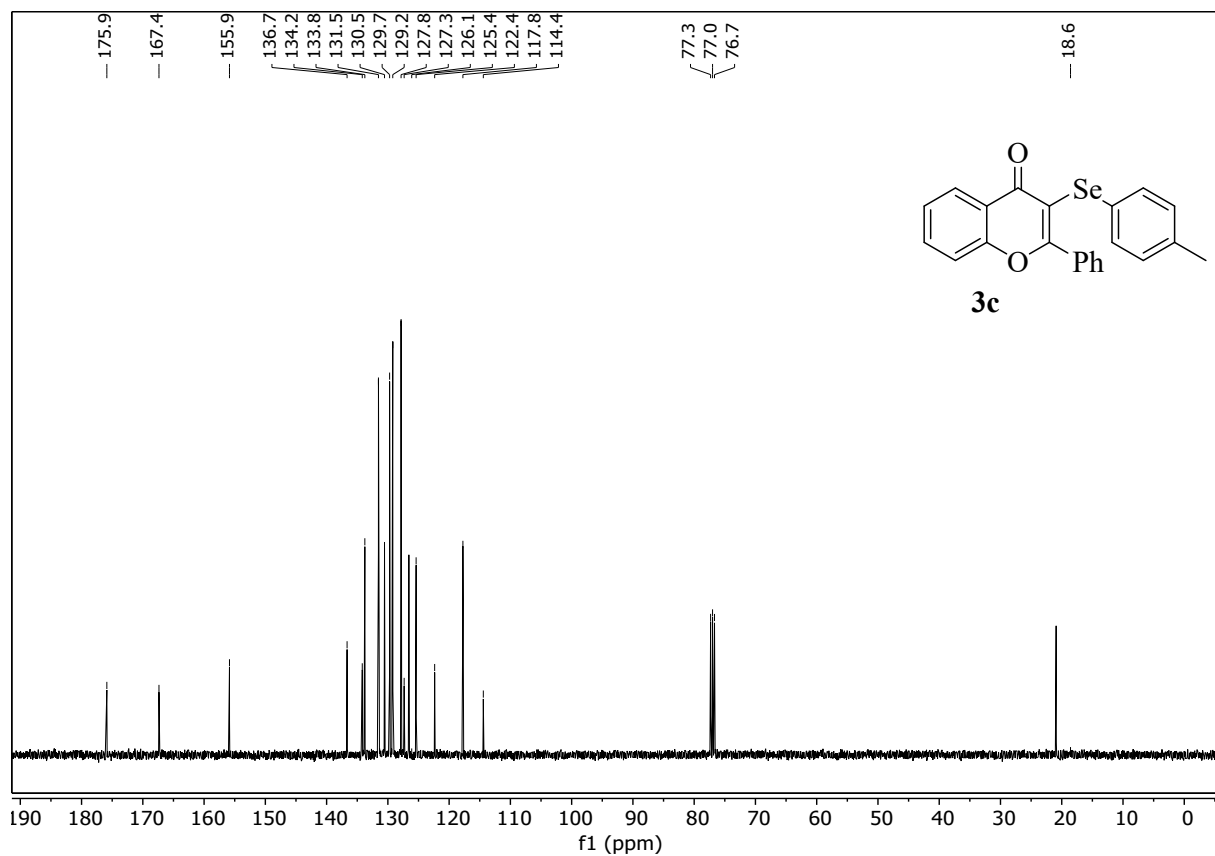
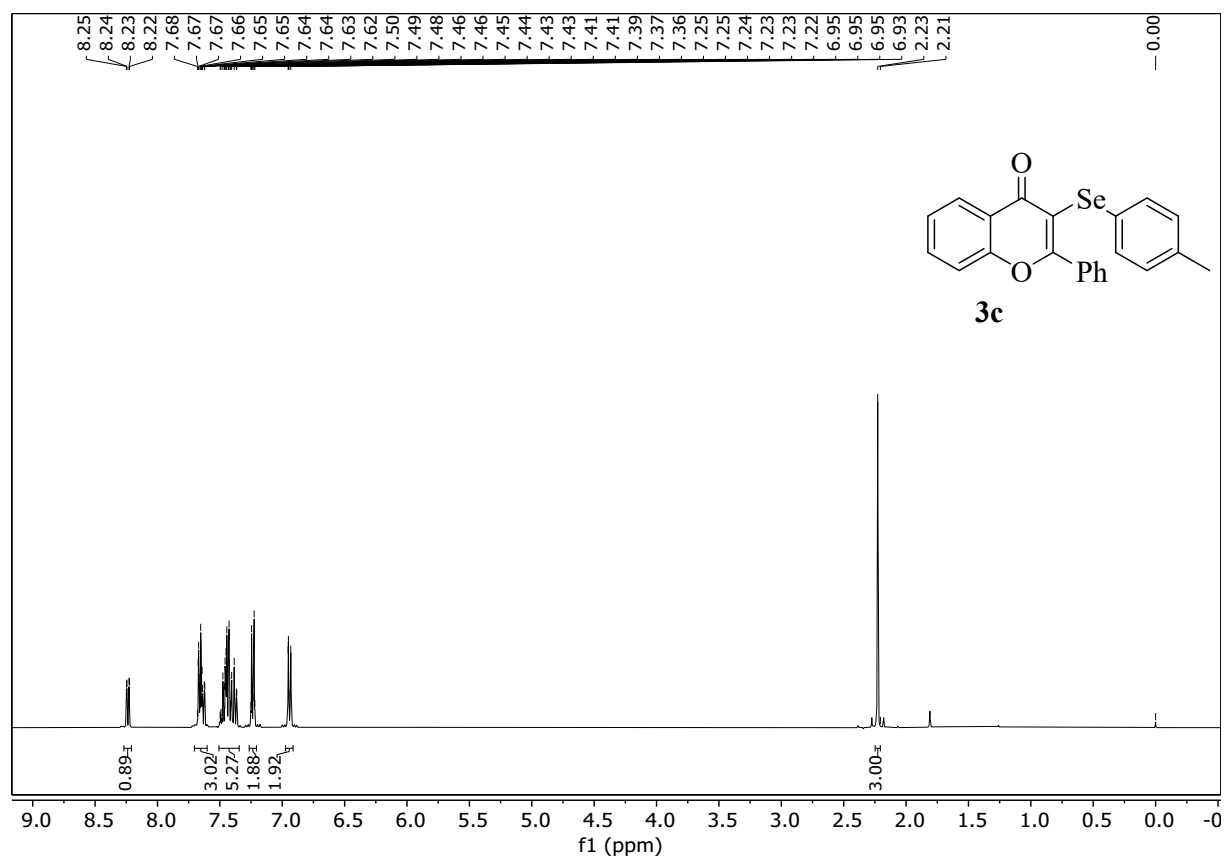


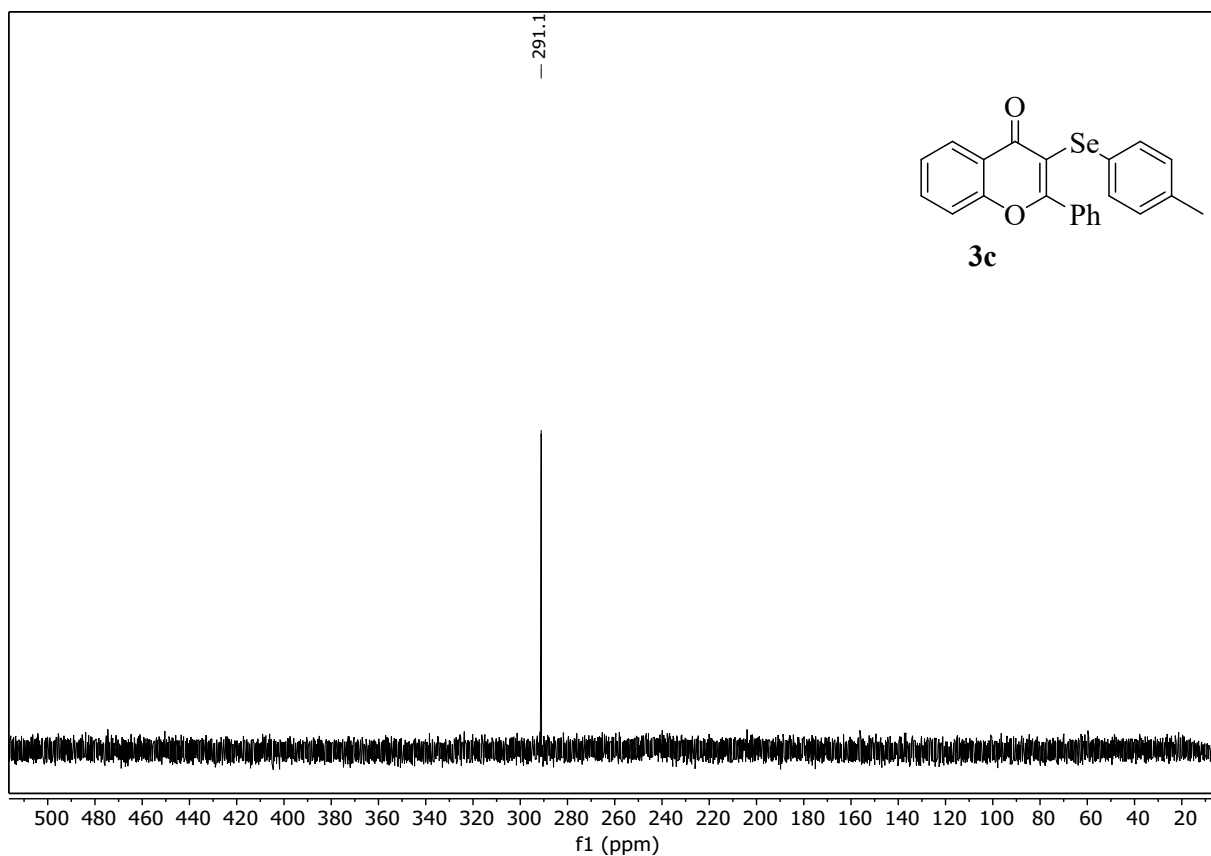
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3b** in CDCl<sub>3</sub>.



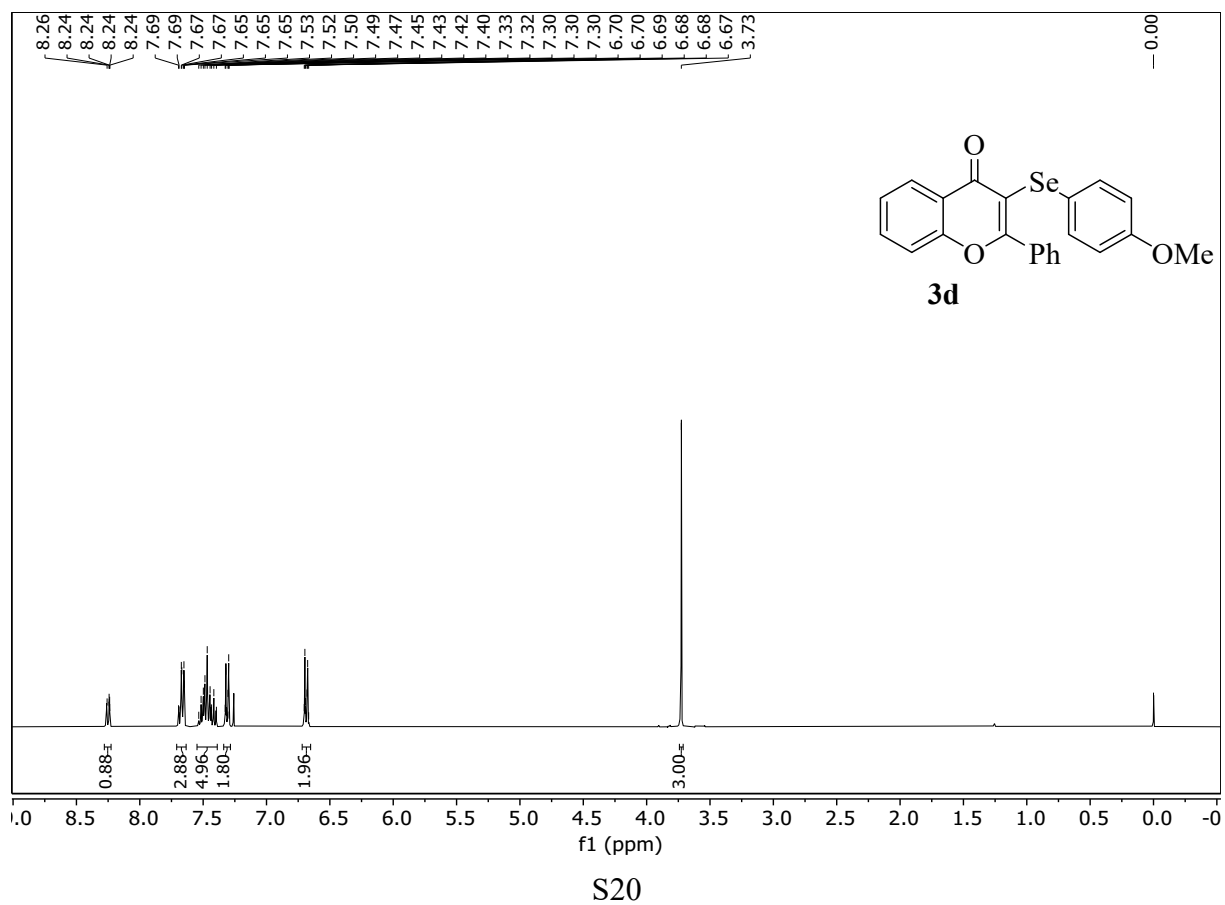


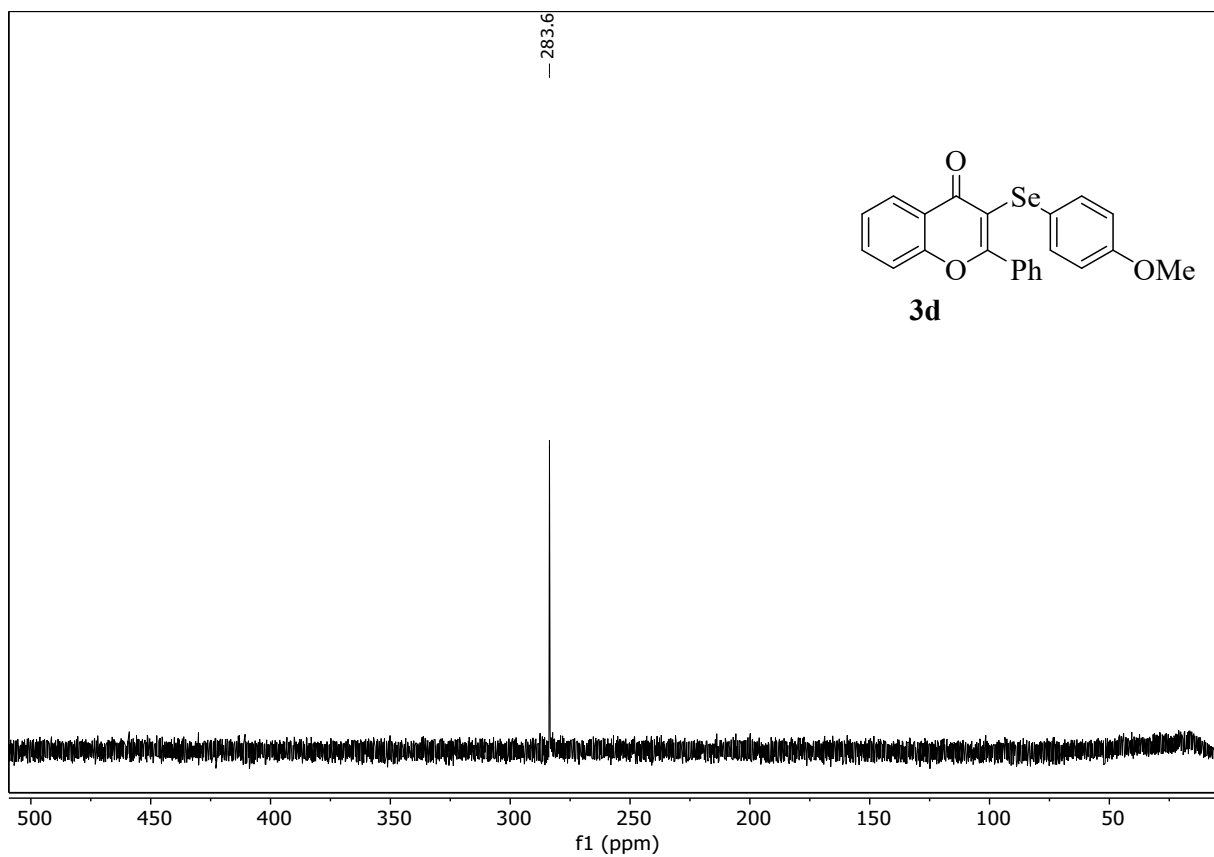
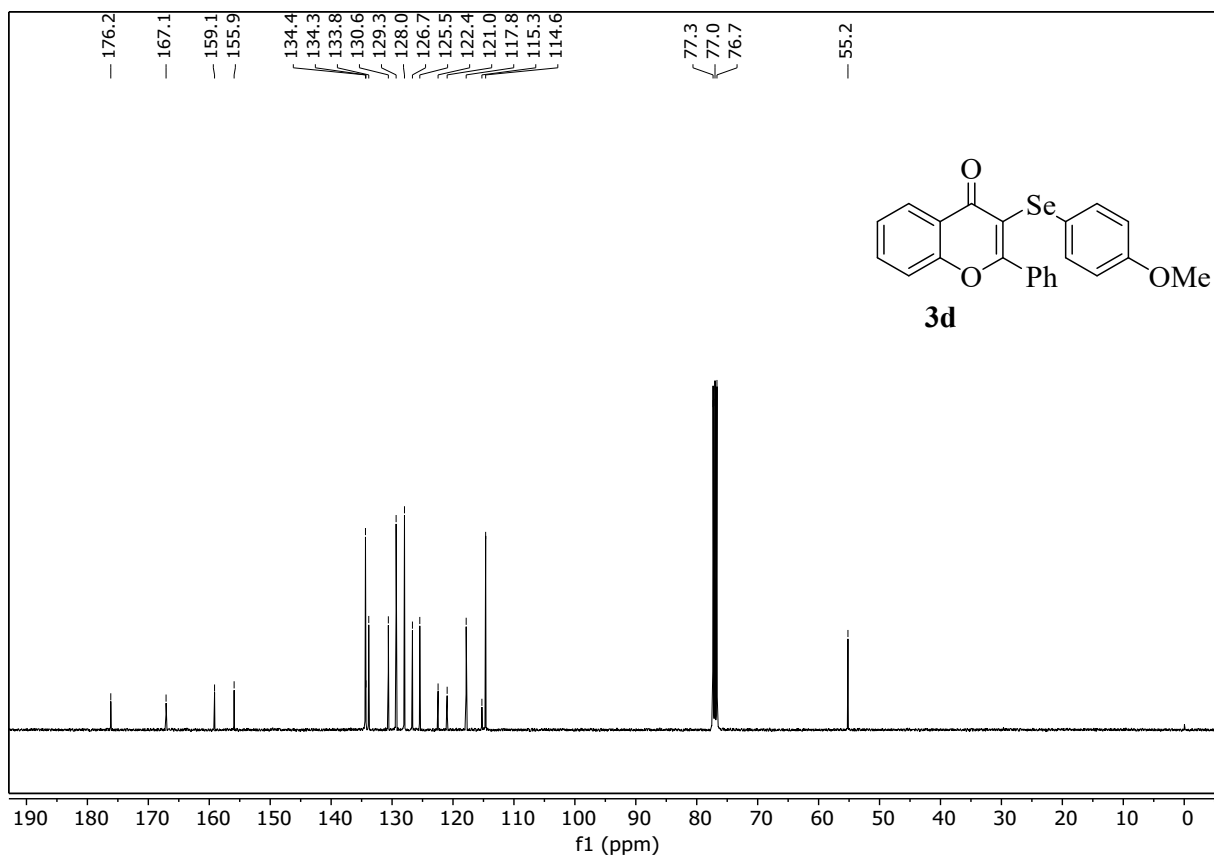
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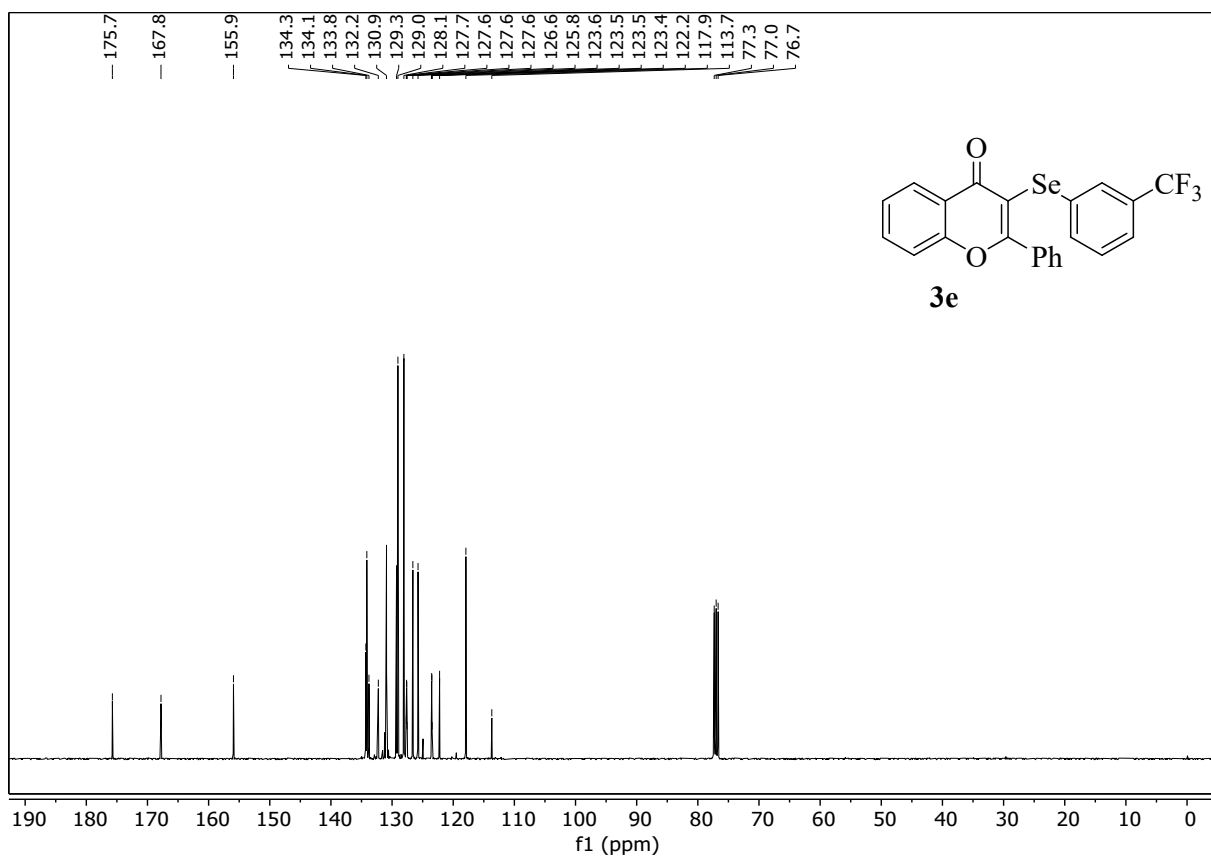
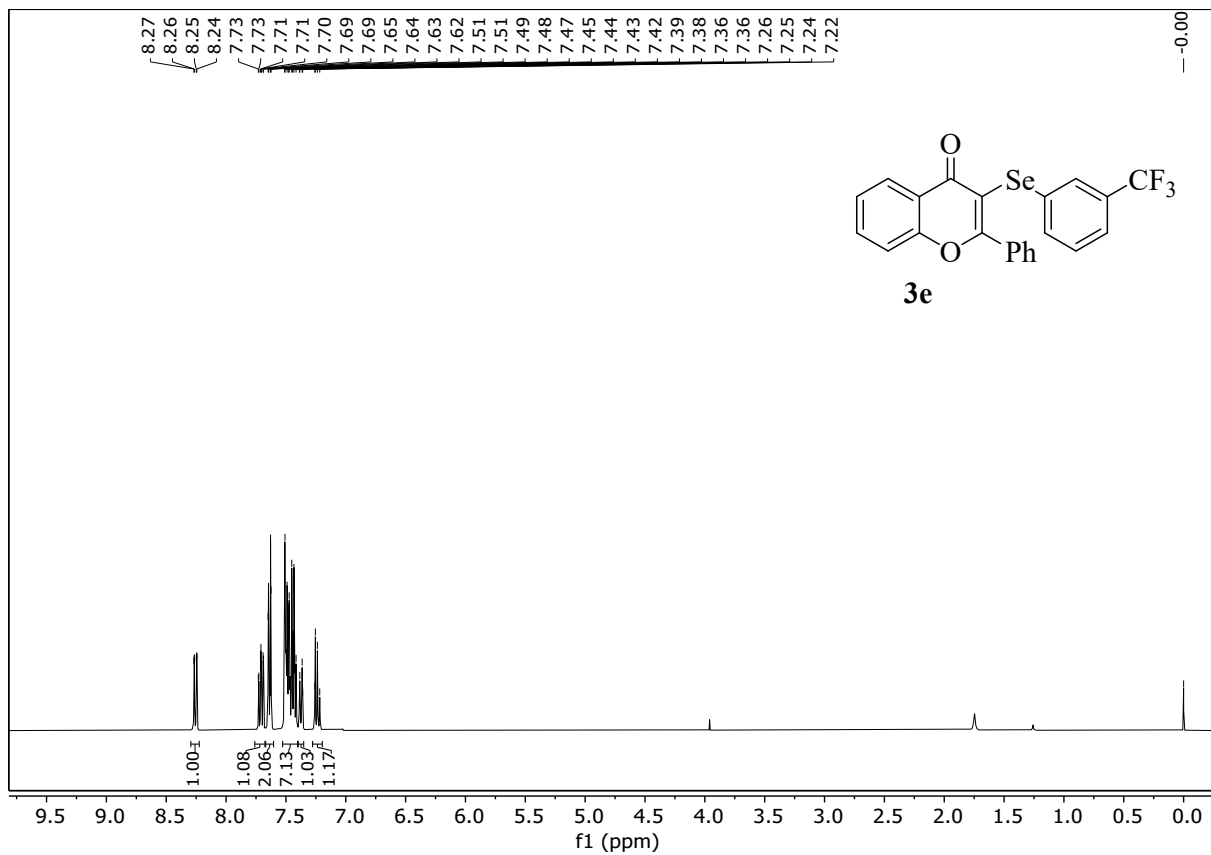


