Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iridium(III) dipyridylamine complexes: Synthesis, characterization and catalytic activities in photoredox reactions

Elodie Sauvageot,[a,b] Ronan Marion, [a,b] Fabien Sguerra,[c] Adèle Grimault,[a,b] Richard Daniellou, [d,e] Matthieu Hamel,[c] Sylvain Gaillard,*[,a,b] Jean-Luc Renaud*[,a,b]

Table of Content

Part 1: Synthesis of complexes **1-6** and dipyridylamine derivatives **b-e** S2-S17

Part 2: Emission and absorption spectra of complexes **1-6** S18-S23

Part 3: Cyclic Voltammetry S24-S34

Part 4: General procedure for catalytic assays S35-S36

Part 5: Crystallographic data of complexes **1c** and **2c** S38-S53

Part 6: ^{1}H and ^{13}C NMR spectra of compounds **1-8** and **b-e** S54-S101

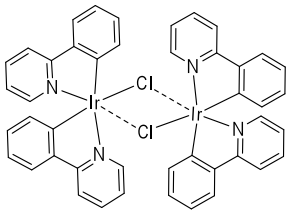
General Considerations. Solvents were purchased from Carlo Erba and degassed prior to use by bubbling argon gas directly in the solvent. Dipyridylamine (CAS: 1202-34-2) was purchased from Sigma-Aldrich®. Solvents for NMR spectroscopy were dried over molecular sieves. NMR spectra were recorded on a 400 MHz and 500 MHz Brücker spectrometer. Proton (^{1}H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet), coupling constant(s) (*J*) in Hertz (Hz), number of protons. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved and br indicates the signal in question broadened. Carbon (^{13}C) NMR spectra are reported in ppm (δ) relative to residual $CHCl_3$ (δ 77.0) unless noted otherwise. HRMS analyses were performed by LCMT analytical services. NMR solvent was passed through a pad of basic alumina before uses. UV-vis spectra were measured at room temperature in chloroform on a Jenway 6715 UV/visible spectrometer. Wavelengths λ are given in nm and extinction coefficients ε are presented in $L.mol^{-1}.cm^{-1}$. Steady-state emission spectra were recorded on chloroform on a Horiba Jobin-Yvon Fluoromax-4 spectrofluorometer in all-transparent quartz cuvettes.

Part 1: Synthesis of complexes 1 to 6

General Procedure for $[Ir_2(\mu\text{-}Cl)_2(C\text{^}N)_2]$ complexes[1]

In a dry flamed Schlenk tube under argon atmosphere, $IrCl_3.xH_2O$ (1 eq.) and C^N ligand (2.2 eq.) were introduced in a degassed 3:1 mixture of ethylene glycol monomethyl ether/water (16 mL). The resulting reaction mixture was heated under stirring at 120 °C for 14h. After cooling down the reaction to room temperature, water (20 mL) was added. The resulting precipitate was collected on a frit. The solid was successively washed with water (3x5 mL), diethyl ether (2x5 mL) and pentane (2x5 mL) and finally dried under vacuum to afford pure iridium dimer complex.

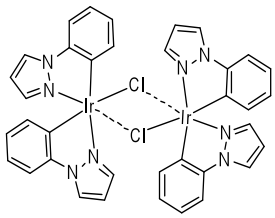
bis-[μ-Chloro-bis-(2-phenylpyridinato-*C*^{2},*N*)iridium(III)][1]



Yellow solid. Isolated yield: 88%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 5.93 (d, J = 7.6 Hz, 4H), 6.56 (t, J = 7.2 Hz, 4H), 6.74 (t, J = 7.6 Hz, 4H), 6.77 (t, J = 6.0 Hz, 4H), 7.48 (d, J = 7.6 Hz, 4H), 7.73 (t, J = 7.2 Hz, 4H), 7.87 (d, J = 8.0 Hz, 4H), 9.24 (d, J = 5.2 Hz, 4H) ppm.

bis-[μ-Chloro-(2-phenylpyrazolato-*C*^{2},*N*)iridium(III)]

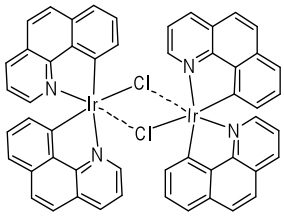


White solid. Isolated yield: 82%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 6.00 (d, J = 7.6 Hz, 4H), 6.53 (t, J = 7.2 Hz, 4H), 6.65 (t, J = 2.8 Hz, 4H), 6.77 (t, J = 7.2 Hz, 4H), 7.10 (d, J = 6.8 Hz, 4H), 7.84 (d, J = 1.6 Hz, 4H), 8.12 (d, J = 2.4 Hz, 4H) ppm.

bis-[μ-Chloro-bis-(benzoquinolinato-*C*,*N*)iridium(III)]

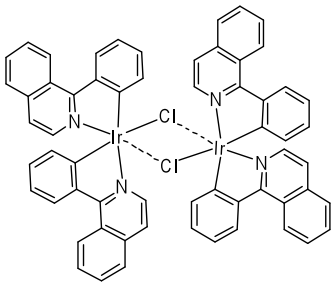
[1] Nonoyama, M. *Bull. Chem. Soc. Jpn.* 1974, **47**, 767.



Orange solid. Isolated yield: 77%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 5.99 (d, J = 7.2 Hz, 4H), 6.82 (t, J = 7.2 Hz, 4H), 7.16 (t, J = 6.0 Hz, 4H), 7.20 (d, J = 8.0 Hz, 4H), 7.68 (d, J = 8.8 Hz, 4H), 7.75 (d, J = 8.8 Hz, 4H), 8.27 (d, J = 8.0 Hz, 4H), 6.36 (d, J = 4.8 Hz, 4H) ppm.

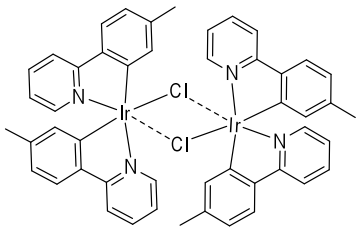
bis-[μ-Chloro-bis(2-phenylisoquinolinato-*C*^{2},*N*)iridium(III)]



Red solid. Isolated yield: 73%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 6.03 (d, J = 8.0 Hz, 4 H), 6.50 (t, J = 7.6 Hz, 4H), 6.56 (d, J = 6.4 Hz, 4H), 6.81 (t, J = 6.8 Hz, 4H), 7.76 (t, J = 6.8 Hz, 4H), 7.81-7.85 (m, 8H), 8.12 (d, J = 7.6 Hz, 4H), 8.97 (d, J = 8.0 Hz, 4H), 9.05 (d, J = 6.0 Hz, 4H) ppm.

bis-[μ-Chloro-bis(2-(4-methylphenyl)-pyridinato-*C*^{2},*N*)iridium(III)][2]

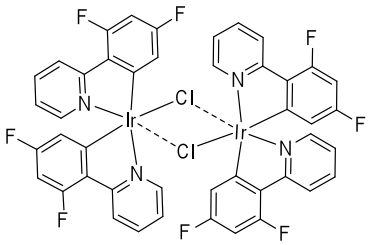


Yellow solid. Isolated yield: 99%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 9.16 (d, J = 5.6 Hz, 4 H), 7.80 (d, J = 8.0 Hz, 4 H), 7.69 (dt, J = 1.8; 8.0 Hz, 4 H), 7.36 (d, J = 7.7 Hz, 4 H), 6.71 (dt, J = 1.8; 5.6 Hz, 4 H), 6.55 (d, J = 7.7 Hz, 4 H), 5.73 (s, 4 H), 1.92 (s, 12 H).

[2] Liaptsis, G.; Hertel, D.; Meerholz, K.; *Angew. Chem. Int. Ed*., 2013, **52**, 9563-9567.

bis-[μ-Chloro-bis-(2-(4,6-difluorophenyl)pyridinato-C^2,N)iridium(III)][3]



Yellow solid. Isolated yield: 82%.

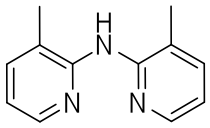
^{1}H-NMR ($CDCl_3$, 400MHz): δ 9.11 (d, J = 5.6 Hz, 4 H), 8.30 (d, J = 8.4 Hz, 4 H), 7.80 (t, J = 8.4 Hz, 4 H), 6.82 (t, J = 7.0 Hz, 4 H), 6.33 (dt, J = 9.3; 2.0 Hz, 4 H), 5.28 (dd, J = 9.3; 2.0 Hz, 4 H).

Synthesis of substituted dipyridylamine ligands b-e.

General procedure

In a dry flamed Schlenck tube under azote atmosphere, $Pd_2(dba)_3$ (0.02 eq.) and dppp (0.04 eq.) were dissolved in 25 ml of degazed toluene. 2-bromomethylpyridine (1 eq.), 2-aminomethylpyridine (1.2 eq.) and potassium *tert*-butoxide (1.4 eq.) were successively added. The mixture was heated at 110°C overnight. After cooling to room temperature, the mixture was filtered over a pad of celite®. The cake was washed with ethyl acetate. The filtrate was concentrated *in vacuum* leading to a brown oil. The crude product was purified over column chromatography with pentane/ethyl acetate (2/1) giving pure dpa derivatives.

3,3'-dimethyl-2,2'-dipyridylamine b

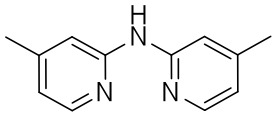


White powder. Isolated yield: 37%.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 6H), 6.40-6.51 (s, 1H), 6.88 (t, J = 6.0 Hz, 2H), 7.46 (d, J = 7.3 Hz, 2H), 8.14 (d, J = 3.9 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 18.0 (qx2), 118.0 (dx2), 123.5 (sx2), 138.7 (dx2), 145.4 (dx2), 153.5 (sx2) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_{14}N_3$ $[M+H]^+$: 200.1188; found: 200.1180 . IR (neat): ν 3169, 3061, 2964, 2911, 1579, 1506, 1407, 1281, 1118, 993, 777 cm^{-1}.

[3] Baranoff, E.; Curcho, B.F.E.; Monti, F.; Steimer, F.; Accorsi, G.; Tavernelli, I.; Rothlisberger, U.; Scopelliti, R.; Gratzel, M.; Nazeeruddin, Md.K.; *Inorg. Chem.*, 2012, **51**, 799–811.

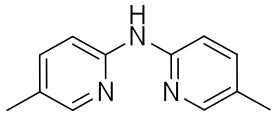
4,4'-dimethyl-2,2'-dipyridylamine c



Pale yellow powder. Isolated yield: 84%.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.34 (s, 6H), 6.69 (d, *J* = 5.1 Hz, 2H), 7.36 (s, 2H), 8.12 (d, *J* = 5.1 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 21.3 (qx2), 111.9 (dx2), 117.7 (dx2), 147.2 (dx2), 149.0 (sx2), 154.2 (sx2) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_{14}N_3$ $[M+H]^+$: 200.1188; found: 200.1191 . IR (neat): ν 3270, 3106, 3046, 2919, 1601, 1528, 1490, 1418, 1299, 1175, 984, 800 cm^{-1}.

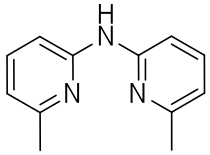
5,5'-dimethyl-2,2'-dipyridylamine d



Pale yellow powder. Isolated yield: 77%.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.25 (s, 6H), 7.40 (s, 4H), 8.06 (s, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 17.7 (qx2), 111.1 (dx2), 125.1 (sx2), 138.6 (dx2), 147.4 (dx2), 152.2 (sx2) ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_{14}N_3$ $[M+H]^+$: 200.1188; found: 200.1180. IR (neat): ν 3268, 3177, 3007, 2922, 1602, 1573, 1494, 1468, 1389, 1338, 1024, 815 cm^{-1}.

6,6'-dimethyl-2,2'-dipyridylamine[4,5] e



Pale yellow crystals. Isolated yield: 97%.

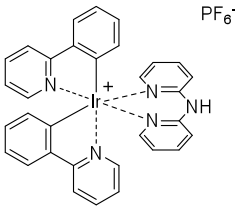
^{1}H-NMR ($CDCl_3$, 400 MHz): δ 2.45 (s, 6H), 6.68 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.41-7.46 (s, 1H), 7.46 (t, *J* = 8.0 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 24.3 (qx2), 108.3 (dx2), 115.5 (dx2), 138.0 (dx2), 153.5 (sx2), 156.6 (sx2) ppm.

[4] Tlili, A. ; Monnier, F.; Taillefer, M.; *Chem. Commun.,* 2012, **48**, 6408-6410.
[5] Gaillard, S.; Elmkaddem, M. K.; Fischmeister, C.; Thomas, C. M.; Renaud, J.-L. *Tetrahedron Lett.* 2008, **49**, 3471-3474.

General procedure for $[Ir(C^N)_2(N^N)][PF_6]$ complexes 1-6.

In a dry flamed Schlenk tube under argon atmosphere, iridium dimer (1 eq.) and N^N ligand (2.2 eq.) were introduced in degassed 2:1 mixture of dichloromethane/methanol mixture (8 mL). The reaction mixture was stirred at 50 °C for 6 h. After cooling down the solution to room temperature, excess of KPF_6 (10 eq.) was added affording a precipitate. The inorganic solid was filtered off and the filtrate was evaporated. The solid was washed on a frit with diethyl ether (3x5 mL) and dried under vacuum to afford pure cationic iridium $[Ir(C^N)_2(N^N)][PF_6]$ complex.

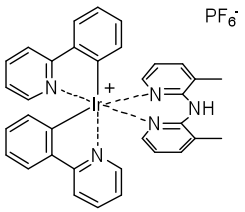
[(bis(pyridyn-2yl)amine)bis-(2-phenylpyridinato-C^2,N)iridium(III)] hexafluorophosphate, $[Ir(ppy)_2(Hdpa)][PF_6]$ 1a [6]



Yellow solid. Isolated yield: 80%.

^{1}H-NMR (d_6-DMSO, 400MHz): δ 6.06 (d, J = 7.7 Hz, 2H), 6.80-6.86 (m, 4H), 6.94 (t, J = 7.1 Hz, 2H), 7.35 (d, J = 4.7 Hz, 2H), 7.86 (t, J = 8.0 Hz, 4H), 8.02 (t, J = 8.2 Hz, 2H), 8.27 (d, J = 7.3 Hz, 4H), 10.61 (s, 1H) ppm. ^{13}C-NMR (d_6-DMSO, 100MHz): δ 116.1 (dx2), 119.6 (dx2), 120.6 (dx2), 122.6 (dx2), 124.0 (dx2), 125.5 (dx2), 130.5 (dx2), 131.6 (dx2), 139.3 (dx2), 140.1 (dx2), 144.4 (sx2), 149.5 (dx2), 150.0 (dx2), 150.5 (sx2), 151.7 (sx2), 167.3 (sx2) ppm. IR (neat): ν 3384, 3044, 1633, 1608, 1475, 1269, 1231, 1165, 842 cm^{-1}.

[(bis(3-methylpyridin-2-yl)amine)bis-(2-phenylpyridinato-C^2,N)iridium(III)] hexafluorophosphate, $[Ir(ppy)_2(3\text{-}MeHdpa)][PF_6]$ 1b



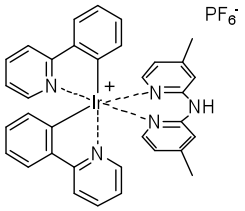
Yellow solid. Isolated yield: 91%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 2.65 (s, 6H), 6.14 (d, J = 7.2 Hz, 2H), 6.60 (t, J = 6.6 Hz, 2H), 6.80 (t, J = 7.2 Hz, 2H), 6.93 (t, J = 7.2 Hz, 2H), 7.53 (d, J = 6.6 Hz, 4H), 7.58 (d, J = 8.1 Hz, 2H), 7.76-7.83 (m, 4H), 7.88 (d, J = 8.1 Hz, 2H), 8.31 (d, J = 4.8 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 18.5

[6] Tseng, M. C.; Su, W. L.; Yu, Y. C.; Wang, S. P.; Huang, W. L. *Inorg. Chim. Acta* 2006, **359**, 4144-4148.

(qx2), 119.4 (dx2), 119.6 (dx2), 122.3 (dx2), 123.5 (dx2), 124.5 (dx2), 125.2 (sx2), 130.4 (dx2), 131.8 (dx2), 138.0 (dx2), 140.5 (dx2), 143.7 (sx2), 147.8 (dx2), 149.9 (sx2), 150.3 (dx2), 150.5 (sx2), 167.5 (sx2) ppm. IR (neat): ν 3441, 3044, 1607, 1583, 1522, 1465, 1269, 1227, 1122, 839 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{34}H_{29}IrN_5$ $[M - PF_6]^+$: 700.2052; found: 700.2045.

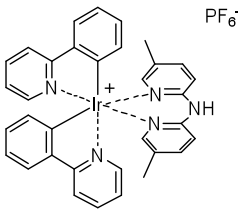
[(bis(4-methylpyridin-2-yl)amine)bis-(2-phenylpyridinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppy)$_2$(4-MeHdpa)][PF$_6$] 1c



Yellow solid. Isolated yield: 88%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 2.23 (s, 6H), 6.14 (d, J = 7.9 Hz, 2H), 6.40 (d, J = 5.9 Hz, 2H), 6.80 (t, J = 7.4 Hz, 2H), 6.94 (t, J = 7.4 Hz, 2H), 7.11 (t, J = 6.5 Hz, 2H), 7.36 (d, J = 6.2 Hz, 2H), 7.59 (d, J = 6.5 Hz, 4H), 7.79 (t, J = 7.9 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 8.15 (d, J = 5.3 Hz, 2H), 9.52 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 21.0 (qx2), 116.5 (dx2), 119.5 (dx2), 120.7 (dx2), 122.2 (dx2), 122.8 (dx2), 124.6 (dx2), 130.4 (dx2), 131.8 (dx2), 137.9 (dx2), 143.6 (sx2), 148.6 (dx2), 149.4 (dx2), 150.4 (sx2), 151.3 (sx4), 167.9 (sx2) ppm. IR (neat): ν 3383, 3041, 1640, 1607, 1583, 1477, 1227, 1194, 842 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{34}H_{29}IrN_5$ $[M - PF_6]^+$: 700.2052; found: 700.2046.

[(bis(5-methylpyridin-2-yl)amine)bis-(2-phenylpyridinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppy)$_2$(5-MeHdpa)][PF$_6$] 1d

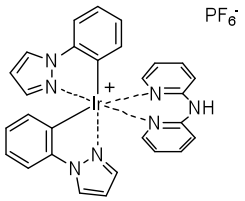


Yellow solid. Isolated yield: 88%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 1.87 (s, 6H), 6.14 (d, J = 7.0 Hz, 2H), 6.81 (t, J = 7.0 Hz, 2H), 6.94 (t, J = 7.5 Hz, 2H), 7.12 (t, J = 6.2 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.80 (t, J = 7.8 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H), 8.14 (d, J = 5.4 Hz, 2H), 9.61 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 17.5 (qx2), 116.1 (dx2), 119.5 (dx2), 122.3 (dx2), 122.9 (dx2), 124.7 (dx2), 128.0 (sx2), 130.5 (dx2), 131.8 (dx2), 137.9 (dx2), 140.4 (dx2), 143.6 (sx2), 148.5 (dx2), 149.4 (dx2), 149.8 (sx2), 150.3 (dx2), 167.8 (sx2) ppm. IR (neat): ν 3385, 3040, 1635, 1607, 1583,

1489, 1477, 1239, 838 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{34}H_{29}IrN_5$ $[M - PF_6]^+$: 700.2052; found: 700.2048.

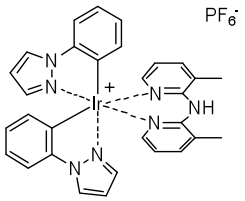
[(bis(5-methylpyridin-2-yl)amine)bis-(2-phenylpyridinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppz)$_2$(Hdpa)][PF$_6$] 2a



Grey solid. Isolated yield: 82%.

^{1}H-NMR (d_6-DMSO, 400MHz): δ 5.98 (d, J = 6.8 Hz, 2H), 6.74 (t, J = 7.4 Hz, 2H), 6.84 (t, J = 2.5 Hz, 2H), 6.88 (t, J = 6.3 Hz, 2H), 6.95 (t, J = 7.3 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.61-7.64 (m, 4H), 7.67 (d, J = 2.1 Hz, 2H), 7.69 (t, J = 8.4 Hz, 2H), 8.90 (d, J = 2.8 Hz, 2H), 10.73 (s, 1H) ppm. ^{13}C-NMR (d_6-DMSO, 100MHz): δ 109.0 (dx2), 112.5 (dx2), 115.7 (dx2), 119.6 (dx2), 123.2 (dx2), 126.6 (dx2), 129.3 (dx2), 132.4 (sx2), 133.3 (dx2), 140.2 (dx2), 140.4 (dx2), 143.5 (sx2), 150.0 (dx2), 152.3 (sx2) ppm. IR (neat): ν 3383, 3144, 3056, 1627, 1585, 1472, 1057, 1035, 1415, 834 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{23}IrN_7$ $[M - PF_6]^+$: 650.1644; found: 650.1641.

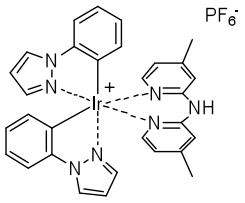
[(bis(3-methylpyridin-2-yl)amine)bis-(2-phenylpyrazolinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppz)$_2$(3-MeHdpa)][PF$_6$] 2b



White solid. Isolated yield: 87%.

^{1}H-NMR (CDCl3, 400MHz): δ 2.65 (s, 6H), 6.09 (d, J = 7.5 Hz, 2H), 6.66 (t, J = 6.5 Hz, 2H), 6.72-6.76 (m, 4H), 6.93 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.61-7.67 (m, 4H), 8.07 (d, J = 2.7 Hz, 2H) ppm. ^{13}C-NMR (CDCl3, 100MHz): δ 19.4 (qx2), 108.4 (dx2), 111.1 (dx2), 119.5 (dx2), 122.8 (dx2), 126.5 (dx4), 126.6 (sx2), 132.3 (sx2), 133.6 (dx2), 140.5 (dx2), 140.7 (dx2), 142.9 (sx2), 147.7 (dx2), 151.6 (sx2) ppm. IR (neat): ν 3442, 3151, 3056, 1619, 1592, 1519, 1463, 1410, 839 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{27}IrN_7$ $[M - PF_6]^+$: 678.1957; found: 678.1951.

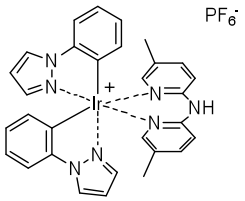
[(bis(4-methylpyridin-2-yl)amine)bis-(2-phenylpyrazolinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppz)$_2$(4-MeHdpa)][PF$_6$] 2c



White solid. Isolated yield: 96%.

^{1}H-NMR (CDCl3, 400MHz): δ 2.25 (s, 6H), 6.08 (d, J = 7.5 Hz, 2H), 6.44 (d, J = 5.8 Hz, 2H), 6.64 (t, J = 2.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 2H), 6.94 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 2.1 Hz, 2H), 7.49 (d, J = 6.1 Hz, 2H), 7.67 (s, 2H), 8.09 (d, J = 2.7 Hz, 2H), 9.74 (s, 1H) ppm. ^{13}C-NMR (CDCl3, 100MHz): δ 21.1 (qx2), 108.2 (dx2), 111.4 (dx2), 116.4 (dx2), 120.6 (dx2), 123.0 (dx2), 126.7 (dx2), 126.8 (dx2), 132.4 (sx2), 133.8 (dx2), 139.3 (dx2), 143.0 (sx2), 149.0 (dx2), 151.6 (sx2), 152.3 (sx2) ppm. IR (neat): ν 3383, 3140, 3055, 1639, 1476, 1410, 1073, 1057, 1035, 839 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{27}IrN_7$ $[M - PF_6]^+$: 678.1957; found: 678.1953.

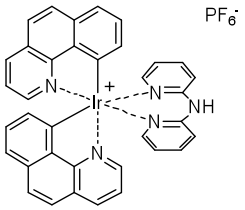
[(bis(5-methylpyridin-2-yl)amine)bis-(2-phenylpyrazolinato-C^2,N)iridium(III)] hexafluorophosphate, [Ir(ppz)$_2$(5-MeHdpa)][PF$_6$] 2d



White solid. Isolated yield: 96%.

^{1}H-NMR (CDCl3, 400MHz): δ 1.76 (s, 6H), 5.93 (d, J = 7.0 Hz, 2H), 6.49 (d, J = 2.3 Hz, 2H), 6.59 (t, J = 5.7 Hz, 2H), 6.76 (t, J = 7.2 Hz, 2H), 7.07 (d, J = 7.3 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.26 (s, 2H), 7.29 (s, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.99 (t, J = 2.7 Hz, 2H), 9.78 (s, 1H) ppm. ^{13}C-NMR (CDCl3, 100MHz): δ 17.4 (qx2), 108.2 (dx2), 111.4 (dx2), 115.6 (dx2), 123.0 (dx2), 126.6 (dx2), 126.8 (dx2), 128.1 (sx2), 132.0 (sx2), 133.5 (dx2), 139.2 (dx2), 140.5 (dx2), 142.8 (sx2), 148.9 (dx2), 150.6 (sx2) ppm. IR (neat): ν 3384, 3142, 3058, 1634, 1479, 1265, 1239, 1056, 1034, 836, 730 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{30}H_{27}IrN_7$ $[M - PF_6]^+$: 678.1957; found: 678.1951.

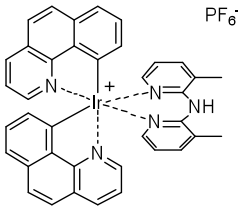
[(bis(pyridin-2-yl)amine)bis-(benzoquinolinato-*C,N*)iridium(III)] hexafluorophosphate, [Ir(bzq)$_2$(Hdpa)][PF$_6$] 3a



Yellow solid. Isolated yield: 51%.

^{1}H-NMR (d$_6$-DMSO, 400MHz): δ 5.99 (d, J = 7.2 Hz, 2H), 6.72 (t, J = 6.3 Hz, 2H), 7.04 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 5.3 Hz, 2H), 7.78-7.84 (m, 4H), 7.88-7.91 (m, 4H), 8.64 (d, J = 8.1 Hz, 2H), 8.70 (d, J = 5.0 Hz, 2H), 10.72 (s, 1H) ppm. ^{13}C-NMR (d$_6$-DMSO, 100MHz): δ 116.1 (dx2), 119.7 (dx2), 120.6 (dx2), 123.1 (dx2), 124.7 (dx2), 127.4 (sx2), 129.0 (dx2), 129.9 (dx4), 134.2 (sx2), 138.3 (dx2), 140.3 (dx2), 140.7 (sx2), 147.2 (sx2), 149.9 (dx4), 151.9 (sx2), 156.9 (dx2) ppm. IR (neat): ν 3381, 3041, 1629, 1585, 1568, 1475, 1329, 1165, 844 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{36}H_{25}IrN_5$ [M – PF$_6$]$^+$: 720.1739; found: 720.1724.

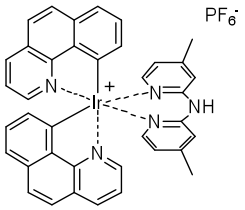
[(bis(3-methylpyridin-2-yl)amine)bis-(benzoquinolinato-*C,N*)iridium(III)] hexafluorophosphate, [Ir(bzq)$_2$(3-MeHdpa)][PF$_6$] 3b



Orange solid. Isolated yield: 55%.

^{1}H-NMR (d$_6$-DMSO, 400MHz): δ 2.59 (s, 6H), 5.98 (d, J = 5.8 Hz, 2H), 6.76 (t, J = 5.3 Hz, 2H), 7.04 (t, J = 6.1 Hz, 2H), 7.43 (d, J = 6.3 Hz, 2H), 7.46 (d, J = 4.0 Hz, 2H), 7.76-7.79 (m, 4H), 7.91 (d, J = 2.1 Hz, 4H), 8.64-8.66 (m, 4H) ppm. ^{13}C-NMR (d$_6$-DMSO, 100MHz): δ 18.2 (qx2), 120.4 (dx2), 120.5 (dx2), 123.0 (dx2), 124.7 (dx2), 125.9 (sx2), 127.3 (sx2), 128.9 (dx2), 129.8 (dx2), 134.2 (sx2), 138.2 (dx2), 139.9 (dx2), 140.8 (sx2), 141.3 (dx2), 147.6 (sx2), 147.9 (dx2), 150.2 (dx2), 151.3 (sx2), 157.0 (sx2) ppm. IR (neat): ν 3437, 3038, 1620, 1592, 1568, 1520, 1463, 1446, 1406, 1329, 842 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{38}H_{29}IrN_5$ [M – PF$_6$]$^+$: 748.2052; found: 748.2057.

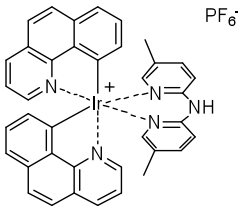
[(bis(3-methylpyridin-2-yl)amine)bis-(benzoquinolinato-*C,N*)iridium(III)] hexafluorophosphate, [Ir(bzq)$_2$(4-MeHdpa)][PF$_6$] 3c



Orange solid. Isolated yield: 65%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 2.34 (s, 6H), 6.06 (d, J = 7.2 Hz, 2H), 6.27 (d, J = 5.6 Hz, 2H), 6.74 (d, J = 4.4 Hz, 2H), 7.01 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 6.8 Hz, 4H), 7.43 (s, 2H), 7.54 (dd, J = 7.7; 5.5 Hz, 4H), 7.61 (s, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 5.2 Hz, 2H), 8.30 (d, J = 7.8 Hz, 2H), 8.51 (d, J = 5.1 Hz, 2H), 9.59 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 21.1 (qx2), 116.6 (dx2), 120.3 (dx2), 120.8 (dx2), 121.8 (dx2), 123.8 (dx2), 127.3 (sx2), 128.8 (sx2), 129.3 (dx2), 129.8 (dx2), 130.1 (dx2), 134.4 (sx2), 137.1 (dx2), 140.9 (sx2), 147.0 (sx2), 148.6 (dx2), 149.2 (dx2), 151.4 (sx2), 157.8 (sx2) ppm. IR (neat): ν 3382, 3037, 1640, 1604, 1525, 1480, 1446, 1329, 1192, 844 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{38}H_{29}IrN_5$ $[M - PF_6]^+$: 748.2052; found: 748.2042.

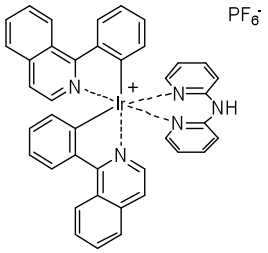
[(bis(5-methylpyridin-2-yl)amine)bis-(benzoquinolinato-*C,N*)iridium(III)] hexafluorophosphate, [Ir(bzq)$_2$(5-MeHdpa)][PF$_6$] 3d



Yellow solid. Isolated yield: 57%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 1.72 (s, 6H), 6.07 (d, J = 7.1 Hz, 2H), 7.02 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.9 Hz, 4H), 7.52 (s, 2H), 7.56 (dd, J = 7.9 Hz et J = 5.5 Hz, 2H), 7.66 (t, J = 8.5 Hz, 4H), 7.81 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 7.9 Hz, 2H), 8.51 (d, J = 5.2 Hz, 2H), 9.51 (s, 1H) ppm. 13C-NMR (CDCl3, 100MHz): δ 17.3 (qx2), 115.9 (dx2), 120.3 (dx2), 121.8 (dx2), 123.7 (dx2), 127.2 (sx2), 128.0 (sx2), 129.1 (dx2), 129.6 (dx2), 129.9 (dx2), 134.2 (sx2), 137.1 (dx2), 140.3 (dx2), 140.7 (sx2), 146.7 (sx2), 148.5 (dx2), 149.0 (dx2), 150.0 (sx2), 157.5 (sx2) ppm. IR (neat): ν 3382, 3036, 1603, 1567, 1489, 1446, 1328, 1240, 842 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{38}H_{29}IrN_5$ $[M - PF_6]^+$: 748.2052; found: 748.2054.

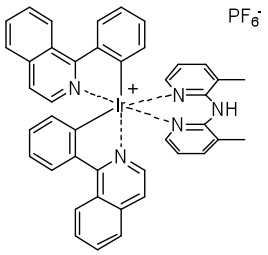
[(bis(pyridin-2-yl)amine)bis-(2-phenyl(1-isoquinolinato)-C^2,*N*)iridium(III)] hexafluorophosphate, [Ir(piq)$_2$(Hdpa)][PF$_6$] 4a



Red solid. Isolated yield: 84%.

^{1}H-NMR (d_6-DMSO, 400MHz): δ 6.16 (d, J = 7.5 Hz, 2H), 6.80 (q, J = 8.0 Hz, 4H), 7.04 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 5.3 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 6.5 Hz, 2H), 7.83 (t, J = 8.4 Hz, 2H), 7.90 (qui, J = 8.8 Hz, 4H), 8.16 (d, J = 7.8 Hz, 2H), 8.21 (d, J = 6.4 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 8.96 (d, J = 8.4 Hz, 2H), 10.88 (s, 1H) ppm. ^{13}C-NMR (d_6-DMSO, 100MHz): δ 116.1 (dx2), 119.6 (dx2), 122.1 (dx2), 122.6 (dx2), 126.1 (sx2), 126.9 (dx2), 128.2 (dx2), 129.7 (dx2), 130.6 (dx2), 131.1 (dx2), 132.5 (dx2), 137.1 (sx2), 140.3 (dx2), 142.0 (dx2), 145.7 (sx2), 149.6 (dx2), 151.8 (sx2), 153.9 (sx2), 168.24 (sx2) ppm. IR (neat): ν 3384, 3042, 1641, 1578, 1540, 1477, 1435, 1162, 843 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{40}H_{29}IrN_5$ $[M - PF_6]^+$: 772.2052; found: 772.2045.

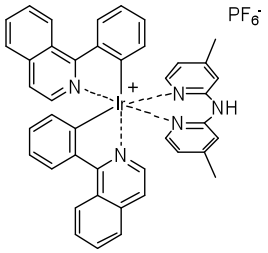
[(bis(3-methylpyridin-2-yl)amine)bis-(2-phenyl-(1-isoquinolinato)-*C*^{2},*N*)iridium(III)] hexafluorophosphate, [Ir(piq)$_2$(3-MeHdpa)][PF$_6$] 4b



Orange solid. Isolated yield: quantitative.

^{1}H-NMR (d_6-DMSO, 400MHz): δ 2.58 (s, 6H), 6.13 (d, J = 7.6 Hz, 2H), 6.80 (t, J = 7.7 Hz, 2H), 6.82 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.3 Hz, 2H), 7.35 (d, J = 5.0 Hz, 2H), 7.75-7.78 (m, 4H), 7.87 (t, J = 8.3 Hz, 2H), 7.92 (t, J = 6.8 Hz, 2H), 8.15 (t, J = 6.9 Hz, 4H), 8.27 (s, 1H), 8.29 (d, J = 8.1 Hz, 2H), 8.95 (d, J = 8.4 Hz, 2H) ppm. ^{13}C-NMR (d_6-DMSO, 100MHz): 18.2 (qx2), 120.4 (dx2), 122.1 (dx2), 122.5 (dx2), 126.0 (sx2), 126.1 (sx2), 126.9 (dx2), 128.1 (dx2), 129.7 (dx2), 130.5 (dx2), 131.0 (dx2), 131.9 (dx2), 132.5 (dx2), 137.1 (sx2), 141.4 (dx2), 142.2 (dx2), 145.7 (sx2), 147.7 (dx2), 151.2 (sx2), 154.3 (sx2), 168.3 (sx2) ppm. IR (neat): ν 3438, 3044, 1619, 1592, 1576, 1522, 1465, 1122, 842 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{42}H_{33}IrN_5$ $[M - PF_6]^+$: 800.2365; found: 800.2364.

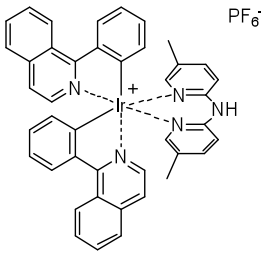
[(bis(4-methylpyridin-2-yl)amine)bis-(2-phenyl-(1-isoquinolinato)-*C*^{2},*N*)iridium(III)] hexafluorophosphate, [Ir(piq)$_2$(4-MeHdpa)][PF$_6$] 4c



Orange solid. Isolated yield: 82%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 2.18 (s, 6H), 6.20 (d, J = 7.4 Hz, 2H), 6.36 (d, J = 5.9 Hz, 2H), 6.77 (t, J = 7.2 Hz, 2H), 7.01 (t, J = 7.2 Hz, 2H), 7.22 (d, J = 6.1 Hz, 2H), 7.44 (d, J = 6.4 Hz, 2H), 7.56 (s, 2H), 7.72-7.79 (m, 4H), 7.94 (d, J = 7.4 Hz, 2H), 8.07 (d, J = 6.4 Hz, 2H), 8.20 (d, J = 7.9 Hz, 2H), 8.90 (d, J = 8.1 Hz, 2H), 9.47 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 21.0 (qx2), 116.4 (dx2), 120.7 (dx2), 121.3 (dx2), 122.0 (dx2), 126.4 (sx2), 126.9 (dx2), 127.6 (dx2), 128.5 (dx2), 130.4 (dx2), 130.6 (dx2), 131.6 (dx2), 132.2 (dx2), 137.1 (sx2), 141.3 (dx2), 145.5 (sx2), 148.8 (dx2), 151.3 (sx2), 151.4 (sx2), 153.7 (sx2), 169.0 (sx2) ppm. IR (neat): ν 3381, 3045, 1637, 1576, 1480, 1194, 841 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{42}H_{33}IrN_5$ $[M - PF_6]^+$: 800.2365; found: 800.2351.

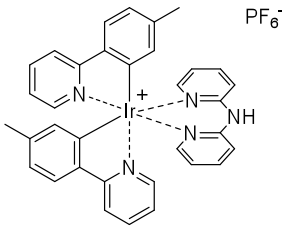
[(bis(5-methylpyridin-2-yl)amine)bis-(2-phenyl-(1-isoquinolinato)-*C*^{2},*N*)iridium(III)] hexafluorophosphate, [Ir(piq)$_2$(5-MeHdpa)][PF$_6$] 4d



Orange solid. Isolated yield: 92%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 1.79 (s, 6H), 6.17 (d, J = 7.2 Hz, 2H), 6.79 (t, J = 7.0 Hz, 2H), 7.02 (t, J = 7.2 Hz, 2H), 7.07 (s, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 6.4 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.73-7.79 (m, 4H), 7.94 (d, J = 7.9 Hz, 2H), 8.08 (d, J = 6.4 Hz, 2H), 8.19 (d, J = 7.9 Hz, 2H), 8.89 (d, J = 8.1 Hz, 2H), 9.84 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 17.6 (qx2), 116.0 (dx2), 121.4 (dx2), 122.0 (dx2), 126.4 (sx2), 126.9 (dx2), 127.6 (dx2), 128.0 (sx2), 128.5 (dx2), 130.4 (dx2), 130.6 (dx2), 131.6 (dx2), 132.2 (dx2), 137.1. HRMS (ESI): *m/z* calcd for $C_{42}H_{33}F_6IrN_5P$ $[M - PF_6]^+$: 798.2327; found: 798.2342.

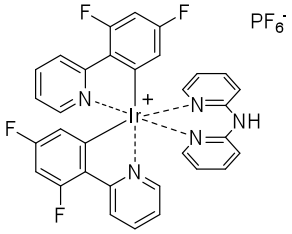
[(bis(pyridin-2-yl)amine)bis-(2-(4-methylphenyl)pyridinato-*C*^{2},*N*)iridium(III)] hexafluorophosphate, [Ir(4-Me-ppy)$_2$(Hdpa)][PF$_6$] 5a



Yellow solid. Isolated yield: 39%.

1H-NMR (d_6-DMSO, 400MHz): δ 2.0 (s, 6H), 5.86 (s, 2H), 6.76 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 6.4 Hz, 2H), 7.28 (t, J = 6.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 5.6 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.82 (t, J = 7.2 Hz, 2H), 7.97 (t, J = 8.0 Hz), m (8.21, 4H) ppm. 13C-NMR (d_6-DMSO, 100MHz): δ 21.95 (qx1), 116.2 (dx2), 119.4 (dx2), 120.2 (dx2), 123.4 (dx2), 123.6 (dx2), 125.5 (dx2), 132.3 (dx2), 139.2 (dx2), 139.8 (sx2), 140.0 (dx2), 141.8 (sx2), 149.5 (dx2), 149.9 (dx2), 150.9 (sx2), 151.7 (sx2), 167.4 (sx2) ppm. IR (neat): n 3378, 3081, 2924, 1601, 1474, 1294, 1164, 989, 839 cm-1. HRMS (ESI): *m/z* calcd for $C_{34}H_{29}F_6IrN_5P$ $[M - PF_6]^+$: 698.2032; found: 698.2029.

[(bis(pyridin-2-yl)amine)bis-(2-(4,6-difluorophenyl)pyridinato-*C*^{2},*N*)iridium(III)] hexafluorophosphate, [Ir(2,4-F-ppy)$_2$(Hdpa)][PF$_6$] 6a



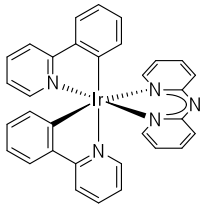
Yellow solid. Isolated yield: 94%.

1H-NMR (d_6-DMSO, 400MHz): δ 5.52 (dd, J = 8.4 Hz et J = 2.0 Hz, 2H), 6.89 (m, 4H), 7.42 (t, J = 6.2 Hz, 6H), 7.86 (t, J = 7.5 Hz, 2H), 8.11 (t, J = 7.7 Hz, 2H), 8.31 (d, J = 8.6 Hz, 2H), 8.36 (d, J = 5.5 Hz, 2H) ppm. 13C-NMR (d_6-DMSO, 100MHz): δ 99.3 (dx2), 113.7 (dx2), 113.8 (dx2), 116.7 (dx2), 119.8 (dx2), 123.8 (dx2), 124.0 (dx2), 124.6 (dx2), 128.2 (sx2), 140.5 (dx2), 140.6 (dx2), 149.4 (dx2), 150.9 (dx2), 151.8 (sx2), 163.2 (sx2), 163.3 (sx2) ppm. IR (neat): n 3381, 3038, 2921, 1583, 1475, 1264, 1162, 838, 728 cm-1. HRMS (ESI): *m/z* calcd for $C_{32}H_{21}F_{10}IrN_5P$ $[M - PF_6]^+$: 742.1351; found: 472.1339.

