

*Supporting Information for*

## **Fluorination of Allylic Alcohols: Synthesis of Z-Fluoroalkenes via Cleavage of Non-activated Carbon-Carbon Bond**

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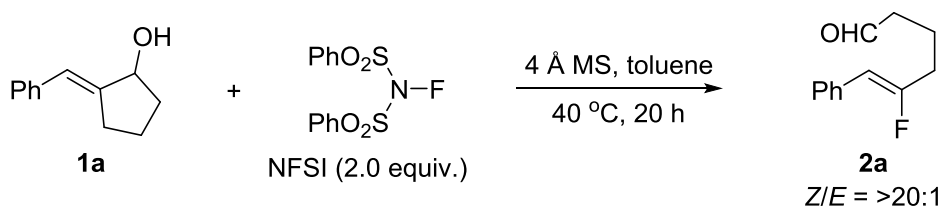
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## I. General information

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker 500 or 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform  $\delta$  7.26), carbon (chloroform  $\delta$  77.0) or fluorine ( $\text{CFCl}_3$   $\delta$  0.00). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra (HRMS) were obtained on a Finnigan/MAT 95XL-T spectrometer or micrOTOF-Q II 10269 spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

All the fluorination reactions were carried out under ambient atmosphere. Commercially available reagents were used as received without further purification. The substrates **1** and **8** were prepared by reduction of the corresponding enones which according to the literature procedure.<sup>1</sup>

## II. Synthesis and characterization of **2a**

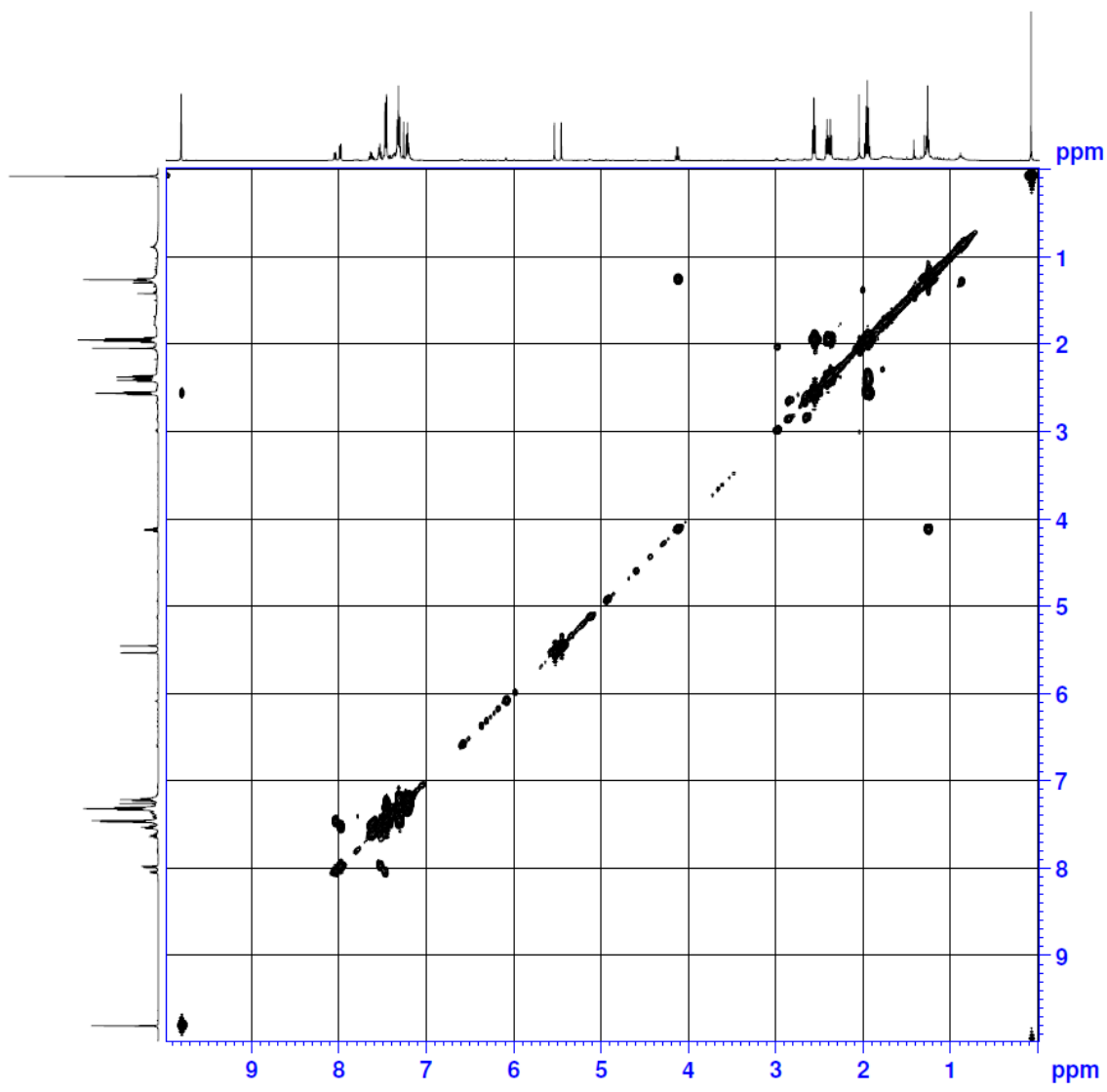


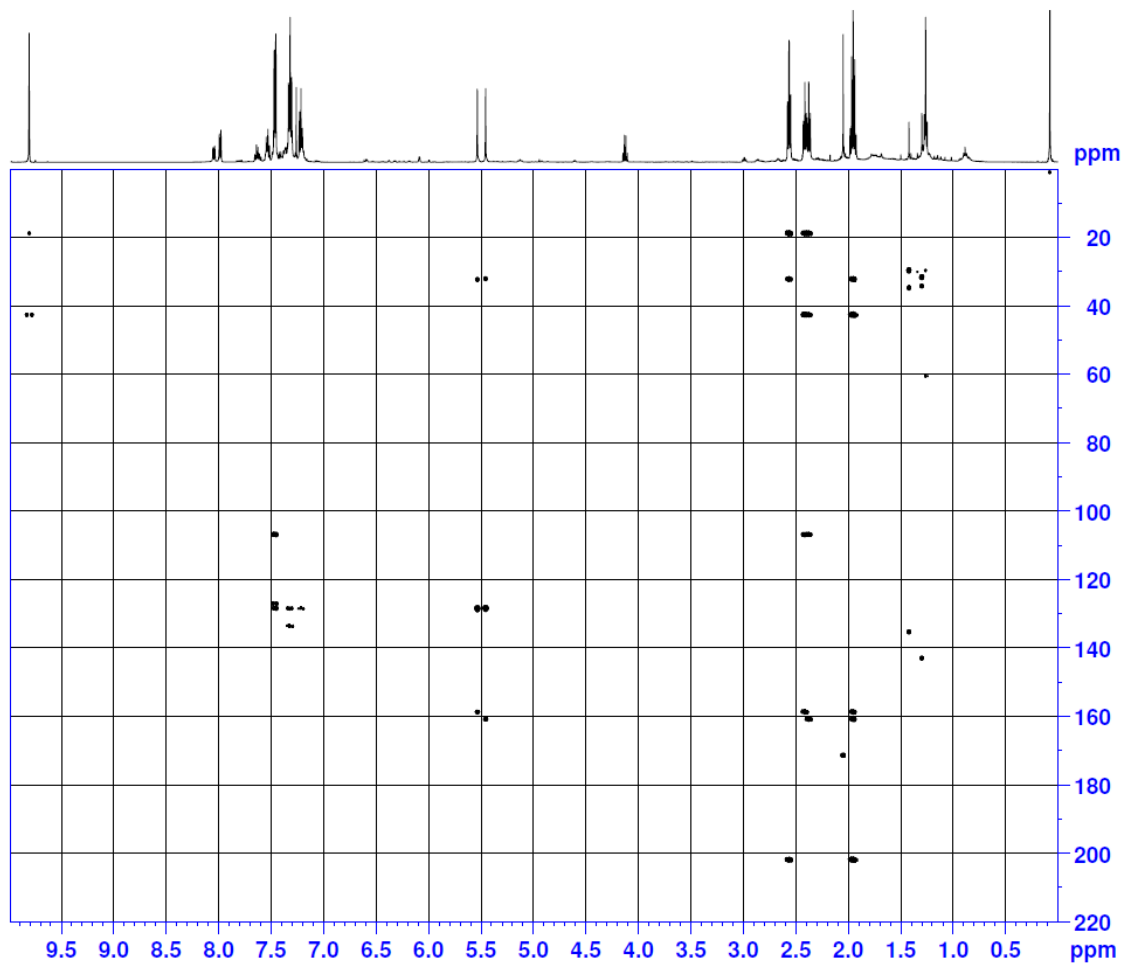
**(Z)-5-fluoro-6-phenylhex-5-enal (2a):** To a solution of allylic alcohol **1a** (34.8 mg, 0.200 mmol) in 1 mL of toluene were added 4 Å MS and NFSI (126 mg, 0.400 mmol). The resulting mixture was allowed to stir at 40 °C for 20 h. The crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness and then directly

analyzed by  $^1\text{H}$  NMR to determine the *Z/E* ratio. The residue was then purified by column chromatography (hexanes:ethyl acetate = 5:1) to yield the product **2a** in 60% yield as an oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  9.80 (t,  $J = 1.0$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.22 (t,  $J = 7.5$  Hz, 1H), 5.50 (d,  $J = 39.0$  Hz, 1H), 2.56 (t,  $J = 7.5$  Hz, 2H), 2.43-2.36 (m, 2H), 1.98-1.94 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  201.6, 159.6 (d,  $J = 264.8$  Hz), 133.4 (d,  $J = 2.5$  Hz), 128.4, 128.3 (d,  $J = 7.4$  Hz), 126.9 (d,  $J = 2.3$  Hz), 106.7 (d,  $J = 8.5$  Hz), 42.6, 32.2 (d,  $J = 26.9$  Hz), 18.8.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -102.07 (dt,  $J = 39.2$  Hz, 18.6 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{13}\text{OF}$   $[\text{M}]^+$ : 192.0950; found: 192.0949.

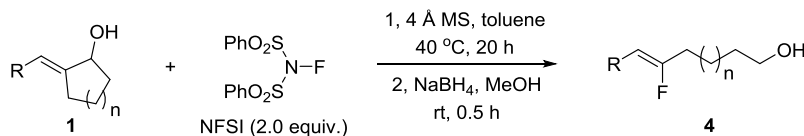
The *Z* configuration of **2a** was determined by 2D ( $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{13}\text{C}$ ) NMR measurement as shown below (Figure S1).





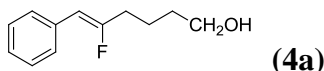
**Figure S1.** 2D ( $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{13}\text{C}$ ) NMR spectra of **2a**.

### III. General procedure for the synthesis of **4**



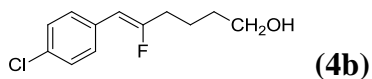
To a solution of allylic alcohols **1** (0.20 mmol) in 1 mL of toluene were added 4 Å MS and NFSI (0.40 mmol). The resulting mixture was allowed to stir at 40 °C for ~20 h. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness, which was then directly analyzed by <sup>1</sup>H NMR analysis to determine the *Z/E* ratios. 1 mL of methanol was then added followed by NaBH<sub>4</sub> (0.30 mmol). The resulting mixture was allowed to stir at ambient temperature for 0.5 h, quenched by saturated brine, extracted with ethyl acetate, concentrated and purified by column chromatography (hexanes:ethyl acetate) to afford the products **4** as an oil.

### IV. Characterization of compounds **4**



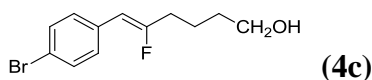
#### (Z)-5-fluoro-6-phenylhex-5-en-1-ol

The title compound was prepared according to the general procedure as described above in 82% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.49 (d, *J* = 39.5 Hz, 1H), 3.69 (t, *J* = 6.0 Hz, 2H), 2.41-2.34 (m, 2H), 1.72-1.65 (m, 4H), 1.57 (brs, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 160.7 (d, *J* = 264.9 Hz), 133.7 (d, *J* = 2.4 Hz), 128.4, 128.2 (d, *J* = 7.3 Hz), 126.6 (d, *J* = 2.1 Hz), 106.0 (d, *J* = 8.8 Hz), 62.5, 32.8 (d, *J* = 26.5 Hz), 31.9, 22.6. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -101.18 (dt, *J* = 39.5 Hz, 18.0 Hz). HRMS (EI): *m/z* calcd. for C<sub>12</sub>H<sub>15</sub>OF [M]<sup>+</sup>: 194.1107; found: 194.1112.



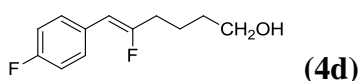
**(Z)-6-(4-chlorophenyl)-5-fluorohex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 53% yield. *Z/E* = 12:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.38 (d,  $J$  = 8.5 Hz, 2H), 7.27 (d,  $J$  = 8.5 Hz, 2H), 5.44 (d,  $J$  = 39.0 Hz, 1H), 3.69 (t,  $J$  = 6.0 Hz, 2H), 2.40-2.33 (m, 2H), 1.71-1.64 (m, 4H), 1.54 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.2 (d,  $J$  = 265.9 Hz), 132.2, 129.5 (d,  $J$  = 7.6 Hz), 128.5, 105.0 (d,  $J$  = 8.6 Hz), 62.5, 32.8 (d,  $J$  = 26.4 Hz), 31.8, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.19 (dt,  $J$  = 38.9 Hz, 18.0 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{12}\text{H}_{14}\text{OCIF}$  [ $\text{M}$ ] $^+$ : 228.0717; found: 228.0712.



**(Z)-6-(4-bromophenyl)-5-fluorohex-5-en-1-ol**

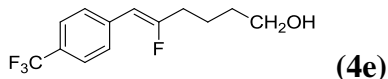
The title compound was prepared according to the general procedure as described above in 63% yield. *Z/E* = 15:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.42 (d,  $J$  = 8.5 Hz, 2H), 7.32 (d,  $J$  = 8.5 Hz, 2H), 5.43 (d,  $J$  = 39.0 Hz, 1H), 3.69 (t,  $J$  = 6.0 Hz, 2H), 2.37-2.32 (m, 2H), 1.71-1.64 (m, 4H), 1.55 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.3 (d,  $J$  = 266.3 Hz), 132.7, 131.5, 129.8 (d,  $J$  = 7.6 Hz), 120.3 (d,  $J$  = 3.5 Hz), 105.1 (d,  $J$  = 8.8 Hz), 62.5, 32.8 (d,  $J$  = 26.3 Hz), 31.8, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -99.77 (dt,  $J$  = 38.6 Hz, 18.3 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{12}\text{H}_{14}\text{OBrF}$  [ $\text{M}$ ] $^+$ : 272.0212; found: 272.0201.



**(Z)-5-fluoro-6-(4-fluorophenyl)hex-5-en-1-ol**

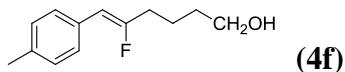
The title compound was prepared according to the general procedure as described above in 91% yield. *Z/E* = 17:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.44-7.41 (m, 2H), 7.01-6.97 (m, 2H), 5.44 (d,  $J$  = 39.0 Hz, 1H), 3.69 (t,  $J$  = 6.0 Hz, 2H), 2.39-2.32 (m, 2H), 1.71-1.66 (m, 5H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.4 (d,  $J$  = 244.8 Hz), 160.4 (d,  $J$  = 264.3 Hz), 129.8 (t,  $J$  = 7.6 Hz), 115.2 (d,  $J$  = 21.3 Hz), 104.9 (d,  $J$  = 8.9 Hz), 62.5, 32.7

(d,  $J = 26.5$  Hz), 31.8, 22.6.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -102.48 (dt,  $J = 39.5$  Hz, 18.1 Hz), -115.04 - -115.15 (m, 1F). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{14}\text{OF}_2$   $[\text{M}]^+$ : 212.1013; found: 212.1016.



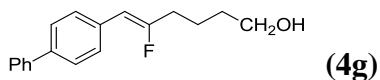
#### **(Z)-5-fluoro-6-(4-(trifluoromethyl)phenyl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 65% yield.  $Z/E = 10:1$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.55 (m, 4H), 5.54 (d,  $J = 38.5$  Hz, 1H), 3.71 (t,  $J = 6.0$  Hz, 2H), 2.43-2.37 (m, 2H), 1.74-1.66 (m, 4H), 1.60 (brs, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  162.5 (d,  $J = 268.4$  Hz), 137.3, 128.3 (d,  $J = 7.6$  Hz), 125.3 (q,  $J = 3.9$  Hz), 124.2 (q,  $J = 272.5$  Hz), 115.9, 105.1 (d,  $J = 8.3$  Hz), 62.5, 32.8 (d,  $J = 26.1$  Hz), 31.8, 22.6.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -62.51 (s, 3F), -97.63 (dt,  $J = 38.6$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{OF}_4$   $[\text{M}]^+$ : 262.0981; found: 262.0983.



#### **(Z)-5-fluoro-6-(p-tolyl)hex-5-en-1-ol**

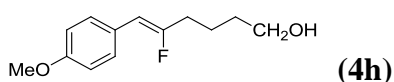
The title compound was prepared according to the general procedure as described above in 67% yield.  $Z/E = 14:1$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.36 (d,  $J = 8.0$  Hz, 2H), 7.12 (d,  $J = 8.0$  Hz, 2H), 5.45 (d,  $J = 39.5$  Hz, 1H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.39-2.33 (m, 5H), 1.69-1.67 (m, 4H), 1.49 (brs, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  160.1 (d,  $J = 263.8$  Hz), 136.4 (d,  $J = 2.4$  Hz), 130.9, 129.1, 128.1 (d,  $J = 7.3$  Hz), 105.8 (d,  $J = 8.9$  Hz), 62.5, 32.8 (d,  $J = 26.6$  Hz), 31.9, 22.7, 21.1.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -102.24 (dt,  $J = 39.8$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{17}\text{OF}$   $[\text{M}]^+$ : 208.1263; found: 208.1263.



#### **(Z)-6-([1,1'-biphenyl]-4-yl)-5-fluorohex-5-en-1-ol**

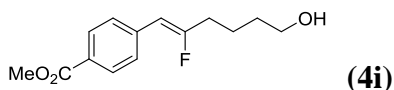


The title compound was prepared according to the general procedure as described above in 93% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.61-7.53 (m, 6H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.34 (t,  $J = 7.5$  Hz, 1H), 5.53 (d,  $J = 39.5$  Hz, 1H), 3.71 (t,  $J = 6.0$  Hz, 2H), 2.43-2.37 (m, 2H), 1.73-1.67 (m, 4H), 1.59 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  160.9 (d,  $J = 265.4$  Hz), 140.8, 139.4, 132.8, 128.75, 128.65 (d,  $J = 7.4$  Hz), 127.2, 127.0, 126.9, 105.7 (d,  $J = 8.6$  Hz), 62.6, 32.9 (d,  $J = 26.4$  Hz), 31.9, 22.7.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.58 (dt,  $J = 39.5$  Hz, 18.0 Hz). **HRMS (EI)**:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{19}\text{OF}$   $[\text{M}]^+$ : 270.1420; found: 270.1419.



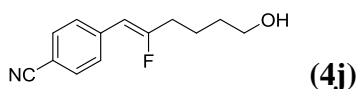
**(Z)-5-fluoro-6-(4-methoxyphenyl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 76% yield. *Z/E* = 15:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.40 (d,  $J = 8.5$  Hz, 2H), 6.85 (d,  $J = 8.5$  Hz, 2H), 5.42 (d,  $J = 40.0$  Hz, 1H), 3.80 (s, 3H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.38-2.32 (m, 2H), 1.71-1.63 (m, 4H), 1.54 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.3 (d,  $J = 263.8$  Hz), 158.2, 129.4 (d,  $J = 7.4$  Hz), 126.5 (d,  $J = 2.3$  Hz), 113.8, 105.4 (d,  $J = 9.1$  Hz), 62.5, 55.2, 32.7 (d,  $J = 26.6$  Hz), 31.9, 22.7.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -104.14 (dt,  $J = 39.8$  Hz, 18.3 Hz). **HRMS (EI)**:  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{F}$   $[\text{M}]^+$ : 224.1213; found: 224.1213.



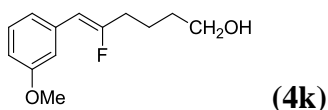
**methyl (Z)-4-(2-fluoro-6-hydroxyhex-1-en-1-yl)benzoate**

The title compound was prepared according to the general procedure as described above in 80% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  7.97 (d,  $J = 8.4$  Hz, 2H), 7.51 (t,  $J = 8.4$  Hz, 2H), 5.54 (d,  $J = 38.8$  Hz, 1H), 3.90 (s, 3H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.43-2.35 (m, 2H), 1.73-1.56 (m, 5H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  166.9, 162.6 (d,  $J = 268.8$  Hz), 138.4 (d,  $J = 2.5$  Hz), 129.7, 128.1 (d,  $J = 7.7$  Hz), 105.5 (d,  $J = 8.3$  Hz), 62.5, 52.0, 33.9 (d,  $J = 26.1$  Hz), 31.9, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -96.9 (dt,  $J = 39.1$  Hz, 18.0 Hz).



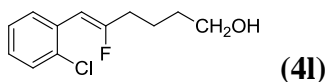
**(Z)-4-(2-fluoro-6-hydroxyhex-1-en-1-yl)benzonitrile**

The title compound was prepared according to the general procedure as described above in 68% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  7.57 (d,  $J = 8.4$  Hz, 2H), 7.52 (d,  $J = 8.4$  Hz, 2H), 5.52 (d,  $J = 38.4$  Hz, 1H), 3.59 (t,  $J = 6.0$  Hz, 2H), 2.44-2.36 (m, 2H), 1.73-1.50 (m, 5H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  163.6 (d,  $J = 270.4$  Hz), 138.4 (d,  $J = 2.5$  Hz), 132.2, 128.6 (d,  $J = 8.0$  Hz), 119.0, 109.8 (d,  $J = 3.0$  Hz), 105.1 (d,  $J = 8.1$  Hz), 62.4, 32.9 (d,  $J = 25.8$  Hz), 31.8, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -95.18 (dt,  $J = 37.2$  Hz, 18.4 Hz).



**(Z)-5-fluoro-6-(3-methoxyphenyl)hex-5-en-1-ol**

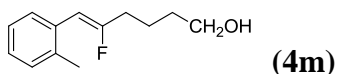
The title compound was prepared according to the general procedure as described above in 82% yield. *Z/E* = 11:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.22 (t,  $J = 8.0$  Hz, 1H), 7.06-7.02 (m, 2H), 6.78-6.76 (m, 1H), 5.46 (d,  $J = 39.0$  Hz, 1H), 3.81 (s, 3H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.40-2.33 (m, 2H), 1.70-1.66 (m, 5H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  160.9 (d,  $J = 265.5$  Hz), 159.5, 129.3, 126.4, 120.9 (d,  $J = 6.9$  Hz), 113.6 (d,  $J = 8.1$  Hz), 112.5, 106.0 (d,  $J = 8.3$  Hz), 62.5, 55.2, 32.8 (d,  $J = 26.5$  Hz), 31.9, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.31 (dt,  $J = 39.2$  Hz, 18.0 Hz). **HRMS (EI)**:  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{F}$   $[\text{M}]^+$ : 224.1213; found: 224.1213.



**(Z)-6-(3-chlorophenyl)-5-fluorohex-5-en-1-ol**

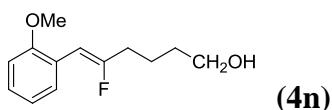
The title compound was prepared according to the general procedure as described above in 22% yield. *Z/E* = 9:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.78 (d,  $J = 8.0$  Hz, 1H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.23 (t,  $J = 8.0$  Hz, 1H), 7.14 (t,  $J = 8.0$  Hz, 1H), 5.89 (d,  $J =$

38.5 Hz, 1H), 3.71 (t,  $J = 6.0$  Hz, 2H), 2.45-2.39 (m, 2H), 1.74-1.67 (m, 4H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  161.8 (d,  $J = 267.3$  Hz), 132.3, 131.6, 130.3 (d,  $J = 11.9$  Hz), 129.3, 127.8, 126.6, 102.1 (d,  $J = 7.3$  Hz), 62.5, 32.9 (d,  $J = 26.4$  Hz), 31.9, 22.6.  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -100.82 (dt,  $J = J = 39.4$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for C<sub>12</sub>H<sub>14</sub>OCIF [M]<sup>+</sup>: 228.0717; found: 228.0714.



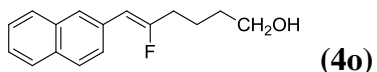
**(Z)-5-fluoro-6-(o-tolyl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 42% yield.  $Z/E = 9:1$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>, TMS, 500 MHz):  $\delta$  7.60 (d,  $J = 7.5$  Hz, 1H), 7.19-7.13 (m, 3H), 5.61 (d,  $J = 38.5$  Hz, 1H), 3.71 (t,  $J = 6.0$  Hz, 2H), 2.42-2.37 (m, 2H), 2.30 (s, 3H), 1.74-1.67 (m, 4H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  160.2 (d,  $J = 263.5$  Hz), 135.3, 132.2, 129.9, 129.1 (d,  $J = 9.4$  Hz), 126.8, 125.8, 103.4 (d,  $J = 10.0$  Hz), 62.5, 32.8 (d,  $J = 26.9$  Hz), 31.9, 22.7, 20.1.  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -103.61 (dt,  $J = 38.4$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for C<sub>13</sub>H<sub>17</sub>OF [M]<sup>+</sup>: 208.1263; found: 208.1267.



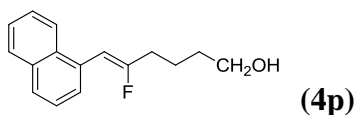
**(Z)-5-fluoro-6-(4-methoxyphenyl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 50% yield.  $Z/E = 9:1$ .  $^1\text{H}$  NMR (CDCl<sub>3</sub>, TMS, 500 MHz):  $\delta$  7.75 (d,  $J = 8.0$  Hz, 1H), 7.19 (t,  $J = 8.0$  Hz, 1H), 6.94 (t,  $J = 8.0$  Hz, 1H), 6.85 (d,  $J = 8.0$  Hz, 1H), 5.90 (d,  $J = 40.5$  Hz, 1H), 3.83 (s, 3H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.42-2.36 (m, 2H), 1.71-1.58 (m, 5H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  160.6 (d,  $J = 263.1$  Hz), 155.8, 129.7 (d,  $J = 12.5$  Hz), 127.8, 122.5, 120.6, 110.4, 99.3 (d,  $J = 7.3$  Hz), 62.6, 55.5, 33.0 (d,  $J = 26.9$  Hz), 31.9, 22.7.  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -102.85 (dt,  $J = 40.6$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for C<sub>13</sub>H<sub>17</sub>O<sub>2</sub>F [M]<sup>+</sup>: 224.1213; found: 224.1222.



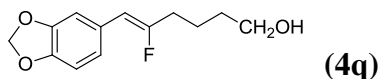
**(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 60% yield. *Z/E* = 13:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.91 (s, 1H), 7.82-7.79 (m, 3H), 7.69-7.67 (m, 1H), 7.48-7.45 (m, 2H), 5.65 (d,  $J = 39.5$  Hz, 1H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.45-2.39 (m, 2H), 1.86 (brs, 1H), 1.75-1.67 (m, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.0 (d,  $J = 265.5$  Hz), 133.4, 132.2, 131.3 (d,  $J = 2.5$  Hz), 127.9, 127.8, 127.4, 126.9 (d,  $J = 7.4$  Hz), 126.5 (d,  $J = 7.6$  Hz), 126.0, 125.6, 106.05 (d,  $J = 8.3$  Hz), 62.4, 32.8 (d,  $J = 26.4$  Hz), 31.8, 22.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.44 (dt,  $J = 39.5$  Hz, 18.3 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{16}\text{H}_{17}\text{OF}$   $[\text{M}]^+$ : 244.1263; found: 244.1263.



**(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-en-1-ol**

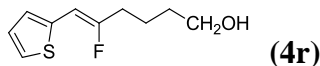
The title compound was prepared according to the general procedure as described above in 64% yield. *Z/E* = 9:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  8.03 (d,  $J = 8.0$  Hz, 1H), 7.85 (d,  $J = 8.5$  Hz, 1H), 7.78-7.76 (m, 2H), 7.54-7.47 (m, 3H), 6.14 (d,  $J = 37.5$  Hz, 1H), 3.72 (t,  $J = 6.0$  Hz, 2H), 2.53-2.47 (m, 2H), 1.79-1.73 (m, 5H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.1 (d,  $J = 263.6$  Hz), 133.6, 131.2, 129.7, 128.5, 127.3, 127.1 (d,  $J = 8.0$  Hz), 125.9, 125.5, 125.4, 124.0, 102.6 (d,  $J = 10.8$  Hz), 62.4, 32.8 (d,  $J = 26.8$  Hz), 31.9, 22.7.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -102.35 (dt,  $J = 36.9$  Hz, 17.8 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{16}\text{H}_{17}\text{OF}$   $[\text{M}]^+$ : 244.1263; found: 244.1263.



**(Z)-6-(benzo[d][1,3]dioxol-5-yl)-5-fluorohex-5-en-1-ol**

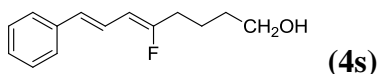
The title compound was prepared according to the general procedure as described above in 54% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.09 (s, 1H), 6.84 (d,  $J = 8.0$  Hz, 1H), 6.75 (d,  $J = 8.0$  Hz, 1H), 5.94 (s, 2H), 5.39 (d,  $J = 39.0$  Hz, 1H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.36-2.31 (m, 2H), 1.68-1.66 (m, 4H), 1.57 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.5 (d,  $J = 263.1$  Hz), 147.7, 127.9, 122.1 (d,  $J = 5.9$  Hz), 108.5 (d,  $J = 9.8$  Hz), 108.2, 105.7 (d,  $J = 8.8$  Hz), 100.9, 62.6, 32.7 (d,  $J = 26.6$  Hz), 31.9, 31.6, 22.7.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -103.20 (dt,  $J = 39.2$  Hz, 18.0 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{15}\text{O}_3\text{F}$   $[\text{M}]^+$ : 238.1005; found: 238.1004.



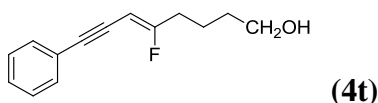
**(Z)-5-fluoro-6-(naphthalen-2-yl)hex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 60% yield.  $Z/E = 20:1$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.22 (d,  $J = 5.0$  Hz, 1H), 7.00-6.96 (m, 2H), 5.82 (d,  $J = 38.5$  Hz, 1H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.41-2.35 (m, 2H), 1.69-1.65 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.4 (d,  $J = 263.9$  Hz), 135.9 (d,  $J = 3.5$  Hz), 126.5, 125.6 (d,  $J = 3.8$  Hz), 124.9 (d,  $J = 9.0$  Hz), 100.7 (d,  $J = 12.8$  Hz), 62.5, 32.1 (d,  $J = 25.5$  Hz), 31.8, 22.5.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -97.93 (dtd,  $J = 38.4$  Hz, 17.8 Hz, 1.7 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{13}\text{OFS}$   $[\text{M}]^+$ : 200.0671; found: 200.0672.



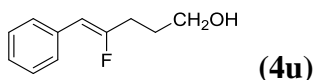
**(5Z,7E)-5-fluoro-8-phenylocta-5,7-dien-1-ol**

The title compound was prepared according to the general procedure as described above in 56% yield.  $Z/E = 6:1$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.40 (d,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.5$  Hz, 1H), 7.02 (dd,  $J = 16.5$  Hz, 10.5 Hz, 1H), 6.44 (d,  $J = 16.5$  Hz, 1H), 5.43 (dd,  $J = 35.5$  Hz, 10.5 Hz, 1H), 3.69 (t,  $J = 6.0$  Hz, 2H), 2.34-2.29 (m, 2H), 1.66-1.64 (m, 4H), 1.57 (brs, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.0 (d,  $J = 263.1$  Hz), 137.5, 130.0 (d,  $J = 4.5$  Hz), 128.6, 127.3, 126.2, 120.7 (d,  $J = 5.5$  Hz), 107.2 (d,  $J = 12.0$  Hz), 62.5, 32.0 (d,  $J = 26.1$  Hz), 31.9, 22.5.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -103.12 (dt,  $J = 35.3$  Hz, 17.8 Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{17}\text{OF}$   $[\text{M}]^+$ : 220.1263; found: 220.1263.



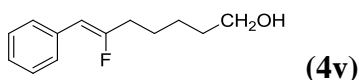
**(Z)-5-fluoro-8-phenyloct-5-en-7-yn-1-ol**

The title compound was prepared according to the general procedure as described above in 69% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz)  $\delta$  7.44 (m, 2H), 7.30 (m, 3H), 5.03 (d,  $J = 33.5$  Hz, 1H), 3.68 (t,  $J = 6.0$  Hz, 2H), 2.35-2.32 (m, 2H), 1.66-1.64 (m, 4H), 1.56 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  169.0 (d,  $J = 270.4$  Hz), 131.4, 128.2, 128.1, 123.3, 93.0 (d,  $J = 5.6$  Hz), 87.9 (d,  $J = 14.6$  Hz), 81.6, 62.4, 31.9 (d,  $J = 24.5$  Hz), 31.7, 22.3.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz)  $\delta$  -88.10 (dt,  $J = 33.3$  Hz, 17.2 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{14}\text{H}_{15}\text{OF}$   $[\text{M}]^+$ : 218.1107; found: 218.1110.



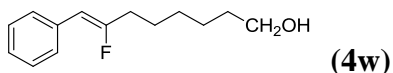
#### **(Z)-4-fluoro-5-phenylpent-4-en-1-ol**

The title compound was prepared according to the general procedure as described above in 83% yield. *Z/E* = 5:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.47 (d,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.5$  Hz, 1H), 5.52 (d,  $J = 35.5$  Hz, 1H), 3.75 (t,  $J = 6.0$  Hz, 2H), 2.49-2.42 (m, 2H), 1.91-1.85 (m, 2H), 1.52 (brs, 1H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  160.4 (d,  $J = 264.8$  Hz), 133.7, 128.4, 128.3 (d,  $J = 7.3$  Hz), 126.7 (d,  $J = 2.3$  Hz), 106.2 (d,  $J = 8.6$  Hz), 61.8, 29.5 (d,  $J = 26.9$  Hz), 29.3.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -101.31 (dt,  $J = 39.5$  Hz, 18.6 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{11}\text{H}_{13}\text{OF}$   $[\text{M}]^+$ : 180.0950; found: 180.0950.



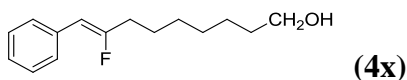
#### **(Z)-6-fluoro-7-phenylhept-6-en-1-ol**

The title compound was prepared according to the general procedure as described above in 56% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.46 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.20 (t,  $J = 7.5$  Hz, 1H), 5.47 (d,  $J = 39.5$  Hz, 1H), 3.67 (t,  $J = 6.0$  Hz, 2H), 2.38-2.32 (m, 2H), 1.66-1.42 (m, 7H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  160.9 (d,  $J = 265.0$  Hz), 133.8, 128.4, 128.2 (d,  $J = 7.4$  Hz), 126.6 (d,  $J = 2.0$  Hz), 105.9 (d,  $J = 8.6$  Hz), 62.8, 33.0 (d,  $J = 26.5$  Hz), 32.4, 26.2, 25.1.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -101.03 (dt,  $J = 39.5$  Hz, 18.3 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{13}\text{H}_{17}\text{OF}$   $[\text{M}]^+$ : 208.1263; found: 208.1264.



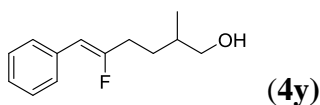
**(Z)-7-fluoro-8-phenyloct-7-en-1-ol**

The title compound was prepared according to the general procedure as described above in 45% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.46 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.20 (t,  $J = 7.5$  Hz, 1H), 5.46 (d,  $J = 39.5$  Hz, 1H), 3.65 (t,  $J = 6.5$  Hz, 2H), 2.35-2.31 (m, 2H), 1.64-1.41 (m, 9H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.1 (d,  $J = 265.0$  Hz), 133.9, 128.4, 128.2 (d,  $J = 7.3$  Hz), 126.6, 105.7 (d,  $J = 8.8$  Hz), 62.9, 33.0 (d,  $J = 26.4$  Hz), 32.6, 28.7, 26.3, 25.5.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.86 (dt,  $J = 39.5$  Hz, 18.0 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{14}\text{H}_{19}\text{OF}$   $[\text{M}]^+$ : 222.1420; found: 222.1419.



**(Z)-8-fluoro-9-phenylnon-8-en-1-ol**

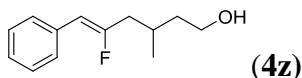
The title compound was prepared according to the general procedure as described above in 42% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.46 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.20 (t,  $J = 7.5$  Hz, 1H), 5.46 (d,  $J = 39.5$  Hz, 1H), 3.65 (t,  $J = 6.5$  Hz, 2H), 2.36-2.29 (m, 2H), 1.64-1.38 (m, 11H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  161.1 (d,  $J = 265.1$  Hz), 133.9, 128.4, 128.2 (d,  $J = 7.3$  Hz), 126.6 (d,  $J = 2.3$  Hz), 105.7 (d,  $J = 8.8$  Hz), 63.0, 33.0 (d,  $J = 26.4$  Hz), 32.7, 29.1, 28.9, 26.3, 25.6.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -100.77 (dt,  $J = 39.5$  Hz, 18.3 Hz). **HRMS (EI)**: *m/z* calcd. for  $\text{C}_{15}\text{H}_{21}\text{OF}$   $[\text{M}]^+$ : 236.1576; found: 236.1578.



**(Z)-5-fluoro-2-methyl-6-phenylhex-5-en-1-ol**

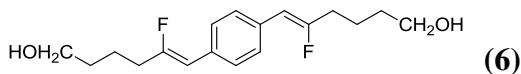
The title compound was prepared according to the general procedure as described above in 66% yield. *Z/E* = >20:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.46 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.20 (t,  $J = 7.0$  Hz, 1H), 5.49 (d,  $J = 39.5$  Hz, 1H),

3.56-3.49 (m, 1H), 2.45-2.32 (m, 2H), 1.78-1.43 (m, 5H), 1.28 (d,  $J = 19.5$  Hz, 3H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz):  $\delta$  161.0 (d,  $J = 266.6$  Hz), 133.8 (d,  $J = 2.4$  Hz), 128.4, 128.3 (d,  $J = 7.3$  Hz), 126.6 (d,  $J = 2.1$  Hz), 105.8 (d,  $J = 8.9$  Hz), 68.0, 35.1, 30.7 (d,  $J = 26.7$  Hz), 29.8, 16.4. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -100.89 (dt,  $J = 39.5$  Hz, 18.1 Hz). **HRMS (EI)**:  $m/z$  calcd. for C<sub>12</sub>H<sub>15</sub>OF [M]<sup>+</sup>: 208.1263; found: 208.1265.



**(Z)-5-fluoro-3-methyl-6-phenylhex-5-en-1-ol**

The title compound was prepared according to the general procedure as described above in 66% yield.  $Z/E = >20:1$ . **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz):  $\delta$  7.47 (d,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.5$  Hz, 1H), 5.48 (d,  $J = 39.5$  Hz, 1H), 3.76-3.70 (m, 2H), 2.37-2.32 (m, 1H), 2.23-2.17 (m, 1H), 2.04-2.02 (m, 1H), 1.75-1.71 (m, 1H), 1.57 (brs, 1H), 1.49-1.45 (m, 1H), 1.02 (d,  $J = 6.5$  Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz):  $\delta$  159.8 (d,  $J = 166.8$  Hz), 133.7, 128.4 (d,  $J = 16.7$  Hz), 128.2 (d,  $J = 7.4$  Hz), 126.7 (d,  $J = 1.8$  Hz), 107.3 (d,  $J = 9.1$  Hz), 60.9, 40.8 (d,  $J = 25.8$  Hz), 39.2, 27.6, 19.4. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -100.09 (ddd,  $J = 40.7$  Hz, 22.2 Hz, 19.6 Hz). **HRMS (EI)**:  $m/z$  calcd. for C<sub>12</sub>H<sub>15</sub>OF [M]<sup>+</sup>: 208.1263; found: 208.1265 .



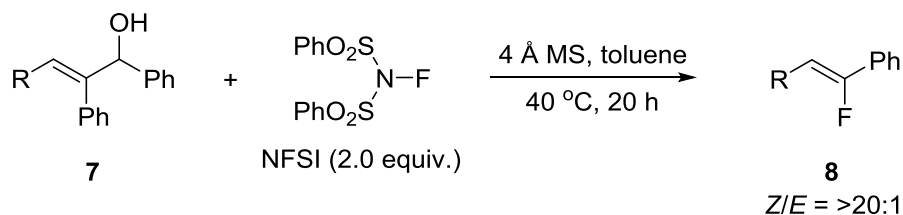
**(5Z,5'Z)-6,6'-(1,4-phenylene)bis(5-fluorohex-5-en-1-ol)**

The title compound was prepared according to the general procedure as described above in 46% yield.  $Z/E = >20:1$ . **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz):  $\delta$  7.41 (s, 4H), 5.46 (d,  $J = 40.0$  Hz, 2H), 3.69 (t,  $J = 6.0$  Hz, 4H), 2.38-2.35 (m, 4H), 1.70-1.65 (m, 10H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz):  $\delta$  160.7 (d,  $J = 265.1$  Hz), 132.2, 129.1, 128.3 (d,  $J = 7.5$  Hz), 126.4, 105.8 (d,  $J = 8.6$  Hz), 62.6, 32.8 (d,  $J = 26.6$  Hz), 31.9, 22.7. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -100.75 (dt,  $J = 39.8$  Hz, 18.0 Hz). **HRMS (EI)**:  $m/z$  calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>F<sub>2</sub> [M]<sup>+</sup>: 310.1744; found: 310.1750.



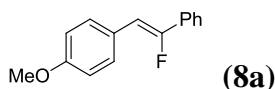


## V. General Procedure for the Synthesis of Compounds 8



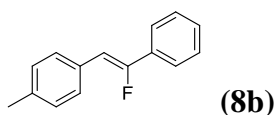
To a solution of allylic alcohol **7** (0.20 mmol) in 1 mL of toluene were added 4 Å MS and NFSI (0.40 mmol). The resulting mixture was allowed to stir at 40 °C for 20 h. The crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness and then directly analyzed by <sup>1</sup>H NMR to determine the *Z/E* ratio. The residue was then purified by column chromatography (100% hexanes) to yield the product **8** in pure form.

## VI. Characterization of Compounds 8



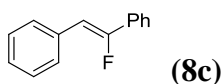
### (*Z*)-1-(2-fluoro-2-phenylvinyl)-4-methoxybenzene.<sup>2</sup>

The title compound was prepared according to the general procedure as described above in 70% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 7.67-7.61 (m, 4H), 7.45-7.36 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.30 (d, *J* = 39.9 Hz, 1H), 3.85 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 158.8 (d, *J* = 2.9 Hz), 156.0 (d, *J* = 254.1 Hz), 133.1 (d, *J* = 27.8 Hz), 130.3 (d, *J* = 7.9 Hz), 128.6, 128.5 (d, *J* = 1.9 Hz), 126.4 (d, *J* = 2.9 Hz), 124.0 (d, *J* = 7.4 Hz), 114.0, 105.4 (d, *J* = 10.8 Hz), 55.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -117.08 (d, *J* = 39.8 Hz).



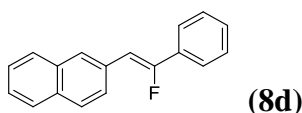
**(Z)-1-(2-fluoro-2-phenylvinyl)-4-methylbenzene.<sup>3</sup>**

The title compound was prepared according to the general procedure as described above in 33% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 39.5 Hz, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 156.7 (d, *J* = 255.8 Hz), 137.2, 133.1 (d, *J* = 11.6 Hz), 130.8 (d, *J* = 2.9 Hz), 129.3, 128.9, 128.8 (d, *J* = 8.5 Hz), 128.5 (d, *J* = 2.0 Hz), 124.2 (d, *J* = 7.4 Hz), 105.8 (d, *J* = 7.0 Hz), 21.3. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -115.17 (d, *J* = 39.8 Hz).



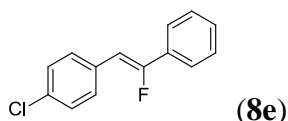
**(Z)-(1-fluoroethene-1,2-diyl)dibenzene.<sup>2</sup>**

The title compound was prepared according to the general procedure as described above in 28% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.67-7.64 (m, 4H), 7.44-7.35 (m, 5H), 7.29-7.26 (m, 1H), 6.32 (d, *J* = 39.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 157.2 (d, *J* = 257.0 Hz), 133.7 (d, *J* = 3.1 Hz), 132.9 (d, *J* = 27.6 Hz), 129.0, 128.9 (d, *J* = 7.9 Hz), 128.59, 128.57, 127.3 (d, *J* = 2.5 Hz), 124.3 (d, *J* = 7.4 Hz), 105.7 (d, *J* = 10.5 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -114.14 (d, *J* = 39.5 Hz).



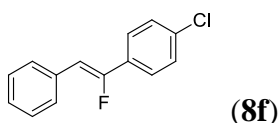
**(Z)-2-(2-fluoro-2-phenylvinyl)naphthalene.<sup>4</sup>**

The title compound was prepared according to the general procedure as described above in 33% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 8.09 (s, 1H), 7.86-7.81 (m, 4H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.49-7.39 (m, 5H), 5.49 (d, *J* = 39.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 157.5 (d, *J* = 257.4 Hz), 133.6, 132.9 (d, *J* = 27.8 Hz), 132.6, 131.3, 129.1, 128.6 (d, *J* = 2.0 Hz), 128.1, 128.1, 127.6, 126.8 (d, *J* = 8.1 Hz), 126.2, 126.1, 124.4, 124.3, 106.0 (d, *J* = 10.3 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -133.77 (d, *J* = 39.5 Hz).



**(Z)-1-chloro-4-(2-fluoro-2-phenylvinyl)benzene.**<sup>3</sup>

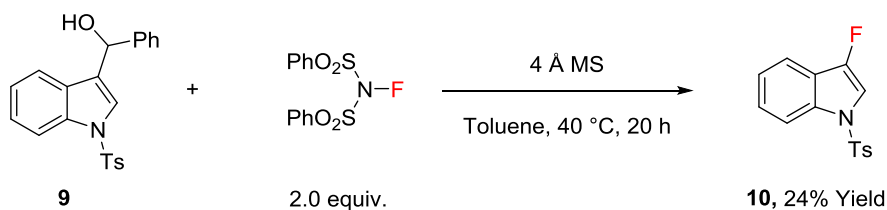
The title compound was prepared according to the general procedure as described above in 16% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.46-7.40 (m, 3H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.29 (d, *J* = 39.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 157.6 (d, *J* = 257.6 Hz), 132.9 (d, *J* = 3.8 Hz), 132.6 (d, *J* = 27.6 Hz), 132.2 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.3 Hz), 129.2, 128.8, 128.6 (d, *J* = 2.1 Hz), 124.4 (d, *J* = 7.5 Hz), 104.8 (d, *J* = 10.5 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -116.34 (d, *J* = 38.9 Hz).



