Iridium Abnormal N-Heterocyclic Carbene Complexes via Highly Selective C-H Activation

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General descriptions ----------S2

Synthesis of phosphine-imidazolium ligands ----------S2-S9

The kinetic studies for the conversion of 4 to 5 ----------S9-S10

The chemical equilibrium between complexes 7 and 8 ----------S11-S12

^{19}F-^{1}H HOESY spectra of complexes 5 and 8a-(PF_6) ----------S13

X-ray data for complex 5 ----------S14-S23

X-ray data for complex 8a-(PF_6) ----------S24-S33

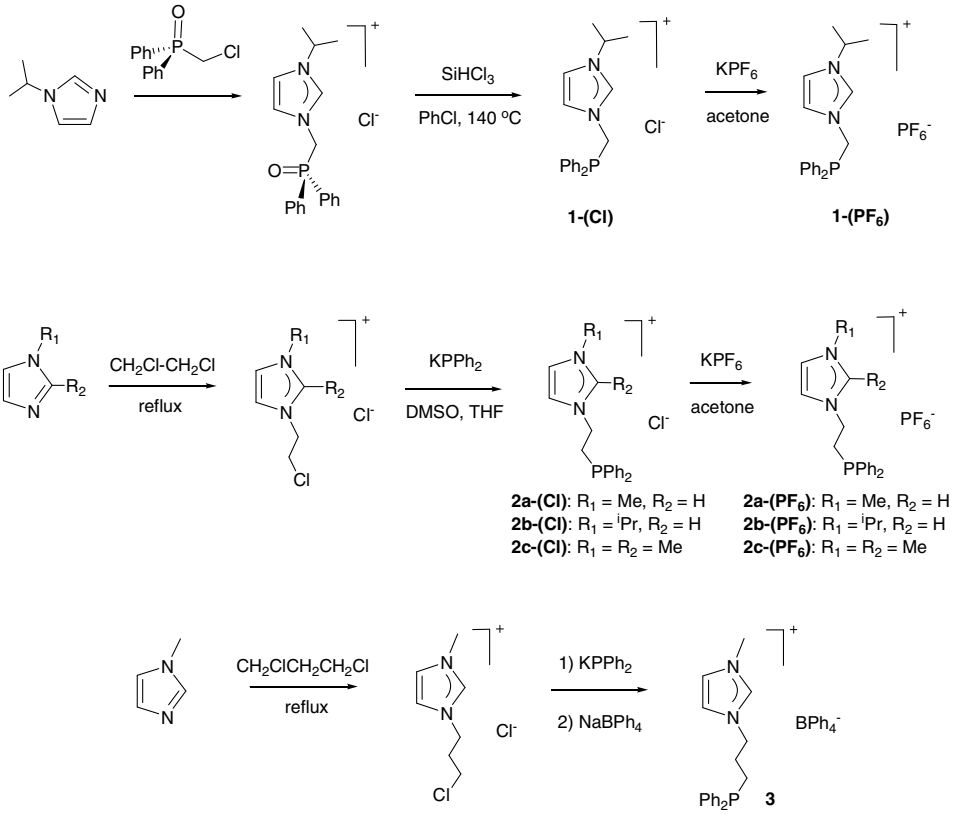
NMR spectra ----------S34-S54

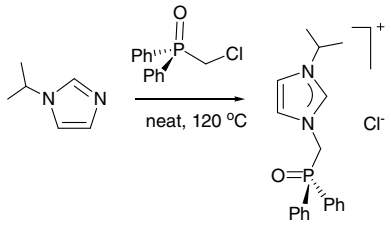
General Descriptions

All manipulations were performed using standard Schlenk techniques or in a nitrogen-filled glove box. All solvents were distilled under N_2 and were stored in a glove-box. $CDCl_3$ was degassed and dried by 4Å molecular sieves. CD_2Cl_2, CD_3CN, and DMSO-d_6 were obtained from CIL in sealed ampules and were used as received. Air-sensitive chemicals were stored and weighted inside a glove box.

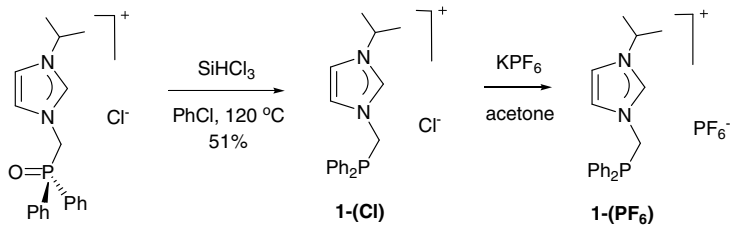
NMR spectra were recorded on Bruker DPX 300, Bruker AMX 400 or Bruker 500 spectrometers. All spectra were obtained at 298K unless otherwise specified. Temperatures (≥ 290 K) of NMR samples for kinetic and thermodynamic studies were calibrated by using 80% ethylene glycol in DMSO-d_6. The chemical shifts are given as δ values and are referenced relative to tetramethylsilane for ^{1}H and ^{13}C NMR spectroscopy and relative to 85% H_3PO_4 for ^{31}P NMR spectroscopy. Elemental analyses were performed in the Division of Chemistry and Biological Chemistry, Nanyang Technological University and were not performed for imidazolium chlorides, which are highly hydroscopic. Instead, their PF_6^- salt derivatives were analyzed. HRMS spectra were obtained in ESI or EI mode on a Finnigan MAT95XP GC/HRMS spectrometer (Thermo Electron Corp.). X-ray crystallographic data was collected on a Bruker X8 APEX diffractometer.

Synthesis of Phosphine-Imidazoliums Ligands





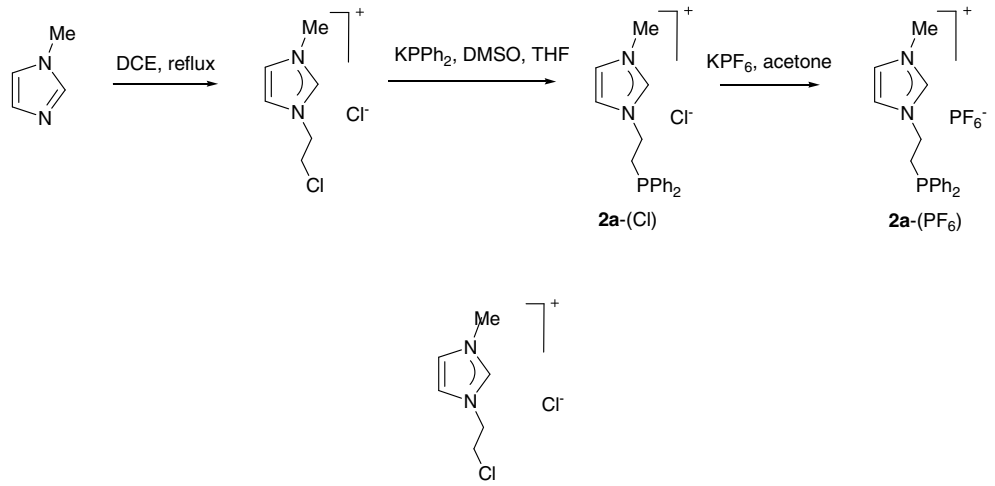
This imidazolium phosphine oxide was synthesized by following a literature report.[1] Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.66 (s, 1H, imidazole H2), 8.11-8.15 (m, 4H, PPh_2), 7.80 (s, 1H, imidazole H4/5), 7.53-7.57 (m, 6H, PPh_2), 7.09 (s, 1H, imidazole H4/5), 5.87 (d, $^{2}J_{P\text{-}H}$ = 5.1 Hz, 2H, N-CH_2), 4.45 (heptet, ^{3}J = 5.4 Hz, 1H, CH of ^{i}Pr), 1.42 (d, ^{3}J = 5.6 Hz, 6H, 2CH_3). ^{31}P {^{1}H} NMR (161 MHz, $CDCl_3$): δ 27.73. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0 (s, imidazole C2), 133. 1 (s, PPh_2), 131.4 (d, $J_{P\text{-}C}$ = 10.0 Hz, PPh_2), 129.2 (d, $J_{P\text{-}C}$ = 12.4 Hz, PPh_2), 127.6 (d, $J_{P\text{-}C}$ = 103 Hz, *ipso*-PPh_2), 123.7 (s, imidazole C4/5), 119.2 (s, imidazole C4/5), 53.5 (s, CH of ^{i}Pr), 49.1 (d, $J_{P\text{-}C}$ = 33.7 Hz, CH_2), 22.9 (s, 2CH_3). HRMS (m/z, ESI^{+}): 325.1475; Calcd for $[C_{19}H_{22}OPN_2]^{+}$: 325.1464.



3-[2-(Diphenylphosphino)methyl]-1-isopropyl-imidazolium chloride [1-(Cl)] and hexafluorophosphate [1-(PF_6)]

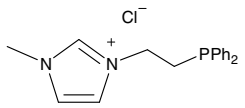
A mixture of the imidazolium phosphine oxide (1.8 g, 5.0 mmol) and chlorobenzene (30 ml) was placed into a glass pressure tube. Trichlorosilane (4 ml, 28.8 mmol) was added to the suspension at room temperature. The mixture was sealed, heated to 120 °C for 3 hour, and cooled to room temperature. After addition of dichloromethane (50 ml), any excess amount of trichlorosilane was quenched by careful addition of degassed aq NaOH solution (10%) at 0 °C. The organic layer was separated by syringe and the aqueous phase was washed with dichloromethane. The organic layers were combined and dried (Na_2SO_4). All volatiles were removed under vacuum and the residue was washed with diethyl ether to give **1-**(Cl) as a white hydroscopic solid in 51% yield (880 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.71 (s, 1H, imidazole H2), 7.52-7.58 (m, 4H, PPh_2), 7.38-7.39 (m, 6H, PPh_2), 7.32 (m, 1H, imidazole H4/5), 7.06 (m, 1H, imidazole H4/5), 5.25 (d, $^{2}J_{P\text{-}H}$ = 5.64 Hz, 2H, N-CH_2-P), 4.65 (heptet, 1H, J = 6.7 Hz, CH of ^{i}Pr), 1.46 (d, J = 6.7 Hz, 6H, 2CH_3). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -11.46 (s). No satisfactory microanalysis was obtained for **1**-(Cl) due to its hydroscopicity. Instead, satisfactory microanalysis was obtained for the PF_6^{-} salt [1-(PF_6)]. Compound **1-**(PF_6) was obtained by anion exchange between **1-**(Cl) and KPF_6. Compound **1**-(Cl) (300 mg, 0.868 mmol) was dissolved in acetone (10 mL), to which was added KPF_6 (1.0 g, 5.4 mmol). The mixture was stirred for 12 h followed by removal of all the solvent under reduced pressure. To this residue was added CH_2Cl_2 (15 mL) and all the insolubles were removed by filtration. Removal of all the CH_2Cl_2 gave a white solid and was dried under

vacuum to give analytically pure **1**-(PF_6). ^{1}H NMR (400 MHz, $CDCl_3$) of **1**-(PF_6): δ 8.92 (s, 1H imidazole H2), 7.80-7.82 (m, 2H, imidazole H4 and H5), 7.45-7.55 (m, 10H, PPh_2), 5.13 (m, 2H, N-CH_2-P), 4.54 (m, 1H, CH of ^{i}Pr), 1.34 (d, 6H, 2CH_3). ^{31}P {^{1}H} NMR (161 MHz, DMSO-d_6): δ -11.60 (s, PPh2), -144.2 (heptet, $J_{P\text{-}F}$ = 707 Hz, PF_6^-). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 135.0 (s, imidazole C2), 134.0 (d, $J_{P\text{-}C}$ = 12.5 Hz, *ipso*-PPh_2), 133.2 (d, $J_{P\text{-}C}$ = 19.3Hz, PPh_2), 130.5 (s, PPh_2), 129.5 (d, $J_{P\text{-}C}$ = 6.7 Hz, PPh_2), 123.3 (s, imidazole C4/5), 121.4 (s, imidazole C4/5), 52.8 (s, CH of ^{i}Pr), 47.9 (d, $J_{P\text{-}C}$ = 20 Hz, N-CH_2-P), 22.7 (s, CH_3 of ^{i}Pr). Anal. Calcd for $C_{19}H_{22}F_6N_2P_2$ (454.1): C, 50.23; H, 4.88; N, 6.17; Found: C, 50.12; H, 4.62; N, 6.09.



3-(2-chloroethyl)-1-methylimidazolium chloride

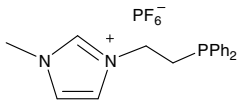
1-methylimidazole (1.0 g) was dissolved in 1,2-dichloroethane (15ml) and the solution was stirred under reflux for 20 h. 1,2-Dichloroethane was then removed under vacuum and the resulting residue was dissolved in hot acetonitrile (40 mL). Cooling of this solution to -20 ^{o}C gave precipitates which were mostly the dicationic side product. The precipitates were rapidly removed by filtration while the solution was cold. Removal of all the acetonitrile of the filtrate gave a colorless viscous liquid which slowly solidified to give a white hydroscopic solid. Yield: 75% (1.65 g). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.31 (s, 1H, imidazole H2), 8.00-8.01 (m, 1H, imidazole H4/5), 7.87-7.88 (m, 1H, imidazole H4/5), 4.61 (t, ^3J = 5.2 Hz, N-CH_2), 4.07 (t, ^3J = 5.6 Hz, Cl-CH_2), 3.86 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 137.2 (s, C2), 124.2 (s, C4/5), 122.2 (s, C4/5), 51.4 (s, N-CH_2), 43.9 (s, Cl-CH_2), 35.8 (s, CH_3). HRMS (ESI$^+$): 146.0598. Calcd for $[C_6H_{10}{}^{35}ClN]^+$ 146.0605.



3-[2-(Diphenylphosphino)ethyl]-1-methylimidazolium chloride [2a-(Cl)]

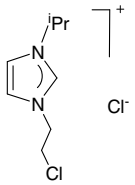
Potassium diphenylphosphide in THF solution (0.5 M, 10 mL, 5 mmol) was added dropwise to a solution of 3-(2-chloroethyl)-1-methylimidazolium chloride (910 mg, 5 mmol) in DMSO (10 ml). The mixture was stirred at room temperature for 3 hours, followed by removal of DMSO under

reduced pressure. Methanol (5 ml) was then added and the mixture was stirred for 20 min followed by removal of all volatiles under vacuum. The residue was then dissolved in dichloromethane (15 mL) and was filtered to remove inorganic salts. All the solvent was then removed under vacuum to afford 3-[2-(Diphenylphosphino)ethyl]-1-methylimidazolium chloride as a white solid after washing with diethyl ether (5 × 10 mL). Yield: 1.52 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.67(s, 1H, imidazole H2), 7.33-7.52(m, 12H, PPh_2 + imidazole CH), 4.39-4.45 (m, 2H, N-CH_2), 3.99 (s, 3H, CH_3), 2.74-2.79 (m, 2H, P-CH_2). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -21.33 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9 (s, imidazole C2), 136.1 (d, $J_{P\text{-}C}$ = 11.6 Hz, *ipso*- PPh_2), 132.7 (d, $J_{P\text{-}C}$ = 19.3 Hz, PPh_2), 129.3 (s, PPh_2), 128.8 (d, $J_{P\text{-}C}$ = 7.0 Hz, PPh_2), 123.4 (s, imidazole C4/5), 122.1 (s, imidazole C4/5), 47.6 (d, $J_{P\text{-}C}$ = 23.2 Hz, N-CH_2), 36.4 (s, CH_3), 29.1 (d, $J_{P\text{-}C}$ = 15.8 Hz, P-CH_2). No satisfactory microanalysis could be obtained for ligand **2a**-(Cl) due to its hydrocsopicity. The microanalysis of the PF_6^- salt gave satisfactory data [see **2a-(PF_6)**].



3-[2-(Diphenylphosphino)ethyl]-1-methylimidazolium hexafluorophosphate [2a-(PF_6)]

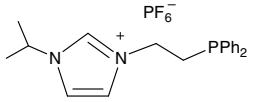
KPF_6 (900mg 4.9 mmol) was added to a suspension of **2a-(Cl)** (300 mg, 0.9 mmol) in acetone (10 mL) and the mixture was stirred at room temperature for 8 h. Acetone was then removed under vacuum and to this residue was added dichloromethane (15 mL). A clear solution was obtained after filtration. Removal of the solvent followed by addition of diethyl ether gave **2a**-(PF_6) as an oil which solidified slowly to give a white solid in 95% yield (377 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, 1H, imidazole H2), 7.77 (d, J = 1.7 Hz, 1H, imidazole H4/5), 7.59 (d, J = 1.7 Hz, 1H, imidazole H4/5), 7.39-7.47(m, 10H, PPh_2), 4.25-4.33 (m, 2H, N-CH_2), 3.78 (s, 3H, CH_3), 2.74 (apparent t, J = 7.7 Hz, 2H, P-CH_2). ^{31}P {^{1}H} NMR (121 MHz, DMSO-d_6): δ -21.8 (s, PPh_2), -144.5 (heptet, $J_{P\text{-}F}$ = 706 Hz, PF_6^-). ^{13}C NMR (100 MHz, CD_3CN): δ 136.8 (d, J_{PC} = 12 Hz, *ipso*-PPh_2) 135.8 (s, imidazole C2), 132.6 (d, $J_{P\text{-}C}$ = 19.3 Hz, PPh_2), 129.3 (s, PPh_2), 128.8 (d, $J_{P\text{-}C}$ = 7.0 Hz, PPh_2), 123.6 (s, imidazole C4/5), 122.3 (s, imidazole C4/5), 47.6 (d, $J_{P\text{-}C}$ = 24 Hz, N-CH_2), 35.8 (s, CH_3), 27.9 (d, $J_{P\text{-}C}$ = 15.0 Hz, P-CH_2). Anal. Calcd for $C_{18}H_{20}F_6N_2P_2$: C, 49.10; H, 4.58; N, 6.36; Found: C, 49.42; H, 4.78; N, 6.24.



3-(2-chloroethyl)-1-isopropylimidazolium chloride [2b-(Cl)]

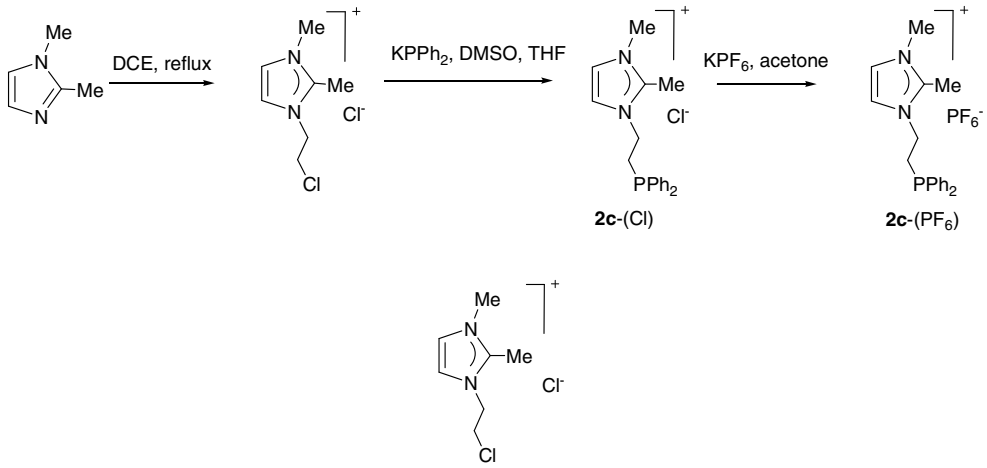
3-(2-chloroethyl)-1-isopropylimidazolium chloride was synthesized by a method directly analogous to that for 3-(2-chloroethyl)-1-methylimidazolium chloride. Compound **2b**-(Cl) was obtained as a sticky oil which failed to solidify after a few days. Yield: 89%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.73 (s, 1H, imidazole H2), 8.04 (m, 1H, imidazole H4/5), 7.98 (m, 1H, imidazole H4/5), 4.66-4.75 (heptet, ^3J=6.7, 1H), 4.59 (t, ^3J = 5.7 Hz, N-CH_2), 4.14 (t, ^3J = 5.5 Hz, ClCH_2), 1.49 (d, ^{3}J = 6.7 Hz, 6H, 2CH_3). ^{13}C{^{1}H} NMR (75 MHz, DMSO-*d6*): δ 136.2 (s, imidazole C2),

123.2 (s, imidazole C4/5), 121.2 (s, imidazole C4/5), 52.8 (s), 50.7 (s), 43.5 (s, Cl-CH_2), 22.8 (s, CH_3). Due to the hydroscopicity of this chloride salt, no satisfactory microanalysis could be obtained.



