Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Materials for

Fluoride, Bifluoride and Trifluoromethyl Complexes of Iridium(I) and Rhodium(I)

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This PDF file includes:

Other Supplementary Materials for this manuscript includes the following:

X-ray crystallographic data for complexes ‡CCDC-1000750 (**1**), 1000751 (**3**), 1000752 (**5**), 1001354 (**6**), 1000753 (**7**), 1000754 (**8**), 1000755 (**9**), 1000756 (**11**), 1000757 (**13**).

GENERAL CONSIDERATIONS

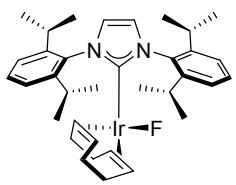
All manipulations and reactions were performed inside an Argon-filled Innovative Technologies glovebox or on an Argon-supplied Schlenk line unless stated otherwise. All reagents were supplied by Aldrich and used without further purification. Solvents were distilled and dried as required. NMR data was obtained using either a Bruker 300, 400 or 500 MHz spectrometer at 303 K (unless stated otherwise) in the specified deuterated solvent. All chemical shifts are given in ppm and coupling constants in Hz. Signals on the $^{13}C\{^{1}H\}$ NMR spectra are singlets unless otherwise stated. Spectra were referenced to residual protonated solvent signals (for ^{1}H) or solvent signals (for ^{13}C): (C_6D_6: ^{1}H δ 7.16 ppm, ^{13}C δ 128.06 ppm, CD_2Cl_2 ^{1}H δ 5.32 ppm, ^{13}C δ 53.84 ppm). Infrared spectra (ν) were recorded on a Shimadzu Fourier transform IR Affinity-1 Infrared spectrometer using a MIRacle^{TM} single reflection horizontal ATR (diamond). Samples were placed directly on the crystal (ATR) in the solid state. Only characteristic peaks have been quoted. Elemental analyses were performed at the London Metropolitan University. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Known compounds were prepared acoording to literature procedures: [M(cod)(NHC)Cl] (M = Rh/Ir) were prepared from $[M(cod)Cl]_2$ and the free NHC or $[Ag(NHC)Cl]_2$ according to reported procedures.[1]

[Ir(cod)(NHC)(OH)] complexes were prepared according to reported procedures.[2]

[Rh(cod)(NHC)(OH)] complexes were prepared according to reported procedures.[3]

SYNTHETIC PROCEDURES AND CHARACTERISATION DATA



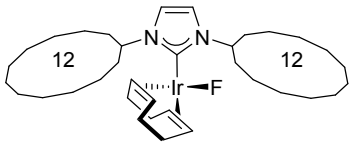
[Ir(cod)(IPr)(F)] **1**

Method A: A vial was charged with [Ir(cod)(IPr)(Cl)] (50 mg, 0.071 mmol) and AgF (43.8 mg, 0.35 mmol) in CH_2Cl_2 (1 mL) and the reaction mixture was stirred at rt in the

dark for 16 h. Once complete, pentane (1 mL) was added to the mixture and left to stand for 10 mins. The reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL), taken up in a mixture of THF (0.2 mL) and pentane (1 mL) and filtered through a PTFE syringe filter (0.2 μm) to remove residual Ag compounds. The product was dried *in vacuo* to give [Ir(cod)(IPr)(F)] (**1**) (45 mg, 90%) as a yellow solid.

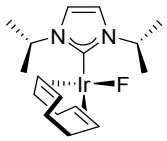
Method B: A vial was charged with [Ir(cod)(IPr)(OH)] (20 mg, 0.028 mmol) and KHF_2 (6.6 mg, 0.085 mmol) in THF (1 mL) and the reaction mixture was stirred at rt for 5 h. Once complete, the reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL) and dried *in vacuo* to give [Ir(cod)(IPr)(F)] (**1**) (20 mg, 99%) as a yellow solid.

Method C: A Schlenk tube was charged with [Ir(cod)(IPr)(OH)] (50 mg, 0.071 mmol) in benzene (1 mL). $NEt_3.3HF$ (4.0 μL, 0.024 mmol) was added under Ar and the reaction mixture was stirred at rt for 4.5 h. The product was reduced *in vacuo* and azeotroped with hexane (2 x 2 mL) to give a yellow solid. The solid was washed with hexane (2 x 1 mL) and dried *in vacuo* to give [Ir(cod)(IPr)(F)] (**1**) (35 mg, 70%) as a yellow solid. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.51 (t, 2H, $^3J_{HH}$ = 7.7, *p*-ArH), 7.34 (d, 4H, $^3J_{HH}$ = 7.7, *m*-ArH), 7.02 (s, 2H, N-(C*H*)$_2$-N), 4.02 – 3.92 (m, 2H, cod-CH), 2.95 (sept., 4H, $^3J_{HH}$ = 6.8, C*H*$(CH_3)_2$), 2.64 – 2.58 (m, 2H, cod-CH), 1.73 – 1.64 (m, 2H, cod-CH_2), 1.59 – 1.49 (m, 2H, cod-CH_2), 1.37 (d, 12H, $^3J_{HH}$ = 6.7, CH_3), 1.28 – 1.18 (m, 4H, cod-CH_2), 1.10 (d, 12H, $^3J_{HH}$ = 6.8, CH_3). **^{19}F NMR** (282 MHz, C_6D_6): δ -221 (br.). **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 183.6 (Ir-$C_{carbene}$), 146.9 (ArC), 136.3 (ArC), 129.9 (ArCH), 124.4 (ArCH), 123.9 (N-(*C*H)$_2$-N), 83.3 (d, $^2J_{FC}$ = 4, cod-CH), 45.0 (d, $^2J_{FC}$ = 4, cod-CH), 34.2 (cod-CH_2), 29.1 (*C*H$(CH_3)_2$), 28.4 (cod-CH_2), 26.3 (CH_3), 22.8 (CH_3). **FTIR (ATR)** ν = 800.5 (s), 756.1 (s) cm^{-1}. **Anal. Calcd.** for $C_{35}H_{48}FIrN_2$ (MW 707.98): C, 59.38; H, 6.83; N, 3.96. Found: C, 59.38; H, 6.97; N, 4.01.



[Ir(cod)(IDD)(F)] **2**

A vial was charged with [Ir(cod)(IDD)(Cl)] (50.0 mg, 0.068 mmol) and AgF (43.0 mg, 0.34 mmol) in CH_2Cl_2 (1 mL) and the reaction mixture was stirred at rt in the dark for 16 h. Once complete, pentane (1 mL) was added to the mixture and left to stand for 10 mins. The reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL), taken up in a mixture of THF (0.2 mL) and pentane (1 mL) and filtered through a PTFE syringe filter (0.2 μm) to remove residual Ag compounds. The product was dried *in vacuo* to give [Ir(cod)(IDD)(F)] (**2**) (48 mg, 98%) as a yellow solid. **^{1}H NMR** (400 MHz, C_6D_6): δ 6.43 (s, 2H, N-(C*H*)$_2$-N), 5.78 – 5.68 (m, 2H, N-C*H*(IDD)), 5.04 – 4.96 (m, 2H, cod-CH), 2.97 – 2.90 (m, 2H, cod-CH), 2.60 – 2.39 (m, 4H, cod-CH_2), 2.17 – 2.03 (m, 2H, IDD-CH_2), 2.00 – 1.84 (m, 4H, cod-CH_2), 1.83 – 1.61 (m, 12H, IDD-CH_2), 1.52 – 1.17 (m, 30H, IDD-CH_2). **^{19}F{^{1}H} NMR** (470 MHz, C_6D_6): δ -219.7 (s). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 182.0 (Ir-$C_{carbene}$), 117.0 (N-(*C*H)$_2$-N), 84.3 (cod-CH), 56.8 (cod-CH), 43.3 (N-*C*H$(CH_3)_2$), 35.1 (cod-CH_2), 32.5, 31.7, 29.5, 25.3, 25.1, 24.1, 23.8, 23.7, 23.5, 23.4, 23.3, 22.4. **Anal. Calcd.** for $C_{35}H_{60}FIrN_2$ (MW 720.09): C, 58.38; H, 8.40; N, 3.89. Found: C, 58.44; H, 8.48; N, 3.91.



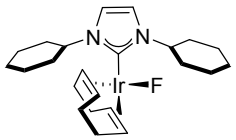
[Ir(cod)(I^{i}Pr)(F)] **3**

<u>*Method A:*</u> A vial was charged with [Ir(cod)(I^{i}Pr)(Cl)] (50.0 mg, 0.102 mmol) and AgF (65.0 mg, 0.512 mmol) in CH_2Cl_2 (1 mL) and the reaction mixture was stirred at rt in the dark for 16 h. Once complete, pentane (1 mL) was added to the mixture and left to stand for 10 mins. The reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL), taken up in a mixture of THF (0.2 mL) and pentane (1 mL) and filtered through a PTFE syringe filter

(0.2 μm) to remove residual Ag compounds. The product was dried *in vacuo* to give [Ir(cod)(I^{i}Pr)(F)] (**3**) (47 mg, 98%) as a yellow solid.

Method B: A vial was charged with [Ir(cod)(I^{i}Pr)(OH)] (20 mg, 0.043 mmol) and KHF_2 (10.0 mg, 0.13 mmol) in THF (1 mL) and the reaction mixture was stirred at rt for 5 h. Once complete, the reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL) and dried *in vacuo* to give [Ir(cod)(I^{i}Pr)(F)] (**3**) (15 mg, 74%) as a yellow solid.

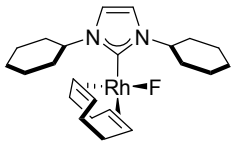
Method C: A Schlenk tube was charged with [Ir(cod)(I^{i}Pr)(OH)] (100 mg, 0.213 mmol) in benzene (1 mL). $NEt_3.3HF$ (12 μL, 0.07 mmol) was added under Ar and the reaction mixture was stirred at rt for 4.5 h. The product was reduced *in vacuo* and azeotroped with hexane (2 x 2 mL) to give a yellow solid. The solid was washed with pentane (3 x 1 mL) and dried to give [Ir(cod)(I^{i}Pr)(F)] (**3**) (97.9 mg, 97%) as a yellow solid. **^{1}H NMR** (300 MHz, C_6D_6): δ 6.28 (s, 2H, N-(C*H*)$_2$-N), 5.80 (sept., 2H, $^3J_{HH}$ = 6.8, N-C*H*$(CH_3)_2$), 5.10 – 4.97 (m, 2H, cod-CH), 2.96 – 2.87 (m, 2H, cod-CH), 2.45 – 2.22 (m, 4H, cod-CH_2), 1.80 – 1.58 (m, 4H, cod-CH_2), 1.21 (app. d, 6H, $^3J_{HH}$ = 6.4 CH_3), 1.11 (app. d, 6H, $^3J_{HH}$ = 6.8, CH_3). **^{19}F NMR** (282 MHz, C_6D_6): δ -227 (br). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6): δ 180.7 (Ir-$C_{carbene}$), 116.2 (N-(*C*H)$_2$-N), 84.4 (cod-CH), 52.5 (cod-CH), 43.8 (N-*C*H$(CH_3)_2$), 34.9 (cod-CH_2), 29.5 (cod-CH_2), 24.3 (CH_3), 23.0 (CH_3). **FTIR (ATR)** ν = 1413.8 (s), 1211.3 (s), 881.5 (w) cm^{-1}. **Anal. Calcd.** for $C_{17}H_{28}FIrN_2$ (MW 471.63): C, 43.29; H, 5.98; N, 5.94. Found: C, 43.23; H, 6.05; N, 6.05.



[Ir(cod)(ICy)(F)] **4**

A vial was charged with [Ir(cod)(ICy)(Cl)] (50 mg, 0.088 mmol) and AgF (56 mg, 0.44 mmol) in CH_2Cl_2 (1 mL) and the reaction mixture was stirred at rt in the dark for 16 h. Once complete, pentane (1 mL) was added to the mixture and left to stand for 10 mins. The reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL), taken up in a mixture of THF (0.2 mL) and pentane (1 mL) and filtered through a PTFE syringe filter (0.2 μm)

to remove residual Ag compounds. The product was dried *in vacuo* to give [Ir(cod)(ICy)(F)] (**4**) (44 mg, 90%) as a yellow solid. **^{1}H NMR** (300 MHz, C_6D_6): δ 6. 35 (s, 2H, N-(C*H*)$_2$-N), 5.46 (tt, 2H, $^3J_{HH}$ = 11.7, 3.6 N-C*H*(ICy)), 5.02 – 4.92 (m, 2H, cod-CH), 3.00 – 2.89 (m, 2H, cod-CH), 2.51 – 2.23 (m, 6H, cod-CH_2, ICy-CH_2), 1.94 – 1.81 (m, 2H, ICy-CH_2), 1.81 – 1.02 (m, 18H, ICy-CH_2), 1.02 – 0.80 (m, 2H, ICy-CH_2). **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6): δ -227 (s). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6): δ 181.2 (Ir-$C_{carbene}$), 116.6 (N-(*C*H)$_2$-N), 84.1 (cod-CH), 60.3 (cod-CH), 43.8 (N-*C*H(CH_3)$_2$), 35.1 (cod-CH_2), 34.4 (ICy-CH_2), 29.7 (cod-CH_2), 26.3, 25.7, 22.7, 14.3 (ICy-CH_2). **Anal. Calcd.** for $C_{23}H_{36}FIrN_2$ (MW 551.77): C, 50.07; H, 6.58; N, 5.08. Found: C, 49.96; H, 6.65; N, 5.12.

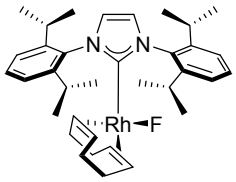


[Rh(cod)(ICy)F] **5**

Method A: A vial was charged with [Rh(cod)(ICy)(OH)] (20 mg, 0.032 mmol) and KHF_2 (8.0 mg, 0.10 mmol) in THF (1 mL) and the reaction mixture was stirred at rt for 5 h. Once complete, the reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL) and dried *in vacuo* to give [Rh(cod)(ICy)(F)] (**5**) (16 mg, 81%) as a yellow solid.

Method B: A Schlenk tube was charged with [Rh(cod)(ICy)OH] (50 mg, 0.11 mmol) in benzene (1 mL). NEt_3.3HF (6.0 µL, 0.036 mmol) was added under Ar and the reaction mixture was stirred at rt for 3.5 h. The product was reduced *in vacuo* and azeotroped with hexane (2 x 2 mL) to give a yellow solid. The solid was washed with pentane (2 x 1 mL) and dried to give [Rh(cod)(ICy)(F)] (**5**) (43 mg, 86%) as a yellow solid. **^{1}H NMR** (500 MHz, C_6D_6): δ 6.39 (s, 2H, N-(C*H*)$_2$-N), 5.69 – 5.56 (m, 2H, NCH), 5.38 – 5.26 (m, 2H, cod-CH), 3.14 – 3.04 (m, 2H, cod-CH), 2.69 – 2.51 (m, 2H, ICy-CH_2), 2.52 – 2.29 (m, 4H, cod-CH_2), 1.96 – 1.80 (m, 4H, cod-CH_2), 1.80 – 1.71 (m, 2H, ICy-CH_2), 1.71 – 1.58 (m, 4H, ICy-CH_2), 1.57 – 1.05 (m, 10H, ICy-CH_2), 1.05 – 0.85 (m, 2H, ICy-CH_2). **^{19}F{^{1}H} NMR** (470 MHz, C_6D_6): δ -257 (br, Rh-F). **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 181.0 (Rh-$C_{carbene}$, from HMBC), 117.4 (N-(*C*H)$_2$-N), 98.0 (br, cod-CH), 62.3 (br, cod-CH), 60.8 (N-$(CH)_2$-N), 35.1 (ICy-CH_2), 34.6 (ICy-CH_2), 33.7 (cod-CH_2), 28.7 (cod-

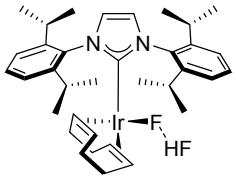
CH_2), 26.5 (ICy-CH_2), 26.4 (ICy-CH_2), 25.8 (ICy-CH_2). **FTIR (ATR)** ν = 706.0 (s), 1990.2 (w, br), 2924.1 (s) cm^{-1}. **Anal. Calcd.** for $C_{23}H_{36}FRhN_2$ (MW 462.45): C, 59.74; H, 7.85; N, 6.06. Found: C, 59.58; H, 7.66; N, 6.18.



[Rh(cod)(IPr)(F)] **6**

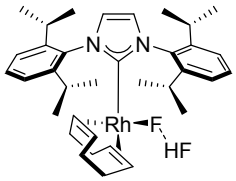
Method A: A Schlenk tube was charged with [Rh(cod)(IPr)(OH)] (50 mg, 0.081 mmol) in benzene (1 mL). NEt_3.3HF (4.5 µL, 0.027 mmol) was added under Ar and the reaction mixture was stirred at rt for 3.5 h. The product was reduced *in vacuo* and azeotroped with hexane (2 x 2 mL) to give a yellow solid. The solid was washed with hexane (2 x 1 mL) and dried to give [Rh(cod)(IPr)(F)] (**6**) (41.5 mg, 83%) as a yellow solid.

Method B: A vial was charged with [Rh(cod)(IPr)(OH)] (20 mg, 0.032 mmol) and KHF_2 (8.0 mg, 0.098 mmol) in THF (1 mL) and the reaction mixture was stirred at rt for 5 h. Once complete, the reaction mixture was filtered through celite and concentrated *in vacuo* to give a yellow solid. The solid was washed with cold pentane (3 x 1 mL) and dried *in vacuo* to give [Rh(cod)(IPr)(F)] (**6**) (15.5 mg, 78%) as a yellow solid. **^{1}H NMR** (300 MHz, C_6D_6): δ 7.33 (t, 2H, $^3J_{HH}$ = 7.6, *p*-ArH), 7.25 (d, 4H, $^3J_{HH}$ = 7.6, *m*-ArH), 6.57 (s, 2H, N-(C*H*)$_2$-N), 4.96 – 4.75 (m, 2H, cod-CH), 3.39 – 3.08 (m, 4H, C*H*$(CH_3)_2$), 3.04 – 2.85 (m, 2H, cod-CH), 1.99 – 1.76 (m, 4H, cod-CH_2), 1.52 (d, 12H, $^3J_{HH}$ = 6.7, CH_3), 1.45 – 1.20 (m, 4H, cod-CH_2), 1.05 (d, 12H, $^3J_{HH}$ = 6.9, CH_3). **^{19}F{^{1}H} NMR** (282 MHz, C_6D_6): δ -252.8 (d, $^1J_{RhF}$ = 77). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6): δ 189.1 (d, $^1J_{RhC}$ = 54, Rh-$C_{carbene}$), 147.2 (ArC), 136.7 (ArC), 130.1 (ArCH), 124.0 (N-(*C*H)$_2$-N), 123.9 (ArCH), 97.0 (d, $^1J_{RhC}$ = 5, cod-CH), 61.4 (d, $^1J_{RhC}$ = 15, cod-CH), 33.6 (cod-CH_2), 28.9 (*C*H$(CH_3)_2$), 28.2 (cod-CH_2), 26.5 (CH_3), 23.2 (CH_3). **FTIR (ATR)** ν = 800.5 (s), 754.2 (s) cm^{-1}. **Anal. Calcd.** for $C_{35}H_{48}FRhN_2$ (MW 618.67): C, 67.95; H, 7.82; N, 4.53. Found: C, 68.04; H, 7.76; N, 4.39.



[Ir(cod)(IPr)(HF_2)] **7**

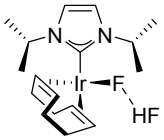
A Schlenk tube was charged with [Ir(cod)(IPr)(OH)] (400 mg, 0.57 mmol) in THF (2 mL). NEt_3.3HF (63 µL, 0.38 mmol) was added under Ar and the reaction mixture was stirred at rt for 4.5 h. The product was reduced *in vacuo* and azeotroped with pentane (3 x 2 mL) to give a yellow solid. The solid was washed with hexane (3 x 2 mL) and dried to give [Ir(cod)(IPr)(HF_2)] (**7**) (384 mg, 93%) as a yellow solid. **^{1}H NMR** (300 MHz, C_6D_6): δ 11.32 (d, 1H, $^1J_{FH}$ = 395.0, F-*H*F), 7.27 (t, 2H, $^3J_{HH}$ = 7.7, *p*-ArH), 7.17 (d, 4H, $^3J_{HH}$ = 7.7, *m*-ArH), 6.49 (s, 2H, N-(C*H*)$_2$-N), 4.67 – 4.57 (m, 2H, cod-CH), 3.04 (sept., 4H, $^3J_{HH}$ = 6.8, C*H*(CH_3)$_2$), 2.91 – 2.82 (m, 2H, cod-CH), 1.75 – 1.58 (m, 4H, cod-CH_2), 1.50 (d, 12H, $^3J_{HH}$ = 6.7, CH_3), 1.25 – 1.15 (m, 4H, cod-CH_2), 1.02 (d, 12H, $^3J_{HH}$ = 6.8, CH_3); ^{1}H NMR (500 MHz, 200K, CD_2Cl_2): δ 11.73 (app. dd, 1H, $^1J_{FH}$ = 395.0, $^1J_{FH}$ = 40.0, Ir-F-*H*F). **^{19}F NMR** (282 MHz, C_6D_6): δ -185.2 (br. d, $^1J_{HF}$ = 395, Ir-F-H*F*), -236.2 (br s., Ir-*F*-HF). **^{19}F NMR** (470 MHz, 200K, CD_2Cl_2): δ -177.9 (dd, $^1J_{HF}$ = 395, $^2J_{FF}$ = 120, Ir-F-H*F*), - 238.9 (dd, $^2J_{FF}$ = 120, $^1J_{HF}$ = 40, Ir-*F*-HF). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6): δ 183.7 (Ir-$C_{carbene}$), 146.8 (ArC), 136.0 (ArC), 130.3 (ArCH), 124.1 (N-(*C*H)$_2$-N), 123.9 (ArCH), 84.7 (d, $^2J_{FC}$ = 2, cod-CH), 45.0 (d, $^2J_{FC}$ = 4, cod-CH), 34.3 (cod-CH_2), 29.1 (*C*H(CH_3)$_2$), 28.4 (cod-CH_2), 26.4 (CH_3), 22.9 (CH_3). **FTIR (ATR)** ν = 2623.2 (s, br, HF_2), 1807.3 (w, HF_2), 1215.2 (s) cm^{-1}. **Anal. Calcd.** for $C_{35}H_{49}F_2IrN_2$ (MW 727.99): C, 57.74; H, 6.78; N, 3.85. Found: C, 57.90; H, 6.83; N, 3.80.



[Rh(cod)(IPr)(HF_2)] **8**

A Schlenk tube was charged with [Rh(cod)(IPr)(OH)] (400 mg, 0.65 mmol) in THF (2 mL). NEt_3.3HF (72 µL, 0.43 mmol) was added under Ar and the reaction mixture was stirred at rt for 4.5 h. The product was reduced *in vacuo* and azeotroped with hexane (3 x

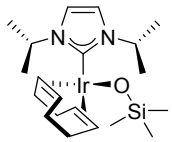
2 mL) to give a yellow solid. The solid was washed with pentane (3 x 1 mL) and dried to give [Rh(cod)(IPr)(HF_2)] (**8**) (375 mg, 90%) as a yellow solid. **^{1}H NMR** (400 MHz, C_6D_6): δ 12.4 (d, 1H, $^1J_{FH}$ = 350.0, Rh-F-*H*F), 7.31 (t, 2H, $^3J_{HH}$ = 7.7, *p*-ArH), 7.22 (d, 4H, $^3J_{HH}$ = 7.7, *m*-ArH), 6.49 (s, 2H, N-(C*H*)$_2$-N), 4.94 – 4.84 (m, 2H, cod-CH), 3.09 – 2.93 (m, 6H, C*H*(CH_3)$_2$, cod-CH), 1.83 – 1.68 (m, 4H, cod-CH_2), 1.51 (d, 12H, $^3J_{HH}$ = 6.7, CH_3), 1.45 – 1.25 (m, 4H, cod-CH_2), 1.02 (d, 12H, $^3J_{HH}$ = 6.9, CH_3); ^{1}H NMR (500 MHz, 200K, CD_2Cl_2): δ 12.89 (app. dd, $^1J_{FH}$ = 350.0, $^1J_{FH}$ = 25.0, Rh-F-*H*F); ^{19}F{^{1}H} NMR (470 MHz, C_6D_6): δ -181.5 (br., Rh-F-H*F*), -255.7 (br, Rh-*F*-HF). **^{19}F NMR** (470 MHz, 200 K, CD_2Cl_2): δ -173.1 (dd, $^1J_{FH}$ = 350, $^2J_{FF}$ = 150, Rh-FH*F*), -253.6 (app. dd, $^2J_{FF}$ = 150, $^1J_{FH}$ = 50, Rh-*F*-HF). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 186.3 (d, $^1J_{RhC}$ = 52, Rh-$C_{carbene}$), 147.1 (ArC), 136.3 (ArC), 130.3 (ArCH), 124.4 (N-(*C*H)$_2$-N), 124.1 (ArCH), 97.9 (d, $^1J_{RhC}$ = 8, cod-CH), 62.3 (d, $^1J_{RhC}$ = 15, cod-CH), 33.3 (cod-CH_2), 29.0 (*C*H(CH_3)$_2$), 27.9 (cod-CH_2), 26.5 (CH_3), 23.0 (CH_3). **FTIR (ATR)** ν = 2530.6 (s, br, HF_2), 1890.2 (s, br, HF_2) 758.0 (s) cm^{-1}. **Anal. Calcd.** for $C_{35}H_{49}F_2N_2Rh$ (MW 638.68): C, 65.82; H, 7.73; N, 4.39. Found: C, 66.0; H, 7.85; N, 4.26.