**(Z)-1-chloro-4-(1-fluoro-2-phenylvinyl)benzene.**<sup>5</sup>

The title compound was prepared according to the general procedure as described above in 14% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.39-7.36 (m, 4H), 7.29-7.26 (m, 1H), 6.30 (d, *J* = 39.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 156.2 (d, *J* = 256.6 Hz), 134.9, 133.4 (d, *J* = 5.6 Hz), 131.4 (d, *J* = 28.4 Hz), 129.0 (d, *J* = 7.9 Hz), 128.9 (d, *J* = 2.0 Hz), 128.6, 127.6 (d, *J* = 2.4 Hz), 125.6 (d, *J* = 7.4 Hz), 106.4 (d, *J* = 10.4 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -114.49 (d, *J* = 39.2 Hz).

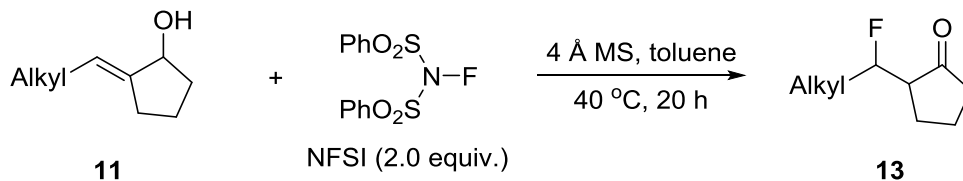
## VII. Synthesis and characterization of 10



**3-fluoro-1-tosyl-1H-indole:** To a solution of allylic alcohol **9** (0.20 mmol) in 1 mL of toluene were added 4Å MS and NFSI (0.40 mmol). The resulting mixture was allowed to stir at 40 °C for 20 h. The crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness. The residue was then purified by column chromatography (hexanes:ethyl acetate = 200:1) to yield the product **10** in 24% yield.

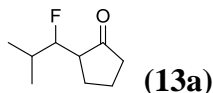
<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 500 MHz): δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 148.9 (d, *J* = 253.9 Hz), 145.1, 134.8, 132.8 (d, *J* = 5.1 Hz), 129.9, 126.8, 126.0, 123.6, 121.6 (d, *J* = 18.9 Hz), 117.7 (d, *J* = 2.5 Hz), 114.1 (d, *J* = 1.1 Hz), 108.8 (d, *J* = 28.5 Hz), 21.5. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -165.6 (d, *J* = 2.5 Hz). HRMS (EI): *m/z* calcd. for C<sub>15</sub>H<sub>12</sub>FNO<sub>2</sub>S [M]<sup>+</sup>: 289.0573; found: 289.0571.

## VIII. General Procedure for the Synthesis of Compounds **13** and **14**



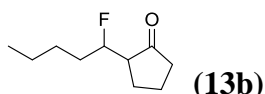
To a solution of allylic alcohol **11** (0.20 mmol) in 1 mL of toluene were added 4Å MS and NFSI (0.40 mmol). The resulting mixture was allowed to stir at 40 °C for 20 h. The crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness and then directly analyzed by <sup>1</sup>H NMR to determine the *Z/E* ratio. The residue was then purified by column chromatography to yield the product **13** in pure form.

## IX. Characterization of Compounds **13**



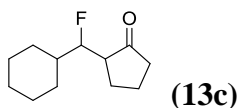
### 2-(1-fluoro-2-methylpropyl)cyclopentan-1-one.

The title compound was prepared according to the general procedure as described above in 42% yield. *Trans:cis* = 2:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  4.54 (ddd,  $J$  = 2.4 Hz, 6.8 Hz, 46.8 Hz, 1H), 2.36-1.74 (m, 7H), 1.03-0.87 (m, 6H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  218.5, 96.7 (d,  $J$  = 172.0 Hz), 50.6 (d,  $J$  = 2.3 Hz), 38.7, 30.9 (d,  $J$  = 19.8 Hz), 22.8 (d,  $J$  = 4.0 Hz), 20.8, 18.4 (d,  $J$  = 20.6 Hz), 18.3 (d,  $J$  = 23.6 Hz).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -192.3 (ddd,  $J$  = 12.0 Hz, 35.6 Hz, 47.0 Hz).



### 2-(1-fluoropentyl)cyclopentan-1-one.

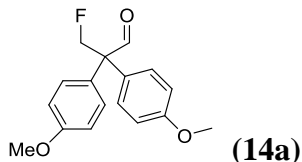
The title compound was prepared according to the general procedure as described above in 60% yield. *Trans:cis* = 3.3:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  4.93-4.81 (m, 1H), 2.31-2.27 (m, 1H), 2.16-1.90 (m, 4H), 1.76-1.68 (m, 2H), 1.58-1.47 (m, 1H), 1.43-1.23 (m, 5H), 0.89-0.86 (m, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  218.1, 91.9 (d,  $J$  = 169.4 Hz), 52.6 (d,  $J$  = 22.8 Hz), 38.7, 33.1 (d,  $J$  = 20.5 Hz), 27.3 (d,  $J$  = 5.0 Hz), 23.0 (d,  $J$  = 3.8 Hz), 22.4, 20.7, 13.9.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -189.4 - -189.7 (m).



### 2-(cyclohexylfluoromethyl)cyclopentan-1-one.

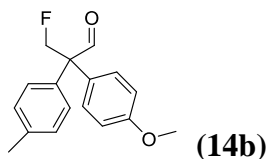
The title compound was prepared according to the general procedure as described above in 73% yield. *Trans:cis* = 2:1.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  4.60 (ddd,  $J$  = 2.5 Hz, 9.0 Hz, 47.5 Hz, 1H), 2.34-2.28 (m, 2H), 2.16-1.95 (m, 5H), 1.78-1.50 (m, 5H), 1.28-1.14 (m, 4H), 1.04-0.95 (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  218.9, 95.8 (d,  $J$  = 170.9 Hz), 50.3 (d,  $J$  = 23.6 Hz), 40.2 (d,  $J$  = 19.3 Hz), 38.8, 28.8 (d,  $J$  = 4.9 Hz), 28.3 (d,  $J$  = 7.6 Hz), 26.1, 25.8, 25.4, 22.7 (d,  $J$  = 3.8 Hz), 20.8.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -194.3 (ddd,  $J$  = 11.6 Hz, 36.1 Hz, 47.4 Hz).

## X. Characterization of Compounds 14



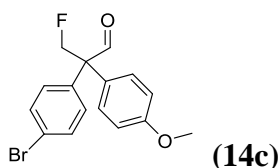
### 3-fluoro-2,2-bis(4-methoxyphenyl)propanal.

The title compound was prepared according to the general procedure as described above in 86% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  9.85 (d,  $J = 2.5$  Hz, 1H), 7.14 (d,  $J = 9.0$  Hz, 4H), 6.93 (d,  $J = 9.0$  Hz, 4H), 5.10 (d,  $J = 47.0$  Hz, 2H), 3.82 (s, 6H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  197.5 (d,  $J = 3.4$  Hz), 159.2, 130.0 (d,  $J = 1.4$  Hz), 129.0 (d,  $J = 2.8$  Hz), 84.3 (d,  $J = 177.2$  Hz), 62.8 (d,  $J = 17.9$  Hz), 55.3.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -126.8 (dd,  $J = 3.8$  Hz, 54.5 Hz). **HRMS (APCI)**:  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{18}\text{FO}_3$   $[\text{M}+\text{H}]^+$ : 289.1234; found: 289.1227.



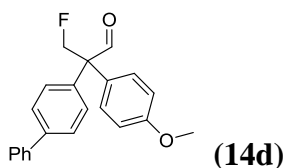
### 3-fluoro-2-(4-methoxyphenyl)-2-(p-tolyl)propanal.

The title compound was prepared according to the general procedure as described above in 82% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  9.86 (d,  $J = 2.5$  Hz, 1H), 7.21 (d,  $J = 8.0$  Hz, 2H), 7.14-7.09 (m, 4H), 6.92 (d,  $J = 8.0$  Hz, 2H), 5.10 (d,  $J = 47.0$  Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  197.5 (d,  $J = 3.4$  Hz), 159.2, 137.8, 134.1 (d,  $J = 3.8$  Hz), 130.0, 129.7, 128.7, 114.3, 84.4 (d,  $J = 177.3$  Hz), 63.2 (d,  $J = 17.6$  Hz), 55.3, 21.0.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -126.8 (dd,  $J = 1.9$  Hz, 54.5 Hz). **HRMS (APCI)**:  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{18}\text{FO}_2$   $[\text{M}+\text{H}]^+$ : 273.1285; found: 273.1281.



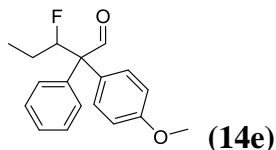
### 2-(4-bromophenyl)-3-fluoro-2-(4-methoxyphenyl)propanal.

The title compound was prepared according to the general procedure as described above in 81% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  9.84 (d,  $J = 2.4$  Hz, 1H), 7.52 (d,  $J = 8.4$  Hz, 2H), 7.11-7.07 (m, 4H), 6.93 (d,  $J = 8.8$  Hz, 2H), 5.20-5.00 (m, 2H), 3.82 (s, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  196.8 (d,  $J = 3.7$  Hz), 159.5, 136.6 (d,  $J = 2.1$  Hz), 132.1, 130.6 (d,  $J = 1.5$  Hz), 129.8 (d,  $J = 1.2$  Hz), 122.3, 114.6, 84.1 (d,  $J = 177.8$  Hz), 63.2 (d,  $J = 17.9$  Hz), 55.3.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -125.1- -127.9 (m). **HRMS (APCI)**:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{15}\text{BrFO}_2$   $[\text{M}+\text{H}]^+$ : 337.0234; found: 337.0231.



### 2-([1,1'-biphenyl]-4-yl)-3-fluoro-2-(4-methoxyphenyl)propanal.

The title compound was prepared according to the general procedure as described above in 76% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  9.93 (d,  $J = 2.8$  Hz, 1H), 7.64-7.59 (m, 4H), 7.46 (t,  $J = 7.2$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 8.8$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 5.18 (dd,  $J = 2.8$  Hz, 47.2 Hz, 2H), 3.83 (s, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  197.4 (d,  $J = 3.5$  Hz), 159.3, 140.9, 140.2, 136.2 (d,  $J = 2.5$  Hz), 130.1, 129.3, 128.8, 127.6, 127.1, 114.5, 84.3 (d,  $J = 177.5$  Hz), 63.3 (d,  $J = 17.9$  Hz), 55.3.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -125.7- -127.5 (m). **HRMS (APCI)**:  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{20}\text{FO}_2$   $[\text{M}+\text{H}]^+$ : 335.1442; found: 335.1446.

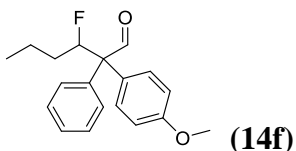


### 3-fluoro-2-(4-methoxyphenyl)-2-phenylpentanal.

The title compound was prepared according to the general procedure as described above in 75% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 400 MHz):  $\delta$  9.73 (d,  $J = 5.2$  Hz, 1H), 7.39-7.36 (m, 3H), 7.20-7.16 (m, 4H), 6.91 (d,  $J = 7.2$  Hz, 2H), 5.60 (ddd,  $J = 1.2$  Hz, 9.6 Hz, 47.2 Hz, 1H), 3.81 (s, 3H), 1.70-1.63 (m, 1H), 1.13-1.03 (m, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  196.1 (d,  $J = 6.2$  Hz), 159.1, 137.3 (d,  $J = 1.8$  Hz), 131.2 (d,  $J = 1.1$  Hz),



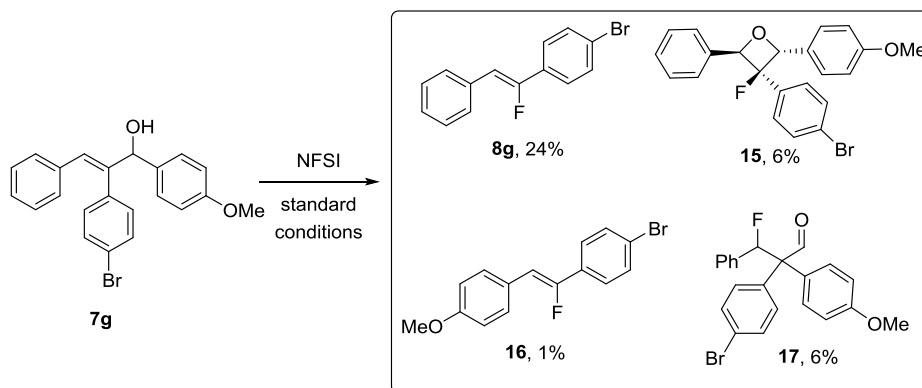
129.6 (d,  $J = 1.4$  Hz), 128.6, 127.9, 114.0, 94.5 (d,  $J = 176.4$  Hz), 67.0 (d,  $J = 19.0$  Hz), 55.2, 24.9 (d,  $J = 21.4$  Hz), 10.4 (d,  $J = 2.9$  Hz).  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -194.3 (t,  $J = 49.3$  Hz). HRMS (APCI):  $m/z$  calcd. for C<sub>18</sub>H<sub>18</sub>FO<sub>2</sub> [M+H]<sup>+</sup>: 285.1296; found: 285.1298.



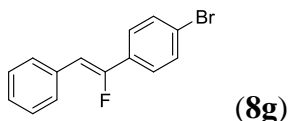
### 3-fluoro-2-(4-methoxyphenyl)-2-phenylhexanal.

The title compound was prepared according to the general procedure as described above in 73% yield.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  9.73 (d,  $J = 5.2$  Hz, 1H), 7.39-7.36 (m, 3H), 7.20-7.16 (m, 4H), 6.91 (d,  $J = 7.2$  Hz, 2H), 5.60 (ddd,  $J = 1.2$  Hz, 9.6 Hz, 47.2 Hz, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  196.1 (d,  $J = 6.2$  Hz), 159.1, 137.3 (d,  $J = 1.9$  Hz), 131.3 (d,  $J = 1.3$  Hz), 129.7 (d,  $J = 1.4$  Hz), 128.7, 128.3 (d,  $J = 2.2$  Hz), 127.9, 114.1, 92.8 (d,  $J = 175.6$  Hz), 66.9 (d,  $J = 19.1$  Hz), 55.3, 33.7 (d,  $J = 21.1$  Hz), 19.2 (d,  $J = 2.1$  Hz), 13.8.  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 282 MHz):  $\delta$  -194.3 (t,  $J = 50.4$  Hz).

## XI. Mechanistic studies

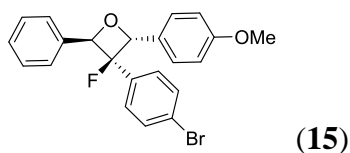


To a solution of allylic alcohol **7g** (0.50 mmol) in 3 mL of toluene were added 4Å MS and NFSI (1.00 mmol). The resulting mixture was allowed to stir at 40 °C for 20 h. The crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness and then directly analyzed by <sup>1</sup>H NMR to determine the ratio of major product and the byproduct. The residue was then purified by column chromatography to yield the product **8g**, **15** and **17** in pure form.



### **(Z)-1-bromo-4-(1-fluoro-2-phenylvinyl)benzene.<sup>3</sup>**

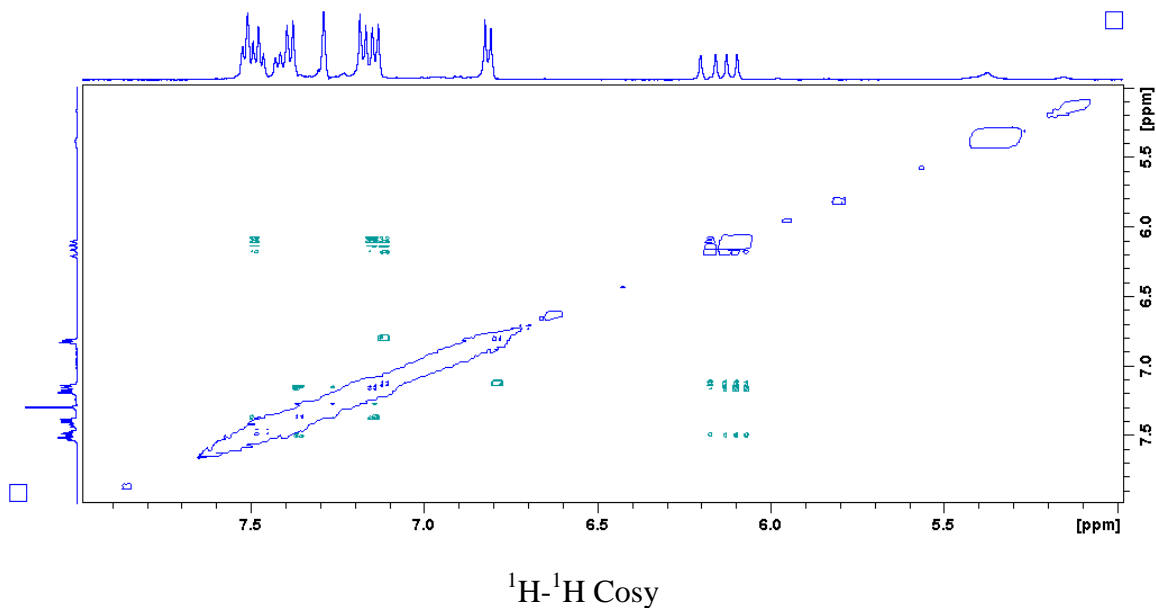
The title compound was prepared according to the general procedure as described above in 24% yield. *Z/E* = >20:1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz): δ 7.55 (d, *J* = 6.8 Hz, 2H), 7.47-7.41 (m, 4H), 7.30 (d, *J* = 6.8 Hz, 2H), 6.22 (d, *J* = 39.2 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 156.2 (d, *J* = 256.6 Hz), 133.3 (d, *J* = 3.1 Hz), 131.8 (d, *J* = 28.3 Hz), 131.8 (d, *J* = 2.2 Hz), 129.0 (d, *J* = 7.9 Hz), 128.6, 127.6 (d, *J* = 2.6 Hz), 125.8 (d, *J* = 7.4 Hz), 123.1, 106.5 (d, *J* = 10.3 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ -114.6 (d, *J* = 39.5 Hz).

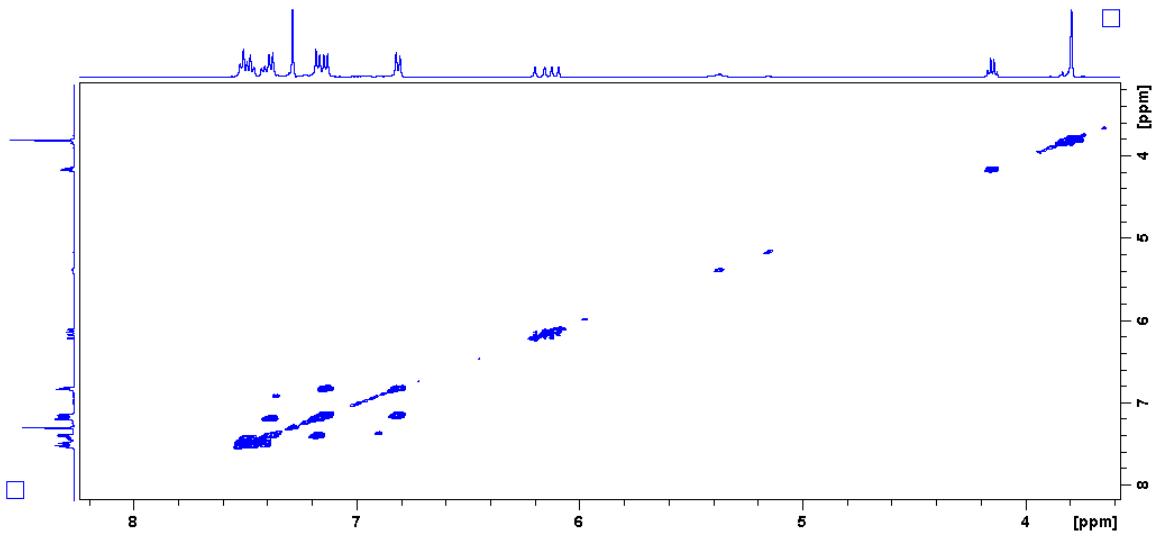


### 3-(4-bromophenyl)-3-fluoro-2-(4-methoxyphenyl)-4-phenyloxetane.

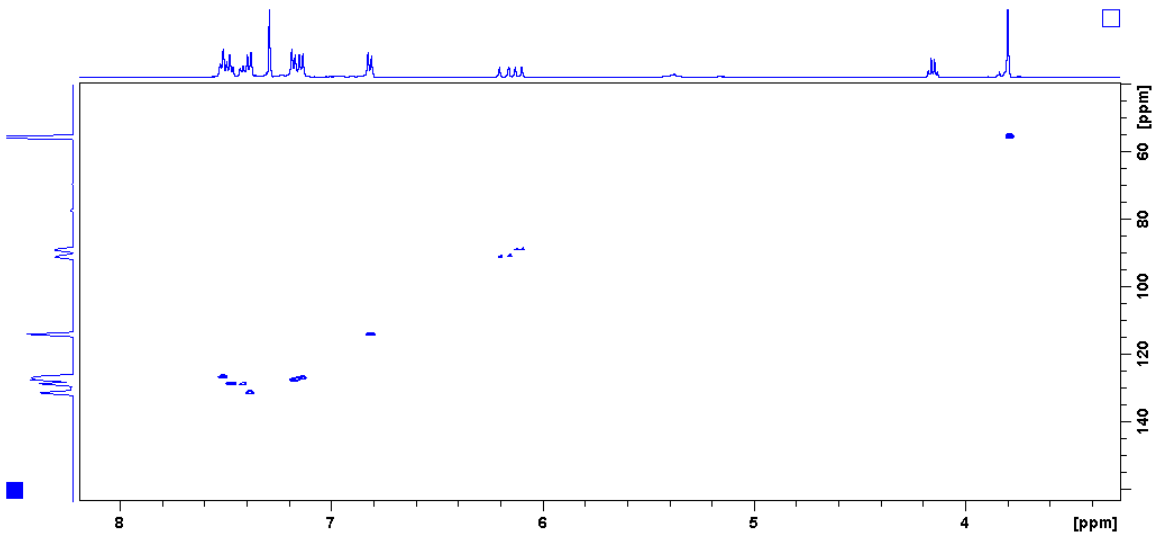
The title compound was prepared according to the general procedure as described above in 6% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.50-7.49 (m, 4H), 7.40-7.39 (m, 1H), 7.36 (d,  $J = 9.0$  Hz, 2H), 7.15 (d,  $J = 8.5$  Hz, 2H), 7.11 (d,  $J = 8.5$  Hz, 2H), 6.79 (d,  $J = 8.5$  Hz, 2H), 6.15 (d,  $J = 21.5$  Hz, 1H), 6.09 (d,  $J = 15.0$  Hz, 1H), 3.77 (s, 3H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  159.3, 135.5 (d,  $J = 5.0$  Hz), 134.6 (d,  $J = 24.4$  Hz), 131.2, 128.5 (d,  $J = 12.5$  Hz), 128.3 (d,  $J = 6.5$  Hz), 127.2 (d,  $J = 9.5$  Hz), 126.8, 126.3, 122.6 (d,  $J = 1.9$  Hz), 113.8, 98.4 (d,  $J = 214.0$  Hz), 90.6 (d,  $J = 30.3$  Hz), 88.6 (d,  $J = 21.6$  Hz), 55.2.  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -151.8 (dd,  $J = 15.0$  Hz, 21.4 Hz). **HRMS (APCI):**  $m/z$  Calcd. for  $[\text{C}_{22}\text{H}_{18}\text{BrFO}_2, \text{M}+\text{H}]^+$ : 412.0469; Found: 412.0466.

The configuration of **15** was determined by 2D ( $^1\text{H}$ - $^1\text{H}$  Cosy, NOESY and  $^1\text{H}$ - $^{13}\text{C}$  HMQC, HMBC) NMR measurement as shown below (Figure S2).

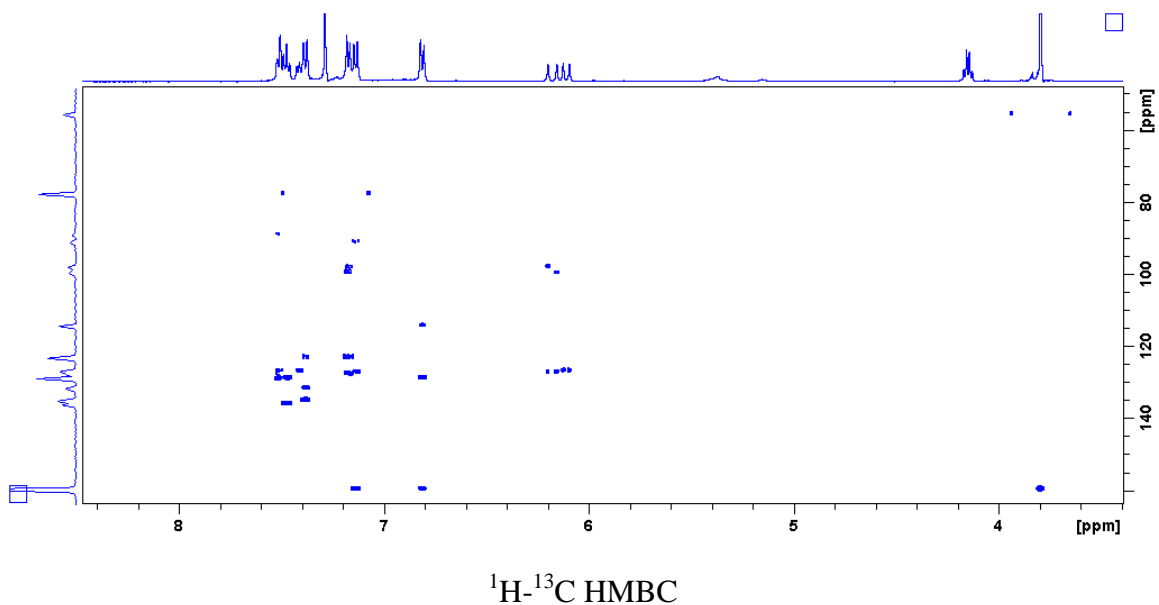




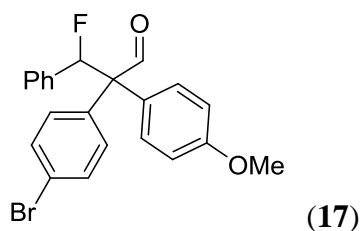
$^1\text{H}$ - $^1\text{H}$  NOESY



$^1\text{H}$ - $^{13}\text{C}$  HMQC



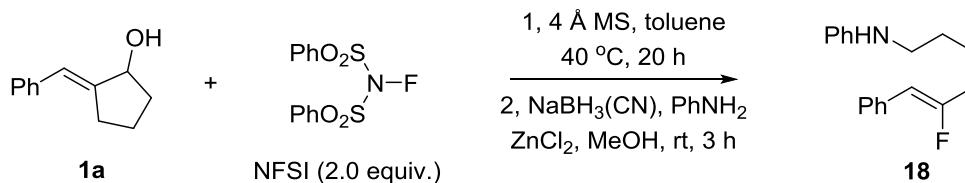
**Figure S2.** 2D ( $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{13}\text{C}$ ) NMR spectra of **15**.



**2-(4-bromophenyl)-3-fluoro-2-(4-methoxyphenyl)-3-phenylpropanal.**

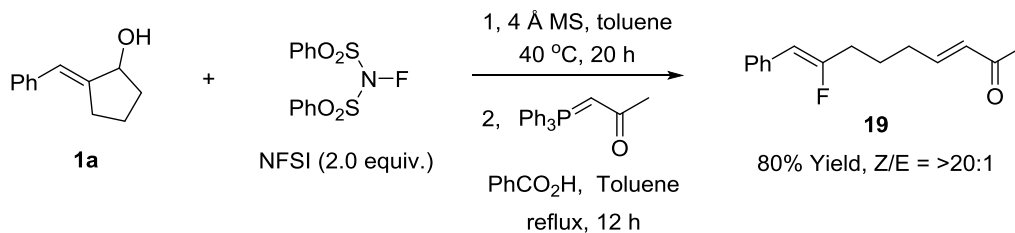
The title compound was prepared according to the general procedure as described above in 6% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  9.75 (d,  $J = 5.5$  Hz, 1H), 7.48 (d,  $J = 9.0$  Hz, 2H), 7.22 (t,  $J = 7.0$  Hz, 2H), 7.15-7.12 (m, 4H), 6.93 (d,  $J = 8.5$  Hz, 2H), 6.85-6.83 (m, 4H), 6.75 (d,  $J = 44.0$  Hz, 1H), 3.82 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  195.3 (d,  $J = 7.6$  Hz), 159.4, 135.9 (d,  $J = 26.3$  Hz), 132.0, 131.6 (d,  $J = 4.6$  Hz), 128.5, 127.7 (d,  $J = 8.0$  Hz), 127.5, 122.2, 113.8, 93.0 (d,  $J = 224.6$  Hz), 68.6 (d,  $J = 27.8$  Hz), 55.32.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -186.1 (dd,  $J = 44.0$  Hz). HRMS (APCI):  $m/z$  Calcd. for  $[\text{C}_{22}\text{H}_{18}\text{BrFO}_2, \text{M}+\text{H}]^+$ : 412.0469; Found: 412.0465.

## XII. Synthesis and characterization of 18-23



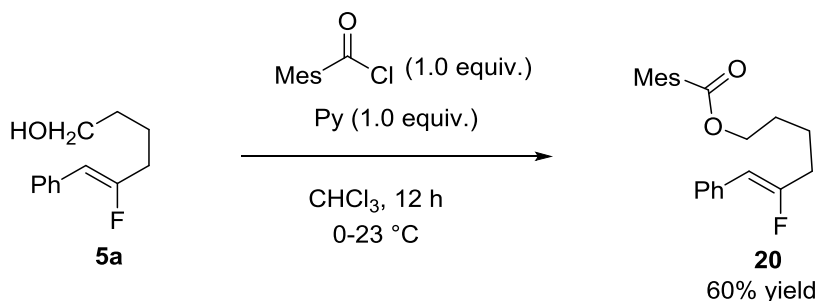
**(Z)-N-(5-fluoro-6-phenylhex-5-en-1-yl)aniline (18):** To a solution of allylic alcohol **1a** (34.8 mg, 0.200 mmol) in 1 mL of toluene were added 4 Å MS and NFSI (126 mg, 0.400 mmol). The resulting mixture was allowed to stir at 40 °C for ~20 h. Once the starting material was completely consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. 1 mL of methanol and PhNH<sub>2</sub> (74.4 mg, 0.800 mmol) were then added sequentially. To the above mixture at room temperature were added a solution of sodium cyanoborohydride (12.6 mg, 0.200 mmol) and zinc chloride (13.4 mg, 0.100 mmol) in methanol (0.5 mL). The resulting solution was stirred at room temperature for 2 h and was taken up in 0.1 N NaOH (2 mL). After methanol was evaporated under reduced pressure, the aqueous solution was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with water and brine, dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (hexanes:ethyl acetate = 5:1) to produce compound **18** in 56% yield as an oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25-7.17 (m, 3H), 6.74-6.61 (m, 3H), 5.50 (d, *J* = 39.3 Hz, 1H), 3.20-3.13 (m, 2H), 2.85 (s, 1H), 2.43-2.35 (m, 2H), 1.76-1.72 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 160.5 (d, *J* = 265.0 Hz), 148.3, 133.7, 129.2, 128.4, 128.3 (d, *J* = 7.3 Hz), 126.7, 117.3, 112.7, 106.1 (d, *J* = 8.8 Hz), 43.6, 32.8 (d, *J* = 26.6 Hz), 28.8, 23.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz): δ -101.32 (dt, *J* = 39.5 Hz, 18.0 Hz). HRMS (EI): *m/z* calcd. for C<sub>18</sub>H<sub>20</sub>NF [M]<sup>+</sup>: 269.1580; found: 269.1576.



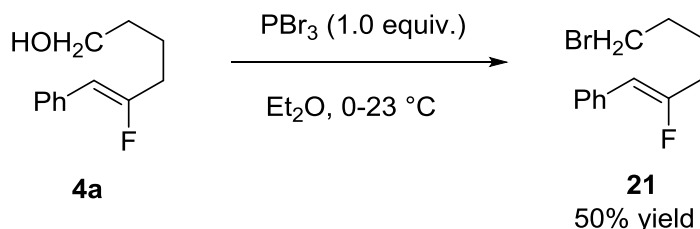
**(3E,8Z)-8-fluoro-9-phenylnona-3,8-dien-2-one (19):** To a solution of allylic alcohol **1a** (34.8 mg, 0.200 mmol) in 1 mL of toluene were added 4 Å MS and NFSI (126 mg, 0.400 mmol). The resulting mixture was allowed to stir at 40 °C for ~20 h. Once the starting material was completely consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. 1 mL of toluene was then added, which was followed by the addition of PhCO<sub>2</sub>H (4.9 mg, 0.040 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (95 mg, 0.300 mmol). The resulting solution was heated to reflux for 12 h and then cooled to room temperature. After toluene was evaporated under reduced pressure, the residue was purified by column chromatography (hexanes:ethyl acetate = 20:1) to give compound **19** in 80% yield as an oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 300 MHz): δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.80 (dt, *J* = 7.0 Hz, 16.0 Hz, 1H), 6.14-6.10 (m, 1H), 5.49 (d, *J* = 39.5 Hz, 1H), 2.41-2.31 (m, 4H), 2.25 (s, 3H), 1.83-1.77 (m, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 198.4, 159.9 (d, *J* = 264.9 Hz), 147.0, 133.5, 131.8, 131.6, 128.4, 128.3 (d, *J* = 7.1 Hz), 126.8 (d, *J* = 2.1 Hz), 106.6 (d, *J* = 8.6 Hz), 32.5 (d, *J* = 26.8 Hz), 31.4, 27.0, 24.8. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz): δ -101.83 (dt, *J* = 39.2 Hz, 18.3 Hz). **HRMS (EI):** *m/z* calcd. for C<sub>15</sub>H<sub>17</sub>FO [M]<sup>+</sup>: 232.1263; found: 232.1269.



**(Z)-5-fluoro-6-phenylhex-5-en-1-yl 2,4,6-trimethylbenzoate (20):** To a solution of **5a** (38.8 mg, 0.200 mmol) in 1 mL CHCl<sub>3</sub> was added dropwise a solution of pyridine (15.8 mg, 0.200 mmol) and 2,4,6-trimethylbenzoyl chloride (36.4 mg, 0.200 mmol) in 1 mL CHCl<sub>3</sub> at 0 °C. The mixture was allowed to stir at room temperature for 12 h and then diluted with ether and a solution of aqueous sodium chloride. The aqueous phase was extracted with diethyl ether for three times. The combined organic phase was dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness. The residue was purified by column chromatography (hexanes:ethyl acetate = 20:1) to give the corresponding ester **20** in 60% yield.

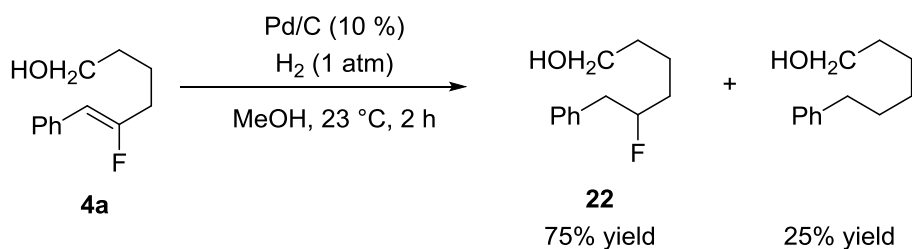
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 6.90 (s, 2H), 5.52 (d, *J* = 39.5 Hz, 1H), 4.40 (t, *J* = 6.0 Hz, 2H), 2.46-2.32 (m, 11H), 1.90-1.78 (m, 4H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 170.1, 160.2 (d, *J* = 265.0 Hz), 139.2, 134.9, 133.6 (d, *J* = 2.3 Hz), 131.0, 128.3, 128.2 (d, *J* = 7.4 Hz), 126.7, 106.2 (d, *J* = 8.6 Hz), 64.3, 32.5 (d, *J* = 26.8 Hz), 27.8, 23.0, 21.0, 19.7. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz): δ -101.44 (dt, *J* = 39.2 Hz, 18.3 Hz). **HRMS (EI):** *m/z* calcd. for C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>F [M]<sup>+</sup>: 340.1839; found: 340.1844.



**(Z)-(6-bromo-2-fluorohex-1-en-1-yl)benzene (21):** To a solution of **4a** (38.8 mg, 0.200 mmol) in 1 mL Et<sub>2</sub>O was added PBr<sub>3</sub> (53.5 mg, 0.200 mmol) at 0 °C. The mixture was allowed to warm to ambient temperature and stir overnight. The reaction mixture was quenched with NaHCO<sub>3</sub> (saturated aqueous solution) and extracted with Et<sub>2</sub>O. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography (hexanes:ethyl acetate = 20:1) to give the corresponding product **21** in 50% yield.



**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.49 (d, *J* = 39.5 Hz, 1H), 3.45 (t, *J* = 6.5 Hz, 2H), 2.41-2.34 (m, 2H), 1.99-1.93 (m, 2H), 1.81-1.75 (m, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 160.1 (d, *J* = 264.9 Hz), 133.6, 128.4, 128.3 (d, *J* = 7.3 Hz), 126.8, 106.3 (d, *J* = 8.6 Hz), 33.2, 32.2 (d, *J* = 26.8 Hz), 31.8, 24.9. **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz): δ -101.52 (dt, *J* = 39.2 Hz, 18.3 Hz). **HRMS (EI)**: *m/z* calcd. for C<sub>12</sub>H<sub>14</sub>BrF [M]<sup>+</sup>: 256.0263; found: 256.0260.

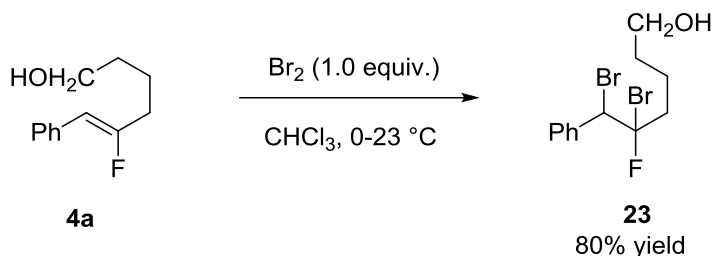


**5-fluoro-6-phenylhexan-1-ol (22)**: A vial was charged with **4a** (38.8 mg, 0.200 mmol) and Pd/C (3.9 mg) and MeOH (1 mL). The vial was purged three times with H<sub>2</sub>, and the reaction mixture was allowed to stir under H<sub>2</sub> atmosphere at room temperature for 1 h. After the reaction was completed, the hydrogen was released and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexane:ethyl acetate = 10:1) to produce the products **22** in 75% yield. The corresponding defluorinated product was also isolated in 25% yield.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.24-7.21 (m, 3H), 4.77-4.62 (m, 1H), 3.64 (t, *J* = 6.0 Hz, 2H), 3.01-2.83 (m, 2H), 1.72-1.47 (m, 7H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 137.3 (d, *J* = 4.8 Hz), 129.3, 128.4, 126.5, 94.4 (d, *J* = 169.9 Hz), 62.6, 41.6 (d, *J* = 21.4 Hz), 34.3 (d, *J* = 20.8 Hz), 32.4, 21.4 (d, *J* = 4.1 Hz). **<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 282 MHz): δ -178.56--179.06 (m, 1F). **HRMS (ESI)**: *m/z* calcd. for C<sub>12</sub>H<sub>17</sub>ONaF [M+Na]<sup>+</sup>: 219.1156; found: 219.1164.

**The defluorinated product: 6-phenylhexan-1-ol**: **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, TMS, 500 MHz): δ 7.29-7.27 (m, 2H), 7.19-7.17 (m, 3H), 3.63 (t, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 7.5

Hz, 2H), 1.67-1.38 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  142.7, 128.4, 128.2, 125.6, 63.0, 35.8, 32.7, 31.4, 29.0, 25.6.



**5,6-dibromo-5-fluoro-6-phenylhexan-1-ol (23):** To a solution of **4a** (38.8 mg, 0.200 mmol) in 1 mL  $\text{CHCl}_3$  was added bromine (63.2 mg, 0.400 mmol) dropwise at 0  $^\circ\text{C}$ . The mixture was allowed to warm to ambient temperature and stir overnight. The reaction mixture was quenched with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was washed with brine, dried over  $\text{MgSO}_4$  and concentrated. The residue was purified by column chromatography (hexanes:ethyl acetate = 1:1) to give the corresponding product **23** in 80% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 500 MHz):  $\delta$  7.52-7.51 (m, 2H), 7.37-7.36 (m, 3H), 5.20 (d,  $J = 24.5$  Hz, 1H), 3.72 (t,  $J = 6.0$  Hz, 2H), 2.58-2.36 (m, 2H), 1.80-1.66 (m, 4H), 1.60 (brs, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  137.5, 129.8 (d,  $J = 2.6$  Hz), 129.1, 128.3, 111.8 (d,  $J = 263.9$  Hz), 62.4, 57.7 (d,  $J = 21.0$  Hz), 43.1 (d,  $J = 20.4$  Hz), 31.8, 21.5 (d,  $J = 5.4$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 282 MHz):  $\delta$  -108.59 (t,  $J = 21.2$  Hz). HRMS (EI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{15}\text{Br}_2\text{FO}$   $[\text{M}]^+$ : 353.9453; found: 353.9461.

The *trans* configuration of **23** was determined by 2D ( $^1\text{H}$ - $^1\text{H}$ ) NMR measurement as shown below (Figure S3).

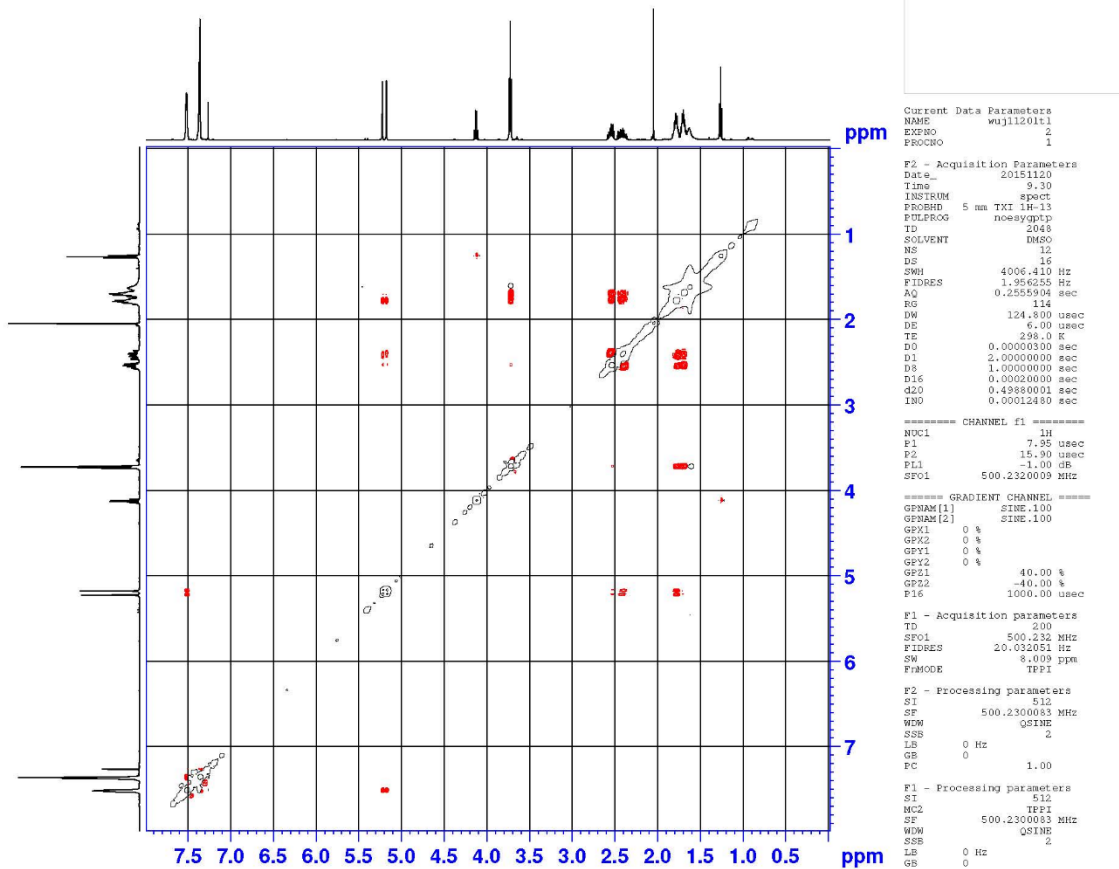


Figure S3. 2D ( $^1\text{H}$ - $^1\text{H}$ ) NMR spectra of **23**.

### **XIII. References**

- 1) Lu, S.-M., Bolm, C. *Angew. Chem. Int. Ed.* **2008**, *47*, 8920–8923.
- 2) Xu, J., Burton, D. J., *J. Org. Chem.* **2006**, *71*, 3743–3747.
- 3) Zhang, W., Huang, W., Hu, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 9858–9861.
- 4) Zhao, Y., Jiang, F., Hu, J. *J. Am. Chem. Soc.* **2015**, *137*, 5199–5203.
- 5) Chen, C., Wilcoxon, K., Zhu, Y.-F., Kim, K., McCarthy, J. R. *J. Org. Chem.* **1999**, *64*, 3476–3482.