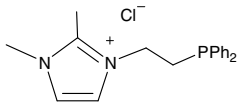
3-[2-(Diphenylphosphino)ethyl]-1-isopropylimidazolium hexafluorophosphate [2b-(PF_6)]

Ion exchange of **2b-(Cl)** to **2b-(PF_6)** was carried out. Yield (after phosphination and anion exchange): 72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (s, 1H, *H*2), 7.79-7.82 (m, 2H, *H*4 and *H*5), 7.38-7.45(m, 10H C*H* of PPh_2), 4.53(heptet, J = 6.6Hz, 1H, C*H* of iPr), 4.25-4.31 (m, 2H, N-CH_2), 2.76 (apparent t, J = 7.6Hz, 2H, P-CH_2), 1.42 (d, J = 6.8 Hz, 6H, 2CH_3). ^{31}P{^{1}H} NMR (161 MHz, DMSO-d_6): δ -21.96 (s, PPh_2), -144.4 (heptet, $J_{P\text{-}F}$ = 707 Hz, PF_6^-). ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.2 (d, $J_{P\text{-}C}$ = 12.2 Hz, *ipso*-PPh_2), 135.2 (s, C2), 132.9 (d, $J_{P\text{-}C}$ = 19.2 Hz, *o*-PPh_2), 129.6 (s, *p*-PPh_2), 129.2 (d, $J_{P\text{-}C}$ = 6.8 Hz, *m*-PPh_2), 123.0 (s, C4/5), 120.9 (s, C4/5), 52.68 (s, CH of ^{i}Pr), 47.3 (d, $J_{P\text{-}C}$ = 27 Hz, N-CH_2), 36.4 (s, CH_3), 27.6 (d, $J_{P\text{-}C}$ = 14 Hz, P-CH_2), 22.72 (s, CH_3 of ^{i}Pr). Anal. Calcd for $C_{20}H_{24}F_6N_2P_2$ (468.1): C, 51.29; H, 5.17; N, 5.98; Found: C, 51.12; H, 5.42; N, 5.97.



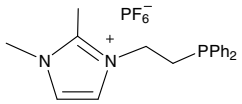
3-(2-chloroethyl)-1,2-dimethylimidazolium chloride

1,2-Dimethylimidazole (1.0 g, 0.0104 mol) was dissolved in 1, 2-dichloroethane (15 ml) and the mixture was stirred under reflux for 24 h. All the 1, 2-Dichloroethane was then removed under vacuum and the residue was washed with diethyl ether (3 ×10 mL) to give 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride as a white solid in 91% yield (1.84 g). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.90 (s, 1H, imidazole H4/5), 7.85 (s, 1H, imidazole H4/5), 4.60 (t, ^3J = 4.0 Hz, N-CH_2), 4.08 (t, ^3J = 4.0 Hz, Cl-CH_2), 3.83 (s, 3H, CH_3), 2.67 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 145.6 [s, imidazole N-*C*(Me)-N], 123.0 (s, imidazole C4/5), 121.8 (s, imidazole C4/5), 49.2 (s, N-CH_2), 43.7 (s, Cl-CH_2), 35.3 (s, CH_3), 10.1 (s, CH_3). HRMS (ESI$^+$): 159.0674, Calcd for [$C_7H_{12}{}^{35}ClN_2{}^+$] 159.0684.



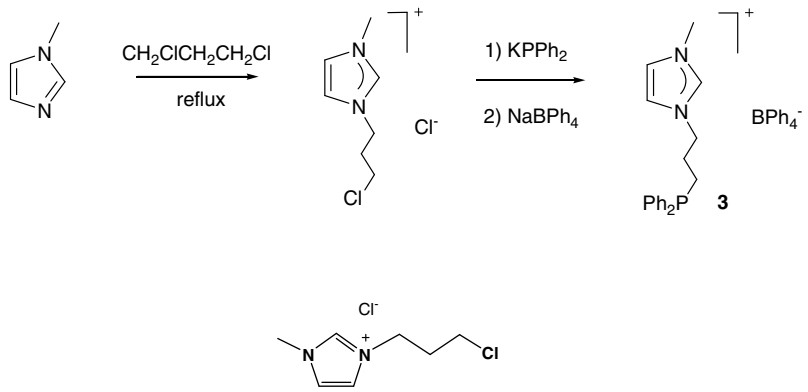
3-[2-(Diphenylphosphino)ethyl]-1,2-dimethylimidazolium chloride [2c-(Cl)]

This ligand was prepared (81% yield) by following a directly analogous method for the synthesis of **2a**-(Cl) starting from 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride and $KPPh_2$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H, imidazole H4/5), 7.71(s, 1H, imidazole C4/5), 7.34-7.38(m, 10H, PPh_2), 4.33-4.41 (m, 2H, N-CH_2), 3.88 (s, 3H, CH_3), 2.66 (apparent t, J = 7.0 Hz, 2H, P-CH_2), 2.58 (s, 3H, CH_3). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ -21.79 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.42 (s, imidazole C2), 136.0 (d, $J_{P\text{-}C}$ = 11.6 Hz, *ipso*-PPh_2), 132.6 (d, $J_{P\text{-}C}$ = 21.7 Hz, PPh_2), 129.4 (s, PPh_2), 128.8 (d, $J_{P\text{-}C}$ = 7.0 Hz, PPh_2), 123.2 (s, imidazole C4/5), 121.3 (s, imidazole C4/5), 46.3 (d, $J_{P\text{-}C}$ = 21 Hz, N-CH_2), 35.7 (s, CH_3), 29.1 (d, $J_{P\text{-}C}$ = 16.5 Hz, P-CH_2), 10. 51 (d, $J_{P\text{-}C}$ = 3 Hz, CH_3). No satisfactory microanalysis could be obtained for ligand **2c**-(Cl) due to its hydrocsopicity. The microanalysis of the PF_6^- salt **2c**-(PF_6) gave satisfactory data.



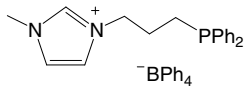
3-[2-(Diphenylphosphino)ethyl]-1,2-dimethylimidazolium hexafluophosphate [2c-(PF_6)]

2c-(PF_6) was obtained in 92% yield by anion exchange of **2c**-(Cl) using an excess amount of KPF_6 in acetone. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25-7.40 (m, 10H, PPh_2), 7.07 (s, 1H), 7.02 (s, 1H), 4.11 (m, 2H, PCH_2), 3.58 (s, 3H, NCH_3), 2.55 (apparent t, J = 7.3 Hz, 2H, PCH_2), 2.33 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ -21.77 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7 (s, imidazole C2), 136.0 (d, $J_{P\text{-}C}$ = 11.4 Hz, *ipso*-PPh_2), 132.6 (d, $J_{P\text{-}C}$ = 21.8 Hz, PPh_2), 129.4 (s, PPh_2), 128.8 (d, $J_{P\text{-}C}$ = 7.0 Hz, PPh_2), 122.5 (s, imidazole C4/5), 120.6 (s, imidazole C4/5), 46.0 (d, $J_{P\text{-}C}$ = 23 Hz, N-CH_2), 34.9 (s, CH_3), 28.6 (d, $J_{P\text{-}C}$ = 15.8 Hz, P-CH_2), 9.3 (s, CH_3). Anal. Calcd for $C_{19}H_{22}F_6N_2P_2$ (468.1): C, 50.23; H, 4.88; N, 6.17; Found: C, 50.10; H, 5.08; N, 6.12.



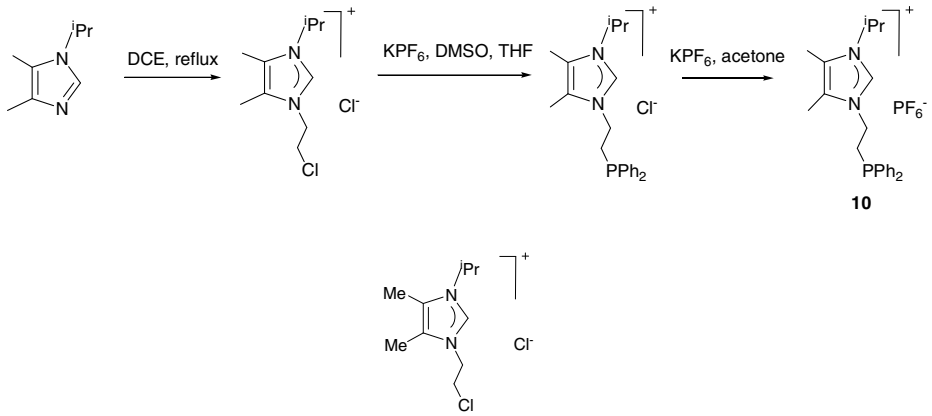
3-(3-chloropropyl)-1-methylimidazolium chloride

3-(3-chloropropyl)-1-isopropylimidazolium chloride was synthesized by a method directly analogous to the synthesis of 3-(2-chloroethyl)-1-methylimidazolium chloride. Yield: 67%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.0 (s, 1H, imidazole H2), 7.40 (s, 1H, imidazole H4/5), 7.33 (m, 1H, imidazole H4/5), 4.60 (t, ^3J = 6.93 Hz, 2H, N-CH_2), 4.10 (s, CH_3), 3.64 (t, ^3J = 5.9 Hz, Cl-CH_2), 2.51 (quintet, ^3J = 6.1 Hz, CH_2-CH_2-CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 137.4 (s, imidazole C2), 124.1 (s, C4/5), 122.8 (s, C4/5), 46.8 (s, N-CH_2), 42.2 (s, Cl-CH_2), 36.2 (s, N-CH_3), 32.5 (s, C-CH_2-C). HRMS (ESI$^+$): 159.0653; Calcd for $[C_7H_{12}{}^{35}ClN_2]^+$: 159.0684.



3-[2-(Diphenylphosphino)propyl]-1-methylimidazolium Tetraphenylborate (3)

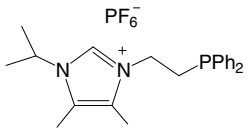
The synthesis of **3** was performed by following a literature report,[2] using 3-(3-chloropropyl)-1-methylimidazolium chloride and $KPPh_2$, followed by anion exchange with $NaBPh_4$ without the isolation of the chloride salt.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (br, 8H, BPh_4), 7.33-7.39 (m, 10H, PPh_2), 6.88-6.92 (m, 8H, BPh_4), 6.69-6.72 (m, 4H, *para*-BPh_4), 5.78 (s, 1H, imidazole H4), 5.65 (s, 1H, imidazole, H5), 4.28 (s, 1H, imidazole H2), 3.13 (apparent t, d = 7.6 Hz, 2H, N-CH_2), 2.70 (s, 3H, CH_3), 1.79 (apparent t, d = 7.8 Hz, 2H, P-CH_2), 1.39-1.46 (m, 2H, C-CH_2-C). ^{1}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -16.9 (s). ^{13}C NMR (75 MHz, $CDCl_3$): 164.1 (q, $^1J_{B\text{-}C}$ = 48.4 Hz, *ipso*-BPh_4), 137.3 (d, $J_{P\text{-}C}$ = 12.1 Hz, *ipso*-PPh_2), 135.7 (s, BPh_4), 135.1 (s, imidazole C2), 132.6 (d, $J_{P\text{-}C}$ = 18.7 Hz, *o*- or *m*-PPh_2), 129.2 (s, PPh_2), 128.7 (d, $J_{P\text{-}C}$ = 6.9 Hz, *o* or *m*-PPh_2), 126.0 (s, *m*-BPh_4), 122.4 (s, imidazole C4/5), 122.0 (s, *p*-BPh_4), 120.3 (s, imidazole C4/5), 49.7 (d, $J_{P\text{-}C}$ = 13.6 Hz, N-CH_2), 35.6 (s, CH_3), 26.6 (d, $J_{P\text{-}C}$ = 18.8 Hz, P-CH_2), 24.5 (d, $J_{P\text{-}C}$ = 13.3 Hz, C-CH_2-C). Anal. Calcd for $C_{43}H_{42}BN_2P$ (628.59): C, 82.16; H, 6.73; N, 4.46; Found: C, 81.93; H, 6.56; N, 6.68.



3-(2-chloroethyl)-1-isopropyl-4,5-dimethyl-imidazolium chloride

This imidazolium salt was synthesized by a method directly analogous to that for 3-(2-chloroethyl)-1,2-dimethylimidazolium chloride. Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.84 (s, 1H, imidazole H2), 4.72 (t, ^3J = 5.04 Hz, 2H, N-CH_2), 4.41 (heptet, J = 6.6, 1H, C*H* of iPr), 4.14 (t, ^3J = 5.04 Hz, Cl-CH_2), 2.29 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.63 (d, J = 6.6 Hz, 6H, 2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6 (s, imidazole C2), 127.3 (s, C4/5), 125.2 (s, C4/5), 50.8 (s, CH of ^{i}Pr), 48.2 (s, N-CH_2), 43.8 (s, Cl-CH_2), 22.8 (s, 2CH_3 of ^{i}Pr), 8.8 (s, CH_3), 8.7 (s, CH_3). Due to

the hydroscopicity of this chloride salt, no satisfactory microanalysis could be obtained. It was used directly for the next step.



3-[2-(Diphenylphosphino)ethyl]-1-isopropyl-4,5-dimethylimidazolium hexafluorophosphate (10)

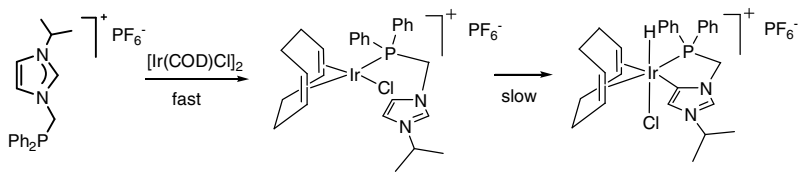
Compound (10) was synthesized by directly following the synthesis of compound **2a**-(PF_6). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.10 (s, 1H, imidazole H2), 7.39-7.64 (m, 10H, PPh_2), 4.43 (heptet, J = 6.6 Hz, 1H, CH of ^{i}Pr), 4.21-4.27 (m, 2H, N-CH_2), 2.72 (apparent t, J = 7.5 Hz, P-CH_2), 2.16 (s, 6H, 2CH_3), 1.40 (d, J = 6.8 Hz, 6H, 2CH_3). ^{31}P{^{1}H} NMR (161 MHz, DMSO-d_6): δ -21.60 (s, PPh_2), -144.18 (heptet, $J_{P\text{-}F}$ = 702 Hz, PF_6^-). ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.2 (d, $J_{P\text{-}C}$ = 12.3 Hz, *ipso*-PPh_2), 133.0 (s, PPh_2), 132.8 (s, imidazole C2), 129.6 (s, PPh_2), 129.15 (d, $J_{P\text{-}C}$ = 6.8 Hz, PPh2), 126.8 (s, imidazole C4/5), 126.3 (s, imidazole C4/5), 49.8 (s, CH of ^{i}Pr), 44.9 (d, $J_{P\text{-}C}$ = 25 Hz, N-CH_2), 27.3 (d, $J_{P\text{-}C}$ = 14 Hz, P-CH_2), 22.6 (s, 2CH_3), 8.19 (s, CH_3), 8.16 (s, CH_3). Anal. Calcd for $C_{22}H_{28}F_6N_2P_2$ (496.16): C, 53.23; H, 5.69; N, 5.64. Found: C, 53.01; H, 5.66; N, 5.53.

References:

(1) A. A. Danopoulos, N. Tsoureas, S. A. Macgregor, C. Smith, *Organometallics* **2007**, *26*, 253.

Kinetic Studies of the Conversion of Complex 4 to 5 (oxidative addition).

In a typical experiment, ligand **1-**(PF_6) (13 mg, 0.0286 mmol), $[Ir(COD)Cl]_2$ (9.6 mg, 0.0143 mmol) and an internal standard 1,3,5-trimethoxylbenzene (1.0 mg, 0.00595 mmol) was dissolved in $CDCl_3$ (0.6 ml) at -30 ^{o}C and the solution was loaded into a J-Young NMR tube and was analyzed on an NMR spectrometer with a preset temperature. The signals of the imidazole H(2) of **4** (8.70 ppm) and H(2) of **5** (8.80 ppm) and internal standard (6.11 ppm) were used to calculate the conversion of **4** and the formation of **5.** The slope of the plot of ln[**4**] against t give the 1st order rate constant k (Figure S1). The Eyring plot [ln(k/T) against 1/T, gives$\Delta H^{\neq}$ and$\Delta S^{\neq}$ based on the Eyring equation $\ln(k/T) = -\Delta H^{\neq}/RT + \ln(k_b/h) + \Delta S^{\neq}/R$ (Figure S2).



1-(PF_6) **4** **5**

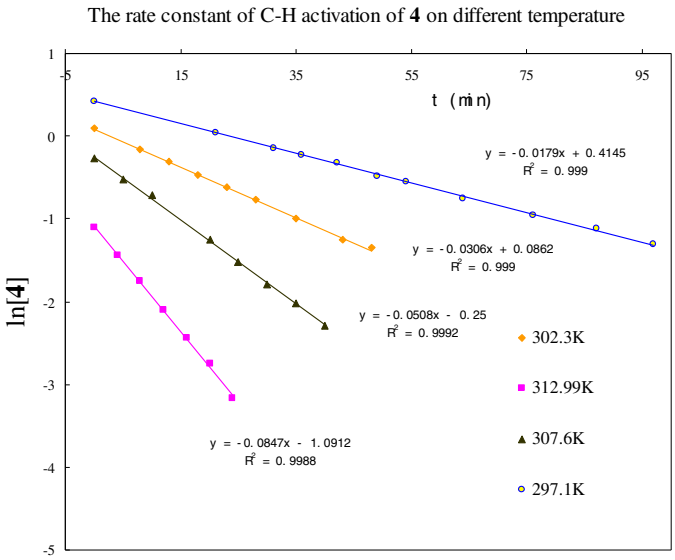


Figure S1

$$\ln[\mathbf{4}] = -kt + C$$

$$k\ (297.1\text{K}) = 0.0179\ \text{min}^{-1}$$

$$k\ (302.3\text{K}) = 0.0306\ \text{min}^{-1}$$

$$k\ (307.6\text{K}) = 0.0508\ \text{min}^{-1}$$

$$k\ (312.9\text{K}) = 0.0847\ \text{min}^{-1}$$

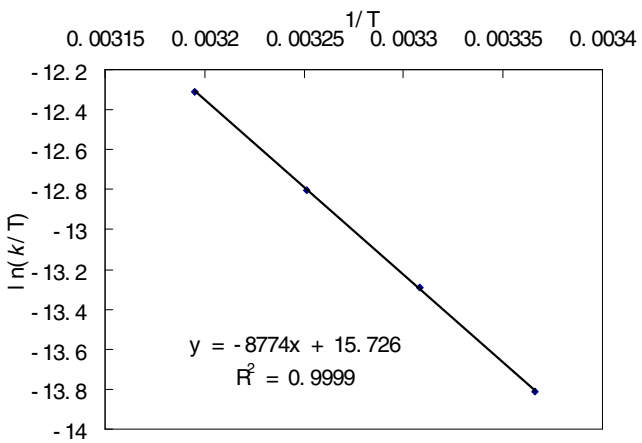


Figure S2

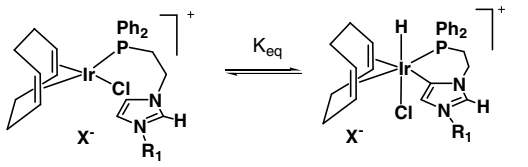
$$\ln(k/T) = -\Delta H^{\neq}/RT + \ln(k_b/h) + \Delta S^{\neq}/R$$

$$\Delta H^{\neq} = 17.4\ \text{kcal/mol}$$

$$\Delta S^{\neq} = -66.8\ \text{J mol}^{-1}\ \text{K}^{-1} = -16\ \text{eu}$$

The Chemical Equilibrium between Ir(I) and Ir(III) Complexes.

Complex **8a**-(Cl), **8a**-(PF_6), **or 8b**-(PF_6) (15 mg) was dissolved in CD_3CN (0.6 mL) and the solution was loaded into a J-Young NMR tube. The $^{31}P\{^1H\}$ spectra were detected at different temperatures. The resonance signals of Ir(I) and Ir(III) were used to calculate the ratio (K_{eq}) of [Ir(III)] to [Ir(I)]. The results are showed in Table S1. ΔH^o and ΔS^o were obtained by the equation $\ln K_{eq} = -\Delta H^o/(RT) + \Delta S^o/R$ (Figure S3).



