

## Supporting Information for

# Palladium-Catalyzed and Alcohol-Enabled Transformation of Nitrile: A Novel Method to Synthesize Benzocyclic Ketones

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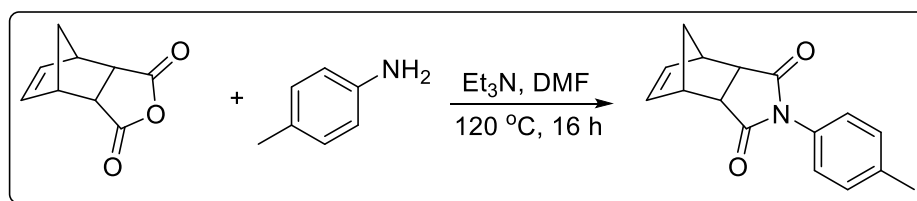
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## 1 General information

**Experimental:** All carbonylation reactions were carried out under an inert atmosphere of nitrogen in standard Schlenk tube. All solvents were dried by standard methods before use. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Bruker Avance 400 (400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) instruments. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard (for  $\text{CDCl}_3$ ,  $^1\text{H}$  NMR: 7.26 ppm,  $^{13}\text{C}$  NMR: 77.16 ppm). Coupling constants ( $J$ ) were reported in Hz. Mass spectra (EI, 70 eV) were recorded on an Agilent 5975 instrument. High resolution mass spectra (HRMS) were recorded on Waters Micromass GCT instrument. All commercially available reagents were used as received.

## 2 Substrates Preparation

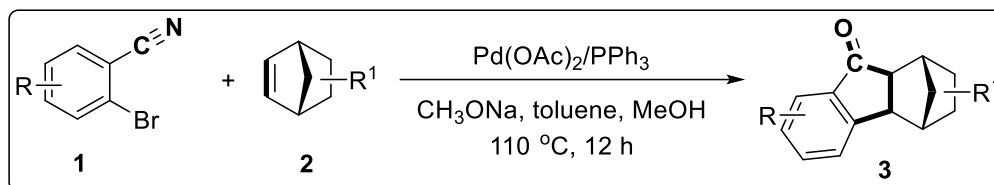
### 2.1 The Synthesis of *Endo*-Norbornenesuccinimides (2a, 2b)<sup>1</sup>:



Triethylamine (6.6 mmol, 0.92 mL) and the desired anhydride (6 mmol) were added to a solution of 4-toluidine (6 mmol) in 5 mL of N, N-dimethylformamide (DMF). The solution was heated for 16 h at 120 °C. After it returned to room temperature, the resulting mixture was treated with water, and extracted with ethyl ether and washed with 1 N HCl (20 mL). The combined organic layer was washed with brine, dried over magnesium sulfate and concentrated *in vacuo*, purified by chromatography on a column of silica gel with PE/EA=3/1 to afford the pure products as white solid (86% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.25 (d,  $J$  = 8.0 Hz, 2H), 7.03 (d,  $J$  = 8.0 Hz, 2H), 6.28 (s, 2H), 3.52 (s, 2H), 3.43-3.44 (m, 2H), 2.38 (s, 3H), 1.80 (d,  $J$  = 8.8 Hz, 2H), 1.62 (d,  $J$  = 8.8 Hz, 2H).

### 3 Palladium-Catalyzed and Alcohol-Enabled Transformation of Nitrile to Synthesize Benzocyclic Ketones

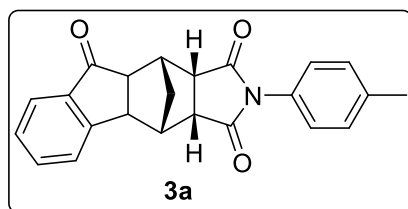
#### 3.1 General Procedures for the Carbonylation



To a flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar, 2-bromobenzonitriles **1** (0.55 mmol, 1.2 equiv.), norbornene derivatives **2** (0.5 mmol, 1.0 equiv.), MeOH (0.05 mL), Pd(OAc)<sub>2</sub> (11.22 mg, 0.05 mmol, 10 mol%), PPh<sub>3</sub> (28.85 mg, 0.11 mmol, 22 mol%), CH<sub>3</sub>ONa (81.04 mg, 1.5 mmol, 3.0 equiv.), and toluene (2.0 mL) were added sequentially under nitrogen. The tube was sealed with a Teflon lined cap, the reaction mixture was stirred at 110 °C for 12 h. After completion of the reaction, the resulting mixture was cooled down to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography to afford the product **3**

#### 3.2 Experimental Characterization of Products

(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-methanoindeno-

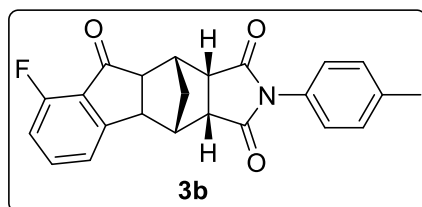


[1,2-*f*]isoindole-1,3,9(2H)-trione(**3a**): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent

of petroleum ether/EtOAc (10/1→2/1) to give white solid, 167.0 mg, 93 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.38-3.46 (m, 3H), 3.21 (d, *J* = 4.8 Hz, 1H), 3.05 (d, *J* = 4.8 Hz, 1H), 2.71 (dd, *J* = 6.0 Hz, 0.4 Hz, 1H), 2.37 (s, 3H), 1.43 (d, *J* = 11.2 Hz, 1H), 1.24 (d, *J* = 11.2

Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.8, 176.6, 175.9, 155.0, 139.0, 138.9, 135.6, 130.0, 128.9, 128.2, 126.4, 126.3, 123.6, 50.5, 48.0, 47.6, 44.1, 42.8, 42.7, 36.0, 21.2; **HRMS (EI)** calcd. for  $\text{C}_{23}\text{H}_{19}\text{NO}_3$  [ $\text{M}^+$ ]: 357.1365, found: 357.1368.

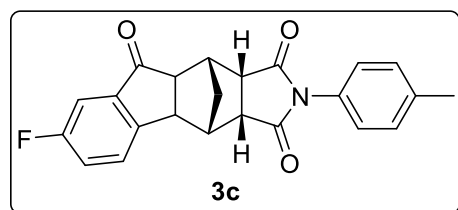
**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-8-fluoro-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3b):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a

gradient eluent of petroleum ether/EtOAc (10/1  $\rightarrow$  2/1) to give white solid, 146.3 mg, 78 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.66 (m, 1H), 7.31 (d,  $J = 7.6$  Hz, 1H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.12 (d,  $J = 8.8$  Hz, 2H), 7.04(t,  $J = 9.2$  Hz, 1H), 3.38-3.47 (m, 3H), 3.25 (d,  $J = 4.8$  Hz, 1H), 3.05 (d,  $J = 4.8$  Hz, 1H), 2.73 (d,  $J = 4.8$  Hz, 1H), 2.38 (s, 3H), 1.48 (d,  $J = 11.2$  Hz, 1H), 1.32 (d,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.0 (d,  $J_{\text{C-F}} = 1.7$  Hz), 176.5, 175.6, 158.6 (d,  $J_{\text{C-F}} = 263.2$  Hz), 157.1, 139.1, 137.6 (d,  $J_{\text{C-F}} = 9.1$  Hz), 130.0, 128.8, 126.7 (d,  $J_{\text{C-F}} = 12.7$  Hz), 126.3, 122.1 (d,  $J_{\text{C-F}} = 3.8$  Hz), 115.2 (d,  $J_{\text{C-F}} = 18.8$  Hz), 50.9, 48.0, 47.4, 44.3, 42.9, 42.8, 36.1, 21.2; **HRMS (EI)** calcd. for  $\text{C}_{23}\text{H}_{18}\text{FNO}_3$  [ $\text{M}^+$ ]: 375.1271, found: 375.1269.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-fluoro-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

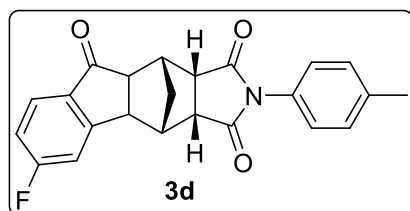


**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3c):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel

with a gradient eluent of petroleum ether/EtOAc (10/1  $\rightarrow$  2/1) to give white solid, 161.3 mg, 86 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.53 (m, 1H), 7.38 (d,  $J = 7.6$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 3.37-3.46 (m, 3H), 3.21 (d,  $J = 4.8$  Hz, 1H), 3.01 (d,  $J = 4.8$  Hz, 1H), 2.75 (d,  $J = 5.6$  Hz, 1H), 1.45 (d,  $J = 11.2$  Hz, 1H), 1.23 (d,  $J = 10.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.7, 176.5, 175.7, 162.7 (d,  $J_{\text{C-F}} = 248.1$  Hz), 150.4, 140.8 (d,  $J_{\text{C-F}} = 8.0$  Hz), 139.1, 130.0, 128.8, 127.7 (d,  $J_{\text{C-F}} = 8.1$  Hz), 126.3, 123.5, 123.2, 109.5 (d,  $J_{\text{C-F}} = 21.9$  Hz), 51.3, 47.9, 47.4, 44.0, 42.8, 42.4, 36.0, 21.2; **HRMS (EI)** calcd. for  $\text{C}_{23}\text{H}_{18}\text{FNO}_3$  [ $\text{M}^+$ ]: 375.1271, found:

375.1268.

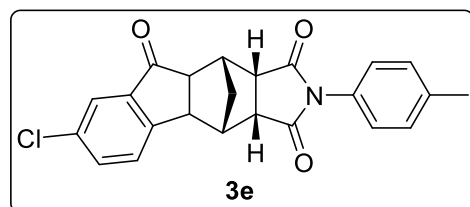
**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-6-fluoro-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3d):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a

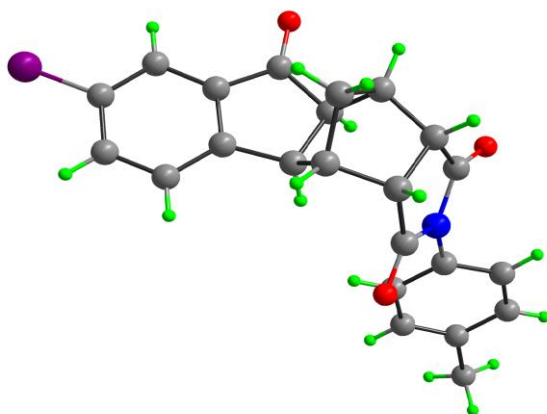
gradient eluent of petroleum ether/EtOAc (10/1 → 2/1) to give white solid, 153.8 mg, 82 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 8.8 Hz, 5.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.09-7.14 (m, 3H), 3.37-3.47 (m, 3H), 3.21 (d, *J* = 5.2 Hz, 1H), 3.03 (d, *J* = 5.2 Hz, 1H), 2.73 (d, *J* = 5.2 Hz, 1H), 2.38 (s, 3H), 1.46 (d, *J* = 11.2 Hz, 1H), 1.25 (d, *J* = 11.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.8, 176.4, 175.7, 167.6 (d, *J*<sub>C-F</sub> = 313.4 Hz), 139.1, 135.3, 130.0, 128.8, 126.3, 126.0 (d, *J*<sub>C-F</sub> = 9.9 Hz), 116.6 (d, *J*<sub>C-F</sub> = 24.3 Hz), 113.0 (d, *J*<sub>C-F</sub> = 21.9 Hz), 50.8, 48.0, 47.5, 44.0, 42.7, 36.0, 21.2; HRMS (EI) calcd. for C<sub>23</sub>H<sub>18</sub>FNO<sub>3</sub> [M<sup>+</sup>]: 375.1271, found: 375.1268.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-chloro-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3e):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel

with a gradient eluent of petroleum ether/EtOAc (10/1 → 2/1) to give white solid, 170.1 mg, 87 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 3.37-3.49 (m, 3H), 3.21 (d, *J* = 4.4 Hz, 1H), 3.02 (d, *J* = 4.8 Hz, 1H), 2.74 (d, *J* = 5.6 Hz, 1H), 2.38 (s, 3H), 1.45 (d, *J* = 11.2 Hz, 1H), 1.22 (d, *J* = 12.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 204.4, 176.5, 175.7, 153.0, 140.4, 139.1, 135.6, 134.9, 130.0, 128.8, 127.5, 126.3, 123.5, 51.0, 47.9, 47.4, 44.0, 42.8, 42.5, 36.0, 21.2; HRMS (EI) calcd. for C<sub>23</sub>H<sub>18</sub>ClNO<sub>3</sub> [M<sup>+</sup>]: 391.0975, found: 391.0973. The configuration was confirmed by X-ray analysis (Figure S1) and undoubtedly determined that methylenecyclopropane moiety was formed

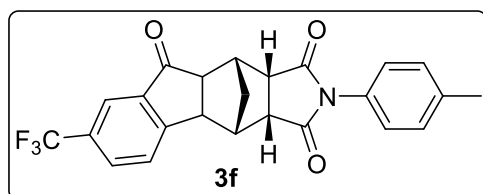


**Figure S1.** ORTEP drawing of product **3e**

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-2-(p-tolyl)-7-(trifluoromethyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-**

**4,10-methanoindeno[1,2-*f*]isoindole-**

**1,3,9(2*H*)-trione(3f):** The title compound was prepared according to the general procedure and purified by flash column chromatography

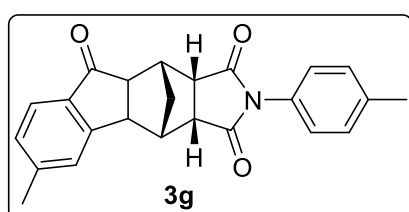


on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 2/1) to give white solid, 142.4 mg, 67 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 7.91 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.40-3.50 (m, 3H), 3.08 (d, *J* = 4.8 Hz, 1H), 2.79 (d, *J* = 6.4 Hz, 1H), 2.38 (s, 3H), 1.49 (d, *J* = 11.2 Hz, 1H), 1.23(d, *J* = 11.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 204.4, 176.3, 175.5, 158.0, 139.3, 139.1, 132.1 (q, *J*<sub>C-F</sub> = 3.8 Hz), 130.0, 129.8 (q, *J*<sub>C-F</sub> = 245.8 Hz), 128.8; 127.1, 126.3, 120.9 (q, *J*<sub>C-F</sub> = 3.9 Hz), 50.8, 48.0, 47.4, 44.1, 42.9, 42.9, 36.1, 21.2; **HRMS (EI)** calcd. for C<sub>24</sub>H<sub>18</sub>F<sub>3</sub>NO<sub>3</sub> [M<sup>+</sup>]: 425.1239, found: 425.1237.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-6-methyl-2-(p-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-**

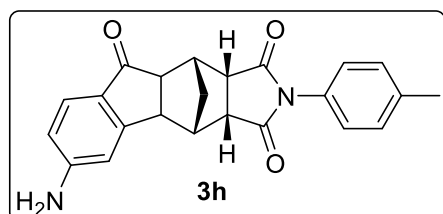
**trione(3g):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a



gradient eluent of petroleum ether/EtOAc (10/1 → 2/1) to give white solid, 168.9 mg, 91 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.38-3.45 (m,

2H), 3.35 (d,  $J = 6.4$  Hz, 1H), 3.20 (d,  $J = 4.4$  Hz, 1H), 3.02 (d,  $J = 4.8$  Hz, 1H), 2.69 (d,  $J = 6.0$  Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 1.41 (d,  $J = 11.6$  Hz, 1H), 1.25 (d,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.2, 176.7, 175.9, 155.5, 147.0, 139.0, 136.7, 129.9, 129.5, 128.9, 126.6, 126.4, 123.5, 50.7, 48.0, 47.6, 44.1, 42.6, 36.0, 22.1, 21.2; HRMS (EI) calcd. for  $\text{C}_{24}\text{H}_{21}\text{NO}_3$  [ $\text{M}^+$ ]: 371.1521, found: 371.1518.

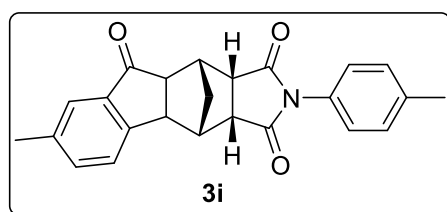
**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-6-amino-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3h):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a

gradient eluent of petroleum ether/EtOAc (10/1  $\rightarrow$  2/1) to give white solid, 156.3 mg, 84 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.8$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 6.61 (d,  $J = 7.2$  Hz, 2H), 4.45 (s, 2H), 3.35-3.42 (m, 2H), 3.22 (d,  $J = 6.4$  Hz, 1H), 3.15 (d,  $J = 4.8$  Hz, 1H), 2.95 (d,  $J = 4.4$  Hz, 1H), 2.63 (d,  $J = 6.0$  Hz, 1H), 2.37 (s, 3H), 1.37 (d,  $J = 11.2$  Hz, 1H), 1.35 (d,  $J = 10.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.1, 176.9, 176.1, 158.2, 153.9, 139.0, 129.9, 129.4, 128.9, 126.4, 125.7, 115.3, 109.2, 50.8, 48.1, 47.7, 44.1, 42.5, 42.4, 36.0, 21.2; HRMS (EI) calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_3$  [ $\text{M}^+$ ]: 372.1474, found: 372.1476.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-methyl-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

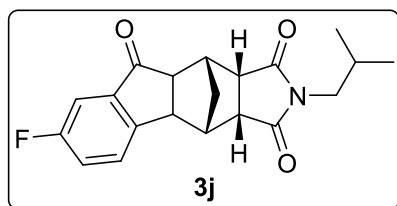


**methanoindeno[1,2-*f*]isoindole-1,3,9(2H)-trione(3i):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel

with a gradient eluent of petroleum ether/EtOAc (10/1  $\rightarrow$  2/1) to give white solid, 178.2 mg, 96 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (s, 1H), 7.48 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.26 (d,  $J = 8.4$  Hz, 2H), 7.12 (d,  $J = 8.0$  Hz, 2H), 3.39-3.45 (m, 2H), 3.35 (d,  $J = 5.2$  Hz, 1H), 3.19 (d,  $J = 5.2$  Hz, 1H), 3.00 (d,  $J = 5.2$  Hz, 1H), 2.70 (d,  $J = 6.0$  Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H), 1.41 (d,  $J = 11.2$  Hz, 1H), 1.23 (d,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.9, 176.7, 175.9, 152.4, 139.1, 139.0, 138.4, 136.9, 129.9, 128.9, 126.4, 125.9, 123.6, 50.8, 48.0, 47.5, 44.1, 42.7, 42.5,

36.0, 21.2, 21.1; **HRMS (EI)** calcd. for C<sub>24</sub>H<sub>21</sub>NO<sub>3</sub> [M<sup>+</sup>]: 371.1521, found: 371.1518.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-fluoro-2-isobutyl-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

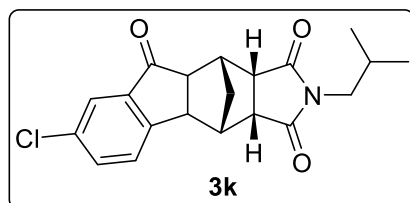


**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione**

**(3j):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of

petroleum ether/EtOAc (10/1→2/1) to give white solid, 141.6 mg, 83 % yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.53 (m, 1H), 7.35-7.40 (m, 2H), 3.34 (d, *J* = 7.2 Hz, 2H), 3.23-3.31 (m, 2H), 3.20 (d, *J* = 6.0 Hz, 1H), 3.12 (d, *J* = 4.4 Hz, 1H), 2.93 (d, *J* = 4.8 Hz, 1H), 2.58 (d, *J* = 6.0 Hz, 1H), 1.99-2.10 (m, 1H), 1.40 (d, *J* = 11.6 Hz, 1H), 1.19 (d, *J* = 11.6 Hz, 1H), 0.91 (s, 3H), 0.89 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 204.9 (d, *J*<sub>C-F</sub> = 3.4 Hz), 177.5, 176.7, 162.7 (d, *J*<sub>C-F</sub> = 247.8 Hz), 150.5 (d, *J*<sub>C-F</sub> = 2.0 Hz), 140.7 (d, *J*<sub>C-F</sub> = 7.2 Hz), 127.7 (d, *J*<sub>C-F</sub> = 8.2 Hz), 123.3 (d, *J*<sub>C-F</sub> = 23.0 Hz), 109.4 (d, *J*<sub>C-F</sub> = 21.9 Hz), 51.3, 47.9, 47.4, 46.3, 43.4, 42.3, 42.2, 36.0, 27.2, 20.4; **HRMS (EI)** calcd. for C<sub>20</sub>H<sub>20</sub>FNO<sub>3</sub> [M<sup>+</sup>]: 341.1427, found: 341.1429.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-chloro-2-isobutyl-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



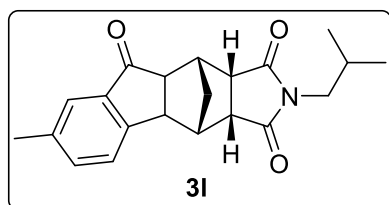
**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione**

**(3k):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent

of petroleum ether/EtOAc (10/1→2/1) to give white solid, 151.8 mg, 85 % yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 3.34 (d, *J* = 7.2 Hz, 2H), 3.23-3.30 (m, 2H), 3.19 (d, *J* = 6.0 Hz, 1H), 3.12 (d, *J* = 5.2 Hz, 1H), 2.93 (d, *J* = 4.8 Hz, 1H), 2.56 (d, *J* = 6.4 Hz, 1H), 1.99-2.09 (m, 1H), 1.40 (d, *J* = 10.8 Hz, 1H), 1.18 (d, *J* = 10.0 Hz, 1H), 0.91 (s, 3H), 0.89 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 204.6, 177.4, 176.6, 153.1, 140.3, 135.6, 134.8, 127.4, 123.4, 51.0, 47.9, 47.4, 46.3, 43.4, 42.5, 42.2, 36.1, 27.2, 20.4; **HRMS (EI)** calcd. for C<sub>20</sub>H<sub>20</sub>ClNO<sub>3</sub> [M<sup>+</sup>]: 357.1132, found: 357.1135.



**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-7-methyl-2-isobutyl-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

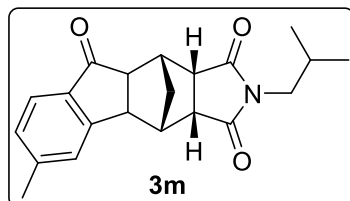


**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione**

**(3l):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of

petroleum ether/EtOAc (10/1→2/1) to give white solid, 155.1 mg, 92 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (s, 1H), 7.47 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 3.33 (d, *J* = 7.2 Hz, 2H), 3.21-3.29 (m, 2H), 3.17 (d, *J* = 5.6 Hz, 1H), 3.10 (d, *J* = 4.8 Hz, 1H), 2.91 (d, *J* = 4.4 Hz, 1H), 2.52 (d, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 1.99-2.09 (m, 1H), 1.35 (d, *J* = 11.2 Hz, 1H), 1.19 (d, *J* = 10.8 Hz, 1H), 0.90 (s, 3H), 0.89 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.2, 177.7, 176.9, 152.4, 139.1, 138.3, 136.8, 125.9, 123.5, 50.8, 48.0, 47.6, 46.3, 43.5, 42.4, 42.1, 36.1, 27.2, 21.1, 20.4; HRMS (EI) calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub> [M<sup>+</sup>]: 337.1678, found: 337.1679.

