

# Radical [3+2]-Cycloaddition Reaction for the Synthesis of Difluorocyclopentanones

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## 1. General experimental details

Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70,  $\nu_{\max}$  in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual  $\text{CHCl}_3$  signal as internal standard ( $\text{CDCl}_3$ :  $\delta$  7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( $\text{CDCl}_3$ :  $\delta$  77.16).  $^{19}\text{F-NMR}$  spectra were recorded on BRUKER AVANCE III HD (376MHz) and VARIAN DD2-600 (564MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT Premier<sup>TM</sup> and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

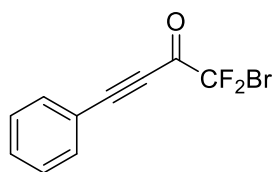
## 2. General procedure for the radical cyclization

Alkenes **1** (0.2 mmol, 1.0 equiv.), bromodifluoromethyl alkynyl ketone **2** and *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 2 mol %) were loaded in a flask which was subjected to evacuation/flushing with nitrogen for three times. DMA (2.0 mL) was added to the mixture via syringe and the mixture was then irradiated by 30 W green LEDs. The reaction was stirred at rt for 4 h. The mixture was then diluted with ethyl acetate (30 mL). The resultant organic solution was washed by H<sub>2</sub>O and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the corresponding product **3**.

## 3. Synthesis of starting materials

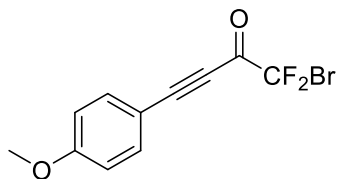
To a stirred solution of alkynes (15 mmol, 1.0 equiv.) in anhydrous THF (40 mL) was added *n*-BuLi (2.5 M in hexane, 18 mmol, 1.2 equiv.) dropwise at -78 °C. The resulting solution was stirred at the same temperature for 30 min, at which time a solution of ethyl bromodifluoroacetate (18 mmol, 1.2 equiv.) and BF<sub>3</sub>·OEt<sub>2</sub> (18 mmol, 1.2 equiv.) in anhydrous THF (8 mL) was added dropwise. After reaction was complete (ca. 1 h), water and saturated NH<sub>4</sub>Cl solution was added. The aqueous layer was separated and extracted with ethyl acetate (2 x 25 mL). The combined organic extracts were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated to give the crude product, which was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford compound **2**.

## 4. Characterization of new starting materials

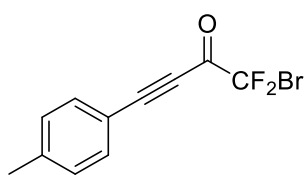


**2a**: 4.5 g, 87% yield, colorless oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.66 (m, 2H), 7.59-7.53 (m, 1H), 7.49-7.42 (m, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5 (t,  $J_{\text{C-F}}$  = 32.0 Hz), 133.9, 132.4, 128.9, 118.3, 112.9 (t,  $J_{\text{C-F}}$  = 315.0 Hz), 100.6, 82.2;  $^{19}\text{F NMR}$

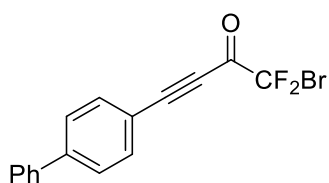
(376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.0 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3064, 2187, 1697, 1288, 684. HRMS [ESI] calcd for C<sub>10</sub>H<sub>6</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 258.9565, found 258.9567.



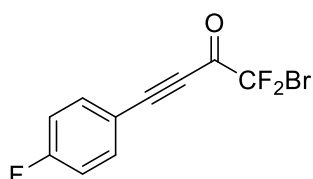
**2aa:** 0.85 g, 59% yield, brown oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65-7.60 (m, 2H), 6.96-6.92 (m, 2H), 3.87 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (t,  $J_{C-F}$  = 31.8 Hz), 163.1, 136.2, 114.8, 113.0 (t,  $J_{C-F}$  = 315.1 Hz), 110.0, 102.5, 82.8, 55.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.5 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 2938, 2842, 2173, 1794, 1419, 1297, 682. HRMS [EI] calcd for C<sub>11</sub>H<sub>7</sub>BrF<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup> 287.9597, found 287.9596.



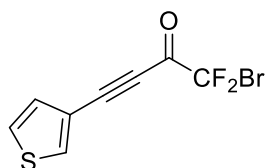
**2ab:** 1.12 g, 82% yield, colorless oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58-7.52 (m, 2H), 7.27-7.22 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (t,  $J_{C-F}$  = 32.2 Hz), 143.7, 133.9, 129.8, 115.2, 113.0 (t,  $J_{C-F}$  = 315.2 Hz), 101.6, 82.3, 21.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.8 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3649, 2181, 1694, 1603, 1148, 1046. HRMS [EI] calcd for C<sub>11</sub>H<sub>7</sub>BrF<sub>2</sub>O [M]<sup>+</sup> 271.9648, found 271.9647.



**2ac:** 1.30 g, 78% yield, yellow solid, m.p. 45-46 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.72 (m, 2H), 7.71-7.60 (m, 4H), 7.55-7.48 (m, 2H), 7.48-7.42 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (t,  $J_{C-F}$  = 32.1 Hz), 145.3, 139.4, 134.5, 129.2, 128.7, 127.5, 127.2, 116.9, 113.0 (t,  $J_{C-F}$  = 314.9 Hz), 100.9, 83.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.7 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3629, 2181, 1691, 1406, 1151, 1051. HRMS [EI] calcd for C<sub>16</sub>H<sub>9</sub>BrF<sub>2</sub>O [M]<sup>+</sup> 333.9805, found 333.9803.

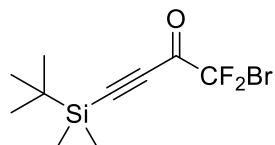


**2ad:** 1.0 g, 72% yield, colorless oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72-7.66 (m, 2H), 7.18-7.11 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.3 (t,  $J_{C-F}$  = 32.3 Hz), 165.0 (d,  $J_{C-F}$  = 255.2 Hz), 136.4 (d,  $J_{C-F}$  = 9.3 Hz), 116.6 (d,  $J_{C-F}$  = 22.4 Hz), 114.5 (d,  $J_{C-F}$  = 3.5 Hz), 112.8 (t,  $J_{C-F}$  = 315.0 Hz), 99.4, 82.2 (d,  $J_{C-F}$  = 1.0 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.1 (s), -102.8 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3107, 2186, 1697, 1236, 685. HRMS [ESI] calcd for C<sub>10</sub>H<sub>5</sub>BrF<sub>3</sub>O [M+H]<sup>+</sup> 276.9470, found 276.9478.

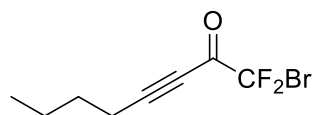


**2ae:** 0.1 g, 76% yield, brown oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97-7.94 (m, 1H), 7.42-7.38 (m, 1H), 7.32-7.29 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (t,  $J_{C-F}$  = 32.3 Hz), 137.0, 130.4, 126.9, 117.8, 112.8 (t,  $J_{C-F}$  = 315.0 Hz), 96.1, 82.8; <sup>19</sup>F NMR

(376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.9 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3113, 2184, 1691, 1272, 697. HRMS [ESI] calcd for C<sub>8</sub>H<sub>4</sub>BrF<sub>2</sub>OS [M+H]<sup>+</sup> 264.9129, found 264.9116.

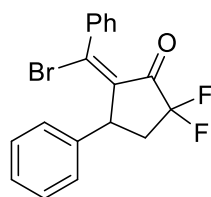


**2af:** 0.99 g, 67% yield, colorless oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 200/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.99 (s, 9H), 0.24 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.6 (t,  $J_{C-F}$  = 32.3 Hz), 112.7 (t,  $J_{C-F}$  = 314.9 Hz), 109.4, 95.8, 25.8, 16.7, -5.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.7 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 2947, 2159, 1708, 1387, 1240, 678. HRMS [CI] calcd for C<sub>10</sub>H<sub>16</sub>BrF<sub>2</sub>OSi [M+H]<sup>+</sup> 297.0116, found 297.0119.

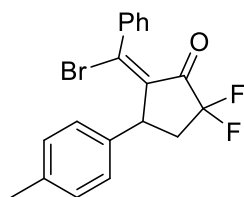


**2ag:** 1.26 g, 58% yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.51 (t,  $J$  = 7.2 Hz, 2H), 1.68-1.59 (m, 2H), 1.52-1.41 (m, 2H), 0.95 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (t,  $J_{C-F}$  = 31.9 Hz), 112.8 (t,  $J_{C-F}$  = 314.9 Hz), 105.2, 74.8, 29.2, 21.9, 19.2, 13.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.4 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>) 2962, 2213, 1707, 1258, 1158, 1126, 945. HRMS [EI] calcd for C<sub>8</sub>H<sub>9</sub>BrF<sub>2</sub>O [M]<sup>+</sup> 237.9805, found 237.9806.

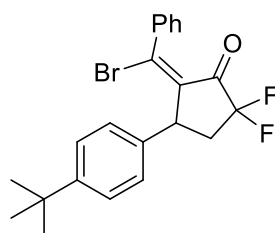
## 5. Characterization of products



**3a:** 65.2 mg, 90% yield, yellow solid, m.p. 60-61 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50-7.42 (m, 5H), 7.42-7.36 (m, 2H), 7.34-7.27 (m, 3H), 4.47 (dd,  $J$  = 9.6 Hz,  $J$  = 4.0 Hz, 1H), 2.98-2.81 (m, 1H), 2.57-2.44 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8 (t,  $J_{C-F}$  = 26.9 Hz), 148.2, 141.7, 137.9, 134.9 (t,  $J_{C-F}$  = 3.0 Hz), 130.9, 129.1, 128.9, 128.2, 127.4, 127.2, 118.0 (t,  $J_{C-F}$  = 253.4 Hz), 45.0 (dd,  $J_{C-F}$  = 4.7, 2.6 Hz), 39.3 (t,  $J_{C-F}$  = 20.6 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -104.5 (d,  $J$  = 271.5 Hz), -106.3 (d,  $J$  = 271.8 Hz). FT-IR:  $\nu$  (cm<sup>-1</sup>) 3059, 2921, 2851, 1746, 1647, 1618, 1589, 1492, 1347, 1226. HRMS [ESI] calcd for C<sub>18</sub>H<sub>13</sub>BrF<sub>2</sub>NaO [M+Na]<sup>+</sup> 385.0010, found 384.9992.

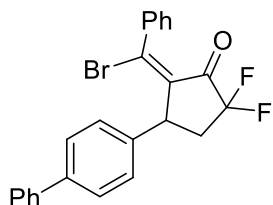


**3b:** 68.4 mg, 91% yield, yellow solid, m.p. 89-90 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48-7.38 (m, 5H), 7.21-7.14 (m, 4H), 4.43 (dd,  $J$  = 9.6, 3.6 Hz, 1H), 2.95-2.78 (m, 1H), 2.54-2.41 (m, 1H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.9 (t,  $J_{C-F}$  = 26.9 Hz), 148.0, 138.6, 138.0, 136.9, 135.1 (t,  $J_{C-F}$  = 2.3 Hz), 130.8, 129.7, 128.9, 128.2, 127.3, 118.0 (t,  $J_{C-F}$  = 253.8 Hz), 44.6 (dd,  $J_{C-F}$  = 4.5, 2.2 Hz), 39.4 (t,  $J_{C-F}$  = 20.3 Hz), 21.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -104.5 (d,  $J$  = 271.5 Hz), -106.3 (d,  $J$  = 271.5 Hz). FT-IR:  $\nu$  (cm<sup>-1</sup>) 2921, 2852, 1736, 1611, 1587, 1513, 1488, 1378, 1225. HRMS [CI] calcd for C<sub>19</sub>H<sub>16</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 377.0347, found 377.0351.

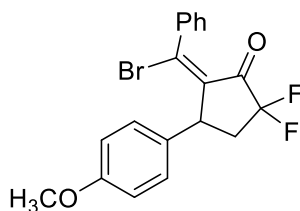


**3c:** 74.5 mg, 89% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.36 (m, 7H), 7.23-7.18 (m, 2H), 4.45 (dd,  $J$  = 9.6, 3.6 Hz, 1H), 2.96-2.79 (m, 1H), 2.58-2.45 (m, 1H),

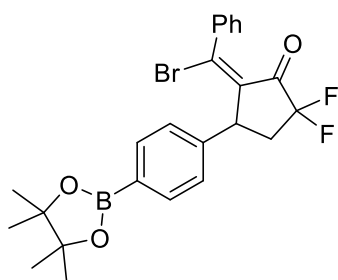
1.35 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.9 (t,  $J_{\text{C-F}} = 26.9$  Hz), 150.0, 147.9, 138.5, 138.0, 135.2 (t,  $J_{\text{C-F}} = 2.5$  Hz), 130.8, 129.0, 128.1, 127.1, 125.9, 118.0 (t,  $J_{\text{C-F}} = 253.7$  Hz), 44.5 (dd,  $J_{\text{C-F}} = 4.4$ , 2.2 Hz), 39.2 (t,  $J_{\text{C-F}} = 20.4$  Hz), 34.5, 31.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.5 (d,  $J = 271.5$  Hz), -106.0 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3056, 2962, 2867, 1736, 1585, 1517, 1487, 1394, 1251. HRMS [CI] calcd for  $\text{C}_{22}\text{H}_{22}\text{BrF}_2\text{O}$   $[\text{M}+\text{H}]^+$  419.0817, found 419.0819.



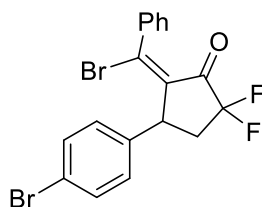
**3d:** 76.2 mg, 87% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65-7.60 (m, 4H), 7.52-7.41 (m, 7H), 7.40-7.33 (m, 3H), 4.52 (dd,  $J = 9.6$ , 4.0 Hz, 1H), 3.01-2.84 (m, 1H), 2.62-2.49 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.7 (t,  $J_{\text{C-F}} = 26.8$  Hz), 148.3, 140.7, 140.5, 140.1, 137.9, 134.9 (t,  $J_{\text{C-F}} = 2.6$  Hz), 130.9, 128.9, 128.9, 128.2, 127.9, 127.7, 127.5, 127.1, 118.0 (t,  $J_{\text{C-F}} = 253.8$  Hz), 44.7 (dd,  $J_{\text{C-F}} = 4.5$ , 2.2 Hz), 39.2 (t,  $J_{\text{C-F}} = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.2 (d,  $J = 271.8$  Hz), -106.2 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3030, 2924, 2853, 1736, 1602, 1587, 1518, 1486, 1338, 1218. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{17}\text{BrF}_2\text{NaO}$   $[\text{M}+\text{Na}]^+$  461.0323, found 461.0328.



**3e:** 71.3 mg, 91% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.38 (m, 5H), 7.22-7.17 (m, 2H), 6.93-6.88 (m, 2H), 4.42 (dd,  $J = 9.6$ , 4.0 Hz, 1H), 3.82 (s, 3H), 2.94-2.77 (m, 1H), 2.54-2.41 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.9 (t,  $J_{\text{C-F}} = 26.8$  Hz), 158.7, 148.0, 138.0, 135.3 (t,  $J_{\text{C-F}} = 2.5$  Hz), 133.7, 130.8, 128.9, 128.5, 128.2, 118.0 (t,  $J_{\text{C-F}} = 253.6$  Hz), 114.4, 55.3, 44.2 (dd,  $J_{\text{C-F}} = 4.6$ , 2.1 Hz), 39.4 (t,  $J_{\text{C-F}} = 20.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.3 (d,  $J = 271.5$  Hz), -106.4 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3002, 2934, 2837, 1735, 1647, 1610, 1583, 1463, 1339, 1221. HRMS [CI] calcd for  $\text{C}_{19}\text{H}_{16}\text{BrF}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  393.0296, found 393.0307.

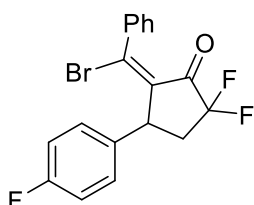


**3f:** 54.6 mg, 56% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 60/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.80 (m, 2H), 7.46-7.39 (m, 5H), 7.30-7.25 (m, 2H), 4.45 (dd,  $J = 10.0$ , 4.0 Hz, 1H), 2.97-2.82 (m, 1H), 2.53-2.40 (m, 1H), 1.34 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.7 (t,  $J_{\text{C-F}} = 26.7$  Hz), 148.3, 144.8, 137.9, 135.5, 134.7 (t,  $J_{\text{C-F}} = 2.4$  Hz), 130.9, 128.9, 128.2, 126.8, 117.9 (t,  $J_{\text{C-F}} = 253.7$  Hz), 83.9, 45.1 (dd,  $J_{\text{C-F}} = 4.1$ , 2.4 Hz), 39.2 (t,  $J_{\text{C-F}} = 20.6$  Hz), 24.9, 24.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.7 (d,  $J = 271.5$  Hz), -106.3 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2978, 2926, 1737, 1610, 1585, 1517, 1488, 1398, 1251. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{24}\text{BBrF}_2\text{NaO}_3$   $[\text{M}+\text{Na}]^+$  511.0862, found 511.0856.

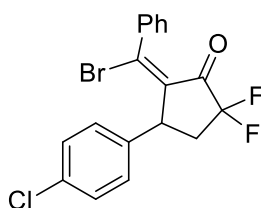


**3g:** 66.8 mg, 76% yield, yellow solid, m.p. 73-74 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.48 (m, 2H), 7.48-7.39

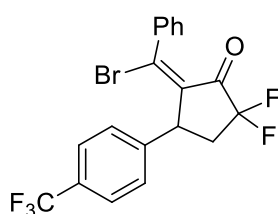
(m, 5H), 7.19-7.14 (m, 2H), 4.42 (dd,  $J = 9.6, 3.6$  Hz, 1H), 2.96-2.79 (m, 1H), 2.52-2.39 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.4 (t,  $J_{\text{C-F}} = 26.8$  Hz), 148.8, 140.7, 137.7, 134.4 (t,  $J_{\text{C-F}} = 1.8$  Hz), 132.2, 131.1, 129.2, 128.9, 128.2, 121.2, 117.9 (t,  $J_{\text{C-F}} = 253.8$  Hz), 44.5 (dd,  $J_{\text{C-F}} = 4.8, 2.0$  Hz), 39.0 (t,  $J_{\text{C-F}} = 20.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.1 (d,  $J = 271.8$  Hz), -106.7 (d,  $J = 272.2$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3061, 2918, 2849, 1737, 1613, 1588, 1487, 1336, 1225. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{12}\text{Br}_2\text{F}_2\text{NaO}$   $[\text{M}+\text{Na}]^+$  462.9115, found 462.9111.



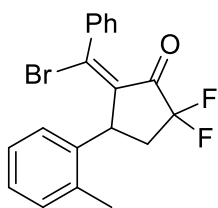
**3h:** 65.3 mg, 86% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.40 (m, 5H), 7.30-7.22 (m, 2H), 7.12-7.01 (m, 2H), 4.46 (dd,  $J = 9.6, 3.2$  Hz, 1H), 2.96-2.79 (m, 1H), 2.54-2.39 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.5 (t,  $J_{\text{C-F}} = 26.8$  Hz), 161.9 (d,  $J_{\text{C-F}} = 244.5$  Hz), 148.6, 137.8, 137.4 (d,  $J_{\text{C-F}} = 3.3$  Hz), 134.7 (t,  $J_{\text{C-F}} = 2.4$  Hz), 131.0, 129.0 (dd,  $J_{\text{C-F}} = 7.9, 0.9$  Hz), 128.9, 128.2, 117.9 (t,  $J_{\text{C-F}} = 253.9$  Hz), 116.0 (d,  $J_{\text{C-F}} = 21.6$  Hz), 44.3 (dd,  $J_{\text{C-F}} = 4.5, 1.9$  Hz), 39.2 (t,  $J_{\text{C-F}} = 20.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.1 (d,  $J = 272.6$  Hz), -106.6 (d,  $J = 271.5$  Hz), -115.1 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2958, 2919, 2849, 1736, 1645, 1601, 1584, 1466, 1377, 1206. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{12}\text{BrF}_3\text{NaO}$   $[\text{M}+\text{Na}]^+$  402.9916, found 402.9898.



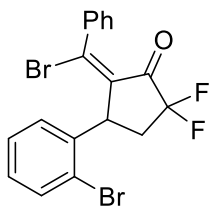
**3i:** 70.5 mg, 89% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.48 (m, 2H), 7.47-7.39 (m, 5H), 7.19-7.14 (m, 2H), 4.42 (dd,  $J = 9.6, 3.6$  Hz, 1H), 2.96-2.79 (m, 1H), 2.52-2.39 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.4 (t,  $J_{\text{C-F}} = 26.9$  Hz), 148.7, 140.1, 137.7, 134.4 (t,  $J_{\text{C-F}} = 2.5$  Hz), 133.1, 131.0, 129.2, 128.9, 128.8 (t,  $J_{\text{C-F}} = 0.9$  Hz), 128.2, 117.8 (t,  $J_{\text{C-F}} = 254.1$  Hz), 44.4 (dd,  $J_{\text{C-F}} = 4.5, 2.0$  Hz), 39.1 (t,  $J_{\text{C-F}} = 20.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.1 (d,  $J = 271.8$  Hz), -106.7 (d,  $J = 272.2$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3059, 2920, 2849, 1735, 1584, 1491, 1408, 1338, 1206. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{13}\text{BrClF}_2\text{O}$   $[\text{M}+\text{H}]^+$  396.9801, found 396.9793.



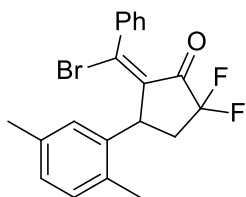
**3j:** 68.7 mg, 80% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.62 (m, 2H), 7.54-7.38 (m, 7H), 4.53 (dd,  $J = 9.6, 3.6$  Hz, 1H), 3.99-2.83 (m, 1H), 2.54-2.41 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.3 (t,  $J_{\text{C-F}} = 26.7$  Hz), 149.0, 145.7, 137.7, 134.1 (t,  $J_{\text{C-F}} = 2.0$  Hz), 131.1, 129.6 (q,  $J_{\text{C-F}} = 30.5$  Hz), 128.9, 128.3, 127.9, 126.1 (q,  $J_{\text{C-F}} = 3.6$  Hz), 124.1 (q,  $J_{\text{C-F}} = 270.6$  Hz), 117.8 (dd,  $J_{\text{C-F}} = 254.7, 252.9$  Hz), 44.8 (dd,  $J_{\text{C-F}} = 4.4, 1.6$  Hz), 38.9 (t,  $J_{\text{C-F}} = 20.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.5 (s), -103.9 (d,  $J = 273.0$  Hz), -106.8 (d,  $J = 272.2$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2921, 1737, 1584, 1507, 1489, 1444, 1322, 1207. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{13}\text{BrF}_5\text{O}$   $[\text{M}+\text{H}]^+$  431.0064, found 431.0073.



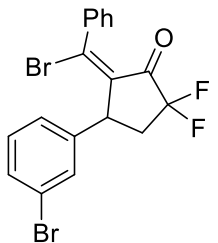
**3k:** 63.8 mg, 85% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.40 (m, 5H), 7.25-7.18 (m, 3H), 7.16-7.10 (m, 1H), 4.61 (dd,  $J = 10.0, 4.8$  Hz, 1H), 2.97-2.81 (m 1H), 2.47 (s, 3H), 2.42-2.28 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.8 (t,  $J_{\text{C-F}} = 26.9$  Hz), 147.7, 140.2, 137.9, 135.7, 135.5 (t,  $J_{\text{C-F}} = 2.3$  Hz), 130.9, 130.8, 129.0, 128.2, 127.3, 126.8, 125.7, 118.2 (t,  $J_{\text{C-F}} = 253.7$  Hz), 41.5 (t,  $J_{\text{C-F}} = 3.1$  Hz), 37.7 (t,  $J_{\text{C-F}} = 20.5$  Hz), 19.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.4 (d,  $J = 270.7$  Hz), -106.1 (d,  $J = 270.3$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3062, 2921, 2851, 1735, 1584, 1488, 1461, 1381, 1253. HRMS [CI] calcd for  $\text{C}_{19}\text{H}_{16}\text{BrF}_2\text{O}$   $[\text{M}+\text{H}]^+$  377.0347, found 377.0355.



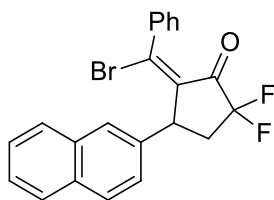
**3l:** 61.6 mg, 70% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.62 (m, 1H), 7.51-7.40 (m, 5H), 7.35-7.29 (m, 1H), 7.24-7.15 (m, 2H), 4.82 (dd,  $J = 9.6, 4.0$  Hz, 1H), 3.00-2.83 (m, 1H), 2.54-2.40 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.5 (t,  $J_{\text{C-F}} = 27.0$  Hz), 148.1, 140.4, 137.7, 134.3 (t,  $J_{\text{C-F}} = 2.5$  Hz), 133.5, 131.0, 128.9, 128.9, 128.2, 128.0, 124.3, 118.0 (t,  $J_{\text{C-F}} = 253.8$  Hz), 44.9 (t,  $J_{\text{C-F}} = 3.2$  Hz), 37.2 (t,  $J_{\text{C-F}} = 20.9$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -109.6 (d,  $J = 270.2$  Hz), -113.2 (d,  $J = 270.2$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3059, 2920, 2850, 1736, 1658, 1632, 1584, 1469, 1338, 1208. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{13}\text{Br}_2\text{F}_2\text{O}$   $[\text{M}+\text{H}]^+$  440.9296, found 440.9288.



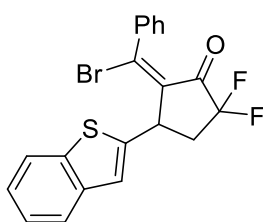
**3m:** 64.7 mg, 83% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.41 (m, 5H), 7.15-7.10 (m, 1H), 7.07-7.01 (m, 1H), 6.91 (s, 1H), 4.57 (dd,  $J = 9.6, 4.4$  Hz, 1H), 2.97-2.80 (m, 1H), 2.43 (s, 3H), 2.41-2.27 (m, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  187.0 (t,  $J_{\text{C-F}} = 26.8$  Hz), 147.5, 140.1, 137.9, 136.3, 135.7 (t,  $J_{\text{C-F}} = 2.3$  Hz), 132.5, 130.9, 130.6, 129.0, 128.2, 127.9, 126.4, 118.2 (t,  $J_{\text{C-F}} = 253.8$  Hz), 41.5 (t,  $J_{\text{C-F}} = 3.3$  Hz), 37.8 (t,  $J_{\text{C-F}} = 20.3$  Hz), 21.3, 19.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.7 (d,  $J = 271.1$  Hz), -105.7 (d,  $J = 270.7$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2922, 1736, 1584, 1500, 1489, 1380, 1253. HRMS [CI] calcd for  $\text{C}_{20}\text{H}_{18}\text{BrF}_2\text{O}$   $[\text{M}+\text{H}]^+$  391.0504, found 391.0522.



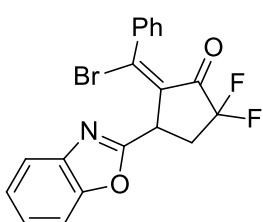
**3n:** 73.6 mg, 84% yield, yellow solid, m.p. 73-74 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.40 (m, 7H), 7.28-7.18 (m, 2H), 4.43 (dd,  $J = 9.6, 3.2$  Hz, 1H), 2.96-2.80 (m, 1H), 2.54-2.41 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.3 (t,  $J_{\text{C-F}} = 26.9$  Hz), 148.9, 143.9, 137.6, 134.1 (t,  $J_{\text{C-F}} = 2.4$  Hz), 131.1, 130.8, 130.6, 130.5, 128.9, 128.2, 125.8, 123.1, 117.8 (t,  $J_{\text{C-F}} = 253.7$  Hz), 44.6 (dd,  $J_{\text{C-F}} = 4.4, 2.1$  Hz), 39.0 (t,  $J_{\text{C-F}} = 20.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.2 (d,  $J = 271.8$  Hz), -106.6 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2923, 1737, 1684, 1591, 1541, 1457, 1374, 1220. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{13}\text{Br}_2\text{F}_2\text{O}$   $[\text{M}+\text{H}]^+$  440.9296, found 440.9302.



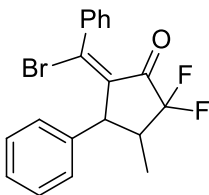
**3o:** 69.9 mg, 85% yield, yellow solid, m.p. 114-115 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91-7.81 (m, 3H), 7.73 (s, 1H), 7.55-7.42 (m, 7H), 7.42-7.37 (m, 1H), 4.63 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.04-2.87 (m, 1H), 2.65-2.51 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.8 (t, *J*<sub>C-F</sub> = 26.9 Hz), 148.5, 138.9, 137.9, 134.8 (t, *J*<sub>C-F</sub> = 2.5 Hz), 133.5, 132.5, 130.9, 129.1, 128.9, 128.2, 127.9, 127.7, 126.5, 126.3, 126.1, 125.3, 118.0 (t, *J*<sub>C-F</sub> = 253.8 Hz), 45.1 (dd, *J*<sub>C-F</sub> = 4.4, 2.4 Hz), 39.2 (t, *J*<sub>C-F</sub> = 20.7 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -104.4 (d, *J* = 271.5 Hz), -106.0 (d, *J* = 271.5 Hz). FT-IR: ν (cm<sup>-1</sup>) 3057, 2927, 1736, 1647, 1598, 1583, 1488, 1367, 1232. HRMS [CI] calcd for C<sub>22</sub>H<sub>16</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 413.0347, found 413.0340.



**3p:** 46.8 mg, 56% yield, yellow solid, m.p. 119-120 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 40/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84-7.79 (m, 1H), 7.77-7.72 (m, 1H), 7.54-7.42 (m, 5H), 7.41-7.30 (m, 2H), 7.20 (s, 1H), 4.81 (dd, *J* = 9.2, 1.6 Hz, 1H), 3.00-2.83 (m, 1H), 2.83-2.72 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 185.9 (t, *J*<sub>C-F</sub> = 26.8 Hz), 149.1, 144.8, 139.5, 139.4, 137.6, 134.3 (dd, *J*<sub>C-F</sub> = 3.2, 2.3 Hz), 131.2, 128.9, 128.3, 124.6, 124.5, 123.6, 122.4, 121.9, 117.6 (dd, *J*<sub>C-F</sub> = 254.8, 253.7 Hz), 41.2 (dd, *J*<sub>C-F</sub> = 5.7, 1.1 Hz), 39.0 (t, *J*<sub>C-F</sub> = 21.1 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -102.5 (d, *J* = 273.0 Hz), -106.4 (d, *J* = 273.0 Hz). FT-IR: ν (cm<sup>-1</sup>) 3056, 2959, 2919, 1736, 1698, 1647, 1584, 1473, 1338, 1235. HRMS [ESI] calcd for C<sub>20</sub>H<sub>14</sub>BrF<sub>2</sub>OS [M+H]<sup>+</sup> 418.9911, found 418.9912.

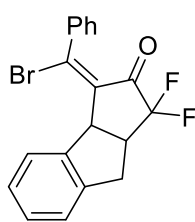


**3q:** 39.1 mg, 46% yield, yellow solid, m.p. 125-126 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 30/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79-7.72 (m, 1H), 7.59-7.49 (m, 3H), 7.49-7.41 (m, 3H), 7.41-7.34 (m, 2H), 4.81 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.02-2.80 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 184.9 (t, *J*<sub>C-F</sub> = 26.5 Hz), 164.1, 150.9, 149.8, 141.1, 137.3, 131.3, 130.6 (t, *J*<sub>C-F</sub> = 2.7 Hz), 129.0, 128.2, 125.4, 124.7, 120.3, 117.2 (t, *J*<sub>C-F</sub> = 253.8 Hz), 110.8, 39.8 (dd, *J*<sub>C-F</sub> = 4.7, 2.9 Hz), 35.6 (t, *J*<sub>C-F</sub> = 22.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -105.7 (d, *J* = 273.0 Hz), -106.7 (d, *J* = 272.6 Hz). FT-IR: ν (cm<sup>-1</sup>) 3064, 2921, 2849, 1746, 1645, 1583, 1561, 1474, 1361, 1231. HRMS [ESI] calcd for C<sub>19</sub>H<sub>12</sub>BrF<sub>2</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 425.9912, found 425.9917.

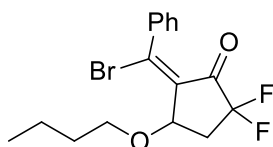


**3r:** 30.1 mg, 40% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.36 (m, 7H), 7.35-7.27 (m, 3H), 3.81 (d, *J* = 8.8 Hz, 1H), 2.47-2.30 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.7 (t, *J*<sub>C-F</sub> = 27.0 Hz), 147.7, 141.1, 138.1, 134.7 (dd, *J*<sub>C-F</sub> = 2.6, 2.4 Hz), 130.9, 129.2, 129.0, 128.0, 127.9, 127.2, 118.1 (dd, *J*<sub>C-F</sub> = 258.6, 251.9 Hz), 53.3 (d, *J*<sub>C-F</sub> = 5.7 Hz), 44.9 (dd, *J*<sub>C-F</sub> = 20.8, 18.5 Hz), 10.1 (d, *J*<sub>C-F</sub> = 7.3 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -117.0 (d, *J* = 262.4 Hz), -120.3 (d, *J* = 263.2 Hz). FT-IR: ν (cm<sup>-1</sup>) 3061, 2975, 2850, 1741, 1583, 1569, 1454, 1382, 1228. HRMS [ESI] calcd for C<sub>19</sub>H<sub>16</sub>BrF<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 377.0347, found 377.0360.

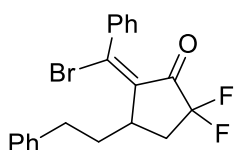




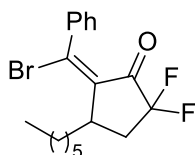
**3s:** 60.6 mg, 81% yield, yellow solid, m.p. 120-121 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75-7.70 (m, 1H), 7.48-7.38 (m, 5H), 7.33-7.22 (m, 3H), 5.09-5.02 (m, 1H), 3.42-3.24 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.4 (t, *J*<sub>C-F</sub> = 28.0 Hz), 144.5, 142.4, 139.7, 137.4, 134.5 (t, *J*<sub>C-F</sub> = 3.4 Hz), 130.3, 128.4, 127.9, 127.7, 126.7, 124.7, 124.3, 117.4 (t, *J*<sub>C-F</sub> = 256.4 Hz), 51.5 (d, *J*<sub>C-F</sub> = 6.7 Hz), 44.1 (dd, *J*<sub>C-F</sub> = 21.8, 18.9 Hz), 30.6 (d, *J*<sub>C-F</sub> = 9.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -104.9 (d, *J* = 276.7 Hz), -112.0 (d, *J* = 276.7 Hz). FT-IR: ν (cm<sup>-1</sup>) 3062, 2955, 2852, 1731, 1646, 1607, 1585, 1457, 1346, 1220. HRMS [ESI] calcd for C<sub>19</sub>H<sub>14</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 375.0191, found 375.0194.



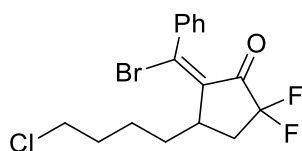
**3t:** 35.8 mg, 50% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49-7.37 (m, 5H), 4.82-4.77 (m, 1H), 3.69-3.56 (m, 2H), 2.71-2.60 (m, 1H), 2.55-2.39 (m, 1H), 1.68-1.59 (m, 2H), 1.49-1.38 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.1 (t, *J*<sub>C-F</sub> = 26.7 Hz), 149.8, 137.3, 133.5 (t, *J*<sub>C-F</sub> = 2.7 Hz), 131.2, 129.0, 128.1, 117.6 (t, *J*<sub>C-F</sub> = 254.6 Hz), 75.8 (d, *J*<sub>C-F</sub> = 7.8 Hz), 69.6, 36.7 (t, *J*<sub>C-F</sub> = 20.7 Hz), 31.8, 19.4, 13.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -101.3 (d, *J* = 274.1 Hz), -106.0 (d, *J* = 273.7 Hz). FT-IR: ν (cm<sup>-1</sup>) 2958, 2932, 2871, 1739, 1587, 1573, 1488, 1420, 1379, 1226. HRMS [ESI] calcd for C<sub>16</sub>H<sub>17</sub>BrF<sub>2</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 381.0272, found 381.0276.



**3u:** 32.7 mg, 42% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.29 (m, 7H), 7.27-7.21 (m, 3H), 3.28-3.18 (m, 1H), 2.95-2.85 (m, 1H), 2.77-2.67 (m, 1H), 2.56-2.25 (m, 3H), 1.94-1.82 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.0 (t, *J*<sub>C-F</sub> = 27.1 Hz), 144.8, 140.7, 138.0, 136.8 (dd, *J*<sub>C-F</sub> = 4.1, 2.0 Hz), 130.6, 128.7, 128.6, 128.6, 128.2, 126.4, 118.2 (dd, *J*<sub>C-F</sub> = 257.1, 250.3 Hz), 39.3 (d, *J*<sub>C-F</sub> = 5.9 Hz), 34.2, 33.7, 33.6 (dd, *J*<sub>C-F</sub> = 21.3, 19.4 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -99.9 (d, *J* = 274.5 Hz), -107.0 (d, *J* = 274.5 Hz). FT-IR: ν (cm<sup>-1</sup>) 3062, 2919, 2850, 1737, 1684, 1633, 1541, 1470, 1346, 1260. HRMS [ESI] calcd for C<sub>20</sub>H<sub>18</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 391.0504, found 391.0516.

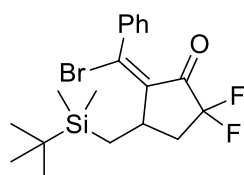


**3v:** 37.6 mg, 51% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.36 (m, 5H), 3.27-3.19 (m, 1H), 2.49-2.30 (m, 2H), 2.05-1.92 (m, 1H), 1.62-1.32 (m, 9H), 0.98-0.90 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.2 (t, *J*<sub>C-F</sub> = 27.1 Hz), 144.3, 138.1, 137.2 (dd, *J*<sub>C-F</sub> = 4.0, 2.1 Hz), 130.5, 128.7, 128.1, 118.2 (dd, *J*<sub>C-F</sub> = 256.6, 250.7 Hz), 39.9 (d, *J*<sub>C-F</sub> = 5.8 Hz), 33.9 (dd, *J*<sub>C-F</sub> = 21.1, 19.2 Hz), 32.8, 31.8, 28.9, 27.4, 22.6, 14.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -100.1 (d, *J* = 274.1 Hz), -106.4 (d, *J* = 274.5 Hz). FT-IR: ν (cm<sup>-1</sup>) 2954, 2925, 2855, 1741, 1586, 1488, 1444, 1377, 1228. HRMS [ESI] calcd for C<sub>19</sub>H<sub>16</sub>Br<sub>2</sub>F<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 371.0817, found 371.0814.

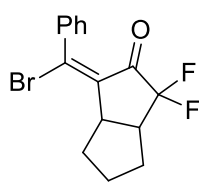


**3w:** 22.5 mg, 30% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether =

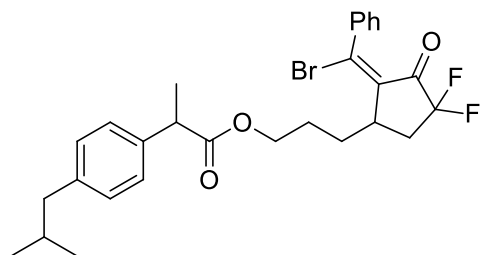
100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.35 (m, 5H), 3.66-3.55 (m, 2H), 3.28-3.19 (m, 1H), 2.50-2.32 (m, 2H), 2.06-1.80 (m, 3H), 1.76-1.52 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.9 (t, *J*<sub>C-F</sub> = 27.2 Hz), 144.8, 137.9, 136.7 (dd, *J*<sub>C-F</sub> = 4.0, 1.9 Hz), 130.6, 128.7, 128.2, 118.1 (dd, *J*<sub>C-F</sub> = 257.1, 250.1 Hz), 44.7, 39.8 (d, *J*<sub>C-F</sub> = 5.9 Hz), 33.8 (dd, *J*<sub>C-F</sub> = 21.4, 19.4 Hz), 32.0, 32.0, 24.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -99.9 (d, *J* = 274.9 Hz), -106.8 (d, *J* = 274.9 Hz). FT-IR: ν (cm<sup>-1</sup>) 2940, 2864, 1740, 1586, 1507, 1458, 1345, 1228. HRMS [ESI] calcd for C<sub>16</sub>H<sub>17</sub>BrClF<sub>2</sub>O [M+H]<sup>+</sup> 377.0114, found 377.0115.



**3x:** 38.0 mg, 46% yield, yellow solid, m.p. 109-110 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32-7.25 (m, 5H), 3.29-3.20 (m, 1H), 2.44-2.12 (m, 2H), 1.28-1.21 (m, 1H), 0.87-0.79 (m, 1H), 0.83 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.2 (t, *J*<sub>C-F</sub> = 27.0 Hz), 143.3, 139.5 (dd, *J*<sub>C-F</sub> = 3.7, 2.1 Hz), 138.0, 130.5, 128.7, 128.1, 118.3 (dd, *J*<sub>C-F</sub> = 256.6, 250.6 Hz), 36.4 (dd, *J*<sub>C-F</sub> = 13.5, 7.6 Hz), 36.3 (dd, *J*<sub>C-F</sub> = 21.1, 18.8 Hz), 26.4, 17.3, 16.7, -4.5, -5.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -99.3 (d, *J* = 274.1 Hz), -106.9 (d, *J* = 274.5 Hz). FT-IR: ν (cm<sup>-1</sup>) 2956, 2918, 2849, 1740, 1698, 1653, 1585, 1461, 1361, 1231. HRMS [ESI] calcd for C<sub>19</sub>H<sub>26</sub>BrF<sub>2</sub>OSi [M+H]<sup>+</sup> 415.0899, found 415.0905.

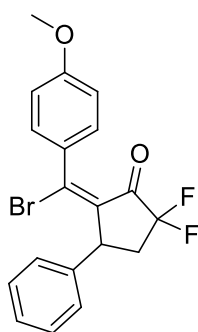


**3y:** 22.8 mg, 35% yield, yellow solid, m.p. 57-58°C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.36 (m, 5H), 3.60-3.51 (m, 1H), 2.95-2.79 (m, 1H), 2.52-2.40 (m, 1H), 2.04-1.68 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.8 (t, *J*<sub>C-F</sub> = 28.1 Hz), 144.5, 138.0, 136.7 (dd, *J*<sub>C-F</sub> = 3.8, 2.4 Hz), 130.5, 128.8, 128.1, 118.6 (dd, *J*<sub>C-F</sub> = 258.0, 250.8 Hz), 46.1 (dd, *J*<sub>C-F</sub> = 3.6, 2.0 Hz), 44.2 (dd, *J*<sub>C-F</sub> = 21.1, 18.9 Hz), 33.1, 26.7, 25.7 (dd, *J*<sub>C-F</sub> = 6.0, 3.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -101.7 (d, *J* = 270.3 Hz), -116.2 (d, *J* = 270.3 Hz). FT-IR: ν (cm<sup>-1</sup>) 3056, 2958, 2850, 1735, 1606, 1587, 1541, 1471, 1353, 1221. HRMS [ESI] calcd for C<sub>15</sub>H<sub>14</sub>BrF<sub>2</sub>O [M+H]<sup>+</sup> 327.0191, found 327.0194.

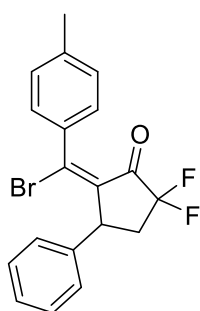


**3z:** 36.0 mg, 34% yield, *dr* = 1:1, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 30/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.34 (m, 5H, two isomers), 7.25-7.21 (m, 2H, two isomers), 7.13-7.09 (m, 2H, two isomers), 4.24-4.12 (m, 2H, two isomers), 3.73 (q, *J* = 6.8 Hz, 1H, two isomers), 3.23-3.12 (m, 1H, two isomers), 2.45 (d, *J* = 7.2 Hz, 2H, two isomers), 2.40-2.25 (m, 2H, two isomers), 2.05-1.94 (m, 1H, two isomers), 1.91-1.66 (m, 3H, two isomers), 1.62-1.49 (m, 1H, two isomers), 1.52 (d, *J* = 7.2 Hz, 3H, two isomers), 0.90 (d, *J* = 6.4 Hz, 6H, two isomers); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 186.8 (t, *J*<sub>C-F</sub> = 27.0 Hz, two isomers), 174.7 (two isomers), 144.9 (one isomer), 144.9 (one isomer), 140.6 (two isomers), 137.9 (two isomers), 137.7 (one isomer), 137.7 (one isomer), 136.6 (dd, *J*<sub>C-F</sub> = 6.2, 2.1 Hz, two isomers), 130.6 (two isomers), 129.4 (two isomers), 128.7 (two isomers), 128.2 (two isomers), 127.2 (two isomers), 118.1 (dd, *J*<sub>C-F</sub> = 257.1, 250.5 Hz, two isomers), 64.0 (one isomer), 64.0 (one isomer), 45.2 (one isomer), 45.0 (one isomer), 39.4 (d, *J*<sub>C-F</sub> = 5.7 Hz, one isomer), 33.8 (t, *J*<sub>C-F</sub> = 20.2 Hz, one isomer),

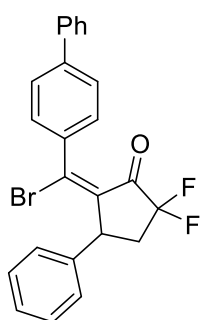
30.2 (one isomer), 29.4 (one isomer), 29.3 (one isomer), 26.5 (one isomer), 26.5 (one isomer), 22.4 (two isomers), 18.5 (one isomer), 18.5 (one isomer);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.9 (d,  $J = 274.5$  Hz, one isomer), -99.9 (d,  $J = 274.9$  Hz, one isomer), -106.9 (d,  $J = 274.5$  Hz, one isomer), -106.9 (d,  $J = 274.5$  Hz, one isomer). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3062, 2947, 2858, 1700, 1684, 1576, 1540, 1464, 1383, 1246. HRMS [ESI] calcd for  $\text{C}_{28}\text{H}_{31}\text{BrF}_2\text{NaO}_3$  [ $\text{M}+\text{Na}$ ] $^+$  555.1317, found 555.1313.



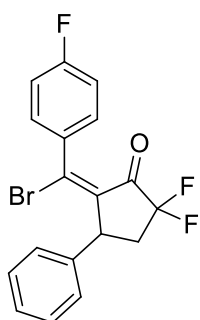
**3aa:** 53.1 mg, 68% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.47 (m, 2H), 7.40-7.33 (m, 2H), 7.31-7.25 (m, 3H), 6.95-6.89 (m, 2H), 4.46 (dd,  $J = 9.6, 4.0$  Hz, 1H), 3.87 (s, 3H), 2.96-2.79 (m, 1H), 2.54-2.40 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.5 (t,  $J_{\text{C-F}} = 26.7$  Hz), 162.1, 149.2, 142.0, 133.6 (t,  $J_{\text{C-F}} = 2.5$  Hz), 131.6, 129.9, 129.0, 127.4, 127.1, 118.2 (t,  $J_{\text{C-F}} = 253.5$  Hz), 113.4, 55.5, 45.3 (dd,  $J_{\text{C-F}} = 3.9, 2.5$  Hz), 39.3 (t,  $J_{\text{C-F}} = 20.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.3 (d,  $J = 270.7$  Hz), -105.9 (d,  $J = 270.3$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3028, 2920, 2847, 1732, 1600, 1576, 1504, 1454, 1342, 1223. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{15}\text{BrF}_2\text{NaO}_2$  [ $\text{M}+\text{Na}$ ] $^+$  415.0116, found 415.0127.



