

# Direct Radical Trifluoromethylthiolation and Thiocyanation of Aryl Alkynoate Esters: Mild and Facile Synthesis of 3- Trifluoromethylthiolated and 3-Thiocyanated Coumarins

Yao-Fu Zeng, Dong-Hang Tan, Yunyun Chen, Wen-Xin Lv, Xu-Ge Liu, Qingjiang Li, Honggen Wang\*

*School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006*

## Supporting Information

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## 1. General information

The solvents used were dried by distillation over the drying agents indicated in parentheses and were transferred under argon: toluene (Na-benzophenone), 1,2-dichloroethane (CaH<sub>2</sub>). Anhydrous CH<sub>3</sub>CN, DMF and DMSO were purchased from Acros Organics and stored under argon. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton (<sup>1</sup>H), Fluorine (<sup>19</sup>F) and Carbon NMR (<sup>13</sup>C) were recorded at 400 MHz, 376 MHz and 100 MHz NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV<sub>254</sub> plates. Visualization was accomplished with short wave UV light, or KMnO<sub>4</sub> staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use..

No attempts were made to optimize yields for substrate synthesis.

## 2. Synthesis of the starting materials

Substrates **1a-z** were prepared according to the reported procedure<sup>1-2</sup>.

AgSCF<sub>3</sub> and CuSCF<sub>3</sub> were synthesized according to the reported literature<sup>3-4</sup>.

## 3. General procedure for synthesis of 3-trifluoromethylthiolated and 3-thiocyanated coumarins

### (1) Synthesis of 3-trifluoromethylthiolated coumarins

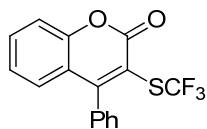
A mixture of **1** (0.2 mmol), AgSCF<sub>3</sub> (0.4 mmol) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.8 mmol) in DMSO (1 mL) was stirred under an atmosphere of Ar at 30 °C for 15 h. After completion of the reaction, the resulting mixture was diluted with ethyl acetate and water and filtered through a pad of celite. Then the filtrate was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent.

### (2) Synthesis of 3-thiocyanated coumarins

A mixture of **1** (0.2 mmol), AgSCN (0.4 mmol) and ammonium nitrate (0.4 mmol) in DMSO (2 mL) was stirred under an atmosphere of air at 60 °C for 15 h. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate and water and filtered through a pad of celite. Then the filtrate was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent.

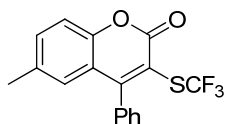
## 4. Characterization of products

### 4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2a)



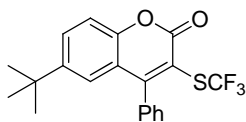
White solid; (50.3 mg, 78%).  $R_F = 0.30$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (t,  $J = 7.6$  Hz, 1H), 7.55 (d,  $J = 1.6$  Hz, 3H), 7.43 (d,  $J = 8.3$  Hz, 1H), 7.25 - 7.20 (m, 3H), 7.10 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 159.3, 154.0, 134.1, 134.0, 129.5, 129.3, 128.7 (q,  $J = 311.6$  Hz), 128.6, 128.2, 124.1, 120.2, 117.1, 113.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.40. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 323.0348, found: 323.0342.

### 6-methyl-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2b)



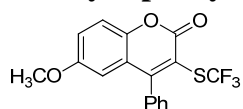
White solid; (48.4 mg, 72%).  $R_F = 0.30$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 - 7.52 (m, 3H), 7.23 (s, 3H), 7.02 (d,  $J = 8.2$  Hz, 2H), 6.96 (d,  $J = 8.2$  Hz, 0H), 2.47 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 159.7, 154.1, 146.0, 134.2, 129.4, 129.0, 128.8 (q,  $J = 311.5$  Hz), 128.5, 128.2, 126.0, 117.9, 117.2, 111.5, 21.9;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.68. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 337.0505, found: 337.0499.

### 6-(tert-butyl)-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2c)



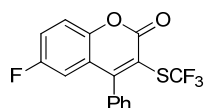
White solid; (47.7 mg, 63%).  $R_F = 0.44$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 - 7.54 (m, 3H), 7.43 (s, 1H), 7.25 - 7.23 (m, 3H), 7.03 (d,  $J = 8.5$  Hz, 1H), 1.35 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 159.7, 159.1, 154.1, 134.2, 129.4, 128.8, 128.7 (q,  $J = 311.6$  Hz), 128.5, 128.2, 122.3, 117.8, 113.8, 111.8, 35.5, 30.9;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.67. **ESI-MS:** calcd for  $\text{C}_{20}\text{H}_{18}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 379.0974, found: 379.0970.

### 6-methoxy-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2d)



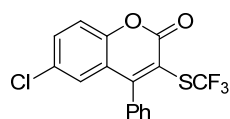
White solid; (41.6 mg, 59%).  $R_F = 0.50$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.53 (m, 3H), 7.22 (dd,  $J = 6.4, 2.8$  Hz, 2H), 6.99 (d,  $J = 9.0$  Hz, 1H), 6.89 (d,  $J = 2.4$  Hz, 1H), 6.76 (dd,  $J = 8.9, 2.4$  Hz, 1H), 3.90 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 164.7, 159.9, 156.2, 134.4, 130.5, 129.4, 128.8 (d,  $J = 312.1$  Hz), 128.5, 128.2, 113.9, 113.2, 108.6, 100.6, 56.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -41.06. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_3\text{S}$   $[\text{M} + \text{H}]^+$ : 353.0454, found: 353.0453

### 6-fluoro-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2e)



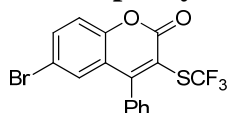
Yellow oil; (34.7 mg, 51%).  $R_F = 0.33$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 - 7.57 (m, 3H), 7.24 - 7.23 (m, 2H), 7.12 - 7.09 (m, 2H), 6.95 (td,  $J = 8.7, 2.4$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8 (d,  $J = 258.2$  Hz), 165.1, 159.0, 155.3 (d,  $J = 13.5$  Hz), 133.9, 131.4 (d,  $J = 10.5$  Hz), 129.7, 128.7, 128.6 (q,  $J = 311.3$  Hz), 128.1, 117.1, 113.0 (d,  $J = 22.6$  Hz), 111.9, 104.6 (d,  $J = 25.7$  Hz);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.49, -101.05. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_4\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 341.0254, found: 341.0262.

### 6-chloro-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2f)



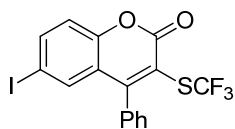
White solid; (41.4 mg, 58%).  $R_F = 0.41$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 2.3$  Hz, 3H), 7.43 (s, 1H), 7.25 - 7.17 (m, 3H), 7.04 (d,  $J = 8.6$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 158.7, 154.2, 140.3, 133.7, 130.2, 129.8, 128.8, 128.6 (q,  $J = 312.2$  Hz), 128.1, 125.4, 118.9, 117.4, 113.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.31. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_3\text{O}_2\text{SCl}$   $[\text{M} + \text{H}]^+$ : 356.9958, found: 356.9958.

### 6-bromo-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2g)



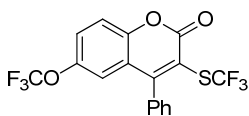
White solid; (48.1 mg, 60%).  $R_F = 0.41$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (s, 1H), 7.56 (d,  $J = 2.7$  Hz, 3H), 7.34 (d,  $J = 8.6$  Hz, 1H), 7.22 (d,  $J = 3.3$  Hz, 2H), 6.95 (d,  $J = 8.6$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 158.6, 154.0, 133.6, 130.2, 129.8, 128.8, 128.6, 128.5 (q,  $J = 311.7$  Hz), 128.3, 128.1, 120.3, 119.2, 113.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.28. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_3\text{O}_2\text{SBr}$   $[\text{M} + \text{H}]^+$ : 400.9453, found: 400.9458.

### 6-iodo-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2h)



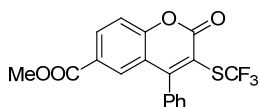
White solid; (49.3 mg, 55%).  $R_F = 0.44$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 1.5$  Hz, 1H), 7.57 - 7.53 (m, 4H), 7.22 (dd,  $J = 6.4, 2.8$  Hz, 2H), 6.78 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 158.5, 153.6, 134.1, 133.6, 130.0, 129.7, 128.8, 128.5 (q,  $J = 311.6$  Hz), 128.1, 126.3, 119.7, 113.6, 100.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.26. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_3\text{O}_2\text{SI}$   $[\text{M} + \text{H}]^+$ : 448.9315, found: 448.9335.

### 4-phenyl-6-(trifluoromethoxy)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2i)



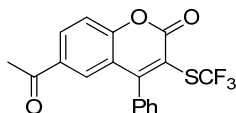
Yellow oil; (45.5 mg, 56%).  $R_F = 0.48$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 - 7.57 (m, 3H), 7.29 (s, 1H), 7.25 - 7.23 (m, 2H), 7.16 (d,  $J = 8.9$  Hz, 1H), 7.06 (dd,  $J = 8.9, 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 158.6, 154.7, 152.8, 133.6, 130.9, 129.8, 128.8, 128.6 (q,  $J = 311.8$  Hz), 128.1, 120.2 (q,  $J = 260.5$  Hz), 118.5, 116.7, 113.2, 108.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.30, -57.72. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_8\text{F}_6\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 407.0171, found: 407.0184.

**methyl 2-oxo-4-phenyl-3-((trifluoromethyl)thio)-2H-chromene-6-carboxylate (2j)**



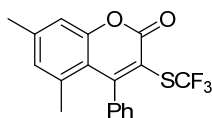
Yellow solid; (40.3 mg, 53%).  $R_F = 0.42$  (PE:EA = 5:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 1H), 7.84 (d,  $J = 8.3$  Hz, 1H), 7.58 (s, 3H), 7.27 - 7.25 (m, 2H), 7.18 (d,  $J = 8.3$  Hz, 1H), 3.98 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 164.3, 158.7, 153.5, 134.8, 133.6, 129.8, 129.4, 128.8, 128.5 (q,  $J = 311.7$  Hz), 128.1, 125.2, 123.2, 118.2, 115.6, 52.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -39.90. **ESI-MS:**  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}_4\text{S}$   $[\text{M} + \text{H}]^+$ : 384.0403, found: 384.0406.

**6-acetyl-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2k)**



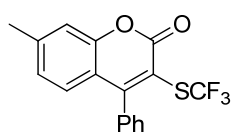
Yellow solid; (26.2 mg, 36%).  $R_F = 0.40$  (PE:EA = 5:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 1.3$  Hz, 1H), 7.75 (dd,  $J = 8.3, 1.5$  Hz, 1H), 7.59 - 7.58 (m, 3H), 7.26 - 7.24 (m, 2H), 7.21 (d,  $J = 8.3$  Hz, 1H), 2.66 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 164.2, 158.7, 153.8, 140.8, 133.5, 129.8, 129.7, 128.8, 128.5 (q,  $J = 311.9$  Hz), 128.1, 123.7, 123.2, 116.9, 115.7, 26.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -39.87. **ESI-MS:** calcd for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}_3\text{S}$   $[\text{M} + \text{H}]^+$ : 365.0454, found: 365.0465.

**5,7-dimethyl-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2l)**



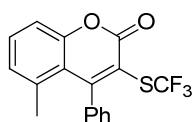
Yellow solid; (55.4 mg, 79%).  $R_F = 0.41$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 - 7.54 (m, 3H), 7.30 (s, 1H), 7.23 - 7.21 (m, 2H), 6.66 (s, 1H), 2.48 (s, 3H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 159.6, 150.6, 136.6, 134.5, 133.7, 129.3, 128.8 (q,  $J = 311.5$  Hz), 128.5, 128.2, 126.6, 126.3, 119.8, 112.5, 20.8, 15.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.58. **ESI-MS:** calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 351.0661, found: 351.0650.

### 7-methyl-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2m)



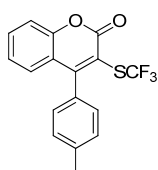
Yellow solid; (30.3 mg, 45%).  $R_F = 0.37$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 - 7.55 (m, 3H), 7.43 (dd,  $J = 8.5, 1.9$  Hz, 1H), 7.32 (d,  $J = 8.4$  Hz, 1H), 7.24 - 7.22 (m, 2H), 6.84 (s, 1H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 159.5, 152.2, 135.2, 134.6, 134.2, 129.4, 128.8, 128.7 (q,  $J = 311.4$  Hz), 128.6, 128.2, 119.9, 116.7, 113.0, 20.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.44. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 337.0505, found: 337.0501.

### 5-methyl-4-phenyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2m')



Yellow solid; (20.9 mg, 31%).  $R_F = 0.35$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (s, 3H), 7.50 (d,  $J = 7.3$  Hz, 1H), 7.29 - 7.25 (m, 2H), 7.13 (t,  $J = 7.6$  Hz, 1H), 6.94 (d,  $J = 7.9$  Hz, 1H), 2.55 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 159.4, 152.4, 135.4, 134.4, 129.4, 128.7 (q,  $J = 311.6$  Hz), 128.5, 128.2, 127.1, 126.7, 124.2, 120.1, 112.7, 15.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.51. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 337.0505, found: 337.0511.

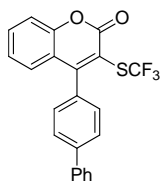
### 4-(p-tolyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2o)



White solid; (48.4 mg, 72%).  $R_F = 0.33$  (PE:EA = 10:1)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (t,  $J = 7.7$  Hz, 1H), 7.42 (d,  $J = 8.3$  Hz, 1H), 7.36 (d,  $J = 7.8$  Hz, 2H), 7.21 (t,  $J = 7.6$  Hz, 1H), 7.13 (d,  $J = 7.9$  Hz, 3H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 159.4, 153.9, 139.7, 133.9, 131.1, 129.4, 129.3, 128.7 (q,  $J = 311.7$  Hz), 128.2, 124.7, 120.4, 117.1, 113.0, 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.43. **ESI-MS:**  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 337.0505, found: 337.0497.

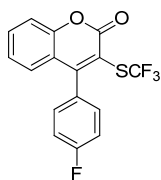


#### 4-([1,1'-biphenyl]-4-yl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2p)



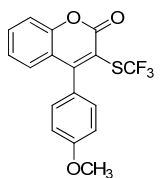
Yellow solid; (57.4 mg, 72%).  $R_F = 0.30$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 7.3$  Hz, 2H), 7.72 (d,  $J = 7.6$  Hz, 2H), 7.67 (t,  $J = 7.6$  Hz, 1H), 7.53 (t,  $J = 7.3$  Hz, 2H), 7.48 – 7.43 (m, 2H), 7.35 (d,  $J = 7.5$  Hz, 2H), 7.29 – 7.21 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 159.2, 154.1, 142.4, 139.9, 134.1, 132.8, 129.3, 128.9, 128.8, 128.6 (q,  $J = 311.6$  Hz), 128.0, 127.2, 127.1, 124.7, 120.2, 117.1, 113.2;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.33. **ESI-MS:** calcd for  $\text{C}_{22}\text{H}_{14}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 399.0661, found: 399.0668.

#### 4-(4-fluorophenyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2q)



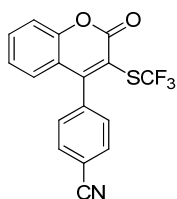
Yellow solid; (53.1 mg, 78%).  $R_F = 0.30$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (ddd,  $J = 8.6, 7.4, 1.5$  Hz, 1H), 7.44 (dd,  $J = 8.3, 0.9$  Hz, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 3H), 7.10 (dd,  $J = 8.1, 1.5$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 163.3 (d,  $J = 261.1$  Hz), 159.1, 154.0, 134.3, 130.4 (d,  $J = 8.4$  Hz), 129.9 (d,  $J = 3.6$  Hz), 129.1, 128.6 (q,  $J = 311.6$  Hz), 124.8, 120.1, 117.2, 115.9 (d,  $J = 22.0$  Hz), 113.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.38, -110.67. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_4\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 341.0254, found: 341.0250.

#### 4-(4-methoxyphenyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2r)



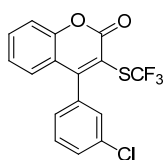
Yellow solid; (46.5 mg, 66%).  $R_F = 0.42$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.60 (m, 1H), 7.42 (d,  $J = 8.3$  Hz, 1H), 7.25 – 7.16 (m, 4H), 7.07 (d,  $J = 8.6$  Hz, 2H), 3.92 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 160.5, 159.4, 153.9, 133.9, 129.9, 129.4, 128.8 (q,  $J = 311.6$  Hz), 126.1, 124.7, 120.5, 117.1, 114.0, 113.1, 55.4;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.48. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_3\text{S}$   $[\text{M} + \text{H}]^+$ : 353.0454, found: 353.0447.

#### 4-(2-oxo-3-((trifluoromethyl)thio)-2H-chromen-4-yl)benzonitrile (2s)



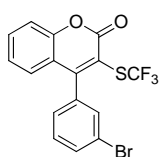
Yellow oil; (42.4 mg, 61%).  $R_F = 0.23$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.87 (m, 2H), 7.68 (ddd,  $J = 8.6, 7.4, 1.5$  Hz, 1H), 7.47 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.40 (d,  $J = 8.3$  Hz, 2H), 7.28 – 7.23 (m, 1H), 6.97 (dd,  $J = 8.1, 1.4$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 158.7, 154.1, 138.5, 134.7, 132.5, 129.2, 128.6, 128.4 (q,  $J = 311.8$  Hz), 125.1, 119.4, 117.9, 117.5, 113.8, 113.5;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.19. **ESI-MS:** calcd for  $\text{C}_{17}\text{H}_8\text{F}_3\text{NO}_2\text{S}$   $[\text{M} + \text{Na}]^+$ : 370.0120, found: 370.0116.

#### 4-(3-chlorophenyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2t)



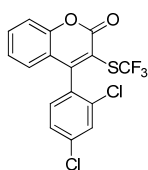
Yellow solid; (52.8 mg, 74%).  $R_F = 0.30$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (t,  $J = 7.7$  Hz, 1H), 7.55 – 7.43 (m, 3H), 7.26 – 7.23 (m, 2H), 7.14 (d,  $J = 7.1$  Hz, 1H), 7.07 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 158.9, 154.0, 135.6, 134.9, 134.4, 130.1, 129.8, 128.9, 128.6 (q,  $J = 311.6$  Hz), 128.2, 126.4, 124.9, 119.8, 117.3, 113.5;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.25. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_3\text{O}_2\text{SCl}$   $[\text{M} + \text{H}]^+$ : 356.9958, found: 356.9957.

#### 4-(3-bromophenyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2u)



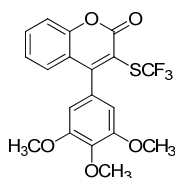
Yellow solid; (57.0 mg, 71%).  $R_F = 0.24$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.63 (m, 2H), 7.47 – 7.41 (m, 3H), 7.27 – 7.23 (m, 1H), 7.20 (d,  $J = 7.6$  Hz, 1H), 7.08 (dd,  $J = 8.1, 1.5$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 158.9, 154.0, 135.8, 134.4, 132.7, 131.0, 130.3, 129.0, 128.6 (q,  $J = 311.8$  Hz), 126.9, 124.9, 122.8, 119.8, 117.2, 113.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.24. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{F}_3\text{O}_2\text{SBr}$   $[\text{M} + \text{H}]^+$ : 400.9453, found: 400.9460.

#### 4-(2,4-dichlorophenyl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2v)



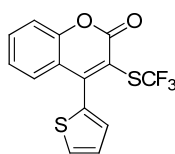
Yellow solid; (62.6 mg, 80%).  $R_F = 0.23$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.65 (m, 1H), 7.62 (d,  $J = 2.0$  Hz, 1H), 7.47 (dt,  $J = 9.4, 4.8$  Hz, 2H), 7.25 (dd,  $J = 11.4, 4.2$  Hz, 1H), 7.19 (d,  $J = 8.3$  Hz, 1H), 6.98 (dd,  $J = 8.0, 1.5$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 158.8, 154.2, 136.6, 134.5, 133.3, 131.5, 130.6, 129.9, 128.6 (q,  $J = 311.9$  Hz), 128.2, 127.6, 125.1, 119.0, 117.4, 114.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -39.65. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_8\text{F}_3\text{O}_2\text{SCl}_2$   $[\text{M} + \text{H}]^+$ : 390.9569, found: 390.9561.

#### 3-((trifluoromethyl)thio)-4-(3,4,5-trimethoxyphenyl)-2H-chromen-2-one (2w)



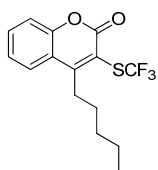
Yellow solid; (46.2 mg, 56%).  $R_F = 0.30$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.62 (m, 1H), 7.43 (d,  $J = 8.4$  Hz, 1H), 7.28 – 7.20 (m, 3H), 6.46 (s, 1H), 3.97 (s, 3H), 3.86 (s, 6H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 159.2, 153.9, 153.5, 138.7, 134.1, 129.3, 129.2, 128.8 (q,  $J = 311.2$  Hz), 124.8, 120.2, 117.1, 113.2, 105.5, 61.1, 56.3;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.21. **ESI-MS:** calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{O}_5\text{S}$   $[\text{M} + \text{H}]^+$ : 413.0665, found: 413.0665.

#### 4-(thiophen-2-yl)-3-((trifluoromethyl)thio)-2H-chromen-2-one (2x)



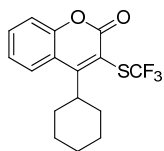
Yellow solid; (30.9 mg, 47%).  $R_F = 0.27$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.63 (m, 2H), 7.43 – 7.37 (m, 2H), 7.29 – 7.24 (m, 2H), 7.16 (d,  $J = 3.4$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 158.8, 153.7, 134.2, 132.9, 130.2, 129.1, 128.7, 128.6 (q,  $J = 313.1$  Hz), 127.4, 124.9, 120.4, 117.1, 115.3;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.21. **ESI-MS:** calcd for  $\text{C}_{14}\text{H}_8\text{F}_3\text{O}_2\text{S}_2$   $[\text{M} + \text{H}]^+$ : 328.9912, found: 328.9904.

#### 4-pentyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2y)



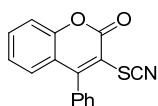
Yellow oil; (38.6 mg, 61%).  $R_F = 0.31$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.1$  Hz, 1H), 7.64 (t,  $J = 7.5$  Hz, 1H), 7.37 (t,  $J = 8.2$  Hz, 2H), 3.27 – 3.23 (m, 2H), 1.69 – 1.62 (m, 2H), 1.54 – 1.47 (m, 2H), 1.45 – 1.38 (m, 2H), 0.94 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 159.2, 153.9, 133.9, 128.9 (q,  $J = 311.5$  Hz), 126.3, 124.8, 118.7, 117.7, 112.0, 32.1, 31.7, 29.6, 22.3, 13.9;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.82. **ESI-MS:** calcd for  $\text{C}_{15}\text{H}_{16}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 317.0818, found: 317.0806.

#### 4-cyclohexyl-3-((trifluoromethyl)thio)-2H-chromen-2-one (2z)



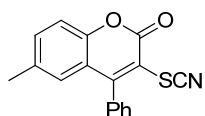
Yellow oil; (16.4 mg, 25%).  $R_F = 0.35$  (PE:EA = 10:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 6.8$  Hz, 1H), 7.64 – 7.57 (m, 1H), 7.38 (dd,  $J = 8.3, 1.2$  Hz, 1H), 7.33 (t,  $J = 7.7$  Hz, 1H), 4.17 – 4.11 (m, 1H), 2.12 – 2.15 (m, 2H), 1.98 – 1.83 (m, 5H), 1.54 – 1.39 (m, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 159.4, 153.8, 133.5, 129.0 (q,  $J = 311.0$  Hz), 127.9, 123.9, 118.2, 117.9, 112.2, 45.8, 30.5, 26.6, 25.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -41.45. **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{O}_2\text{S}$   $[\text{M} + \text{H}]^+$ : 329.0818, found: 329.0805.

#### 4-phenyl-3-thiocyanato-2H-chromen-2-one (3a)



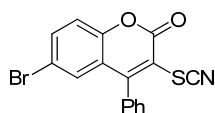
White solid; (26.8 mg, 48%).  $R_F = 0.27$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 – 7.60 (m, 4H), 7.46 (d,  $J = 8.3$  Hz, 1H), 7.33 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.16 (dd,  $J = 8.1, 1.5$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 157.4, 153.5, 134.1, 133.2, 130.3, 129.3, 128.7, 128.0, 125.1, 119.8, 117.3, 112.8, 108.1; **ESI-MS:** calcd for  $\text{C}_{16}\text{H}_9\text{NO}_2\text{S}$   $[\text{M} + \text{Na}]^+$ : 302.0246, found: 302.0239.

### 6-methyl-4-phenyl-3-thiocyanato-2H-chromen-2-one (3b)



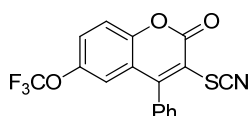
White solid; (25.2 mg, 43%).  $R_F = 0.27$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.60 (m, 3H), 7.30 (dd,  $J = 6.6, 2.9$  Hz, 2H), 7.26 (d,  $J = 2.8$  Hz, 1H), 7.07 – 7.02 (m, 2H), 2.49 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 157.7, 153.7, 146.1, 133.4, 130.2, 129.2, 128.4, 128.0, 126.3, 117.5, 117.3, 111.1, 108.5, 21.9; **ESI-MS**: calcd for  $\text{C}_{17}\text{H}_{11}\text{NO}_2\text{S}$   $[\text{M} + \text{Na}]^+$ : 316.0403, found: 316.0399.

### 6-bromo-4-phenyl-3-thiocyanato-2H-chromen-2-one (3g)



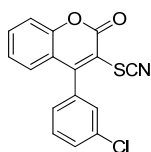
White solid; (35.8 mg, 50%).  $R_F = 0.31$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.62 (m, 4H), 7.38 (dd,  $J = 8.6, 1.9$  Hz, 1H), 7.31 – 7.27 (m, 2H), 7.02 (d,  $J = 8.6$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 156.7, 153.5, 132.7, 130.6, 129.5, 129.4, 128.6, 128.4, 127.9, 120.5, 118.8, 113.0, 107.8; **ESI-MS**: calcd for  $\text{C}_{16}\text{H}_8\text{NO}_2\text{SBr}$   $[\text{M} + \text{Na}]^+$ : 379.9351, found: 379.9343.