**(3<sup>a</sup>R,4S,10R,10<sup>a</sup>S)-6-methyl-2-isobutyl-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**

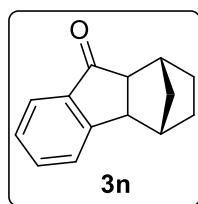


**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione(3m):**

The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum

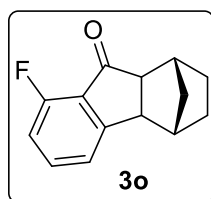
ether/EtOAc (10/1→2/1) to give white solid, 148.4 mg, 88 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 0.8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 3.33 (d, *J* = 7.2 Hz, 2H), 3.21-3.30 (m, 2H), 3.16 (d, *J* = 6.0 Hz, 1H), 3.10 (d, *J* = 4.4 Hz, 1H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.51 (d, *J* = 6.0 Hz, 1H), 2.46 (s, 3H), 1.99-2.09 (m, 1H), 1.36 (d, *J* = 11.2 Hz, 1H), 1.20 (d, *J* = 11.2 Hz, 1H), 0.90 (s, 3H), 0.89 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.4, 177.6, 176.9, 155.6, 146.9, 136.6, 129.4, 126.5, 123.4, 50.7, 48.0, 47.6, 46.3, 43.5, 42.6, 42.1, 36.1, 27.2, 22.1, 20.4; HRMS (EI) calcd. for C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub> [M<sup>+</sup>]: 337.1678, found: 337.1675.

**(1R,4S)-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one(3n):** The title



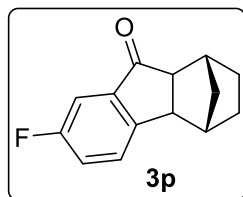
compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 89.2 mg, 90 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.15 (d, *J* = 6.0 Hz, 1H), 2.60 (d, *J* = 3.6 Hz, 1H), 2.50 (d, *J* = 6.0 Hz, 1H), 2.41 (d, *J* = 3.6 Hz, 1H), 1.60-1.76 (m, 2H), 1.44-1.50 (m, 1H), 1.34-1.41 (m, 1H), 0.95 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H), 0.81 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.9, 157.2, 139.1, 135.0, 127.4, 126.2, 123.2, 55.8, 48.1, 41.3, 40.4, 32.2, 28.9, 28.7; HRMS (EI) calcd. for C<sub>14</sub>H<sub>14</sub>O [M<sup>+</sup>]: 198.1045, found: 198.1043.

**(1R,4S)-8-fluoro-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one (3o):** The



title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 80.0 mg, 74 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.60 (m, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 8.8 Hz, 1H), 3.16 (d, *J* = 6.4 Hz, 1H), 2.63 (d, *J* = 4.0 Hz, 1H), 2.52 (d, *J* = 6.0 Hz, 1H), 2.42 (d, *J* = 4.4 Hz, 1H), 1.60-1.76 (m, 2H), 1.43-1.49 (m, 1H), 1.33-1.40 (m, 1H), 0.99 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 0.89 (dt, *J* = 10.4 Hz, 1.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.2 (d, *J*<sub>C-F</sub> = 3.0 Hz), 158.5 (d, *J*<sub>C-F</sub> = 262.0 Hz), 136.8 (d, *J*<sub>C-F</sub> = 8.2 Hz), 126.8 (d, *J*<sub>C-F</sub> = 12.2 Hz), 122.0 (d, *J*<sub>C-F</sub> = 4.1 Hz), 114.2 (d, *J*<sub>C-F</sub> = 19.5 Hz), 56.3, 48.0, 41.6, 40.6, 32.3, 28.8, 28.6; HRMS (EI) calcd. for C<sub>14</sub>H<sub>13</sub>FO [M<sup>+</sup>]: 216.0950, found: 216.0947.

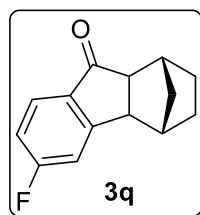
**(1R,4S)-7-fluoro-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one (3p):** The



title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow solid, 91.8 mg, 85 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.48 (m, 1H), 7.30-7.35 (m, 2H), 3.12 (d, *J* = 6.4 Hz, 1H), 2.60 (d, *J* = 4.0 Hz, 1H), 2.55 (d, *J* = 5.6 Hz, 1H), 2.39 (d, *J* = 4.0 Hz, 1H), 1.60-1.76 (m, 2H), 1.43-1.49 (m, 1H),

1.33-1.40 (m, 1H), 0.97 (dt,  $J = 10.4$  Hz, 1.6 Hz, 1H), 0.80 (dt,  $J = 10.8$  Hz, 1.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  207.8 (d,  $J_{\text{C-F}} = 2.8$  Hz), 162.3 (d,  $J_{\text{C-F}} = 246.5$  Hz), 152.7 (d,  $J_{\text{C-F}} = 2.0$  Hz), 140.8 (d,  $J_{\text{C-F}} = 7.7$  Hz), 127.5 (d,  $J_{\text{C-F}} = 8.1$  Hz), 122.6 (d,  $J_{\text{C-F}} = 23.6$  Hz), 108.9 (d,  $J_{\text{C-F}} = 20.6$  Hz), 56.6, 47.5, 41.2, 40.5, 32.1, 28.8, 28.6; **HRMS (EI)** calcd. for  $\text{C}_{14}\text{H}_{13}\text{FO}$  [ $\text{M}^+$ ]: 216.0950, found: 216.0948.

**(1R,4S)-6-fluoro-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one (3q):** The

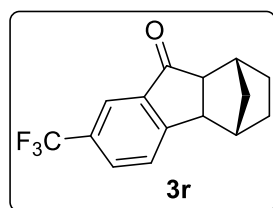


title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 87.5 mg, 81 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (dd,  $J = 8.4$  Hz,

5.2 Hz, 1H), 7.15 (dd,  $J = 8.8$  Hz, 2.0 Hz, 1H), 7.05 (dt,  $J = 8.4$  Hz, 2.0 Hz, 1H), 3.13 (d,  $J = 6.0$  Hz, 1H), 2.60 (d,  $J = 3.6$  Hz, 1H), 2.53 (d,  $J = 6.0$  Hz, 1H), 2.41 (d,  $J = 4.0$  Hz, 1H), 1.61-1.77 (m, 2H), 1.43-1.50 (m, 1H), 1.34-1.41 (m, 1H), 0.98 (dt,  $J = 10.4$  Hz, 1.6 Hz, 1H), 0.82 (dt,  $J = 10.8$  Hz, 1.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.8, 167.5 (d,  $J_{\text{C-F}} = 254.8$  Hz), 160.1 (d,  $J_{\text{C-F}} = 8.9$  Hz), 135.5 (d,  $J_{\text{C-F}} = 10.9$  Hz), 125.5 (d,  $J_{\text{C-F}} = 10.7$  Hz), 115.7 (d,  $J_{\text{C-F}} = 24.7$  Hz), 112.7 (d,  $J_{\text{C-F}} = 21.6$  Hz), 56.2, 47.9 (d,  $J_{\text{C-F}} = 2.8$  Hz), 41.3, 40.4, 32.2, 28.8, 28.6; **HRMS (EI)** calcd. for  $\text{C}_{14}\text{H}_{13}\text{FO}$  [ $\text{M}^+$ ]: 216.0950, found: 216.0947.

**(1R,4S)-7-trifluoromethyl-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one**

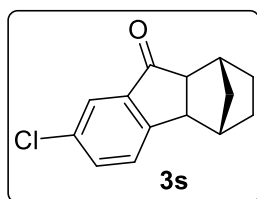
**(3r):** The title compound was prepared according to the general procedure and purified



by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 86.5 mg, 65 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H), 7.85 (dd,  $J = 8.0$  Hz, 1.2 Hz, 1H), 7.64 (dd,  $J = 8.0$  Hz,  $J$

$= 0.4$  Hz, 1H), 3.22 (d,  $J = 10.4$  Hz, 1H), 2.64 (d,  $J = 3.6$  Hz, 1H), 2.58 (d,  $J = 6.0$  Hz, 1H), 2.46 (d,  $J = 4.0$  Hz, 1H), 1.63-1.80 (m, 2H), 1.47-1.54 (m, 1H), 1.37-1.43 (m, 1H), 0.80 (dt,  $J = 10.4$  Hz, 1.6 Hz, 1H), 0.78 (dt,  $J = 11.2$  Hz, 1.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  207.5, 160.3, 139.4, 131.4 (q,  $J_{\text{C-F}} = 3.2$  Hz), 130.2 (d,  $J_{\text{C-F}} = 32.3$  Hz), 127.0, 123.8 (q,  $J_{\text{C-F}} = 270.9$  Hz), 120.4 (q,  $J_{\text{C-F}} = 4.0$  Hz), 56.1, 48.1, 41.3, 40.6, 32.3, 28.9, 28.5; **HRMS (EI)** calcd. for  $\text{C}_{15}\text{H}_{13}\text{F}_3\text{O}$  [ $\text{M}^+$ ]: 266.0918, found: 266.0920.

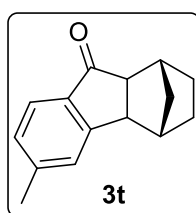
**(1R,4S)-7-chloro-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one (3s):** The



title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 90.5 mg, 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

7.66 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 3.12 (d, *J* = 4.8 Hz, 1H), 2.60 (d, *J* = 4.0 Hz, 1H), 2.53 (d, *J* = 6.0 Hz, 1H), 2.40 (d, *J* = 4.0 Hz, 1H), 1.60-1.76 (m, 1H), 1.43-1.49 (m, 1H), 1.34-1.40 (m, 1H), 0.97 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H), 0.79 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 207.4, 155.3, 140.6, 134.9, 133.8, 127.4, 123.0, 56.3, 47.7, 41.2, 40.5, 32.2, 28.8, 28.6; HRMS (EI) calcd. for C<sub>14</sub>H<sub>13</sub>ClO [M<sup>+</sup>]: 232.0655, found: 232.0657.

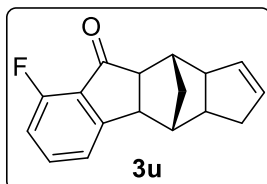
**(1R,4S)-6-methyl-1,2,3,4,4<sup>a</sup>,9<sup>a</sup>-hexahydro-9H-1,4-methanofluoren-9-one (3t):** The



title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 95.5 mg, 90 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.6 Hz,

1H), 7.29 (s, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.09 (d, *J* = 6.4 Hz, 1H), 2.58 (d, *J* = 3.6 Hz, 1H), 2.48 (d, *J* = 6.0 Hz, 1H), 2.45 (s, 3H), 2.39 (d, *J* = 3.6 Hz, 1H), 1.59-1.75 (m, 2H), 1.42-1.48 (m, 1H), 1.33-1.39 (m, 1H), 0.93 (d, *J* = 10.8 Hz, 1H), 0.81 (d, *J* = 10.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.3, 157.8, 146.1, 136.8, 128.7, 126.5, 123.0, 56.1, 47.9, 41.2, 40.3, 32.2, 28.9, 28.7, 22.1; HRMS (EI) calcd. for C<sub>15</sub>H<sub>16</sub>O [M<sup>+</sup>]: 212.1201, found: 212.1200.

**(4R,10S)-8-fluoro-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-methanocyclopenta[*b*]fluoren-**

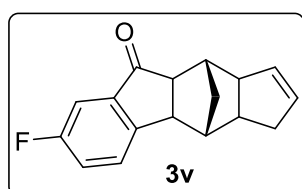


**9(3H)-one (3u):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 90.2 mg, 71 %

yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52-7.58 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 8.4 Hz, 1H), 5.63-5.76 (m, 2H), 3.17-3.28 (m, 2H), 2.64-2.76 (m, 1H), 2.51-2.56 (m, 2H), 2.32-2.43 (m, 3H), 1.24 (dt, *J* = 10.8 Hz, 1.2 Hz, 1H), 1.04 (t, *J* = 8.0 Hz, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.2 (d,  $J_{\text{C-F}} = 1.4$  Hz), 160.5 (d,  $J_{\text{C-F}} = 1.7$  Hz), 158.5 (d,  $J_{\text{C-F}} = 262.0$  Hz), 136.6 (d,  $J_{\text{C-F}} = 7.6$  Hz), 132.0, 131.4, 127.2 (d,  $J_{\text{C-F}} = 12.5$  Hz), 121.5 (d,  $J_{\text{C-F}} = 3.8$  Hz), 113.9 (d,  $J_{\text{C-F}} = 4.4$  Hz), 53.0, 52.5, 49.6, 45.2, 44.3, 41.7, 35.1, 32.1; **HRMS (EI)** calcd. for  $\text{C}_{17}\text{H}_{15}\text{FO}$  [ $\text{M}^+$ ]: 254.1107, found: 254.1104.

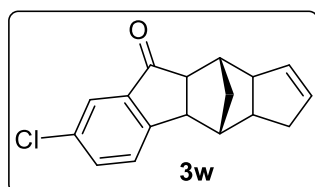
**(4R,10S)-7-fluoro-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-methanocyclopenta[*b*]fluoren-**



**9(3H)-one (3v):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 96.6 mg,

76 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.42 (m, 1H), 7.28-7.35 (m, 2H), 5.70-5.76 (m, 2H), 3.14-3.29 (m, 2H), 2.64-2.77 (m, 1H), 2.55-2.59 (m, 1H), 2.29-2.50 (m, 4H), 1.19-1.23 (m, 1H), 0.92-0.96 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.9 (d,  $J_{\text{C-F}} = 2.9$  Hz), 162.2 (d,  $J_{\text{C-F}} = 246.3$  Hz), 153.4 (d,  $J_{\text{C-F}} = 1.7$  Hz), 141.2 (d,  $J_{\text{C-F}} = 7.2$  Hz), 131.8 (d,  $J_{\text{C-F}} = 19.2$  Hz), 131.5 (d,  $J_{\text{C-F}} = 14.0$  Hz), 127.1 (d,  $J_{\text{C-F}} = 7.9$  Hz), 122.5 (d,  $J_{\text{C-F}} = 22.9$  Hz), 108.9 (d,  $J_{\text{C-F}} = 21.3$  Hz), 53.0, 50.0, 45.2, 43.9, 43.2, 41.7, 35.1, 32.1; **HRMS (EI)** calcd. for  $\text{C}_{17}\text{H}_{15}\text{FO}$  [ $\text{M}^+$ ]: 254.1107, found: 254.1103.

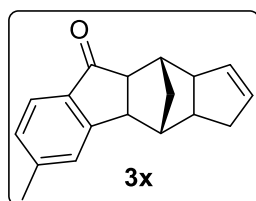
**(4R,10S)-7-chloro-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanocyclopenta[*b*]fluoren-9(3H)-one (3w):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give

light yellow sticky oil, 108.0 mg, 80 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 2.0$  Hz, 1H), 7.54 (dt,  $J = 8.0$  Hz, 2.0 Hz, 1H), 7.38 (d,  $J = 8.4$  Hz, 1H), 5.63-5.76 (m, 2H), 3.14-3.28 (m, 2H), 2.63-2.75 (m, 1H), 2.53-2.57 (m, 1H), 2.50 (d,  $J = 4.4$  Hz, 1H), 2.29-2.43 (m, 3H), 1.19-1.23 (m, 1H), 0.91-0.95 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 156.1, 140.9, 134.8, 132.0, 131.5, 127.1, 127.0, 122.9, 53.0, 49.6, 45.2, 43.9, 43.3, 41.7, 35.1, 32.1; **HRMS (EI)** calcd. for  $\text{C}_{17}\text{H}_{15}\text{ClO}$  [ $\text{M}^+$ ]: 270.0811, found: 270.0808.

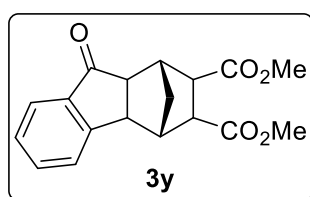
**(4*R*,10*S*)-6-methyl-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanocyclopenta[*b*]fluoren-9(3*H*)-one (3x):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow

sticky oil, 107.6 mg, 86 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.64-5.75 (m, 2H), 3.11-3.27 (m, 2H), 2.63-2.76 (m, 1H), 2.49-2.52 (m, 2H), 2.43 (s, 3H), 2.29-2.42 (m, 3H), 1.18 (d, *J* = 10.4 Hz, 1H), 0.93-0.97 (d, *J* = 10.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 209.6, 158.6, 146.0, 137.2, 131.9, 131.6, 128.5, 126.1, 123.0, 53.1, 49.3, 44.9, 44.0, 43.5, 41.8, 35.2, 32.1, 22.1; HRMS (EI) calcd. for C<sub>18</sub>H<sub>18</sub>O [M<sup>+</sup>]: 250.1358, found: 250.1360.

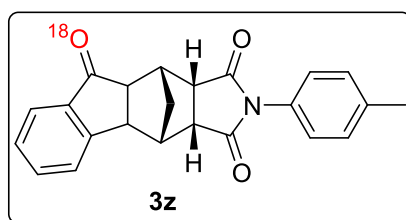
**dimethyl (1*R*,4*S*)-9-oxo-2,3,4,4<sup>a</sup>,9,9<sup>a</sup>-hexahydro-1*H*-1,4-methanofluorene-2,3-di-**



**carboxylate (3y):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→2/1) to give light yellow

sticky oil, 131.9 mg, 84 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 6.0 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.23 (dd, *J* = 11.6 Hz, 4.0 Hz, 1H), 3.11 (dd, *J* = 12.8 Hz, 4.0 Hz, 1H), 2.98 (d, *J* = 6.0 Hz, 1H), 2.95 (d, *J* = 4.0 Hz, 1H), 2.72 (d, *J* = 2.4 Hz, 1H), 1.13 (d, *J* = 11.2 Hz, 1H), 1.06 (d, *J* = 10.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.4, 172.3, 156.8, 139.3, 135.2, 127.6, 126.3, 123.3, 51.9, 51.6, 50.5, 46.7, 46.1, 44.5, 43.8, 41.6, 33.5; HRMS (EI) calcd. For C<sub>18</sub>H<sub>18</sub>O<sub>5</sub> [M<sup>+</sup>]: 314.1154, found: 314.1157.

**(3<sup>a</sup>*R*,4*S*,10*R*,10<sup>a</sup>*S*)-2-(*p*-tolyl)-3<sup>a</sup>,4,4<sup>a</sup>,9<sup>a</sup>,10,10<sup>a</sup>-hexahydro-4,10-**



**methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione-<sup>18</sup>O (3z):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a

gradient eluent of petroleum ether/EtOAc (10/1→2/1) to give white solid, 134.7 mg, 75 % yield. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 6.0 Hz, 1H), 7.66 (t, *J* = 6.0 Hz, 1H), 7.54 (d, *J* = 6.4 Hz, 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 3.38-3.46 (m, 3H), 3.22 (d, *J* = 4.0 Hz, 1H), 3.05 (d, *J* = 4.0 Hz, 1H), 2.71 (d, *J* = 4.8 Hz, 1H), 2.38 (s, 3H), 1.43 (d, *J* = 9.2 Hz, 1H), 1.24 (d, *J* = 8.2 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 205.7, 176.6, 175.8, 154.9, 139.1, 138.9, 135.6, 130.0, 128.9, 128.2, 126.3, 126.2, 123.7, 50.5, 48.0, 47.5, 44.1, 42.8, 42.7, 36.0, 21.2; **HRMS (ESI)** calcd. For C<sub>23</sub>H<sub>20</sub>NO<sub>2</sub><sup>18</sup>O [M+H]<sup>+</sup>: 360.1486, found: 360.1480.

#### 4 References

- (1) Lanier, M.; Schade, D.; Willems, E.; Tsuda, M.; Spiering, S.; Kalisiak, J.; Mercola, M.; Cashman, J. R. *J. Med. Chem.* **2012**, *55*, 697.

#### 5 Copies for <sup>1</sup>H NMR and <sup>13</sup>C NMR

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7.262  
7.242  
7.045  
7.025

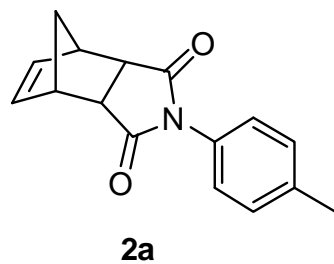
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0.000



2.05 2.00

2.01

2.01 2.03

3.08

1.03 1.02

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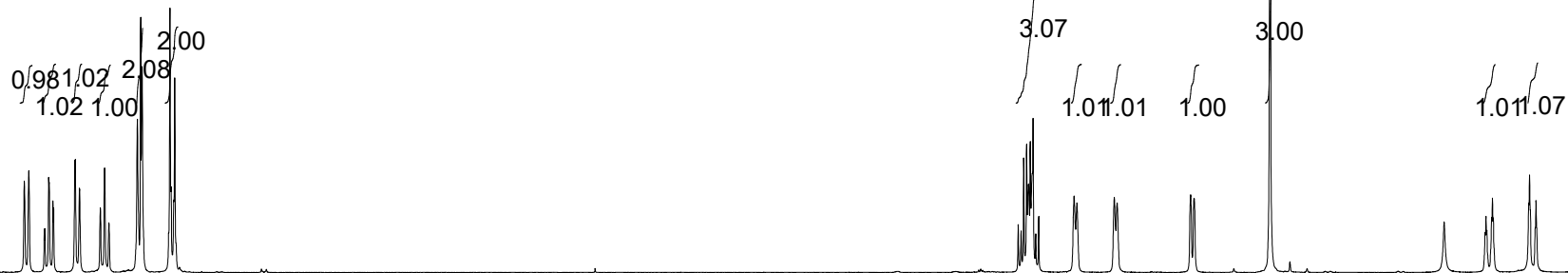
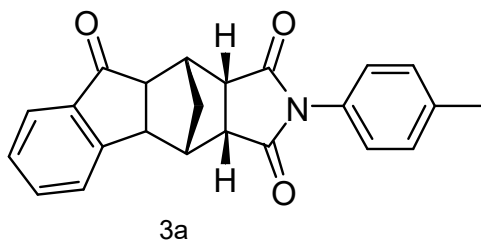


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7.399  
7.276  
7.255  
7.135  
7.114

3.463  
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3.427  
3.411  
3.398  
3.375  
3.222  
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3.035  
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2.717  
2.703  
2.701  
2.374

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-0.000



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USER: nmr -- DATE: Wed Sep 06 07:35:52 2017

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SW1: 8224

OF1: 2467.0

PTS1d: 32768

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PD: 1.0 sec

NA: 8

LB: 0.0

Nuts - \$pdata

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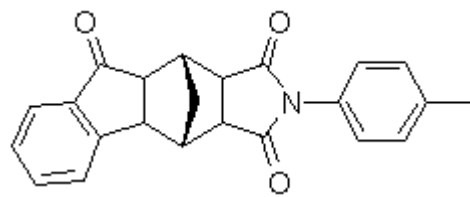
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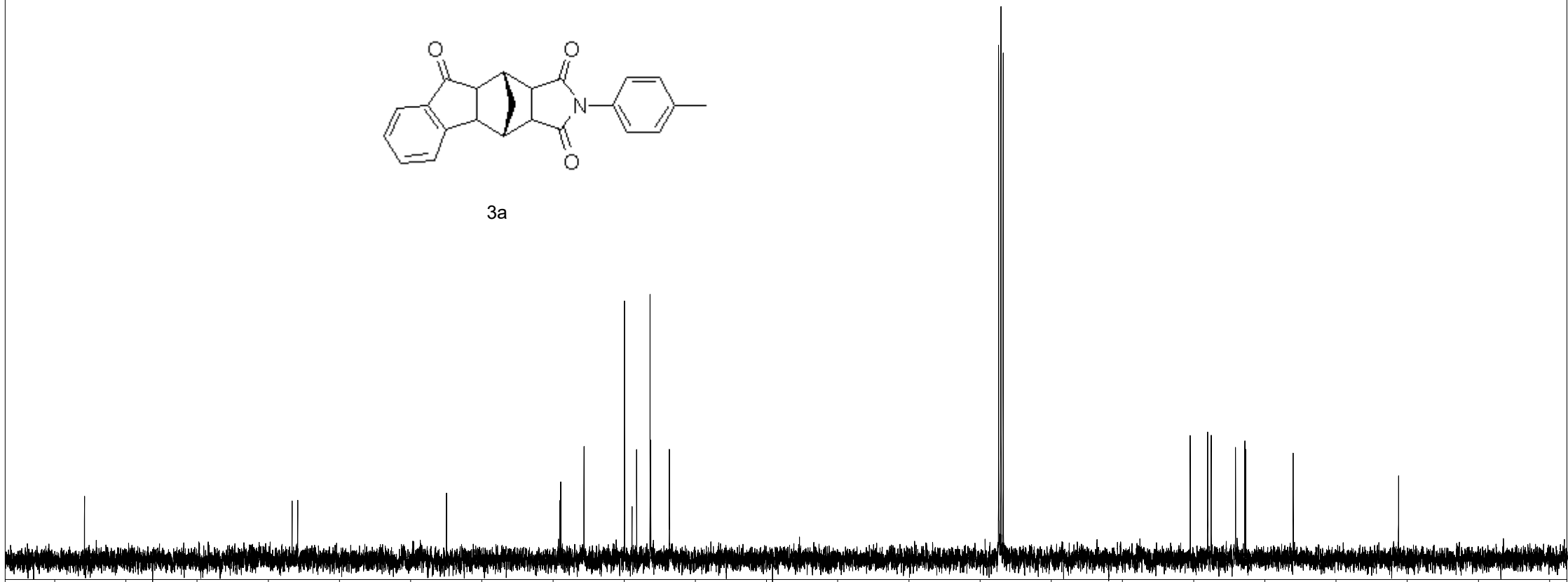
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21.227