**3ab:** 68.9 mg, 92% yield, yellow solid, m.p. 95-96 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.35 (m, 4H), 7.34-7.26 (m, 3H), 7.26-7.21 (m, 2H), 4.47 (dd,  $J = 9.6, 4.0$  Hz, 1H), 2.97-2.80 (m, 1H), 2.56-2.39 (m, 1H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.7 (t,  $J_{\text{C-F}} = 26.7$  Hz), 148.9, 141.8, 141.6, 135.1, 134.4 (t,  $J_{\text{C-F}} = 2.5$  Hz), 129.2, 129.0, 128.8, 127.4, 127.2, 118.1 (t,  $J_{\text{C-F}} = 253.7$  Hz), 45.1 (dd,  $J_{\text{C-F}} = 4.4, 2.4$  Hz), 39.3 (t,  $J_{\text{C-F}} = 20.6$  Hz), 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.4 (d,  $J = 271.5$  Hz), -106.1 (d,  $J = 271.1$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3690, 2988, 1792, 1636, 1486, 1266, 1163, 1049. HRMS [EI] calcd for  $\text{C}_{19}\text{H}_{15}\text{BrF}_2\text{O}$  [ $\text{M}$ ] $^+$  376.0274, found 376.0269.

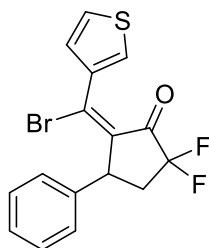


**3ac:** 75.3 mg, 86% yield, yellow solid, m.p. 127-128 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71-7.63 (m, 4H), 7.63-7.56 (m, 2H), 7.53-7.46 (m, 2H), 7.45-7.37 (m, 3H), 7.36-7.29 (m, 3H), 4.51 (dd,  $J = 9.6, 4.0$  Hz, 1H), 3.01-2.84 (m, 1H), 2.61-2.46 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.8 (t,  $J_{\text{C-F}} = 26.8$  Hz), 148.2, 143.8, 141.8, 140.0, 136.6, 134.9 (t,  $J_{\text{C-F}} = 2.3$  Hz), 129.8, 129.1, 129.0, 128.1, 127.5, 127.3, 127.3, 126.8, 118.1 (t,  $J_{\text{C-F}} = 253.7$  Hz), 45.2 (dd,  $J_{\text{C-F}} = 4.1, 2.2$  Hz), 39.3 (t,  $J_{\text{C-F}} = 20.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.3 (d,  $J = 271.5$  Hz), -106.0 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3329, 2923, 1693, 1671, 1494, 1340, 1192, 1053. HRMS [EI] calcd for  $\text{C}_{24}\text{H}_{17}\text{BrF}_2\text{O}$  [ $\text{M}$ ] $^+$  438.0431, found 438.0431.

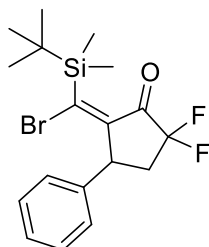


**3ad:** 73.5 mg, 91% yield, yellow solid, m.p. 67-68 °C. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.44 (m, 2H), 7.41-7.34 (m, 2H), 7.33-7.29 (m, 1H), 7.29-7.24 (m, 2H), 7.14-7.07 (m, 2H), 4.45 (dd,  $J = 9.6, 4.0$  Hz, 1H), 2.97-2.81 (m, 1H), 2.56-2.43 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.7

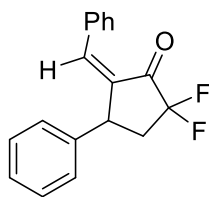
(t,  $J_{C-F} = 27.1$  Hz), 164.1 (d,  $J_{C-F} = 250.9$  Hz), 146.8, 141.6, 135.2 (t,  $J_{C-F} = 2.1$  Hz), 133.8 (d,  $J_{C-F} = 3.5$  Hz), 131.4 (d,  $J_{C-F} = 8.8$  Hz), 129.1, 127.4, 127.3, 117.9 (t,  $J_{C-F} = 253.6$  Hz), 115.3 (d,  $J_{C-F} = 22.0$  Hz), 45.0 (dd,  $J_{C-F} = 4.2, 2.5$  Hz), 39.2 (t,  $J_{C-F} = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.6 (d,  $J = 271.8$  Hz), -106.1 (d,  $J = 271.8$  Hz), -108.2 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2923, 2852, 1739, 1645, 1600, 1502, 1450, 1373, 1234. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{12}\text{BrF}_3\text{NaO}$  [ $\text{M}+\text{Na}$ ] $^+$  402.9916, found 402.9896.



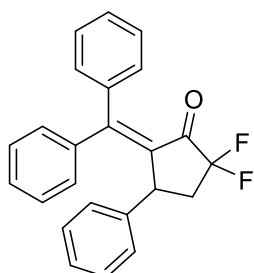
**3ae:** 45.4 mg, 62% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99-7.94 (m, 1H), 7.42-7.34 (m, 3H), 7.34-7.23 (m, 4H), 4.54-4.45 (m, 1H), 2.99-2.81 (m, 1H), 2.57-2.42 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  186.5 (t,  $J_{C-F} = 26.7$  Hz), 142.0, 141.7, 137.7, 134.0 (t,  $J_{C-F} = 2.1$  Hz), 131.1, 129.1, 129.0, 127.4, 127.2, 124.9, 118.2 (dd,  $J_{C-F} = 252.9, 251.1$  Hz), 45.6 (t,  $J_{C-F} = 3.4$  Hz), 39.3 (t,  $J_{C-F} = 20.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.4 (d,  $J = 270.0$  Hz), -105.4 (d,  $J = 270.0$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3028, 2923, 2851, 1731, 1559, 1508, 1493, 1363, 1218. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{11}\text{BrF}_2\text{NaOS}$  [ $\text{M}+\text{Na}$ ] $^+$  390.9574, found 390.9573.



**3af:** 45.7 mg, 57% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.18-7.13 (m, 2H), 4.47 (dd,  $J = 10.0, 2.8$  Hz, 1H), 2.94-2.77 (m, 1H), 2.55-2.42 (m, 1H), 1.03 (s, 9H), 0.41 (s, 3H), 0.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.8 (t,  $J_{C-F} = 26.6$  Hz), 160.3, 149.0, 141.7, 129.0, 127.2, 127.0, 117.5 (t,  $J_{C-F} = 253.6$  Hz), 46.5 (dd,  $J_{C-F} = 3.9, 3.0$  Hz), 39.3 (t,  $J_{C-F} = 20.4$  Hz), 27.5, 19.6, -1.7, -3.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -104.8 (d,  $J = 271.5$  Hz), -105.6 (d,  $J = 270.3$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3063, 2946, 2867, 1739, 1646, 1603, 1542, 1465, 1385, 1217. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{23}\text{BrF}_2\text{NaOSi}$  [ $\text{M}+\text{Na}$ ] $^+$  423.0562, found 423.0554.

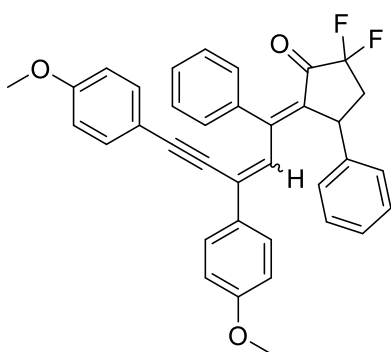


**4:** 23.1 mg, 82% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 2.0$  Hz, 1H), 7.38-7.16 (m, 10H), 4.62-4.55 (m, 1H), 2.92-2.75 (m, 1H), 2.61-2.47 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.2 (t,  $J_{C-F} = 25.6$  Hz), 141.9, 141.1, 133.2, 132.5 (t,  $J_{C-F} = 2.4$  Hz), 131.9, 131.1, 129.1, 128.7, 127.3, 127.2, 117.6 (t,  $J_{C-F} = 253.3$  Hz), 40.8 (dd,  $J_{C-F} = 5.3, 1.7$  Hz), 40.8 (t,  $J_{C-F} = 19.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.9 (d,  $J = 275.6$  Hz), -111.0 (d,  $J = 275.6$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 2925, 1732, 1611, 1447, 1188, 1073, 1002. HRMS [EI] calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_2\text{O}$  [ $\text{M}$ ] $^+$  284.1013, found 284.1013.



**5:** 54.1 mg, 75% yield, yellow oil. The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.33 (m, 3H), 7.28-7.04 (m, 8H), 6.98-6.92 (m, 2H), 6.90-6.85 (m, 2H), 4.36 (dd,  $J = 8.4, 7.2$  Hz, 1H), 2.92-2.77 (m, 1H), 2.45-2.30 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2 (t,  $J_{C-F} = 25.3$  Hz), 160.4, 143.3, 140.4, 139.0, 132.4 (t,  $J_{C-F} = 2.6$  Hz), 129.8, 129.7, 129.0,

129.0, 128.5, 128.0, 128.0, 127.4, 126.5, 117.7 (dd,  $J_{C-F} = 254.9, 250.3$  Hz), 42.1 (t,  $J_{C-F} = 3.3$  Hz), 40.3 (dd,  $J_{C-F} = 21.3, 19.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.6 (d,  $J = 271.5$  Hz), -108.5 (d,  $J = 271.5$  Hz). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3026, 2957, 2853, 1713, 1577, 1549, 1455, 1325, 1233. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_2\text{NaO}$   $[\text{M}+\text{Na}]^+$  383.1218, found 383.1233.



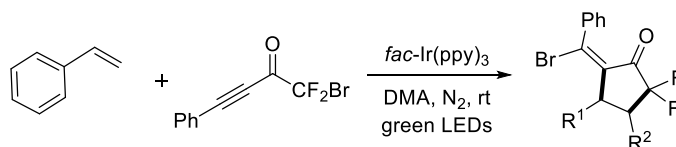
**6:** 41.3 mg, 76% yield, Z/E = 15.7:1, red solid, m.p. 165-166 °C.

The crude product was purified by flash column chromatography (eluent: ethyl acetate/petroleum ether = 100/1). Major isomer:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (s, 1H), 7.86-7.80 (m, 2H), 7.18-7.03 (m, 6H), 7.01-6.85 (m, 6H), 6.85-6.79 (m, 2H), 6.73-6.67 (m, 2H), 4.11 (dd,  $J = 9.2, 3.6$  Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 2.83-2.65 (m, 1H), 2.42-2.26 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3 (t,  $J_{C-F} = 25.7$  Hz), 160.8, 159.9, 157.2, 144.6, 137.8, 133.6, 133.4, 132.4 (t,  $J_{C-F} = 2.4$  Hz), 132.1,

129.0, 128.9, 128.7, 128.4, 128.4, 127.9, 127.4, 126.3, 118.0 (t,  $J_{C-F} = 251.7$  Hz), 114.6, 114.0, 113.5, 104.9, 86.8, 55.4, 55.3, 41.9 (dd,  $J_{C-F} = 4.2, 2.4$  Hz), 40.0 (t,  $J_{C-F} = 20.5$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -103.1 (d,  $J = 271.5$  Hz, Z isomer), -105.9 (d,  $J = 271.5$  Hz, Z isomer), -107.1 (d,  $J = 268.8$  Hz, E isomer), -108.9 (d,  $J = 268.8$  Hz, E isomer). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 1698, 1601, 1509, 1375, 1251, 1032, 1019. HRMS [EI] calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_2\text{O}$   $[\text{M}]^+$  546.2007, found 546.2010.

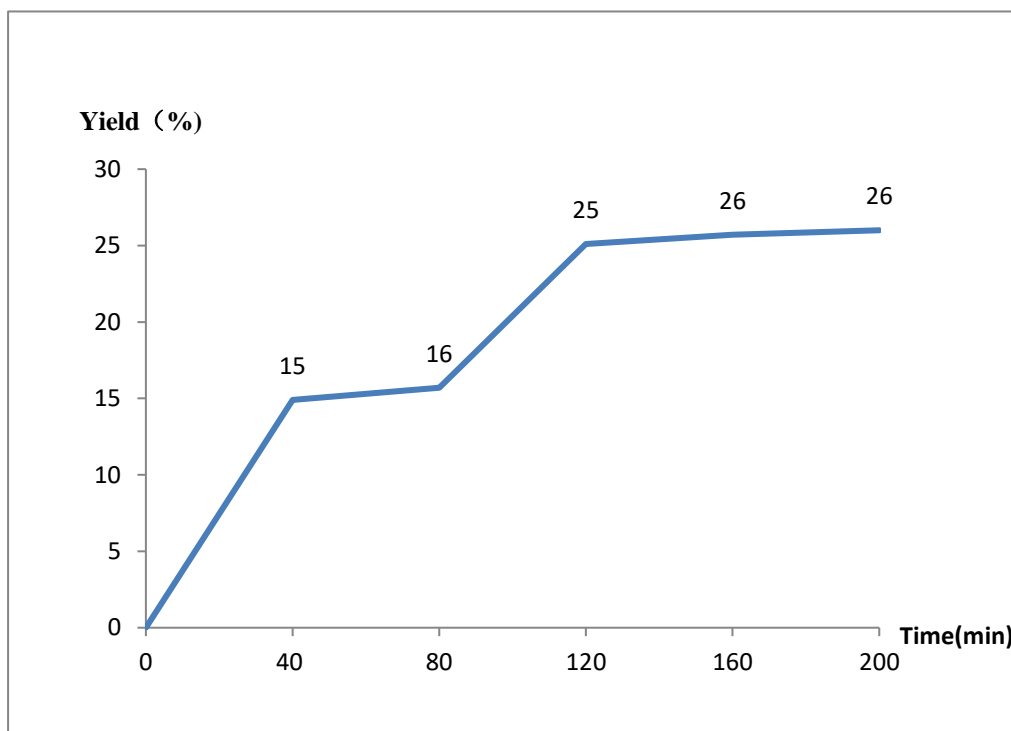
## 6. Light on-off experiments



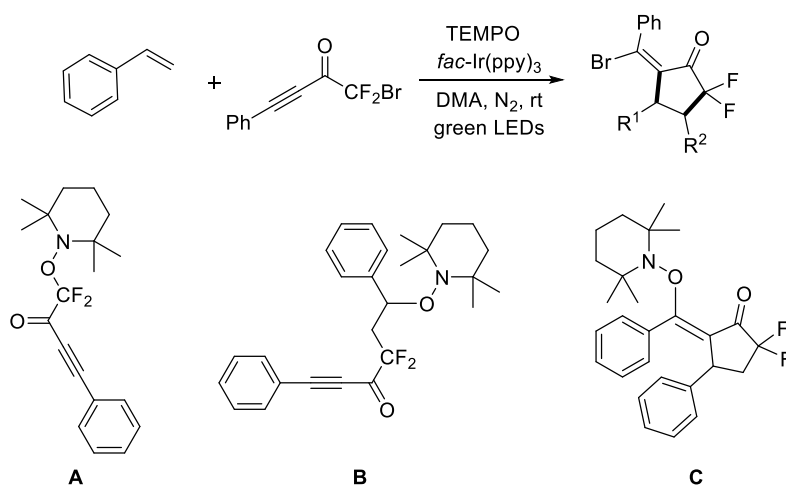
For one clean tubes, according to the general procedure, the 0.2 mmol scale model reaction solution was stirred for light on 40 min and light off 12h. Yields of isolated products are given.

Time	light on (40 min)	light off (12 h)
Yield	14%	16%

For five clean tubes, according to the general procedure, the 0.2 mmol scale model reaction solution was stirred for specified time intervals (40 min, 80 min, 120 min, 160 min and 200 min) with regular interval time of light on and light off (light on 40 min, light off 40 min, light on 40 min...). Yields of isolated products are given.



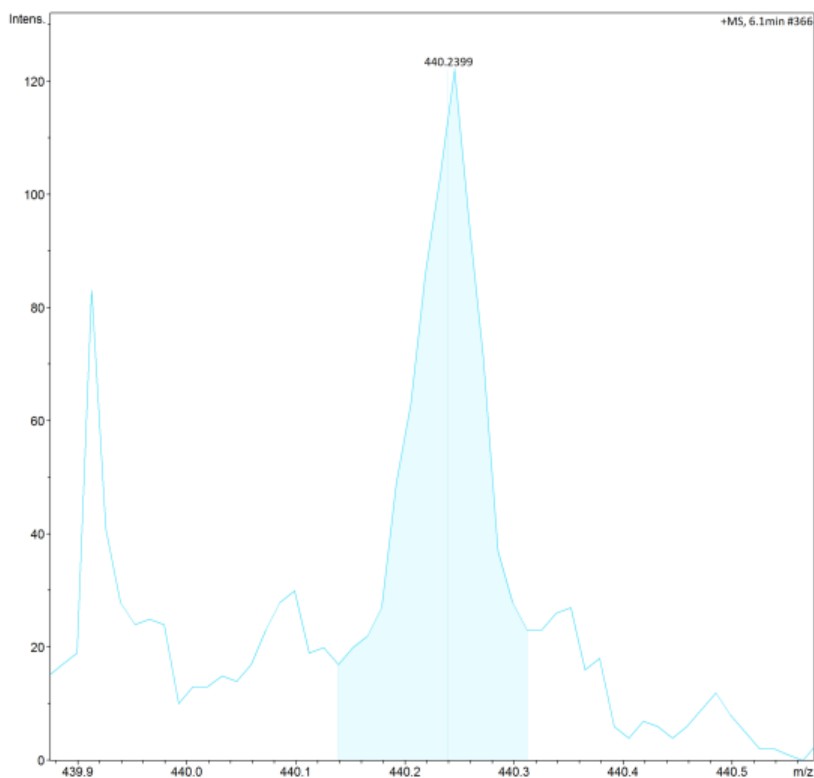
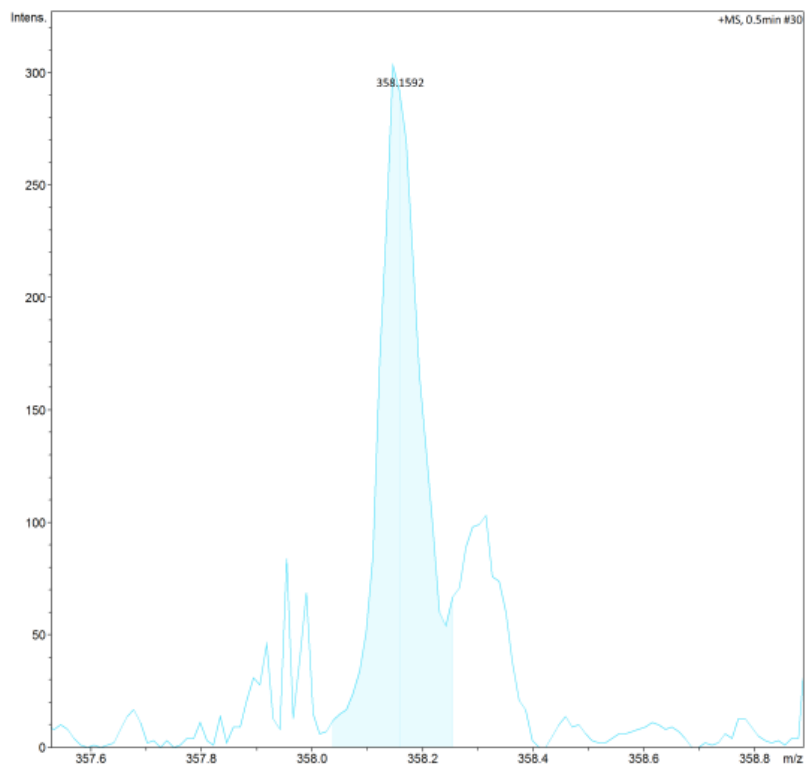
## 7. Radical-trapping experiments



Exact Mass	A	B	C
M	335.1697	439.2323	439.2323
[M+H] <sup>+</sup>	336.1770	440.2396	440.2396
[M+Na] <sup>+</sup>	358.1589	462.2215	462.2215

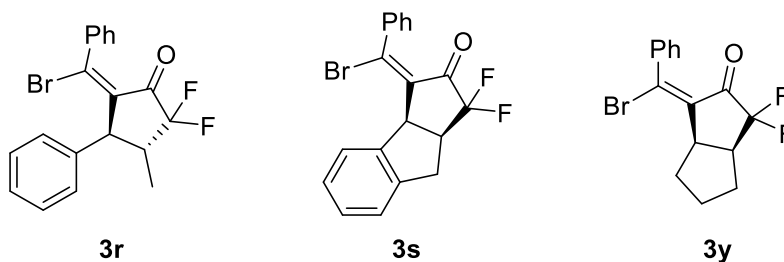
Styrene (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.) TEMPO (0.3 mmol, 1.5 equiv.) and *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 2 mol %) were loaded in a flask which was subjected to evacuation/flushing with nitrogen for three times. DMA (2.0 mL) was added to the mixture via syringe and the mixture was then irradiated by 30 W green LEDs. The reaction was stirred at rt for 4 h. The resultant organic solution were measured with high resolution mass spectrometry (HRMS). The results are following: **A**

HRMS [ESI] calcd for  $C_{19}H_{23}F_2NNaO_2$   $[M+Na]^+$  358.1589, found 358.1592. **B** or **C** HRMS [ESI] calcd for  $C_{27}H_{32}F_2NO_2$   $[M+H]^+$  440.2396, found 440.2399. These result indicate that the formation of radical **A** from **2** and intermediates **B** or **C** was involved in this transformation. The radical trap experiment proved that a radical process is present in the catalytic system.



## 8. Configuration determination of compound 3r, 3s and 3y

Configuration determination of compound 3r, 3s and 3y by comparing the calculated  $J$  values with the tested ones by NMR:



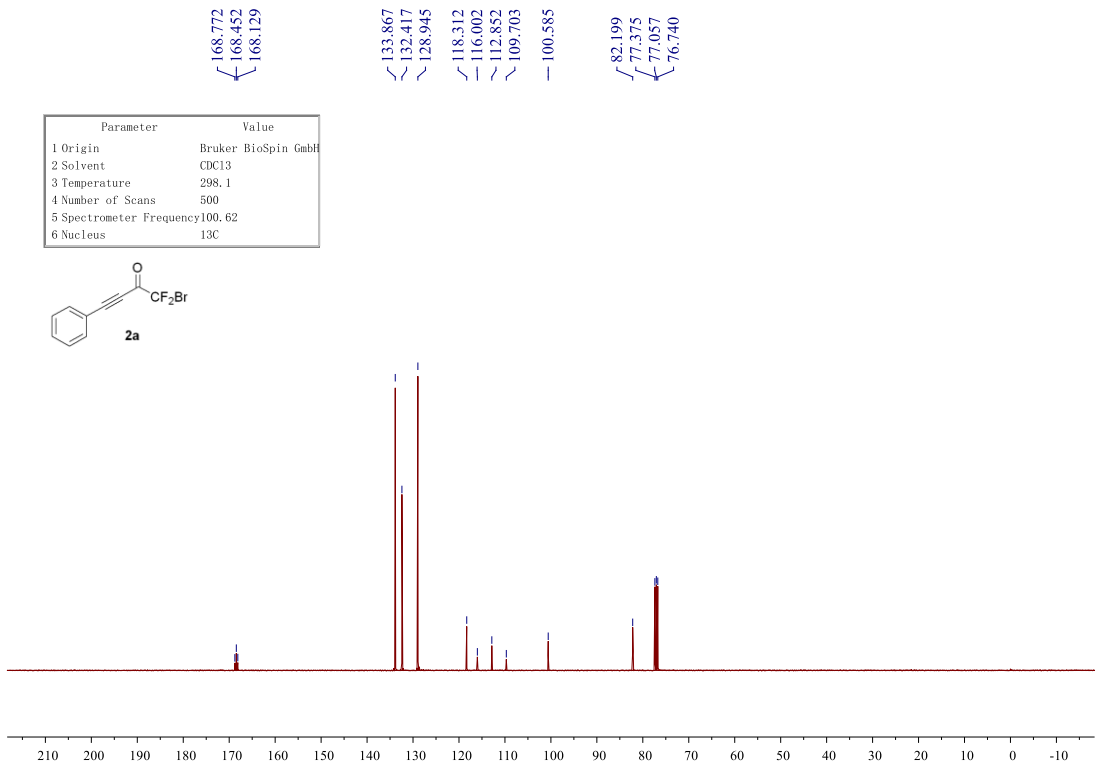
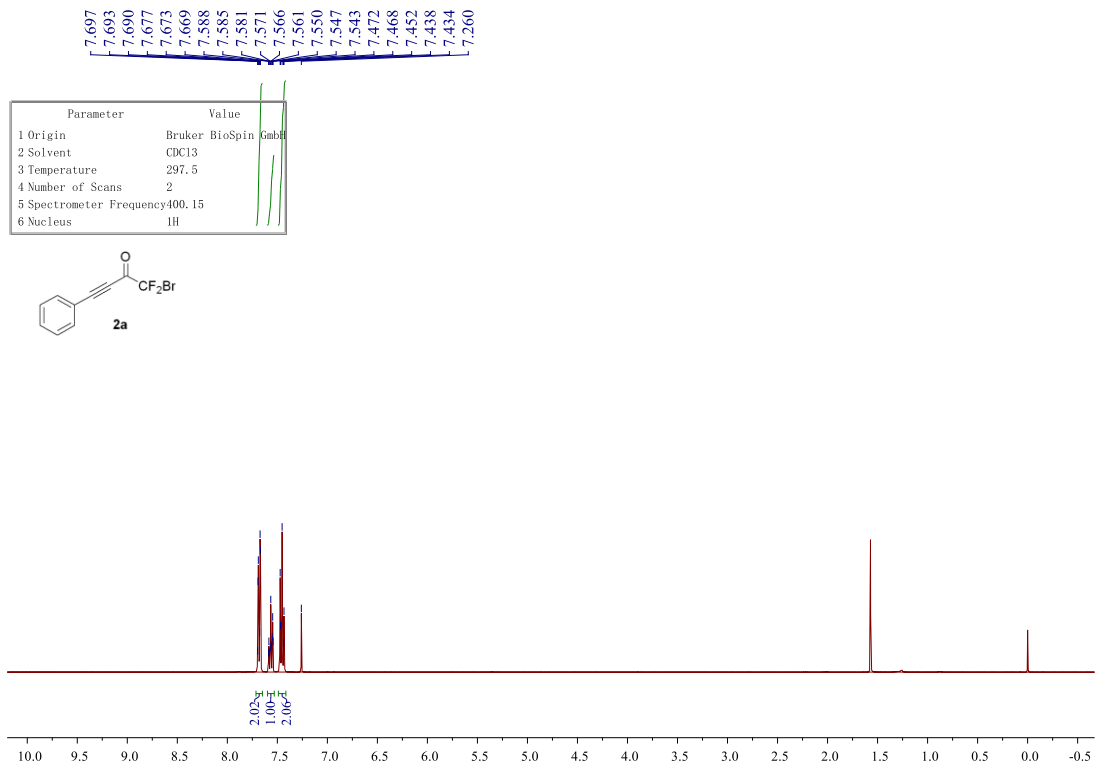
$${}^3J = 4.22 - 0.5 \cos \varphi + 4.5 \cos^2 \varphi$$

( $\varphi$  = dihedral angle of two C-H bonds)

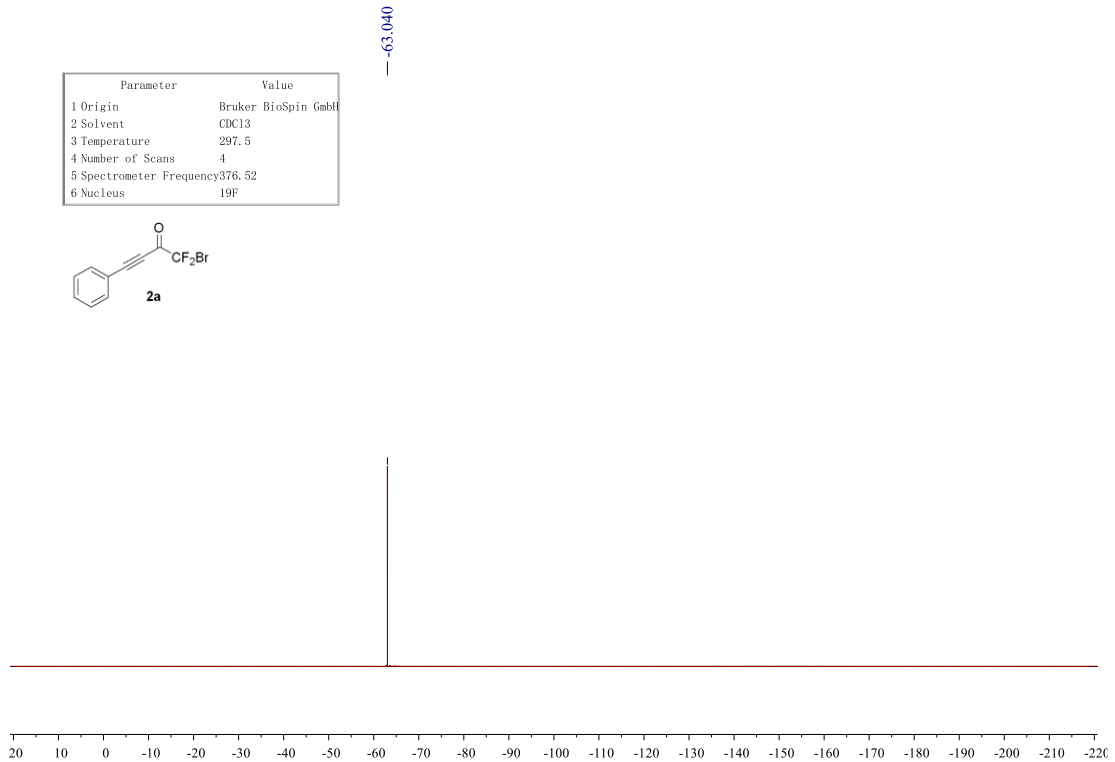
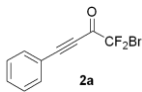
	<b>3r</b>	<b>3s</b>	<b>3y</b>
Calculated dihedral angle of <i>trans</i> -configuration	159.0°	178.9°	178.7°
Calculated ${}^3J$ of <i>trans</i> -configuration	8.6	9.2	9.2
Calculated dihedral angle of <i>cis</i> -configuration	33.2°	28.1°	32.7°
Calculated ${}^3J$ of <i>cis</i> -configuration	7.0	7.3	7.0
Exact $J$ value of ${}^1\text{H}$ NMR	<b>8.4</b>	<b>7.2</b>	<b>7.2</b>
Proposed configuration	<b><i>trans</i></b>	<b><i>cis</i></b>	<b><i>cis</i></b>
H-F HOSEY result	<b><i>trans</i></b>	-	<b><i>cis</i></b>



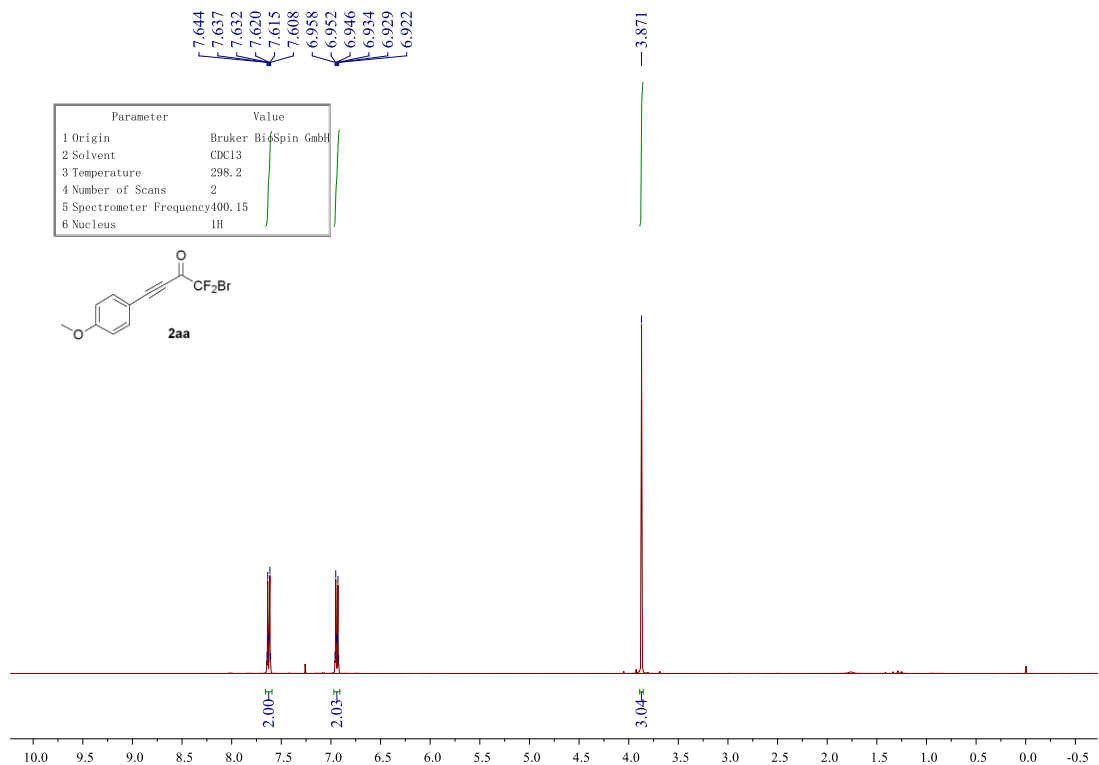
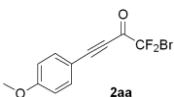
## 9. $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.5
4 Number of Scans	4
5 Spectrometer Frequency	376.52
6 Nucleus	<sup>19</sup> F

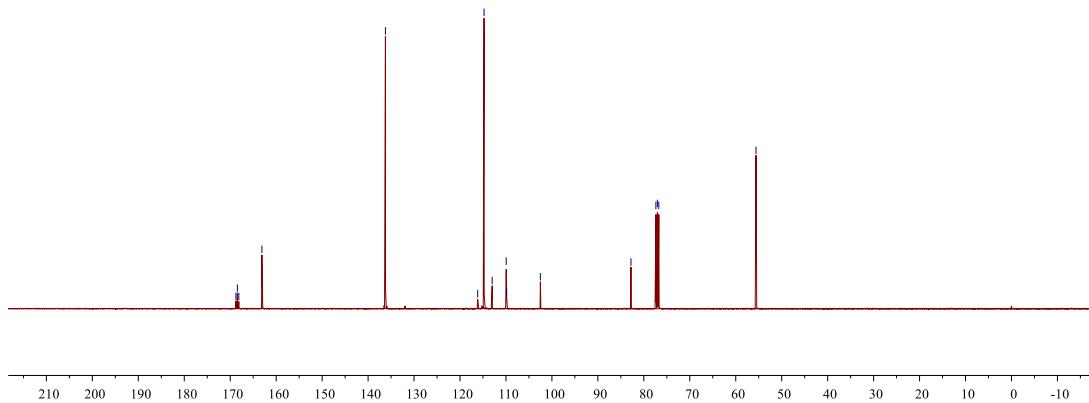
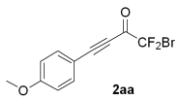


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	<sup>1</sup> H



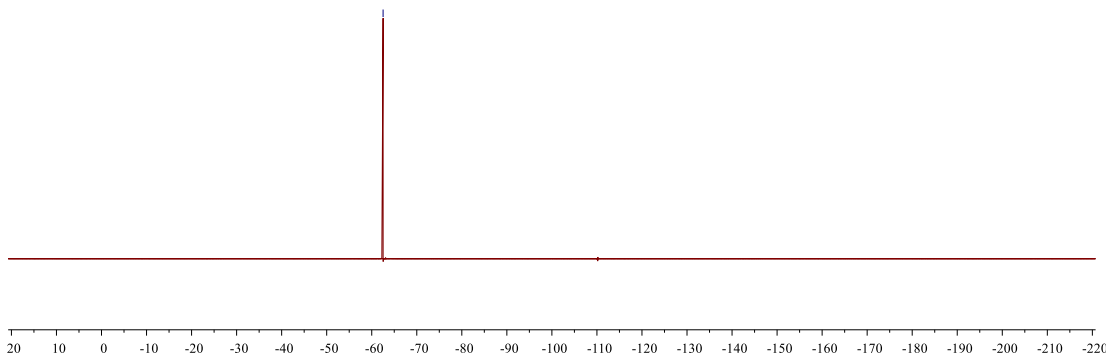
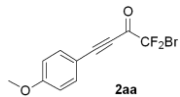
168.758  
168.440  
168.121  
163.105  
136.226  
116.153  
114.764  
113.002  
109.950  
109.853  
102.510  
82.801  
77.374  
77.056  
76.739  
55.591

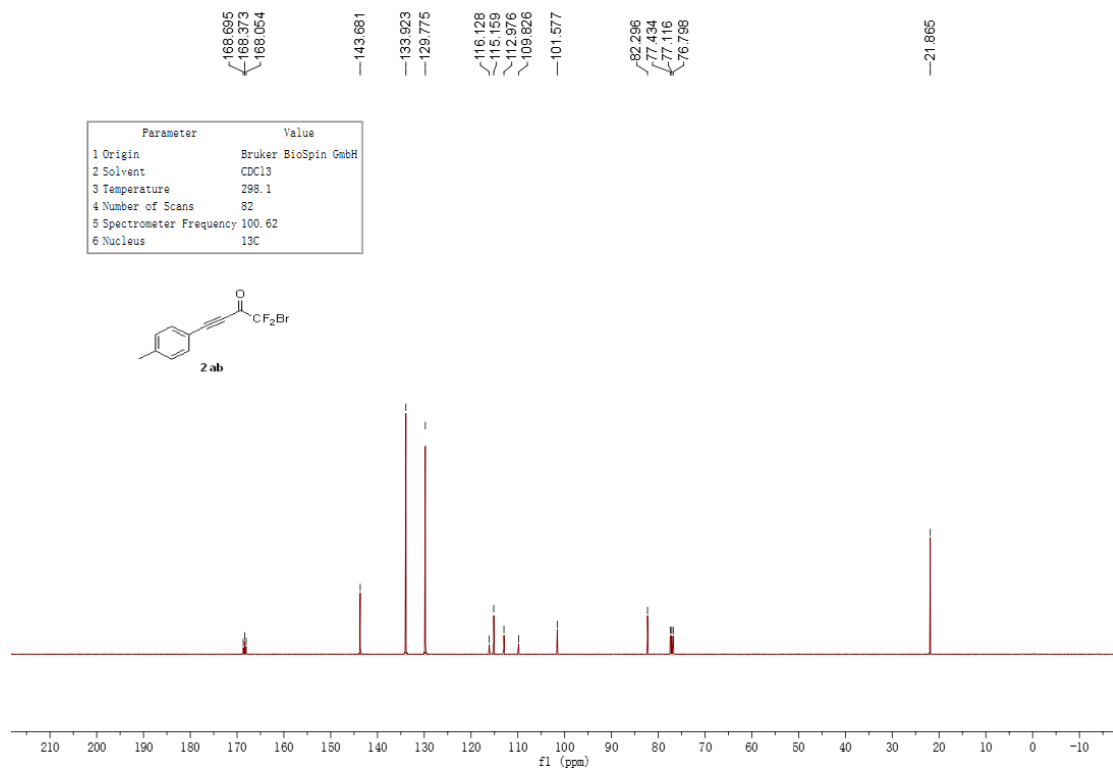
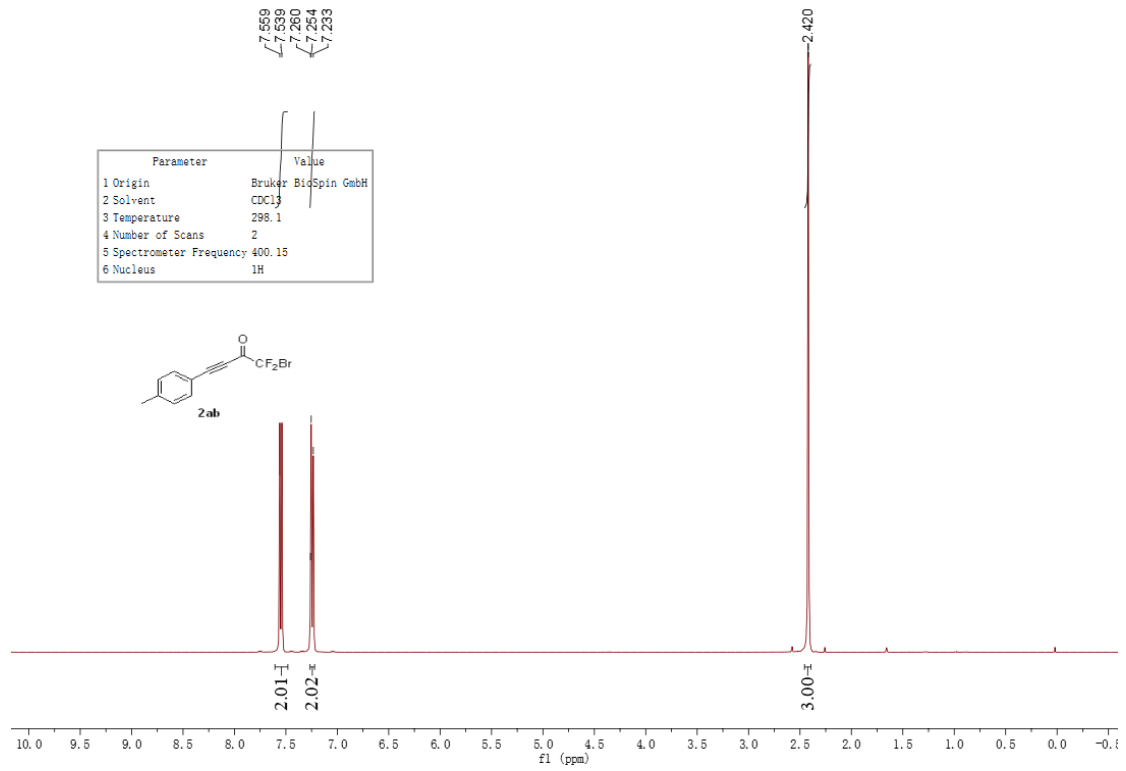
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C

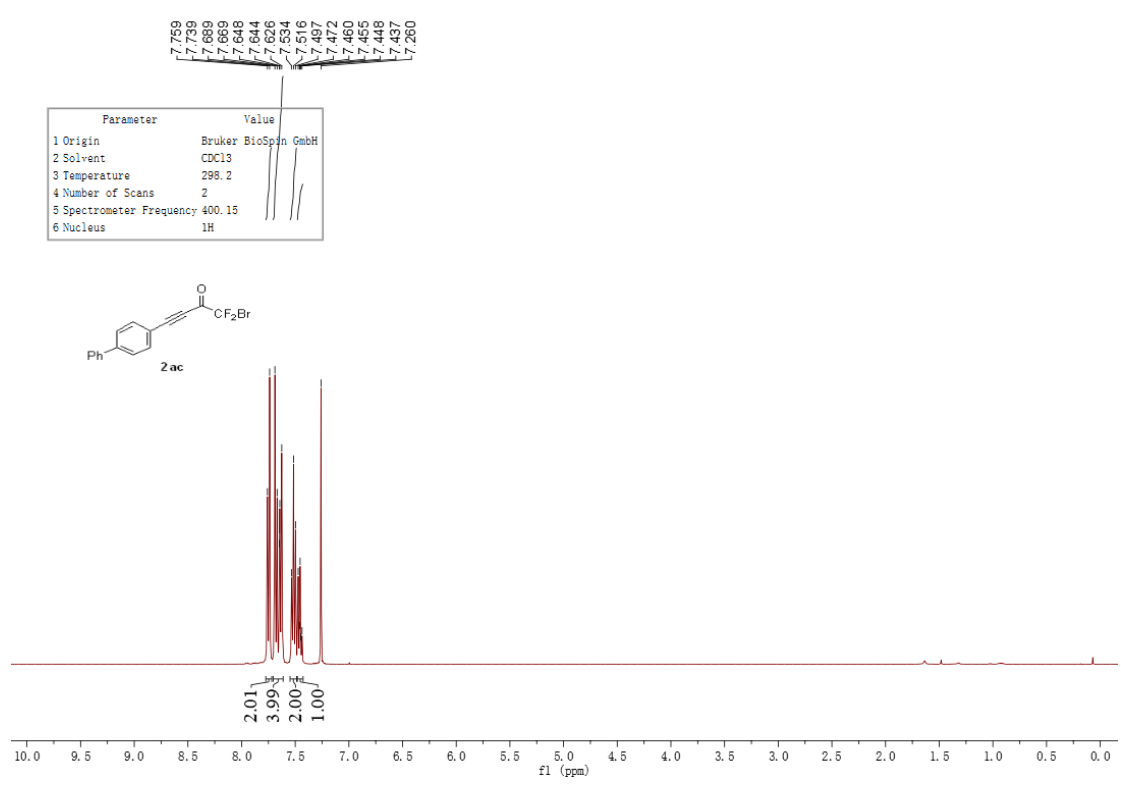
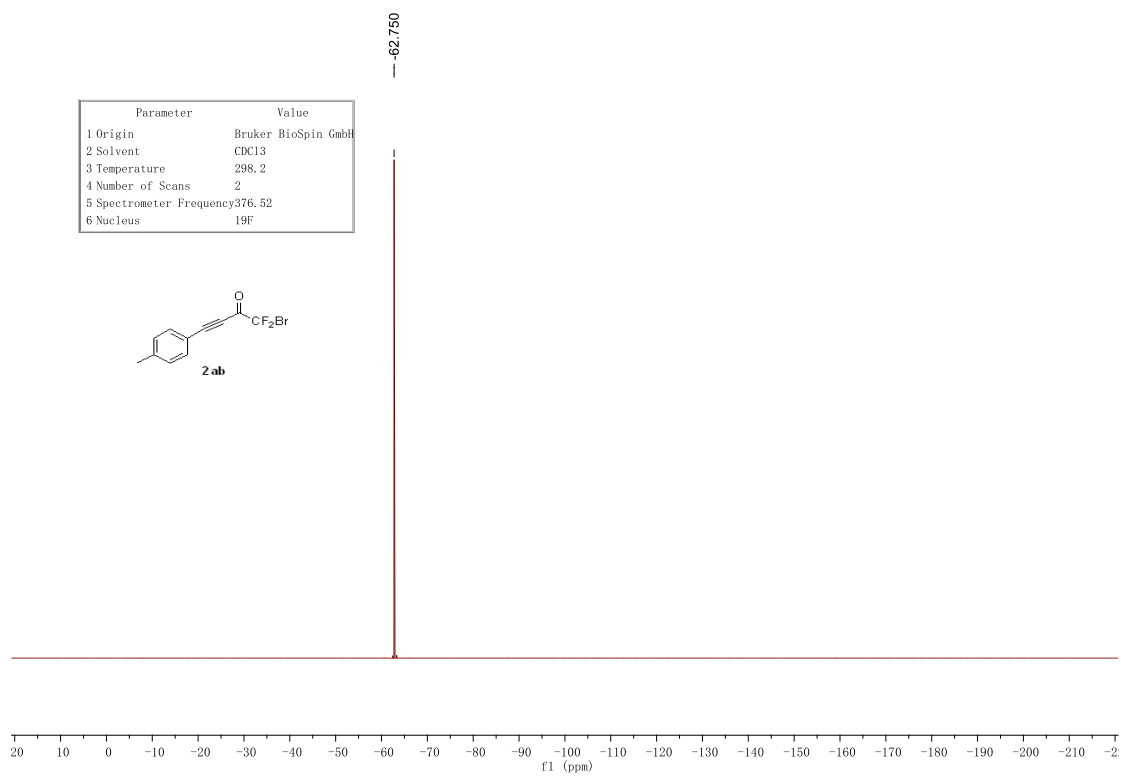


62.521

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

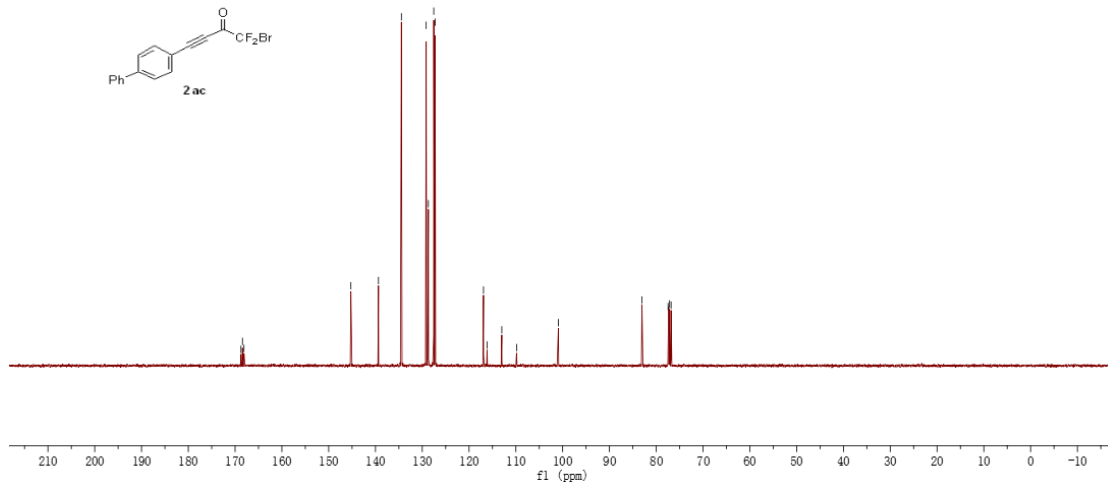
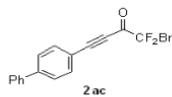