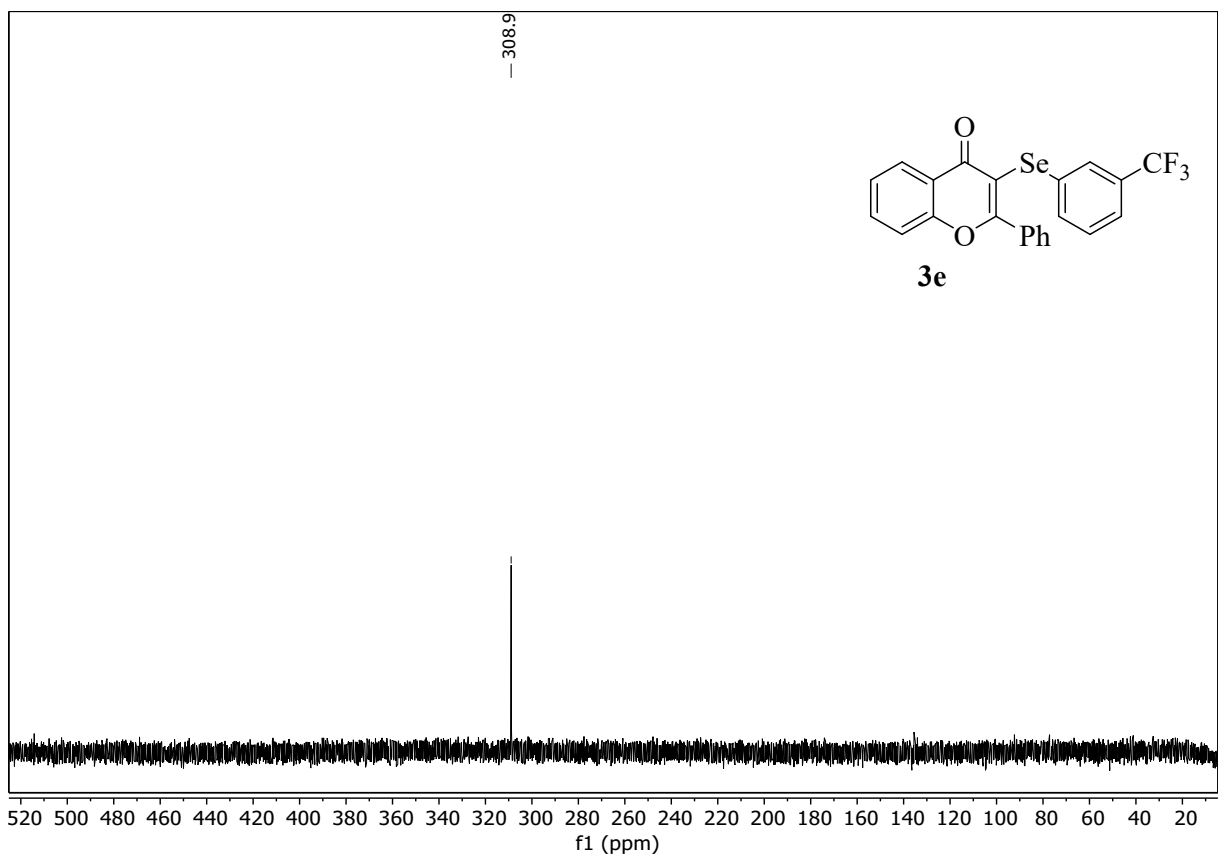
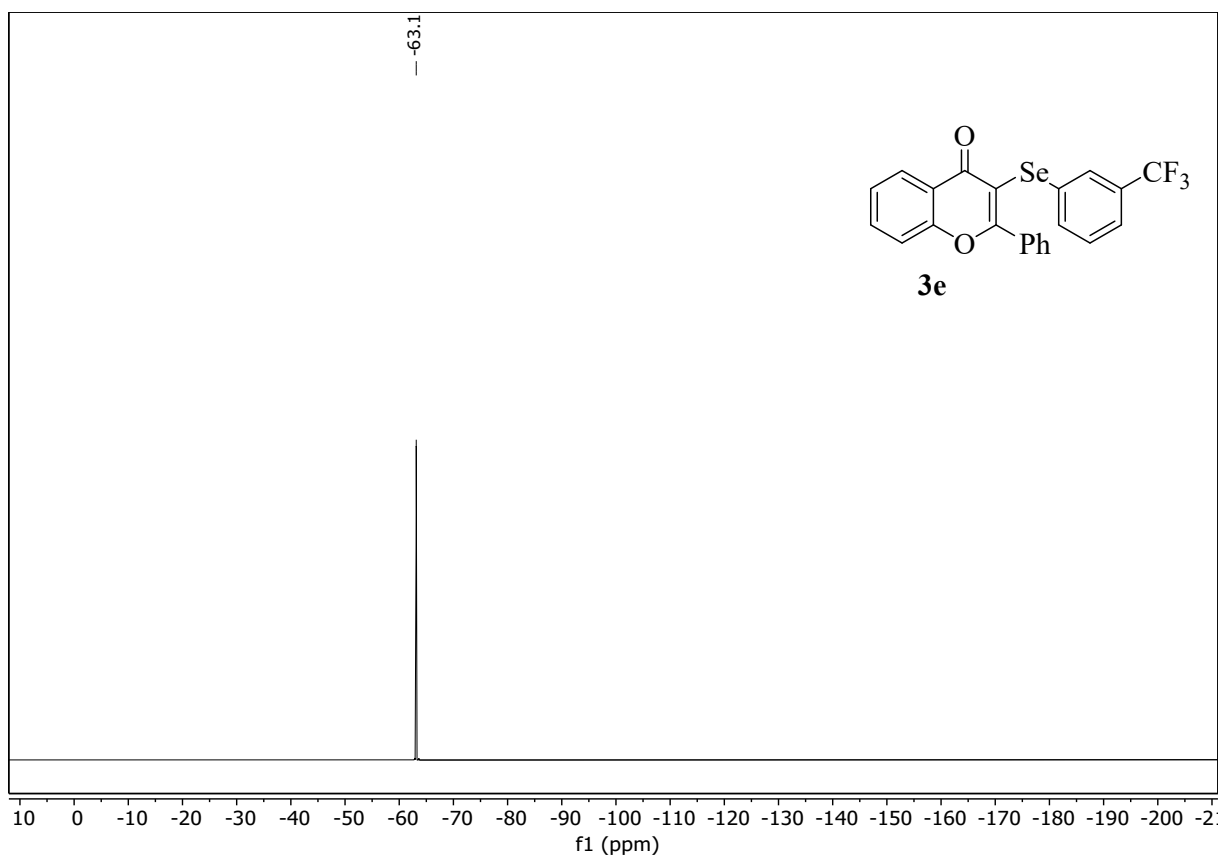
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3d** in CDCl<sub>3</sub>.



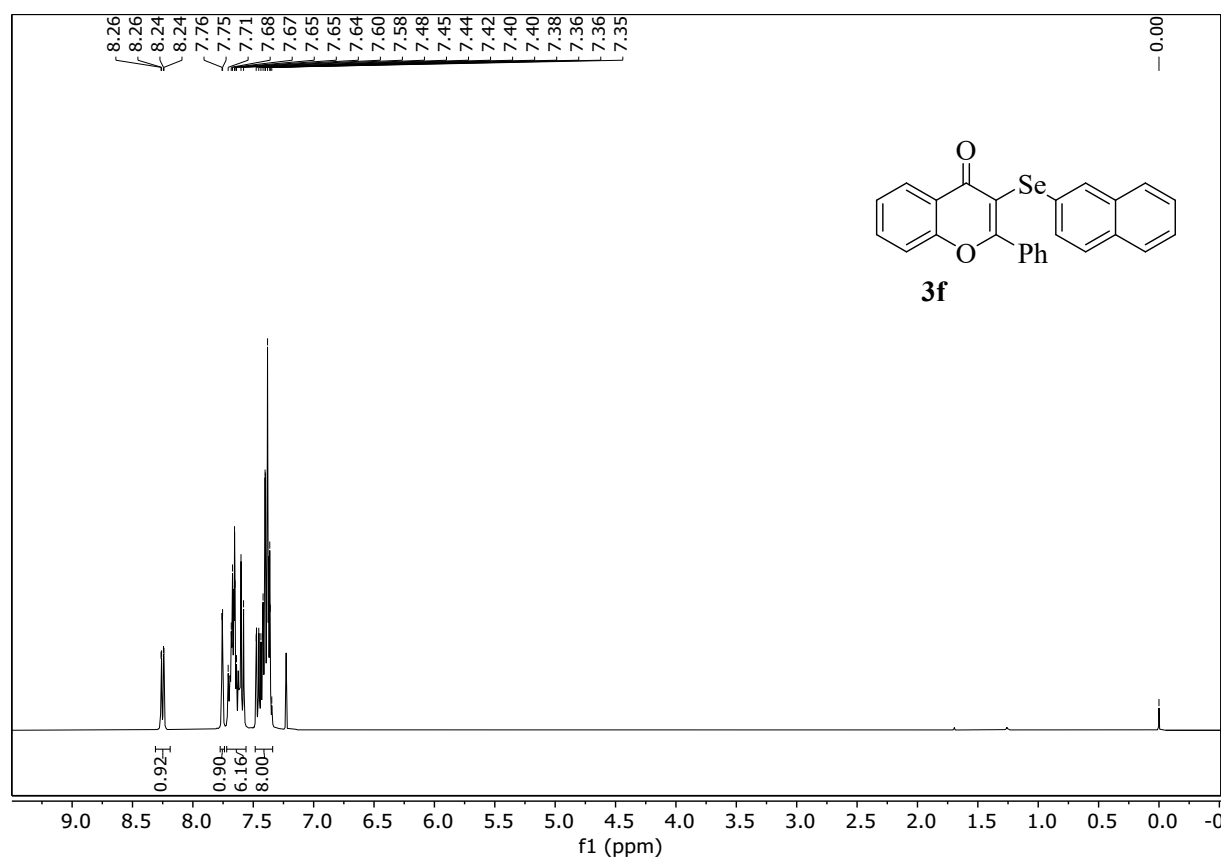


The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz),  $^{19}\text{F}$  (375 MHz) and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3e** in  $\text{CDCl}_3$ .

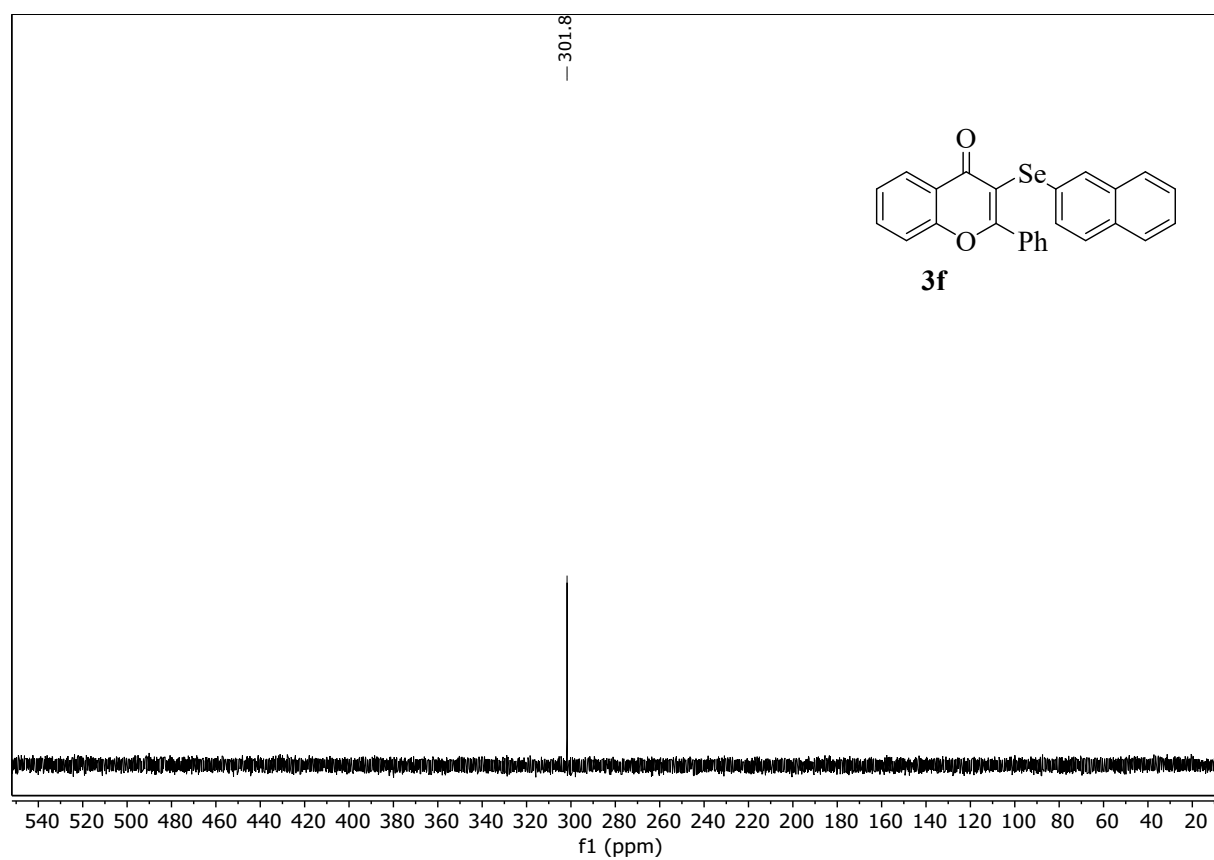
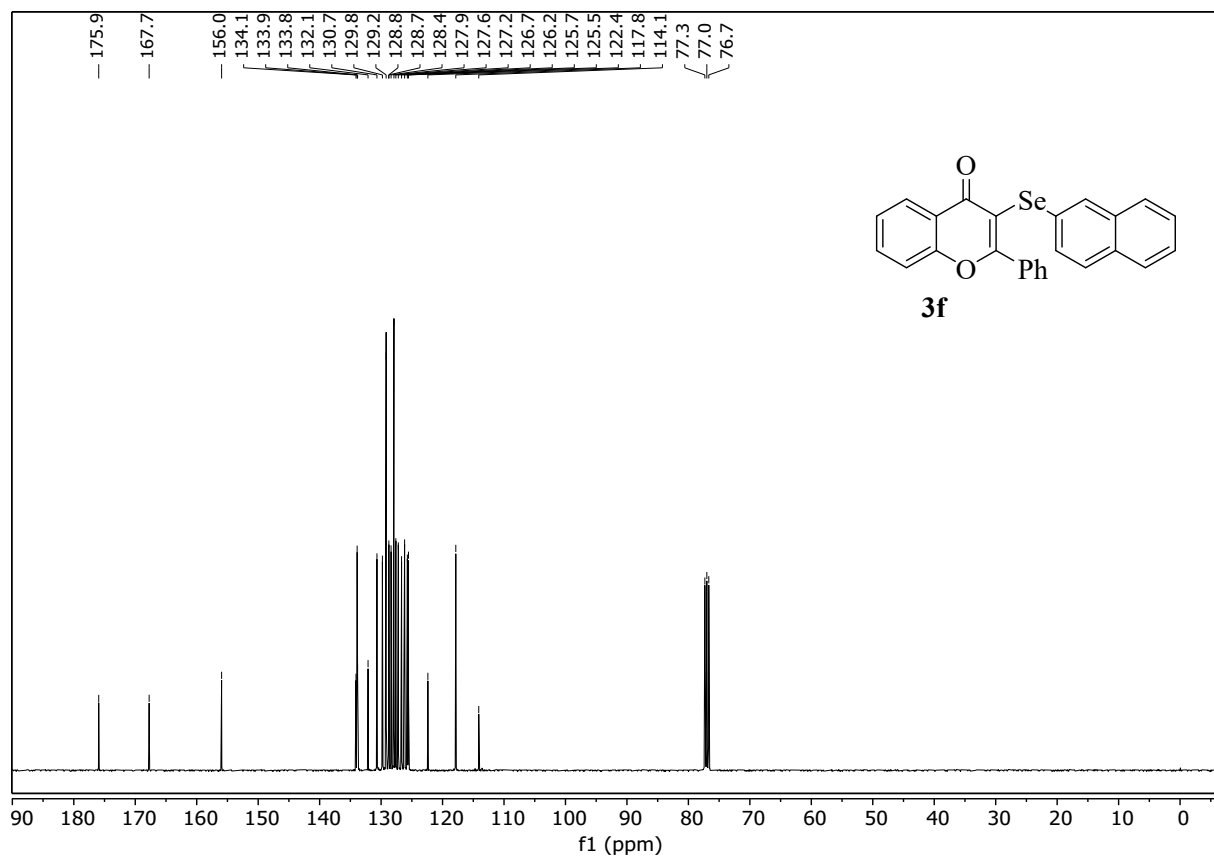




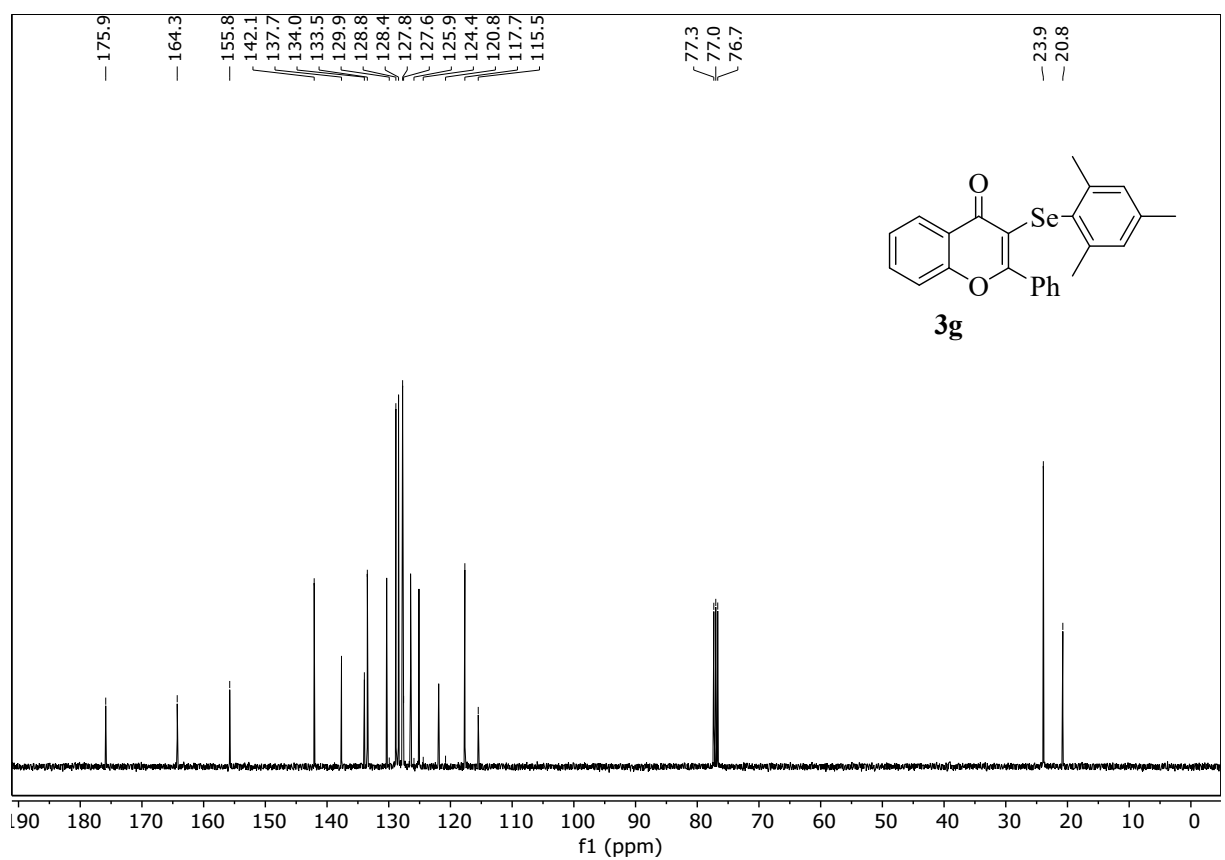
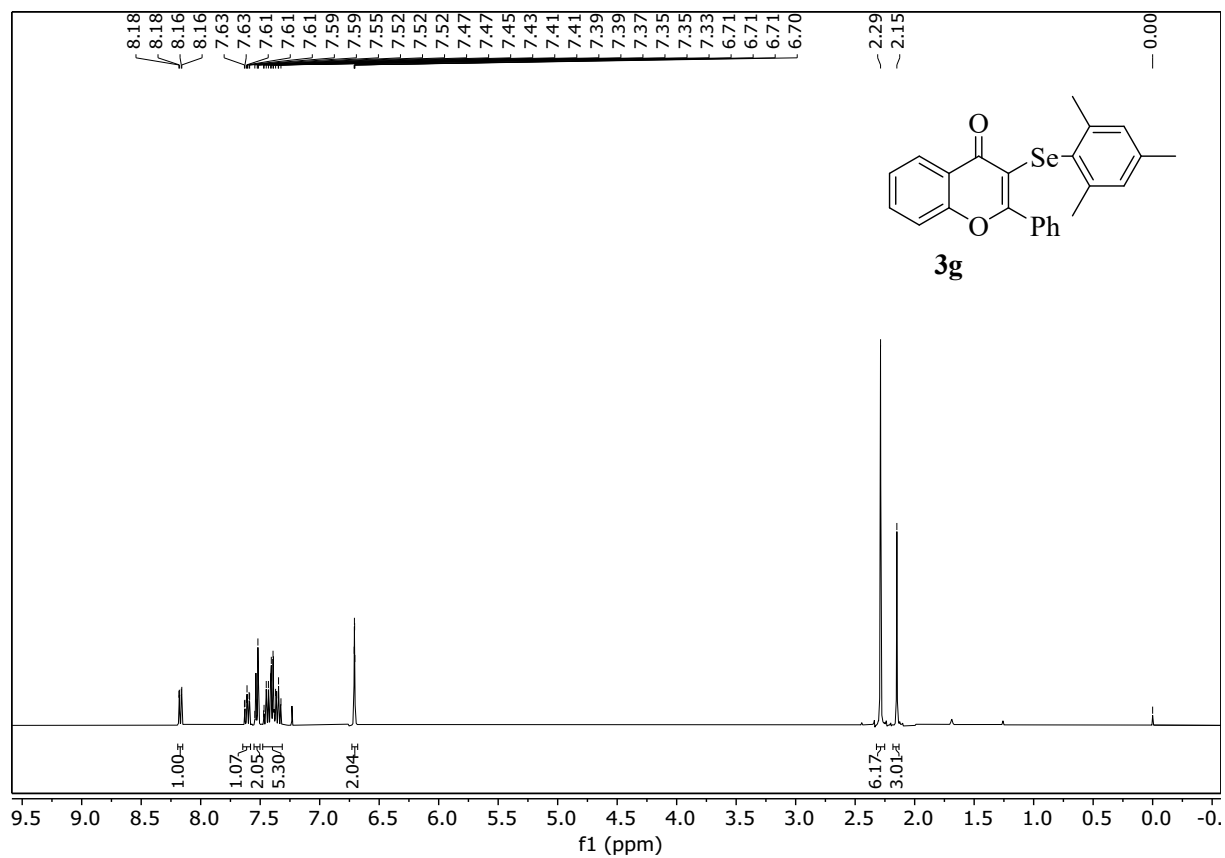
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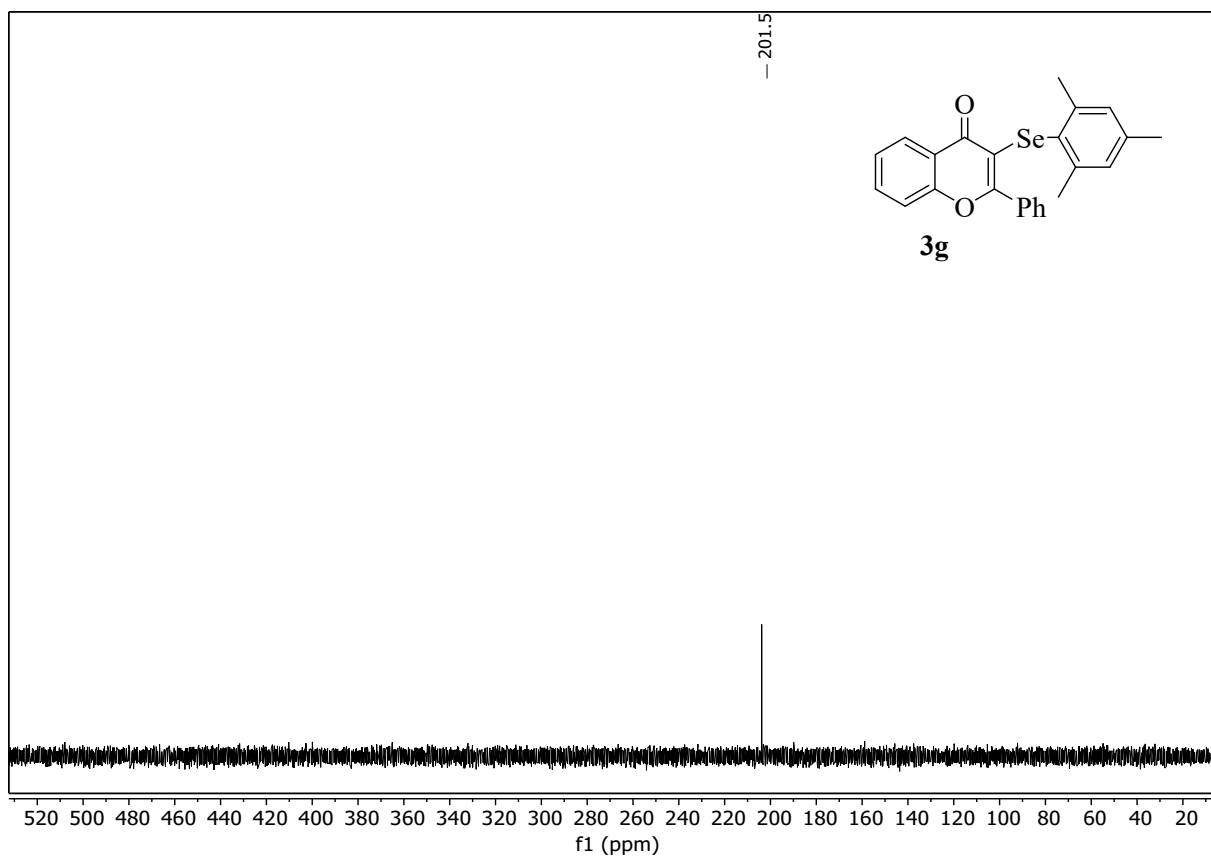




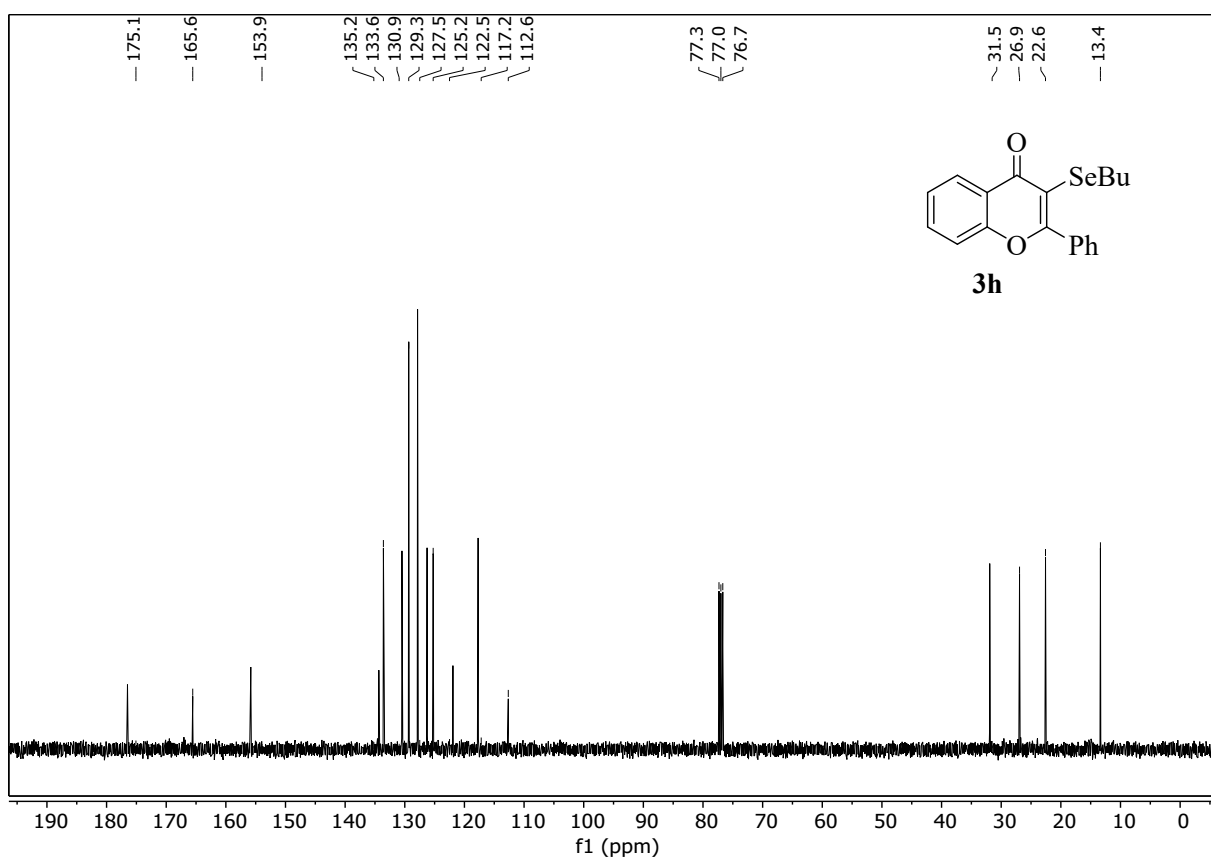
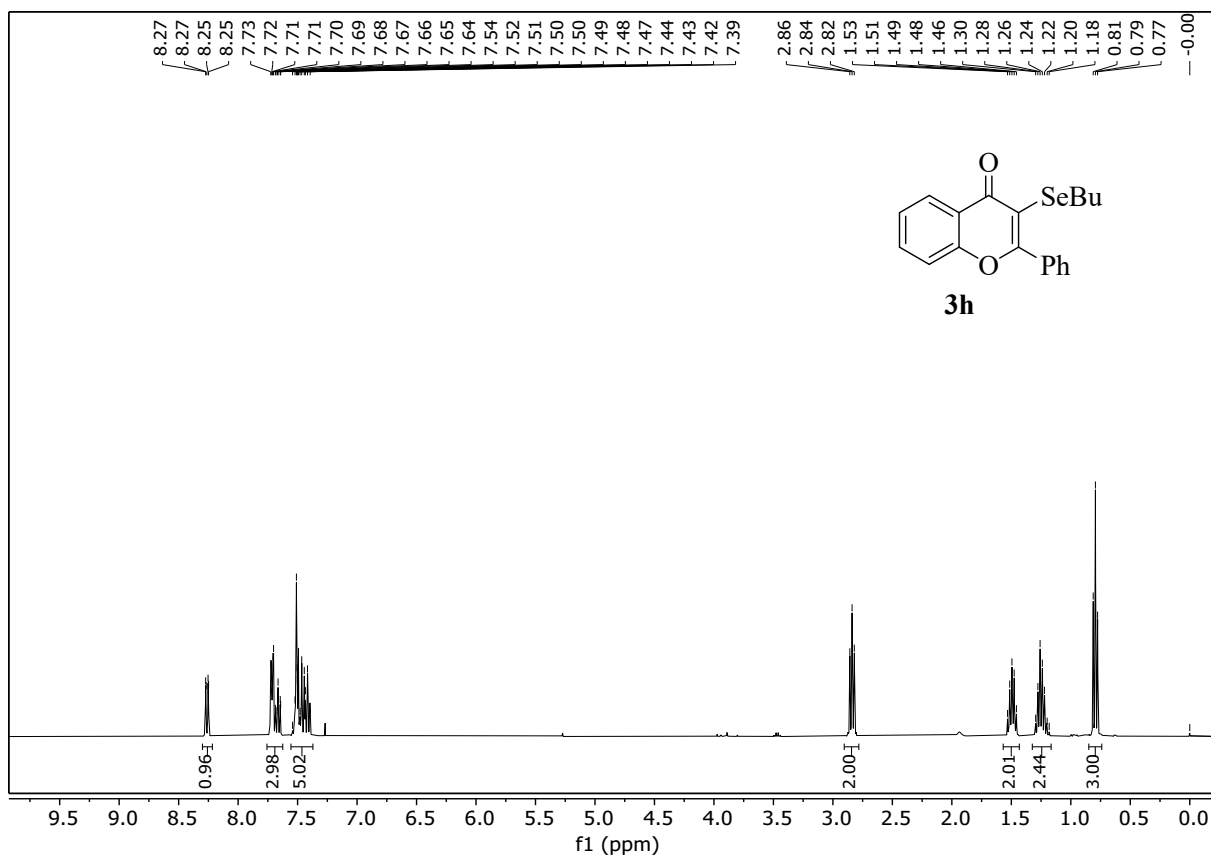


