

**Supporting Information  
for**

**Three-component synthesis of C<sub>2</sub>F<sub>5</sub>-substituted pyrazoles from  
C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>·HCl, NaNO<sub>2</sub> and electron-deficient alkynes**

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**Experimental procedures and copies of NMR spectra for all new compounds**

### Experimental part

Dichloromethane was purified by distillation. All reagents were available from Enamine Ltd. Melting points are uncorrected. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 500 spectrometer (at 499.9 MHz and 124.9 MHz, respectively). <sup>19</sup>F-NMR spectra were recorded on a Varian Unity Plus 400 spectrometer (at 376.7 Hz). Chemical shifts are reported in ppm downfield from Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C) or upfield from CFCl<sub>3</sub> (<sup>19</sup>F) using conventional deuterium lock referencing as internal standards. MS analysis was performed on an LCMS instrument with chemical ionization.

**General procedure:** To a stirred suspension of C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>·HCl (90 mg, 0.48 mmol, 3.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) / water (0.2 mL), sodium nitrite (54 mg, 0.78 mmol, 5.0 eq.) and alkyne (0.16 mmol, 1.0 eq.) was added. The reaction mixture was vigorously stirred 72 h at 20 °C. Water (1.0 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL) were added. The organic layer was separated. The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 3 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum to provide the pure product.

#### Methyl 3-(pentafluoroethyl)-1H-pyrazole-5-carboxylate (1a)

Compound **1a** was obtained as a white solid (39 mg, 99%) following the general procedure. M.p. = 79-80 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 11.81 (broad s, 1H, NH), 7.11 (s, 1H, CH), 3.96 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 159.0 (s, CO), 142.8 (broad s, C), 135.5 (broad s, C), 118.6 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 110.2 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 108.6 (s, CH), 52.7 (s, CH<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -85.1 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 245 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>7</sub>H<sub>5</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 34.44; H, 2.06; N, 11.48. Found: C, 34.14; H, 2.34; N, 11.68.

#### Ethyl 3-(pentafluoroethyl)-1H-pyrazole-5-carboxylate (2a)

Compound **2a** was obtained as a white solid (41 mg, 98%) following the general procedure. M.p. = 90 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 11.89 (broad s, 1H, NH), 7.13 (s, 1H, CH), 4.45 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.42 (t, *J* = 7.0 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 158.3 (s, CO), 142.2 (broad s, C), 135.4 (broad s, C), 118.3 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.3 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 109.8 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.0 Hz, CF<sub>2</sub>CF<sub>3</sub>), 108.2 (s, CH), 61.8 (s, OCH<sub>2</sub>), 13.7 (s, CH<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -85.1 (t, <sup>3</sup>*J*(F,F) = 3.8 Hz, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (q, <sup>3</sup>*J*(F,F) = 3.8 Hz, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 259 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>8</sub>H<sub>7</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 37.22; H, 2.73; N, 10.85. Found: C, 37.51; H, 3.02; N, 10.74.

#### Isopropyl 3-(pentafluoroethyl)-1H-pyrazole-5-carboxylate (3a)

Compound **3a** was obtained as a white solid (42 mg, 97%) following the general procedure. M.p. = 85-86 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 7.12 (s, 1H, CH), 5.31 (m,  $J = 6.5$  Hz, 1H, CHCH<sub>3</sub>), 1.38 (6,  $J = 6.5$  Hz, 6H, CHCH<sub>3</sub>).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 158.0 (s, CO), 141.8 (t,  $^2J_{\text{C-F}} = 30.0$  Hz, CCF<sub>2</sub>), 135.7 (broad s, C), 118.2 (qt,  $^1J_{\text{C-F}} = 285.3$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz, CF<sub>2</sub>CF<sub>3</sub>), 109.9 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.0$  Hz, CF<sub>2</sub>CF<sub>3</sub>), 108.1 (s, CH), 70.1 (s, OCH), 21.3 (s, CH<sub>3</sub>).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -85.1 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI):  $m/z$  (%) = 273 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>9</sub>H<sub>9</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 39.72; H, 3.33; N, 10.29. Found: C, 39.59; H, 3.61; N, 10.14.

#### ***N*-Methyl-3-(pentafluoroethyl)-1*H*-pyrazole-5-carboxamide (4a)**

The reaction was performed in toluene (4.0 mL) /water (0.2 mL) at 45 °C following the general procedure. The crude product was washed with cyclohexane (0.3 mL) to give the pure compound **4a** as a white solid (30 mg, 78%). M.p. = 172-173 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CD}_3\text{OD}$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 7.09 (s, 1H, CH), 2.90 (s, 3H, CH<sub>3</sub>).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CD}_3\text{OD}$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 158.9 (s, CO), 144.3 (s, C), 140.8 (broad s, C), signals of CF<sub>2</sub>CF<sub>3</sub> are not seen, 103.4 (s, CH), 24.5 (s, CH<sub>3</sub>).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CD}_3\text{OD}$ ;  $\text{CFCl}_3$ ),  $\delta$ : -85.4 (broad s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.3 (broad s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI):  $m/z$  (%) = 244 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>7</sub>H<sub>6</sub>F<sub>5</sub>N<sub>3</sub>O: C, 34.58; H, 2.49; N, 17.28. Found: C, 34.25; H, 2.77; N, 17.51.

#### ***N*-(2-bromophenyl)-3-(pentafluoroethyl)-1*H*-pyrazole-5-carboxamide (5a)**

The reaction was performed in in toluene (4.0 mL) /water (0.2 mL) at 45 °C following the general procedure. The crude product was washed with chloroform (0.3 mL) to give the pure compound **5a** as a white solid (54 mg, 78%). M.p. = 152-153 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 14.81 (s, 1H, NH), 10.37 (s, 1H, NH), 7.74 (d,  $^3J(\text{H,H}) = 10.5$  Hz, 1H, Ph), 7.57 (s, 1H, CH), 7.52 (broad s, 1H, Ph), 7.46 (t,  $^3J_{\text{H-H}} = 9.0$  Hz, 1H, Ph), 7.27 (t,  $^3J(\text{H,H}) = 9.0$  Hz, 1H, Ph).

$^{13}\text{C}$  NMR (125 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 156.7 (s, CO), 139.9 (t,  $^2J_{\text{C-F}} = 31.1$  Hz, CCF<sub>2</sub>), 138.7 (s), signals of CF<sub>2</sub>CF<sub>3</sub> are not seen, 135.2 (s), 133.0 (s), 129.4 (s), 128.8 (s), 128.4 (s), 120.9 (s), 105.5 (s, CH).

$^{19}\text{F}$  NMR (375 MHz;  $\text{DMSO-d}_6$ ;  $\text{CFCl}_3$ ),  $\delta$ : -83.2 (broad s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -110.6 (broad s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI):  $m/z$  (%) = 383, 385 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>12</sub>H<sub>7</sub>BrF<sub>5</sub>N<sub>3</sub>O: C, 37.52; H, 1.84; N, 10.94. Found: C, 37.73; H, 2.07; N, 10.58.

#### **Cyclobutyl[3-(pentafluoroethyl)-1*H*-pyrazol-5-yl]methanone (6a)**

Compound **6a** was obtained as a yellow solid (43 mg, 99%) following the general procedure. M.p. = 67-68 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 11.78 (broad s, 1H, NH), 6.56 (s, 1H, CH), 3.82 (qv,  $J = 7.0$  Hz, 1H, CH), 2.46 (m, 2H), 2.33 (m, 2H), 2.14 (m, 1H), 1.98 (m, 1H).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 191.5 (s, CO), 142.2 ( $^2J_{\text{C-F}} = 31.3$  Hz,  $\text{CCF}_2$ ), 140.4 (broad s, C), 118.3 (qt,  $^1J_{\text{C-F}} = 285.3$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 109.8 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.0$  Hz,  $\text{CF}_2\text{CF}_3$ ), 107.2 (s, CH), 42.5 (s, CH), 24.3 (s,  $\text{CH}_2$ ), 17.8 (s,  $\text{CH}_2$ ).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -85.0 (broad s, 3F,  $\text{CF}_2\text{CF}_3$ ), -113.5 (broad s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 269  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{10}\text{H}_9\text{F}_5\text{N}_2\text{O}$ : C, 44.79; H, 3.38; N, 10.45. Found: C, 45.02; H, 3.61; N, 10.16.

### 1-[3-(Pentafluoroethyl)-1H-pyrazol-5-yl]-2-phenylethanone (7a)

Compound **7a** was obtained as a white solid (49 mg, 98%) following the general procedure. M.p. = 75-76 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 11.67 (broad s, 1H, NH), 7.36-7.26 (m, 5H, Ph), 7.04 (s, 1H, CH), 4.16 (s, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 187.8 (s, CO), 142.0 (t,  $J = 28.7$  Hz,  $\text{CCF}_2$ ), 141.3 (s, C), 132.0 (s, Ph), 129.1 (s, Ph), 128.6 (s, Ph), 127.3 (s, Ph), 118.3 (qt,  $^1J_{\text{C-F}} = 285.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 109.7 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ), 108.9 (s, CH), 46.1 (s,  $\text{CH}_2$ ).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -85.0 (t,  $^3J(\text{F,F}) = 3.8$  Hz, 3F,  $\text{CF}_2\text{CF}_3$ ), -113.5 (q,  $^3J(\text{F,F}) = 3.8$  Hz, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 305  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{13}\text{H}_9\text{F}_5\text{N}_2\text{O}$ : C, 51.33; H, 2.98; N, 9.21. Found: C, 51.61; H, 3.32; N, 9.07.

### 1-[3-(Pentafluoroethyl)-1H-pyrazol-5-yl]-3-phenyl-1-propanone (8a)

Compound **8a** was obtained as a white solid (49 mg, 97%) following the general procedure. M.p. = 57-58 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 7.33-7.21 (m, 5H, Ph), 7.04 (s, 1H, CH), 4.16 (s, 2H,  $\text{CH}_2$ ), 3.25 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 3.09 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 189.7 (s, CO), 142.1 (t,  $J = 28.5$  Hz,  $\text{CCF}_2$ ), 141.5 (s, C), 139.6 (s, Ph), 128.3 (s, Ph), 128.0 (s, Ph), 126.2 (s, Ph), 118.2 (qt,  $^1J_{\text{C-F}} = 281.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 109.5 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ), 107.4 (s, CH), 41.0 (s,  $\text{CH}_2$ ), 29.1 (s,  $\text{CH}_2$ ).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -85.1 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -113.6 (s,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 319  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{13}\text{H}_9\text{F}_5\text{N}_2\text{O}$ : C, 52.84; H, 3.48; N, 8.80. Found: C, 52.51; H, 3.12; N, 8.92.

### 5-(Diphenylphosphoryl)-3-(pentafluoroethyl)-1H-pyrazole (9a)

The synthesis was performed following the general procedure. During the reaction the product partially precipitated from the reaction mixture. After 3 days water (1.0 mL) and  $\text{CH}_2\text{Cl}_2$  (10 mL) were added. Water phase was separated and discarded. The organic suspension was evaporated under vacuum to afford the pure product **9a** as a white solid (59 mg, 95%). M.p. > 200 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 14.81 (broad s, NH), 7.67 (broad s, 6H, Ph+Ph), 7.59 (broad s, 4H, Ph+Ph), 6.82 (s, 1H, CH).

$^{13}\text{C}$  NMR (125 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 140.0 (broad s, C), the signal NCP is not seen, 132.7 (d,  $^4J(\text{C,P}) = 2.5$  Hz, CH, Ph), 131.4 (d,  $^1J(\text{C,P}) = 97.5$  Hz, C, Ph), 131.2 (d,  $^3J(\text{C,P}) = 11.3$  Hz, CH,

Ph), 128.9 (d,  $^2J_{\text{C,P}} = 12.5$  Hz, CH, Ph), 118.5 (qt,  $^1J_{\text{C-F}} = 285.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 112.0 (d,  $^2J_{\text{C,P}} = 16.3$  Hz, CH), 110.6 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ).

$^{19}\text{F}$  NMR (375 MHz DMSO- $d_6$ ;  $\text{CFCl}_3$ ),  $\delta$ : -83.7 (broad s, 3F,  $\text{CF}_2\text{CF}_3$ ), -110.6 (broad s, 2F,  $\text{CF}_2\text{CF}_3$ ).

$^{31}\text{P}$  NMR (202 MHz DMSO- $d_6$ ;  $\text{H}_3\text{PO}_4$ ),  $\delta$ : 8.8 (broad s, P).

MS (CI):  $m/z$  (%) = 387  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_5\text{N}_2\text{OP}$ : C, 52.86; H, 3.13; N, 7.25. Found: C, 53.02; H, 3.41; N, 7.02.

### 2-[3-(pentafluoroethyl)-1H-pyrazol-5-yl]-1,3-benzothiazole (10a)

The reaction was performed in in toluene (4.0 mL) /water (0.2 mL) at 45 °C following the general procedure. The crude product was crystallized from hexane (0.5 mL) to give the pure compound **10a** as a grey solid (24 mg, 45%). M.p. = 142-143 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 12.07 (broad s, 1H, NH), 8.11 (d,  $J = 8.0$  Hz, 1H, CH), 7.96 (d,  $J = 8.0$  Hz, 1H, CH), 7.56 (t,  $J = 8.0$  Hz, 1H, CH), 7.48 (t,  $J = 8.0$  Hz, 1H, CH), 7.13 (s, 1H, CH).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 152.7 (s, NCS), 139.0 (broad s, C), 134.2 (s, CH), 126.6 (s, CH), 125.8 (s, CH), 123.1 (s, CH), 121.5 (s, CH),  $\text{C}_2\text{F}_5$  is not seen, 105.4 (s, CH).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -84.6 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -113.4 (s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 320  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{12}\text{H}_6\text{F}_5\text{N}_3\text{S}$ : C, 45.15; H, 1.89; N, 13.16; S, 10.04. Found: C, 45.47; H, 2.01; N, 12.88; S, 9.77.

### 2-[3-(Pentafluoroethyl)-1H-pyrazol-5-yl]-thiazole (11a)

The reaction was performed in dichloromethane/water at 40 °C for 72 h following the general procedure. The crude product was washed with cyclohexane (0.2 mL) to give the pure compound **11a** as a grey solid (24 mg, 57%). M.p. = 127-128 °C.

$^1\text{H}$  NMR (500 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 14.77 (broad s, 1H, NH), 8.01 (s, 1H, CH), 7.92 (s, 1H, CH), 7.34 (s, 1H, CH).

$^{13}\text{C}$  NMR (125 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 155.2 (broad s, NCS), 143.7 (s, CH), 140.5 (broad s, C), 138.4 (broad s, C), 121.9 (s, CH), 104.4 (s, CH),  $\text{C}_2\text{F}_5$  is not seen.

$^{19}\text{F}$  NMR (375 MHz; DMSO- $d_6$ ;  $\text{CFCl}_3$ ),  $\delta$ : -83.2 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -110.6 (s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 270  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_8\text{H}_4\text{F}_5\text{N}_3\text{S}$ : C, 35.69; H, 1.50; N, 15.61; S, 11.91. Found: C, 35.21; H, 1.38; N, 15.29; S, 12.08.

### 2-[3-((Pentafluoroethyl)-1H-pyrazol-5-yl)- quinoxaline (12a)

The reaction was performed in dichloromethane/water at 40 °C for 72 h following the general procedure. The formed white precipitate was filtered, and dried on air to give the pure product **12a** as a white solid (18 mg, 38%). M.p. > 200 °C.

$^1\text{H}$  NMR (500 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 15.10-14.65 (broad s, 1H, NH), 9.56 (s, 1H, CH), 8.14 (d,  $J = 8.0$  Hz, 2H, CH), 7.91 (m, 2H, CH), 7.99 (s, 1H, CH).

$^{13}\text{C}$  NMR (125 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 143.7 (s), 142.5 (s), 141.5 (s), 141.1 (s), 131.2 (s), 130.6 (s), 129.2 (s), 128.9 (s), 105.6 (s), two tert-C atoms and  $\text{C}_2\text{F}_5$  are not seen.

$^{19}\text{F}$  NMR (375 MHz; DMSO- $d_6$ ;  $\text{CFCl}_3$ ),  $\delta$ : -83.1 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -110.5 (s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 315  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{13}\text{H}_7\text{F}_5\text{N}_4$ : C, 49.69; H, 2.25; N, 17.83. Found: C, 49.33; H, 2.53; N, 17.99.

### Dimethyl 3-(pentafluoroethyl)-1H-pyrazole-4,5-dicarboxylate (15a)

Compound **15a** was obtained as a white solid (48 mg, 99%) following the general procedure. M.p. = 59-60 °C.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 3.97 (s, 3H,  $\text{CH}_3$ ), 3.95 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 162.0 (s, CO), 158.0 (s, CO), 139.9 (t,  $J = 28.7$  Hz,  $\text{CCF}_2$ ), 134.1 (s, C), 118.4 (qt,  $^1J_{\text{C-F}} = 285.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 117.1 (s, C), 110.1 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ), 53.3 (s,  $\text{CH}_3$ ), 53.2 (s,  $\text{CH}_3$ ).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -84.3 (t,  $^3J(\text{F,F}) = 3.8$  Hz, 3F,  $\text{CF}_2\text{CF}_3$ ), -112.3 (q,  $^3J(\text{F,F}) = 3.8$  Hz, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 303  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_9\text{H}_7\text{F}_5\text{N}_2\text{O}_4$ : C, 35.78; H, 2.34; N, 9.27. Found: C, 35.49; H, 2.57; N, 9.10.

### Diethyl 3-(pentafluoroethyl)-1H-pyrazole-4,5-dicarboxylate (16a)

Compound **16a** was obtained as a colorless oil (52 mg, 98%) following the general procedure.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 12.05 (broad s, 1H, NH), 4.41 (m, 4H,  $\text{CH}_2+\text{CH}_2$ ), 1.37 (m, 6H,  $\text{CH}_3+\text{CH}_3$ ).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 161.2 (s, CO), 157.2 (s, CO), 139.4 (t,  $J = 28.7$  Hz,  $\text{CCF}_2$ ), 133.7 (s, C), 117.9 (qt,  $^1J_{\text{C-F}} = 285.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 117.1 (s, C), 109.9 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ), 62.3 (s,  $\text{OCH}_2$ ), 62.0 (s,  $\text{OCH}_2$ ), 13.5 (s,  $\text{CH}_3$ ), 13.4 (s,  $\text{CH}_3$ ).

$^{19}\text{F}$  NMR (375 MHz;  $\text{CDCl}_3$ ;  $\text{CFCl}_3$ ),  $\delta$ : -84.3 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -112.2 (s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 331  $[\text{M}+1]^+$ .

Anal. calcd for  $\text{C}_{11}\text{H}_{11}\text{F}_5\text{N}_2\text{O}_4$ : C, 40.01; H, 3.26; N, 8.48. Found: C, 39.88; H, 3.59; N, 8.35.

### 3-(Pentafluoroethyl)-4,5-bis(trifluoromethyl)-1H-pyrazole (17a)

A solution of *bis*-trifluoromethylacetylene (**17**) in dry  $\text{CH}_2\text{Cl}_2$  was prepared at -30 °C (Flask 1). An aliquot of a solution of **17** (100 mg, 0.62 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (ca. 5 mL) was added to a previously generated solution (flask 2) of  $\text{C}_2\text{F}_5\text{CHN}_2$  (obtained from  $\text{C}_2\text{F}_5\text{CH}_2\text{NH}_2\cdot\text{HCl}$  (115 mg, 0.62 mmol, 1.0 eq)) in dichloromethane at -10 °C. The reaction mixture was allowed to warm slowly to a room temperature and was left for 12 h. The organic layer was separated, dried over sodium sulfate and gently concentrated under vacuum (20 mm) without external heating to give pyrazole **17a** (129 mg, 0.40 mmol, 65% yield) as a yellowish liquid. *The product is volatile!*

$^{13}\text{C}$  NMR (125 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ),  $\delta$ : 137.8-136.0 (broad s,  $\text{CF}_3-\text{C}=\text{N}+\text{C}_2\text{F}_5-\text{C}=\text{N}$ ), 119.4 (q,  $^1J_{\text{C-F}} = 267.5$  Hz,  $\text{CF}_3$ ), 118.2 (q,  $^1J_{\text{C-F}} = 268.8$  Hz,  $\text{CF}_3$ ), 117.7 (qt,  $^1J_{\text{C-F}} = 285.0$  Hz,  $^2J_{\text{C-F}} = 36.3$  Hz,  $\text{CF}_2\text{CF}_3$ ), 112.3 (q,  $^2J_{\text{C-F}} = 41.3$  Hz,  $\text{CCF}_3$ ), 109.0 (tq,  $^1J_{\text{C-F}} = 250.0$  Hz,  $^2J_{\text{C-F}} = 38.9$  Hz,  $\text{CF}_2\text{CF}_3$ ).

$^{19}\text{F}$  NMR (375 MHz; DMSO- $d_6$ ;  $\text{CFCl}_3$ ),  $\delta$ : -55.7 (s, 3F,  $\text{CF}_3$ ), -61.4 (s, 3F,  $\text{CF}_3$ ), -84.2 (s, 3F,  $\text{CF}_2\text{CF}_3$ ), -111.7 (s, 2F,  $\text{CF}_2\text{CF}_3$ ).

MS (CI):  $m/z$  (%) = 321  $[\text{M}-1]^+$ .

Anal. calcd for  $\text{C}_7\text{HF}_{11}\text{N}_2$ : C, 26.10; H, 0.31; N, 8.70. Found: C, 26.47; H, 0.65; N, 9.03.

**Ethyl 3-(pentafluoroethyl)-4-(trifluoromethyl)-1H-pyrazole-5-carboxylate (18a),****Ethyl 3-(pentafluoroethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate (18b)**

Compound **18** was obtained as two inseparable regioisomers (2.6/1) as colorless oil (51 mg, 99%) following the general procedure.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 4.49, 4.39 (2 q, *J* = 7.0 Hz, OCH<sub>2</sub>), 1.43, 1.37 (2 t, *J* = 7.0 Hz, CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si; signals of major isomer **18a**), δ: 156.7 (s, CO) 139.8 (t, *J* = 31.5 Hz, CCF<sub>2</sub>), 134.8 (s, C), 120.0 (q, <sup>1</sup>*J*<sub>C-F</sub> = 267.5 Hz, CF<sub>3</sub>), CF<sub>2</sub>CF<sub>3</sub> and CCF<sub>3</sub> are not seen, 109.9 (tq, <sup>1</sup>*J*<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>*J*<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 62.9 (s, OCH<sub>2</sub>), 13.4 (s, CH<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -55.1, -61.6 (2 s, 3F, CF<sub>3</sub>), -83.1, -83.6 (2 s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -109.5, -111.0 (2 s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 327 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>9</sub>H<sub>6</sub>F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 33.14; H, 1.85; N, 8.59. Found: C, 33.45; H, 1.98; N, 8.31.

**1-[3-(Pentafluoroethyl)-5-(trimethylsilyl)-1H-pyrazol-4-yl]ethanone (19b)**

The reaction was performed at 40 °C following the general procedure. The crude product was washed with cold cyclohexane (0.1 mL) to give the pure compound **19b** as a white solid (35 mg, 73%). M.p. = 102-103 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 10.51 (broad s, 1H, NH), 2.56 (s, 3H, CH<sub>3</sub>), 0.38 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 193.4 (s, CO), 150.4 (s, C), 139.5 (t, *J* = 28.7 Hz, CCF<sub>2</sub>), 128.8 (s, C), 118.2 (qt, <sup>1</sup>*J*<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>*J*<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 111.1 (tq, <sup>1</sup>*J*<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>*J*<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 29.9 (t, <sup>5</sup>*J*<sub>CF</sub> = 7.5 Hz, CH<sub>3</sub>), -2.3 (s, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -82.4 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -104.9 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 301 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>10</sub>H<sub>13</sub>F<sub>5</sub>N<sub>2</sub>OSi: C, 40.00; H, 4.36; N, 9.33. Found: C, 39.76; H, 4.45; N, 9.61.

**2-Chloro-1-[3-(pentafluoroethyl)-5-(trimethylsilyl)-1H-pyrazol-4-yl]ethanone (20b)**

The reaction was performed at 40 °C following the general procedure. The crude product (a 4/1 mixture of diastereomers **20b/a**) was washed with cold hexane (0.2 mL) to give the pure compound **20b** as a white solid (29 mg, 55%). M.p. = 107-108 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 10.60 (broad s, 1H, NH), 4.68 (s, 2H, CH<sub>2</sub>), 0.40 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 187.1 (s, CO), 151.7 (s, C), 139.2 (t, *J* = 31.5 Hz, CCF<sub>2</sub>), 125.6 (s, C), C<sub>2</sub>F<sub>5</sub> is not seen, 48.3 (t, <sup>5</sup>*J*<sub>CF</sub> = 7.5 Hz, CH<sub>2</sub>), -2.5 (s, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -82.4 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -105.2 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 336 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>10</sub>H<sub>12</sub>ClF<sub>5</sub>N<sub>2</sub>OSi: C, 35.88; H, 3.61; N, 8.37. Found: C, 36.16; H, 3.33; N, 8.05.

**2,2-Difluoro-1-[3-(pentafluoroethyl)-4-(trimethylsilyl)-1H-pyrazol-5-yl]ethanone (21a),****2,2-Difluoro-1-[3-(pentafluoroethyl)-5-(trimethylsilyl)-1H-pyrazol-4-yl]ethanone (21b)**

Compound **21b/a** was obtained as two inseparable regioisomers (2.6/1) as colorless oil (48 mg, 89%) following the general procedure.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 10.79 (broad s, 1H, NH), 6.56, 6.32 (2 t, <sup>2</sup>J<sub>HF</sub> = 53.6 Hz, 1H, CHF<sub>2</sub>), 0.38, 0.30 (2 s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si; major isomer **21b**), δ: 185.3 (t, <sup>2</sup>J<sub>C-F</sub> = 26.3 Hz, COCHF<sub>2</sub>), 151.8 (s, C), 139.9 (t, <sup>2</sup>J<sub>C-F</sub> = 31.3 Hz, CCF<sub>2</sub>), 123.2 (s, C), 118.4 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 110.4 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 107.4 (tt, <sup>1</sup>J<sub>C-F</sub> = 247.5 Hz, <sup>5</sup>J<sub>C-F</sub> = 7.5 Hz, CHF<sub>2</sub>), -2.6 (s, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -83.1, -83.8 (s + broad s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -107.2, -108.4 (s + broad s, 2F, CF<sub>2</sub>CF<sub>3</sub>), -127.3, 127.0 (broad s + dt, <sup>2</sup>J<sub>FF</sub> = 52.6 Hz, <sup>6</sup>J<sub>FF</sub> = 7.5 Hz, 2F, CHF<sub>2</sub>),

MS (CI): *m/z* (%) = 337 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>10</sub>H<sub>11</sub>F<sub>7</sub>N<sub>2</sub>OSi: C, 35.72; H, 3.30; N, 8.33. Found: C, 35.45; H, 3.13; N, 8.54.

### 1-[3-(Trifluoromethyl)-5-(trimethylsilyl)-1H-pyrazol-4-yl]-ethanone (**23**)

To a stirred suspension of CF<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>\*HCl (65 mg, 0.48 mmol, 3.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) / water (0.2 mL), sodium nitrite (54 mg, 0.78 mmol, 5.0 eq.) and alkyne **19** (22 mg, 0.16 mmol, 1.0 eq.) was added. The reaction mixture was vigorously stirred 168 h at RT. Water (1.0 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL) were added. The organic layer was separated. The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 3 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum to provide the crude material (*no starting material was left*). The tarry solid was washed with cold cyclohexane (0.1 mL) to give the pure product **23** (30 mg, 0.12 mmol, 75% yield) as a white solid. M.p. = 120-122 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 11.16 (broad s, 1H, NH), 2.57 (s, 3H, CH<sub>3</sub>), 0.39 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 192.6 (s, CO), 151.3 (s, C), 141.0 (q, <sup>2</sup>J(C,F) = 36.1 Hz, CCF<sub>3</sub>), 127.1 (s), 120.8 (q, <sup>1</sup>J(C,F) = 270.0 Hz, CF<sub>3</sub>), 29.2 (s, CH<sub>3</sub>), 2.6 (s, Si(CH<sub>3</sub>)<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -58.1 (s, CF<sub>3</sub>).

Anal. calcd for C<sub>9</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>OSi: C, 43.19; H, 5.24; N, 11.19. Found: C, 43.42; H, 5.53; N, 10.94.

MS (CI): *m/z* (%) = 251 [M+1]<sup>+</sup>.

### 1-[3-(Pentafluoroethyl)-1H-pyrazol-4-yl]-ethanone (**24**)

Compound **19b** (50 mg, 0.17 mmol) was dissolved in methanol (3 mL). Water (0.5 mL), and KHF<sub>2</sub> (5 mg) were added. The reaction mixture was heated at reflux for 10h. After cooling to a room temperature, the methanol was evaporated under vacuum. Water (1 mL) was added and the mixture was extracted with dichloromethane (3×2 mL). The organic fractions were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum to afford pyrazole **24** (17 mg, 0.08 mmol, 46% yield) as a white solid. M.p. = 152-153 °C.

<sup>1</sup>H NMR (500 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si), δ: 8.75 (s, 1H, CH), 2.44 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz DMSO-d<sub>6</sub>; Me<sub>4</sub>Si), δ: 190.2 (s, CO), 137.9 (t, *J* = 28.7 Hz, CCF<sub>2</sub>), 136.7 (s), 121.5 (s), 119.1 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 110.9 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 29.0 (s, CH<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; DMSO-d<sub>6</sub>; CFCl<sub>3</sub>), δ: -80.9 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -107.4 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 229 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>7</sub>H<sub>5</sub>F<sub>5</sub>N<sub>2</sub>O: C, 36.86; H, 2.21; N, 12.38. Found: C, 36.51; H, 2.44; N, 12.17.

### 3-(Pentafluoroethyl)-1H-pyrazole-5-carboxylic acid (**25**)

To a solution of pyrazole **1a** (93 mg, 0.38 mmol) in MeOH (0.5 mL) was added 1N NaOH (1.6 mL, 1.60 mmol). The reaction mixture was vigorously stirred at room temperature for 20 h. The solvent



was evaporated under vacuum, and water (5 mL) was added. The water phase was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 \* 1mL). Organic layer was discarded. Water phase was acidified with conc. HCl to pH = 1. White precipitate was formed. The suspension was extracted EtOAc (3 \* 5mL). The combined organic layer was dried over sodium sulfate, and evaporated under vacuum to afford the pure acid **25** (71 mg, 0.31 mmol, 81% yield) as a white solid. M.p.= 134-135 °C.

<sup>1</sup>H NMR (500 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si), δ: 14.78 (s, 1H, NH), 7.20 (s, 1H, CH).

<sup>13</sup>C NMR (125 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si), δ: 159.6 (s, CO<sub>2</sub>H), 140.2 (t, <sup>2</sup>J(C,F) = 28.8 Hz, CCF<sub>2</sub>), 136.8 (s, C), 118.3 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 112.4 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 108.1 (s, CH).

<sup>19</sup>F NMR (375 MHz; DMSO-d<sub>6</sub>; CFCl<sub>3</sub>), δ: -85.2 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 231 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>6</sub>H<sub>3</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 31.32; H, 1.31; N, 12.17. Found: C, 31.63; H, 1.02; N, 12.48.

#### **1-Methyl-3-(pentafluoroethyl)-1H-pyrazole-5-carboxylic acid, methyl ester (26)**

Pyrazole **1a** (450 mg, 1.8 mmol) was dissolved in dry DMF (5 mL). Dry K<sub>2</sub>CO<sub>3</sub> (472 mg, 3.6 mmol), and MeI (523 mg, 3.6 mmol) were added. The reaction mixture was vigorously stirred at room temperature for 20 h. The reaction mixture was then subjected to column chromatography on silicagel using hexane/EtOAc = 4/1 as an eluent. R<sub>f</sub> = 0.6. Colorless liquid **26** (328 mg, 1.2 mmol, 69% yield).

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 7.10 (s, 1H, CH), 4.25 (s, 3H, CH<sub>3</sub>), 3.92 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 158.9 (s, CO), 139.0 (t, <sup>2</sup>J(C,F) = 28.8 Hz, CCF<sub>2</sub>), 133.5 (s, C), 118.3 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.3 Hz, CF<sub>2</sub>CF<sub>3</sub>), 108.6 (s, CH), 110.4 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 52.0 (s, CH<sub>3</sub>), 40.0 (s, CH<sub>3</sub>).

<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -85.2 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 259 [M+1]<sup>+</sup>.

Anal. calcd for C<sub>8</sub>H<sub>7</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 37.22; H, 2.73; N, 10.85. Found: C, 37.48; H, 2.91; N, 10.56.

#### **1-Methyl-3-(pentafluoroethyl)-1H-pyrazole-5-carboxylic acid (27)**

To a solution of pyrazole **26** (100 mg, 0.38 mmol) in MeOH (0.5 mL) was added 1N NaOH (0.8 mL, 0.80 mmol). The reaction mixture was vigorously stirred at room temperature for 20 h. The solvent was evaporated under vacuum, and water (5 mL) was added. The water phase was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 \* 1mL). Organic layer was discarded. Water phase was acidified with conc. HCl to pH = 1. White precipitate was formed. The suspension was extracted CH<sub>2</sub>Cl<sub>2</sub> (3 \* 5mL). The combined organic layer was dried over sodium sulfate, and evaporated under vacuum to afford the pure acid **27** (92 mg, 0.37 mmol, 97% yield) as a white solid. M.p.= 125-126 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 7.25 (s, 1H, CH), 4.28 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si), δ: 162.4 (s, CO), 139.4 (t, <sup>2</sup>J(C,F) = 28.5 Hz, CCF<sub>2</sub>), 132.8 (s, C), 118.2 (qt, <sup>1</sup>J<sub>C-F</sub> = 285.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 36.5 Hz, CF<sub>2</sub>CF<sub>3</sub>), 109.8 (tq, <sup>1</sup>J<sub>C-F</sub> = 250.0 Hz, <sup>2</sup>J<sub>C-F</sub> = 38.9 Hz, CF<sub>2</sub>CF<sub>3</sub>), 112.0 (s, CH), 40.0 (s, CH<sub>3</sub>).

