Supporting Information for

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

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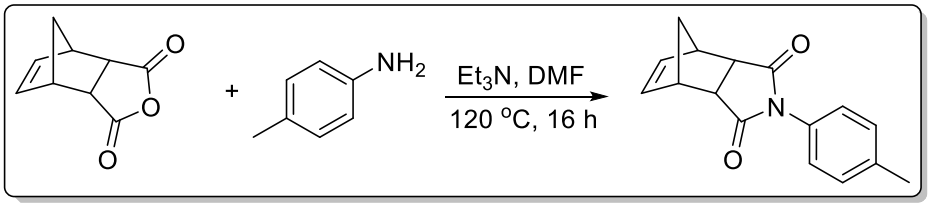
1 General information

Experimental: All carboylation 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}H; 100 MHz for ^{13}C) instruments. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}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

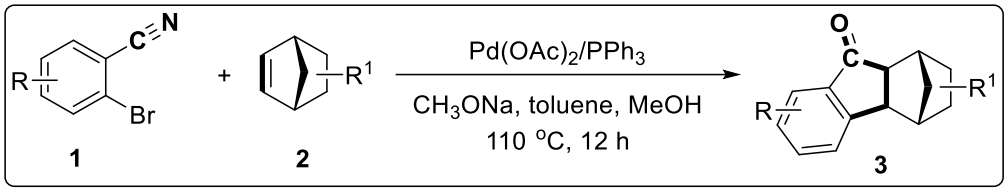
2.1 The Synthesis of *Endo*-Norbornenesuccinimides (2a, 2b)[1]:



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}H NMR** ($CDCl_3$, 400 MHz) δ 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

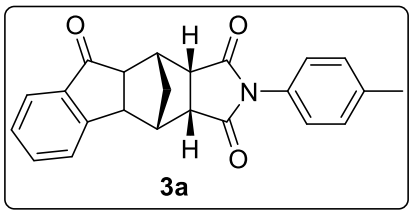
3.1 General Procedures for the Carbonylation



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 derivants **2** (0.5 mmol, 1.0 equiv.), MeOH (0.05 mL), $Pd(OAc)_2$ (11.22 mg, 0.05 mmol, 10 mol%), PPh_3 (28.85 mg, 0.11 mmol, 22 mol%), CH_3ONa (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_2Cl_2 (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**

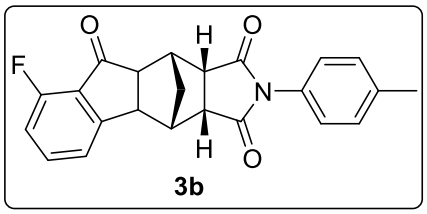
3.2 Experimental Characterization of Products

(3^a*R*,4*S*,10*R*,10^a*S*)-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno-[1,2-*f*]isoindole-1,3,9(2*H*)-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. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 7.6 Hz, 0.8Hz, 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



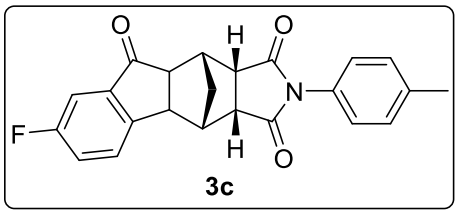
Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.8, 176.6, 175.9, 155.0, 139.0, 138.9, 135.6, 130.0, 128.9, 128.2, 126.4, 126.3, 123.6, 50.5, 48.0, 47.6, 44.1, 42.8, 42.7, 36.0, 21.2; **HRMS (EI)** calcd. for $C_{23}H_{19}NO_3$ [M^+]: 357.1365, found: 357.1368.

(3^a*R*,4*S*,10*R*,10^a*S*)-8-fluoro-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-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→2/1) to give white solid, 146.3 mg, 78 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 202.0 (d, J_{C-F} = 1.7 Hz), 176.5, 175.6, 158.6 (d, J_{C-F} = 263.2 Hz), 157.1, 139.1, 137.6 (d, J_{C-F} = 9.1 Hz), 130.0, 128.8, 126.7 (d, J_{C-F} = 12.7 Hz), 126.3, 122.1 (d, J_{C-F} = 3.8 Hz), 115.2 (d, J_{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 $C_{23}H_{18}FNO_3$ [M^+]: 375.1271, found: 375.1269.



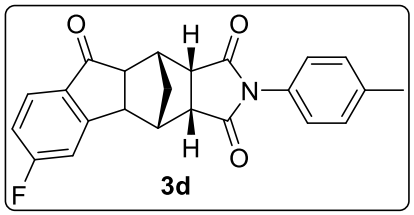
3b

(3^a*R*,4*S*,10*R*,10^a*S*)-7-fluoro-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-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→2/1) to give white solid, 161.3 mg, 86 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 204.7, 176.5, 175.7, 162.7 (d, J_{C-F} = 248.1 Hz), 150.4, 140.8 (d, J_{C-F} = 8.0 Hz), 139.1, 130.0, 128.8, 127.7 (d, J_{C-F} = 8.1 Hz), 126.3, 123.5, 123.2, 109.5 (d, J_{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 $C_{23}H_{18}FNO_3$ [M^+]: 375.1271, found:



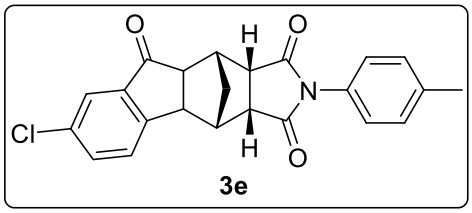
3c

375.1268.

(3^a*R*,4*S*,10*R*,10^a*S*)-6-fluoro-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione(3d): 

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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.8, 176.4, 175.7, 167.6 (d, J_{C-F} = 313.4 Hz), 139.1, 135.3, 130.0, 128.8, 126.3, 126.0 (d, J_{C-F} = 9.9 Hz), 116.6 (d, J_{C-F} = 24.3 Hz), 113.0 (d, J_{C-F} = 21.9 Hz), 50.8, 48.0, 47.5, 44.0, 42.7, 36.0, 21.2; **HRMS (EI)** calcd. for $C_{23}H_{18}FNO_3$ [M^+]: 375.1271, found: 375.1268.

(3^a*R*,4*S*,10*R*,10^a*S*)-7-chloro-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione(3e): 

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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{23}H_{18}ClNO_3$ [M^+]: 391.0975, found: 391.0973. The configuration was confirmed by X-ray analysis (Figure S1) and undoubtedly determined that methylenecyclopropane moiety was formed

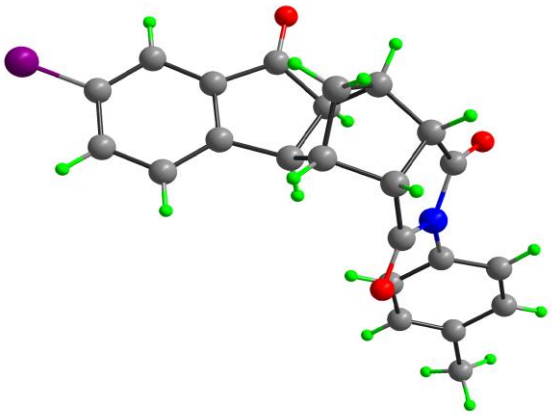
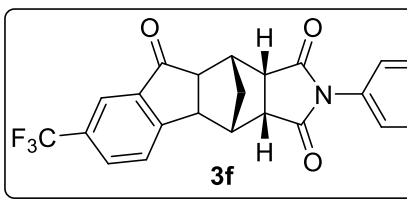
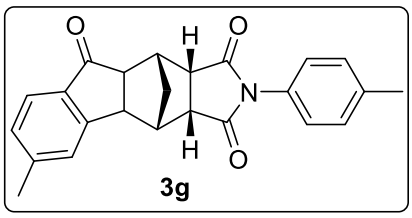


Figure S1. ORTEP drawing of product **3e**

(3^a*R*,4*S*,10*R*,10^a*S*)-2-(*p*-tolyl)-7-(trifluoromethyl)-3^a,4,4^a,9^a,10,10^a-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.4, 176.3, 175.5, 158.0, 139.3, 139.1, 132.1 (q, J_{C-F} = 3.8 Hz), 130.0, 129.8 (q, J_{C-F} = 245.8 Hz), 128.8, 127.1, 126.3, 120.9 (q, J_{C-F} = 3.9 Hz), 50.8, 48.0, 47.4, 44.1, 42.9, 42.9, 36.1, 21.2; **HRMS (EI)** calcd. for $C_{24}H_{18}F_3NO_3$ [M^+]: 425.1239, found: 425.1237.

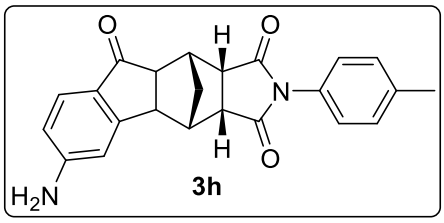


(3^a*R*,4*S*,10*R*,10^a*S*)-6-methyl-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione(3g): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→2/1) to give white solid, 168.9 mg, 91 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 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,



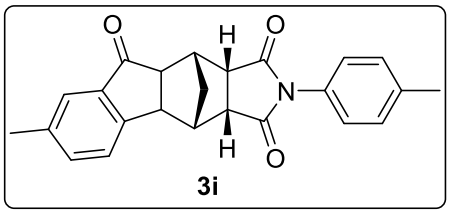
2H), 3.35 (d, *J* = 6.4 Hz, 1H), 3.20 (d, *J* = 4.4 Hz, 1H), 3.02 (d, *J* = 4.8 Hz, 1H), 2.69 (d, *J* = 6.0 Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 1.41 (d, *J* = 11.6 Hz, 1H), 1.25 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.2, 176.7, 175.9, 155.5, 147.0, 139.0, 136.7, 129.9, 129.5, 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 $C_{24}H_{21}NO_3$ [M^+]: 371.1521, found: 371.1518.

(3^a*R*,4*S*,10*R*,10^a*S*)-6-amino-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-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→2/1) to give white solid, 156.3 mg, 84 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 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 $C_{23}H_{20}N_2O_3$ [M^+]: 372.1474, found: 372.1476.



3h

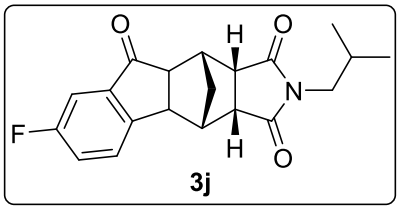
(3^a*R*,4*S*,10*R*,10^a*S*)-7-methyl-2-(*p*-tolyl)-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione(3i): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→2/1) to give white solid, 178.2 mg, 96 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 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,



3i

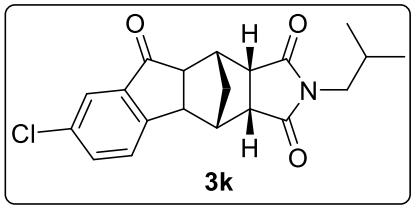
36.0, 21.2, 21.1; **HRMS (EI)** calcd. for $C_{24}H_{21}NO_3$ [M^+]: 371.1521, found: 371.1518.

(3^a*R*,4*S*,10*R*,10^a*S*)-7-fluoro-2-isobutyl-3^a,4,4^a,9^a,10,10^a-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.9 (d, $J_{C\text{-}F}$ = 3.4 Hz), 177.5, 176.7, 162.7 (d, $J_{C\text{-}F}$ = 247.8 Hz), 150.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 140.7 (d, $J_{C\text{-}F}$ = 7.2 Hz), 127.7 (d, $J_{C\text{-}F}$ = 8.2 Hz), 123.3 (d, $J_{C\text{-}F}$ = 23.0 Hz), 109.4 (d, $J_{C\text{-}F}$ = 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 $C_{20}H_{20}FNO_3$ [M^+]: 341.1427, found: 341.1429.



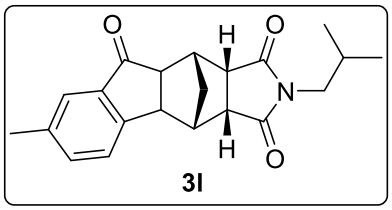
3j

(3^a*R*,4*S*,10*R*,10^a*S*)-7-chloro-2-isobutyl-3^a,4,4^a,9^a,10,10^a-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{20}H_{20}ClNO_3$ [M^+]: 357.1132, found: 357.1135.



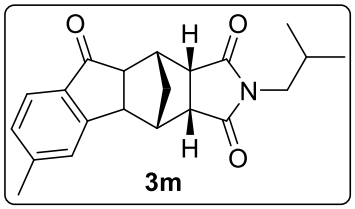
3k

(3^a*R*,4*S*,10*R*,10^a*S*)-7-methyl-2-isobutyl-3^a,4,4^a,9^a,10,10^a-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{21}H_{23}NO_3$ [M^+]: 337.1678, found: 337.1679.



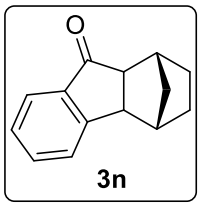
3l

(3^a*R*,4*S*,10*R*,10^a*S*)-6-methyl-2-isobutyl-3^a,4,4^a,9^a,10,10^a-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{21}H_{23}NO_3$ [M^+]: 337.1678, found: 337.1675.

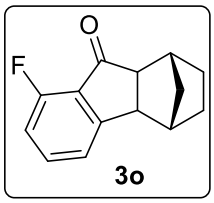


3m

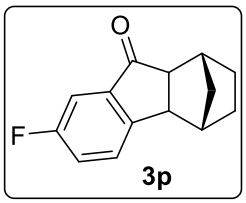
(1*R*,4*S*)-1,2,3,4,4^a,9^a-hexahydro-9*H*-1,4-methanofluoren-9-one(3n): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 89.2 mg, 90 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{14}H_{14}O$ [M^+]: 198.1045, found: 198.1043.



(1*R*,4*S*)-8-fluoro-1,2,3,4,4^a,9^a-hexahydro-9*H*-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 158.5 (d, $J_{C\text{-}F}$ = 262.0 Hz), 136.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.8 (d, $J_{C\text{-}F}$ = 12.2 Hz), 122.0 (d, $J_{C\text{-}F}$ = 4.1 Hz), 114.2 (d, $J_{C\text{-}F}$ = 19.5 Hz), 56.3, 48.0, 41.6, 40.6, 32.3, 28.8, 28.6; **HRMS (EI)** calcd. for $C_{14}H_{13}FO$ [M^+]: 216.0950, found: 216.0947.

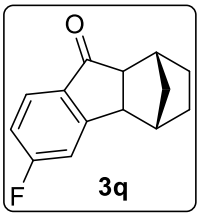


(1*R*,4*S*)-7-fluoro-1,2,3,4,4^a,9^a-hexahydro-9*H*-1,4-methanofluoren-9-one (3p): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow solid, 91.8 mg, 85 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 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),



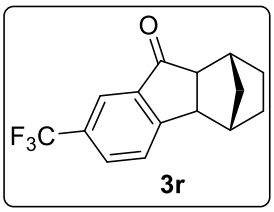
1.33-1.40 (m, 1H), 0.97 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H), 0.80 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.8 (d, $J_{C\text{-}F}$ = 2.8 Hz), 162.3 (d, $J_{C\text{-}F}$ = 246.5 Hz), 152.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 140.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 122.6 (d, $J_{C\text{-}F}$ = 23.6 Hz), 108.9 (d, $J_{C\text{-}F}$ = 20.6 Hz), 56.6, 47.5, 41.2, 40.5, 32.1, 28.8, 28.6; **HRMS (EI)** calcd. for $C_{14}H_{13}FO$ [M^+]: 216.0950, found: 216.0948.

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



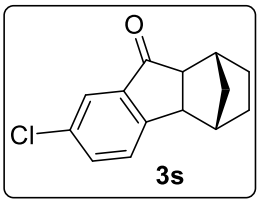
title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 87.5 mg, 81 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.4 Hz, 5.2 Hz, 1H), 7.15 (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}C NMR** (100 MHz, $CDCl_3$) δ 206.8, 167.5 (d, $J_{C\text{-}F}$ = 254.8 Hz), 160.1 (d, $J_{C\text{-}F}$ = 8.9 Hz), 135.5 (d, $J_{C\text{-}F}$ = 10.9 Hz), 125.5 (d, $J_{C\text{-}F}$ = 10.7 Hz), 115.7 (d, $J_{C\text{-}F}$ = 24.7 Hz), 112.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 56.2, 47.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 41.3, 40.4, 32.2, 28.8, 28.6; **HRMS (EI)** calcd. for $C_{14}H_{13}FO$ [M^+]: 216.0950, found: 216.0947.

(1*R*,4*S*)-7-trifluoromethyl-1,2,3,4,4^a,9^a-hexahydro-9*H*-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}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 207.5, 160.3, 139.4, 131.4 (q, $J_{C\text{-}F}$ = 3.2 Hz), 130.2 (d, $J_{C\text{-}F}$ = 32.3 Hz), 127.0, 123.8 (q, $J_{C\text{-}F}$ = 270.9 Hz), 120.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 56.1, 48.1, 41.3, 40.6, 32.3, 28.9, 28.5; **HRMS (EI)** calcd. for $C_{15}H_{13}F_3O$ [M^+]: 266.0918, found: 266.0920.

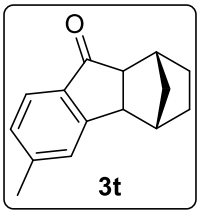
(1*R*,4*S*)-7-chloro-1,2,3,4,4^a,9^a-hexahydro-9*H*-1,4-methanofluoren-9-one (3s): The



3s

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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{14}H_{13}ClO$ [M^+]: 232.0655, found: 232.0657.

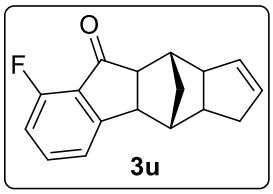
(1*R*,4*S*)-6-methyl-1,2,3,4,4^a,9^a-hexahydro-9*H*-1,4-methanofluoren-9-one (3t): The



3t

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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{15}H_{16}O$ [M^+]: 212.1201, found: 212.1200.

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

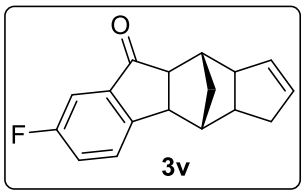


3u

9(3*H*)-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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);

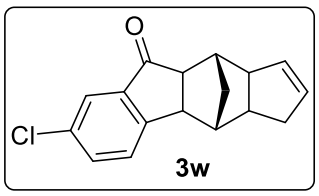
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2 (d, J_{C-F} = 1.4 Hz), 160.5 (d, J_{C-F} = 1.7 Hz), 158.5 (d, J_{C-F} = 262.0 Hz), 136.6 (d, J_{C-F} = 7.6 Hz), 132.0, 131.4, 127.2 (d, J_{C-F} = 12.5 Hz), 121.5 (d, J_{C-F} = 3.8 Hz), 113.9 (d, J_{C-F} = 4.4 Hz), 53.0, 52.5, 49.6, 45.2, 44.3, 41.7, 35.1, 32.1; **HRMS (EI)** calcd. for $C_{17}H_{15}FO$ [M^+]: 254.1107, found: 254.1104.

(4*R*,10*S*)-7-fluoro-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanocyclopenta[*b*]fluoren-9(3*H*)-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}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 208.9 (d, J_{C-F} = 2.9 Hz), 162.2 (d, J_{C-F} = 246.3 Hz), 153.4 (d, J_{C-F} = 1.7 Hz), 141.2 (d, J_{C-F} = 7.2 Hz), 131.8 (d, J_{C-F} = 19.2 Hz), 131.5 (d, J_{C-F} = 14.0 Hz), 127.1 (d, J_{C-F} = 7.9 Hz), 122.5 (d, J_{C-F} = 22.9 Hz), 108.9 (d, J_{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 $C_{17}H_{15}FO$ [M^+]: 254.1107, found: 254.1103.



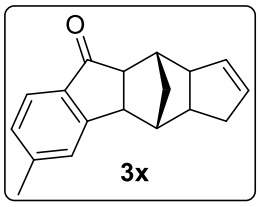
3v

(4*R*,10*S*)-7-chloro-3^a,4,4^a,9^a,10,10^a-hexahydro-4,10-methanocyclopenta[*b*]fluoren-9(3*H*)-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}H NMR** (400 MHz, $CDCl_3$) δ 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}C NMR** (100 MHz, $CDCl_3$) δ 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 $C_{17}H_{15}ClO$ [M^+]: 270.0811, found: 270.0808.



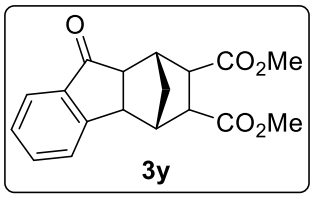
3w

(4*R*,10*S*)-6-methyl-3^{a},4,4^{a},9^{a},10,10^{a}-hexahydro-4,10-



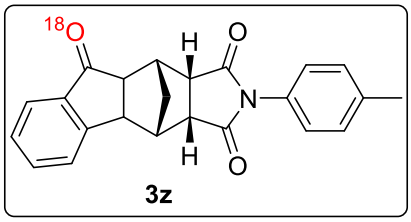
methanocyclopenta[*b*]fluoren-9(3*H*)-one (3x): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 107.6 mg, 86 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{18}H_{18}O$ [M^+]: 250.1358, found: 250.1360.

dimethyl (1*R*,4*S*)-9-oxo-2,3,4,4^{a},9,9^{a}-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. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{18}H_{18}O_5$ [M^+]: 314.1154, found: 314.1157.

(3^{a}*R*,4*S*,10*R*,10^{a}*S*)-2-(*p*-tolyl)-3^{a},4,4^{a},9^{a},10,10^{a}-hexahydro-4,10-



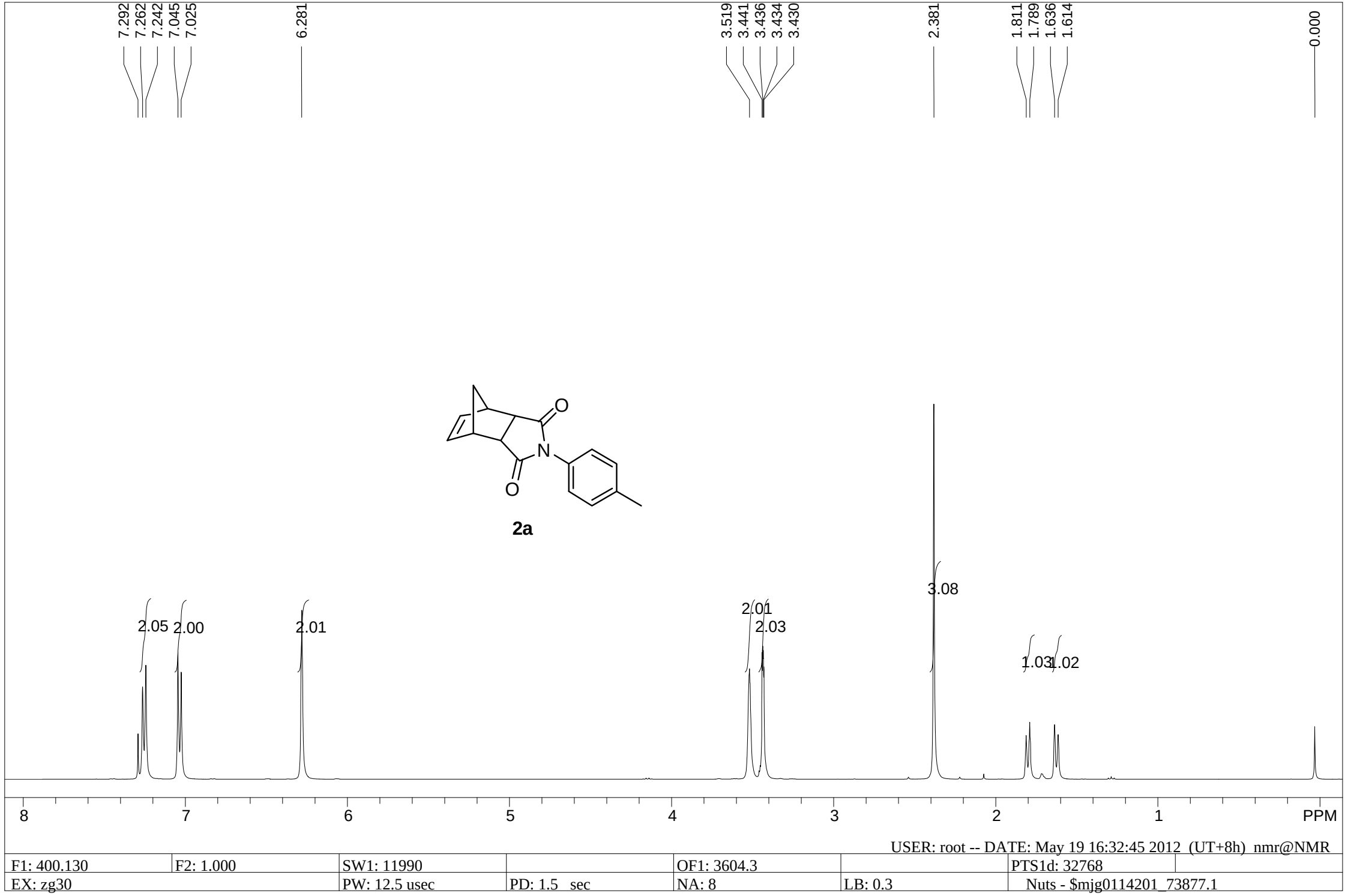
methanoindeno[1,2-*f*]isoindole-1,3,9(2*H*)-trione-^{18}O (3z): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a

gradient eluent of petroleum ether/EtOAc (10/1→2/1) to give white solid, 134.7 mg, 75 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) 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); **^{13}C NMR** (100 MHz, $CDCl_3$) 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 $C_{23}H_{20}NO_2{}^{18}O$ $[M+H]^+$: 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 ^{1}H NMR and ^{13}C NMR