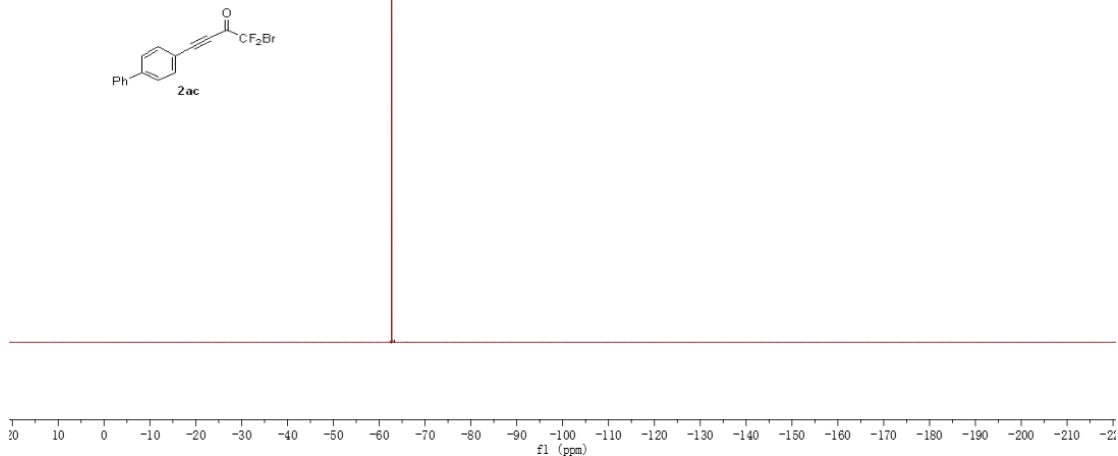
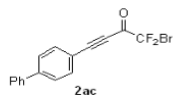
$\delta$  168.747  
 $\delta$  168.426  
 $\delta$  168.105  
 $\delta$  145.261  
 $\delta$  139.962  
 $\delta$  134.465  
 $\delta$  129.167  
 $\delta$  128.696  
 $\delta$  127.546  
 $\delta$  127.249  
 $\delta$  116.917  
 $\delta$  116.151  
 $\delta$  113.002  
 $\delta$  109.852  
 $\delta$  100.912  
 $\delta$  83.061  
 $\delta$  77.466  
 $\delta$  77.148  
 $\delta$  76.830

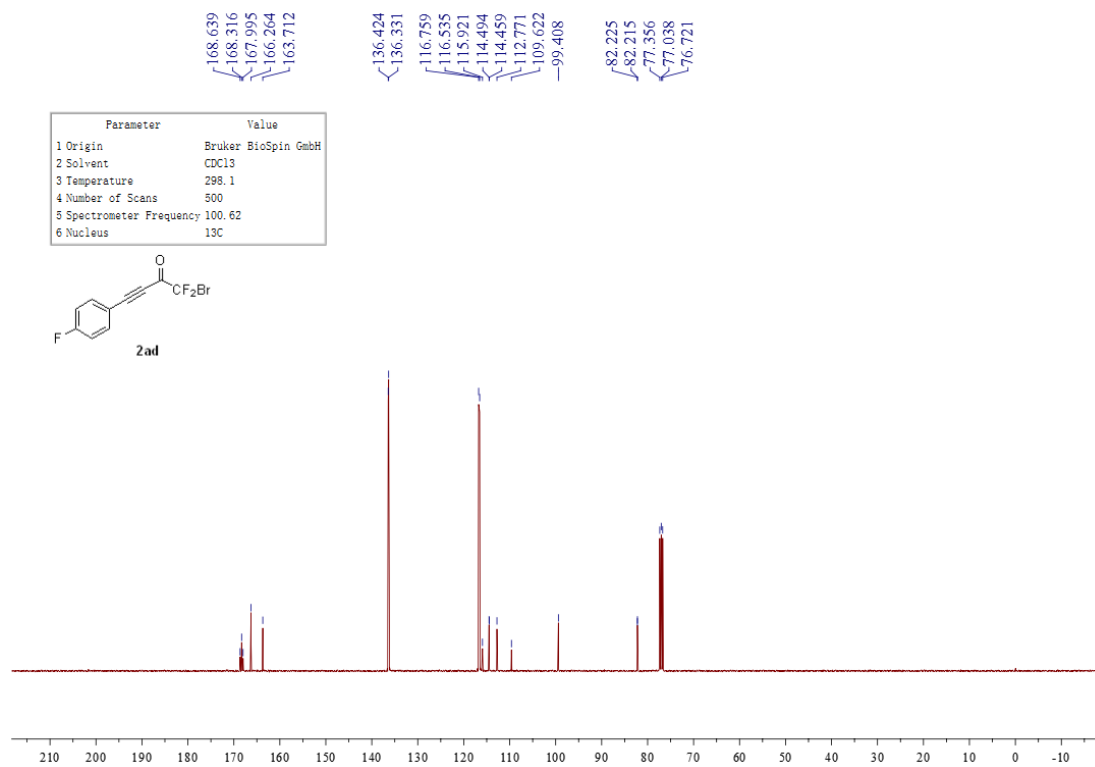
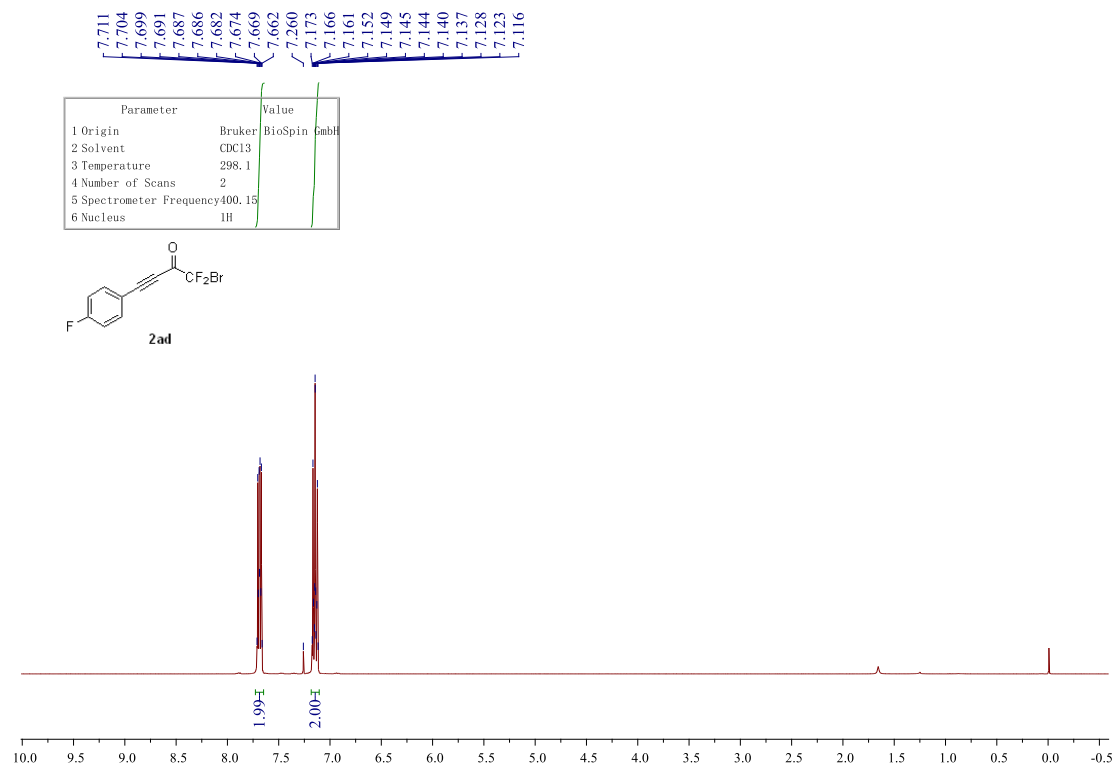
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.2
4 Number of Scans	34
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C



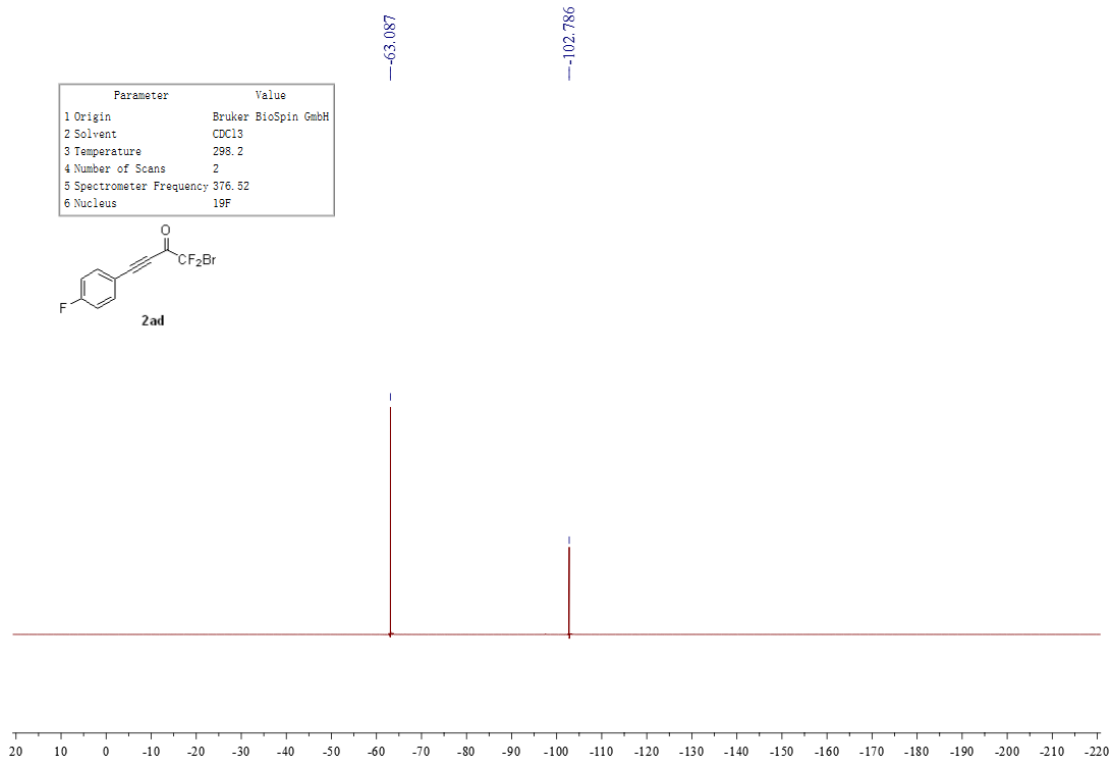
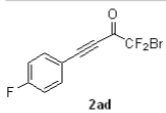
$\delta$  62.717

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.32
6 Nucleus	<sup>19</sup> F



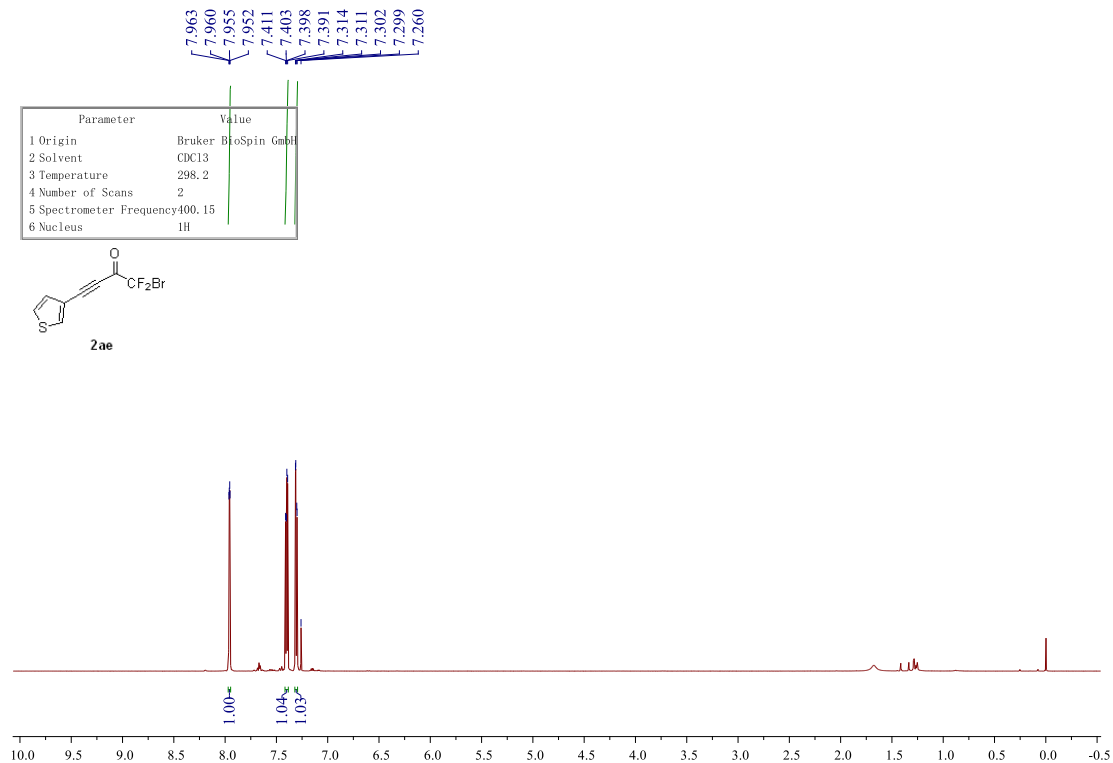
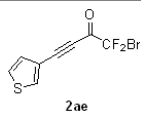


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



7.963  
7.960  
7.955  
7.952  
7.411  
7.403  
7.398  
7.391  
7.314  
7.311  
7.302  
7.299  
7.260

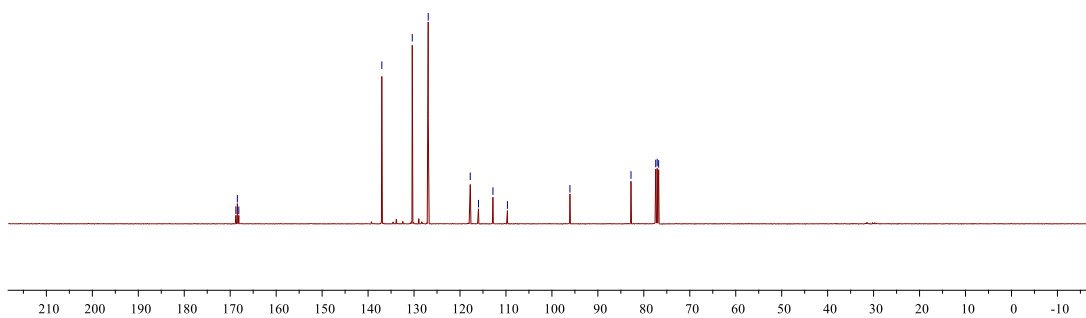
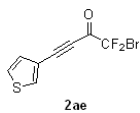
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H





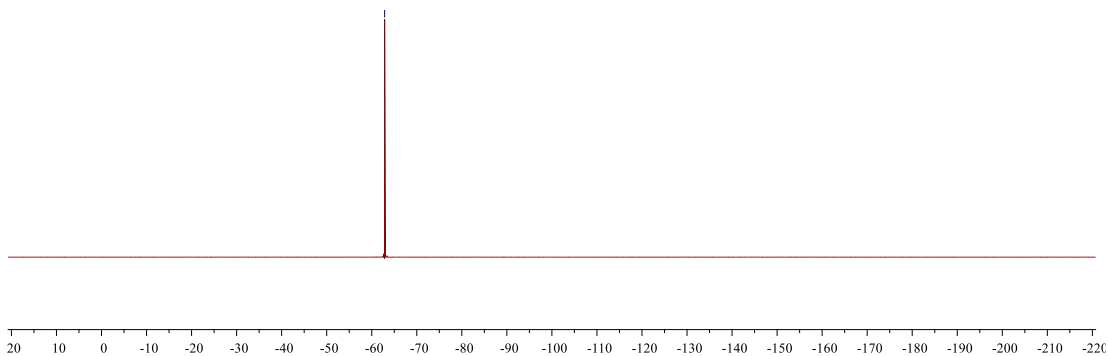
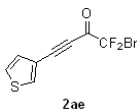
168.768  
 168.445  
 168.125  
 137.008  
 130.389  
 126.914  
 117.768  
 115.980  
 112.830  
 109.679  
 -96.078  
 82.793  
 77.409  
 77.092  
 76.774

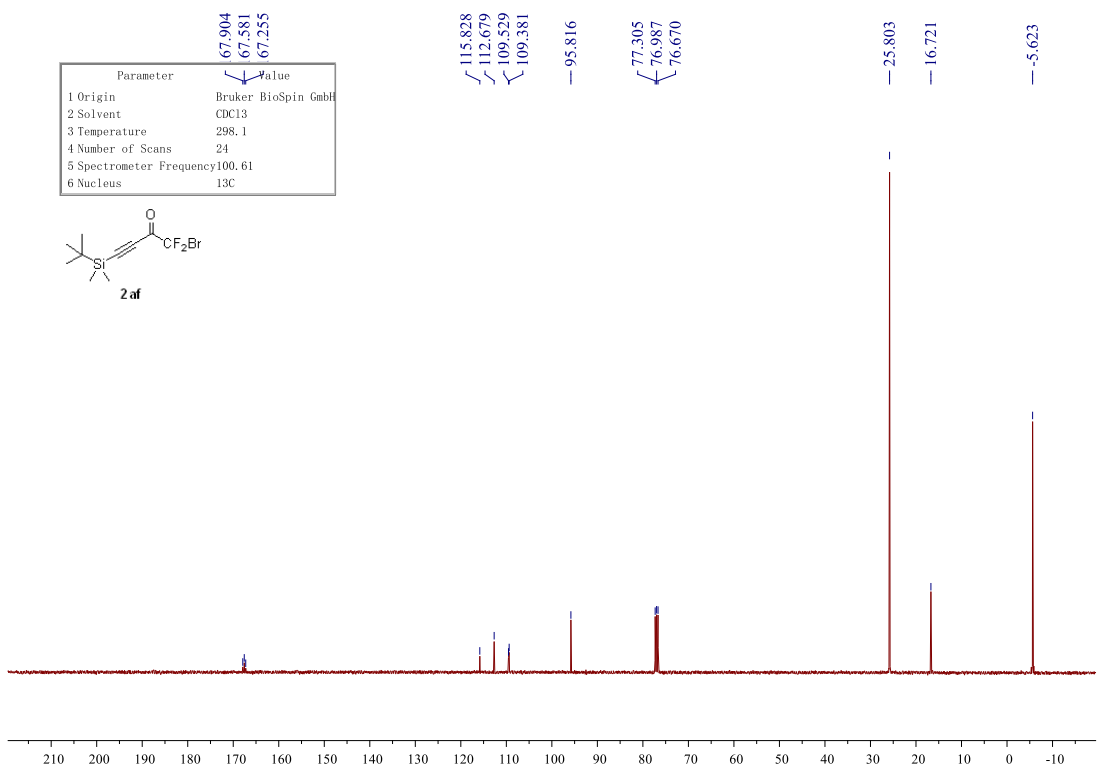
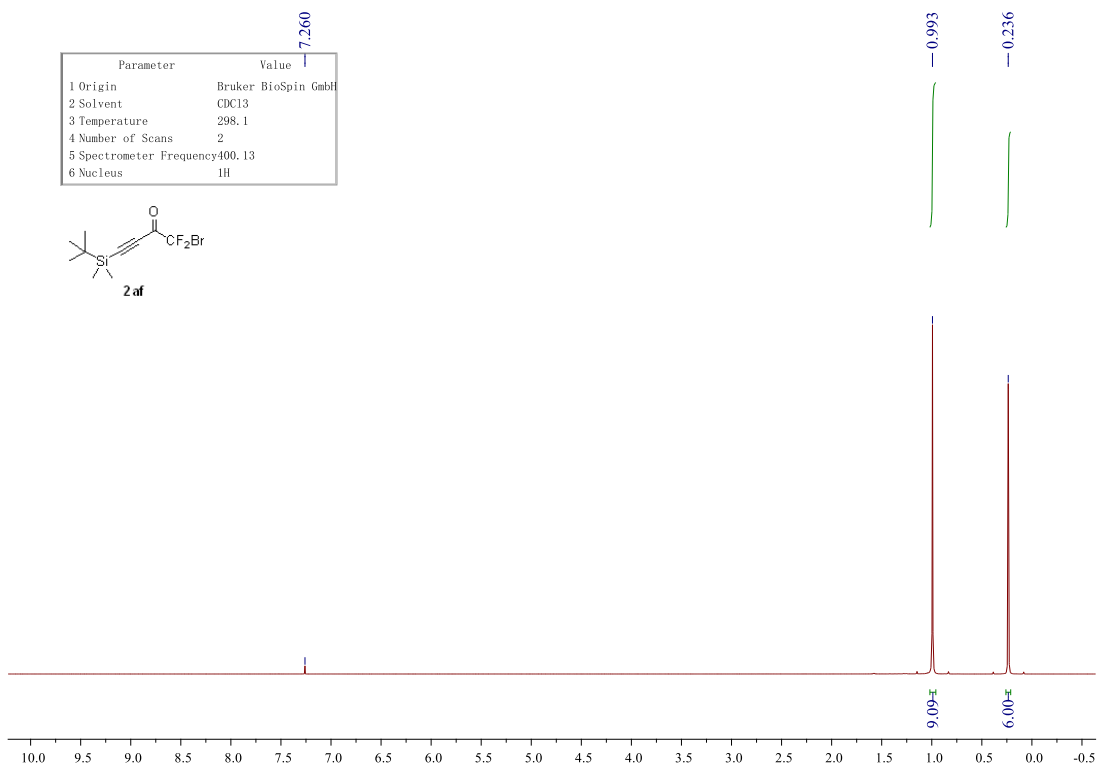
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	297.9
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C

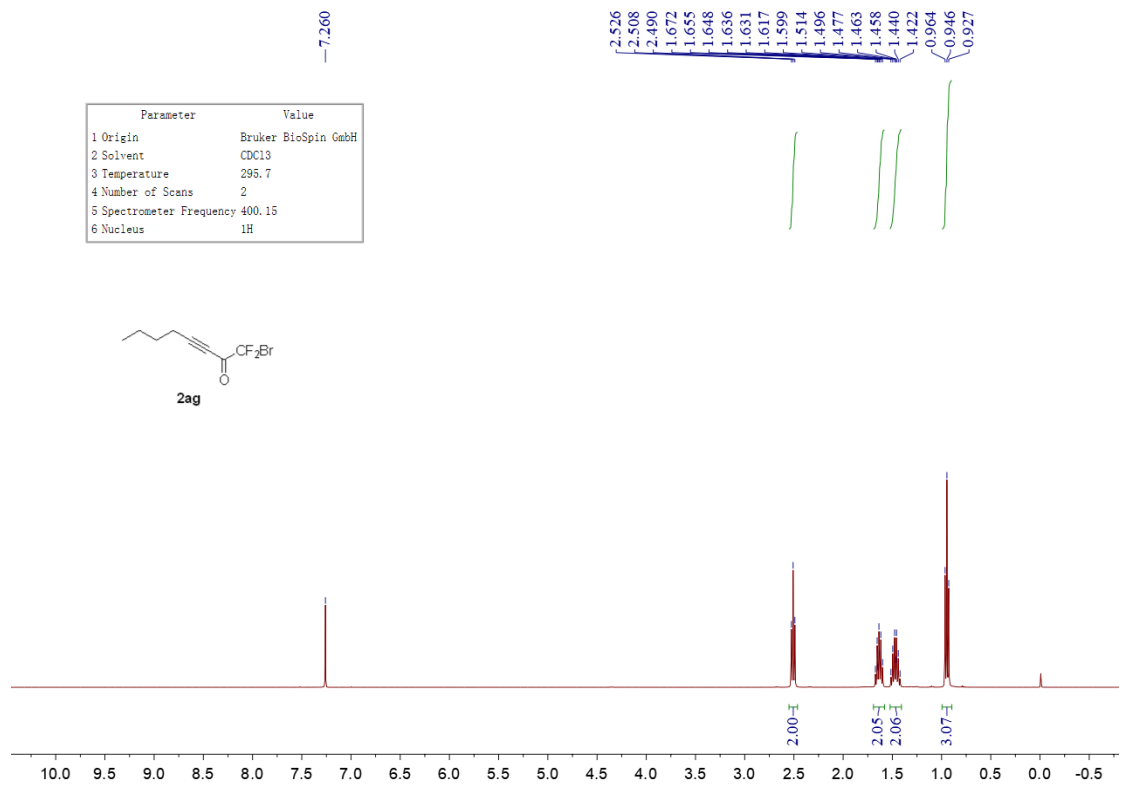
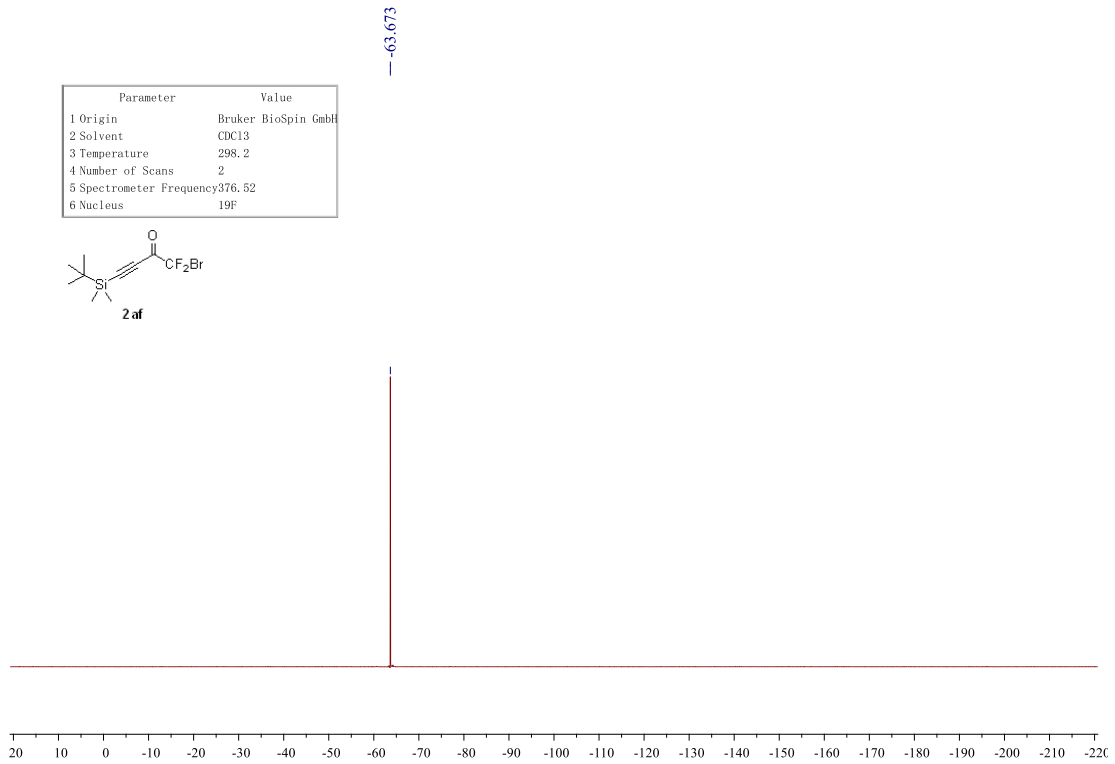


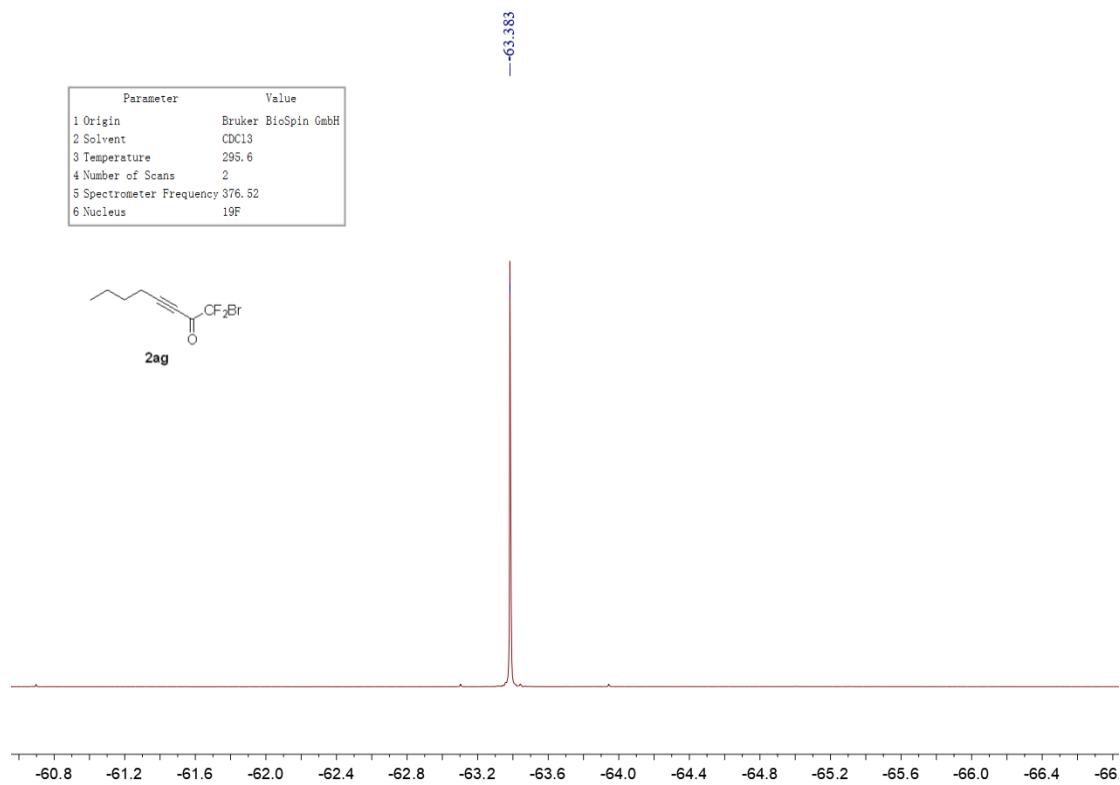
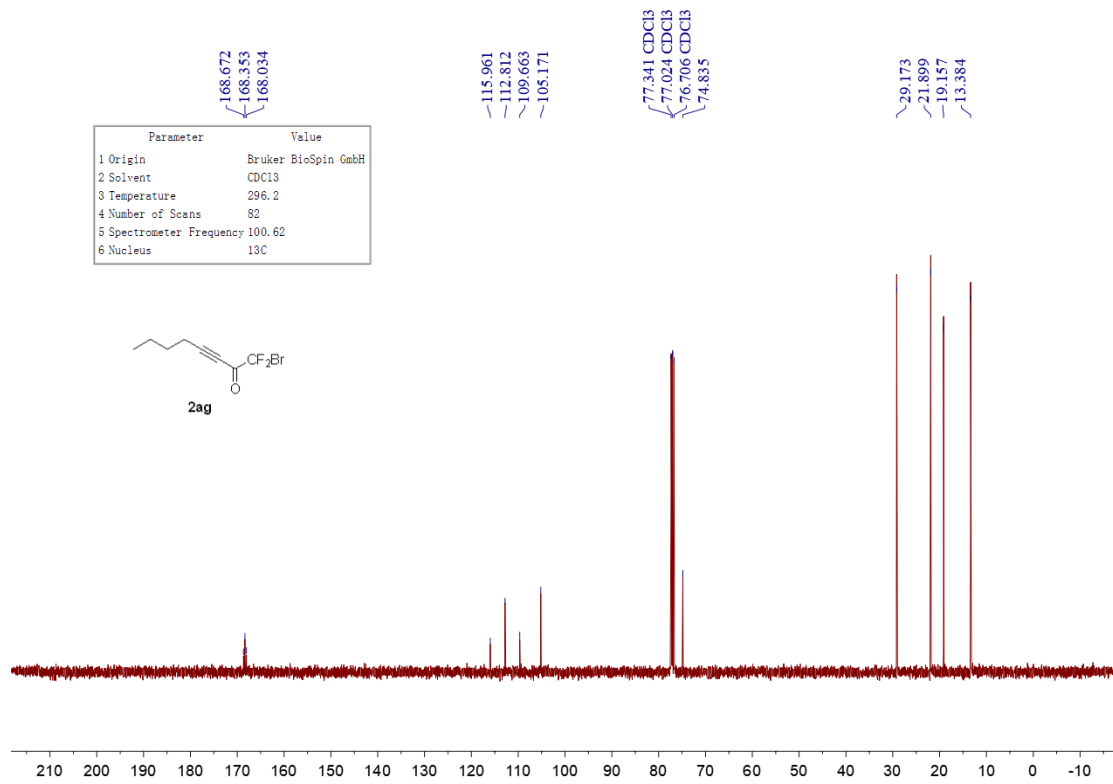
-62.863

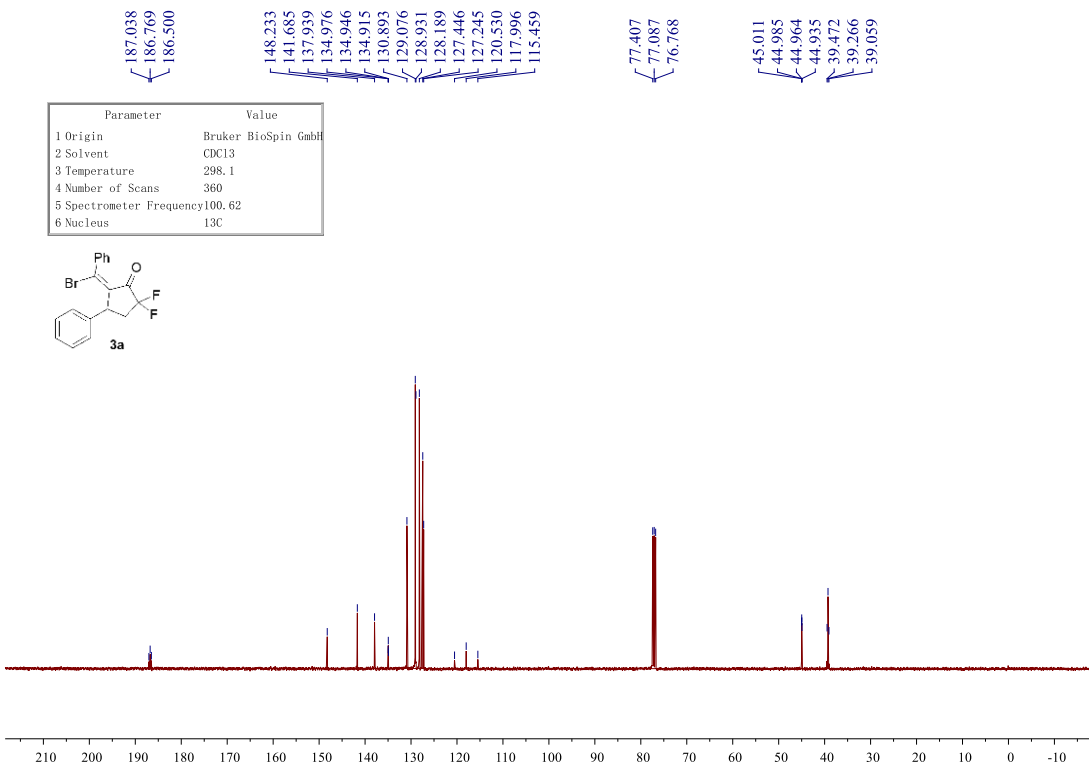
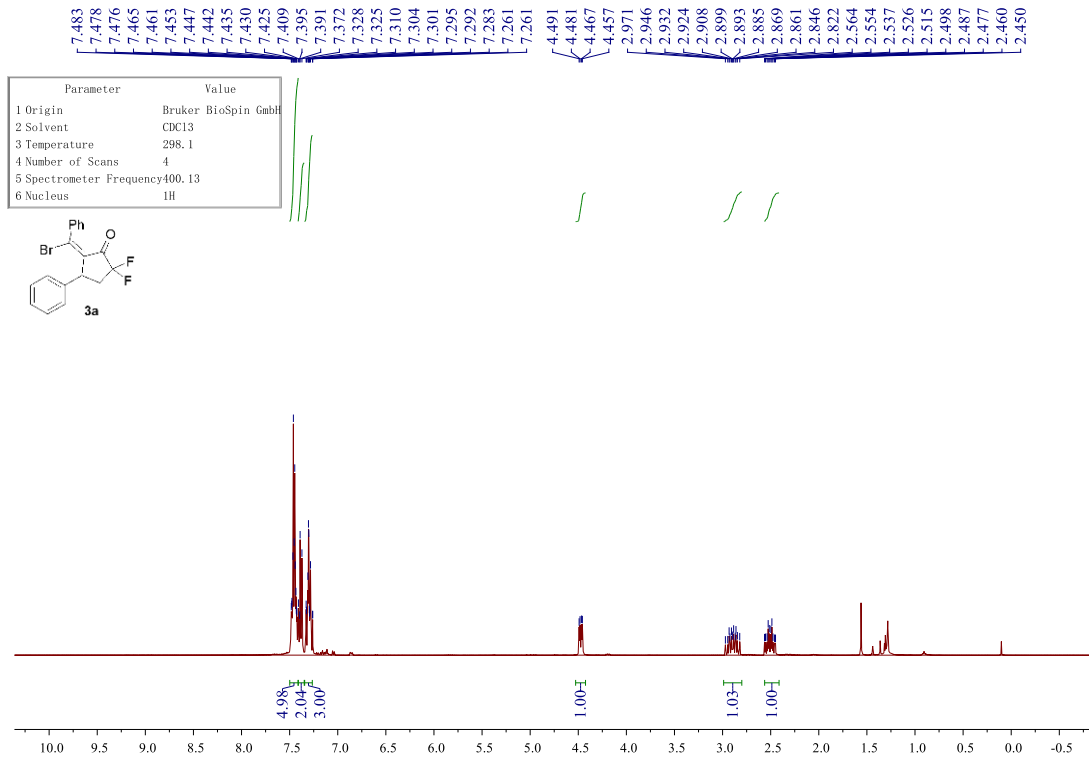
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	<sup>19</sup> F



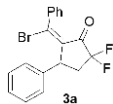




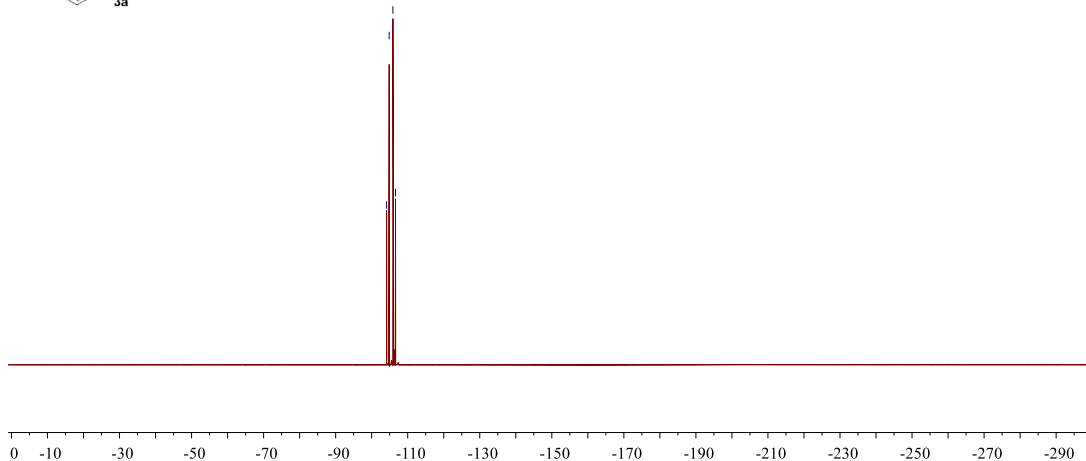




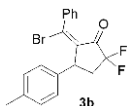
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	376.44
6 Nucleus	19F



-104.138  
-104.860  
-105.891  
-106.614

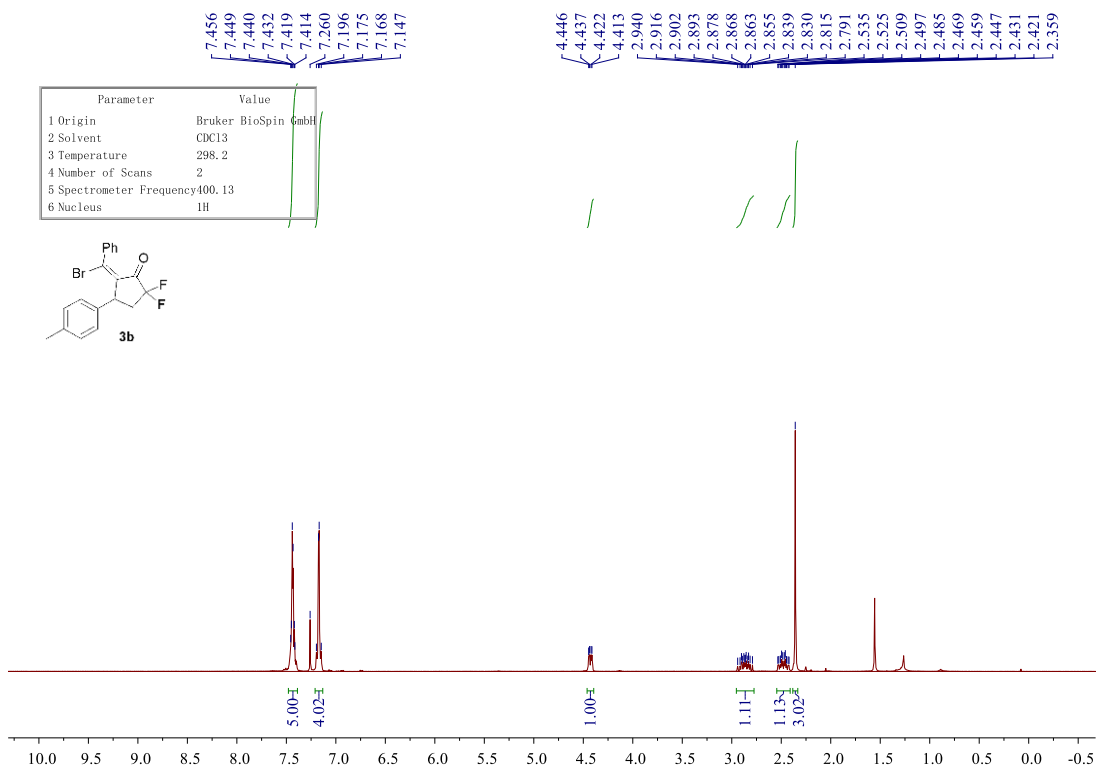


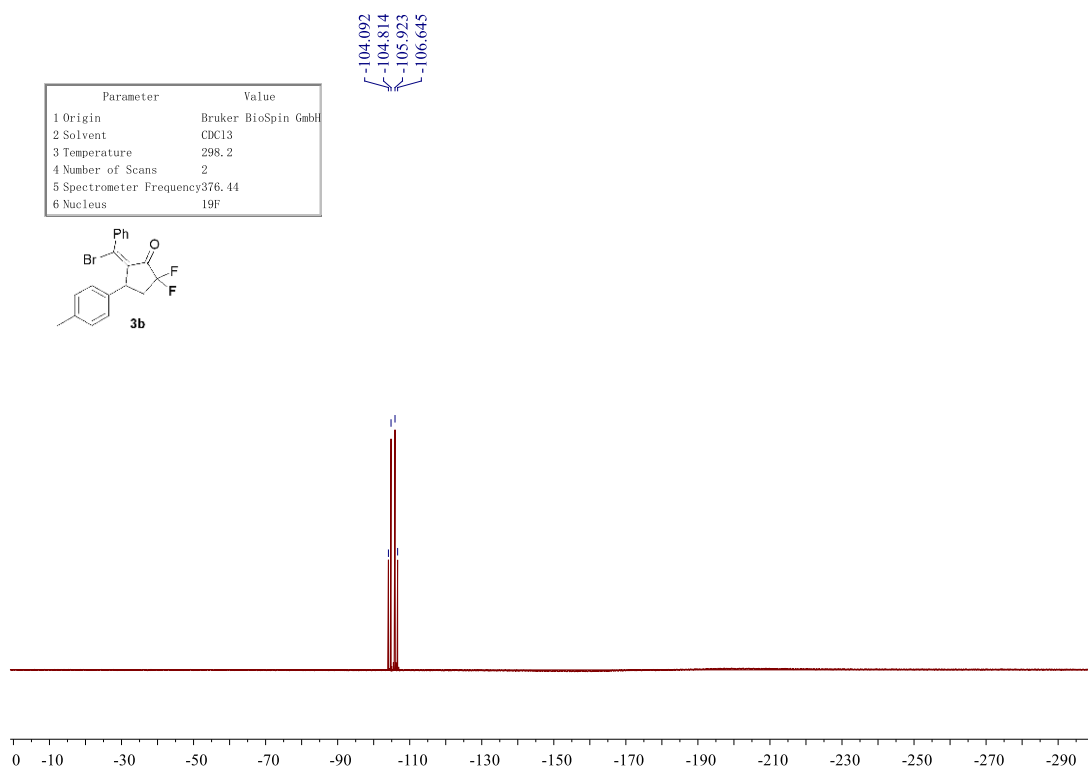
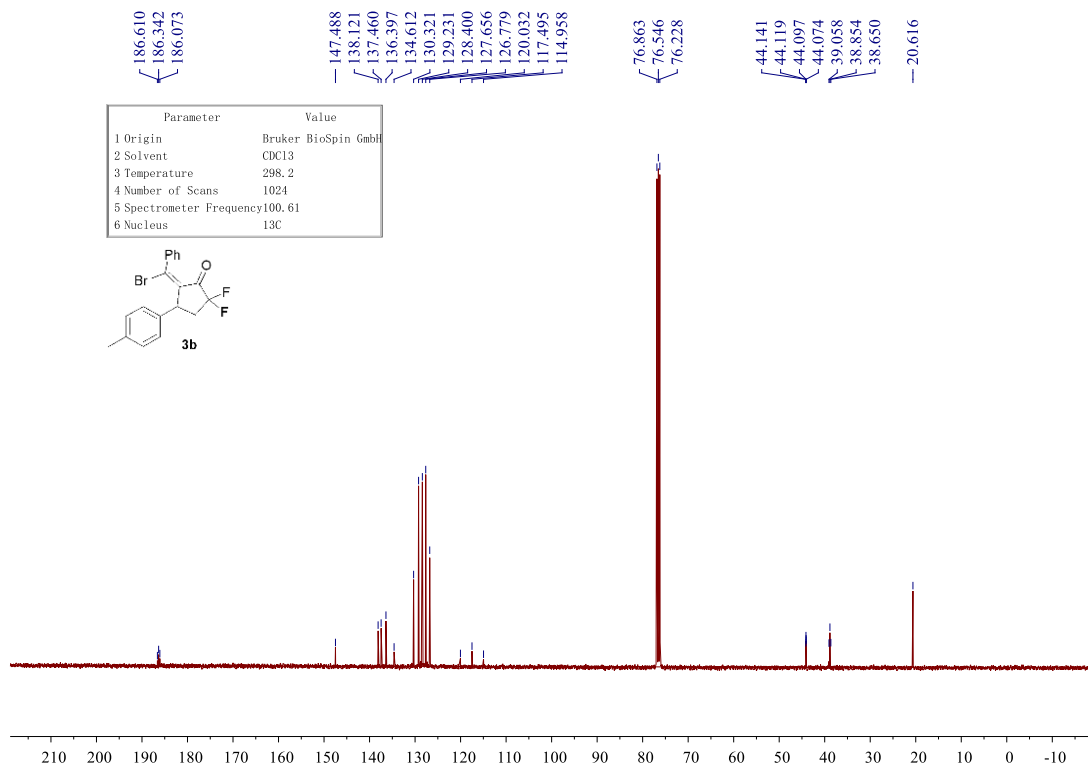
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	100.13
6 Nucleus	1H