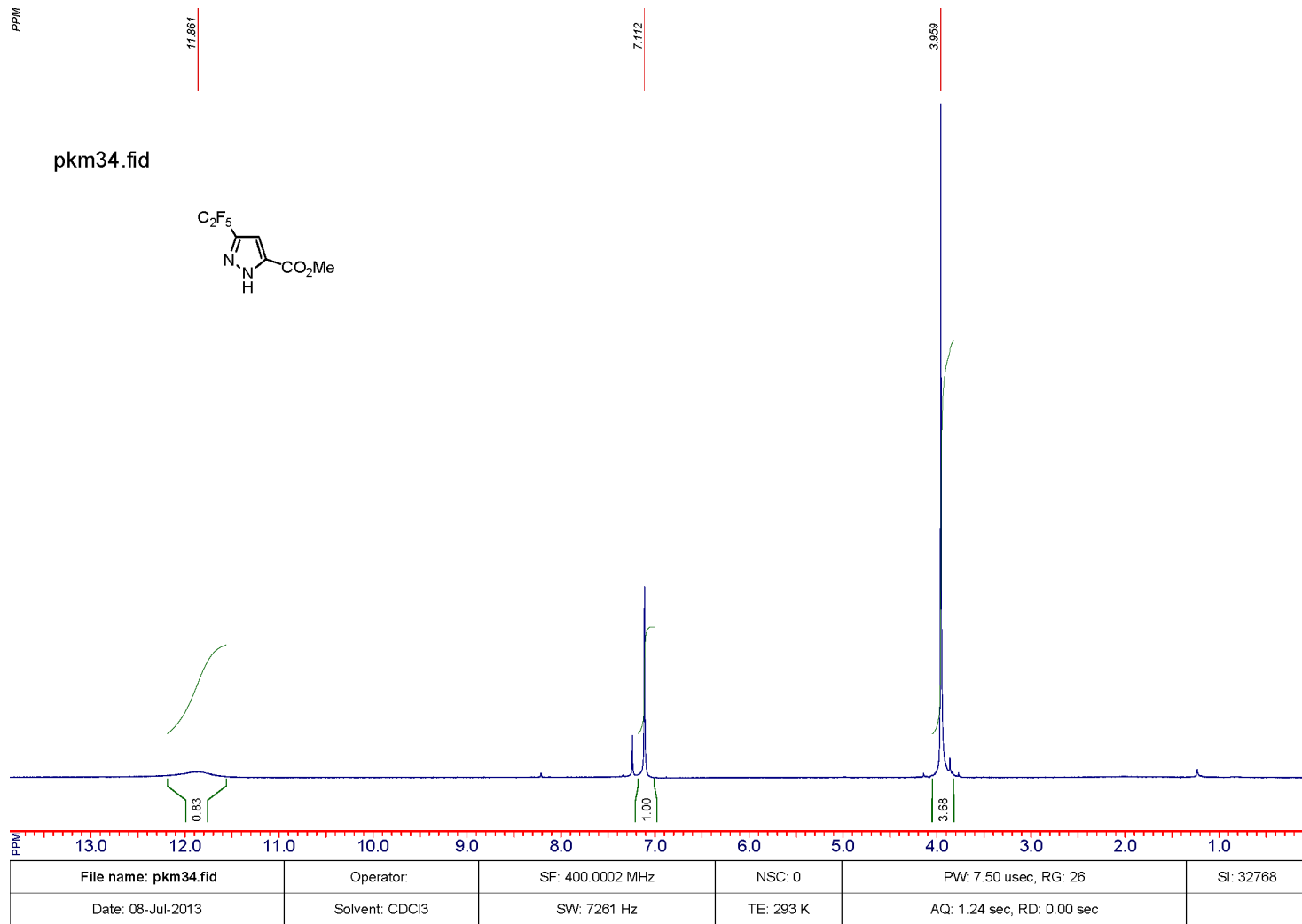
<sup>19</sup>F NMR (375 MHz; CDCl<sub>3</sub>; CFCl<sub>3</sub>), δ: -85.1 (s, 3F, CF<sub>2</sub>CF<sub>3</sub>), -113.8 (s, 2F, CF<sub>2</sub>CF<sub>3</sub>).

MS (CI): *m/z* (%) = 243 [M-1]<sup>+</sup>.

Anal. calcd for C<sub>7</sub>H<sub>5</sub>F<sub>5</sub>N<sub>2</sub>O<sub>2</sub>: C, 34.44; H, 2.06; N, 11.48. Found: C, 34.17; H, 1.91; N, 11.37.

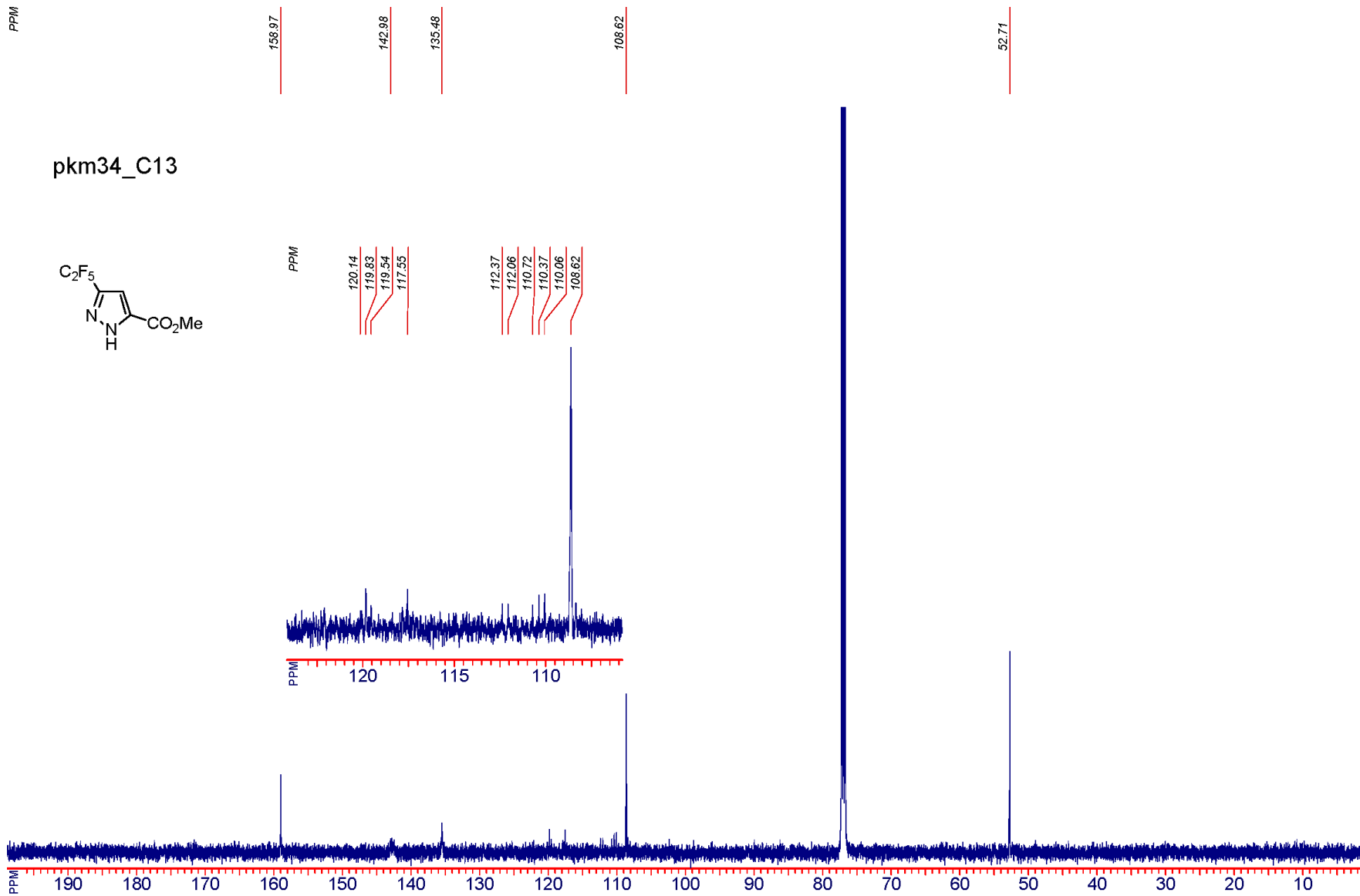
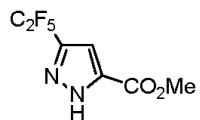
# Compound 1a

## Copies of NMR spectra.



PPM

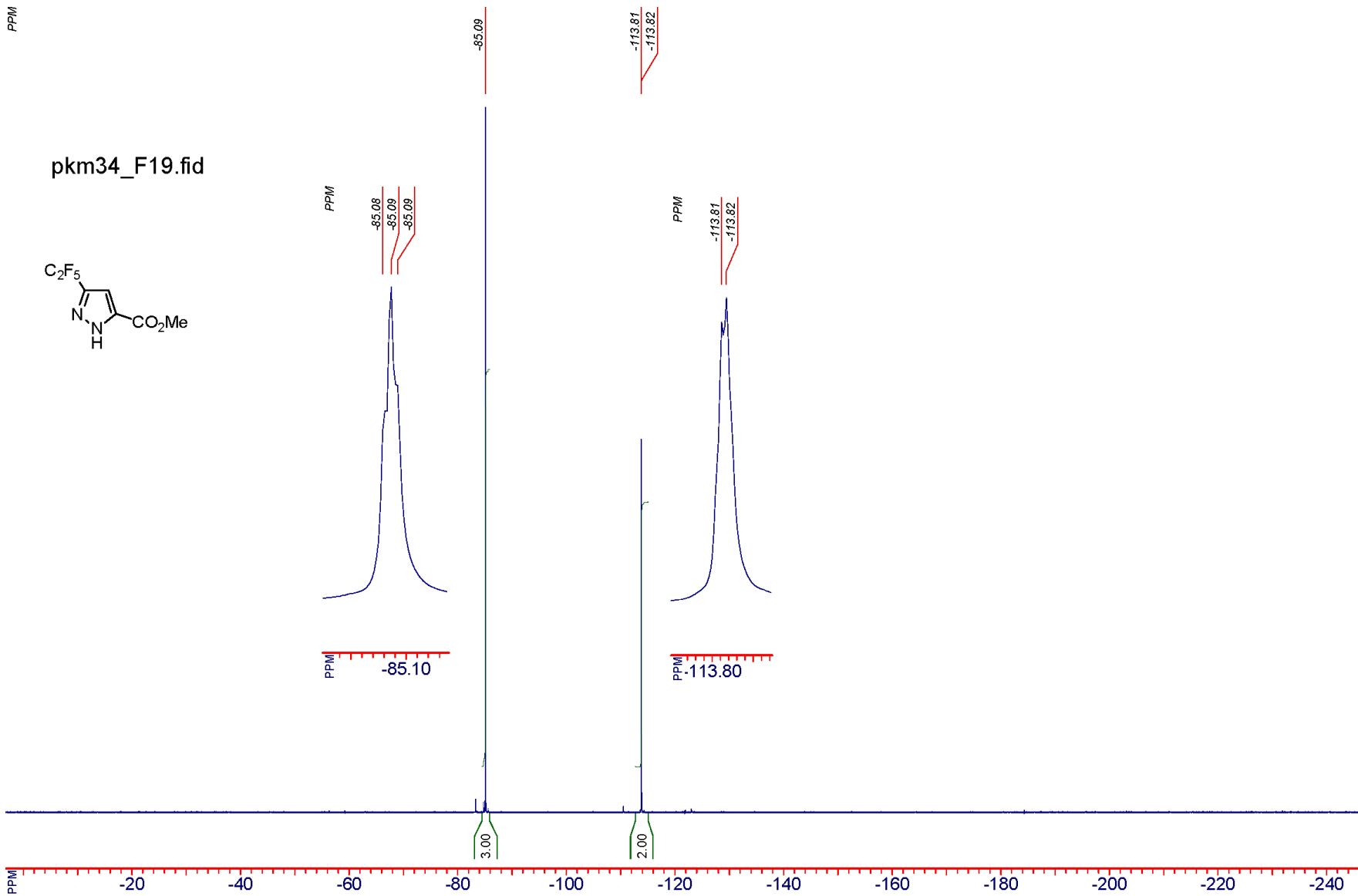
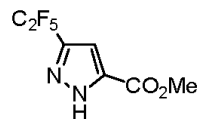
pkm34\_C13



File name: pkm34_C13	Operator: root	SF: 125.7422 MHz	NSC: 1125	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 10-Jul-2013	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM

pkm34\_F19.fid



File name: pkm34_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 11-Jul-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	

# Compound 2a

PPM

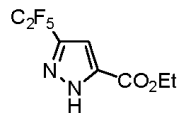
11.884

7.131

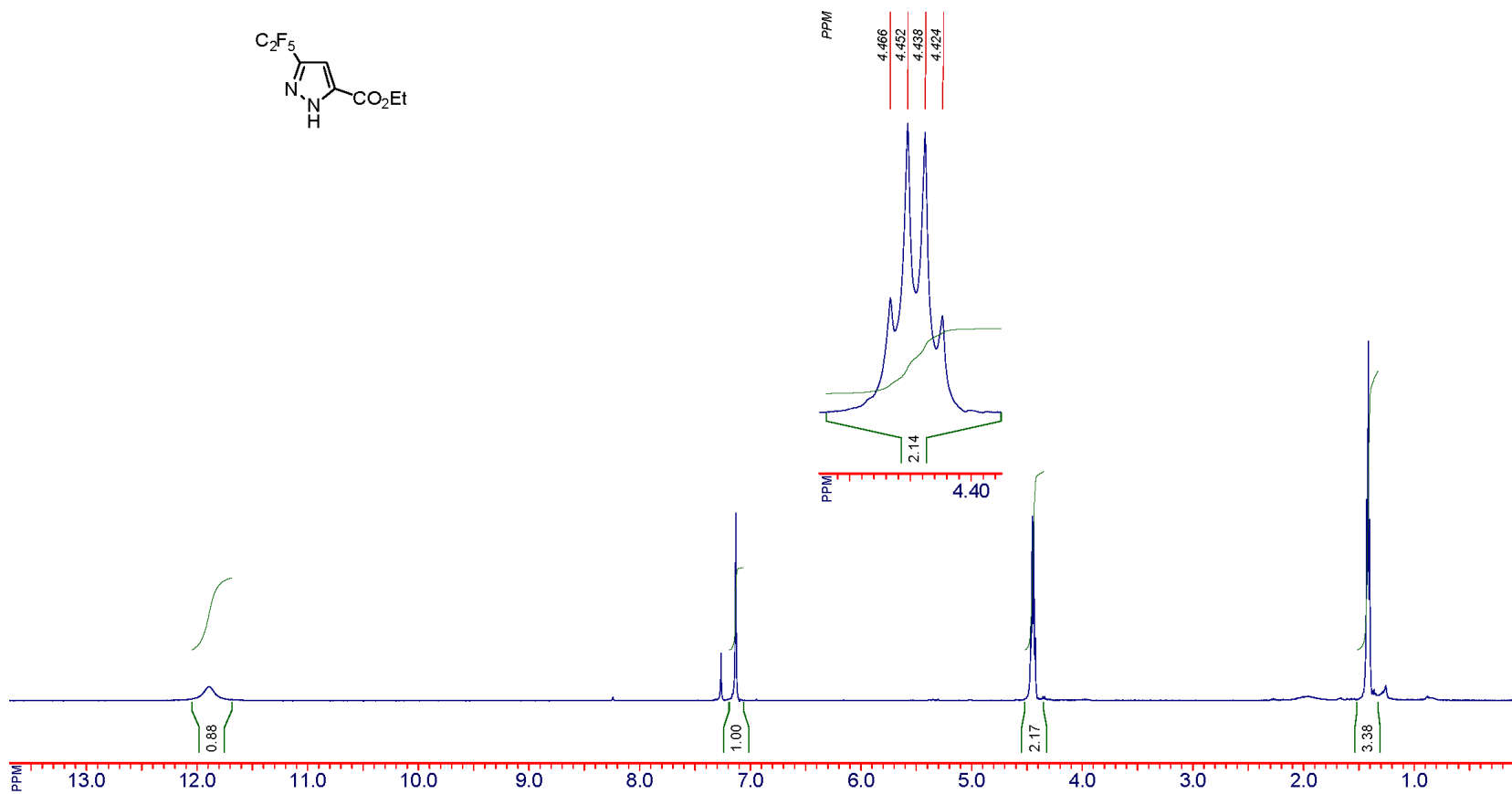
4.466  
4.452  
4.438  
4.424

1.431  
1.417  
1.402

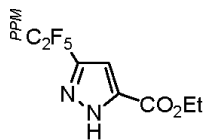
## pkm91



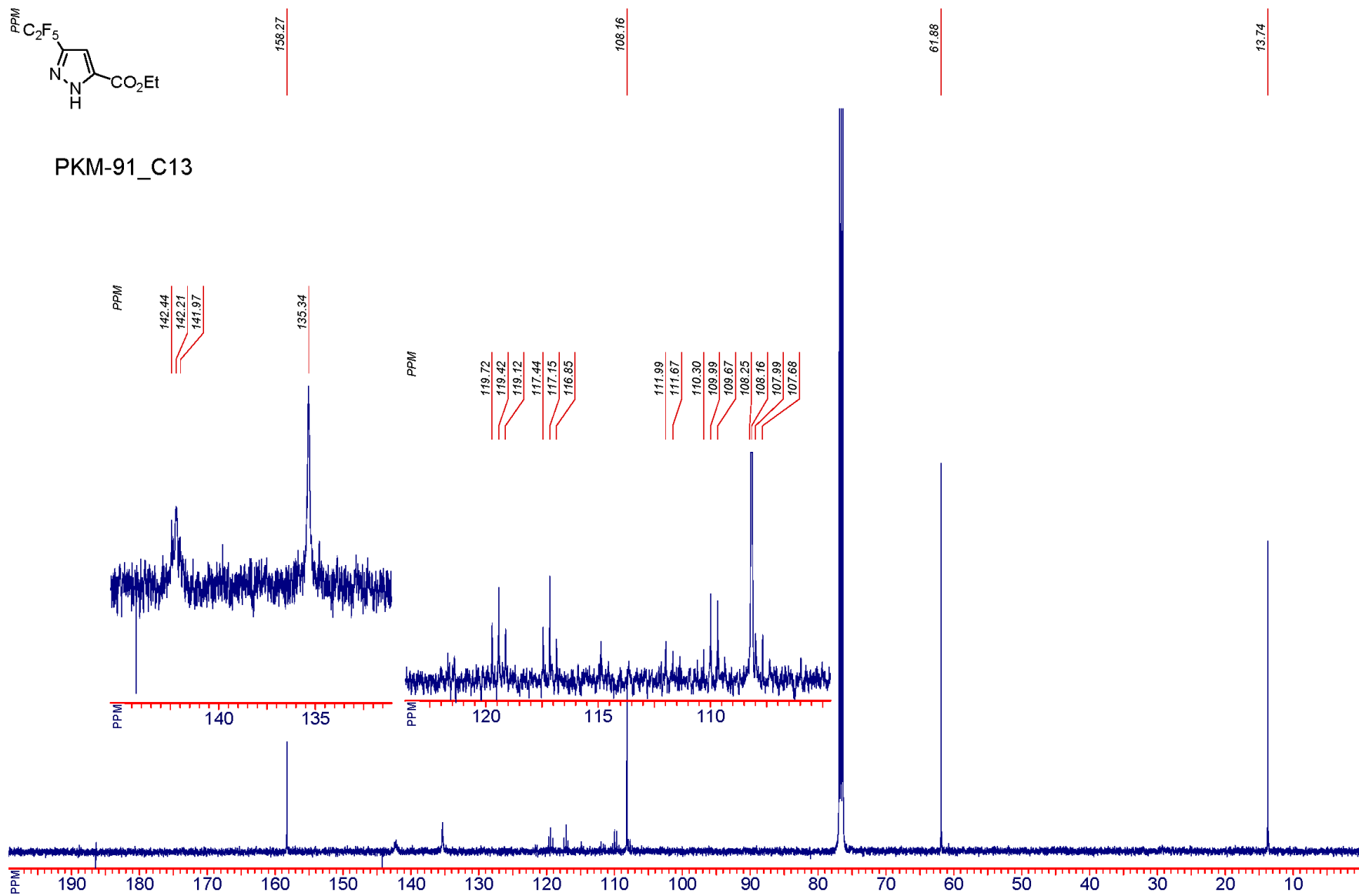
PPM  
4.466  
4.452  
4.438  
4.424



File name: pkm91	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 24	SI: 32768
Date: 21-Oct-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5



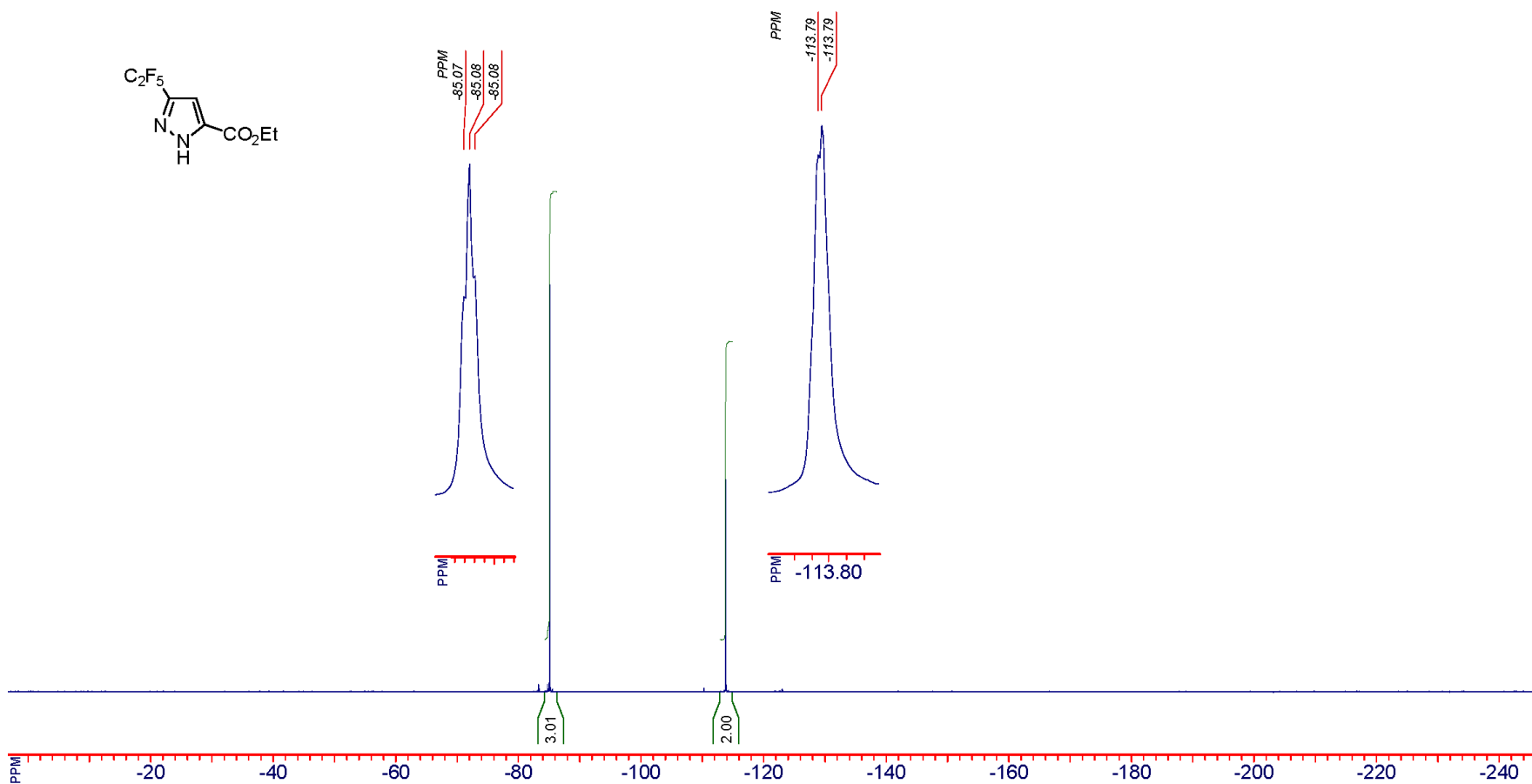
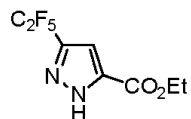
PKM-91\_C13



File name: PKM-91_C13	Operator: root	SF: 125.7126 MHz	NSC: 2651	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 22-Oct-2013	Solvent: DMSO	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM

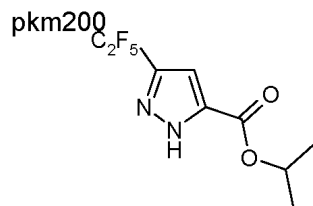
pkm-91\_F19.fid



File name: pkm-91_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 24-Oct-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	

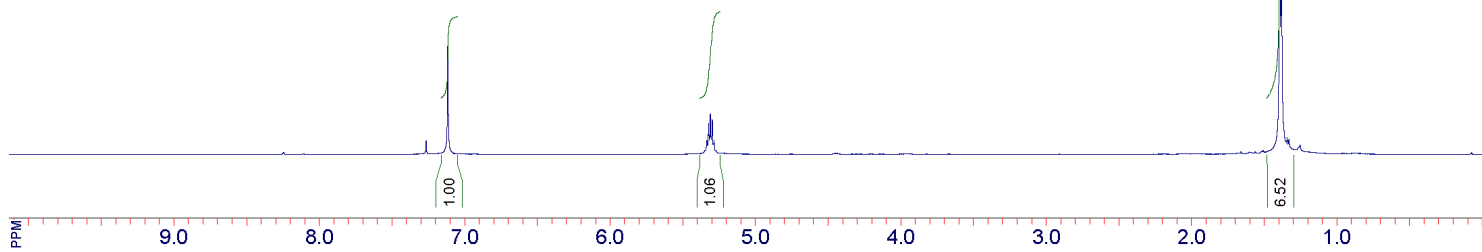
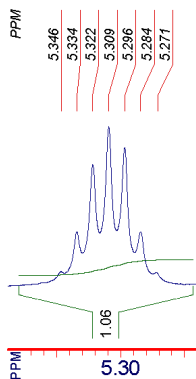
# Compound 3a

PPM



7.115

1.393  
1.361



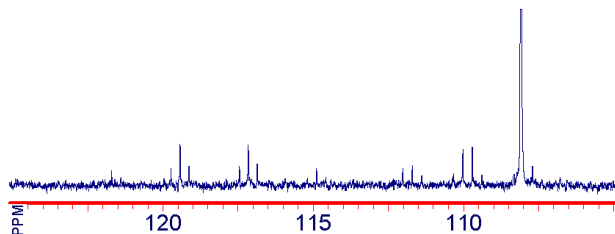
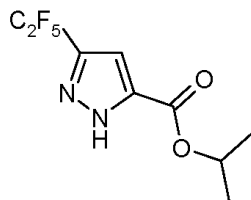
File name: pkm200	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 200	SI: 32768
Date: 12-May-2014	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5



PPM



pkm200\_C13



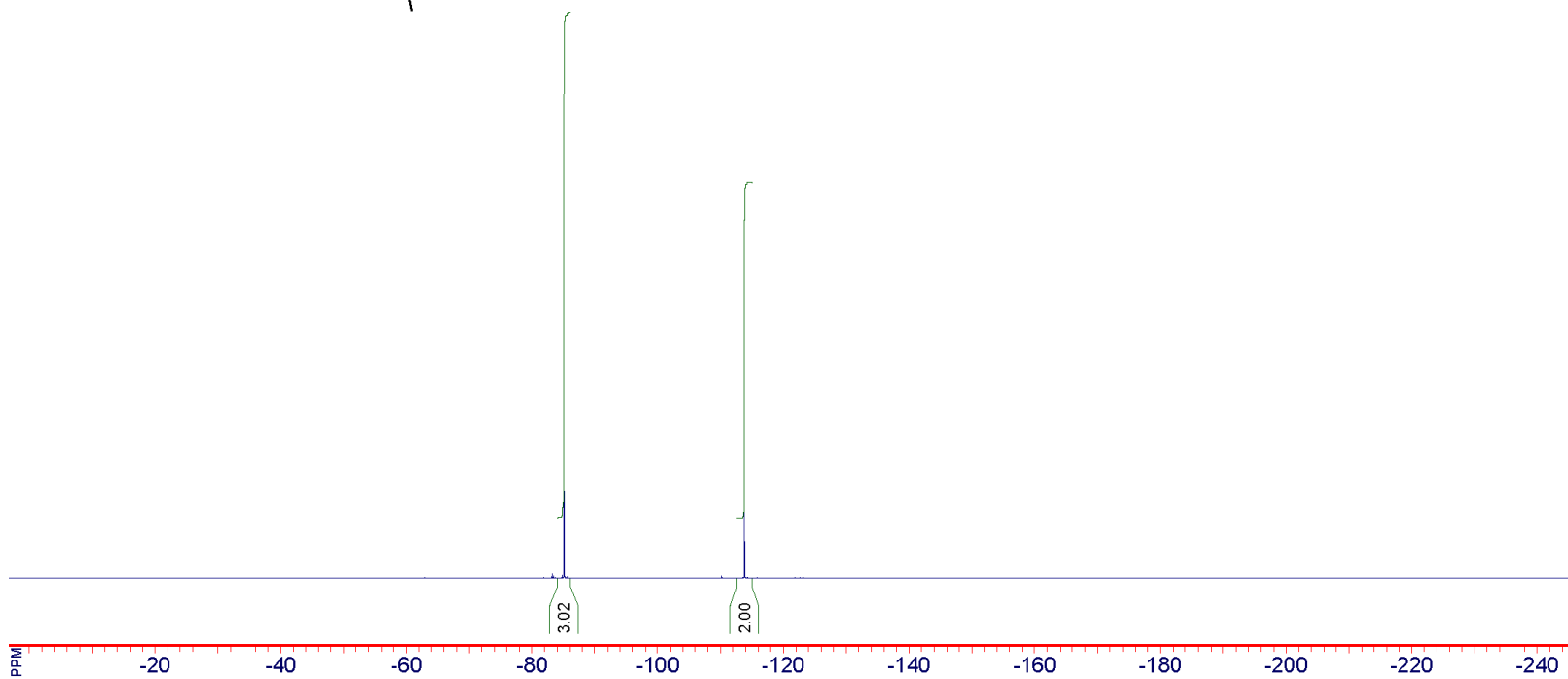
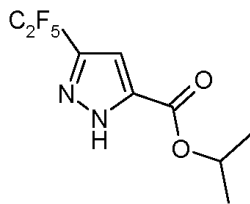
File name: pkm200_C13	Operator: root	SF: 125.7126 MHz	NSC: 1619	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 14-May-2014	Solvent: CDCl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWMN-NMR Version 3.5

PPM

-65.14

-113.80

Pkm200\_F19.fid

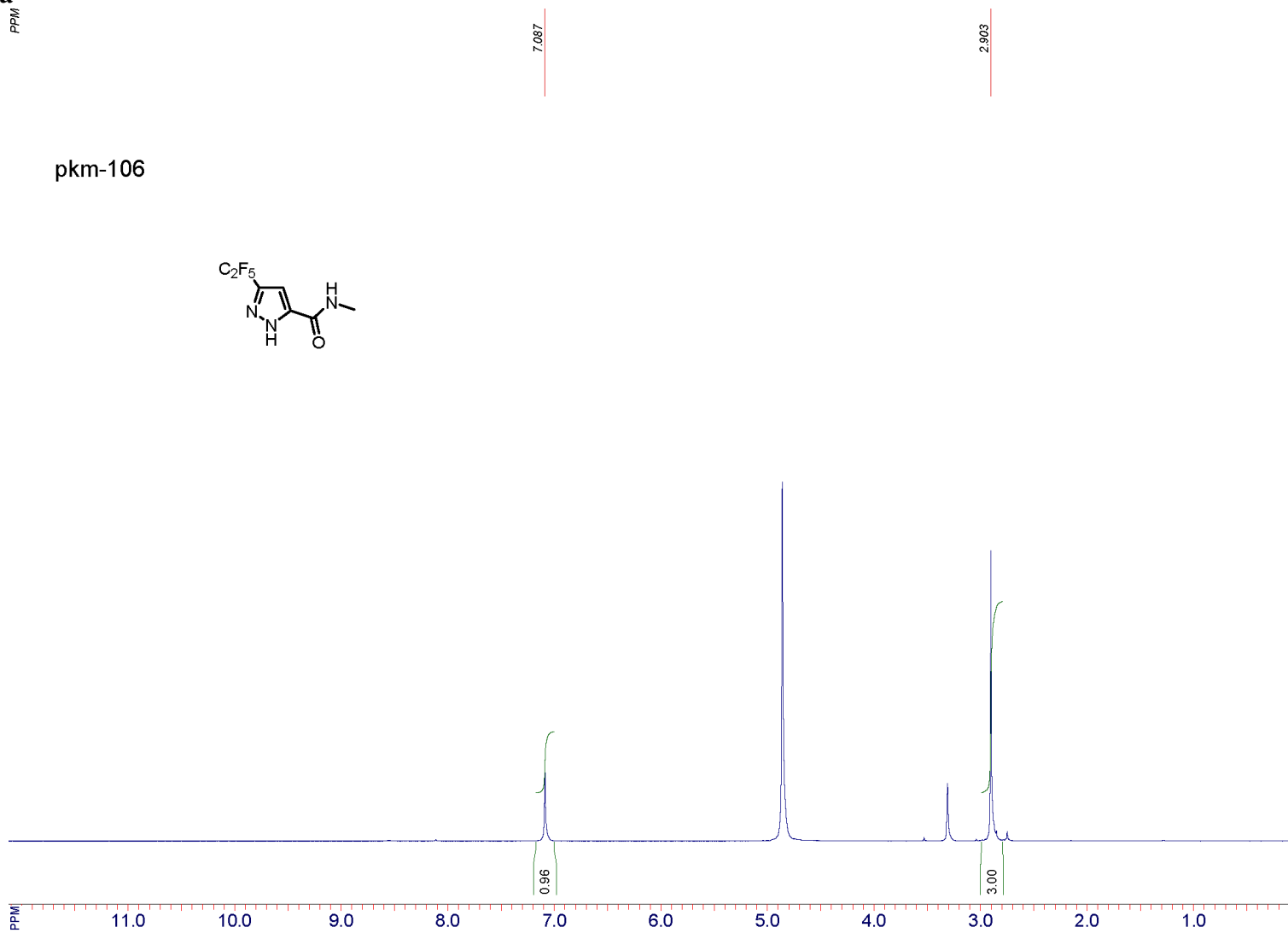
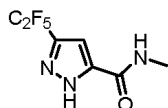


File name: Pkm200_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□

# Compound 4a

PPM

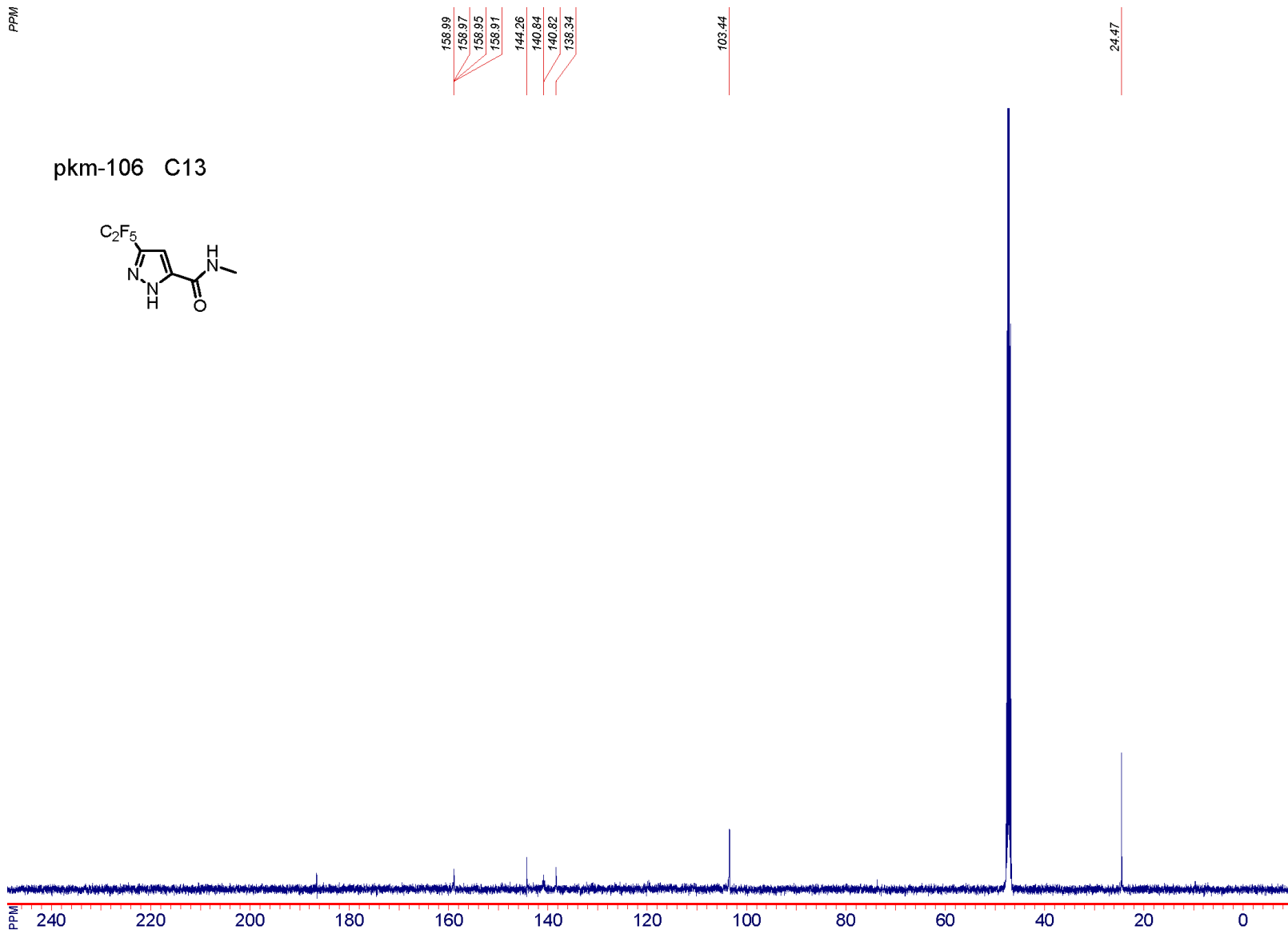
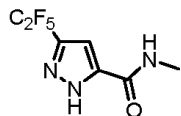
pkm-106