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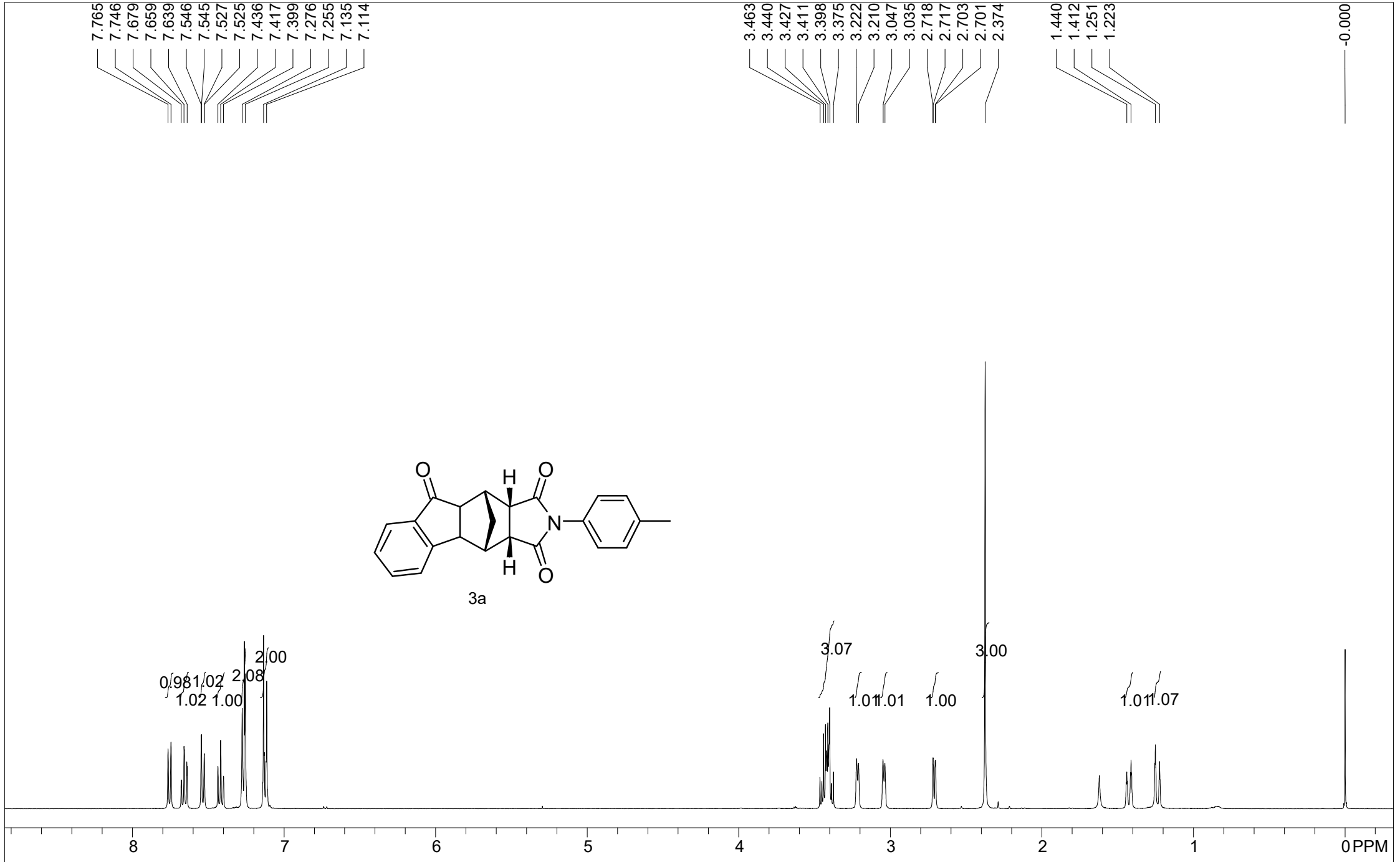

spect, CDCl3,

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

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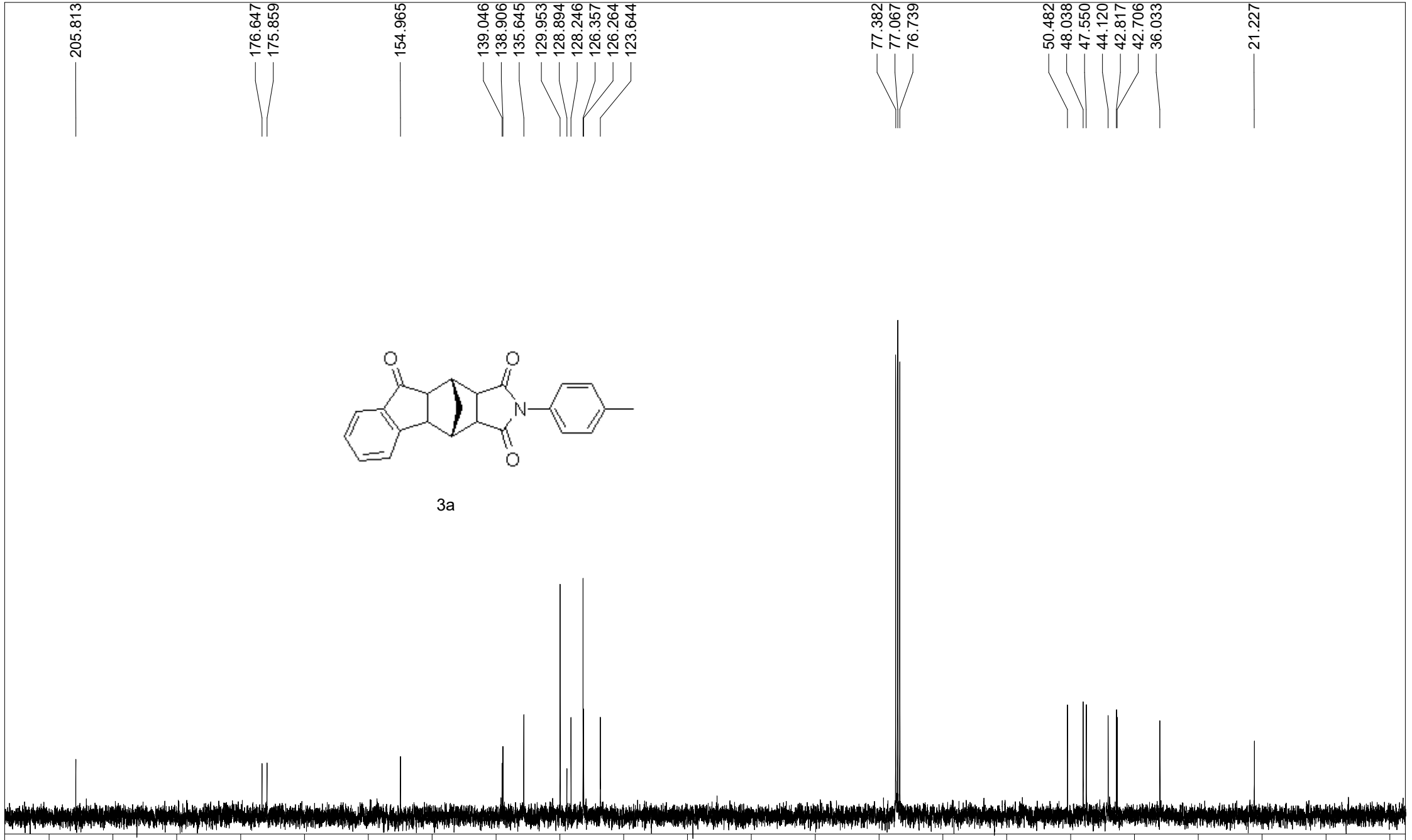

spect, CDCl3,

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

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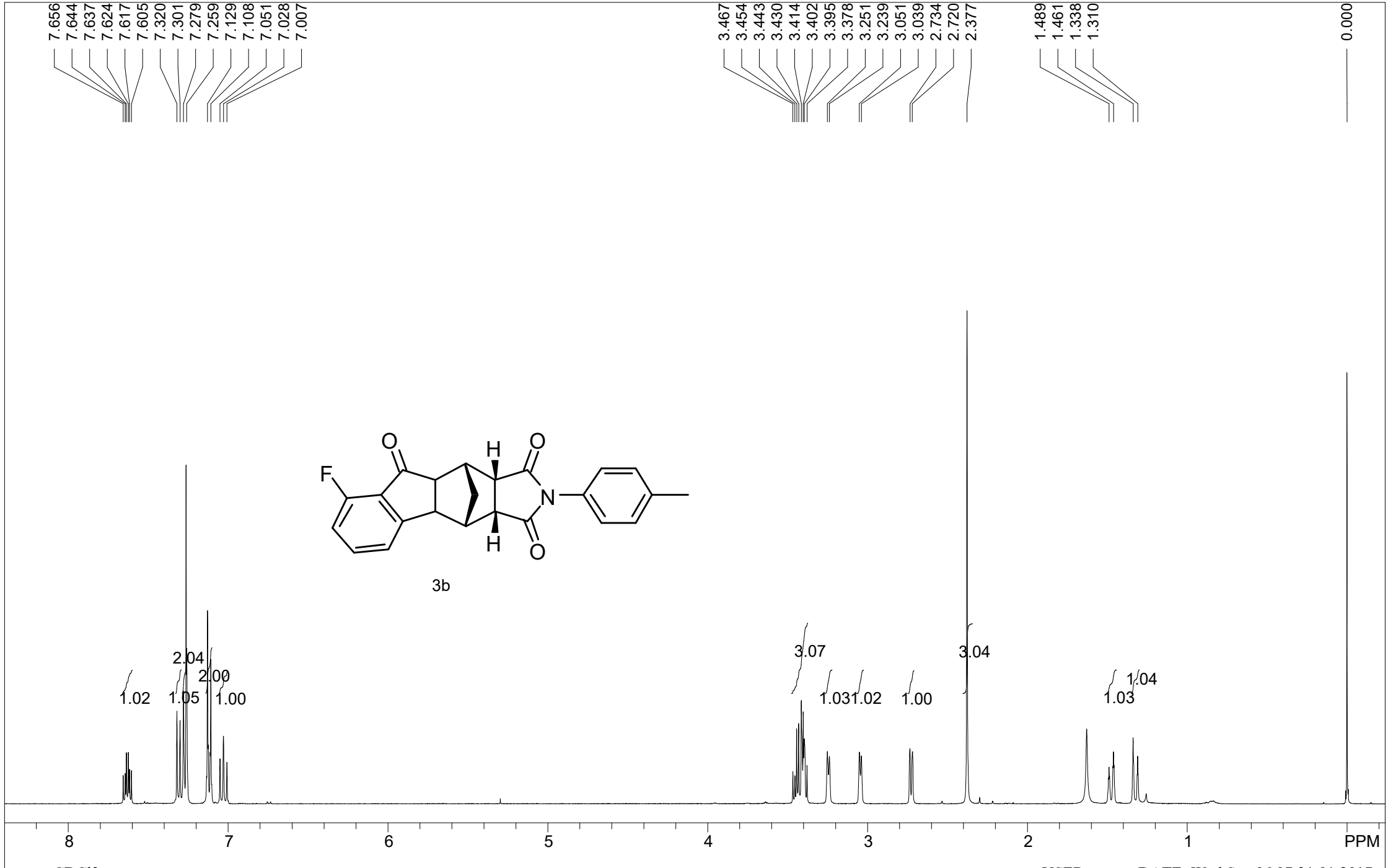

spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 07:31:01 2017

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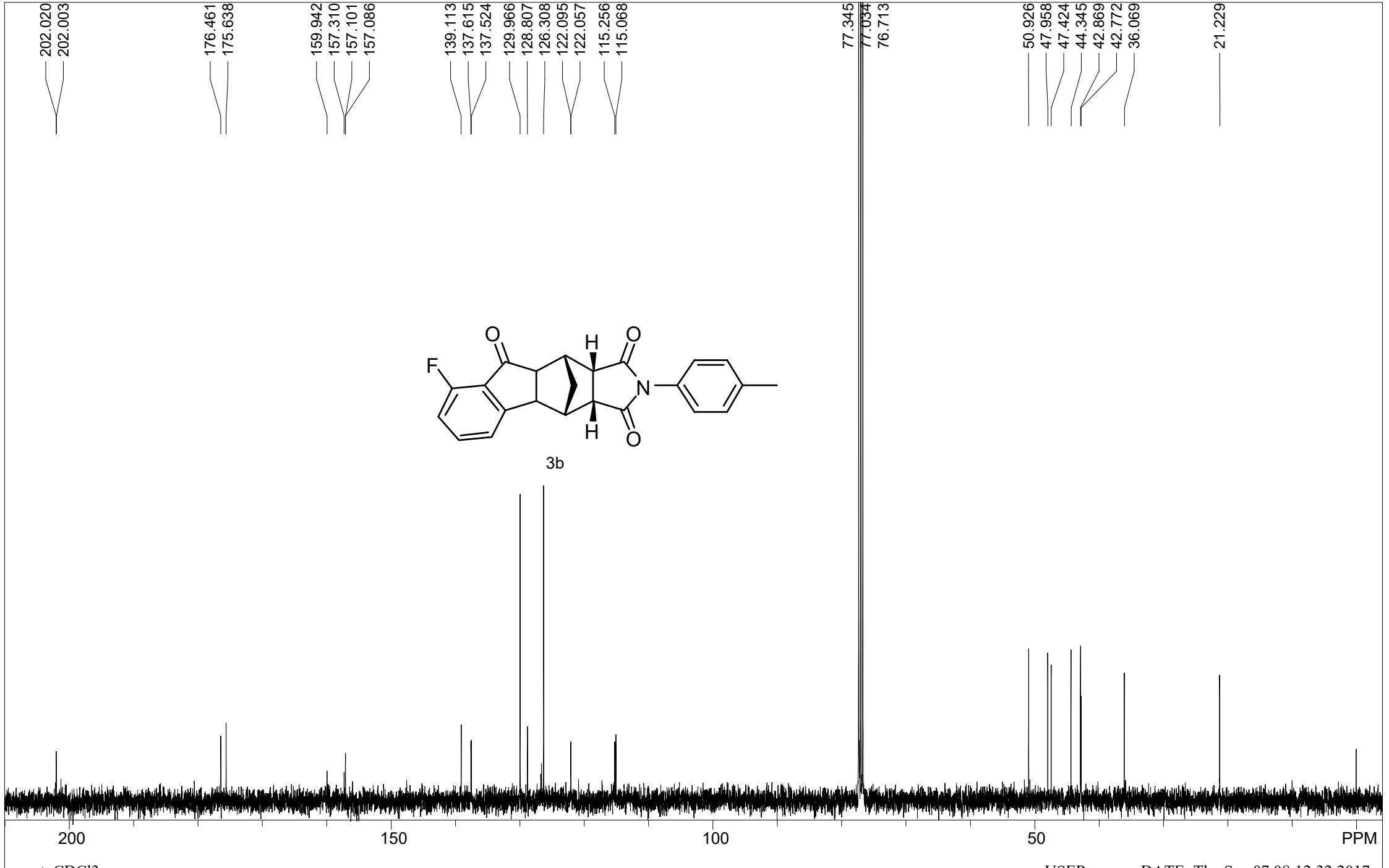

3b

spect, CDCl3,

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

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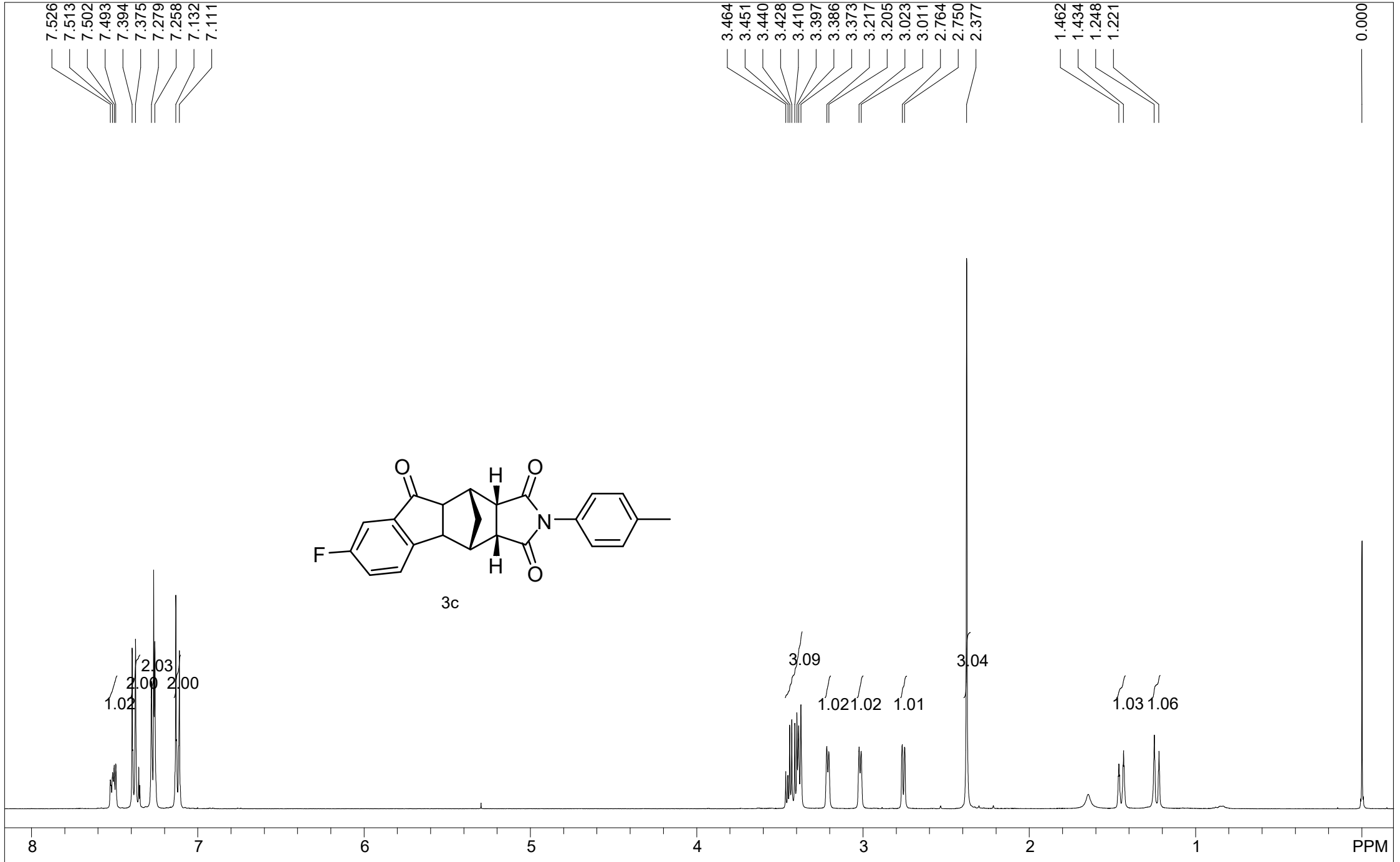

spect, CDCl3,

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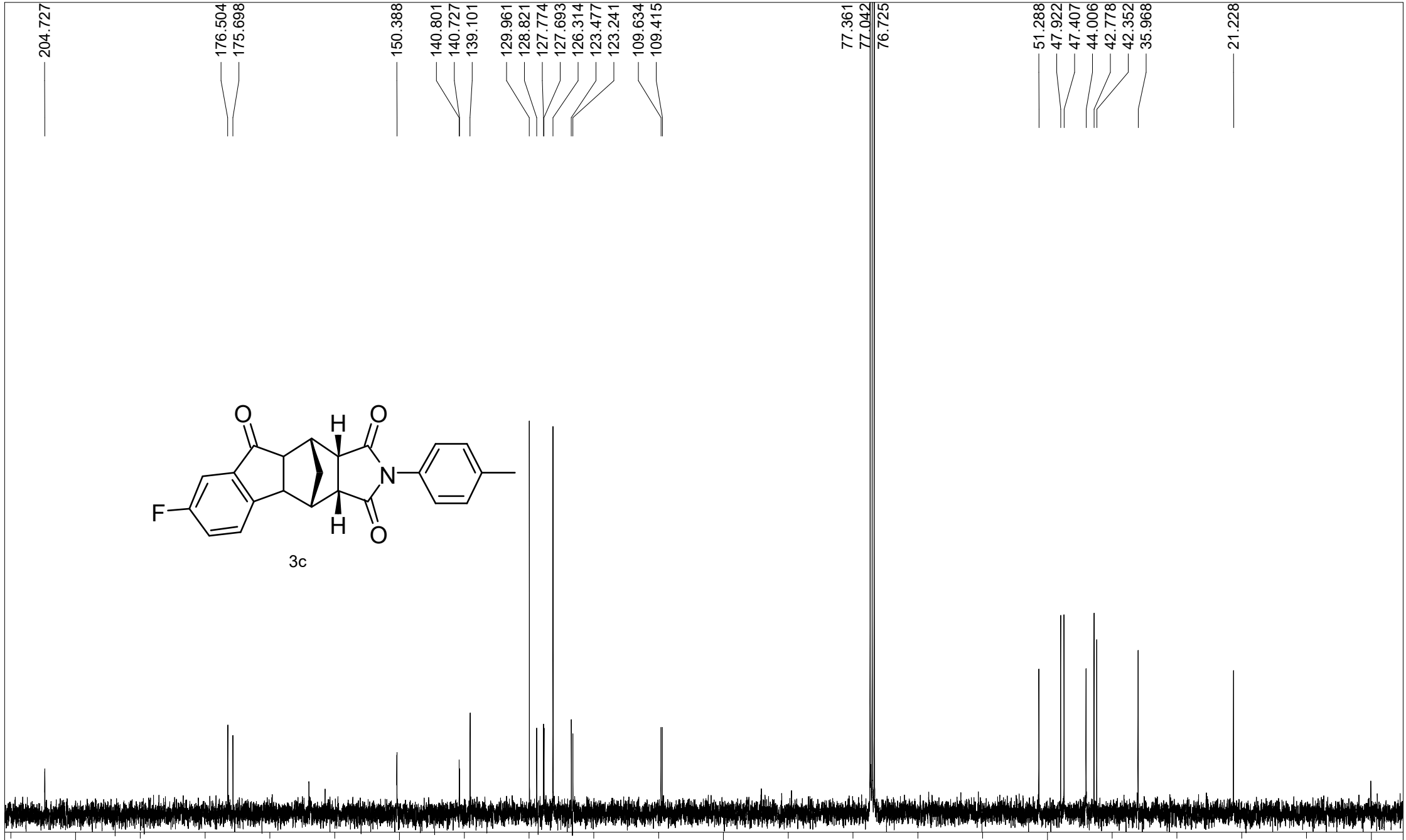

spect, CDCl3,

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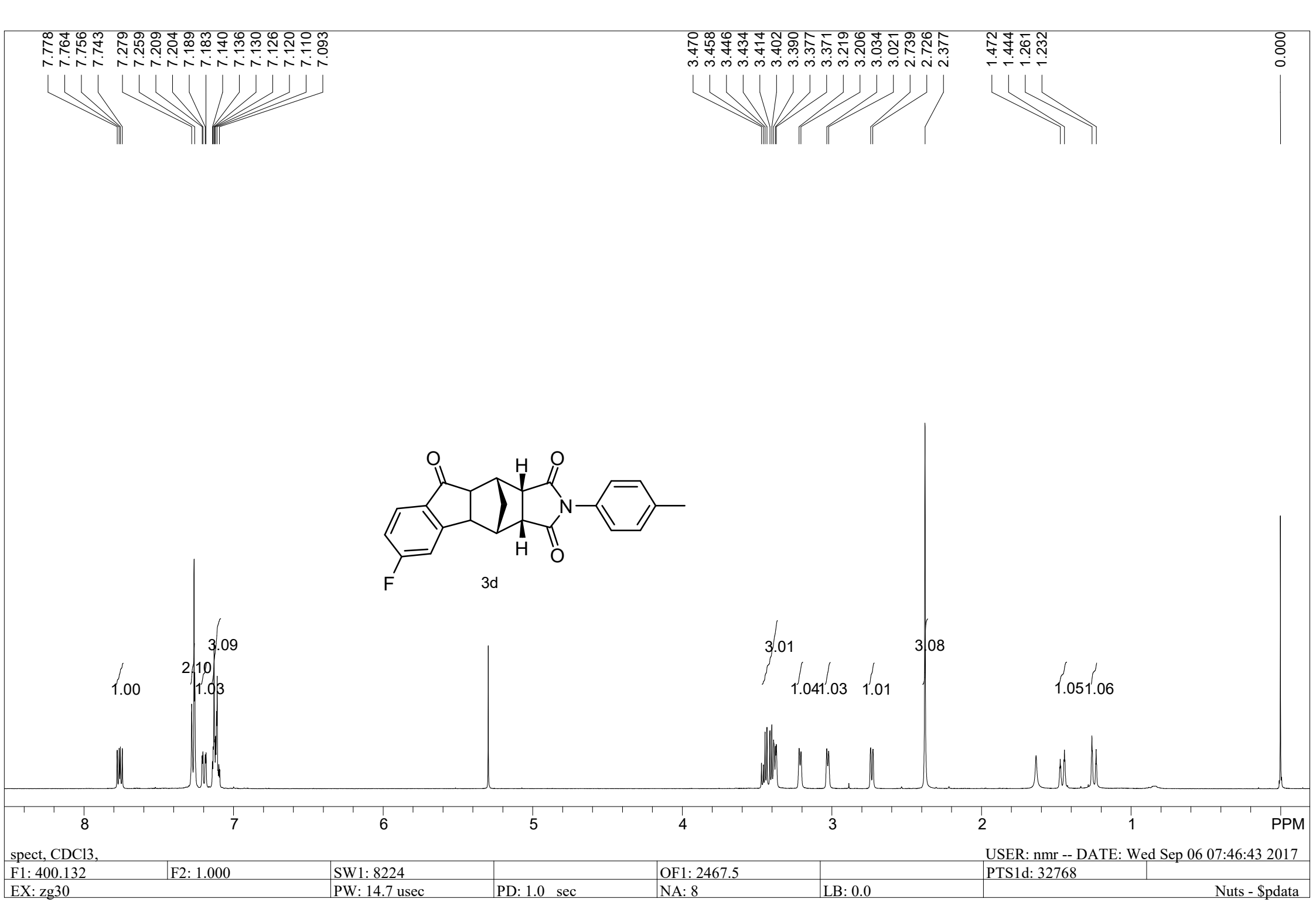

spect, CDCl3,

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

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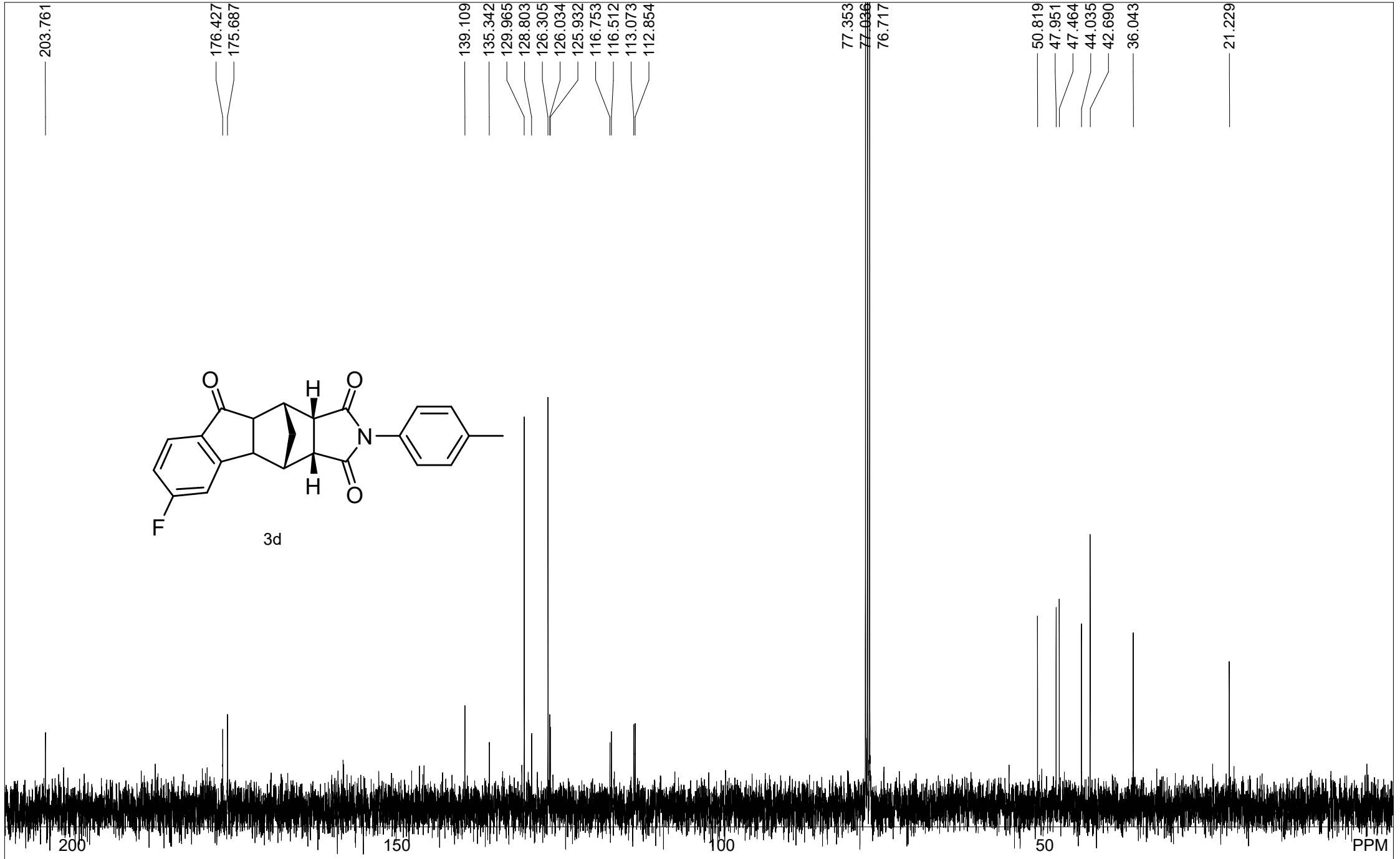