7a-(Cl$^-$): R_1 = Me
7a-(PF_6^-): R_1 = Me
7b-(PF_6^-): R_1 = ^{i}Pr

8a-(Cl$^-$): R_1 = Me
8a-(PF_6^-): R_1 = Me
8b-(PF_6^-): R_1 = ^{i}Pr

Table S1

Temp (K)	**8a**-(PF_6)		**8b**-(PF_6)		**8a**-(Cl)	
	K_{eq}	$\ln K_{eq}$	K_{eq}	$\ln K_{eq}$	K_{eq}	$\ln K_{eq}$
298.0	18.17	2.9	15.75	2.757	10.85	2.384
308.0	11.80	2.47	10.85	2.384	8.26	2.112
318.0	8.36	2.123	7.64	2.034	5.93	1.7814
323.0	7.10	1.96	6.11	1.81	5.317	1.671
328.0	6.21	1.826	5.20	1.649	4.711	1.55
330.0			4.63	1.533		
338.0	4.43	1.49	3.97	1.378	3.781	1.33

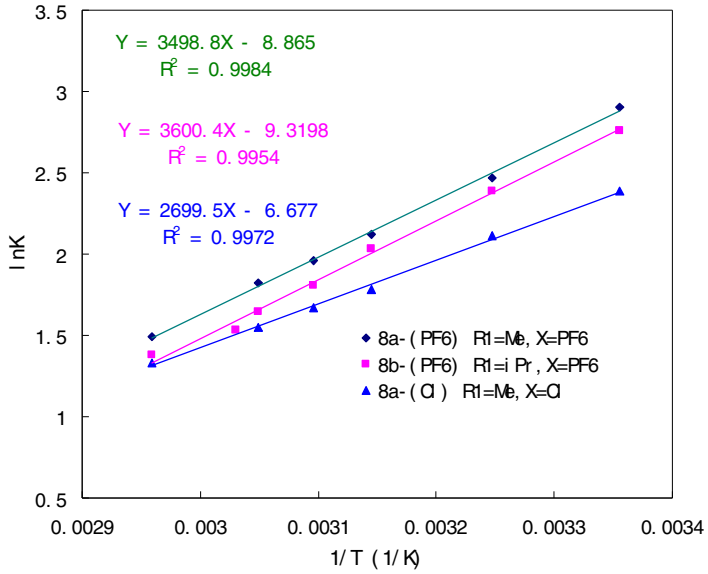


Figure S3. The Van't Hoff Plot

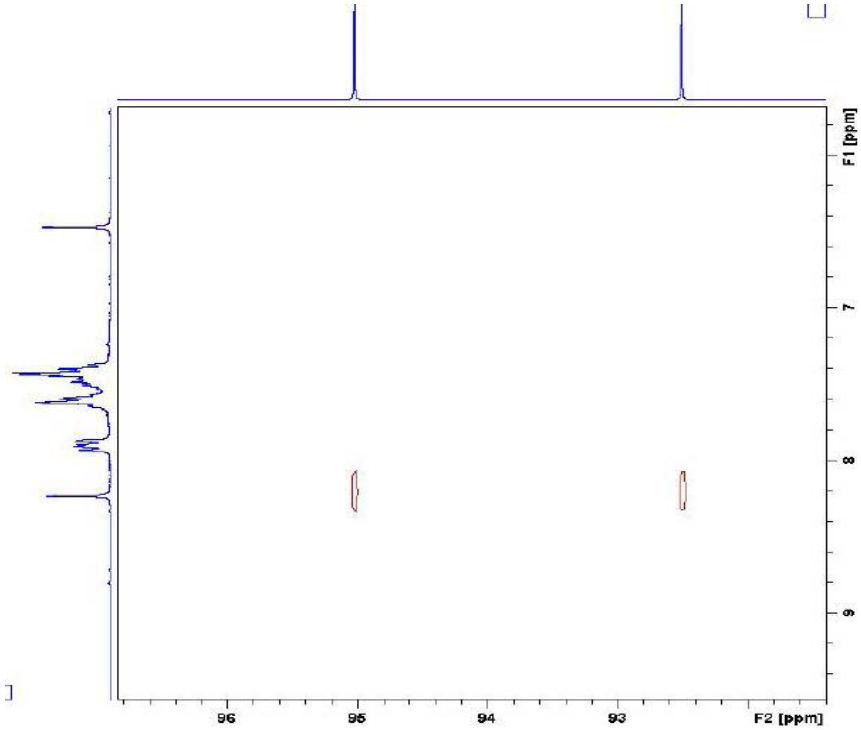
$$\ln K_{eq} = -\Delta H^{o}/(RT) + \Delta S^{o}/R$$

8a-(PF_6) R_1 = Me, ΔH^o = -29.1 kcal/mol; ΔS^o = -73.9 J/K/mol

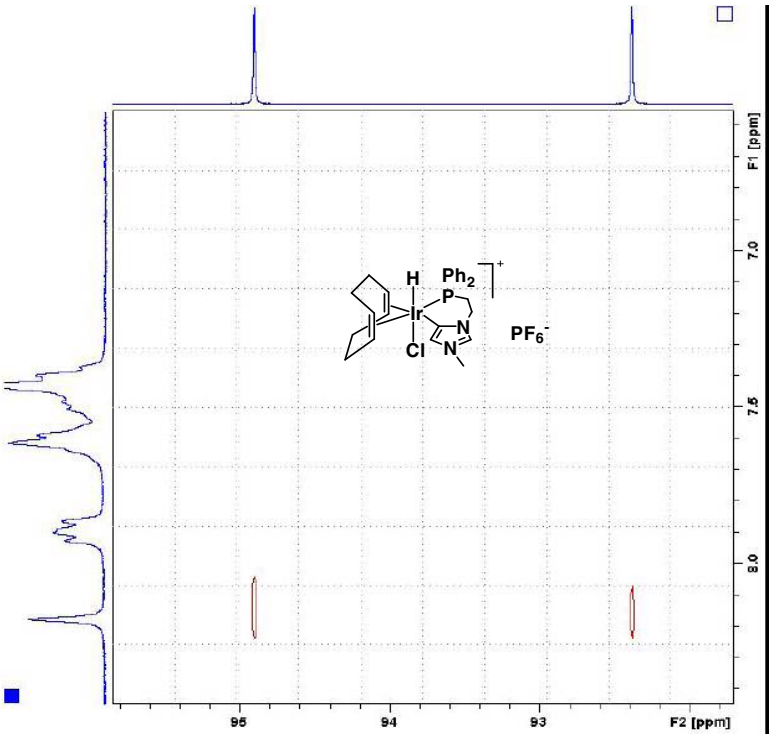
8b-(PF_6) R_1 = ^{i}Pr, ΔH^o = -29.9 kcal/mol; ΔS^o = -77.5 J/K/mol

8a-(Cl) R_1=Me, ΔH^o = -22.4 kcal/mol; ΔS^o = -55.5 J/K/mol

Part of the ^{19}F-^{1}H HOESY Spectrum of Complex 5 (CD_2Cl_2)



Part of the ^{19}F-^{1}H HOESY Spectrum (CD_2Cl_2) of Complex 8a-(PF_6)



Crystal Data of Complex 5

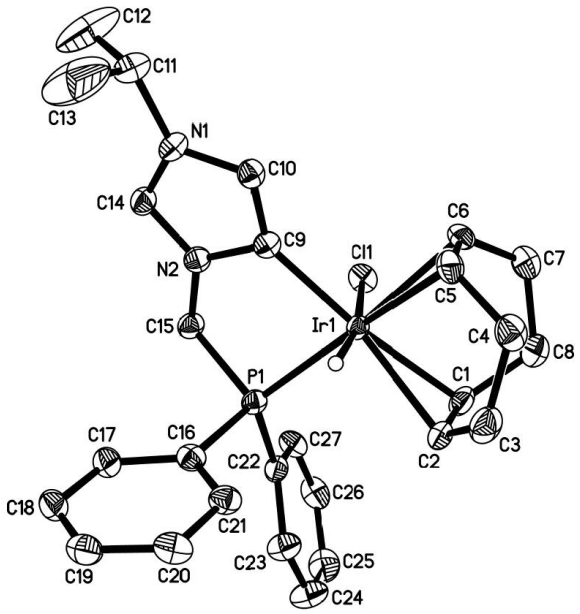


Table 1. Crystal data and structure refinement for complex **5.**

Identification code	lxw16r	
Empirical formula	C27 H34 Cl F6 Ir N2 P2	
Formula weight	790.15	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.8370(5) Å	α= 90°.
	b = 18.8931(8) Å	β= 90°.
	c = 23.3920(10) Å	γ = 90°.
Volume	5673.3(4) $Å^3$	
Z	8	
Density (calculated)	1.850 Mg/m^3	
Absorption coefficient	4.975 mm^{-1}	
F(000)	3104	
Crystal size	0.25 x 0.10 x 0.06 mm^3	
Theta range for data collection	2.11 to 26.50°.	
Index ranges	-14<=h<=16, -23<=k<=23, -27<=l<=29	
Reflections collected	29836	
Independent reflections	5873 [R(int) = 0.0365]	
Completeness to theta = 26.50°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7545 and 0.3694
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5873 / 66 / 358
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0568
R indices (all data)	R1 = 0.0356, wR2 = 0.0650
Largest diff. peak and hole	1.366 and -1.003 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	2397(1)	10362(1)	6946(1)	17(1)
C(1)	2041(3)	10382(2)	5991(2)	25(1)
C(2)	2940(3)	9990(2)	6074(2)	25(1)
C(3)	4038(3)	10245(2)	5978(2)	33(1)
C(4)	4280(3)	10977(2)	6219(2)	29(1)
C(5)	3677(3)	11175(2)	6754(2)	24(1)
C(6)	2736(3)	11522(2)	6734(2)	24(1)
C(7)	2167(3)	11723(2)	6192(2)	30(1)
C(8)	2033(4)	11133(2)	5758(2)	33(1)
C(9)	2402(3)	10495(2)	7815(2)	19(1)
C(10)	2915(3)	10891(2)	8209(2)	21(1)
C(11)	2958(4)	11037(3)	9294(2)	33(1)
C(12)	2105(5)	11147(4)	9714(2)	78(2)
C(13)	3854(5)	10619(4)	9523(3)	83(2)
C(14)	1852(3)	10208(2)	8702(2)	23(1)
C(15)	1023(3)	9554(2)	7883(2)	22(1)
C(16)	2563(3)	8597(2)	7404(2)	21(1)
C(17)	2338(3)	8142(2)	7860(2)	25(1)
C(18)	3036(3)	7619(2)	8018(2)	29(1)
C(19)	3945(3)	7519(2)	7710(2)	30(1)
C(20)	4165(3)	7944(2)	7248(2)	29(1)
C(21)	3489(3)	8487(2)	7101(2)	24(1)
C(22)	734(3)	8912(2)	6724(2)	21(1)

C(23)	1061(3)	8366(2)	6367(2)	29(1)
C(24)	418(3)	8107(3)	5941(2)	36(1)
C(25)	-572(4)	8388(2)	5872(2)	36(1)
C(26)	-911(3)	8919(2)	6232(2)	30(1)
C(27)	-265(3)	9192(2)	6651(2)	25(1)
Cl(1)	581(1)	10848(1)	6999(1)	24(1)
F(1)	3507(3)	2185(2)	4811(2)	68(1)
F(2)	4115(3)	2399(2)	3922(1)	65(1)
F(3)	3472(3)	1336(2)	4153(2)	84(1)
F(4)	4589(3)	1265(2)	4882(1)	87(1)
F(5)	5167(3)	1469(2)	3997(2)	85(1)
F(6)	5217(3)	2335(3)	4650(2)	91(1)
N(1)	2562(2)	10715(2)	8752(1)	23(1)
N(2)	1738(2)	10062(2)	8144(1)	20(1)
P(1)	1675(1)	9305(1)	7208(1)	18(1)
P(2)	4352(1)	1834(1)	4411(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for complex **5**.

Ir(1)-C(9)	2.049(4)
Ir(1)-C(2)	2.267(4)
Ir(1)-C(1)	2.280(4)
Ir(1)-P(1)	2.2851(10)
Ir(1)-C(6)	2.289(4)
Ir(1)-C(5)	2.294(4)
Ir(1)-Cl(1)	2.5097(9)
C(1)-C(2)	1.385(6)
C(1)-C(8)	1.522(6)
C(2)-C(3)	1.506(6)
C(3)-C(4)	1.526(6)
C(4)-C(5)	1.519(5)
C(5)-C(6)	1.374(6)
C(6)-C(7)	1.512(6)
C(7)-C(8)	1.517(6)
C(9)-C(10)	1.356(5)
C(9)-N(2)	1.410(5)
C(10)-N(1)	1.388(5)

C(11)-C(12)	1.486(7)
C(11)-C(13)	1.493(7)
C(11)-N(1)	1.497(5)
C(14)-N(1)	1.328(5)
C(14)-N(2)	1.341(5)
C(15)-N(2)	1.461(5)
C(15)-P(1)	1.850(4)
C(16)-C(21)	1.400(5)
C(16)-C(17)	1.399(6)
C(16)-P(1)	1.816(4)
C(17)-C(18)	1.384(6)
C(18)-C(19)	1.384(6)
C(19)-C(20)	1.377(6)
C(20)-C(21)	1.386(6)
C(22)-C(23)	1.392(5)
C(22)-C(27)	1.397(5)
C(22)-P(1)	1.814(4)
C(23)-C(24)	1.382(6)
C(24)-C(25)	1.386(6)
C(25)-C(26)	1.379(6)
C(26)-C(27)	1.385(6)
F(1)-P(2)	1.580(3)
F(2)-P(2)	1.594(3)
F(3)-P(2)	1.589(4)
F(4)-P(2)	1.569(3)
F(5)-P(2)	1.583(3)
F(6)-P(2)	1.563(4)

C(9)-Ir(1)-C(2)	158.46(15)
C(9)-Ir(1)-C(1)	166.07(15)
C(2)-Ir(1)-C(1)	35.46(15)
C(9)-Ir(1)-P(1)	80.98(11)
C(2)-Ir(1)-P(1)	95.46(11)
C(1)-Ir(1)-P(1)	101.27(11)
C(9)-Ir(1)-C(6)	95.50(15)
C(2)-Ir(1)-C(6)	92.49(15)
C(1)-Ir(1)-C(6)	79.08(15)
P(1)-Ir(1)-C(6)	166.39(10)

C(9)-Ir(1)-C(5)	96.27(15)
C(2)-Ir(1)-C(5)	79.14(15)
C(1)-Ir(1)-C(5)	86.63(15)
P(1)-Ir(1)-C(5)	158.20(11)
C(6)-Ir(1)-C(5)	34.90(14)
C(9)-Ir(1)-Cl(1)	84.78(10)
C(2)-Ir(1)-Cl(1)	116.31(11)
C(1)-Ir(1)-Cl(1)	81.69(11)
P(1)-Ir(1)-Cl(1)	85.98(3)
C(6)-Ir(1)-Cl(1)	80.60(10)
C(5)-Ir(1)-Cl(1)	115.44(10)
C(2)-C(1)-C(8)	123.7(4)
C(2)-C(1)-Ir(1)	71.8(2)
C(8)-C(1)-Ir(1)	111.6(3)
C(1)-C(2)-C(3)	126.1(4)
C(1)-C(2)-Ir(1)	72.8(2)
C(3)-C(2)-Ir(1)	108.8(3)
C(2)-C(3)-C(4)	115.1(3)
C(3)-C(4)-C(5)	115.1(3)
C(6)-C(5)-C(4)	122.5(4)
C(6)-C(5)-Ir(1)	72.4(2)
C(4)-C(5)-Ir(1)	111.1(3)
C(5)-C(6)-C(7)	124.9(4)
C(5)-C(6)-Ir(1)	72.7(2)
C(7)-C(6)-Ir(1)	109.3(3)
C(6)-C(7)-C(8)	115.6(3)
C(7)-C(8)-C(1)	116.4(3)
C(10)-C(9)-N(2)	104.1(3)
C(10)-C(9)-Ir(1)	138.0(3)
N(2)-C(9)-Ir(1)	117.9(3)
C(9)-C(10)-N(1)	109.3(3)
C(12)-C(11)-C(13)	113.9(5)
C(12)-C(11)-N(1)	111.6(4)
C(13)-C(11)-N(1)	110.6(4)
N(1)-C(14)-N(2)	108.0(3)
N(2)-C(15)-P(1)	103.9(2)
C(21)-C(16)-C(17)	118.1(4)
C(21)-C(16)-P(1)	120.9(3)

C(17)-C(16)-P(1)	121.0(3)
C(18)-C(17)-C(16)	120.5(4)
C(17)-C(18)-C(19)	120.3(4)
C(20)-C(19)-C(18)	120.1(4)
C(19)-C(20)-C(21)	119.9(4)
C(20)-C(21)-C(16)	121.0(4)
C(23)-C(22)-C(27)	118.9(4)
C(23)-C(22)-P(1)	118.5(3)
C(27)-C(22)-P(1)	122.2(3)
C(24)-C(23)-C(22)	121.0(4)
C(23)-C(24)-C(25)	119.7(4)
C(26)-C(25)-C(24)	119.8(4)
C(25)-C(26)-C(27)	120.9(4)
C(26)-C(27)-C(22)	119.7(4)
C(14)-N(1)-C(10)	108.4(3)
C(14)-N(1)-C(11)	126.9(3)
C(10)-N(1)-C(11)	124.6(3)
C(14)-N(2)-C(9)	110.2(3)
C(14)-N(2)-C(15)	127.6(3)
C(9)-N(2)-C(15)	122.2(3)
C(22)-P(1)-C(16)	105.95(18)
C(22)-P(1)-C(15)	109.64(17)
C(16)-P(1)-C(15)	104.82(18)
C(22)-P(1)-Ir(1)	117.40(13)
C(16)-P(1)-Ir(1)	117.16(13)
C(15)-P(1)-Ir(1)	100.93(13)
F(6)-P(2)-F(4)	91.5(3)
F(6)-P(2)-F(1)	91.2(2)
F(4)-P(2)-F(1)	90.2(2)
F(6)-P(2)-F(3)	178.5(2)
F(4)-P(2)-F(3)	90.0(2)
F(1)-P(2)-F(3)	89.2(2)
F(6)-P(2)-F(5)	90.8(2)
F(4)-P(2)-F(5)	90.2(2)
F(1)-P(2)-F(5)	177.9(2)
F(3)-P(2)-F(5)	88.8(2)
F(6)-P(2)-F(2)	89.2(2)
F(4)-P(2)-F(2)	178.8(2)

F(1)-P(2)-F(2)	90.7(2)
F(3)-P(2)-F(2)	89.3(2)
F(5)-P(2)-F(2)	88.77(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for complex **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	16(1)	18(1)	16(1)	0(1)	2(1)	0(1)
C(1)	30(2)	31(2)	14(2)	0(2)	-1(2)	-2(2)
C(2)	33(2)	25(2)	16(2)	1(2)	5(2)	2(2)
C(3)	32(2)	39(3)	28(2)	1(2)	10(2)	4(2)
C(4)	24(2)	29(2)	35(2)	4(2)	7(2)	-1(2)
C(5)	21(2)	25(2)	26(2)	5(2)	2(2)	-5(2)
C(6)	29(2)	16(2)	26(2)	-1(2)	6(2)	-5(2)
C(7)	33(2)	25(2)	32(2)	6(2)	-1(2)	1(2)
C(8)	42(3)	34(2)	23(2)	3(2)	-3(2)	-1(2)
C(9)	16(2)	22(2)	20(2)	-1(2)	2(1)	1(1)
C(10)	19(2)	22(2)	23(2)	1(2)	3(2)	1(2)
C(11)	38(2)	36(2)	26(2)	-9(2)	-2(2)	-1(2)
C(12)	60(3)	131(6)	43(3)	-46(3)	3(3)	-6(4)
C(13)	73(4)	109(5)	66(4)	-39(4)	-41(3)	36(4)
C(14)	28(2)	23(2)	19(2)	1(2)	5(2)	3(2)
C(15)	21(2)	24(2)	20(2)	-1(2)	4(2)	-2(2)
C(16)	20(2)	21(2)	23(2)	-2(2)	-4(2)	-3(2)
C(17)	28(2)	23(2)	25(2)	2(2)	1(2)	-3(2)
C(18)	39(2)	21(2)	26(2)	2(2)	-4(2)	-5(2)
C(19)	34(2)	25(2)	31(2)	-4(2)	-13(2)	6(2)
C(20)	23(2)	27(2)	37(2)	-5(2)	0(2)	0(2)
C(21)	22(2)	23(2)	28(2)	-2(2)	3(2)	1(2)
C(22)	22(2)	23(2)	17(2)	1(2)	0(2)	-4(2)
C(23)	27(2)	33(2)	28(2)	-6(2)	-3(2)	4(2)
C(24)	35(2)	42(3)	31(2)	-14(2)	-3(2)	2(2)
C(25)	37(3)	38(3)	32(2)	1(2)	-10(2)	-9(2)
C(26)	24(2)	28(2)	39(2)	6(2)	-6(2)	-2(2)
C(27)	23(2)	20(2)	33(2)	1(2)	1(2)	-1(2)
Cl(1)	17(1)	24(1)	32(1)	1(1)	1(1)	2(1)
F(1)	54(2)	82(3)	67(2)	-20(2)	26(2)	5(2)
F(2)	95(3)	45(2)	55(2)	10(2)	-1(2)	15(2)
F(3)	106(3)	64(2)	81(3)	-14(2)	-23(2)	-30(2)
F(4)	89(3)	126(4)	47(2)	49(2)	14(2)	35(2)

F(5)	121(3)	72(2)	62(2)	15(2)	54(2)	46(2)
F(6)	60(2)	135(4)	78(3)	-25(3)	-2(2)	-41(2)
N(1)	22(2)	29(2)	17(2)	-2(1)	-1(1)	0(1)
N(2)	19(2)	21(2)	20(2)	-1(1)	2(1)	2(1)
P(1)	16(1)	20(1)	18(1)	-1(1)	2(1)	0(1)
P(2)	40(1)	41(1)	21(1)	-5(1)	1(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for complex **5**.

	x	y	z	U(eq)
H(1)	1393	10169	6085	30
H(2)	2857	9517	6203	30
H(3A)	4175	10251	5561	39
H(3B)	4523	9900	6152	39
H(4A)	4132	11334	5920	35
H(4B)	5034	11001	6306	35
H(5)	3961	11055	7117	29
H(6)	2420	11644	7088	29
H(7A)	2550	12116	6007	36
H(7B)	1469	11903	6297	36
H(8A)	2596	11175	5471	39
H(8B)	1364	11209	5556	39
H(10)	3434	11234	8126	25
H(11)	3234	11516	9194	40
H(12A)	1571	11454	9546	117
H(12B)	2386	11371	10059	117
H(12C)	1794	10690	9814	117
H(13A)	3611	10150	9642	124
H(13B)	4155	10867	9852	124
H(13C)	4385	10568	9225	124
H(14)	1488	9987	9007	28
H(15A)	336	9774	7808	26
H(15B)	924	9136	8132	26
H(17)	1702	8193	8063	31

H(18)	2890	7328	8339	34
H(19)	4417	7156	7818	36
H(20)	4778	7866	7030	35
H(21)	3657	8789	6789	29
H(23)	1735	8168	6416	35
H(24)	653	7739	5697	43
H(25)	-1015	8216	5578	43
H(26)	-1598	9100	6191	36
H(27)	-500	9567	6889	30
H(1M)	3460(20)	9956(15)	7010(20)	75(19)

Crystal Data of Complex 8a-(PF_6)

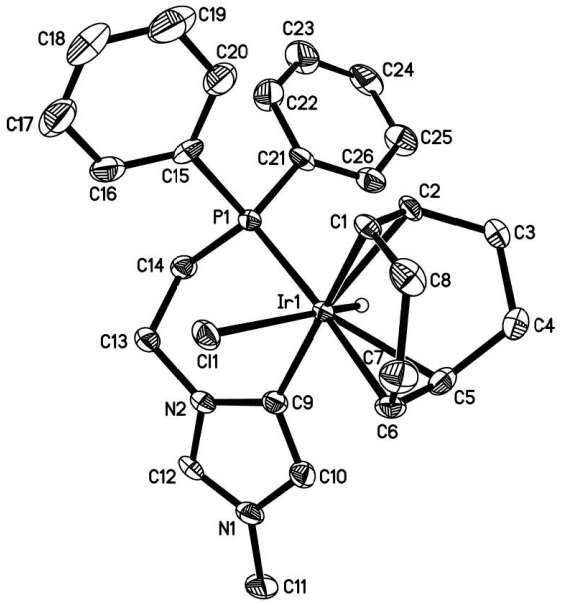


Table 1. Crystal data and structure refinement for complex **8a**-(PF_6).