File name: pkm-106	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 06-Nov-2013	Solvent: MeOD	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWMN-NMR Version 3.5

PPM

pkm-106 C13



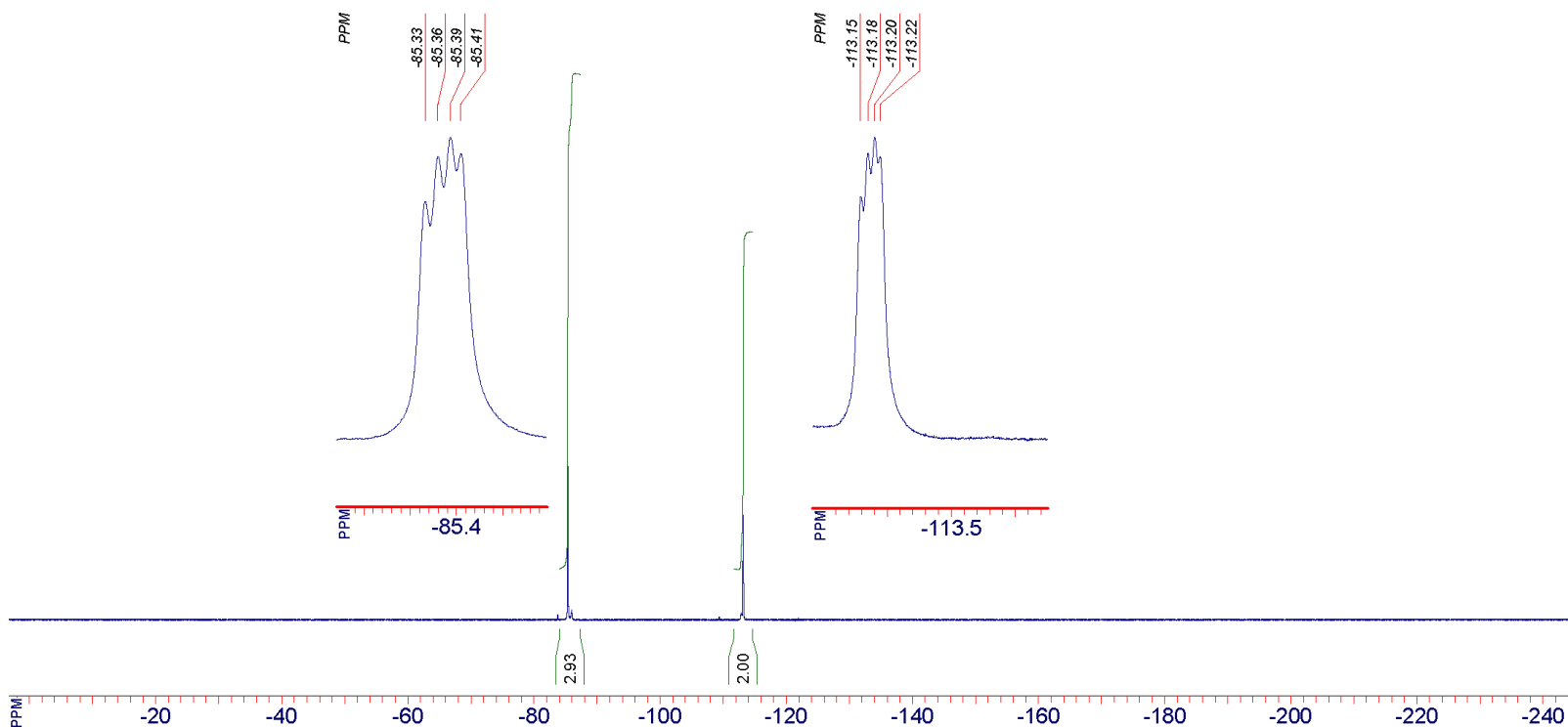
File name: pkm-106 C13	Operator: root	SF: 125.7126 MHz	NSC: 9466	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 08-Nov-2013	Solvent: MeOD	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-85.33  
-85.36  
-85.39  
-85.41

-113.15  
-113.18  
-113.20  
-113.22

pkm106\_F19.fid



File name: pkm106_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 12-Nov-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

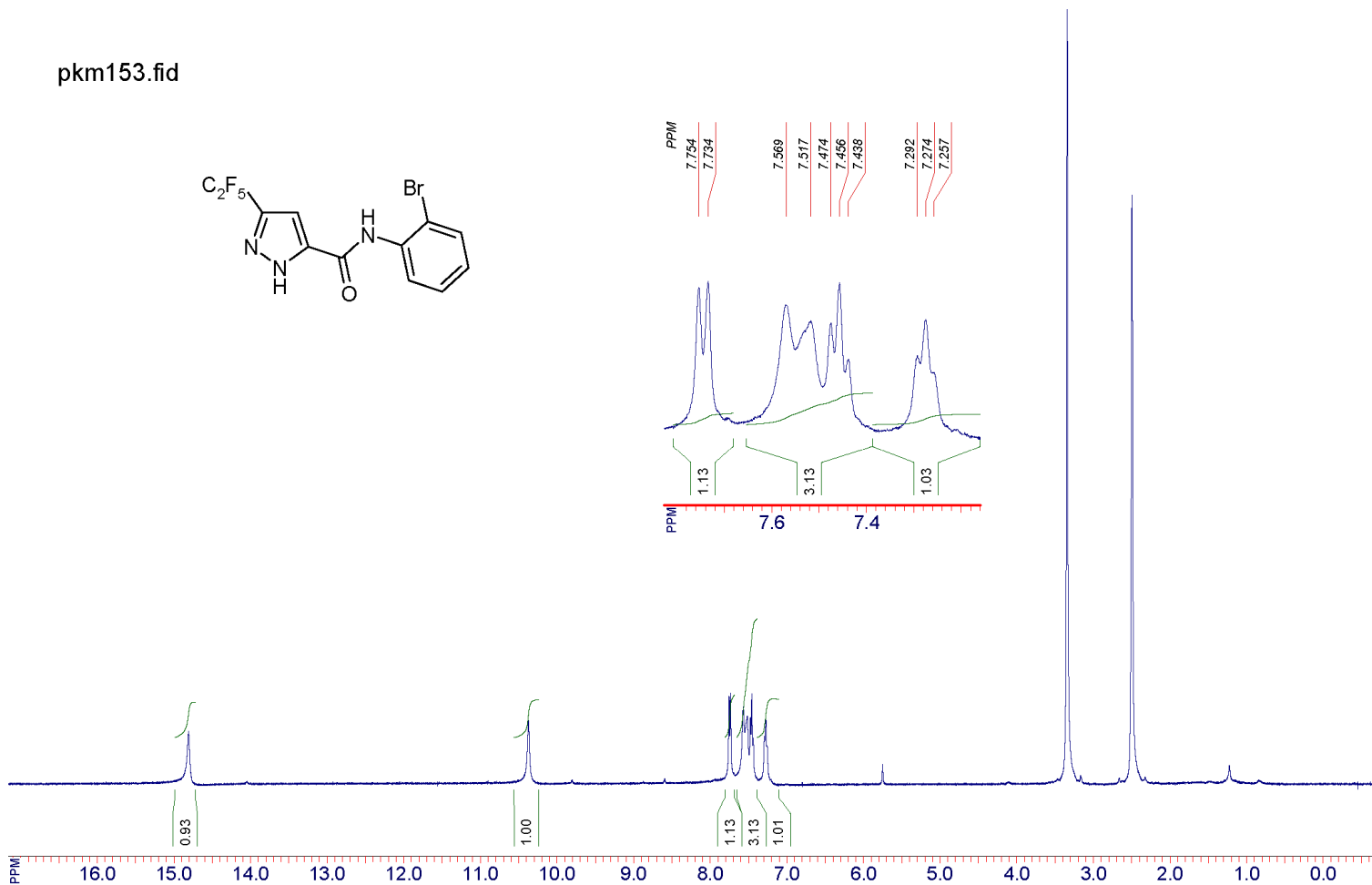
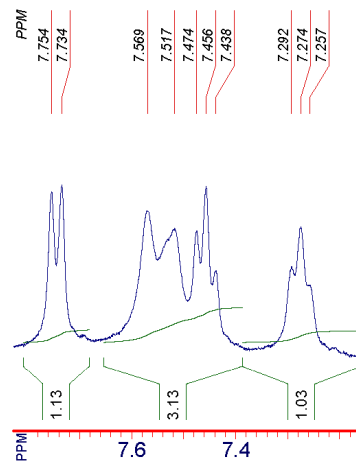
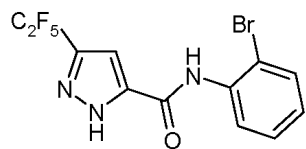
# Compound 5a

PPM

14.807

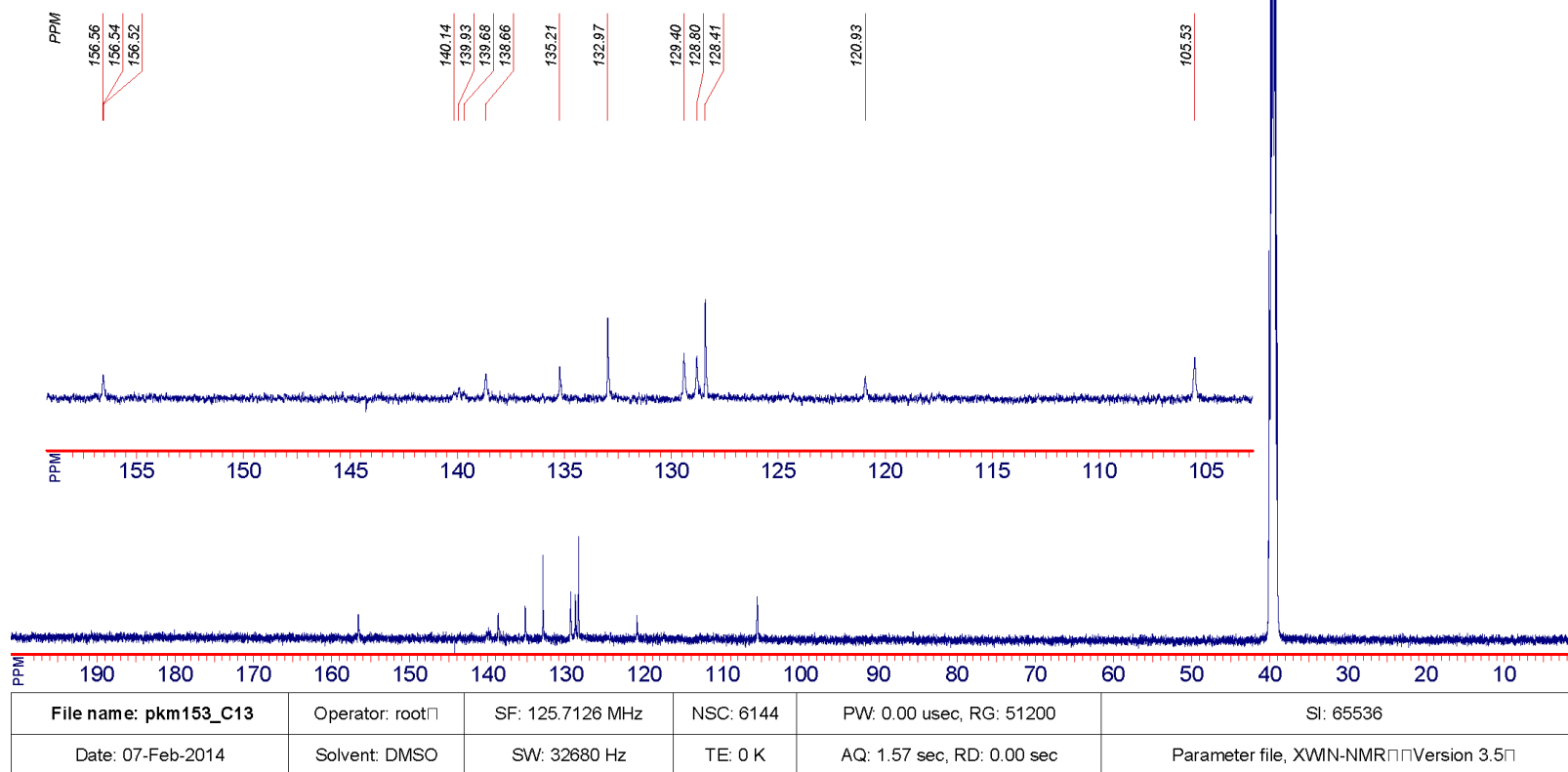
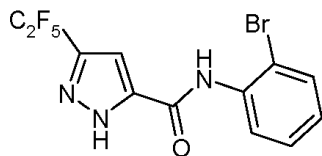
10.371

pkm153.fid



File name: pkm153.fid	Operator:	SF: 400.0019 MHz	NSC: 0	PW: 7.50 usec, RG: 26	SI: 32768
Date: 31-Jan-2014	Solvent: dms0_d6	SW: 7175 Hz	TE: 293 K	AQ: 1.67 sec, RD: 0.00 sec	□

pkm153\_C13

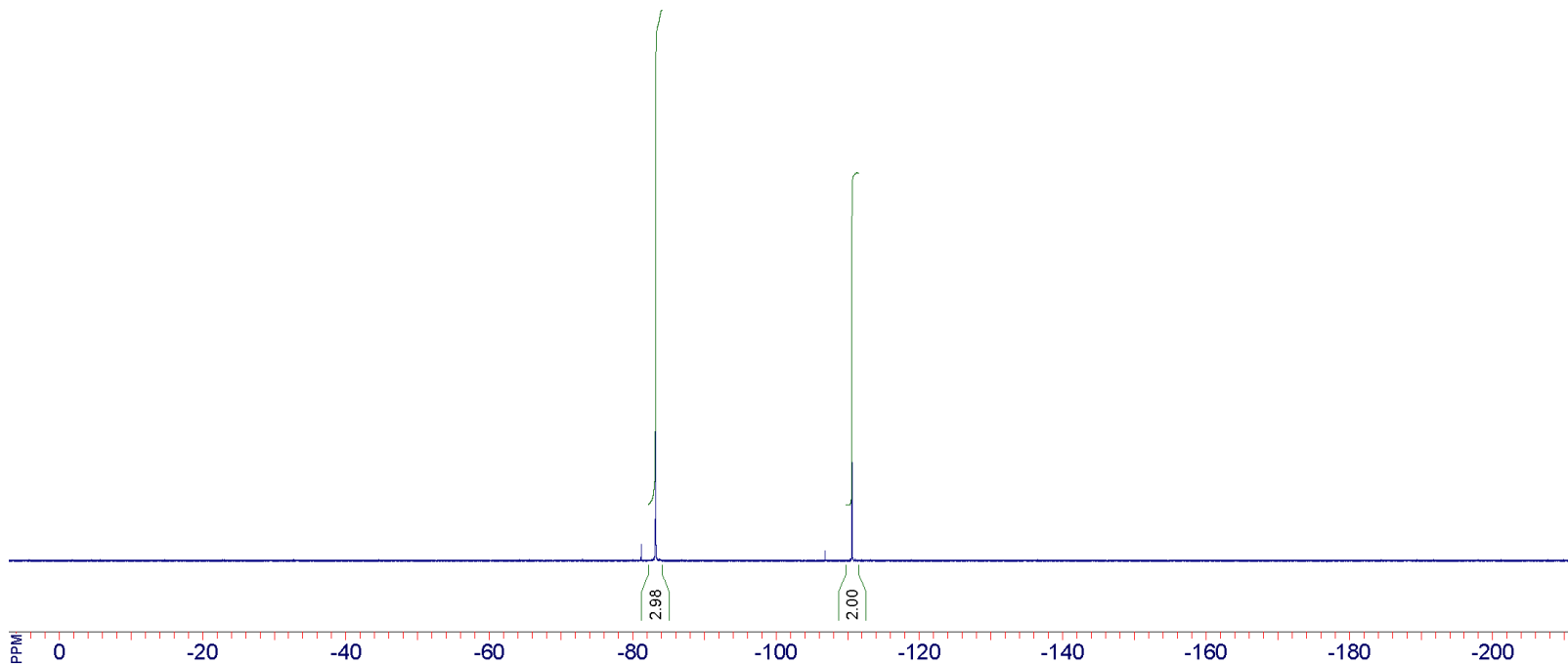
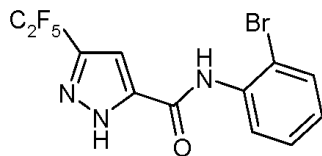


PPM

-83.21

-110.59

pkm153-F19.fid



File name: pkm153-F19.fid	Operator:	SF: 376.3274 MHz	NSC: 0	PW: 3.00 usec, RG: 60	SI: 65536
Date: 06-Mar-2014	Solvent: dmsol-d6	SW: 82816 Hz	TE: 293 K	AQ: 0.39 sec, RD: 0.00 sec	□



Compound 6a

PPM

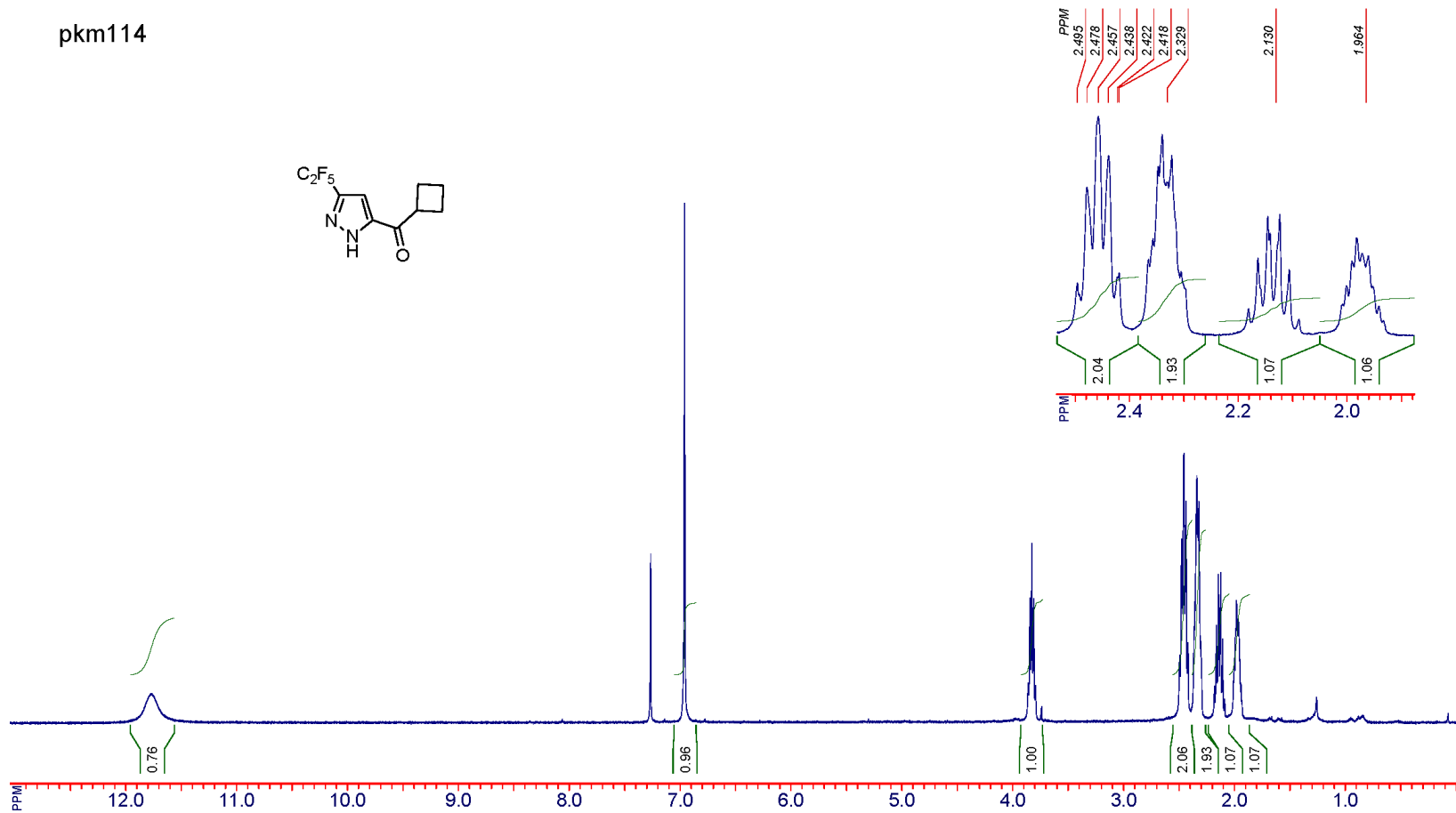
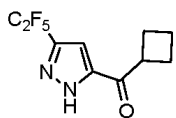
11.775

6.959

3.860  
3.844  
3.827  
3.810  
3.793

pkm114

PPM  
2.495  
2.478  
2.457  
2.438  
2.422  
2.418  
2.329  
2.130  
1.964



File name: pkm114	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 100	SI: 32768
Date: 21-Nov-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM

191.52

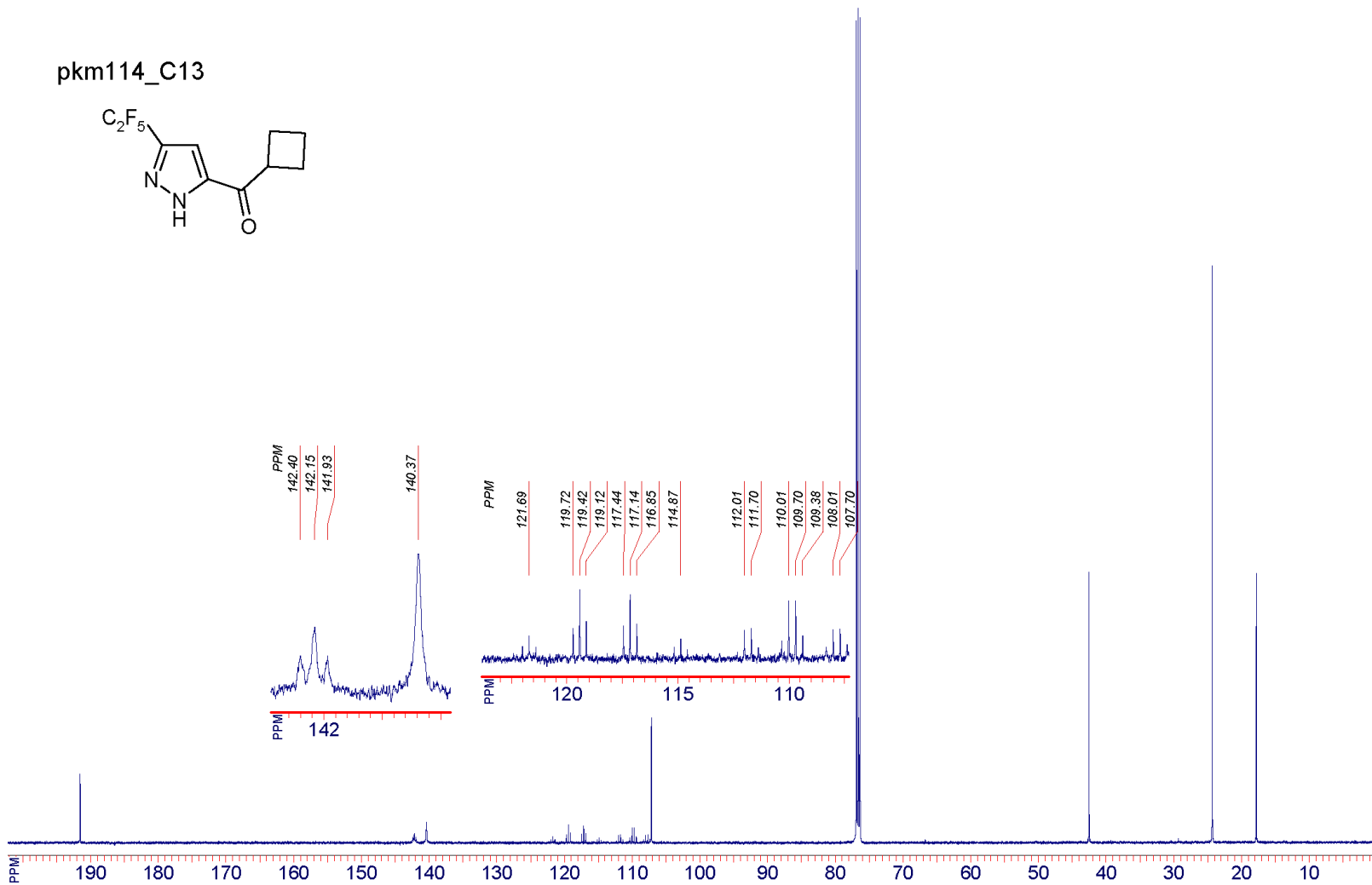
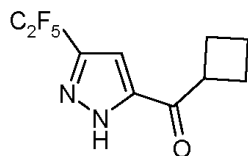
107.15

42.51

24.33

17.82

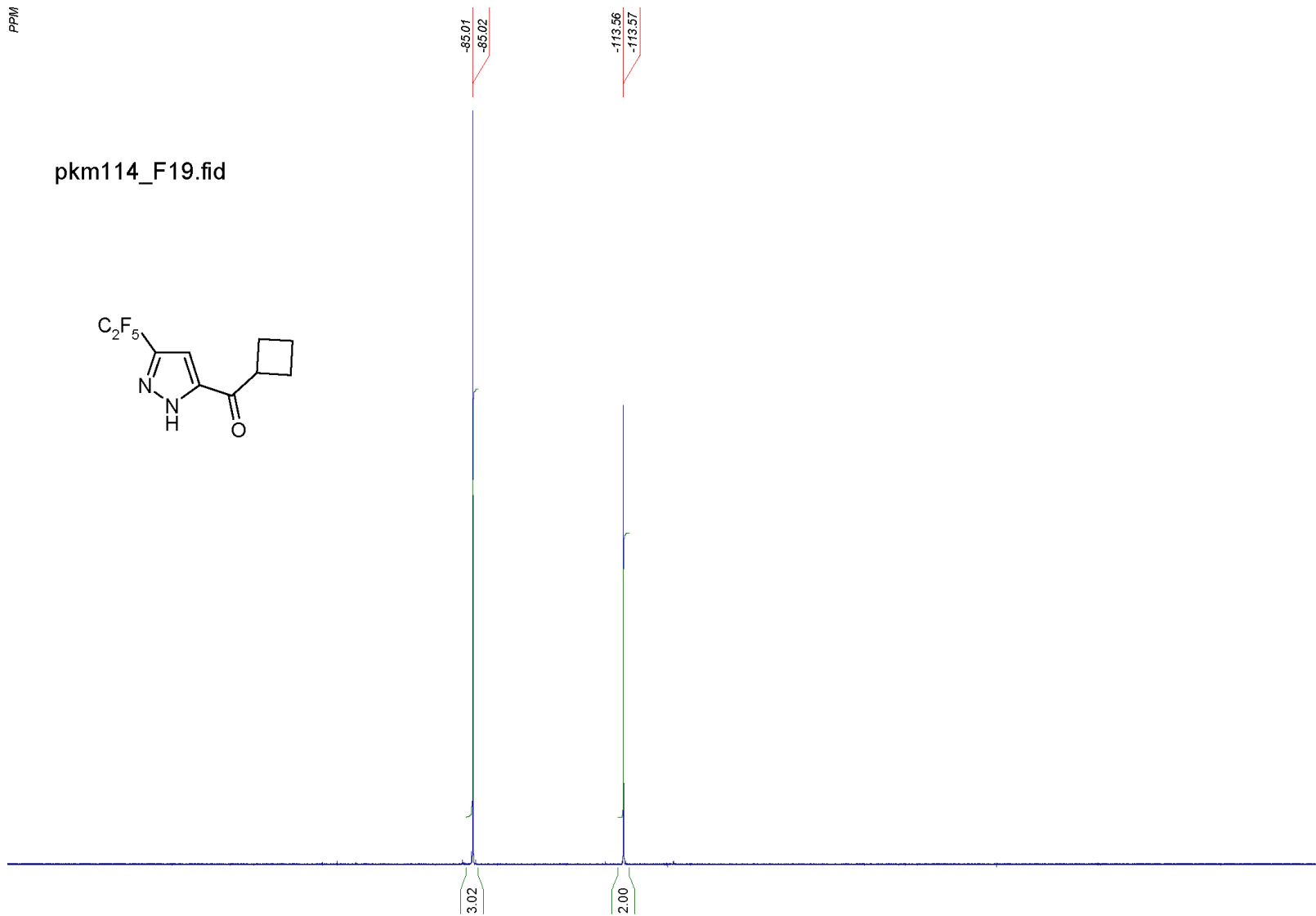
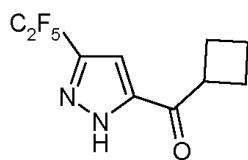
pkm114\_C13



File name: pkm114_C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 07-Dec-2013	Solvent: dms	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

pkm114\_F19.fid



File name: pkm114_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 10-Dec-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

# Compound 7a

PPM

11.672

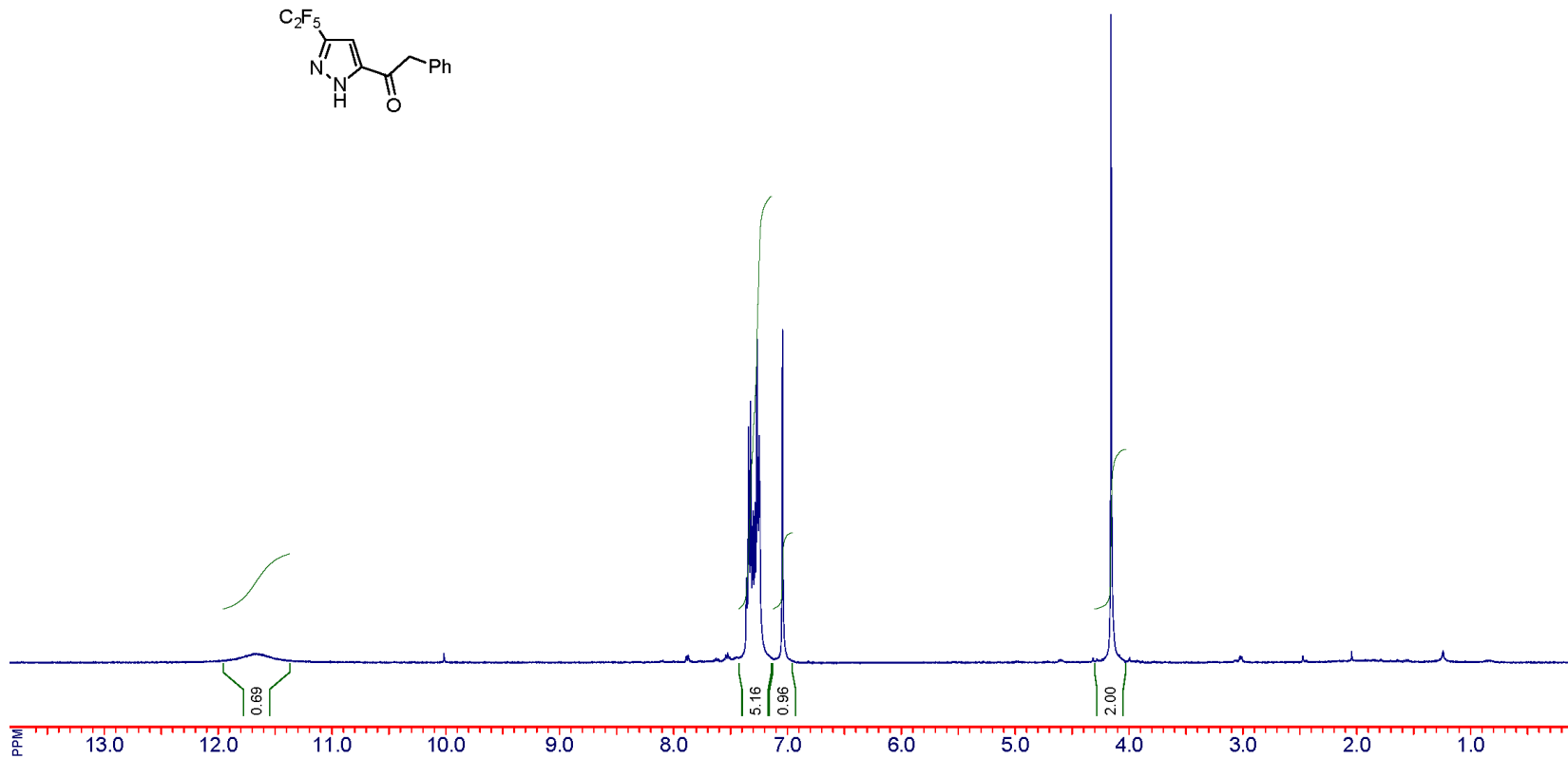
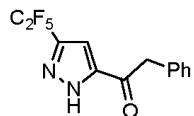
7.962

7.248

7.044

4.158

pkm82.fid



File name: pkm82.fid	Operator:	SF: 400.0002 MHz	NSC: 0	PW: 7.50 usec, RG: 26	SI: 32768
Date: 10-Oct-2013	Solvent: CDCl3	SW: 7261 Hz	TE: 293 K	AQ: 1.24 sec, RD: 0.00 sec	

PPM

187.80

142.00

141.34

132.01

129.07

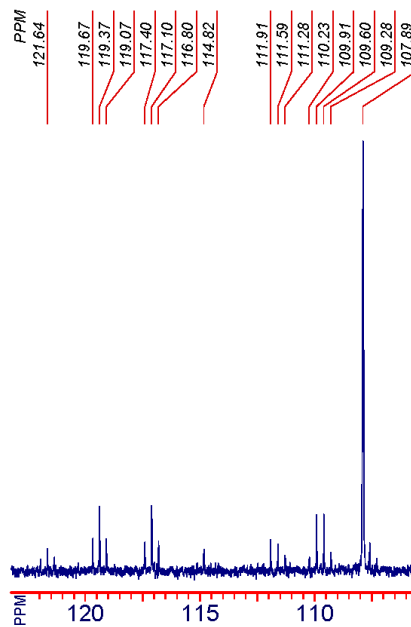
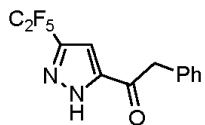
128.61