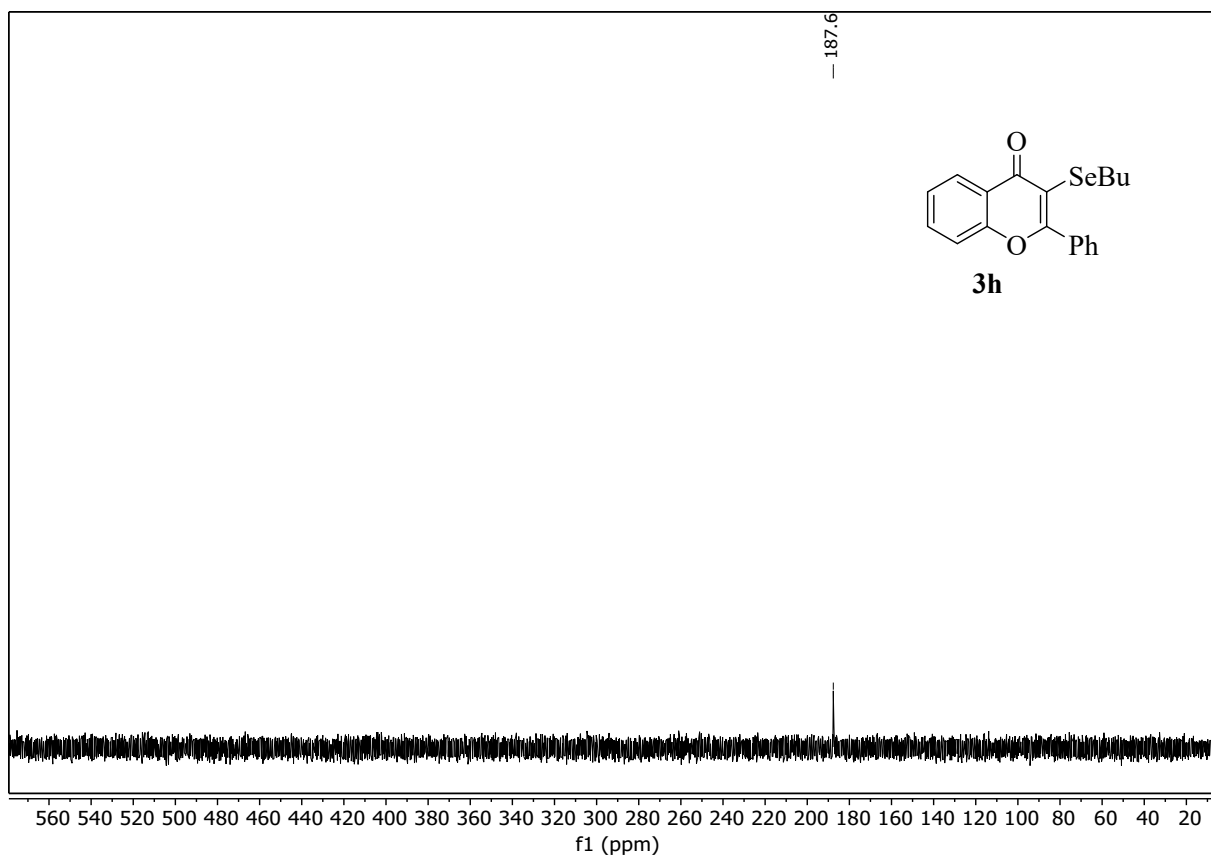
The <sup>1</sup>H (400 MHz), <sup>13</sup>C {<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3g** in CDCl<sub>3</sub>.



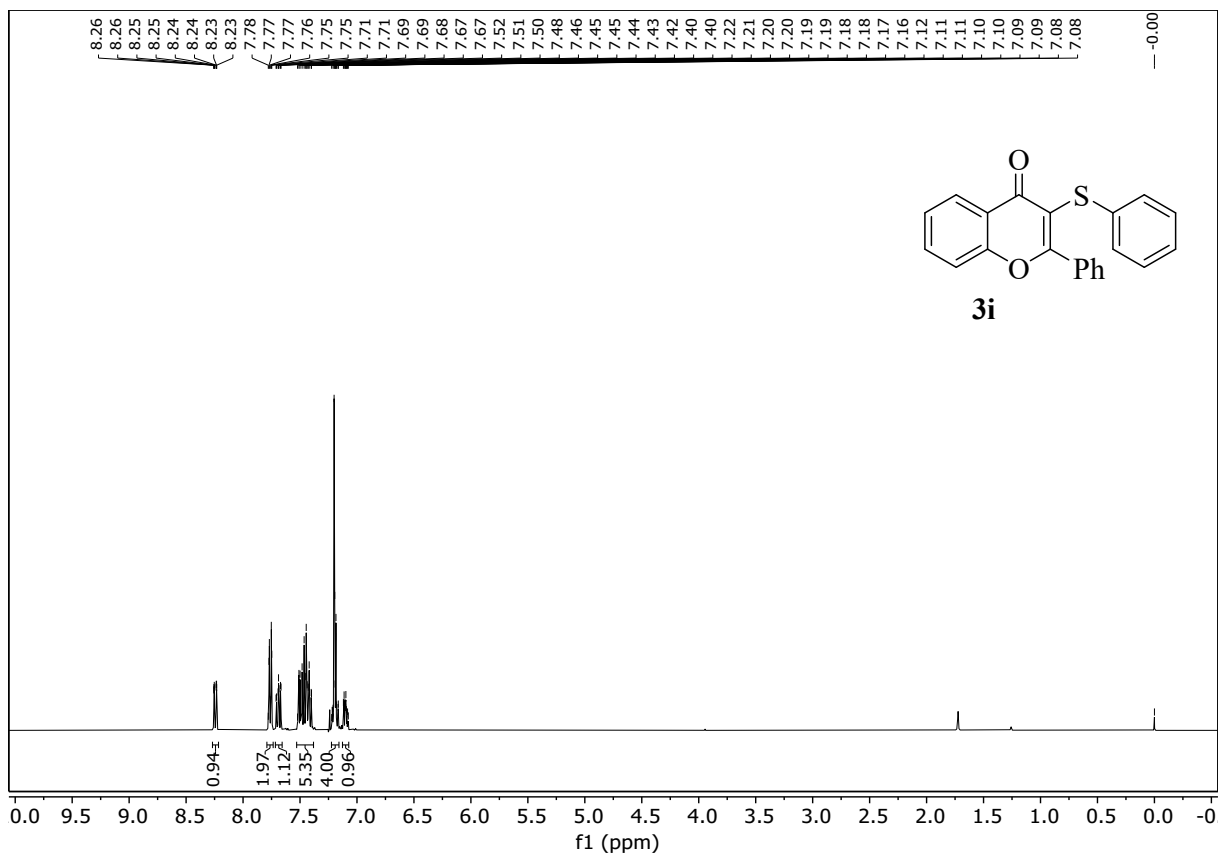


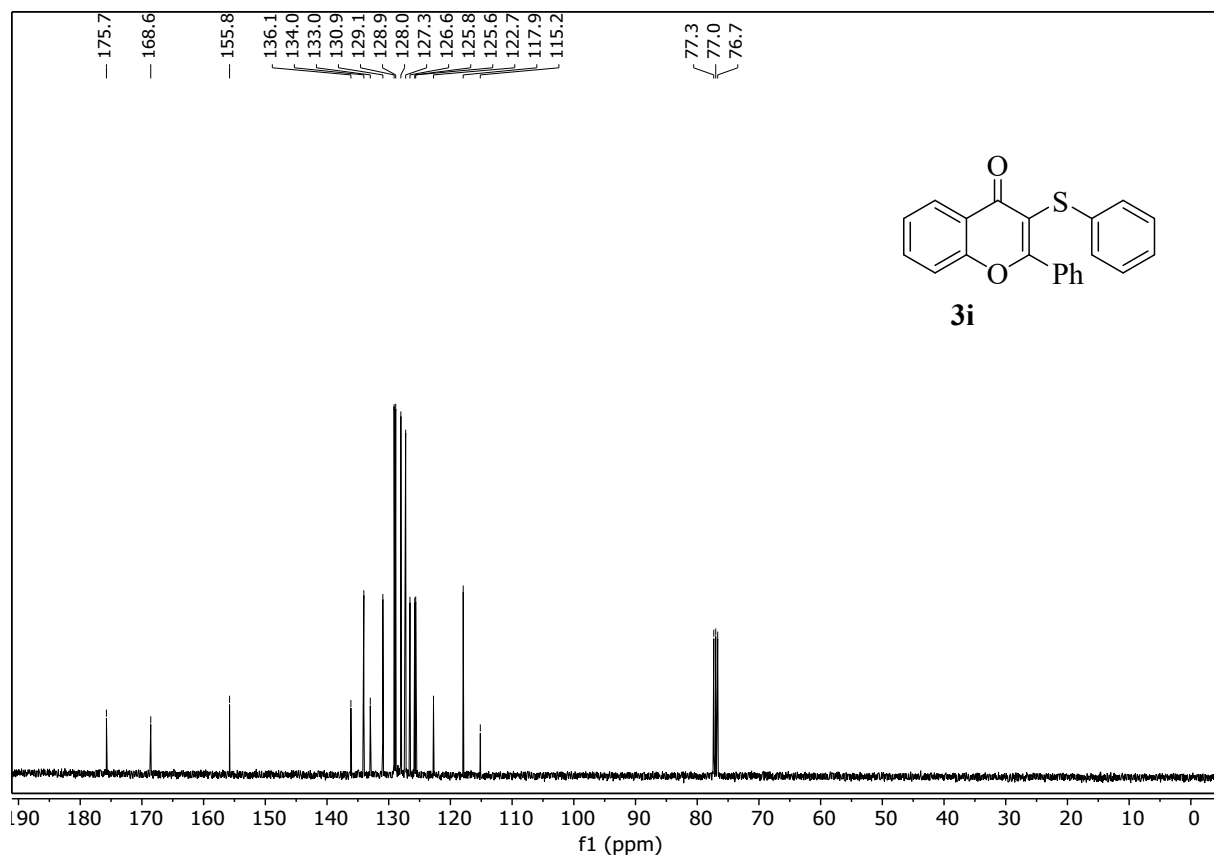
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3h** in CDCl<sub>3</sub>.



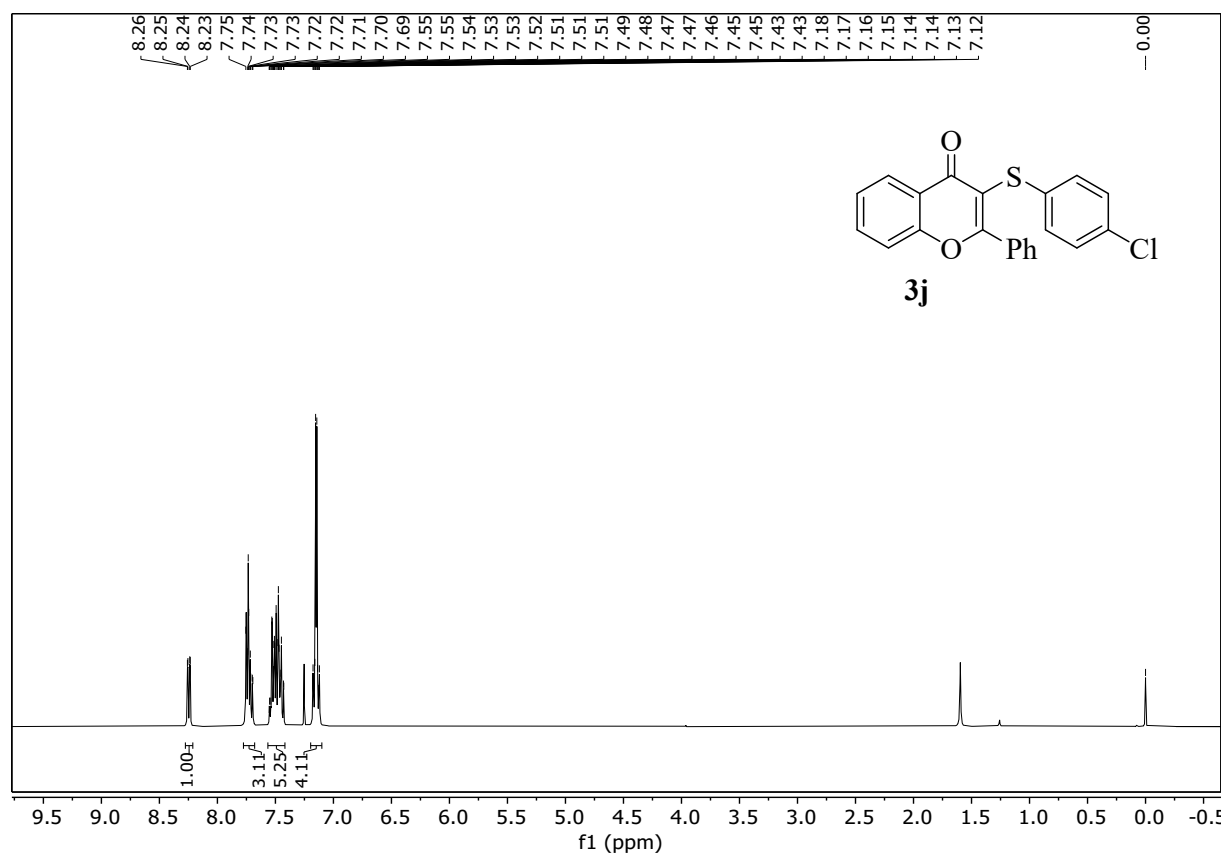


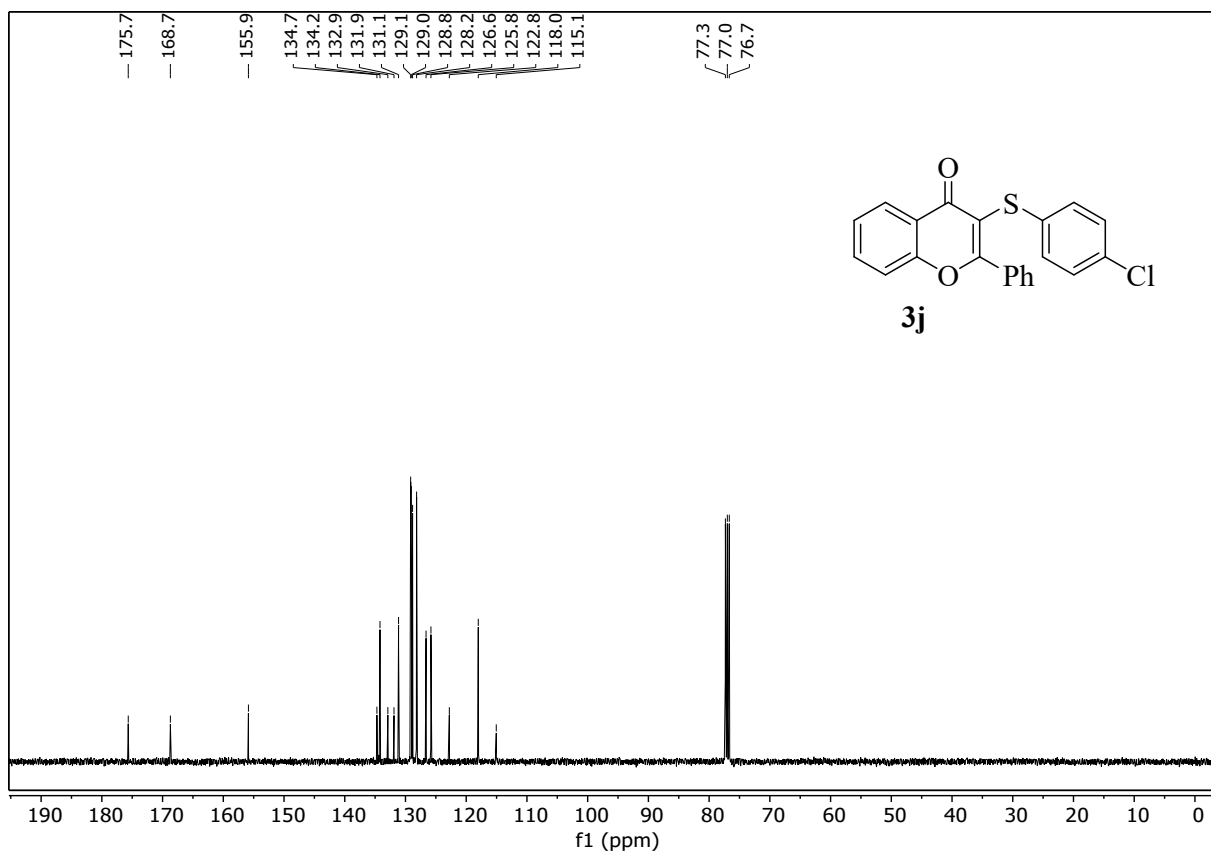
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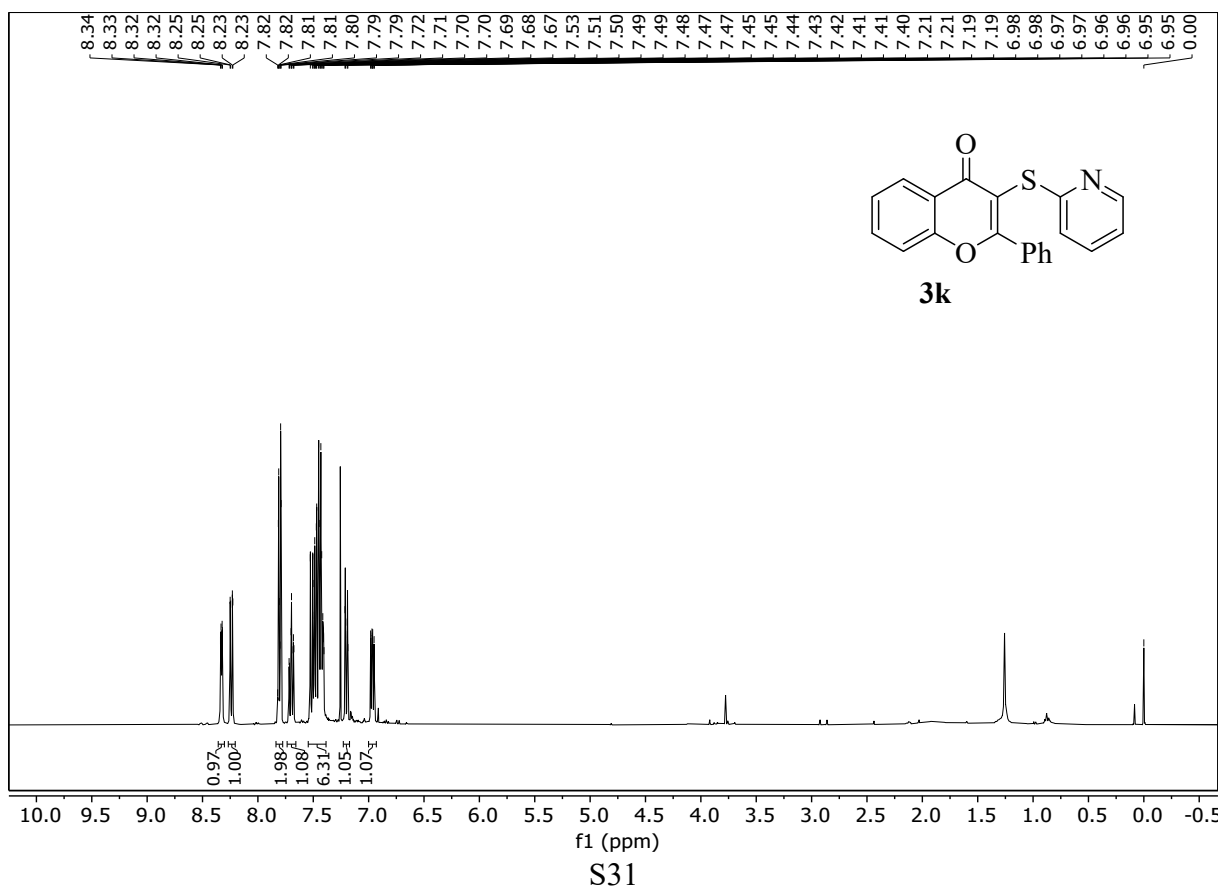


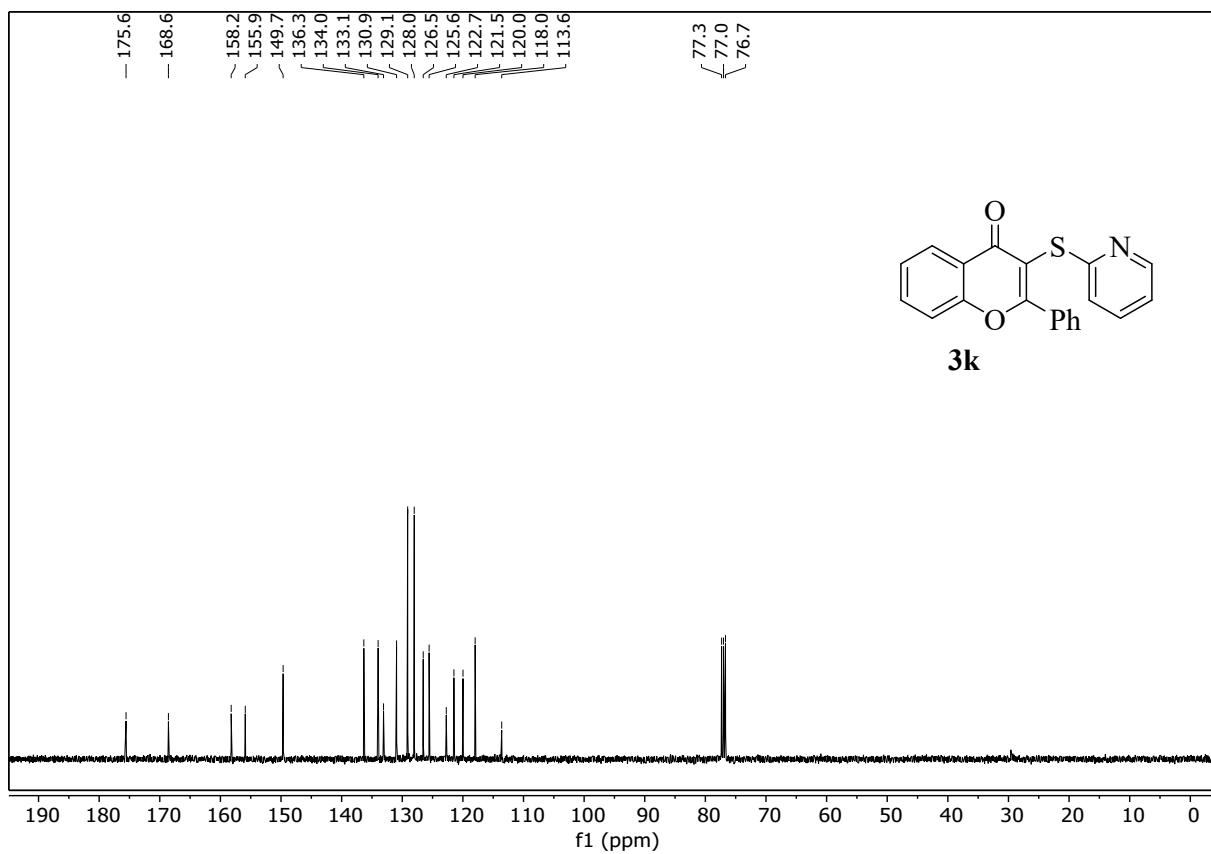
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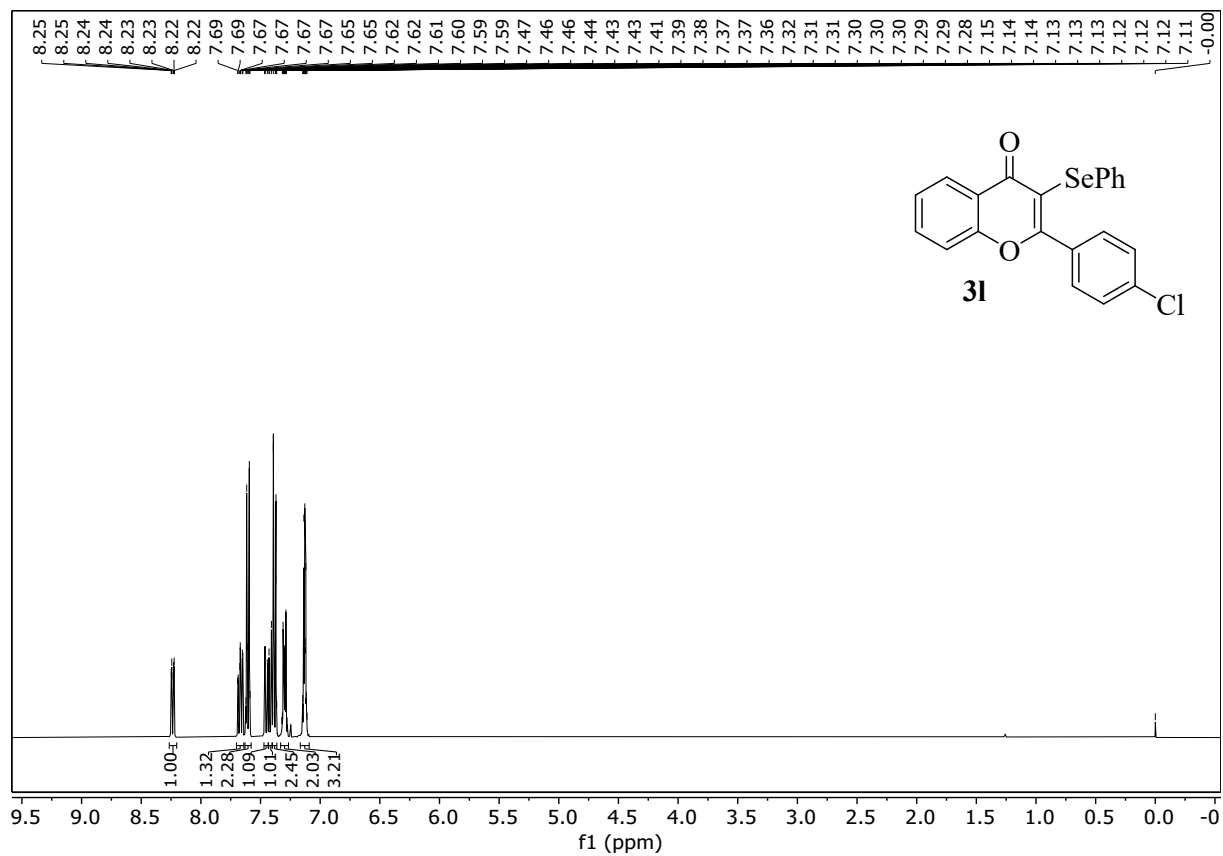


The <sup>1</sup>H (400 MHz) and <sup>13</sup>C{<sup>1</sup>H} (100 MHz) NMR spectra of **3k** in CDCl<sub>3</sub>.