General procedure for neutral [Ir(C^N)$_2$(dpa)] complexes 1f, 2f and 4f.

In a dry flamed Schlenk tube under argon atmosphere, $[Ir(ppy)_2(Hdpa)][PF_6]$ (1 eq.) and K_2CO_3 (3 eq.) were introduced in dry dichloromethane. The reaction mixture was stirred at room temperature for 24 h then filtered over a pad of celite©. The filtrate was concentrated under vacuum to 1 mL. A large amount of pentane (20 mL) was added to the residue affording a precipitate. The resulting precipitate was collected on a frit. The solid was washed with pentane (3x5 mL) and dried under vacuum to afford pure neutral $[Ir(C^N)_2(dpa)]$ complex.

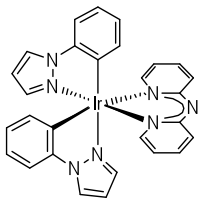
[(bis(pyridin-2-yl)amido)bis-(2-phenylpyridynato-*C*^{2},*N*)iridium(III)], [Ir(ppy)$_2$(dpa)] 1f



Yellow solid. Isolated yield: 70%.

^{1}H-NMR ($CDCl_3$, 400MHz): δ 6.17 (d, J = 7.5 Hz, 2H), 6.32 (t, J = 6.3 Hz, 2H), 6.79 (t, J = 7.5 Hz, 2H), 6.92 (t, J = 7.7 Hz, 2H), 7.10 (t, J = 7.2 Hz, 2H), 7.21-7.26 (m, 2H, overlapped with $CHCl_3$), 7.42 (d, J = 5.8 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.76 (t, J = 7.8 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 8.28 (d, J = 5.5 Hz, 2H) ppm. ^{13}C-NMR ($CDCl_3$, 100MHz): δ 114.9 (dx2), 119.2 (dx2), 120.1 (dx2), 121.6 (dx2), 122.4 (dx2), 124.5 (dx2), 130.2 (dx2), 131.9 (dx2), 136.7 (dx2), 137.3 (dx2), 143.7 (sx2), 149.3 (dx2), 149.5 (dx2), 153.0 (sx2), 154.0 (sx2), 168.1 (qx2) ppm. IR (neat): ν 3041, 1604, 1582, 1537, 1440, 1161, 843 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{32}H_{25}IrN_5$ $[M+H]^+$: 672.1739; found: 672.1734.

[(bis(pyridin-2-yl)amido)bis-(2-phenylpyrazolinato-*C*^{2},*N*)iridium(III)], [Ir(ppz)$_2$(dpa)] 2f

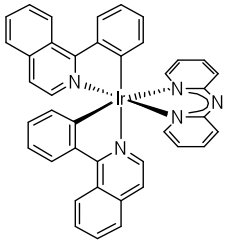


Light yellow solid. Isolated yield: 54%.

^{1}H-NMR (d_6-DMSO, 400MHz): δ 5.97 (d, J = 7.4 Hz, 2H), 6.18 (t, J = 6.4 Hz, 2H), 6.67 (t, J = 7.4 Hz, 2H), 6.78-6.82 (m, 4H), 6.87 (t, J = 7.6 Hz, 2H), 7.33-7.37 (m, 4H), 7.50 (s, 2H), 7.56 (d, J = 7.9 Hz, 2H), 8.83 (d, J = 1.92 Hz, 2H) ppm. ^{13}C-NMR (d_6-DMSO, 100MHz): δ 108.5 (dx2), 112.1 (dx2), 113.5 (dx2), 120.8 (dx2), 122.4 (dx2), 126.4 (dx2), 128.6 (dx2), 133.6 (dx2), 136.0 (sx2), 136.8 (dx2), 139.2 (dx2), 143.7 (sx2), 149.6 (dx2), 155.4 (sx2) ppm. IR (neat): ν 3134, 3054, 1598, 1474, 1439,

1416, 1054, 1033, 1009, 840 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{28}H_{23}IrN_7$ $[M+H]^+$: 650.1644; found: 650.1639.

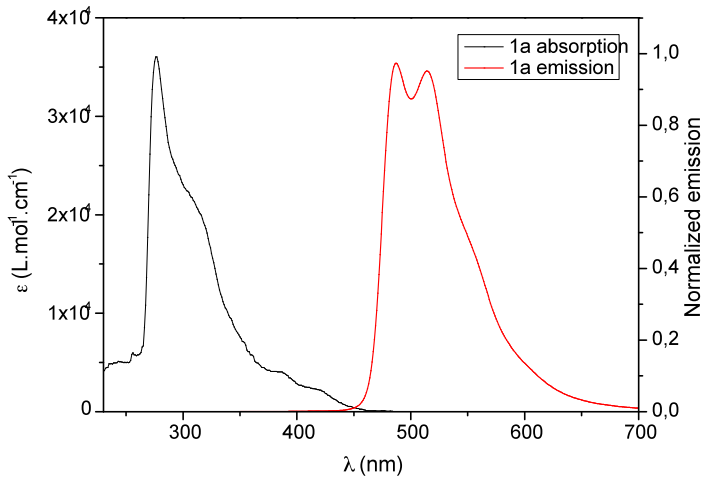
[(bis(pyridin-2-yl)amido)bis-(2-phenyl-(1-isoquinolinato)-*C*^{2},*N*)iridium(III)], [Ir(piq)$_2$(dpa)] 4f

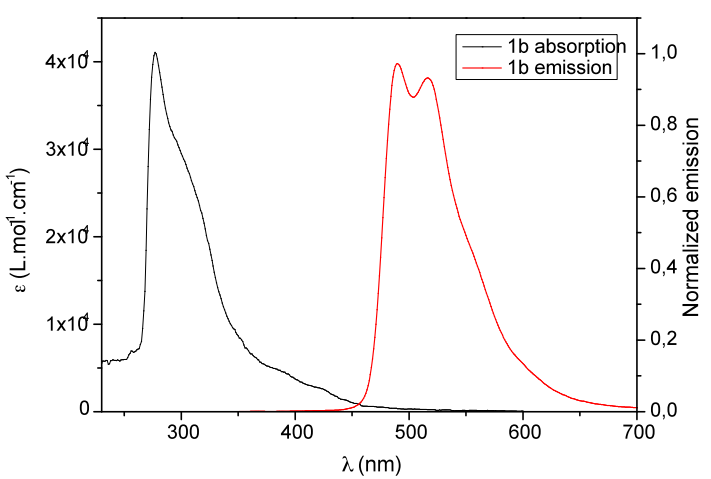


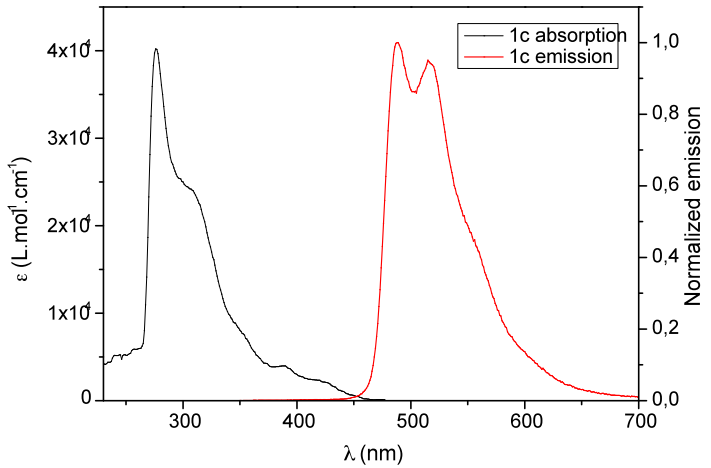
Orange solid. Isolated yield: 54%.

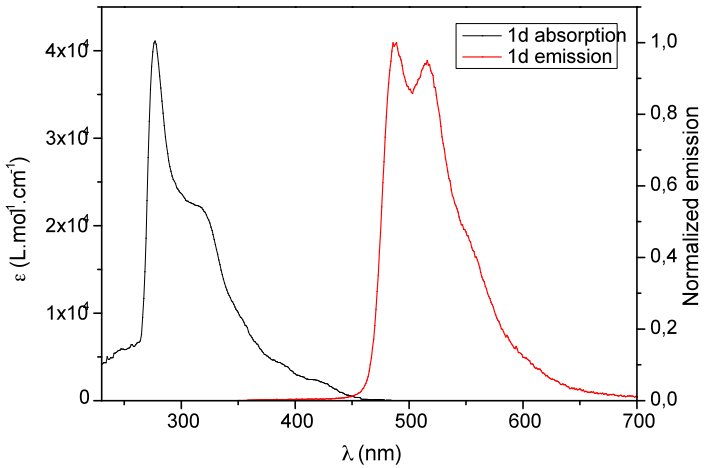
^{1}H-NMR (d_6-DMSO, 400MHz): δ 6.13 (d, J = 7.6 Hz, 2H), 6.24 (t, J = 6.2 Hz, 2H), 6.75 (t, J = 7.4 Hz, 2H), 6.99 (t, J = 7.3 Hz, 4H), 7.13 (d, J = 5.9 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.74 (d, J = 6.5 Hz, 2H), 7.85 (t, J = 7.6 Hz, 2H), 7.89 (t, J = 6.7 Hz, 2H), 8.11 (d, J = 7.6 Hz, 2H), 8.25 (t, J = 8.5 Hz, 4H), 8.94 (d, J = 8.2 Hz, 2H) ppm. ^{13}C-NMR (d_6-DMSO, 100 MHz): δ 114.9 (dx2), 120.5 (dx2), 121.7 (dx2), 121.9 (dx2), 126.1 (sx2), 126.8 (dx2), 128.1 (dx2), 129.5 (dx2), 130.3 (dx2), 130.9 (dx2), 132.0 (dx2), 132.2 (dx2), 137.0 (sx2), 137.4 (dx2), 141.7 (dx2), 145.7 (sx2), 149.3 (dx2), 154.1 (sx2), 157.1 (sx2), 168.3 (sx2) ppm. IR (neat): ν 3042, 1598, 1576, 1539, 1440, 1269, 1157, 841, 731 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{40}H_{29}IrN_5$ $[M+H]^+$: 772.2052; found: 772.2044.

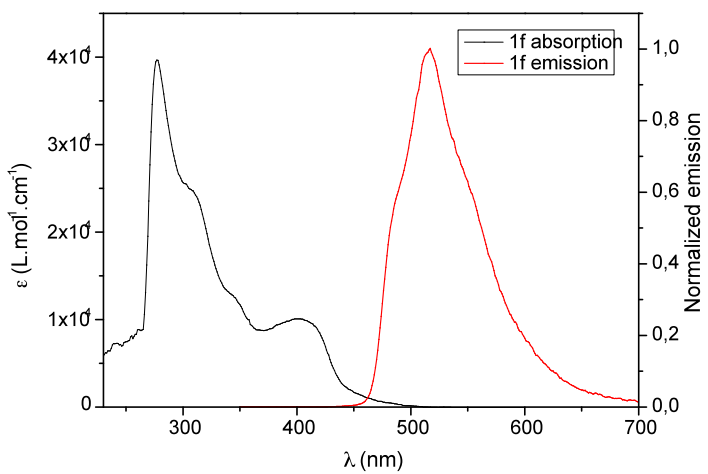
Part 2: Emission and absorption spectra of complexes 1-6

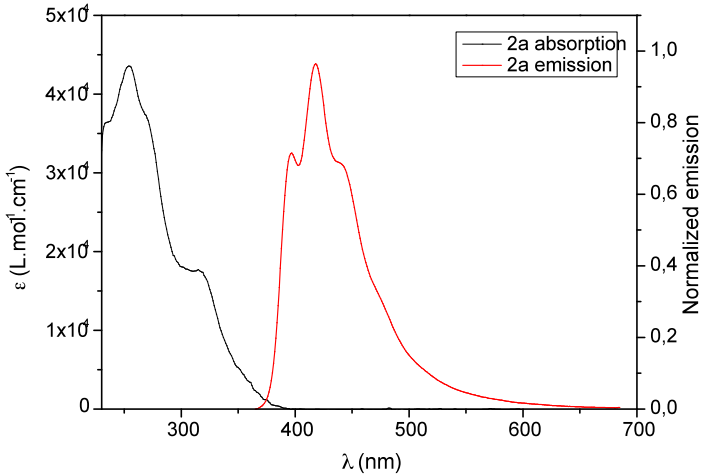


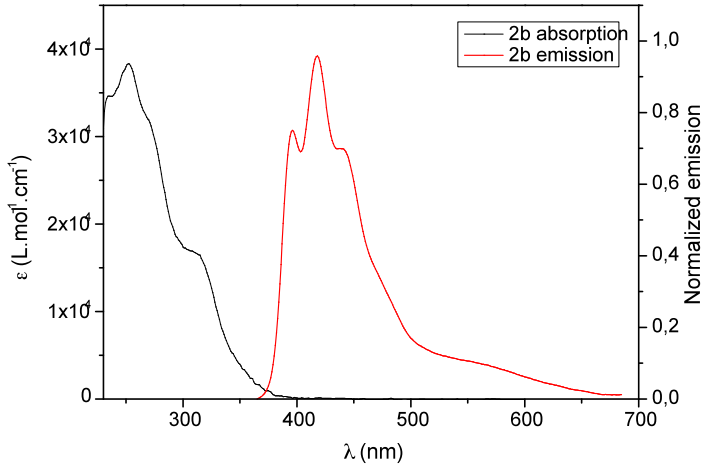


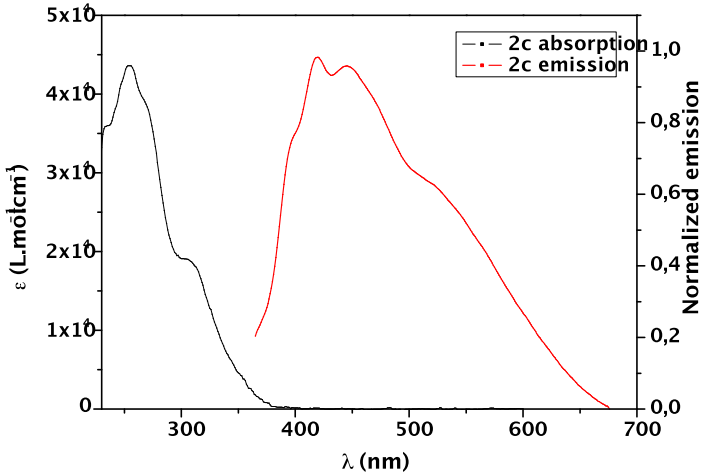


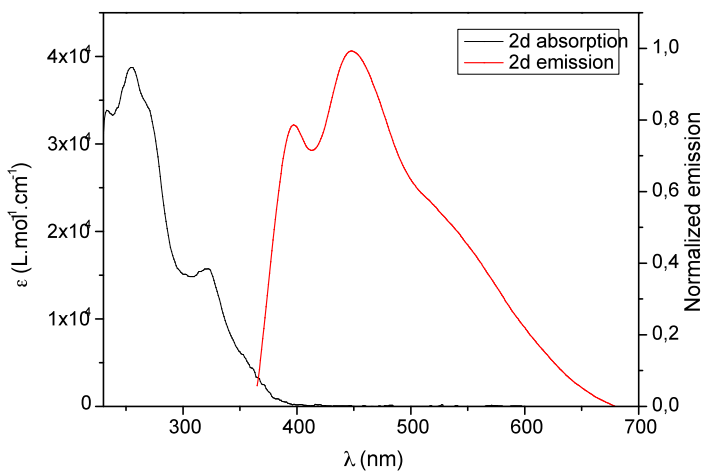


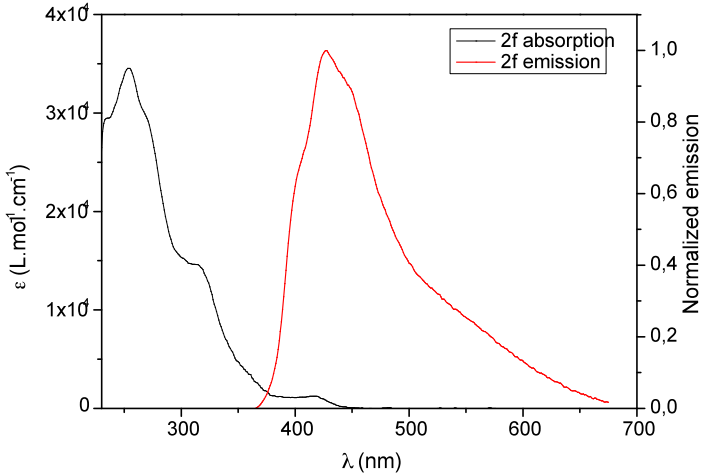

1f absorption
1f emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

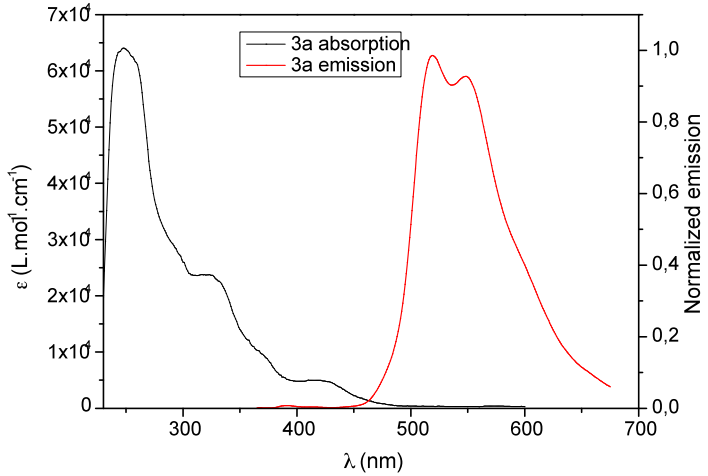

2a absorption
2a emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

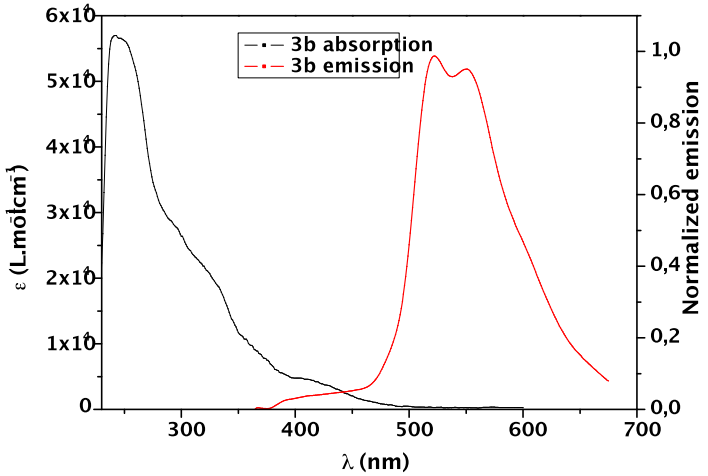

2b absorption
2b emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

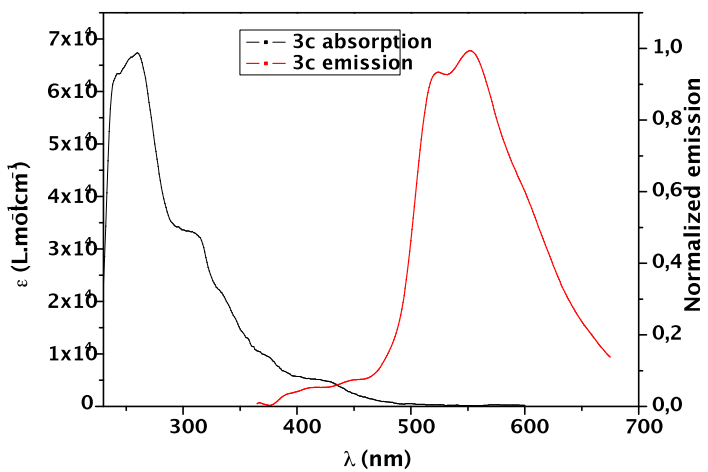

2c absorption
2c emission
ε (L.molcm-1)
Normalized emission
λ (nm)

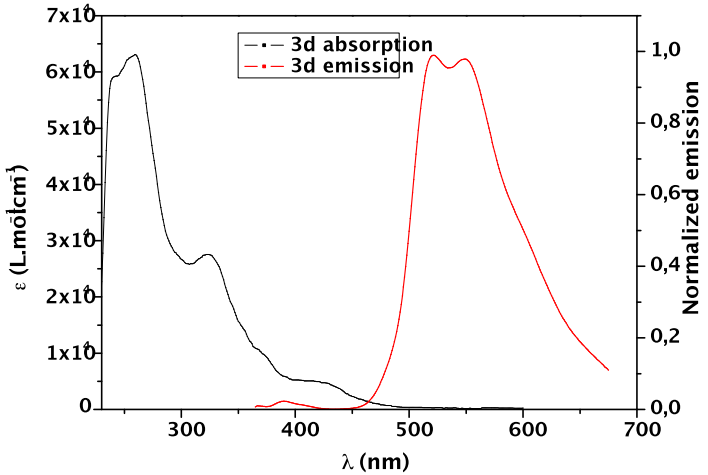

2d absorption
2d emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

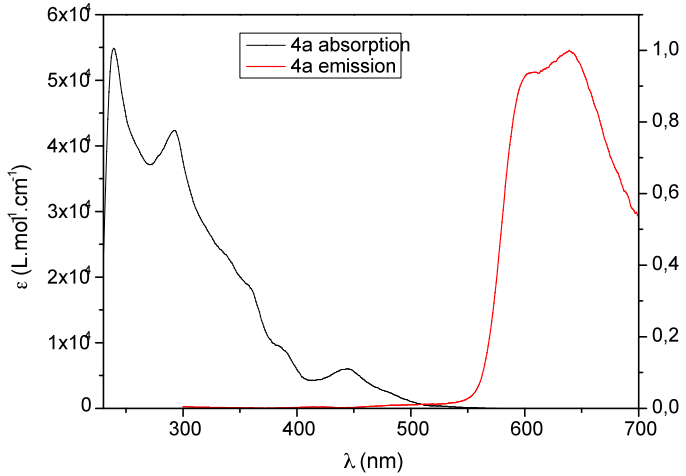

2f absorption
2f emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

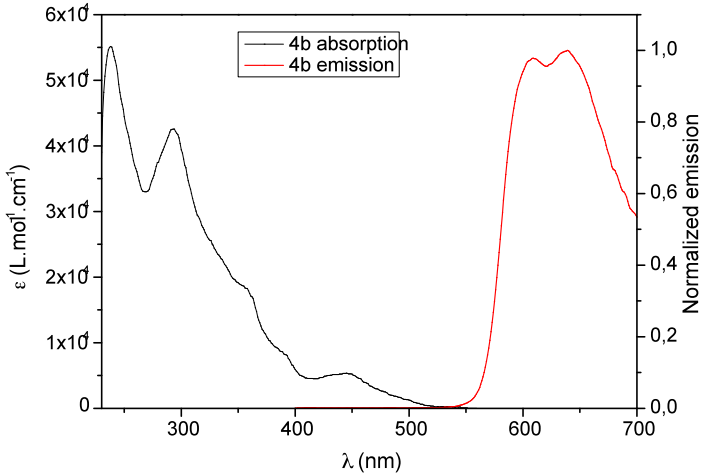

3a absorption
3a emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

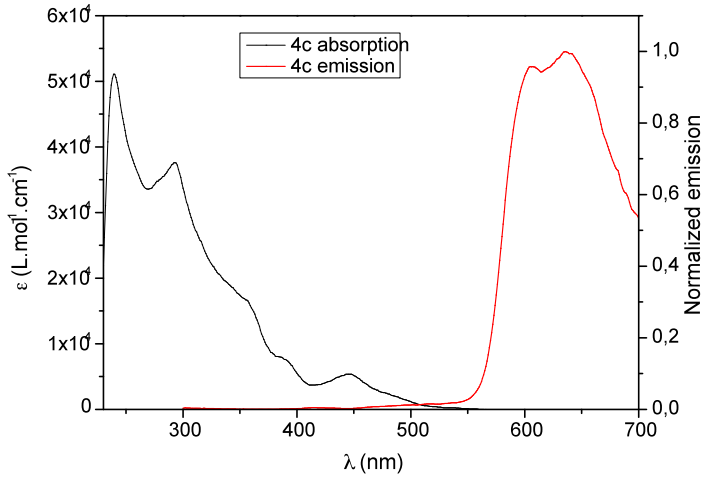

3b absorption
3b emission
ε (L.mol-1cm-1)
Normalized emission
λ (nm)

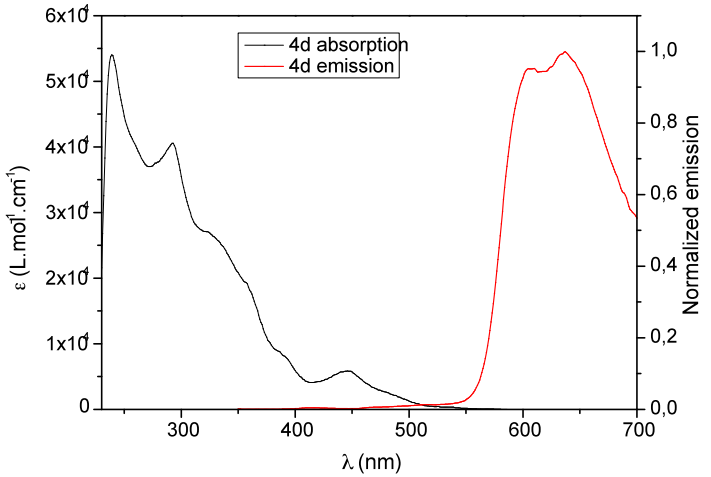

3c absorption
3c emission
ε (L.mol.cm)
Normalized emission
λ (nm)

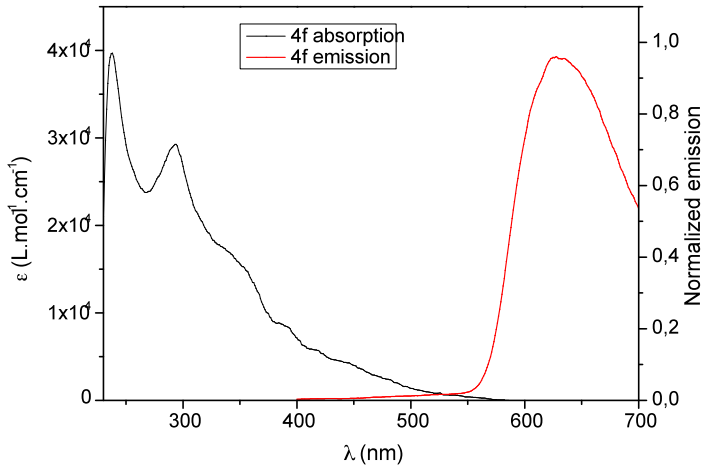

3d absorption
3d emission
ε (L.mol.cm)
Normalized emission
λ (nm)

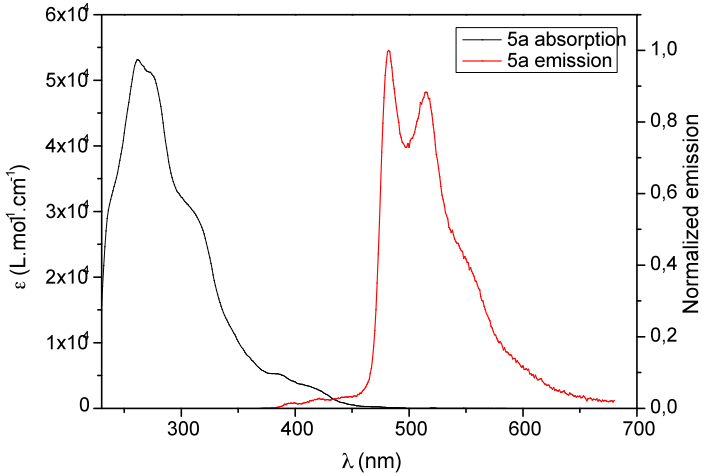

4a absorption
4a emission
ε (L.mol.cm)
λ (nm)

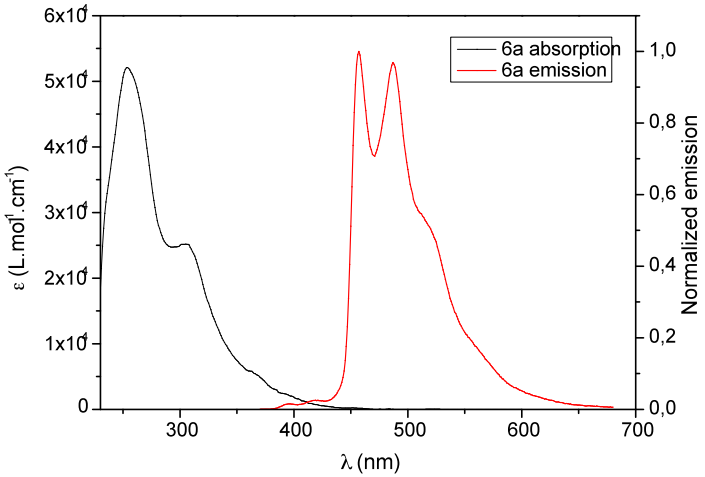

4b absorption
4b emission
ε (L.mol.cm)
Normalized emission
λ (nm)


4c absorption
4c emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)


4d absorption
4d emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

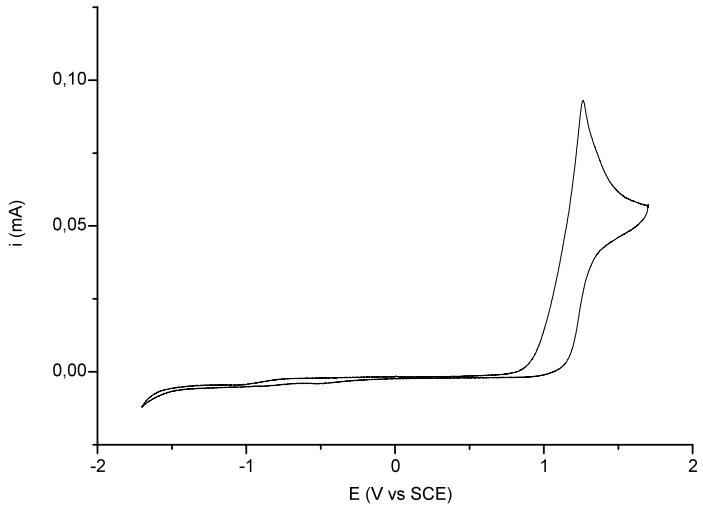

4f absorption
4f emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)


5a absorption
5a emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)

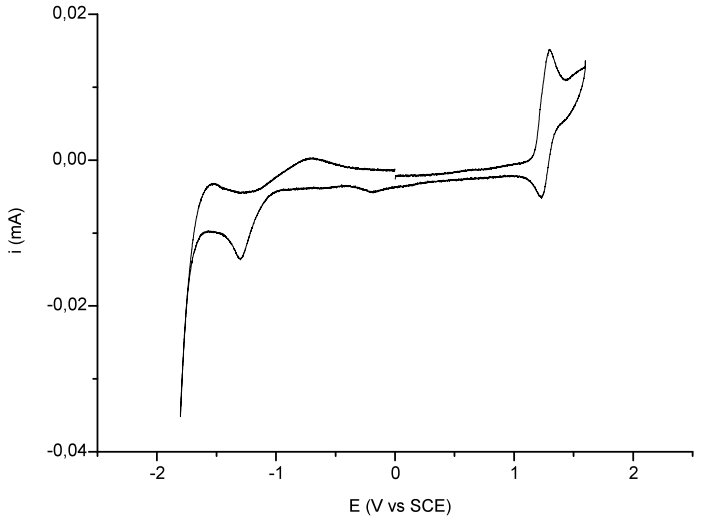

6a absorption
6a emission
ε (L.mol-1.cm-1)
Normalized emission
λ (nm)
0
1x10
2x10
3x10
4x10
5x10
6x10
0,0
0,2
0,4
0,6
0,8
1,0
300
400
500
600
700

Voltammetric experiments were carried out using a Biologic potentiostat unit, with the EC-Lab software package. A platinum wire working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Cyclic voltammetries were performed in anhydrous acetonitrile, containing 0.1 M tetrabutylammonium hexafluorophosphate, at a 50 $mV.s^{-1}$ scan rate, under a nitrogen atmosphere.

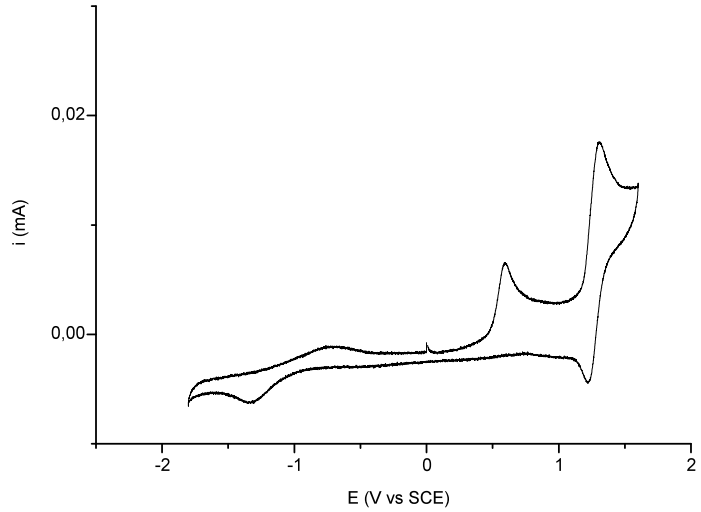
Hdpa



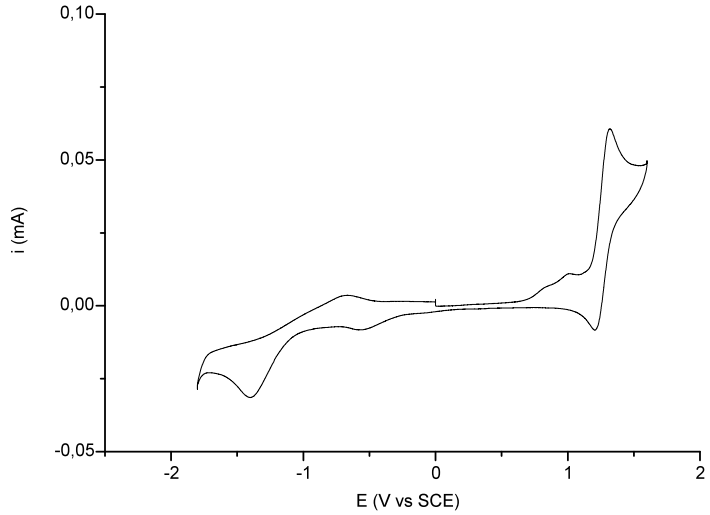
$[Ir(ppy)_2(Hdpa)][PF_6]$ **1a**



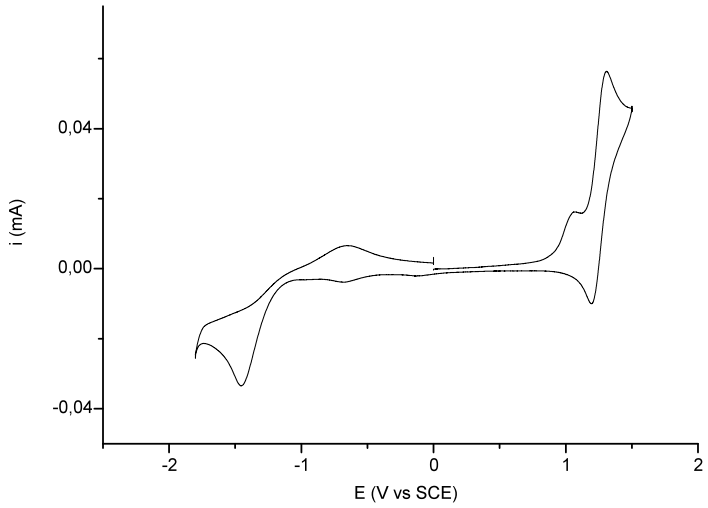
$Ir(ppy)_2(dpa)$ **1f**



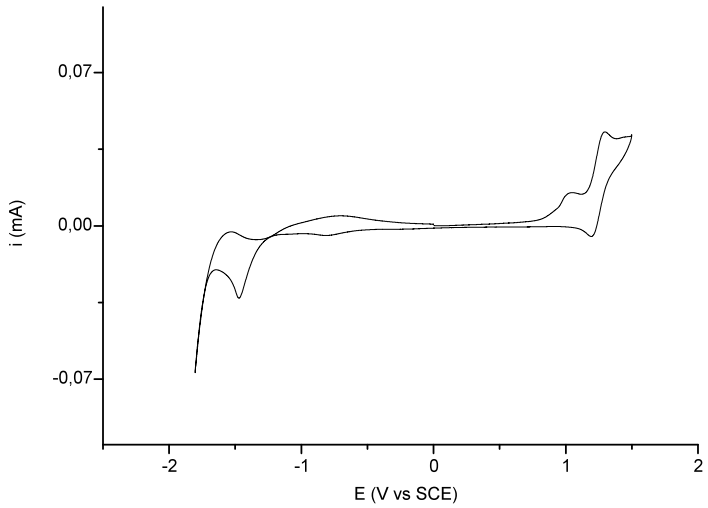
$[Ir(ppy)_2(3\text{-Me-Hdpa})][PF_6]$ **1b**



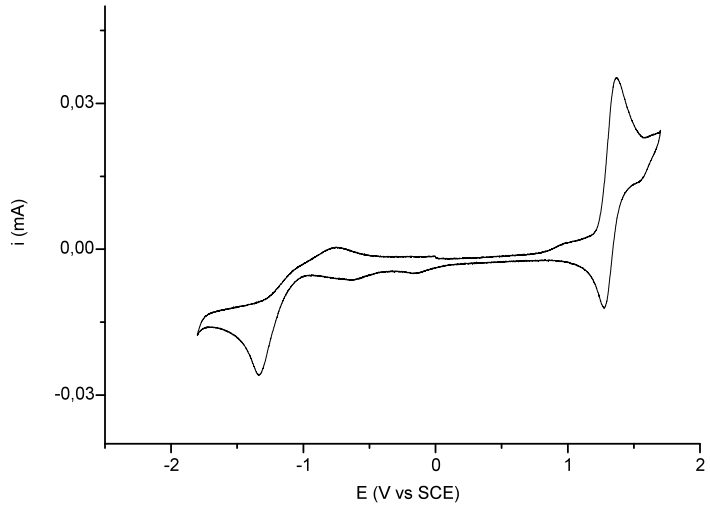
$[Ir(ppy)_2(4\text{-Me-Hdpa})][PF_6]$ **1c**



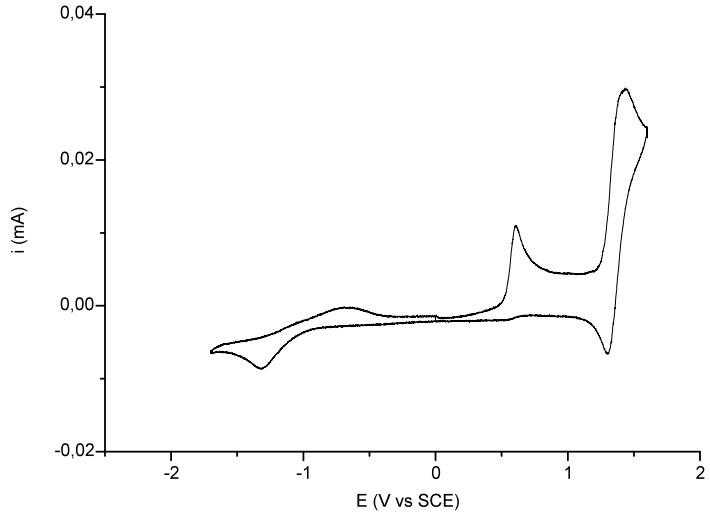
$[Ir(ppy)_2(5\text{-Me-Hdpa})][PF_6]$ **1d**