127.29

107.89

46.12

pkm82\_C13



PPM

File name: pkm82\_C13

Operator: root

SF: 125.7126 MHz

NSC: 6144

PW: 0.00 usec, RG: 51200

SI: 65536

Date: 13-Oct-2013

Solvent: CDCl3

SW: 32680 Hz

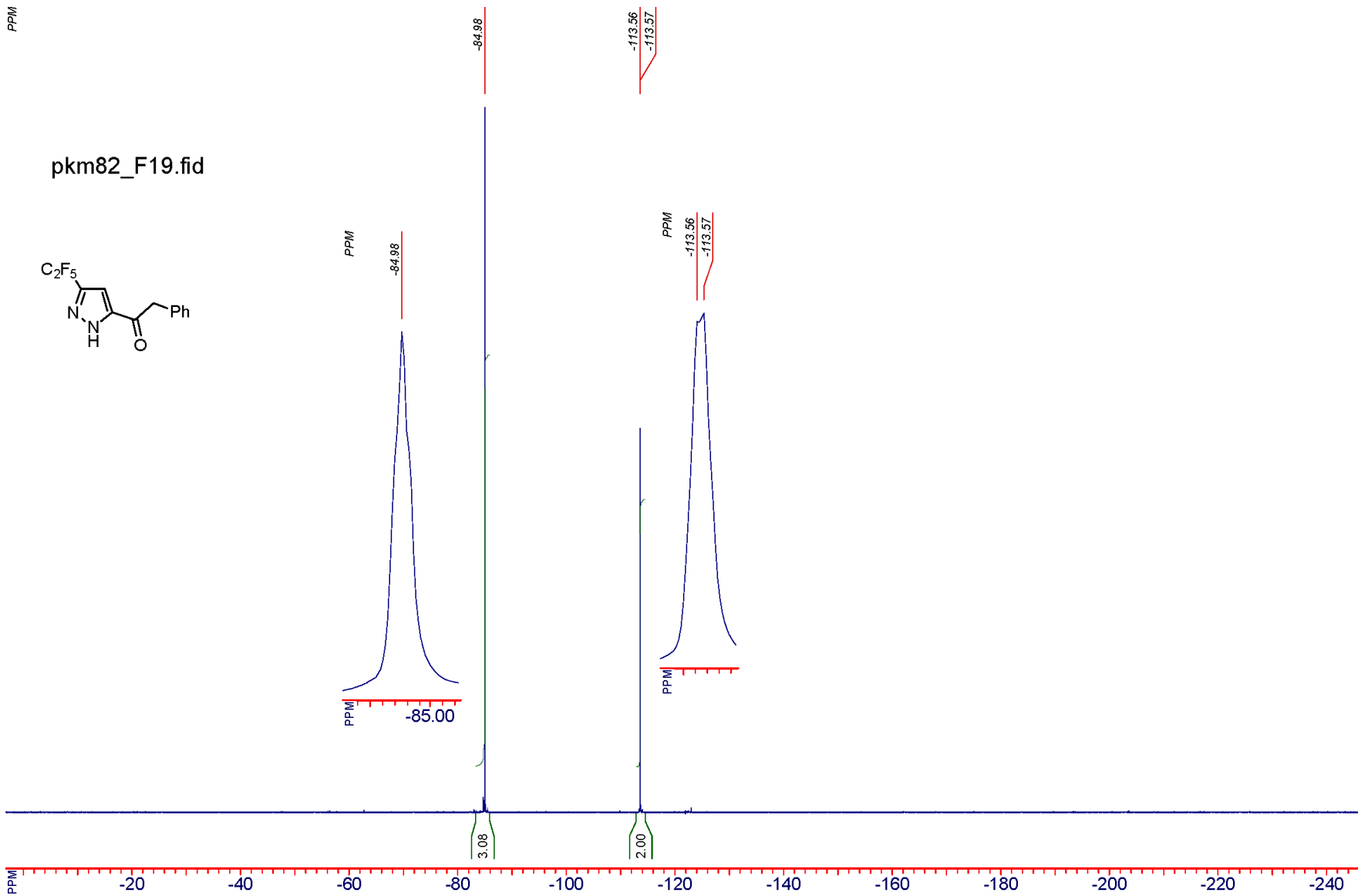
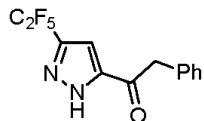
TE: 0 K

AQ: 1.57 sec, RD: 0.00 sec

Parameter file, XWIN-NMRVersion 3.5

PPM

pkm82\_F19.fid



File name: pkm82_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 15-Oct-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	

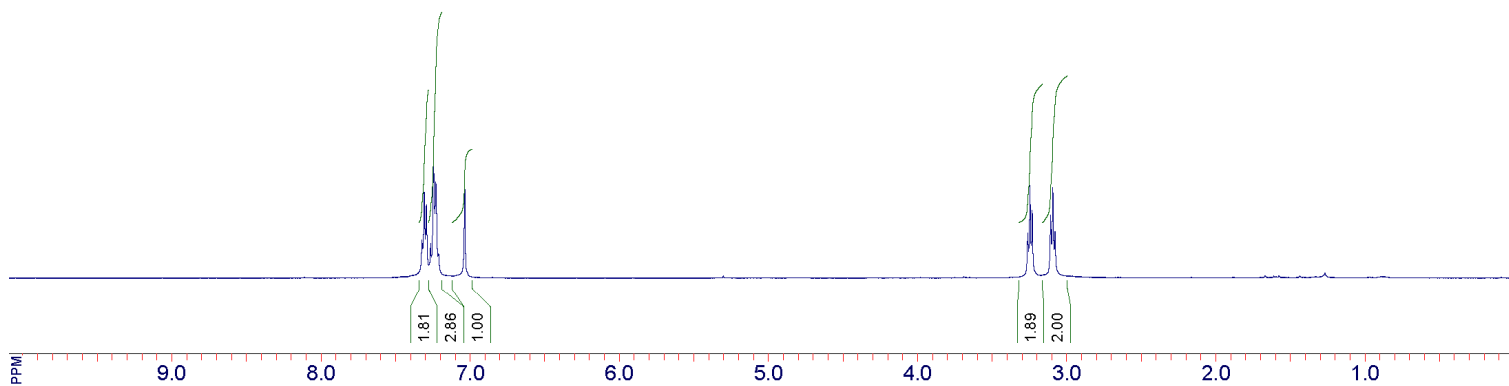
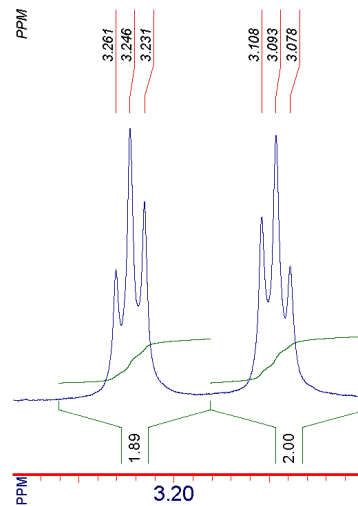
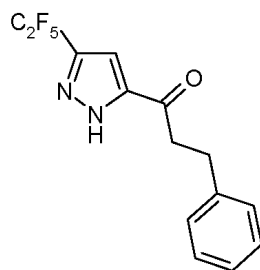
# Compound 8a

PPM

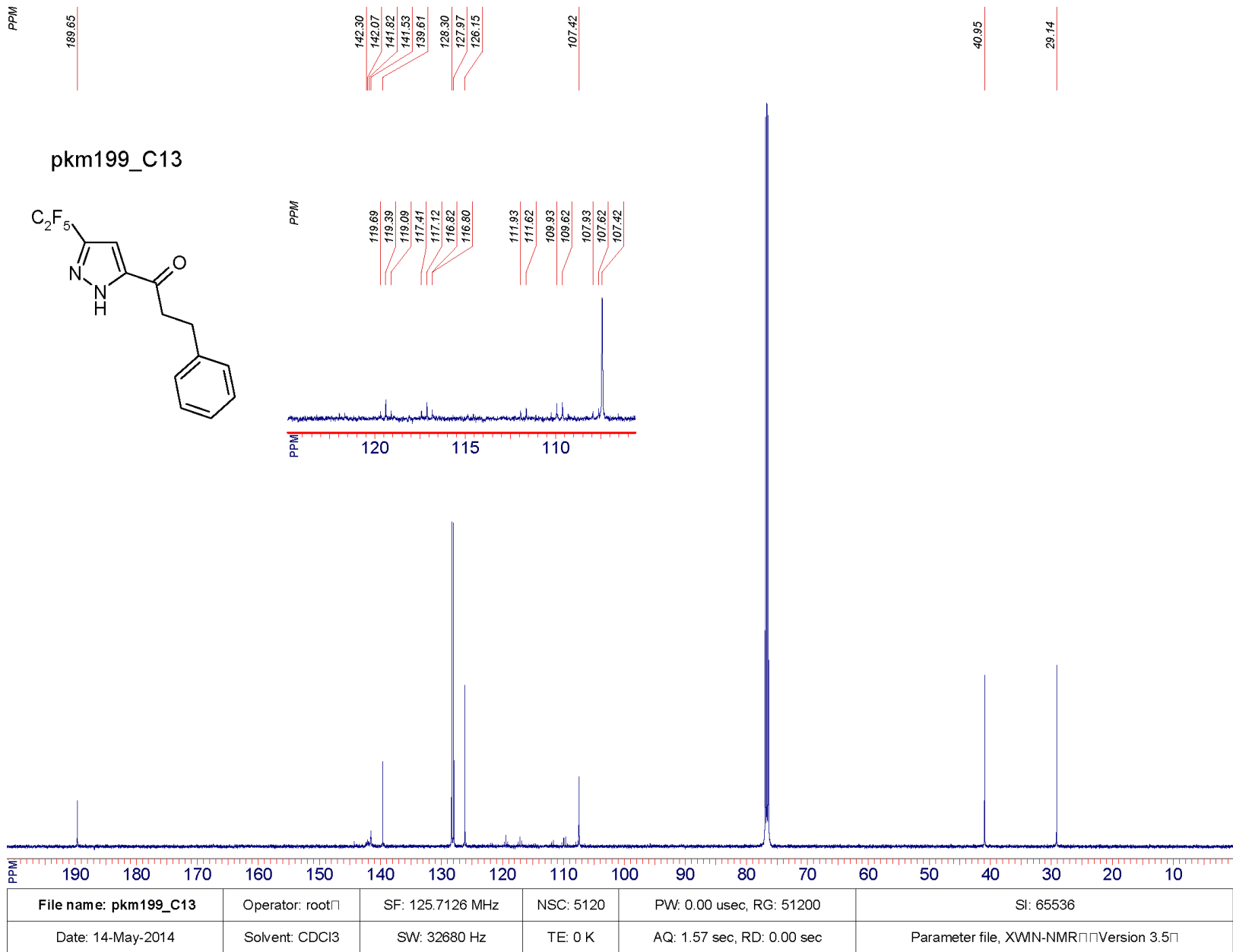
7.322  
7.307  
7.293  
7.245  
7.230  
7.036

3.261  
3.246  
3.231  
3.108  
3.093  
3.078

pkm199



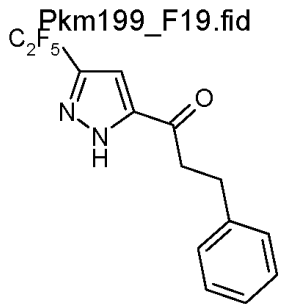
File name: pkm199	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 12-May-2014	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5



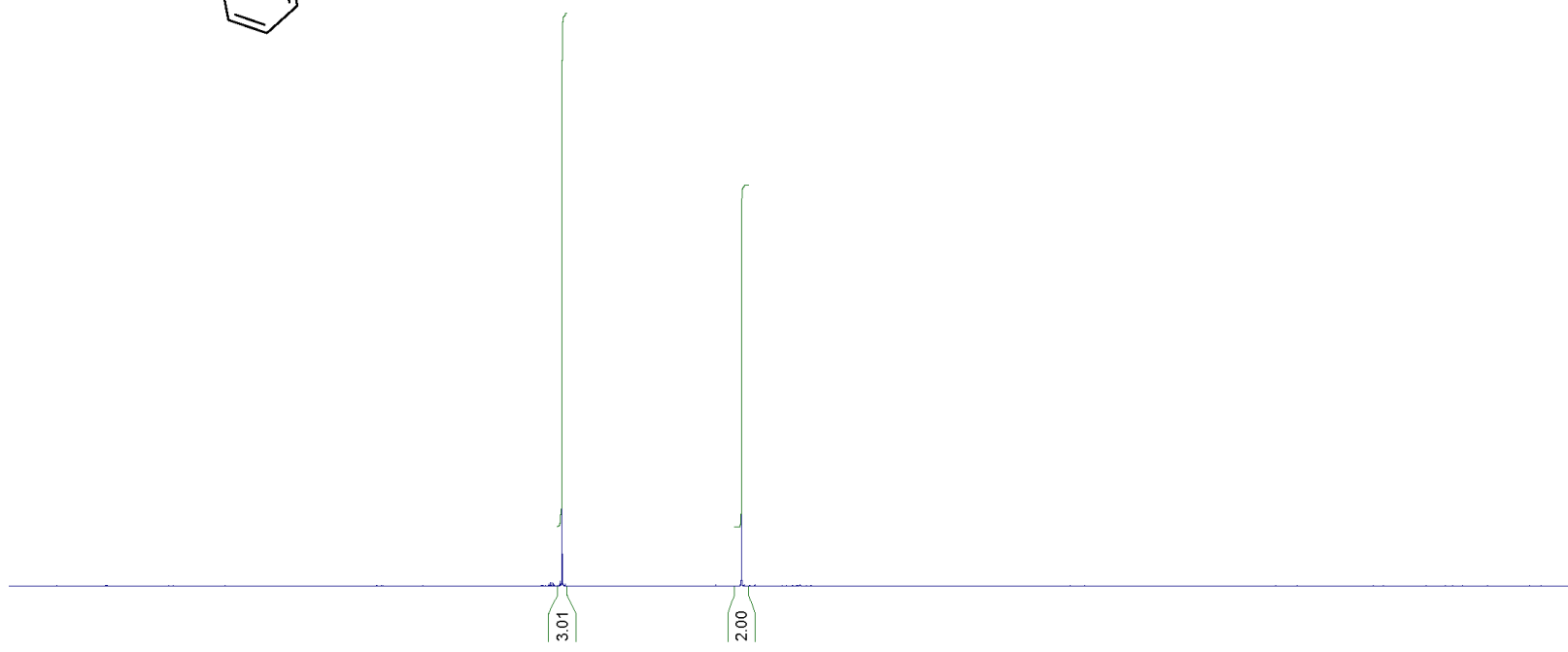


PPM

Pkm199\_F19.fid



-65.01  
-113.63



File name: Pkm199_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□

# Compound 9a

PPM

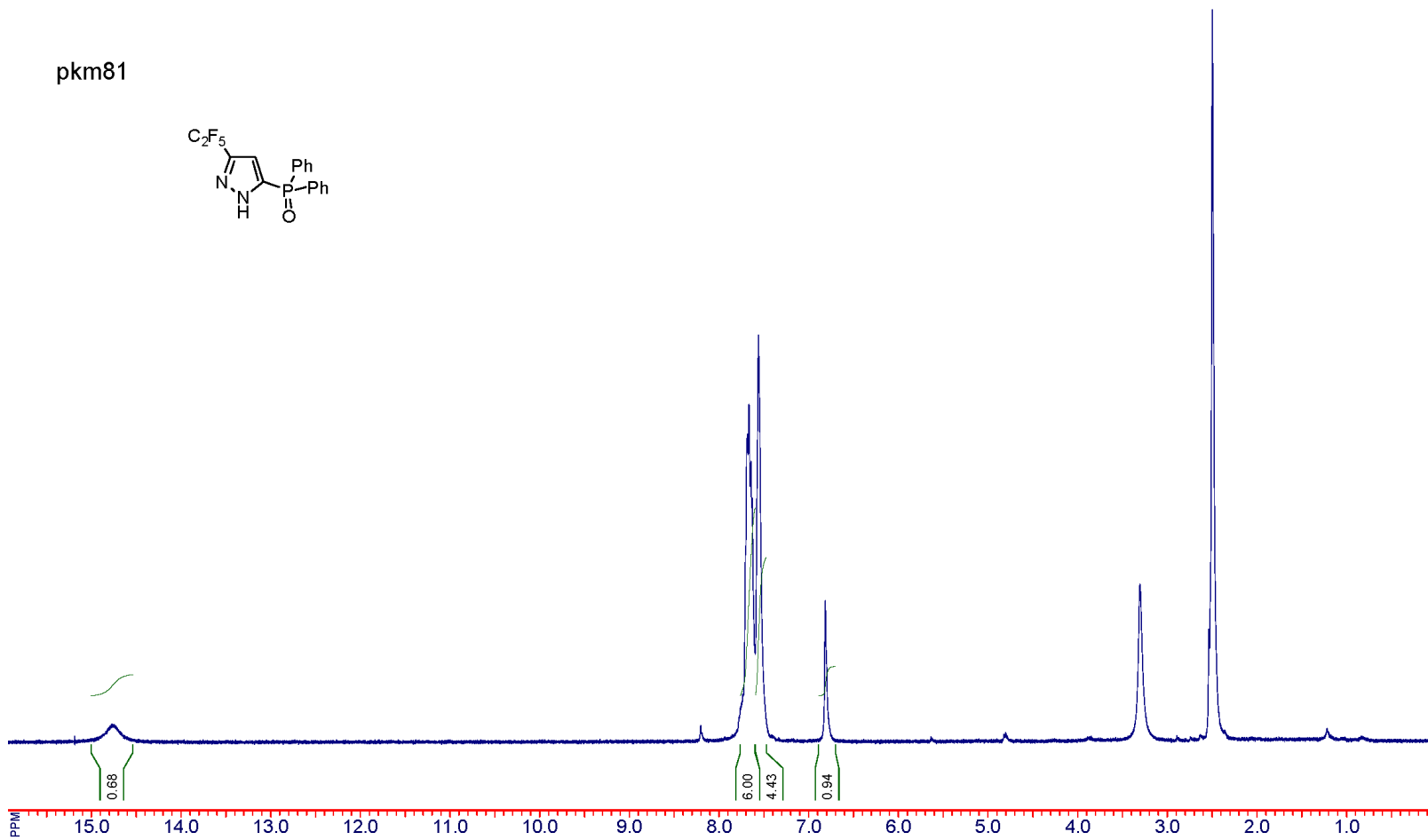
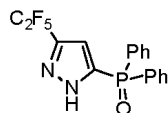
14.776

7.666

7.559

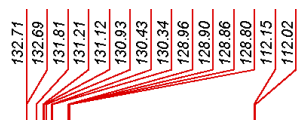
6.815

pkm81

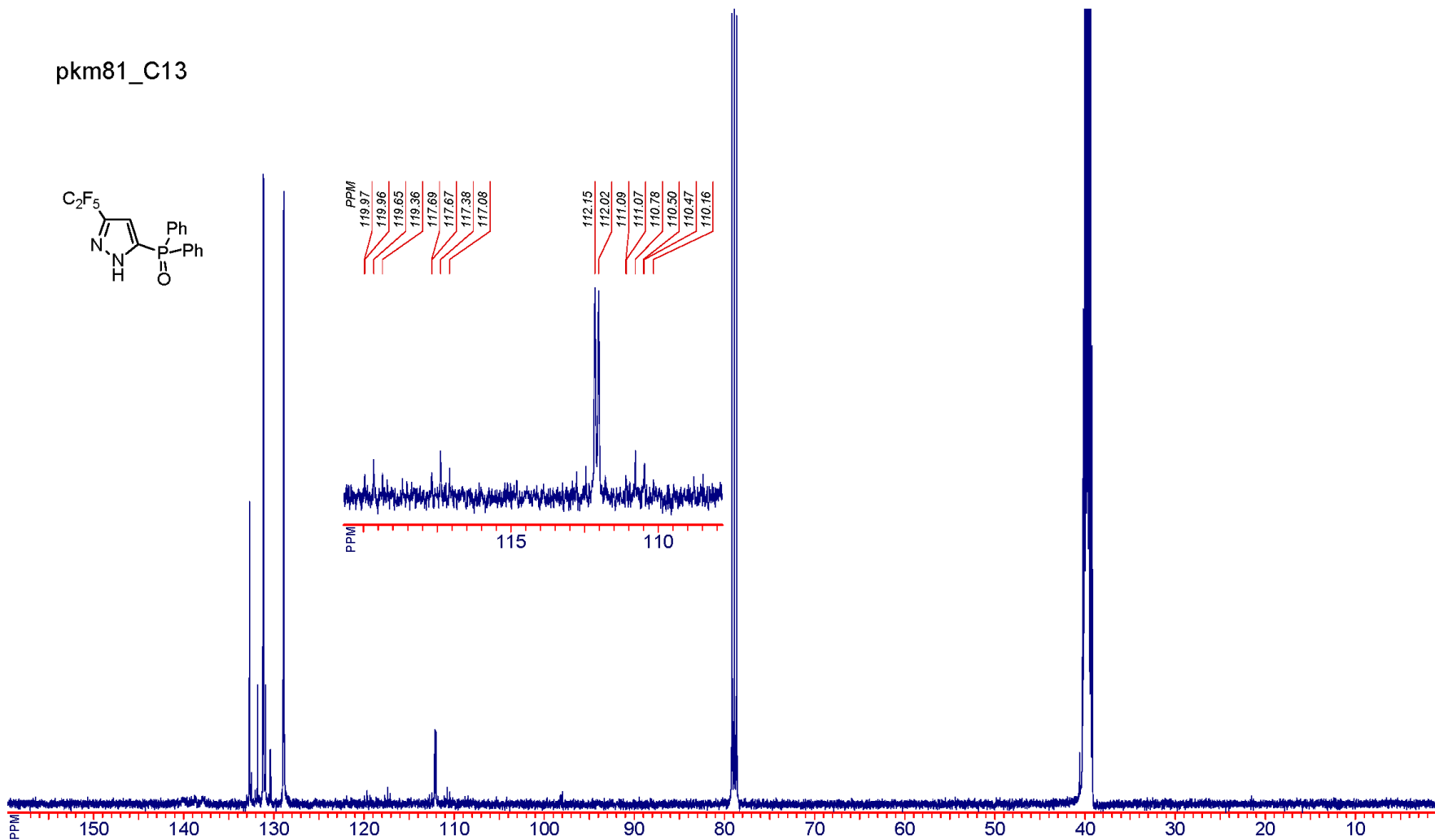
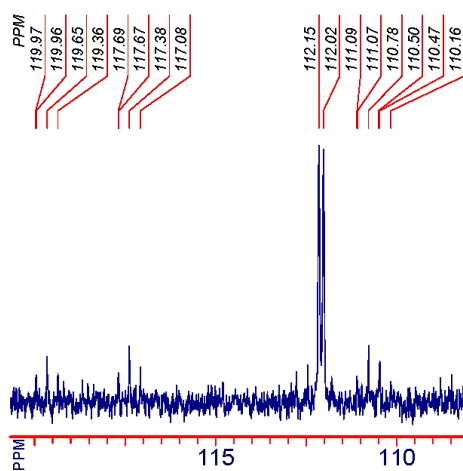
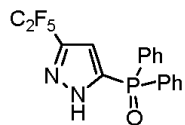


File name: pkm81	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 10-Oct-2013	Solvent: DMSO	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM



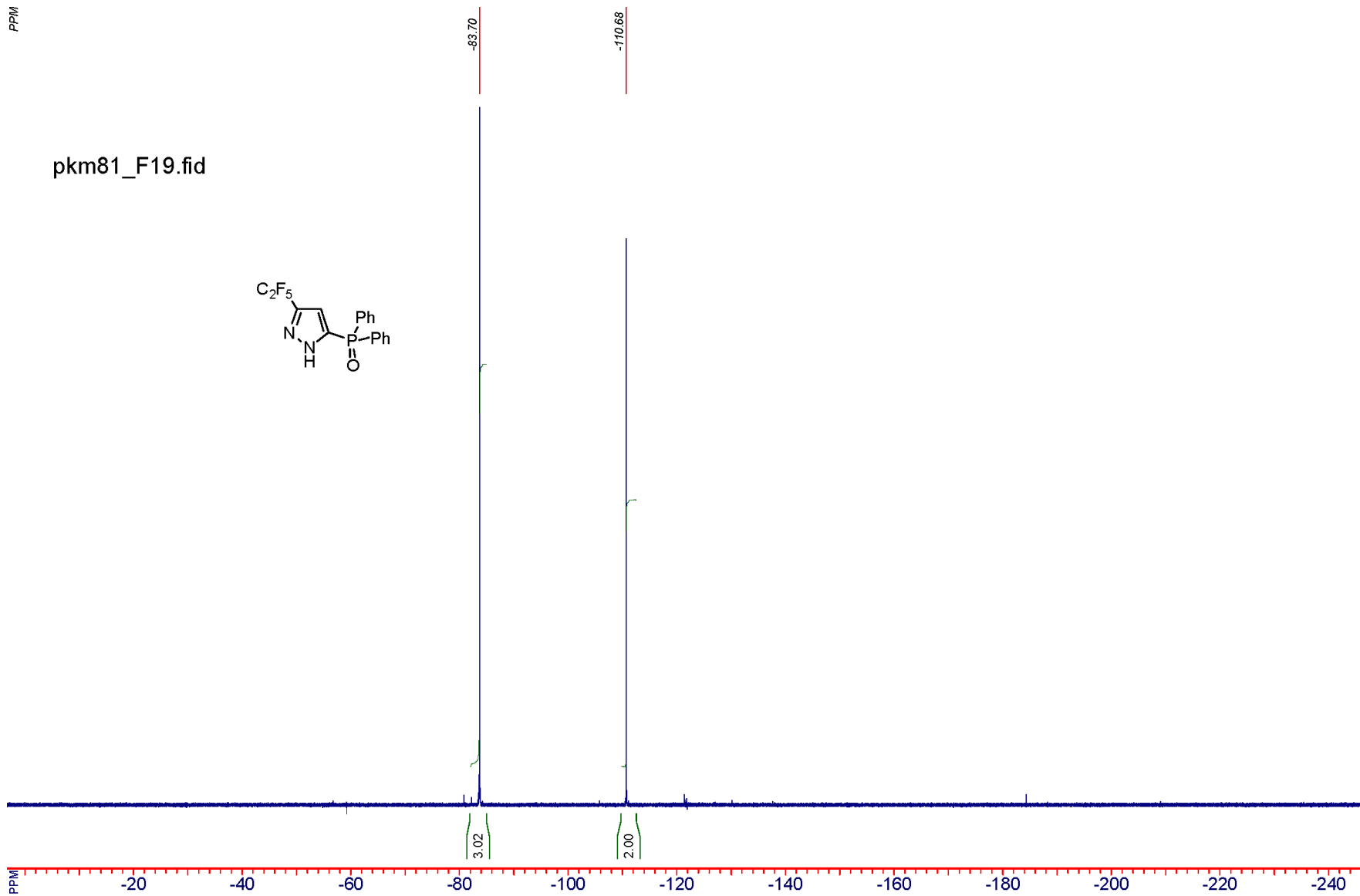
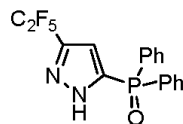
pkm81\_C13



File name: pkm81_C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 12-Oct-2013	Solvent: DMSO	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWMN-NMRVersion 3.5

PPM

pkm81\_F19.fid

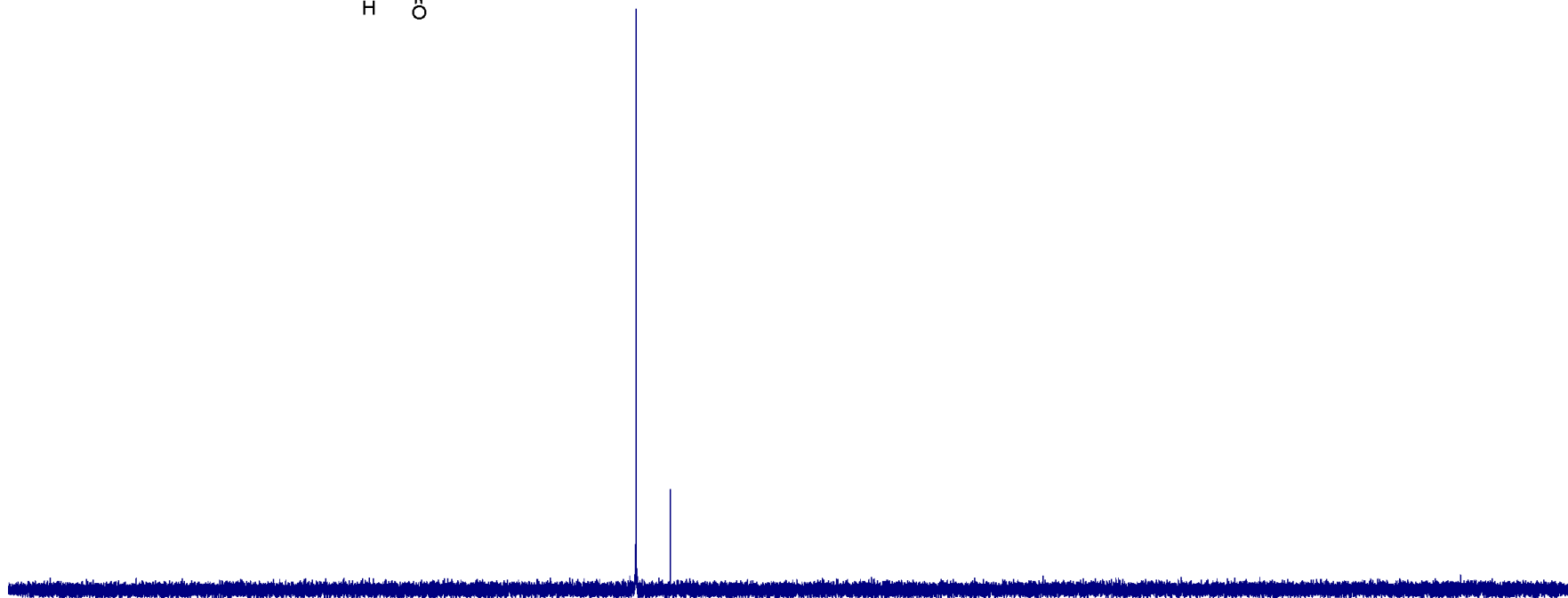
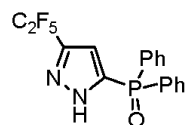


File name: pkm81_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 22-Oct-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	

PPM

8.75

pkm81\_P31



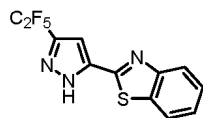
File name: pkm81_P31	Operator: root	SF: 202.3833 MHz	NSC: 12	PW: 0.00 usec, RG: 512	SI: 65536
Date: 24-Oct-2013	Solvent: CDCl3	SW: 80645 Hz	TE: 0 K	AQ: 0.81 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

# Compound 10a

PPM

12.070

pkm105

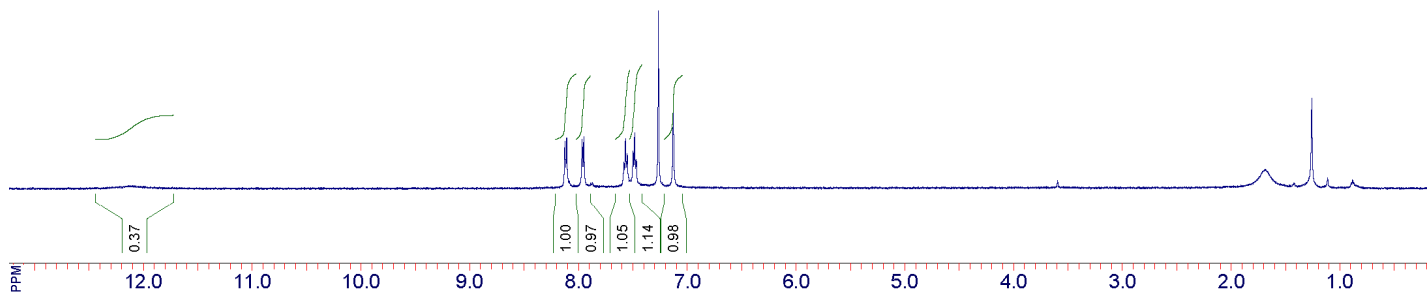
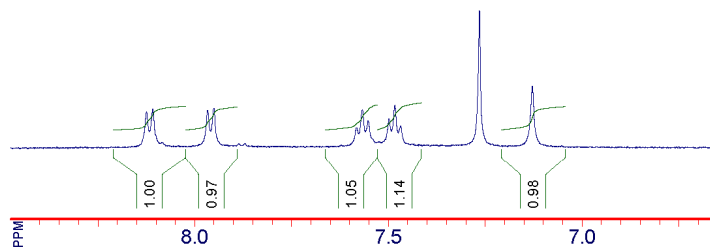


PPM

8.124  
8.116  
8.107  
7.966  
7.950

7.582  
7.567  
7.552  
7.489  
7.483  
7.468

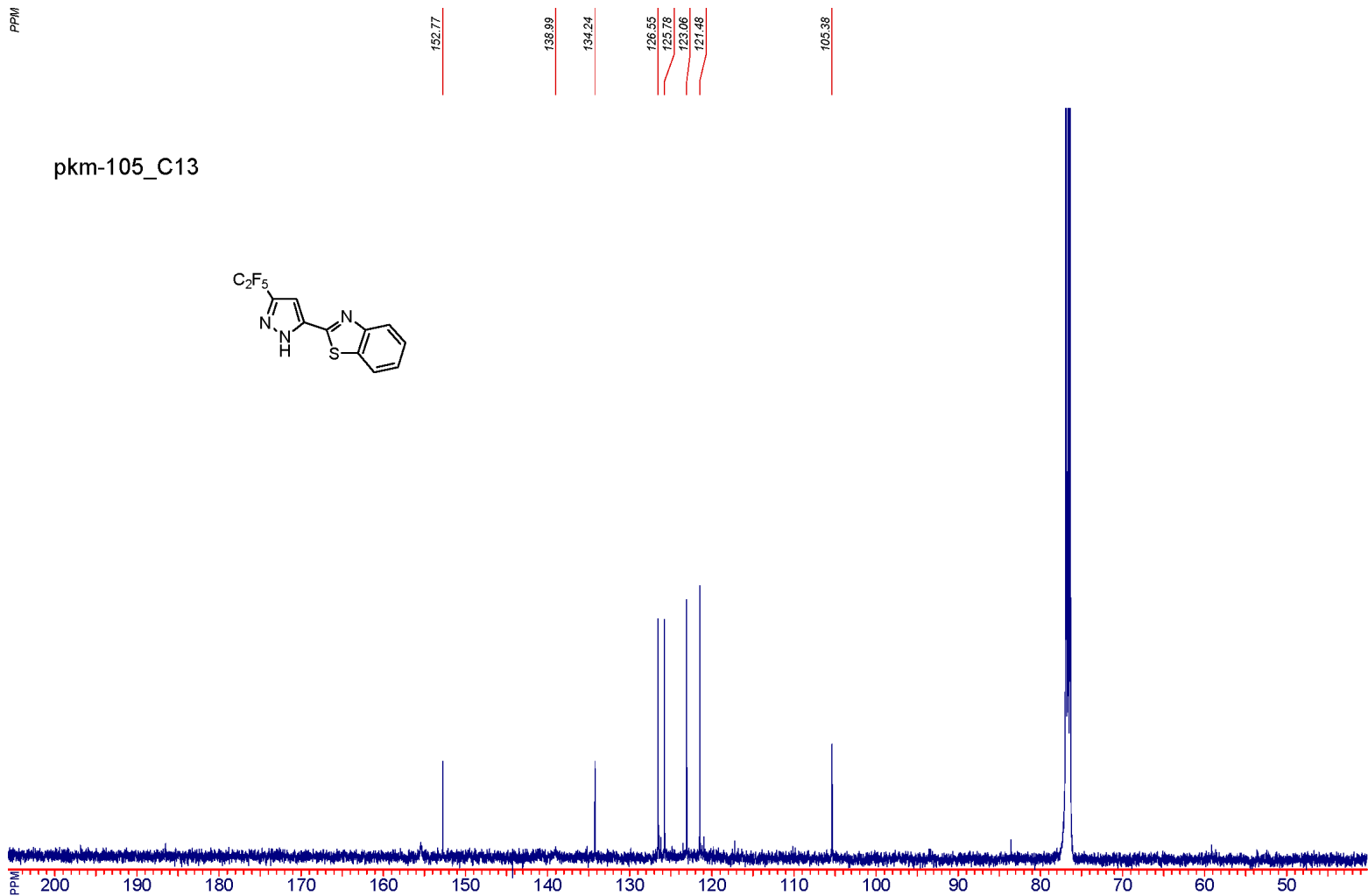
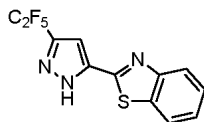
7.128