### 4-phenyl-3-thiocyanato-6-(trifluoromethoxy)-2H-chromen-2-one (3i)



Yellow oil; (37.1 mg, 51%).  $R_F = 0.35$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.61 (m, 3H), 7.32 – 7.29 (m, 3H), 7.22 (d,  $J = 8.9$  Hz, 1H), 7.12 – 7.09 (m, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 156.7, 154.2, 152.7, 132.7, 130.6, 130.3, 129.4, 127.9, 120.2 (q,  $J = 260.5$  Hz), 118.1, 117.1, 112.9, 109.0, 107.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.72; **ESI-MS**: calcd for  $\text{C}_{17}\text{H}_8\text{NO}_3\text{F}_3\text{S}$   $[\text{M} + \text{Na}]^+$ : 386.0069, found: 386.0062.

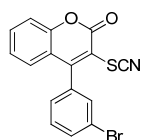
### 4-(3-chlorophenyl)-3-thiocyanato-2H-chromen-2-one (3t)



Yellow oil; (26.4 mg, 42%).  $R_F = 0.27$  (PE:EA = 5:1)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.66 (m, 1H), 7.56 – 7.59 (m 2H), 7.47 (d,  $J = 8.3$  Hz, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.13 (dd,  $J = 8.1, 1.4$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 157.1, 153.5, 135.5, 134.7,

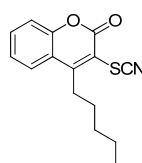
134.4, 130.8, 130.5, 128.4, 127.9, 126.3, 125.3, 119.4, 117.4, 113.2, 107.8; **ESI-MS**: calcd for C<sub>16</sub>H<sub>8</sub>NO<sub>2</sub>SCl [M + Na]<sup>+</sup>: 335.9856, found: 335.9851.

#### 4-(3-bromophenyl)-3-thiocyanato-2H-chromen-2-one (3u)



Yellow oil; (33.7 mg, 47%). *R*<sub>F</sub> = 0.25 (PE:EA = 5:1) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.66 (m, 1H), 7.56 – 7.59 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.13 (dd, *J* = 8.1, 1.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.0, 157.1, 153.5, 134.9, 134.4, 133.5, 130.9, 130.7, 128.4, 126.7, 125.3, 123.4, 119.4, 117.4, 113.2, 107.8; **ESI-MS**: calcd for C<sub>16</sub>H<sub>8</sub>NO<sub>2</sub>SBr [M + Na]<sup>+</sup>: 379.9351, found: 379.9341.

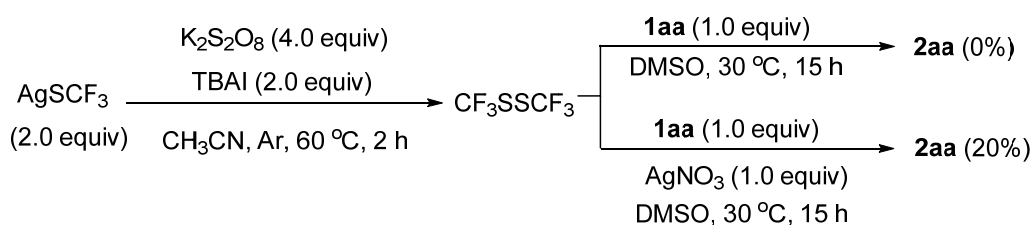
#### 4-pentyl-3-thiocyanato-2H-chromen-2-one (3y)



Yellow oil; (12.0 mg, 22%). *R*<sub>F</sub> = 0.31 (PE:EA = 5:1) <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 7.94 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.74 (ddd, *J* = 8.5, 7.4, 1.5 Hz, 1H), 7.50 – 7.44 (m, 2H), 3.32 – 3.25 (m, 2H), 1.77 – 1.69 (m, 2H), 1.59 – 1.52 (m, 2H), 1.50 – 1.41 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>OD) δ 163.8, 157.8, 153.4, 133.9, 126.3, 125.0, 118.5, 117.0, 111.5, 108.9, 31.6, 31.3, 29.0, 22.0, 12.9; **ESI-MS**: calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>S [M + Na]<sup>+</sup>: 296.0716, found: 296.0704.

## 5. Mechanistic study

Role of the silver experiments<sup>5</sup>



**Experiment of 6:** A mixture of AgSCF<sub>3</sub> (41.8 mg, 0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108.1, 0.4 mmol) and tetrabutylammonium iodide (TBAI) (73.9 mg, 0.2 mmol) in CH<sub>3</sub>CN (0.5 mL) was

stirred under an atmosphere of Ar at 60 °C for 2 h. After cooling to the room temperature, **1a** (22.2 mg, 0.1mmol) in DMSO (0.5 mL) was added and stirred at 30 °C for another 15 h. Afterwards, methyl 4-bromobenzoate (21.5mg, 0.1mmol) was added and the resulting mixture was diluted with ethyl acetate and water and filtered through a pad of celite. Then the filtrate was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The yield of **2a** was determined by <sup>1</sup>H NMR resonance using methyl 4-bromobenzoate as the internal standard. (0%, <sup>1</sup>H NMR yield)

**Experiment of eq 7:** A mixture of AgSCF<sub>3</sub> (41.8 mg, 0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108.1, 0.4 mmol) and tetrabutylammonium iodide (TBAI) (73.9 mg, 0.2 mmol) in CH<sub>3</sub>CN (0.5 mL) was stirred under an atmosphere of Ar at 60 °C for 2 h. After cooling to the room temperature, AgNO<sub>3</sub> (17.0 mg, 0.1 mmol) and **1a** (22.2 mg, 0.1mmol) in DMSO (0.5 mL) was added and stirred at 30 °C for another 15 h. Afterwards, methyl 4-bromobenzoate (21.5 mg, 0.1mmol) was added and the resulting mixture was diluted with ethyl acetate and water and filtered through a pad of celite. Then the filtrate was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The yield of **2a** was determined by <sup>1</sup>H NMR resonance using methyl 4-bromobenzoate as the internal standard. (20%, <sup>1</sup>H NMR yield)

## 6. X-ray Crystal Structure Data for **2g**

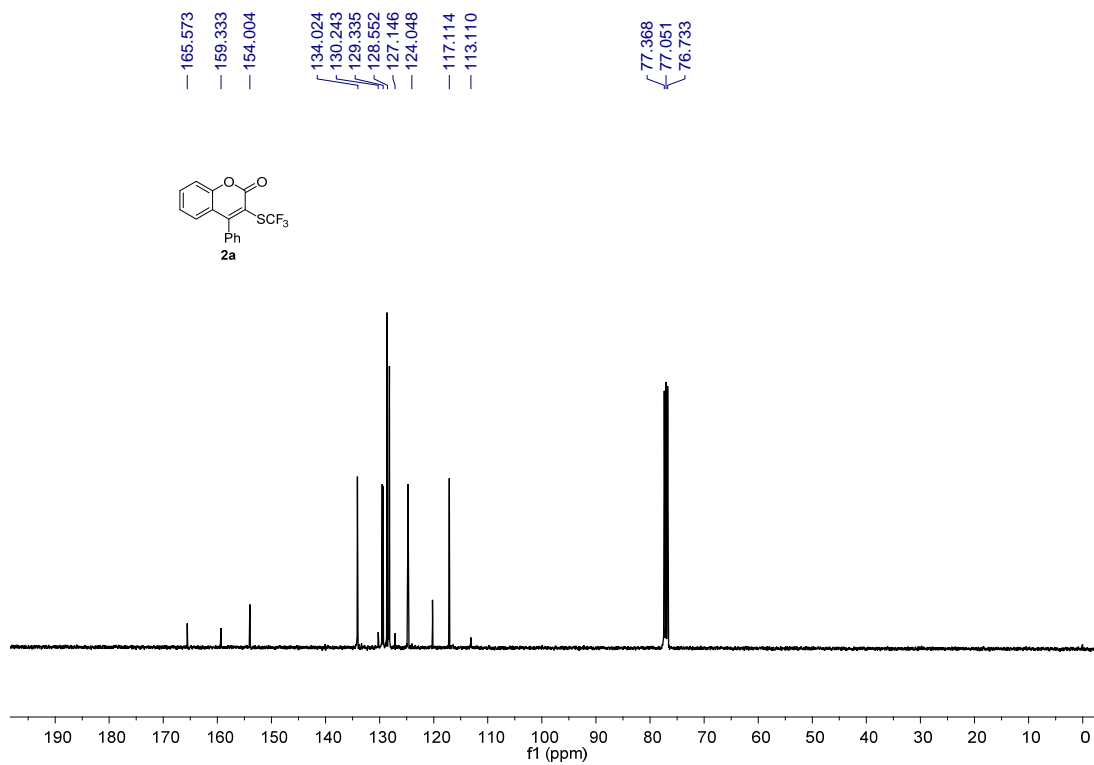
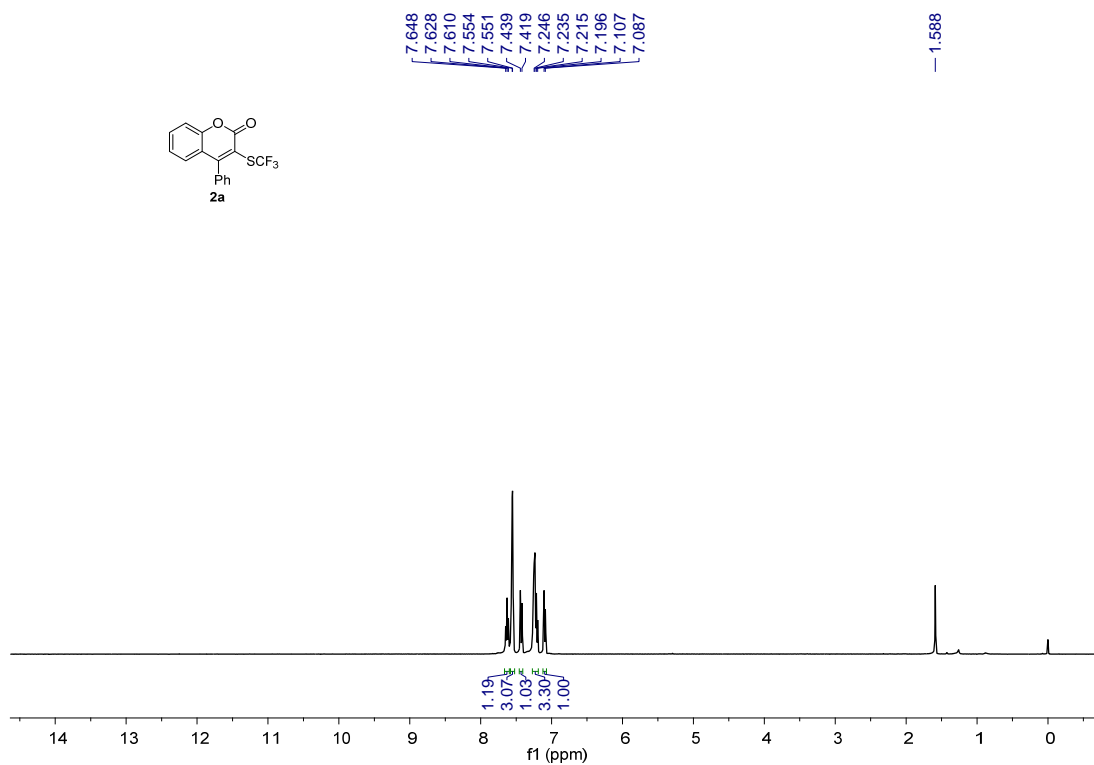
The structure of **2g** was determined by the X-ray diffraction. And it was recrystallized from DCM/ petroleum ether. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1409264.

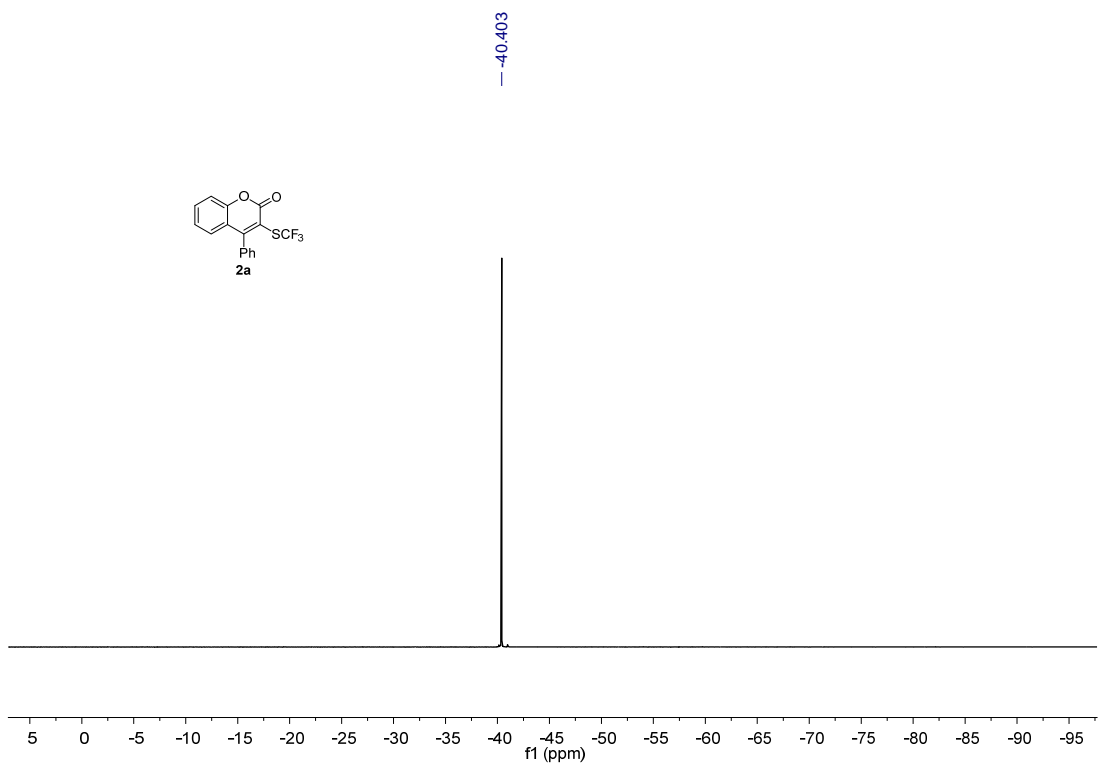
## 7. References

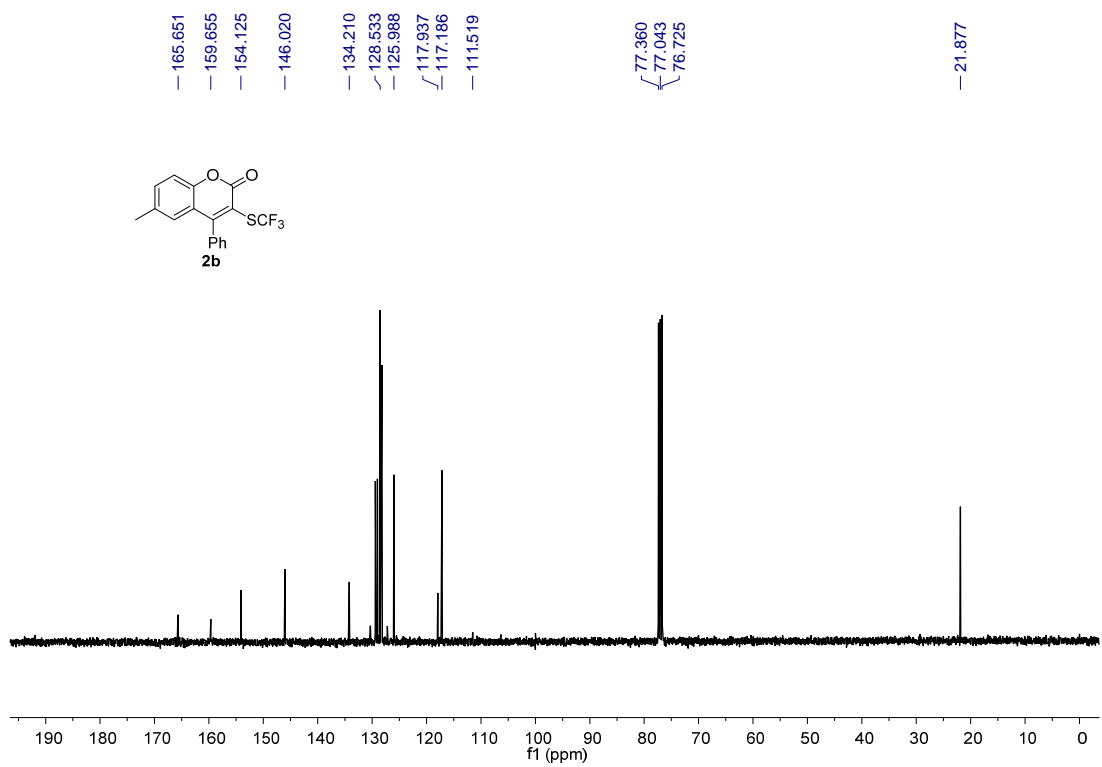
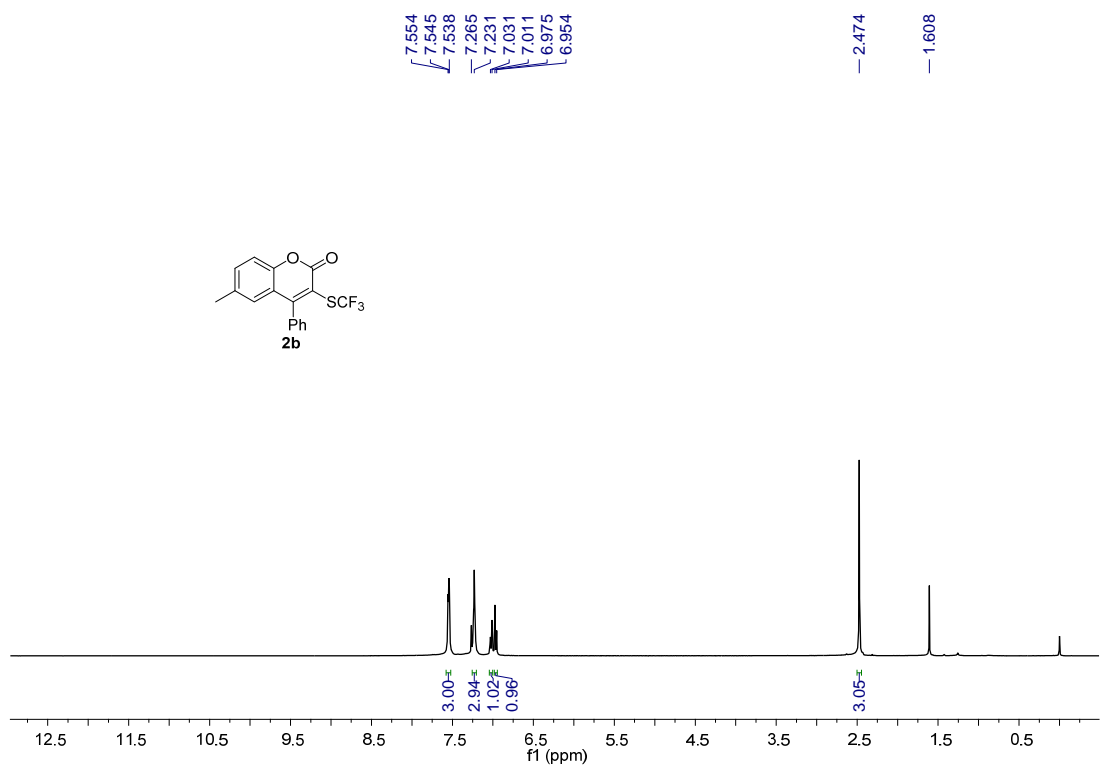
- (1) Song, C. E.; Jung, D.; Choung, S. Y.; Roh, E. J.; Lee, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 6183.
- (2) Kawate, T.; Iwase, N.; Shimizu, M.; Stanley, S. A.; Wellington, S.; Kazyanskaya, E.; Hung, D. T. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 6052.
- (3) Teverovskiy, G.; Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 7312.
- (4) Clark, J. H.; Jones, C. W.; Kybett, A. P.; McClinton, M. A. *J. Fluor. Chem.* **1990**, *48*, 249.
- (5) (a) Yin, F.; Wang, X. *Org. Lett.* **2014**, *16*, 1128. (b) Guo, S.; Zhang, X.; Tang, P. *Angew. Chem. Int. Ed.* **2015**, *54*, 4065.

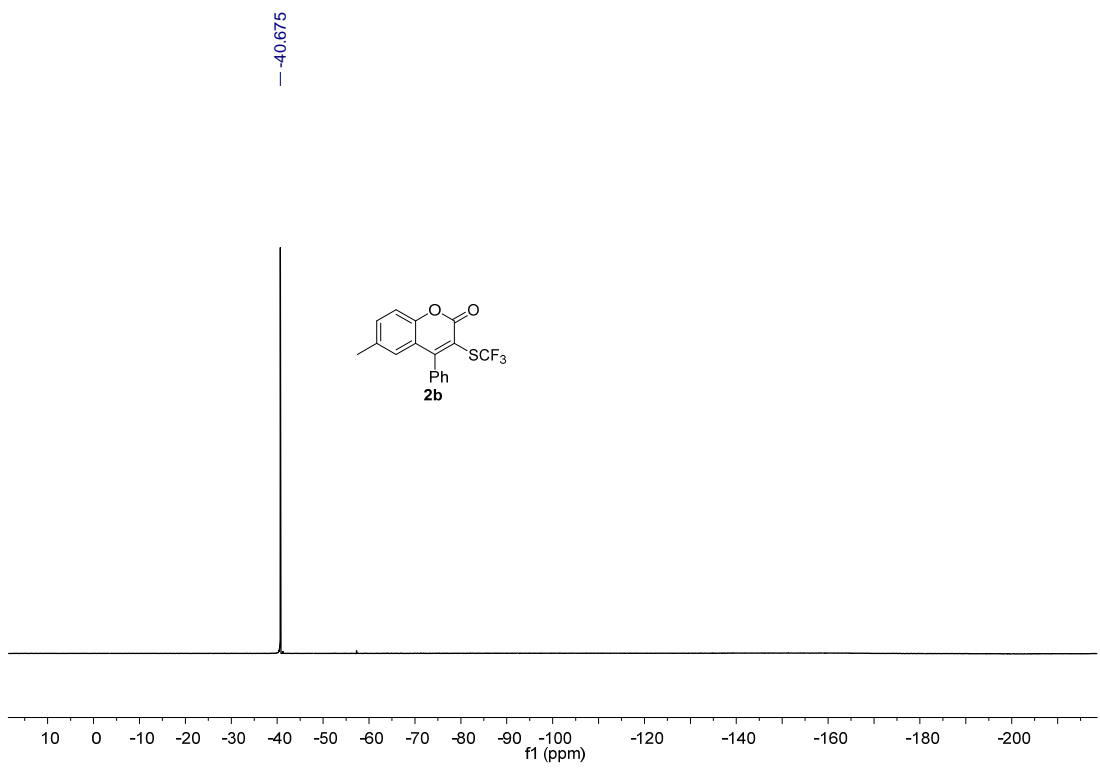


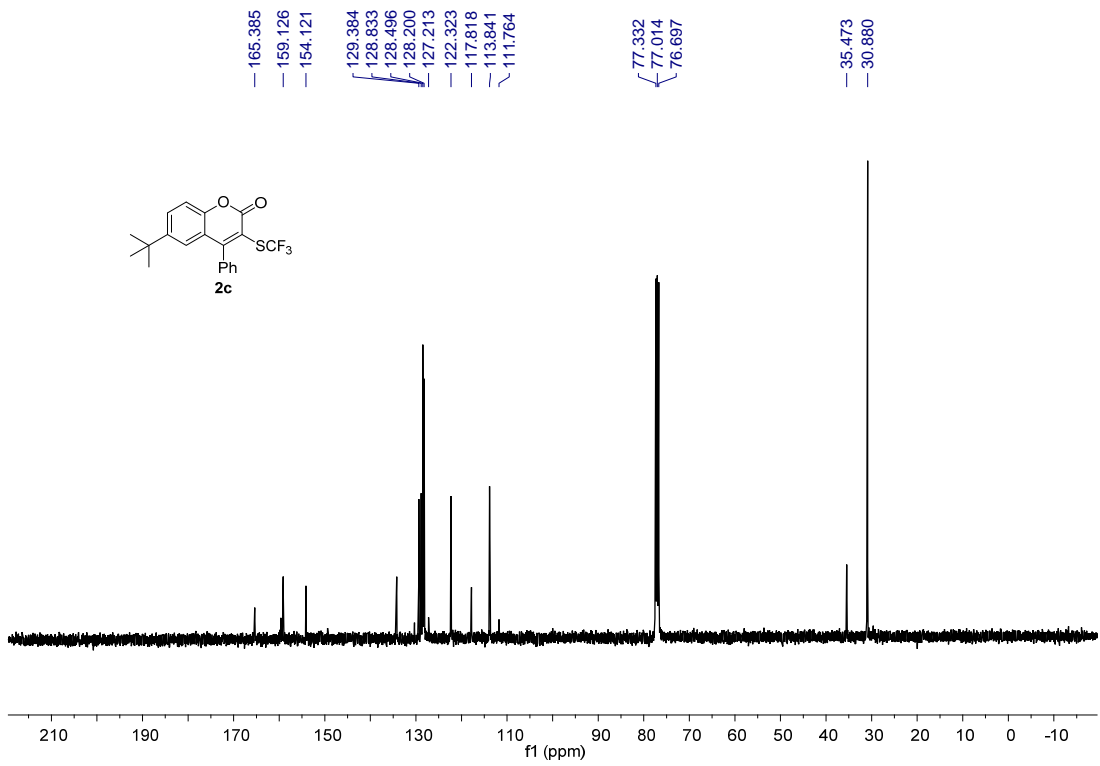
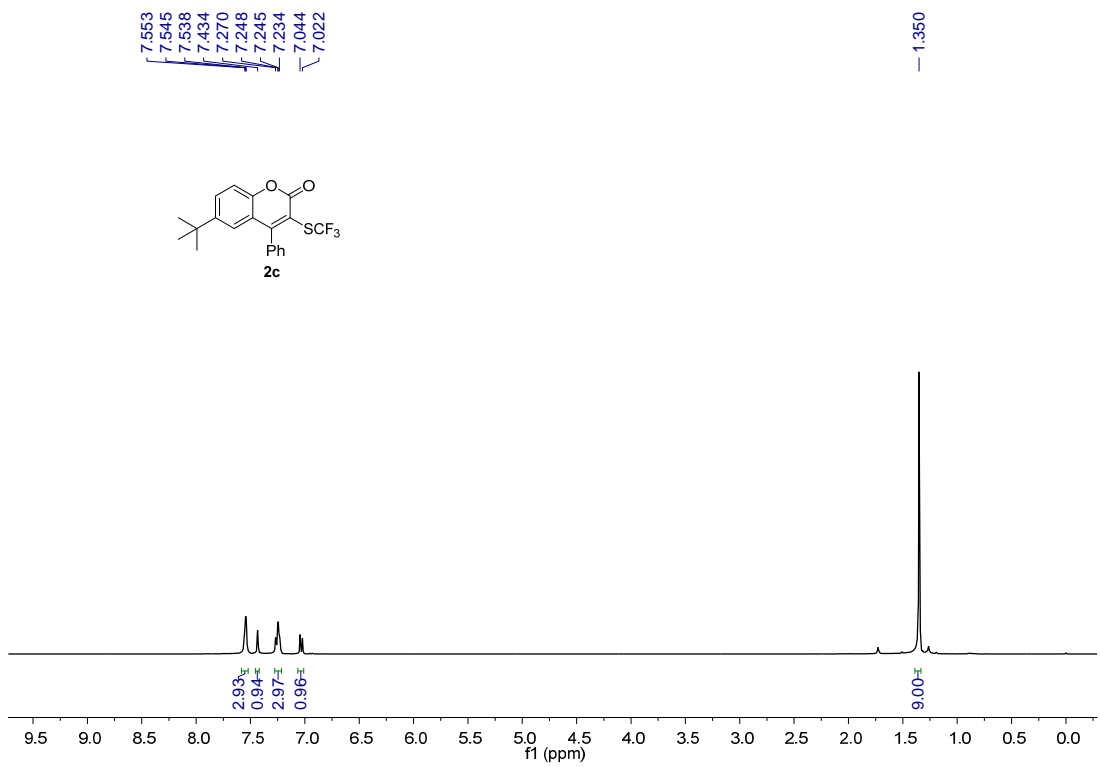
## 8. NMR Spectrum of Products