Identification code	lxw3m	
Empirical formula	C26 H32 Cl F6 Ir N2 P2	
Formula weight	776.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.5058(4) Å	α= 90°.
	b = 7.2918(2) Å	β= 95.284(2)°.
	c = 29.6570(11) Å	γ = 90°.
Volume	2692.92(15) $Å^3$	
Z	4	
Density (calculated)	1.914 Mg/m^3	
Absorption coefficient	5.238 mm^{-1}	
F(000)	1520	
Crystal size	0.15 x 0.04 x 0.04 mm^3	
Theta range for data collection	1.38 to 25.05°.	
Index ranges	-14<=h<=14, -8<=k<=8, -35<=l<=35	
Reflections collected	38359	
Independent reflections	4762 [R(int) = 0.0564]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.8178 and 0.5071
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4762 / 0 / 356
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0330, wR2 = 0.0849
R indices (all data)	R1 = 0.0391, wR2 = 0.0980
Largest diff. peak and hole	4.945 and -0.961 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) complex **8a**-(PF_6). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	7847(1)	3388(1)	870(1)	14(1)
C(1)	8435(5)	698(8)	1203(2)	21(1)
C(2)	9101(4)	2100(9)	1382(2)	19(1)
C(3)	10215(5)	2514(10)	1249(2)	26(1)
C(4)	10293(5)	2503(11)	738(2)	31(2)
C(5)	9283(5)	3146(9)	452(2)	23(1)
C(6)	8494(5)	1930(9)	274(2)	23(1)
C(7)	8531(6)	-88(9)	366(2)	30(1)
C(8)	8767(5)	-660(9)	859(2)	29(1)
C(9)	7093(4)	5248(8)	422(2)	19(1)
C(10)	7369(5)	5817(9)	12(2)	23(1)
C(11)	6650(6)	8043(11)	-605(2)	35(2)
C(12)	5843(5)	7181(9)	101(2)	21(1)
C(13)	5439(5)	5996(10)	840(2)	24(1)
C(14)	6058(5)	6412(8)	1295(2)	21(1)
C(15)	6291(5)	2957(9)	1786(2)	23(1)
C(16)	5208(6)	2683(11)	1674(2)	35(2)
C(17)	4671(7)	1268(13)	1880(3)	48(2)
C(18)	5187(7)	217(11)	2207(3)	46(2)
C(19)	6260(7)	561(13)	2337(3)	56(2)
C(20)	6811(6)	1856(10)	2123(3)	37(2)
C(21)	7907(5)	5778(9)	1912(2)	21(1)
C(22)	7547(6)	6081(12)	2335(2)	38(2)
C(23)	8145(6)	7162(13)	2654(3)	47(2)

C(24)	9090(6)	7933(11)	2553(2)	36(2)
C(25)	9473(6)	7642(10)	2140(2)	33(2)
C(26)	8887(5)	6564(8)	1819(2)	26(2)
Cl(1)	6247(1)	1379(2)	666(1)	23(1)
F(1)	6502(5)	2320(12)	3470(3)	102(2)
F(2)	7821(6)	4272(9)	3736(3)	107(3)
F(3)	7497(6)	4(9)	3684(4)	123(3)
F(4)	8787(6)	1889(12)	3967(4)	152(5)
F(5)	8140(9)	1973(18)	3258(3)	181(6)
F(6)	7140(6)	2248(15)	4177(2)	109(3)
N(1)	6593(4)	7009(7)	-183(2)	23(1)
N(2)	6114(4)	6137(7)	464(2)	18(1)
P(1)	7034(1)	4608(2)	1474(1)	16(1)
P(2)	7660(2)	2135(3)	3710(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for complex **8a**-(PF_6).

Ir(1)-C(9)	2.065(6)
Ir(1)-C(6)	2.276(6)
Ir(1)-C(5)	2.282(6)
Ir(1)-C(2)	2.282(5)
Ir(1)-C(1)	2.286(6)
Ir(1)-P(1)	2.3164(14)
Ir(1)-Cl(1)	2.5076(14)
C(1)-C(2)	1.393(9)
C(1)-C(8)	1.507(9)
C(2)-C(3)	1.514(8)
C(3)-C(4)	1.527(9)
C(4)-C(5)	1.530(9)
C(5)-C(6)	1.394(9)
C(6)-C(7)	1.496(9)
C(7)-C(8)	1.525(9)
C(9)-C(10)	1.358(8)
C(9)-N(2)	1.401(7)
C(10)-N(1)	1.389(8)
C(11)-N(1)	1.469(8)
C(12)-N(1)	1.324(8)
C(12)-N(2)	1.337(8)
C(13)-N(2)	1.464(8)
C(13)-C(14)	1.522(8)
C(14)-P(1)	1.840(6)
C(15)-C(16)	1.380(9)
C(15)-C(20)	1.394(9)
C(15)-P(1)	1.824(6)
C(16)-C(17)	1.402(11)
C(17)-C(18)	1.352(12)
C(18)-C(19)	1.385(13)
C(19)-C(20)	1.361(11)
C(21)-C(22)	1.390(9)
C(21)-C(26)	1.403(9)
C(21)-P(1)	1.828(6)
C(22)-C(23)	1.393(10)
C(23)-C(24)	1.367(12)

C(24)-C(25)	1.372(10)
C(25)-C(26)	1.390(9)
F(1)-P(2)	1.559(6)
F(2)-P(2)	1.572(7)
F(3)-P(2)	1.568(7)
F(4)-P(2)	1.549(7)
F(5)-P(2)	1.522(7)
F(6)-P(2)	1.585(6)

C(9)-Ir(1)-C(6)	88.9(2)
C(9)-Ir(1)-C(5)	92.0(2)
C(6)-Ir(1)-C(5)	35.6(2)
C(9)-Ir(1)-C(2)	160.6(2)
C(6)-Ir(1)-C(2)	93.1(2)
C(5)-Ir(1)-C(2)	78.7(2)
C(9)-Ir(1)-C(1)	162.0(2)
C(6)-Ir(1)-C(1)	79.1(2)
C(5)-Ir(1)-C(1)	86.0(2)
C(2)-Ir(1)-C(1)	35.5(2)
C(9)-Ir(1)-P(1)	92.24(16)
C(6)-Ir(1)-P(1)	173.29(17)
C(5)-Ir(1)-P(1)	150.83(17)
C(2)-Ir(1)-P(1)	88.10(15)
C(1)-Ir(1)-P(1)	98.16(15)
C(9)-Ir(1)-Cl(1)	85.50(16)
C(6)-Ir(1)-Cl(1)	82.67(17)
C(5)-Ir(1)-Cl(1)	118.27(17)
C(2)-Ir(1)-Cl(1)	113.86(16)
C(1)-Ir(1)-Cl(1)	79.70(16)
P(1)-Ir(1)-Cl(1)	90.83(5)
C(2)-C(1)-C(8)	123.2(6)
C(2)-C(1)-Ir(1)	72.1(3)
C(8)-C(1)-Ir(1)	111.7(4)
C(1)-C(2)-C(3)	125.4(6)
C(1)-C(2)-Ir(1)	72.4(3)
C(3)-C(2)-Ir(1)	109.7(4)
C(2)-C(3)-C(4)	113.8(5)
C(3)-C(4)-C(5)	115.1(5)

C(6)-C(5)-C(4)	122.3(6)
C(6)-C(5)-Ir(1)	72.0(4)
C(4)-C(5)-Ir(1)	111.9(4)
C(5)-C(6)-C(7)	123.3(6)
C(5)-C(6)-Ir(1)	72.4(4)
C(7)-C(6)-Ir(1)	108.9(4)
C(6)-C(7)-C(8)	116.3(5)
C(1)-C(8)-C(7)	115.4(5)
C(10)-C(9)-N(2)	103.5(5)
C(10)-C(9)-Ir(1)	129.7(5)
N(2)-C(9)-Ir(1)	126.7(4)
C(9)-C(10)-N(1)	109.8(5)
N(1)-C(12)-N(2)	108.4(5)
N(2)-C(13)-C(14)	112.2(5)
C(13)-C(14)-P(1)	112.6(4)
C(16)-C(15)-C(20)	118.2(6)
C(16)-C(15)-P(1)	120.5(5)
C(20)-C(15)-P(1)	121.2(5)
C(15)-C(16)-C(17)	120.0(7)
C(18)-C(17)-C(16)	120.9(8)
C(17)-C(18)-C(19)	119.0(7)
C(20)-C(19)-C(18)	120.9(8)
C(19)-C(20)-C(15)	120.8(7)
C(22)-C(21)-C(26)	118.2(6)
C(22)-C(21)-P(1)	119.6(5)
C(26)-C(21)-P(1)	121.8(5)
C(21)-C(22)-C(23)	120.3(7)
C(24)-C(23)-C(22)	120.4(7)
C(23)-C(24)-C(25)	120.7(6)
C(24)-C(25)-C(26)	119.6(7)
C(25)-C(26)-C(21)	120.8(6)
C(12)-N(1)-C(10)	107.6(5)
C(12)-N(1)-C(11)	125.9(6)
C(10)-N(1)-C(11)	126.2(5)
C(12)-N(2)-C(9)	110.6(5)
C(12)-N(2)-C(13)	122.2(5)
C(9)-N(2)-C(13)	127.3(5)
C(15)-P(1)-C(21)	104.3(3)

C(15)-P(1)-C(14)	105.3(3)
C(21)-P(1)-C(14)	102.0(3)
C(15)-P(1)-Ir(1)	114.8(2)
C(21)-P(1)-Ir(1)	116.9(2)
C(14)-P(1)-Ir(1)	112.2(2)
F(5)-P(2)-F(4)	90.6(7)
F(5)-P(2)-F(1)	91.8(6)
F(4)-P(2)-F(1)	177.0(6)
F(5)-P(2)-F(3)	86.6(6)
F(4)-P(2)-F(3)	91.0(4)
F(1)-P(2)-F(3)	87.3(4)
F(5)-P(2)-F(2)	93.5(5)
F(4)-P(2)-F(2)	89.1(5)
F(1)-P(2)-F(2)	92.6(5)
F(3)-P(2)-F(2)	179.9(5)
F(5)-P(2)-F(6)	178.2(6)
F(4)-P(2)-F(6)	90.2(6)
F(1)-P(2)-F(6)	87.4(4)
F(3)-P(2)-F(6)	91.8(6)
F(2)-P(2)-F(6)	88.1(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for complex **8a**-(PF_6). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

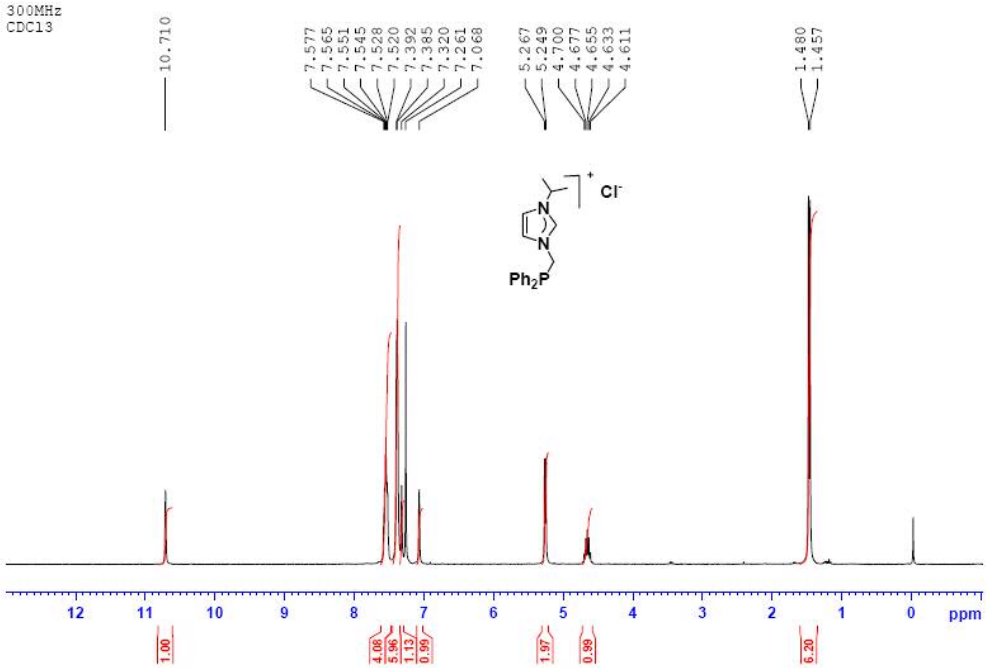
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	14(1)	16(1)	12(1)	0(1)	-1(1)	0(1)
C(1)	19(3)	24(3)	19(3)	8(2)	-1(2)	9(2)
C(2)	14(3)	23(3)	17(3)	1(2)	-4(2)	6(2)
C(3)	17(3)	36(4)	24(3)	1(3)	-3(2)	2(3)
C(4)	20(3)	48(5)	27(3)	-1(3)	6(3)	3(3)
C(5)	26(3)	24(4)	21(3)	2(3)	10(3)	4(3)
C(6)	27(3)	30(3)	12(3)	-1(2)	1(3)	8(3)
C(7)	36(4)	27(4)	26(3)	-5(3)	2(3)	1(3)
C(8)	31(4)	21(3)	34(4)	-3(3)	-4(3)	8(3)
C(9)	20(3)	22(3)	16(3)	0(2)	-1(2)	-2(2)
C(10)	21(3)	23(3)	23(3)	6(3)	0(2)	3(2)
C(11)	34(4)	47(4)	23(3)	21(3)	-2(3)	-2(3)
C(12)	18(3)	24(3)	19(3)	1(2)	-8(2)	1(2)
C(13)	19(3)	35(4)	19(3)	2(3)	0(2)	7(3)
C(14)	23(3)	24(3)	17(3)	-1(2)	3(2)	4(2)
C(15)	29(3)	24(3)	16(3)	-1(2)	11(2)	-3(3)
C(16)	37(4)	51(5)	17(3)	3(3)	2(3)	-11(3)
C(17)	44(5)	69(6)	34(4)	-5(4)	14(4)	-27(4)
C(18)	54(5)	40(5)	47(5)	2(4)	31(4)	-8(4)
C(19)	66(6)	57(6)	50(5)	26(4)	32(4)	23(5)
C(20)	33(4)	42(4)	37(4)	14(3)	14(3)	8(3)
C(21)	22(3)	24(3)	16(3)	-3(2)	-6(2)	6(2)
C(22)	30(4)	61(5)	23(3)	-16(3)	4(3)	-2(3)
C(23)	41(4)	74(6)	24(4)	-19(4)	-5(3)	4(4)
C(24)	39(4)	38(4)	28(4)	-14(3)	-14(3)	3(3)
C(25)	34(4)	29(4)	33(4)	-4(3)	-7(3)	-8(3)
C(26)	28(4)	29(4)	21(3)	0(3)	-4(3)	-2(3)
Cl(1)	19(1)	25(1)	24(1)	1(1)	-5(1)	-5(1)
F(1)	62(4)	140(6)	99(5)	3(5)	-25(4)	27(4)
F(2)	113(6)	48(4)	166(7)	-8(4)	44(5)	-21(4)
F(3)	99(5)	48(4)	214(9)	-3(5)	-25(5)	-15(4)
F(4)	52(4)	117(7)	272(13)	-41(7)	-61(6)	16(4)
F(5)	173(10)	276(14)	112(7)	-84(8)	112(7)	-90(9)

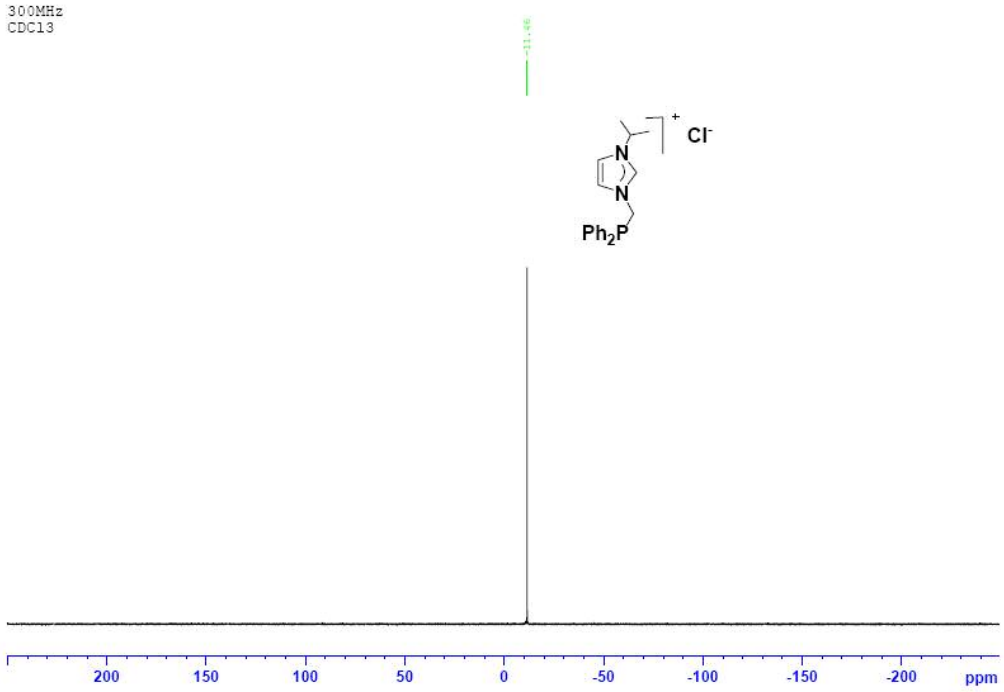
F(6)	106(6)	169(8)	55(4)	-4(4)	21(4)	-51(5)
N(1)	24(3)	25(3)	18(3)	6(2)	-4(2)	-2(2)
N(2)	19(2)	18(2)	16(2)	2(2)	-3(2)	1(2)
P(1)	16(1)	20(1)	13(1)	-1(1)	0(1)	0(1)
P(2)	26(1)	34(1)	46(1)	0(1)	9(1)	0(1)

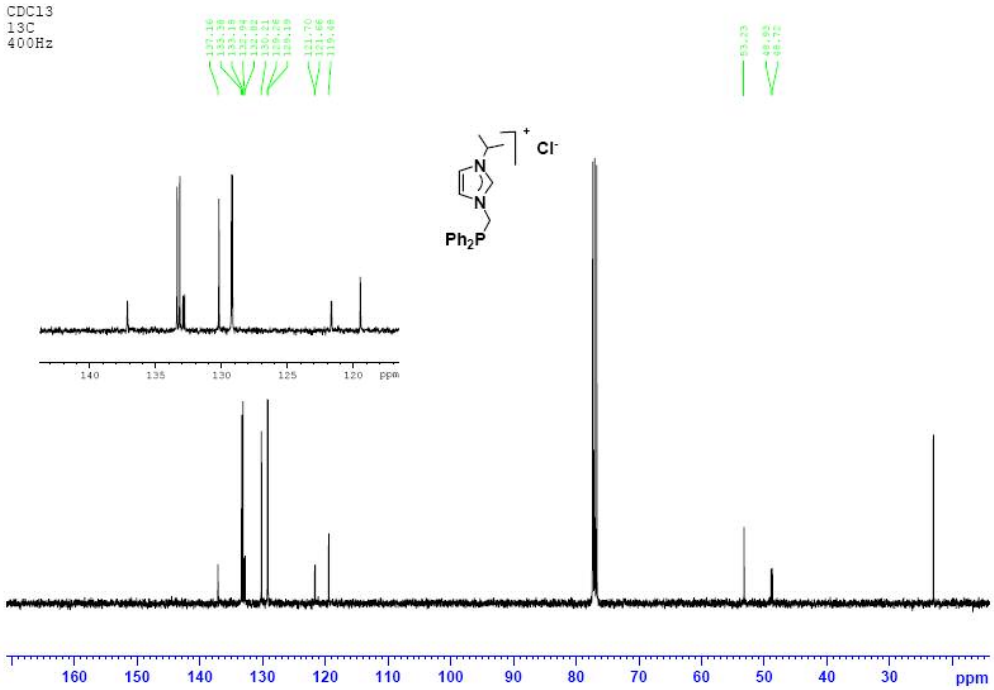
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **8a**-(PF_6).

