

# Supporting Information for: Transmetallation of Alkyl Ligands from $\text{Cp}^*(\text{PMe}_3)\text{IrR}^1\text{R}^2$ to $(\text{cod})\text{PtR}^3\text{X}$

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## Materials

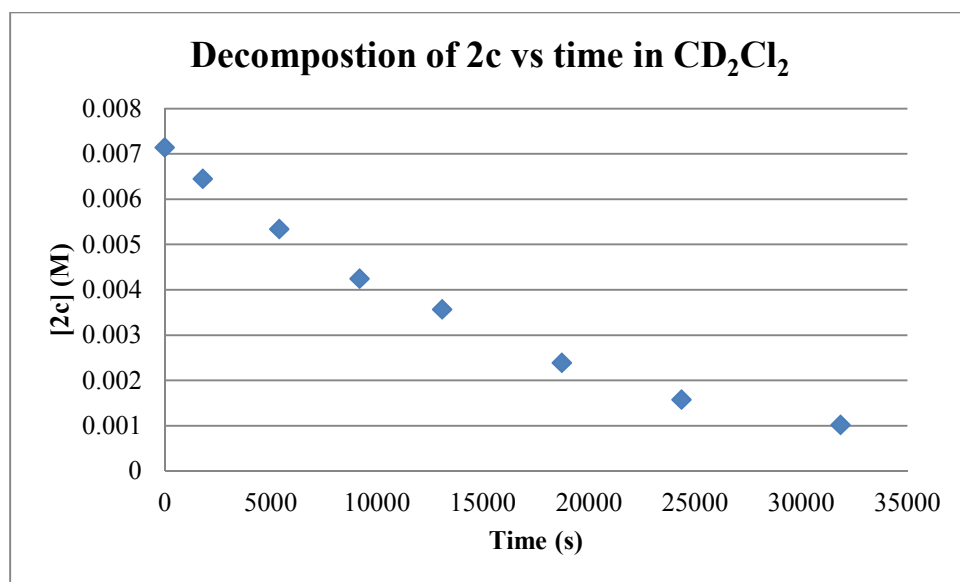
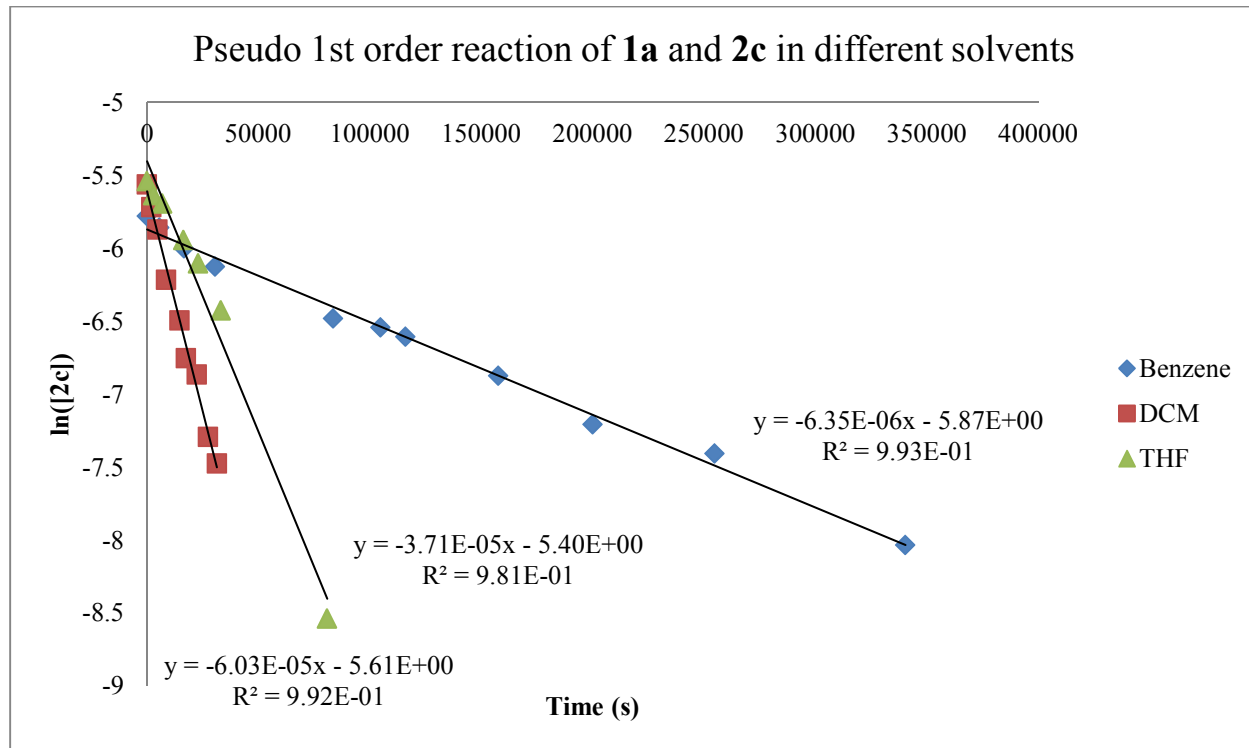
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), toluene, and pentane were obtained from an Innovative Technologies solvent purification system (solvent deoxygenated by N<sub>2</sub> sparge and dried over alumina). Acetone was dried over MgSO<sub>4</sub>, distilled under N<sub>2</sub> into a Schlenk flask, and degassed by three freeze-pump-thaw cycles. Benzene-d<sub>6</sub> was degassed by three freeze-pump-thaw cycles in a glass tube sealed with a Kontes stopper and stored over 3 Å molecular sieves. THF-d<sub>6</sub> was dried over sodium/benzophenone ketyl and vacuum transferred to a glass storage vessel with a Kontes stopper. Methylene chloride-d<sub>2</sub> was dried over CaH<sub>2</sub>, distilled into a Schlenk flask, and stored under N<sub>2</sub>. Molecular sieves were activated in an oven set to 150 °C. Alumina, silica, and celite that were used in the glove box were all rigorously flame dried in a Schlenk flask under vacuum. IrCl<sub>3</sub>·3H<sub>2</sub>O was purchased from Pressure Chemicals and (cod)PtCl<sub>2</sub> was purchased from Strem. Complete analytical data and preparations have been reported for Cp\*(PMe<sub>3</sub>)IrCl<sub>2</sub>,<sup>1</sup> Cp\*(PMe<sub>3</sub>)IrMe<sub>2</sub>,<sup>2</sup> Cp\*(PMe<sub>3</sub>)IrMeCl,<sup>2</sup> Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub>,<sup>3</sup> Cp\*(PMe<sub>3</sub>)Ir(*p*-Tolyl)H,<sup>4</sup> Cp\*(PMe<sub>3</sub>)IrPhCl,<sup>5</sup> (cod)PtMe<sub>2</sub>,<sup>6</sup> (cod)PtMeCl,<sup>7</sup> and (cod)PtMeBn.<sup>8</sup>

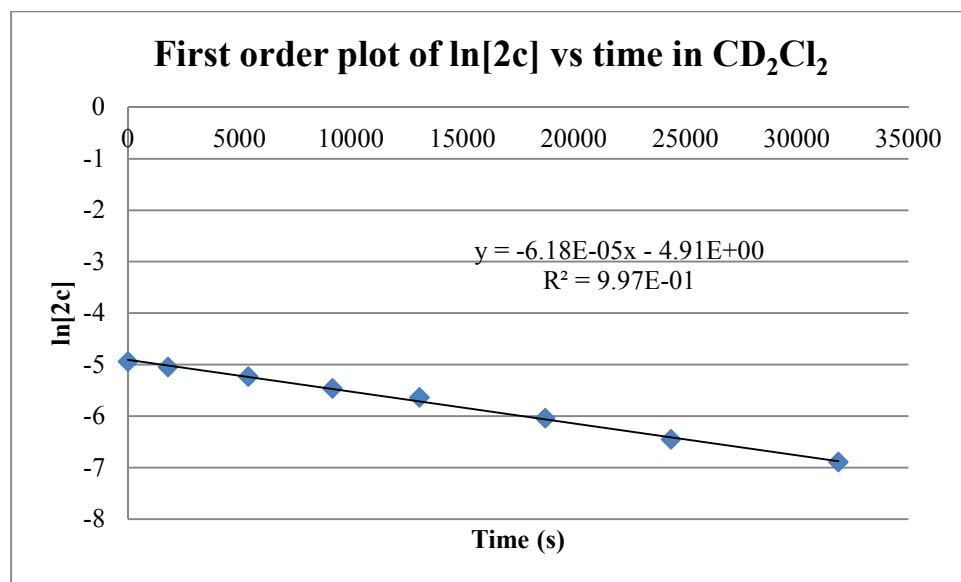
## General Procedures

Unless otherwise noted, all reactions and manipulations were performed under a circulating nitrogen atmosphere in an Innovative Technologies glove box, or using standard Schlenk technique. Glassware was dried in an oven set to 150 °C before use. Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P) were obtained using a Bruker 500 MHz spectrometer at room temperature. Chemical shifts are reported in ppm and coupling constants are reported in Hz. <sup>1</sup>H resonances are referenced to residual protonated solvent (CHCl<sub>3</sub>, 7.26 ppm; C<sub>6</sub>D<sub>6</sub>, 7.16 ppm)<sup>9</sup> while <sup>31</sup>P resonances are referenced to a phosphoric acid external standard (0.0 ppm). It has been reported that the –CF<sub>3</sub> carbon in complexes of the form Cp\*(PMe<sub>3</sub>)IrR(O<sub>3</sub>SCF<sub>3</sub>) may not be observable in the <sup>13</sup>C NMR in a reasonable number of scans.<sup>10</sup> The same phenomenon was often observed for the trifluoroacetate carbons in the complexes reported below. Yields determined by NMR were calculated from 1,3,5-trimethoxybenzene internal standard and are reported as the average of two trials set up in parallel. Products of reactions monitored by *in situ* NMR were confirmed by comparison to authentic material prepared by either the procedures listed above in the materials section or below in the experimental section. Mass spectra were obtained from the University of Chicago mass spectrometry facility using an Agilent Technologies 6224 TOF LC/MS.

All kinetic experiments were set up in an inert atmosphere dry box. All trials for each kinetic experiment were set up in parallel using stock solutions of reagents which were dispensed using gas tight syringes. In order to prevent any reaction from occurring during the unavoidable lag time between setting up an experiment and data acquisition, the contents of the NMR tubes were frozen in a bath of aluminum beads cooled to -30 °C in the glovebox and transferred frozen from the glovebox to an ice bath. Individual samples were thawed immediately before being lowered into the spectrometer. Full time course kinetic experiments were performed in J. Young NMR tubes in an equilibrated oil bath. Samples were cooled in an ice bath during transport between the oil bath and the spectrometer to ensure no reaction occurred during this time. Single pulse spectra were acquired with a delay (d1) of five times the longest measured spin lattice relaxation time of any protons that were interrogated. The decomposition of (cod)PtMeX complexes was monitored by the disappearance of the olefin resonance *trans* to the trifluoroacetate ligand.

### Representative Kinetic Data





## Experimental Procedures

**Cp\*(PMe<sub>3</sub>)IrBn<sub>2</sub> (1a):** In an inert atmosphere dry box, a 20 mL scintillation vial containing a stir bar was charged with Cp\*(PMe<sub>3</sub>)Cl<sub>2</sub> (500mg, 1.04 mmol) and Et<sub>2</sub>O ( 3.0 mL) and stirred rapidly. BnMgCl (3.12 mL, 3.12 mmol, 1.0 M in Et<sub>2</sub>O) was added dropwise via syringe to the stirring suspension and the vial was capped. After 16 hours of stirring, the mixture was diluted with 5 mL Et<sub>2</sub>O and filtered over a 1 cm pad of dry basic alumina, then eluted with additional Et<sub>2</sub>O. The red filtrate was concentrated to dryness *in vacuo* to afford a brown solid. The crude material was removed from the dry box and purified by basic alumina column chromatography using a hexane/Et<sub>2</sub>O (4:1) eluent. The first yellow band to elute was concentrated to afford **1a** as an air stable yellow solid in 71% yield (432 mg, 0.738mmol). Analytically pure samples were obtained by crystallization from hot pentane at -20 °C: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.35 (d, *J* = 7.3 Hz, 4H), 7.20 (t, *J* = 7.6 Hz, 4H), 7.07 (t, *J* = 7.3 Hz, 2H), 3.23 (m, 2H), 2.94 (m, 2H), 1.38 (d, *J*<sub>HP</sub> = 1.8 Hz, 15H), 0.91 (d, *J*<sub>HP</sub> = 9.4 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 154.03 (d, *J* = 4.0 Hz), 129.71 (s), 127.84 (s), 123.13 (s), 92.73 (d, *J*<sub>CP</sub> = 3.5 Hz), 14.49 (d, *J*<sub>CP</sub> = 35.0 Hz), 9.21 (s), 2.45 (d, *J*<sub>CP</sub> = 8.2 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -42.51 (s); MS (ESI): *m/z* 585.22 (M<sup>+</sup> and base), 495.17 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>).

**Cp\*(PMe<sub>3</sub>)Ir(*p*-Tol)<sub>2</sub> (1c):** Under air atmosphere, Cp\*(PMe<sub>3</sub>)IrCl<sub>2</sub> (200 mg, 0.417 mmol) was added to an oven dried 10 mL round bottom flask containing a stir bar. The flask was capped with a rubber septum, purged using three cycles of evacuation and N<sub>2</sub> backfill, and Et<sub>2</sub>O (1.0 mL) was added via syringe. The suspension was rapidly stirred and *p*-TolMgCl (1.51 mL, 1.25 mmol, 0.83 M in THF) was added dropwise at room temperature. After stirring for 16 hours, the reaction vessel was cooled to 0 °C and H<sub>2</sub>O (5 mL) was added slowly to quench any excess Grignard reagent. The organic layer was extracted with Et<sub>2</sub>O (3 x 10 mL), dried over Na<sub>2</sub>CO<sub>3</sub>, and concentrated. The crude mixture was purified by silica gel chromatography using 19:1 hexane:EtOAc eluent and concentrated to afford **1c** as a white solid in 9% yield (23.0 mg, 0.039 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.55 (d, *J* = 7.4 Hz, 4H), 7.00 (d, *J* = 7.3 Hz, 4H), 2.34 (s, 6H), 1.47 (s, 15H), 1.04 (d, *J*<sub>CP</sub> = 9.9 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 143.32 (d, *J*<sub>CP</sub> = 2.6 Hz), 132.47 (d, *J* = 14.7 Hz), 130.14 (s), 95.34 (d, *J*<sub>CP</sub> = 3.5 Hz), 21.34 (s), 14.95 (d, *J*<sub>CP</sub> = 38.4 Hz), 9.98 (s), 1.61 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -38.80 (s); MS (ESI): *m/z* 586.23, (M<sup>+</sup> and base), 495.17 M<sup>+</sup> - C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). (It should be noted that the major product of this reaction, Cp\*(PMe<sub>3</sub>)Ir(*p*-Tol)Cl, can be easily isolated with high purity by eluting the crude mixture with 9:1 hexane:EtOAc.)

**Cp\*(PMe<sub>3</sub>)IrBnCl (3aa):** In an inert atmosphere dry box, a 20 mL scintillation vial containing a stir bar was charged with **1a** (60.0 mg, 0.103 mmol) and dry, deoxygenated acetone (2.5 mL). Anilinium

hydrochloride (13.3 mg, 0.103 mmol) was added in portions to the rapidly stirring solution and allowed to stir for 1 h. After 1h, the volatiles were removed *in vacuo* and the remaining yellow solid was taken up in Et<sub>2</sub>O and filtered over silica, then eluted with additional Et<sub>2</sub>O. The resulting yellow solution was concentrated to afford **3aa** in 93% yield (51mg, 0.096 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 4.11 (m, 1H), 3.17 (m, 1H), 1.29 (s, 15H), 1.13 (d, *J*<sub>HP</sub> = 10.2 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 152.97 (d, *J*<sub>HP</sub> = 5.2 Hz), 129.68 (s), 127.58 (s), 123.21 (s), 91.64 (d, *J*<sub>HP</sub> = 3.3 Hz), 13.53 (d, *J*<sub>HP</sub> = 37.0 Hz), 8.74 (s), 5.75 (d, *J*<sub>HP</sub> = 9.0 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -34.73; MS (ESI): *m/z* 495.17 (M<sup>+</sup> - Cl and base).

**Cp\*(PMe<sub>3</sub>)IrBnOAc (3ab):** Under air atmosphere, **3aa** (11.5 mg, 0.021 mmol) and AgOAc (3.8 mg, 0.023) were weighed into a 1.5 mL centrifuge tube with a sealable cap and DCM (1.0 mL) was added. The reaction vessel was agitated by continuous rotation for 1 h, the insoluble materials were pelleted by centrifugation (4000 rpm, 10 min, 4 °C), and the supernatant was decanted and concentrated. The crude material was crystallized from Et<sub>2</sub>O/hexanes to afford **3ab** as a yellow solid in 48% yield (5.6 mg, 0.0101 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.76-3.70 (m, 1H), 2.79-2.73 (m, 1H), 2.35 (s, 3H), 1.34 (s, 15H), 1.20 (d, *J* = 10.2 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 177.91 (s), 152.99 (d, *J*<sub>CP</sub> = 5.5 Hz), 128.83 (s), 127.73 (s), 123.18 (s), 89.98 (d, *J*<sub>CP</sub> = 3.5 Hz), 23.76 (s), 13.79 (d, *J*<sub>CP</sub> = 35.6 Hz), 8.73 (s), 7.13 (d, *J*<sub>CP</sub> = 7.9 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -30.84; MS (ESI): *m/z* 495.17 (M<sup>+</sup> - CH<sub>3</sub>COO), 463.13 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 437.11 (base).

**Cp\*(PMe<sub>3</sub>)IrBnTFA (3ac):** In an inert atmosphere dry box, a 20 mL scintillation vial containing a stir bar was charged with **3aa** (56.0 mg, 0.106 mmol) and DCM (6 mL). To the stirring mixture was added solid AgTFA (23.5 mg, 0.106 mmol) and the vial was capped. The mixture was allowed to stir for 10 minutes, filtered over celite, and then the filtrate was concentrated *in vacuo*. The crude material was taken up in a minimal amount of Et<sub>2</sub>O and precipitated with pentane at -30 °C to afford **3ac** as a yellow solid in 40 % yield (25.6 mg, 0.042 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.67 (m, 1H), 2.65 (m, 1H), 1.15 (d, *J*<sub>HP</sub> = 2.2 Hz, 2H), 1.02 (d, *J*<sub>HP</sub> = 10.2 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 151.90 (d, *J*<sub>CP</sub> = 5.5 Hz), 128.79 (s), 127.94 (s), 123.60 (s), 90.40 (d, *J*<sub>CP</sub> = 3.3 Hz), 13.55 (d, *J*<sub>CP</sub> = 35.9 Hz), 8.71 (d, *J*<sub>CP</sub> = 7.8 Hz), 8.53 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -30.67 (s); <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>) δ -174.70 (s); MS (ESI): *m/z* 517.10 (M<sup>+</sup> - CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 495.17 (M<sup>+</sup> - CF<sub>3</sub>COO and base), 437.11.

**Cp\*(PMe<sub>3</sub>)IrMeTFA (4bc):** In an inert atmosphere dry box, a 20 mL scintillation vial containing a stir bar was charged with Cp\*(PMe<sub>3</sub>)IrMeCl (42.0 mg, 0.093 mmol) and DCM (7 mL). To

the stirring mixture was added solid AgTFA (20.4 mg, 0.093 mmol) and the vial was capped. The mixture was allowed to stir for 10 minutes, filtered over celite, and then the filtrate was concentrated *in vacuo*. The crude material was taken up in minimal Et<sub>2</sub>O and precipitated with pentane at -30 °C to afford **3ac** as a yellow solid in 84% yield (41.4 mg, 0.078 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.36 (d, *J*<sub>HP</sub> = 2.0 Hz, 1H), 1.08 (d, *J*<sub>HP</sub> = 10.3 Hz, 1H), 0.94 (d, *J*<sub>HP</sub> = 6.8 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 89.91 (d, *J*<sub>CP</sub> = 3.4 Hz), 13.81 (d, *J*<sub>CP</sub> = 36.5 Hz), 8.86 (s), -13.33 (d, *J*<sub>CP</sub> = 10.0 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -29.45 (s); <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>) δ -174.56 (s); MS (ESI): *m/z* 517.10 (M<sup>+</sup> - CH<sub>3</sub>), 437.12, 419.14 (M<sup>+</sup> - CF<sub>3</sub>COO and base).