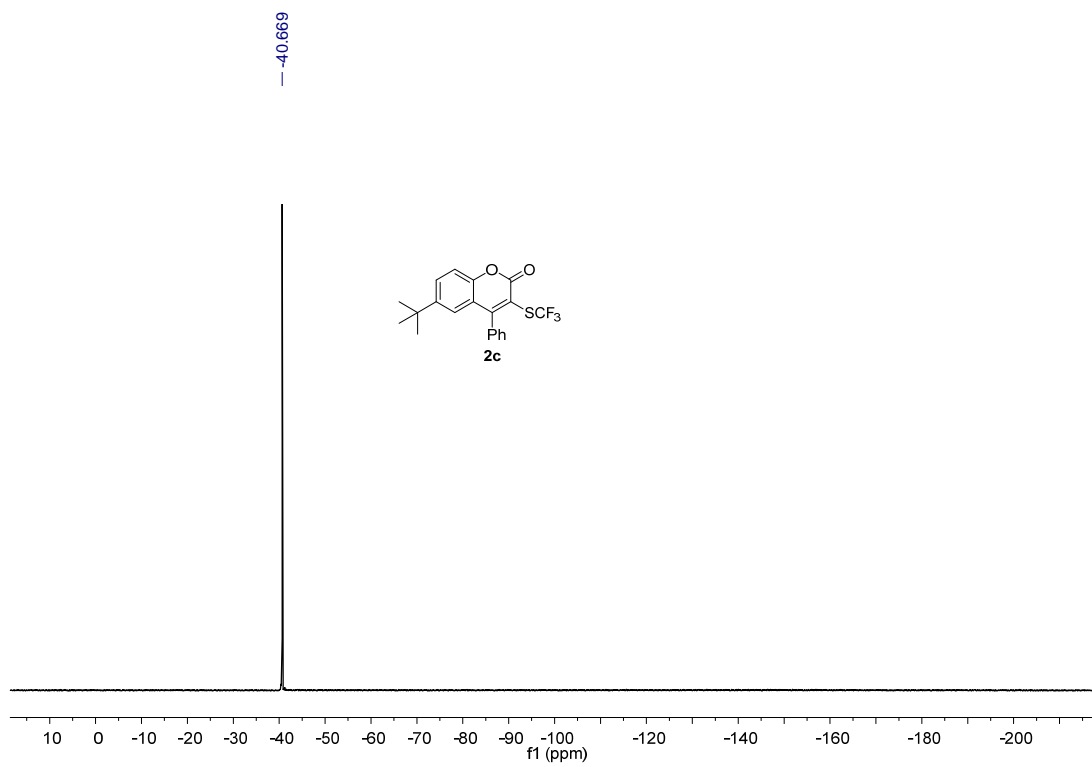


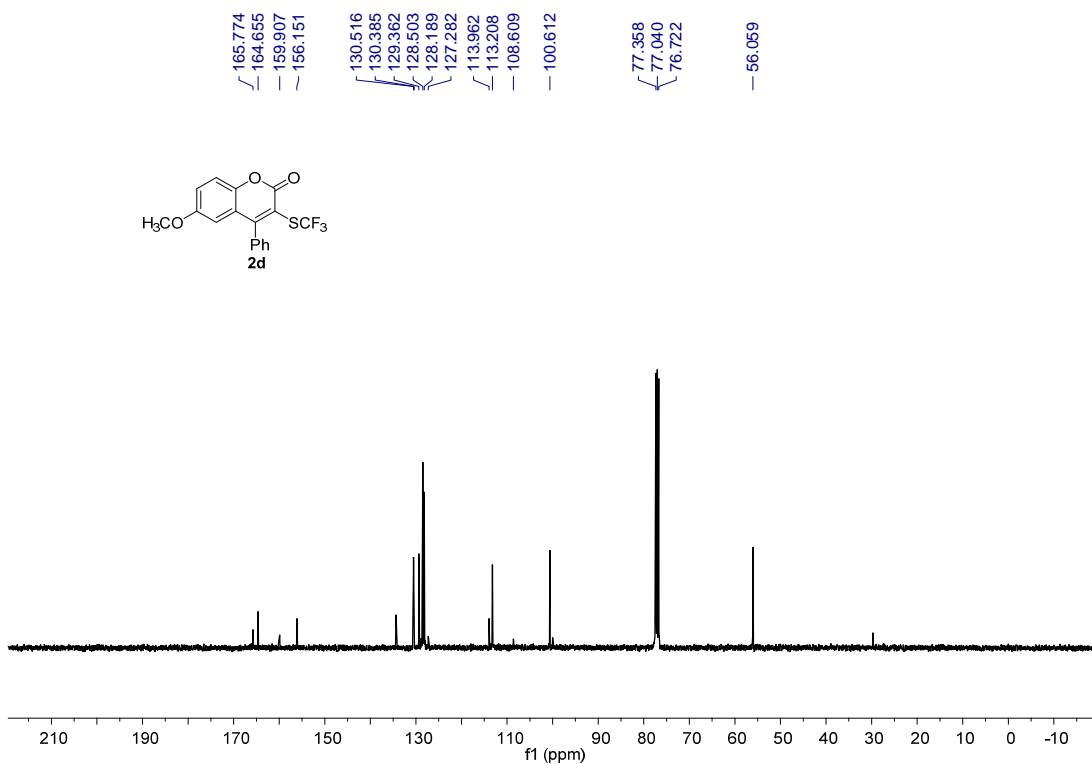
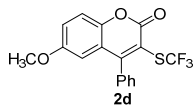
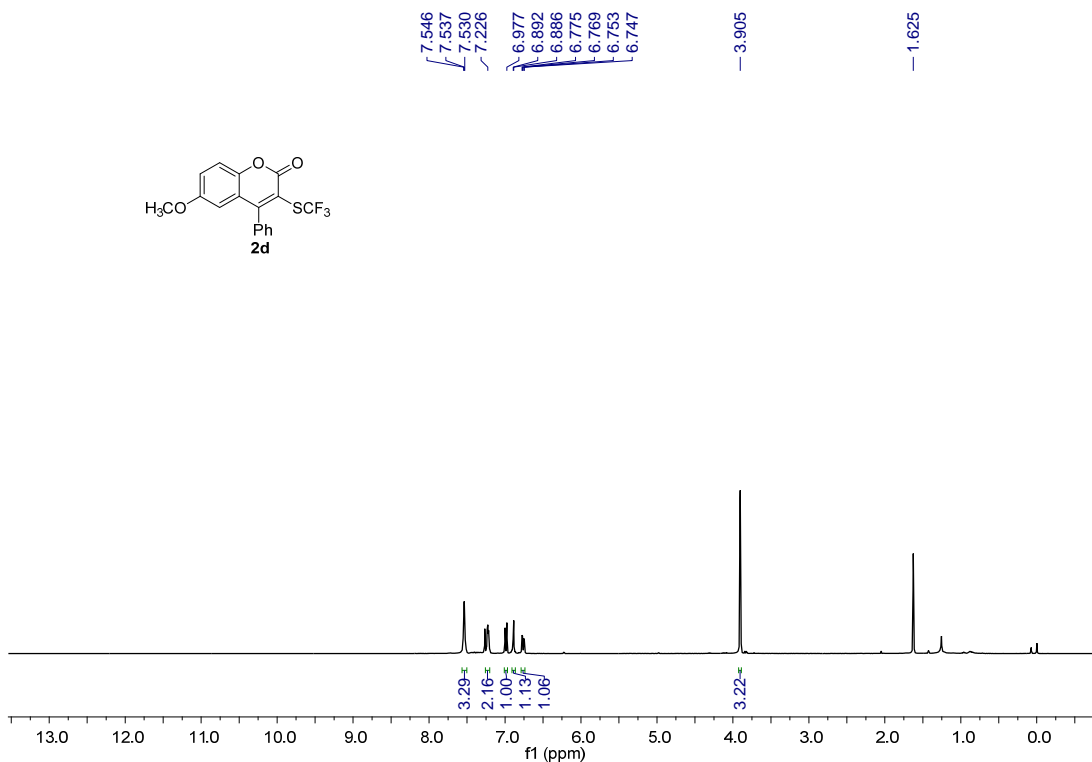
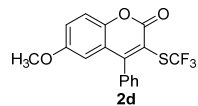




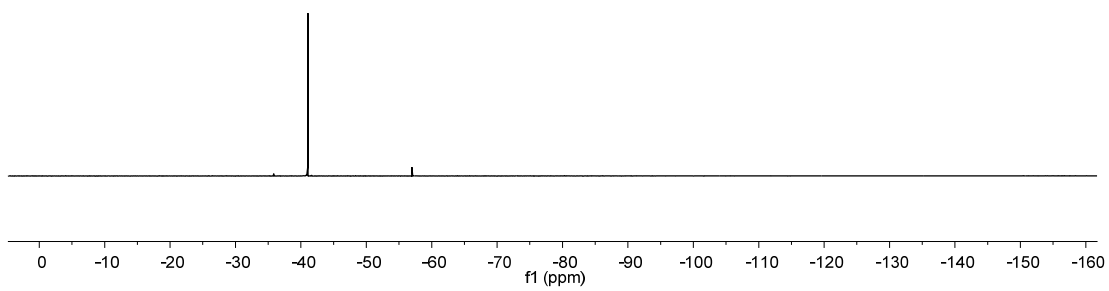
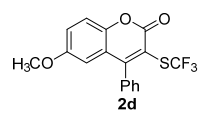




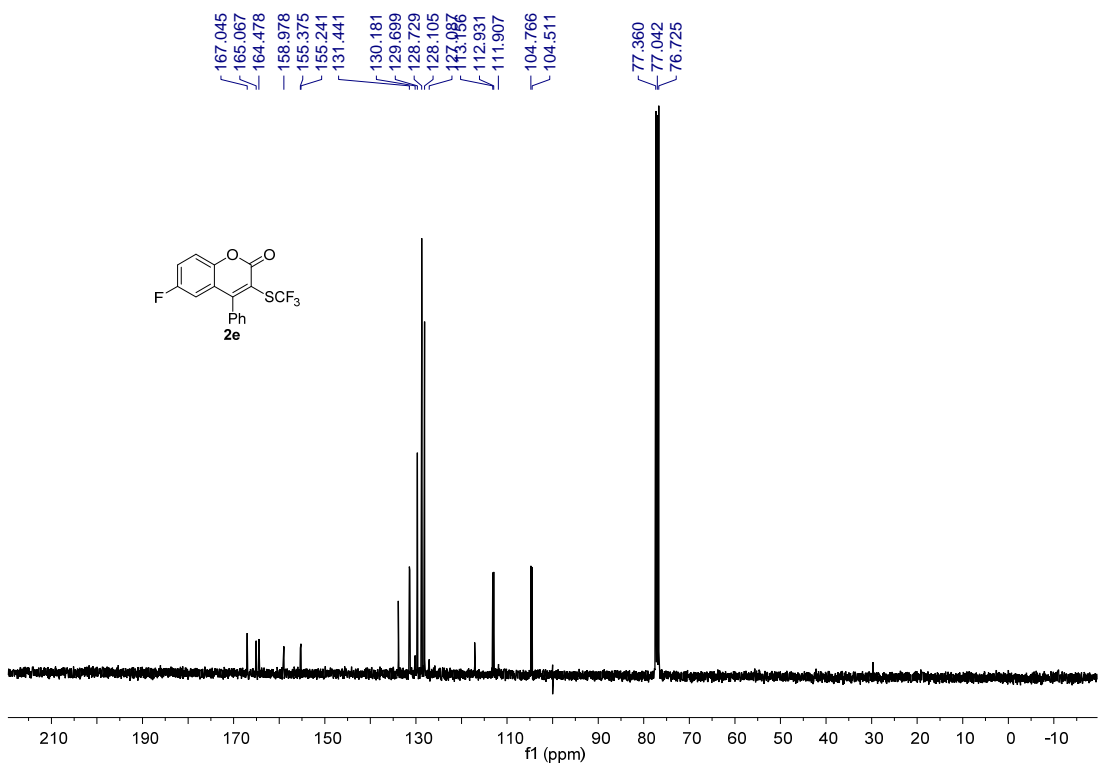
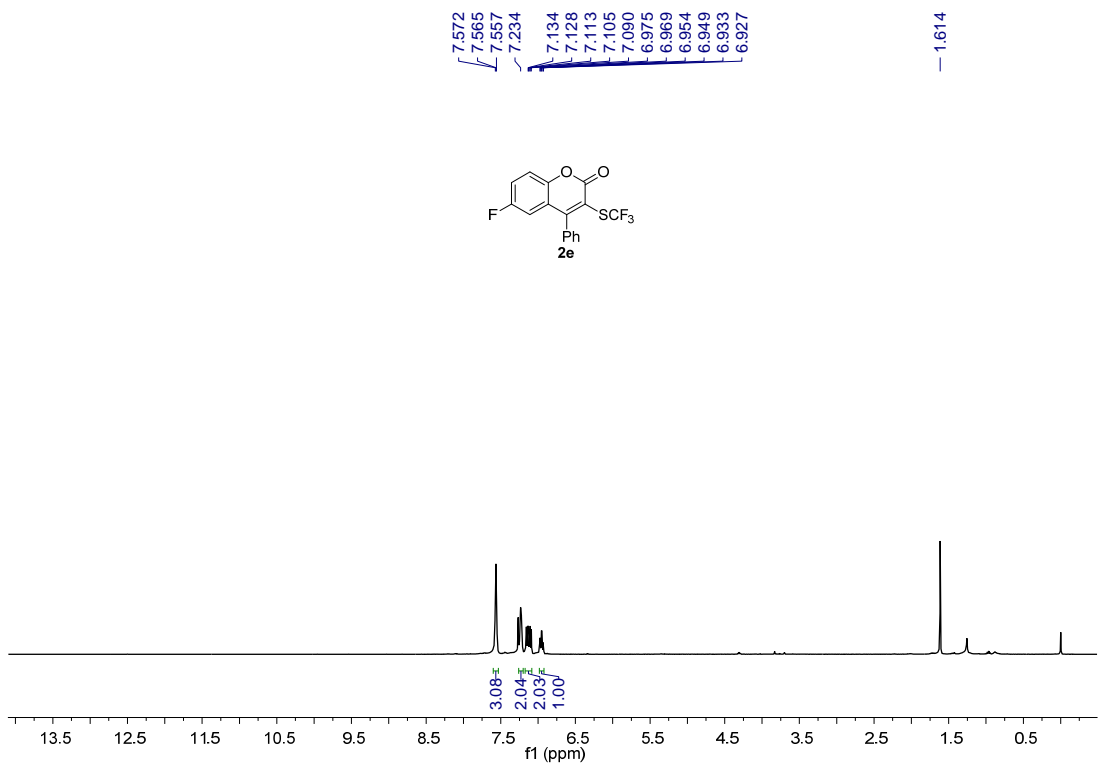


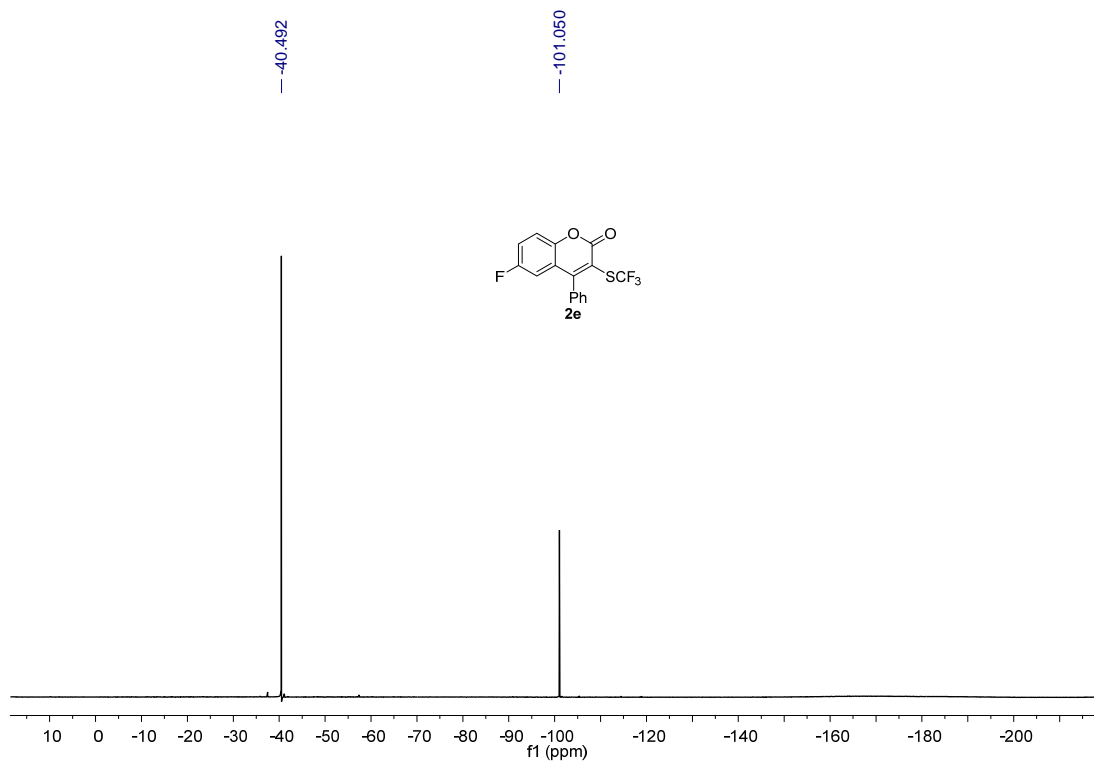


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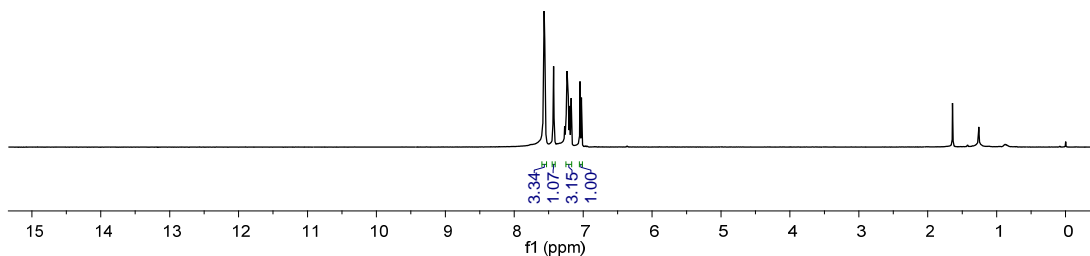
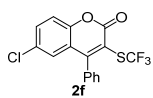




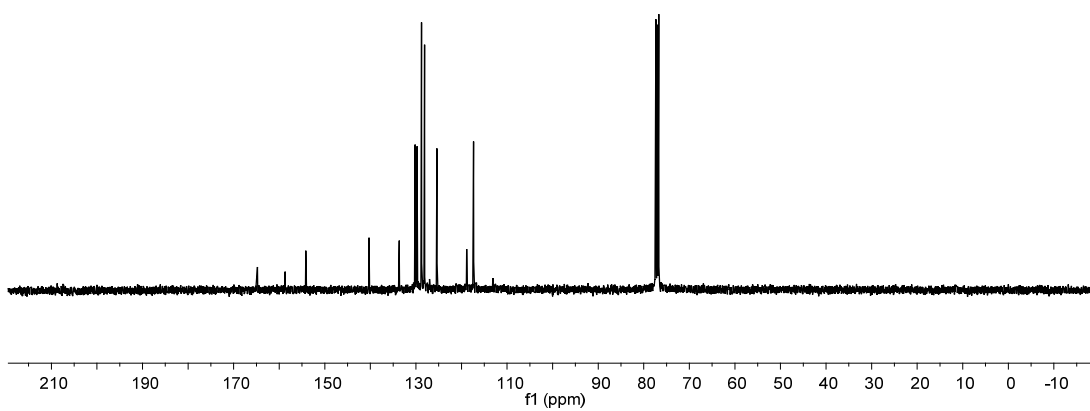
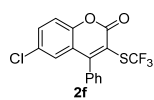