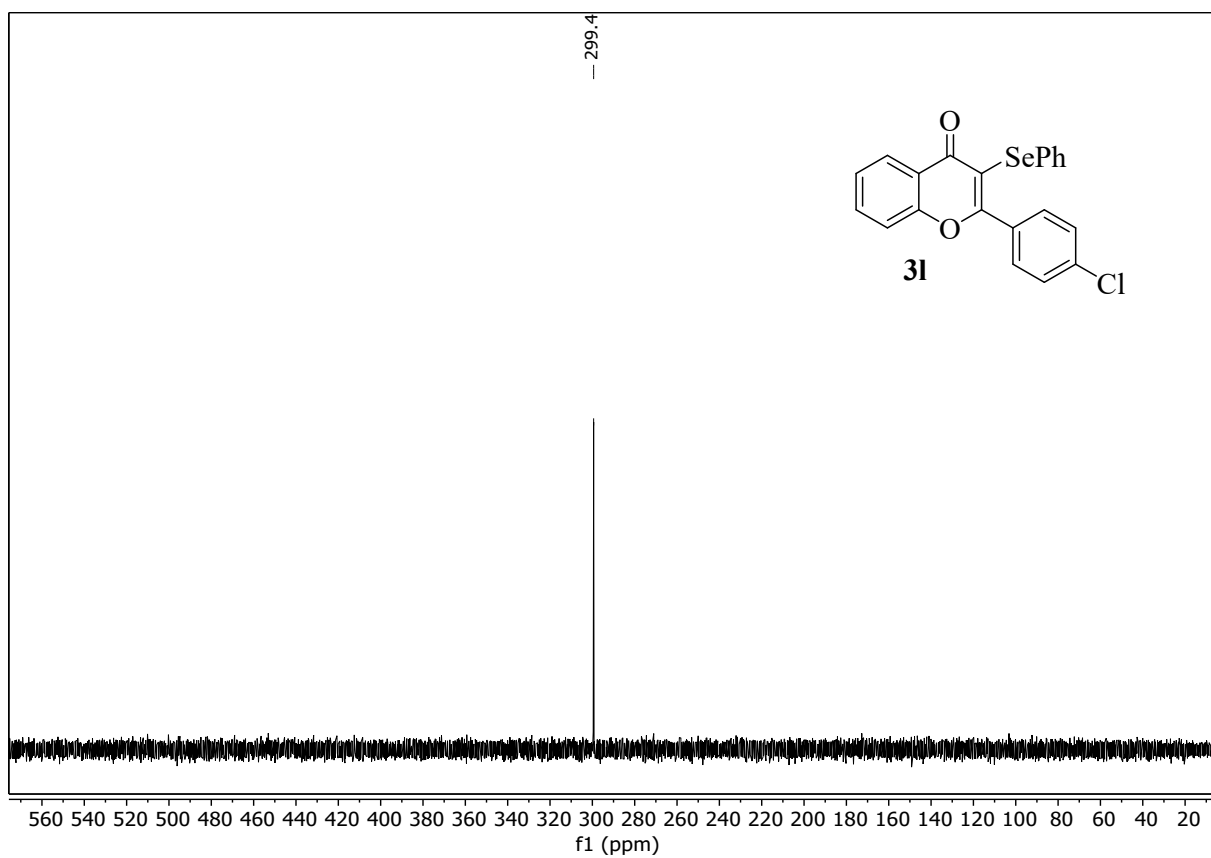
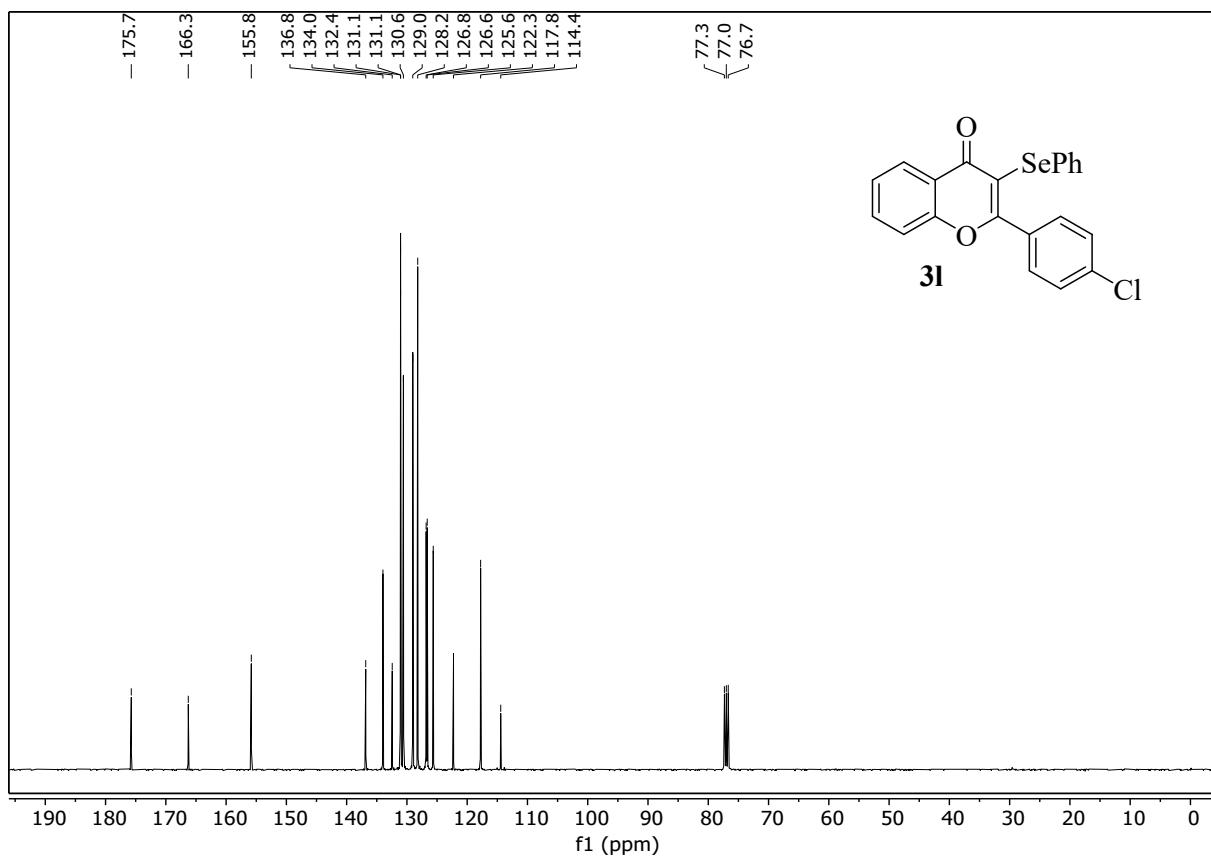




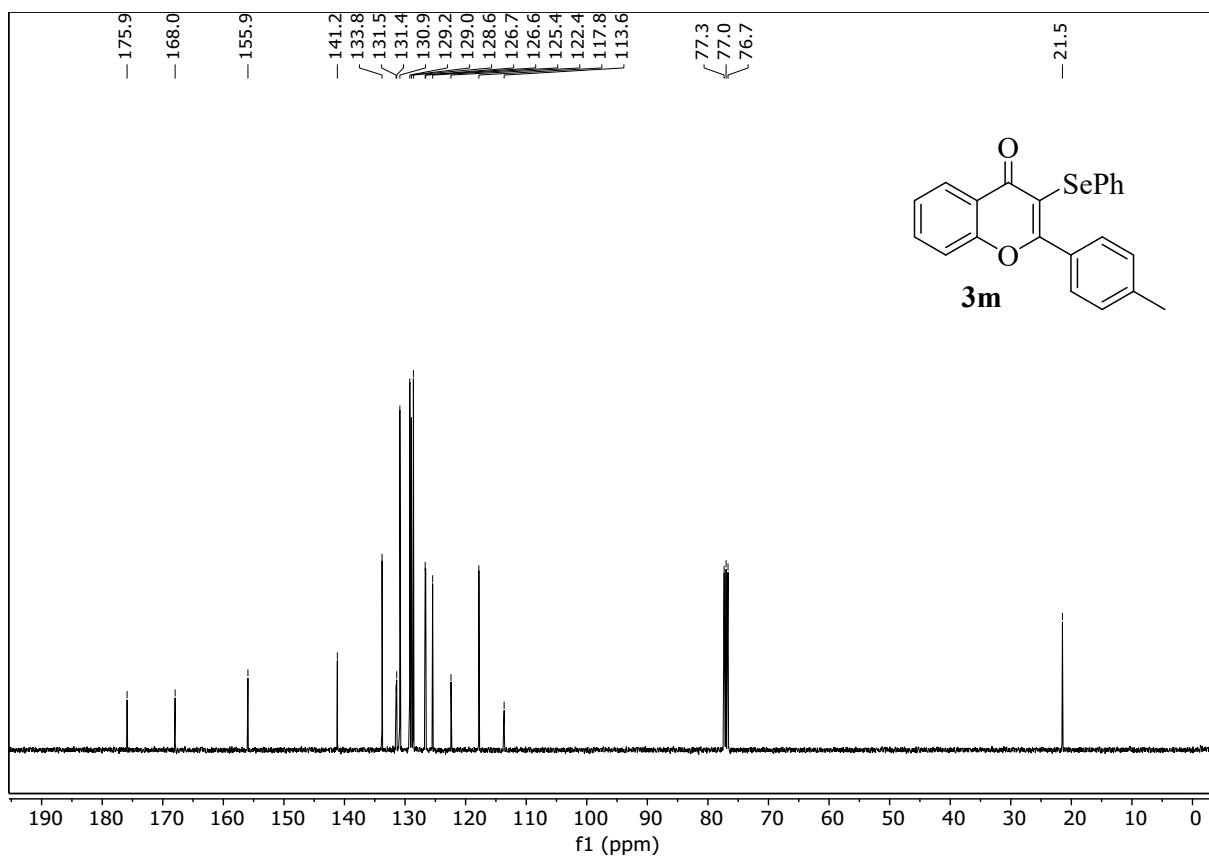
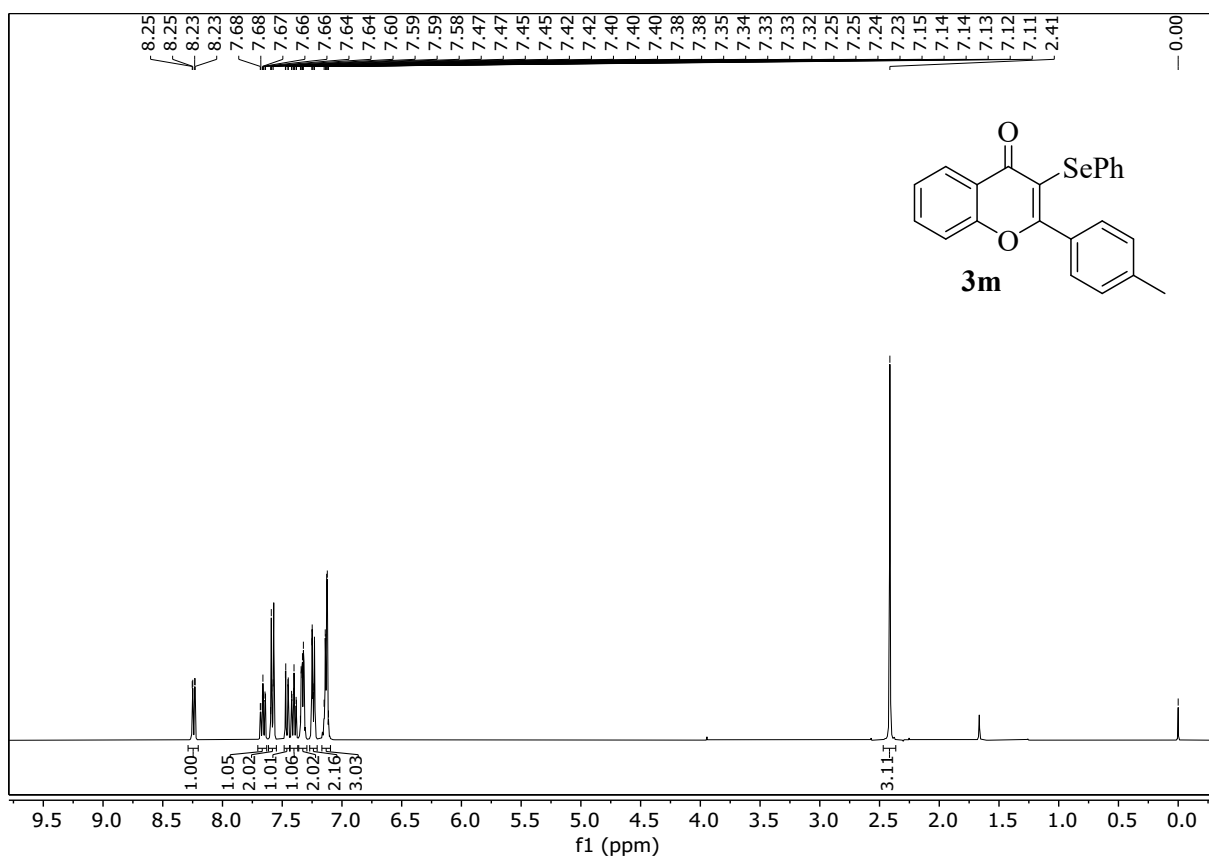
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3l** in CDCl<sub>3</sub>.

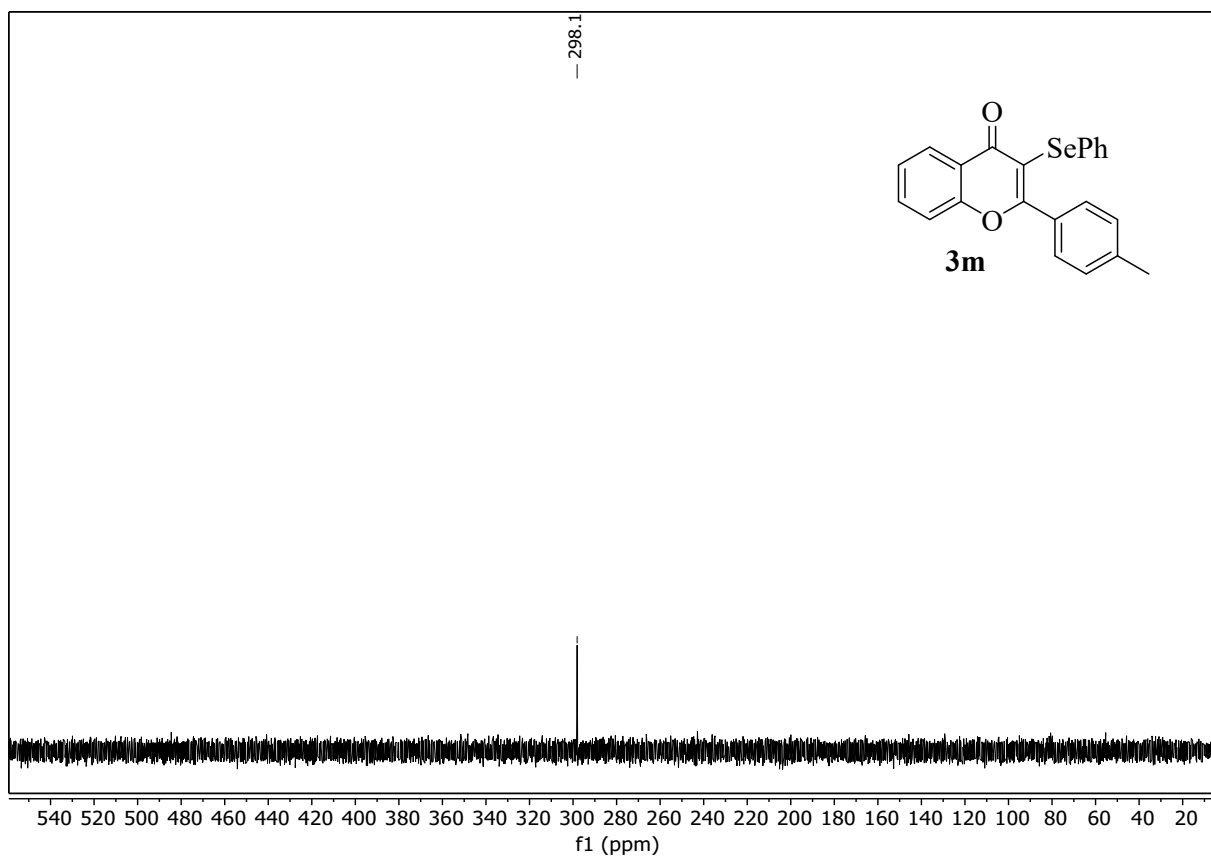




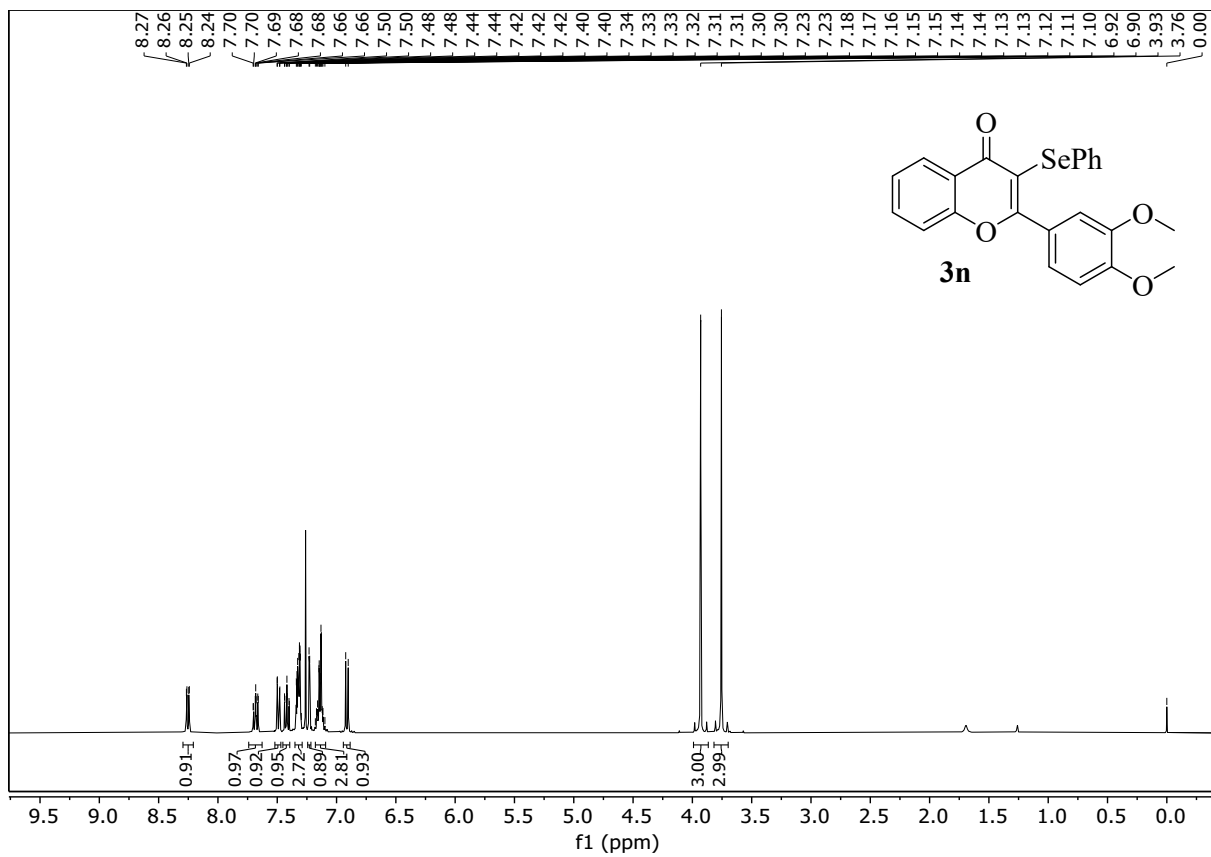


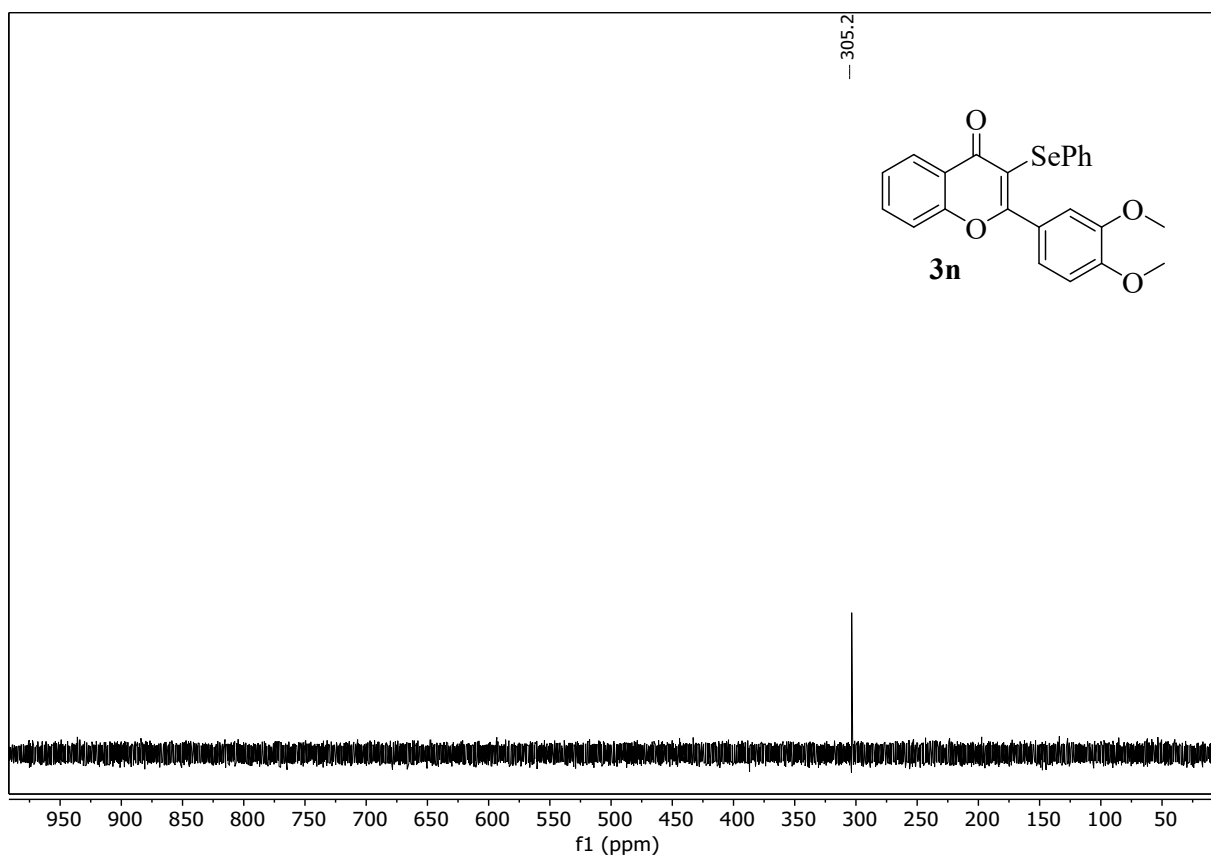
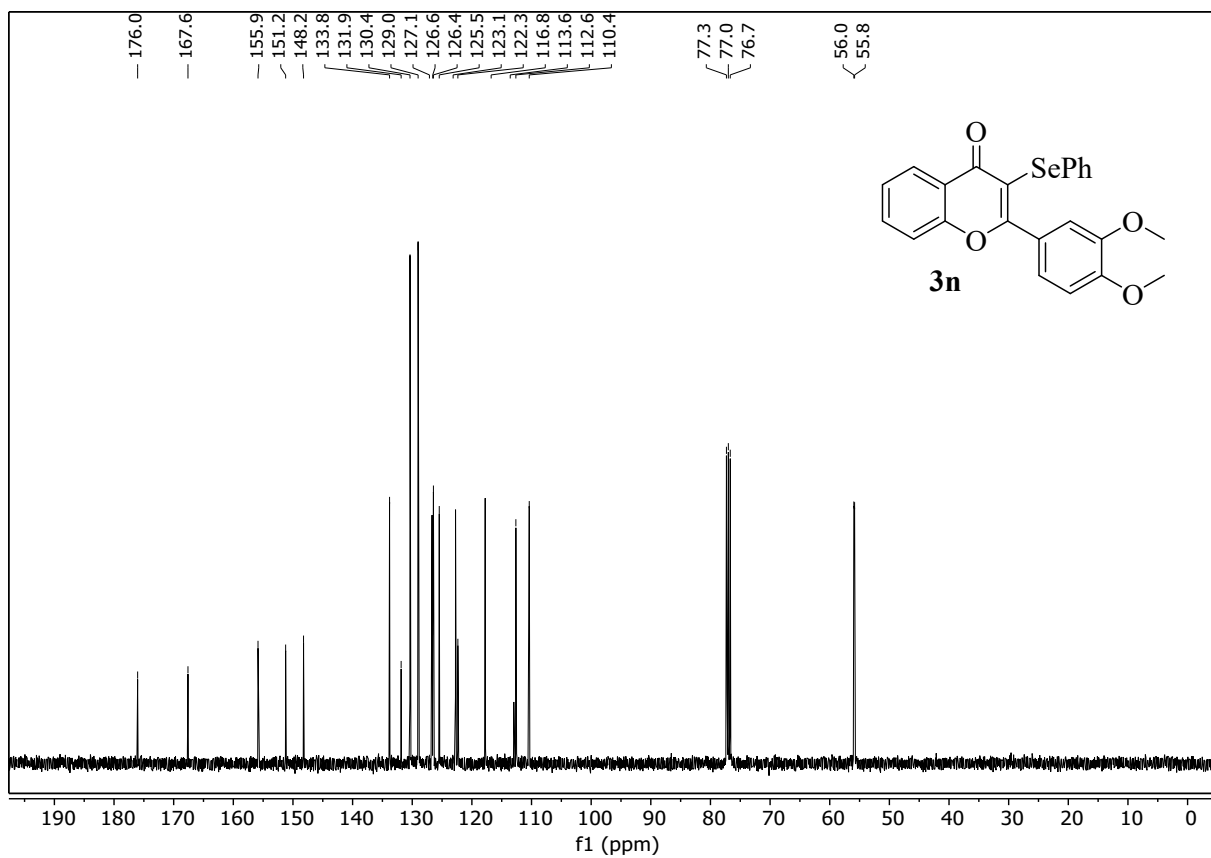
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3m** in  $\text{CDCl}_3$ .