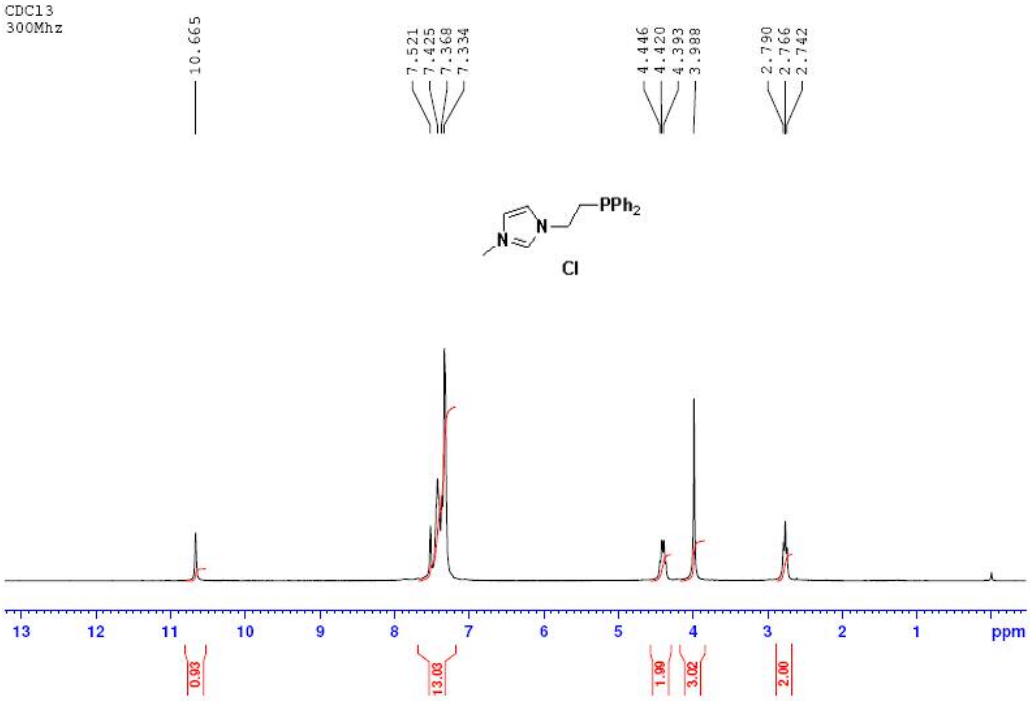
	x	y	z	U(eq)
H(1M)	8440(50)	4840(90)	970(20)	21(16)
H(1)	7736	593	1303	25
H(2)	8834	2859	1607	22
H(3A)	10722	1594	1391	31
H(3B)	10440	3733	1370	31
H(4A)	10463	1240	645	38
H(4B)	10900	3299	671	38
H(5)	9290(50)	4200(110)	340(20)	26(19)
H(6)	8070(60)	2420(110)	10(20)	30(18)
H(7A)	9085	-637	190	36
H(7B)	7831	-622	250	36
H(8A)	8398	-1837	905	35
H(8B)	9549	-881	919	35
H(10)	7999	5454	-120	27
H(11A)	5943	8563	-701	52
H(11B)	6869	7220	-841	52
H(11C)	7176	9035	-555	52
H(12)	5217	7921	55	25
H(13A)	5139	4741	847	29
H(13B)	4831	6864	789	29
H(14A)	5544	6550	1527	25
H(14B)	6442	7592	1273	25
H(16)	4825	3454	1457	42
H(17)	3934	1043	1789	58
H(18)	4820	-742	2345	55

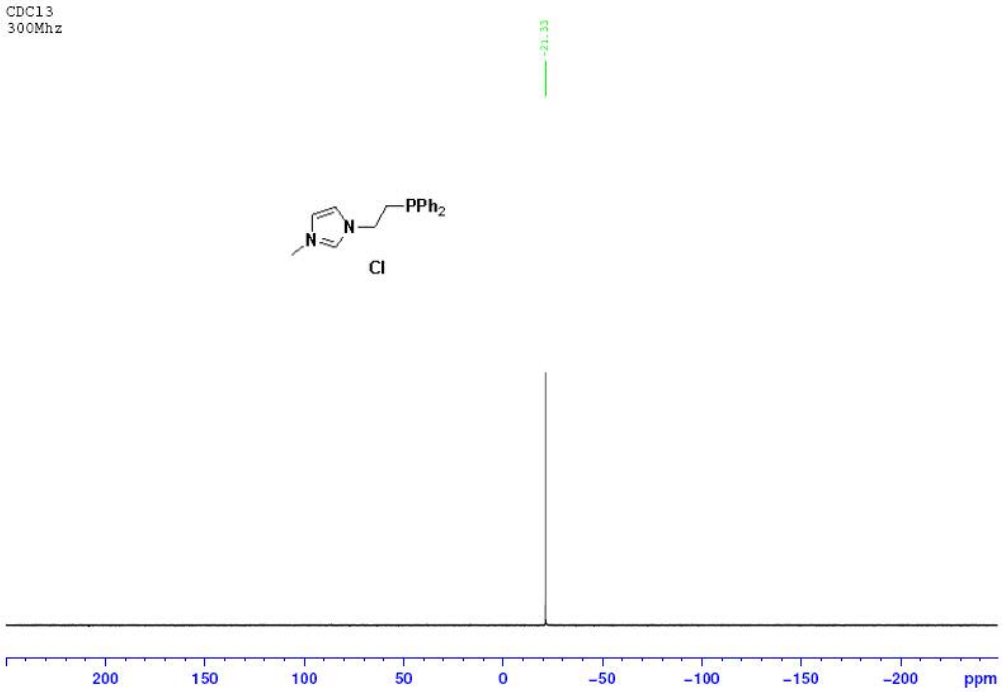
H(19)	6617	-118	2580	67
H(20)	7558	2013	2204	44
H(22)	6891	5549	2408	45
H(23)	7893	7364	2942	56
H(24)	9487	8678	2772	43
H(25)	10134	8174	2074	39
H(26)	9154	6357	1534	32

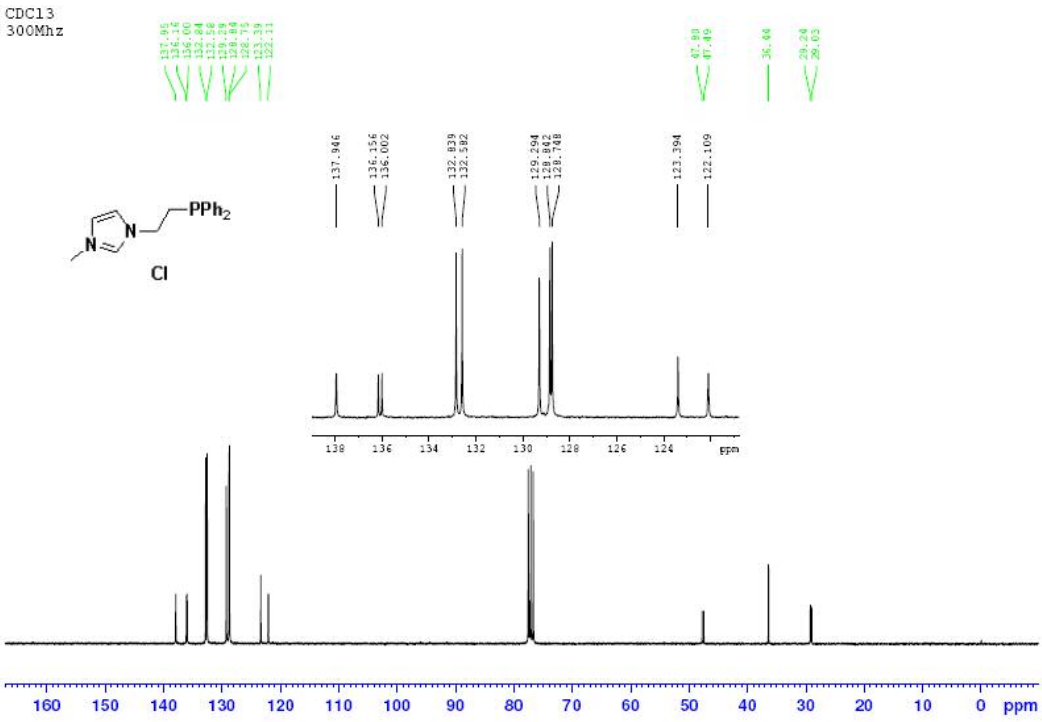

300MHz
CDCl3
10.710
7.577
7.565
7.551
7.545
7.528
7.520
7.392
7.385
7.320
7.261
7.068
5.267
5.249
4.700
4.677
4.655
4.633
4.611
1.480
1.457
Cl-
Ph2P
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.08
5.96
1.13
0.99
1.97
0.99
6.20

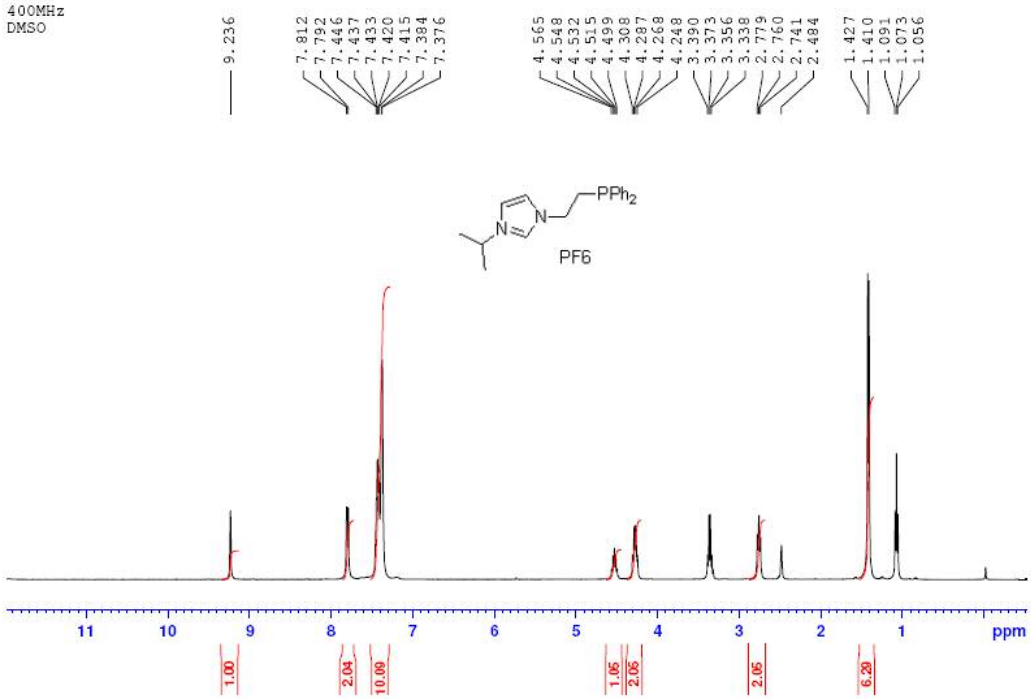

300MHz
CDCl3
-11.46
Cl-
Ph2P
200
150
100
50
0
-50
-100
-150
-200
ppm

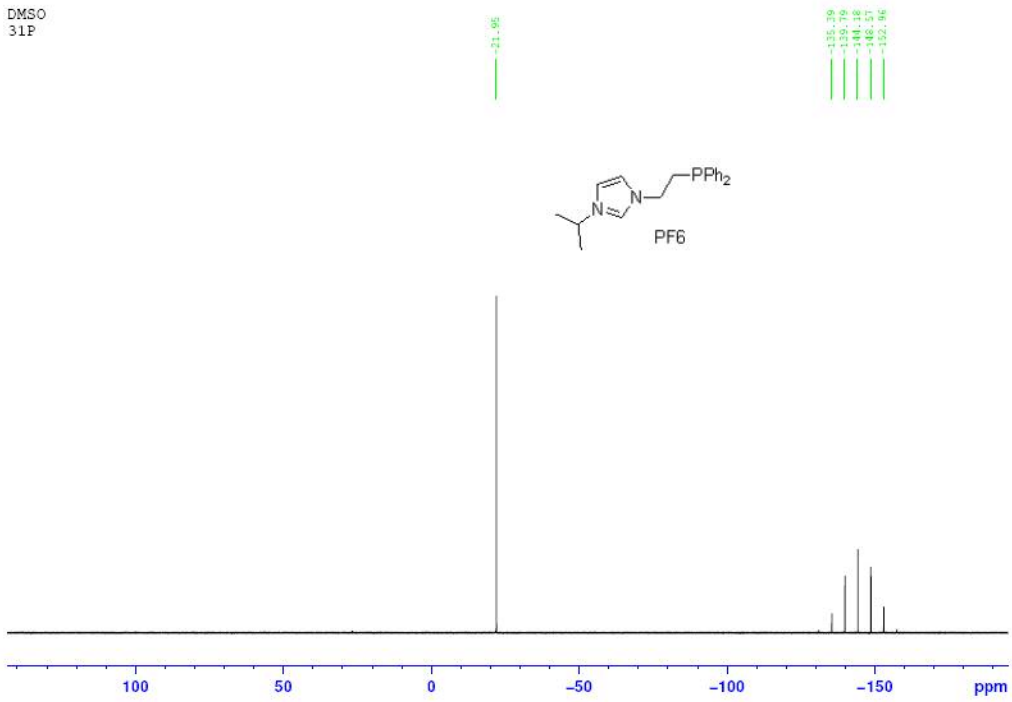

CDCl3
13C
400Hz
Cl-
Ph2P
ppm

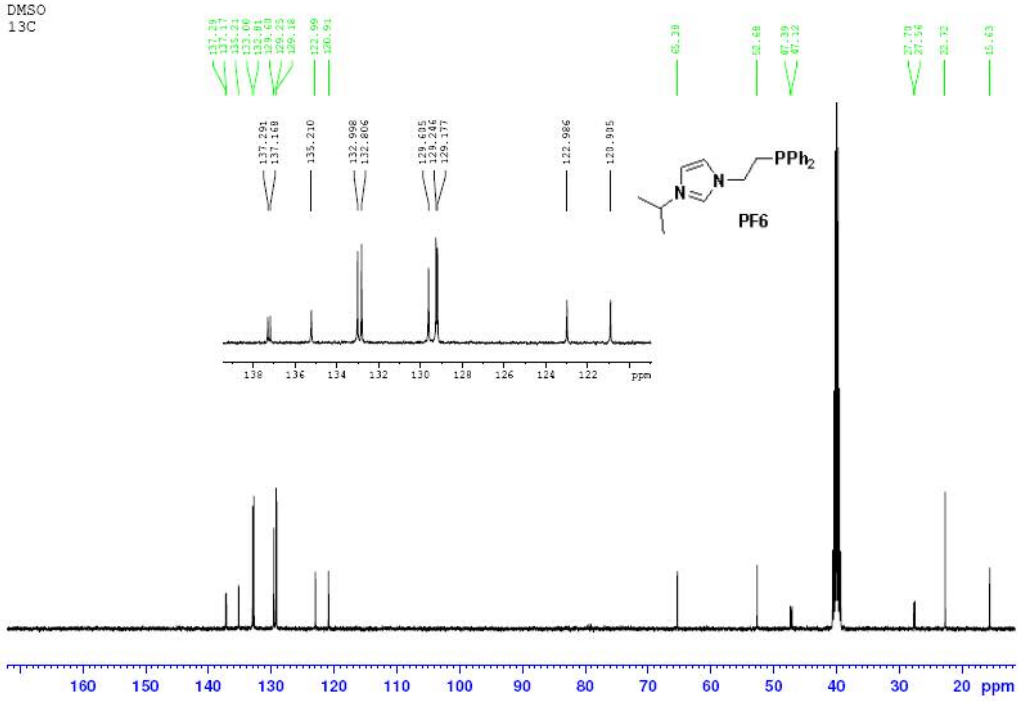

CDCl3
300Mhz
10.665
7.521
7.425
7.368
7.334
4.446
4.420
4.393
3.988
2.790
2.766
2.742
PPh2
N
N
Cl
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.93
13.03
1.99
3.02
2.00

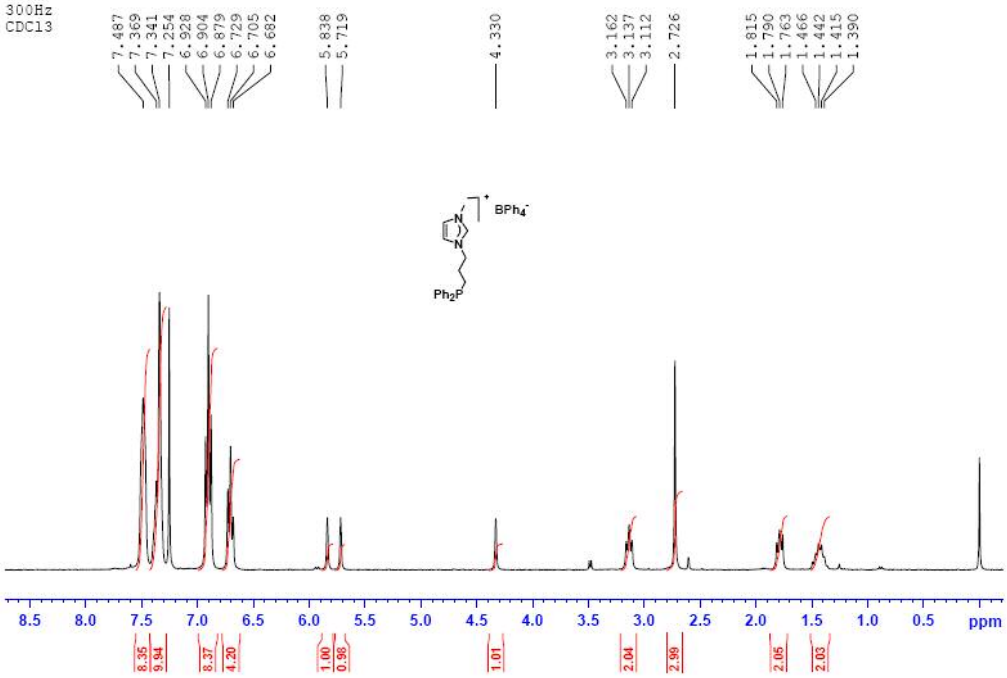

CDCl3
300Mhz
-21.33
PPh2
N
N
Cl
200
150
100
50
0
-50
-100
-150
-200
ppm

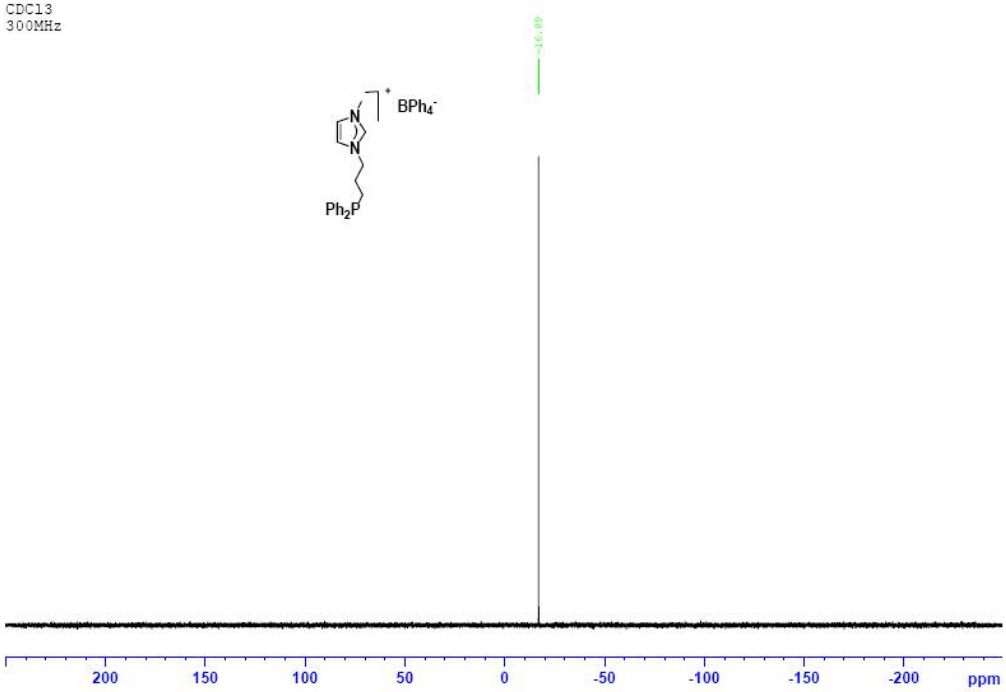

CDCl3
300Mhz
PPh2
N
N
Cl
137.946
136.156
136.002
132.839
132.582
129.294
129.042
128.748
123.394
122.109
47.90
47.49
36.44
29.24
28.03
ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