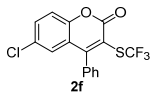


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7.025

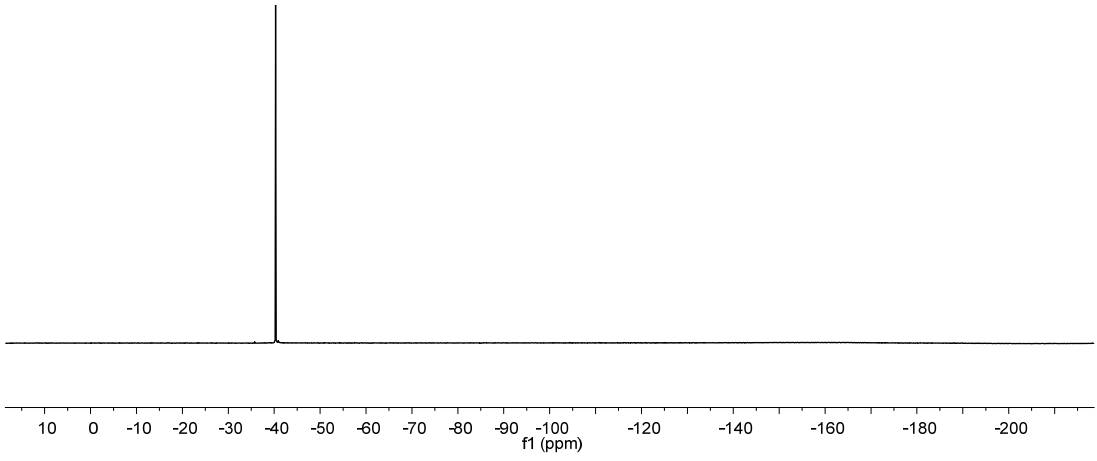


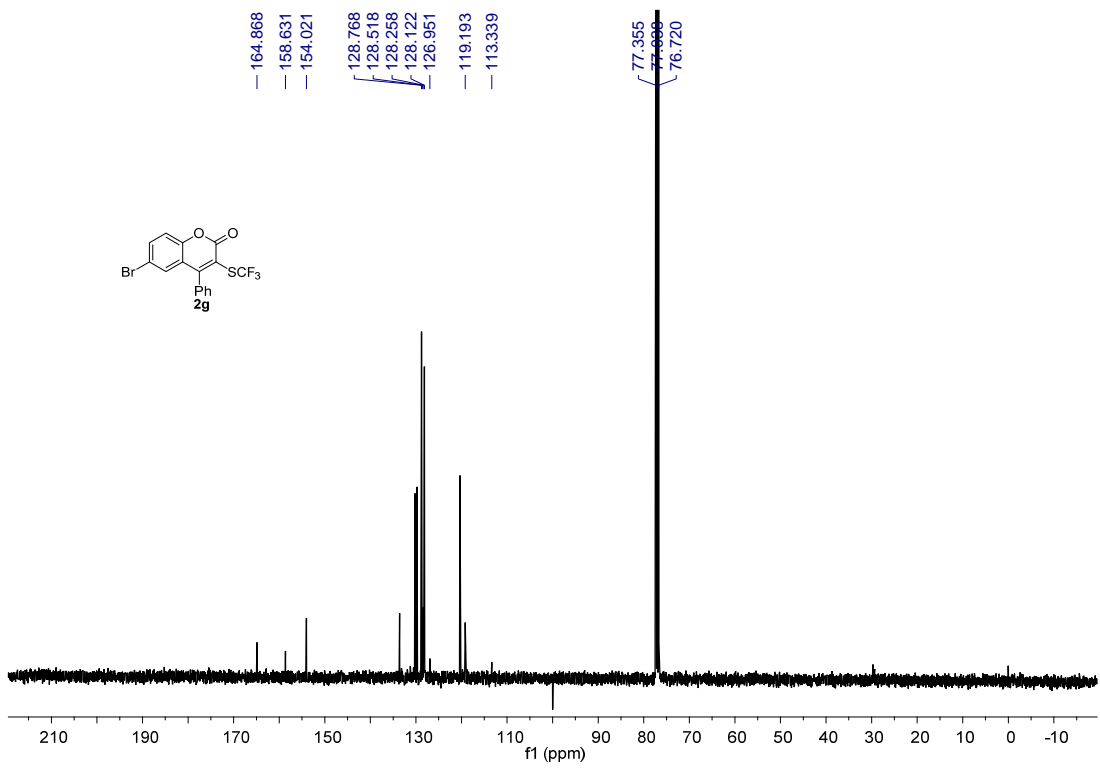
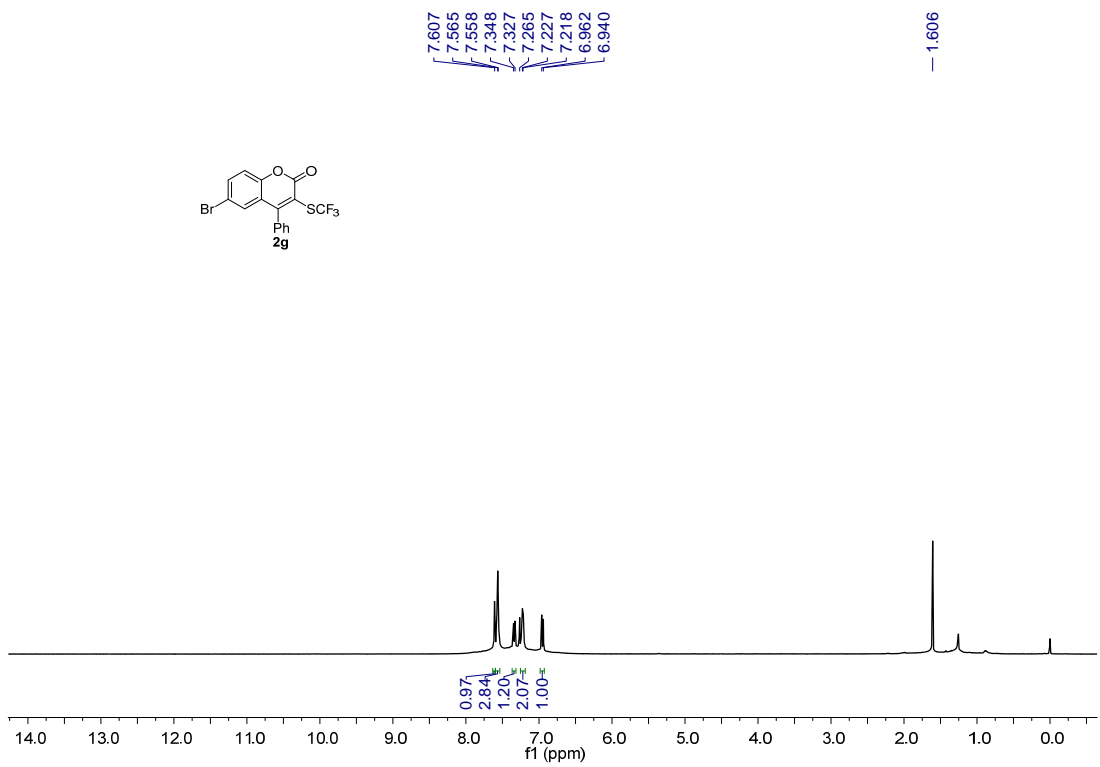
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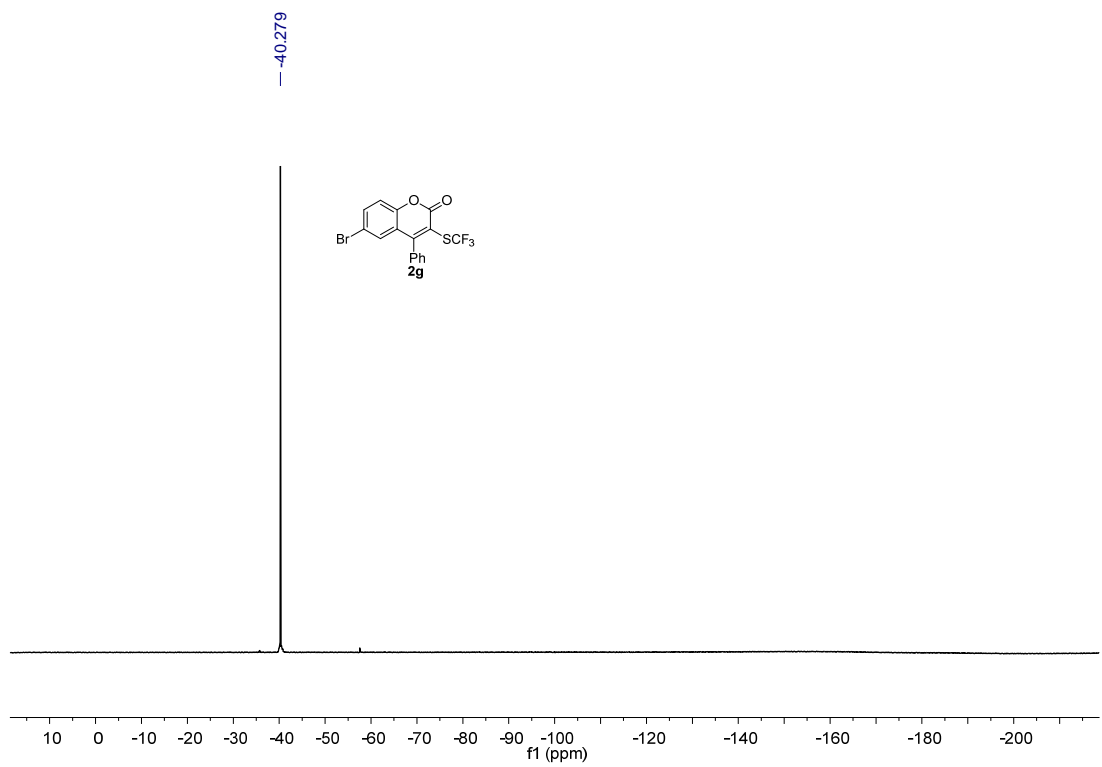


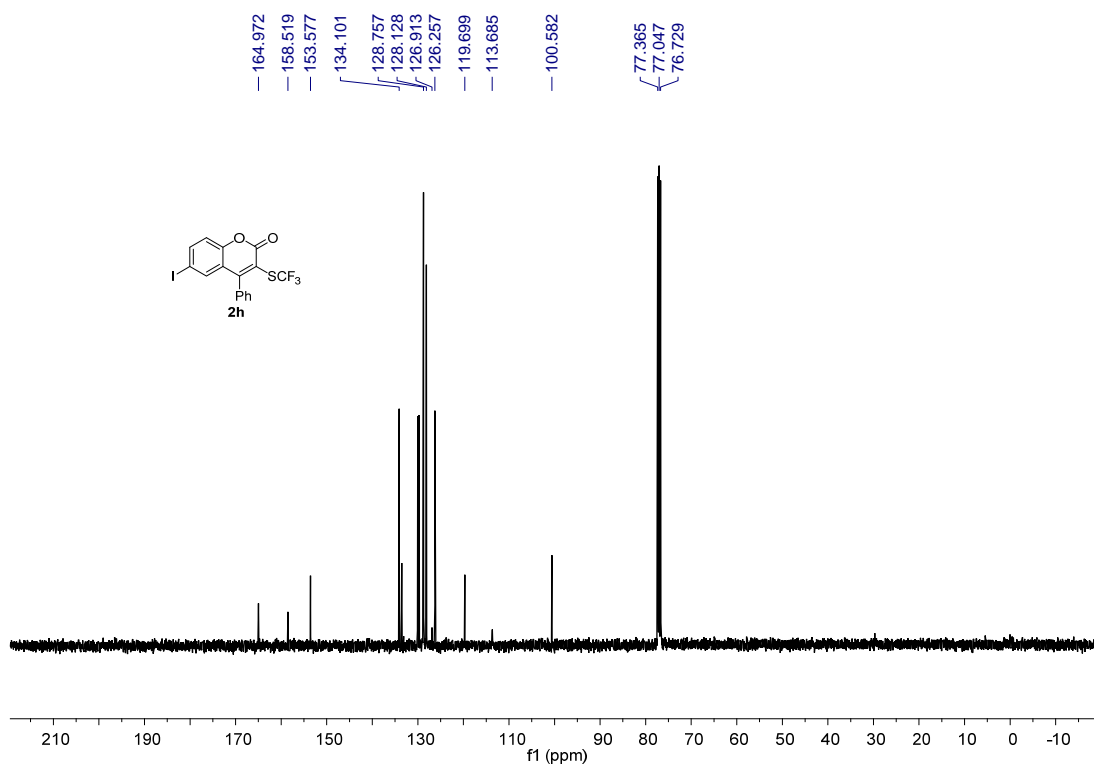
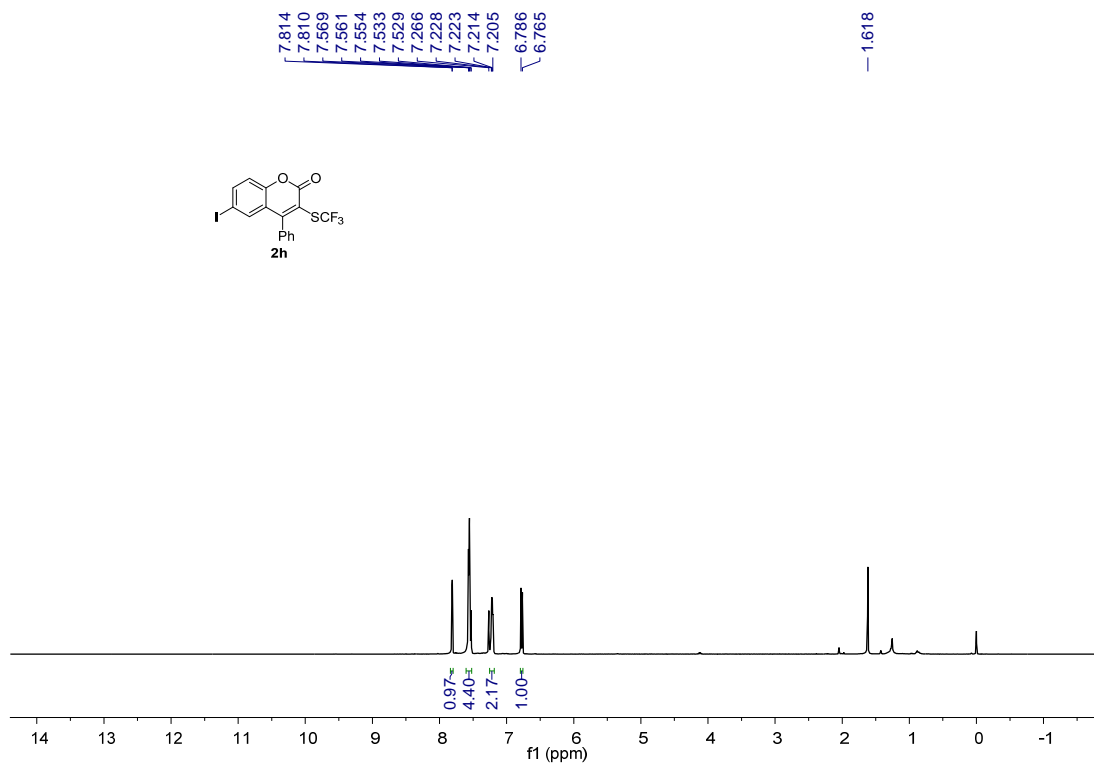


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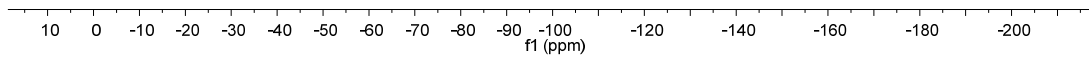
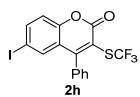




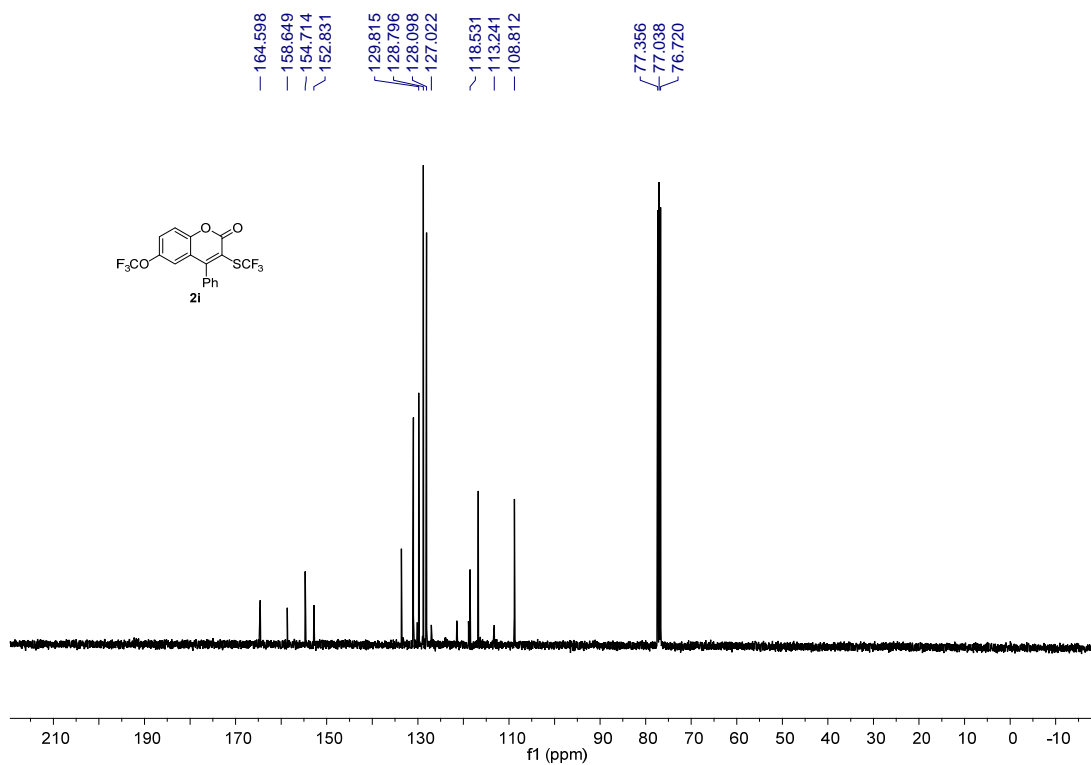
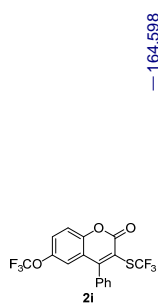
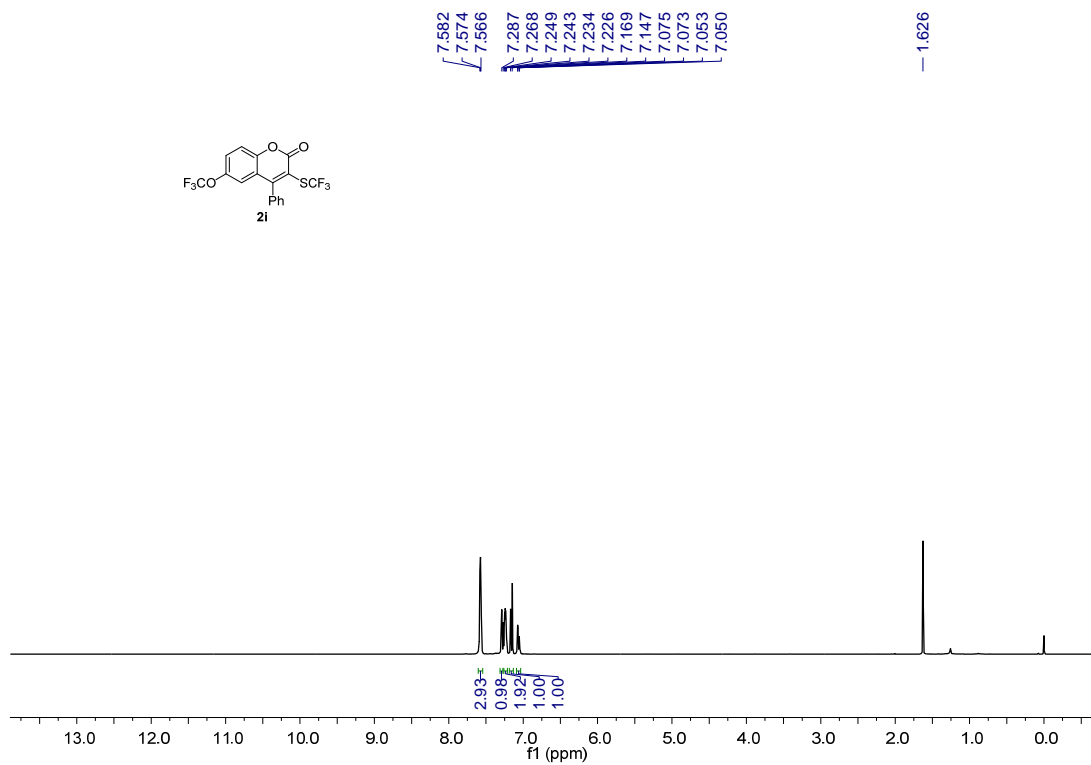
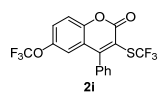


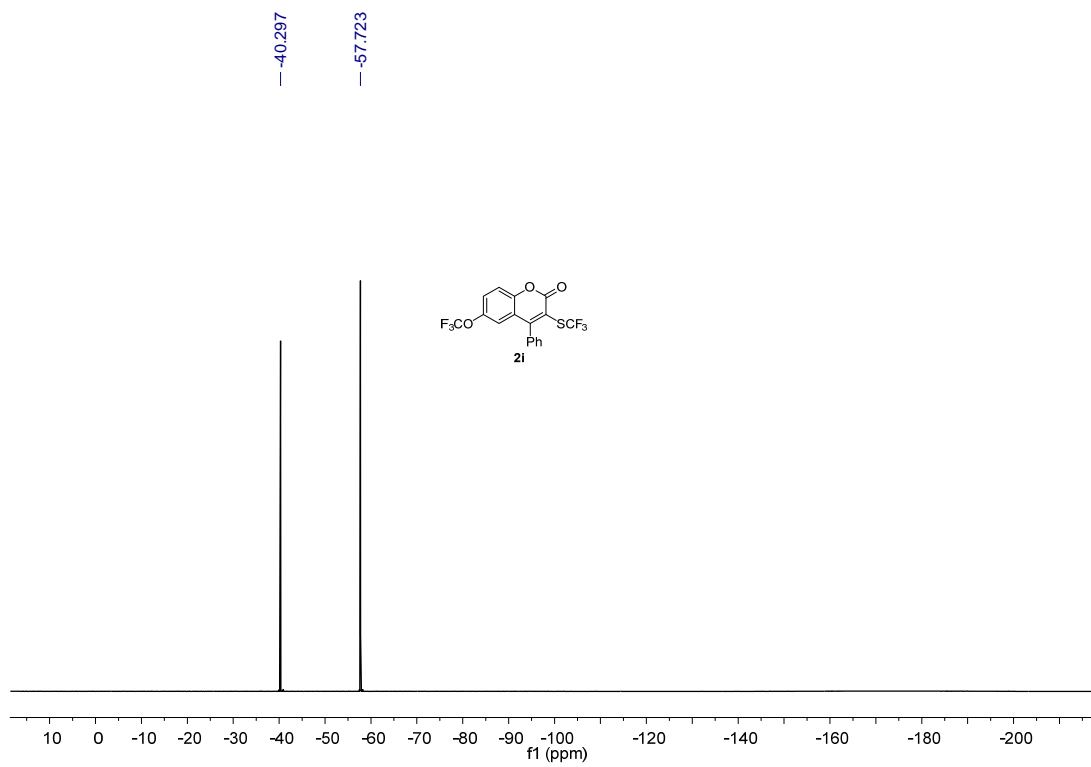


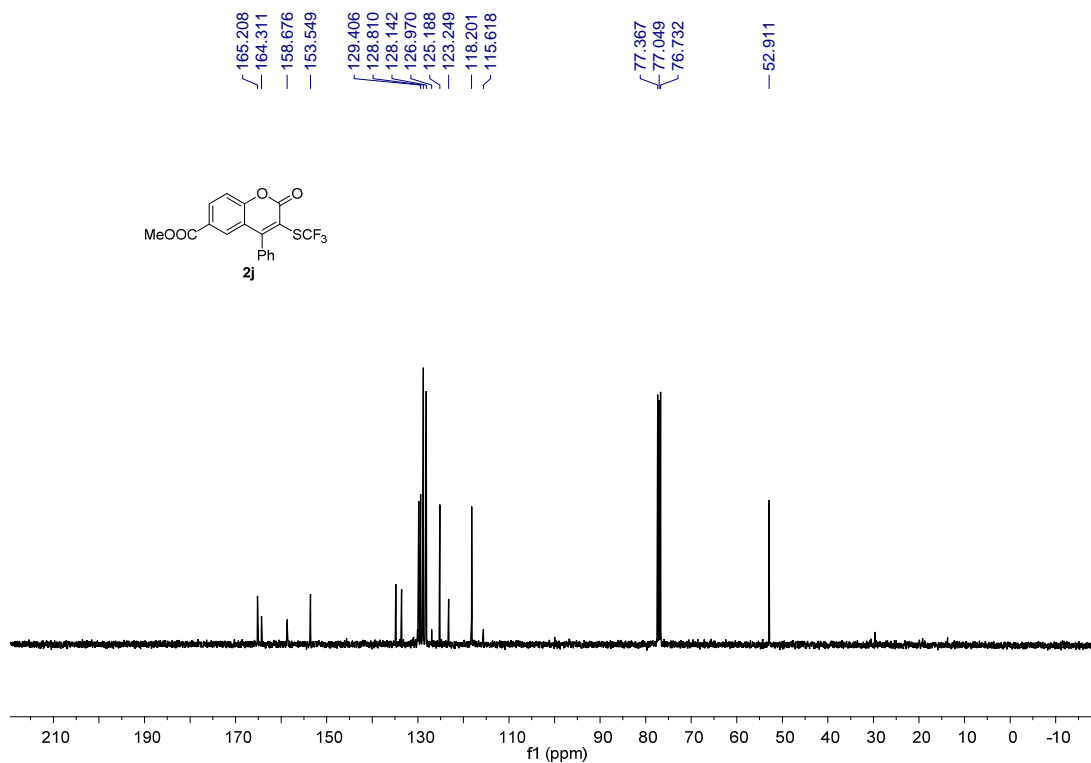
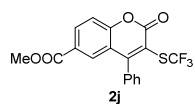
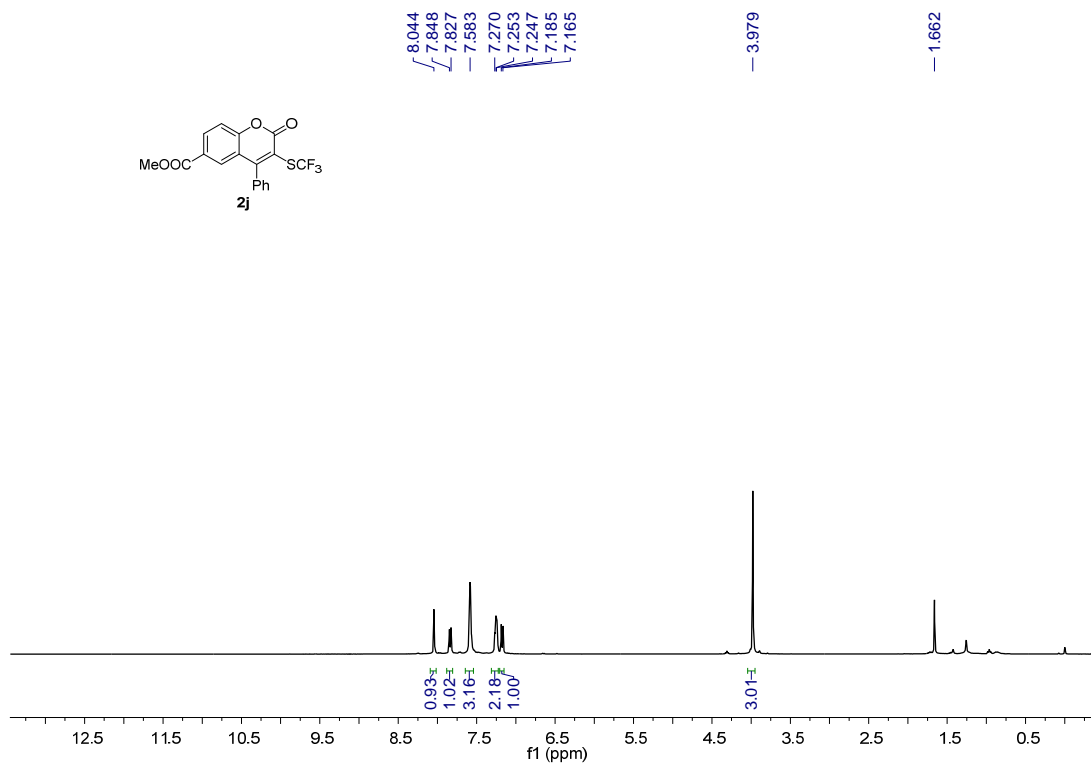
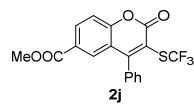
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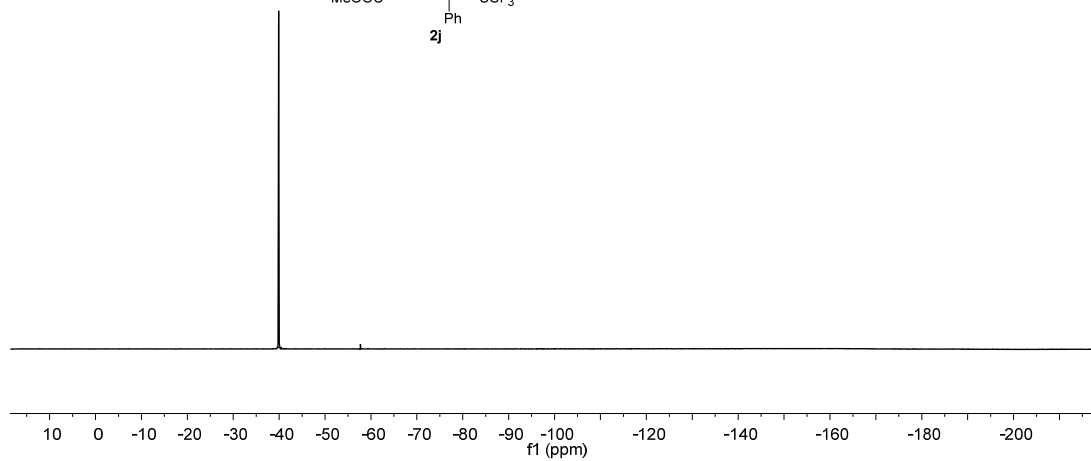
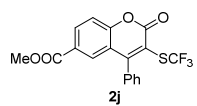