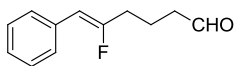
# XIV. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR Spectra

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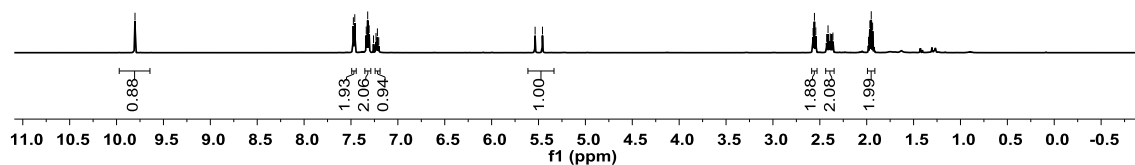
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5.458

2.572  
2.557  
2.543  
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1.952  
1.937



2a



201.559

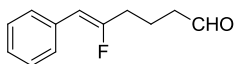
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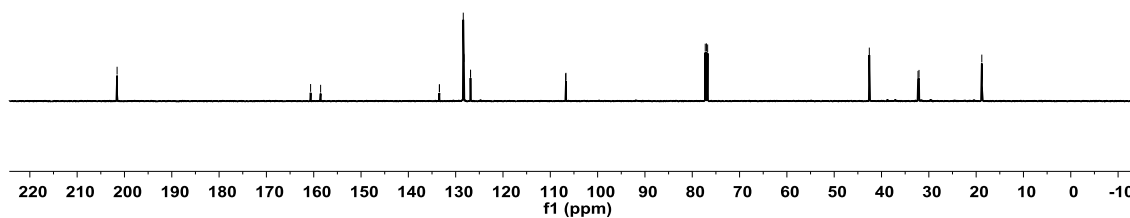
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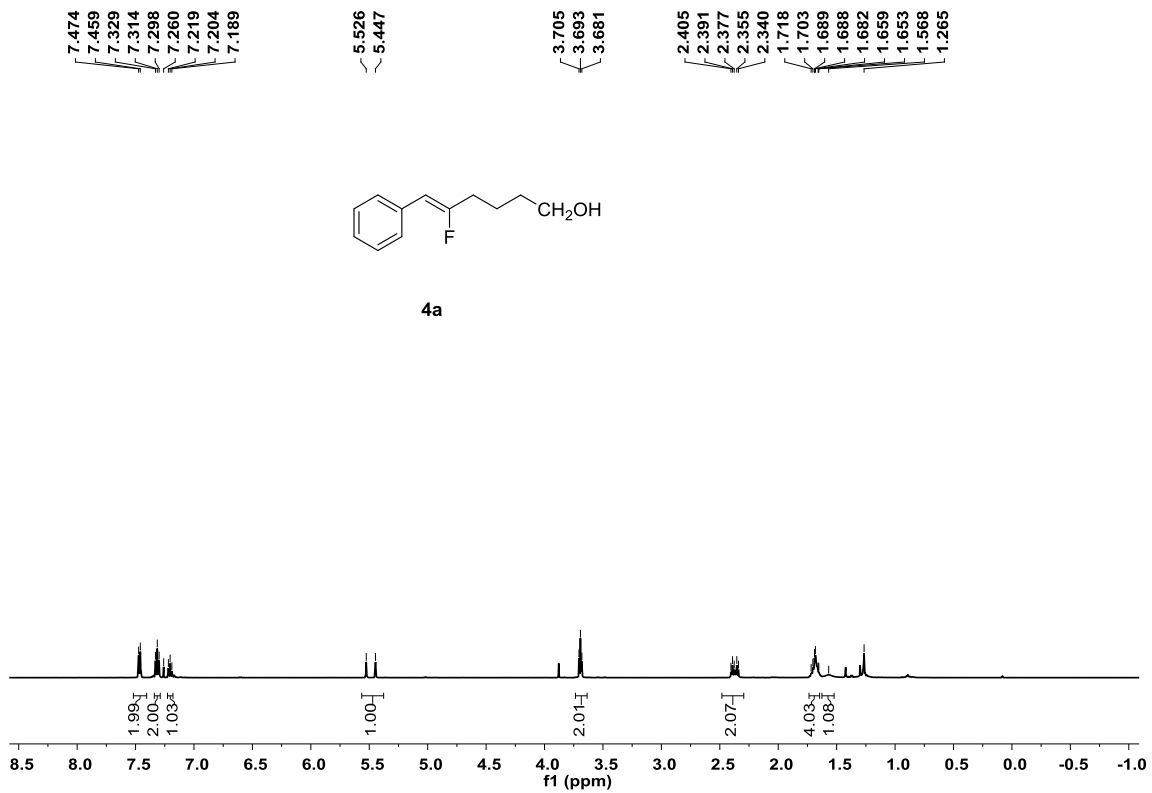
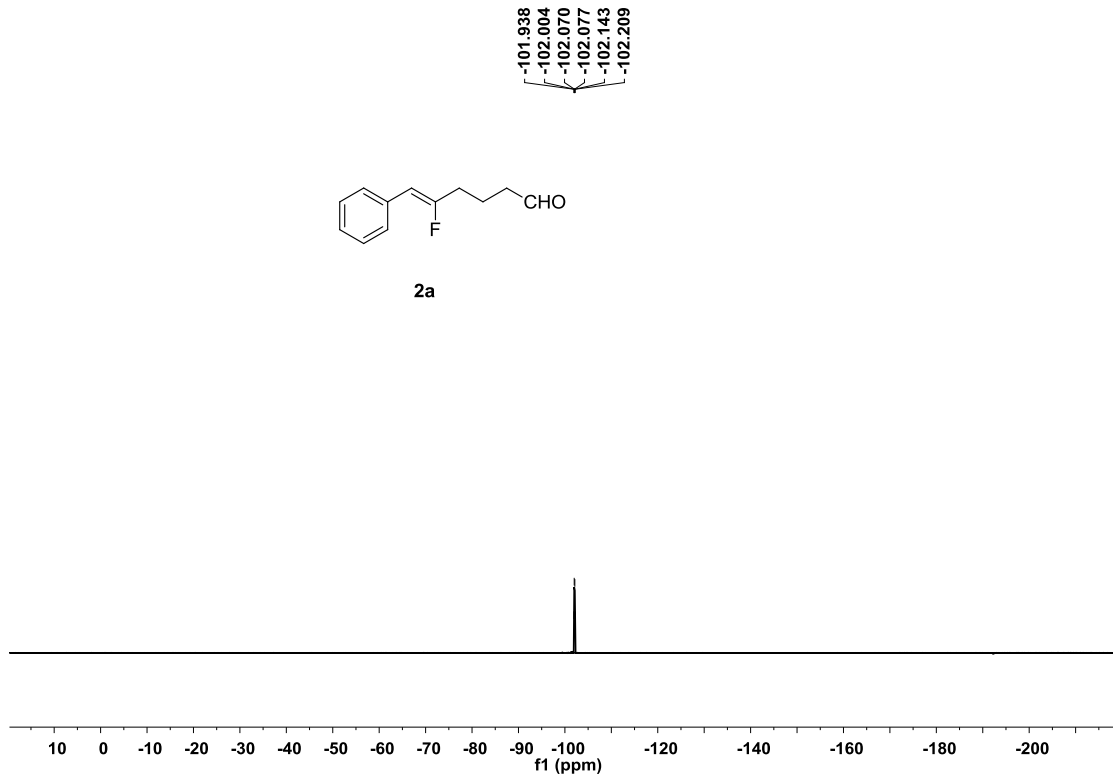
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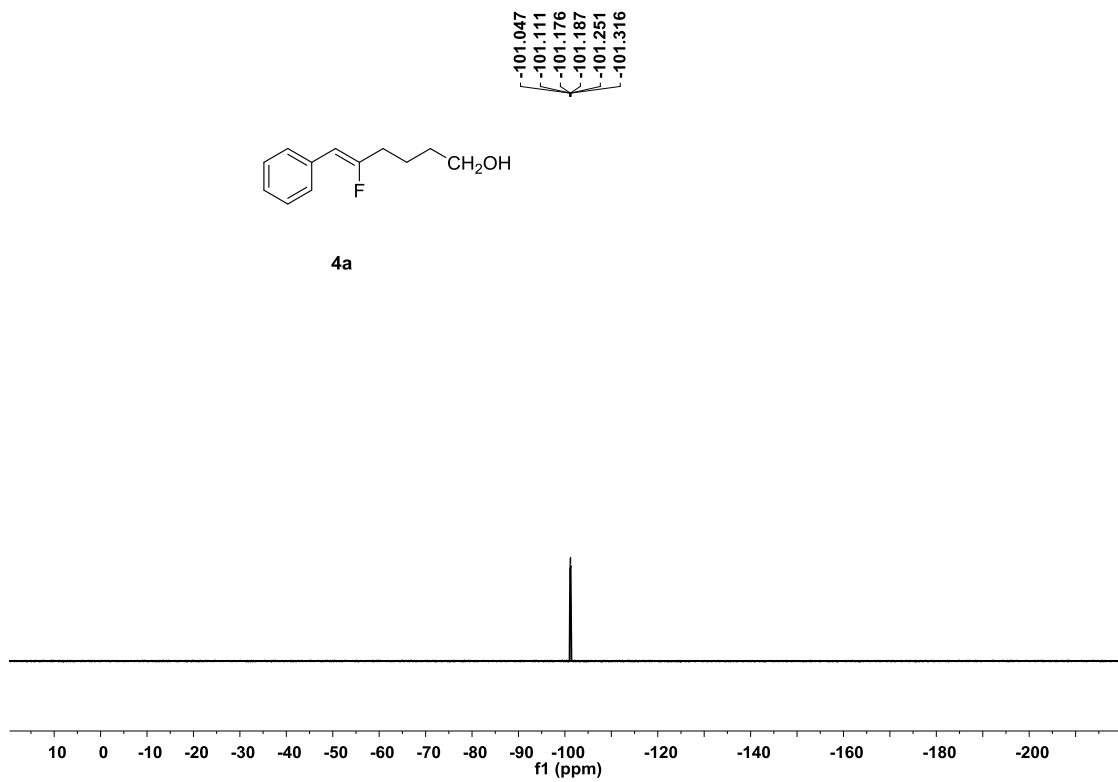
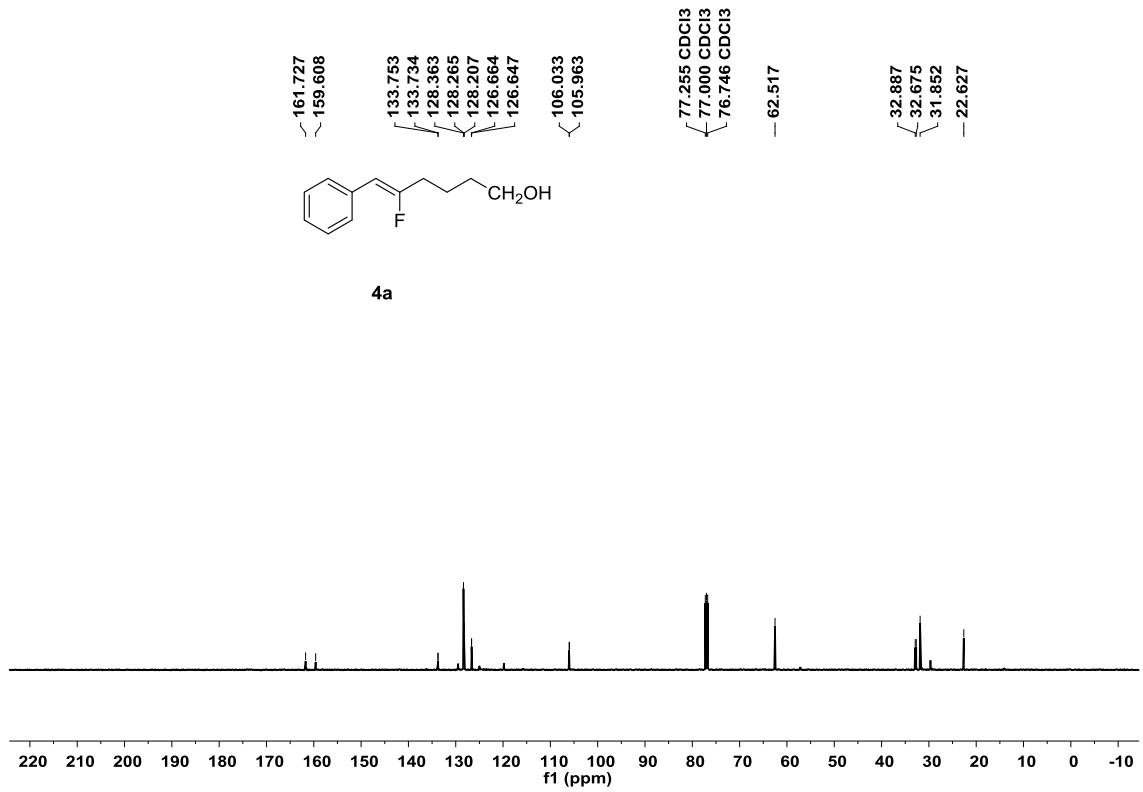
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2a





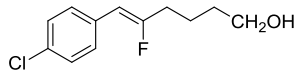


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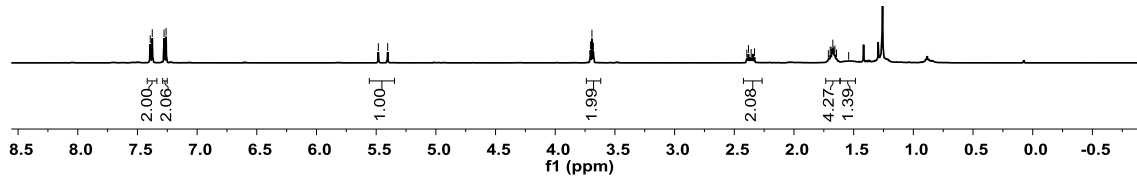
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4b



162.248  
160.121

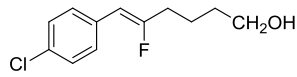
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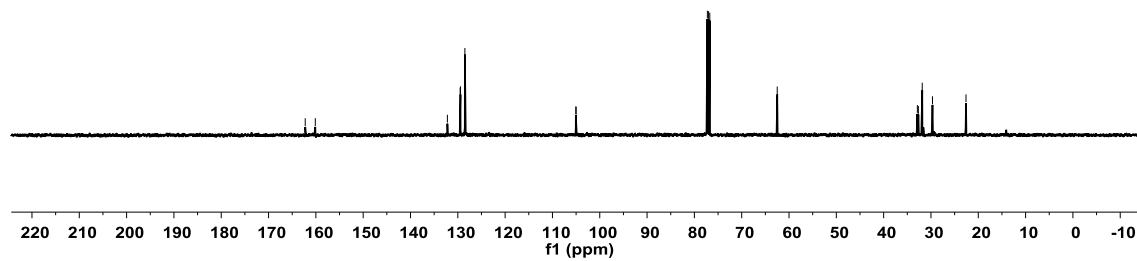
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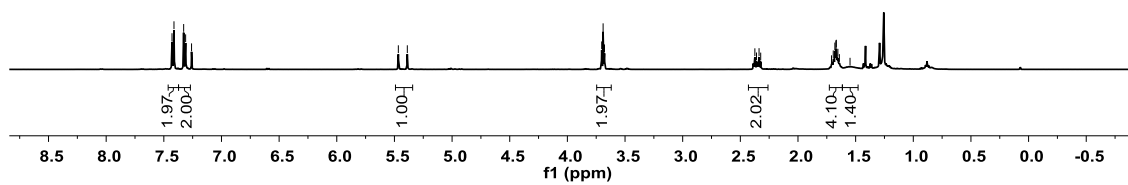
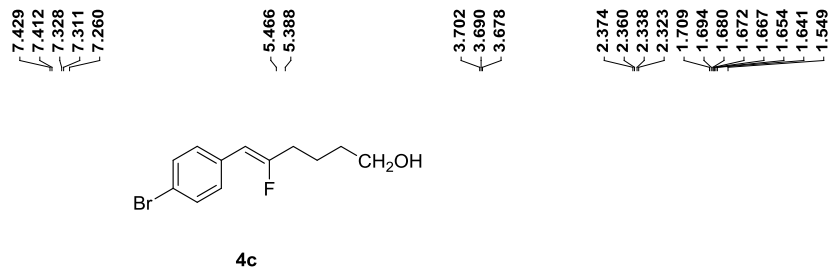
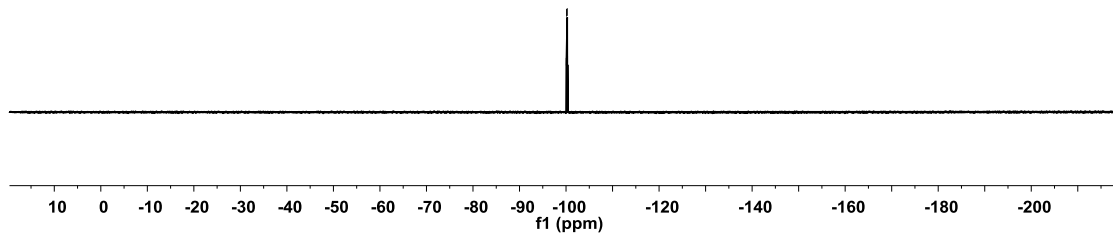
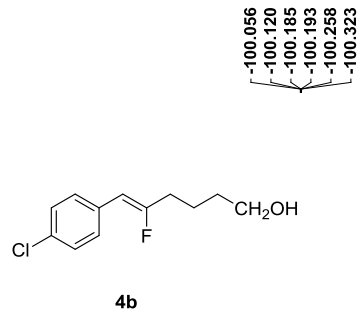
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4b







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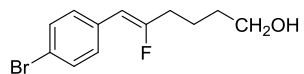
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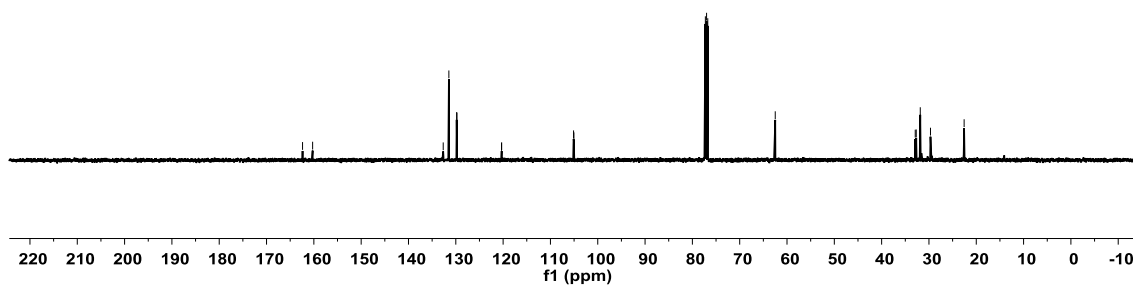
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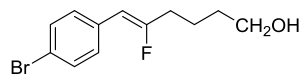
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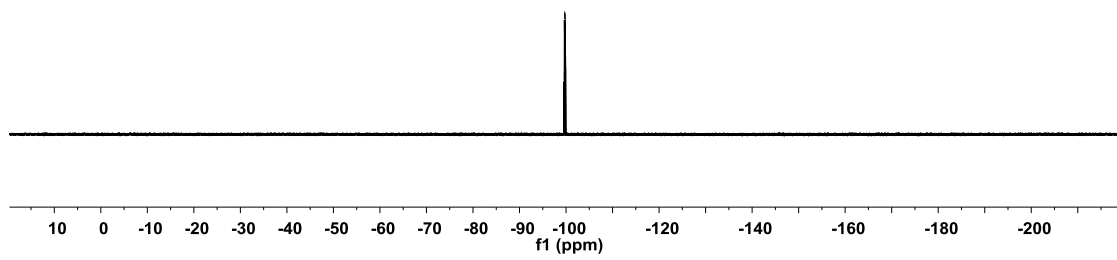
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4c

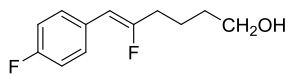


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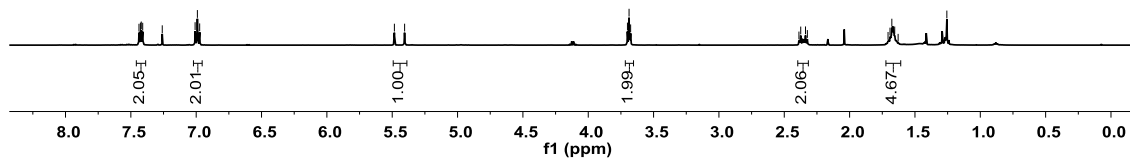
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4d



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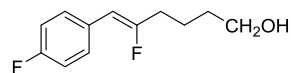
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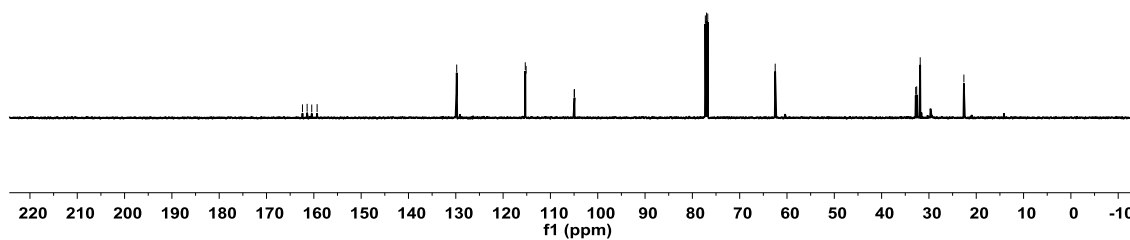
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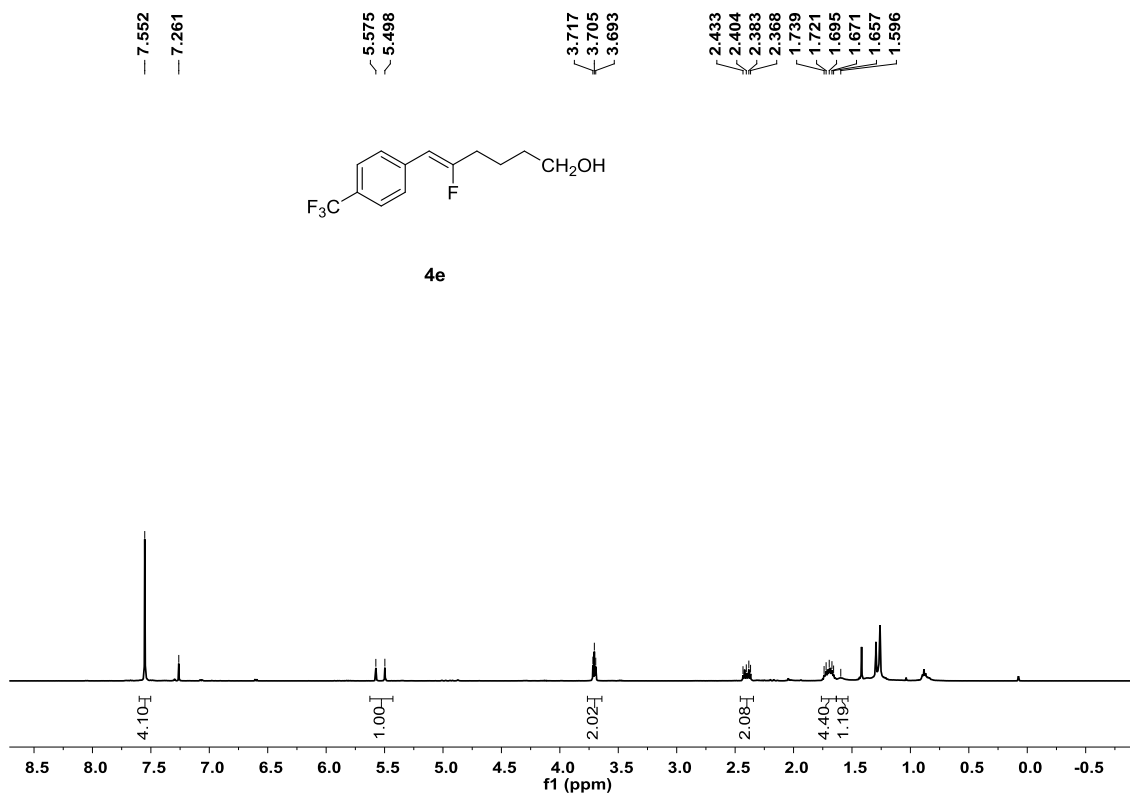
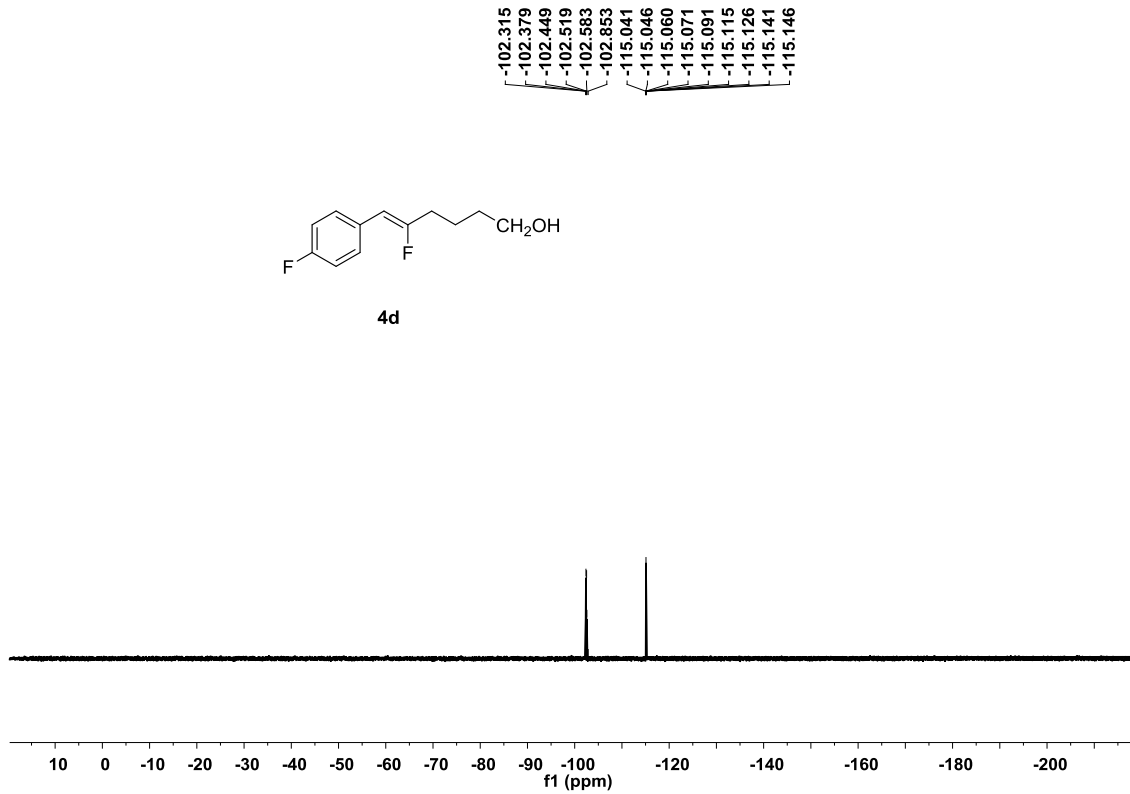
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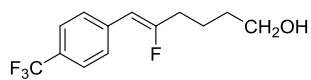


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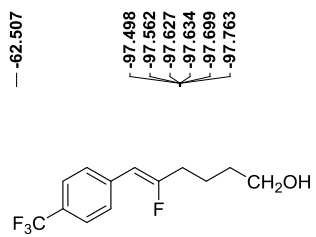
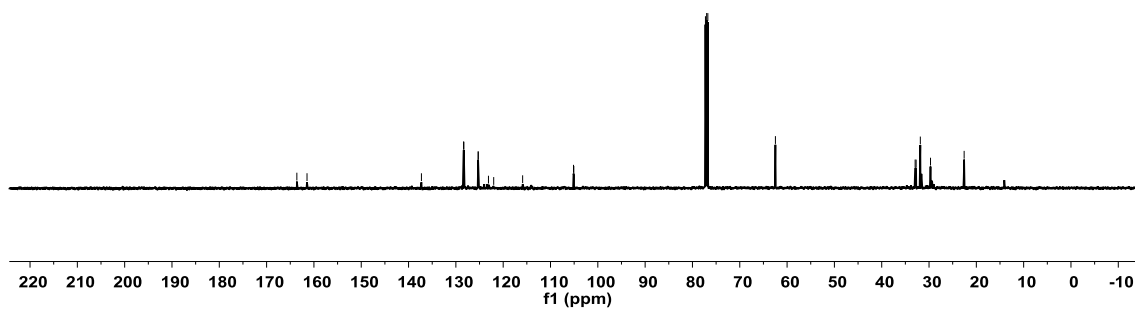




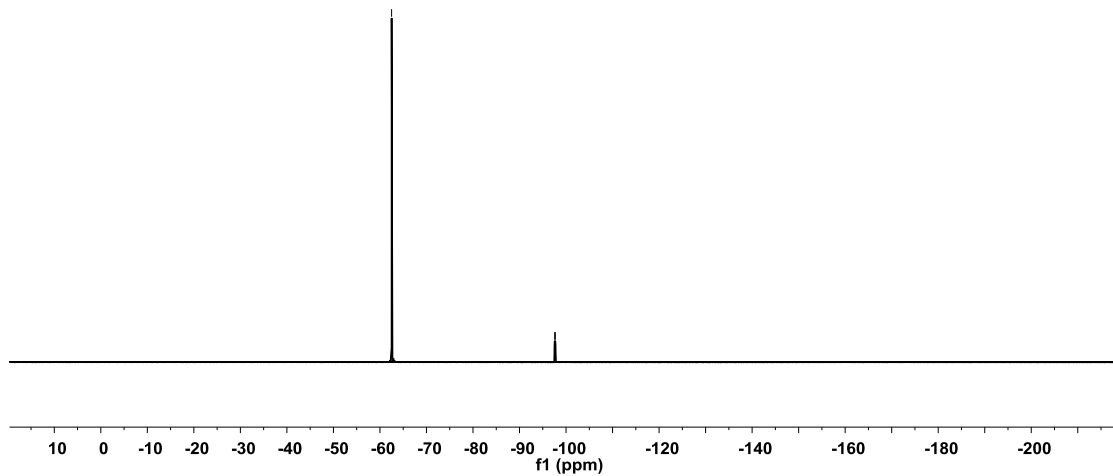
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4e



4e

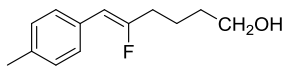


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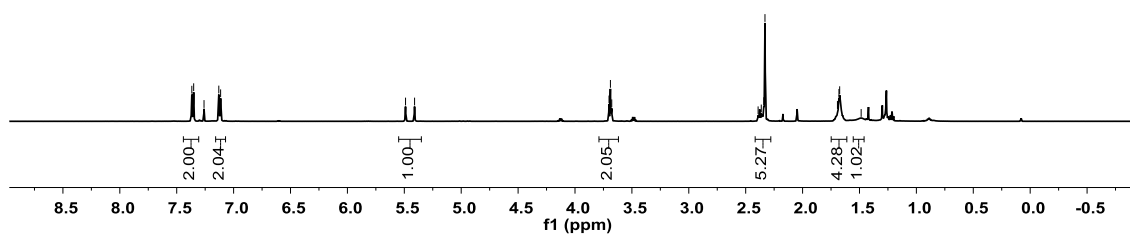
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4f



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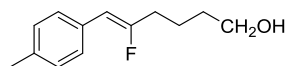
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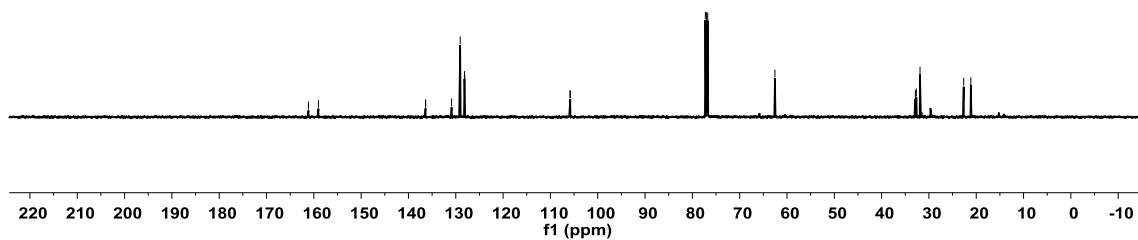
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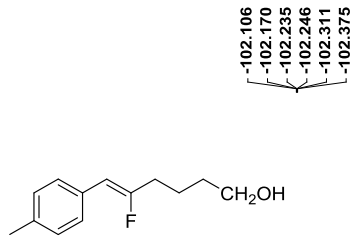
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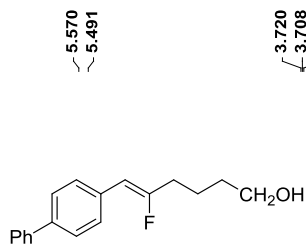
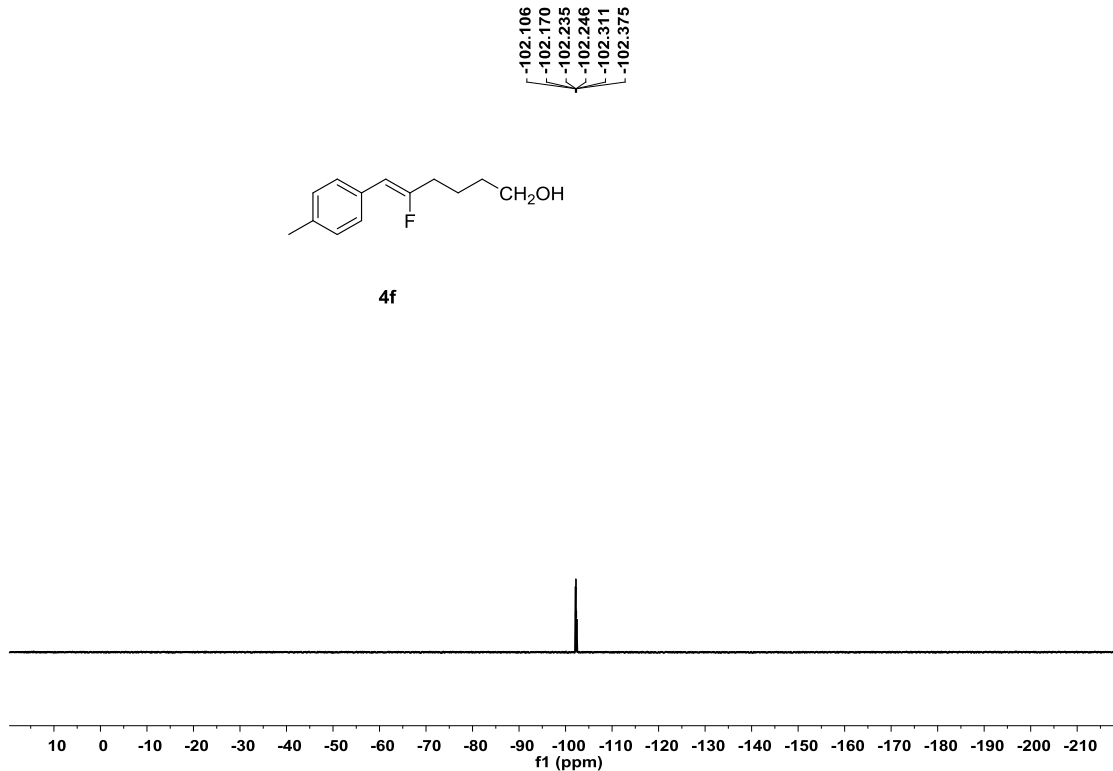


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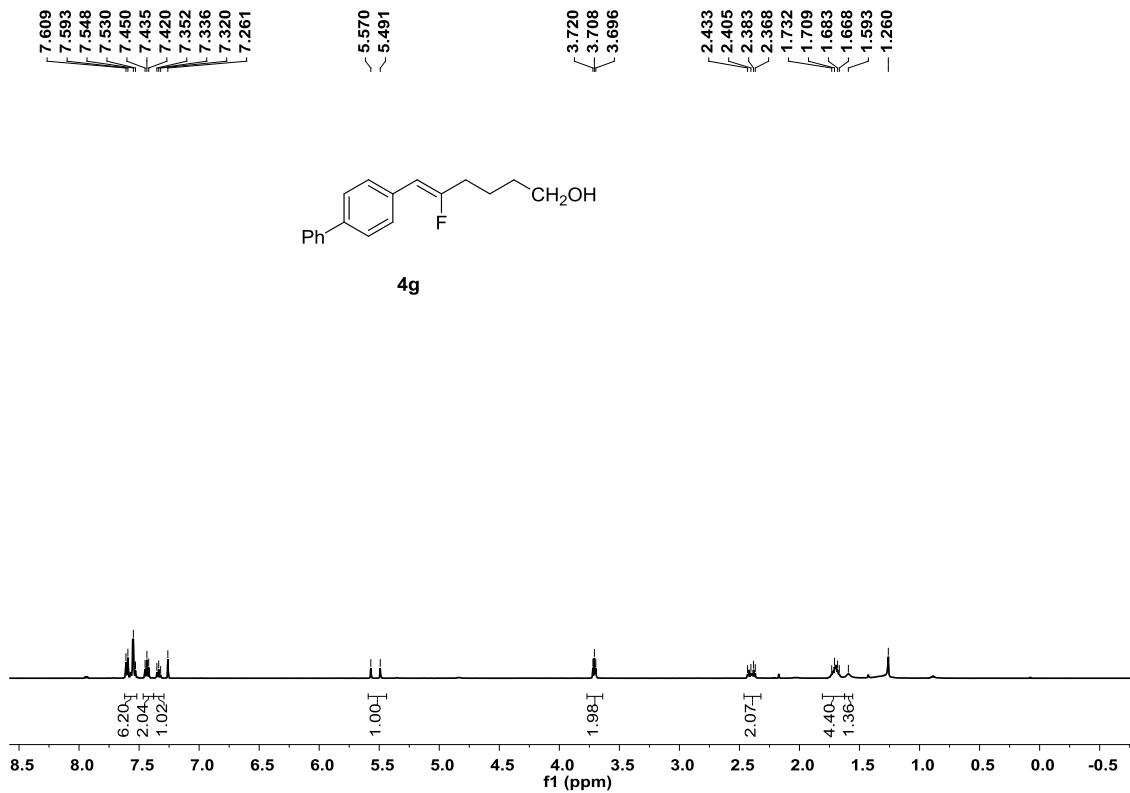


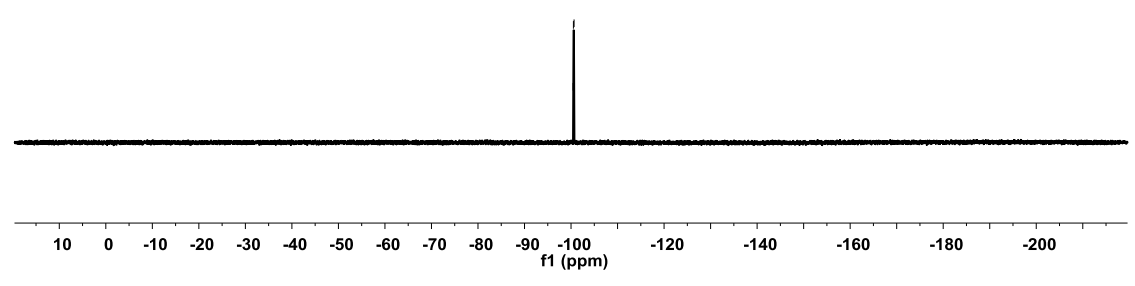
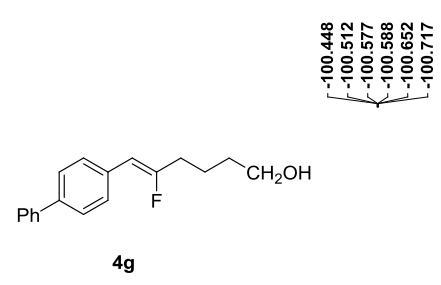
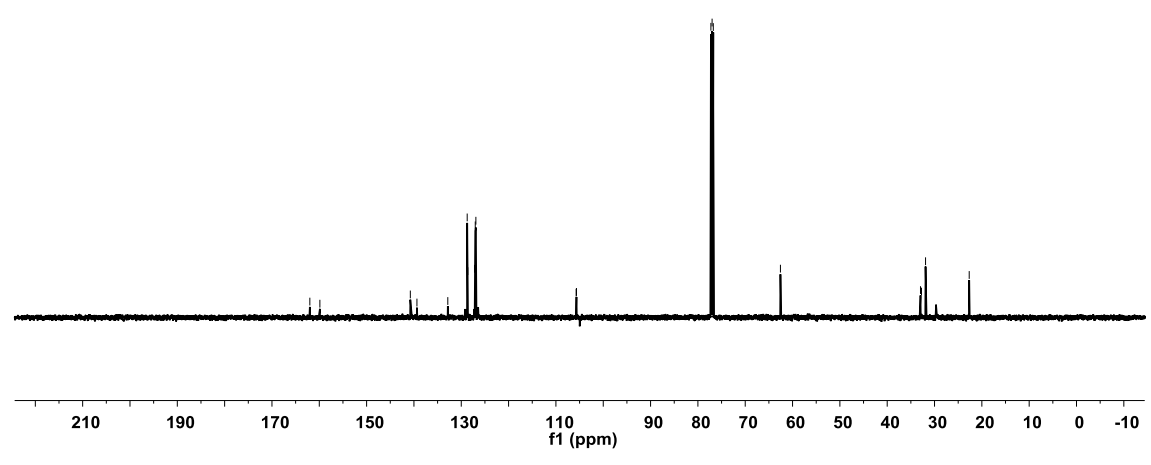
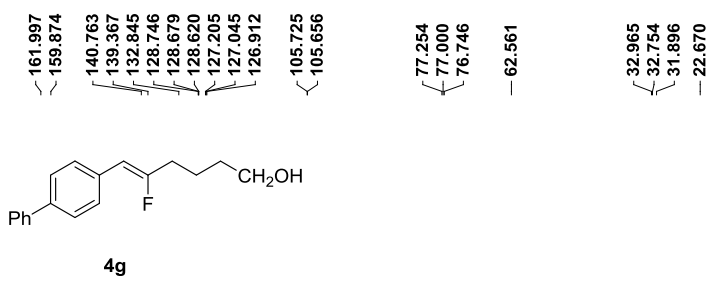


4f



4g





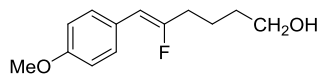


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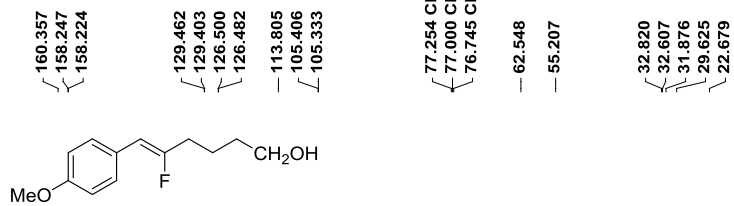
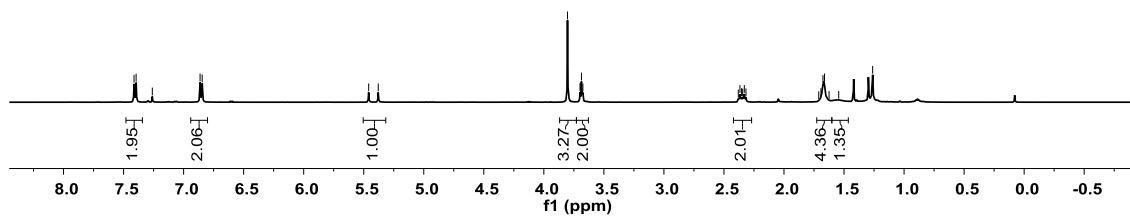
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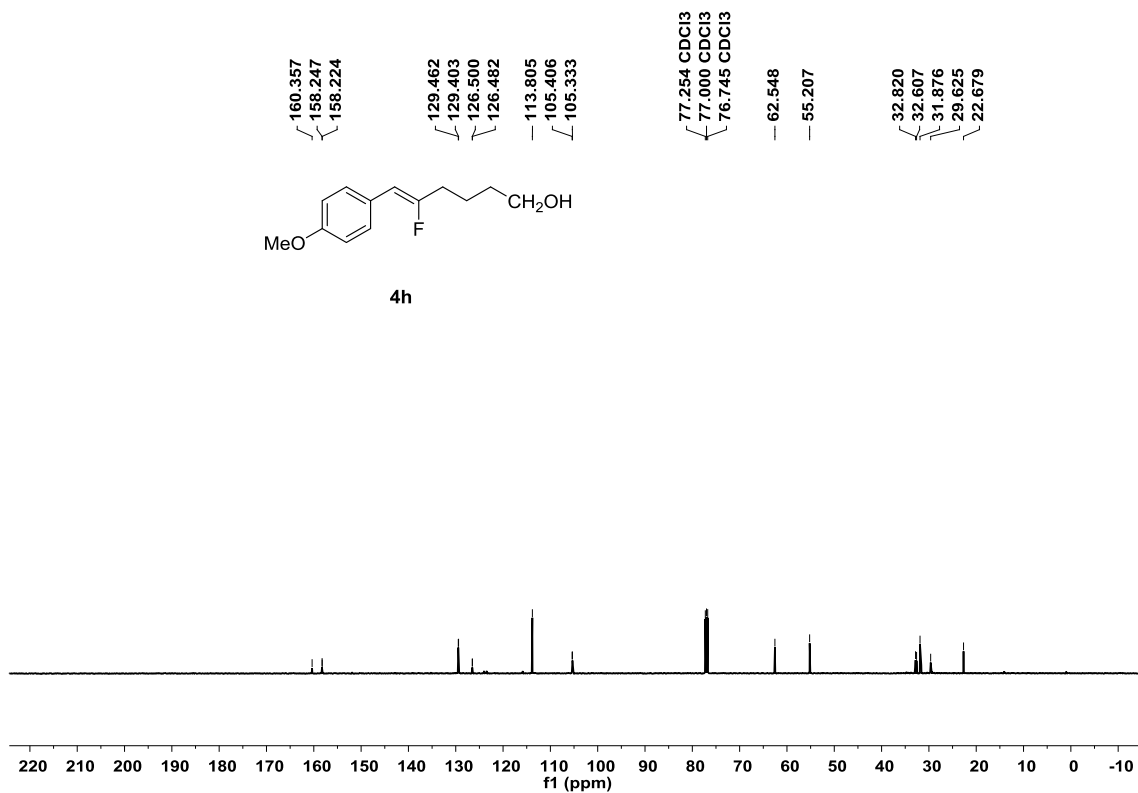
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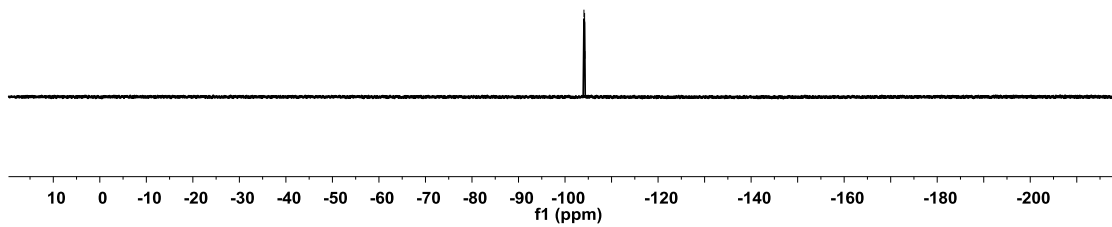
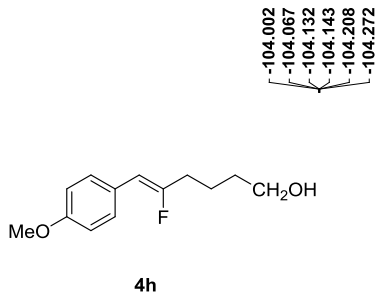


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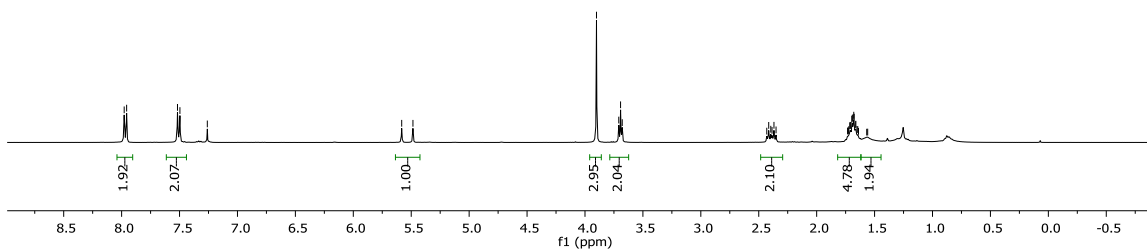
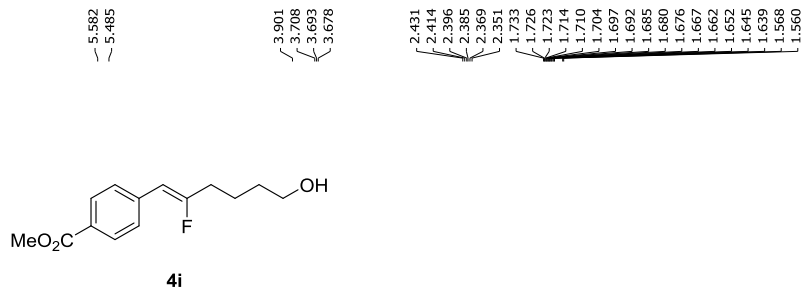