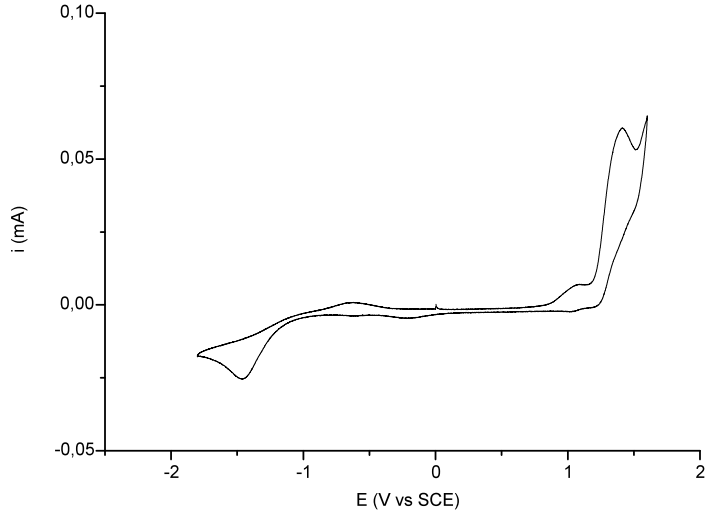
$[Ir(ppz)_2(Hdpa)][PF_6]$ **2a**



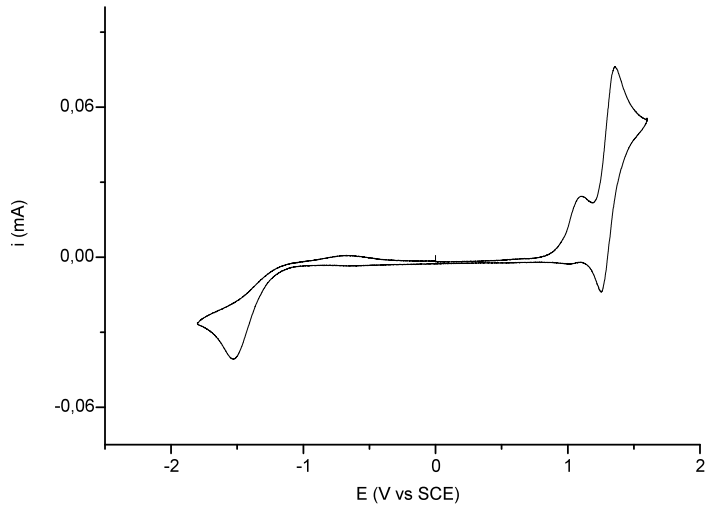
$Ir(ppz)_2(dpa)$ **2f**



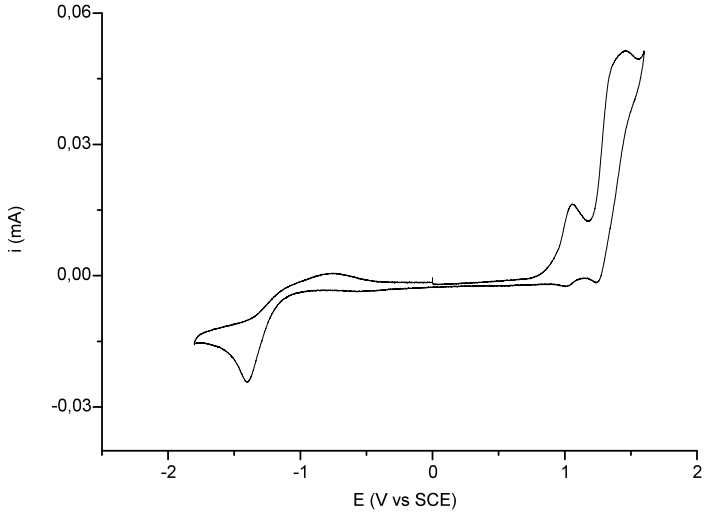
[Ir(ppz)$_2$(3-Me-Hdpa)][PF$_6$] **2b**



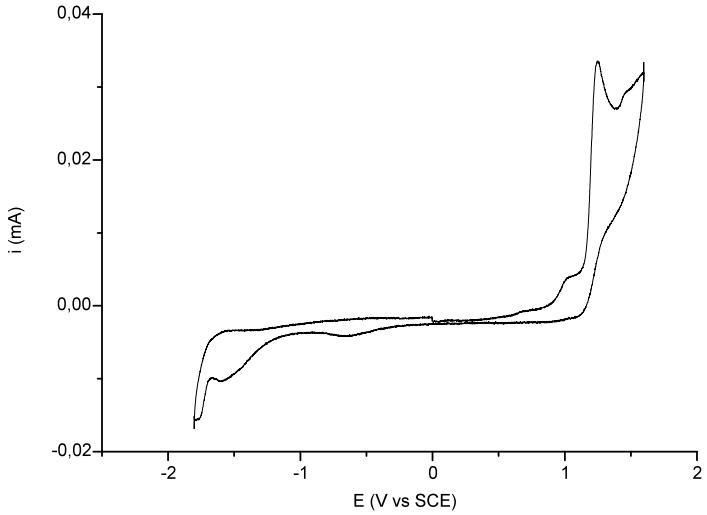
[Ir(ppz)$_2$(4-Me-Hdpa)][PF$_6$] **2c**



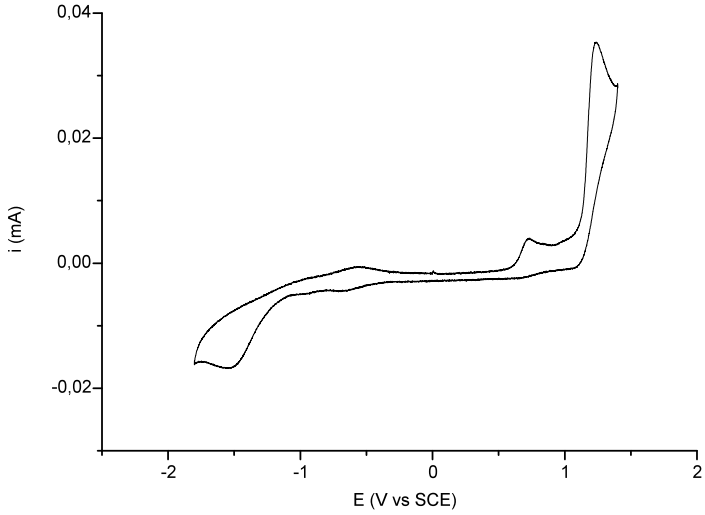
$[Ir(ppz)_2(5\text{-Me-Hdpa})][PF_6]$ **2d**



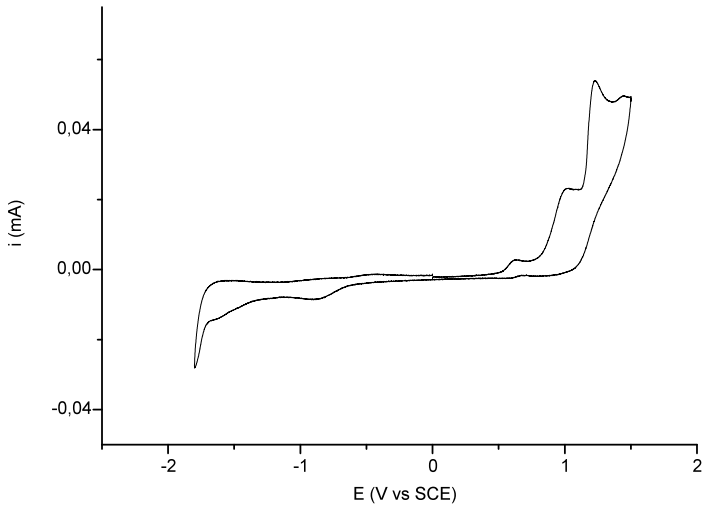
$[Ir(bzq)_2(Hdpa)][PF_6]$ **3a**



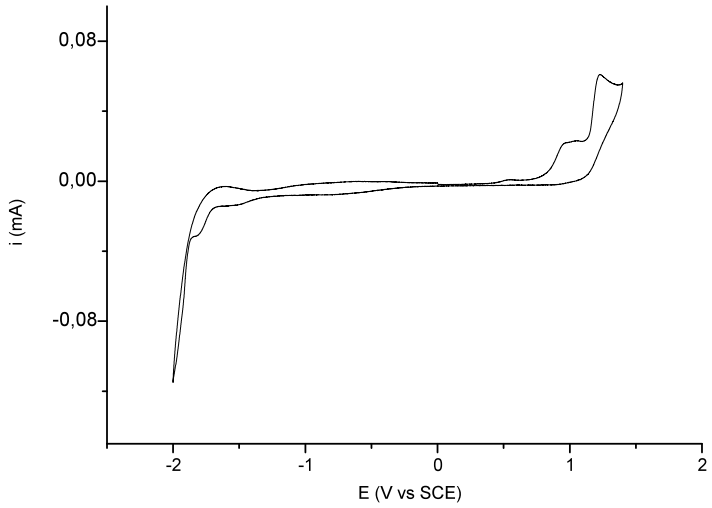
[Ir(bzq)$_2$(3-Me-Hdpa)][PF$_6$] **3b**



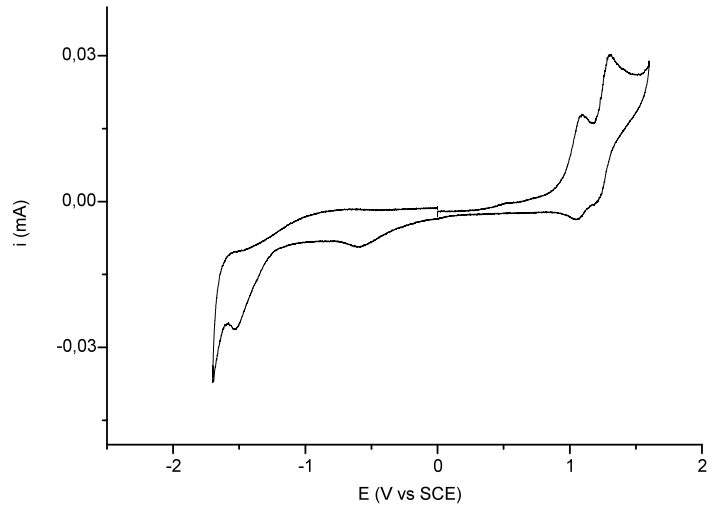
[Ir(bzq)$_2$(4-Me-Hdpa)][PF$_6$] **3c**



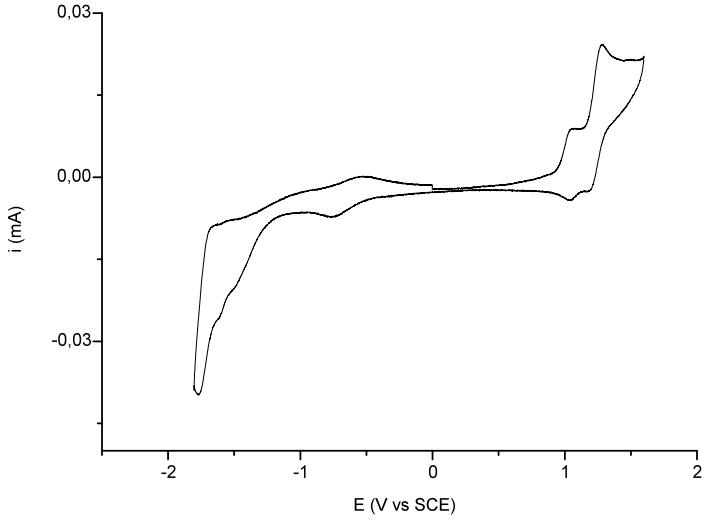
$[Ir(bzq)_2(5\text{-Me-Hdpa})][PF_6]$ **3d**



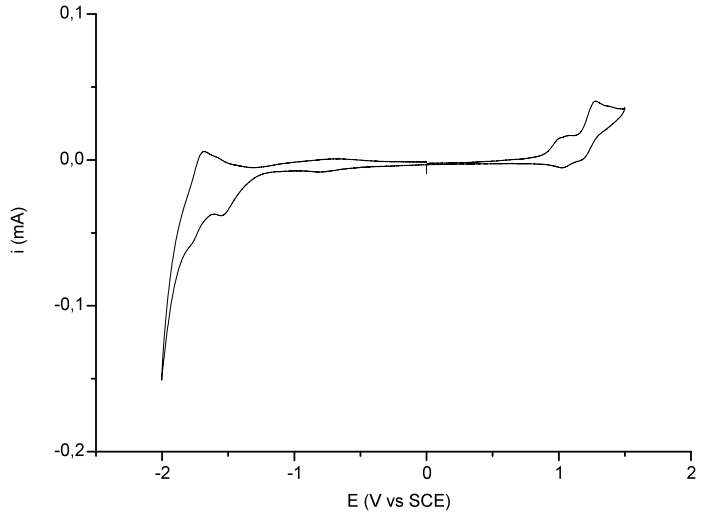
$[Ir(piq)_2(Hdpa)][PF_6]$ **4a**



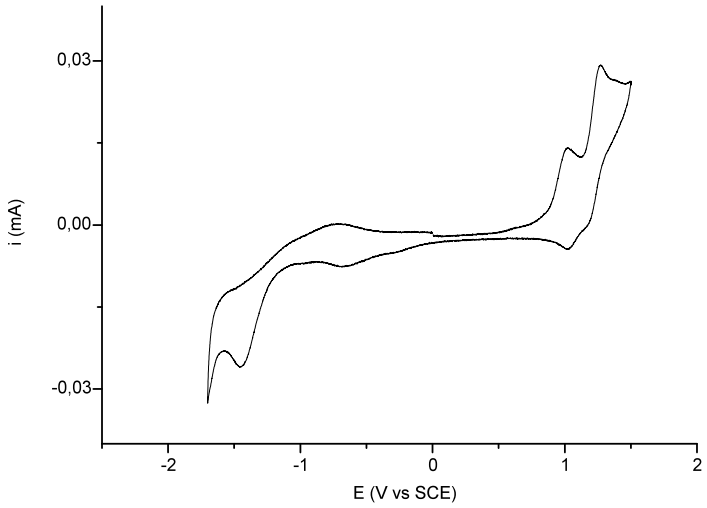
[Ir(piq)$_2$(3-Me-Hdpa)][PF$_6$] **4b**



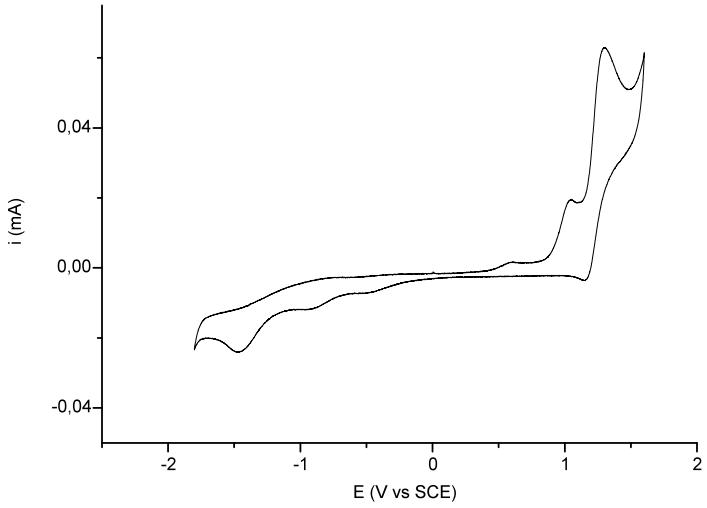
[Ir(piq)$_2$(4-Me-Hdpa)][PF$_6$] **4c**



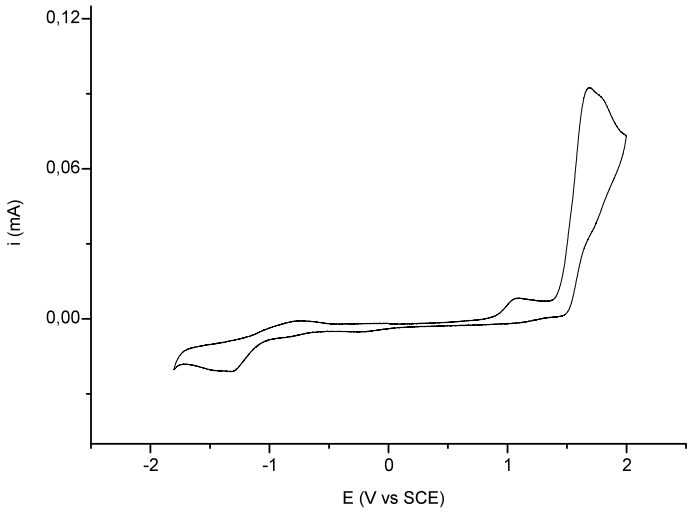
[Ir(piq)$_2$(5-Me-Hdpa)][PF$_6$] **4d**



[Ir(4-Me-ppy)$_2$(Hdpa)][PF$_6$] **5a**



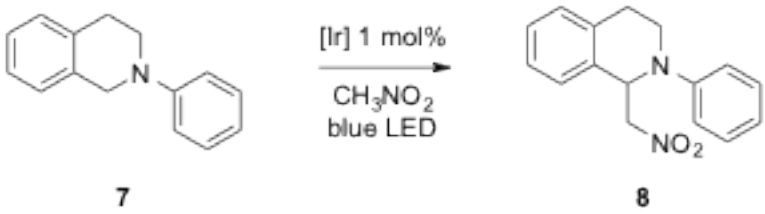
[Ir(2,4-F-ppy)$_2$(Hdpa)][PF$_6$] **6a**



Part 3: General procedure for catalysis assays.

General procedure for the iridium(III)-catalysed CH functionalization of compound 7.[7]

In an open tube equipped with a $CaCl_2$ drying tube, iridium catalyst (25 μmol, 0.01 eq) was added to a tetrahydroisoquinoline **7** (52 mg, 0.25 mmol, 1 eq) in dry distilled nitromethane (1 ml). The reaction mixture was stirred under irradiation of a blue LED strip (1 cm between the tube and the FlexLed inspire®, 2.4 W/m) at room temperature for 11h. Solvent was removed under vacuum and the residue was taken up with dichloromethane (0.1 mL). Diethyl ether (10 mL) was added and the solution was filtered over a pad of Celite® in order to remove the precipitated catalyst. Cake was washed with dietyl ether and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent pentane/ethyl acetate 95:5) to afford **8** as pale yellow oil.



Scheme 1. Iridium(III)-catalysed CH functionalization of compound **7**.

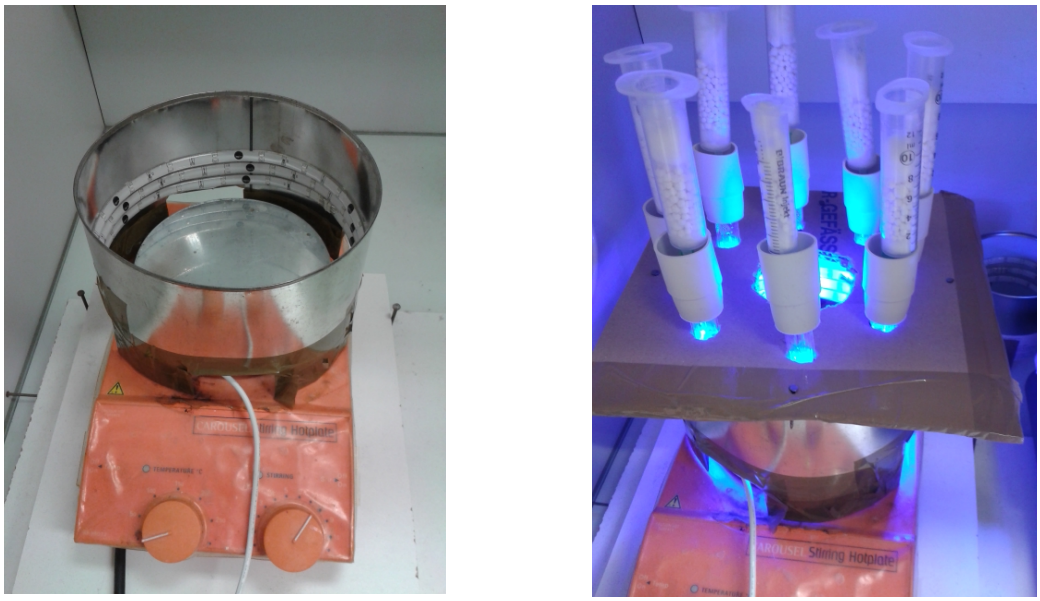


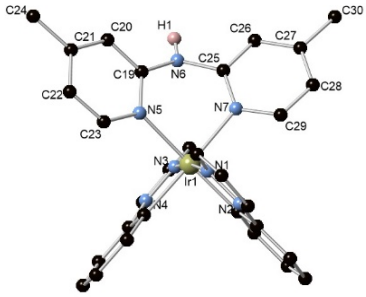
Figure 1. Picture of the light chamber equipped with blue LED strips (left) and picture of the light chamber during catalytic assays (right).

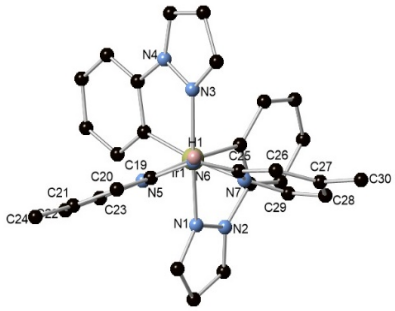
[7] Condie, A.G.; Gonzalez-Gomez, J.C.; Stephenson, C.R.J.; *J. Am. Chem. Soc.*, 2010, **132**, 1464-1465.

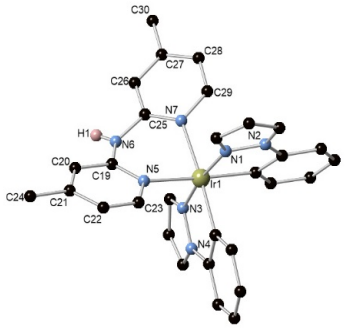
Table 1. Iridium(III)-catalysed C-H functionalisation.

Entry	Complex	Conv.[a] (%)
1	$[Ir(ppy)_2(dpa)][PF_6]$	92
2	$[Ir(ppy)_2(3\text{-}Medpa)][PF_6]$	69
3	$[Ir(ppy)_2(4\text{-}Medpa)][PF_6]$	93
4	$[Ir(ppy)_2(5\text{-}Medpa)][PF_6]$	91
5	$[Ir(ppy)_2(dpa)]$	88
6	$[Ir(ppz)_2(dpa)][PF_6]$	8
7	$[Ir(ppz)_2(3\text{-}Medpa)][PF_6]$	5
8	$[Ir(ppz)_2(4\text{-}Medpa)][PF_6]$	8
9	$[Ir(ppz)_2(5\text{-}Medpa)][PF_6]$	6
10	$[Ir(ppz)_2(dpa)]$	13
11	$[Ir(bzq)_2(dpa)][PF_6]$	98
12	$[Ir(bzq)_2(3\text{-}Medpa)][PF_6]$	94
13	$[Ir(bzq)_2(4\text{-}Medpa)][PF_6]$	87
14	$[Ir(bzq)_2(5\text{-}Medpa)][PF_6]$	96
15	$[Ir(piq)_2(dpa)][PF_6]$	98
16	$[Ir(piq)_2(3\text{-}Medpa)][PF_6]$	99
17	$[Ir(piq)_2(4\text{-}Medpa)][PF_6]$	97
18	$[Ir(piq)_2(5\text{-}Medpa)][PF_6]$	97
19	$[Ir(piq)_2(dpa)]$	96
20	$[Ir(4\text{-}Me\text{-}ppy)_2(dpa)][PF_6]$	88
21	$[Ir(2,4\text{-}F\text{-}ppy)_2(dpa)][PF_6]$	81
22	$[Ir(ppy)_2(dtbbpy)][PF_6]$	100

Part 4: Crystallographic data of complexes 1c and 2c.







	Complex **2c**
Formula	$C_{30}H_{27}F_6IrN_7P$
M/g.mol^{-1}	821.75
Crystal system	Monoclinic
Flack parameter	
Space group	*P*2(1)/c
a/ Å	9.3281(6)
b/ Å	15.4516(10)
c/ Å	23.6282(17)
α/ °	90.00
β/ °	92.742(3)
γ/ °	90.00
V/ Å^3	3401.7(4)
Z	4
ρcalcd/ g.cm^{-3}	1.605
μ(Mo K$_α$)/ mm^{-1}	4.035
T/ K	150(2)
No of reflections	61905
No of unique reflections	7497
R_{int}	0.0547
*R*1, wR_2 (I > 2*σ*(I))	0.0311, 0.0665
*R*1, wR_2 (all data)	0.0405, 0.0691
GOF	1.066

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir1	0.717365 (15)	0.566033 (9)	0.696282 (6)	0.02075 (5)
P1	0.92343 (18)	0.26978 (11)	0.99413 (7)	0.0595 (4)
F1	0.8827 (5)	0.2685 (4)	1.05769 (18)	0.1188 (18)

F2	0.9647 (7)	0.2683 (4)	0.9322 (2)	0.154 (2)
F3	0.8465 (5)	0.1775 (2)	0.98894 (18)	0.0941 (13)
F4	0.7771 (5)	0.3132 (3)	0.9752 (3)	0.127 (2)
F5	0.9911 (6)	0.3621 (3)	1.0035 (3)	0.134 (2)
F6	1.0691 (4)	0.2249 (3)	1.0135 (2)	0.1171 (18)
N7	0.9096 (3)	0.51677 (19)	0.66084 (14)	0.0230 (7)
N6	0.7773 (4)	0.4347 (2)	0.59190 (16)	0.0307 (8)
N5	0.6207 (3)	0.44688 (19)	0.66704 (14)	0.0244 (7)
N4	0.5346 (4)	0.6774 (2)	0.62708 (16)	0.0343 (8)
N3	0.6574 (3)	0.6296 (2)	0.62391 (15)	0.0280 (7)
N2	0.8429 (4)	0.5797 (2)	0.80935 (15)	0.0334 (8)
N1	0.7771 (4)	0.5199 (2)	0.77409 (14)	0.0278 (7)
C29	1.0397 (4)	0.5436 (3)	0.68090 (19)	0.0301 (9)
H29	1.0461	0.5726	0.7164	0.036*
C28	1.1631 (4)	0.5313 (3)	0.6529 (2)	0.0333 (10)
H28	1.2529	0.5492	0.6697	0.040*
C27	1.1567 (4)	0.4927 (3)	0.59998 (18)	0.0279 (9)
C26	1.0259 (4)	0.4614 (3)	0.58050 (18)	0.0269 (9)
H26	1.0175	0.4326	0.5450	0.032*
C25	0.9054 (4)	0.4714 (2)	0.61249 (17)	0.0232 (8)
C19	0.6625 (4)	0.4034 (3)	0.62187 (17)	0.0234 (8)
C23	0.5088 (4)	0.4123 (3)	0.69478 (19)	0.0304 (9)
H23	0.4790	0.4408	0.7278	0.036*
C22	0.4377 (5)	0.3390 (3)	0.67756 (19)	0.0347 (10)
H22	0.3610	0.3175	0.6985	0.042*
C21	0.4782 (4)	0.2958 (3)	0.62899 (19)	0.0325 (9)
C20	0.5932 (4)	0.3288 (3)	0.60142 (18)	0.0275 (9)
H20	0.6252	0.3007	0.5685	0.033*
C24	0.3998 (6)	0.2167 (3)	0.6070 (2)	0.0462 (12)
H24B	0.3090	0.2340	0.5877	0.069*
H24C	0.3802	0.1783	0.6387	0.069*
H24A	0.4591	0.1862	0.5803	0.069*
C30	1.2880 (5)	0.4858 (3)	0.5652 (2)	0.0433 (12)
H30B	1.2693	0.4449	0.5341	0.065*
H30A	1.3695	0.4653	0.5894	0.065*
H30C	1.3106	0.5428	0.5498	0.065*
C10	0.5305 (4)	0.6184 (3)	0.71973 (18)	0.0271 (9)
C15	0.4600 (5)	0.6101 (3)	0.7699 (2)	0.0396 (11)
H15	0.4991	0.5741	0.7993	0.048*
C14	0.3312 (5)	0.6548 (3)	0.7774 (2)	0.0478 (13)

H14	0.2841	0.6480	0.8119	0.057*
C13	0.2723 (5)	0.7076 (3)	0.7363 (3)	0.0524 (15)
H13	0.1859	0.7379	0.7425	0.063*
C12	0.3376 (5)	0.7170 (3)	0.6860 (2)	0.0463 (13)
H12	0.2971	0.7532	0.6570	0.056*
C11	0.4643 (4)	0.6724 (3)	0.6786 (2)	0.0345 (10)
C16	0.7117 (6)	0.6476 (3)	0.5750 (2)	0.0436 (12)
H16	0.7977	0.6238	0.5618	0.052*
C17	0.6233 (7)	0.7075 (4)	0.5454 (3)	0.0668 (17)
H17	0.6376	0.7314	0.5090	0.080*
C18	0.5135 (6)	0.7242 (4)	0.5793 (2)	0.0563 (15)
H18	0.4353	0.7622	0.5708	0.068*
C1	0.8137 (4)	0.6725 (2)	0.73004 (17)	0.0243 (8)
C2	0.8650 (4)	0.6635 (3)	0.78608 (18)	0.0283 (9)
C7	0.7699 (6)	0.4478 (3)	0.8033 (2)	0.0426 (12)
H7	0.7303	0.3951	0.7889	0.051*
C8	0.8282 (7)	0.4592 (4)	0.8581 (2)	0.0582 (15)
H8	0.8351	0.4174	0.8876	0.070*
C9	0.8737 (6)	0.5435 (4)	0.8604 (2)	0.0519 (14)
H9	0.9189	0.5715	0.8923	0.062*
C3	0.9333 (5)	0.7282 (3)	0.8174 (2)	0.0422 (12)
H3	0.9671	0.7184	0.8554	0.051*
C4	0.9508 (5)	0.8066 (3)	0.7919 (3)	0.0503 (14)
H4	0.9973	0.8523	0.8125	0.060*
C5	0.9015 (5)	0.8200 (3)	0.7368 (2)	0.0450 (13)
H5	0.9135	0.8751	0.7198	0.054*
C6	0.8343 (5)	0.7537 (3)	0.7056 (2)	0.0355 (10)
H6	0.8021	0.7637	0.6675	0.043*
H1	0.787 (5)	0.411 (3)	0.565 (2)	0.029 (14)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.01845 (8)	0.02037 (8)	0.02343 (8)	0.00032 (6)	0.00102 (5)	−0.00254 (6)
P1	0.0610 (10)	0.0605 (9)	0.0555 (10)	−0.0165 (7)	−0.0133 (7)	0.0212 (8)
F1	0.097 (3)	0.191 (5)	0.069 (3)	−0.041 (3)	0.005 (2)	−0.007 (3)
F2	0.228 (7)	0.169 (5)	0.068 (3)	0.000 (5)	0.042 (4)	0.039 (3)
F3	0.123 (3)	0.063 (2)	0.093 (3)	−0.026 (2)	−0.028 (3)	0.025 (2)
F4	0.097 (3)	0.082 (3)	0.193 (5)	0.000 (2)	−0.078 (3)	0.021 (3)
F5	0.118 (4)	0.087 (3)	0.192 (6)	−0.054 (3)	−0.035 (4)	0.012 (4)
F6	0.061 (3)	0.140 (4)	0.151 (4)	0.009 (3)	0.009 (3)	0.057 (4)

N7	0.0190 (16)	0.0189 (15)	0.0308 (19)	0.0019 (12)	−0.0004 (13)	−0.0021 (13)
N6	0.0274 (19)	0.038 (2)	0.027 (2)	−0.0067 (16)	0.0041 (15)	−0.0102 (18)
N5	0.0214 (16)	0.0226 (16)	0.0290 (18)	−0.0034 (13)	0.0001 (13)	−0.0033 (13)
N4	0.0289 (19)	0.035 (2)	0.038 (2)	0.0043 (15)	−0.0059 (16)	0.0015 (16)
N3	0.0204 (17)	0.0322 (18)	0.0312 (19)	0.0034 (14)	−0.0018 (14)	0.0000 (15)
N2	0.034 (2)	0.038 (2)	0.0281 (19)	0.0069 (16)	−0.0038 (15)	−0.0054 (16)
N1	0.0313 (19)	0.0296 (18)	0.0224 (18)	0.0026 (14)	0.0018 (14)	−0.0036 (14)
C29	0.023 (2)	0.028 (2)	0.039 (3)	0.0008 (16)	−0.0030 (18)	−0.0100 (18)
C28	0.018 (2)	0.035 (2)	0.046 (3)	−0.0021 (17)	−0.0006 (18)	−0.008 (2)
C27	0.022 (2)	0.027 (2)	0.035 (2)	0.0034 (16)	0.0031 (17)	0.0035 (17)
C26	0.027 (2)	0.028 (2)	0.026 (2)	−0.0009 (16)	0.0061 (17)	−0.0035 (16)
C25	0.0216 (19)	0.0205 (18)	0.027 (2)	−0.0017 (15)	0.0006 (16)	0.0023 (16)
C19	0.0184 (19)	0.0285 (19)	0.023 (2)	0.0004 (15)	−0.0007 (15)	0.0000 (16)
C23	0.024 (2)	0.034 (2)	0.033 (2)	−0.0031 (17)	0.0074 (17)	−0.0028 (18)
C22	0.030 (2)	0.041 (2)	0.034 (2)	−0.0093 (19)	0.0083 (19)	0.0004 (19)
C21	0.031 (2)	0.032 (2)	0.034 (2)	−0.0099 (18)	−0.0050 (18)	0.0023 (19)
C20	0.025 (2)	0.027 (2)	0.030 (2)	−0.0051 (16)	−0.0006 (17)	−0.0053 (17)
C24	0.052 (3)	0.042 (3)	0.044 (3)	−0.021 (2)	−0.001 (2)	0.001 (2)
C30	0.028 (2)	0.052 (3)	0.051 (3)	0.003 (2)	0.006 (2)	−0.003 (2)
C10	0.0198 (19)	0.027 (2)	0.035 (2)	−0.0010 (16)	0.0057 (17)	−0.0116 (17)
C15	0.037 (3)	0.039 (3)	0.043 (3)	−0.007 (2)	0.010 (2)	−0.011 (2)
C14	0.039 (3)	0.042 (3)	0.065 (4)	−0.004 (2)	0.023 (3)	−0.019 (3)
C13	0.031 (3)	0.038 (3)	0.090 (4)	0.003 (2)	0.015 (3)	−0.021 (3)
C12	0.028 (2)	0.035 (3)	0.075 (4)	0.0055 (19)	0.001 (2)	−0.006 (2)
C11	0.023 (2)	0.027 (2)	0.053 (3)	0.0023 (17)	0.0003 (19)	−0.007 (2)
C16	0.052 (3)	0.049 (3)	0.031 (3)	0.009 (2)	0.006 (2)	0.008 (2)
C17	0.084 (4)	0.073 (4)	0.044 (3)	0.027 (3)	0.004 (3)	0.017 (3)
C18	0.057 (3)	0.061 (4)	0.049 (3)	0.023 (3)	−0.015 (3)	0.015 (3)
C1	0.0172 (18)	0.0224 (18)	0.033 (2)	0.0027 (14)	0.0033 (16)	−0.0080 (16)
C2	0.021 (2)	0.032 (2)	0.032 (2)	0.0014 (16)	−0.0006 (17)	−0.0115 (18)
C7	0.057 (3)	0.030 (2)	0.041 (3)	0.006 (2)	0.003 (2)	0.006 (2)
C8	0.079 (4)	0.052 (3)	0.042 (3)	0.011 (3)	−0.009 (3)	0.018 (3)
C9	0.061 (3)	0.065 (4)	0.029 (3)	0.014 (3)	−0.011 (2)	0.001 (2)
C3	0.029 (2)	0.051 (3)	0.046 (3)	0.000 (2)	−0.001 (2)	−0.023 (2)
C4	0.035 (3)	0.043 (3)	0.073 (4)	−0.007 (2)	0.006 (3)	−0.032 (3)
C5	0.038 (3)	0.026 (2)	0.071 (4)	−0.0052 (19)	0.014 (3)	−0.009 (2)
C6	0.032 (2)	0.029 (2)	0.046 (3)	−0.0029 (18)	0.008 (2)	−0.0038 (19)

Geometric parameters (Å, °)

Ir1—C1	2.020 (4)	C21—C20	1.379 (6)

Ir1—C10	2.023 (4)	C21—C24	1.504 (6)
Ir1—N1	2.025 (3)	C20—H20	0.9500
Ir1—N3	2.027 (3)	C24—H24B	0.9800
Ir1—N5	2.150 (3)	C24—H24C	0.9800
Ir1—N7	2.154 (3)	C24—H24A	0.9800
P1—F2	1.531 (5)	C30—H30B	0.9800
P1—F1	1.567 (5)	C30—H30A	0.9800
P1—F4	1.567 (4)	C30—H30C	0.9800
P1—F5	1.572 (4)	C10—C15	1.388 (6)
P1—F6	1.574 (4)	C10—C11	1.403 (6)
P1—F3	1.598 (4)	C15—C14	1.404 (6)
N7—C25	1.339 (5)	C15—H15	0.9500
N7—C29	1.348 (5)	C14—C13	1.365 (8)
N6—C25	1.390 (5)	C14—H14	0.9500
N6—C19	1.397 (5)	C13—C12	1.367 (8)
N6—H1	0.74 (5)	C13—H13	0.9500
N5—C19	1.335 (5)	C12—C11	1.387 (6)
N5—C23	1.367 (5)	C12—H12	0.9500
N4—C18	1.347 (6)	C16—C17	1.404 (7)
N4—N3	1.369 (5)	C16—H16	0.9500
N4—C11	1.411 (6)	C17—C18	1.356 (8)
N3—C16	1.313 (6)	C17—H17	0.9500
N2—C9	1.348 (6)	C18—H18	0.9500
N2—N1	1.369 (5)	C1—C2	1.393 (6)
N2—C2	1.425 (5)	C1—C6	1.397 (6)
N1—C7	1.314 (5)	C2—C3	1.381 (6)
C29—C28	1.368 (6)	C7—C8	1.391 (7)
C29—H29	0.9500	C7—H7	0.9500
C28—C27	1.384 (6)	C8—C9	1.371 (8)
C28—H28	0.9500	C8—H8	0.9500
C27—C26	1.372 (6)	C9—H9	0.9500
C27—C30	1.511 (6)	C3—C4	1.366 (7)
C26—C25	1.393 (5)	C3—H3	0.9500
C26—H26	0.9500	C4—C5	1.376 (8)
C19—C20	1.398 (5)	C4—H4	0.9500
C23—C22	1.364 (6)	C5—C6	1.394 (6)
C23—H23	0.9500	C5—H5	0.9500
C22—C21	1.395 (6)	C6—H6	0.9500
C22—H22	0.9500		

C1—Ir1—C10	86.51 (15)	C21—C22—H22	120.2
C1—Ir1—N1	80.23 (15)	C20—C21—C22	117.3 (4)
C10—Ir1—N1	95.46 (15)	C20—C21—C24	120.9 (4)
C1—Ir1—N3	92.20 (15)	C22—C21—C24	121.8 (4)
C10—Ir1—N3	80.25 (15)	C21—C20—C19	119.9 (4)
N1—Ir1—N3	171.56 (13)	C21—C20—H20	120.0
C1—Ir1—N5	175.00 (15)	C19—C20—H20	120.0
C10—Ir1—N5	94.39 (14)	C21—C24—H24B	109.5
N1—Ir1—N5	94.78 (13)	C21—C24—H24C	109.5
N3—Ir1—N5	92.81 (13)	H24B—C24—H24C	109.5
C1—Ir1—N7	94.51 (13)	C21—C24—H24A	109.5
C10—Ir1—N7	172.77 (15)	H24B—C24—H24A	109.5
N1—Ir1—N7	91.76 (13)	H24C—C24—H24A	109.5
N3—Ir1—N7	92.55 (13)	C27—C30—H30B	109.5
N5—Ir1—N7	85.21 (12)	C27—C30—H30A	109.5
F2—P1—F1	178.3 (4)	H30B—C30—H30A	109.5
F2—P1—F4	89.4 (3)	C27—C30—H30C	109.5
F1—P1—F4	91.8 (3)	H30B—C30—H30C	109.5
F2—P1—F5	91.8 (4)	H30A—C30—H30C	109.5
F1—P1—F5	89.5 (3)	C15—C10—C11	115.8 (4)
F4—P1—F5	89.4 (3)	C15—C10—Ir1	130.3 (4)
F2—P1—F6	91.0 (3)	C11—C10—Ir1	113.9 (3)
F1—P1—F6	87.8 (3)	C10—C15—C14	120.4 (5)
F4—P1—F6	179.1 (3)	C10—C15—H15	119.8
F5—P1—F6	91.4 (3)	C14—C15—H15	119.8
F2—P1—F3	92.6 (3)	C13—C14—C15	121.4 (5)
F1—P1—F3	86.2 (3)	C13—C14—H14	119.3
F4—P1—F3	88.8 (2)	C15—C14—H14	119.3
F5—P1—F3	175.2 (3)	C14—C13—C12	120.1 (4)
F6—P1—F3	90.4 (3)	C14—C13—H13	120.0
C25—N7—C29	116.7 (3)	C12—C13—H13	120.0
C25—N7—Ir1	121.7 (3)	C13—C12—C11	118.4 (5)
C29—N7—Ir1	120.5 (3)	C13—C12—H12	120.8
C25—N6—C19	129.1 (4)	C11—C12—H12	120.8
C25—N6—H1	111 (4)	C12—C11—C10	123.9 (4)
C19—N6—H1	113 (4)	C12—C11—N4	121.1 (4)
C19—N5—C23	116.5 (3)	C10—C11—N4	115.0 (3)
C19—N5—Ir1	123.6 (3)	N3—C16—C17	109.7 (5)
C23—N5—Ir1	119.9 (3)	N3—C16—H16	125.1
C18—N4—N3	109.5 (4)	C17—C16—H16	125.1

C18—N4—C11	134.2 (4)	C18—C17—C16	105.8 (5)
N3—N4—C11	116.2 (3)	C18—C17—H17	127.1
C16—N3—N4	107.0 (4)	C16—C17—H17	127.1
C16—N3—Ir1	137.9 (3)	N4—C18—C17	108.0 (5)
N4—N3—Ir1	114.4 (3)	N4—C18—H18	126.0
C9—N2—N1	109.6 (4)	C17—C18—H18	126.0
C9—N2—C2	133.9 (4)	C2—C1—C6	115.7 (4)
N1—N2—C2	116.6 (3)	C2—C1—Ir1	114.8 (3)
C7—N1—N2	106.6 (4)	C6—C1—Ir1	129.4 (3)
C7—N1—Ir1	139.1 (3)	C3—C2—C1	124.4 (4)
N2—N1—Ir1	114.3 (3)	C3—C2—N2	121.5 (4)
N7—C29—C28	123.5 (4)	C1—C2—N2	114.1 (3)
N7—C29—H29	118.2	N1—C7—C8	110.7 (5)
C28—C29—H29	118.2	N1—C7—H7	124.6
C29—C28—C27	119.7 (4)	C8—C7—H7	124.6
C29—C28—H28	120.2	C9—C8—C7	105.3 (5)
C27—C28—H28	120.2	C9—C8—H8	127.4
C26—C27—C28	117.1 (4)	C7—C8—H8	127.4
C26—C27—C30	121.6 (4)	N2—C9—C8	107.8 (5)
C28—C27—C30	121.3 (4)	N2—C9—H9	126.1
C27—C26—C25	120.4 (4)	C8—C9—H9	126.1
C27—C26—H26	119.8	C4—C3—C2	117.9 (5)
C25—C26—H26	119.8	C4—C3—H3	121.1
N7—C25—N6	120.1 (3)	C2—C3—H3	121.1
N7—C25—C26	122.0 (4)	C3—C4—C5	120.6 (5)
N6—C25—C26	117.9 (4)	C3—C4—H4	119.7
N5—C19—N6	119.5 (4)	C5—C4—H4	119.7
N5—C19—C20	122.9 (4)	C4—C5—C6	120.7 (5)
N6—C19—C20	117.6 (4)	C4—C5—H5	119.7
C22—C23—N5	123.6 (4)	C6—C5—H5	119.7
C22—C23—H23	118.2	C5—C6—C1	120.6 (5)
N5—C23—H23	118.2	C5—C6—H6	119.7
C23—C22—C21	119.7 (4)	C1—C6—H6	119.7
C23—C22—H22	120.2		