3a



200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 06:15:32 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

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PD: 2.0 sec

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LB: 0.0

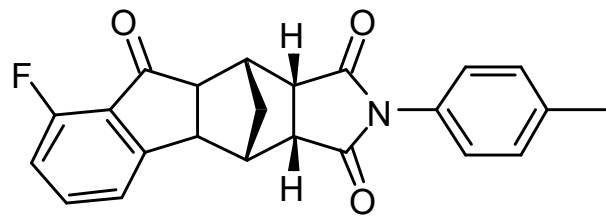
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7.259  
7.129  
7.108  
7.051  
7.028  
7.007

3.467  
3.454  
3.443  
3.430  
3.414  
3.402  
3.395  
3.378  
3.251  
3.239  
3.051  
3.039  
2.734  
2.720  
2.377

1.489  
1.461  
1.338  
1.310

0.000



3b

1.02 1.05 2.04 2.00 1.00 3.07 1.03 1.02 1.00 3.04 1.03 1.04

8 7 6 5 4 3 2 1 PPM

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139.113  
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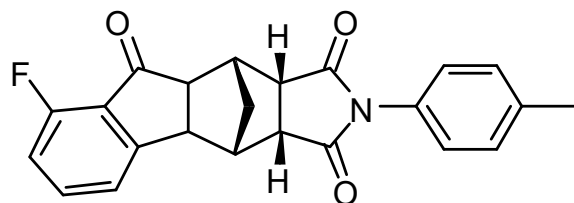
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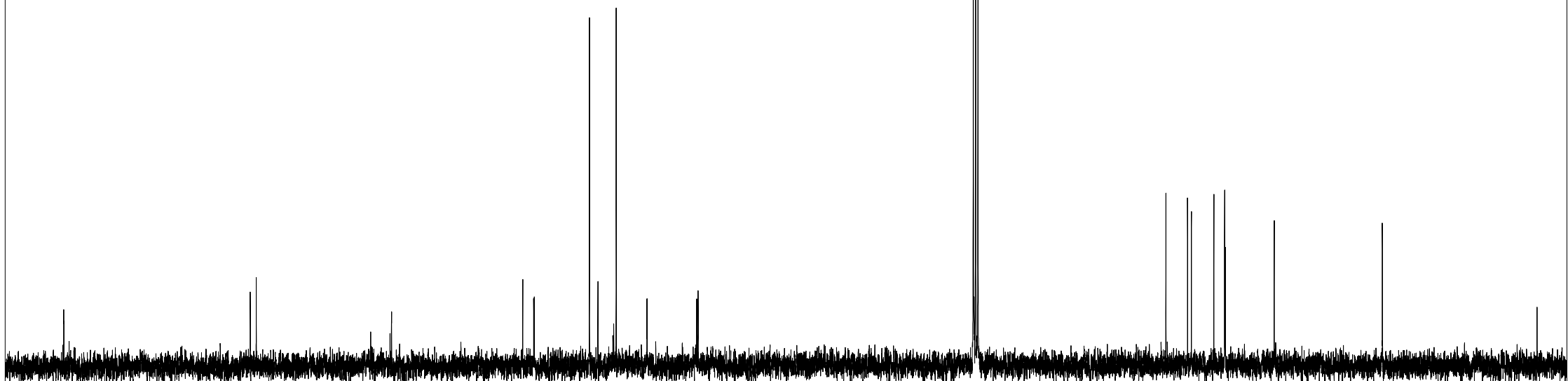
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21.229



3b



200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 08:12:32 2017

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F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

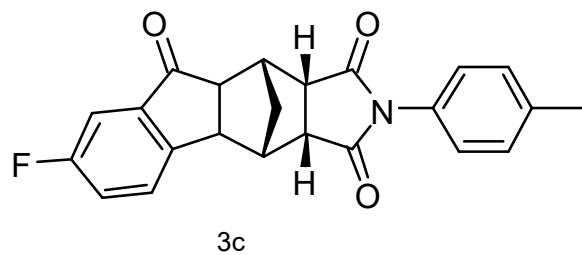
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LB: 0.0

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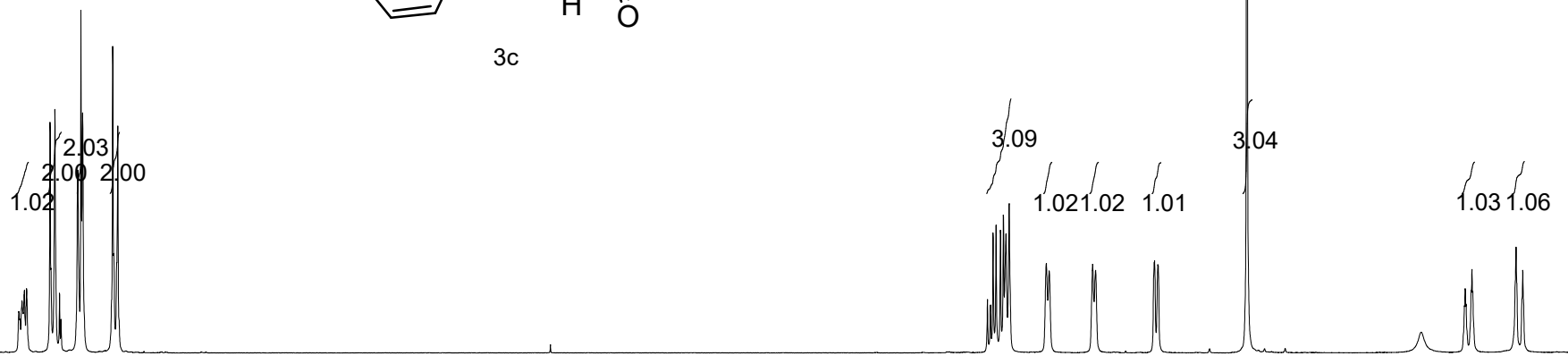


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7.279  
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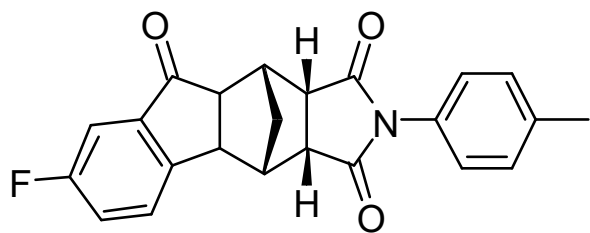
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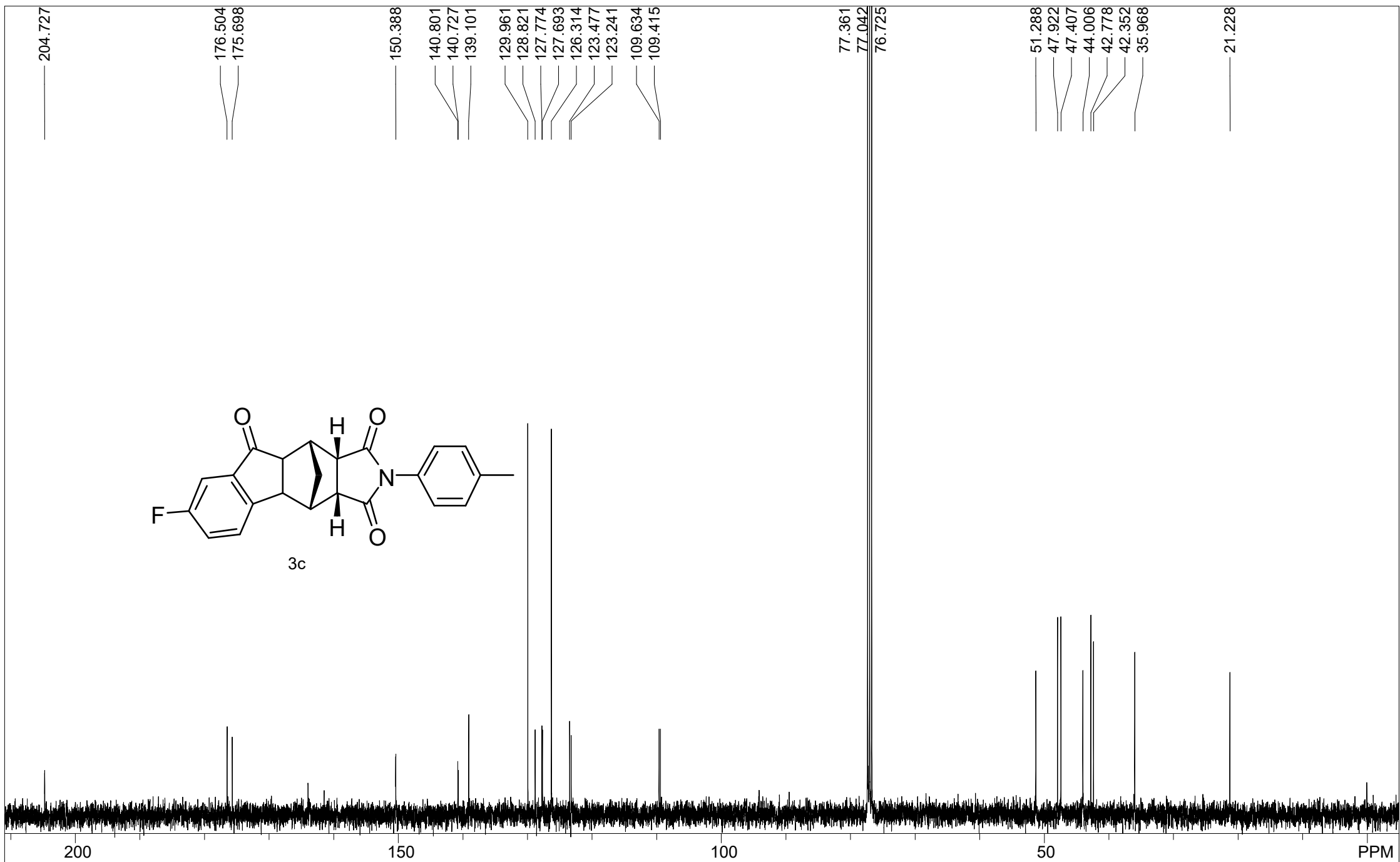
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3c



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21.228

200

150

100

50

PPM

spect, CDCl<sub>3</sub>,

USER: nmr -- DATE: Thu Sep 07 08:38:04 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

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PD: 2.0 sec

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LB: 0.0

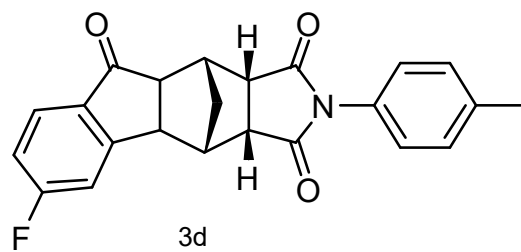
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7.140  
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3.446  
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3.402  
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1.04  
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3.08

1.05  
1.06

8

7

6

5

4

3

2

1

PPM

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USER: nmr -- DATE: Wed Sep 06 07:46:43 2017

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OF1: 2467.5

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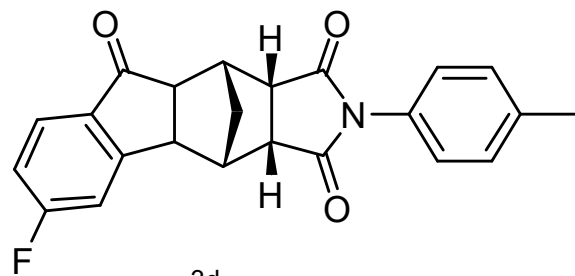
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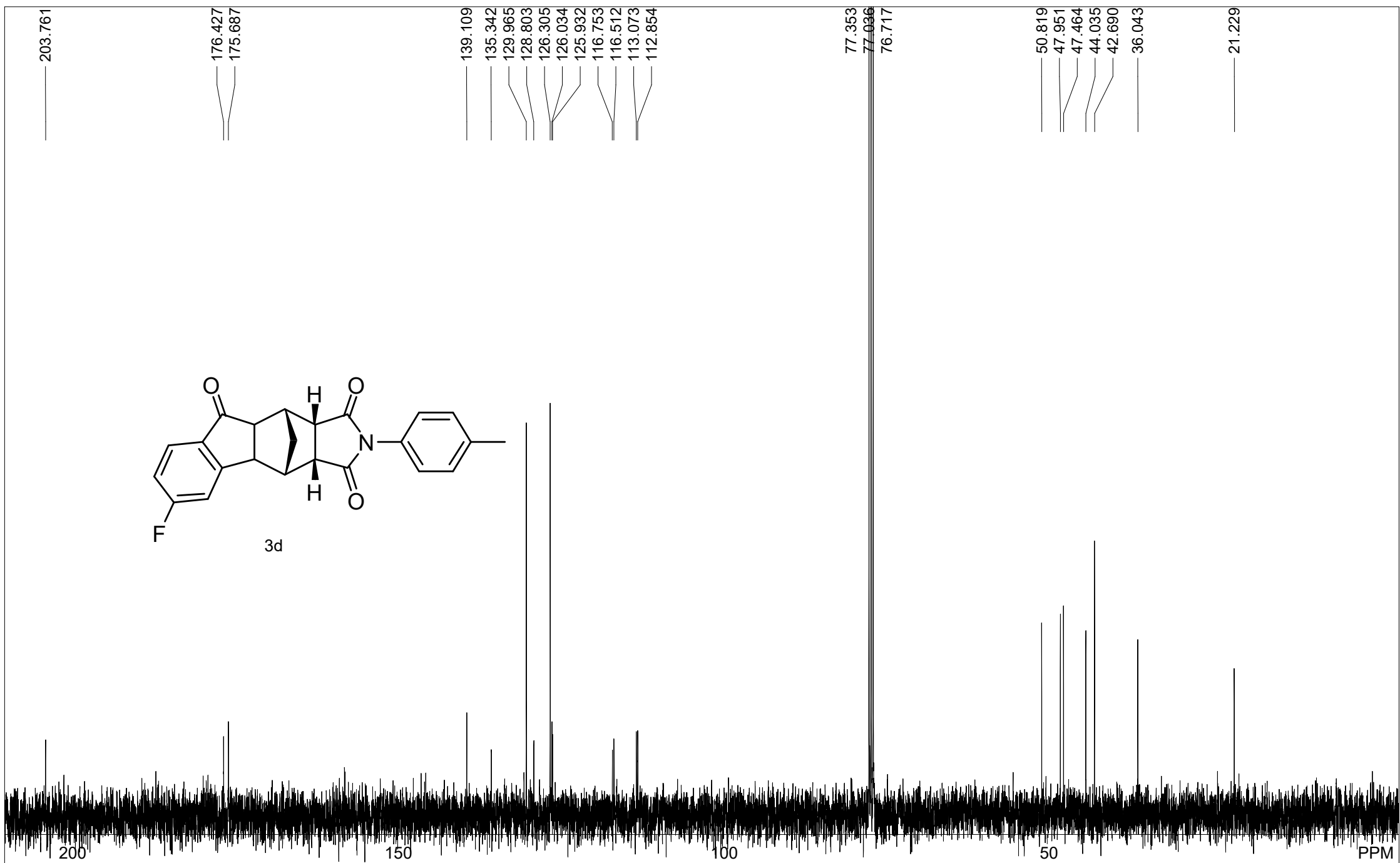
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Nuts - \$pdata



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					Nuts - \$pdata

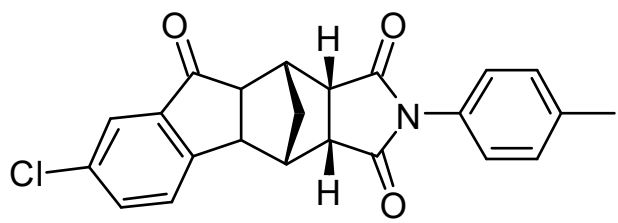


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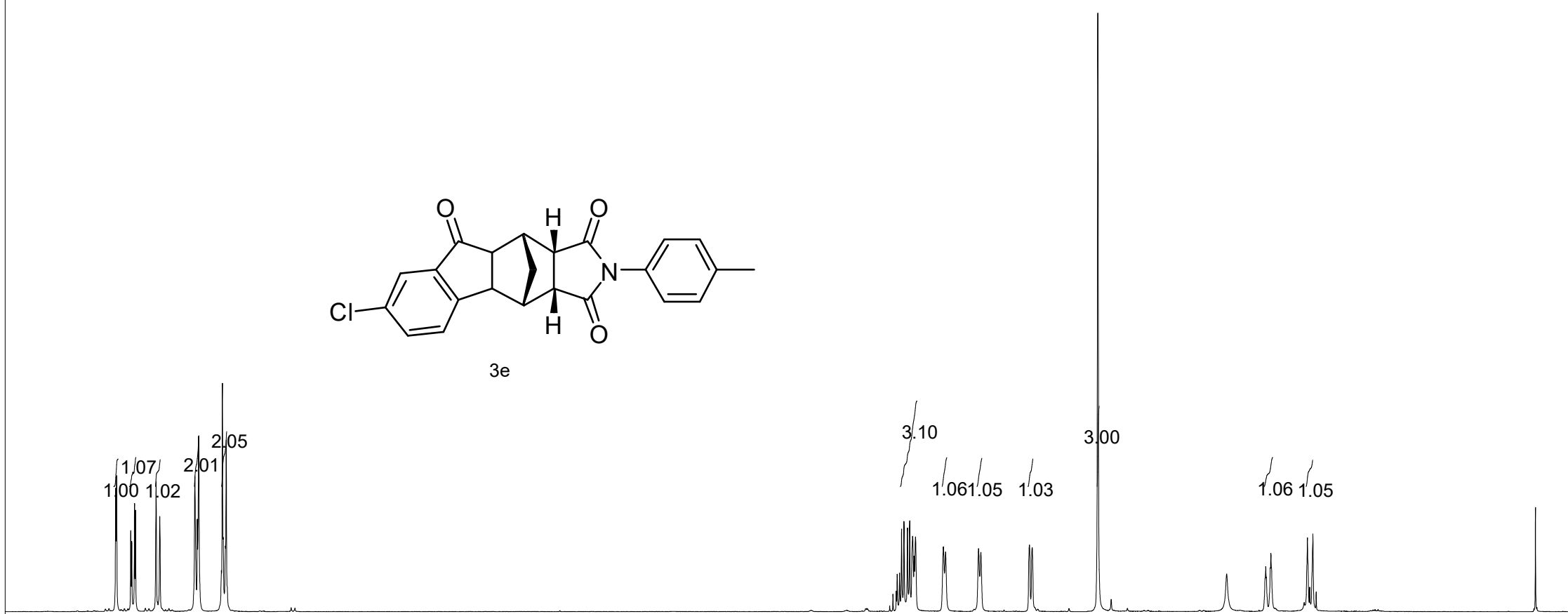
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3.023  
3.011  
2.747  
2.733  
2.376

1.465  
1.437  
1.239  
1.208

-0.000



3e



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Wed Sep 06 09:00:15 2017				
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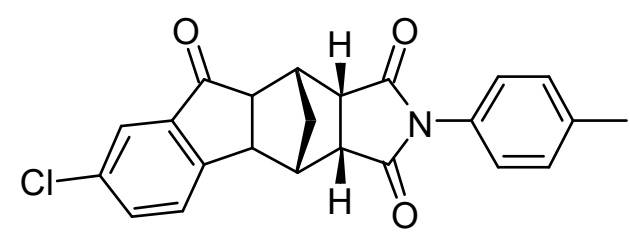
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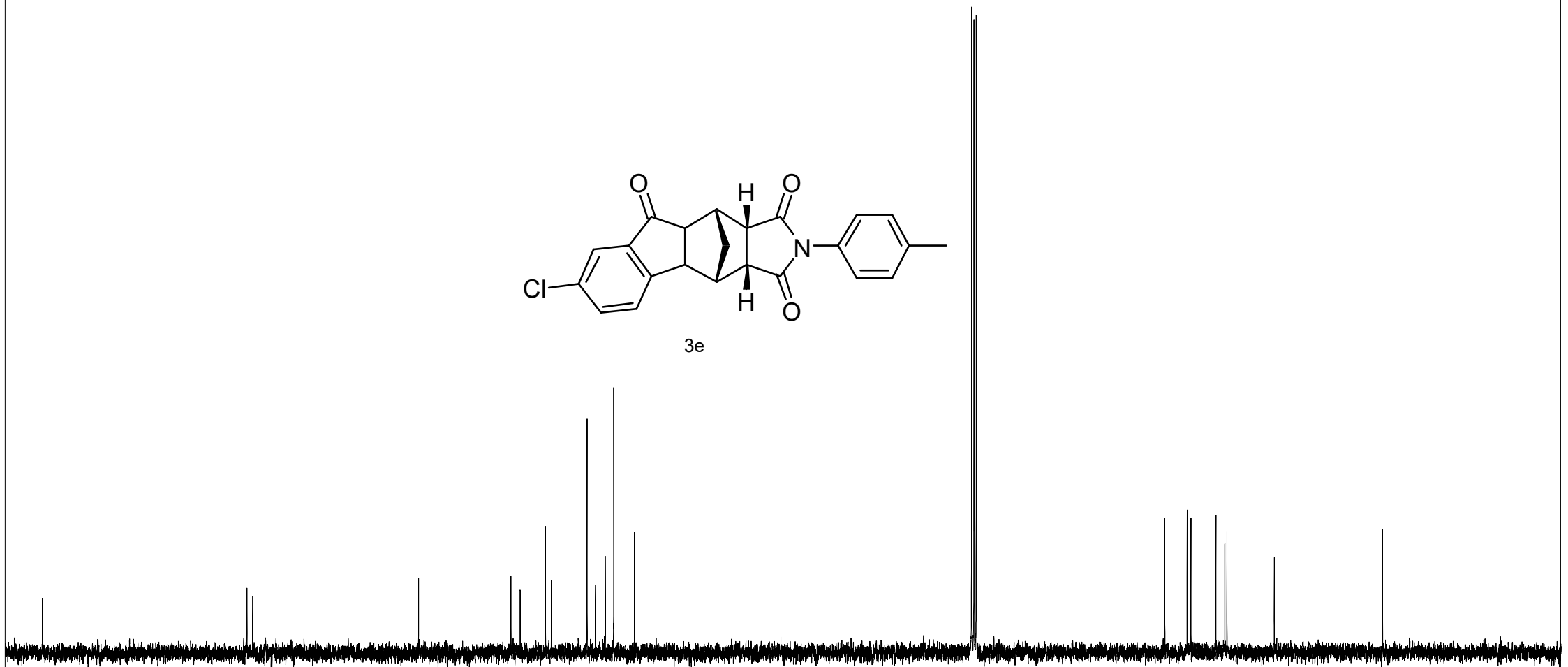
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43.994  
42.771  
42.490  
36.015