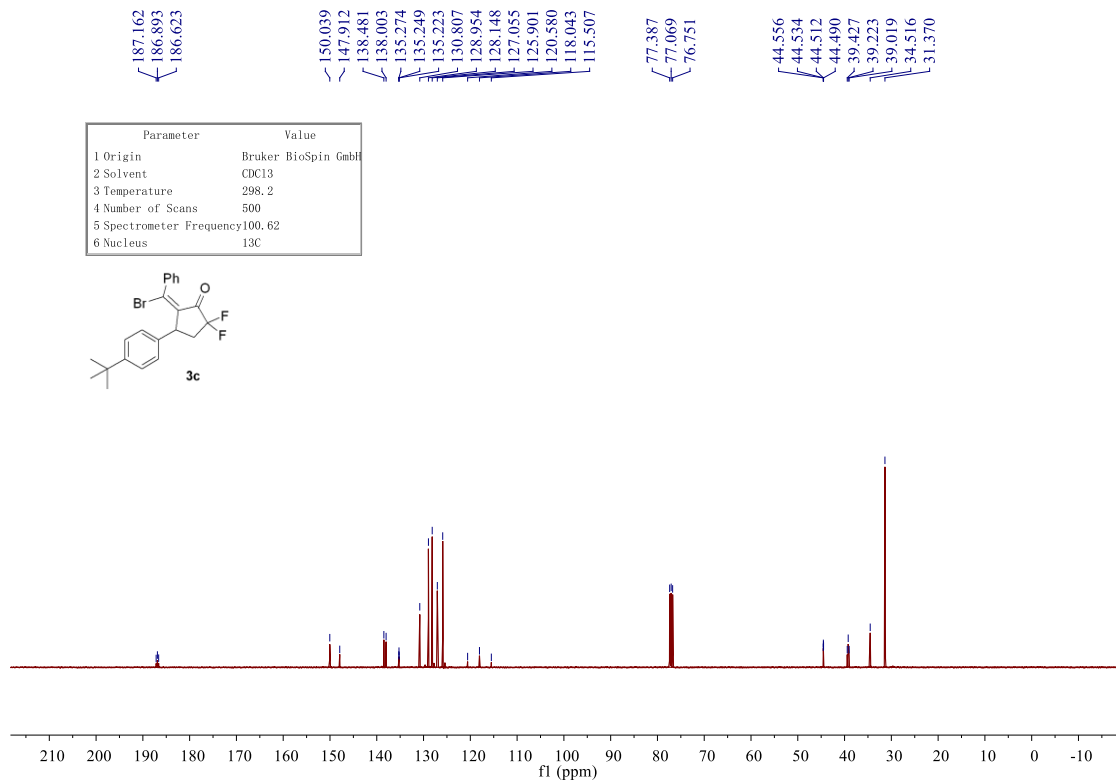
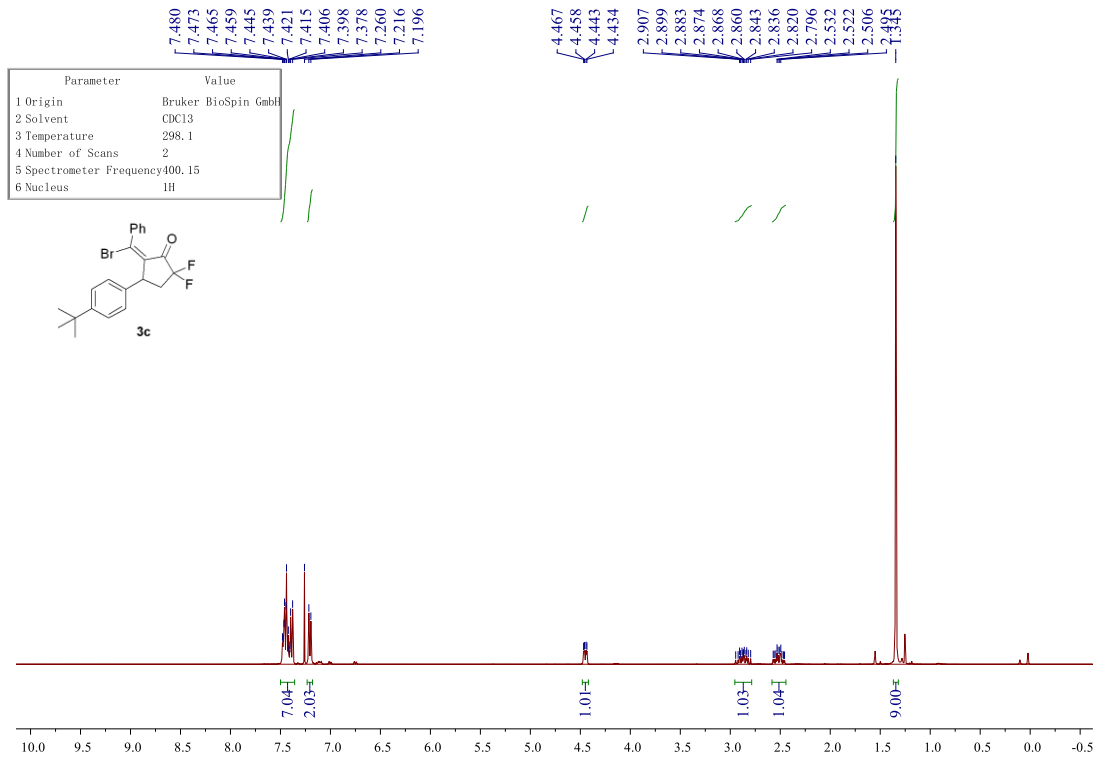


7.456  
7.449  
7.440  
7.432  
7.419  
7.414  
7.260  
7.196  
7.175  
7.168  
7.147

4.446  
4.437  
4.422  
4.413  
2.940  
2.916  
2.902  
2.893  
2.878  
2.868  
2.863  
2.855  
2.839  
2.830  
2.815  
2.791  
2.535  
2.525  
2.509  
2.497  
2.485  
2.469  
2.459  
2.447  
2.431  
2.421  
2.359

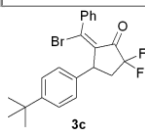




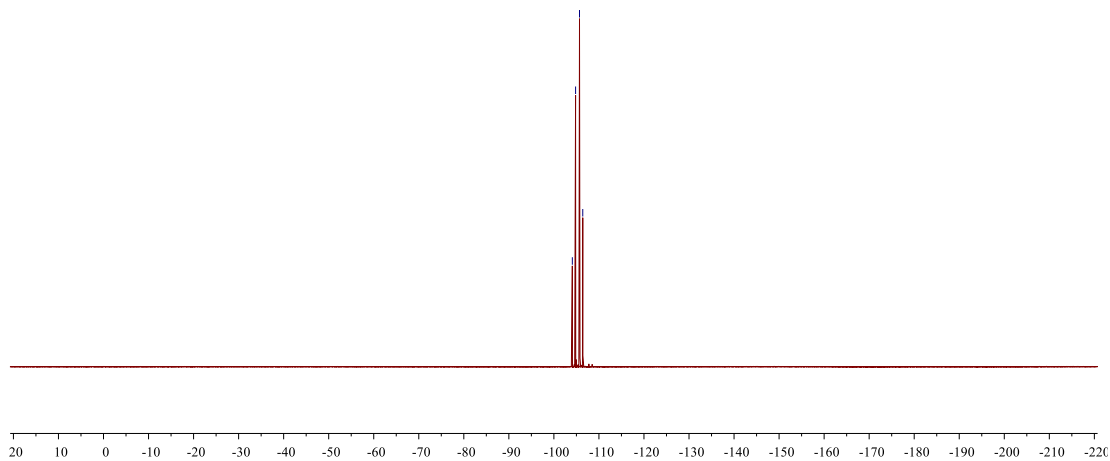




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	376.52
6 Nucleus	19F

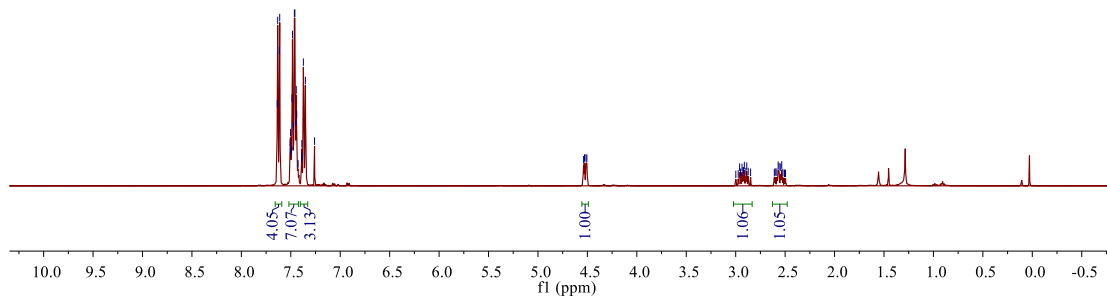
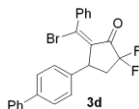


-104.094  
-104.816  
-105.688  
-106.410



7.637 7.633 7.616 7.612 7.507 7.503 7.498 7.496 7.494 7.488 7.483 7.473 7.464 7.459 7.449 7.445 7.440 7.426 7.391 7.388 7.385 7.373 7.352 7.260 4.539 4.529 4.515 4.505 2.999 2.975 2.960 2.951 2.936 2.926 2.922 2.913 2.897 2.888 2.874 2.849 2.610 2.600 2.584 2.570 2.560 2.545 2.534 2.522 2.506 2.496

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.7
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



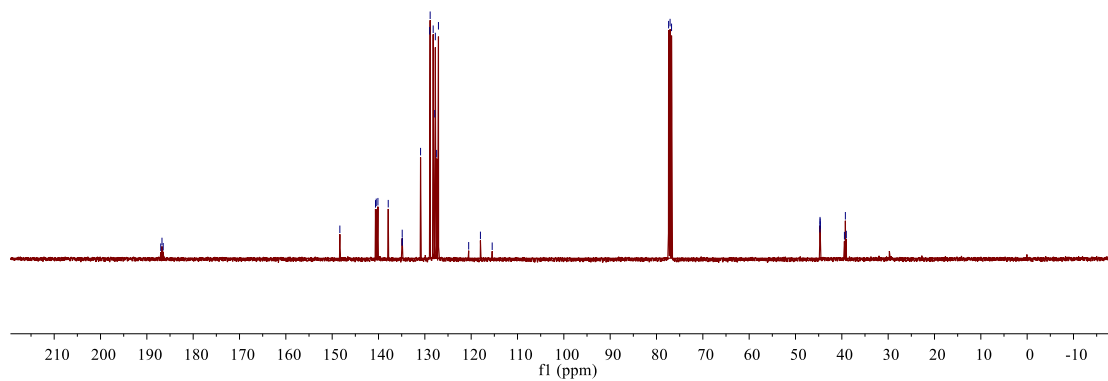
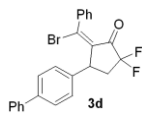
187.002  
186.734  
186.466

148.341  
140.652  
140.491  
140.128  
137.901  
134.911  
134.885  
134.858  
130.925  
128.949  
128.852  
128.199  
127.862  
127.734  
127.452  
127.063  
120.539  
118.001  
115.464

77.388  
77.071  
76.753

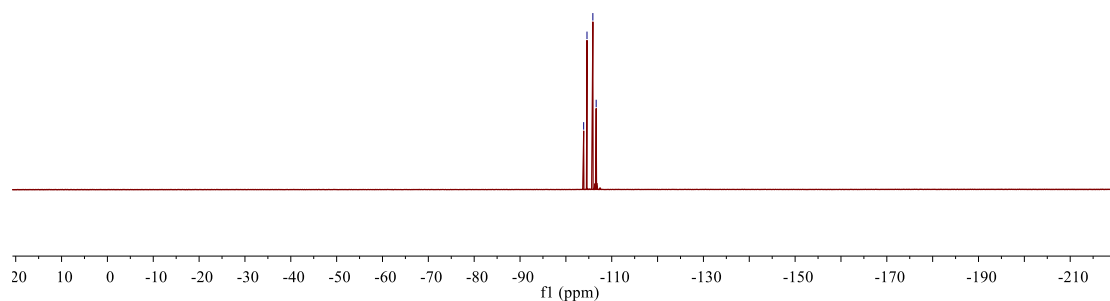
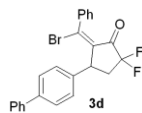
44.725  
44.703  
44.680  
44.658  
39.442  
39.237  
39.033

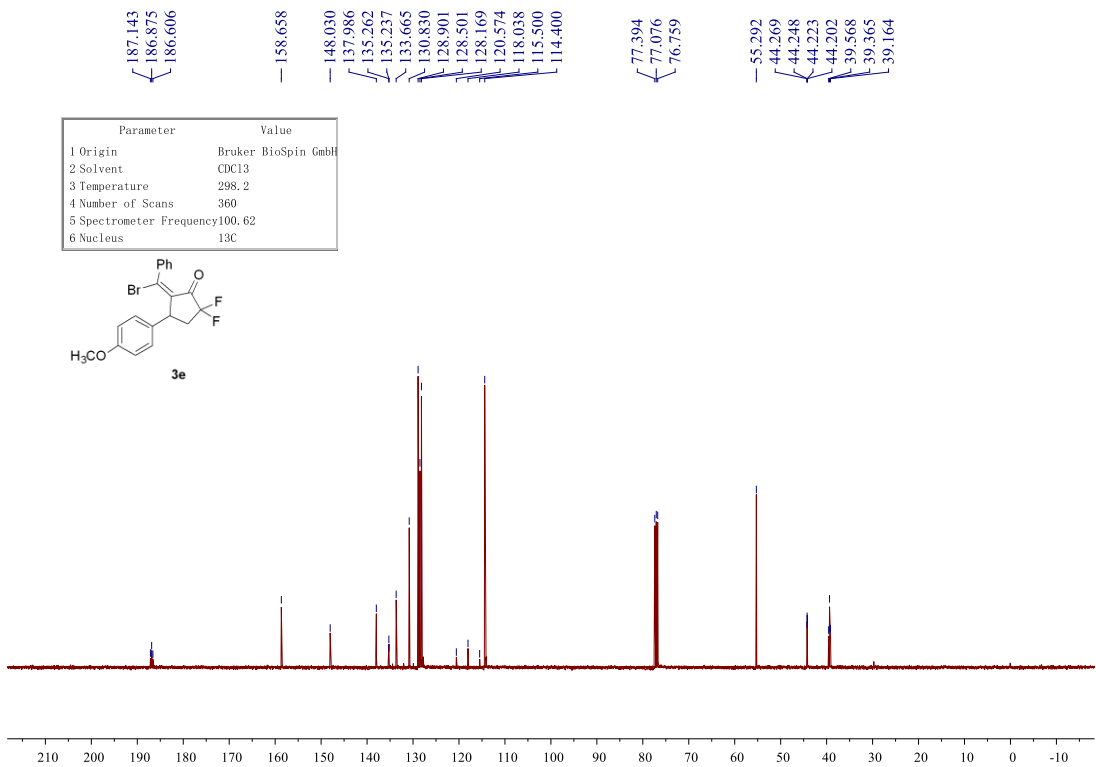
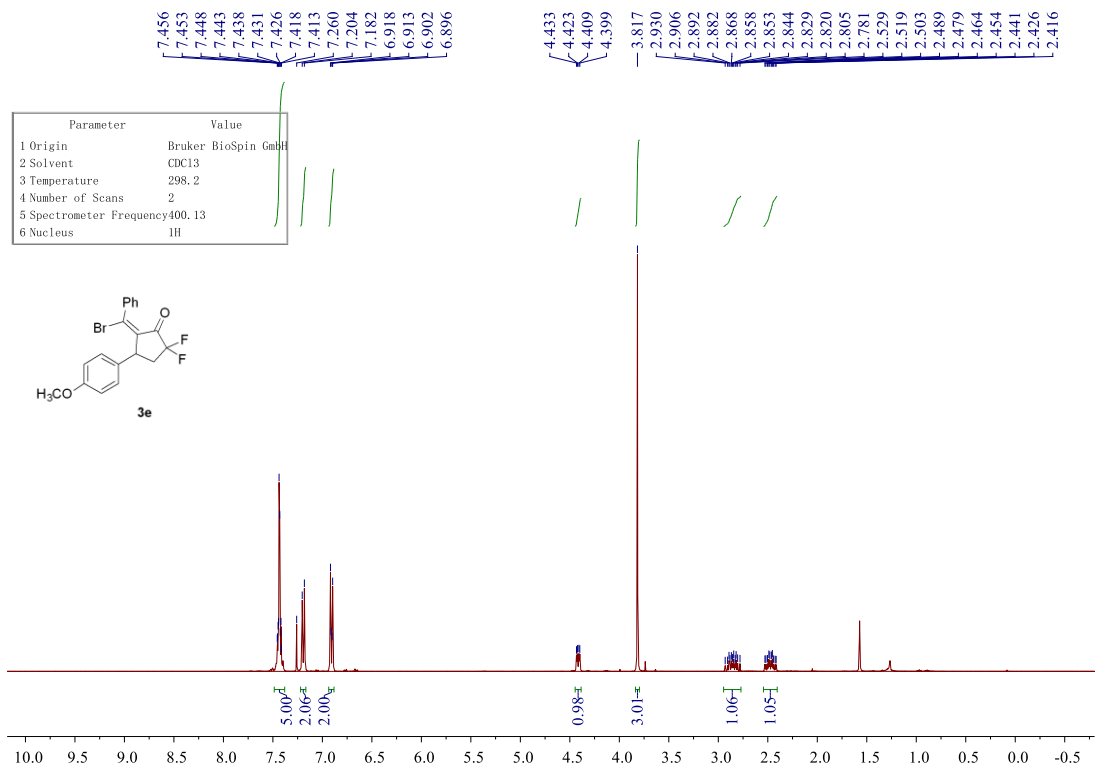
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.5
4 Number of Scans	271
5 Spectrometer Frequency	100.61
6 Nucleus	13C



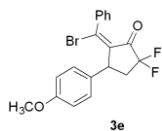
103.880  
104.603  
105.886  
106.608

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.7
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

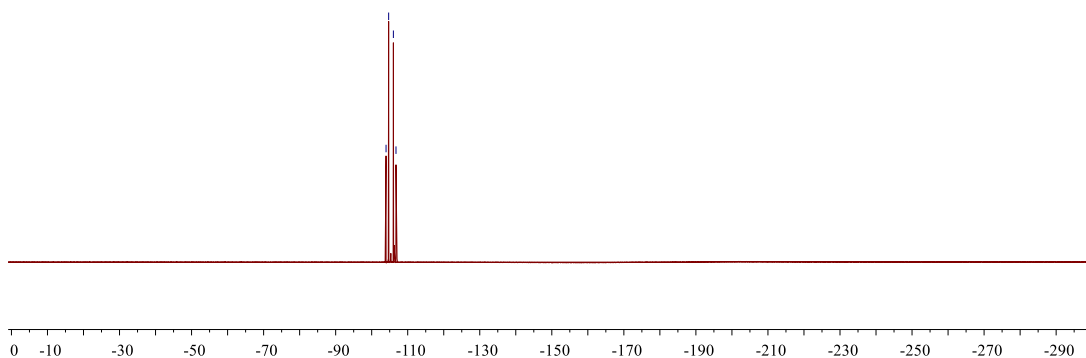




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.44
6 Nucleus	19F



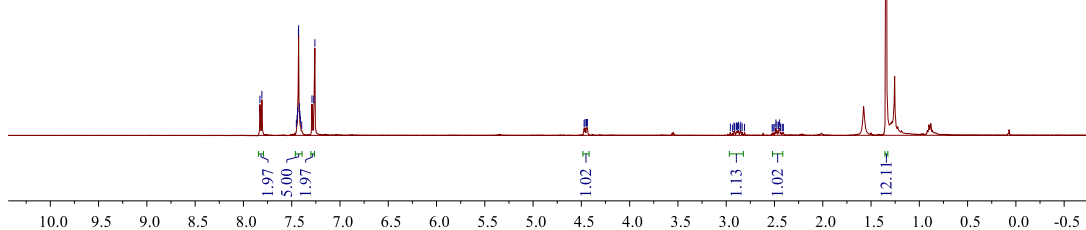
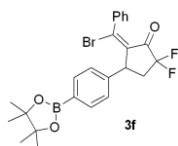
-103.987  
-104.709  
-106.024  
-106.746



7.829  
7.809  
7.452  
7.444  
7.439  
7.430  
7.428  
7.421  
7.415  
7.410  
7.396  
7.290  
7.270  
7.260

4.472  
4.462  
4.447  
4.437  
2.957  
2.919  
2.912  
2.895  
2.887  
2.880  
2.874  
2.849  
2.834  
2.485  
2.475  
2.457  
1.347

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



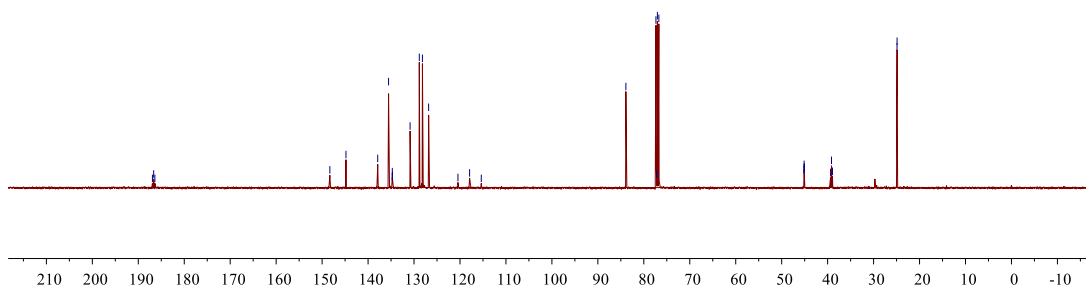
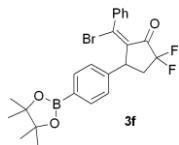
186.925  
186.658  
186.390

148.315  
144.808  
137.901  
135.541  
134.749  
134.725  
134.699  
130.857  
128.857  
128.170  
126.824  
120.445  
117.908  
115.369

83.903  
77.361  
77.247  
77.044  
76.726

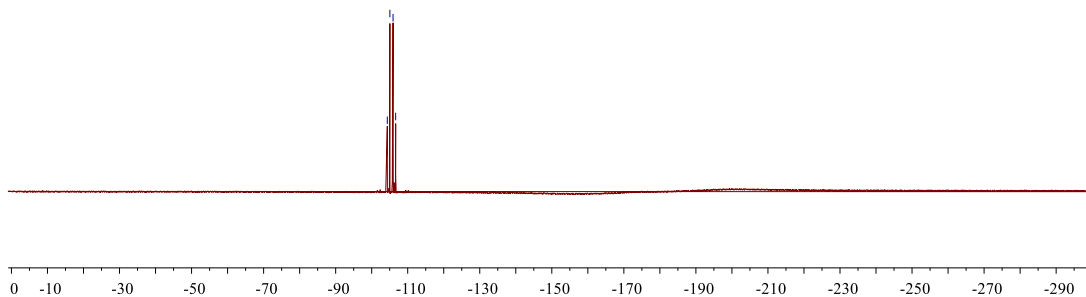
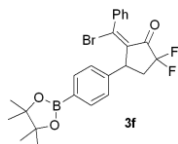
45.141  
45.117  
45.100  
45.075  
39.363  
39.157  
38.950  
24.903  
24.892

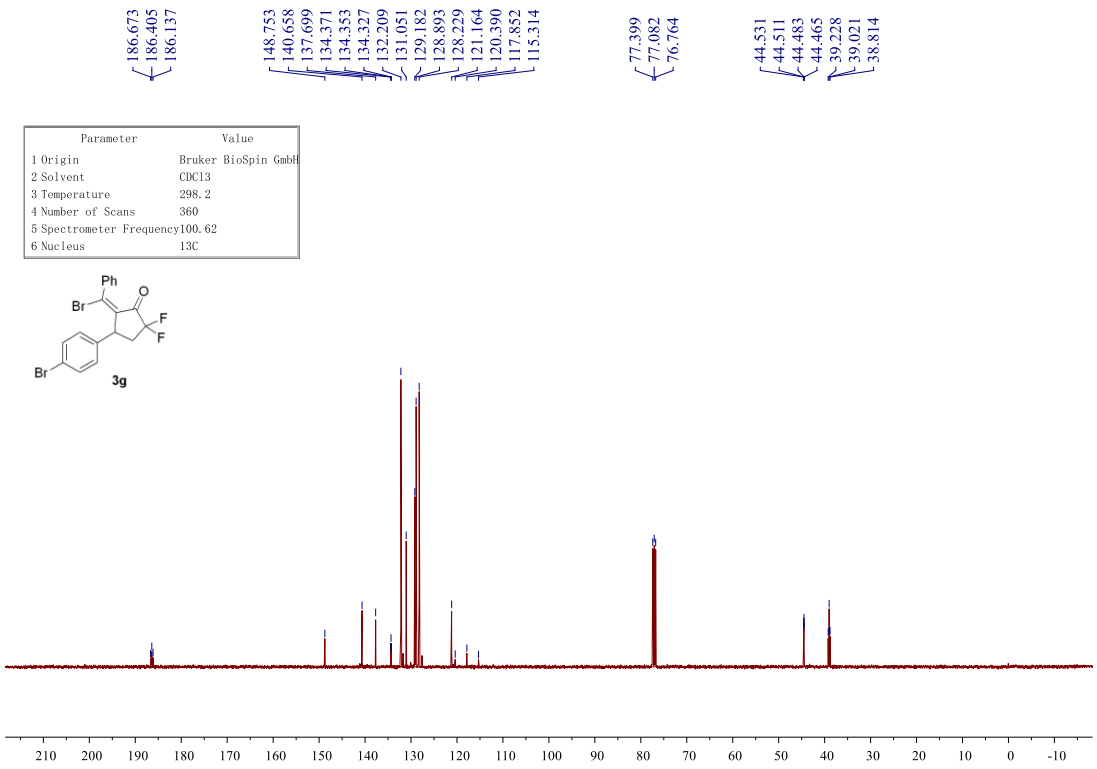
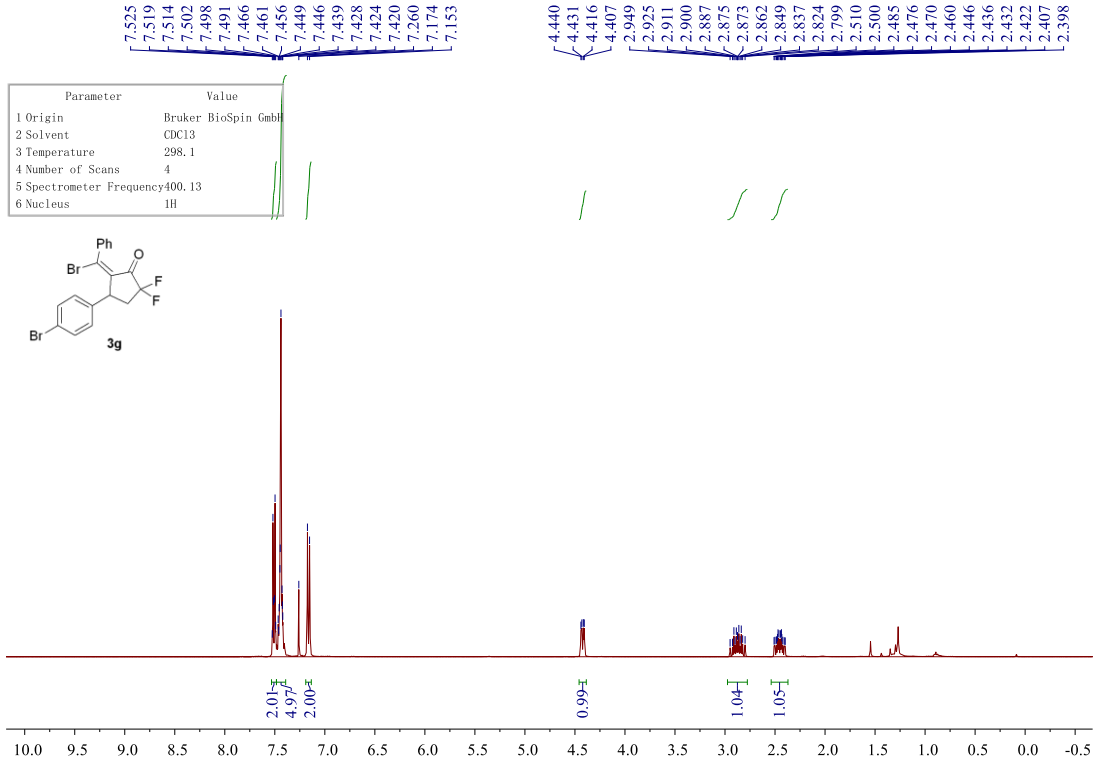
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.4
4 Number of Scans	500
5 Spectrometer Frequency	100.62
6 Nucleus	13C



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.44
6 Nucleus	19F

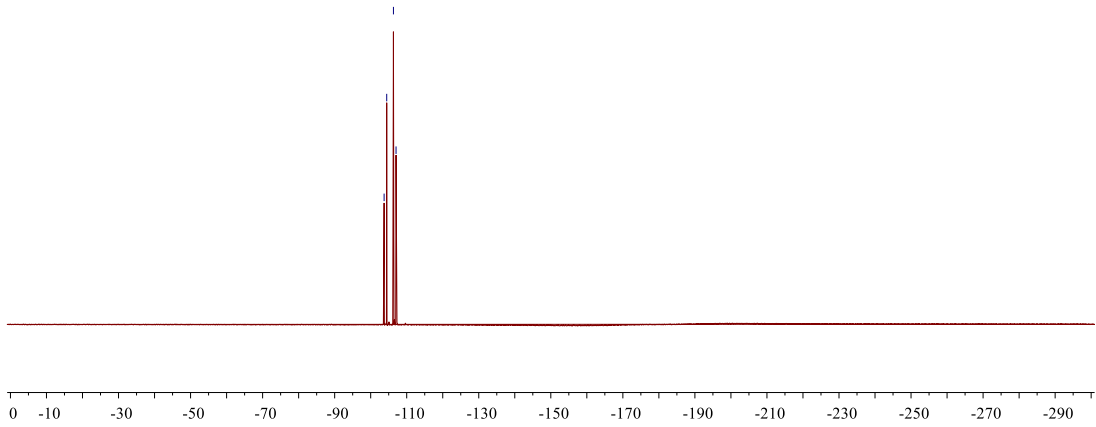
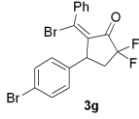
-104.331  
-105.053  
-105.935  
-106.657





Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.44
6 Nucleus	19F

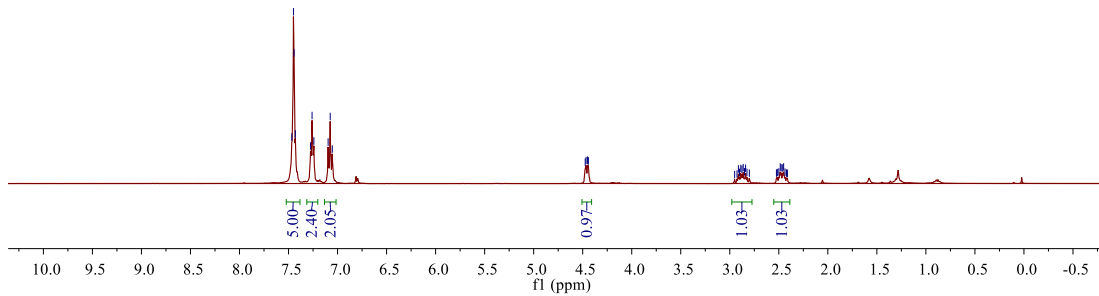
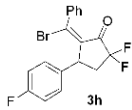
-103.726  
-104.449  
-106.316  
-107.040



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

7.467  
7.450  
7.444  
7.430  
7.276  
7.260  
7.242  
7.096  
7.075  
7.053

4.474  
4.466  
4.450  
4.442  
2.950  
2.926  
2.912  
2.901  
2.888  
2.875  
2.863  
2.850  
2.839  
2.825  
2.800  
2.524  
2.515  
2.500  
2.485  
2.476  
2.460  
2.451  
2.437  
2.422  
2.412



186.802  
186.534  
186.265

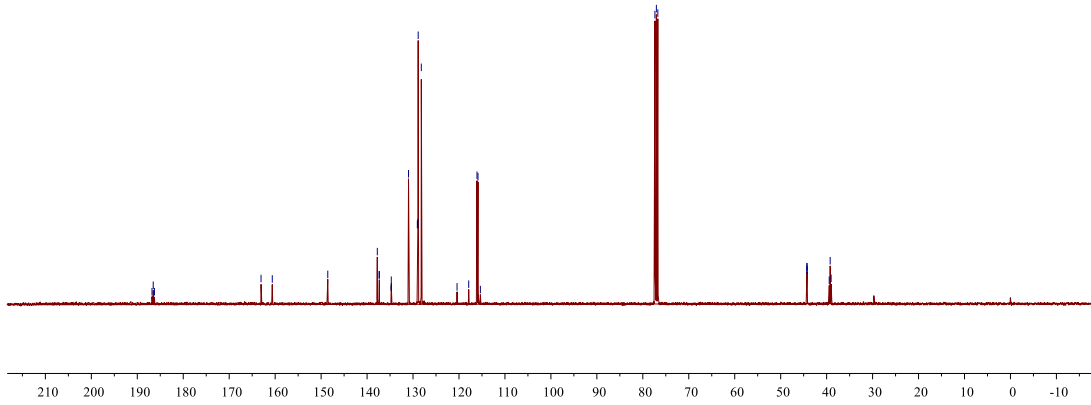
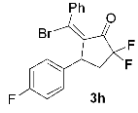
163.075  
160.630

148.550

137.775  
137.369  
137.336  
134.733  
134.707  
130.980  
129.049  
129.040  
128.970  
128.961  
128.878  
128.202  
117.883  
116.082  
115.866  
77.049  
76.732

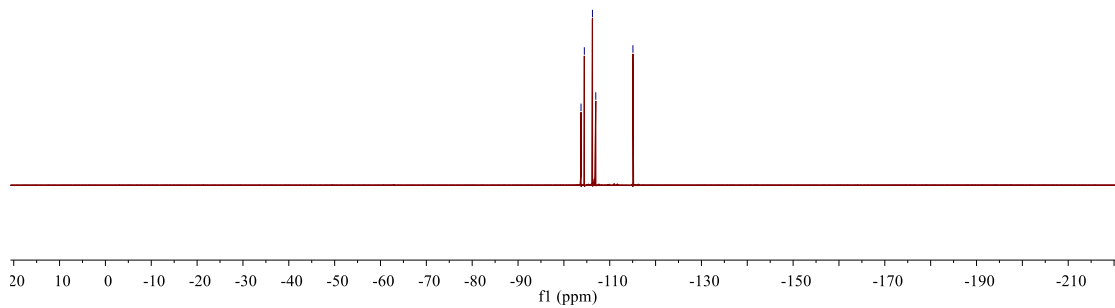
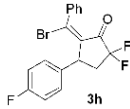
44.309  
44.290  
44.264  
44.244  
39.437  
39.230  
39.026

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C

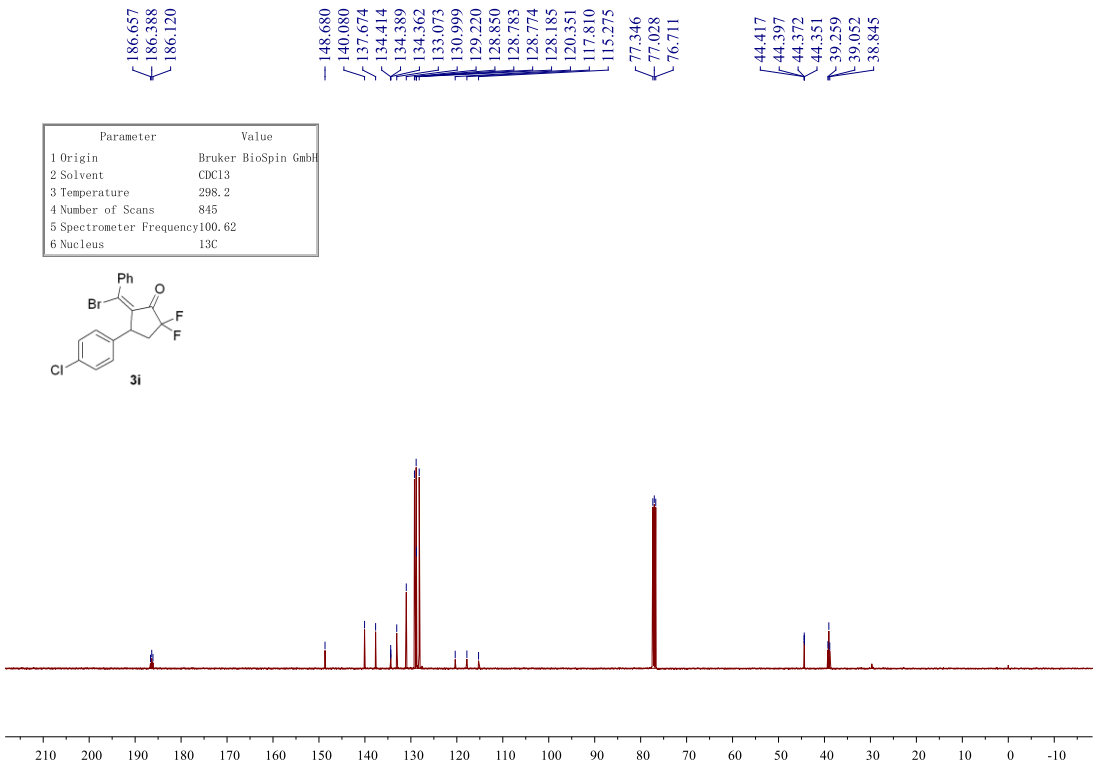
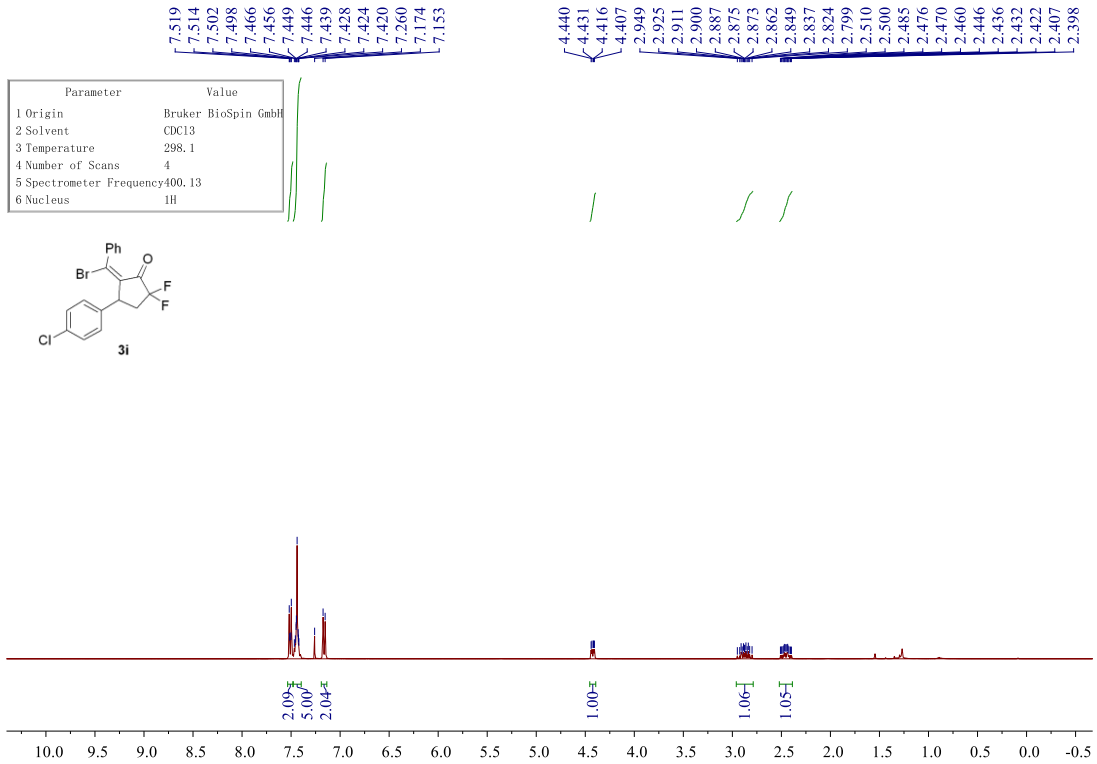


103.738  
104.463  
106.232  
106.954  
115.057

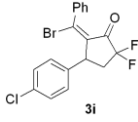
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	<sup>19</sup> F



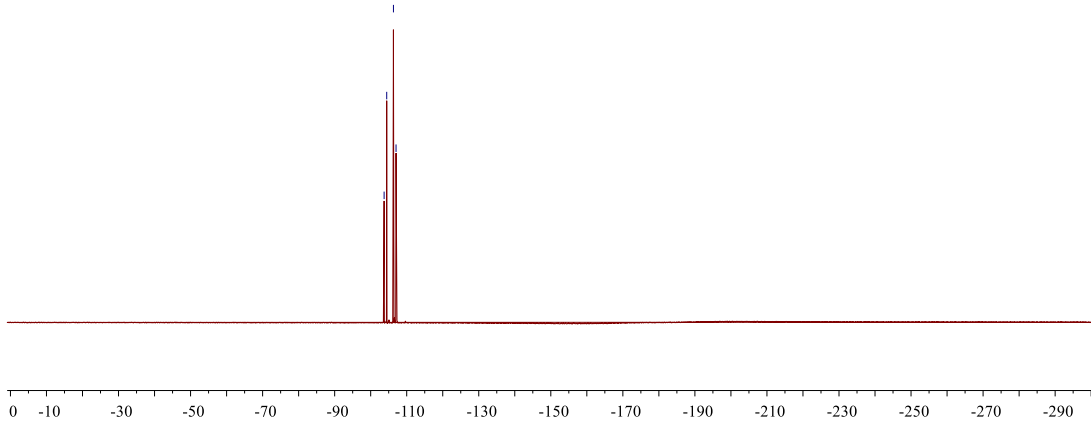




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.44
6 Nucleus	19F

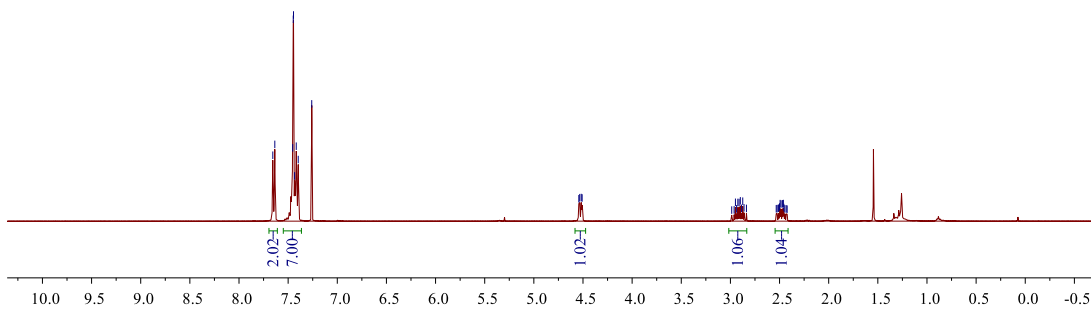
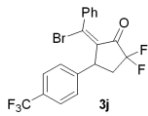


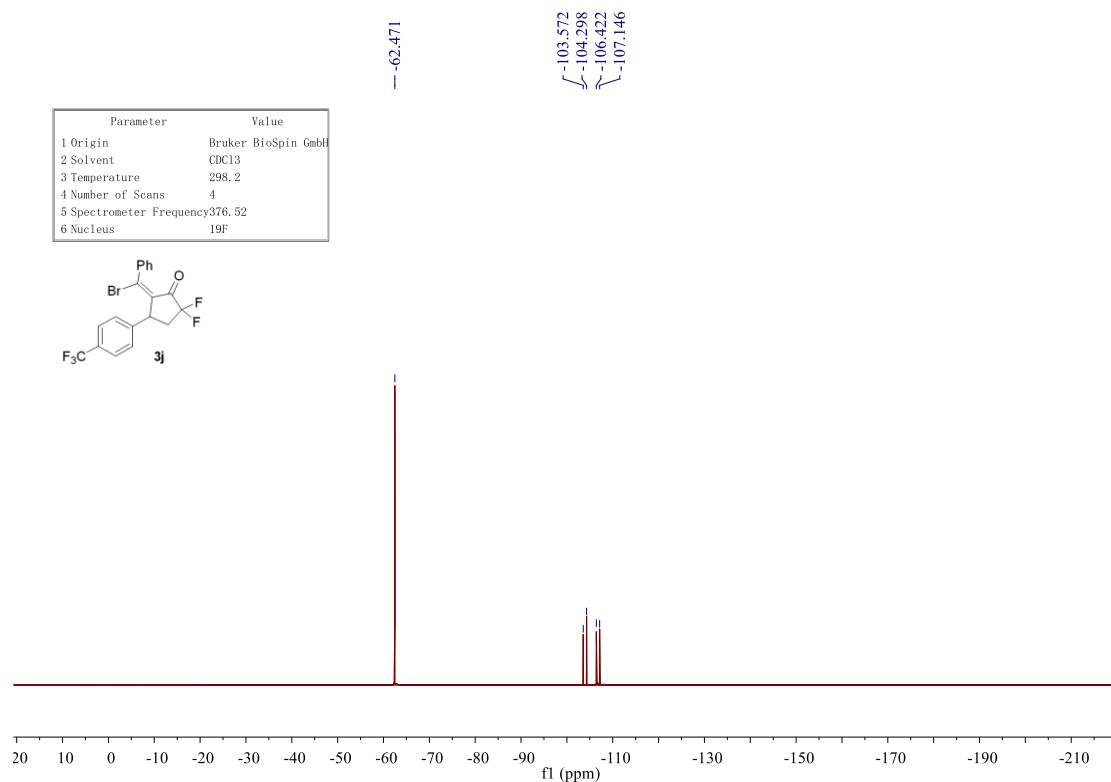
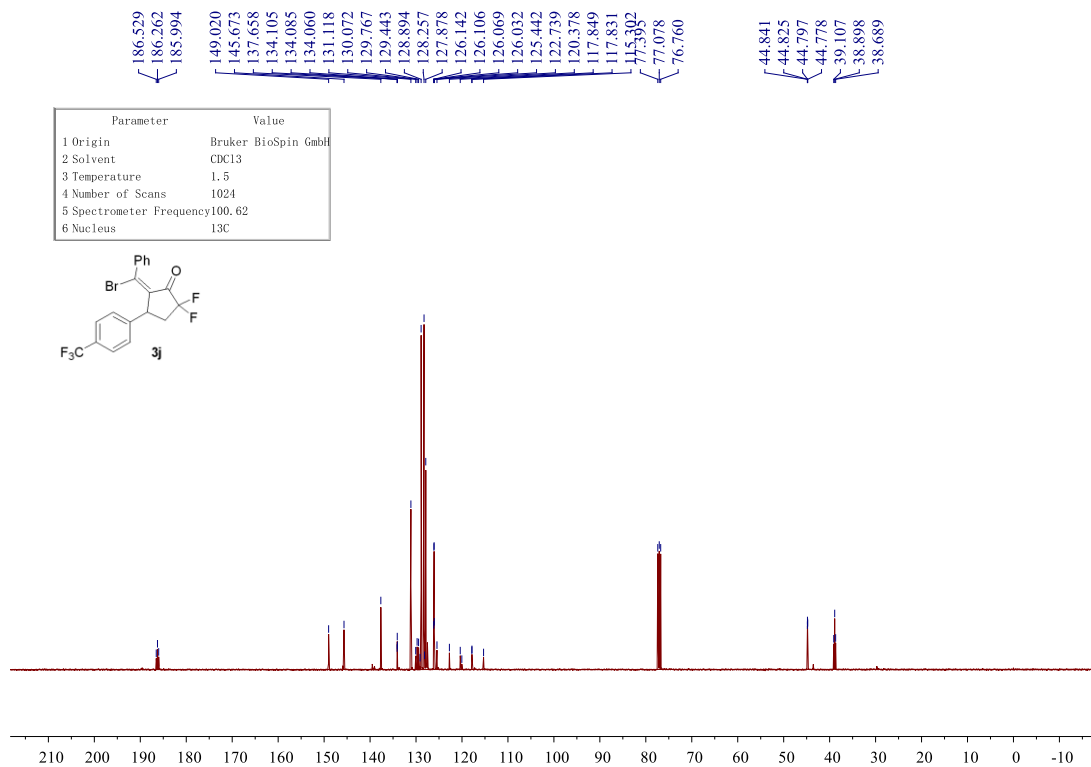
-103.726  
-104.449  
-106.316  
-107.040