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 06:22:14 2017

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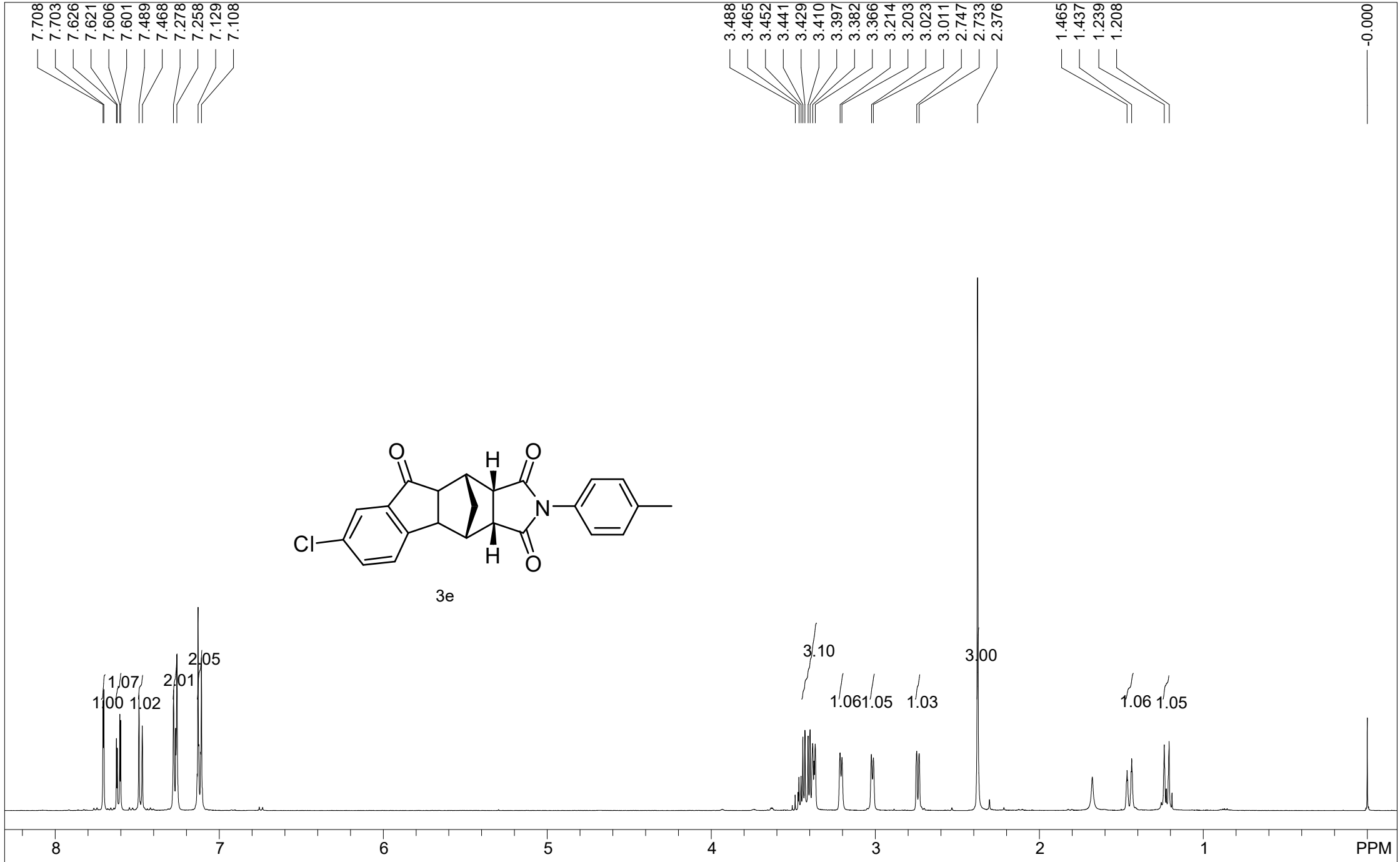

spect, CDCl3,

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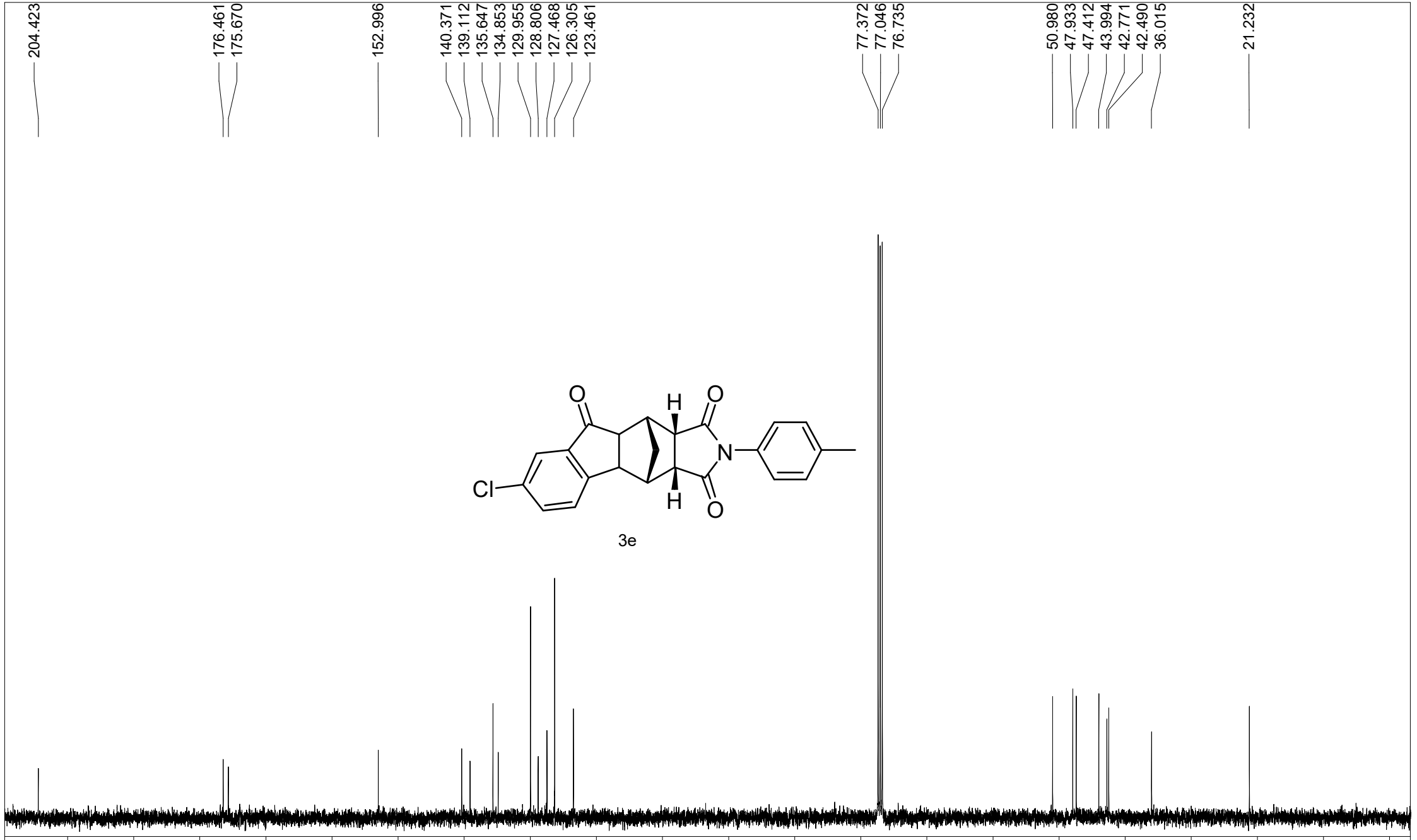

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 07:27:44 2017

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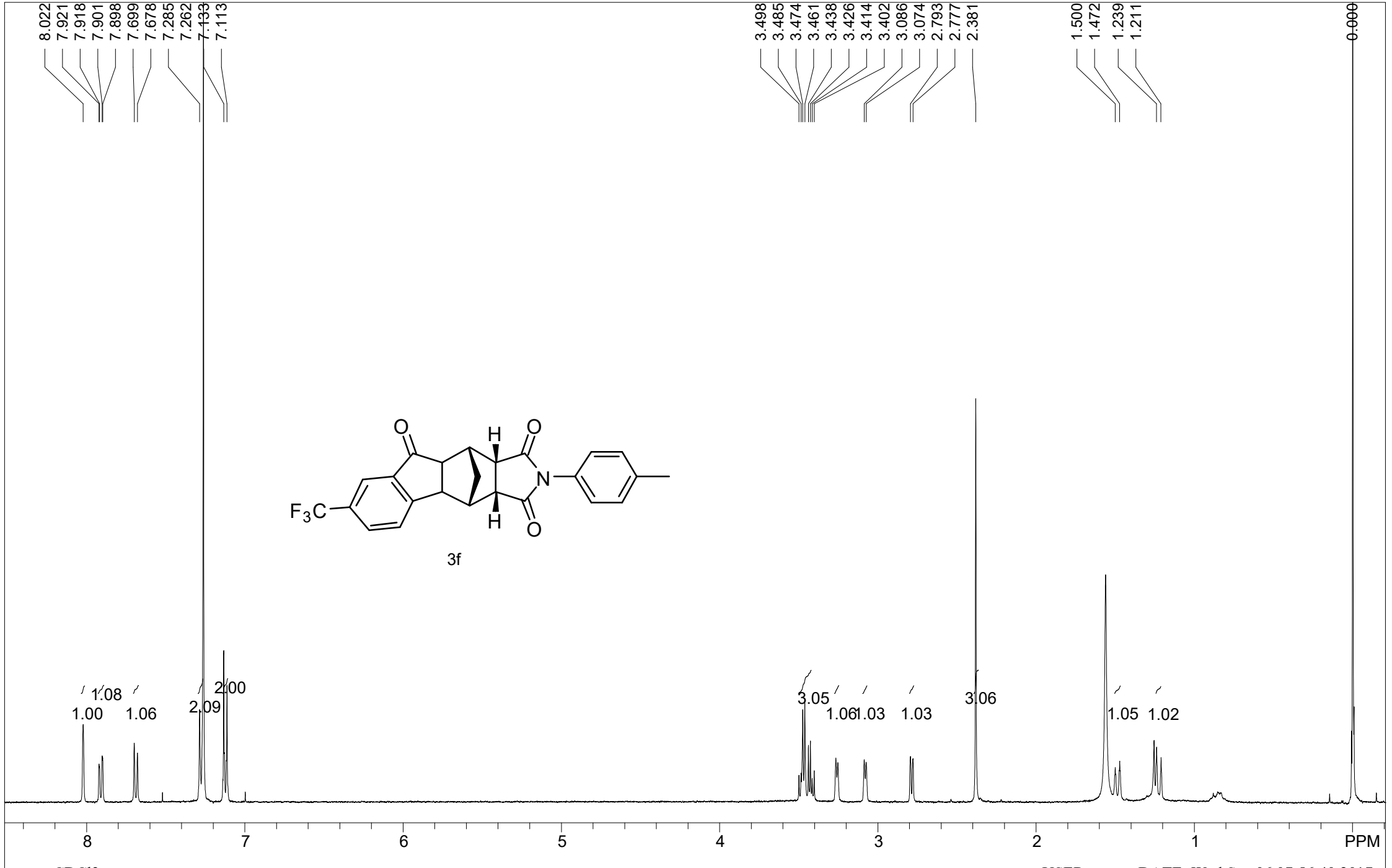

3f

spect, CDCl3,

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

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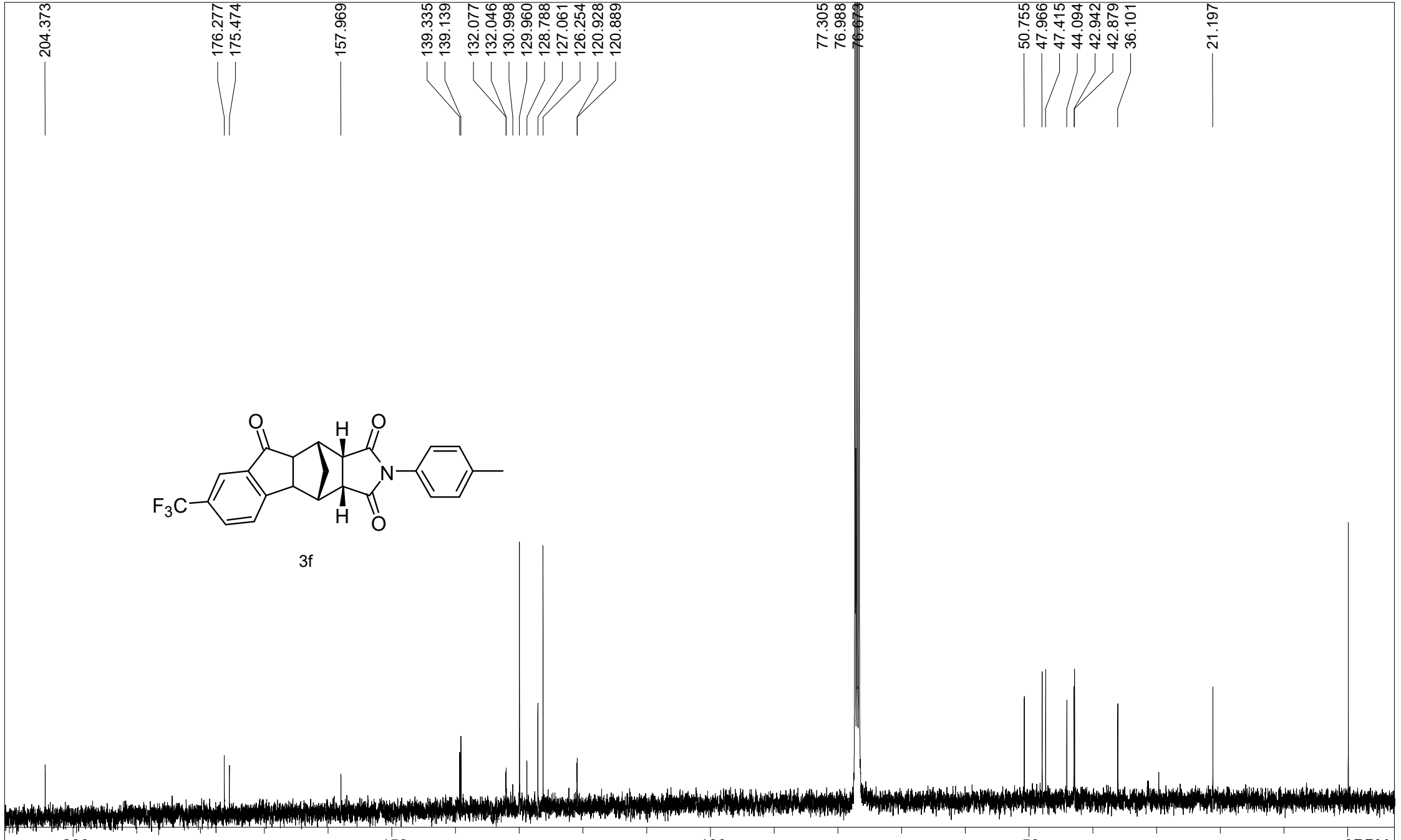

3f

spect, CDCl3,

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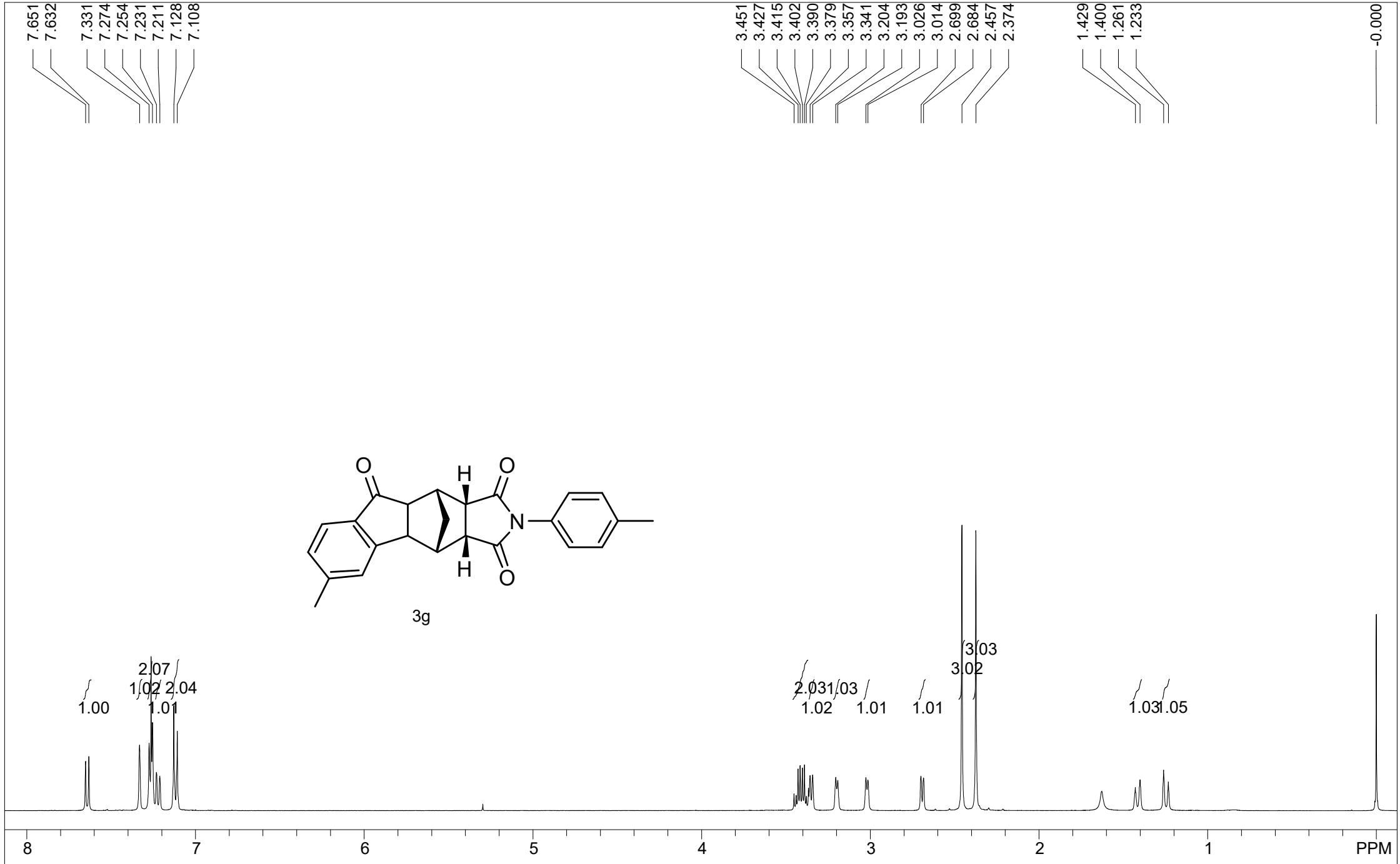

spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 08:05:47 2017

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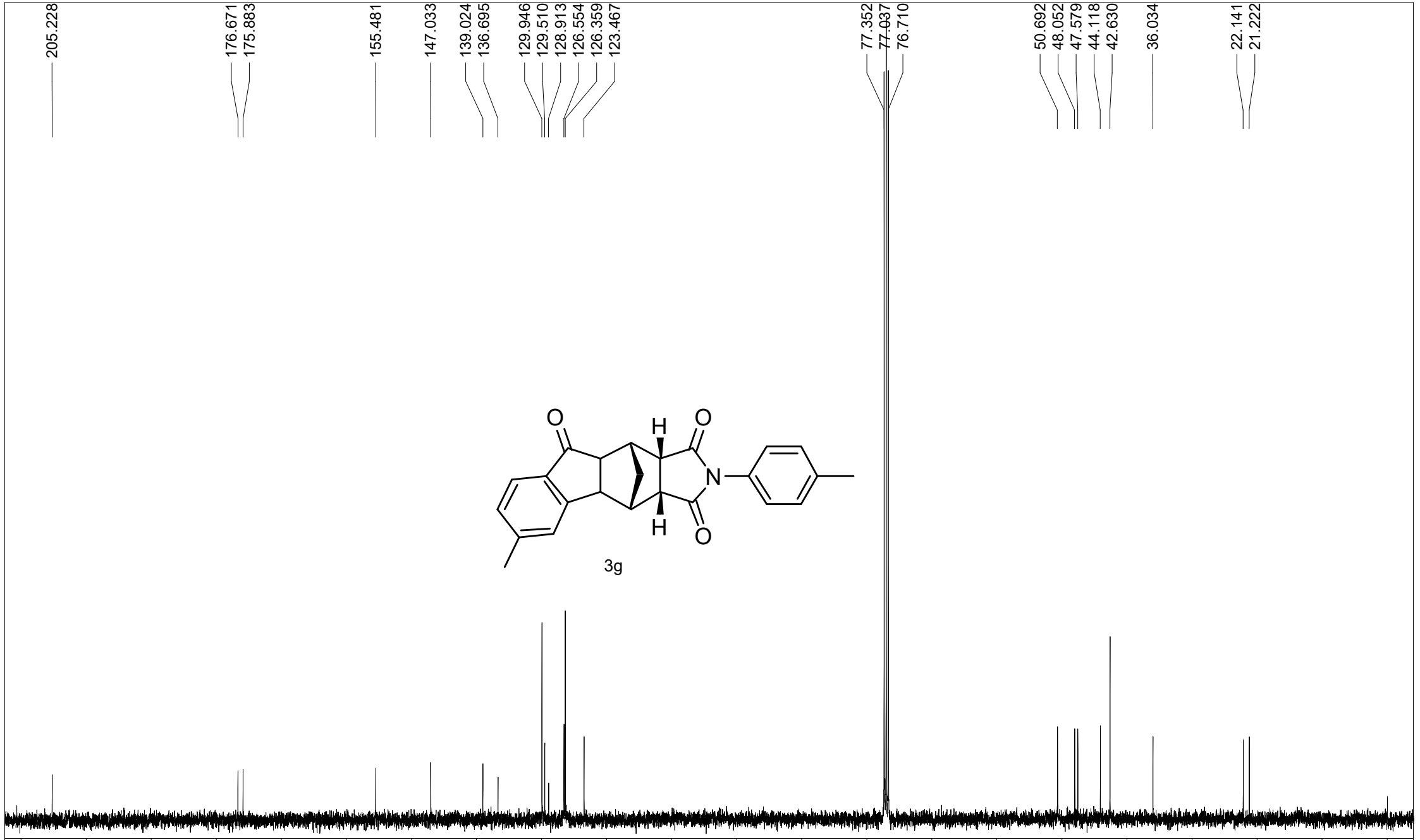

spect, CDCl3,

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

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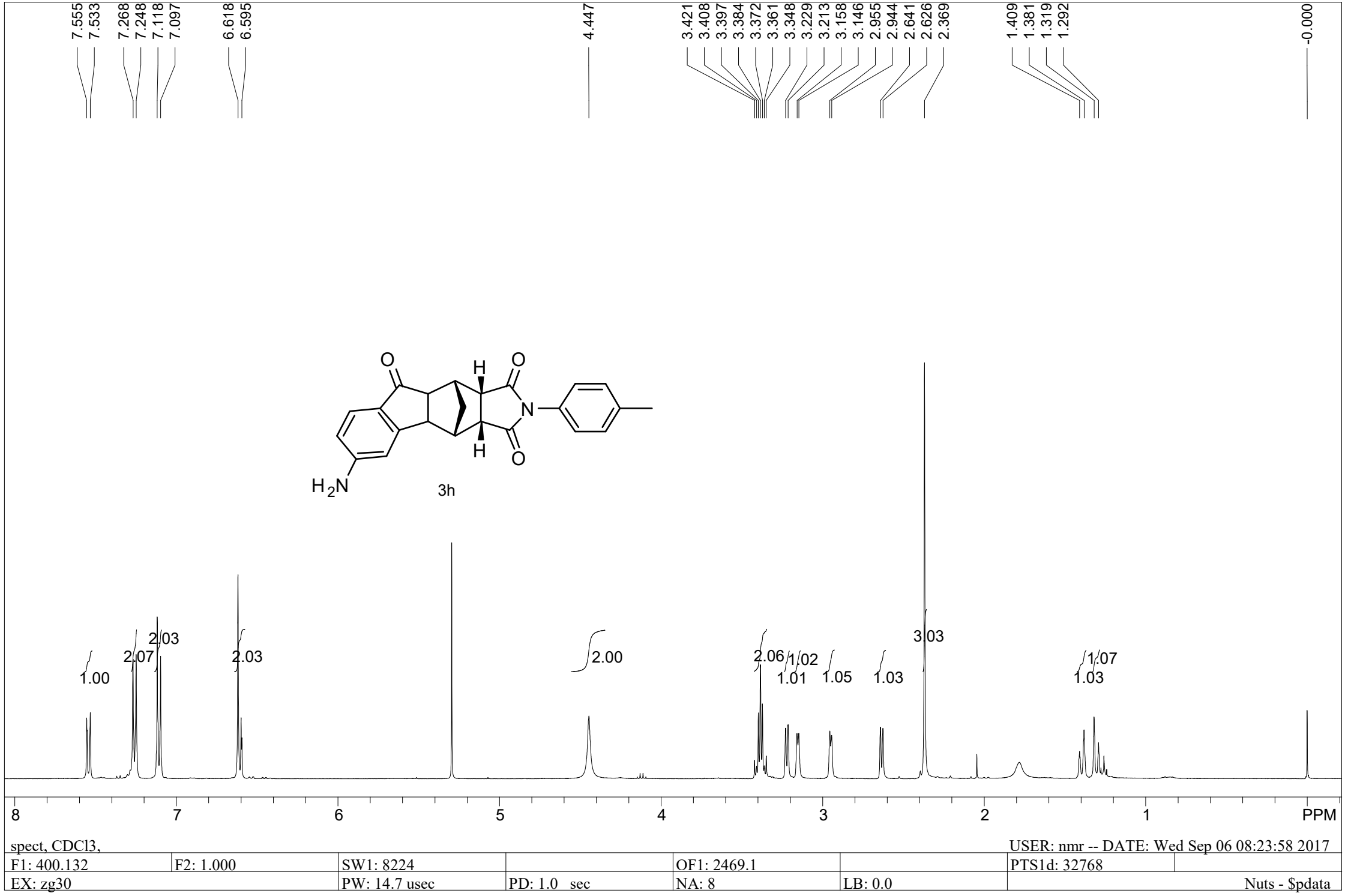

spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 08:23:58 2017

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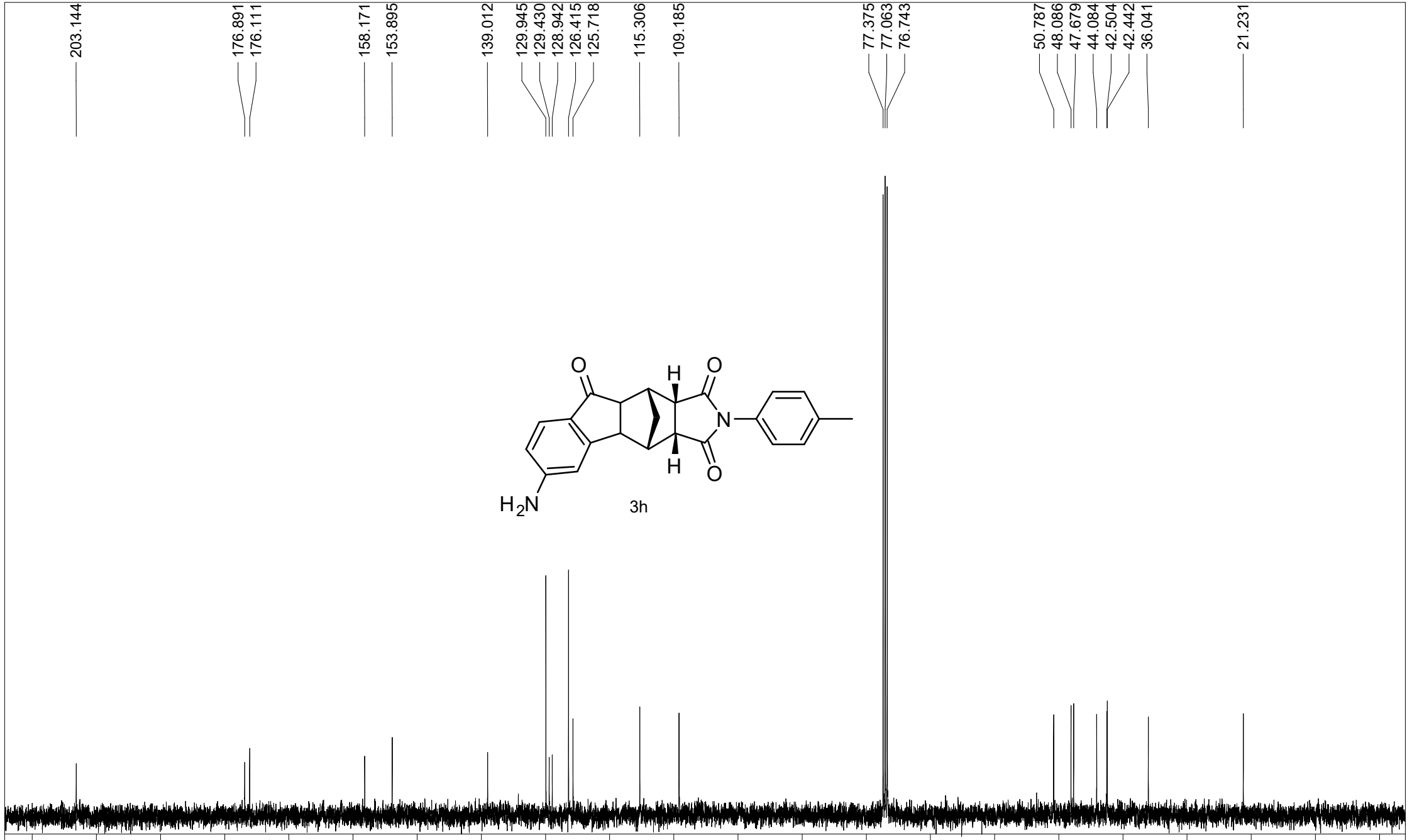

spect, CDCl3,

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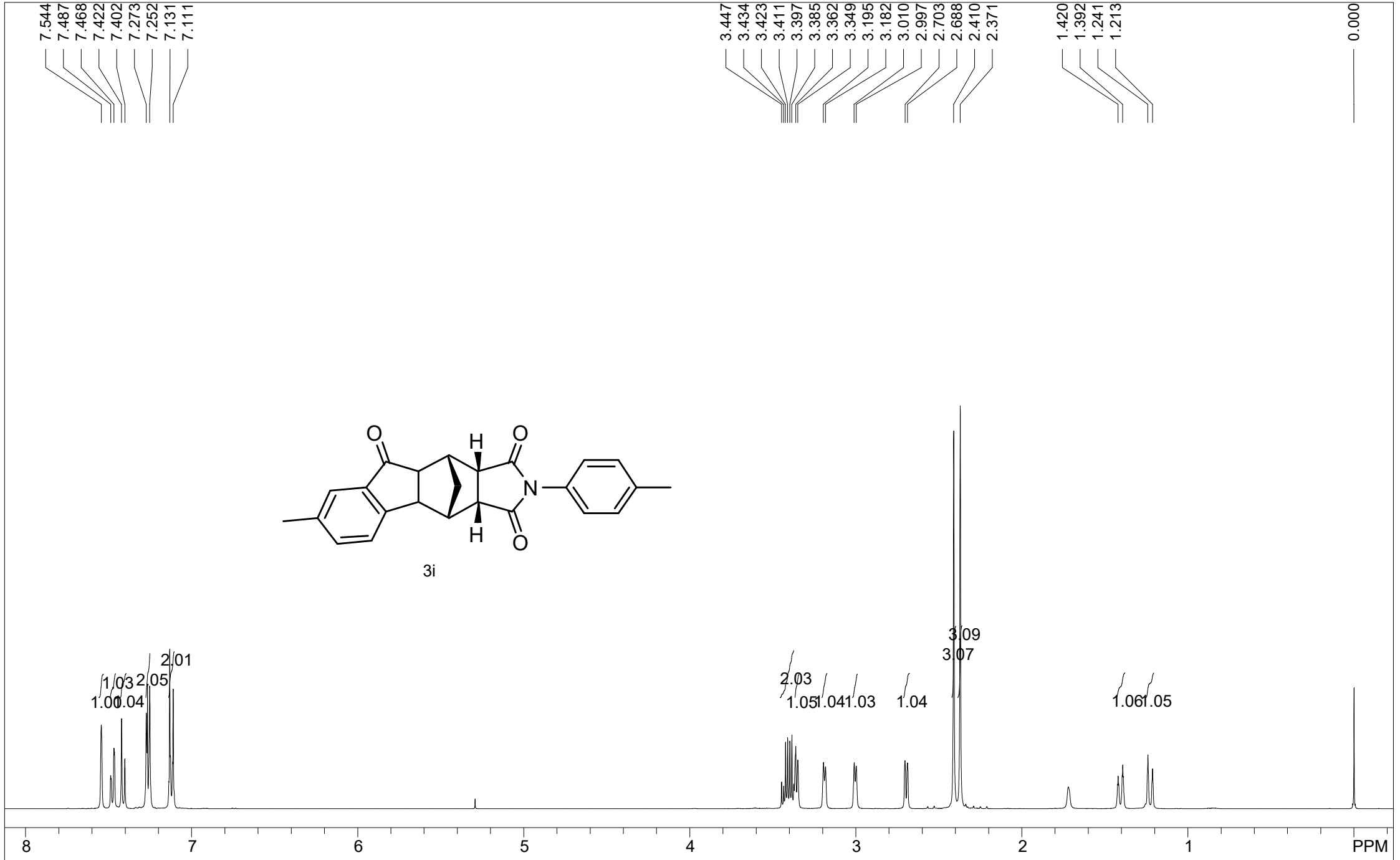

spect, CDCl3,

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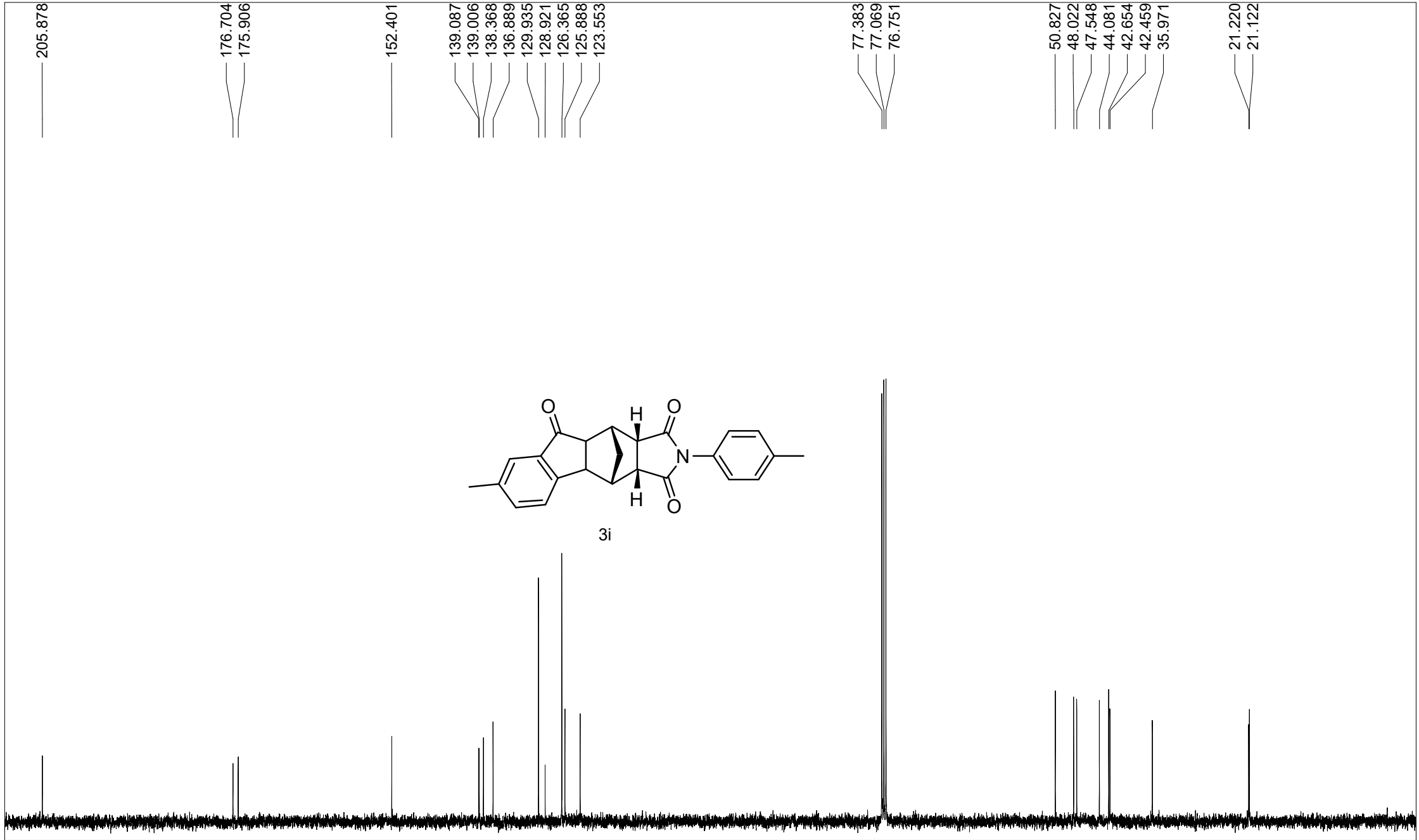

spect, CDCl3,

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

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
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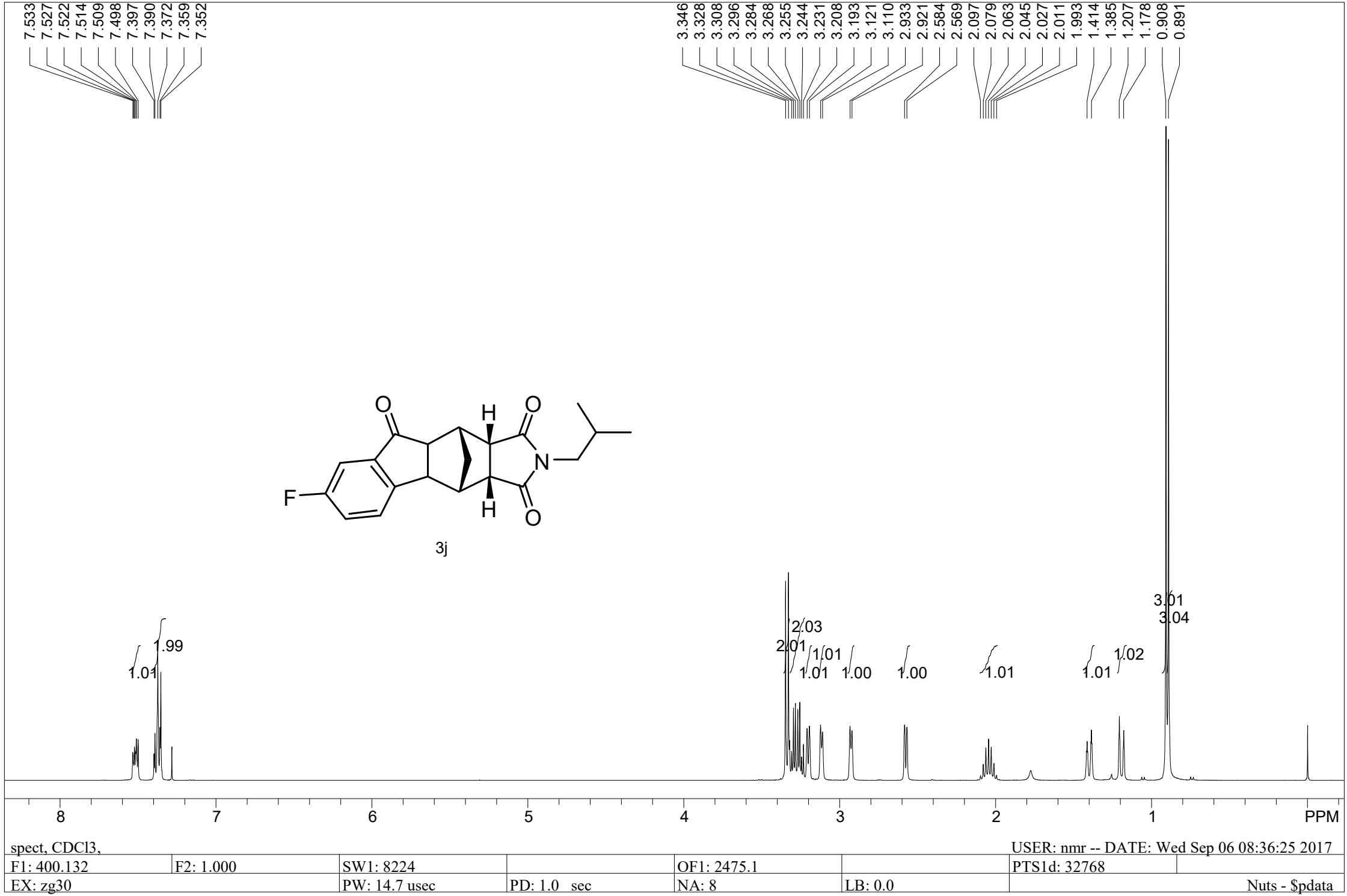
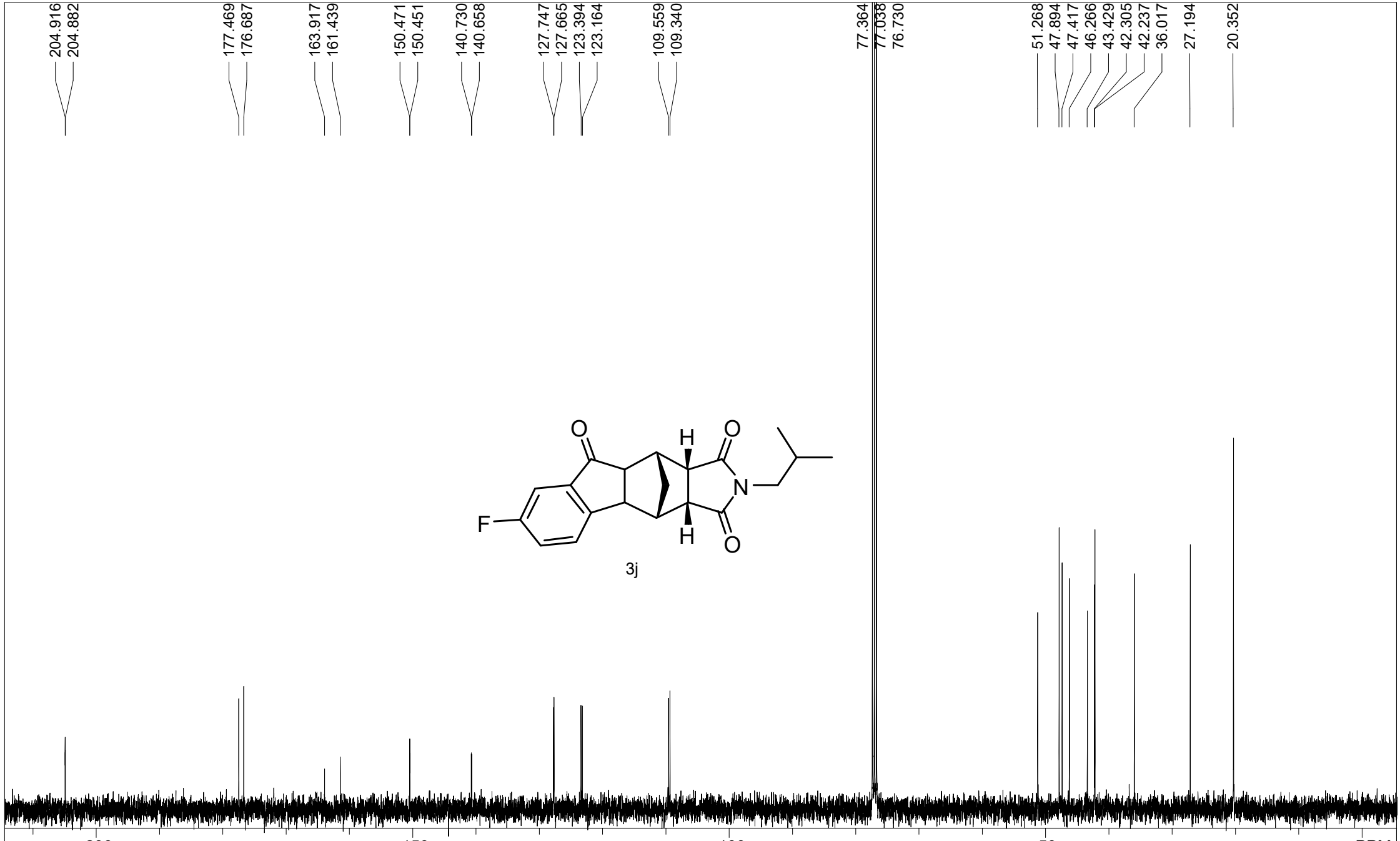


spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 08:36:25 2017

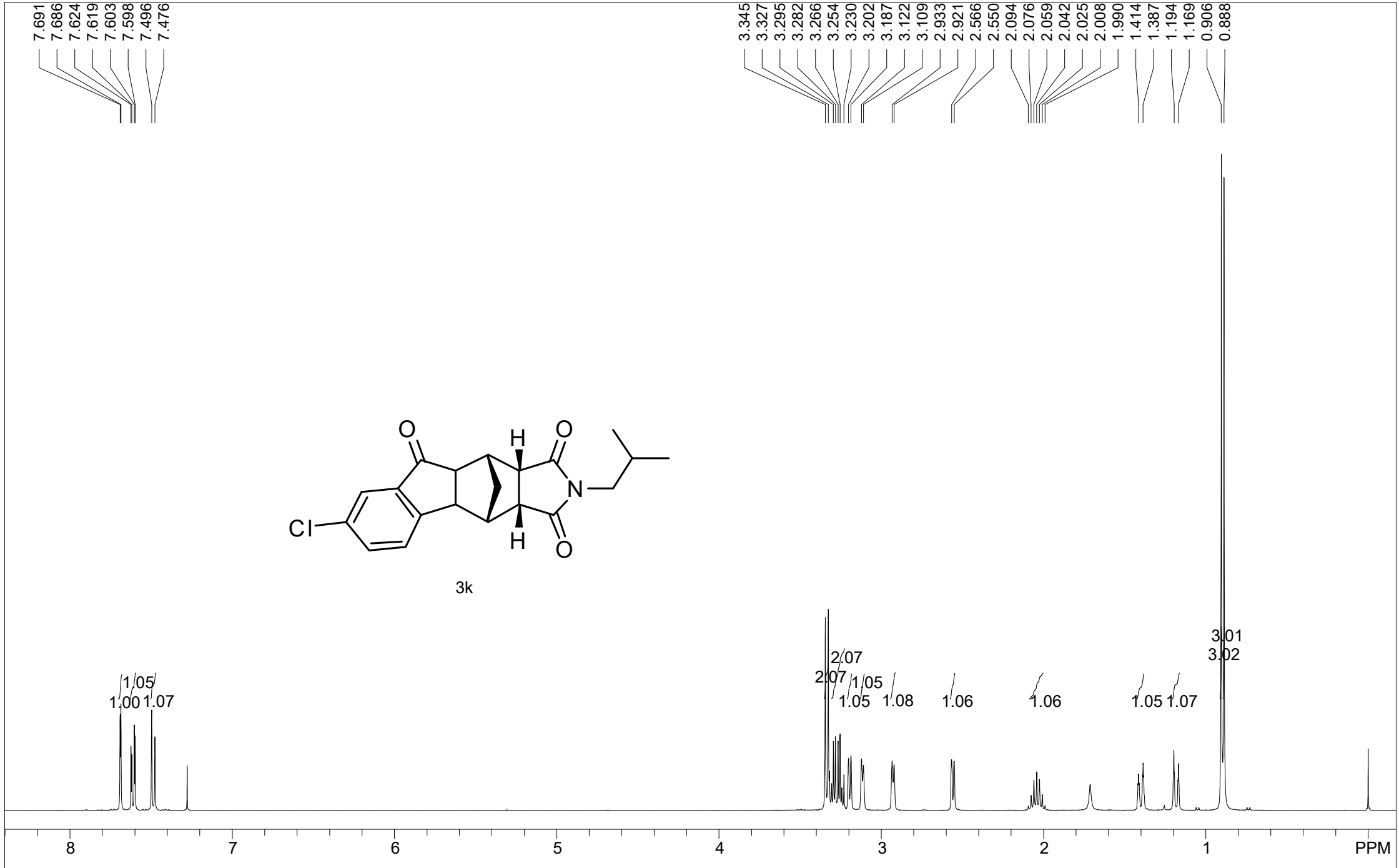
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2475.1		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 07:33:44 2017

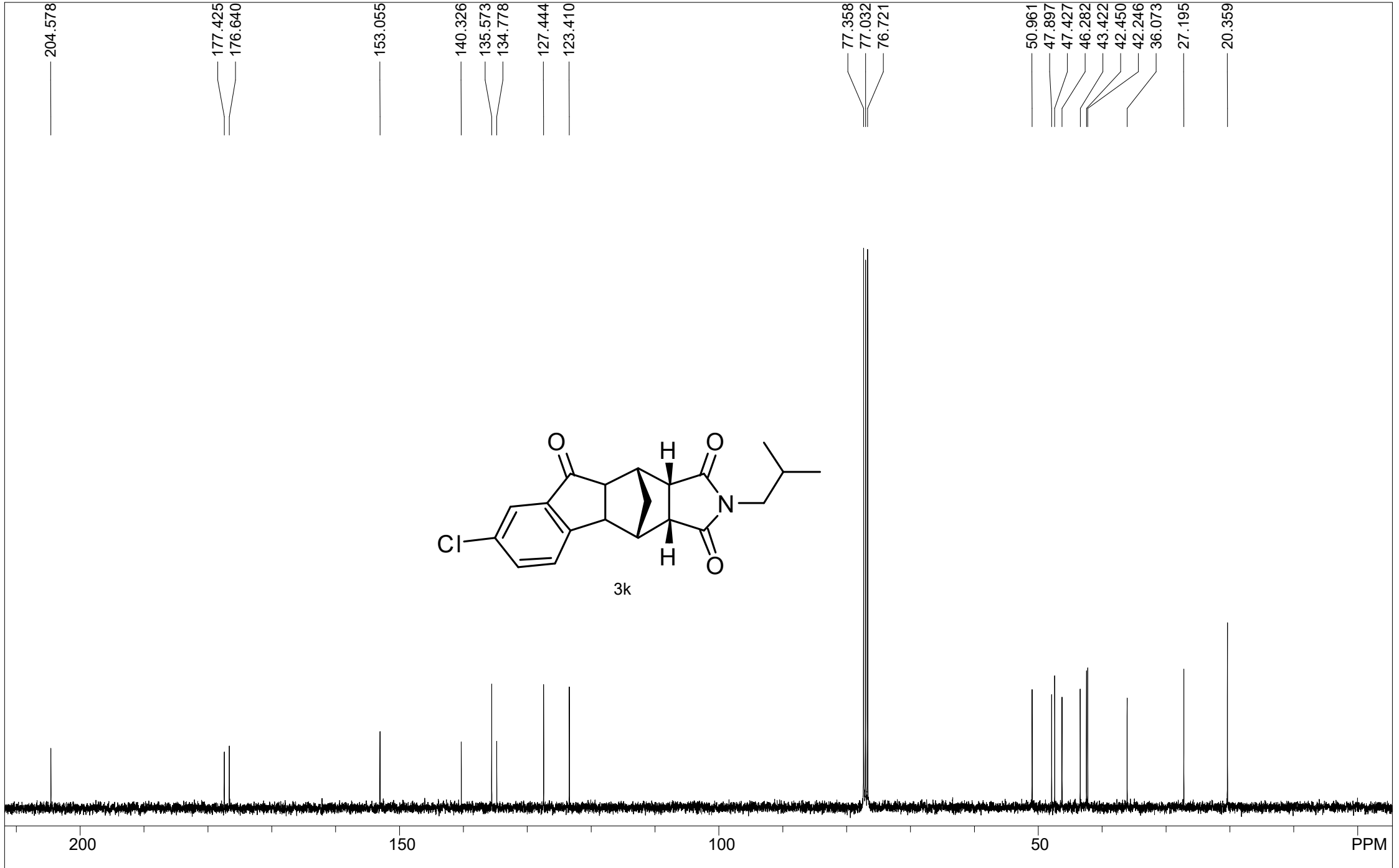
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 40	LB: 0.0	Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 09:04:21 2017