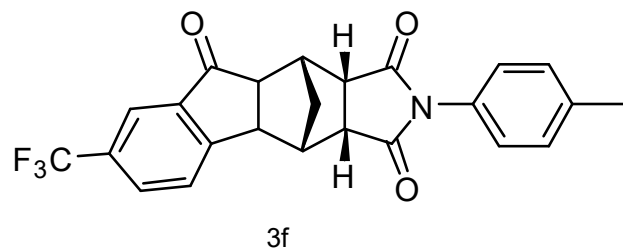
21.232



3e



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Thu Sep 07 07:27:44 2017				
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 60	LB: 0.0	Nuts - \$pdata



8.022  
7.921  
7.918  
7.901  
7.898  
7.699  
7.678  
7.285  
7.262  
7.133  
7.113

3.498  
3.485  
3.474  
3.461  
3.438  
3.426  
3.414  
3.402  
3.086  
3.074  
2.793  
2.777  
2.381

1.500  
1.472  
1.239  
1.211

0.000

1.00 1.08 1.06 2.09 2.00

3.05 1.06 1.03 1.03 3.06 1.05 1.02

8

7

6

5

4

3

2

1

PPM

spect, CDCl<sub>3</sub>,

USER: nmr -- DATE: Wed Sep 06 07:56:40 2017

F1: 400.132

F2: 1.000

SW1: 8224

OF1: 2466.6

PTS1d: 32768

EX: zg30

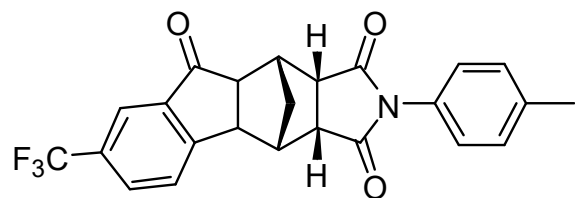
PW: 14.7 usec

PD: 1.0 sec

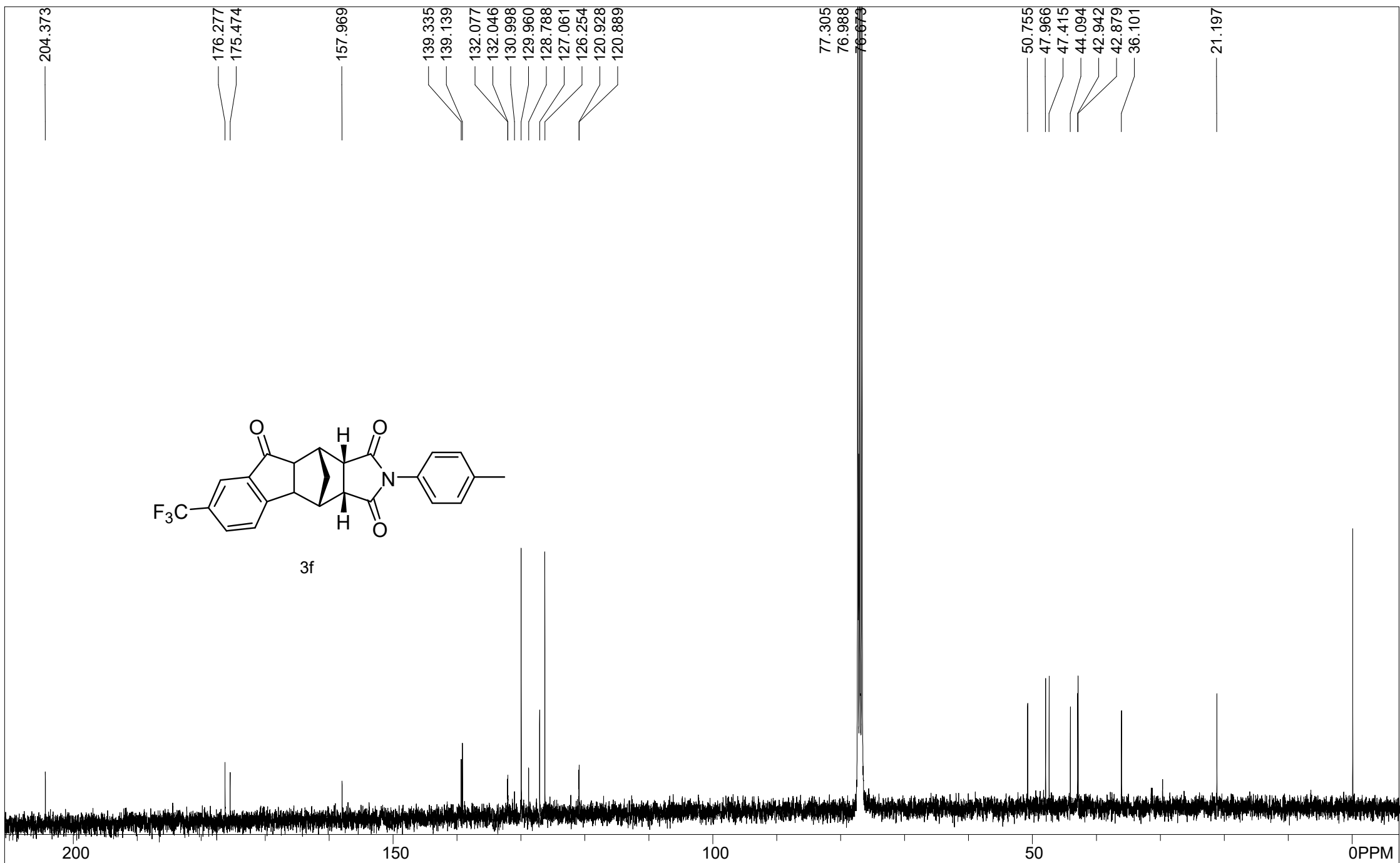
NA: 8

LB: 0.0

Nuts - \$pdata



3f



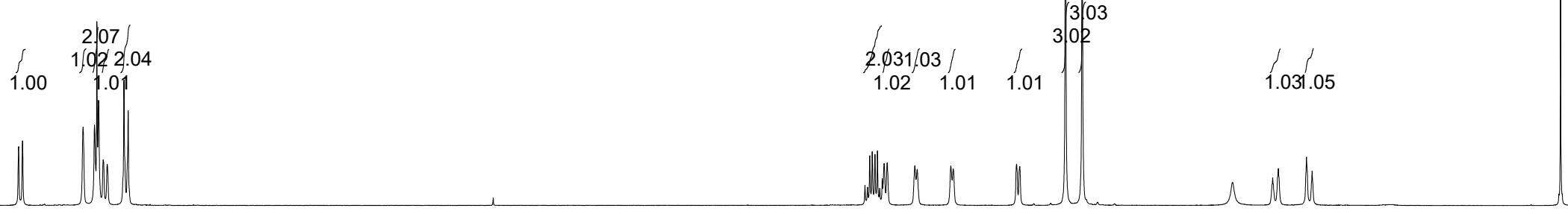
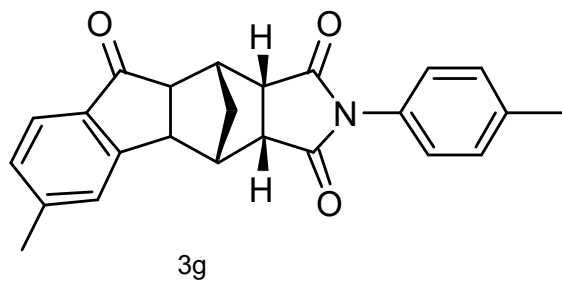
spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Thu Sep 07 13:41:58 2017				
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 5000	LB: 0.0	Nuts - \$pdata

7.651  
7.632  
7.331  
7.274  
7.254  
7.231  
7.211  
7.128  
7.108

3.451  
3.427  
3.415  
3.402  
3.390  
3.379  
3.357  
3.341  
3.204  
3.193  
3.026  
3.014  
2.699  
2.684  
2.457  
2.374

1.429  
1.400  
1.261  
1.233

-0.000



spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 06 08:05:47 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2467.3		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

205.228

176.671  
175.883

155.481

147.033

139.024  
136.695

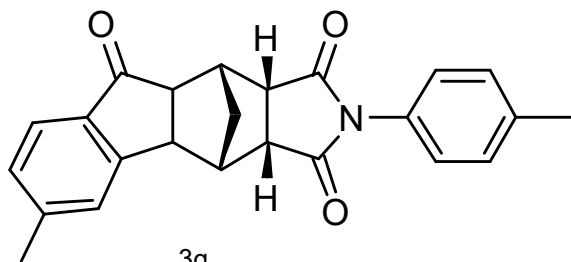
129.946  
129.510  
128.913  
126.554  
126.359  
123.467

77.352  
77.037  
76.710

50.692  
48.052  
47.579  
44.118  
42.630

36.034

22.141  
21.222



200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 07:44:57 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

NA: 120

LB: 0.0

Nuts - \$pdata

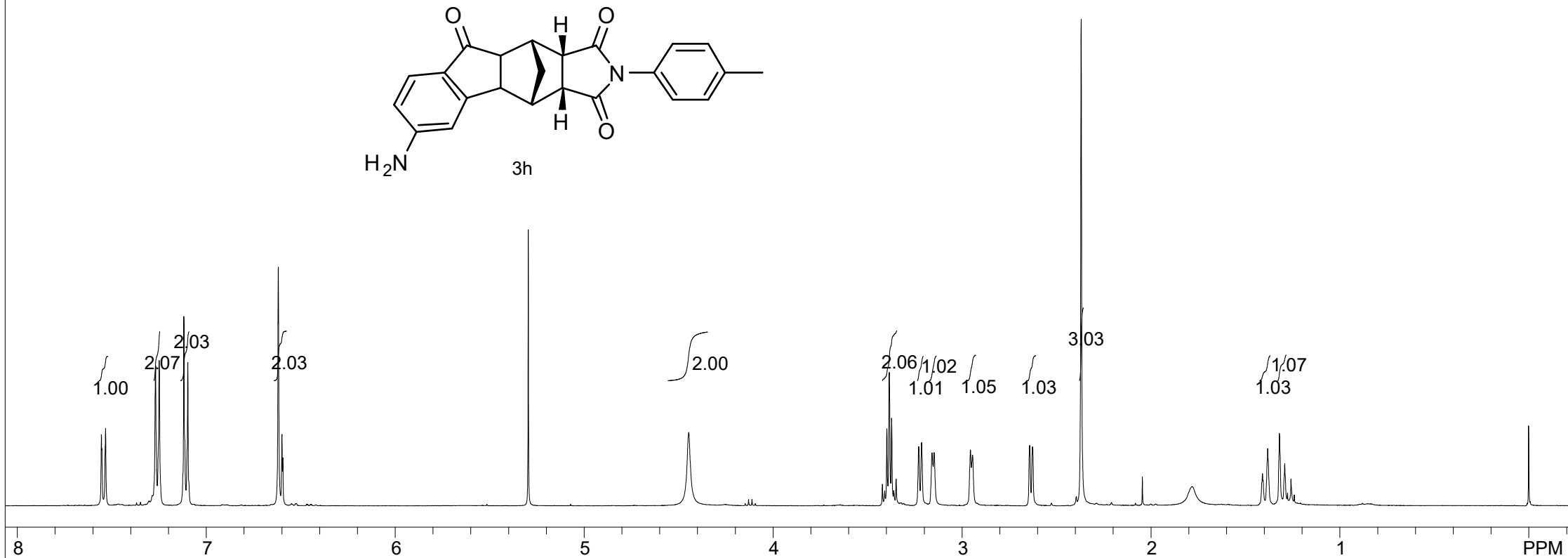
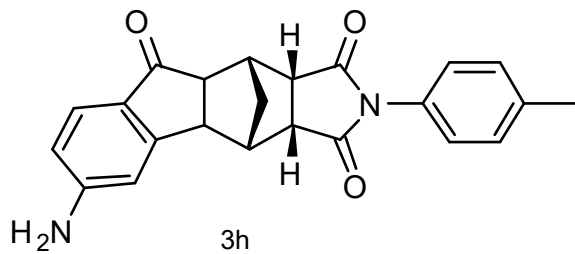
7.555  
7.533  
7.268  
7.248  
7.118  
7.097  
6.618  
6.595

4.447

3.421  
3.408  
3.397  
3.384  
3.372  
3.361  
3.348  
3.229  
3.213  
3.158  
3.146  
2.955  
2.944  
2.641  
2.626  
2.369

1.409  
1.381  
1.319  
1.292

-0.000



spect, CDCl3,		USER: nmr -- DATE: Wed Sep 06 08:23:58 2017				
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2469.1	PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	
					Nuts - \$pdata	

203.144

176.891  
176.111

158.171  
153.895

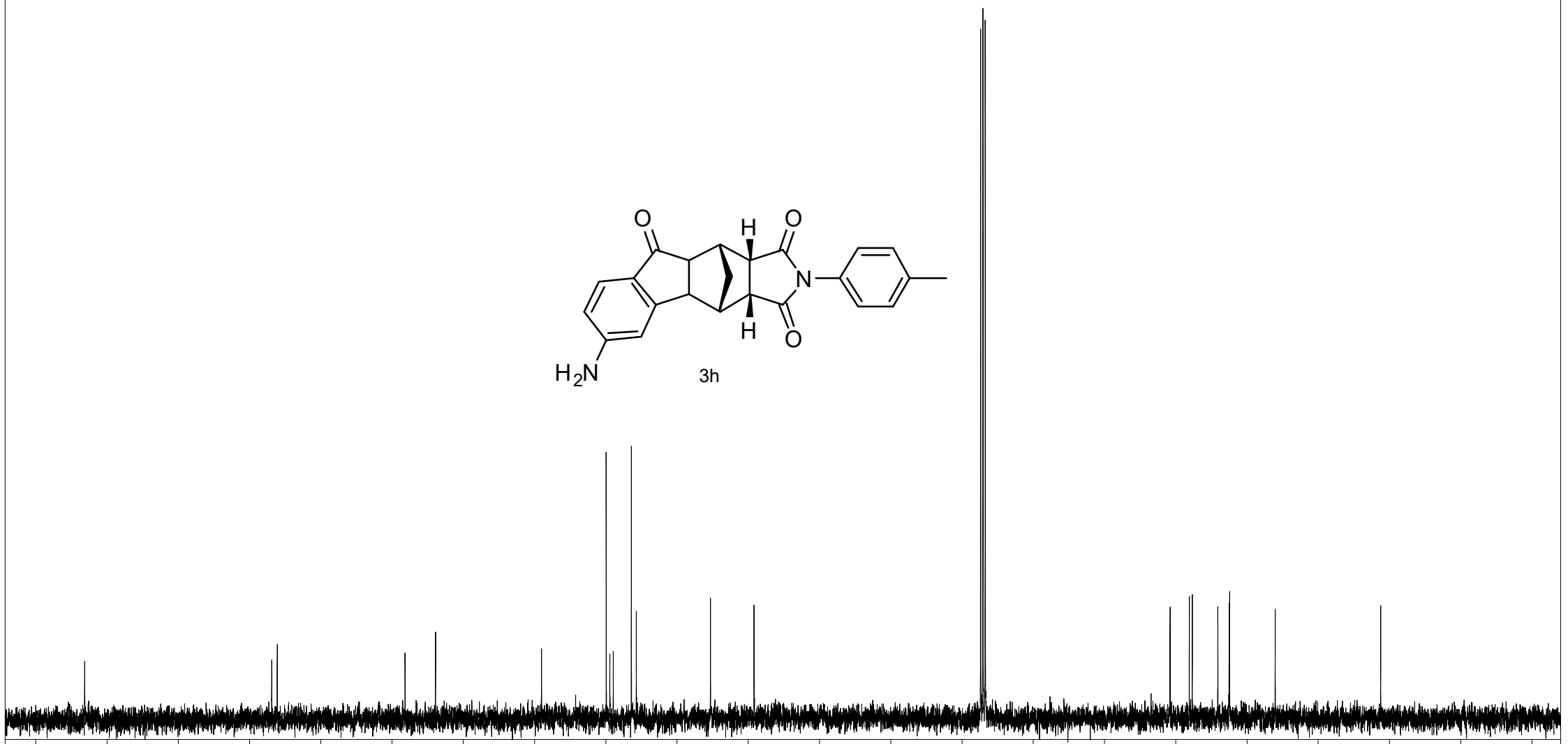
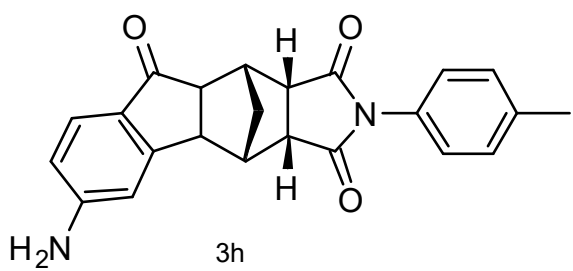
139.012  
129.945  
129.430  
128.942  
126.415  
125.718

115.306  
109.185

77.375  
77.063  
76.743

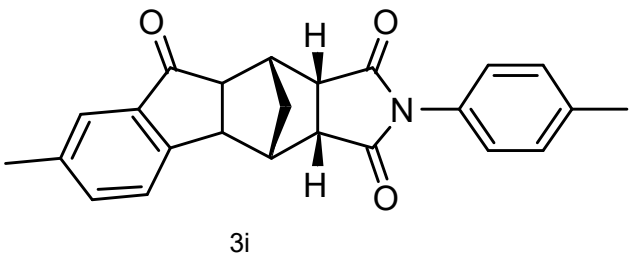
50.787  
48.086  
47.679  
44.084  
42.504  
42.442  
36.041

21.231



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Thu Sep 07 06:57:49 2017	
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 40
		LB: 0.0	PTS1d: 32768
			Nuts - \$pdata



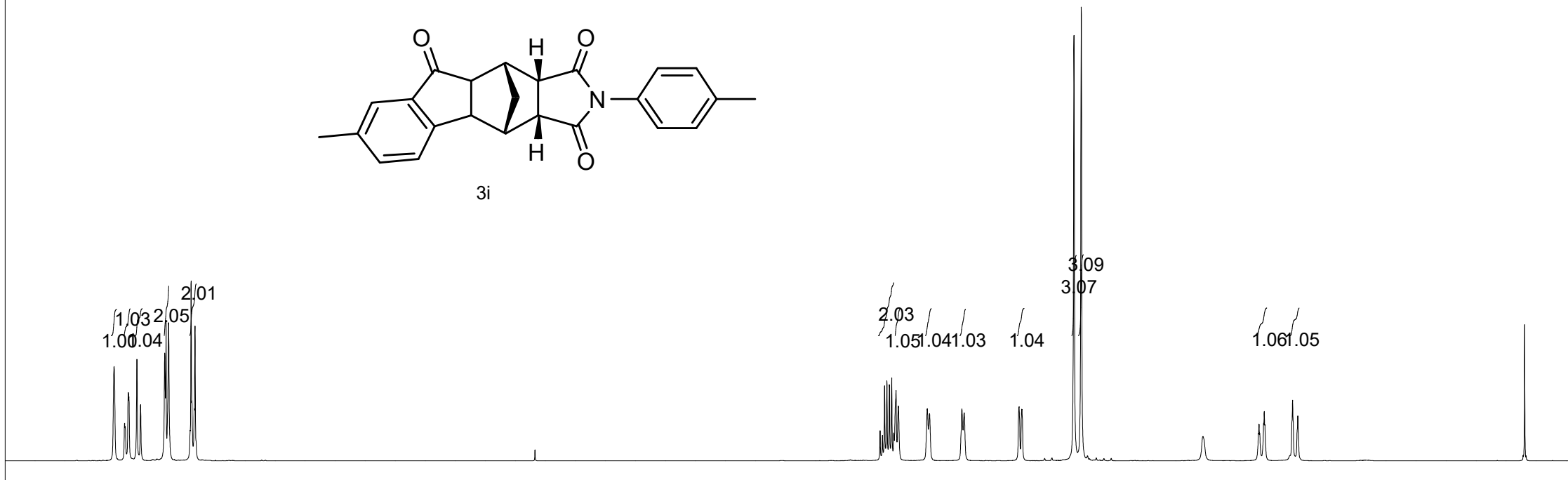


7.544  
7.487  
7.468  
7.422  
7.402  
7.273  
7.252  
7.131  
7.111

3.447  
3.434  
3.423  
3.411  
3.397  
3.385  
3.362  
3.349  
3.195  
3.182  
3.010  
2.997  
2.703  
2.688  
2.410  
2.371

1.420  
1.392  
1.241  
1.213

0.000



spect, CDCl3,		USER: nmr -- DATE: Wed Sep 06 08:14:50 2017				
F1: 400.132	F2: 1.000	SW1: 8224	OF1: 2468.5	PTS1d: 32768		
EX: zg30	PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$pdata	

205.878

176.704

175.906

152.401

139.087

139.006

138.368

136.889

129.935

128.921

126.365

125.888

123.553

77.383

77.069

76.751

50.827

48.022

47.548

44.081

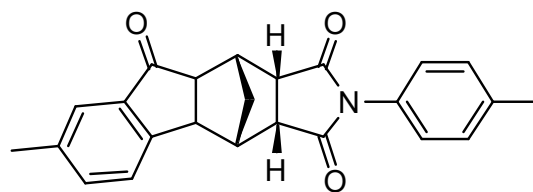
42.654

42.459

35.971

21.220

21.122



3i

200

150

100

50

PPM

spect, CDCl<sub>3</sub>,

USER: nmr -- DATE: Thu Sep 07 07:51:58 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

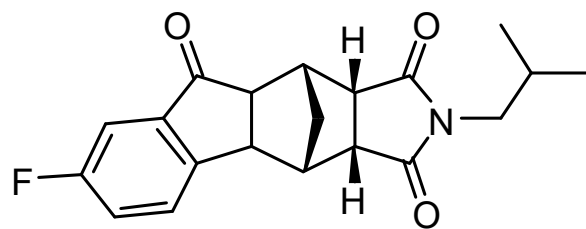
NA: 50

LB: 0.0

Nuts - \$pdata

7.533  
7.527  
7.522  
7.514  
7.509  
7.498  
7.397  
7.390  
7.372  
7.359  
7.352

3.346  
3.328  
3.308  
3.296  
3.284  
3.268  
3.255  
3.244  
3.231  
3.208  
3.193  
3.121  
3.110  
2.933  
2.921  
2.584  
2.569  
2.097  
2.079  
2.063  
2.045  
2.027  
2.011  
1.993  
1.414  
1.385  
1.207  
1.178  
0.908  
0.891

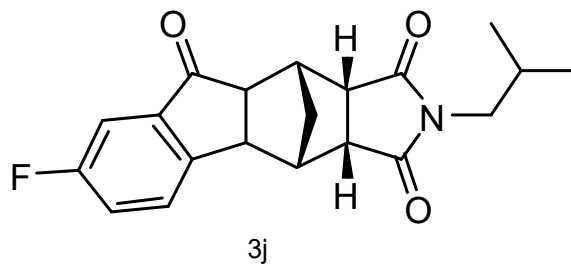


3j



spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 06 08:36:25 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2475.1		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

204.916  
204.882  
177.469  
176.687  
163.917  
161.439  
150.471  
150.451  
140.730  
140.658  
127.747  
127.665  
123.394  
123.164  
109.559  
109.340  
77.364  
77.036  
76.730  
51.268  
47.894  
47.417  
46.266  
43.429  
42.305  
42.237  
36.017  
27.194  
20.352