C1—Ir1—N7—C25	−147.6 (3)	Ir1—N5—C23—C22	177.1 (3)
C10—Ir1—N7—C25	−49.8 (12)	N5—C23—C22—C21	−0.4 (7)
N1—Ir1—N7—C25	132.1 (3)	C23—C22—C21—C20	2.0 (7)
N3—Ir1—N7—C25	−55.2 (3)	C23—C22—C21—C24	−177.7 (4)
N5—Ir1—N7—C25	37.4 (3)	C22—C21—C20—C19	−1.0 (6)

C1—Ir1—N7—C29	20.3 (3)	C24—C21—C20—C19	178.6 (4)
C10—Ir1—N7—C29	118.2 (11)	N5—C19—C20—C21	−1.6 (6)
N1—Ir1—N7—C29	−60.0 (3)	N6—C19—C20—C21	−179.2 (4)
N3—Ir1—N7—C29	112.7 (3)	C1—Ir1—C10—C15	−89.8 (4)
N5—Ir1—N7—C29	−154.6 (3)	N1—Ir1—C10—C15	−9.9 (4)
C1—Ir1—N5—C19	−116.5 (14)	N3—Ir1—C10—C15	177.4 (4)
C10—Ir1—N5—C19	143.4 (3)	N5—Ir1—C10—C15	85.3 (4)
N1—Ir1—N5—C19	−120.8 (3)	N7—Ir1—C10—C15	171.9 (9)
N3—Ir1—N5—C19	62.9 (3)	C1—Ir1—C10—C11	89.1 (3)
N7—Ir1—N5—C19	−29.4 (3)	N1—Ir1—C10—C11	168.9 (3)
C1—Ir1—N5—C23	64.3 (15)	N3—Ir1—C10—C11	−3.7 (3)
C10—Ir1—N5—C23	−35.8 (3)	N5—Ir1—C10—C11	−95.8 (3)
N1—Ir1—N5—C23	60.0 (3)	N7—Ir1—C10—C11	−9.2 (12)
N3—Ir1—N5—C23	−116.2 (3)	C11—C10—C15—C14	−0.5 (6)
N7—Ir1—N5—C23	151.4 (3)	Ir1—C10—C15—C14	178.4 (3)
C18—N4—N3—C16	0.7 (5)	C10—C15—C14—C13	−0.5 (7)
C11—N4—N3—C16	−175.5 (4)	C15—C14—C13—C12	1.0 (8)
C18—N4—N3—Ir1	173.2 (3)	C14—C13—C12—C11	−0.6 (7)
C11—N4—N3—Ir1	−3.0 (4)	C13—C12—C11—C10	−0.4 (7)
C1—Ir1—N3—C16	86.8 (5)	C13—C12—C11—N4	178.1 (4)
C10—Ir1—N3—C16	172.9 (5)	C15—C10—C11—C12	0.9 (6)
N1—Ir1—N3—C16	112.8 (9)	Ir1—C10—C11—C12	−178.2 (4)
N5—Ir1—N3—C16	−93.2 (5)	C15—C10—C11—N4	−177.7 (4)
N7—Ir1—N3—C16	−7.8 (5)	Ir1—C10—C11—N4	3.3 (5)
C1—Ir1—N3—N4	−82.4 (3)	C18—N4—C11—C12	6.2 (8)
C10—Ir1—N3—N4	3.7 (3)	N3—N4—C11—C12	−178.8 (4)
N1—Ir1—N3—N4	−56.4 (10)	C18—N4—C11—C10	−175.2 (5)
N5—Ir1—N3—N4	97.6 (3)	N3—N4—C11—C10	−0.2 (5)
N7—Ir1—N3—N4	−177.0 (3)	N4—N3—C16—C17	−0.5 (6)
C9—N2—N1—C7	−0.9 (5)	Ir1—N3—C16—C17	−170.2 (4)
C2—N2—N1—C7	178.8 (4)	N3—C16—C17—C18	0.1 (7)
C9—N2—N1—Ir1	177.9 (3)	N3—N4—C18—C17	−0.7 (6)
C2—N2—N1—Ir1	−2.4 (4)	C11—N4—C18—C17	174.5 (5)
C1—Ir1—N1—C7	−179.5 (5)	C16—C17—C18—N4	0.4 (7)
C10—Ir1—N1—C7	95.0 (5)	C10—Ir1—C1—C2	94.2 (3)
N3—Ir1—N1—C7	154.1 (8)	N1—Ir1—C1—C2	−1.9 (3)
N5—Ir1—N1—C7	0.1 (5)	N3—Ir1—C1—C2	174.3 (3)
N7—Ir1—N1—C7	−85.2 (5)	N5—Ir1—C1—C2	−6.3 (16)
C1—Ir1—N1—N2	2.3 (3)	N7—Ir1—C1—C2	−92.9 (3)
C10—Ir1—N1—N2	−83.2 (3)	C10—Ir1—C1—C6	−84.8 (4)

N3—Ir1—N1—N2	−24.1 (10)	N1—Ir1—C1—C6	179.0 (4)
N5—Ir1—N1—N2	−178.0 (3)	N3—Ir1—C1—C6	−4.7 (4)
N7—Ir1—N1—N2	96.6 (3)	N5—Ir1—C1—C6	174.7 (13)
C25—N7—C29—C28	4.1 (6)	N7—Ir1—C1—C6	88.0 (4)
Ir1—N7—C29—C28	−164.5 (3)	C6—C1—C2—C3	−0.3 (6)
N7—C29—C28—C27	2.8 (7)	Ir1—C1—C2—C3	−179.5 (3)
C29—C28—C27—C26	−5.8 (6)	C6—C1—C2—N2	−179.6 (3)
C29—C28—C27—C30	174.0 (4)	Ir1—C1—C2—N2	1.2 (4)
C28—C27—C26—C25	2.1 (6)	C9—N2—C2—C3	1.1 (7)
C30—C27—C26—C25	−177.7 (4)	N1—N2—C2—C3	−178.5 (4)
C29—N7—C25—N6	174.1 (4)	C9—N2—C2—C1	−179.6 (5)
Ir1—N7—C25—N6	−17.6 (5)	N1—N2—C2—C1	0.8 (5)
C29—N7—C25—C26	−7.9 (6)	N2—N1—C7—C8	1.0 (5)
Ir1—N7—C25—C26	160.5 (3)	Ir1—N1—C7—C8	−177.3 (4)
C19—N6—C25—N7	−31.0 (6)	N1—C7—C8—C9	−0.7 (6)
C19—N6—C25—C26	150.9 (4)	N1—N2—C9—C8	0.4 (6)
C27—C26—C25—N7	4.9 (6)	C2—N2—C9—C8	−179.2 (5)
C27—C26—C25—N6	−177.0 (4)	C7—C8—C9—N2	0.2 (6)
C23—N5—C19—N6	−179.3 (4)	C1—C2—C3—C4	0.6 (6)
Ir1—N5—C19—N6	1.5 (5)	N2—C2—C3—C4	179.8 (4)
C23—N5—C19—C20	3.1 (6)	C2—C3—C4—C5	0.0 (7)
Ir1—N5—C19—C20	−176.1 (3)	C3—C4—C5—C6	−0.7 (7)
C25—N6—C19—N5	40.3 (6)	C4—C5—C6—C1	0.9 (7)
C25—N6—C19—C20	−142.0 (4)	C2—C1—C6—C5	−0.4 (6)
C19—N5—C23—C22	−2.1 (6)	Ir1—C1—C6—C5	178.6 (3)

	Complex **1c**
Formula	$C_{34}H_{29}F_6IrN_5P$
M/g.mol^{-1}	844.79
Crystal system	Monoclinic
Flack parameter	
Space group	*P*2(1)/c
a/ Å	13.828(3)
b/ Å	16.821(4)
c/ Å	15.516(2)
α/ °	90.00
β/ °	90.367(13)
γ/ °	90.00

V/ Å^3	3609.2(13)
Z	4
ρcalcd/ g.cm^{-3}	1.555
μ(Mo K$_\alpha$)/ mm^{-1}	3.804
T/ K	150(2)
No of reflections	58333
No of unique reflections	10078
R_{int}	0.0420
*R*1, wR_2 (I > 2σ(I))	0.0265, 0.0649
*R*1, wR_2 (all data)	0.0484, 0.0701
GOF	1.007

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir1	0.663585 (7)	0.252039 (6)	0.516815 (6)	0.01848 (4)
P3	0.10389 (7)	0.08037 (5)	0.12781 (5)	0.0357 (2)
N3	0.79463 (18)	0.26122 (13)	0.44263 (15)	0.0235 (5)
N5	0.72735 (16)	0.34022 (13)	0.60131 (14)	0.0193 (5)
C29	0.7904 (2)	0.39505 (17)	0.57550 (18)	0.0234 (6)
N1	0.72249 (17)	0.15425 (14)	0.57409 (14)	0.0224 (5)
N2	0.59026 (18)	0.34343 (14)	0.45888 (14)	0.0241 (5)
N4	0.83570 (18)	0.38896 (15)	0.49637 (15)	0.0312 (6)
H4	0.8561	0.4345	0.4753	0.037*
C23	0.8545 (2)	0.32399 (17)	0.44485 (17)	0.0245 (6)
C24	0.9350 (2)	0.32969 (19)	0.3919 (2)	0.0361 (8)
H24	0.9751	0.3755	0.3948	0.043*
C7	0.6927 (2)	0.08237 (17)	0.54232 (17)	0.0241 (6)
C11	0.7856 (2)	0.15604 (18)	0.64104 (18)	0.0292 (7)
H11	0.8068	0.2060	0.6624	0.035*
C1	0.6243 (2)	0.08893 (17)	0.47064 (17)	0.0226 (6)
C12	0.5405 (2)	0.24871 (16)	0.58476 (18)	0.0221 (5)
C18	0.4995 (2)	0.35753 (18)	0.48983 (18)	0.0287 (7)
C6	0.5825 (2)	0.02277 (18)	0.43029 (17)	0.0270 (7)
H6	0.5994	−0.0293	0.4486	0.032*
C17	0.5167 (2)	0.19676 (18)	0.65135 (18)	0.0282 (7)
H17	0.5614	0.1566	0.6680	0.034*
C13	0.4720 (2)	0.30675 (18)	0.56160 (18)	0.0282 (7)
C3	0.5355 (2)	0.17551 (18)	0.37650 (17)	0.0265 (6)
H3	0.5191	0.2273	0.3568	0.032*
C22	0.6228 (2)	0.38779 (19)	0.39233 (18)	0.0323 (7)
H22	0.6856	0.3773	0.3705	0.039*
C8	0.7269 (2)	0.01289 (18)	0.57880 (18)	0.0326 (7)

H8	0.7064	−0.0369	0.5562	0.039*
C16	0.4290 (3)	0.2025 (2)	0.6938 (2)	0.0389 (8)
H16	0.4142	0.1663	0.7389	0.047*
C21	0.5695 (3)	0.4466 (2)	0.3555 (2)	0.0424 (9)
H21	0.5952	0.4774	0.3097	0.051*
C9	0.7901 (3)	0.0150 (2)	0.6473 (2)	0.0440 (9)
H9	0.8133	−0.0328	0.6726	0.053*
C2	0.6014 (2)	0.16674 (16)	0.44416 (17)	0.0213 (6)
C10	0.8195 (3)	0.0883 (2)	0.6788 (2)	0.0393 (8)
H10	0.8630	0.0913	0.7263	0.047*
C4	0.4935 (2)	0.1096 (2)	0.33737 (19)	0.0321 (7)
H4A	0.4482	0.1170	0.2918	0.039*
C19	0.4425 (3)	0.4164 (2)	0.4518 (2)	0.0393 (8)
H19	0.3789	0.4257	0.4722	0.047*
C5	0.5169 (2)	0.0333 (2)	0.36402 (19)	0.0324 (8)
H5	0.4879	−0.0114	0.3368	0.039*
C15	0.3631 (3)	0.2605 (2)	0.6710 (2)	0.0429 (9)
H15	0.3033	0.2642	0.7004	0.052*
C20	0.4779 (3)	0.4610 (2)	0.3853 (2)	0.0458 (9)
H20	0.4394	0.5016	0.3600	0.055*
C14	0.3837 (2)	0.3132 (2)	0.6054 (2)	0.0396 (8)
H14	0.3386	0.3534	0.5900	0.048*
C32	0.7113 (2)	0.41281 (17)	0.73406 (18)	0.0265 (6)
H32	0.6829	0.4162	0.7895	0.032*
C26	0.8966 (3)	0.2025 (2)	0.3356 (2)	0.0364 (8)
H26	0.9090	0.1588	0.2985	0.044*
C33	0.6913 (2)	0.35000 (17)	0.68152 (17)	0.0244 (6)
H33	0.6490	0.3102	0.7027	0.029*
C27	0.8200 (2)	0.20074 (19)	0.38967 (19)	0.0327 (7)
H27	0.7815	0.1540	0.3905	0.039*
C25	0.9573 (3)	0.2687 (2)	0.3346 (2)	0.0376 (8)
C31	0.7736 (2)	0.47183 (18)	0.7058 (2)	0.0335 (8)
C30	0.8131 (2)	0.46201 (19)	0.6249 (2)	0.0341 (8)
H30	0.8560	0.5010	0.6028	0.041*
F2	0.03970 (15)	0.01848 (12)	0.07511 (14)	0.0565 (6)
F1	0.02853 (19)	0.14757 (12)	0.10424 (14)	0.0688 (7)
F4	0.16998 (17)	0.14168 (15)	0.17722 (17)	0.0840 (9)
F3	0.17831 (16)	0.01077 (13)	0.14954 (13)	0.0583 (6)
F6	0.16313 (19)	0.09582 (15)	0.04134 (14)	0.0731 (8)
F5	0.04644 (16)	0.06208 (15)	0.21217 (12)	0.0664 (7)

C34	0.7986 (3)	0.5416 (2)	0.7620 (3)	0.0681 (14)
H34A	0.8668	0.5382	0.7794	0.102*
H34B	0.7578	0.5410	0.8134	0.102*
H34C	0.7877	0.5910	0.7299	0.102*
C28	1.0413 (3)	0.2745 (3)	0.2760 (3)	0.0668 (14)
H28A	1.0194	0.2679	0.2162	0.100*
H28B	1.0882	0.2327	0.2903	0.100*
H28C	1.0720	0.3267	0.2827	0.100*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.01906 (6)	0.01975 (6)	0.01663 (6)	−0.00010 (5)	−0.00143 (4)	0.00088 (5)
P3	0.0400 (5)	0.0315 (5)	0.0357 (5)	−0.0016 (4)	−0.0005 (4)	−0.0039 (4)
N3	0.0238 (12)	0.0266 (14)	0.0202 (12)	−0.0004 (10)	0.0022 (10)	−0.0022 (9)
N5	0.0165 (12)	0.0191 (12)	0.0222 (12)	0.0021 (9)	−0.0017 (10)	0.0005 (9)
C29	0.0215 (15)	0.0209 (14)	0.0278 (15)	0.0014 (12)	0.0022 (12)	0.0005 (11)
N1	0.0242 (13)	0.0208 (12)	0.0221 (12)	0.0014 (10)	−0.0024 (10)	0.0055 (10)
N2	0.0264 (13)	0.0230 (13)	0.0226 (12)	0.0008 (10)	−0.0095 (11)	−0.0002 (10)
N4	0.0405 (16)	0.0236 (13)	0.0297 (14)	−0.0079 (12)	0.0153 (13)	−0.0019 (10)
C23	0.0280 (16)	0.0249 (15)	0.0206 (14)	−0.0004 (12)	0.0016 (13)	0.0012 (11)
C24	0.0355 (19)	0.0298 (18)	0.043 (2)	−0.0066 (15)	0.0116 (16)	−0.0003 (14)
C7	0.0270 (15)	0.0235 (15)	0.0218 (14)	−0.0011 (12)	0.0031 (12)	0.0017 (11)
C11	0.0337 (18)	0.0286 (16)	0.0252 (15)	0.0034 (14)	−0.0077 (14)	−0.0029 (12)
C1	0.0259 (15)	0.0241 (15)	0.0180 (13)	−0.0039 (12)	0.0036 (12)	0.0004 (11)
C12	0.0199 (12)	0.0261 (14)	0.0202 (13)	−0.0048 (13)	−0.0021 (10)	−0.0079 (12)
C18	0.0326 (17)	0.0251 (16)	0.0284 (16)	0.0024 (13)	−0.0101 (13)	−0.0066 (12)
C6	0.0354 (18)	0.0243 (15)	0.0214 (14)	−0.0090 (13)	0.0062 (13)	0.0020 (12)
C17	0.0259 (16)	0.0317 (17)	0.0271 (16)	−0.0061 (13)	0.0037 (13)	−0.0019 (13)
C13	0.0247 (16)	0.0306 (16)	0.0294 (16)	0.0016 (13)	−0.0066 (13)	−0.0061 (13)
C3	0.0253 (16)	0.0307 (16)	0.0236 (15)	−0.0015 (13)	−0.0010 (12)	−0.0004 (12)
C22	0.0409 (19)	0.0339 (18)	0.0219 (15)	−0.0046 (15)	−0.0044 (14)	0.0073 (13)
C8	0.044 (2)	0.0235 (16)	0.0302 (16)	−0.0009 (14)	−0.0057 (15)	−0.0001 (13)
C16	0.033 (2)	0.052 (2)	0.0314 (18)	−0.0104 (17)	0.0080 (15)	−0.0010 (16)
C21	0.053 (2)	0.042 (2)	0.0320 (18)	−0.0028 (18)	−0.0133 (17)	0.0097 (15)
C9	0.060 (3)	0.0277 (18)	0.044 (2)	0.0090 (17)	−0.0085 (19)	0.0034 (15)
C2	0.0229 (15)	0.0232 (15)	0.0179 (13)	−0.0023 (12)	0.0015 (12)	−0.0047 (11)
C10	0.049 (2)	0.0364 (19)	0.0320 (17)	0.0059 (17)	−0.0167 (16)	0.0035 (14)
C4	0.0271 (17)	0.046 (2)	0.0237 (15)	−0.0084 (15)	−0.0018 (13)	−0.0051 (14)
C19	0.040 (2)	0.0370 (19)	0.0404 (18)	0.0131 (16)	−0.0162 (15)	−0.0077 (15)
C5	0.0365 (19)	0.0367 (19)	0.0241 (16)	−0.0143 (15)	0.0023 (14)	−0.0062 (13)

C15	0.0225 (16)	0.066 (3)	0.040 (2)	−0.0023 (17)	0.0084 (15)	−0.0065 (18)
C20	0.063 (3)	0.0302 (19)	0.044 (2)	0.0174 (18)	−0.0231 (19)	0.0006 (15)
C14	0.0276 (18)	0.049 (2)	0.0418 (19)	0.0108 (16)	−0.0030 (15)	−0.0085 (16)
C32	0.0288 (16)	0.0279 (16)	0.0227 (14)	0.0025 (13)	0.0028 (12)	−0.0030 (12)
C26	0.040 (2)	0.0339 (19)	0.0360 (18)	−0.0024 (16)	0.0095 (16)	−0.0114 (15)
C33	0.0240 (15)	0.0261 (15)	0.0233 (15)	−0.0016 (12)	−0.0022 (12)	0.0030 (12)
C27	0.0352 (18)	0.0314 (18)	0.0315 (17)	−0.0056 (14)	0.0046 (15)	−0.0077 (14)
C25	0.0356 (19)	0.040 (2)	0.0374 (19)	−0.0019 (15)	0.0119 (16)	−0.0063 (14)
C31	0.0365 (19)	0.0259 (16)	0.0382 (19)	−0.0045 (14)	0.0062 (15)	−0.0095 (14)
C30	0.0338 (18)	0.0298 (18)	0.0390 (19)	−0.0104 (14)	0.0112 (16)	−0.0065 (14)
F2	0.0493 (13)	0.0451 (13)	0.0749 (15)	0.0014 (11)	−0.0135 (11)	−0.0212 (11)
F1	0.0906 (19)	0.0403 (13)	0.0752 (15)	0.0257 (13)	−0.0176 (14)	−0.0056 (11)
F4	0.0528 (16)	0.0853 (19)	0.114 (2)	−0.0179 (14)	0.0046 (15)	−0.0606 (17)
F3	0.0498 (14)	0.0703 (16)	0.0548 (13)	0.0230 (12)	−0.0056 (11)	−0.0018 (11)
F6	0.094 (2)	0.0709 (18)	0.0545 (13)	−0.0084 (15)	0.0277 (14)	0.0072 (13)
F5	0.0520 (14)	0.103 (2)	0.0446 (12)	0.0145 (14)	0.0123 (11)	0.0090 (12)
C34	0.082 (3)	0.055 (3)	0.068 (3)	−0.038 (2)	0.038 (3)	−0.036 (2)
C28	0.062 (3)	0.057 (3)	0.083 (3)	−0.020 (2)	0.046 (3)	−0.024 (2)

Geometric parameters (Å, °)

Ir1—C12	2.008 (3)	C3—C4	1.389 (4)
Ir1—C2	2.014 (3)	C3—C2	1.394 (4)
Ir1—N1	2.037 (2)	C3—H3	0.9500
Ir1—N2	2.046 (2)	C22—C21	1.358 (4)
Ir1—N3	2.159 (2)	C22—H22	0.9500
Ir1—N5	2.164 (2)	C8—C9	1.372 (5)
P3—F5	1.566 (2)	C8—H8	0.9500
P3—F4	1.574 (2)	C16—C15	1.380 (5)
P3—F1	1.579 (2)	C16—H16	0.9500
P3—F2	1.591 (2)	C21—C20	1.373 (5)
P3—F3	1.593 (2)	C21—H21	0.9500
P3—F6	1.598 (2)	C9—C10	1.387 (5)
N3—C23	1.342 (3)	C9—H9	0.9500
N3—C27	1.355 (4)	C10—H10	0.9500
N5—C29	1.332 (3)	C4—C5	1.387 (4)
N5—C33	1.354 (3)	C4—H4A	0.9500
C29—N4	1.386 (3)	C19—C20	1.368 (5)
C29—C30	1.397 (4)	C19—H19	0.9500
N1—C11	1.352 (4)	C5—H5	0.9500
N1—C7	1.368 (4)	C15—C14	1.380 (5)

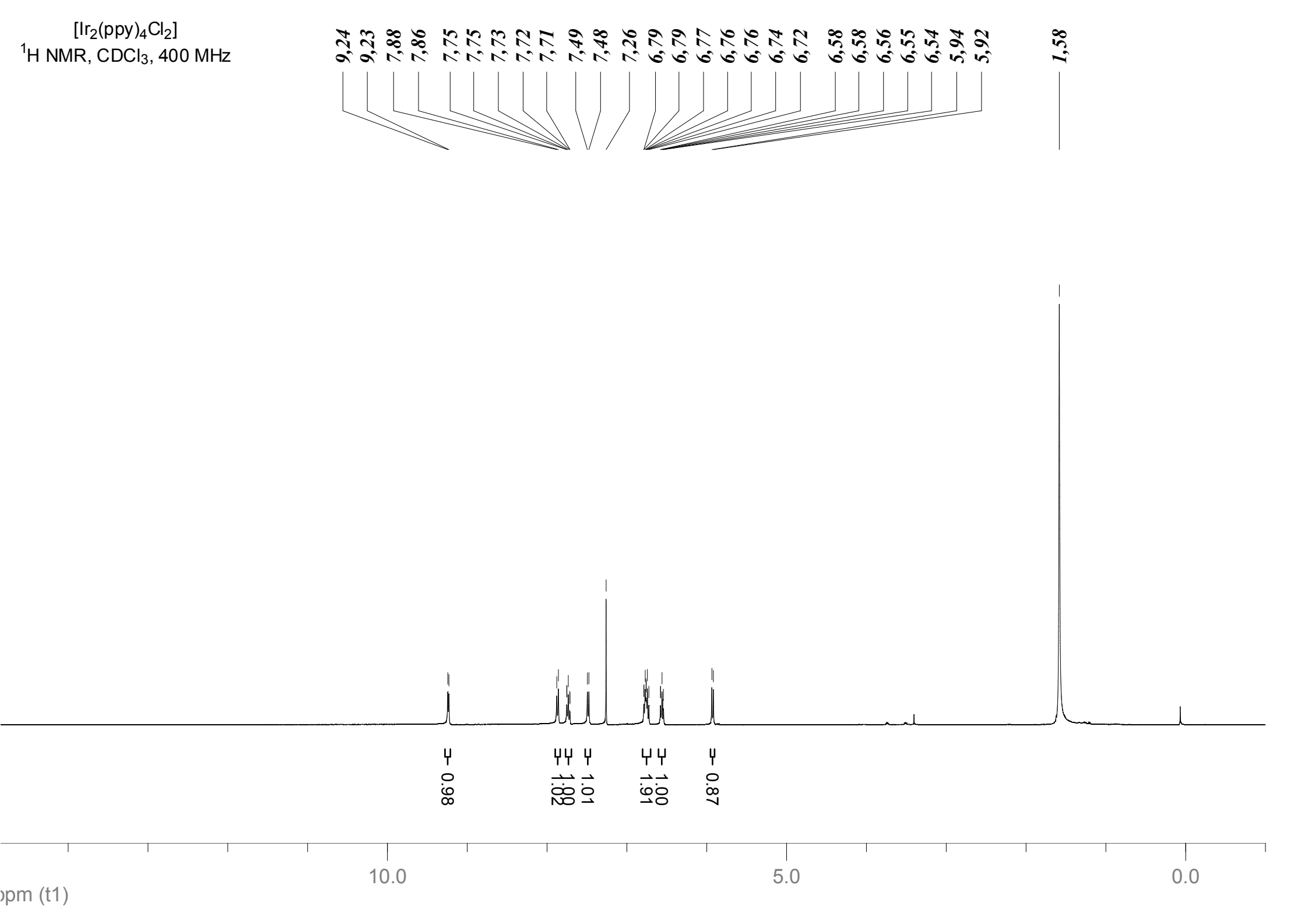
N2—C22	1.354 (4)	C15—H15	0.9500
N2—C18	1.368 (4)	C20—H20	0.9500
N4—C23	1.380 (3)	C14—H14	0.9500
N4—H4	0.8800	C32—C33	1.362 (4)
C23—C24	1.391 (4)	C32—C31	1.387 (4)
C24—C25	1.393 (4)	C32—H32	0.9500
C24—H24	0.9500	C26—C27	1.357 (4)
C7—C8	1.381 (4)	C26—C25	1.393 (5)
C7—C1	1.459 (4)	C26—H26	0.9500
C11—C10	1.362 (4)	C33—H33	0.9500
C11—H11	0.9500	C27—H27	0.9500
C1—C6	1.400 (4)	C25—C28	1.484 (5)
C1—C2	1.407 (4)	C31—C30	1.381 (4)
C12—C17	1.395 (4)	C31—C34	1.501 (4)
C12—C13	1.406 (4)	C30—H30	0.9500
C18—C19	1.394 (4)	C34—H34A	0.9800
C18—C13	1.456 (4)	C34—H34B	0.9800
C6—C5	1.378 (4)	C34—H34C	0.9800
C6—H6	0.9500	C28—H28A	0.9800
C17—C16	1.387 (4)	C28—H28B	0.9800
C17—H17	0.9500	C28—H28C	0.9800
C13—C14	1.405 (4)		

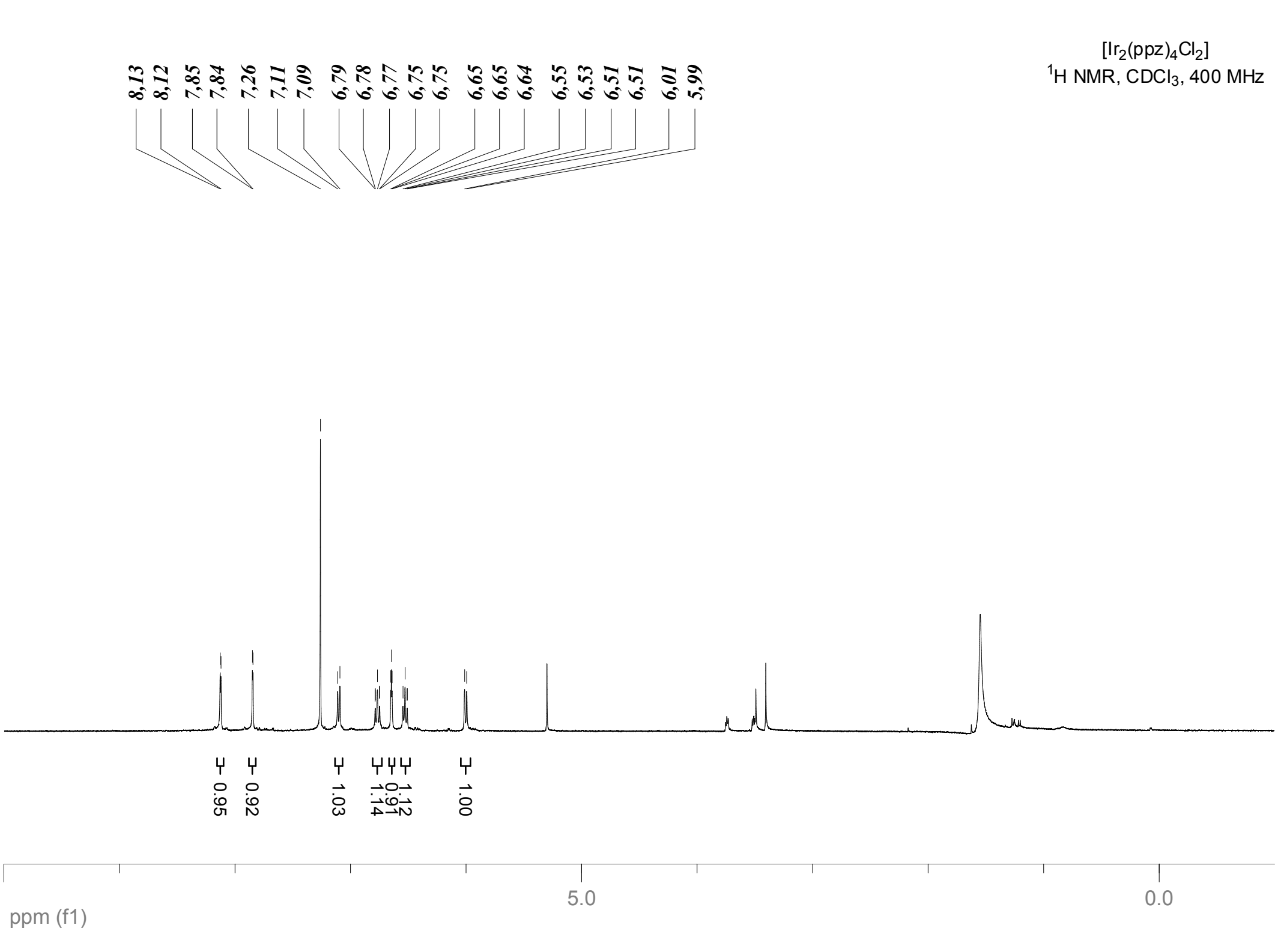
C12—Ir1—C2	85.07 (11)	C12—C13—C18	115.1 (3)
C12—Ir1—N1	94.95 (10)	C4—C3—C2	121.0 (3)
C2—Ir1—N1	80.62 (11)	C4—C3—H3	119.5
C12—Ir1—N2	80.35 (11)	C2—C3—H3	119.5
C2—Ir1—N2	94.64 (11)	N2—C22—C21	122.7 (3)
N1—Ir1—N2	173.64 (9)	N2—C22—H22	118.7
C12—Ir1—N3	177.41 (10)	C21—C22—H22	118.7
C2—Ir1—N3	96.27 (10)	C9—C8—C7	120.7 (3)
N1—Ir1—N3	87.46 (9)	C9—C8—H8	119.6
N2—Ir1—N3	97.31 (9)	C7—C8—H8	119.6
C12—Ir1—N5	92.54 (9)	C15—C16—C17	120.3 (3)
C2—Ir1—N5	176.74 (9)	C15—C16—H16	119.8
N1—Ir1—N5	97.41 (10)	C17—C16—H16	119.8
N2—Ir1—N5	87.13 (9)	C22—C21—C20	119.1 (3)
N3—Ir1—N5	86.21 (9)	C22—C21—H21	120.4
F5—P3—F4	91.01 (14)	C20—C21—H21	120.4
F5—P3—F1	89.81 (13)	C8—C9—C10	118.6 (3)

F4—P3—F1	91.37 (14)	C8—C9—H9	120.7
F5—P3—F2	90.96 (13)	C10—C9—H9	120.7
F4—P3—F2	177.98 (13)	C3—C2—C1	117.6 (3)
F1—P3—F2	89.10 (13)	C3—C2—Ir1	128.4 (2)
F5—P3—F3	90.53 (12)	C1—C2—Ir1	113.9 (2)
F4—P3—F3	90.35 (14)	C11—C10—C9	119.5 (3)
F1—P3—F3	178.23 (14)	C11—C10—H10	120.2
F2—P3—F3	89.17 (12)	C9—C10—H10	120.2
F5—P3—F6	178.03 (14)	C5—C4—C3	120.8 (3)
F4—P3—F6	90.19 (14)	C5—C4—H4A	119.6
F1—P3—F6	91.73 (14)	C3—C4—H4A	119.6
F2—P3—F6	87.83 (13)	C20—C19—C18	120.3 (3)
F3—P3—F6	87.89 (12)	C20—C19—H19	119.8
C23—N3—C27	116.4 (3)	C18—C19—H19	119.8
C23—N3—Ir1	124.22 (18)	C6—C5—C4	119.5 (3)
C27—N3—Ir1	119.4 (2)	C6—C5—H5	120.3
C29—N5—C33	116.0 (2)	C4—C5—H5	120.3
C29—N5—Ir1	123.86 (18)	C14—C15—C16	120.3 (3)
C33—N5—Ir1	119.30 (18)	C14—C15—H15	119.9
N5—C29—N4	121.0 (3)	C16—C15—H15	119.9
N5—C29—C30	122.6 (3)	C19—C20—C21	119.5 (3)
N4—C29—C30	116.4 (3)	C19—C20—H20	120.3
C11—N1—C7	119.2 (2)	C21—C20—H20	120.3
C11—N1—Ir1	124.8 (2)	C15—C14—C13	119.5 (3)
C7—N1—Ir1	115.94 (19)	C15—C14—H14	120.3
C22—N2—C18	118.9 (3)	C13—C14—H14	120.3
C22—N2—Ir1	125.6 (2)	C33—C32—C31	119.4 (3)
C18—N2—Ir1	115.43 (19)	C33—C32—H32	120.3
C23—N4—C29	131.3 (2)	C31—C32—H32	120.3
C23—N4—H4	114.4	C27—C26—C25	119.8 (3)
C29—N4—H4	114.4	C27—C26—H26	120.1
N3—C23—N4	121.3 (2)	C25—C26—H26	120.1
N3—C23—C24	122.3 (3)	N5—C33—C32	124.7 (3)
N4—C23—C24	116.2 (3)	N5—C33—H33	117.6
C23—C24—C25	120.5 (3)	C32—C33—H33	117.6
C23—C24—H24	119.8	N3—C27—C26	124.4 (3)
C25—C24—H24	119.8	N3—C27—H27	117.8
N1—C7—C8	119.9 (3)	C26—C27—H27	117.8
N1—C7—C1	113.6 (2)	C26—C25—C24	116.5 (3)
C8—C7—C1	126.5 (3)	C26—C25—C28	122.2 (3)

N1—C11—C10	122.0 (3)	C24—C25—C28	121.3 (3)
N1—C11—H11	119.0	C30—C31—C32	116.8 (3)
C10—C11—H11	119.0	C30—C31—C34	122.0 (3)
C6—C1—C2	121.2 (3)	C32—C31—C34	121.1 (3)
C6—C1—C7	123.0 (3)	C31—C30—C29	120.4 (3)
C2—C1—C7	115.9 (2)	C31—C30—H30	119.8
C17—C12—C13	117.5 (3)	C29—C30—H30	119.8
C17—C12—Ir1	127.7 (2)	C31—C34—H34A	109.5
C13—C12—Ir1	114.7 (2)	C31—C34—H34B	109.5
N2—C18—C19	119.5 (3)	H34A—C34—H34B	109.5
N2—C18—C13	114.3 (3)	C31—C34—H34C	109.5
C19—C18—C13	126.2 (3)	H34A—C34—H34C	109.5
C5—C6—C1	120.0 (3)	H34B—C34—H34C	109.5
C5—C6—H6	120.0	C25—C28—H28A	109.5
C1—C6—H6	120.0	C25—C28—H28B	109.5
C16—C17—C12	121.4 (3)	H28A—C28—H28B	109.5
C16—C17—H17	119.3	C25—C28—H28C	109.5
C12—C17—H17	119.3	H28A—C28—H28C	109.5
C14—C13—C12	121.1 (3)	H28B—C28—H28C	109.5
C14—C13—C18	123.8 (3)		