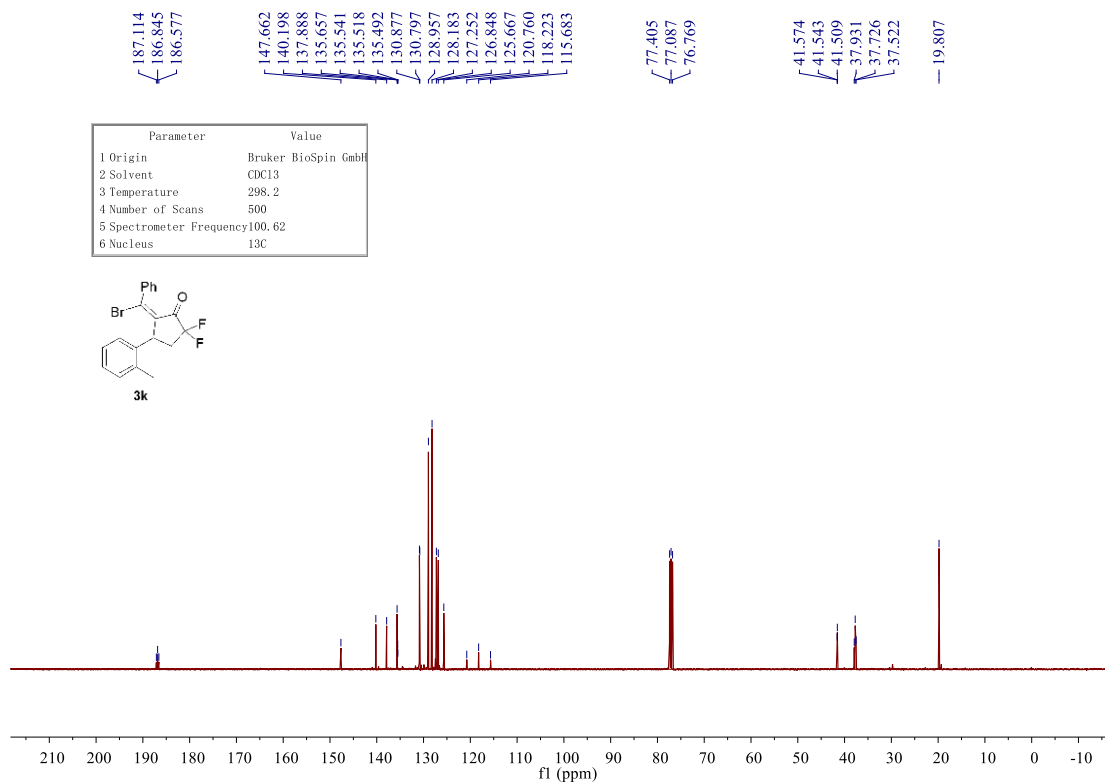
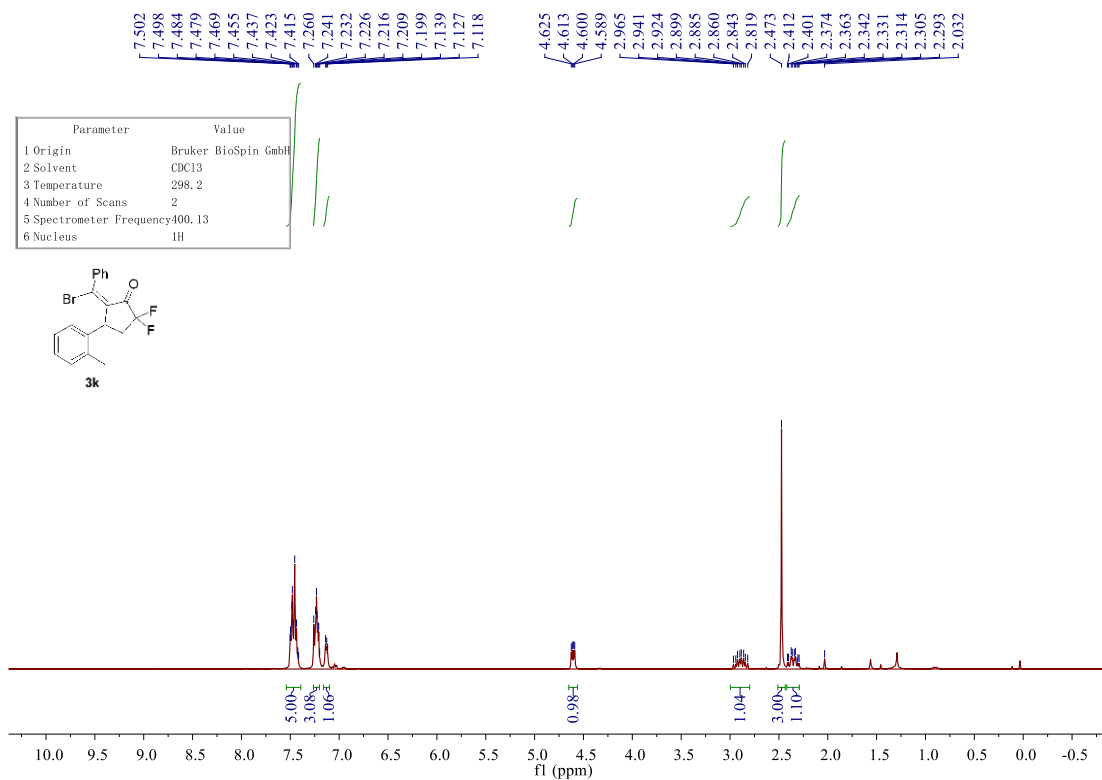


7.656  
7.636  
7.454  
7.448  
7.445  
7.435  
7.418  
7.397  
7.260  
4.542  
4.533  
4.518  
4.509  
2.987  
2.962  
2.949  
2.937  
2.924  
2.912  
2.899  
2.887  
2.875  
2.861  
2.837  
2.534  
2.524  
2.510  
2.500  
2.494  
2.485  
2.471  
2.461  
2.456  
2.446  
2.432  
2.423

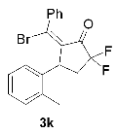
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	4
5 Spectrometer Frequency	400.13
6 Nucleus	1H



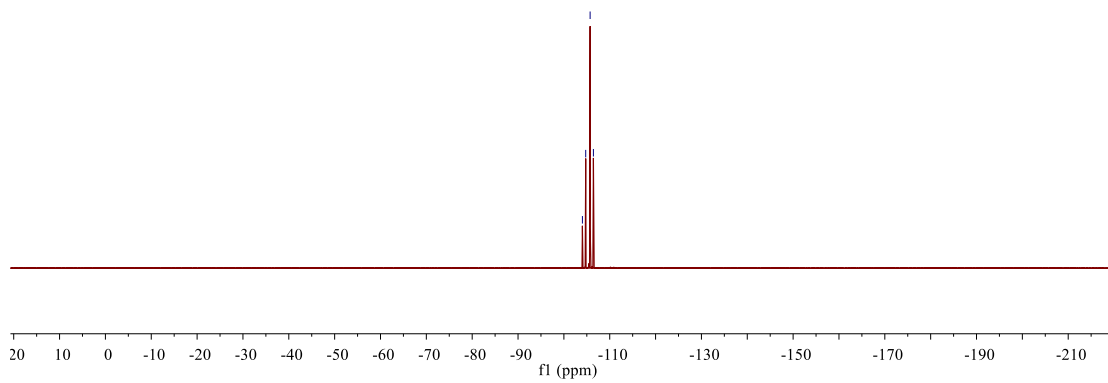




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

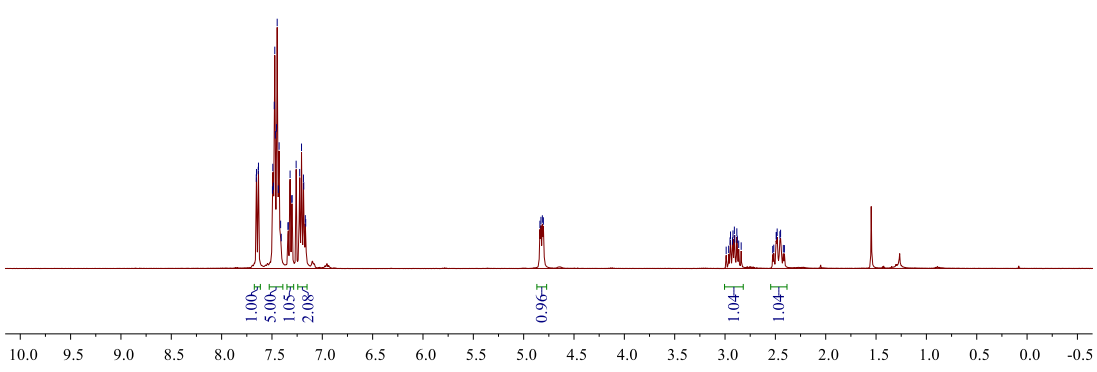
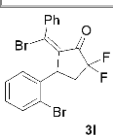


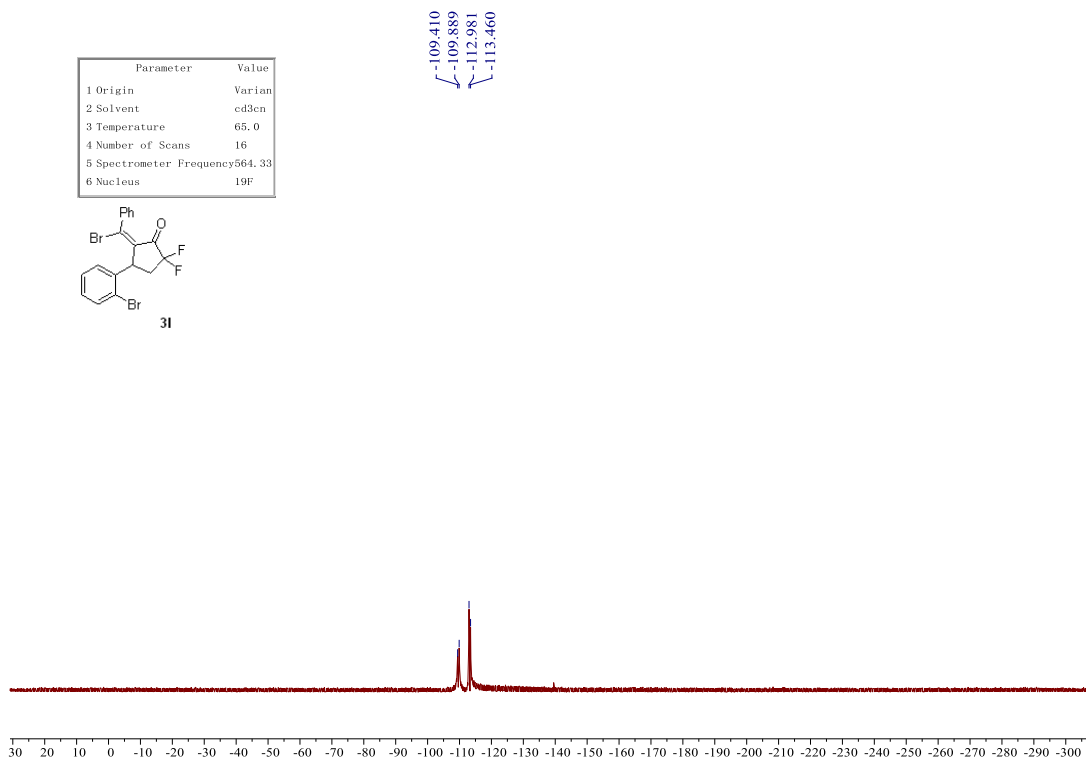
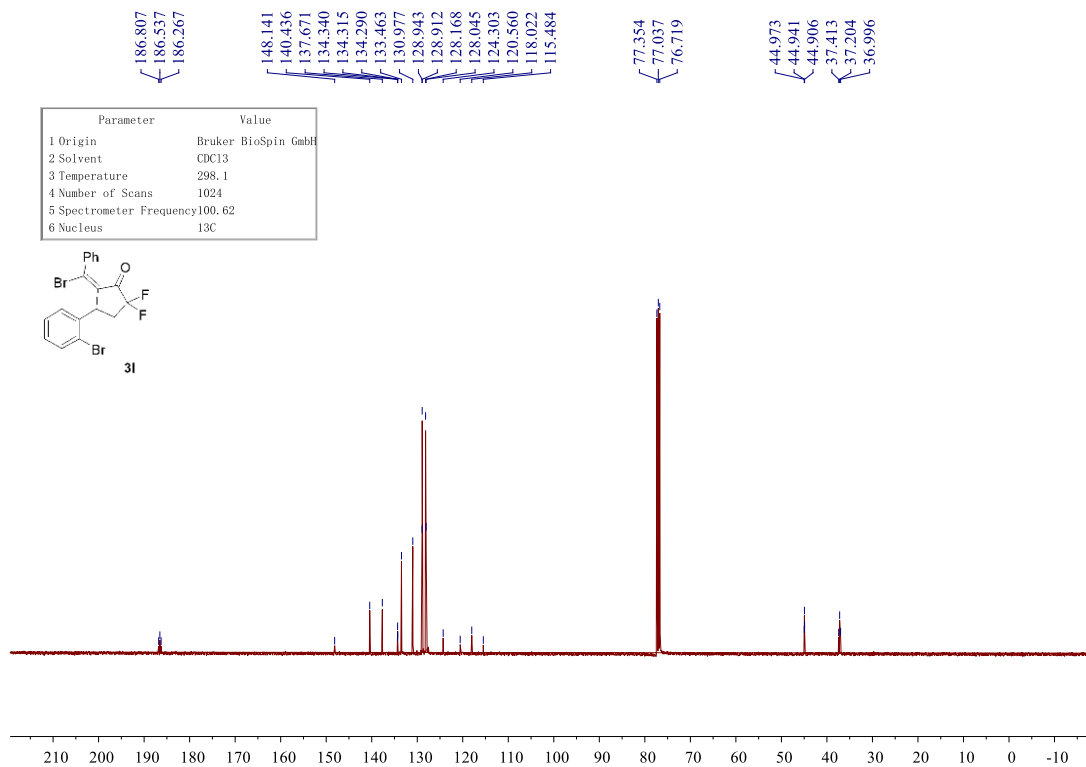
-104.042  
-104.762  
-105.723  
-106.442

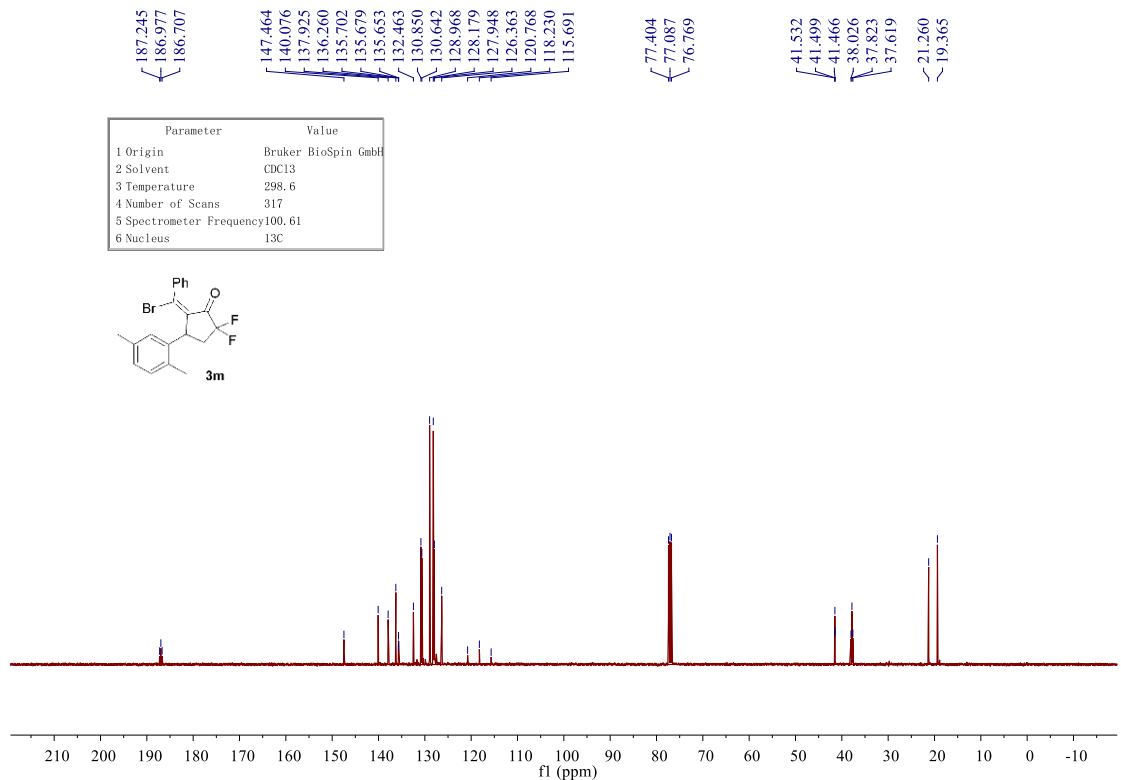
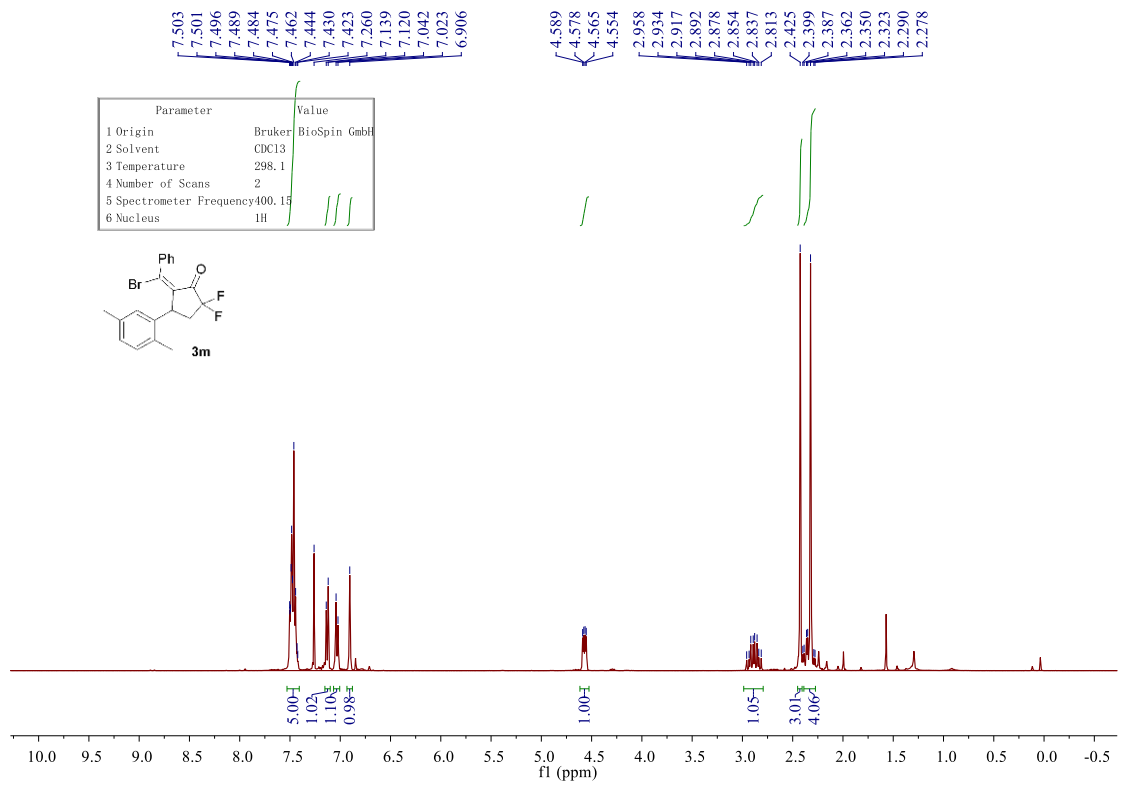


7.656  
7.654  
7.636  
7.634  
7.495  
7.492  
7.486  
7.477  
7.472  
7.466  
7.455  
7.448  
7.437  
7.429  
7.414  
7.338  
7.320  
7.303  
7.300  
7.260  
7.225  
7.207  
7.187  
7.184  
7.169  
7.168  
4.868  
4.828  
4.814  
4.804  
2.989  
2.964  
2.950  
2.946  
2.926  
2.921  
2.907  
2.903  
2.883  
2.878  
2.864  
2.840  
2.526  
2.516  
2.492  
2.489  
2.482  
2.455  
2.448  
2.421  
2.410

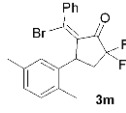
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	4
5 Spectrometer Frequency	400.13
6 Nucleus	1H



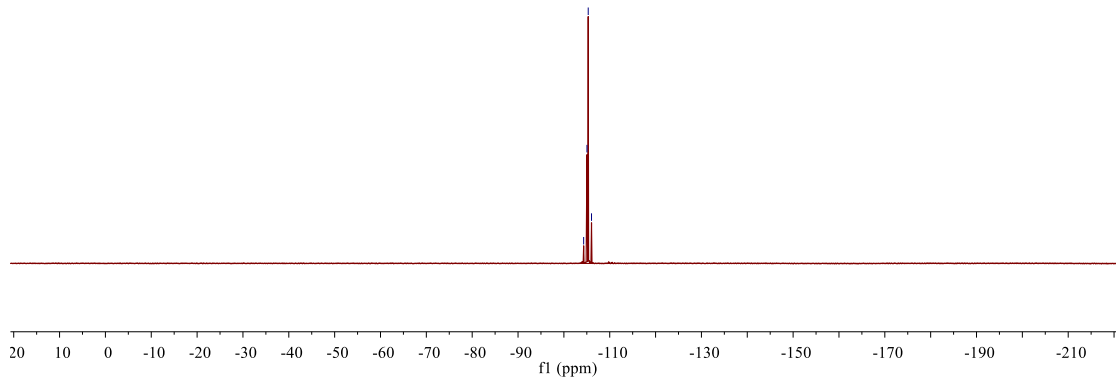




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



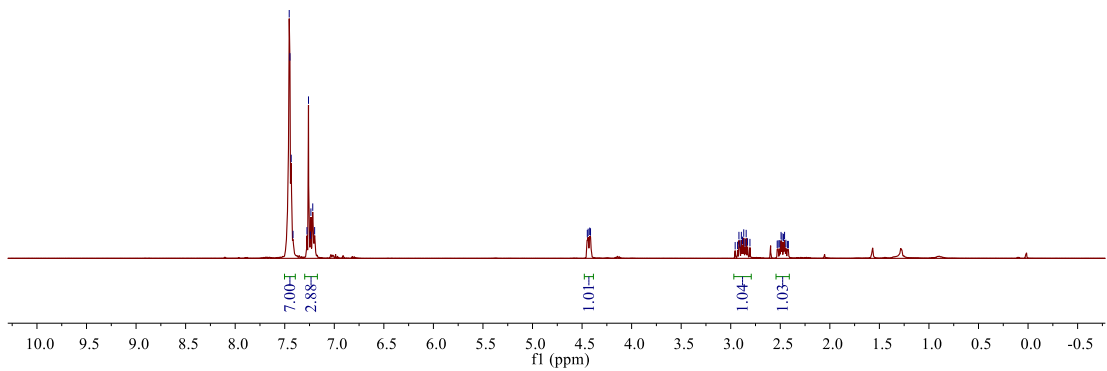
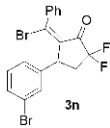
-104.312  
-105.053  
-105.307  
-106.027



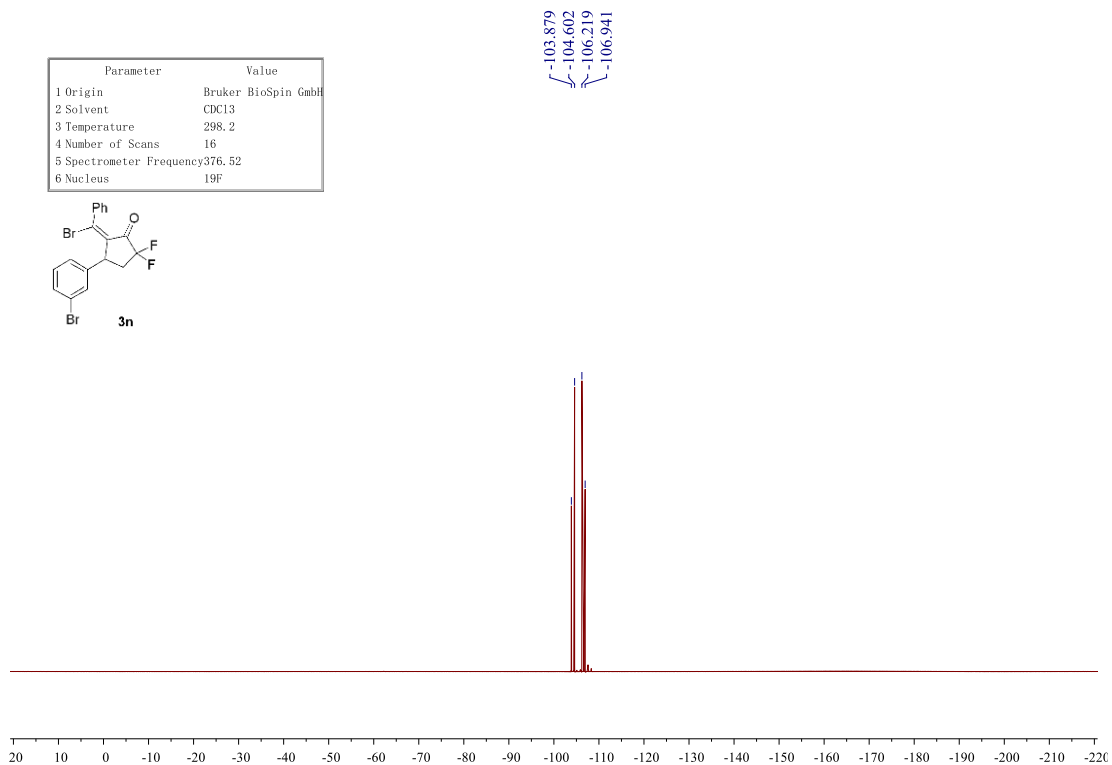
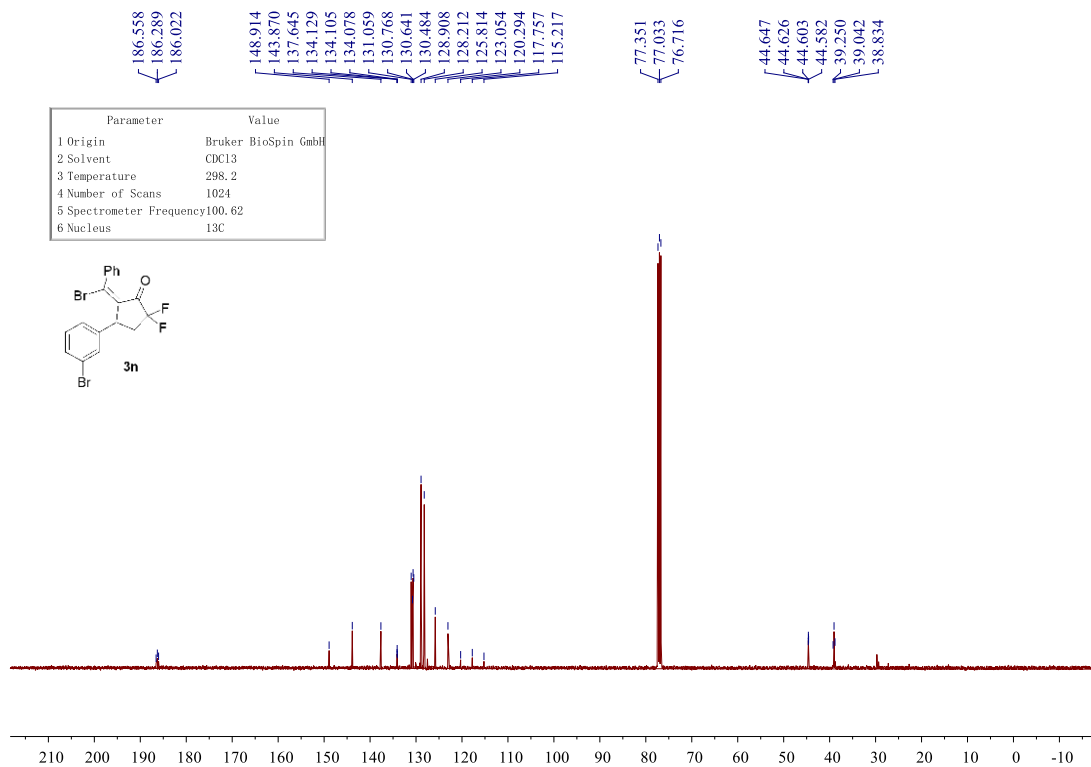
7.455  
7.447  
7.435  
7.416  
7.276  
7.260  
7.242  
7.236  
7.217  
7.198

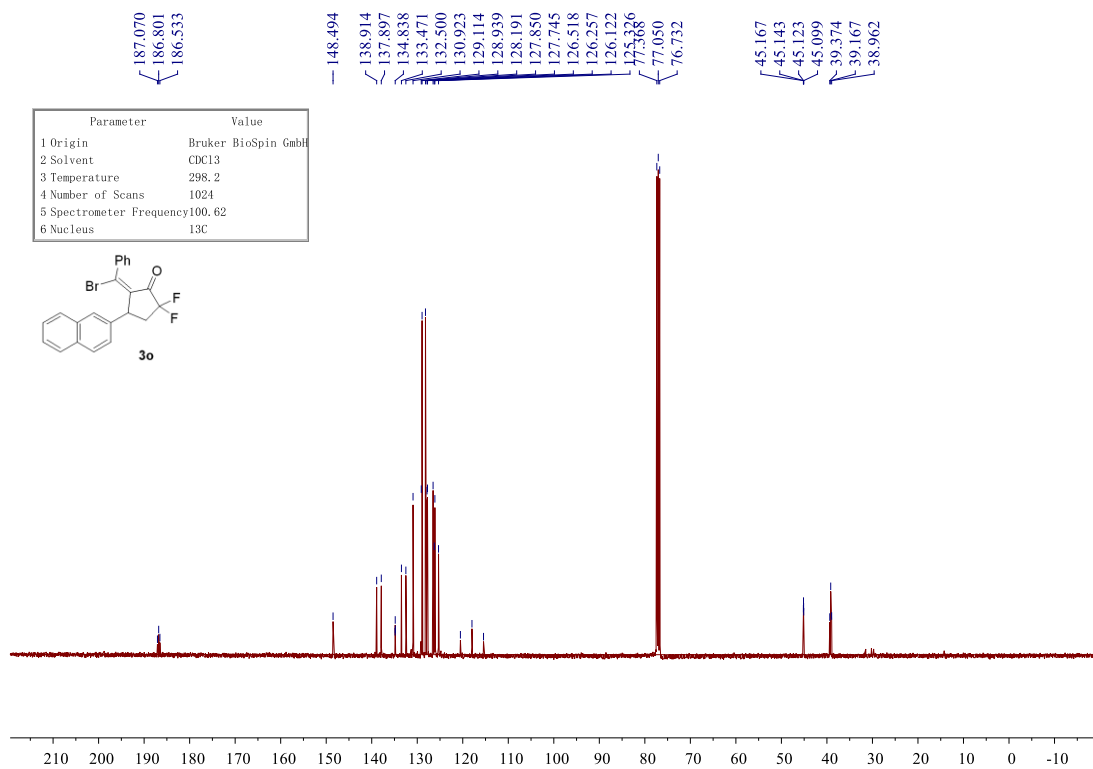
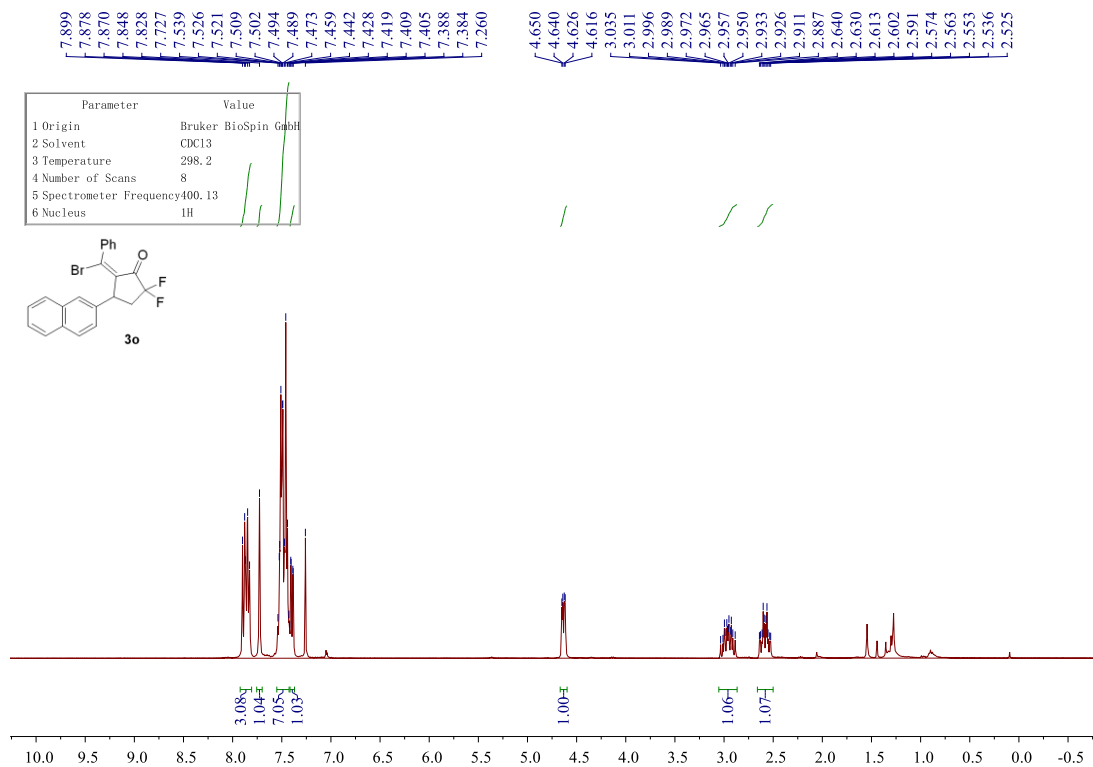
4.447  
4.439  
4.423  
4.415  
2.955  
2.931  
2.917  
2.907  
2.893  
2.882  
2.879  
2.869  
2.855  
2.844  
2.830  
2.806  
2.531  
2.521  
2.506  
2.492  
2.482  
2.467  
2.457  
2.444  
2.428  
2.418

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

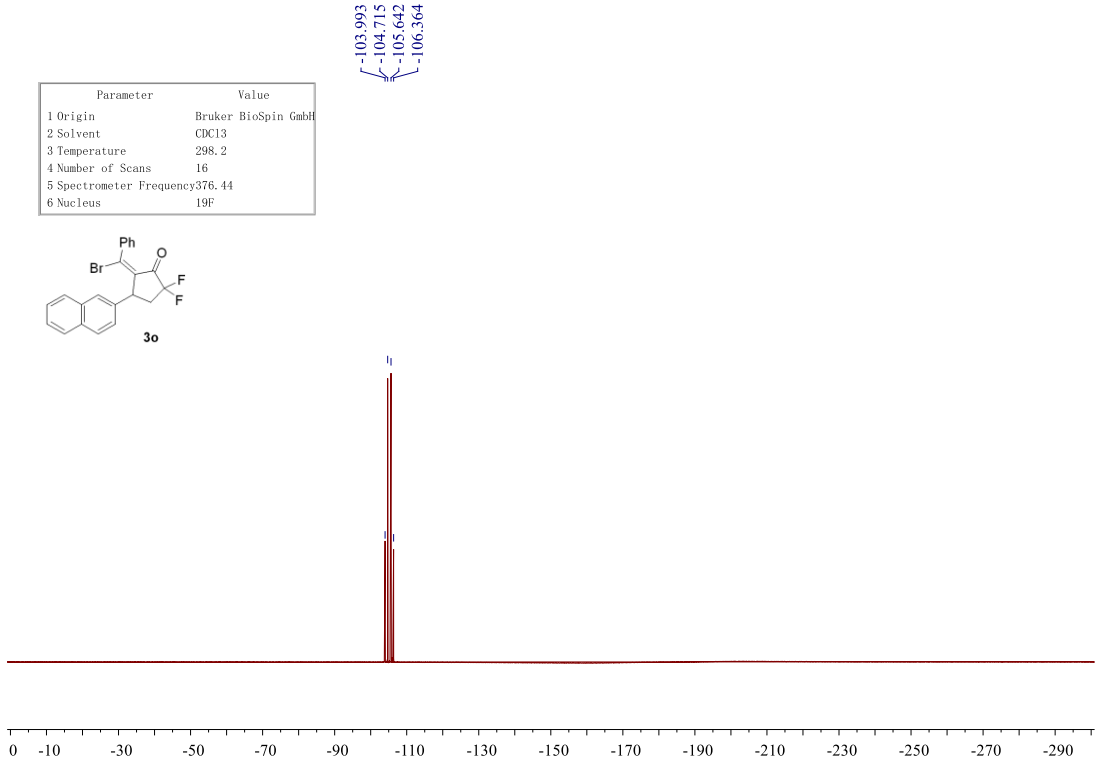
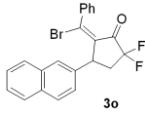






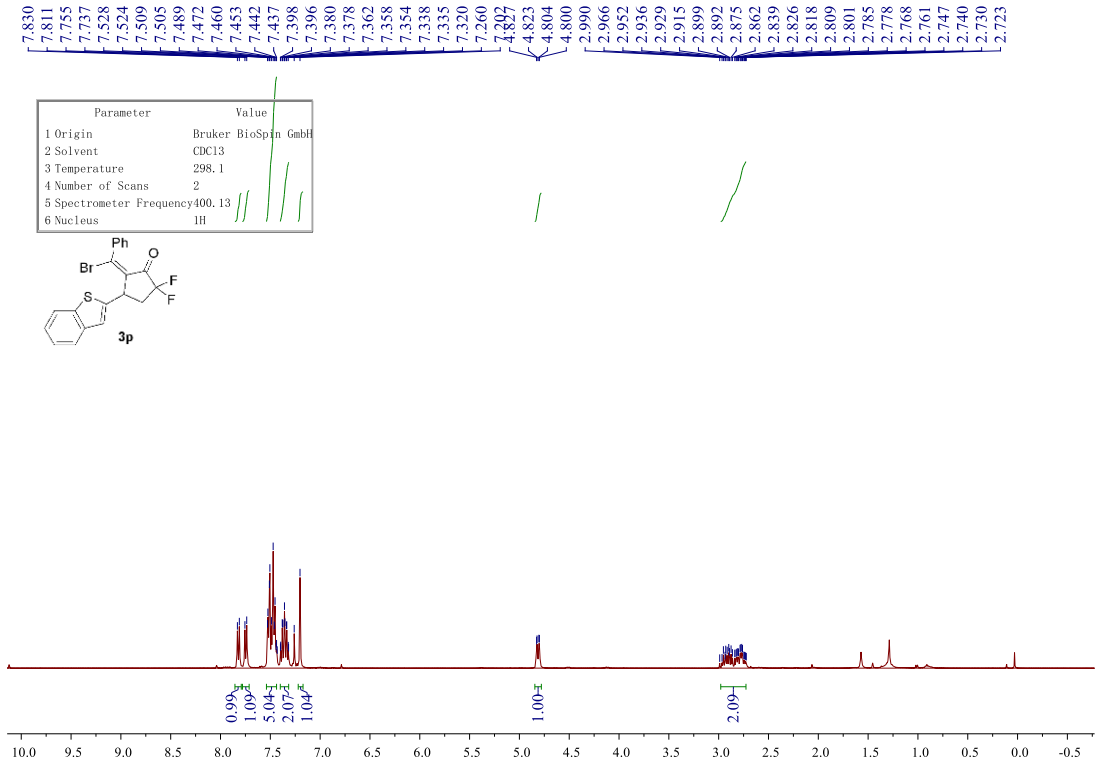
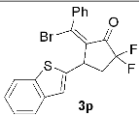


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	376.44
6 Nucleus	19F



7.830  
7.811  
7.755  
7.737  
7.528  
7.524  
7.509  
7.505  
7.489  
7.472  
7.460  
7.453  
7.442  
7.437  
7.398  
7.396  
7.380  
7.378  
7.362  
7.358  
7.354  
7.338  
7.335  
7.320  
7.260  
7.202  
4.823  
4.827  
4.804  
4.800  
2.990  
2.966  
2.952  
2.936  
2.929  
2.915  
2.899  
2.892  
2.875  
2.862  
2.839  
2.826  
2.818  
2.809  
2.801  
2.785  
2.778  
2.768  
2.761  
2.747  
2.740  
2.730  
2.723

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



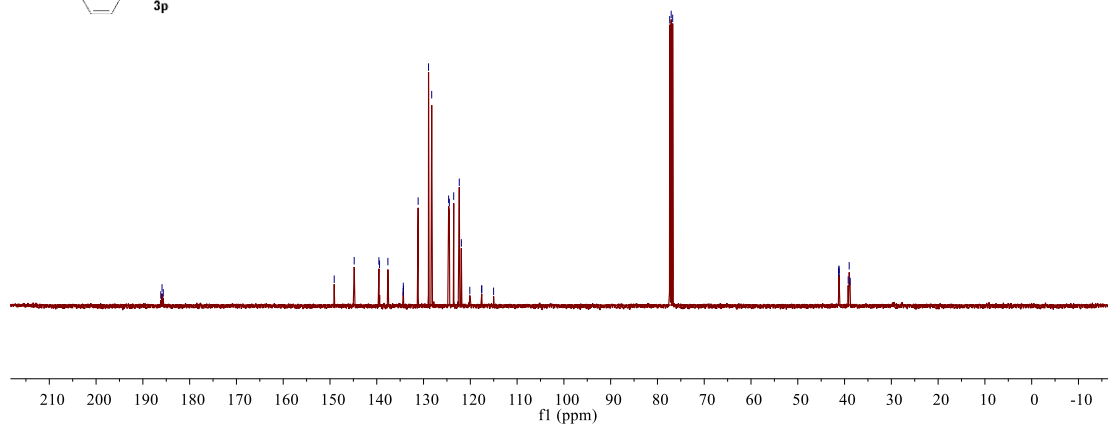
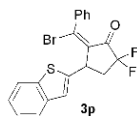
186.170  
185.902  
185.632

149.096  
144.824  
139.546  
139.403  
137.618  
134.355  
134.323  
134.300  
131.152  
128.934  
128.257  
124.638  
124.487  
123.555  
122.362  
121.912  
120.109  
117.572  
117.561  
115.024

77.378  
77.061  
76.743

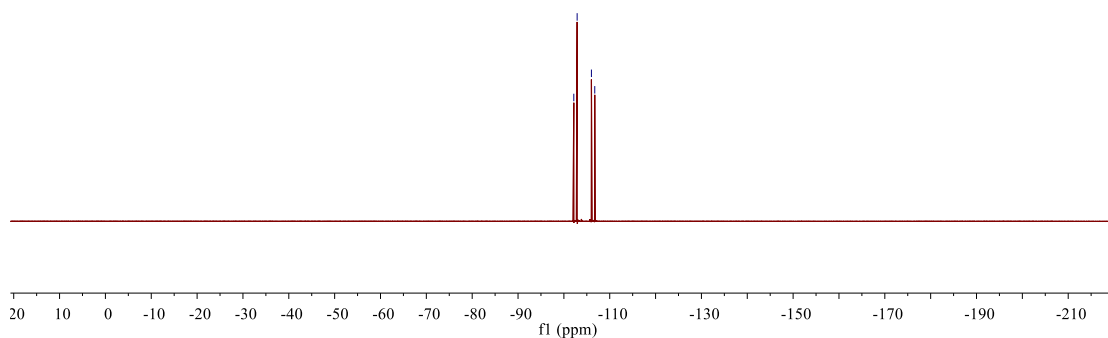
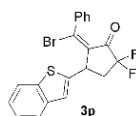
41.245  
41.234  
41.188  
41.178  
39.224  
39.013  
38.804

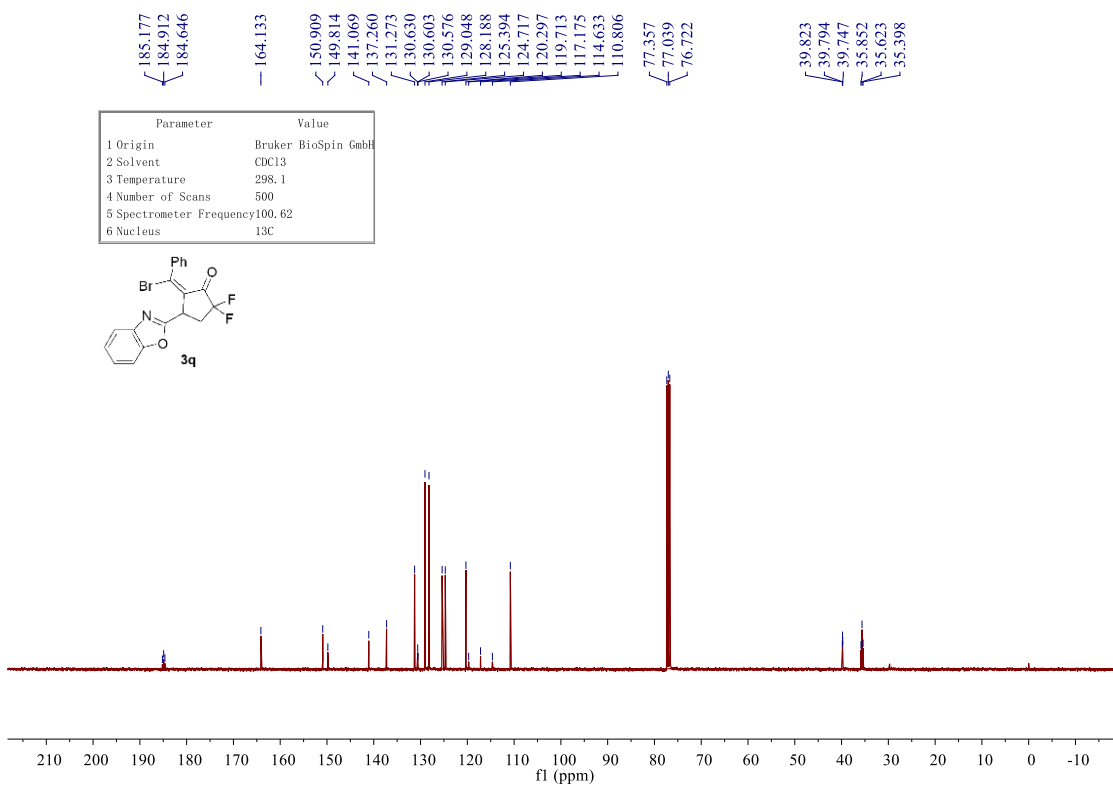
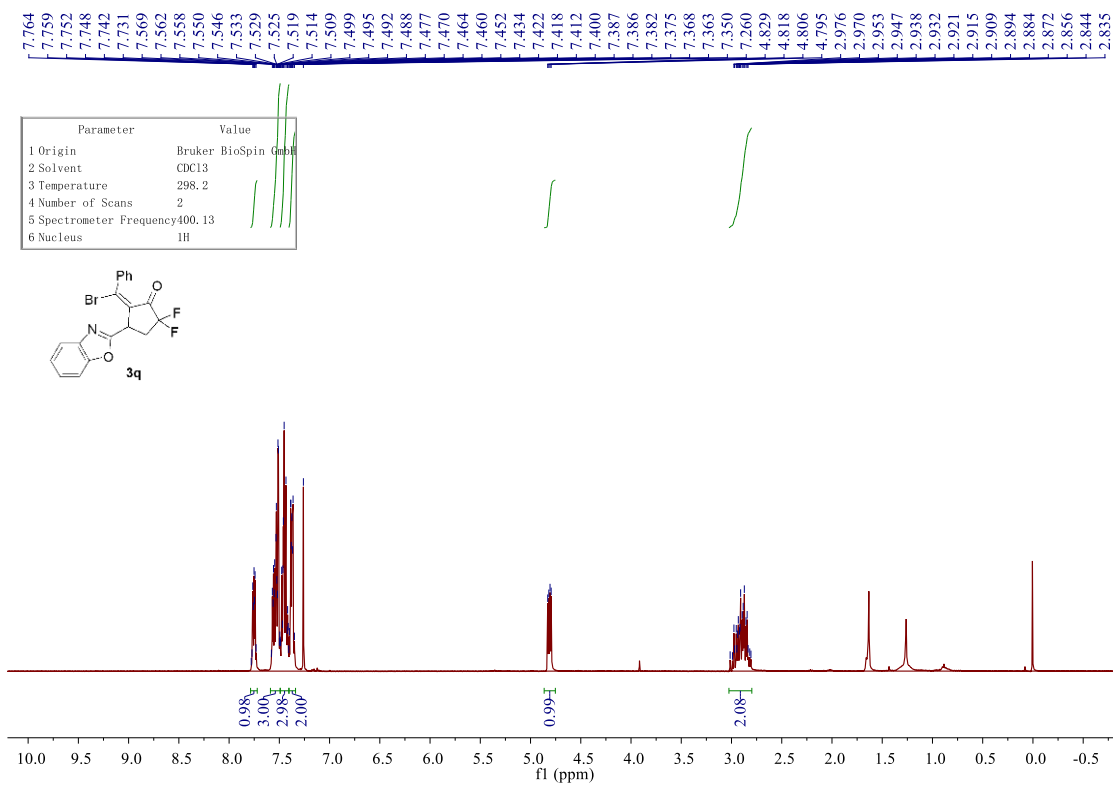
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	301
5 Spectrometer Frequency	100.62
6 Nucleus	13C



