

# Supporting Information

## Ag-Catalyzed Chemoselective Decarboxylative Mono- and *gem*-Di-Fluorination of Malonic Acid Derivatives

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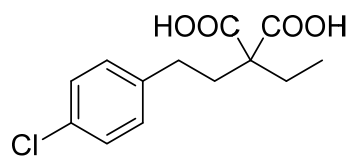
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## 1. General Information

All reagents and organic solvents were purchased from TCI, Sigma-Aldrich, Adamas-beta and Energy Chemical of the highest purity grade and used without further purification unless otherwise noted. Distilled water needs to be degassed before use.  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (J) in Hz. HRMS-ESI and HRMS-EI spectra were recorded on Xevo G2-XS QToF and Waters Micromass GCT Premier. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. Melting points were measured without correction. The substrates were prepared according to the conventional literature methods.<sup>1,2</sup>

## 2. Spectral Characterizations of the Starting Materials



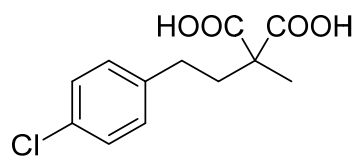
**2-(4-Chlorophenethyl)-2-ethylmalonic acid:** white solid, Mp: 136–138 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.78 (br, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.47 – 2.36 (m, 2H), 2.01 – 1.91 (m, 2H), 1.85 (q, *J* = 7.5 Hz, 2H), 0.80 (t, *J* = 7.5 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 172.8, 140.7, 130.5, 130.1, 128.4, 57.1, 33.3, 29.4, 24.6, 8.5.

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>16</sub>ClO<sub>4</sub> [(M + H)<sup>+</sup>] 271.0737, found 271.0739.

**IR (KBr):** ν (cm<sup>-1</sup>) 2973, 1705, 1617, 1493, 1406, 1270, 1240, 1204, 883, 818, 788.



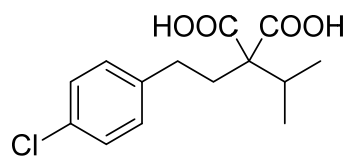
**2-(4-Chlorophenethyl)-2-methylmalonic acid:** white solid, Mp: 160–161 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.78 (br, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.58 – 2.42 (m, 2H), 2.03 – 1.91 (m, 2H), 1.35 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 173.5, 140.8, 130.5, 130.1, 128.4, 52.8, 37.2, 29.8, 19.7.

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>14</sub>ClO<sub>4</sub> [(M + H)<sup>+</sup>] 257.0581, found 257.0580.

**IR (KBr):** ν (cm<sup>-1</sup>) 2985, 2933, 1701, 1494, 1407, 1272, 1213, 1204, 807.



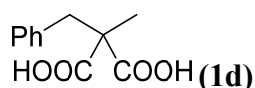
**2-(4-Chlorophenethyl)-2-isopropylmalonic acid:** white solid, Mp: 167–168 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.74 (br, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.55 – 2.48 (m, 2H), 2.33 – 2.14 (m, 1H), 2.03 – 1.85 (m, 2H), 0.97 (d, *J* = 6.8 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 172.3, 141.0, 130.5, 130.0, 128.4, 60.7, 35.4, 31.2, 30.2, 18.6.

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>18</sub>ClO<sub>4</sub> [(M + H)<sup>+</sup>] 285.0894, found 285.0895.

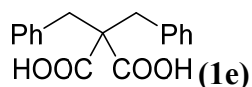
**IR (KBr):** ν (cm<sup>-1</sup>) 2970, 2880, 1690, 1490, 1408, 1265, 910, 804.



**2-Benzyl-2-methylmalonic acid<sup>3</sup>:** white solid.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.82 (br, 2H), 7.30 – 7.19 (m, 3H), 7.16 (d, *J* = 6.8 Hz, 2H), 3.06 (s, 2H), 1.14 (s, 3H).

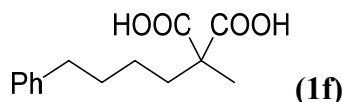
**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 173.2, 136.8, 130.2, 128.1, 126.7, 53.9, 40.5, 19.3.



**2, 2-Dibenzylmalonic acid**<sup>4</sup>: white solid.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  7.35 – 7.15 (m, 10H), 3.02 (s, 4H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  172.3, 136.7, 130.1, 128.2, 126.7, 59.2, 37.6.



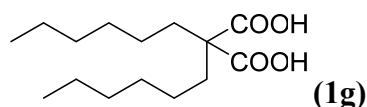
**2-Methyl-2-(4-phenylbutyl) malonic acid**: white solid, Mp: 109–110 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.60 (br, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 2.59 – 2.52 (t,  $J = 7.8$  Hz 2H), 1.79 – 1.69 (m, 2H), 1.61 – 1.50 (m, 2H), 1.27 – 1.16 (m, 5H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  173.7, 142.2, 128.3, 128.3, 125.7, 52.7, 35.0, 31.5, 23.6, 19.7.

HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>19</sub>O<sub>4</sub> [(M + H)<sup>+</sup>] 251.1283, found 251.1285.

IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2936, 1698, 1413, 1283, 1230, 930, 748, 698.



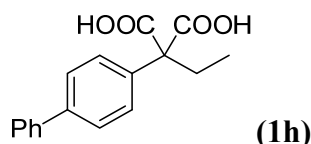
**2, 2-Dihexylmalonic acid**: white solid, Mp: 105–106 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.58 (br, 2H), 1.77 – 1.61 (m, 4H), 1.33 – 1.17 (m, 12H), 1.15 – 1.00 (m, 4H), 0.85 (t,  $J = 6.5$  Hz, 6H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  173.2, 56.6, 31.6, 31.1, 29.1, 23.5, 22.1, 14.0.

HRMS-ESI (m/z) calcd for C<sub>15</sub>H<sub>29</sub>O<sub>4</sub> [(M + H)<sup>+</sup>] 273.2066, found 273.2066.

IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2957, 2927, 2861, 1705, 1467, 1405, 1289, 1246, 914, 786, 725.



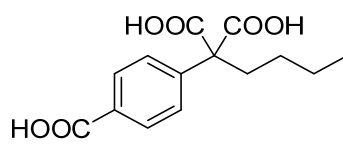
**2-([1, 1'-Biphenyl]-4-yl)-2-ethylmalonic acid**: white solid, Mp: 171–173 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  7.72 – 7.61 (m, 4H), 7.55 – 7.42 (m, 4H), 7.40 – 7.33 (m, 1H), 2.25 (q,  $J = 6.8$  Hz, 2H), 0.84 (t,  $J = 6.7$  Hz, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  172.1, 139.8, 138.8, 136.8, 129.0, 129.0, 127.5, 126.7, 126.1, 62.3, 27.9, 9.5.

HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>17</sub>O<sub>4</sub> [(M + H)<sup>+</sup>] 285.1127, found 285.1132.

IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2970, 2880, 1700, 1396, 1274, 900, 837, 747, 698.



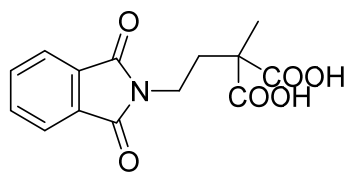
**2-Butyl-2-(4-carboxyphenyl) malonic acid**: white solid, Mp: 180–182 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  7.91 (d,  $J = 8.5$  Hz, 2H), 7.54 (d,  $J = 8.5$  Hz, 2H), 2.25 – 2.10 (m, 2H), 1.33 – 1.21 (m, 2H), 1.17 – 1.05 (m, 2H), 0.82 (t,  $J = 7.3$  Hz, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  171.7, 167.2, 142.9, 129.4, 128.8, 128.5, 62.2, 34.9, 26.7, 22.5, 13.9.

HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>17</sub>O<sub>6</sub> [(M + H)<sup>+</sup>] 281.1025, found 281.1025.

IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2971, 2652, 1709, 1420, 1224, 913, 851, 738.



(1j)

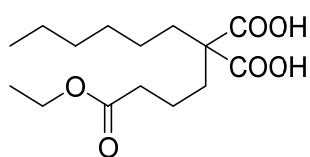
**2-(2-(1,3-Dioxoisindolin-2-yl)ethyl)-2-methylmalonic acid:** white solid, Mp: 176–177 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.83 (br, 2H), 7.99 – 7.71 (m, 4H), 3.62 (t, *J* = 7.4 Hz, 2H), 2.08 (t, *J* = 7.6 Hz, 2H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 173.1, 167.7, 134.3, 131.7, 123.0, 51.5, 33.6, 33.2, 19.5.

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>14</sub>NO<sub>6</sub> [(M + H)<sup>+</sup>] 292.0821, found 292.0822.

**IR (KBr):** ν (cm<sup>-1</sup>) 3063, 1717, 1693, 1449, 1409, 1270, 990, 859, 722.



(1k)

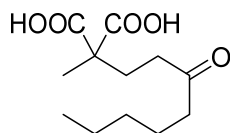
**2-(4-Ethoxy-4-oxobutyl)-2-hexylmalonic acid:** white solid, Mp: 77–79 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 4.01 (q, *J* = 7.1 Hz, 2H), 2.14 (t, *J* = 7.8 Hz, 2H), 1.65 – 1.49 (m, 4H), 1.37 – 1.28 (m, 2H), 1.25 – 1.10 (m, 9H), 1.09 – 0.98 (m, 2H), 0.83 (t, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 177.6, 172.6, 59.7, 55.6, 38.2, 34.0, 31.2, 29.0, 25.4, 22.0, 21.4, 14.2, 14.0.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>27</sub>O<sub>6</sub> [(M + H)<sup>+</sup>] 303.1808, found 303.1809.

**IR (KBr):** ν (cm<sup>-1</sup>) 2956, 2923, 2859, 1740, 1709, 1459, 1415, 1270, 1211, 767.



(1l)

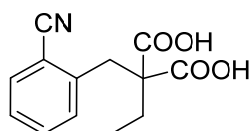
**2-Methyl-2-(3-oxooctyl) malonic acid:** white solid, Mp: 86–88 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 12.70 (br, 2H), 2.43–2.34 (m, 4H), 1.89 (t, *J* = 8.0, 2H), 1.50 – 1.37 (m, 2H), 1.30 – 1.12 (m, 7H), 0.84 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 209.7, 173.5, 52.1, 41.9, 37.4, 30.9, 29.0, 23.0, 22.0, 19.8, 13.9.

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>21</sub>O<sub>5</sub> [(M + H)<sup>+</sup>] 245.1389, found 245.1393.

**IR (KBr):** ν (cm<sup>-1</sup>) 3154, 1748, 1713, 1464, 1411, 1388, 1277, 1210, 953, 830.



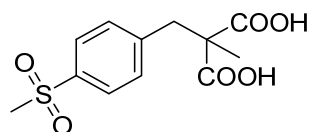
(1m)

**2-(2-Cyanobenzyl)-2-ethylmalonic acid:** white solid, Mp: 145–146 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):** δ 13.05 (br, 2H), 7.79 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.63 (td, *J* = 7.8, 1.2 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 3.33 (s, 2H), 1.64 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):** δ 172.2, 140.5, 133.2, 133.0, 130.3, 127.8, 118.2, 113.3, 58.4, 35.2, 24.6, 8.9.

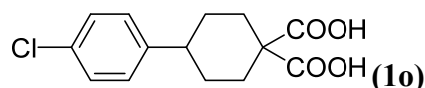
**HRMS-ESI** (m/z) calcd for  $C_{13}H_{14}NO_4$  [(M + H)<sup>+</sup>] 248.0923, found 248.0924.  
**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2989, 2227, 1705, 1443, 1394, 1297, 1243, 904, 765.



(1n)

**2-Methyl-2-(4-(methylsulfonyl) benzyl) malonic acid:** white solid, Mp: 139–141 °C.  
**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  7.83 (d,  $J$  = 8.1 Hz, 2H), 7.43 (d,  $J$  = 8.2 Hz, 2H), 3.20 (s, 3H), 3.18 (s, 2H), 1.17 (s, 3H).  
**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  173.0, 143.2, 139.3, 131.1, 126.7, 53.8, 43.6, 40.3, 19.4.

**HRMS-ESI** (m/z) calcd for  $C_{12}H_{15}O_6S$  [(M + H)<sup>+</sup>] 287.0589, found 287.0591.  
**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3041, 2935, 1754, 1713, 1288, 1146, 968, 836, 761.



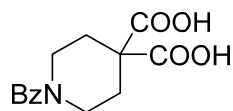
(1o)

**4-(4-Chlorophenyl) cyclohexane-1, 1-dicarboxylic acid:** white solid, Mp: 187–189 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.74 (br, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 7.19 (d,  $J$  = 8.5 Hz, 2H), 2.52 – 1.62 (m, 1H), 2.35 – 2.25 (m, 2H), 1.82 – 1.63 (m, 4H), 1.55 – 1.38 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  173.7, 172.3, 145.5, 130.5, 128.5, 128.3, 53.4, 41.5, 31.0, 30.1.

**HRMS-ESI** (m/z) calcd for  $C_{14}H_{16}ClO_4$  [(M + H)<sup>+</sup>] 283.0737, found 283.0733.  
**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2943, 2868, 1698, 1494, 1452, 1407, 1290, 943, 924, 832, 786.



(1p)

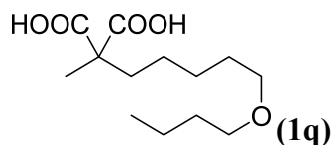
**1-Benzoylpiperidine-4, 4-dicarboxylic acid:** white solid, Mp: 170–171 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  13.04 (br, 2H), 7.52 – 7.27 (m, 5H), 3.70 – 3.26 (m, 4H), 2.10 – 1.75 (m, 4H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  172.1, 169.1, 136.1, 129.5, 128.5, 126.8, 52.6, 44.5, 30.8, 30.1.

**HRMS-ESI** (m/z) calcd for  $C_{14}H_{16}NO_5$  [(M + H)<sup>+</sup>] 278.1028, found 278.1028.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3173, 2936, 1728, 1699, 1589, 1570, 1448, 1273, 1212, 956, 710.



(1q)

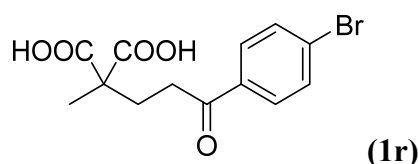
**2-(5-Butoxypentyl)-2-methylmalonic acid:** white solid, Mp: 76–78 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.58 (br, 2H), 3.38 – 3.27 (m, 4H), 1.76 – 1.64 (m, 2H), 1.53 – 1.39 (m, 4H), 1.37 – 1.12 (m, 9H), 0.87 (t,  $J$  = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  173.8, 69.9, 69.7, 52.8, 35.3, 31.5, 29.2, 26.3, 23.9, 19.7, 19.0, 13.9.

**HRMS-ESI** (m/z) calcd for  $C_{13}H_{25}O_5$  [(M + H)<sup>+</sup>] 261.1702, found 261.1702.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2942, 2864, 1711, 1465, 1407, 1285, 1224, 1194, 975, 677.



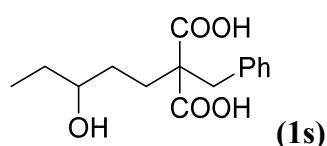
**2-(3-(4-Bromophenyl)-3-oxopropyl)-2-methylmalonic acid:** white solid, Mp: 172–174 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.76 (br, 2H), 7.87 (d,  $J$  = 8.4 Hz, 2H), 7.72 (d,  $J$  = 8.4 Hz, 2H), 2.99 (t,  $J$  = 7.6 Hz, 2H), 2.07 (t,  $J$  = 7.6 Hz, 2H), 1.32 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  198.5, 173.5, 135.5, 131.9, 130.0, 127.3, 52.2, 33.8, 29.5, 19.9.

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>14</sub>O<sub>5</sub>Br [(M + H)<sup>+</sup>] 329.0025, found 329.0030.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2948, 1711, 1682, 1585, 1408, 1289, 953, 833, 777.



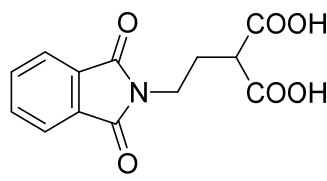
**2-Benzyl-2-(3-hydroxypentyl)malonic acid:** white solid, Mp: 106–108 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.81 (br, 2H), 7.30 – 7.17 (m, 3H), 7.14 (d,  $J$  = 7.3 Hz, 2H), 4.35 (br, 1H), 3.30 – 3.18 (m, 1H), 3.05 (s, 2H), 1.75 (td,  $J$  = 13.2, 4.6 Hz, 1H), 1.48 (td,  $J$  = 13.2, 4.6 Hz, 1H), 1.42 – 1.20 (m, 4H), 0.83 (t,  $J$  = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  172.7, 136.8, 129.9, 128.1, 126.7, 71.4, 57.8, 37.0, 31.2, 29.7, 27.3, 10.1.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>20</sub>NaO<sub>5</sub> [(M + Na)<sup>+</sup>] 303.1208, found 303.1208.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3276, 2970, 2926, 1731, 1470, 1120, 773, 706.



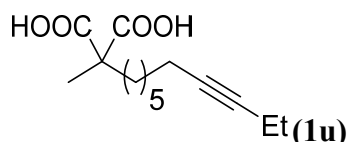
**2-(2-(1,3-Dioxoisindolin-2-yl)ethyl) malonic acid:** white solid, Mp: 164–165 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.77 (br, 2H), 7.95 – 7.75 (m, 4H), 3.64 (t,  $J$  = 6.8 Hz, 2H), 3.30 (t,  $J$  = 7.2 Hz, 1H), 2.06 (q,  $J$  = 6.9 Hz, 2H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  170.5, 168.0, 134.4, 131.7, 123.1, 49.5, 35.8, 27.2.

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>6</sub> [(M + H)<sup>+</sup>] 278.0665, found 278.0668.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3192, 2958, 1741, 1686, 1440, 1406, 1187, 890, 728.



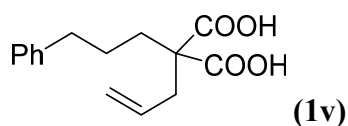
**2-(Dec-7-yn-1-yl)-2-methylmalonic acid:** white solid, Mp: 65–67 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.64 (br, 2H), 2.20 – 2.01 (m, 4H), 1.76 – 1.62 (m, 2H), 1.47 – 1.21 (m, 9H), 1.20 – 1.10 (m, 2H), 1.02 (t,  $J$  = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  173.8, 81.8, 79.6, 52.7, 35.2, 28.9, 28.5, 28.1, 23.9, 19.7, 18.1, 14.3, 11.8.

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>22</sub>NaO<sub>4</sub> [(M + Na)<sup>+</sup>] 277.1416, found 277.1409.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2932, 2858, 1698, 1466, 1411, 1319, 1276, 724.



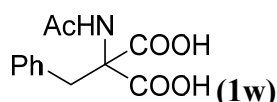
**2-Allyl-2-(3-phenylpropyl)malonic acid:** white solid, Mp: 129–131 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  12.75 (br, 2H), 7.38 – 7.22 (m, 2H), 7.22 – 7.04 (m, 3H), 5.69 – 5.41 (m, 1H), 5.19 – 4.95 (m, 2H), 2.56 (t,  $J$  = 7.3 Hz, 2H), 2.49 (d,  $J$  = 7.6 Hz, 2H), 1.84 – 1.60 (m, 2H), 1.60 – 1.40 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  172.6, 141.8, 133.2, 128.3, 125.8, 118.7, 56.4, 36.2, 35.4, 31.0, 25.5.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>18</sub>NaO<sub>4</sub> [(M + Na)<sup>+</sup>] 285.1103, found 285.1095.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3026, 2959, 1712, 1644, 1462, 1400, 928, 907, 756, 701.



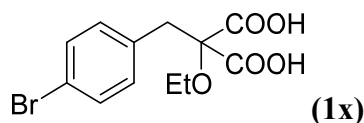
**2-Acetamido-2-benzylmalonic acid:** white solid, Mp: 133–134 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  13.39 (br, 2H), 7.69 (s, 1H), 7.32 – 7.15 (m, 3H), 7.00 (d,  $J$  = 7.0 Hz, 2H), 3.41 (s, 2H), 1.92 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  169.3, 169.1, 136.3, 130.0, 128.2, 126.8, 67.0, 37.3, 22.5.

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>13</sub>NNaO<sub>5</sub> [(M + Na)<sup>+</sup>] 274.0691, found 274.0690.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3359, 3036, 2903, 1742, 1717, 1530, 1424, 732, 700.



**2-(4-Bromobenzyl)-2-ethoxymalonic acid:** white solid, Mp: 121–122 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  13.32 (br, 2H), 7.45 (d,  $J$  = 8.2 Hz, 2H), 7.13 (d,  $J$  = 8.3 Hz, 2H), 3.57 (q,  $J$  = 6.9 Hz, 2H), 3.17 (s, 2H), 1.12 (t,  $J$  = 6.9 Hz, 3H).

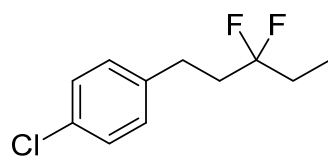
**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):**  $\delta$  169.7, 135.3, 132.4, 130.8, 120.0, 84.2, 60.7, 37.7, 15.4.

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>13</sub>BrNaO<sub>5</sub> [(M + Na)<sup>+</sup>] 338.9844, found 338.9839.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2981, 2889, 1709, 1488, 1404, 1279, 815, 691.

### 3. General Procedure for Silver-Catalyzed Decarboxylative *gem*-Difluorination and Spectral Characterizations of the Products 2

*gem*-Dicarboxylic acid (0.20 mmol), base, AgNO<sub>3</sub> and Selectfluor were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then solvent was added, the resulting reaction mixture was stirred (600 r/min) at room temperature or 55 °C for 12 h. The reaction was quenched with 3M HCl (2 mL), extracted with EtOAc (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, the residue was purified by column chromatography on silica gel or preparative TLC to give the desired product.



#### 1-Chloro-4-(3, 3-difluoropentyl) benzene:

According to the general procedure, a mixture of 2-(4-chlorophenyl)-2-ethylmalonic acid (54.1 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product **2a** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a colorless oil (26.2 mg, 60%). Note: The starting material **1a** was fully consumed, and no major byproducts were observed; 1-(4-chlorophenyl)-3,3-difluoropentyl benzoate and 1-(4-chlorophenyl)pentan-3-one were isolated as two byproducts, but in very low yields (less than 5% for each of them). Since Selectfluor is a strong oxidant, the moderate yield of this reaction may be due to the decomposition of the starting material.<sup>5</sup>

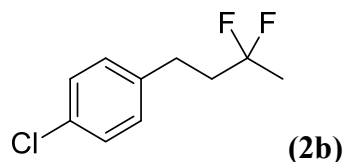
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.83 – 2.72 (m, 2H), 2.18 – 2.01 (m, 2H), 1.97 – 1.79 (m, 2H), 1.03 (t, *J* = 7.5 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -100.8 – -101.0 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 139.4, 132.1, 129.8, 128.8, 124.9 (t, *J* = 240.8 Hz), 37.9 (t, *J* = 25.6 Hz), 29.9 (t, *J* = 26.2 Hz), 28.0 (t, *J* = 5.1 Hz), 6.8 (t, *J* = 5.7 Hz).

**HRMS-EI (m/z)** calcd for C<sub>11</sub>H<sub>13</sub>ClF<sub>2</sub> [M<sup>+</sup>] 218.0674, found 218.0676.

**IR (KBr):** ν (cm<sup>-1</sup>) 2983, 2944, 1493, 1466, 1378, 1194, 1095, 928, 810.



#### 1-Chloro-4-(3, 3-difluorobutyl) benzene:

According to the general procedure, a mixture of 2-(4-chlorophenyl)-2-methylmalonic acid (51.3 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>HPO<sub>4</sub> (69.6 mg, 0.4 mmol, 2.0 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product **2b** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a colorless oil (28.2 mg, 69%).

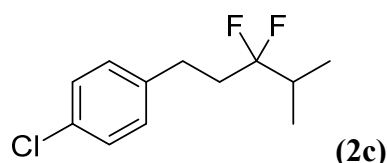
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.83 – 2.72 (m, 2H), 2.20 – 2.04 (m, 2H), 1.63 (t, *J* = 18.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -91.2 – -91.6 (m, 2F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.2, 132.1, 129.8, 128.8, 123.7 (t,  $J = 238.3$  Hz), 39.8 (t,  $J = 25.5$  Hz), 28.3 (t,  $J = 4.9$  Hz), 23.6 (t,  $J = 27.7$  Hz).

HRMS-EI (m/z) calcd for  $\text{C}_{10}\text{H}_{11}\text{ClF}_2$  [ $\text{M}^+$ ] 204.0517, found 204.0527.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2939, 1493, 1393, 1241, 1220, 1206, 1016, 902, 847, 811.



**1-Chloro-4-(3,3-difluoro-4-methylpentyl) benzene:**

According to the general procedure, a mixture of 2-(4-chlorophenethyl)-2-isopropylmalonic acid (56.9 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product **2c** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a colorless oil (23.6 mg, 51%).

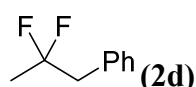
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.26 (d,  $J = 8.3$  Hz, 2H), 7.14 (d,  $J = 8.3$  Hz, 2H), 2.84 – 2.73 (m, 2H), 2.15 – 1.96 (m, 3H), 1.03 (d,  $J = 6.9$  Hz, 6H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -107.7 – -107.8 (m, 2F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.7, 132.0, 129.8, 128.8, 126.0 (t,  $J = 243.2$  Hz), 35.9 (t,  $J = 25.8$  Hz), 34.8 (t,  $J = 24.7$  Hz), 27.6 (t,  $J = 5.0$  Hz), 16.1 (t,  $J = 4.9$  Hz).

HRMS-EI (m/z) calcd for  $\text{C}_{12}\text{H}_{15}\text{ClF}_2$  [ $\text{M}^+$ ] 232.0830, found 232.0836.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2941, 1493, 1457, 1378, 1196, 1095, 929, 810.



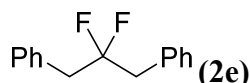
**(2,2-Difluoropropyl) benzene<sup>6</sup>:**

According to the general procedure, a mixture of 2-benzyl-2-methylmalonic acid (41.6 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{K}_2\text{HPO}_4$  (69.6 mg, 0.4 mmol, 2 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The reaction was quenched with 3M HCl (2 mL), extracted with *n*-pentane (3 mL  $\times$  5). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo at 0 °C to obtain **2d** as a yellow oil. (Note: 77%  $^{19}\text{F}$  NMR yield with 4-fluorobenzoic acid as the internal standard, **2d** is very volatile).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 – 7.24 (m, 5H), 3.14 (t,  $J = 15.5$  Hz, 2H), 1.53 (t,  $J = 18.4$  Hz, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -88.7 – -89.0 (m, 2F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.9 (t,  $J = 5.1$  Hz), 130.4, 128.6, 127.5, 123.6 (t,  $J = 239.5$  Hz), 44.6 (t,  $J = 26.3$  Hz), 23.0 (t,  $J = 27.5$  Hz).



**(2,2-Difluoropropane-1,3-diyl) dibenzene<sup>7</sup>:**

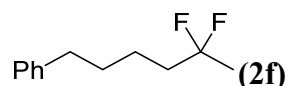
According to the general procedure, a mixture of 2,2-dibenzylmalonic acid (56.8 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product

**2e** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as colorless oil (27.8 mg, 60%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36 – 7.16 (m, 10H), 3.09 (t,  $J$  = 16.4 Hz, 4H).

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -94.6 – -94.8 (m, 2F).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.3, 130.6, 128.5, 127.5, 123.2 (t,  $J$  = 243.7 Hz), 42.5 (t,  $J$  = 25.6 Hz).



**(5, 5-Difluorohexyl) benzene:**

According to the general procedure, a mixture of 2-methyl-2-(4-phenylbutyl) malonic acid (50.1 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2f** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a colorless oil (28.5 mg, 72%).

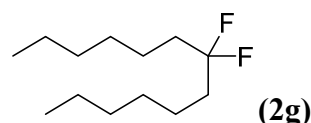
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31 – 7.25(m, 2H), 7.21 – 7.15 (m, 3H), 2.63 (t,  $J$  = 7.6 Hz, 2H), 1.93 – 1.79 (m, 2H), 1.71 – 1.62 (m, 2H), 1.62 – 1.47 (m, 5H).

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -90.1 – -90.4 (m, 2F).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.3, 128.5, 128.5, 125.9, 124.5 (t,  $J$  = 236 Hz), 37.9 (t,  $J$  = 25.3 Hz), 35.9, 31.3, 23.4 (t,  $J$  = 28.0 Hz), 22.6 (t,  $J$  = 4.6 Hz).

**HRMS-EI** (m/z) calcd for  $\text{C}_{12}\text{H}_{16}\text{F}_2$  [ $\text{M}^+$ ] 198.1220, found 198.1225.

**IR** (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2932, 2858, 1455, 1392, 1241, 1192, 1136, 747, 699.



**7, 7-Difluorotridecane:**

According to the general procedure, a mixture of 2,2-dihexylmalonic acid (54.5 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2g** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) as a colorless oil (24.0 mg, 55%).

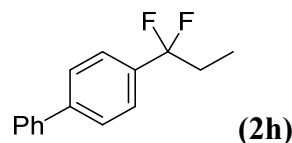
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.88 – 1.72 (m, 4H), 1.50 – 1.39 (m, 4H), 1.37 – 1.23 (m, 12H), 0.89 (t,  $J$  = 6.7 Hz, 6H).

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -97.3 – -97.6 (m, 2F).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  125.7 (t,  $J$  = 239.9 Hz), 36.5 (t,  $J$  = 25.5 Hz), 31.8, 29.2, 22.7, 22.5 (t,  $J$  = 4.5 Hz), 14.2.

**HRMS-EI** (m/z) calcd for  $\text{C}_{13}\text{H}_{25}\text{F}$  [( $\text{M} - \text{HF}$ ) $^+$ ] 200.1940, found 200.1947.

**IR** (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2957, 2931, 2859, 1467, 1379, 1165, 1033, 953.



**4-(1, 1-Difluoropropyl)-1, 1'-biphenyl:**

According to the general procedure, a mixture of 2-([1,1'-biphenyl]-4-yl)-2-ethylmalonic acid (56.9 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2

mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at room temperature for 6 h. The product **2h** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a yellow oil (37.0 mg, 80%).

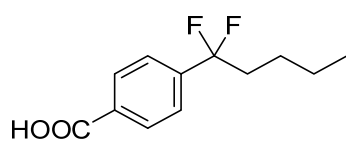
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.68 – 7.57 (m, 4H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.34 (m, 1H), 2.28 – 2.11 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -97.1 (t, *J* = 16.3 Hz, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 142.6 (t, *J* = 1.7 Hz), 140.4, 136.3 (t, *J* = 27.0 Hz), 129.0, 127.9, 127.3, 127.2, 125.7 (t, *J* = 6.2 Hz), 123.6 (t, *J* = 241 Hz), 32.4 (t, *J* = 28.5 Hz), 7.05 (t, *J* = 5.1 Hz).

**HRMS-EI (m/z)** calcd for C<sub>15</sub>H<sub>14</sub>F<sub>2</sub> [M<sup>+</sup>] 232.1064, found 232.1063.

**IR (KBr):** ν (cm<sup>-1</sup>) 2984, 2944, 1489, 1464, 1266, 1166, 841, 729, 691.



#### 4-(1,1-Difluoropentyl) benzoic acid:

According to the general procedure, a mixture of 2-butyl-2-(4-carboxyphenyl) malonic acid (56.1 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>CO<sub>3</sub> (82.9 mg, 0.6 mmol, 3equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in dichloroethane/water (4 mL, 1/1 v/v) was stirred at 55 °C for 12 h. The product **2i** was isolated by preparative TLC (petroleum ether/ethyl acetate = 1/1) as a colorless oil (30.1 mg, 66%).

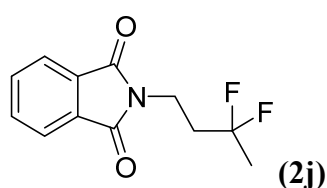
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 2.24 – 2.02 (m, 2H), 1.46 – 1.30 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -96.1 – -96.3 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.8, 143.0 (t, *J* = 26.9 Hz), 130.6, 130.5, 125.4 (t, *J* = 6.1 Hz), 122.8 (t, *J* = 243.1 Hz), 38.9 (t, *J* = 26.8 Hz), 24.6 (t, *J* = 3.9 Hz), 22.5, 13.9.

**HRMS-EI (m/z)** calcd for C<sub>12</sub>H<sub>14</sub>F<sub>2</sub>O<sub>2</sub> [M<sup>+</sup>] 228.0962, found 228.0969.

**IR (KBr):** ν (cm<sup>-1</sup>) 2960, 2921, 1703, 1427, 1288, 1241, 1168, 914, 817.



#### 2-(3,3-Difluorobutyl) isoindoline-1,3-dione:

According to the general procedure, a mixture of 2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-methylmalonic acid (58.2 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>HPO<sub>4</sub> (69.6 mg, 0.4 mmol, 2 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product **2j** was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a white solid (37.0 mg, 77%, Mp: 87–88 °C).

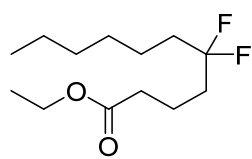
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.89 – 7.81 (m, 2H), 7.76 – 7.69 (m, 2H), 3.92 (t, *J* = 8.0, 2H), 2.38 – 2.20 (m, 2H), 1.68 (t, *J* = 18.5 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -90.9 – -91.2 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 168.1, 134.2, 132.1, 123.4, 123.1 (t, *J* = 236.5 Hz), 36.1 (t, *J* = 25.5 Hz), 32.2 (t, *J* = 5.8 Hz), 23.5 (t, *J* = 27.3 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>12</sub>NO<sub>2</sub>F<sub>2</sub> [(M + H)<sup>+</sup>] 240.0836, found 240.0833.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2956, 1716, 1447, 1396, 1240, 1180, 991, 737, 720.



(2k)

**Ethyl 5,5-difluoroundecanoate:**

According to the general procedure, a mixture of 2-(4-ethoxy-4-oxobutyl)-2-hexylmalonic acid (60.5 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2k** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) as a colorless oil (27.7 mg, 55%).

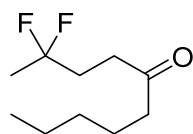
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  4.14 (q,  $J$  = 7.1 Hz, 2H), 2.36 (t,  $J$  = 7.0 Hz, 2H), 1.93 – 1.73 (m, 6H), 1.50 – 1.40 (m, 2H), 1.35 – 1.23 (m, 9H), 0.89 (t,  $J$  = 6.7 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -97.7 – -98.0 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  173.2, 125.2 (t,  $J$  = 240.4 Hz), 60.5, 36.5 (t,  $J$  = 25.2 Hz), 35.6 (t,  $J$  = 25.7 Hz), 33.8, 31.7, 29.2, 22.6, 22.4 (t,  $J$  = 4.6 Hz), 18.1 (t,  $J$  = 4.9 Hz), 14.4, 14.2.

**HRMS-EI (m/z)** calcd for C<sub>13</sub>H<sub>24</sub>FO<sub>2</sub> [(M - F)<sup>+</sup>] 231.1760, found 231.1767.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2959, 2934, 1738, 1464, 1376, 1260, 1188, 1033, 953, 861, 806.



(2l)

**2, 2-Difluorodecan-5-one:**

According to the general procedure, a mixture of 2-methyl-2-(3-oxooctyl) malonic acid (48.9 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2l** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) as a colorless oil (26.4 mg, 69%).

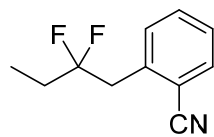
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  2.63 (t,  $J$  = 7.6 Hz, 2H), 2.43 (t,  $J$  = 7.5 Hz, 2H), 2.22 – 2.07 (m, 2H), 1.67 – 1.54 (m, 5H), 1.37 – 1.21 (m, 4H), 0.89 (t,  $J$  = 7.0 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -92.3 – -92.6 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  209.4, 123.8 (t,  $J$  = 237.8 Hz), 43.1, 35.4 (t,  $J$  = 3.4 Hz), 31.8 (t,  $J$  = 25.6 Hz), 31.5, 23.8 (t,  $J$  = 27.7 Hz), 23.7, 22.6, 14.1.

**HRMS-EI (m/z)** calcd for C<sub>10</sub>H<sub>18</sub>F<sub>2</sub>O [M<sup>+</sup>] 192.1326, found 192.1322.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2958, 2934, 1718, 1394, 1299, 1241, 1129, 1083, 897.



(2m)

**2-(2, 2-Difluorobutyl) benzonitrile:**

According to the general procedure, a mixture of 2-(2-cyanobenzyl)-2-ethylmalonic acid (49.5 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h.

The product **2m** was isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1) as a yellow oil (24.2 mg, 62%).

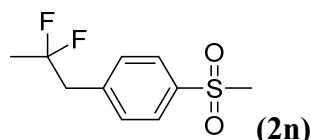
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.67 (dd,  $J$  = 7.9, 0.9 Hz, 1H), 7.57 (td,  $J$  = 7.7, 1.1 Hz, 1H), 7.48 (d,  $J$  = 7.8 Hz, 1H), 7.40 (td,  $J$  = 7.6, 0.9 Hz, 1H), 3.40 (t,  $J$  = 16.1 Hz, 2H), 2.03 – 1.82 (m, 2H), 1.08 (t,  $J$  = 7.6 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -99.1 – -99.4 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  137.2, 133.0, 132.8, 131.8, 128.1, 123.6 (t,  $J$  = 243.2 Hz), 118.1, 114.4, 40.9 (t,  $J$  = 26.5 Hz), 29.8 (t,  $J$  = 25.5 Hz), 6.5 (t,  $J$  = 5.4 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>11</sub>H<sub>12</sub>F<sub>2</sub>N [(M + H)<sup>+</sup>] 196.0938, found 196.0938.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2986, 2227, 1466, 1368, 1198, 1136, 984, 762.



#### 1-(2,2-Difluoropropyl)-4-(methylsulfonyl) benzene:

According to the general procedure, a mixture of 2-methyl-2-(4-(methylsulfonyl) benzyl) malonic acid (57.3 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2n** was isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a white solid (39.8 mg, 85%, Mp: 87–88 °C).

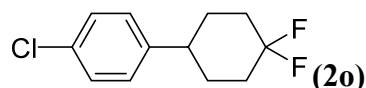
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.91 (d,  $J$  = 8.2 Hz, 2H), 7.49 (d,  $J$  = 8.1 Hz, 2H), 3.24 (t,  $J$  = 15.6 Hz, 2H), 3.07 (s, 3H), 1.59 (t,  $J$  = 18.3 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -89.2 – -89.5 (m, 2F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  134.0 (t,  $J$  = 4.2 Hz), 139.8, 131.4, 127.6, 122.7 (t,  $J$  = 240.1 Hz), 44.6, 44.3 (t,  $J$  = 26.5 Hz), 23.3 (t,  $J$  = 27.3 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>10</sub>H<sub>13</sub>SO<sub>2</sub>F<sub>2</sub> [(M + H)<sup>+</sup>] 235.0604, found 235.0603.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 3010, 2927, 1410, 1304, 1234, 1150, 773, 875.



#### 1-Chloro-4-(4,4-difluorocyclohexyl) benzene:

According to the general procedure, a mixture of 4-(4-chlorophenyl)cyclohexane-1,1-dicarboxylic acid (56.6 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>HPO<sub>4</sub> (69.6 mg, 0.4 mmol, 2 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product **2o** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a white solid (36.4 mg, 79%, Mp: 52–54 °C).

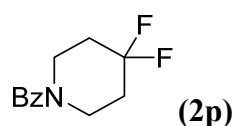
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.27 (d,  $J$  = 8.4 Hz, 2H), 7.15 (d,  $J$  = 8.4 Hz, 2H), 2.64 – 2.52 (m, 1H), 2.29 – 2.14 (m, 2H), 1.98 – 1.66 (m, 6H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -91.7 (d,  $J$  = 236.6 Hz, 1F), -101.6 – -102.9 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  143.8, 132.2, 128.8, 128.2, 123.1 (t,  $J$  = 239.8 Hz), 42.1, 34.1 (dd,  $J$  = 25.6, 22.8 Hz), 30.4 (d,  $J$  = 10.2 Hz).

**HRMS-EI (m/z)** calcd for C<sub>12</sub>H<sub>13</sub>F<sub>2</sub>Cl [M<sup>+</sup>] 230.0674, found 230.0682.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2951, 2868, 1494, 1448, 1269, 1134, 1108, 827, 741.



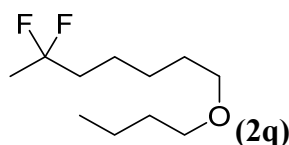
**(4, 4-Difluoropiperidin-1-yl)( phenyl) methanone<sup>8</sup>:**

According to the general procedure, a mixture of 1-benzoylpiperidine-4, 4-dicarboxylic acid (55.5 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (6.8 mg, 0.04 mmol, 0.2 equiv.), K<sub>2</sub>HPO<sub>4</sub> (104.4 mg, 0.6 mmol, 3 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water (4 mL, 1/1 v/v) was stirred at 55 °C for 12 h. The product **2p** was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a white solid (36.4 mg, 81%, Mp: 69–71 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 – 7.35 (m, 5H), 4.03 – 3.39 (m, 4H), 2.17 – 1.83 (m, 4H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -97.4 – -98.0 (m, 2F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 135.3, 130.2, 128.7, 127.0, 121.6 (t, *J* = 242.3 Hz), 44.6, 39.2, 34.6, 34.1.

**1-Butoxy-6, 6-difluoroheptane:**

According to the general procedure, a mixture of 2-(5-butoxypentyl)-2-methylmalonic acid (52.1 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2q** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) as a colorless oil (24.1 mg, 58%).

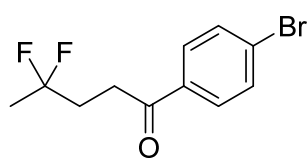
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.40 (t, *J* = 6.7 Hz, 4H), 1.93 – 1.74 (m, 2H), 1.64 – 1.32 (m, 13H), 0.92 (t, *J* = 7.4 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -90.1 – -90.5 (m, 2F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 124.5 (t, *J* = 237.5 Hz), 70.8, 70.7, 38.1 (t, *J* = 25.4 Hz), 32.0, 29.7, 26.2, 23.4 (t, *J* = 28.1 Hz), 22.8 (t, *J* = 4.6 Hz), 19.5, 14.1.

HRMS-EI (*m/z*) calcd for C<sub>11</sub>H<sub>22</sub>F<sub>2</sub>O [*M*<sup>+</sup>] 208.1639, found 208.1645.

IR (KBr): ν (cm<sup>-1</sup>) 2959, 2937, 1466, 1392, 1261, 1112, 911, 805.

**1-(4-Bromophenyl)-4, 4-difluoropentan-1-one:**

According to the general procedure, a mixture of 2-(3-(4-bromophenyl)-3-oxopropyl)-2-methylmalonic acid (65.8 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2r** was isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1) as a white solid (40.8 mg, 74%, Mp: 54–55 °C).

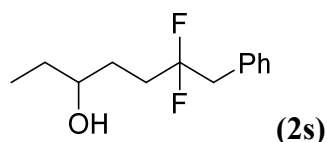
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 7.6 Hz 2H), 2.40 – 2.25 (m, 2H), 1.67 (t, *J* = 18.4 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -92.3 – -92.6 (m, 2F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.3, 135.3, 132.1, 129.7, 128.6, 123.8 (t, *J* = 238.0 Hz), 32.1 (t, *J* = 25.4 Hz), 31.5 (t, *J* = 3.6 Hz), 24.0 (t, *J* = 27.6 Hz).

HRMS-ESI (*m/z*) calcd for C<sub>11</sub>H<sub>12</sub>BrOF<sub>2</sub> [(*M* + *H*)<sup>+</sup>] 277.0040, found 277.0034.

IR (KBr): ν (cm<sup>-1</sup>) 2950, 1683, 1394, 1243, 1208, 1164, 830, 740.



### 6, 6-Difluoro-7-phenylheptan-3-ol:

According to the general procedure, a mixture of 2-benzyl-2-(3-hydroxypentyl)malonic acid (56.1 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), PhCOONa (100.8 mg, 0.7 mmol, 3.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (5 mL, 1/1/3 v/v/v) was stirred at room temperature for 12 h. The product **2s** was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a colorless oil (16.0 mg, 35%). 6, 6-difluoro-7-phenylheptan-3-one was isolated as a by-product (15.0 mg, 33%, colorless oil).

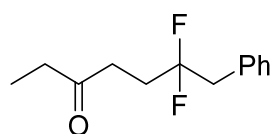
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.38 – 7.16 (m, 5H), 3.50 (tt, *J* = 8.4, 4.6 Hz, 1H), 3.15 (t, *J* = 16.0 Hz, 2H), 2.12 – 1.90 (m, 1H), 1.89 – 1.65 (m, 2H), 1.63 – 1.37 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -96.6 – -97.3 (m, 2F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 133.5, 130.4, 128.6, 127.4, 124.4 (t, *J* = 242.2 Hz), 72.8, 43.4 (t, *J* = 26.2 Hz), 32.2 (t, *J* = 25.0 Hz), 30.5, 29.2 (t, *J* = 3.7 Hz), 10.0.

HRMS-ESI (m/z) calcd for C<sub>13</sub>H<sub>18</sub>NaOF<sub>2</sub> [(M + Na)<sup>+</sup>] 251.1223, found 251.1218.

IR (KBr): ν (cm<sup>-1</sup>) 3374, 2966, 2934, 1497, 1455, 1260, 1105, 737, 700.



### 6, 6-Difluoro-7-phenylheptan-3-one

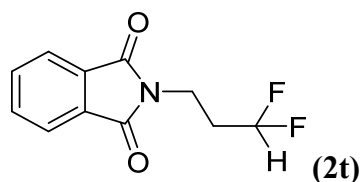
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41 – 7.14 (m, 5H), 3.15 (t, *J* = 16.0 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.45 (q, *J* = 7.3 Hz, 2H), 2.21 – 1.93 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -98.1 – -98.5 (m, 2F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 209.7, 133.2, 130.4, 128.6, 127.5, 123.8 (t, *J* = 242.3 Hz), 43.7 (t, *J* = 26.0 Hz), 36.2, 34.5, 29.9 (t, *J* = 24.9 Hz), 7.9.

HRMS-ESI (m/z) calcd for C<sub>13</sub>H<sub>16</sub>NaOF<sub>2</sub> [(M + Na)<sup>+</sup>] 249.1067, found 249.1063.

IR (KBr): ν (cm<sup>-1</sup>) 2976, 2939, 1718, 1497, 1456, 1356, 1243, 701.



### 2-(3,3-Difluoropropyl)isoindoline-1,3-dione:

According to the general procedure, a mixture of 2-(2-(1,3-dioxoisoindolin-2-yl)ethyl)malonic acid (55.4 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>HPO<sub>4</sub> (139.2 mg, 0.8 mmol, 4 equiv.) and Selectfluor (567 mg, 1.6 mmol, 8 equiv.) in acetonitrile/water (4 mL, 1/1 v/v) was stirred at 55 °C for 12 h. The product **2t** was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a white solid (9.5 mg, 21%, Mp: 58–59 °C). 4-(1,3-dioxoisoindolin-2-yl)-2,2-difluorobutanoic acid was isolated as a by-product (15.1 mg, 28%, white solid, Mp: 204–206 °C).

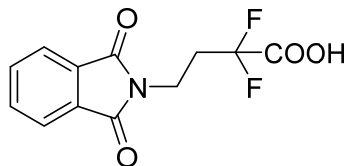
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.3, 3.1 Hz, 2H), 5.94 (tt, *J* = 56.0, 4.4 Hz, 1H), 3.90 (t, *J* = 6.9 Hz, 2H), 2.35 – 2.16 (m, 2H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -116.1 – -116.4 (m, 2F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.2, 134.3, 132.1, 123.6, 115.8 (t,  $J$  = 239.7 Hz), 33.2 (t,  $J$  = 21.5 Hz), 31.7 (t,  $J$  = 7.0 Hz).

HRMS-ESI (m/z) calcd for  $\text{C}_{11}\text{H}_{10}\text{NO}_2\text{F}_2$  [(M + H) $^+$ ] 226.0680, found 226.0676.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2944, 1704, 1613, 1466, 1397, 1137, 954, 900, 718.



**4-(1,3-Dioxoisindolin-2-yl)-2,2-difluorobutanoic acid:**

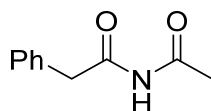
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  7.90 – 7.85 (m, 2H), 7.82 – 7.74 (m, 2H), 3.89 (t,  $J$  = 7.4 Hz, 2H), 2.53 – 2.28 (m, 2H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  -106.5 (t,  $J$  = 16.4 Hz, 2F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  170.5, 170.2, 135.0, 131.3, 123.6, 117.3 (t,  $J$  = 250.1 Hz), 32.5 (t,  $J$  = 24.5 Hz), 31.7 (t,  $J$  = 6.0 Hz).

HRMS-ESI (m/z) calcd for  $\text{C}_{12}\text{H}_{10}\text{NO}_4\text{F}_2$  [(M + H) $^+$ ] 270.0578, found 270.0571.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3332, 1719, 1651, 1401, 1379, 1181, 968, 722.

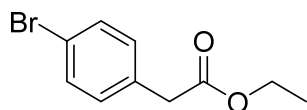


**N-acetyl-2-phenylacetamide<sup>9</sup>:**

According to the general procedure, a mixture of 2-acetamido-2-benzylmalonic acid (50.2 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product N-acetyl-2-phenylacetamide was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a white solid (21.6 mg, 60%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.81 (s, 1H), 7.41 – 7.30 (m, 3H), 7.29 – 7.25 (m, 2H), 3.80 (s, 2H), 2.38 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.7, 171.4, 133.2, 129.6, 129.1, 127.8, 44.4, 25.3.



**Ethyl 2-(4-bromophenyl)acetate<sup>10</sup>:**

According to the general procedure, a mixture of 2-(4-bromobenzyl)-2-ethoxymalonic acid (63.4 mg, 0.2 mmol, 1.0 equiv.),  $\text{AgNO}_3$  (10.2 mg, 0.06 mmol, 0.3 equiv.),  $\text{PhCOONa}$  (72.0 mg, 0.5 mmol, 2.5 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water/hexane (3 mL, 1/1/3 v/v/v) was stirred at 55 °C for 12 h. The product ethyl 2-(4-bromophenyl)acetate was isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1) as a colorless oil (12.0 mg, 25%).

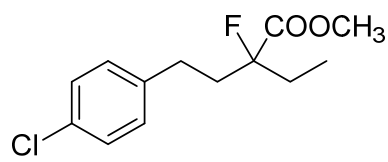
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J$  = 8.4 Hz, 2H), 7.16 (d,  $J$  = 8.4 Hz, 2H), 4.15 (q,  $J$  = 7.1 Hz, 2H), 3.57 (s, 2H), 1.25 (t,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.3, 133.2, 131.8, 131.1, 121.2, 61.2, 40.9, 14.3.

#### 4. General Procedure for Silver-Catalyzed Decarboxylative Monofluorination and Spectral Characterizations of the Products

### 3

*gem*-Dicarboxylic acids (0.20 mmol), K<sub>2</sub>HPO<sub>4</sub> (0.8 mmol), AgNO<sub>3</sub> (0.04 mmol) and Selectfluor (0.4 mmol) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then the mixed solvent CPME/H<sub>2</sub>O (4 mL, 1/1 v/v) was added, the resulting mixture was stirred (600 r/min) at room temperature for 12 h. The reaction was quenched with 3M HCl (2 mL), extracted with ethyl acetate (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was dissolved in DCM/MeOH (5 mL, 4/1 v/v), followed the addition of (trimethylsilyl)diazomethane solution (0.6 mL, 2.0 M in hexanes), monitored the reaction with TLC, after the  $\alpha$ -fluorocarboxylic acid was fully converted to corresponding methyl ester, acetic acid was added to consume the remaining (trimethylsilyl)diazomethane. Then removed solvent under reduced pressure, the crude product was purified by column chromatography on silica gel or preparative TLC to give the desired product. (CPME: cyclopentyl methyl ether).



#### Methyl 4-(4-chlorophenyl)-2-ethyl-2-fluorobutanoate:

Followed the general procedure, the product **3a** was isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1) as a colorless oil (28.1 mg, 54%), 20% yield of starting material was recovered. We found that prolonging the reaction time and increasing the catalyst loading could not improve the yield of **3a**.

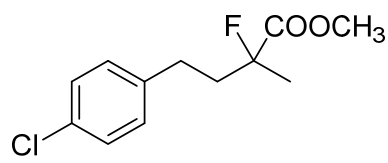
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (d,  $J$  = 8.4 Hz, 2H), 7.10 (d,  $J$  = 8.4 Hz, 2H), 3.76 (s, 3H), 2.85 – 2.70 (m, 1H), 2.57 – 2.45 (m, 1H), 2.27 – 1.76 (m, 4H), 0.95 (t,  $J$  = 7.5 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -168.3 – -168.7 (m, 1F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  171.9 (d,  $J$  = 25.9 Hz), 139.4, 132.0, 129.9, 128.7, 97.8 (d,  $J$  = 188.7 Hz), 52.5, 38.9 (d,  $J$  = 22.3 Hz), 30.8 (d,  $J$  = 22.9 Hz), 29.1 (d,  $J$  = 3.7 Hz), 7.7 (d,  $J$  = 4.3 Hz).

HRMS-ESI (m/z) calcd for C<sub>13</sub>H<sub>17</sub>ClFO<sub>2</sub> [(M + H)<sup>+</sup>] 259.0901, found 259.0901.

IR (KBr):  $\nu$  (cm<sup>-1</sup>) 2954, 1760, 1734, 1493, 1243, 1197, 1176, 1094, 814.



#### Methyl 4-(4-chlorophenyl)-2-fluoro-2-methylbutanoate:

Followed the general procedure, the product **3b** was isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1) as a colorless oil (29.9 mg, 61%).

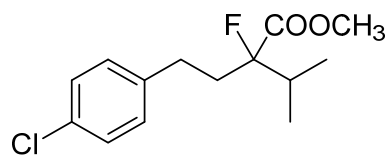
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.25 (d,  $J$  = 8.4 Hz, 2H), 7.11 (d,  $J$  = 8.4 Hz, 2H), 3.76 (s, 3H), 2.85 – 2.70 (m, 1H), 2.60 – 2.48 (m, 1H), 2.32 – 1.99 (m, 2H), 1.60 (d,  $J$  = 21.4 Hz, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -157.1 – -157.5 (m, 1F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.4 (d,  $J = 25.3$  Hz), 139.3, 132.0, 129.9, 128.7, 94.7 (d,  $J = 185.8$  Hz), 52.7, 40.1 (d,  $J = 22.4$  Hz), 29.1 (d,  $J = 3.8$  Hz), 24.0 (d,  $J = 24.2$  Hz).

HRMS-ESI (m/z) calcd for  $\text{C}_{12}\text{H}_{15}\text{ClFO}_2$  [(M + H) $^+$ ] 245.0745, found 245.0746.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2955, 1760, 1742, 1493, 1378, 1265, 1197, 1119, 1092, 1015, 814, 740.



(3c)

**Methyl 2-(4-chlorophenethyl)-2-fluoro-3-methylbutanoate:**

*gem*-Dicarboxylic acid (0.20 mmol),  $\text{PhCOONa}$  (0.7 mmol),  $\text{AgNO}_3$  (0.06 mmol) and Selectfluor (0.8 mmol) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then the mixed solvent CPME/ $\text{H}_2\text{O}$ /acetonitrile/hexane (14 mL, 9/1/1/3 v/v/v/v) was added. The resulting reaction mixture was stirred (600 r/min) at 55  $^\circ\text{C}$  for 12 h. Then followed the general procedure, the crude product was purified by preparative TLC (petroleum ether/ethyl acetate = 20/1), to give the desired product **3c** as a colorless oil (16.3 mg, 30%), and 32% yield of starting material was recovered.

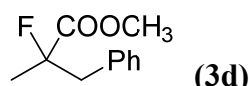
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25 (d,  $J = 8.4$  Hz, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 3.77 (s, 3H), 2.84 – 2.67 (m, 1H), 2.51 – 2.39 (m, 1H), 2.22 – 2.03 (m, 3H), 0.98 (dd,  $J = 11.1, 6.9$  Hz, 6H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -175.5 – -175.8 (m, 1F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.9 (d,  $J = 25.9$  Hz), 139.6, 132.0, 129.9, 128.7, 99.9 (d,  $J = 191.7$  Hz), 52.3, 37.0 (d,  $J = 22.3$  Hz), 35.0 (d,  $J = 22.2$  Hz), 29.4 (d,  $J = 3.7$  Hz), 16.7 (dd,  $J = 127.4, 4.3$  Hz).

HRMS-ESI (m/z) calcd for  $\text{C}_{14}\text{H}_{19}\text{ClFO}_2$  [(M + H) $^+$ ] 273.1058, found 273.1062.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2971, 1760, 1739, 1493, 1254, 1196, 1168, 1093, 1059, 814.



(3d)

**Methyl 2-fluoro-2-methyl-3-phenylpropanoate:**

Followed the general procedure, the product **3d** was isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1) as a colorless oil (29.9 mg, 76%).

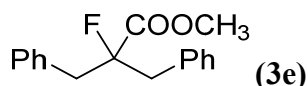
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 – 7.23 (m, 3H), 7.23 – 7.17 (m, 2H), 3.71 (s, 3H), 3.30 – 3.02 (m, 2H), 1.57 (d,  $J = 21.2$  Hz, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -154.9 – -155.2 (m, 1F).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.2 (d,  $J = 25.1$  Hz), 134.6, 130.3, 128.4, 127.3, 95.2 (d,  $J = 187.8$  Hz), 52.6, 44.3 (d,  $J = 21.8$  Hz), 23.3 (d,  $J = 24.2$  Hz).

HRMS-ESI (m/z) calcd for  $\text{C}_{11}\text{H}_{14}\text{FO}_2$  [(M + H) $^+$ ] 197.0978, found 197.0976.

IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2955, 1763, 1742, 1498, 1455, 1376, 1200, 1122, 985, 817, 702.



(3e)

**Methyl 2-benzyl-2-fluoro-3-phenylpropanoate:**

*gem*-Dicarboxylic acid (0.20 mmol),  $\text{PhCOONa}$  (0.7 mmol),  $\text{AgNO}_3$  (0.06 mmol) and Selectfluor (0.8 mmol) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then the mixed solvent CPME/ $\text{H}_2\text{O}$ /acetonitrile/hexane (14 mL, 9/1/1/3 v/v/v/v) was added. The resulting reaction mixture was stirred (600 r/min) at

room temperature for 12 h. Then followed the general procedure, the crude product was purified by preparative TLC (petroleum ether/ethyl acetate = 20/1), to give the desired product **3e** as a white solid (25.6 mg, 47%, Mp: 37–39 °C), 40% yield of starting material was recovered.

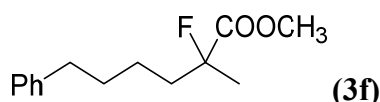
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.33 – 7.17 (m, 10H), 3.53 (s, 3H), 3.33 – 3.05 (m, 4H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -163.7 – -163.9 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.0 (d, *J* = 25.3 Hz), 134.5, 130.3, 128.4, 127.3, 97.8 (d, *J* = 194.7 Hz), 52.3, 43.4 (d, *J* = 21.5 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>17</sub>H<sub>18</sub>FO<sub>2</sub> [(M + H)<sup>+</sup>] 273.1291, found 273.1289.

**IR (KBr):** ν (cm<sup>-1</sup>) 2952, 1764, 1736, 1496, 1236, 1200, 1086, 749, 700.



**Methyl 2-fluoro-2-methyl-6-phenylhexanoate:**

Followed the general procedure, the product **3f** was isolated by preparative TLC (petroleum ether/ethyl acetate = 50/1) as a yellow oil (28.5 mg, 60%).

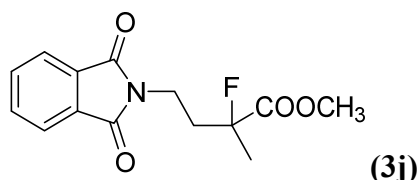
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.31 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 3.77 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.04 – 1.74 (m, 2H), 1.68 – 1.48 (m, 6H), 1.36 – 1.27 (m, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -156.2 – -156.6 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 172.8 (d, *J* = 25.6 Hz), 142.3, 128.5, 128.4, 125.9, 95.4 (d, *J* = 184.7 Hz), 52.6, 38.3 (d, *J* = 22.4 Hz), 35.8, 31.4, 23.8 (d, *J* = 24.3 Hz), 23.1 (d, *J* = 3.3 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>20</sub>FO<sub>2</sub> [(M + H)<sup>+</sup>] 239.1447, found 239.1449.

**IR (KBr):** ν (cm<sup>-1</sup>) 2952, 1762, 1741, 1497, 1454, 1197, 1123, 982, 700.



**Methyl 4-(1,3-dioxoisindolin-2-yl)-2-fluoro-2-methylbutanoate:**

Followed the general procedure, the product **3j** was isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a white solid (51.3 mg, 92%, Mp: 87–89 °C).

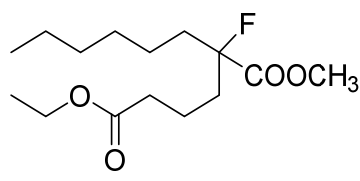
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.93 – 3.69 (m, 5H), 2.46 – 2.17 (m, 2H), 1.63 (d, *J* = 21.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -157.8 – -158.2 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.9 (d, *J* = 25.2 Hz), 168.1, 134.1, 132.2, 123.4, 93.9 (d, *J* = 186.0 Hz), 52.9, 36.2 (d, *J* = 21.7 Hz), 33.0 (d, *J* = 4.7 Hz), 23.8 (d, *J* = 24.1 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>15</sub>FNO<sub>4</sub> [(M + H)<sup>+</sup>] 280.0985, found 280.0984.

**IR (KBr):** ν (cm<sup>-1</sup>) 2955, 1758, 1740, 1713, 1400, 1376, 1190, 750, 721.



**6-Ethyl 1-methyl 2-fluoro-2-hexylhexanedioate:**

Followed the general procedure, the product **3k** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) as a colorless oil (36.3 mg, 63%).

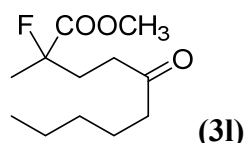
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 4.13 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.71 (m, 5H), 1.66 – 1.37 (m, 2H), 1.34 – 1.14 (m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -166.0 – -166.2 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 173.1, 172.1 (d, *J* = 26.0 Hz), 97.7 (d, *J* = 187.9 Hz), 60.5, 52.5, 37.5 (d, *J* = 22.3 Hz), 36.8 (d, *J* = 22.3 Hz), 34.0, 31.7, 29.3, 23.2 (d, *J* = 2.8 Hz), 22.6, 19.0 (d, *J* = 3.4 Hz), 14.4, 14.2.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>28</sub>FO<sub>4</sub> [(M + H)<sup>+</sup>] 291.1972, found 291.1967.

**IR (KBr):** ν (cm<sup>-1</sup>) 2956, 2931, 1763, 1738, 1459, 1193, 1032, 860, 818.



**Methyl 2-fluoro-2-methyl-5-oxodecanoate:**

Followed the general procedure, the product **3l** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) as a colorless oil (36.4 mg, 78%).

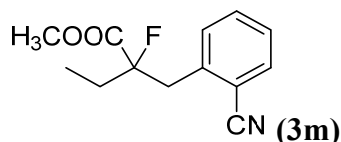
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 3.79 (s, 3H), 2.65 – 2.55 (m, 1H), 2.49 – 2.36 (m, 3H), 2.32 – 2.02 (m, 2H), 1.63 – 1.49 (m, 5H), 1.36 – 1.18 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -156.8 – -157.3 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 209.4, 172.2 (d, *J* = 25.8 Hz), 94.4 (d, *J* = 184.6 Hz), 52.7, 43.0, 36.4 (d, *J* = 2.9 Hz), 32.1 (d, *J* = 22.2 Hz), 31.5, 23.9 (d, *J* = 24.1 Hz), 23.6, 22.5, 14.0.

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>22</sub>FO<sub>3</sub> [(M + H)<sup>+</sup>] 233.1553, found 233.1549.

**IR (KBr):** ν (cm<sup>-1</sup>) 2957, 2934, 1760, 1743, 1717, 1458, 1379, 1203, 1123, 895, 806.



**Methyl 2-(2-cyanobenzyl)-2-fluorobutanoate:**

Followed the general procedure, the product **3m** was isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1) as a yellow oil (34.7 mg, 74%).

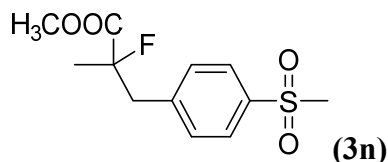
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.64 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.54 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38 (m, 2H), 3.74 (s, 3H), 3.54 – 3.33 (m, 2H), 2.22 – 1.81 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -165.6 – -166.0 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.8 (d, *J* = 26.4 Hz), 138.4, 133.0, 132.8, 131.3, 127.9, 118.0, 114.1, 97.6 (d, *J* = 191.9 Hz), 52.6, 41.1 (d, *J* = 21.5 Hz), 30.5 (d, *J* = 22.7 Hz), 7.7 (d, *J* = 4.0 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>15</sub>FNO<sub>2</sub> [(M + H)<sup>+</sup>] 236.1087, found 236.1083.

**IR (KBr):** ν (cm<sup>-1</sup>) 2977, 2955, 2227, 1760, 1739, 1600, 1489, 1247, 1206, 776.



**Methyl 2-fluoro-2-methyl-3-(4-(methylsulfonyl) phenyl) propanoate:**

Followed the general procedure, the product **3n** was isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a white solid (44.0 mg, 80%, Mp: 41–43 °C).

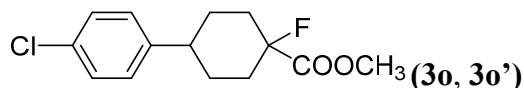
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 3.40 – 3.10 (m, 2H), 3.06 (s, 3H), 1.61 (d, *J* = 21.2 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -155.3 – -155.6 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.6 (d, *J* = 25.1 Hz), 141.1, 139.6, 131.3, 127.5, 94.7 (d, *J* = 189.0 Hz), 52.8, 44.6, 43.9 (d, *J* = 21.8 Hz), 23.7 (d, *J* = 24.0 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>12</sub>H<sub>16</sub>FSO<sub>4</sub> [(M + H)<sup>+</sup>] 275.0753, found 275.0747.

**IR (KBr):** ν (cm<sup>-1</sup>) 2956, 1755, 1739, 1304, 1276, 1149, 1116, 764, 750.

**Methyl 4-(4-chlorophenyl)-1-fluorocyclohexane-1-carboxylate:**

Followed the general procedure, the products **3o** and **3o'** as a pair of diastereomers (dr 3.5/1) were isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1), the major diastereomer **3o** was isolated as a white solid (24.4 mg, 45%, Mp: 110–111 °C), the minor **3o'** was isolated as a colorless oil (7.0 mg, 13%).

The major diastereomer **3o**:

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.27 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 2.66 – 2.52 (m, 1H), 2.22 – 2.10 (m, 2H), 2.09 – 1.87 (m, 2H), 1.86 – 1.77 (m, 4H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -167.0 – -167.3 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 172.9 (d, *J* = 24.6 Hz), 144.7, 132.1, 128.7, 128.3, 93.2 (d, *J* = 186.6 Hz), 52.8, 42.2, 32.9 (d, *J* = 22.7 Hz), 28.3.

**HRMS-EI (m/z)** calcd for C<sub>14</sub>H<sub>16</sub>FO<sub>2</sub>Cl [M<sup>+</sup>] 270.0823, found 270.0819.

**IR (KBr):** ν (cm<sup>-1</sup>) 2959, 2936, 1754, 1489, 1301, 1258, 1126, 1063, 740.

The minor diastereomer **3o'**:

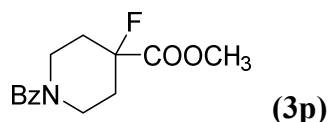
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.72 – 2.54 (m, 1H), 2.42 – 2.31 (m, 2H), 2.01 – 1.90 (m, 2H), 1.88 – 1.74 (m, 4H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -144.2 – -146.0 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.4 (d, *J* = 25.4 Hz), 143.7 (d, *J* = 2.4 Hz), 132.0, 128.7, 128.4, 94.2 (d, *J* = 183.0 Hz), 52.7, 41.4, 33.4 (d, *J* = 21.0 Hz), 30.0 (d, *J* = 9.5 Hz).

**HRMS-EI (m/z)** calcd for C<sub>14</sub>H<sub>16</sub>FO<sub>2</sub>Cl [M<sup>+</sup>] 270.0823, found 270.0819.

**IR (KBr):** ν (cm<sup>-1</sup>) 2951, 1743, 1493, 1311, 1216, 1128, 828, 763.

**Methyl 1-benzoyl-4-fluoropiperidine-4-carboxylate:**

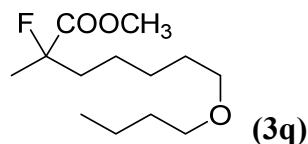
Followed the general procedure, the product **3p** was isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a white solid (46.1 mg, 87%, Mp: 46–48 °C).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.47 – 7.35 (m, 5H), 4.77 – 4.45 (m, 1H), 3.82 (s, 3H), 3.80 – 3.60 (m, 1H), 3.50 – 3.05 (m, 2H), 2.30 – 1.70 (m, 4H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -167.5 – -167.8 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 171.0 (d, *J* = 24.3 Hz), 170.6, 135.5, 130.0, 128.7, 126.9, 92.1 (d, *J* = 187.0 Hz), 53.0, 43.0, 37.4, 32.8, 32.3.

**HRMS-ESI** (m/z) calcd for  $C_{14}H_{17}FNO_3$  [(M + H)<sup>+</sup>] 266.1192, Found: 266.1186.  
**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2932, 1743, 1636, 1434, 1294, 1110, 1070, 750, 711.



**Methyl 7-butoxy-2-fluoro-2-methylheptanoate:**

Followed the general procedure, the product **3q** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) as a colorless oil (39.8 mg, 80%).

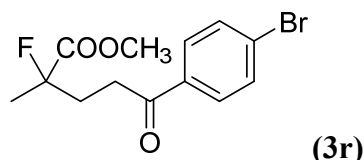
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  3.79 (s, 3H), 3.43 – 3.35 (m, 4H), 2.00 – 1.73 (m, 2H), 1.61 – 1.45 (m, 8H), 1.43 – 1.30 (m, 5H), 0.92 (t,  $J$  = 7.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -156.3 – -156.6 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  172.8 (d,  $J$  = 25.3 Hz), 95.3 (d,  $J$  = 184.6 Hz), 70.8, 70.7, 52.5, 38.5 (d,  $J$  = 22.4 Hz), 32.0, 29.7, 26.2, 23.8 (d,  $J$  = 24.3 Hz), 23.3 (d,  $J$  = 3.4 Hz), 19.5, 14.1.

**HRMS-ESI** (m/z) calcd for  $C_{13}H_{26}FO_3$  [(M + H)<sup>+</sup>] 249.1866, found 249.1864.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2934, 1764, 1742, 1459, 1376, 1195, 1115, 813.



**Methyl 5-(4-bromophenyl)-2-fluoro-2-methyl-5-oxopentanoate:**

Followed the general procedure, the product **3r** was isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1) as a white solid (49.5 mg, 78%, Mp: 61–62 °C).

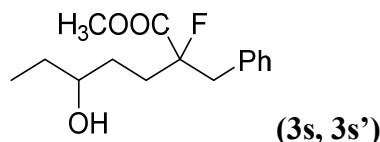
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.82 (d,  $J$  = 8.6 Hz, 2H), 7.61 (d,  $J$  = 8.6 Hz, 2H), 3.80 (s, 3H), 3.23 – 3.12 (m, 1H), 3.00 – 2.89 (m, 1H), 2.51 – 2.19 (m, 2H), 1.64 (d,  $J$  = 21.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -156.7 – -157.0 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  197.4, 172.1 (d,  $J$  = 25.7 Hz), 135.3, 132.0, 129.7, 128.5, 94.5 (d,  $J$  = 184.7 Hz), 52.8, 32.5, 32.3, 24.0 (d,  $J$  = 24.0 Hz).

**HRMS-ESI** (m/z) calcd for  $C_{13}H_{15}FO_3Br$  [(M + H)<sup>+</sup>] 317.0189, found 317.0189.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2954, 1756, 1689, 1585, 1448, 1275, 1207, 825, 790.



**Methyl 2-benzyl-2-fluoro-5-hydroxyheptanoate:**

*gem*-Dicarboxylic acids (0.20 mmol), K<sub>2</sub>HPO<sub>4</sub> (0.8 mmol), AgNO<sub>3</sub> (0.04 mmol) and Selectfluor (0.4 mmol) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then the mixed solvent CPME/H<sub>2</sub>O (4 mL, 1/1 v/v) was added, the resulting mixture was stirred (600 r/min) at room temperature for 2.5 h. The reaction was quenched with 3M HCl (2 mL), extracted with diethyl ether (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo at 0 °C. The residue was dissolved in DCM/MeOH (5 mL, 4/1 v/v), followed the addition of (trimethylsilyl)diazomethane solution (0.6 mL, 2.0 M in hexanes), monitored the reaction with TLC, after the  $\alpha$ -fluorocarboxylic acid was fully converted

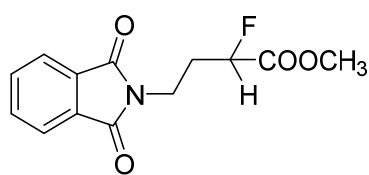
to corresponding methyl ester, acetic acid was added to consume the remaining (trimethylsilyl)diazomethane. Then removed solvent under reduced pressure. **3s** and **3s'** as a pair of diastereomers (dr = 1/1) were isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a colorless oil (41.7 mg, 78%). **3s** and **3s'** were inseparable. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: mixture of diastereomers,  $\delta$  7.35 – 7.21 (m, 3H), 7.21 – 7.15 (m, 2H), 3.70 – 3.64 (m, 3H), 3.53 – 3.40 (m, 1H), 3.27 – 3.04 (m, 2H), 2.30 – 1.76 (m, 2H), 1.75 – 1.54 (m, 1H), 1.52 – 1.38 (m, 3H), 1.34 – 1.22 (m, 1H), 0.96 – 0.87 (m, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**: mixture of diastereomers,  $\delta$  -164.7 – -165.4 (m, 1F)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: mixture of diastereomers,  $\delta$  171.8, 171.7, 171.6, 171.4, 134.5, 130.3, 130.2, 128.4, 127.3, 99.0, 98.7, 97.1, 96.8, 73.0, 72.8, 52.5, 43.9, 43.8, 43.7, 43.5, 30.6, 30.5, 30.5, 30.3, 10.0, 10.0.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>21</sub>NaFO<sub>3</sub> [(M + Na)<sup>+</sup>] 291.1372, found 291.1368.

**IR (KBr)**:  $\nu$  (cm<sup>-1</sup>) 3419, 2962, 2932, 1740, 1497, 1455, 1203, 701.



(3t)

#### Methyl 4-(1,3-dioxoisindolin-2-yl)-2-fluorobutanoate:

Followed the general procedure, a mixture of 2-(2-(1,3-dioxoisindolin-2-yl) ethyl) malonic acid (55.4 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv.), K<sub>2</sub>HPO<sub>4</sub> (139.2 mg, 0.8 mmol, 4 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water (4 mL, 1/4 v/v) was stirred at 55 °C for 12 h. The product **3t** was isolated by preparative TLC (petroleum ether/ethyl acetate = 2/1) as a white solid (21.7 mg, 41%, Mp: 87–88 °C). (Note: 30% <sup>19</sup>F NMR yield of 4-(1,3-dioxoisindolin-2-yl)-2,2-difluorobutanoic acid was observed.)

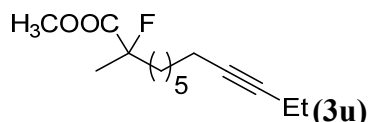
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.86 (dd,  $J$  = 5.5, 3.0 Hz, 2H), 7.73 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 5.01 (ddd,  $J$  = 48.6, 8.1, 4.0 Hz, 1H), 3.91 (t,  $J$  = 6.9 Hz, 2H), 3.78 (s, 3H), 2.43 – 2.20 (m, 2H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**:  $\delta$  -192.8 – -193.2 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  169.6 (d,  $J$  = 23.4 Hz), 168.2, 134.2, 132.1, 123.5, 87.2 (d,  $J$  = 185.8 Hz), 52.7, 34.0, 31.4 (d,  $J$  = 20.7 Hz).

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>13</sub>NFO<sub>4</sub> [(M + H)<sup>+</sup>] 266.0829, found 266.0830.

**IR (KBr)**:  $\nu$  (cm<sup>-1</sup>) 2956, 1767, 1743, 1712, 1441, 1398, 1293, 1219, 1138, 721.



Et(3u)

#### Methyl 2-fluoro-2-methyldodec-9-ynoate:

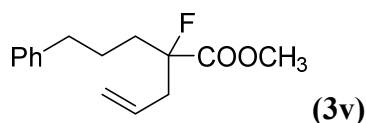
Followed the general procedure, the product **3u** was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) as a colorless oil (28.0 mg, 58%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  3.79 (s, 3H), 2.21 – 2.07 (m, 4H), 2.01 – 1.72 (m, 2H), 1.56 (d,  $J$  = 21.4 Hz, 3H), 1.52 – 1.20 (m, 8H), 1.11 (t,  $J$  = 7.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**:  $\delta$  -156.2 – -156.6 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  172.9 (d,  $J$  = 25.7 Hz), 95.4 (d,  $J$  = 184.2 Hz), 81.9, 79.5, 52.6, 38.6, 38.4, 29.1 (d,  $J$  = 6.0 Hz), 28.7, 23.8 (d,  $J$  = 24.4 Hz), 23.3 (d,  $J$  = 2.9 Hz), 18.8, 14.5, 12.5.

**HRMS-ESI** (m/z) calcd for  $C_{14}H_{23}NaFO_2$  [(M + Na)<sup>+</sup>] 265.1580, found 265.1571.  
**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2936, 2858, 1763, 1742, 1456, 1376, 1198, 1123, 724.



**Methyl 2-fluoro-2-(3-phenylpropyl)pent-4-enoate:**

Followed the general procedure, the product **3v** was isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1) as a colorless oil (6.8 mg, 14%).