**Cp\*(PMe<sub>3</sub>)IrPhTFA (6d)**: Under air atmosphere, a 20 mL scintillation vial containing a stir bar was charged with Cp\*(PMe<sub>3</sub>)IrPhCl (21.6 mg, 0.042 mmol) and DCM (4 mL). To the stirring mixture was added solid AgTFA (9.2 mg, 0.042 mmol) and the vial was capped. The mixture was allowed to stir for 10 minutes, filtered over celite, and then the filtrate was concentrated *in vacuo*. The crude material was taken up in minimal Et<sub>2</sub>O and precipitated with pentane to afford **3ac** as a yellow solid in 84% yield (20.9 mg, 0.035 mmol): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 1.60 (d, *J*<sub>HP</sub> = 1.8 Hz, 15H), 1.39 (d, *J*<sub>HP</sub> = 10.6 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 141.70 (d, *J*<sub>CP</sub> = 14.7 Hz), 136.96 (s), 127.33 (s), 122.29 (s), 92.42 (d, *J*<sub>CP</sub> = 3.1 Hz), 29.85 (s), 14.76 (d, *J*<sub>CP</sub> = 38.0 Hz), 9.45 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -31.01 (s); <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>) δ -174.88 (s); MS (ESI): *m/z* 522.18 (M<sup>+</sup> - CF<sub>3</sub>COO + CH<sub>3</sub>CN), 481.16 (M<sup>+</sup> - CF<sub>3</sub>COO and base).

**Cp\*(PMe<sub>3</sub>)Ir(TFA)<sub>2</sub>**: Under air atmosphere, a 50 mL centrifuge tube with a screw cap was charged with Cp\*(PMe<sub>3</sub>)IrCl<sub>2</sub> (250 mg, 0.530 mmol), AgTFA (235.4 mg, 1.07 mmol), and DCM (12 mL). The vessel was agitated by continuous rotation for 1 h and benzene (20 mL) was added to effect precipitation of all silver salts. The insoluble materials were pelleted by centrifugation (4000 rpm, 10 min, 4 °C) and the supernatant was decanted and concentrated to afford Cp\*(PMe<sub>3</sub>)Ir(TFA)<sub>2</sub> as a yellow solid in 94% yield (313 mg, 0.497 mmol): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.67 (d, *J*<sub>HP</sub> = 2.2 Hz, 15H), 1.57 (d, *J*<sub>HP</sub> = 11.3 Hz, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 162.67 (br), 115.91 (br), 89.75 (d, *J*<sub>CP</sub> = 2.8 Hz), 13.45 (d, *J*<sub>CP</sub> = 36.6 Hz), 9.31 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ -17.56 (s); <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>) δ -174.53 (s); MS (ESI): 517.10 (M<sup>+</sup> - CF<sub>3</sub>COO), 463.13, 437.11 (base).

**Cp\*(PMe<sub>3</sub>)Ir(TFA)H (7ec and 8fc)**: Several methods for preparing **7ec** were attempted. Both addition of NaBH<sub>4</sub> to Cp\*(PMe<sub>3</sub>)Ir(TFA)<sub>2</sub> and reaction between AgTFA and Cp\*(PMe<sub>3</sub>)IrHCl were unsuccessful on first attempt in our hands. It was found that ligand interchange between Cp\*(PMe<sub>3</sub>)Ir(TFA)<sub>2</sub> and Cp\*(PMe<sub>3</sub>)IrH<sub>2</sub> was effective in generating **7ec**. In an inert atmosphere dry box,



$\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$  (8.1 mg, 0.020 mmol) and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{TFA})_2$  were weighed into a J. Young NMR tube, and  $\text{C}_6\text{D}_6$  (0.7 mL) was added. The NMR tube was sealed and heated to 75 °C outside the dry box in an oil bath. The reaction was monitored both by  $^1\text{H}$  and  $^{31}\text{P}$  spectroscopy, and after ca. 3 days of heating an equilibrium between  $\text{Cp}^*(\text{PMe}_3)\text{IrH}_2$ ,  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{TFA})_2$ , and  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{TFA})\text{H}$  was reached. Due to prolonged heating in  $\text{C}_6\text{D}_6$ , some deuterium exchange was observed to produce  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{TFA})\text{D}$  as evidenced by deuterium coupling in the  $^{31}\text{P}$  NMR spectrum. Characteristic  $\text{Cp}^*$  and hydride resonances of **7ec** were observed and were consistent with the products observed in entries 7 and 8 of Table 1. **7ec** was characterized in its equilibrium mixture but was not isolated.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.57 (d,  $J$  = 2.1 Hz, 15H), 1.18 (d,  $J$  = 10.6 Hz, 9H), -12.60 (d,  $J$  = 40.3 Hz, 1H); **7ec**  $^{31}\text{P}\{\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -32.80 (s);  $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{TFA})\text{D}$   $^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -32.72 (t,  $J_{\text{PD}}$  = 12.2 Hz).

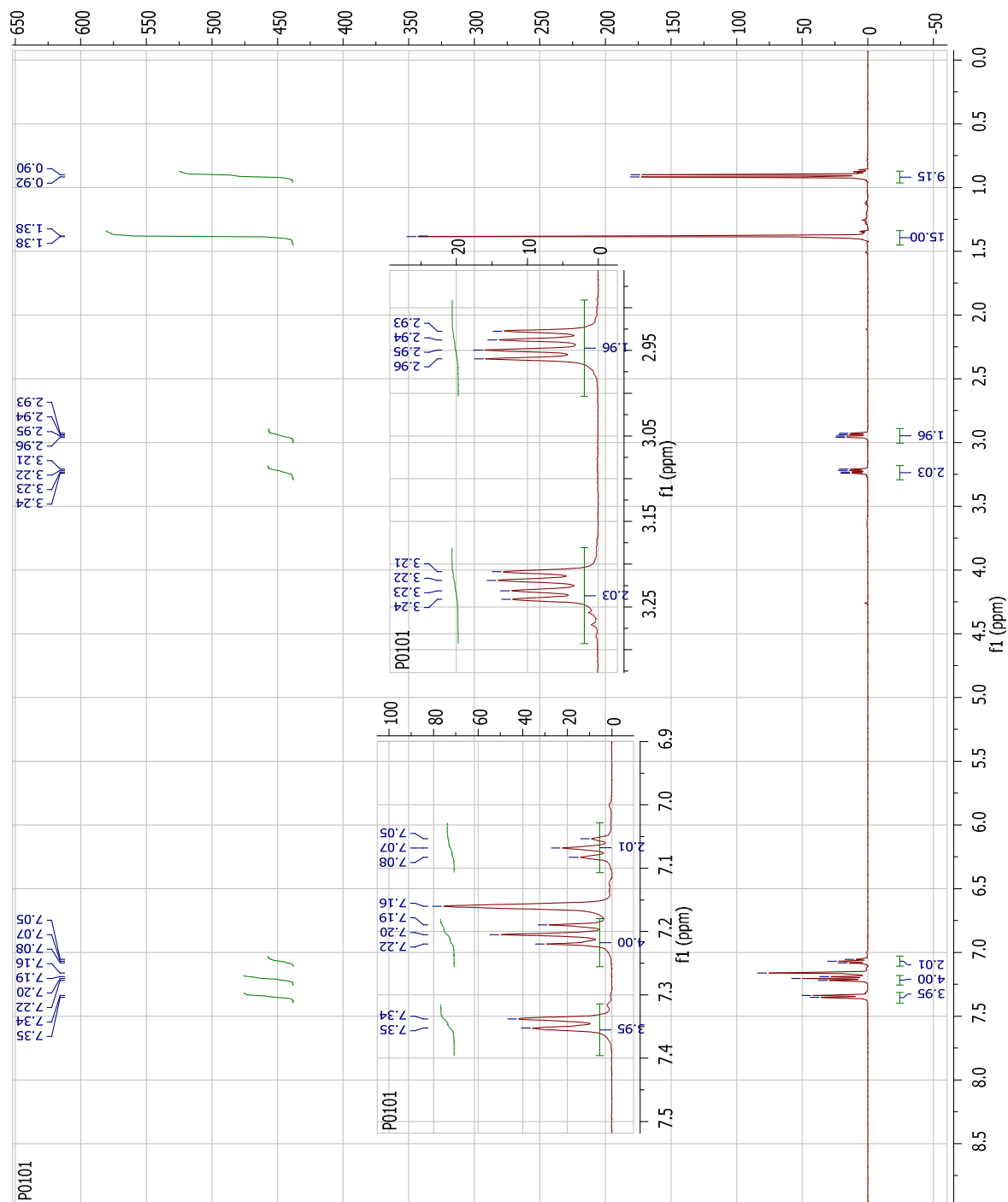
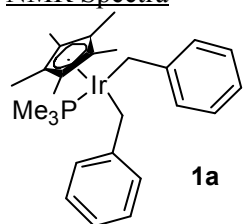
**$\text{Cp}^*(\text{PMe}_3)\text{BnPh}$  (6d)**: Under air atmosphere,  $\text{Cp}^*(\text{PMe}_3)\text{IrPhCl}$  (30.0 mg, 0.058 mmol) was added to a dry, 10 mL round bottomed flask containing a stir bar and the flask was capped with a rubber septum. The vessel was purged by three cycles of evacuation and  $\text{N}_2$  backfill, dry  $\text{Et}_2\text{O}$  was added via syringe, and the mixture was rapidly stirred at room temperature.  $\text{BnMgCl}$  (0.174 mL, 0.174 mmol, 1.0 M in  $\text{Et}_2\text{O}$ ) was added dropwise to the flask, and the mixture was allowed to stir for 18 h.  $\text{H}_2\text{O}$  was added to quench any excess Grignard reagent, and the organics were extracted with DCM (3 x 10 mL). The organic extracts were combined, dried over  $\text{Na}_2\text{CO}_3$ , and concentrated to yield a crude product that was purified by flash chromatography using 19:1 hexane:EtOAc to afford **6d** as a white solid in 70% yield (23.1 mg, 0.040 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.49 (d,  $J$  = 7.2 Hz, 2H), 7.29 (d,  $J$  = 7.4 Hz, 2H), 7.20 (t,  $J$  = 7.3 Hz, 2H), 7.16-7.11 (m, 3H), 7.02 (t,  $J$  = 7.4 Hz, 1H), 3.60 (d,  $J$  = 10.8 Hz, 1H), 2.96 (m,  $J$  = 10.9, 4.3 Hz, 1H), 1.42 (s, 15H), 0.91 (d,  $J_{\text{HP}}$  = 9.6 Hz, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  154.51 (s), 140.95 (d,  $J_{\text{CP}}$  = 3.4 Hz), 138.44 (d,  $J_{\text{CP}}$  = 12.2 Hz), 129.72 (s), 127.77 (s), 127.48 (s), 122.94 (s), 121.68 (s), 93.59 (d,  $J_{\text{CP}}$  = 3.4 Hz), 15.17 (d,  $J_{\text{CP}}$  = 36.0 Hz), 9.48 (s), 5.37 (d,  $J$  = 8.1 Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -39.85 (s); MS (ESI):  $m/z$  522.18 ( $\text{M}^+ - \text{CF}_3\text{COO} + \text{CH}_3\text{CN}$ ), 481.16 ( $\text{M}^+ - \text{CF}_3\text{COO}$  and base).

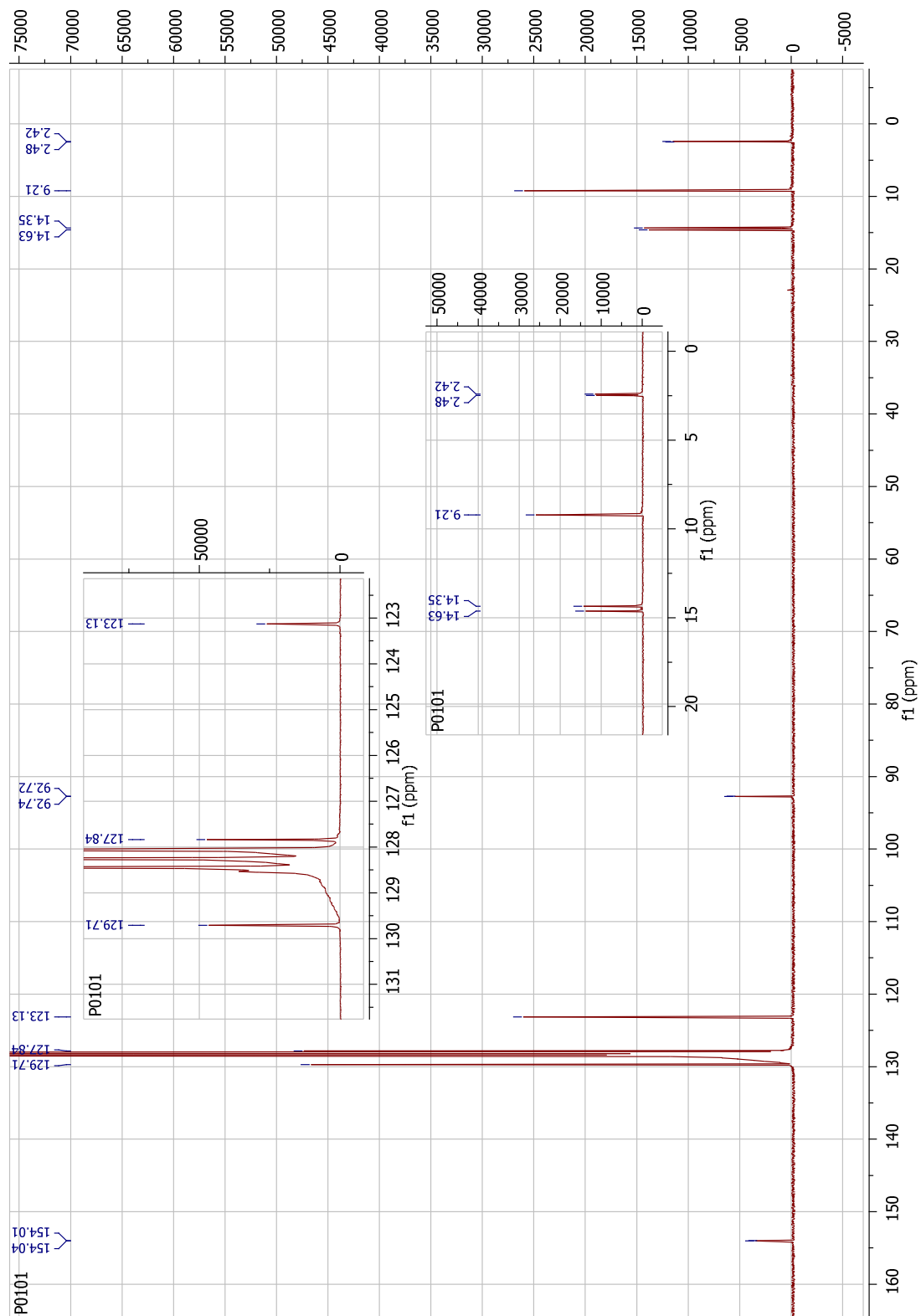
**(cod)PtMeTFA (2c)**: Under air atmosphere, (cod)PtMe<sub>2</sub> (200 mg, 0.60 mmol) and DCM (8 mL) were added to a 20 mL scintillation vial containing a stir bar. To the stirring solution of (cod)PtMe<sub>2</sub>, trifluoroacetic acid (2.0 mL, 0.607 mmol, 0.303 M in DCM) was added dropwise via syringe over 10 min. After the addition, the reaction mixture was allowed to stir until methane evolution ceased (ca. 10 min), and the solvent was removed under reduced pressure. The yellow residue was dissolved in minimal DCM (<1 mL) and diluted with hexanes (10 mL). The solution was concentrated to 1 mL, during which time white crystals formed. The remaining supernatant was decanted away and the crystals were washed with additional hexanes and dried under vacuum to afford **2c** in 70% yield (181 mg, 0.420 mmol):  $^1\text{H}$  NMR

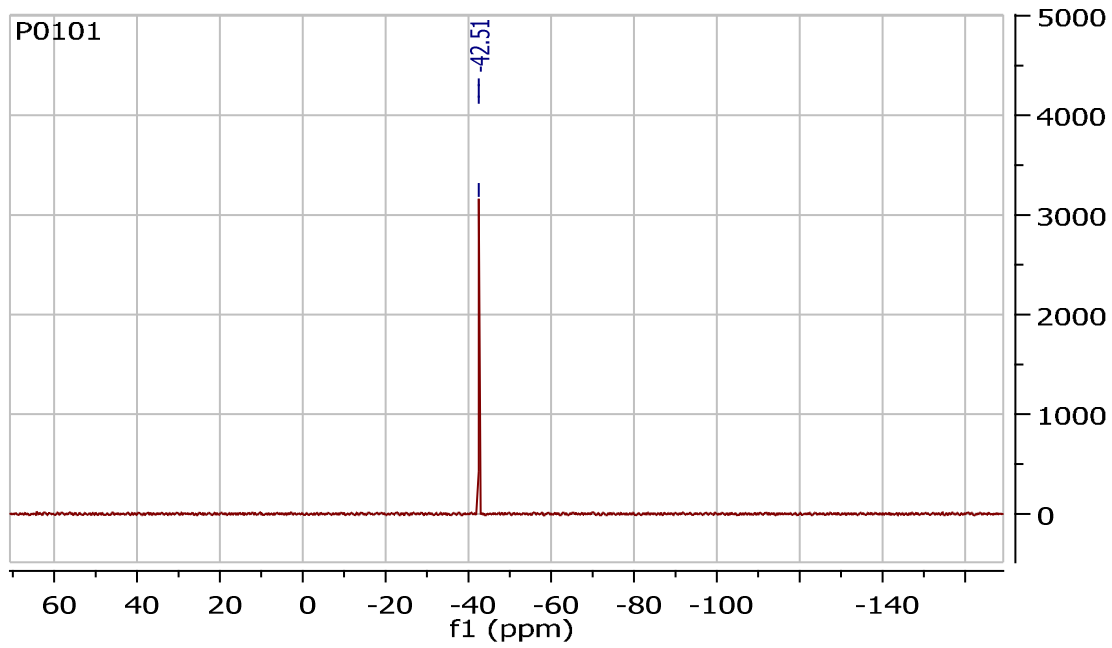
(500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.23 (s w/Pt satellites, 2H,  $^2J_{\text{HPt}} = 5.0$  Hz), 3.68 (s w/Pt satellites, 2H,  $^2J_{\text{HPt}} = 79.2$  Hz), 1.56 (m, 4H), 1.24 (m, 4H), 0.92 (s w/Pt satellites, 3H  $^2J_{\text{HPt}} = 69.6$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  161.20 (br,  $J = 39.0$  Hz), 119.28 (br,  $J = 280.6$  Hz), 112.89 (s w/Pt satellites,  $^2J_{\text{CPt}} = 33.0$  Hz), 79.58 (s w/Pt satellites,  $^2J_{\text{CPt}} = 240.1$  Hz), 30.91 (s w/Pt satellites,  $^2J_{\text{CPt}} = 24.7$  Hz), 27.24 (s w/Pt satellites,  $^2J_{\text{CPt}} = 26.4$  Hz), 5.58 (s w/Pt satellites,  $^2J_{\text{CPt}} = 646.5$  Hz);  $^{19}\text{F}$  NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -174.26 (s); MS (ESI):  $m/z$  681.16, 653.17, 425.15, 359.11 ( $\text{M}^+ - \text{CF}_3\text{COO} + \text{CH}_3\text{CN}$  and base).