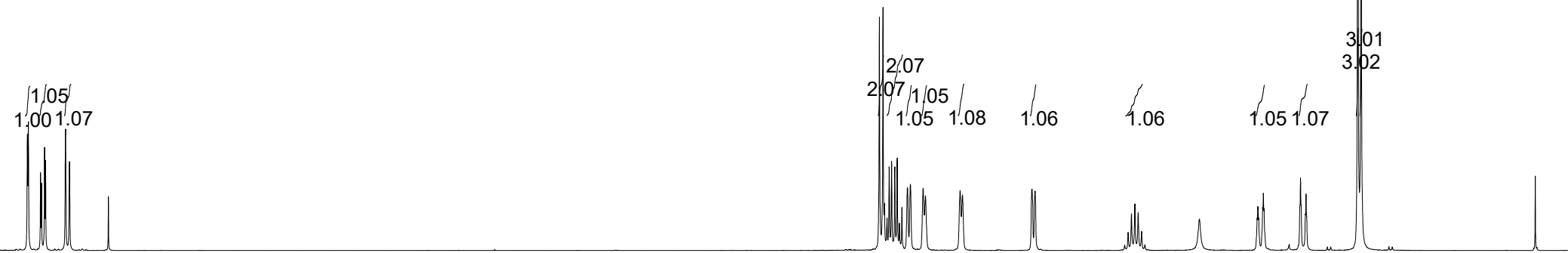
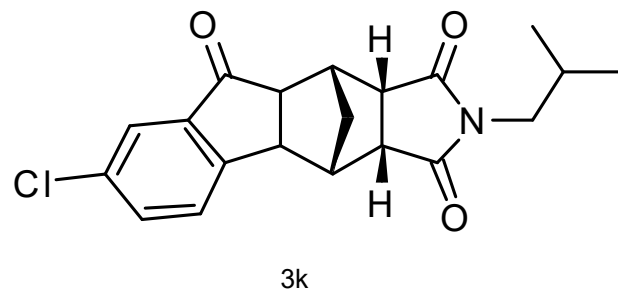


spect, CDCl3, USER: nmr -- DATE: Thu Sep 07 07:33:44 2017

F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0	PTS1d: 32768
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 40	LB: 0.0

7.691  
7.686  
7.624  
7.619  
7.603  
7.598  
7.496  
7.476

3.345  
3.327  
3.295  
3.282  
3.266  
3.254  
3.230  
3.202  
3.187  
3.122  
3.109  
3.109  
2.933  
2.921  
2.566  
2.550  
2.094  
2.076  
2.059  
2.042  
2.025  
2.008  
1.990  
1.414  
1.387  
1.194  
1.169  
0.906  
0.888

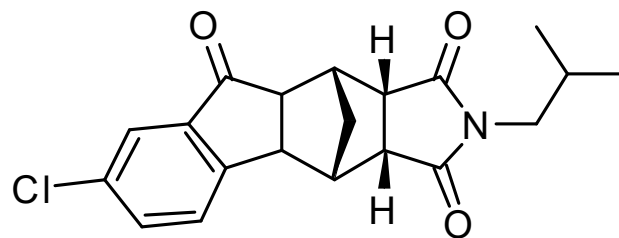


spect, CDCl3,				USER: nmr -- DATE: Wed Sep 06 09:04:21 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2473.2		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

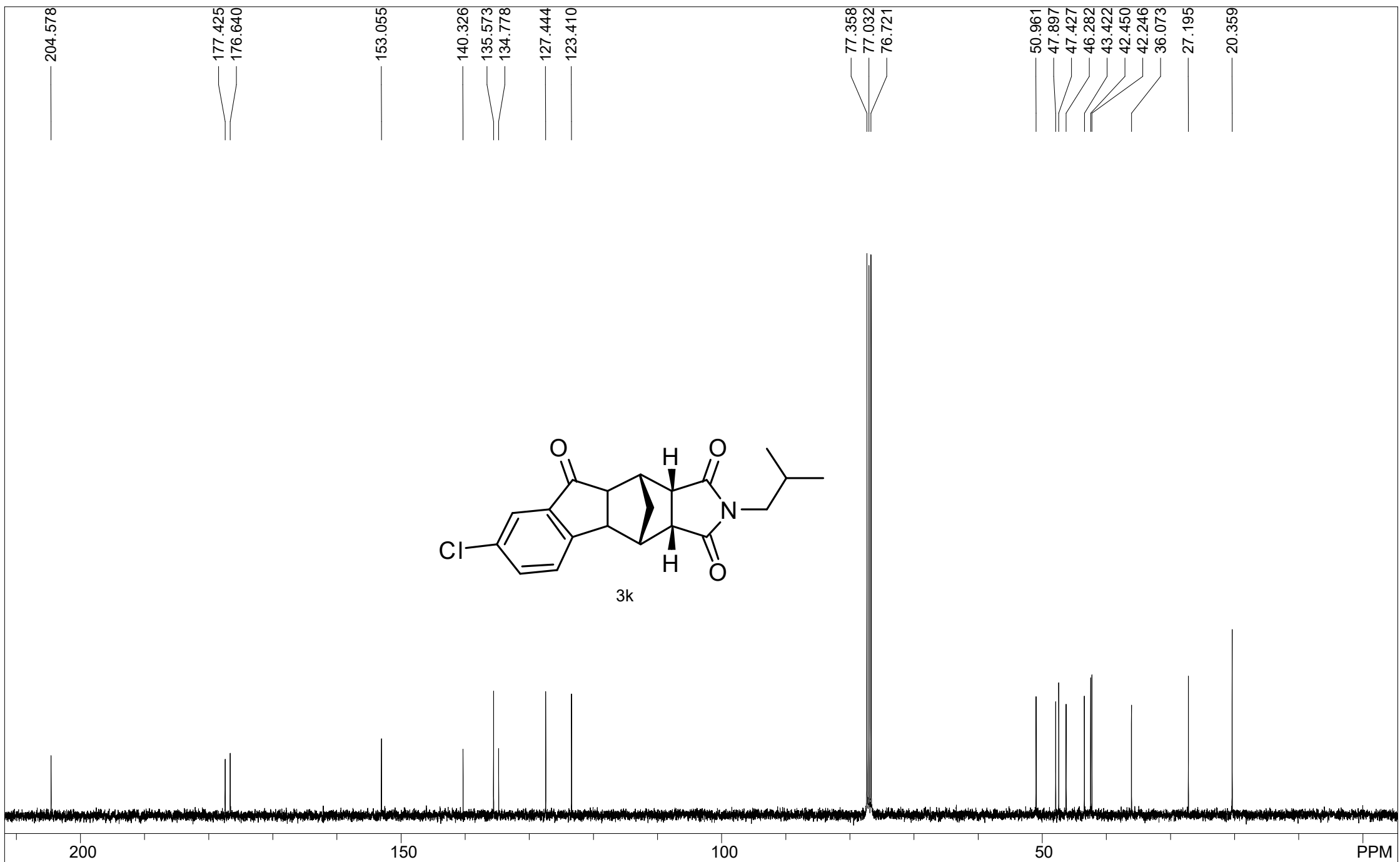
204.578

177.425  
176.640

153.055

140.326  
135.573  
134.778127.444  
123.41077.358  
77.032  
76.72150.961  
47.897  
47.427  
46.282  
43.422  
42.450  
42.246  
36.073  
27.195  
20.359

3k



200

150

100

50

PPM

spect, CDCl<sub>3</sub>,

USER: nmr -- DATE: Thu Sep 07 07:18:13 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

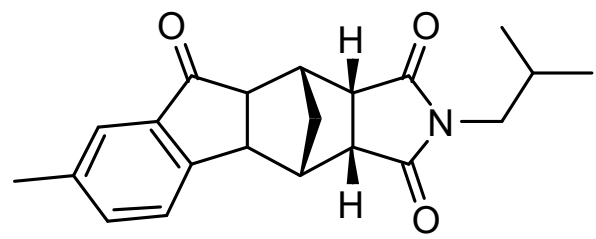
NA: 114

LB: 0.0

Nuts - \$pdata

7.528  
7.480  
7.478  
7.461  
7.458  
7.422  
7.402

3.341  
3.323  
3.292  
3.279  
3.268  
3.255  
3.245  
3.233  
3.222  
3.209  
3.181  
3.167  
3.103  
3.091  
2.914  
2.903  
2.524  
2.508  
2.404  
2.094  
2.077  
2.059  
2.043  
2.026  
2.008  
1.991  
1.364  
1.336  
1.199  
1.172  
0.902  
0.885  
-0.000



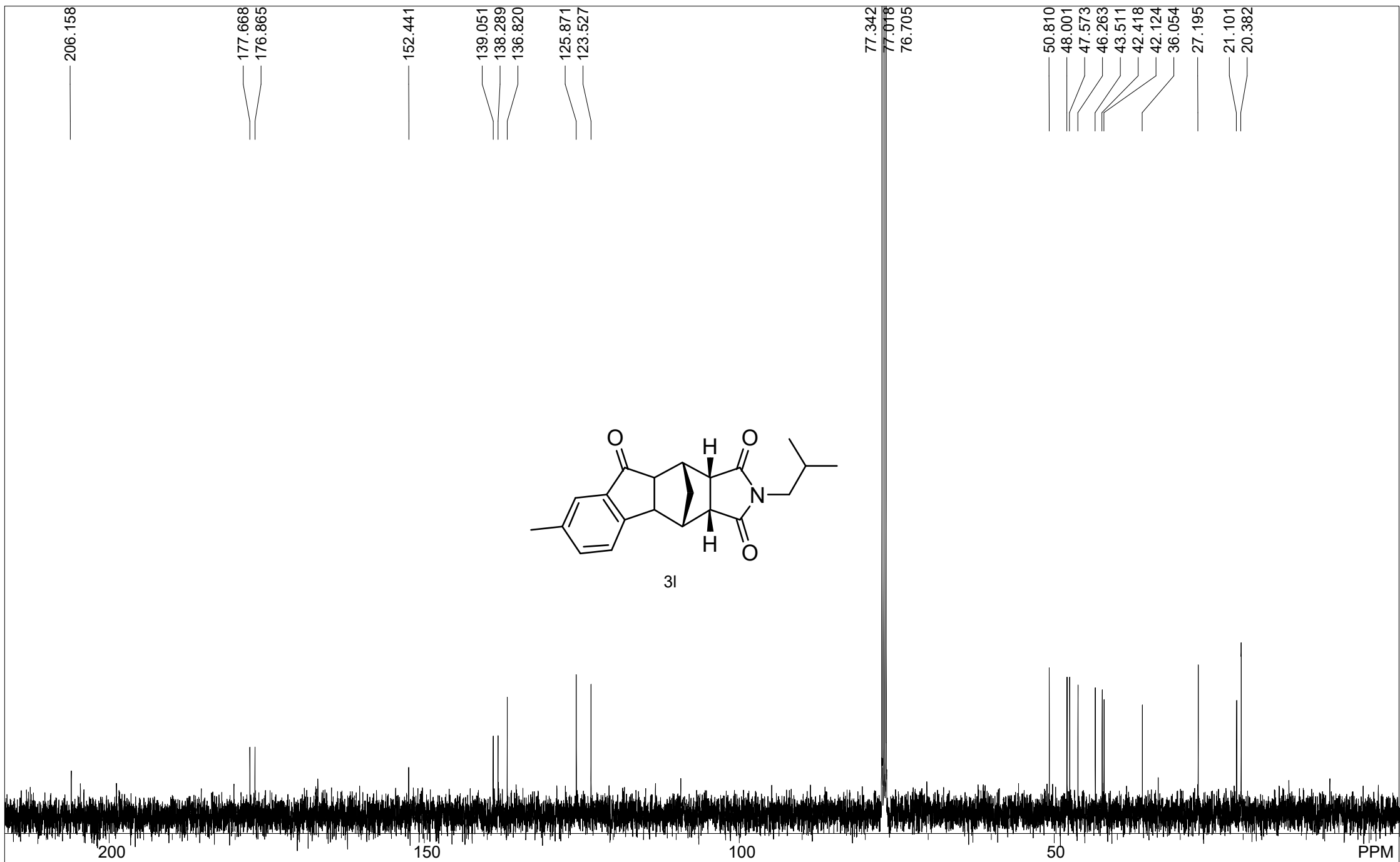
3I

1.03  
1.04  
1.00

2.01  
2.05  
1.01  
1.02  
1.00  
3.01  
1.04  
1.01  
1.02  
3.04  
3.00

8 7 6 5 4 3 2 1 PPM

spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 06 08:28:05 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2468.5		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

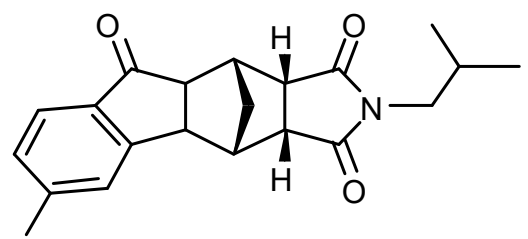


spect, CDC13,				USER: nmr -- DATE: Thu Sep 07 07:07:35 2017			
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 80	LB: 0.0		Nuts - \$pdata

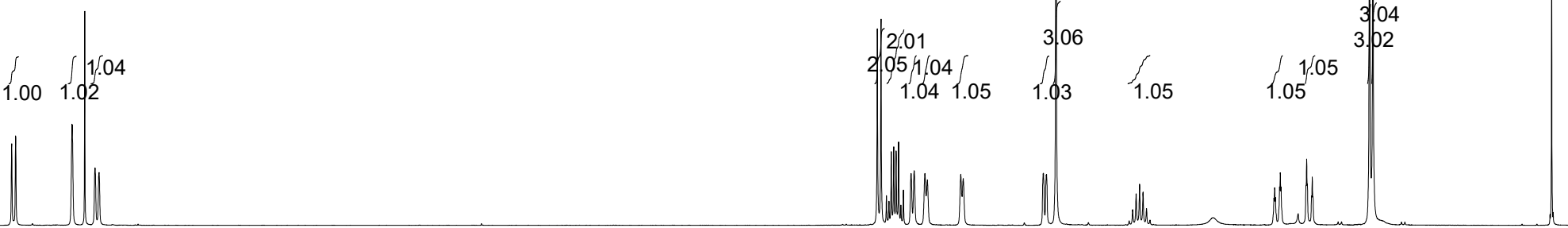


7.633  
7.613  
7.334  
7.332  
7.219  
7.200

3.341  
3.323  
3.296  
3.284  
3.272  
3.260  
3.249  
3.236  
3.225  
3.213  
3.174  
3.159  
3.105  
3.094  
2.928  
2.915  
2.518  
2.503  
2.456  
2.093  
2.076  
2.058  
2.042  
2.025  
2.008  
1.991  
1.373  
1.345  
1.214  
1.186  
0.903  
0.886  
0.000



3m



spect, CDCl3,			USER: nmr -- DATE: Wed Sep 06 08:01:09 2017				
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2470.4		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

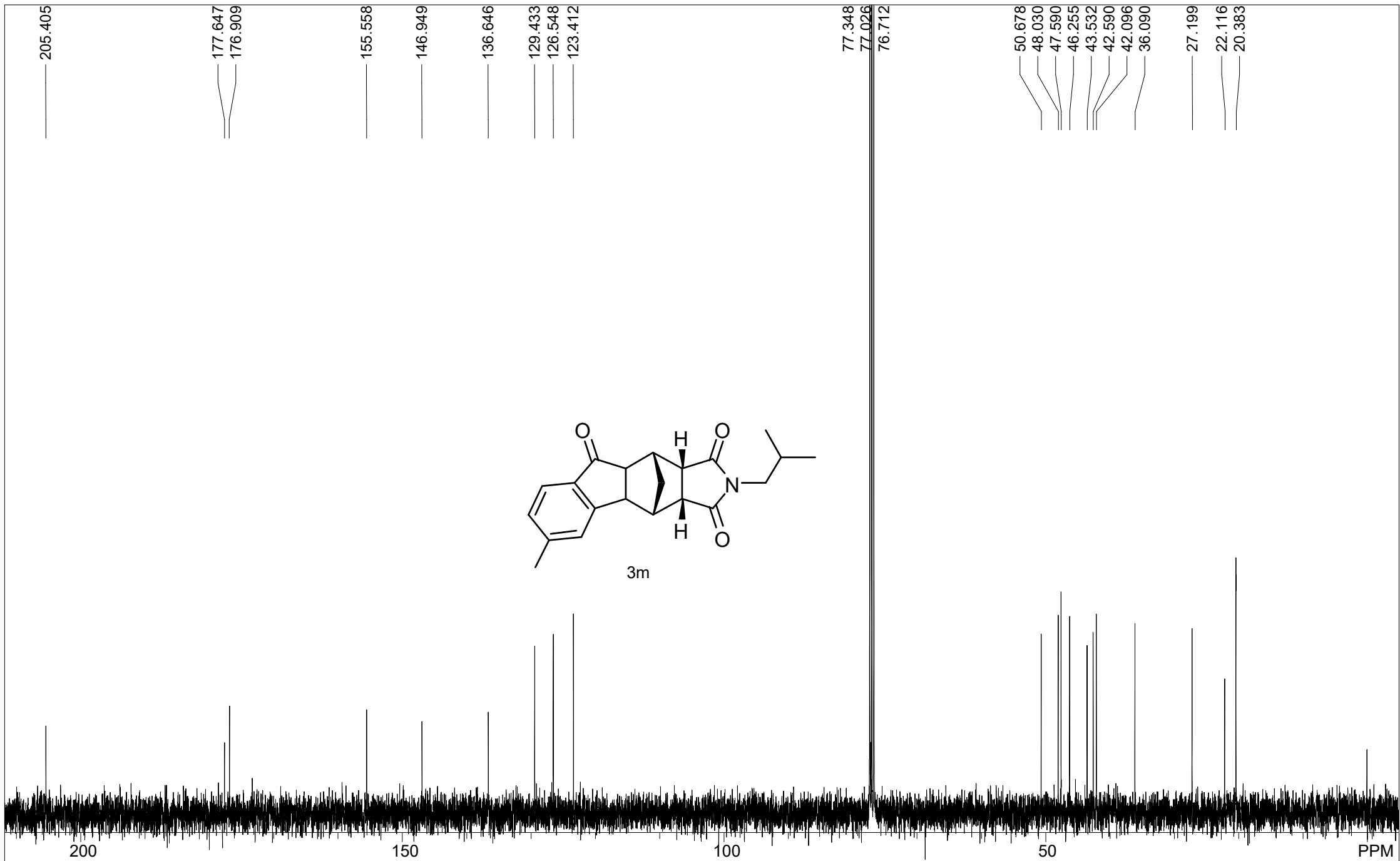
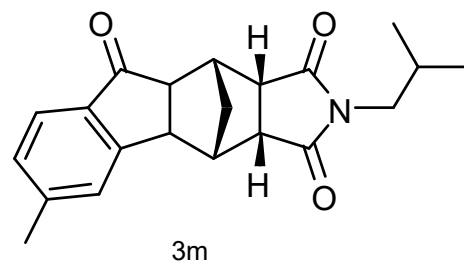
205.405

177.647  
176.909

155.558

146.949

136.646

129.433  
126.548  
123.41277.348  
77.026  
76.71250.678  
48.030  
47.590  
46.255  
43.532  
42.590  
42.096  
36.09027.199  
22.116  
20.383

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 06:41:36 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

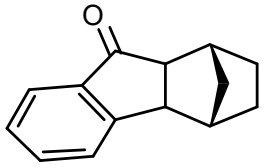
NA: 50

LB: 0.0

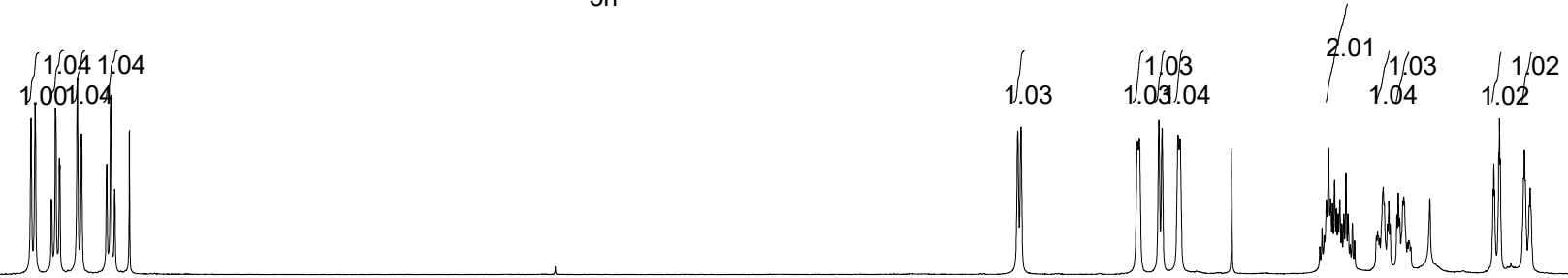
Nuts - \$pdata

7.723  
7.704  
7.629  
7.610  
7.592  
7.509  
7.490  
7.373  
7.355  
7.336

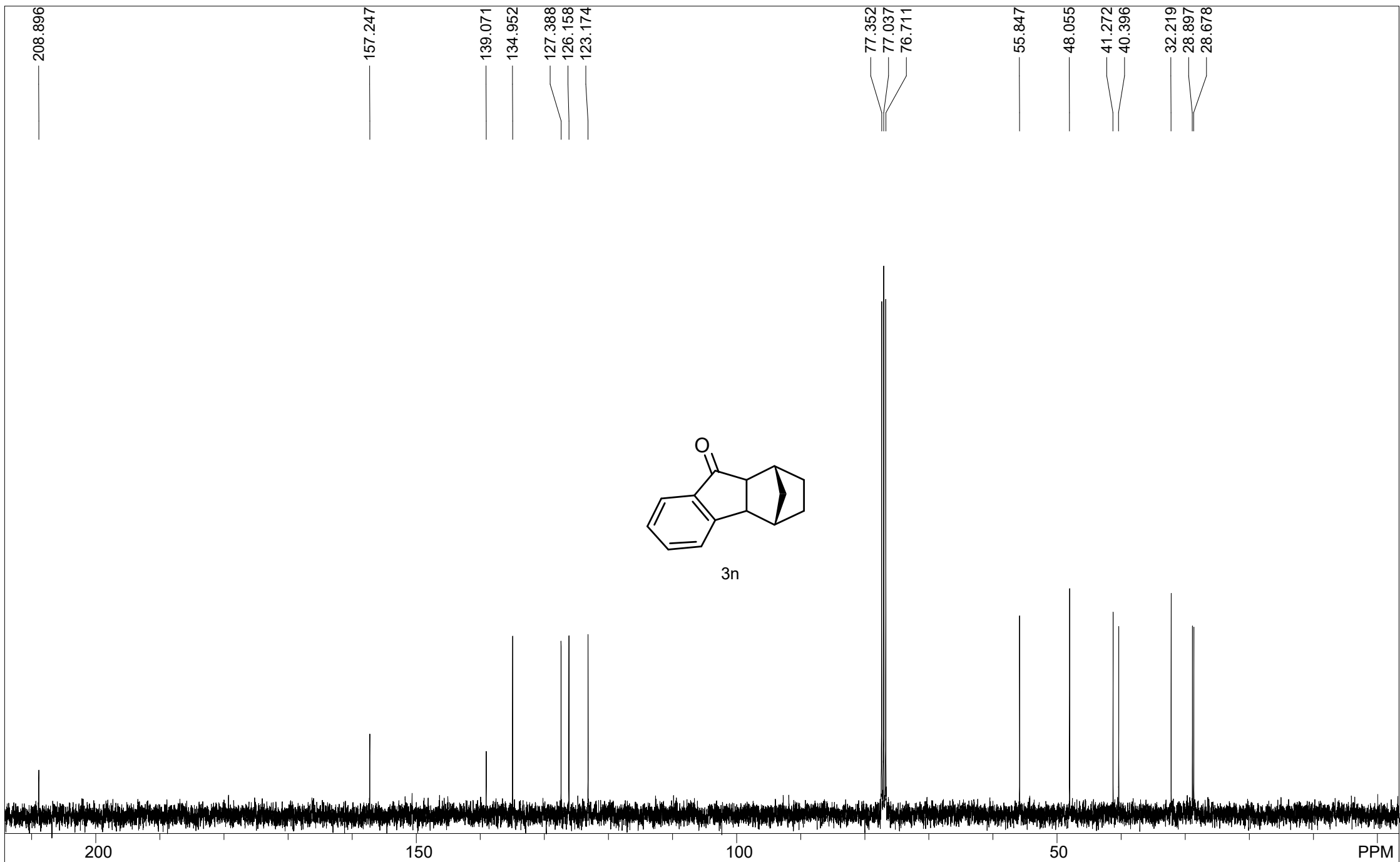
3.161  
3.146  
2.607  
2.598  
2.508  
2.493  
2.419  
2.410  
1.764  
1.724  
1.705  
1.695  
1.653  
1.643  
1.613  
1.602  
1.502  
1.471  
1.465  
1.444  
1.439  
1.408  
1.401  
1.381  
1.352  
1.343  
0.963  
0.959  
0.956  
0.936  
0.933  
0.929  
0.822  
0.818  
0.814  
0.795  
0.792  
0.788  
-0.000