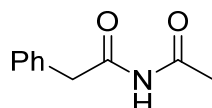
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.35 – 7.25 (m, 2H), 7.24 – 7.09 (m, 3H), 5.85 – 5.69 (m, 1H), 5.21 – 5.07 (m, 2H), 3.75 (s, 3H), 2.72 – 2.47 (m, 4H), 2.06 – 1.71 (m, 3H), 1.64 – 1.50 (m, 1H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -164.4 – -166.4 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  171.7 (d,  $J$  = 25.7 Hz), 141.6, 130.8, 128.5, 126.1, 119.8, 97.5 (d,  $J$  = 189.1 Hz), 52.5, 41.9 (d,  $J$  = 22.2 Hz), 36.6 (d,  $J$  = 22.1 Hz), 35.6, 25.0 (d,  $J$  = 2.7 Hz).

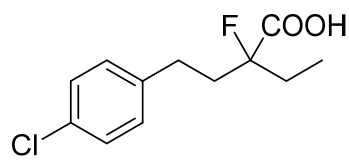
**HRMS-ESI** (m/z) calcd for  $C_{15}H_{20}FO_2$  [(M + H)<sup>+</sup>] 251.1447, found 251.1442.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2926, 2856, 1763, 1741, 1643, 1603, 1497, 1220, 1169, 699.



**N-acetyl-2-phenylacetamide<sup>9</sup>:**

Followed the general procedure, the product N-acetyl-2-phenylacetamide was isolated by preparative TLC (petroleum ether/ethyl acetate = 5/1) as a white solid (23.8 mg, 67%).



**4-(4-Chlorophenyl)-2-ethyl-2-fluorobutanoic acid:**

Followed the general procedure, after extraction and concentration, the residue was directly purified by preparative TLC (dichloromethane/methanol = 10/1) to deliver **3a acid** as a white solid (26.4 mg, 54%, Mp: 64–66 °C).

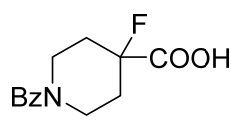
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.19 (d,  $J$  = 8.0 Hz, 2H), 7.03 (d,  $J$  = 8.0 Hz, 2H), 2.85 – 2.70 (m, 1H), 2.63 – 2.57 (m, 1H), 2.34 – 1.78 (m, 4H), 0.97 (t,  $J$  = 7.4 Hz, 3H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):**  $\delta$  -166.6 – -167.8 (m, 1F).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  177.1 (d,  $J$  = 27.5 Hz), 139.2, 132.1, 129.8, 128.7, 97.9 (d,  $J$  = 185.4 Hz), 38.7 (d,  $J$  = 22.2 Hz), 30.5 (d,  $J$  = 22.8 Hz), 29.1 (d,  $J$  = 2.7 Hz), 7.7 (d,  $J$  = 3.8 Hz).

**HRMS-EI** (m/z) calcd for  $C_{12}H_{13}O_2Cl$  [(M – HF)<sup>+</sup>] 224.0604, found 224.0609.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2975, 1728, 1492, 1275, 1260, 809, 764, 750.



**1-Benzoyl-4-fluoropiperidine-4-carboxylic acid:**

Followed the general procedure, after extraction and concentration, the residue was directly purified by preparative TLC (dichloromethane/methanol = 5/1) to deliver **3p acid** as a white solid (40.2 mg, 80%, Mp: 149–151 °C).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.47 – 7.40 (m, 5H), 4.78 – 4.50 (m, 1H), 3.85 – 3.60 (m, 1H), 3.50 – 3.30 (m, 1H), 3.30 – 3.10 (m, 1H), 2.30 – 1.80 (m, 4H).

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -167.4 – -168.3 (m, 1F).

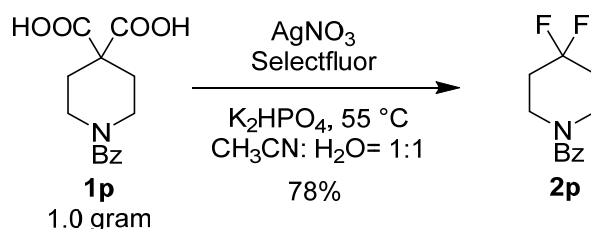
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 173.3 (d, *J* = 24.8 Hz), 171.5, 134.7, 130.4, 128.8, 127.0, 91.6 (d, *J* = 186.5 Hz), 43.3, 37.9, 32.6, 32.0.

**HRMS-ESI (m/z)** calcd for C<sub>13</sub>H<sub>15</sub>FNO<sub>3</sub> [(M + H)<sup>+</sup>] 252.1036, found 252.1034.

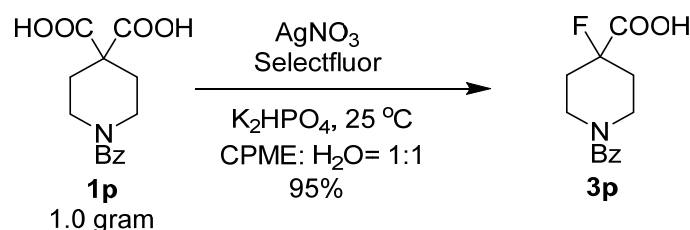
**IR (KBr):** ν (cm<sup>-1</sup>) 2931, 1742, 1591, 1447, 1290, 1258, 1067, 749.

## 5. Synthetic Applications

### 5.1 Gram-Scale Synthesis of 2p and 3p

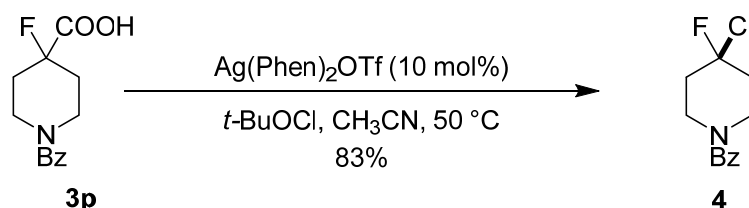


1-Benzoylpiperidine-4,4-dicarboxylic acid (1.00 g, 3.61 mmol, 1.0 equiv.),  $\text{K}_2\text{HPO}_4$  (1.89 g, 10.8 mmol, 3 equiv.),  $\text{AgNO}_3$  (123 mg, 0.72 mmol, 0.2 equiv.) and Selectfluor (7.67 g, 21.7 mmol, 6 equiv.) were placed in a 250 mL flask. The flask was evacuated and filled with nitrogen. Then acetonitrile (36 mL) and water (36 mL) were added at 0 °C, the resulting reaction mixture was stirred (300 r/min) at 0 °C about 5 min and then heated to 55 °C for 4 h. The reaction was quenched with 3M HCl (pH = 2), extracted with EtOAc, the combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo, the residue was purified by column chromatography on silica gel to give the desired product **2p** (634 mg, 78%).



1-Benzoylpiperidine-4,4-dicarboxylic acid (1.00 g, 3.61 mmol, 1.0 equiv.),  $\text{K}_2\text{HPO}_4$  (2.52 g, 14.4 mmol, 4 equiv.),  $\text{AgNO}_3$  (123 mg, 0.72 mmol, 0.2 equiv.) and Selectfluor (2.56 g, 7.22 mmol, 2 equiv.) were placed in a 250 mL flask. The flask was evacuated and filled with nitrogen. Then CPME (36 mL) and water (36 mL) were added at 0 °C, the resulting reaction mixture was stirred (300 r/min) at 0 °C about 5 min and then heated to 25 °C for 5 h. The reaction was quenched with saturated sodium carbonate solution (pH = 11), acetonitrile was removed in vacuo, then washed the aqueous layer with dichloromethane. HCl (3 M) was then added until pH = 2. The acidified aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo, to give the desired product **3p** (860 mg, 95%).

## 5.2 The Transformations of Compound 3p



1-Benzoyl-4-fluoropiperidine-4-carboxylic acid **3p** (25.1 mg, 0.1 mmol, 1.0 equiv.) and Ag(Phen)<sub>2</sub>OTf (6.2 mg, 0.01 mmol, 0.1 equiv.) were dissolved in anhydrous acetonitrile (2 mL), followed the addition of tert-butyl hypochlorite (32.6 mg, 0.3 mmol, 3 equiv) at room temperature. Then the resulting reaction mixture was stirred at 50 °C under nitrogen atmosphere. After 12 h, the reaction mixture was quenched with 3 M HCl (2 mL), extracted with EtOAc. The combined organic extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by preparative TLC (petroleum ether/ethyl acetate = 5/1 v/v), to give the desired product **4** as a white solid (20.1 mg, 83%, Mp: 72–73 °C).

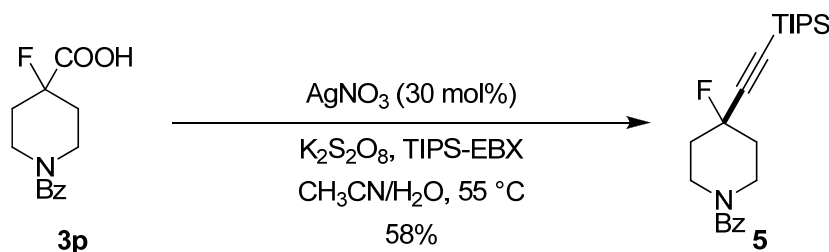
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49 – 7.34 (m, 5H), 4.05 – 3.40 (m, 4H), 2.50 – 2.04 (m, 4H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -100.8 – -102.0 (m, 1F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 135.3, 130.2, 128.8, 127.0, 112.0 (d, *J* = 245.1 Hz), 45.0, 40.1.

HRMS-ESI (*m/z*) calcd for C<sub>12</sub>H<sub>14</sub>ClFNO [(*M* + *H*)<sup>+</sup>] 242.0748, found 242.0744.

IR (KBr): ν (cm<sup>-1</sup>) 2968, 2934, 1634, 1466, 1427, 1351, 1250, 1073, 1027.



The mixture of 1-benzoyl-4-fluoropiperidine-4-carboxylic acid **3p** (25.1 mg, 0.1 mmol, 1.0 equiv.), AgNO<sub>3</sub> (5.1 mg, 0.03 mmol, 0.3 equiv), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (81.0 mg, 0.3 mmol, 3.0 equiv.) and triisopropylsilylethynylbenziodoxolone (85.7 mg, 0.2 mmol, 2.0 equiv) in CH<sub>3</sub>CN (1 mL) and water (1 mL) was stirred at 55 °C under nitrogen atmosphere for 16 h. The resulting mixture was cooled down to room temperature and then extracted with EtOAc. The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC (petroleum ether/ethyl acetate = 5/1 v/v) to give pure product **5** as a yellow solid (22.5 mg, 58%, Mp: 47–49 °C).

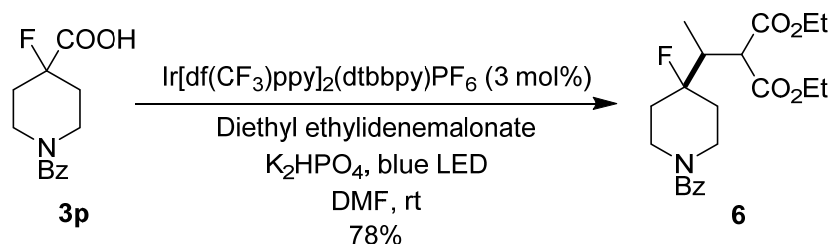
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 – 7.35 (m, 5H), 4.10 – 3.30 (m, 4H), 2.24 – 1.88 (m, 4H), 1.14 – 1.04 (m, 21H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -139.6 – -140.4 (m, 1F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.6, 135.7, 130.0, 128.7, 127.0, 105.0 (d, *J* = 28.4 Hz), 89.8 (d, *J* = 7.7 Hz), 87.9 (d, *J* = 171.6 Hz), 44.5, 39.0, 37.8, 37.3, 18.7, 11.1.

HRMS-ESI (*m/z*) calcd for C<sub>23</sub>H<sub>35</sub>FNOSi [(*M* + *H*)<sup>+</sup>] 388.2472, found 388.2469.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2958, 2943, 2866, 1644, 1464, 1427, 1280, 1250, 1119, 1045, 961, 882, 709.



$\text{Ir}[\text{df}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (3.4 mg, 3  $\mu\text{mol}$ , 0.03 equiv), 1-benzoyl-4-fluoropiperidine-4-carboxylic acid **3p** (25.1 mg, 0.1 mmol, 1.0 equiv.), diethyl ethylidenemalonate (22.3 mg, 0.12 mmol, 1.2 equiv),  $\text{K}_2\text{HPO}_4$  (20.9 mg, 0.12 mmol, 1.2 equiv) were placed in a 2 mL oven-dried vial. The tube was evacuated and filled with nitrogen. Then DMF (0.25 mL) was added at room temperature. The resulting mixture was irradiated with two 15 W blue LED lamps (at approximately 2 cm away from the light source) and stirred at room temperature. After 3.5 d, the reaction mixture was quenched with 3 M HCl (2 mL), extracted with EtOAc. The combined organic extracts were washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by preparative TLC (petroleum ether/ethyl acetate = 2/1 v/v), to give the desired product **6** as a yellow oil (30.6 mg, 78%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.46 – 7.31 (m, 5H), 4.78 – 4.50 (m, 1H), 4.17 (q,  $J$  = 7.1 Hz, 4H), 3.75 – 3.58 (m, 1H), 3.56 (d,  $J$  = 6.8 Hz, 1H), 3.40 – 3.18 (m, 1H), 3.12 – 2.94 (m, 1H), 2.72 – 2.57 (m, 1H), 2.10 – 1.50 (m, 4H), 1.27 – 1.27 (m, 6H), 1.04 (d,  $J$  = 7.2 Hz, 3H).

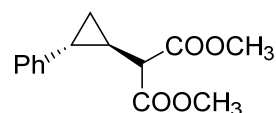
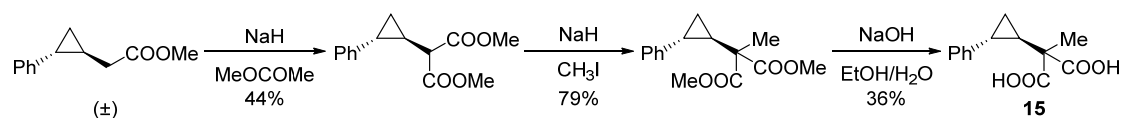
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):**  $\delta$  -164.1 – -164.7 (m, 1F).

**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.5, 169.0, 168.6, 135.8, 129.9, 128.6, 127.0, 96.1 (d,  $J$  = 175.4 Hz), 61.7 (d,  $J$  = 23.7 Hz), 52.3, 43.5, 41.8 (d,  $J$  = 20.2 Hz), 37.9, 33.9 (d,  $J$  = 110.0 Hz), 30.8 (d,  $J$  = 112.6 Hz), 14.1 (d,  $J$  = 5.5 Hz), 12.6 (d,  $J$  = 6.2 Hz).

**HRMS-ESI (m/z)** calcd for  $\text{C}_{21}\text{H}_{29}\text{FNO}_5$  [ $(\text{M} + \text{H})^+$ ] 394.2030, found 394.2027.

**IR (KBr):**  $\nu$  (cm<sup>-1</sup>) 2981, 1732, 1636, 1467, 1435, 1289, 1247, 1031, 915, 732, 711.

## 6. Mechanistic Experiments



### Trans-dimethyl 2-(2-phenylcyclopropyl) malonate:

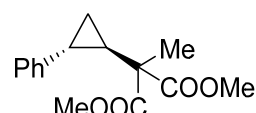
A stirred suspension of NaH (421 mg, 10.5 mmol, 2.0 equiv.) in dimethyl carbonate (6.3 mL) and dry dioxane (1.0 mL) was heated under reflux. To this was added a solution of Methyl 2-(2-phenylcyclopropyl) acetate<sup>11</sup> (1.0 g, 5.3 mmol, 1.0 equiv.) in dimethyl carbonate (1.4 mL) and dry dioxane (1.0 mL) over 20 min. After the addition, the resulting mixture was stirred at reflux overnight, then cooled to room temperature, quenched with sat. aq. ammonium chloride, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 60/1) to give trans-dimethyl 2-(2-phenylcyclopropyl) malonate as a yellow oil (575 mg, 44%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.30 – 7.21 (m, 2H), 7.20 – 7.06 (m, 3H), 3.77 (d, *J* = 12.4 Hz, 6H), 2.91 (d, *J* = 10.1 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.75 – 1.65 (m, 1H), 1.13 – 1.06 (m, 1H), 1.00 – 0.93 (m, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 169.3, 141.5, 128.5, 126.6, 126.1, 56.2, 52.8, 22.5, 21.0, 14.1.

**HRMS-ESI (m/z)** calcd for C<sub>14</sub>H<sub>17</sub>O<sub>4</sub> [(M + H)<sup>+</sup>] 249.1127, found 249.1125.

**IR (KBr):** ν (cm<sup>-1</sup>) 3005, 2954, 1732, 1605, 1499, 1435, 1200, 1146, 756, 699.



### Trans-dimethyl 2-methyl-2-(2-phenylcyclopropyl) malonate:

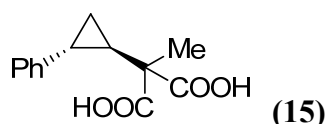
To a solution of NaH (213 mg, 5.3 mmol, 1.2 equiv) in 36 mL THF was added trans-dimethyl 2-(2-phenylcyclopropyl) malonate (1.1 g, 4.4 mmol, in 12 mL THF, 1.0 equiv.) at 0 °C. After stirring for 1h at 0 °C, iodomethane (944 mg, 6.7 mmol, 1.5 equiv.) was added. The reaction was warmed to room temperature and stirred overnight. Then quenched the reaction with sat. aq. ammonium chloride, extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 60/1) to give trans-dimethyl 2-methyl-2-(2-phenylcyclopropyl) malonate as a yellow oil (910 mg, 79%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.29 – 7.21 (m, 2H), 7.20 – 7.11 (m, 3H), 3.74 (d, *J* = 13.0 Hz, 6H), 2.00 – 1.90 (m, 1H), 1.78 – 1.68 (m, 1H), 1.33 (s, 3H), 1.06 – 0.94 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 172.5, 172.4, 142.0, 128.4, 126.6, 126.0, 53.7, 52.8, 52.7, 26.5, 19.3, 18.0, 11.2.

**HRMS-ESI (m/z)** calcd for C<sub>15</sub>H<sub>19</sub>O<sub>4</sub> [(M + H)<sup>+</sup>] 263.1283, found 263.1282.

**IR (KBr):** ν (cm<sup>-1</sup>) 3002, 2953, 1736, 1604, 1499, 1458, 1377, 1117, 699.



**Trans-2-methyl-2-(2-phenylcyclopropyl) malonic acid:**

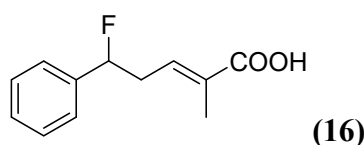
To a solution of trans-dimethyl 2-methyl-2-(2-phenylcyclopropyl) malonate (1.5 g, 5.7 mmol, 1.0 equiv.) in ethanol (10 mL) was added potassium hydroxide aqueous solution (3 M, 15 mL). The resulting mixture was stirred at reflux overnight, ethanol was removed in vacuo, then diluted the reaction with H<sub>2</sub>O and washed the aqueous layer with dichloromethane three times. HCl (3 M) was then added until pH = 2. The acidified aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The solid crude product was finally washed with dichloromethane, and dried under vacuum to give the desired trans-2-methyl-2-(2-phenylcyclopropyl) malonic acid **15** as a white solid (480 mg, 36%, Mp: 142–143 °C).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 12.70 (br, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.08 (m, 3H), 1.98 – 1.83 (m, 1H), 1.65 – 1.56 (m, 1H), 1.14 (s, 3H), 1.01 – 0.85 (m, 2H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 173.3, 173.2, 142.6, 128.2, 126.0, 125.5, 52.7, 26.9, 18.5, 17.0, 11.2.

HRMS-ESI (*m/z*) calcd for C<sub>13</sub>H<sub>15</sub>O<sub>4</sub> [(*M* + *H*)<sup>+</sup>] 235.0970, found 235.0970.

IR (KBr): ν (cm<sup>-1</sup>) 2996, 2886, 1705, 1468, 1413, 1291, 939, 743, 699.



**(E)-5-fluoro-2-methyl-5-phenylpent-2-enoic acid:**

Followed the general procedure of decarboxylative monofluorination, the product **16** was isolated by preparative TLC (dichloromethane/methanol = 20/1) as a white solid (22.5 mg, 54%, Mp: 60–62 °C).

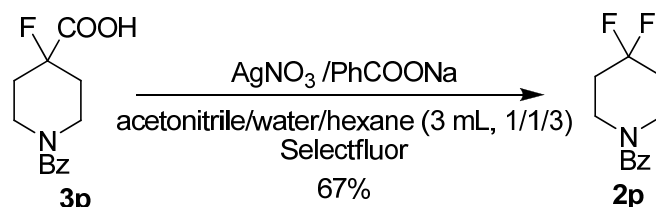
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47 – 7.29 (m, 5H), 6.95 (td, *J* = 7.3, 1.6 Hz, 1H), 5.65 – 5.45 (m, 1H), 3.03 – 2.59 (m, 2H), 1.80 (s, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -174.2 – -174.6 (m, 1F).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 172.8, 139.4 (d, *J* = 19.7 Hz), 138.3 (d, *J* = 5.3 Hz), 130.1, 128.8 (d, *J* = 1.9 Hz), 128.7, 125.5 (d, *J* = 6.8 Hz), 92.9 (d, *J* = 174.4 Hz), 37.0 (d, *J* = 25.0 Hz), 12.4.

HRMS-EI (*m/z*) calcd for C<sub>12</sub>H<sub>13</sub>FO<sub>2</sub> [*M*<sup>+</sup>] 208.0900 found 208.0895.

IR (KBr): ν (cm<sup>-1</sup>) 2962, 1689, 1645, 1289, 1262, 1089, 1014, 699.



1-Benzoyl-4-fluoropiperidine-4-carboxylic acid (**3p**) (50.2 mg, 0.2 mmol, 1.0 equiv.), PhCOONa (72.0 mg, 0.5 mmol, 2.5 equiv.), AgNO<sub>3</sub> (10.2 mg, 0.06 mmol, 0.3 equiv) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then acetonitrile/water/hexane (3 mL, 1/1/3)

was added, the resulting reaction mixture was stirred (600 r/min) at 55 °C for 12 h. The reaction was quenched with 3M HCl (2 mL), extracted with EtOAc (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, the residue was purified by preparative TLC to give the desired product **2p** (30.2 mg, 67%).

## 7. Time Course Study

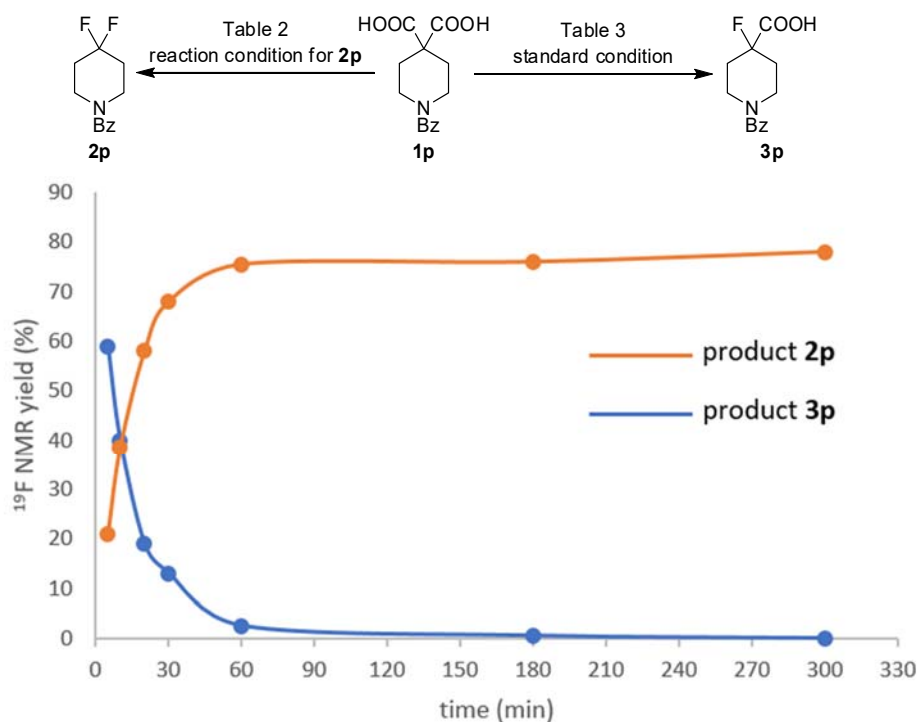


Figure s1. Time course of decarboxylative *gem*-difluorination of substrate **1p**

As for the decarboxylative difluorination (Figure s1):

- the reaction was very fast and could be finished within an hour;
- products **2p** and **3p** were almost formed simultaneously, and in the first ten minutes of the reaction,  $\alpha$ -fluorocarboxylic acid **3p** was generated as the major product;
- $\alpha$ -fluorocarboxylic acid **3p** was converted to *gem*-difluoroalkane **2p** during the course of the reaction, and **2p** was eventually formed exclusively, implying that  $\alpha$ -fluorinated carboxylic acid **3** was the intermediate in the formation of *gem*-difluoroalkanes.

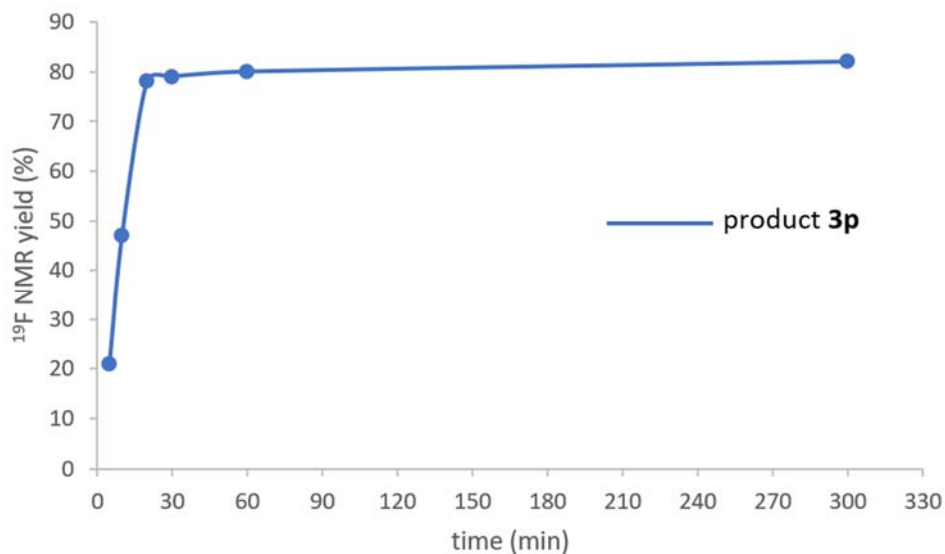


Figure s2. Time course of decarboxylative monofluorination of substrate **1p**

As for the decarboxylative monofluorination (Figure s2):

- the reaction was very fast and could be finished within 30 minutes;
- no *gem*-difluoroalkane **2p** was formed in the course of the reaction.

#### Time course of decarboxylative *gem*-difluorination of substrate **1p**

7 parallel reactions were setup based on the following procedure: a mixture of 1-benzoylpiperidine-4, 4-dicarboxylic acid (55.5 mg, 0.2 mmol, 1.0 equiv.), AgNO<sub>3</sub> (6.8 mg, 0.04 mmol, 0.2 equiv.), K<sub>2</sub>HPO<sub>4</sub> (104.4 mg, 0.6 mmol, 3 equiv.) and Selectfluor (425.2 mg, 1.2 mmol, 6 equiv.) in acetonitrile/water (4 mL, 1/1 v/v) was stirred at 55 °C. After 5 min\10 min\20 min\30 min\60 min\180 min\300 min, quenched the reactions with 3M HCl, respectively, extracted with EtOAc (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, then <sup>19</sup>F-NMR yields of **2p** and **3p** for each of the reactions were determined with 4-fluoro-1,1'-biphenyl as the internal standard.

#### Time course of decarboxylative monofluorination of substrate **1p**

6 parallel reactions were setup based on the following procedure: 1-benzoylpiperidine-4, 4-dicarboxylic acid (55.5 mg, 0.2 mmol, 1.0 equiv.), K<sub>2</sub>HPO<sub>4</sub> (139.2 mg, 0.8 mmol, 4 equiv), AgNO<sub>3</sub> (6.8 mg, 0.04 mmol, 0.2 equiv) and Selectfluor (141.7 mg, 0.4 mmol, 2 equiv) were placed in a Schlenk tube. The tube was evacuated and filled with nitrogen. Then the mixed solvent CPME/H<sub>2</sub>O (4 mL, 1/1 v/v) was added, the resulting mixture was stirred (600 r/min) at room temperature. After 5 min\10 min\20 min\30 min\60 min\300 min, quenched the reaction with 3M HCl, respectively, extracted with ethyl acetate (3 mL × 5), the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo, then <sup>19</sup>F-NMR yields of **2p** and **3p** for each of the reactions were determined with 4-fluoro-1,1'-biphenyl as the internal standard.

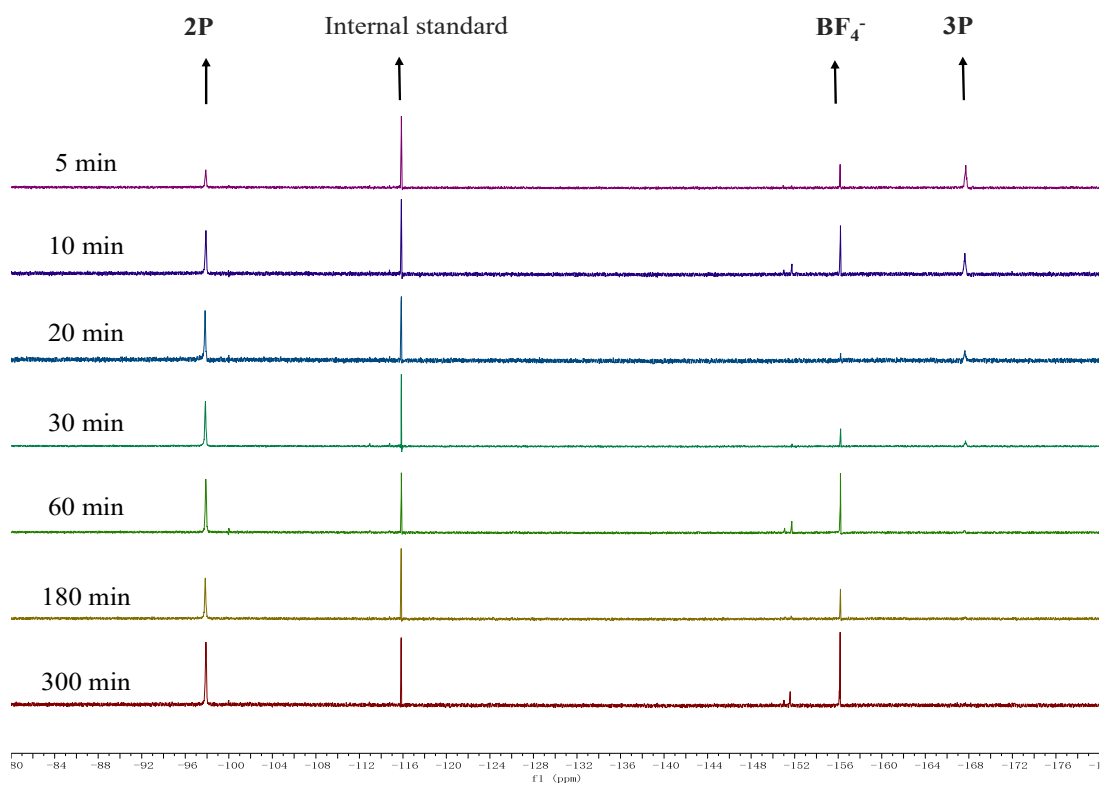


Figure s3.  $^{19}\text{F}$  NMR spectra of decarboxylative *gem*-difluorination of substrate **1p**

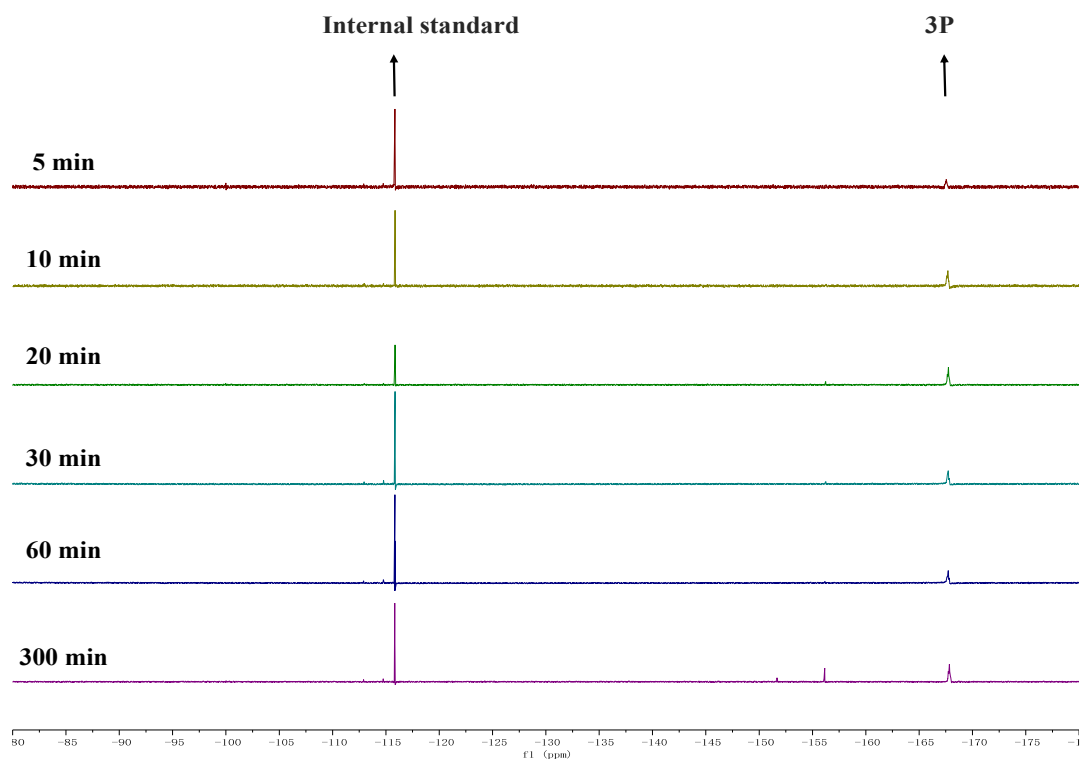
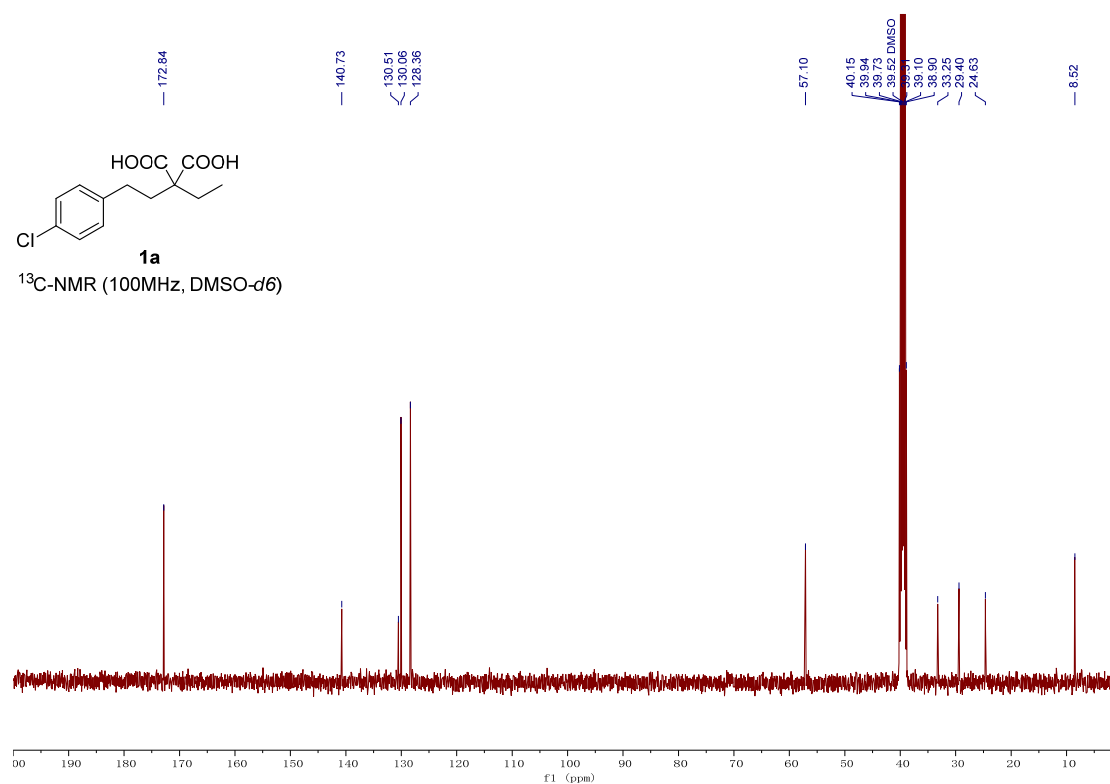
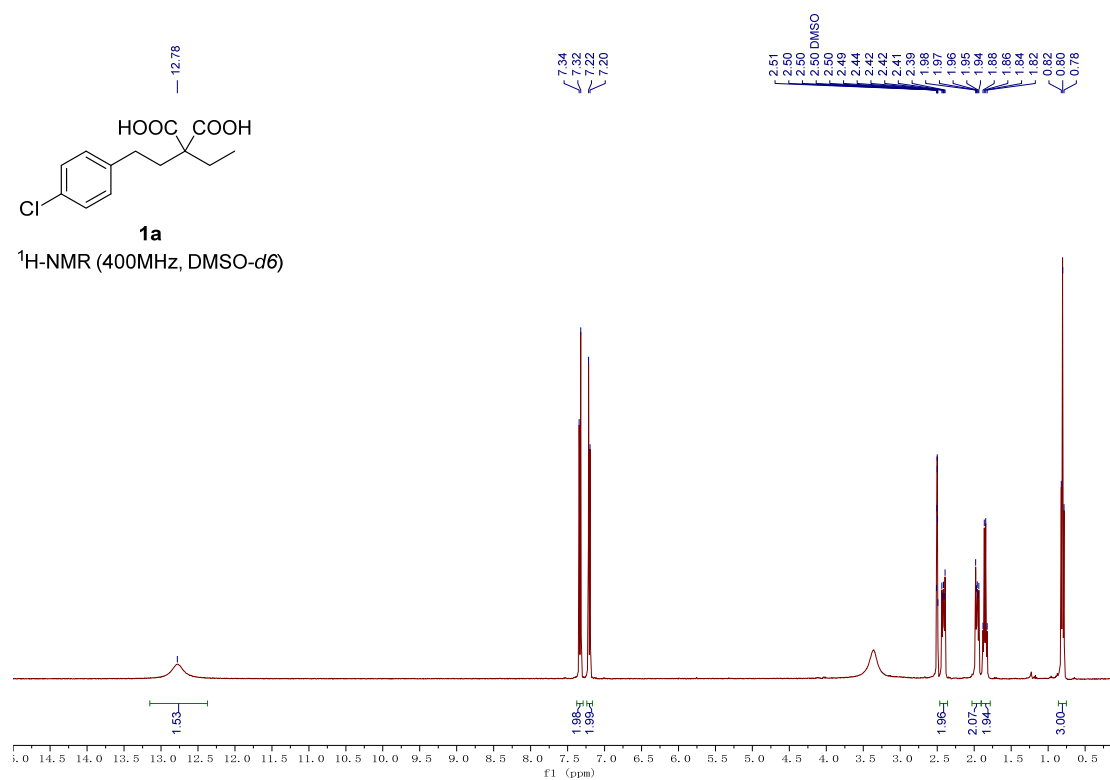
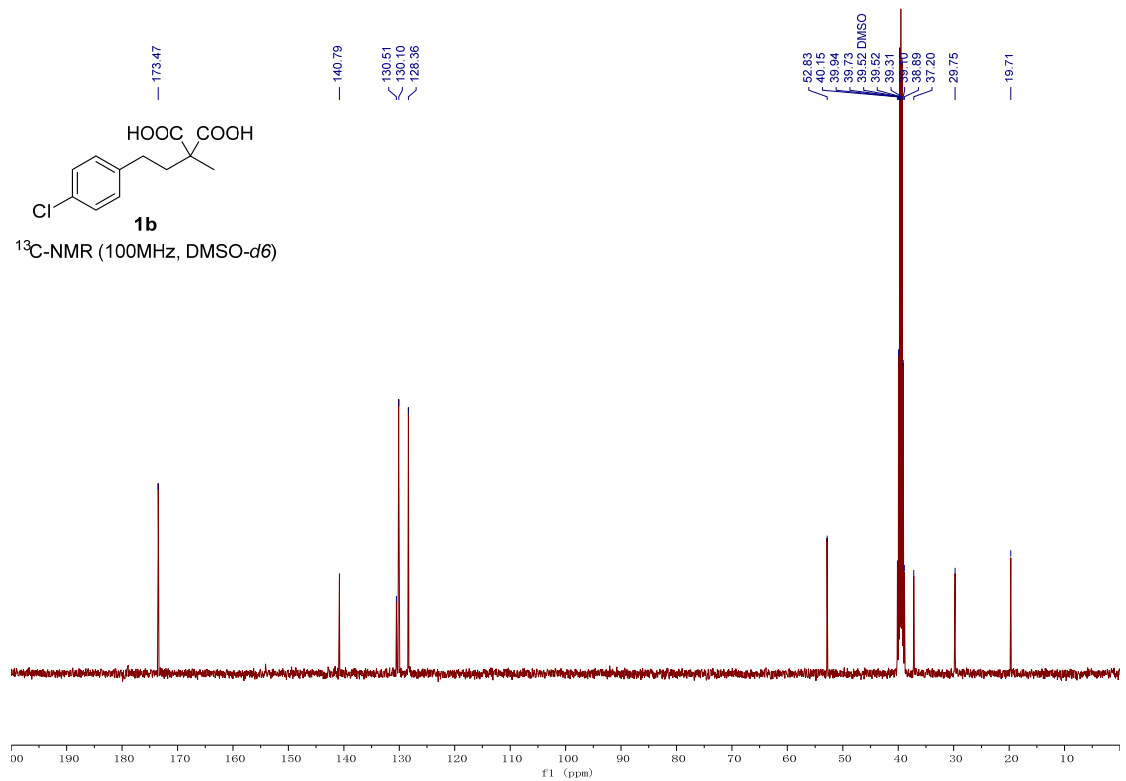
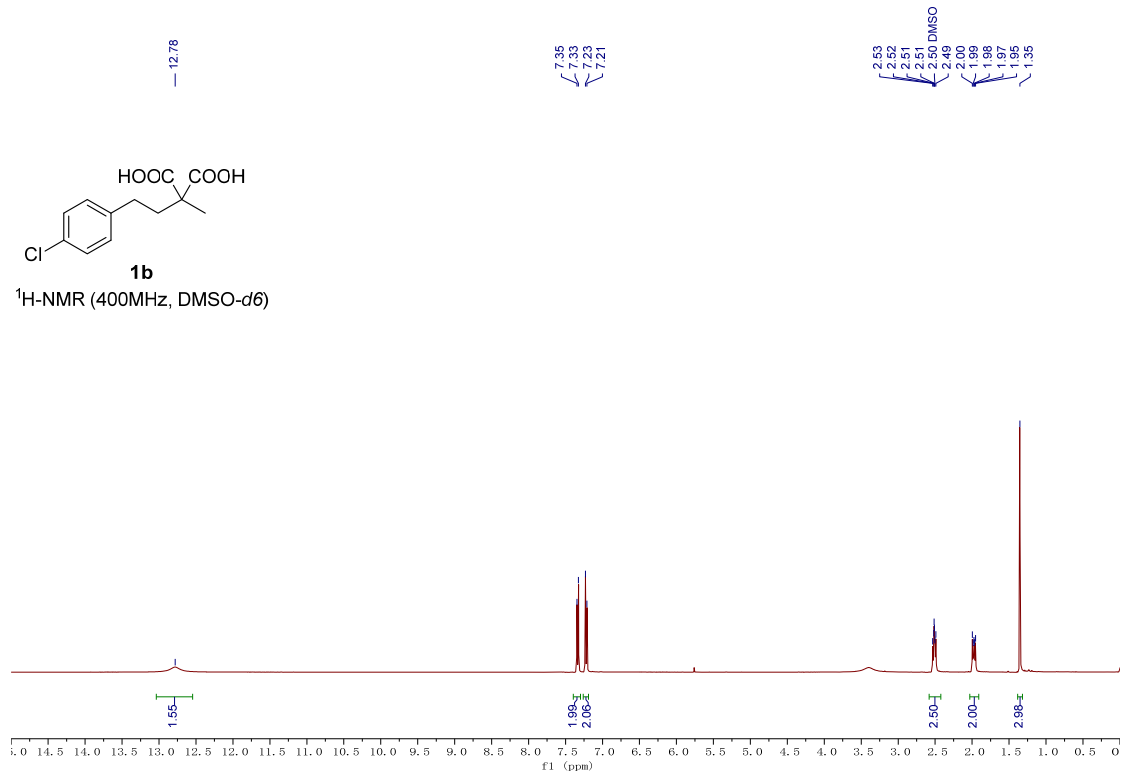


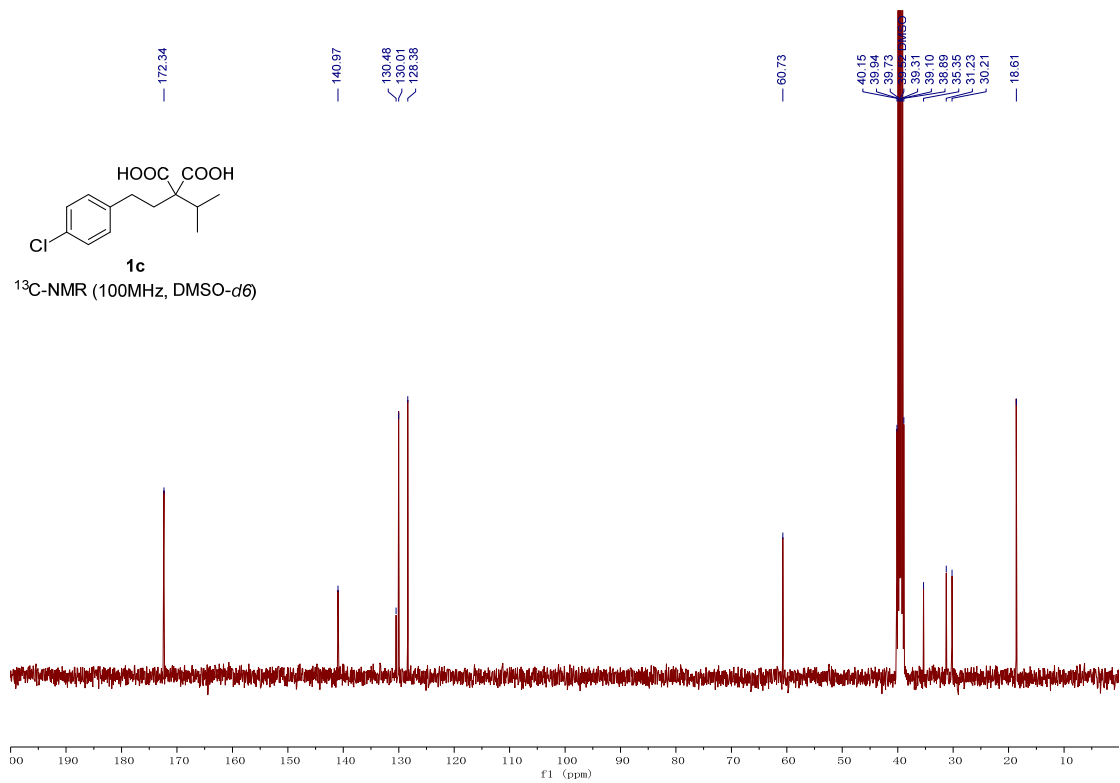
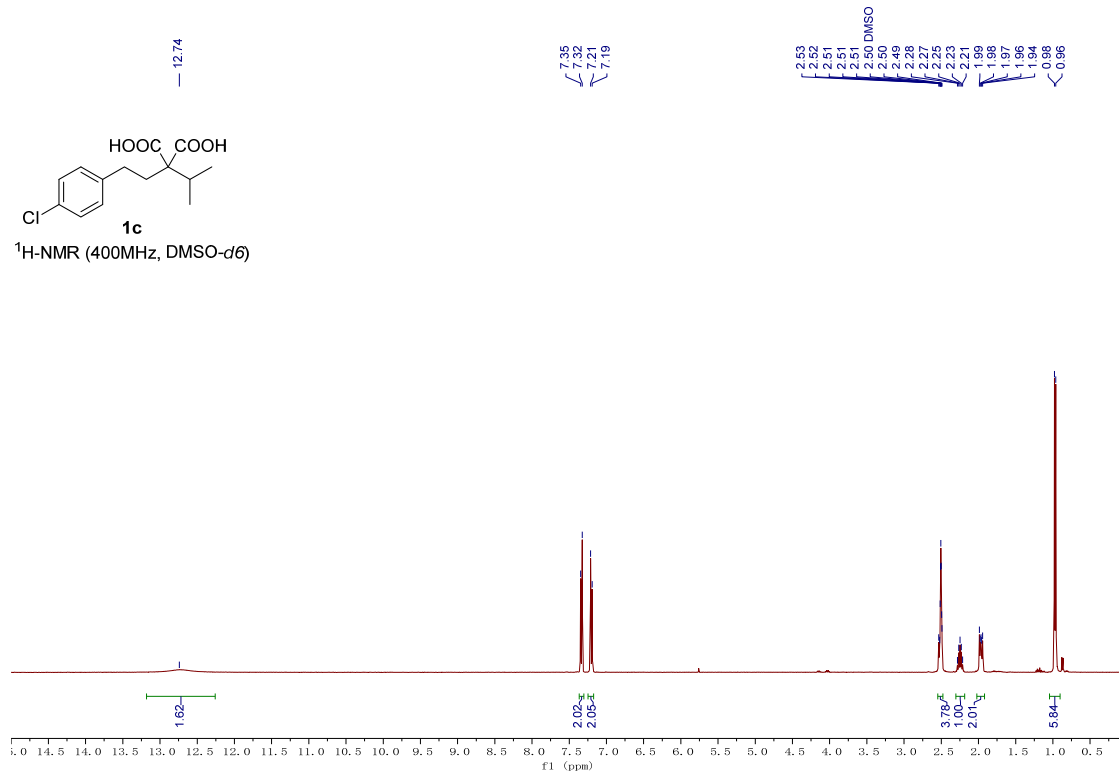
Figure s4.  $^{19}\text{F}$  NMR spectra of decarboxylative monofluorination of substrate **1p**

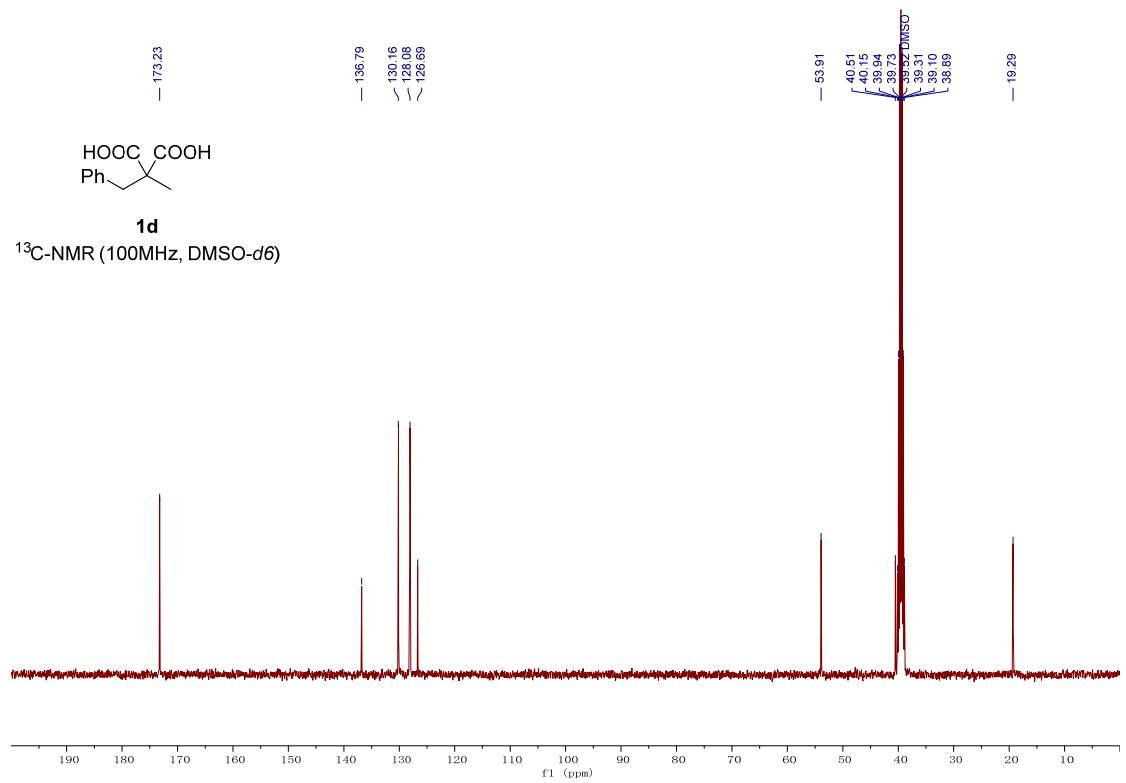
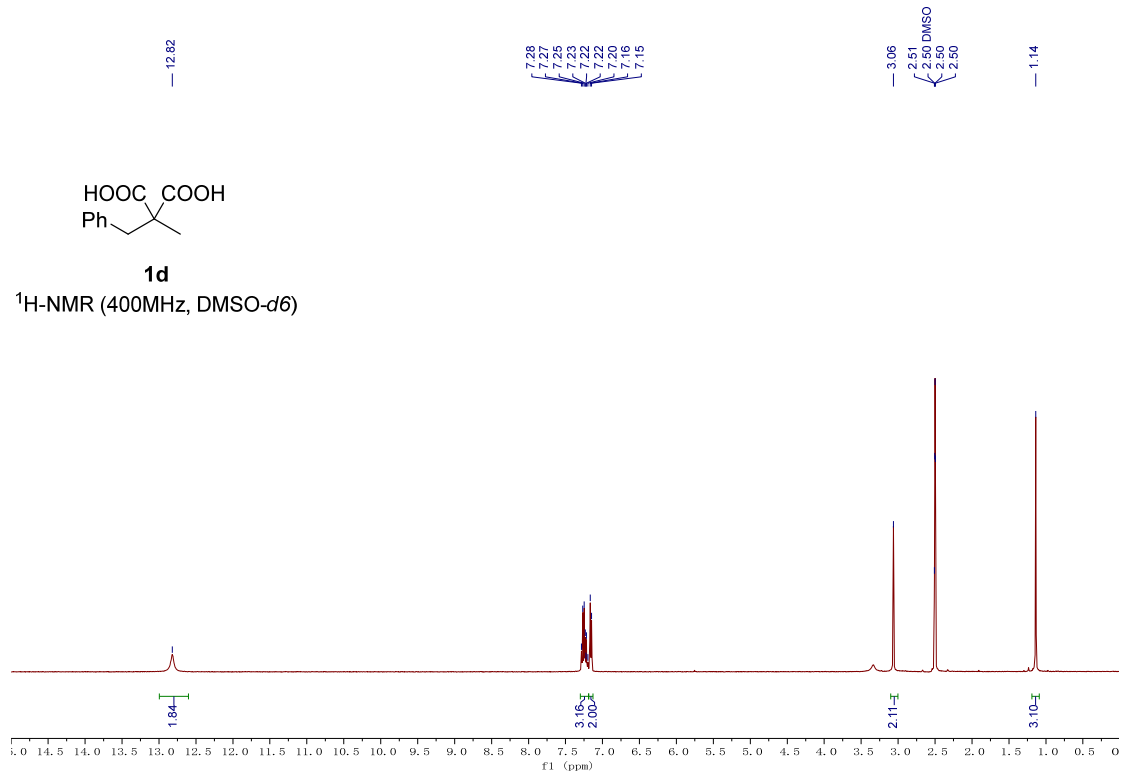
## 8. References

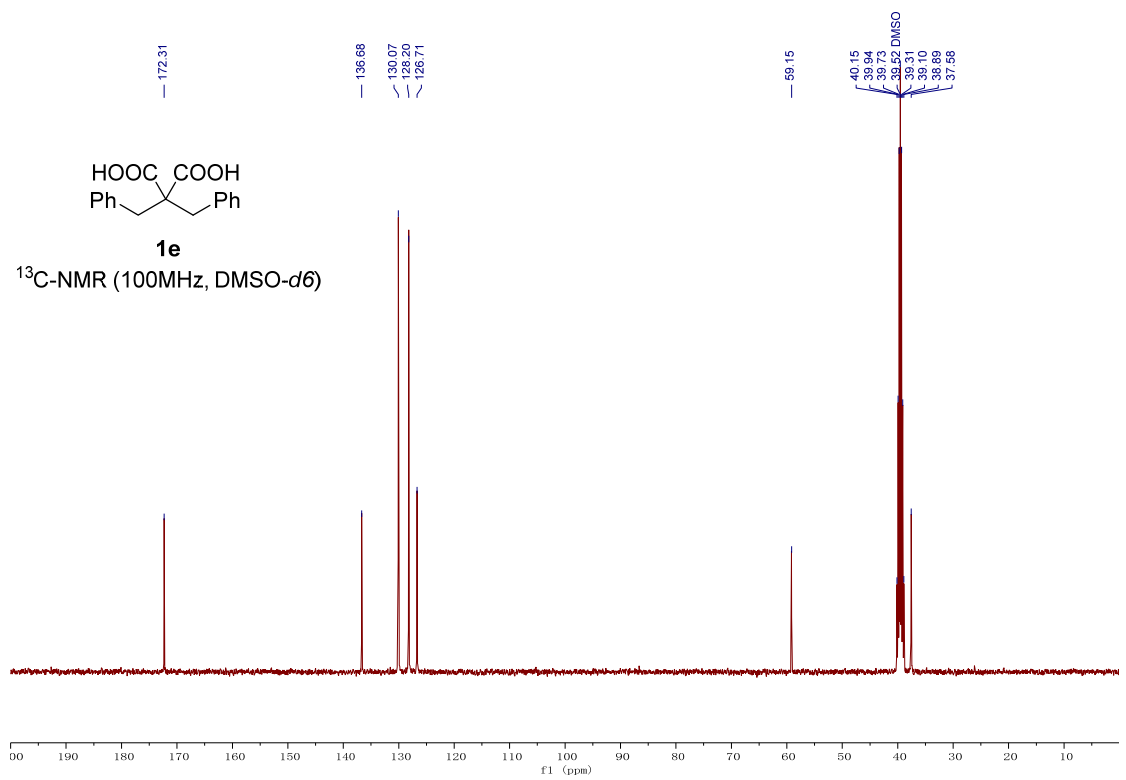
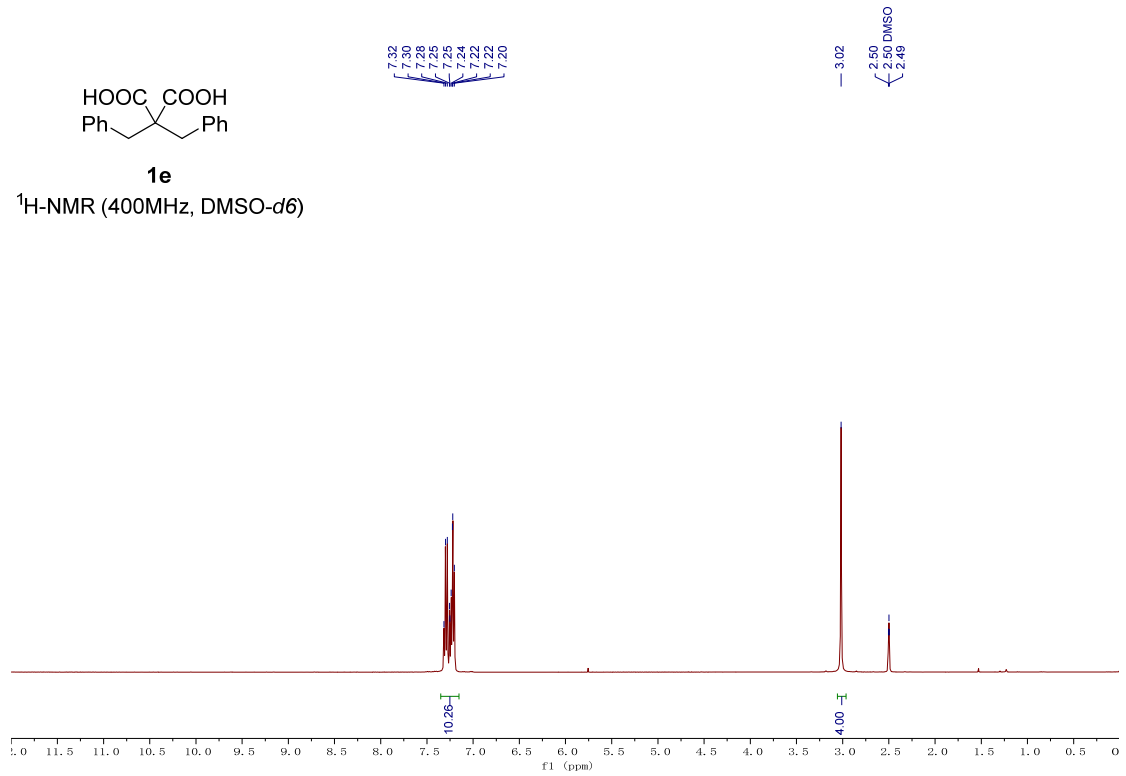
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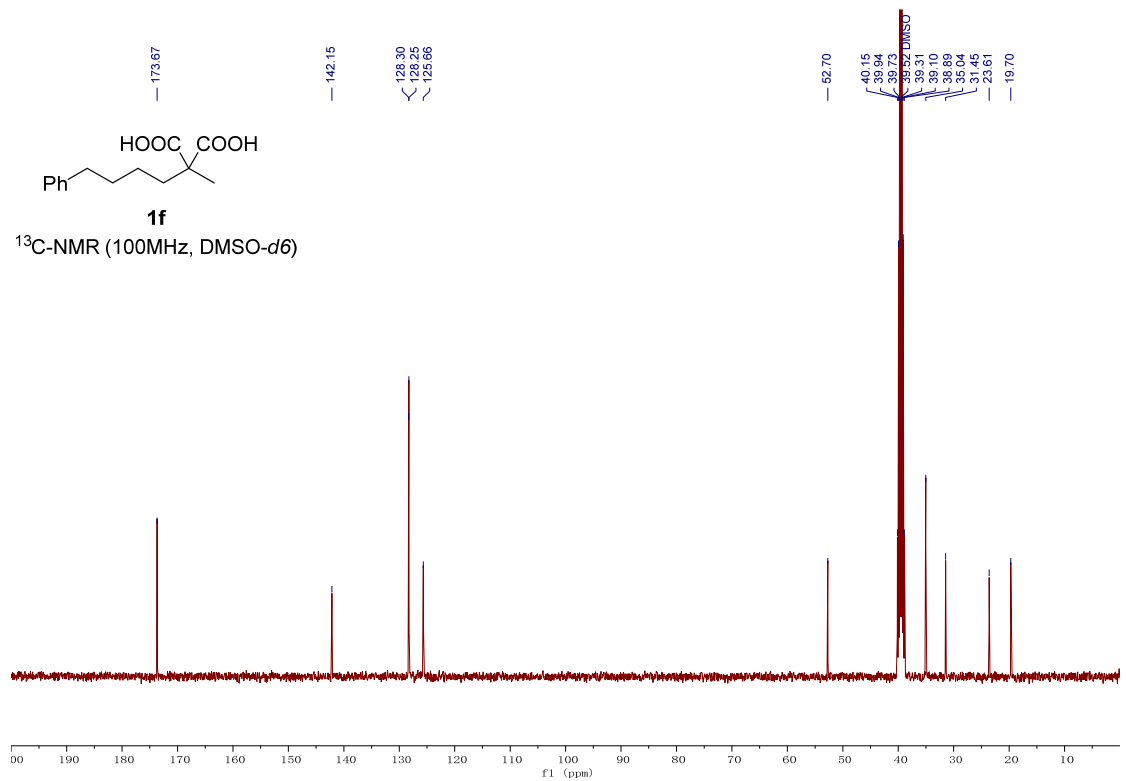
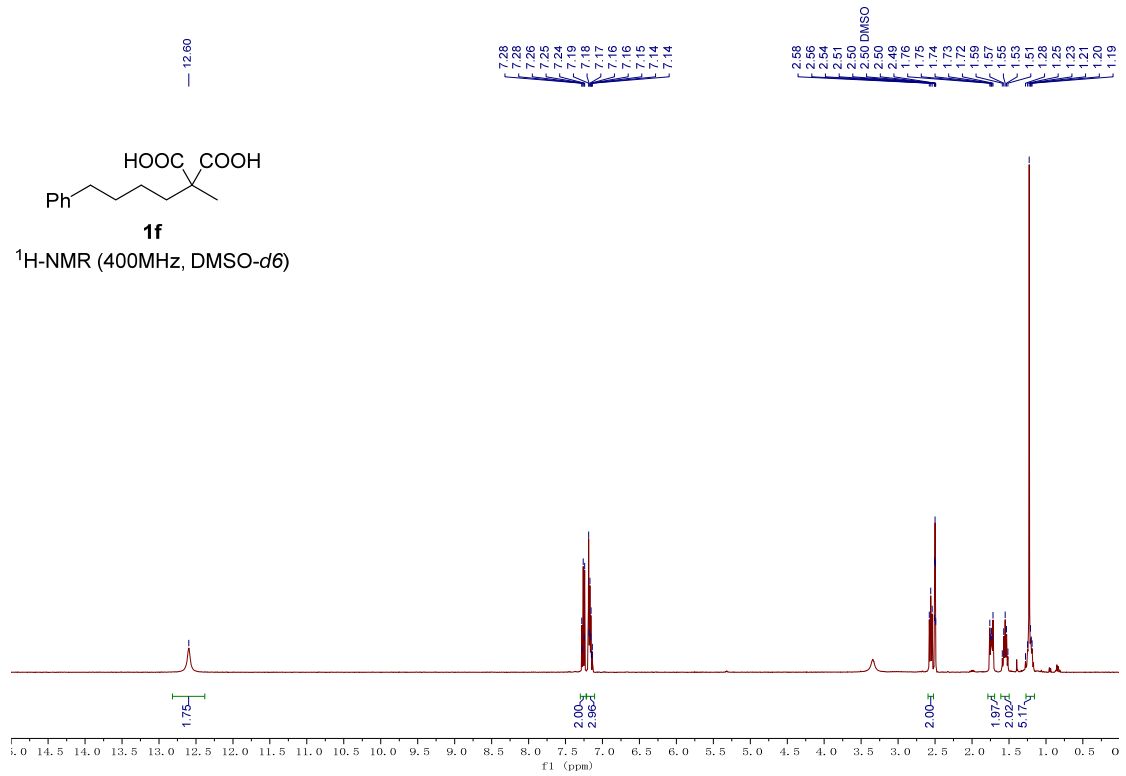
9.  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR Spectra Data

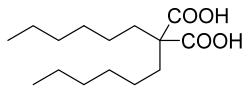




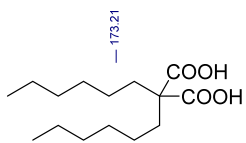
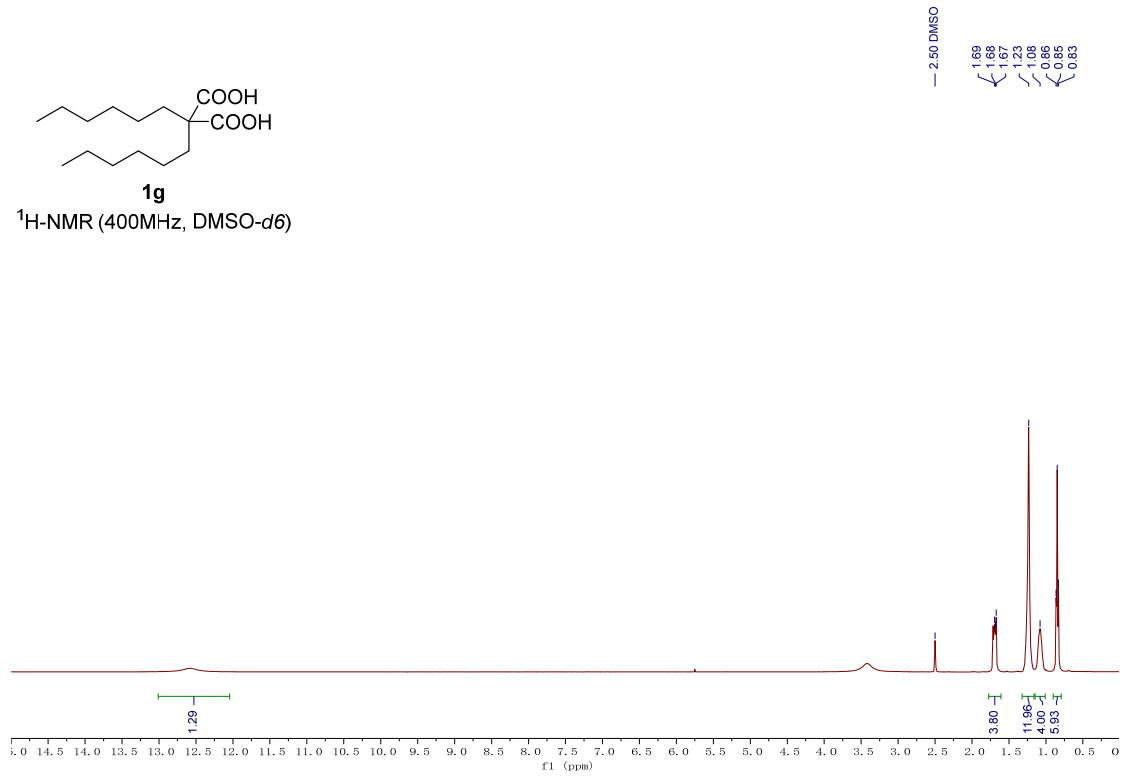




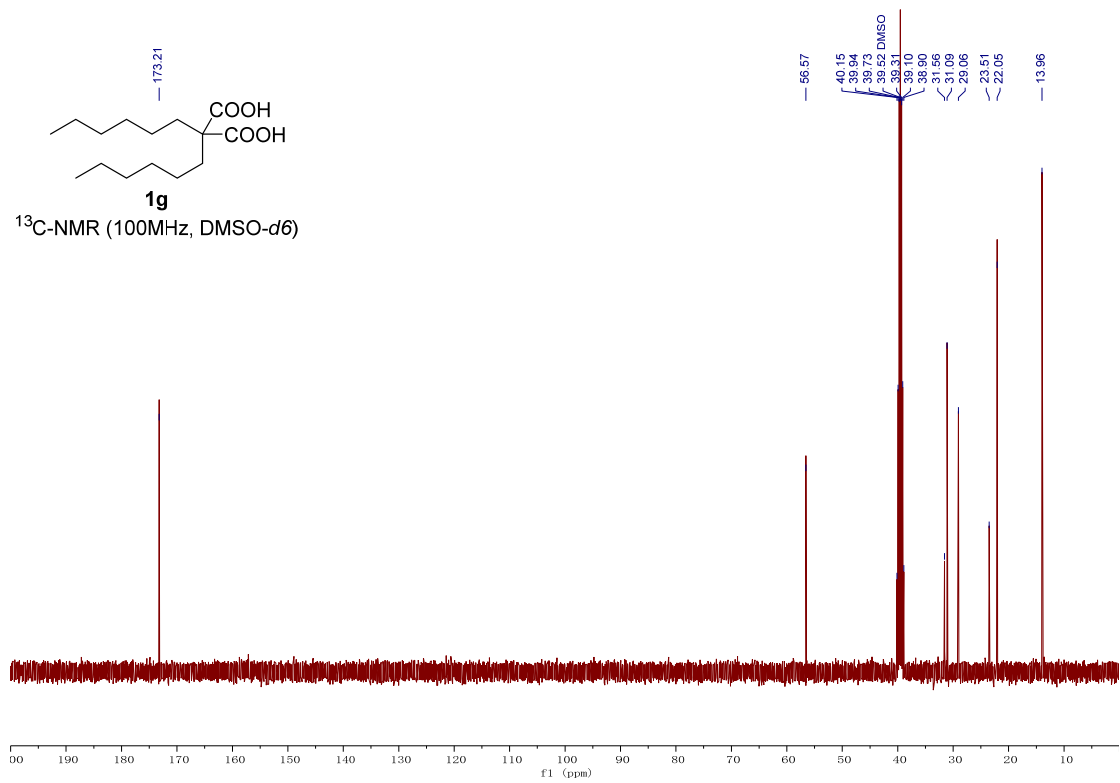


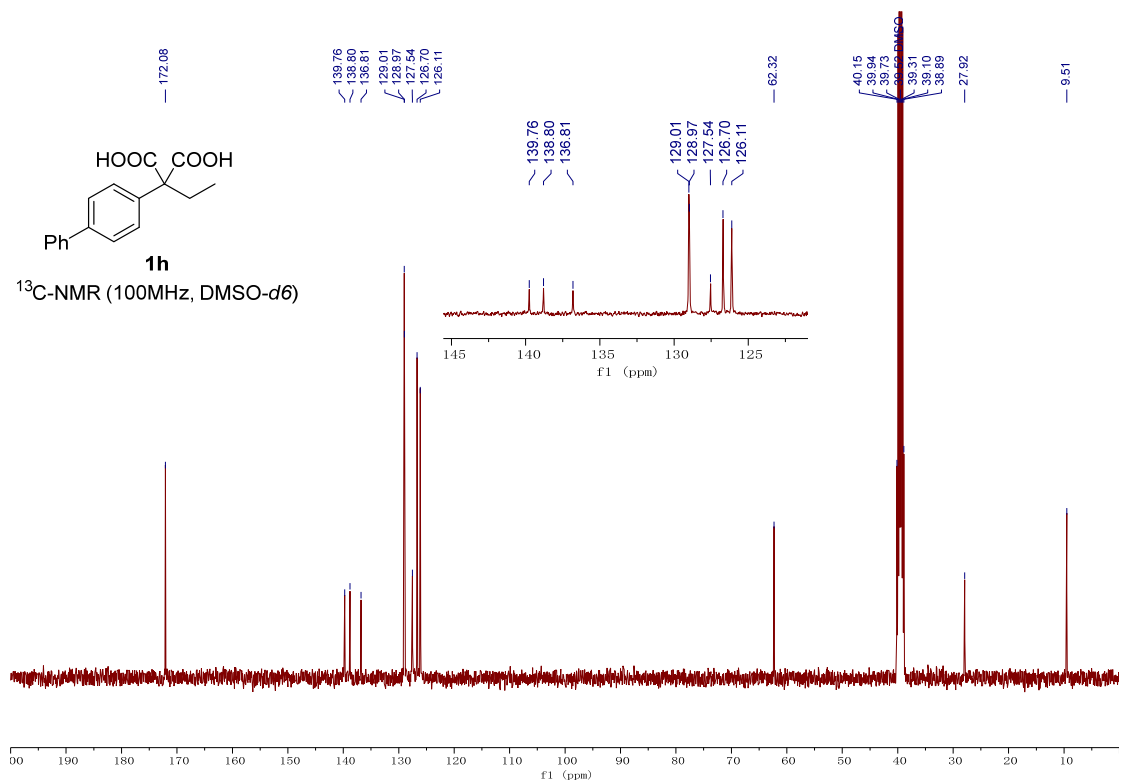
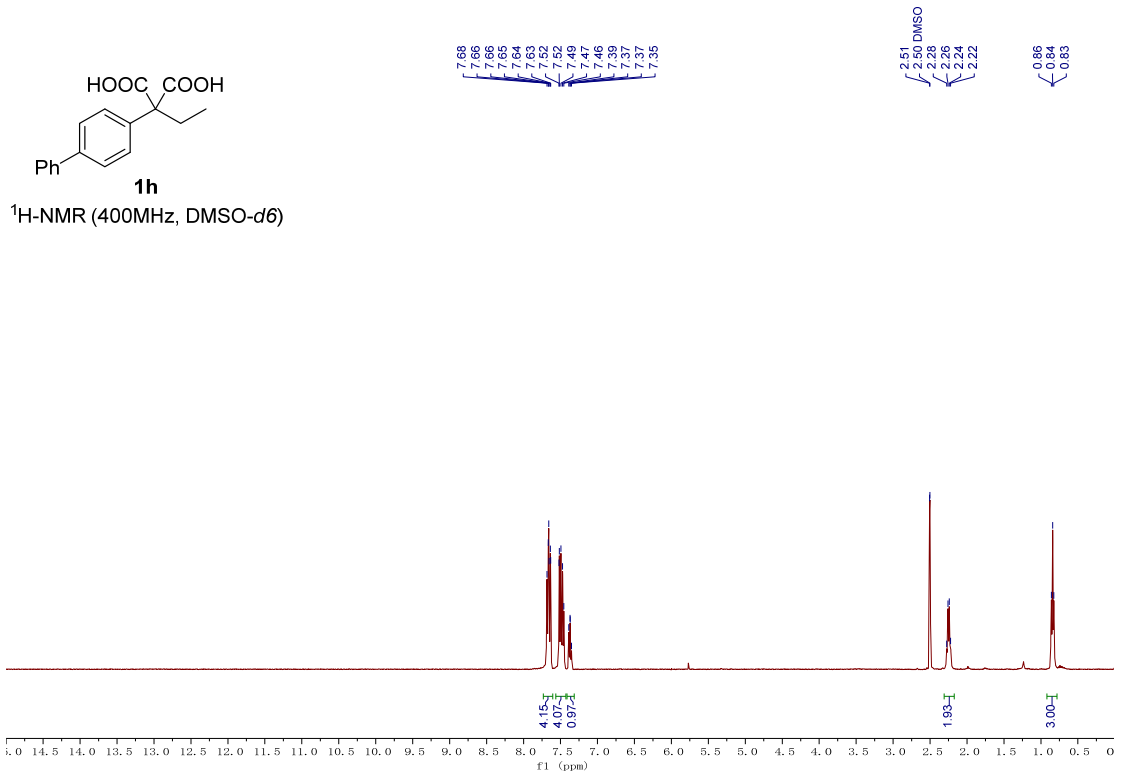