File name: pkm105	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 24	SI: 32768
Date: 05-Nov-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

pkm-105\_C13



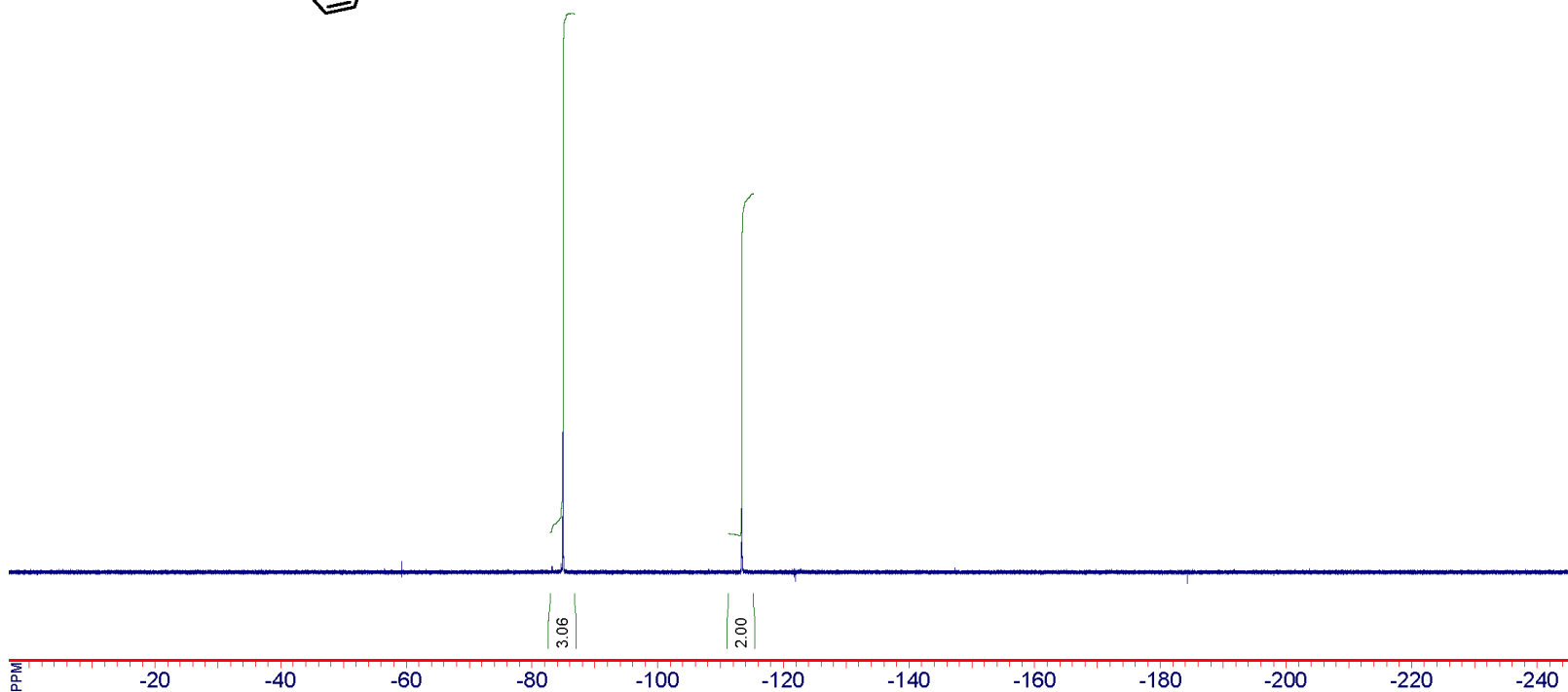
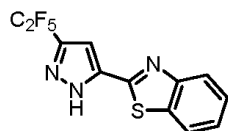
File name: pkm-105_C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 10-Nov-2013	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM

-64.95

-113.40

pkm105\_F19.fid

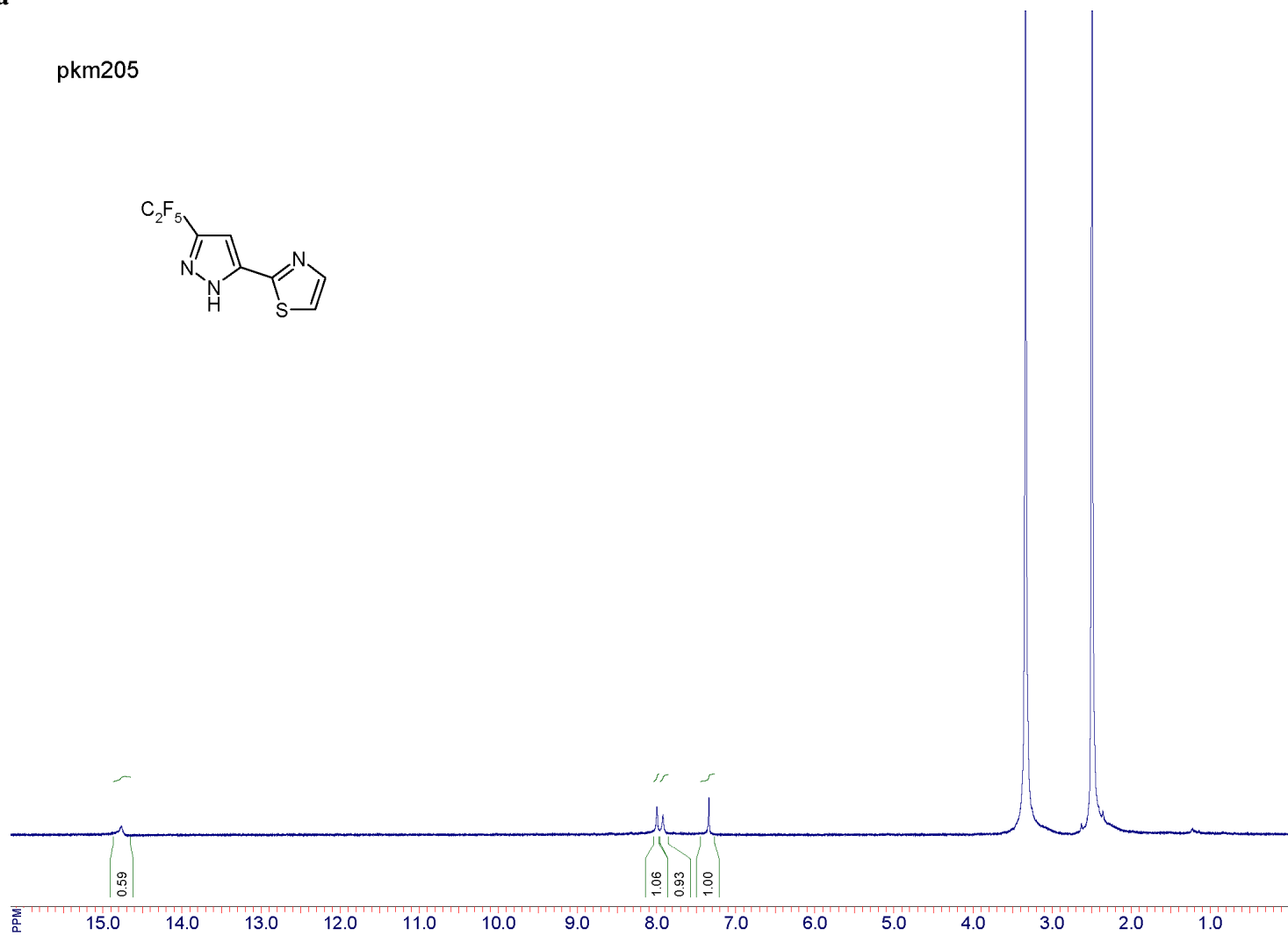
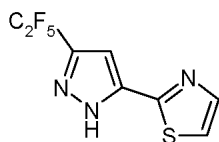


File name: pkm105_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 12-Nov-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□



# Compound 11a

pkm205

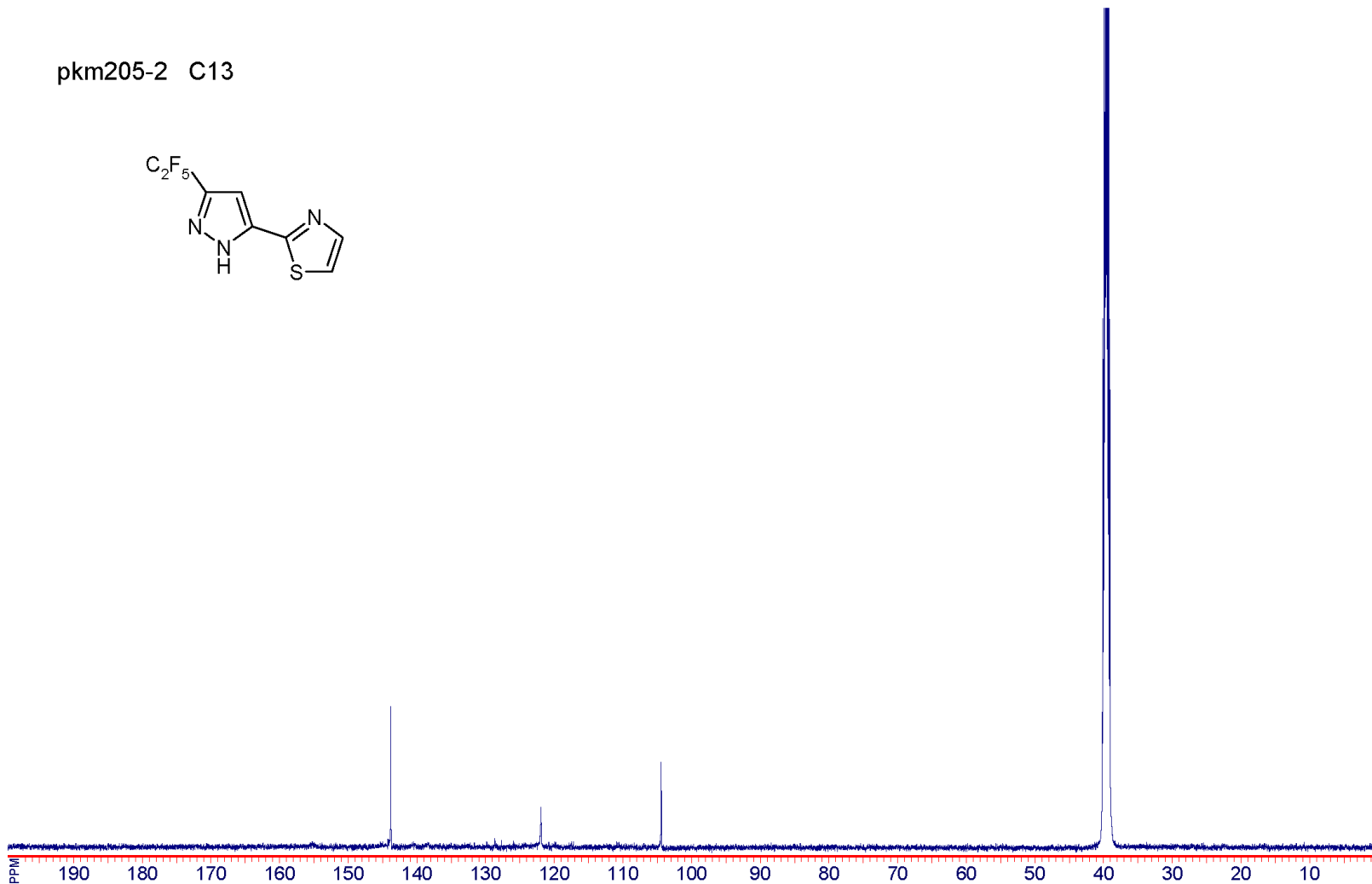
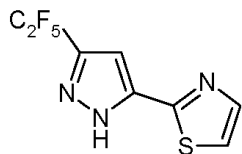


File name: pkm205	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 250	SI: 32768
Date: 14-May-2014	Solvent: DMSO	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

155.14  
143.77  
129.81  
128.63  
127.67  
125.95  
121.92  
104.41

pkm205-2 C13



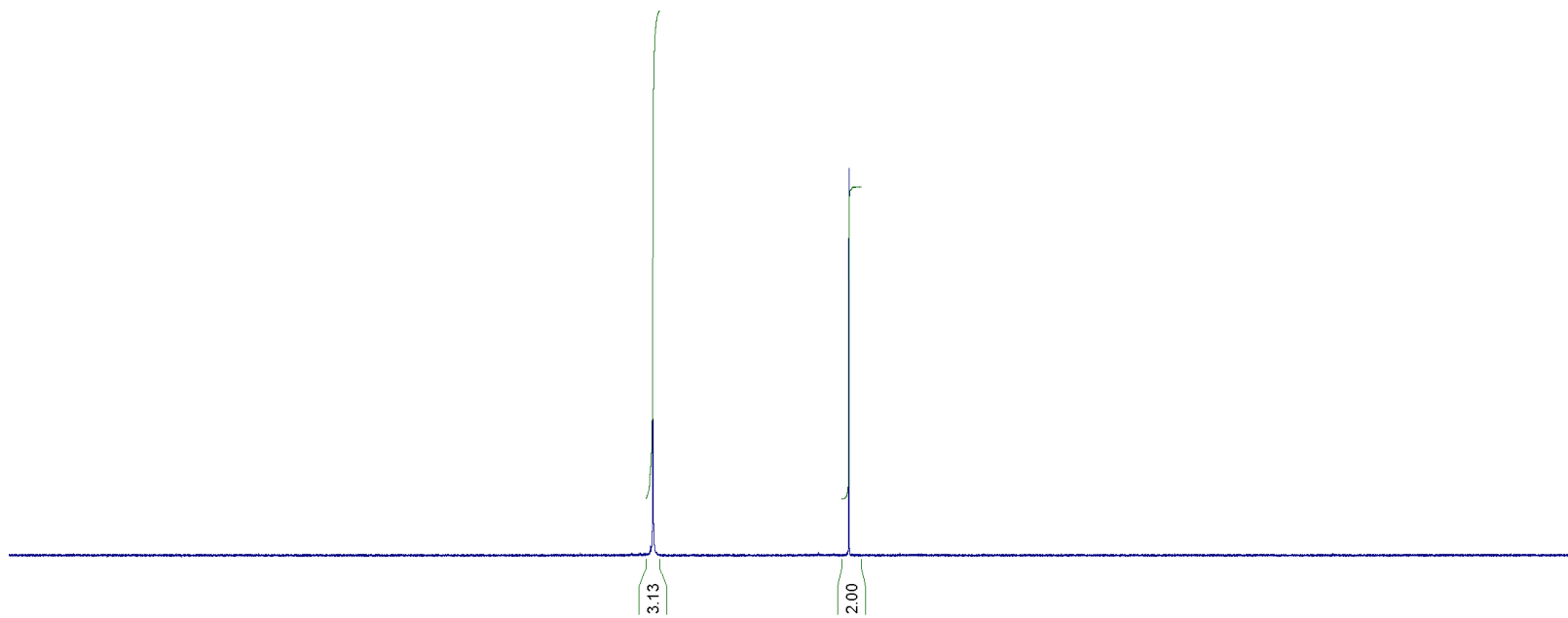
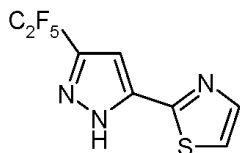
File name: pkm205-2 C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 17-May-2014	Solvent: DMSO	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR\Version 3.5

PPM

-83.78

-110.61

pkm213\_F19.fid

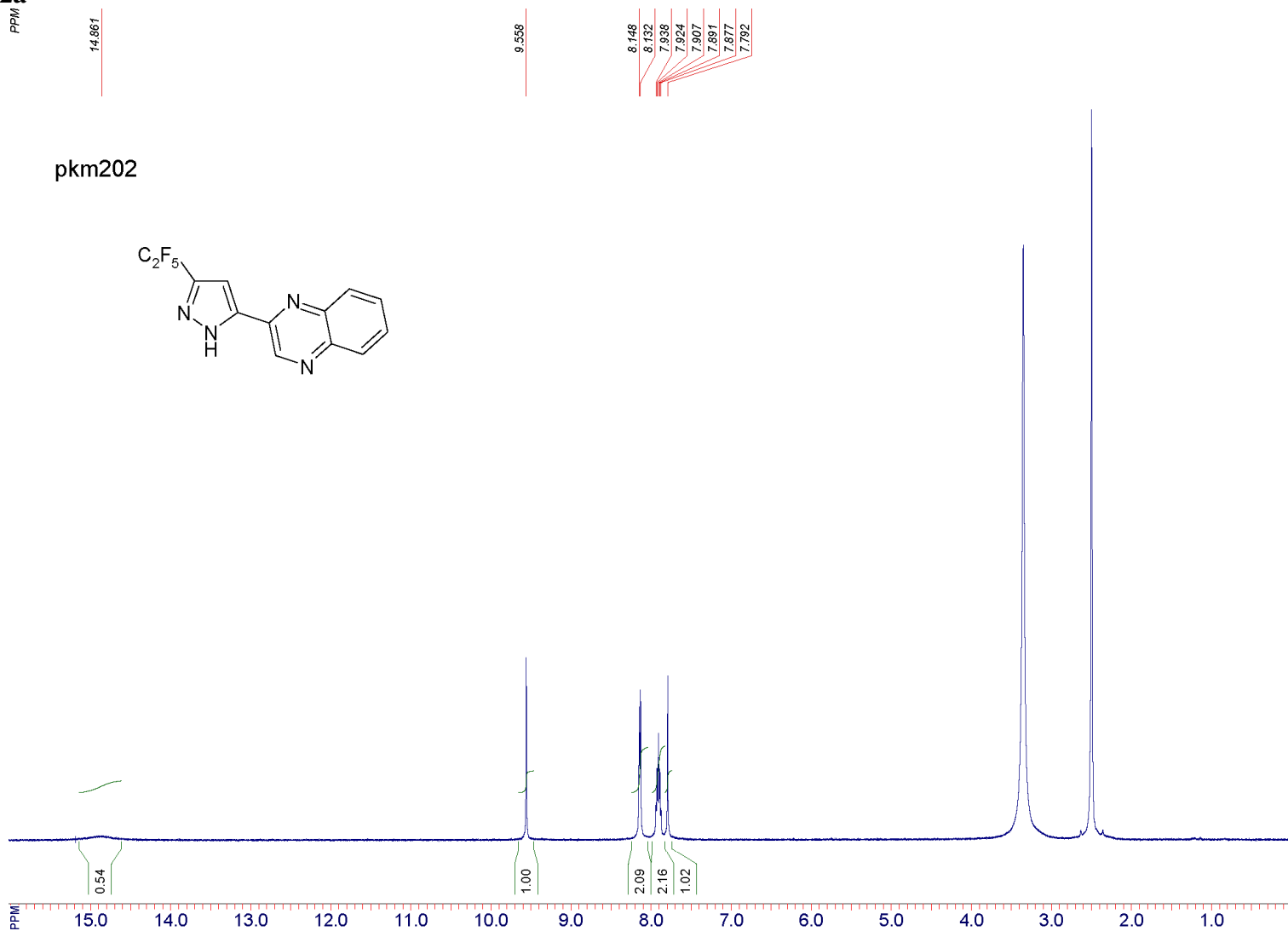
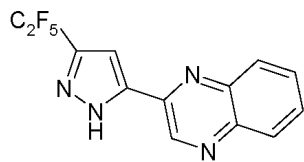


File name: pkm213_F19.fid	Operator:	SF: 376.3274 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 22-May-2014	Solvent: dmsol-d6	SW: 82816 Hz	TE: 293 K	AQ: 0.39 sec, RD: 0.00 sec	□

# Compound 12a

PPM

pkm202

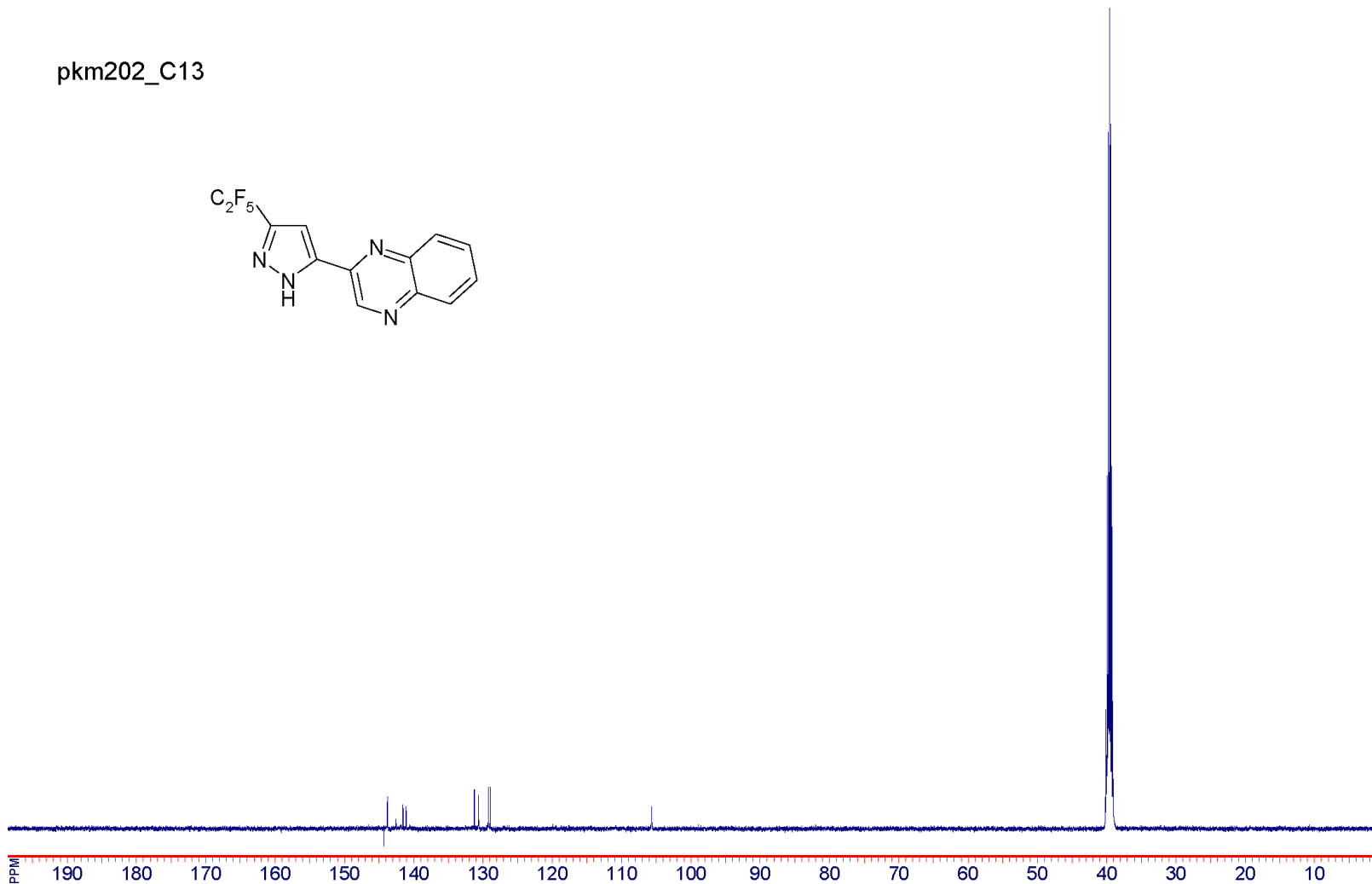
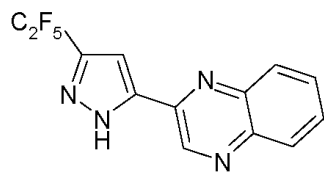


File name: pkm202	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 40	SI: 32768
Date: 12-May-2014	Solvent: DMSO	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR

PPM

142.53  
141.53  
141.07  
131.23  
130.62  
129.22  
128.94  
105.64

pkm202\_C13



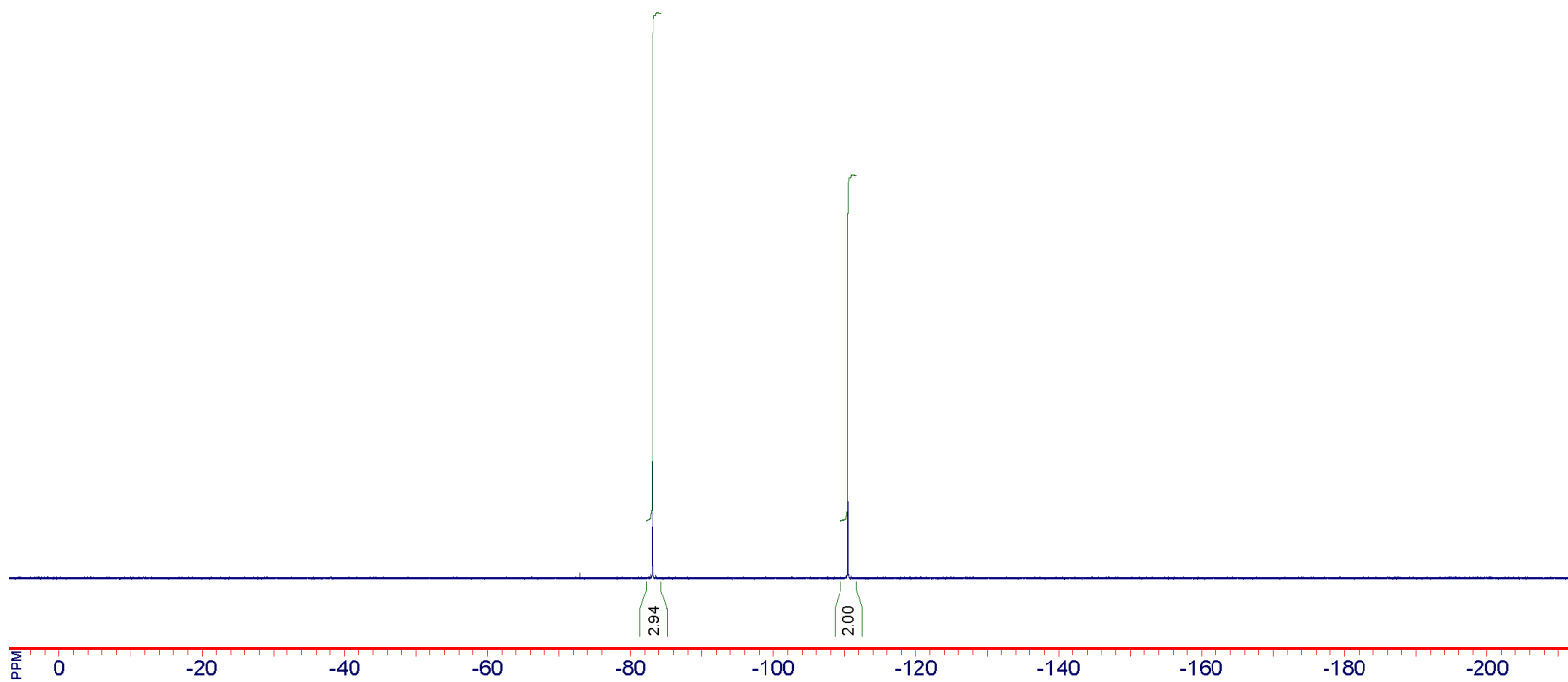
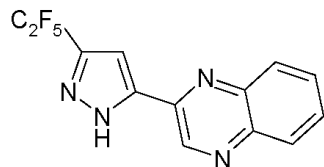
File name: pkm202_C13	Operator: root	SF: 125.7126 MHz	NSC: 1364	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 14-May-2014	Solvent: DMSO	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-83.10

-110.48

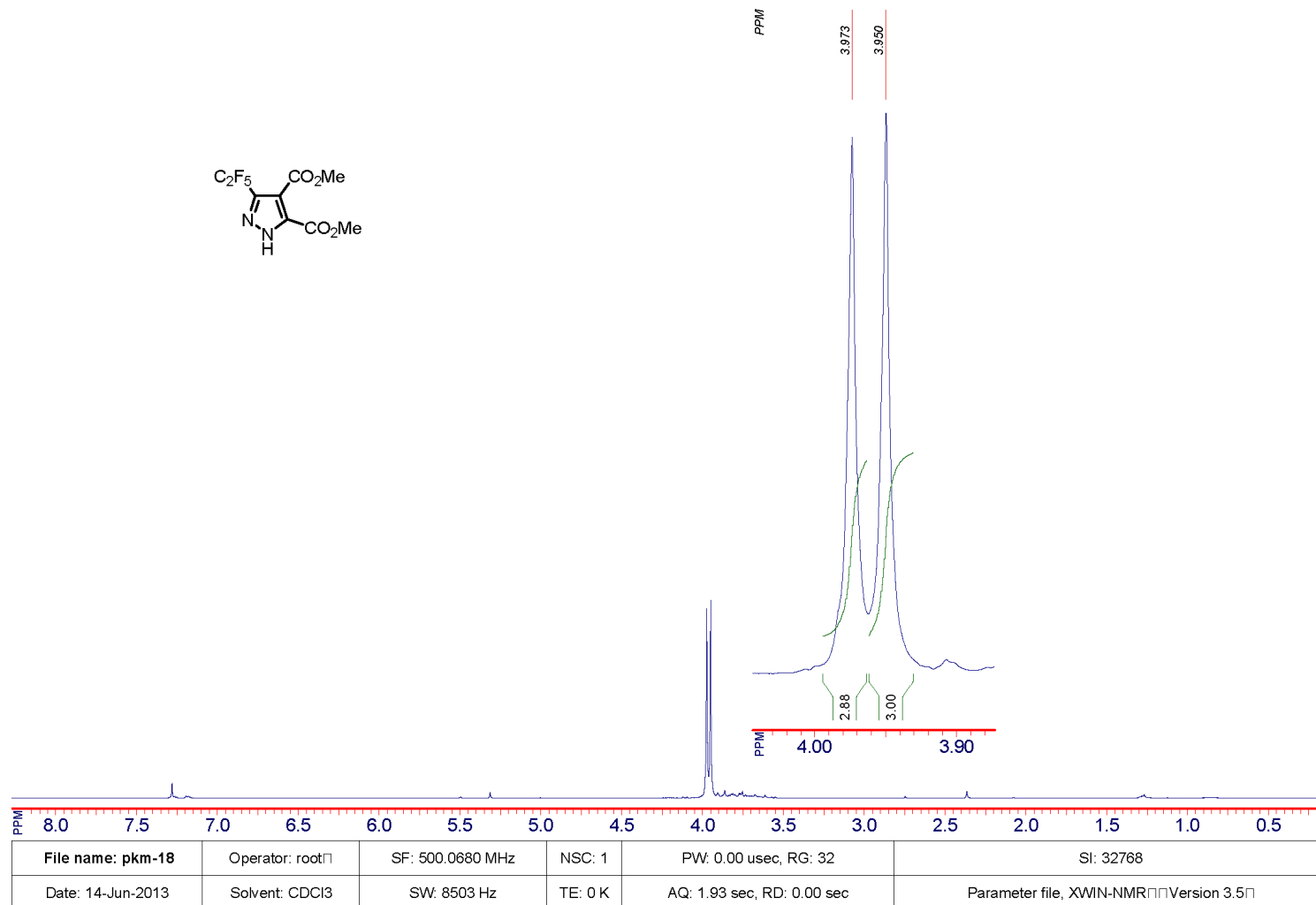
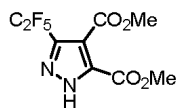
pkm202\_F19.fid



File name: pkm202_F19.fid	Operator:	SF: 376.3274 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: dmsso_d6	SW: 82816 Hz	TE: 293 K	AQ: 0.39 sec, RD: 0.00 sec	□

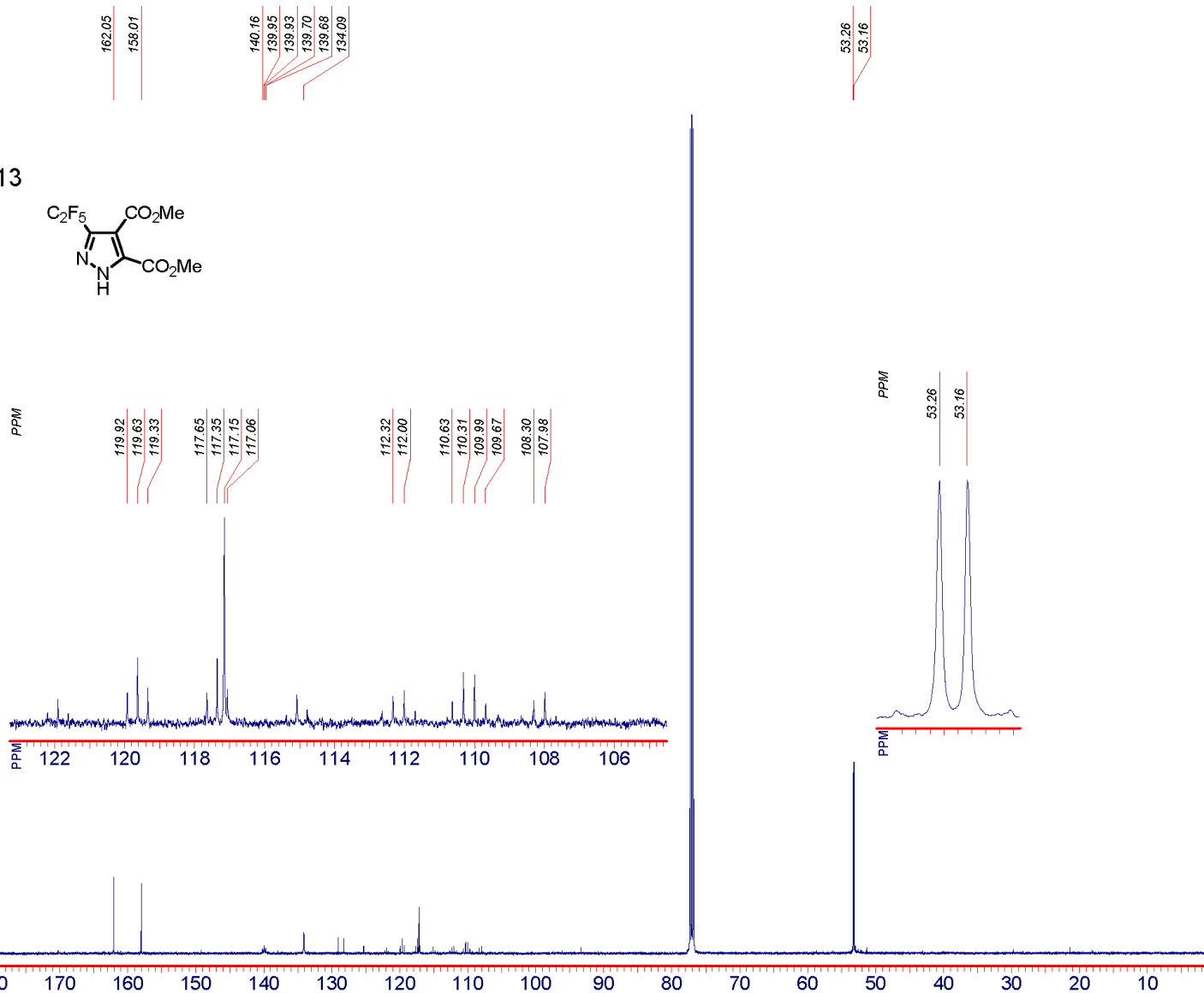
# Compound 15a

pkm-18



PPM

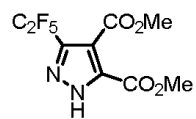
pkm18\_C13



File name: pkm18_C13	Operator: root	SF: 125.7422 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 16-Jun-2013	Solvent: CDCl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR\Version 3.5