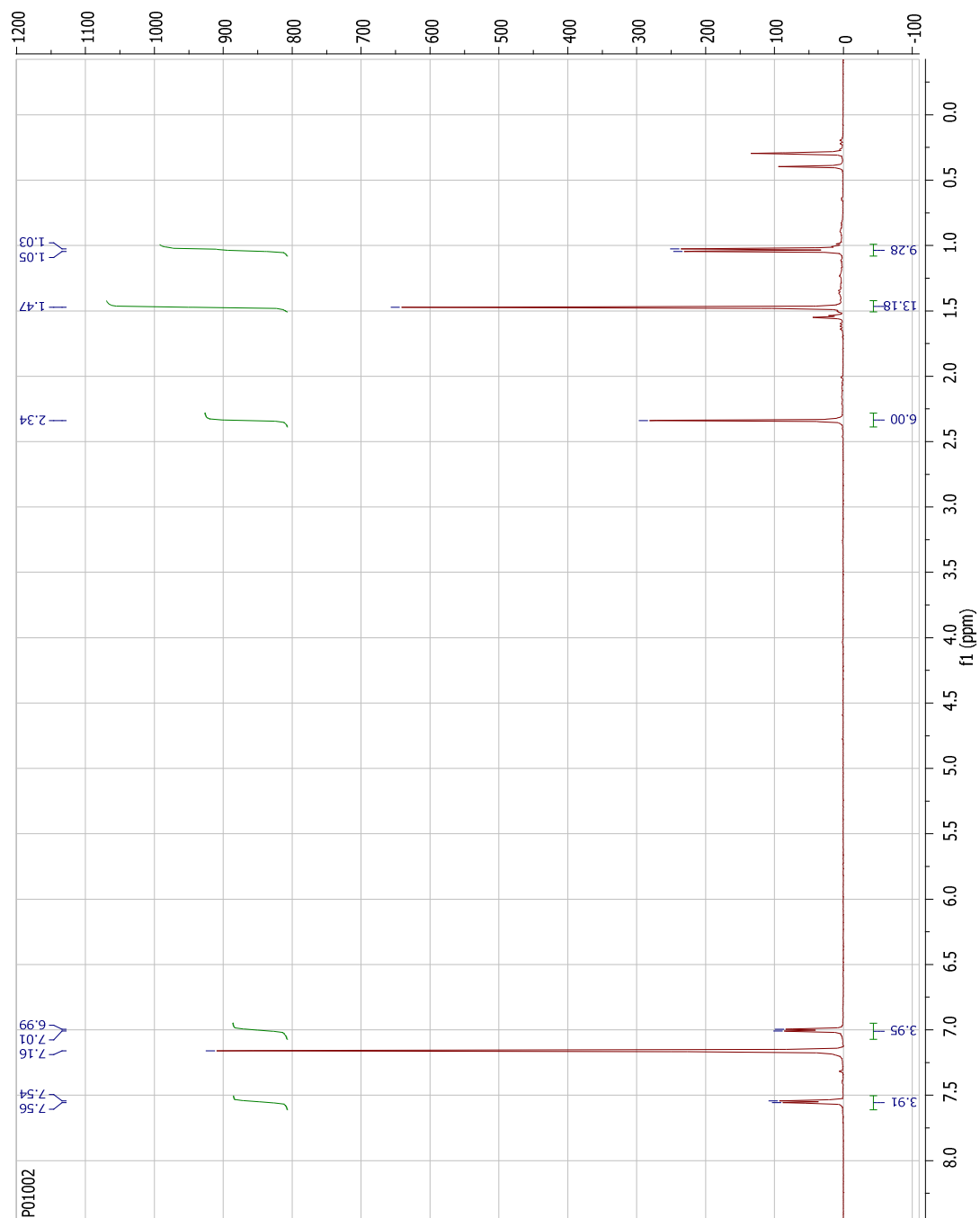
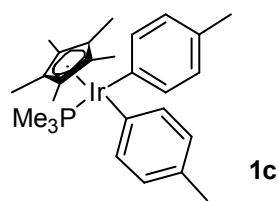
**(cod)PtMeOAc (2b):** Preparation of **2b** by a procedure analogous to that of **2c** was attempted, but was not successful. Instead anion exchange was used. Under air atmosphere, (cod)PtMeCl (345 mg, 0.970 mmol) and AgOAc (164 mg, 0.98 mmol) were weighed into a 50 mL centrifuge tube with a screw cap, and acetone (40 mL) was added. The tube was sealed and agitated by continuous rotation for 1 h, after which time the insoluble materials were pelleted by centrifugation (4000 rpm, 10 min, 4 °C). The supernatant was concentrated to give a crude product that was crystallized from DCM/Et<sub>2</sub>O at 0 °C to afford **2b** as a grey solid in 53% yield (193.7 mg, 0.514 mmol):  $^1\text{H}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.63 (s w/Pt satellites, 2 H,  $^2J_{\text{HPt}} = 27.3$  Hz), 3.69 (s w/Pt satellites, 2 H,  $^2J_{\text{HPt}} = 74.0$  Hz), 2.24 (s, 3 H), 1.79-1.59 (m, 4 H), 1.41-1.26 (m, 4 H), 1.13 (s w/Pt satellites, 3 H,  $^2J_{\text{HPt}} = 68.7$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  175.62 (s), 111.96 (s w/Pt satellites,  $^2J_{\text{CPt}} = 33.8$  Hz), 77.29 (s w/Pt satellites,  $^2J_{\text{CPt}} = 227.8$  Hz), 31.13 (s w/Pt satellites,  $^2J_{\text{CPt}} = 21.7$  Hz), 27.56 (s w/Pt satellites,  $^2J_{\text{CPt}} = 23.6$  Hz), 24.51 (s), 5.66 (s w/Pt satellites,  $^2J_{\text{CPt}} = 673.3$  Hz); MS (ESI):  $m/z$  986.23, 695.17, 653.16 (base), 359.10 ( $\text{M}^+ - \text{CH}_3\text{COO} + \text{CH}_3\text{CN}$ ).

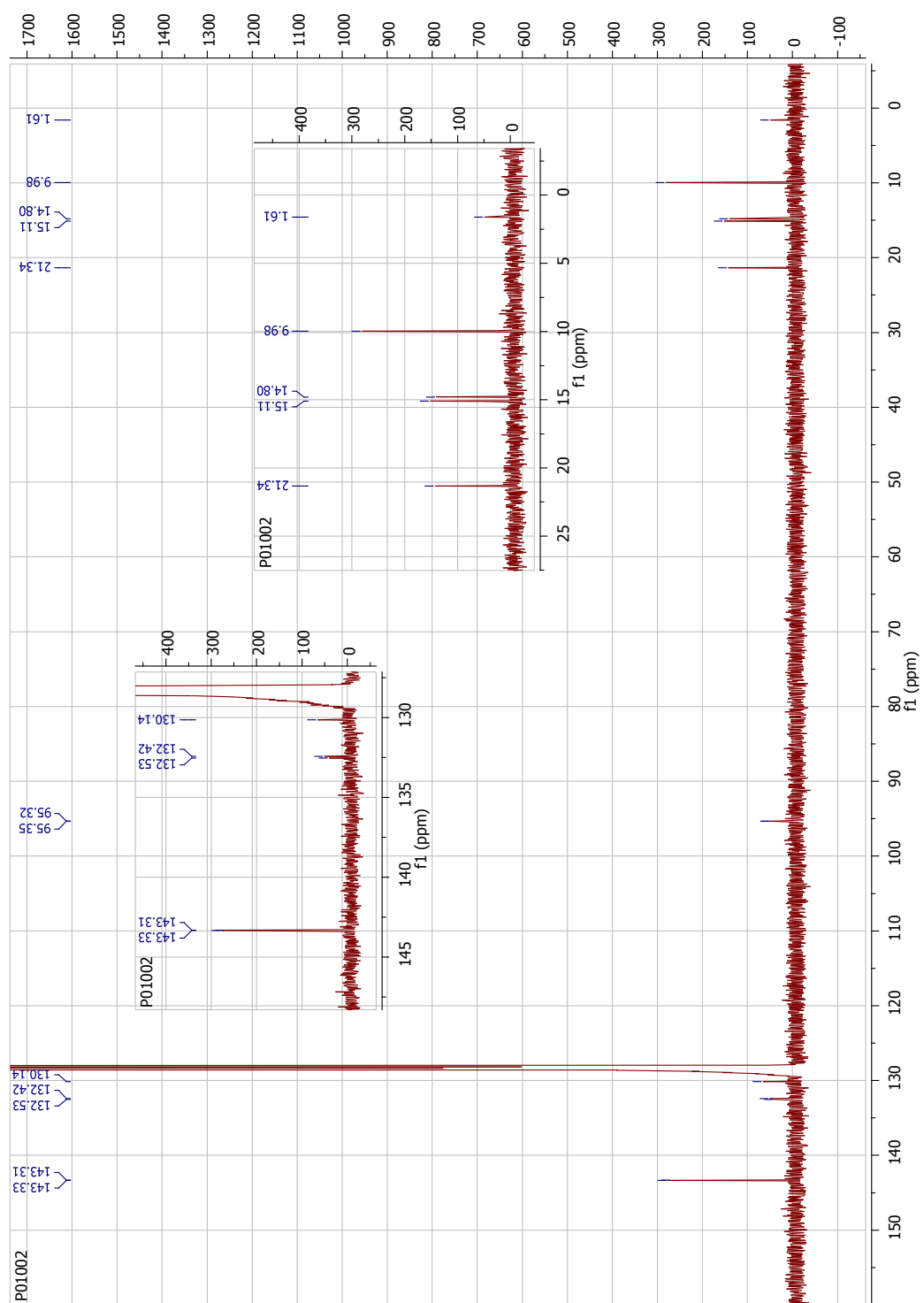
# NMR Spectra

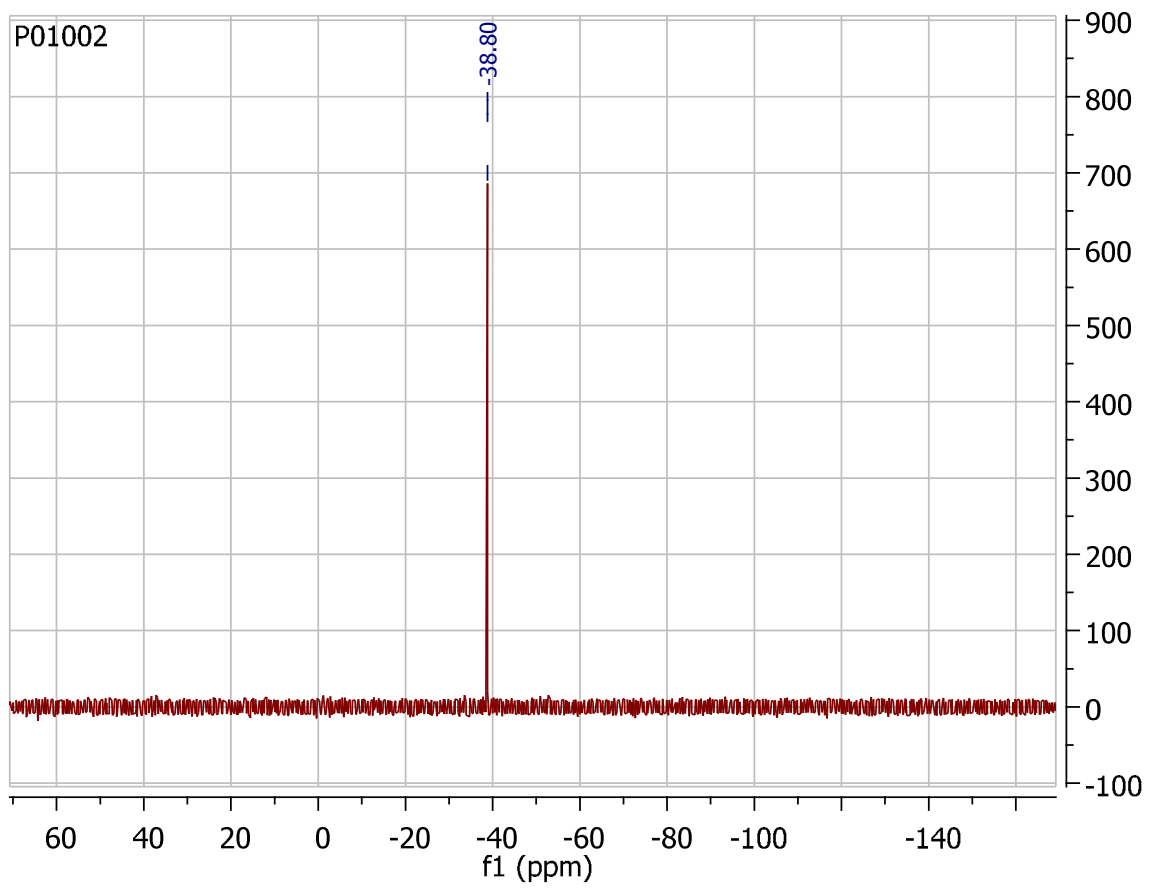




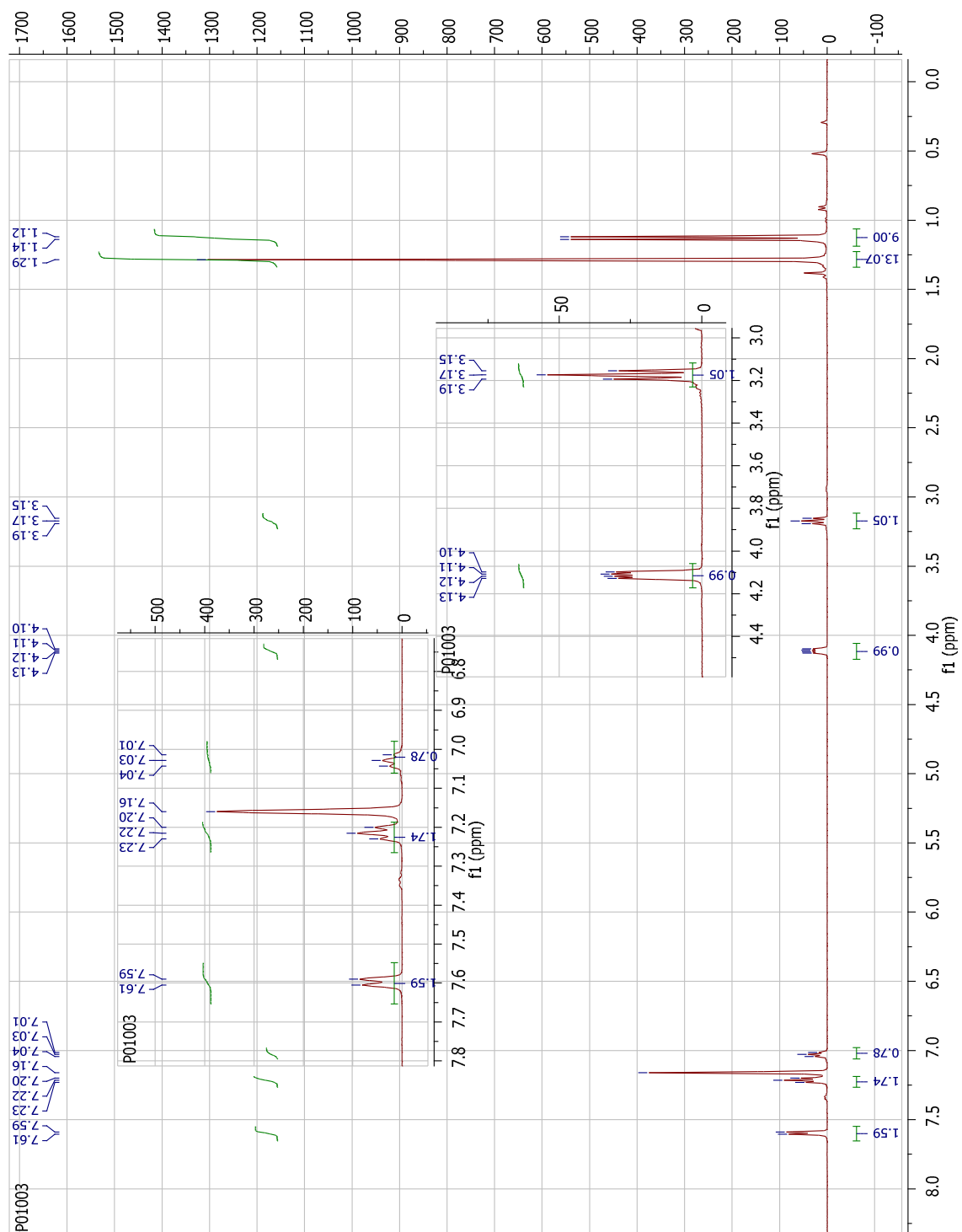
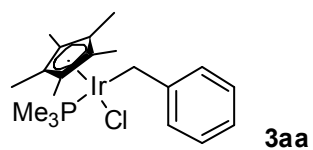