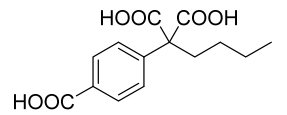
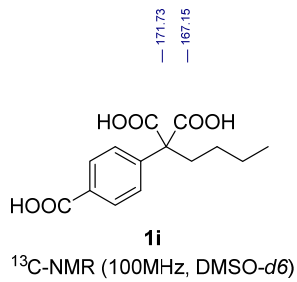
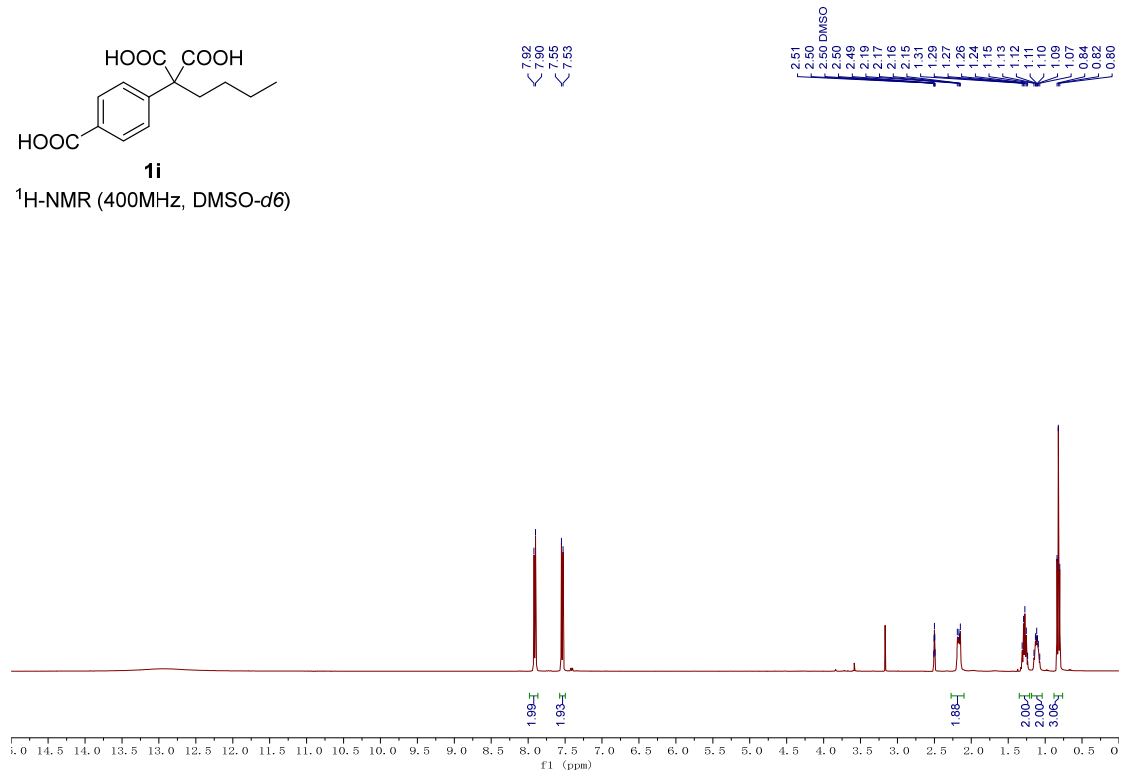
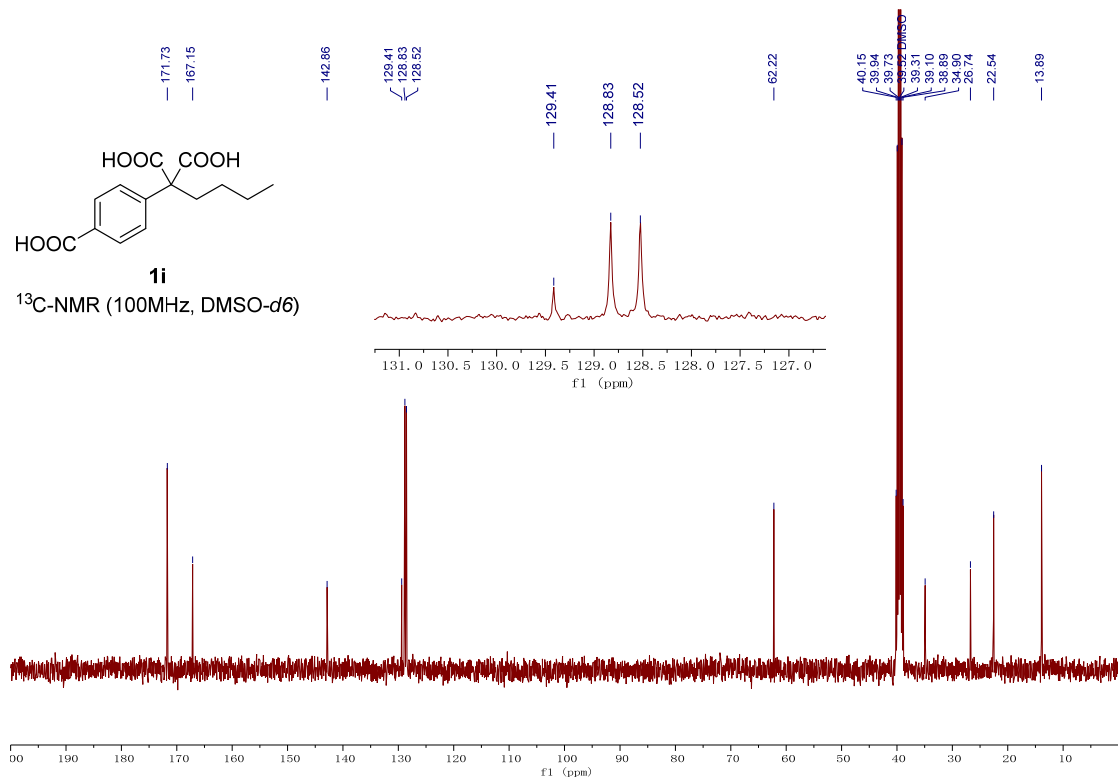
<sup>1</sup>H-NMR (400MHz, DMSO-d<sub>6</sub>)

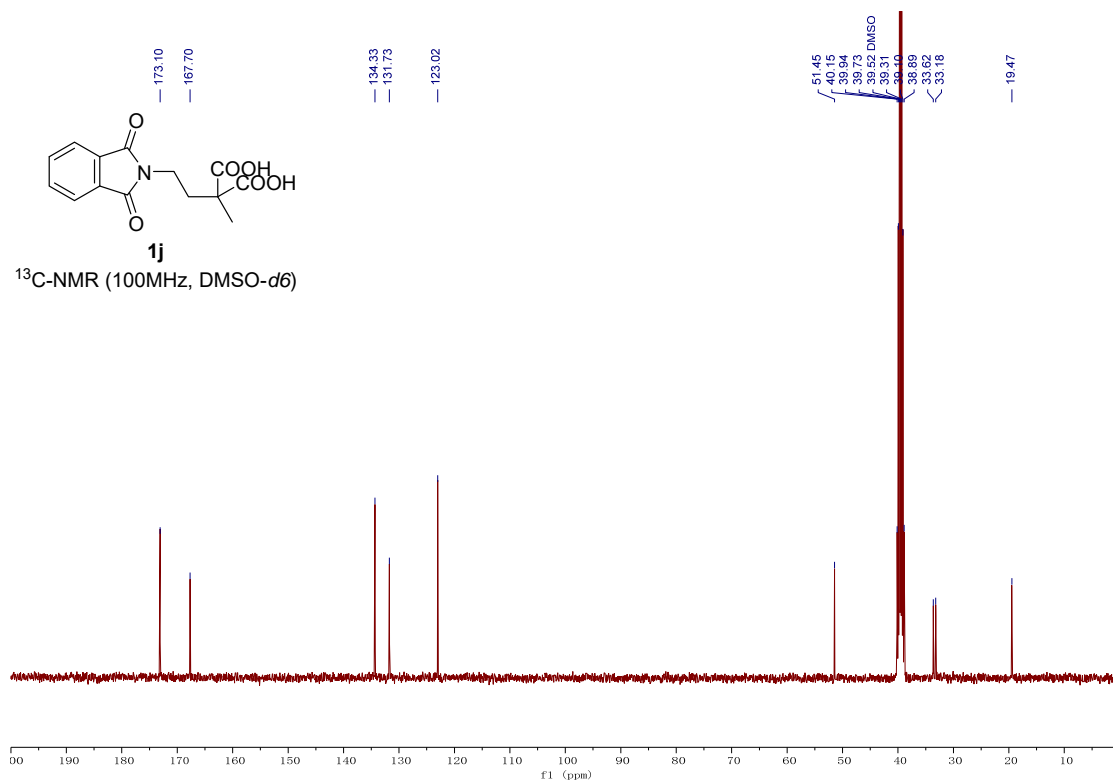
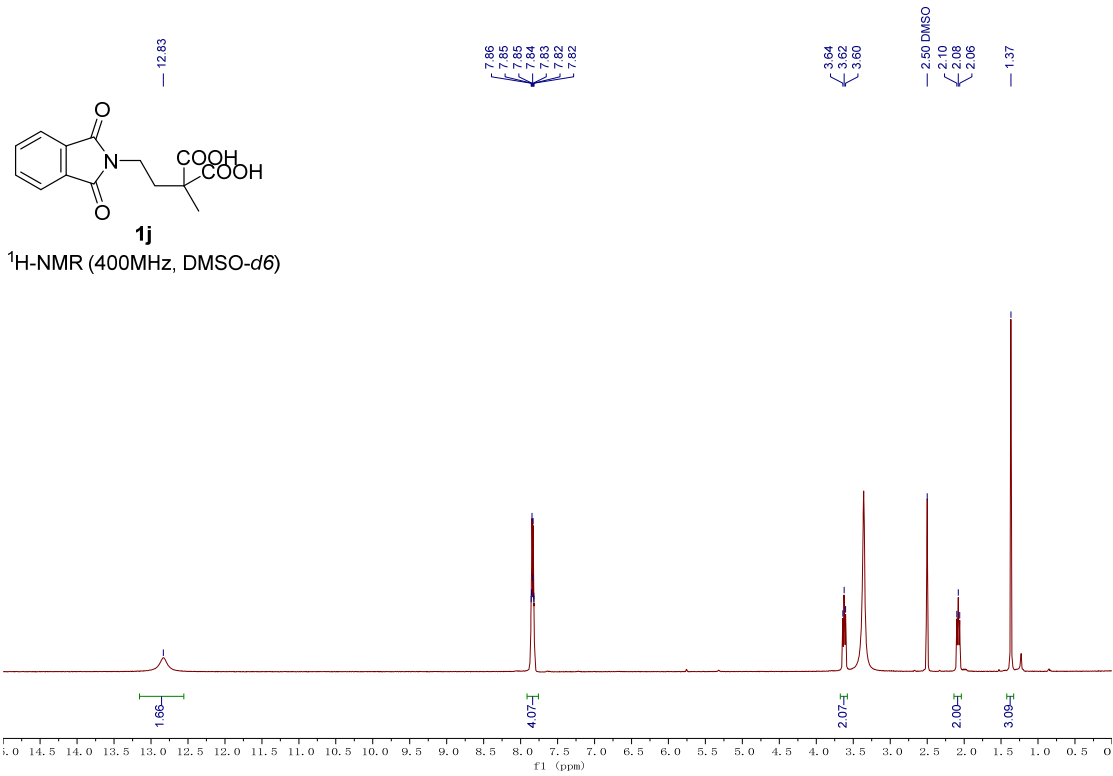


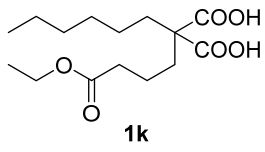
<sup>13</sup>C-NMR (100MHz, DMSO-d<sub>6</sub>)



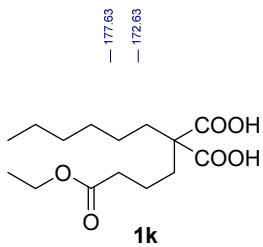
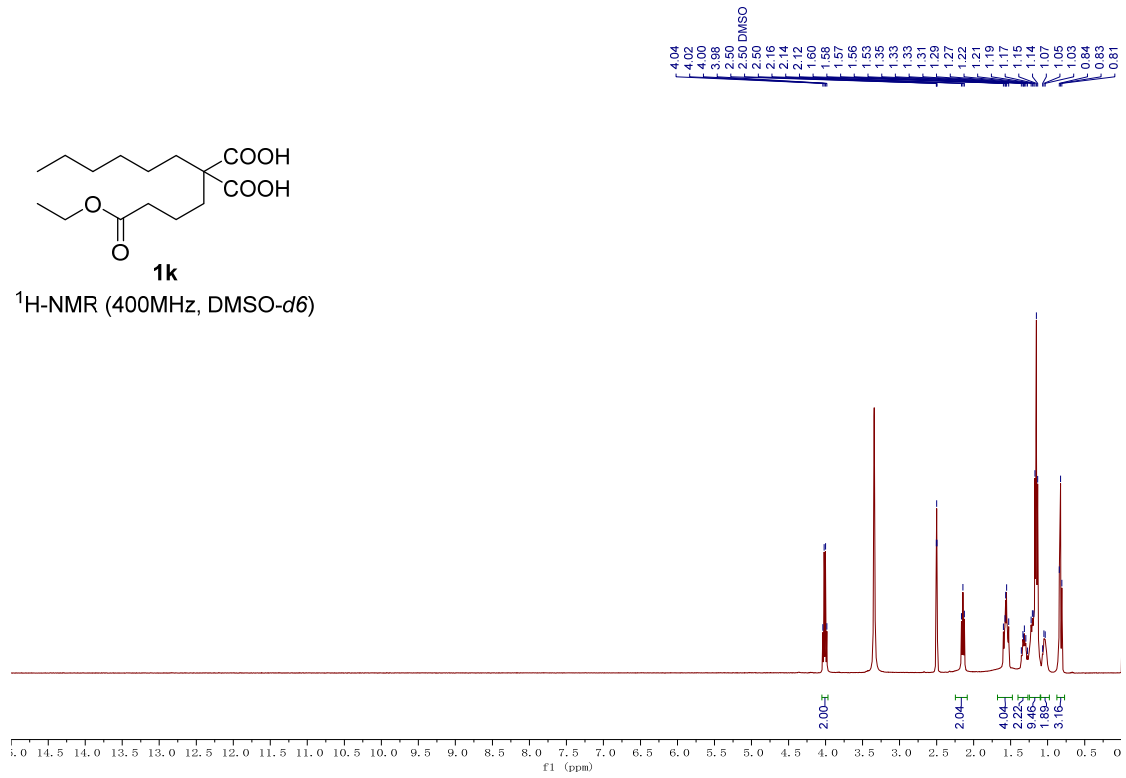


**1i** $^1\text{H-NMR}$  (400MHz, DMSO-*d*<sub>6</sub>)**1i** $^{13}\text{C-NMR}$  (100MHz, DMSO-*d*<sub>6</sub>)

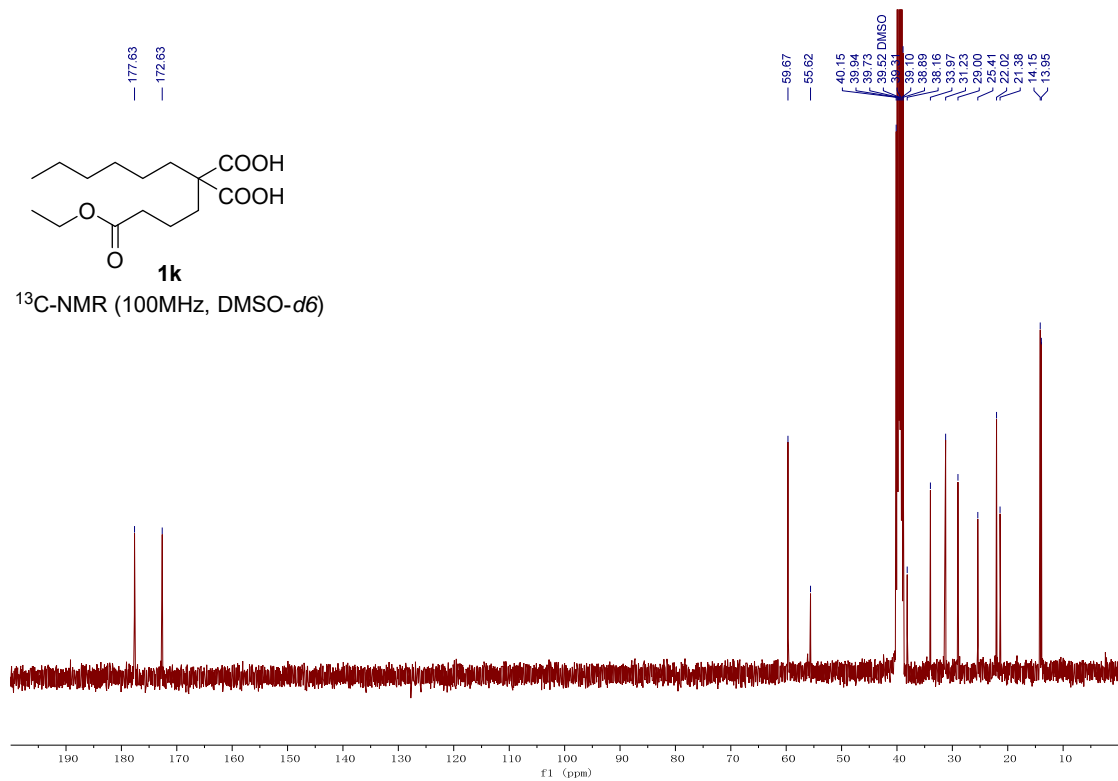


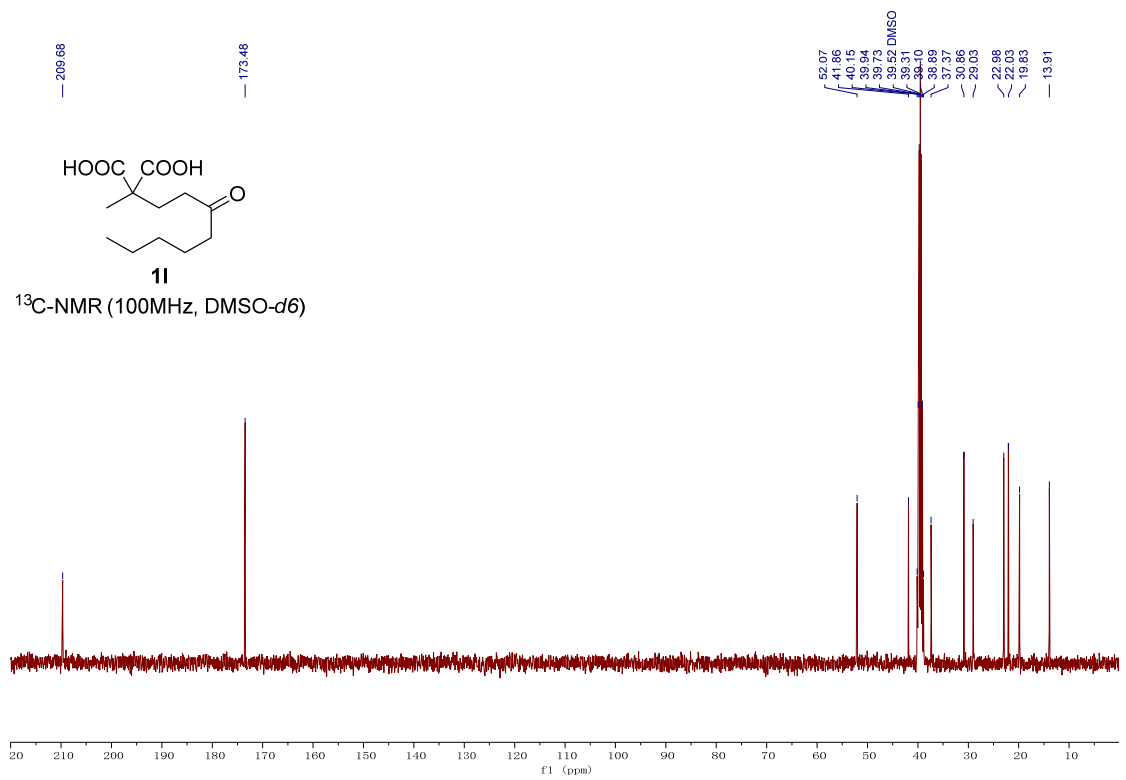
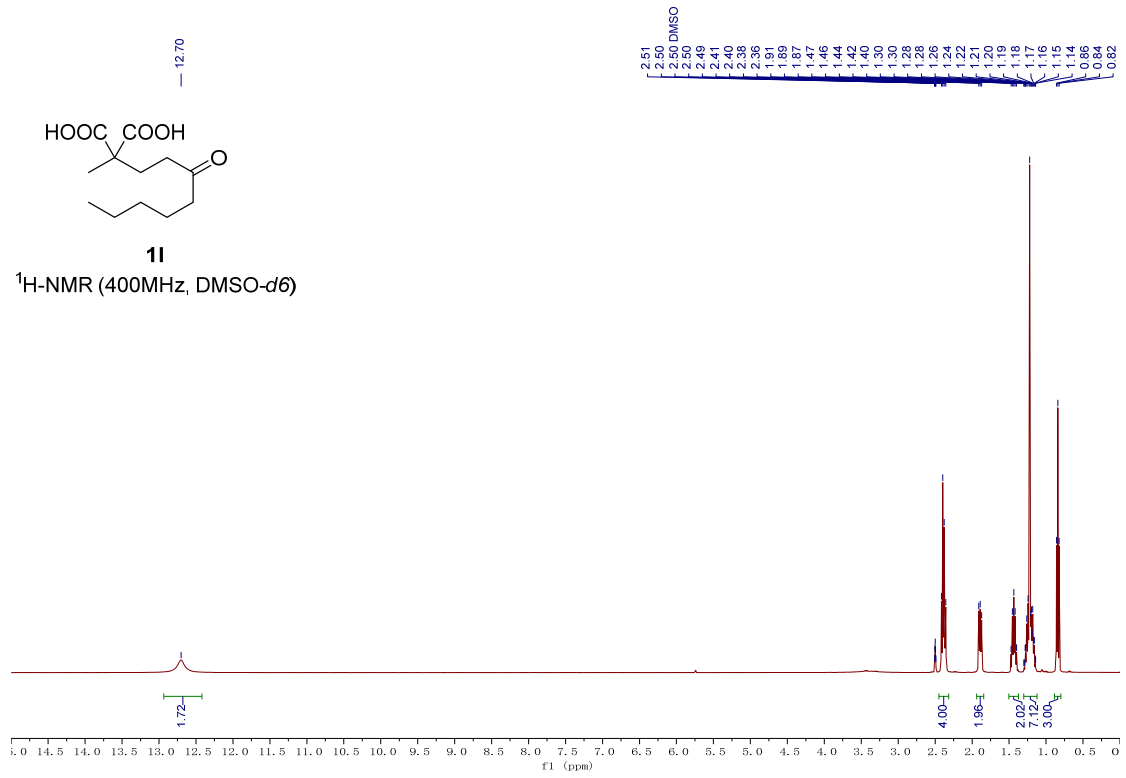


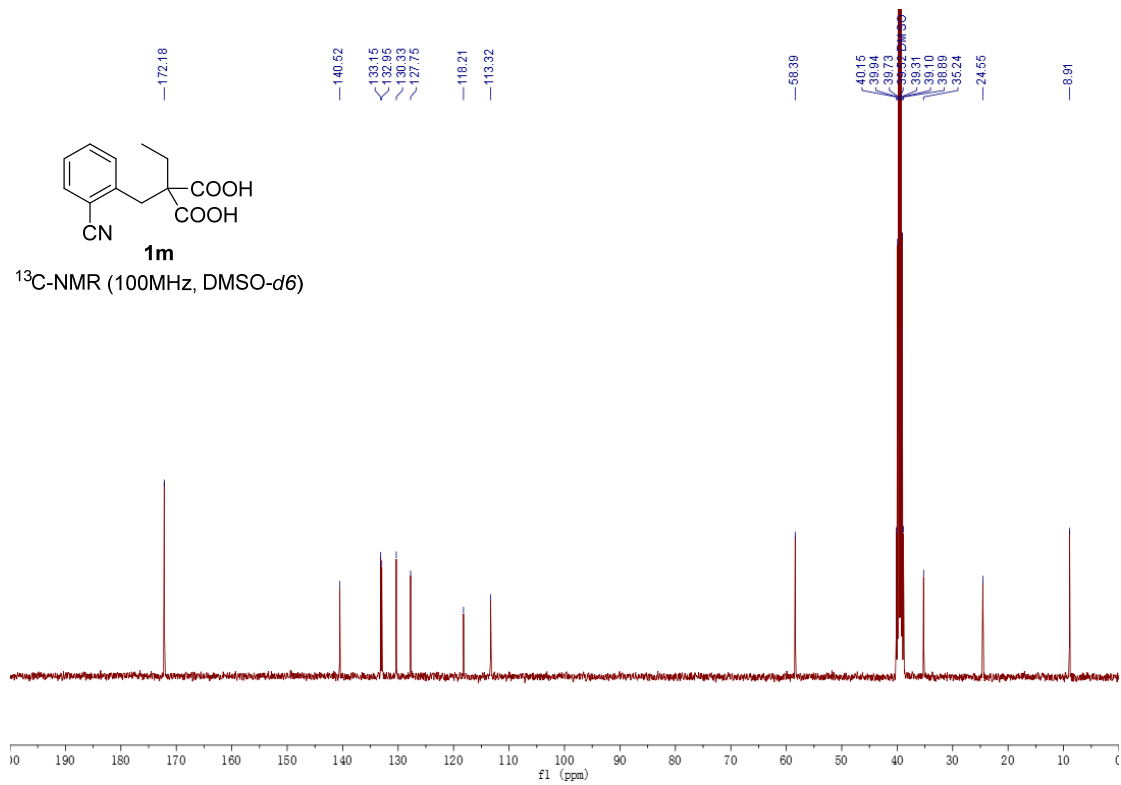
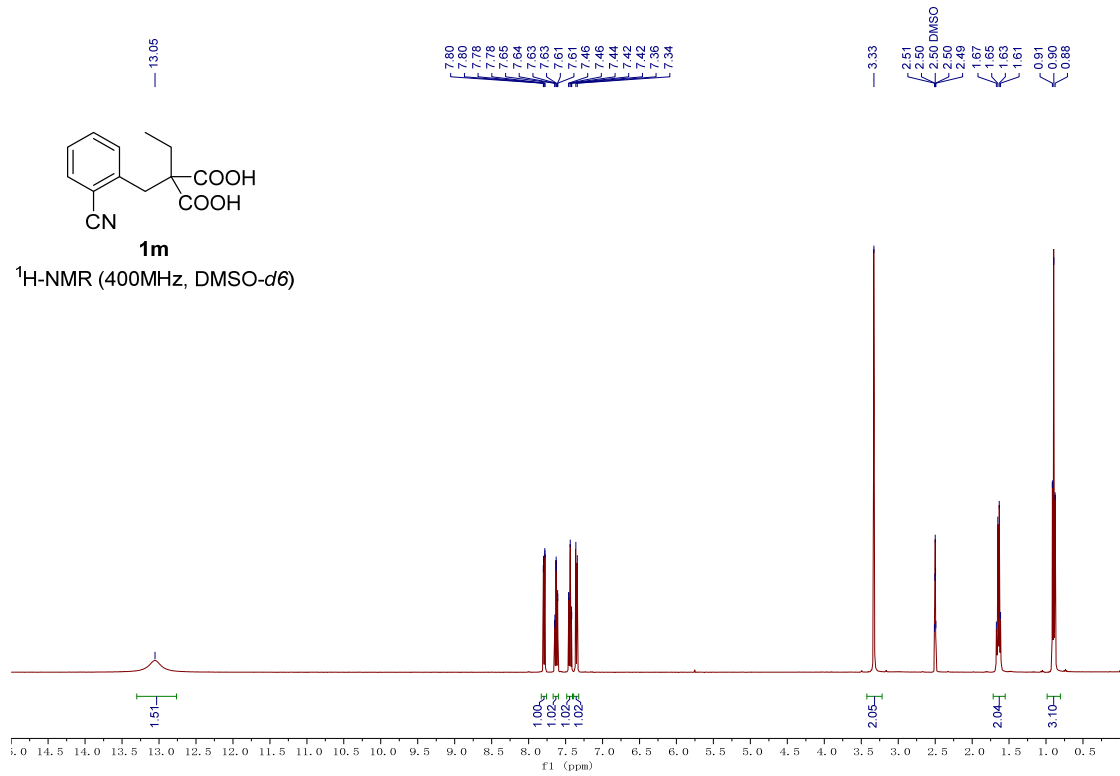
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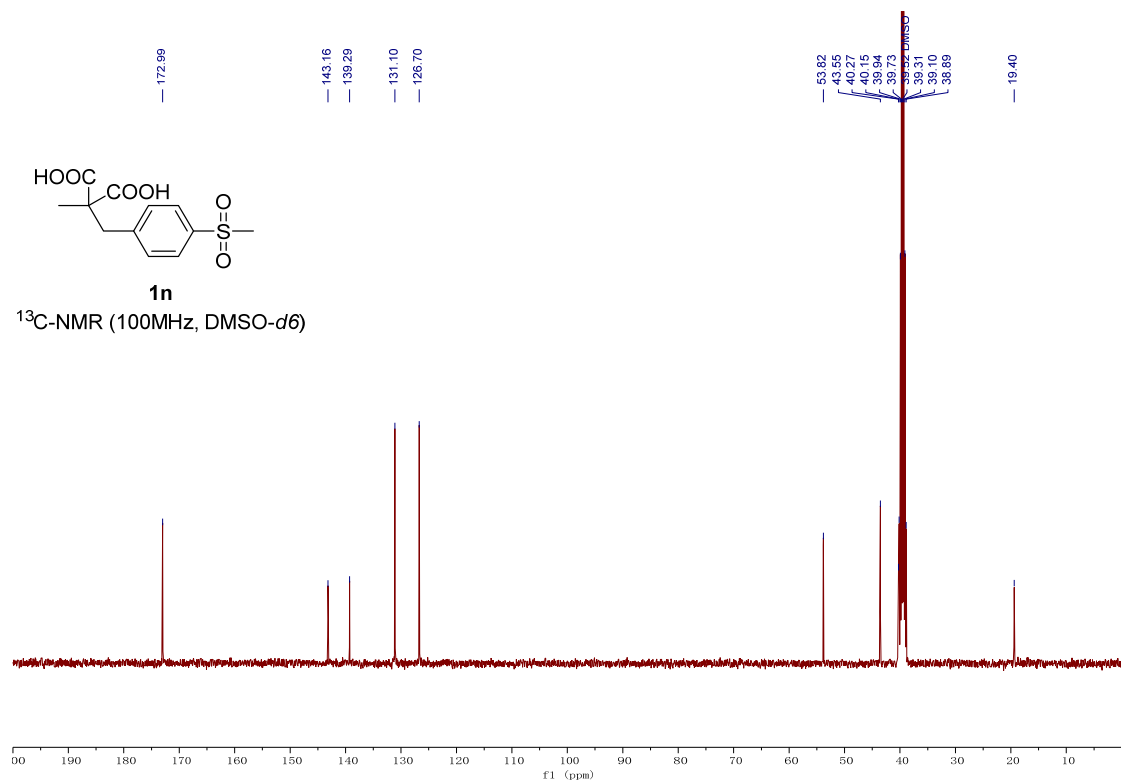
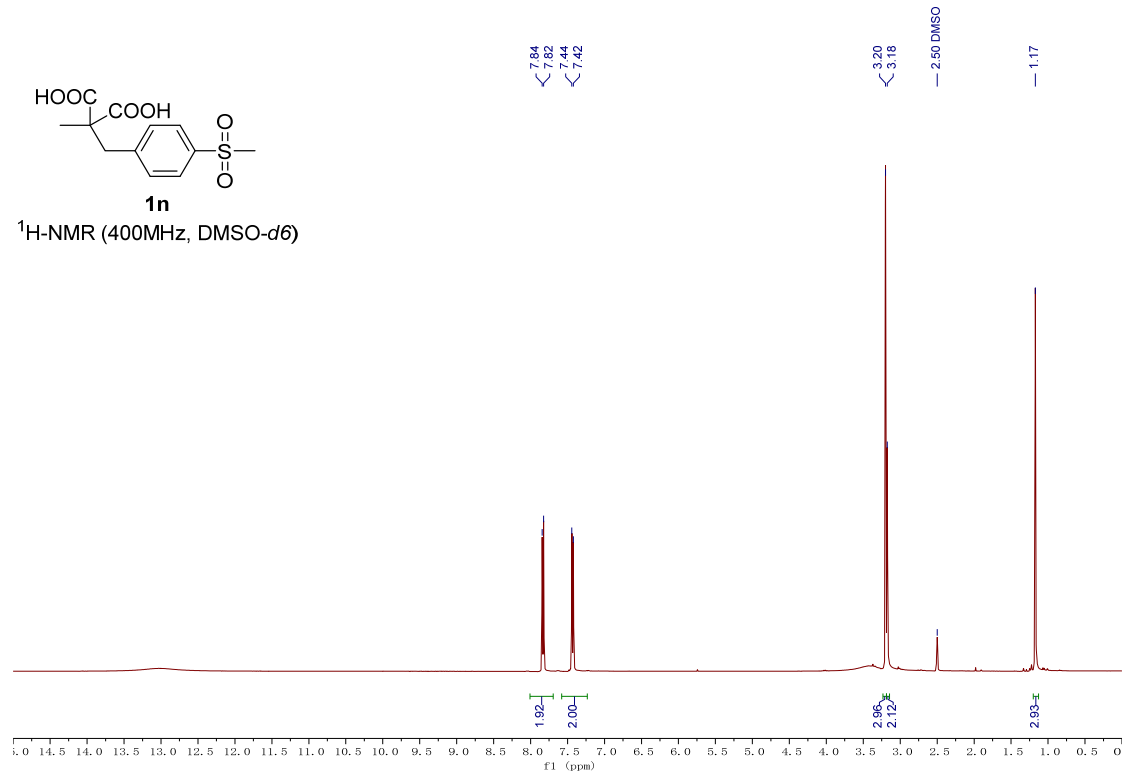


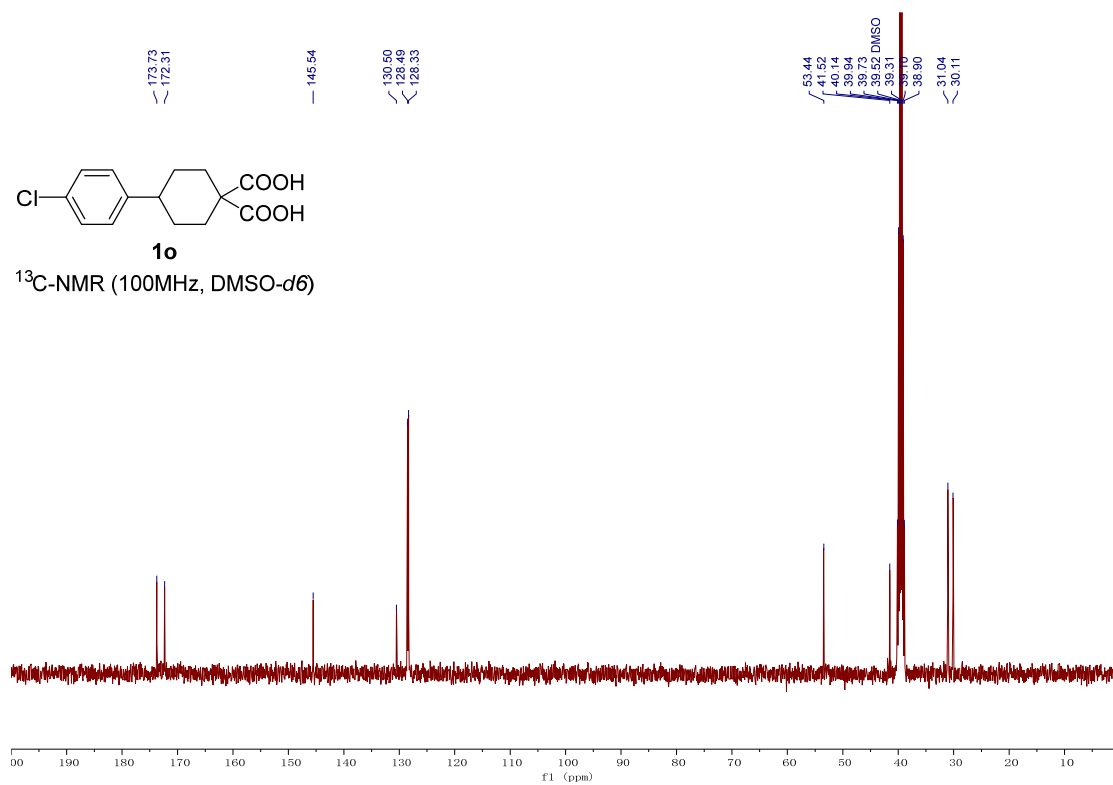
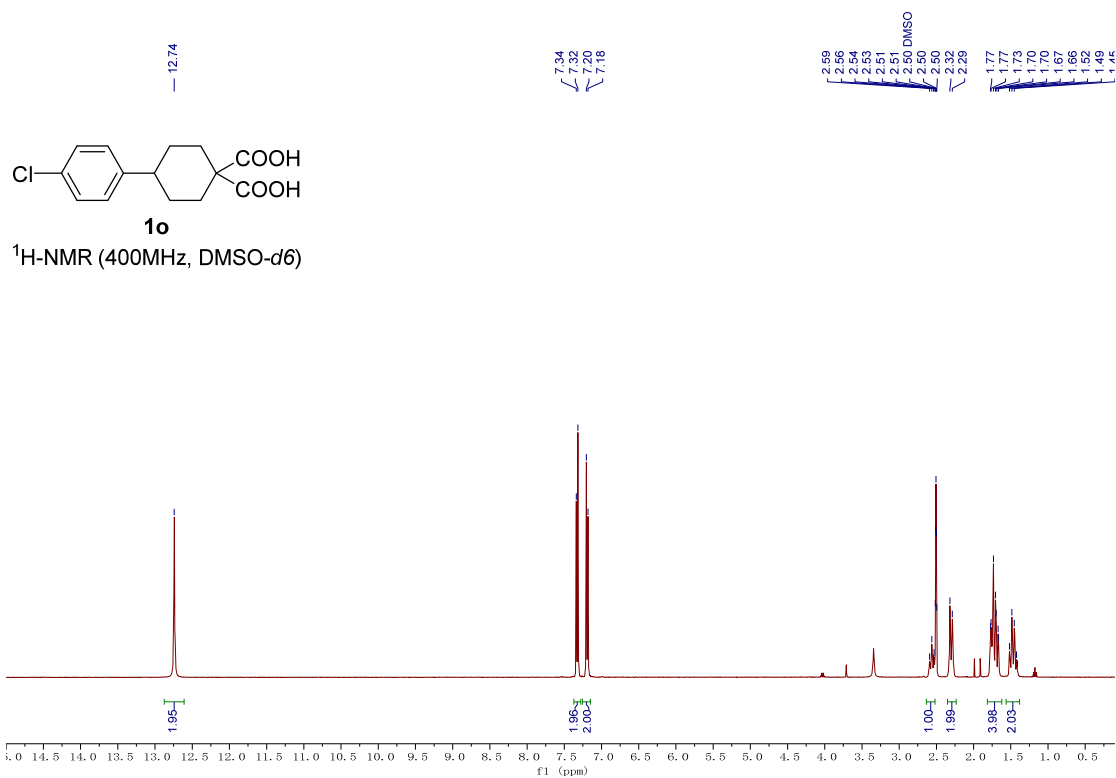
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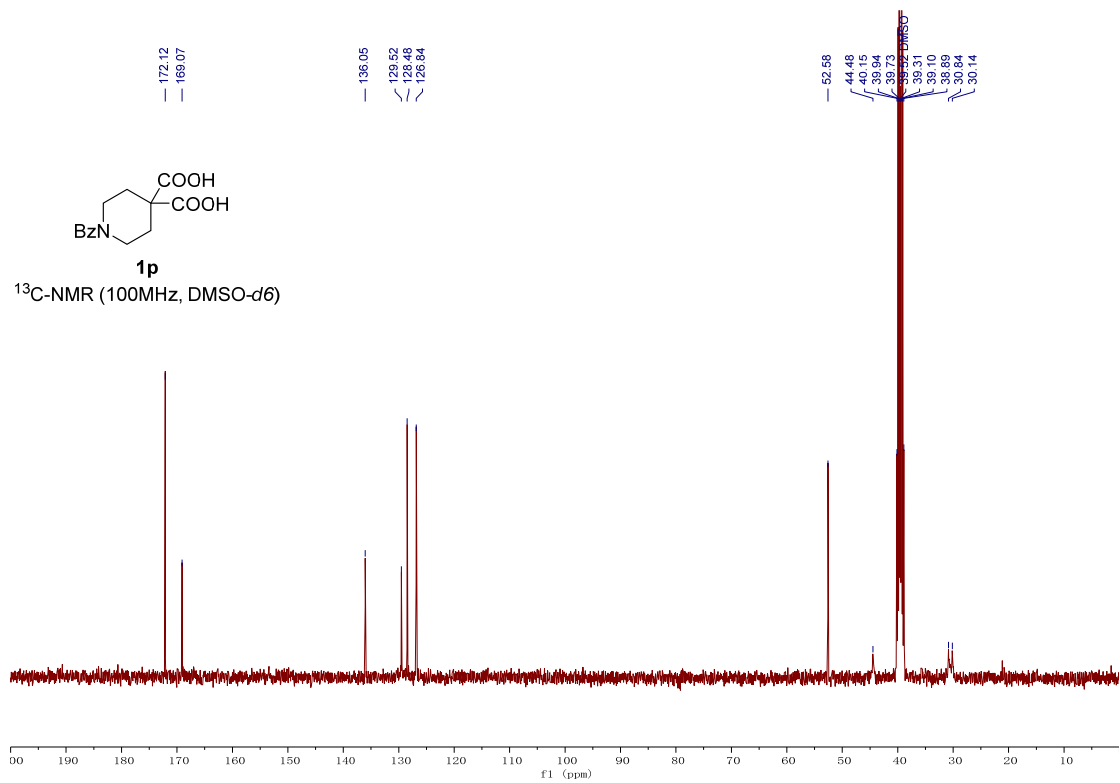
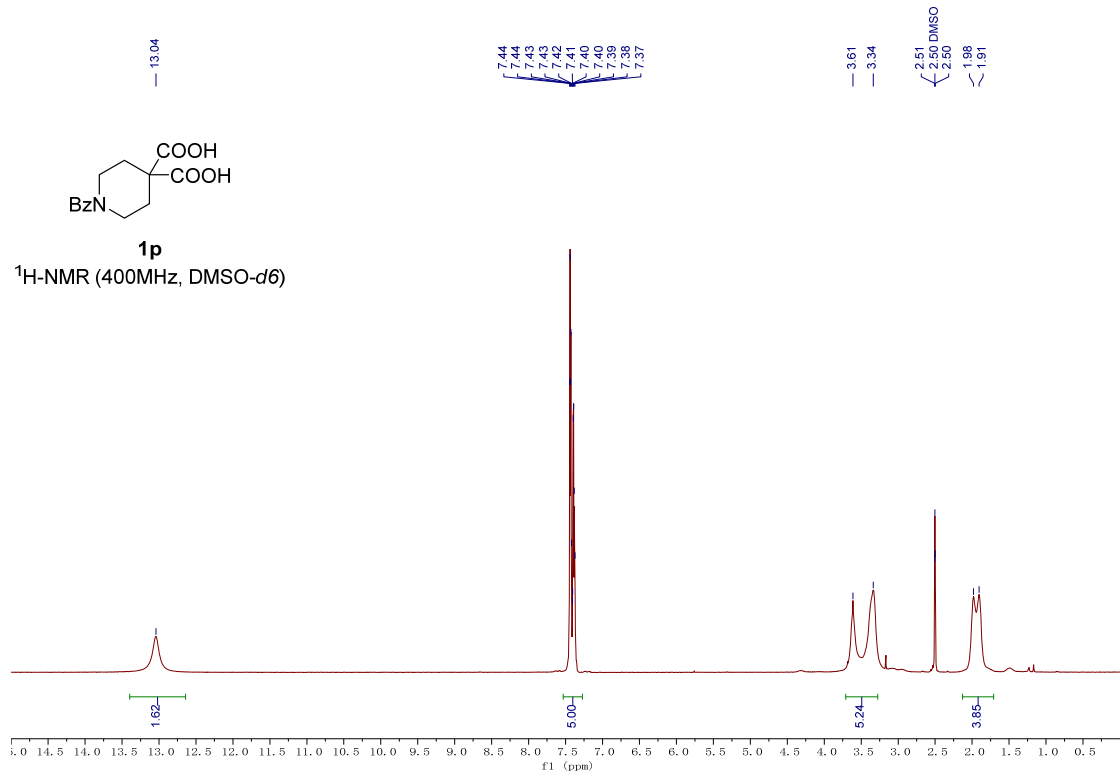


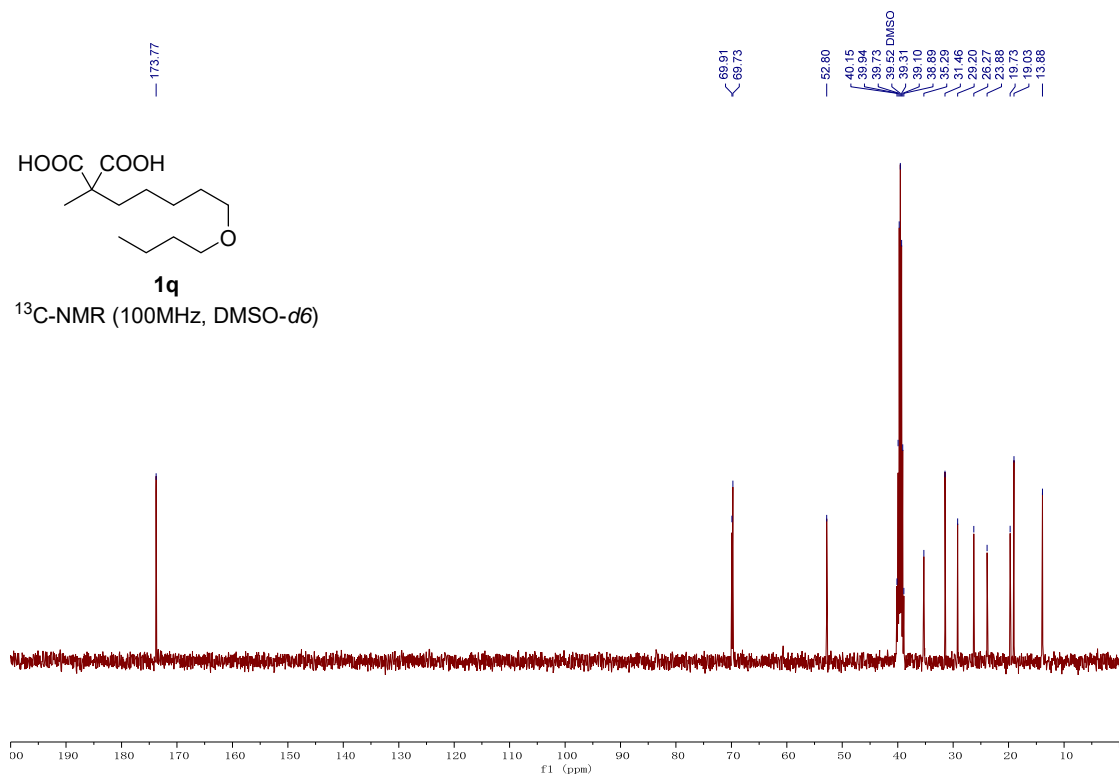
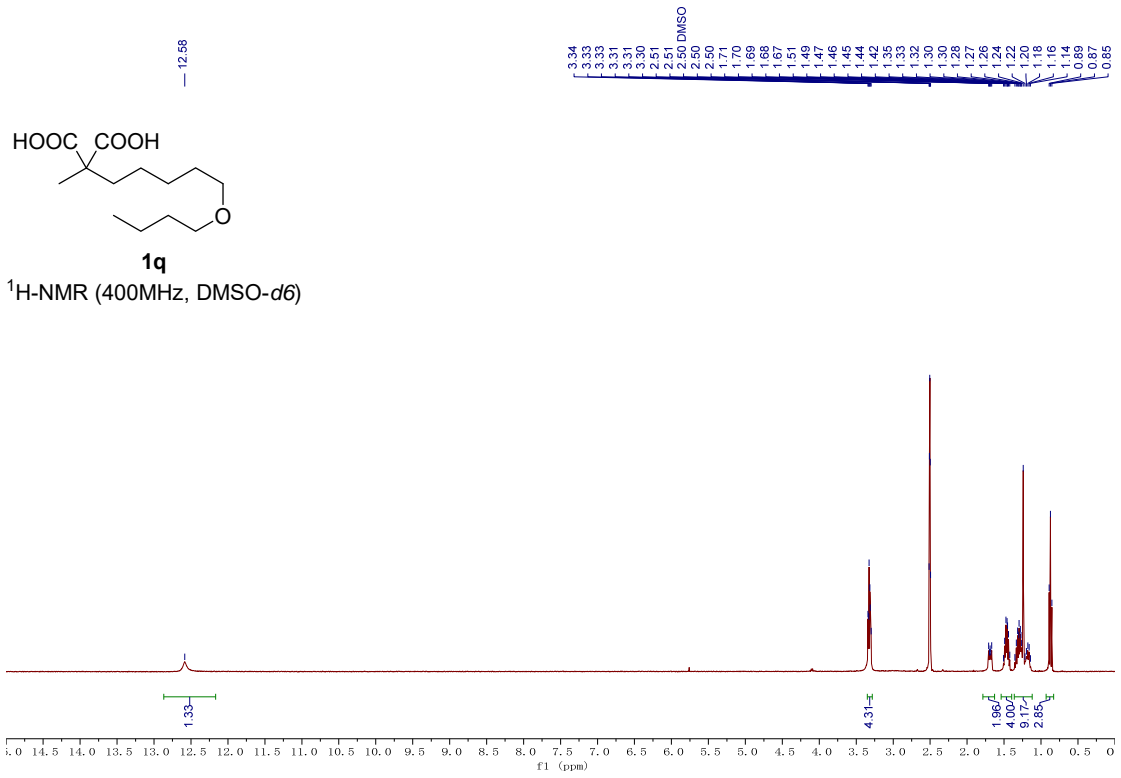


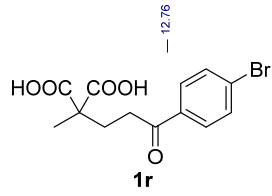




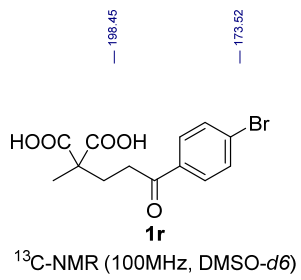
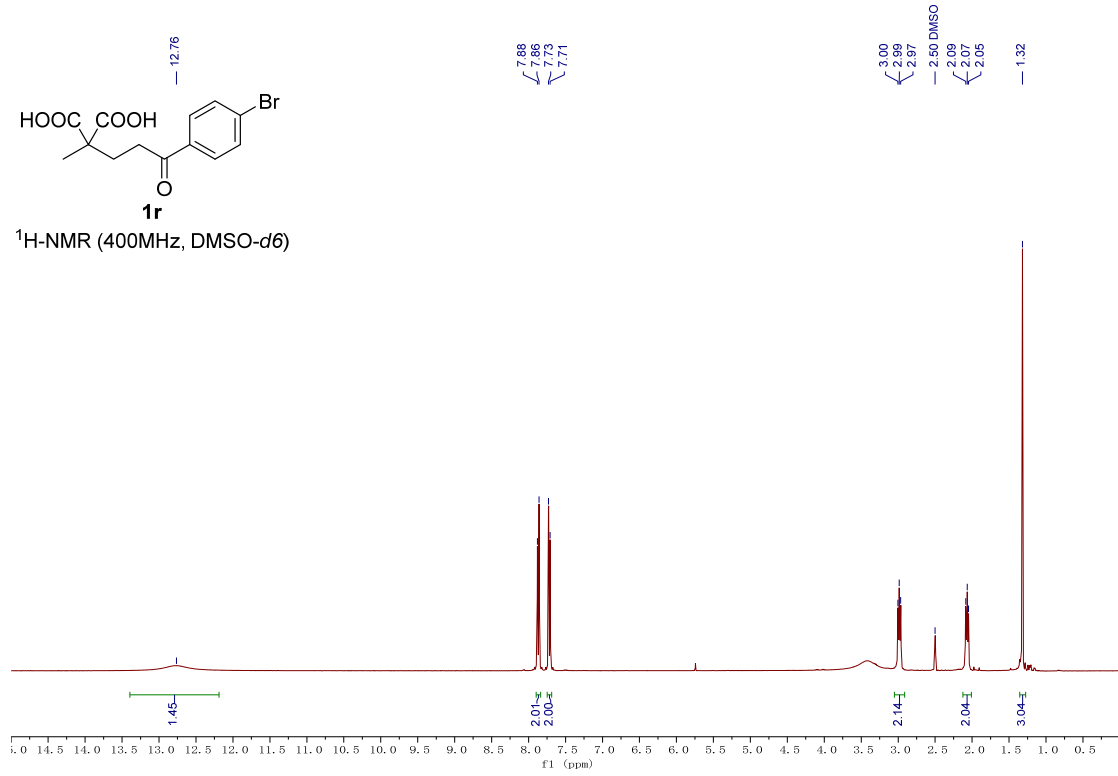




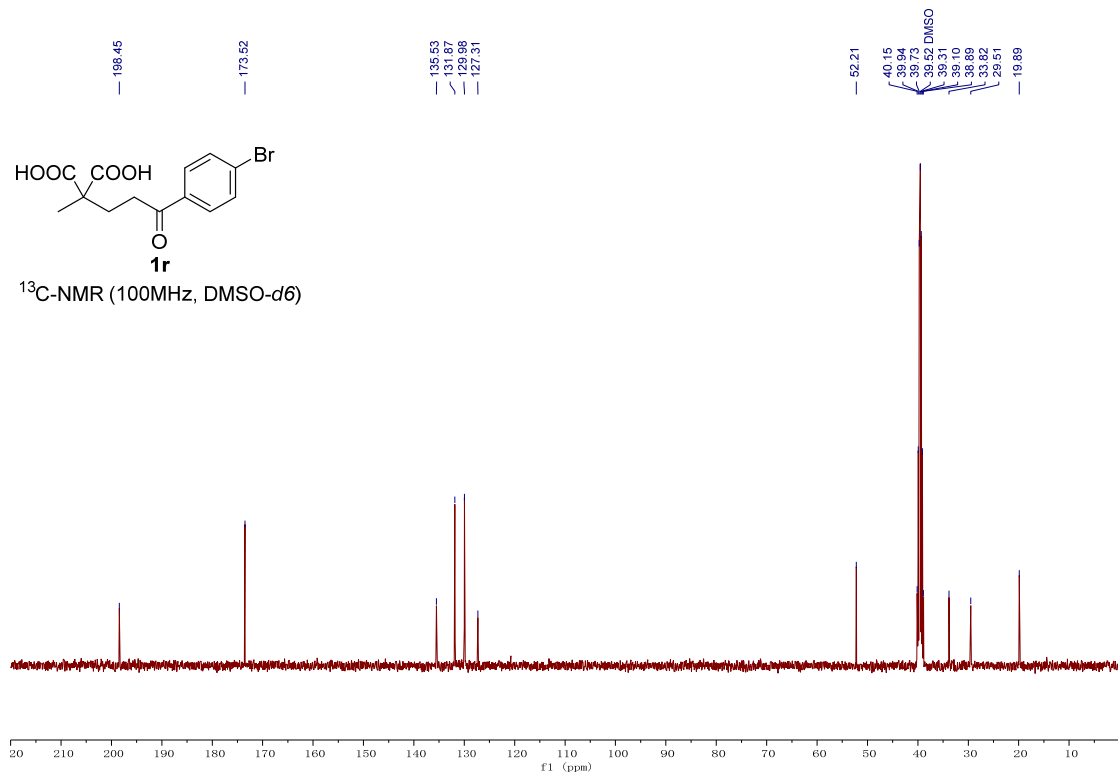


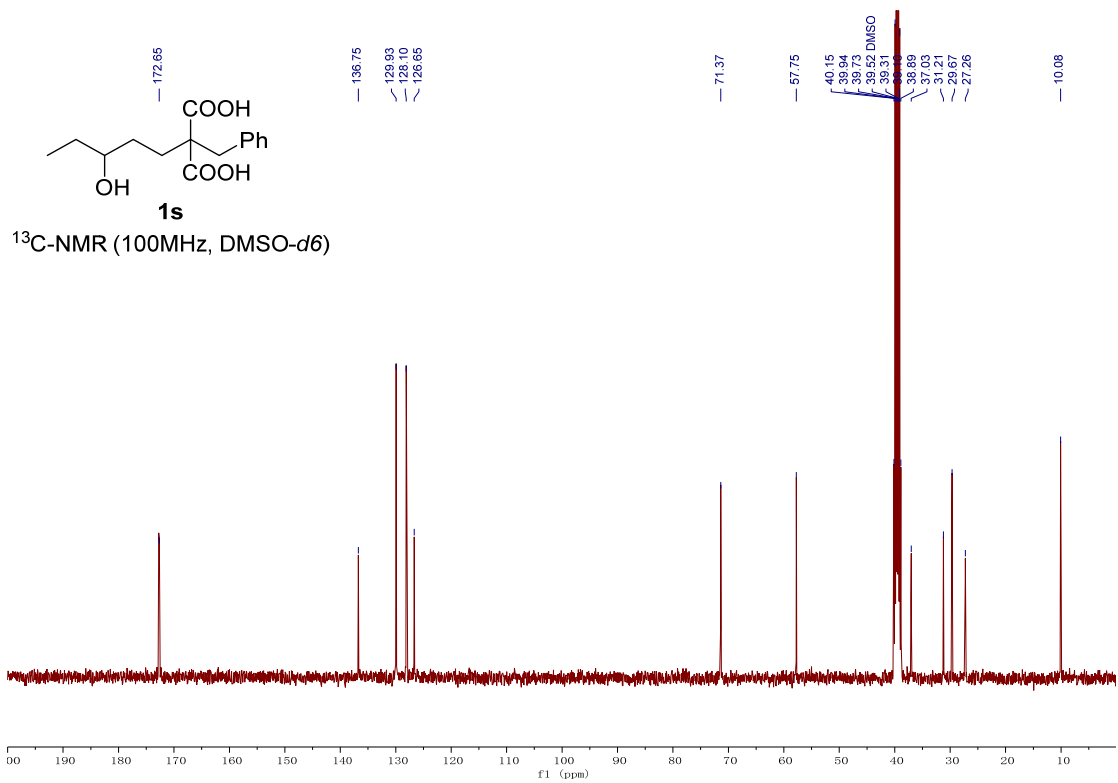
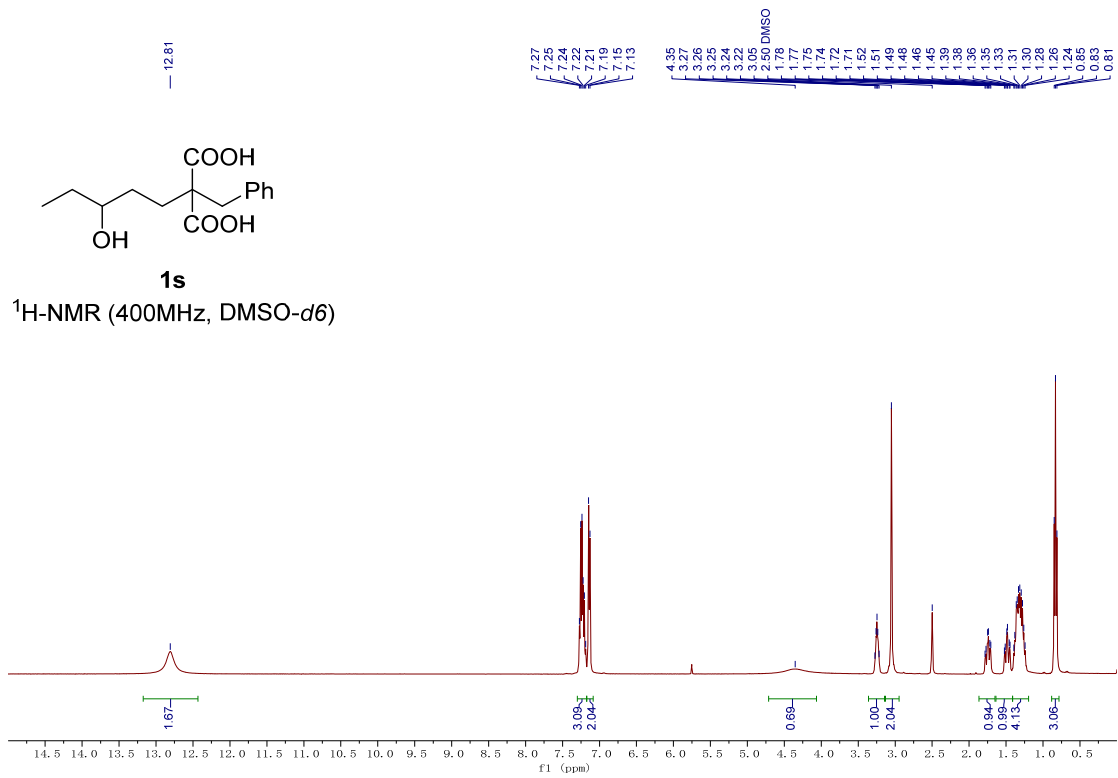


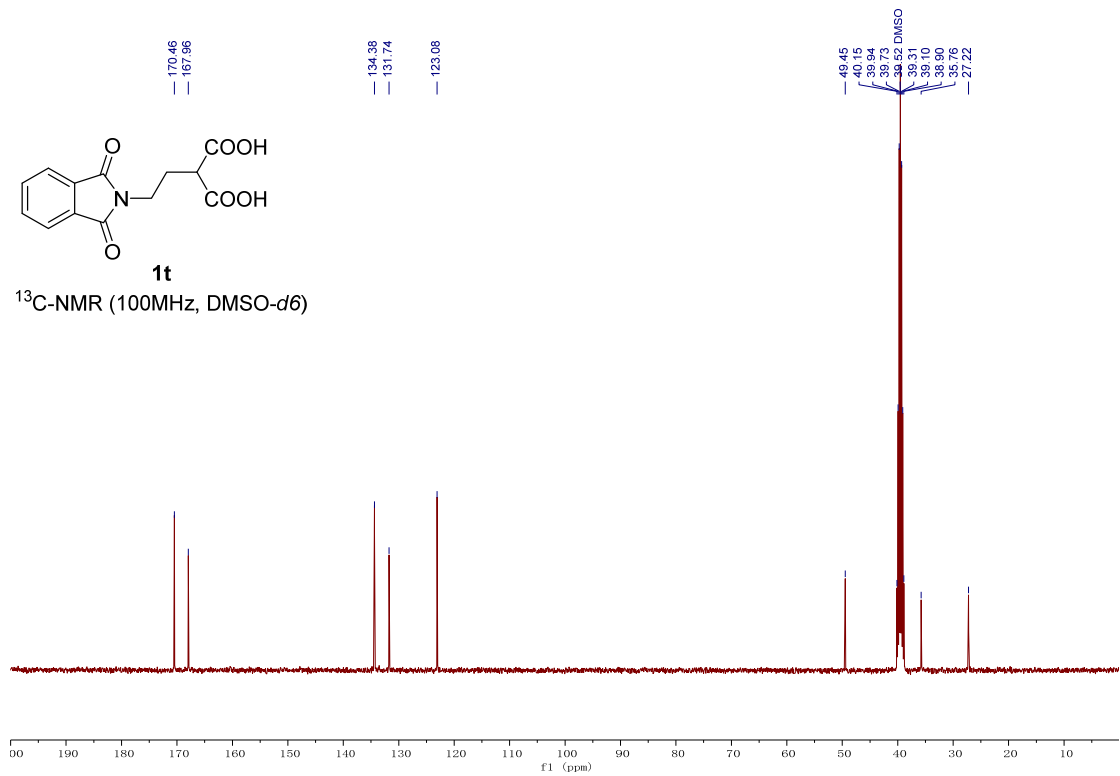
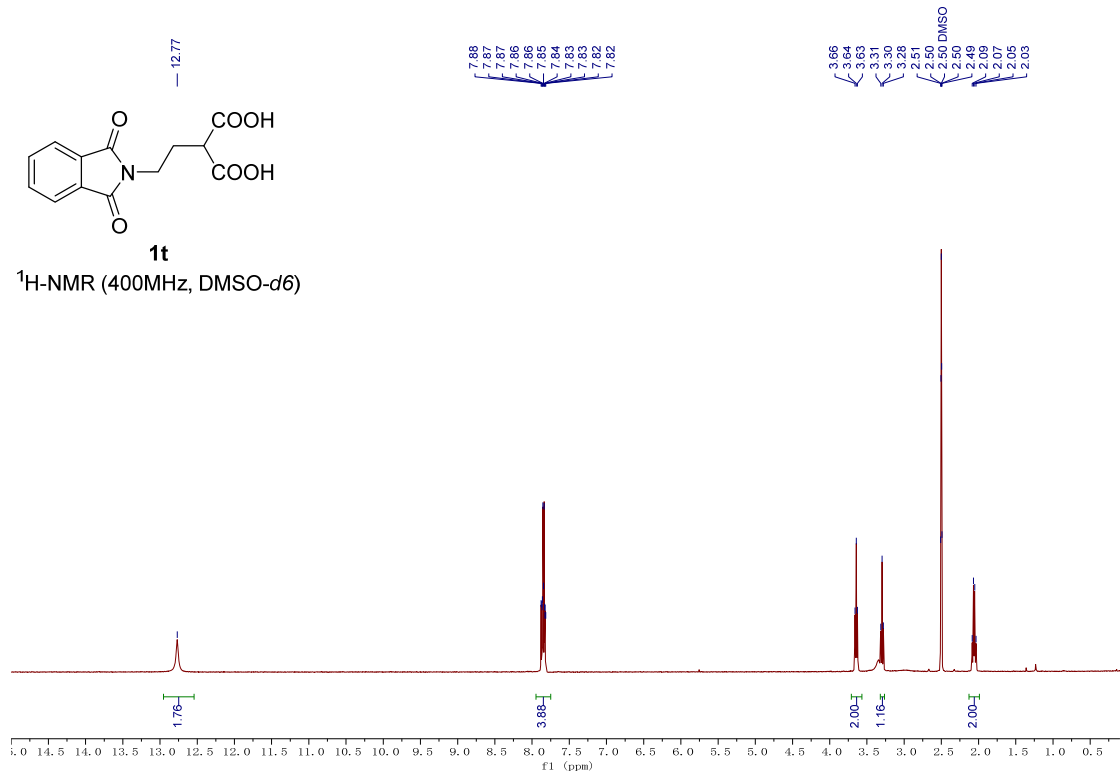
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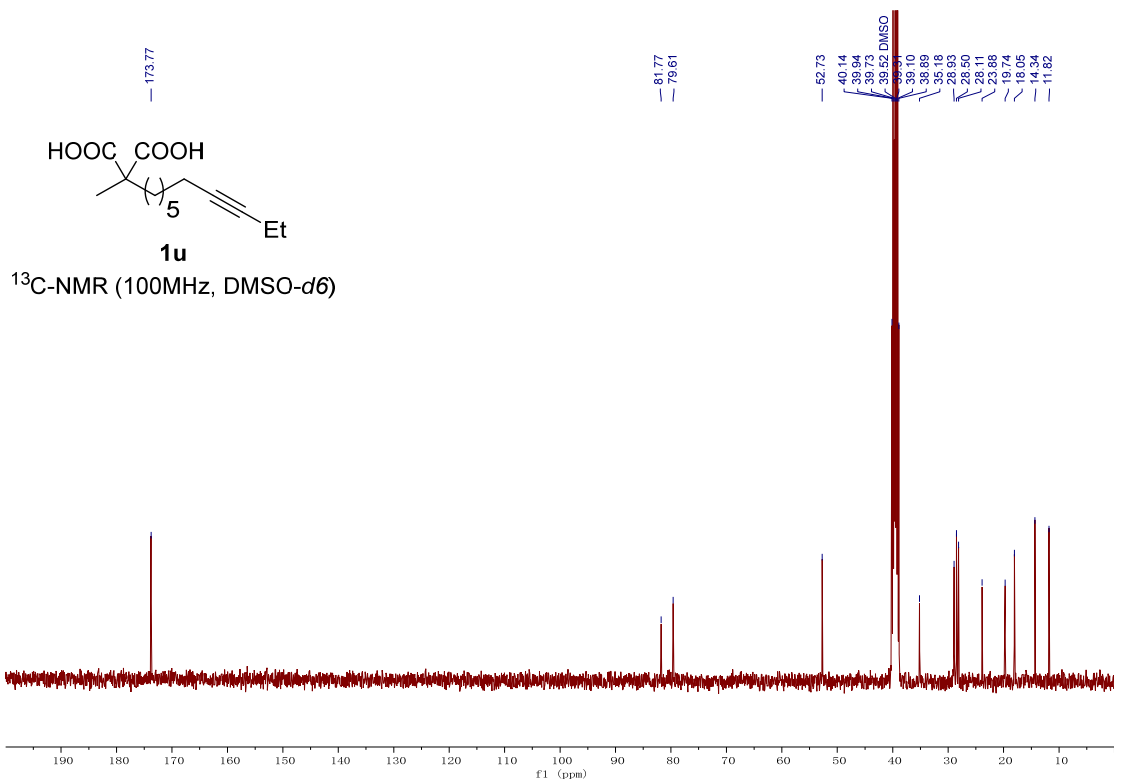
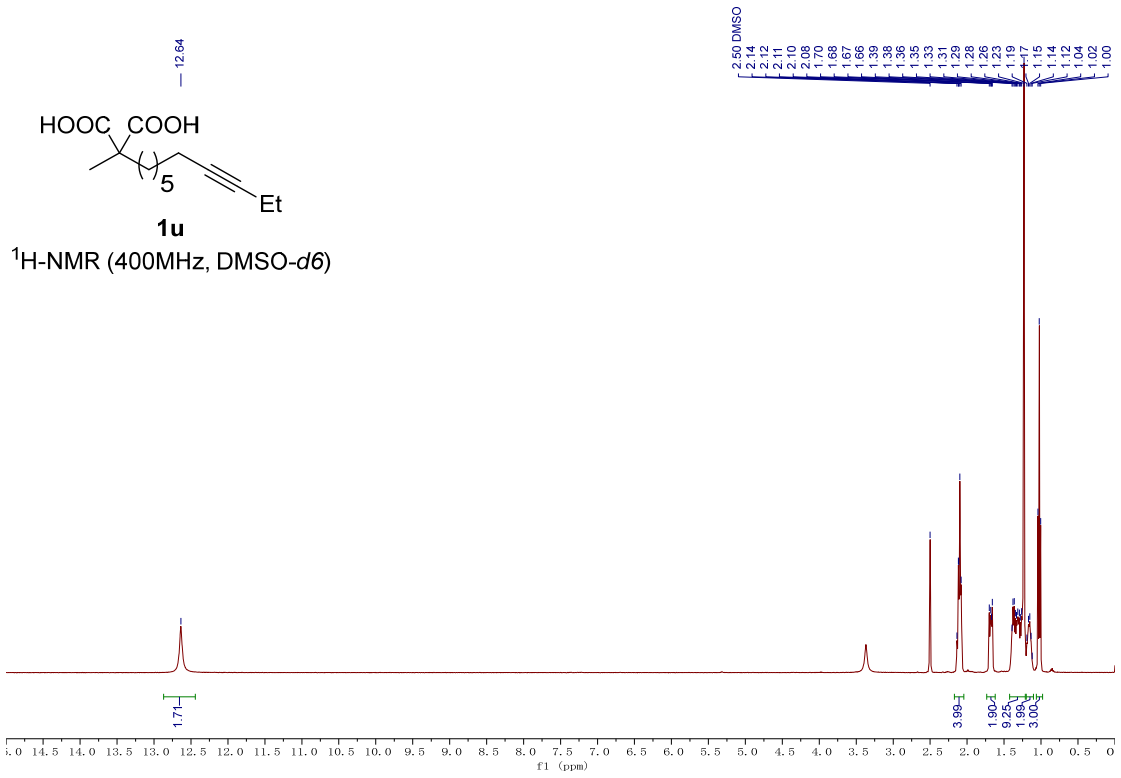


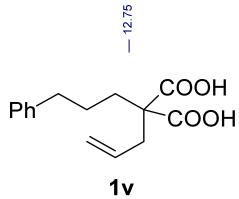
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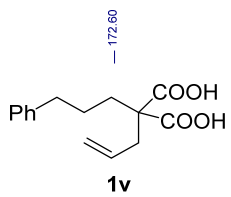
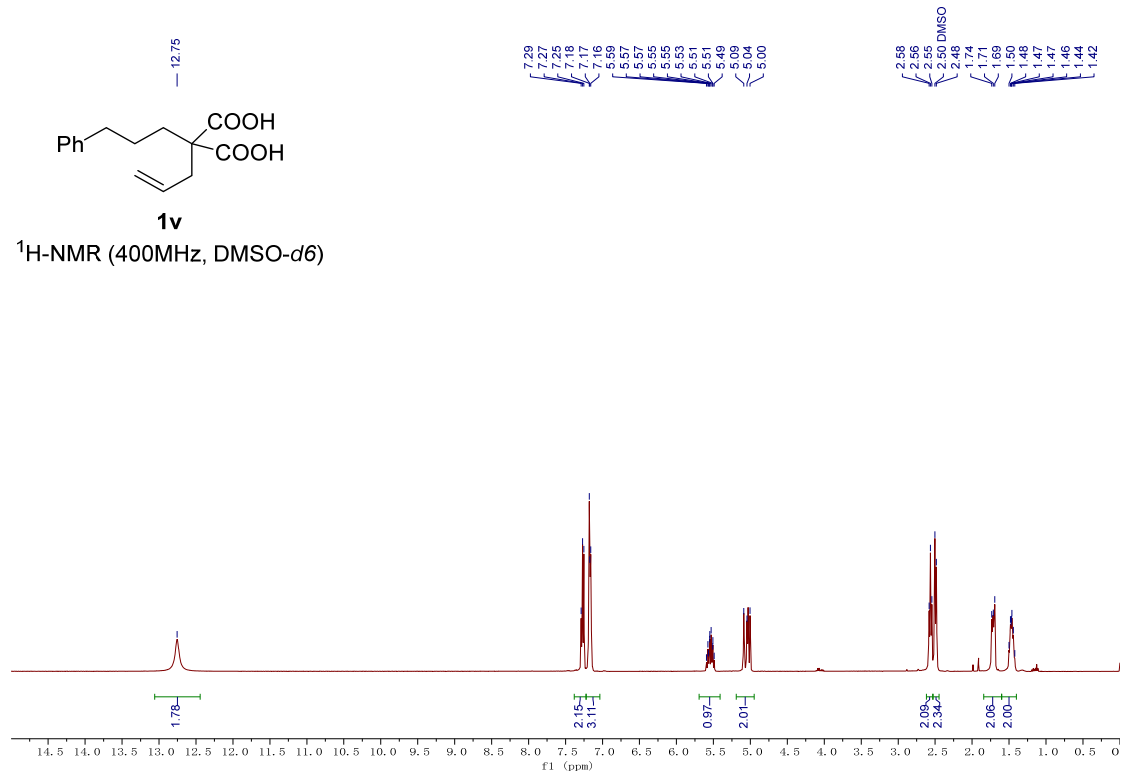