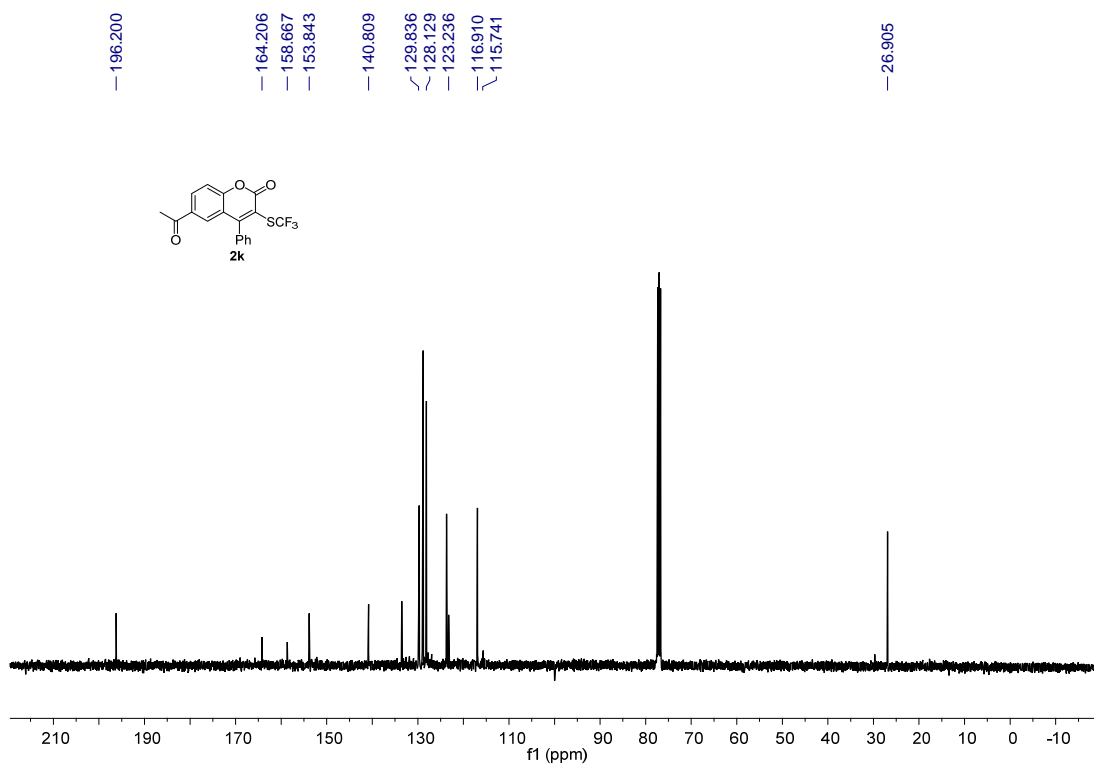
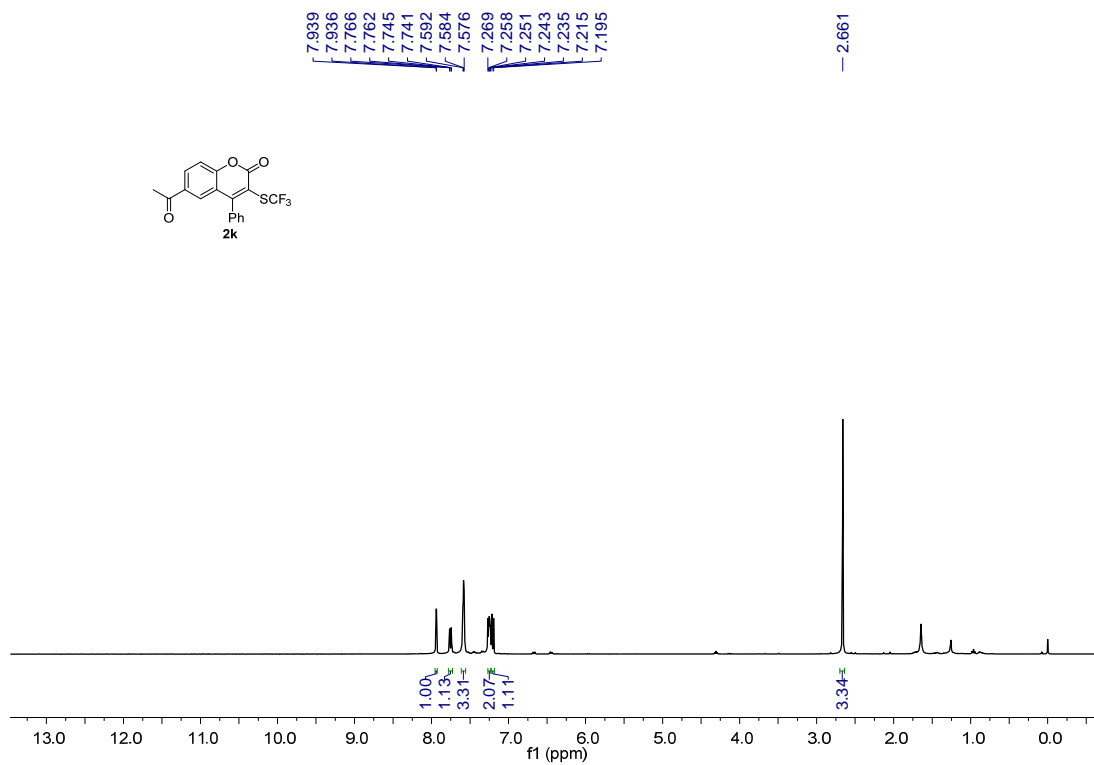




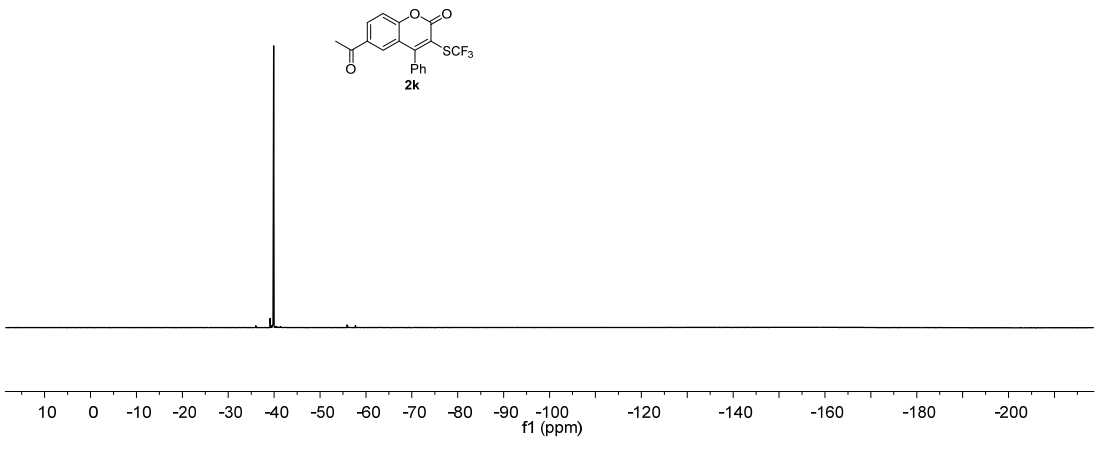


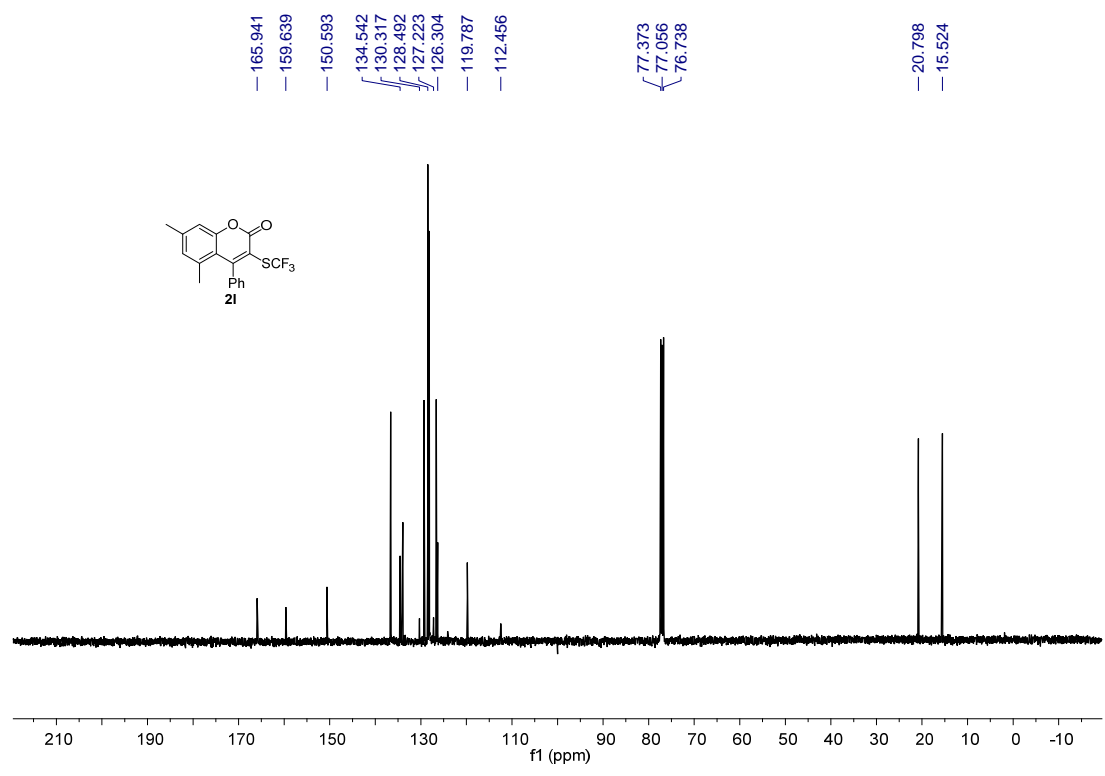
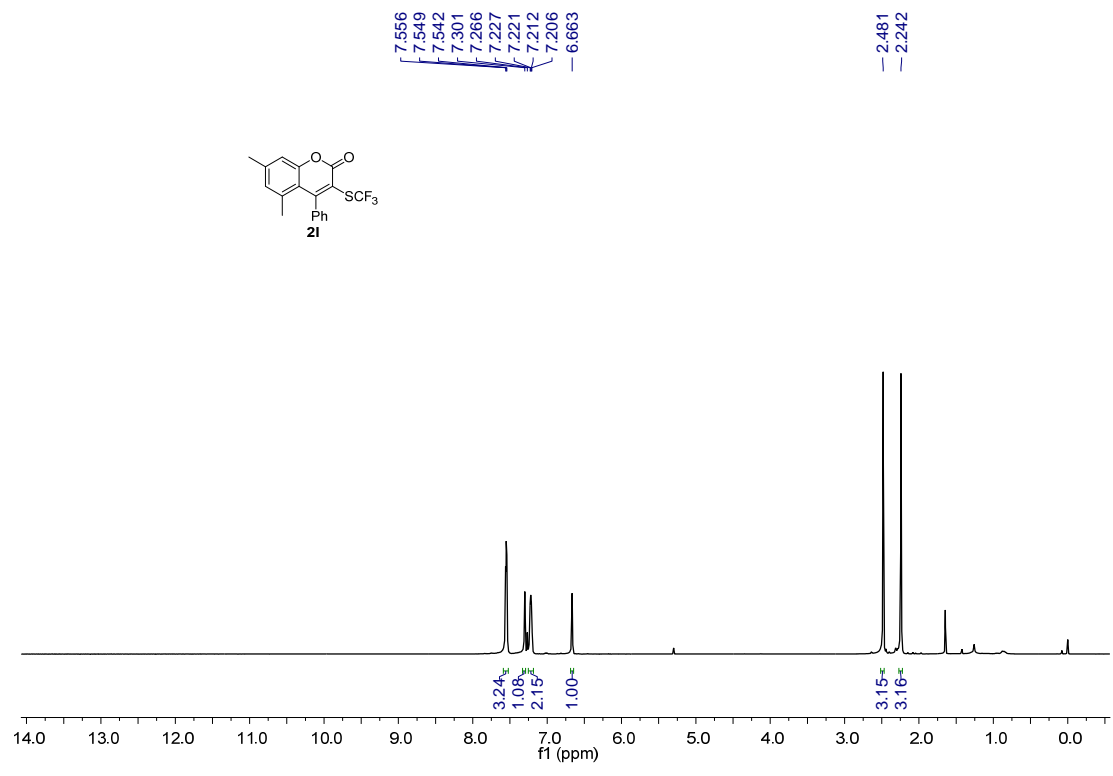
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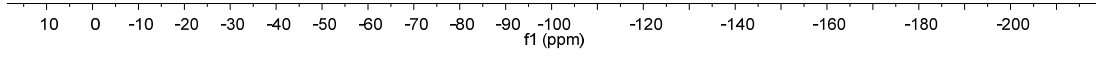
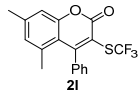


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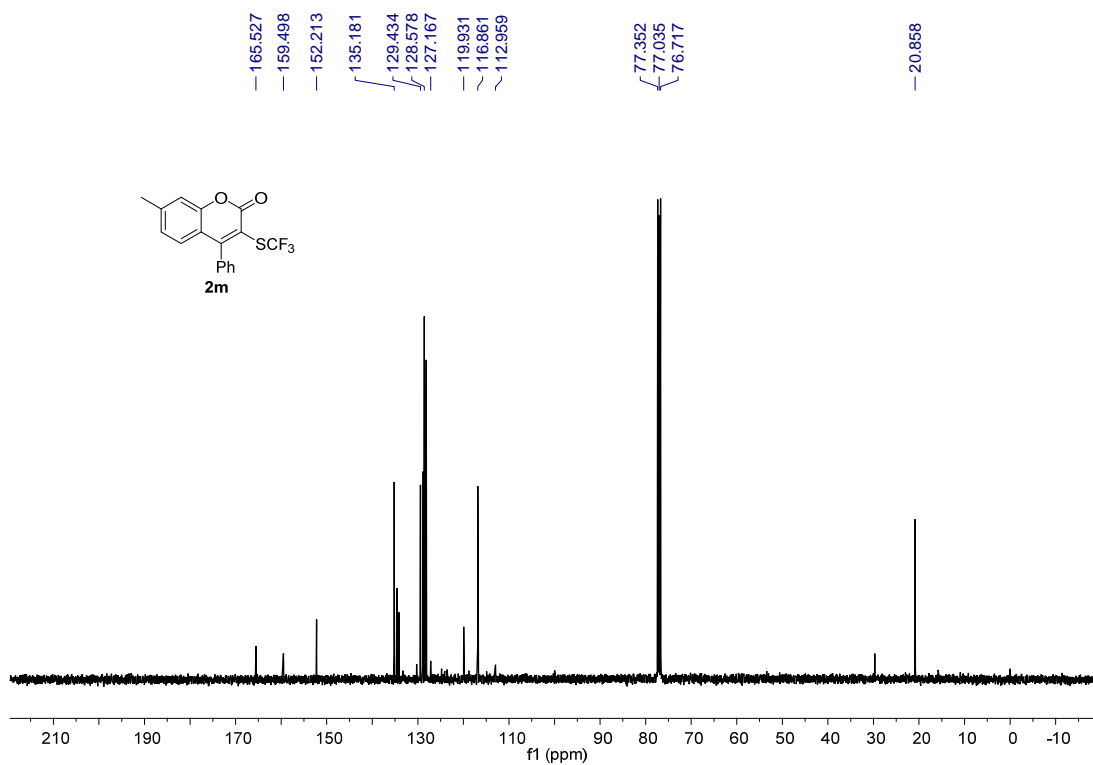
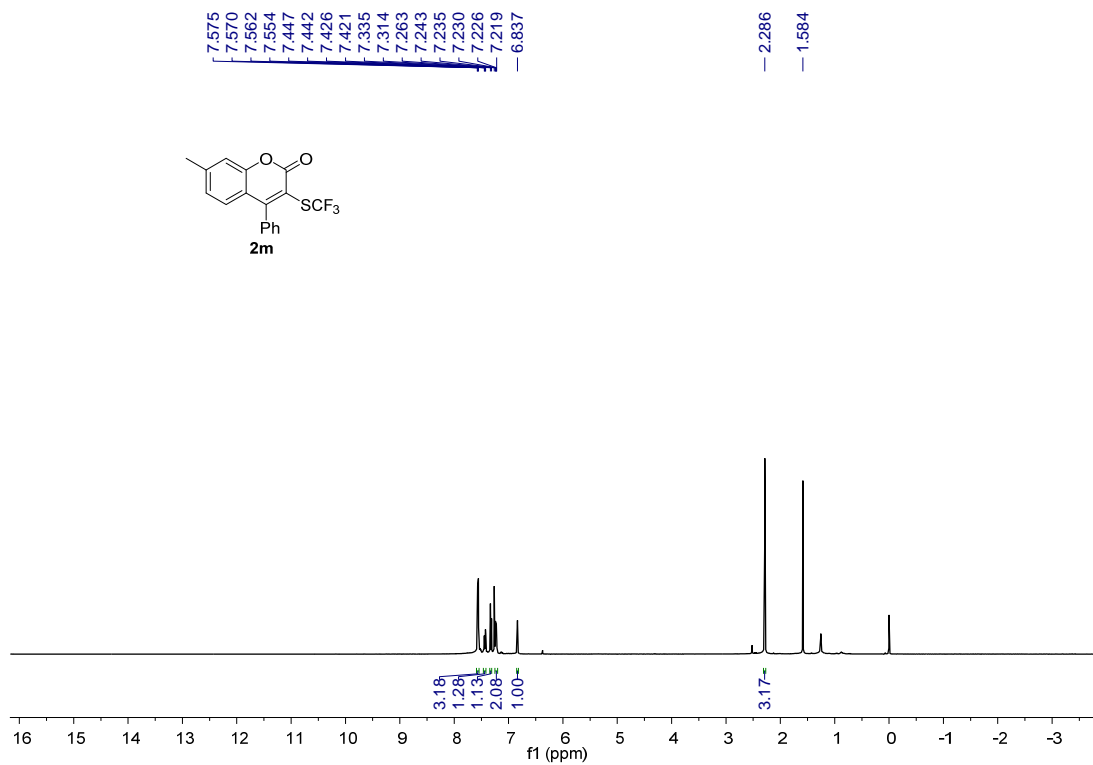




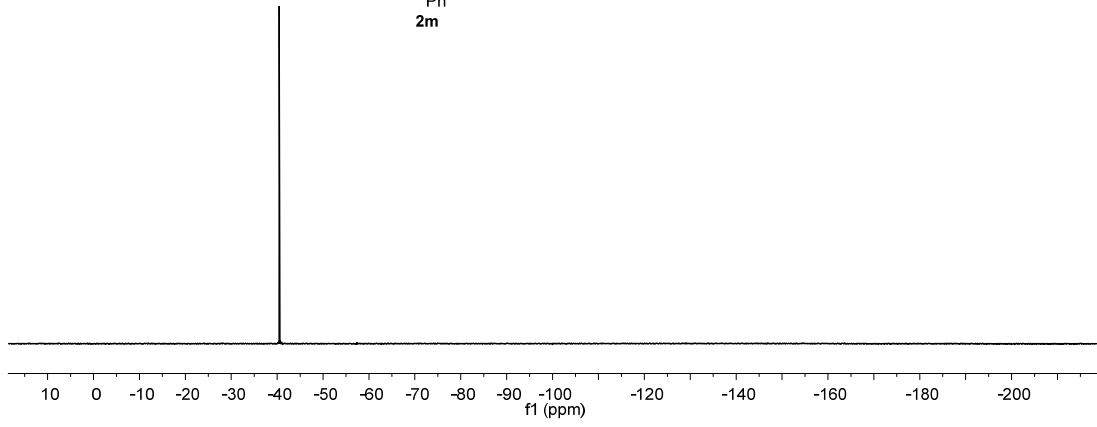
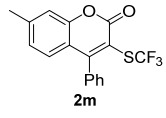
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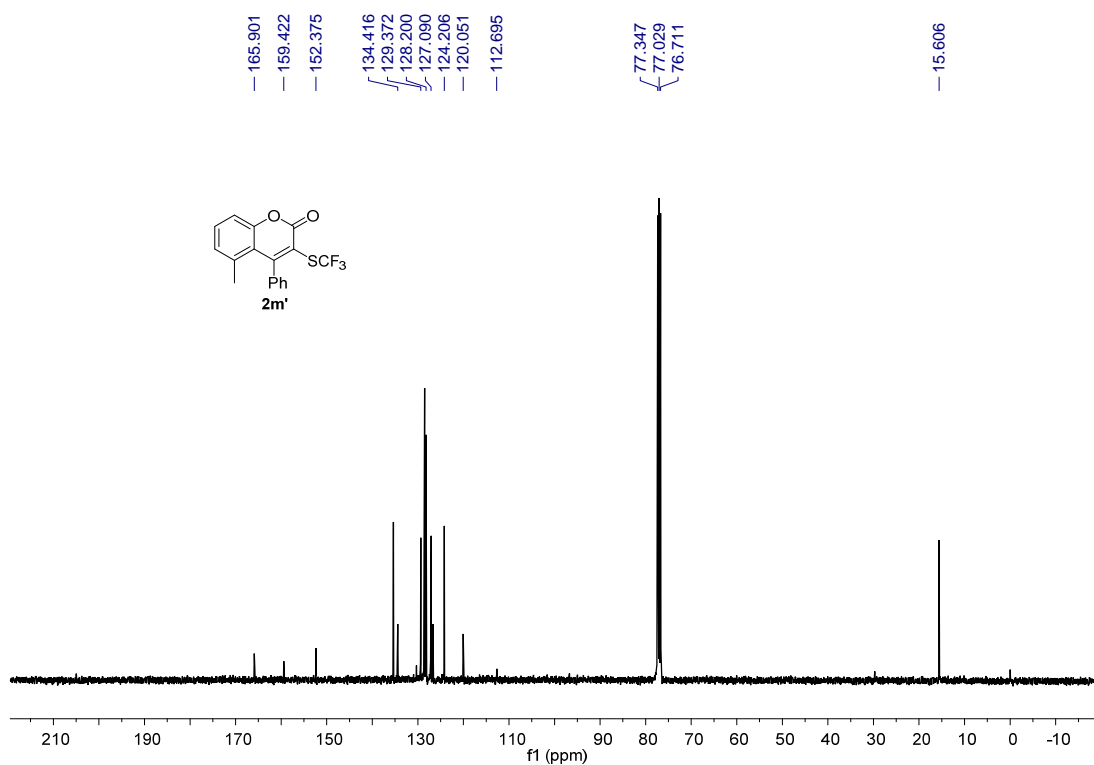
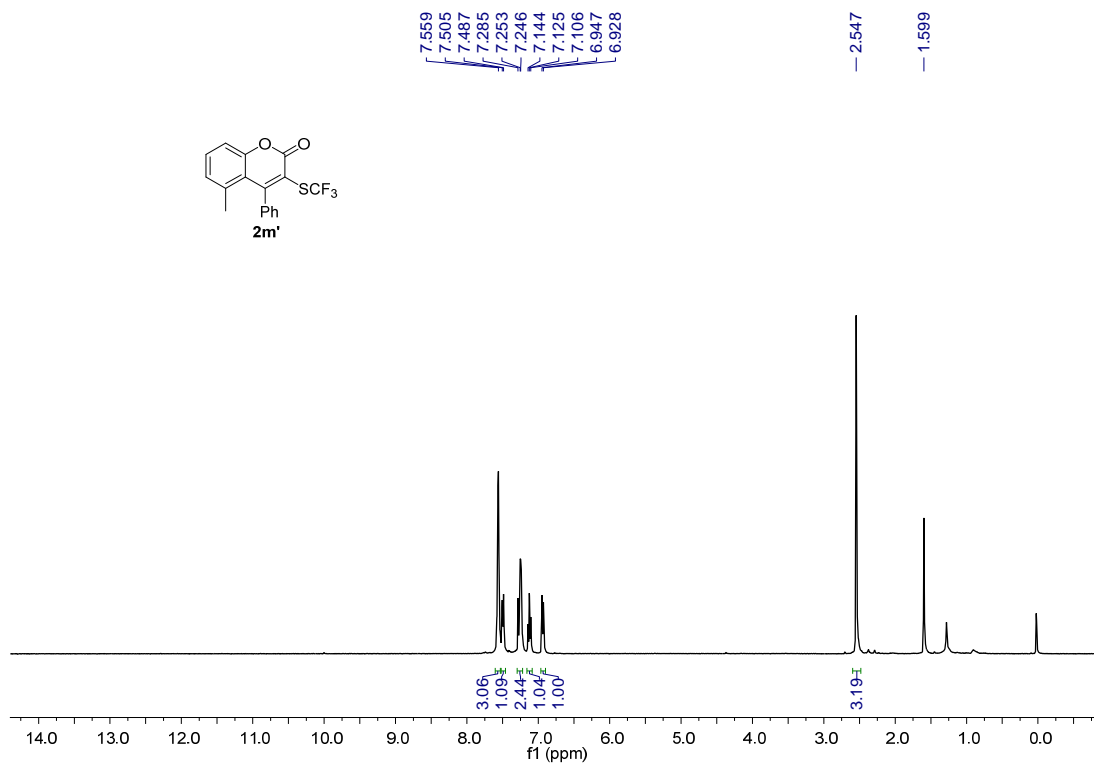




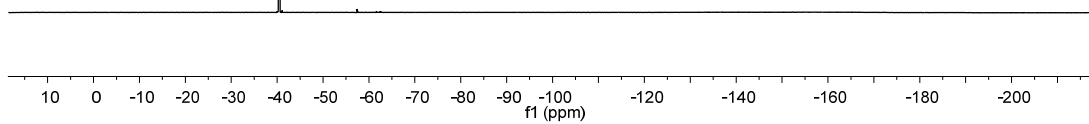
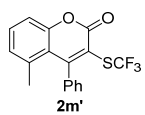