4h





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tl-4-130



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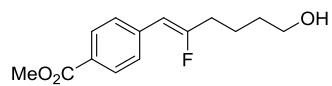
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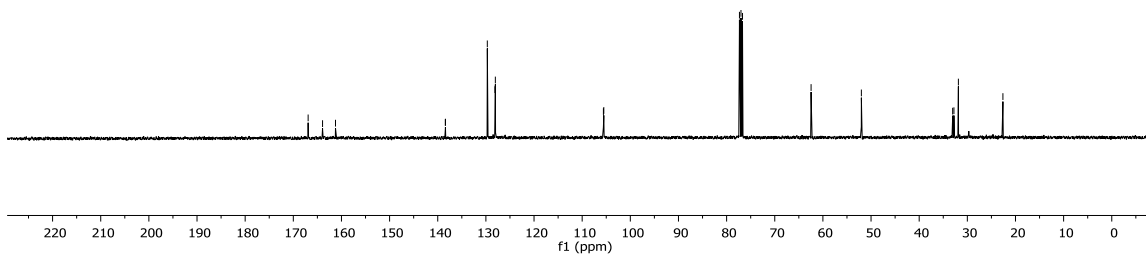
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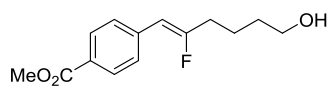


4i

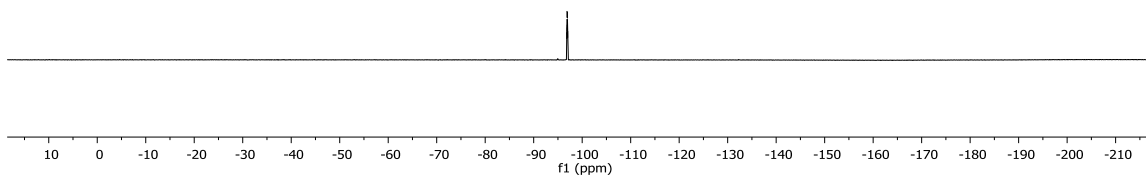


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4i



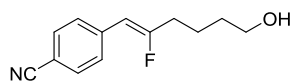
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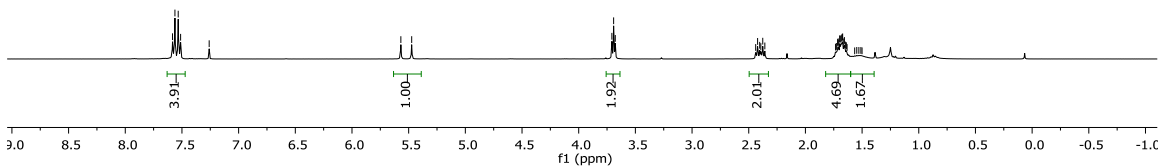
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4j



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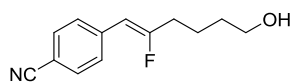
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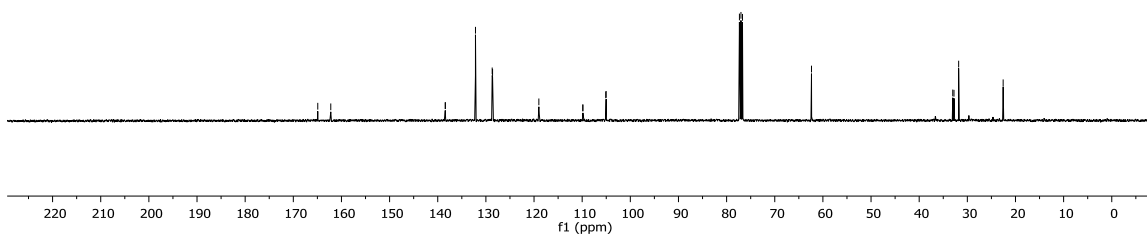
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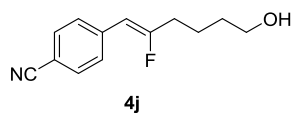
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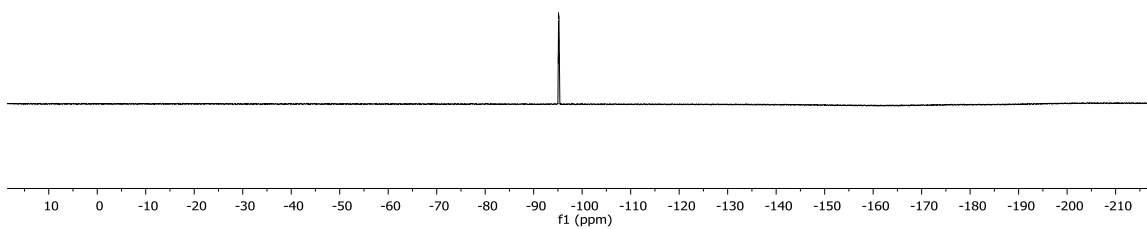


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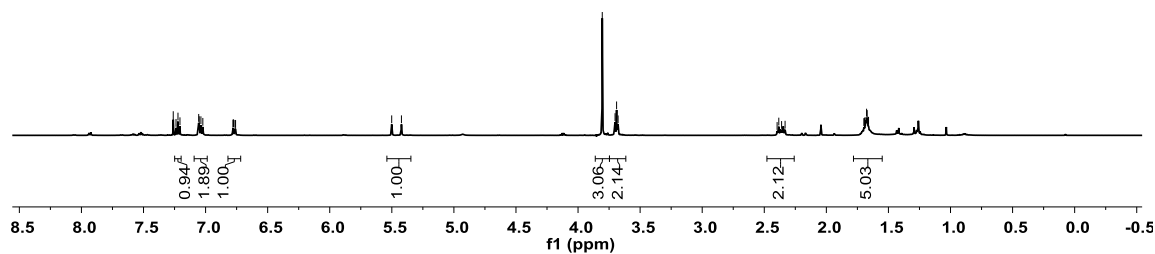
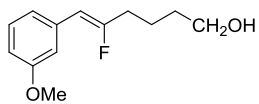


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6.759

5.501  
5.423

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3.702  
3.690  
3.678

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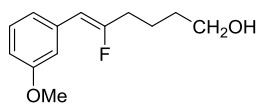
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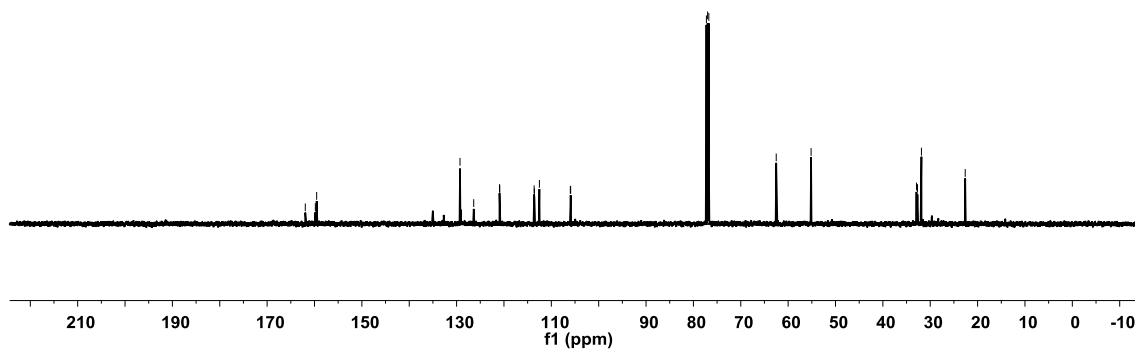
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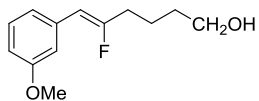
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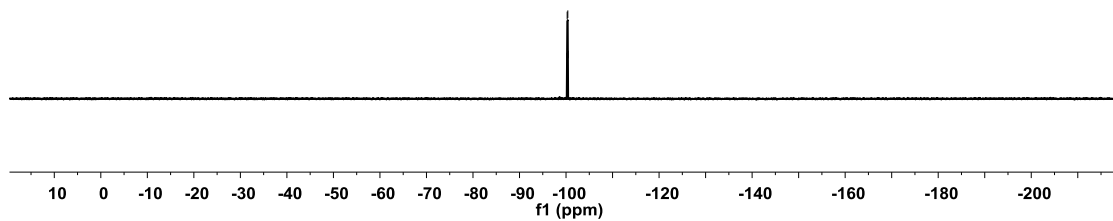
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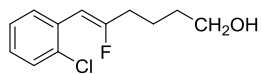
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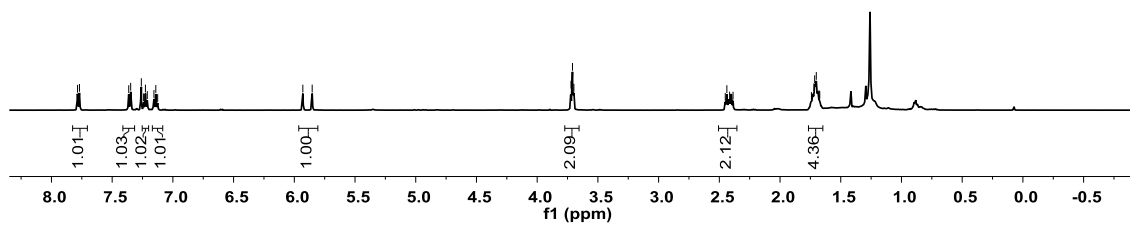
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5.853

3.722  
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3.698

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2.415  
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4l



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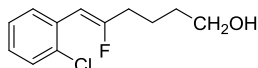
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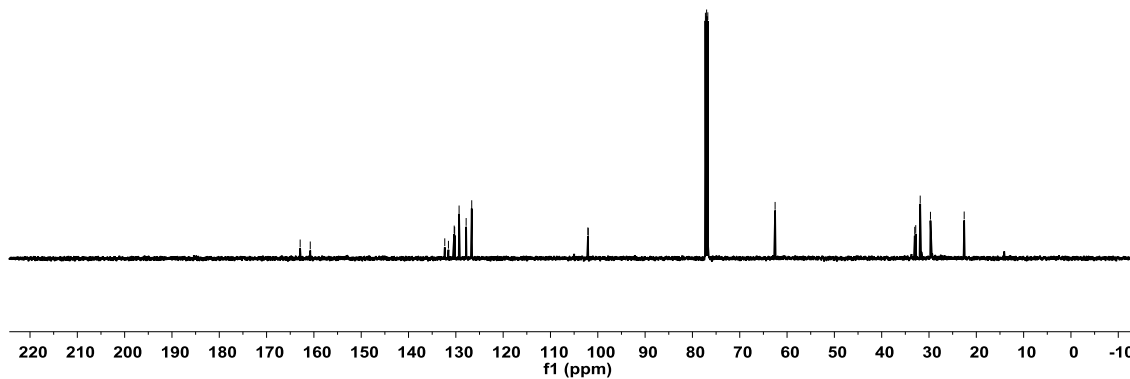
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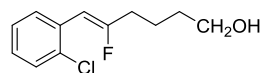
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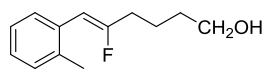
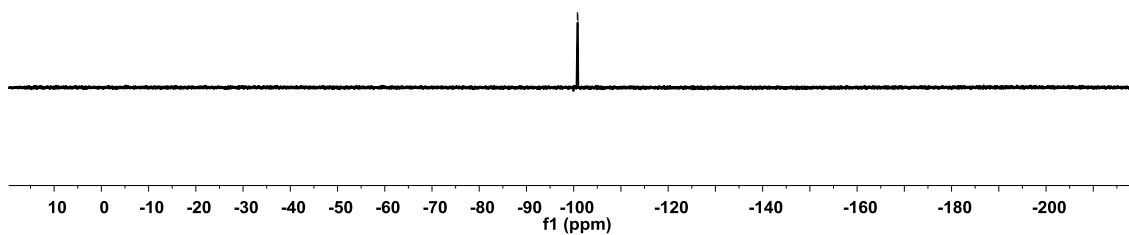
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4l

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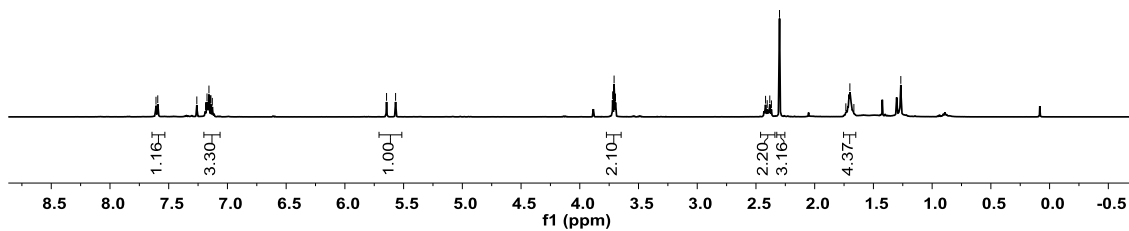
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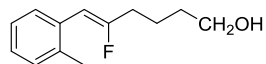
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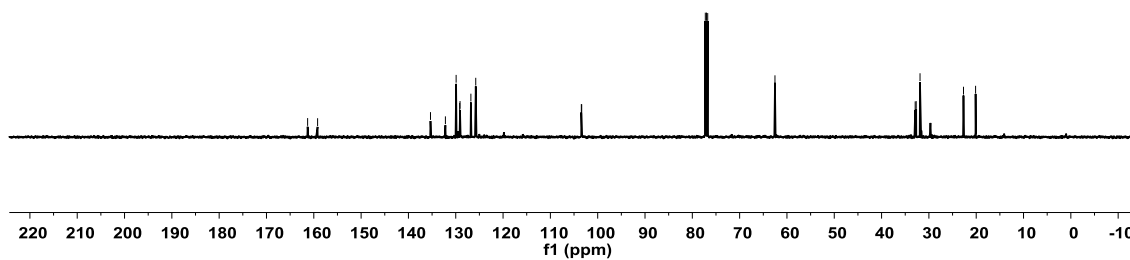
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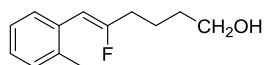
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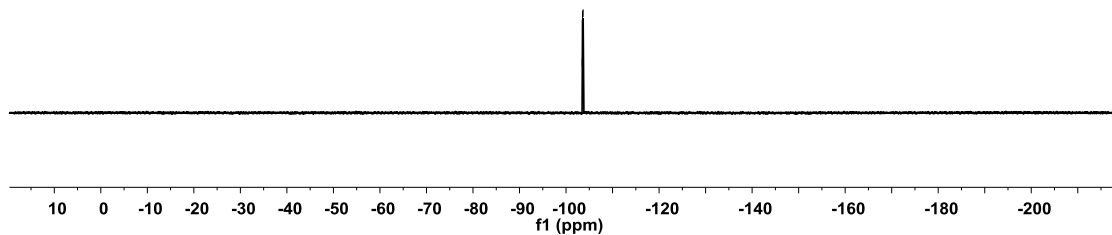
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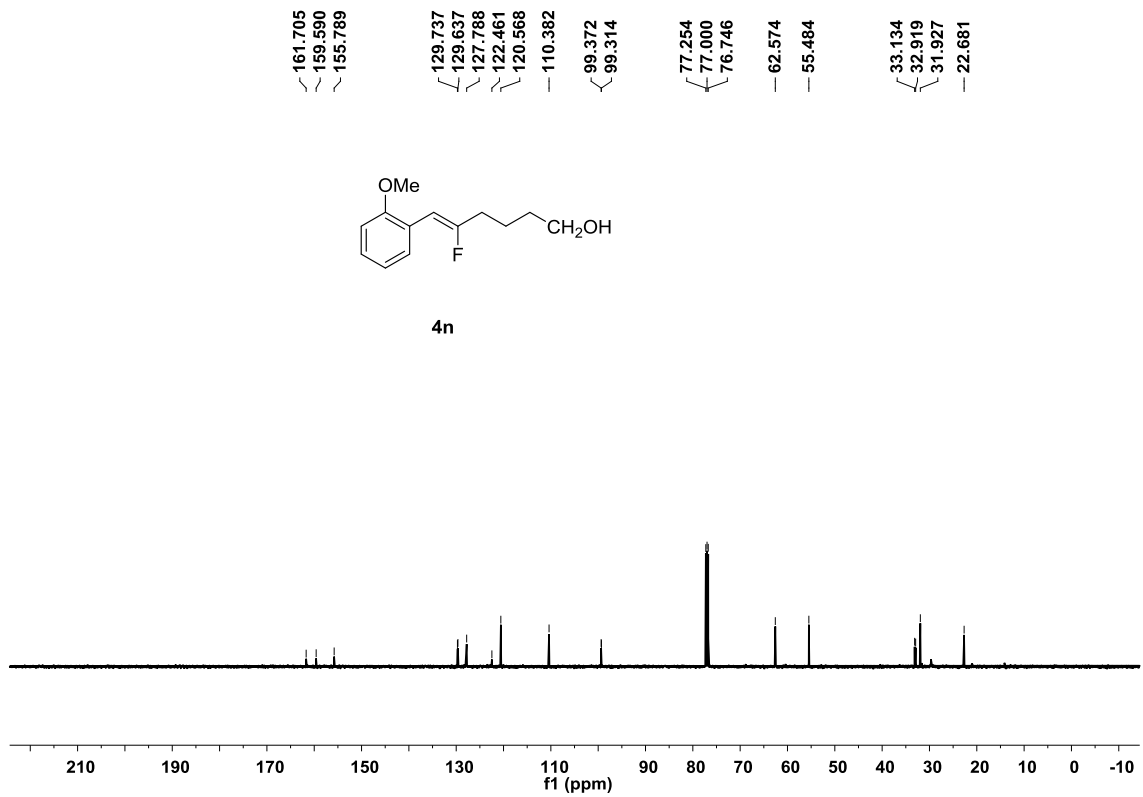
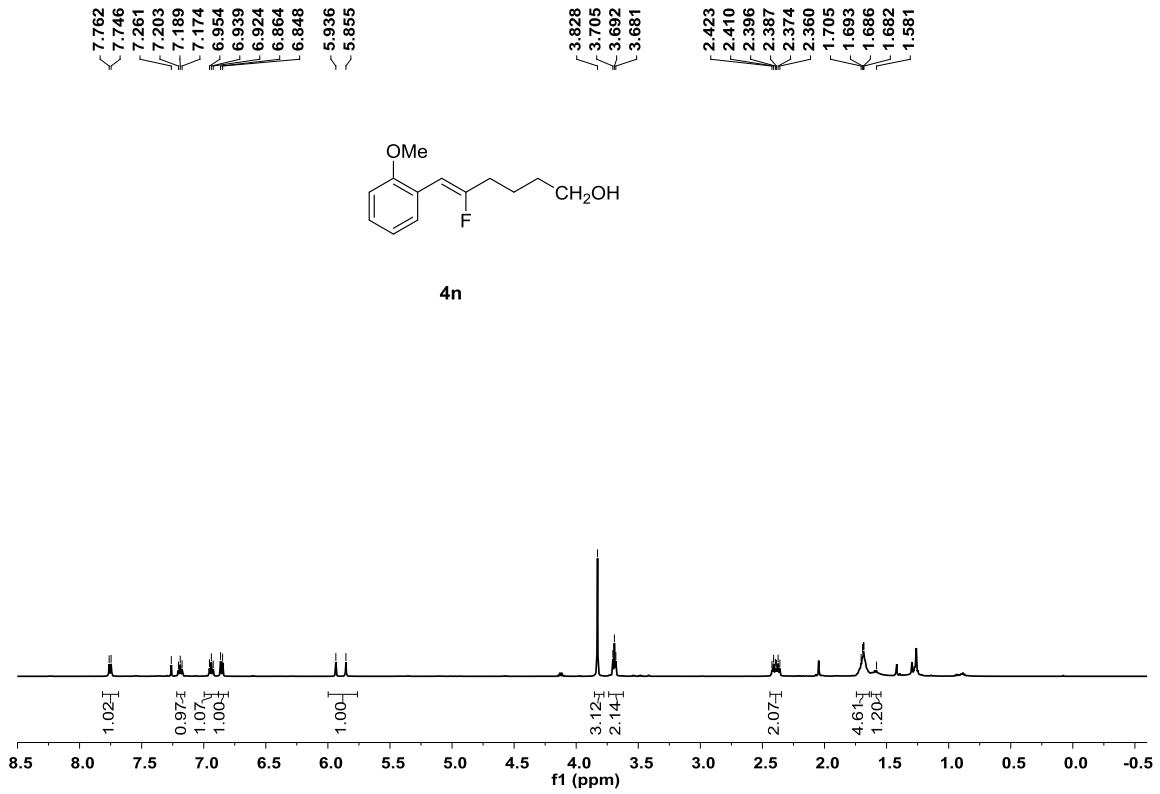


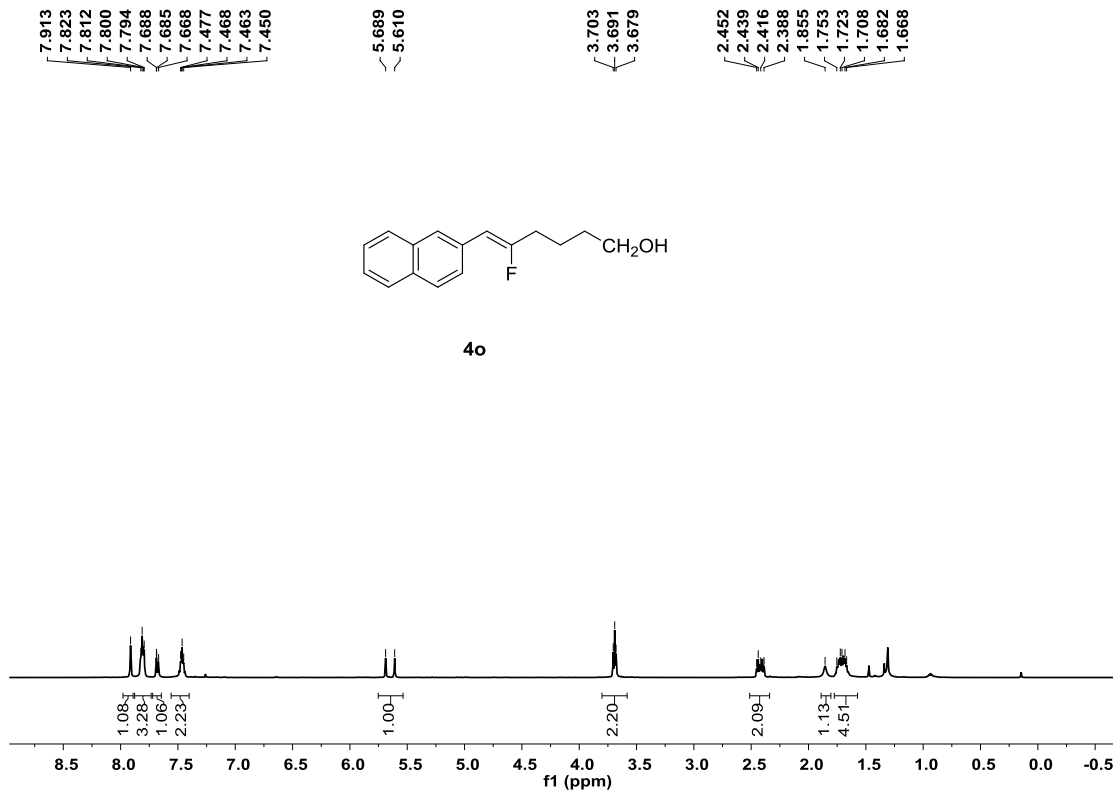
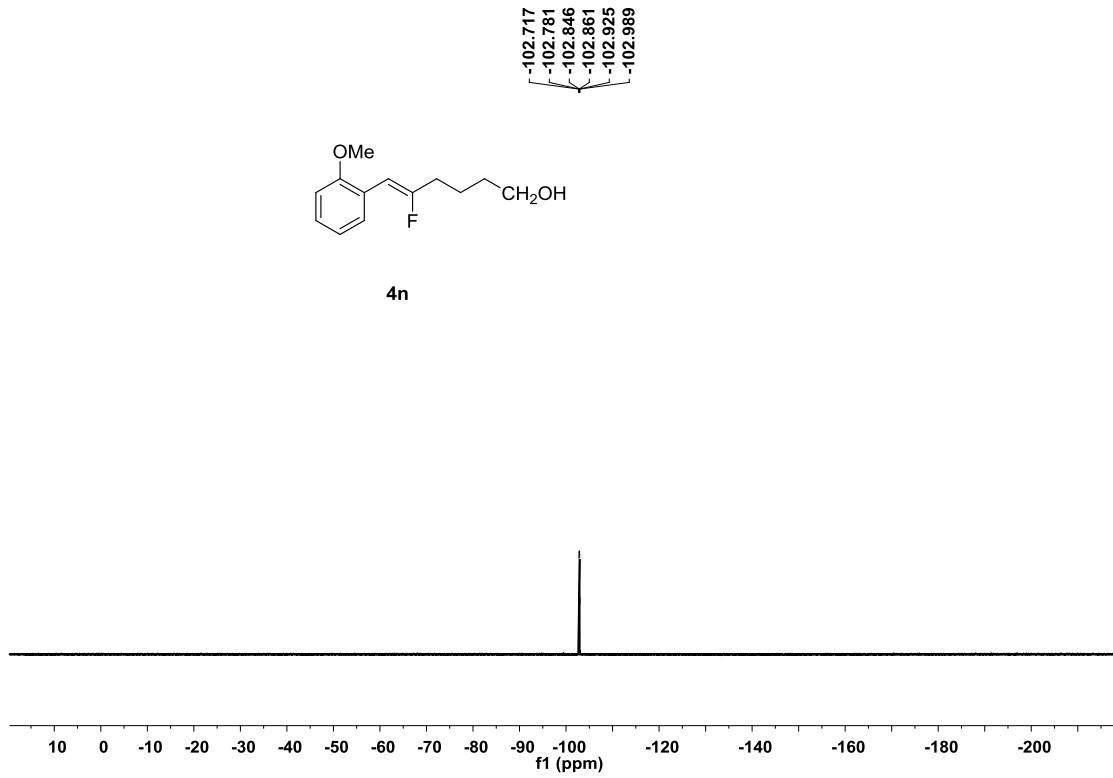
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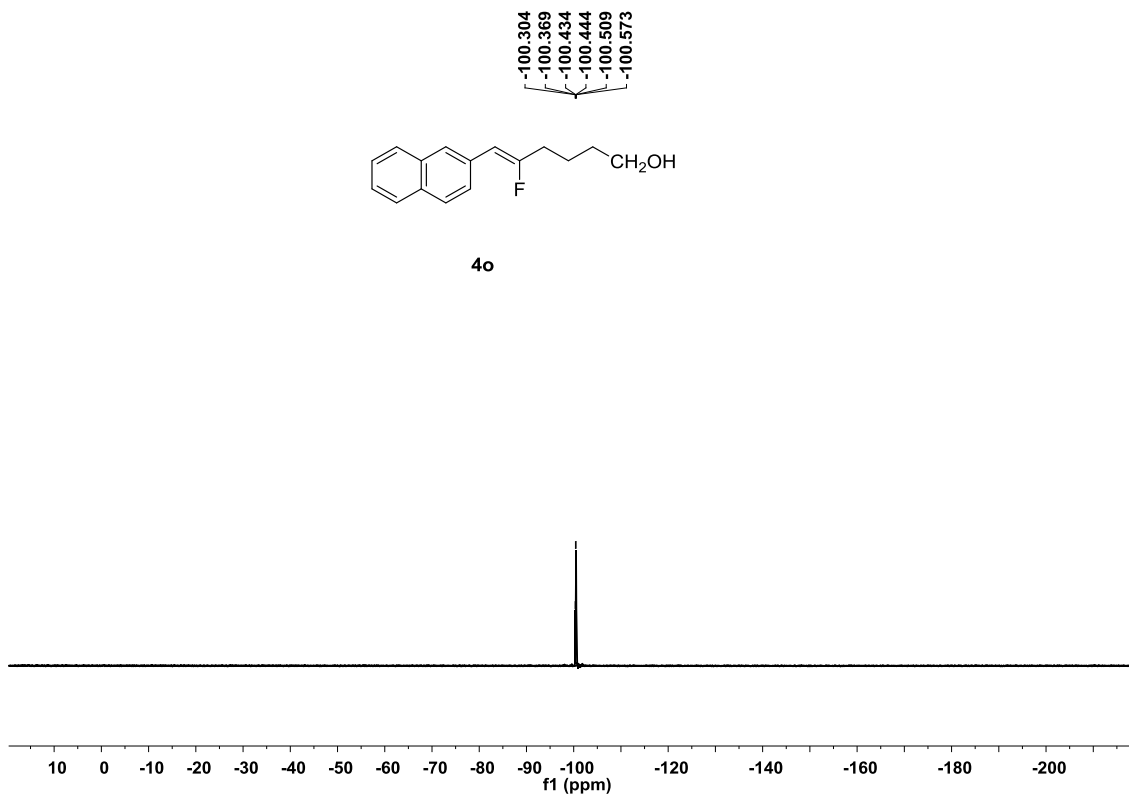
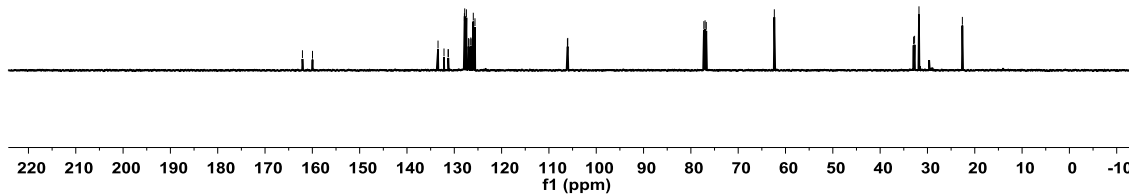
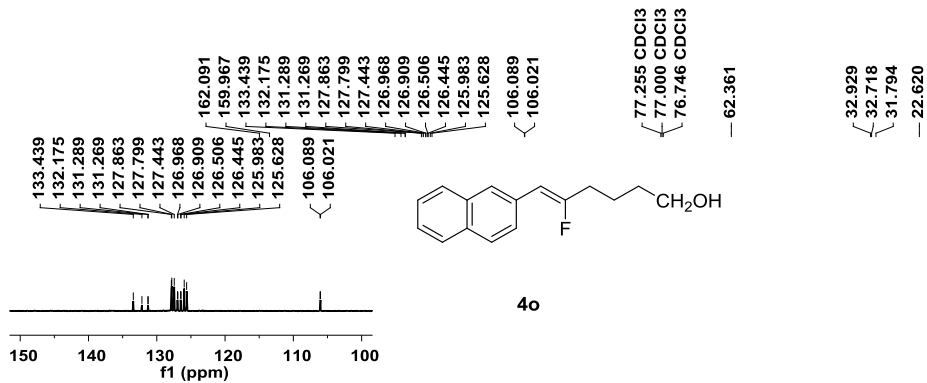


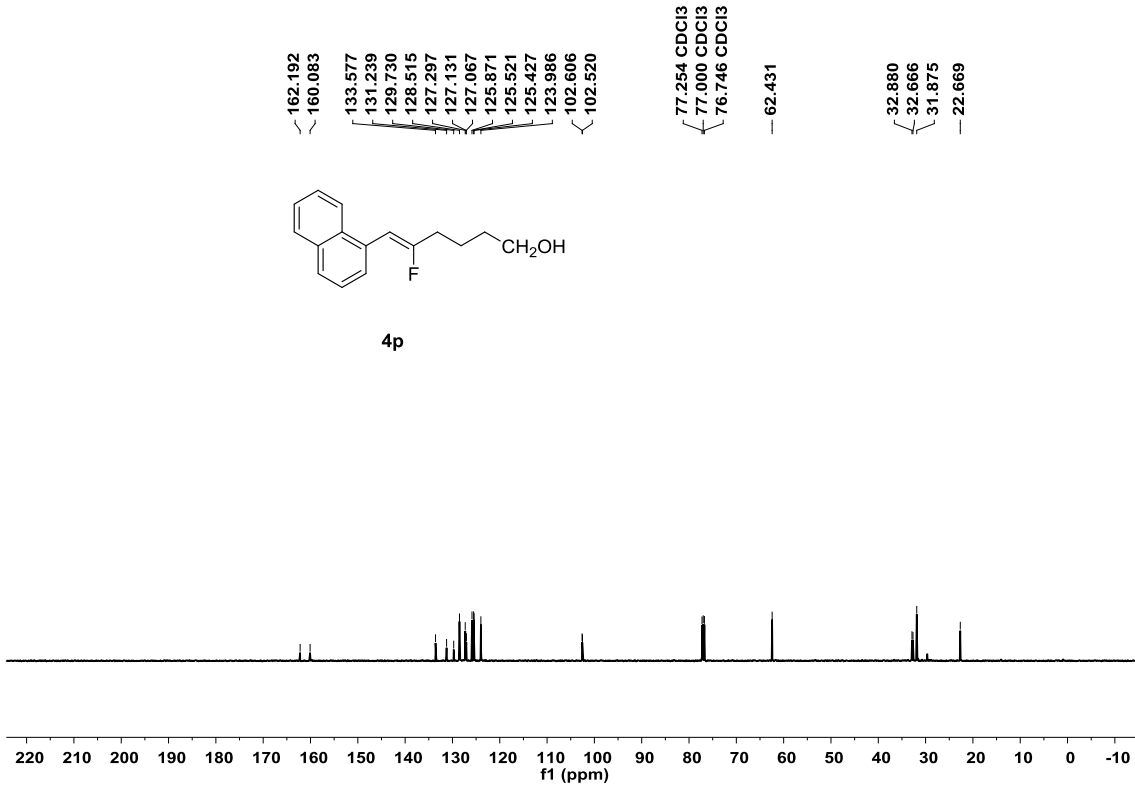
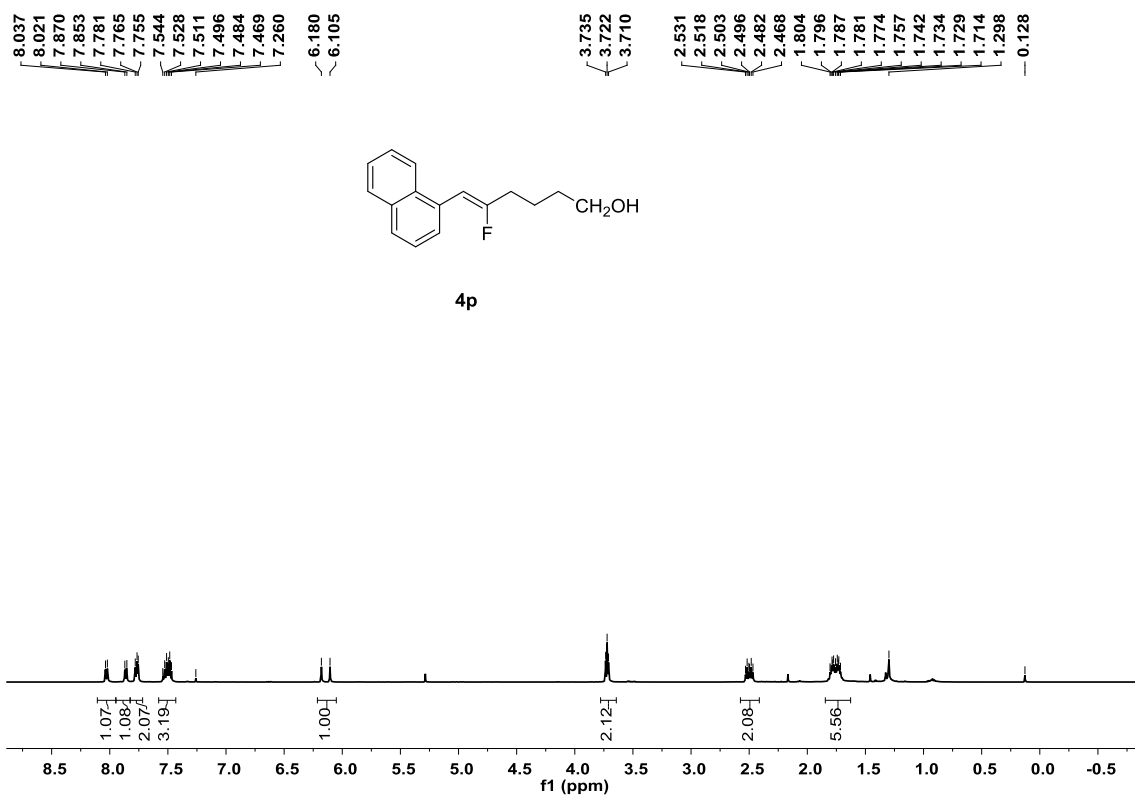
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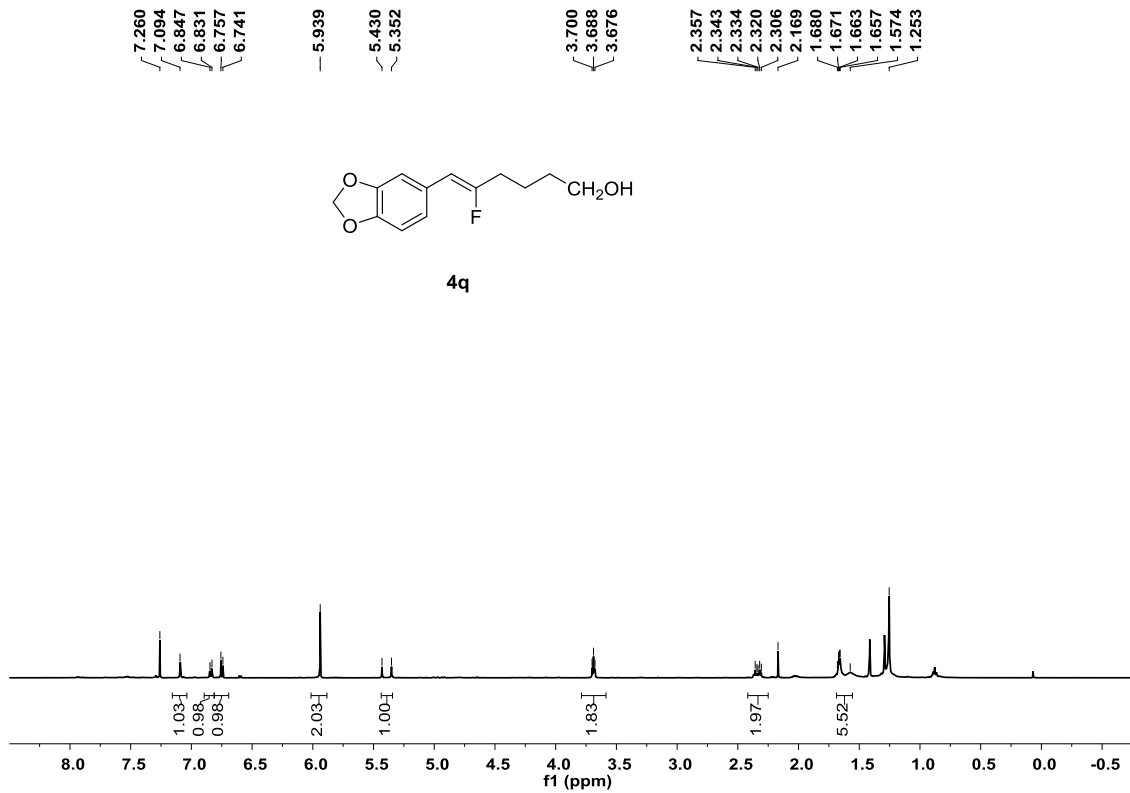
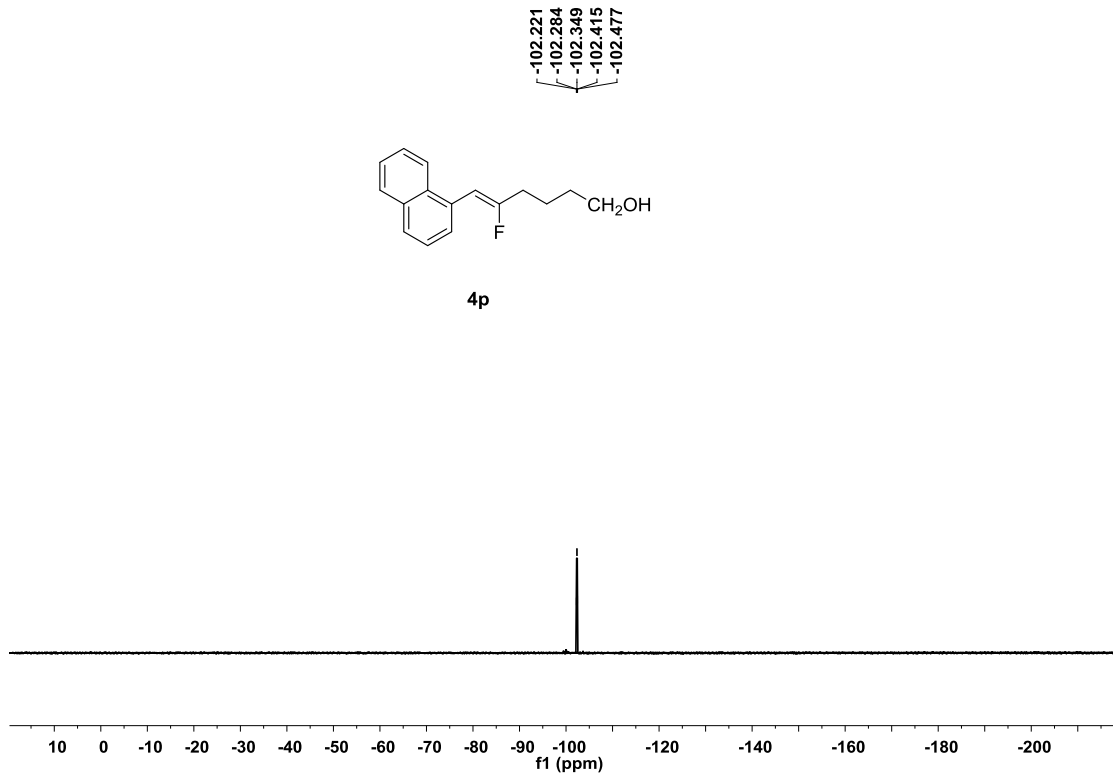


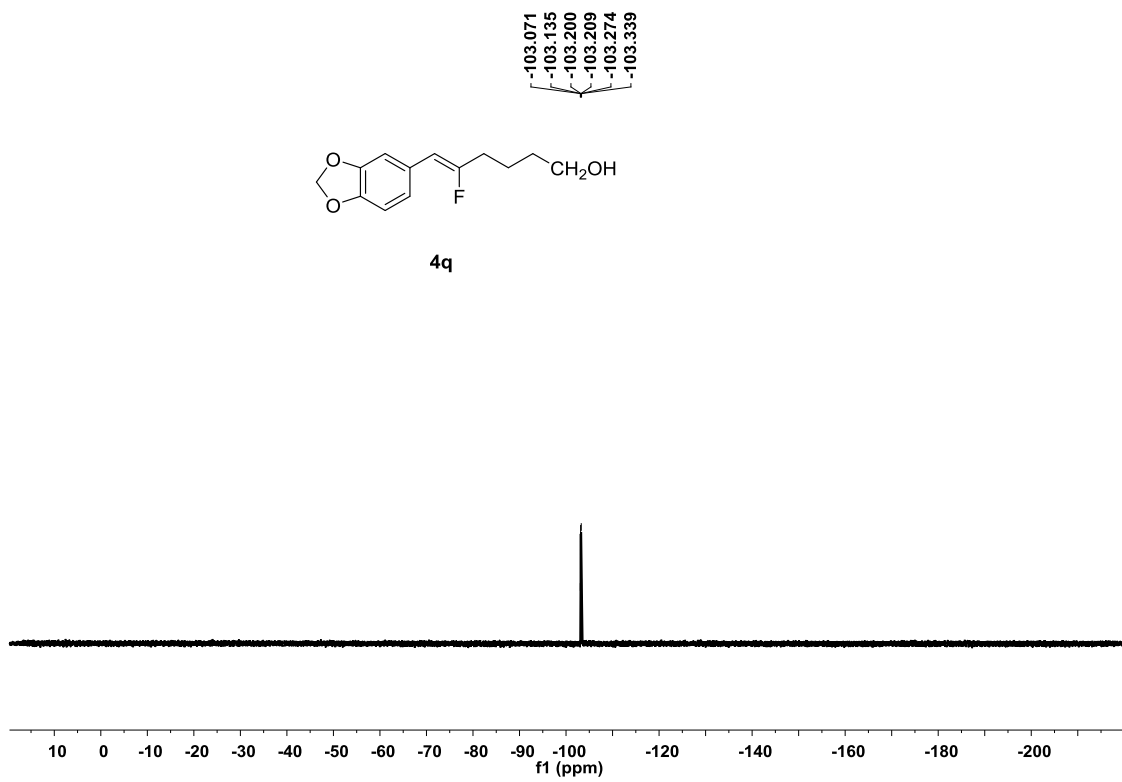
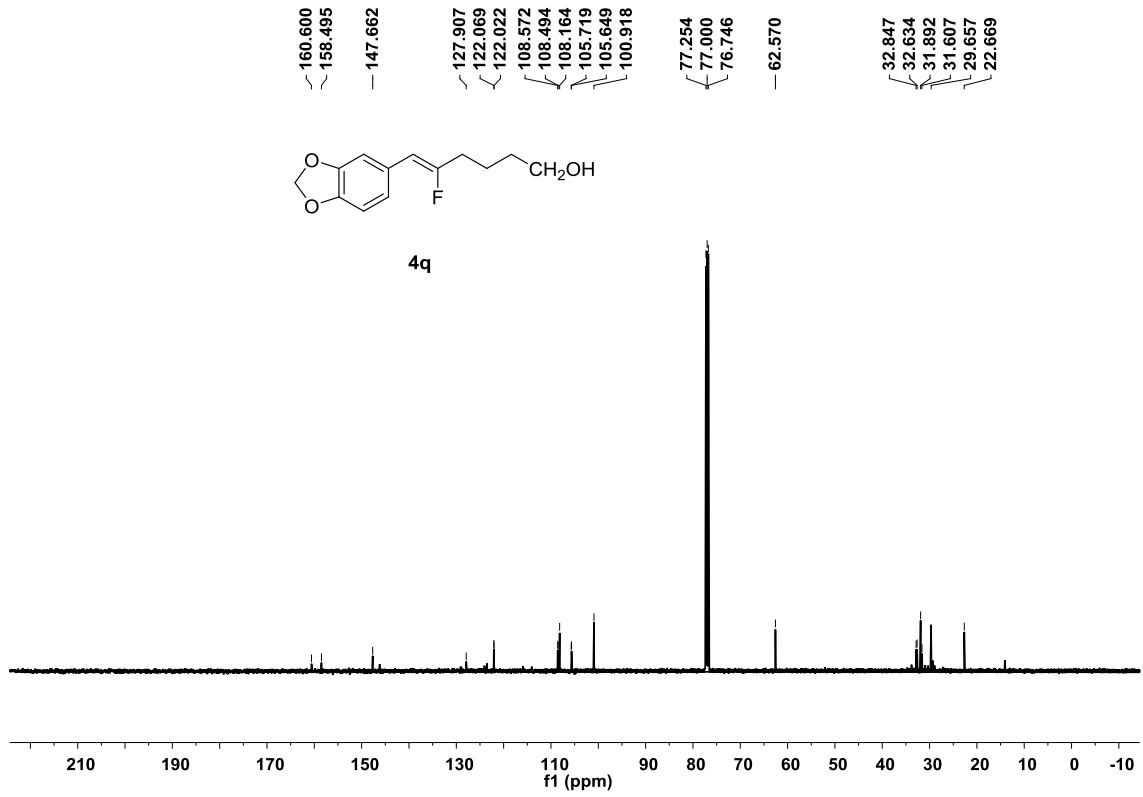