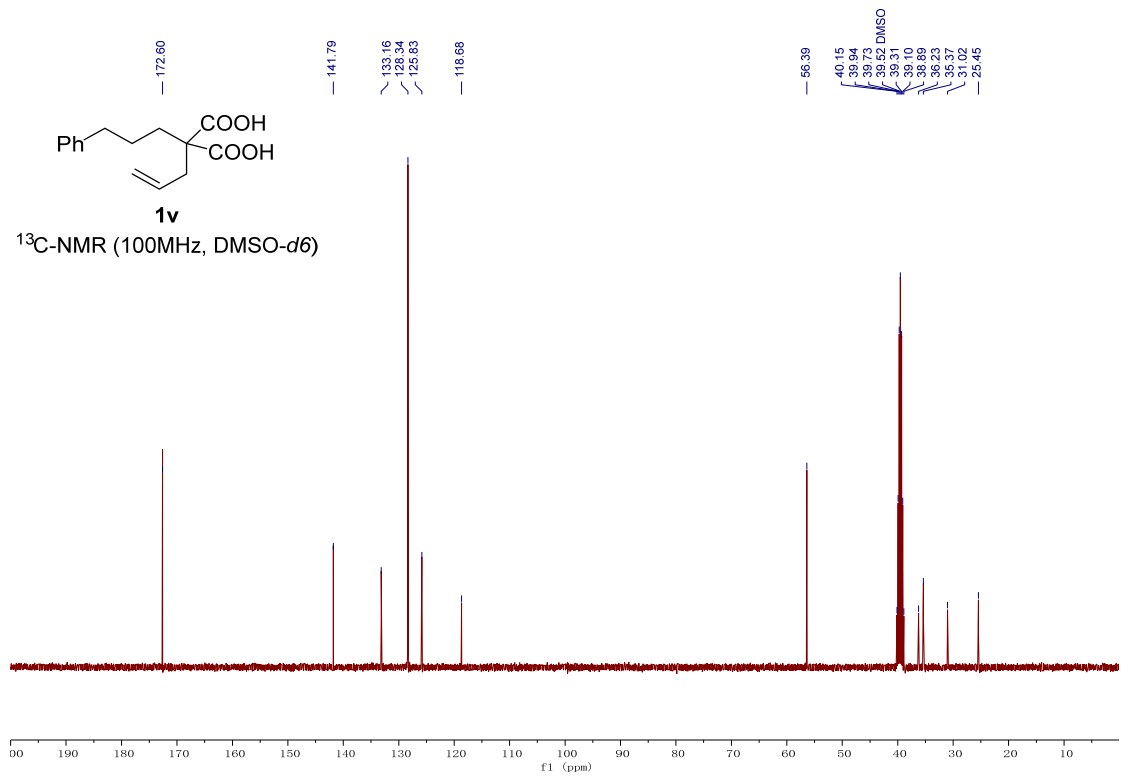


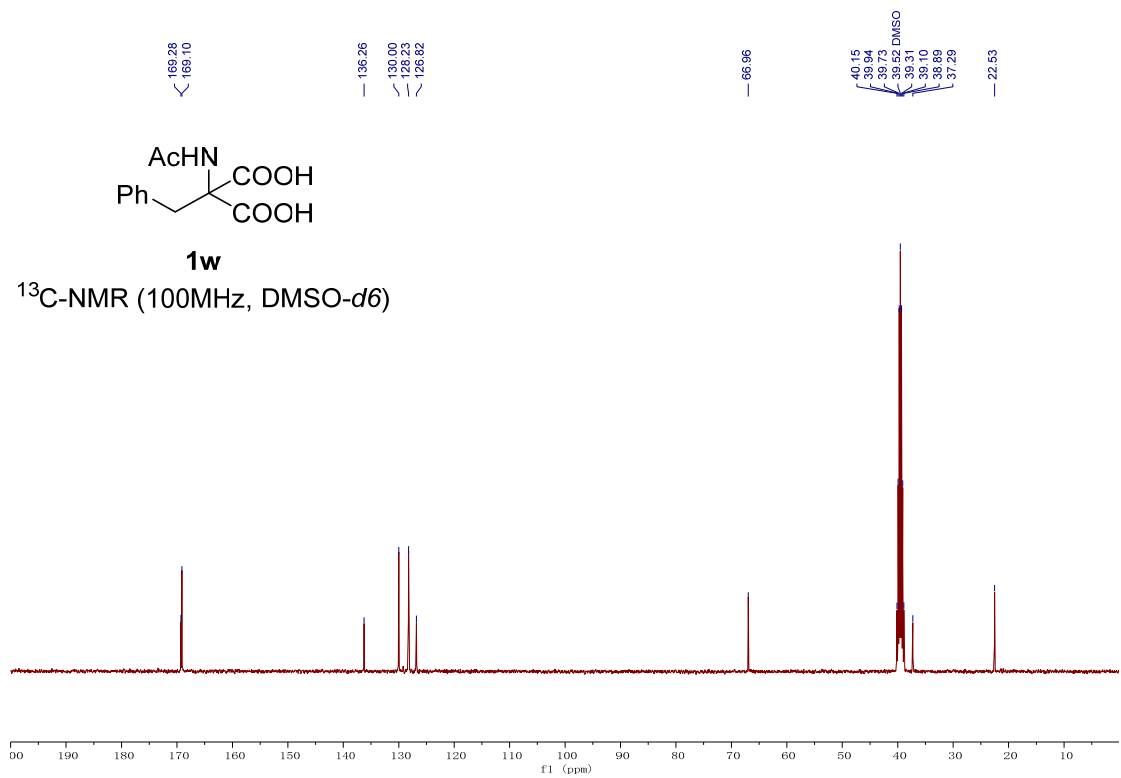
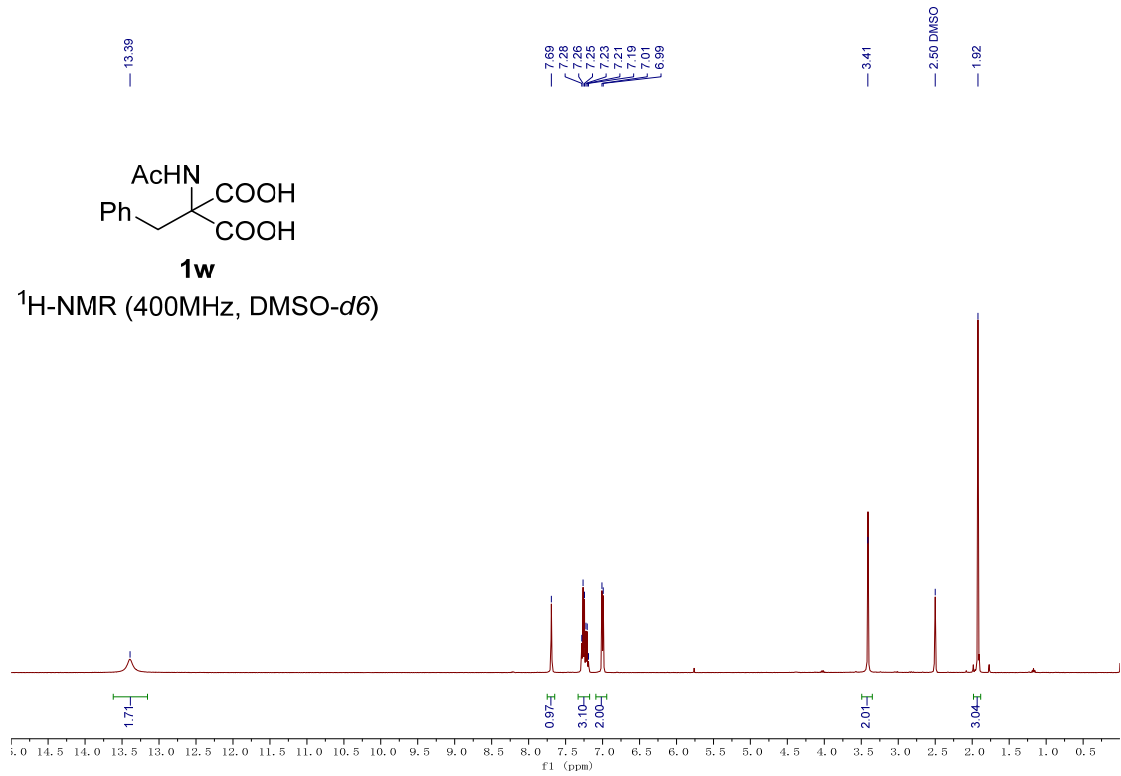


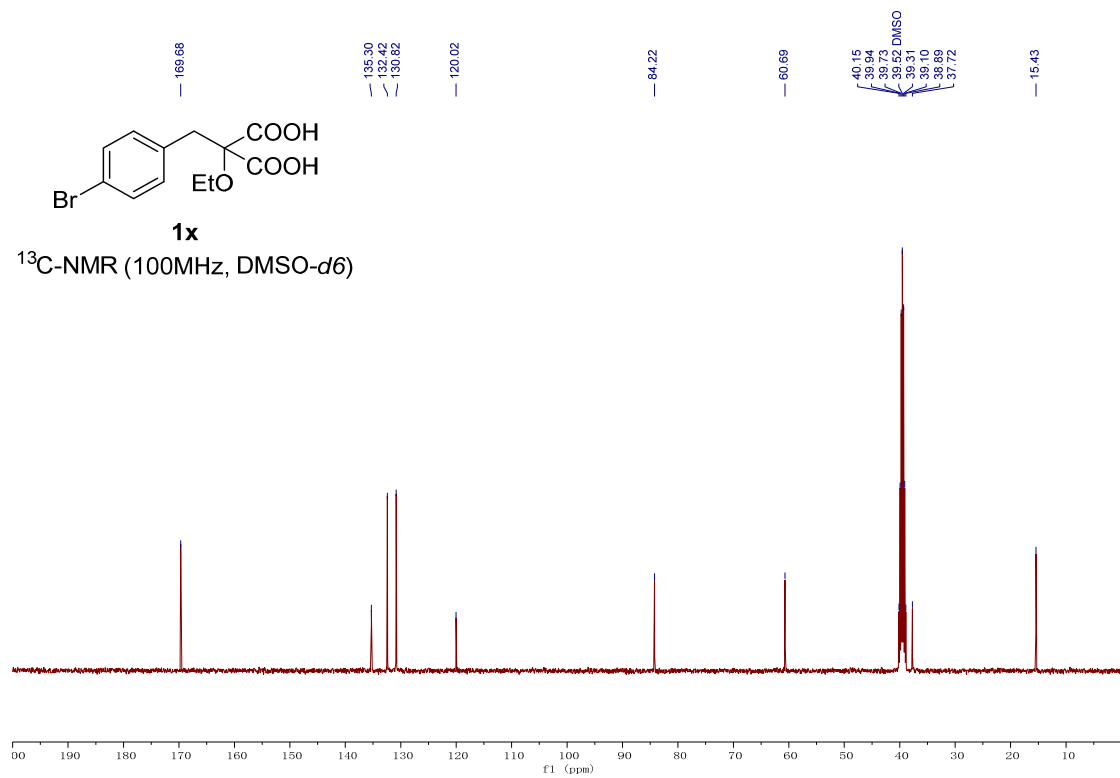
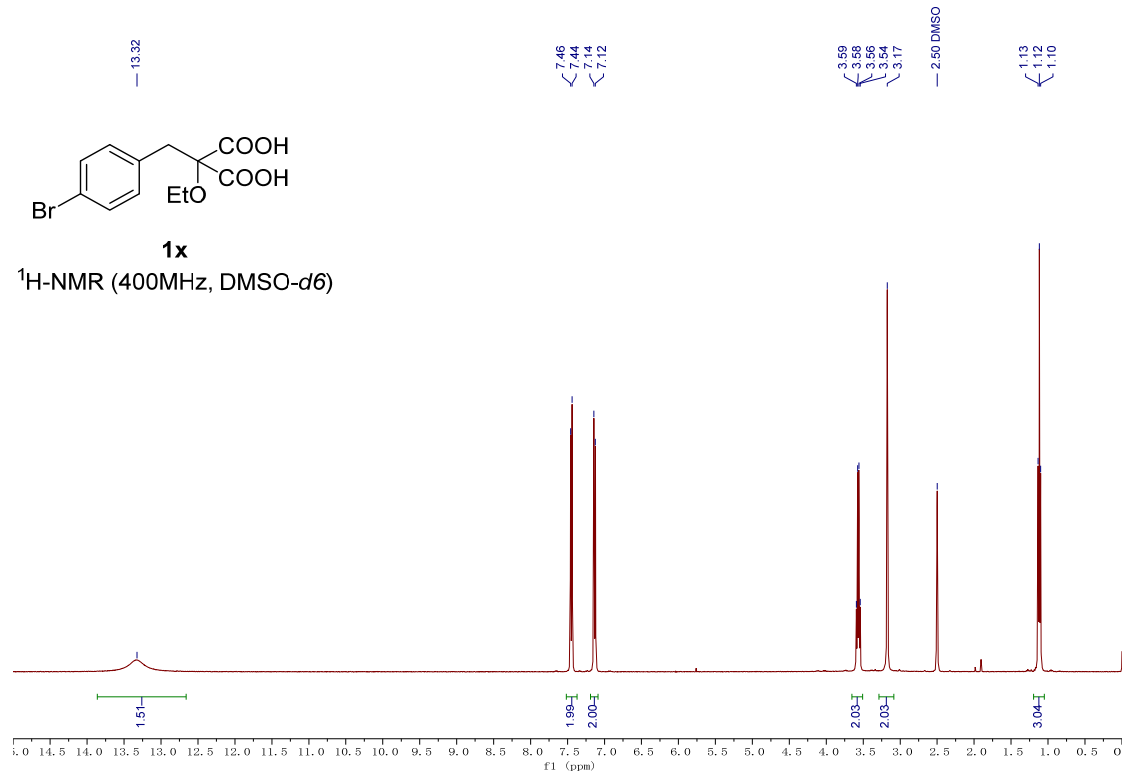
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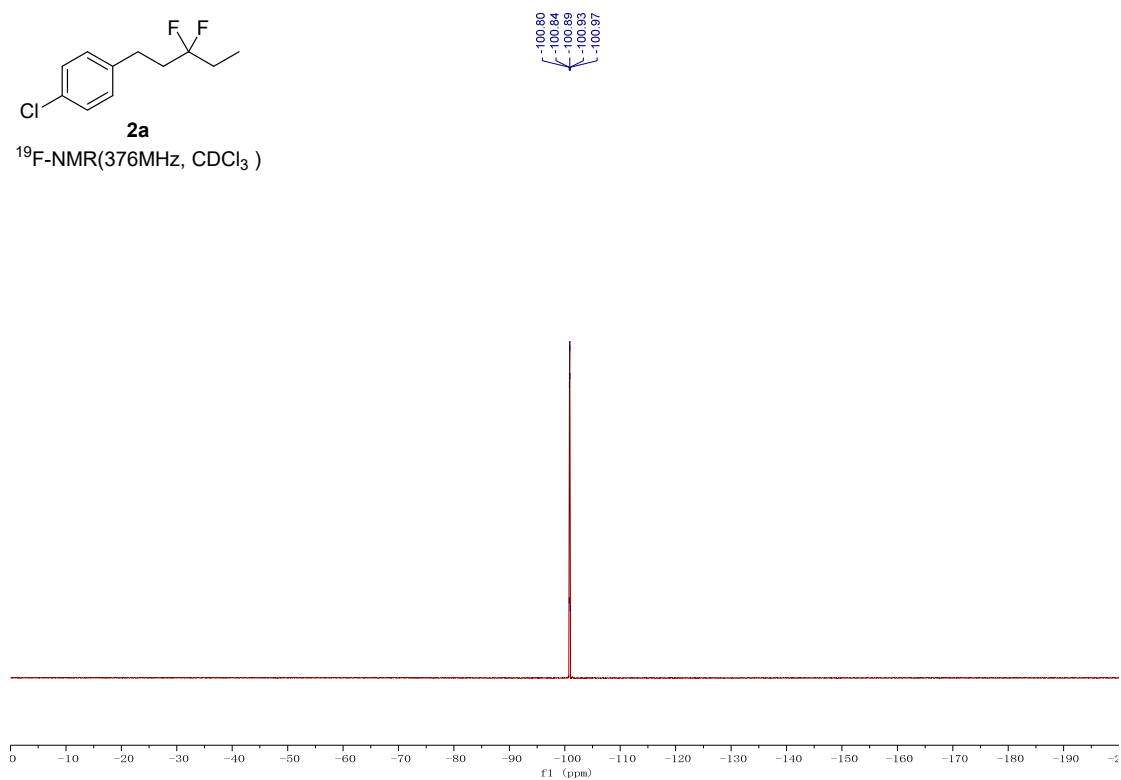
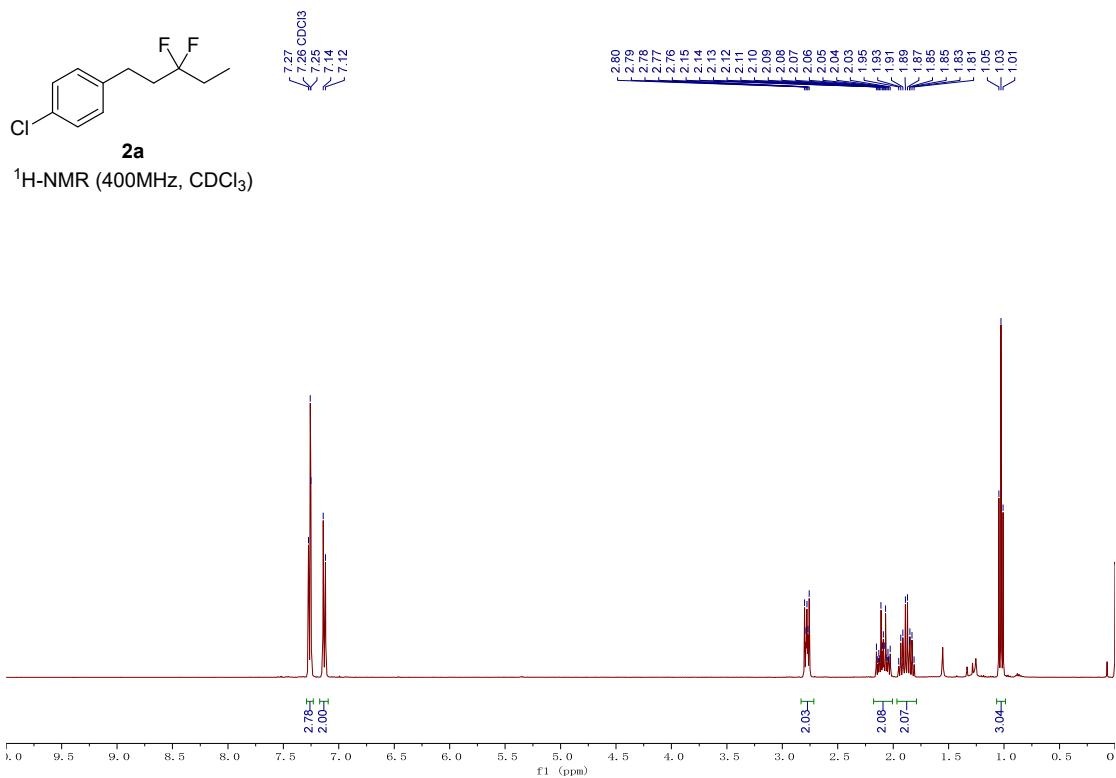


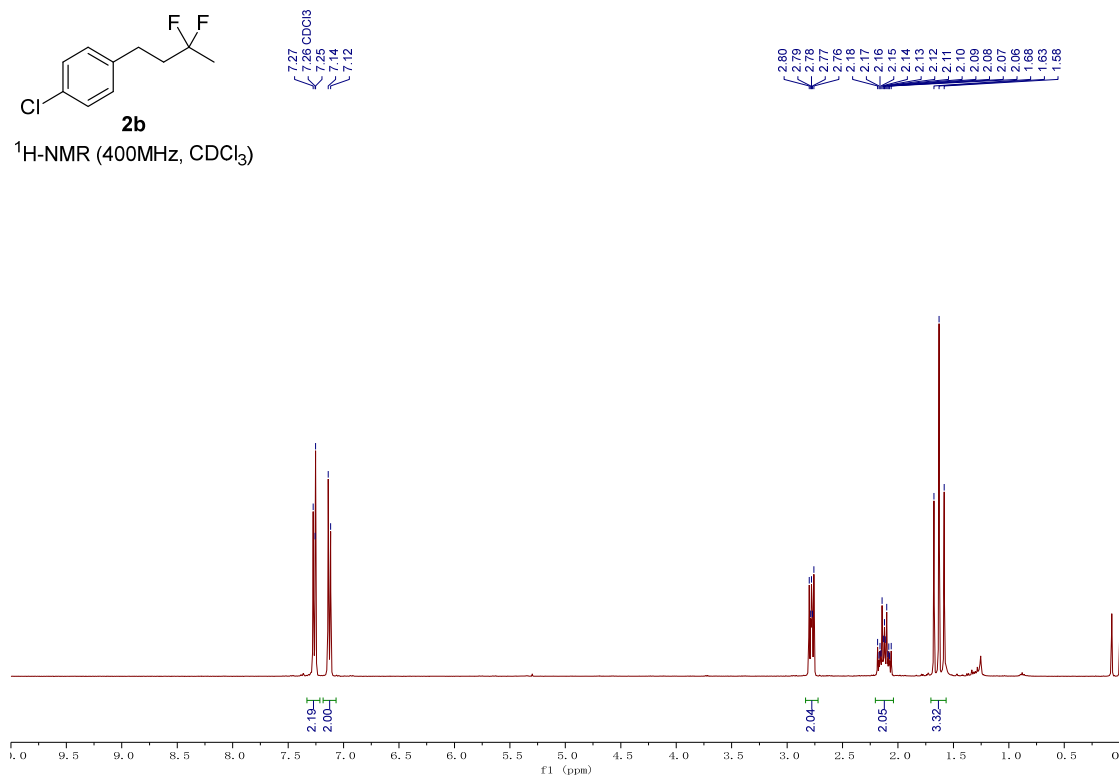
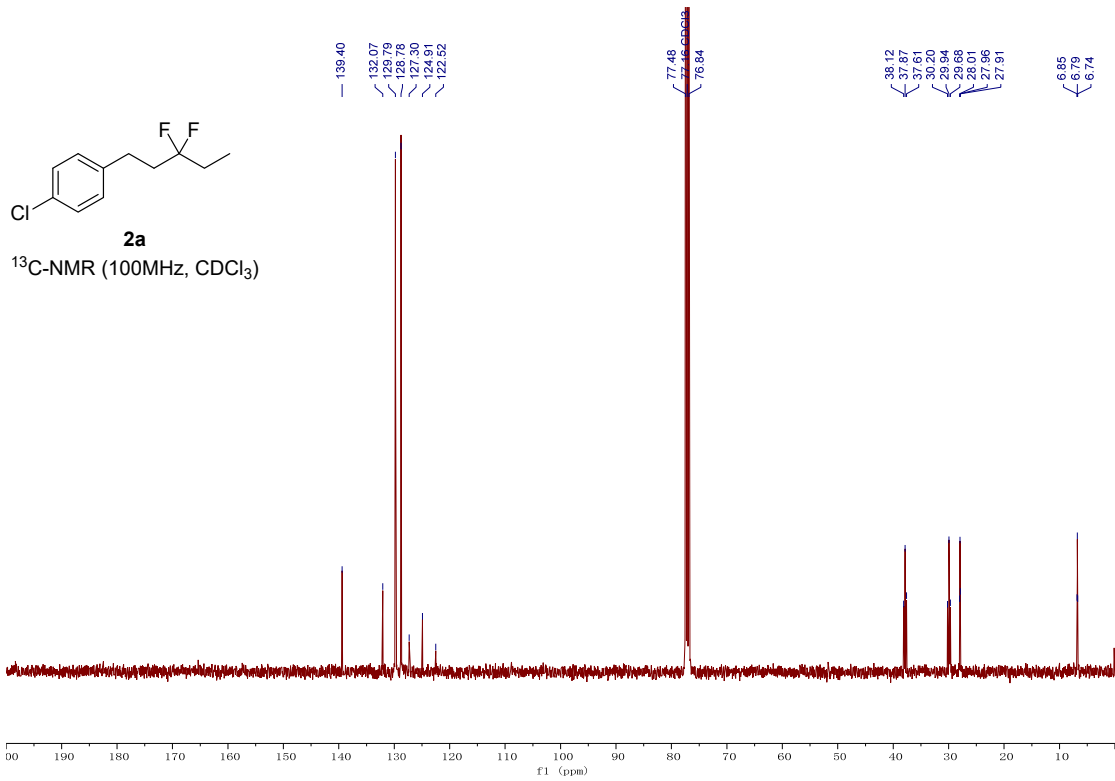
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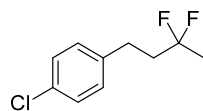




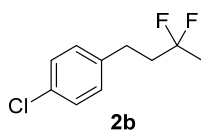
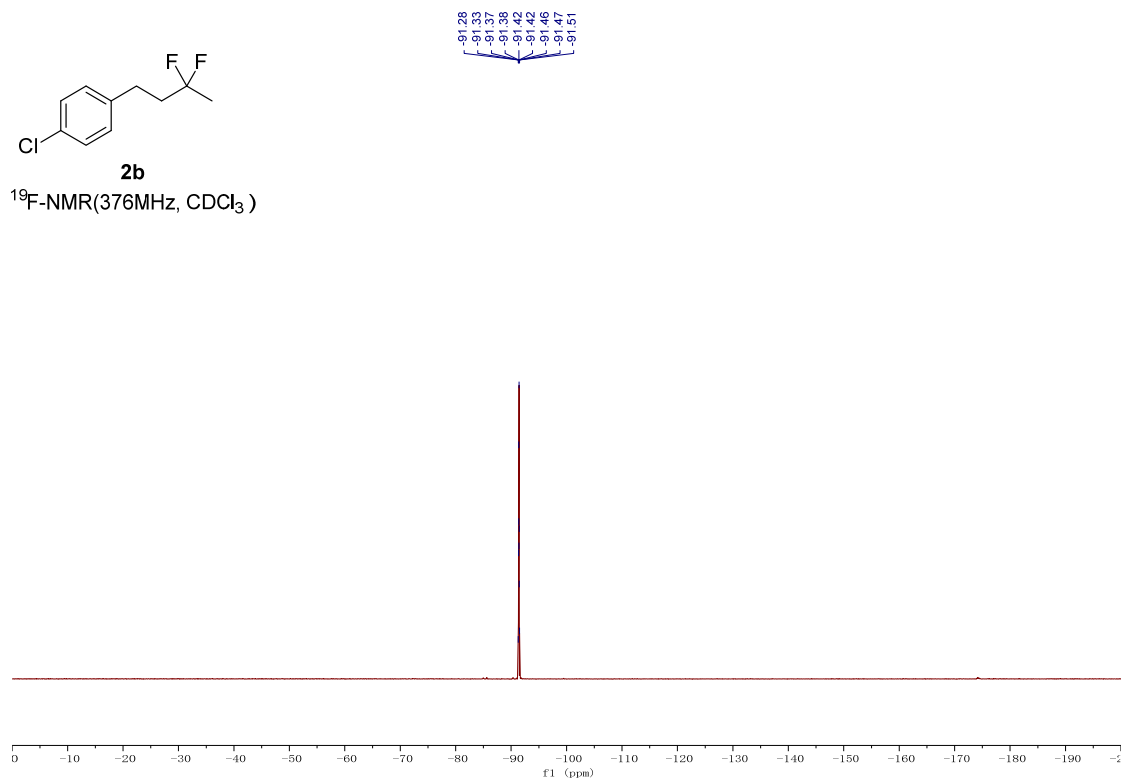




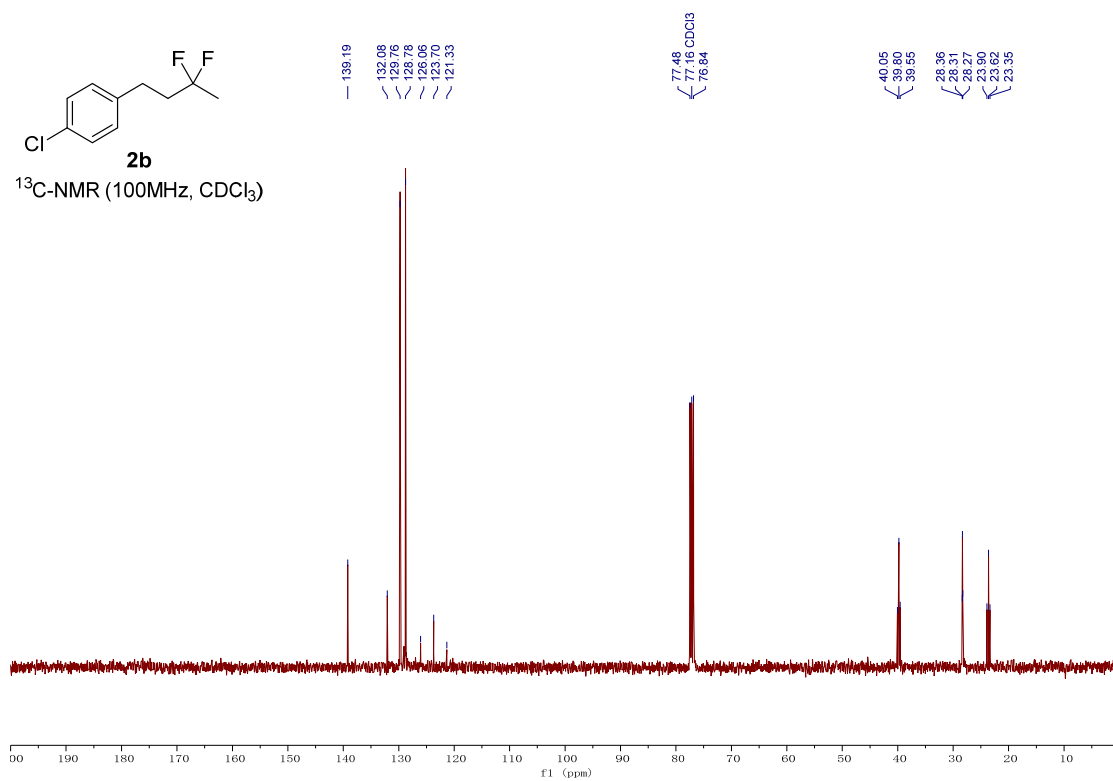


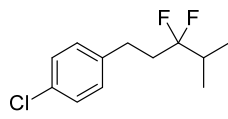


$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )

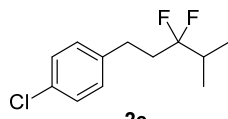
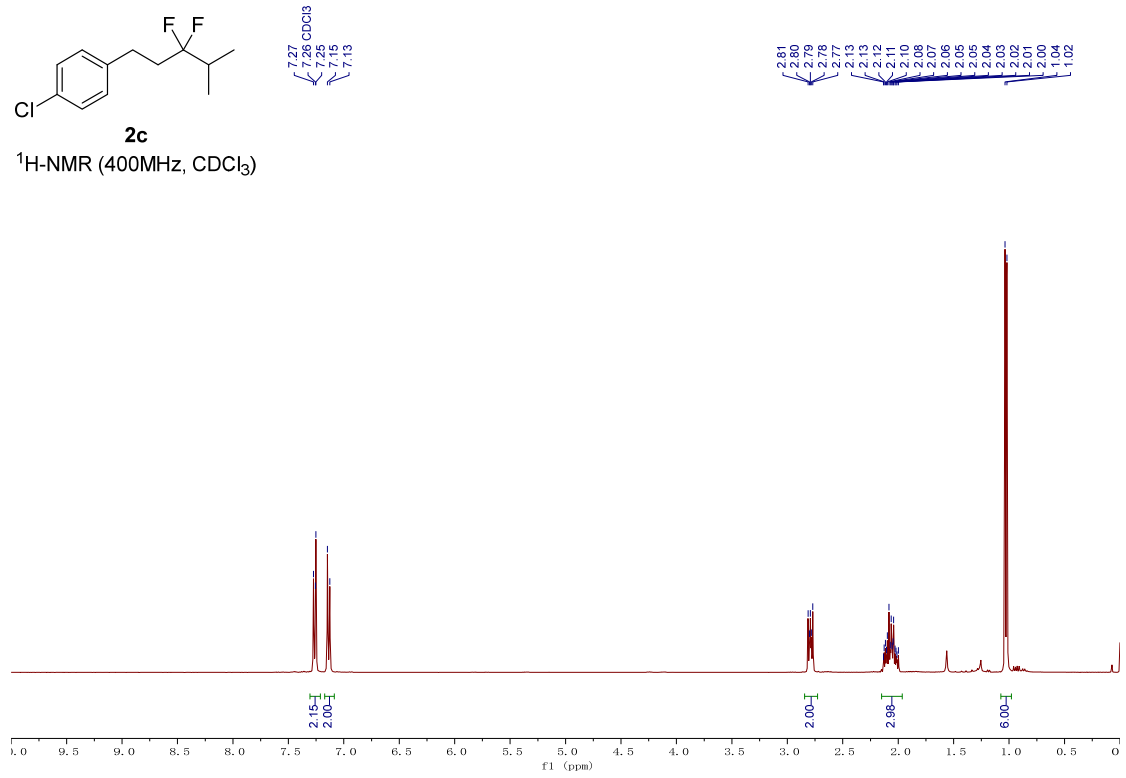


$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

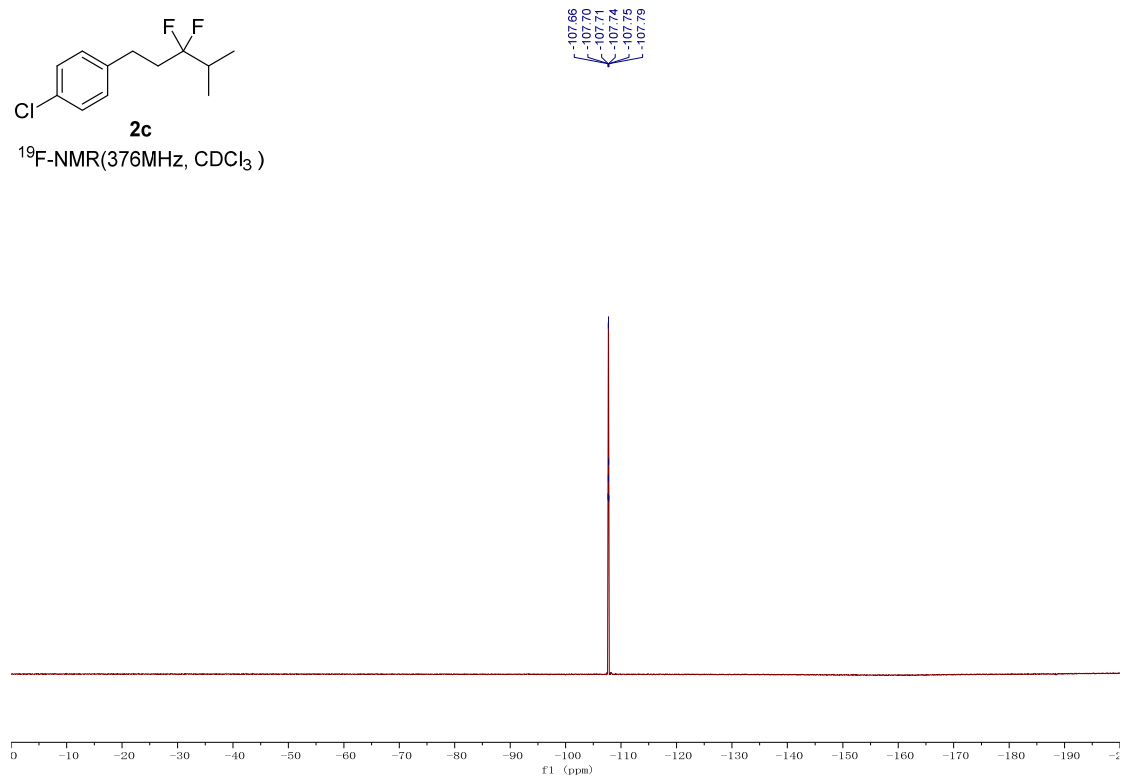


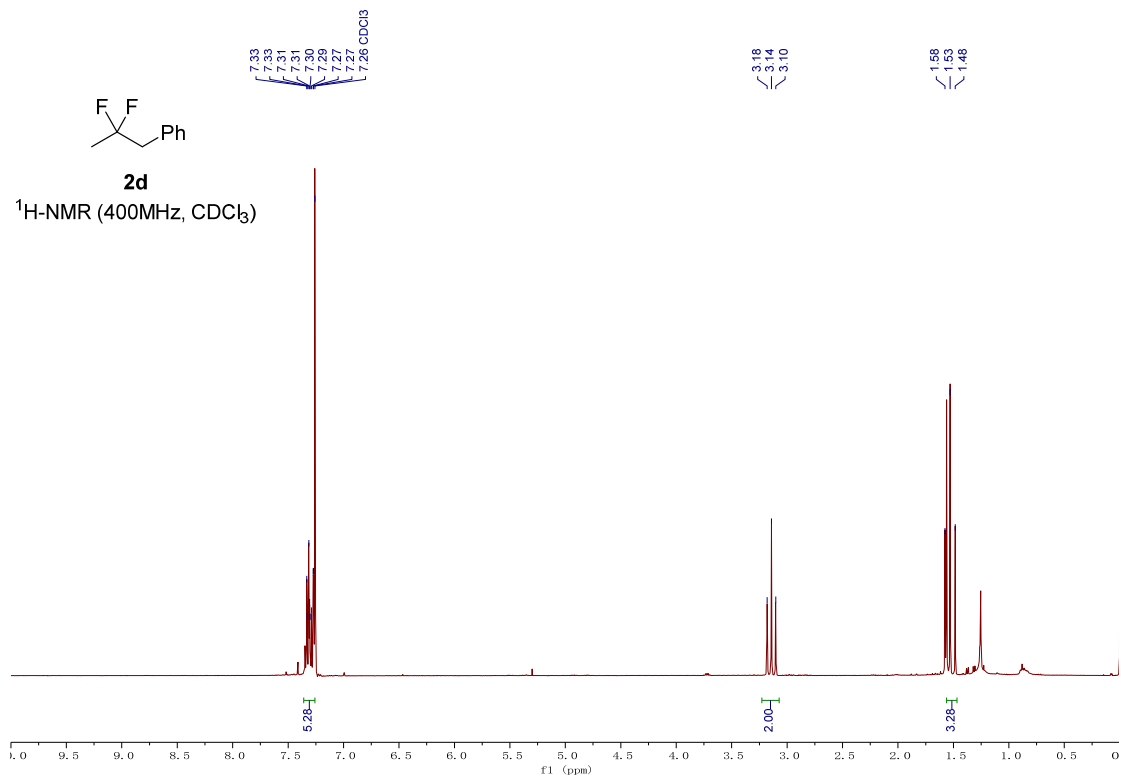
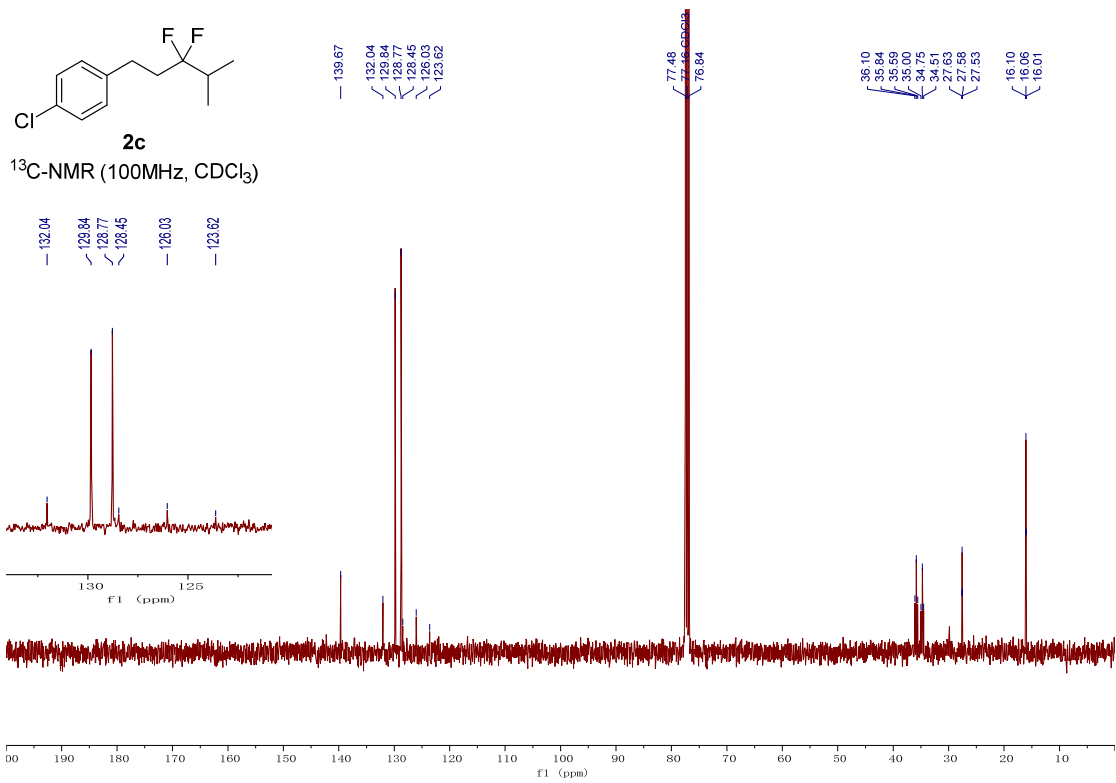


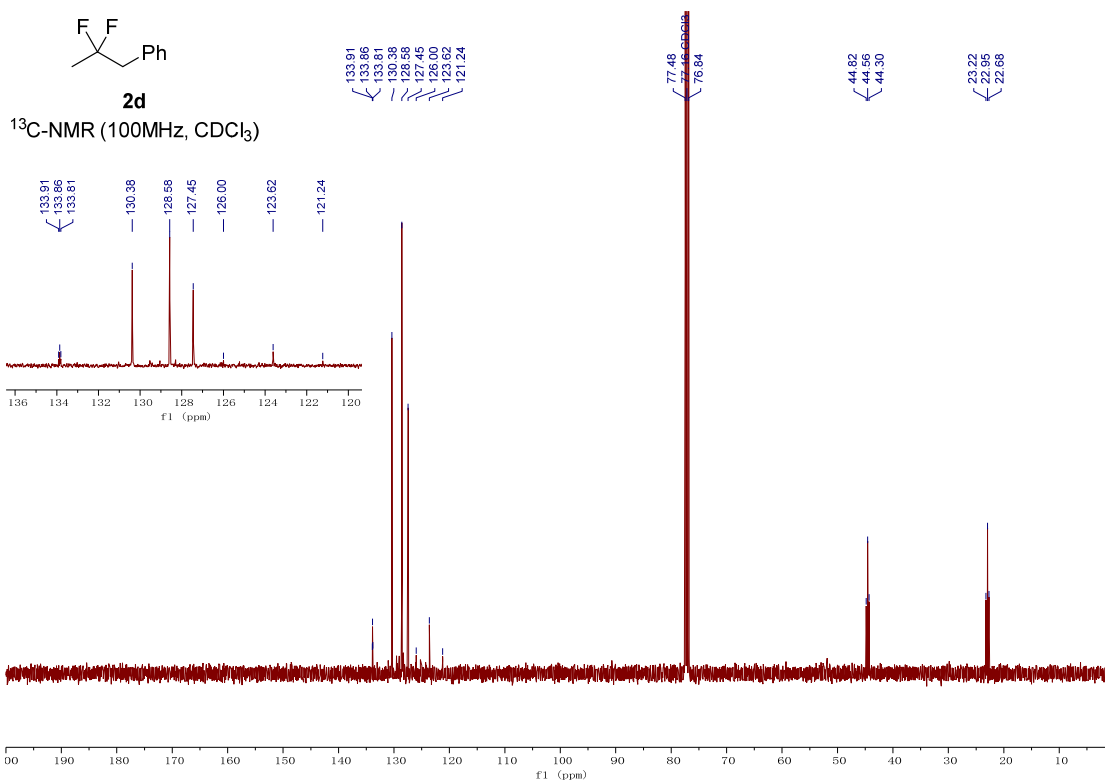
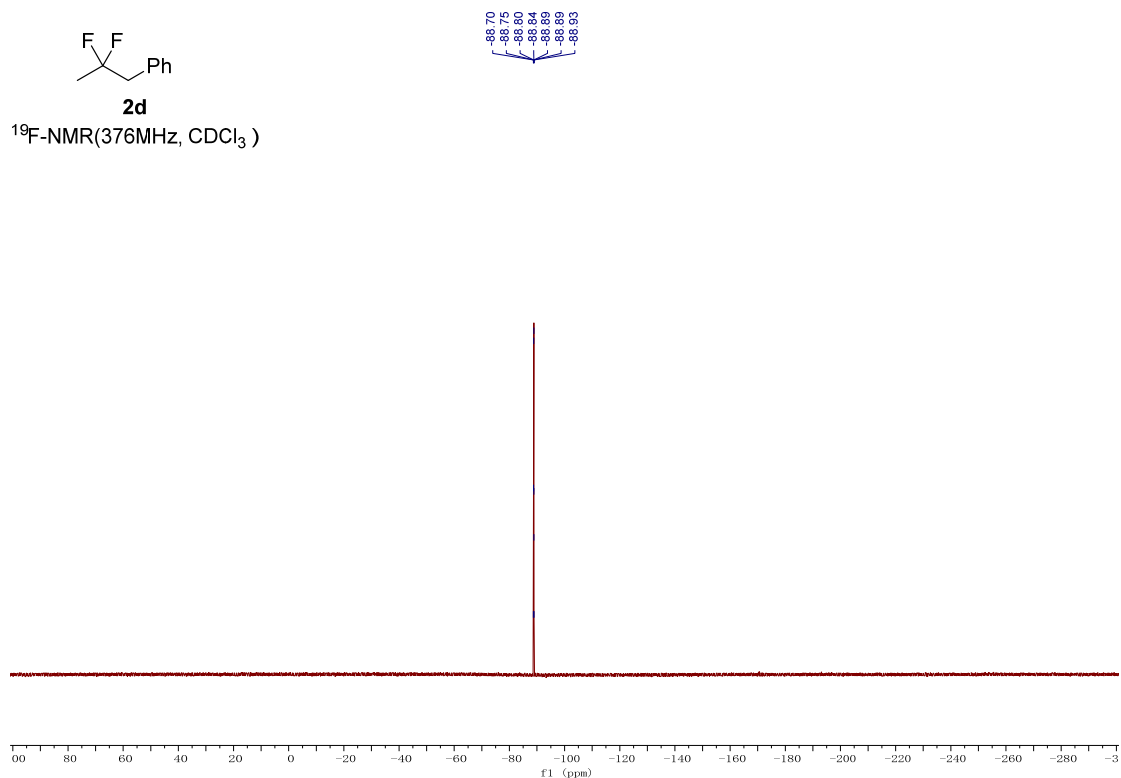
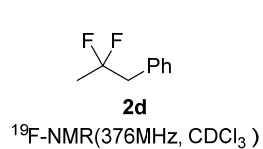
<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>)

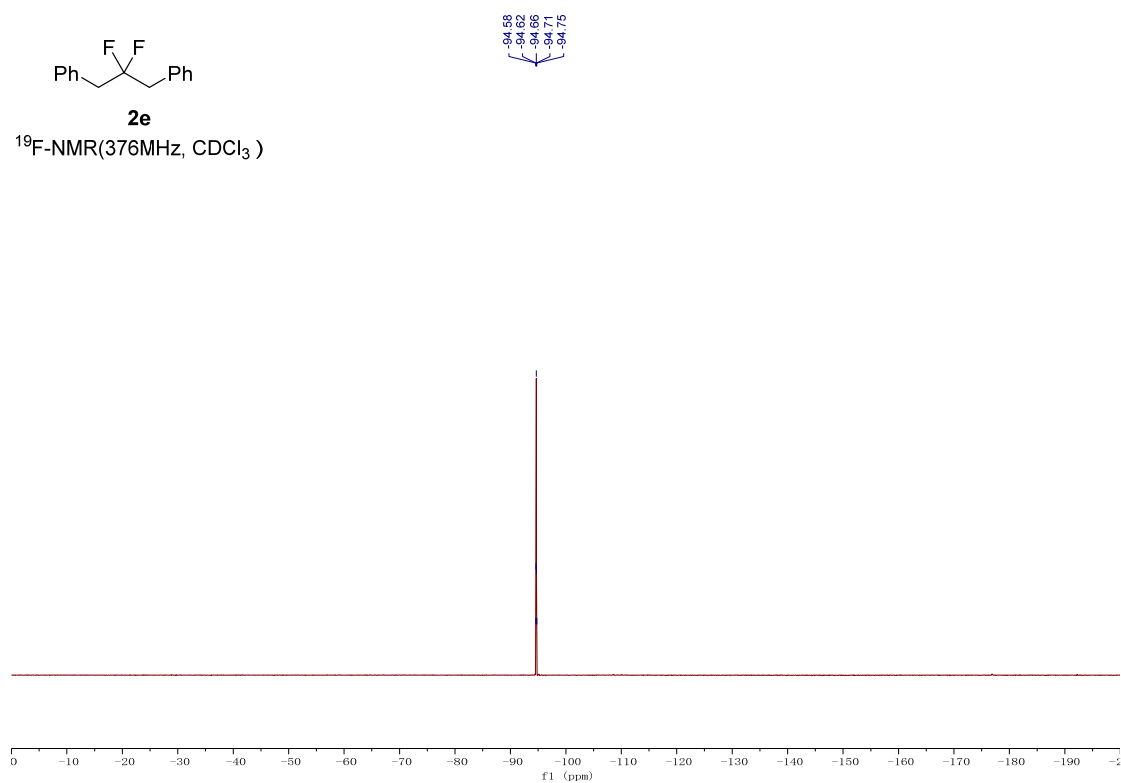
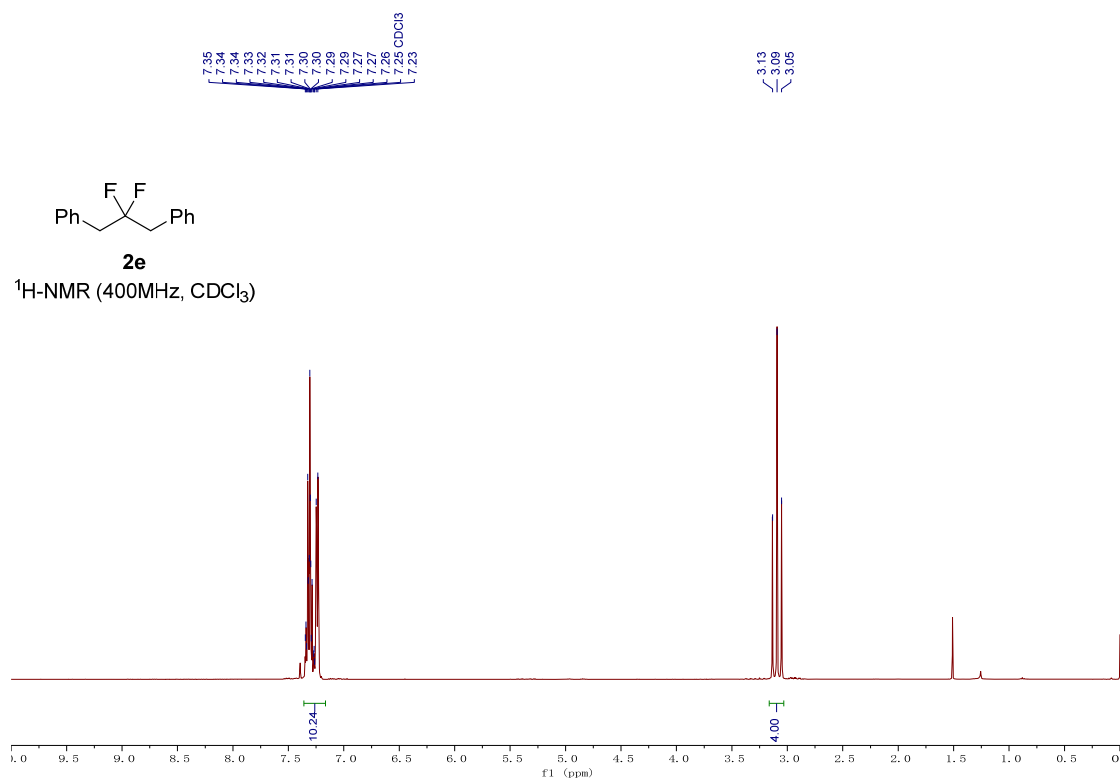


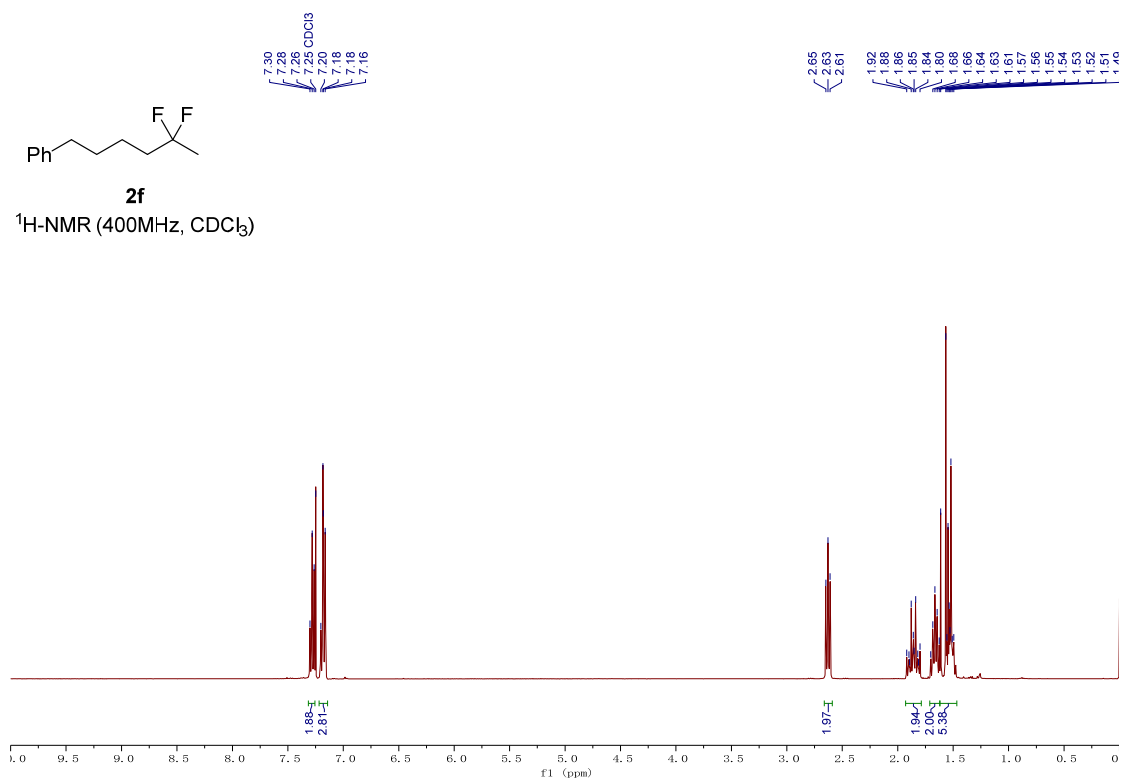
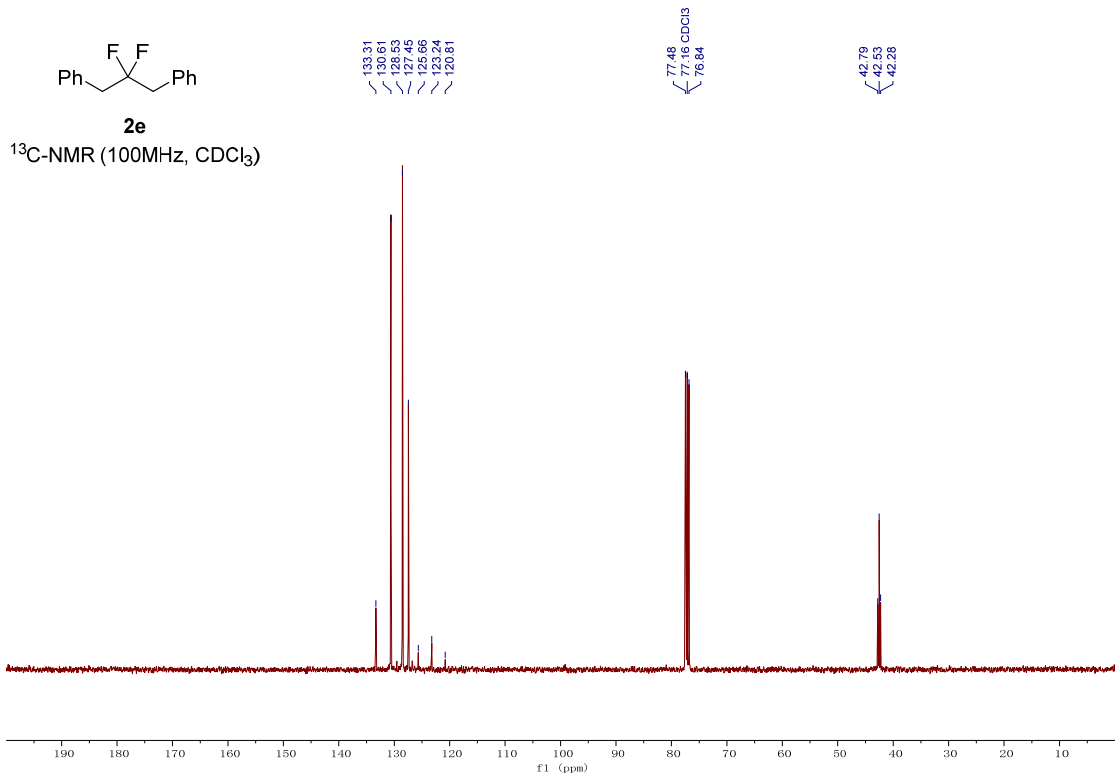
<sup>19</sup>F-NMR(376MHz, CDCl<sub>3</sub>)

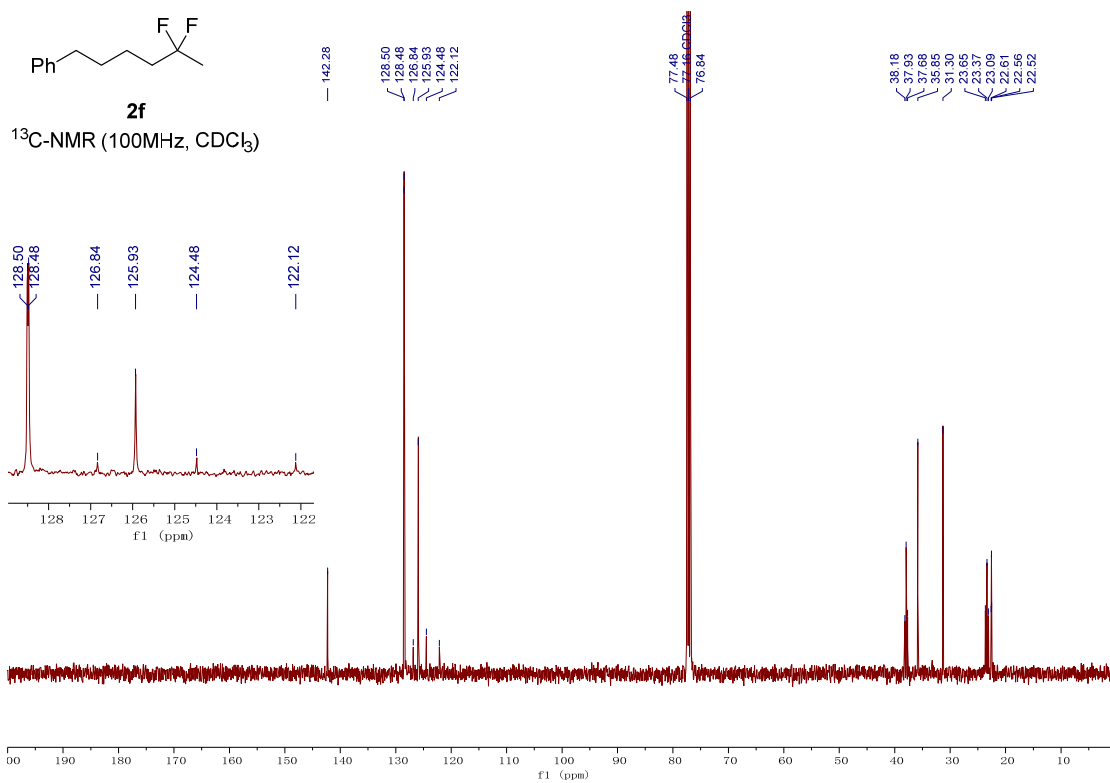
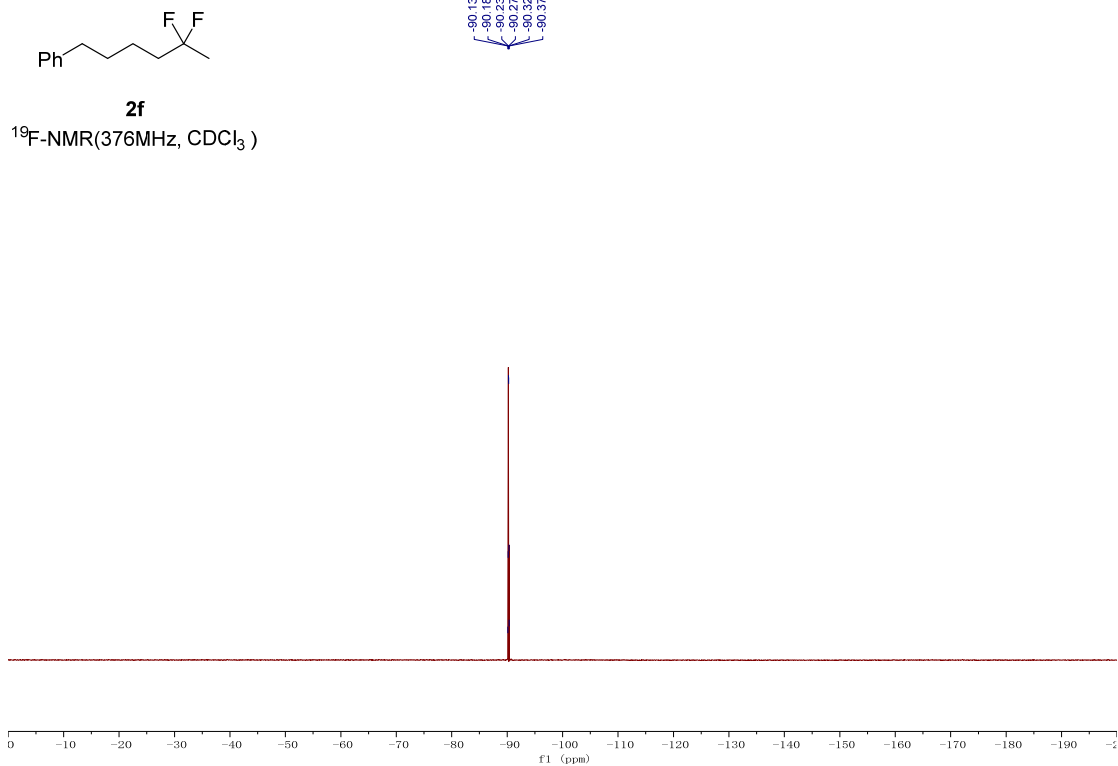


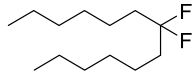
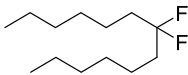
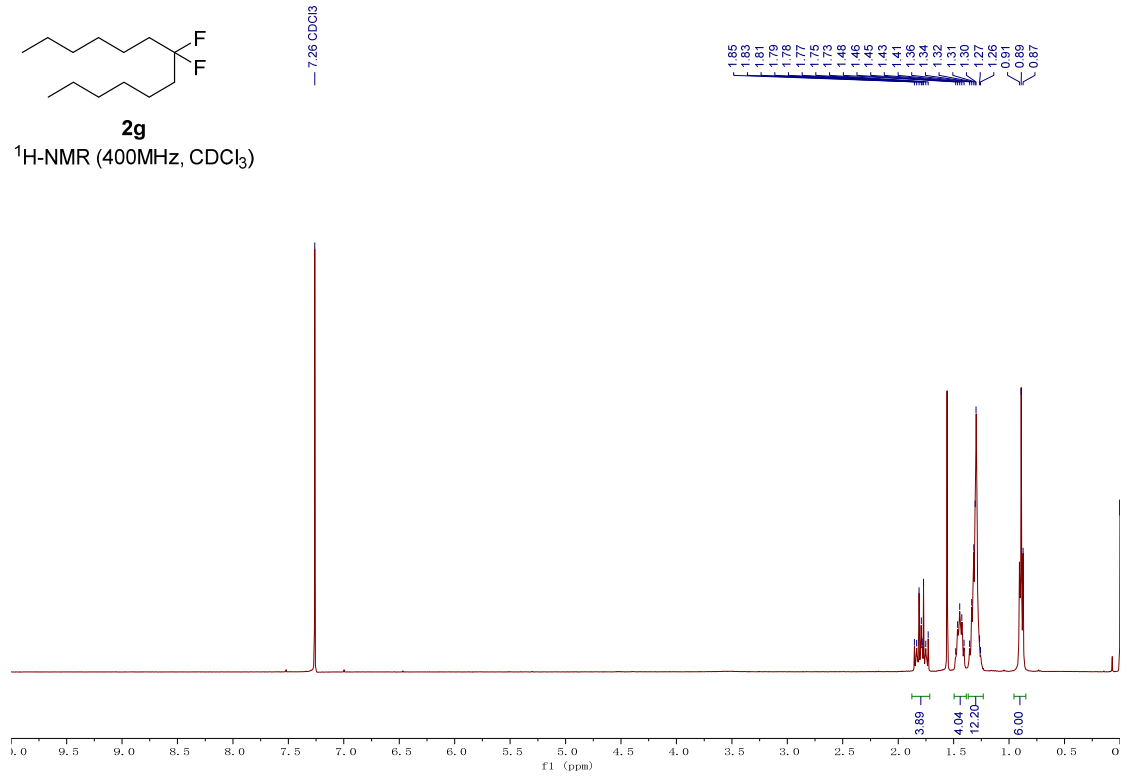
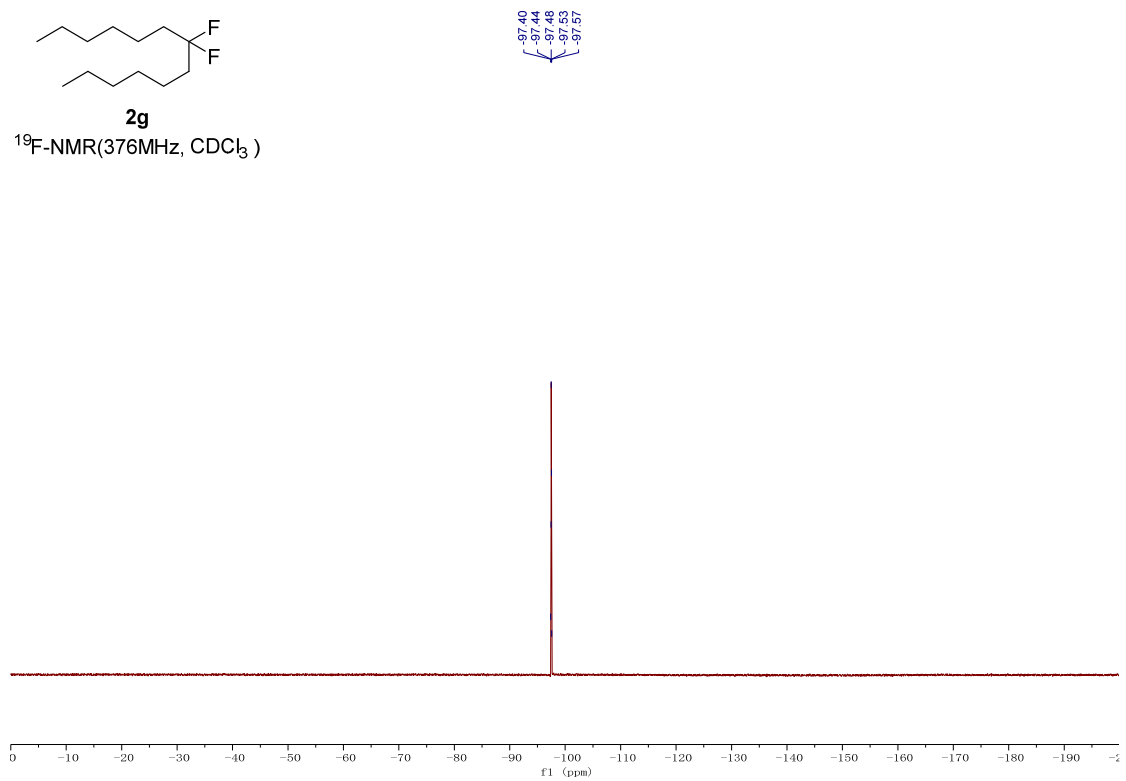




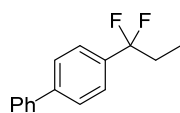
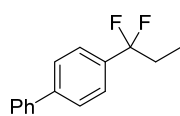
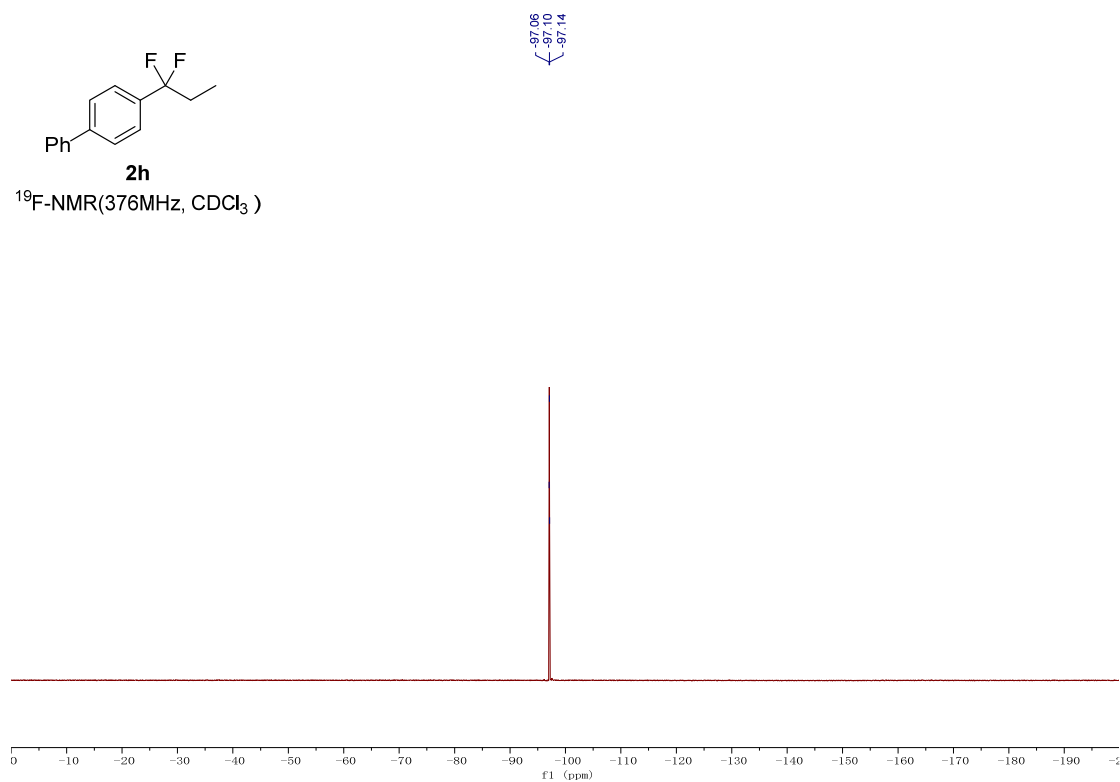
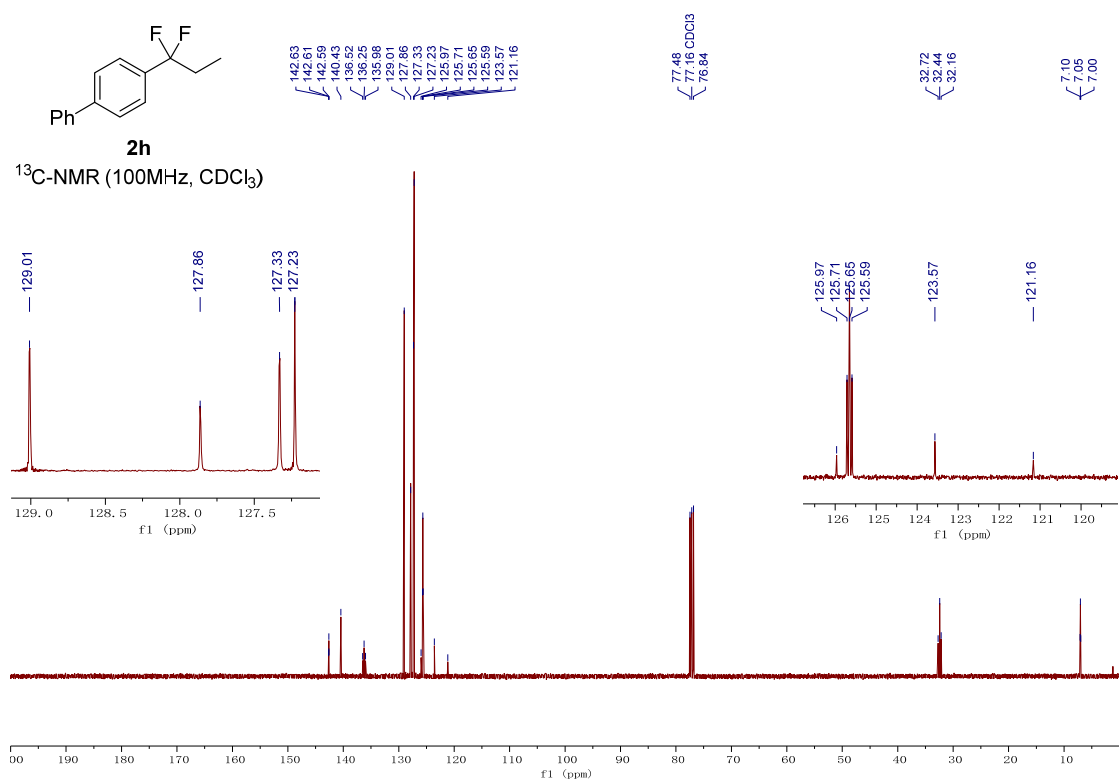


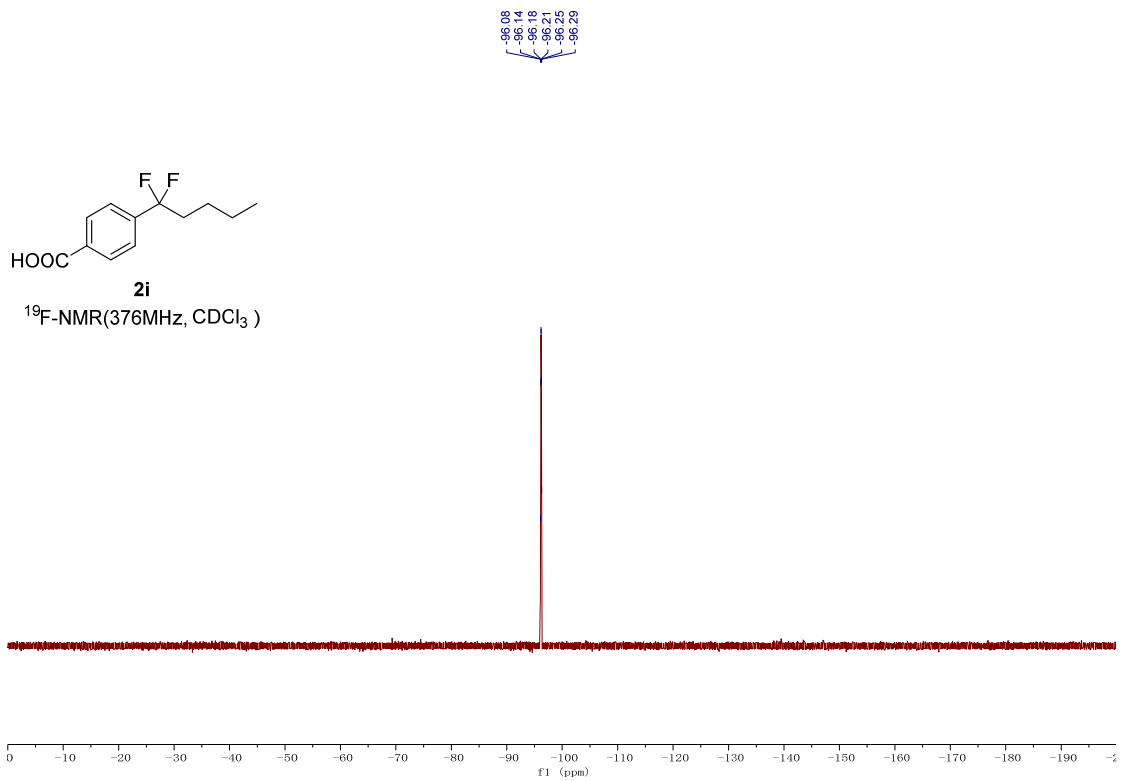
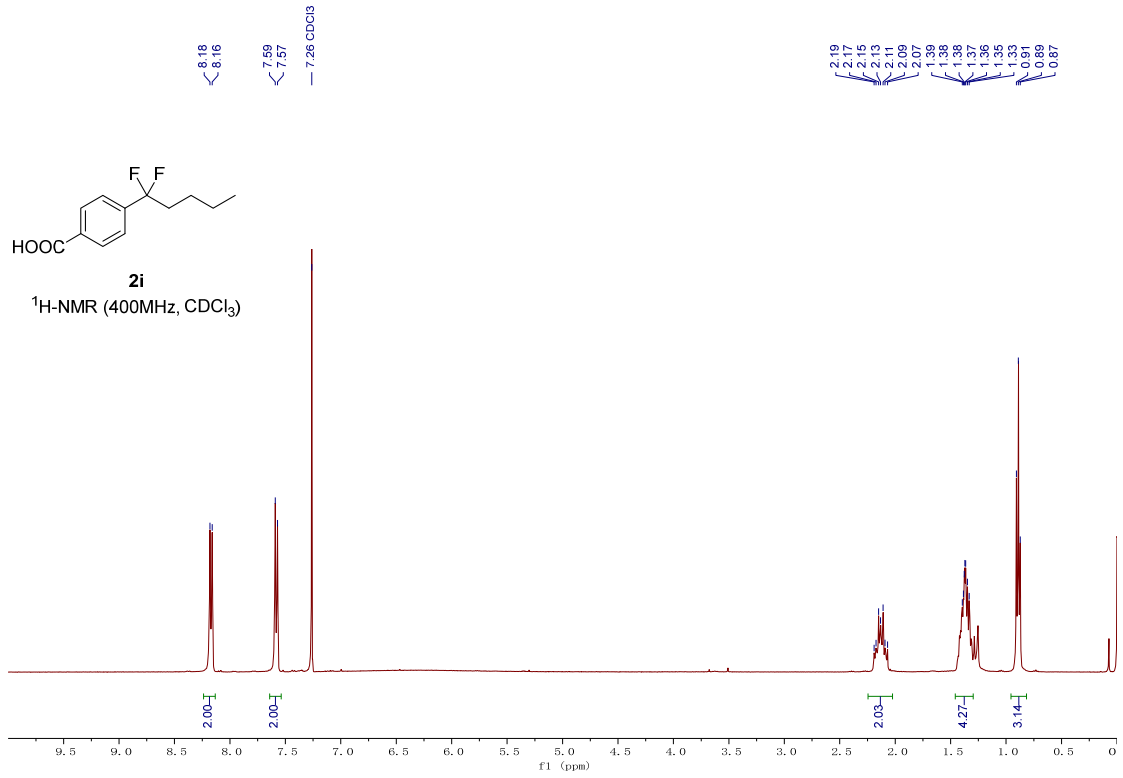