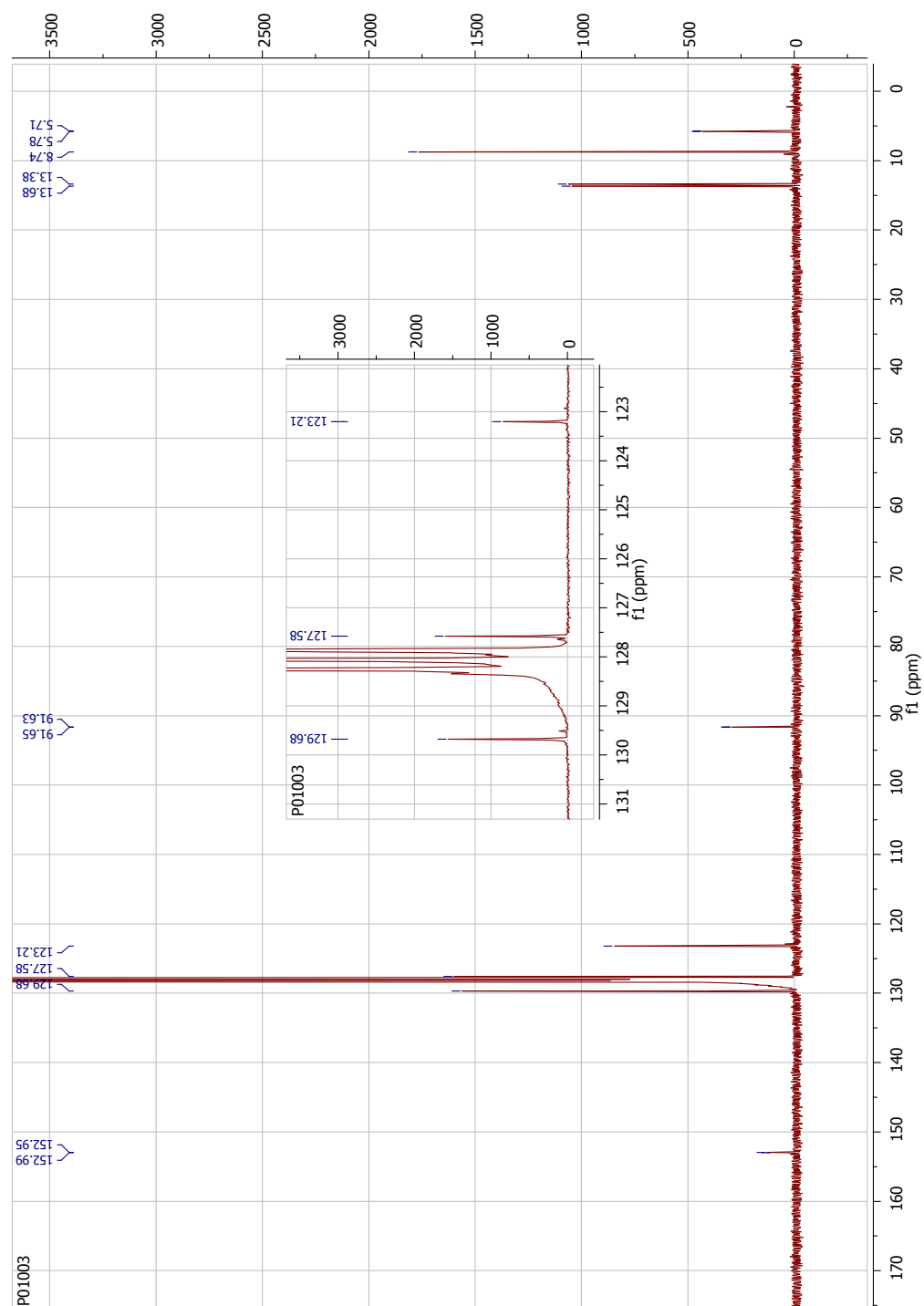


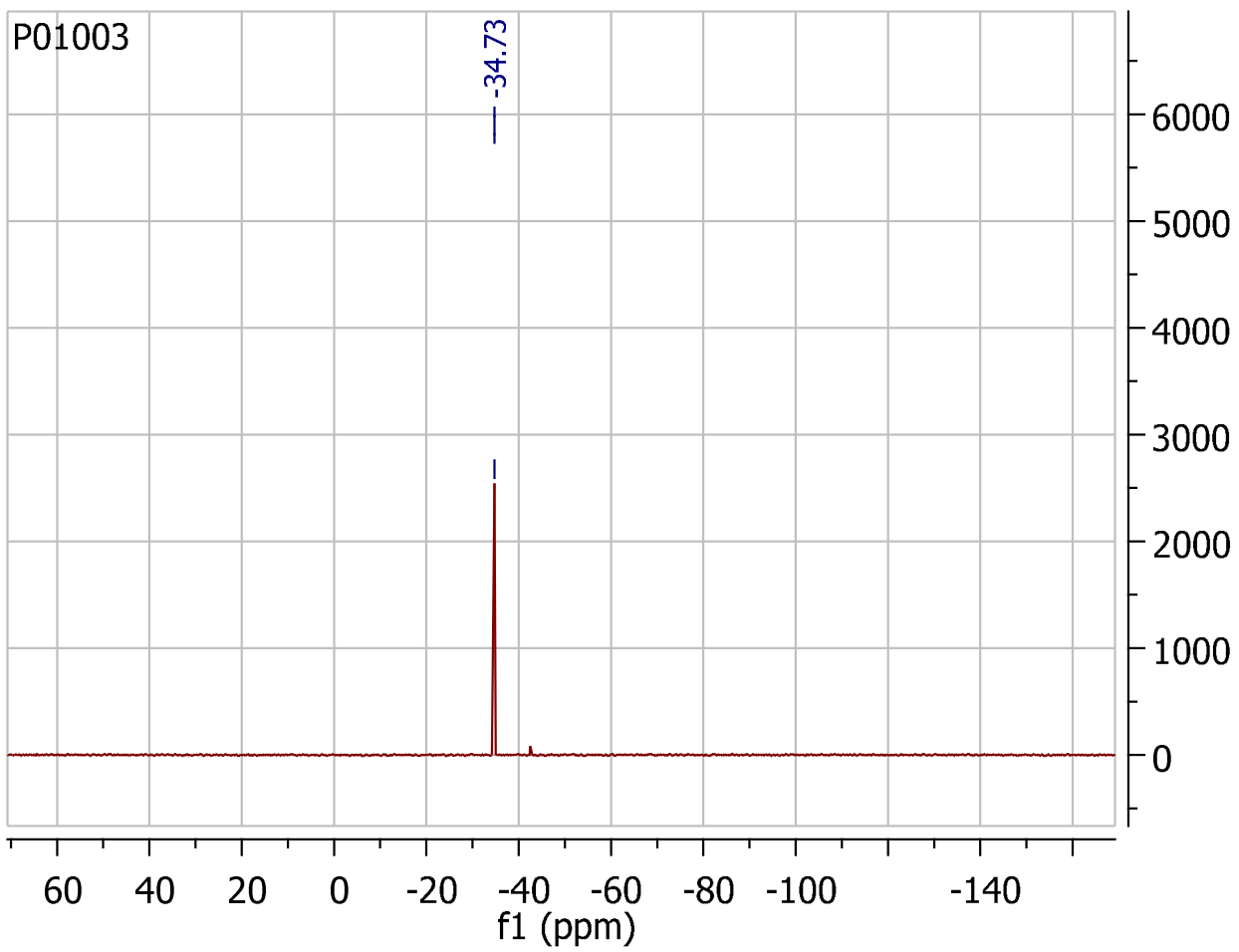




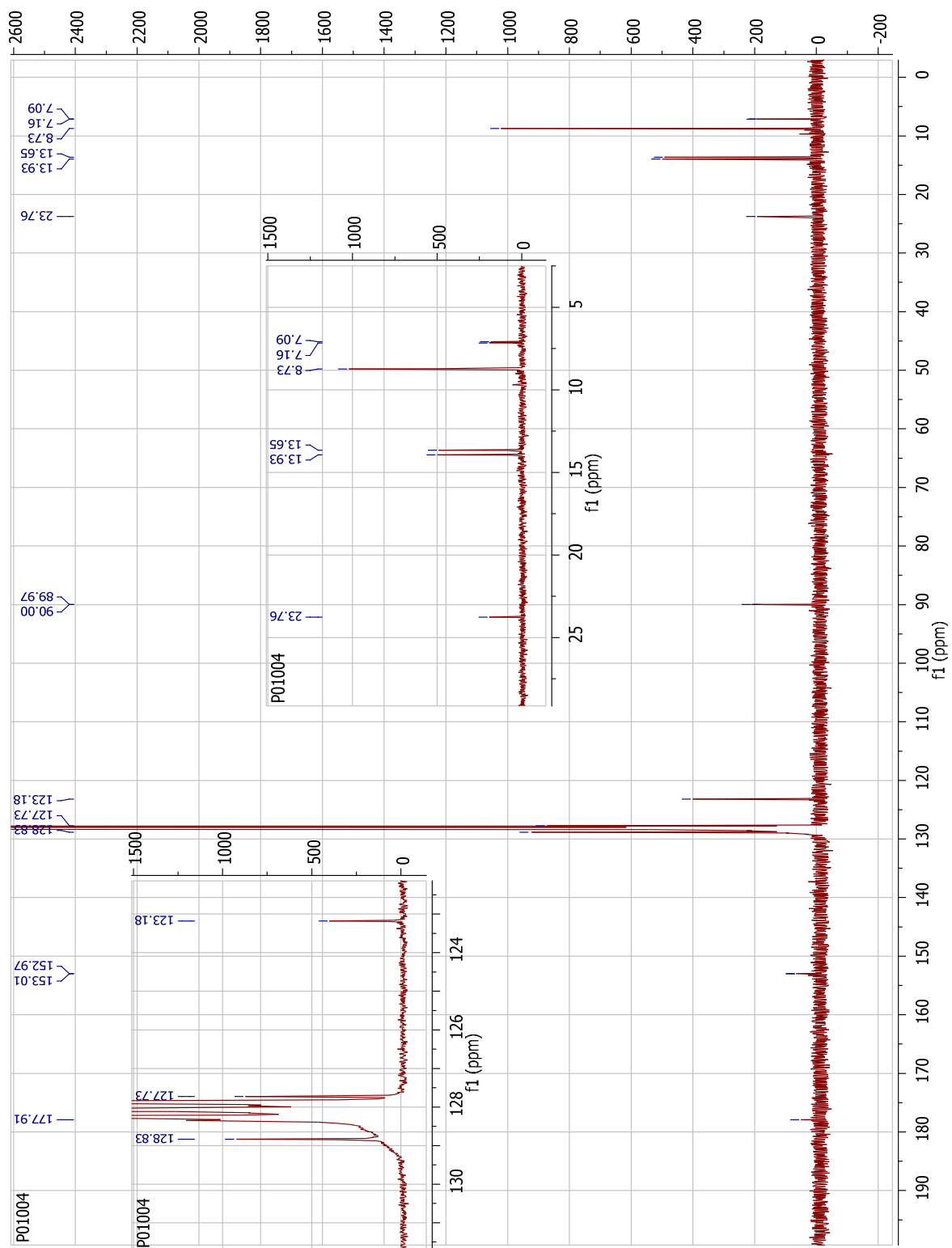


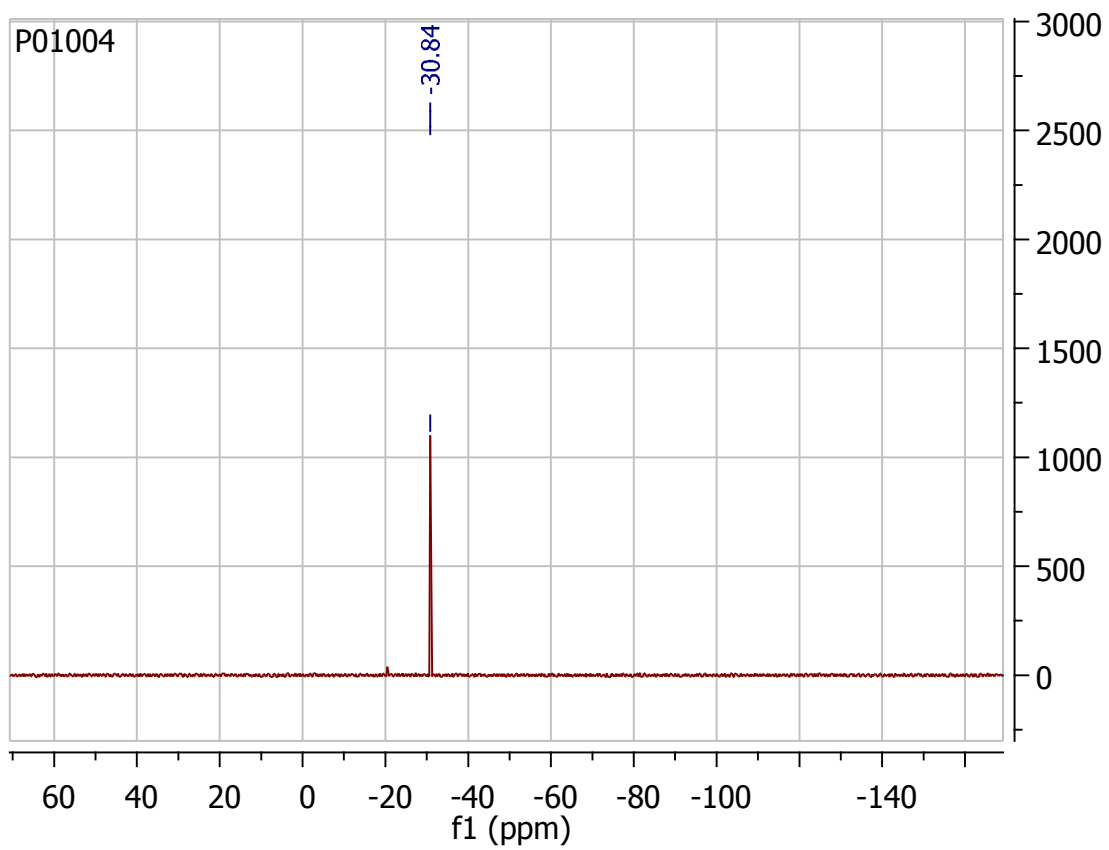


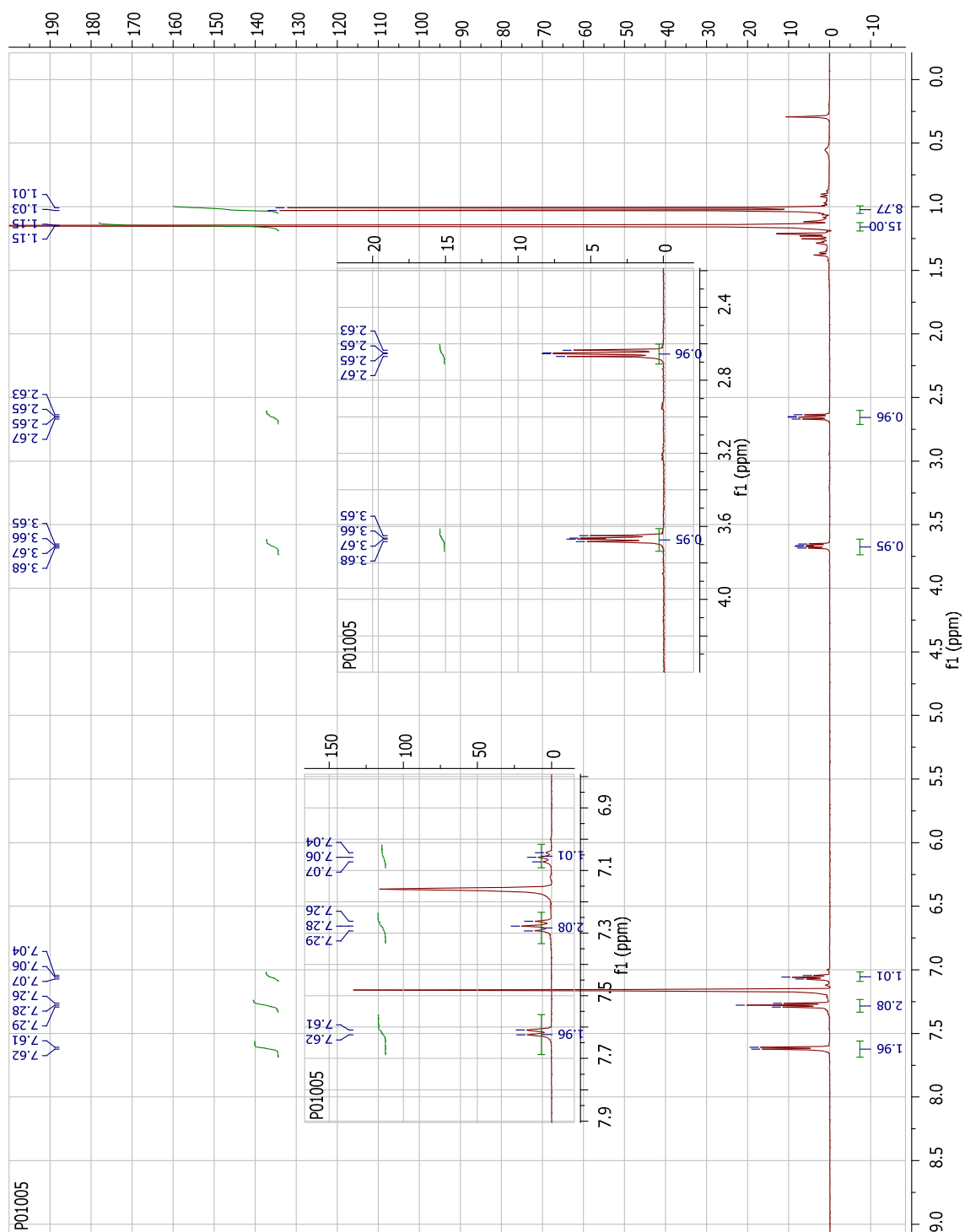
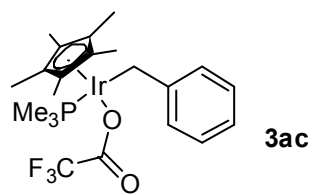