$[Ir_2(ppy)_4Cl_2]$
^1H NMR, $CDCl_3$, 400 MHz



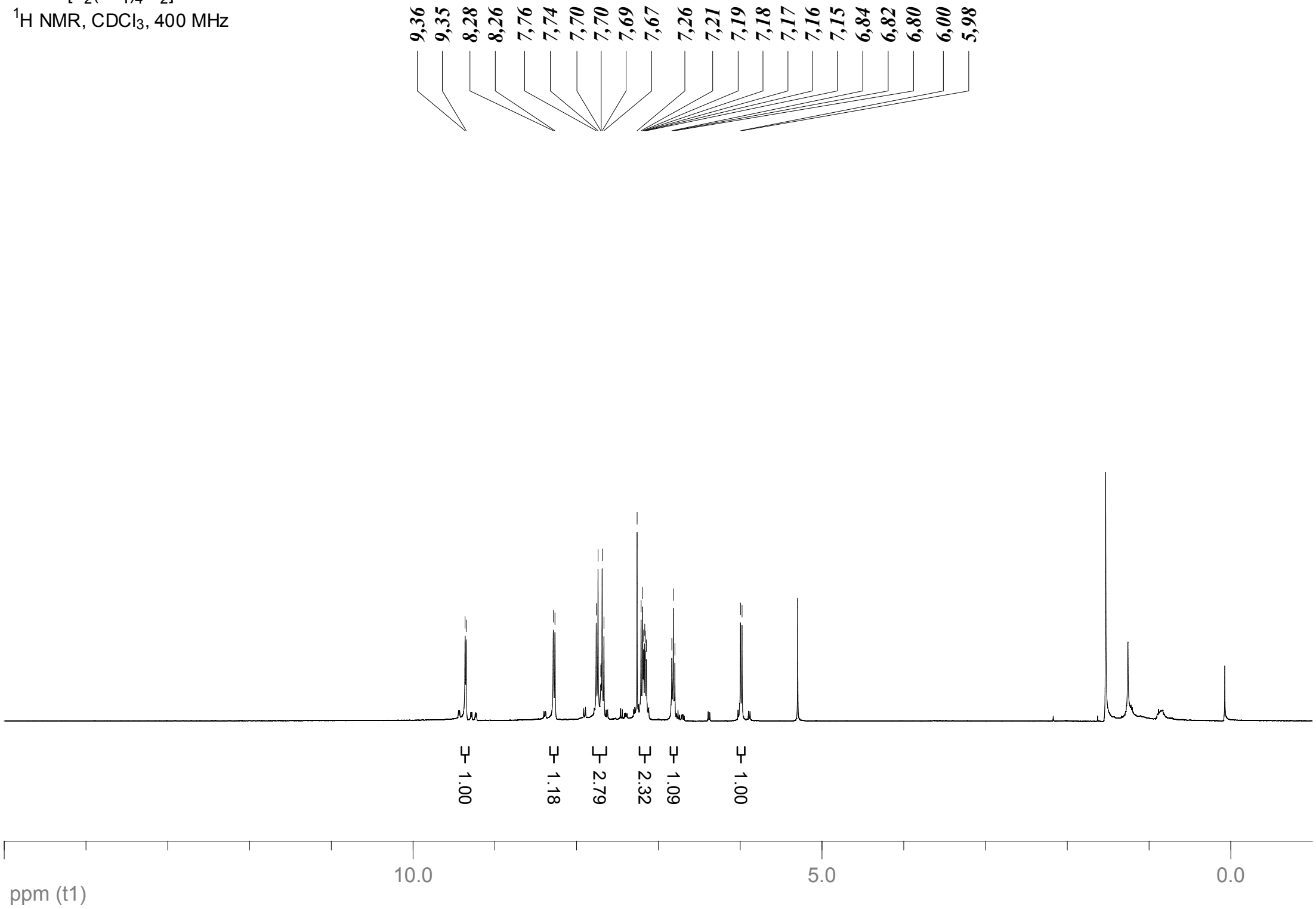


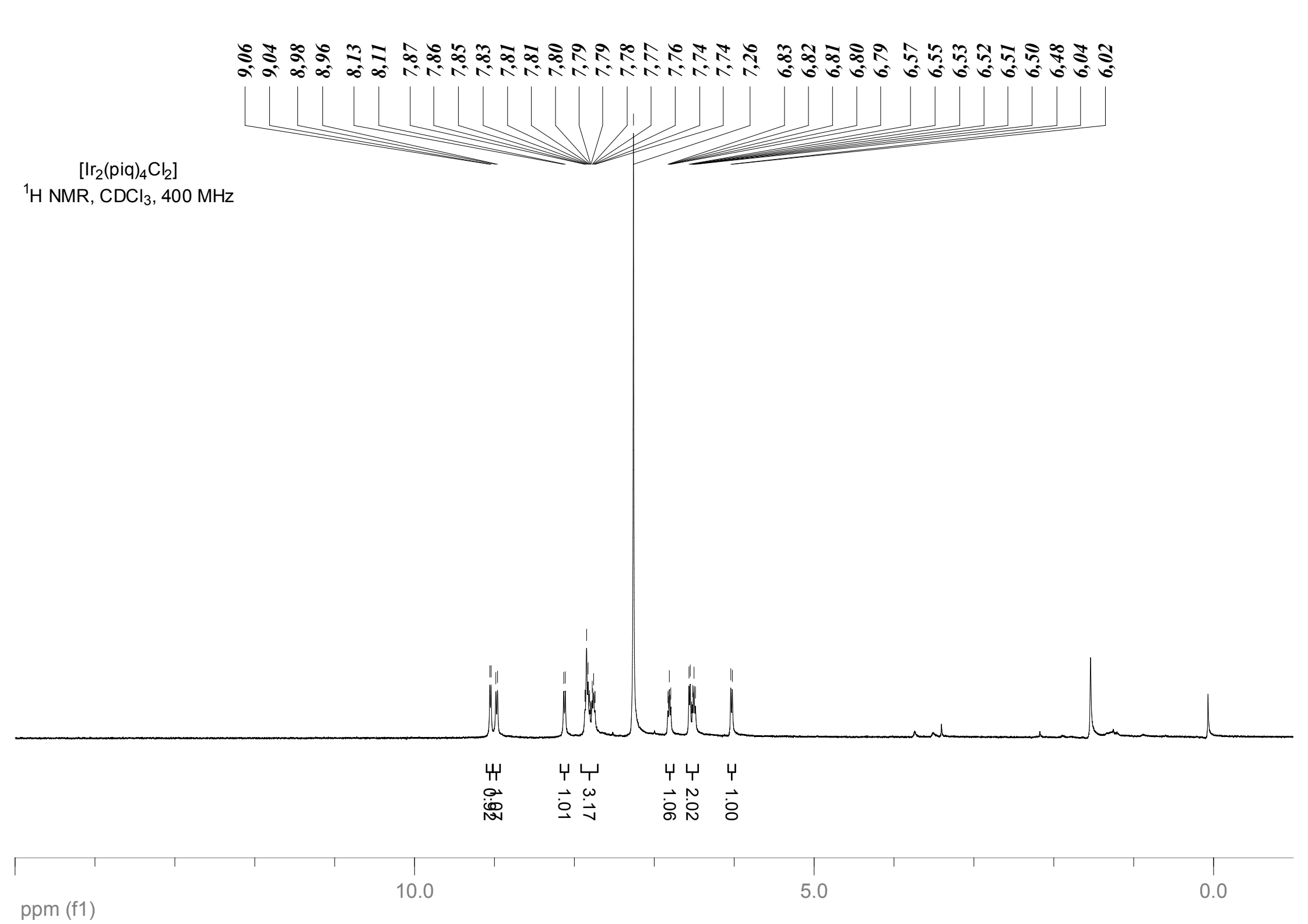
$[Ir_2(ppz)_4Cl_2]$

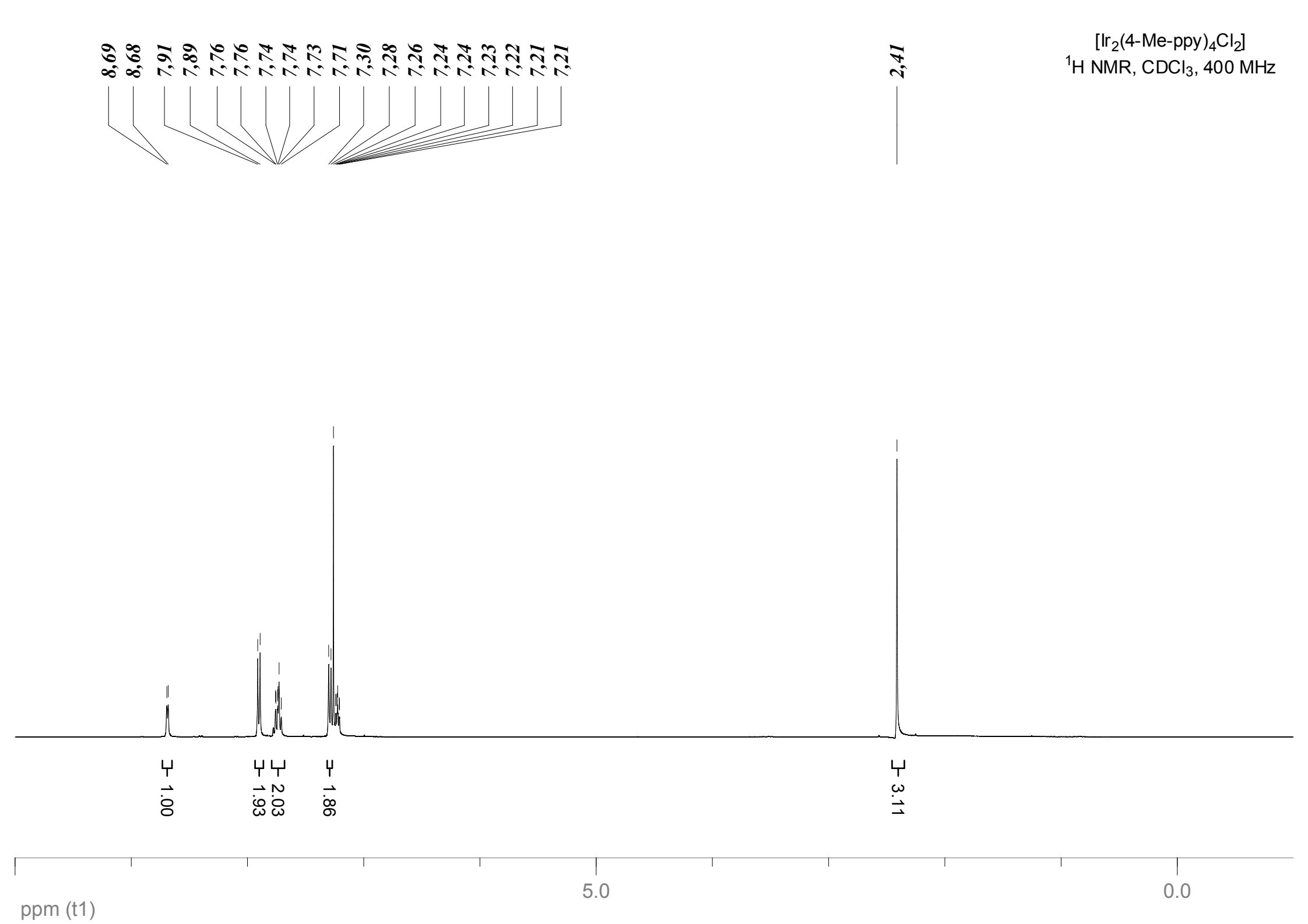
^1H NMR, $CDCl_3$, 400 MHz

$[Ir_2(bzq)_4Cl_2]$

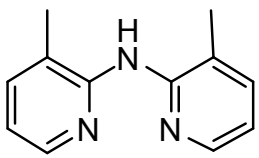
^1H NMR, $CDCl_3$, 400 MHz




9,06
9,04
8,98
8,96
8,13
8,11
7,87
7,86
7,85
7,83
7,81
7,81
7,80
7,79
7,79
7,78
7,77
7,76
7,74
7,74
7,26
6,83
6,82
6,81
6,80
6,79
6,57
6,55
6,53
6,52
6,51
6,50
6,48
6,04
6,02
[Ir2(piq)4Cl2]
1H NMR, CDCl3, 400 MHz
0.92
0.97
1.01
3.17
1.06
2.02
1.00
10.0
5.0
0.0
ppm (f1)


8,69
8,68
7,91
7,89
7,76
7,76
7,74
7,74
7,73
7,71
7,30
7,28
7,26
7,24
7,24
7,23
7,22
7,21
7,21
2,41
[Ir2(4-Me-ppy)4Cl2]
1H NMR, CDCl3, 400 MHz
1.00
1.93
2.03
1.86
3.11
5.0
0.0
ppm (t1)

^{1}H NMR, $CDCl_3$, 400 MHz

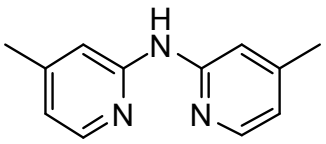


8,14
8,13
7,47
7,45
7,26
6,90
6,88
6,87
6,43
2,24

2.00
2.02
1.93
0.96
5.95

5.0
0.0
ppm (t1)

^{1}H NMR, $CDCl_3$, 400 MHz

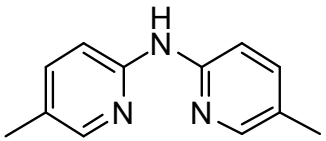


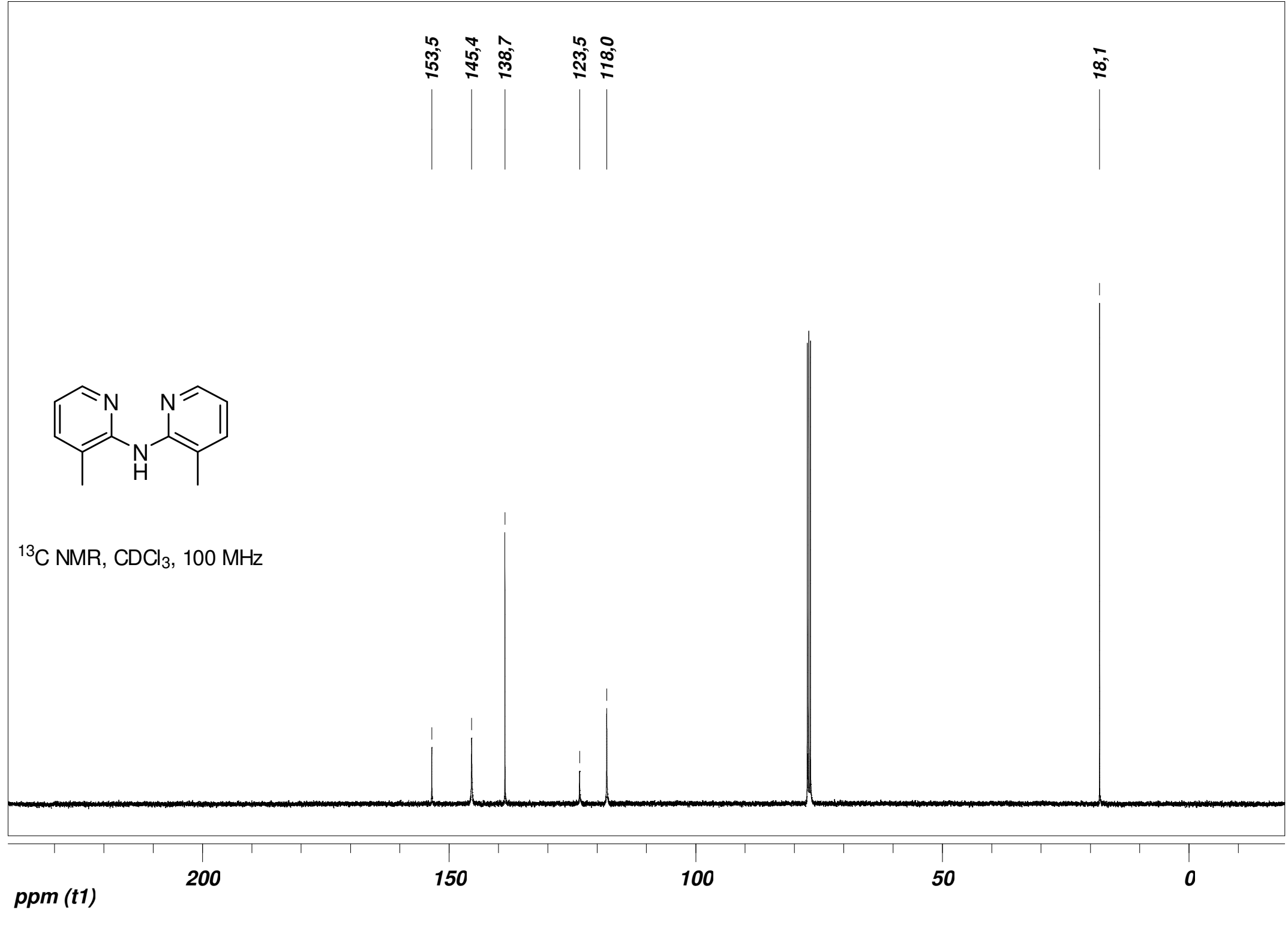
8,12
8,11
7,35
7,26
6,69
6,67
2,33

2.00
2.22
1.99
6.02

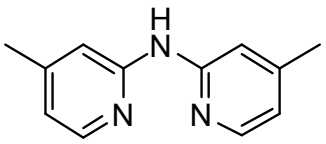
10.0
5.0
0.0
ppm (t1)

^{1}H NMR, $CDCl_3$, 400 MHz




153,5
145,4
138,7
123,5
118,0
18,1
N
N
H
^{13}C NMR, $CDCl_3$, 100 MHz
200
150
100
50
0
ppm (t1)

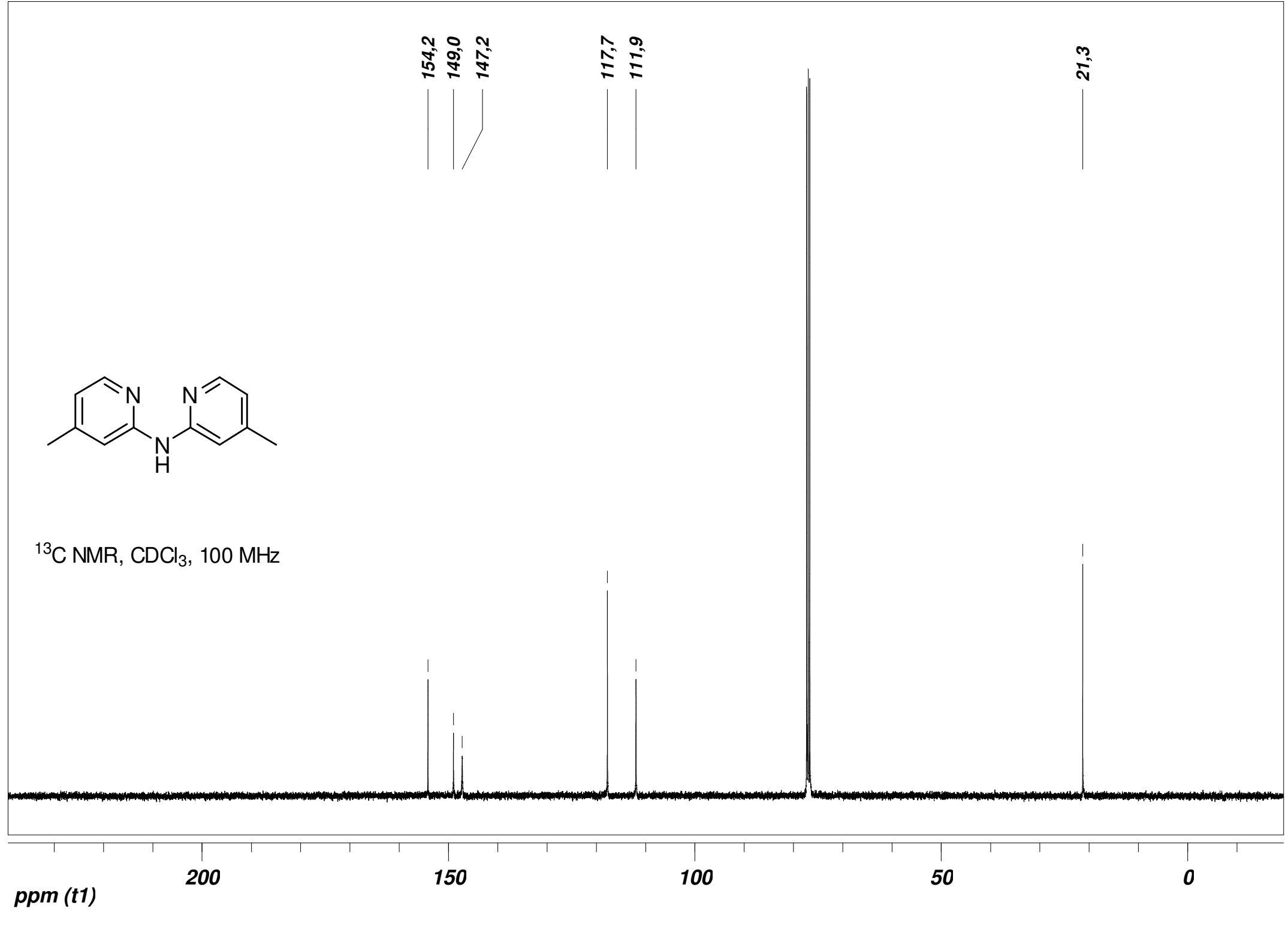
^{1}H NMR, $CDCl_3$, 400 MHz



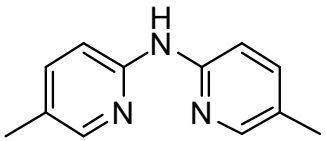
8,12
8,11
7,35
7,26
6,69
6,67
2,33

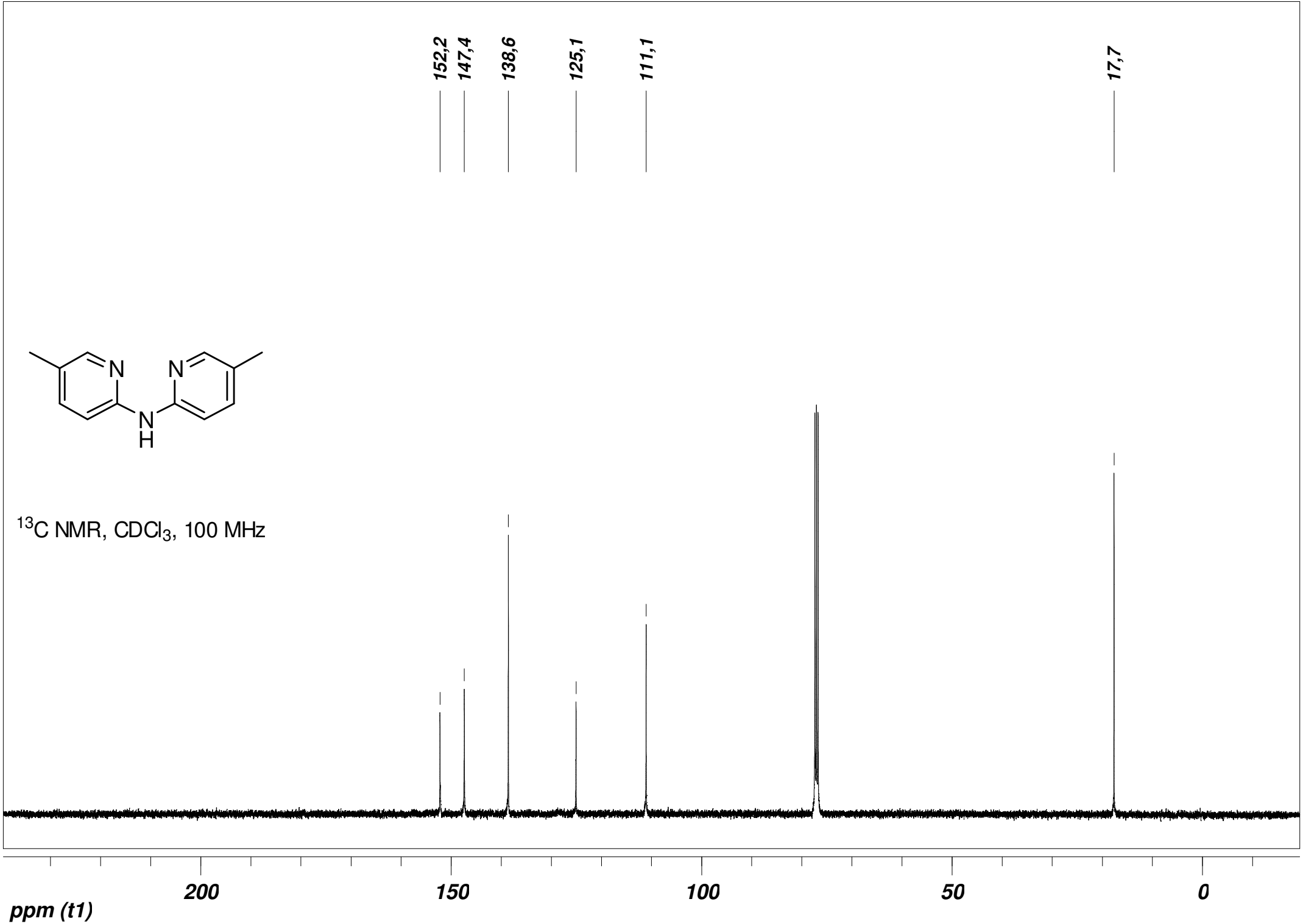
2.00
2.22
1.99
6.02

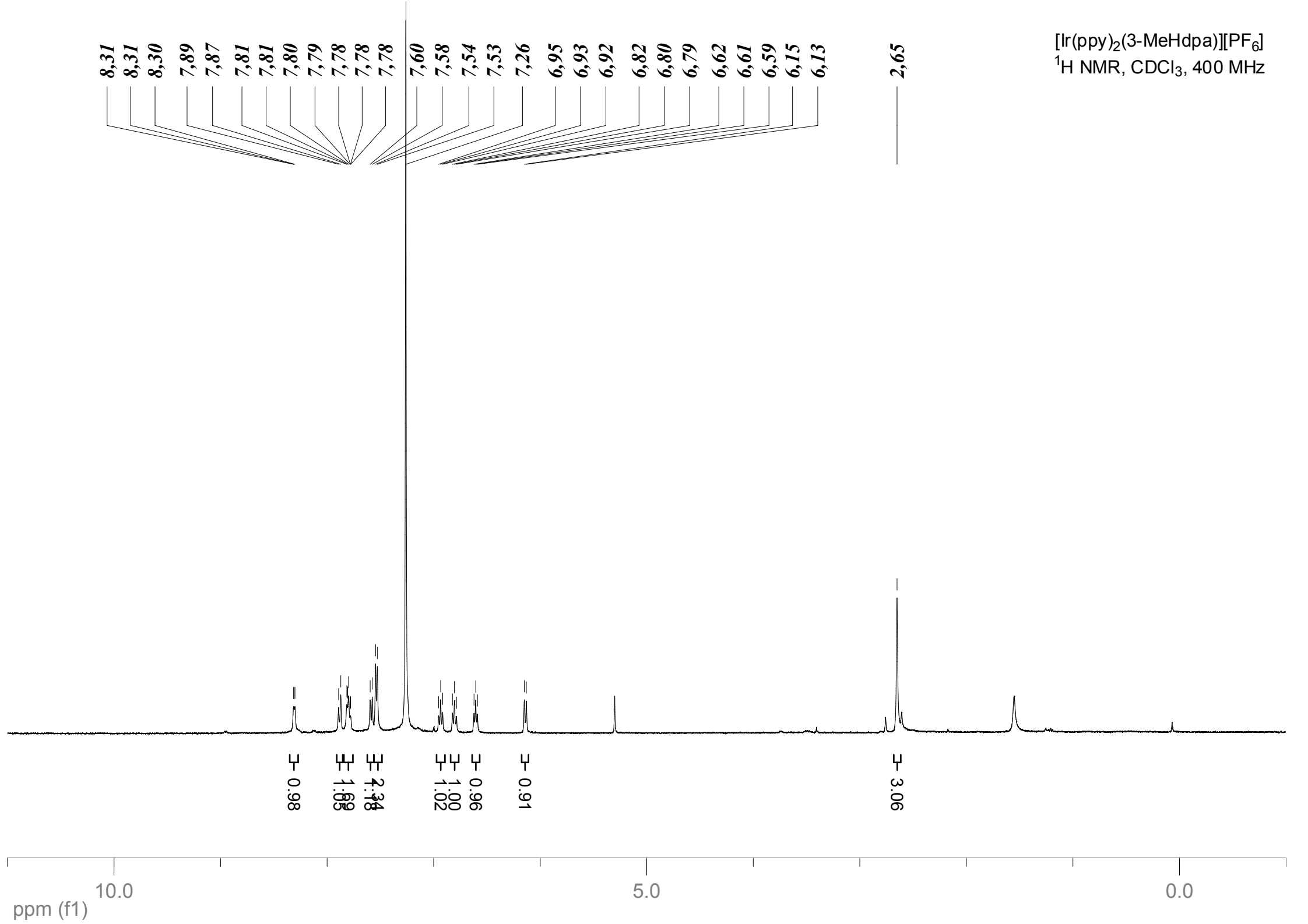
10.0
5.0
0.0
ppm (t1)

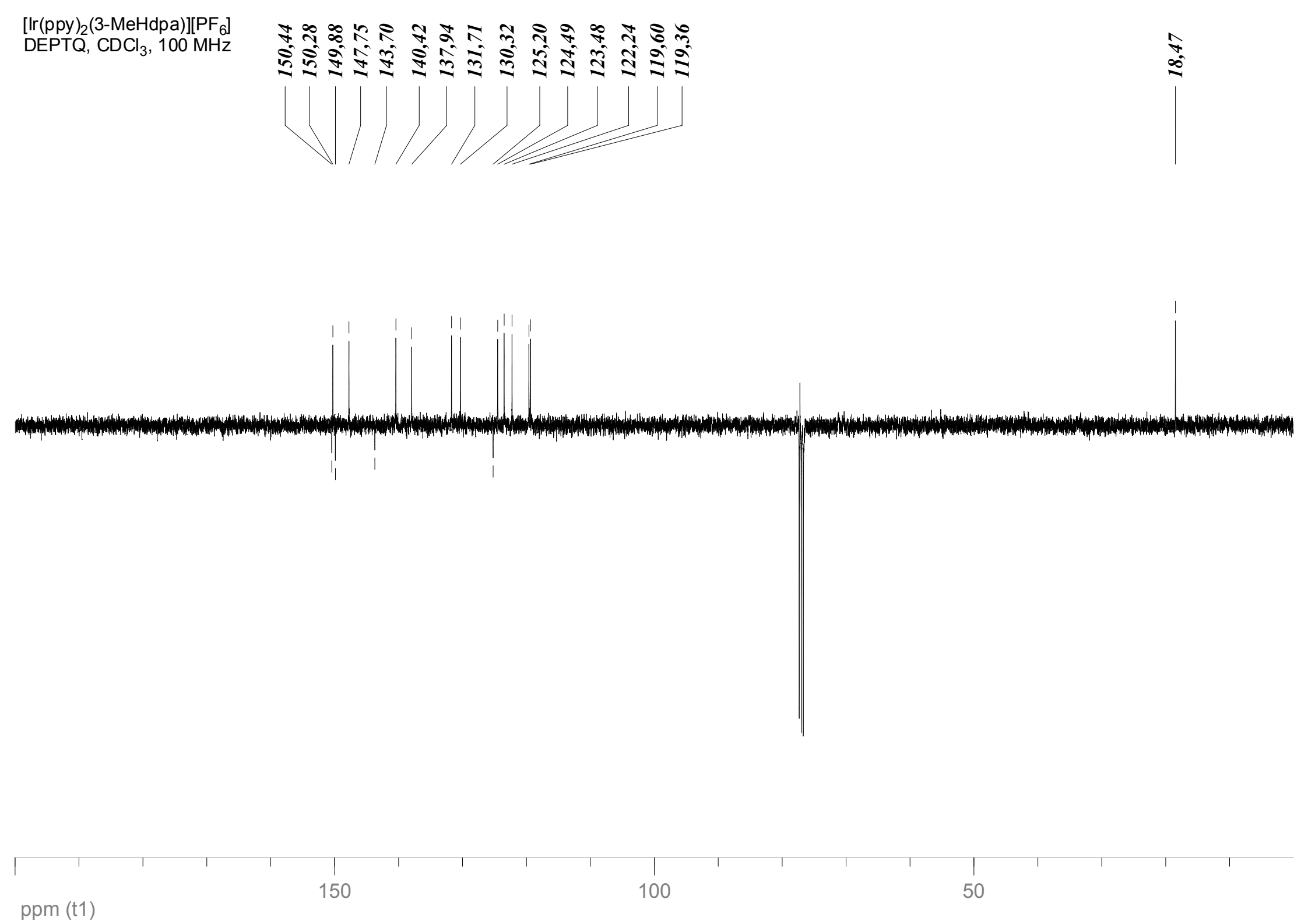

154,2
149,0
147,2
117,7
111,9
21,3
N
N
H
^{13}C NMR, $CDCl_3$, 100 MHz
200
150
100
50
0
ppm (t1)

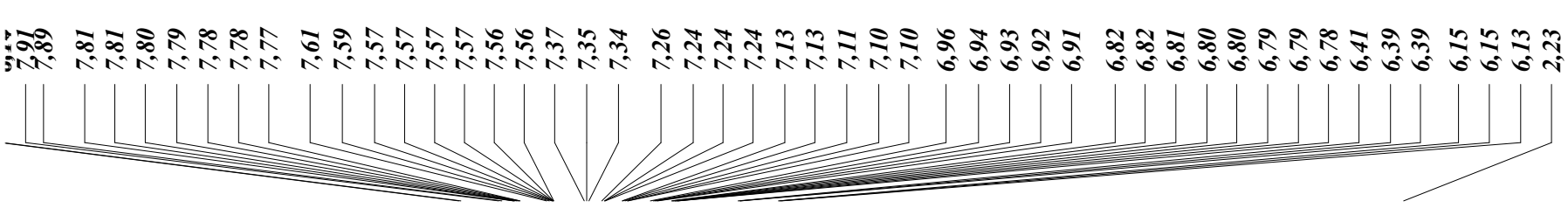
^{1}H NMR, $CDCl_3$, 400 MHz




152,2
147,4
138,6
125,1
111,1
17,7
N
N
H
^{13}C NMR, $CDCl_3$, 100 MHz
200
150
100
50
0
ppm (t1)

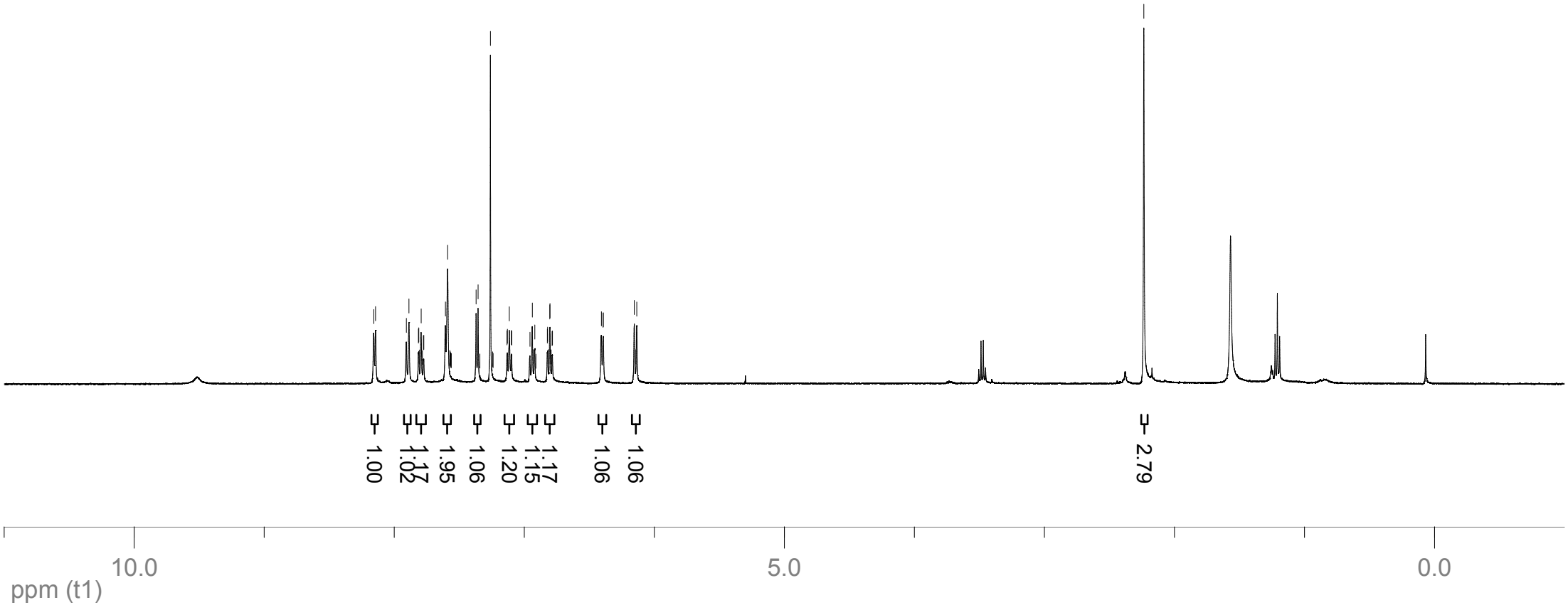

[Ir(ppy)2(3-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
8,31
8,31
8,30
7,89
7,87
7,81
7,81
7,80
7,79
7,78
7,78
7,78
7,60
7,58
7,54
7,53
7,26
6,95
6,93
6,92
6,82
6,80
6,79
6,62
6,61
6,59
6,15
6,13
2,65
0.98
1.03
1.09
2.34
2.18
1.02
1.00
0.96
0.91
3.06
10.0
5.0
0.0
ppm (f1)

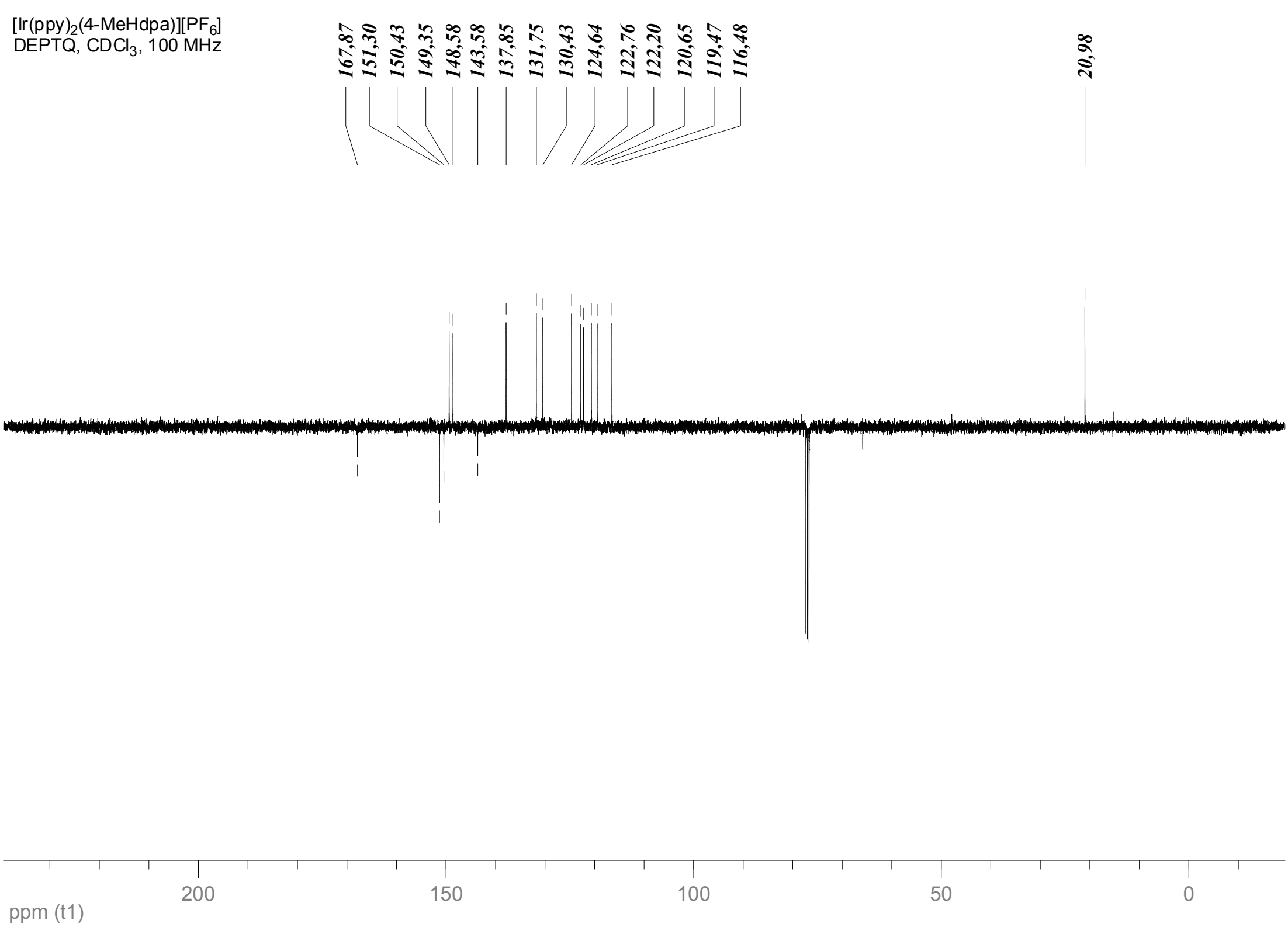

[Ir(ppy)2(3-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
150,44
150,28
149,88
147,75
143,70
140,42
137,94
131,71
130,32
125,20
124,49
123,48
122,24
119,60
119,36
18,47
150
100
50
ppm (t1)