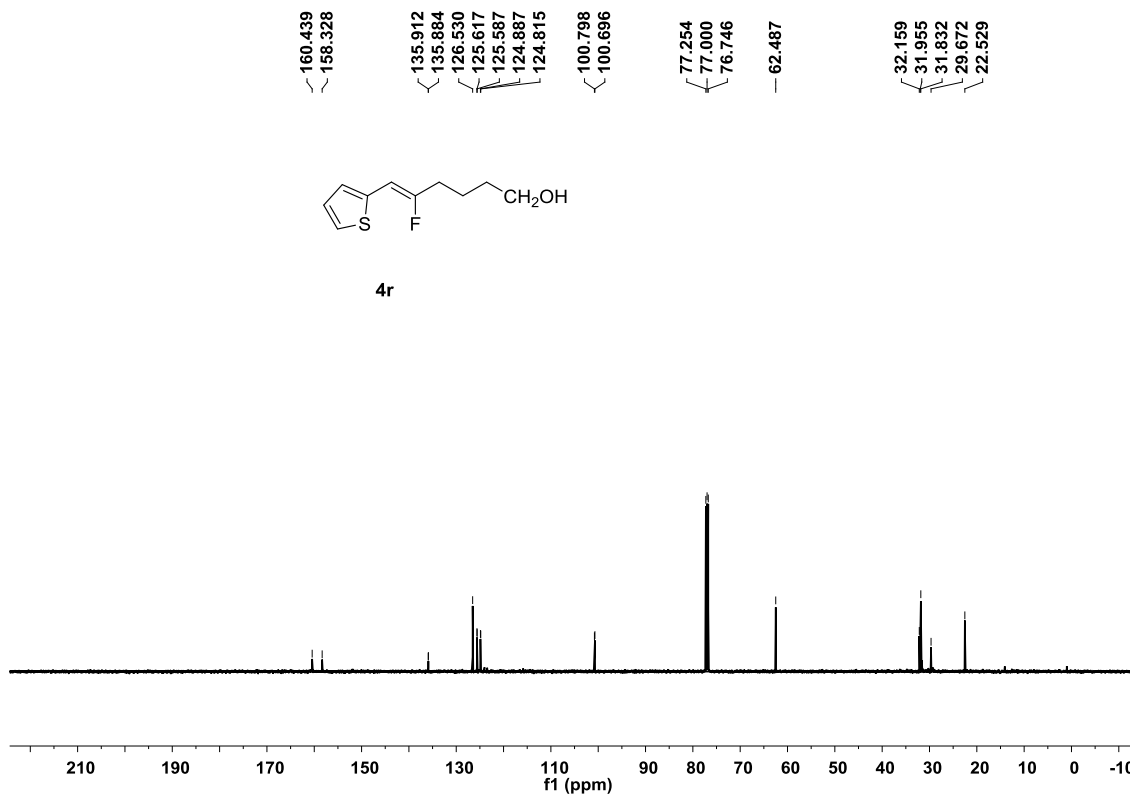
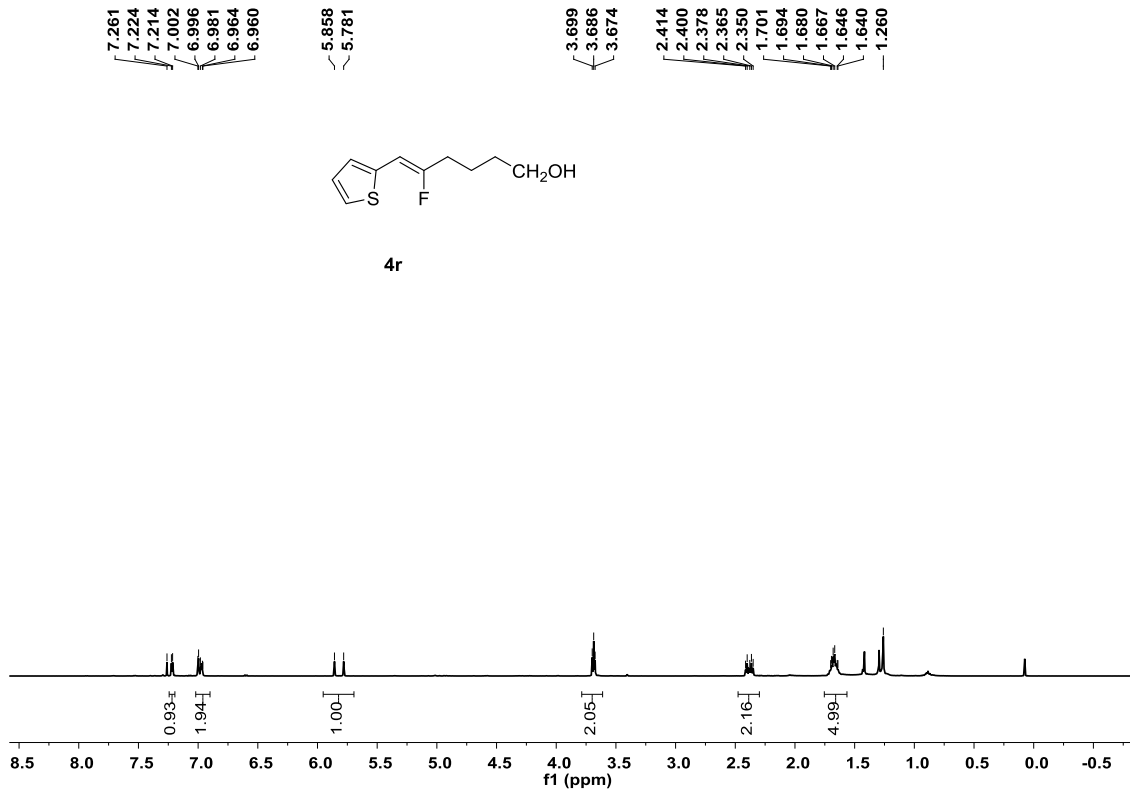






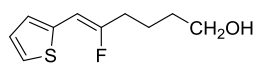




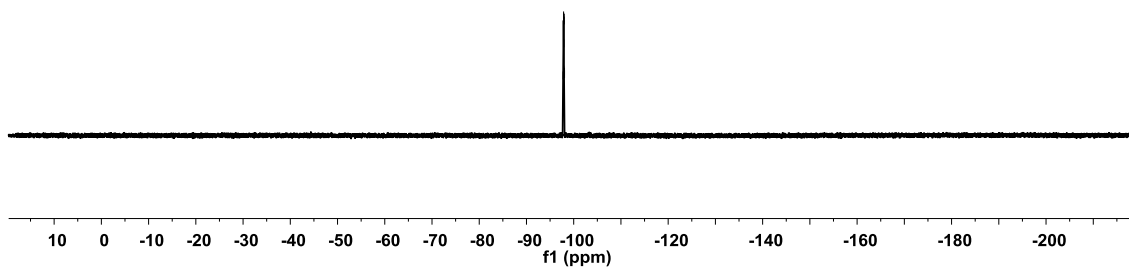




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4r

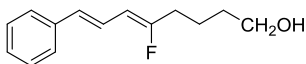


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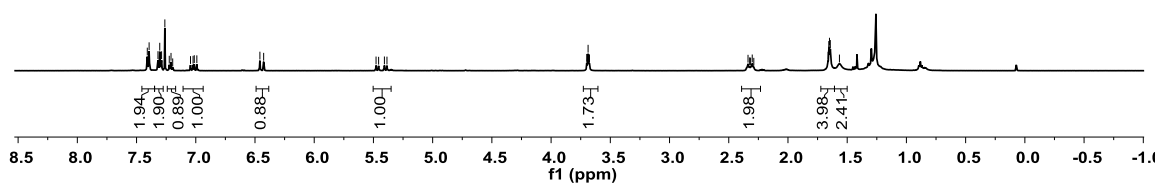
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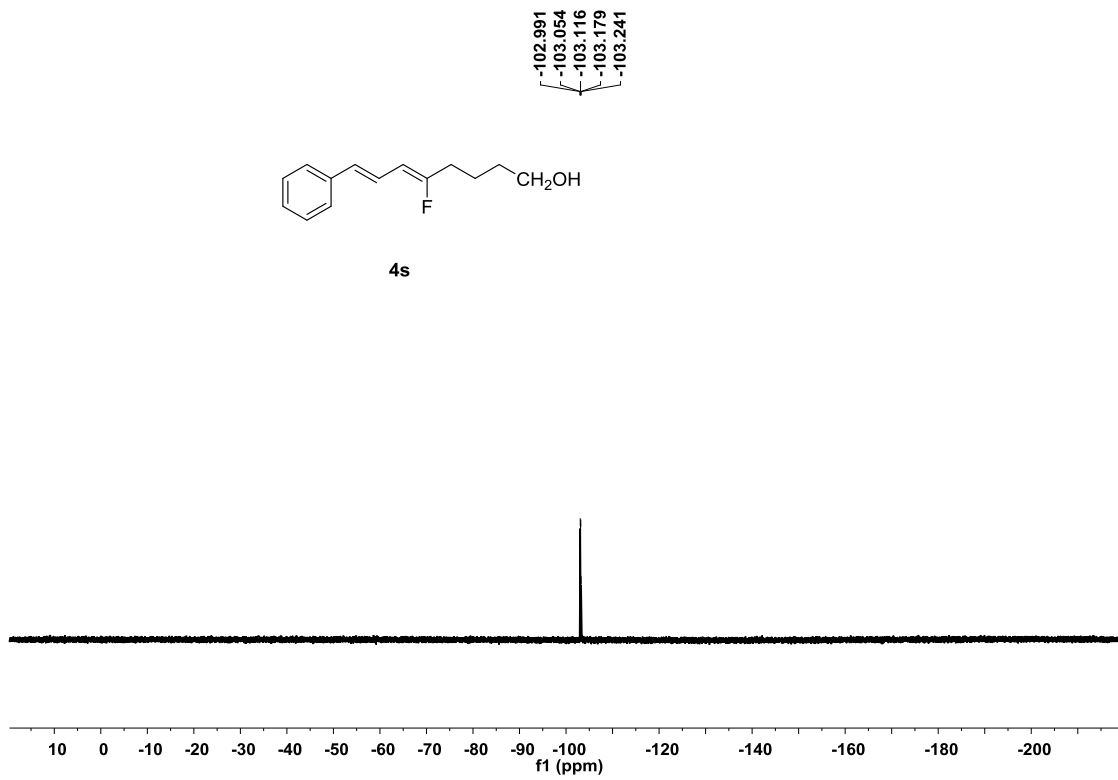
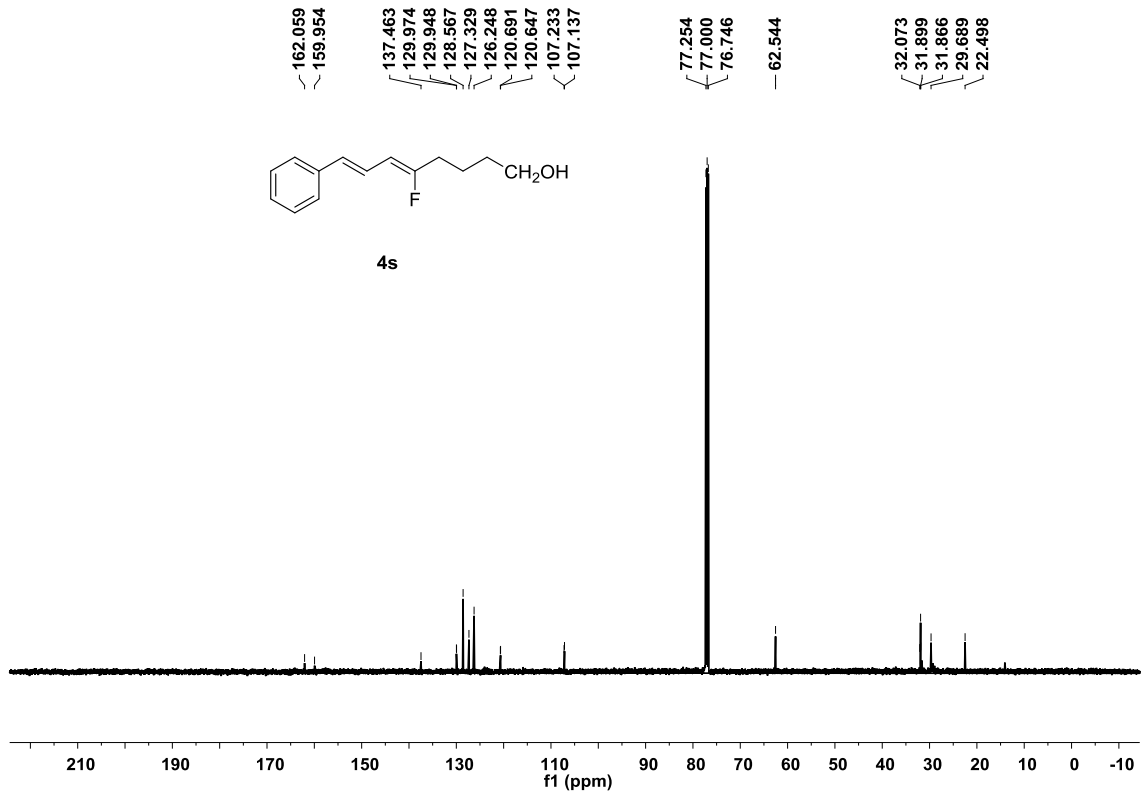
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4s





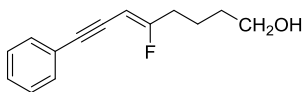
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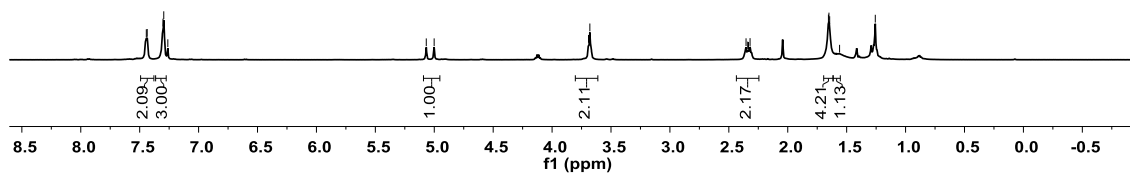
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4t

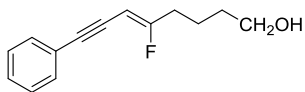


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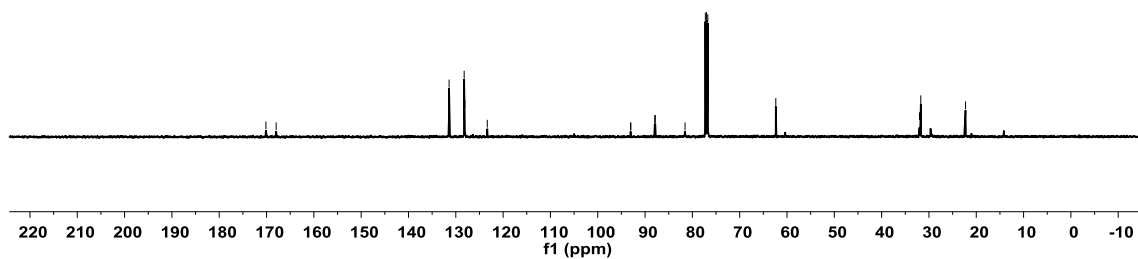
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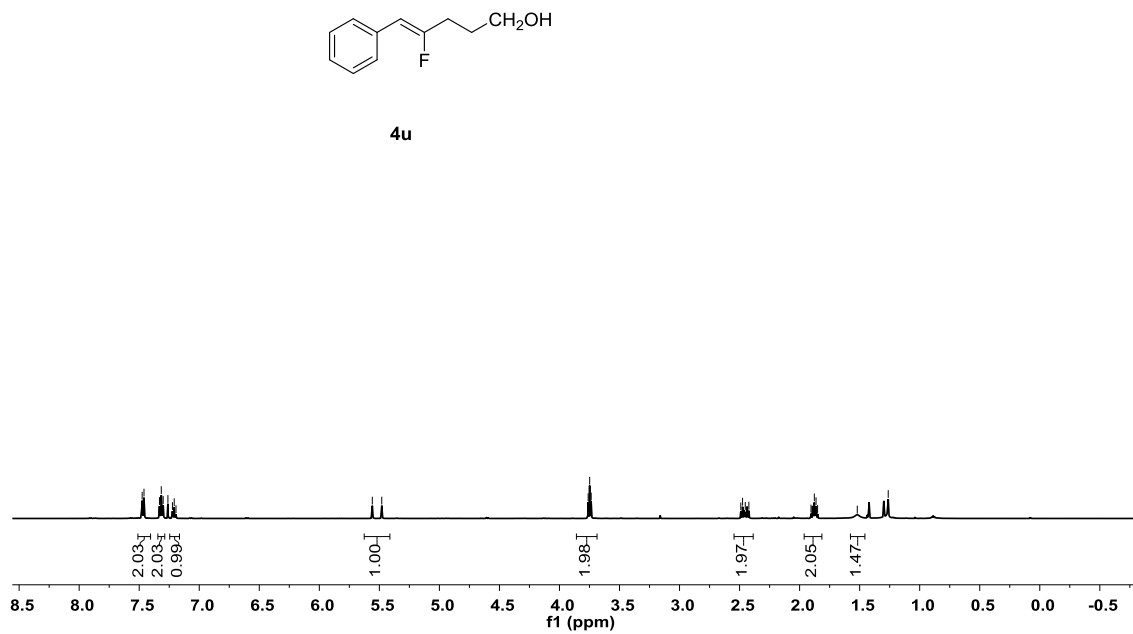
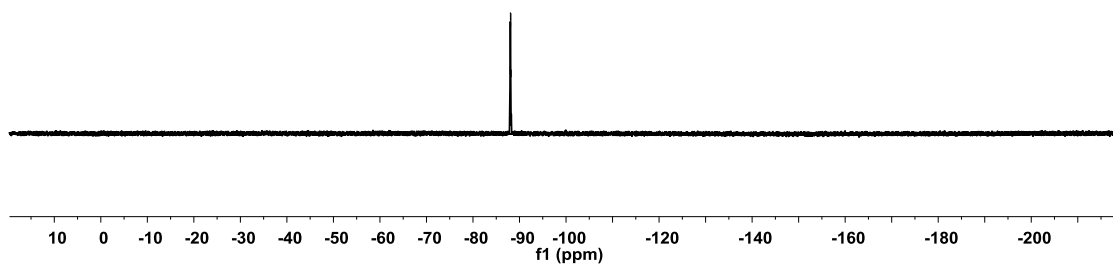
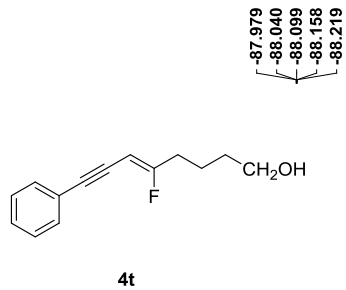
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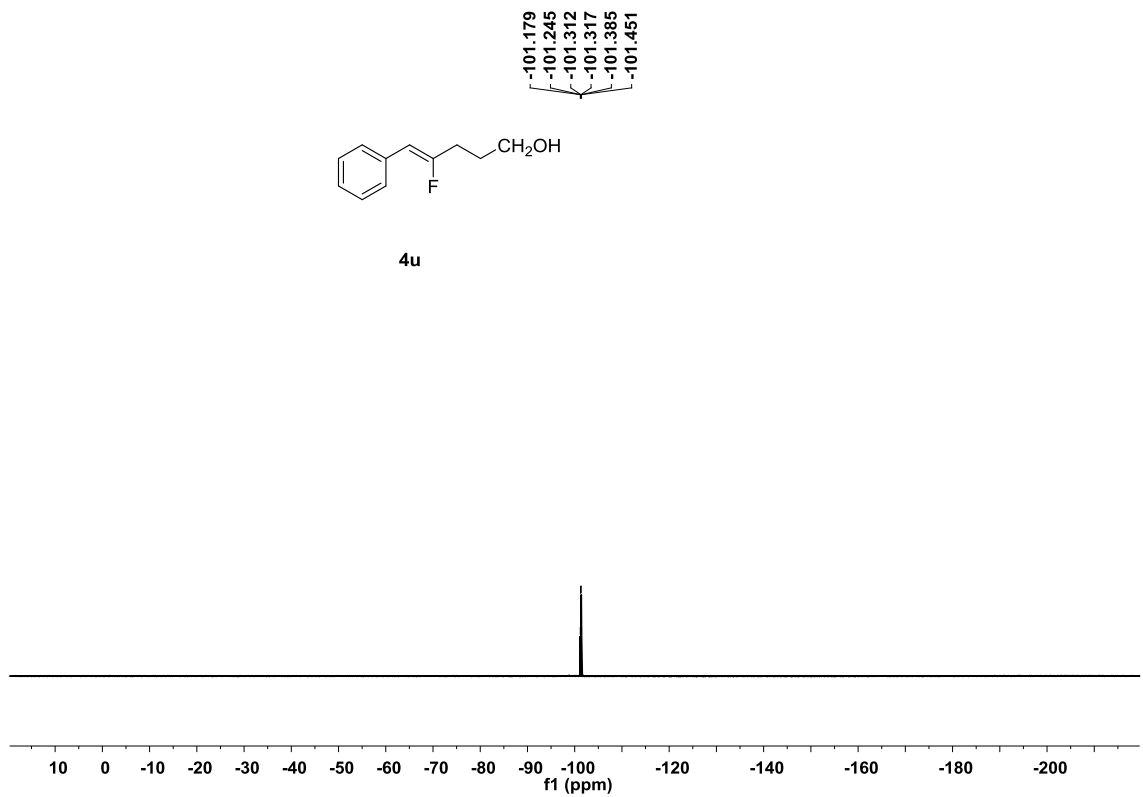
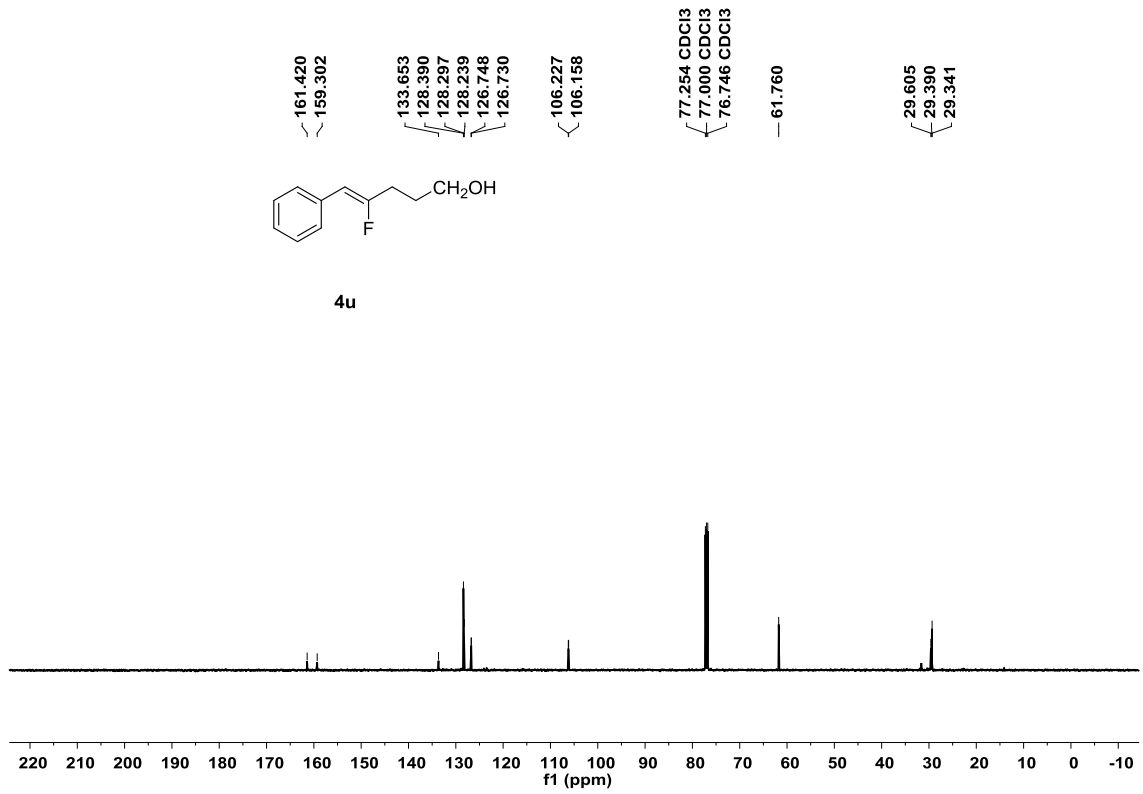
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4t





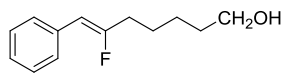


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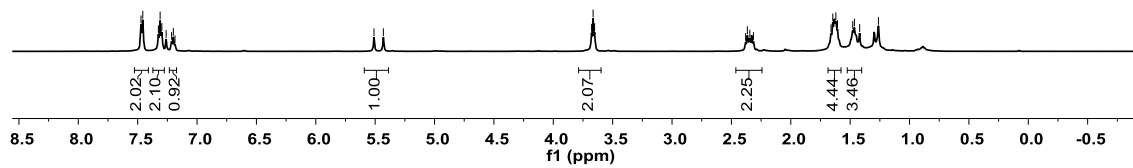
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4v



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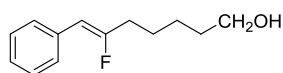
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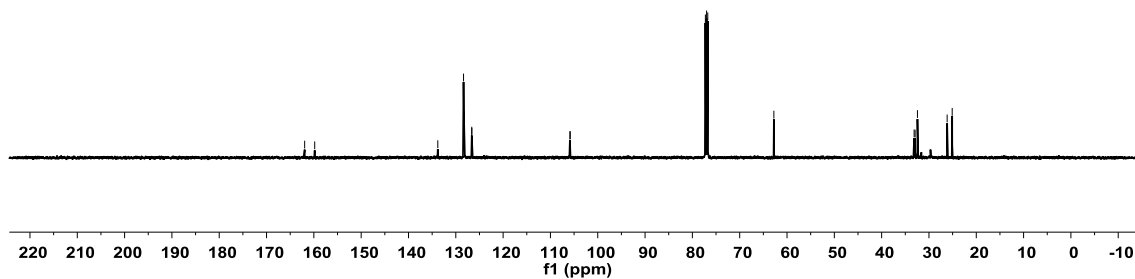
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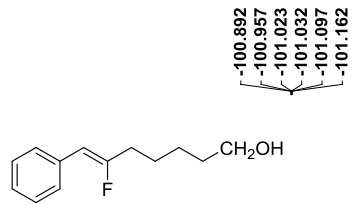
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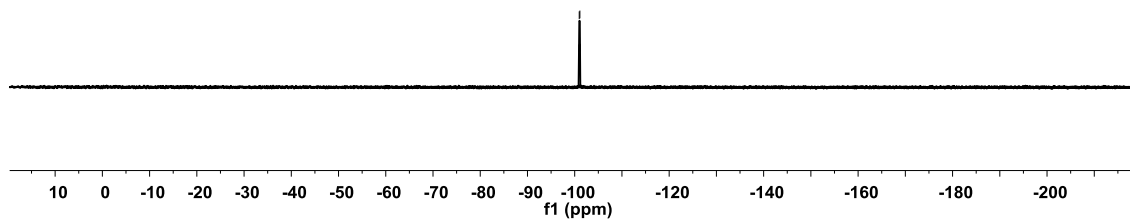


4v





4v

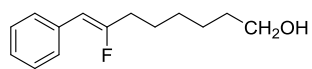


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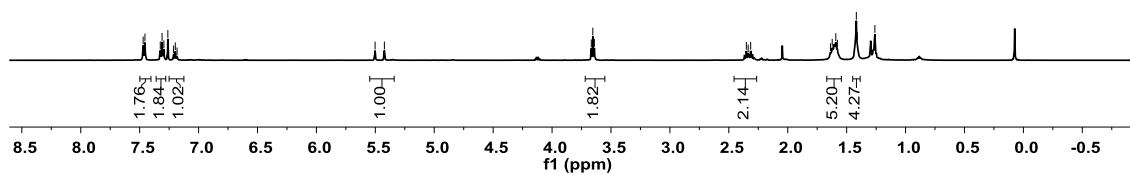
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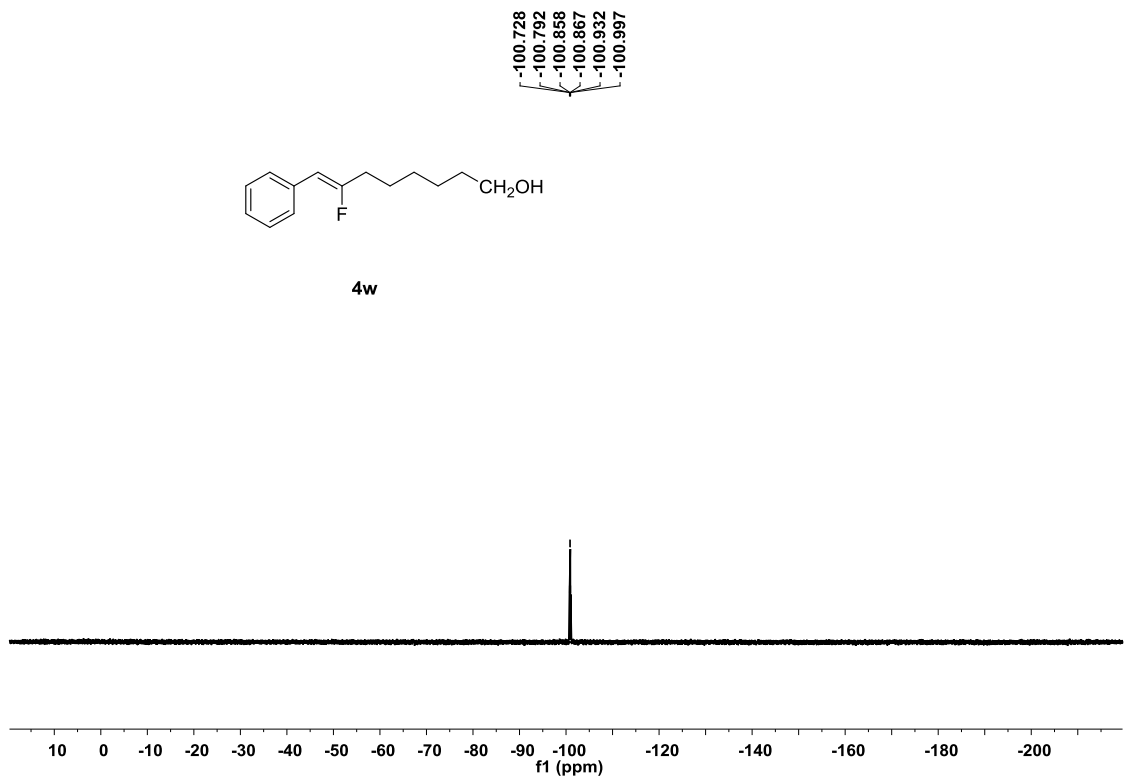
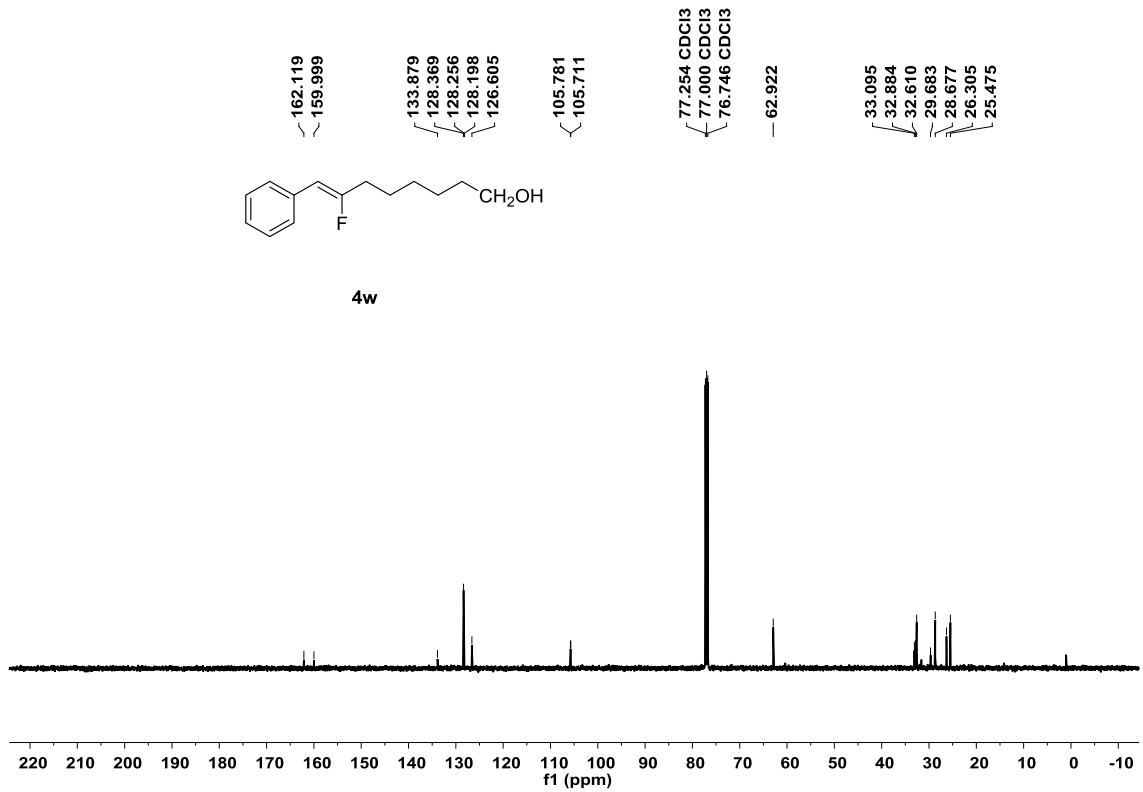
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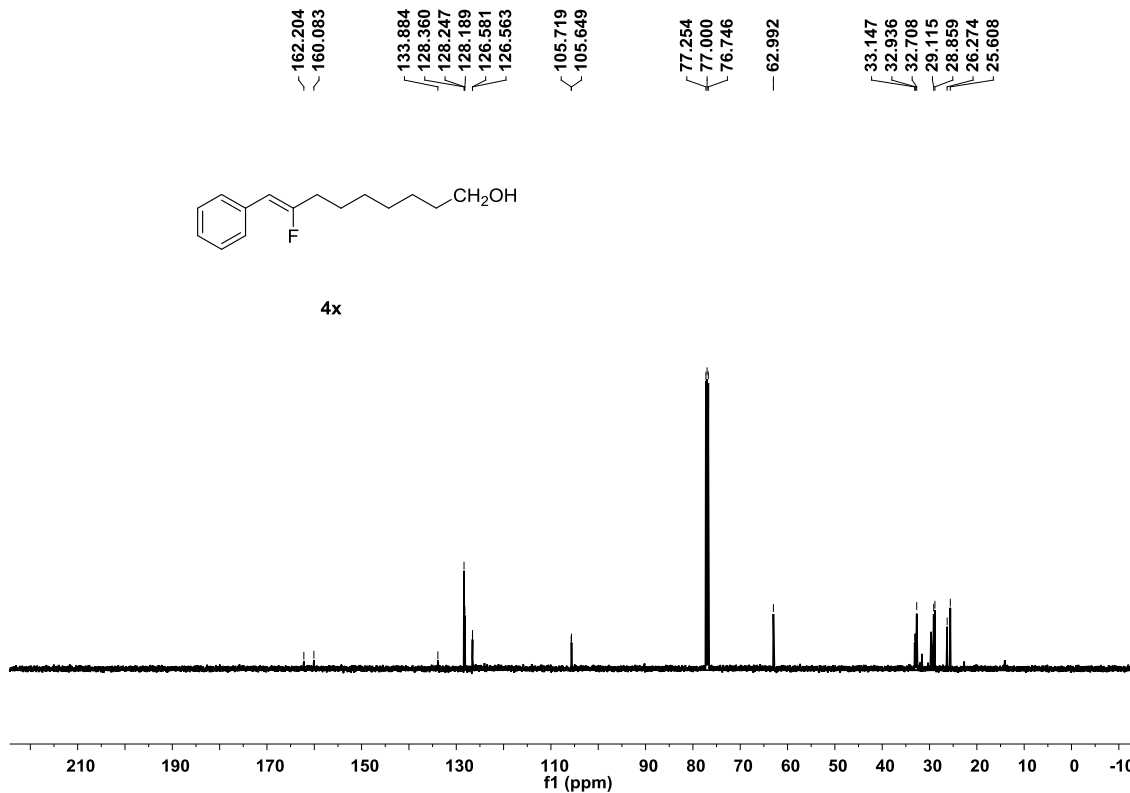
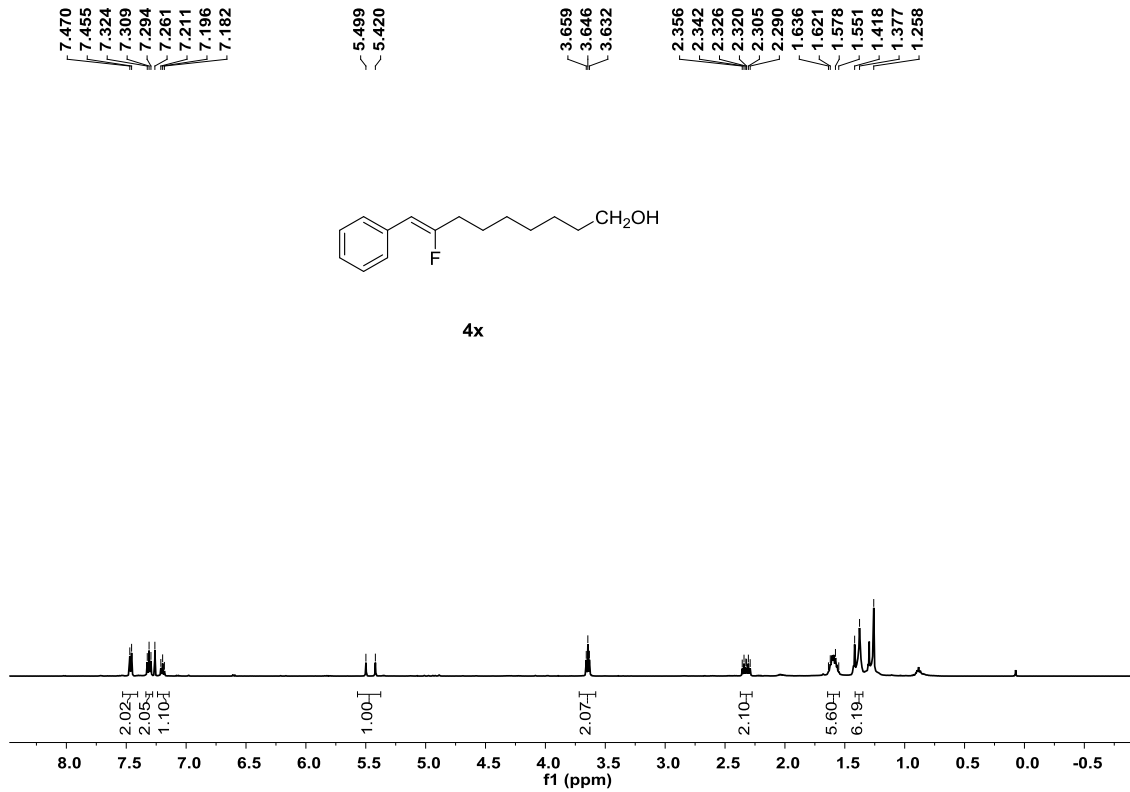


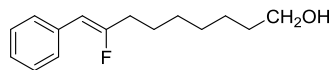
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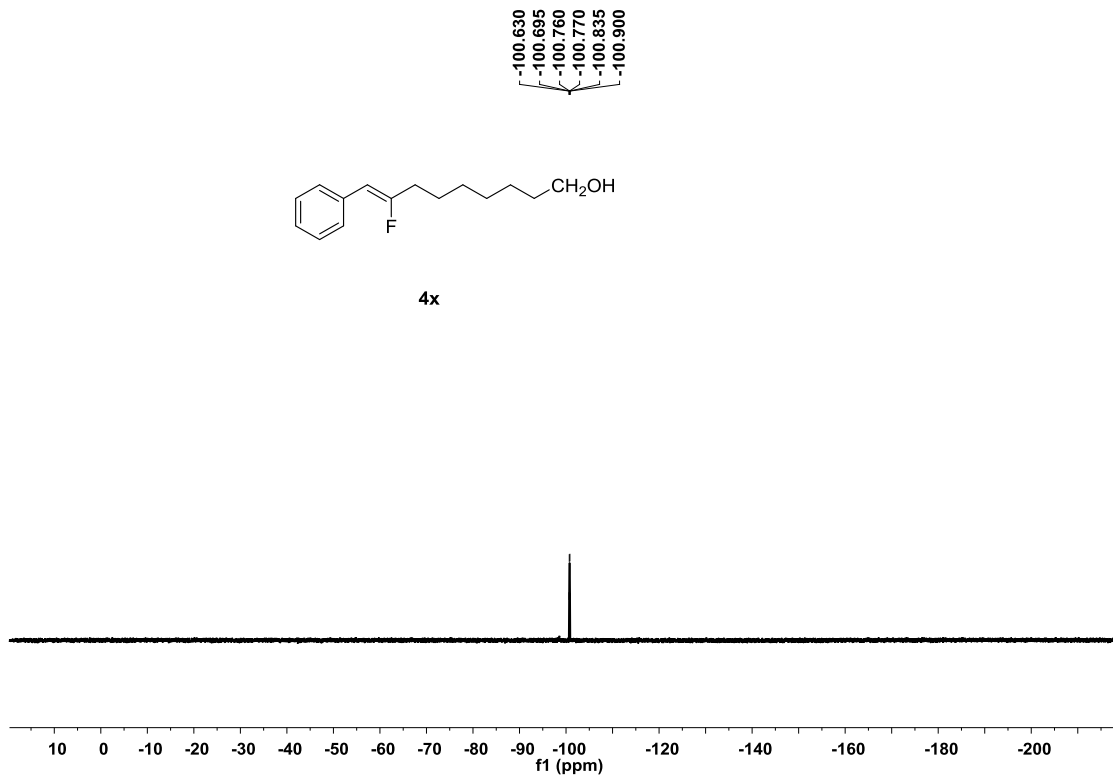






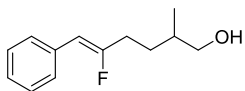


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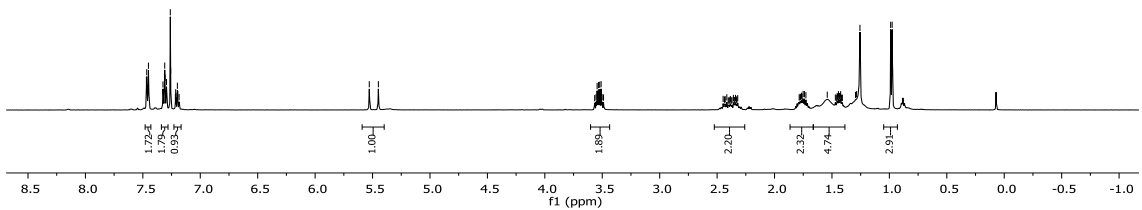


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TL-4-49

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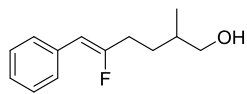


4y

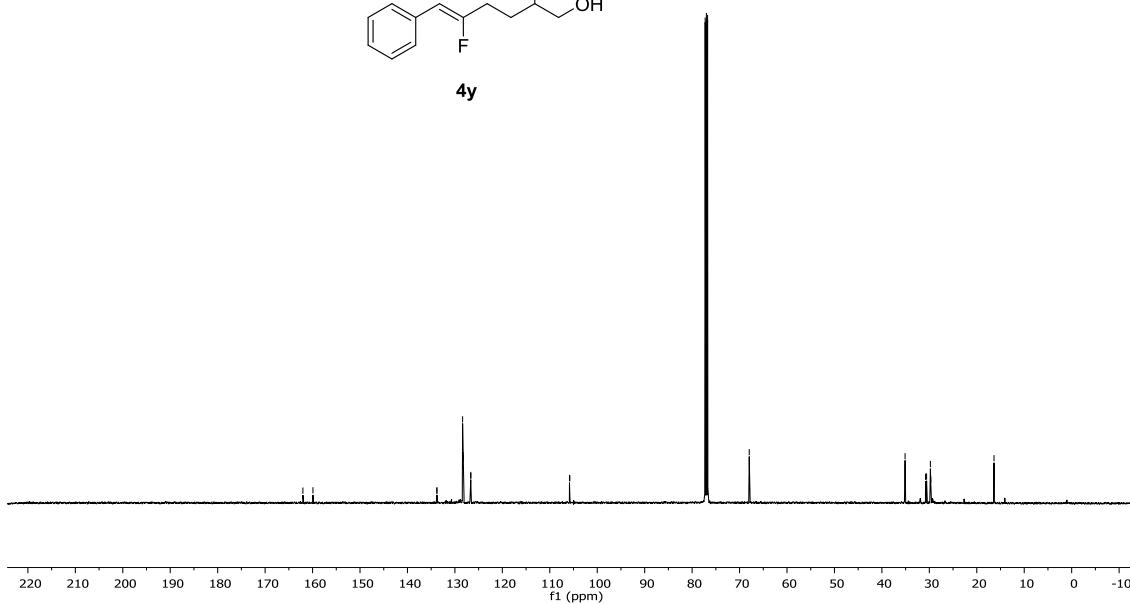


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13C AMX500  
TL-4-49

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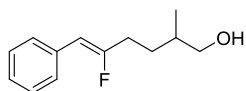


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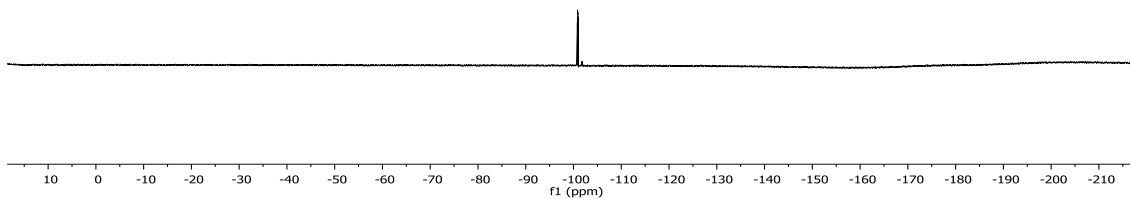


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tl-4-49

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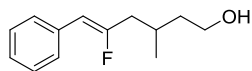


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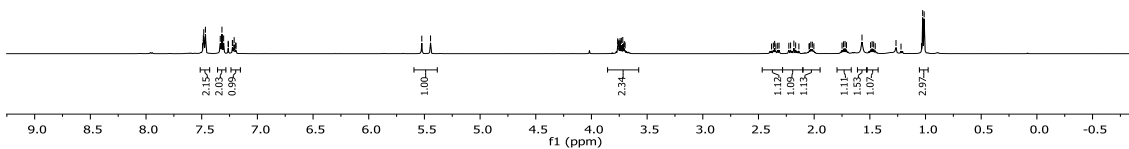


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TL-4-50

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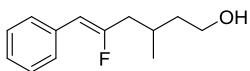


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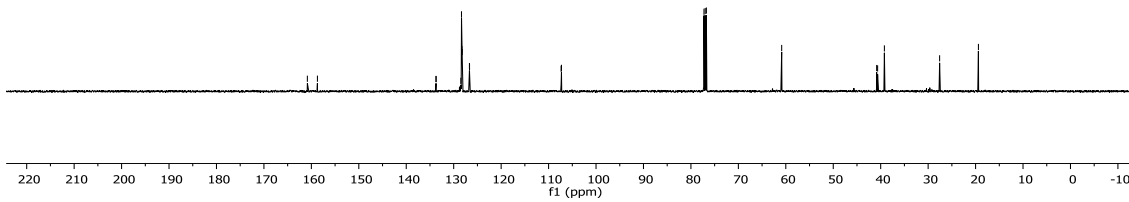


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TL-4-50

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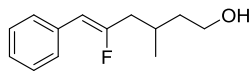