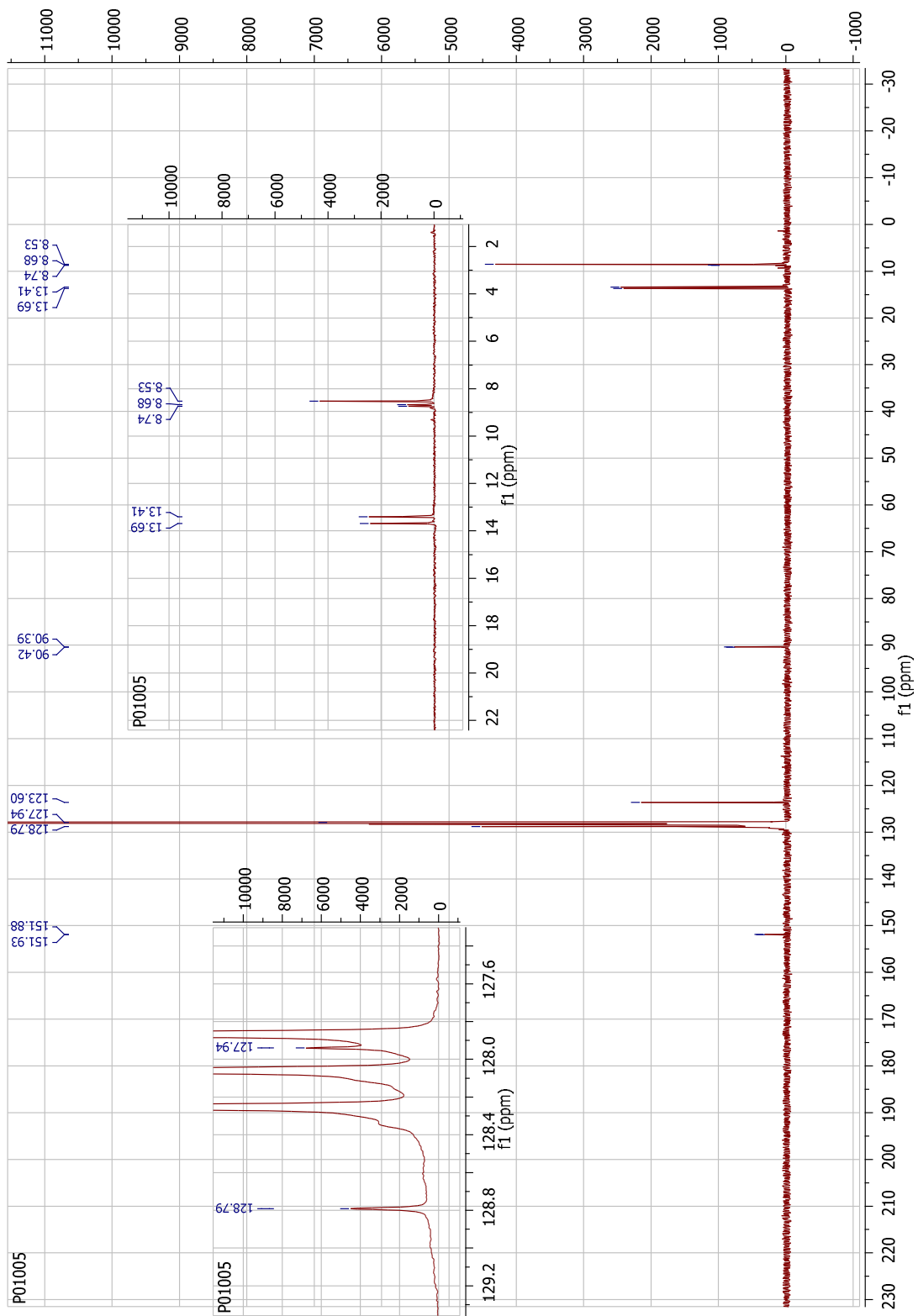




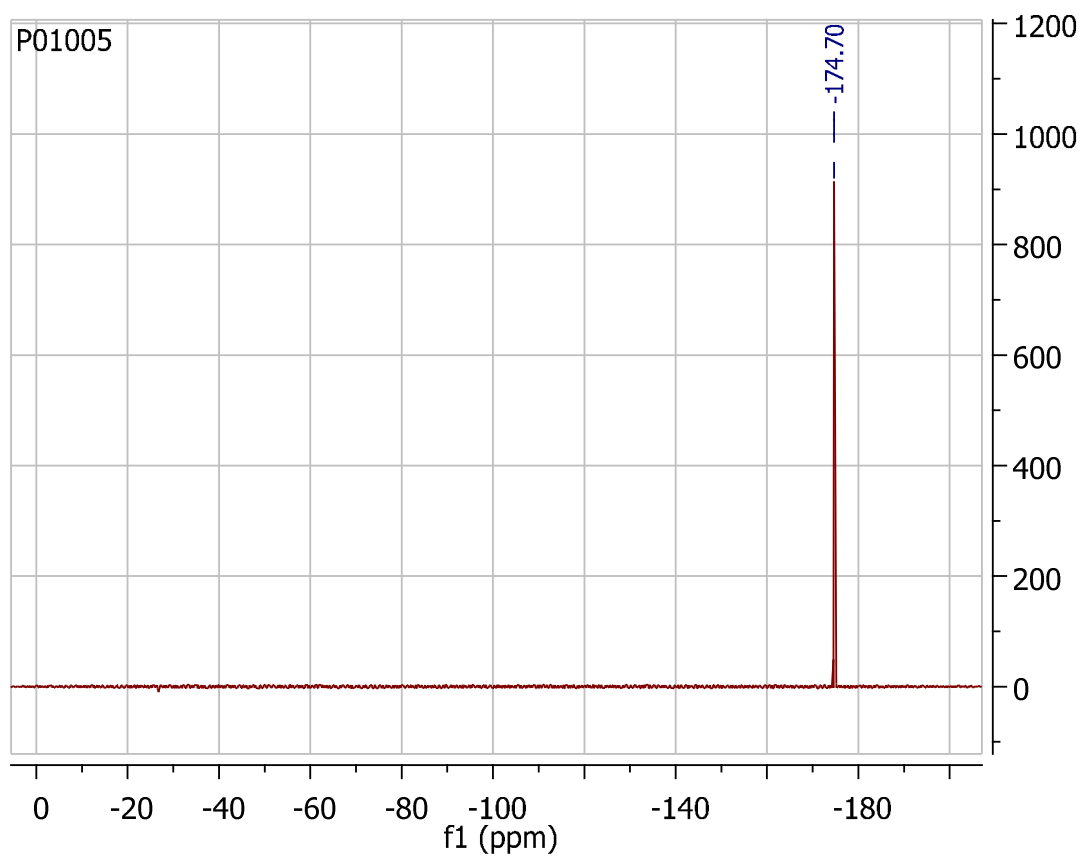
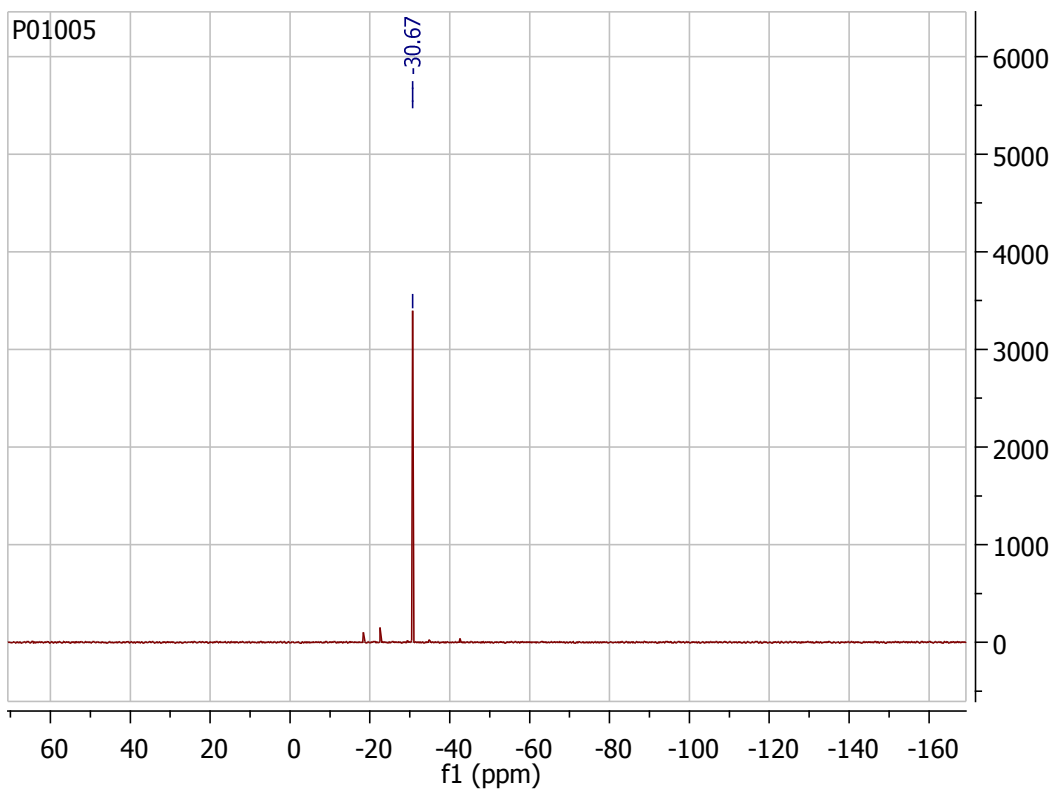


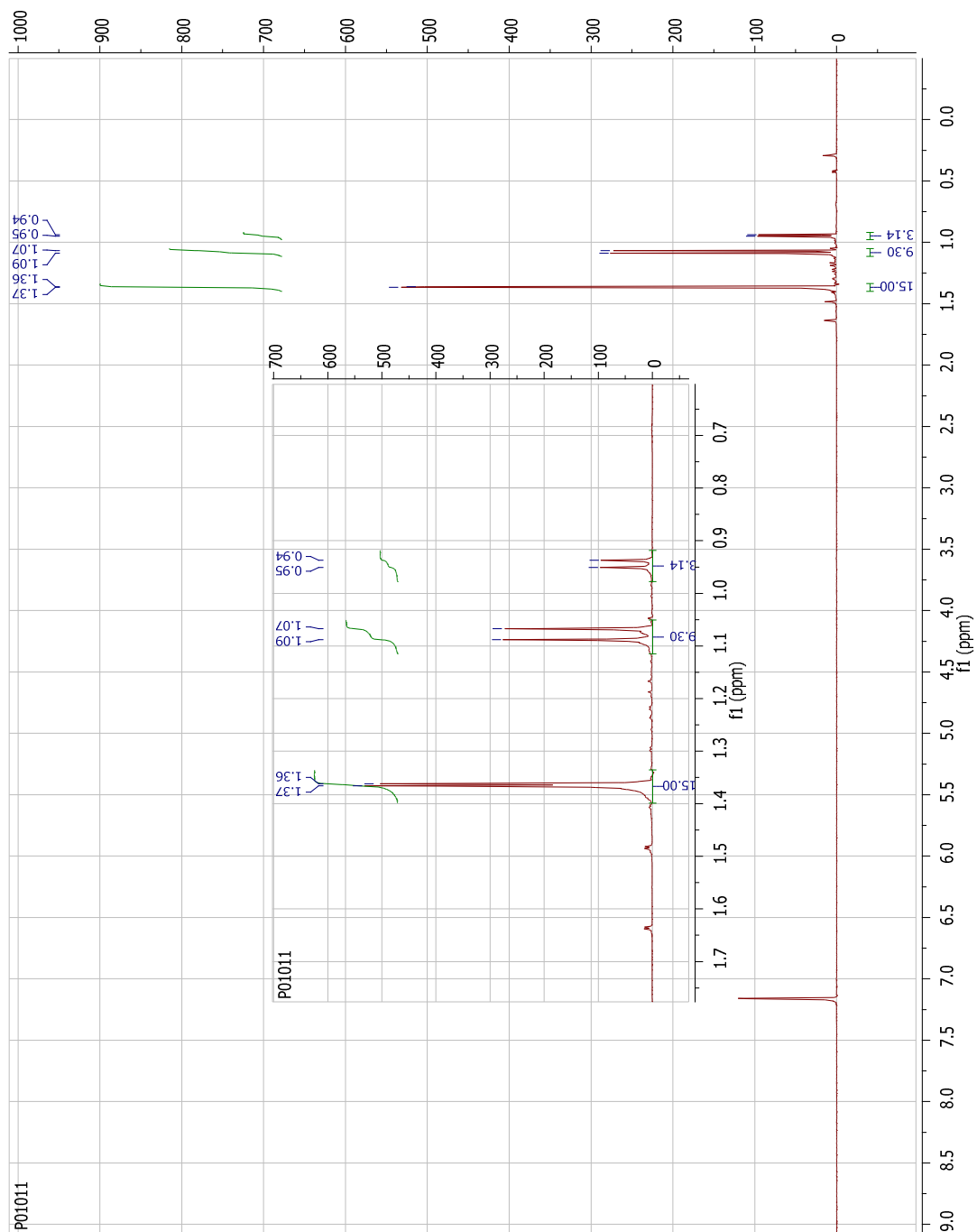
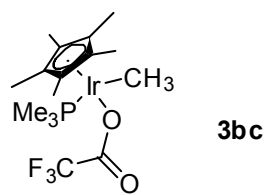


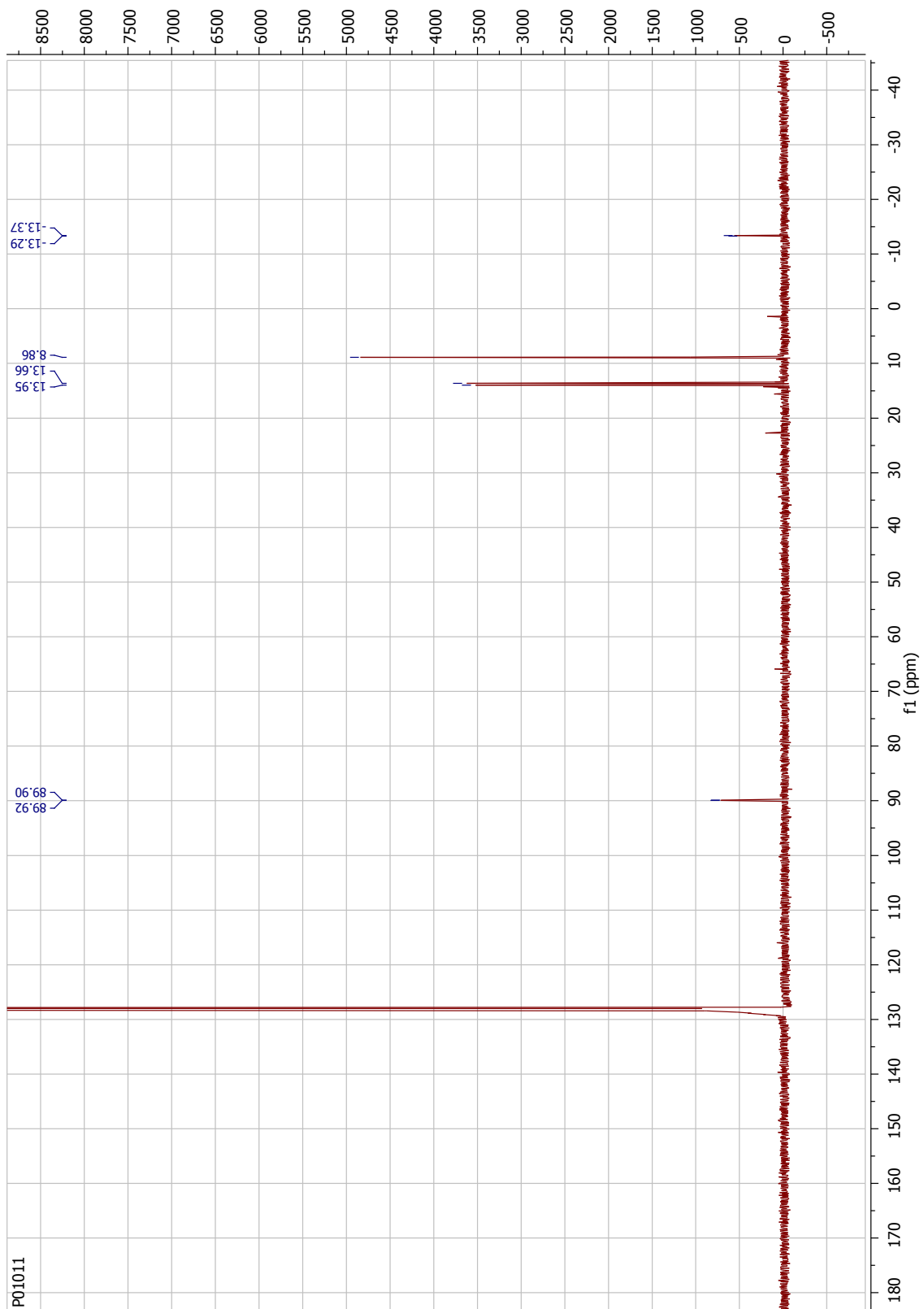


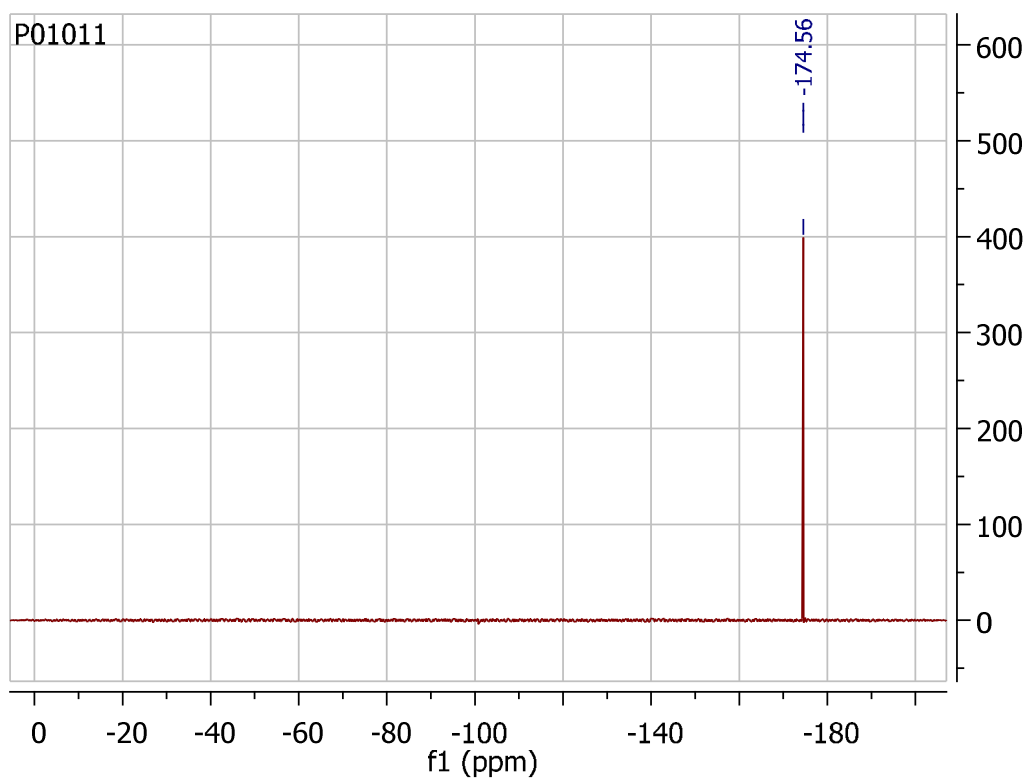
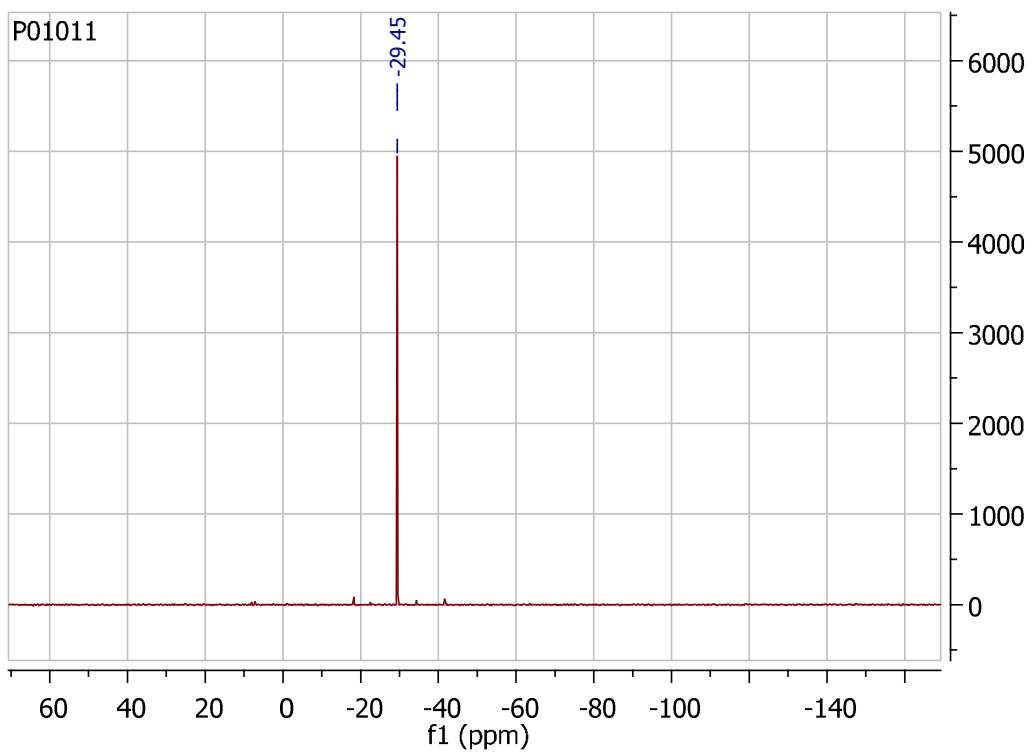


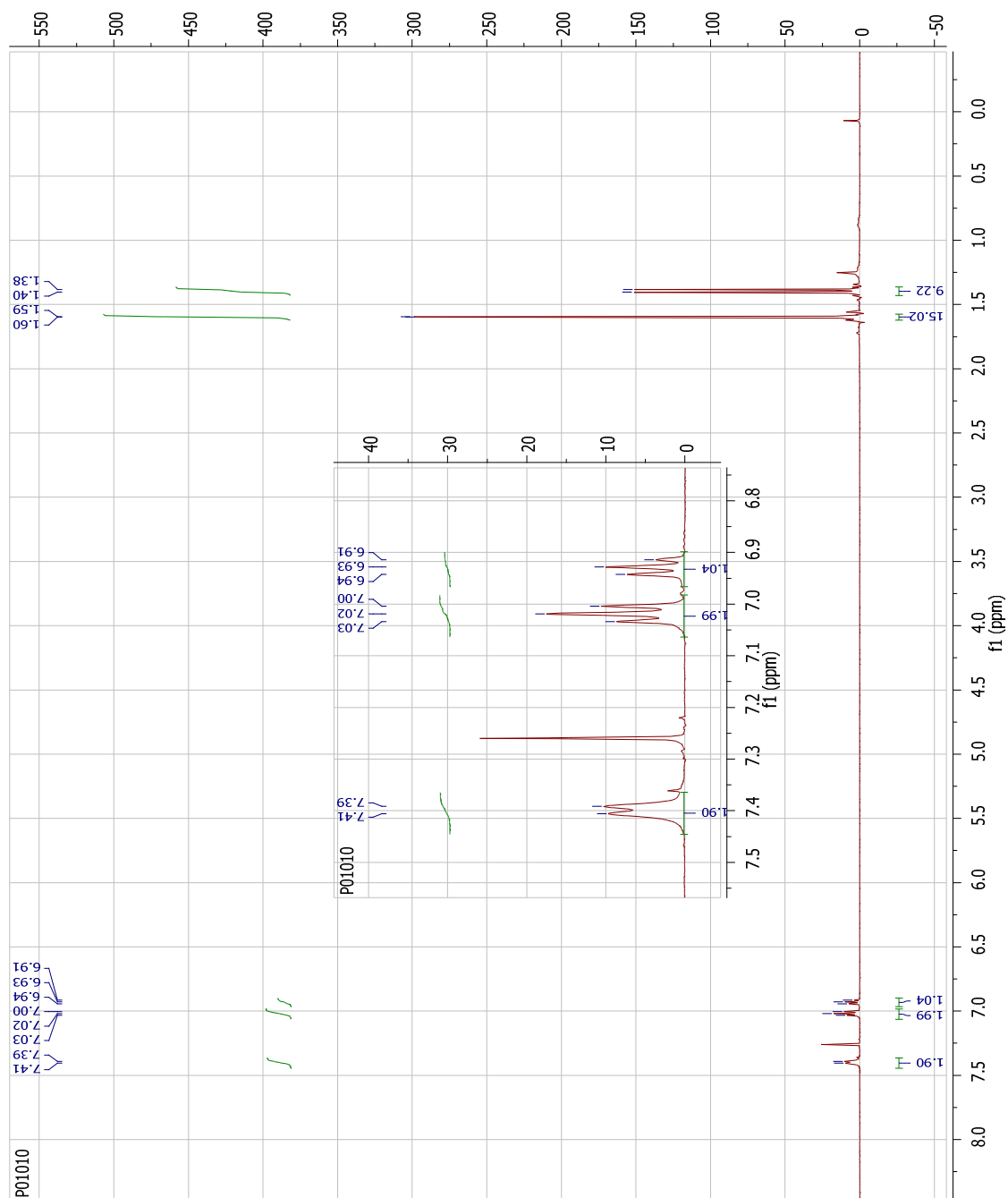
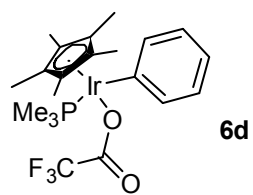