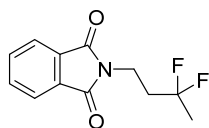
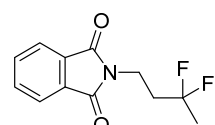
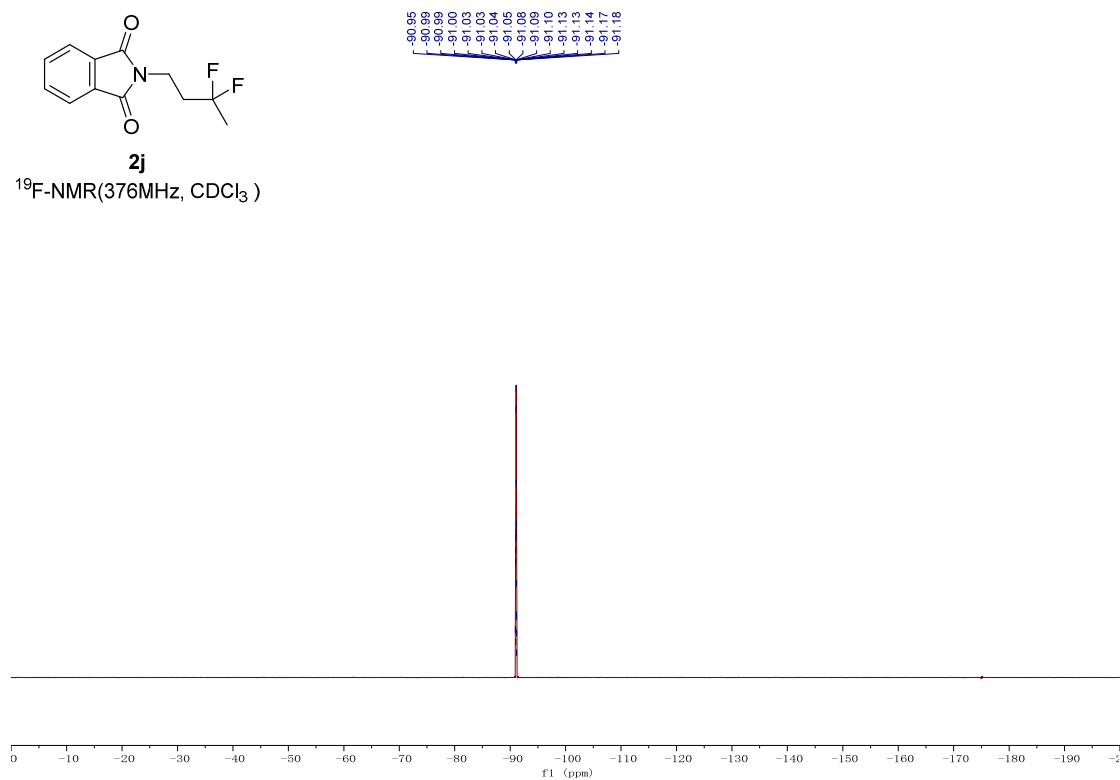
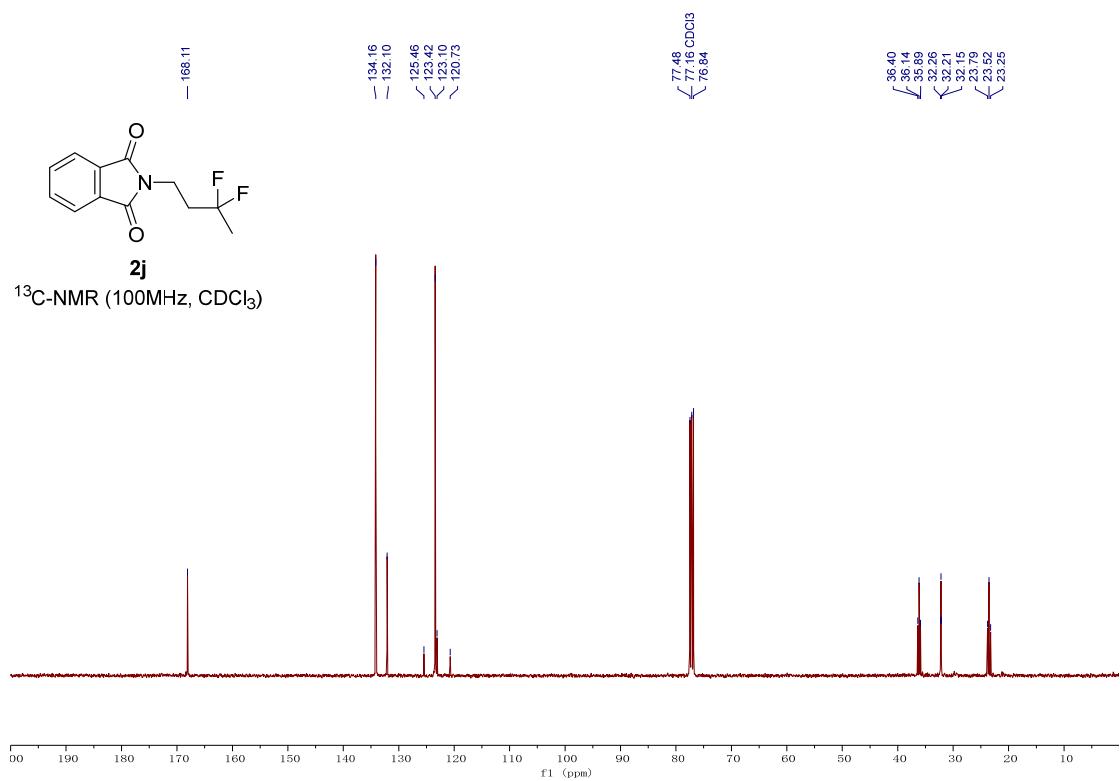
**2g** $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ )**2g** $^{19}\text{F-NMR}$  (376MHz,  $\text{CDCl}_3$ )

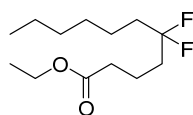
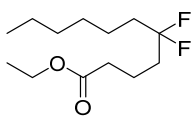
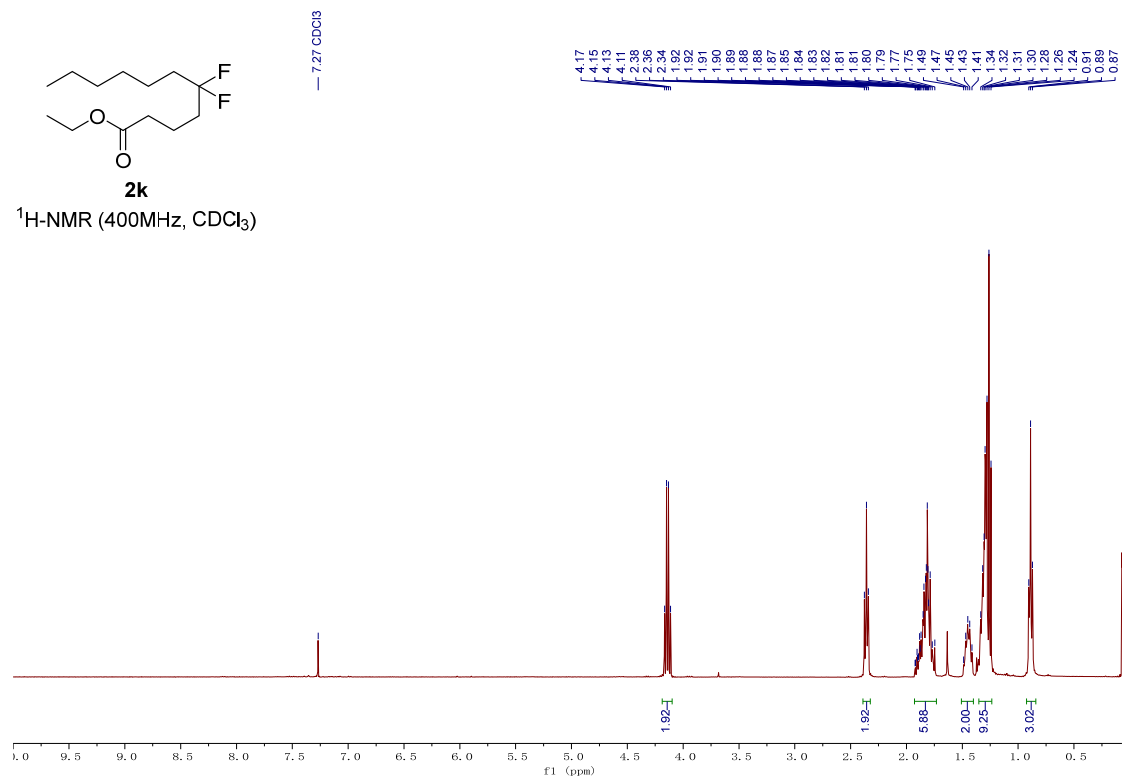
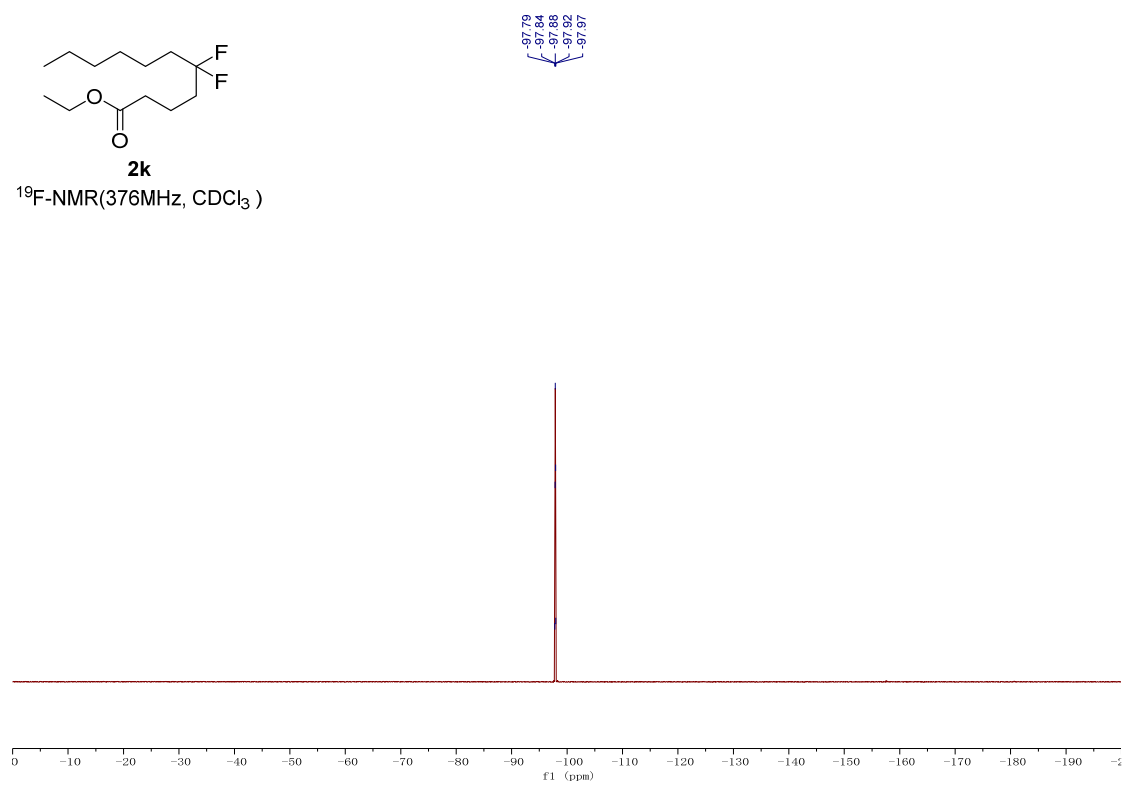


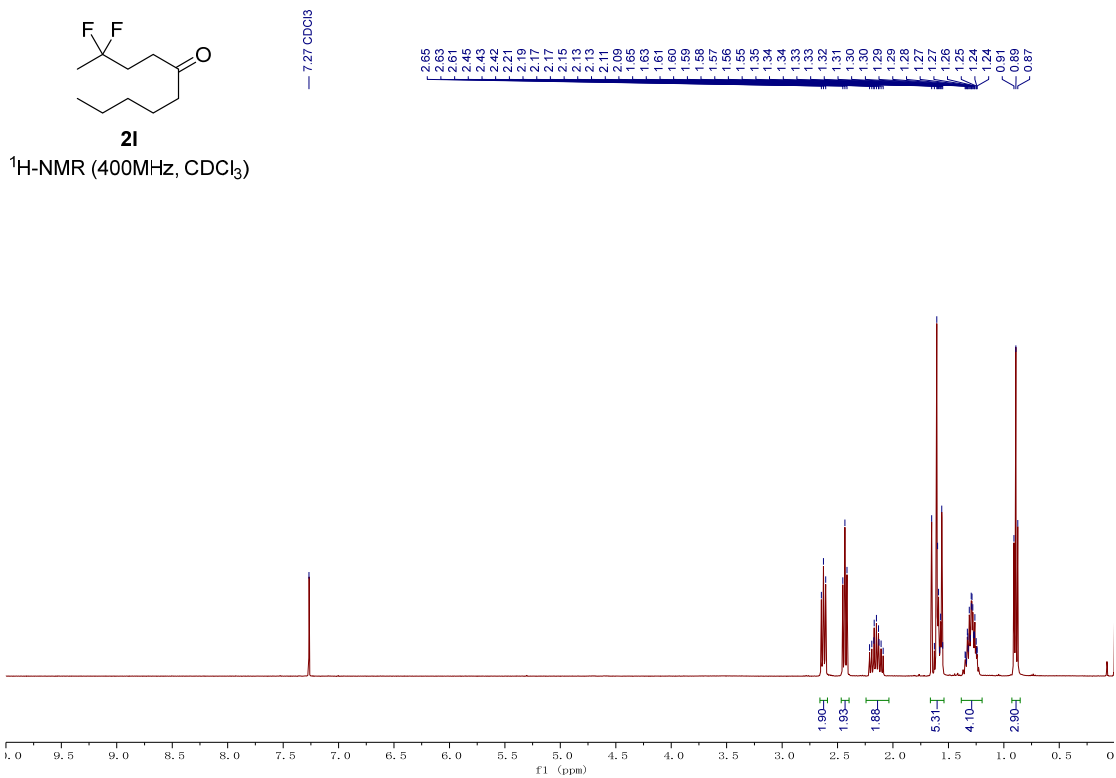
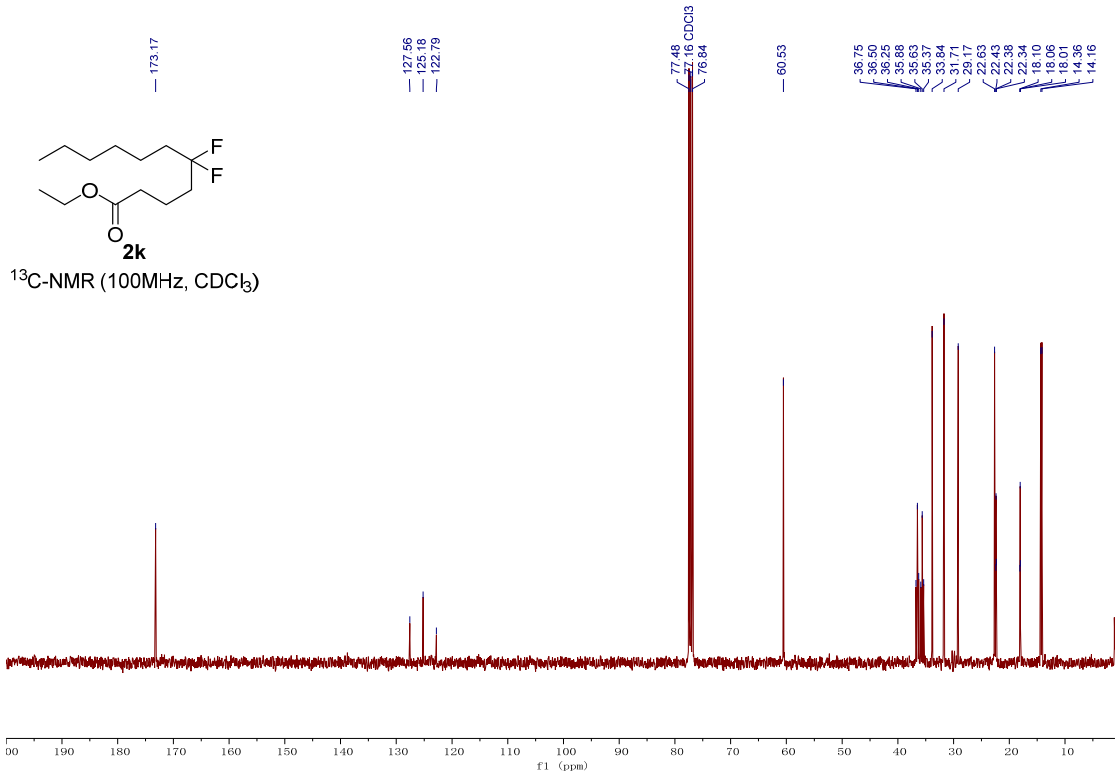
**2h** $^{19}\text{F}$ -NMR(376MHz,  $\text{CDCl}_3$ )**2h** $^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

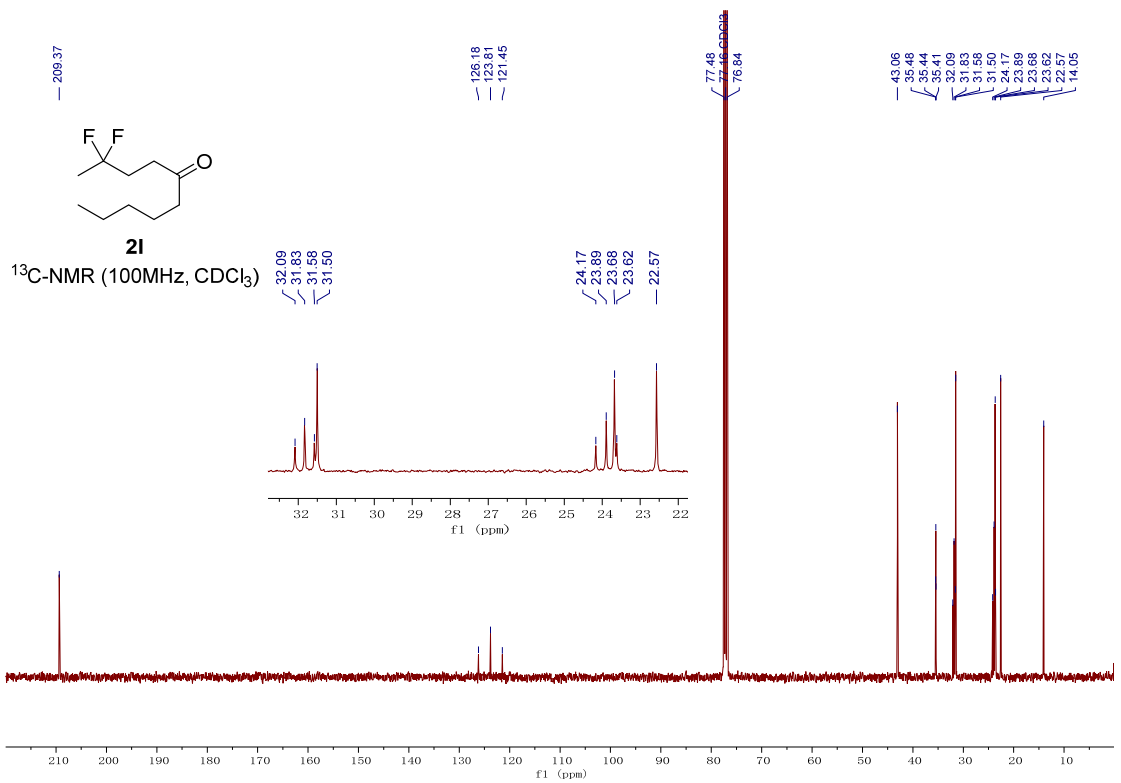
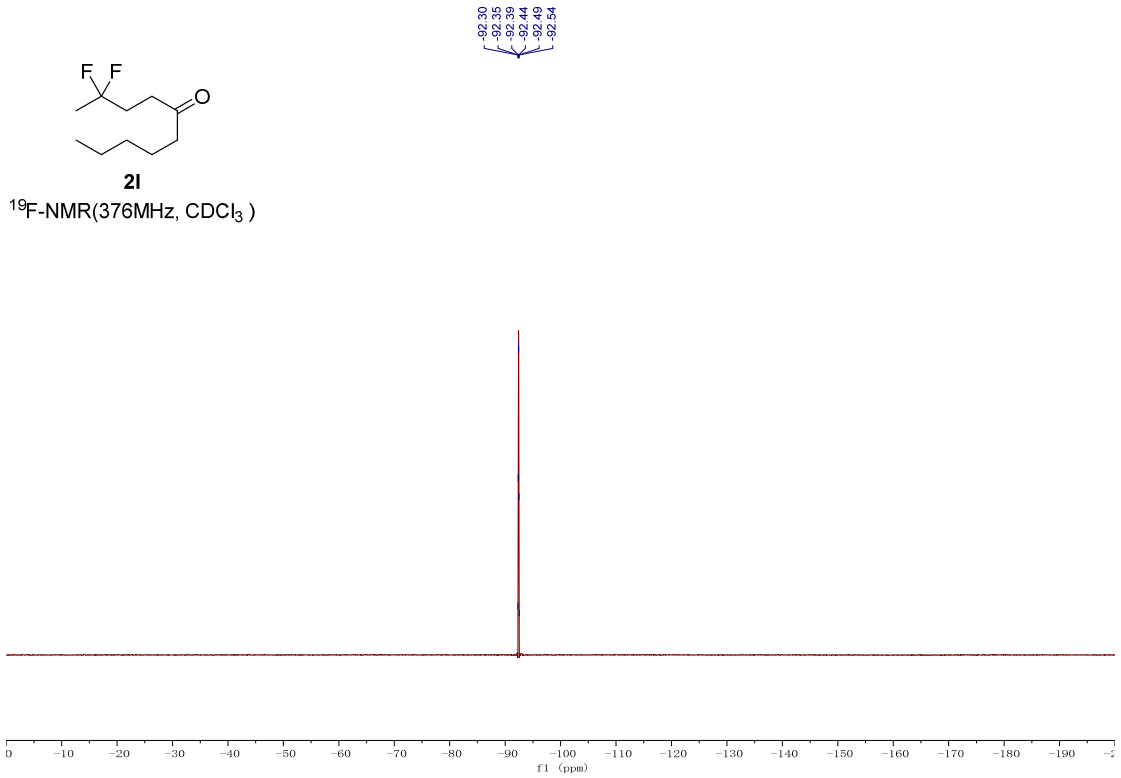


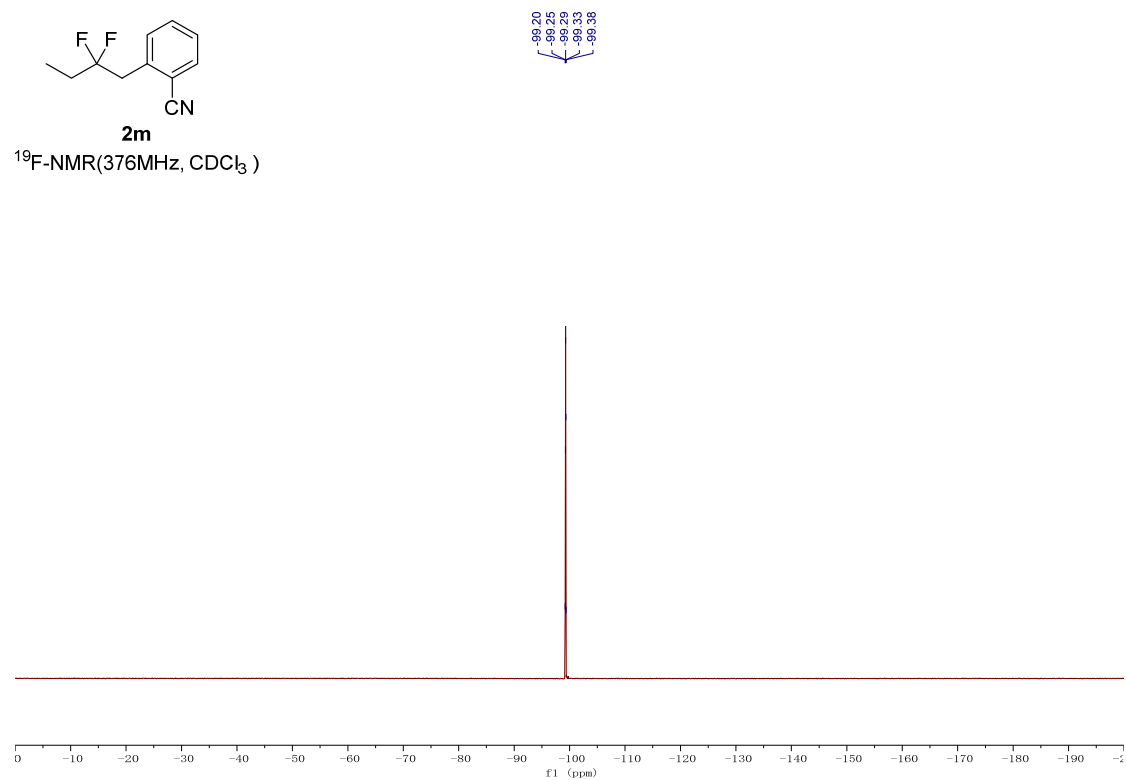
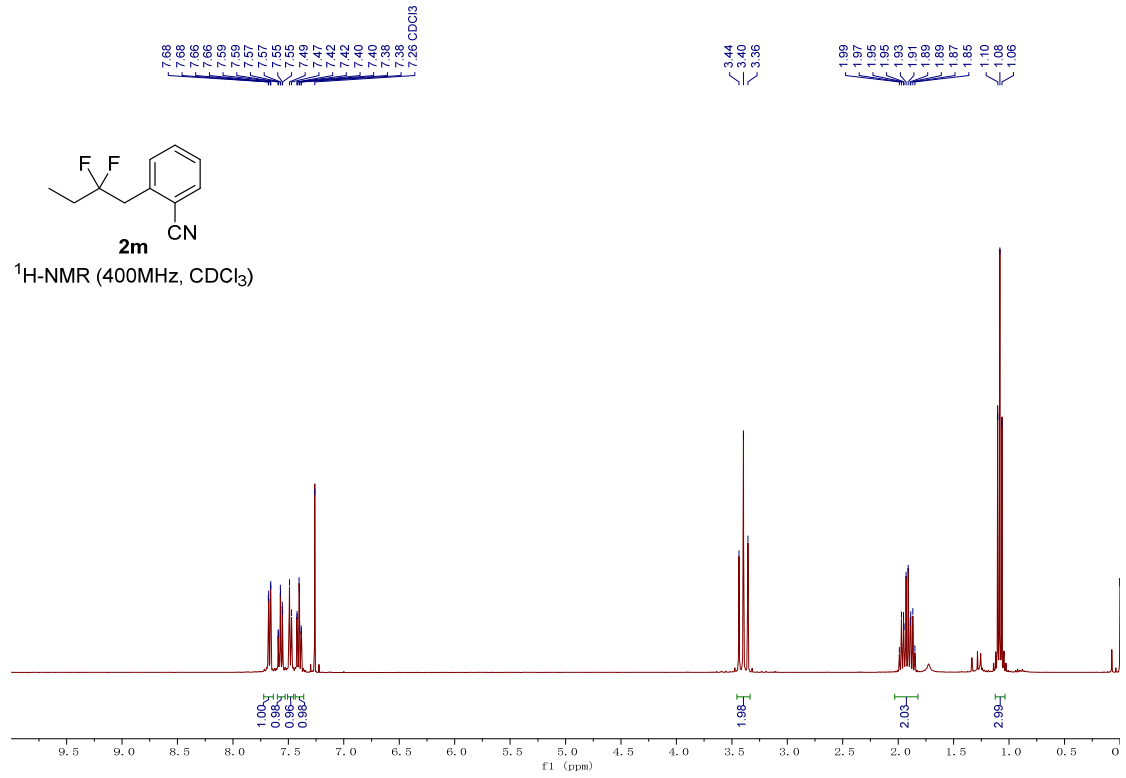


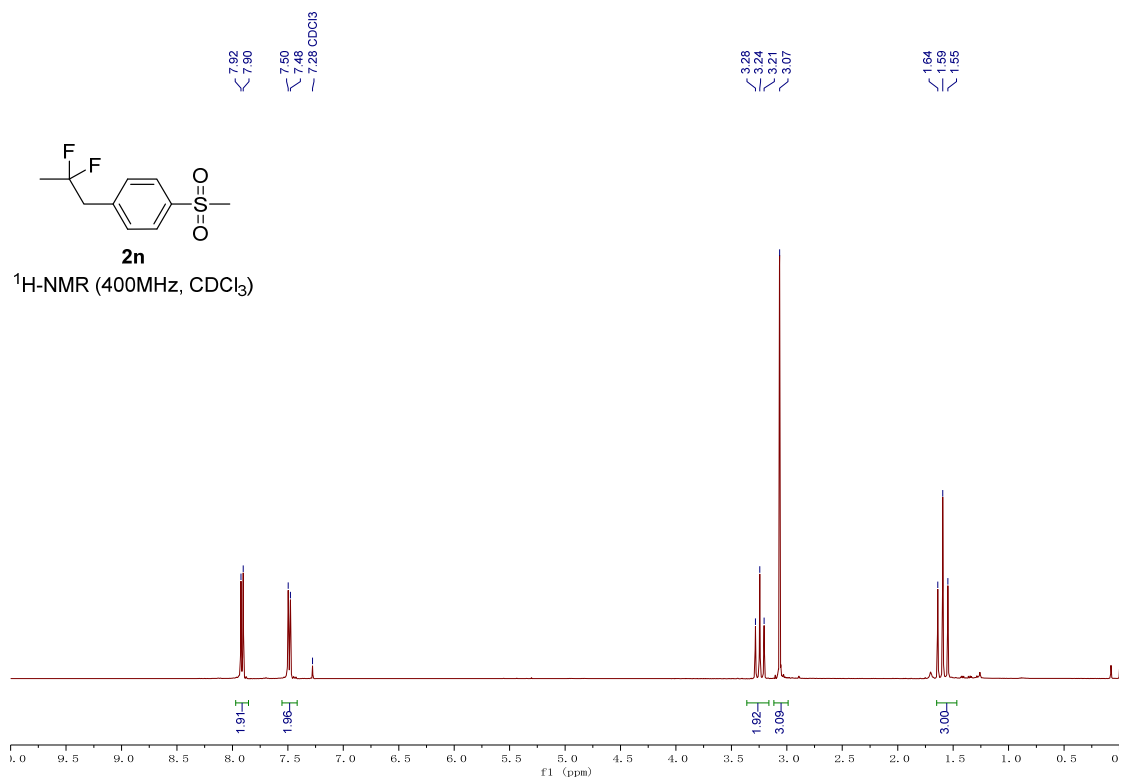
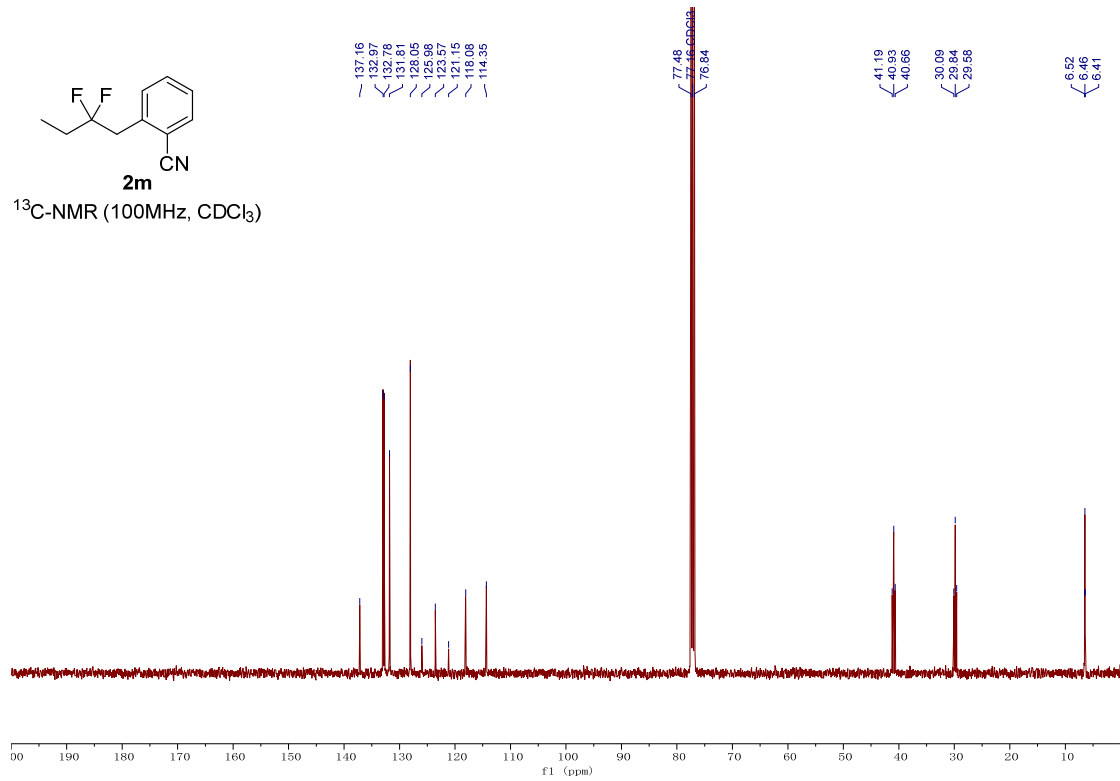
**2j** $^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )**2j** $^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

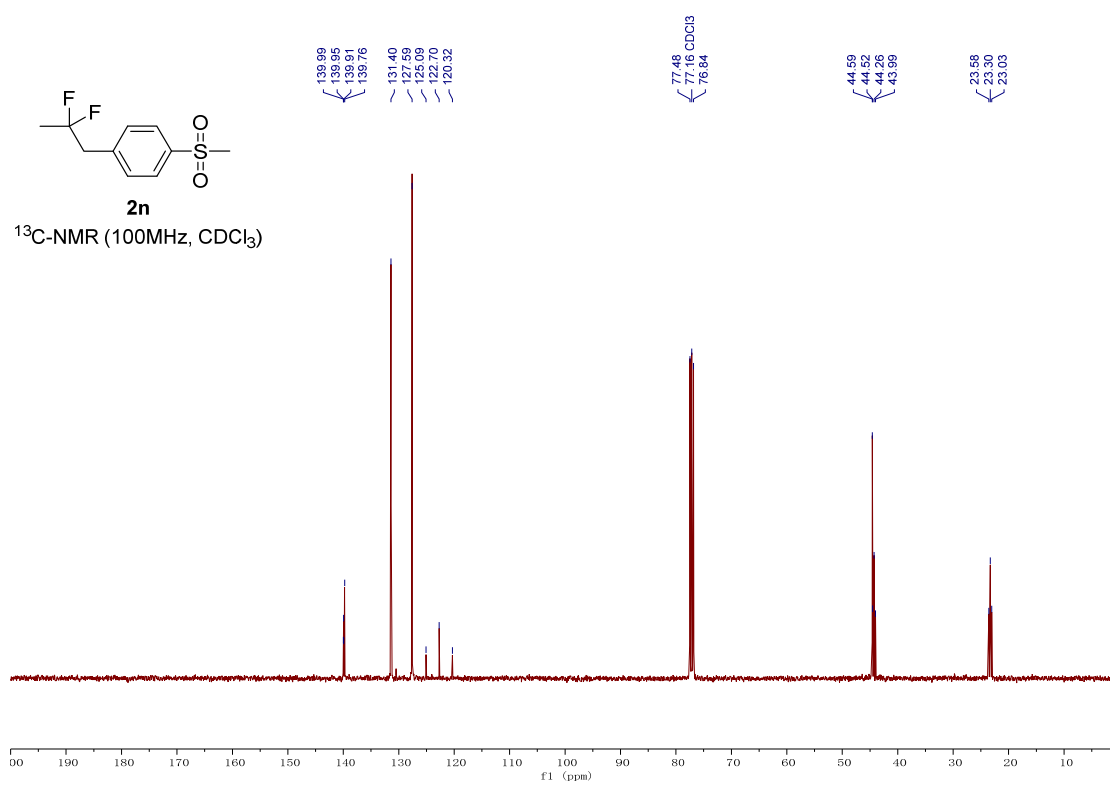
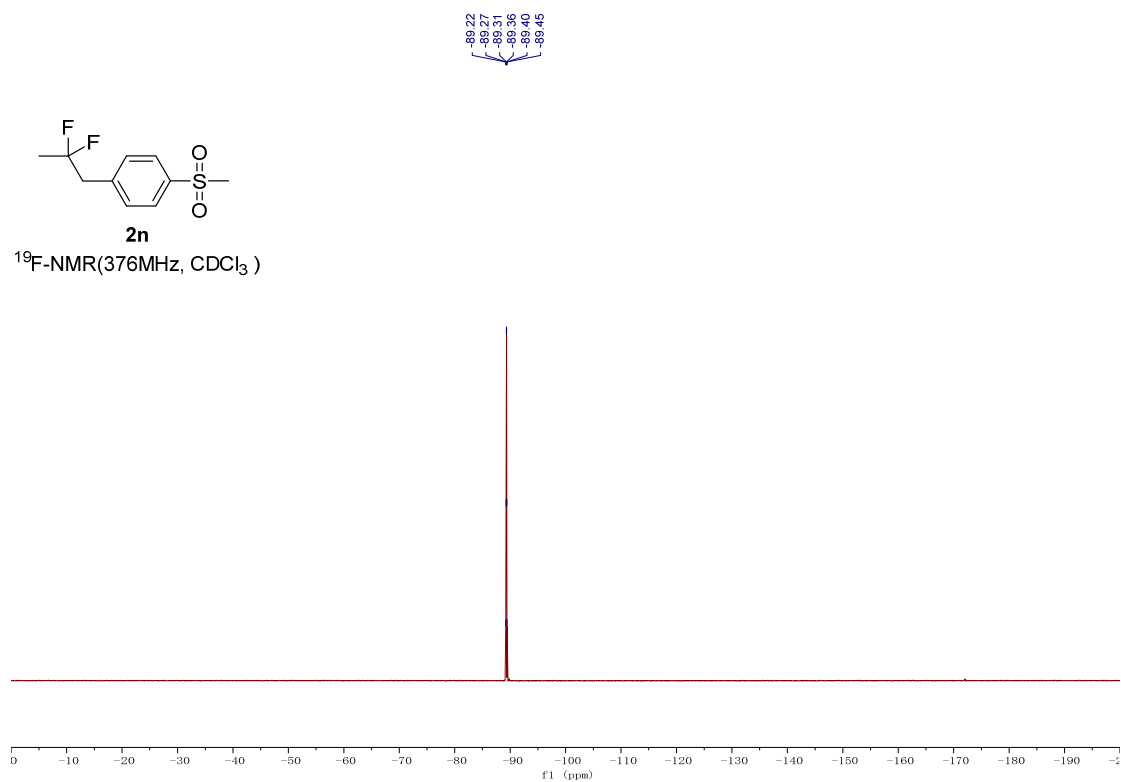
**2k** $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ )**2k** $^{19}\text{F-NMR}$  (376MHz,  $\text{CDCl}_3$ )

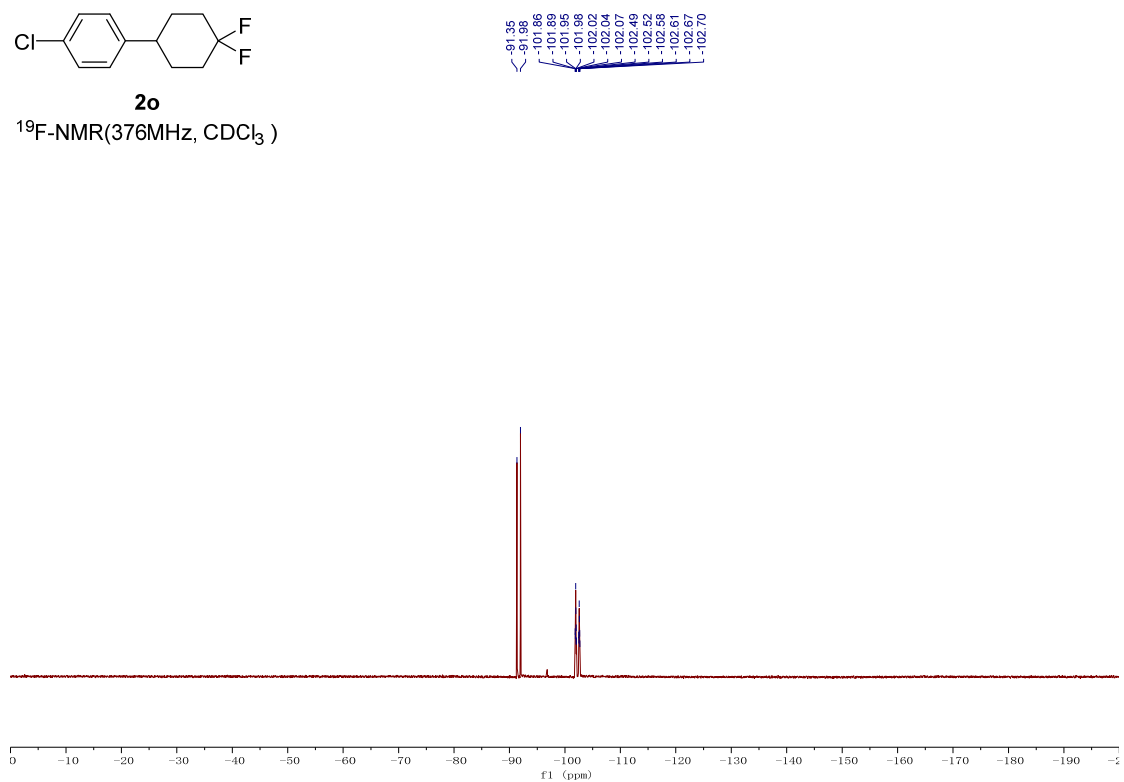
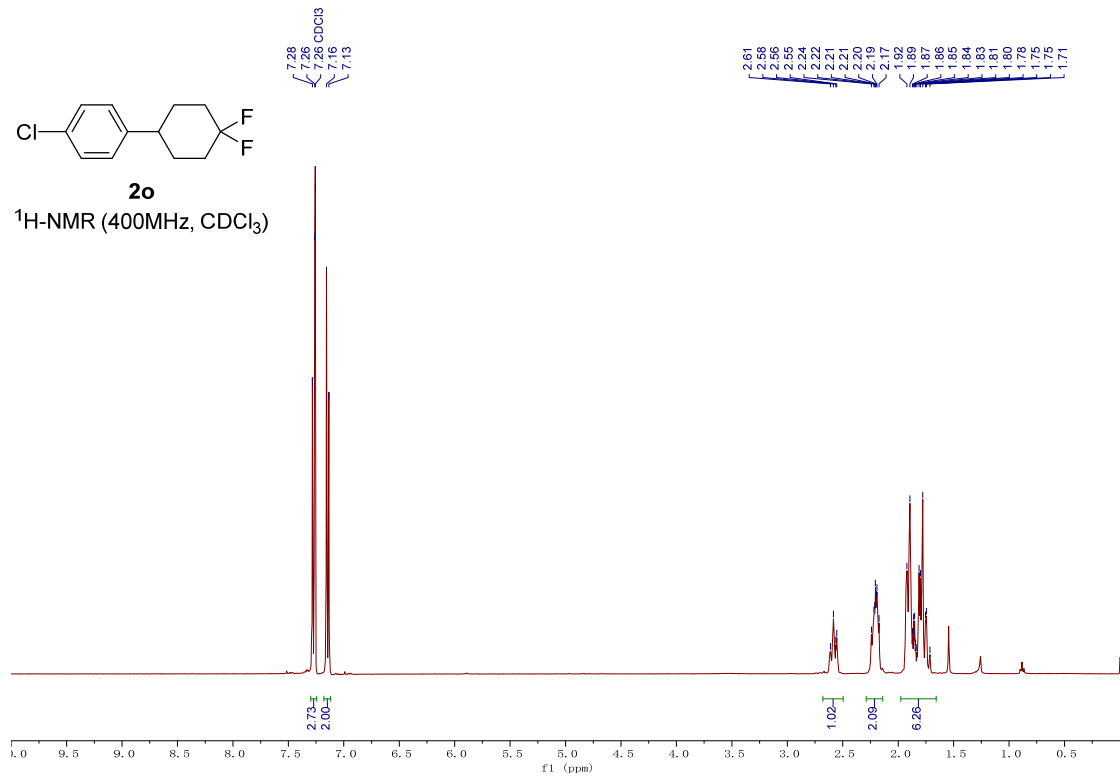


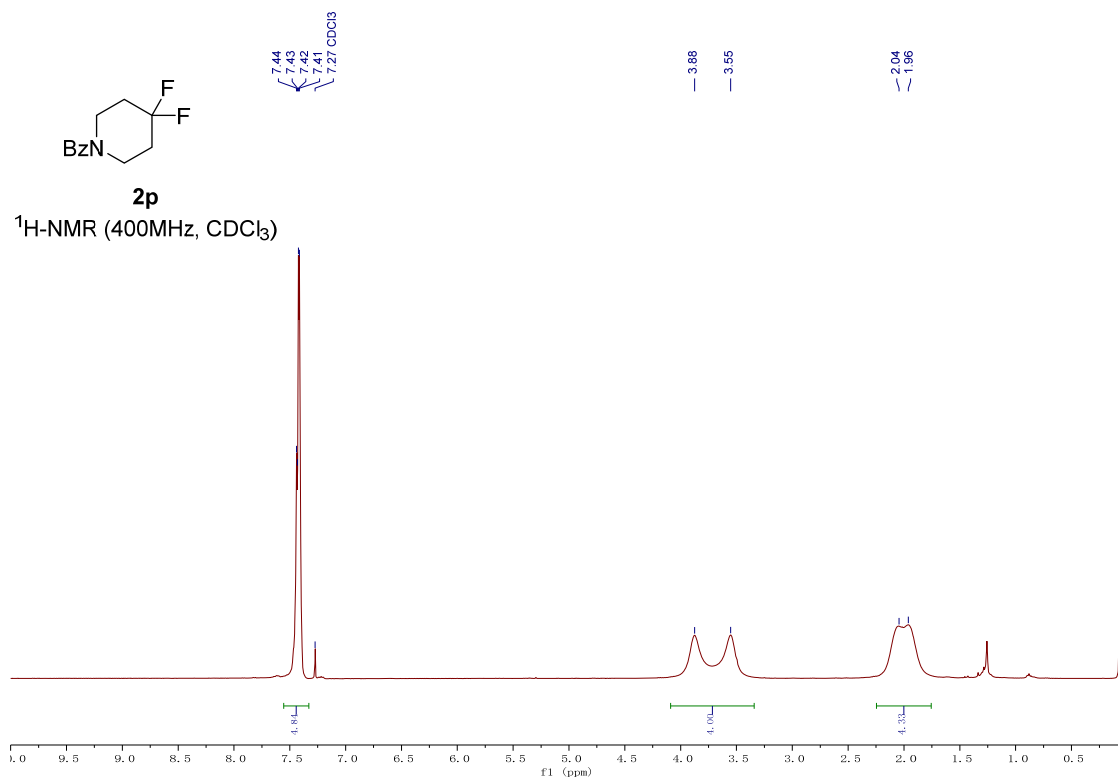
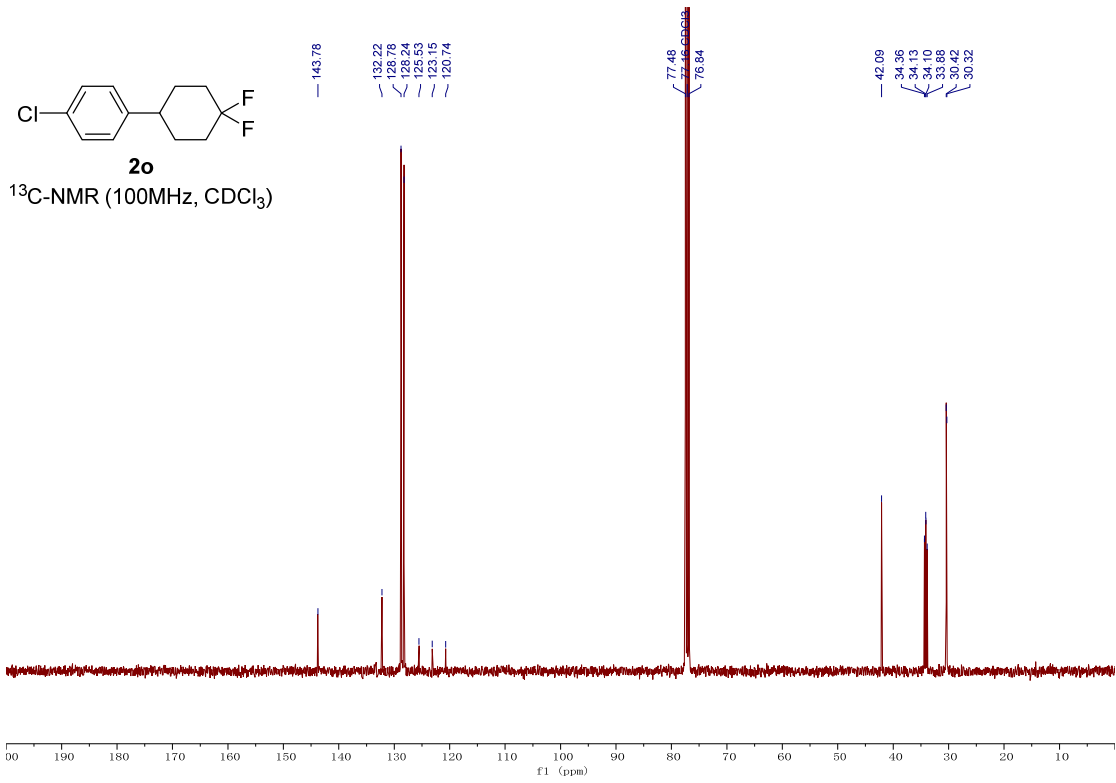


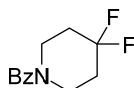
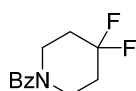
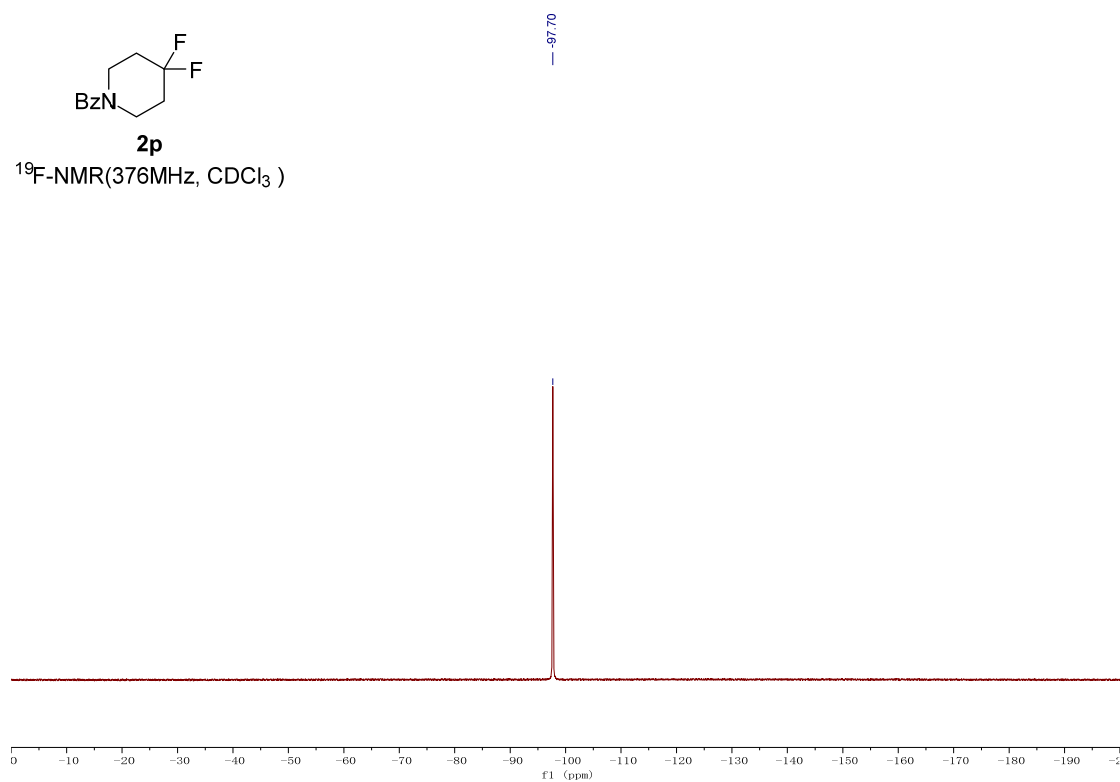
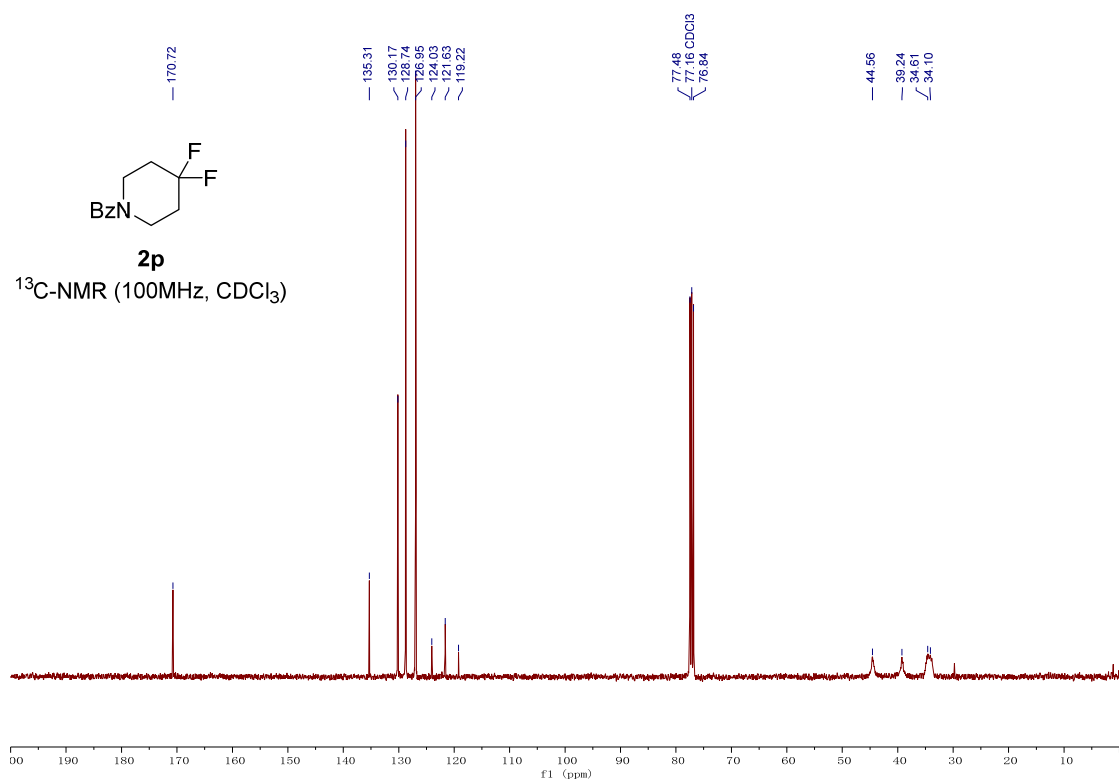


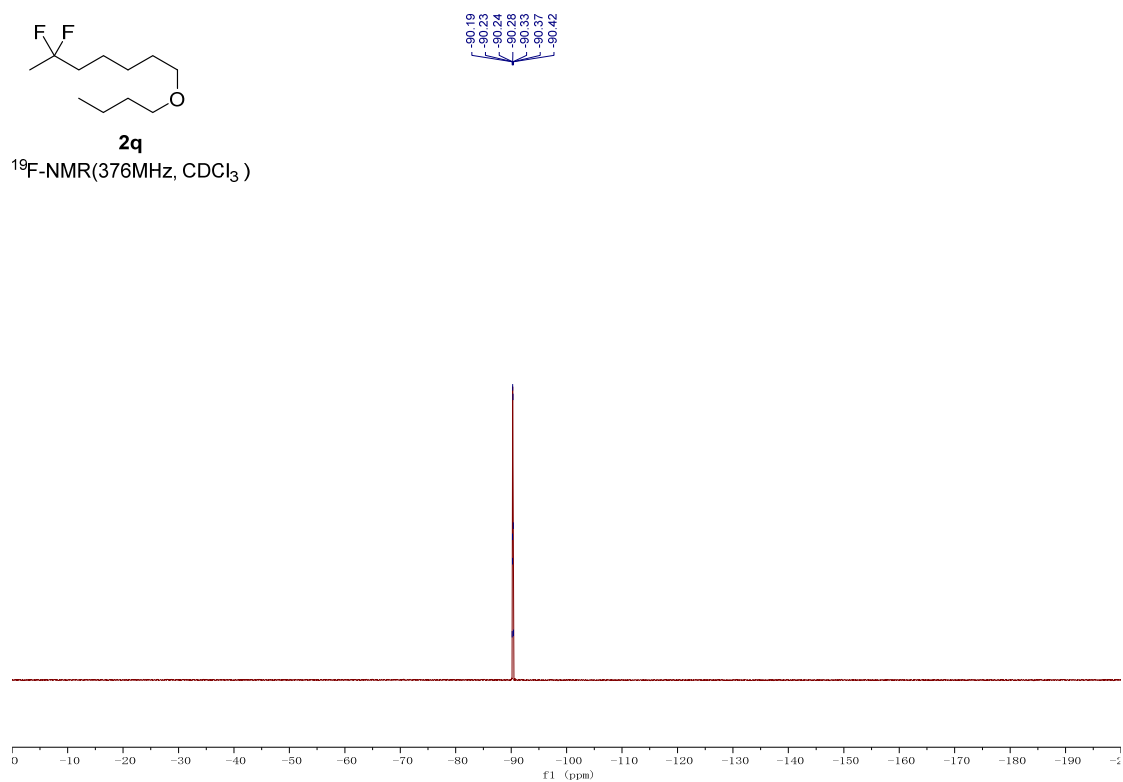
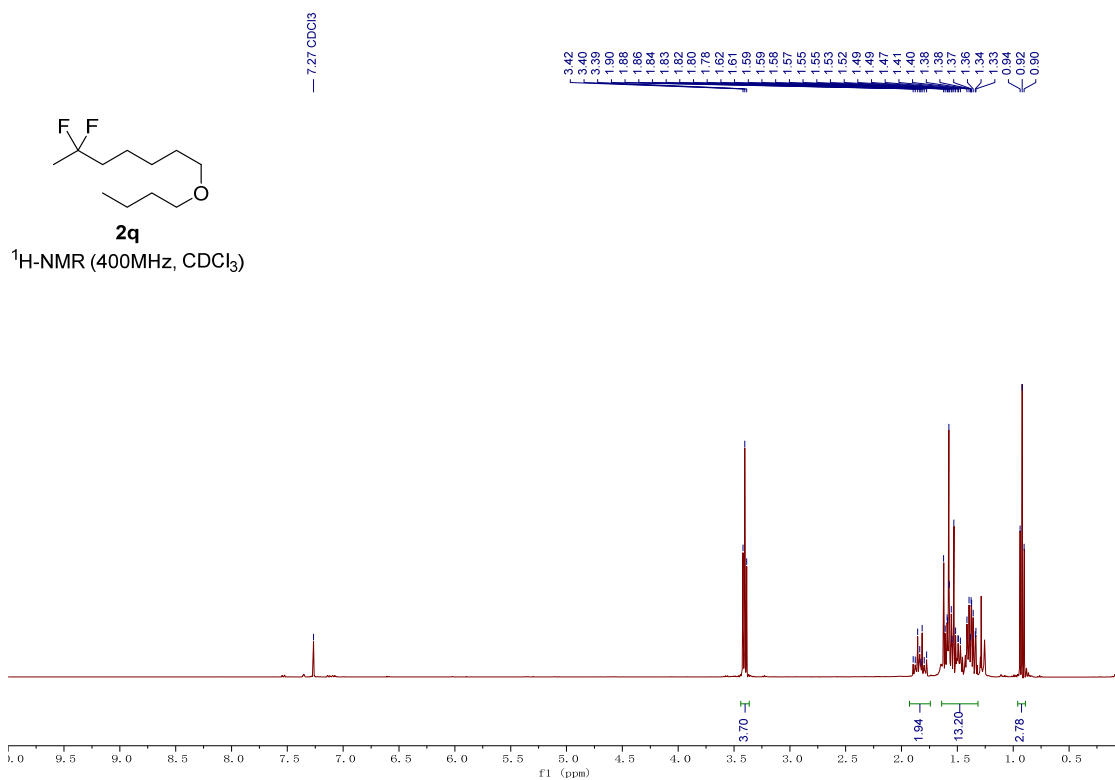


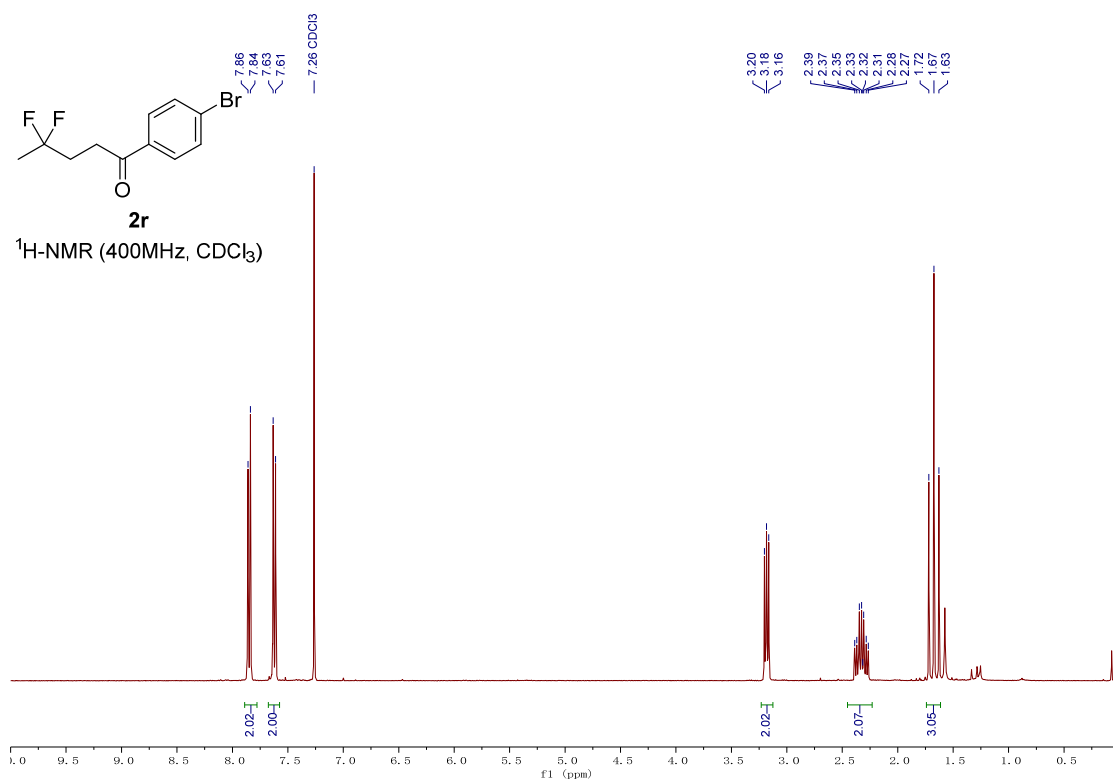
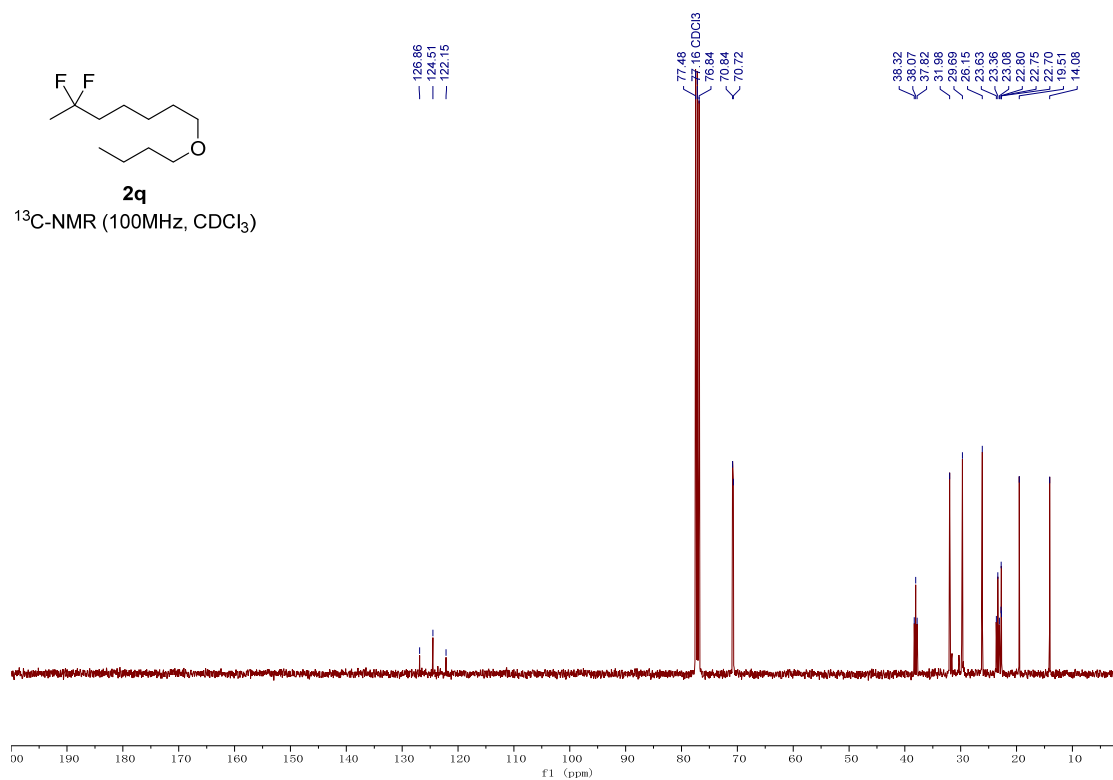


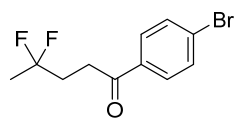
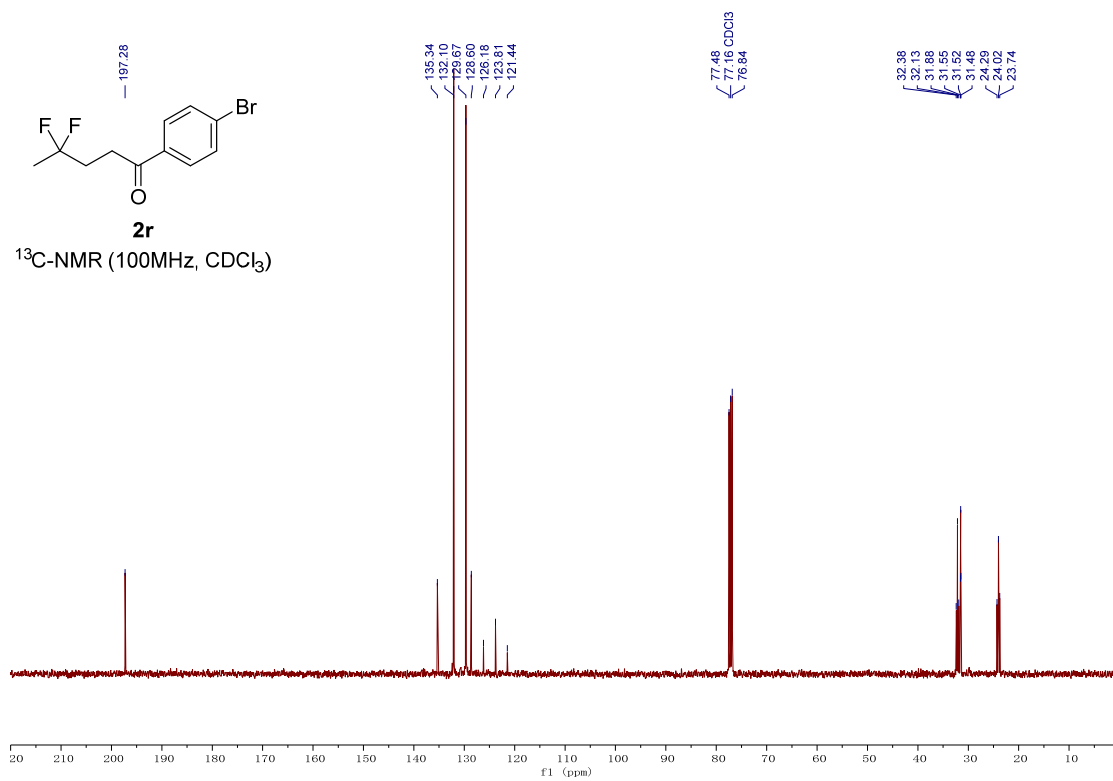
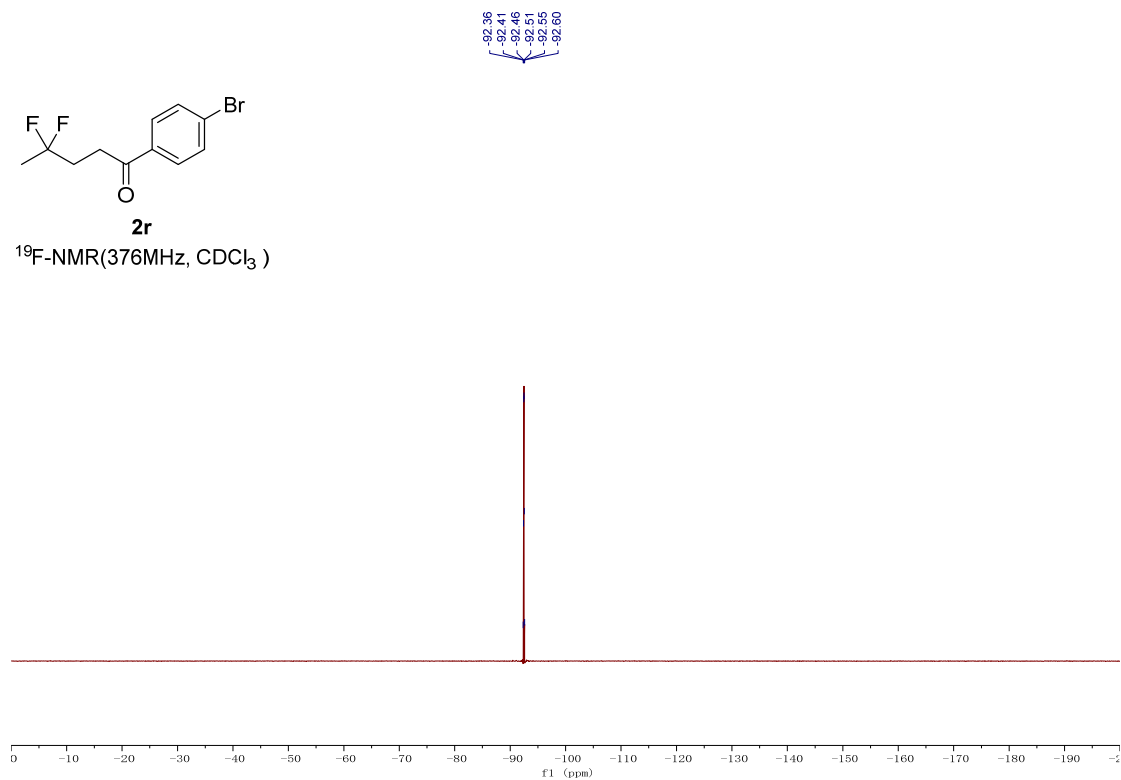


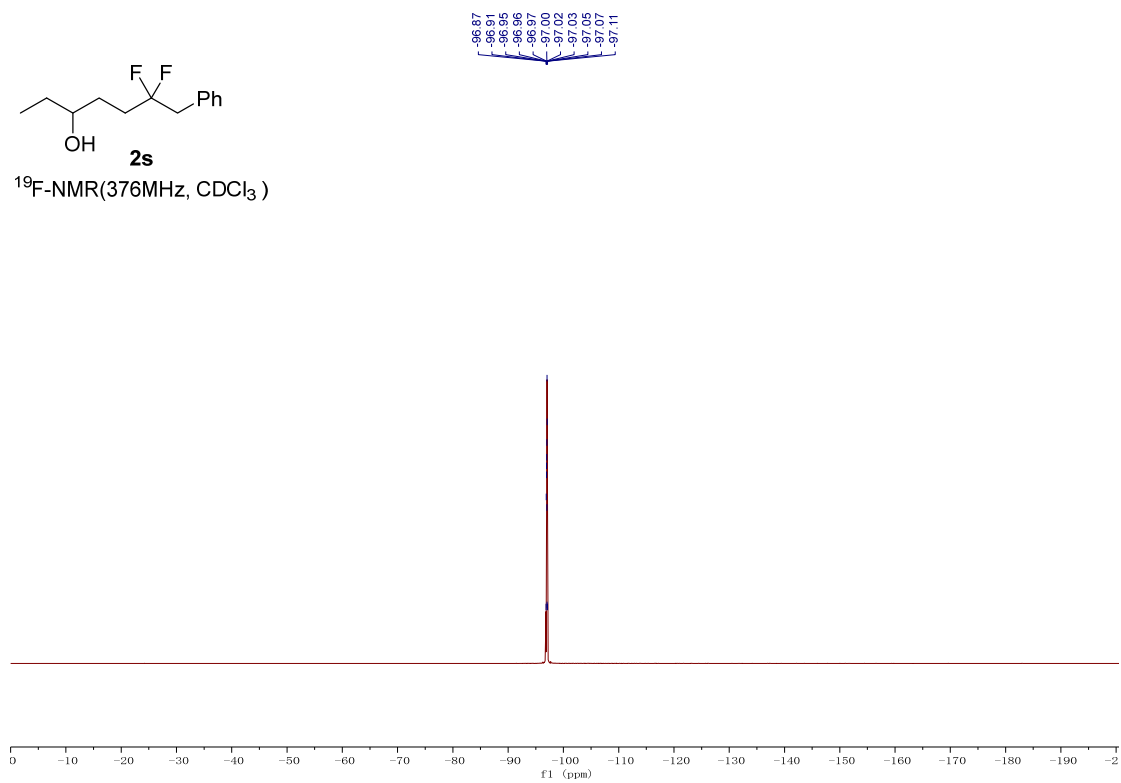
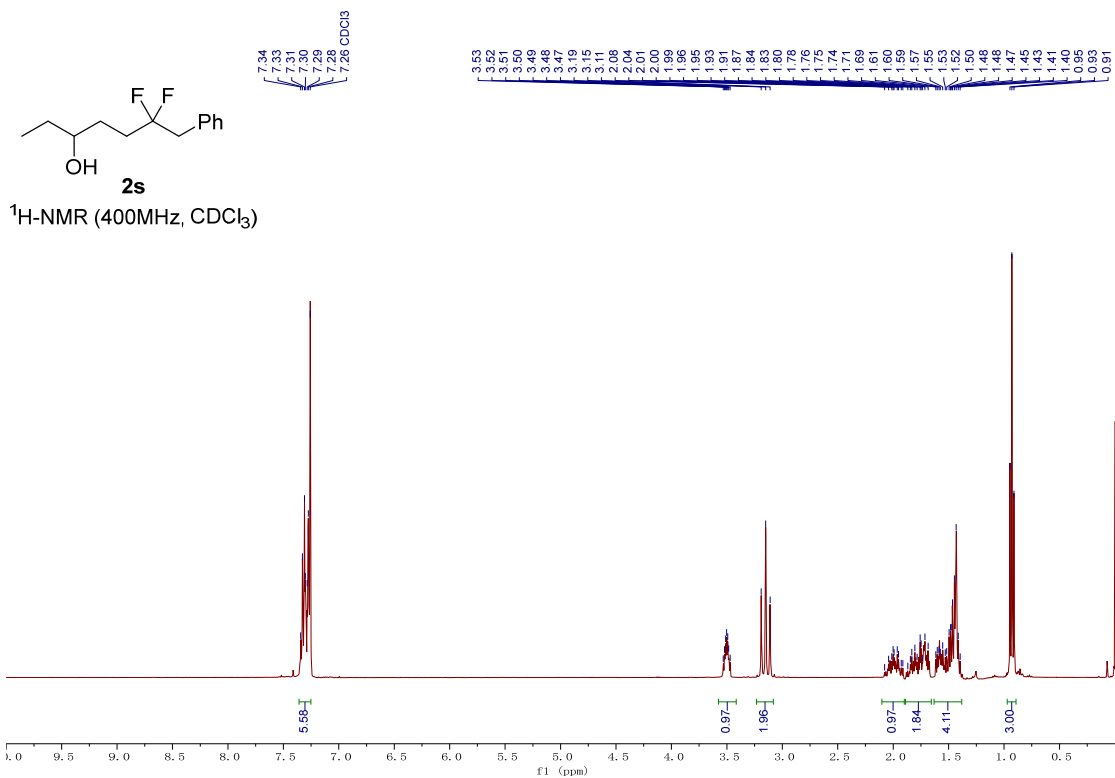