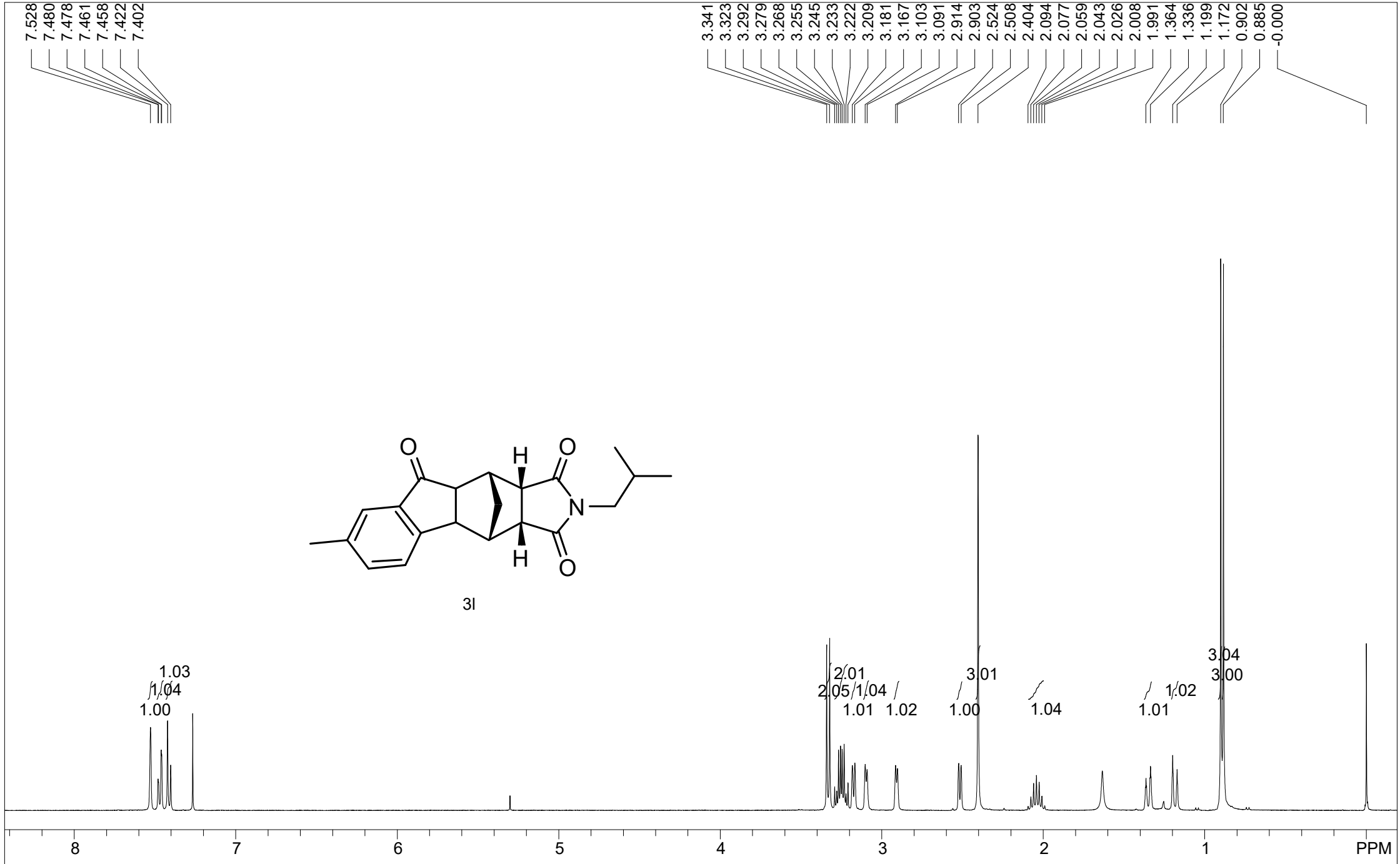
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2473.2		PTS1d: 32768	
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - $pdata



spect, CDCl3,

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

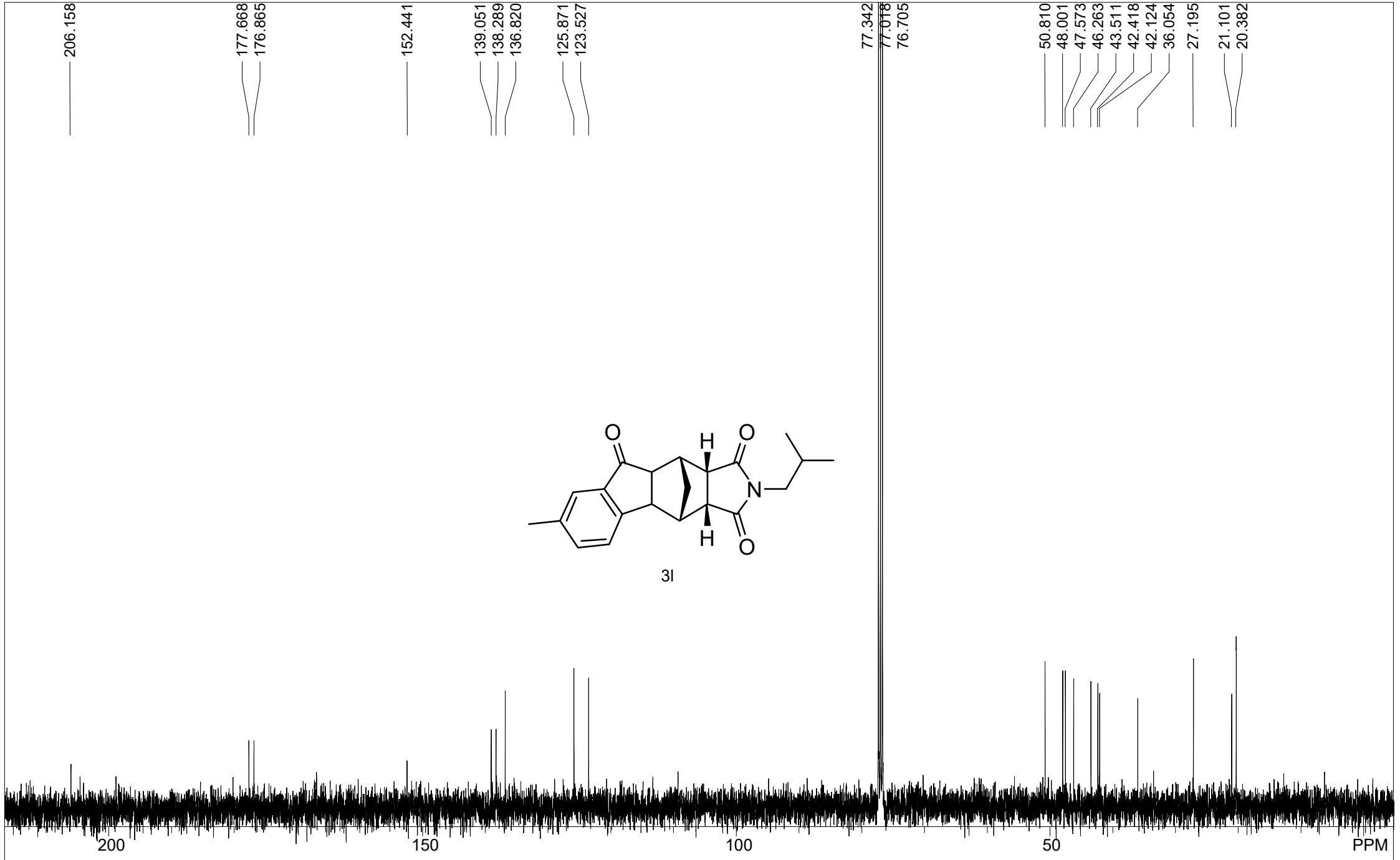
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 114	LB: 0.0	Nuts - $pdata



spect, CDCl3,

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

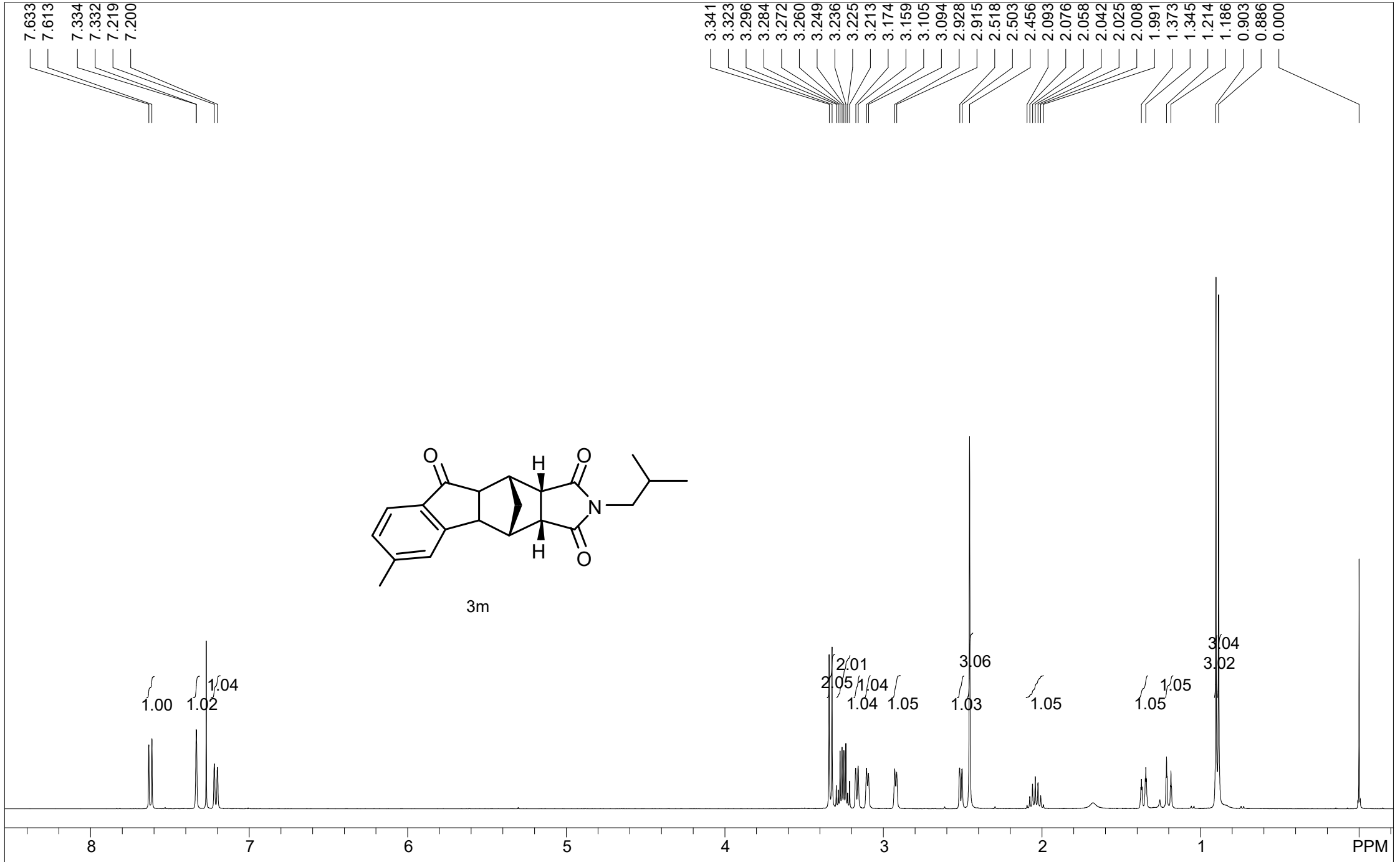


3l

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 07 07:07:35 2017

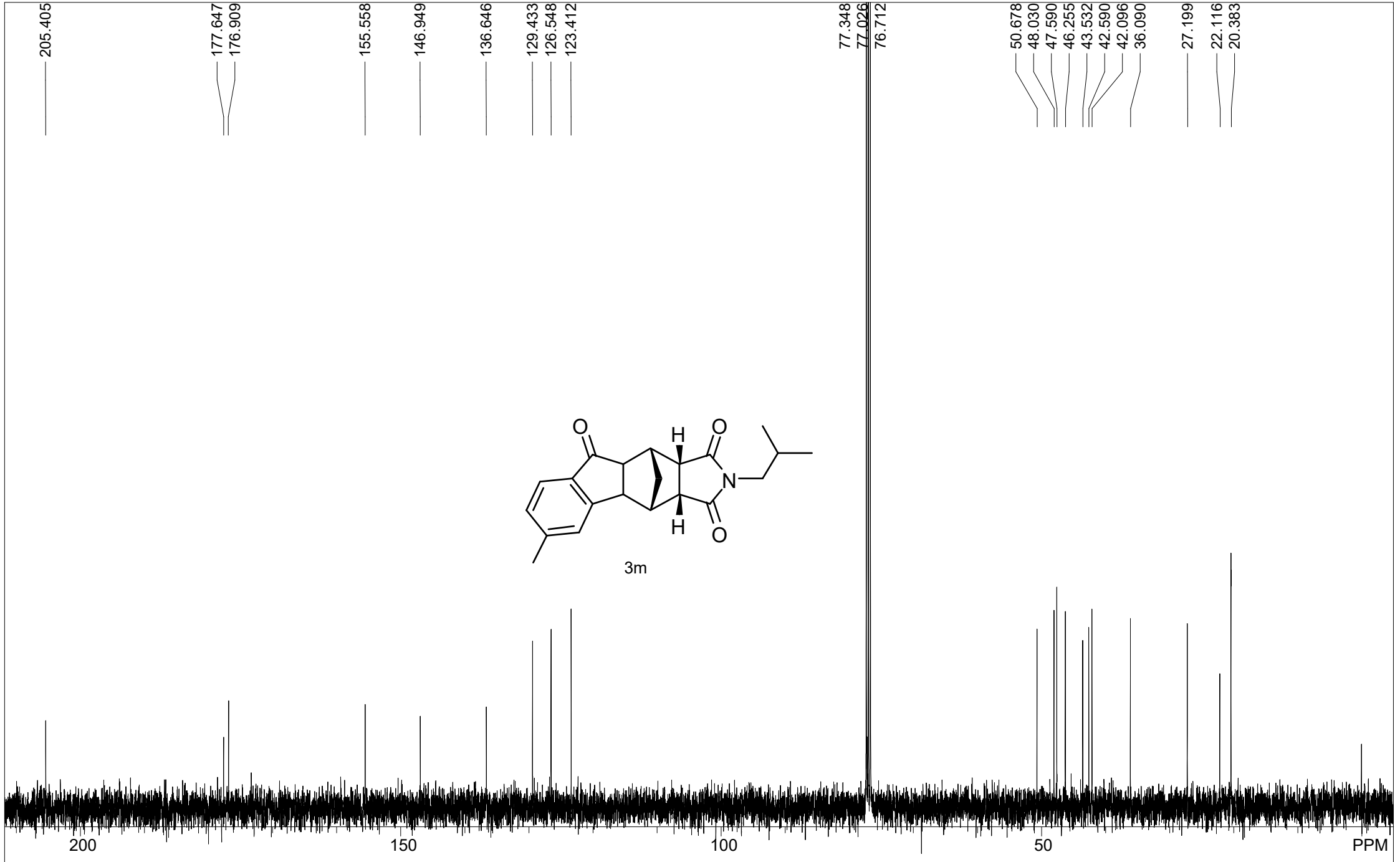
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 80	LB: 0.0		Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 06 08:01:09 2017

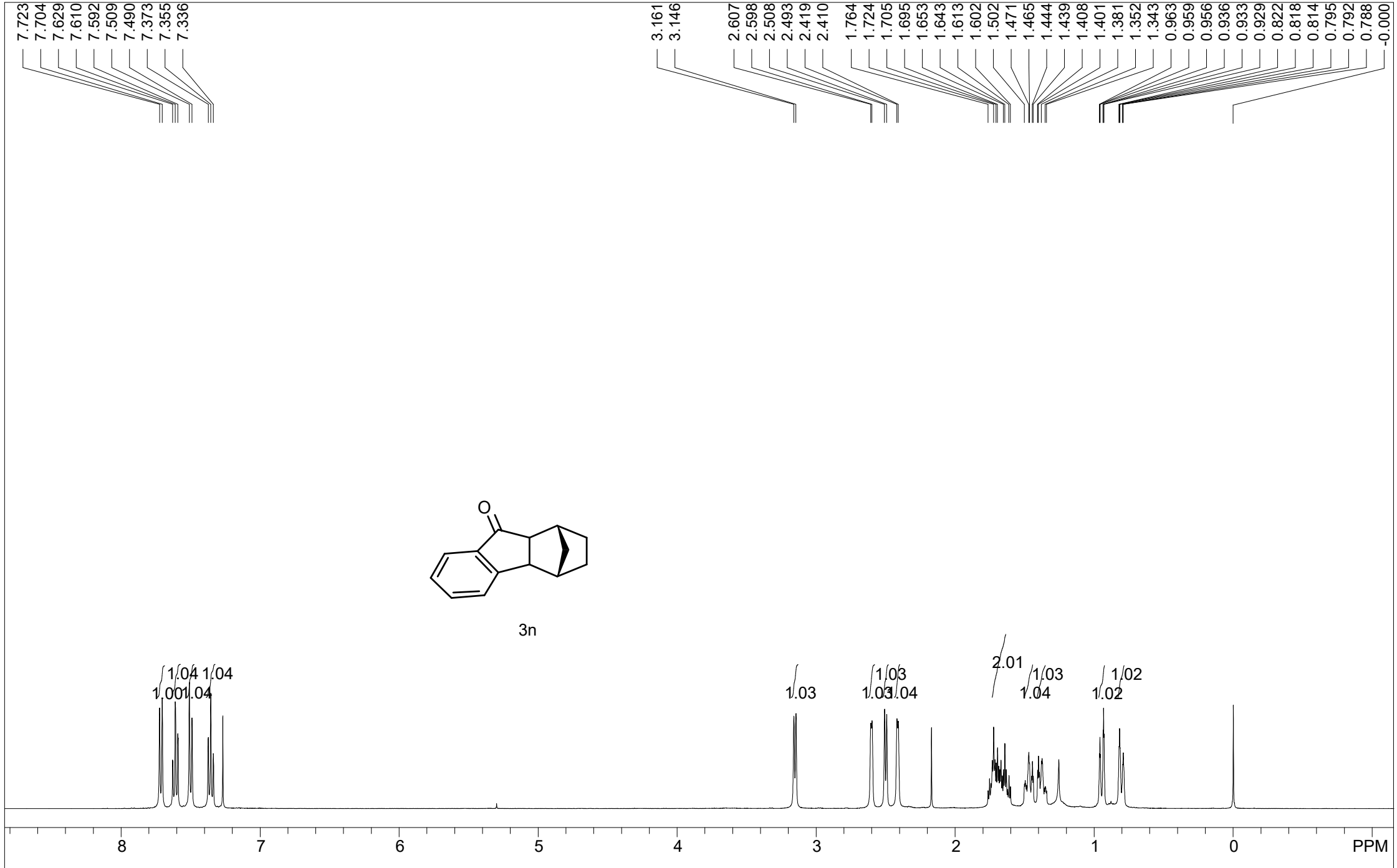
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2470.4		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata



spect, CDCl3,

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

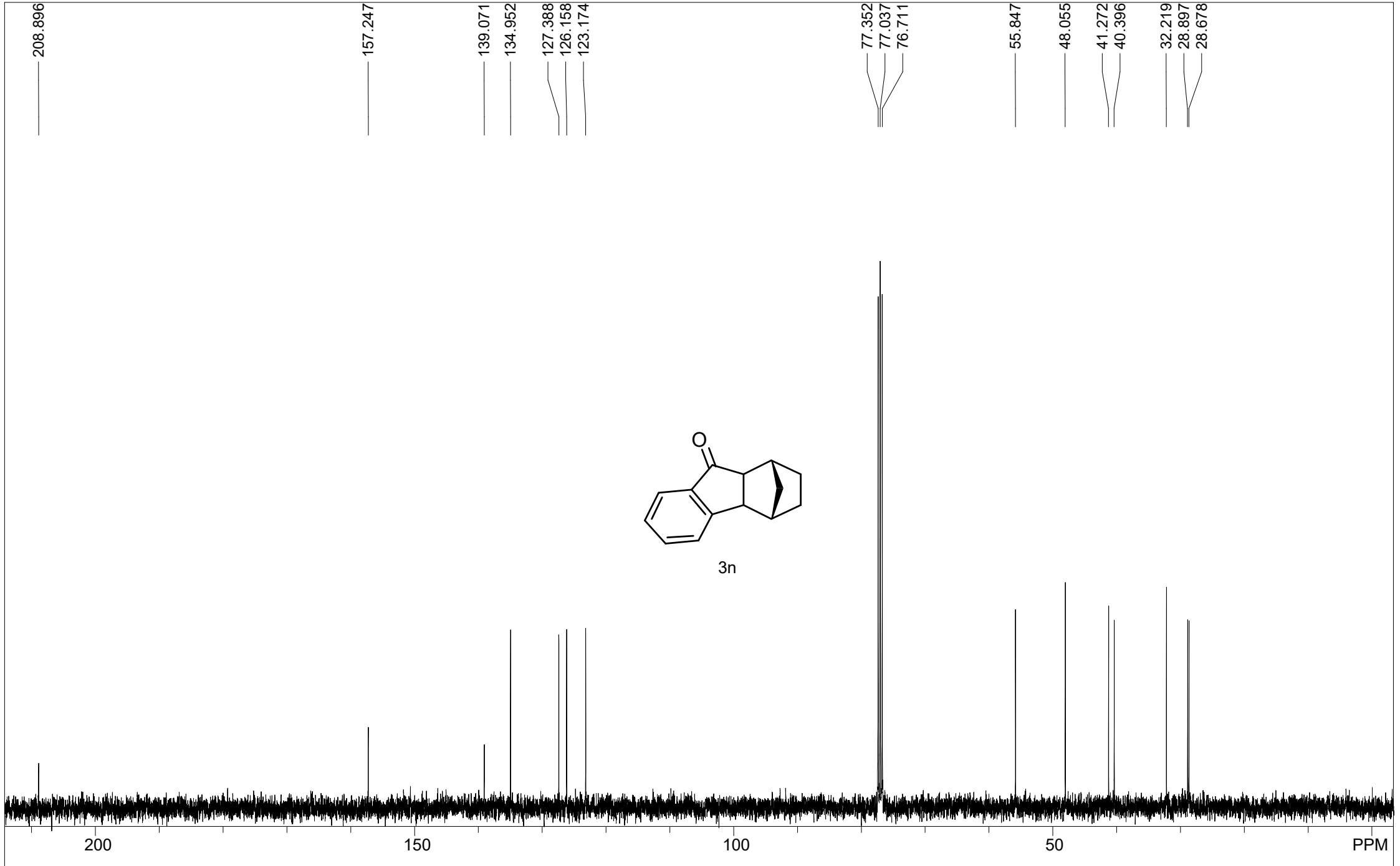
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 50	LB: 0.0		Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:22:22 2017

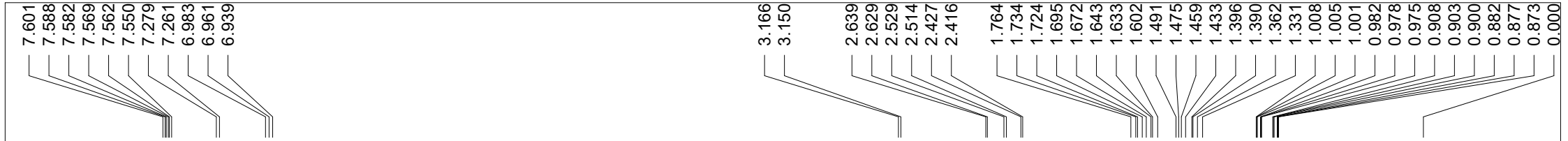
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2469.3		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata

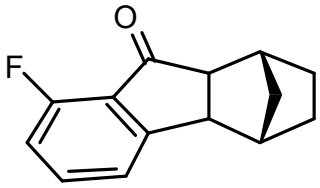


spect, CDCl3,

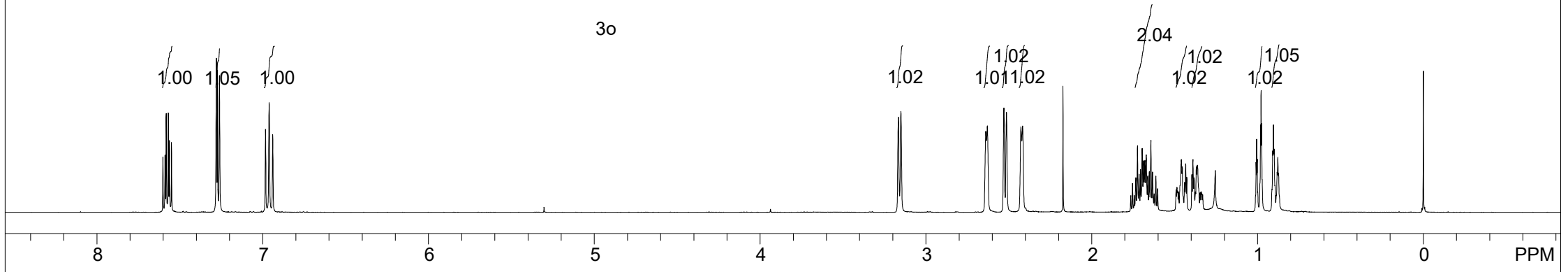
USER: nmr -- DATE: Thu Sep 14 07:00:20 2017