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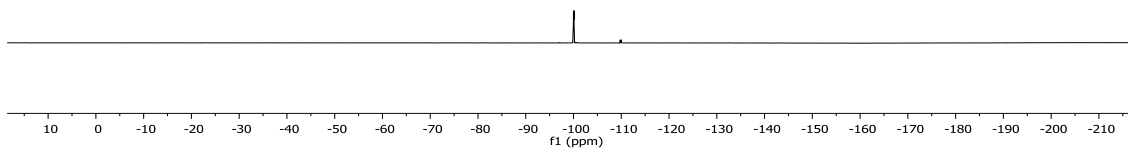


Mar18tl.4.fid  
tl-4-50

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4z



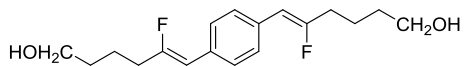
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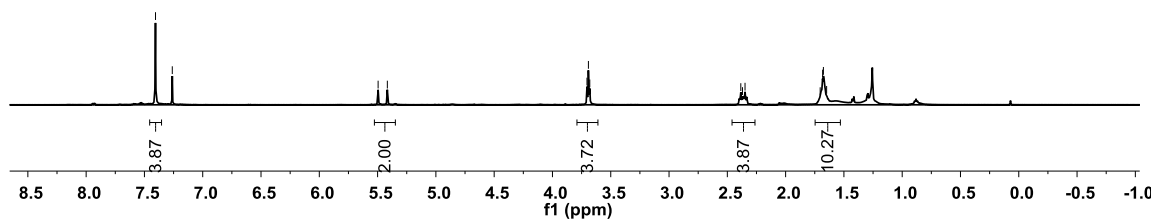
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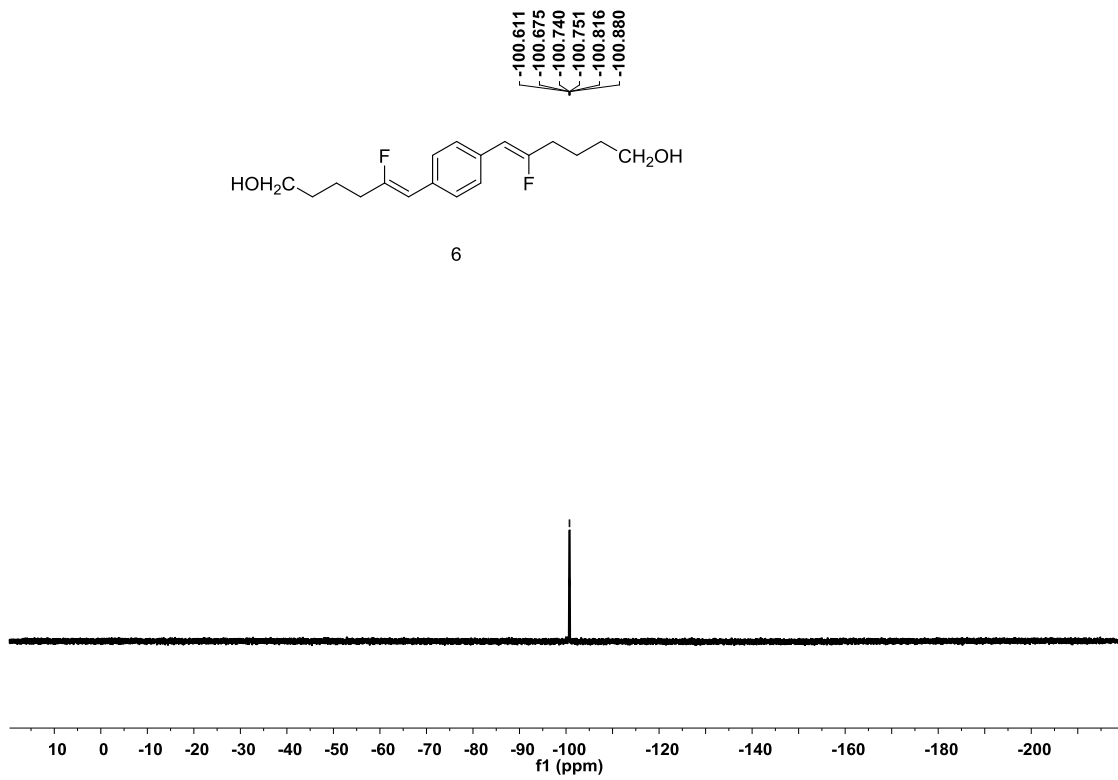
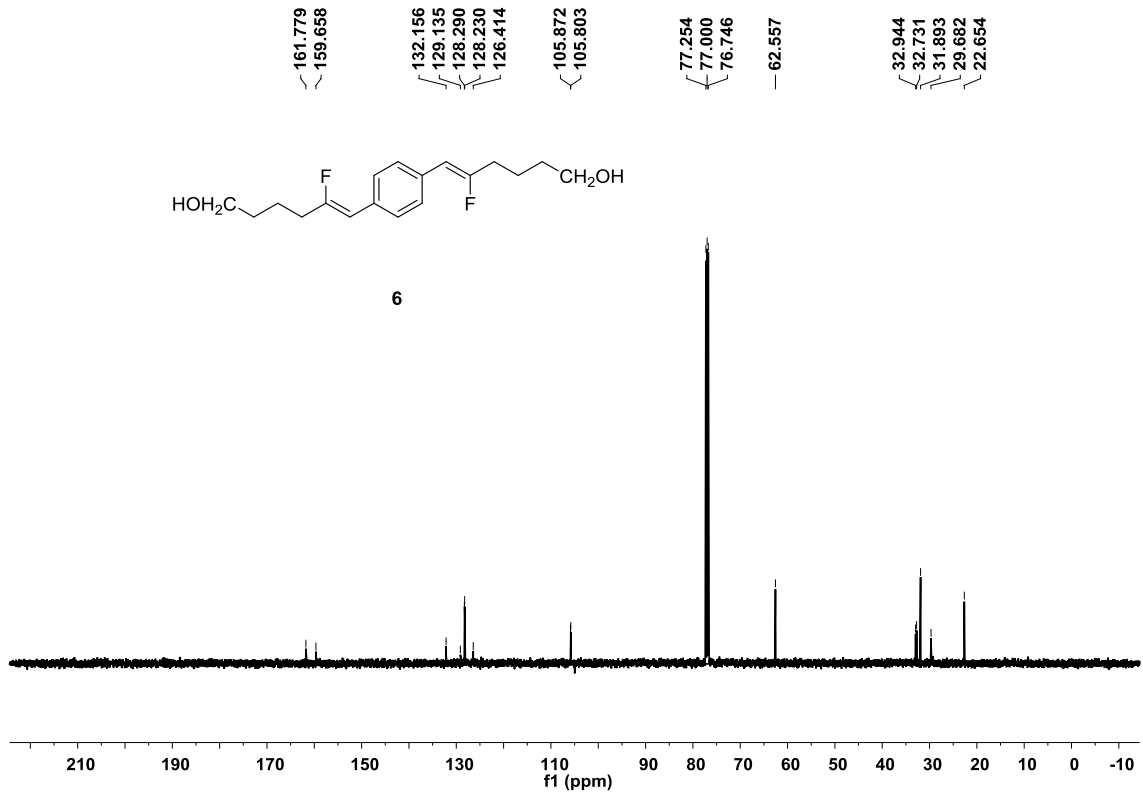
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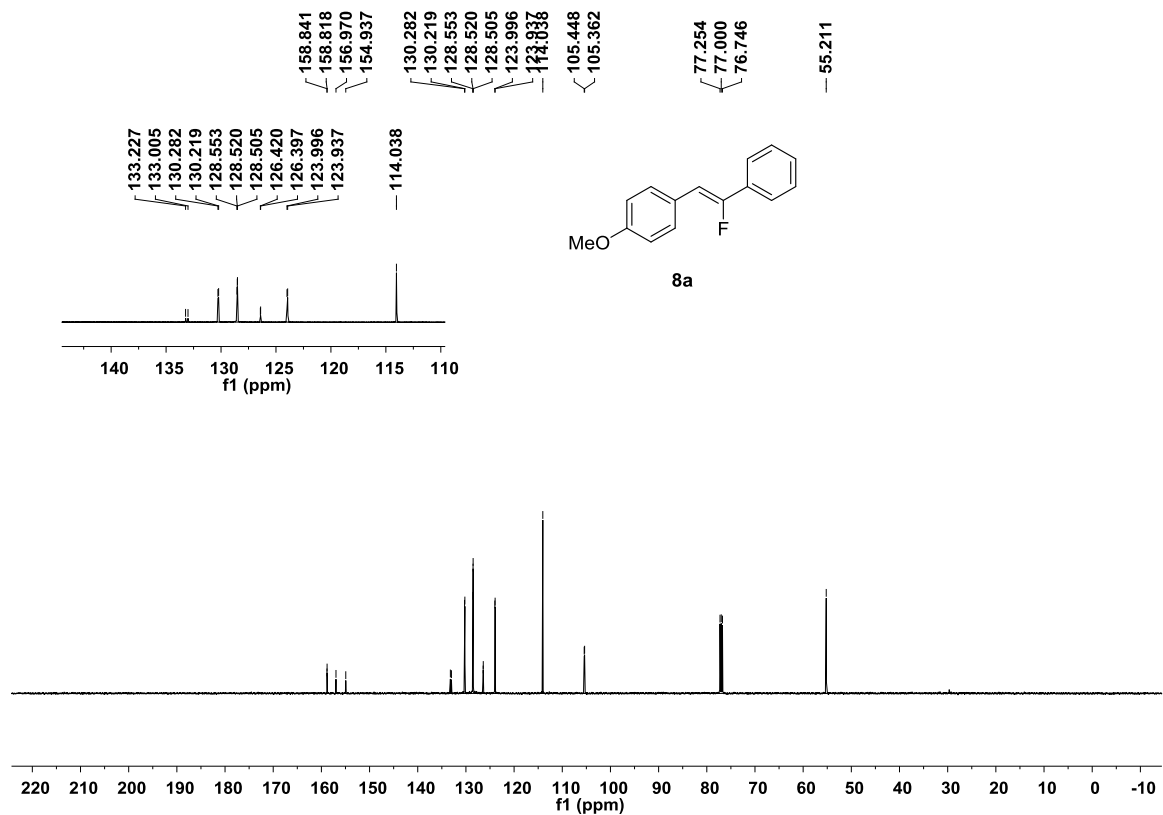
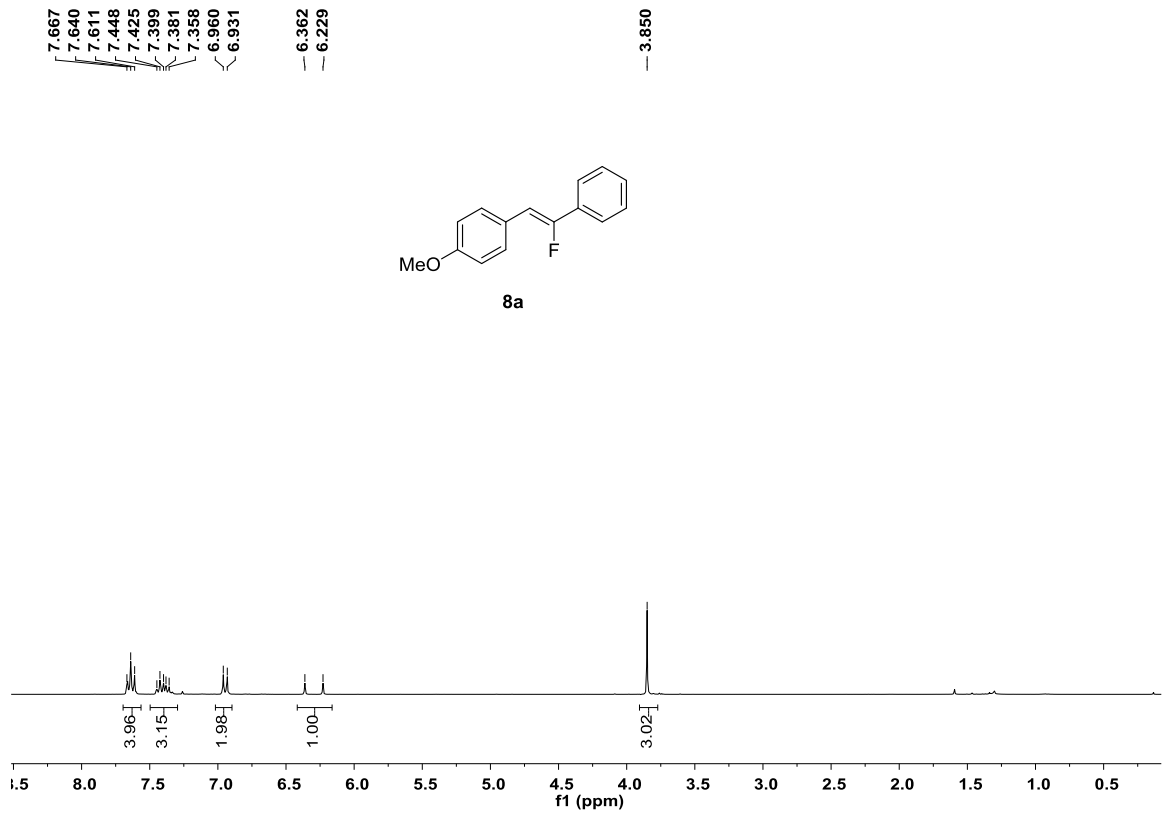
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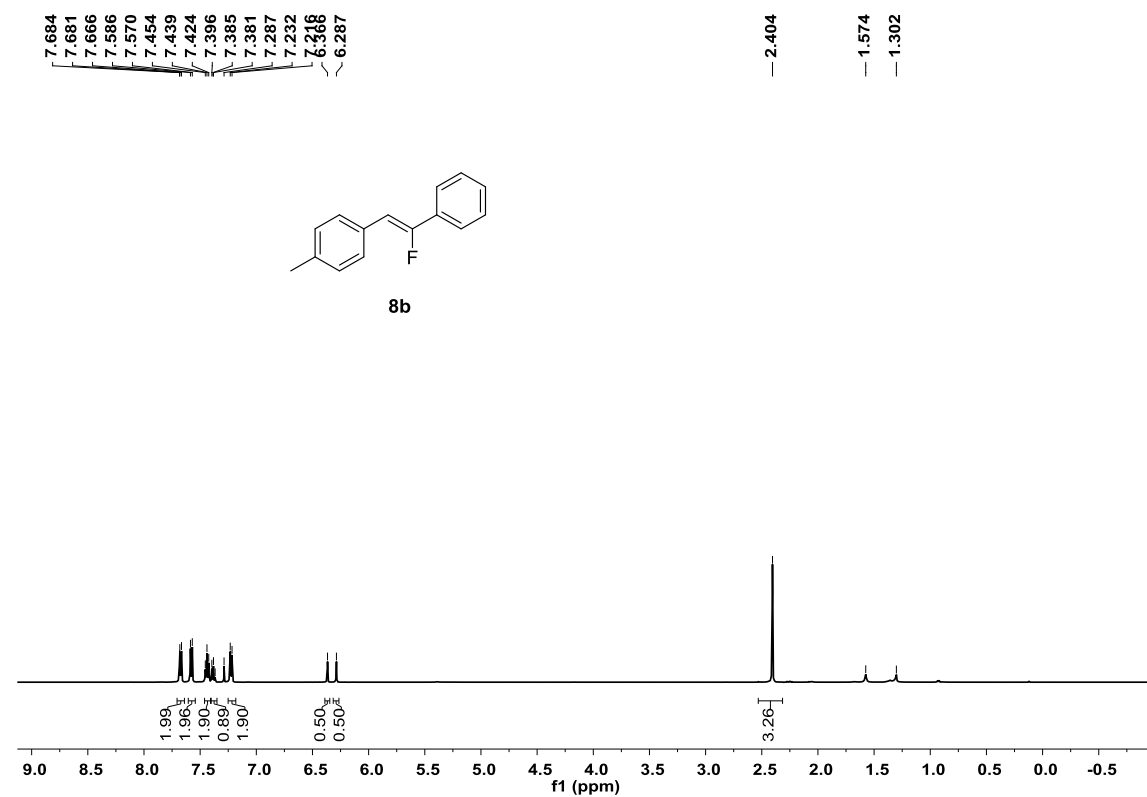
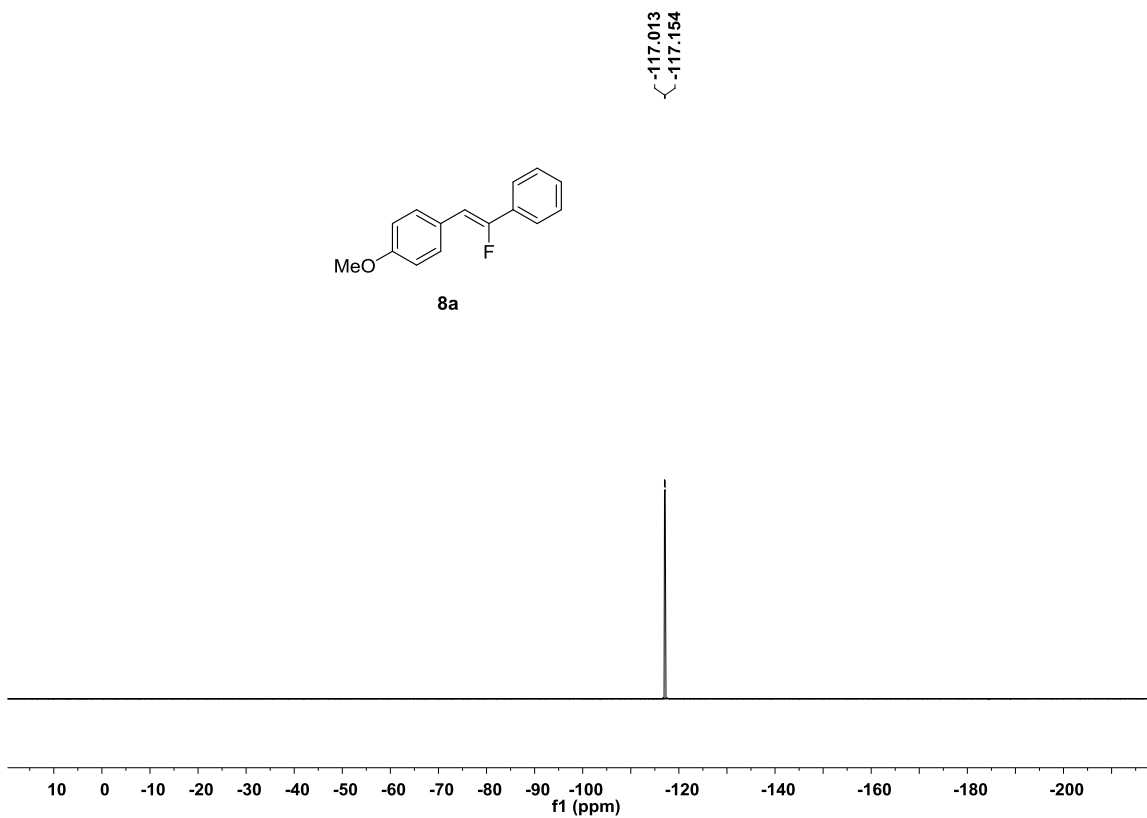


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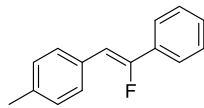




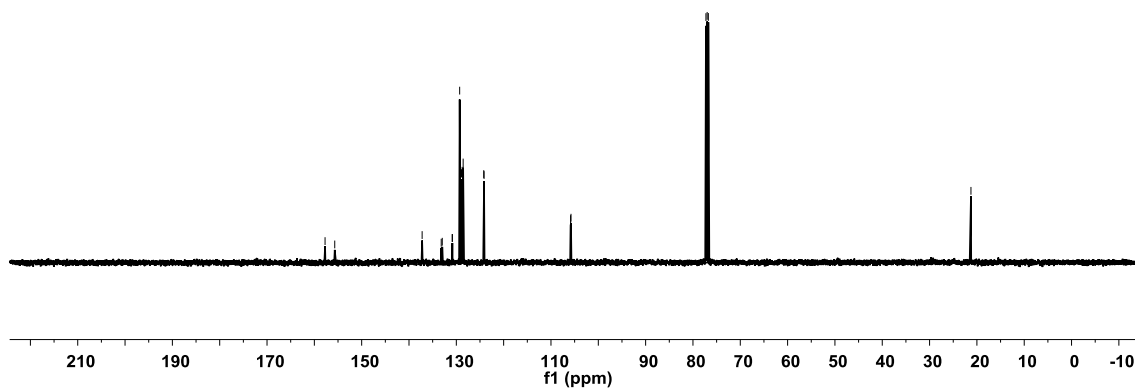
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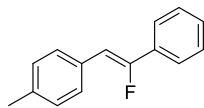
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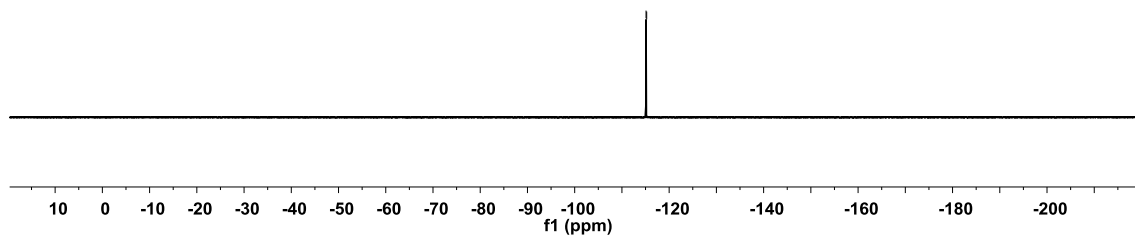
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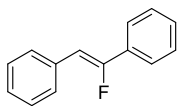
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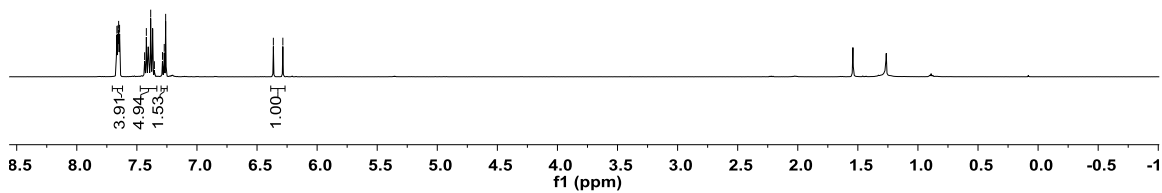
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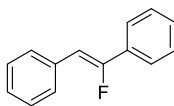
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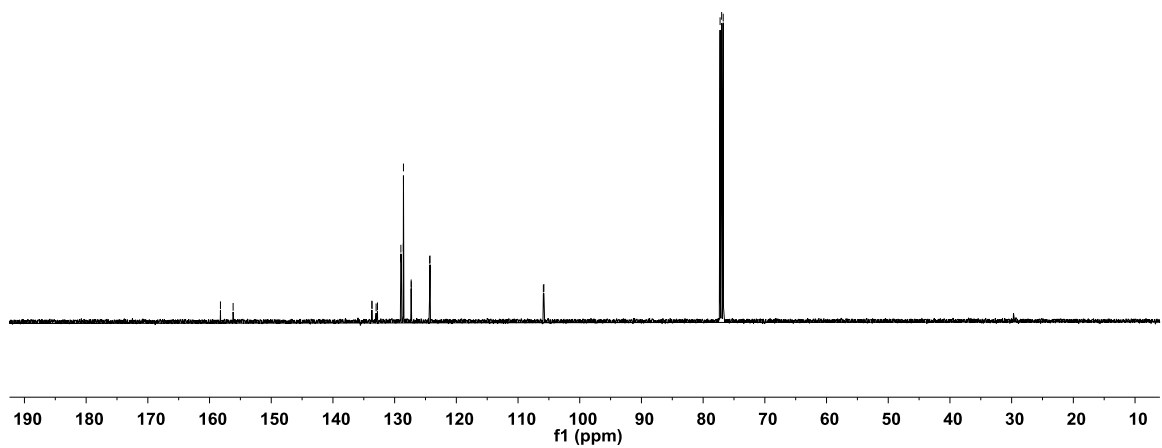
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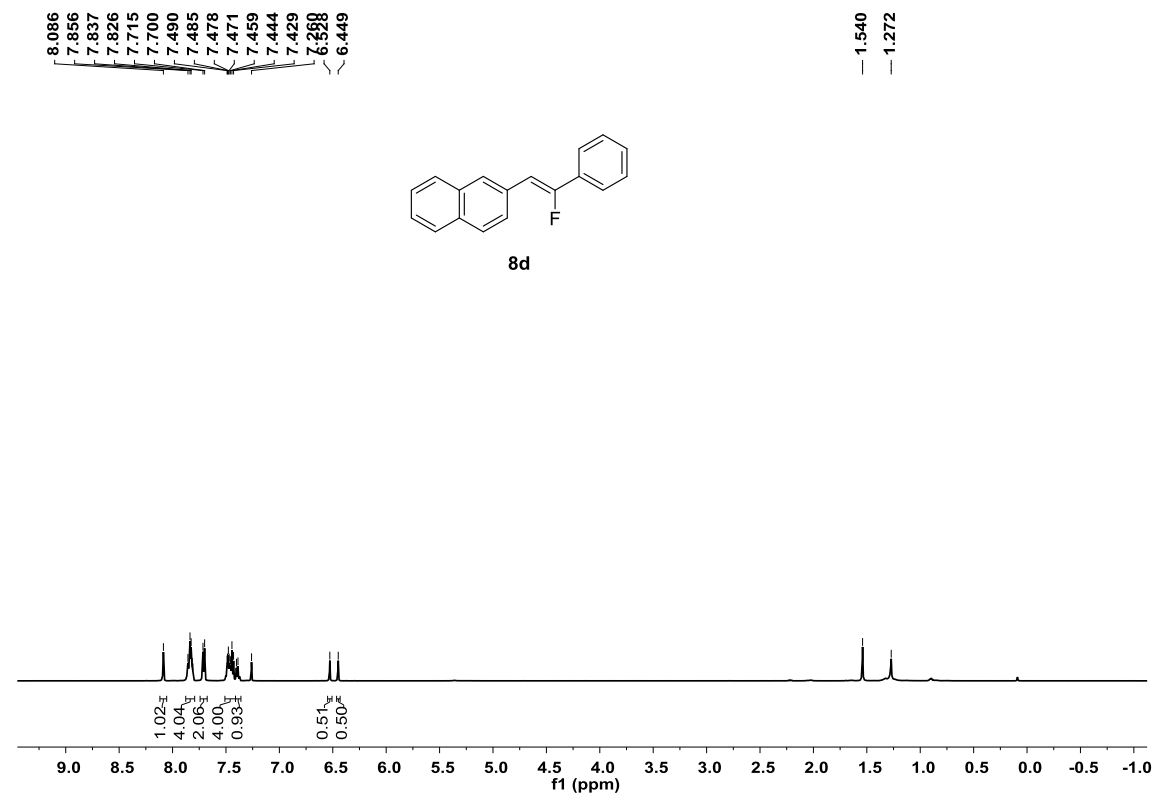
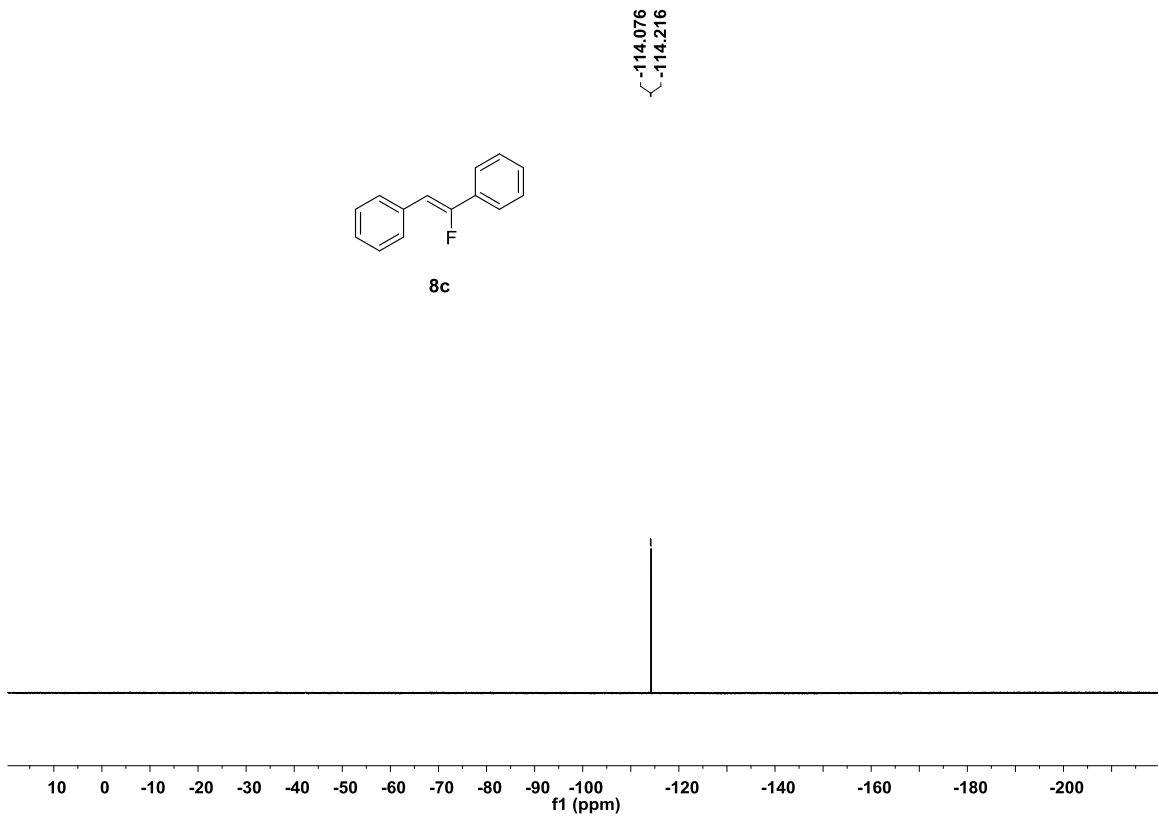


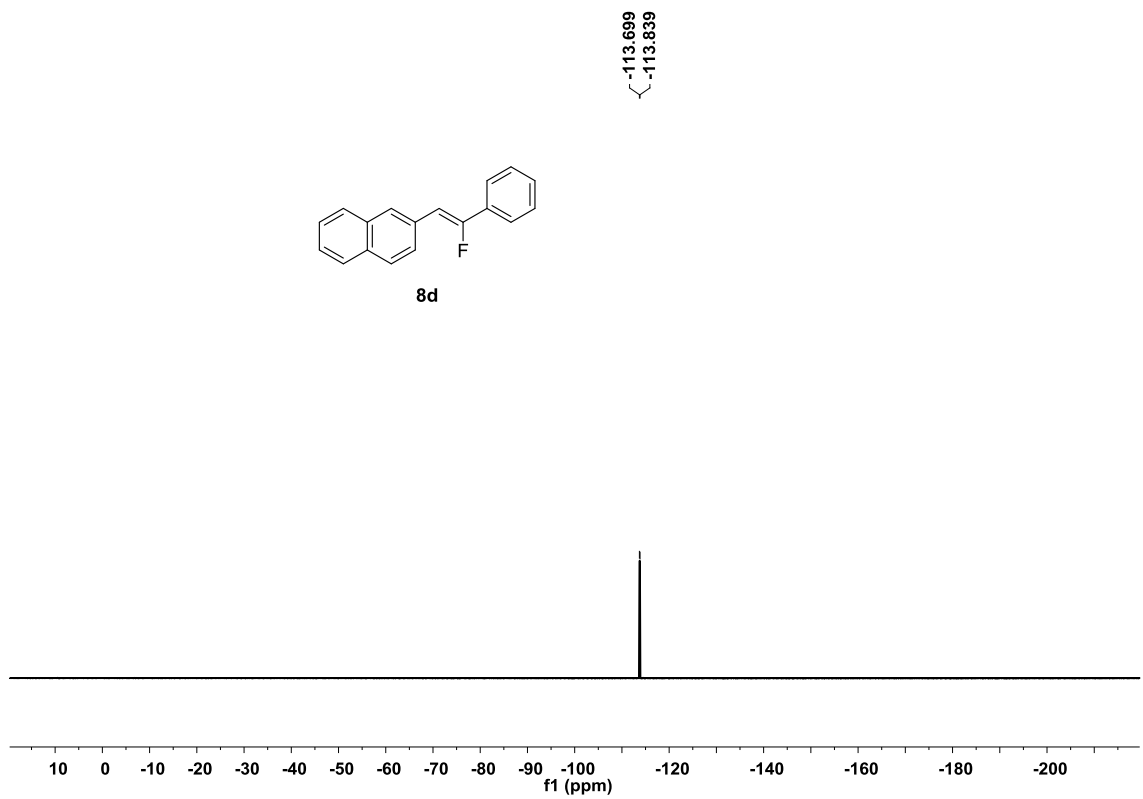
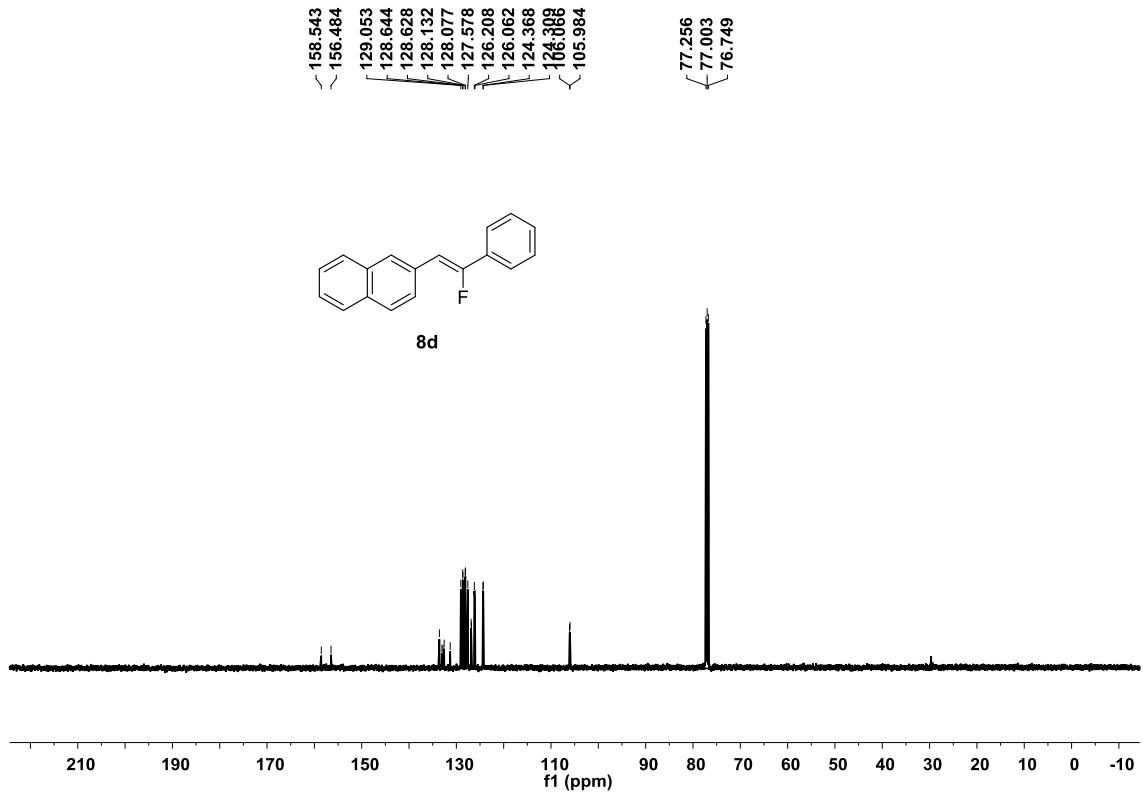
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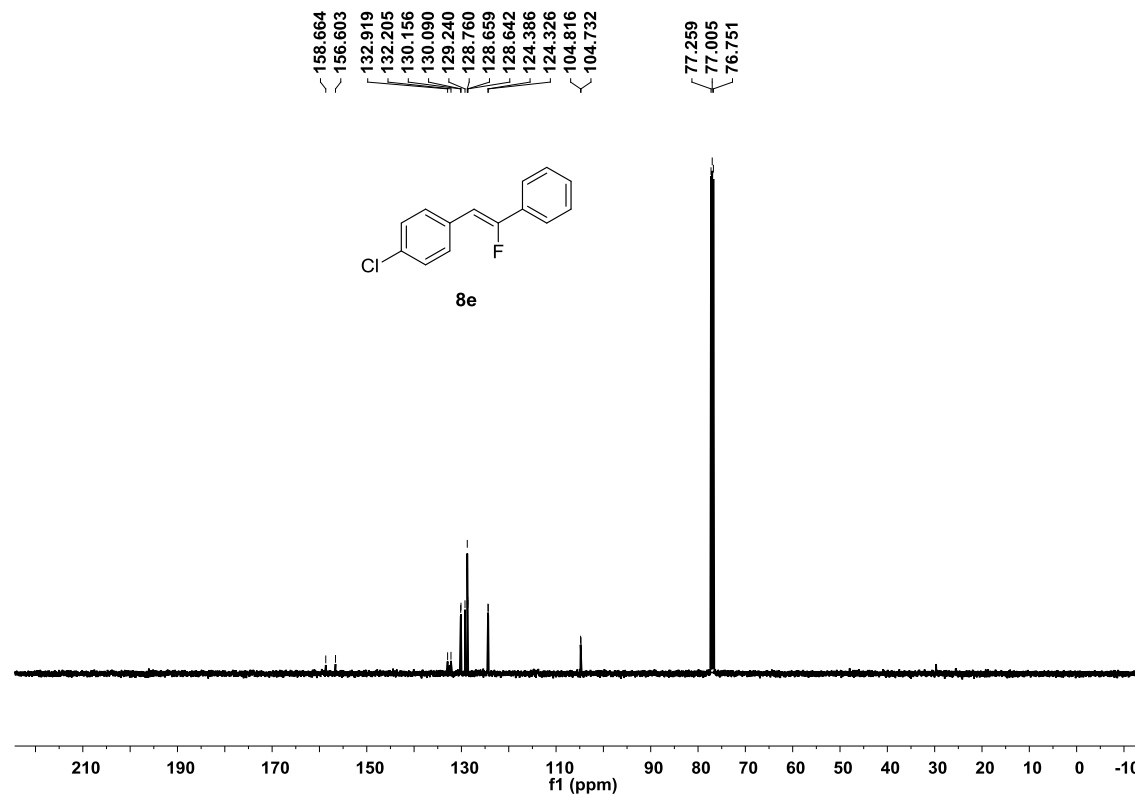
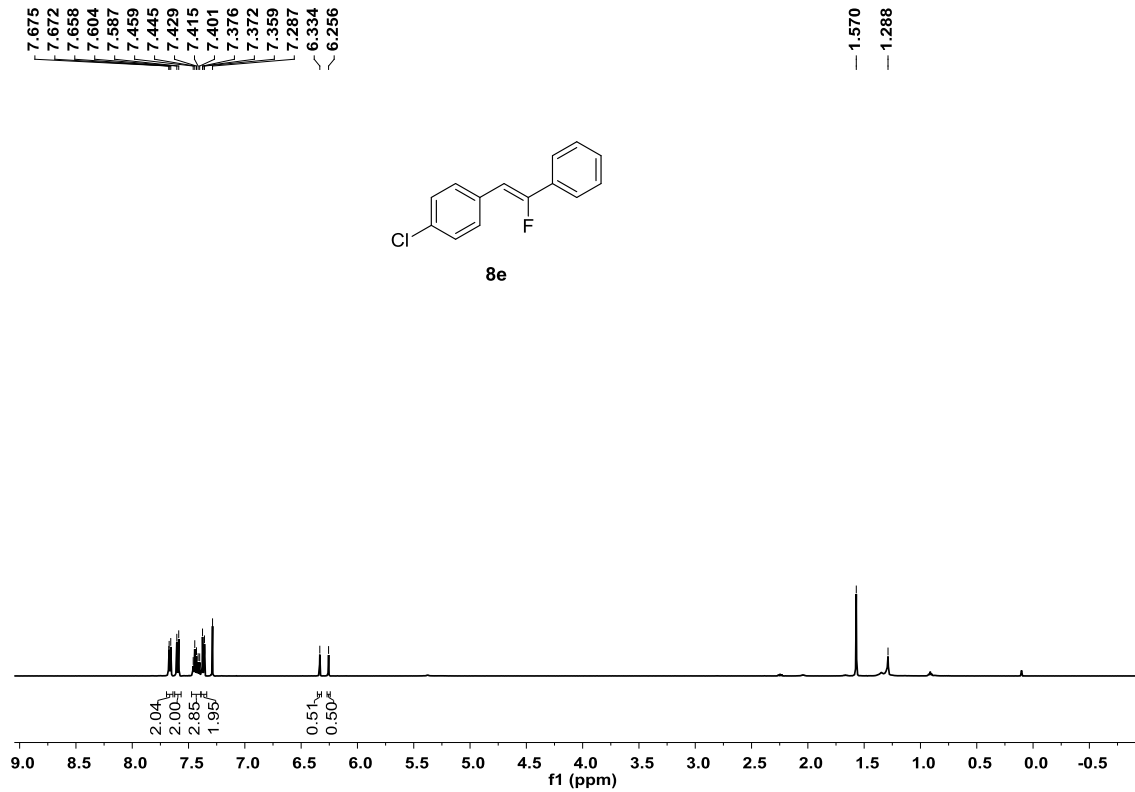


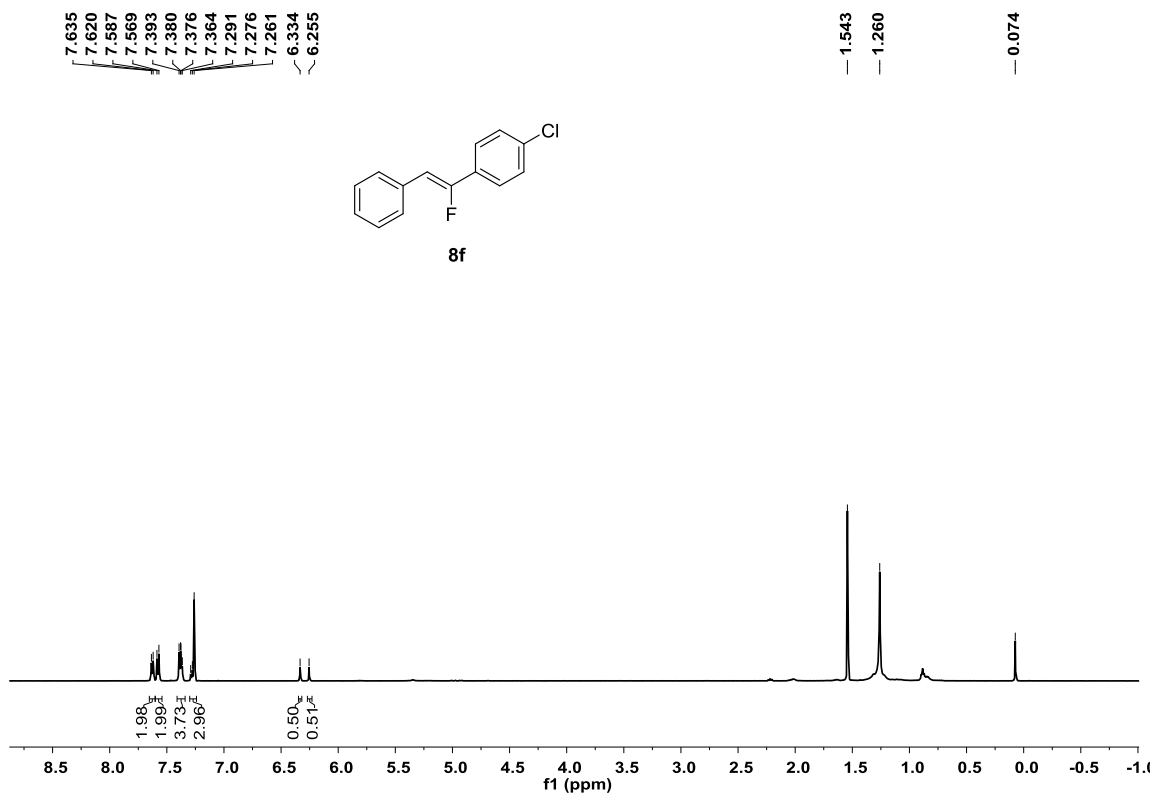
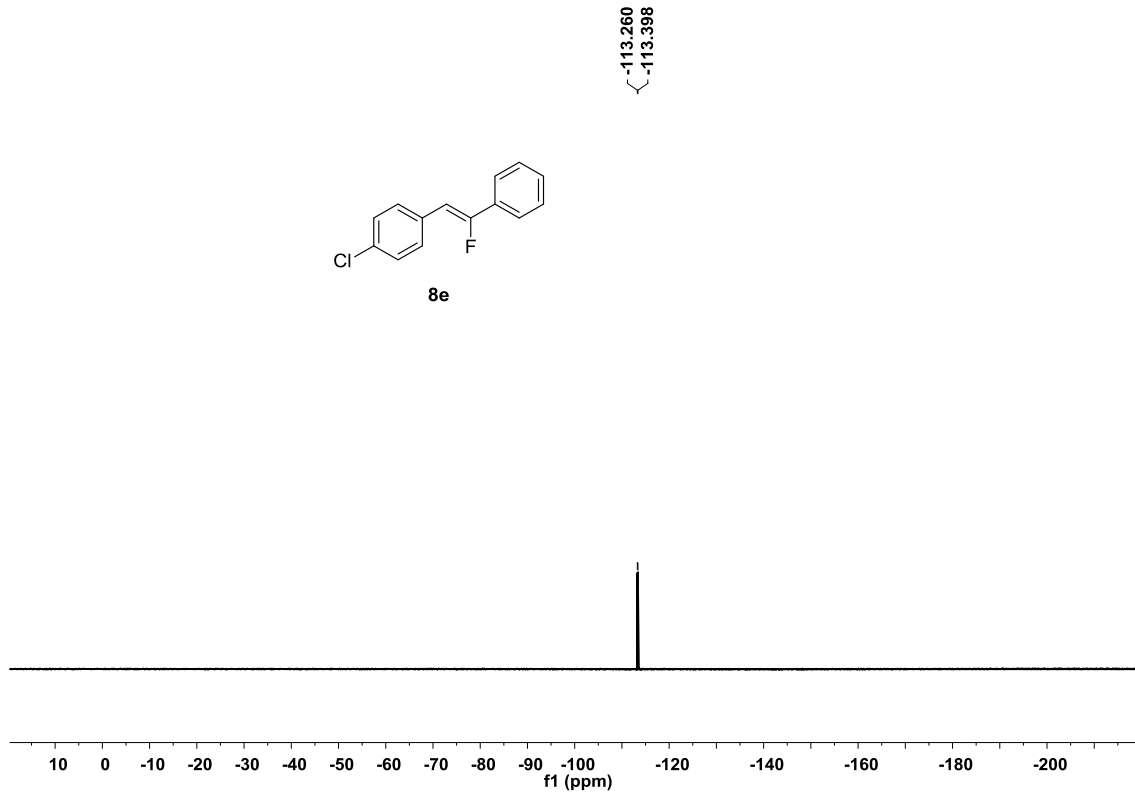
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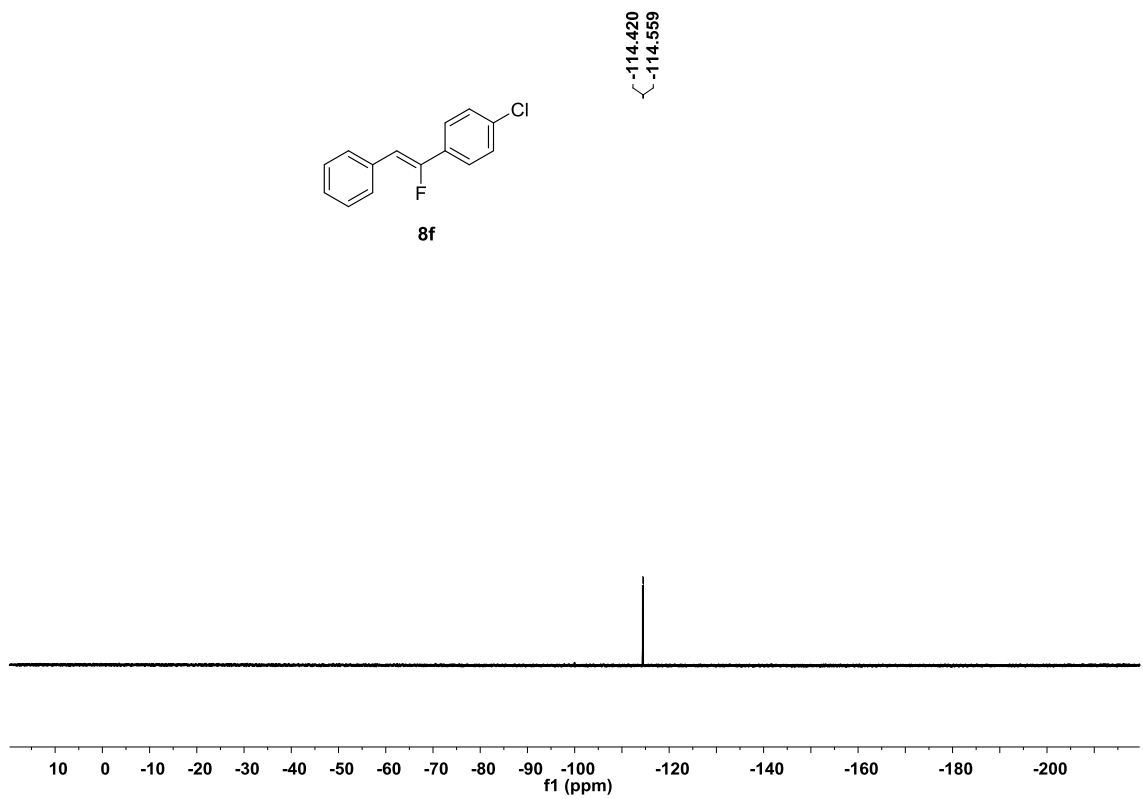
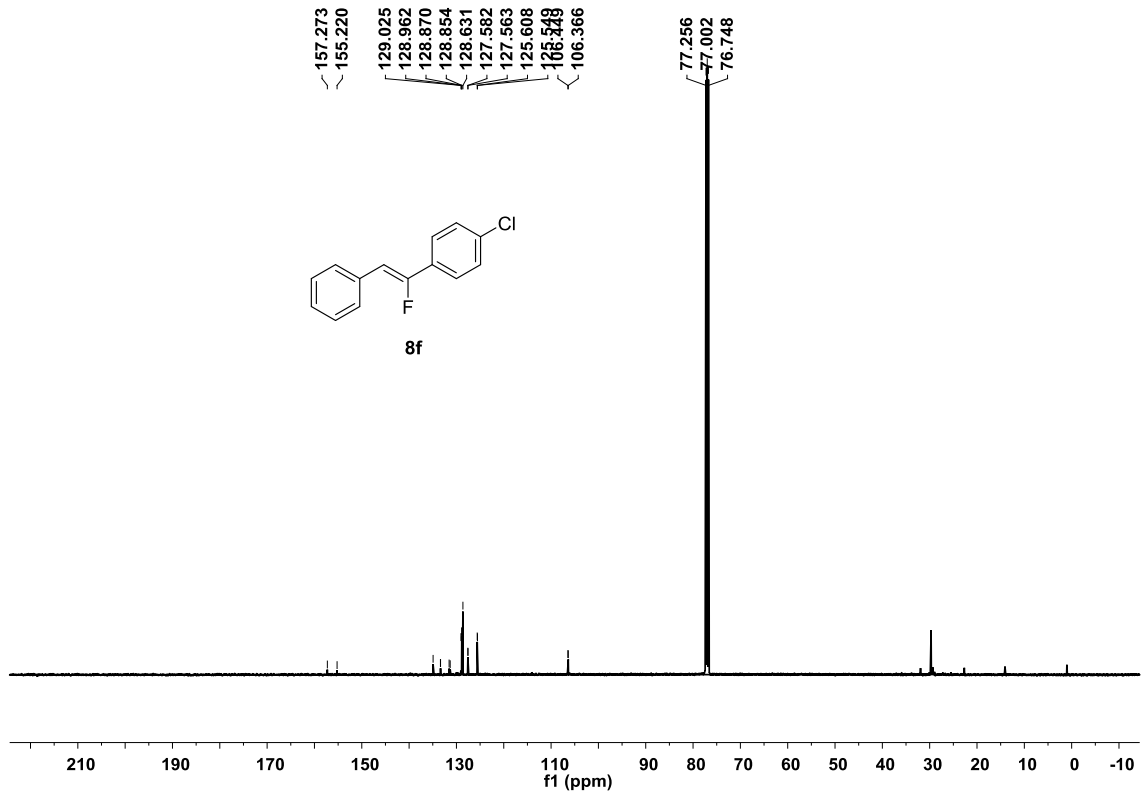