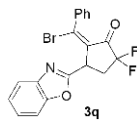
-102.164  
-102.890  
-106.007  
-106.733

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

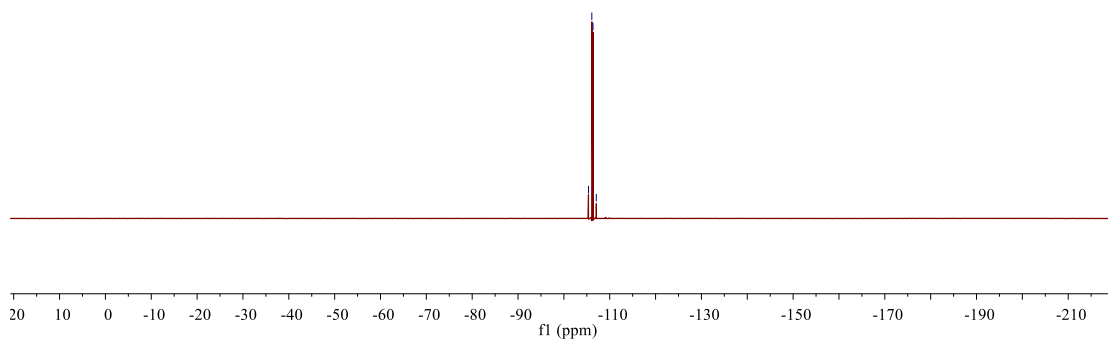




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



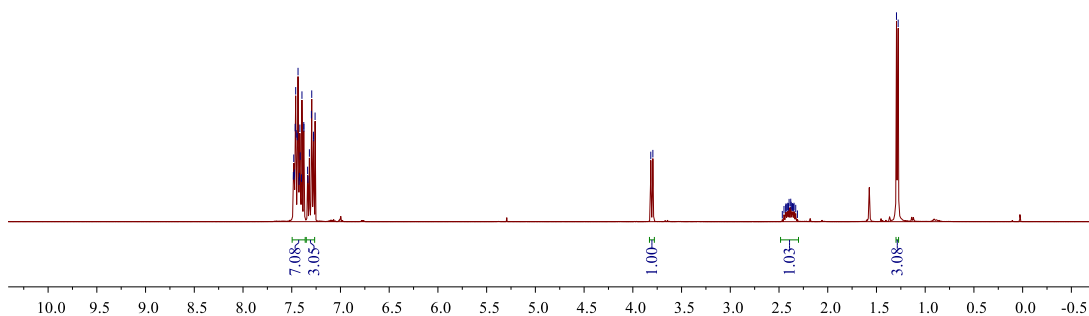
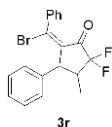
-105.366  
-106.092  
-106.346  
-107.071

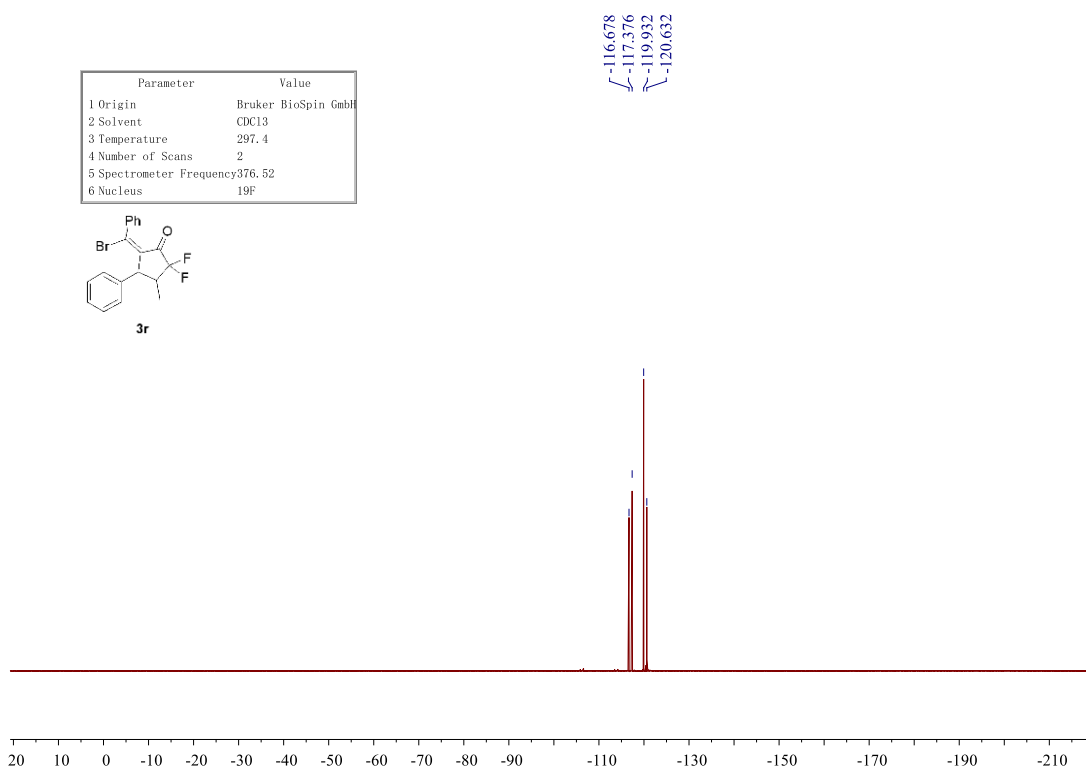
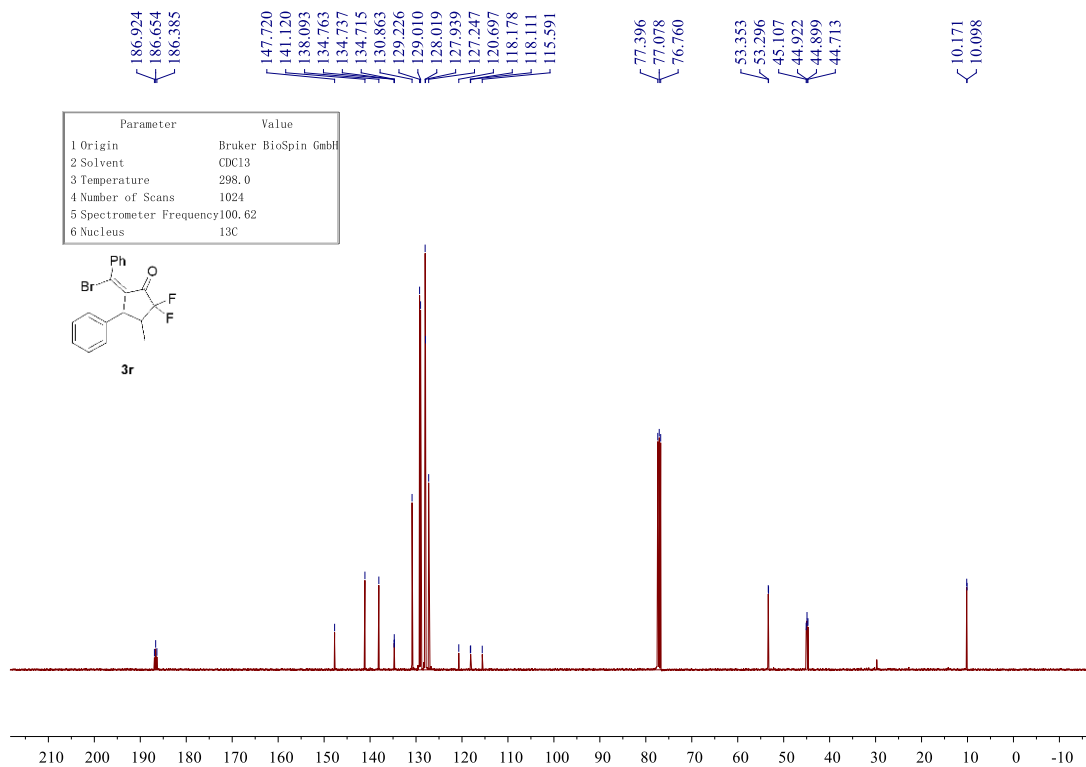


7.483  
7.479  
7.476  
7.474  
7.465  
7.459  
7.454  
7.444  
7.435  
7.425  
7.421  
7.417  
7.413  
7.400  
7.395  
7.376  
7.375  
7.337  
7.334  
7.319  
7.298  
7.295  
7.277  
7.276  
7.260

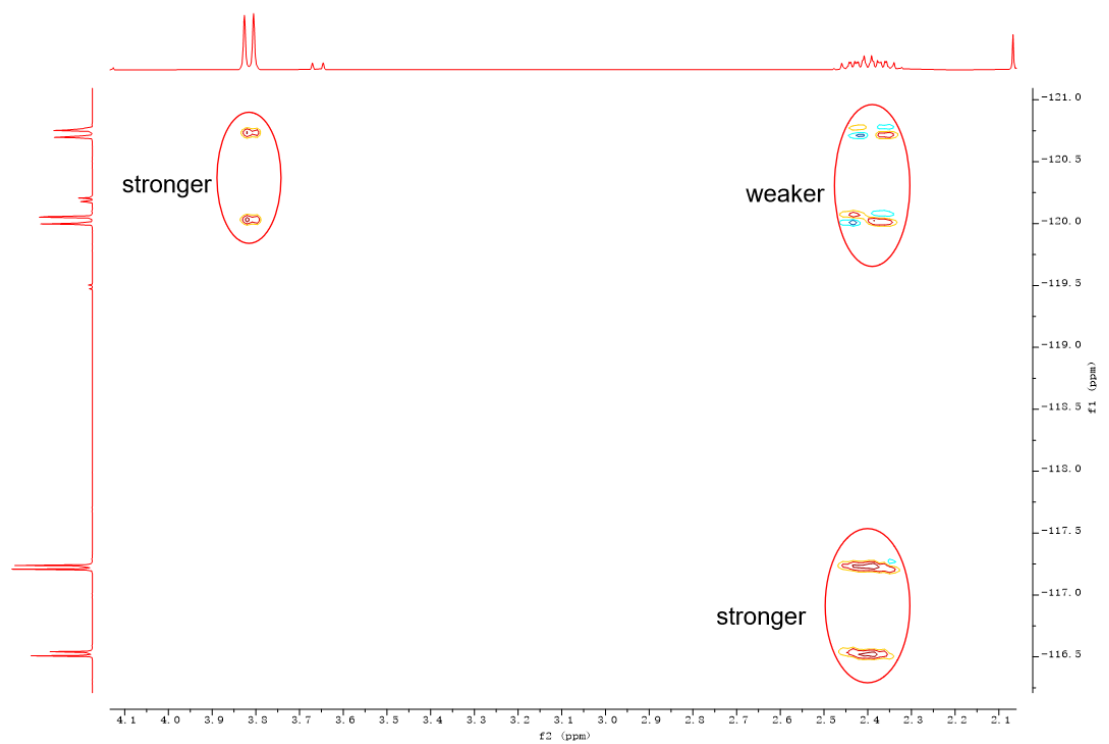
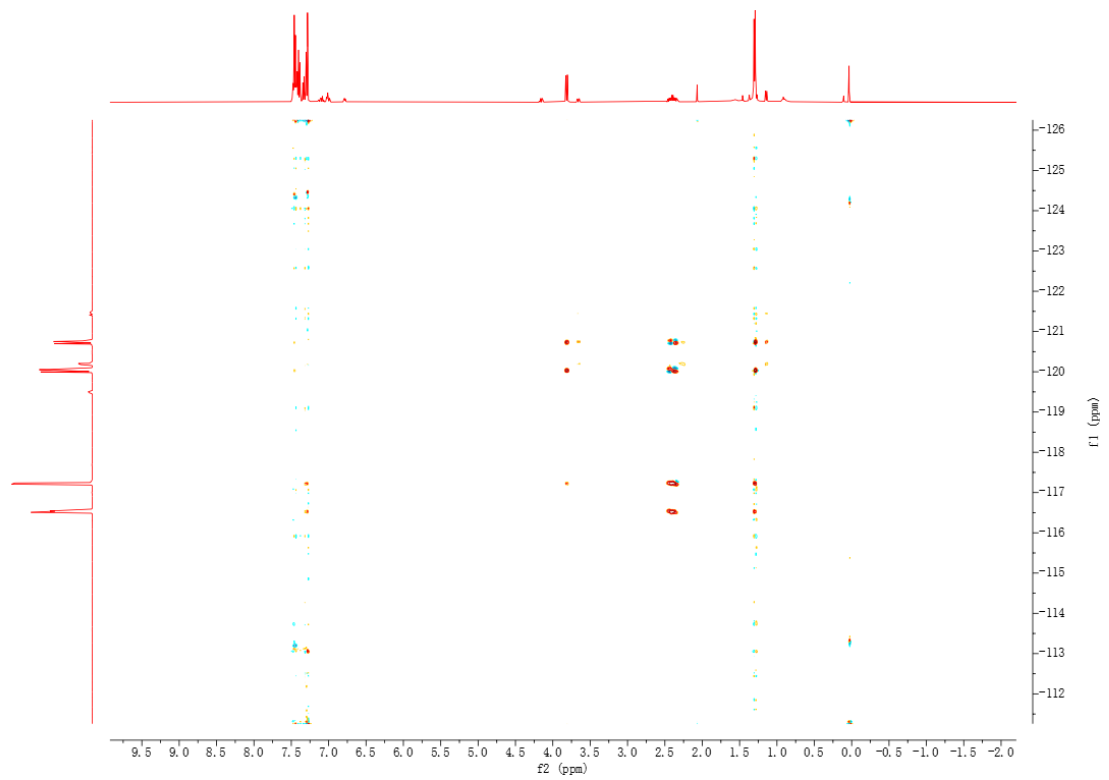
3.816  
3.794  
2.428  
2.411  
2.402  
2.397  
2.380  
2.376  
2.367  
2.363  
2.358  
2.350  
2.346  
1.277

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.3
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

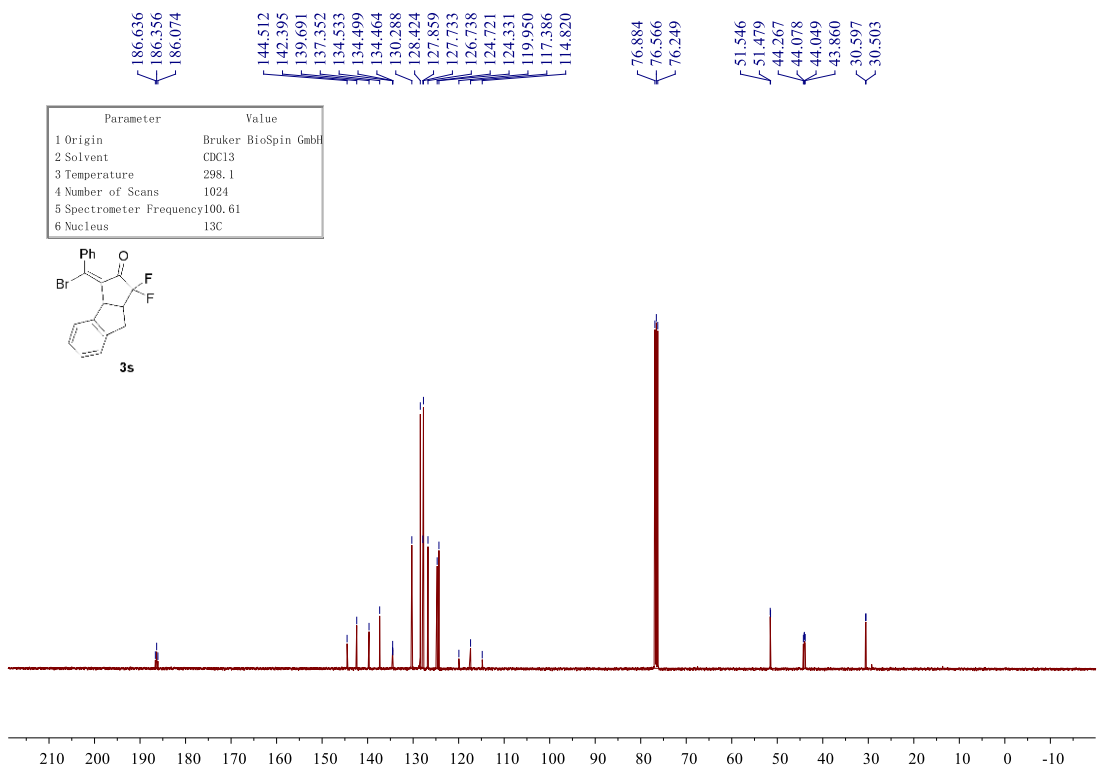
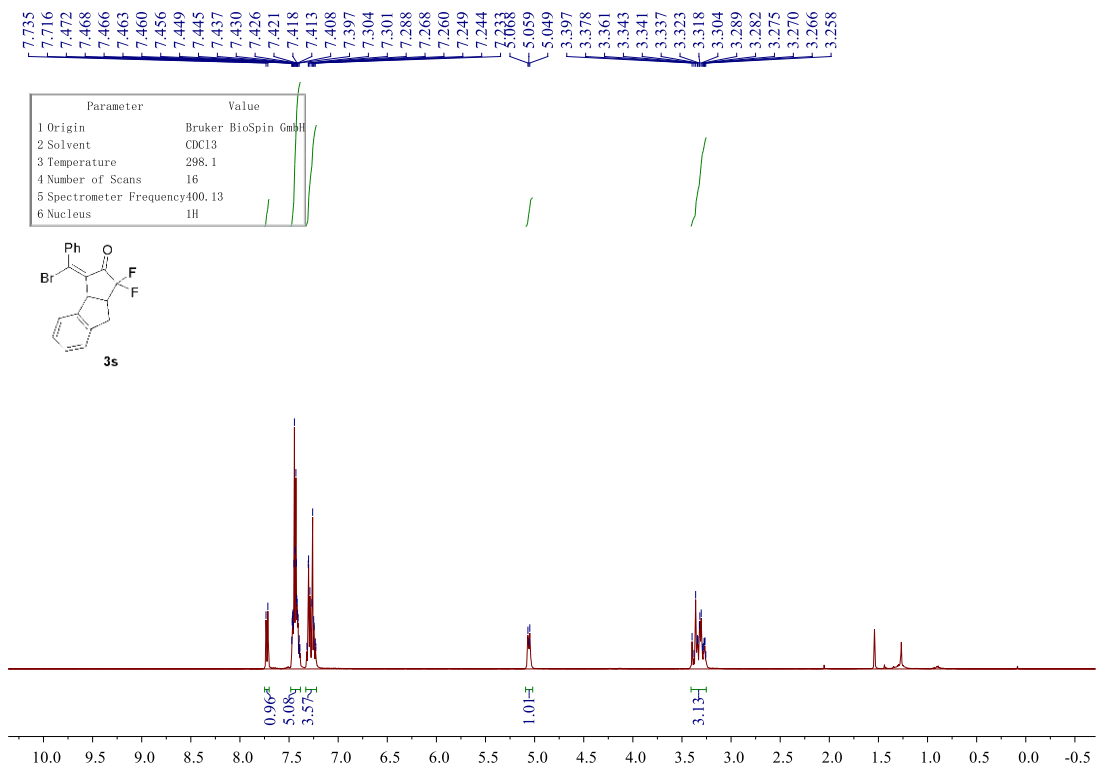




3r (H-F hoesy)

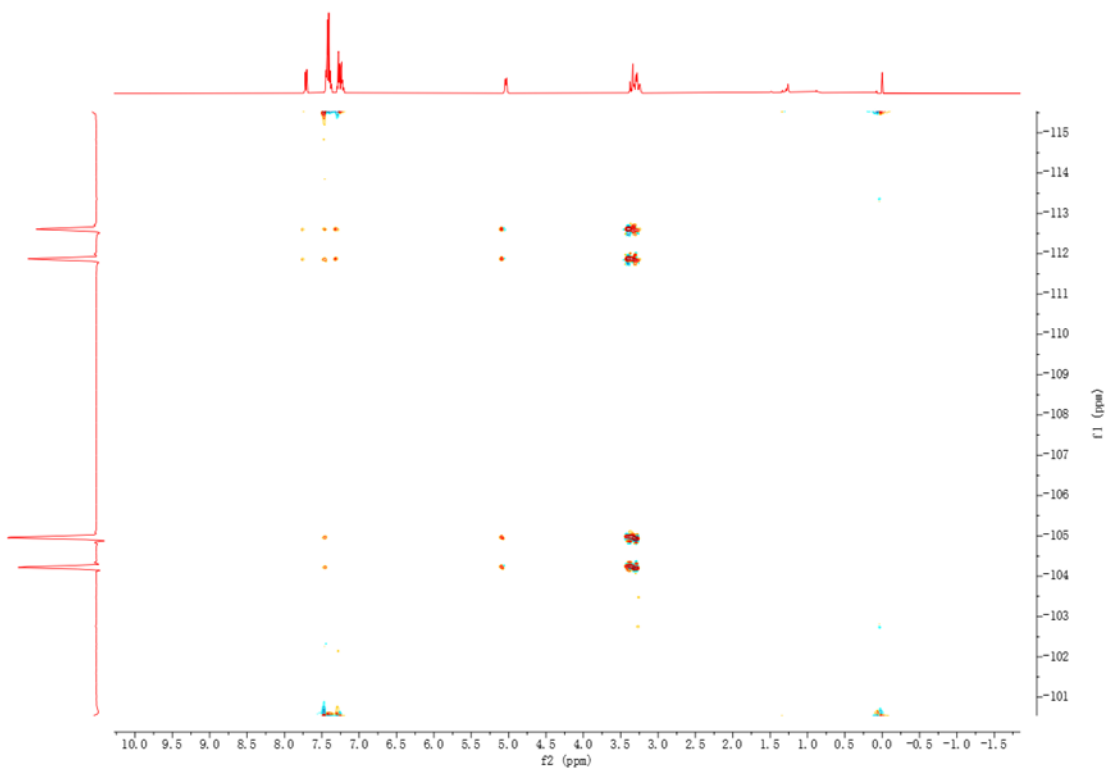
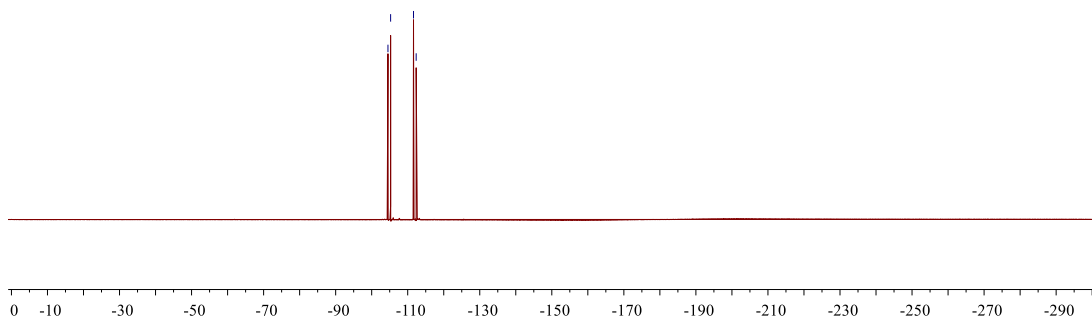
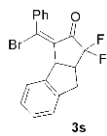


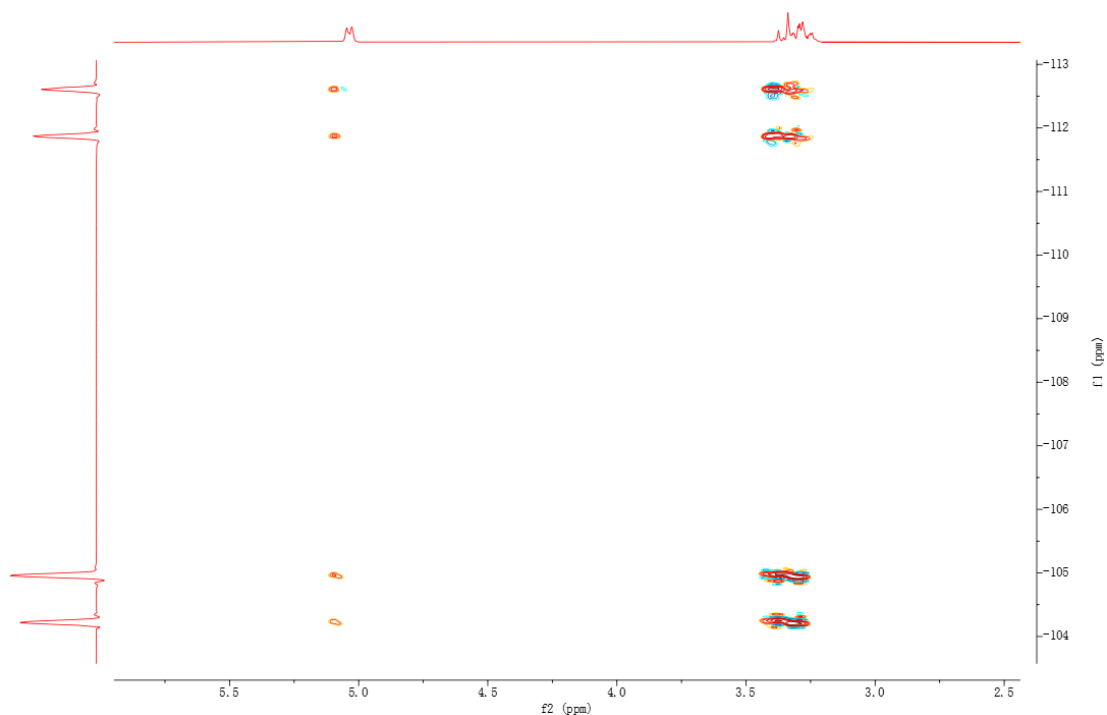




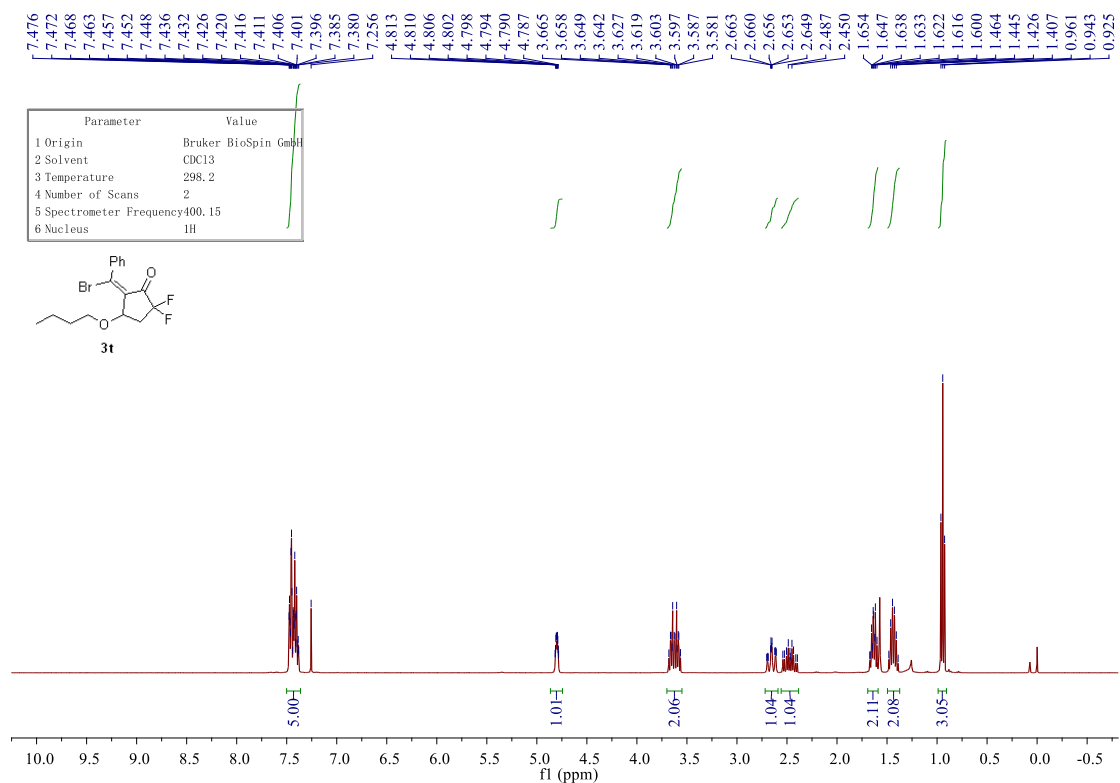
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	376.44
6 Nucleus	19F

-104.518  
 -105.254  
 -111.612  
 -112.348





**NOTE:** According to proposed configuration of Table of Section 8 via comparing calculated formula vs NMR, configuration of 3s is more likely to be *cis*. These results also agreed with configuration confirmation of 3r and 3y via H-F HOSEY.



186.376  
186.109  
185.839

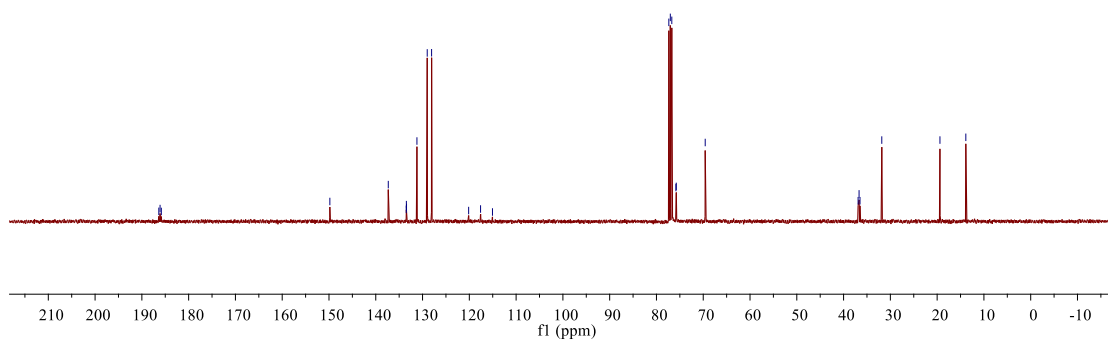
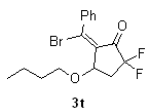
149.815  
137.325  
133.484  
133.457  
133.427  
131.200  
128.999  
128.067  
120.145  
117.599  
115.053

77.354  
77.037  
76.719  
75.841  
75.763  
69.576

36.894  
36.687  
36.488  
31.833

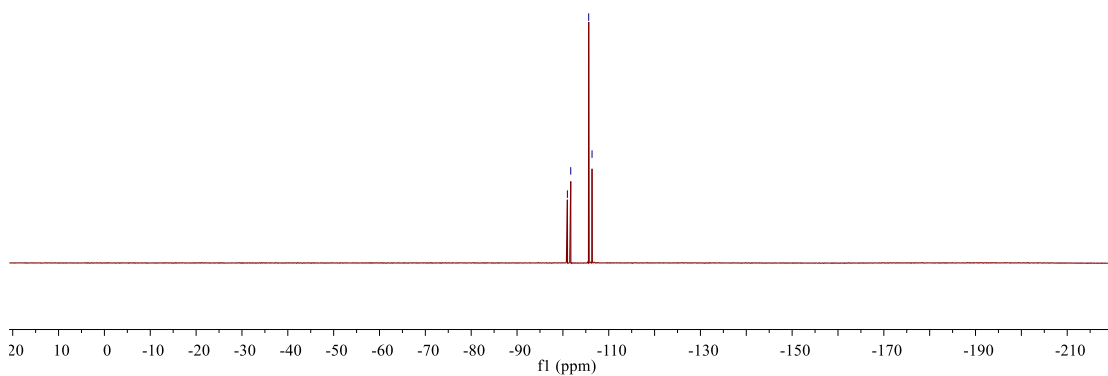
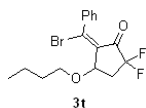
19.400  
13.869

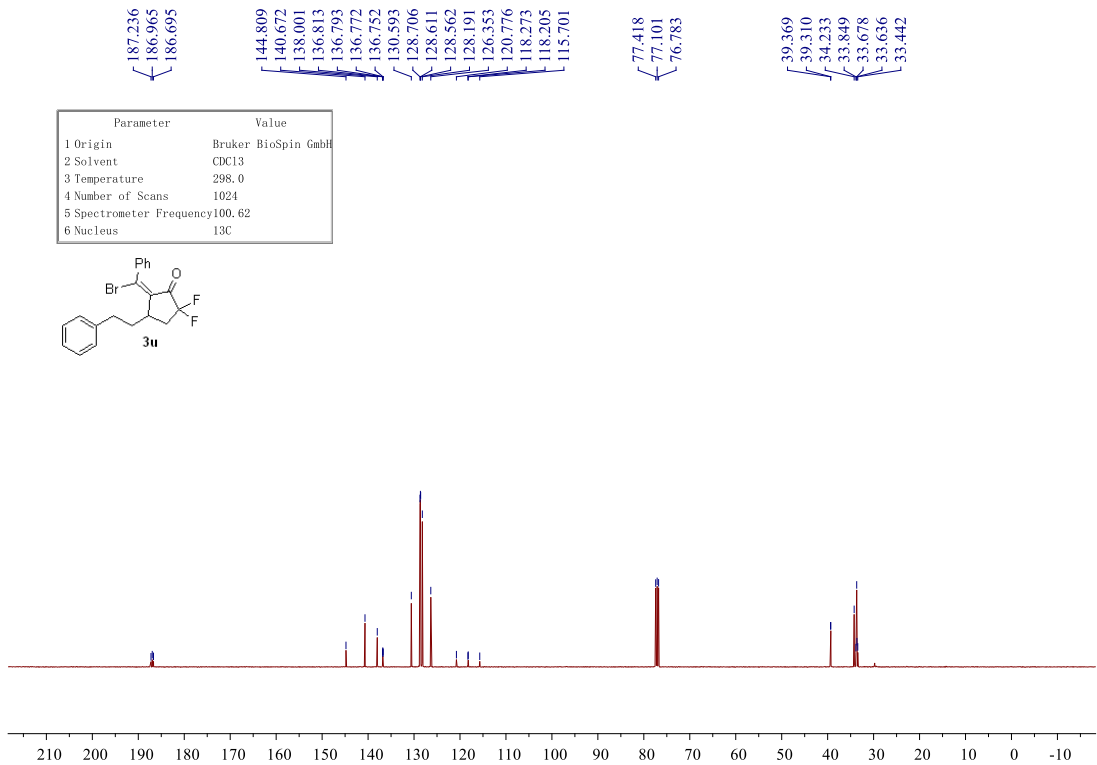
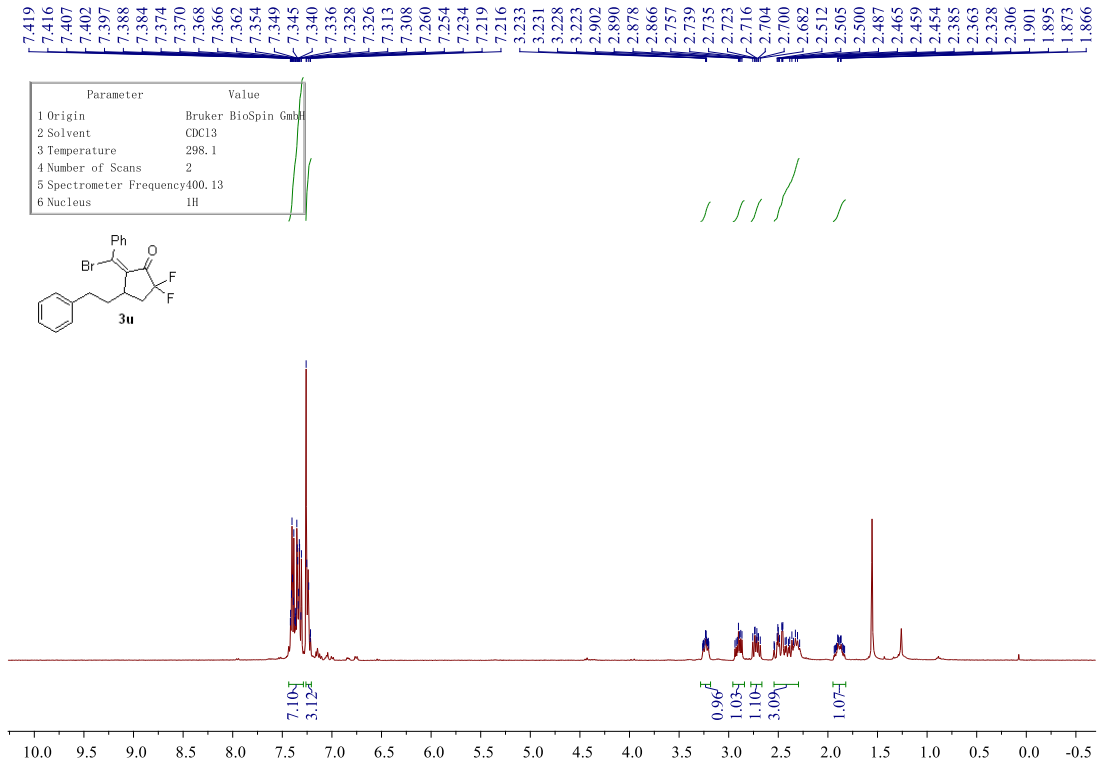
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	325
5 Spectrometer Frequency	100.62
6 Nucleus	13C



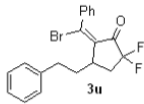
-100.981  
-101.710  
-105.631  
-106.359

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

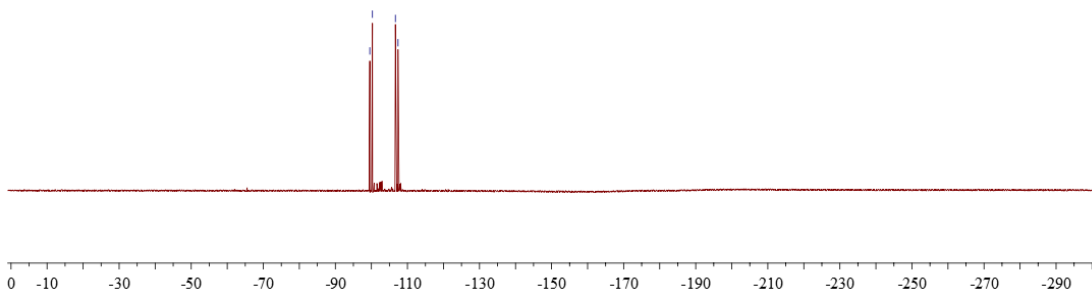




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.44
6 Nucleus	19F

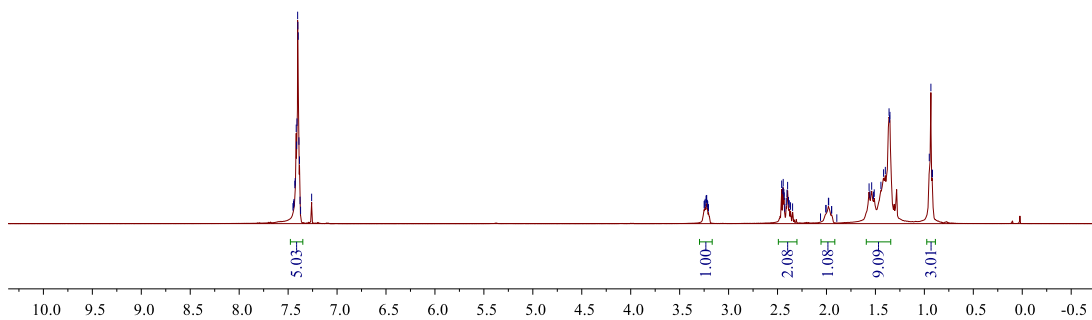
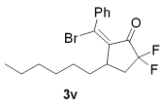


-99.559  
-100.289  
-106.658  
-107.388



7.450  
7.445  
7.440  
7.431  
7.428  
7.417  
7.413  
7.409  
7.403  
7.401  
7.397  
7.390  
7.384  
7.378  
7.260  
3.250  
3.243  
3.239  
3.230  
3.226  
3.224  
3.217  
3.213  
3.206  
2.458  
2.446  
2.442  
2.435  
2.432  
2.426  
2.411  
2.404  
2.397  
2.388  
2.380  
2.367  
2.346  
2.007  
2.005  
1.980  
1.977  
1.948  
1.565  
1.556  
1.538  
1.520  
1.512  
1.444  
1.417  
1.399  
1.361  
1.355  
1.352  
0.950  
0.933  
0.922  
0.918

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	1.5
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



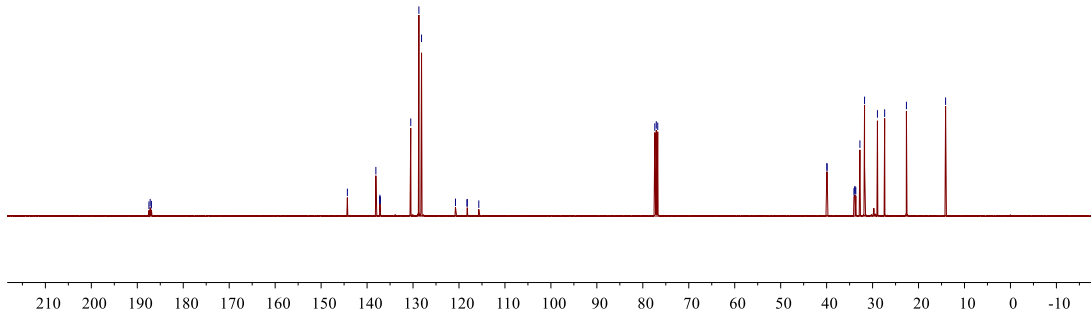
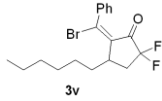
187.471  
187.200  
186.928

144.287  
138.087  
137.226  
137.205  
137.186  
137.165  
130.495  
128.727  
128.146  
120.763  
118.256  
118.197  
115.690

77.388  
77.071  
76.753

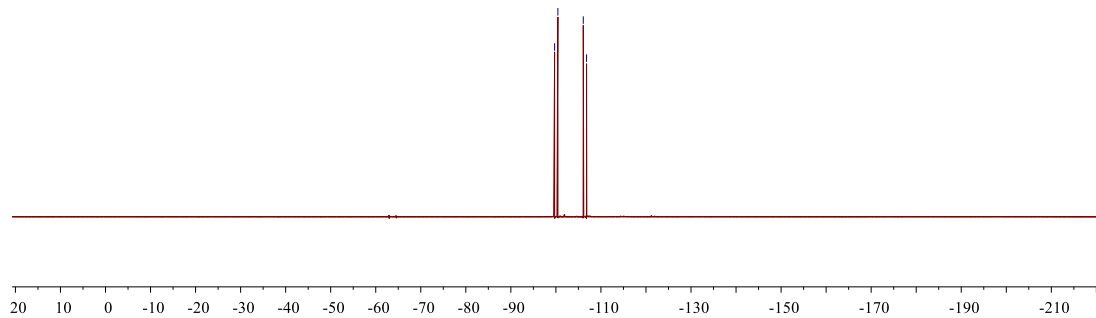
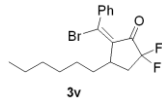
39.953  
39.895  
34.053  
33.861  
33.842  
33.649  
32.759  
31.750  
28.946  
27.373  
22.637  
14.115

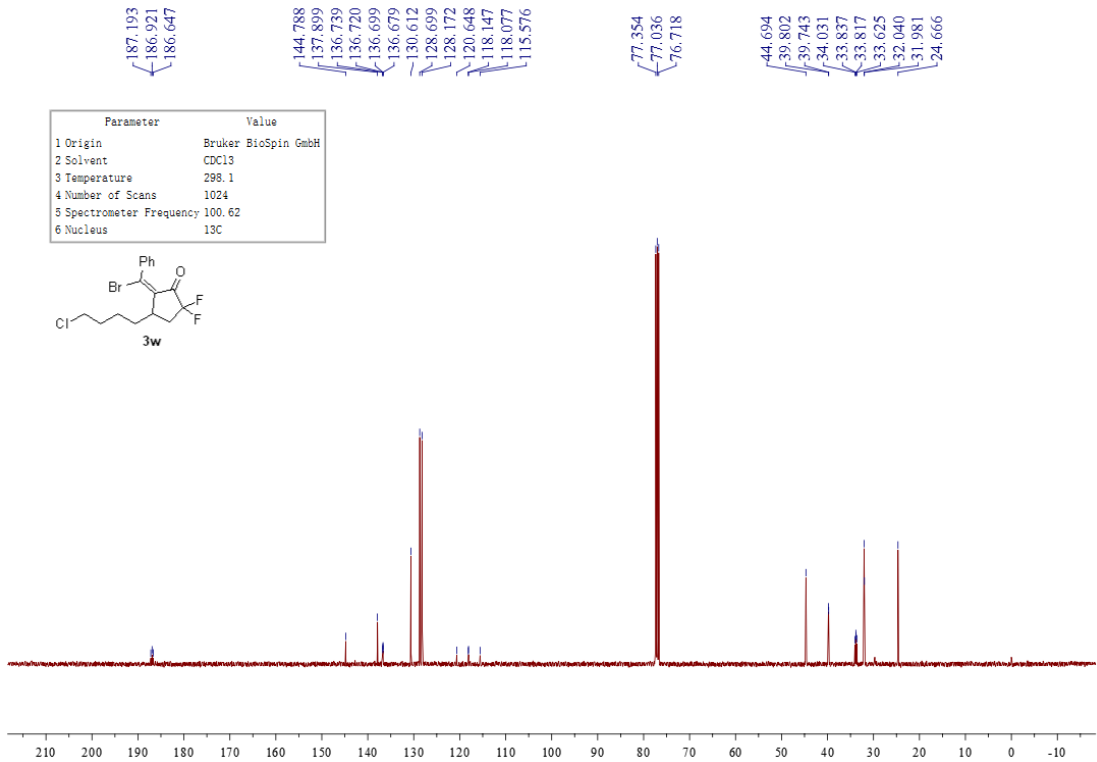
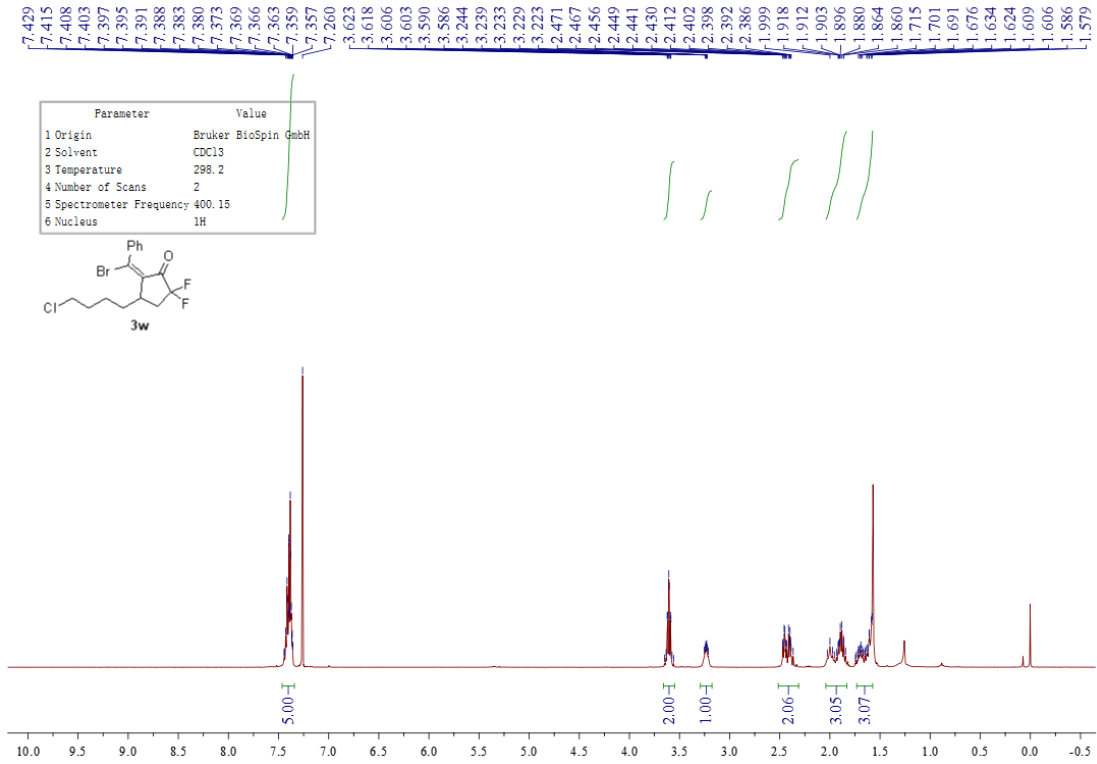
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.7
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.8
4 Number of Scans	4
5 Spectrometer Frequency	376.52
6 Nucleus	19F