[Ir(cod)(I^{i}Pr)(HF_2)] **9**

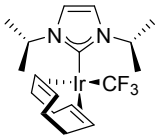
A Schlenk tube was charged with [Ir(cod)^{i}Pr)(OH)] (50.0 mg, 0.107 mmol) in THF (1 mL). NEt_3.3HF (11.8 µL, 0.071 mmol) was added under Ar and the reaction mixture was stirred at rt for 4.5 h. The reaction mixture was reduced *in vacuo* and azeotroped with hexane (2 x 2 mL) to give a yellow solid. The solid was washed with pentane (2 x 2 mL) and dried to give [Ir(cod)(I^{i}Pr)(HF_2)] (**9**) (43.0 mg, 82%) as a yellow solid. **^{1}H NMR** (500 MHz, C_6D_6): δ 12.22 – 11.32 (br s, 1H, Ir-F-*H*F), 6.25 (s, 2H, N-(C*H*)$_2$-N), 5.68 (sept., 2H, $^3J_{HH}$ = 6.8, C*H*(CH_3)$_2$), 4.98 – 4.92 (m, 2H, cod-CH), 2.95 – 2.87 (m, 2H, cod-CH), 2.87 – 2.11 (m, 4H, cod-CH_2), 1.61 – 1.49 (m, 4H, cod-CH_2), 1.26 (d, 6H, $^3J_{HH}$ = 6.6, CH_3), 1.07 (d, 6H, $^3J_{HH}$ = 6.8, CH_3); ^{1}H NMR (500 MHz, 197.5K, CD_2Cl_2): δ 11.53 (dd, $^1J_{FH}$ = 403.0, $^1J_{FH}$ = 44.8, Ir-F-*H*F); ^{19}F NMR (470 MHz, C_6D_6): δ -187.5 (br, Ir-F-H*F*), -243.5 (br, Ir-*F*-HF). **^{19}F NMR** (470 MHz, 197.5K, CD_2Cl_2): δ -184.3 (dd, $^1J_{HF}$ =

403, $^2J_{FF}$ = 99, Ir-F-H*F*), -246.5 (app. dd, $^2J_{FF}$ = 95, $^1J_{HF}$ = 45, Ir-*F*-HF). **^{13}C{^{1}H} NMR** (MHz, C_6D_6): δ 178.1 (Ir-$C_{carbene}$), 116.6 (N-(*C*H)$_2$-N), 85.0 (cod-CH), 52.7 (cod-CH), 44.9 (*C*H(CH$_3$)$_2$), 34.5 (cod-CH$_2$), 29.1 (cod-CH$_2$), 24.1 (CH$_3$), 23.1 (CH$_3$). **FTIR (ATR)** ν = 2546.0 (s, br, HF_2), 1869.0 (s, br HF_2), 1215.2 (s) cm^{-1}. **Anal. Calcd.** for $C_{17}H_{29}F_2IrN_2$ (MW 491.64): C, 41.53; H, 5.95; N, 5.70. Found: C, 41.62; H, 5.87; N, 5.78.



[Ir(cod)(I^{i}Pr)(OSiMe$_3$)] **10**

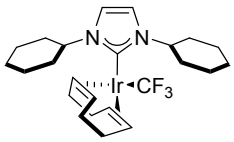
A vial was charged with [Ir(cod)(I^{i}Pr)(OH)] (82.0 mg, 0.17 mmol) in toluene (1 mL). $TMSCF_3$ (31 µL, 0.21 mmol) was added and the reaction mixture was stirred at rt for 2 h. Once complete, the mixture was reduced *in vacuo* and azeotroped with hexane (2 x 1 mL) and washed with hexane (2 x 1 mL). The product was dried *in vacuo* to give [Ir(cod)(I^{i}Pr)(OSiMe$_3$)] (**10**) (88.4 mg, 96%) as a yellow solid. **^{1}H NMR** (300 MHz, C_6D_6): δ 6.19 (s, 2H, N-(C*H*)$_2$-N), 5.76 (sept., 2H, $^3J_{HH}$ = 6.8, N-C*H*(CH$_3$)$_2$), 4.86 – 4.75 (m, 2H, cod-CH), 2.89 – 2.77 (m, 2H, cod-CH), 2.49 – 2.20 (m, 4H, cod-CH$_2$), 1.86 – 1.66 (m, 4H, cod-CH$_2$), 1.20 (d, 6H, $^3J_{HH}$ = 6.7, CHC*H*$_3$), 1.11 (d, 6H, $^3J_{HH}$ = 6.8, CHC*H*$_3$), 0.27 (s, 9H, Si-CH$_3$). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6): δ 180.6 (Ir-$C_{carbene}$), 115.9 (N-(*C*H)$_2$-N), 83.6 (cod-CH), 51.9 (cod-CH), 44.5 (N-*C*H(CH$_3$)$_2$), 34.8 (cod-CH$_2$), 29.9 (cod-CH$_2$), 23.6 (CHC*H*$_3$), 5.0 (Si-CH$_3$). **Anal. Calcd.** for $C_{20}H_{37}IrN_2OSi$ (MW 541.82): C, 44.33; H, 6.88; N, 5.09. Found: C, 44.25; H, 6.70; N, 5.09.



[Ir(cod)(I^{i}Pr)(CF$_3$)] **11**

A Schlenk tube was charged with AgF (78.0 mg, 0.61 mmol) and acetonitrile (2 mL), in the dark and cooled under Ar to -40 °C. $TMSCF_3$ (245 µL, 1.64 mmol) was added and after 15 mins the reaction mixture was warmed to rt, where it was stirred for 30 mins. [Ir(cod)(I^{i}Pr)Cl] (200 mg, 0.410 mmol) was added and the reaction mixture was stirred

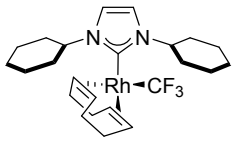
for 16 h. Upon completion, the solvent was removed *in vacuo*, the product dissolved in THF (2 mL) and filtered through a tightly packed celite column to give a red solution. The solvent was removed *in vacuo* and the resultant solid was washed with a cold mixture of pentane/Et_2O (2:1, 3 x 1 mL). The product was dried *in vacuo* to give [Ir(cod)(I^{i}Pr)(CF_3)] (**11**) (160 mg, 75%) as a red solid. **^{1}H NMR** (500 MHz, C_6D_6): δ 6.21 (s, 2H, N-(C*H*)$_2$-N), 5.46 (sept., 2H, $^3J_{HH}$ = 6.8, N-C*H*(CH_3)$_2$), 4.91 – 4.86 (m, 2H, cod-CH), 3.64 – 3.58 (m, 2H, cod-CH), 2.26 – 2.08 (m, 4H, cod-CH_2), 1.84 – 1.76 (m, 4H, cod-CH_2), 1.16 (d, 6H, $^3J_{HH}$ = 6.7, CHC*H*$_3$), 1.04 (d, 6H, $^3J_{HH}$ = 6.8, CHC*H*$_3$). **^{19}F{^{1}H} NMR** (470 MHz, C_6D_6): δ -25.8 (s). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ 180.2 (q, $^3J_{FC}$ = 5, Ir-$C_{carbene}$), 146.3 (q, $^1J_{FC}$ = 346, CF_3), 116.3 (N-(*C*H)$_2$-N), 75.2 (app. q, $^3J_{FC}$ = 1, cod-CH), 71.6 (q, $^3J_{FC}$ = 2, cod-CH), 52.5 (cod-CH_2), 31.8 (cod-CH_2), 31.5 (N-*C*H(CH_3)$_2$), 23.7 (C*H*$_3$), 22.8 (q, $^6J_{FC}$ = 1, CH_3). **Anal. Calcd.** for $C_{18}H_{28}F_3IrN_2$ (MW 521.65): C, 41.45; H, 5.41; N, 5.37. Found: C, 41.31; H, 5.32; N, 5.60. **MS** (+ve EI) for $C_{18}H_{28}F_3IrN_2$ (MW: 521.65, Exact mass calcd. 522.18); m/z 522.1 (100, M^+, ^{193}Ir), 520.1 (64, M^+, ^{191}Ir); **HRMS**: 520.18601 (520.1805 for $C_{18}H_{28}F_3{}^{191}IrN_2$).



[Ir(cod)(ICy)(CF_3)] **12**

A Schlenk tube was charged with AgF (14 mg, 0.11 mmol) and MeCN (1 mL) in the dark. $TMSCF_3$ (44 µL, 0.30 mmol) was added under Ar at -40 °C. After 15 mins the reaction mixture was warmed to rt, where it was stirred for 30 mins. [Ir(cod)(ICy)Cl] (42 mg, 0.074 mmol) was added and the reaction mixture was stirred at rt for 16 h. Upon completion, the solvent was removed *in vacuo*, the product dissolved in THF (2 mL) and filtered through celite to give a red solution. The solvent was removed *in vacuo* and the resultant solid was washed with a cold mixture of pentane/Et_2O (3:1, 3 x 1 mL). The product was dried *in vacuo* to give [Ir(cod)(ICy)(CF_3)] (**12**) (35 mg, 79%) as a red solid. **^{1}H NMR** (500 MHz, C_6D_6): δ 6.34 (s, 2H, N-(C*H*)$_2$-N), 5.19 (tt, 2H, $^3J_{HH}$ = 11.8, $^3J_{HH}$ = 3.6, N-C*H*(ICy)), 4.94 – 4.81 (m, 2H, cod-CH), 3.72 – 3.61 (m, 2H, cod-CH), 2.33 (br. d, 2H, $^3J_{HH}$ = 12.0, ICy-CH_2), 2.27 – 2.10 (m, 4H, cod-CH_2), 1.91 – 1.73 (m, 6H, cod-CH_2,

ICy-CH_2), 1.70 – 1.54 (m, 4H, ICy-CH_2), 1.48 (br. d, 2H, $^3J_{HH}$ = 13.0, ICy-CH_2), 1.44 – 1.30 (m, 4H, ICy-CH_2), 1.23 (qd, 2H, $^3J_{HH}$ = 12.5, $^3J_{HH}$ = 3.5 ICy-CH_2), 1.11 (qd, 2H, $^3J_{HH}$ = 12.0, $^3J_{HH}$ = 3.5 ICy-CH_2), 0.98 – 0.88 (m, 2H, ICy-CH_2). **^{19}F{^{1}H} NMR** (470 MHz, C_6D_6): δ -26.0 (s). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ 180.4 (q, $^3J_{FC}$ = 5, Ir-$C_{carbene}$), 146.1 (q, $^1J_{FC}$ = 347, CF_3), 116.9 (N-(*C*H)$_2$-N), 74.9 (cod-CH), 71.6 (q, $^3J_{FC}$ = 2, cod-CH), 60.4 (N-*C*H(ICy)), 35.2 (ICy-CH_2), 33.6 (q, $^6J_{FC}$ = 1, ICy-CH_2), 32.1 (cod-CH_2), 31.6 (cod-CH_2), 26.3 (ICy-CH_2), 25.9 (ICy-CH_2), 25.6 (ICy-CH_2). **Anal. Calcd.** for $C_{24}H_{36}F_3IrN_2$ (MW 601.77): C, 47.90; H, 6.03; N, 4.66. Found: C, 47.85; H, 5.95; N, 4.75.



[Rh(cod)(ICy)(CF_3)] **13**

A Schlenk tube was charged with AgF (40 mg, 0.31 mmol) and MeCN (1 mL) in the dark and $TMSCF_3$ (110 µL, 0.730 mmol) was added under Ar to -40 °C. After 15 mins the reaction mixture was warmed to rt, where it was stirred for 30 mins. [Rh(cod)(ICy)Cl] (100 mg, 0.21 mmol) was added and the reaction mixture was stirred for 16 h. Upon completion, the reaction mixture was filtered on celite and concentrated *in vacuo*. The resultant solid was dissolved in hexane and filtered on celite. The eluent was concentrated *in vacuo* to give [Rh(cod)(ICy)(CF_3)] (**13**) (57 mg, 53%) as a yellow solid. **^{1}H NMR** (400 MHz, C_6D_6): δ 6.36 (s, 2H, N-(C*H*)$_2$-N), 5.34 (tt, 2H, $^3J_{HH}$ = 12.0, $^3J_{HH}$ = 7.3, N-C*H*(ICy)), 5.27 – 5.18 (m, 2H, cod-CH), 4.16 – 4.08 (m, 2H, cod-CH), 2.40 (br. d, 2H, $^3J_{HH}$ = 12.2, ICy-CH_2), 2.36 – 2.20 (m, 4H, cod-CH_2), 2.05 – 1.95 (m, 4H, cod-CH_2), 1.84 (br. d, 2H, $^3J_{HH}$ = 12.2, ICy-CH_2), 1.70 – 1.57 (m, 4H, ICy-CH_2), 1.47 – 1.38 (m, 4H, ICy-CH_2), 1.25 (qd, 2H, $^3J_{HH}$ = 12.6, $^3J_{HH}$ = 3.6, ICy-CH_2), 1.14 (qd, 2H, $^3J_{HH}$ = 12.4, $^3J_{HH}$ = 3.8, ICy-CH_2), 1.02 – 0.90 (m, 4H, ICy-CH_2). **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ -21.7 (d, $^2J_{RhF}$ = 27 Hz. **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ 185.6 (m, Rh-$C_{carbene}$), 117.0 (N-(*C*H)$_2$-N), 87.7 (d, $^3J_{FC}$ = 9, cod-CH), 86.0 (d, $^3J_{FC}$ = 7, cod-CH), 60.8 (N-*C*H(ICy)), 35.2 (ICy-CH_2), 33.8 (ICy-CH_2), 31.3 (cod-CH_2), 31.2 (cod-CH_2), 26.4 (ICy-CH_2), 26.0 (ICy-CH_2), 25.7 (ICy-CH_2). **Anal. Calcd.** for $C_{24}H_{36}F_3N_2Rh$ (MW

512.47): C, 56.25; H, 7.08; N, 5.47. Found: C, 56.37; H, 7.15; N, 5.64. *(CF_3 not observed by $^{13}C\{^1H\}$ NMR)

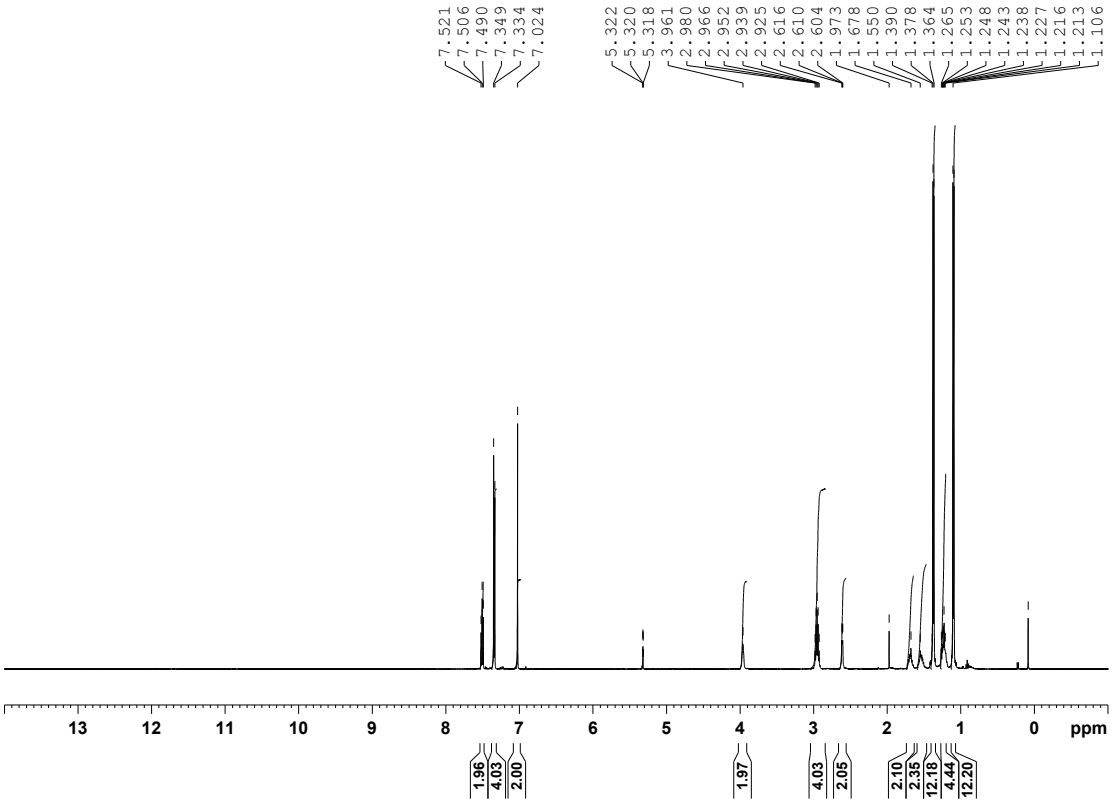


Figure S 1 ^1H NMR (300 MHz, CD_2Cl_2) spectrum for [Ir(cod)(IPr)(F)] **1**

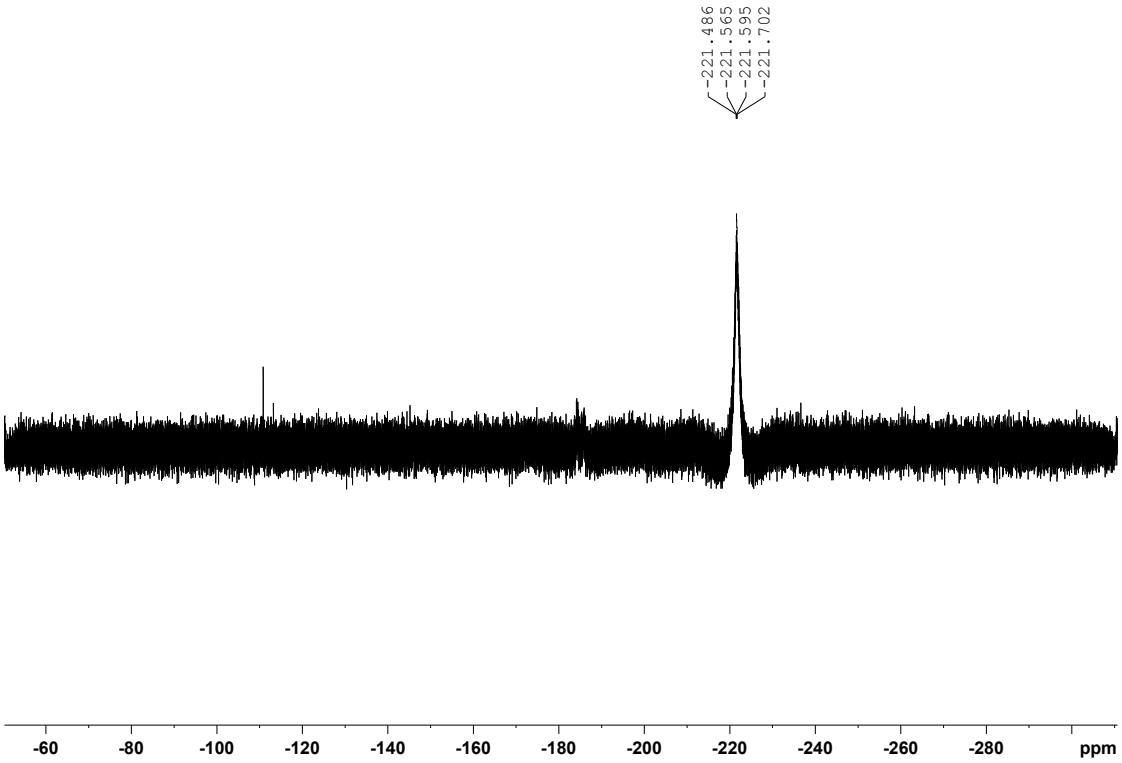


Figure S 2 ^{19}F NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(IPr)(F)] **1**

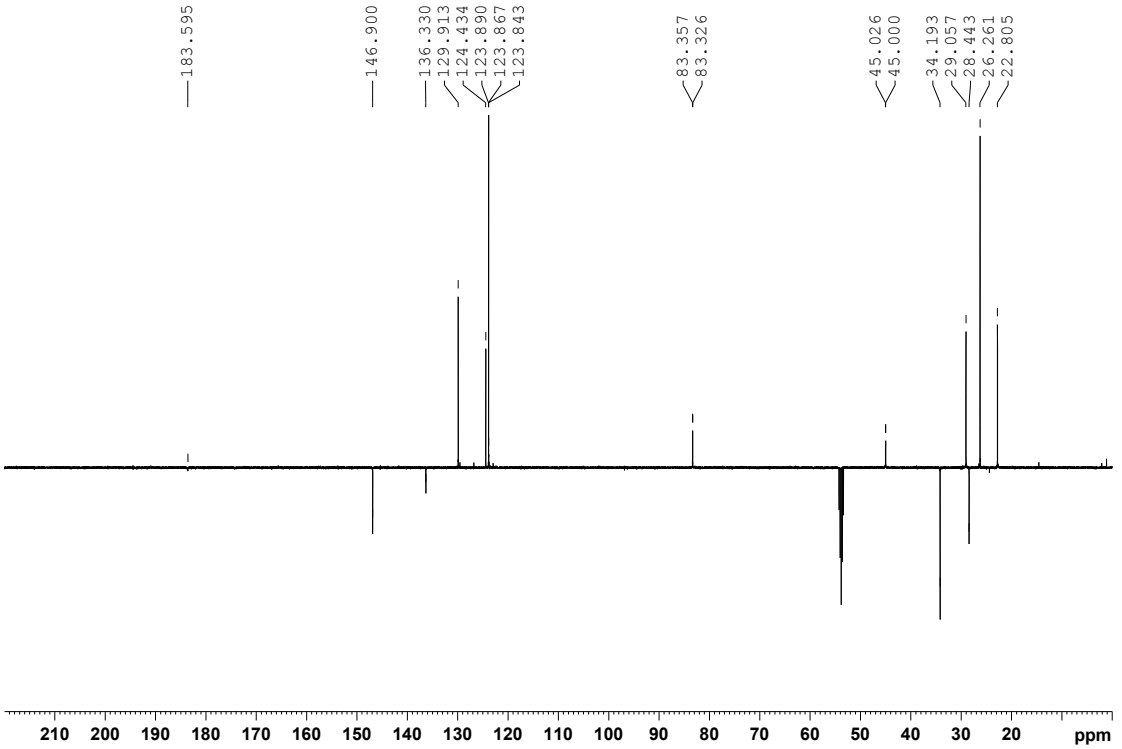


Figure S 3 $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) spectrum for [Ir(cod)(IPr)(F)] **1**