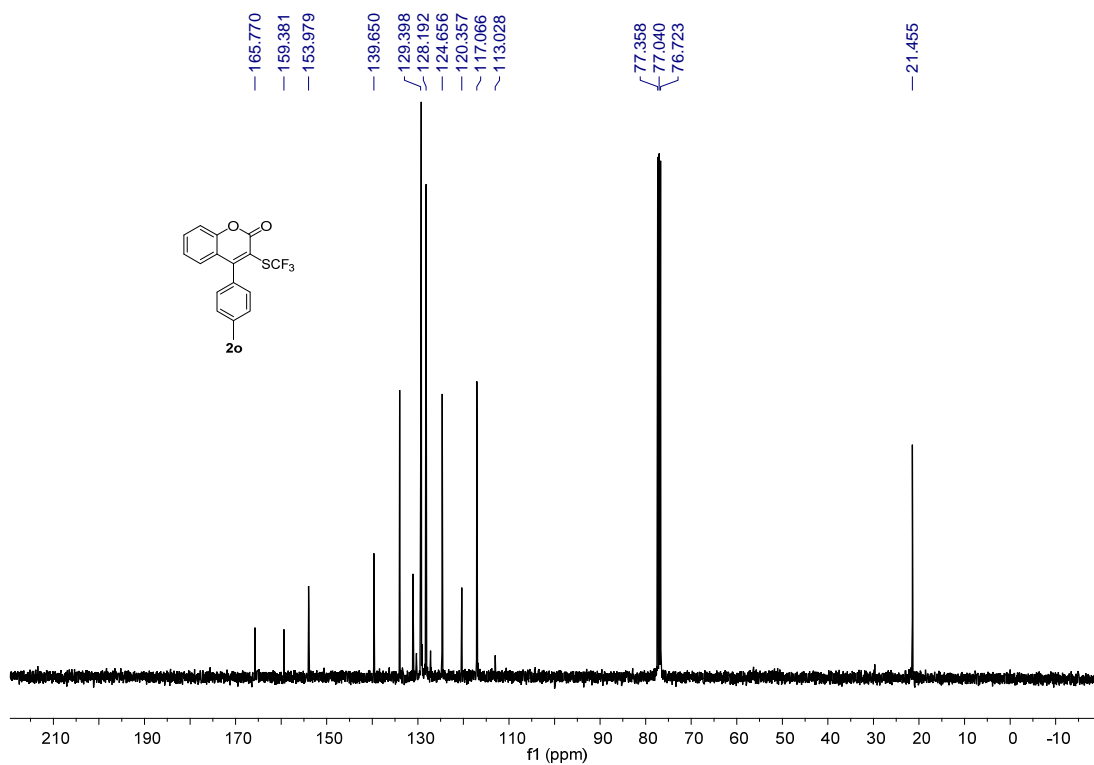
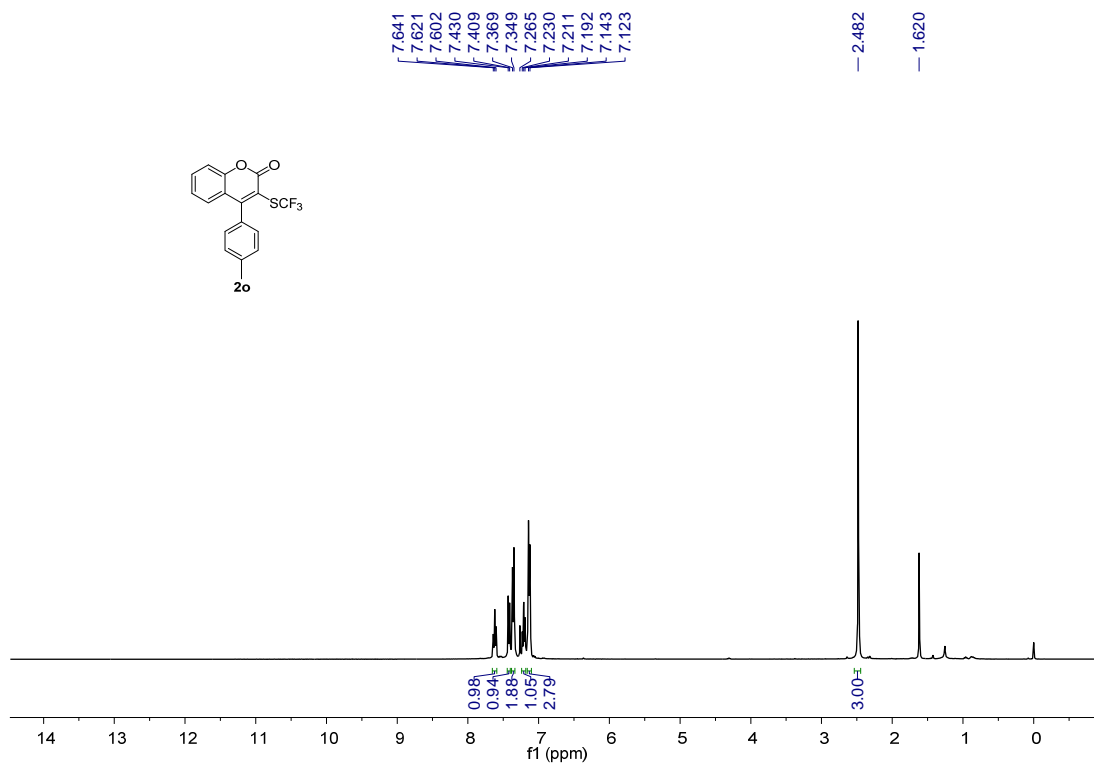
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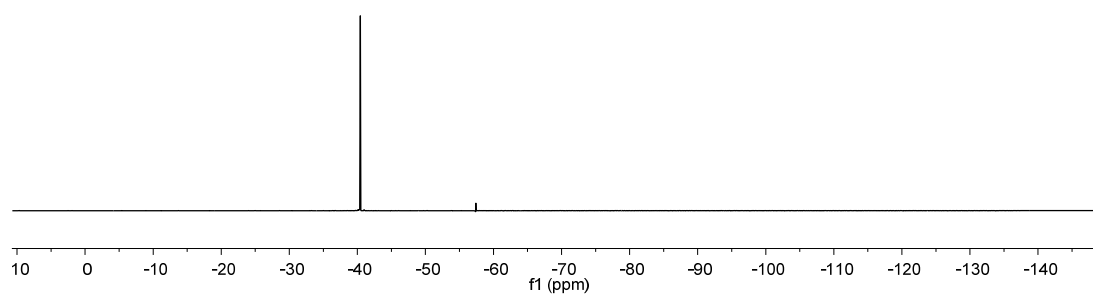
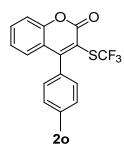


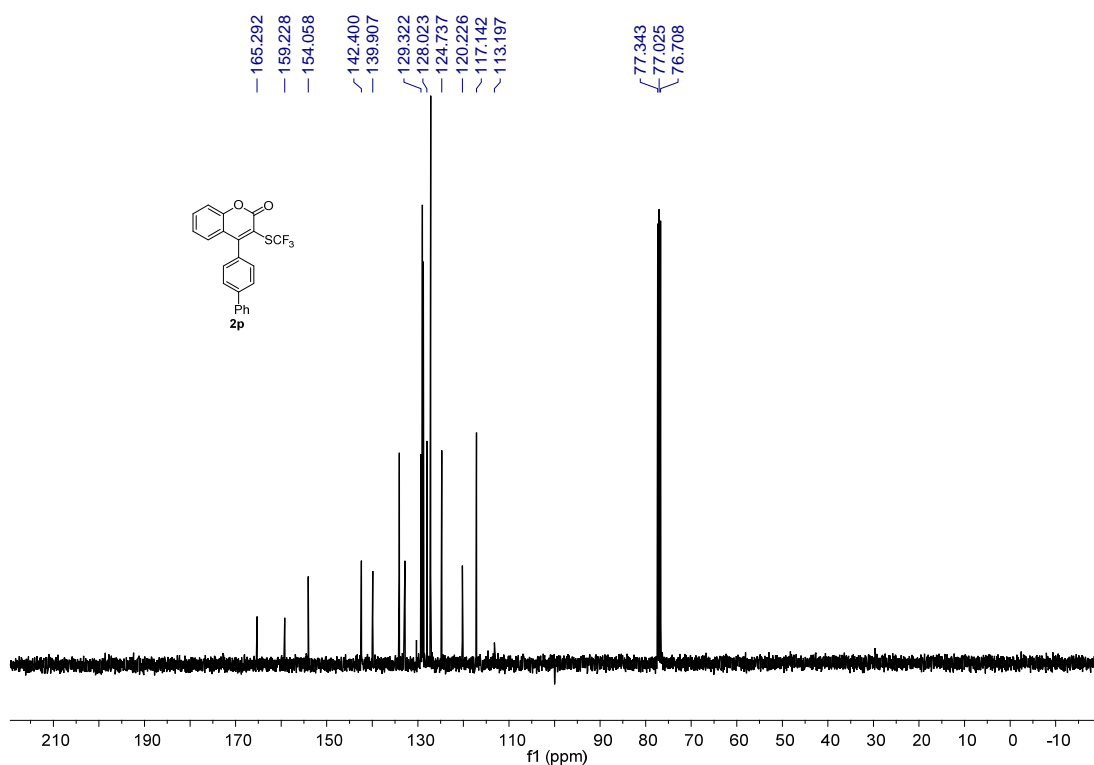
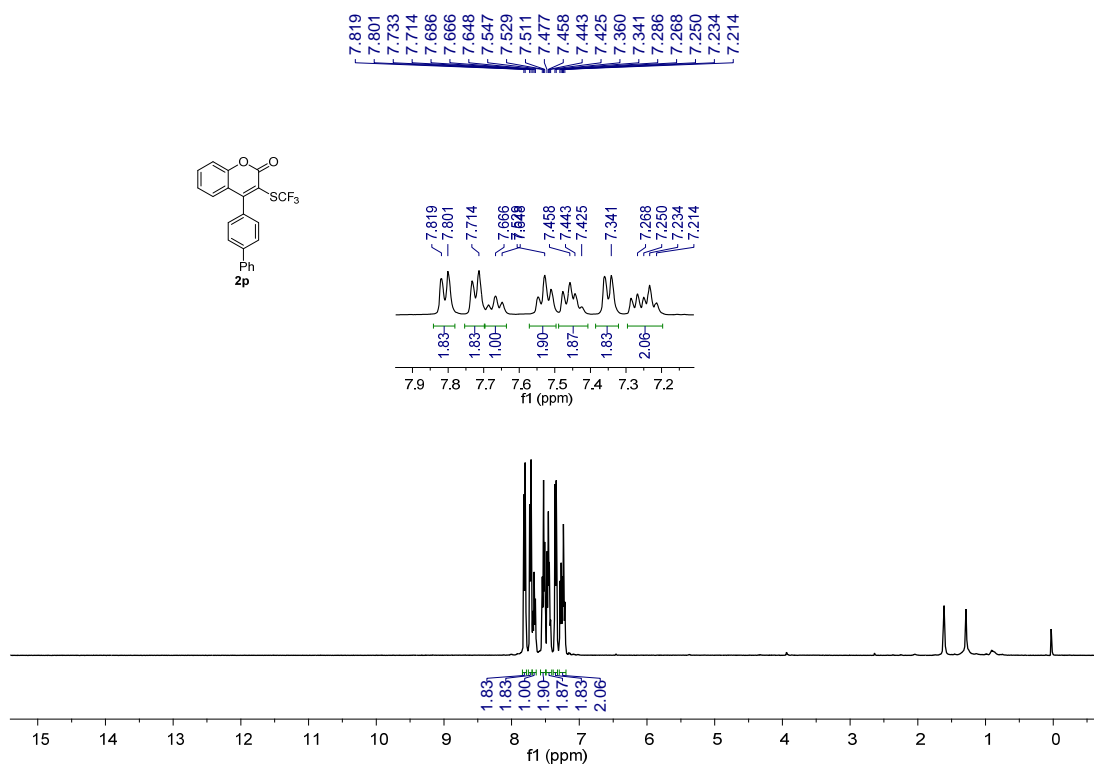
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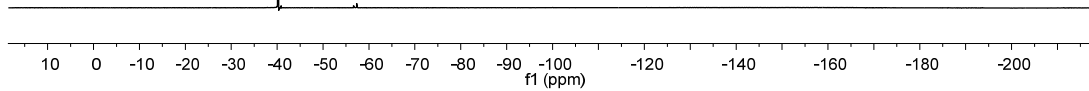
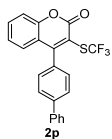


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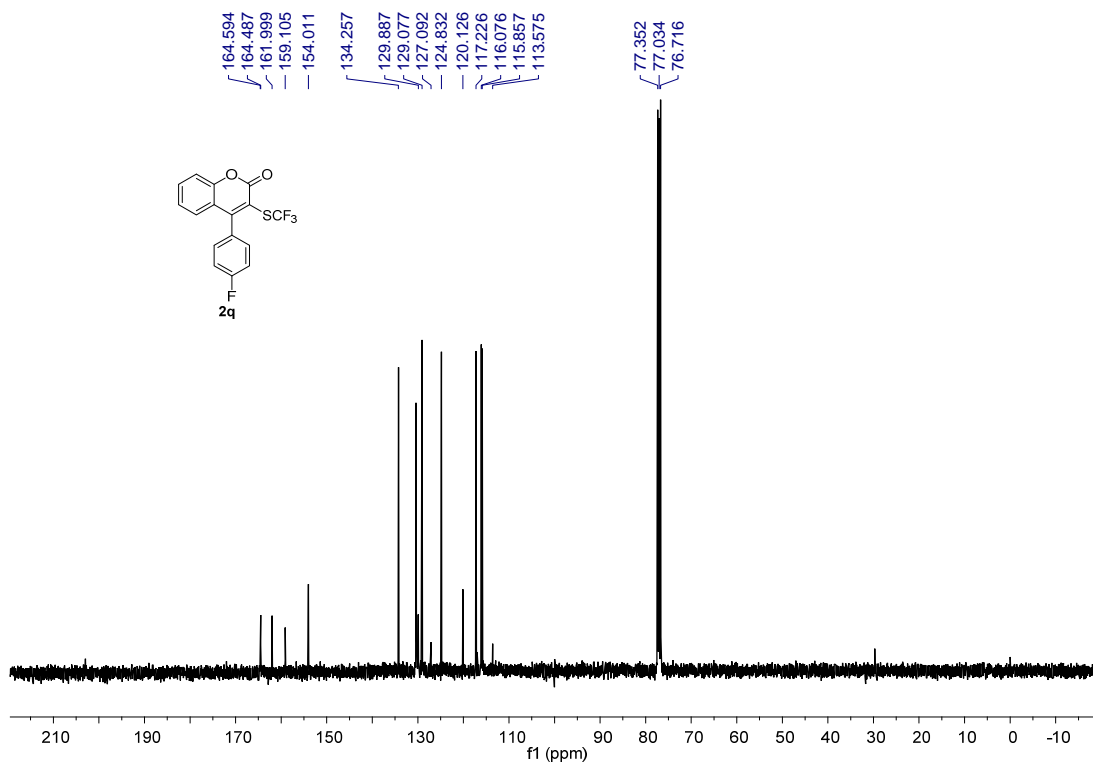
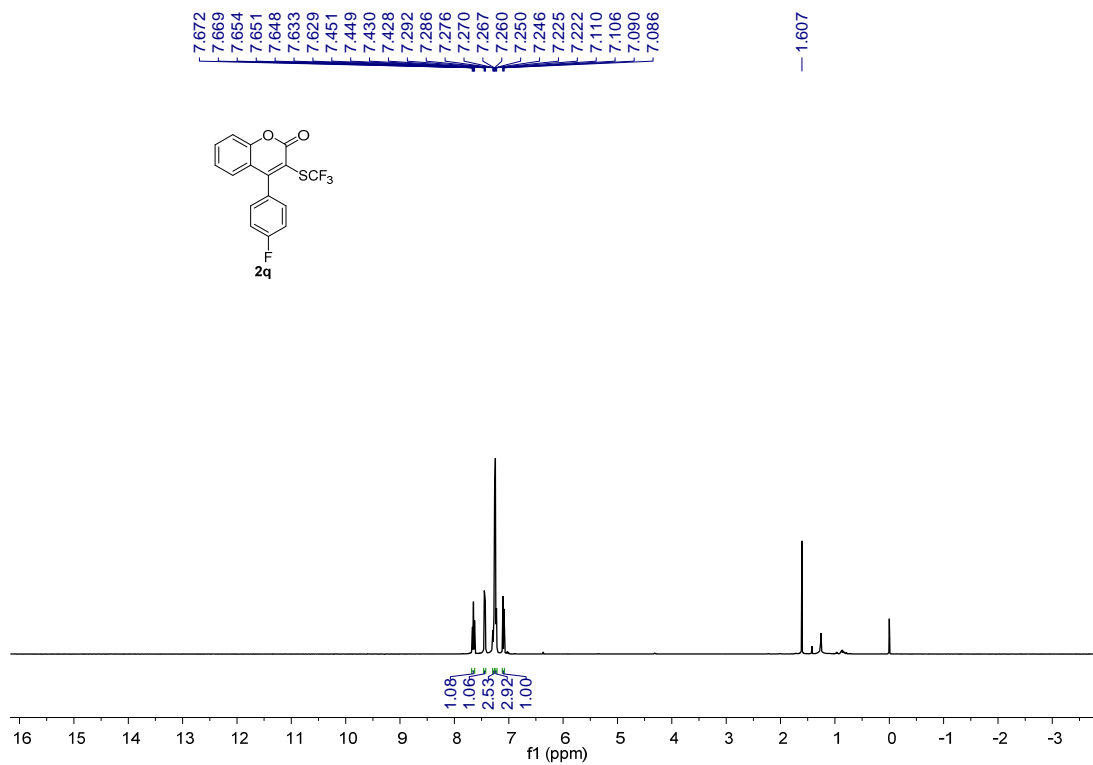


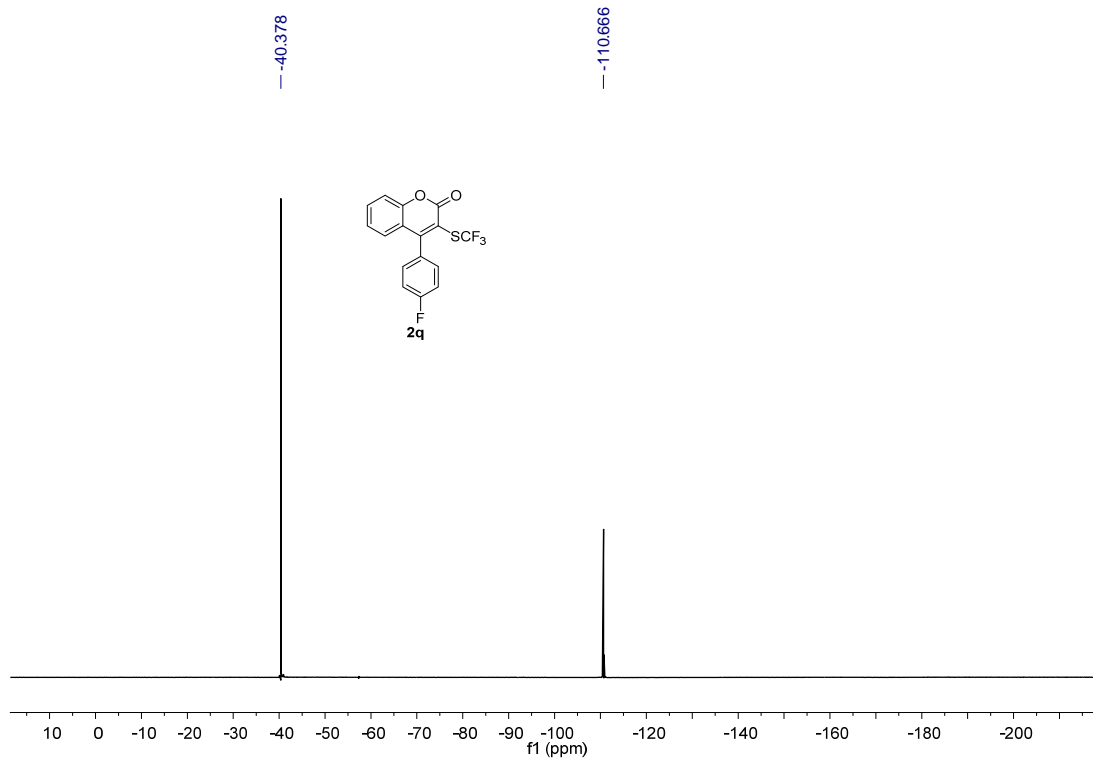


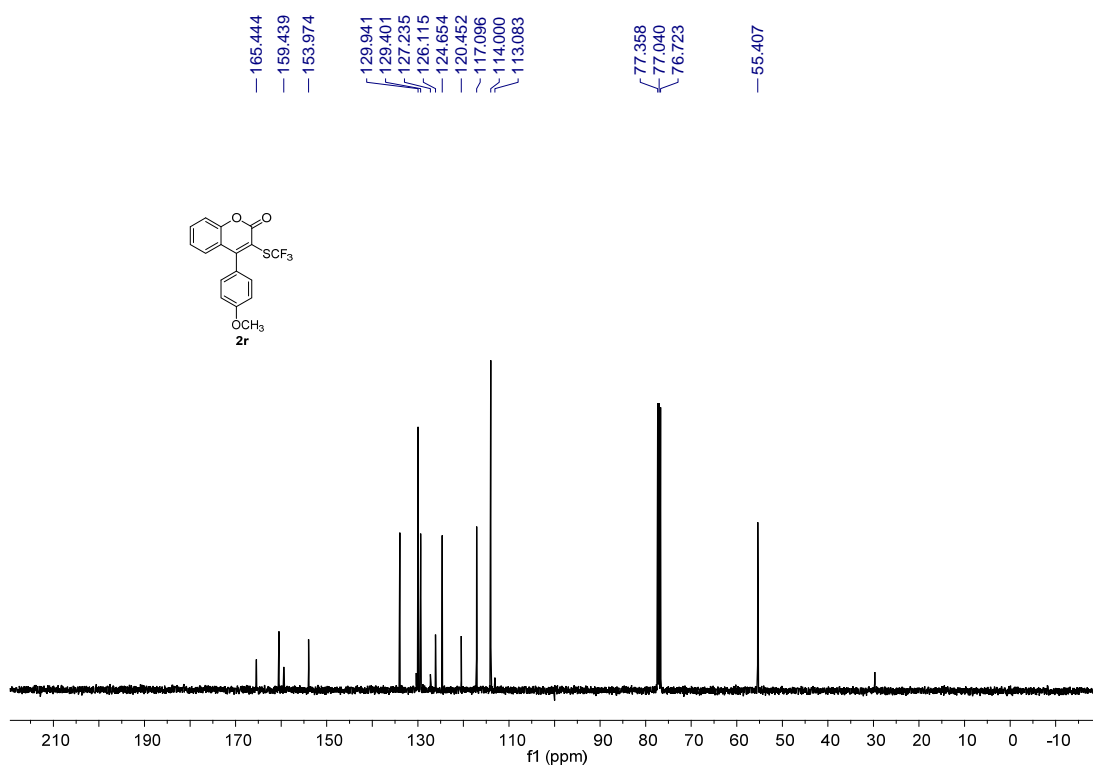
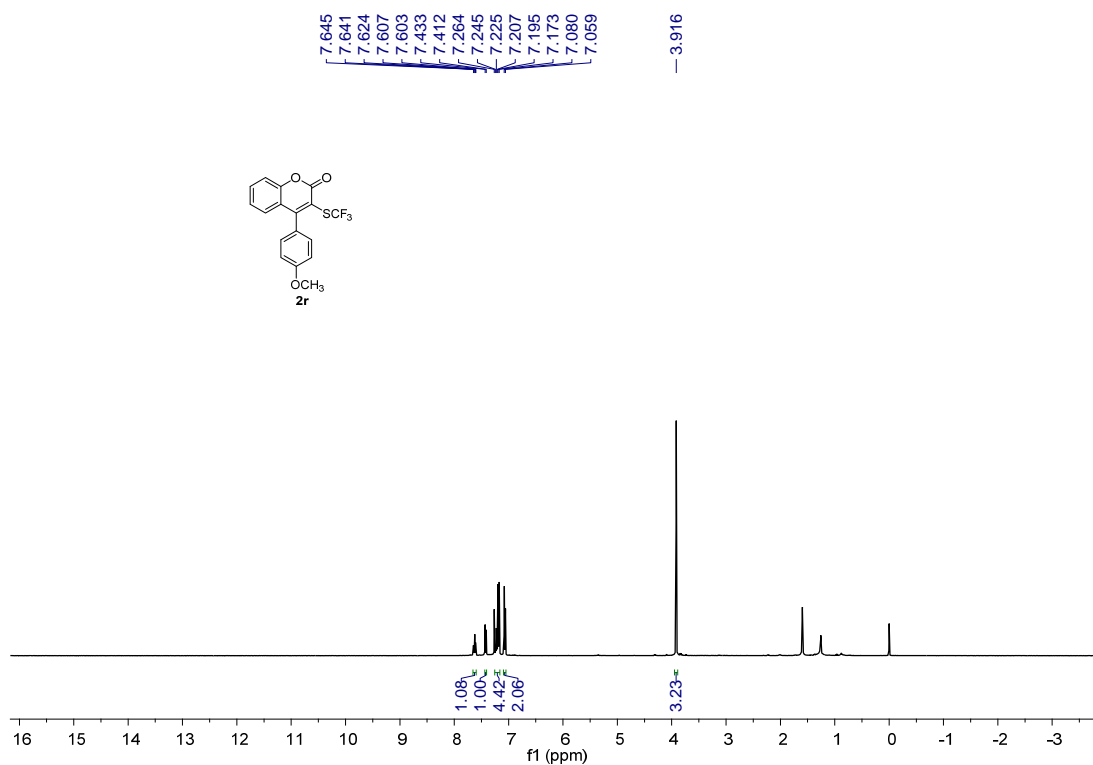
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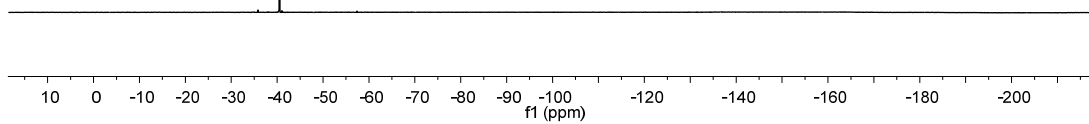
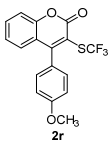