3n



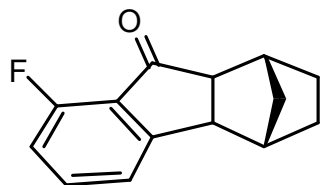
spect, CDCl3,				USER: nmr -- DATE: Wed Sep 13 07:22:22 2017	
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2469.3	PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0
					Nuts - \$pdata



spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Thu Sep 14 07:00:20 2017			
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 60	LB: 0.0		Nuts - \$pdata

7.601  
7.588  
7.582  
7.569  
7.562  
7.550  
7.279  
7.261  
6.983  
6.961  
6.939

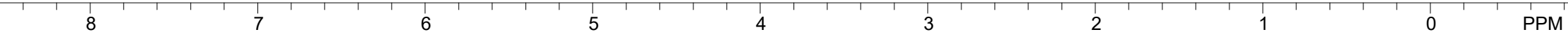
3.166  
3.150  
2.639  
2.629  
2.529  
2.514  
2.427  
2.416  
1.764  
1.734  
1.724  
1.695  
1.672  
1.643  
1.633  
1.602  
1.491  
1.475  
1.459  
1.433  
1.396  
1.390  
1.362  
1.331  
1.008  
1.005  
1.001  
0.982  
0.978  
0.975  
0.908  
0.903  
0.900  
0.882  
0.877  
0.873  
0.000



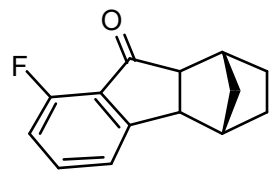
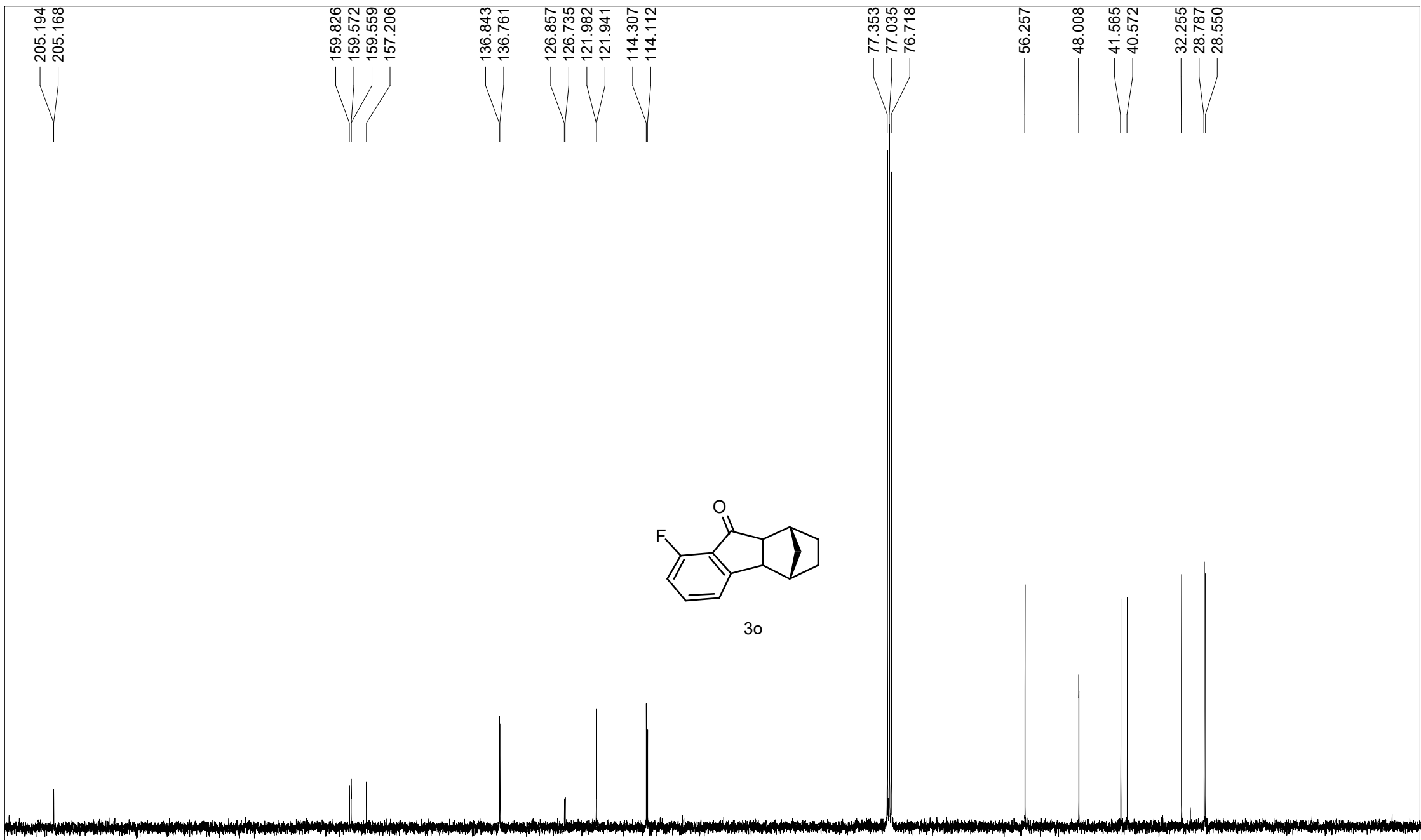
3o

1.00 1.05 1.00

1.02 1.01 1.02 1.02 2.04 1.02 1.02 1.05



spect, CDCl3,		USER: nmr -- DATE: Wed Sep 13 06:47:50 2017				
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2471.0		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$pdata

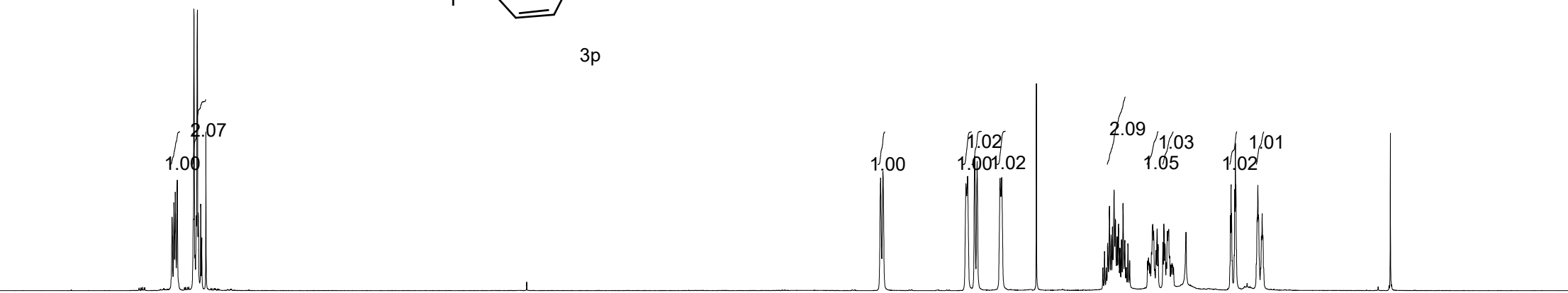
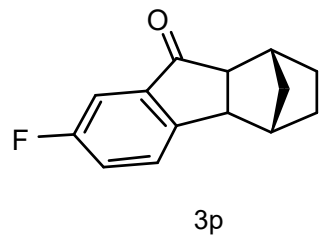


3o

spect, CDCl3,		USER: nmr -- DATE: Thu Sep 14 08:31:57 2017			
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0	PTS1d: 32768	
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 160	LB: 0.0	Nuts - \$pdata

7.480  
7.469  
7.460  
7.449  
7.346  
7.331  
7.324  
7.319  
7.304  
7.297

3.131  
3.115  
2.606  
2.596  
2.552  
2.538  
2.396  
2.386  
1.755  
1.736  
1.725  
1.697  
1.688  
1.651  
1.641  
1.631  
1.600  
1.491  
1.467  
1.453  
1.432  
1.396  
1.391  
1.370  
1.355  
1.332  
0.982  
0.978  
0.975  
0.955  
0.952  
0.948  
0.818  
0.814  
0.810  
0.791  
0.787  
0.783  
0.000



spect, CDCl<sub>3</sub>, USER: nmr -- DATE: Wed Sep 13 07:04:02 2017

F1: 400.132	F2: 1.000	SW1: 8224	OF1: 2471.0	PTS1d: 32768
EX: zg30	PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0
				Nuts - \$pdata

207.811  
207.783

163.543  
161.076

152.678  
152.658

140.874  
140.797

127.569  
127.488  
122.744  
122.508

108.995  
108.789

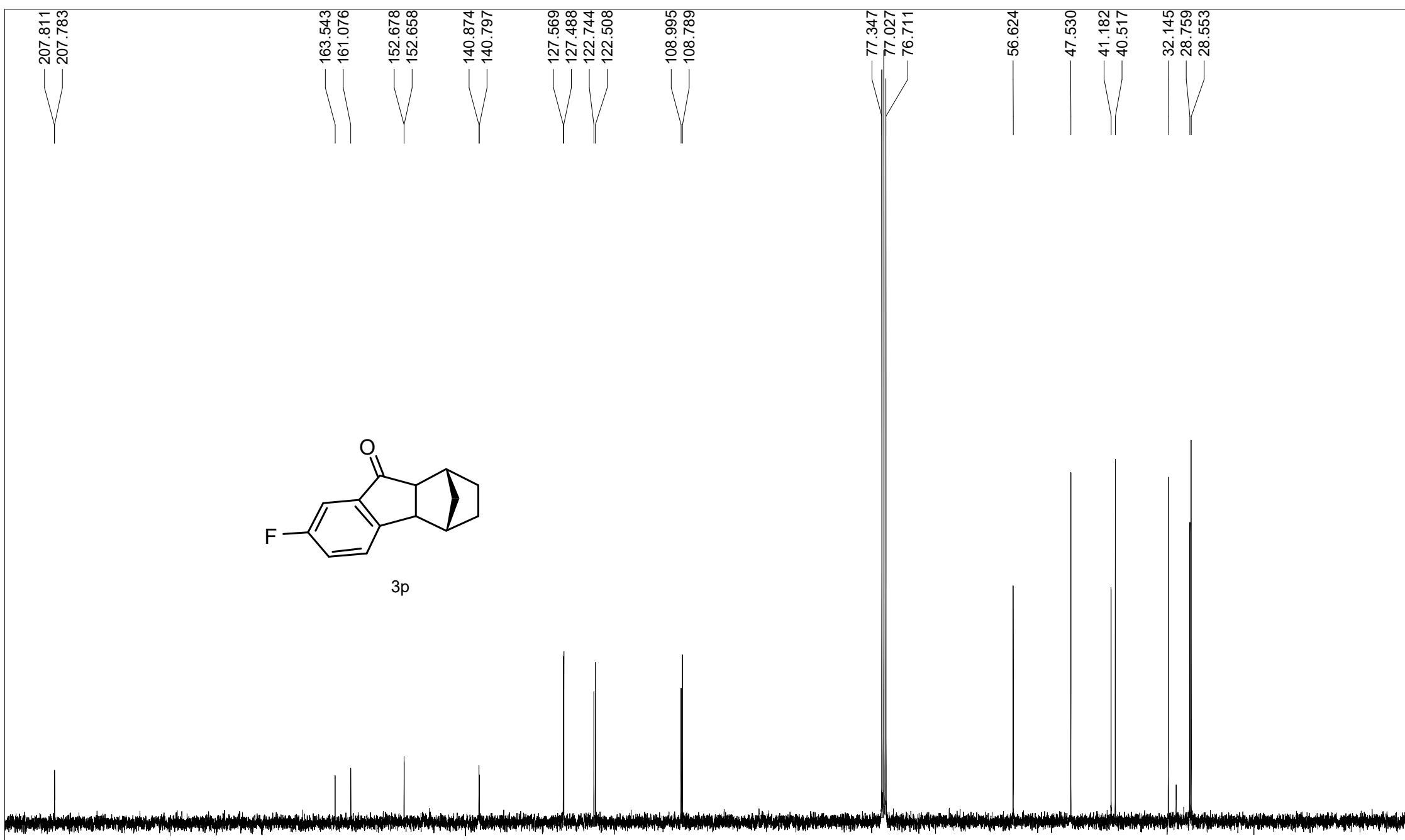
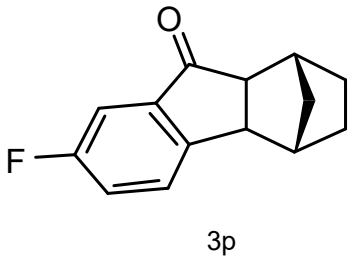
77.347  
77.027  
76.711

56.624

47.530

41.182  
40.517

32.145  
28.759  
28.553



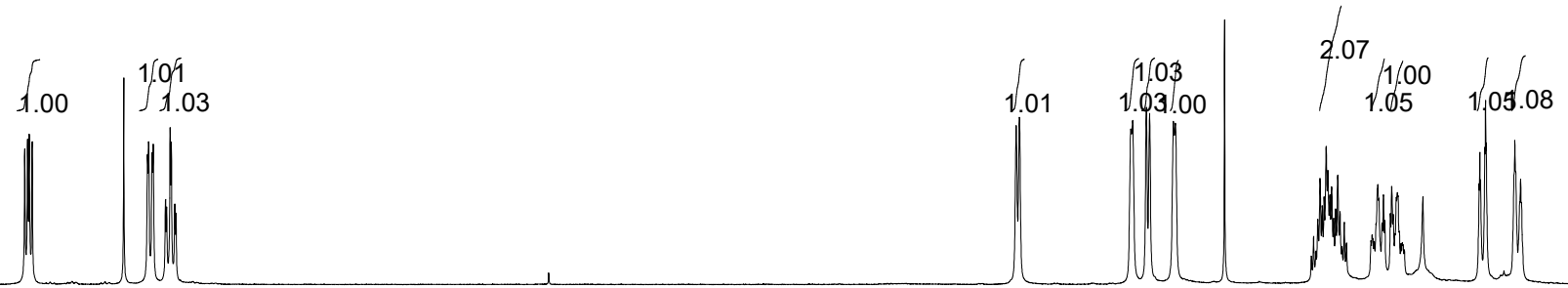
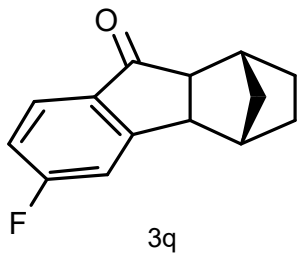
200 150 100 50 PPM

spect, CDCl3,		USER: nmr -- DATE: Thu Sep 14 08:18:15 2017			
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0	PTS1d: 32768	
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 180	LB: 0.0	Nuts - \$pdata



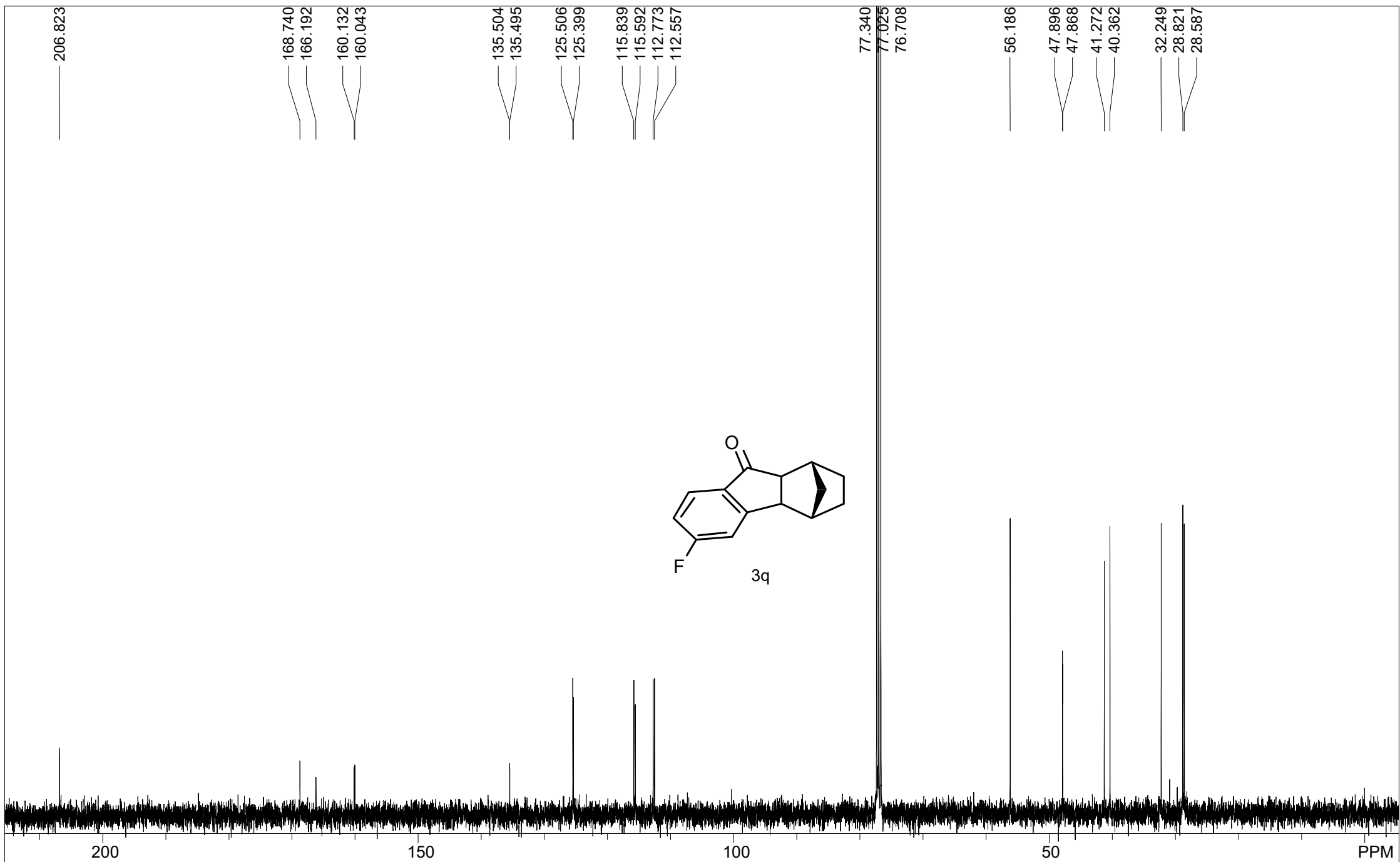
7.729  
7.716  
7.708  
7.694  
7.160  
7.155  
7.138  
7.134  
7.076  
7.072  
7.055  
7.050  
7.034  
7.029

3.138  
3.123  
2.607  
2.598  
2.535  
2.520  
2.410  
2.400  
1.771  
1.731  
1.703  
1.678  
1.649  
1.638  
1.609  
1.495  
1.490  
1.463  
1.437  
1.431  
1.405  
1.399  
1.373  
1.364  
1.341  
0.995  
0.991  
0.988  
0.968  
0.965  
0.962  
0.833  
0.830  
0.825  
0.807  
0.803  
0.799  
0.000



8 6 4 2 0 PPM

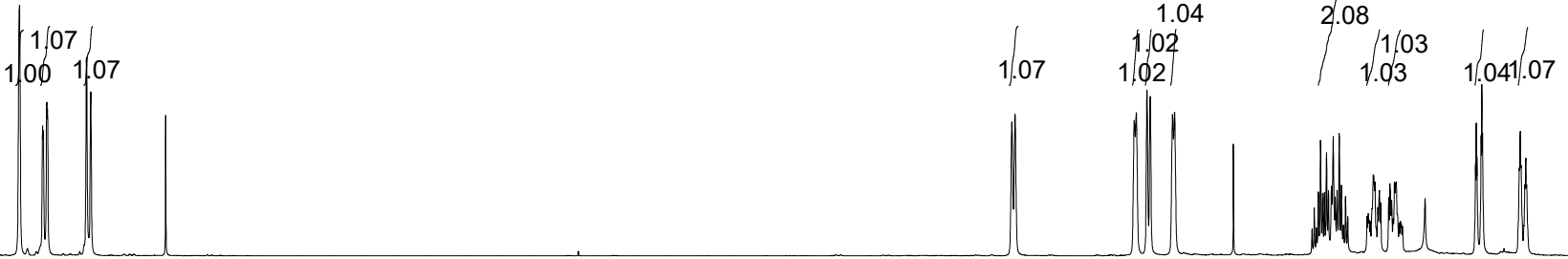
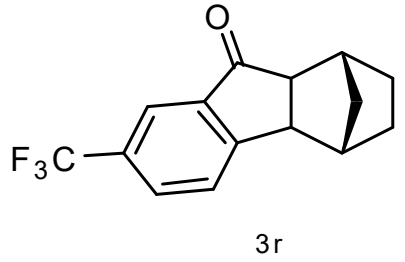
spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 13 07:26:10 2017	
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2470.1	PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0
					Nuts - \$pdata



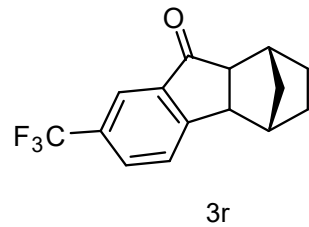
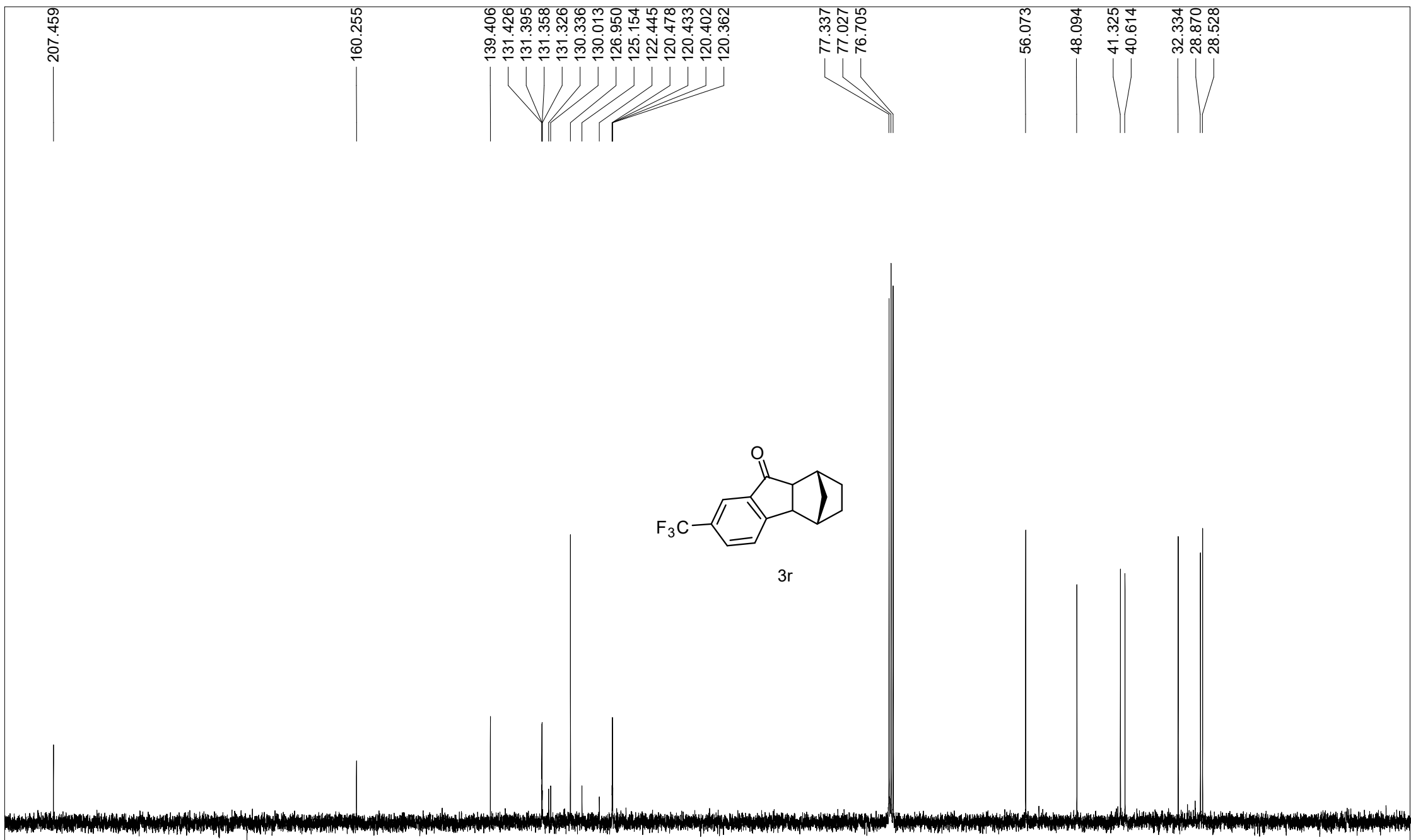
spect, CDCl3,		USER: nmr -- DATE: Thu Sep 14 07:10:39 2017	
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 100
		LB: 0.0	PTS1d: 32768
			Nuts - \$pdata