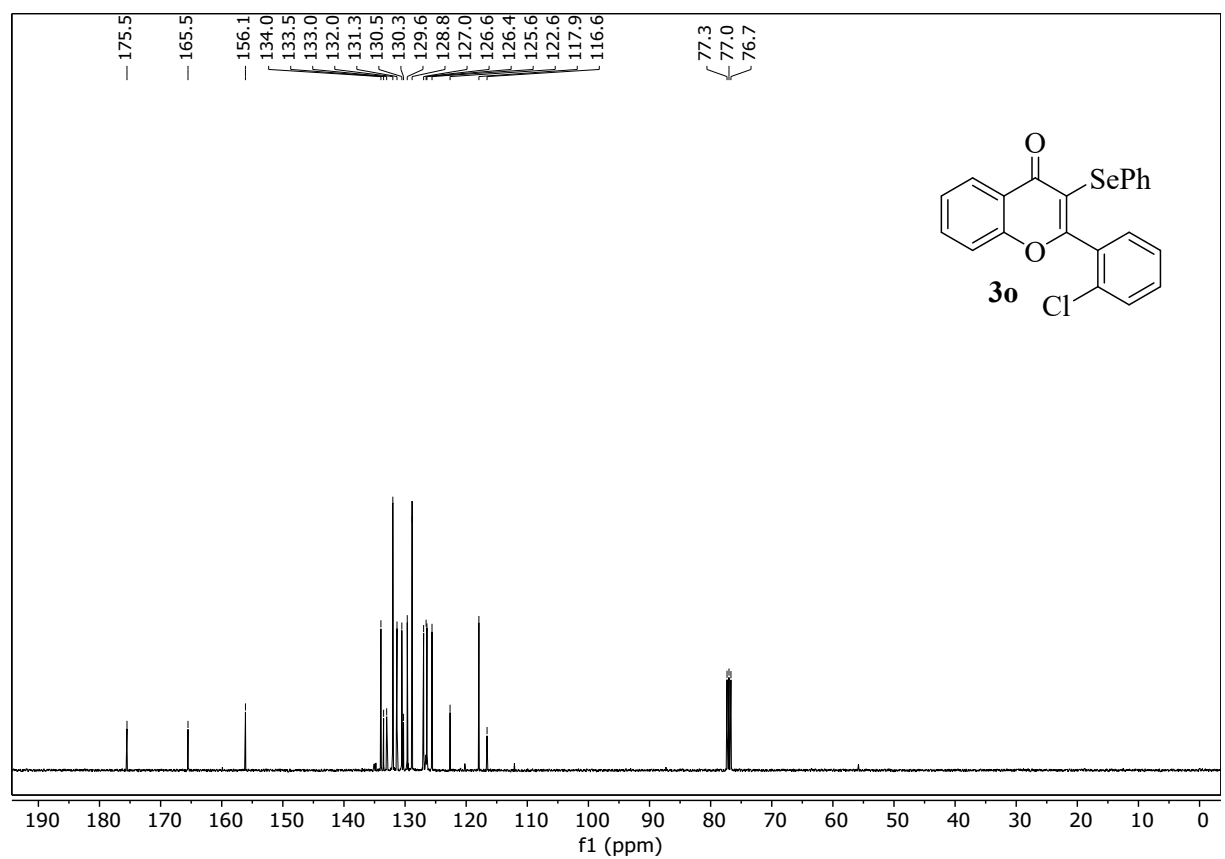
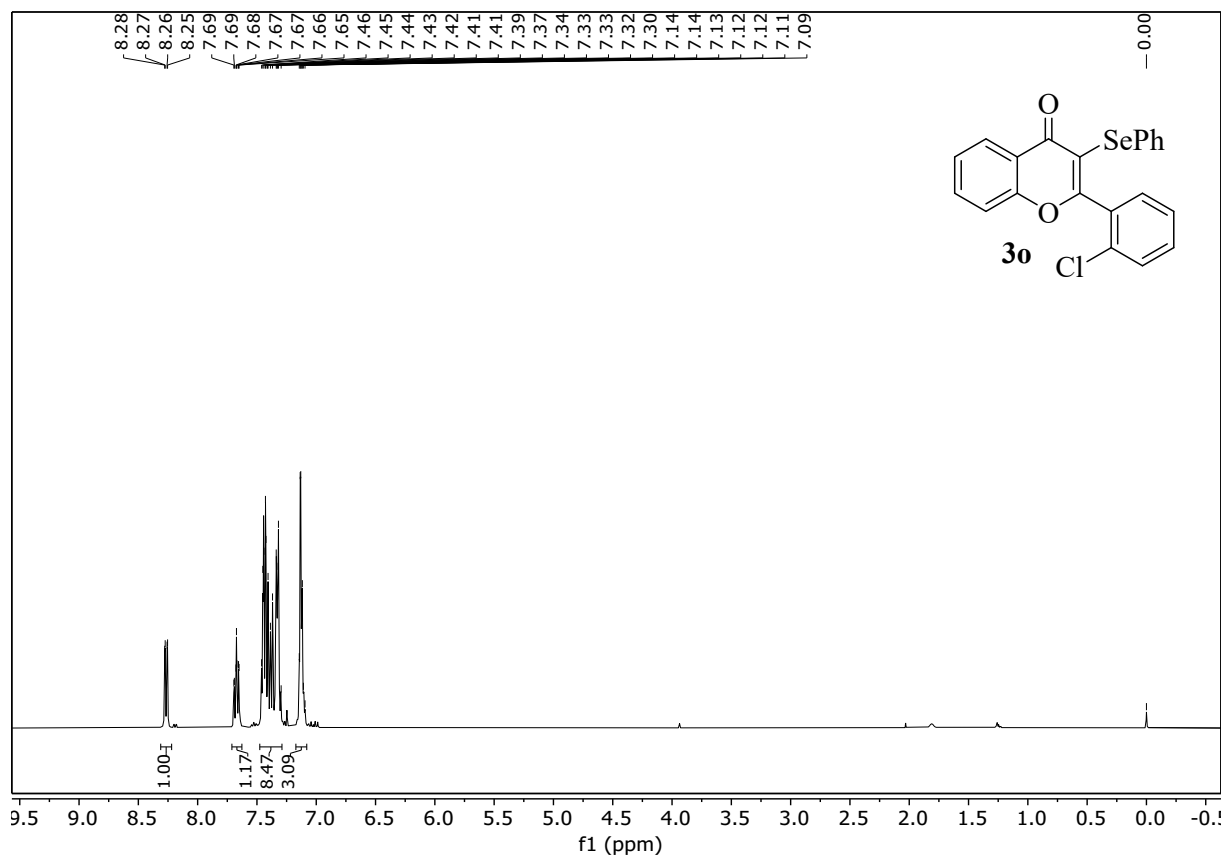


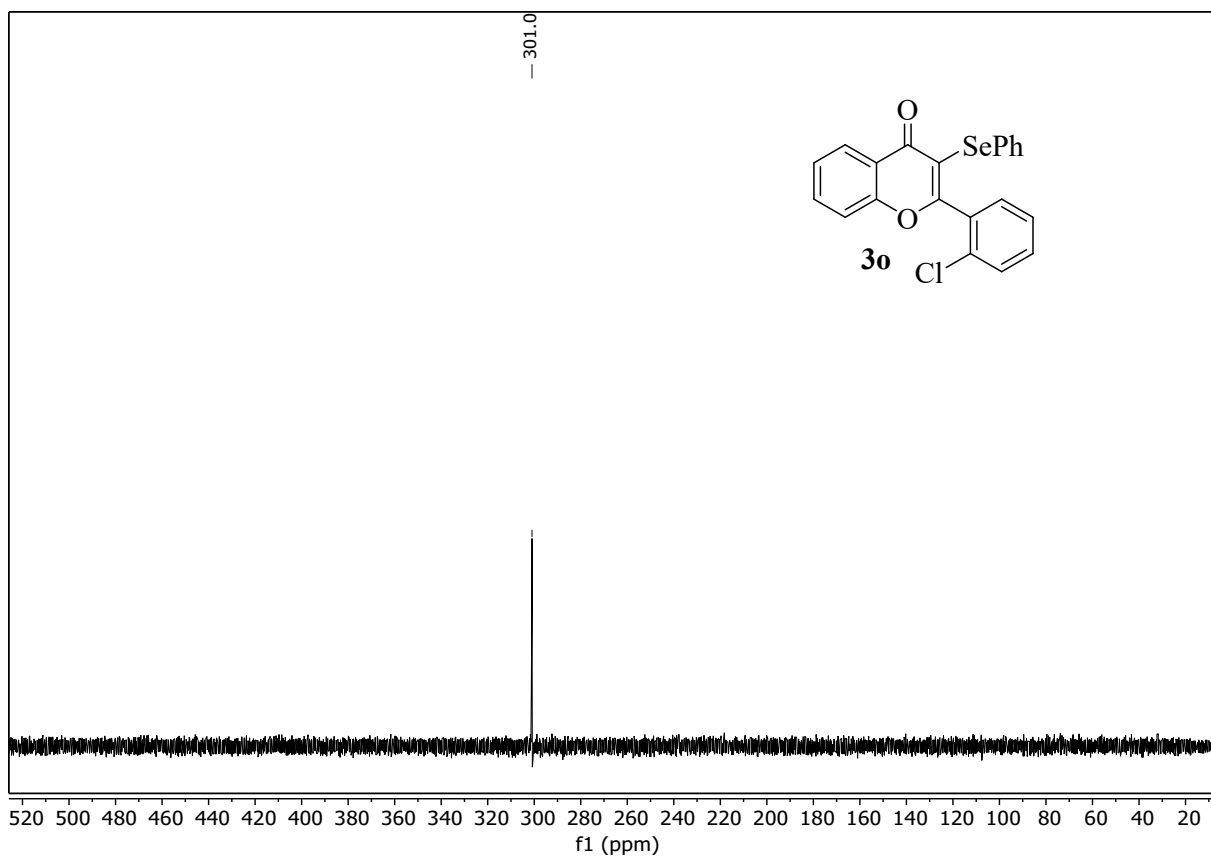
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3n** in CDCl<sub>3</sub>.



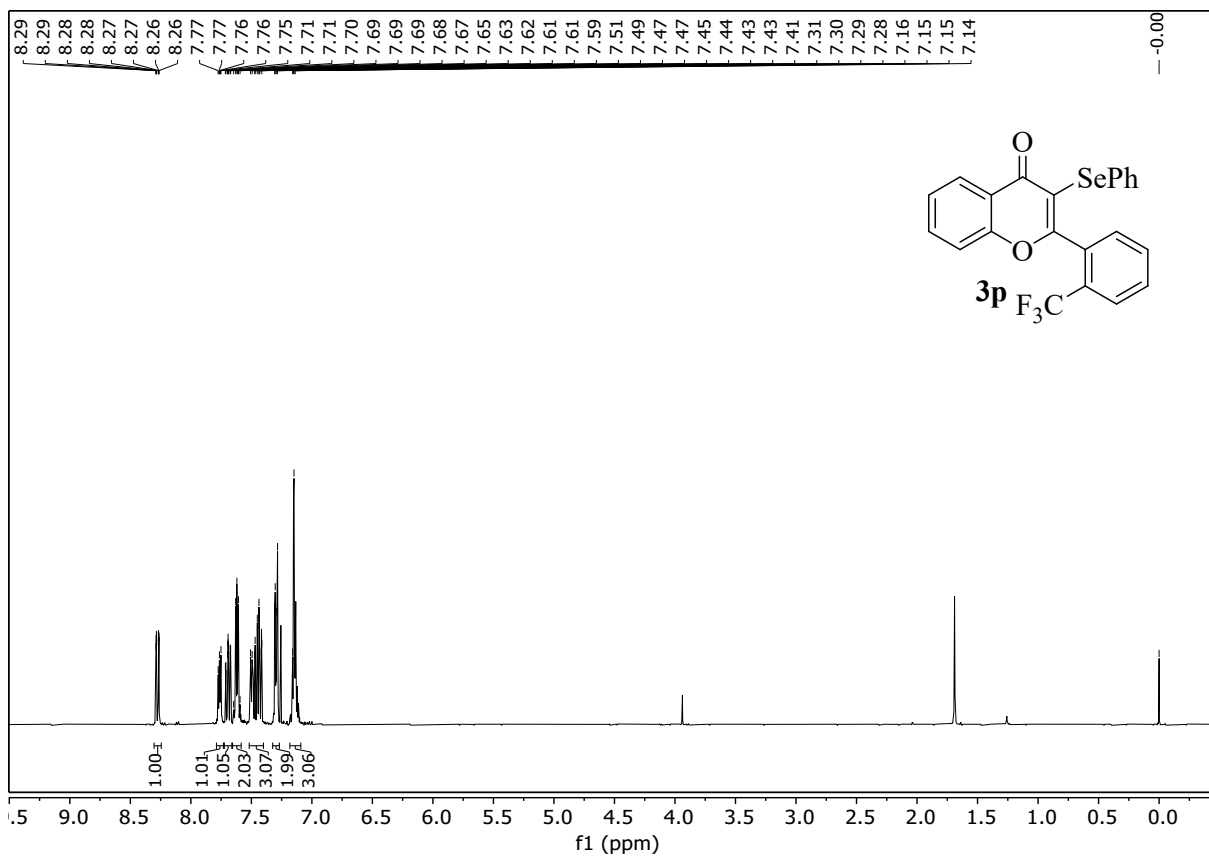


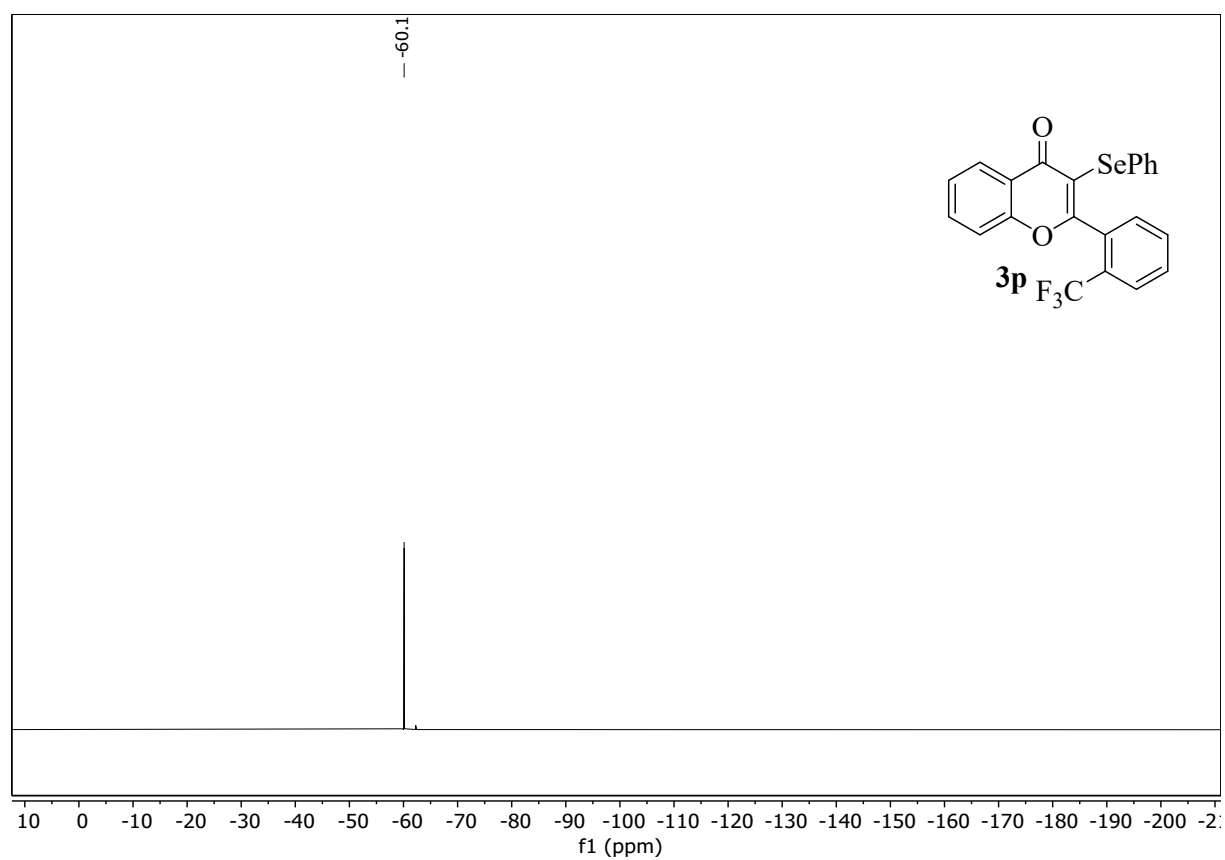
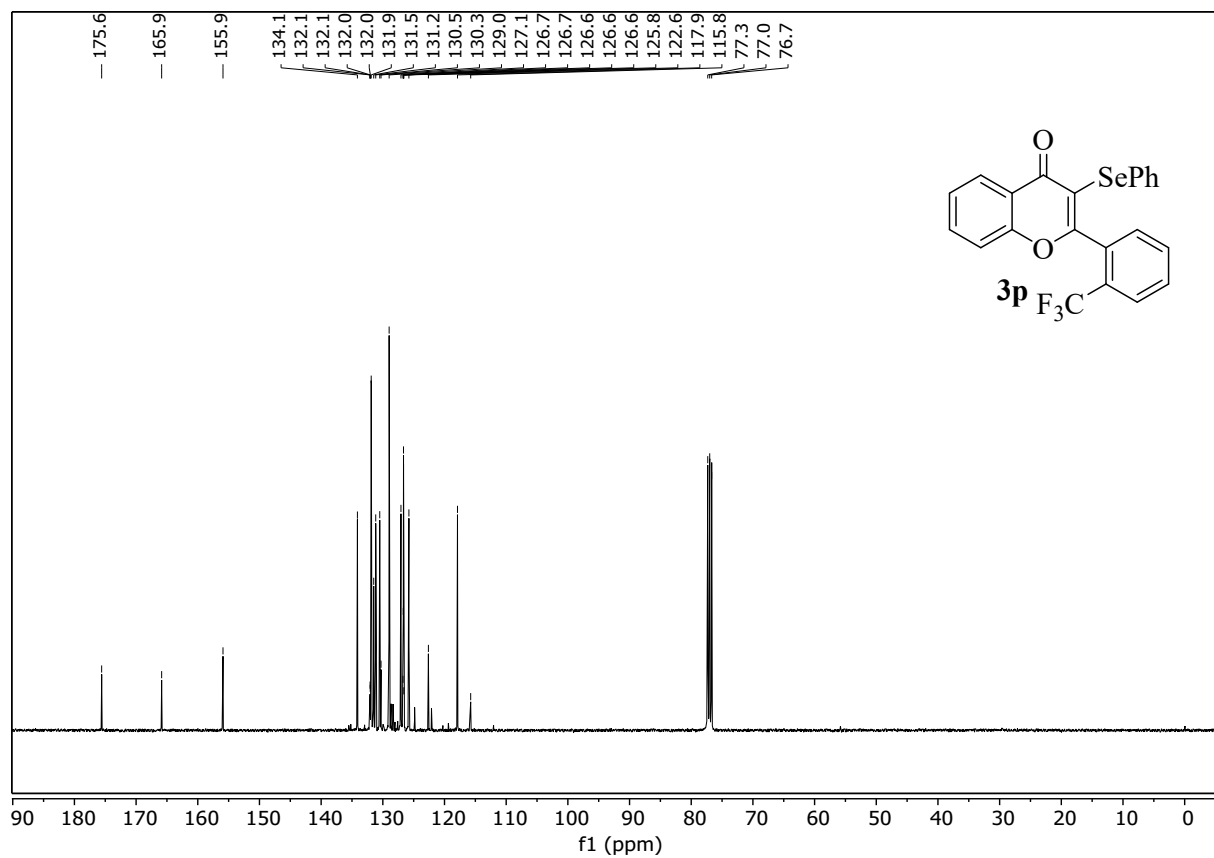
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3o** in  $\text{CDCl}_3$ .

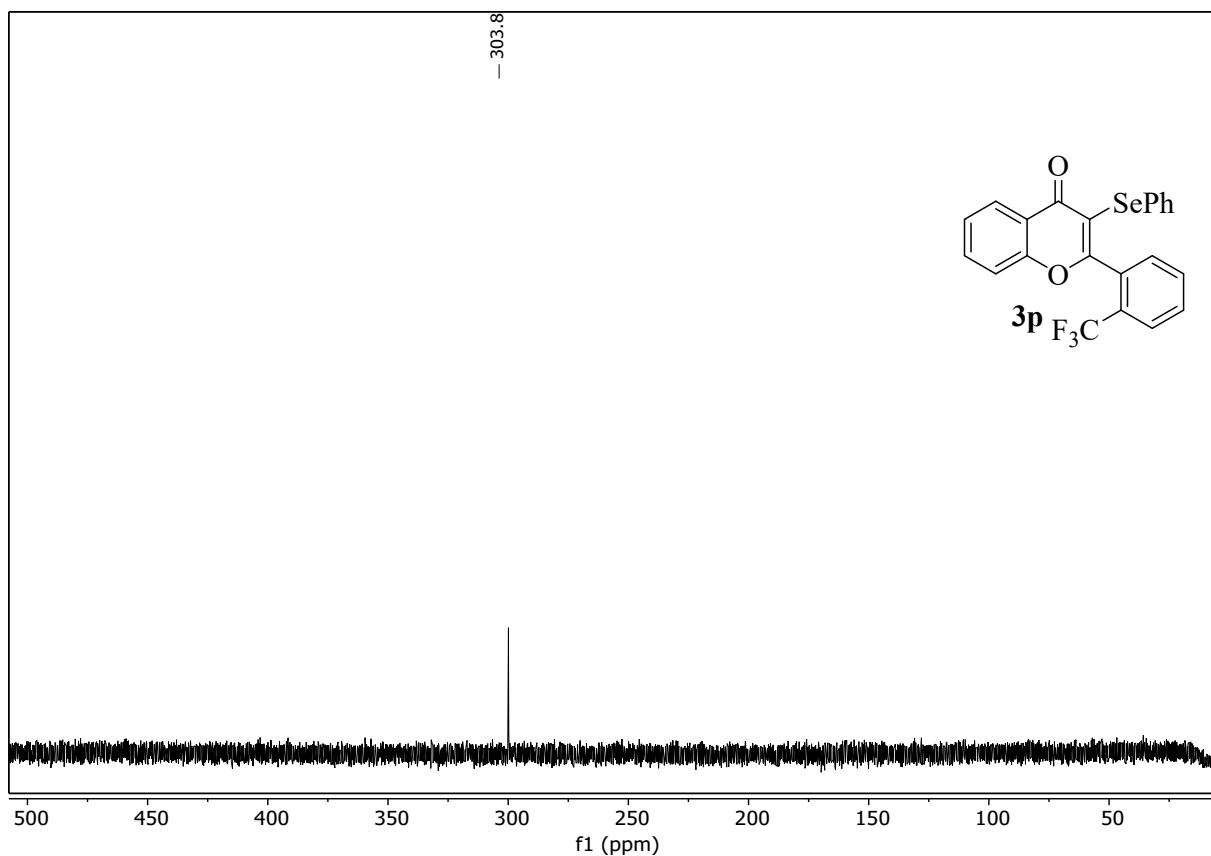




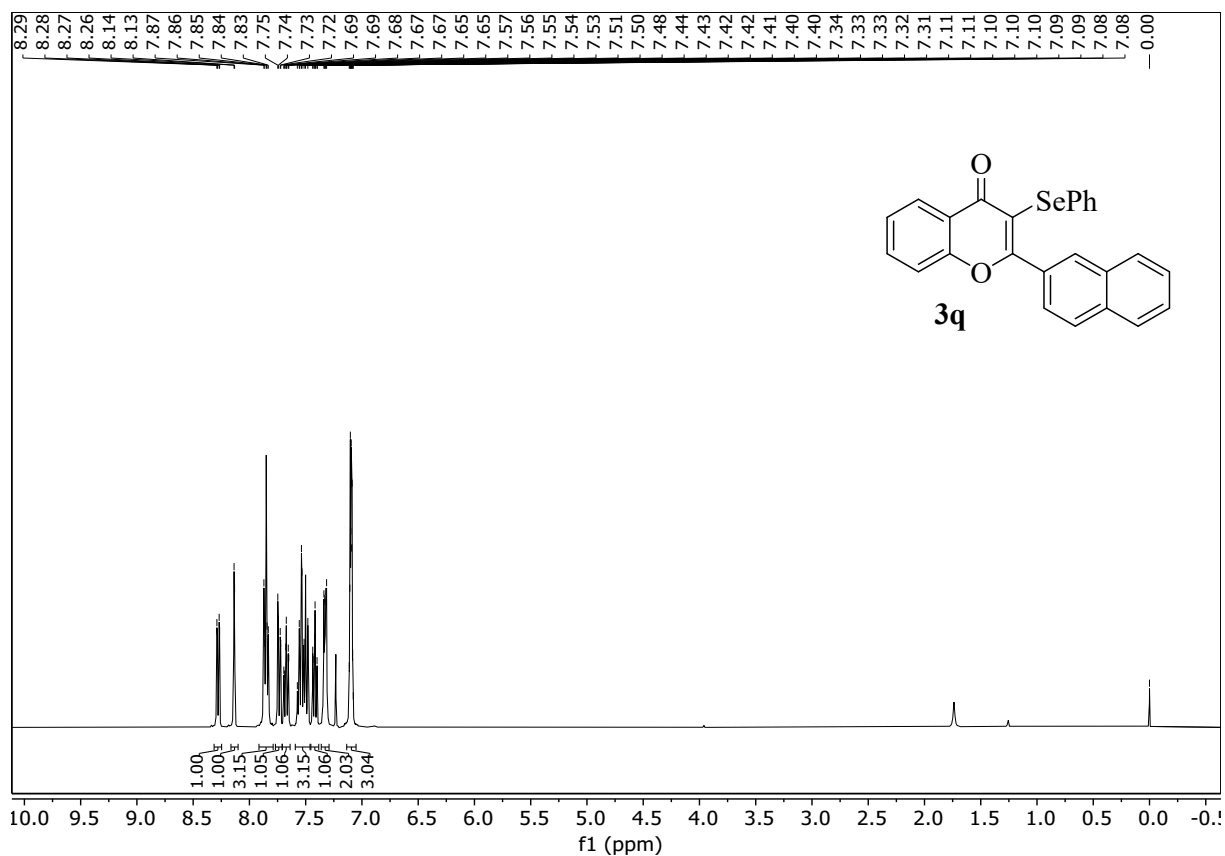
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), <sup>19</sup>F (375 MHz) and <sup>77</sup>Se (76 MHz) NMR spectra of **3p** in CDCl<sub>3</sub>.