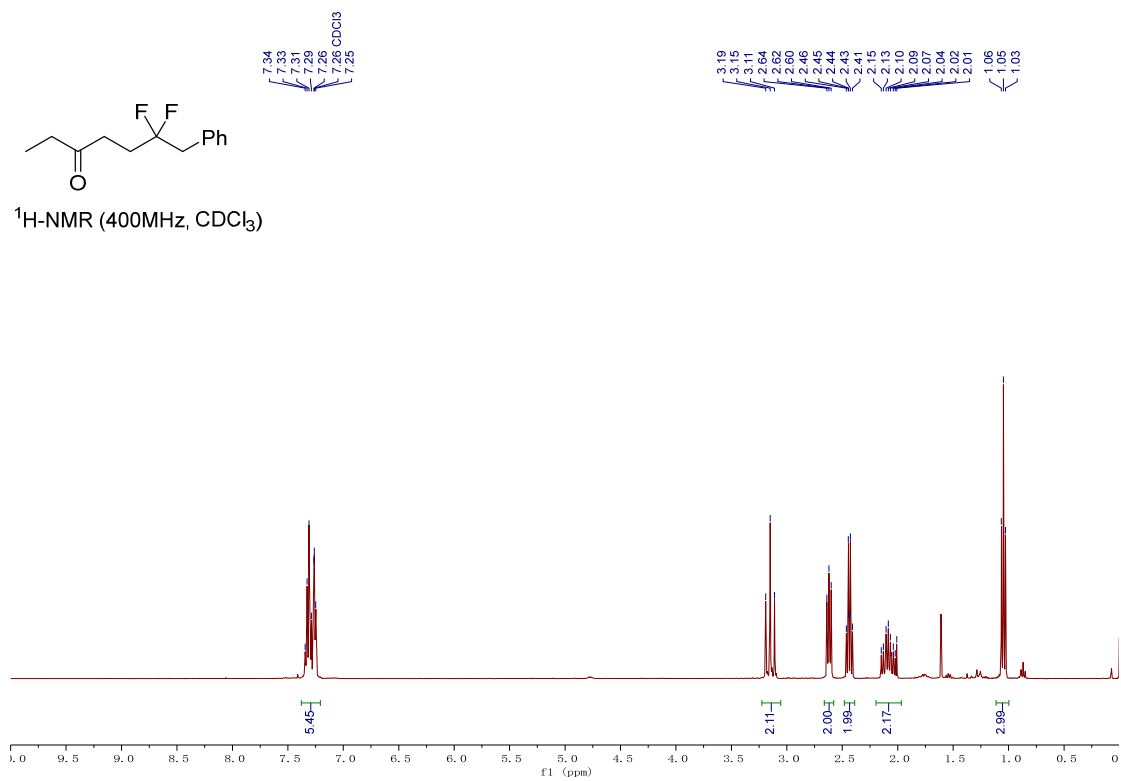
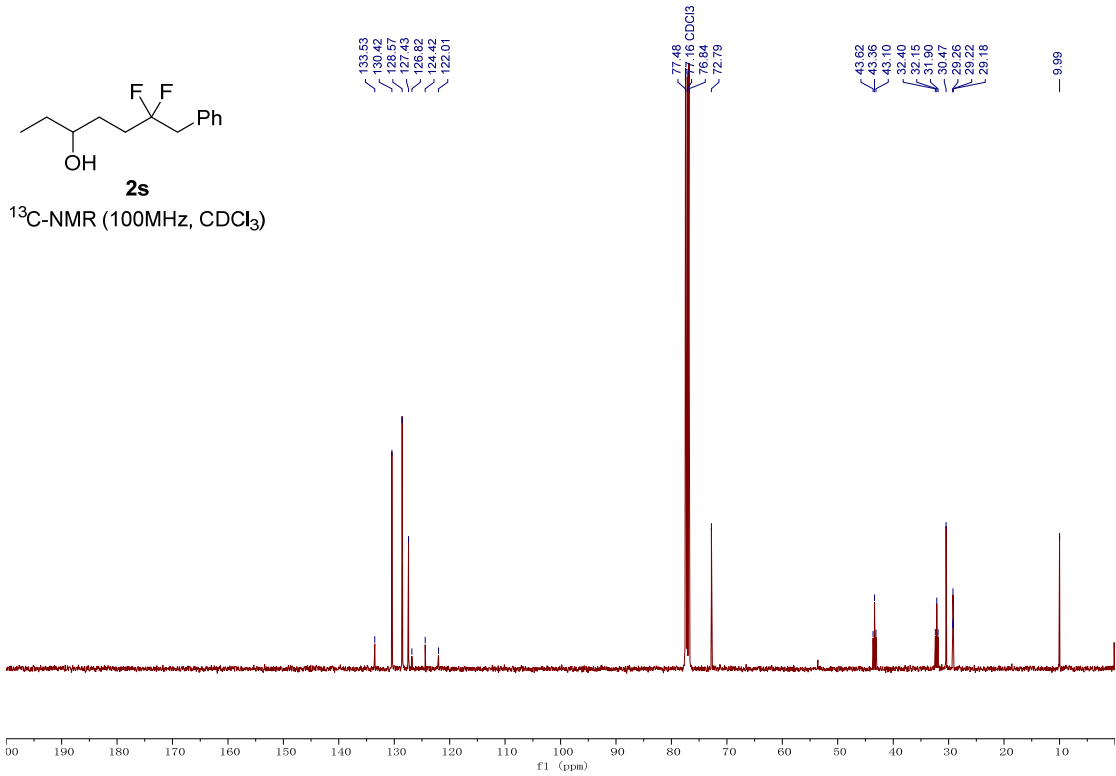
**2p**<sup>19</sup>F-NMR(376MHz, CDCl<sub>3</sub>)**2p**<sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)

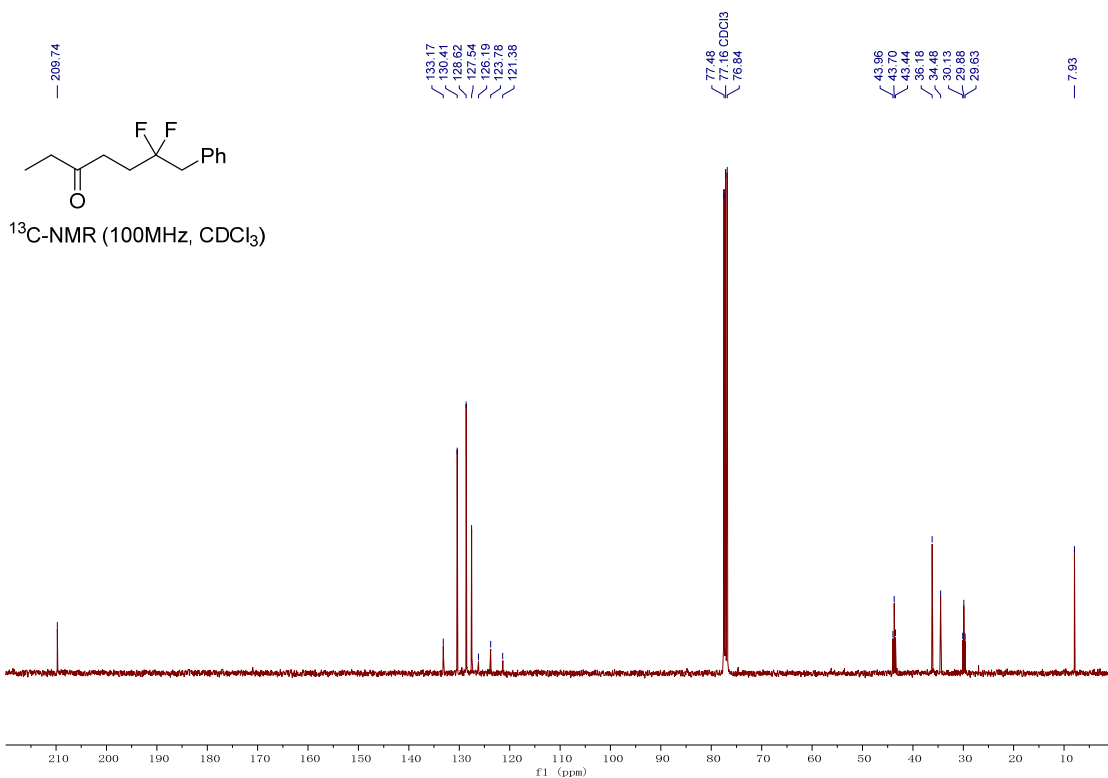
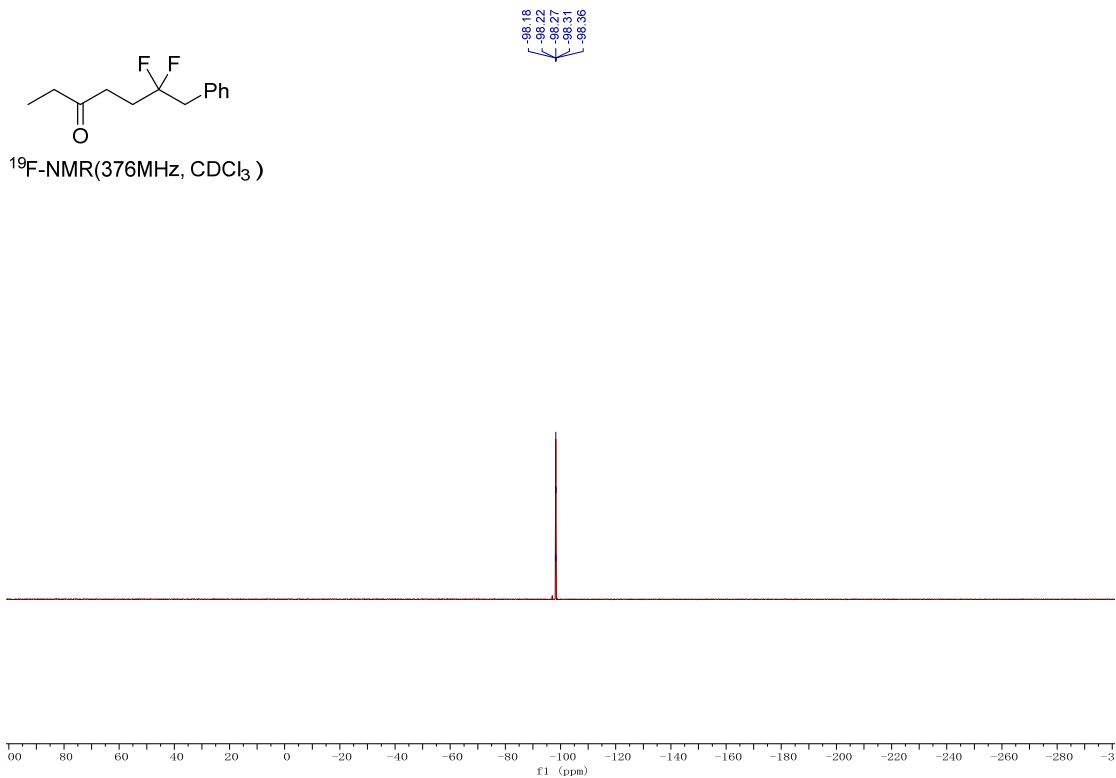


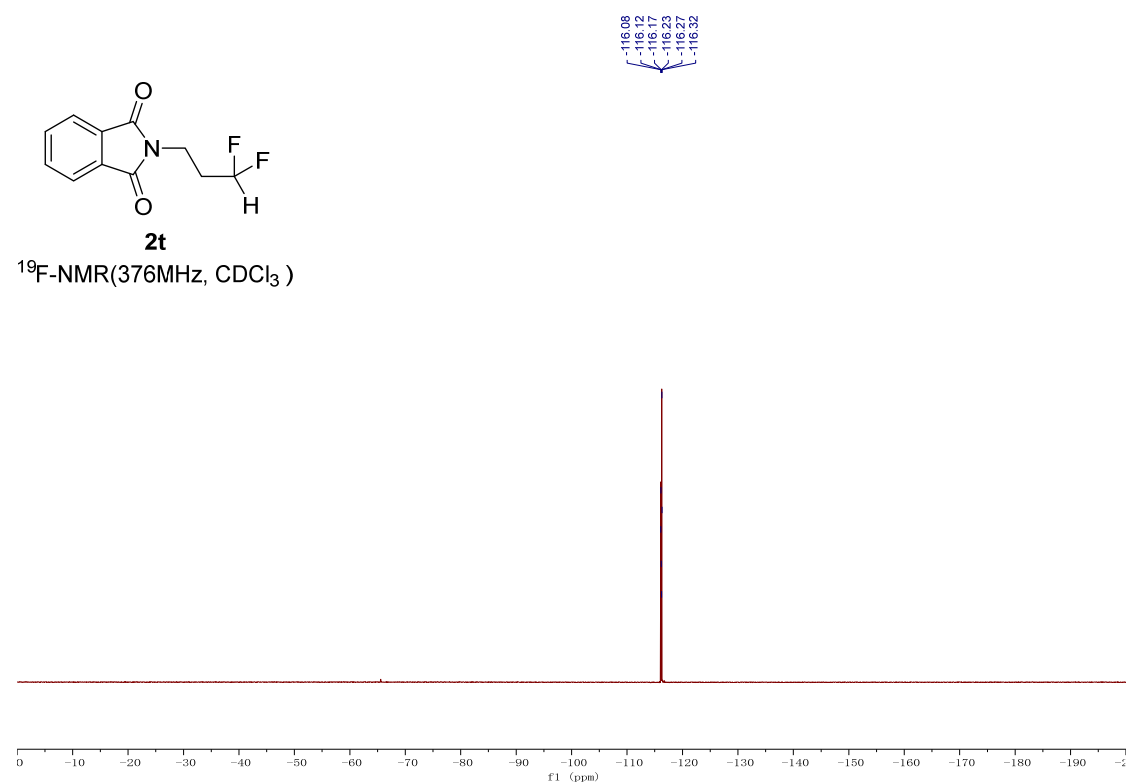
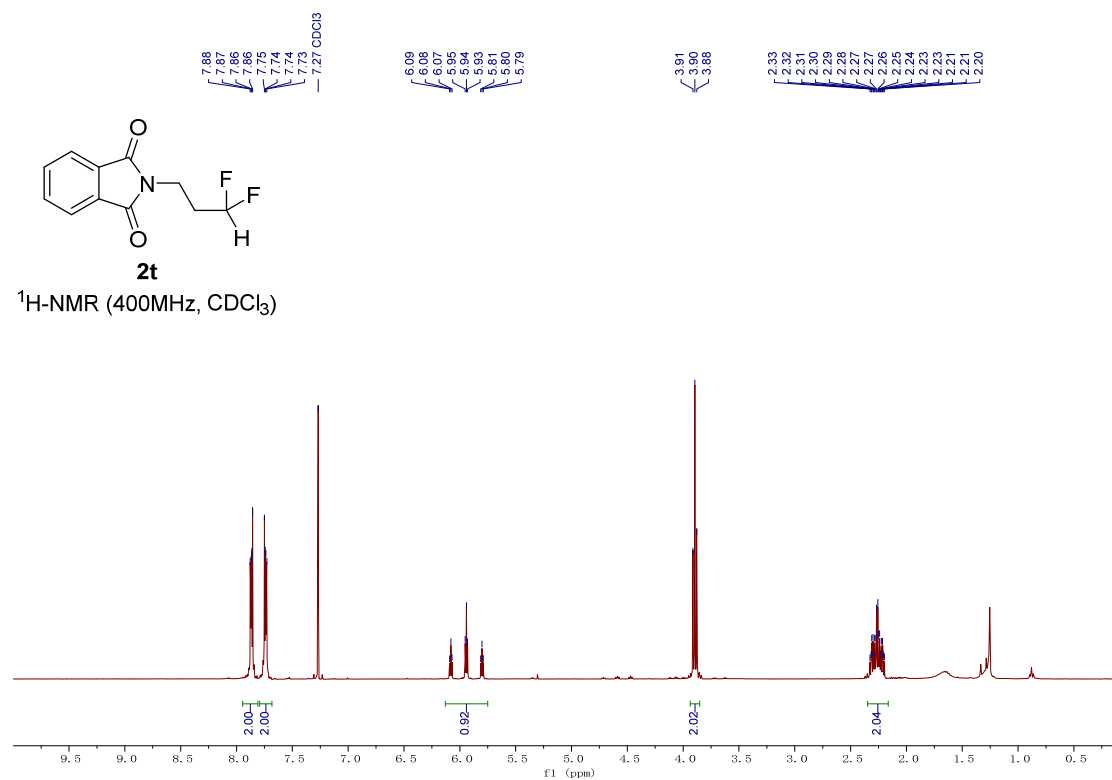


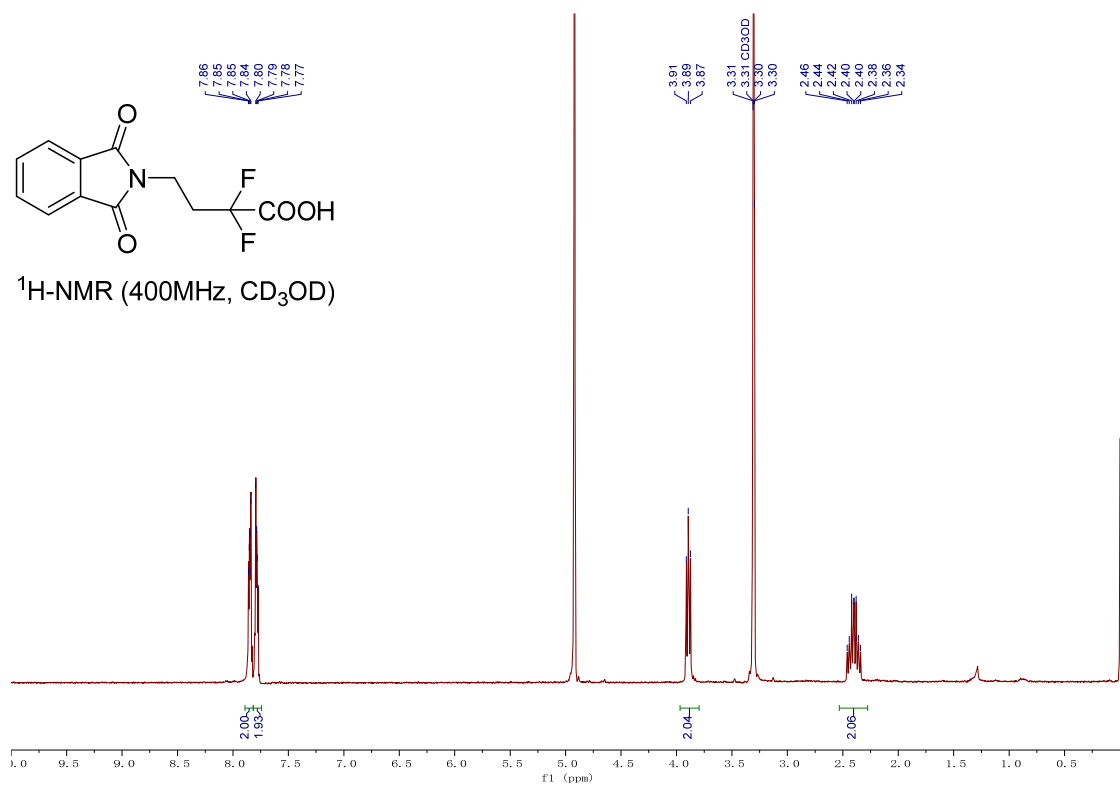
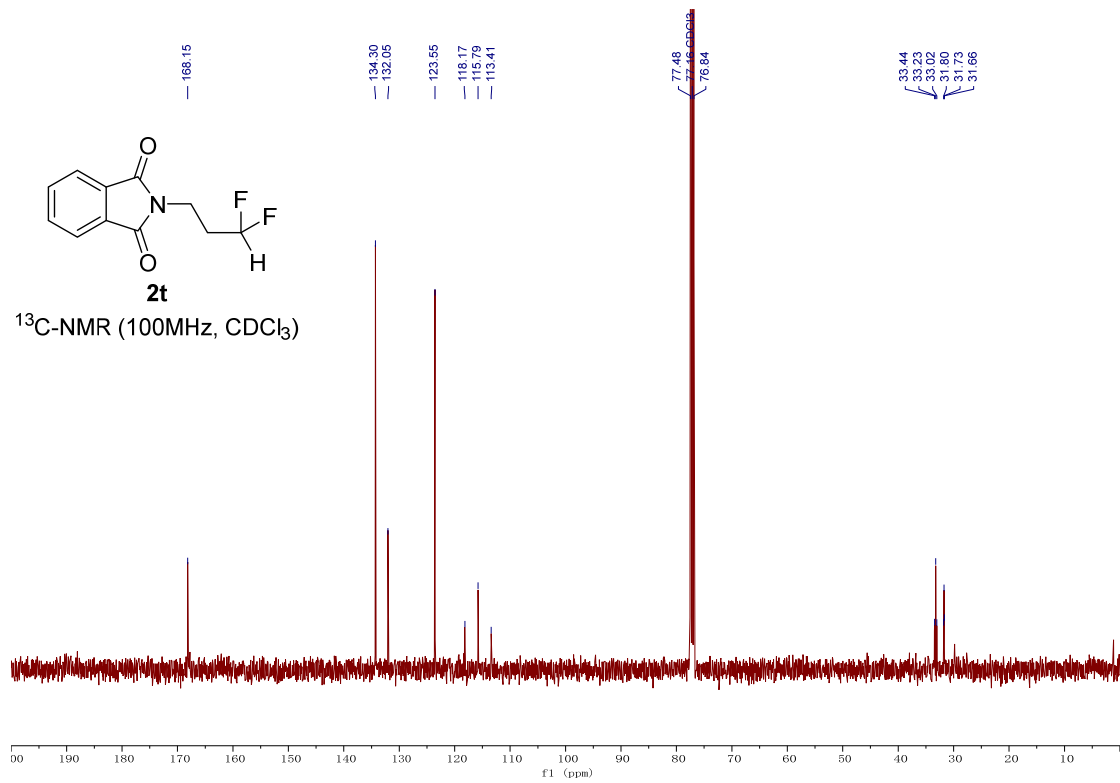
**2r** $^{19}\text{F}$ -NMR(376MHz,  $\text{CDCl}_3$ )

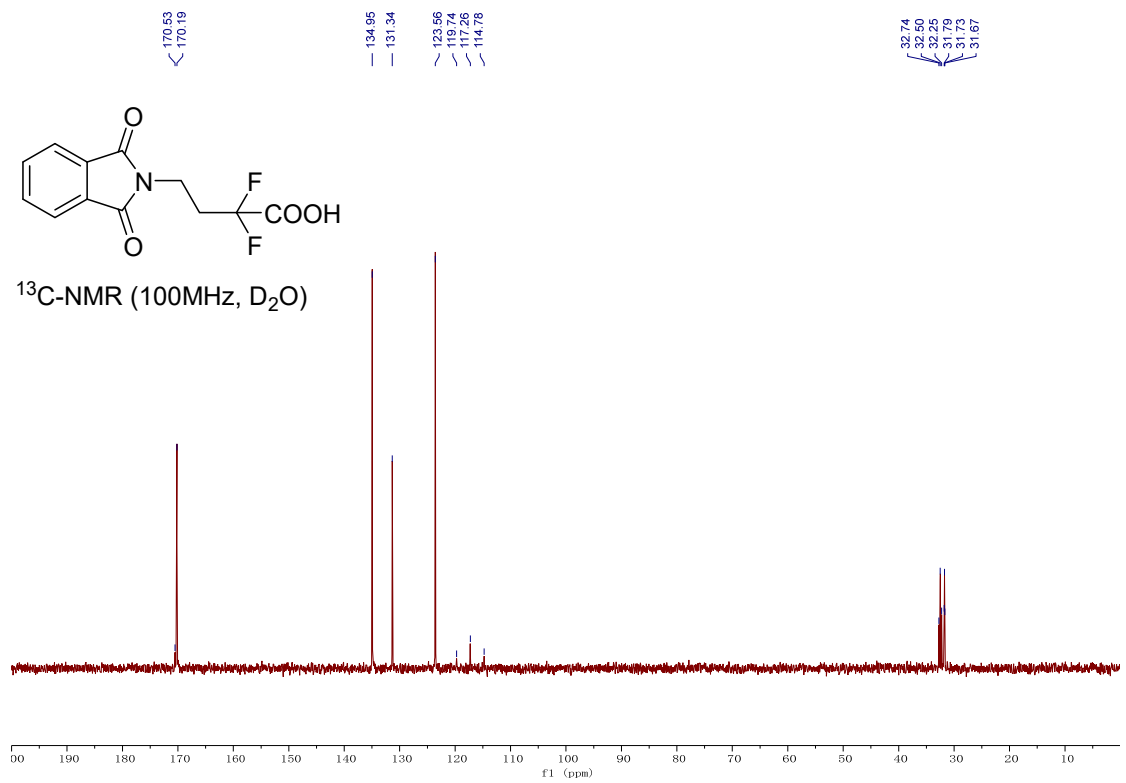
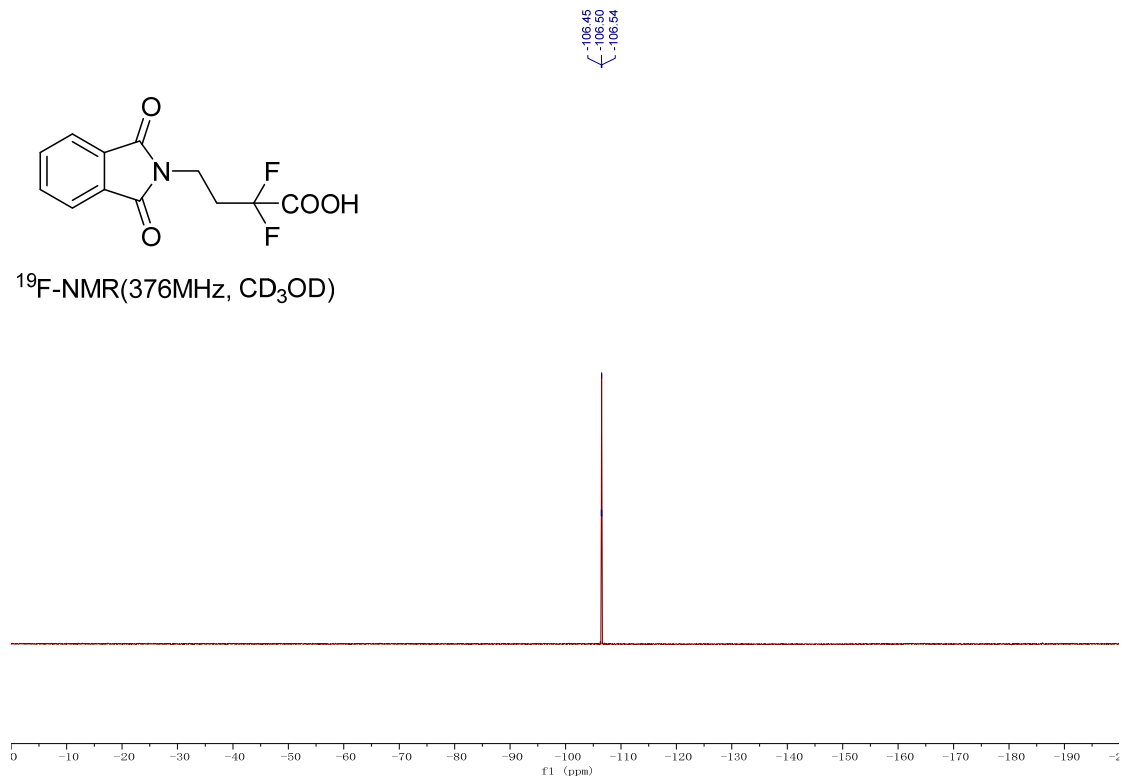


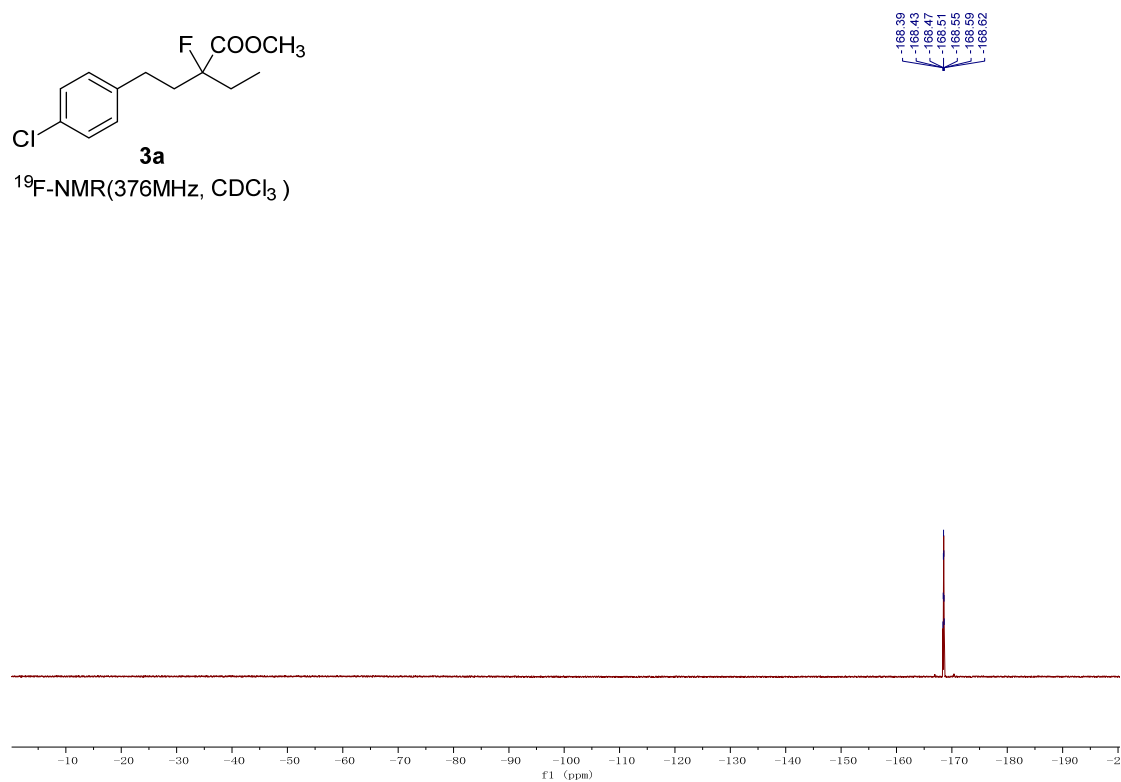
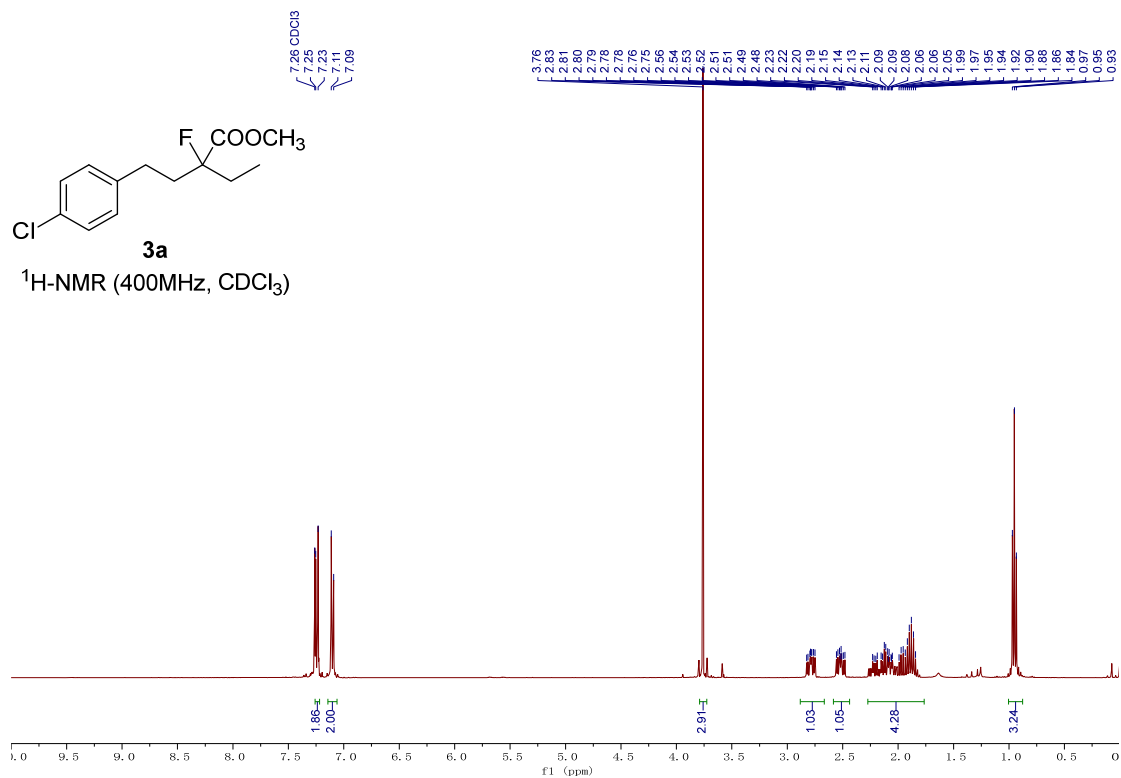


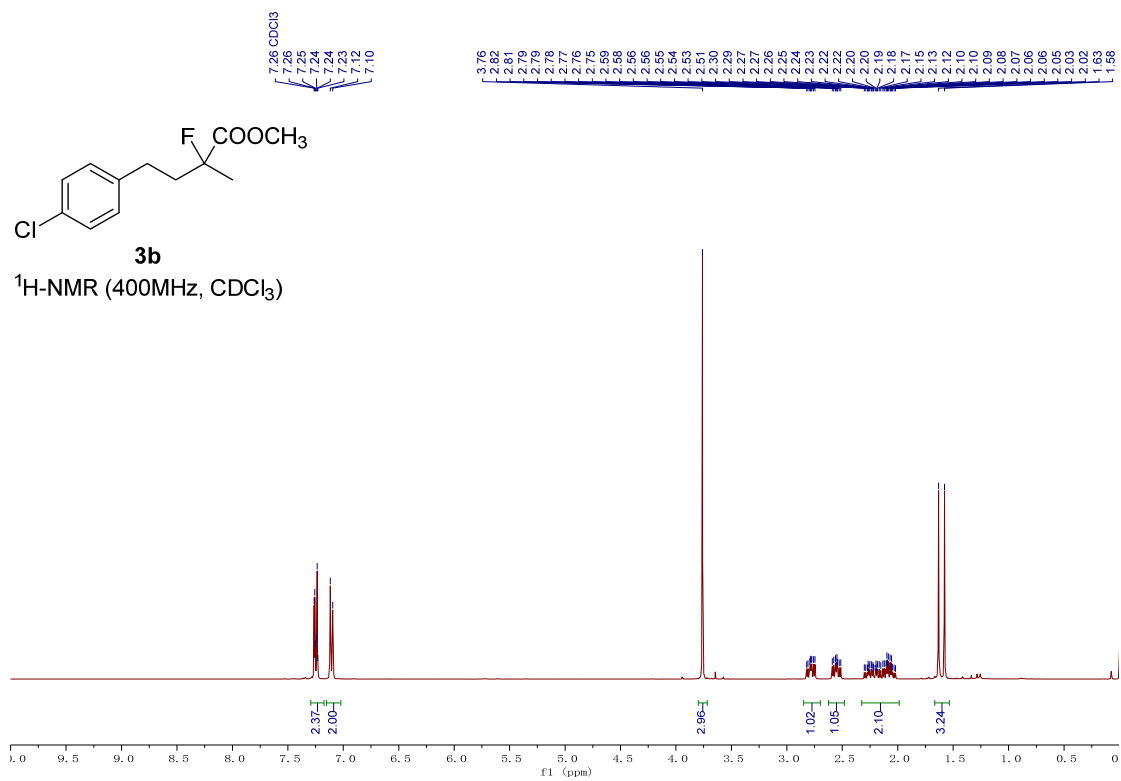
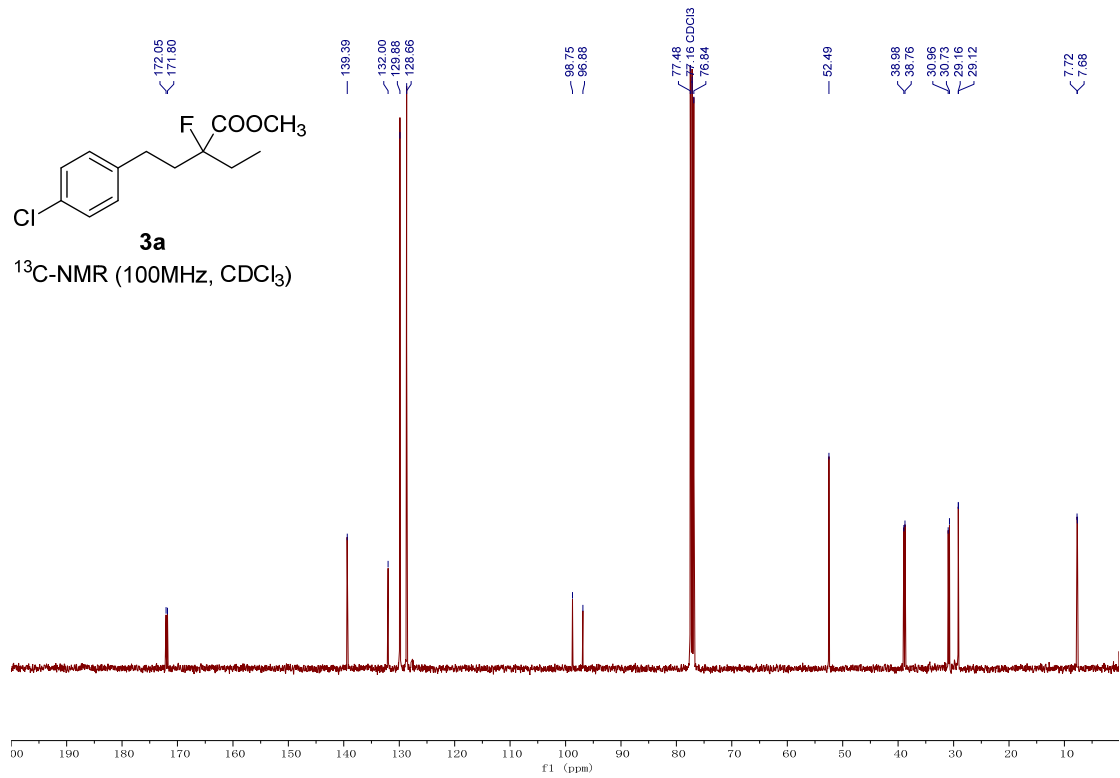


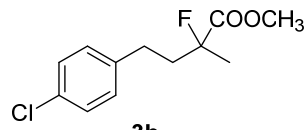




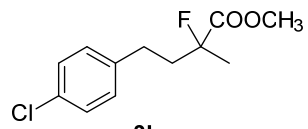
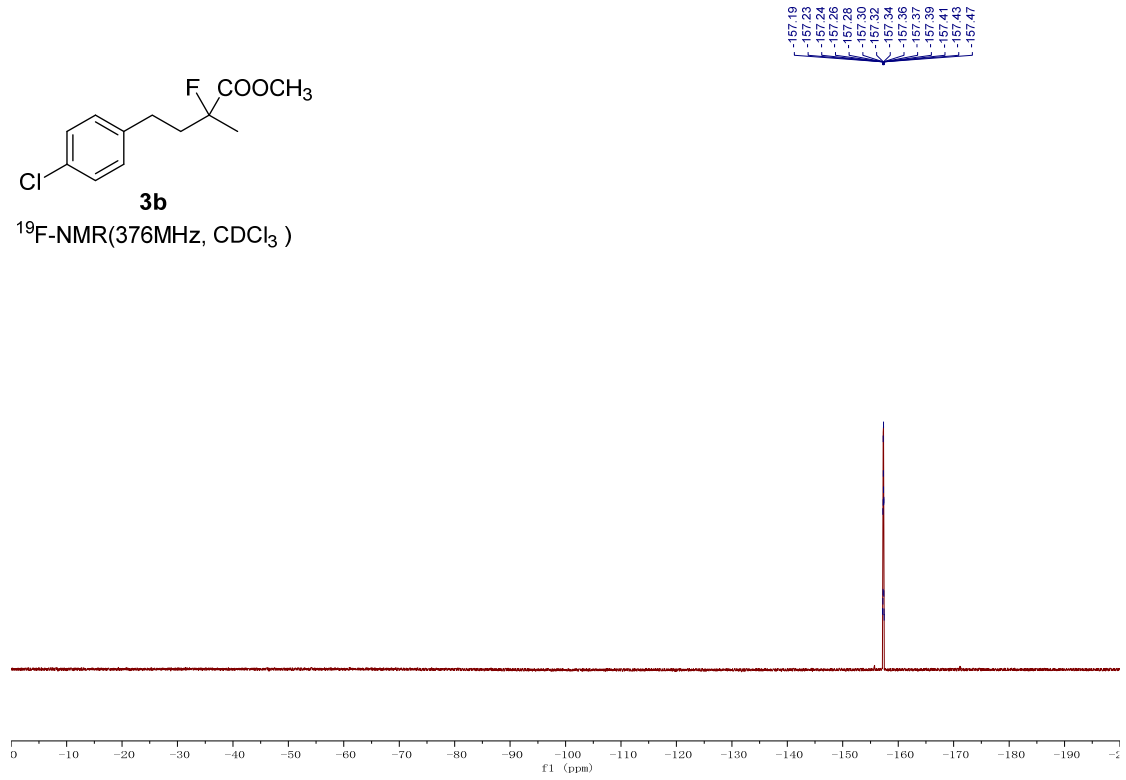




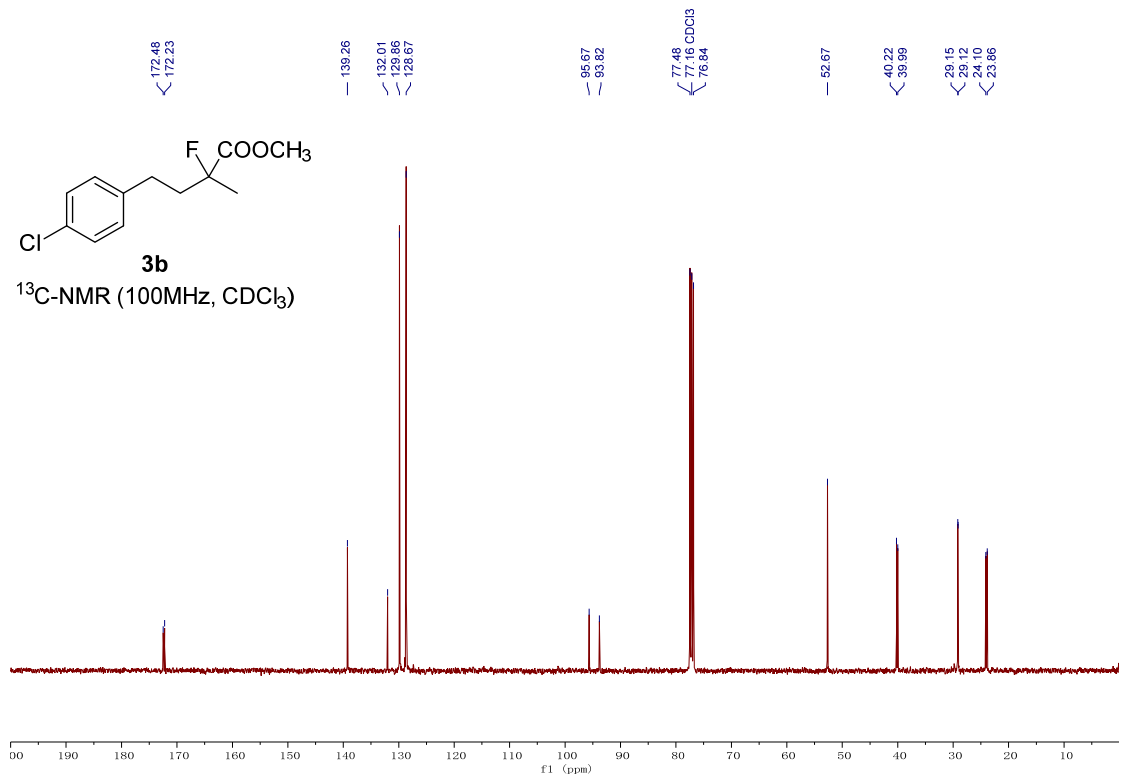


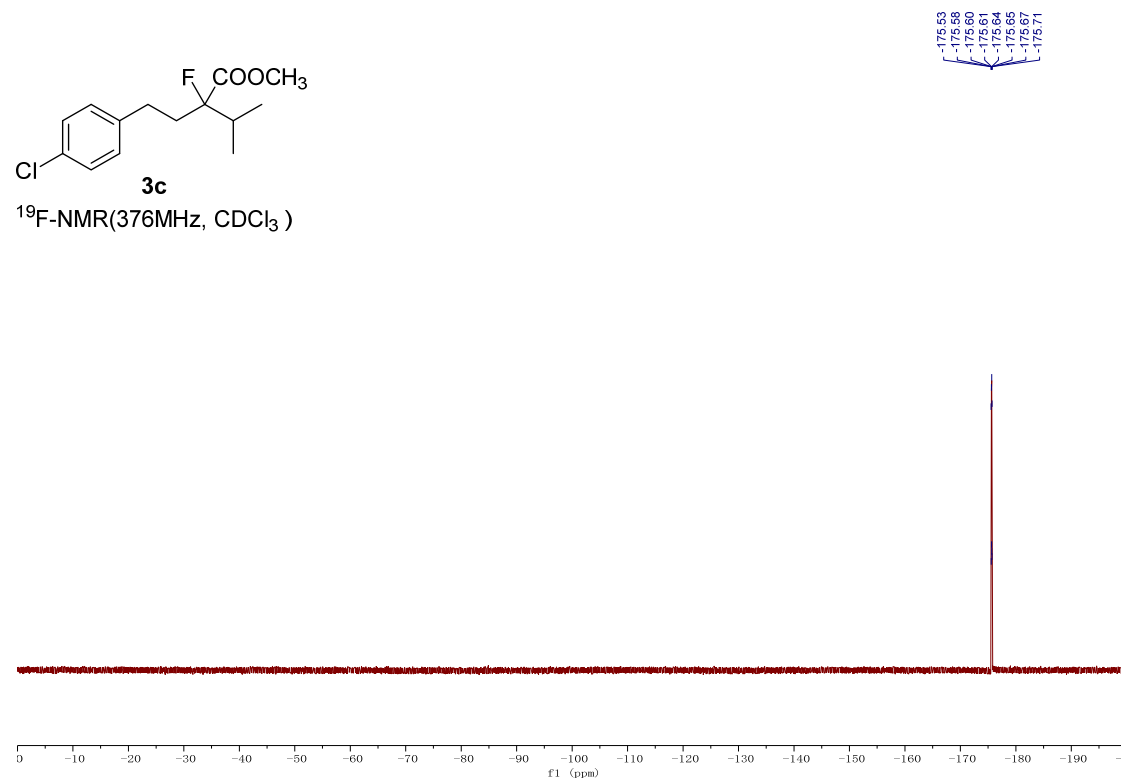
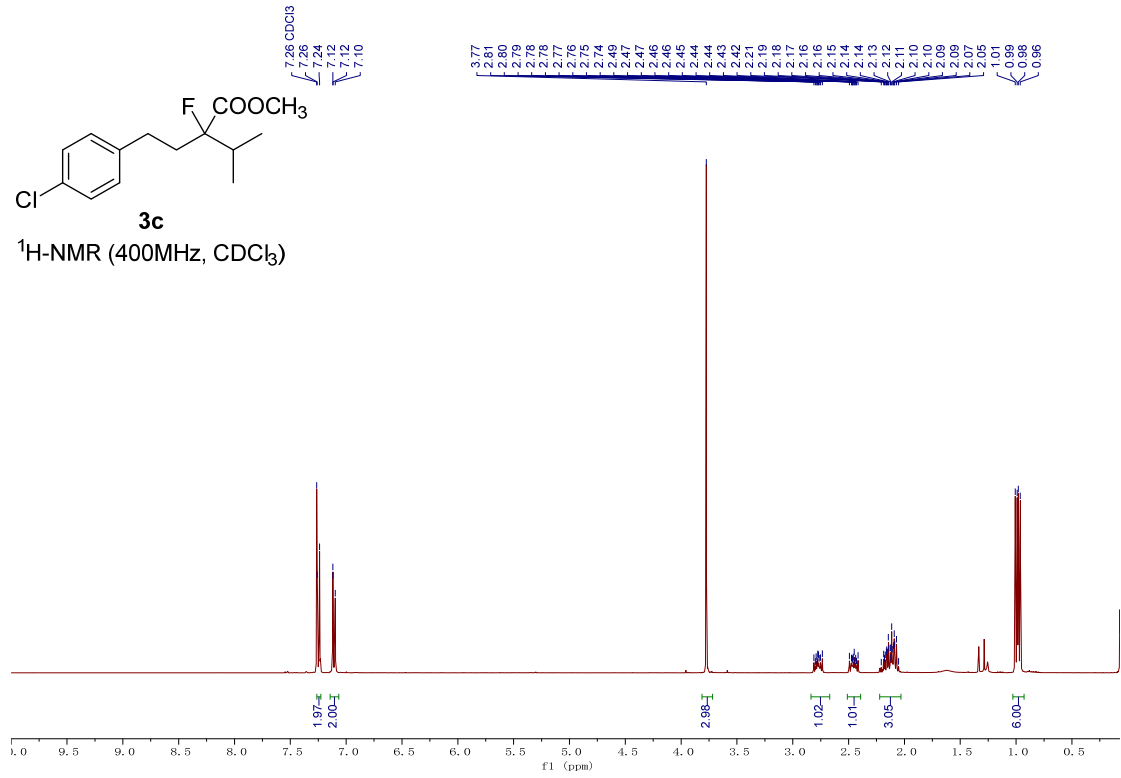


$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )

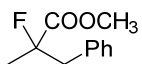
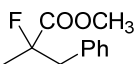
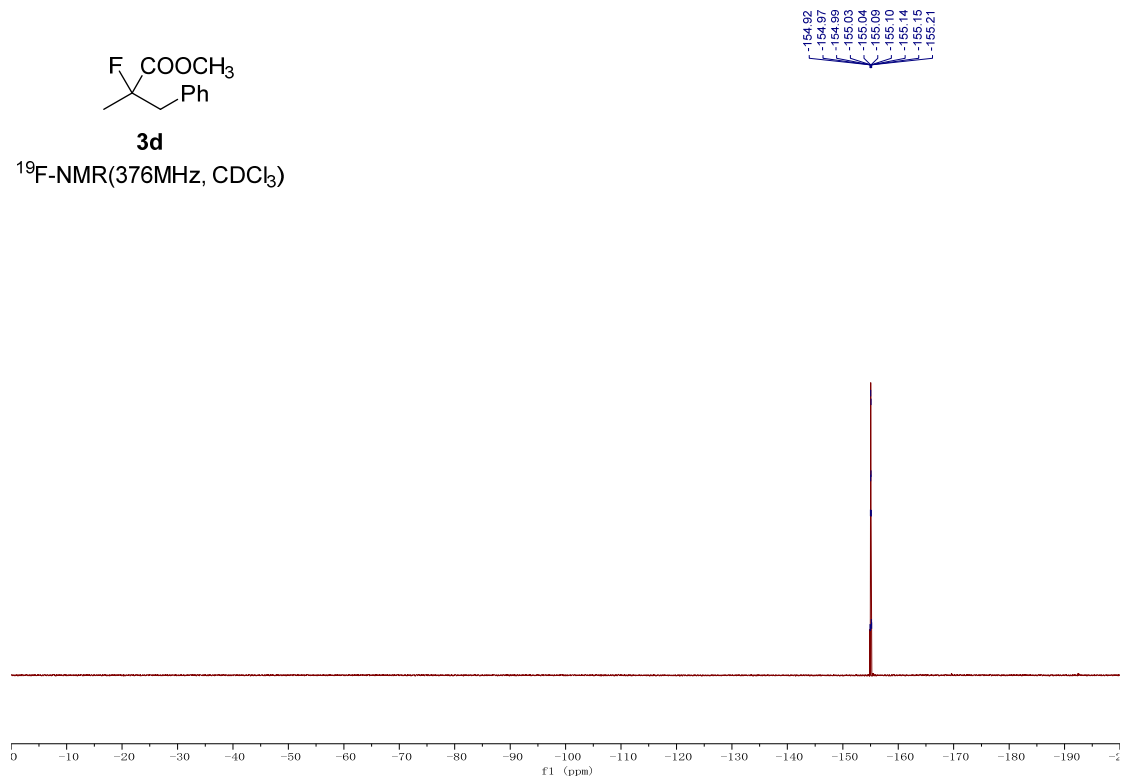
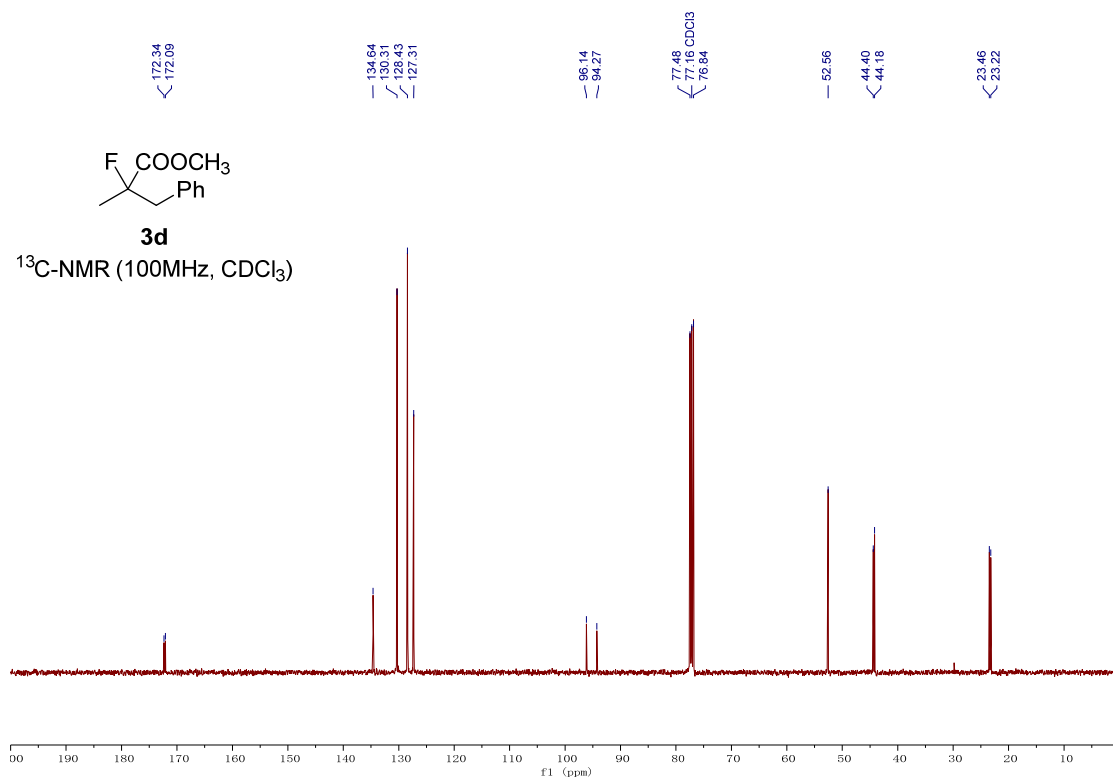


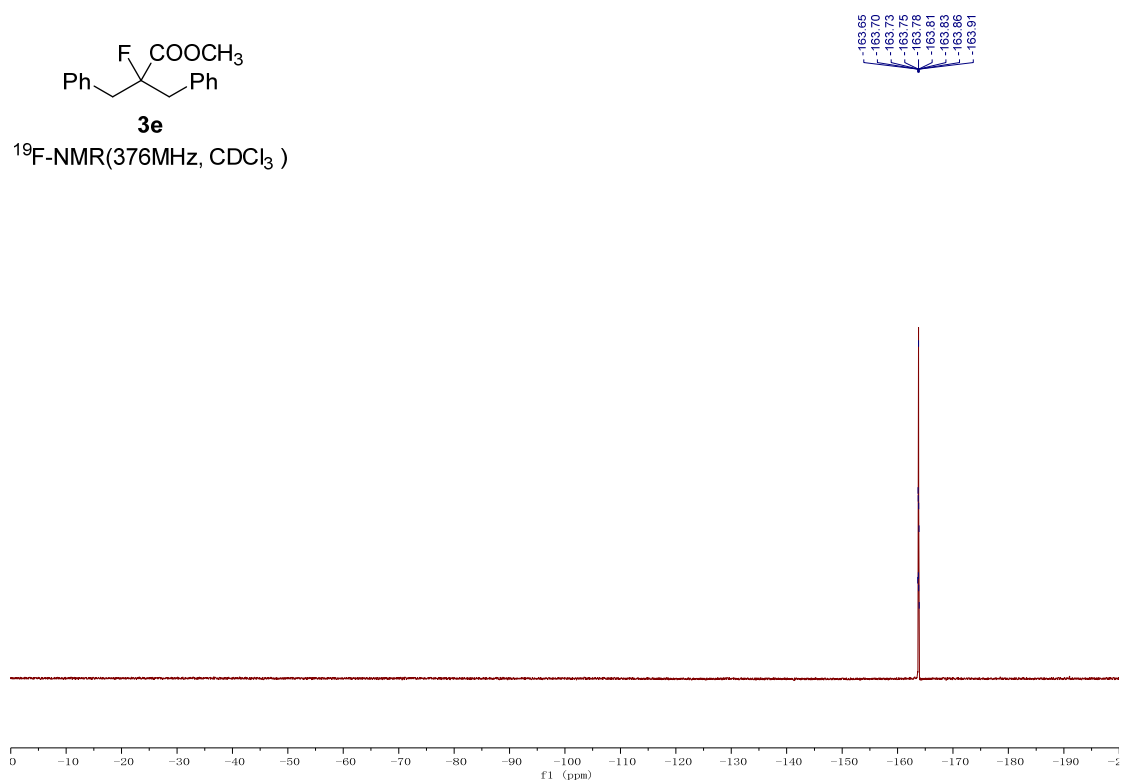
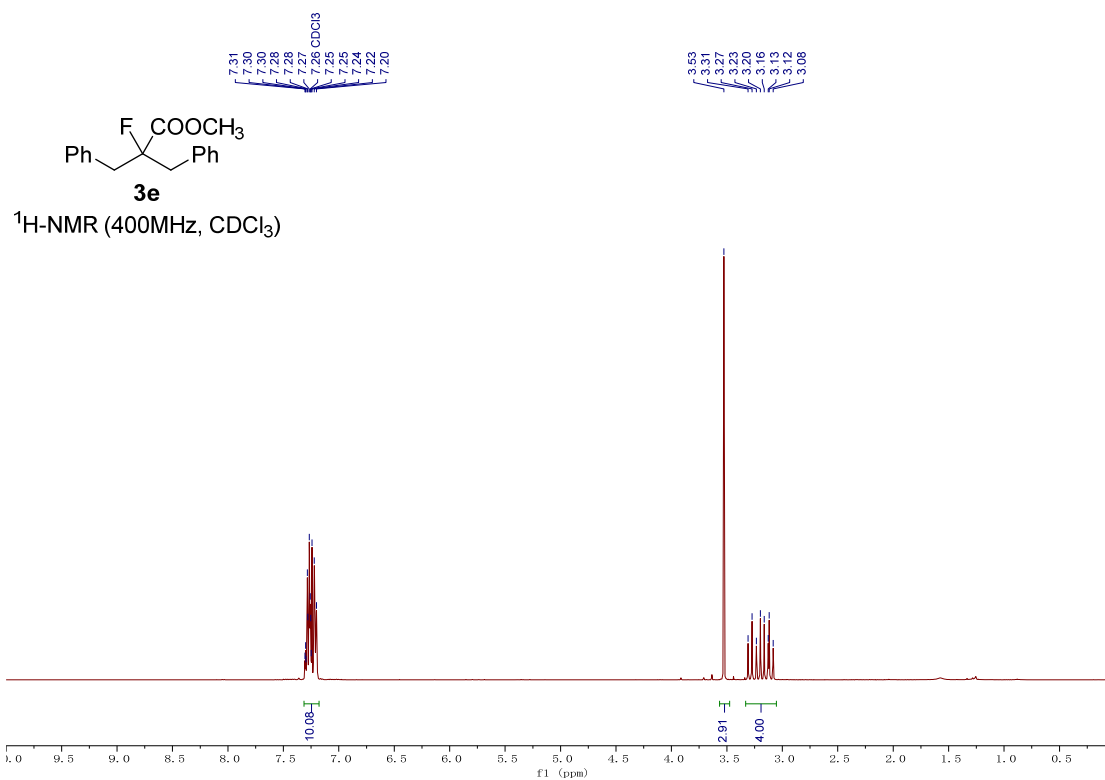
$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

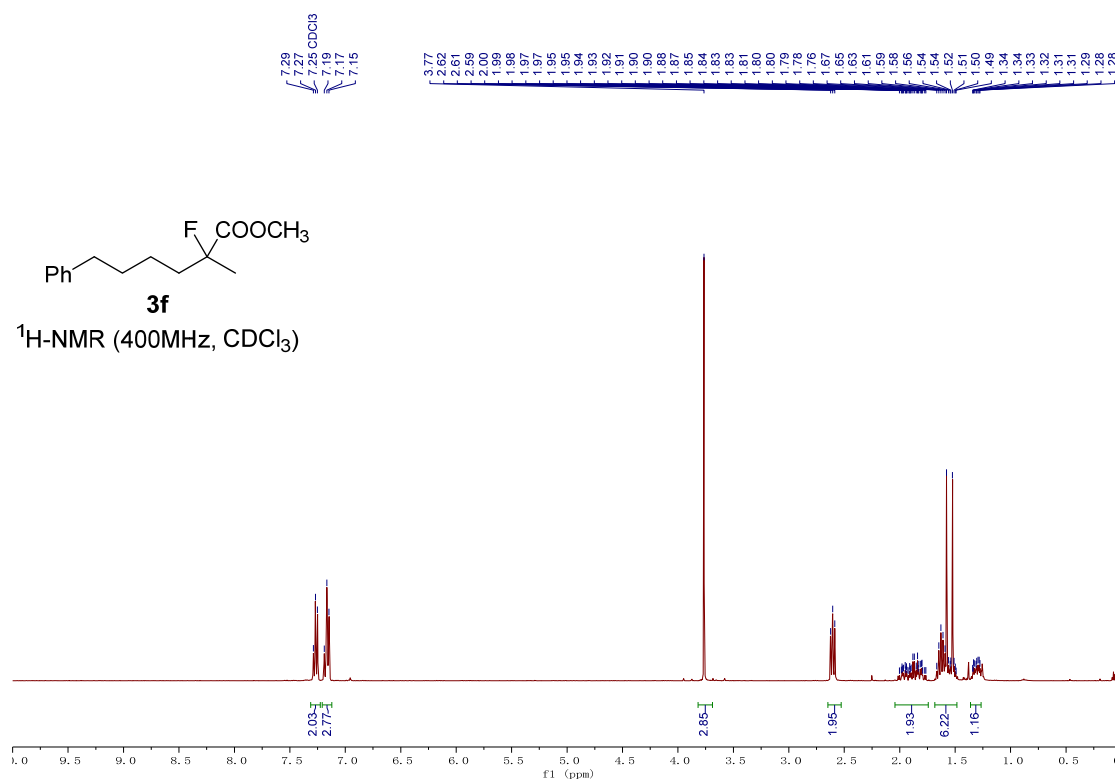
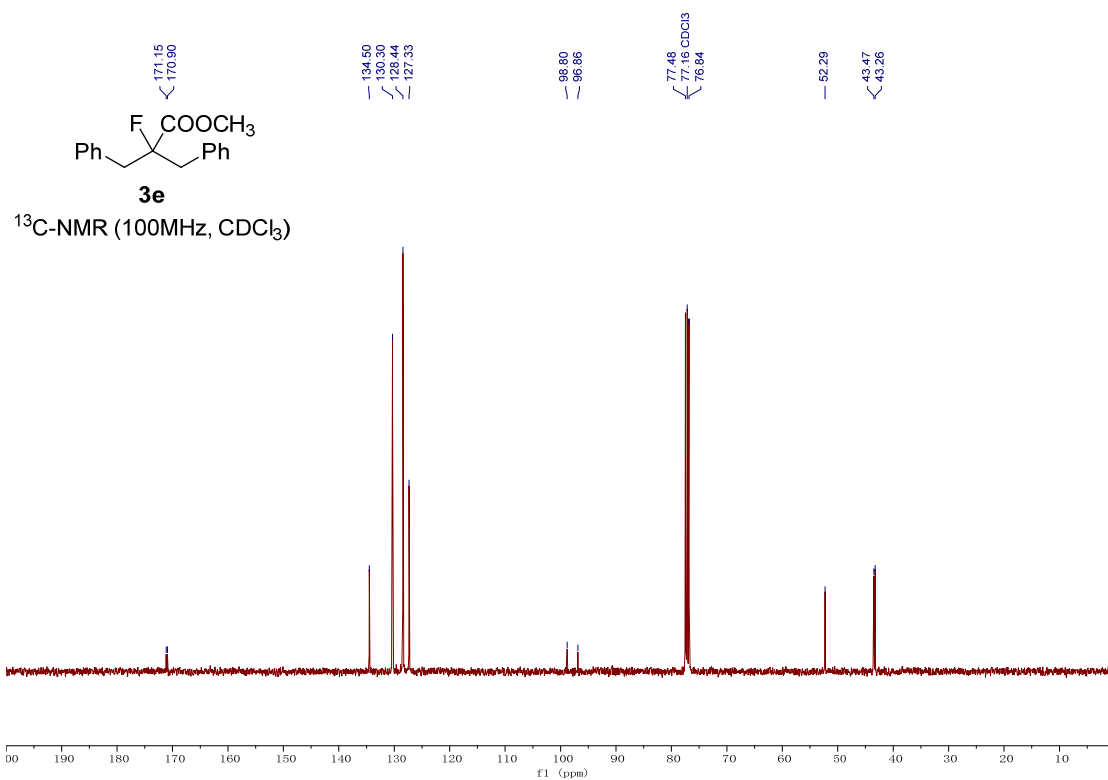


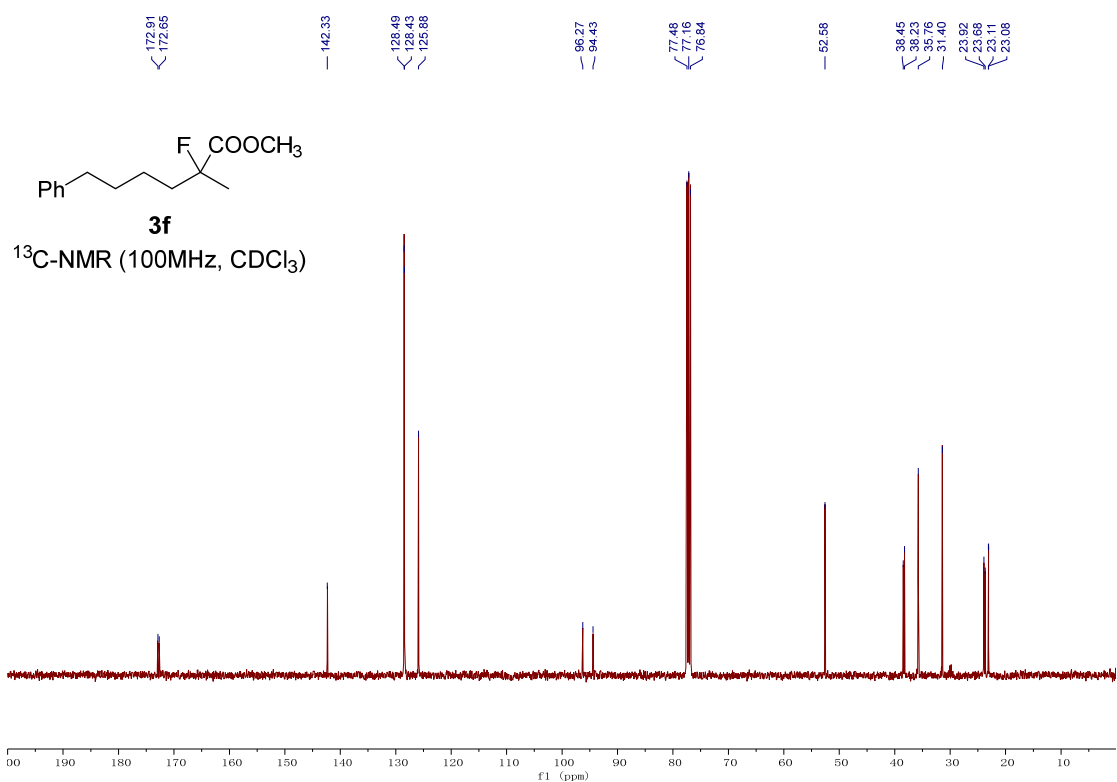
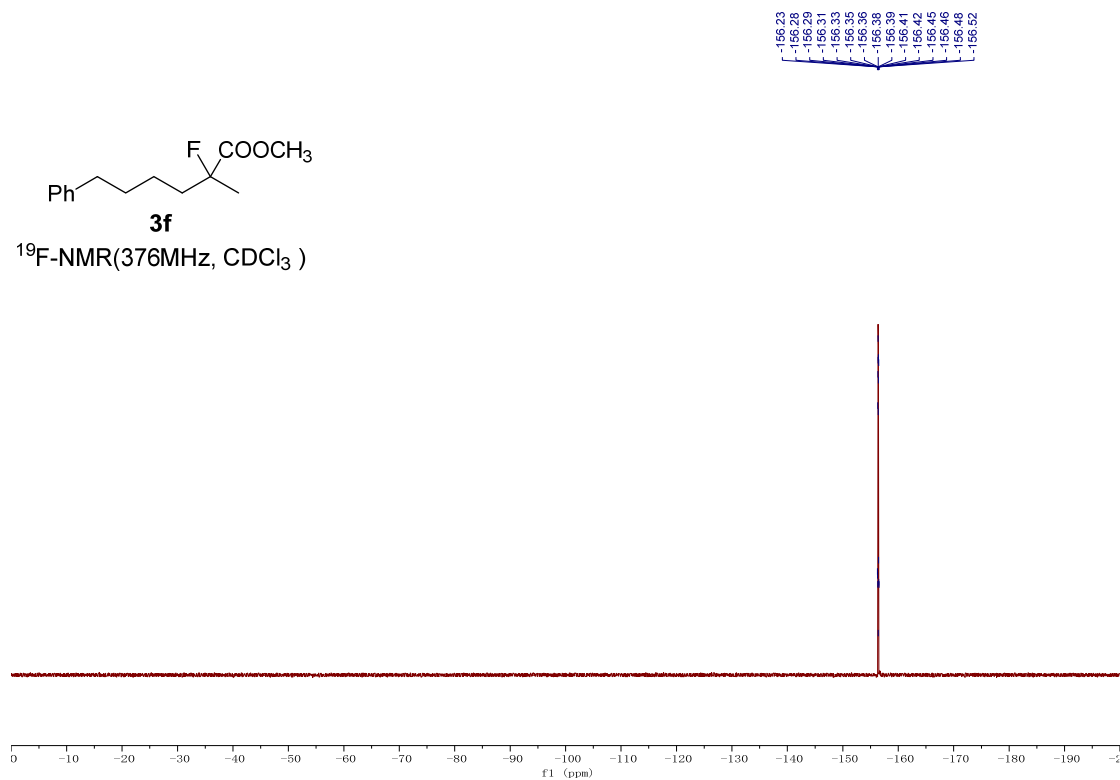
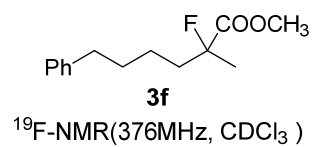


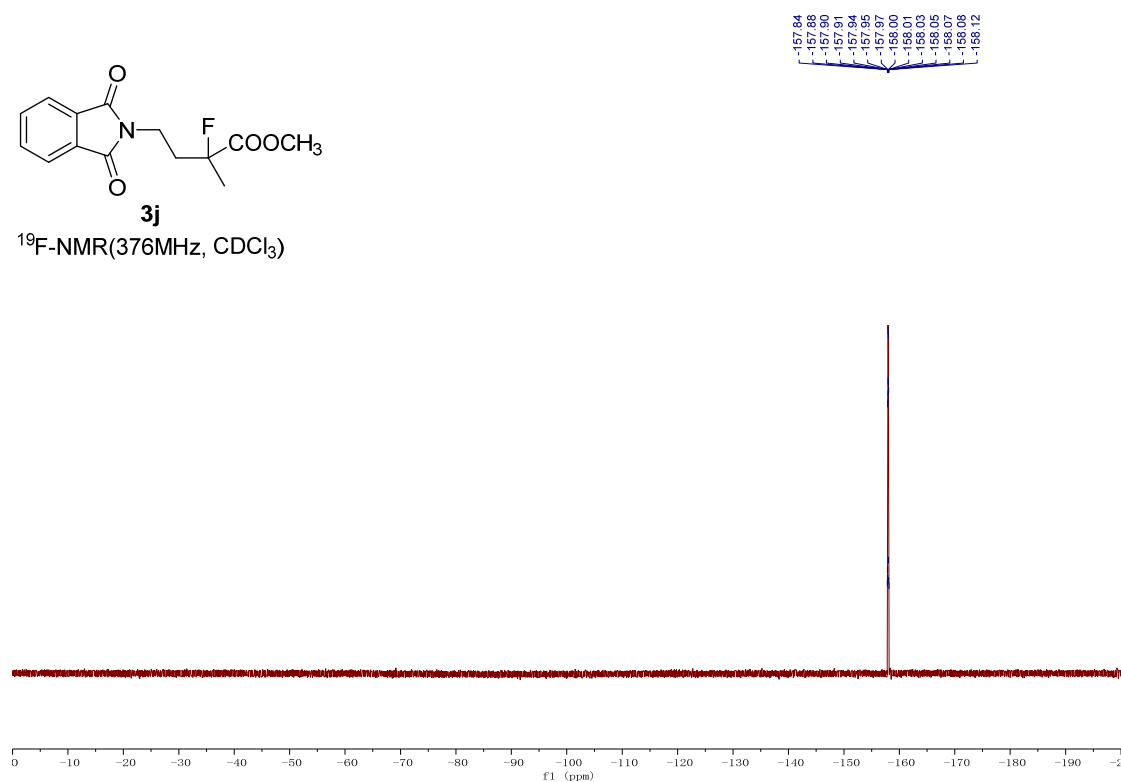
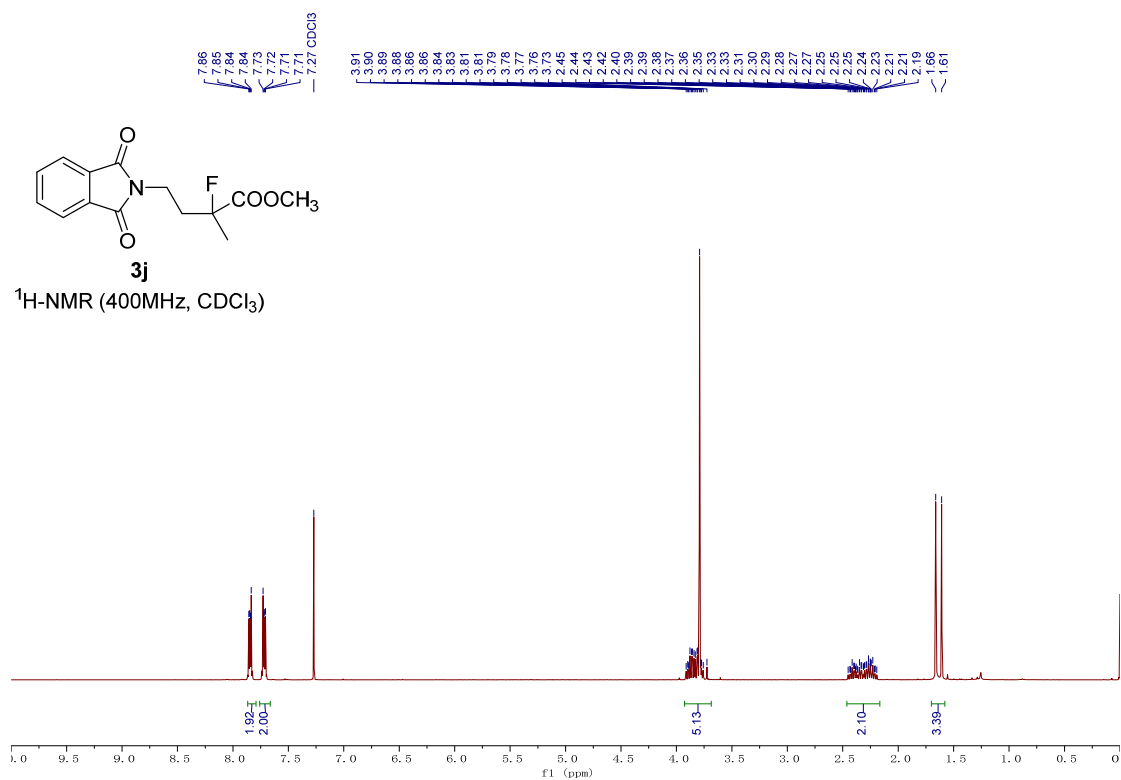


**3d**<sup>19</sup>F-NMR(376MHz, CDCl<sub>3</sub>)**3d**<sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)

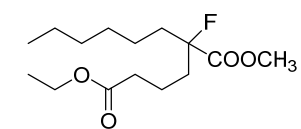




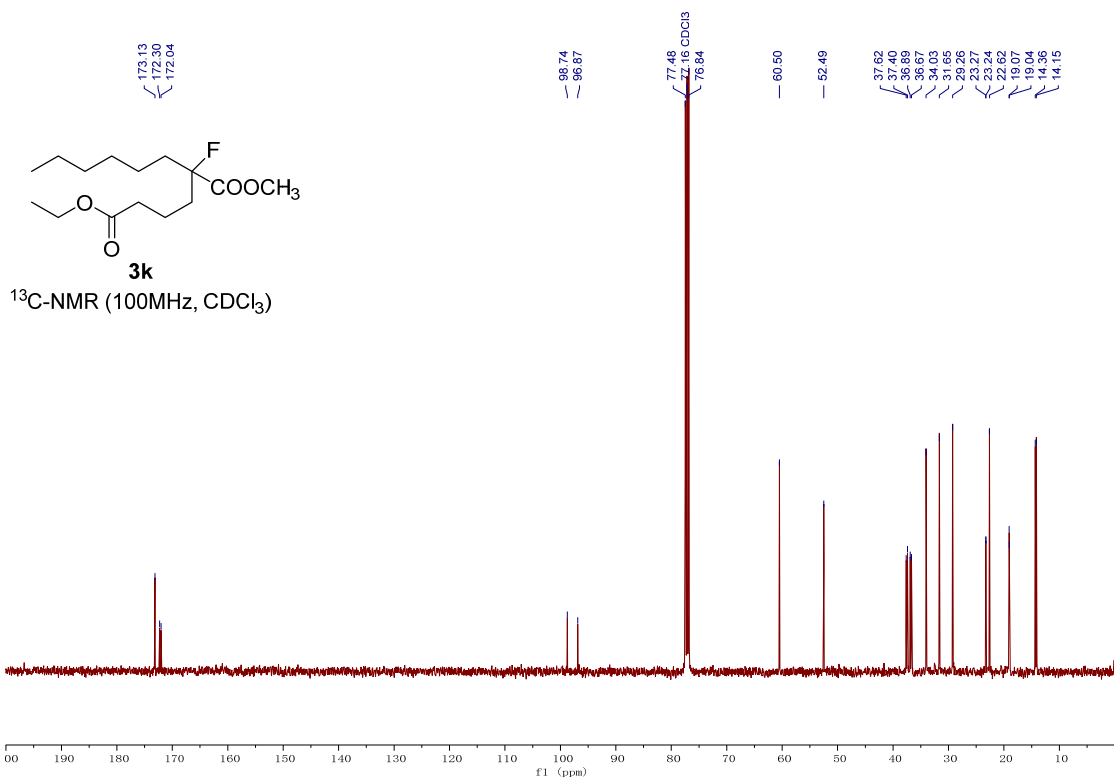
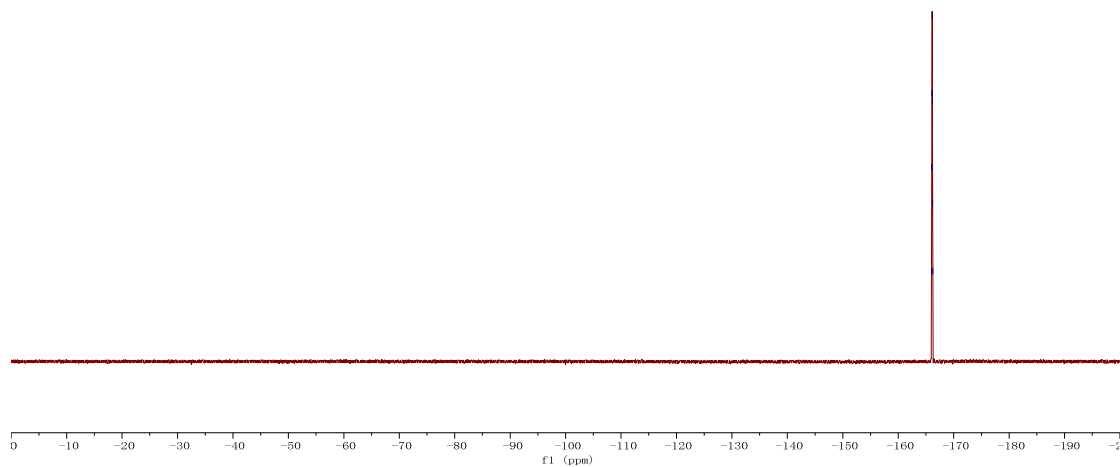