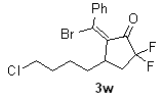
-99.713  
-100.442  
-106.079  
-106.809



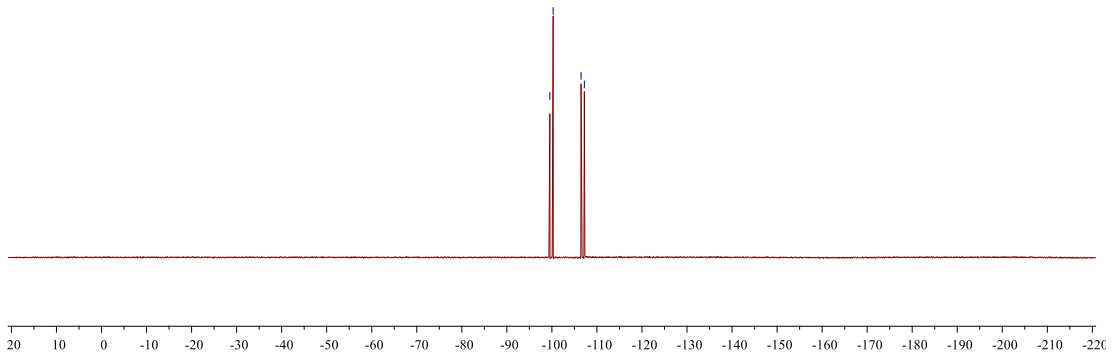




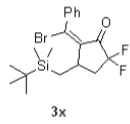
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



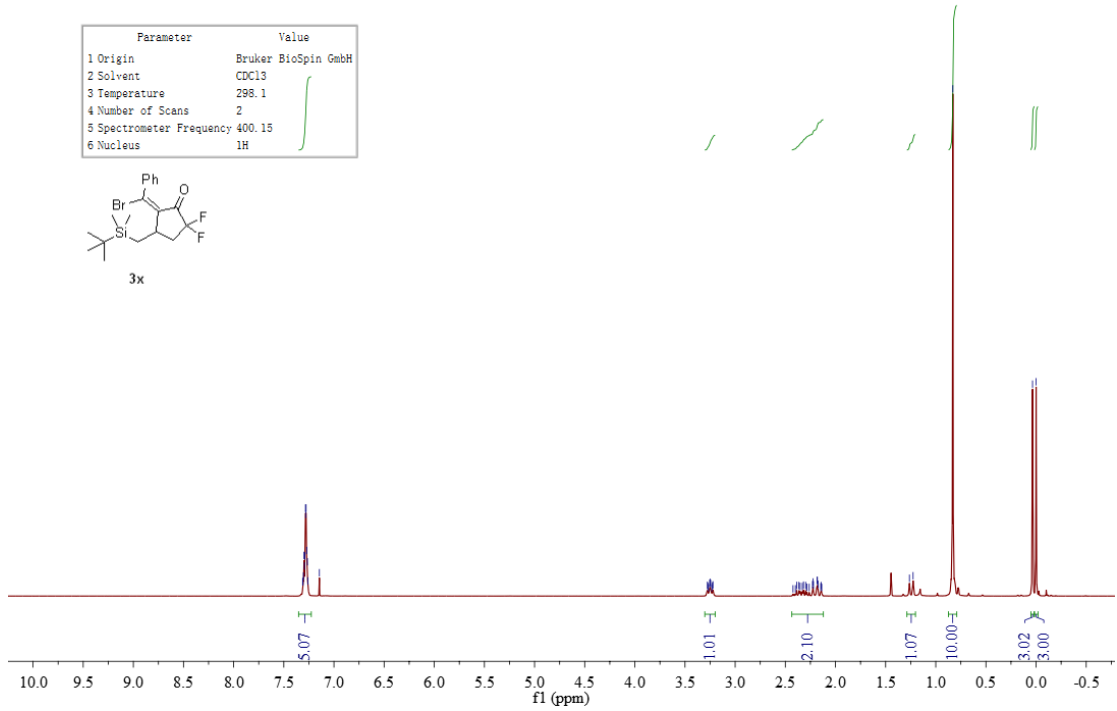
-99.545  
-100.276  
-106.476  
-107.207

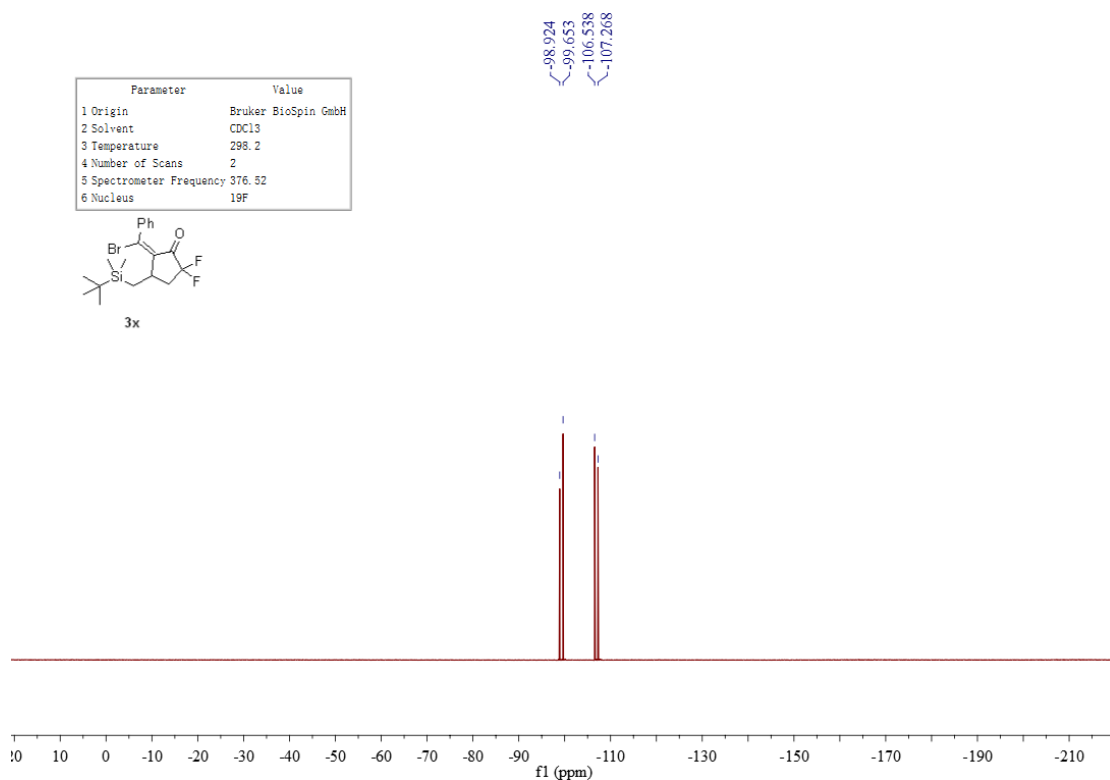
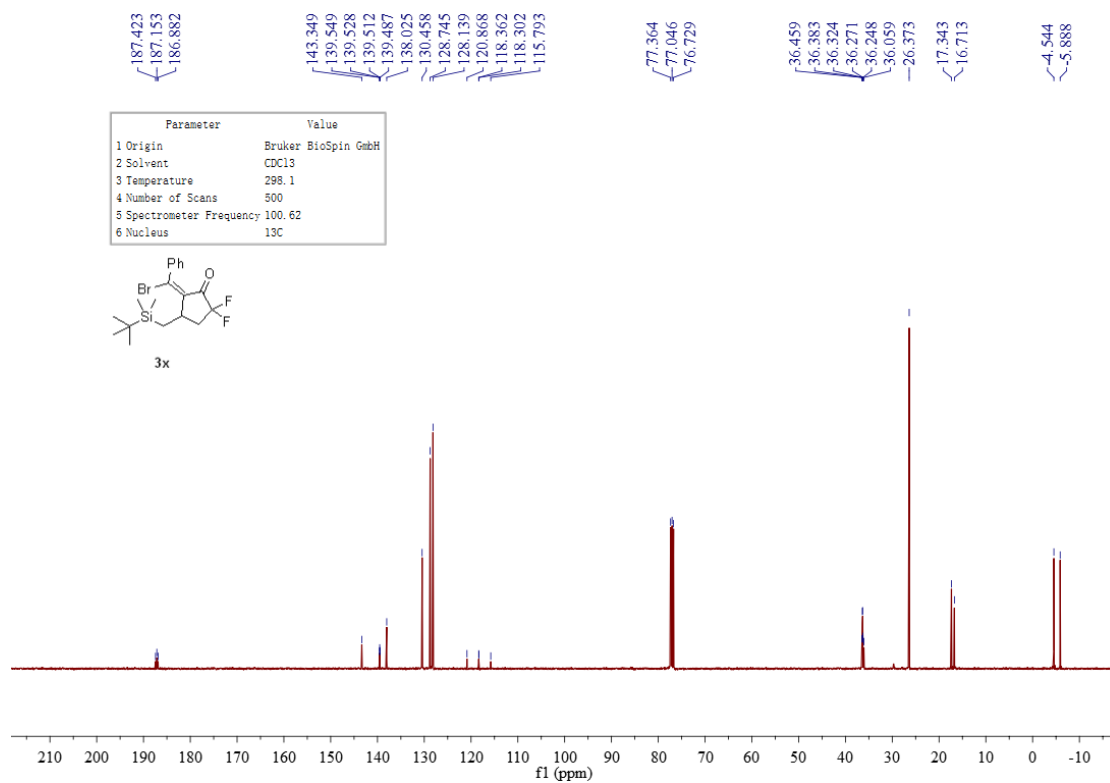


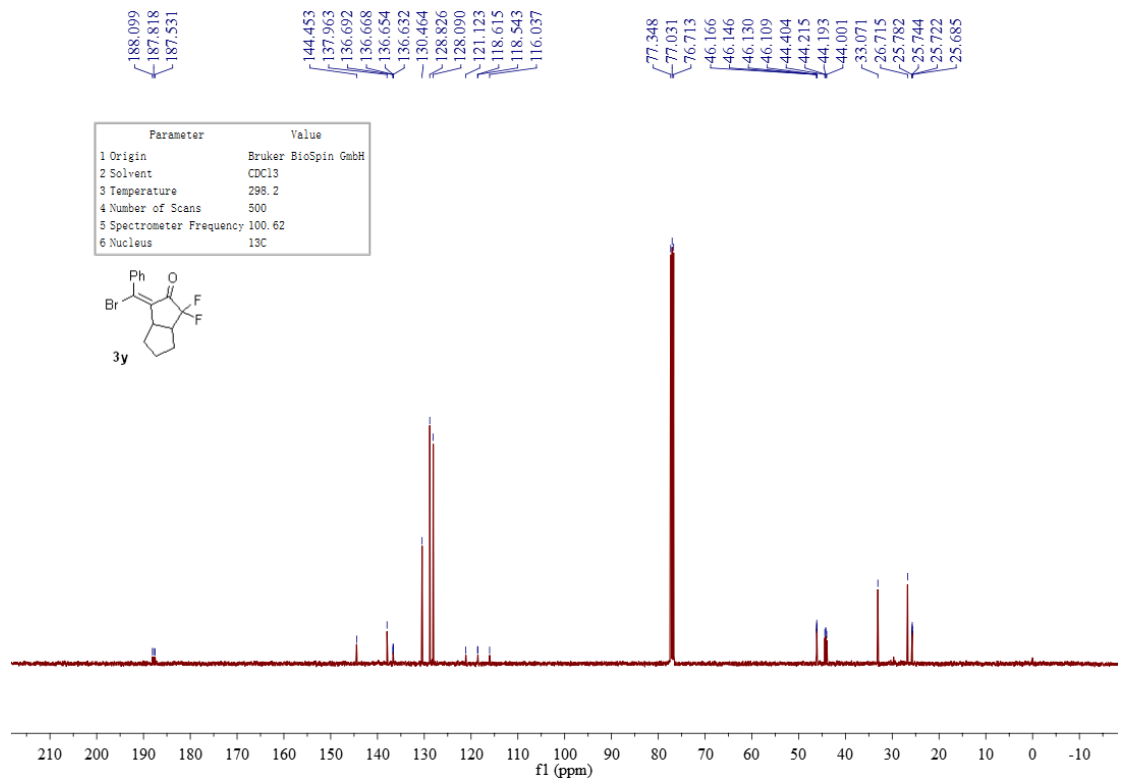
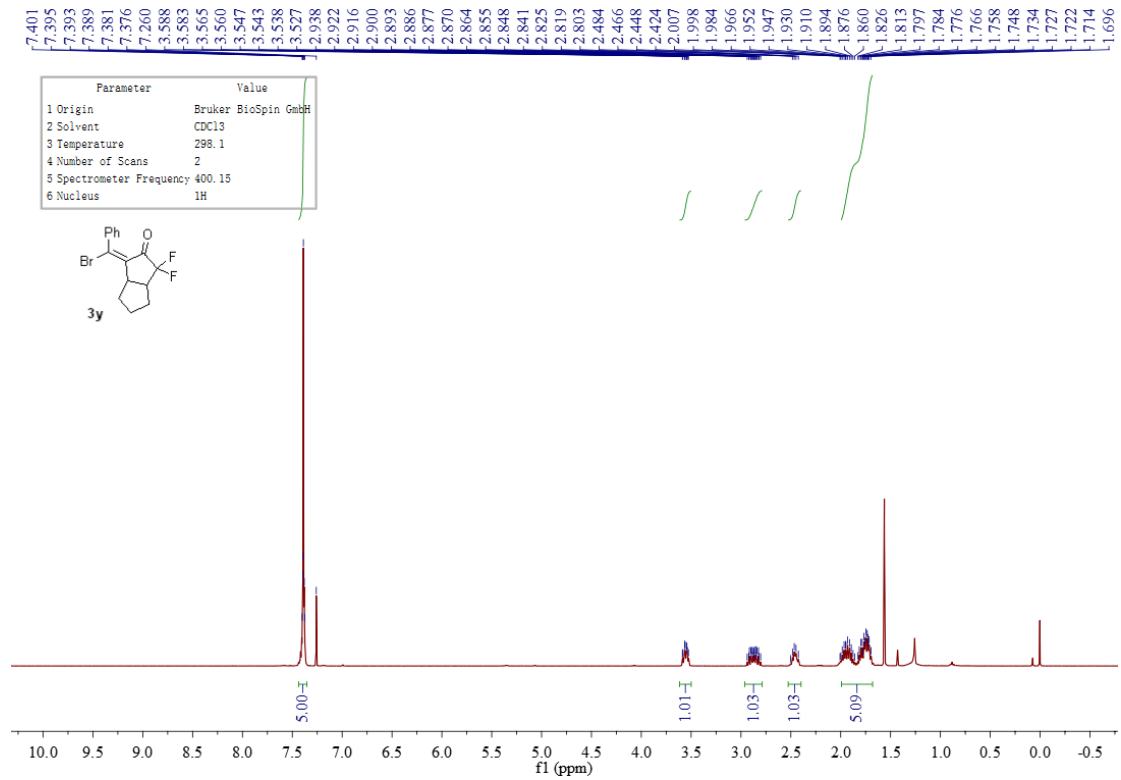
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



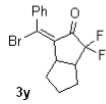
7.312  
7.309  
7.304  
7.298  
7.295  
7.290  
7.284  
7.282  
7.278  
7.272  
7.265  
7.259  
7.145  
3.277  
3.272  
3.265  
3.254  
3.249  
3.244  
3.233  
3.227  
3.222  
2.319  
2.229  
2.224  
2.220  
2.184  
2.180  
1.174  
1.263  
1.226  
-0.830  
0.035  
-0.000



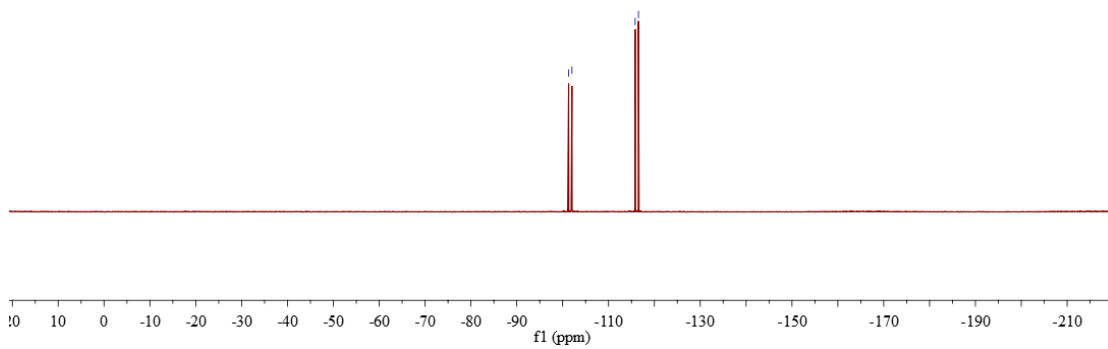




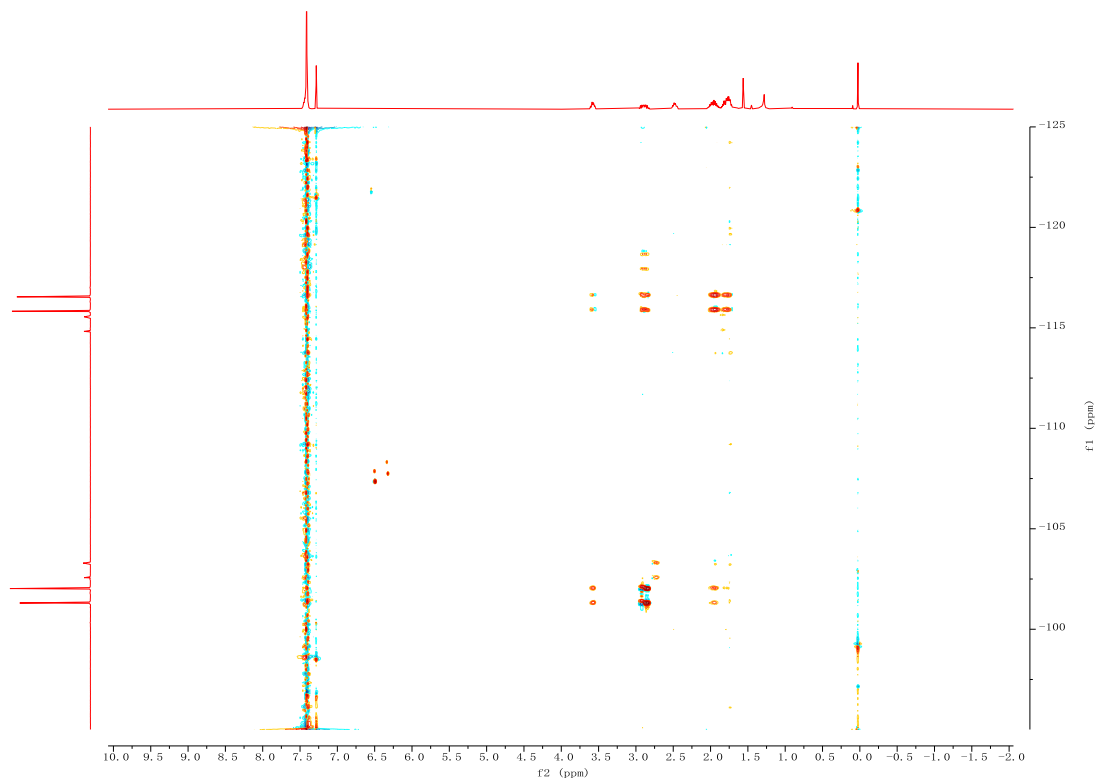
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

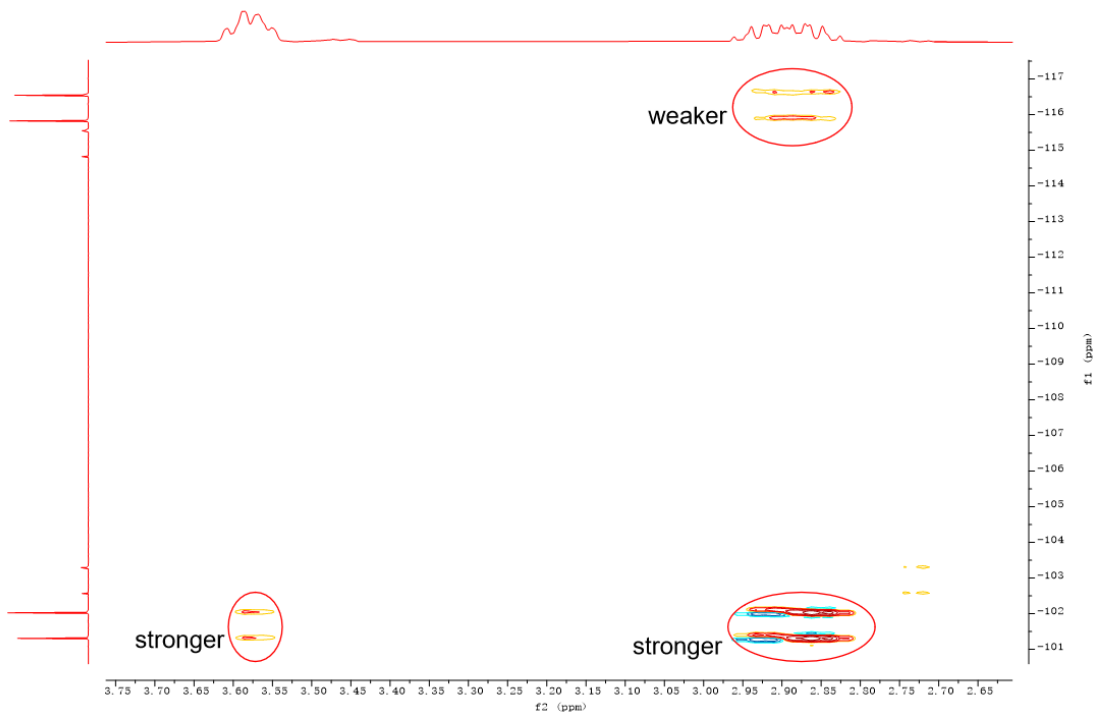


-101.307  
-102.026  
-115.810  
-116.529



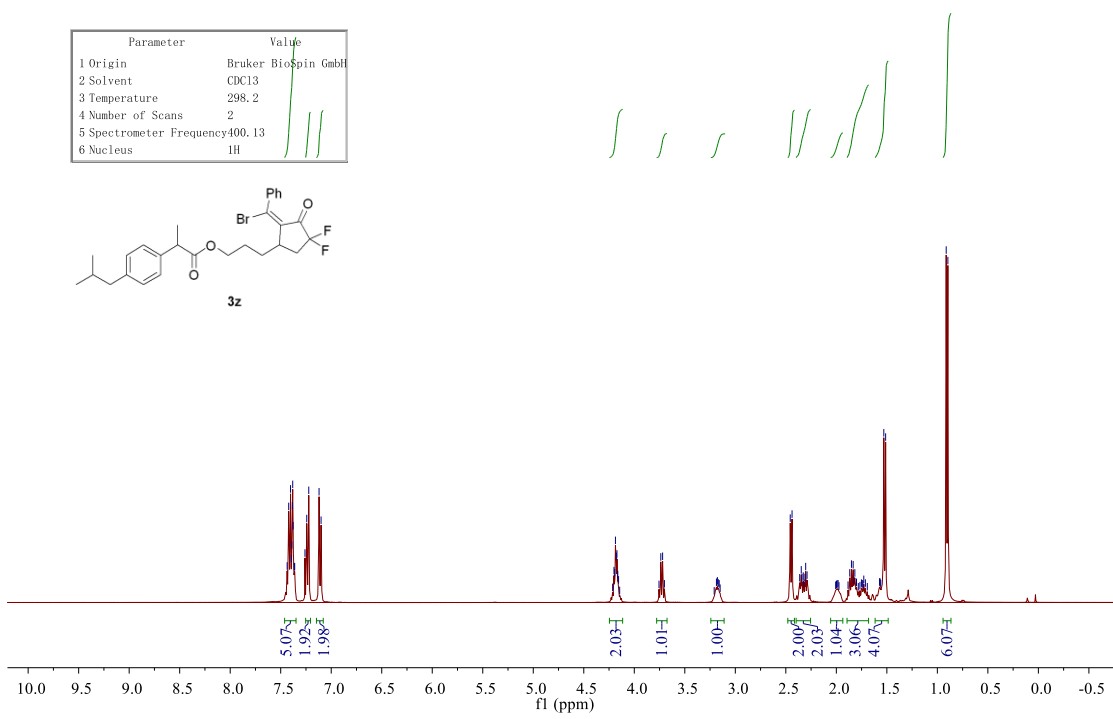
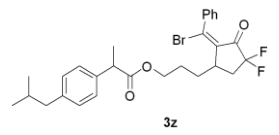
### 3y H-F hoesy





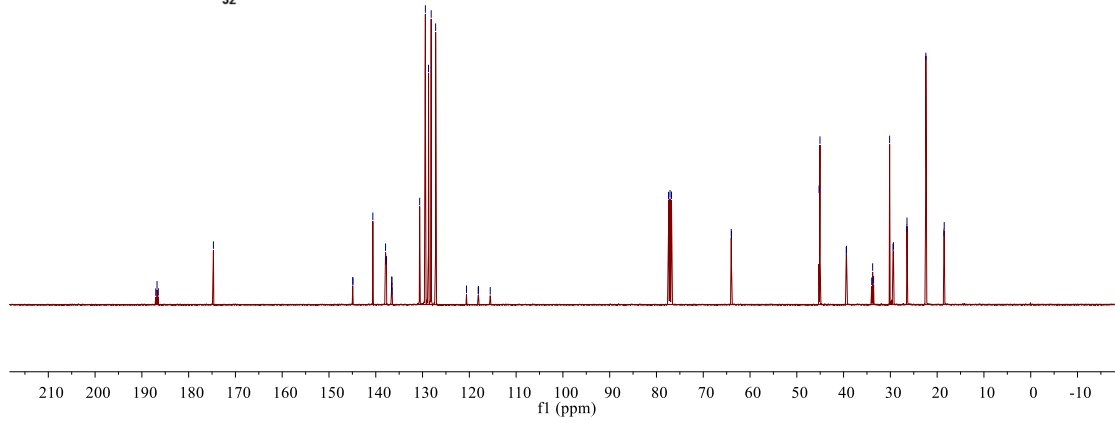
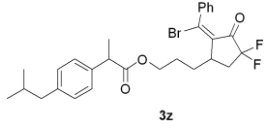
7.436  
7.421  
7.403  
7.396  
7.390  
7.385  
7.381  
7.377  
7.366  
7.362  
7.260  
7.242  
7.222  
7.120  
7.101  
4.201  
4.193  
4.187  
4.178  
4.172  
4.163  
4.156  
3.738  
3.720  
3.702  
3.187  
3.177  
3.168  
3.159  
3.159  
2.456  
2.438  
2.363  
2.347  
2.340  
2.327  
2.321  
2.311  
2.303  
2.290  
1.992  
1.983  
1.867  
1.850  
1.834  
1.825  
1.817  
1.800  
1.752  
1.743  
1.728  
1.712  
1.572  
1.567  
1.561  
1.530  
1.512  
0.912  
0.896

Parameter	Value
1 Origin	Bruker Biospin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



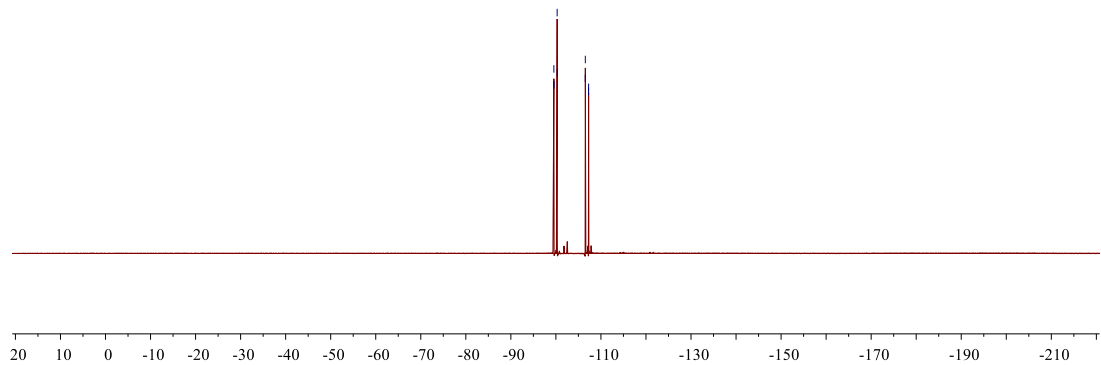
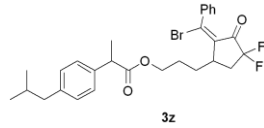
187.028  
186.758  
186.488  
174.703  
144.924  
144.874  
140.628  
137.915  
137.741  
137.718  
136.611  
136.590  
136.549  
136.522  
130.616  
129.398  
128.728  
128.157  
127.203  
120.607  
118.102  
118.036  
115.532  
77.418  
77.100  
76.783  
64.015  
63.960  
45.244  
45.045  
39.430  
39.373  
33.992  
33.790  
33.585  
30.162  
29.431  
29.346  
26.474  
26.450  
22.417  
18.540  
18.492

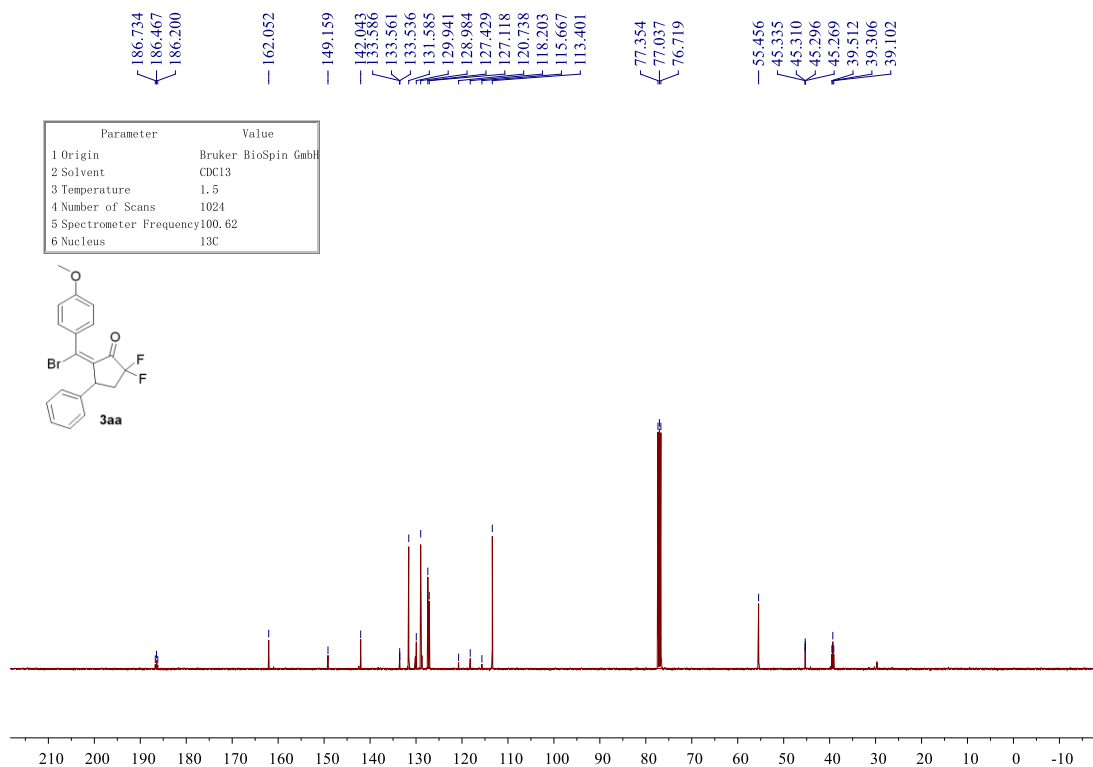
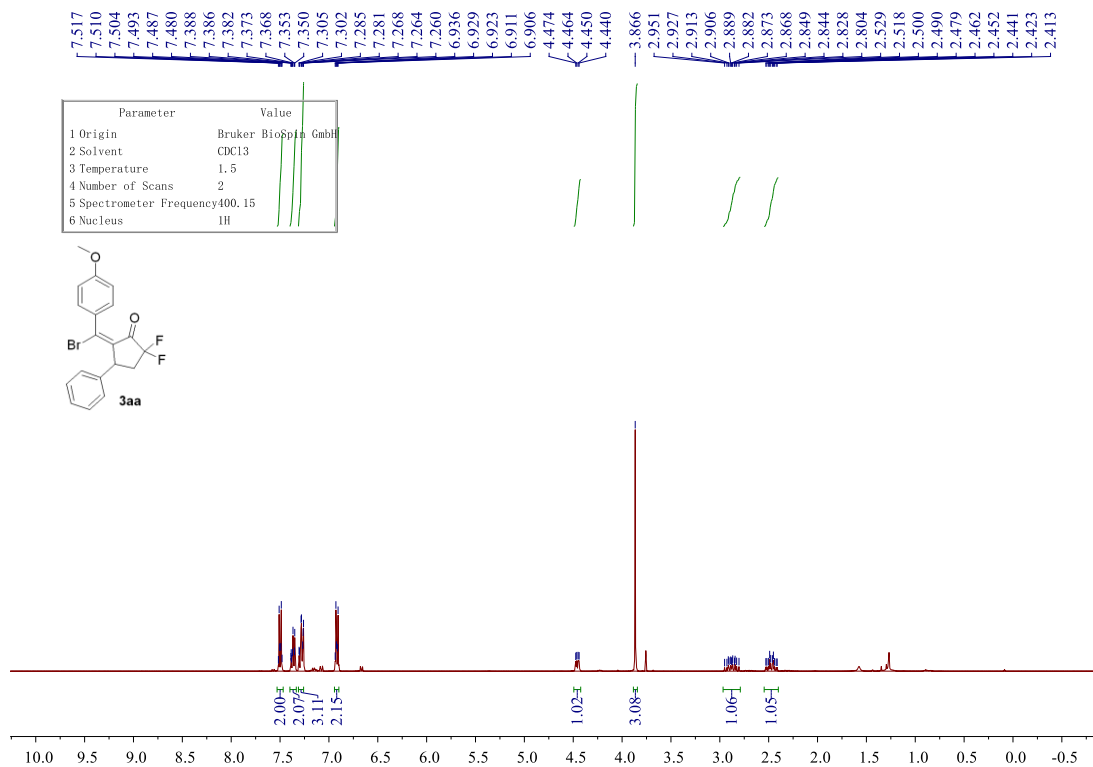
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	1.5
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C



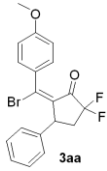
-99.550  
-99.584  
-100.280  
-100.315  
-106.520  
-106.535  
-107.250  
-107.265

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	299.7
4 Number of Scans	4
5 Spectrometer Frequency	376.52
6 Nucleus	19F

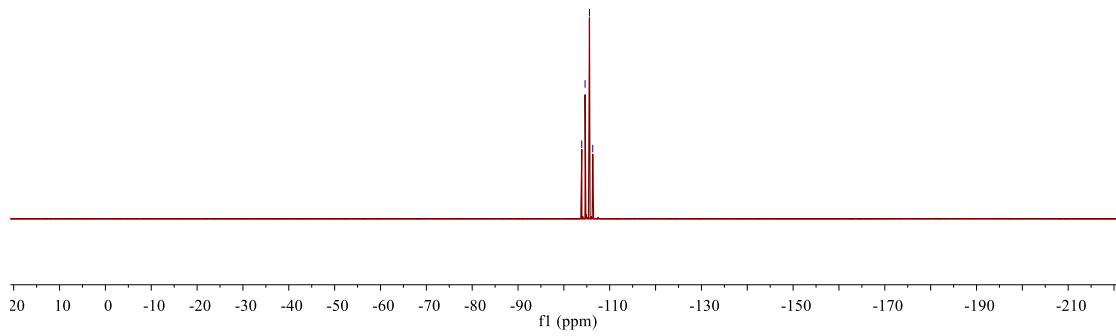




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



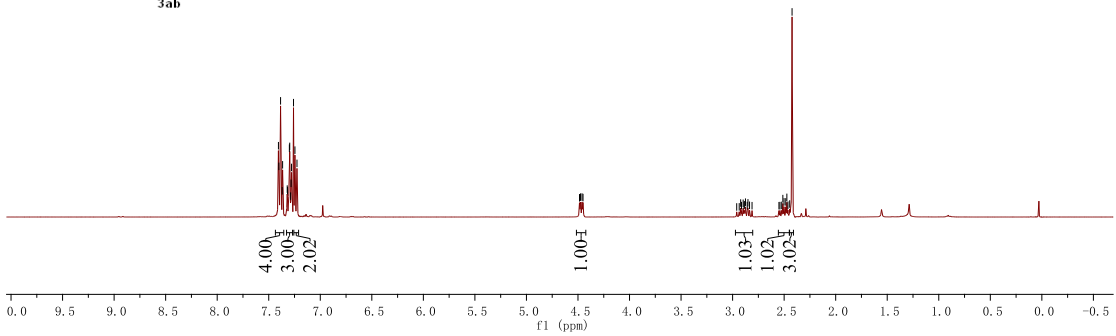
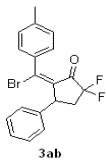
-103.904  
-104.624  
-105.576  
-106.295



7.406  
7.402  
7.385  
7.369  
7.366  
7.321  
7.318  
7.300  
7.296  
7.288  
7.283  
7.279  
7.260  
7.246  
7.226

4.485  
4.475  
4.461  
4.451  
2.960  
2.936  
2.922  
2.913  
2.898  
2.889  
2.883  
2.875  
2.858  
2.851  
2.836  
2.811  
2.550  
2.540  
2.523  
2.513  
2.501  
2.484  
2.474  
2.463  
2.446  
2.423

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



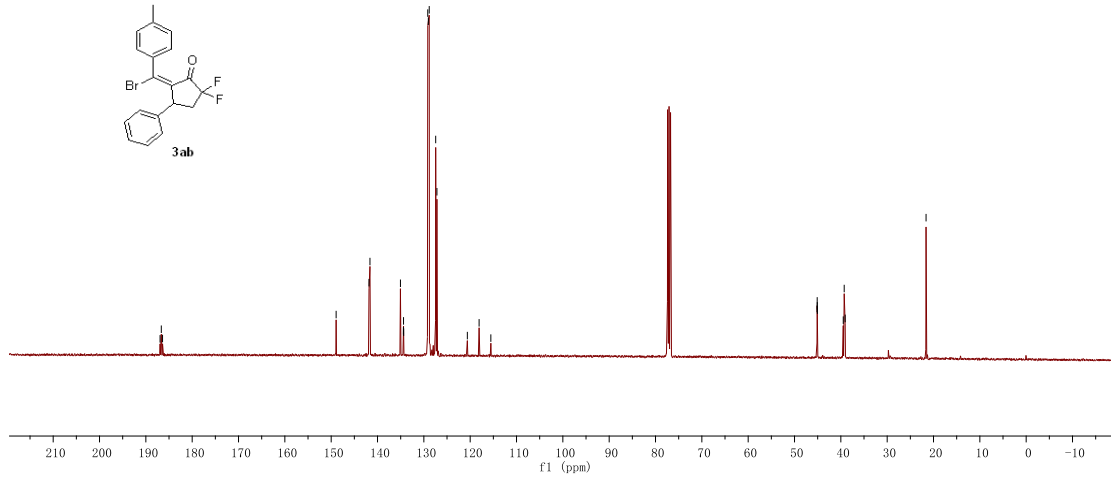
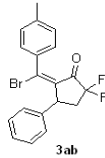


186.932  
186.665  
186.397

148.931  
141.836  
141.630  
135.052  
134.410  
134.385  
134.357  
129.156  
129.029  
128.841  
127.443  
127.177  
120.612  
118.075  
115.539

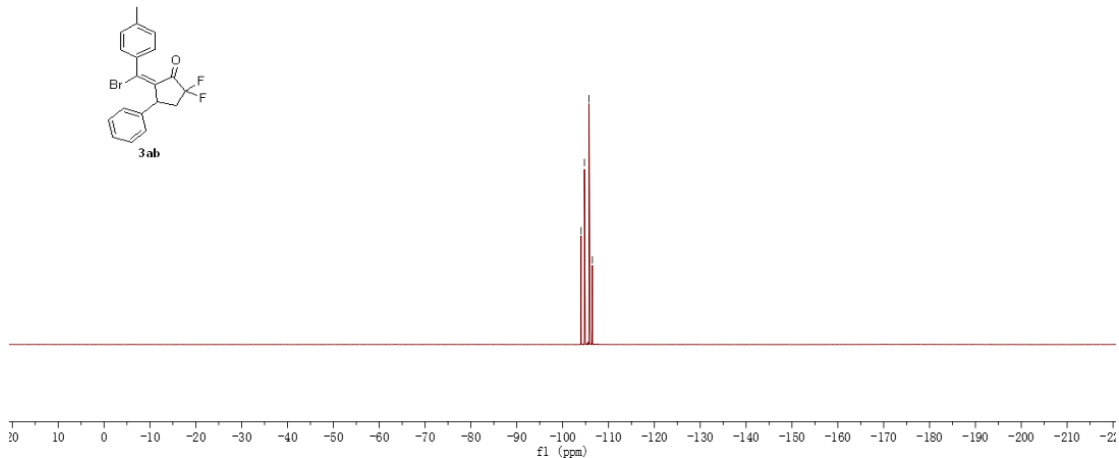
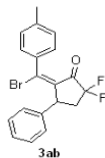
45.130  
45.106  
45.086  
45.062  
39.480  
39.274  
39.070  
21.608

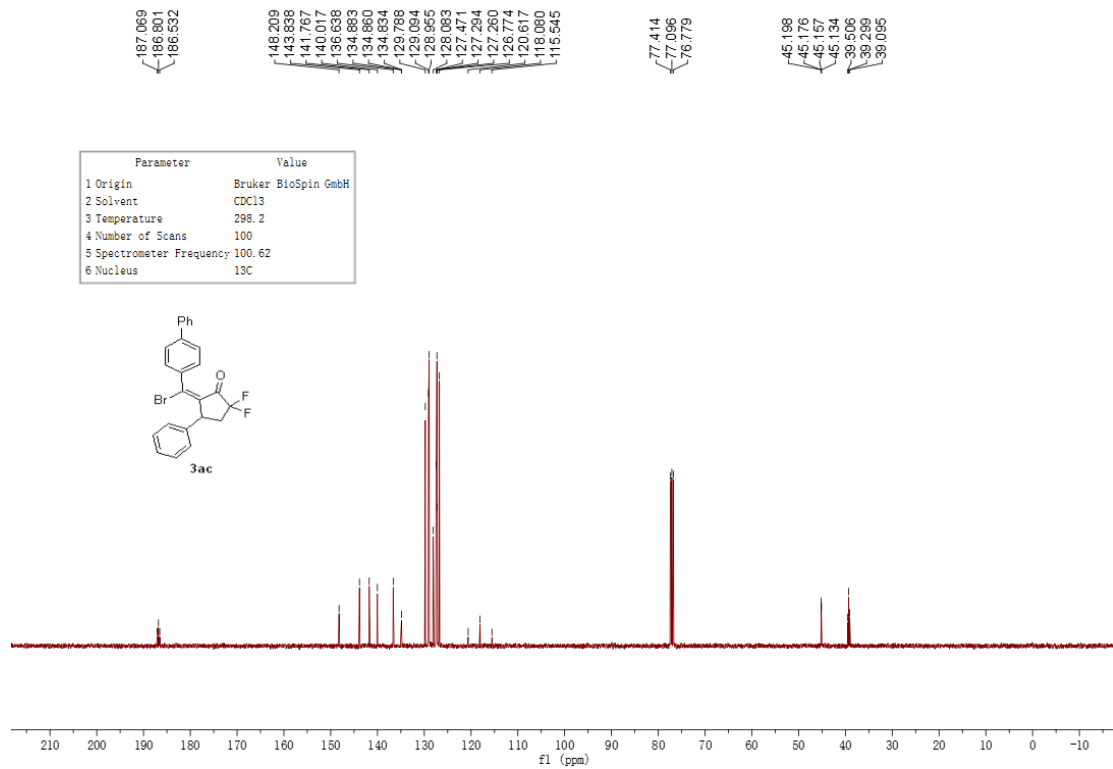
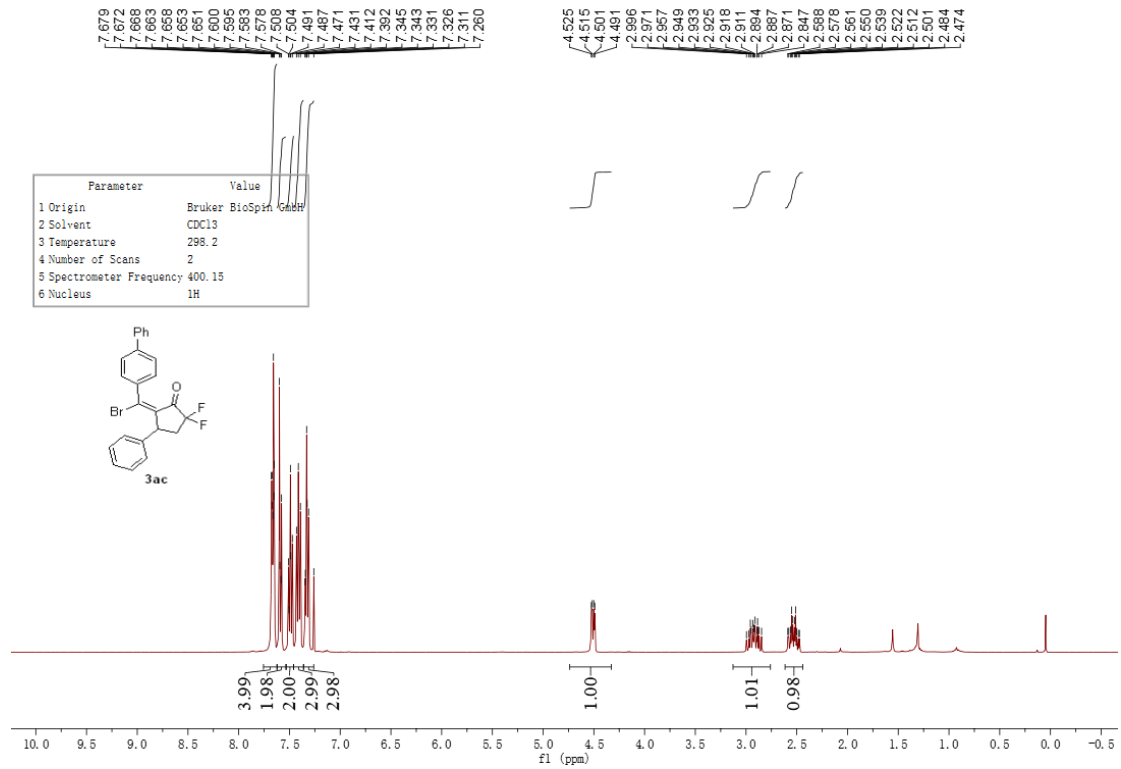
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	1024
5 Spectrometer Frequency	100.61
6 Nucleus	13C