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





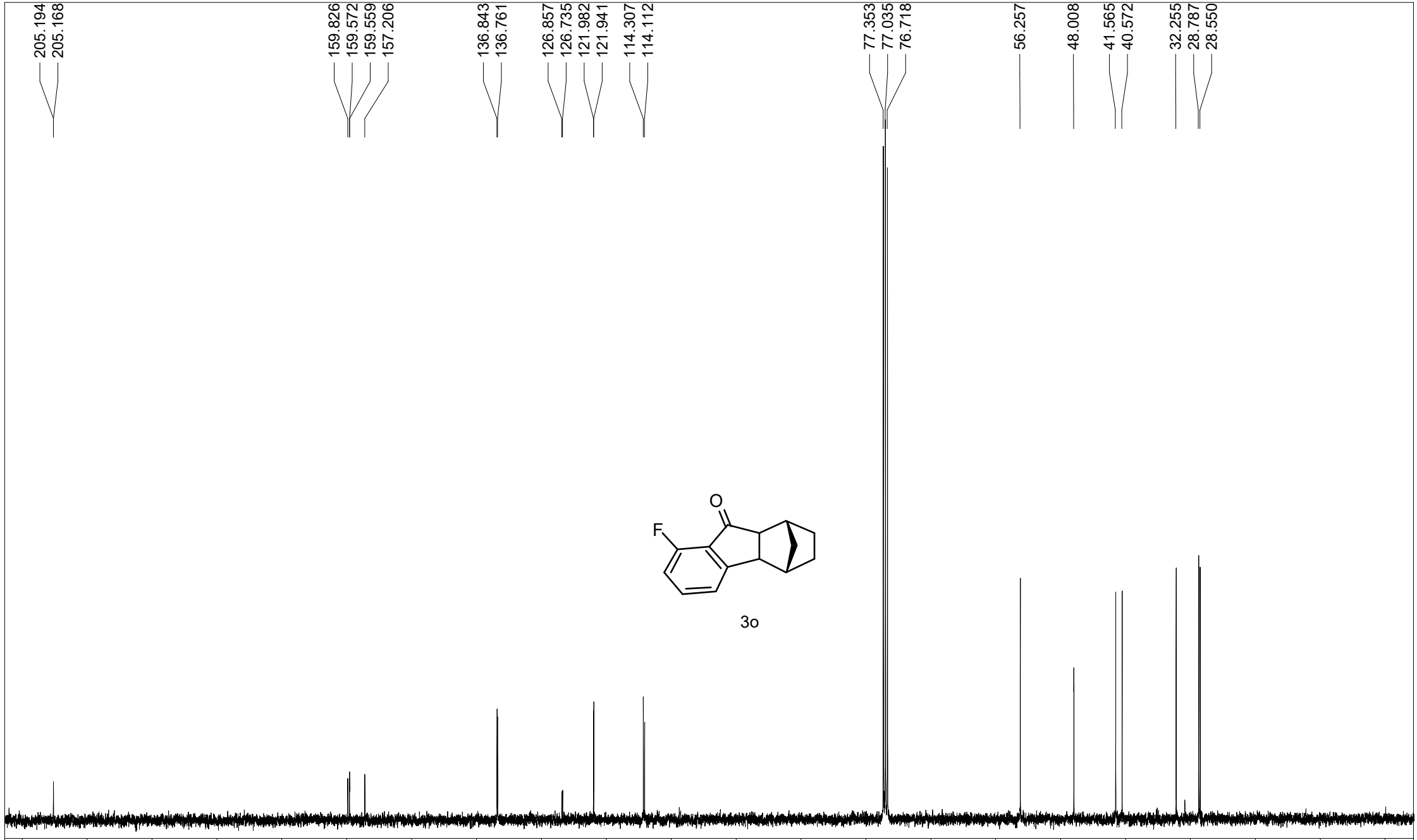
3o



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

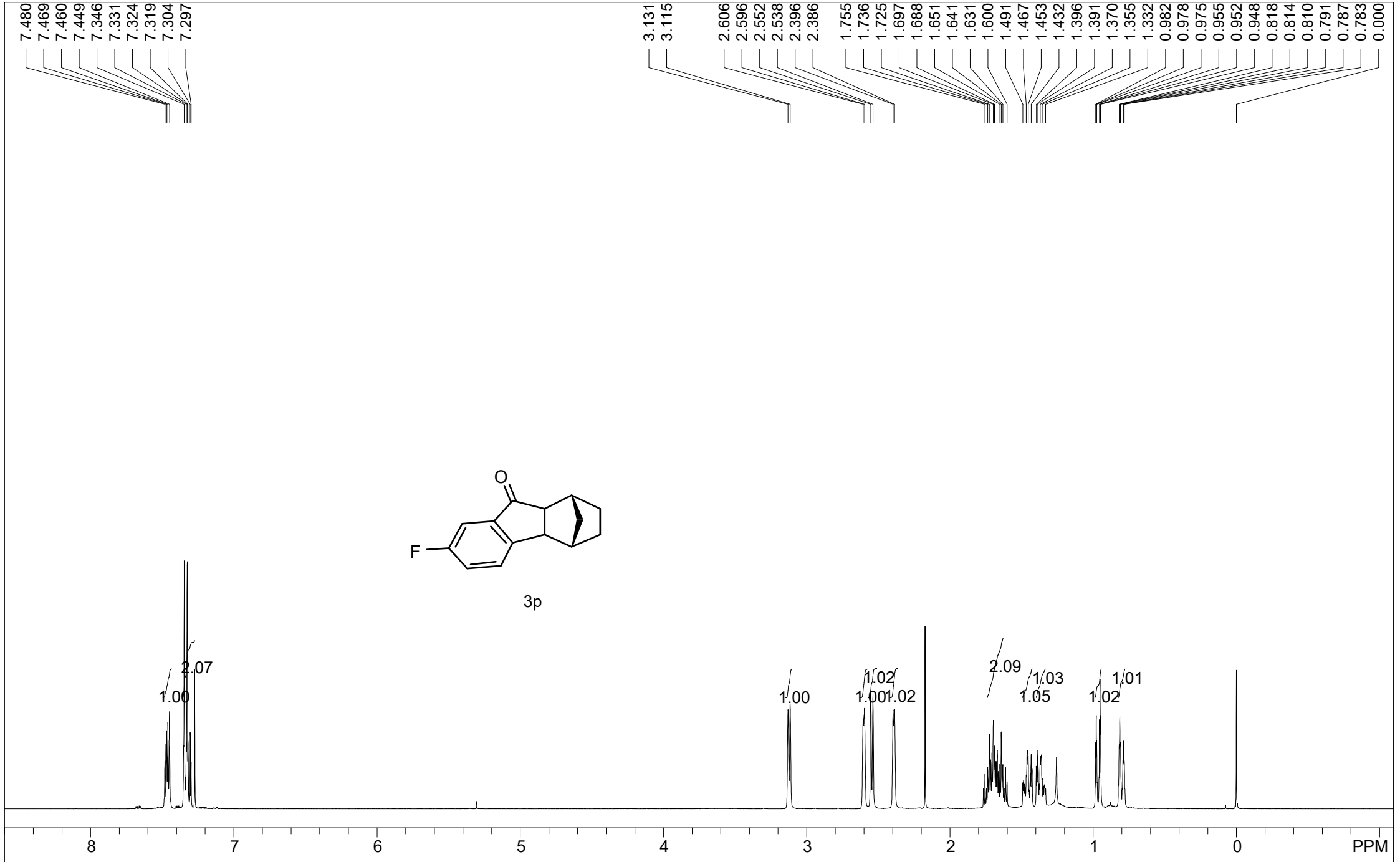


3o

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



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:04:02 2017

F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2471.0		PTS1d: 32768
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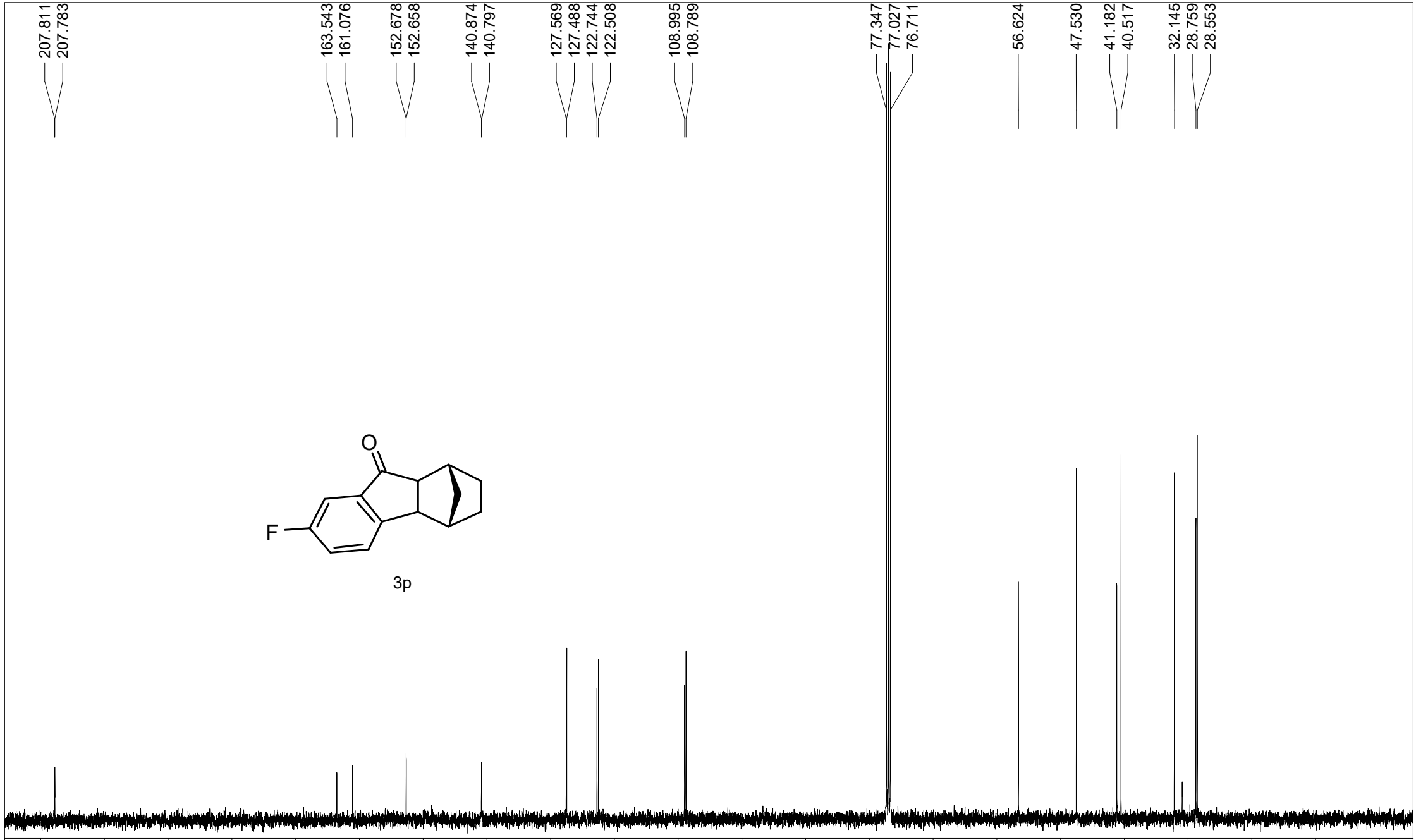
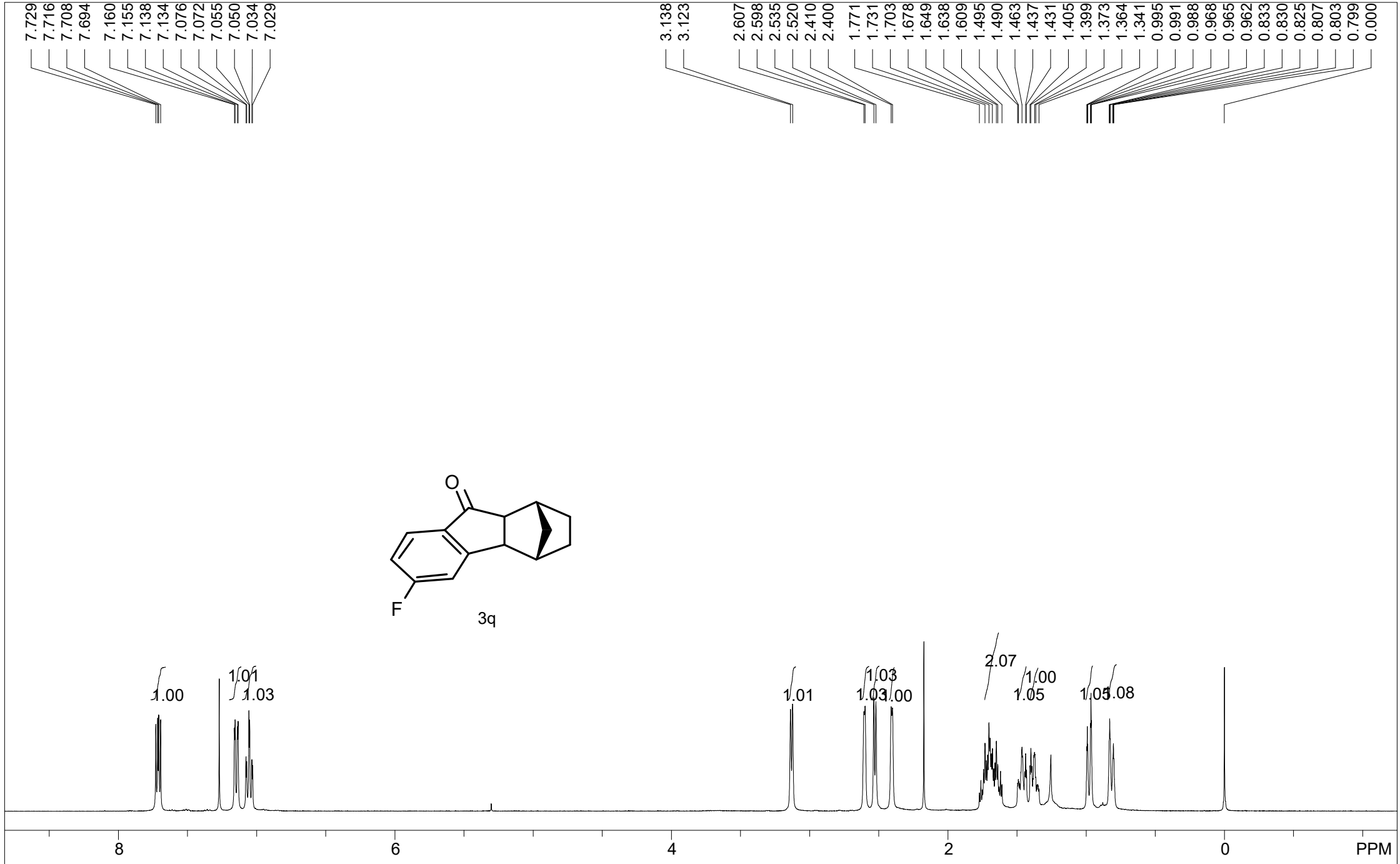


spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 08:18:15 2017

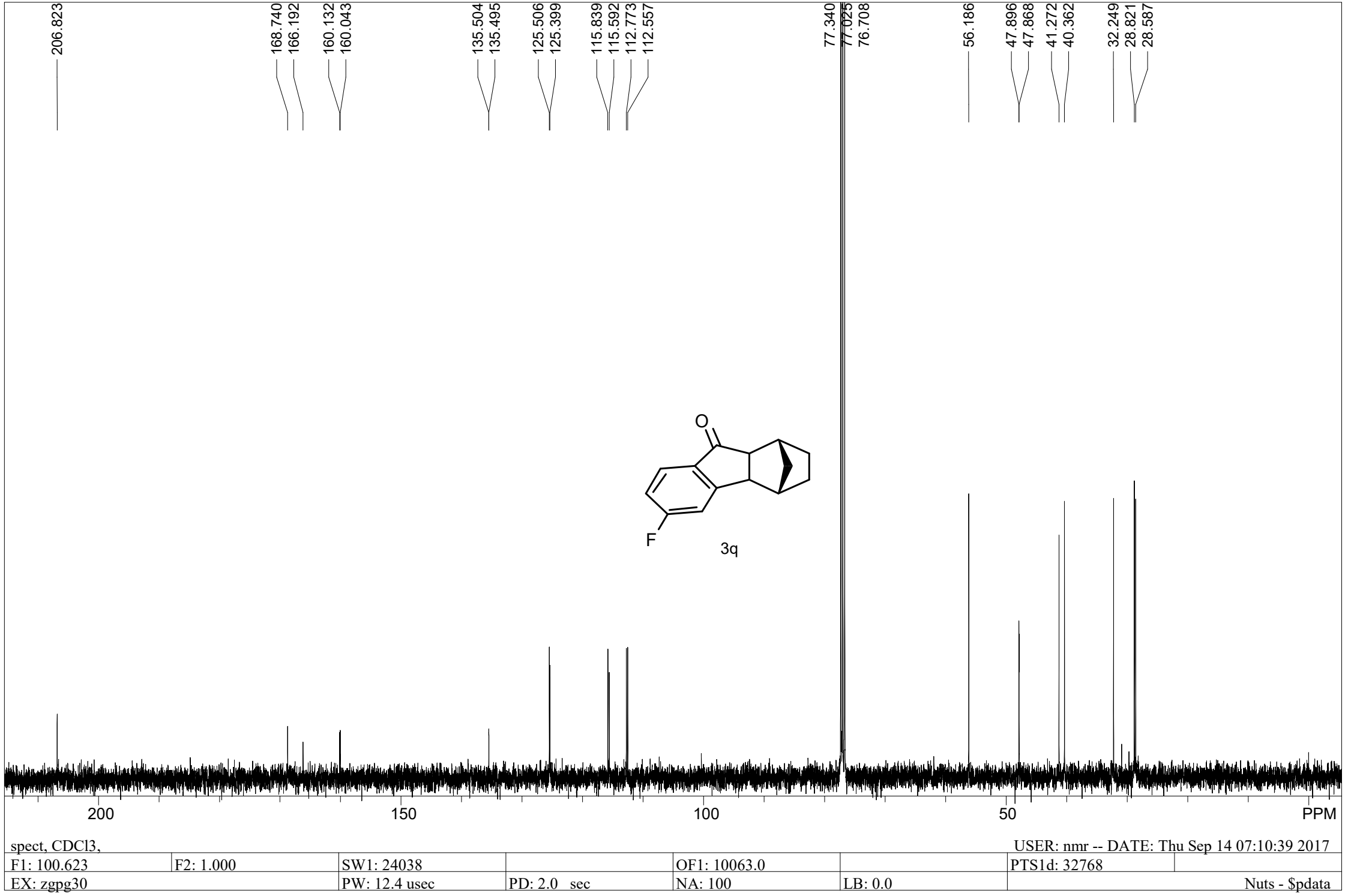
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 180	LB: 0.0		Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:26:10 2017

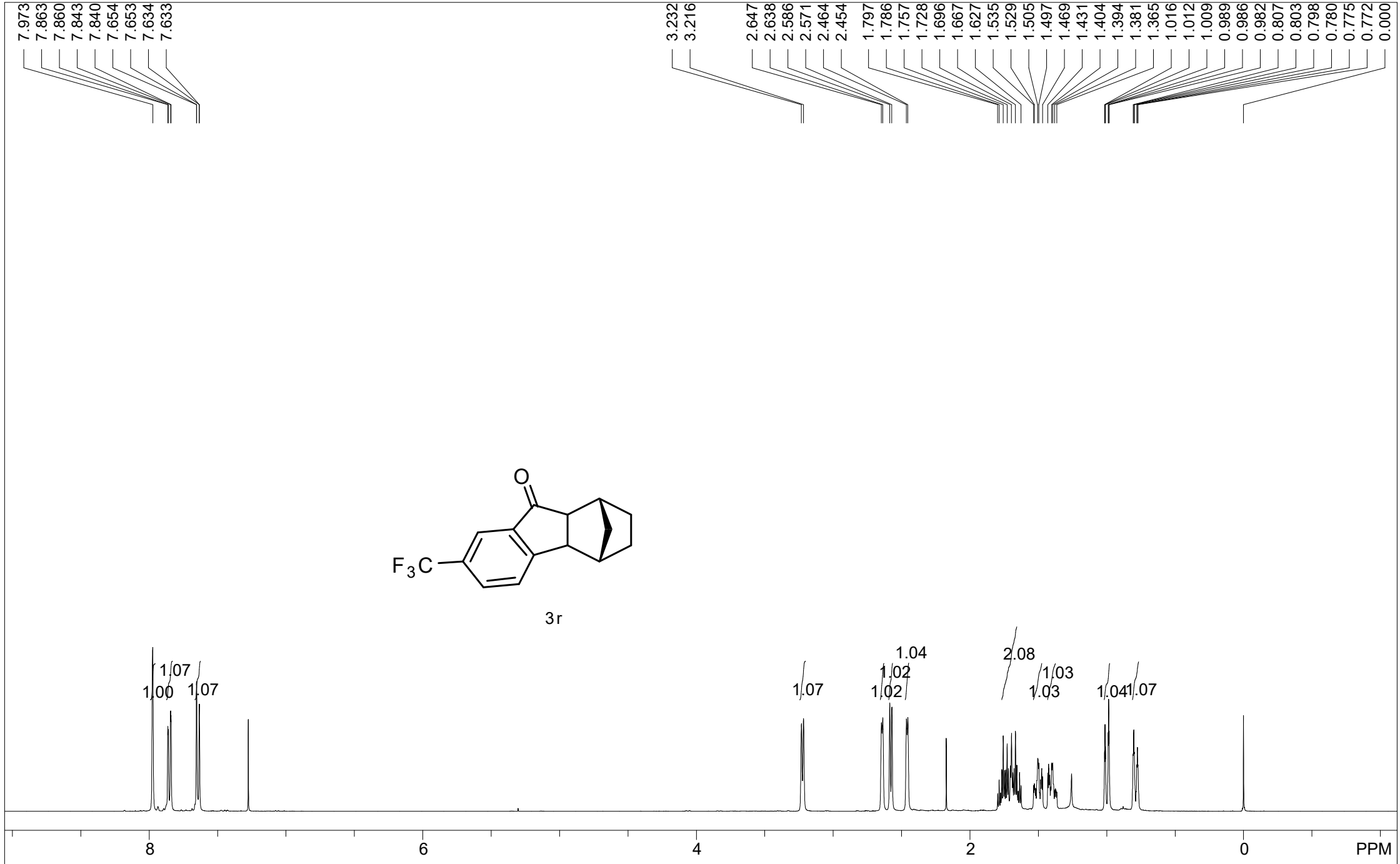
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2470.1		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 07:10:39 2017

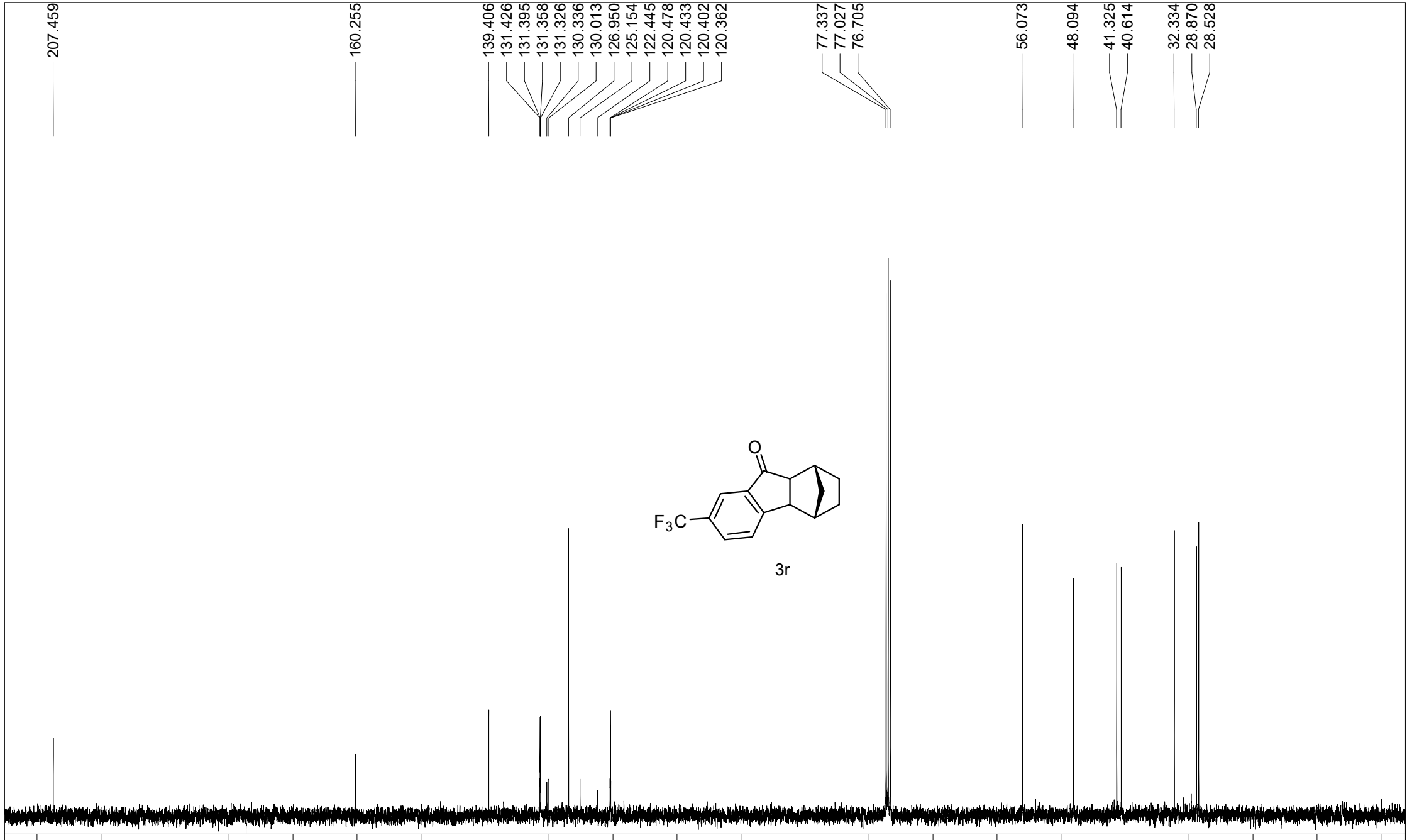
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 100	LB: 0.0	Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:30:21 2017