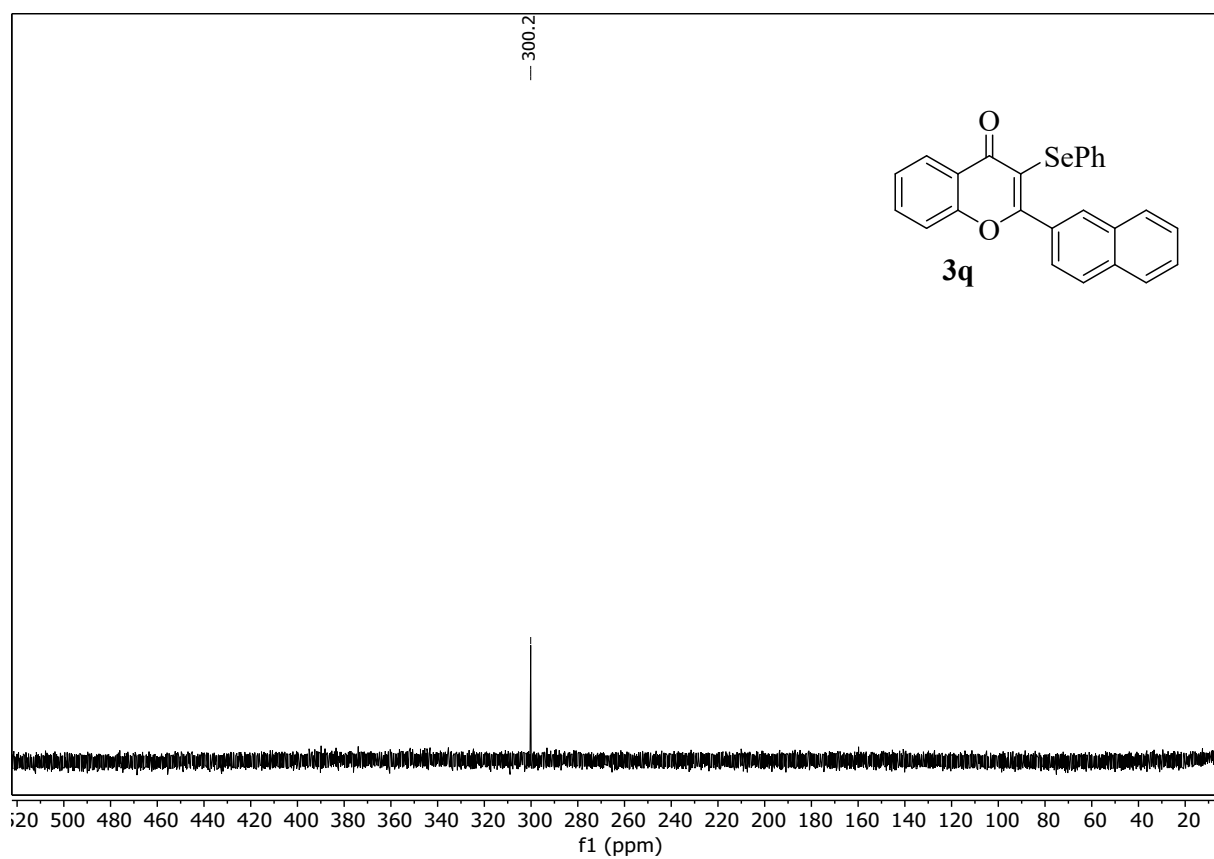
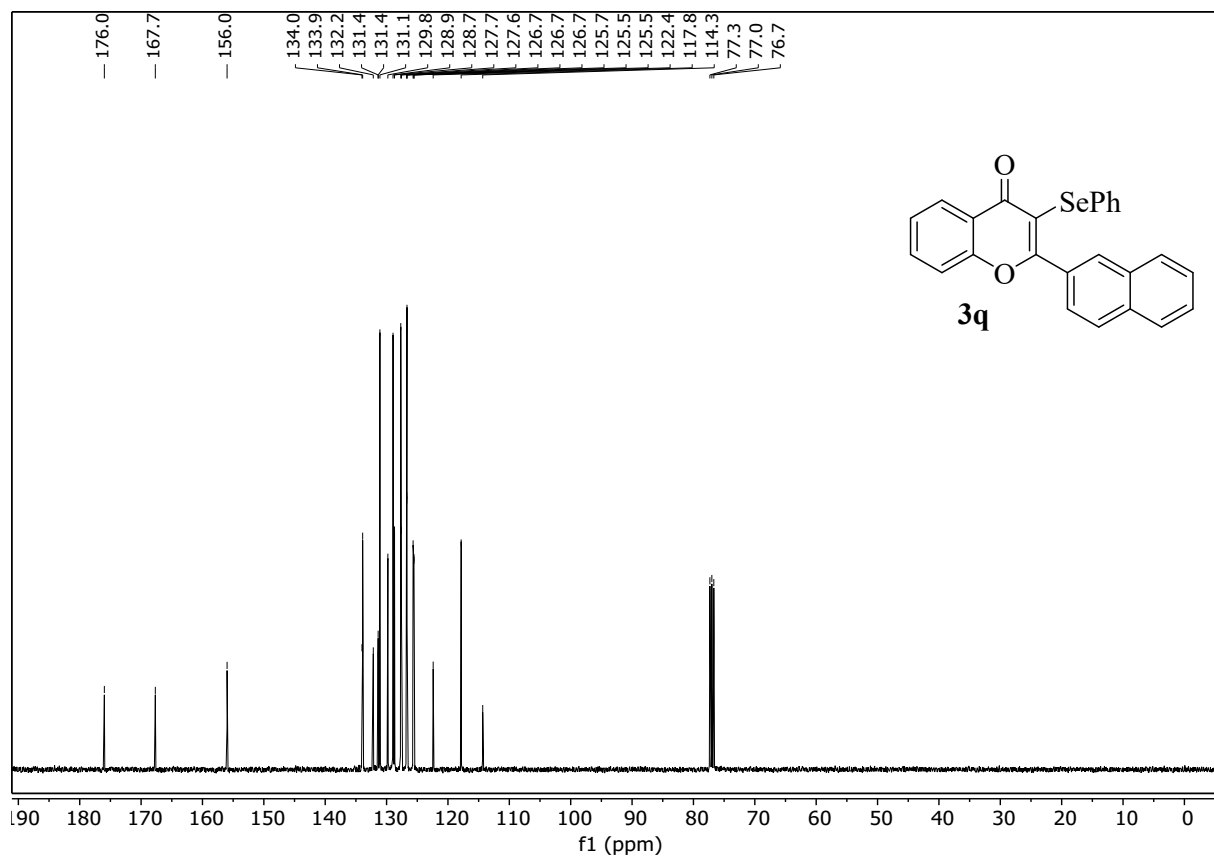




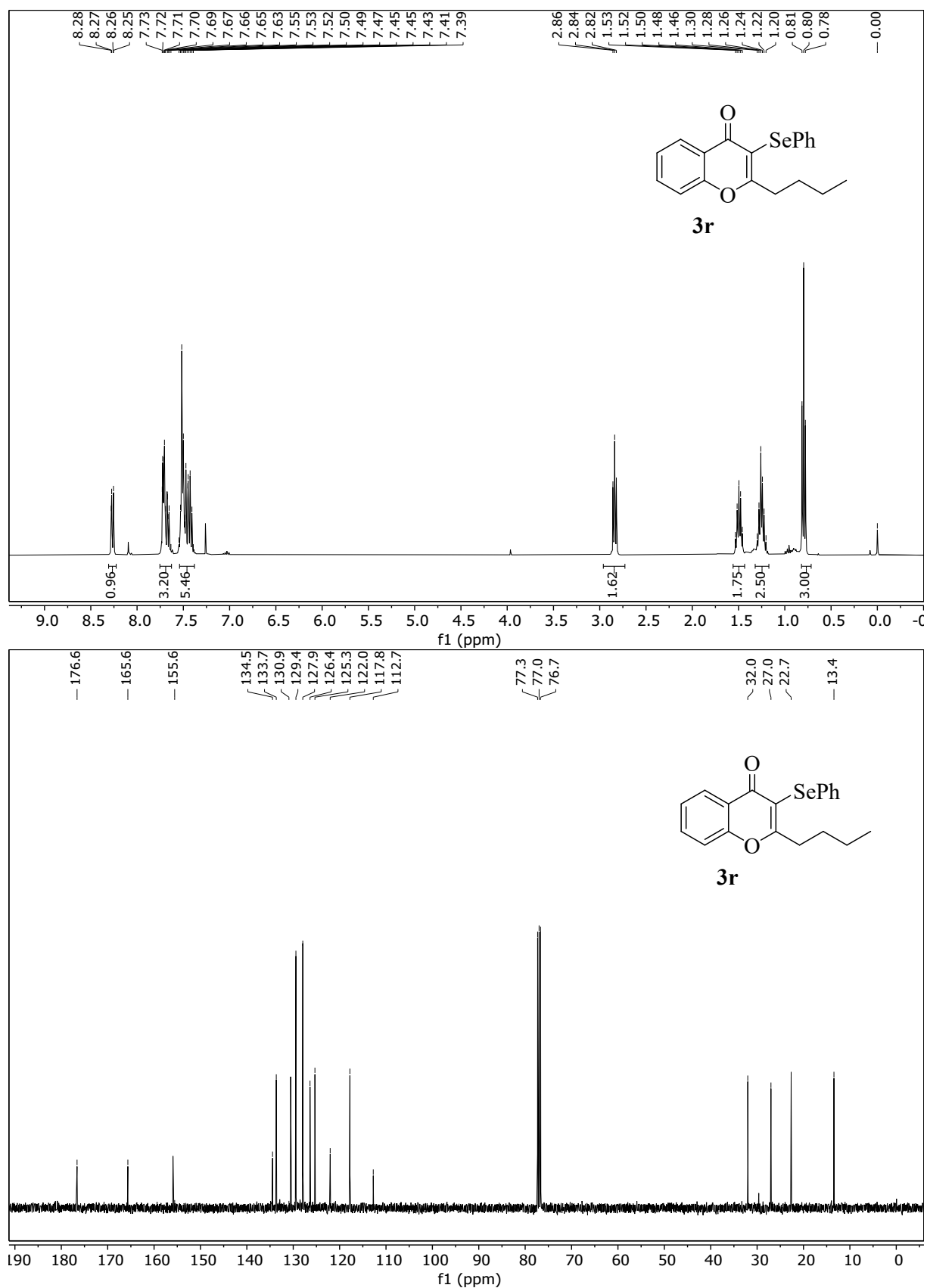
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3q** in CDCl<sub>3</sub>.

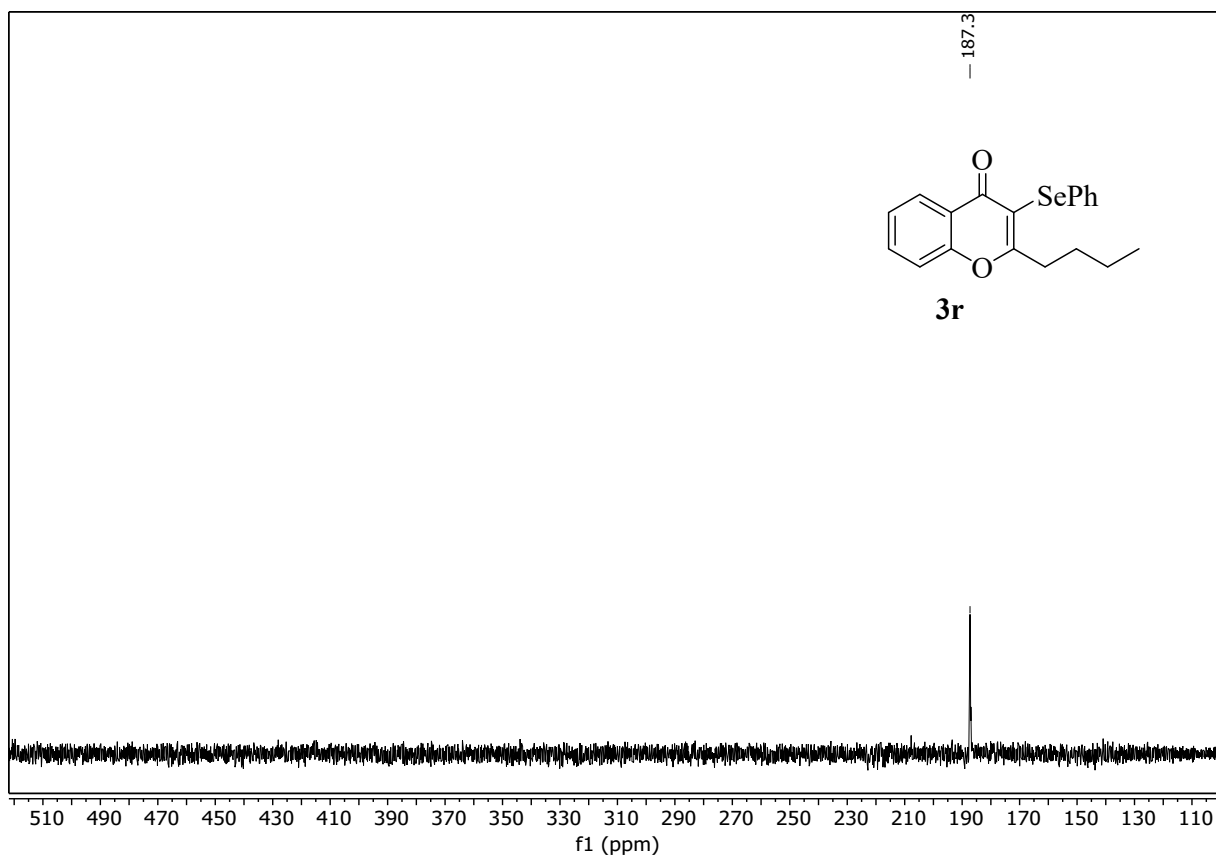




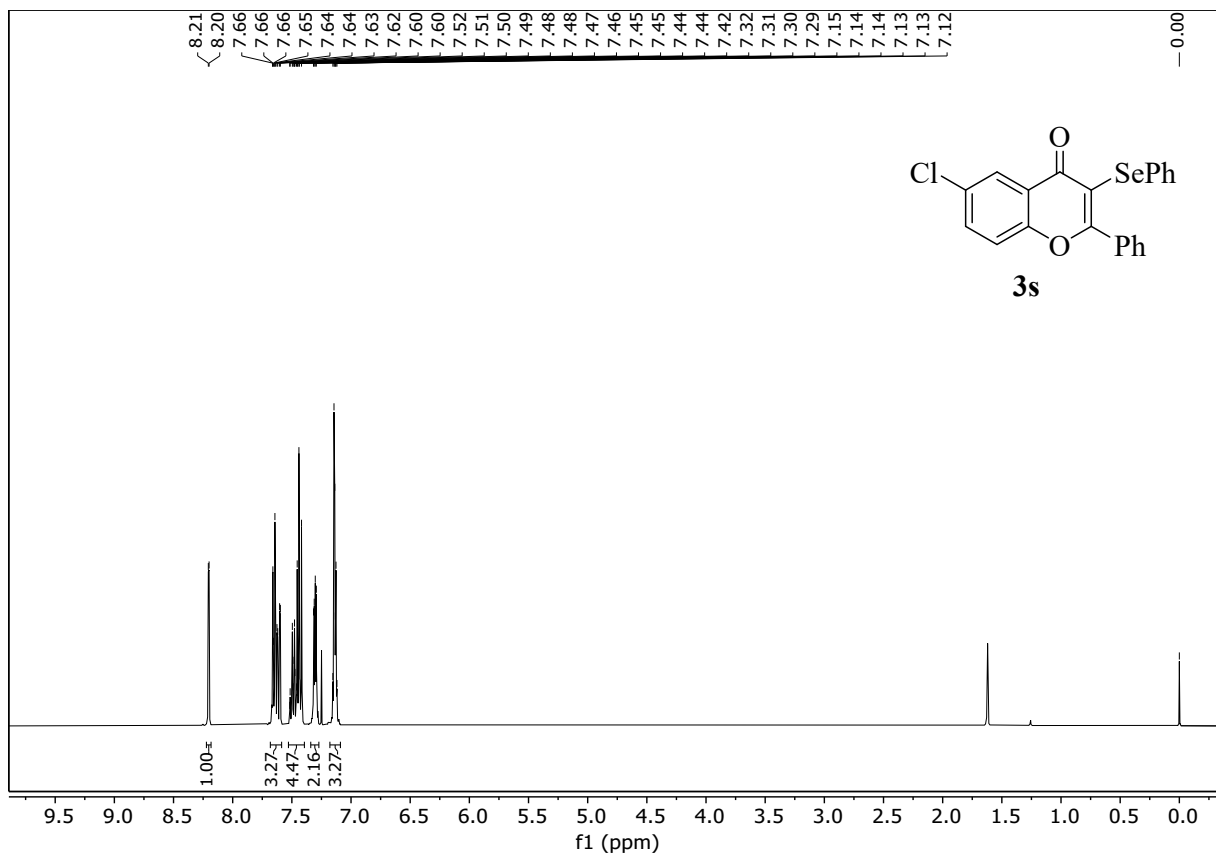


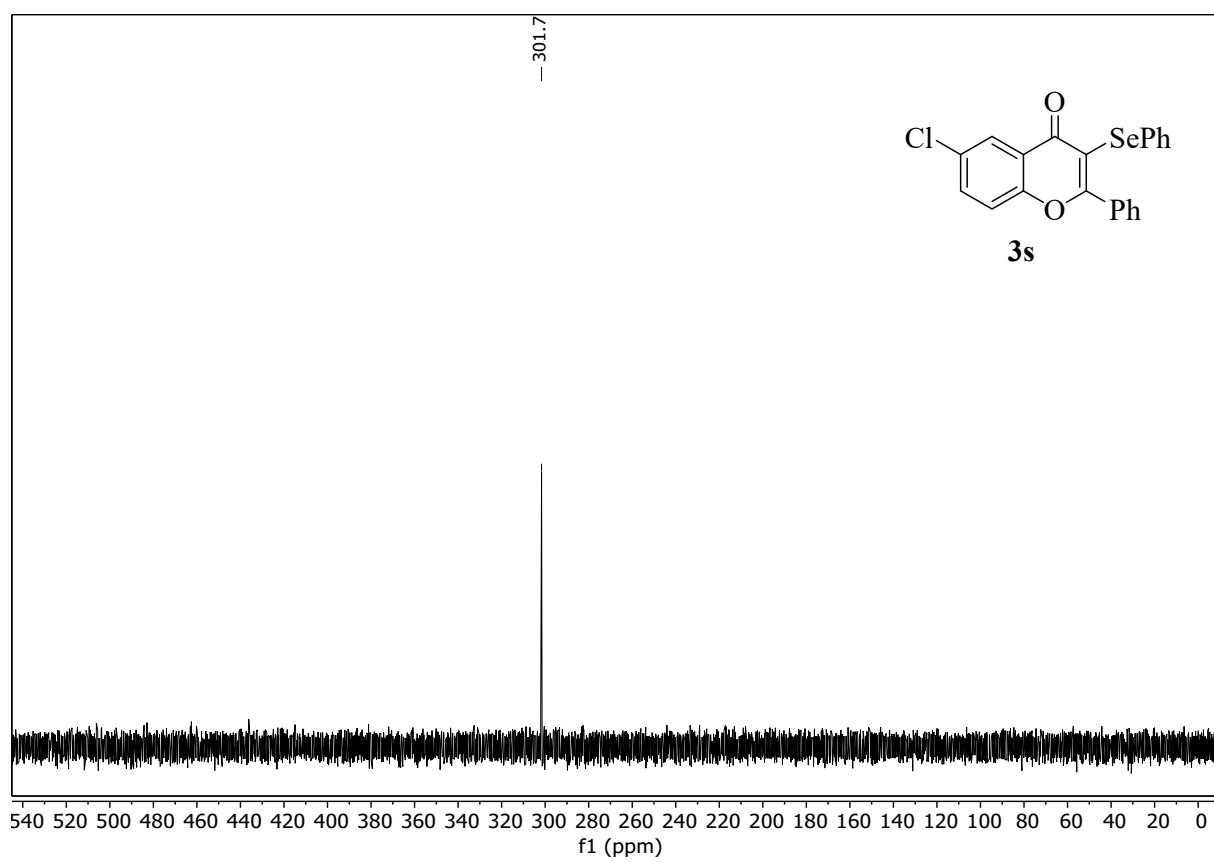
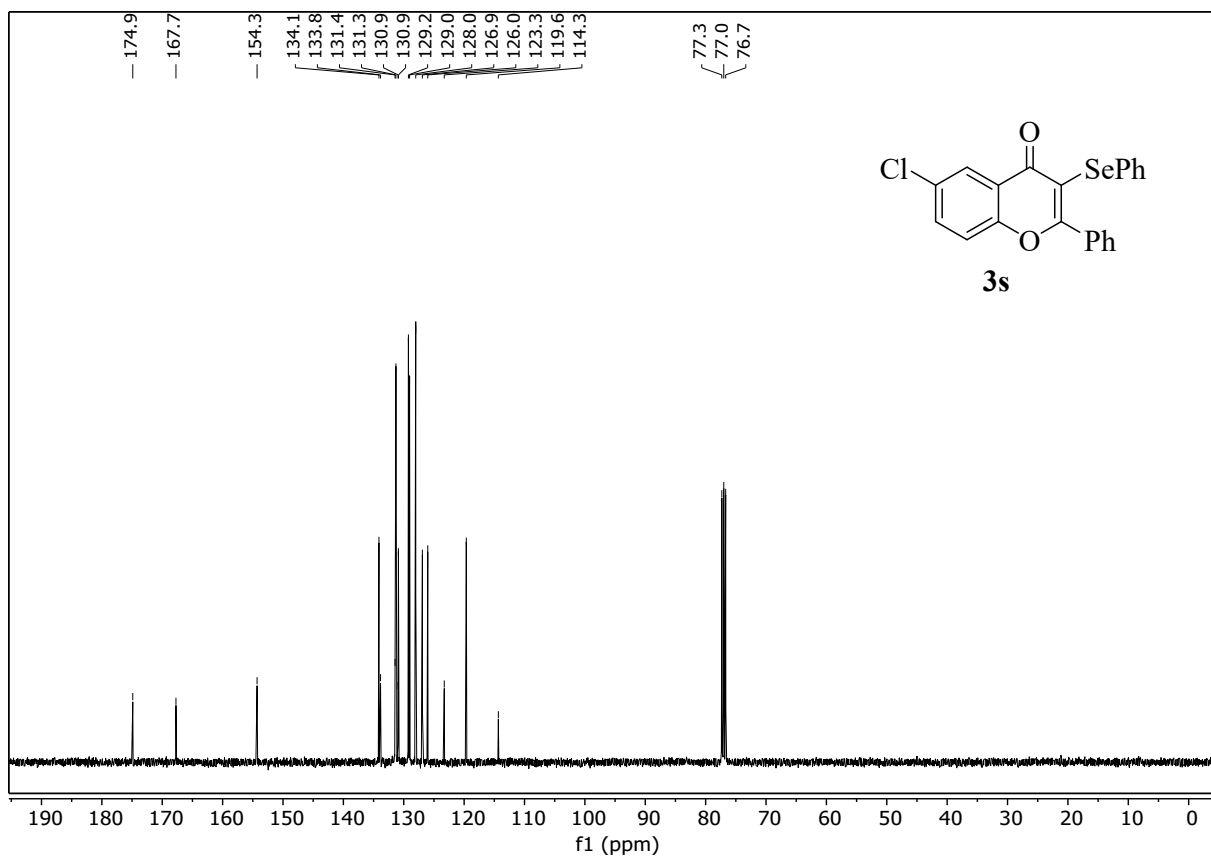
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3r** in  $\text{CDCl}_3$ .



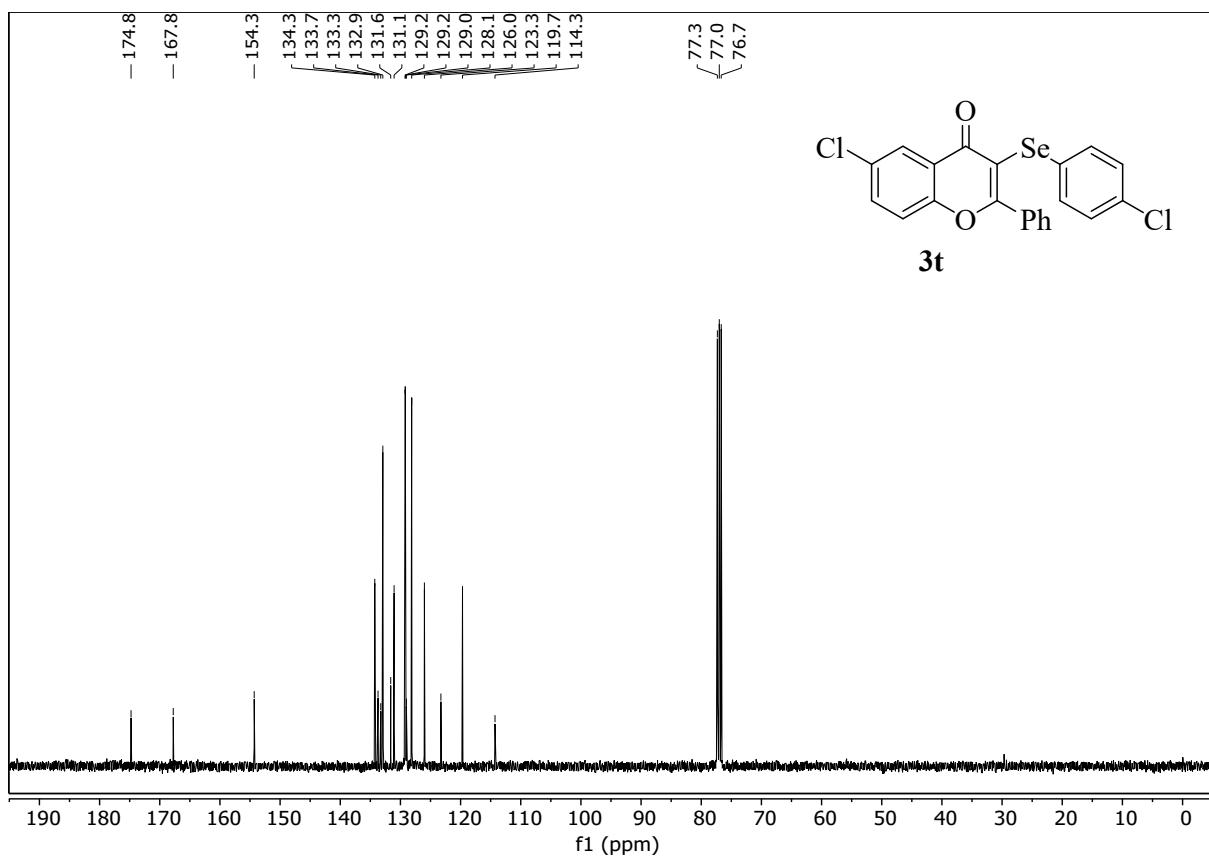
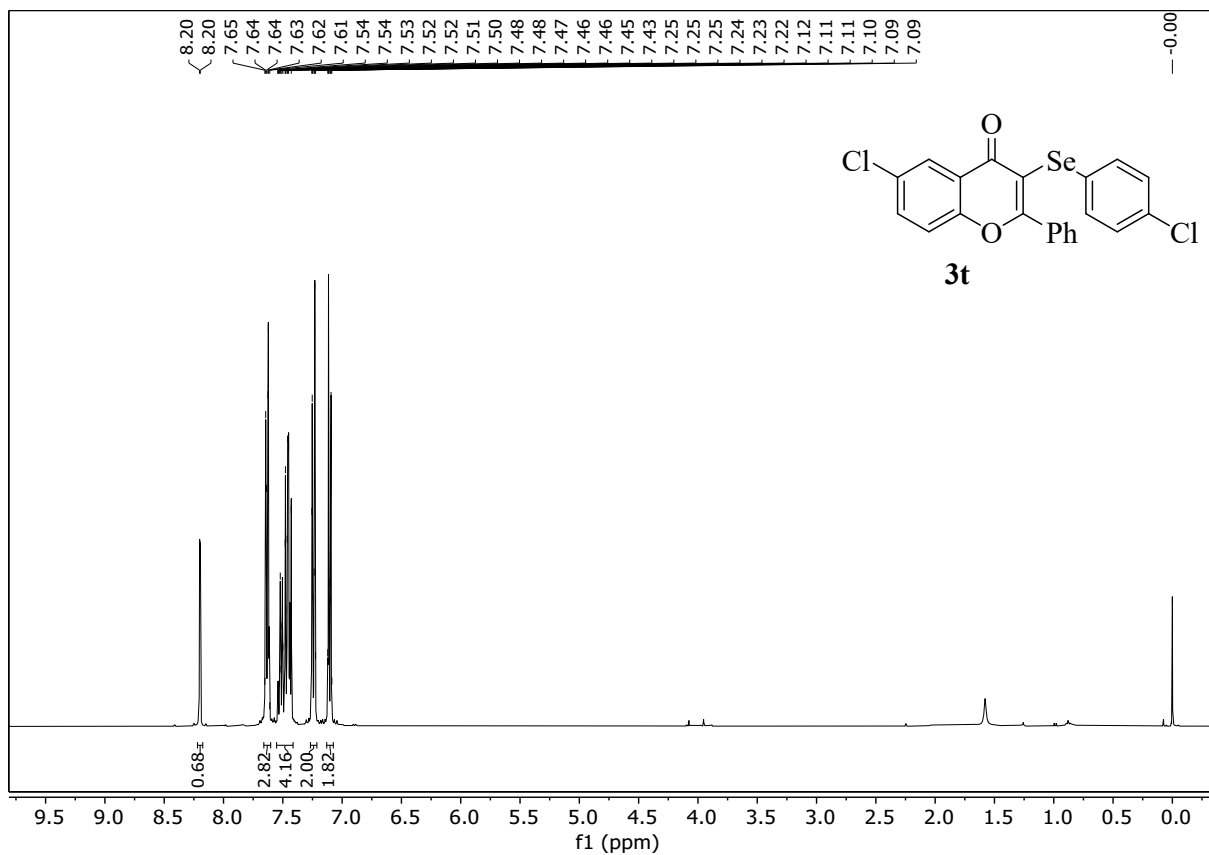


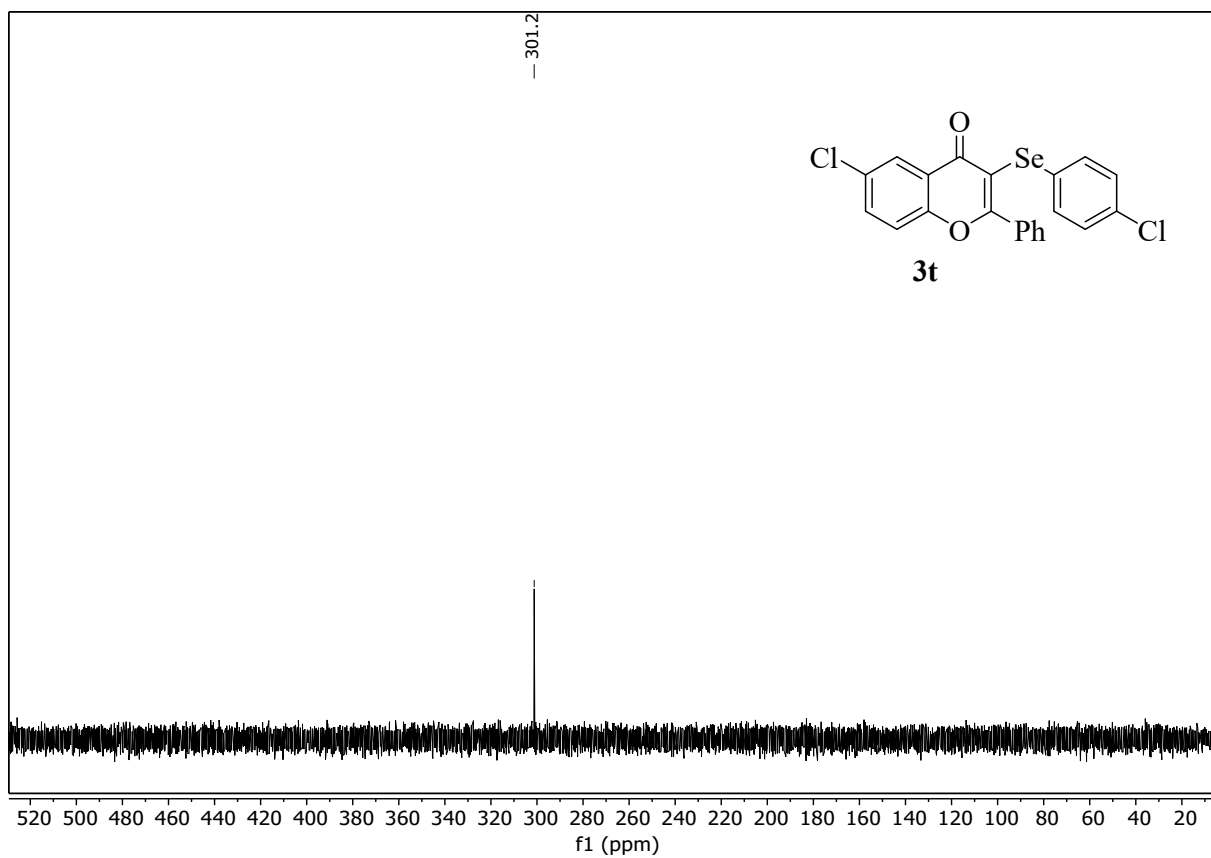
The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3s** in CDCl<sub>3</sub>.