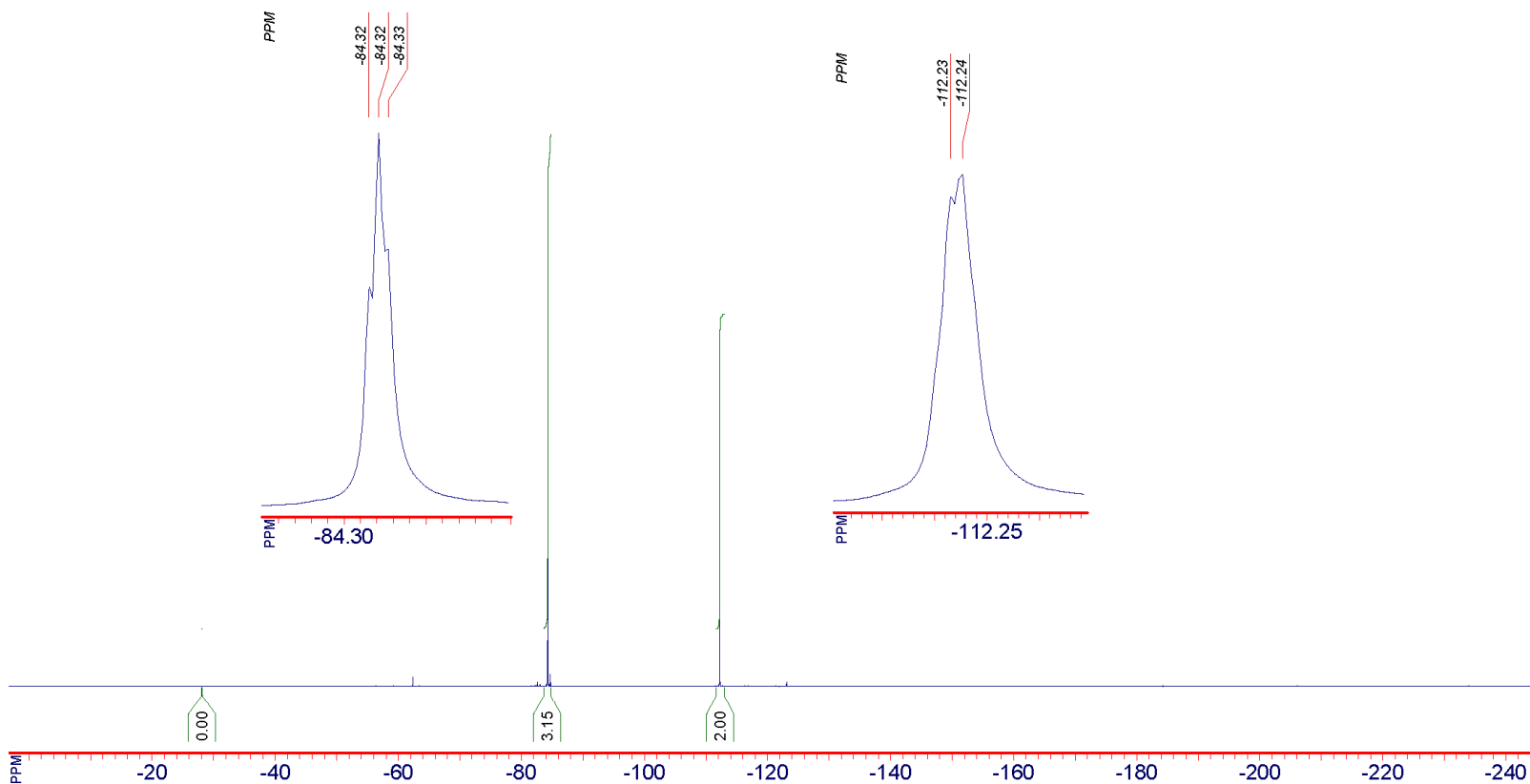
PPM



-84.32  
-84.32  
-84.33

-112.23  
-112.24

pkm-18\_F19.fid



File name: pkm-18_F19.fid	Operator:	SF: 376.3207 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 18-Jun-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

# Compound 16a

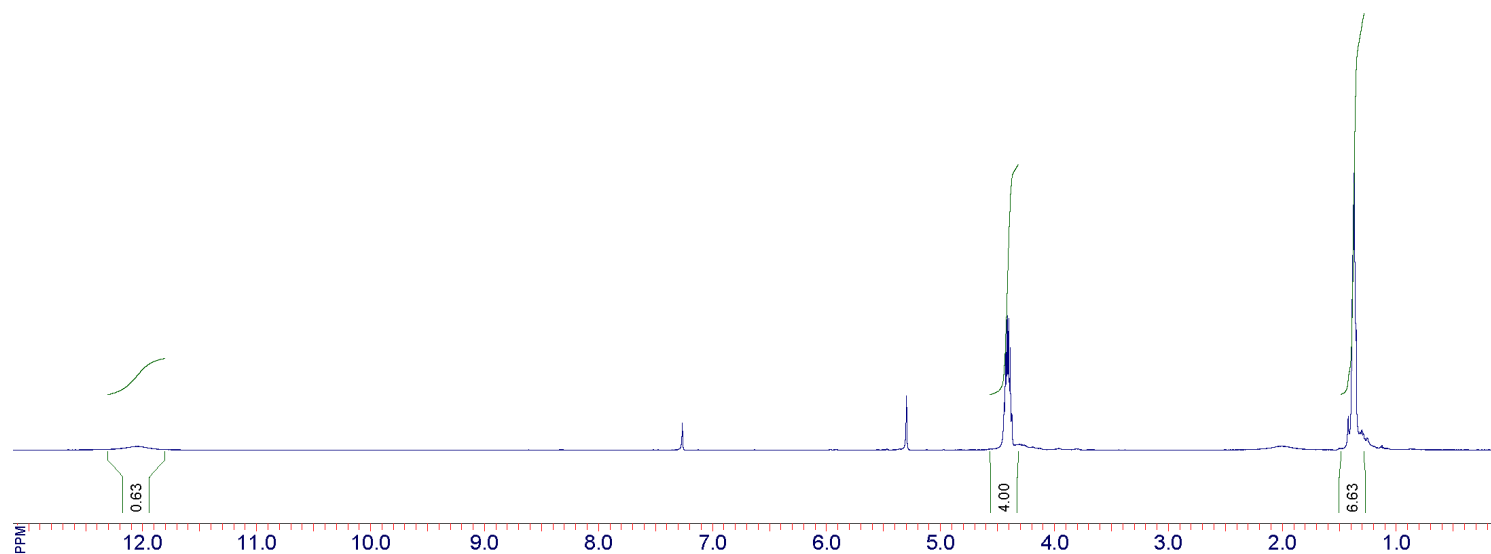
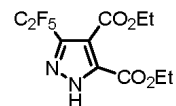
PPM

12.063

4.414

1.375

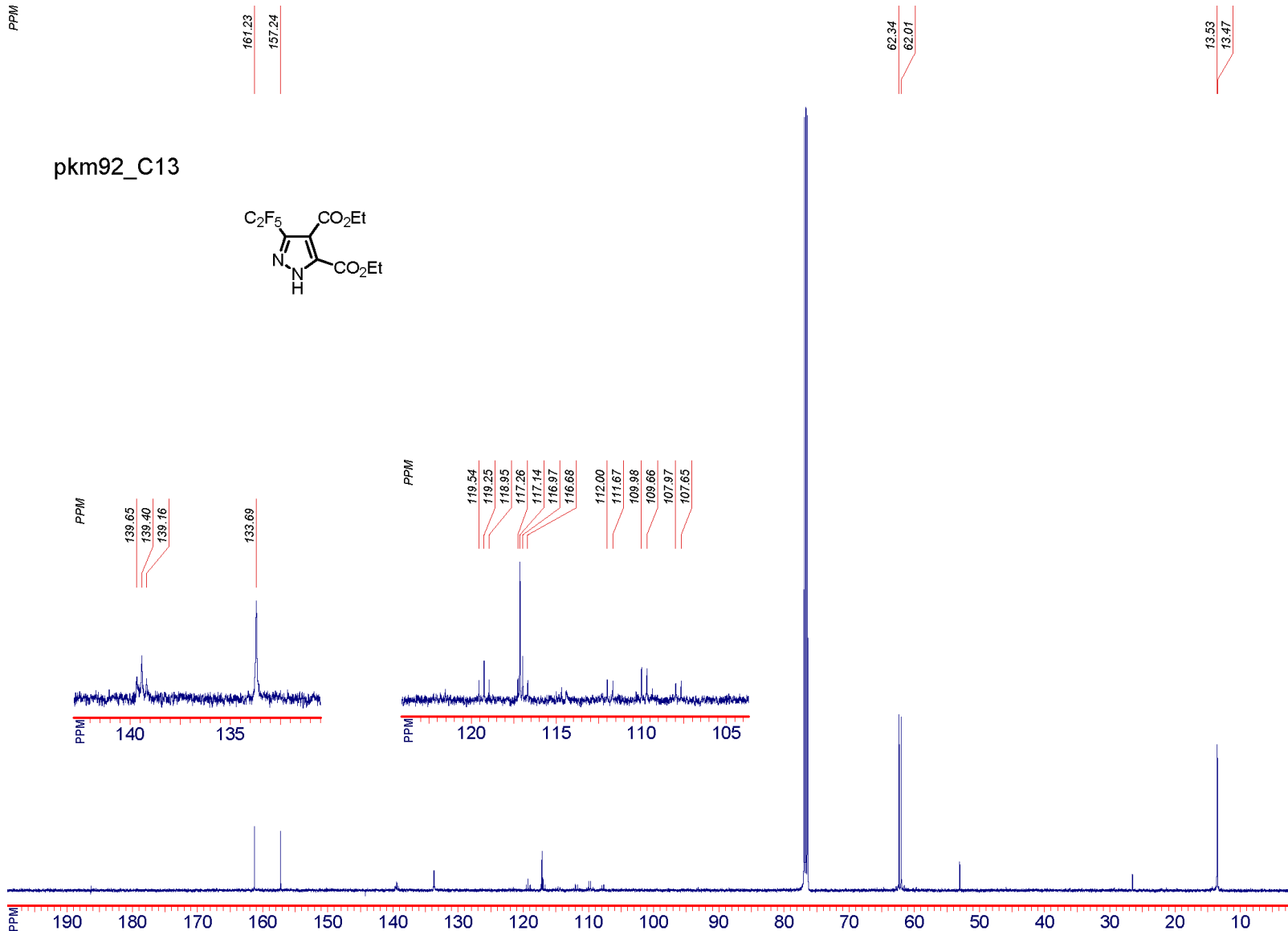
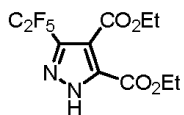
pkm92



File name: pkm92	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 24	SI: 32768
Date: 21-Oct-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

pkm92\_C13



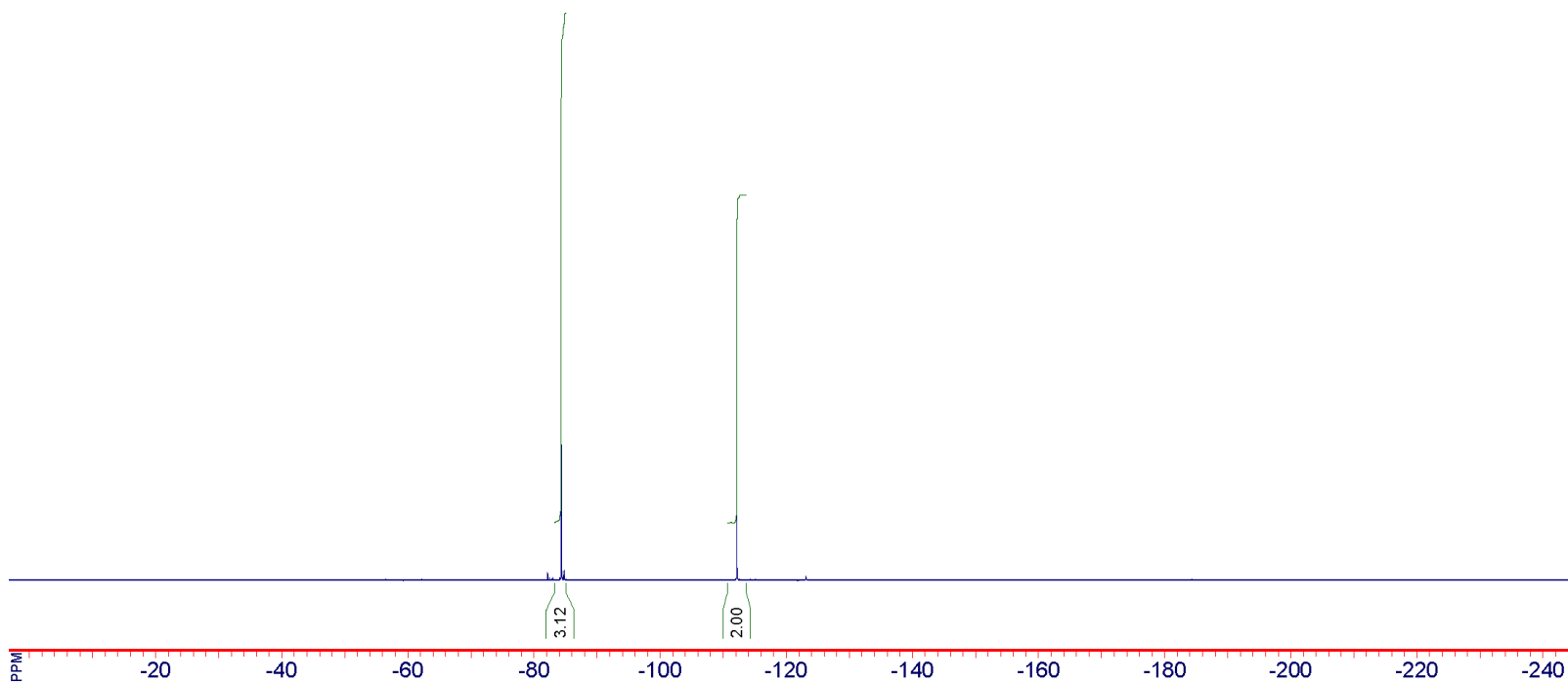
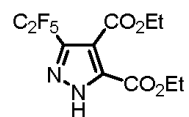
File name: pkm92_C13	Operator: root	SF: 125.7126 MHz	NSC: 5120	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 25-Oct-2013	Solvent: CDCl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-84.34

-112.19

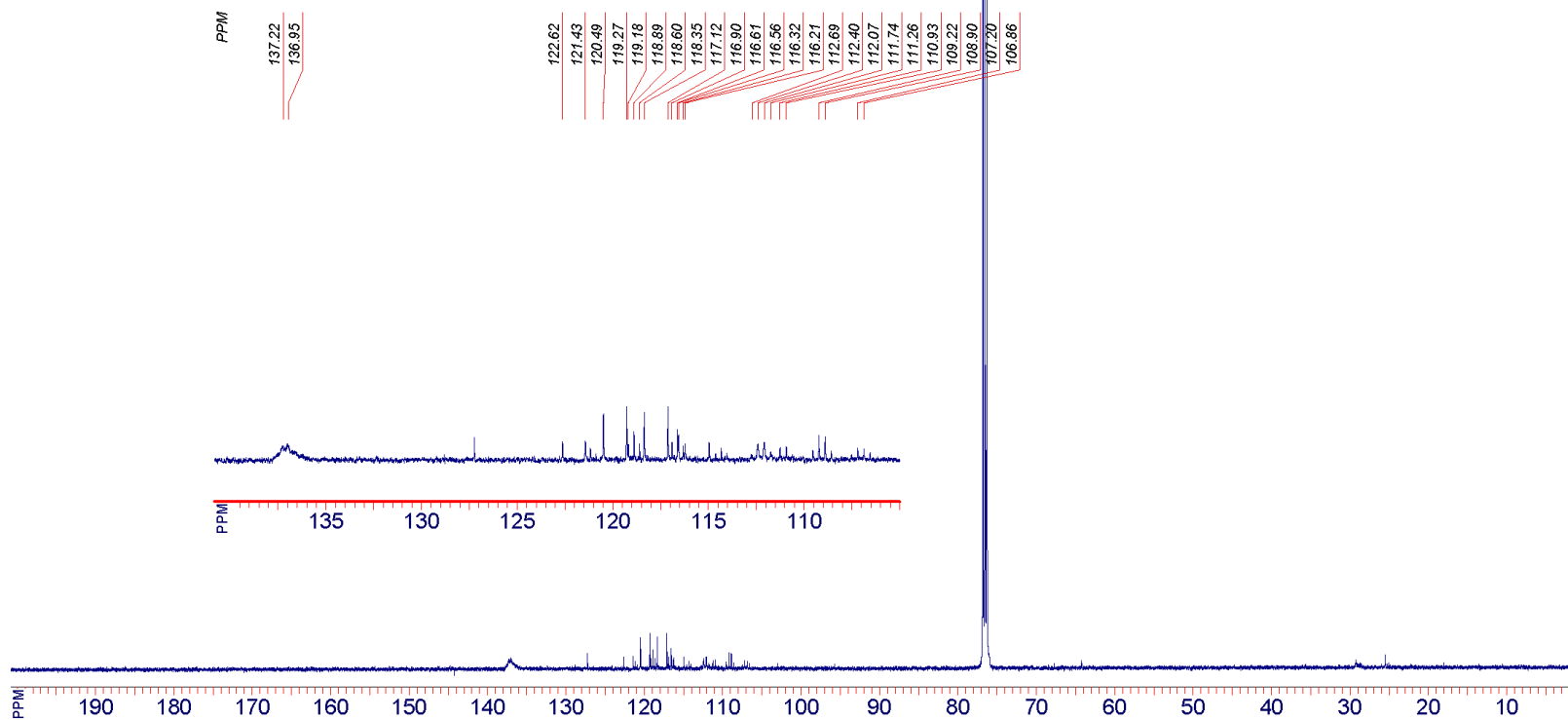
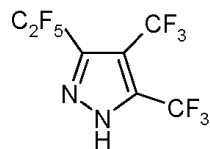
pkm92\_F19.fid



File name: pkm92_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 29-Oct-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

# Compound 17a

pkm217\_C13

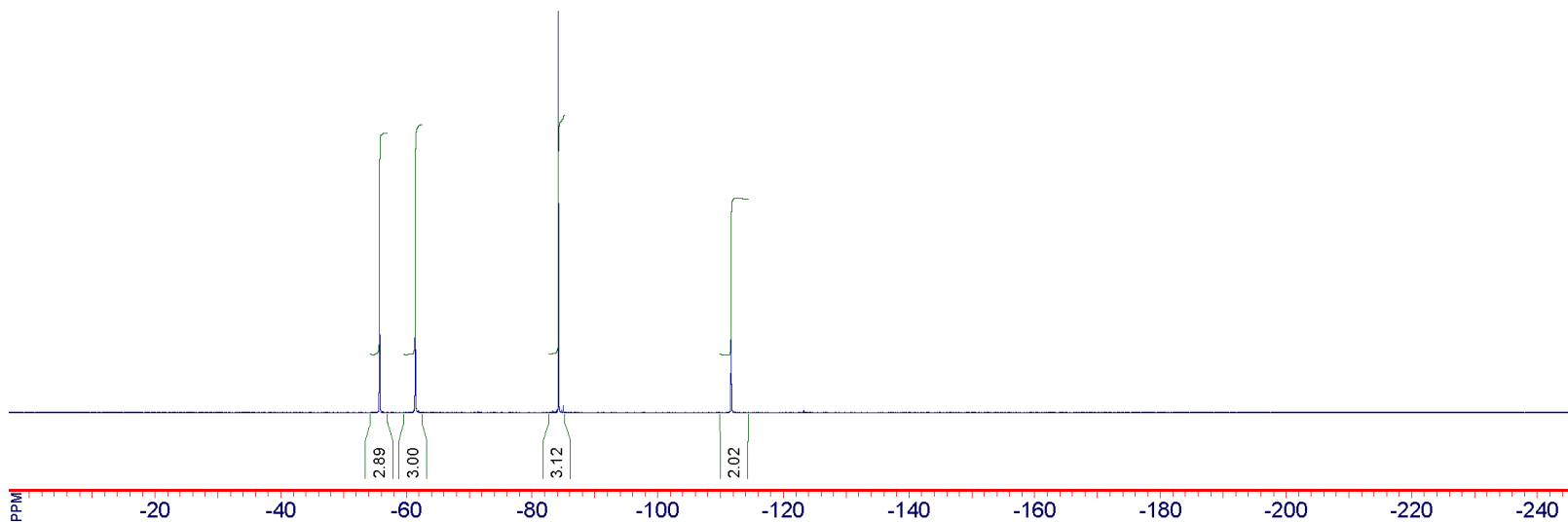


File name: pkm217_C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 25-May-2014	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR\Version 3.5

PPM



pkm217\_F19.fid

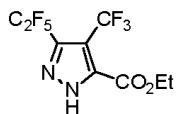


File name: pkm217_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 27-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□

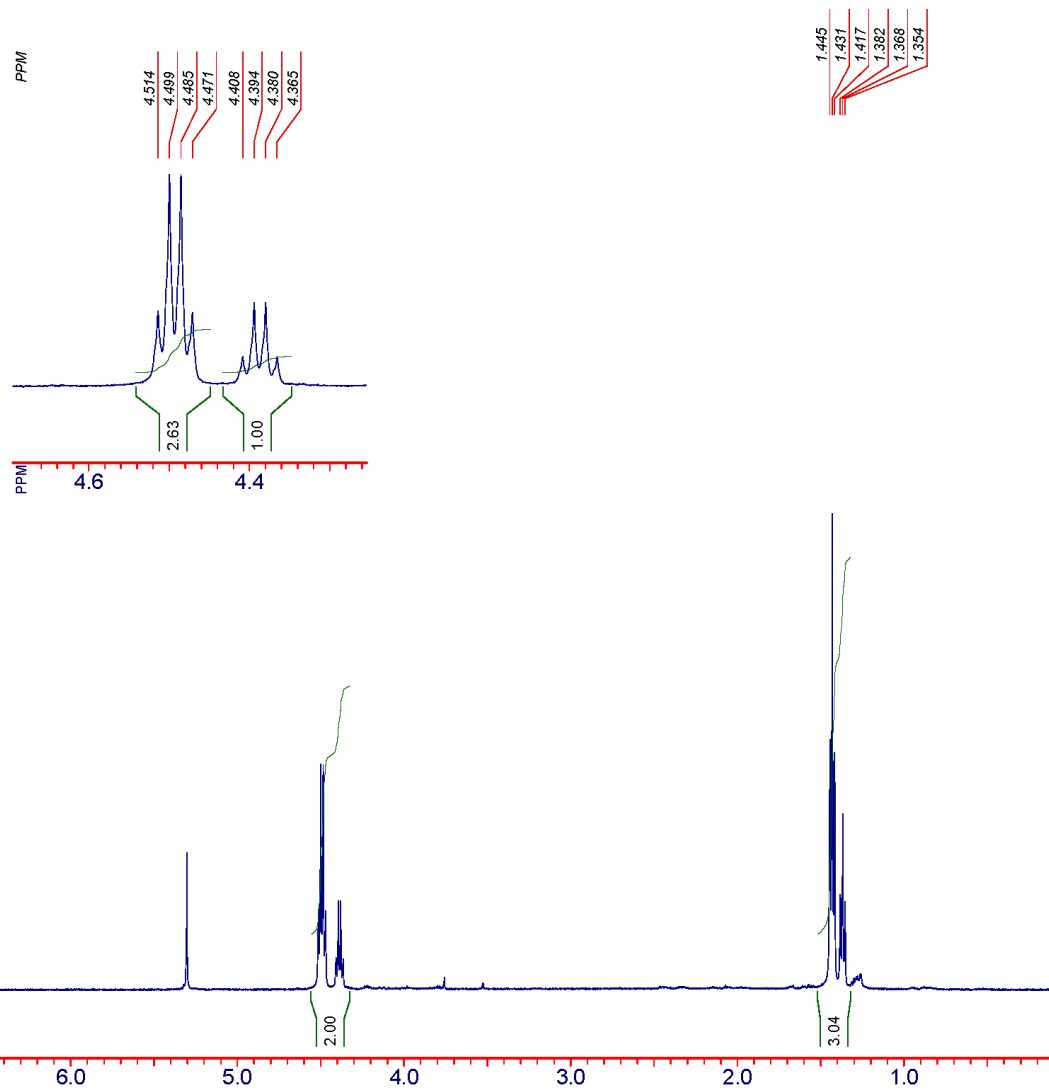
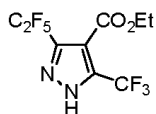
# Compound 18a/18b

PPM

pkm113



+

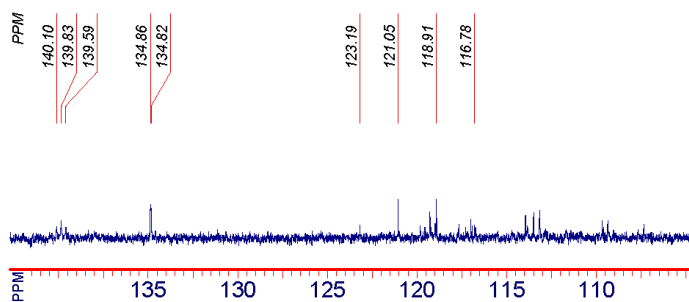
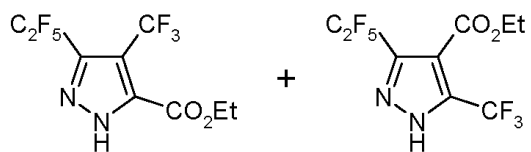


File name: pkm113	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 100	SI: 32768
Date: 21-Nov-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMRVersion 3.5

PPM

158.91  
156.6962.91  
61.7613.40  
13.26

pkm-113\_C13

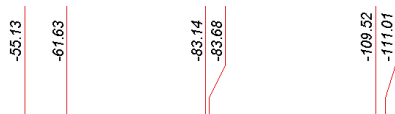
123.19  
121.05  
118.91  
116.78

PPM 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

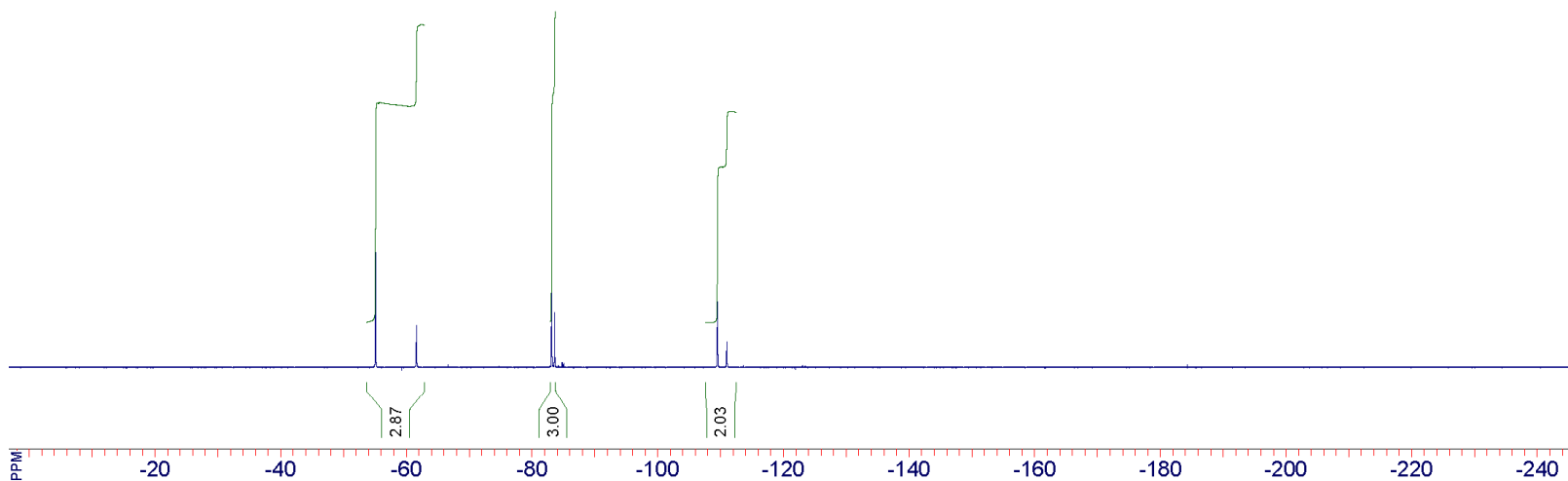
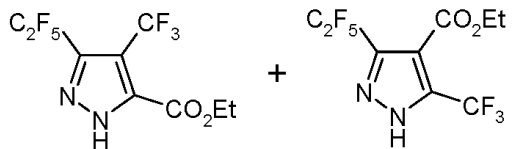
File name: pkm-113_C13	Operator: root	SF: 125.7126 MHz	NSC: 5120	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 06-Dec-2013	Solvent: CDCl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5



PPM



pokm113\_F19.fid

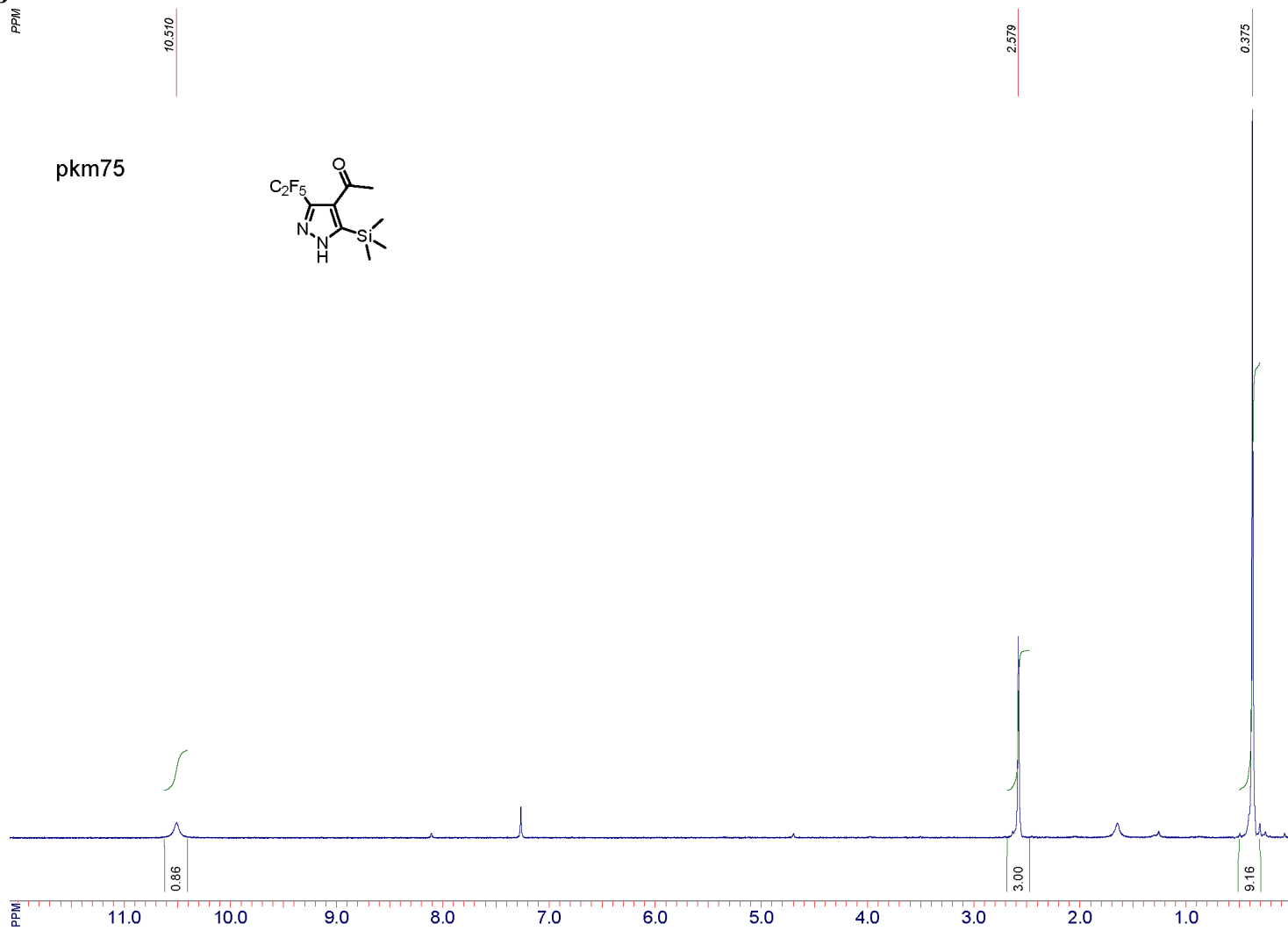
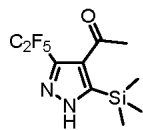


File name: pokm113_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 10-Dec-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

# Compound 19b

PPM

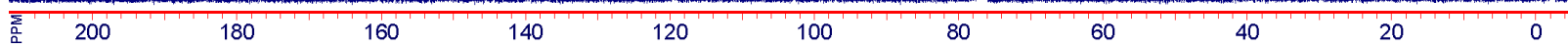
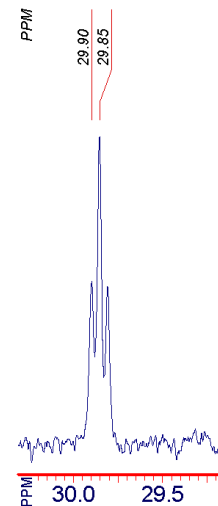
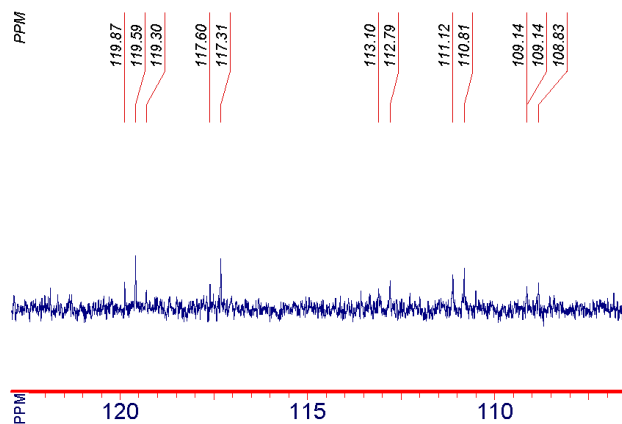
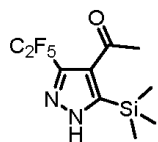
pkm75



File name: pkm75	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 16	SI: 32768
Date: 03-Oct-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5



pkm75\_C13



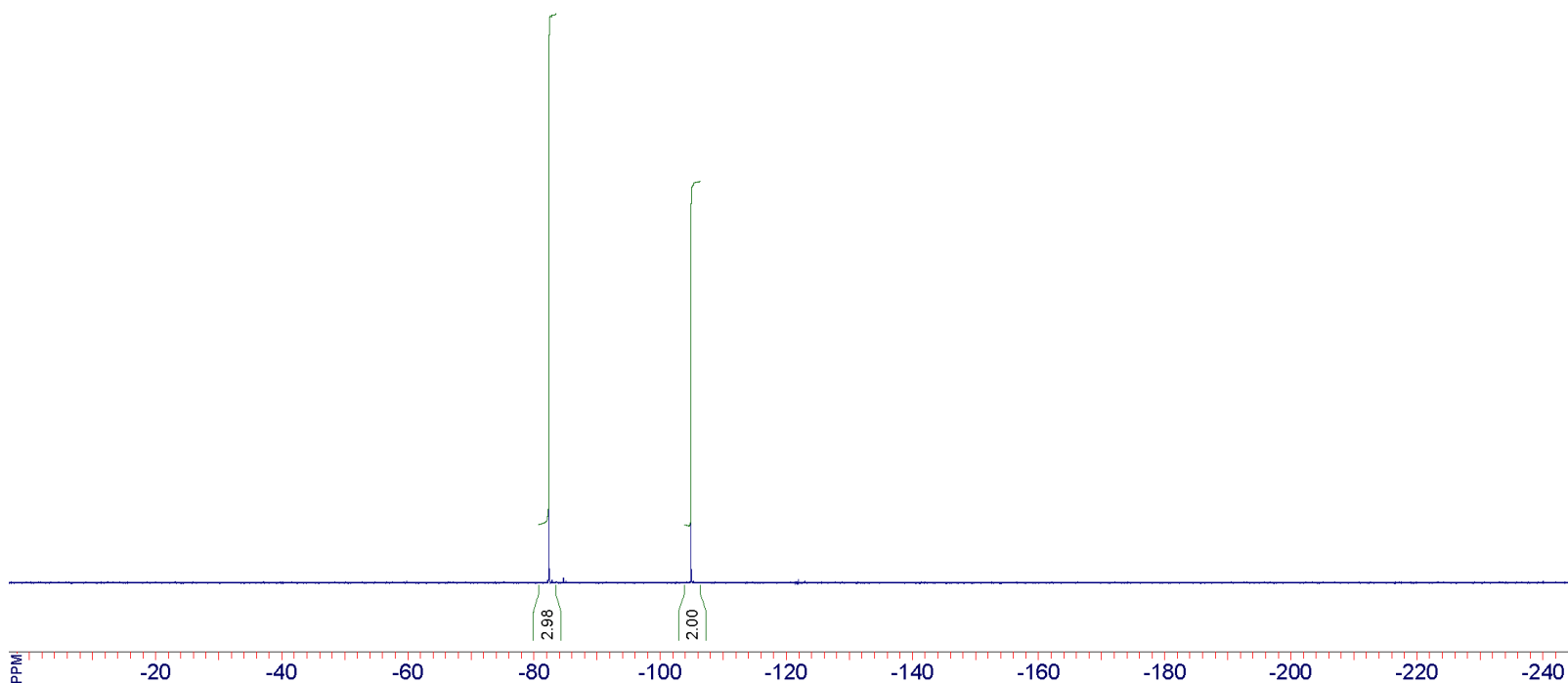
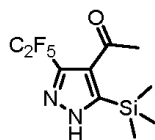
File name: pkm75_C13	Operator: root	SF: 125.7126 MHz	NSC: 7696	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 03-Oct-2013	Solvent: CDCl3	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-82.37