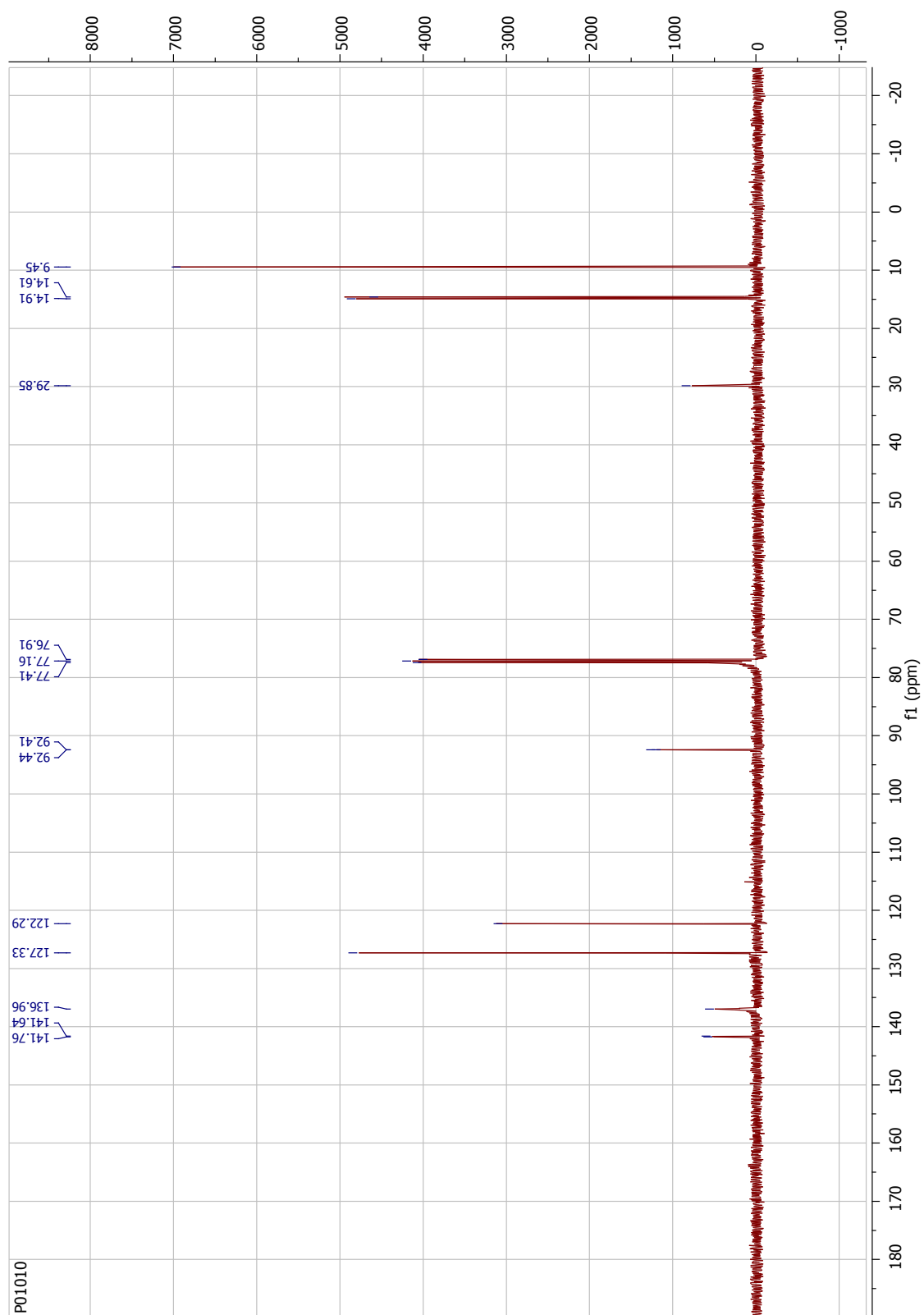


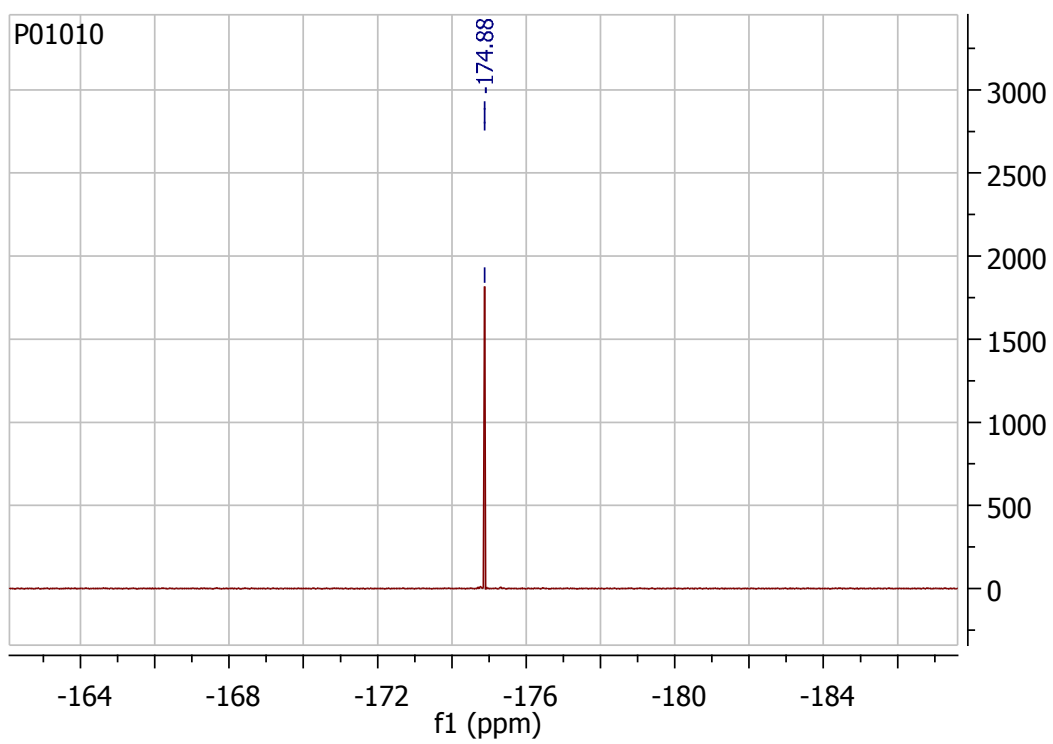
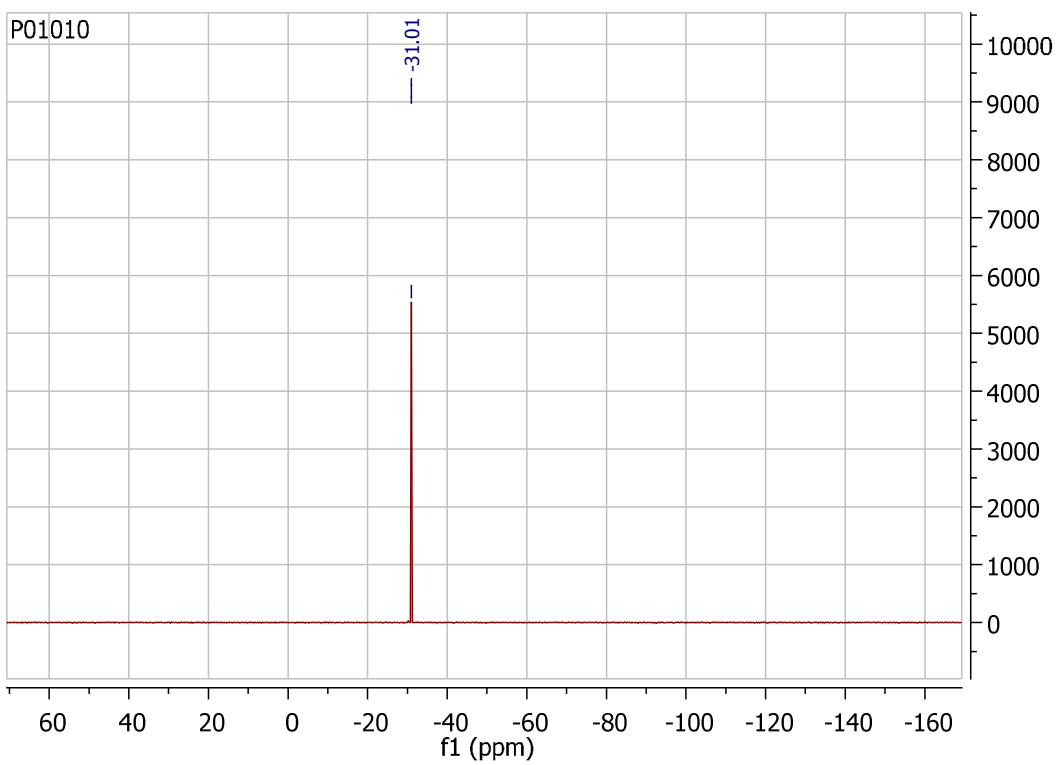


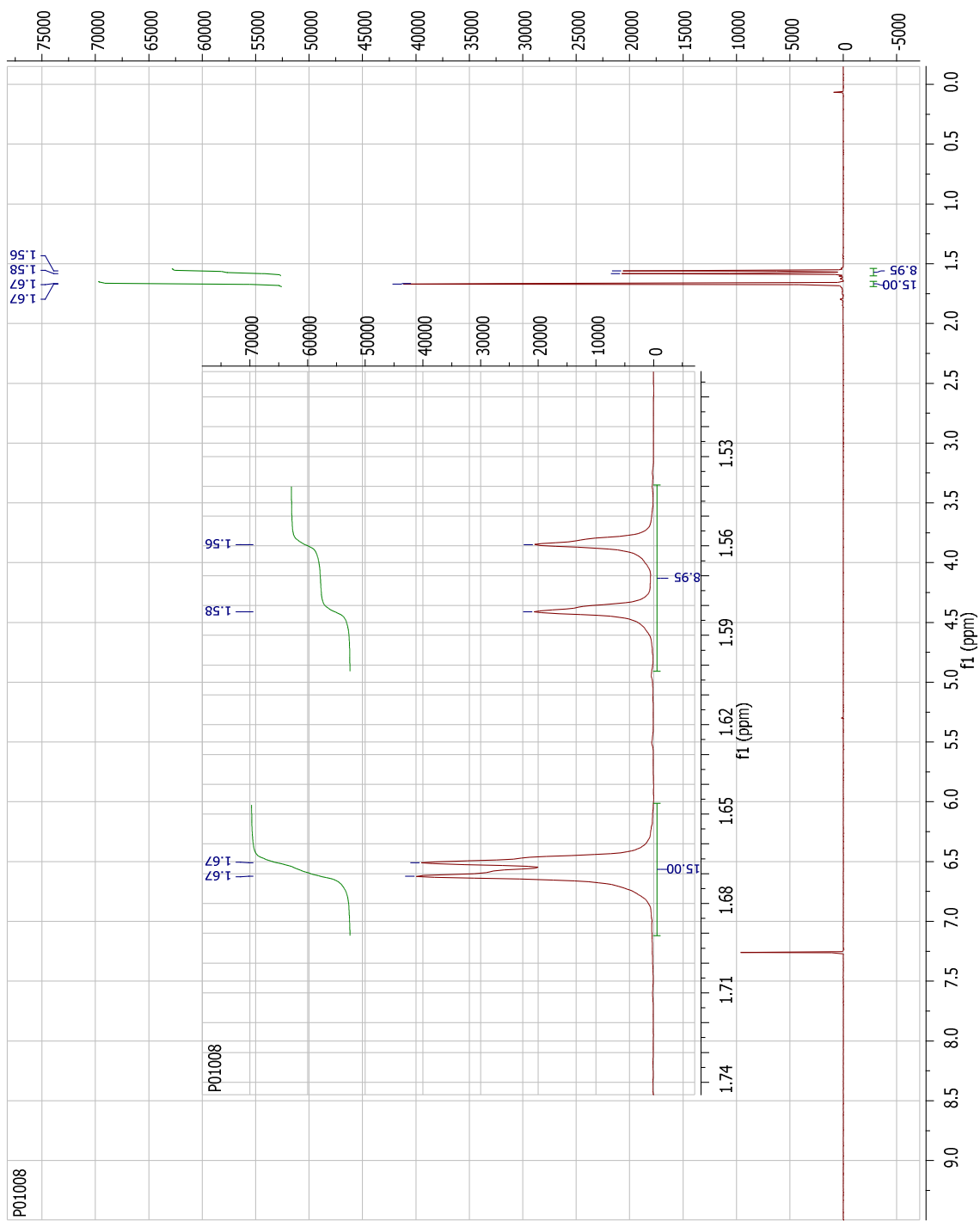
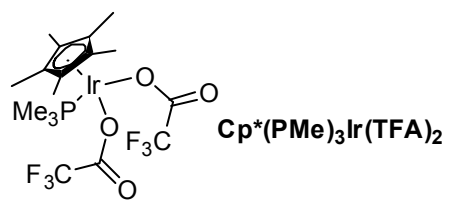




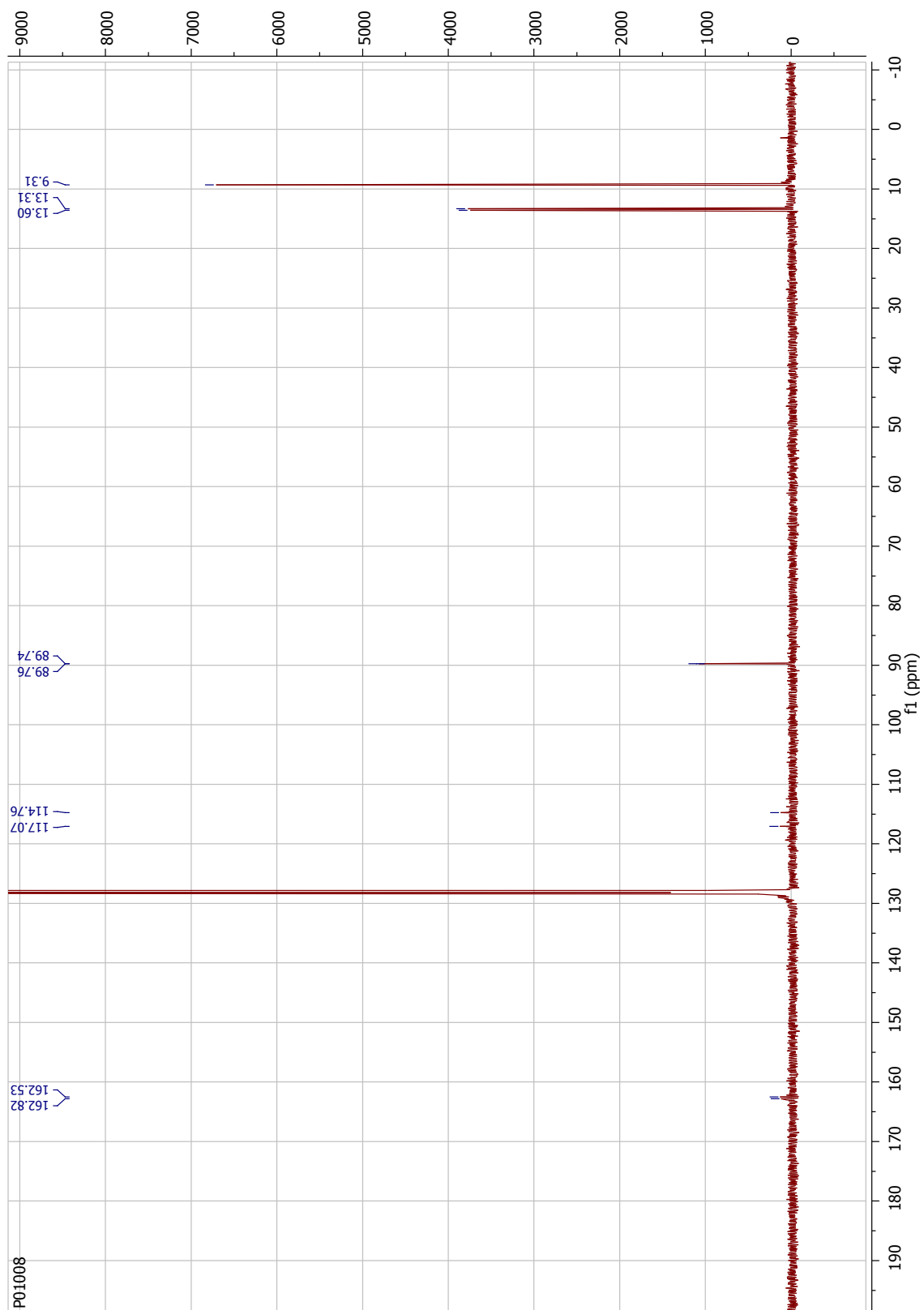


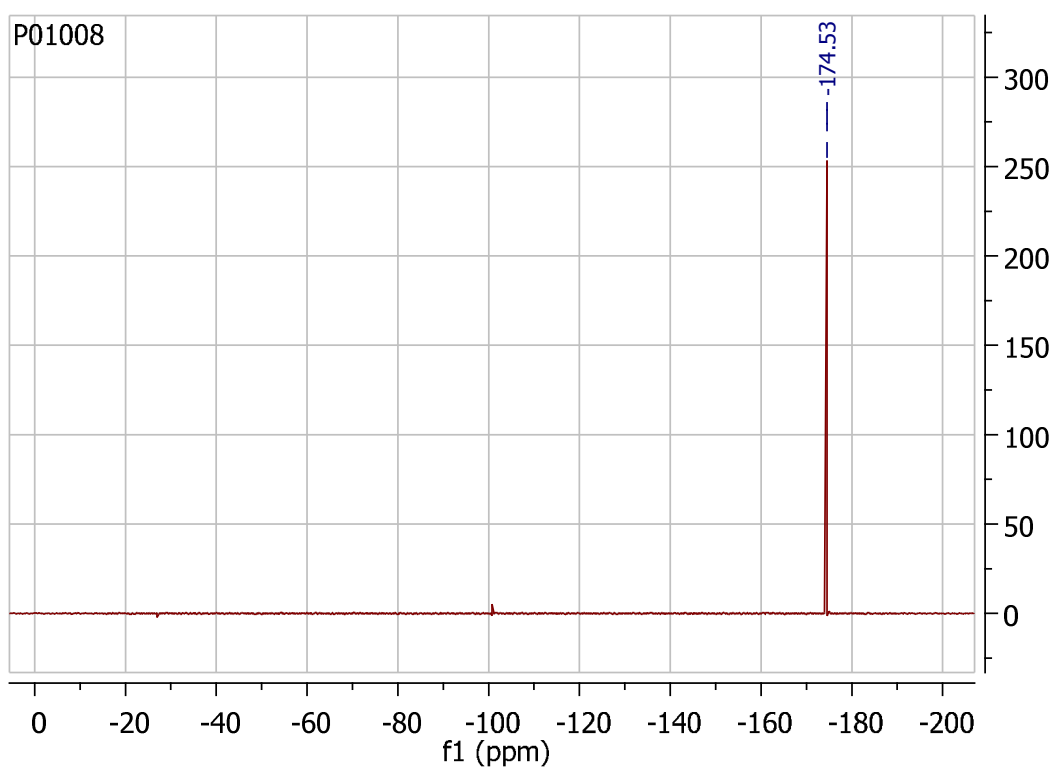
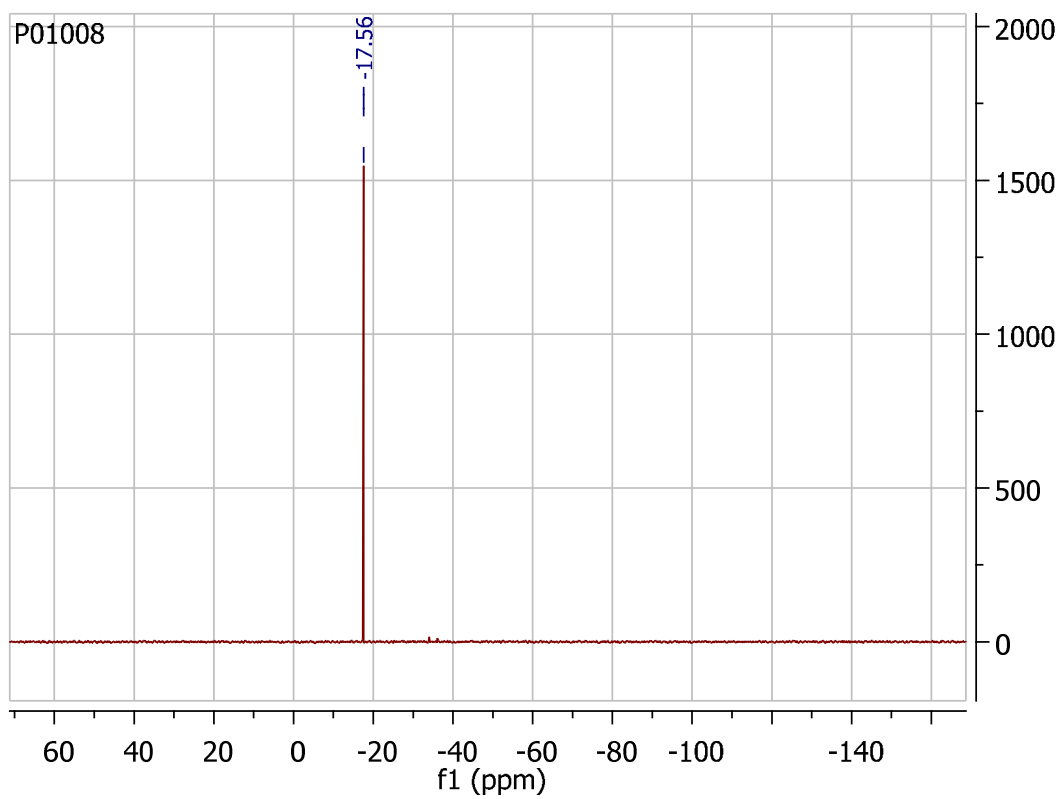