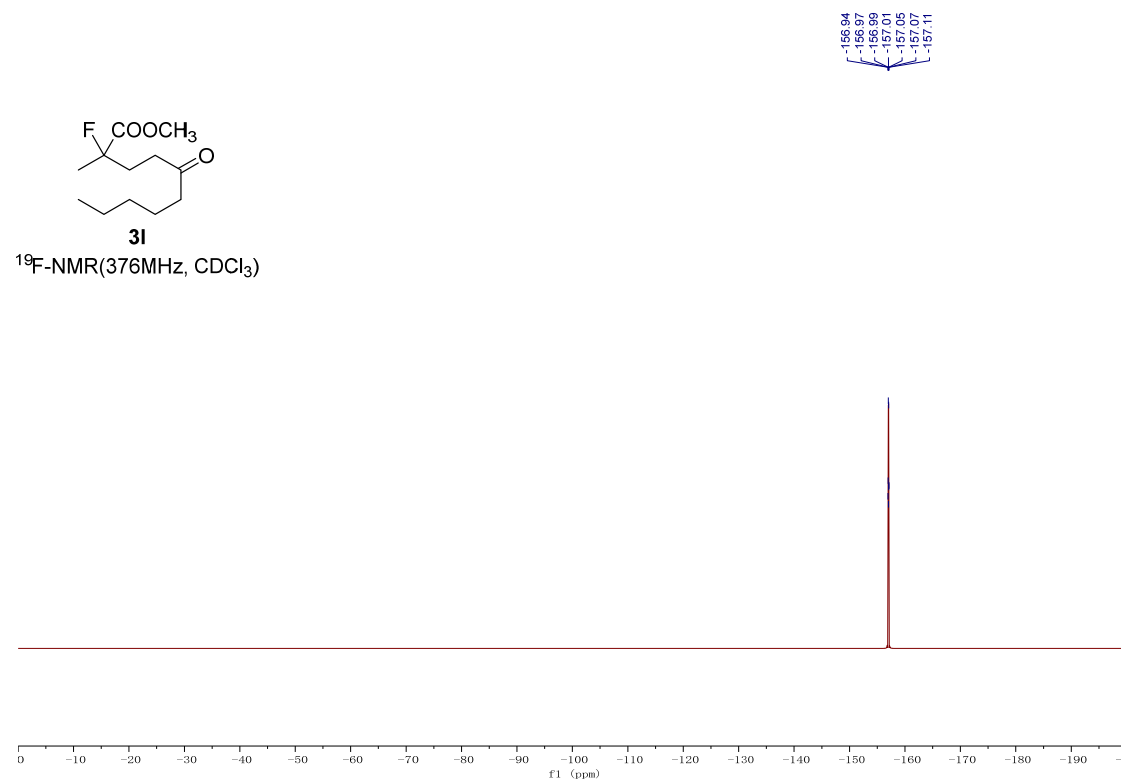
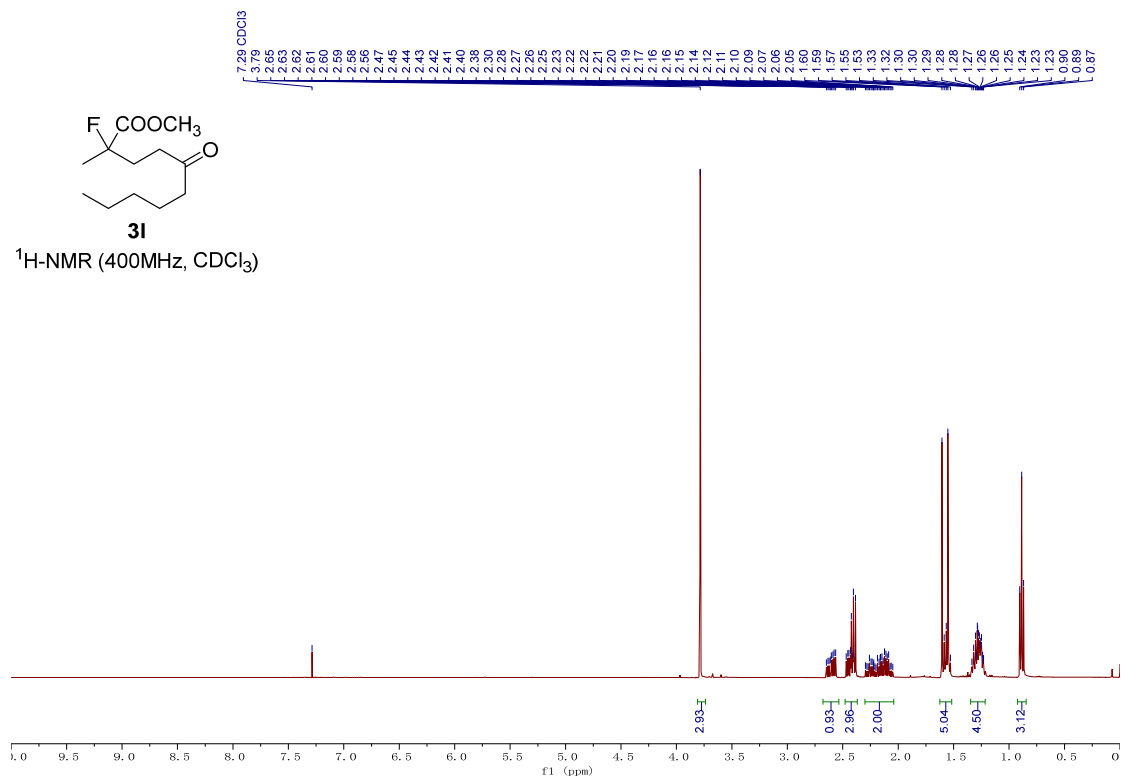


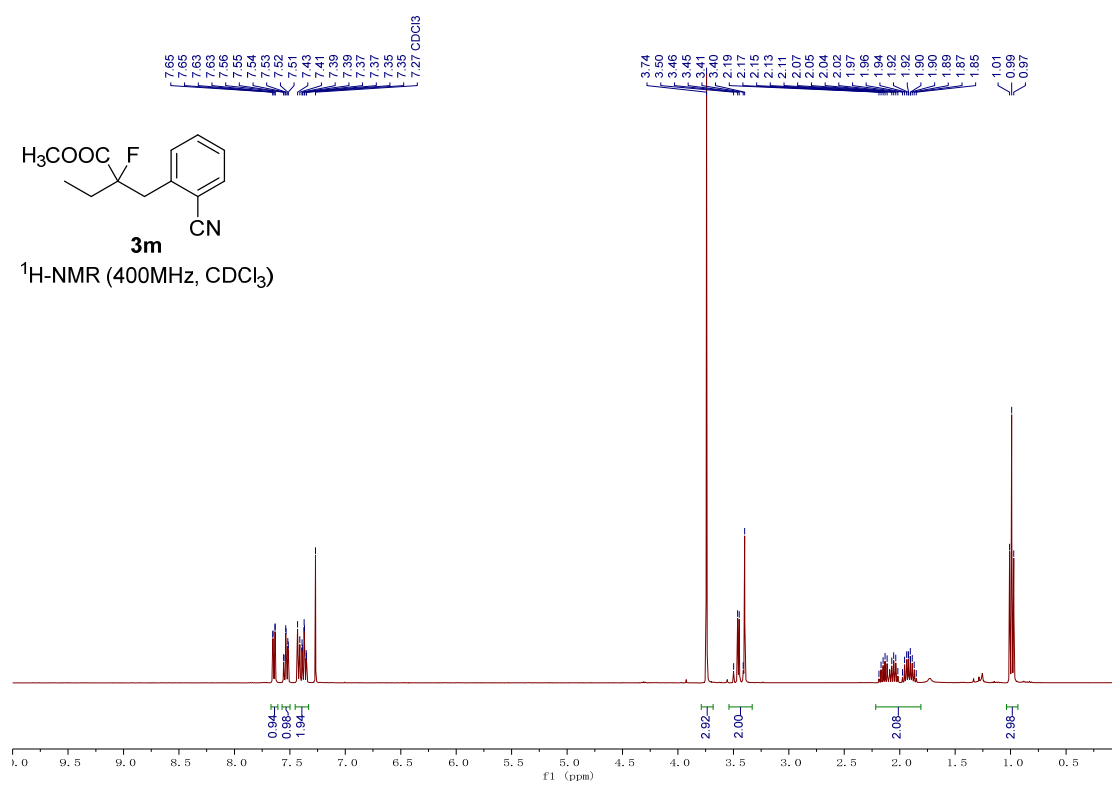
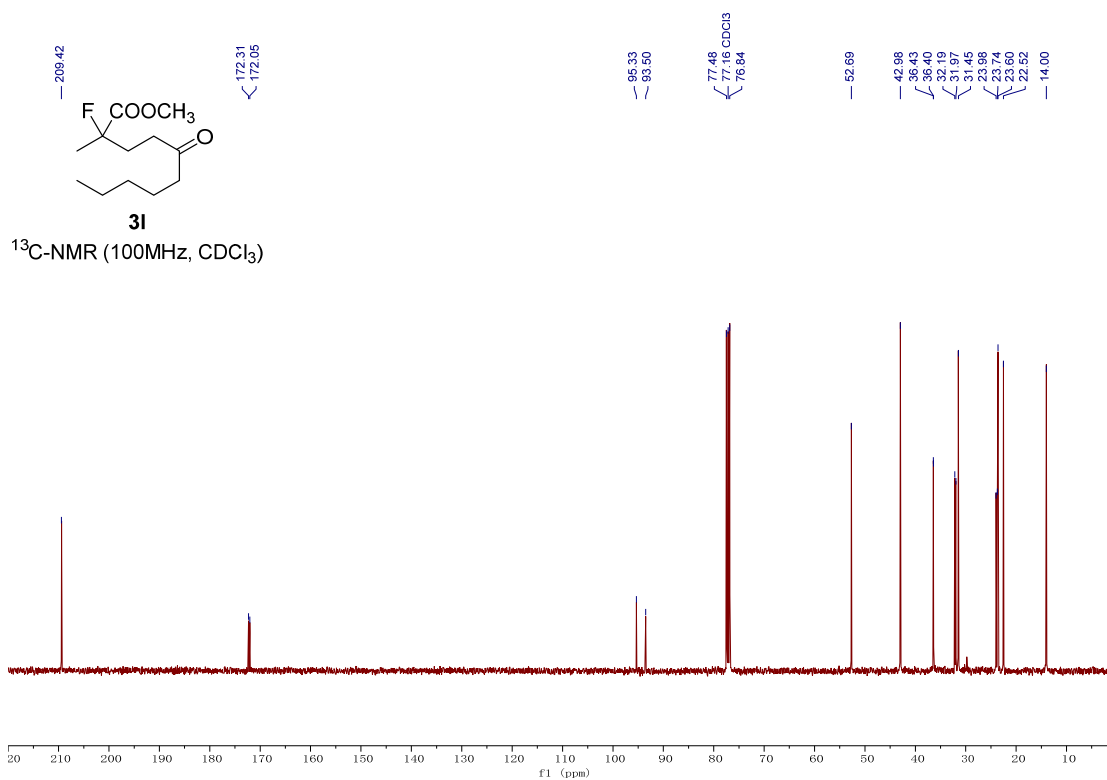


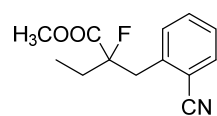
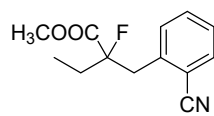
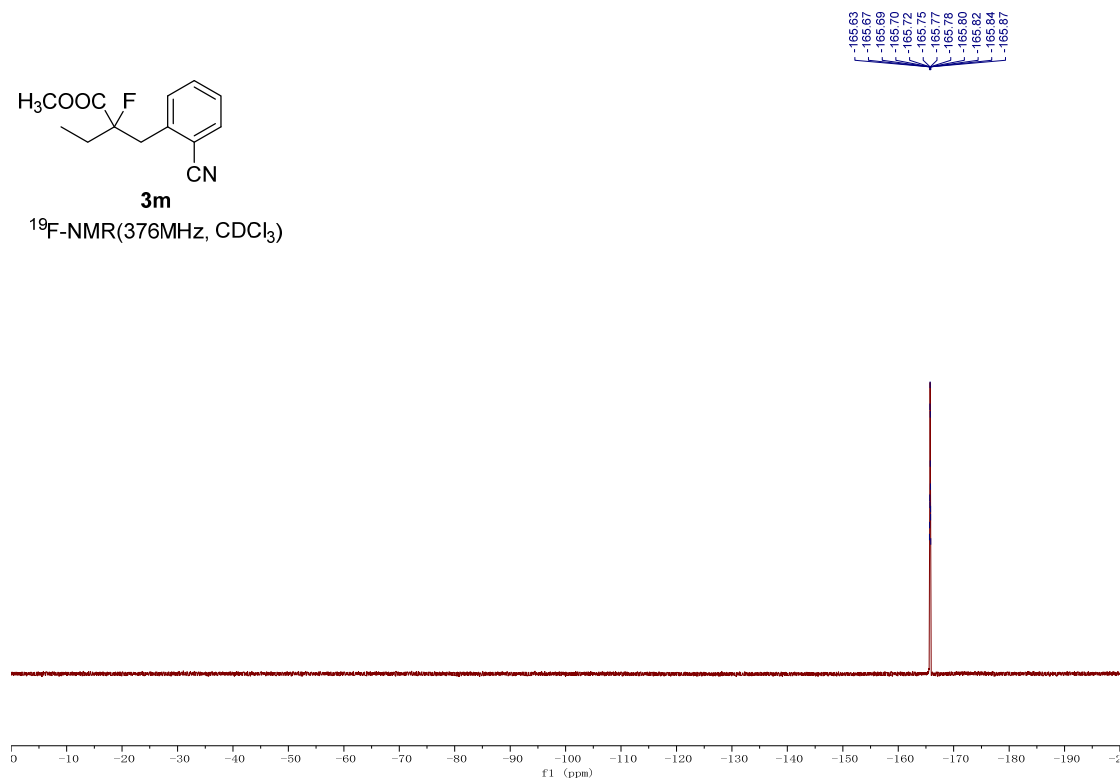
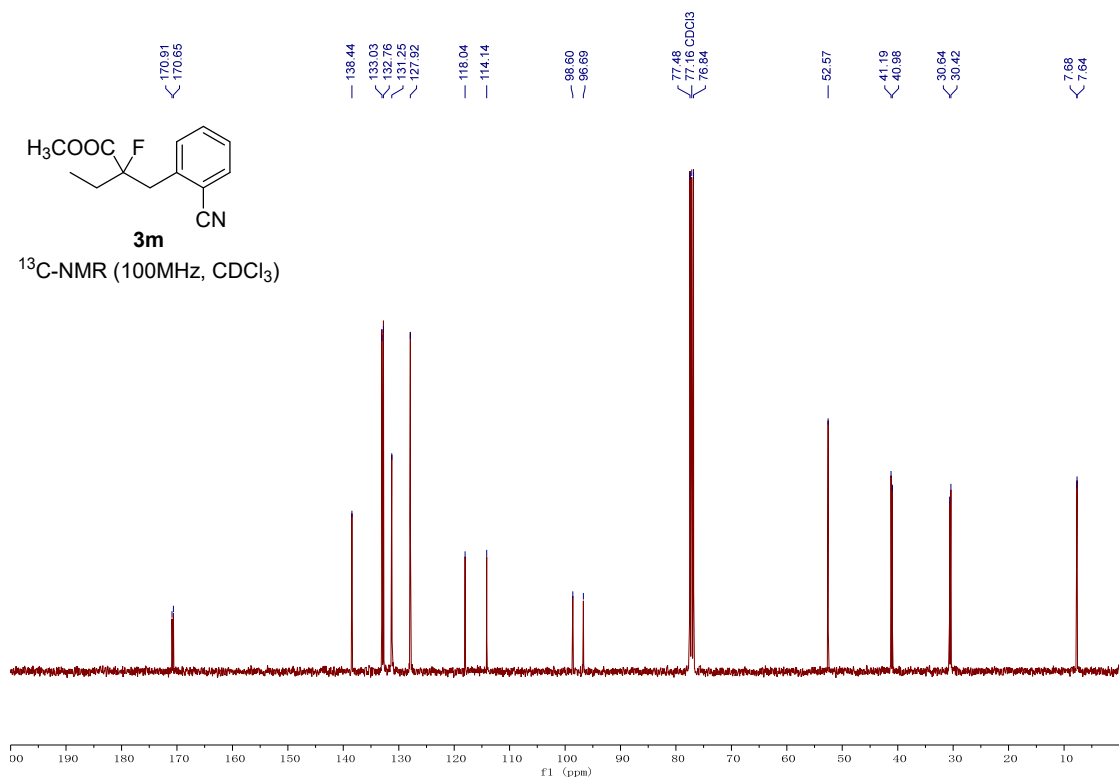


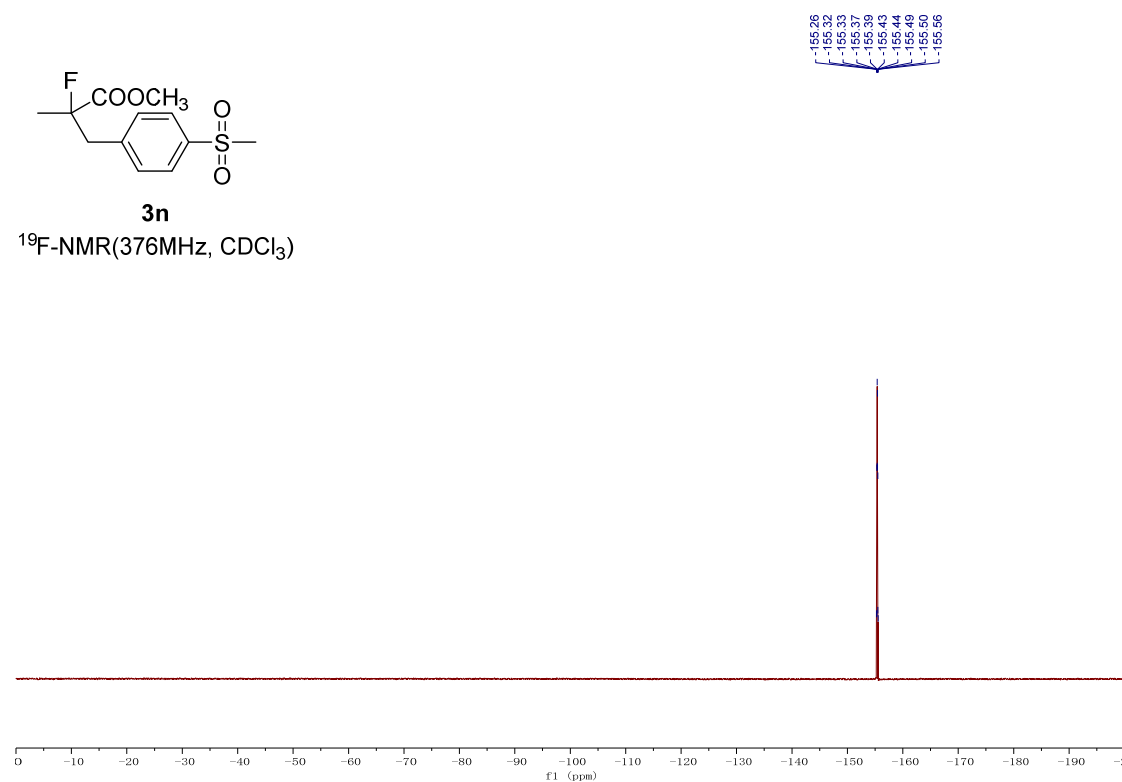
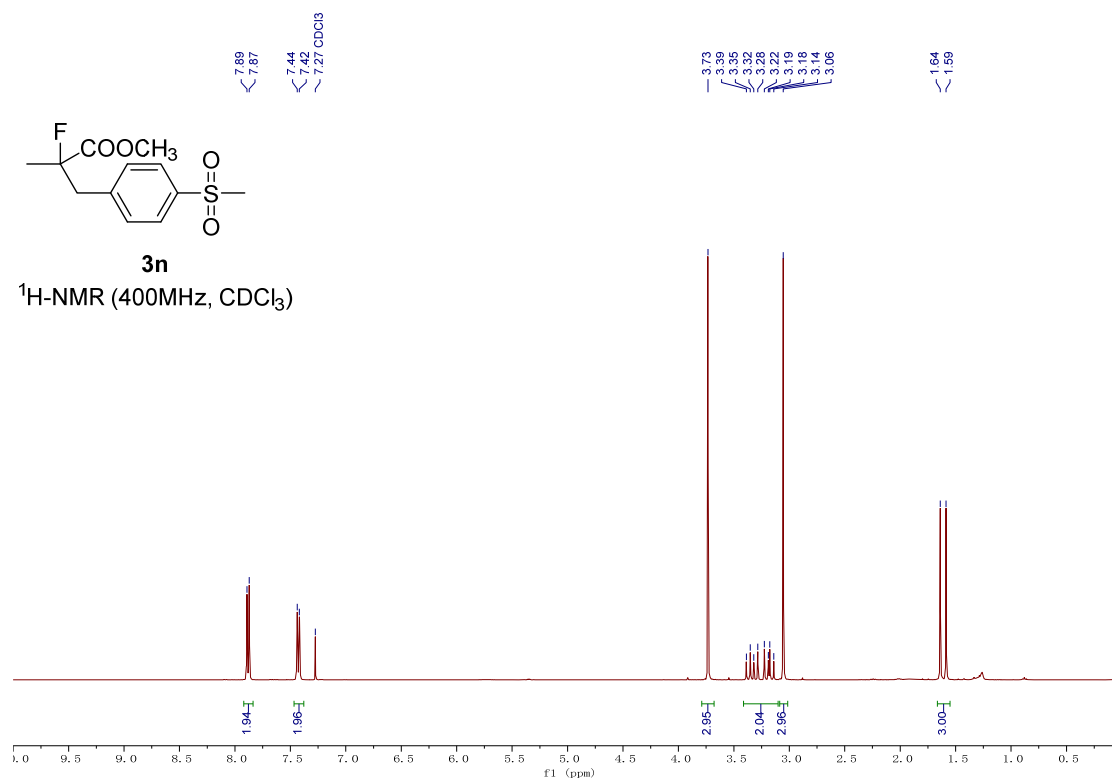
$^{19}\text{F}$ -NMR(376MHz,  $\text{CDCl}_3$ )

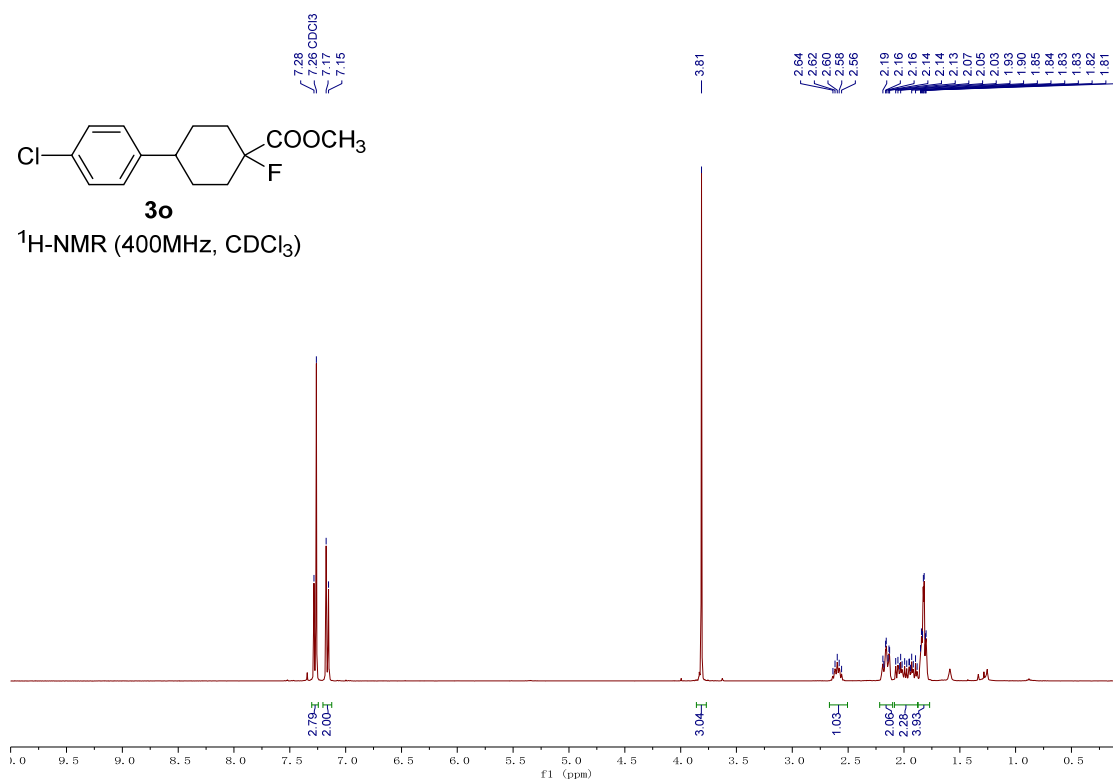
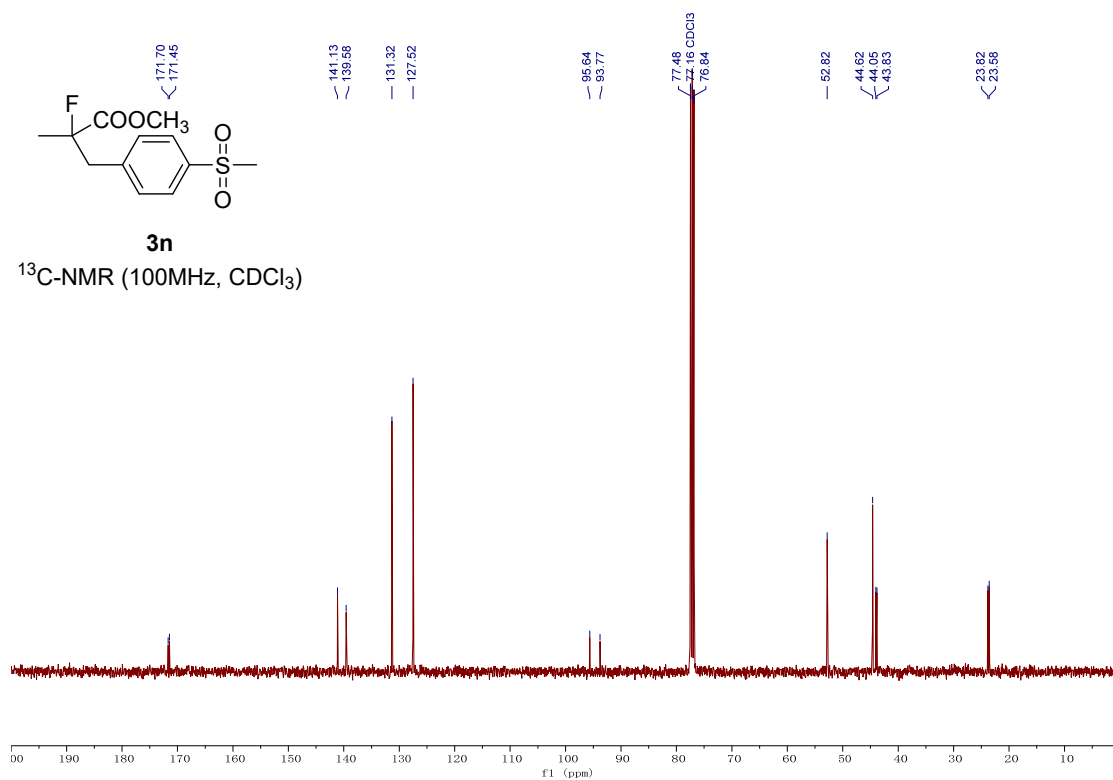




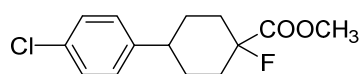


**3m**<sup>19</sup>F-NMR (376MHz, CDCl<sub>3</sub>)**3m**<sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)

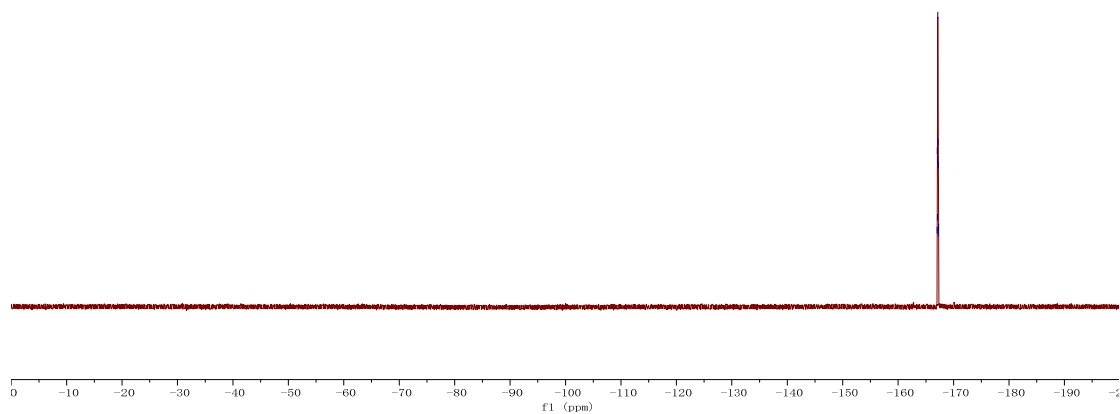




-167.03  
-167.05  
-167.08  
-167.13  
-167.16  
-167.18  
-167.24  
-167.28  
-167.29

**3o**

<sup>19</sup>F-NMR (376MHz, CDCl<sub>3</sub>)



172.97  
172.72

144.68

132.05  
128.70  
128.26

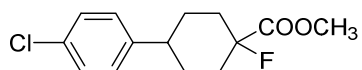
94.11  
92.26

77.48  
77.46  
76.84

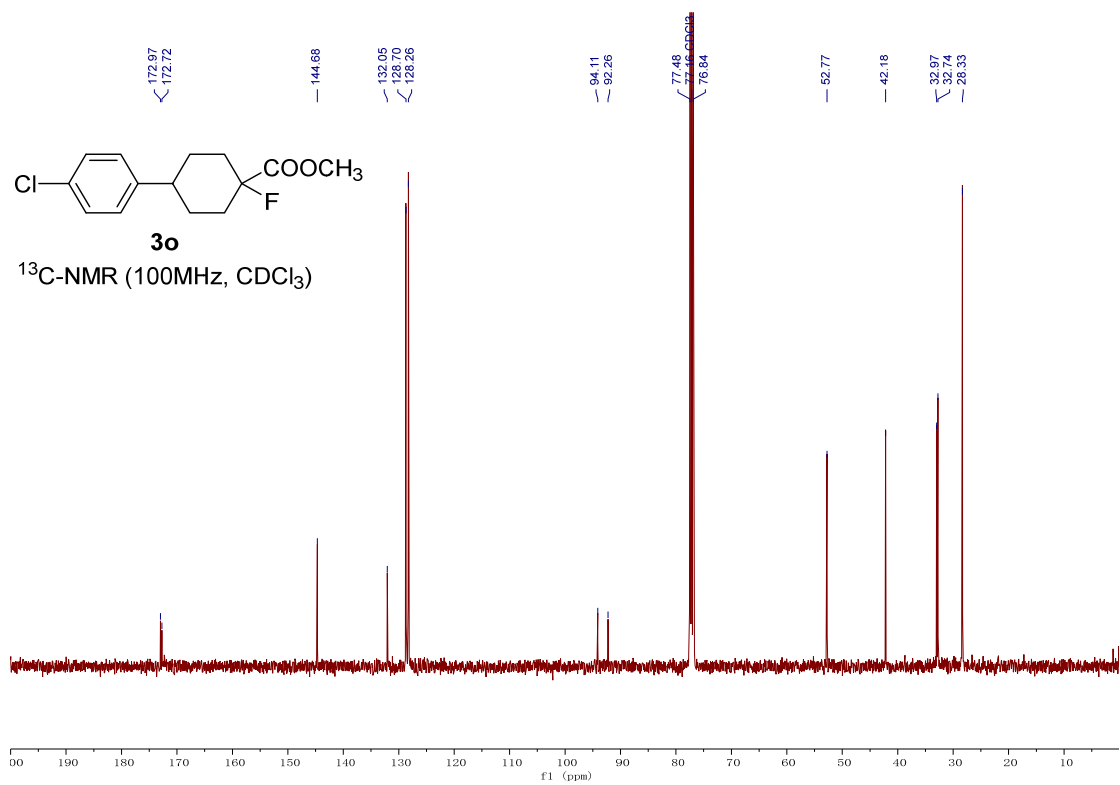
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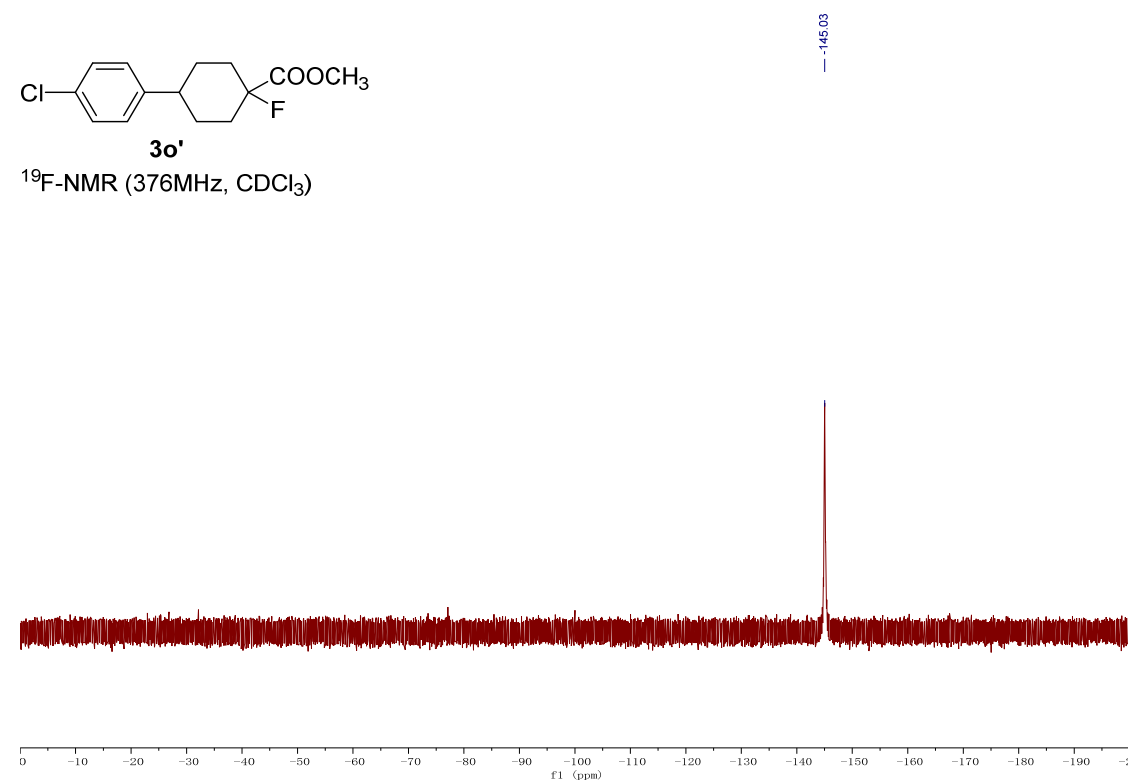
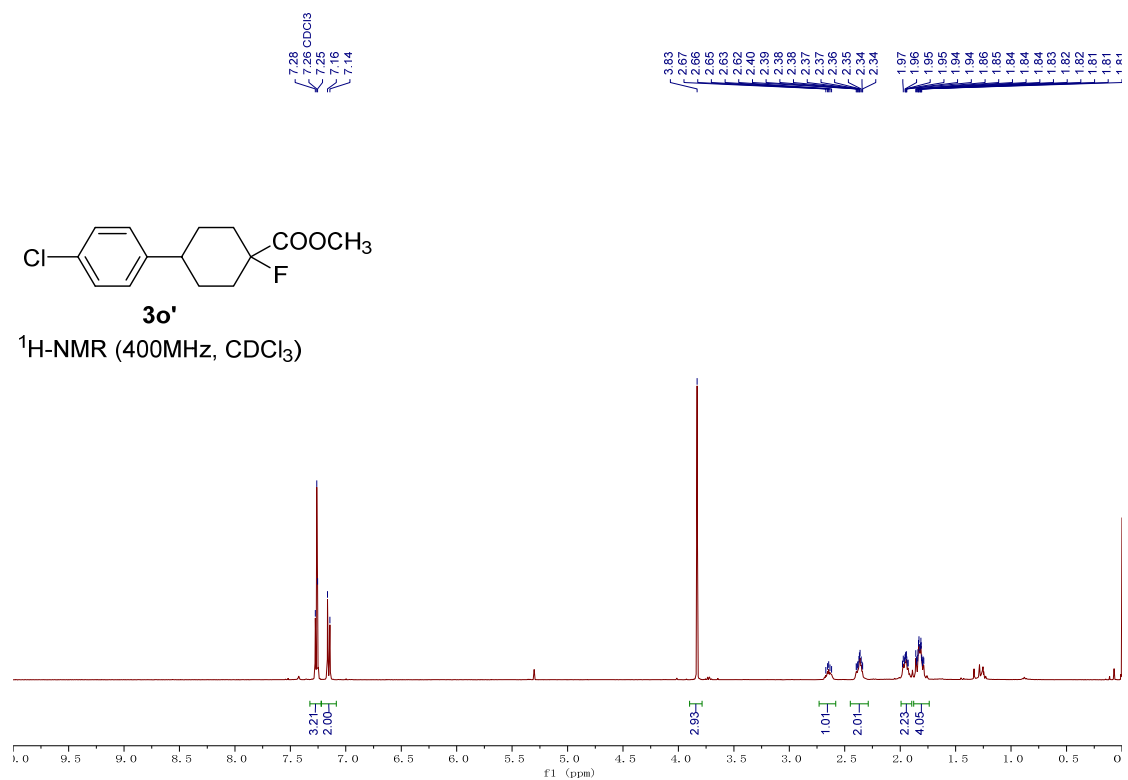
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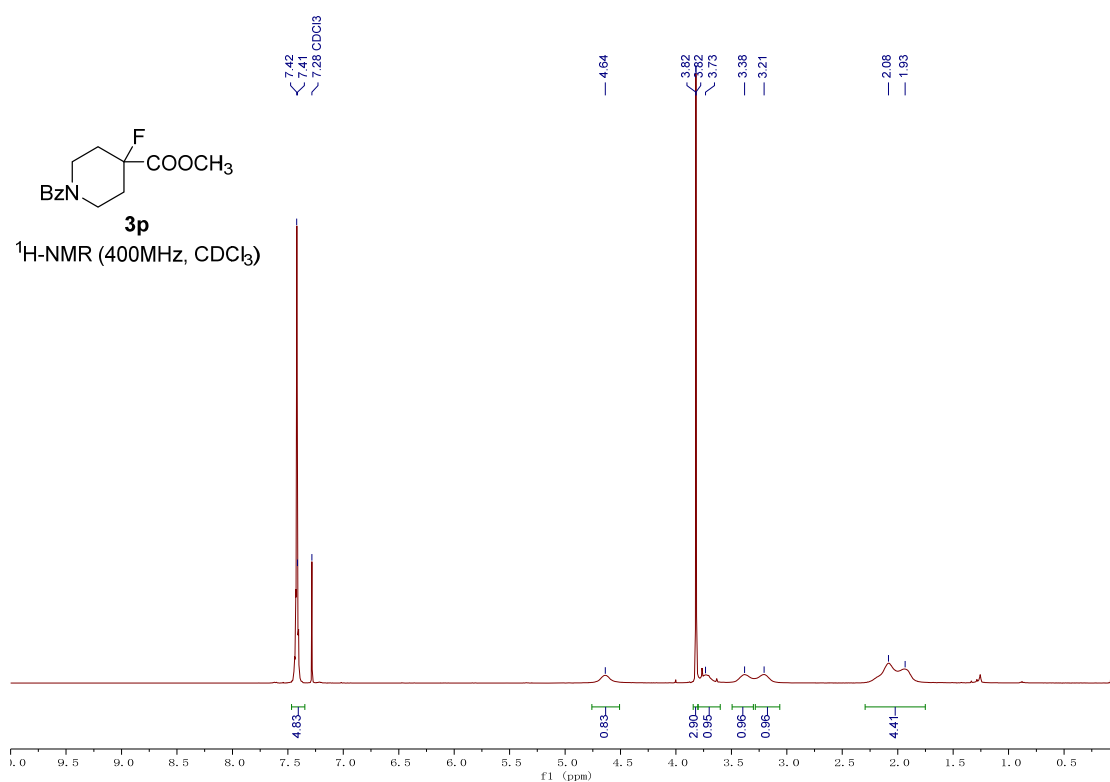
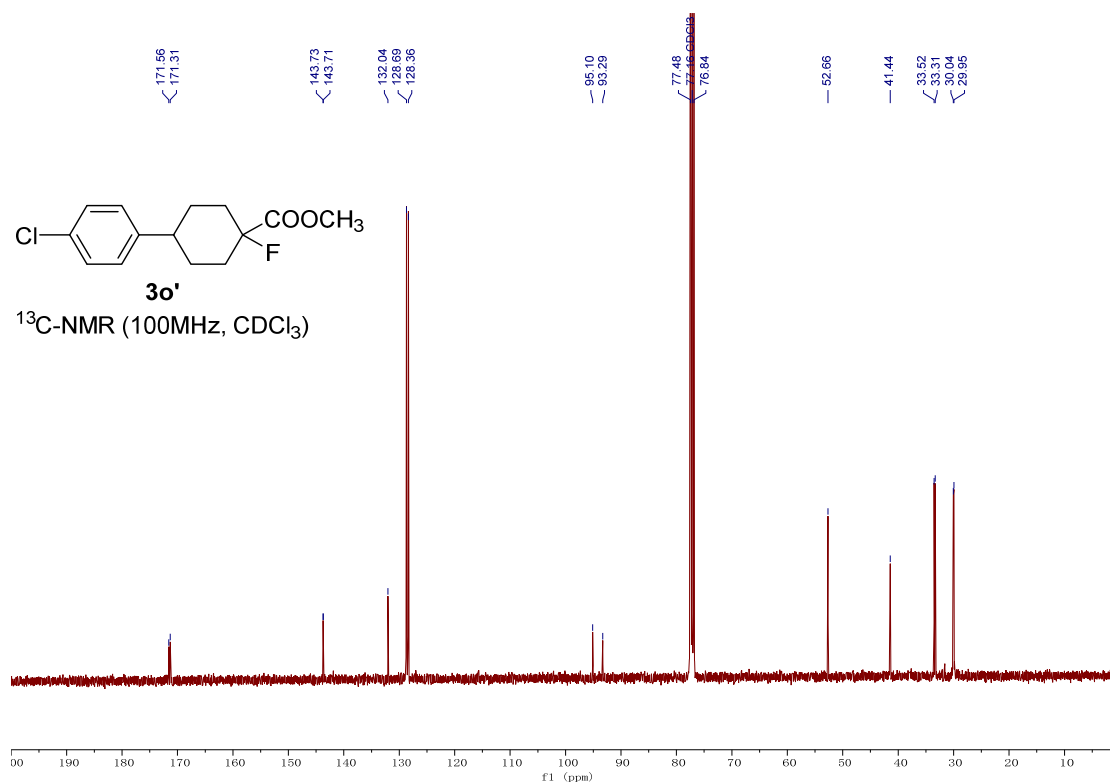
32.97  
32.74  
28.55

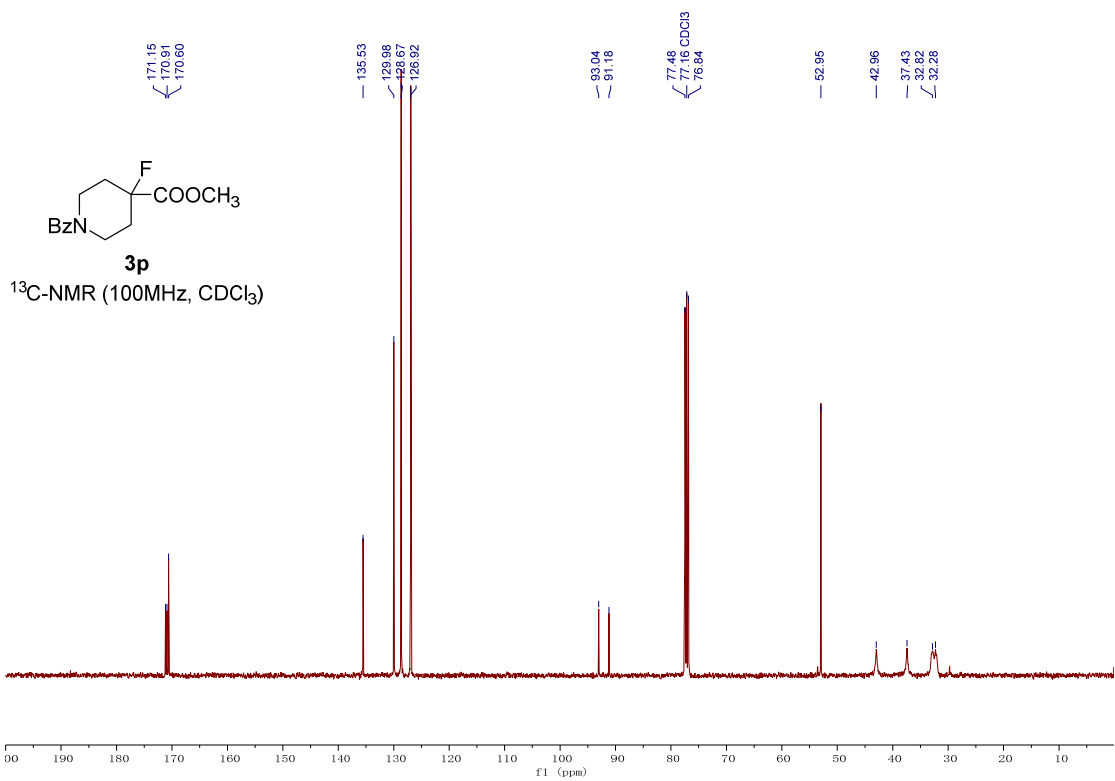
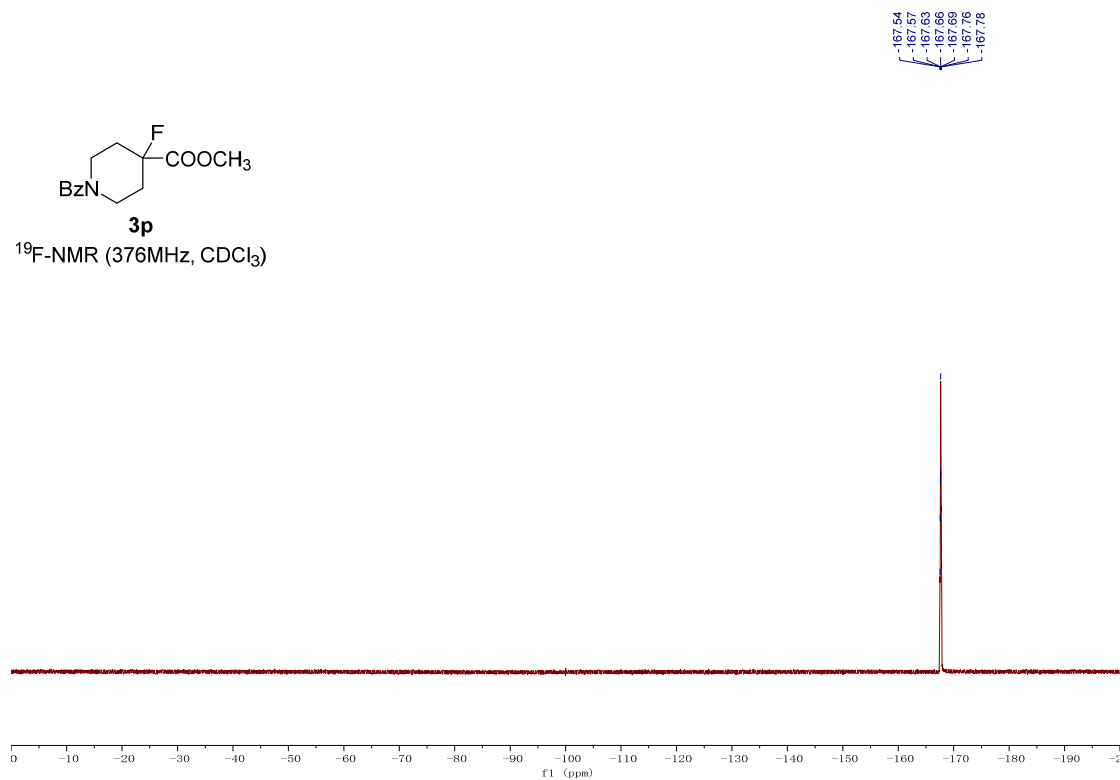
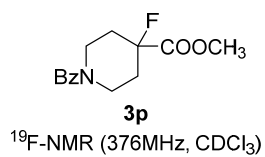
**3o**

<sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>)

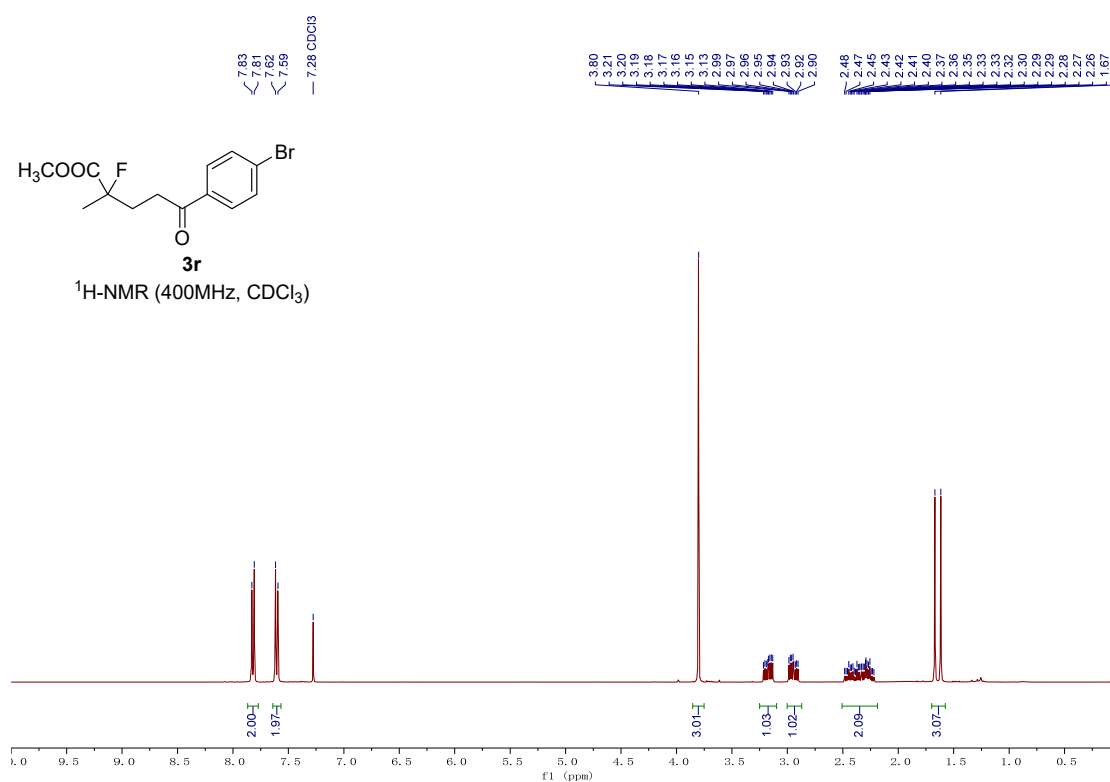
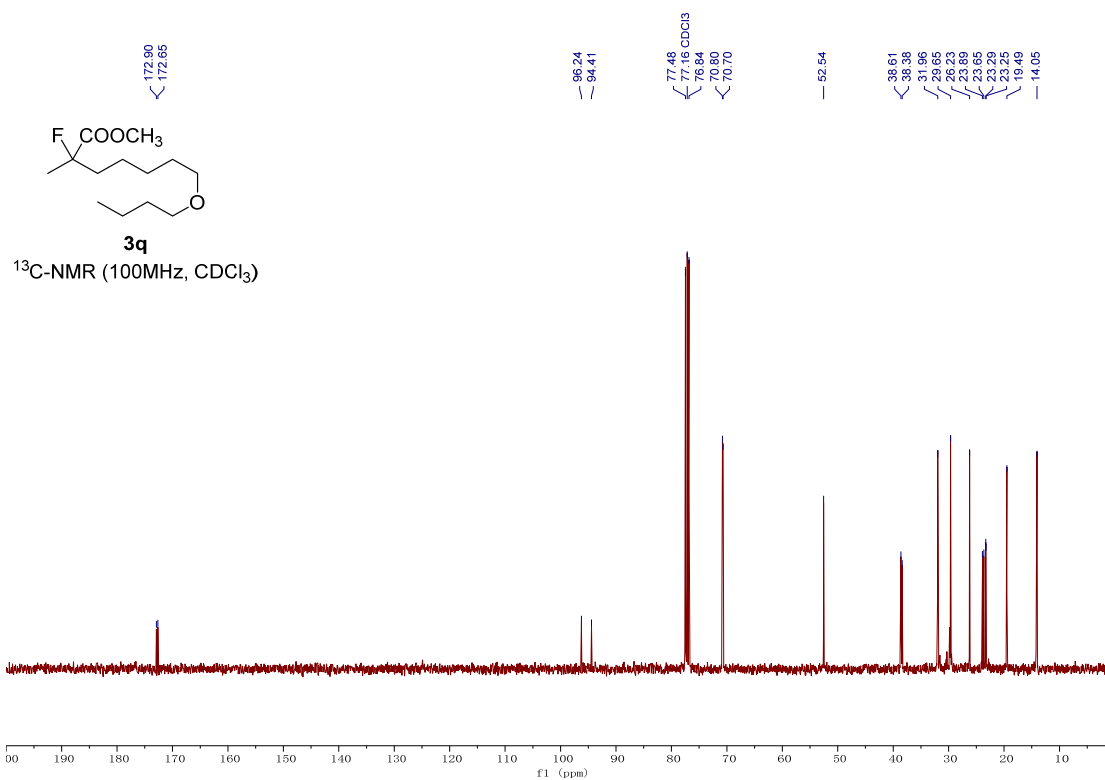


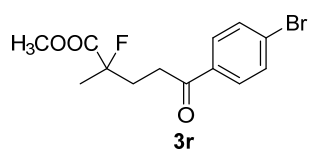




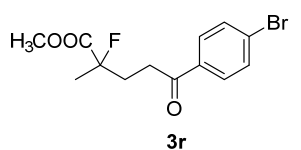
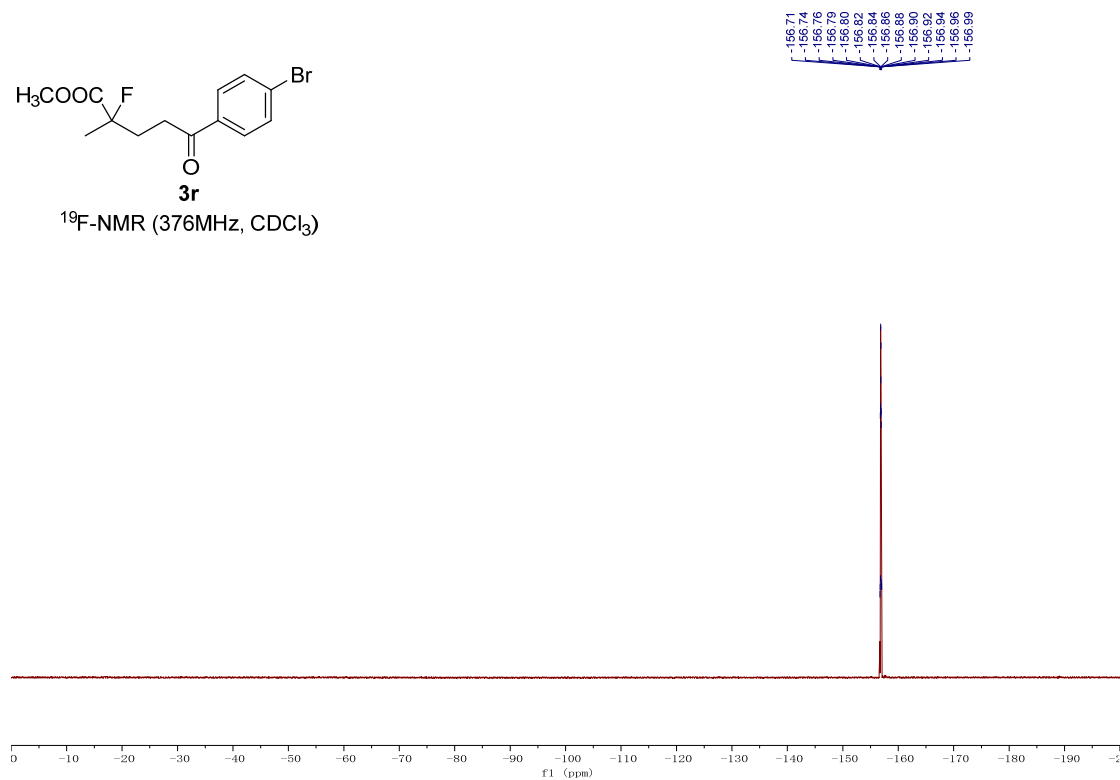




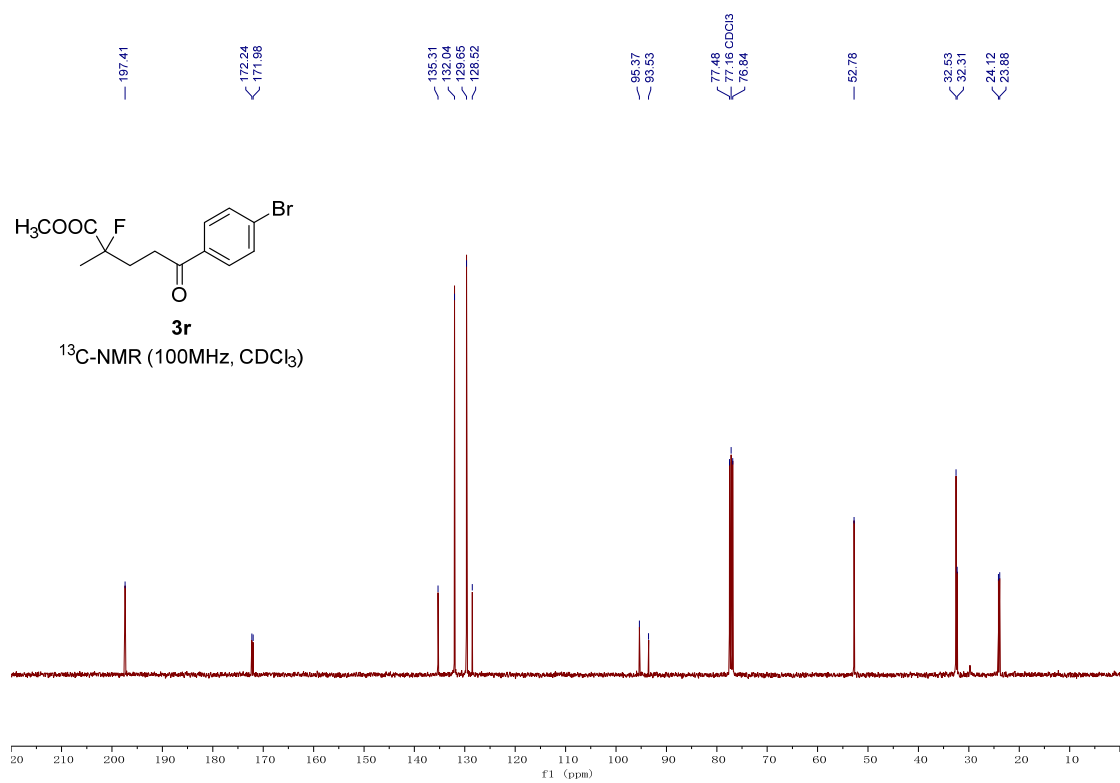


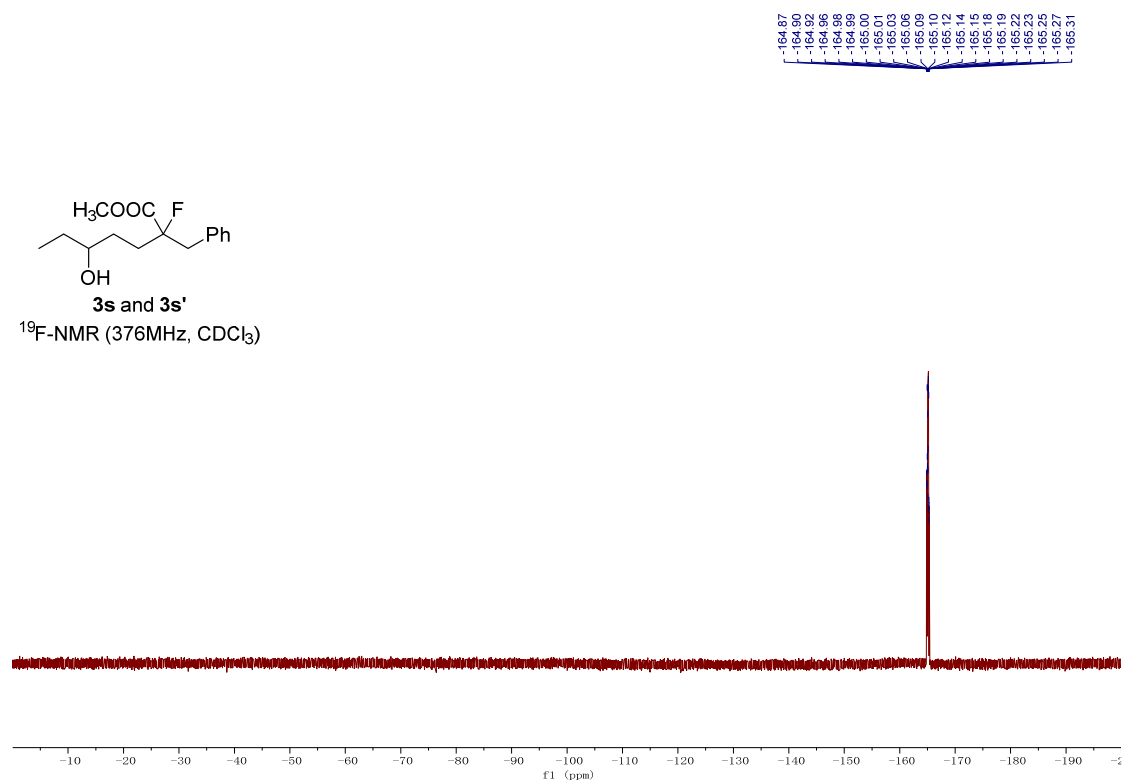
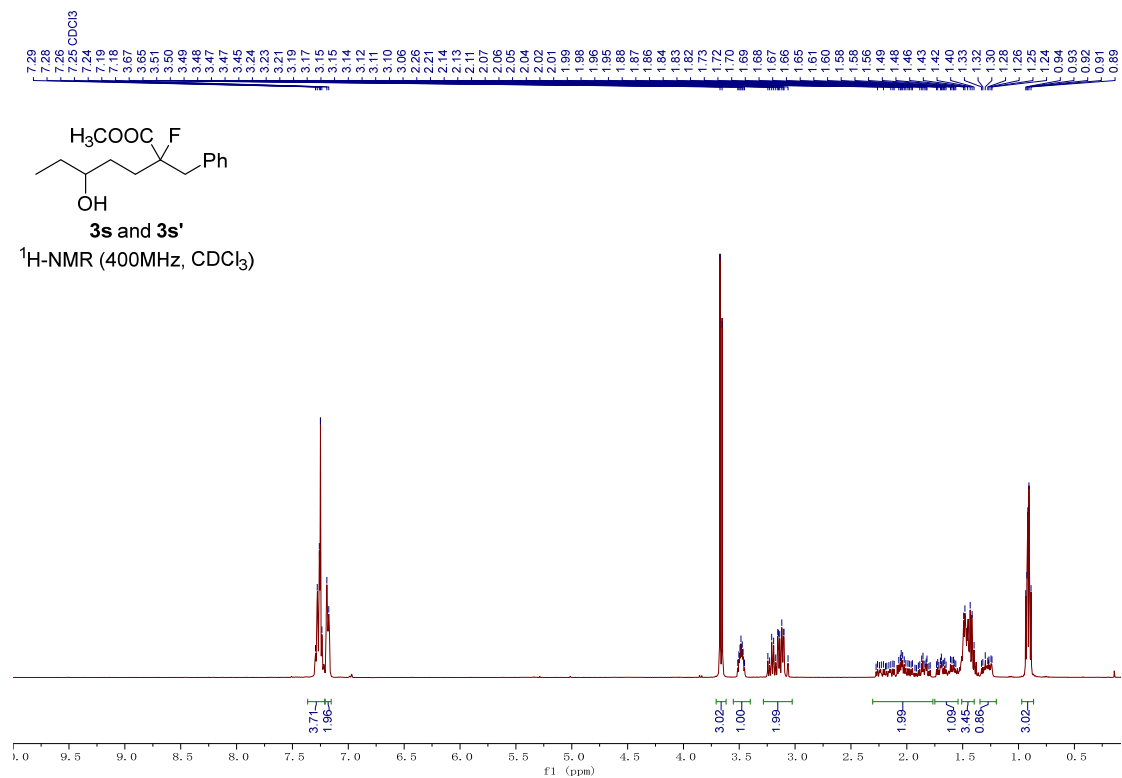


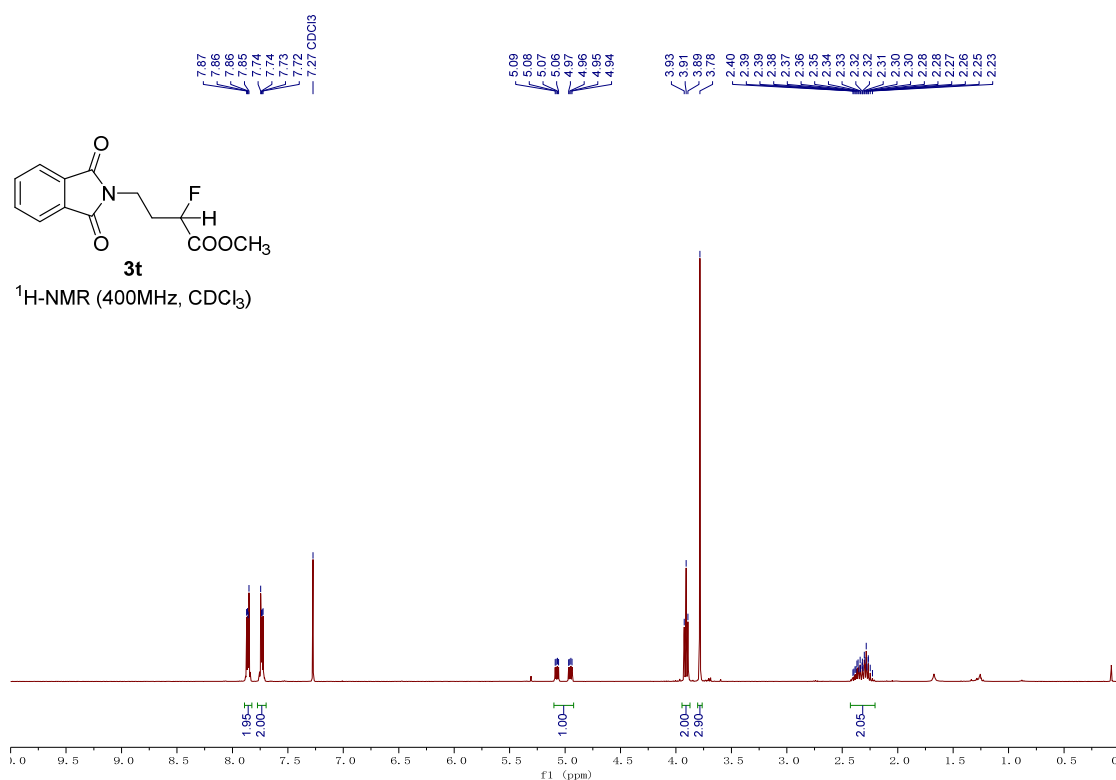
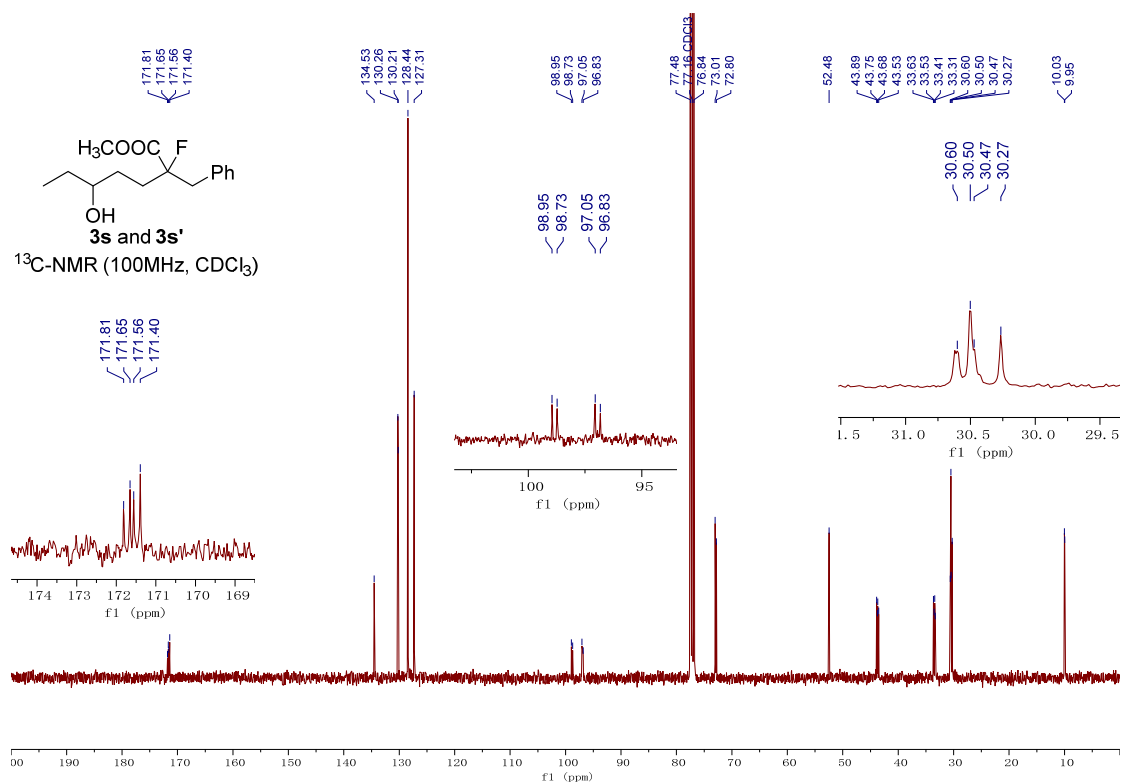
$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )

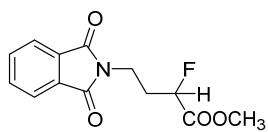


$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

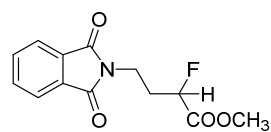
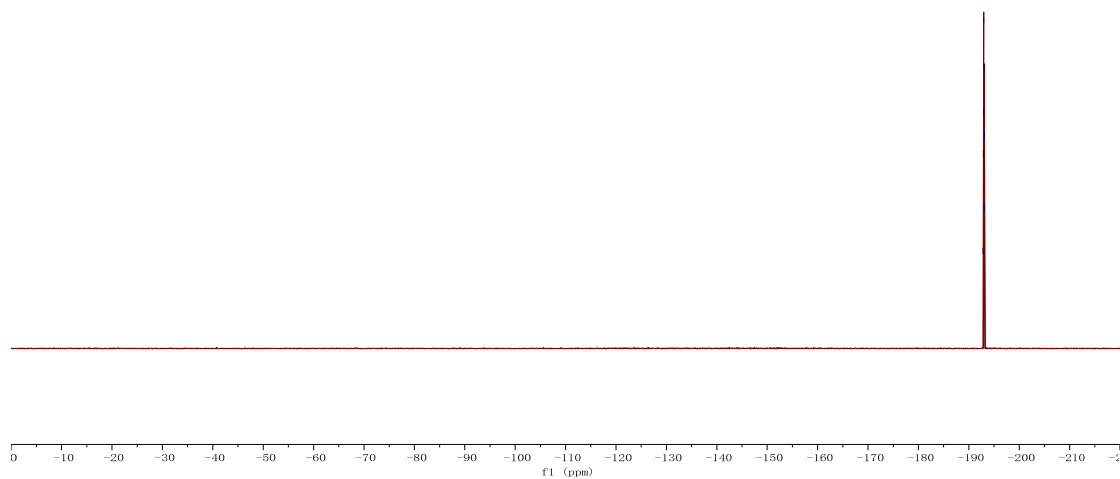