7.973  
7.863  
7.860  
7.843  
7.840  
7.654  
7.653  
7.634  
7.633

3.232  
3.216  
2.647  
2.638  
2.586  
2.571  
2.464  
2.454  
1.797  
1.786  
1.757  
1.728  
1.696  
1.667  
1.627  
1.535  
1.529  
1.505  
1.497  
1.469  
1.431  
1.404  
1.394  
1.381  
1.365  
1.016  
1.012  
1.009  
0.989  
0.986  
0.982  
0.807  
0.803  
0.798  
0.780  
0.775  
0.772  
0.000



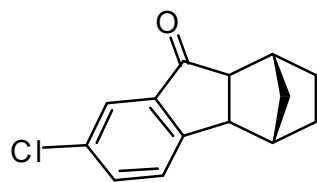
spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 13 07:30:21 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2472.2		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Thu Sep 14 07:18:04 2017	
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 60
			LB: 0.0
			PTS1d: 32768
			Nuts - \$pdata

7.664  
7.659  
7.572  
7.567  
7.552  
7.547  
7.448  
7.428

3.129  
3.115  
2.606  
2.596  
2.537  
2.522  
2.400  
2.390  
1.756  
1.736  
1.726  
1.697  
1.671  
1.662  
1.642  
1.632  
1.612  
1.601  
1.492  
1.460  
1.454  
1.441  
1.434  
1.398  
1.392  
1.377  
1.363  
1.339  
0.985  
0.981  
0.978  
0.958  
0.955  
0.951  
0.811  
0.806  
0.802  
0.784  
0.780  
0.776  
-0.000



3s

1.03  
1.00  
1.07

1.06

1.04  
1.01  
1.05

2.02  
1.06  
1.04

1.01  
1.02

8

6

4

2

0

PPM

spect, CDCl<sub>3</sub>,

USER: nmr -- DATE: Wed Sep 13 07:12:56 2017

F1: 400.132

F2: 1.000

SW1: 8224

OF1: 2470.2

PTS1d: 32768

EX: zg30

PW: 14.7 usec

PD: 1.0 sec

NA: 8

LB: 0.0

Nuts - \$pdata

207.414

155.252

140.553

134.937

133.843

127.374

122.979

77.349

77.031

76.717

56.317

47.661

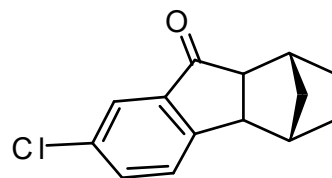
41.199

40.514

32.228

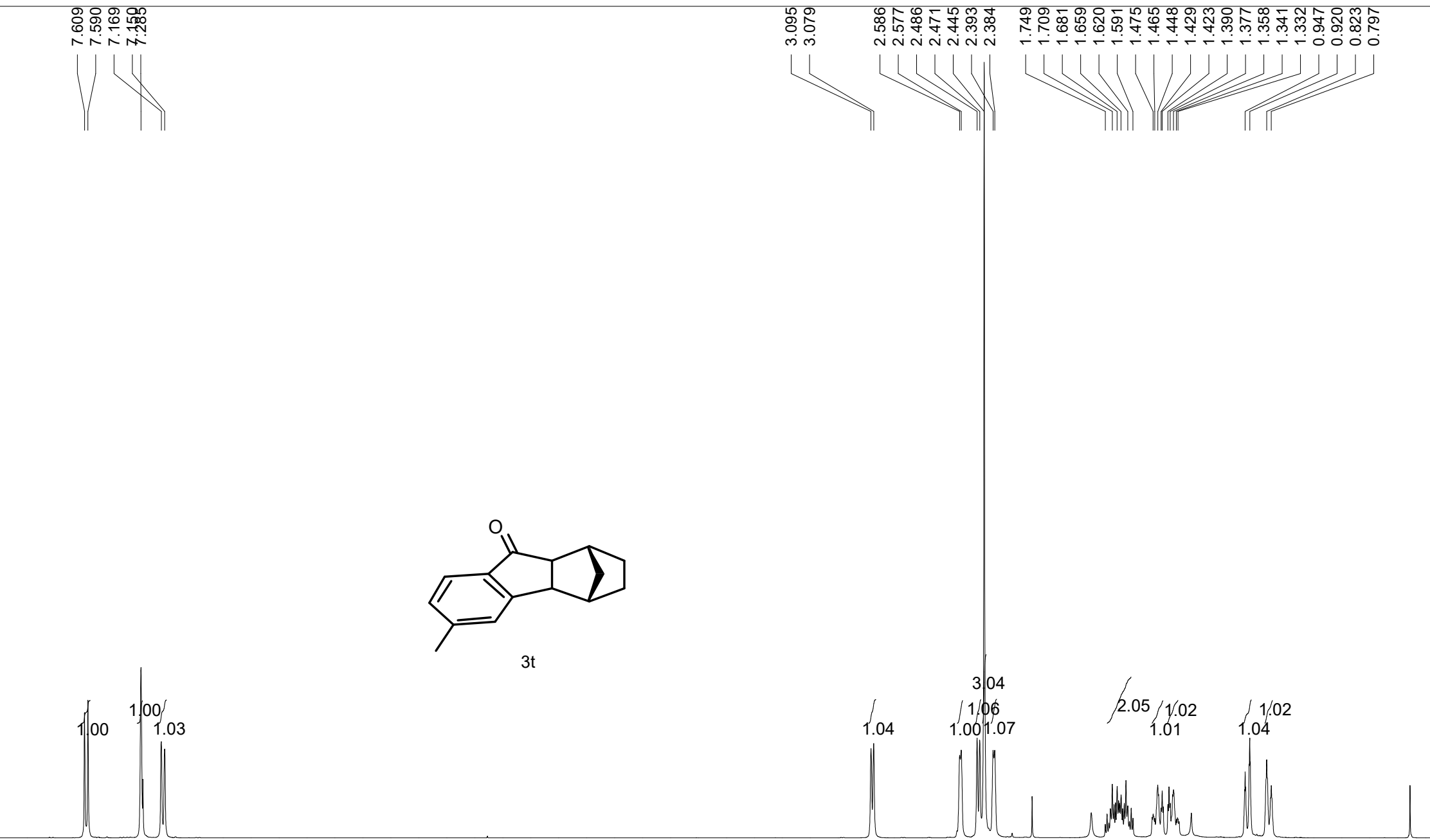
28.808

28.551



3s

spect, CDCl3,				USER: nmr -- DATE: Thu Sep 14 07:48:06 2017			
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 80	LB: 0.0		Nuts - \$pdata



spect, CDCl3,				USER: nmr -- DATE: Wed Sep 13 06:55:56 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2471.9		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

208.333

157.754

146.106

136.839

128.707

126.473

122.998

77.376

77.057

76.739

56.076

47.879

41.240

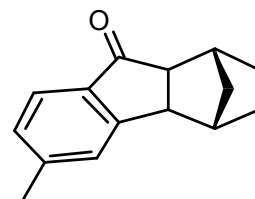
40.270

32.196

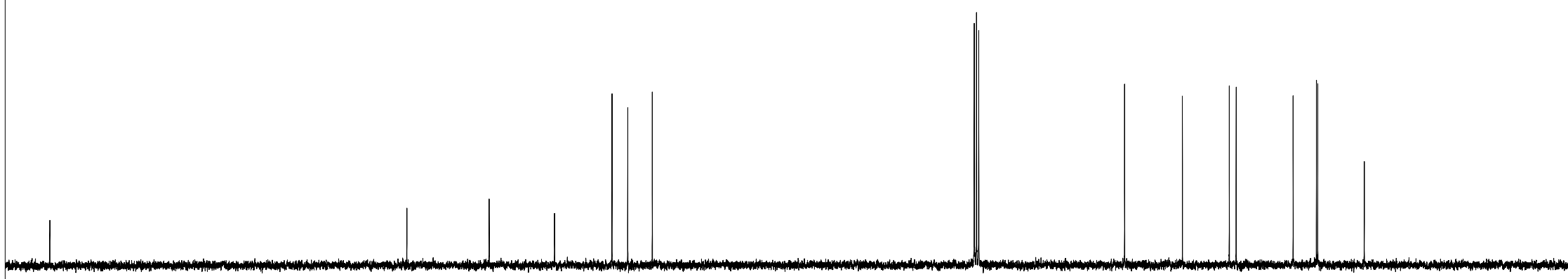
28.895

28.706

22.111



3t



200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 07:24:40 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

NA: 50

LB: 0.0

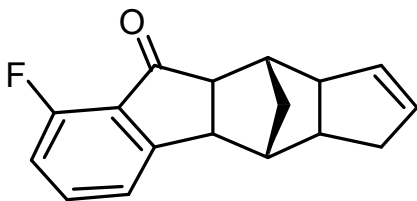
Nuts - \$pdata



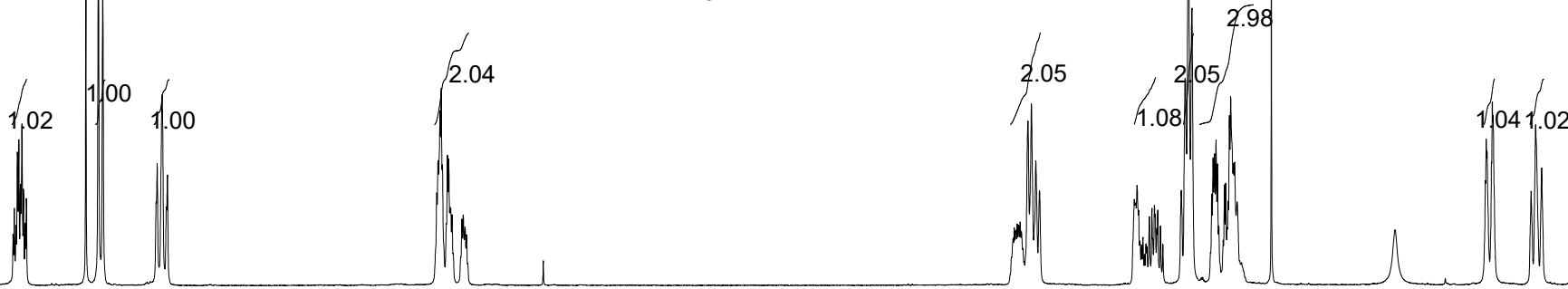
7.581  
7.575  
7.562  
7.556  
7.543  
7.524  
7.214  
7.195  
6.962  
6.941  
6.918

5.760  
5.746  
5.741  
5.736  
5.714  
5.708  
5.694  
5.652  
5.646  
5.632

3.283  
3.270  
3.252  
3.246  
3.218  
3.204  
3.168  
2.761  
2.750  
2.738  
2.711  
2.686  
2.661  
2.639  
2.560  
2.544  
2.529  
2.514  
2.429  
2.411  
2.399  
2.380  
2.353  
2.348  
2.331  
2.319  
1.253  
1.250  
1.247  
1.227  
1.223  
1.220  
1.057  
1.037  
1.011  
-0.000



3u



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Wed Sep 13 06:51:51 2017			
F1: 400.132	F2: 1.000	SW1: 8224	OF1: 2469.3	PTS1d: 32768	
EX: zg30	PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$pdata

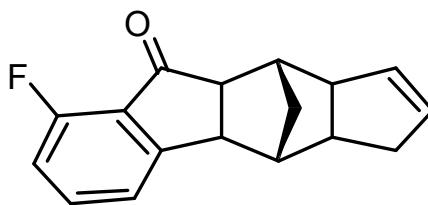
206.214  
206.200

160.483  
160.466  
157.190

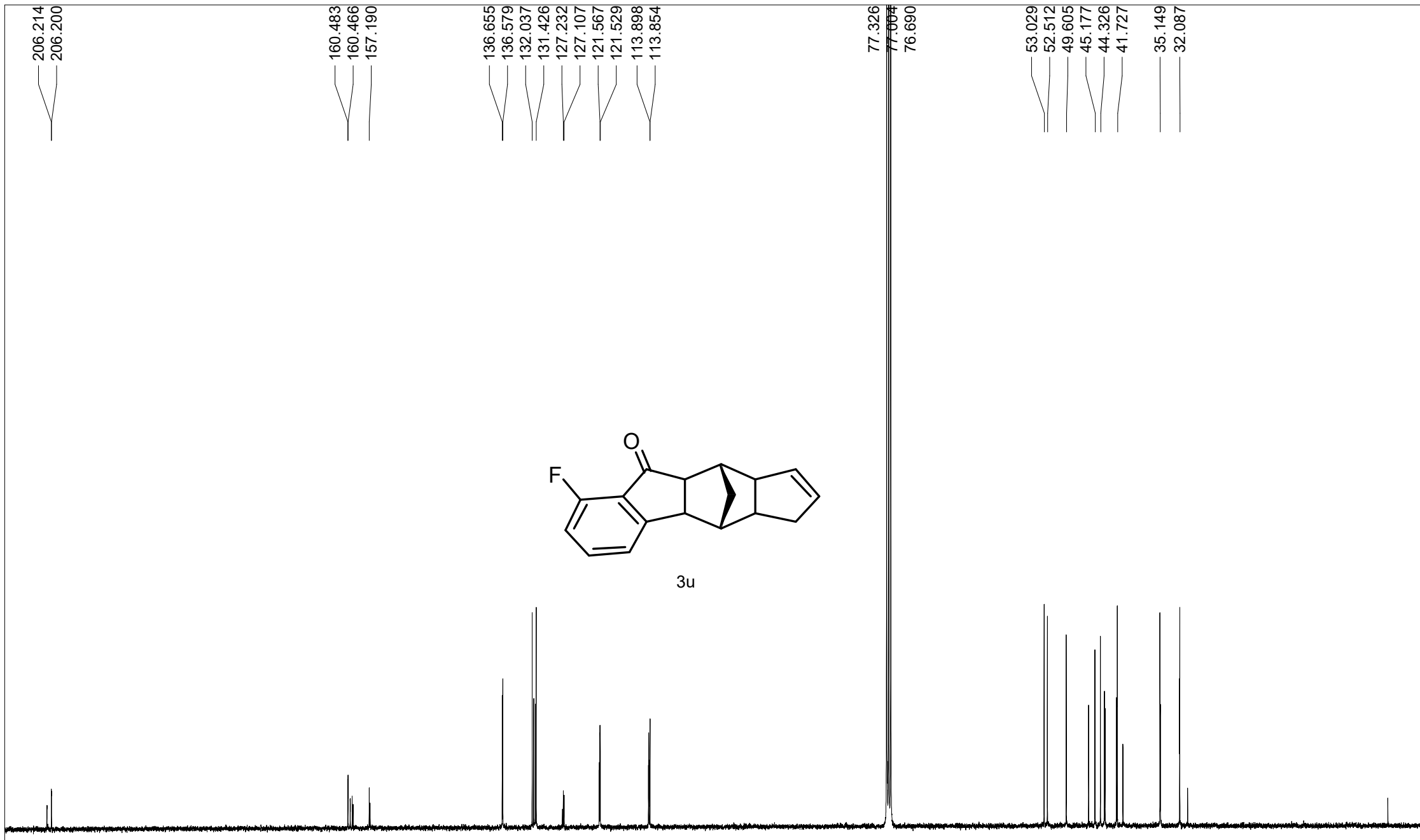
136.655  
136.579  
132.037  
131.426  
127.232  
127.107  
121.567  
121.529  
113.898  
113.854

77.326  
77.004  
76.690

53.029  
52.512  
49.605  
45.177  
44.326  
41.727  
35.149  
32.087



3u



200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 13:31:58 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

PD: 2.0 sec

NA: 5000

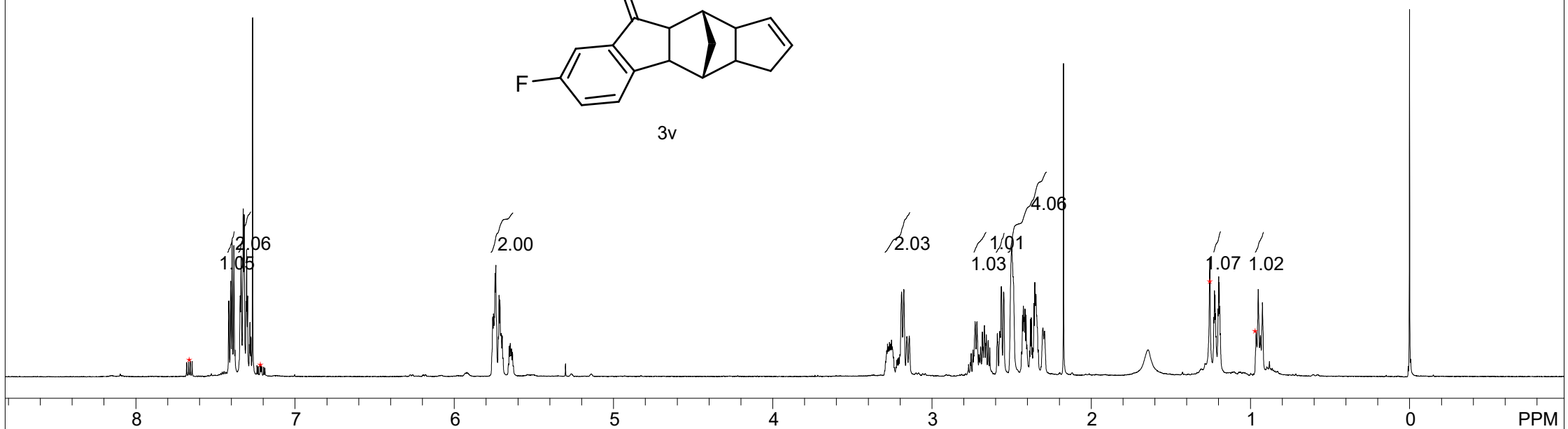
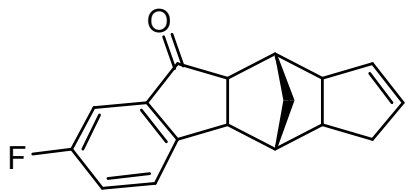
LB: 0.0

Nuts - \$pdata

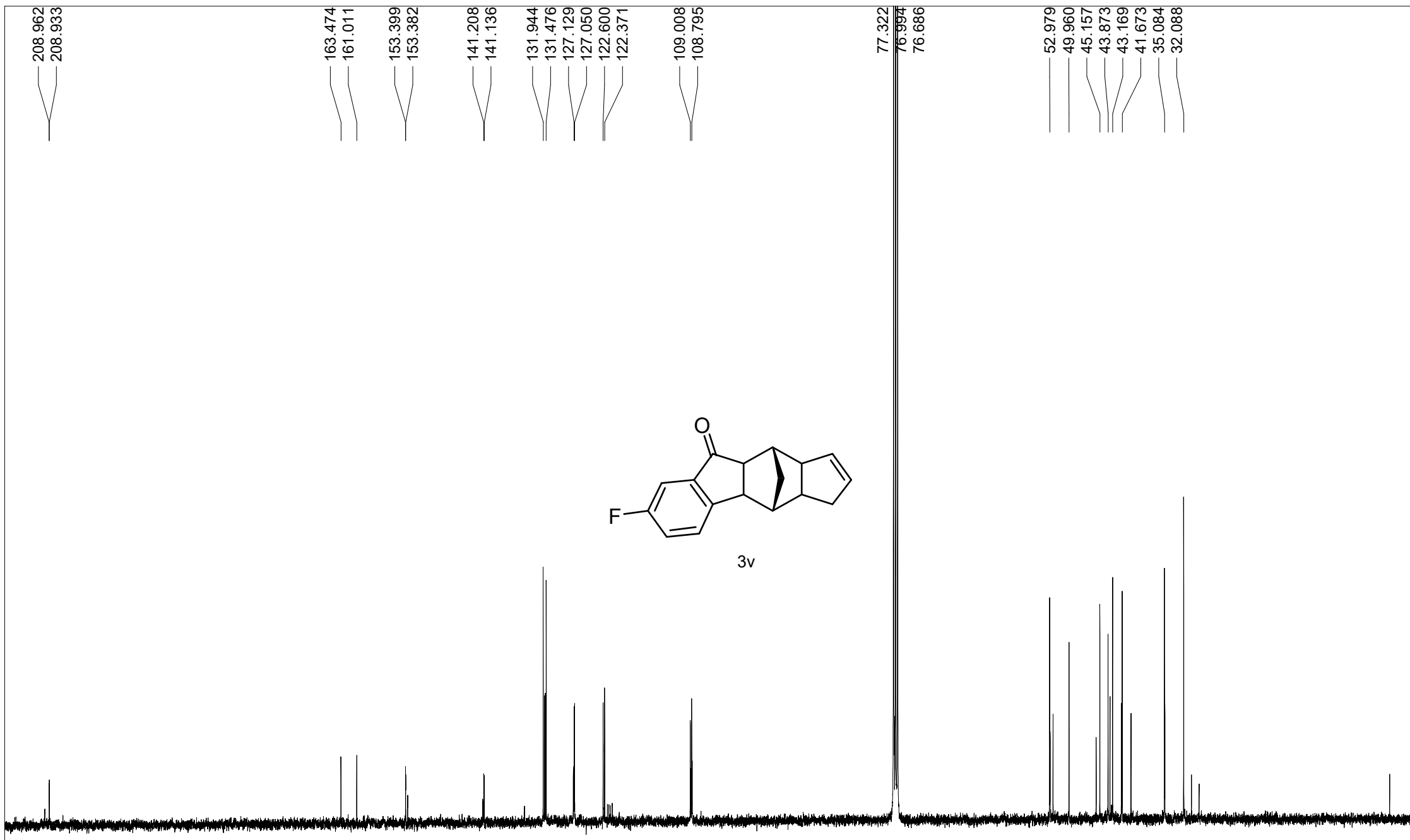
7.415  
7.405  
7.396  
7.383  
7.345  
7.339  
7.325  
7.319  
7.304  
7.298  
7.283  
7.277

5.759  
5.744  
5.739  
5.723  
5.718  
5.713  
5.699  
5.654  
5.635

3.291  
3.283  
3.266  
3.254  
3.190  
3.176  
3.157  
3.142  
2.769  
2.728  
2.716  
2.682  
2.670  
2.658  
2.636  
2.589  
2.574  
2.564  
2.549  
2.498  
2.489  
2.430  
2.420  
2.409  
2.381  
2.375  
2.353  
2.341  
2.303  
2.292  
1.229  
1.225  
1.222  
1.218  
1.214  
1.202  
1.199  
1.195  
1.192  
1.188  
0.963  
0.950  
0.936  
0.923  
0.000



spect, CDCl <sub>3</sub> ,				USER: nmr -- DATE: Wed Sep 13 07:08:52 2017			
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2468.6		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$pdata