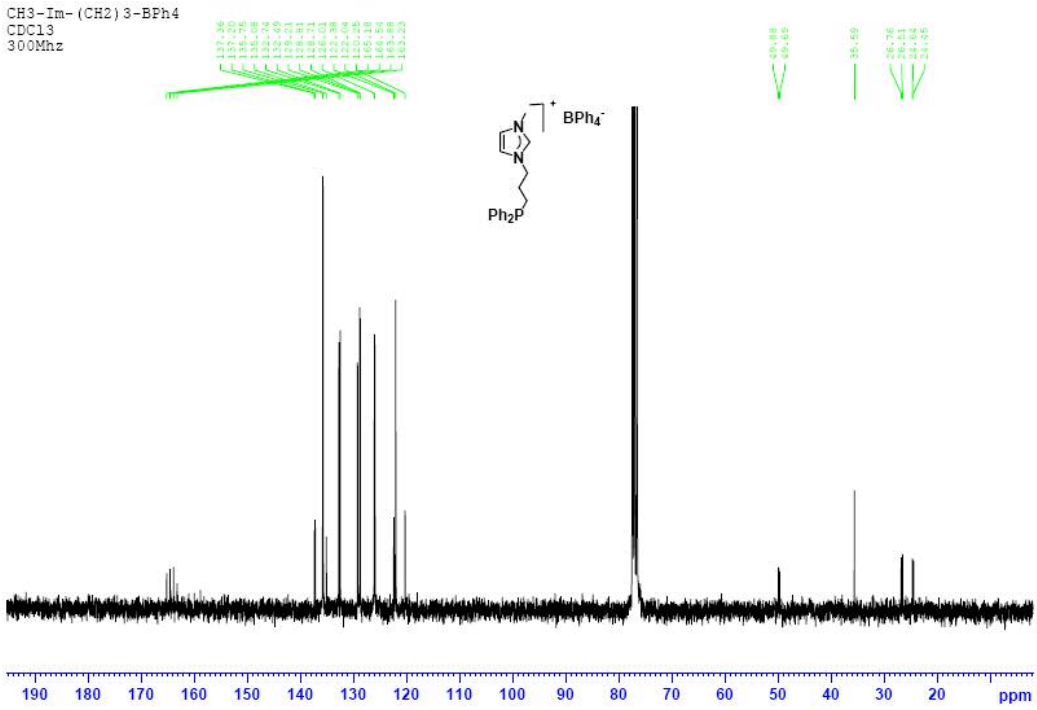

400MHz
DMSO
9.236
7.812
7.792
7.446
7.437
7.433
7.420
7.415
7.384
7.376
4.565
4.548
4.532
4.515
4.499
4.308
4.287
4.268
4.248
3.390
3.373
3.356
3.338
2.779
2.760
2.741
2.484
1.427
1.410
1.091
1.073
1.056
PPh2
PF6
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.04
10.00
1.05
2.05
2.05
6.20

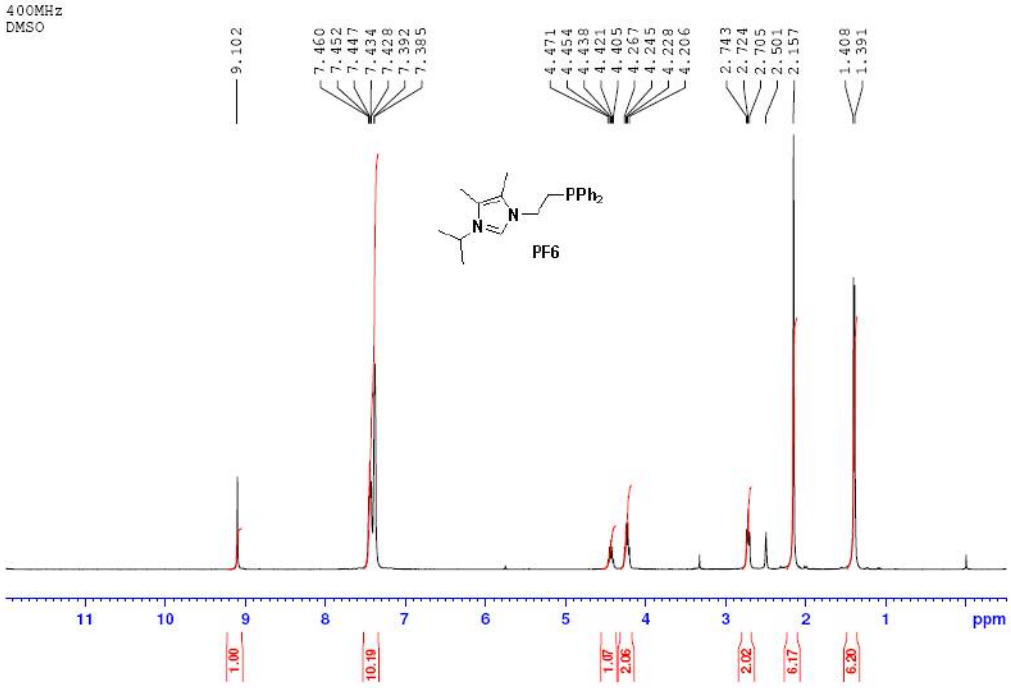

DMSO
31P
-21.95
-135.39
-139.79
-144.18
-148.57
-152.96
PPh2
PF6
100
50
0
-50
-100
-150
ppm

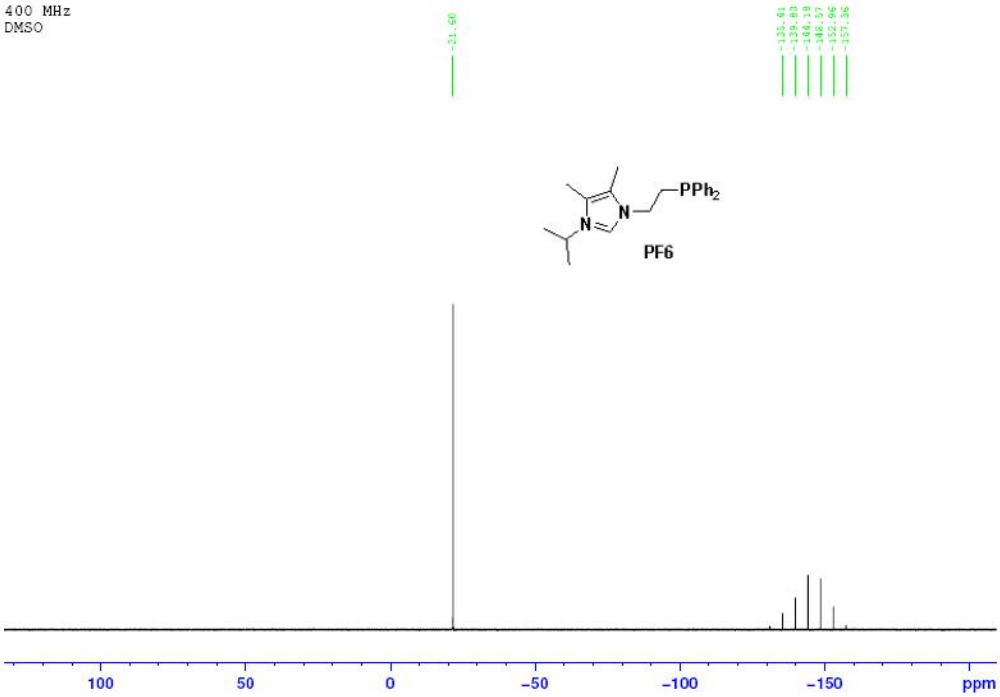

DMSO
13C
PPh2
PF6
ppm

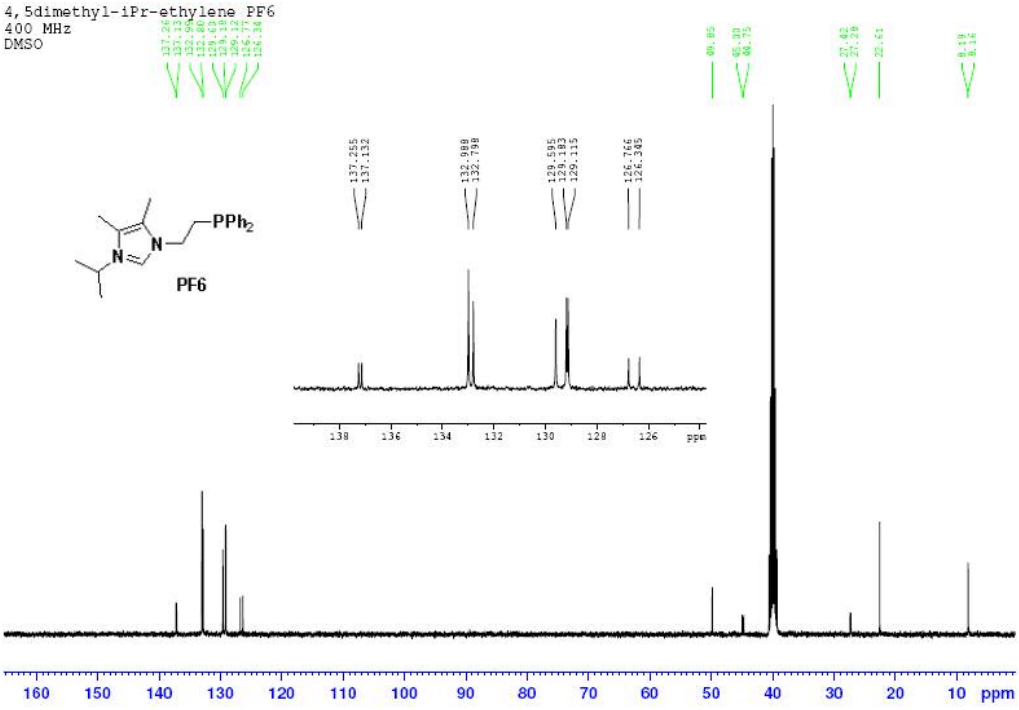

300Hz
CDCl3
7.487
7.369
7.341
7.254
6.928
6.904
6.879
6.729
6.705
6.682
5.838
5.719
4.330
3.162
3.137
3.112
2.726
1.815
1.790
1.763
1.466
1.442
1.415
1.390
BPh4-
Ph2P
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
8.35
9.94
8.37
4.20
1.00
0.98
1.01
2.04
2.99
2.05
2.03

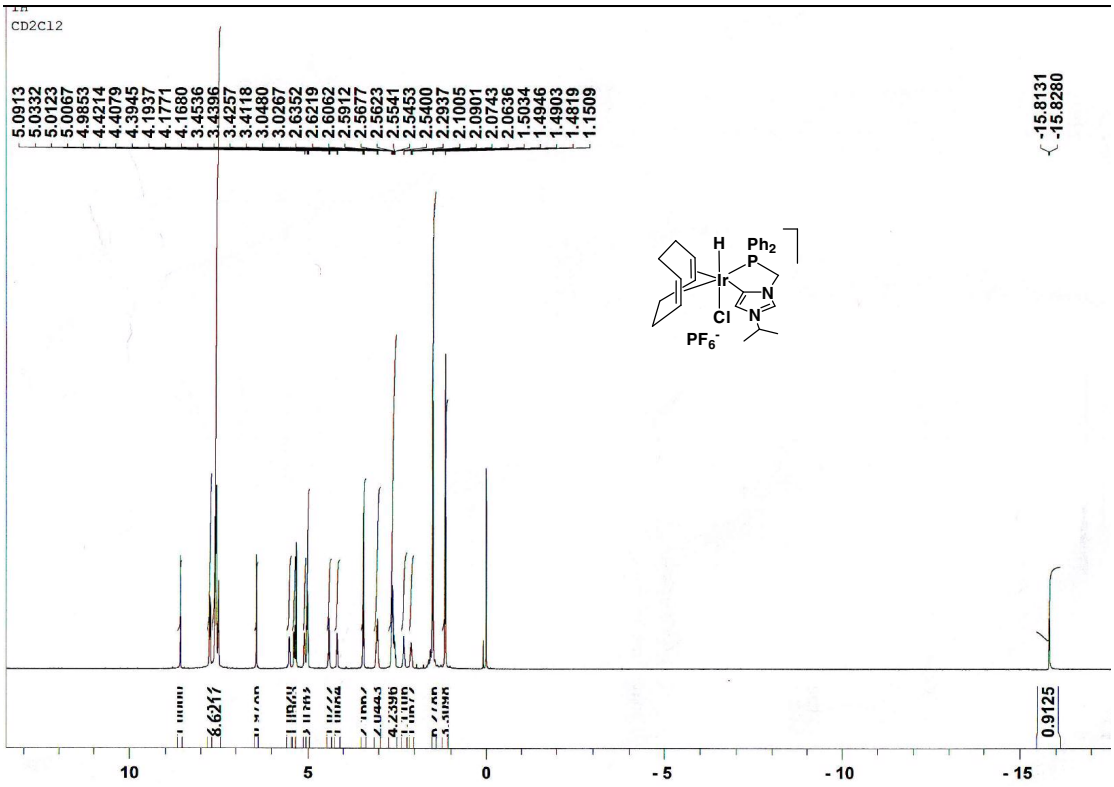

CDCl3
300MHz
-16.89
BPh4-
Ph2P
200
150
100
50
0
-50
-100
-150
-200
ppm

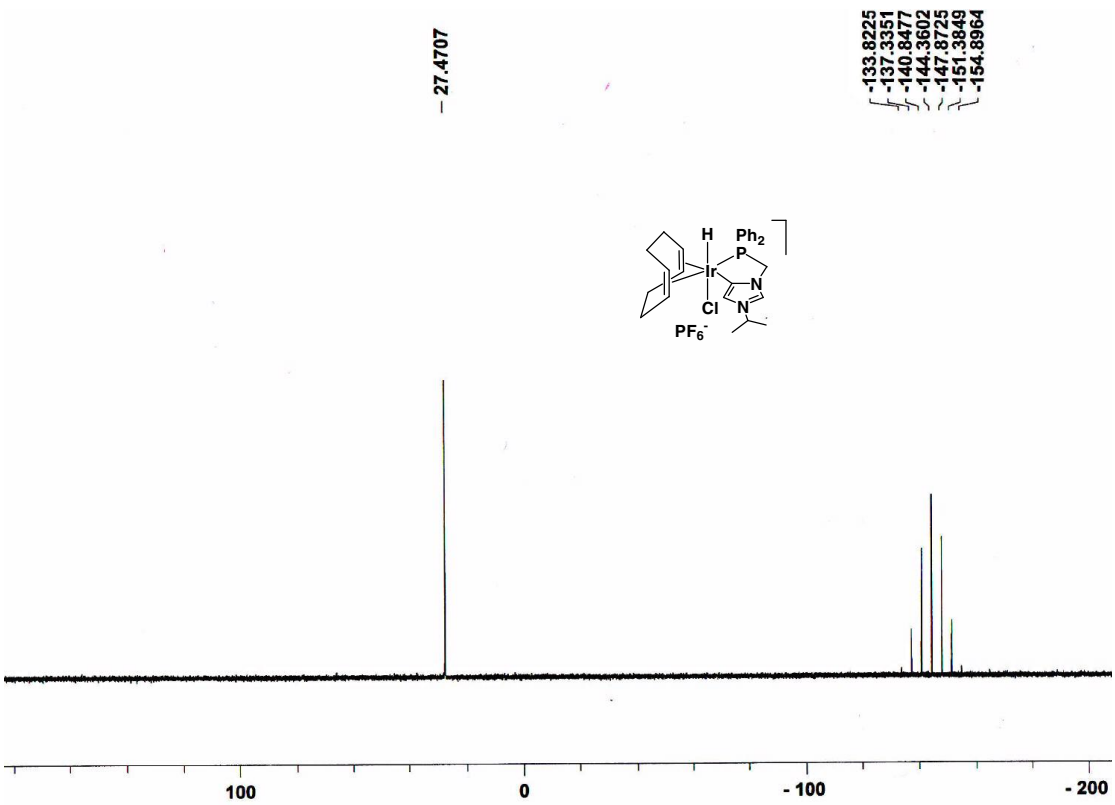

CH3-Im-(CH2)3-BPh4
CDCl3
300Mhz
BPh4-
Ph2P
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

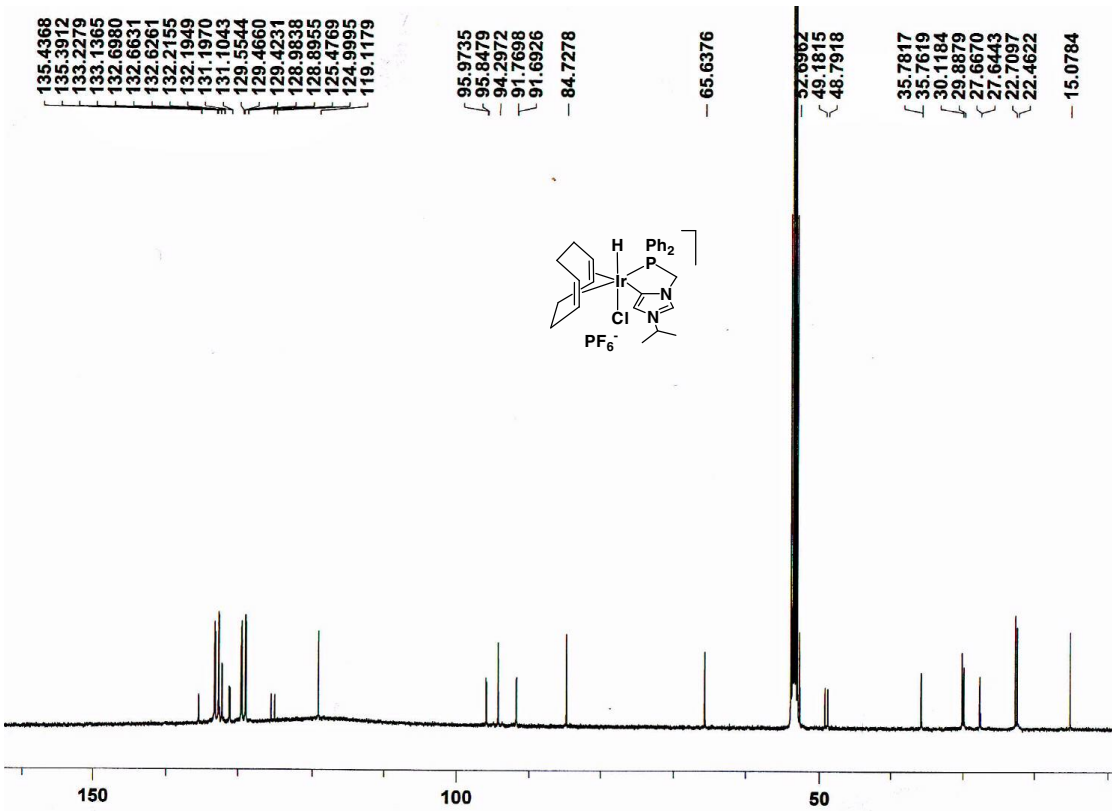

400MHz
DMSO
9.102
7.460
7.452
7.447
7.434
7.428
7.392
7.385
4.471
4.454
4.438
4.421
4.405
4.267
4.245
4.228
4.206
2.743
2.724
2.705
2.501
2.157
1.408
1.391
PPh2
N
N
PF6
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
10.19
1.07
2.06
2.02
6.17
6.20