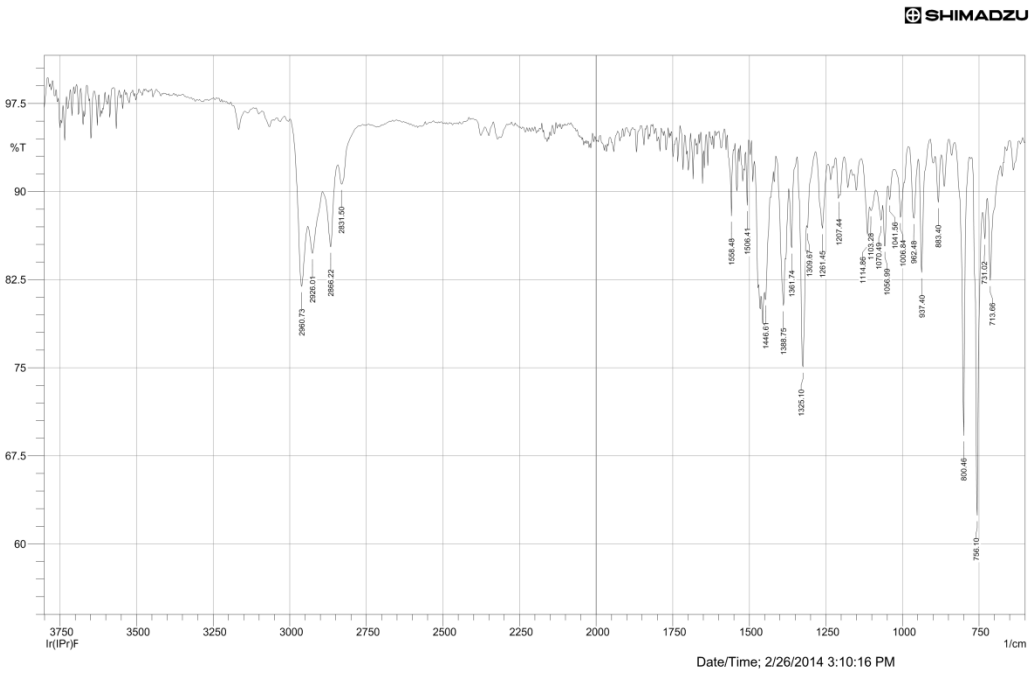


Figure S 4 FTIR (ATR) spectrum for [Ir(cod)(IPr)(F)] **1**

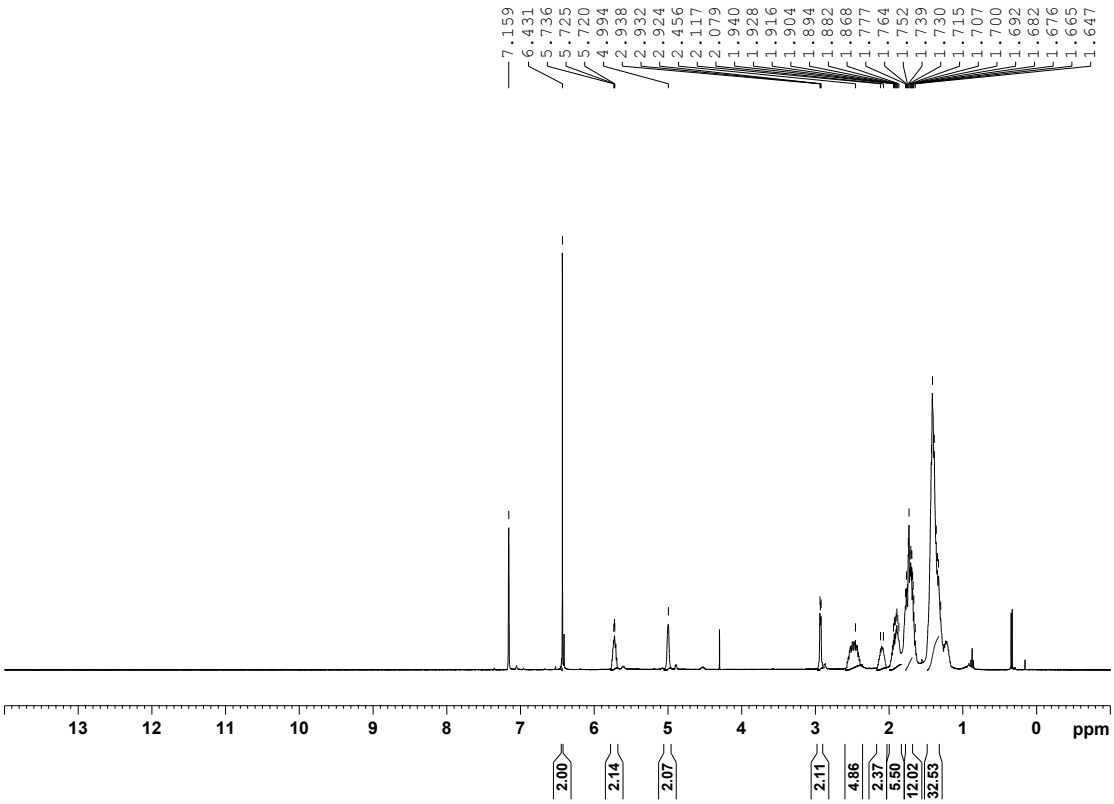


Figure S 5 ^{1}H NMR (400 MHz, C_6D_6) spectrum for [Ir(cod)(IDD)(F)] **2**

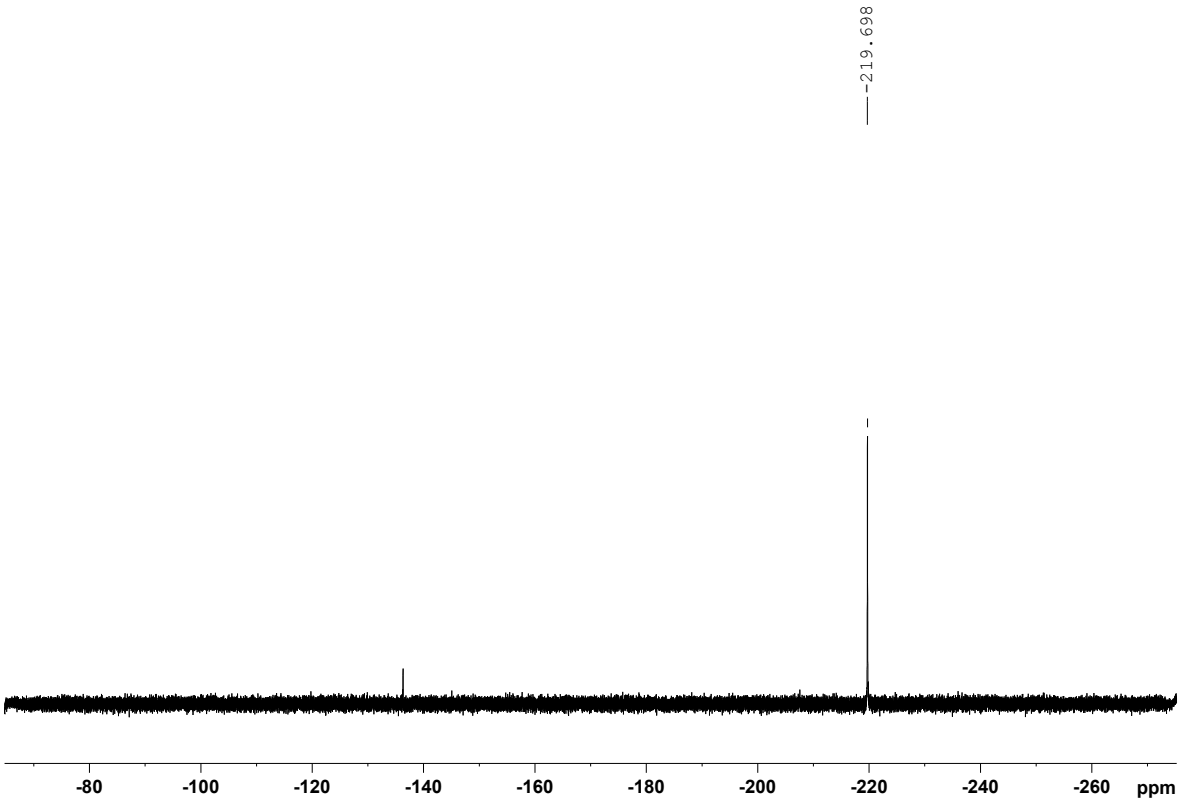


Figure S 6 ^{19}F NMR (470 MHz, C_6D_6) spectrum for [Ir(cod)(IDD)(F)] **2**

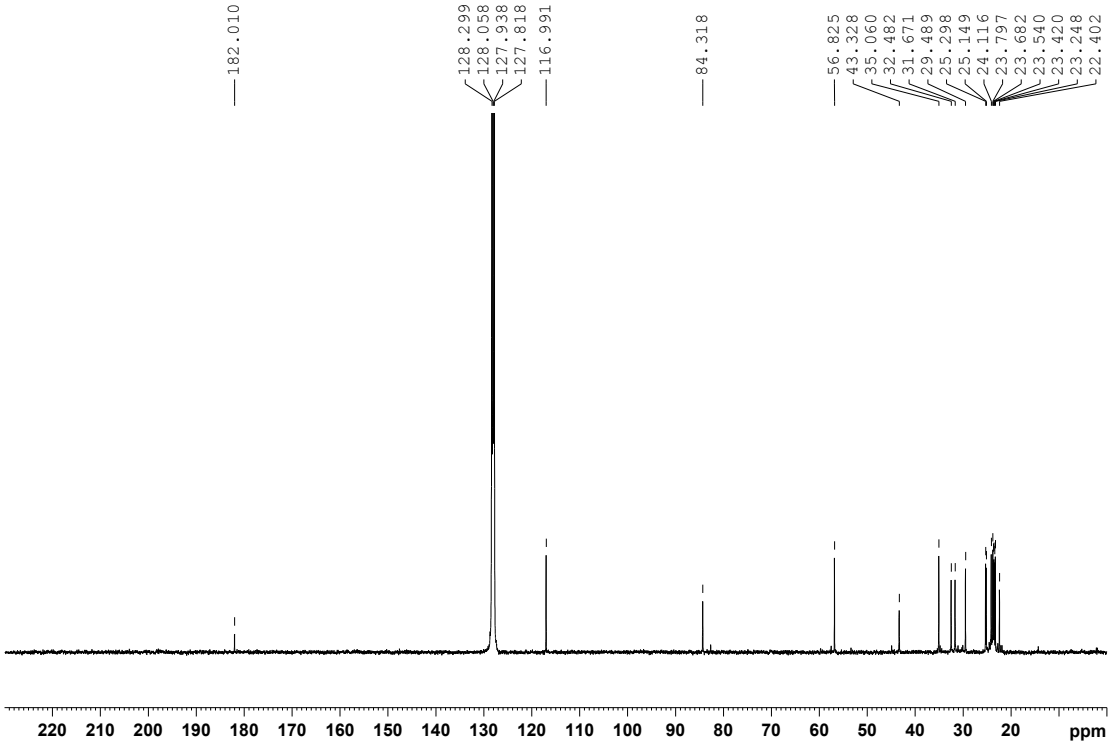


Figure S 7 $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) spectrum for [Ir(cod)(IDD)(F)] **2**

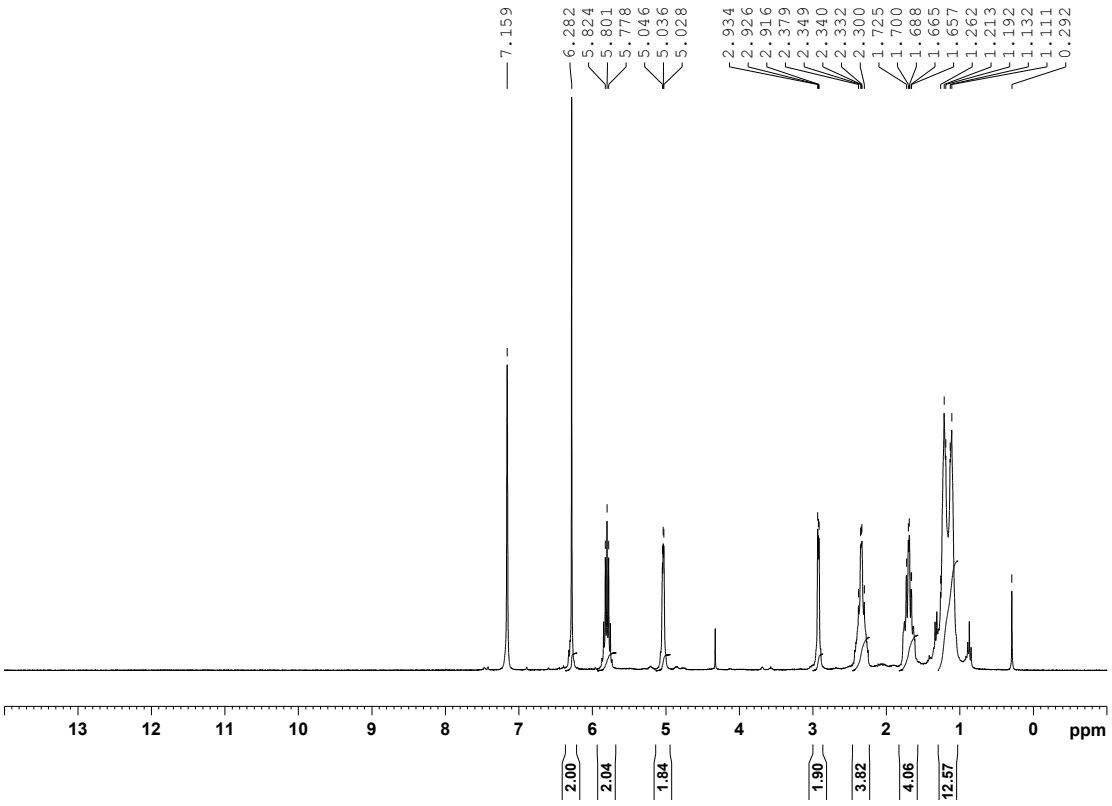


Figure S 8 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(F)] **3**

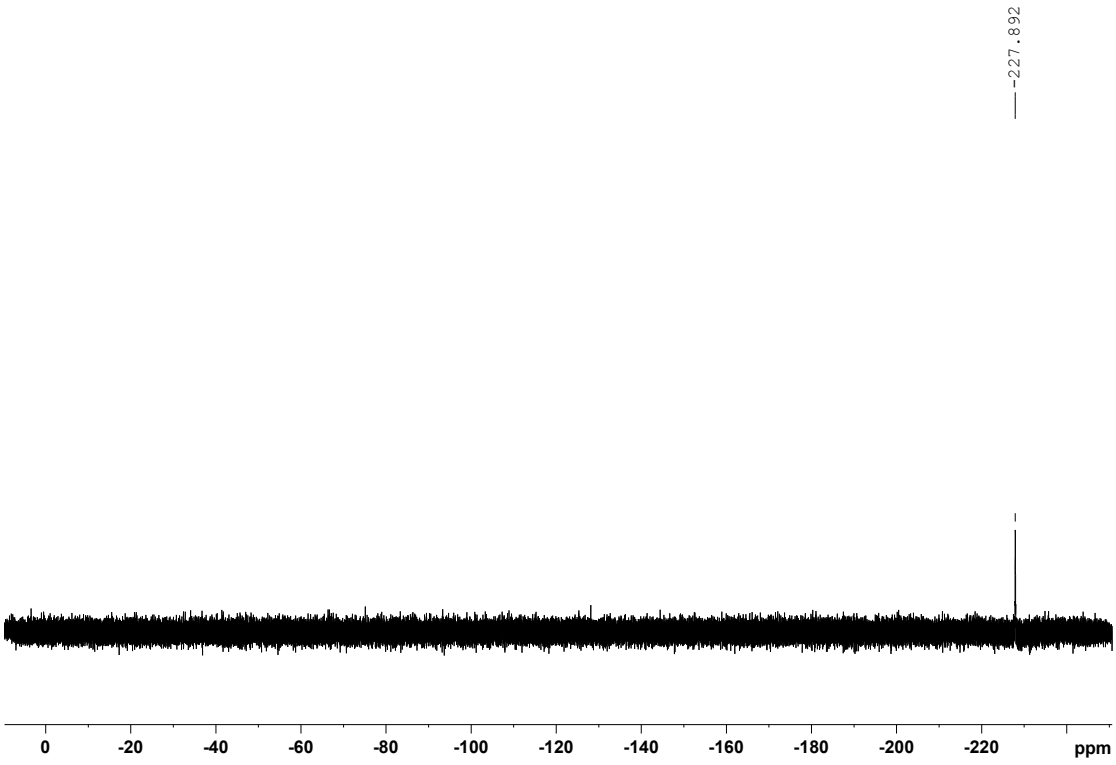


Figure S 9 ^{19}F NMR (282 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(F)] **3**

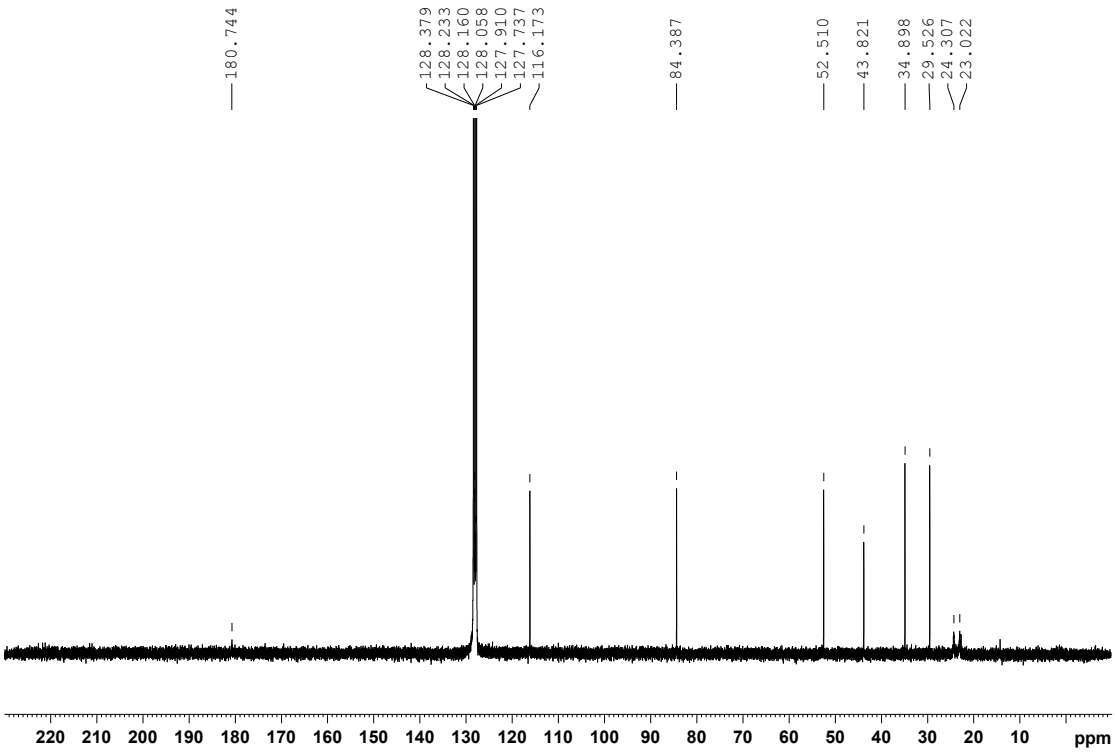


Figure S 10 $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(F)] **3**

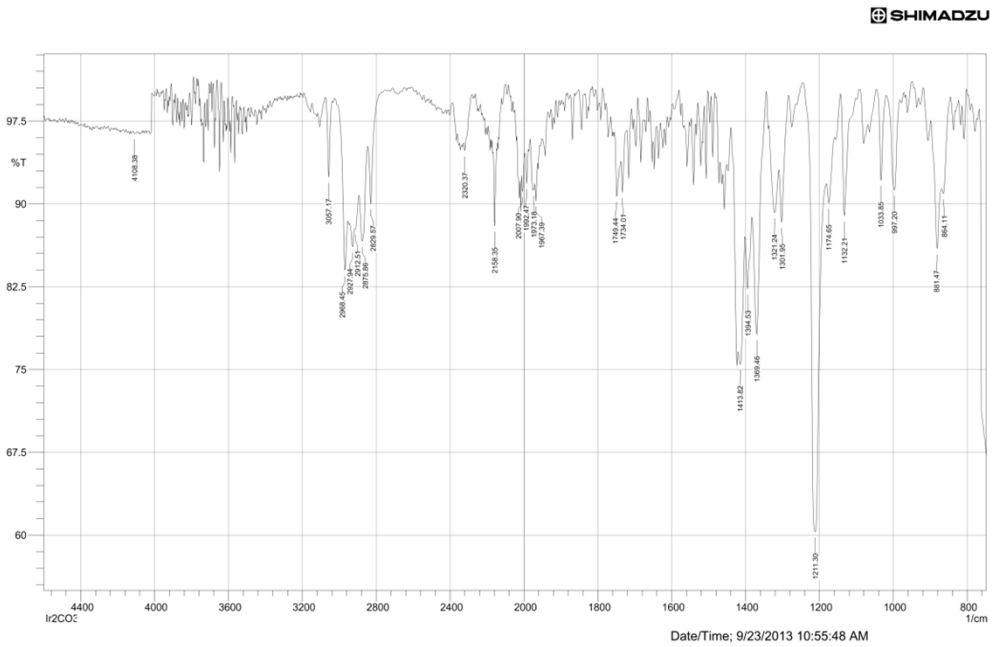


Figure S 11 FTIR (ATR) spectrum for [Ir(cod)(I^{i}Pr)(F)] **3**

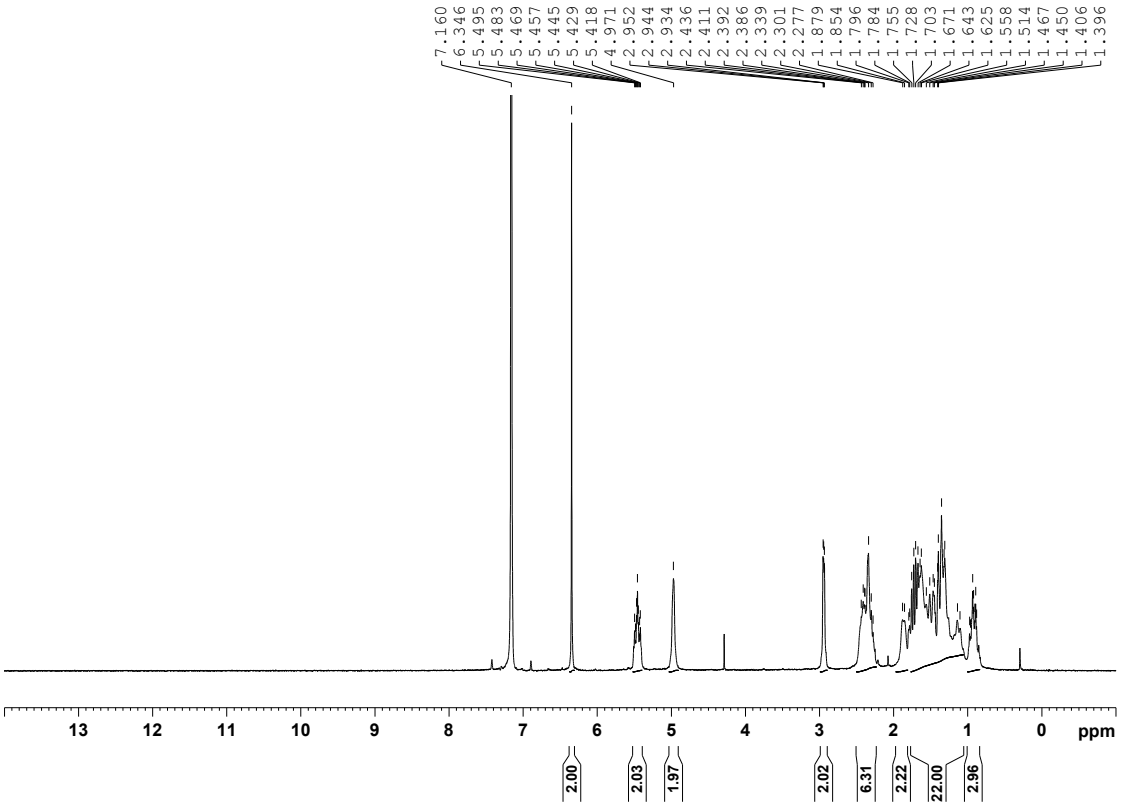


Figure S 12 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(F)] **4**

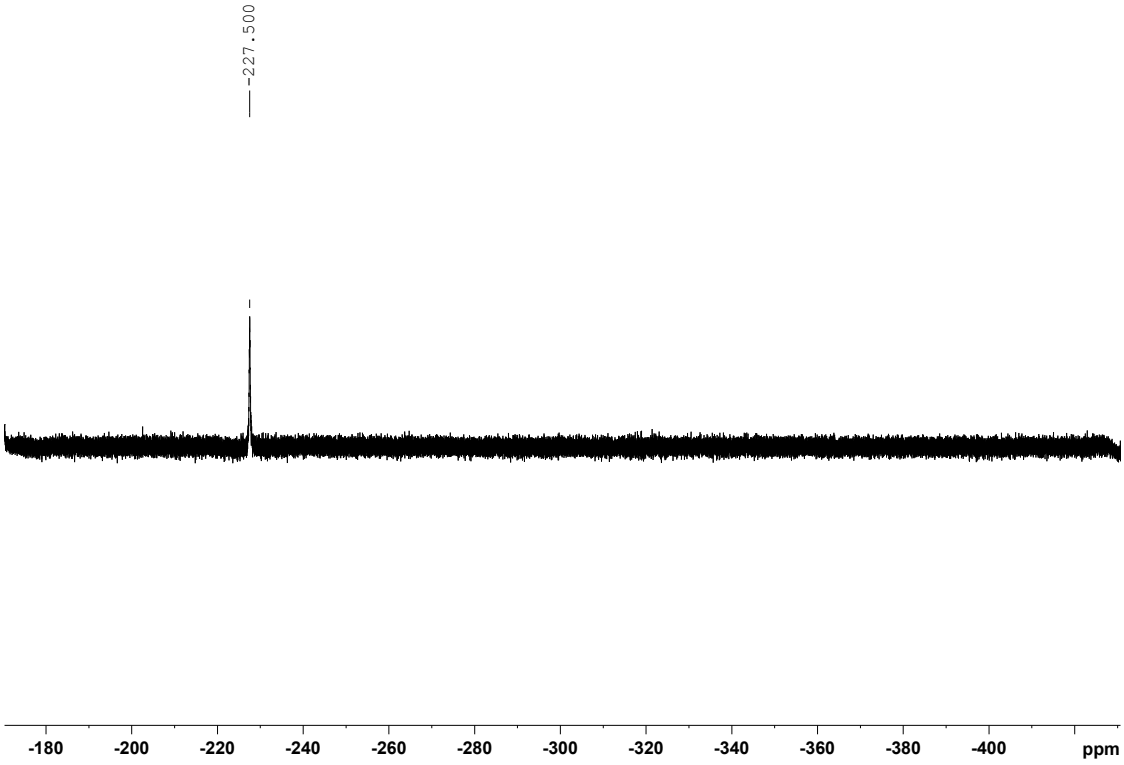


Figure S 13 $^{19}F\{^{1}H\}$ NMR (282 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(F)] **4**

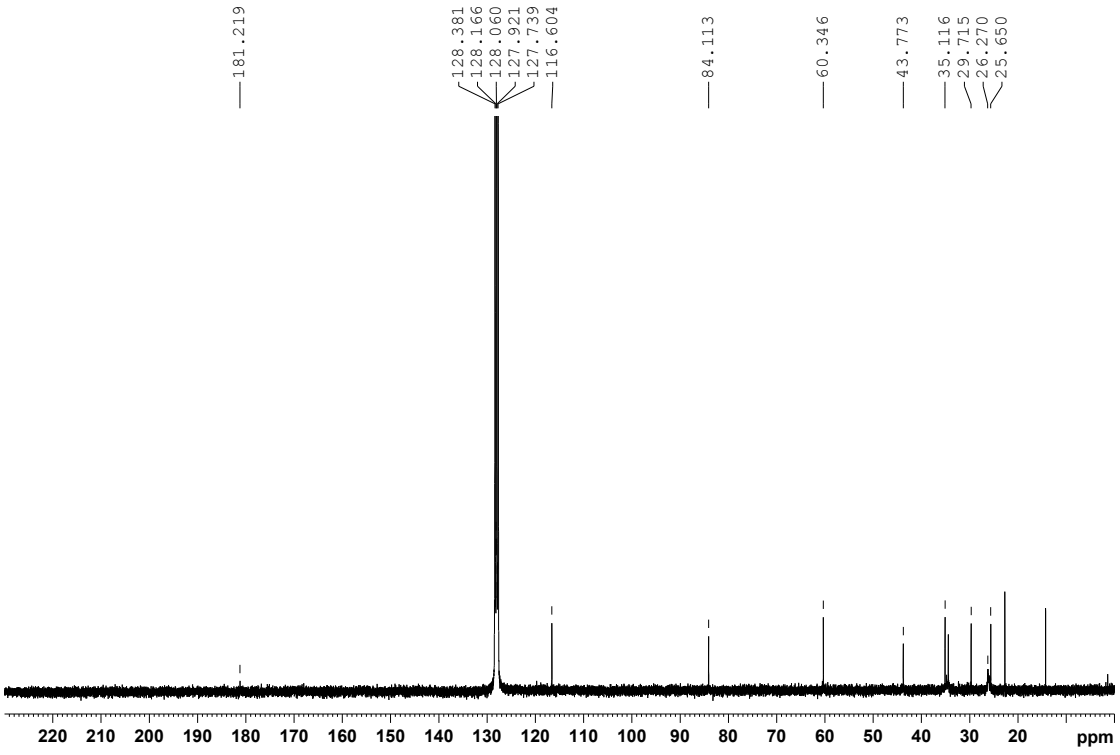


Figure S 14 $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(F)] **4**

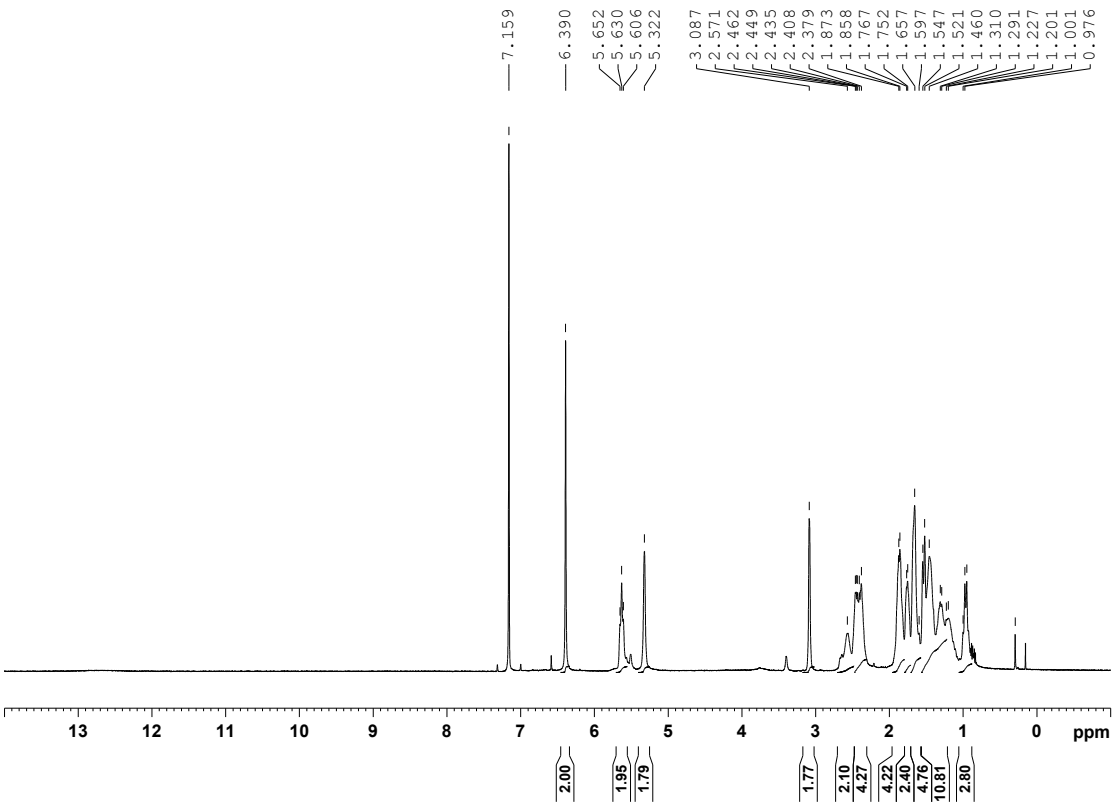


Figure S 15 ^{1}H NMR (500 MHz, C_6D_6) spectrum for [Rh(cod)(ICy)F] **5**

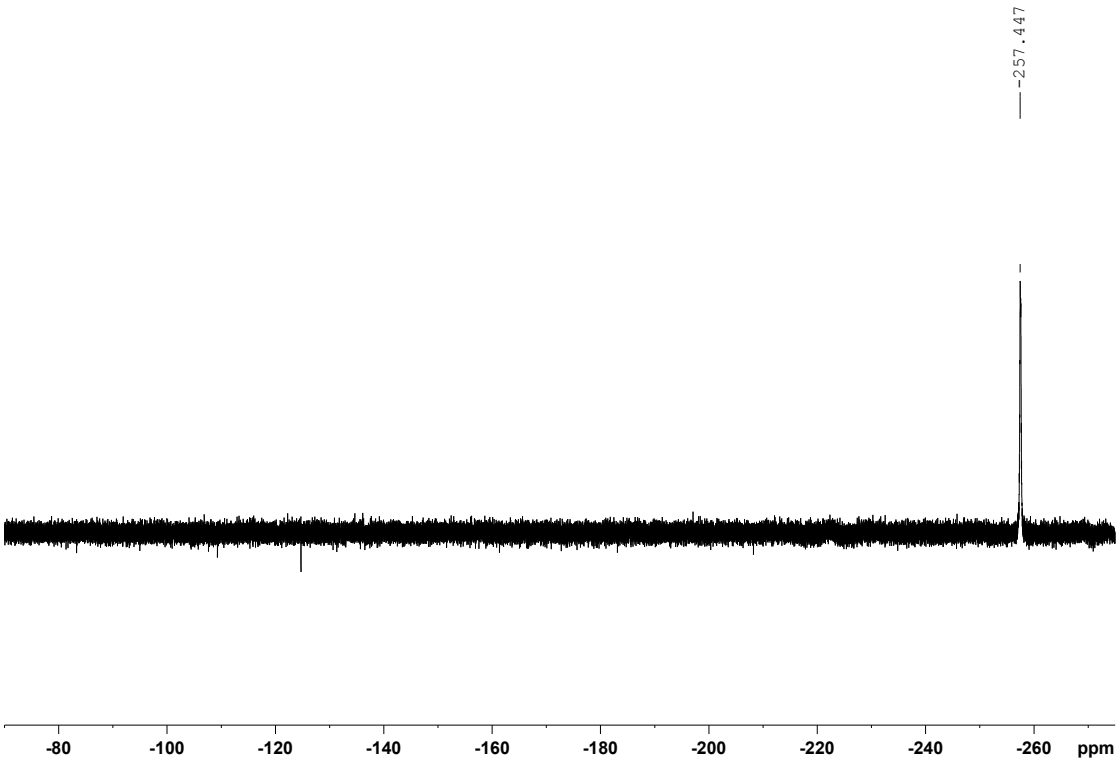


Figure S 16 $^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6) spectrum for [Rh(cod)(ICy)F] **5**

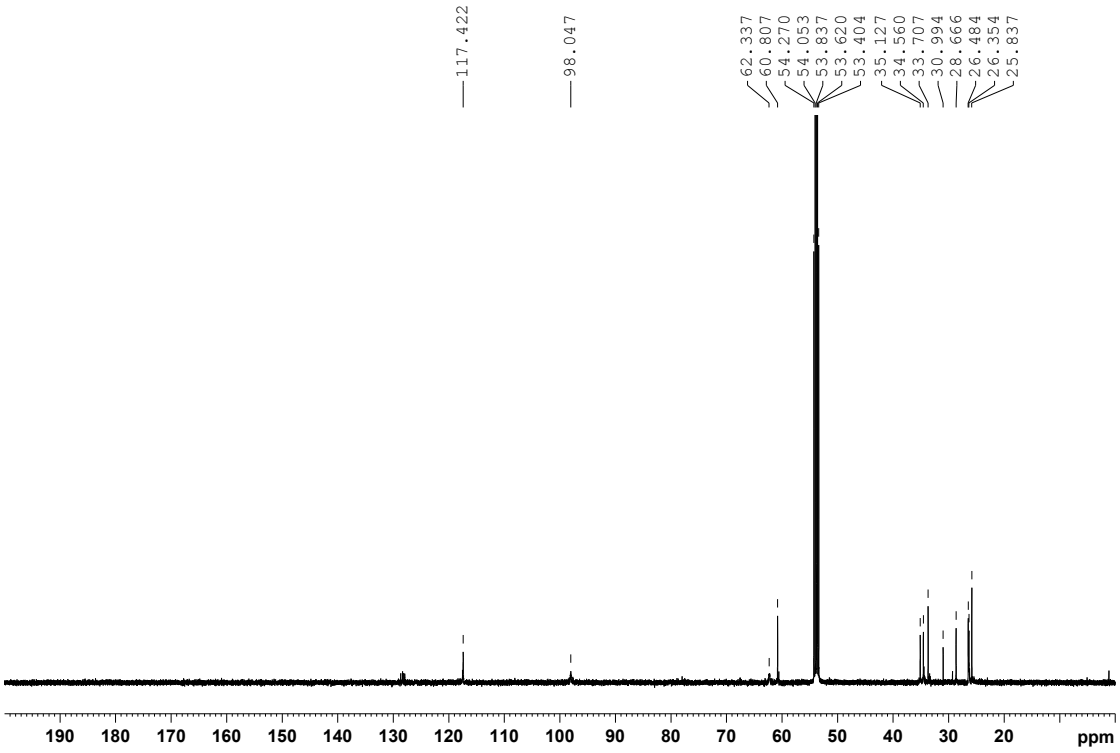


Figure S 17 $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2 spectrum for [Rh(cod)(ICy)F] **5**

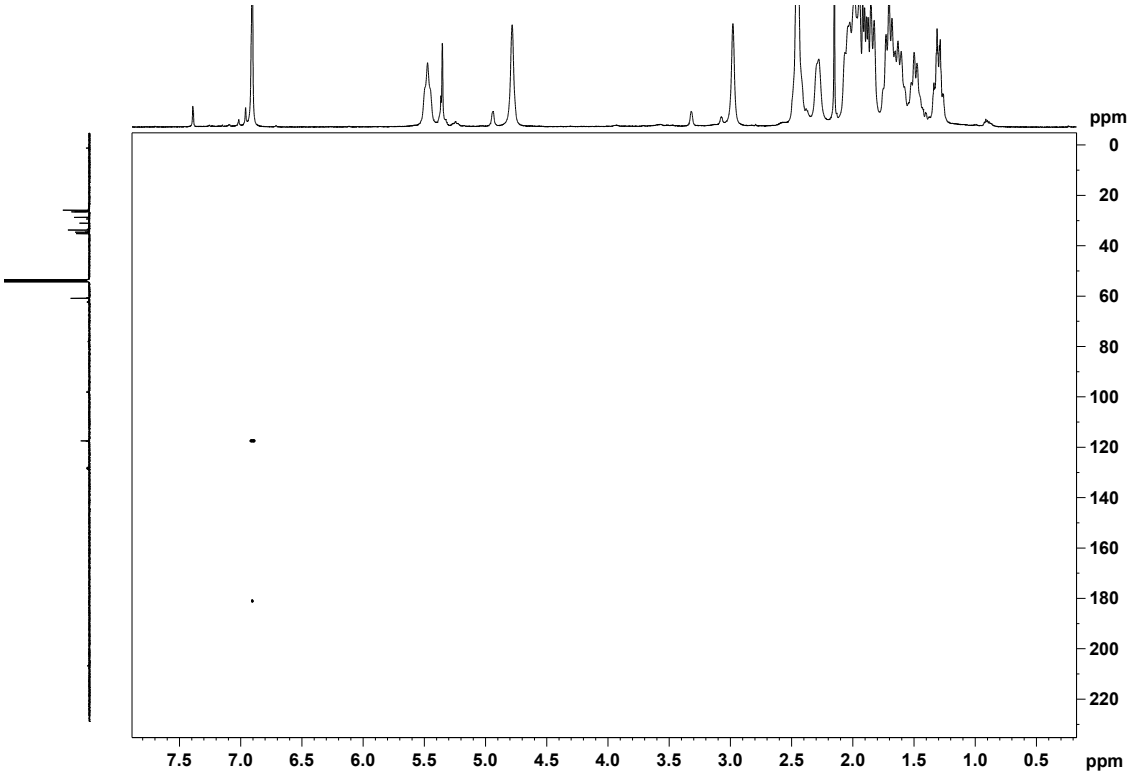


Figure S 18 HMBC NMR (500 MHz, CD_2Cl_2 spectrum for [Rh(cod)(ICy)F] **5**

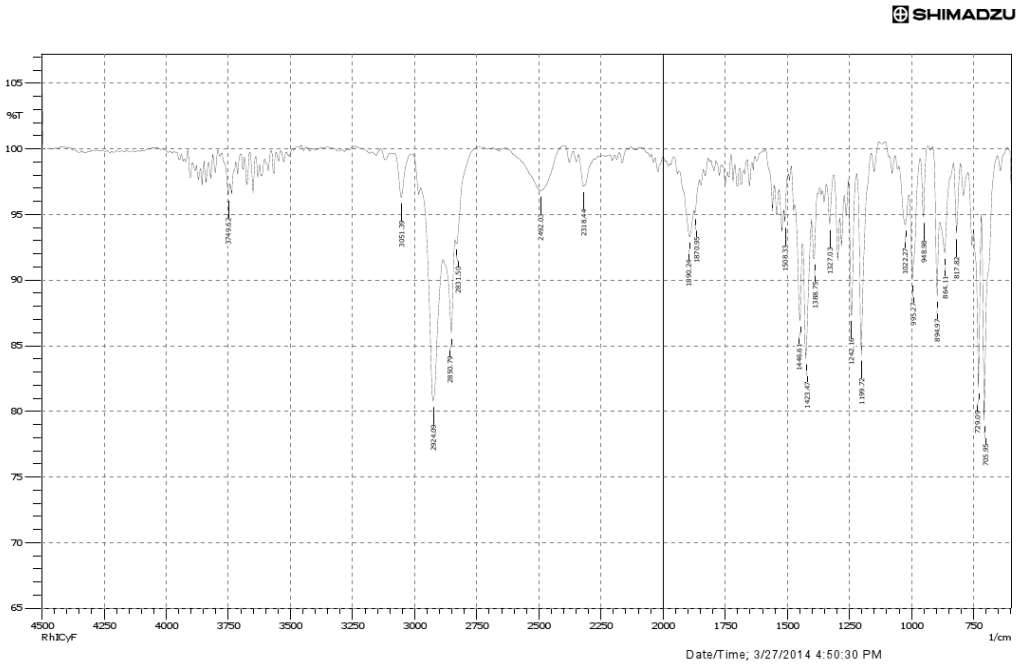


Figure S 19 FTIR (ATR) spectrum for [Rh(cod)(ICy)F] **5**

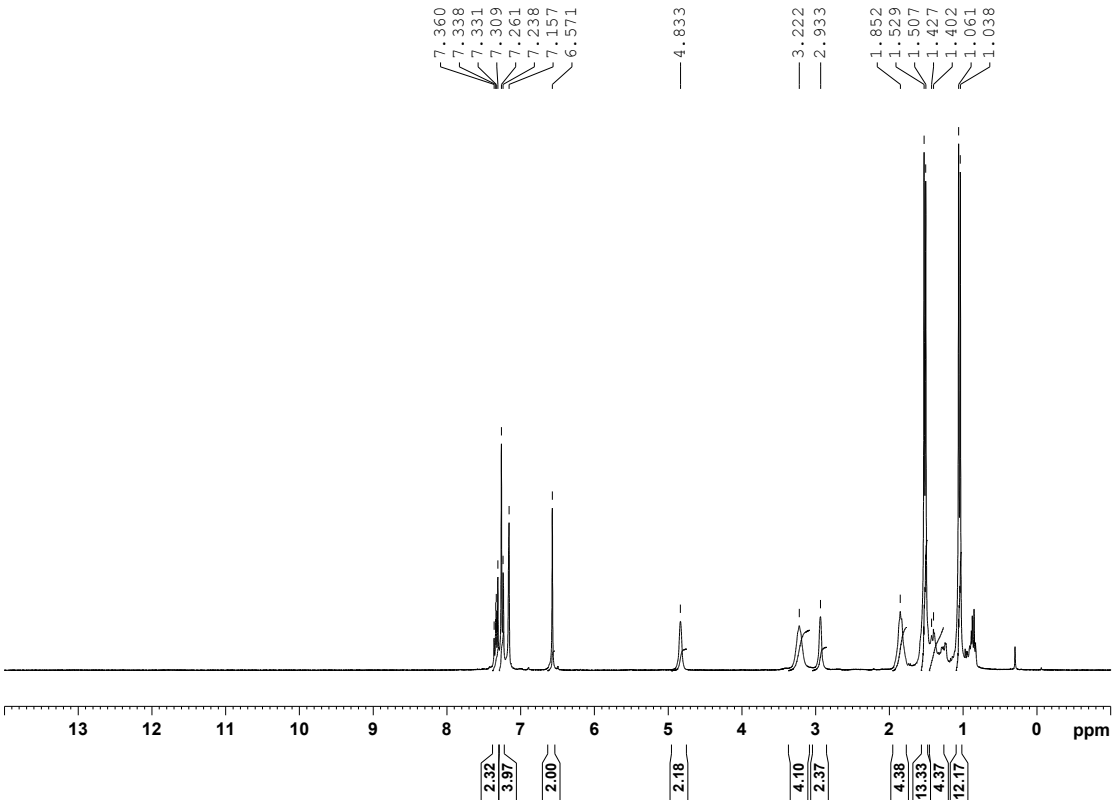


Figure S 20 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(F)] **6**

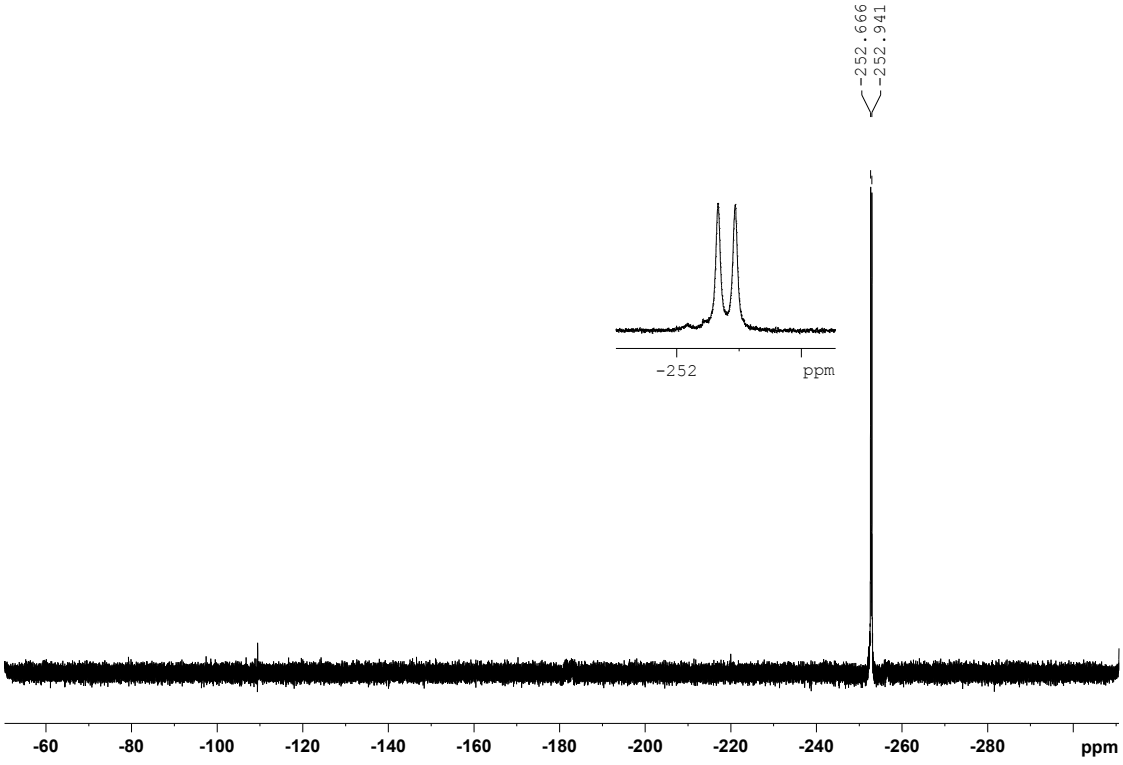


Figure S 21 $^{19}F\{^{1}H\}$ NMR (282 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(F)] **6**

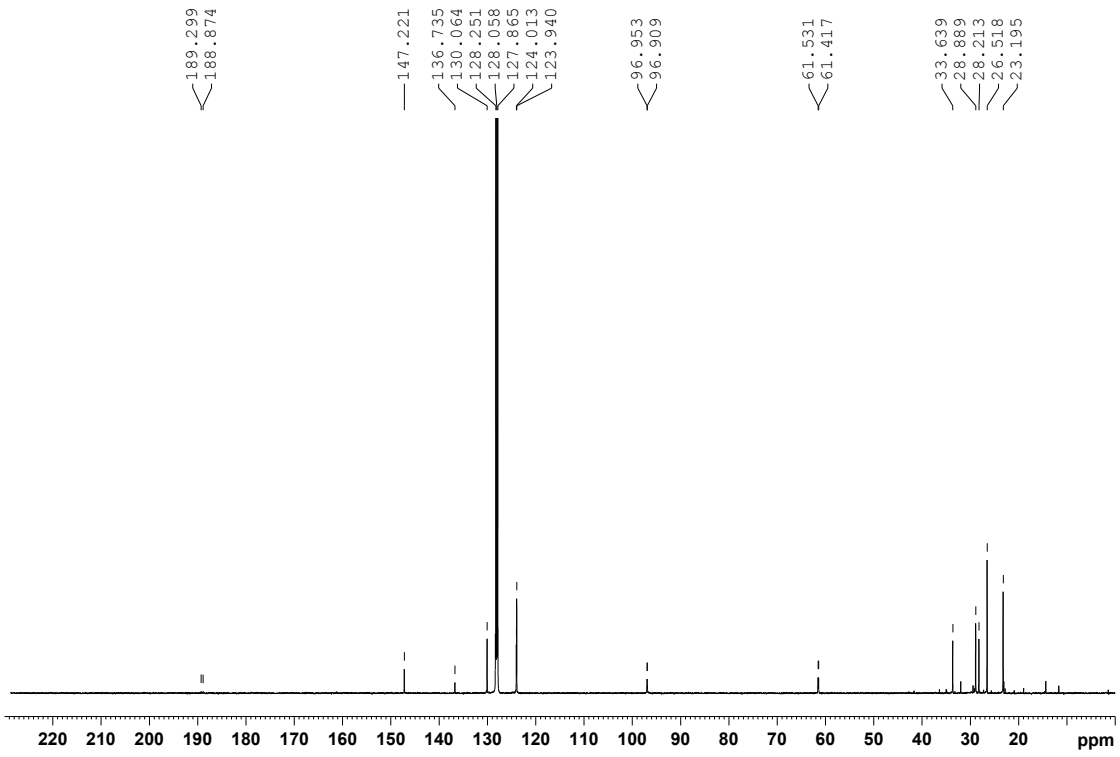


Figure S 22 $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(F)] **6**

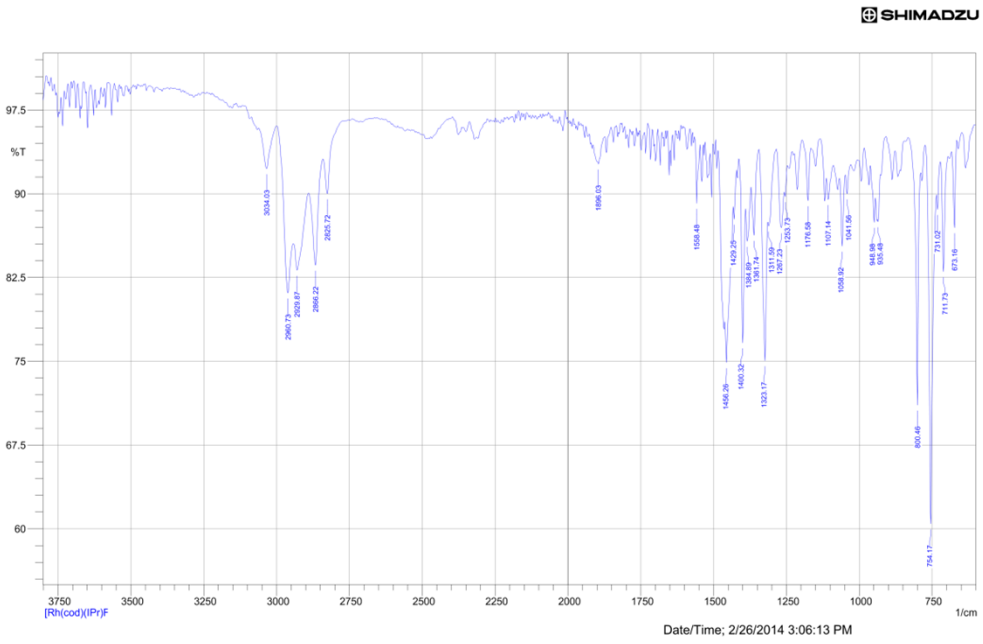


Figure S 23 FTIR (ATR) spectrum for [Rh(cod)(IPr)(F)] **6**

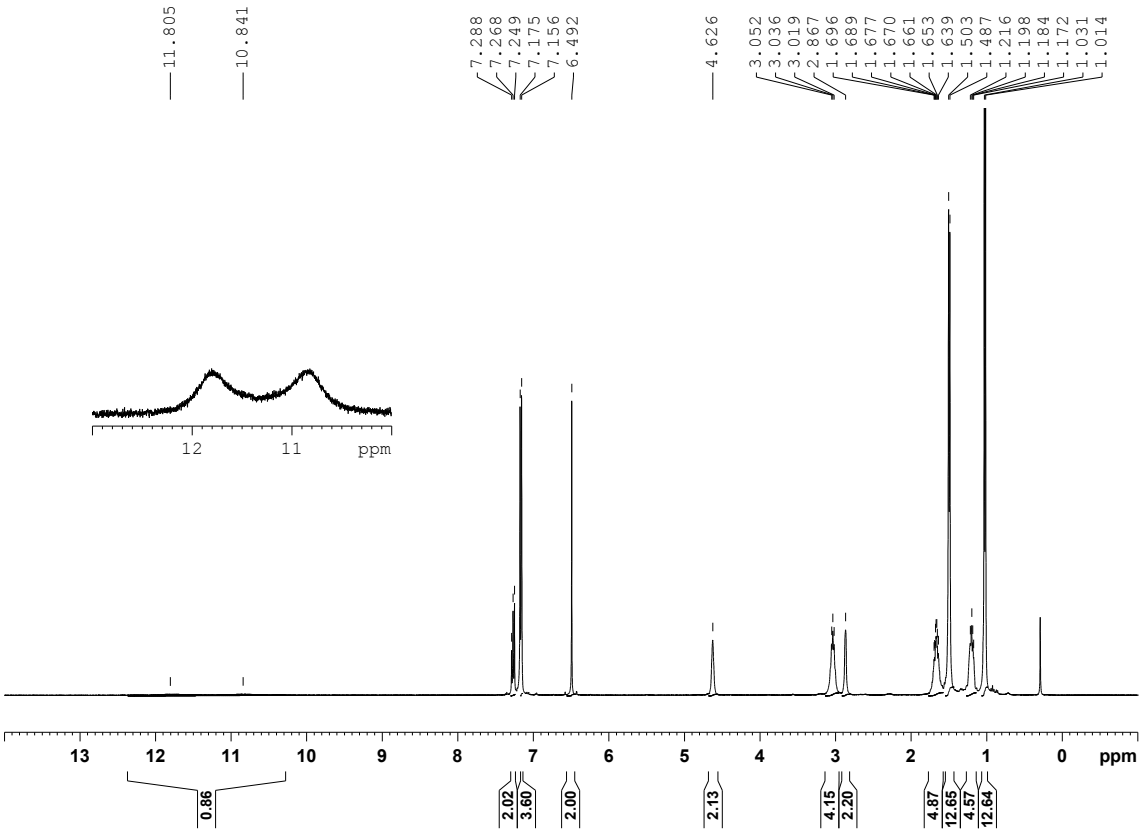


Figure S 24 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

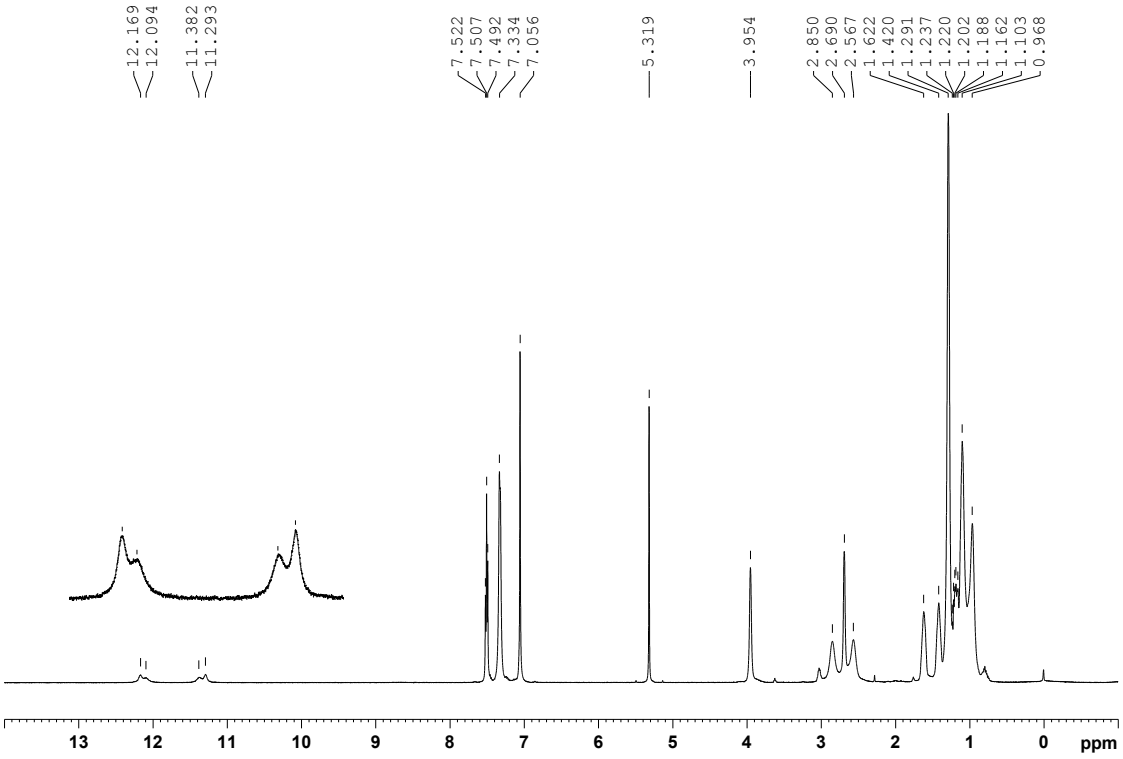


Figure S 25 ^{1}H NMR (500 MHz, 200K, CD_2Cl_2) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

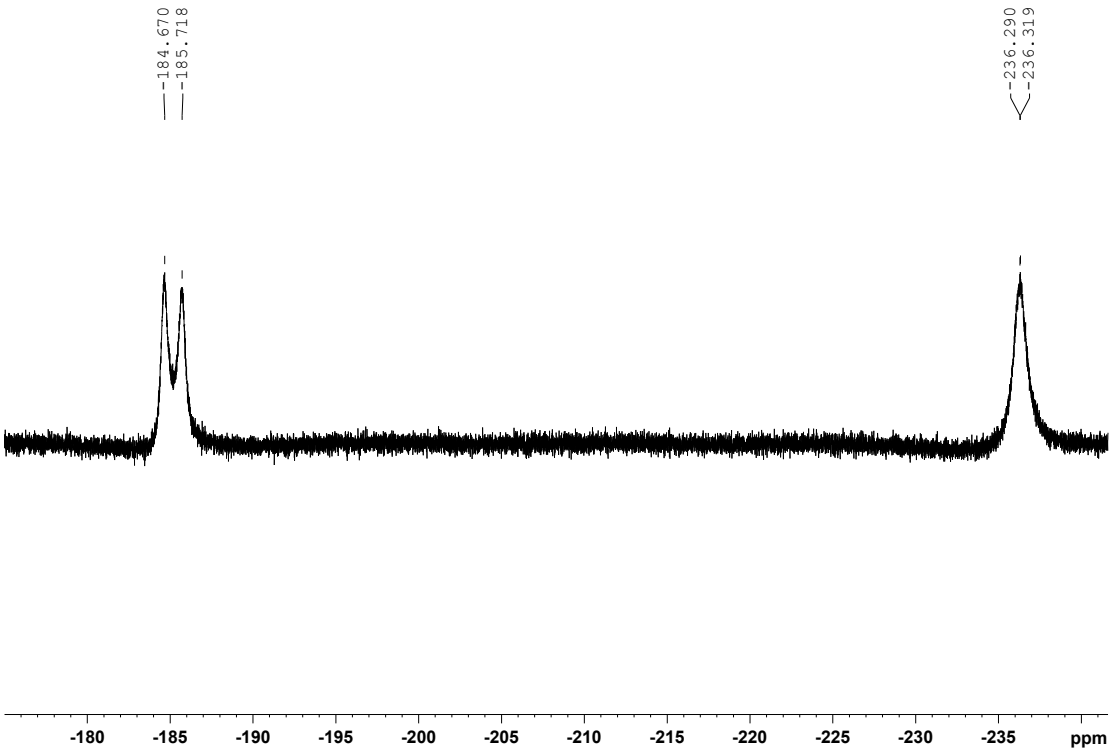


Figure S 26 ^{19}F NMR (282 MHz, 300K, C_6D_6) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

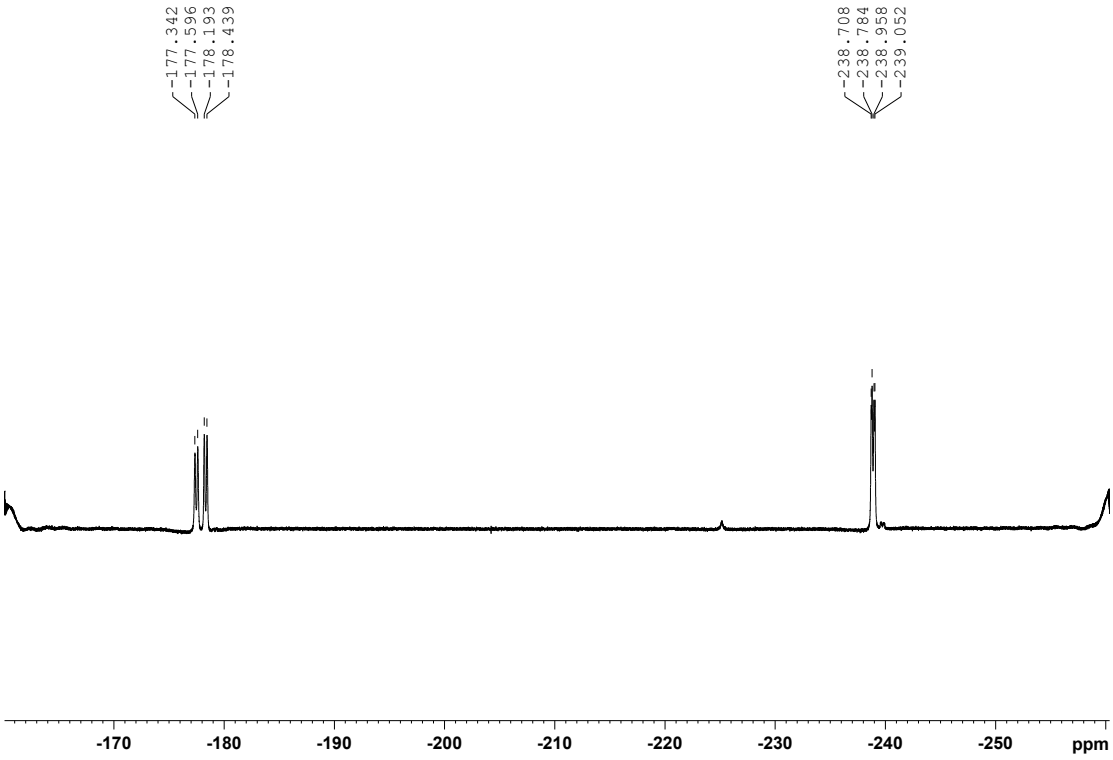


Figure S 27 ^{19}F NMR (282 MHz, 200K, CD_2Cl_2) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

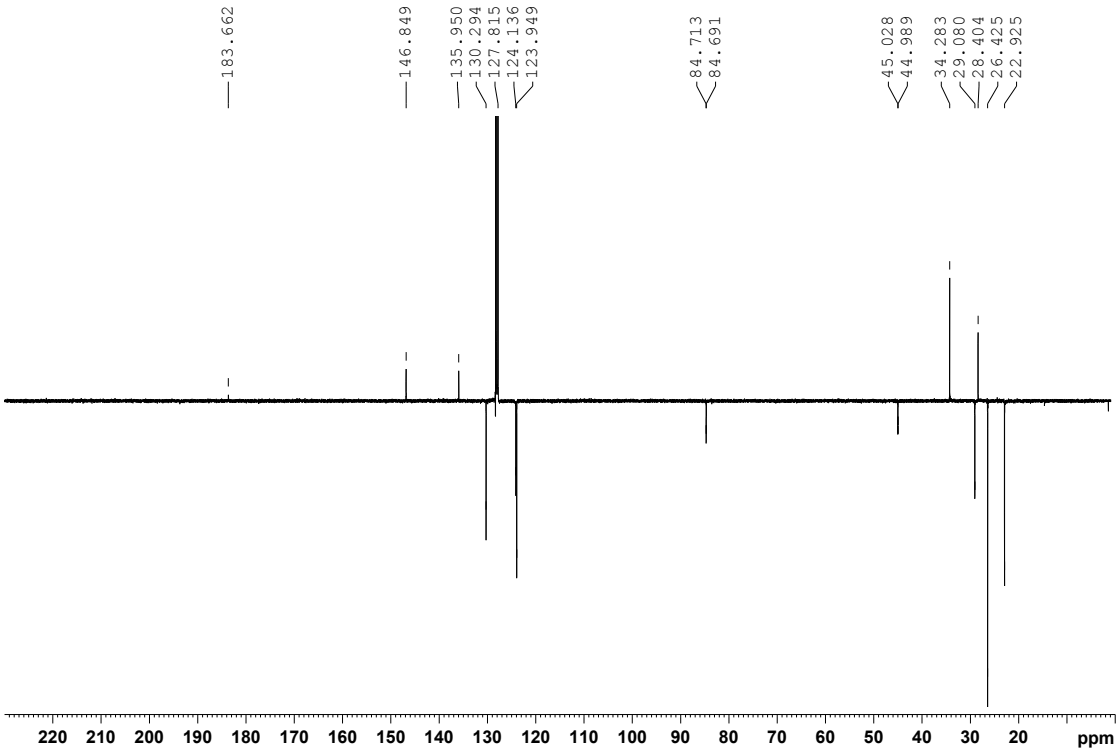


Figure S 28 $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

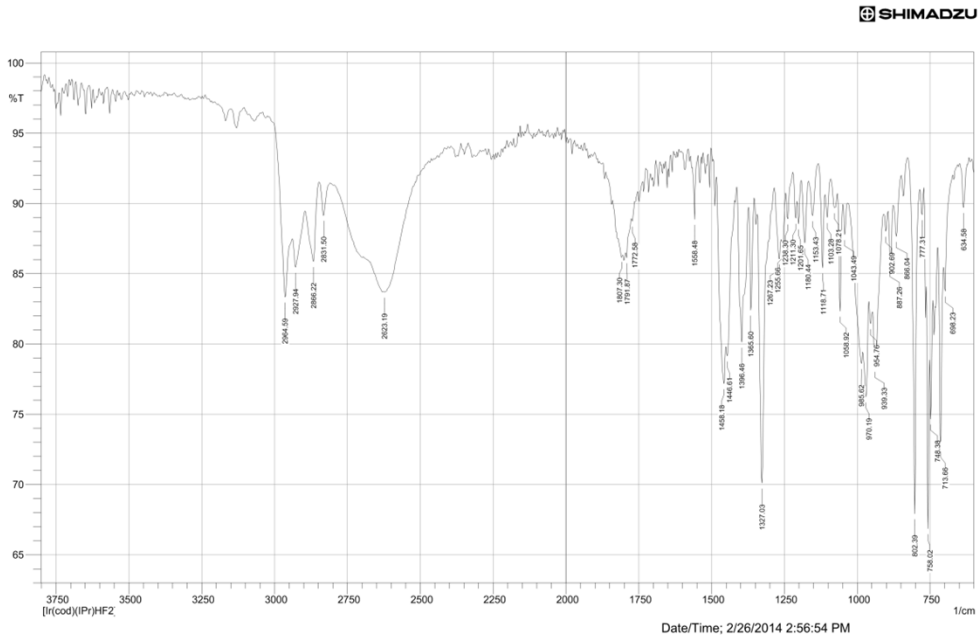


Figure S 29 IR (ATR) spectrum for [Ir(cod)(IPr)(HF_2)] **7**

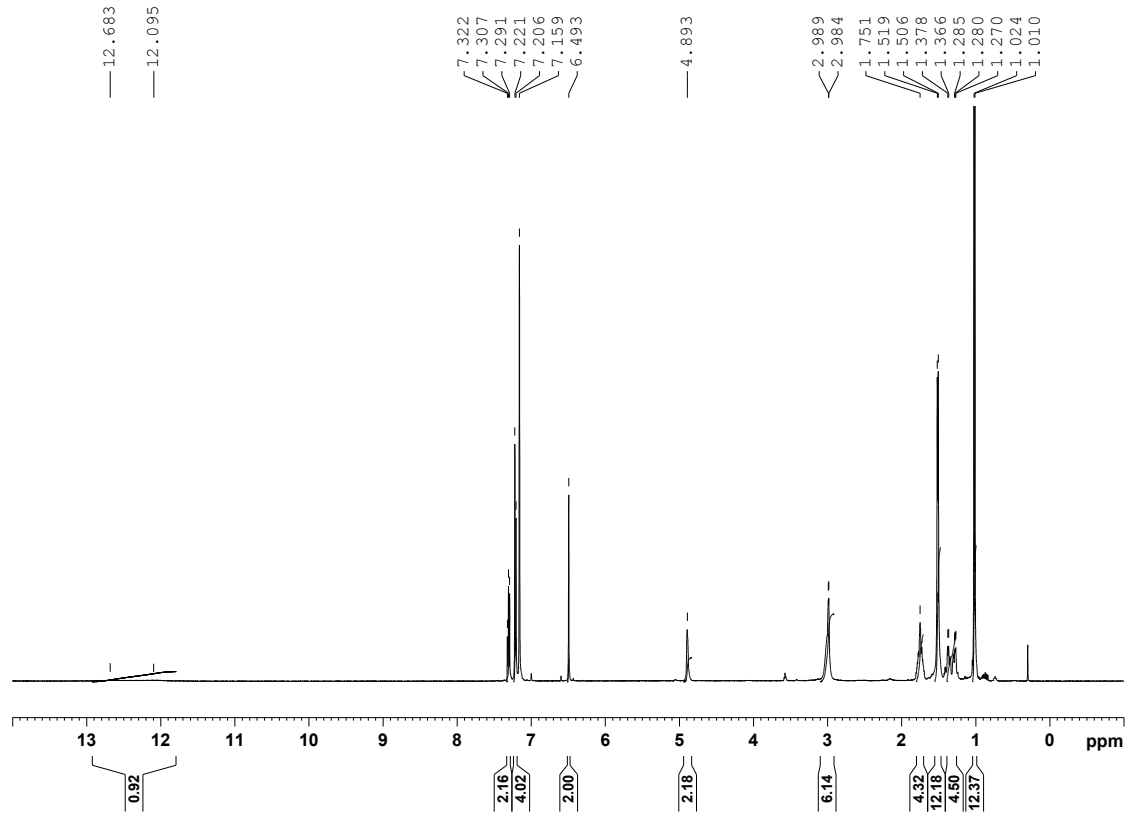


Figure S 30 ^{1}H NMR (400 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

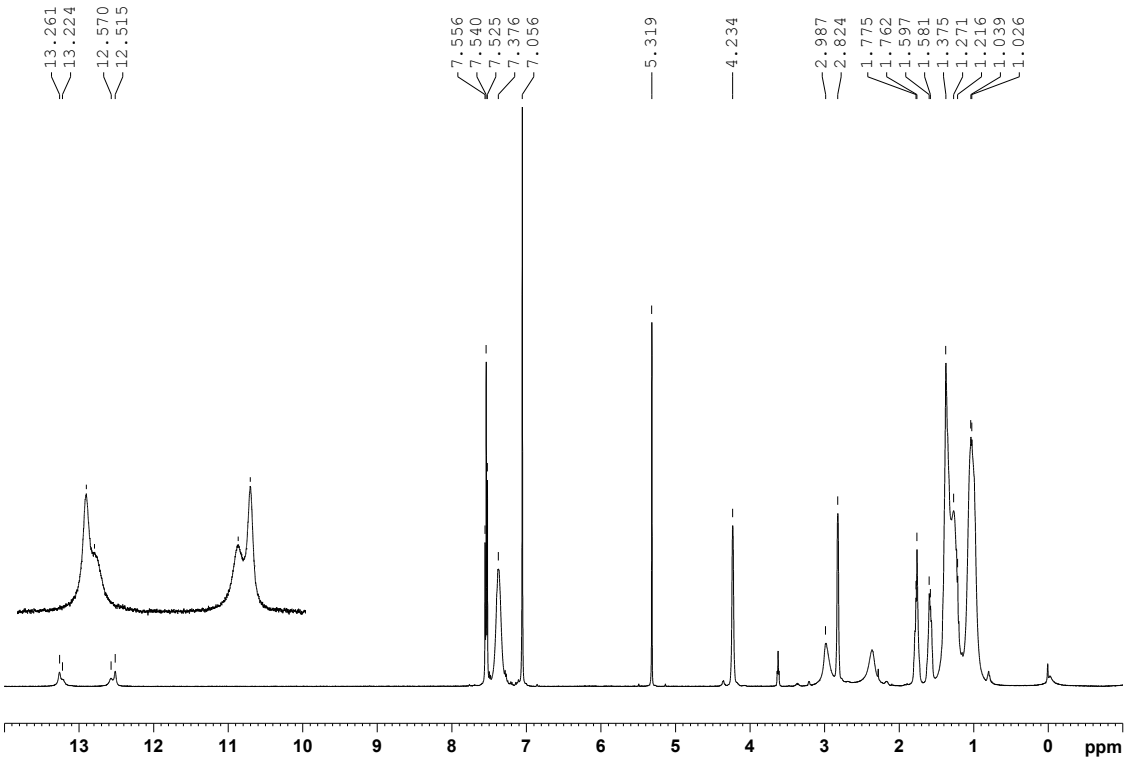


Figure S 31 ^{1}H NMR (500 MHz, 200K, CD_2Cl_2) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

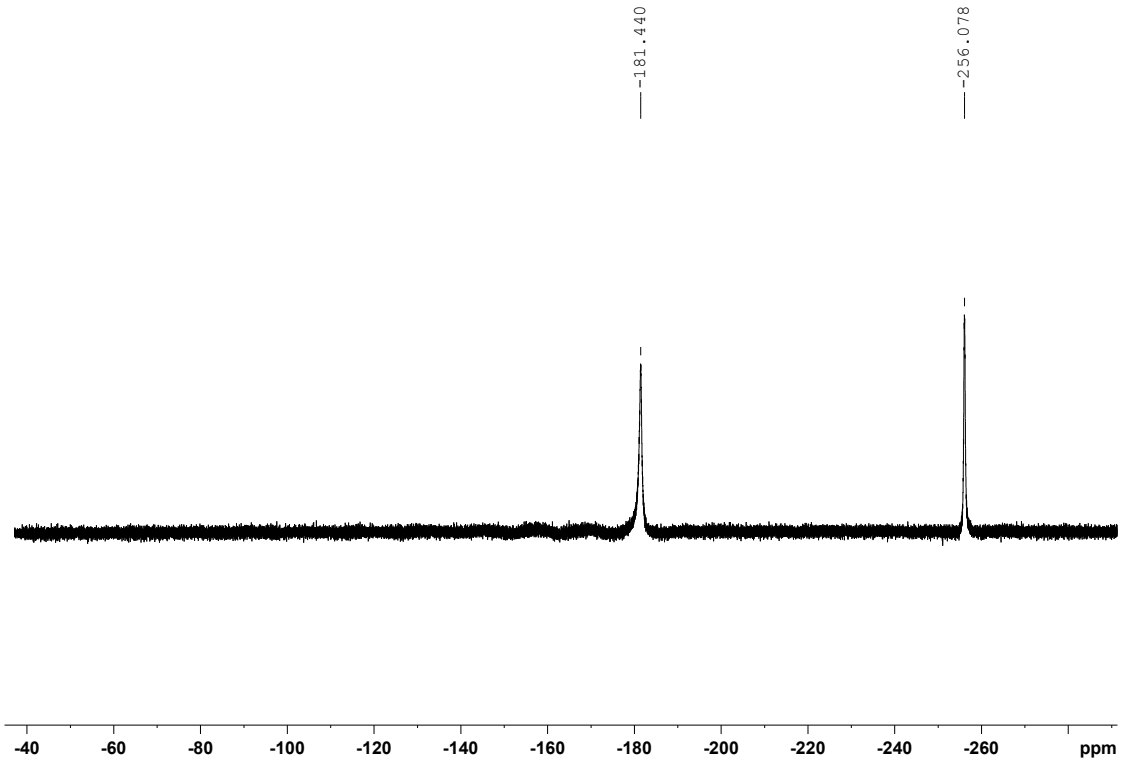


Figure S 32 $^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

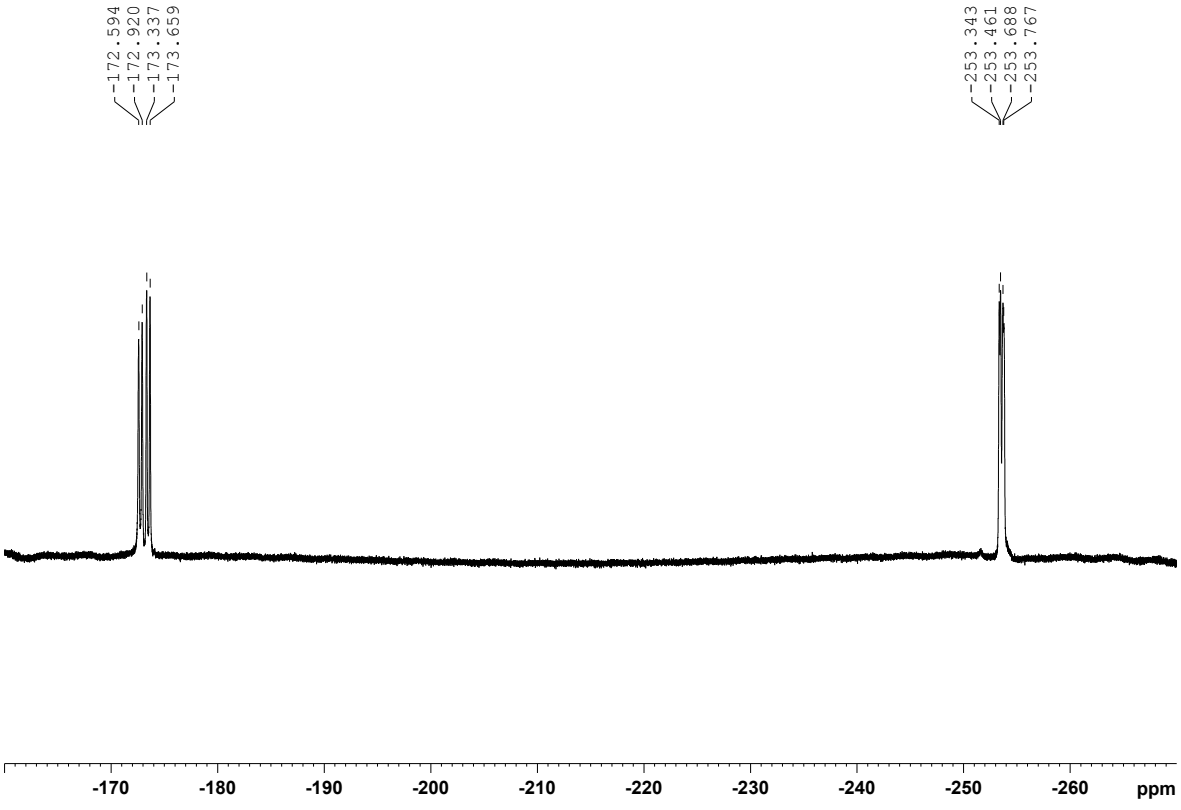


Figure S 33 ^{19}F NMR (470 MHz, 200 K, CD_2Cl_2) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

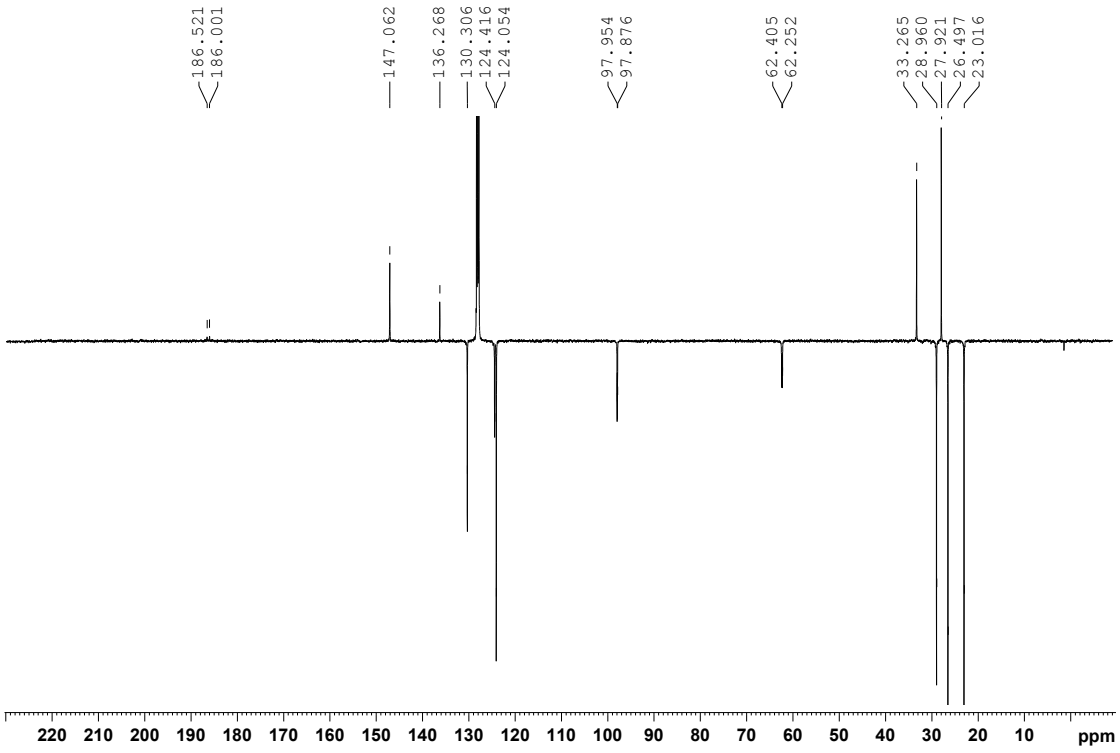


Figure S 34 $^{19}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

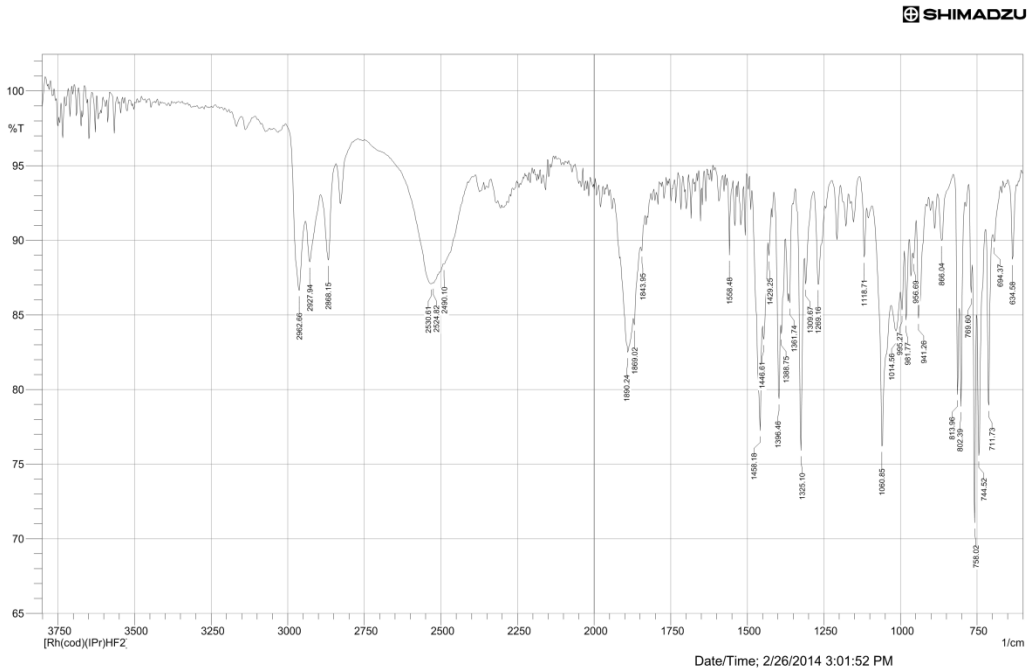


Figure S 35 FTIR (ATR) spectrum for [Rh(cod)(IPr)(HF_2)] **8**

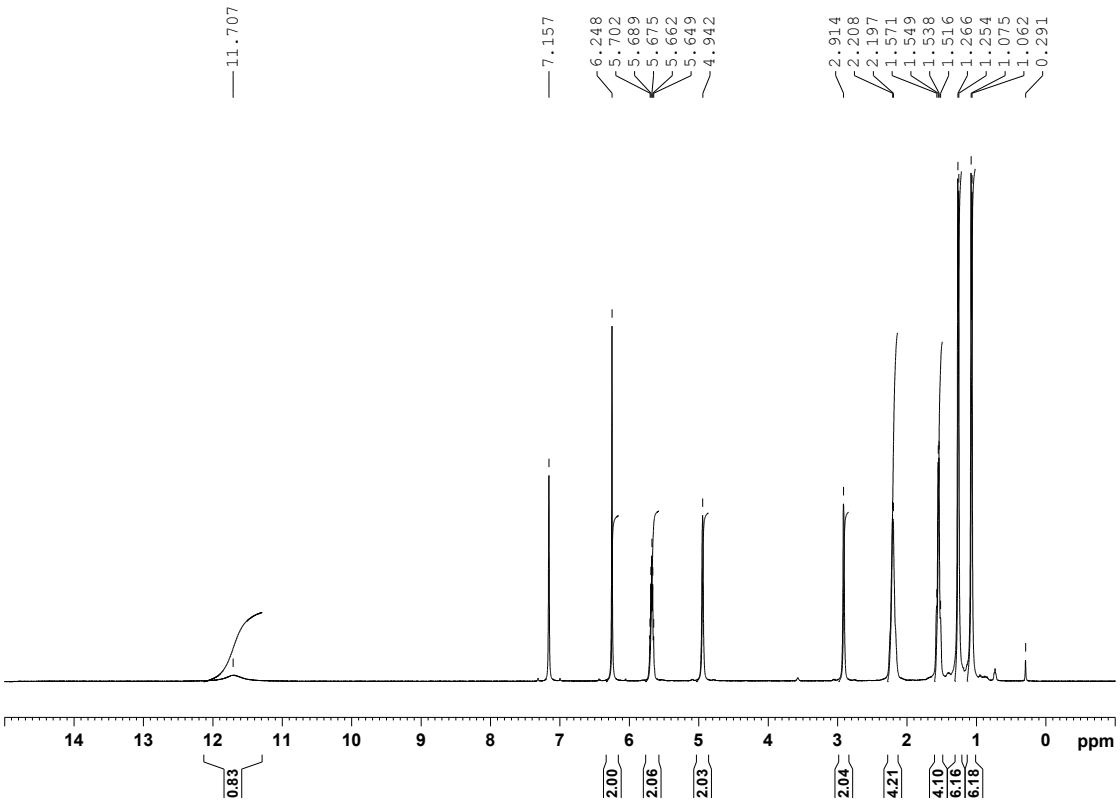


Figure S 36 ^{1}H NMR (500 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

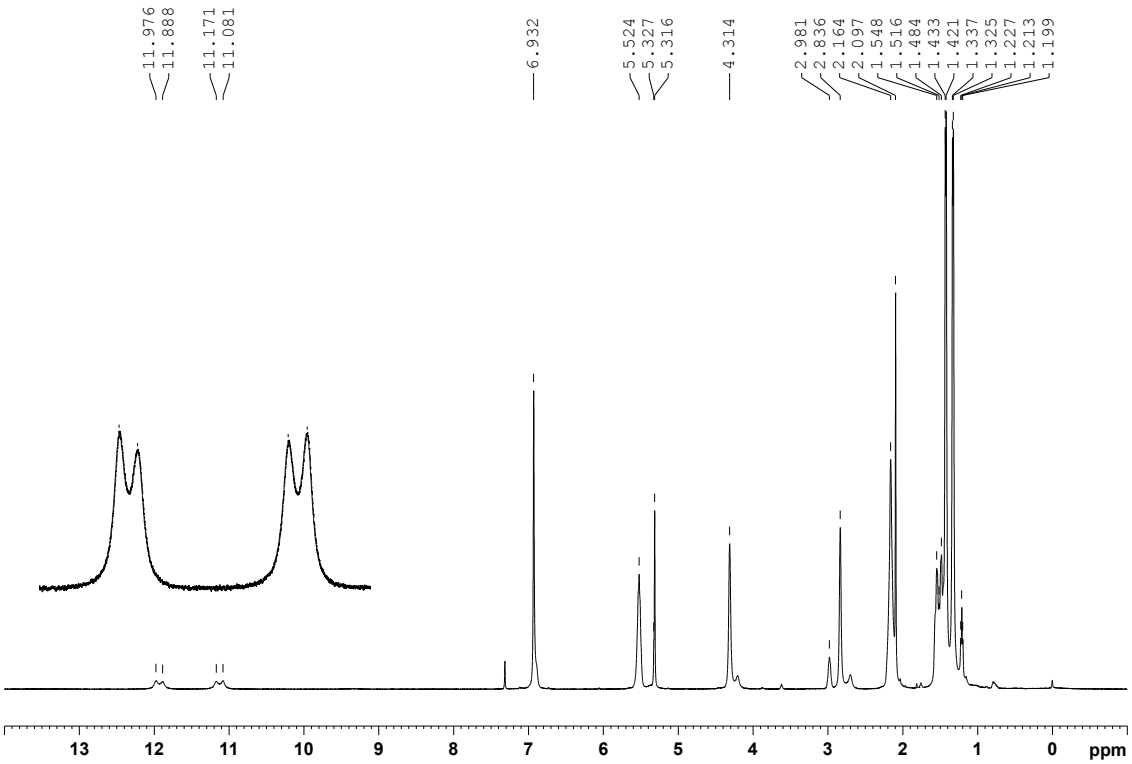


Figure S 37 ^{1}H NMR (500 MHz, 197.5K, CD_2Cl_2) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

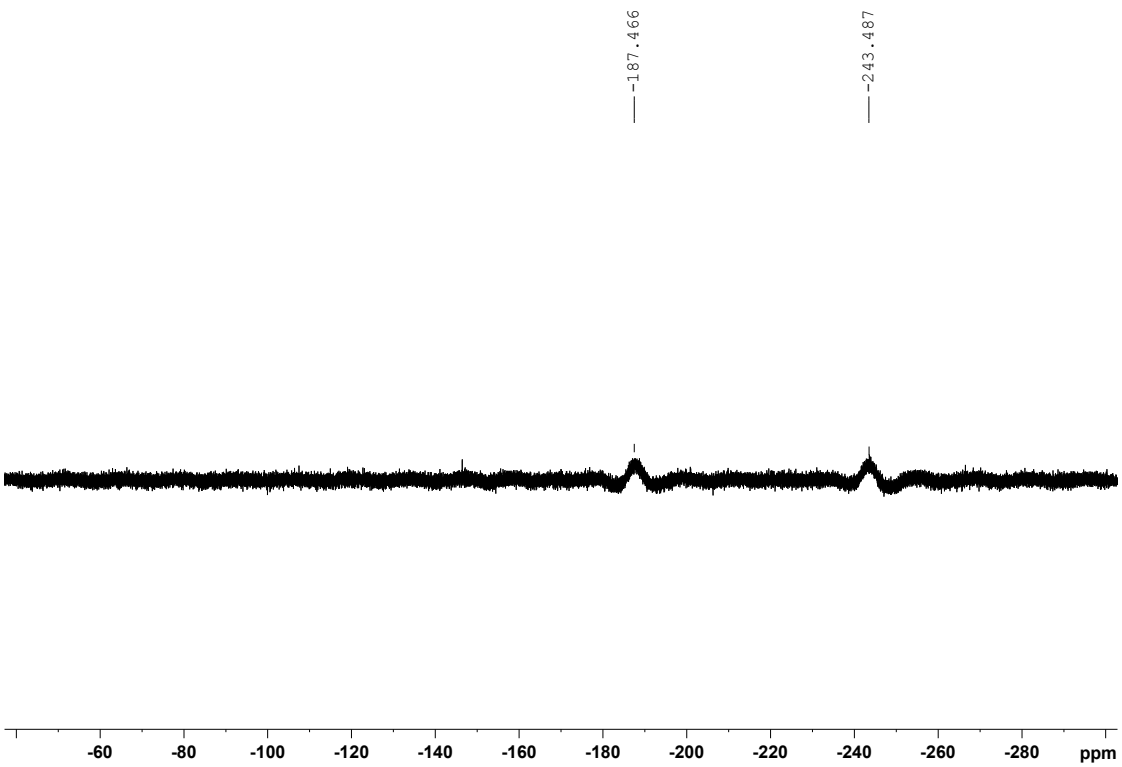


Figure S 38 ^{19}F $\{^{1}H\}$ NMR (470 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

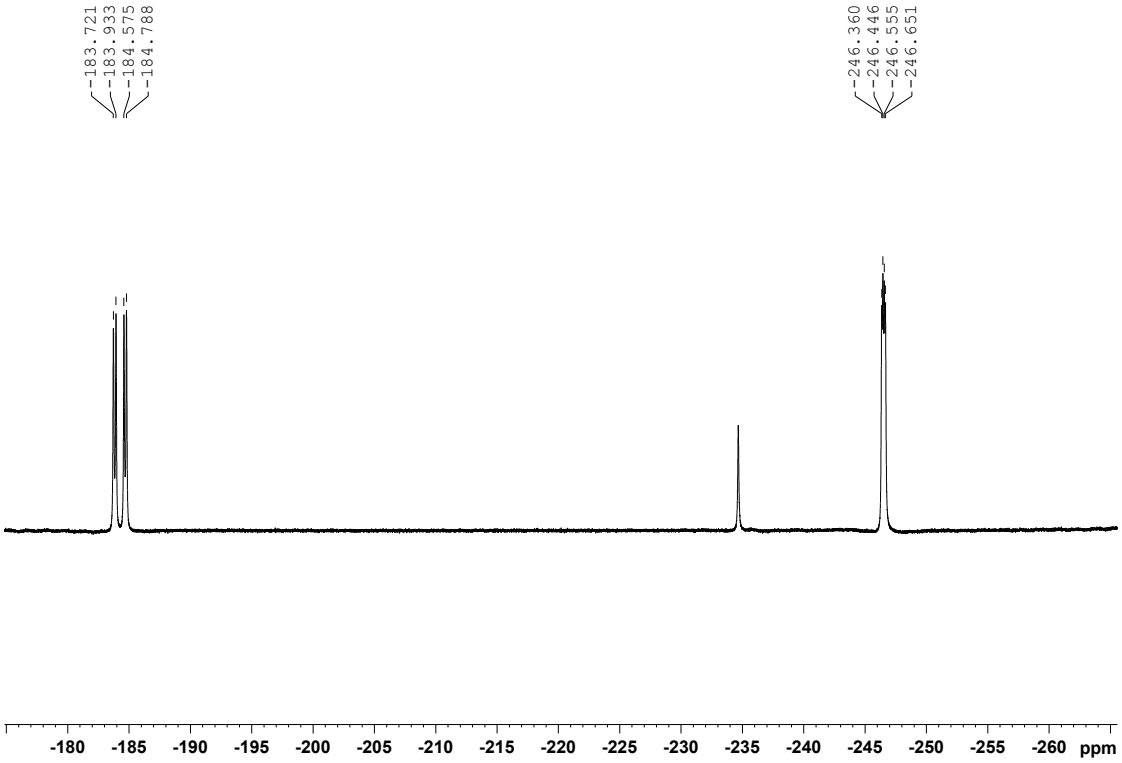


Figure S 39 ^{19}F NMR (470 MHz, 197.5K, CD_2Cl_2) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

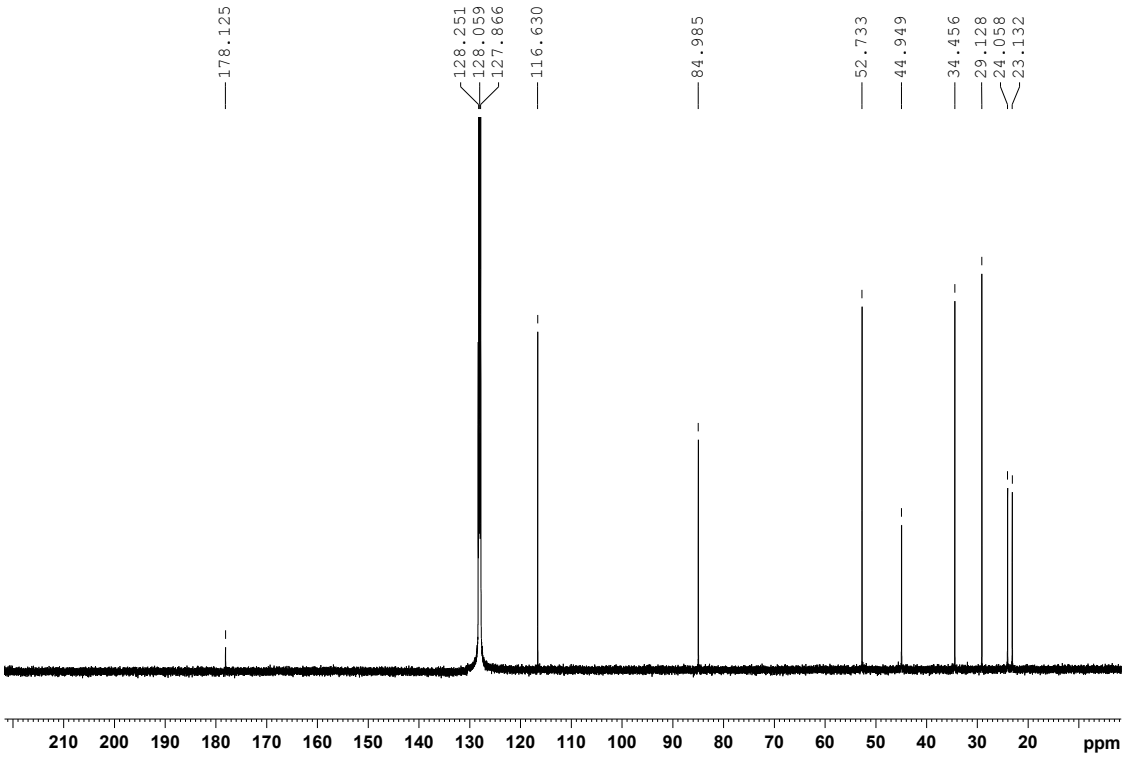


Figure S 40 ^{13}C {^{1}H} NMR (126 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

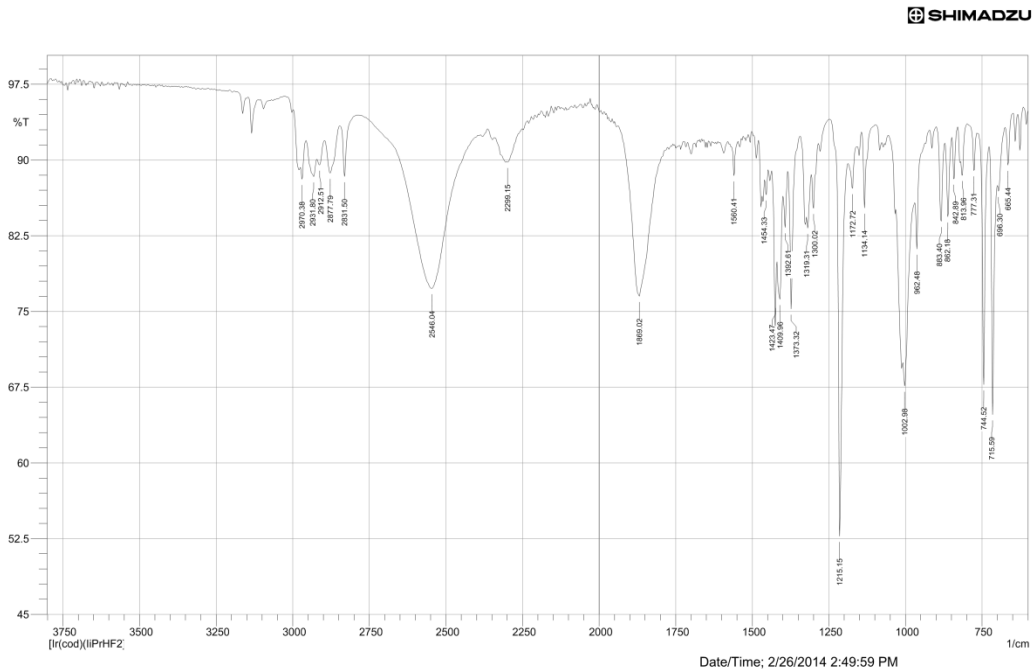


Figure S 41 FTIR (ATR) spectrum for [Ir(cod)(I^{i}Pr)(HF_2)] **9**

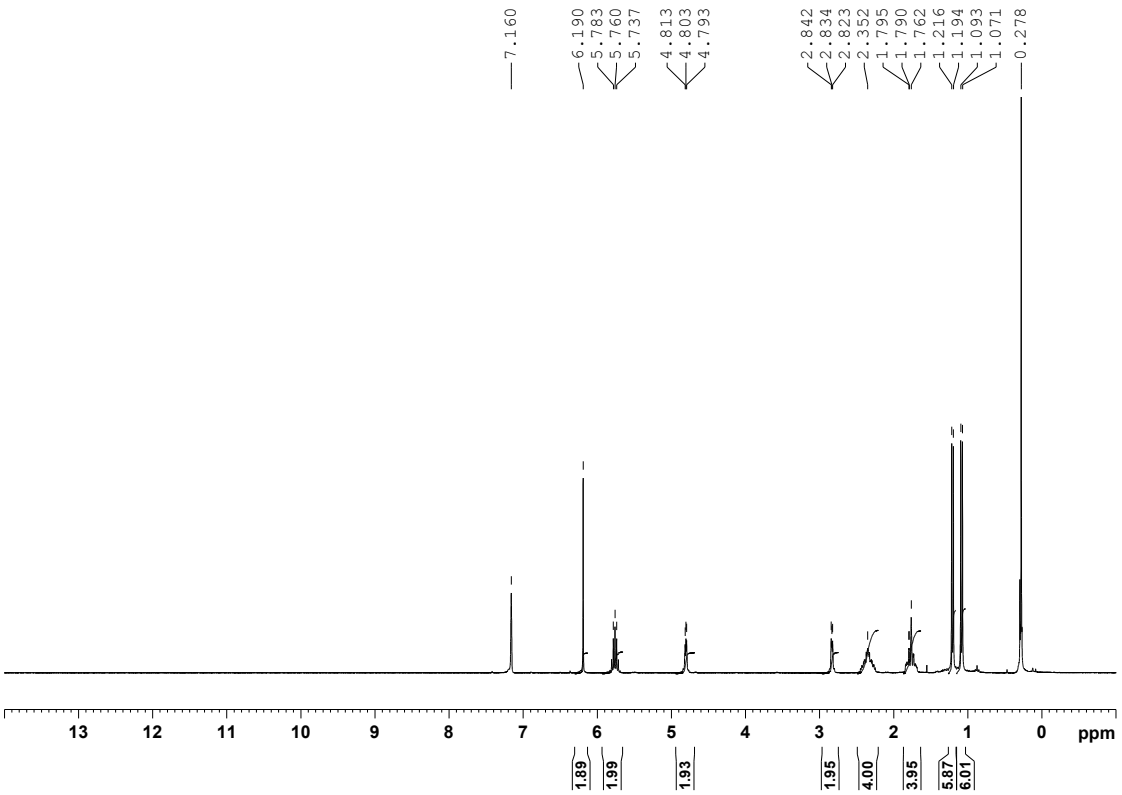


Figure S 42 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(*i*IPr)(OSiMe$_3$)] **10**

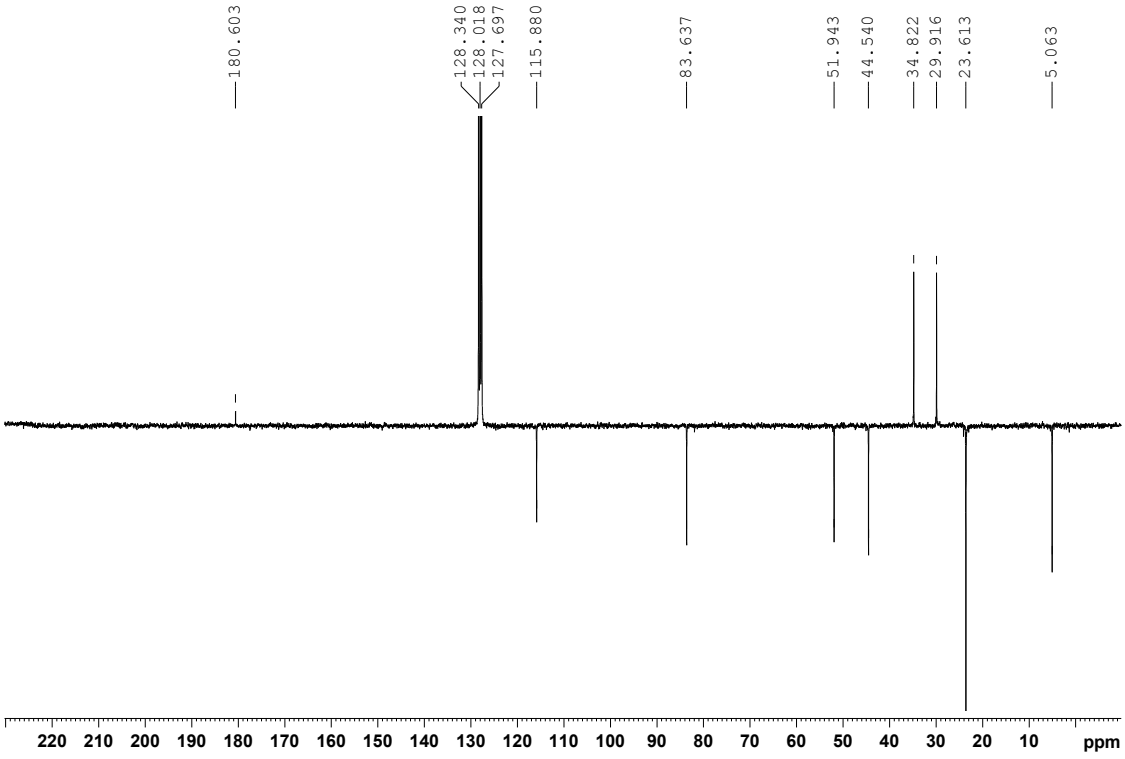


Figure S 43 ^{13}C NMR (75 MHz, C_6D_6) spectrum for [Ir(cod)(*i*IPr)(OSiMe$_3$)] **10**

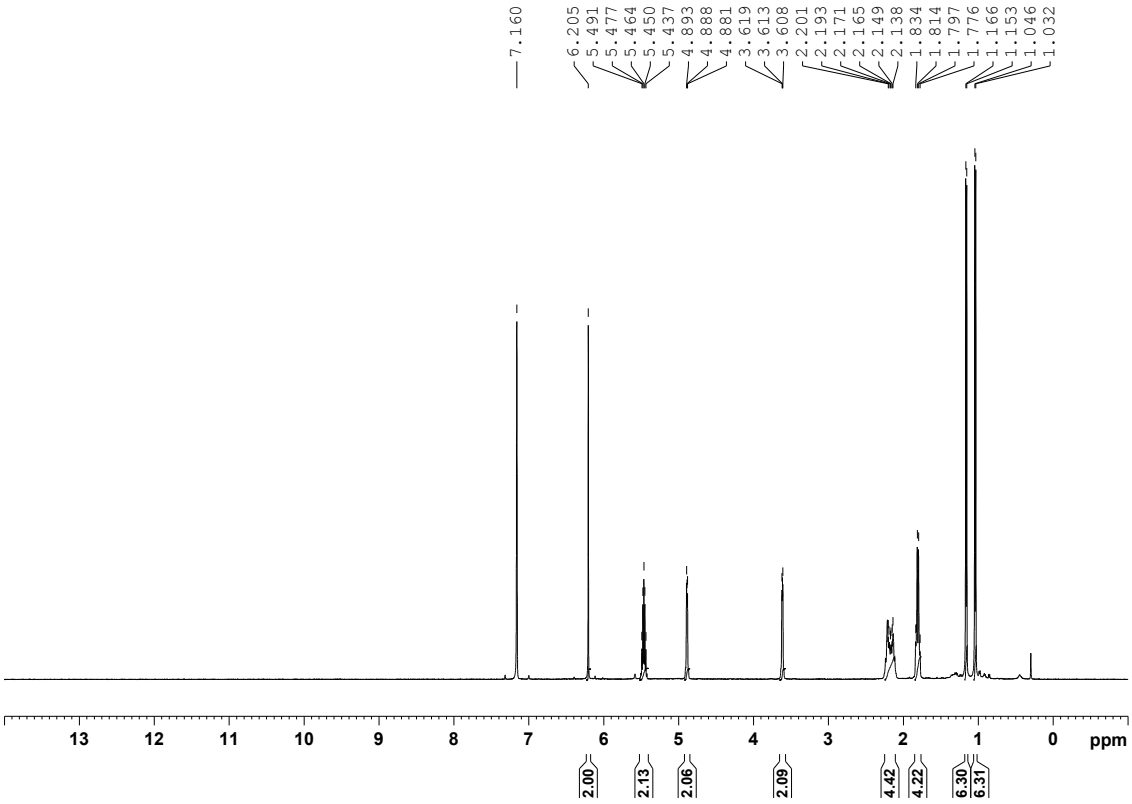


Figure S 44 ^{1}H NMR (500 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

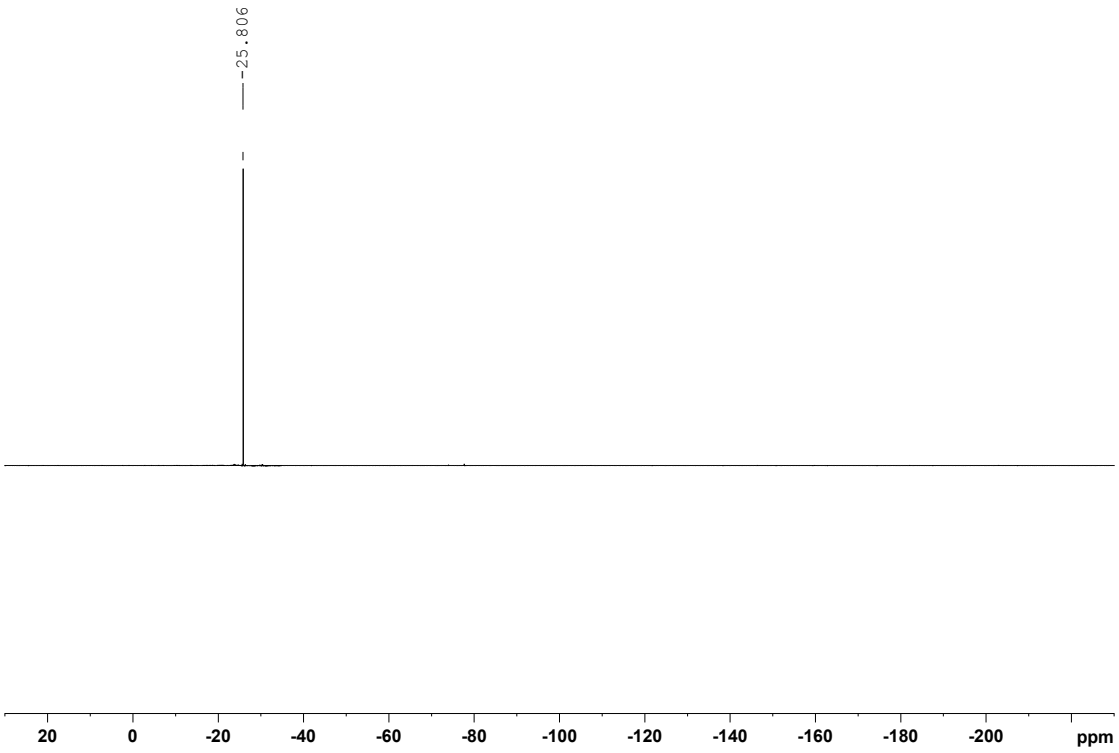


Figure S 45 $^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

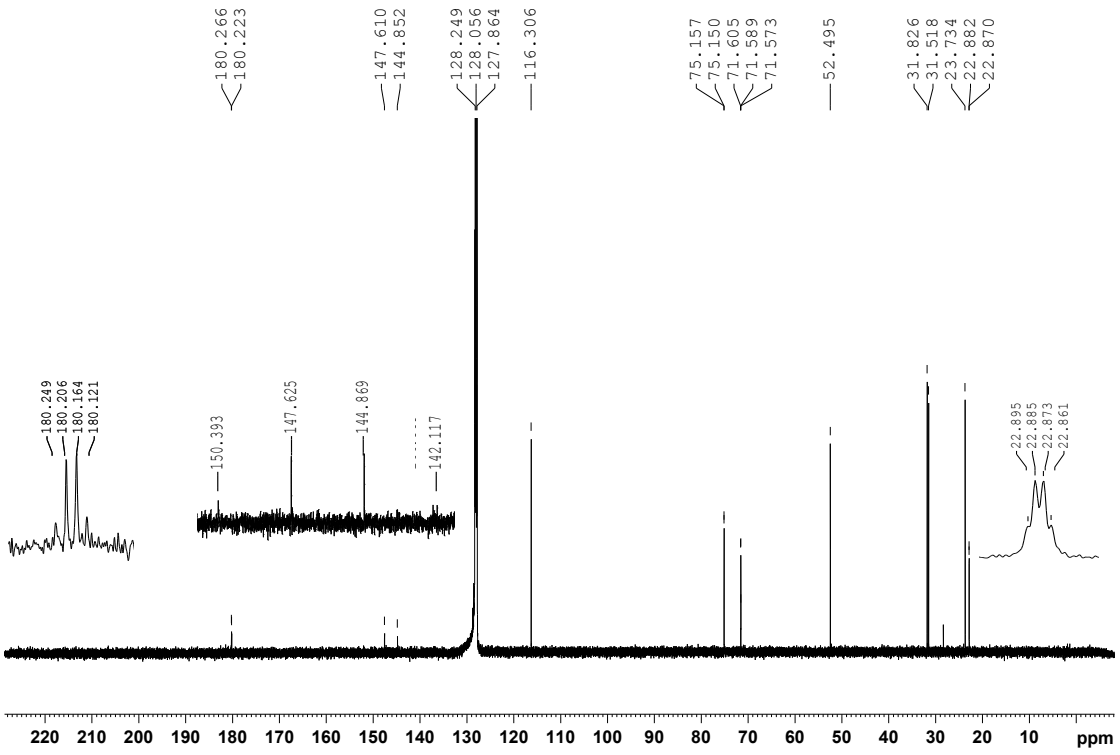


Figure S 46 $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

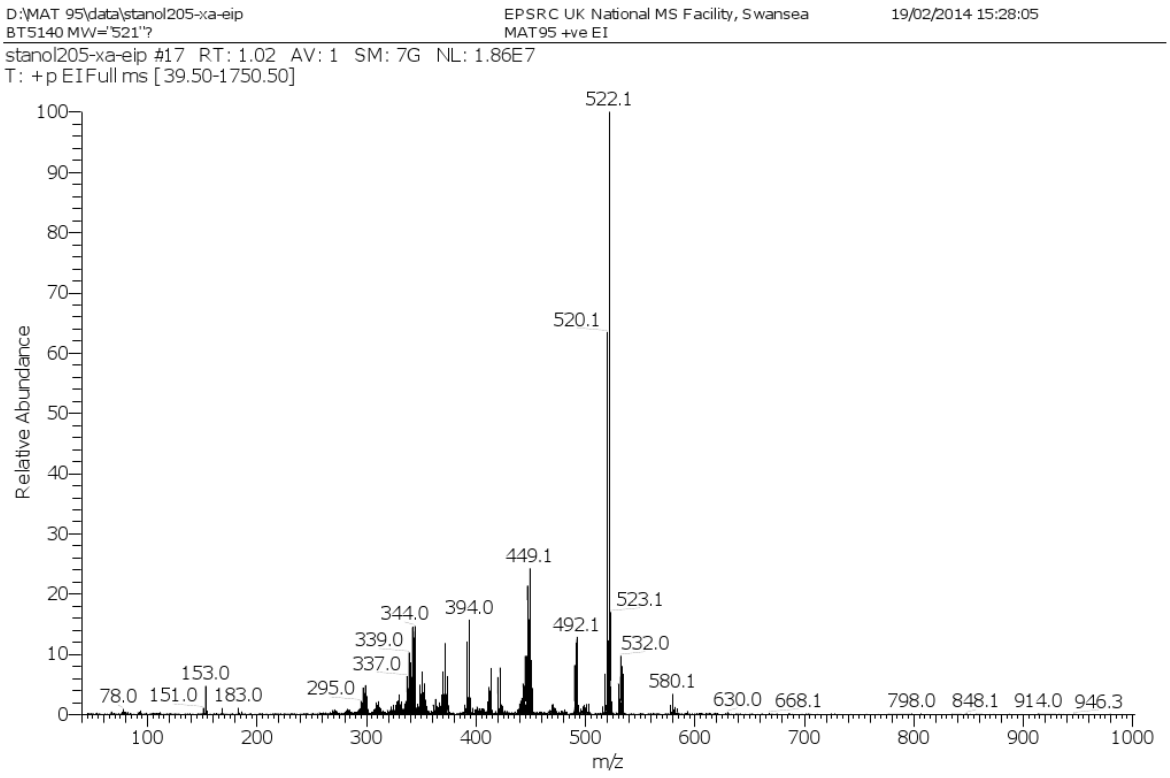


Figure S 47 Mass spectrum (+ve EI) for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

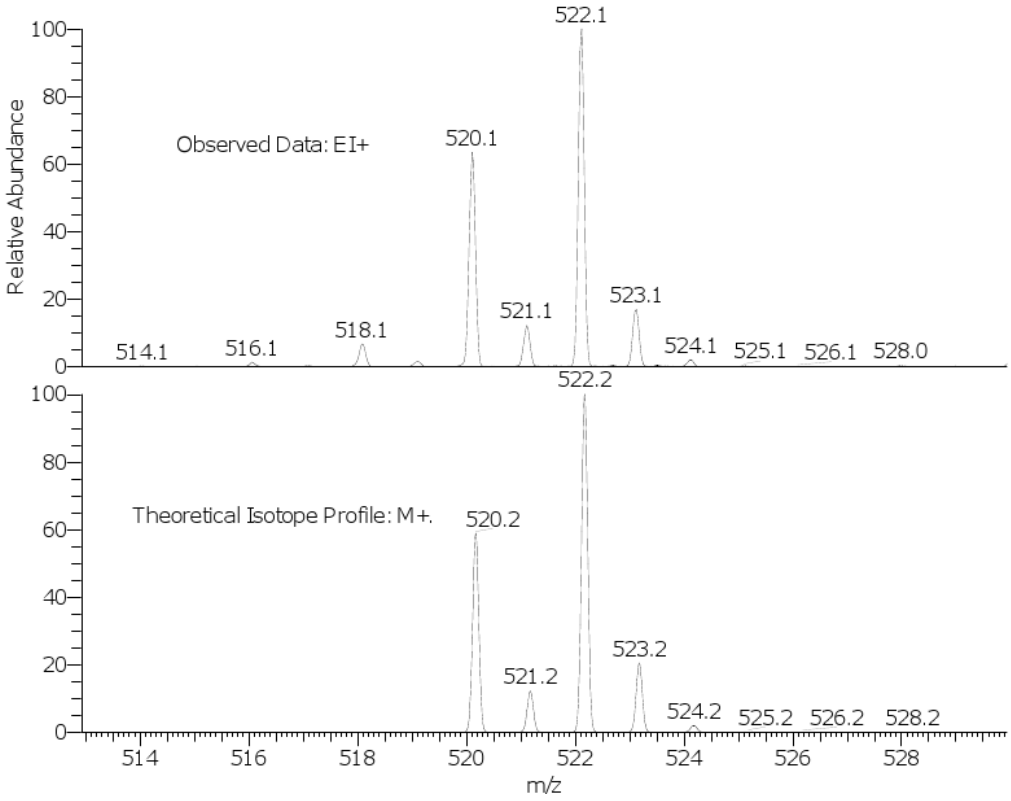


Figure S 48 Mass spectrum isotopic distribution (+ve EI) for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

Isotope:	Min. .. Max.		
12 C	0....80		
1 H	0....120		
16 O	0....12		
14 N	0....12		
191 Ir	0....2		
19 F	0....6		
Tolerance Window:	+- 5.00 ppm		
Db/Ring Equiv:	-3.. 100	N-Rule:	Do not use
Fits:	250	Charge:	1

Mass	Theoretical Mass	Delta [ppm]	RDB	Composition
520.1805	520.1805	-0.0	4.5	$C_{18}H_{29}N_2F_3{}^{191}Ir_1$
	520.1805	0.1	15.0	$C_{25}H_{24}N_6F_6$
	520.1804	0.1	17.0	$C_{29}H_{24}O_5N_2F_2$
	520.1804	0.1	22.5	$C_{38}H_{24}N_6F_2$
	520.1806	-0.2	26.0	$C_{33}H_{24}N_6F_1$
	520.1807	-0.3	18.5	$C_{30}H_{27}N_3F_1$
	520.1803	0.4	1.0	$C_{13}H_{29}N_4F_4{}^{191}Ir_1$
	520.1803	0.5	3.0	$C_{17}H_{31}O_5N_1{}^{191}Ir_1$
	520.1807	-0.5	1.0	$C_{10}H_{27}O_{11}N_{10}F_3$
	520.1803	0.5	8.5	$C_{16}H_{29}N_8{}^{191}Ir_1$
	520.1802	0.5	13.5	$C_{24}H_{28}O_5N_6F_3$
	520.1802	0.5	19.0	$C_{23}H_{31}N_{12}F_3$
	520.1808	-0.6	29.5	$C_{38}H_{22}N_3$
	520.1809	-0.7	22.0	$C_{35}H_{24}F_4$
	520.1801	0.8	-2.5	$C_9H_{26}N_2F_5{}^{191}Ir_1$
	520.1801	0.8	-0.5	$C_{12}H_{31}O_5N_4F_1{}^{191}Ir_1$
	520.1809	-0.8	4.5	$C_{15}H_{29}O_{11}N_2F_2$
	520.1801	0.8	5.0	$C_{11}H_{31}N_{11}F_1{}^{191}Ir_1$
	520.1800	0.9	4.5	$C_{20}H_{30}O_{10}N_2F_4$
	520.1800	0.9	10.0	$C_{19}H_{24}O_5N_8F_4$
	520.1810	-0.9	2.5	$C_{11}H_{29}O_6N_{11}F_6$
	520.1810	-0.9	-3.0	$C_{12}H_{31}O_{11}N_4F_6$
	520.1800	1.0	12.0	$C_{23}H_{28}O_{10}N_4$
	520.1800	1.0	17.5	$C_{22}H_{31}O_5N_{12}$
	520.1811	-1.2	13.5	$C_{19}H_{33}O_6N_{11}F_1$
	520.1811	-1.2	8.0	$C_{20}H_{29}O_{11}N_4F_1$
	520.1798	1.3	1.0	$C_{15}H_{31}O_{10}N_4F_5$
	520.1798	1.3	6.5	$C_{14}H_{27}O_5N_{11}F_5$
	520.1812	-1.3	6.0	$C_{16}H_{25}O_6N_8F_5$
	520.1812	-1.3	0.5	$C_{17}H_{31}O_{11}N_2F_5$
	520.1812	-1.4	1.0	$C_8H_{25}O_3N_{11}F_2{}^{191}Ir_1$

Figure S 49 HRMS analysis of peak 520.18601 for [Ir(cod)(I^{i}Pr)(CF_3)] **11**

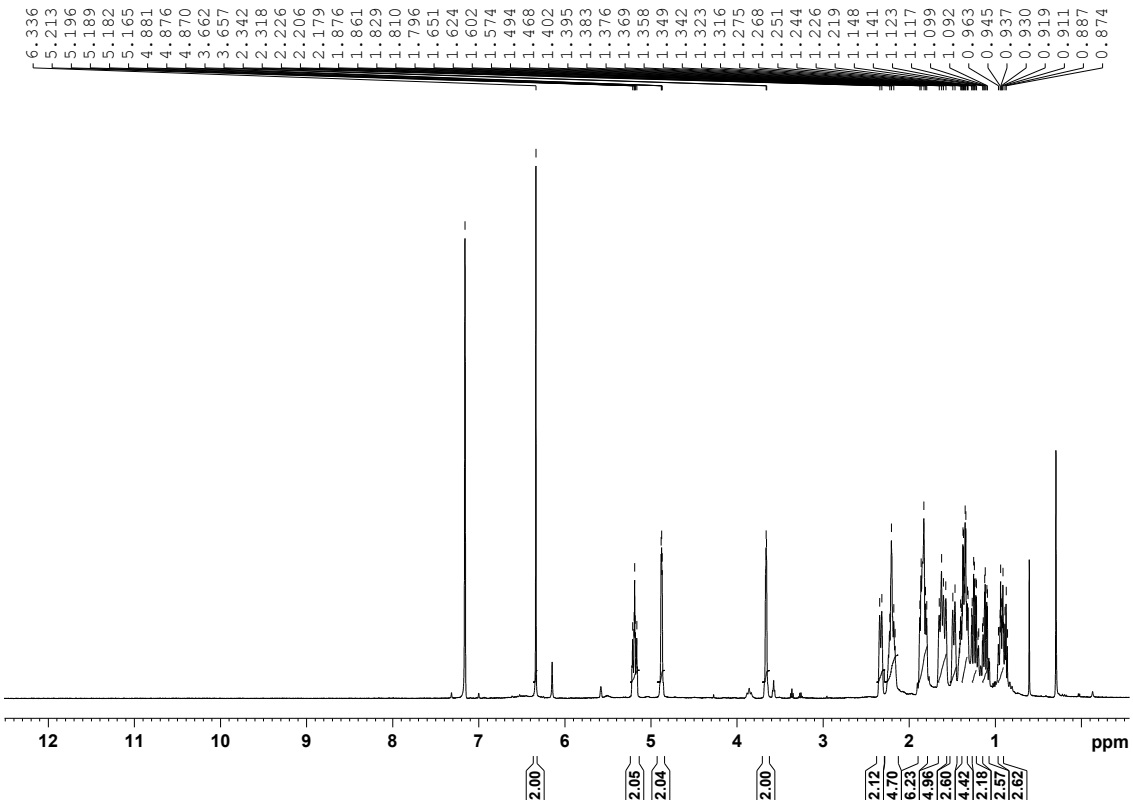


Figure S 50 ^{1}H NMR (300 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(CF_3)] **12**

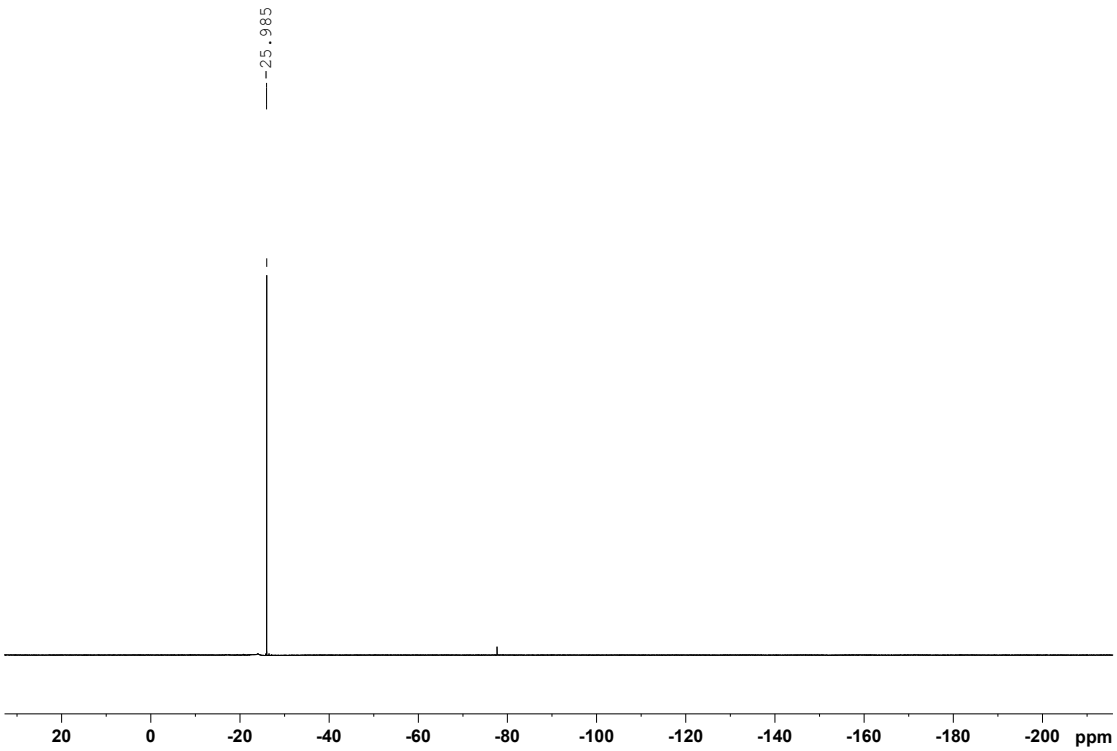


Figure S 51 $^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(CF_3)] **12**

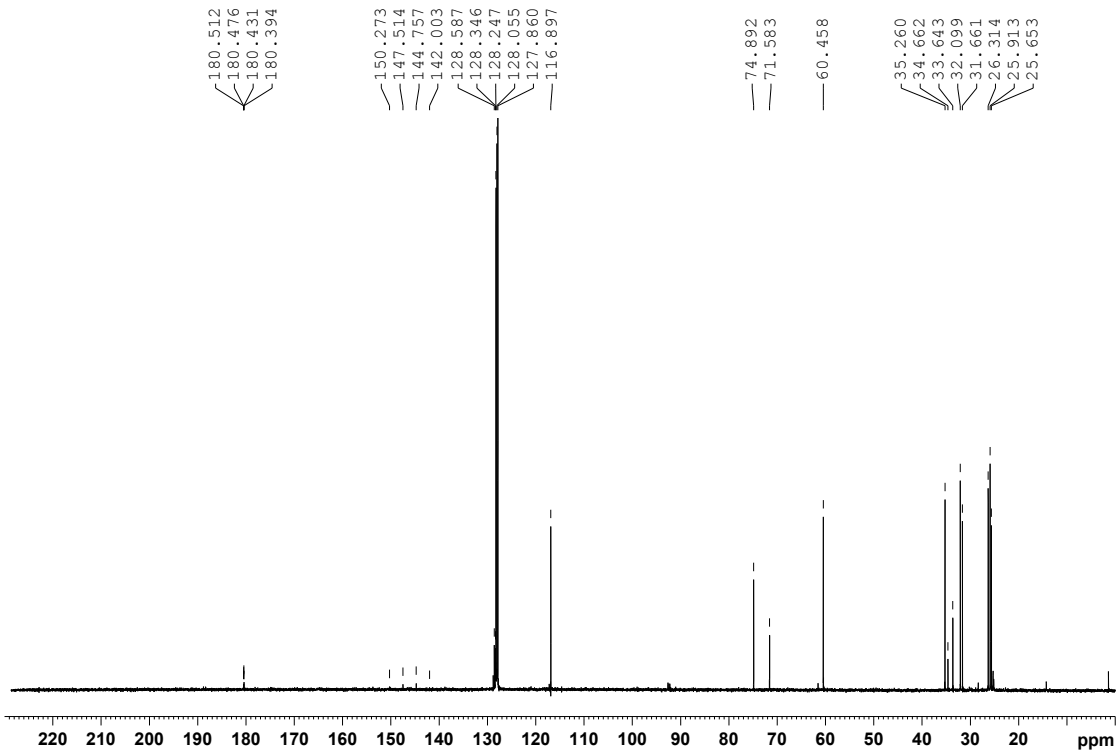


Figure S 52 $^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) spectrum for [Ir(cod)(ICy)(CF_3)] **12**

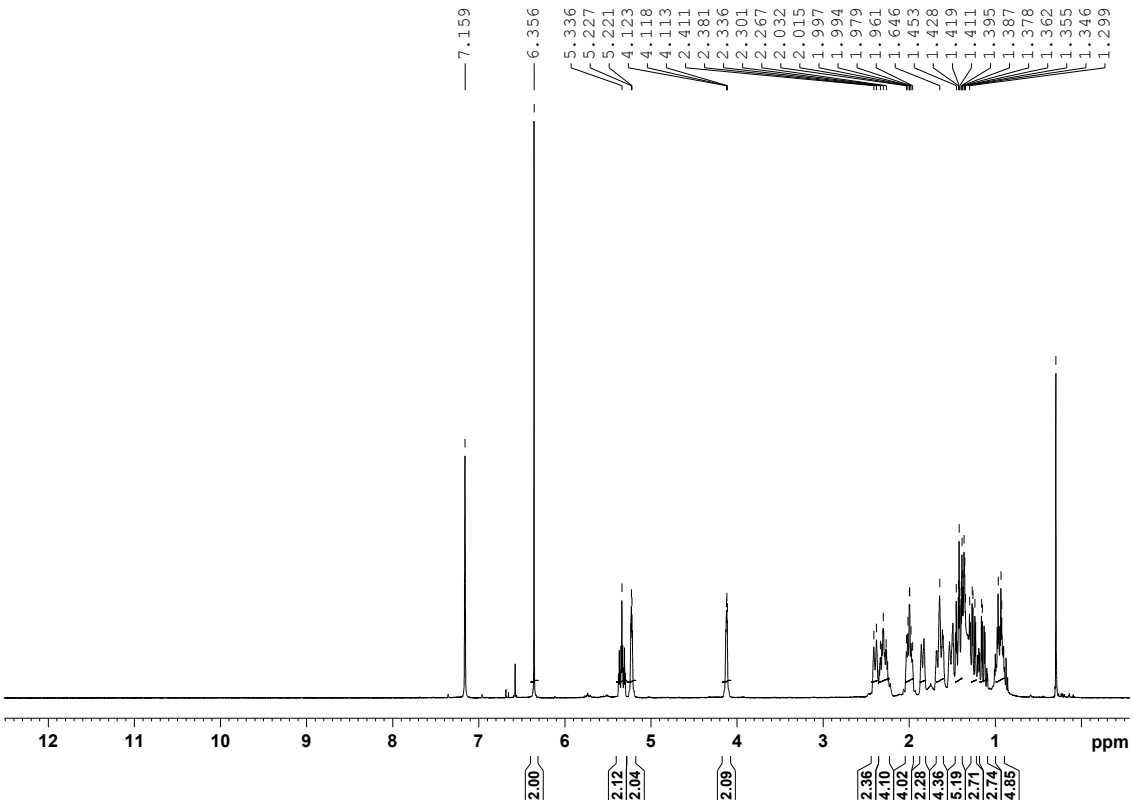


Figure S 53 ^{1}H NMR (400 MHz, C_6D_6) spectrum for [Rh(cod)(ICy)(CF_3)] **13**

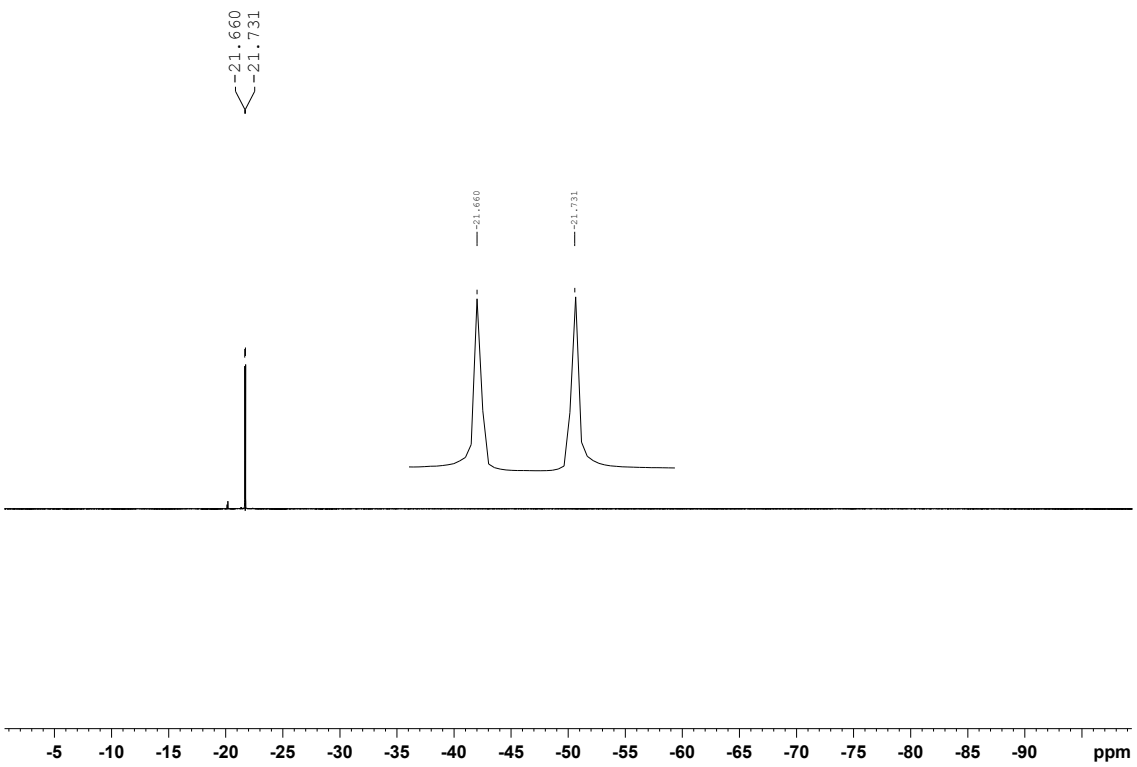


Figure S 54 $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6) spectrum for [Rh(cod)(ICy)(CF_3)] **13**

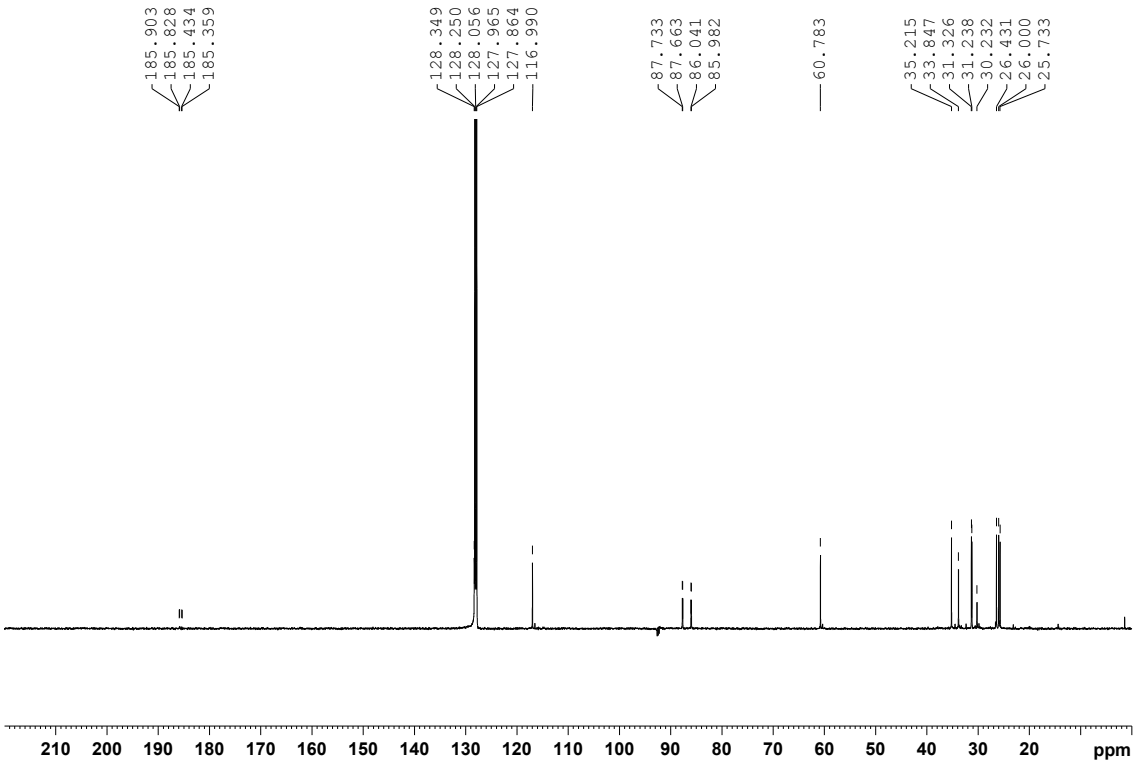


Figure S 55 $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) spectrum for [Rh(cod)(ICy)(CF_3)] **13**

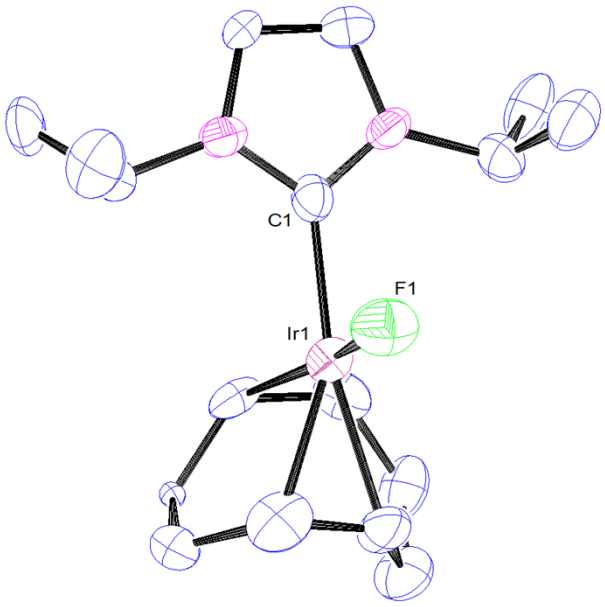


Figure S 56. Thermal ellipsoid representation of complex **3** showing 50% thermal ellipsoid probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°), numbers in parentheses are for second independent molecule: Ir(1)-C(1) 2.038(17),[2.035(16)]; Ir(1)-F(1) 2.002(10), [2.012(9)]; C(1)-Ir(1)-F(1) 88.4(5),[88.6(5)].

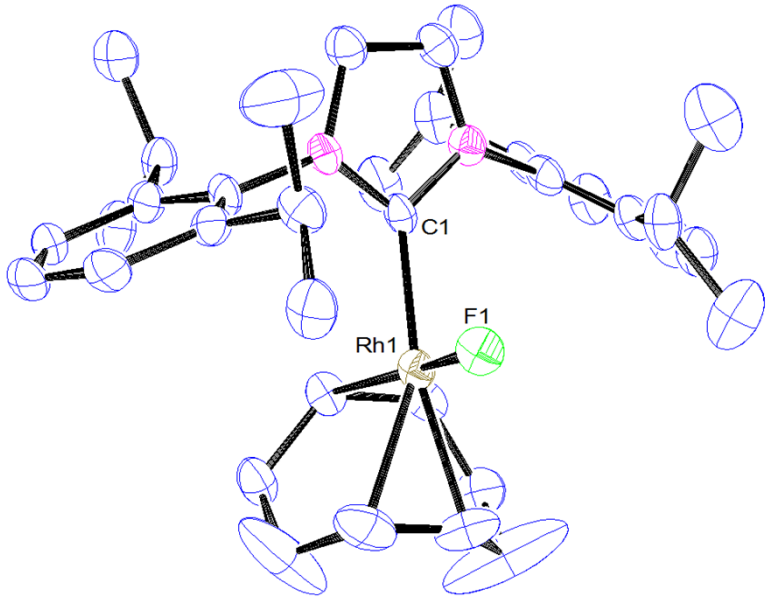


Figure S 57. Thermal ellipsoid representations of complexe **6** showing 50% thermal ellipsoid probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°), numbers in parentheses are for second/third independent molecules: Rh(1)-C(1) 2.044(8), [2.063(8)], [2.035(8)]; Rh(1)-F(1) 2.028(5), [2.086(6)], [2.033(5)]; C(1)-Rh(1)-C(1) 89.1(3), [85.6(3)], [88.0(3)].

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