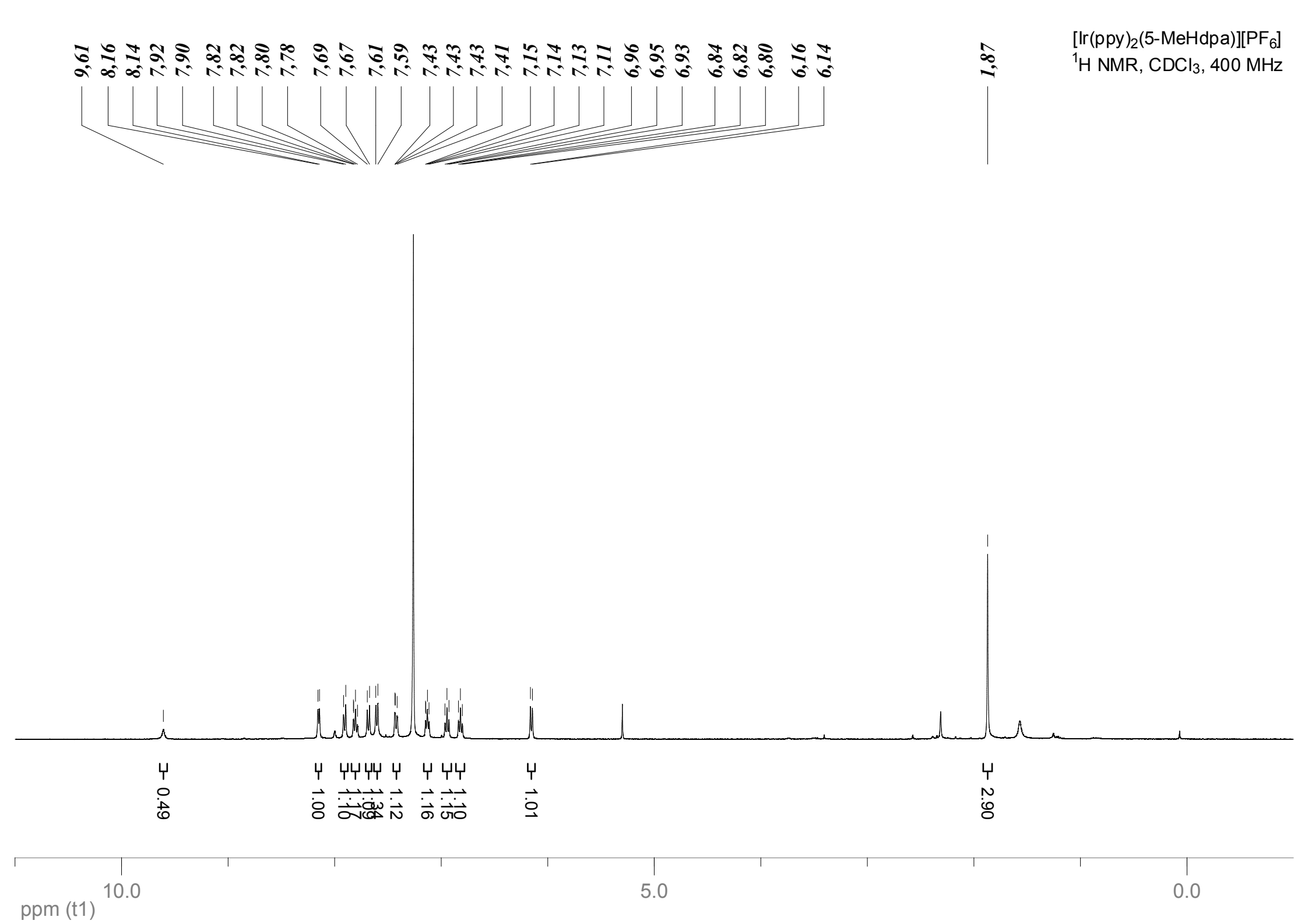


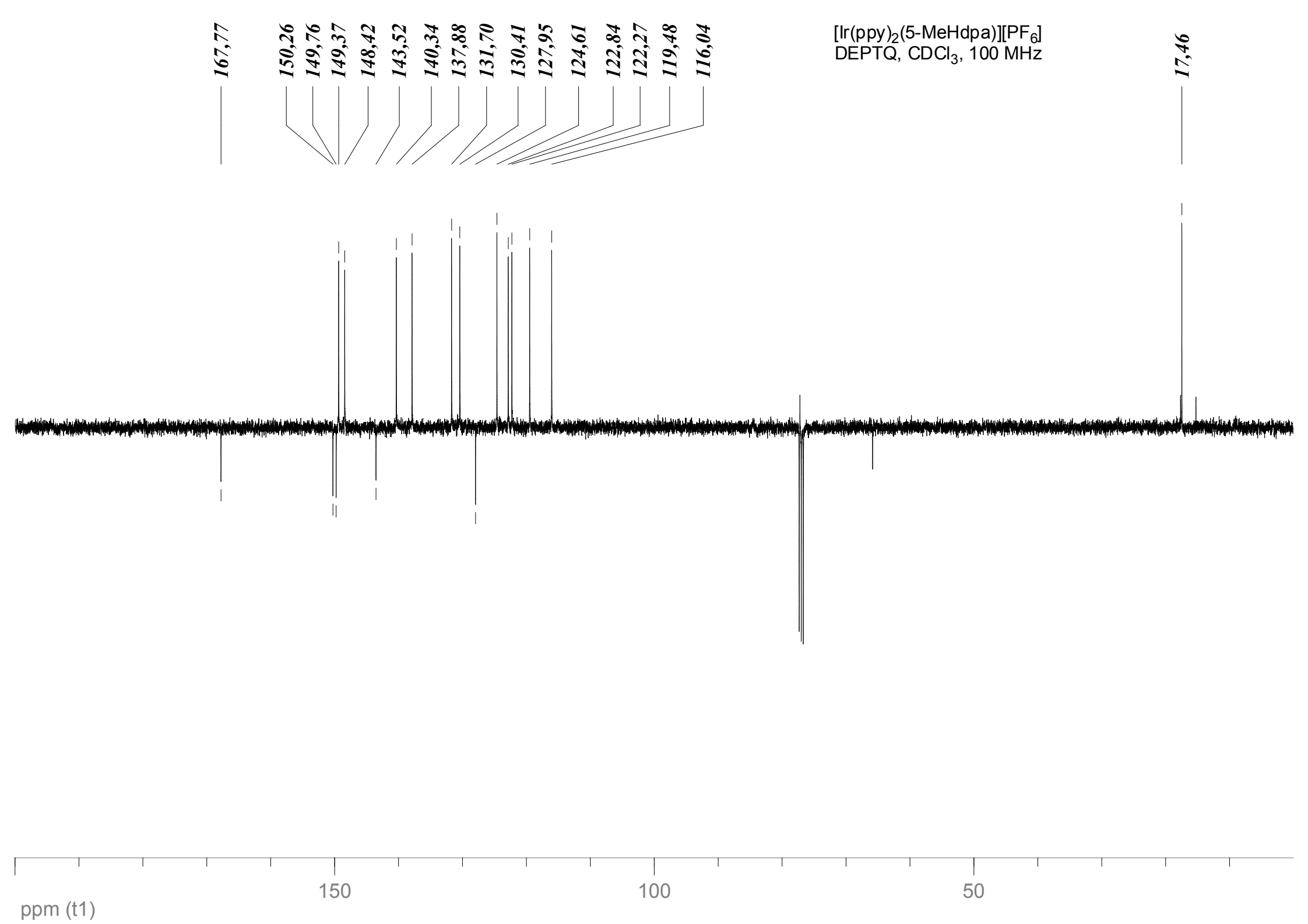
$[Ir(ppy)_2(4\text{-MeHdpa})][PF_6]$

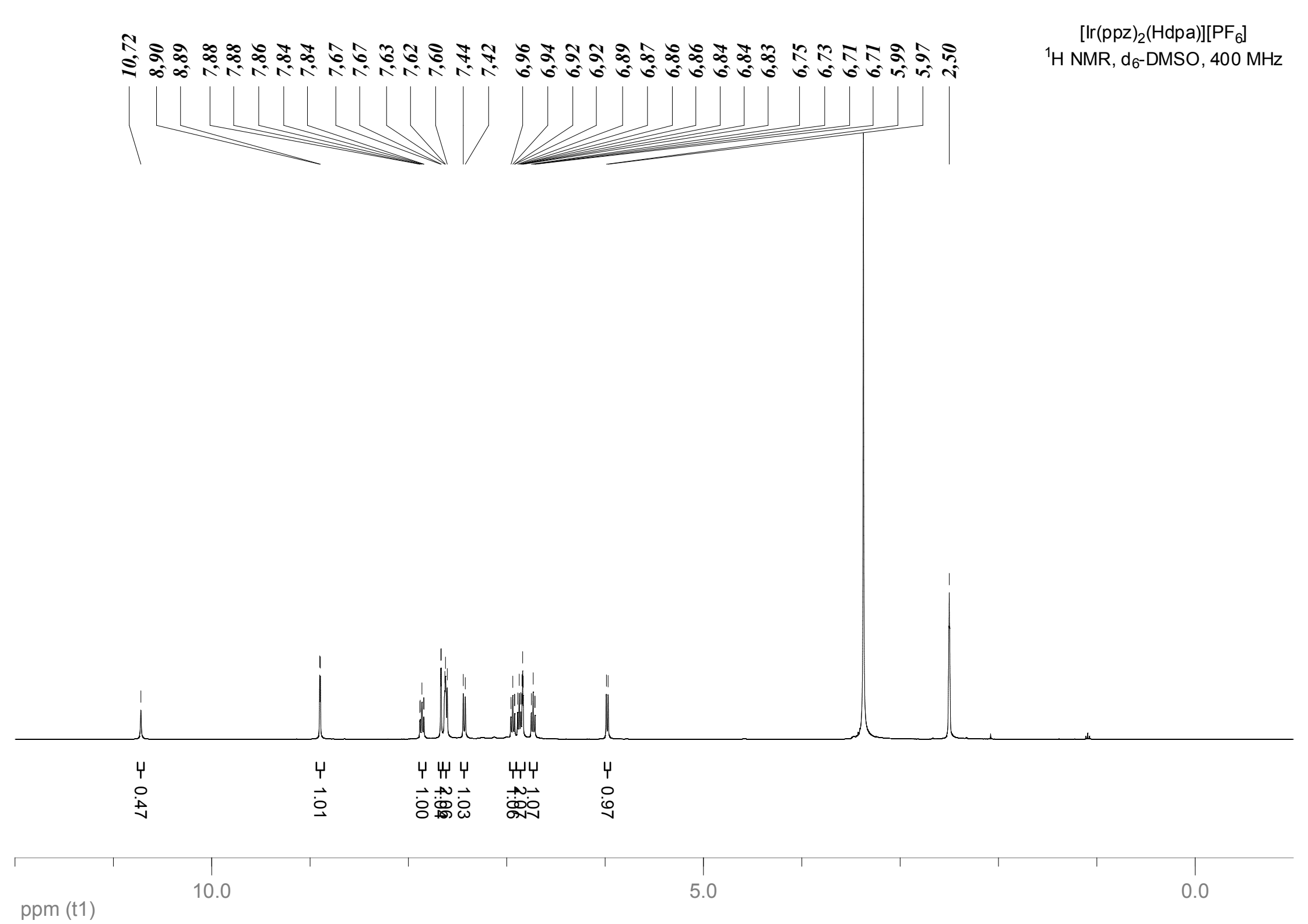
^1H NMR, $CDCl_3$, 400 MHz

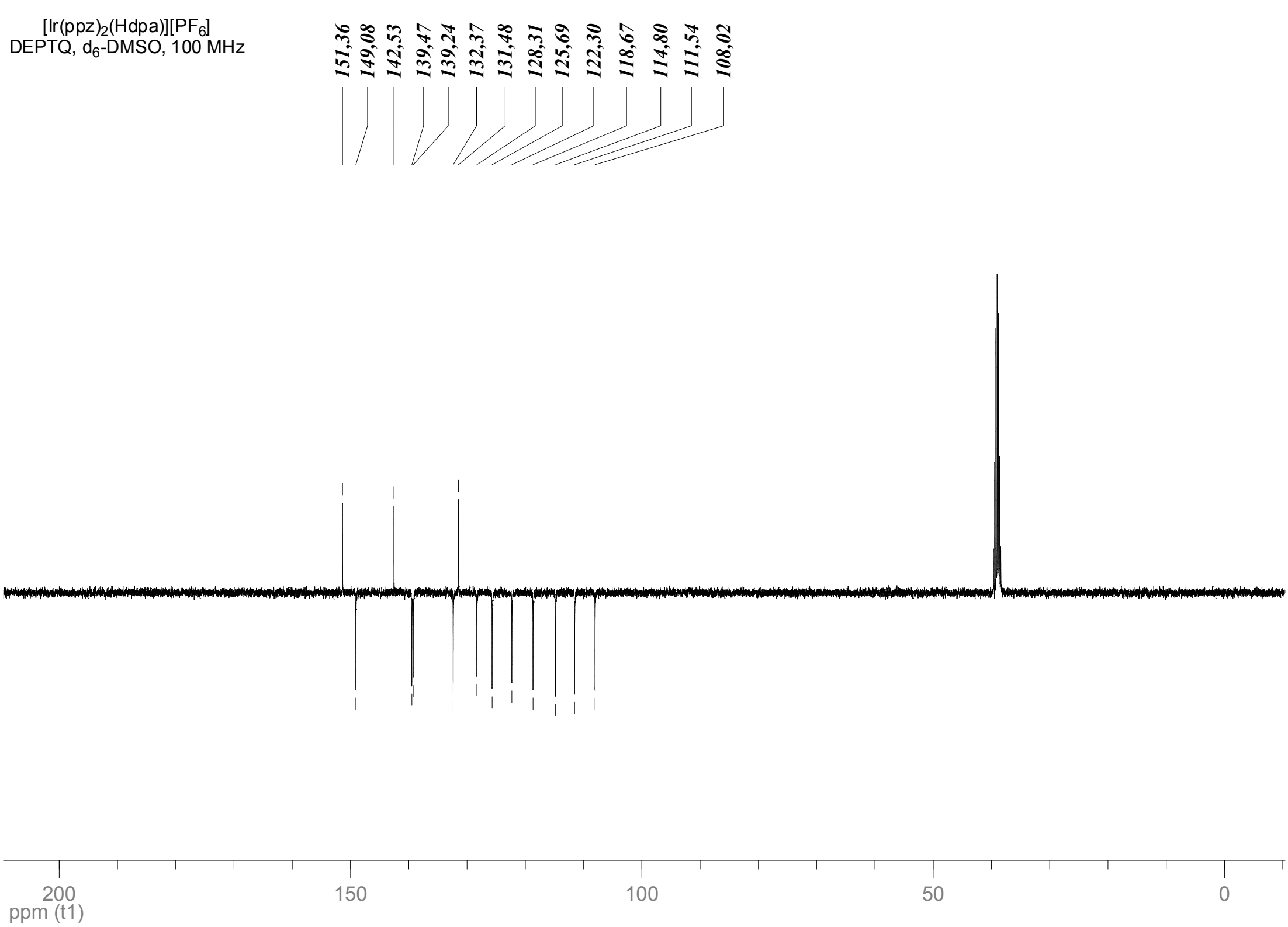


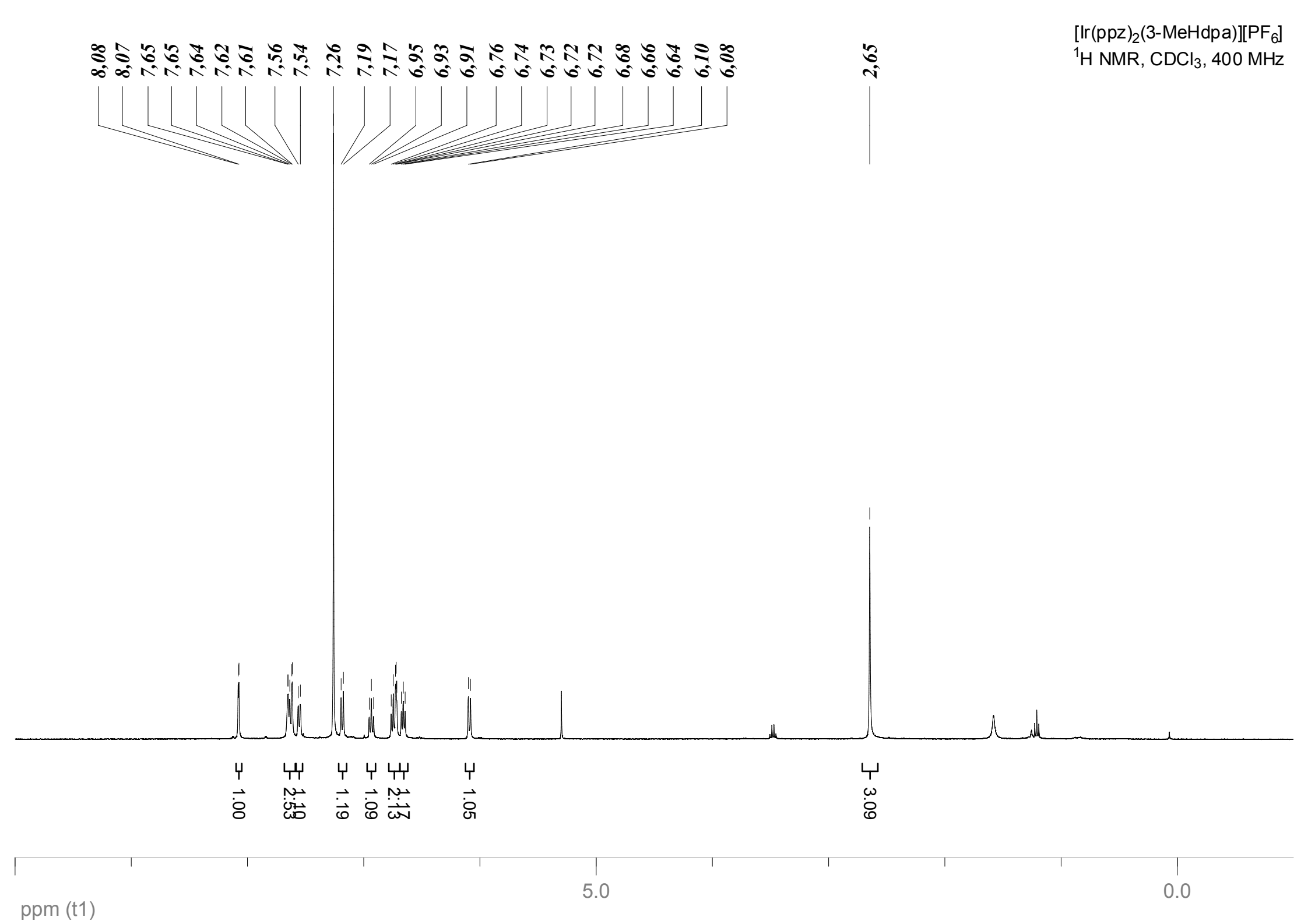

[Ir(ppy)2(4-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
167,87
151,30
150,43
149,35
148,58
143,58
137,85
131,75
130,43
124,64
122,76
122,20
120,65
119,47
116,48
20,98
200
150
100
50
0
ppm (t1)

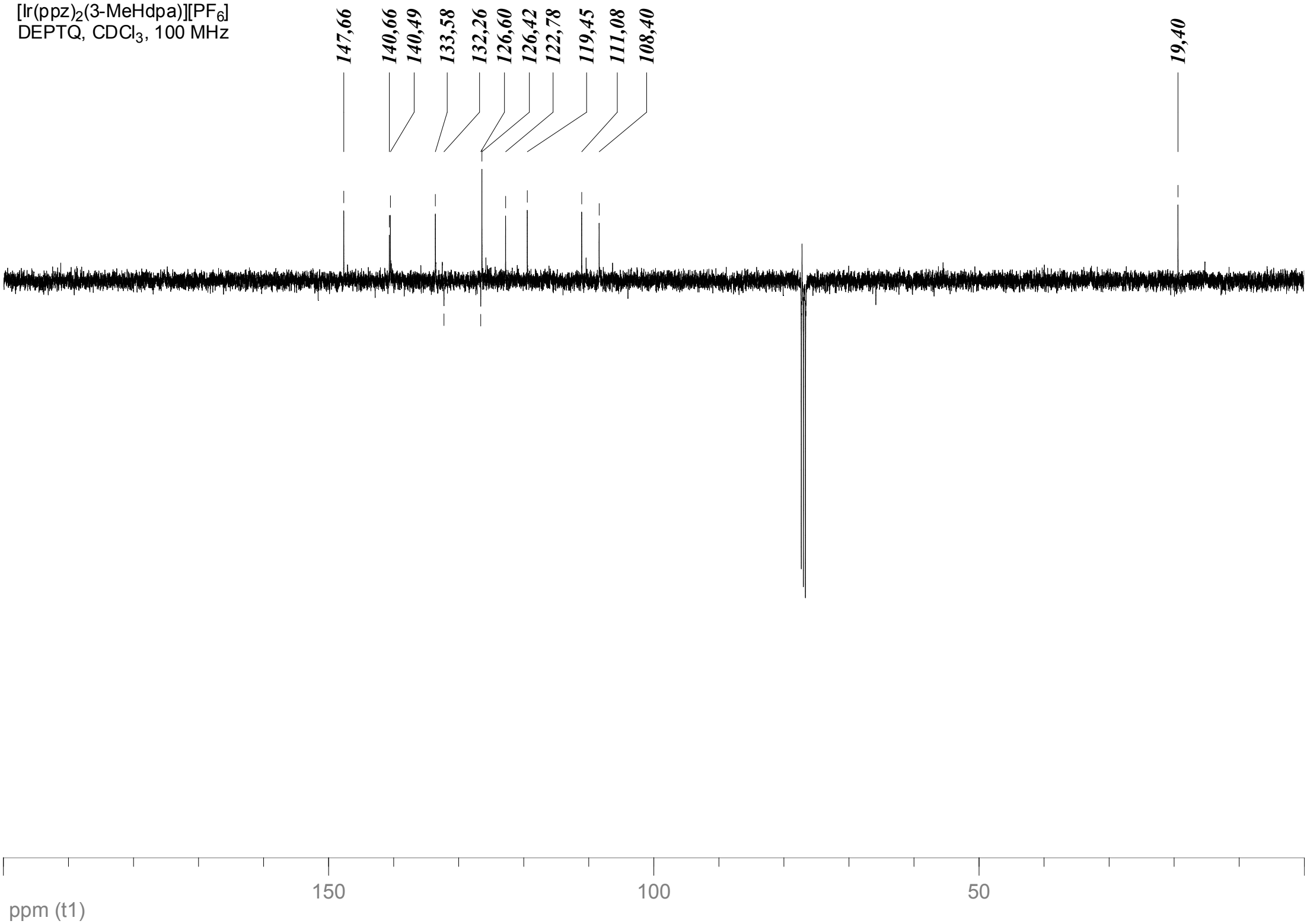

9,61
8,16
8,14
7,92
7,90
7,82
7,82
7,80
7,78
7,69
7,67
7,61
7,59
7,43
7,43
7,43
7,41
7,15
7,14
7,13
7,11
6,96
6,95
6,93
6,84
6,82
6,80
6,16
6,14
1,87
[Ir(ppy)2(5-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
0.49
1.00
1.12
1.16
1.01
2.90
10.0
5.0
0.0
ppm (t1)

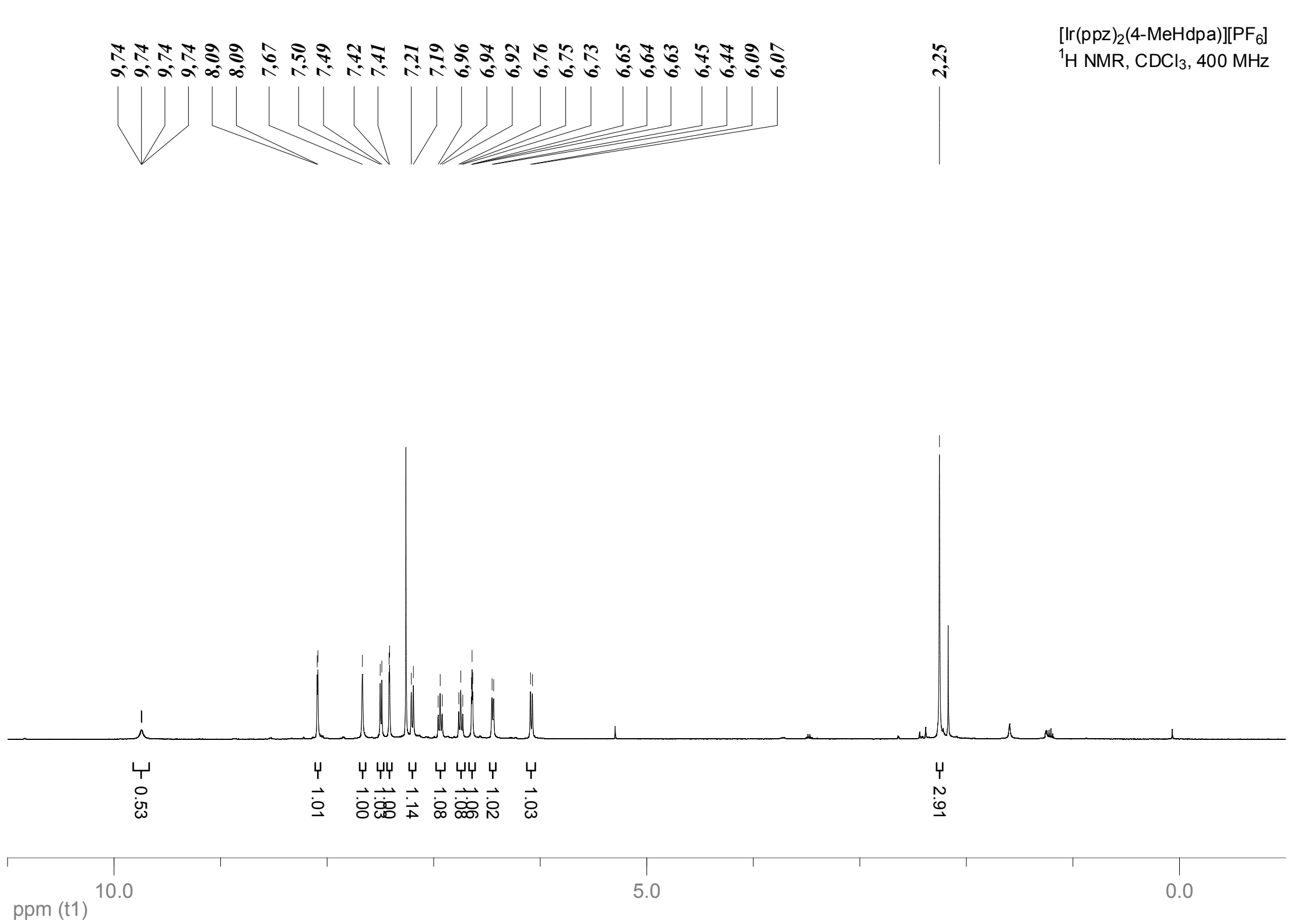

167,77
150,26
149,76
149,37
148,42
143,52
140,34
137,88
131,70
130,41
127,95
124,61
122,84
122,27
119,48
116,04
17,46
[Ir(ppy)2(5-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
150
100
50
ppm (t1)

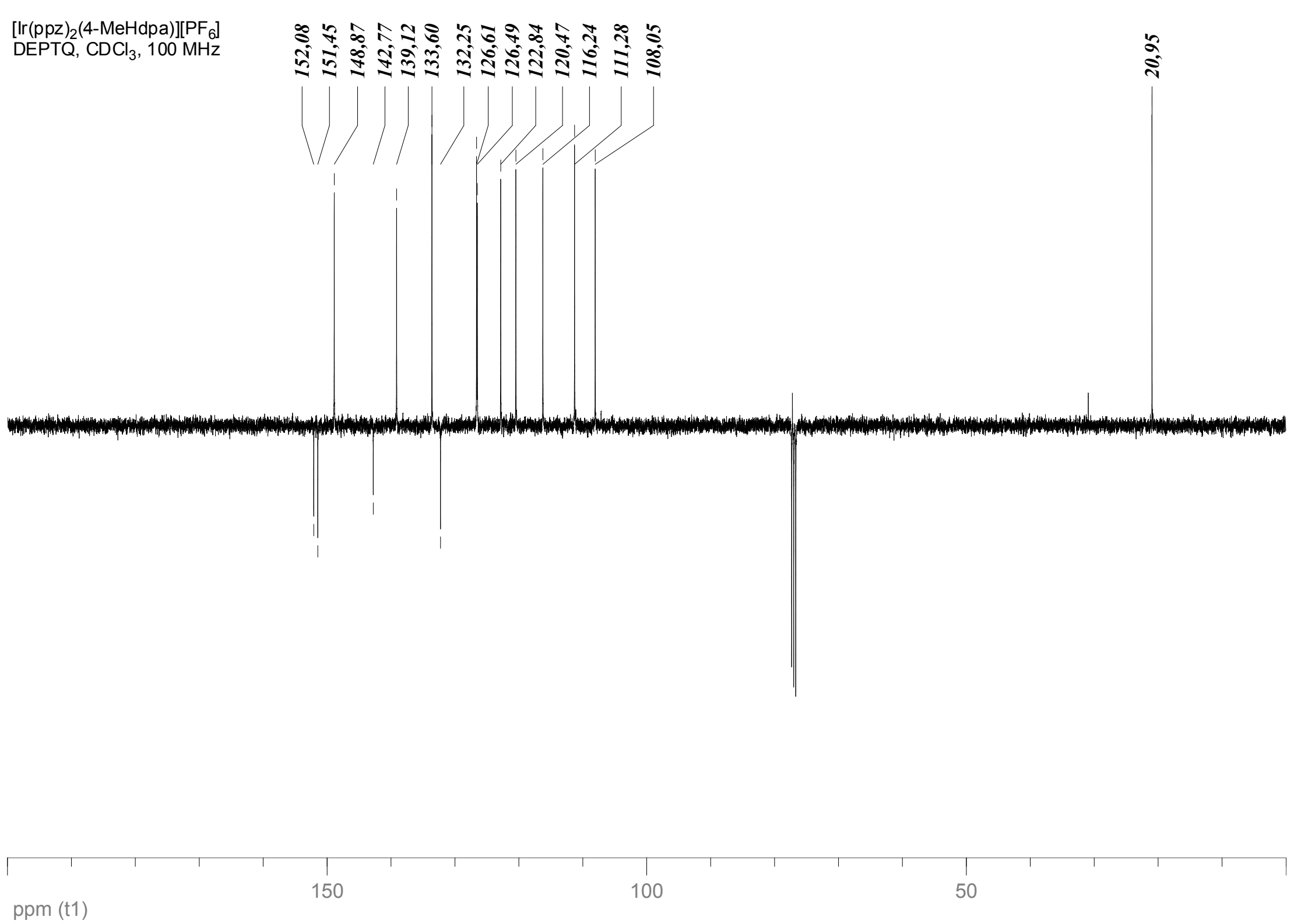

[Ir(ppz)2(Hdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
10,72
8,90
8,89
7,88
7,88
7,86
7,84
7,84
7,67
7,67
7,63
7,62
7,60
7,44
7,42
6,96
6,94
6,92
6,92
6,89
6,87
6,86
6,86
6,84
6,84
6,83
6,75
6,73
6,71
6,71
5,99
5,97
2,50
0.47
1.01
1.00
1.03
1.07
0.97
10.0
5.0
0.0
ppm (t1)

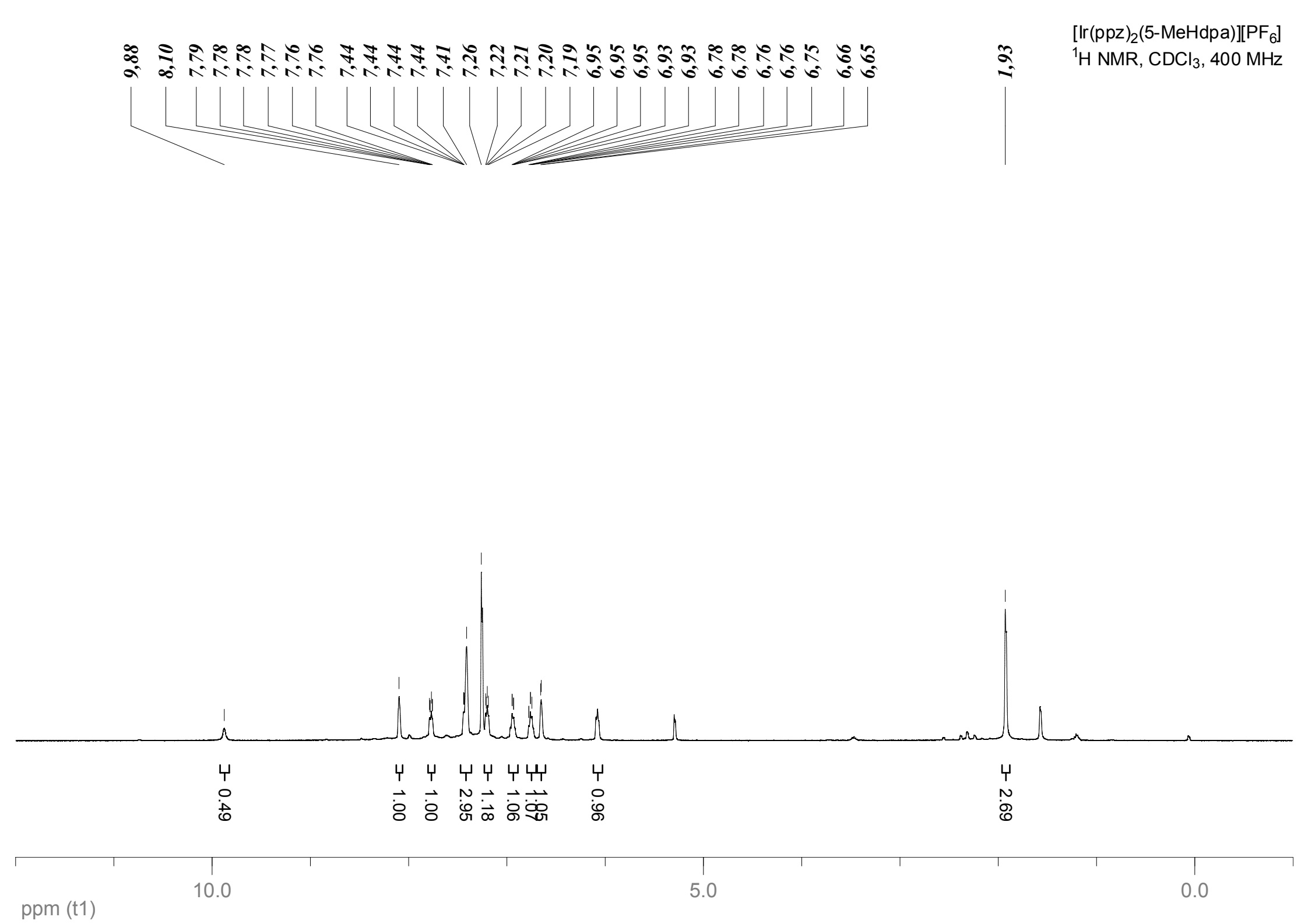

[Ir(ppz)2(Hdpa)][PF6]
DEPTQ, d6-DMSO, 100 MHz
151,36
149,08
142,53
139,47
139,24
132,37
131,48
128,31
125,69
122,30
118,67
114,80
111,54
108,02
200
150
100
50
0
ppm (t1)

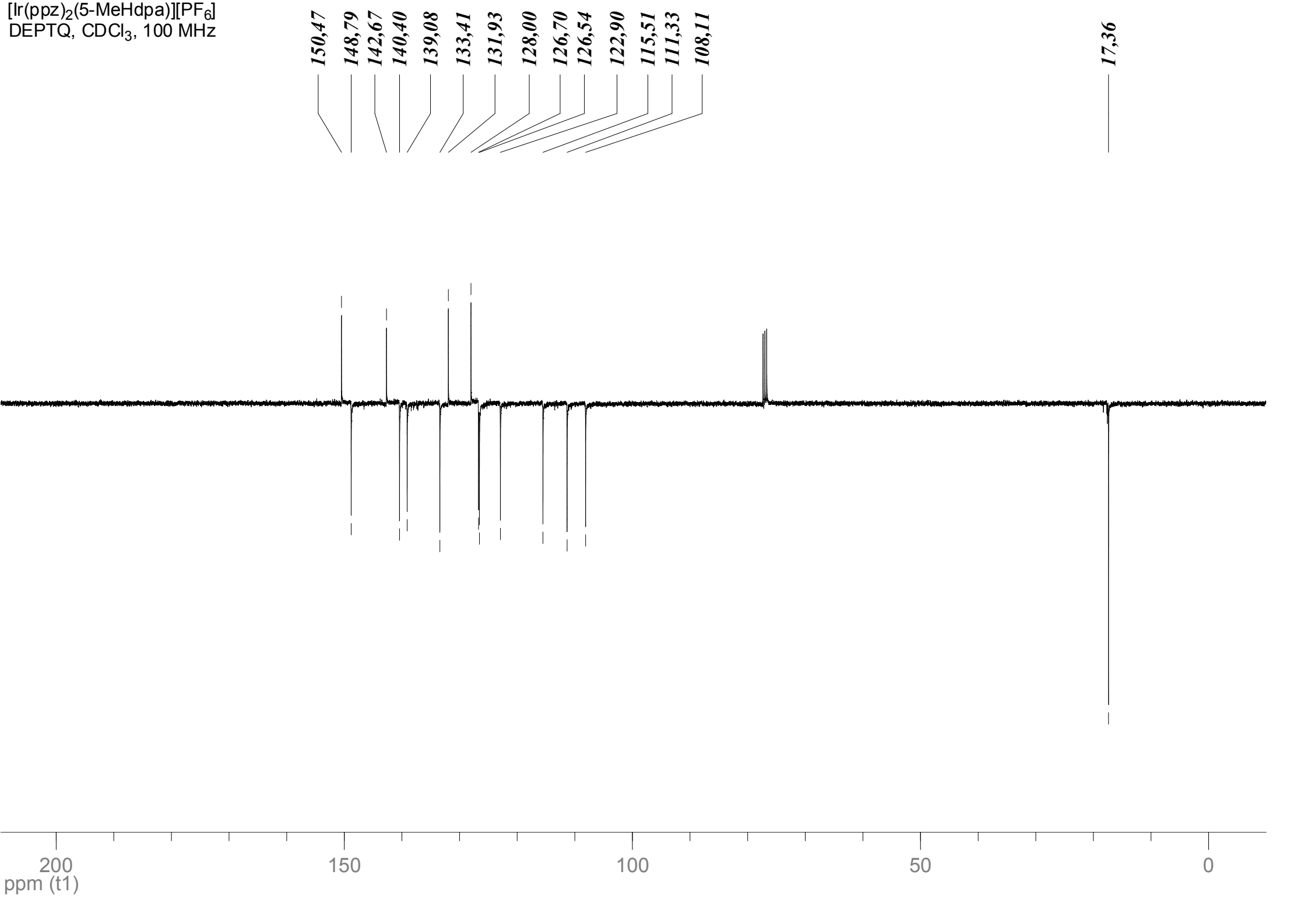

[Ir(ppz)2(3-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
8,08
8,07
7,65
7,65
7,64
7,62
7,61
7,56
7,54
7,26
7,19
7,17
6,95
6,93
6,91
6,76
6,74
6,73
6,72
6,72
6,68
6,66
6,64
6,10
6,08
2,65
1.00
2.53
1.19
1.09
2.13
1.05
3.09
5.0
0.0
ppm (t1)

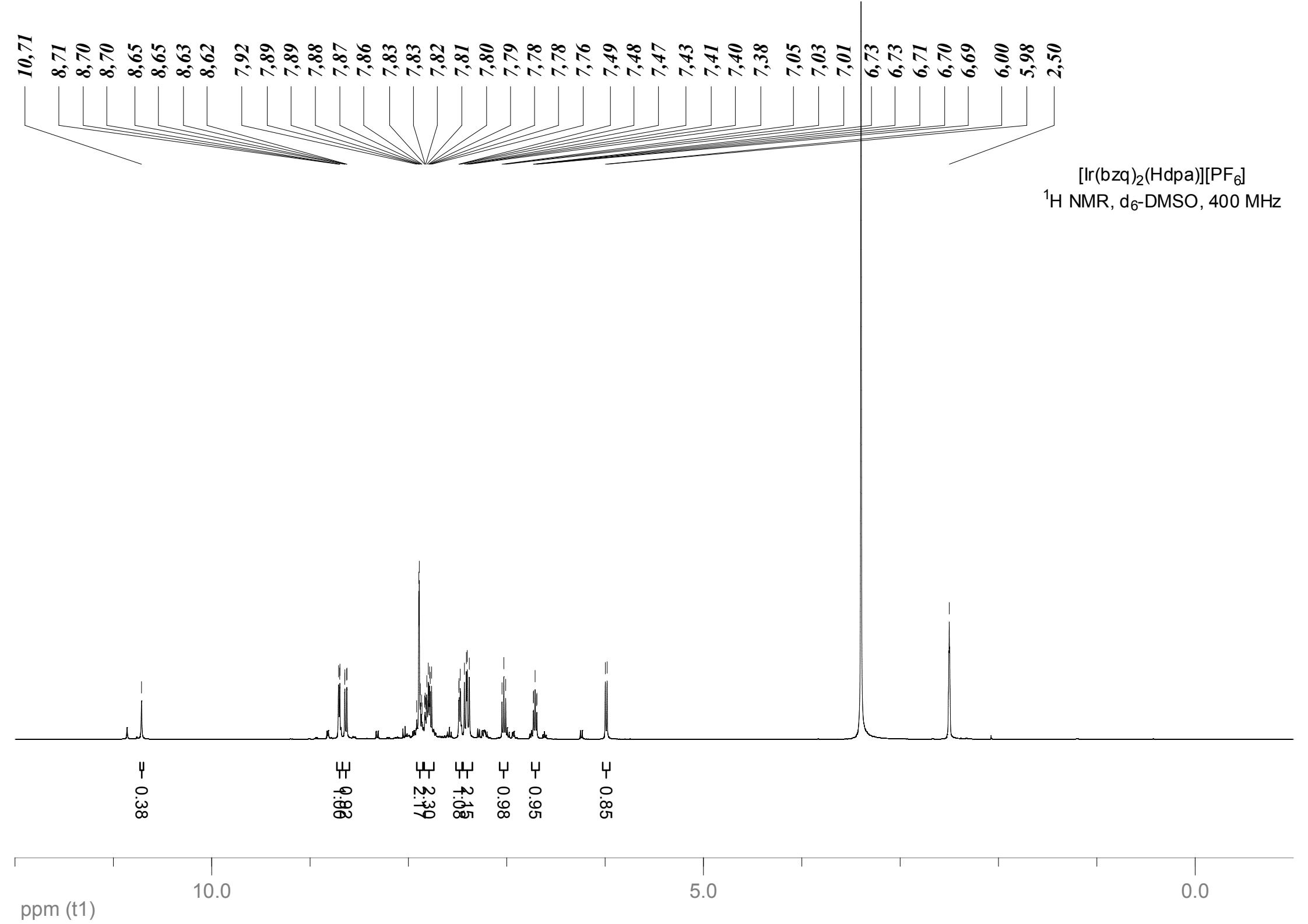

[Ir(ppz)2(3-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
147,66
140,66
140,49
133,58
132,26
126,60
126,42
122,78
119,45
111,08
108,40
19,40
150
100
50
ppm (t1)

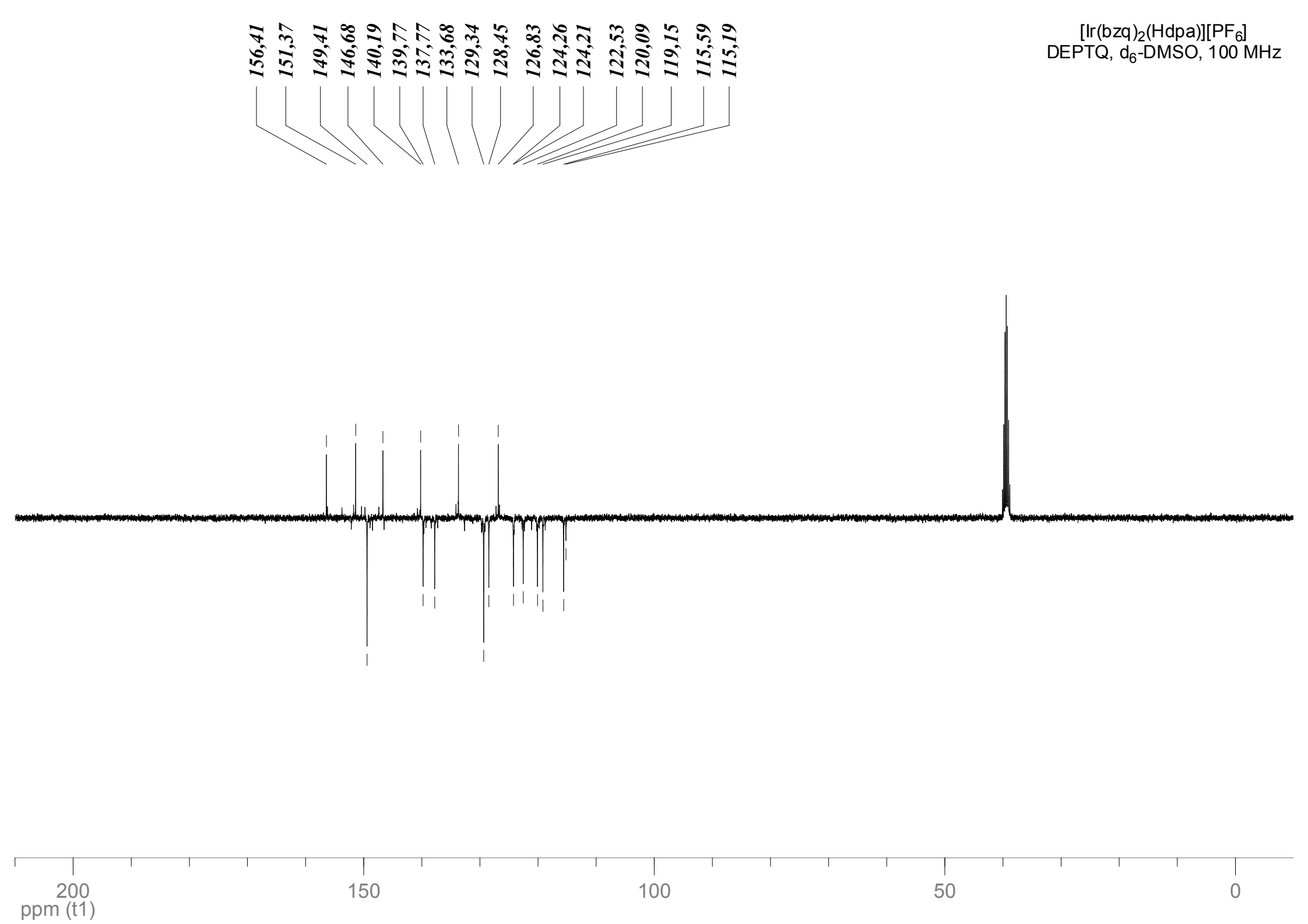

[Ir(ppz)2(4-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
9,74
9,74
9,74
9,74
8,09
8,09
7,67
7,50
7,49
7,42
7,41
7,21
7,19
6,96
6,94
6,92
6,76
6,75
6,73
6,65
6,64
6,63
6,45
6,44
6,09
6,07
2,25
0.53
1.01
1.00
1.14
1.08
1.02
1.03
2.91
10.0
5.0
0.0
ppm (t1)