-104.89

pkm75\_F19.fid



File name: pkm75_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 08-Oct-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

# Compound 20b

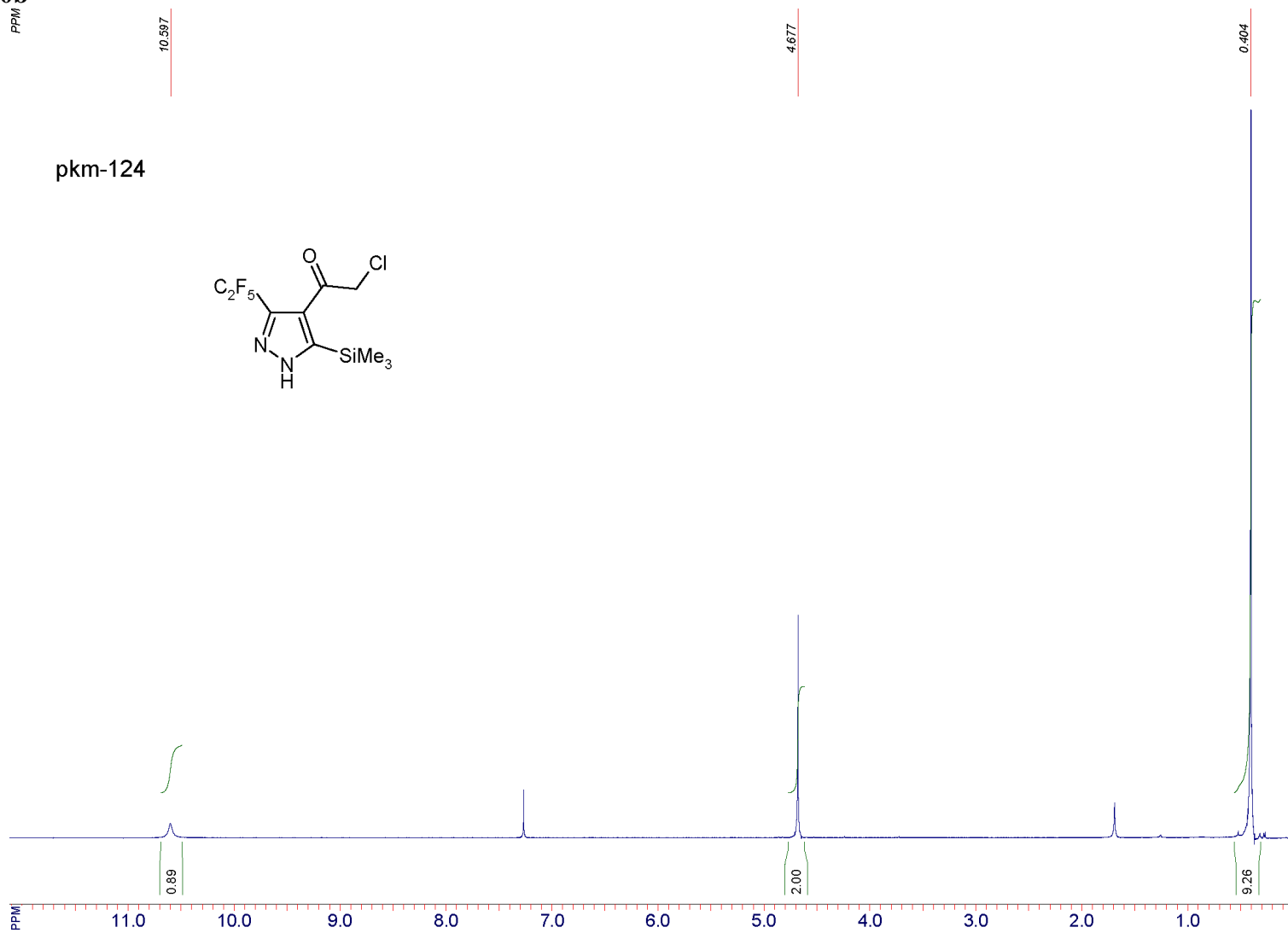
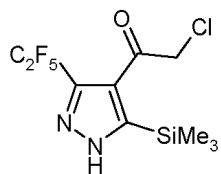
PPM

10.597

4.677

0.404

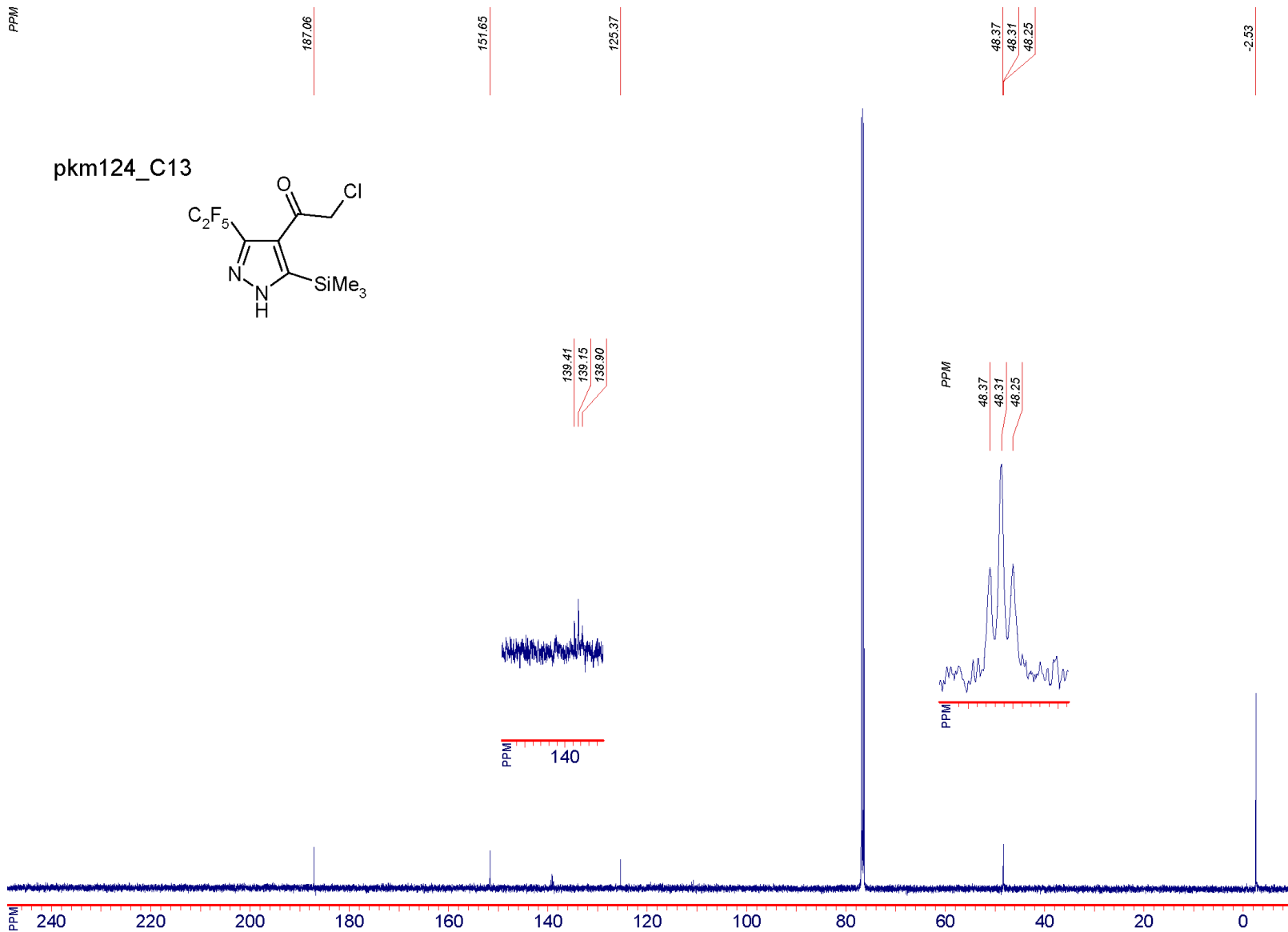
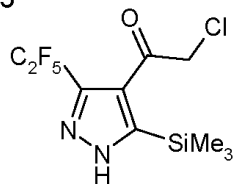
pkm-124



File name: pkm-124	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 50	SI: 32768
Date: 12-Dec-2013	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

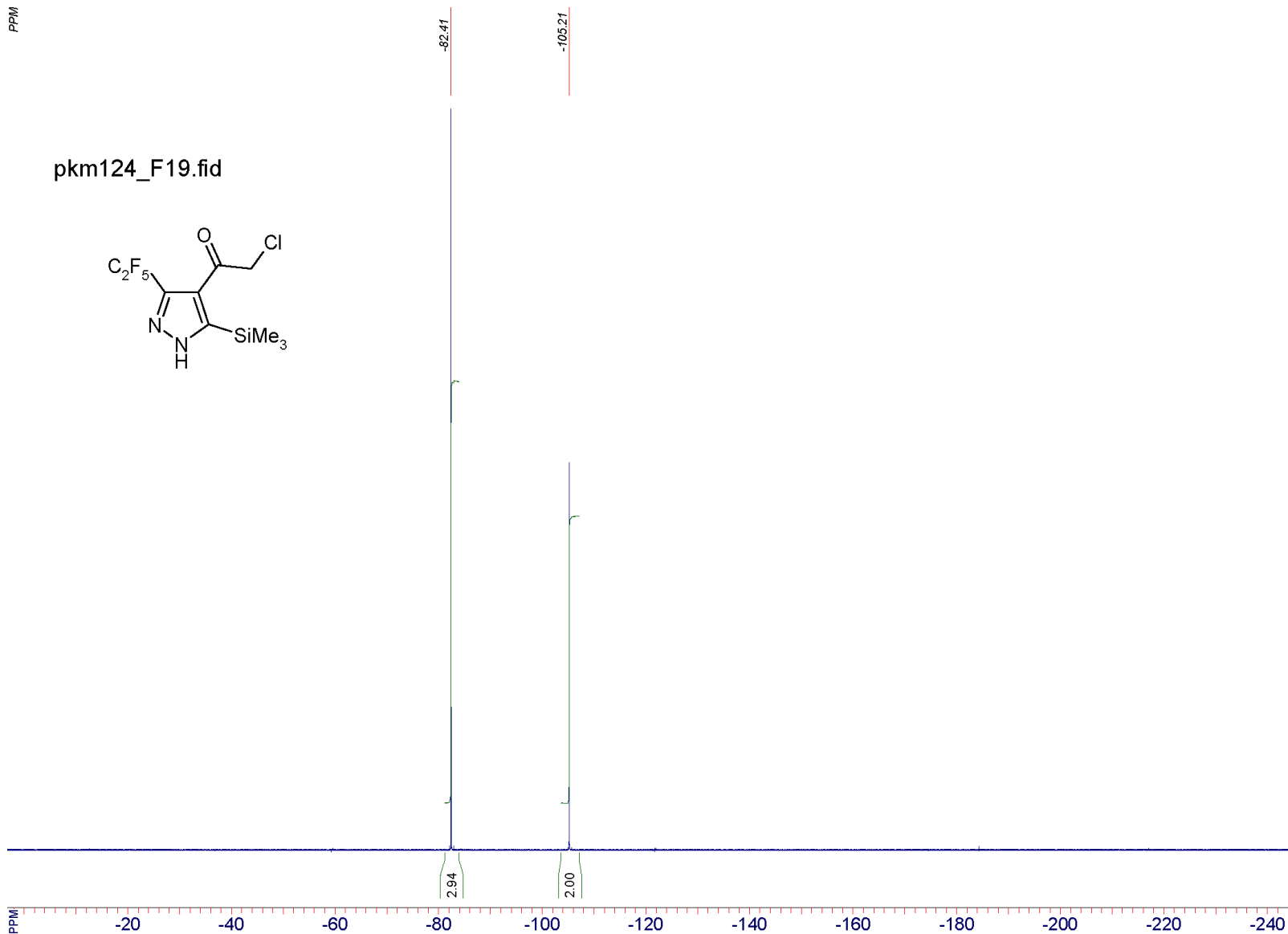
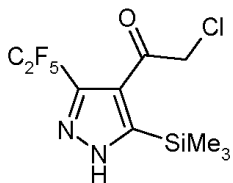
pkm124\_C13



File name: pkm124_C13	Operator: root	SF: 125.7126 MHz	NSC: 1154	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 13-Dec-2013	Solvent: dmsol	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWN-NMR Version 3.5

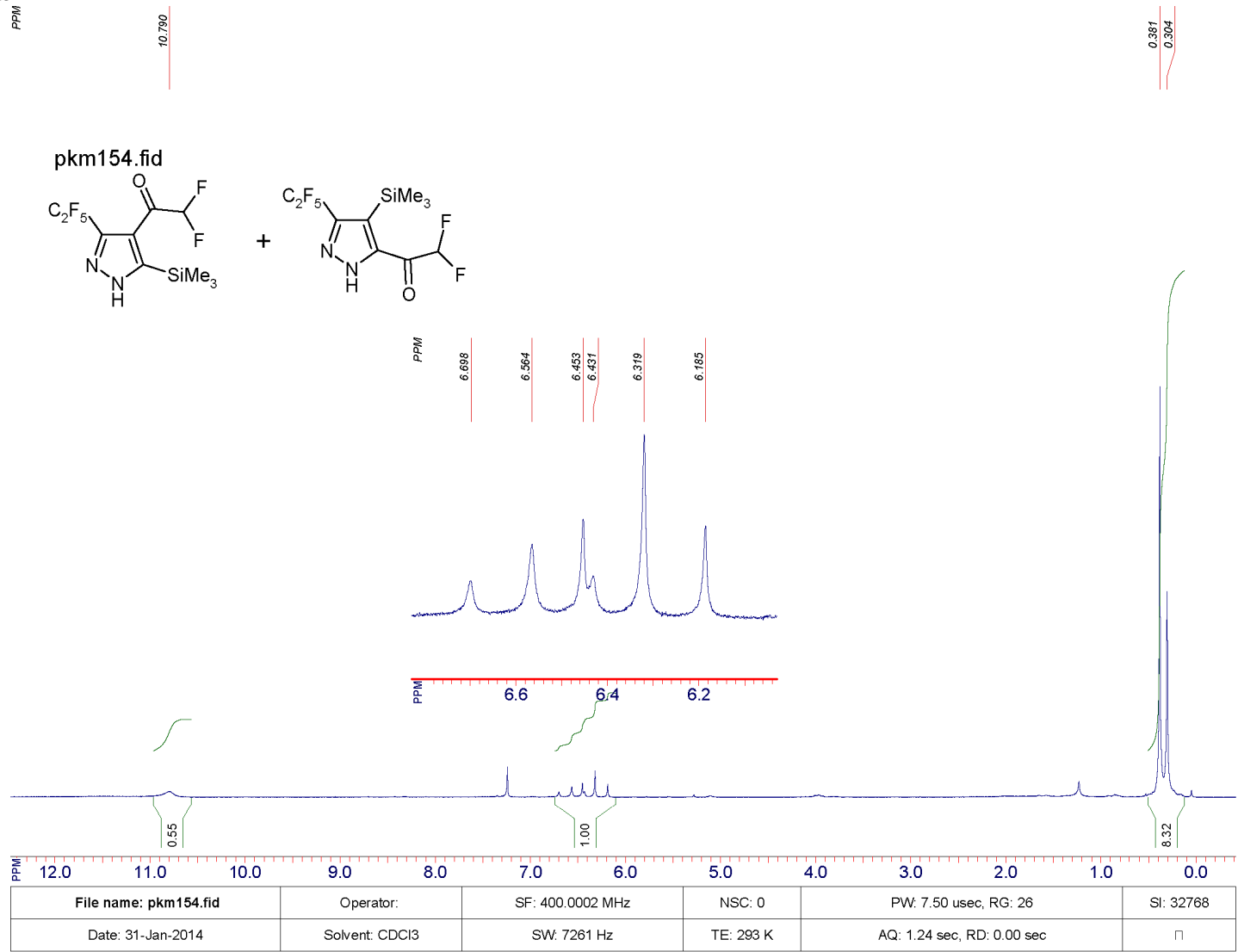
PPM

pkm124\_F19.fid



File name: pkm124_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 17-Dec-2013	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

Compound 21a/b





PPM

165.50  
165.29  
165.08

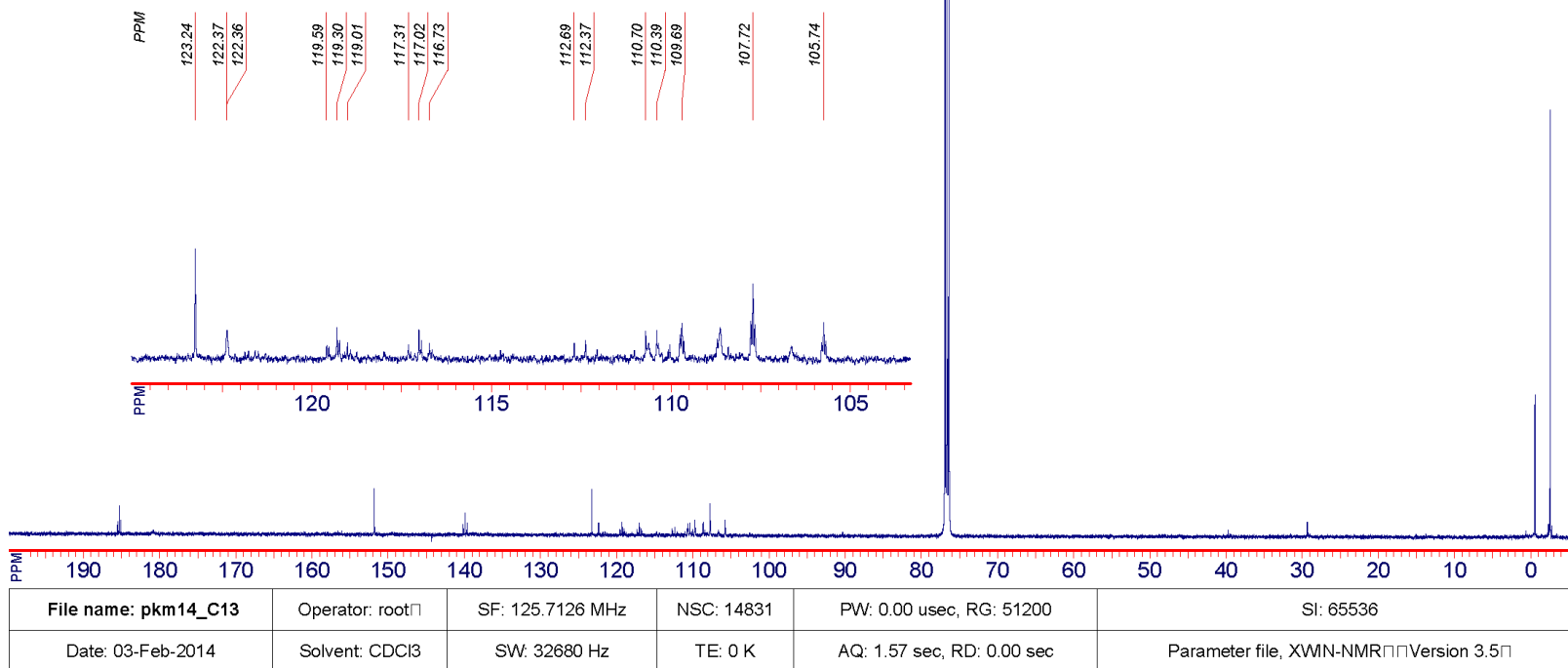
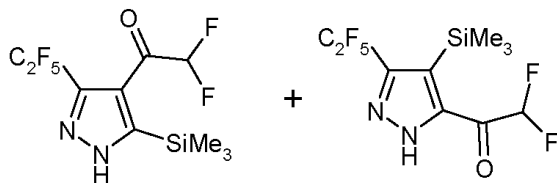
151.80

140.13  
139.89  
139.64

123.24

-0.55  
-2.55

pkm14\_C13

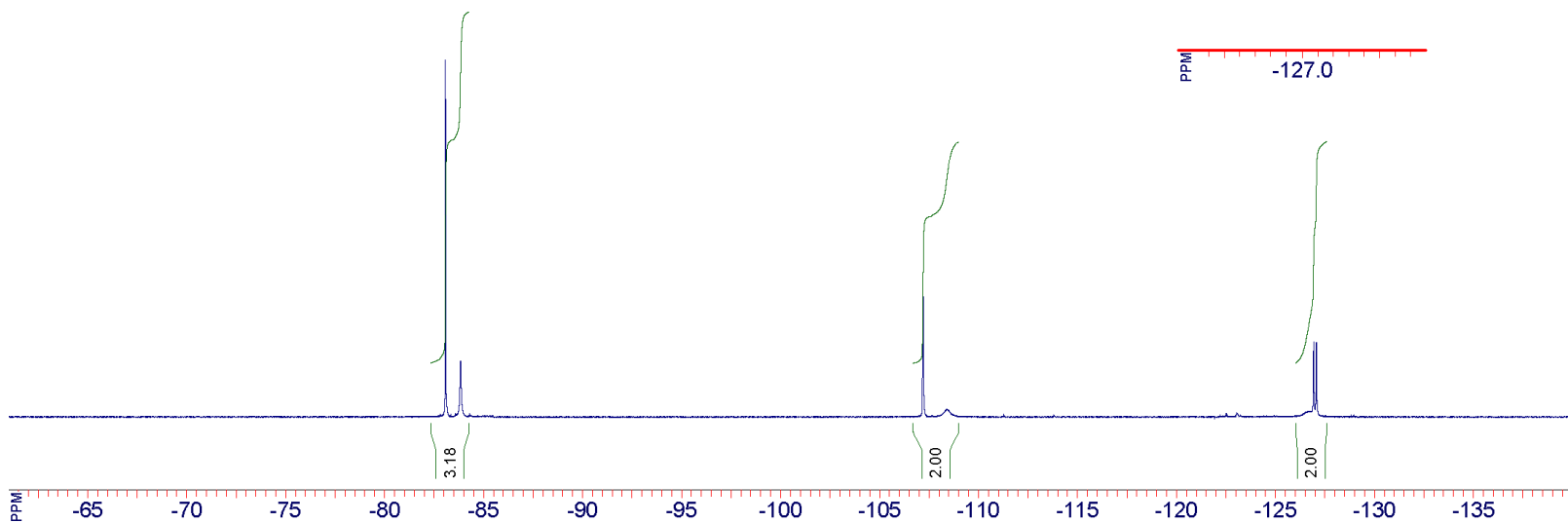
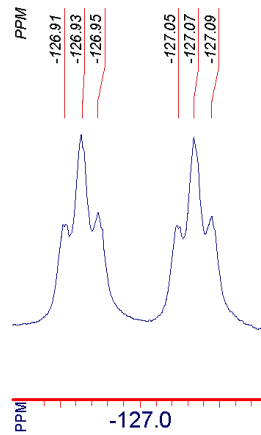
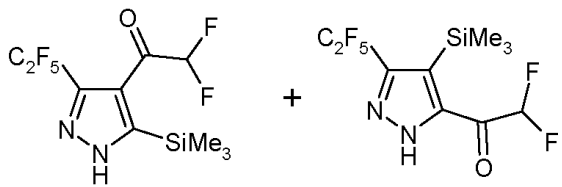


PPM

-63.06  
-63.84

-107.20  
-108.42

pkm154\_F19.fid

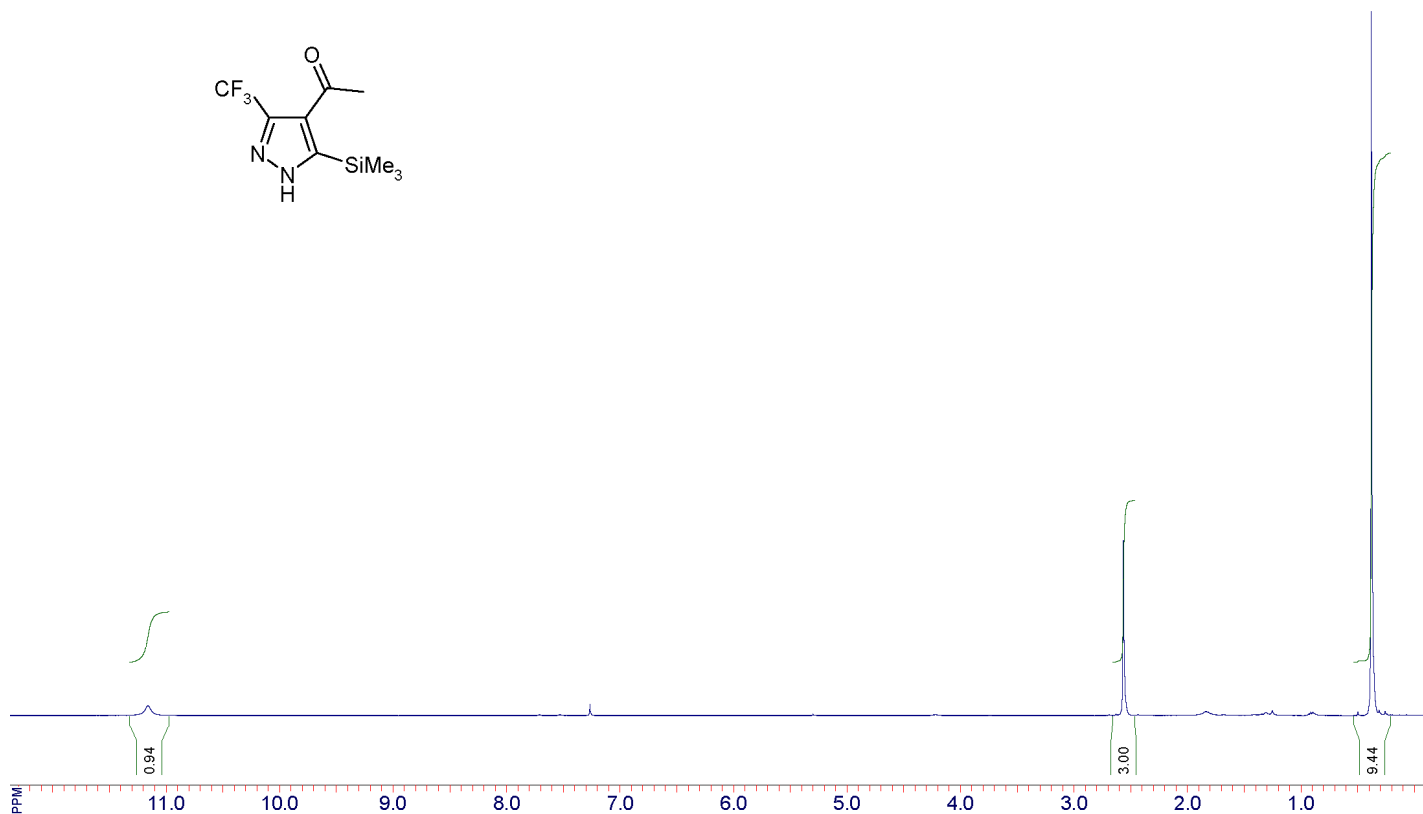
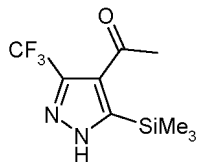


File name: pkm154_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 16	SI: 131072
Date: 04-Feb-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.68 sec, RD: 0.00 sec	□

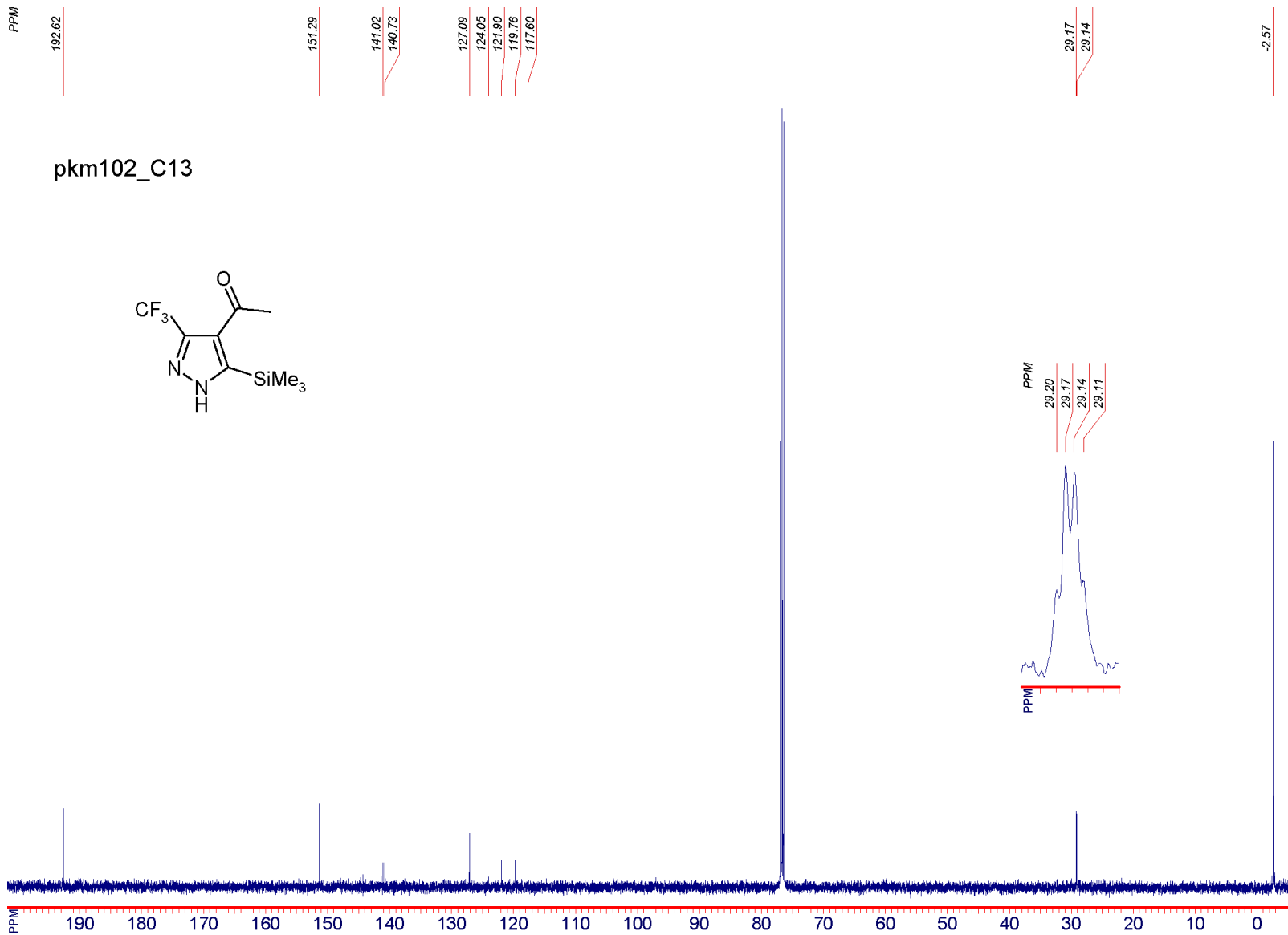
# Compound 23

PPM

pkm102

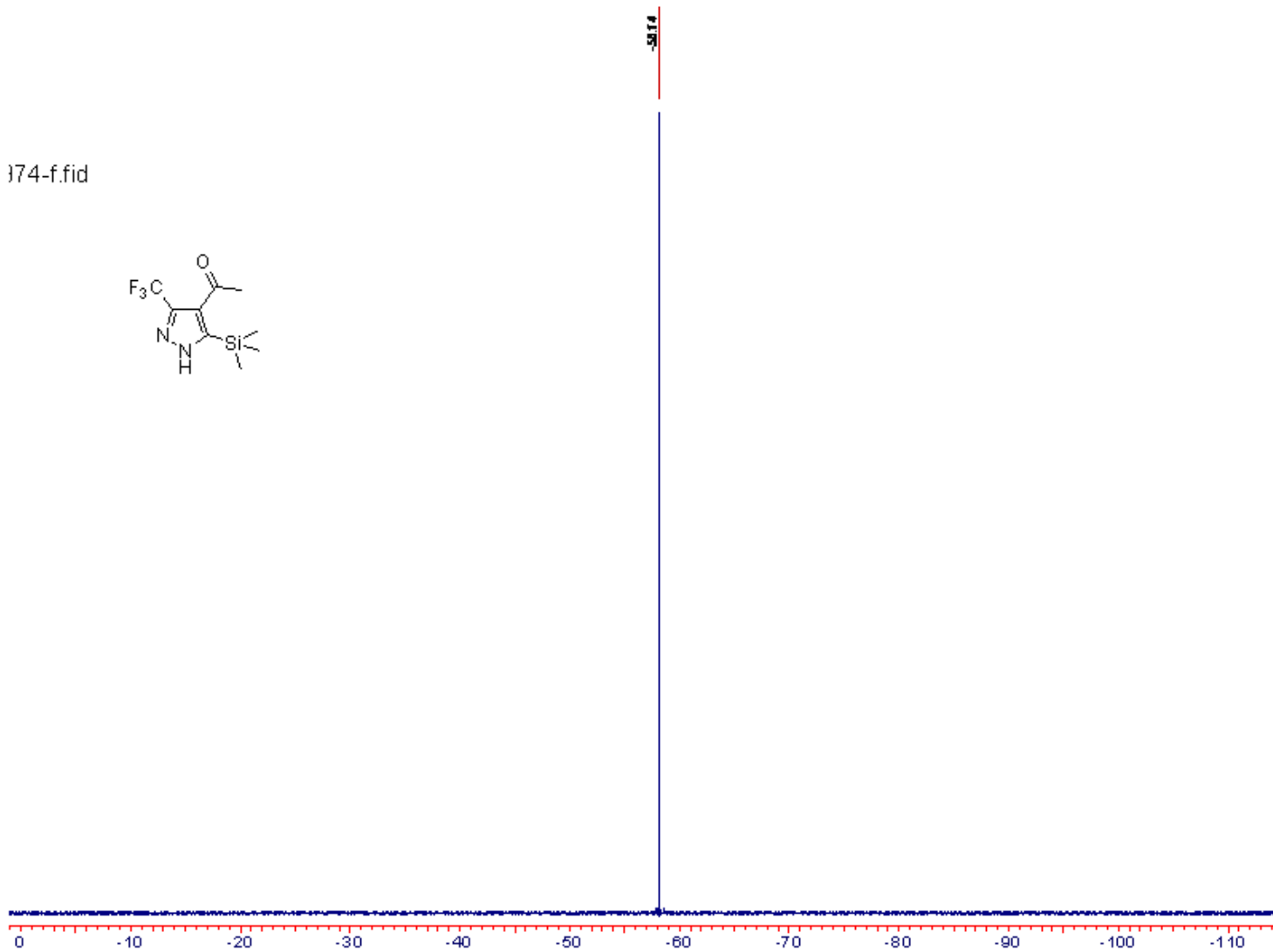
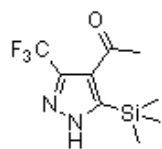