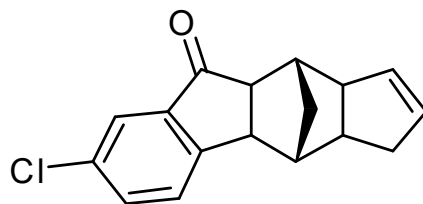


spect, CDCl3,			USER: nmr -- DATE: Thu Sep 14 06:19:00 2017			
F1: 100.623	F2: 1.000	SW1: 24038	OF1: 10063.0	PTS1d: 32768		
EX: zgpg30	PW: 12.4 usec	PD: 2.0 sec	NA: 2818	LB: 0.0	Nuts - \$pdata	

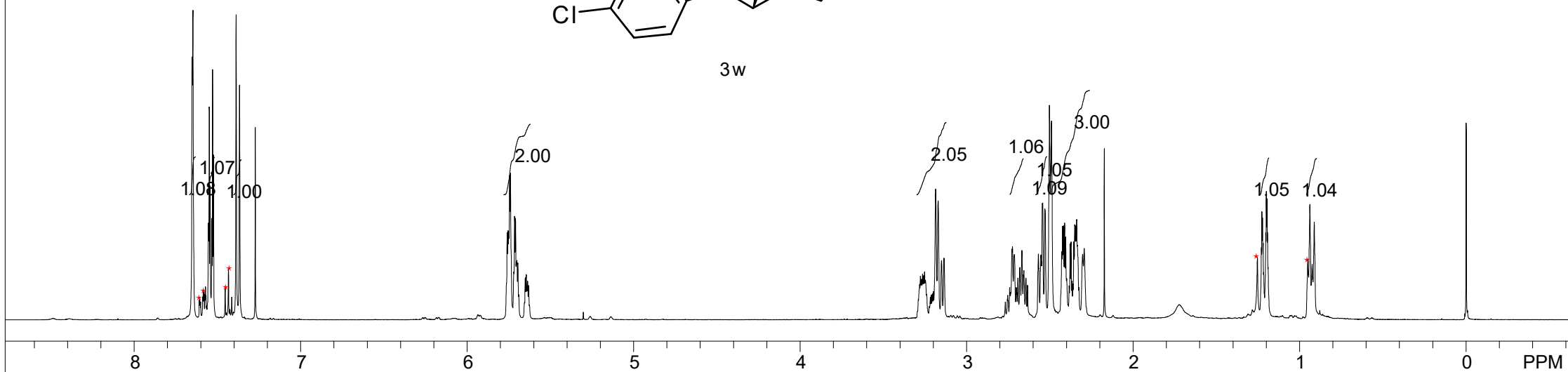
7.652  
7.647  
7.554  
7.549  
7.543  
7.534  
7.529  
7.524  
7.388  
7.367

5.759  
5.754  
5.739  
5.719  
5.714  
5.695  
5.650  
5.637  
5.631

3.283  
3.278  
3.265  
3.247  
3.186  
3.171  
3.151  
3.136  
2.753  
2.728  
2.714  
2.680  
2.668  
2.634  
2.569  
2.557  
2.545  
2.543  
2.530  
2.502  
2.491  
2.429  
2.423  
2.405  
2.356  
2.339  
2.304  
2.294  
1.230  
1.227  
1.223  
1.220  
1.204  
1.201  
1.196  
1.193  
0.951  
0.939  
0.925  
0.913  
0.000



3w



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Wed Sep 13 07:17:18 2017			
F1: 400.132	F2: 1.000	SW1: 8224	OF1: 2471.0	PTS1d: 32768	
EX: zg30	PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$pdata

208.667

156.105

140.887

134.824

132.017

131.467

127.128

127.004

122.946

77.360

77.045

76.717

52.985

49.641

45.159

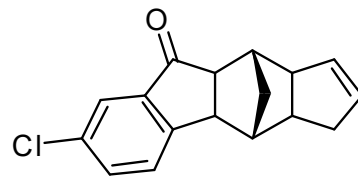
43.905

43.347

41.674

35.131

32.103



3w

200

150

100

50

PPM

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 08:03:29 2017

F1: 100.623

F2: 1.000

SW1: 24038

OF1: 10063.0

PTS1d: 32768

EX: zgpg30

PW: 12.4 usec

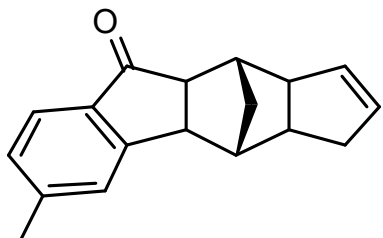
PD: 2.0 sec

NA: 200

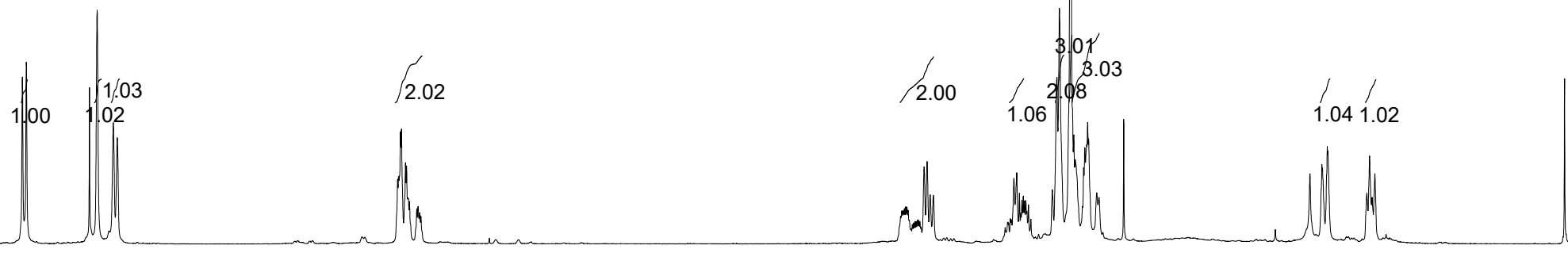
LB: 0.0

Nuts - \$pdata

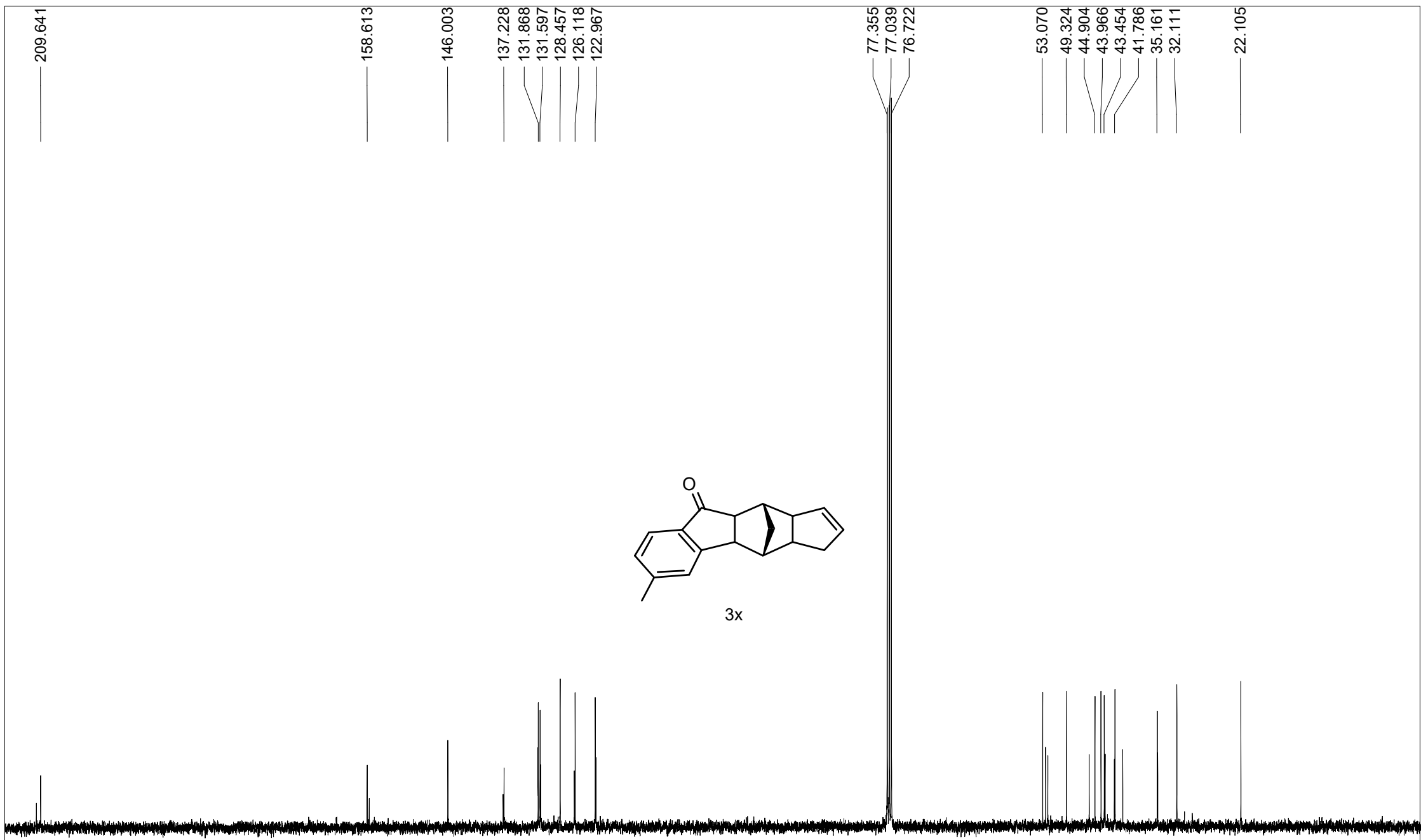
7.599  
7.580  
7.230  
7.151  
7.132  
5.749  
5.736  
5.731  
5.711  
5.691  
5.649  
5.635  
3.270  
3.252  
3.234  
3.207  
3.188  
3.175  
3.155  
3.125  
3.110  
2.756  
2.739  
2.712  
2.685  
2.667  
2.629  
2.523  
2.500  
2.488  
2.434  
2.418  
2.363  
2.354  
2.350  
2.344  
2.304  
2.293  
1.195  
1.169  
0.961  
0.934  
-0.000



3x



spect, CDCl <sub>3</sub> ,		USER: nmr -- DATE: Wed Sep 13 06:59:42 2017			
F1: 400.132	F2: 1.000	SW1: 8224	OF1: 2469.5	PTS1d: 32768	
EX: zg30	PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$pdata



spect, CDC13,			USER: nmr -- DATE: Thu Sep 14 07:38:56 2017			
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 188	LB: 0.0	Nuts - \$pdata



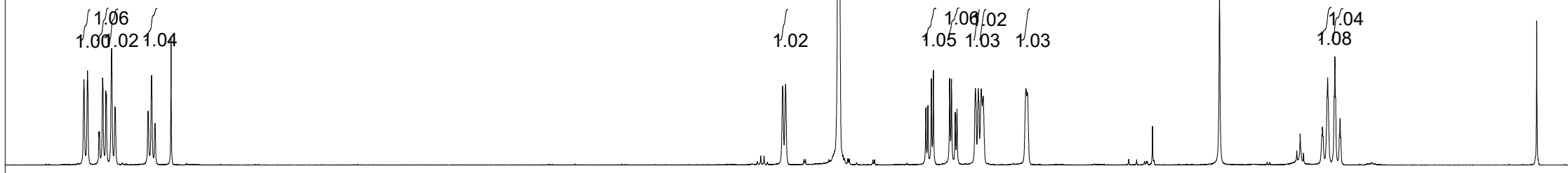
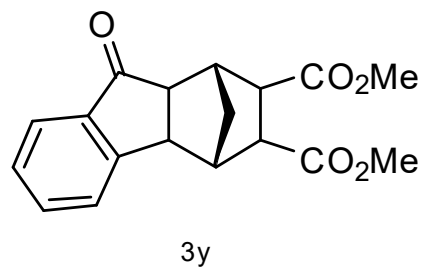
7.733  
7.714  
7.653  
7.634  
7.614  
7.586  
7.568  
7.391  
7.373  
7.355

4.013  
3.998  
3.719  
3.711

3.251  
3.241  
3.222  
3.211  
3.125  
3.115  
3.095  
3.086  
2.988  
2.973  
2.956  
2.946  
2.718  
2.712

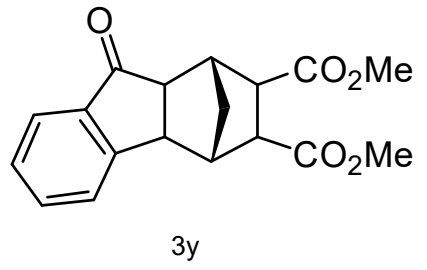
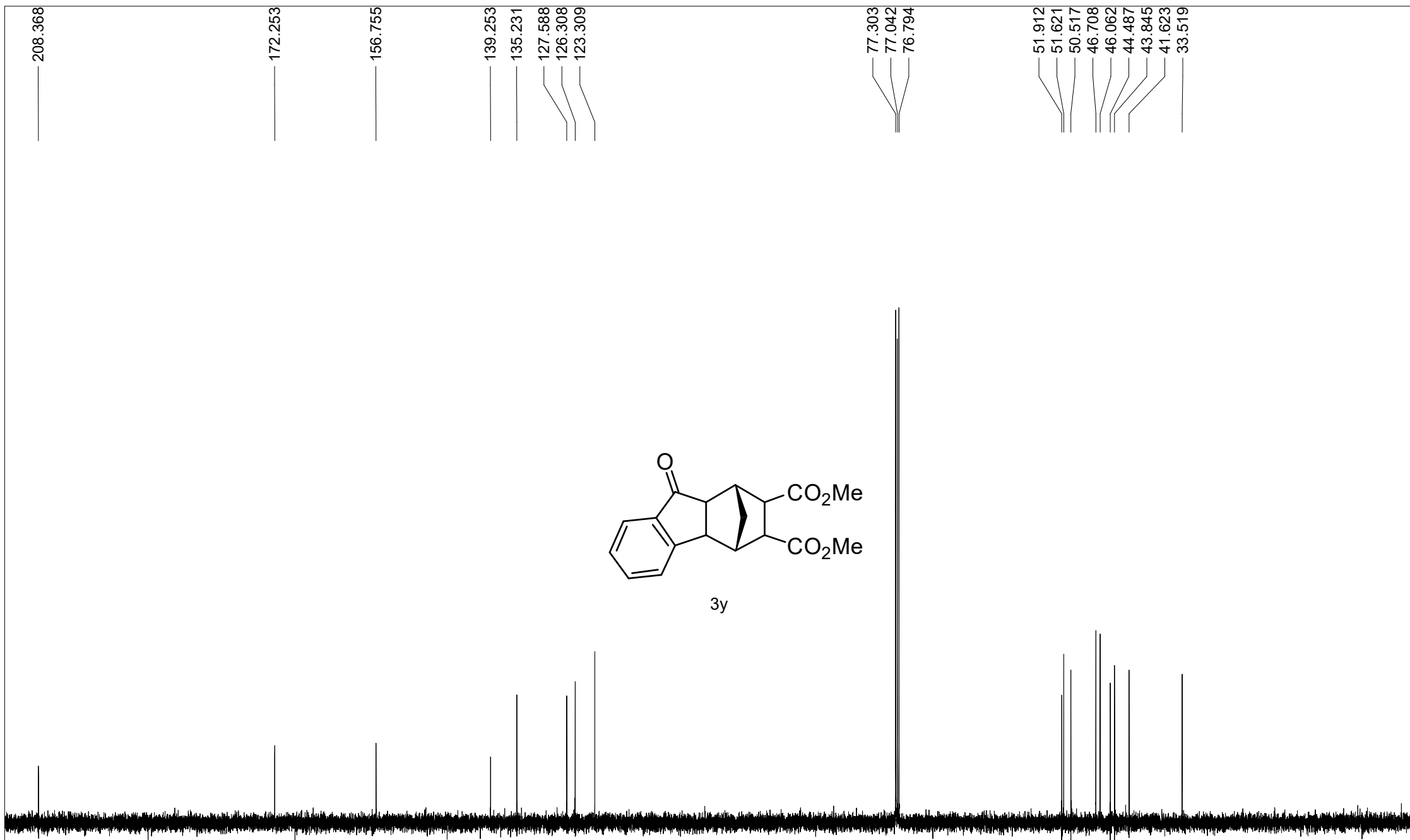
1.141  
1.113  
1.074  
1.047

-0.000



8 7 6 5 4 3 2 1 PPM

spect, CDCl3,		USER: maojgang -- DATE: Wed Jul 25 18:05:54 2018					
F1: 400.132	F2: 1.000	SW1: 5597		OF1: 2394.1		PTS1d: 32768	
EX: zg30		PW: 8.0 usec	PD: 1.0 sec	NA: 16	LB: 0.0		Nuts - \$pdata



200 150 100 50 PPM

AVNEO500, CDCl<sub>3</sub>, USER: jicheng -- DATE: Sat Dec 01 22:28:11 2018

F1: 125.772	F2: 1.000	SW1: 31250	OF1: 13836.6	PTS1d: 32768
EX: zgpg30	PW: 10.0 usec	PD: 2.0 sec	NA: 84	LB: 0.0

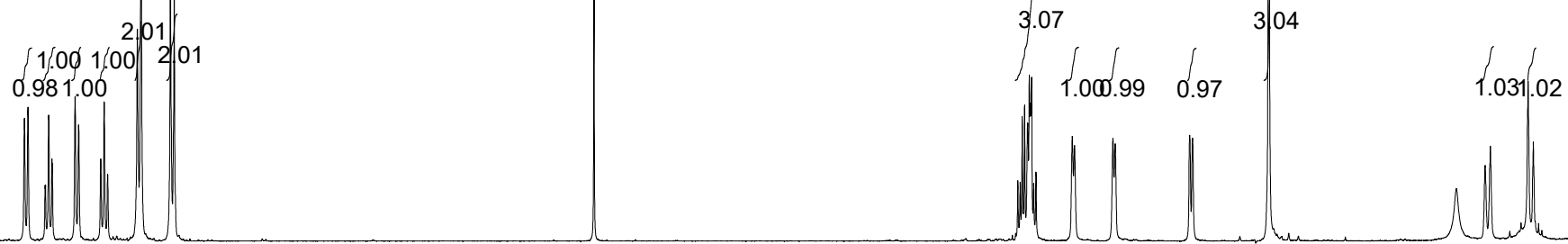
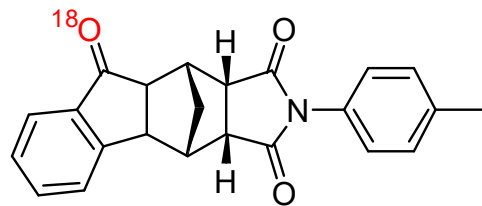
Nuts - \$pdata

7.766  
7.751  
7.677  
7.662  
7.647  
7.547  
7.531  
7.436  
7.421  
7.406  
7.277  
7.261  
7.134  
7.117

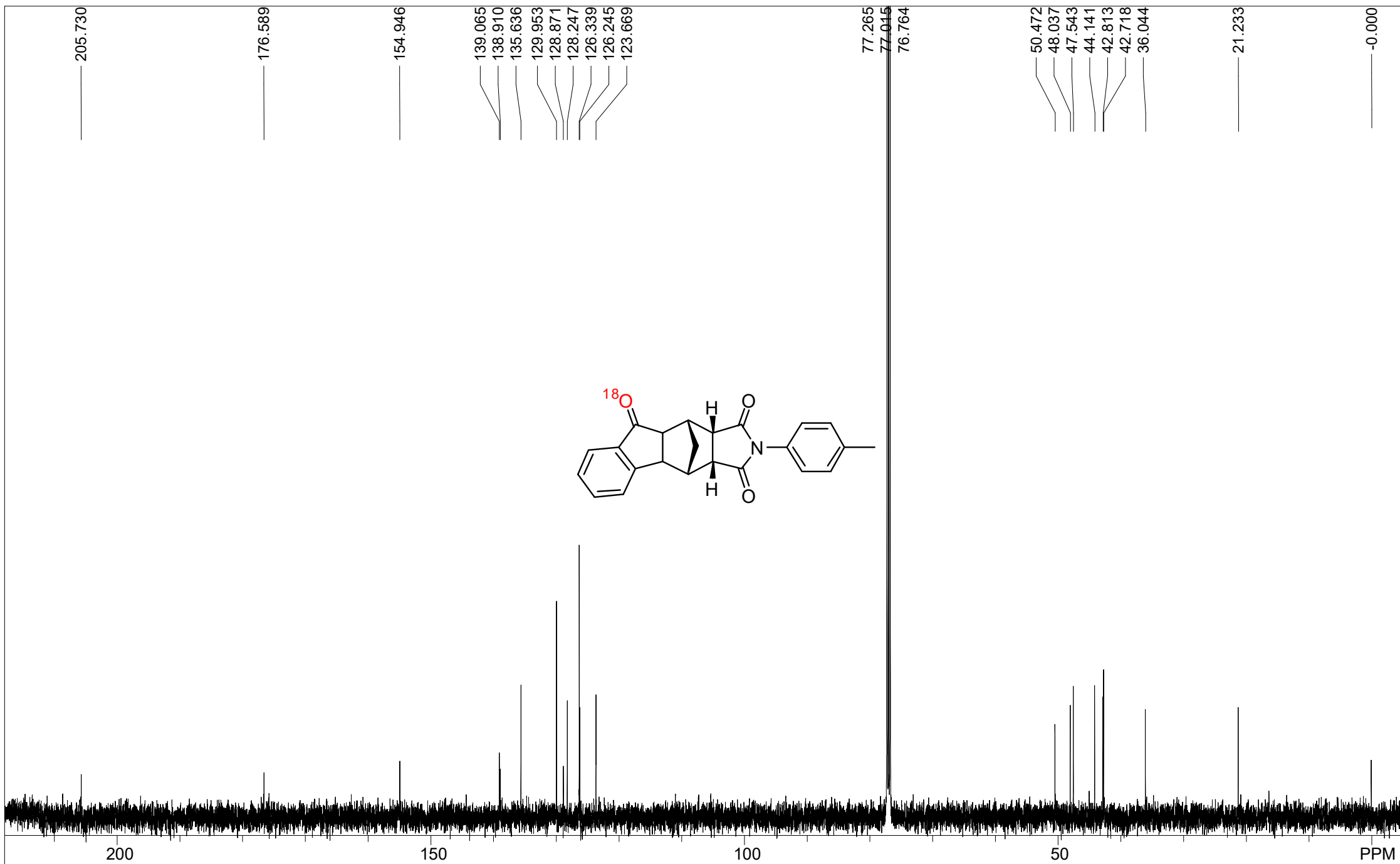
3.463  
3.444  
3.434  
3.420  
3.413  
3.403  
3.384  
3.227  
3.217  
3.051  
3.041  
2.719  
2.707  
2.377

1.440  
1.417  
1.254  
1.232

0.000



spect, CDCl3,		USER: root -- DATE: Tue Jan 14 01:49:50 2020				
F1: 500.133	F2: 1.000	SW1: 10000	OF1: 3075.5	PTS1d: 65536		
EX: zg30	PW: 11.5 usec	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - \$pdata	



spect, CDC13,			USER: root -- DATE: Tue Jan 14 02:01:33 2020			
F1: 125.770	F2: 1.000	SW1: 29762		OF1: 12575.3		PTS1d: 32768
EX: zgpg30		PW: 9.0 usec	PD: 2.0 sec	NA: 256	LB: 0.0	Nuts - \$pdata