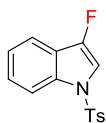




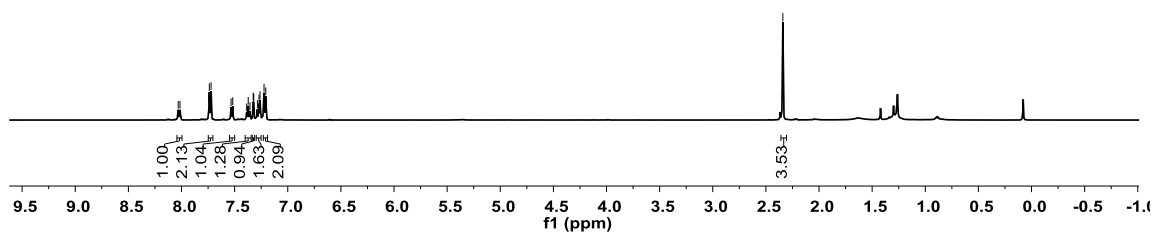


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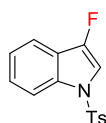
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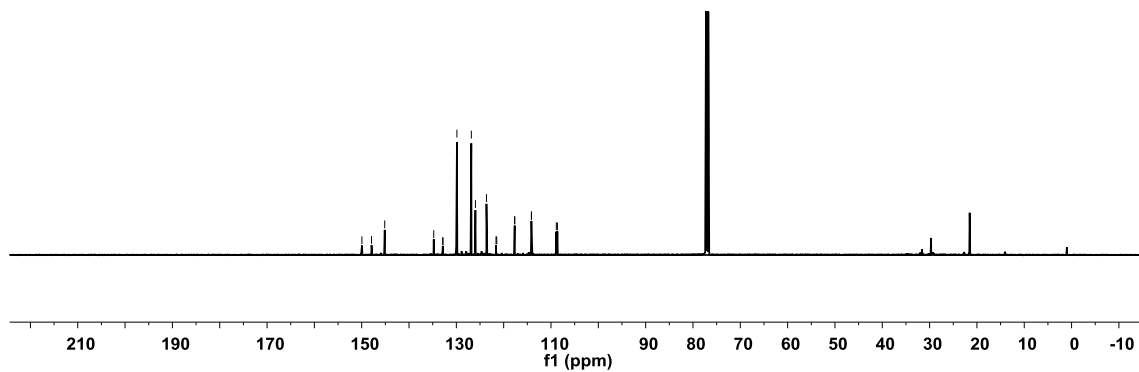
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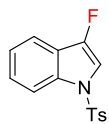
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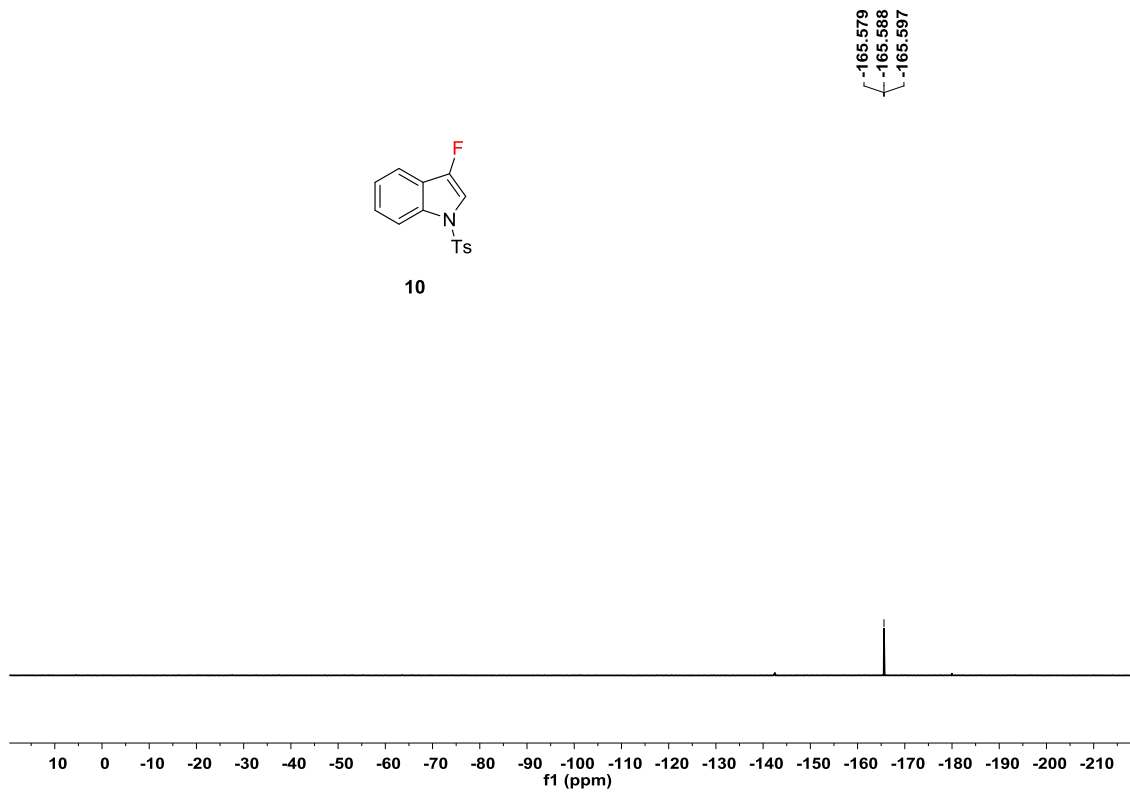
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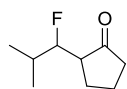




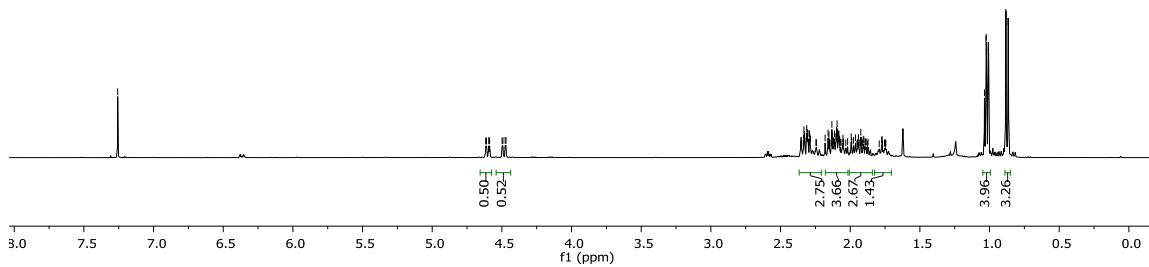
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0.42  
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0.29  
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0.18  
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0.16  
0.15  
0.14  
0.13  
0.12  
0.11  
0.10  
0.09  
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0.06  
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0.03  
0.02  
0.01  
0.00



13a



10913.2.fid  
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iPr  
218.343

97.354  
95.978

77.274  
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76.766

50.716  
50.529

38.721

31.016

30.858

22.858

22.826

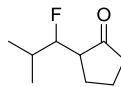
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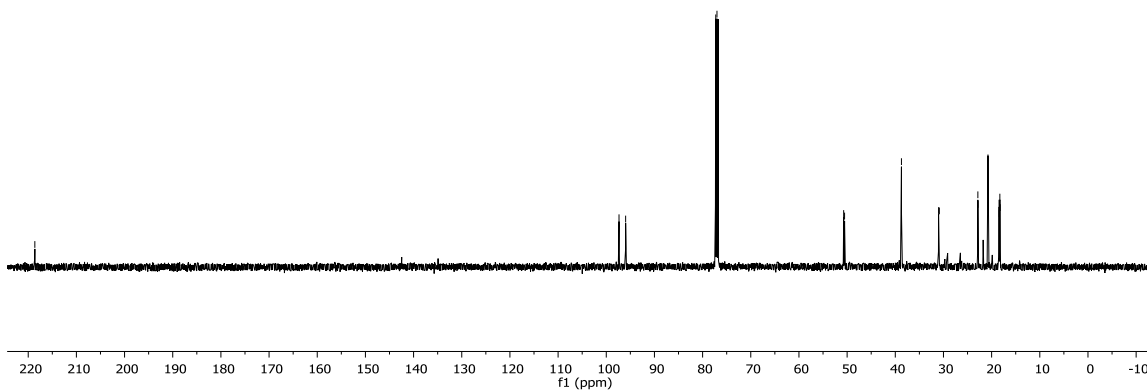
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18.291

18.227

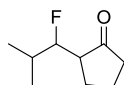


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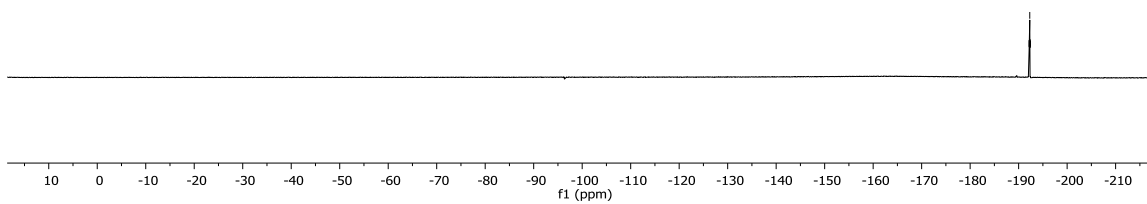


Sep13tl.11.fid  
tl-5-iPr

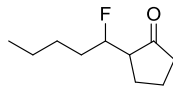
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192.329  
192.389  
192.421



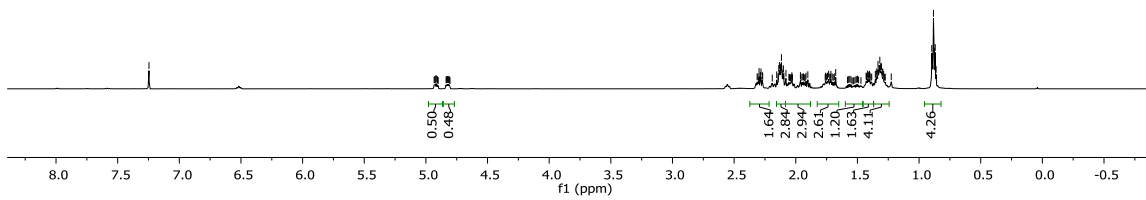
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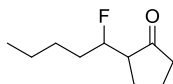
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 7.1867  
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 2.1944  
 2.138  
 2.133  
 2.127  
 2.122  
 2.116  
 2.101  
 2.097  
 2.080  
 2.056  
 2.037  
 2.032  
 1.962  
 1.949  
 1.941  
 1.938  
 1.924  
 1.917  
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 1.758  
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 1.705  
 1.687  
 1.676  
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 1.422  
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 1.413  
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 0.883  
 0.876  
 0.869  
 0.862



**13b**

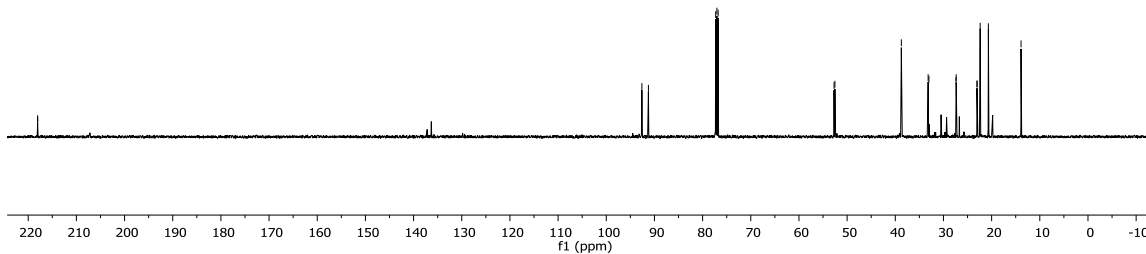


137.0925.fid  
 137.0925  
 211.8323

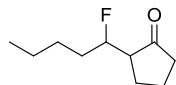


**13b**

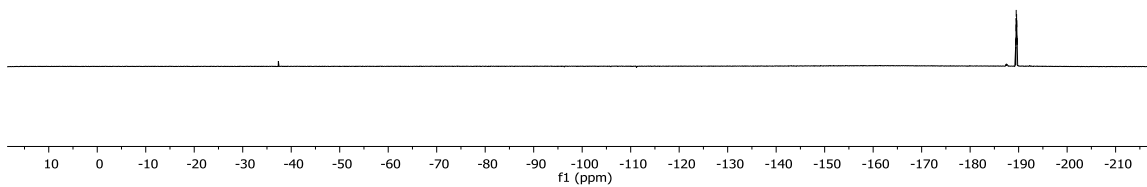
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 91.251  
 77.284  
 77.030  
 76.775  
 52.715  
 52.533  
 38.743  
 33.183  
 33.019  
 27.397  
 27.327  
 23.043  
 23.013  
 22.361  
 20.676  
 13.899



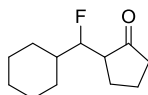
-189.375  
-189.413  
-189.459  
-189.499  
-189.542  
-189.582  
-189.589  
-189.619  
-189.626  
-189.670  
-189.709



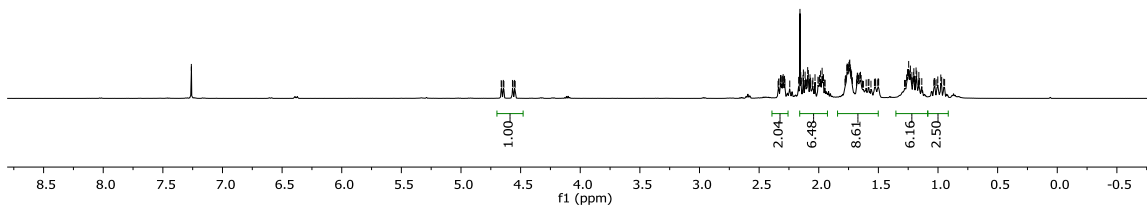
13b



189.375  
189.413  
189.459  
189.499  
189.542  
189.582  
189.589  
189.619  
189.626  
189.670  
189.709



13c

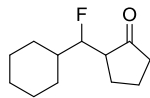


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13C AMX500  
CY-218

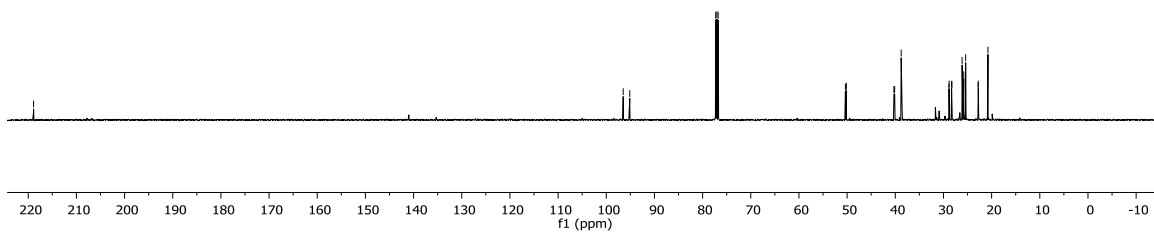
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95.118

77.282  
77.028  
76.775

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50.168  
40.284  
40.130  
38.776  
28.865  
28.826  
28.308  
28.247  
26.127  
25.787  
25.391  
22.799  
22.768  
20.763

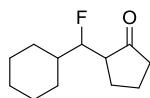


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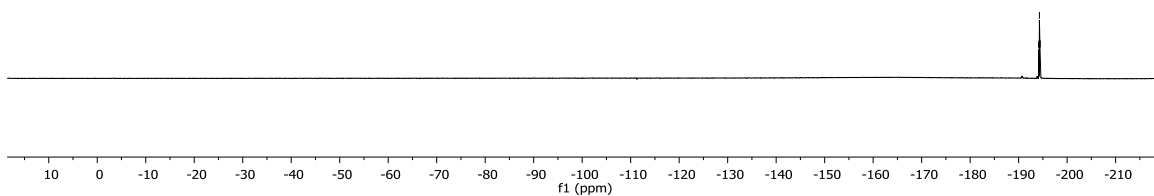


Sep09tl.3.fid  
tl-5-Cy-1

194.160  
194.191  
194.256  
194.286  
194.317  
194.382  
194.412



13c



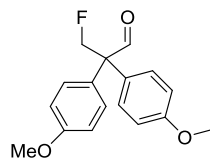
t0916.9.fid

9.852  
9.847

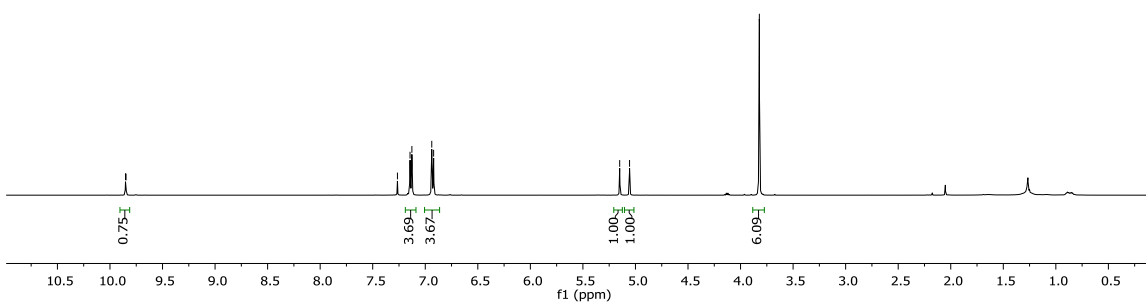
7.265  
7.145  
7.127  
6.938  
6.920

5.150  
5.056

3.821



14a



Sep16tl.12.fid  
tl-5-55-1

197.503  
197.469

159.219

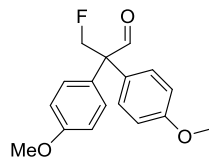
130.010  
129.996  
129.034  
129.006

114.384

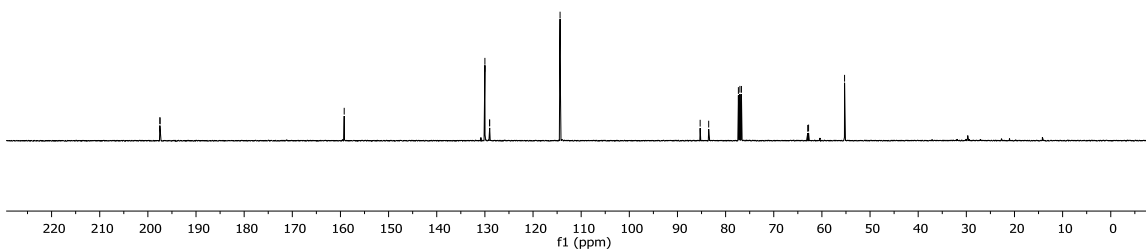
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77.346  
77.028  
76.710

62.946  
62.767

55.293

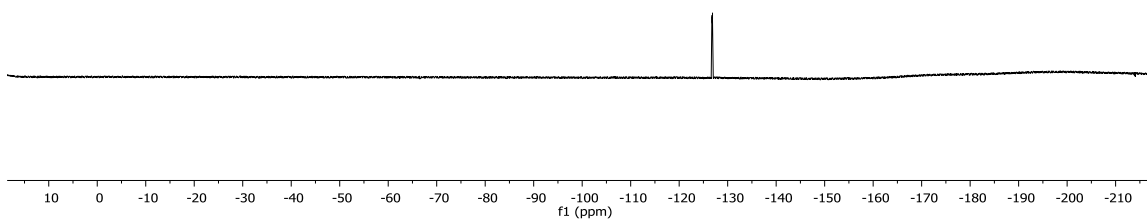
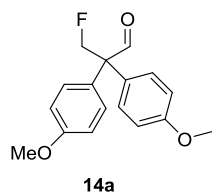


14a



Sep16tl.10.fid  
tl-5-55-1

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-126.731  
-126.866  
-126.876



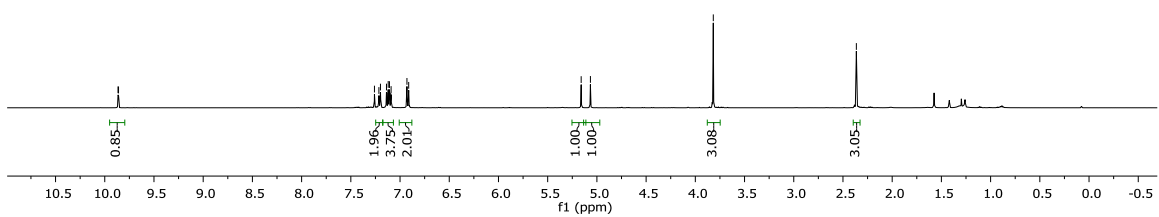
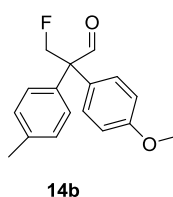
tl0924.1.fid  
1H AMX500  
TL-5-60 p-Me

7.260  
7.215  
7.199  
7.138  
7.125  
7.120  
7.108  
7.095  
7.091  
6.930  
6.912

5.160  
5.066

3.818

2.364



tl0924.2.fid  
13C AMX500  
TL-5-60 p-Me

197.569  
197.542

159.185

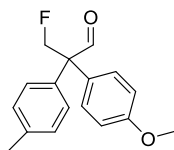
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128.678

114.349

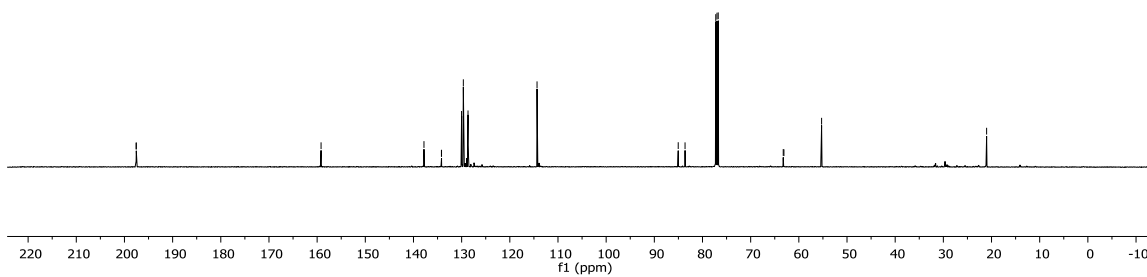
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76.738

63.239  
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21.017

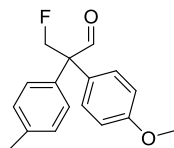


14b

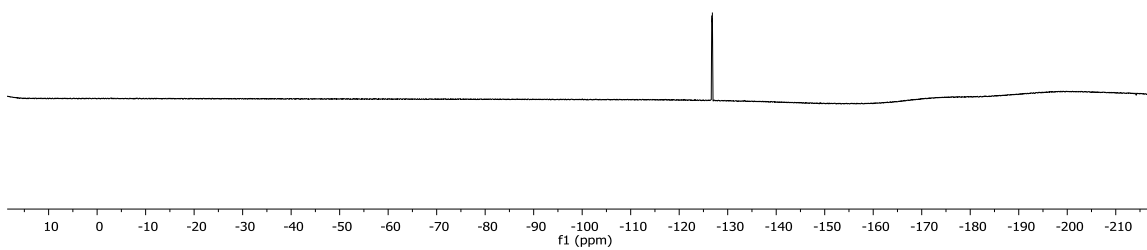


Sep29-2016-tl.4.fid  
tl-5-60 p-Me

126.700  
126.845



14b

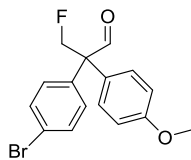




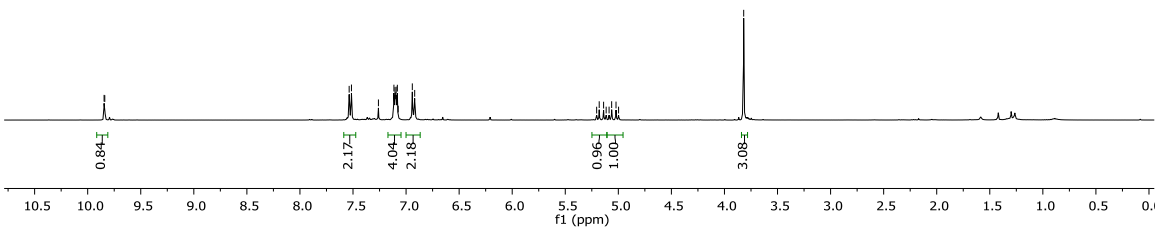
Sep30-2016-tl-5-61 p-Br  
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9.839

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7.515  
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7.114  
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7.089  
7.093  
7.087  
7.082  
7.074  
6.941  
6.919  
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5.180  
5.139  
5.115  
5.087  
5.063  
5.022  
4.998

3.819



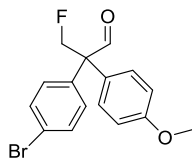
14c



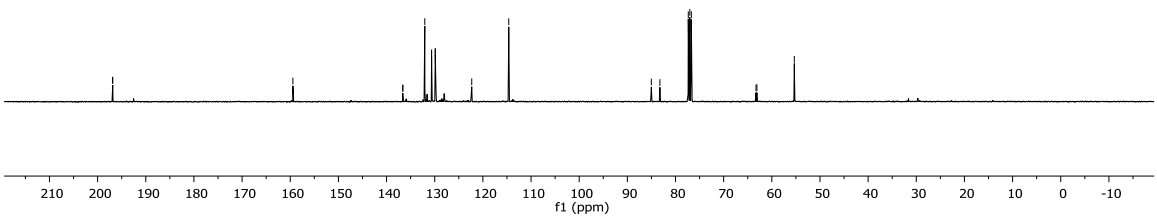
Sep30-2016-tl-5-61 p-Br  
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196.862

159.453  
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129.885  
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85.019  
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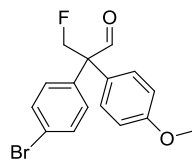


14c

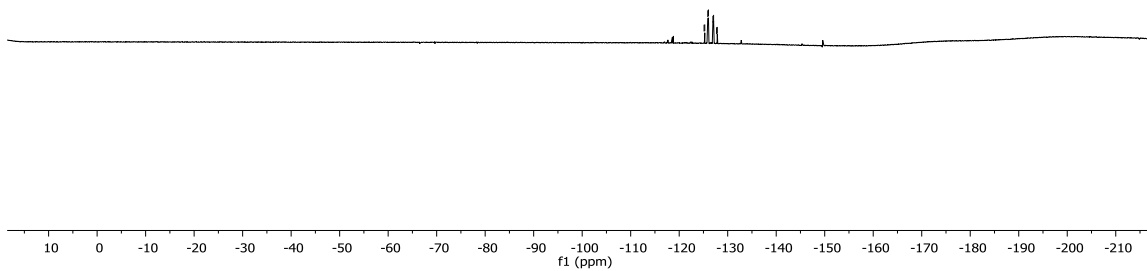


Sep30-2016-tl.4.fid  
tl-5-61 p-Br

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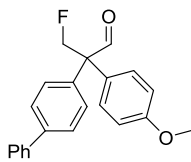
14c



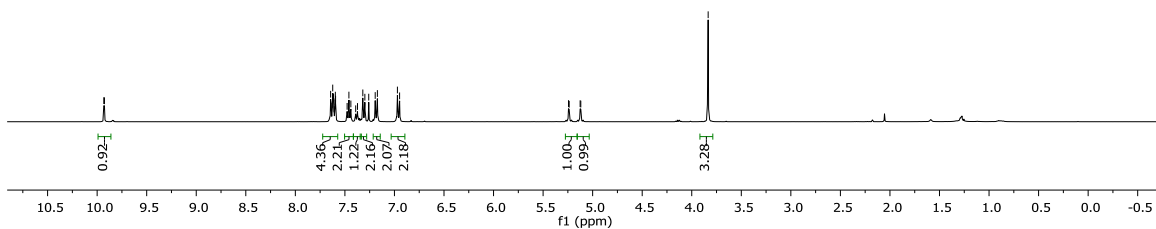
Sep29-2016-855.fid  
tl-5-62 p-Ph

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7.618  
7.614  
7.609  
7.600  
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7.594  
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7.460  
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3.834



14d

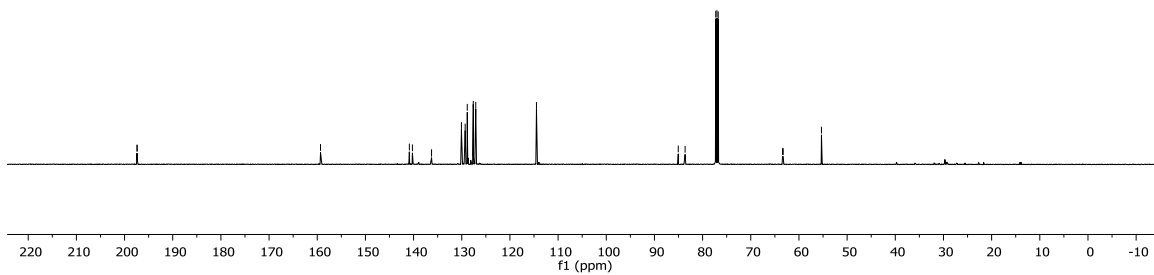
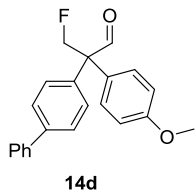


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13C AMX500  
TL-5-62 p-Ph

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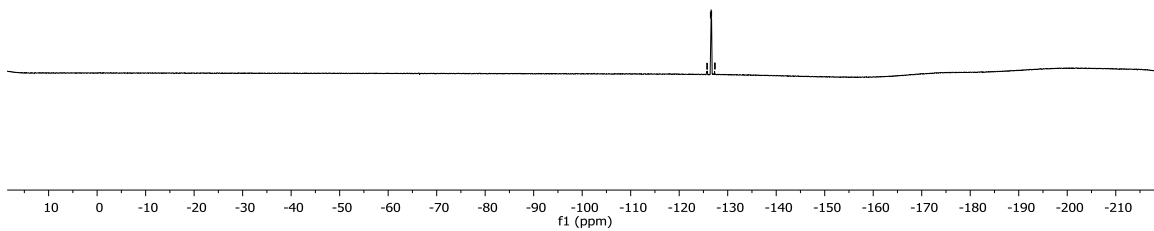
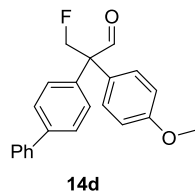
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136.271  
130.066  
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128.858  
127.611  
127.094  
114.491

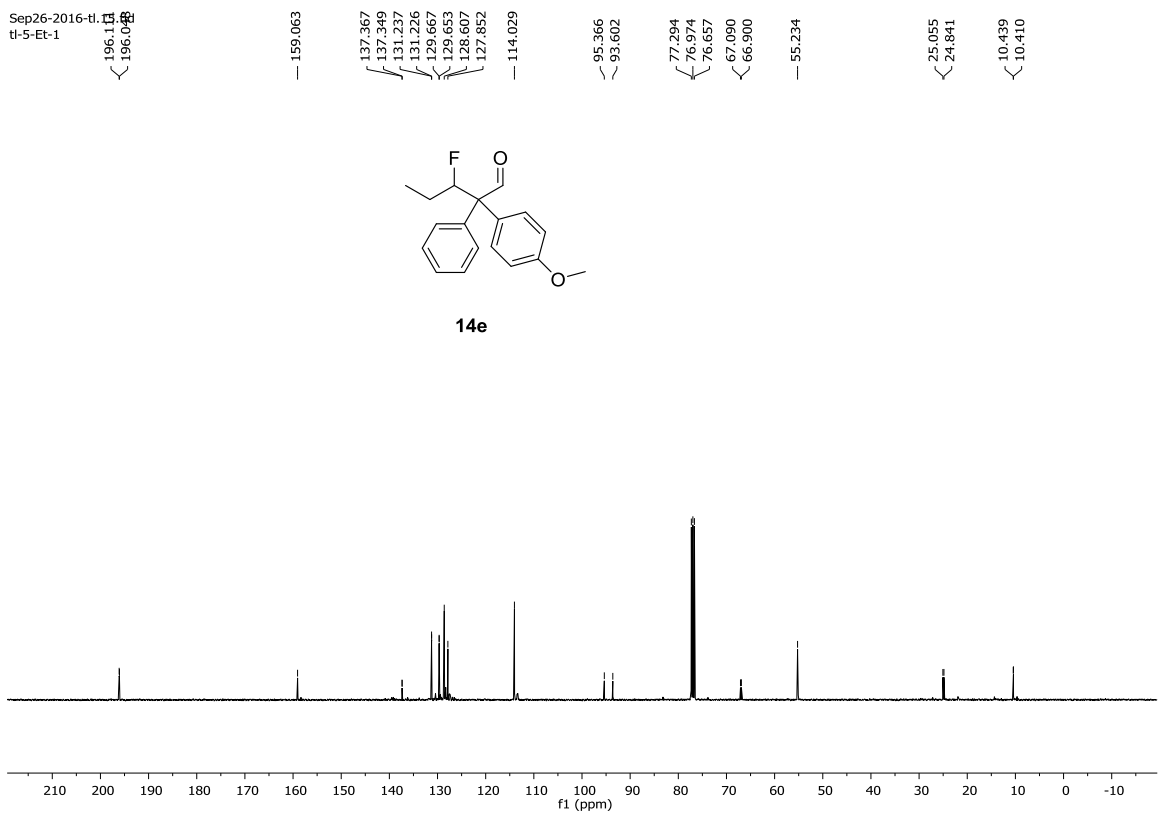
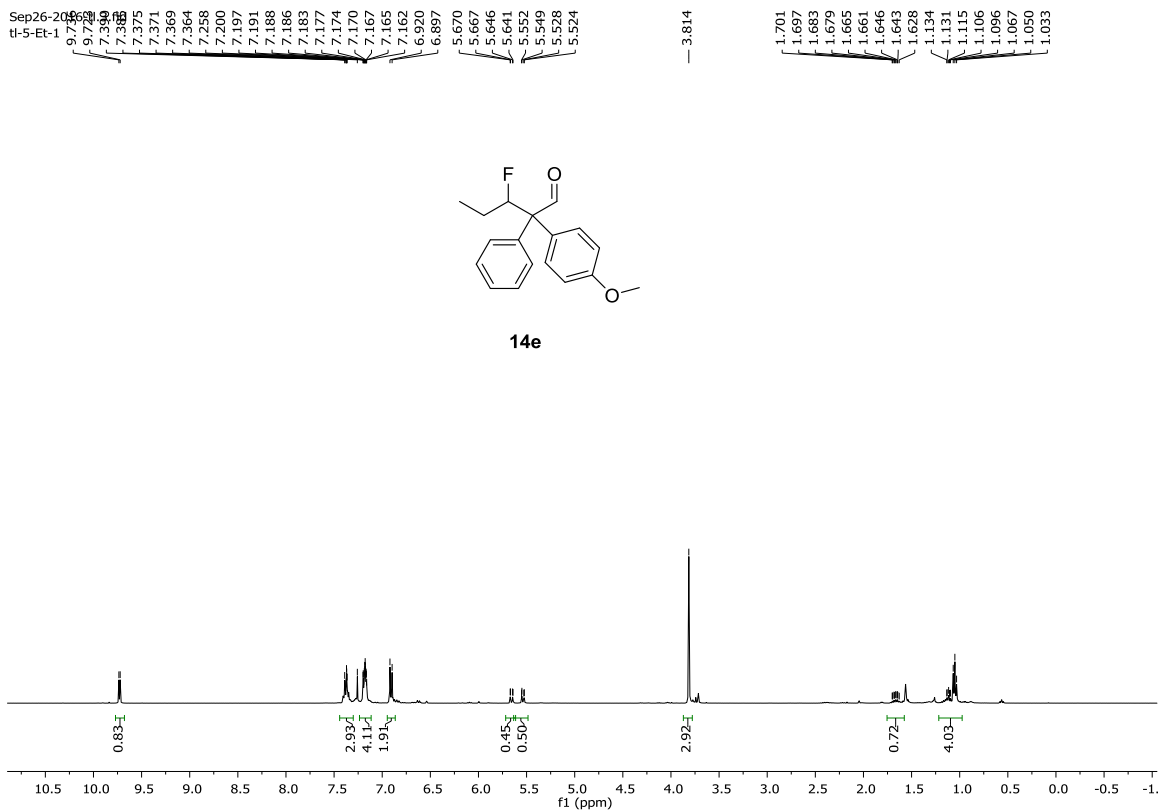
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76.763  
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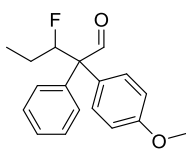
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tl-5-62 p-Ph

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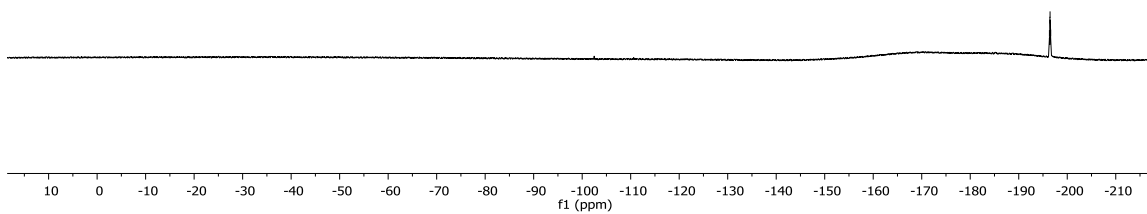




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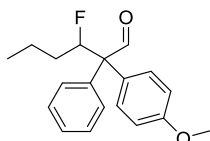


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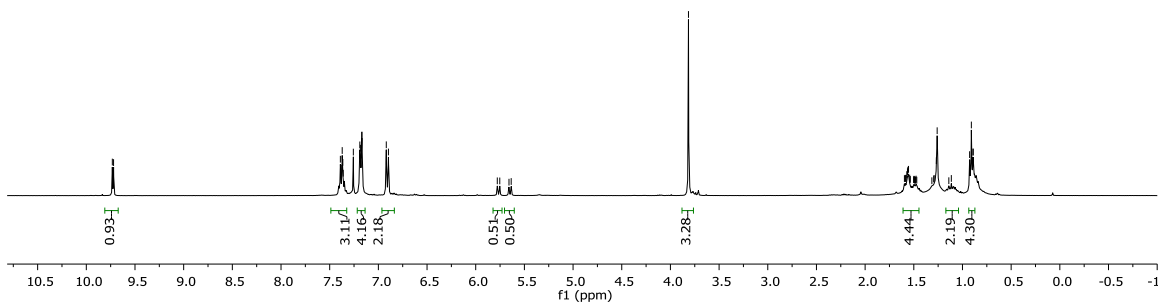


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0.891



14f



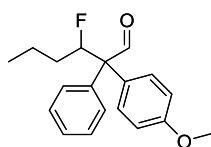
Sep26-2016-tl.8.fid  
tl-5-Pr-1

196.113  
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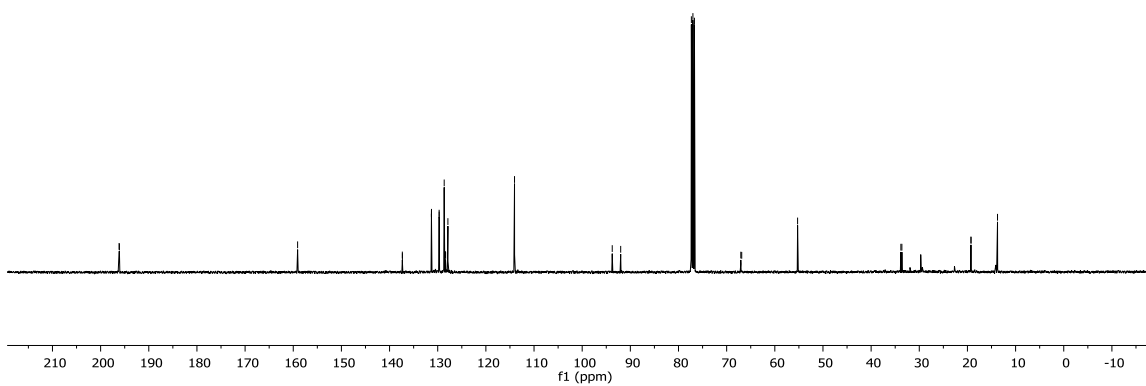
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128.656  
128.382  
128.360  
127.884  
114.054

93.762  
92.006  
77.326  
77.210  
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67.062  
66.871  
55.270

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33.612  
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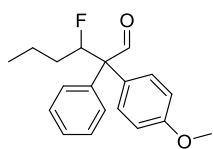


18f

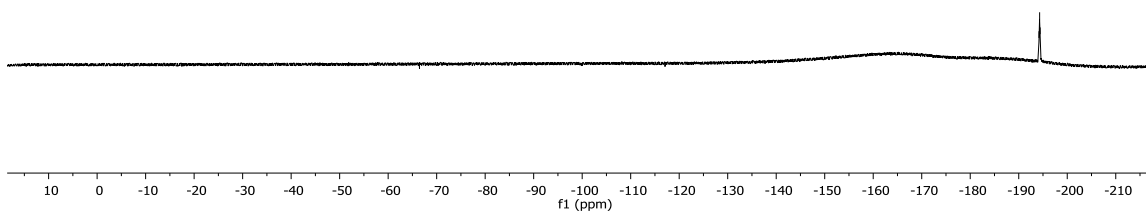


Sep26-2016-tl.8.fid  
tl-5-Pr-1

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194.409

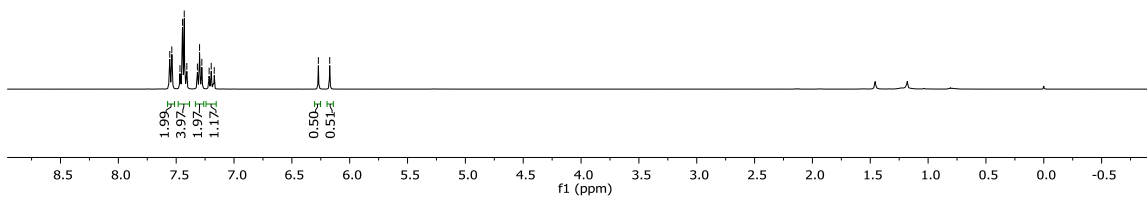
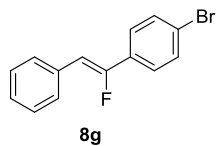