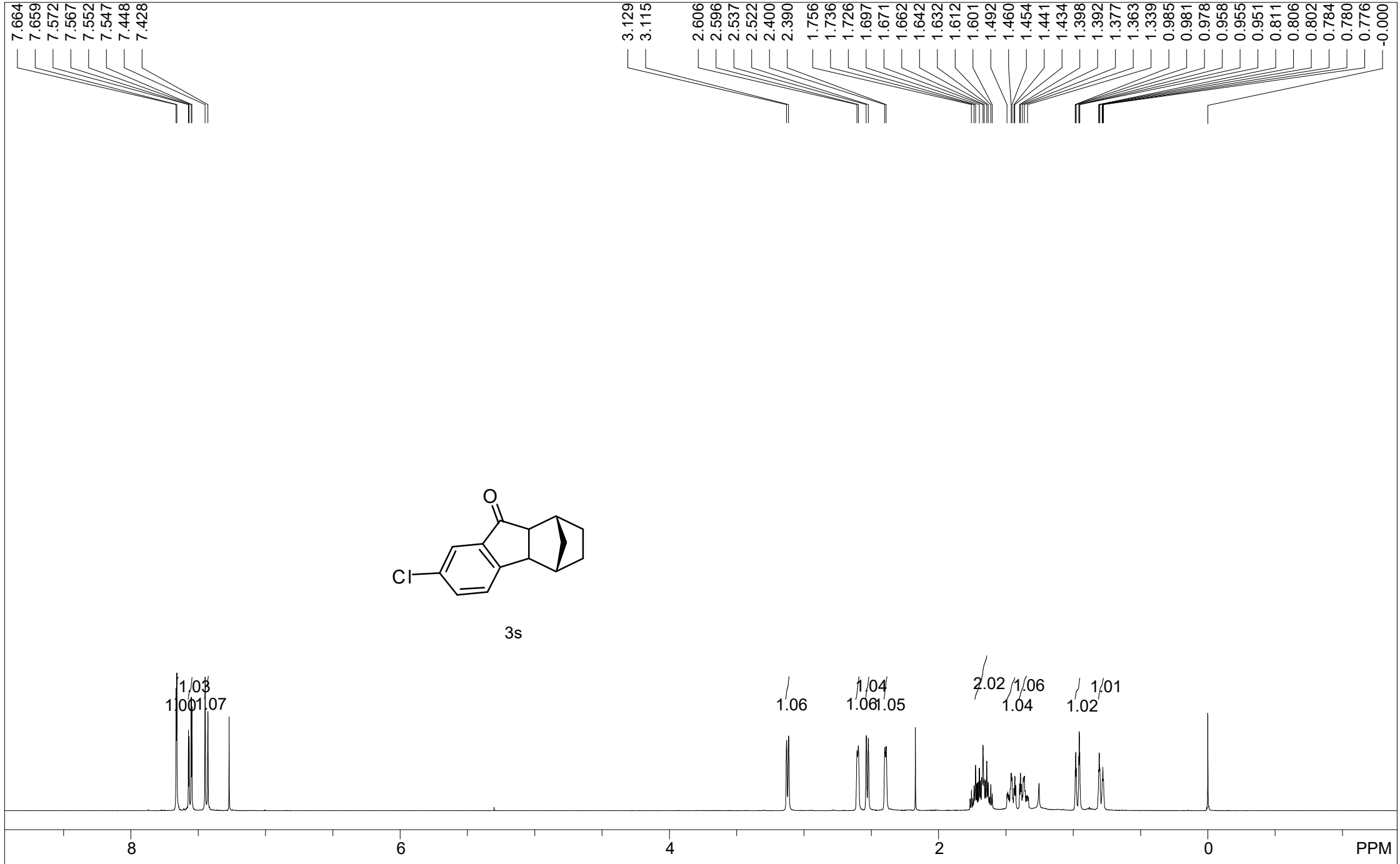
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2472.2		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata



spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 07:18:04 2017

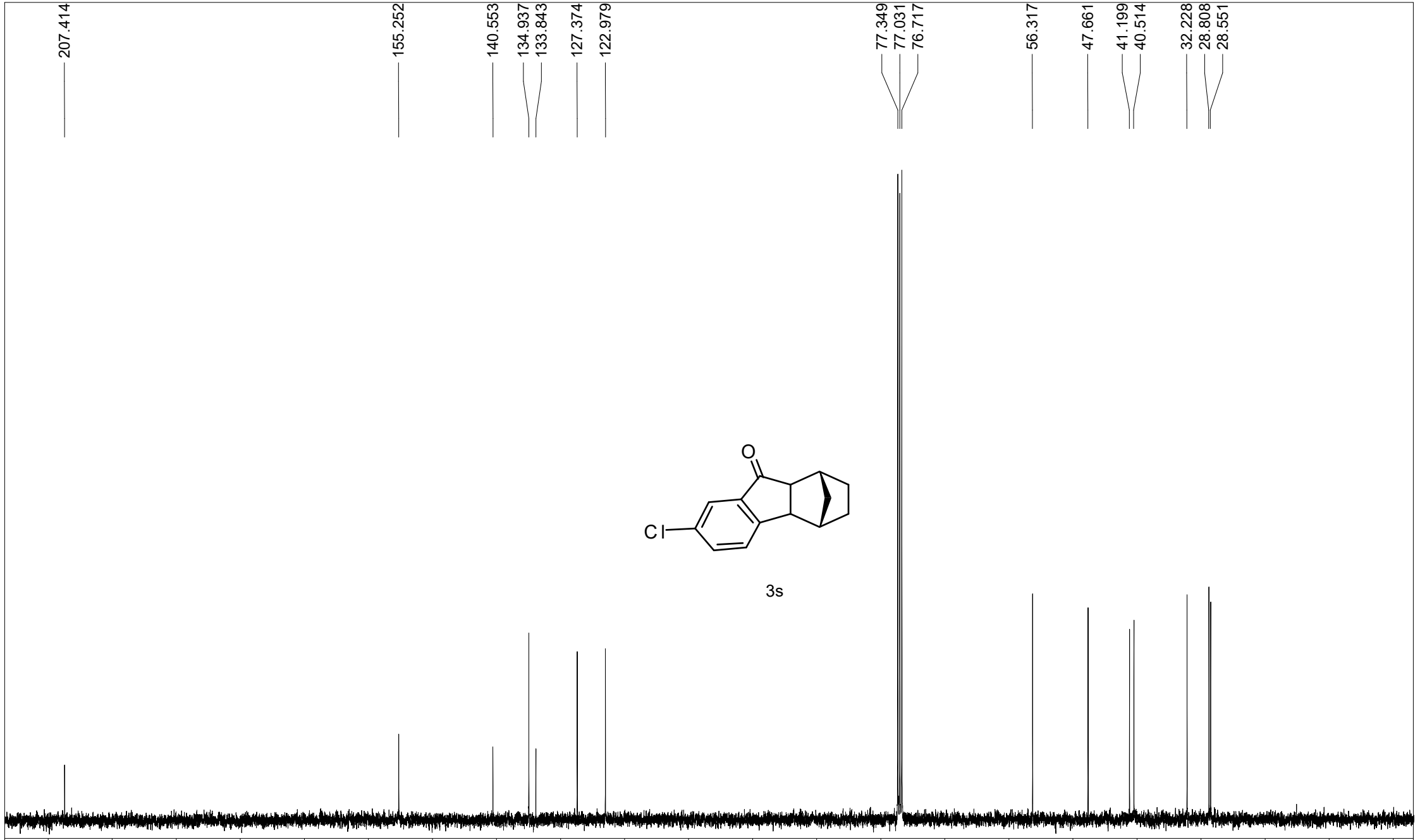
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 60	LB: 0.0		Nuts - $pdata



spect, CDCl3,

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

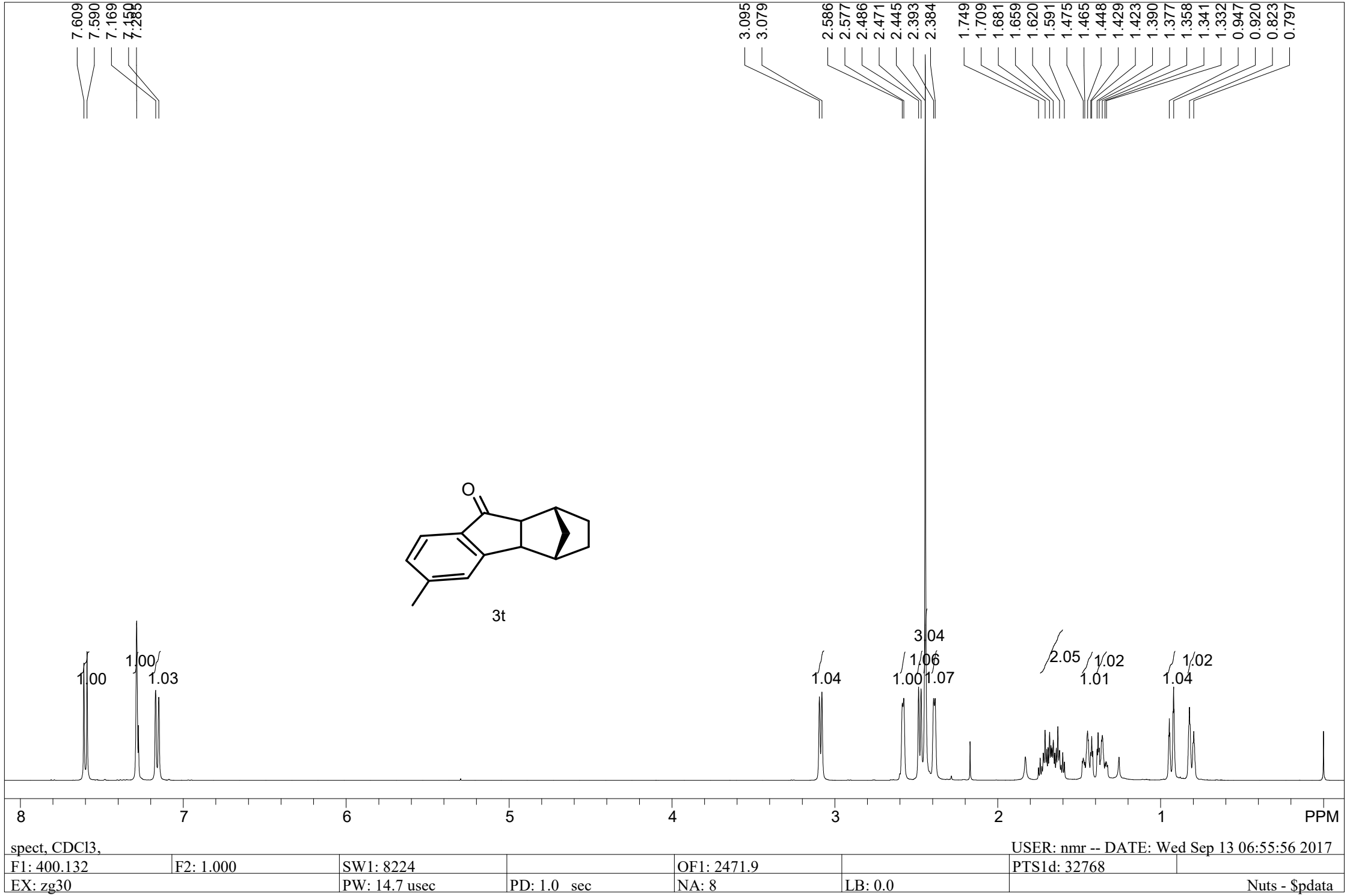
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2470.2		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata



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
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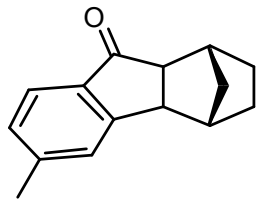
41.240
40.270
32.196
28.895
28.706
22.111



3t

200
150
100
50
0
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	
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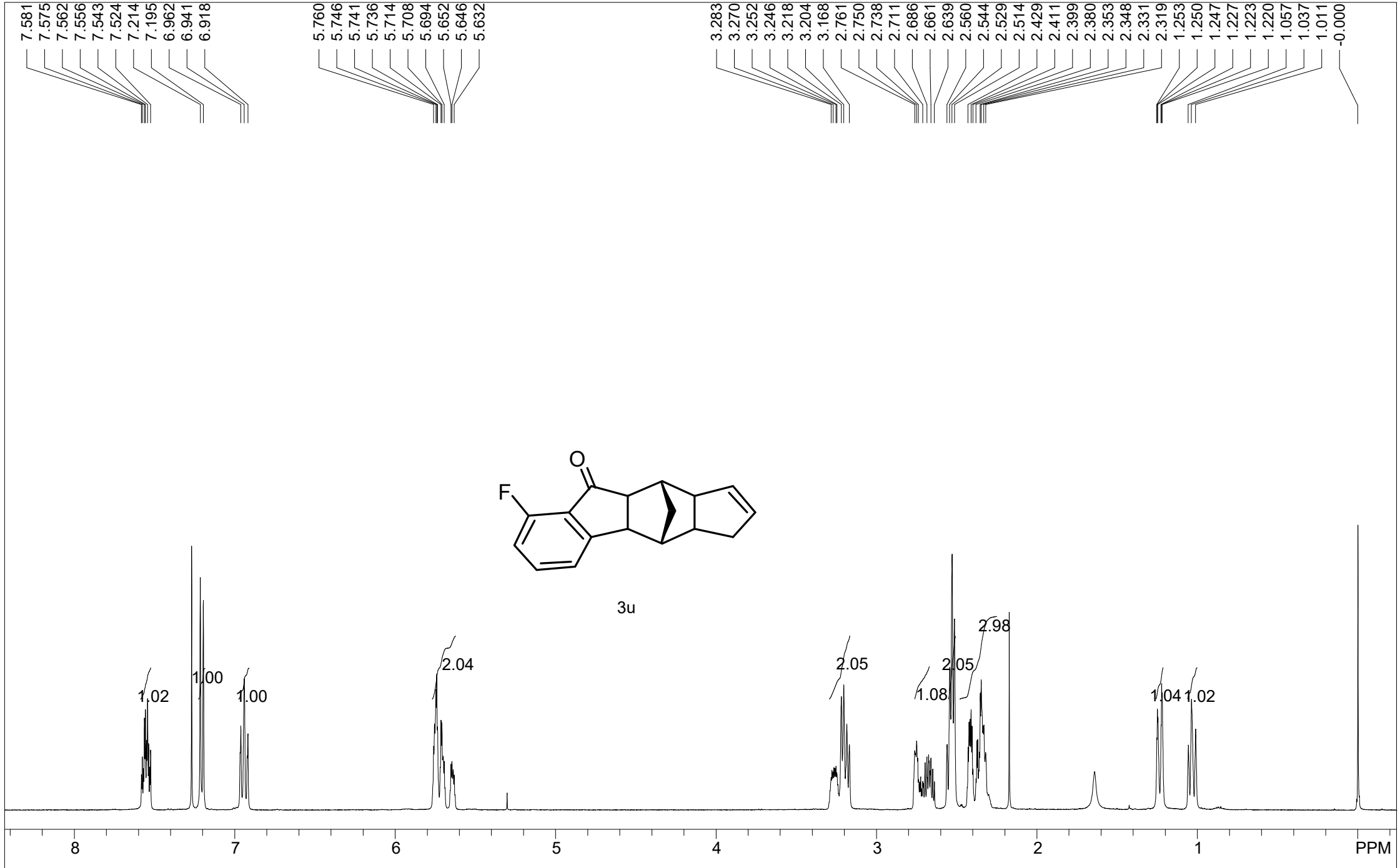

spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 06:51:51 2017

F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2469.3		PTS1d: 32768
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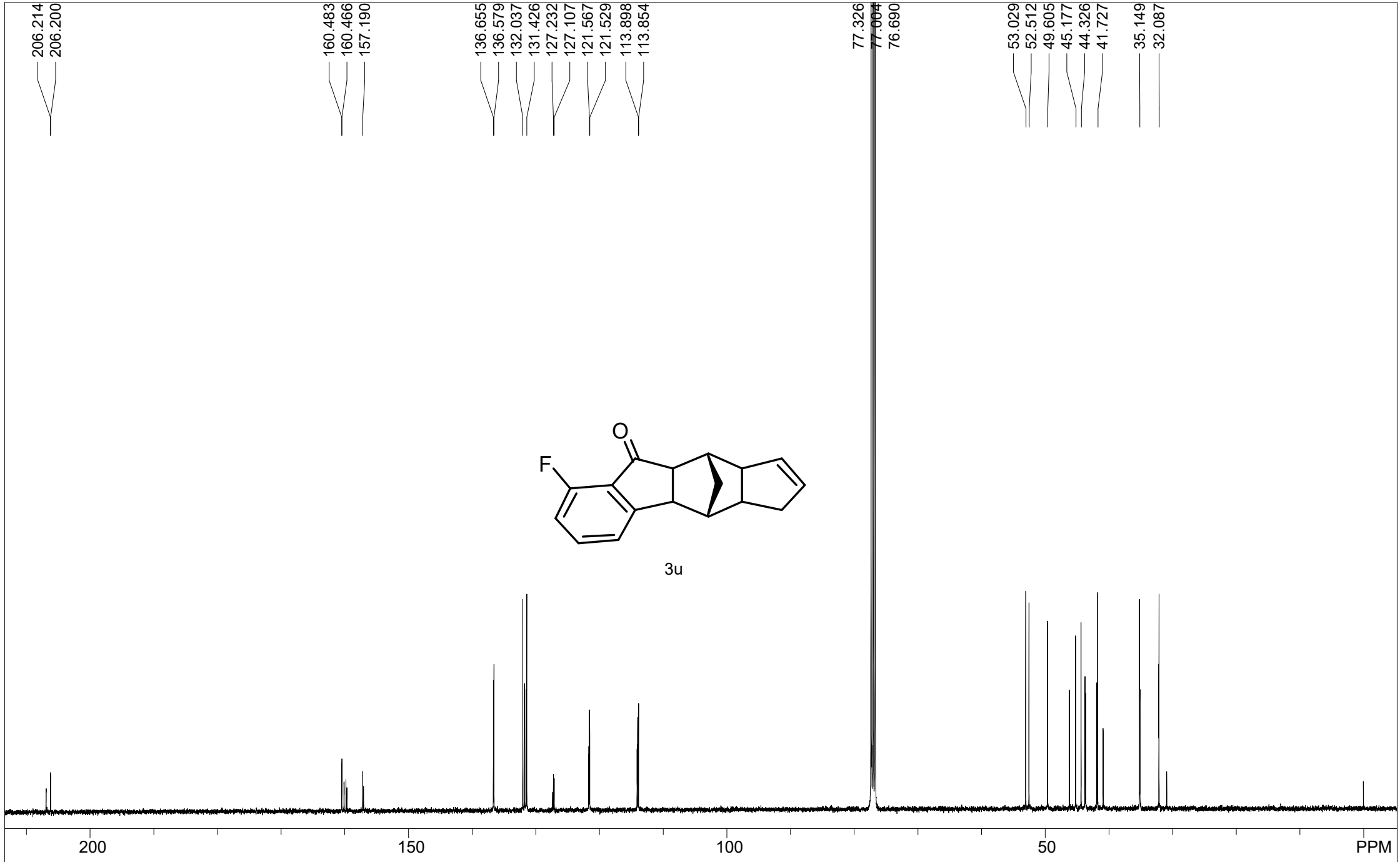

3u

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
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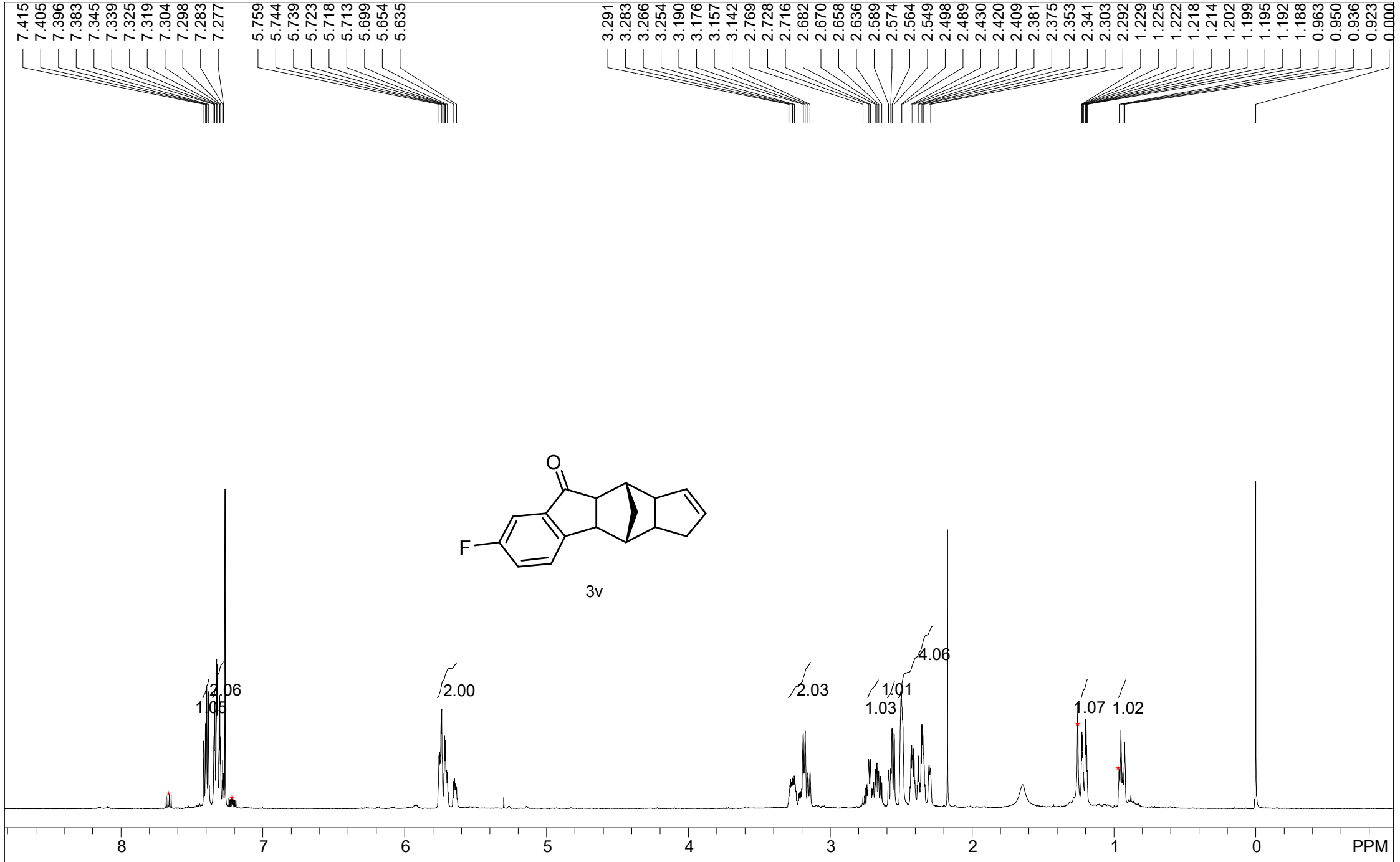
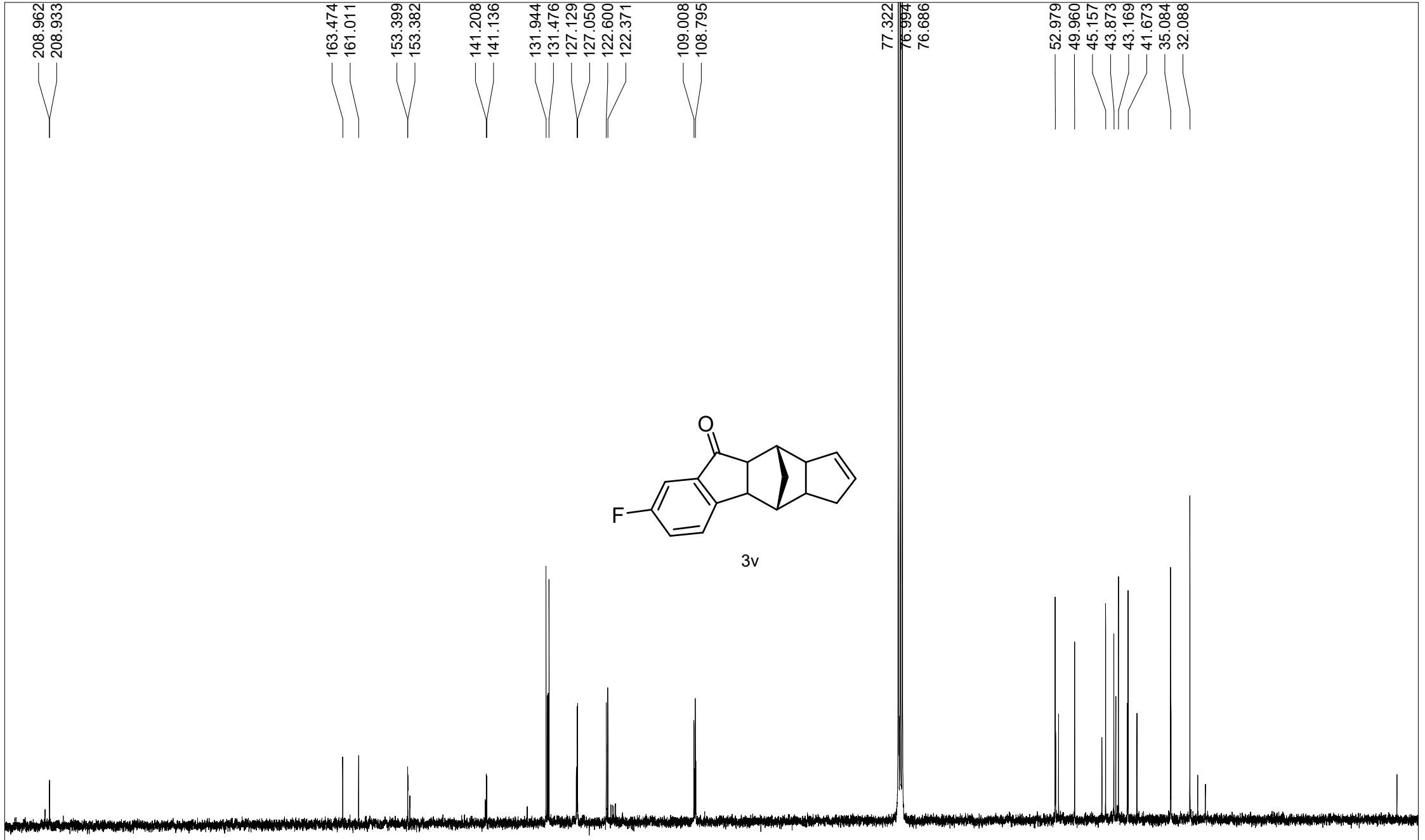


spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:08:52 2017

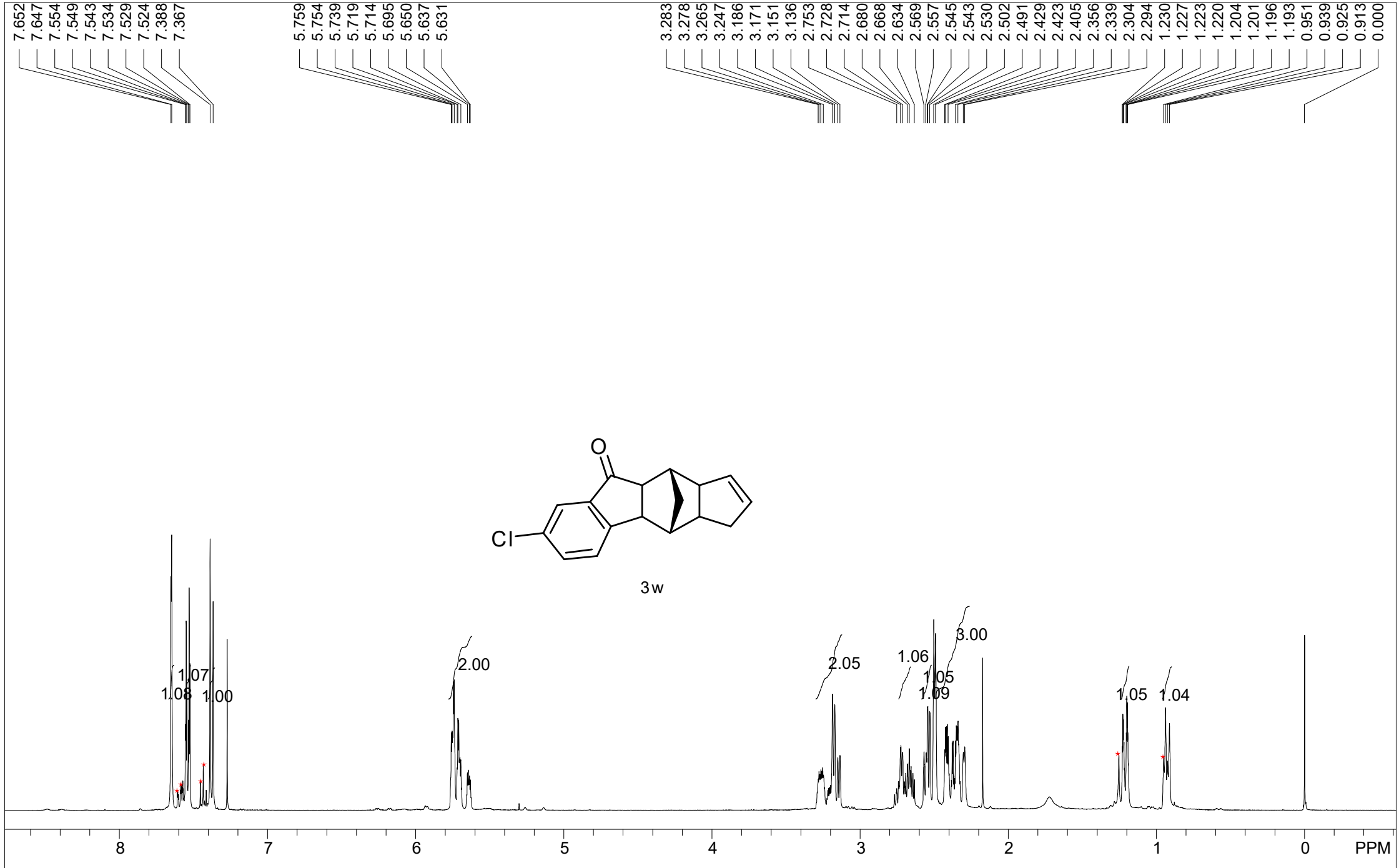
F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2468.6		PTS1d: 32768
EX: zg30		PW: 14.7 usec	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - $pdata