File name: pkm102	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 31-Oct-2013	Solvent: DMSO	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5



File name: pkm102_C13	Operator: root	SF: 125.7126 MHz	NSC: 431	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 31-Oct-2013	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

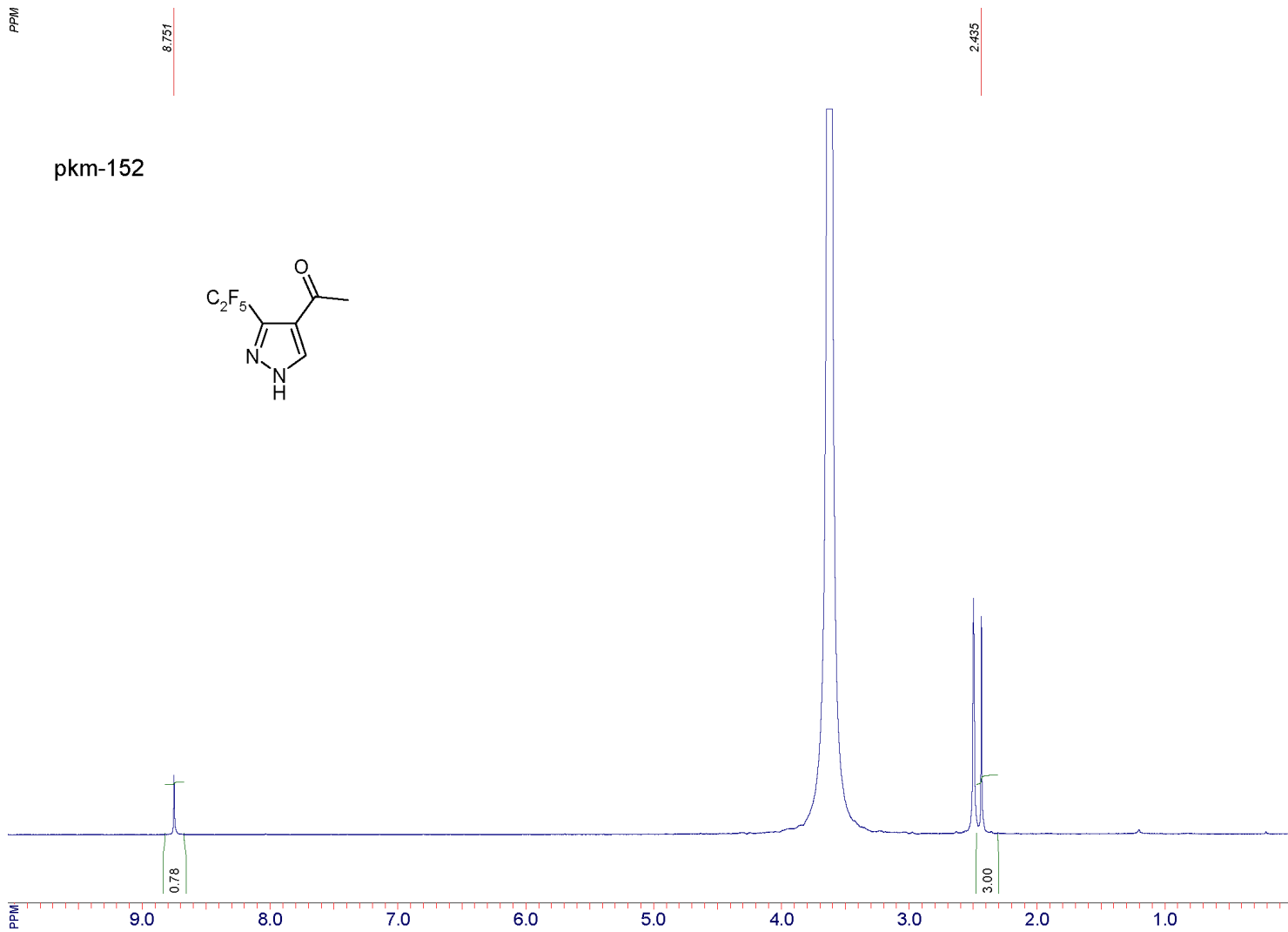
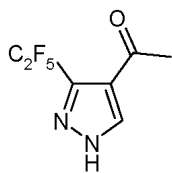
174-f.fid



# Compound 24

PPM

pkm-152



File name: pkm-152	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 28-Jan-2014	Solvent: DMSO	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR\Version 3.5

PPM

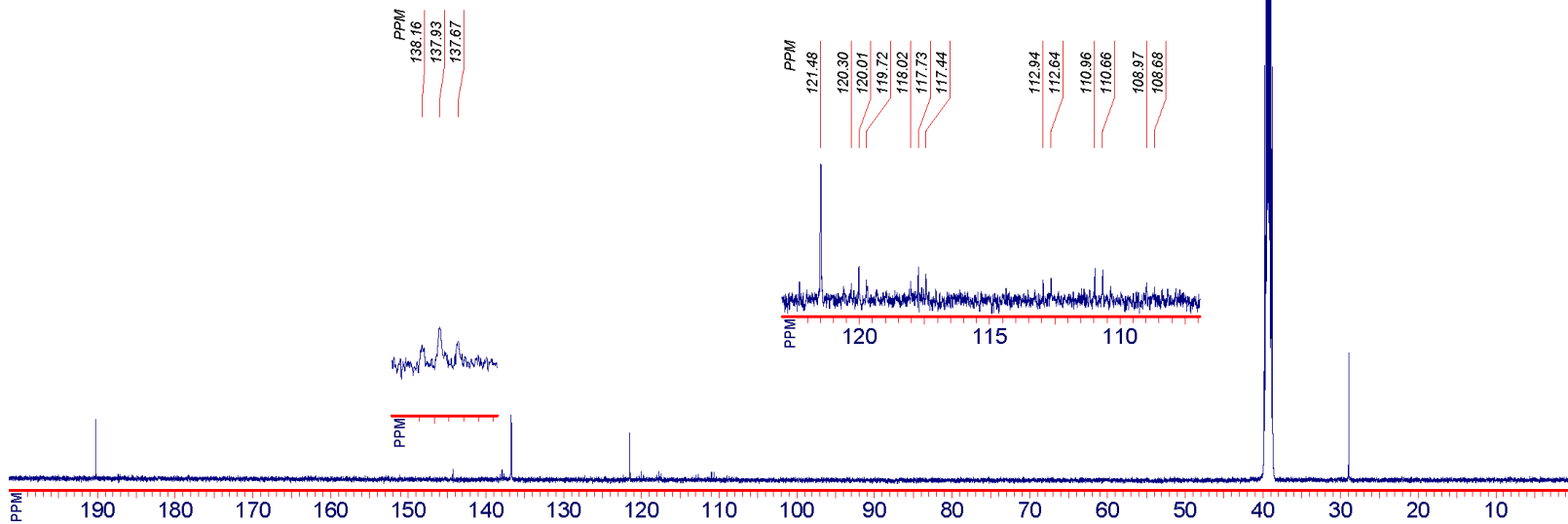
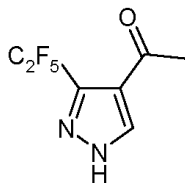
190.22

136.74

121.48

28.95

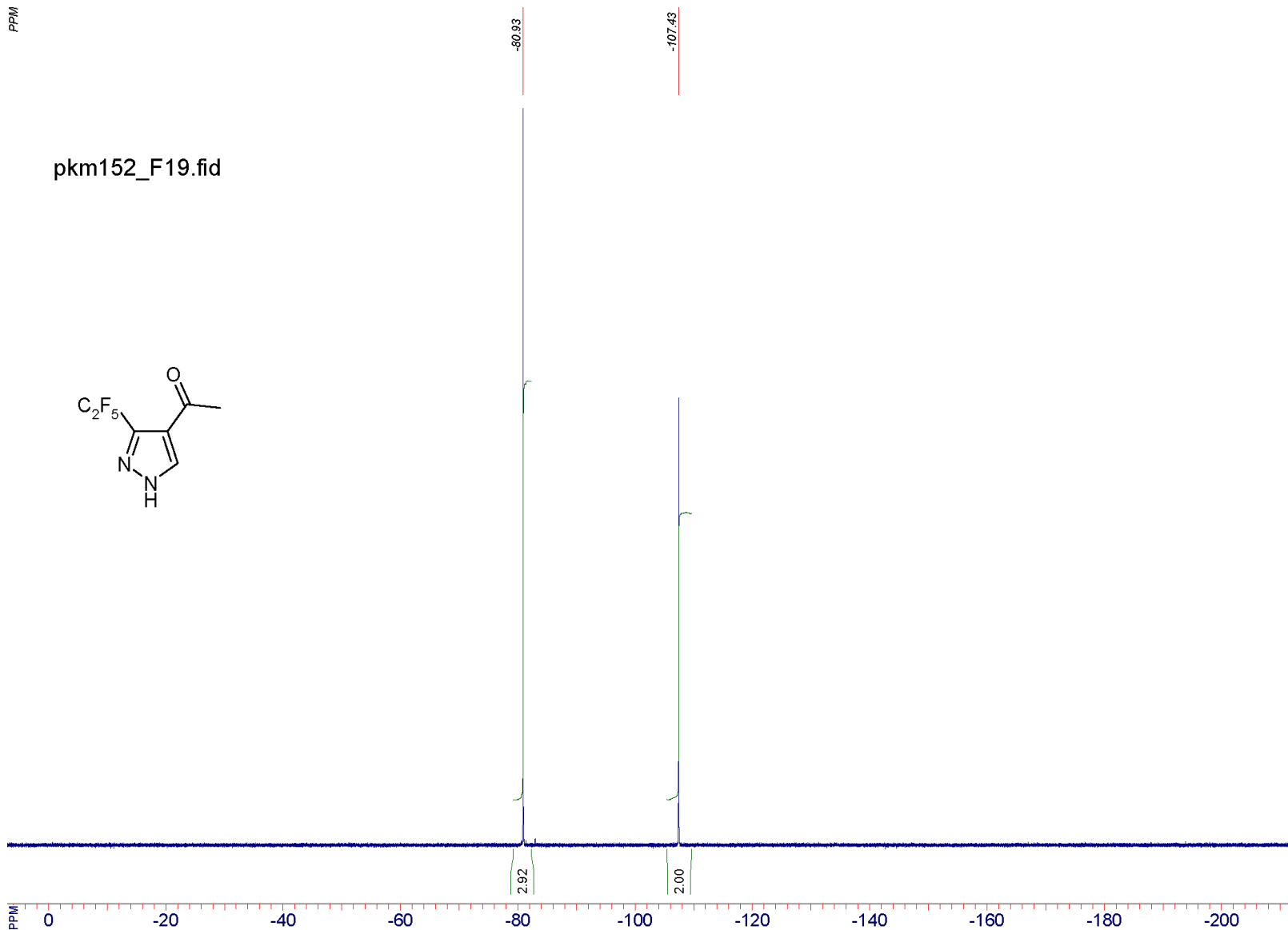
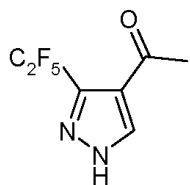
pkm152\_C13



File name: pkm152_C13	Operator: root	SF: 125.7126 MHz	NSC: 10240	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 31-Jan-2014	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

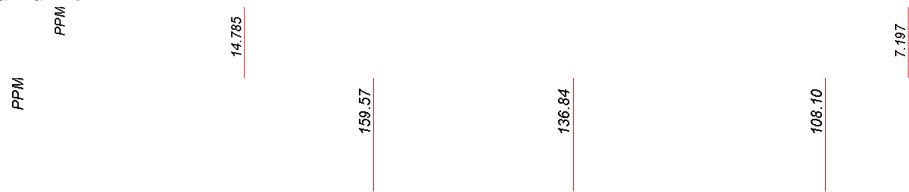
pkm152\_F19.fid



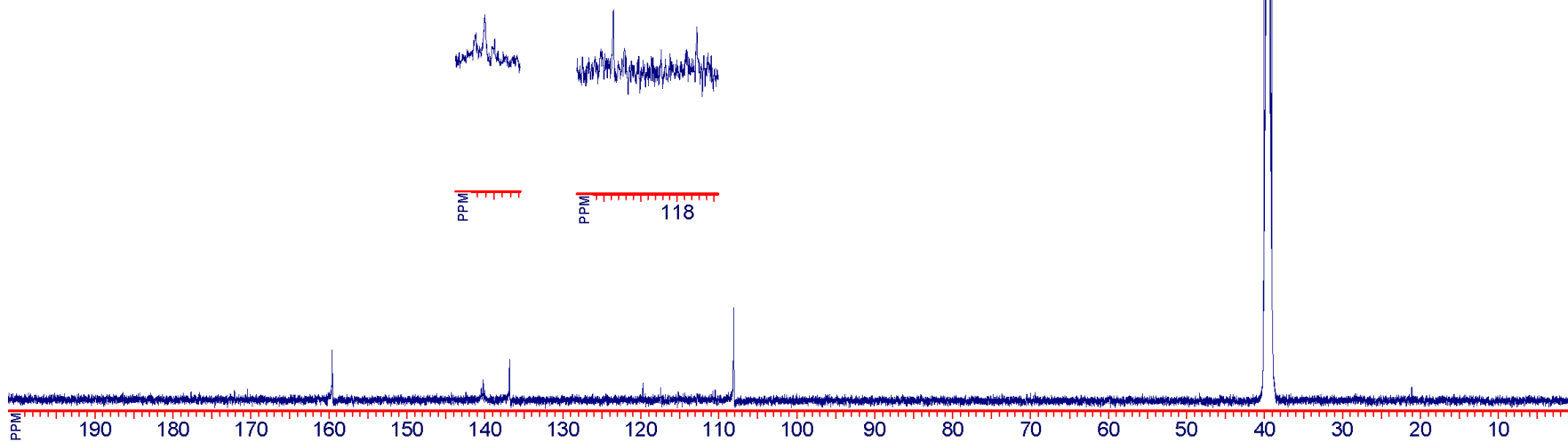
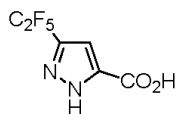
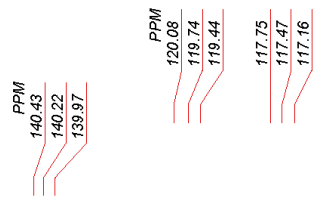
File name: pkm152_F19.fid	Operator:	SF: 376.3274 MHz	NSC: 0	PW: 3.00 usec, RG: 22	SI: 65536
Date: 04-Feb-2014	Solvent: dmsol-d6	SW: 82816 Hz	TE: 293 K	AQ: 0.39 sec, RD: 0.00 sec	□



# Compound 25



acid\_C13



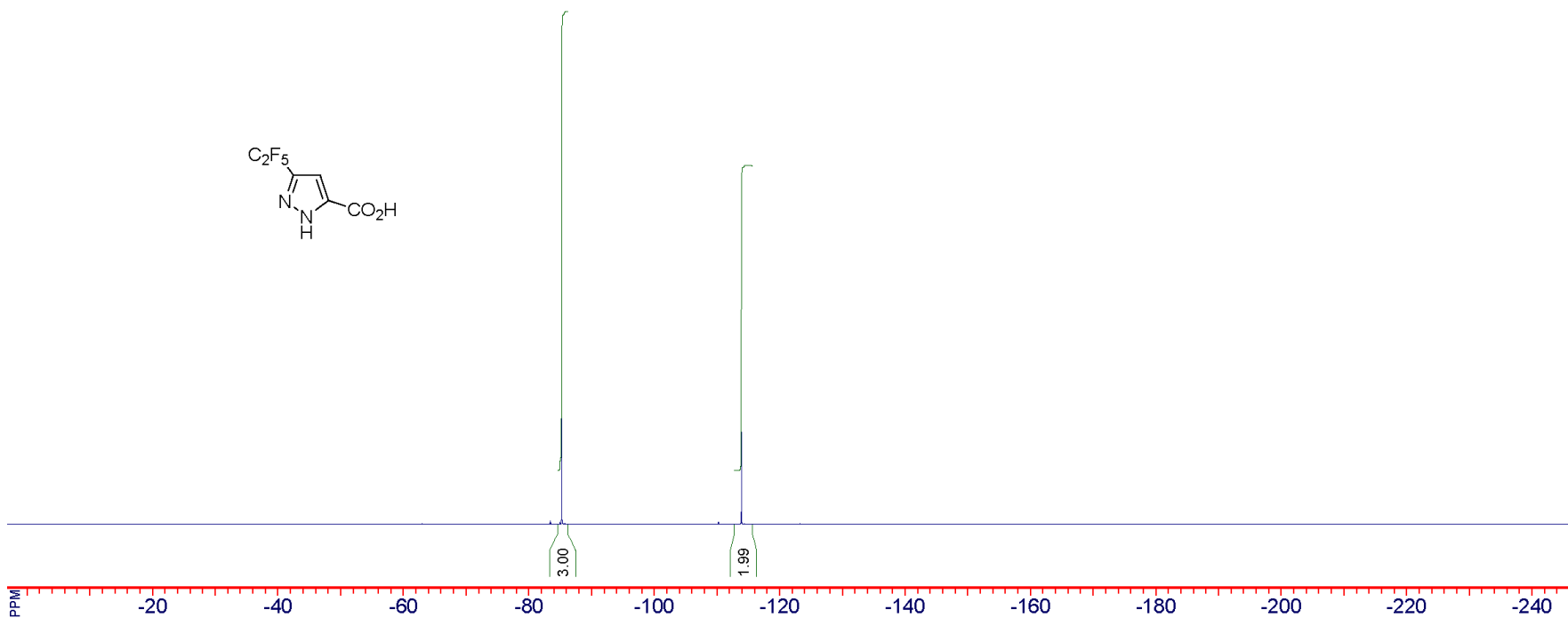
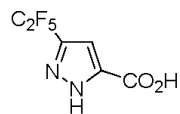
File name: acid_C13	Operator: root	SF: 125.7126 MHz	NSC: 5120	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 18-Jul-2014	Solvent: dmso	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-85.25

-113.91

acid\_F19.fid



File name: acid_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□

# Compound 26

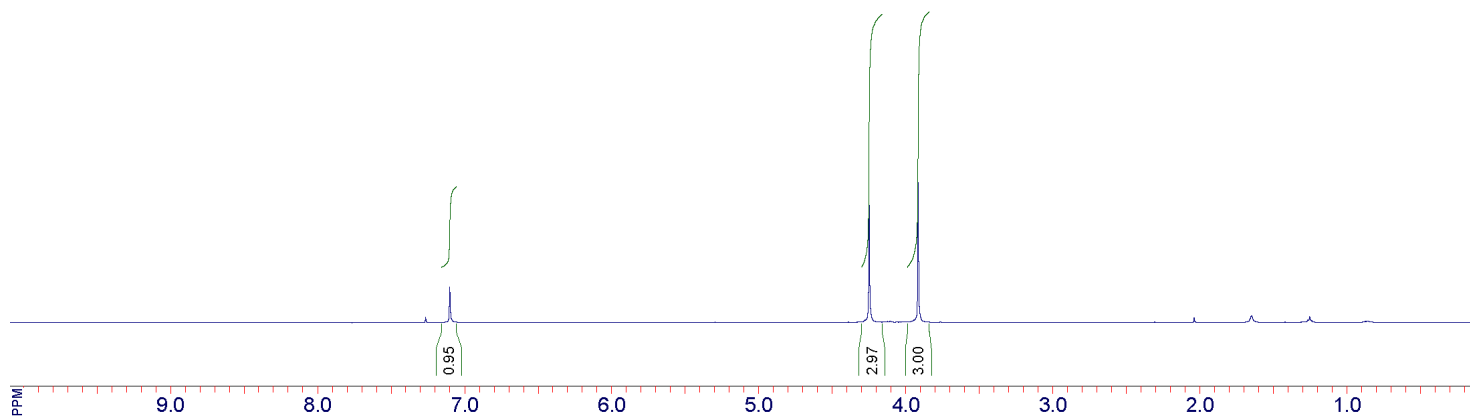
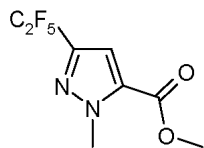
PPM

7.101

4.249

3.916

pkm-209



File name: pkm-209	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 24	SI: 32768
Date: 16-May-2014	Solvent: CDCl3	SW: 8993 Hz	TE: 0 K	AQ: 1.82 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

158.91

139.27

139.04

138.80

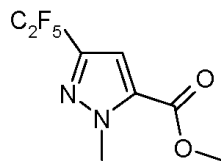
133.48

110.41

51.95

39.99

pkm209 C13



PPM

119.74

119.44

119.14

117.47

117.17

116.87

112.08

111.76

110.41

110.08

109.77

108.08

107.76

PPM

120

115

110

PPM

139.27

139.04

138.80

PPM

PPM

190

180

170

160

150

140

130

120

110

100

90

80

70

60

50

40

30

20

10

File name: pkm209 C13

Operator: root

SF: 125.7126 MHz

NSC: 1501

PW: 0.00 usec, RG: 51200

SI: 65536

Date: 18-May-2014

Solvent: CDCl3

SW: 32680 Hz

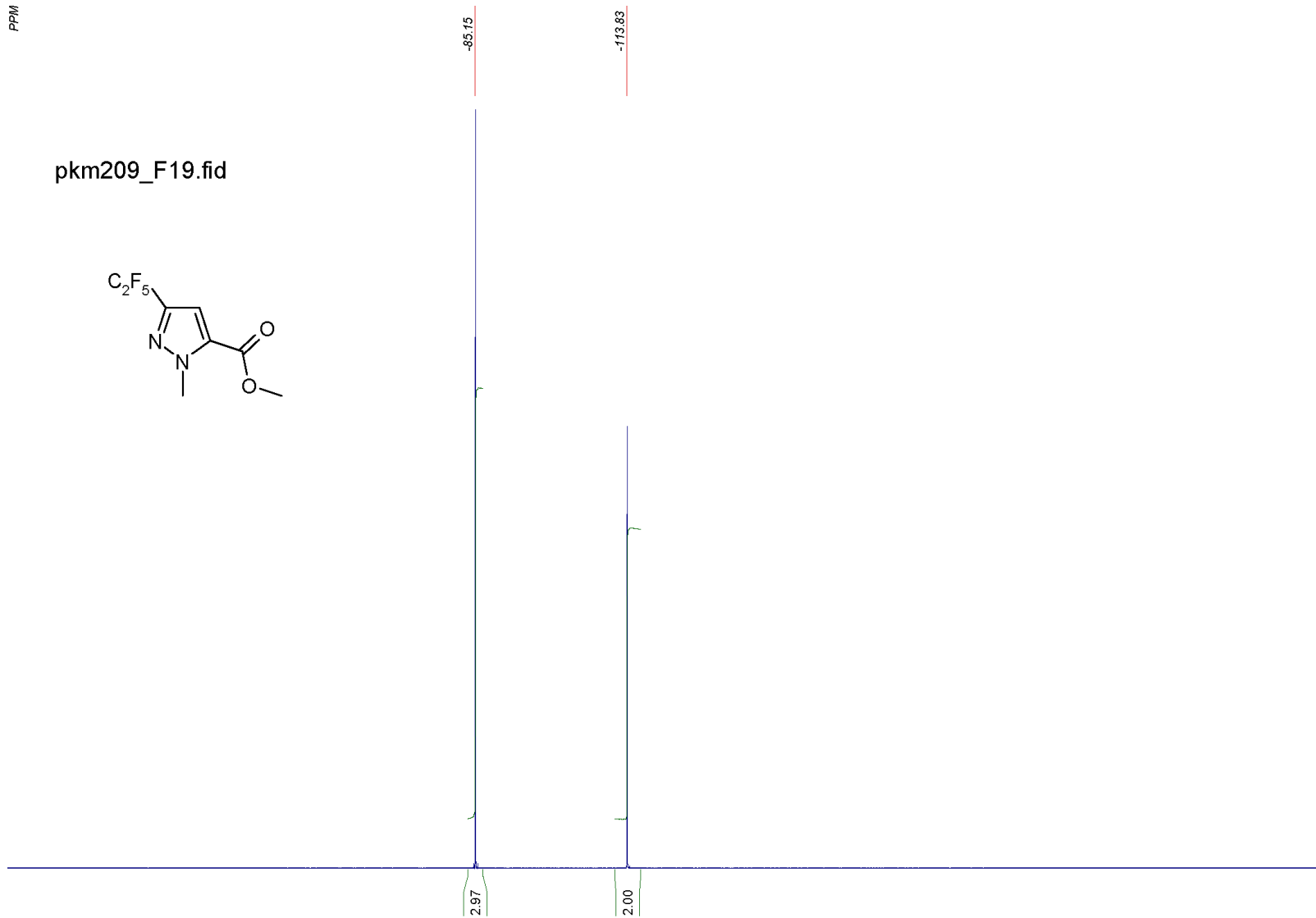
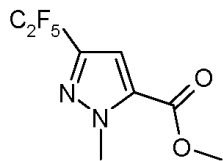
TE: 0 K

AQ: 1.57 sec, RD: 0.00 sec

Parameter file, XWIN-NMR Version 3.5

PPM

pkm209\_F19.fid

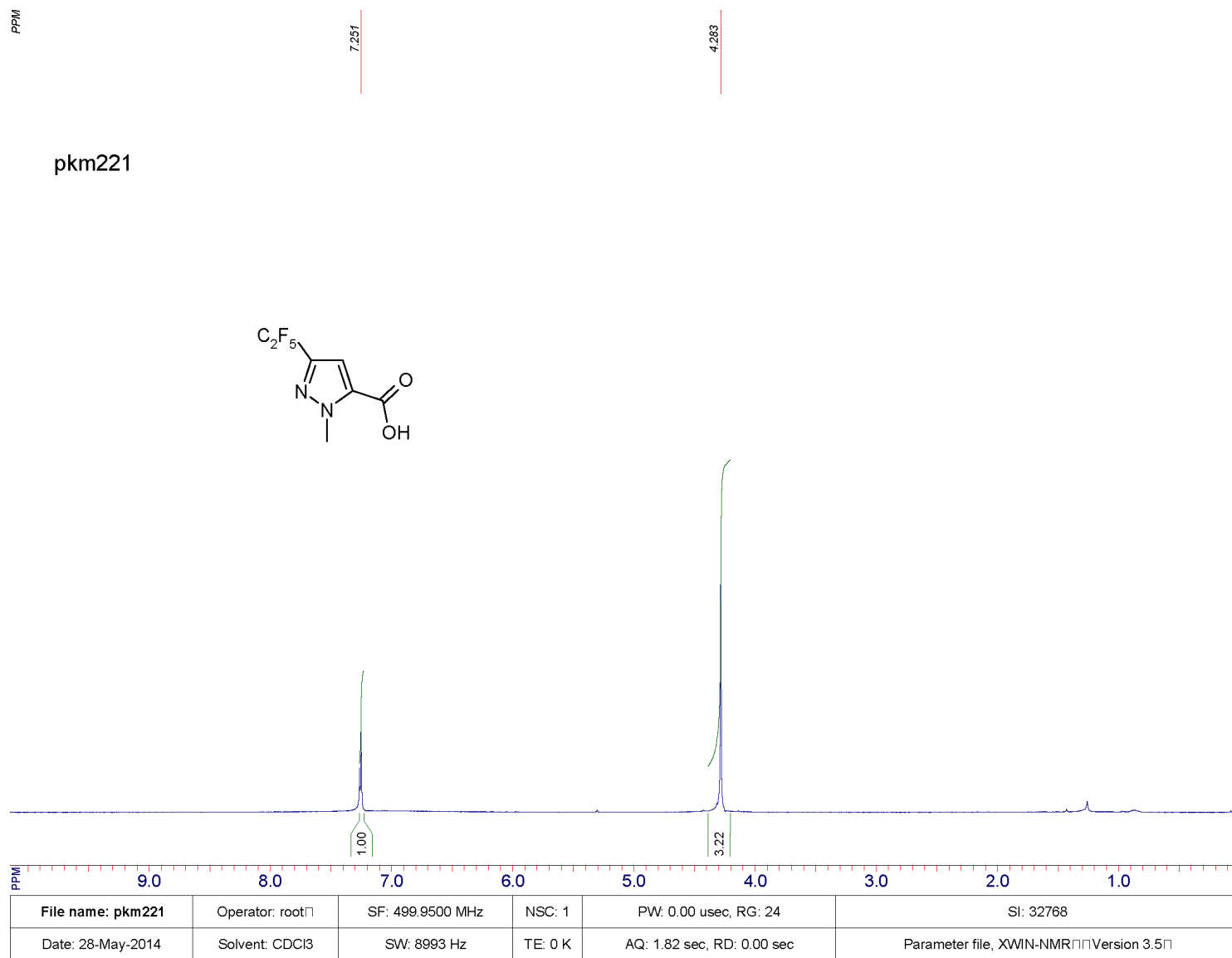
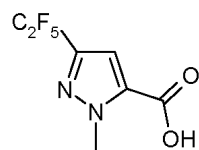


File name: pkm209_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□

# Compound 27

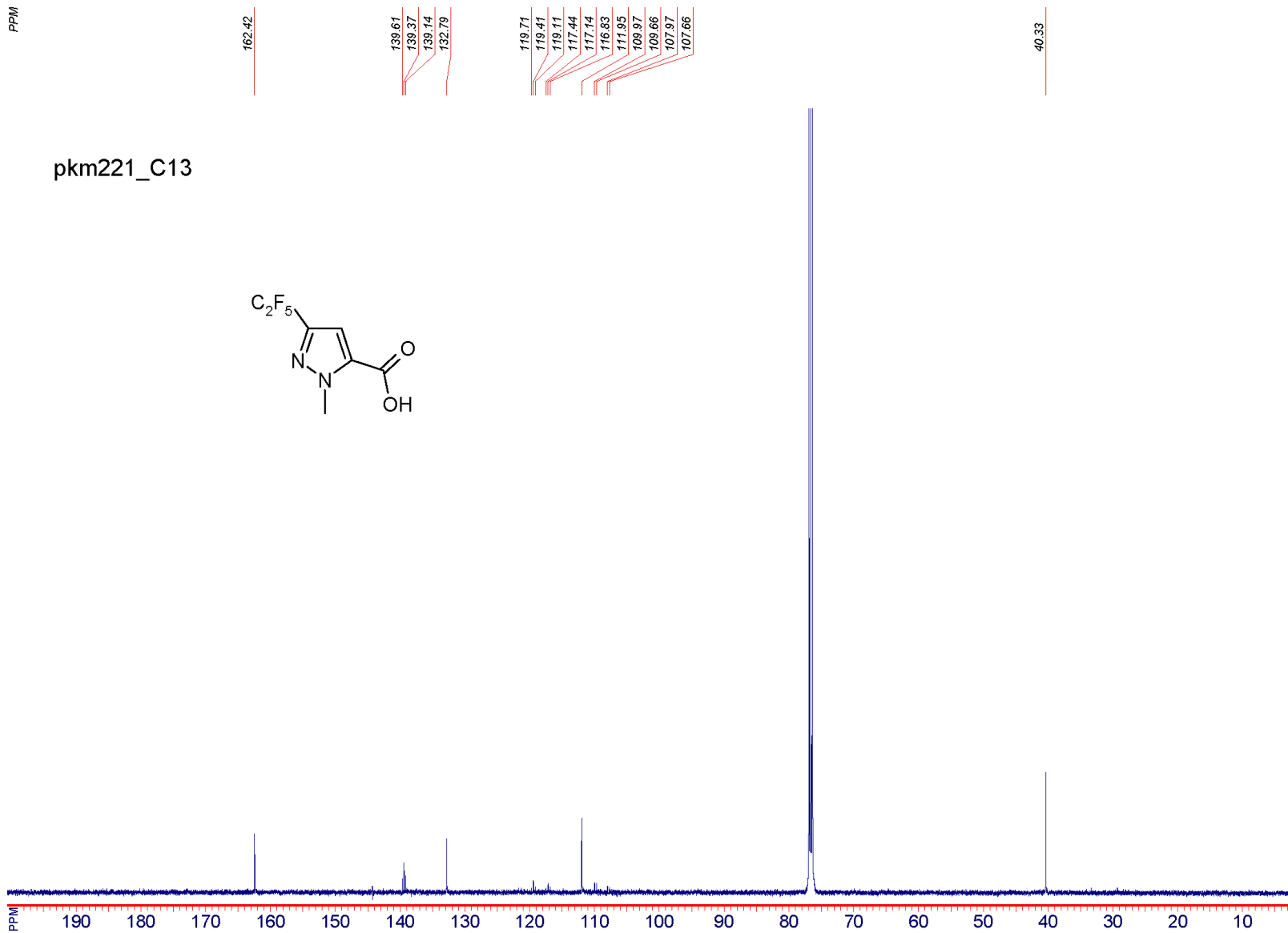
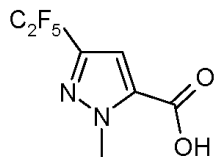
PPM

pkm221



PPM

pkm221\_C13



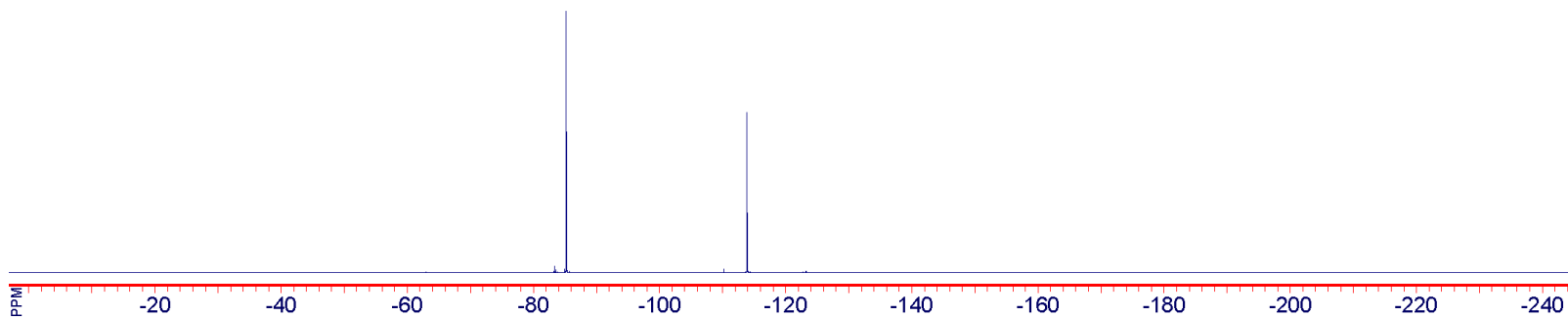
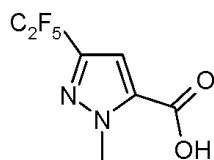
File name: pkm221_C13	Operator: root	SF: 125.7126 MHz	NSC: 3421	PW: 0.00 usec, RG: 51200	SI: 65536
Date: 31-May-2014	Solvent: dms0	SW: 32680 Hz	TE: 0 K	AQ: 1.57 sec, RD: 0.00 sec	Parameter file, XWIN-NMR Version 3.5

PPM

-65.24

-113.90

Pkm221\_m\_F19.fid



File name: Pkm221_m_F19.fid	Operator:	SF: 376.3189 MHz	NSC: 0	PW: 3.00 usec, RG: 32	SI: 65536
Date: 20-May-2014	Solvent: cdcl3	SW: 94118 Hz	TE: 293 K	AQ: 0.34 sec, RD: 0.00 sec	□