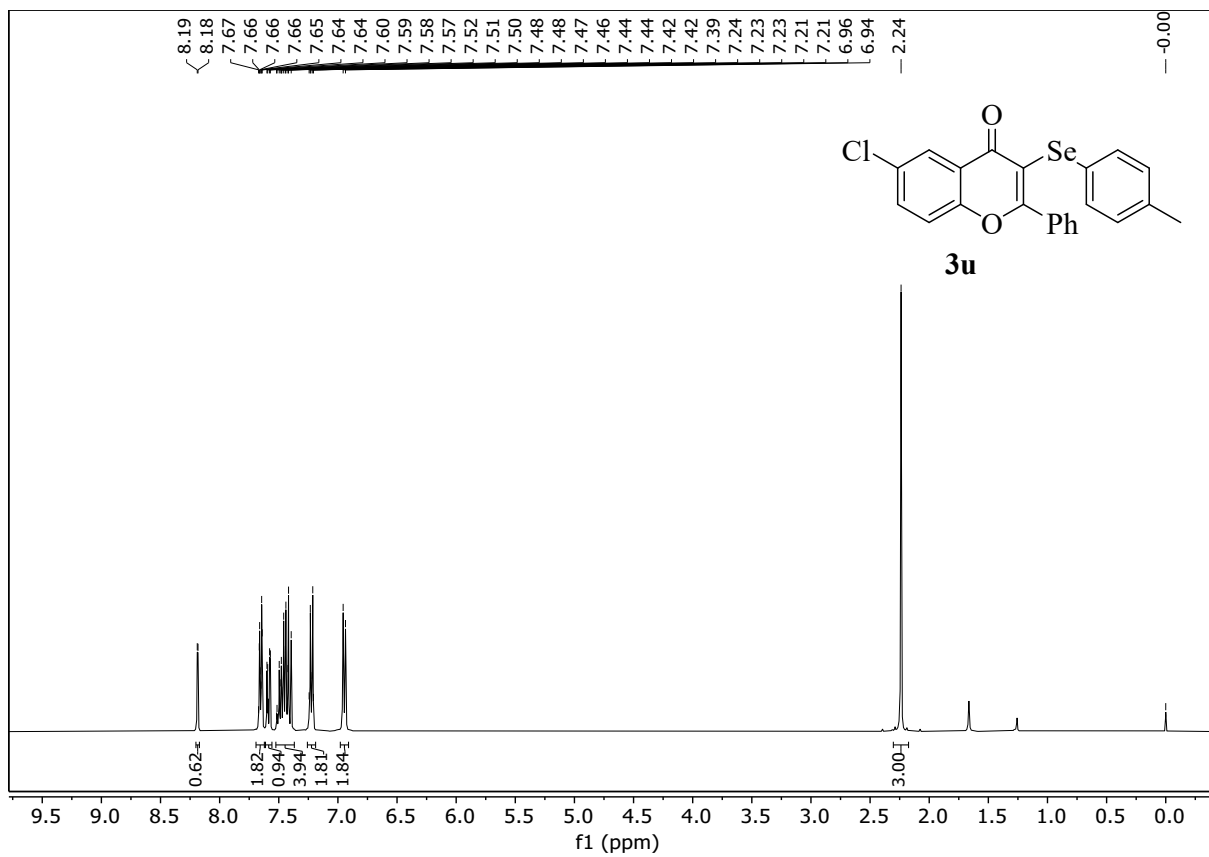


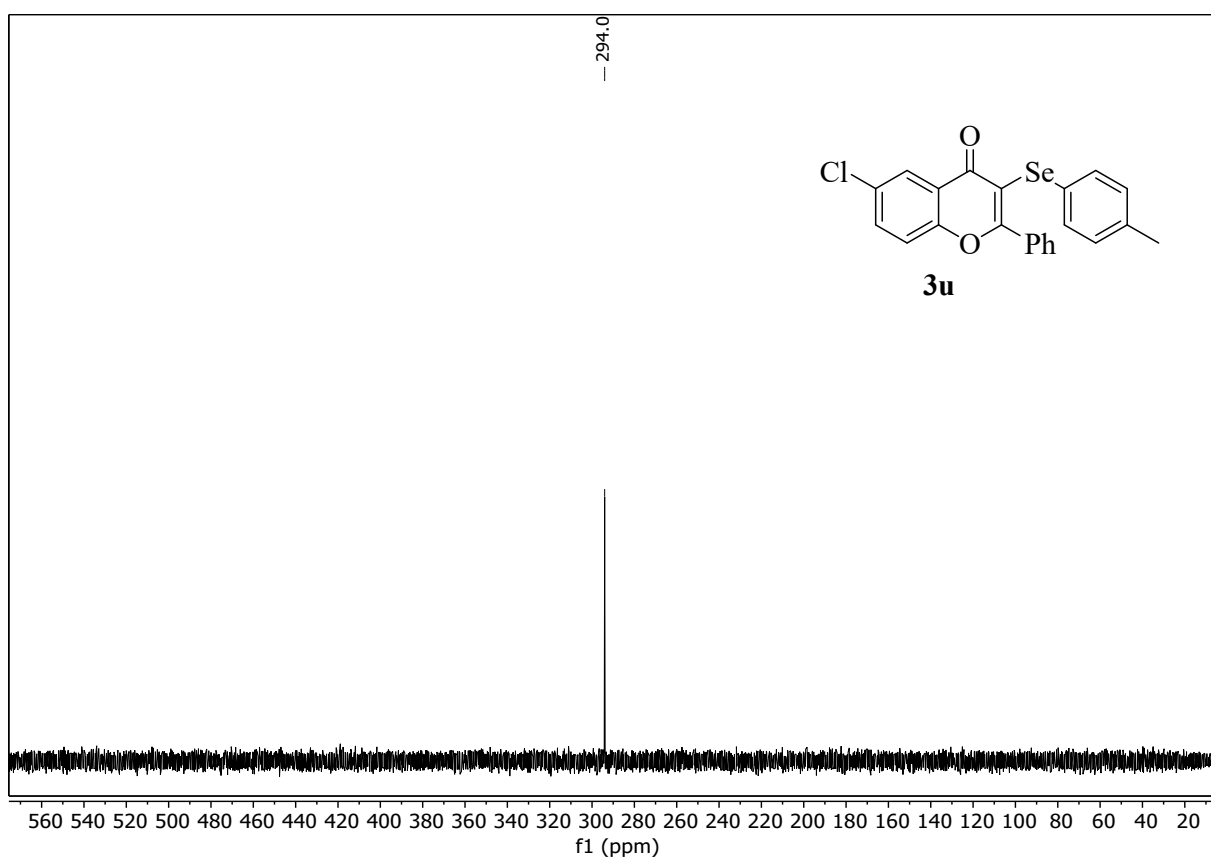
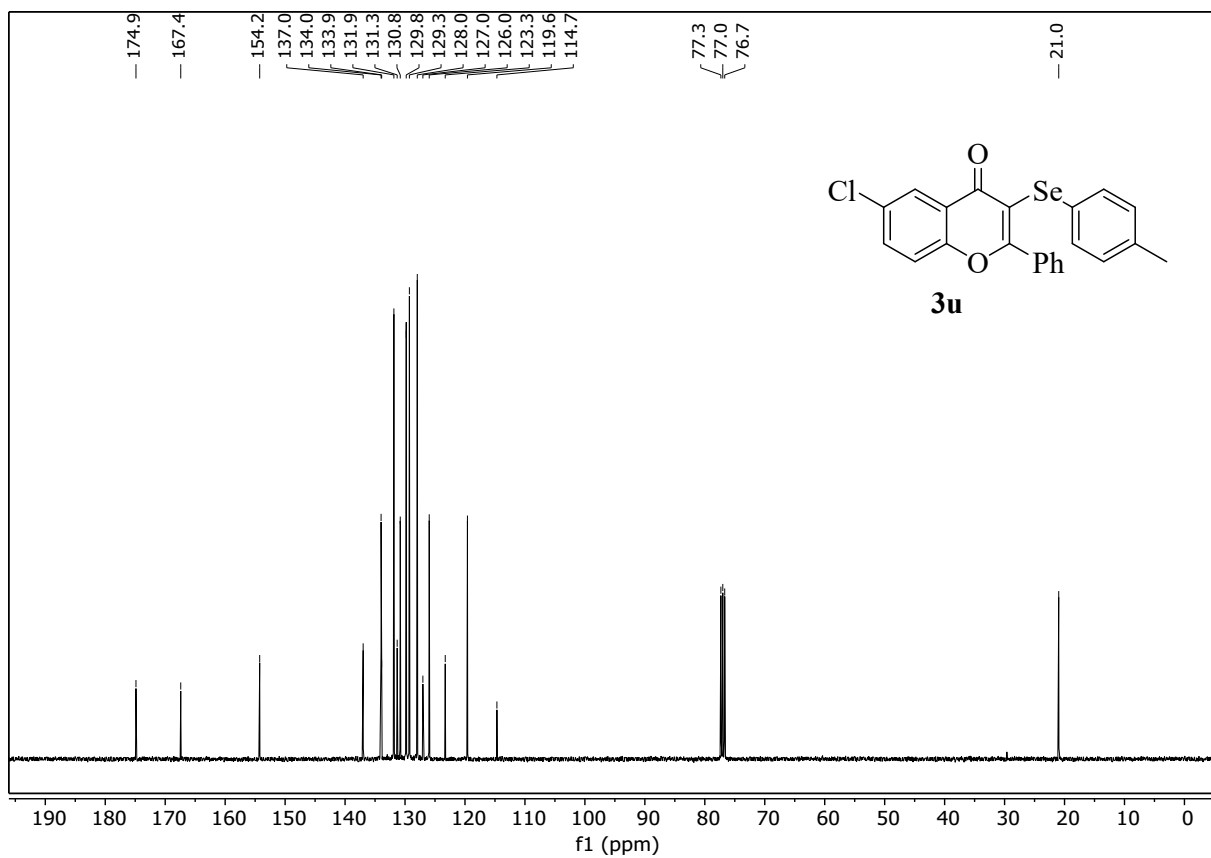
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3t** in  $\text{CDCl}_3$ .



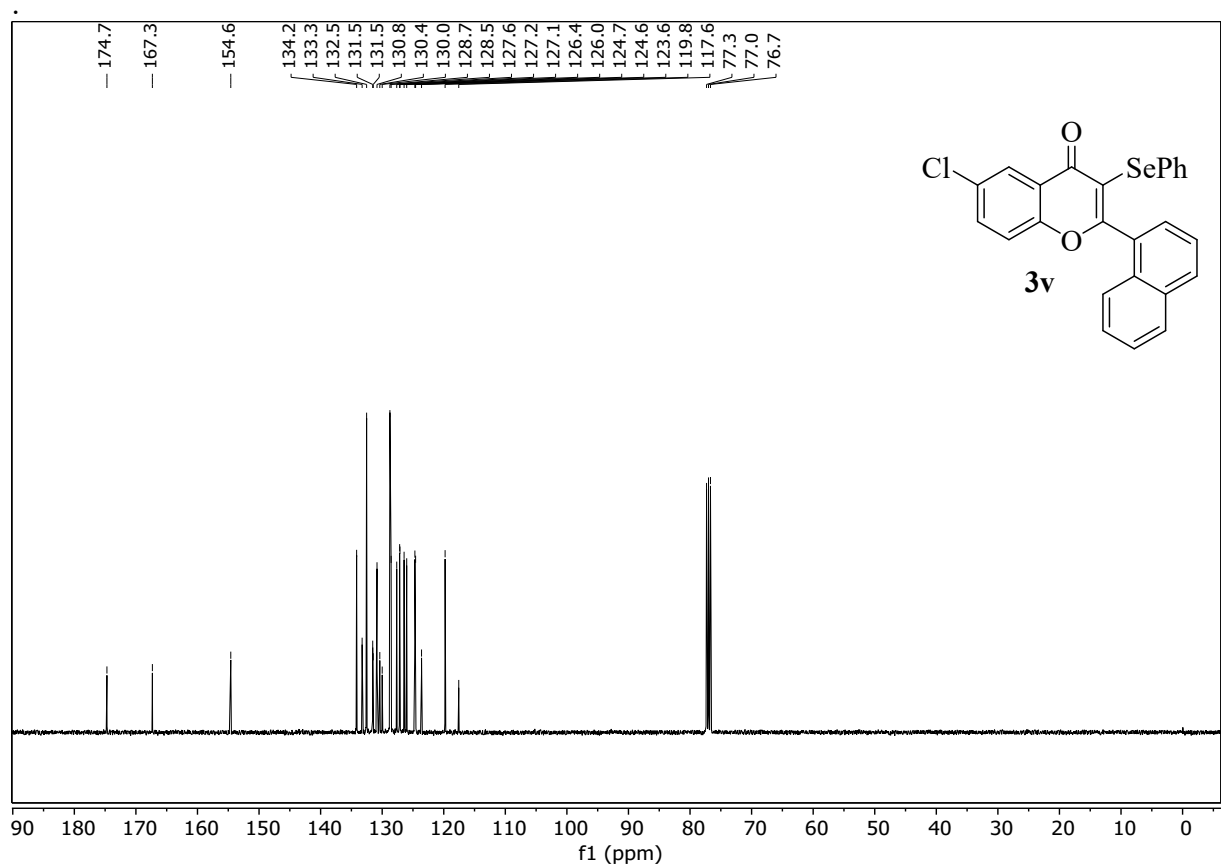
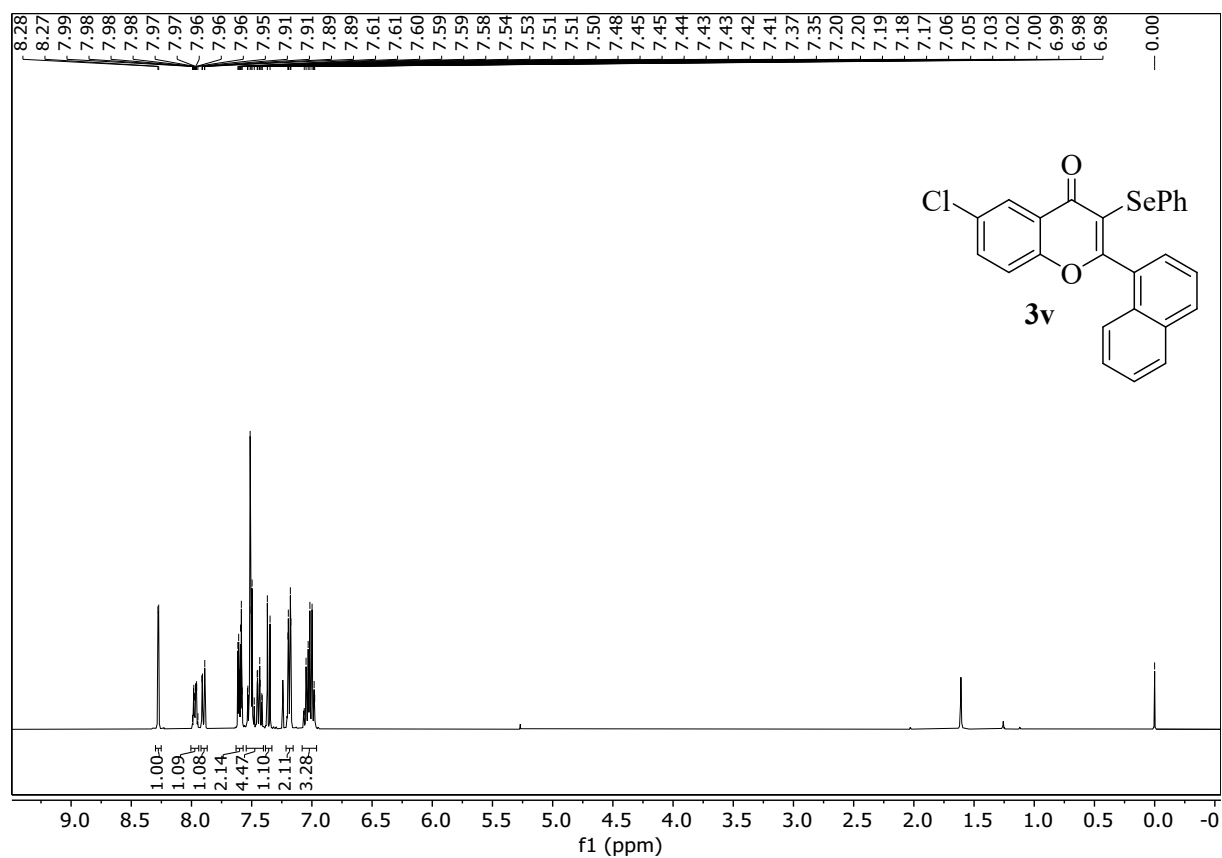


The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3u** in CDCl<sub>3</sub>.

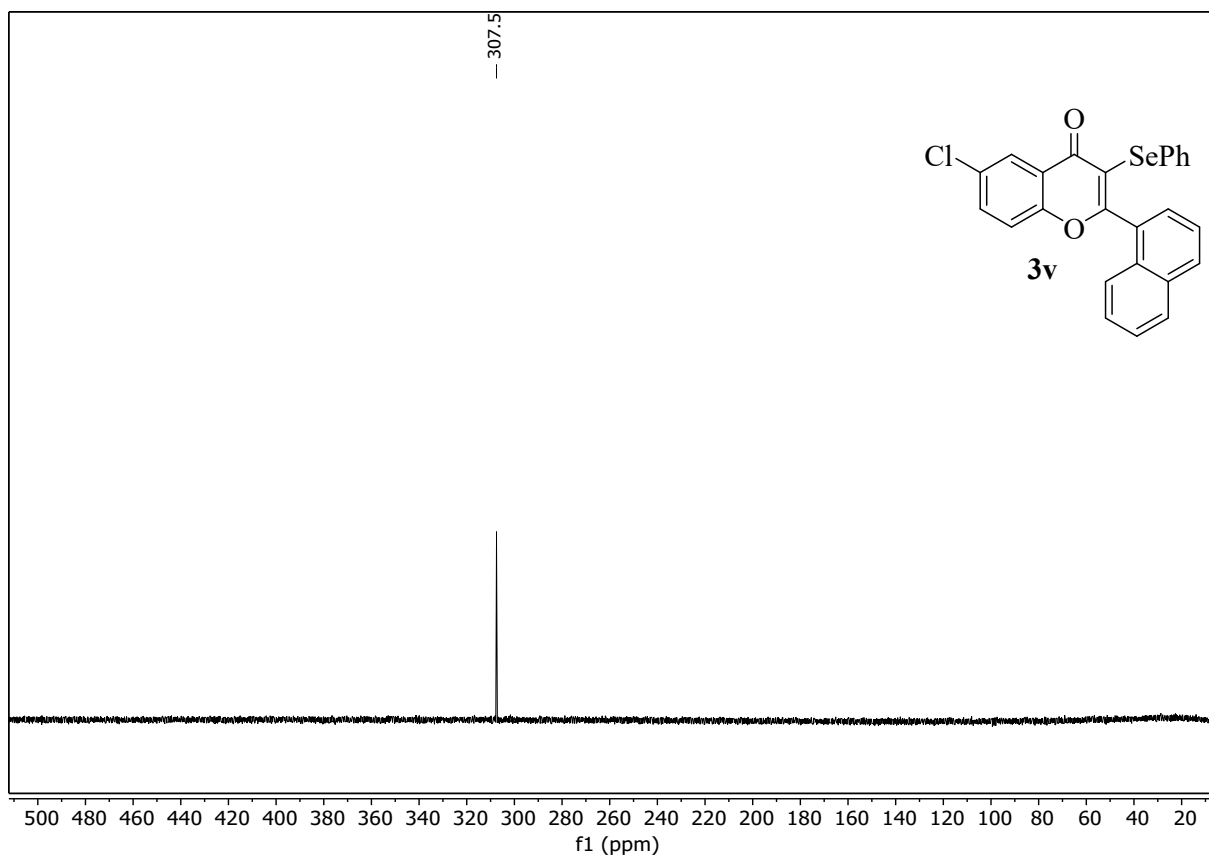




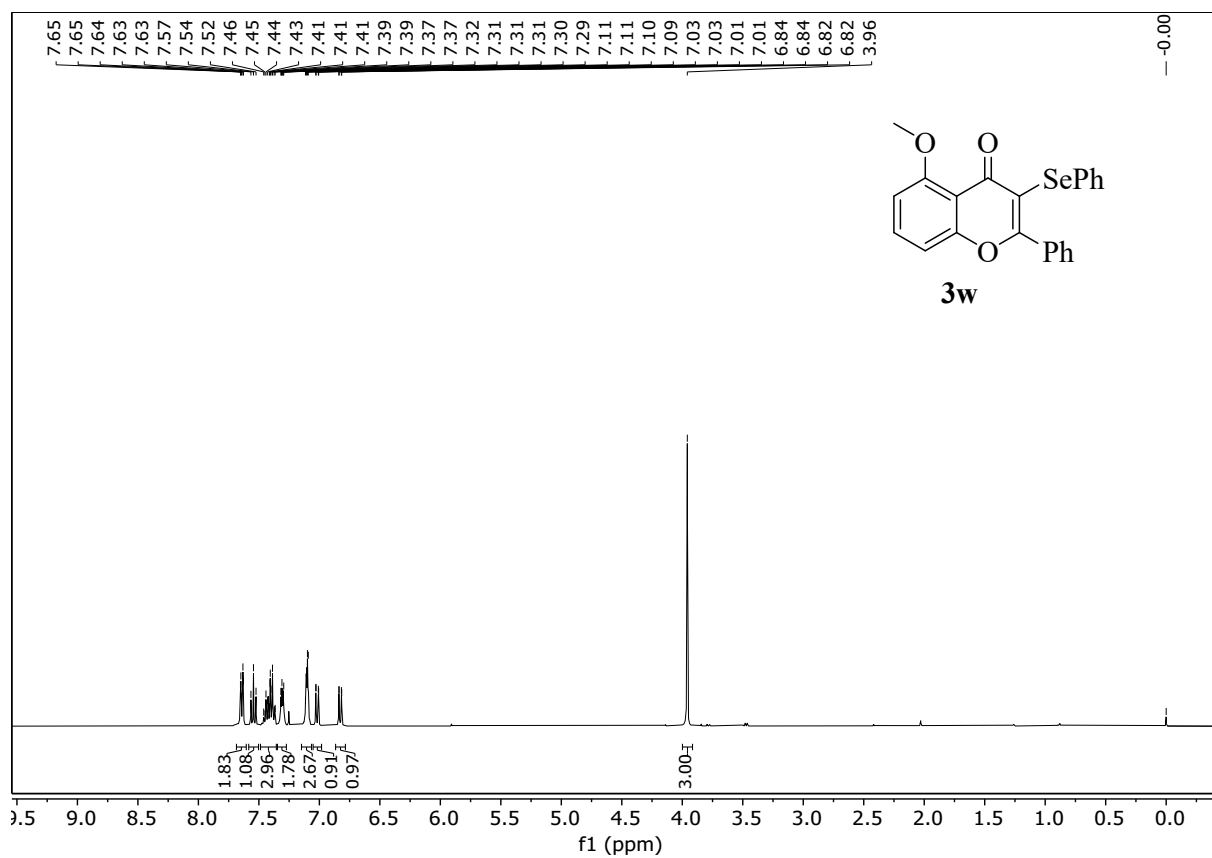
The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz), and  $^{77}\text{Se}$  (76 MHz) NMR spectra of **3v** in  $\text{CDCl}_3$ .