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



spect, CDCl3,

USER: nmr -- DATE: Wed Sep 13 07:17:18 2017

F1: 400.132	F2: 1.000	SW1: 8224		OF1: 2471.0		PTS1d: 32768
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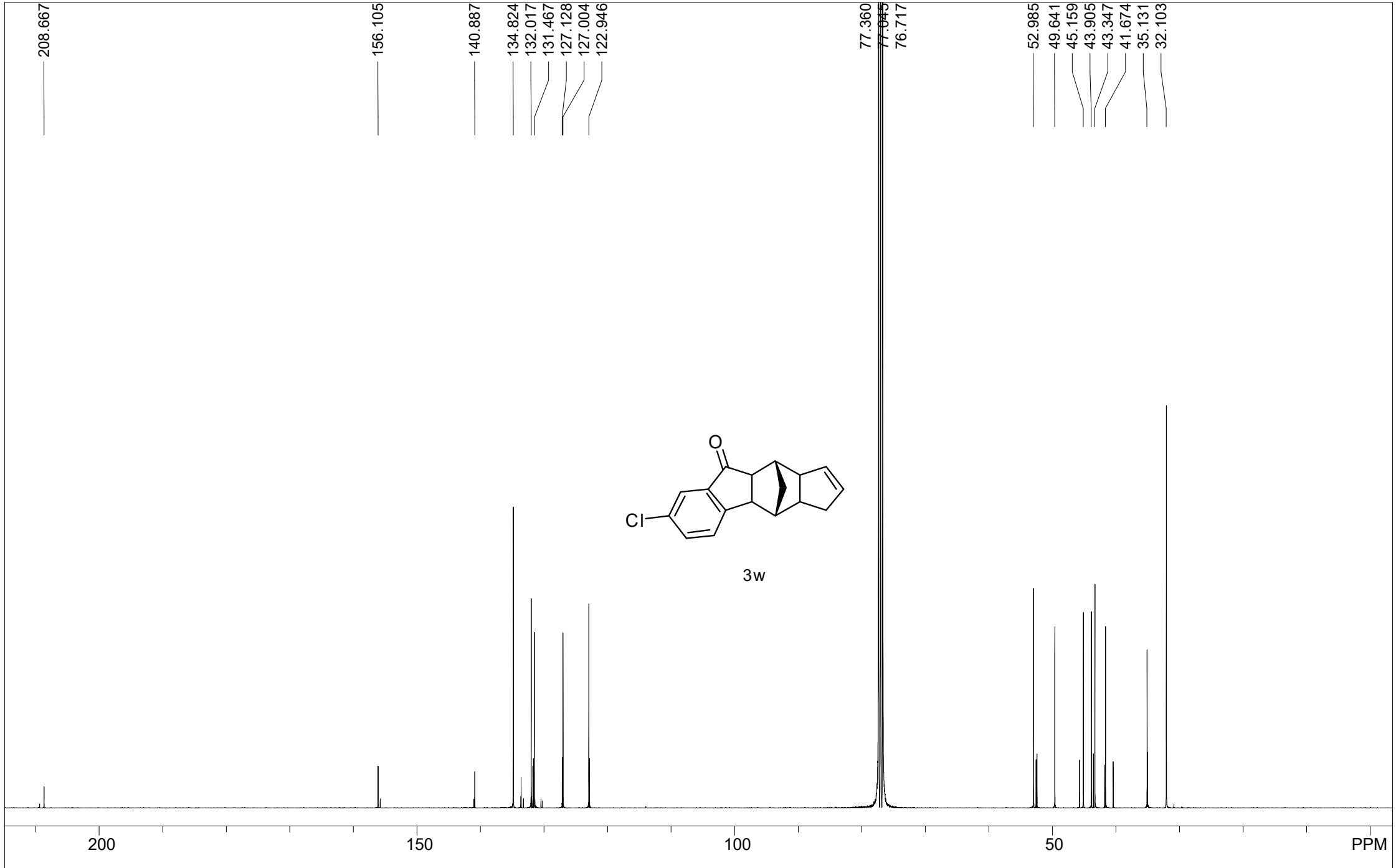

3w

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
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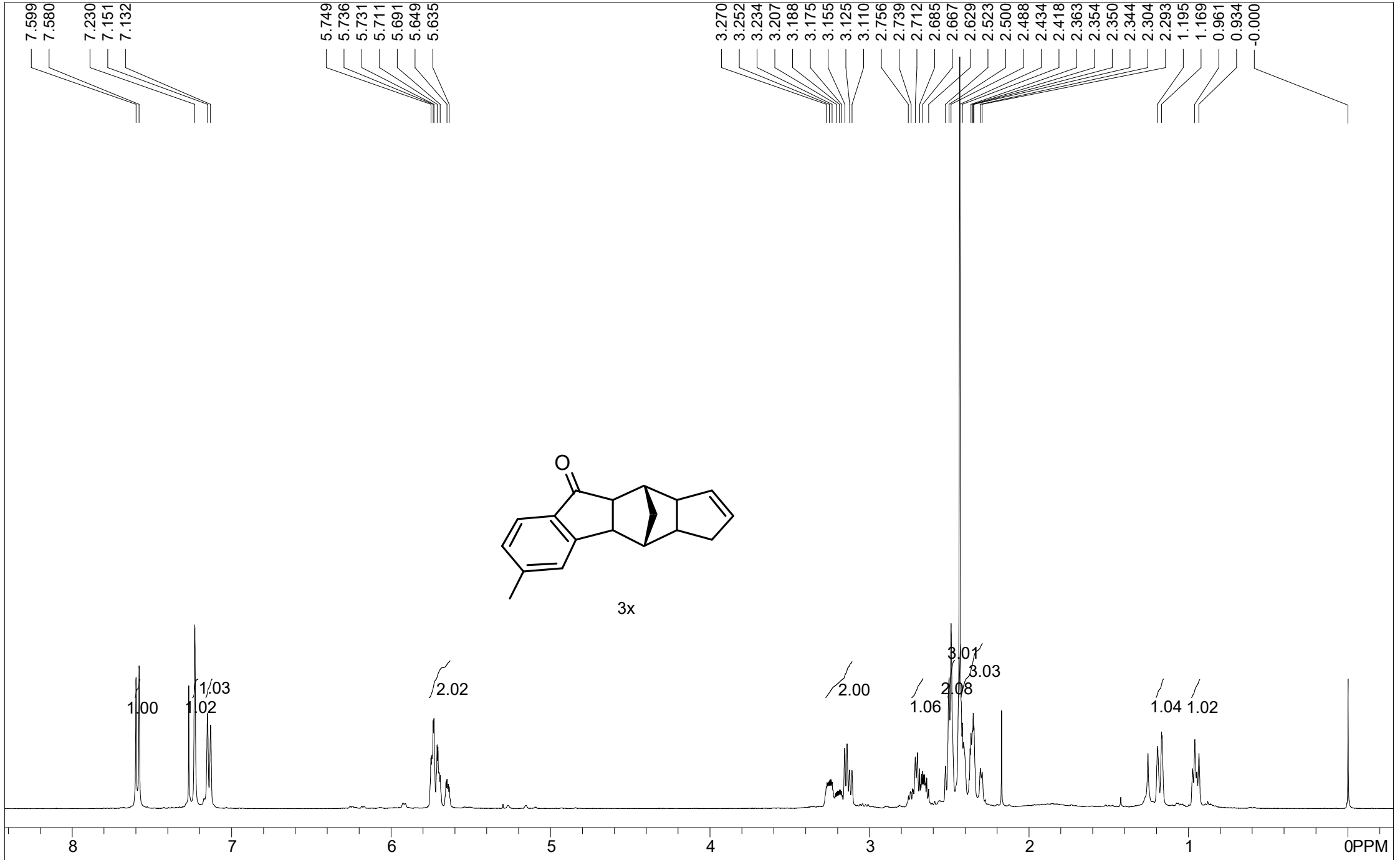
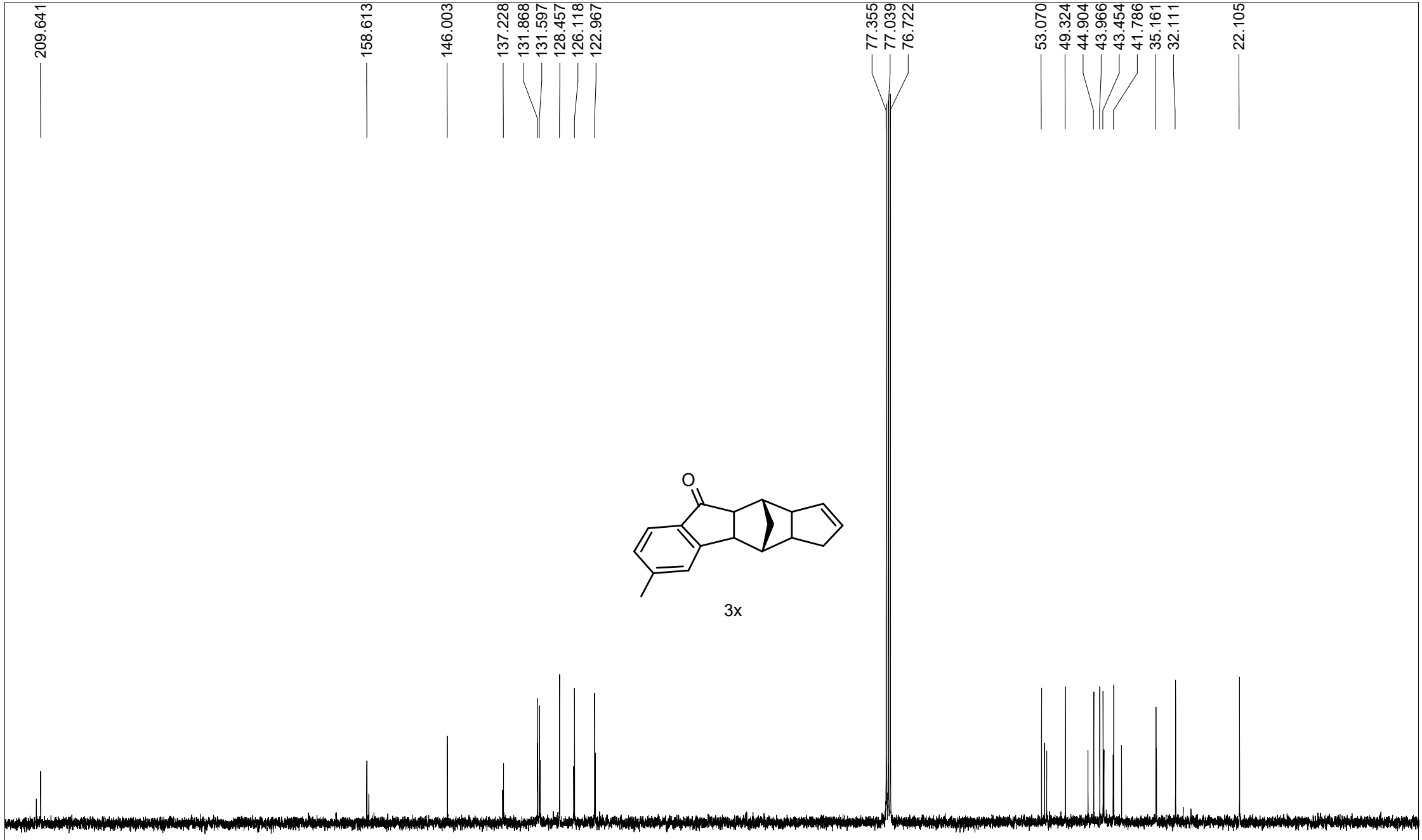


spect, CDCl3,

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

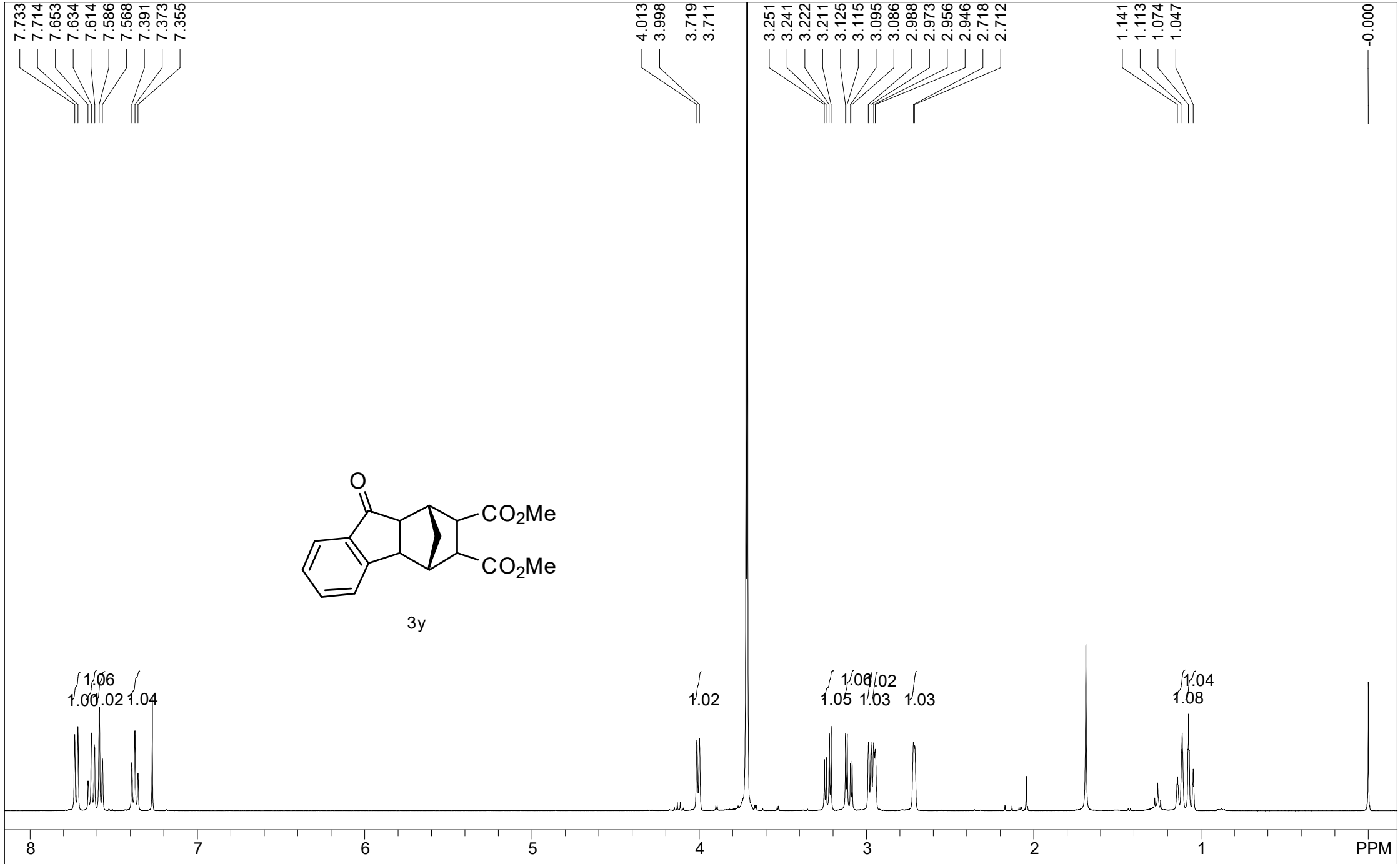


3x

spect, CDCl3,

USER: nmr -- DATE: Thu Sep 14 07:38:56 2017

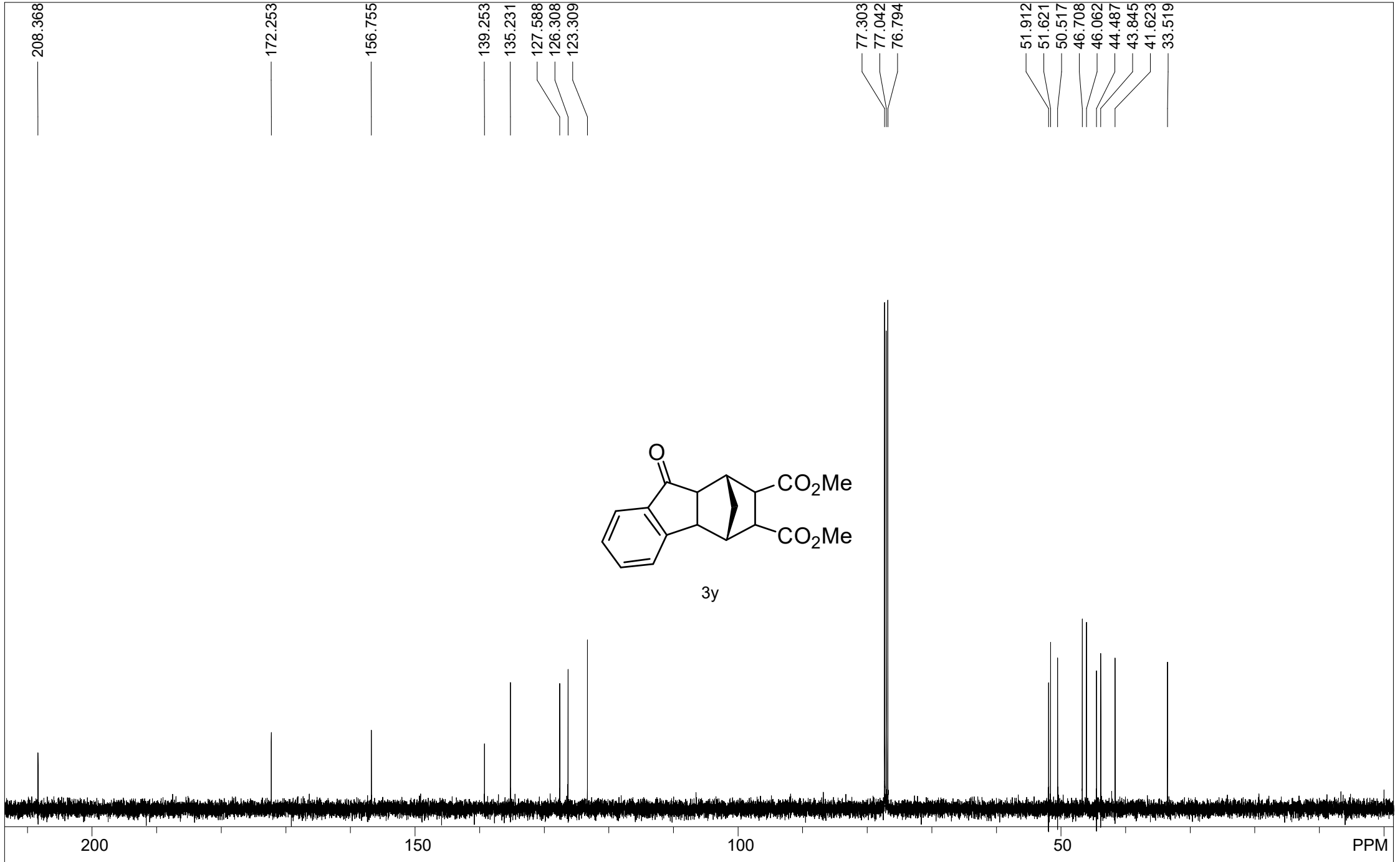
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10063.0		PTS1d: 32768	
EX: zgpg30		PW: 12.4 usec	PD: 2.0 sec	NA: 188	LB: 0.0		Nuts - $pdata



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



AVNEO500, CDCl3,

USER: jicheng -- DATE: Sat Dec 01 22:28:11 2018

F1: 125.772	F2: 1.000	SW1: 31250		OF1: 13836.6		PTS1d: 32768	
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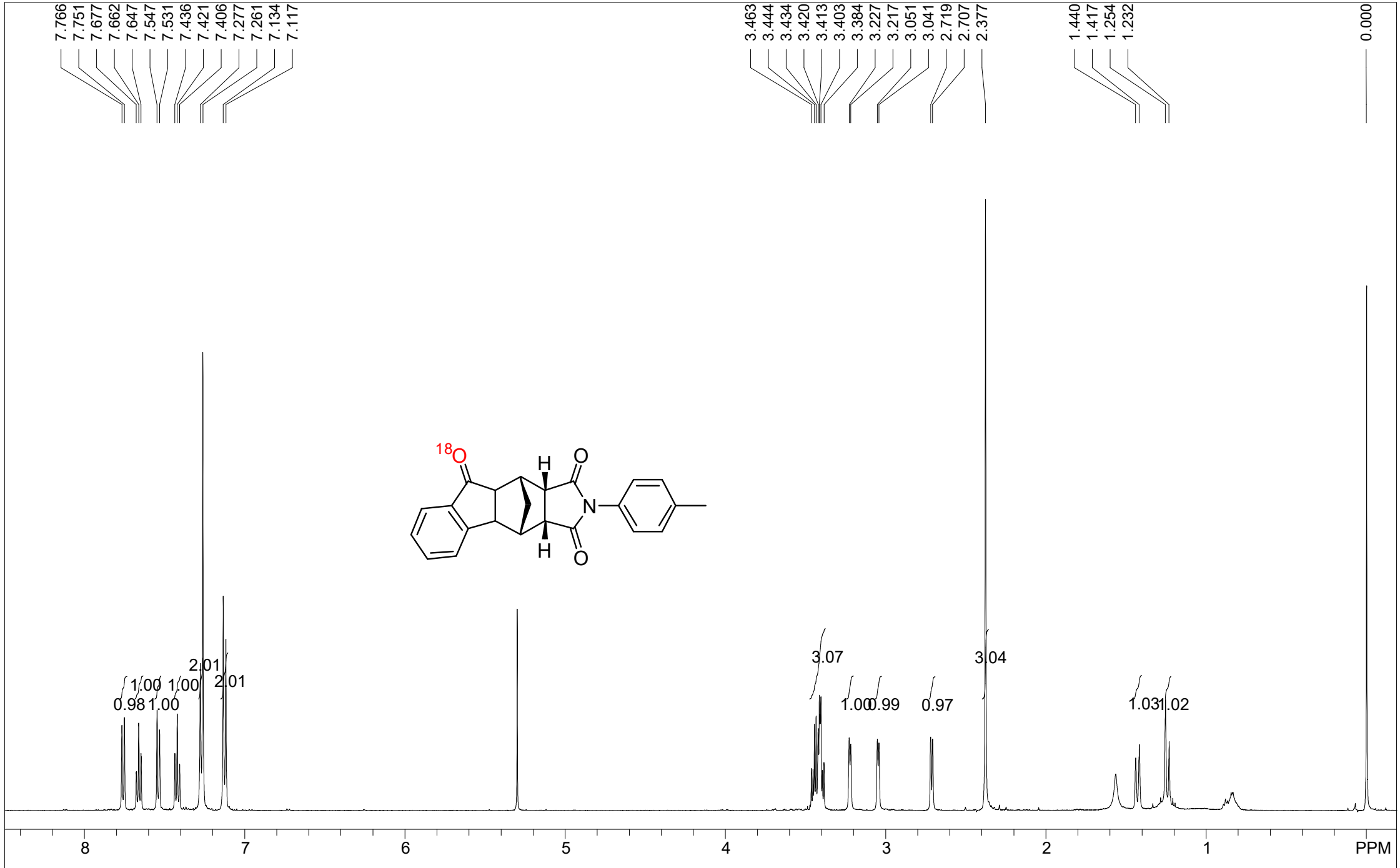
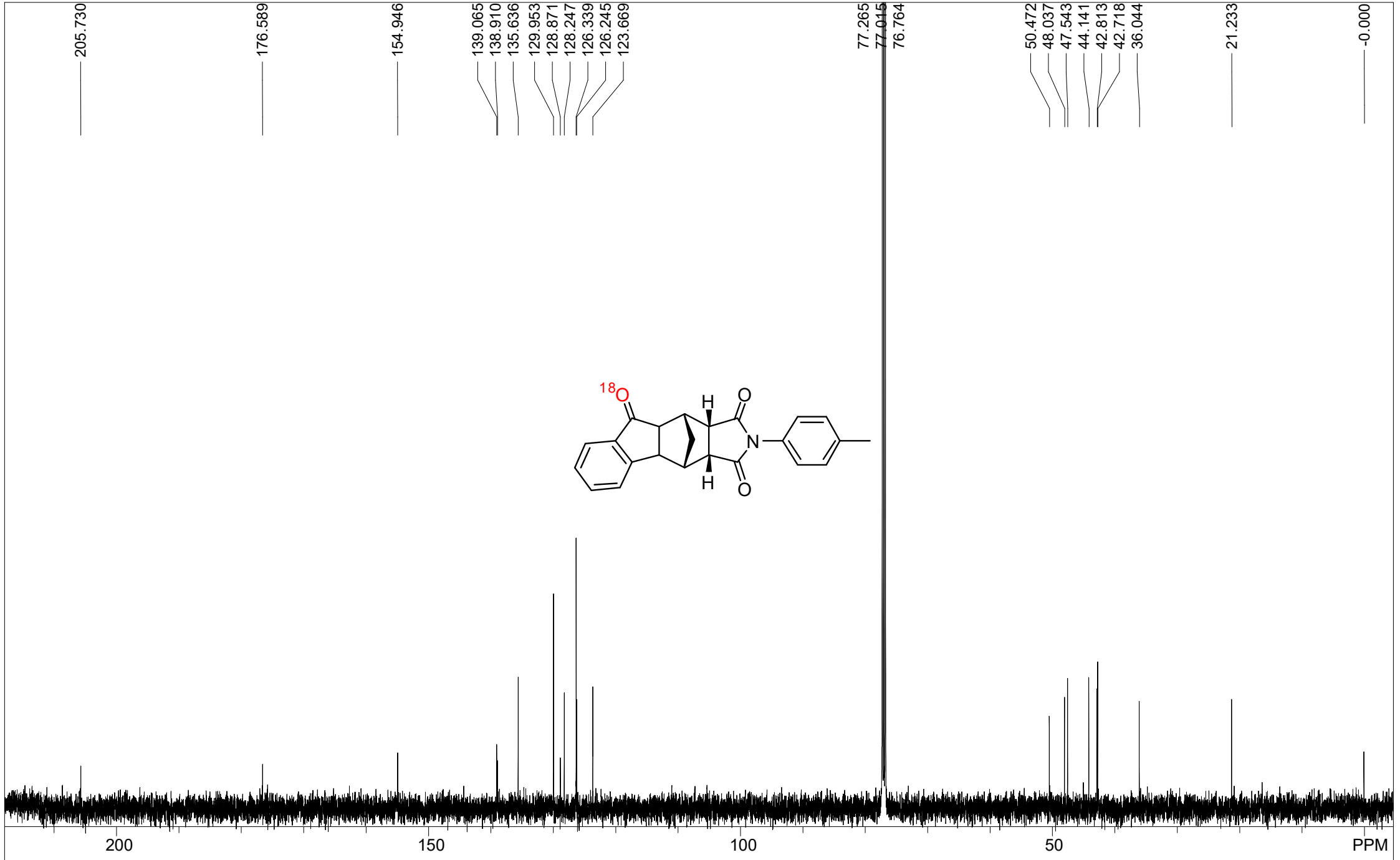


spect, CDCl3,

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, CDCl3,

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