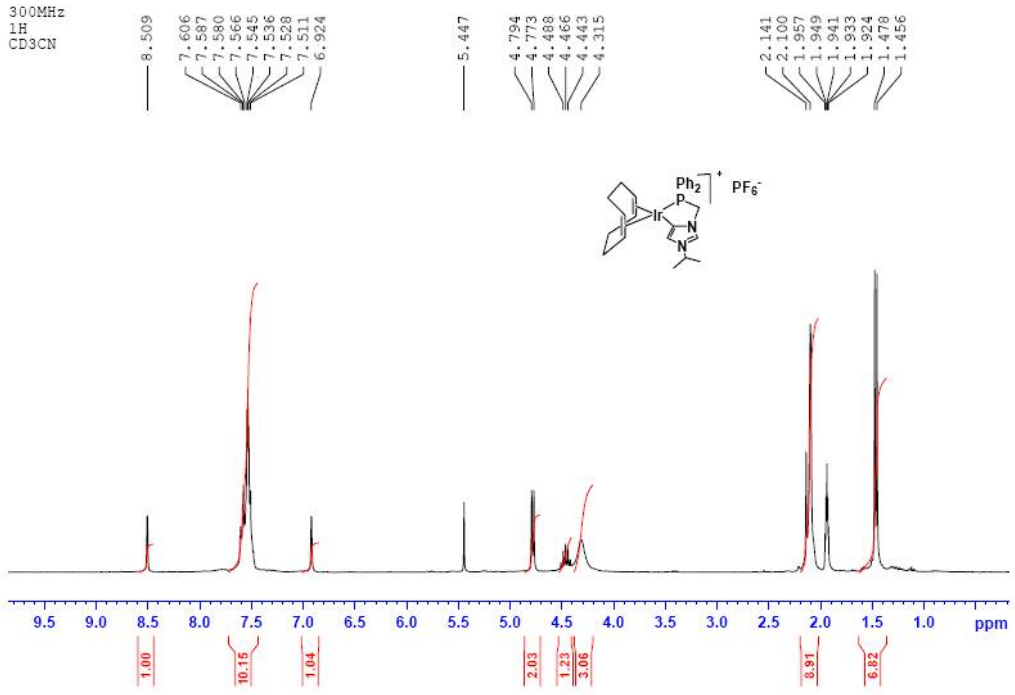

400 MHz
DMSO
-21.60
-135.41
-139.83
-144.19
-148.57
-152.96
-157.36
PPh2
N
N
PF6
100
50
0
-50
-100
-150
ppm

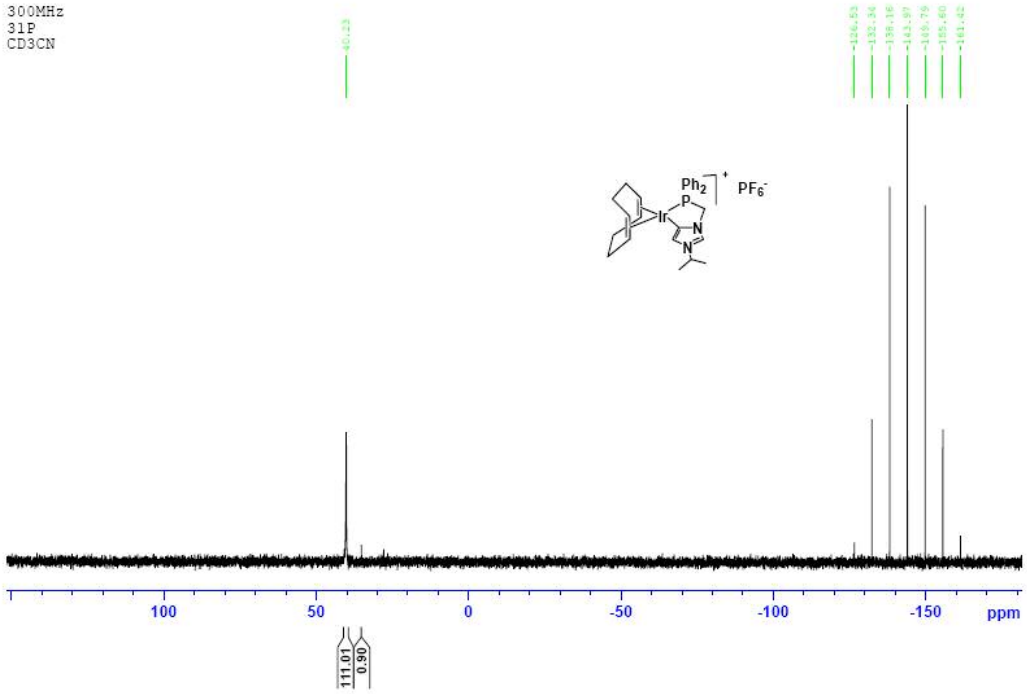

4,5dimethyl-iPr-ethylene PF6
400 MHz
DMSO
PPh2
PF6
137.255
137.132
132.988
132.798
129.595
129.193
129.115
126.766
126.345
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

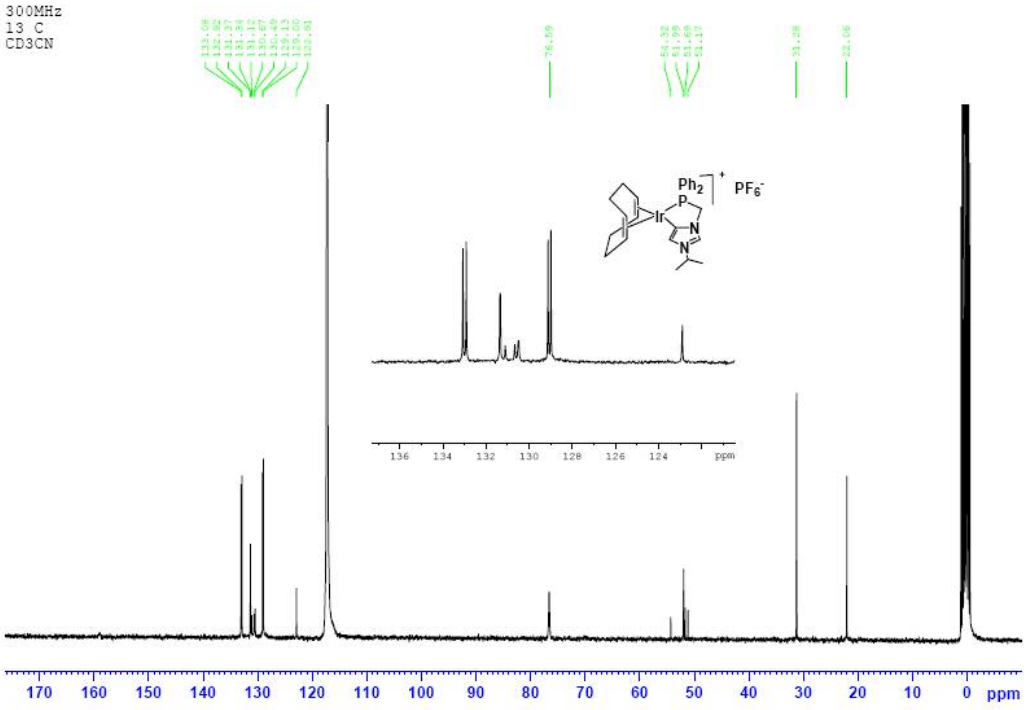

CD2Cl2
5.0913
5.0332
5.0123
5.0067
4.9853
4.4214
4.4079
4.3945
4.1937
4.1771
4.1680
3.4536
3.4396
3.4257
3.4118
3.0480
3.0267
2.6552
2.6219
2.6062
2.5912
2.5677
2.5623
2.5541
2.5453
2.5400
2.2937
2.1005
2.0901
2.0743
2.0636
1.5034
1.4946
1.4903
1.4819
1.1509
-15.8131
-15.8280
H
Ph2
P
Ir
N
N
Cl
PF6-
8.6217
0.9125
10 5 0 - 5 - 10 - 15

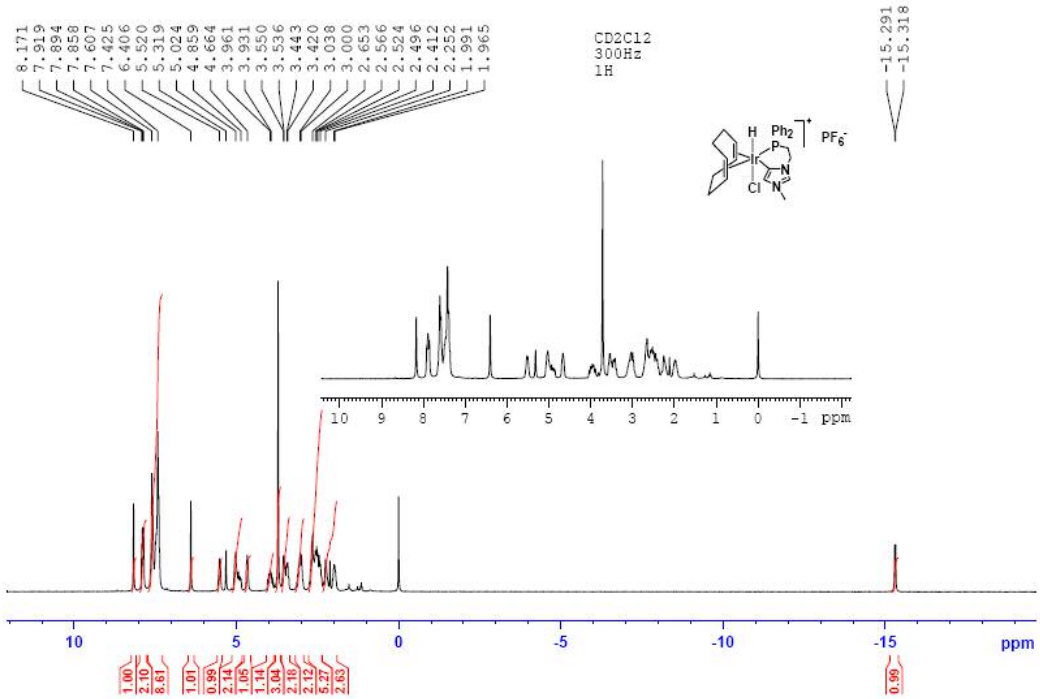

27.4707
-133.8225
-137.3351
-140.8477
-144.3602
-147.8725
-151.3849
-154.8964
H
Ph2
P
Ir
N
N
Cl
PF6-
100
0
- 100
- 200

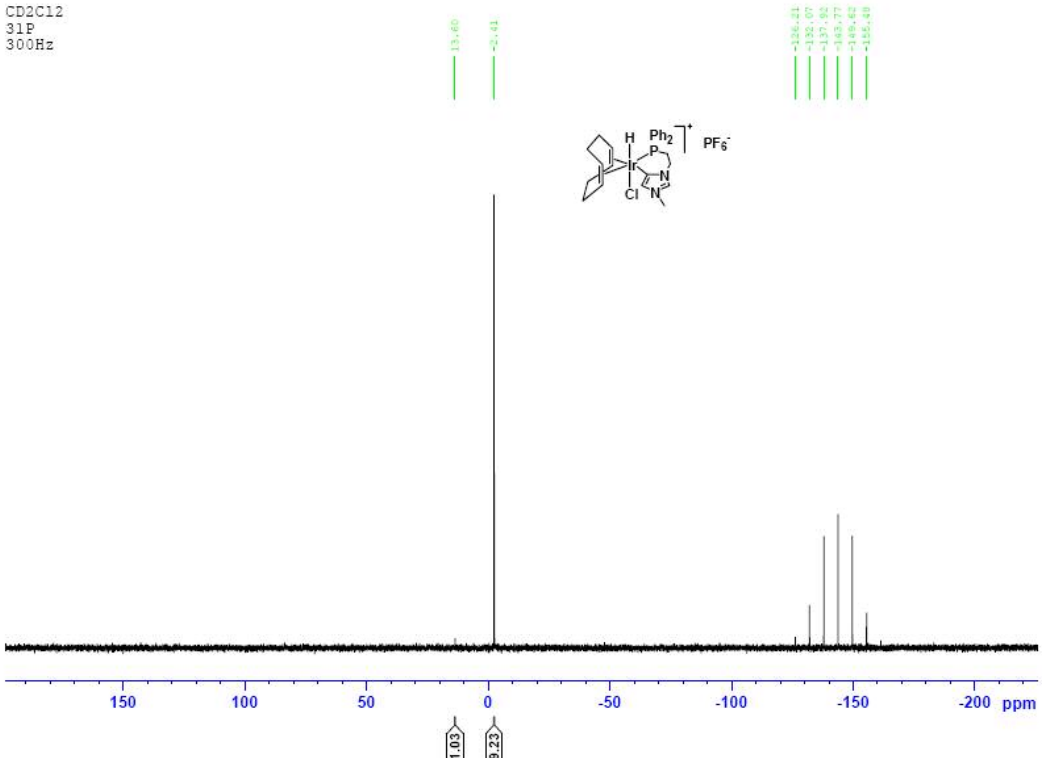

135.4368
135.3912
133.2279
133.1365
132.6980
132.6631
132.6261
132.2155
132.1949
131.1970
131.1043
129.5544
129.4660
129.4231
128.9838
128.8955
125.4769
124.9995
119.1179
95.9735
95.8479
94.2972
91.7698
91.6926
84.7278
65.6376
52.6962
49.1815
48.7918
35.7817
35.7619
30.1184
29.8879
27.6670
27.6443
22.7097
22.4622
15.0784
H
Ph2
P
Ir
N
N
Cl
PF6-
150
100
50

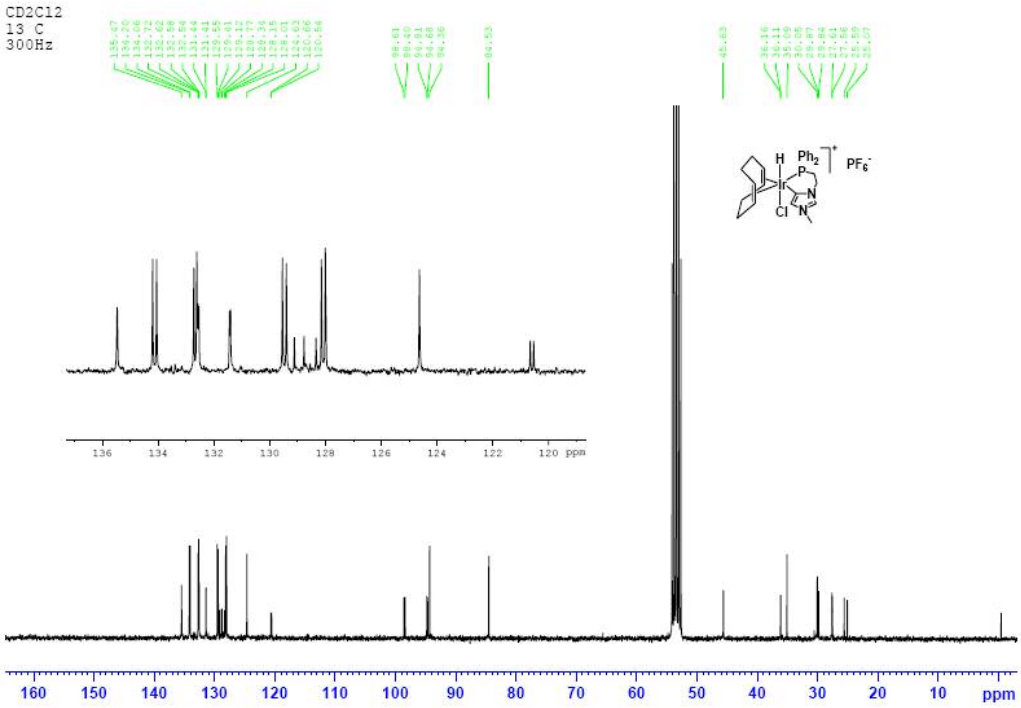

300MHz
1H
CD3CN
8.509
7.606
7.587
7.580
7.566
7.545
7.536
7.528
7.511
6.924
5.447
4.794
4.773
4.488
4.466
4.443
4.315
2.141
2.100
1.957
1.949
1.941
1.933
1.924
1.478
1.456
Ph2
P
Ir
N
N
PF6-
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
10.15
1.04
2.03
1.23
3.06
8.91
6.82

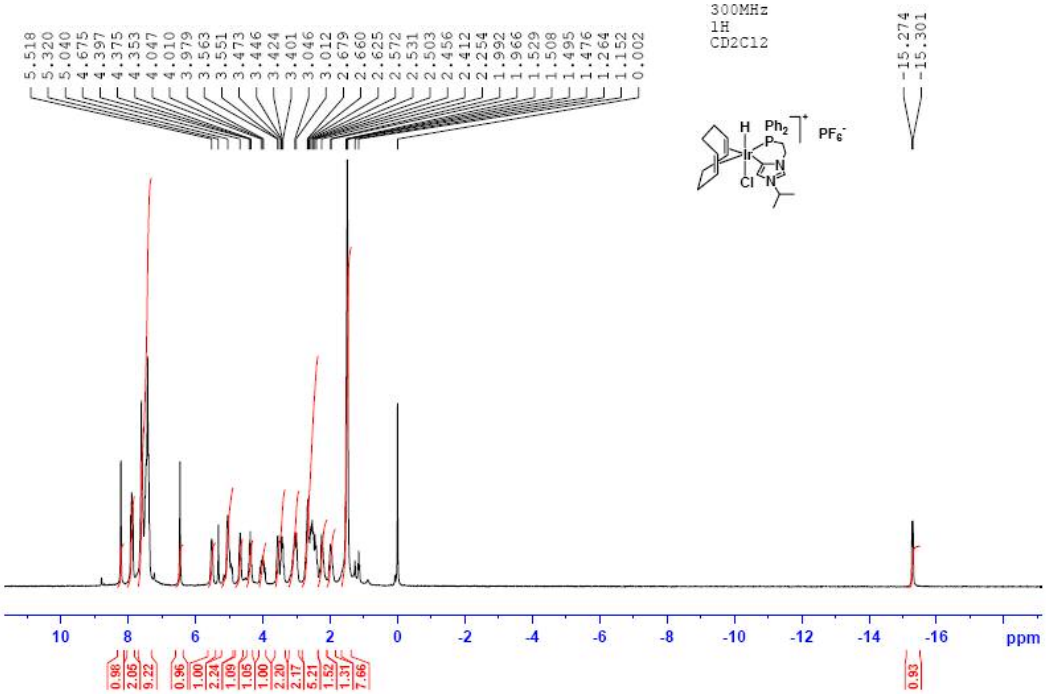

300MHz
31P
CD3CN
40.23
-126.53
-132.54
-138.16
-143.97
-149.79
-155.60
-161.42
Ph2
P
Ir
N
N
PF6-
100 50 0 -50 -100 -150 ppm
111.01
0.90

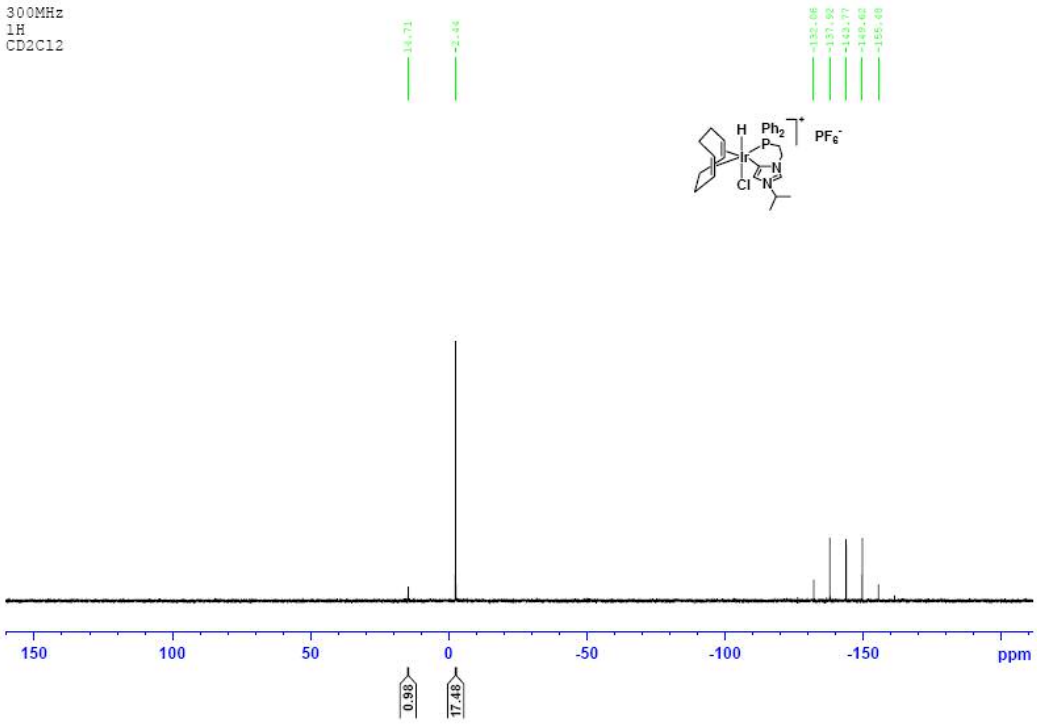

300MHz
13 C
CD3CN
Ph2
PF6-
Ir
P
N
N
136 134 132 130 128 126 124 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