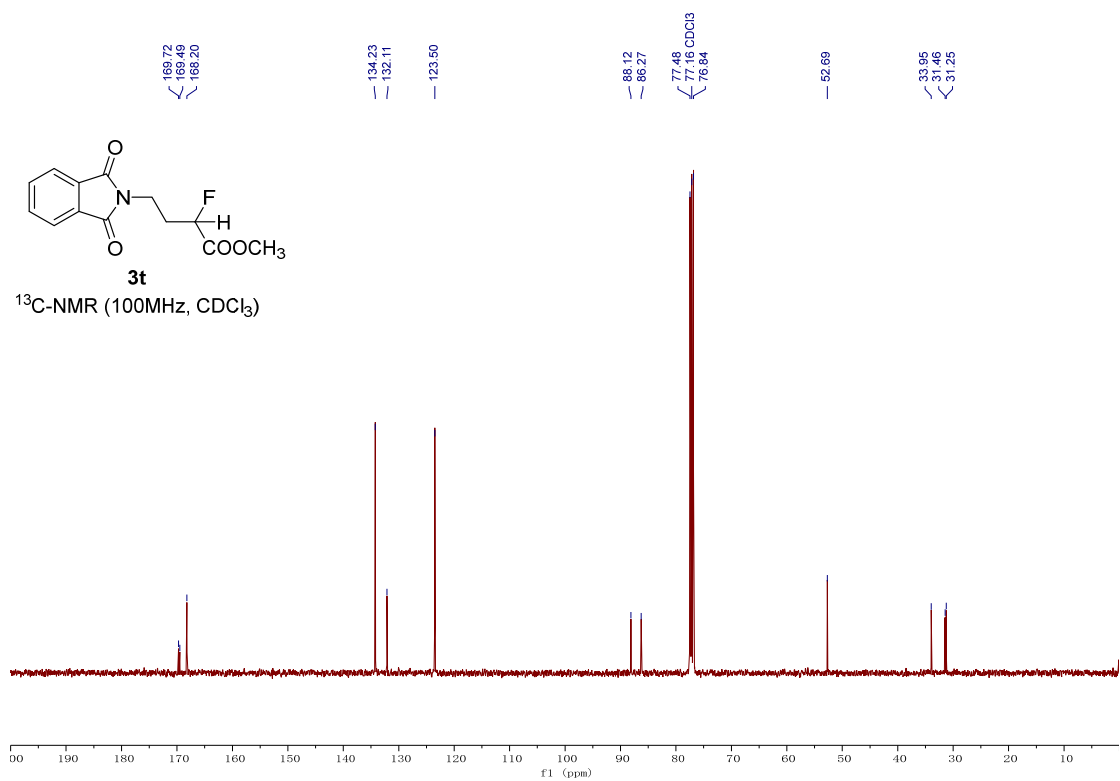


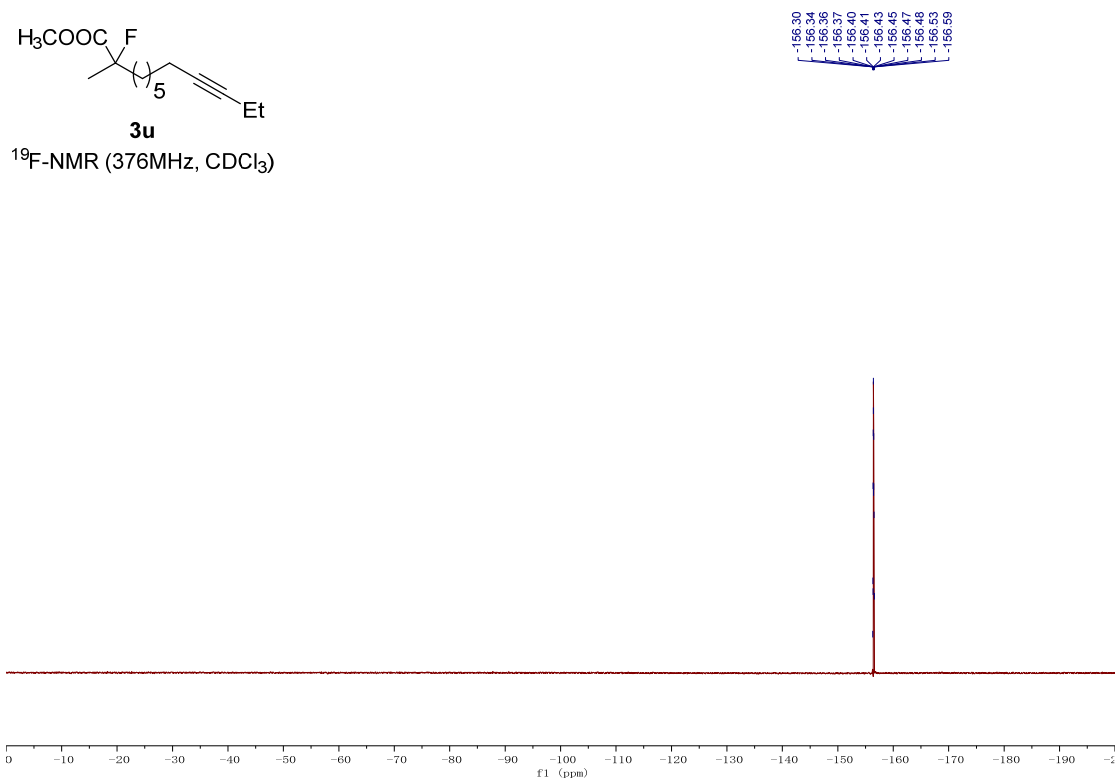
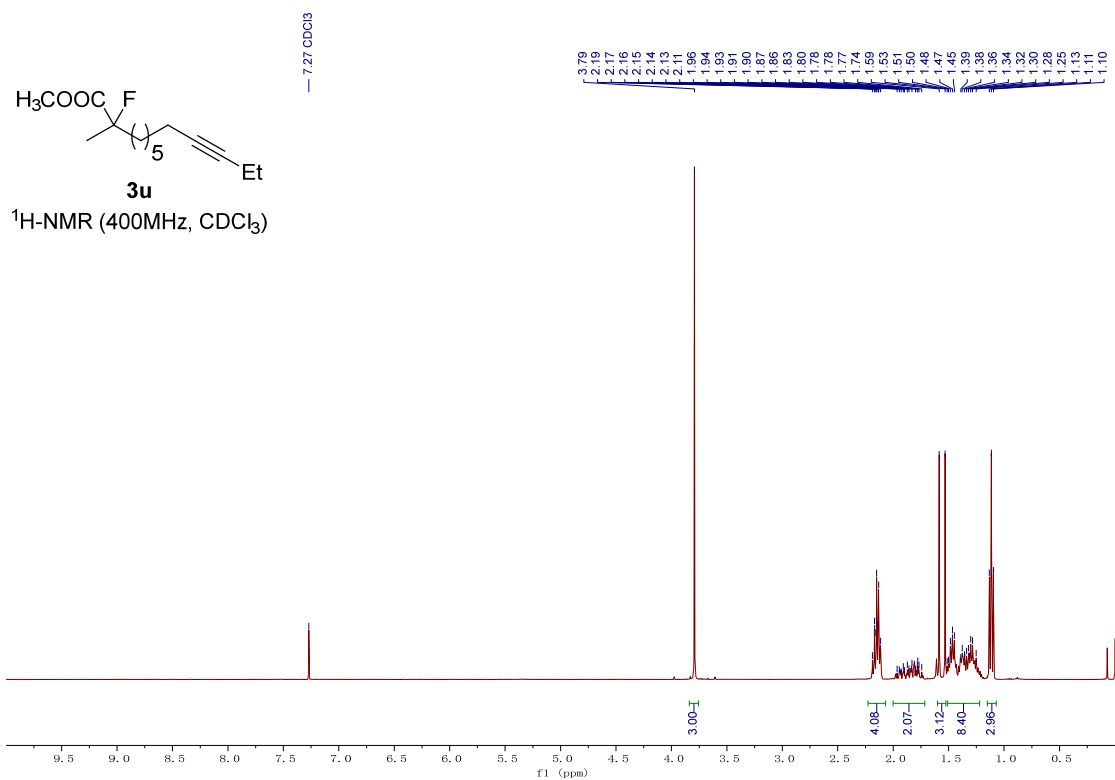


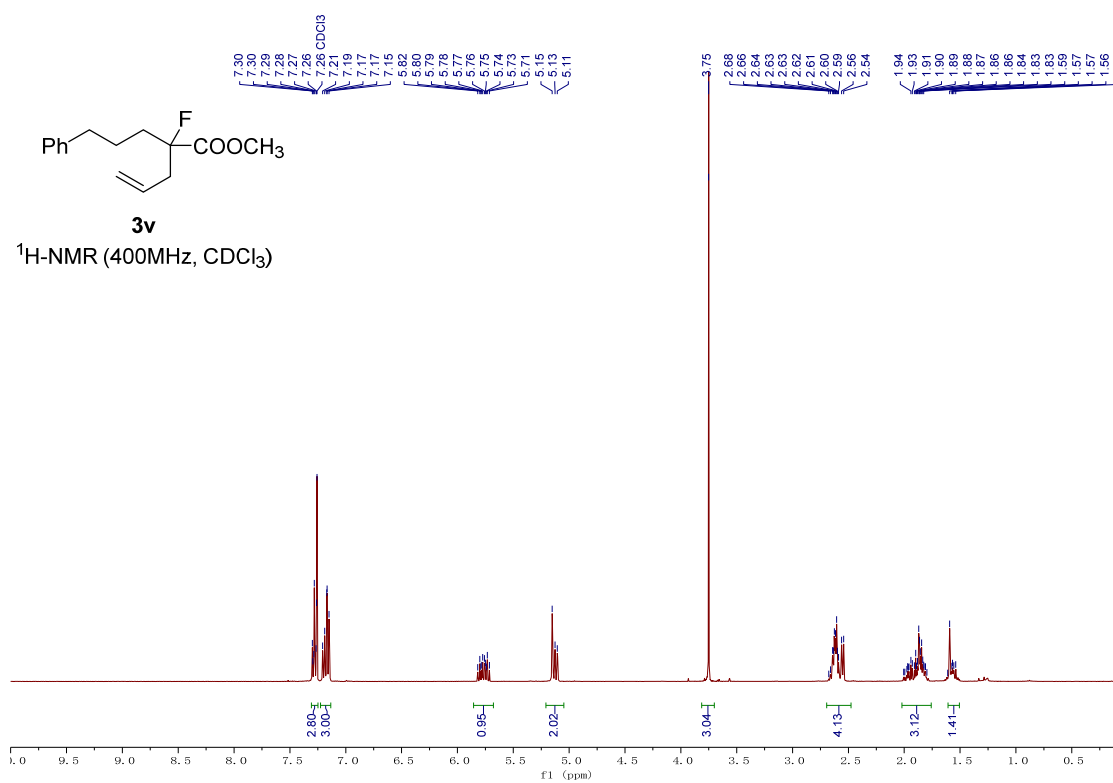
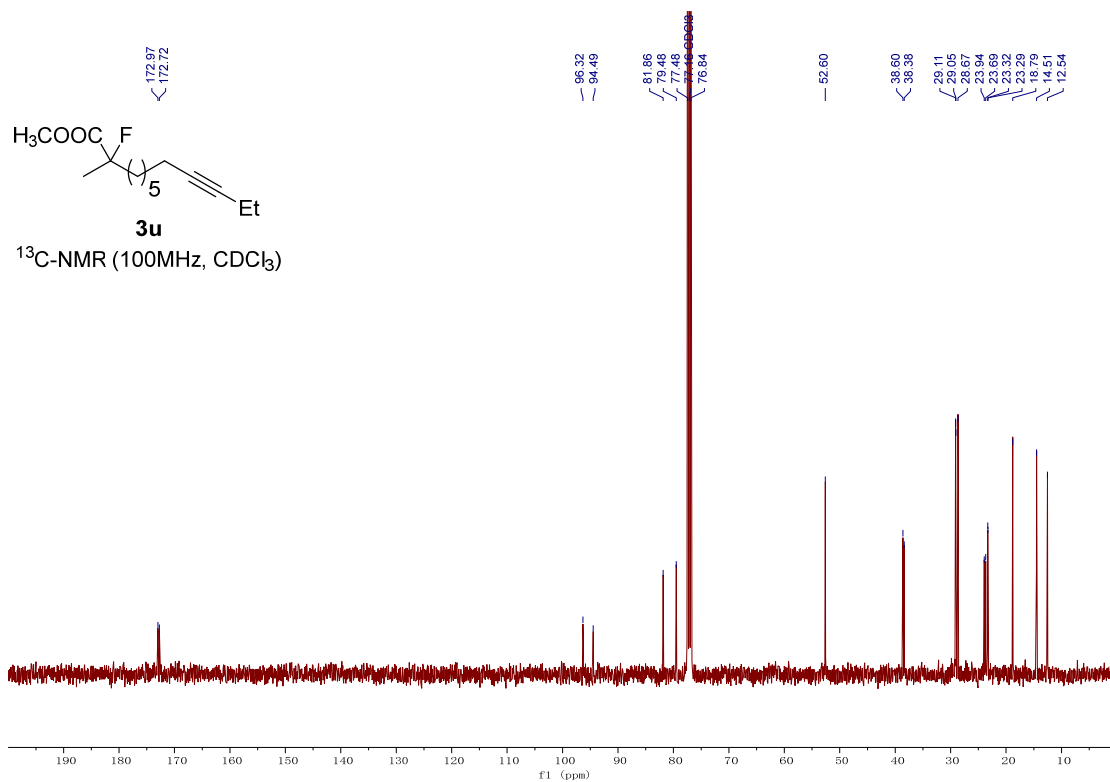
$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )

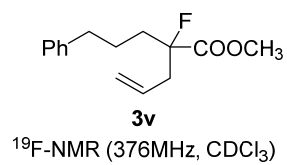


$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

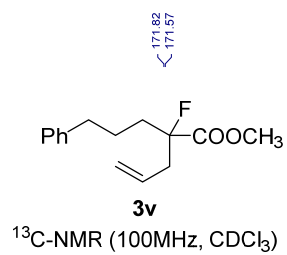
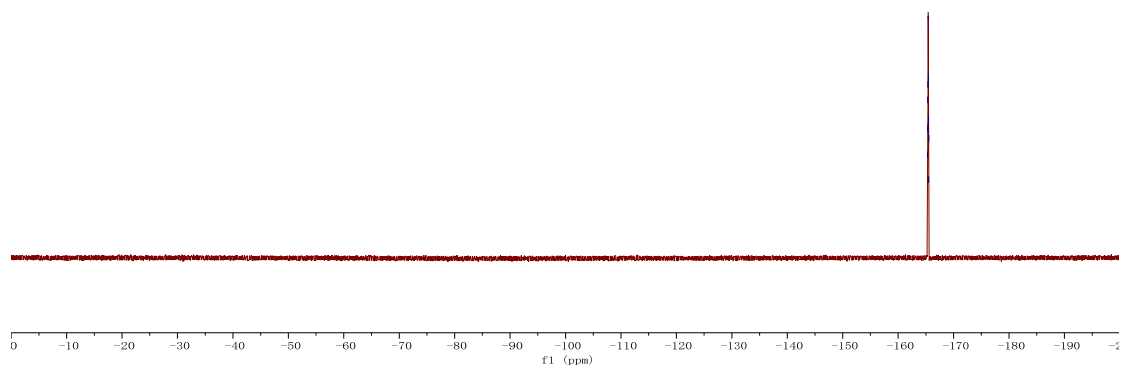








-165.30  
-165.34  
-165.35  
-165.37  
-165.39  
-165.41  
-165.41  
-165.48  
-165.49  
-165.53



171.82  
171.57

141.63

130.84

128.49

126.07

119.81

98.44

96.96

77.48  
77.16  
76.84

52.49

41.96

41.74

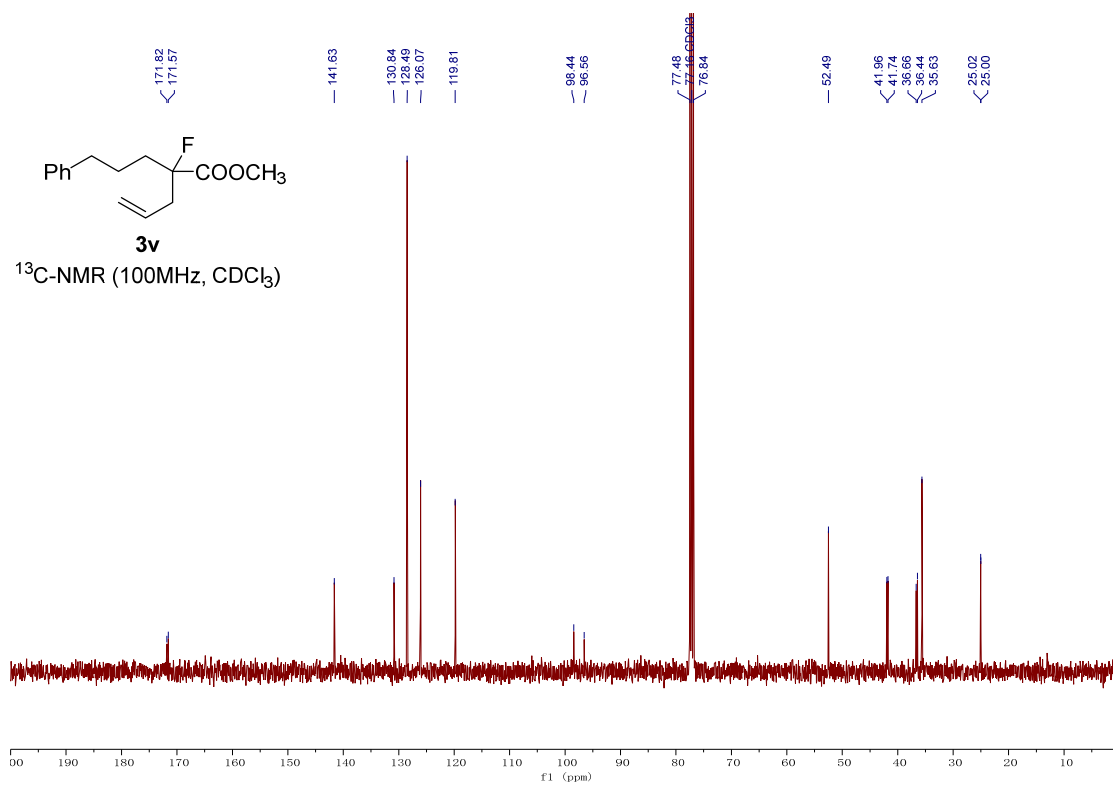
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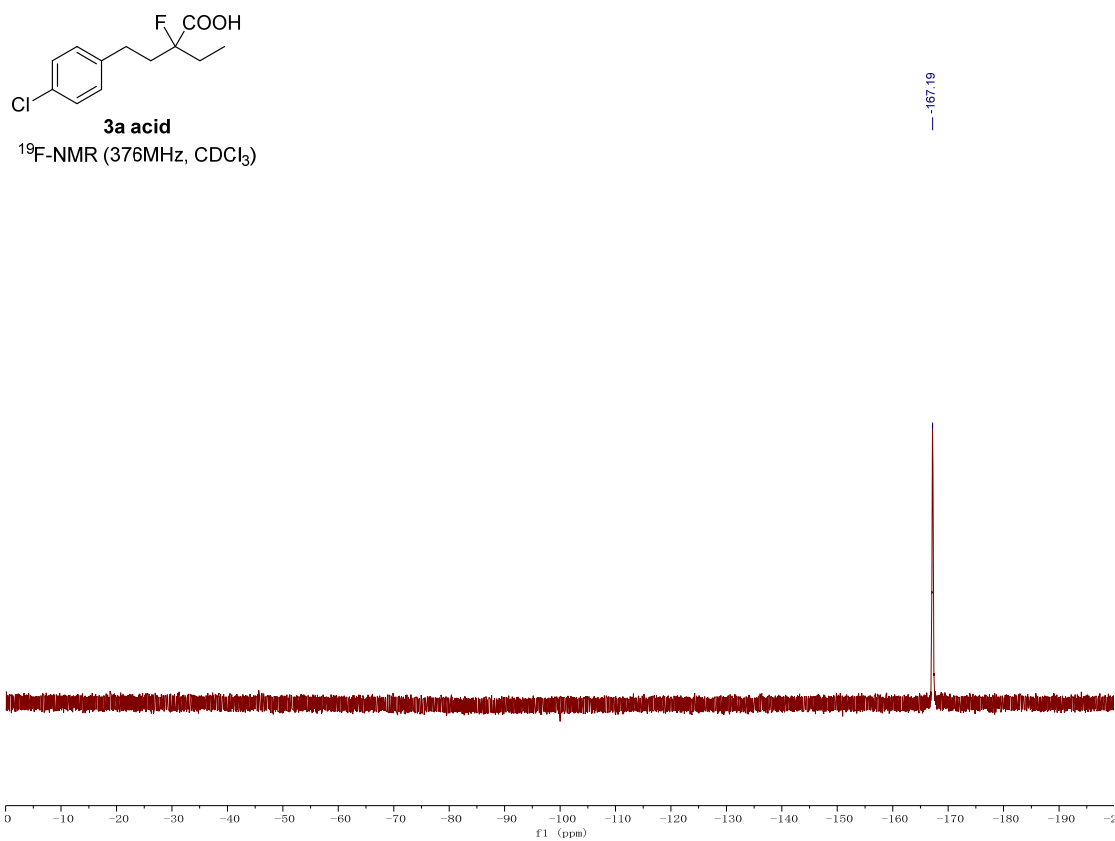
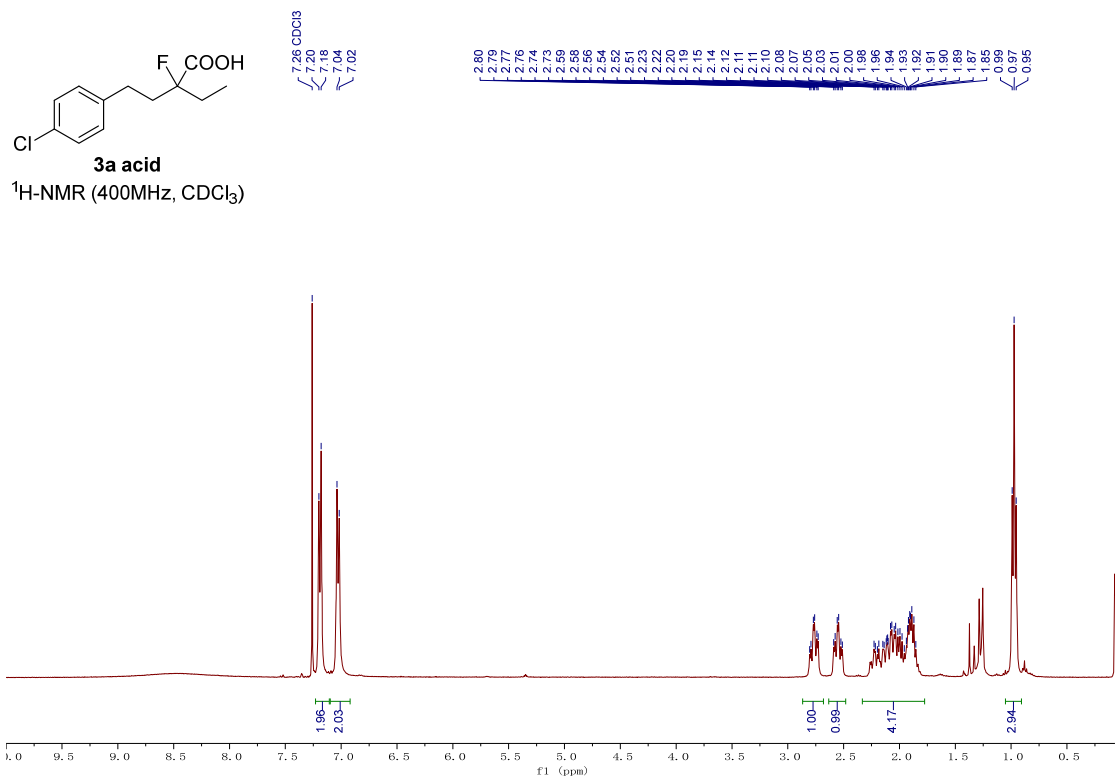
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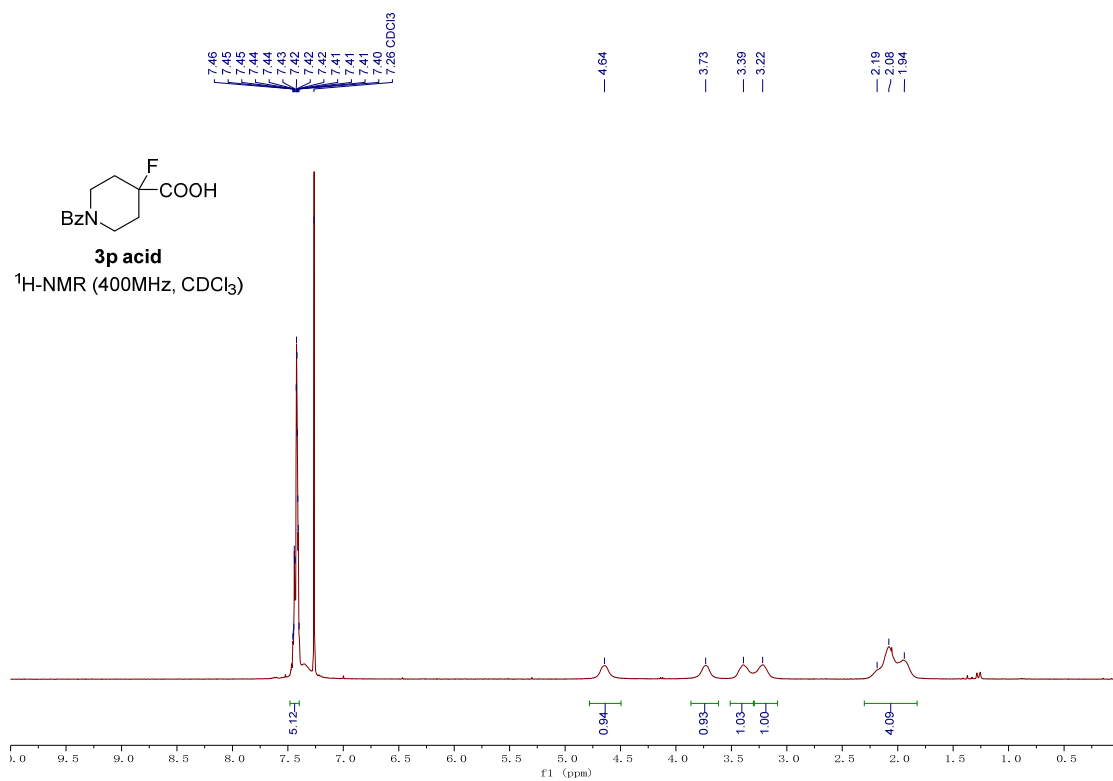
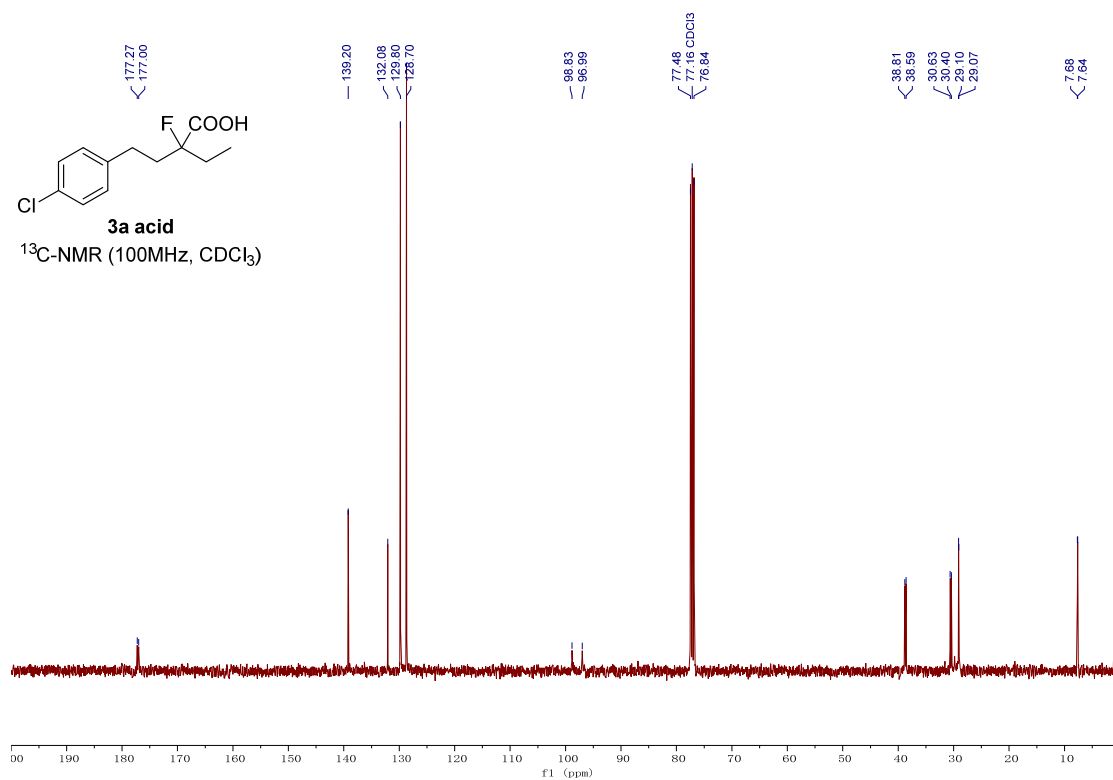
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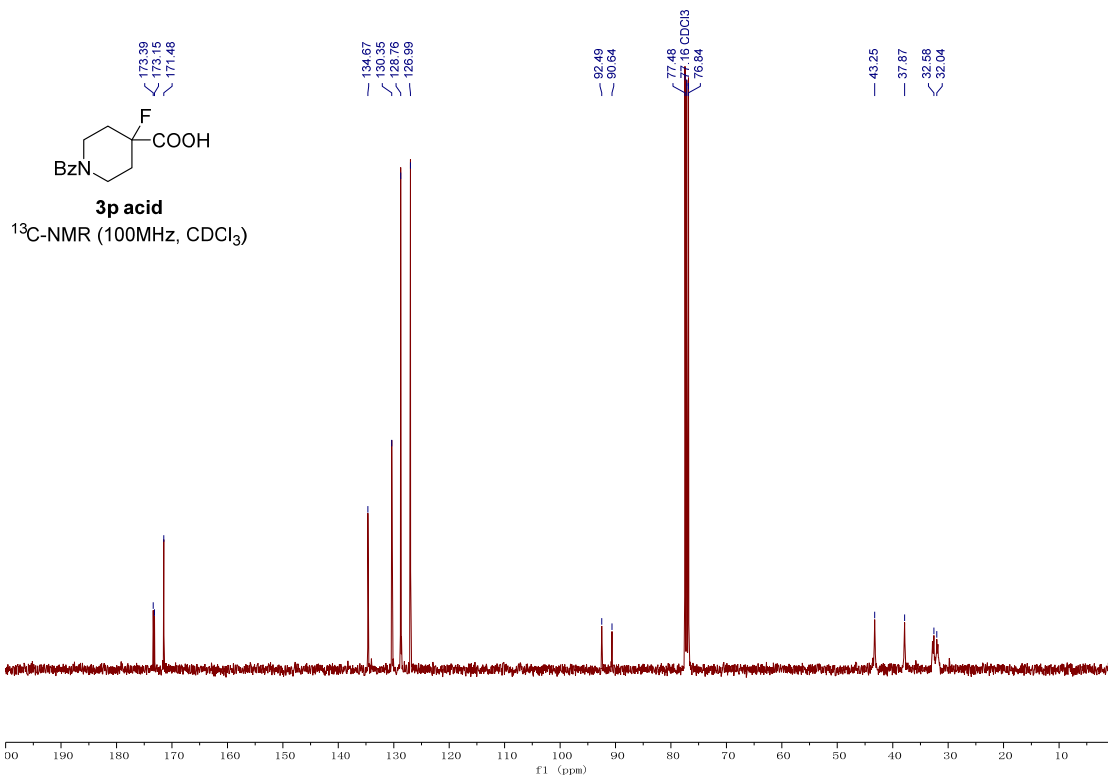
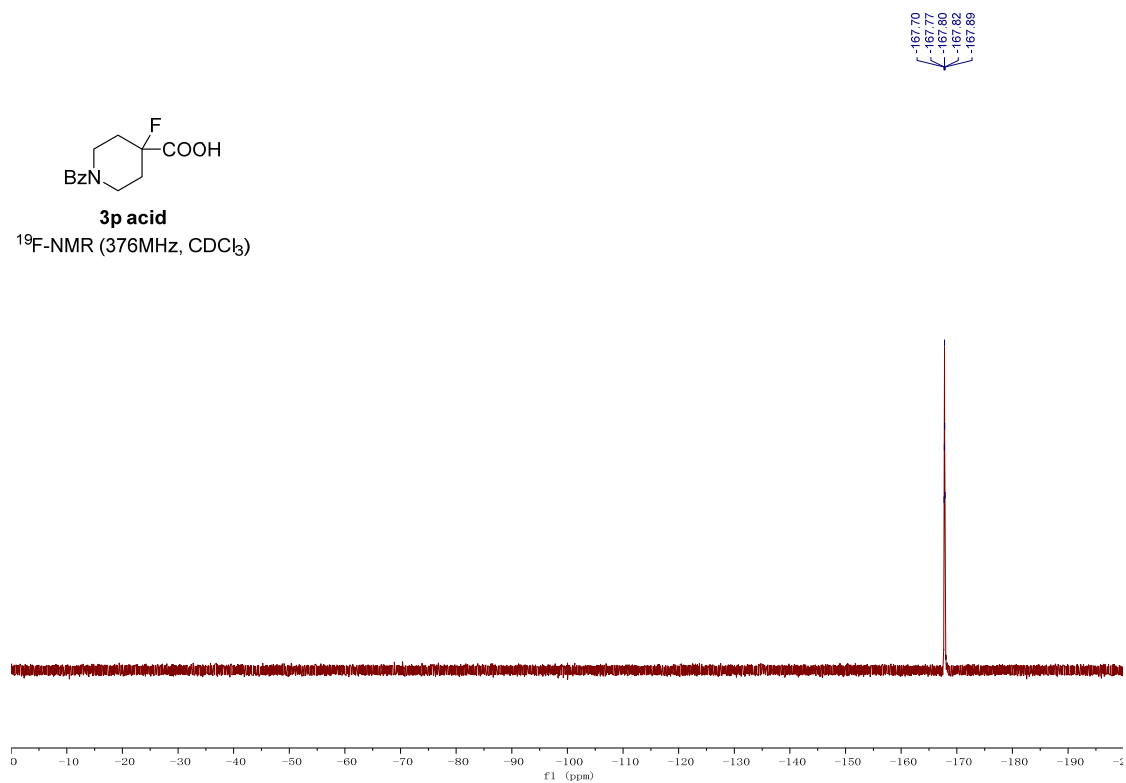
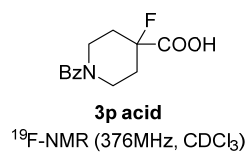
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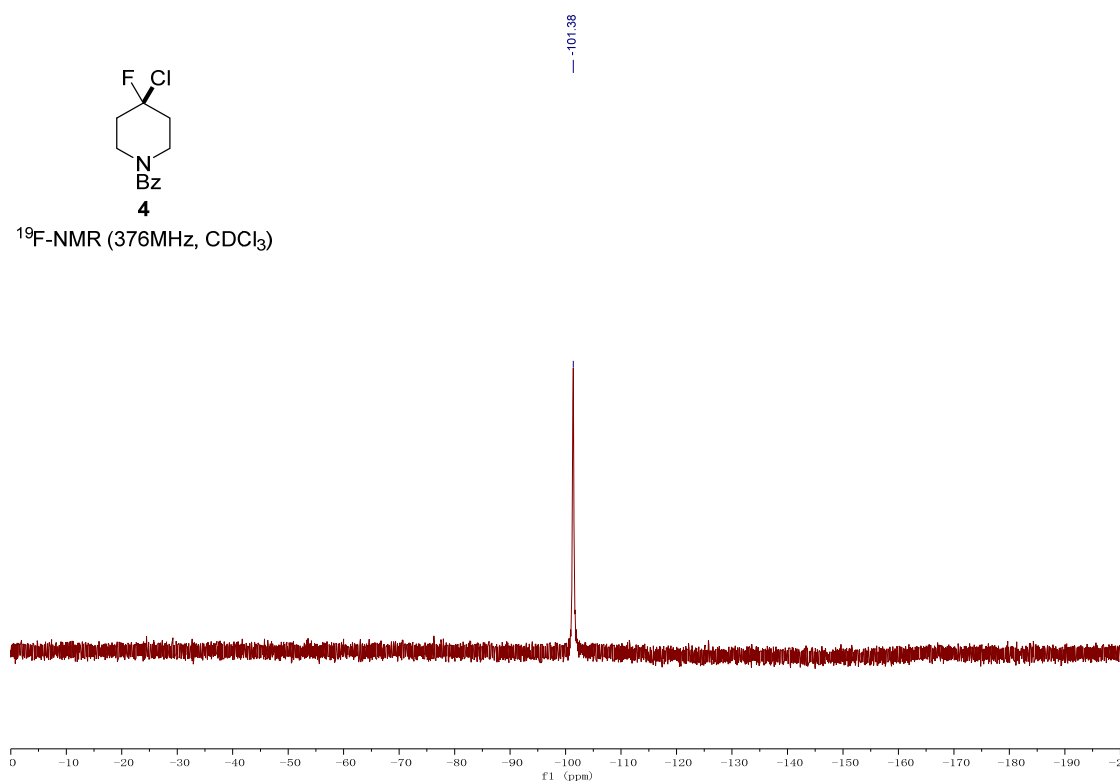
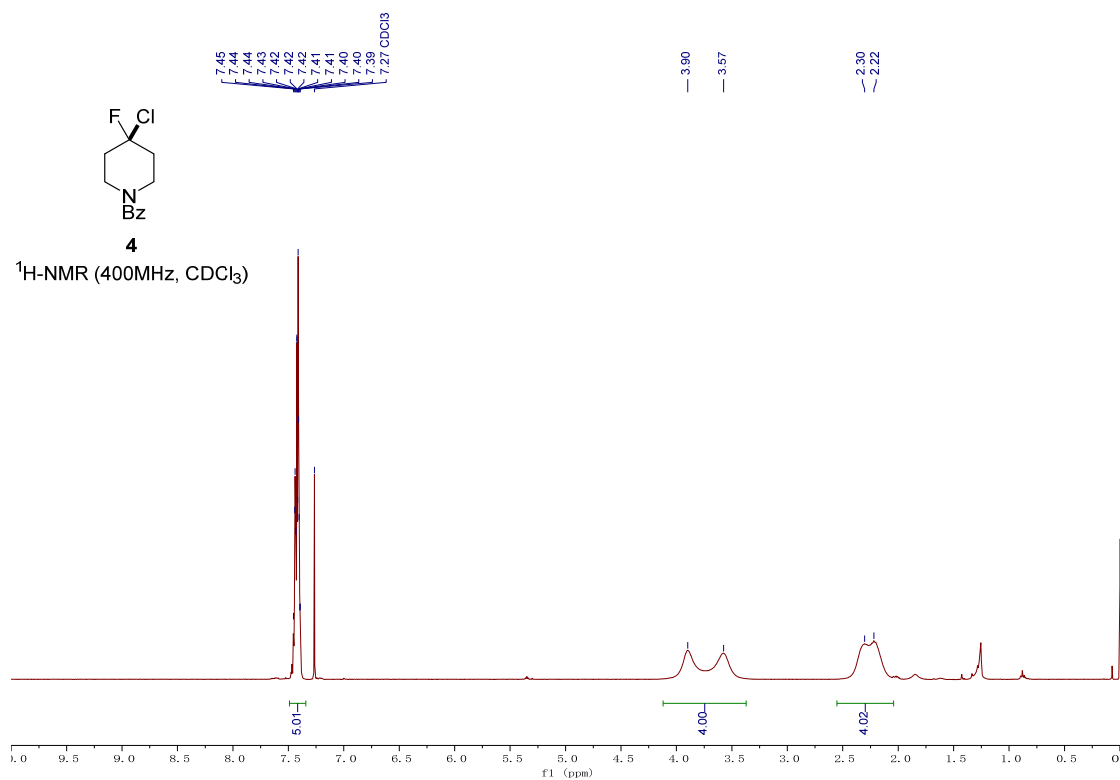
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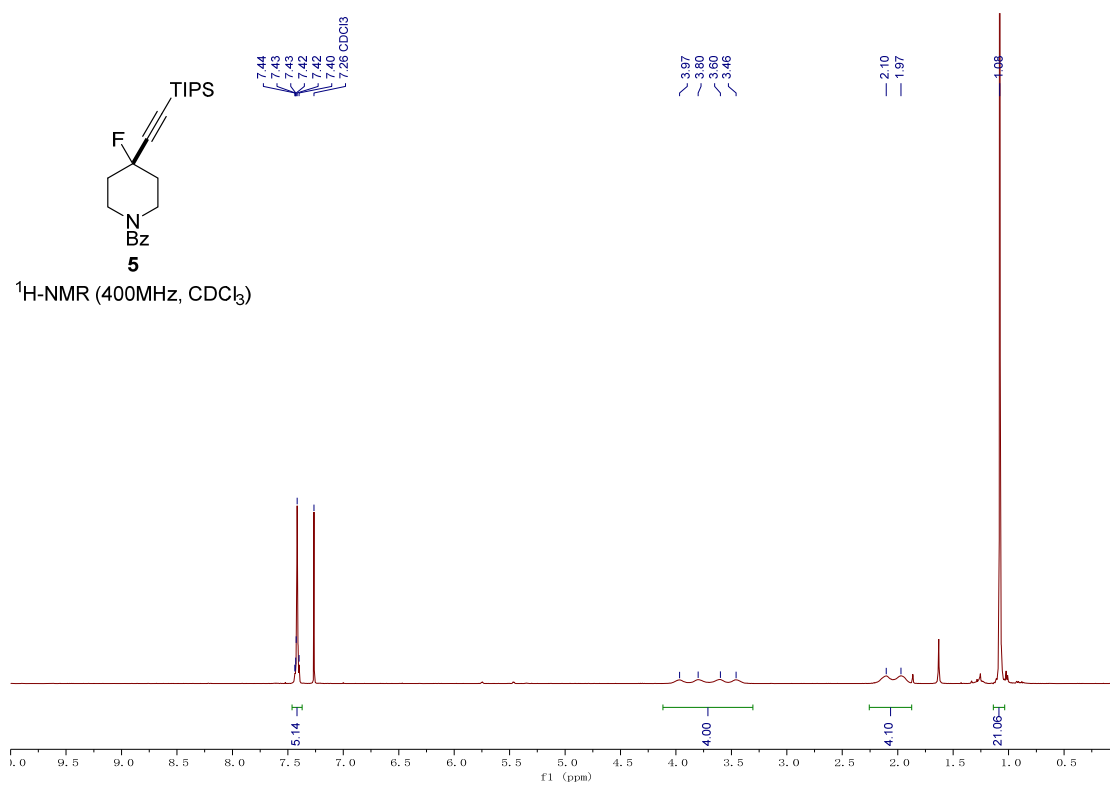
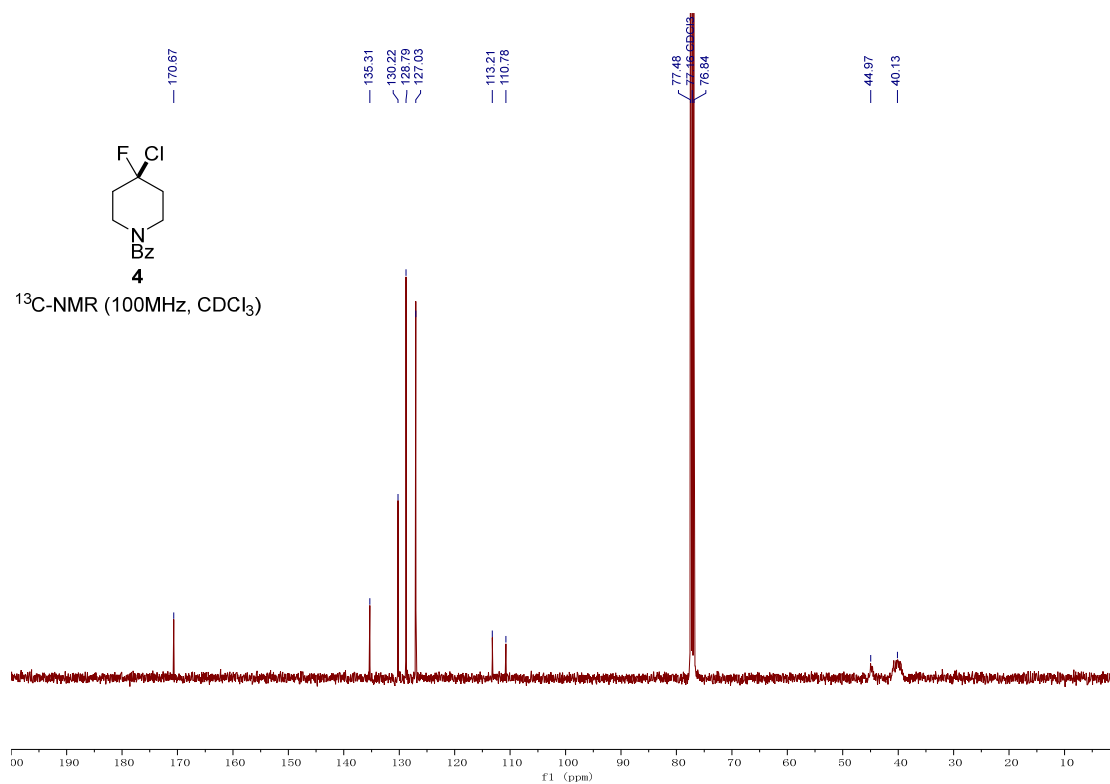


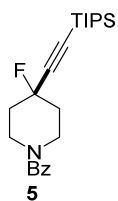




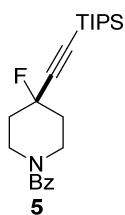
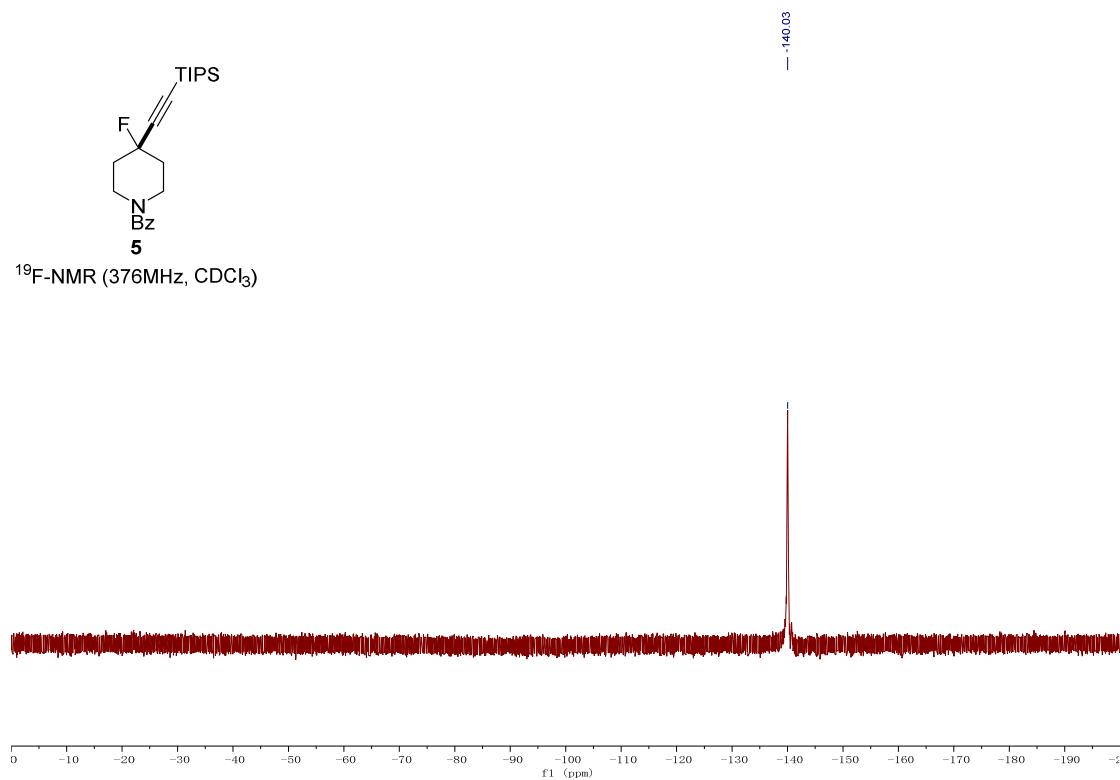




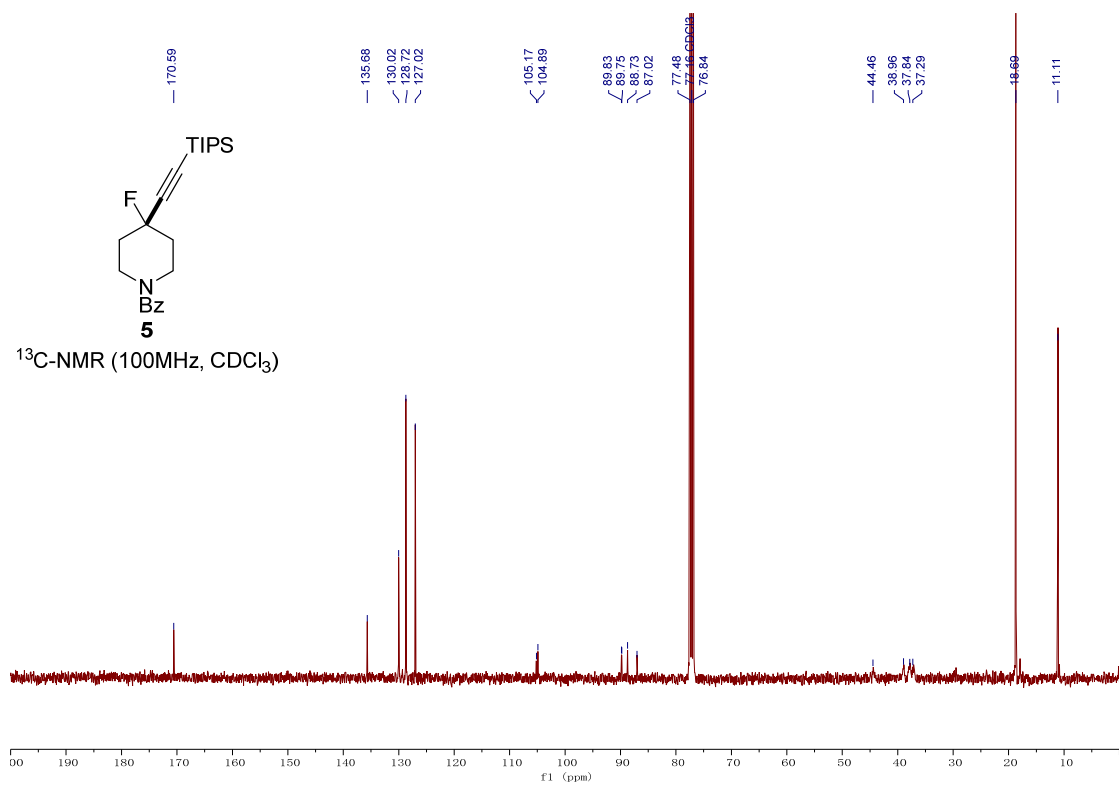


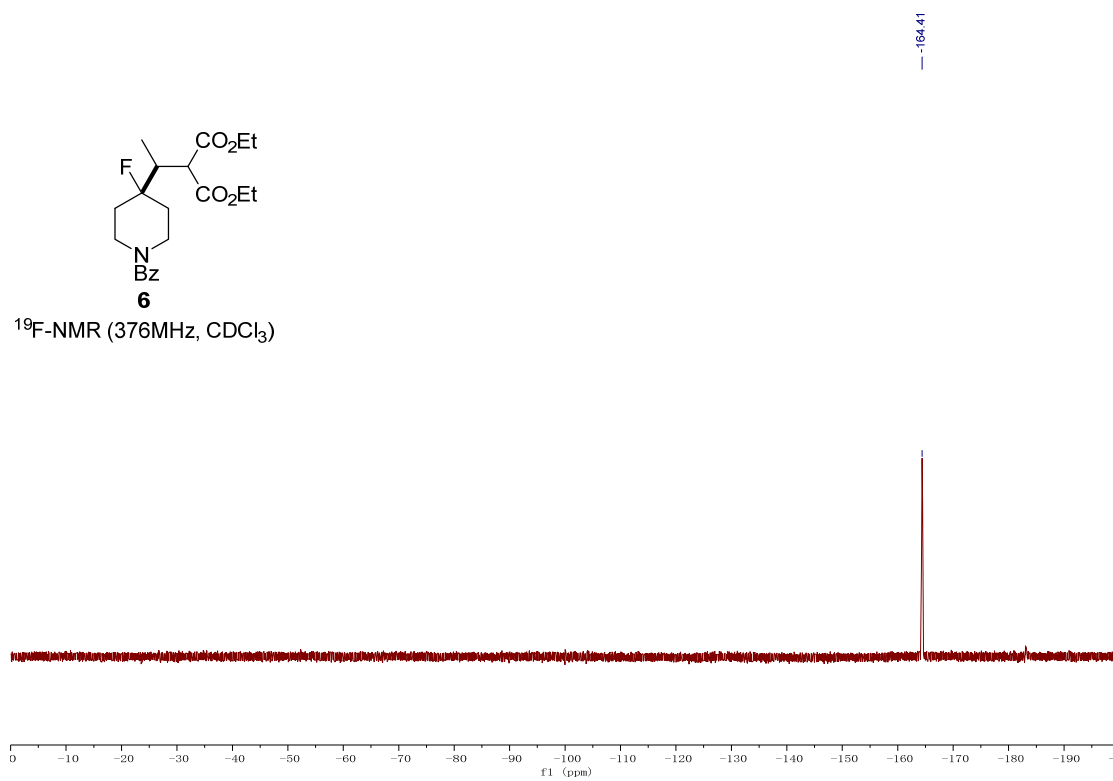
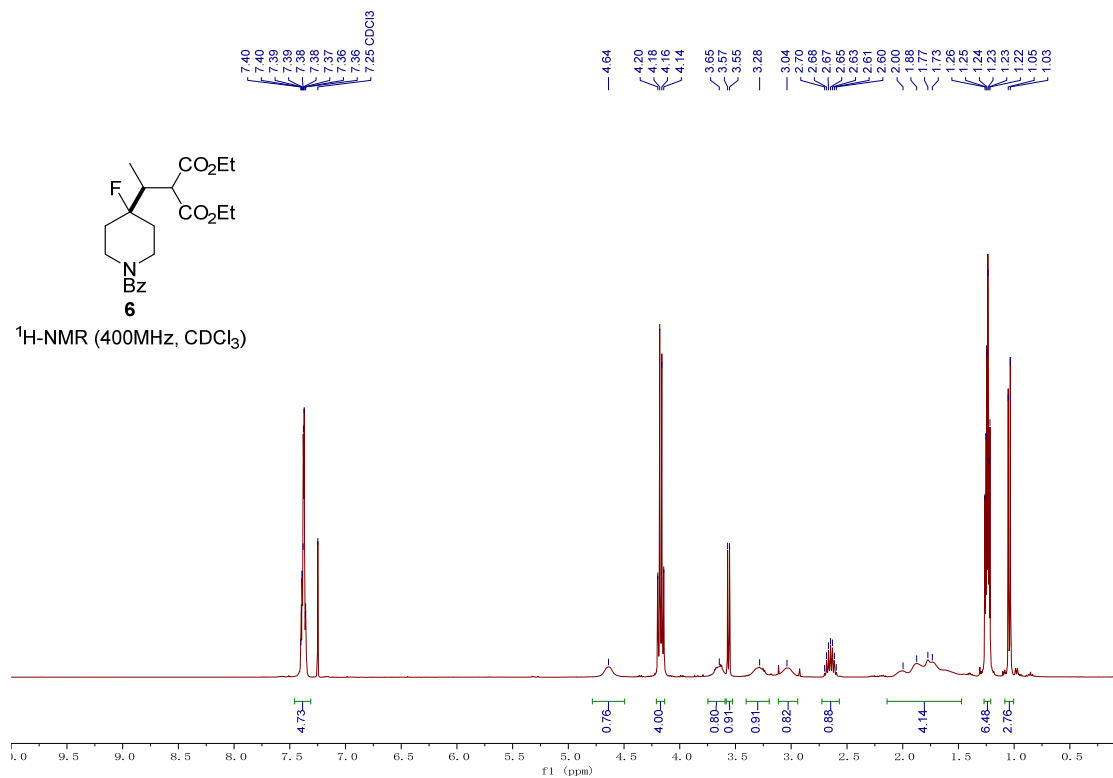


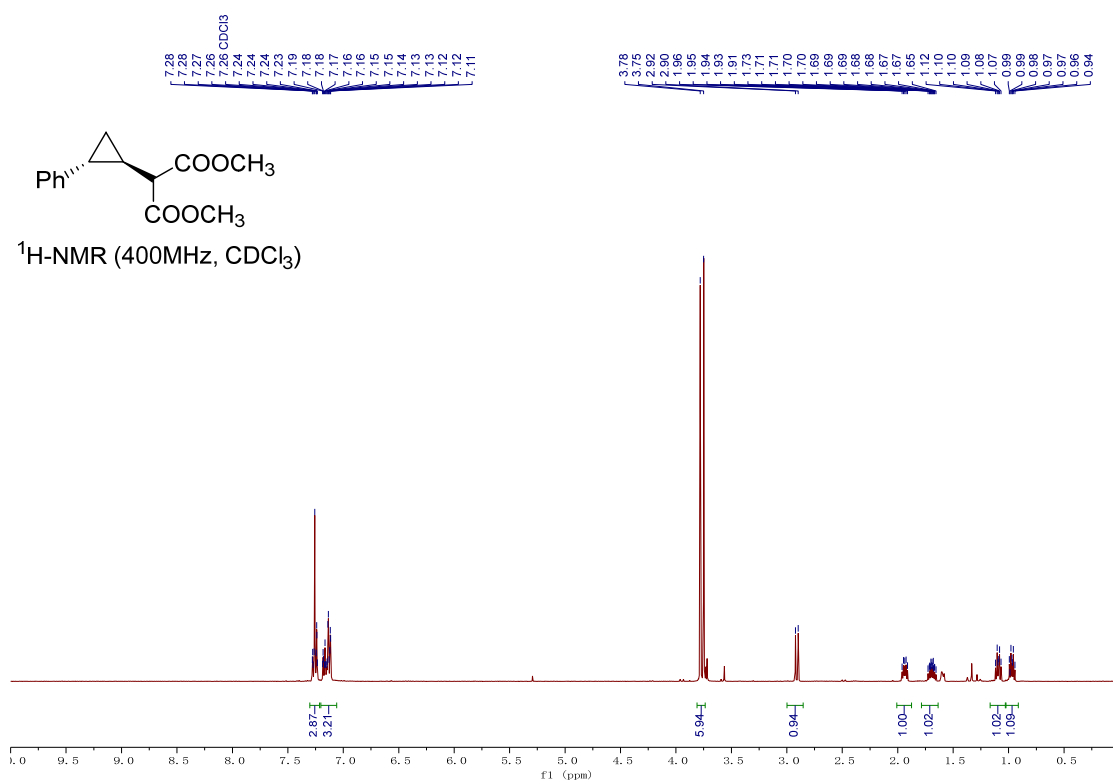
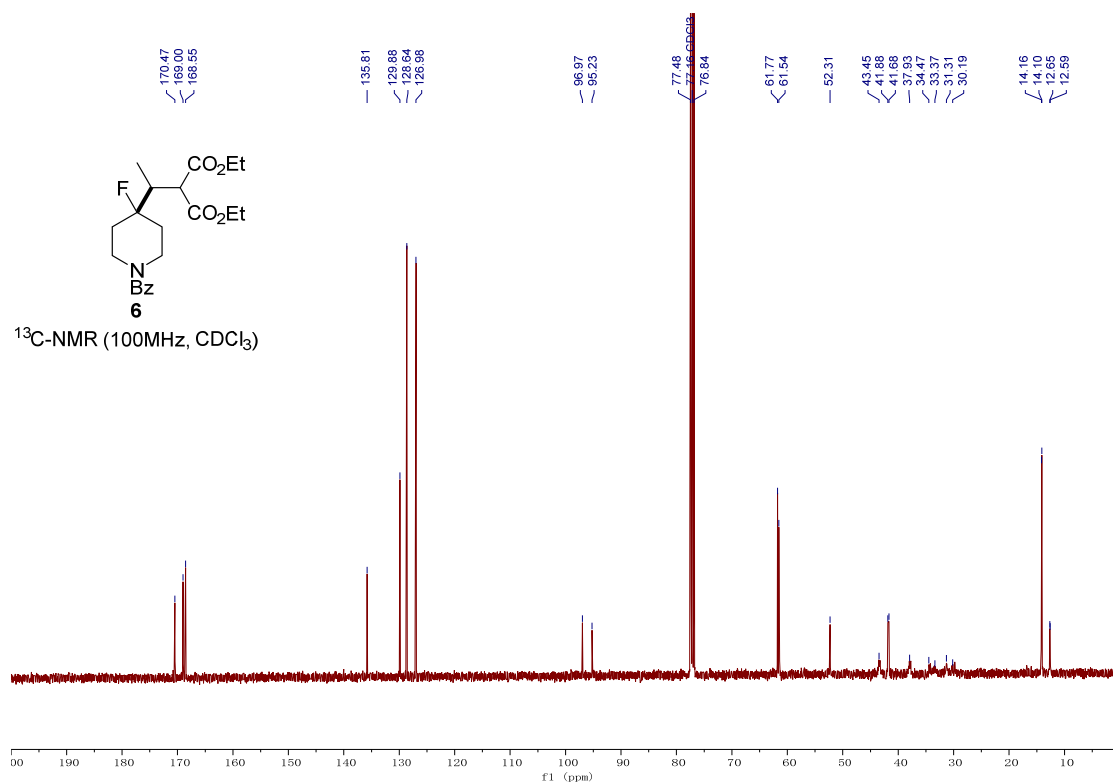
$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )

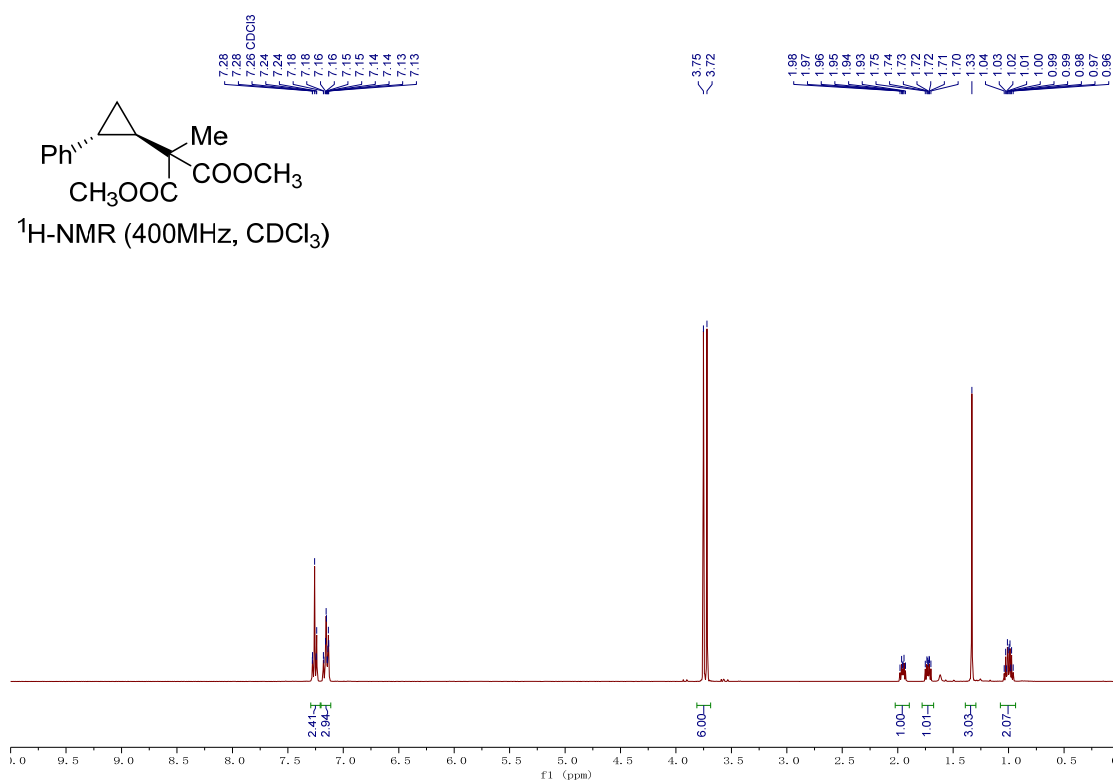
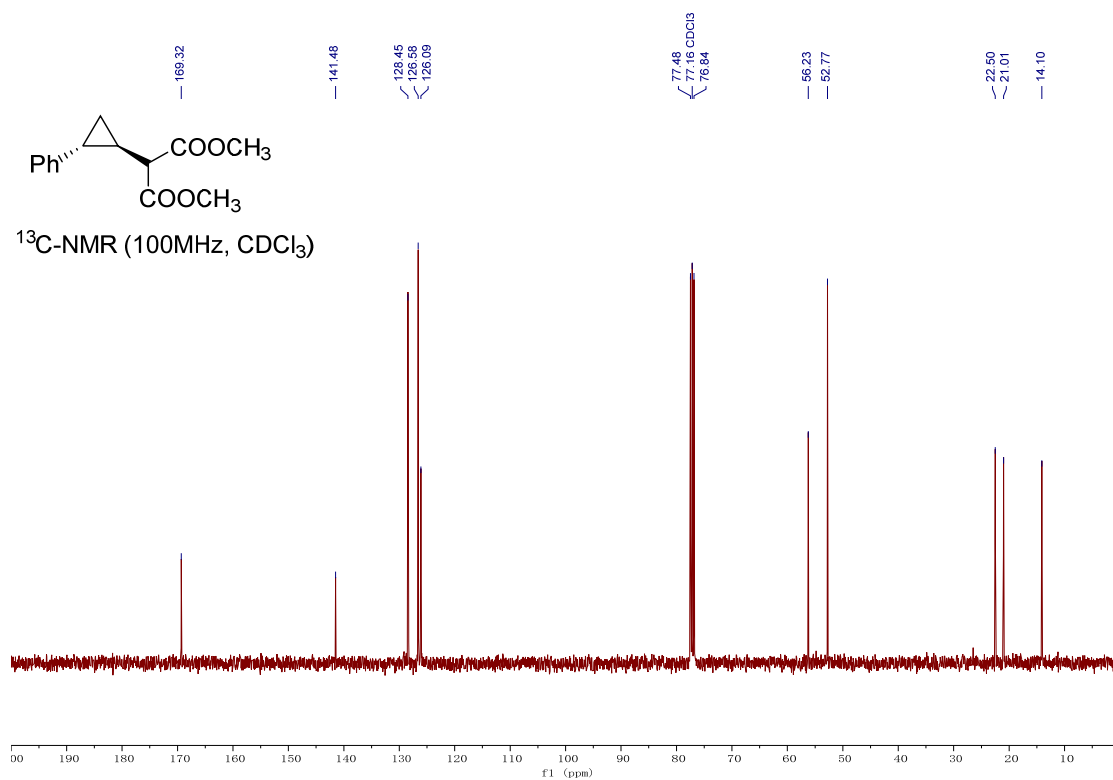


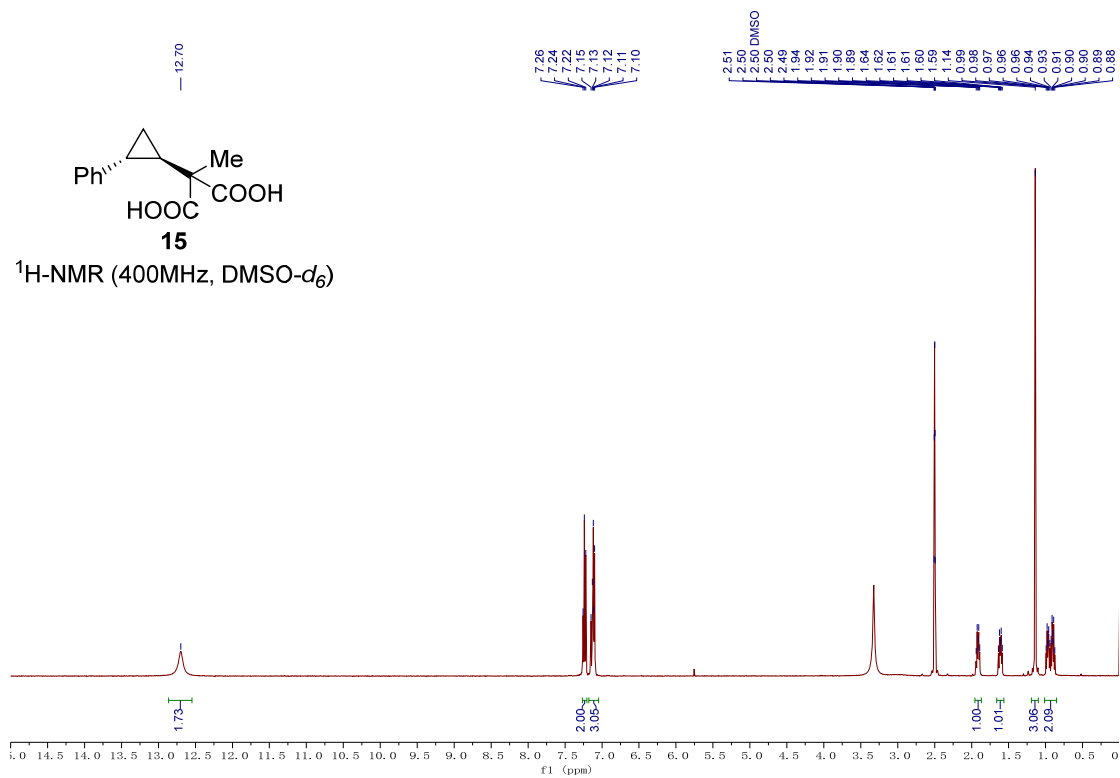
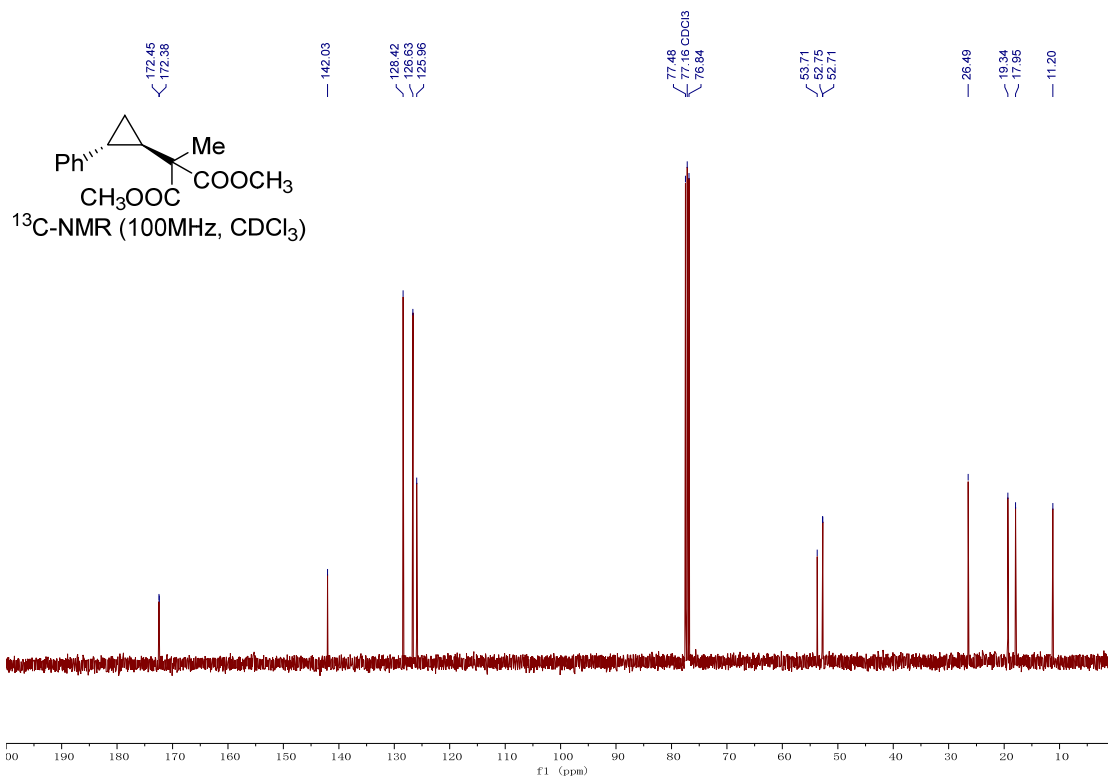
$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

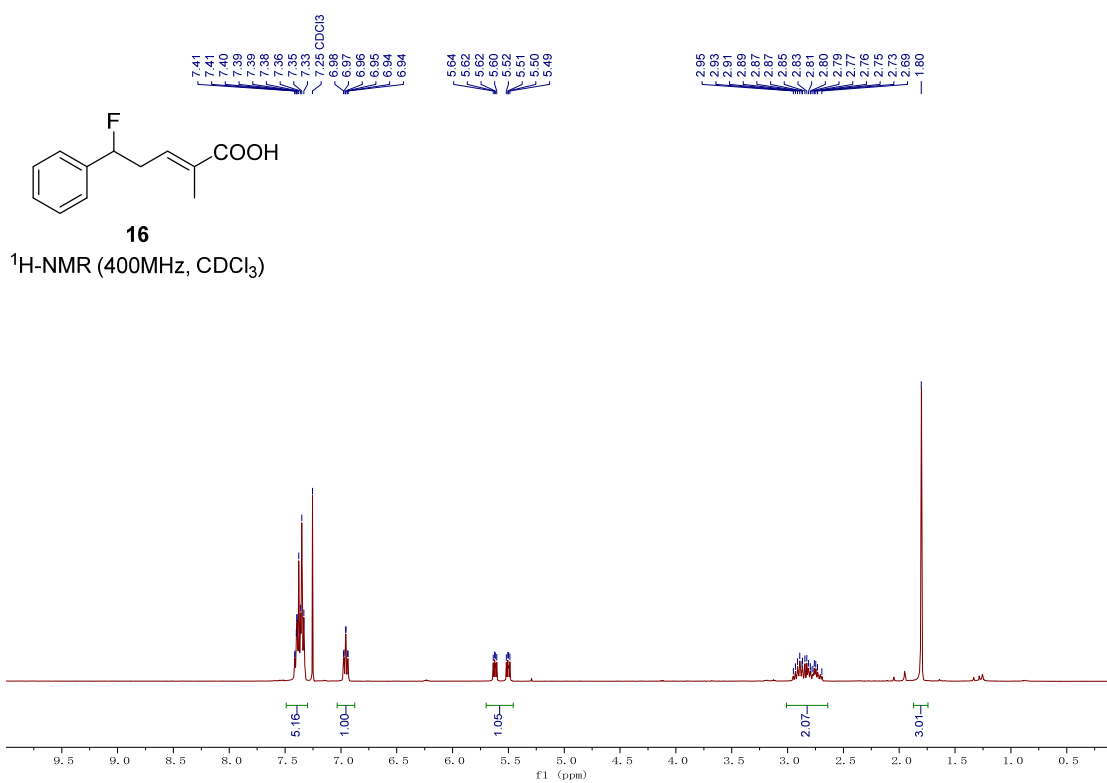
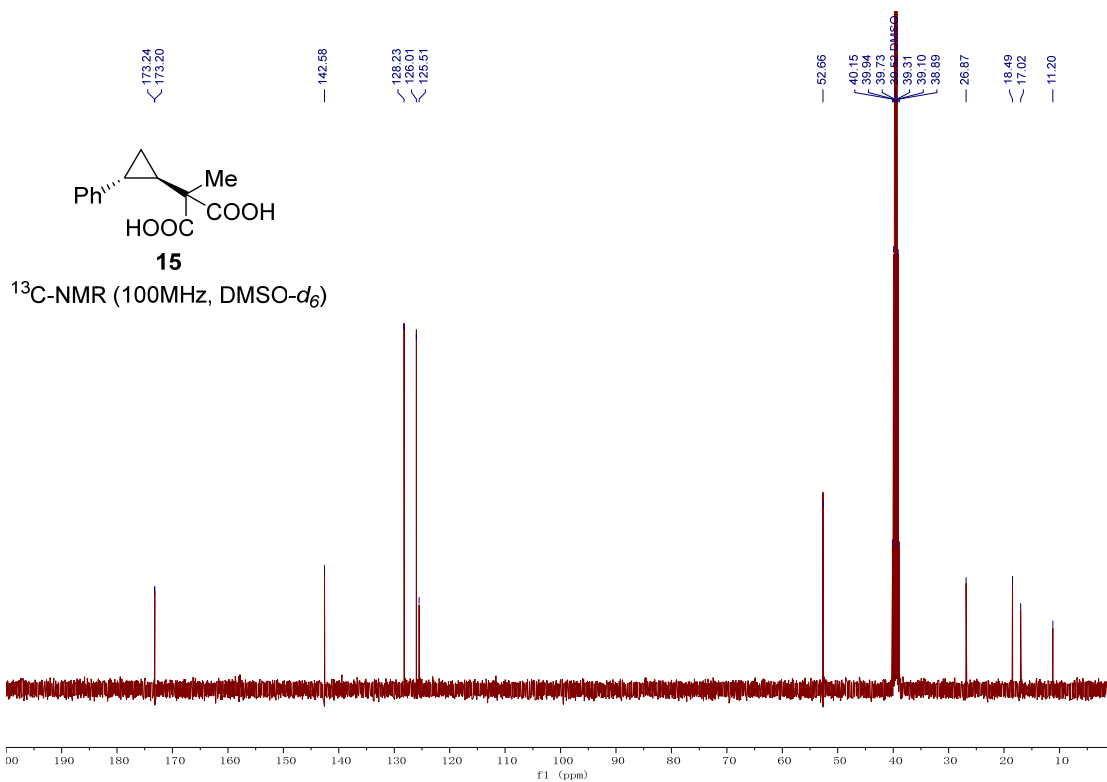


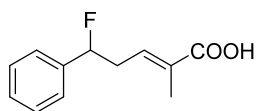




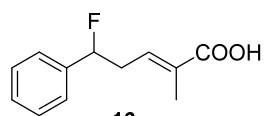
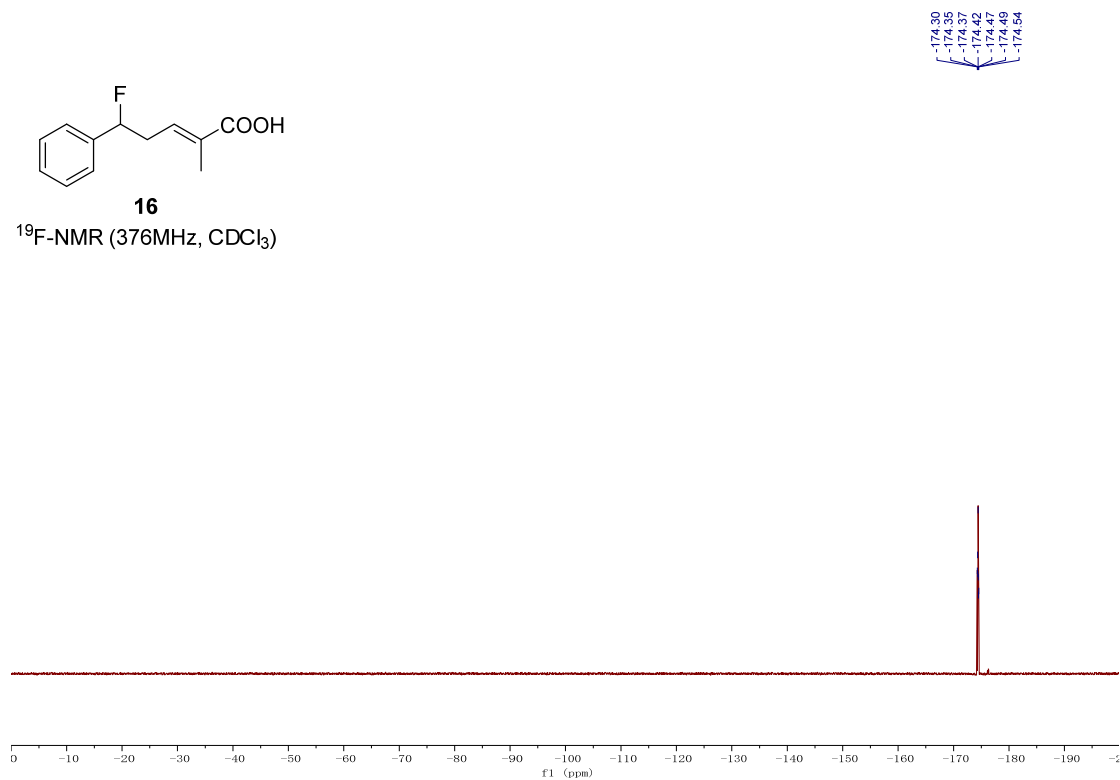








$^{19}\text{F}$ -NMR (376MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR (100MHz,  $\text{CDCl}_3$ )