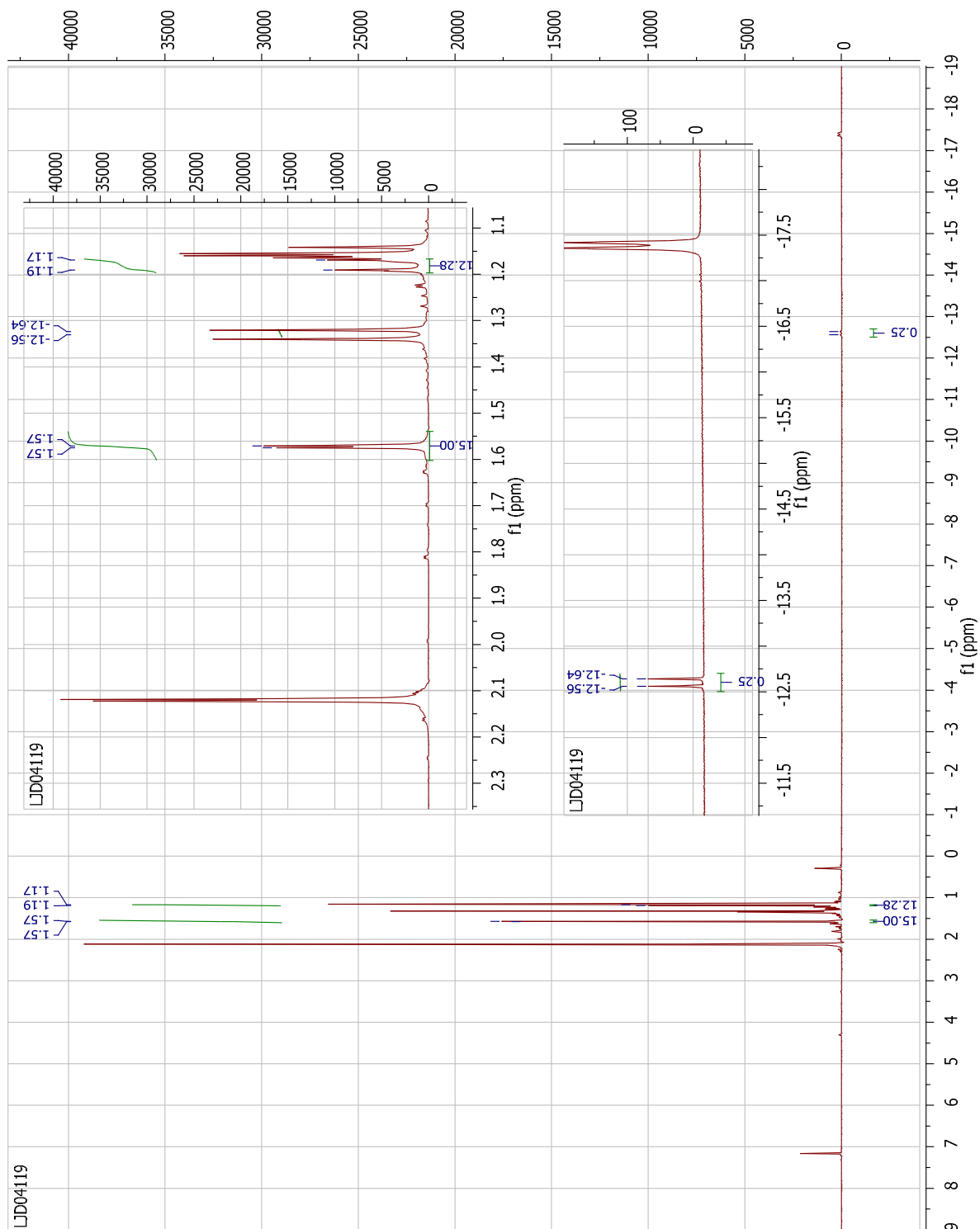


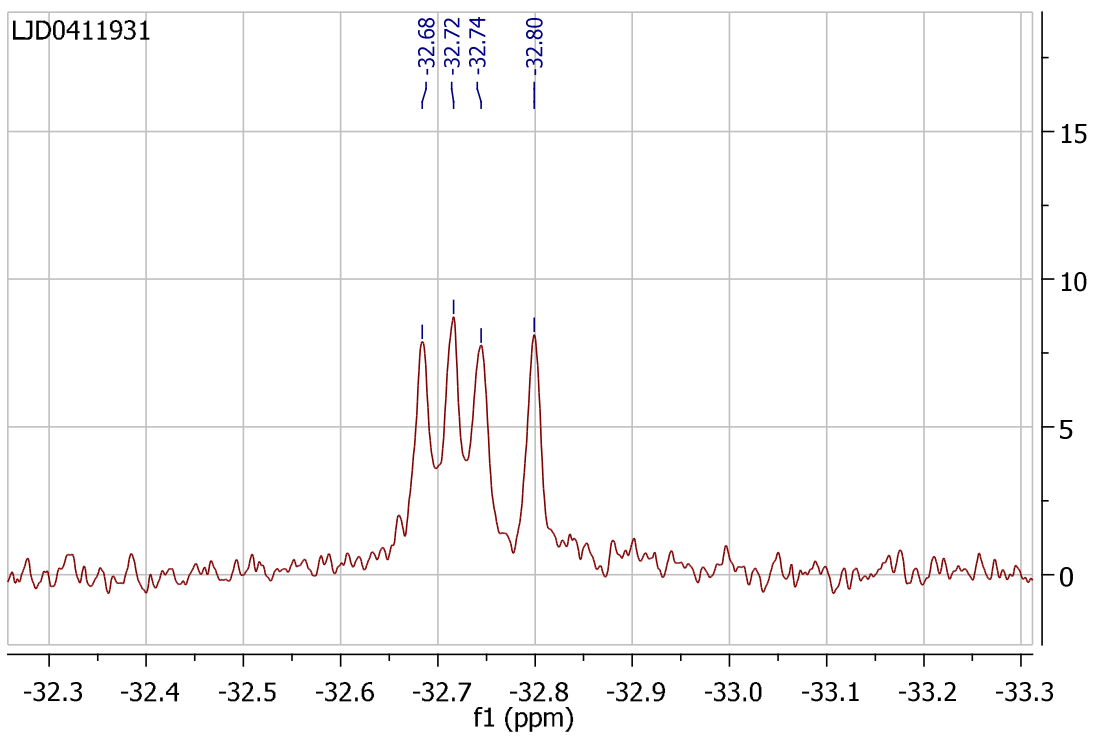
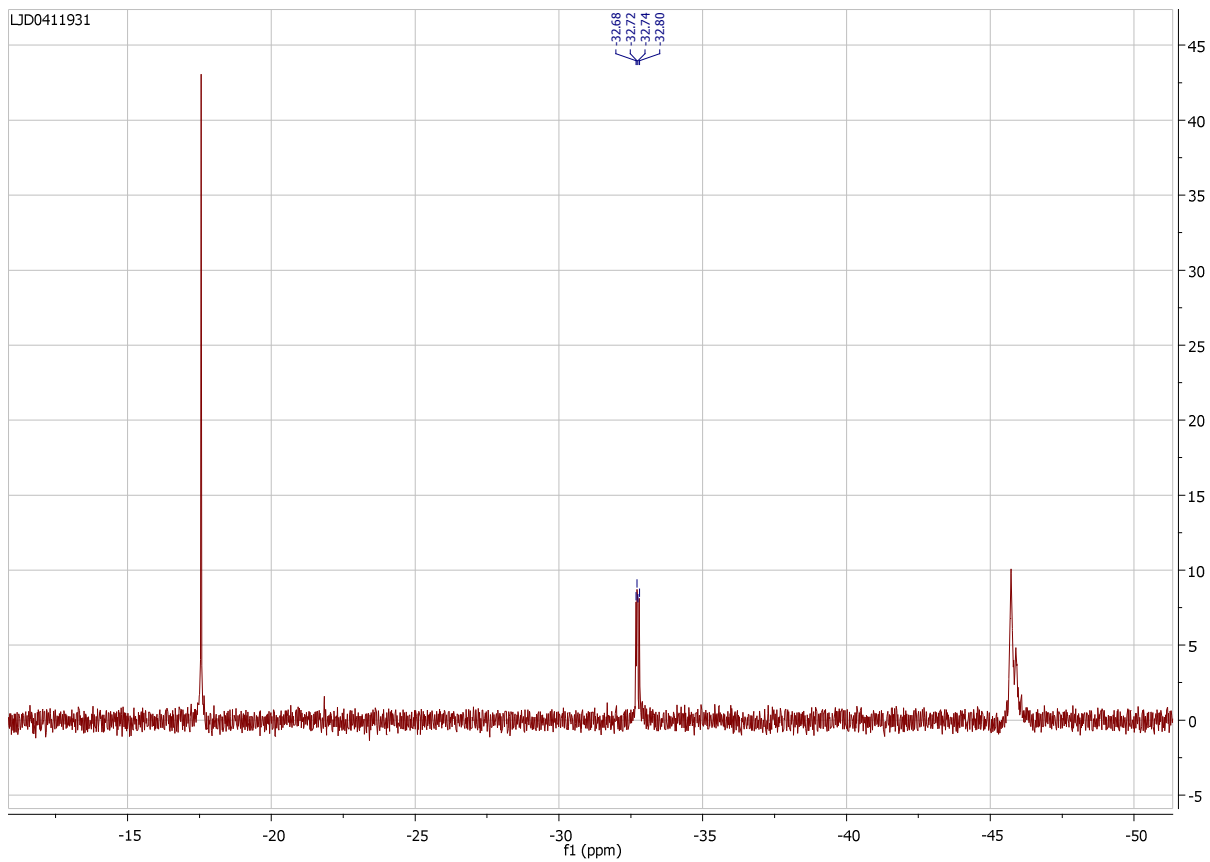