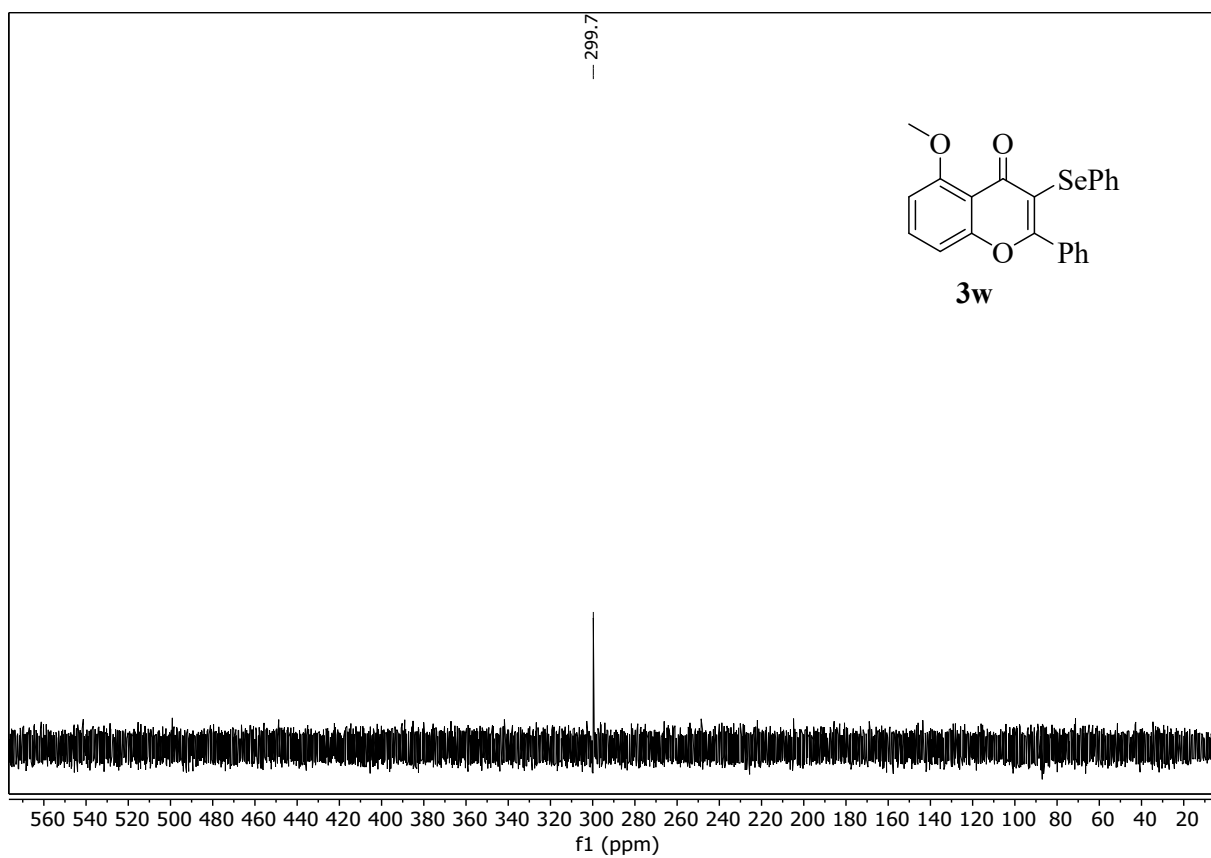
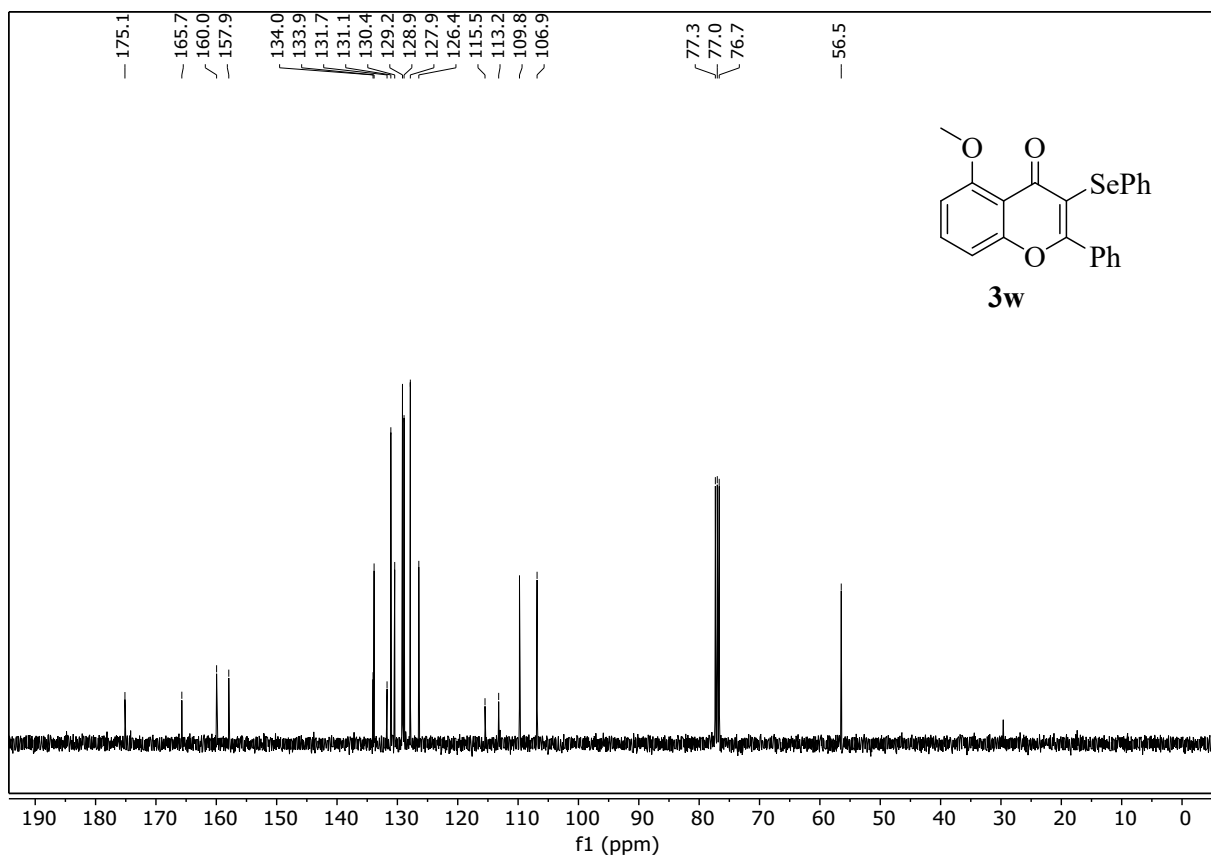






The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3w** in CDCl<sub>3</sub>.

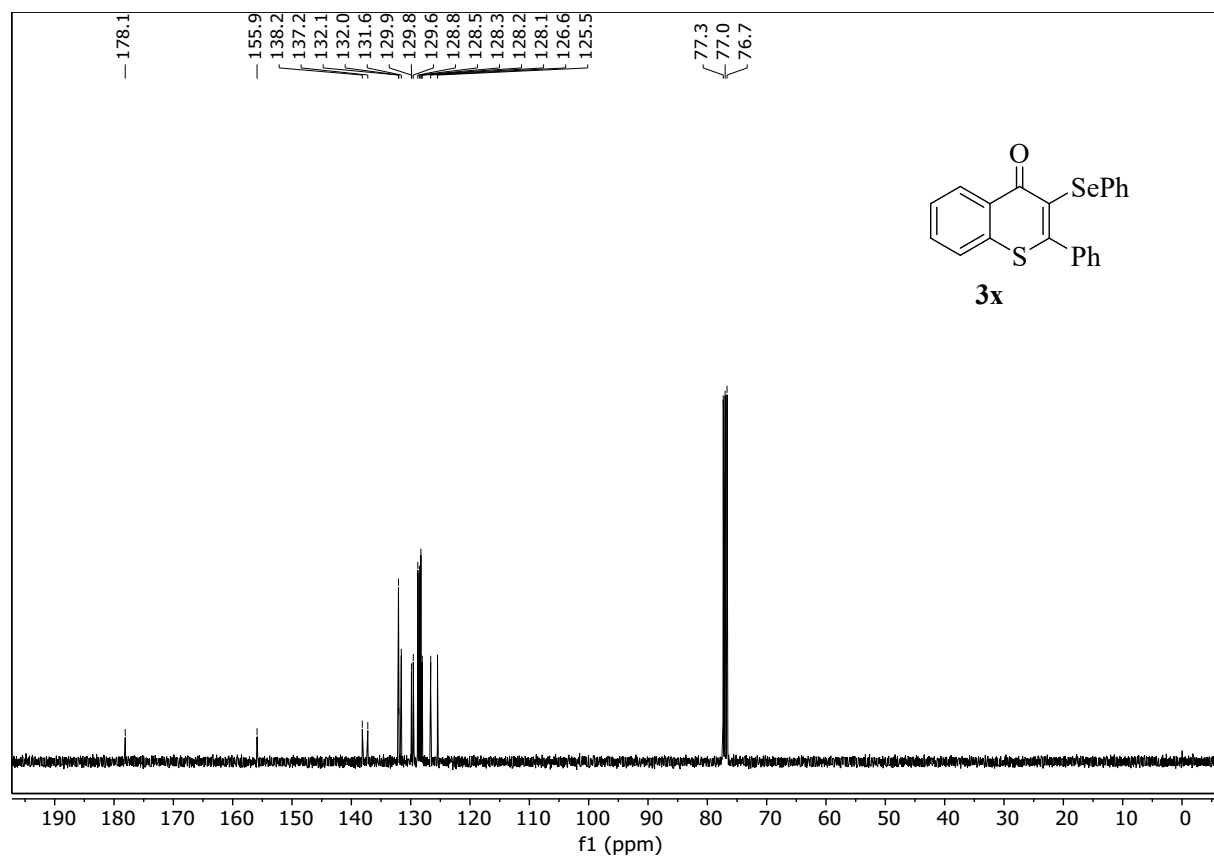


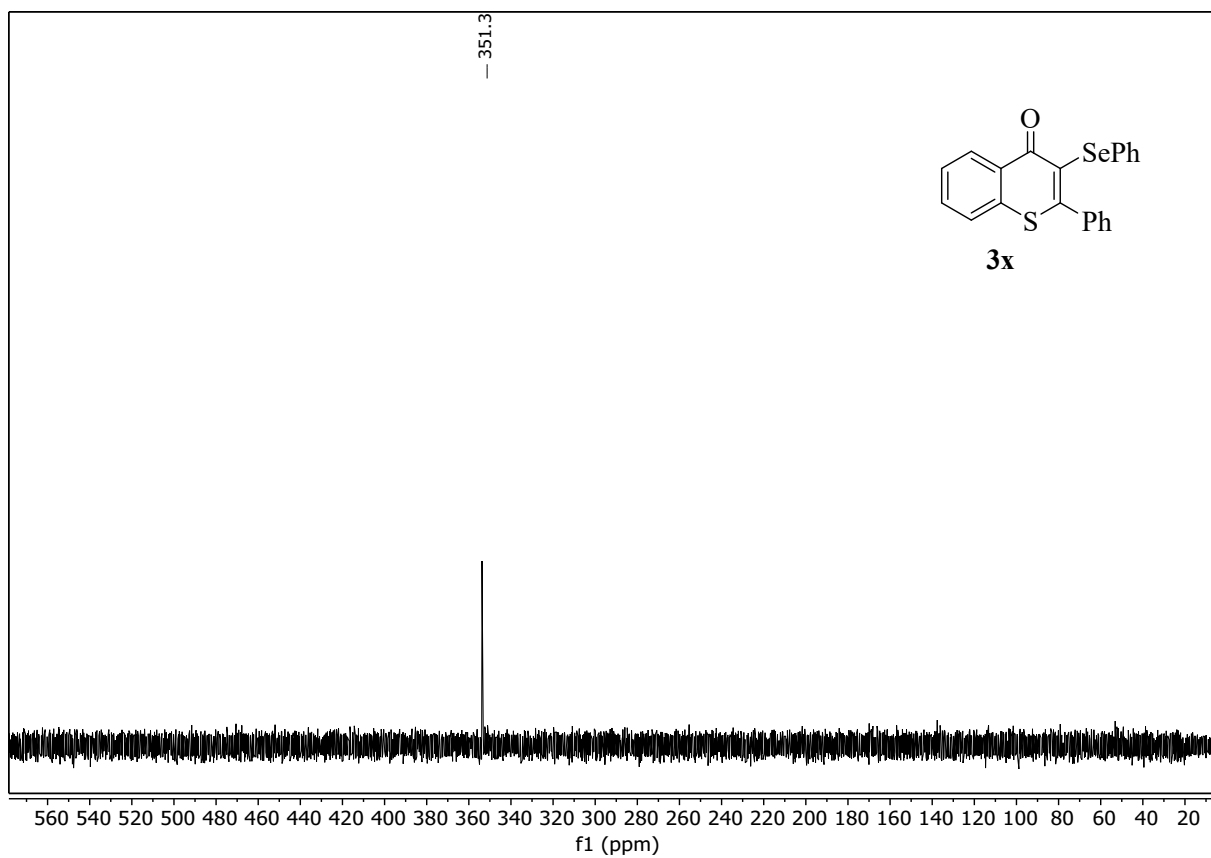


**Chemical structure of 3x:** c1ccc(cc1)c2c(c(s2)C(=O)c3ccccc3)C(=O)c4ccccc4

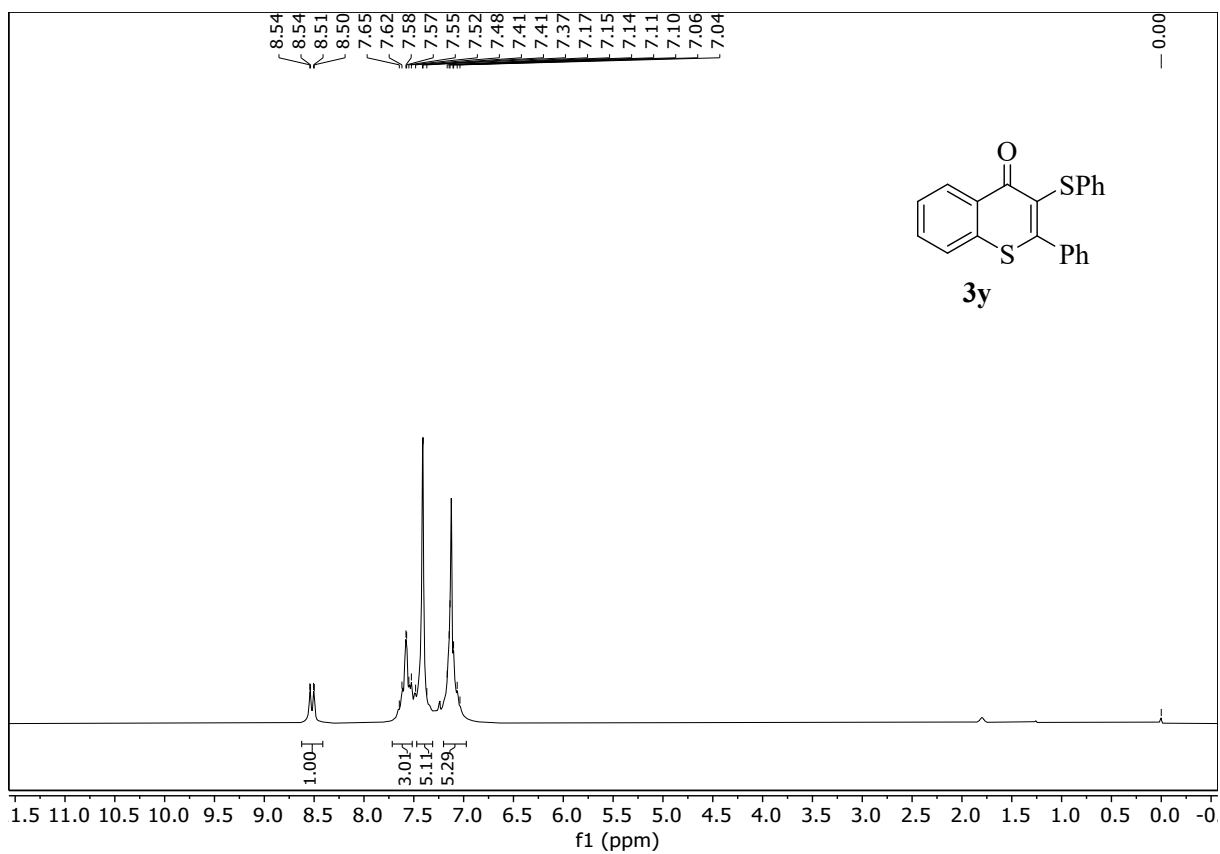
**<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):**

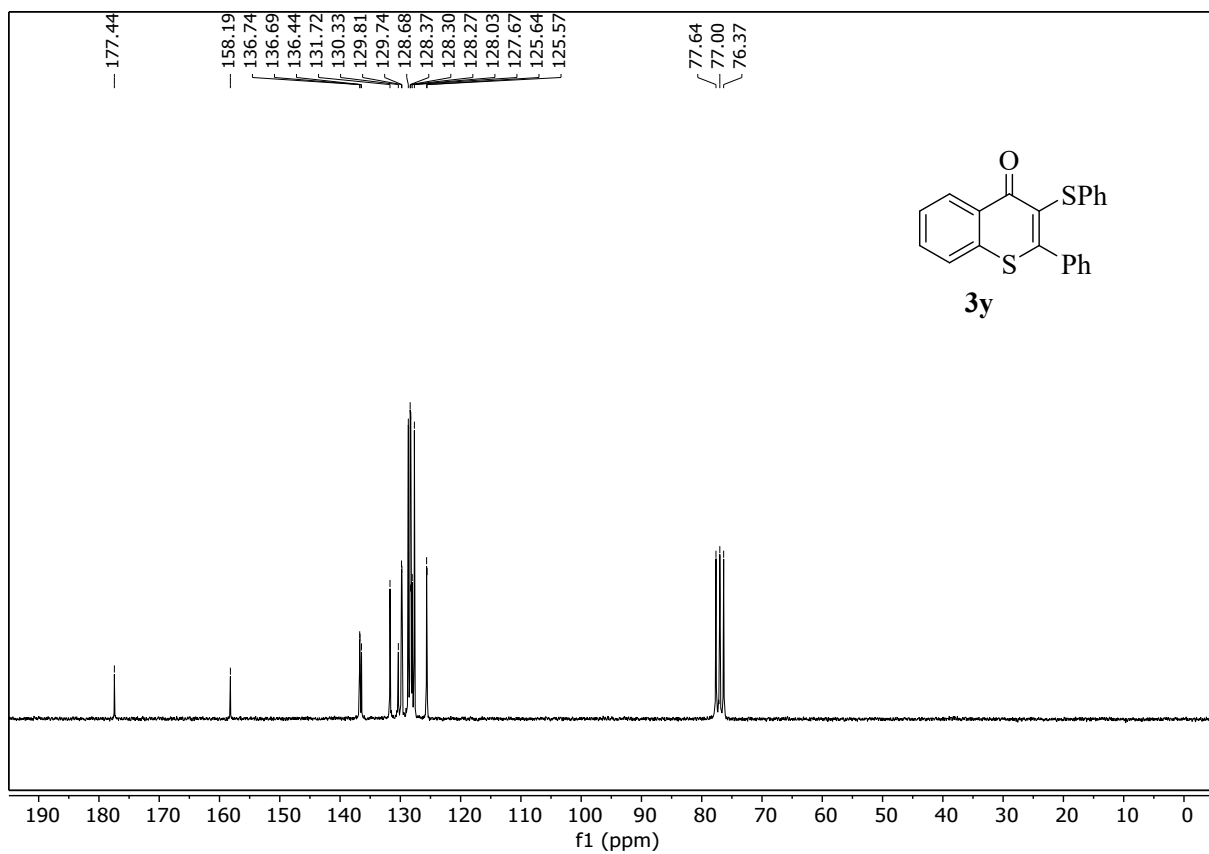
Chemical Shift (ppm)	Integration
8.56, 8.56, 8.54, 8.54	1.00
7.63, 7.63, 7.62, 7.61, 7.60, 7.57, 7.55, 7.54, 7.41, 7.39, 7.38, 7.37, 7.36, 7.34, 7.33, 7.32, 7.31, 7.29, 7.22, 7.22, 7.21, 7.20, 7.11, 7.10, 7.09, 7.08, 7.07, 7.07, 7.06, 7.05	3.17, 5.23, 1.98, 3.09
1.5	
0.0	



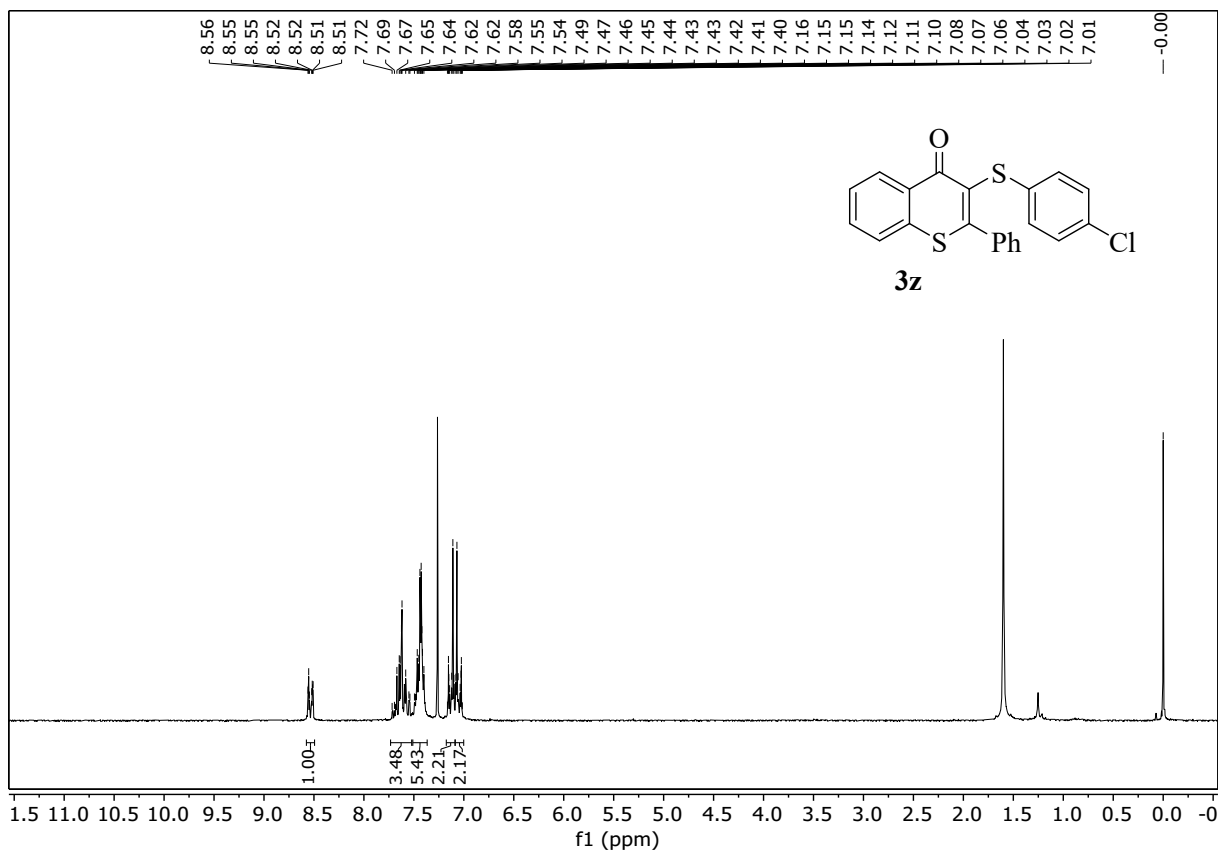


The <sup>1</sup>H (200 MHz) and <sup>13</sup>C {<sup>1</sup>H} (50 MHz) spectra of **3y** in CDCl<sub>3</sub>.

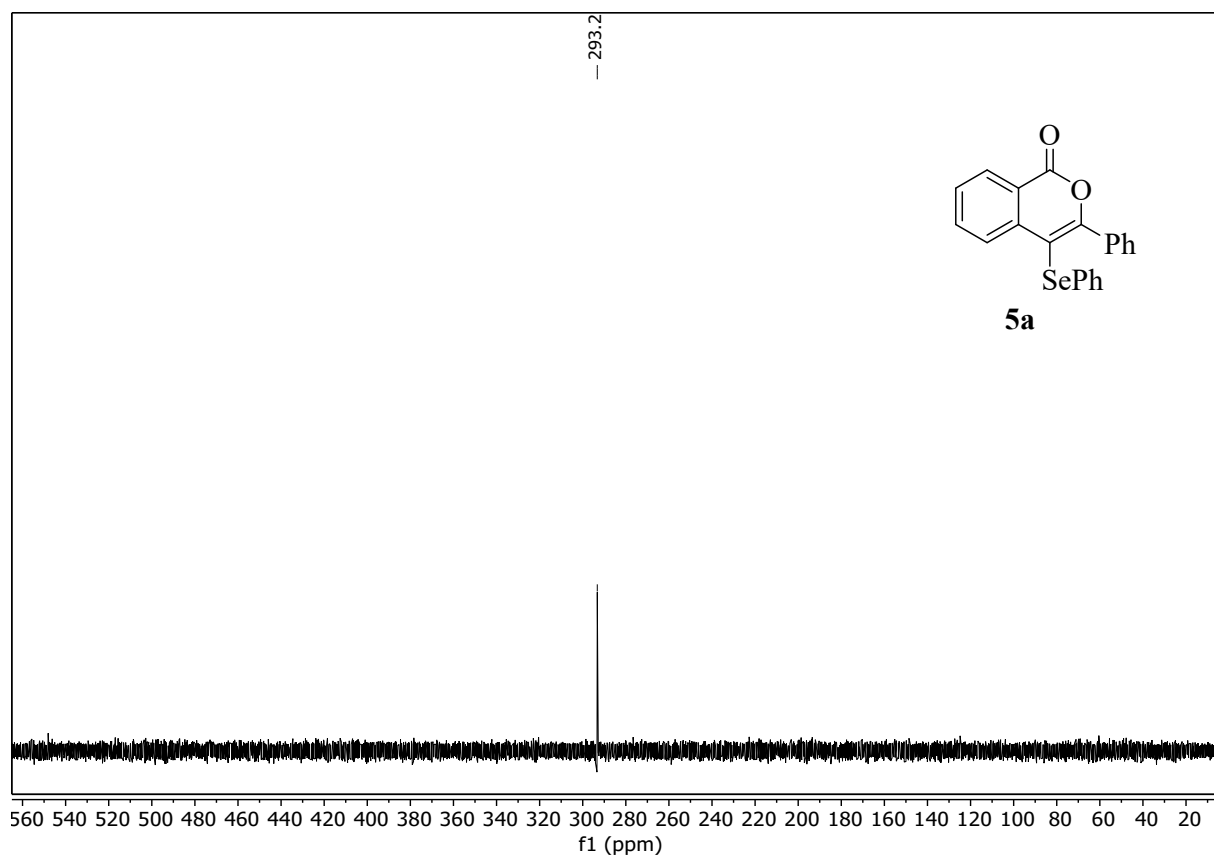
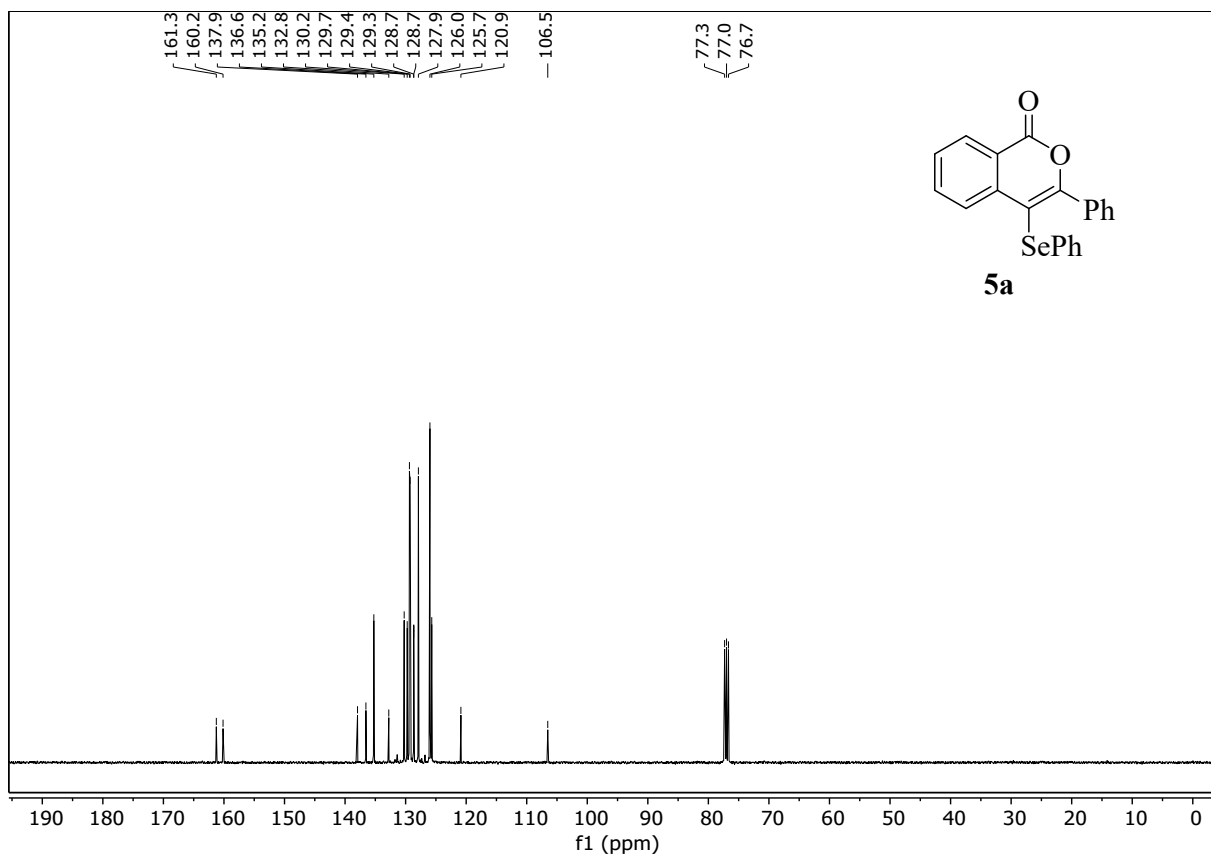




The <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (100 MHz), and <sup>77</sup>Se (76 MHz) NMR spectra of **3z** in CDCl<sub>3</sub>.







The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) NMR spectra of **5b** in  $\text{CDCl}_3$ .