104.021  
104.743  
105.757  
106.478

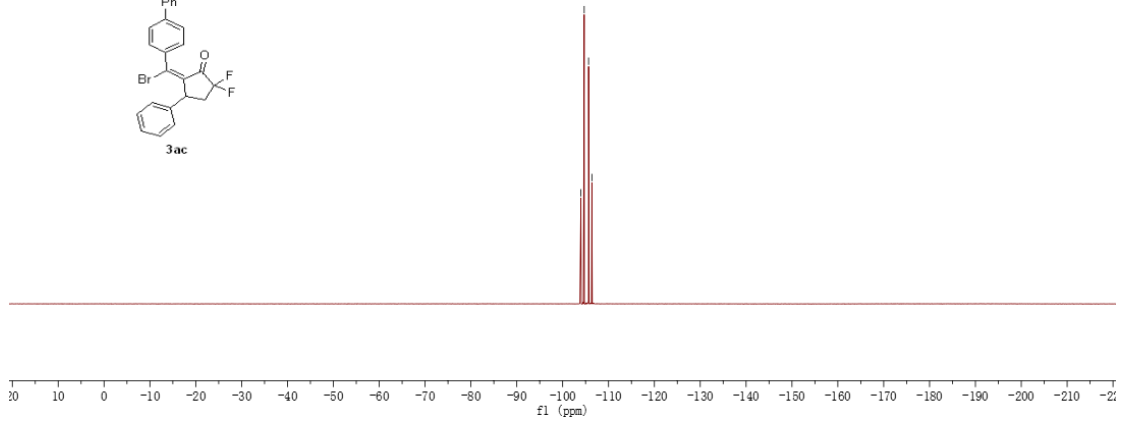
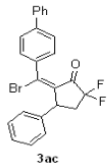
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F





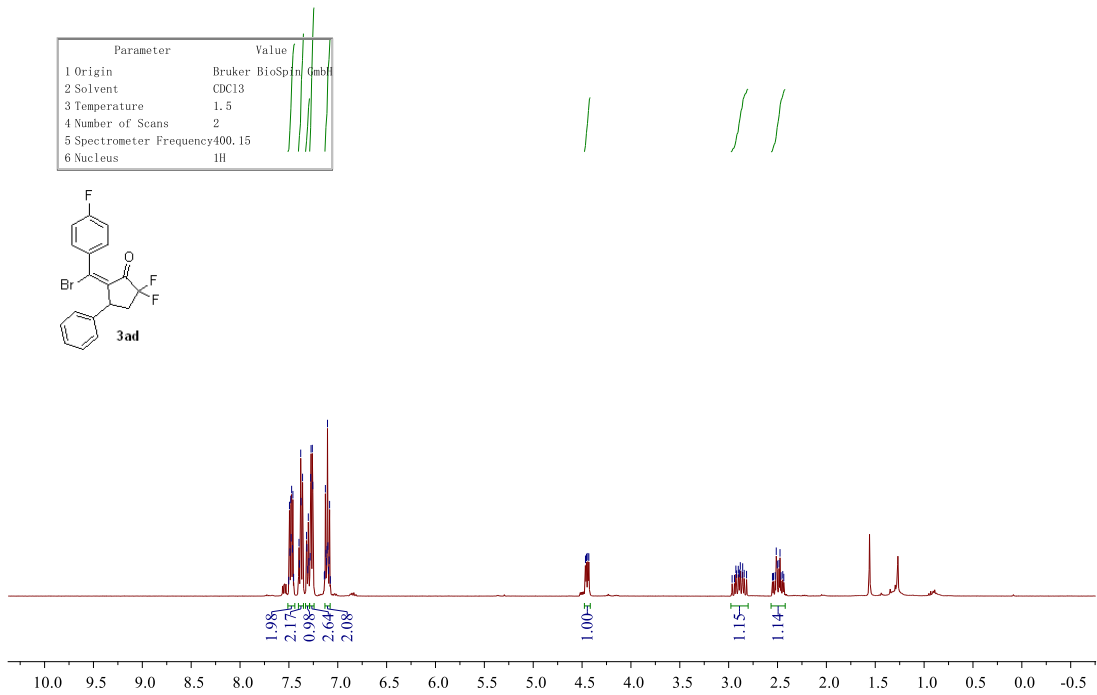
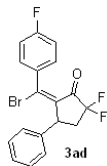
103.977  
104.699  
105.650  
106.372

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



7.494  
7.489  
7.481  
7.477  
7.472  
7.464  
7.459  
7.397  
7.393  
7.379  
7.376  
7.360  
7.320  
7.316  
7.307  
7.301  
7.295  
7.283  
7.277  
7.273  
7.260  
7.256  
7.137  
7.134  
7.127  
7.121  
7.116  
7.110  
7.105  
7.100  
7.095  
7.089  
7.083  
4.465  
4.455  
4.441  
4.431  
2.926  
2.919  
2.902  
2.895  
2.887  
2.881  
2.862  
2.857  
2.841  
2.817  
2.552  
2.541  
2.523  
2.513  
2.503  
2.485  
2.475  
2.464  
2.446  
2.436

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	1.5
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



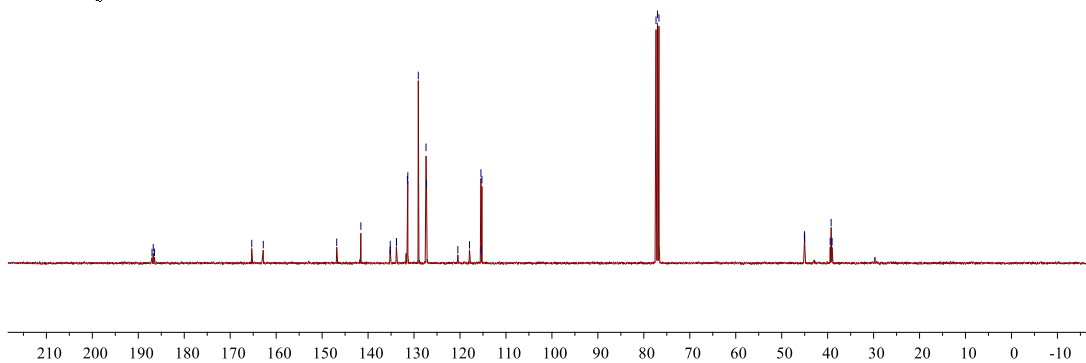
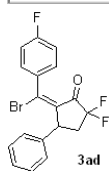
187.017  
186.746  
186.477

165.312  
162.803  
146.824  
141.570  
135.197  
135.176  
135.150  
133.839  
133.804  
131.444  
131.356  
129.074  
127.395  
127.273  
120.466  
117.930  
115.448  
115.392  
115.228

77.344  
77.027  
76.709

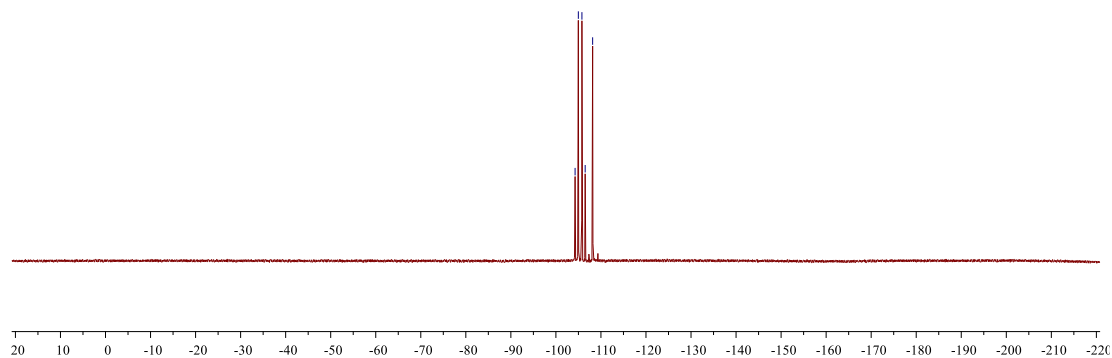
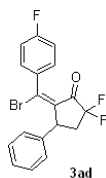
45.066  
45.041  
45.024  
45.000  
39.443  
39.238  
39.034

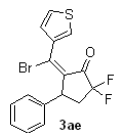
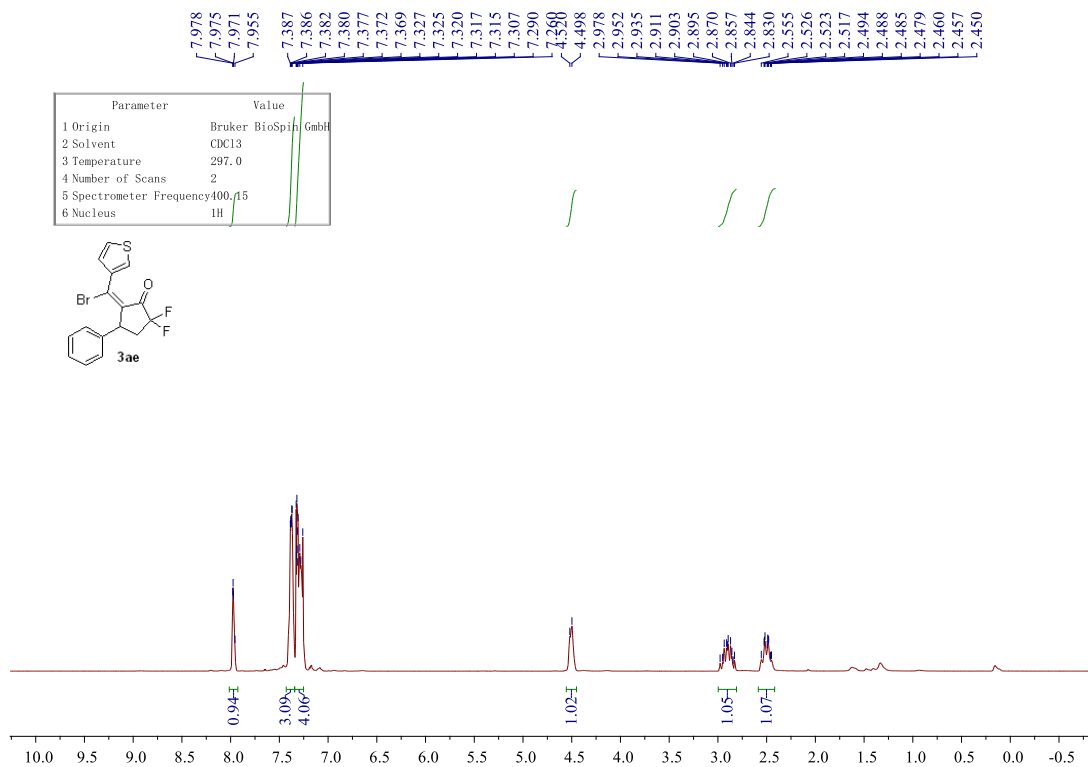
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	1.5
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C



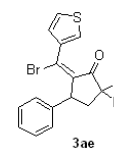
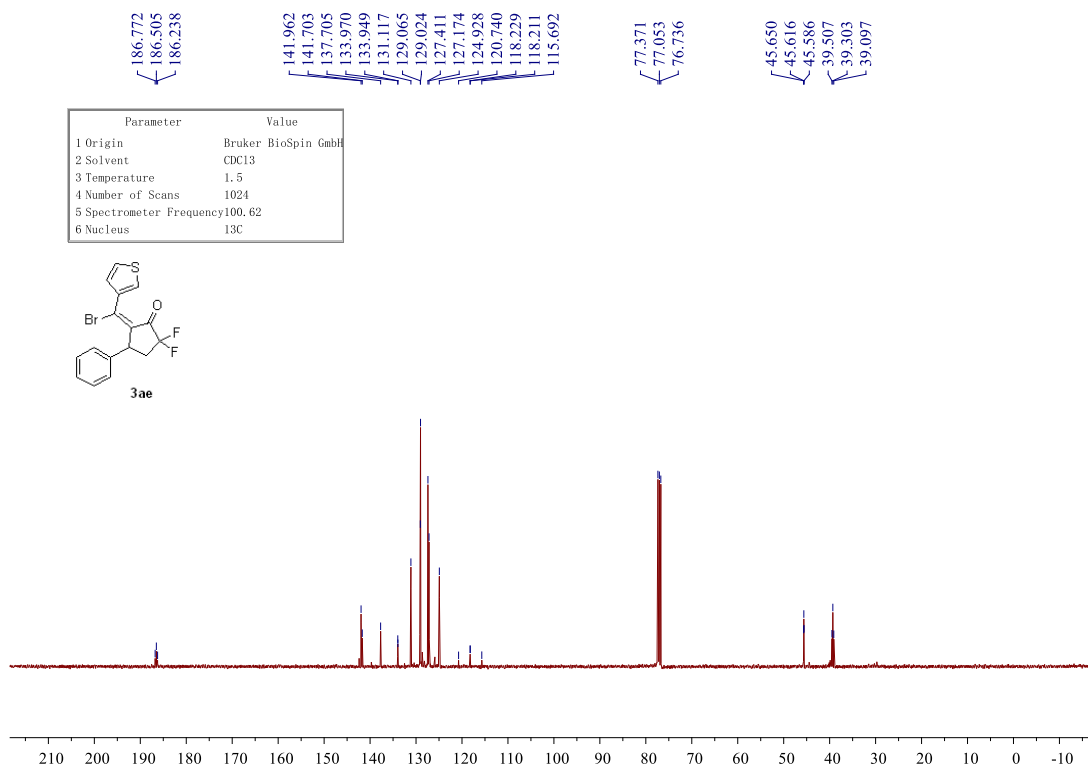
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

-104.259  
-104.982  
-105.777  
-106.500  
-108.156



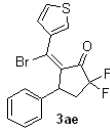


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	297.0
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	<sup>1</sup> H

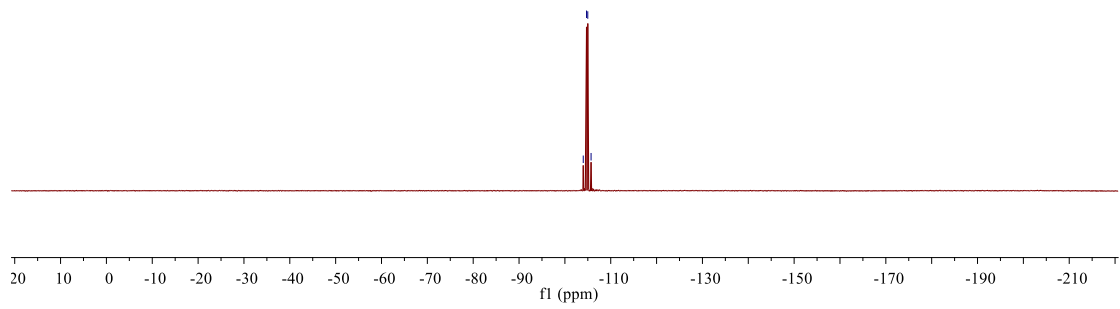


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	1.5
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



-104.005  
-104.723  
-104.993  
-105.711



7.350  
7.333  
7.313  
7.277  
7.274  
7.260  
7.253  
7.243  
7.240  
7.164  
7.145

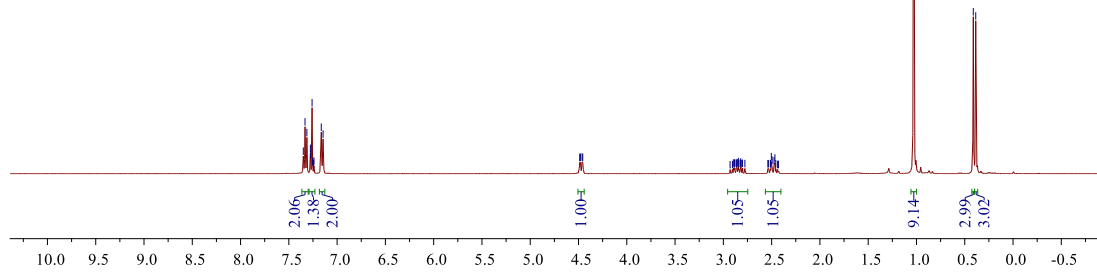
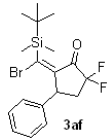
4.488  
4.481  
4.463  
4.456

2.892  
2.883  
2.868  
2.858  
2.849  
2.845  
2.839  
2.824  
2.820  
2.801  
2.777  
2.503  
2.494  
2.475  
2.466

1.056

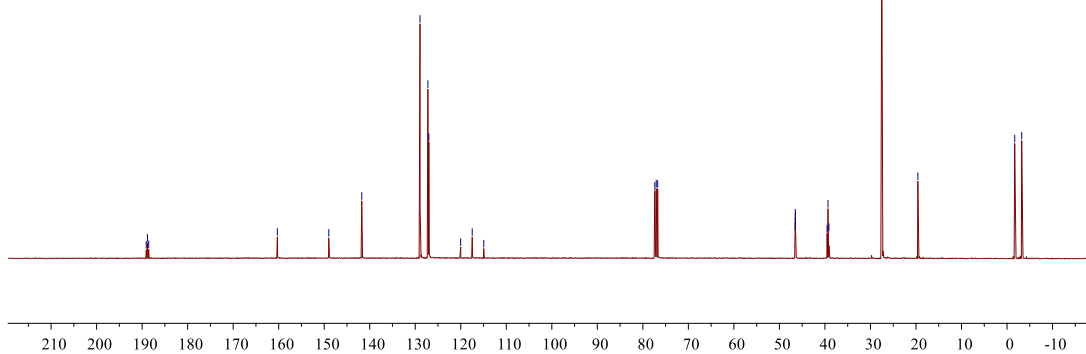
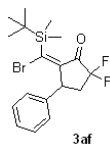
0.411  
0.386

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



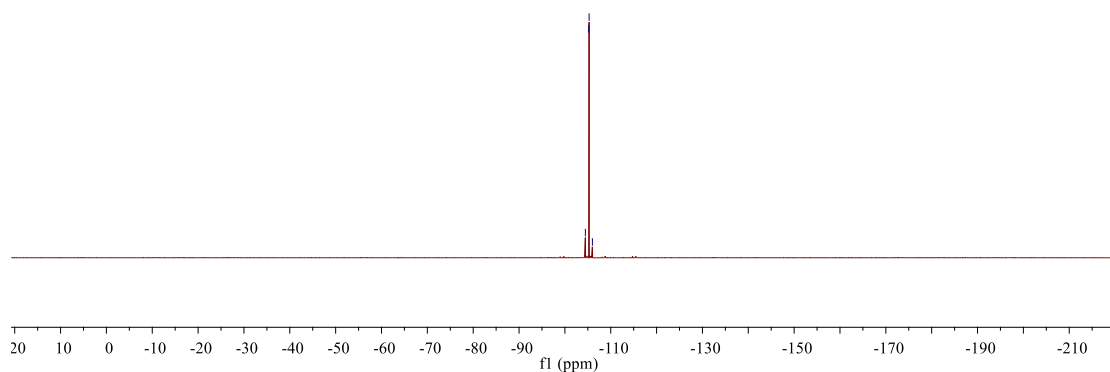
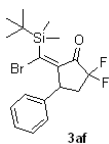
189.090  
 188.824  
 188.557  
 160.289  
 148.997  
 141.749  
 128.952  
 127.223  
 127.004  
 120.021  
 117.485  
 114.949  
 77.378  
 77.060  
 76.743  
 46.542  
 46.512  
 46.503  
 46.473  
 39.528  
 39.324  
 39.122  
 27.495  
 19.584  
 -1.690  
 -3.224

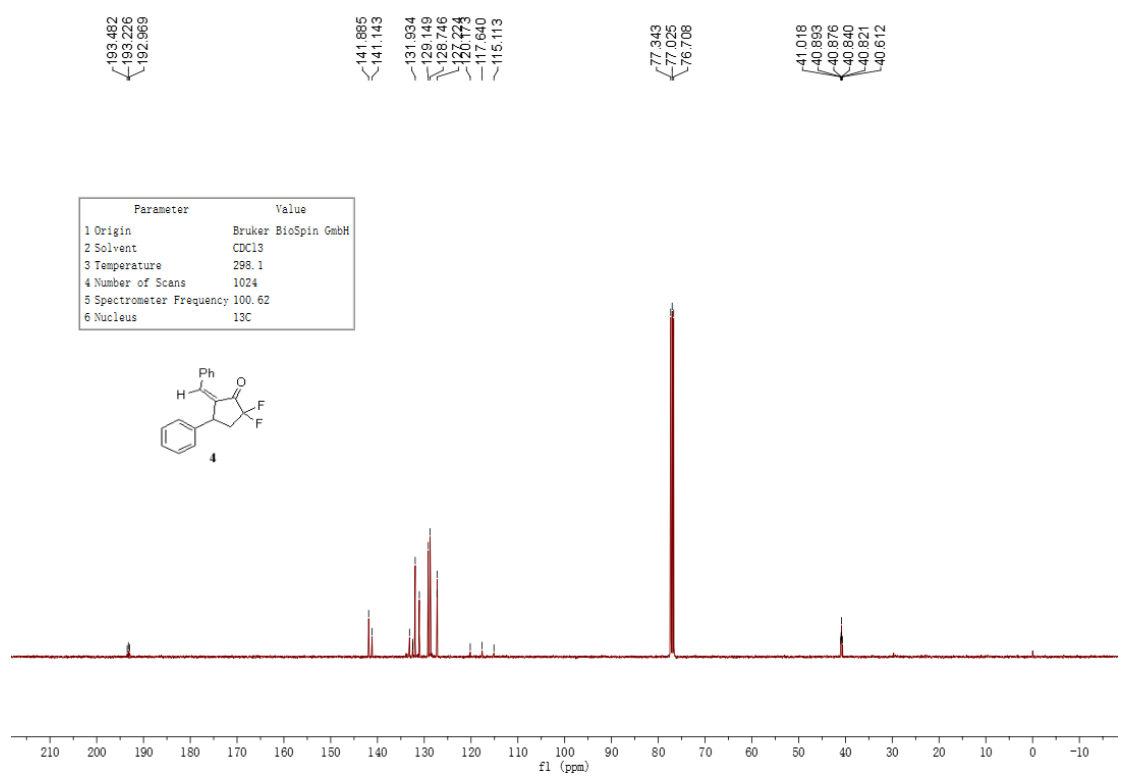
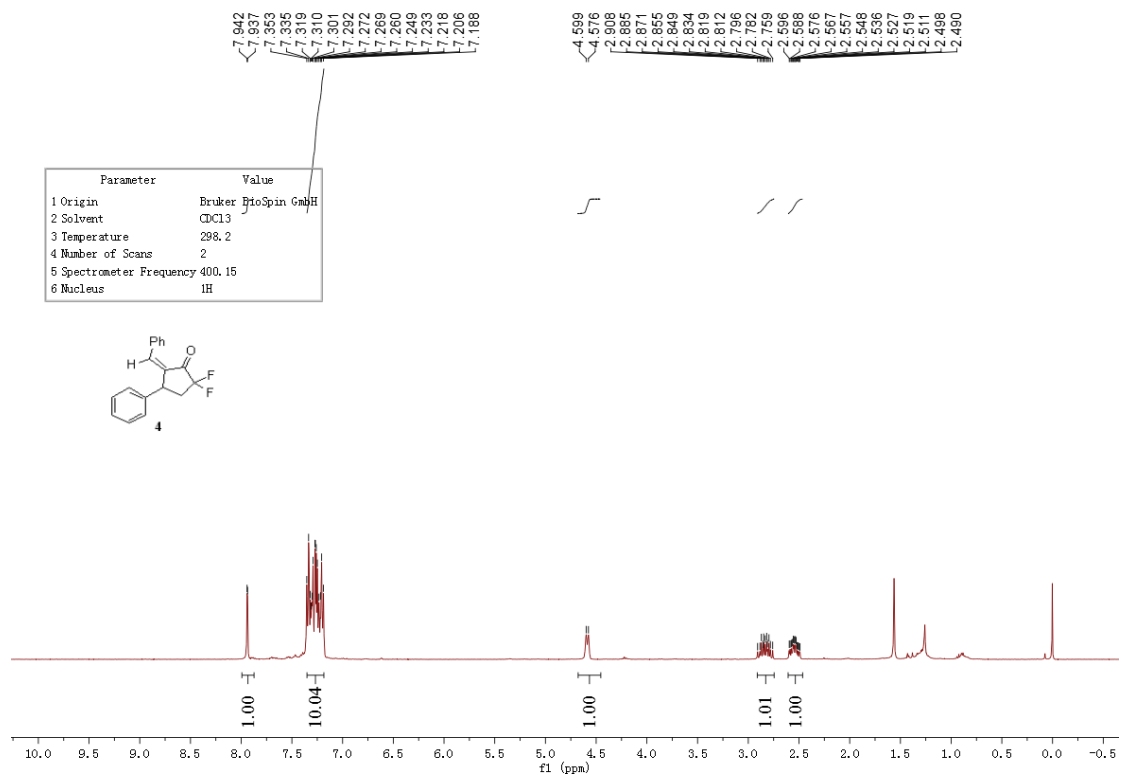
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	500
5 Spectrometer Frequency	100.62
6 Nucleus	13C



-104.467  
 -105.189  
 -105.281  
 -106.000

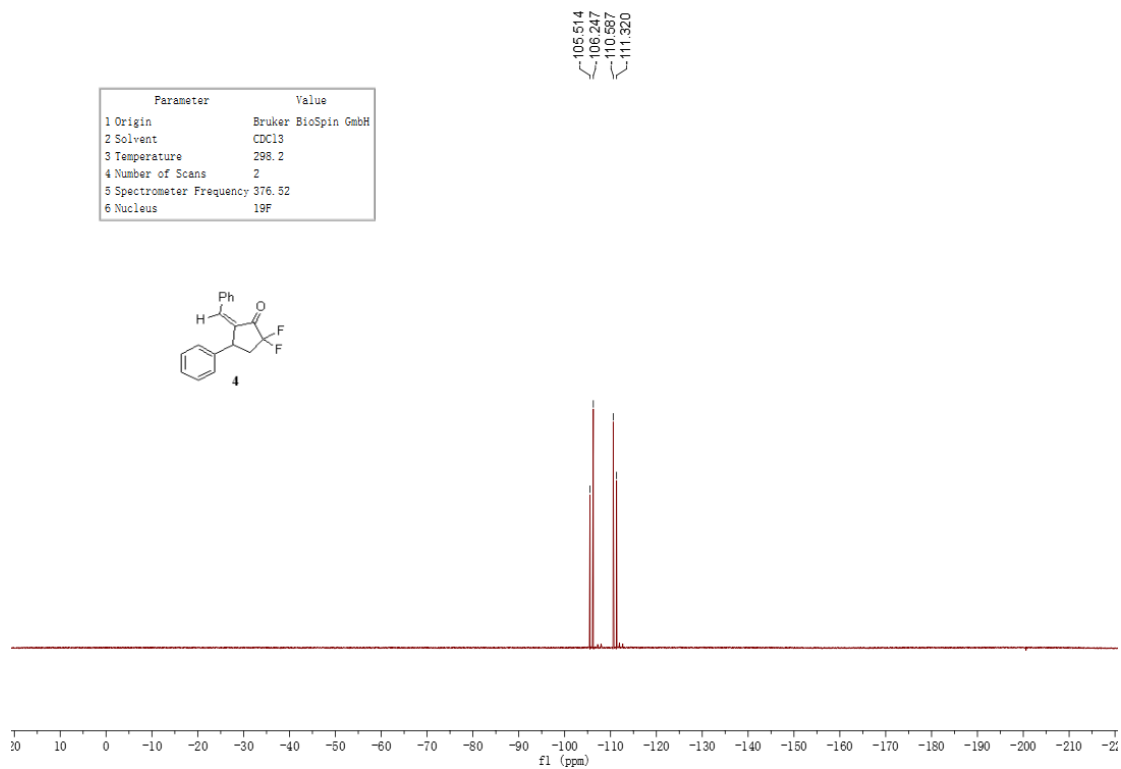
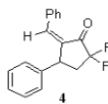
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.52
6 Nucleus	19F





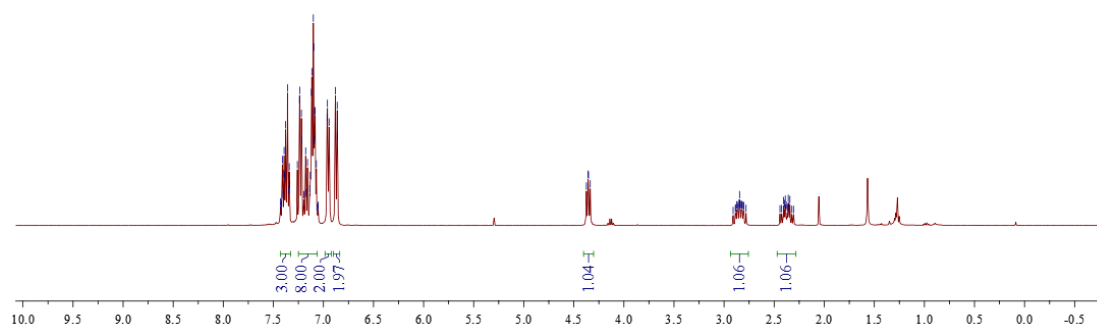
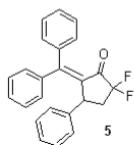


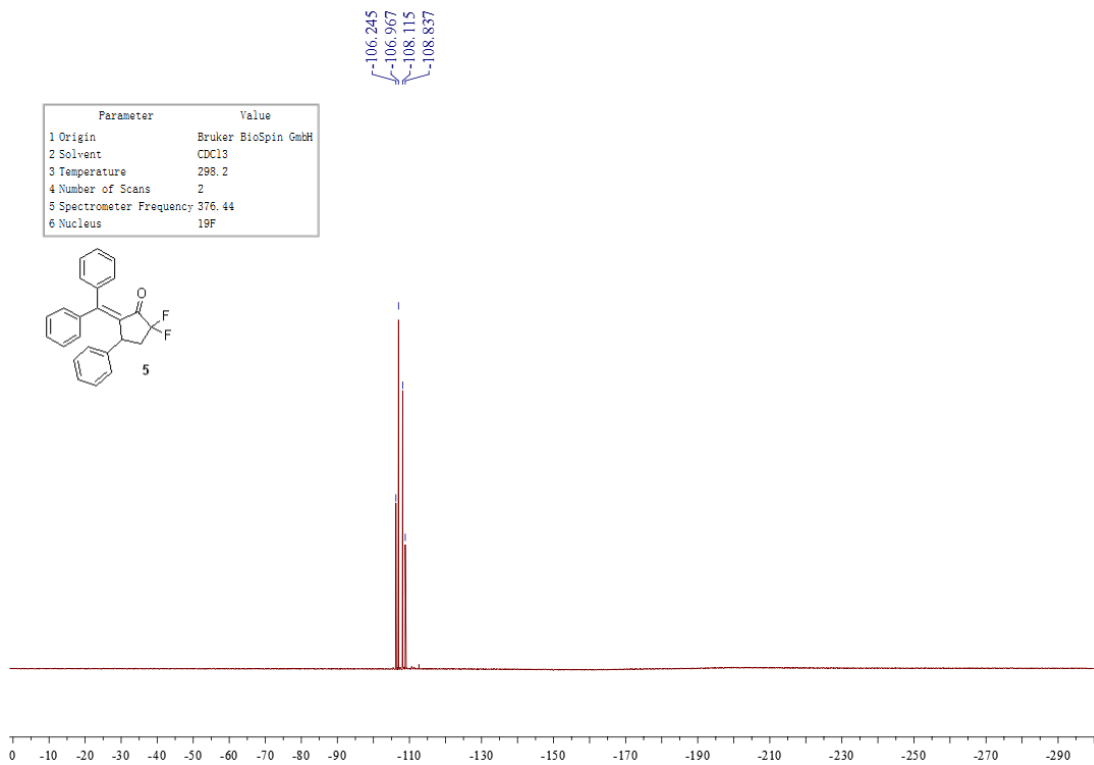
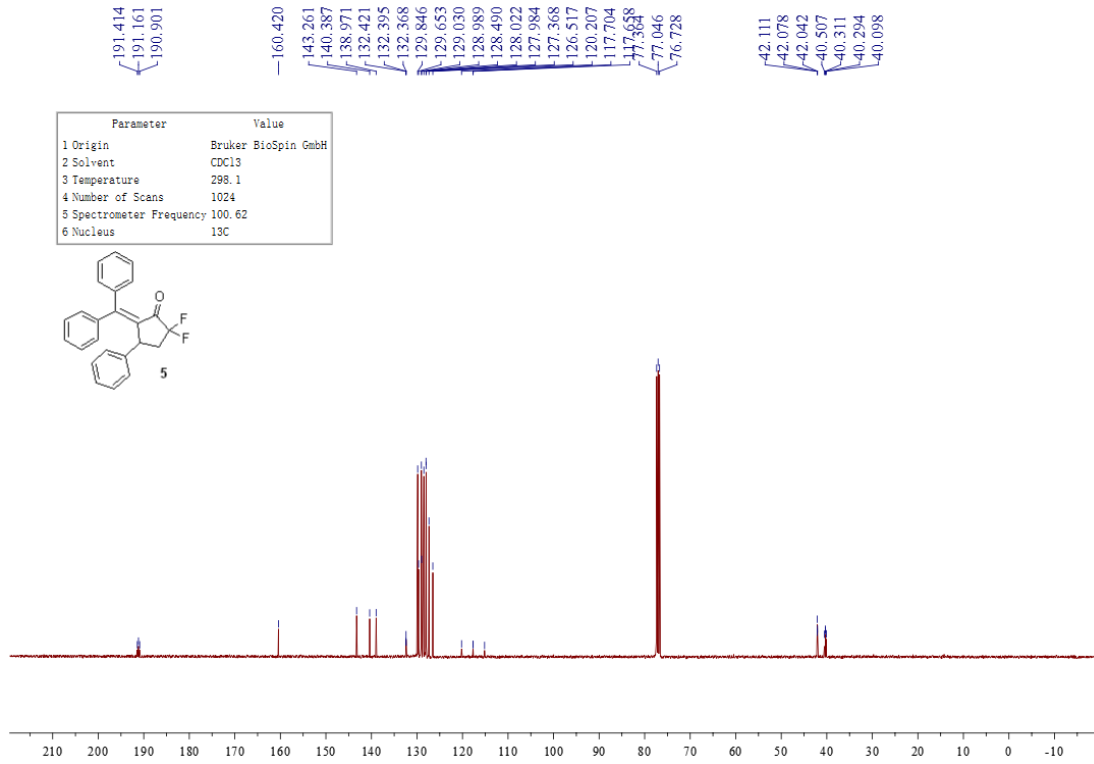
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

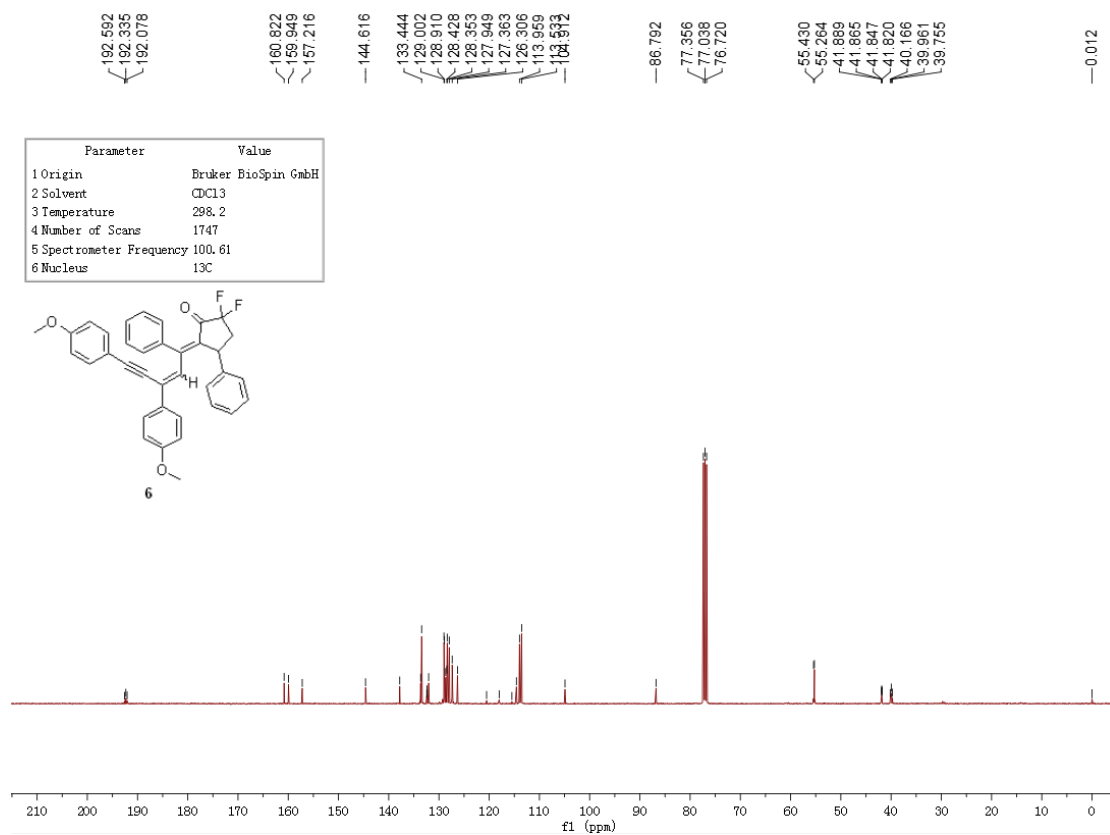
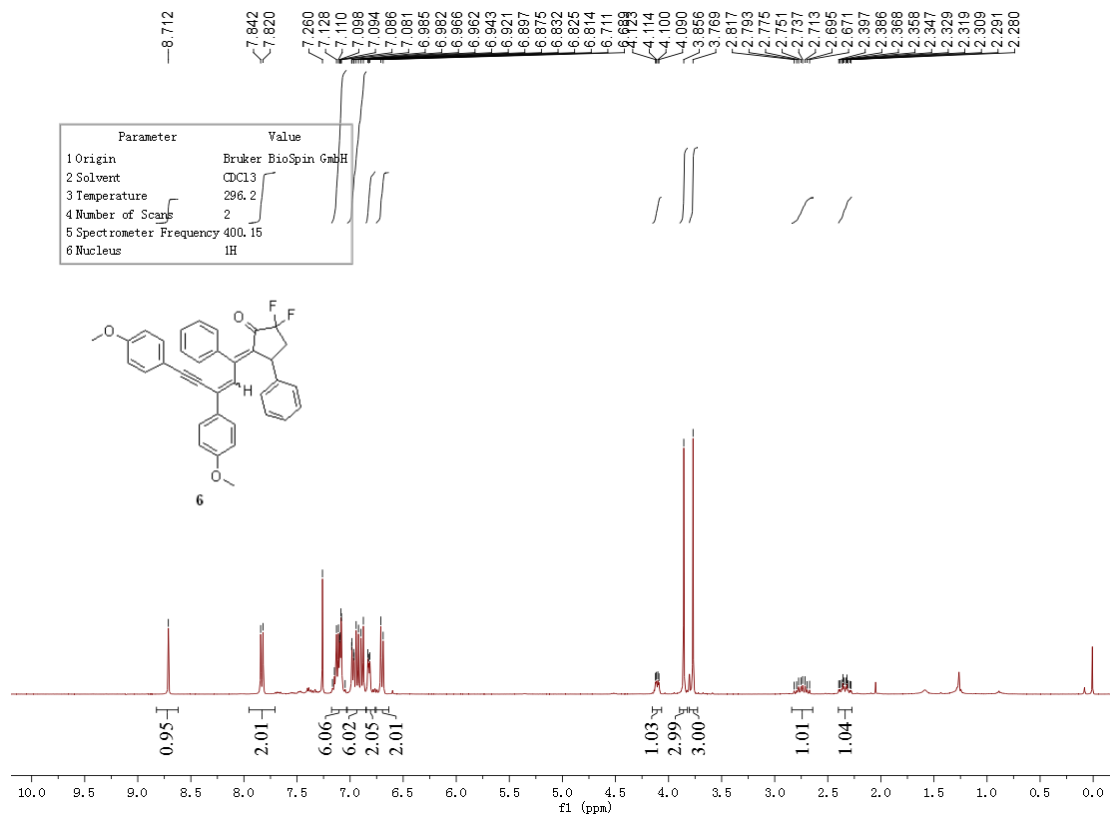


7.428  
7.418  
7.410  
7.404  
7.396  
7.392  
7.389  
7.377  
7.359  
7.346  
7.341  
7.337  
7.260  
7.239  
7.237  
7.220  
7.216  
7.196  
7.178  
7.172  
7.159  
7.137  
7.132  
7.120  
7.116  
7.101  
7.097  
7.091  
7.087  
7.083  
7.070  
7.052  
6.964  
6.960  
6.943  
6.880  
6.862  
6.859  
4.375  
4.357  
4.354  
4.336  
2.872  
2.868  
2.850  
2.845  
2.840  
2.830  
2.823  
2.818  
2.808  
2.405  
2.396  
2.389  
2.379  
2.359  
2.343

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

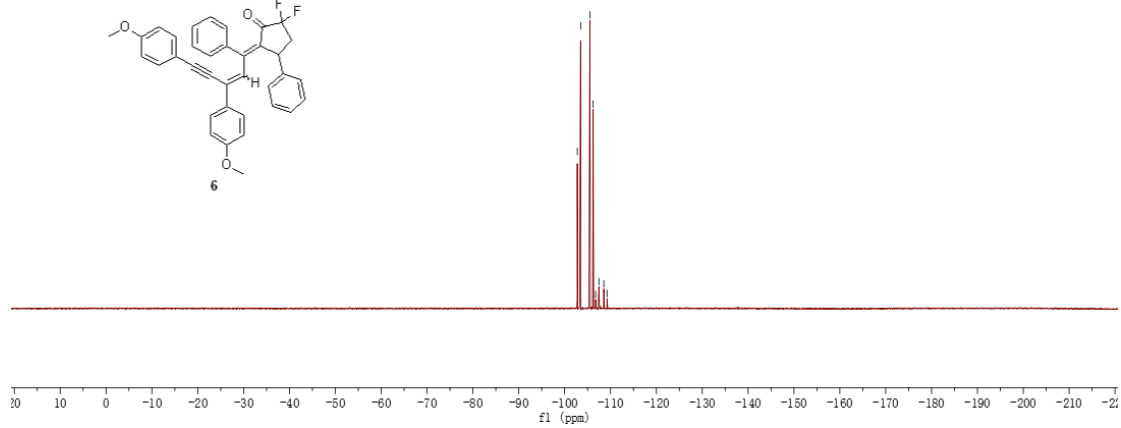
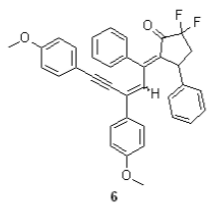




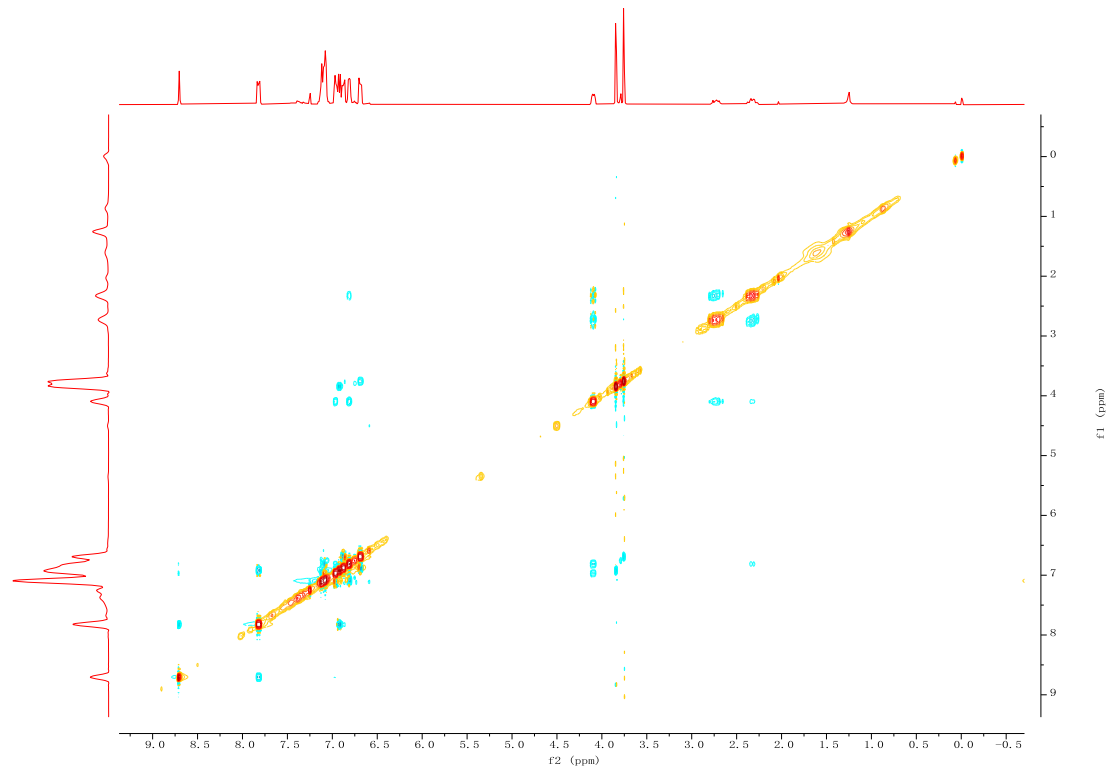


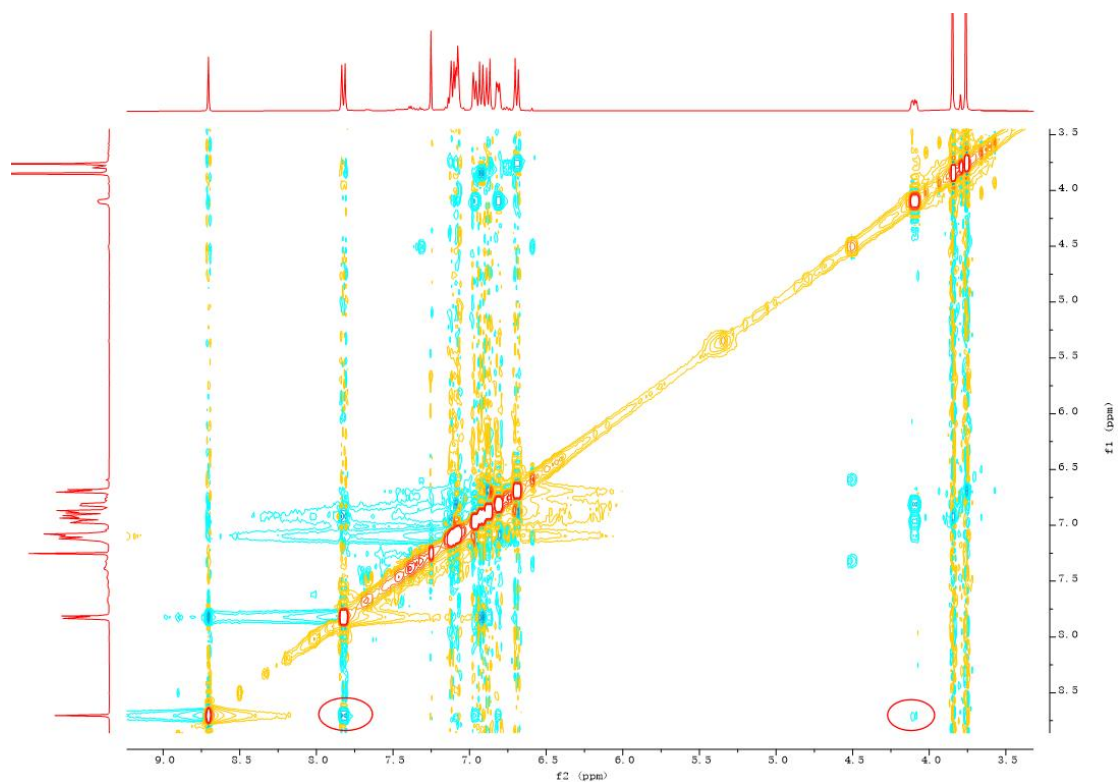
-102.753  
-103.475  
-105.492  
-106.214  
-106.748  
-107.463  
-108.531  
-109.246

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F



6 (noe)





## 10. X-ray crystal structures of compound 3a

CCDC 2059851 contains the supplementary crystallographic data for compound **3a**. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