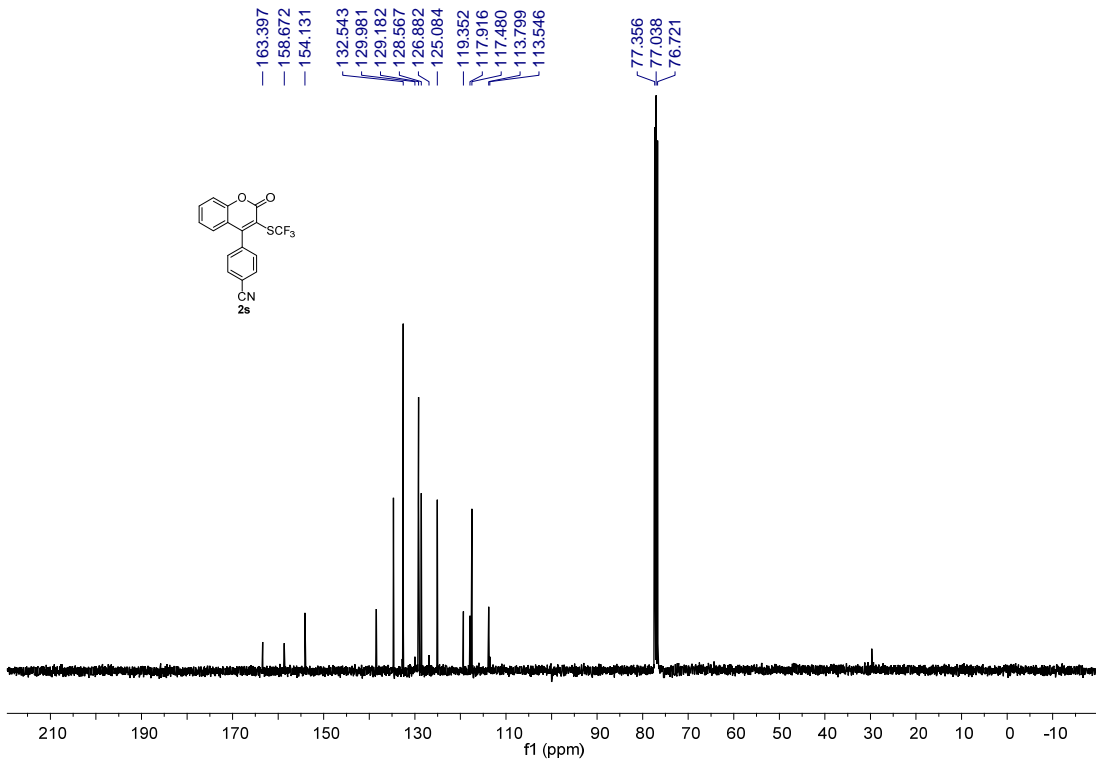
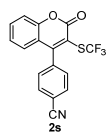
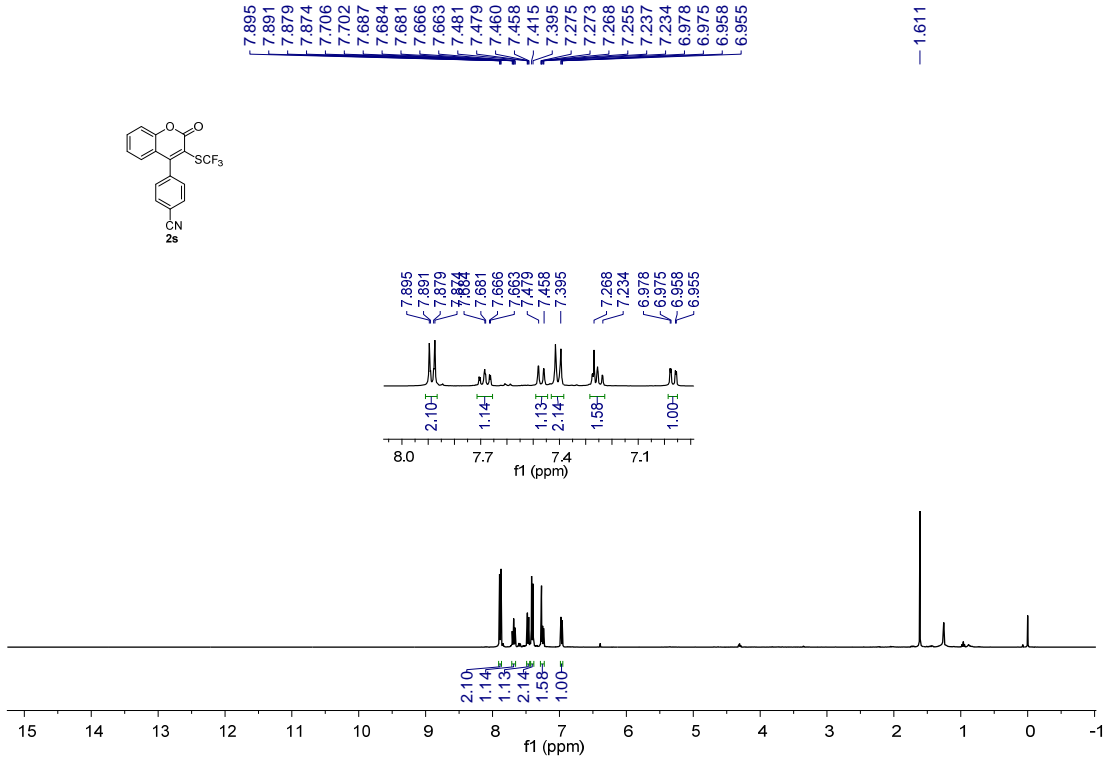
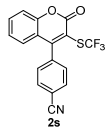


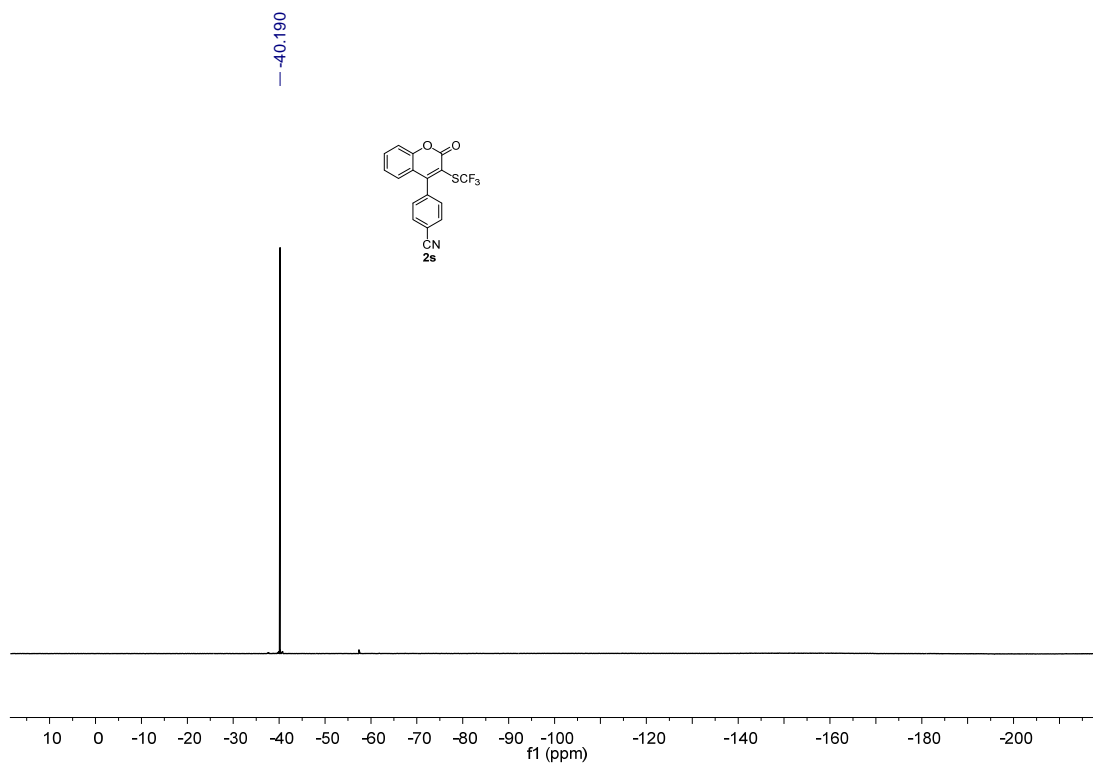


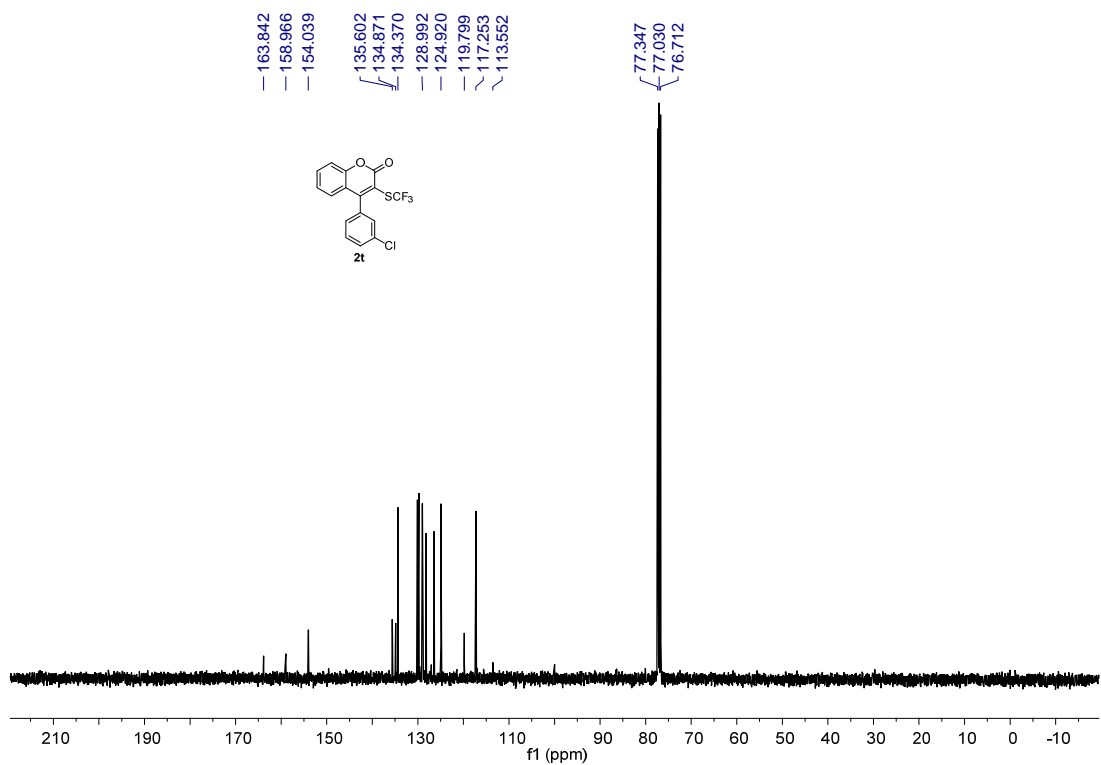
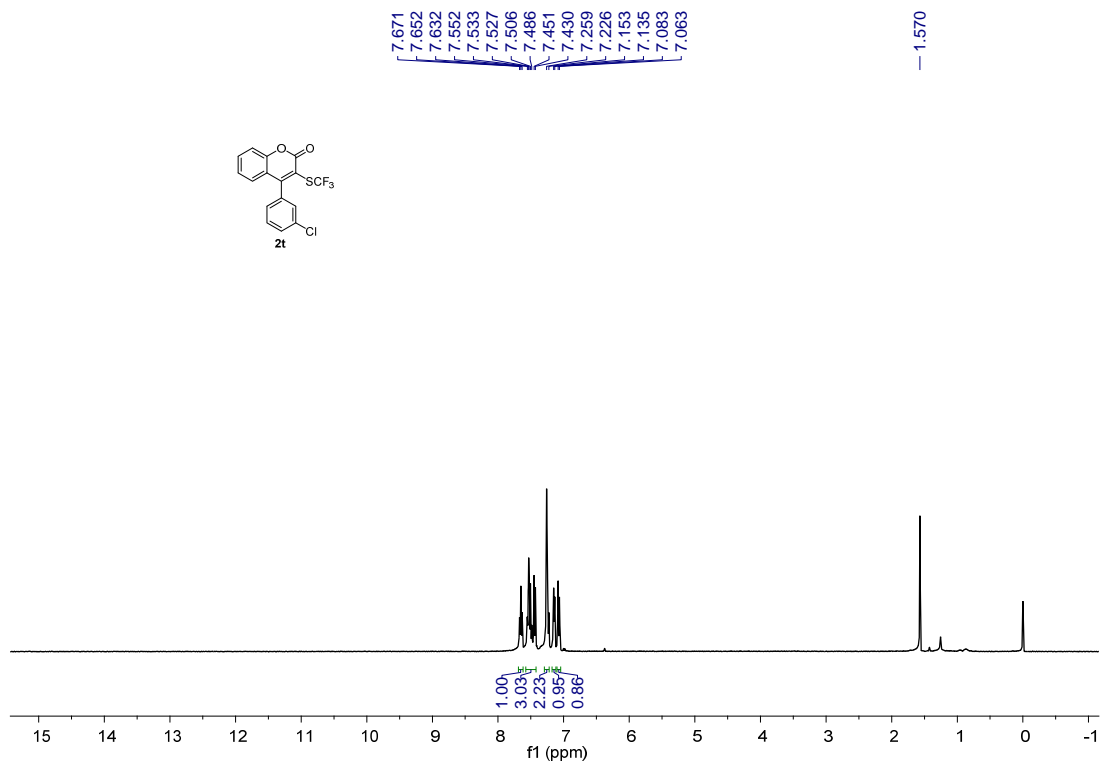


-40.484

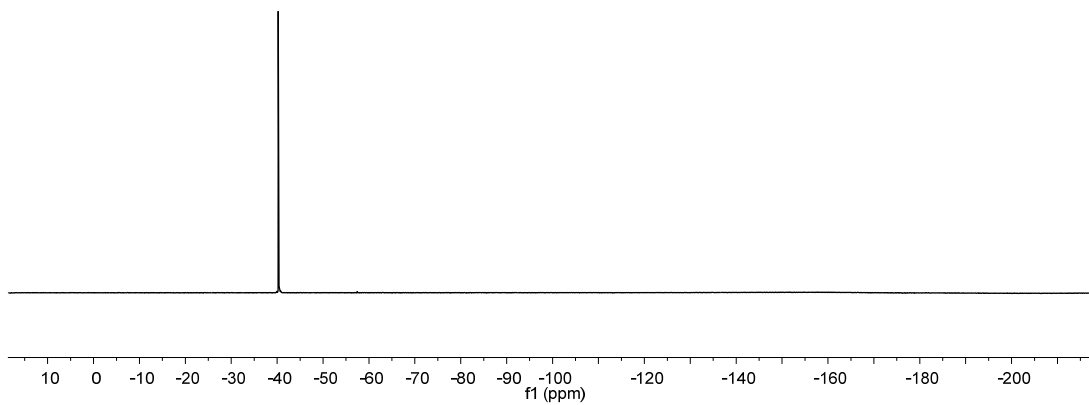
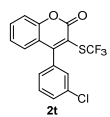




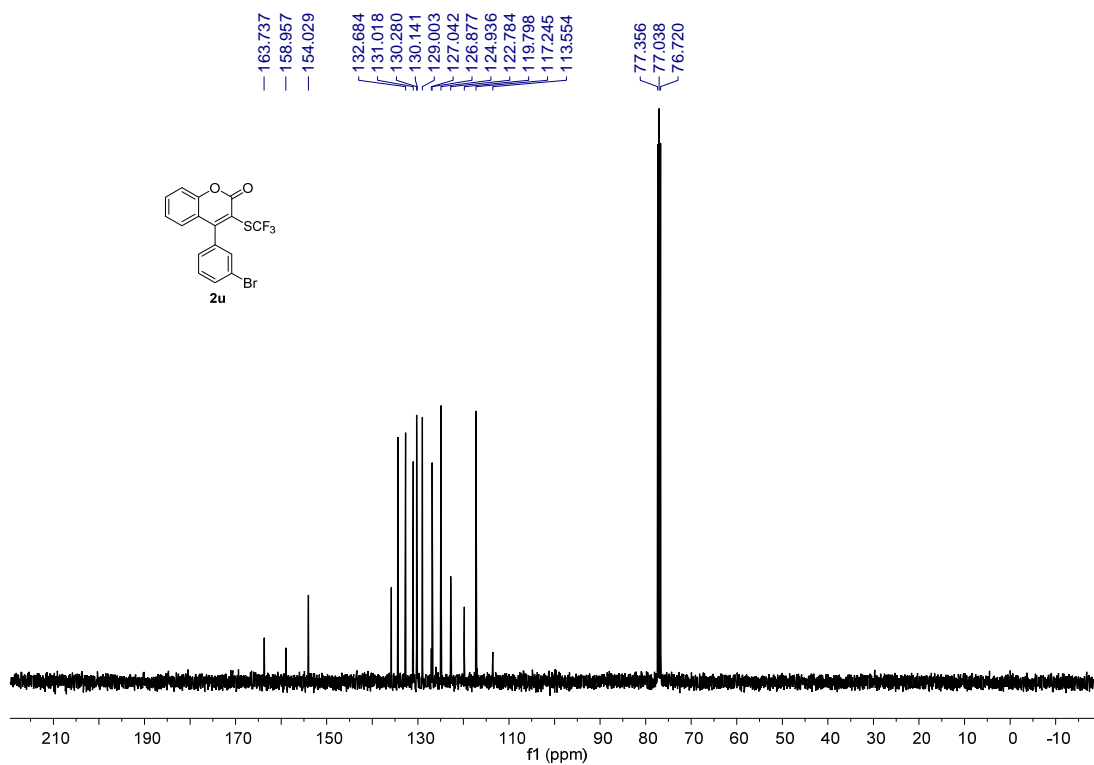
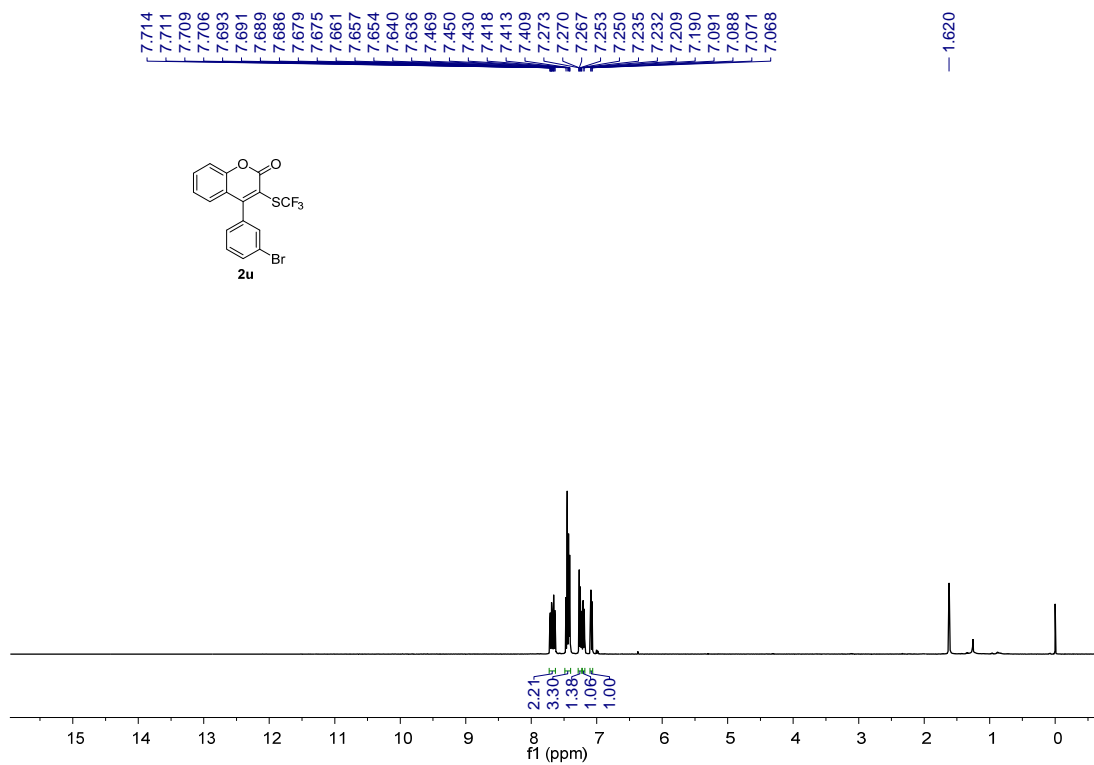




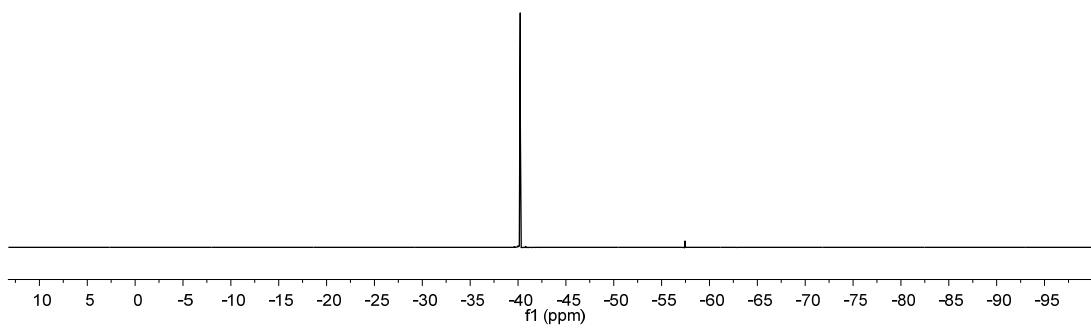
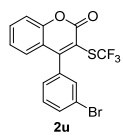
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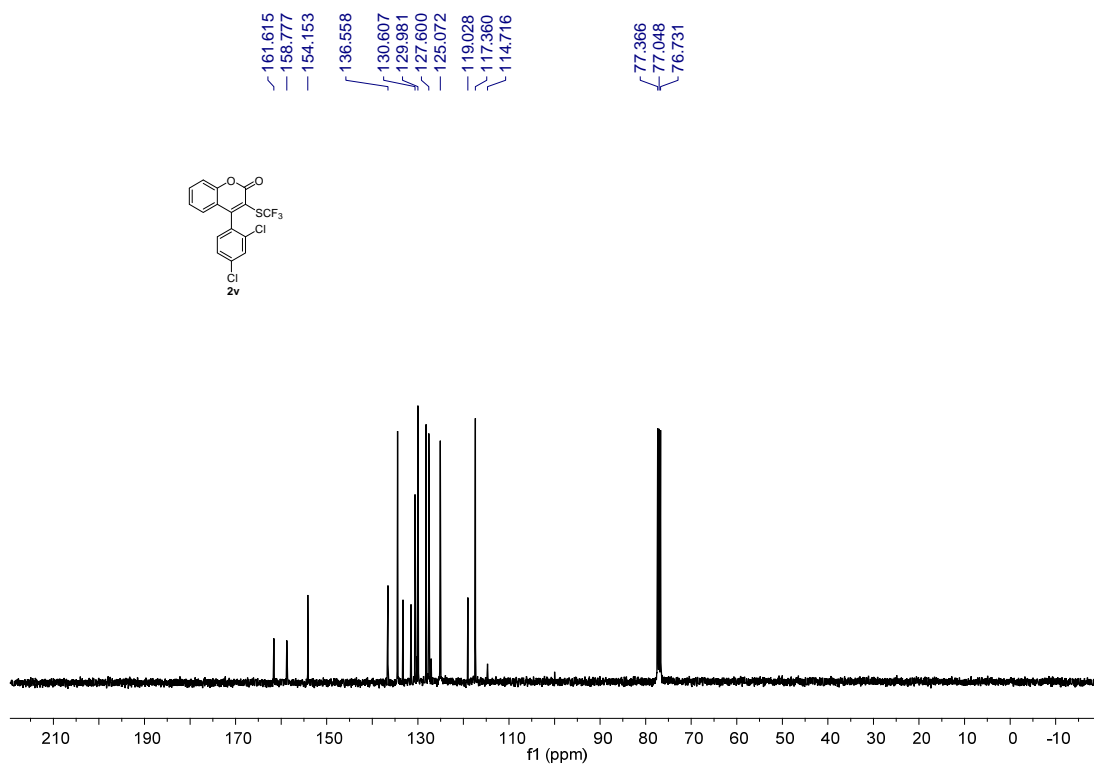
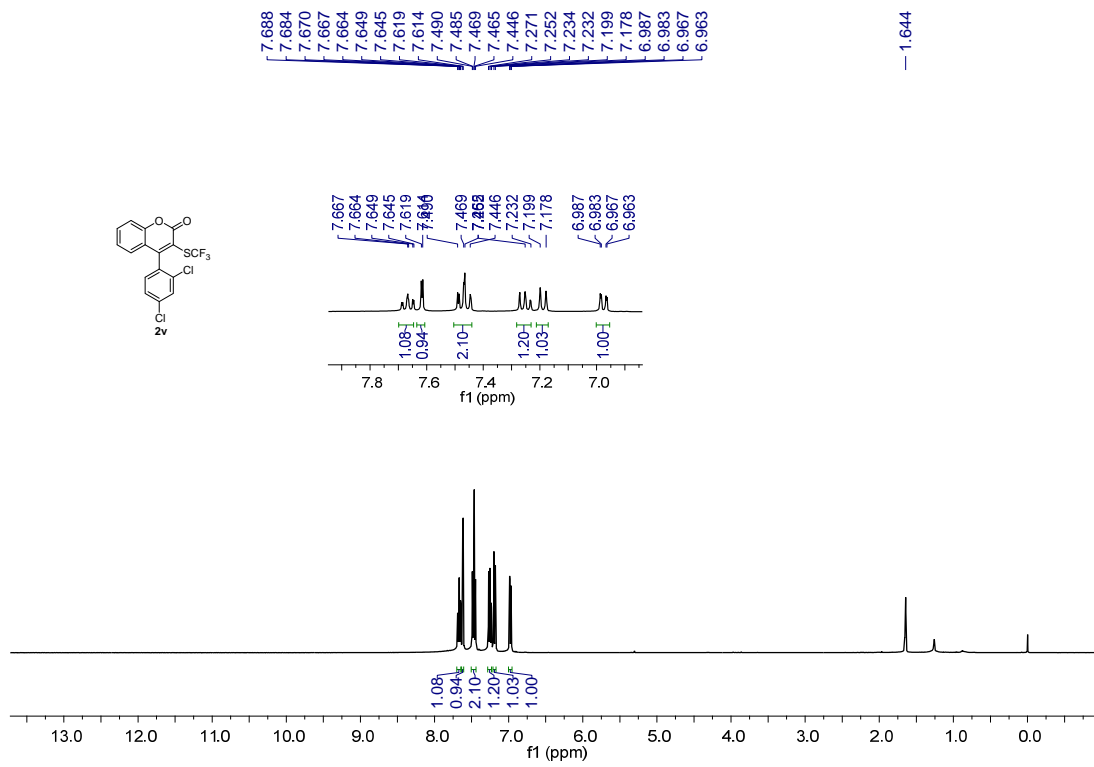