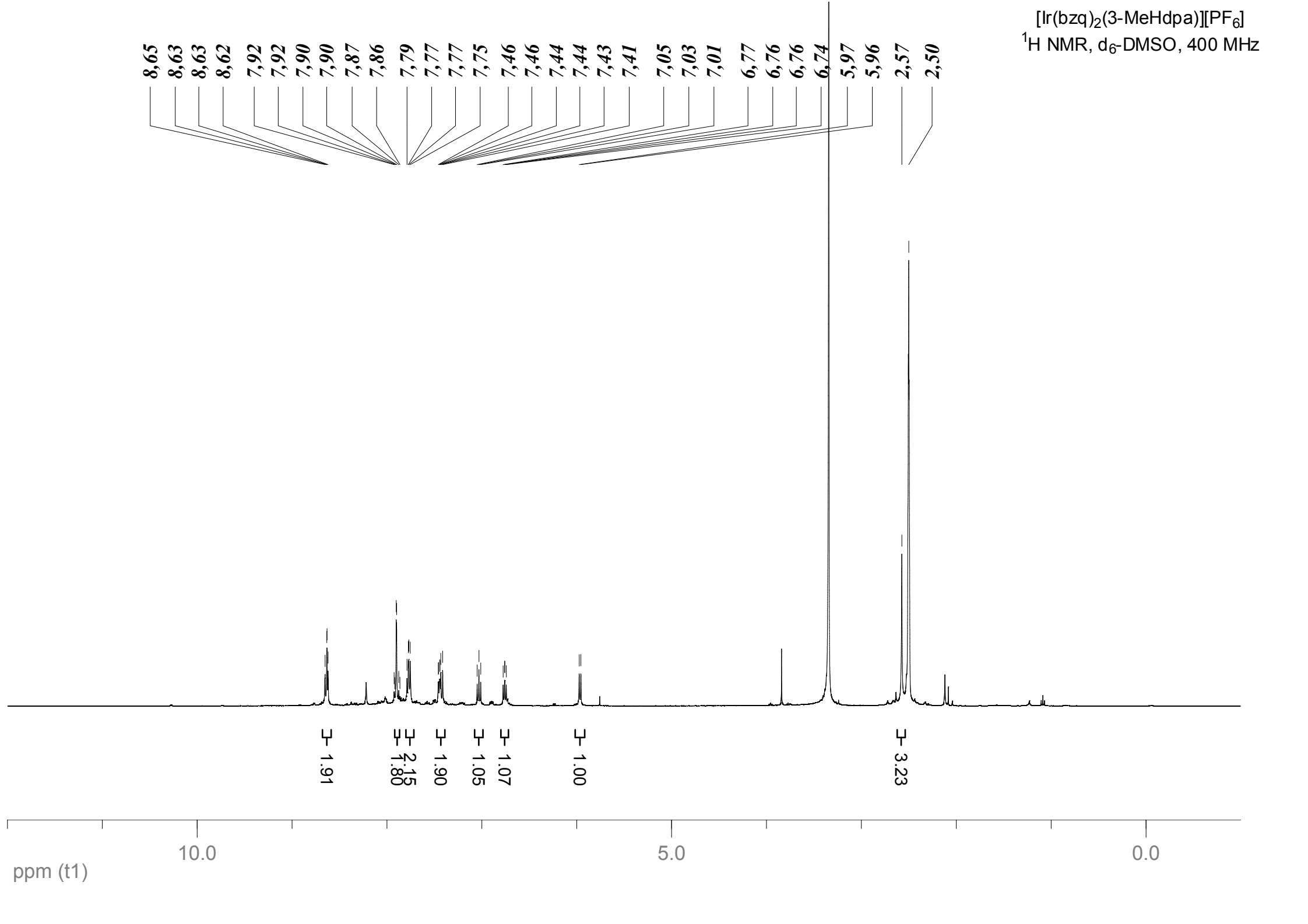

[Ir(ppz)2(4-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
152,08
151,45
148,87
142,77
139,12
133,60
132,25
126,61
126,49
122,84
120,47
116,24
111,28
108,05
20,95
150
100
50
ppm (t1)

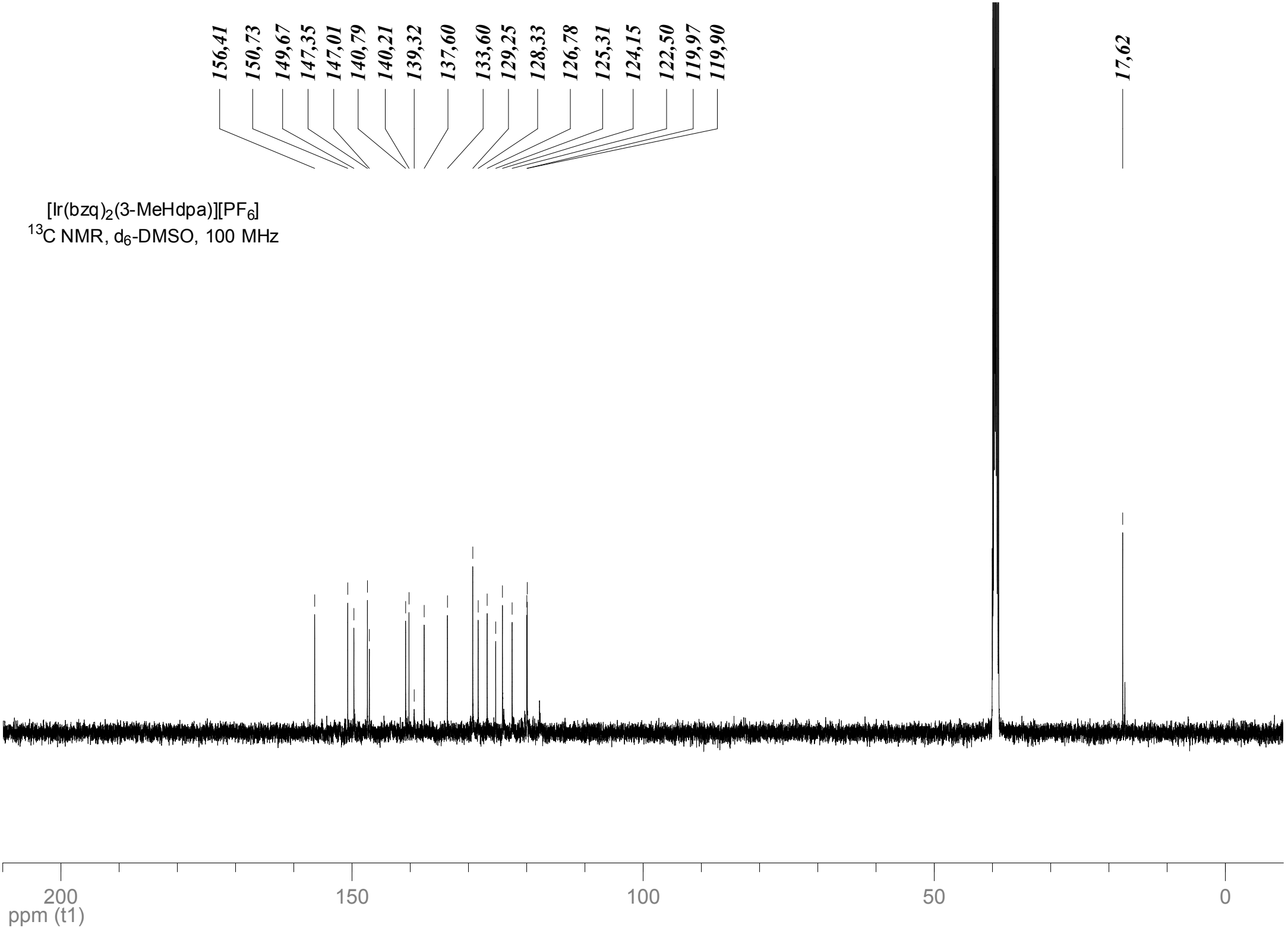

[Ir(ppz)2(5-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
9,88
8,10
7,79
7,78
7,78
7,77
7,76
7,76
7,44
7,44
7,44
7,44
7,41
7,26
7,22
7,21
7,20
7,19
6,95
6,95
6,95
6,93
6,93
6,78
6,78
6,76
6,76
6,75
6,66
6,65
1,93
0.49
1.00
1.00
2.95
1.18
1.06
1.05
1.07
0.96
2.69
10.0
5.0
0.0
ppm (t1)

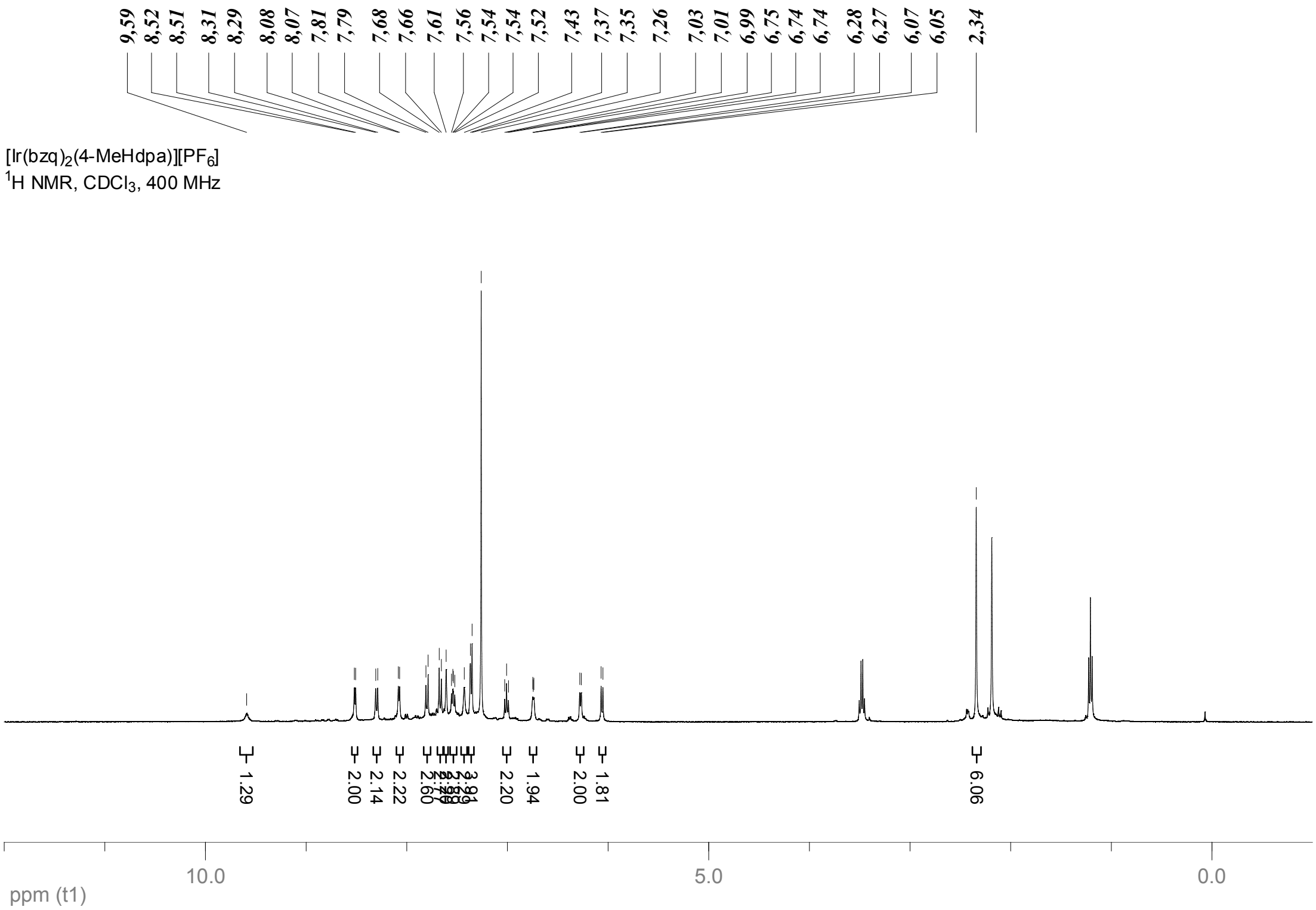

[Ir(ppz)2(5-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
150,47
148,79
142,67
140,40
139,08
133,41
131,93
128,00
126,70
126,54
122,90
115,51
111,33
108,11
17,36
200
150
100
50
0
ppm (t1)

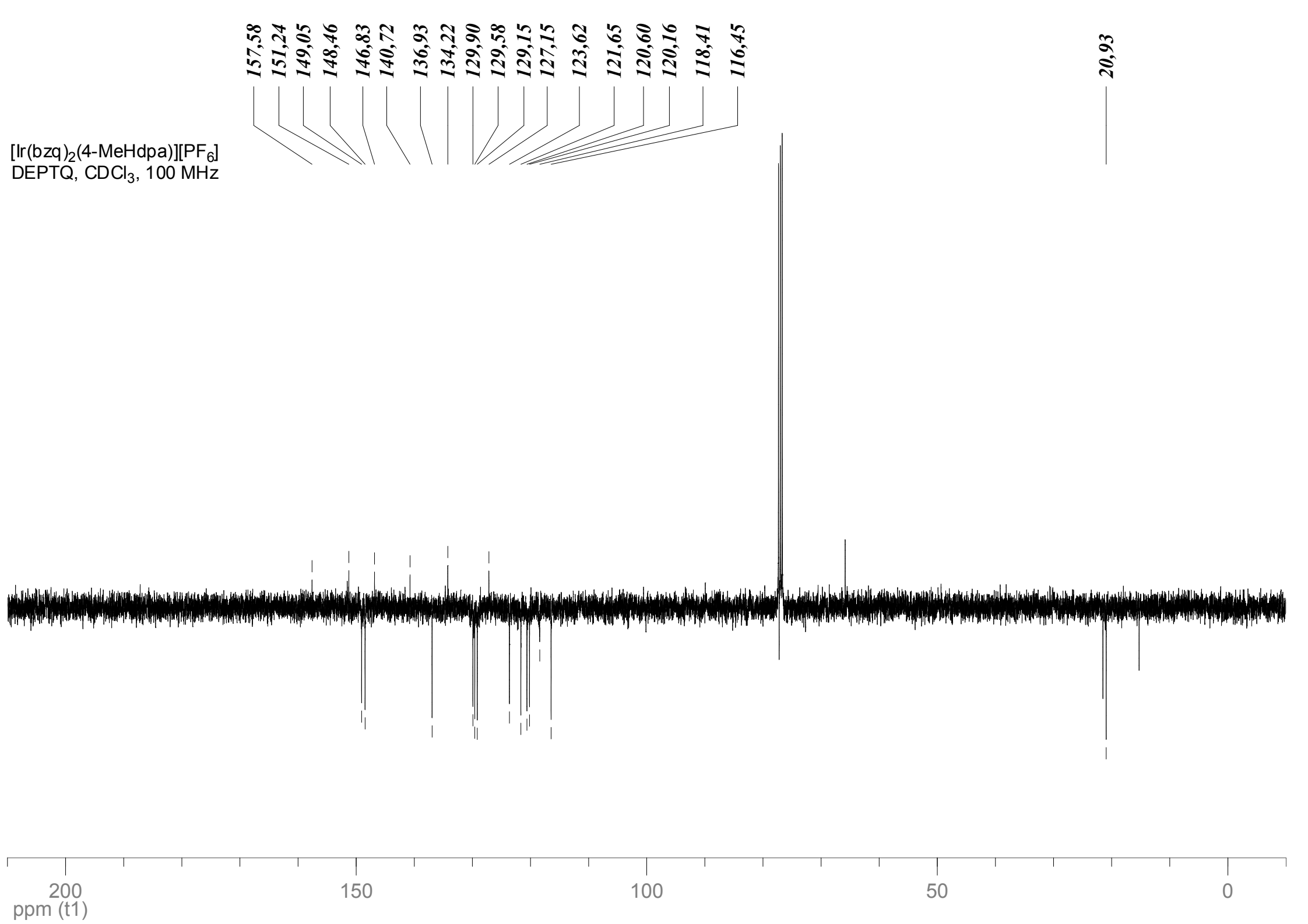

10,71
8,71
8,70
8,70
8,65
8,65
8,63
8,62
7,92
7,89
7,89
7,88
7,87
7,86
7,83
7,83
7,82
7,81
7,80
7,79
7,78
7,78
7,76
7,49
7,48
7,47
7,43
7,41
7,40
7,38
7,05
7,03
7,01
6,73
6,73
6,71
6,70
6,69
6,00
5,98
2,50
[Ir(bzq)2(Hdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
0.38
9.80
2.17
4.08
0.98
0.95
0.85
10.0
5.0
0.0
ppm (t1)

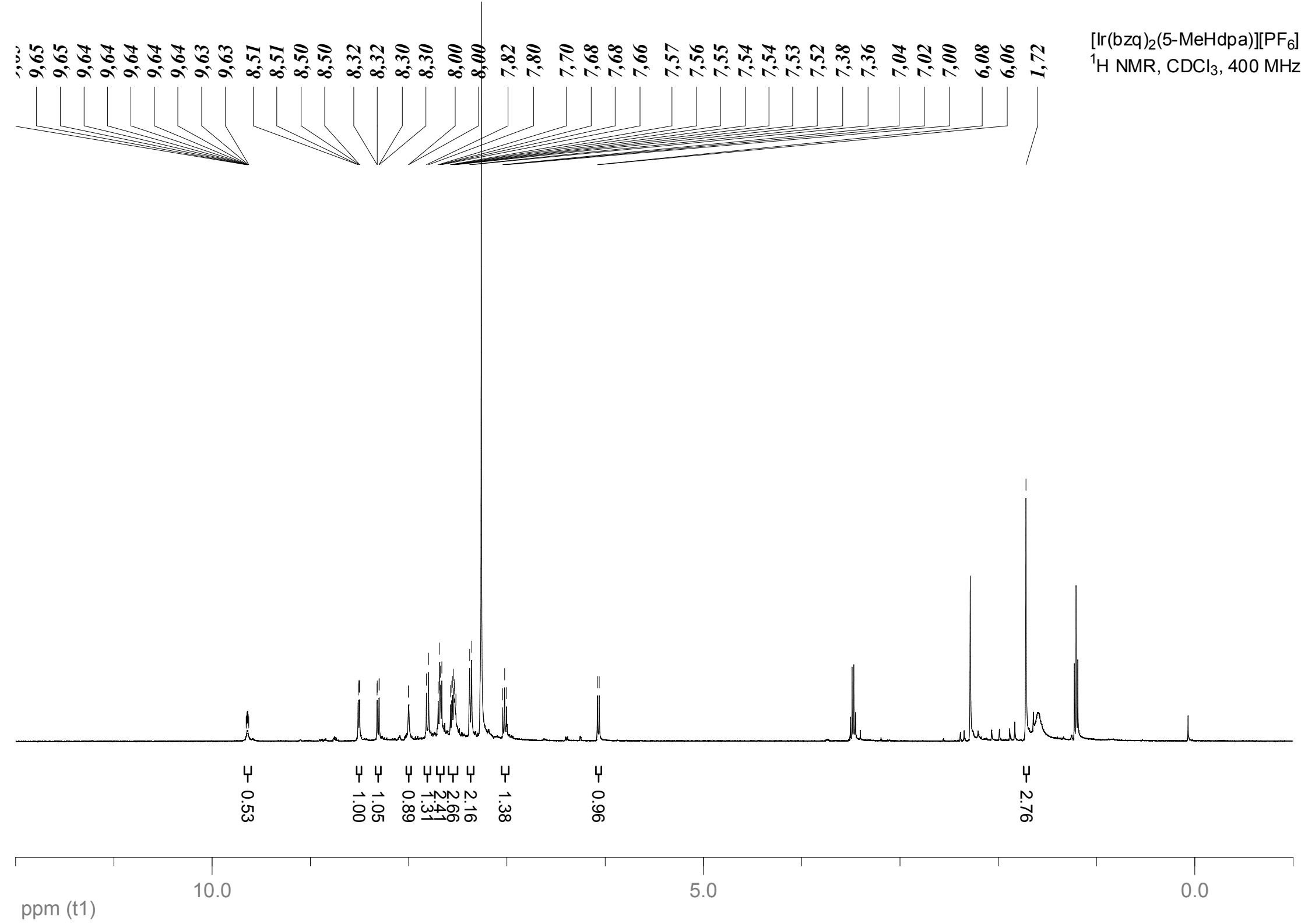

156,41
151,37
149,41
146,68
140,19
139,77
137,77
133,68
129,34
128,45
126,83
124,26
124,21
122,53
120,09
119,15
115,59
115,19
[Ir(bzq)2(Hdpa)][PF6]
DEPTQ, d6-DMSO, 100 MHz
200
150
100
50
0
ppm (t1)

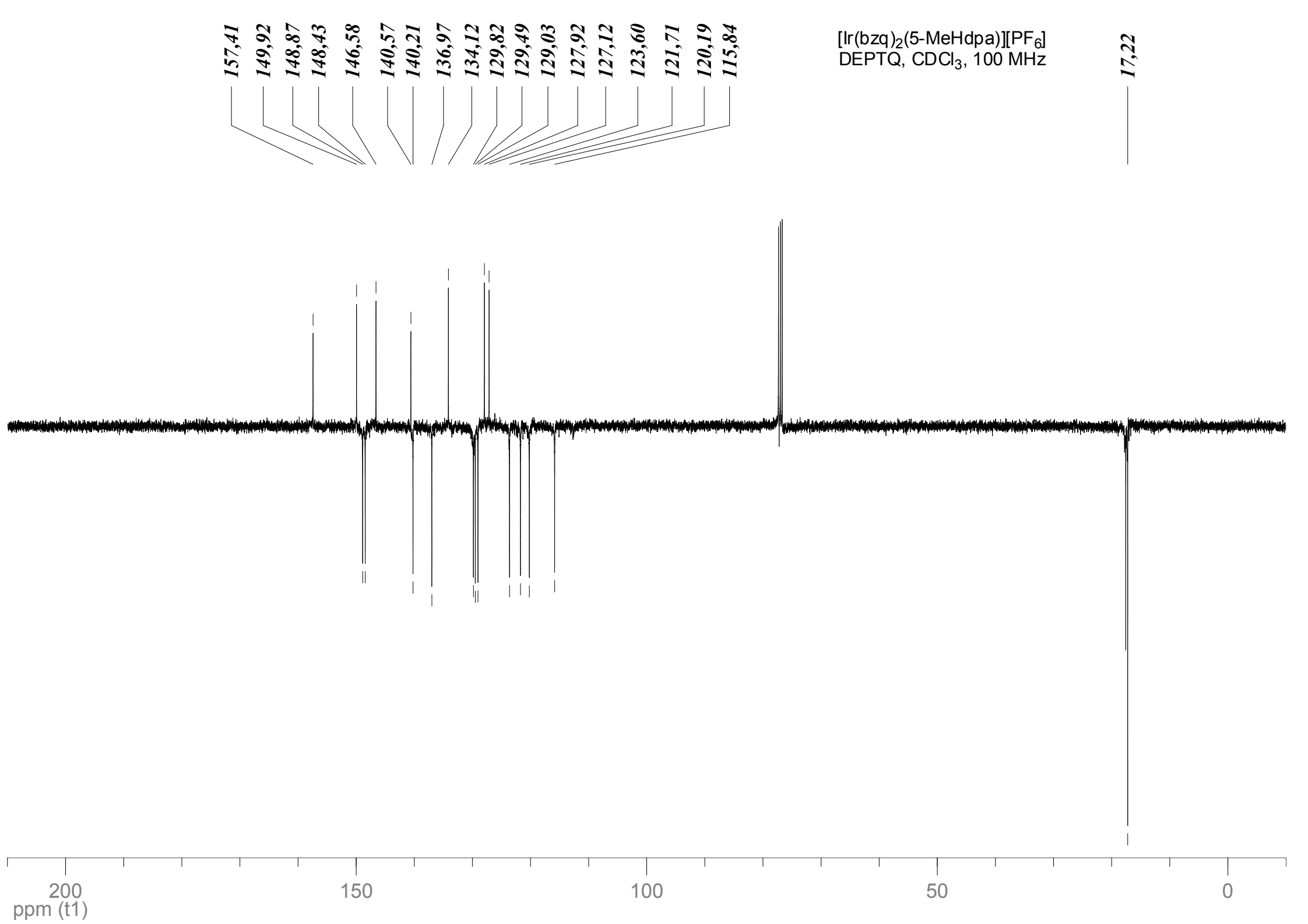

[Ir(bzq)2(3-MeHdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
8,65
8,63
8,63
8,62
7,92
7,92
7,90
7,90
7,87
7,86
7,79
7,77
7,77
7,75
7,46
7,46
7,44
7,44
7,43
7,41
7,05
7,03
7,01
6,77
6,76
6,76
6,74
5,97
5,96
2,57
2,50
1.91
2.15
1.80
1.90
1.05
1.07
1.00
3.23
10.0
5.0
0.0
ppm (t1)

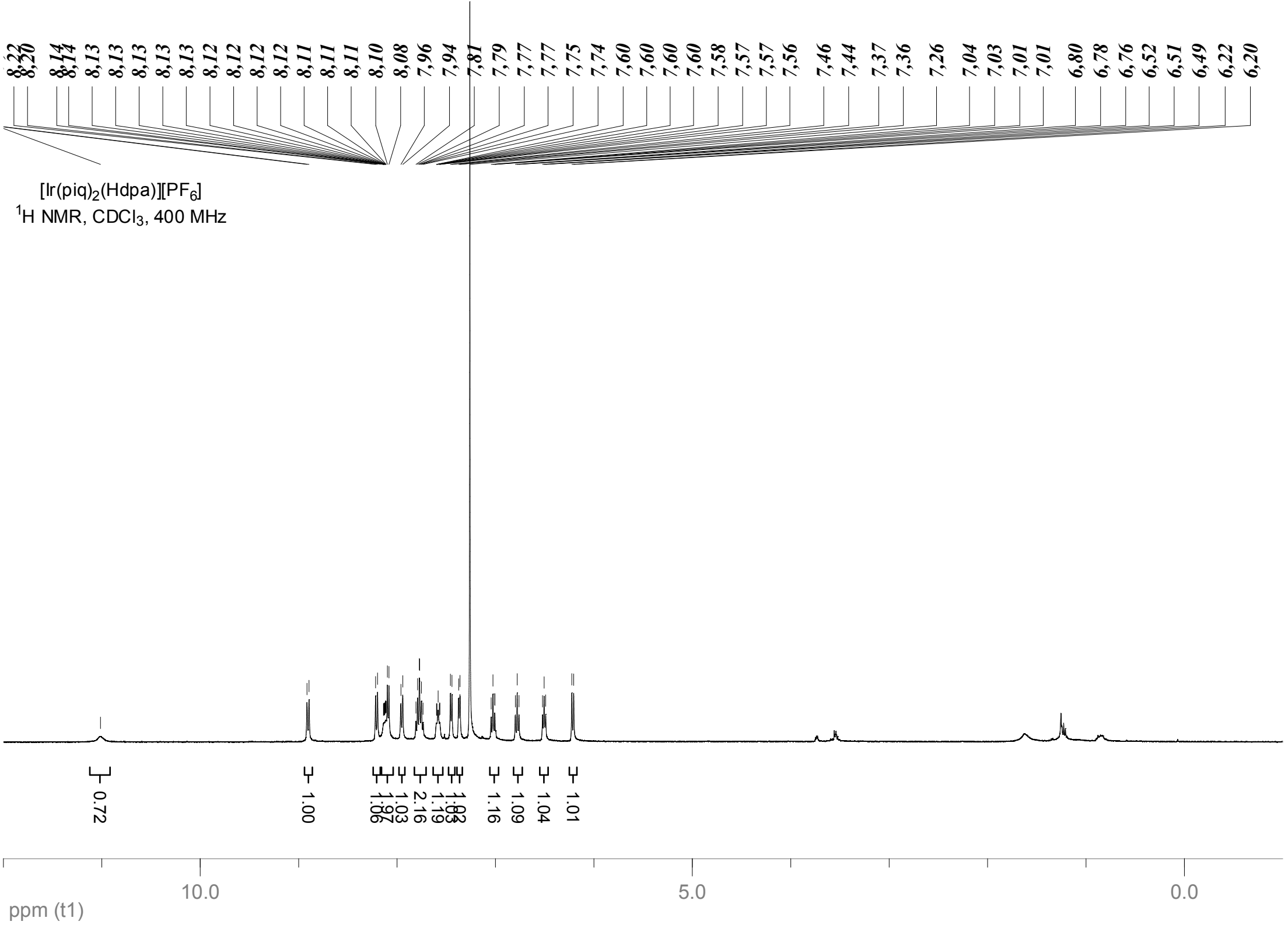

156,41
150,73
149,67
147,35
147,01
140,79
140,21
139,32
137,60
133,60
129,25
128,33
126,78
125,31
124,15
122,50
119,97
119,90
17,62
[Ir(bzq)2(3-MeHdpa)][PF6]
13C NMR, d6-DMSO, 100 MHz
200
150
100
50
0
ppm (t1)

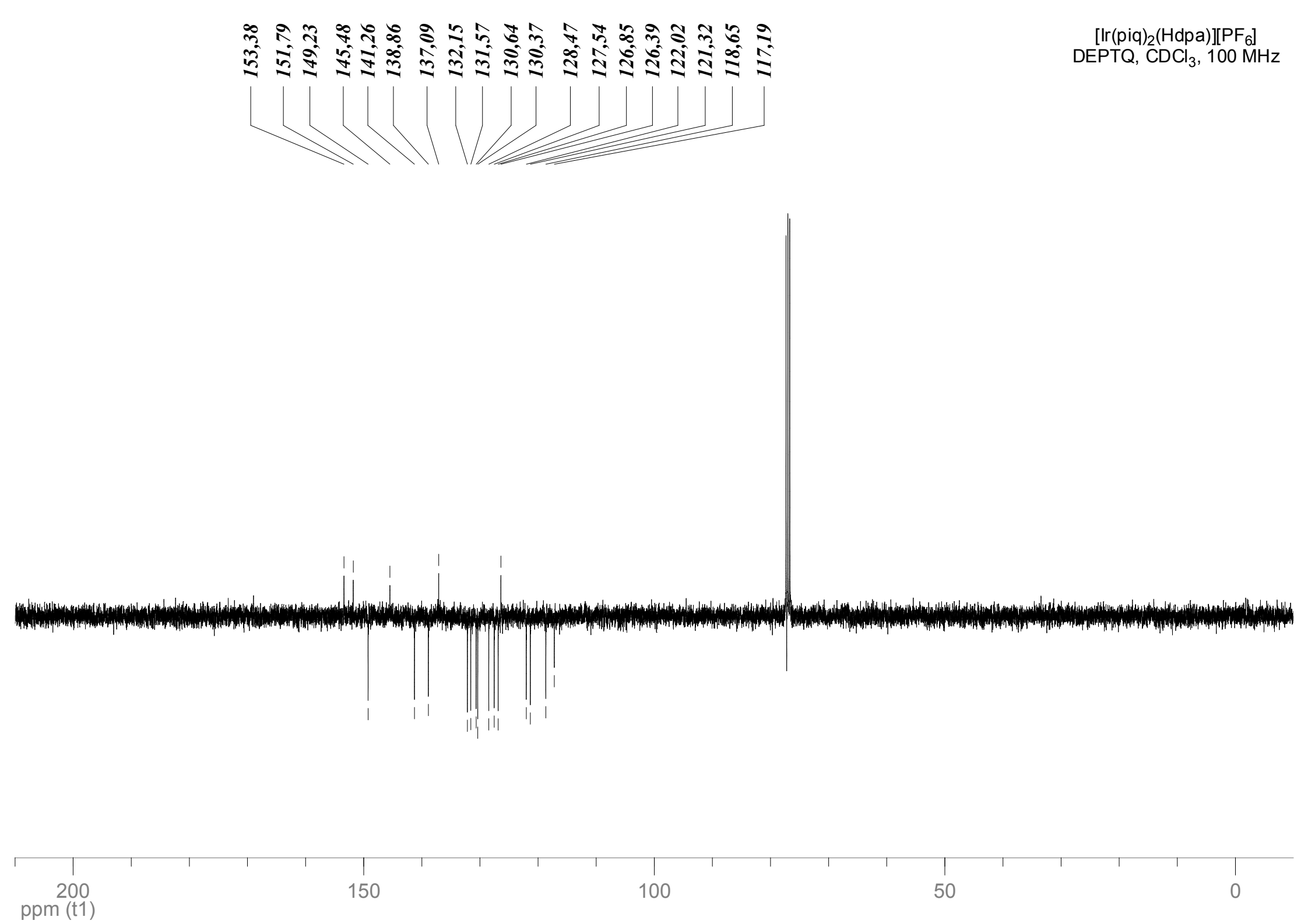

9,59
8,52
8,51
8,31
8,29
8,08
8,07
7,81
7,79
7,68
7,66
7,61
7,56
7,54
7,54
7,52
7,43
7,37
7,35
7,26
7,03
7,01
6,99
6,75
6,74
6,74
6,28
6,27
6,07
6,05
2,34
[Ir(bzq)2(4-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
1.29
2.00
2.14
2.22
2.60
2.20
1.94
2.00
1.81
6.06
10.0
5.0
0.0
ppm (t1)

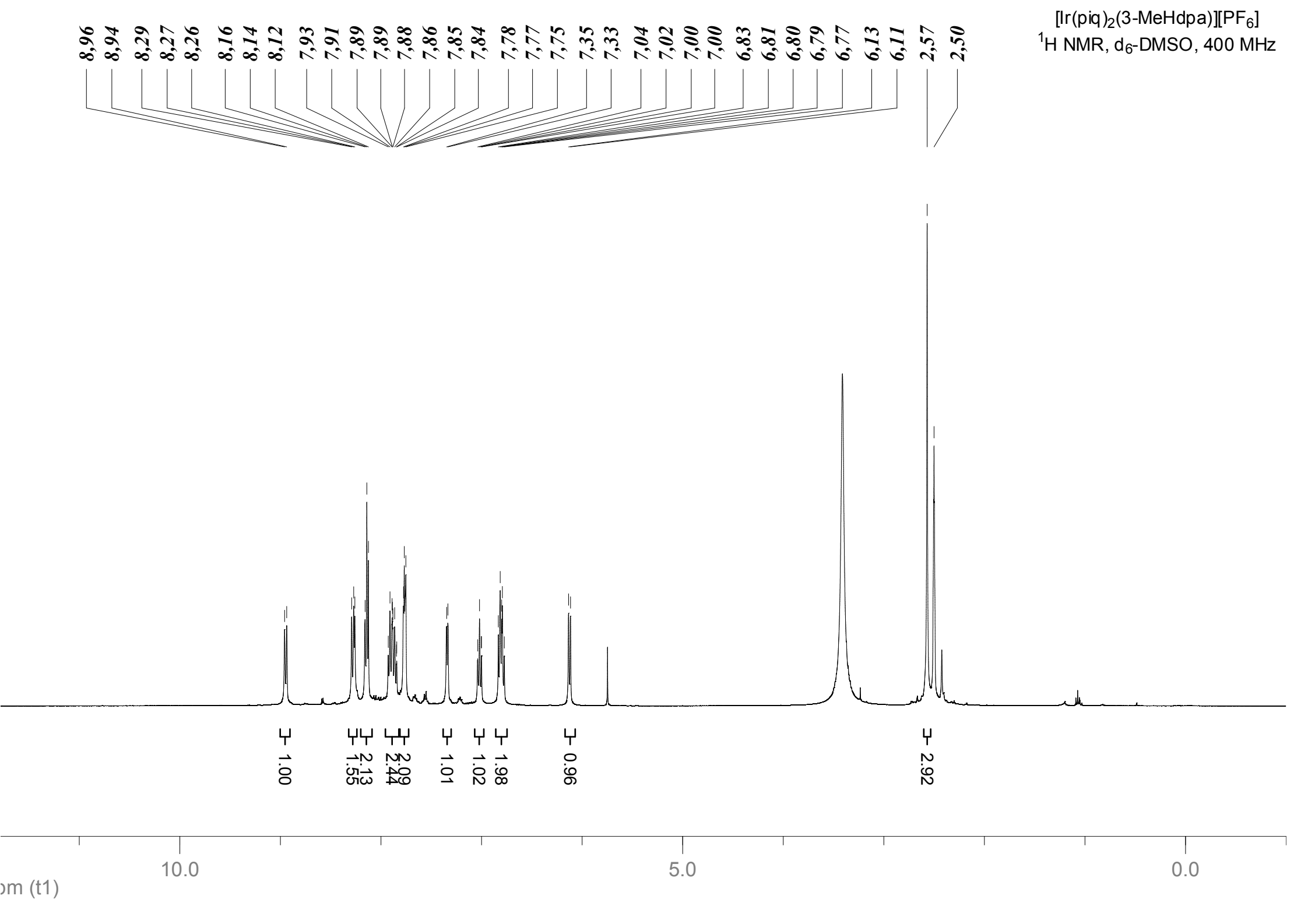

157,58
151,24
149,05
148,46
146,83
140,72
136,93
134,22
129,90
129,58
129,15
127,15
123,62
121,65
120,60
120,16
118,41
116,45
20,93
[Ir(bzq)2(4-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
200
150
100
50
0
ppm (t1)

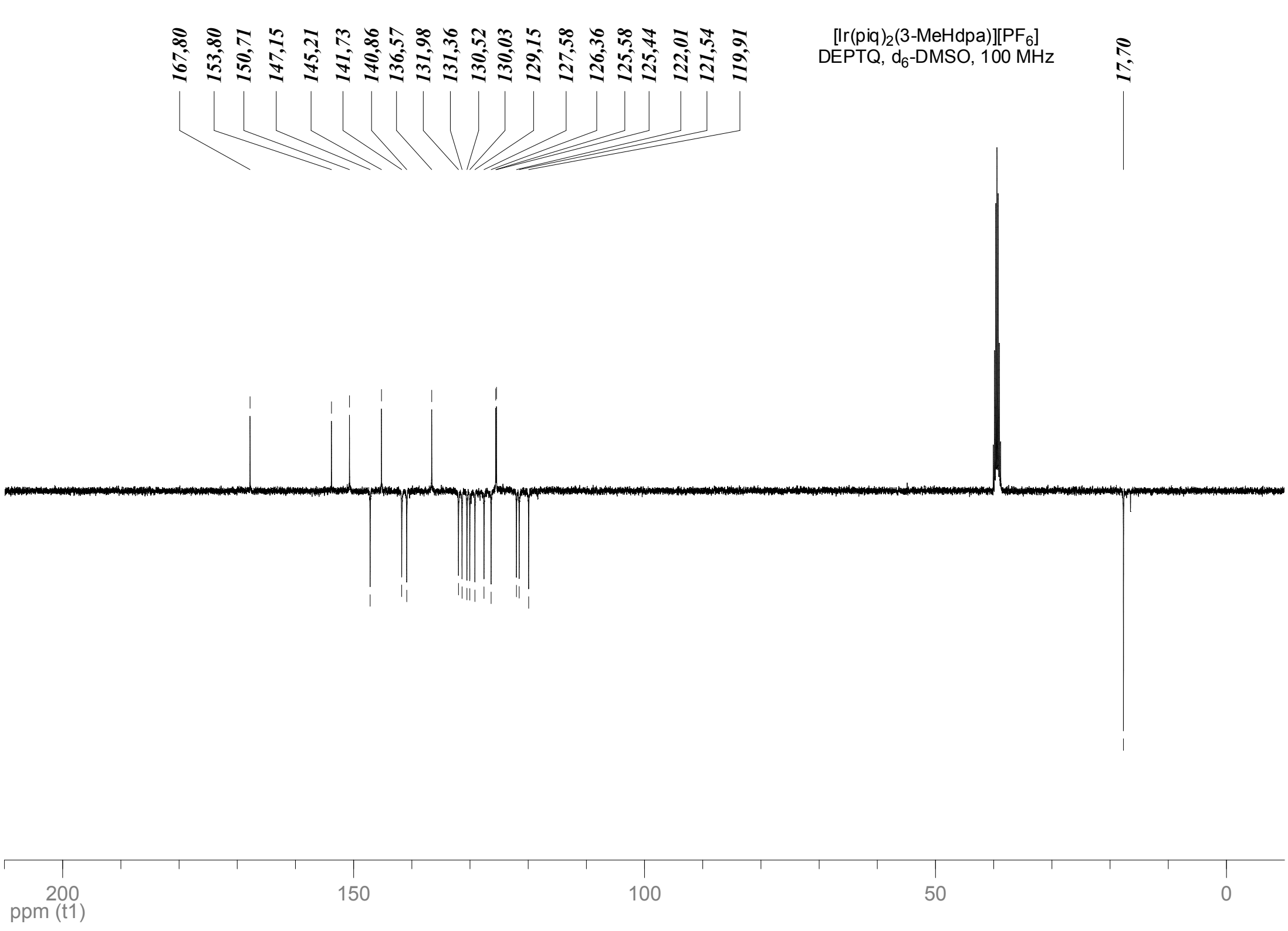

[Ir(bzq)2(5-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
9,65
9,65
9,64
9,64
9,64
9,64
9,64
9,63
9,63
8,51
8,51
8,50
8,50
8,32
8,32
8,30
8,30
8,00
8,00
7,82
7,80
7,70
7,68
7,68
7,66
7,57
7,56
7,55
7,54
7,54
7,53
7,52
7,38
7,36
7,04
7,02
7,00
6,08
6,06
1,72
0.53
1.00
1.05
0.89
1.31
2.41
2.66
2.16
1.38
0.96
2.76
10.0
5.0
0.0
ppm (t1)