14f



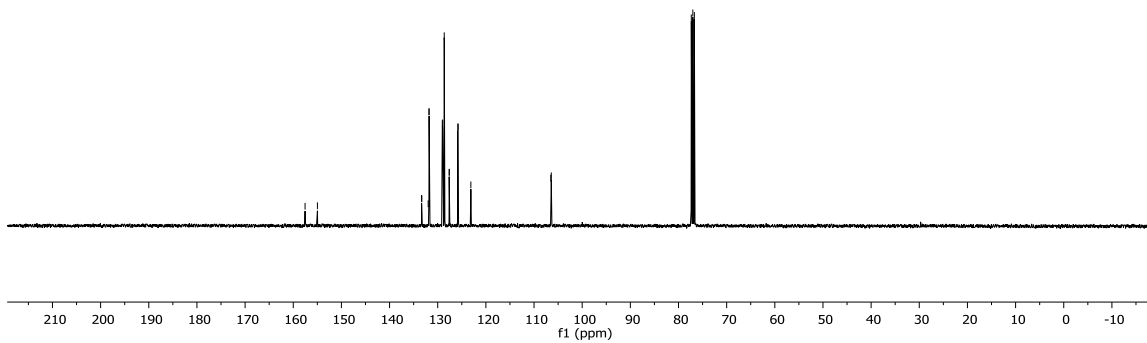
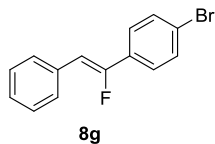
Nov12-2016-tl-16.fid  
 tl-5-83A-1

7.553  
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 7.445  
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 6.173

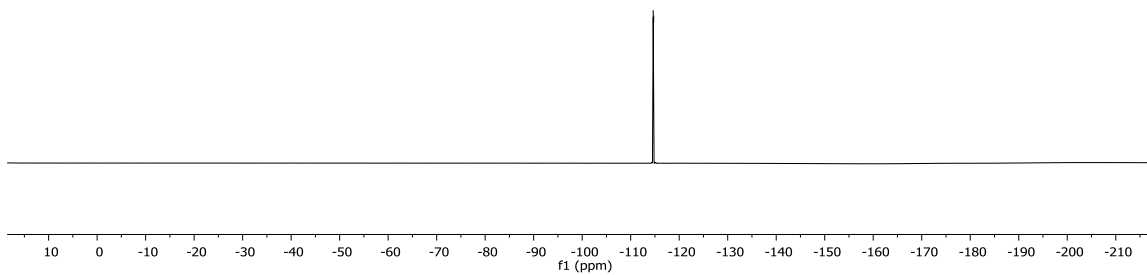
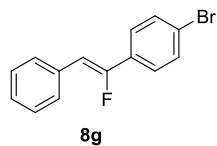


Nov12-2016-tl-16.fid  
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157.545  
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 133.312  
 131.986  
 131.813  
 131.791  
 131.703  
 129.046  
 128.967  
 128.645  
 127.619  
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 125.750  
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 106.416  
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 77.024  
 76.706



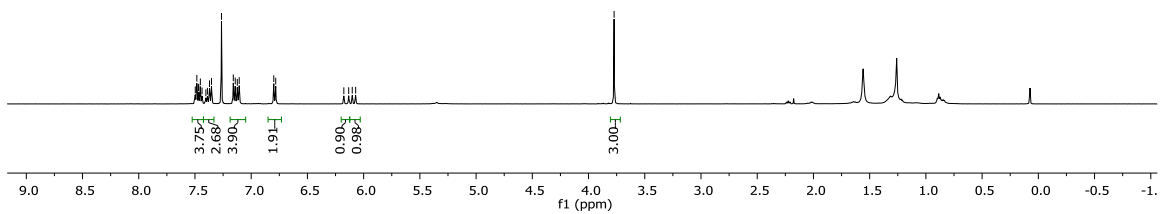
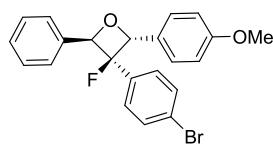
← -114.643  
← -114.748



7.487  
7.485  
7.469  
7.467  
7.452  
7.437  
7.403  
7.389  
7.371  
7.353  
7.264  
7.159  
7.142  
7.124  
7.107  
6.799  
6.782

6.176  
6.133  
6.101  
6.071

— 3.773



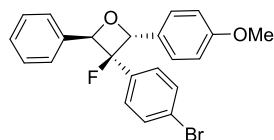


tl1109.3.fid  
13C AMX500  
TL-5-83 Cyclobut

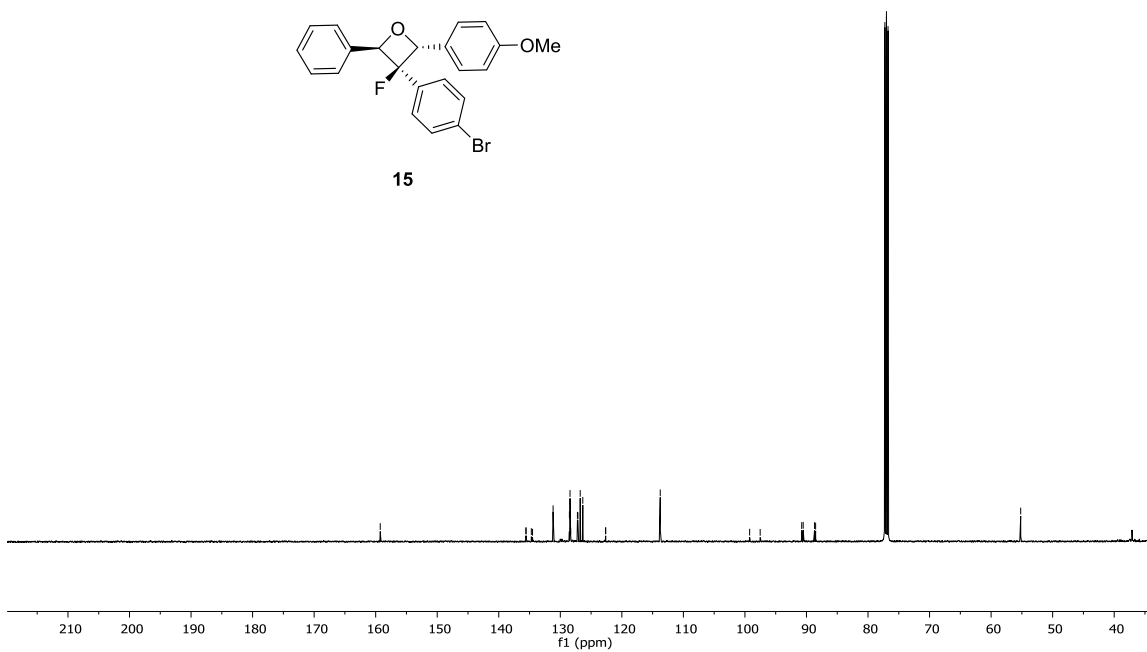
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127.141  
126.765  
126.346  
122.641  
122.626  
113.762

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90.776  
90.534  
88.688  
88.515  
77.259  
77.005  
76.751

55.192

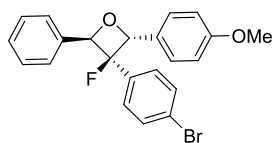


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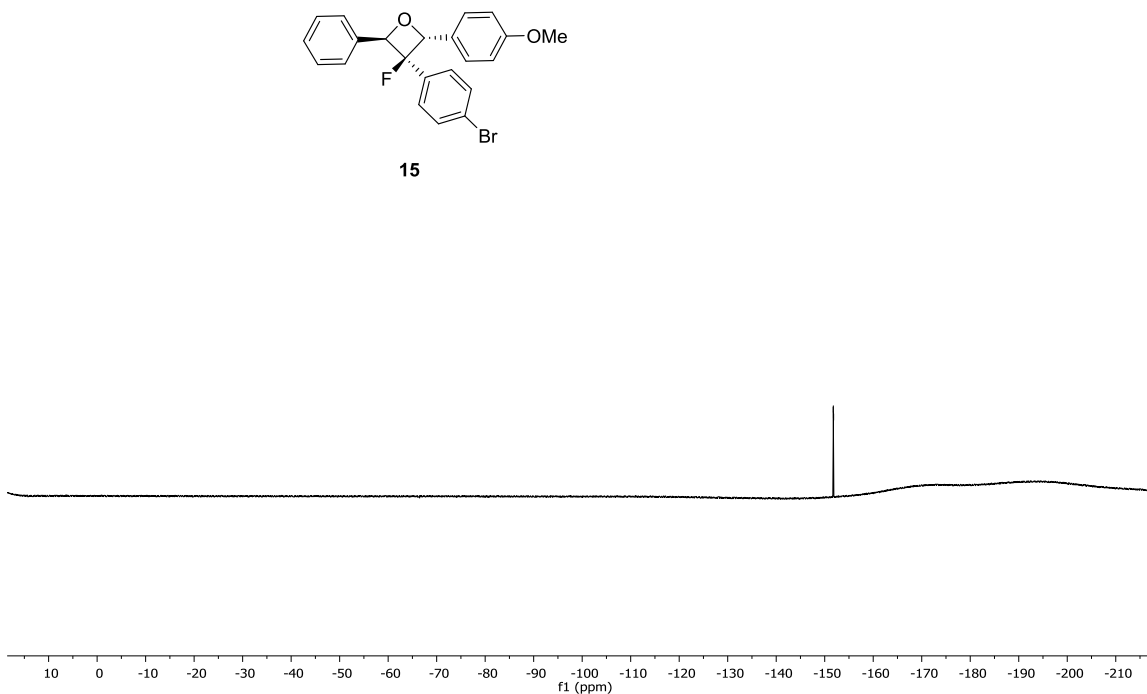


Nov09-2016-tl.2.fid  
tl-5-83 cyclo

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151.796  
151.839



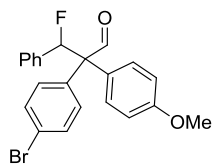
15



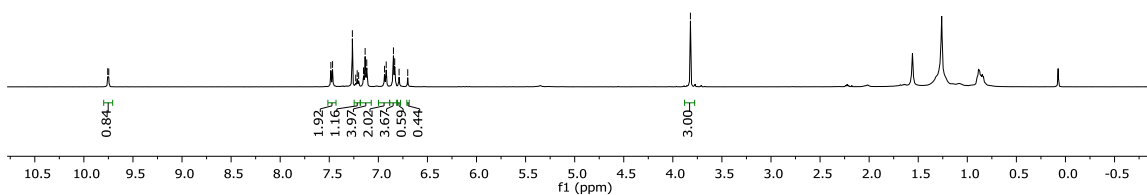
t11107.4.fid  
2  
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9.746

7.484  
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7.230  
7.216  
7.201  
7.151  
7.135  
7.118  
6.937  
6.920  
6.846  
6.833  
6.789  
6.701

3.821



17



Nov09-2016-tl.12.fid  
tl-5-83 aldehyde

195.370  
195.309

159.426

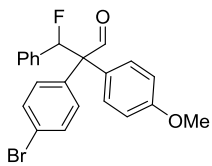
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127.507  
127.486  
127.232  
113.845

93.947  
92.150

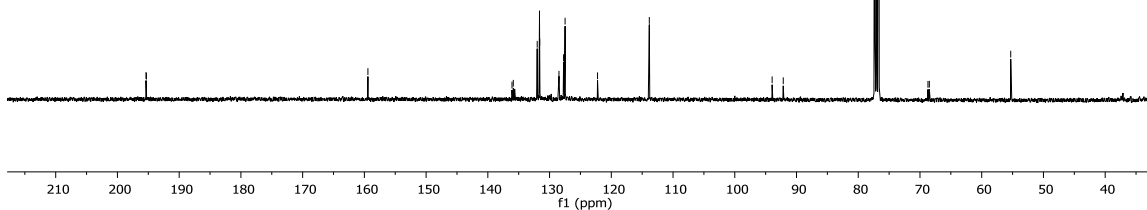
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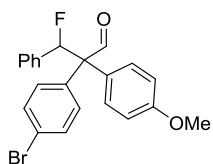
68.706  
68.484

55.299

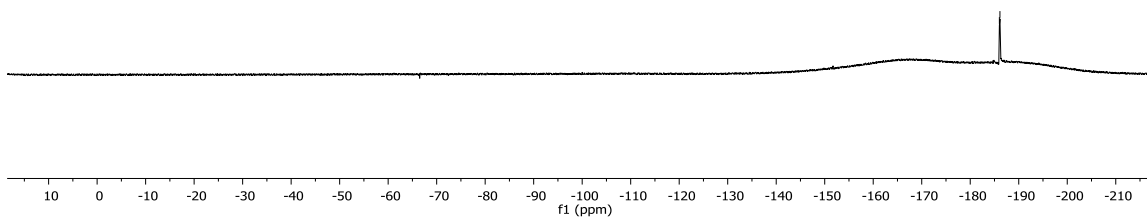


17

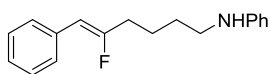




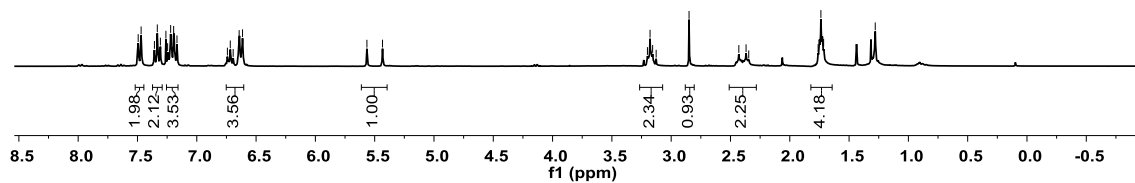
17



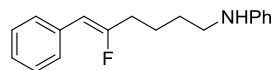
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7.307  
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7.220  
7.195  
6.718  
6.718  
6.693  
6.643  
6.614  
5.565  
5.434  
3.200  
3.178  
3.156  
3.127  
2.849  
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2.369  
2.346  
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1.738  
1.715  
1.279



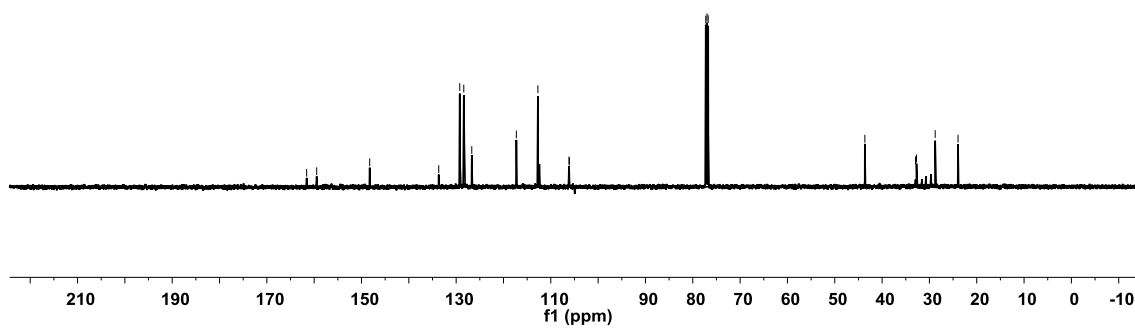
18



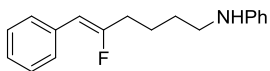
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128.285  
128.227  
126.699  
117.278  
112.727  
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106.084  
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77.000  
76.746  
43.642  
32.934  
32.721  
28.781  
23.949



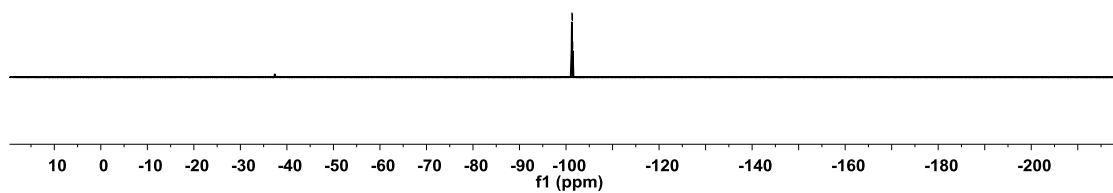
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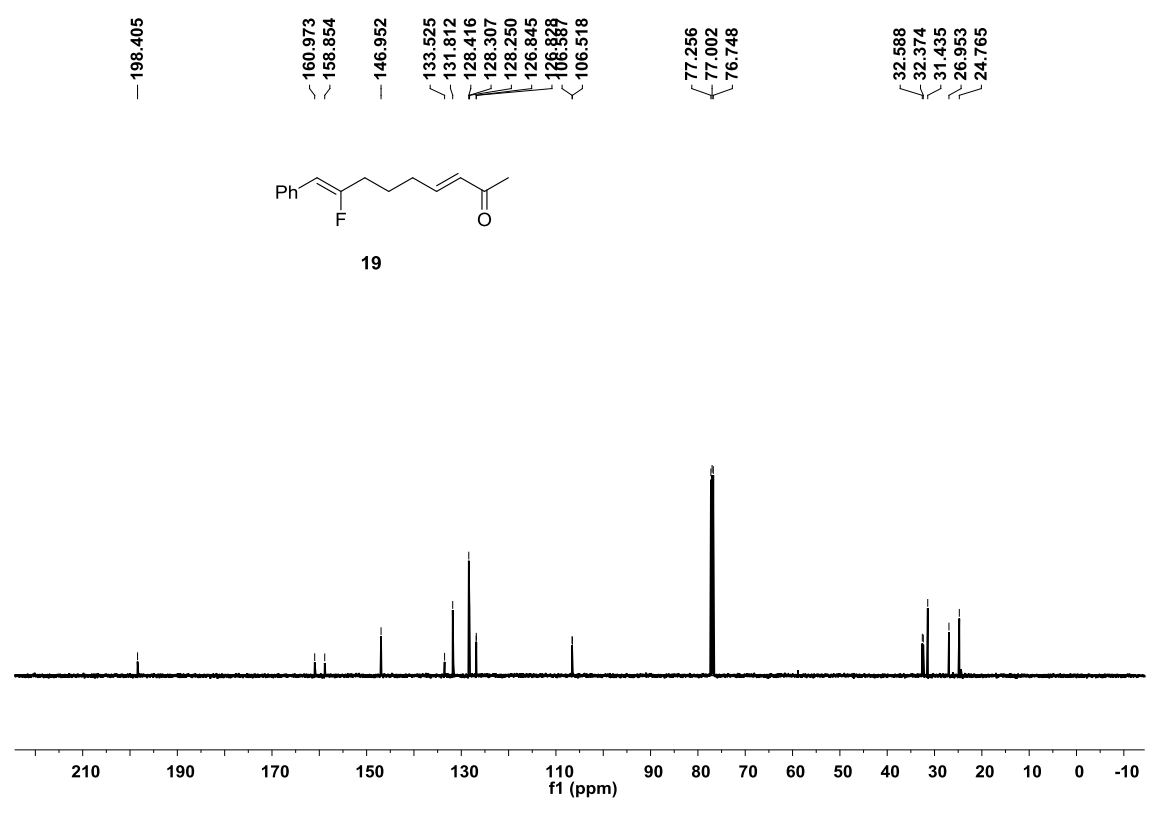
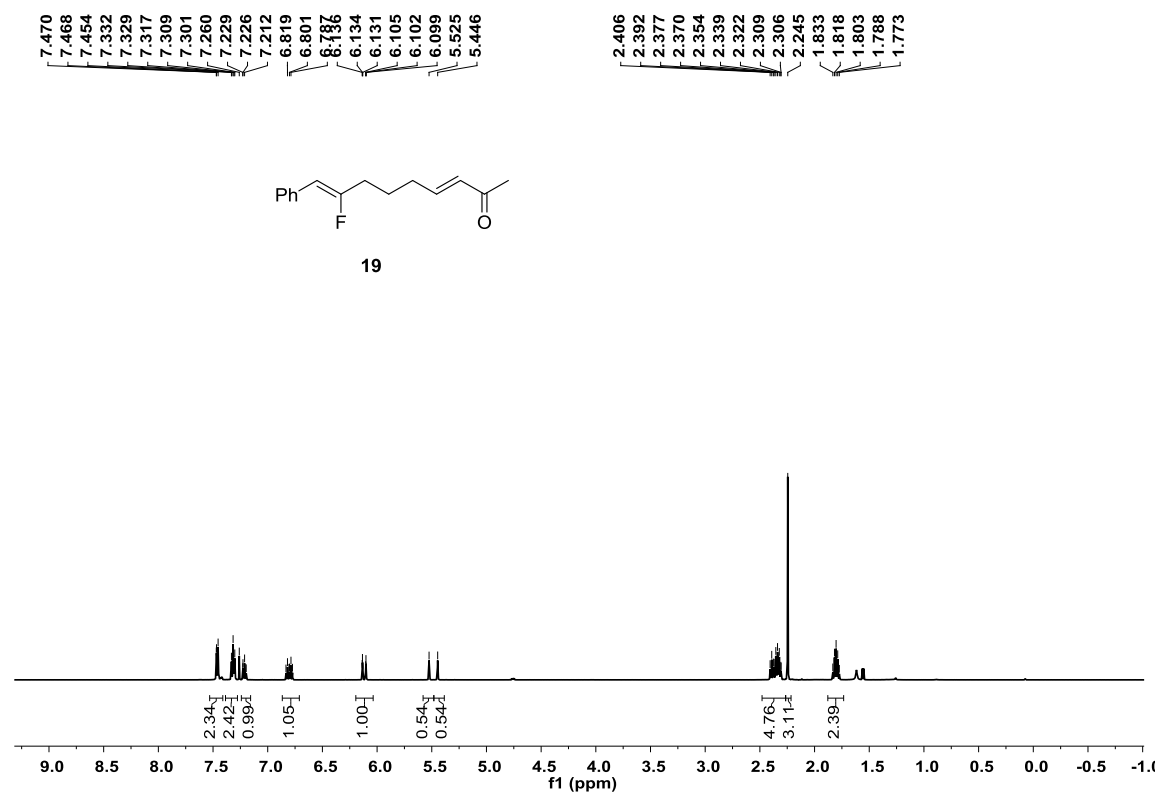


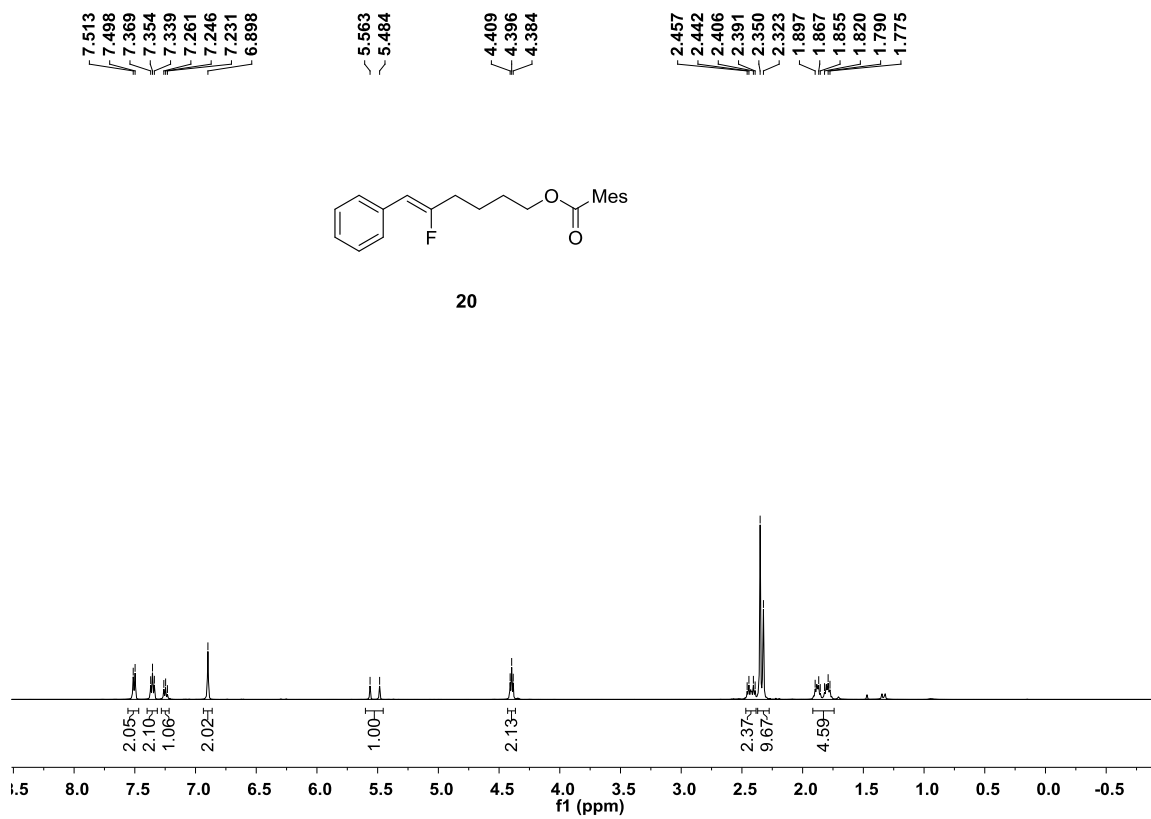
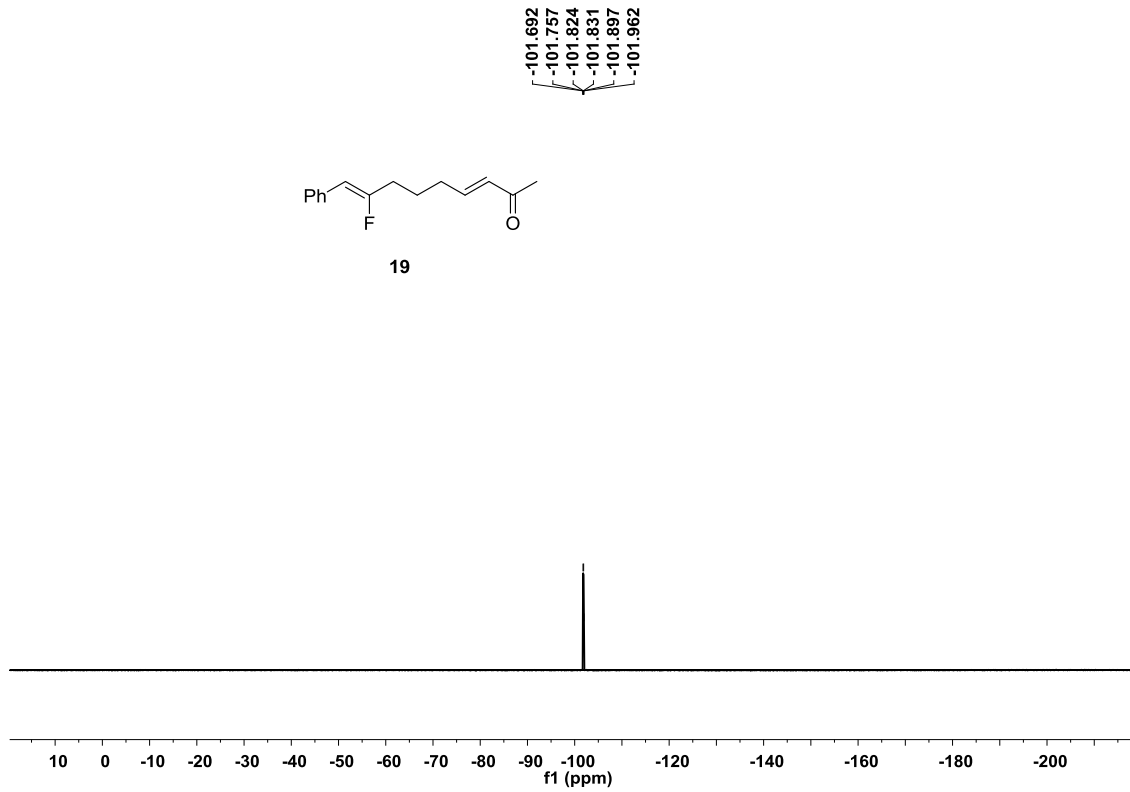
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-101.312  
-101.321  
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-101.451



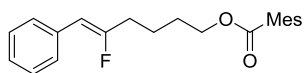
18



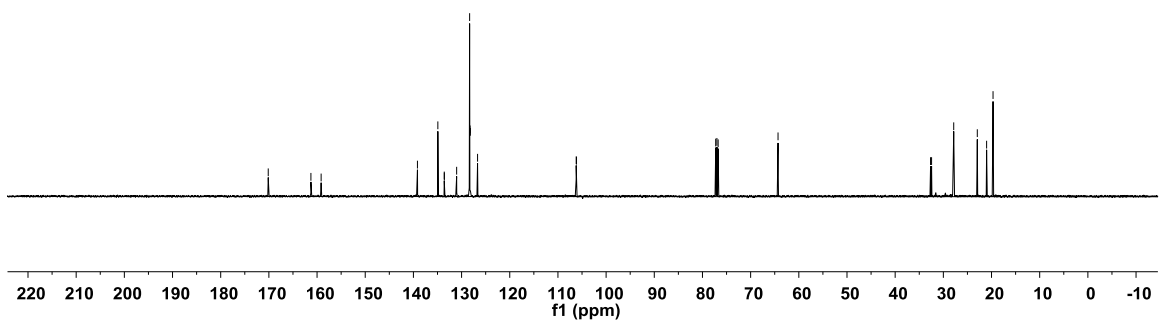




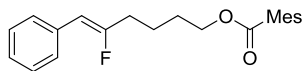
170.132  
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 159.154  
 139.161  
 134.928  
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 133.578  
 131.023  
 128.331  
 128.238  
 128.179  
 126.683  
 106.211  
 106.142  
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 27.846  
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 21.018  
 19.685



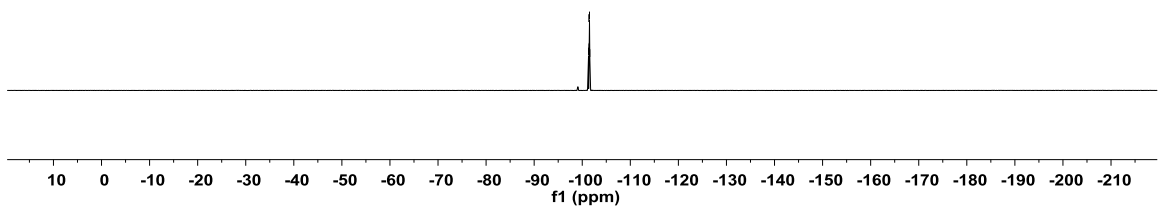
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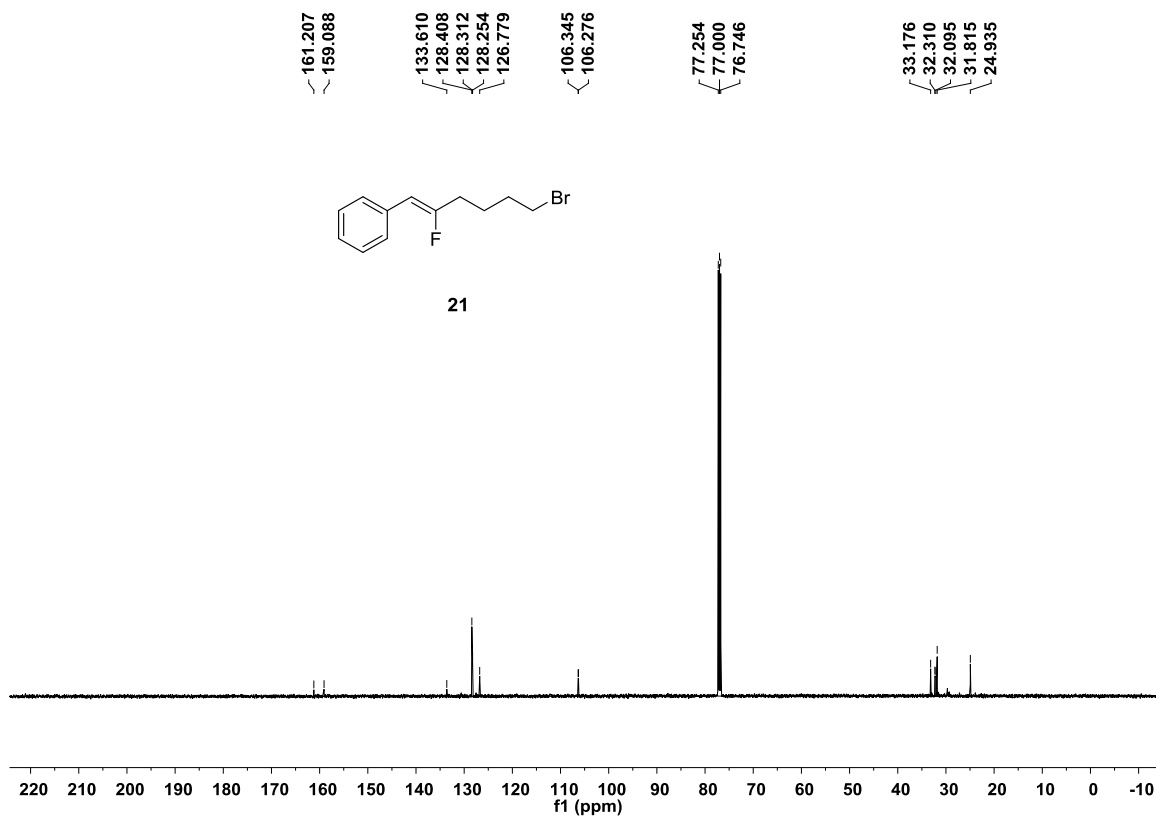
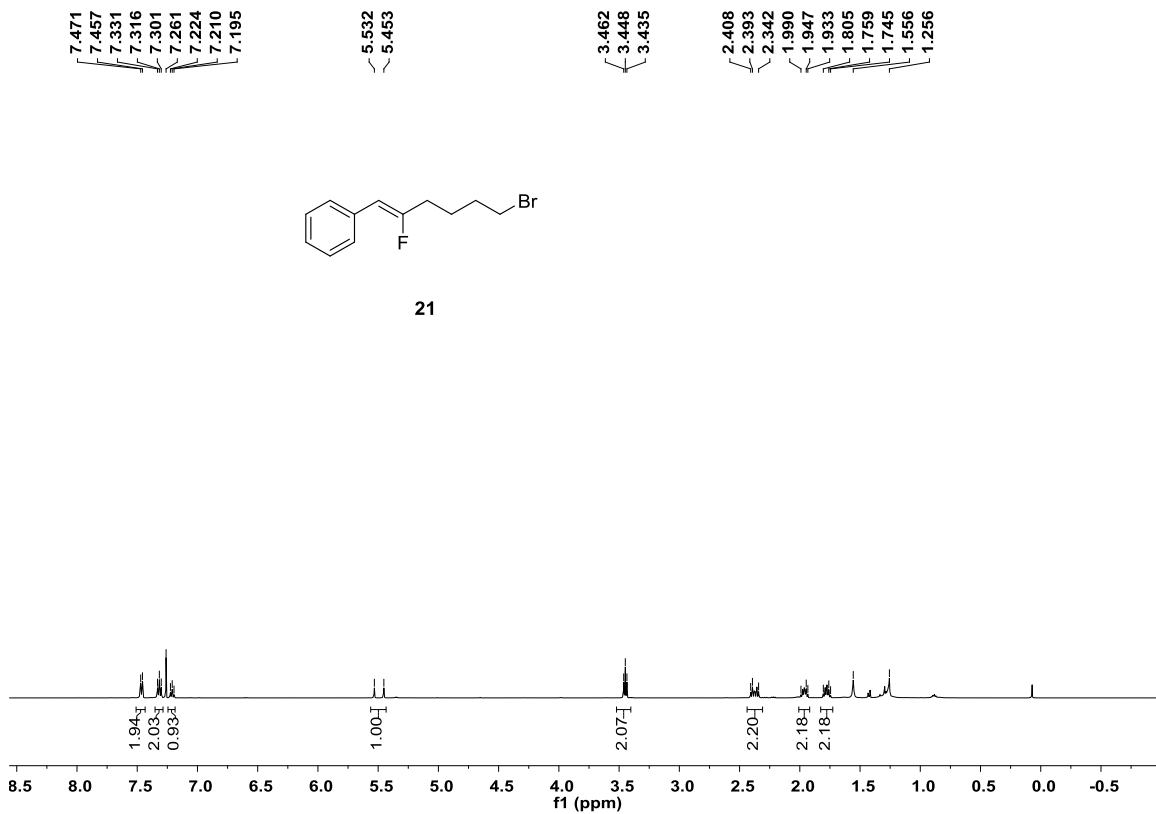


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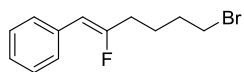


20

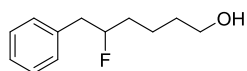
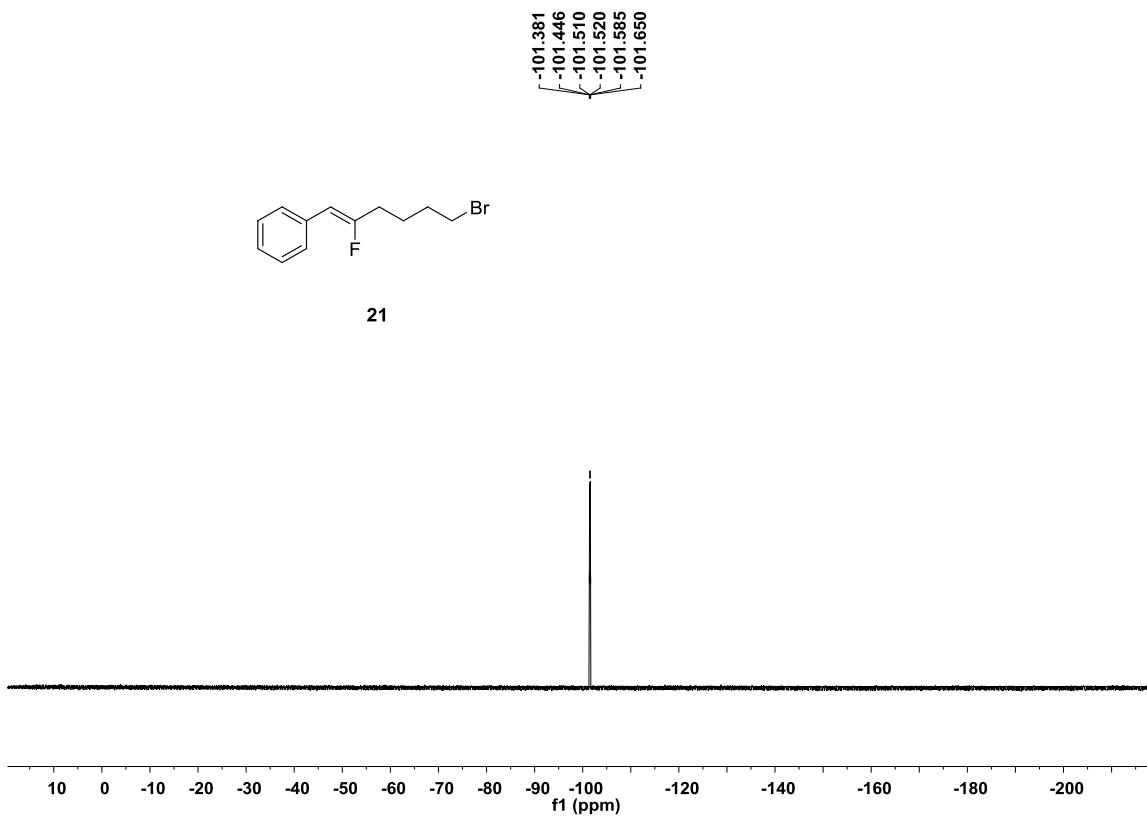




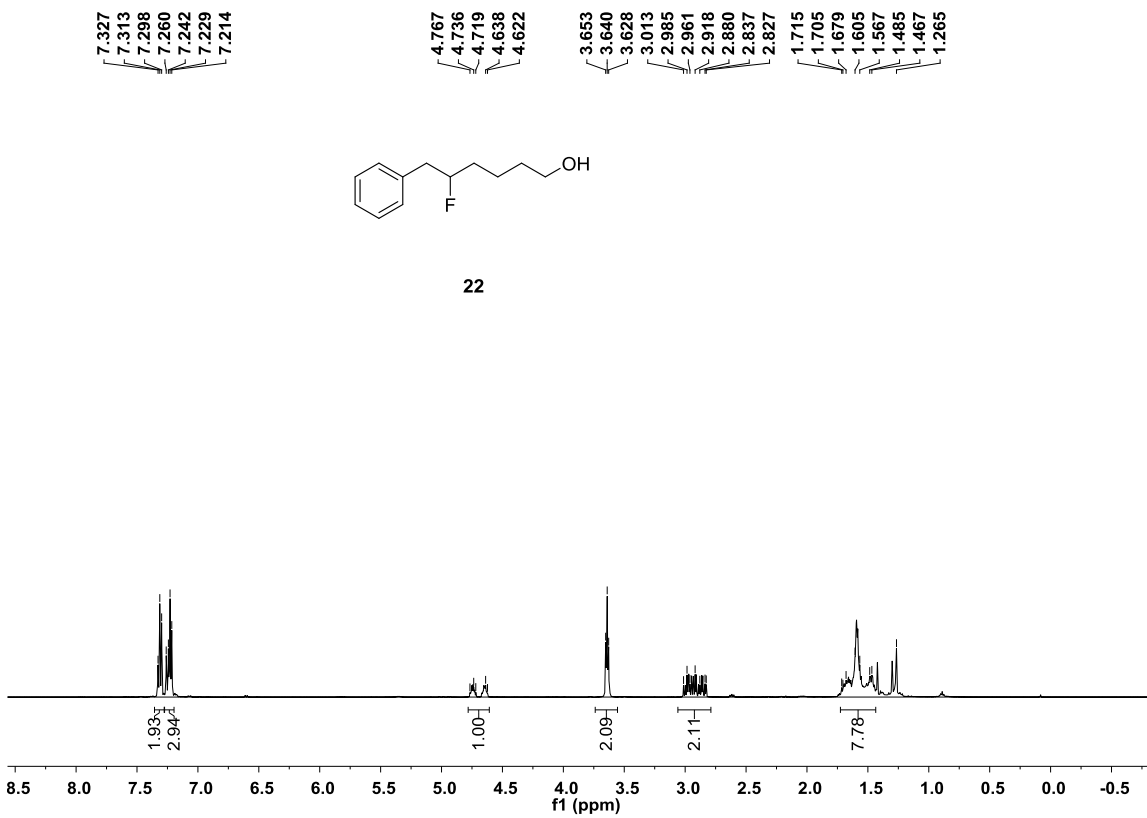




21



22



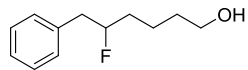
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95.098  
93.739

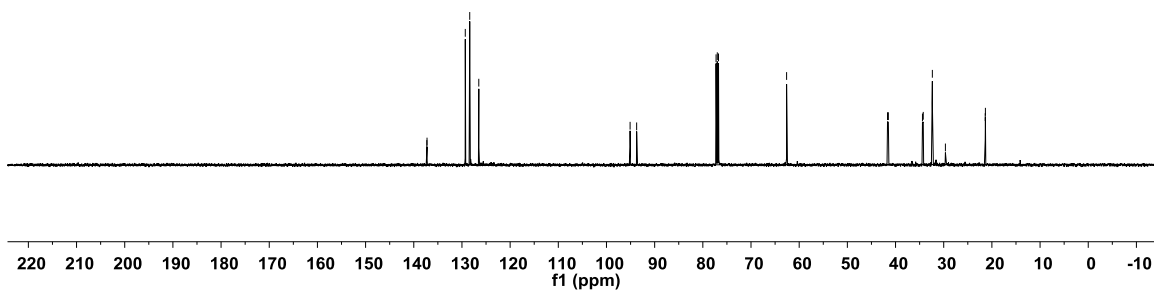
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76.746

62.613

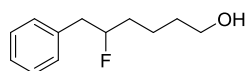
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34.247  
32.359  
29.650  
21.380  
21.347



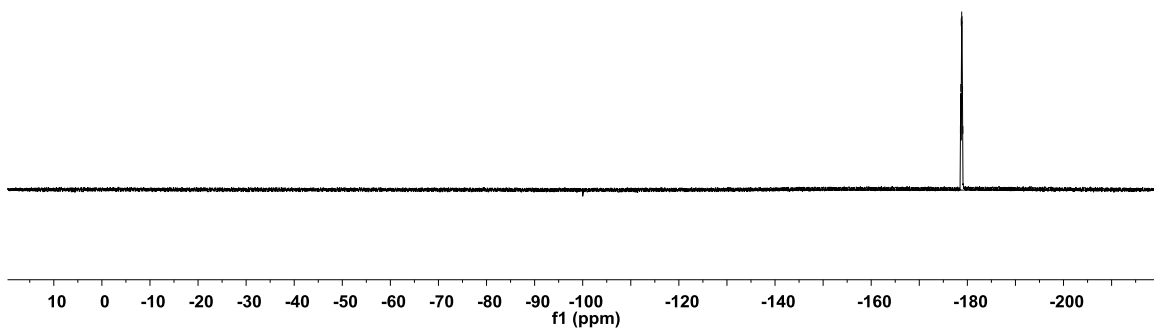
22



-178.559  
-178.627  
-178.652  
-178.732  
-178.763  
-178.825  
-178.893  
-178.997  
-179.064



22

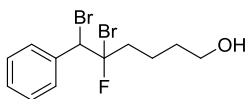


7.522  
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7.507  
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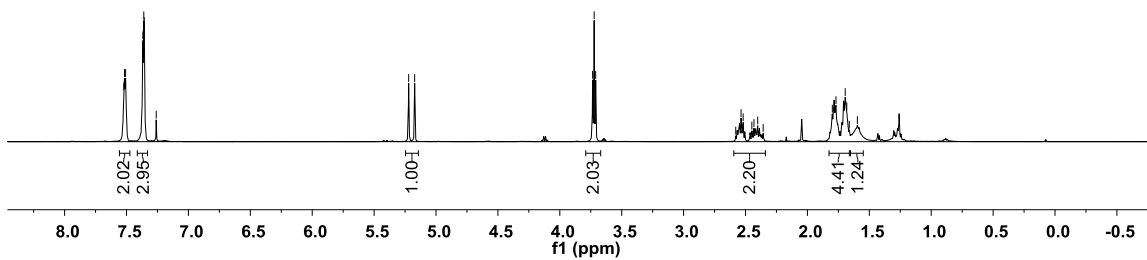
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3.710

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2.519  
2.449  
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2.401  
2.357  
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1.769  
1.695  
1.682  
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1.596



23



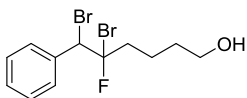
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110.772

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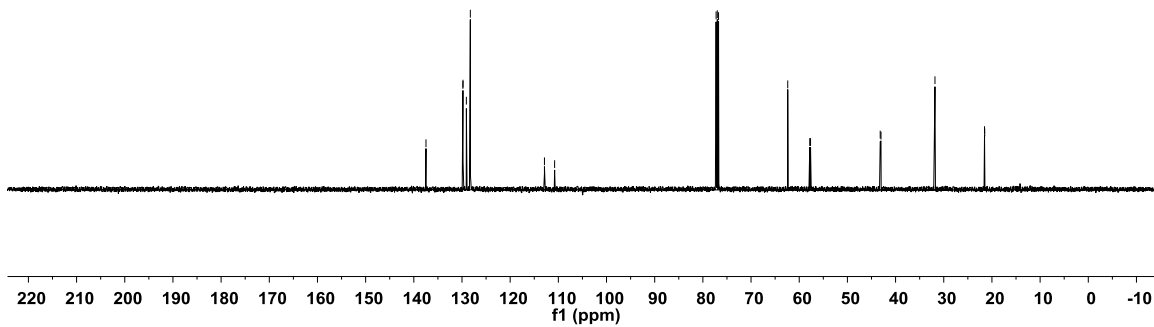
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57.649

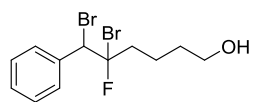
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31.825  
21.540  
21.497



23





23

-108.514  
-108.589  
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