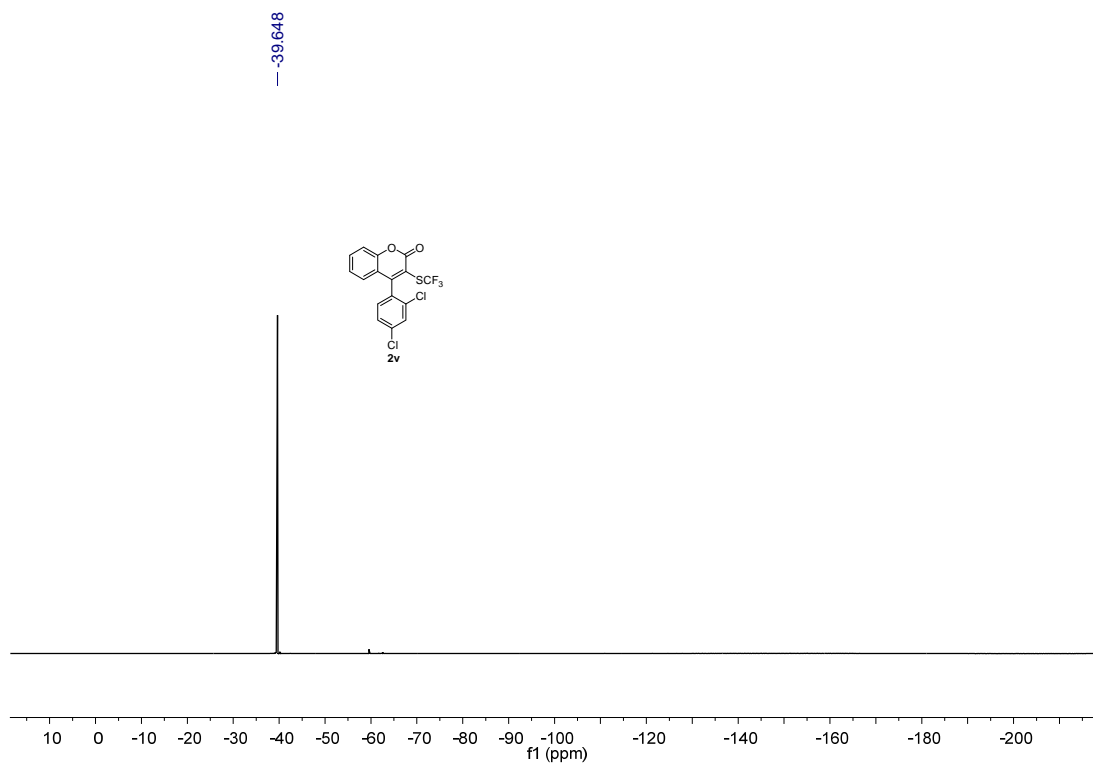


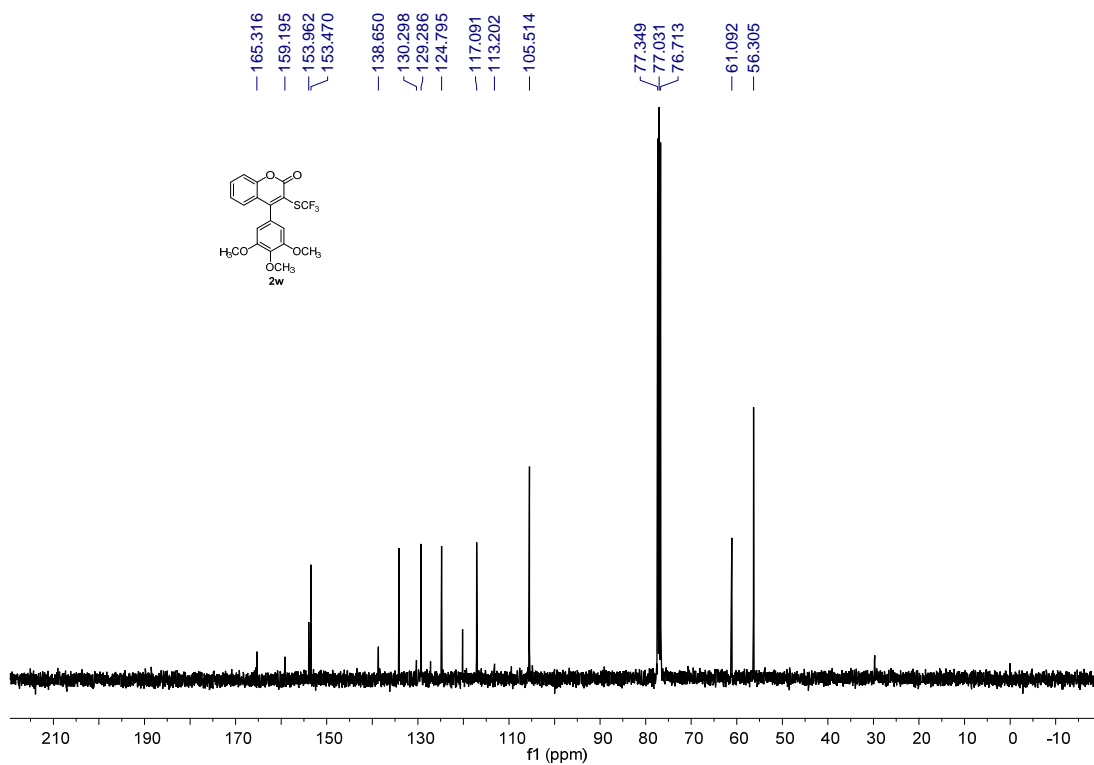
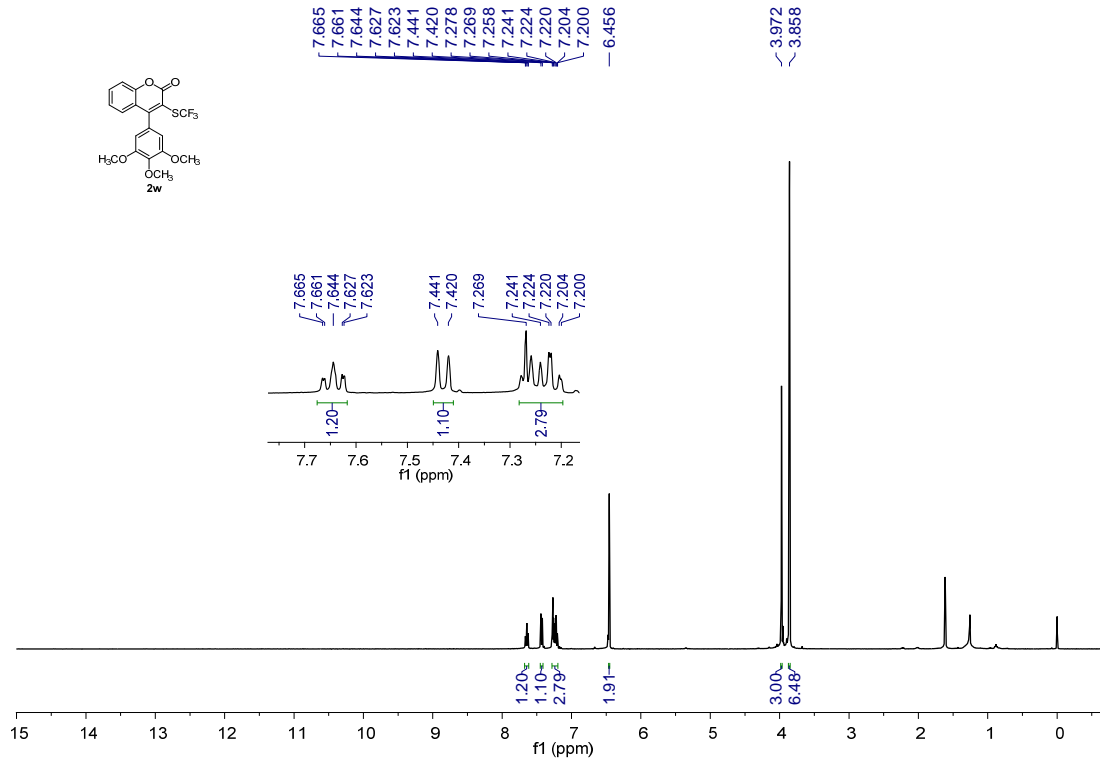


—40.240

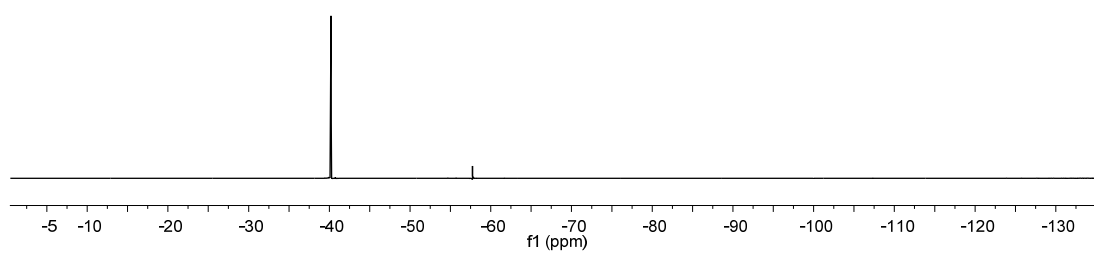
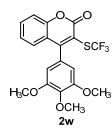


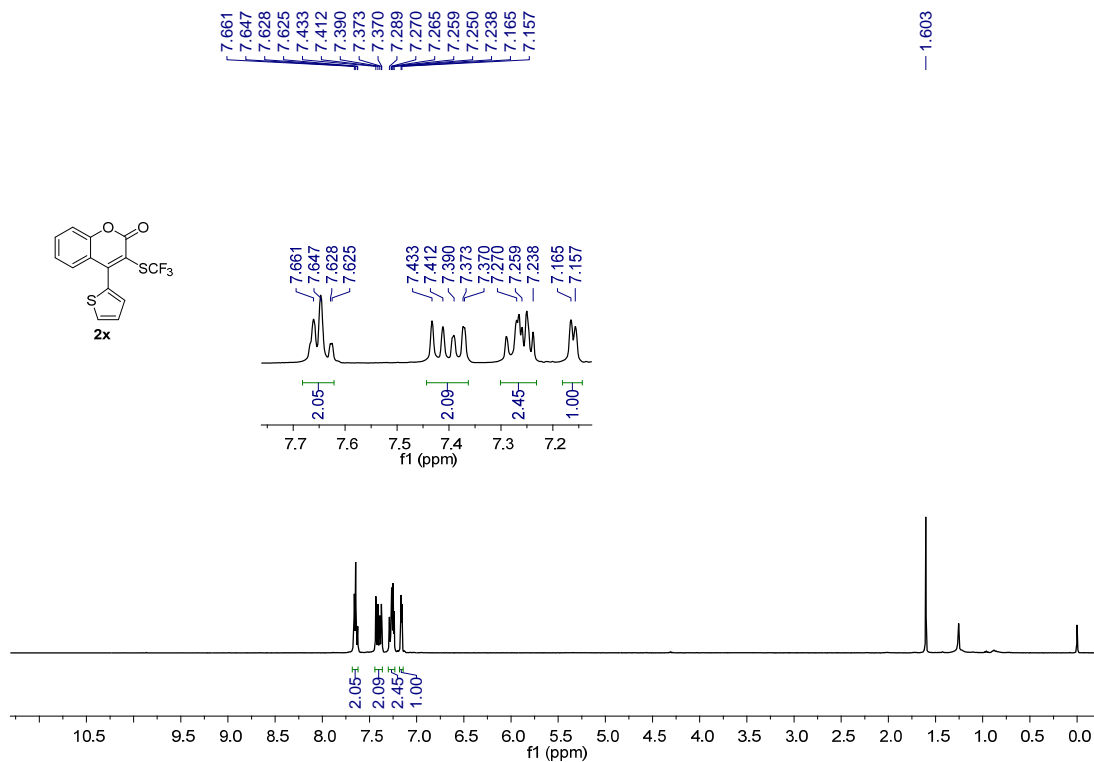




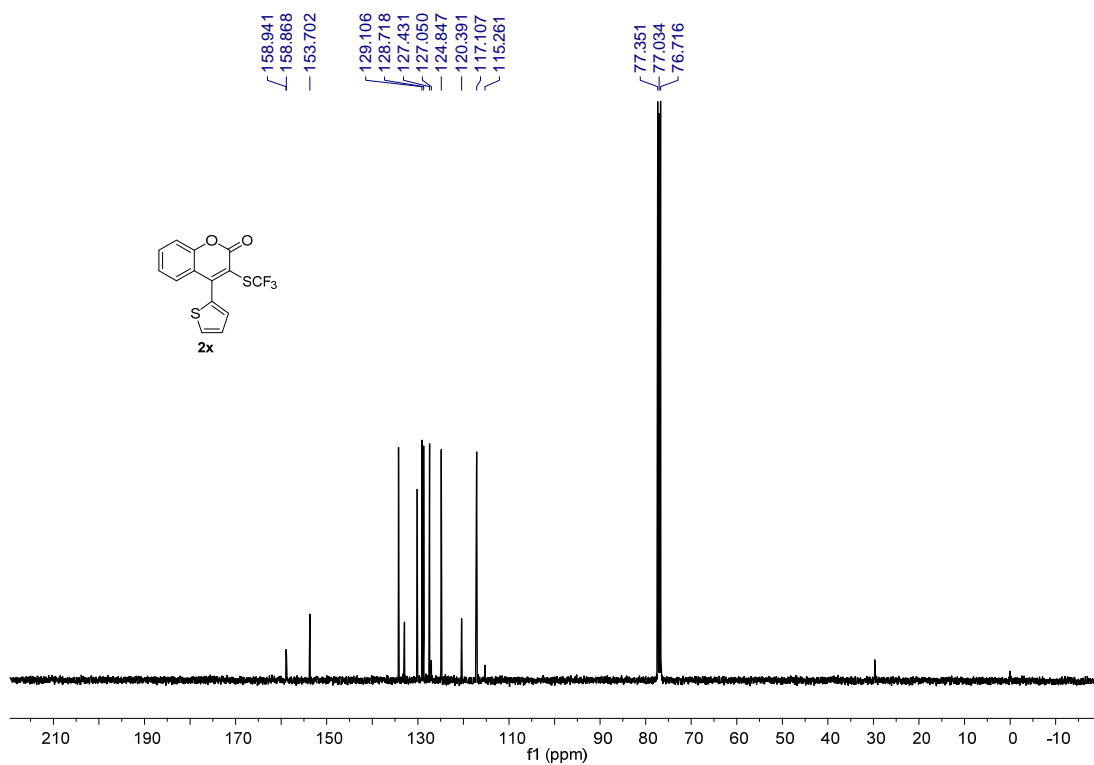


-40.207

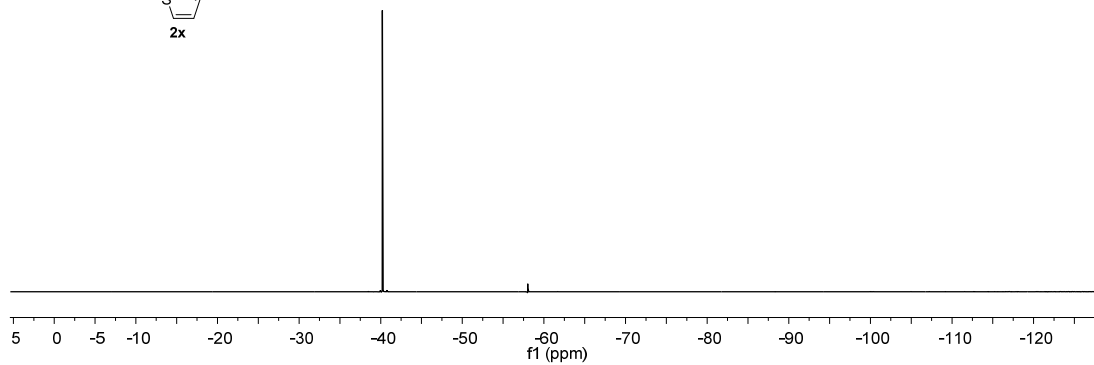
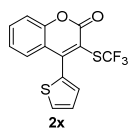




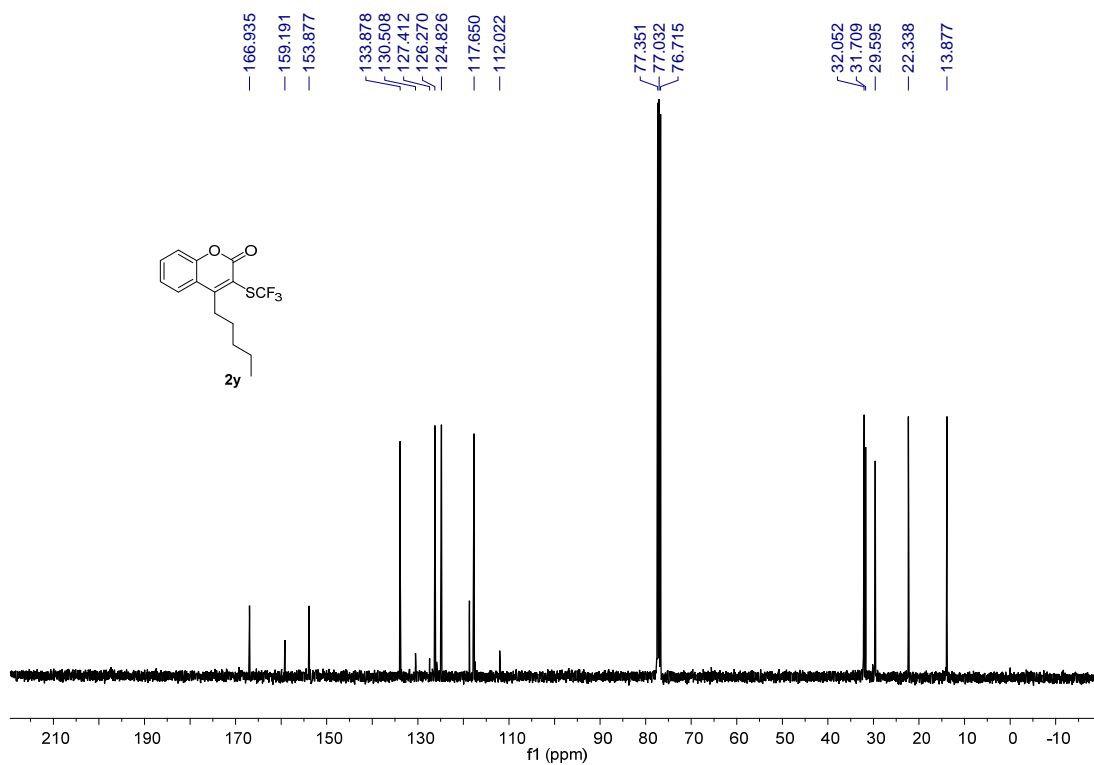
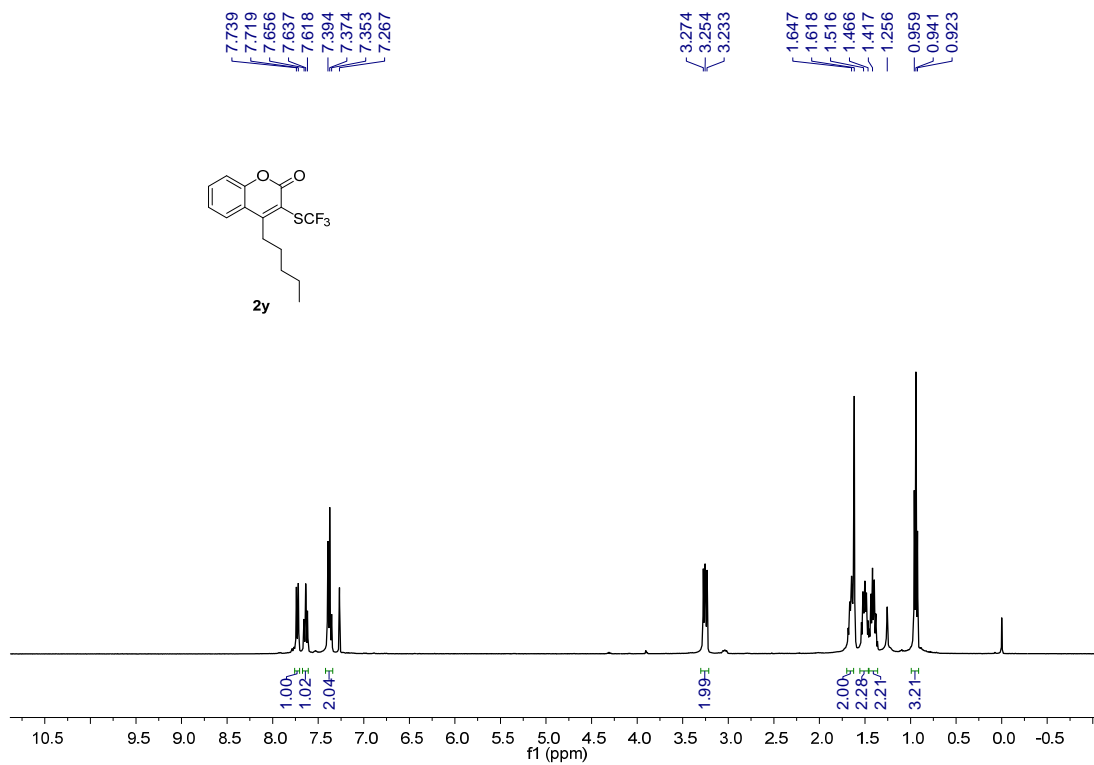
— 1.603



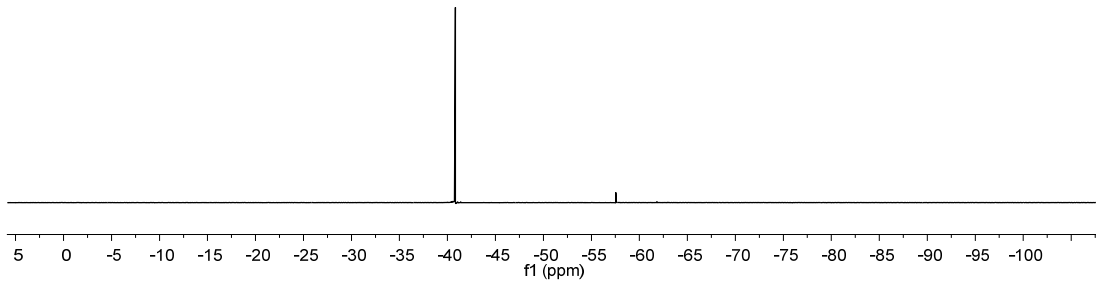
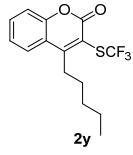
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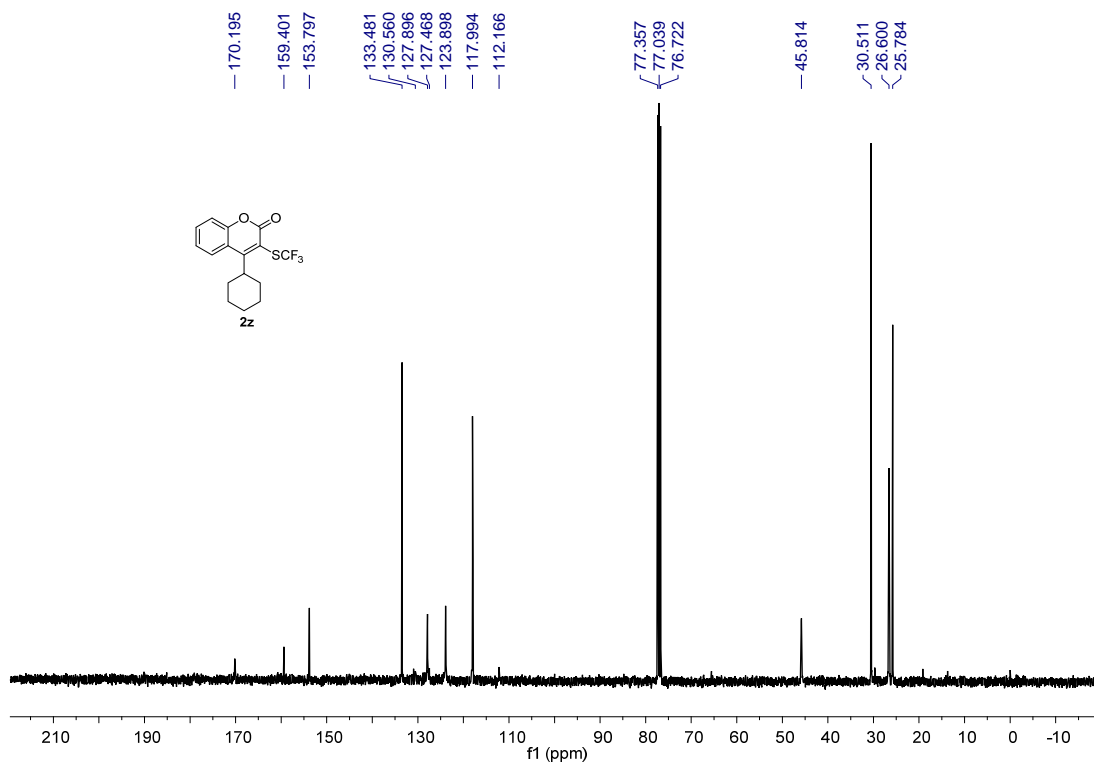
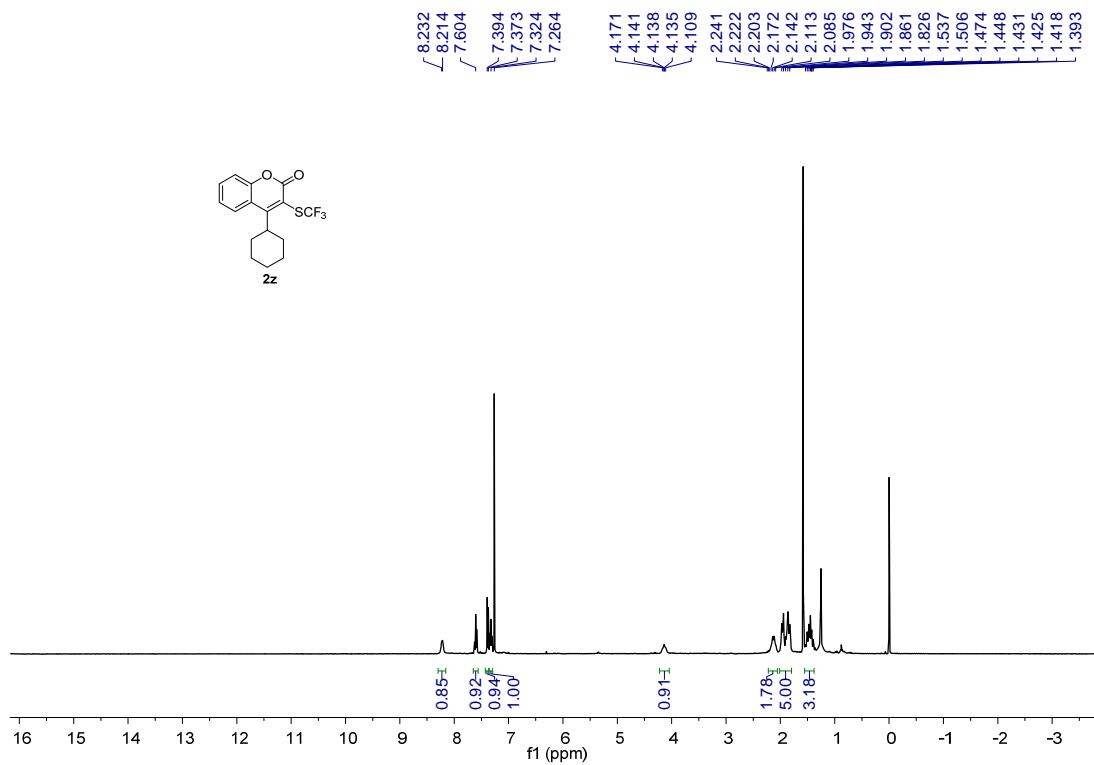






-40.822





-41.446