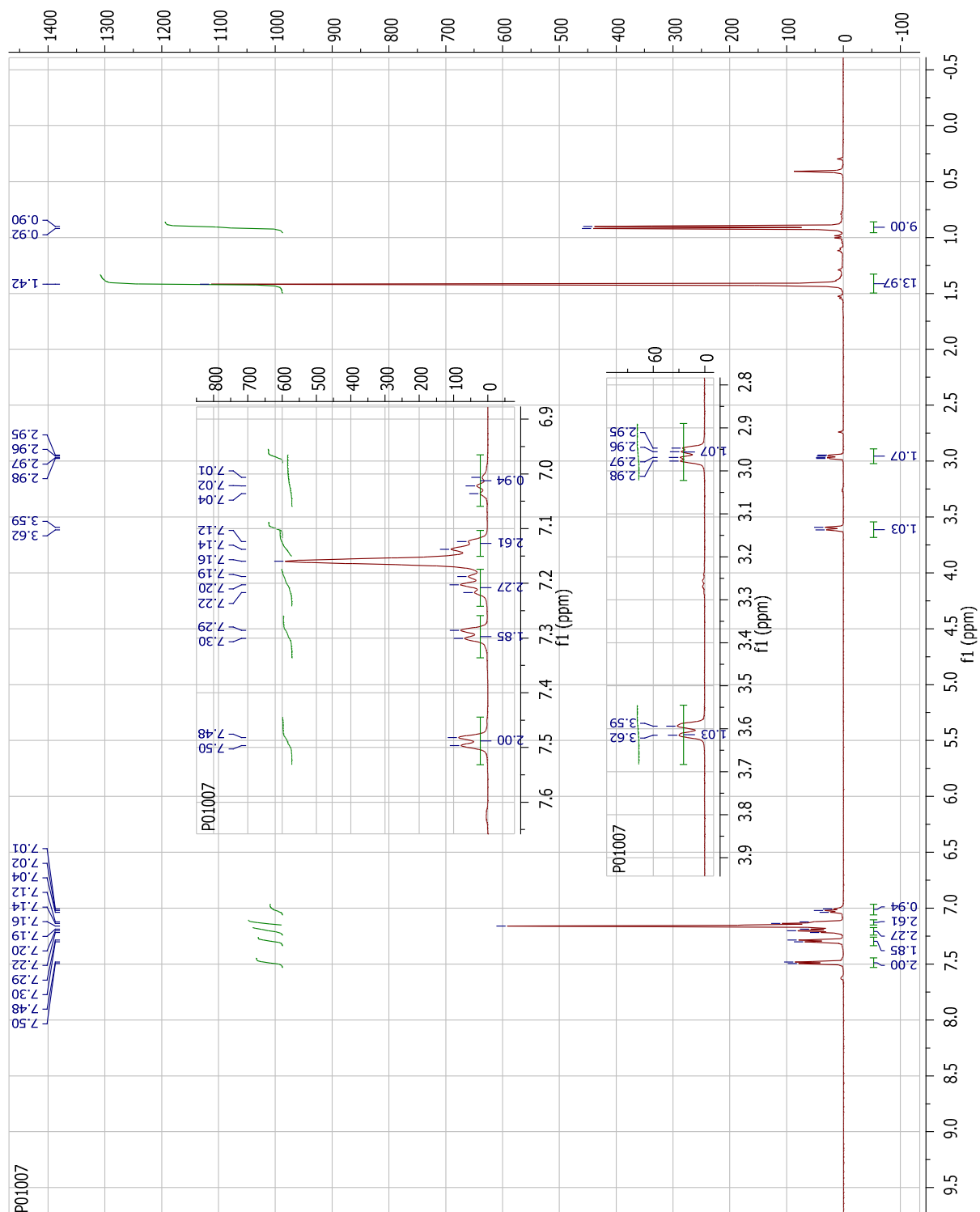


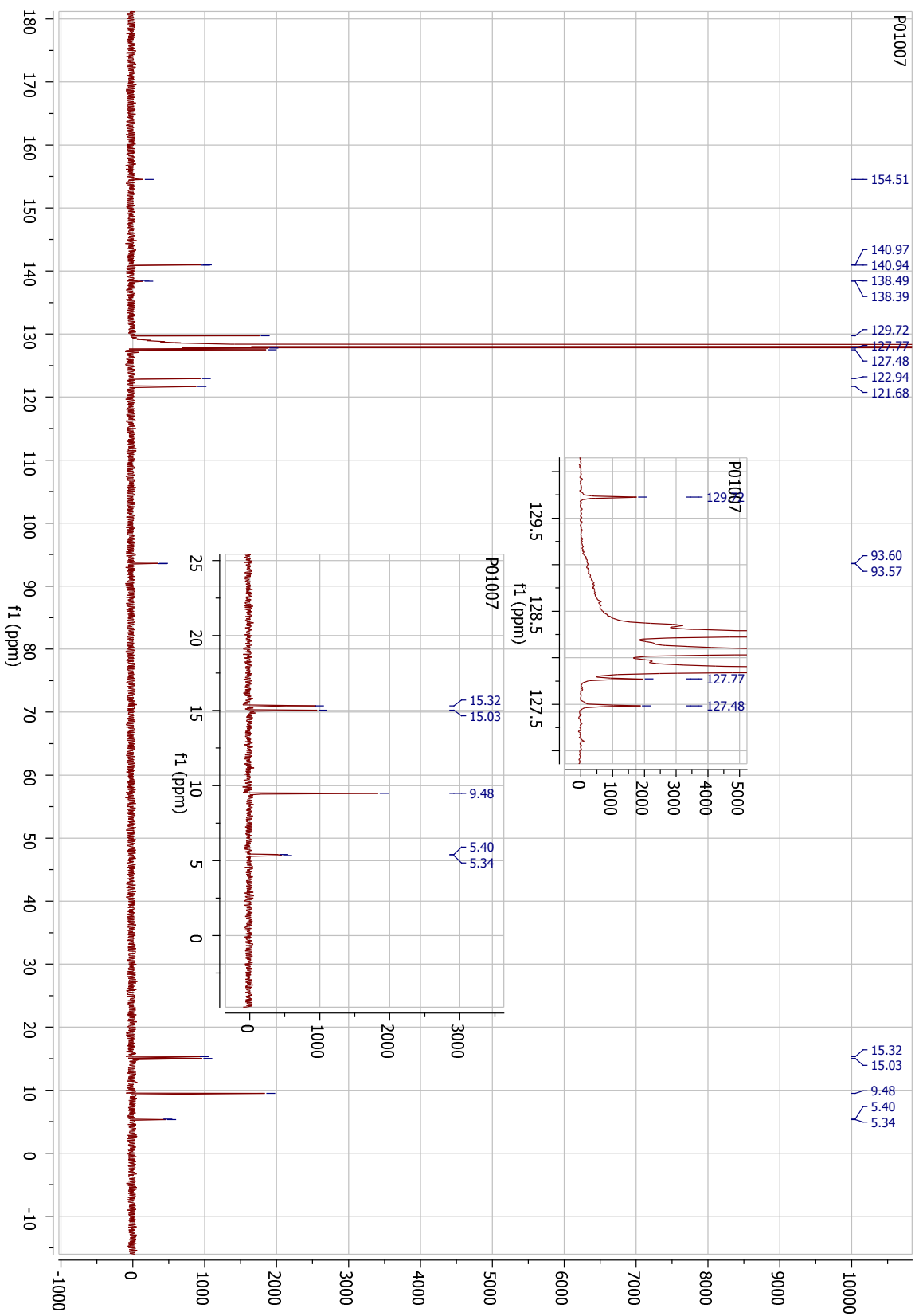


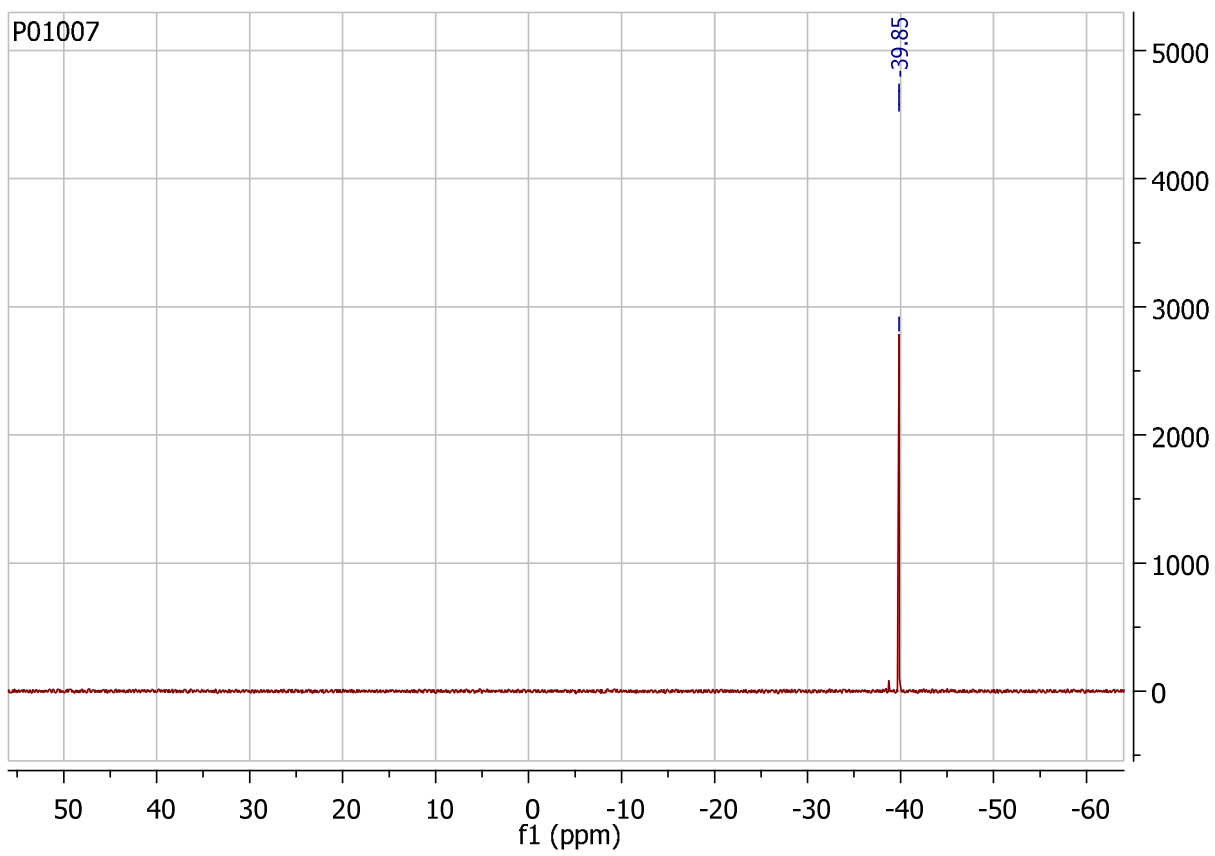


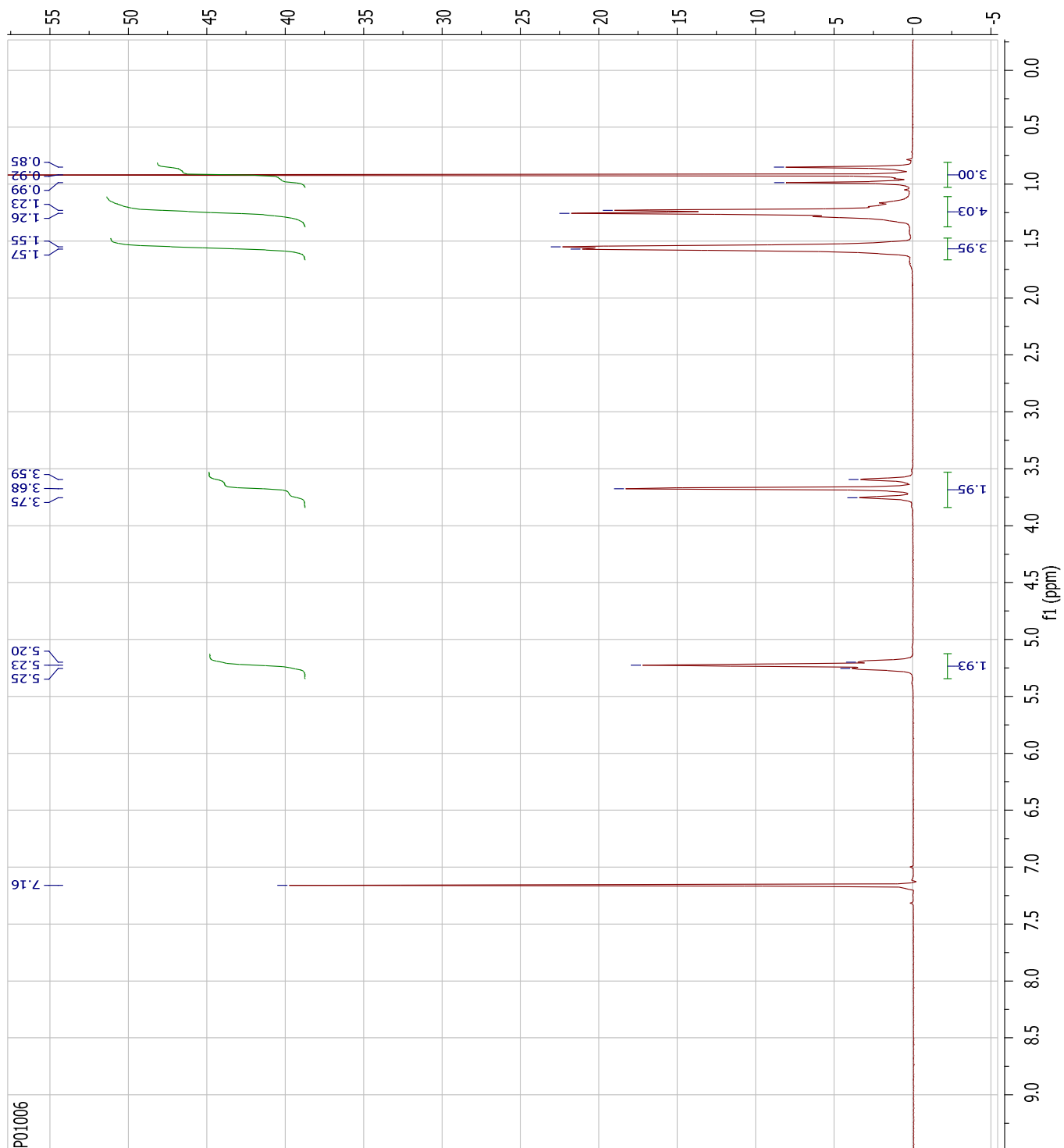
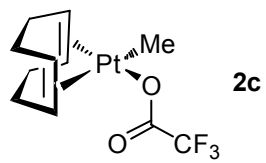




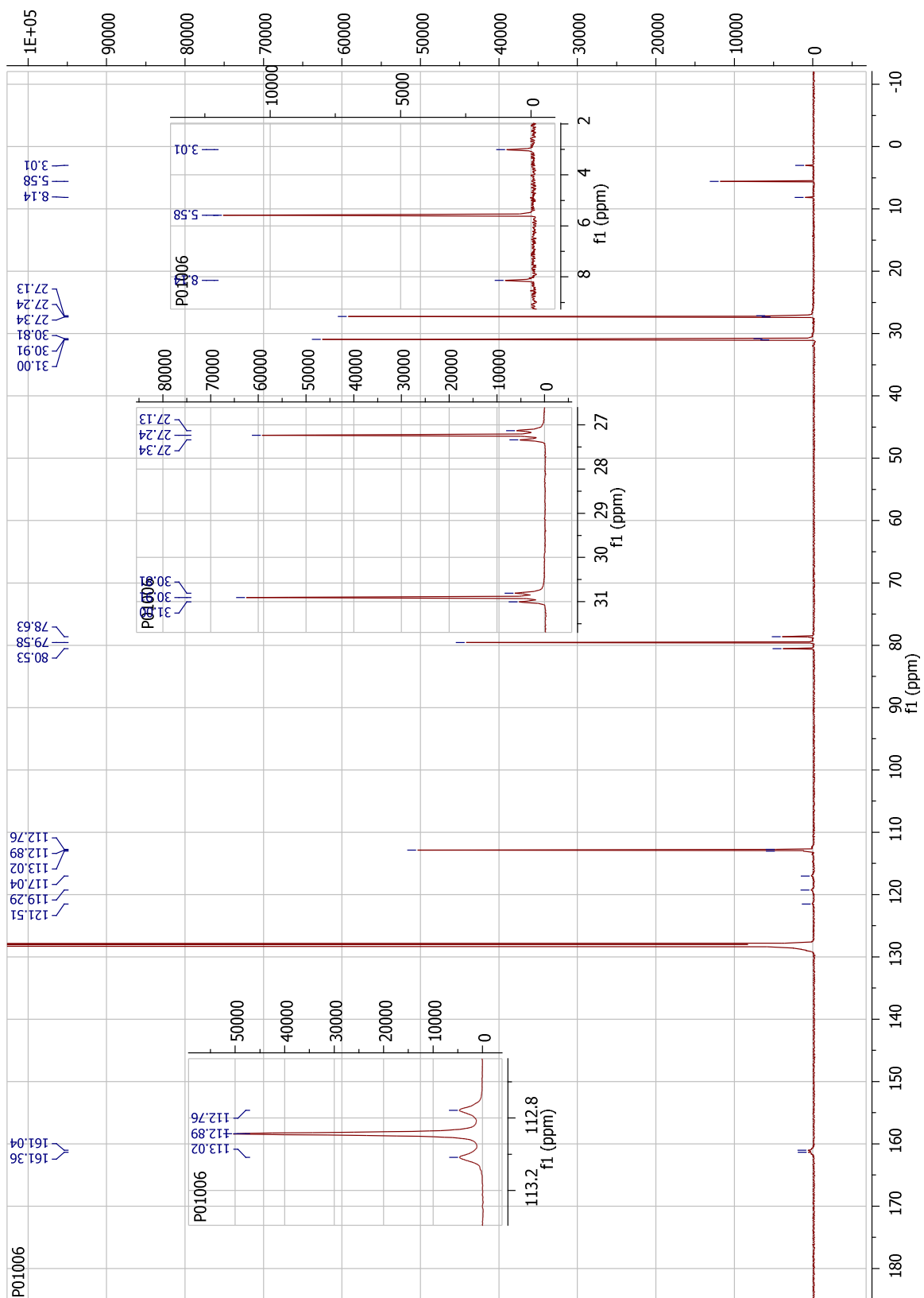


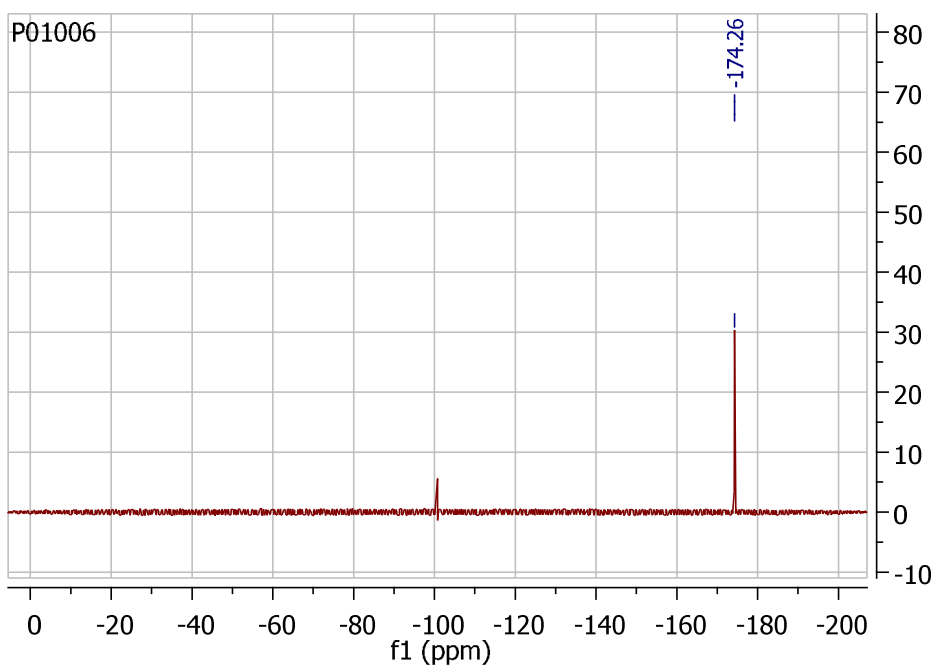


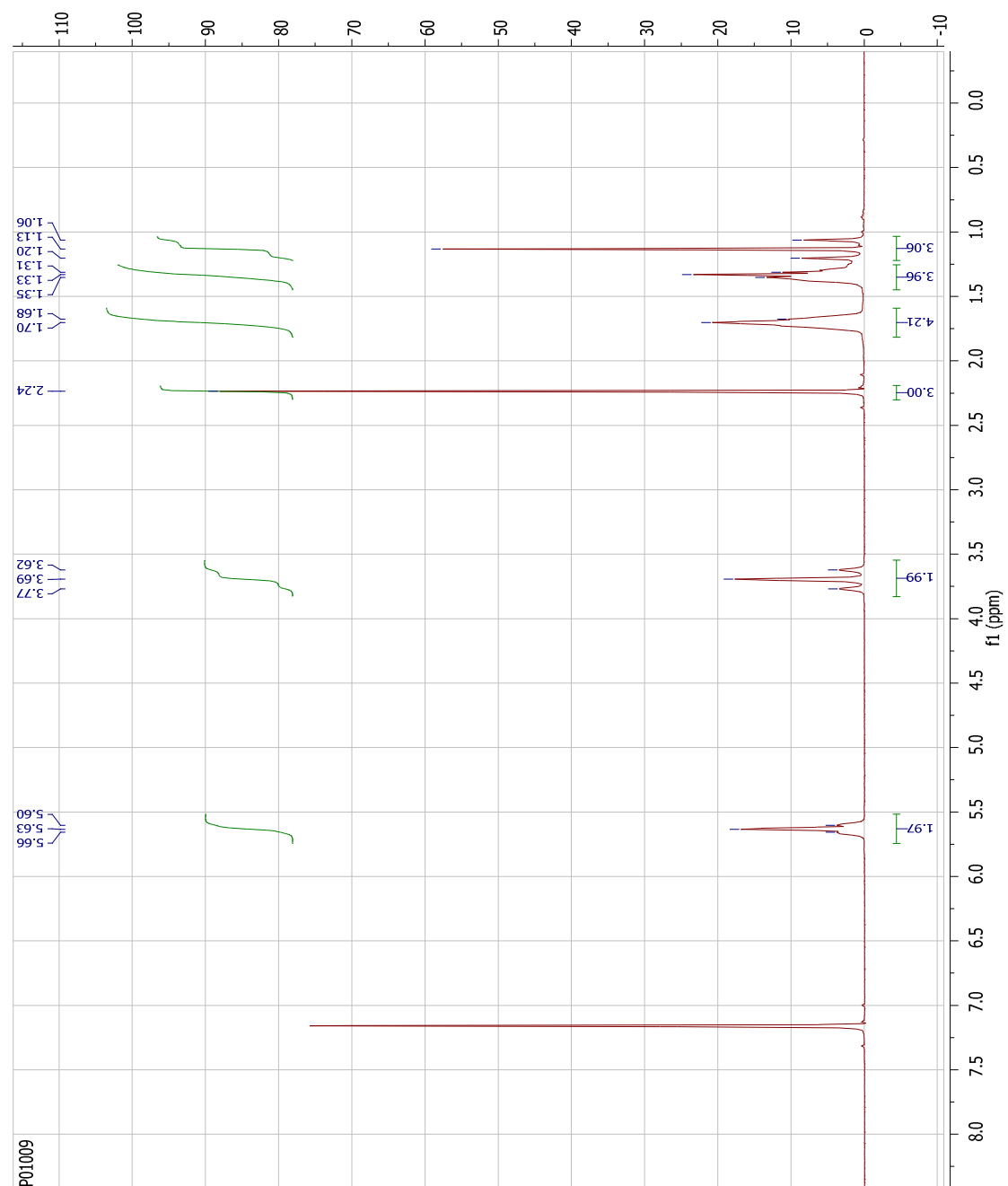
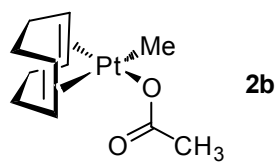


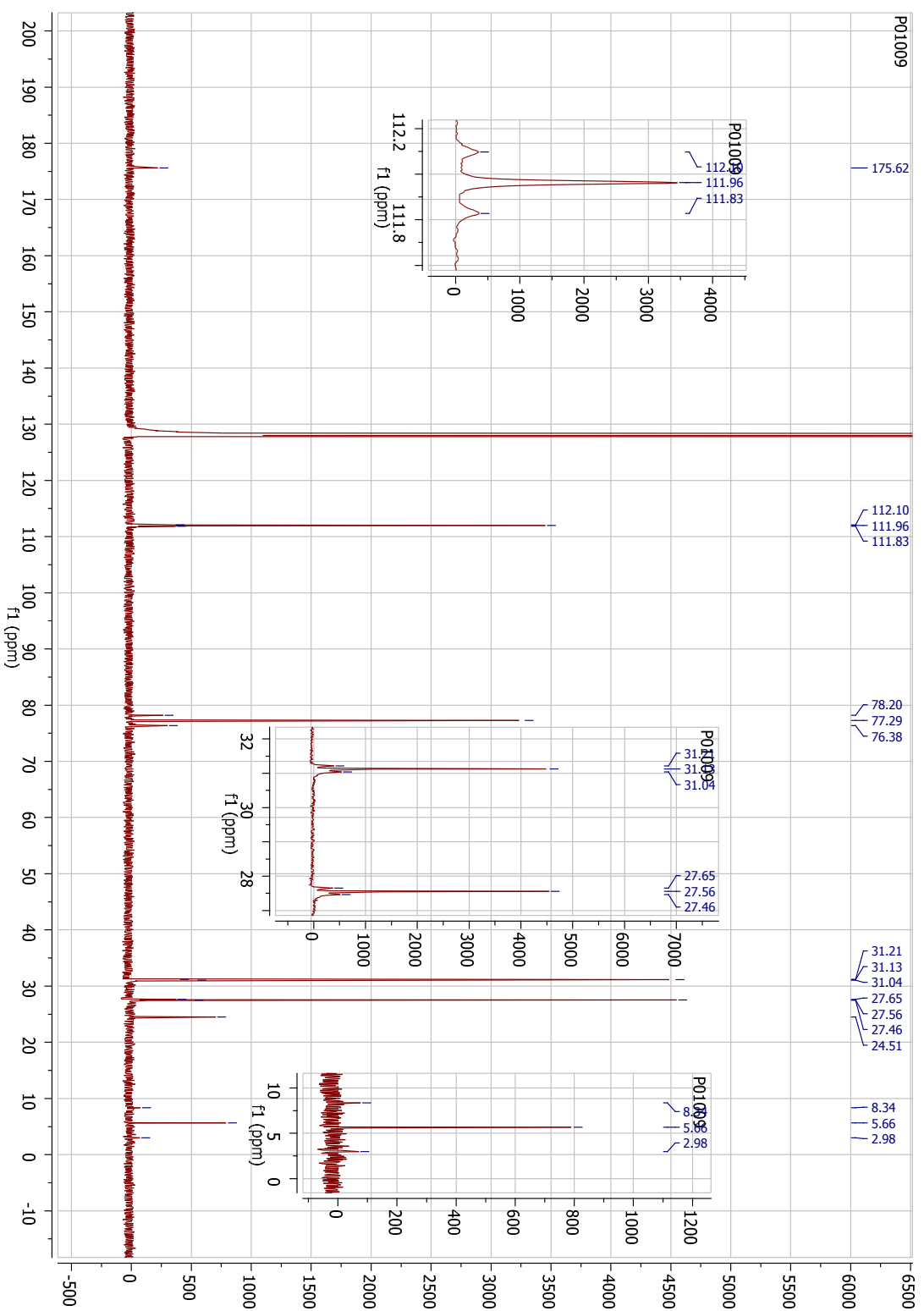












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