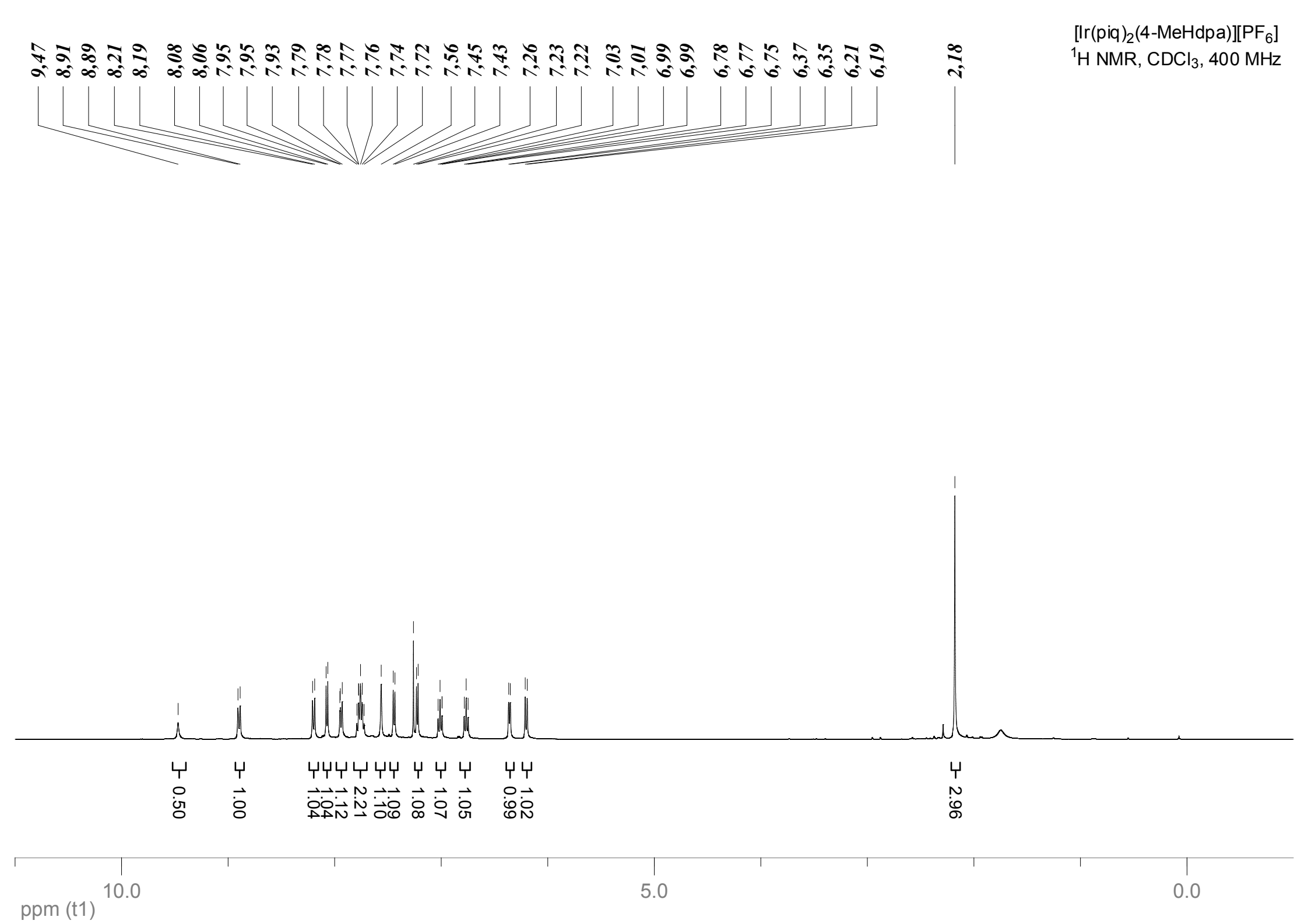

157,41
149,92
148,87
148,43
146,58
140,57
140,21
136,97
134,12
129,82
129,49
129,03
127,92
127,12
123,60
121,71
120,19
115,84
17,22
[Ir(bzq)2(5-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
200
150
100
50
0
ppm (t1)

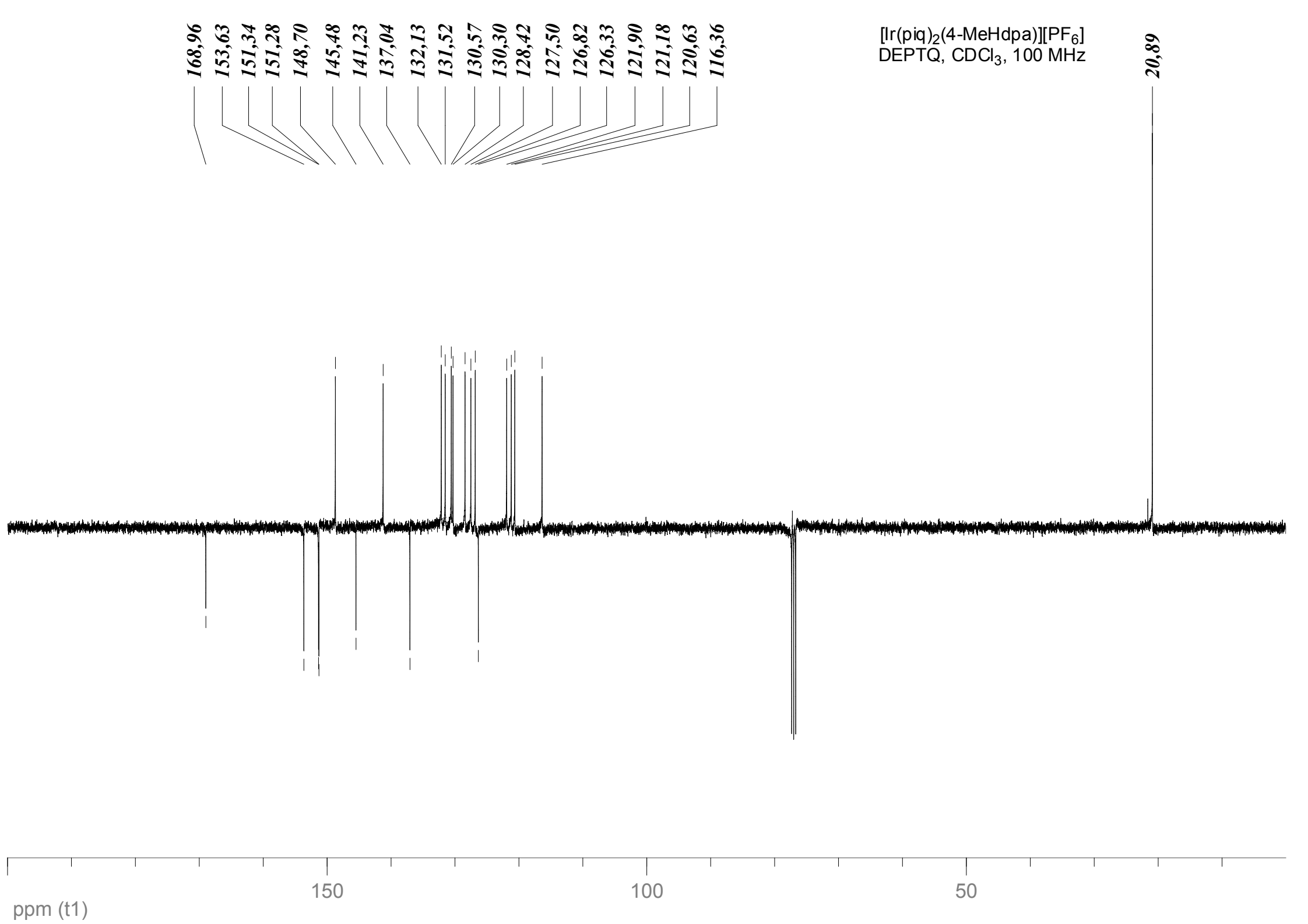

8,22
8,20
8,14
8,14
8,13
8,13
8,13
8,13
8,13
8,12
8,12
8,12
8,12
8,11
8,11
8,11
8,10
8,08
7,96
7,94
7,81
7,79
7,77
7,77
7,75
7,74
7,60
7,60
7,60
7,60
7,58
7,57
7,57
7,56
7,46
7,44
7,37
7,36
7,26
7,04
7,03
7,01
7,01
6,80
6,78
6,76
6,52
6,51
6,49
6,22
6,20
[Ir(piq)2(Hdpa)][PF6]
1H NMR, CDCl3, 400 MHz
0.72
1.00
1.06
1.07
1.03
2.16
1.19
1.16
1.09
1.04
1.01
10.0
5.0
0.0
ppm (t1)

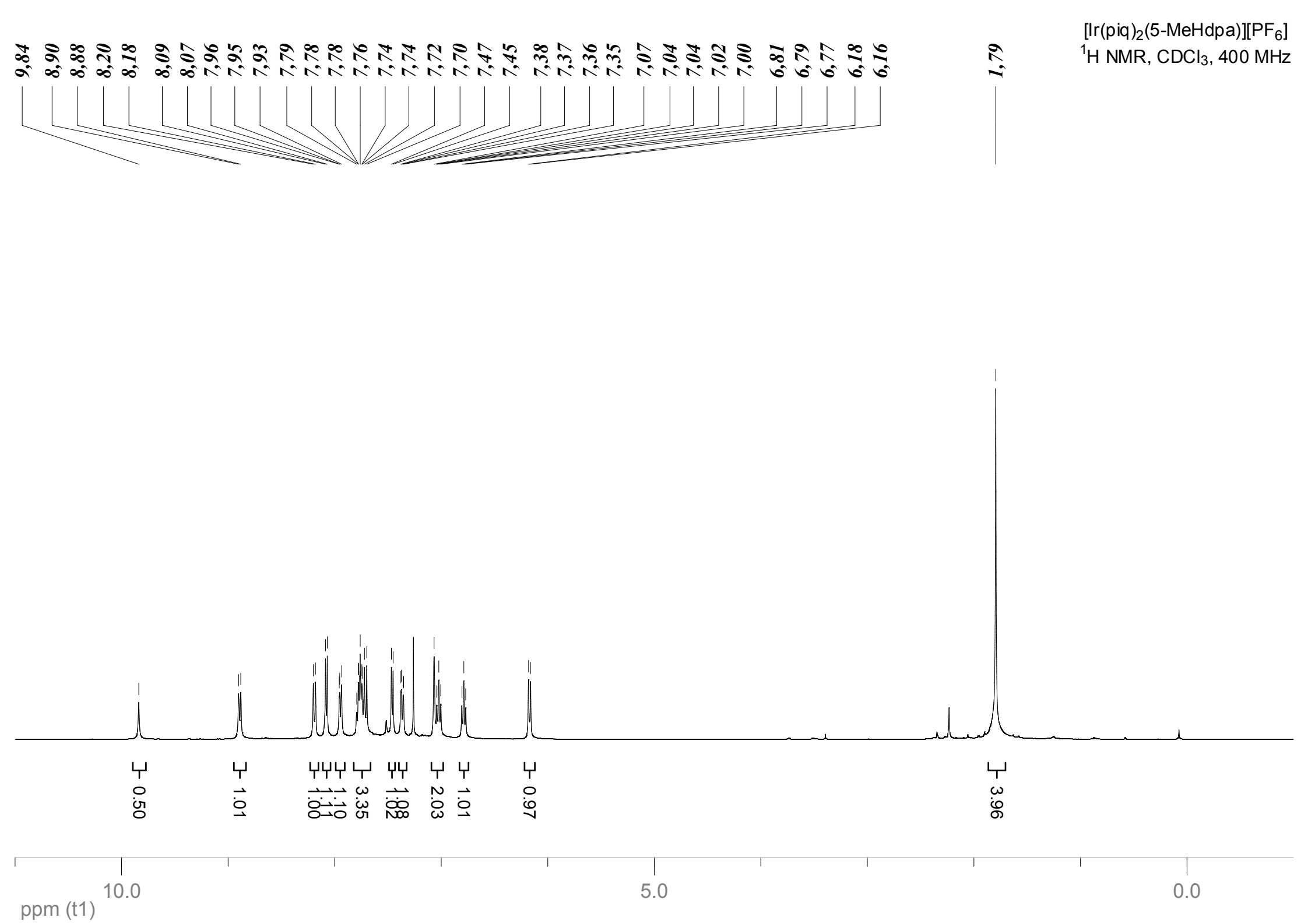

153,38
151,79
149,23
145,48
141,26
138,86
137,09
132,15
131,57
130,64
130,37
128,47
127,54
126,85
126,39
122,02
121,32
118,65
117,19
[Ir(piq)2(Hdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
200
150
100
50
0
ppm (t1)

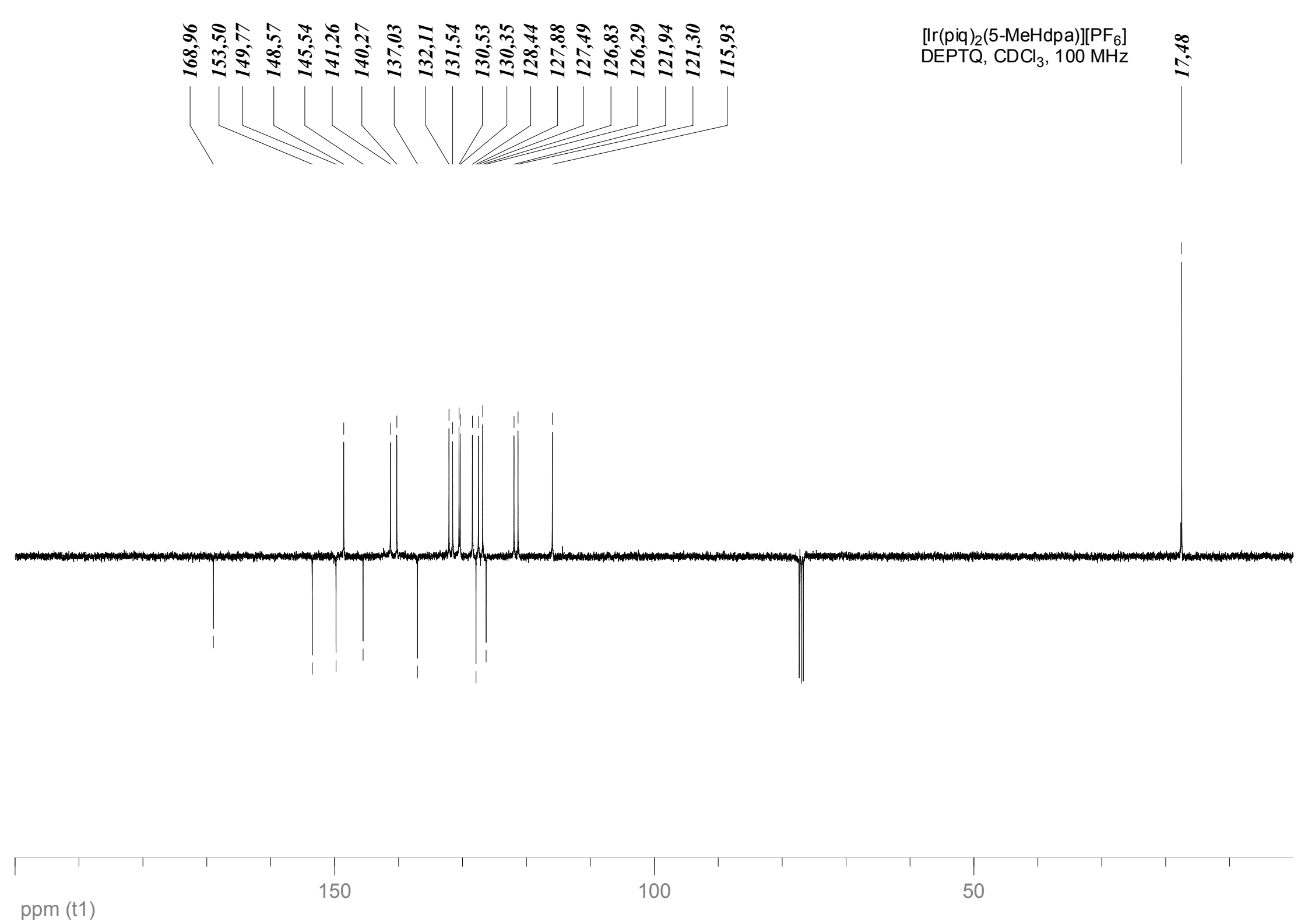

[Ir(piq)2(3-MeHdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
8,96
8,94
8,29
8,27
8,26
8,16
8,14
8,12
7,93
7,91
7,89
7,89
7,88
7,86
7,85
7,84
7,78
7,77
7,75
7,35
7,33
7,04
7,02
7,00
7,00
6,83
6,81
6,80
6,79
6,77
6,13
6,11
2,57
2,50
1.00
2.13
1.55
2.09
2.44
1.01
1.02
1.98
0.96
2.92
10.0
5.0
0.0
pm (t1)

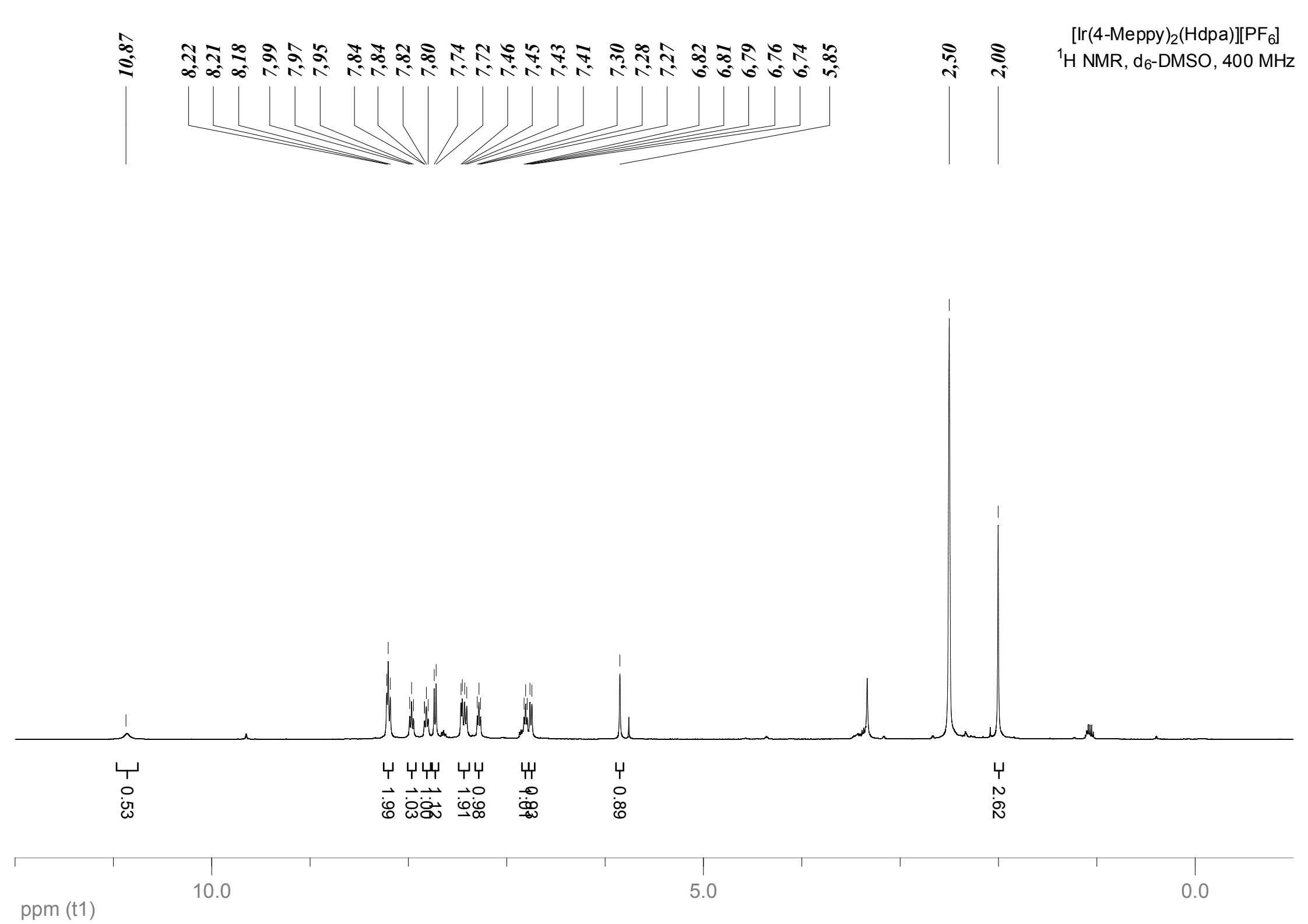

167,80
153,80
150,71
147,15
145,21
141,73
140,86
136,57
131,98
131,36
130,52
130,03
129,15
127,58
126,36
125,58
125,44
122,01
121,54
119,91
17,70
[Ir(piq)2(3-MeHdpa)][PF6]
DEPTQ, d6-DMSO, 100 MHz
200
150
100
50
0
ppm (t1)

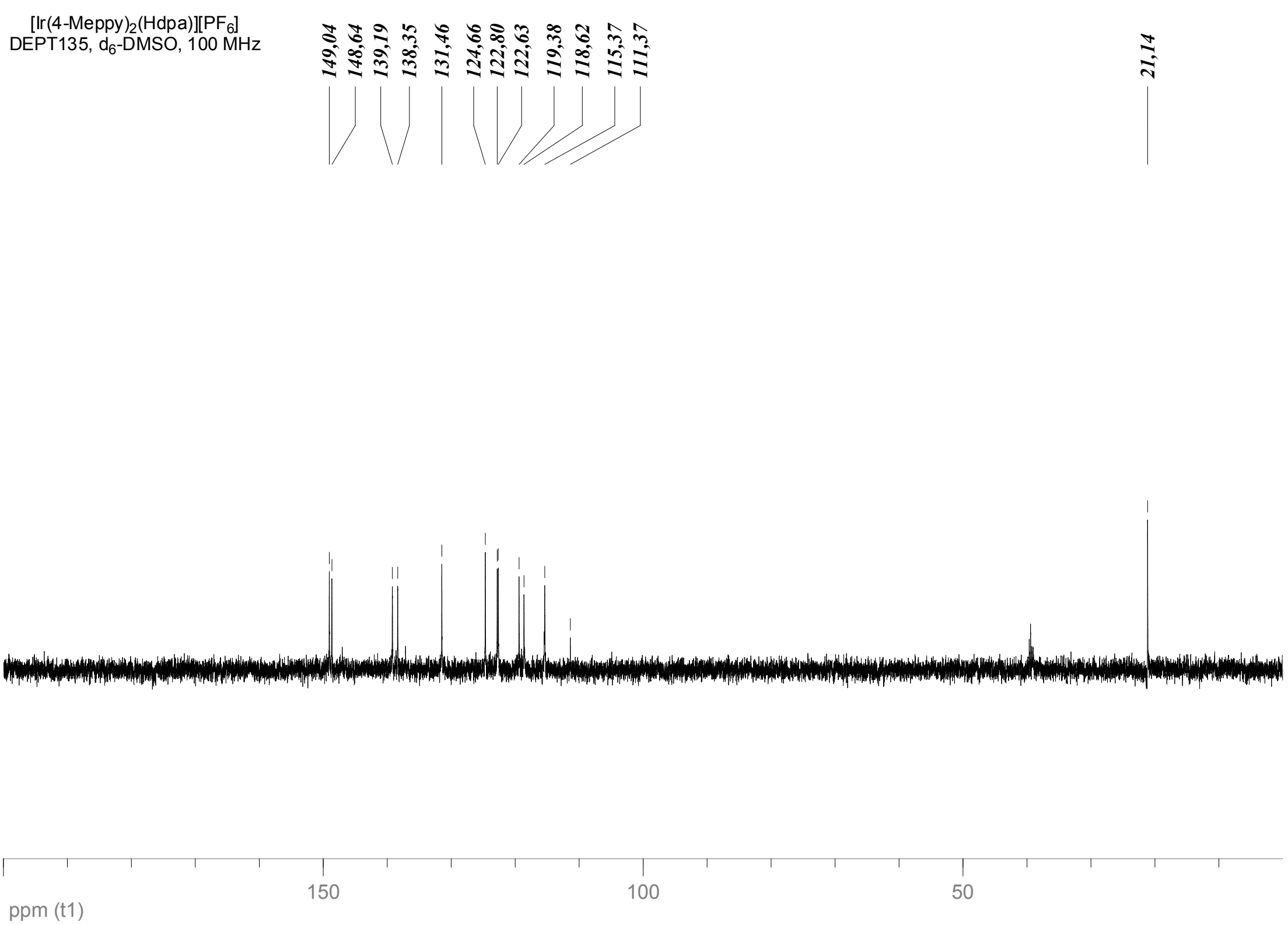

[Ir(piq)2(4-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
9,47
8,91
8,89
8,21
8,19
8,08
8,06
7,95
7,95
7,93
7,79
7,78
7,77
7,76
7,74
7,72
7,56
7,45
7,43
7,26
7,23
7,22
7,03
7,01
6,99
6,99
6,78
6,77
6,75
6,37
6,35
6,21
6,19
2,18
0.50
1.00
1.04
1.04
1.12
2.21
1.10
1.09
1.08
1.07
1.05
0.99
1.02
2.96
10.0
5.0
0.0
ppm (t1)

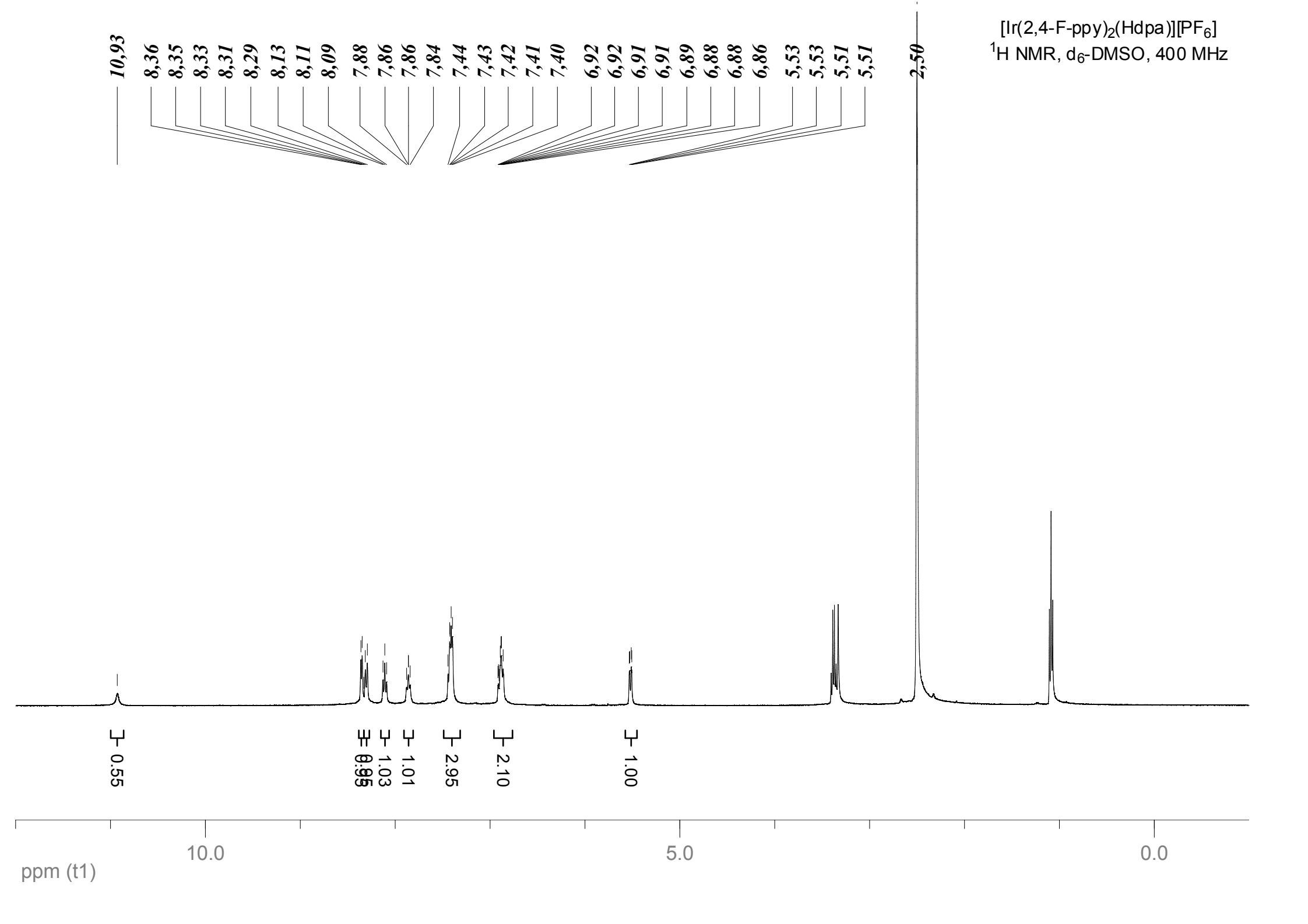

168,96
153,63
151,34
151,28
148,70
145,48
141,23
137,04
132,13
131,52
130,57
130,30
128,42
127,50
126,82
126,33
121,90
121,18
120,63
116,36
20,89
[Ir(piq)2(4-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
150
100
50
ppm (t1)

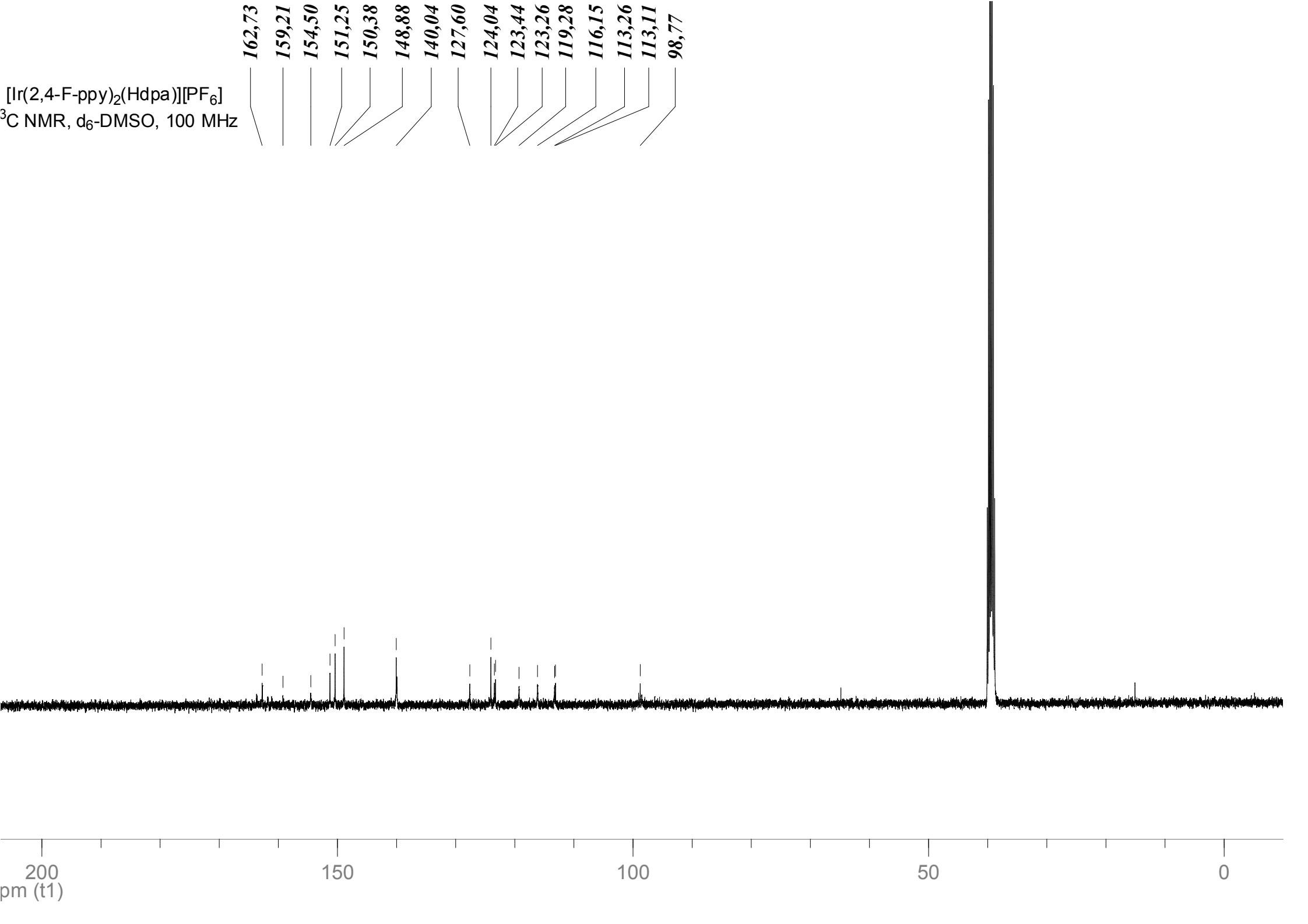

[Ir(piq)2(5-MeHdpa)][PF6]
1H NMR, CDCl3, 400 MHz
9,84
8,90
8,88
8,20
8,18
8,09
8,07
7,96
7,95
7,93
7,79
7,78
7,78
7,76
7,74
7,74
7,72
7,70
7,47
7,45
7,38
7,37
7,36
7,35
7,07
7,04
7,04
7,02
7,00
6,81
6,79
6,77
6,18
6,16
1,79
0.50
1.01
1.00
1.11
1.10
3.35
1.02
1.08
2.03
1.01
0.97
3.96
10.0
5.0
0.0
ppm (t1)

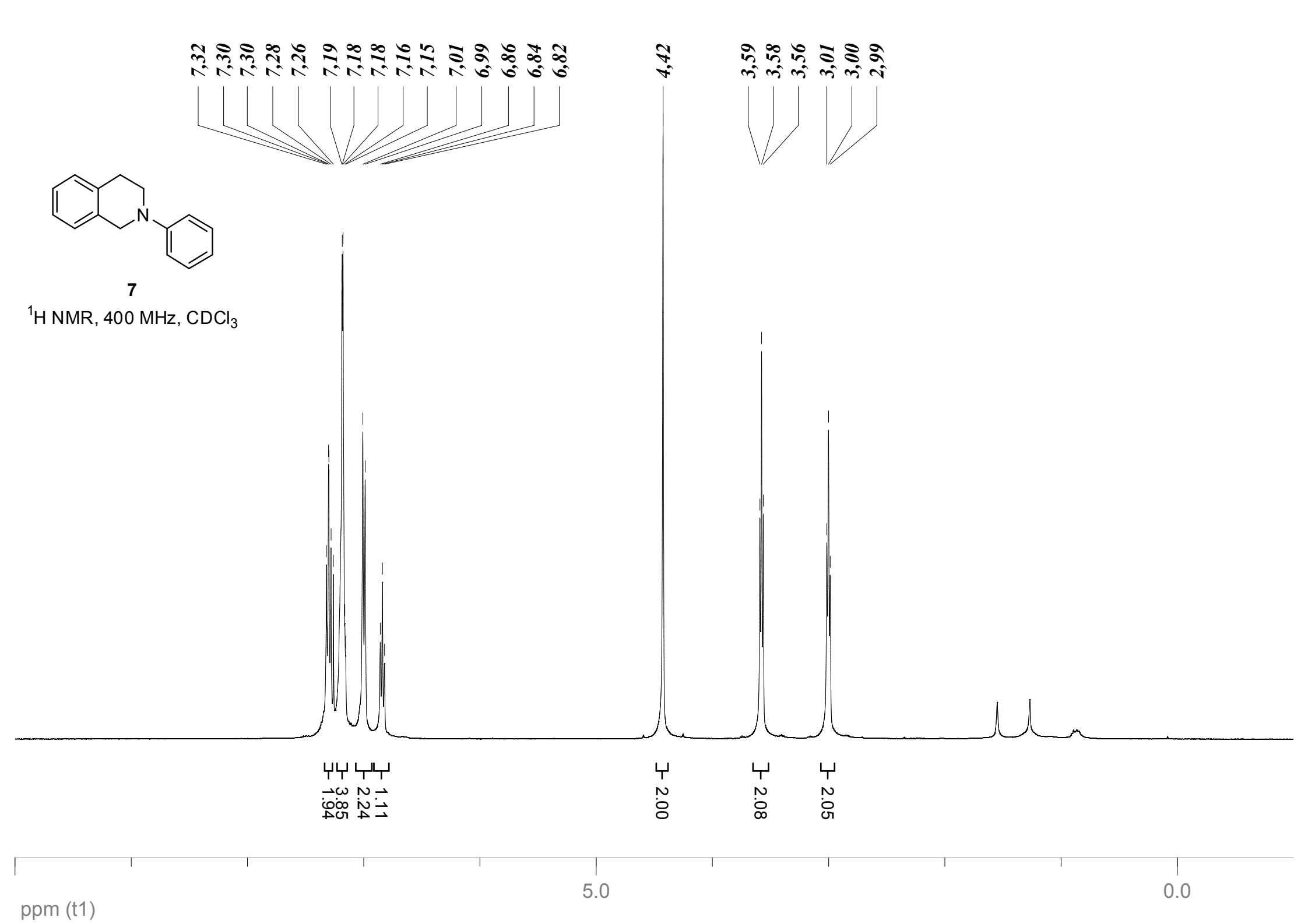

168,96
153,50
149,77
148,57
145,54
141,26
140,27
137,03
132,11
131,54
130,53
130,35
128,44
127,88
127,49
126,83
126,29
121,94
121,30
115,93
17,48
[Ir(piq)2(5-MeHdpa)][PF6]
DEPTQ, CDCl3, 100 MHz
150
100
50
ppm (t1)

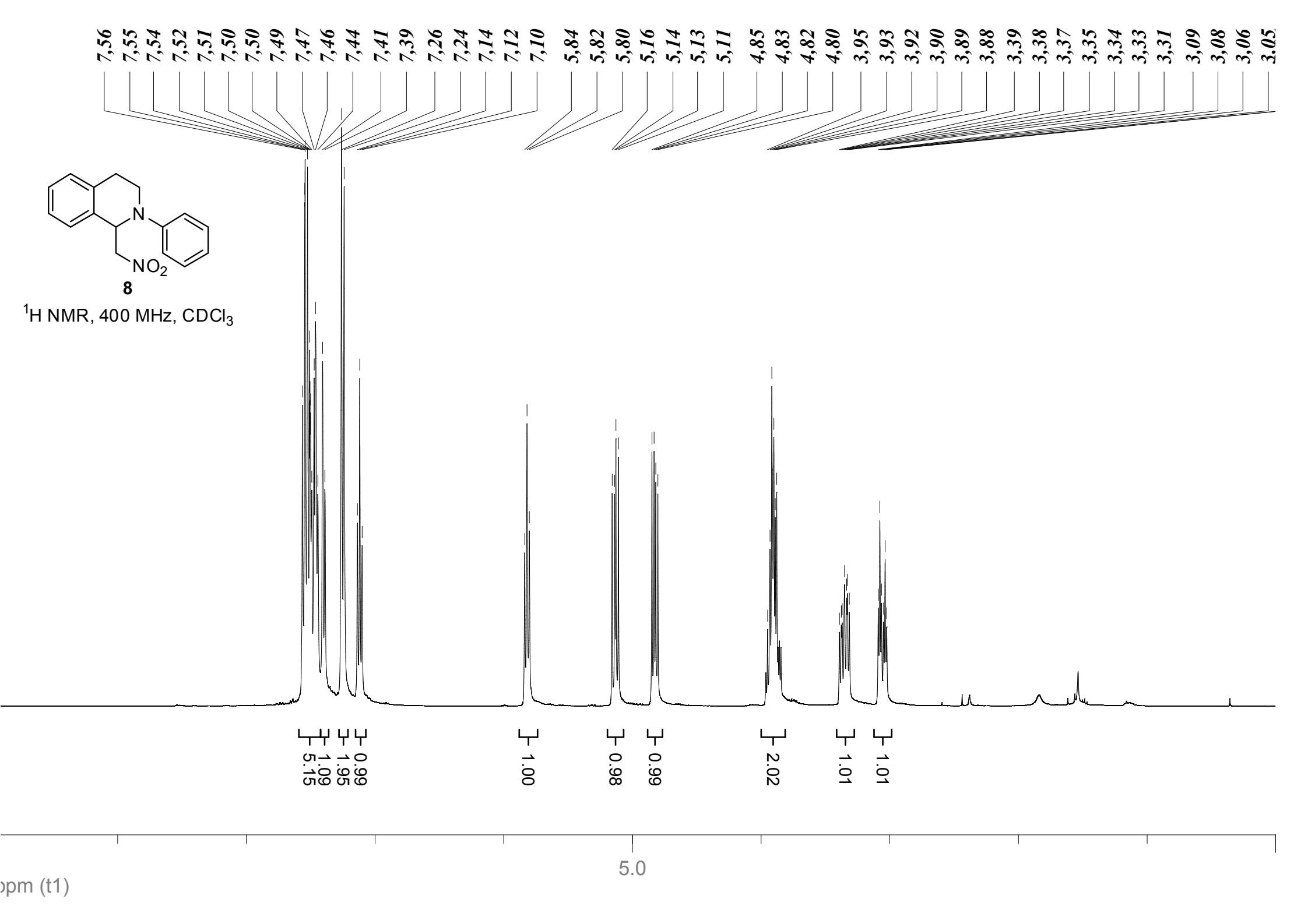

[Ir(4-Meppy)2(Hdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
10,87
8,22
8,21
8,18
7,99
7,97
7,95
7,84
7,84
7,82
7,80
7,74
7,72
7,46
7,45
7,43
7,41
7,30
7,28
7,27
6,82
6,81
6,79
6,76
6,74
5,85
2,50
2,00
0.53
1.99
1.03
0.98
1.91
0.89
2.62
10.0
5.0
0.0
ppm (t1)


[Ir(4-Meppy)2(Hdpa)][PF6]
DEPT135, d6-DMSO, 100 MHz
149,04
148,64
139,19
138,35
131,46
124,66
122,80
122,63
119,38
118,62
115,37
111,37
21,14
150
100
50
ppm (t1)


[Ir(2,4-F-ppy)2(Hdpa)][PF6]
1H NMR, d6-DMSO, 400 MHz
10,93
8,36
8,35
8,33
8,31
8,29
8,13
8,11
8,09
7,88
7,86
7,86
7,84
7,44
7,43
7,42
7,41
7,40
6,92
6,92
6,91
6,91
6,89
6,88
6,88
6,86
5,53
5,53
5,51
5,51
2,50
0.55
1.03
1.01
2.95
2.10
1.00
10.0
5.0
0.0
ppm (t1)


[Ir(2,4-F-ppy)2(Hdpa)][PF6]
13C NMR, d6-DMSO, 100 MHz
162,73
159,21
154,50
151,25
150,38
148,88
140,04
127,60
124,04
123,44
123,26
119,28
116,15
113,26
113,11
98,77
200
150
100
50
0
ppm (t1)


7,32
7,30
7,30
7,28
7,26
7,19
7,18
7,18
7,16
7,15
7,01
6,99
6,86
6,84
6,82
4,42
3,59
3,58
3,56
3,01
3,00
2,99
N
7
1H NMR, 400 MHz, CDCl3
1.94
3.85
2.24
1.11
2.00
2.08
2.05
5.0
0.0
ppm (t1)


7,56
7,55
7,54
7,52
7,51
7,50
7,50
7,49
7,47
7,46
7,44
7,41
7,39
7,26
7,24
7,14
7,12
7,10
5,84
5,82
5,80
5,16
5,14
5,13
5,11
4,85
4,83
4,82
4,80
3,95
3,93
3,92
3,90
3,89
3,88
3,39
3,38
3,37
3,35
3,34
3,33
3,31
3,09
3,08
3,06
3,05
N
NO2
8
1H NMR, 400 MHz, CDCl3
5.15
1.09
1.95
0.99
1.00
0.98
0.99
2.02
1.01
1.01
5.0
ppm (t1)