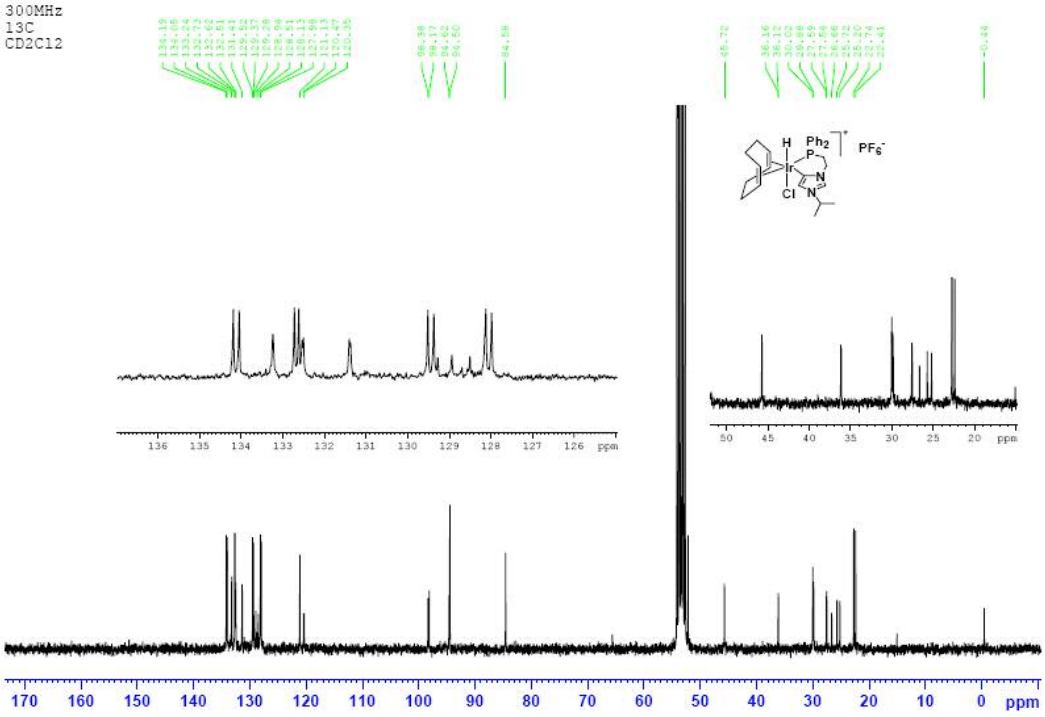

CD2Cl2
300Hz
1H
8.171
7.919
7.894
7.858
7.607
7.425
6.406
5.520
5.319
5.024
4.859
4.664
3.961
3.931
3.550
3.536
3.443
3.420
3.038
3.000
2.653
2.566
2.524
2.496
2.412
2.252
1.991
1.965
-15.291
-15.318
H
Ph2
P
Ir
N
N
Cl
PF6-
10 9 8 7 6 5 4 3 2 1 0 -1 ppm
10 5 0 -5 -10 -15 ppm
1.00
2.10
8.61
1.01
0.89
2.14
1.05
1.14
3.04
2.18
2.12
5.27
2.83
0.96

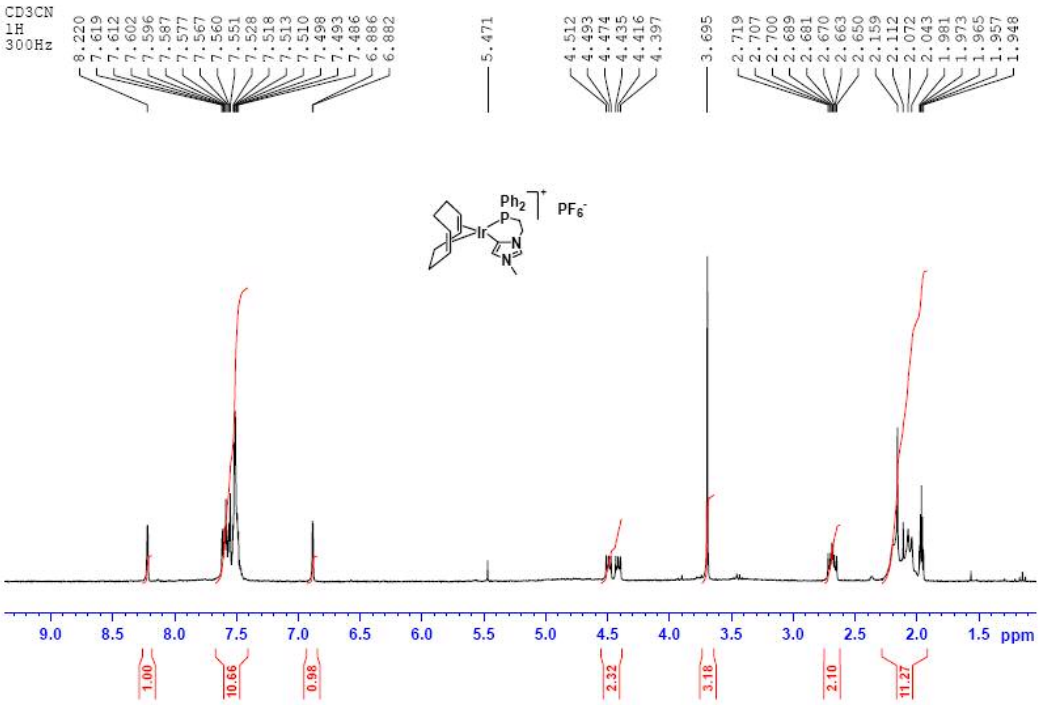

CD2Cl2
31P
300Hz
13.60
-2.41
-126.21
-132.07
-137.92
-143.77
-149.62
-155.49
H
Ph2
P
Ir
N
N
Cl
PF6-
150 100 50 0 -50 -100 -150 -200 ppm
1.03
9.23

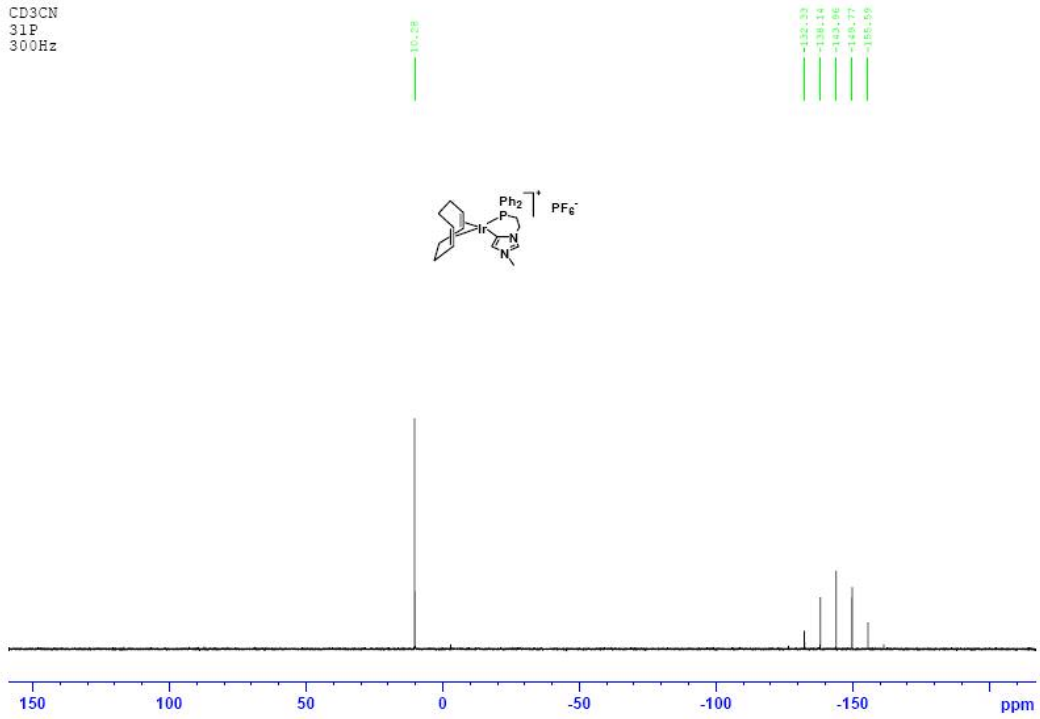

CD2Cl2
13 C
300Hz
PF6-
ppm

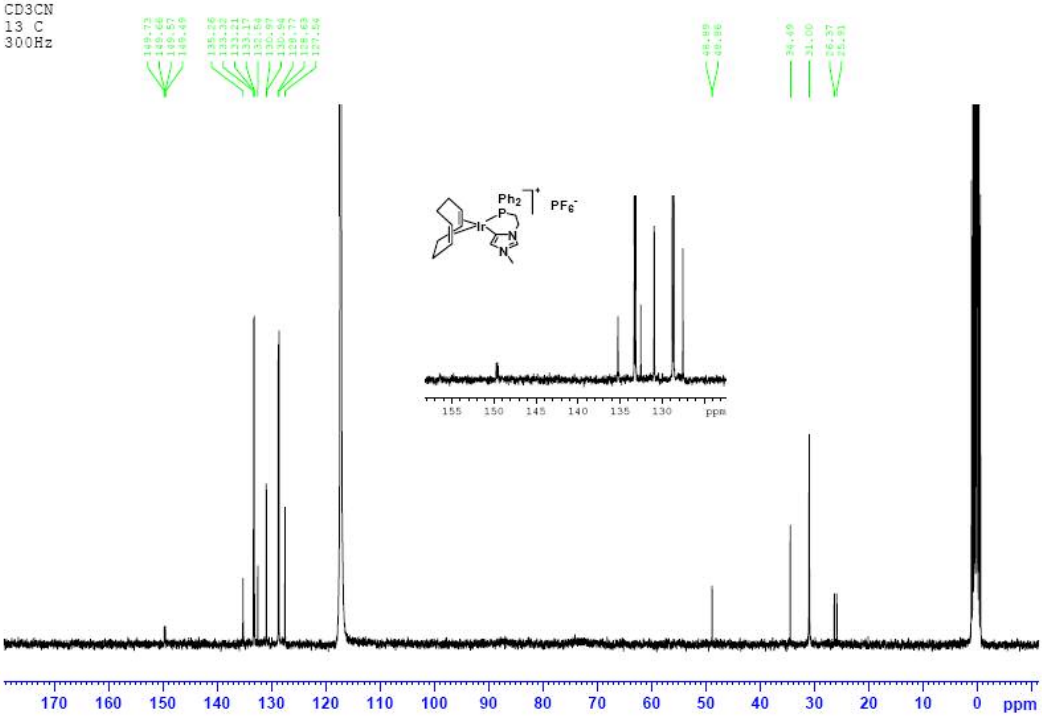

300MHz
1H
CD2C12
5.518
5.320
5.040
4.675
4.397
4.375
4.353
4.047
4.010
3.979
3.563
3.551
3.473
3.446
3.424
3.401
3.046
3.012
2.679
2.660
2.625
2.572
2.531
2.503
2.456
2.412
2.254
1.992
1.966
1.529
1.508
1.495
1.476
1.264
1.152
0.002
-15.274
-15.301
H
Ph2
P
Ir
N
N
Cl
PF6-
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
ppm
0.98
2.05
9.22
0.96
1.00
2.24
1.09
1.05
1.00
2.20
2.17
5.21
1.52
1.31
7.66
0.93

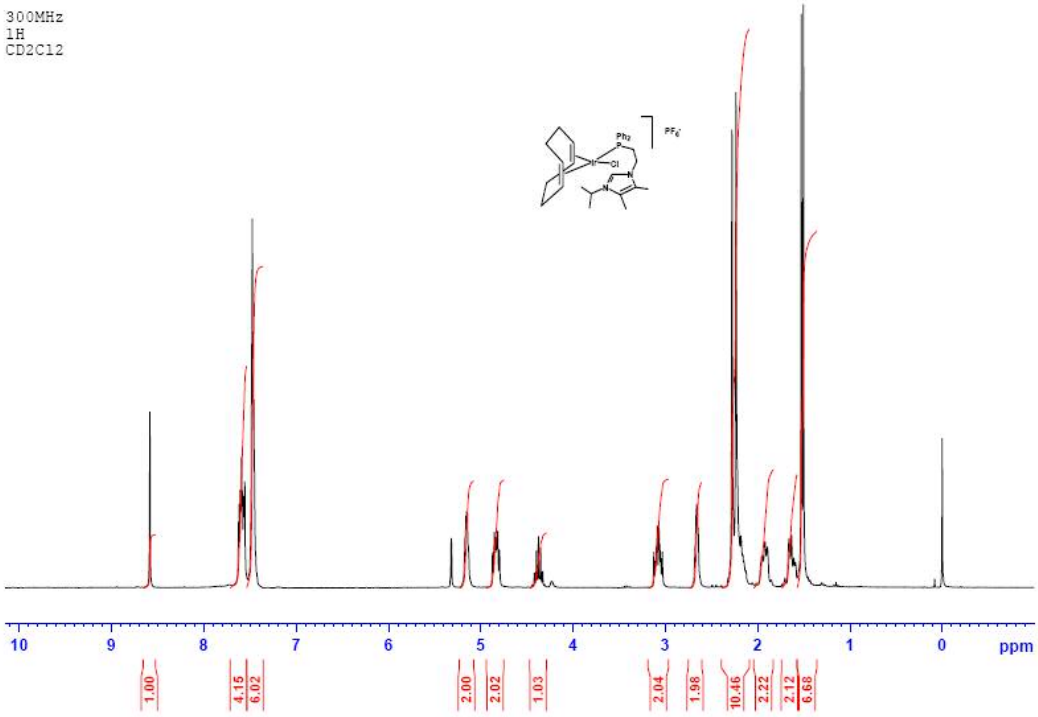

300MHz
1H
CD2C12
14.71
-2.44
-132.06
-137.92
-143.77
-149.62
-155.48
H
Ph2
P
Ir
N
N
Cl
PF6-
150
100
50
0
-50
-100
-150
ppm
0.98
17.48

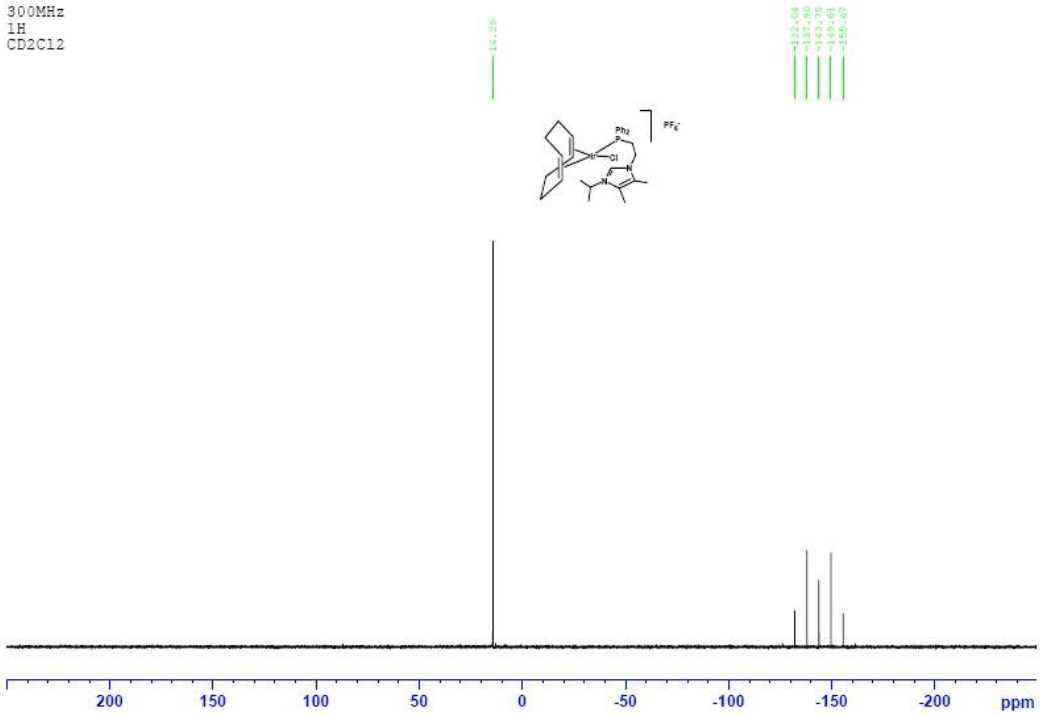

300MHz
13C
CD2C12
H
Ph2
P
Ir
Cl
N
N
PF6-
ppm

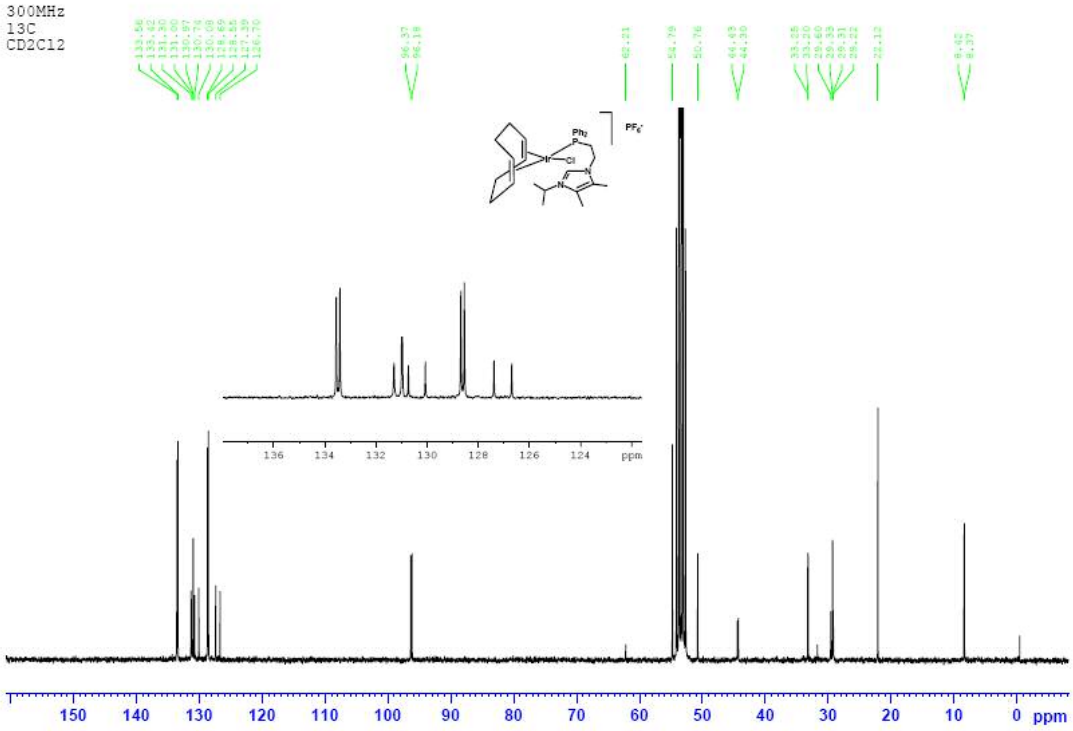

CD3CN
1H
300Hz
8.220
7.619
7.612
7.602
7.596
7.587
7.577
7.567
7.560
7.551
7.528
7.518
7.513
7.510
7.498
7.493
7.486
6.886
6.882
5.471
4.512
4.493
4.474
4.435
4.416
4.397
3.695
2.719
2.707
2.700
2.689
2.681
2.670
2.663
2.650
2.159
2.112
2.072
2.043
1.981
1.973
1.965
1.957
1.948
Ph2
P
Ir
N
N
PF6-
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
10.66
0.98
2.32
3.18
2.10
11.27


CD3CN
31P
300Hz
10.28
-132.33
-138.14
-143.96
-149.77
-155.59
Ph2
P
Ir
N
N
PF6-
150
100
50
0
-50
-100
-150
ppm


CD3CN
13 C
300Hz
Ph2
PF6-
Ir
P
N
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
155 150 145 140 135 130 ppm


300MHz
1H
CD2Cl2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.15
6.02
2.00
2.02
1.03
2.04
1.98
10.46
2.22
2.12
6.68


300MHz
1H
CD2Cl2
14.29
-132.04
-137.90
-143.75
-149.61
-155.47
200
150
100
50
0
-50
-100
-150
-200
ppm


300MHz
13C
CD2C12
133.56
133.42
131.30
131.00
130.97
130.74
130.08
128.69
128.55
127.39
126.70
96.37
96.18
62.21
54.79
50.76
44.43
44.30
33.25
33.20
30.60
29.93
29.31
29.22
22.13
8.42
8.37
Ph2
P
Ir
Cl
N
N
PF6
136
134
132
130
128
126
124
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm