SUPPORTING INFORMATION

Surprising Isomer Preference on Ir^{III}, Favoring Facile H-C(sp^3) Bond Cleavage

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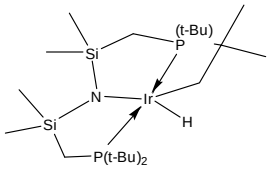
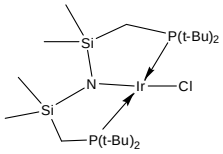
Experimental

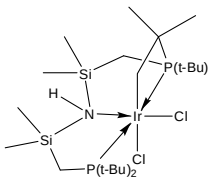
General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. CH_2Cl_2, Pentane and THF were purified using an Innovative Technologies solvent purification system Pure Solv 400-6-MD. Deuterated THF and benzene were also dried under Ph_2CO/Na, vacuum transferred and stored in the glovebox under argon. CD_2Cl_2 was dried with P_2O_5. NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. Coupling constants are given in Hz. ^{31}P NMR spectra are referenced to external standards of H_3PO_4. All NMR spectra were recorded at 25°C with a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P). "PNP" is $N(SiMe_2CH_2P\ ^tBu_2)_2$. Mass spectra were recorded with a MAT-95XP by Thermo Electron Corp. (Waltham, MA).



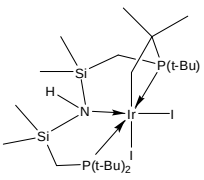
Synthesis of (PNP*)IrH. 200 mg of $[(COE)_2IrCl]_2$ (0.223 mmol) was added with vigorous stirring to a solution of 266 mg of (PNP)MgCl(dioxane) (0.446 mmol) in 20 mL of THF. After 2 h all volatiles were removed from the red solution. The residue was dissolved in 10 mL of pentane. The precipitate ($MgCl_2$) was filtered and the solution was concentrated, then dried in vacuum at room temperature overnight to remove all cyclooctene. Product was collected and used without further purification. Yield: 94%. Samples prepared by this procedure contains less than 5% of $(PNP)IrH_2$. It is also possible to use (PNP)Li(crown)[ref] instead of (PNP)MgCl(dioxane); the main advantages are better accessibility and very low solubility of Li complex in pentane. **^1H NMR (C_6D_{12}):** –21.37 (d.d., 1 H, J = 11.0, 15.6); 0.03, 0.12, 0.21, 0.30 (all s, 3 H each, $SiCH_3$); 1.19 (d, 18 H, J = 12.4, PBu^t_2, accidental degeneracy); 1.31 (d, 9 H, J = 13.7, PBu^t); 1.70-1.80 (m, 1 H, CH_2); other protons in two CH_3 and CH_2 were not located due to overlap with other signals. **$^{31}P\{^1H\}$ NMR (C_6D_{12}):** 15.3 (d, J = 360); 60.1 (d, J = 360). **MS CI** (THF) Exp: 641.2756 $[M]^+$ Calc. 641.2737 ($C_{22}H_{52}N_1Ir_1P_2Si_2$).



Synthesis of (PNP)IrCl. 100 mg of (PNP*)IrH (0.156 mmol) was dissolved in 20 mL of pentane. 75 mg of C_2Cl_6 (0.320 mmol) was added to the solution at 22°C. The mixture was stirred for one hour and the color changed from red to green-yellow. The reaction mixture was then filtered, concentrated to 10 mL and the product crystallized after 12 h at −40°C. Green crystals were collected and washed with minimum amount of cold pentane to give 83 mg (79%) after drying in vacuum. **^{1}H NMR** (C_6D_{12}, 25°C): 1.3 (br.s, 12 H, SiMe), 2.9 (br.s, 36 H, Bu^t), 4.5 (br.s, 4 H, CH_2). **MS CI** (THF) Exp: 676.2419 $[M]^+$ Calc. 676.2431 $C_{22}H_{52}ClIrNP_2Si_2$. This reaction also succeeds, but less cleanly, with N-chlorosuccinimide or $PhICl_2$, with reductive elimination of H with CH_2, to give (PNP)IrCl. All spectra (^{1}H, absence of ^{31}P and EPR, see below) indicate that (PNP)IrCl is a planar d^7 Ir^{II} monomer.

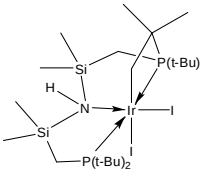


Synthesis of (PN(H)P*)Ir(Cl)$_2$. 21 mg of (PNP)IrCl (0.0314 mmol) was dissolved in 0.5 mL of CH_2Cl_2 and 4.2 mg of N-chlorosuccinimide (0.0314 mmol) were added. NMR observation showed full conversion into the product in 12h. The product was isolated by vacuum removal of solvent, the residue was extracted into pentane to remove succinimide, filtered and the pentane soluble were dried in vacuum. Yield: 19 mg(88%) **^{1}H NMR** (CD_2Cl_2): 0.44 (s, 3 H, $SiCH_3$), 0.50 (s, 9 H, $SiCH_3$, accidental degeneracy), 1.12 (d, 3 H, J = 13.9, CH_3C), 1.27, 1.38 and 1.47 (three d, 9 H each, J = 12.2, 13.7, and 12.4, three Bu^t), 1.70 (d, 3 H, J = 14.3, CH_3C), 2.97 (d, 1 H, J = 8.7, H in Ir-CH_2), 3.52 (m, 1 H, H in Ir-CH_2), 4.47 (br.s, 1 H, NH); two Si-CH_2 groups were not resolved due to overlapping with other signals. **^{31}P{^{1}H} NMR** (CD_2Cl_2): −47.0 (d, J = 410), 8.6 (d, J = 410).

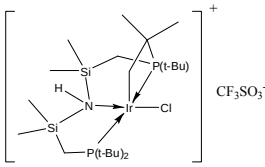


Synthesis of (PN(H)P*)Ir(I)$_2$. 20 mg of (PNP*)IrH (0.0312 mmol) was dissolved in 0.5 mL of benzene and 7.9 mg of I_2 (0.0312 mmol) were added. A precipitate forms and was isolated by filtration after 15 min, washed with pentane and dried to yield 23 mg (83%) of product. **^{1}H NMR** (CD_2Cl_2, 25°C): 0.48 (s, 3 H, $SiCH_3$), 0.55 (s, 6 H, $SiCH_3$, accidental degeneracy), 0.60 (s, 3 H, $SiCH_3$), 1.13 (d, 3

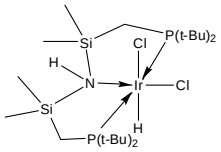
H, *J* = 13.8, CH_3C), 1.35 (br, 9 H, Bu^t), 1.50 and 1.62 (both d, 9 H each, *J* = 13.6 and 12.4, two Bu^t), 1.85 (d, 3 H, *J* = 14.1, CH_3C), 3.16 (d, 1 H, *J* = 7.5, H in Ir-CH_2), 3.93 (m, 1 H, H in Ir-CH_2), 4.40 (br.s, 1 H, NH); two Si-CH_2 groups were not resolved due to overlapping with other signals. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 25°C): −5.3 (d, *J* = 398), −60.2 (d, J = 398). **MS CI** (THF) Exp: 768.1793 $[M-I]^+$ Calc: 768.1787 $C_{22}H_{52}IIrNP_2Si_2$. The reaction proceeds equally well in THF, but the product remains soluble and is isolated pure by vacuum removal of all volatiles.



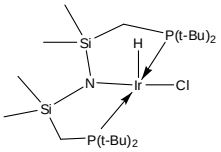
Synthesis of (PN(H)P*)Ir(I)$_2$. 20 mg of (PNP*)IrH (0.0312 mmol) was dissolved in 0.5 mL of THF and 7.9 mg of I_2 (0.0312 mmol) were added. All volatiles were removed in vacuum after 15 min, residue was washed with pentane and dried to yield 23 mg (83%) of product. **^1H NMR** (CD_2Cl_2): 0.48 (s, 3 H, $SiCH_3$), 0.55 (s, 6 H, $SiCH_3$, accidental degeneracy), 0.60 (s, 3 H, $SiCH_3$), 1.13 (d, 3 H, *J* = 13.8, CH_3C), 1.35 (br, 9 H, Bu^t), 1.50 and 1.62 (both d, 9 H each, *J* = 13.6 and 12.4, two Bu^t), 1.85 (d, 3 H, *J* = 14.1, CH_3C), 3.16 (d, 1 H, *J* = 7.5, H in Ir-CH_2), 3.93 (m, 1 H, H in Ir-CH_2), 4.40 (br.s, 1 H, NH); two Si-CH_2 groups were not resolved due to overlapping with other signals. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): −5.3 (d, *J* = 398), −60.2 (d, *J* = 398). **MS CI** (THF) Exp. 768.1793 $[M-I]^+$ Calc. 768.1787 $C_{22}H_{52}IIrNP_2Si_2$.



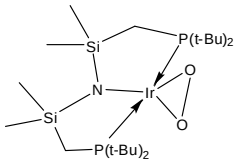
(PN(H)P*)IrCl(OTf). 20 mg of (PNP)IrCl (0.029 mmol) and 9.7 mg of $[Cp_2Fe]OTf$ (0.029 mmol) was dissolved in 0.5 mL of CH_2Cl_2. The green reaction mixture turned to orange in 12h at +40°C. Red crystals formed in 12 h from CH_2Cl_2 layered with pentane. Yield: 21 mg (86%). **^1H NMR** (CD_2Cl_2, 25°C): 0.41, 0.58, 0.68, 0.72 (all s, 3 H each, $SiCH_3$), 1.26 (d, 3 H, *J* = 14.4, CH_3C), 1.29 (d, 9 H, *J* = 13.6, Bu^t), 1.38 and 1.39 (both d, 9 H each, *J* = 13.5 and 14.5, two Bu^t), 1.69 (d, 3 H, *J* = 14.1, CH_3C), 3.54 (br.s, 1 H, NH), 3.88 (d, 1 H, *J* = 6.2, H in Ir-CH_2), 4.25 (d.d.d, 1 H, *J* = 3.7, 6.2, 17.1, H in Ir-CH_2); two Si-CH_2 groups were not resolved due to overlapping with other signals. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 25°C): -19.8 (d, *J* = 362), 24.4 (d, *J* = 362). **$^{19}F\{^1H\}$ NMR** (CD_2Cl_2, 25°C): -79.0 (s).



Synthesis of (PN(H)P)IrH(Cl)$_2$. 16.5 mg (0.025 mmol) of (PNP*)IrH were dissolved in 0.5 mL of Et_2O and 0.026 mL (0.0527 mmol) of a 2M solution of HCl in Et_2O were vacuum transferred at liquid nitrogen temperature. The reaction mixture was then allowed to melt in a Dewar filled with acetone at −40°C. Color of the solution changed from red to yellow after the tube was vigorously shaken. ^{31}P NMR showed complete conversion into the product. Red crystals (15 mg, 87%) formed in 12 h from CD_2Cl_2/pentane. **^{1}H NMR** (CD_2Cl_2, 25°C): −25.22 (t, 1 H, J = 12.9), 0.35, 0.43 (both s, 6 H each, SiMe), 1.10, 1.25 (both m, 2 H each, CH_2), 1.40, 1.48 (both t, 18 H each, J = 6.6, Bu^t), 3.32 (br.s, 1 H, NH). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 25°C): 17.6.



Synthesis of (PNP)Ir(H)(Cl). 10 mg (0.014 mmol) of (PN(H)P)Ir(H)(Cl)$_2$ were dissolved in 2 mL of THF and were reacted with 1.6 mg LiN^iPr_2 (0.014 mmol). The color of the solution changed immediately from yellow to purple. After 1h all volatiles were removed in vacuum, the residue was extracted with pentane, filtered and dried in vacuum. Yield: 8mg (84%). **^{1}H NMR** (C_6D_6, 25°C): −47.0 (t, 1 H, J = 11.7, Ir-H), 0.25, 0.32 (both s, 6 H each, SiMe), 0.77, 0.89 (m, 2 H each, all CH_2), 1.27, 1.40 (both t, 18 H each, J = 6.6, Bu^t). **^{31}P{^{1}H} NMR** (C_6D_6, 25°C): 42.4.



Synthesis of (PNP)Ir(O_2). 18.6 mg of (PNP*)IrH (0.0312 mmol) was dissolved in 0.5 mL of pentane and was degassed through 3 freeze-pump-thaw cycles using liquid N_2. 1 atm. of O_2 (~4 equiv.) was added to the evacuated head space of the frozen solution. The reaction vessel was allowed to warm and the red reaction mixture turned to green-yellow in time of mixing. Pentane was removed in vacuum to give 19 mg (97%) of green powder. NMR observation showed full conversion into the product. **^{1}H NMR** (C_6D_6, 25°C): 0.24 (s, 12 H, $SiCH_3$), 0.66 (t, 4 H, *J* = 4.4, CH_2), 1.32 (t, 36 H, *J* = 6.5, ^{t}Bu). **^{31}P{^{1}H} NMR** (C_6D_6, 25°C): 27.9 (s). **MS CI** (THF) Exp: 673.2632 $[M]^+$ Calc. 673.2641 ($C_{22}H_{52}IrNO_2P_2Si_2$).

Structure determination of (PN(H)P*)IrI$_2$. An orange crystal (approximate dimensions 0.15 × 0.15 × 0.12 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K.

Data collection

The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 5.0 cm. A collection strategy was calculated and complete data to a resolution of 0.71 Å with a redundancy of 6 were collected (five major sections of frames with 0.50º ω and ϕ scans). Data to a resolution of 0.71 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9963 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group P2$_1$/c was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004[3] and refined with SHELXL-97.[4] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0363 and wR2 = 0.0805 (F^2, all data). The remaining electron density is rather large and located near the iodine atoms. The structure was found as proposed with two independent molecules per asymmetric unit.

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1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

2 An empirical correction for absorption anisotropy.
R. Blessing, *Acta Cryst*. A51, 33 - 38 (1995).

3 Sir2004, A Program for Automatic Solution and Refinement of Crystal Structures.
M. C. Burla, R. Caliandro, M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Sagna. Vers. 1.0 (2004).

4 SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.

Structure determination of [(PN(H)P*)IrCl]OTf. A red crystal (approximate dimensions 0.15 × 0.13 × 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K.

Data collection

The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 5.0 cm. A collection strategy was calculated and complete data to a resolution of 0.77 Å with a redundancy of 4 were collected. Three major sections of frames were collected with 0.50º ω and ϕ scans. Data to a resolution of 0.82 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9506 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004[3] and refined with SHELXL-97.[4] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters with the exception of H1n, which is involved in hydrogen bonding and was refined for all parameters. The final full matrix least squares refinement converged to R1 = 0.0316 and wR2 = 0.0815 (F^2, all data). The remaining electron density is located near Ir.

1 SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
2 An empirical correction for absorption anisotropy.
R. Blessing, *Acta Cryst*. A51, 33 - 38 (1995).
3 Sir2004, A Program for Automatic Solution and Refinement of Crystal Structures.
M. C. Burla, R. Caliandro, M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Sagna. Vers. 1.0 (2004).
4 A short history of *SHELX*.
G. M. Sheldrick, *Acta Cryst*. A64, 112 - 122 (2008).

Computational Details

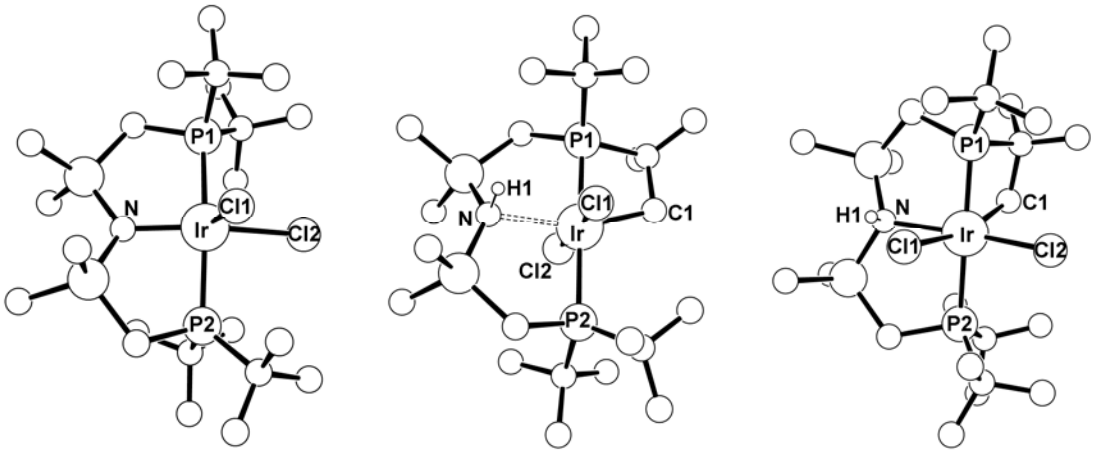
All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the PBE[2] functional and the 6-31G** basis set with no symmetry restrictions. Transition metals were represented using the Los Alamos LACVP basis[3, 4]. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set[5] cc-pVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

The models used in this study consist of ~80 atoms, which represent the non-truncated substrates that were also used in the experimental work. Although a smaller model may also able to reproduce the most important features of the studied reaction qualitatively, we chose to employ the large scale model faithfully construct a realistic model chemistry.

References

1. Jaguar, version 6.0, *Schrödinger, L.L.C, New York, NY, 2005*.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865; Phys. Rev. Lett (Erratum) 1997, 78, 1386.
3. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 270.
4. Wadt, W. R.; Hay, P. J., *J. Chem. Phys.* **1985,** *82*, 284.
5. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007.

S1. Optimized structure of isomers of (PNP)$IrCl_2$ (**F, G1** and **G2**).



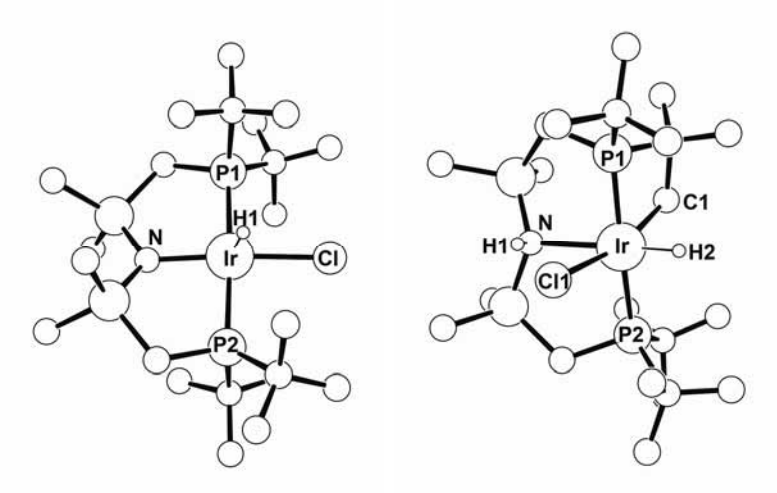
F (+17.76*) **G1** (+14.55) **G2** (0.00)

* Numbers in parenthesis are relative electronic energies in kcal/mol.

Select bond length (in Å) and bond angle (in °).

F		**G1**		**G2**	
Ir-P1	2.425	Ir-P1	2.297	Ir-P1	2.323
Ir-P2	2.407	Ir-P2	2.458	Ir-P2	2.422
Ir-N	2.014	Ir-N	2.367	Ir-N	2.237
Ir-Cl1	2.372	Ir-Cl1	2.436	Ir-Cl1	2.573
Ir-Cl2	2.484	Ir-Cl2	2.430	Ir-Cl2	2.411
P1-Ir-P2	165.0	Ir-C1	2.116	Ir-C1	2.135
N-Ir-Cl2	166.4	N-H1	1.034	N-H1	1.055
N-Ir-Cl1	109.5	P1-Ir-P2	178.1	P1-Ir-P2	171.8
Cl1-Ir-Cl2	83.8	N-Ir-C1	158.6	N-Ir-C12	171.4
		Cl1-Ir-Cl2	175.5	C1-Ir-Cl1	163.5

S1. Optimized structure of isomers of (PNP)IrHCl (**H** and **I**).



H (0.00*) **I** (+2.14)

* Numbers in parenthesis are relative electronic energies in kcal/mol.

Select bond length (in Å) and bond angle (in ˚):

H		**I**	
Ir-P1	2.372	Ir-P1	2.301
Ir-P2	2.364	Ir-P2	2.365
Ir-N	2.073	Ir-N	2.400
Ir-Cl1	2.476	Ir-Cl1	2.595
Ir-H1	1.545	Ir-C1	2.127
P1-Ir-P2	174.9	Ir-H2	1.579
N-Ir-H1	107.9	N-H1	1.047
N-Ir-Cl	79.1	P1-Ir-P2	170.6
H1-Ir-Cl	172.9	C1-Ir-Cl1	163.6
		N-Ir-H2	171.6

S5. Optimized structures.

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F
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Ir	15.355572485	2.407055236	18.589144414
P	16.454177725	0.385855909	19.224254000
P	13.949163108	4.141170552	17.939164750
Si	15.631019323	1.755145155	21.979647669
Si	12.893153182	3.163514093	20.746227904
N	14.688772081	2.802667618	20.806774603
C	17.127554510	2.779637877	22.483412693
H	16.821334138	3.637023501	23.106872621
H	17.670842947	3.169269805	21.607957689
H	17.827805682	2.174001199	23.083301395
C	14.628068977	1.271615507	23.508011402
H	14.215327927	2.156813811	24.020184120
H	15.290180539	0.761615169	24.229387531
H	13.797123334	0.582219725	23.289180071
C	16.110220312	0.156628704	21.049820947
H	16.962938810	-0.332307465	21.552506375
H	15.265453009	-0.545611258	21.154508667
C	15.223934418	-0.819837498	18.393199937
C	18.282160216	-0.058595683	18.953937111
C	12.490107572	4.423422032	22.096891373
H	13.172808926	5.287120674	22.119680363
H	12.542264326	3.934751979	23.084623458
H	11.463521274	4.810498535	21.979161768
C	11.828250883	1.634625661	21.061776193
H	11.835743660	0.889993398	20.251896326
H	10.784510447	1.982654542	21.161471544
H	12.085187047	1.128463249	22.005219722
C	12.433530421	3.831245645	18.975401989
H	11.845264848	3.038090656	18.480809771
H	11.775396485	4.715076880	19.041945715
C	14.246708059	6.029116249	18.037799323
C	13.005331570	6.769579141	17.496872584
H	13.194597231	7.856396189	17.550272375
H	12.093613840	6.572612876	18.083601325
H	12.800973823	6.523058344	16.443024150
C	14.038758939	3.374978715	16.162801780
C	14.965299742	-2.171768077	19.080940947
C	15.591933424	-1.078355090	16.920072679
C	13.953239463	0.058281312	18.487527801
C	18.540998391	-1.558584673	19.192215430
C	19.106612596	0.783538773	19.953180834
C	18.680864633	0.353285446	17.521221334
C	14.162433208	4.314453834	14.952264257
C	12.825237248	2.458372347	15.924753073
C	15.369497208	2.600864501	16.470064392
C	14.460247050	6.375551751	19.526106109
C	15.494589931	6.467400369	17.241150910
H	20.177844792	0.592285205	19.766850248
H	18.908339512	0.514937666	21.003251294
H	18.928774290	1.861884301	19.819857701
H	19.626210316	-1.751645879	19.122662688
H	18.048212545	-2.194047898	18.439204486
H	18.215601136	-1.888836193	20.193189698
H	19.768084095	0.205832356	17.399038301
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H	18.180057359	-0.251731254	16.751152785
H	14.181649113	-2.720611779	18.528141920
H	14.617626774	-2.077361139	20.121803774
H	15.867895588	-2.801663423	19.079687126
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H	16.431163809	-1.786064856	16.836424120
H	15.862714567	-0.159007478	16.381912649
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H	14.087328042	1.093995486	17.977323252
H	13.597388764	0.178522247	19.517996096
H	14.609402689	7.465767108	19.620709622
H	15.362210222	5.883963869	19.927074158
H	13.587260869	6.118085261	20.145972543
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H	15.320212176	6.455414358	16.156773452
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H	15.070751246	4.930130555	14.987241061
H	13.285582866	4.973224811	14.837293480
H	16.245193318	3.201387548	16.171756445
H	13.018399799	1.827107407	15.039511555
H	11.916645304	3.048465316	15.719430977
H	12.598854432	1.781676033	16.763427817
H	15.400605999	1.643752813	15.922020878
Cl	17.205974229	3.817290002	18.846447128
H	15.158932276	3.721242338	20.864992296

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Ir	15.196006387	2.378568316	18.509968144
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Si	15.338904638	1.674248912	21.905495792
Si	12.829443250	3.425939434	20.629121891
N	14.541552305	2.812528948	20.743007802
C	16.319982671	2.754397870	23.117481673
H	15.656926293	3.405566941	23.711661516
H	17.032317787	3.395276883	22.569981382
H	16.901755430	2.134863220	23.821711941
C	14.069310974	0.673167250	22.889918645
H	13.521969506	1.335440097	23.582342493
H	14.586323375	-0.086491808	23.501385631
H	13.334154857	0.153981303	22.258898952
C	16.638914119	0.595765924	20.993134852
H	17.572370925	1.172238138	21.101926131
H	16.794232766	-0.361937356	21.523562770
C	15.554310215	-1.399710827	19.091515617
C	18.227179094	0.178852436	18.389271895
C	12.580119006	4.709094325	22.014671339
H	13.398285375	5.439705182	22.108027742

H	12.499050615	4.181909817	22.981235725
H	11.640829028	5.271222722	21.871444251
C	11.531446138	2.090064965	20.930866901
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H	11.527270087	1.757039645	21.980838951
C	12.530014600	4.233229666	18.876073067
H	11.883218842	3.517482633	18.341437598
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C	14.690188131	6.146530033	18.169887832
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C	14.295608999	-1.317375263	19.984338392
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C	18.191452857	0.911090933	17.032404703
C	14.843380313	4.706458353	15.039280412
C	12.883101396	3.264173583	15.527363574
C	15.271117741	2.579375107	16.404507913
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C	16.050466689	6.473223832	17.514533547
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H	19.404395860	0.299580036	20.251104697
H	19.000967187	1.899829218	19.536939600
H	19.727432883	-1.177373782	17.657461527
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H	19.181650980	0.820672799	16.548036023
H	17.961787317	1.977490777	17.162406192
H	17.440827364	0.477003608	16.350932652
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H	14.627454066	-2.655518067	17.576515017
H	16.032069642	-1.751361846	16.965111491
H	14.479749118	-0.905510678	17.243461042
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H	16.806532165	5.703552369	17.727487752
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H	12.218221322	4.128033593	15.348300430
H	12.384013077	2.553223785	16.198308445
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Cl	17.190753784	3.620742606	19.152137878
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G2

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Ir	15.494673101	2.600220362	18.708528371
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Si	15.002368555	1.205010412	21.845516279
Si	12.804205119	3.242634709	20.736375269
N	14.472432545	2.532869310	20.697616541
C	15.661550577	2.051786721	23.404652432
H	14.874795846	2.604305756	23.944672265
H	16.461342014	2.761570647	23.135257485
H	16.083447128	1.305796563	24.100181928
C	13.557848762	0.090408937	22.362391262
H	12.879741620	0.632718800	23.043065009
H	13.957150132	-0.770608933	22.926648676
H	12.962974826	-0.304175155	21.526834947
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H	17.338619227	0.810540401	21.402876443
H	16.513068875	-0.761850710	21.344648359
C	15.675160684	-1.115347798	18.504656276
C	18.477619454	0.258666545	18.878342998
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H	12.350261750	3.073666132	23.218765954
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C	11.469242311	1.991491052	20.266765058
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H	10.523624743	2.521789885	20.059440540
H	11.278114086	1.297632992	21.100786427
C	12.945546358	4.738317274	19.575999342
H	11.972825424	5.064656663	19.171635203
H	13.327250269	5.563753672	20.202306725
C	14.781695155	6.234762666	17.787546936
C	13.587774731	7.078000276	17.297759634
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H	13.153758179	6.682147547	16.364966600
C	13.312182693	3.462720448	16.872412776
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C	19.103887406	-0.787469740	19.828400185
C	19.163256869	1.609269334	19.165116785
C	18.779871615	-0.135906813	17.417457650
C	13.798545459	3.790851768	15.449389233
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C	13.910419471	2.095577920	17.369508144
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C	15.893142089	6.193159048	16.720059412
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H	19.872055210	-0.069091542	17.259695953
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H	15.119205775	3.308897596	21.000537640

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H

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Si	15.409987556	1.700121985	21.928517624
Si	13.110978657	3.228641348	20.634273114
N	14.706915407	2.492231166	20.522816414
C	16.341667730	2.951864668	23.018731653
H	15.665700805	3.727455818	23.415438931
H	17.127102864	3.464595950	22.436996312
H	16.824855318	2.457401457	23.879776324
C	14.175222943	0.785317662	23.060473528
H	13.438098160	1.466744629	23.516598558
H	14.721227954	0.298725055	23.888157948
H	13.615845168	0.003986173	22.520550374
C	16.699314642	0.446869449	21.293437984
H	17.689461796	0.832157350	21.588008269
H	16.596756400	-0.543576706	21.768513962
C	15.858526299	-1.365357138	19.068377535
C	18.580221531	0.283492319	19.028820750
C	12.883453508	4.283404246	22.206841924
H	13.647129472	5.075835381	22.277031491
H	12.939497978	3.685103439	23.131172578
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C	11.709049127	1.944829970	20.562264649
H	11.796055417	1.346971054	19.638640787
H	10.717712002	2.431605465	20.561094704
H	11.739795399	1.247870627	21.415456633
C	12.871829094	4.353623716	19.105732999
H	11.969627560	3.997885002	18.580227723
H	12.699038765	5.413835625	19.357541033
C	15.418728196	5.672305323	18.293452278
C	14.792305517	7.000378436	17.827999253
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H	14.713355465	7.069989074	16.732324516
C	13.510626053	4.240534626	16.199481052
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C	14.477432713	-1.319034457	19.759213023
C	19.410391932	-0.517604619	20.056183081
C	19.032709487	1.761232203	19.067774651
C	18.856478425	-0.290106024	17.624277417
C	12.355029538	5.263096415	16.140340145
C	12.947655113	2.830682283	15.911505686
C	14.548583655	4.591753376	15.113946948
C	15.641505554	5.749881522	19.820464426
C	16.790895456	5.465407235	17.617705636
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H	18.541043222	2.343485010	18.272459155
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H	14.721596650	6.023078946	20.363006833
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H	14.468788065	1.249749437	17.867349541

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Si	12.754399682	3.226685343	20.770045208
N	14.401625788	2.529948717	20.862747964
C	15.754258937	1.982723706	23.478970224
H	14.982926654	2.505621832	24.069426355
H	16.531734196	2.714220625	23.202191749
H	16.215205003	1.218859002	24.128953100
C	13.618196652	0.046942765	22.466653958
H	12.981586668	0.570443028	23.201011294
H	14.035440126	-0.839281690	22.975751140
H	12.973091594	-0.308483667	21.650494707
C	16.466019562	0.327181659	21.008751077
H	17.355156849	0.889541511	21.350597153
H	16.597214781	-0.717327936	21.345028462
C	15.628760685	-1.122423066	18.547316366
C	18.399293624	0.332513043	18.717295012
C	12.235673267	3.950230910	22.448918034
H	12.978944638	4.676682947	22.819087536
H	12.132014298	3.160256899	23.212393610
H	11.265082764	4.471263632	22.378675015
C	11.461125257	1.948069436	20.255144361
H	11.750621031	1.379783965	19.358251113
H	10.505707380	2.456875733	20.038412403
H	11.271114520	1.230342732	21.069548339
C	12.898096160	4.688609174	19.544481851
H	11.924305094	4.957134476	19.099469526
H	13.214044022	5.553203216	20.154385087
C	14.832080850	6.200068218	17.831266792
C	13.719416257	7.038503378	17.174626607
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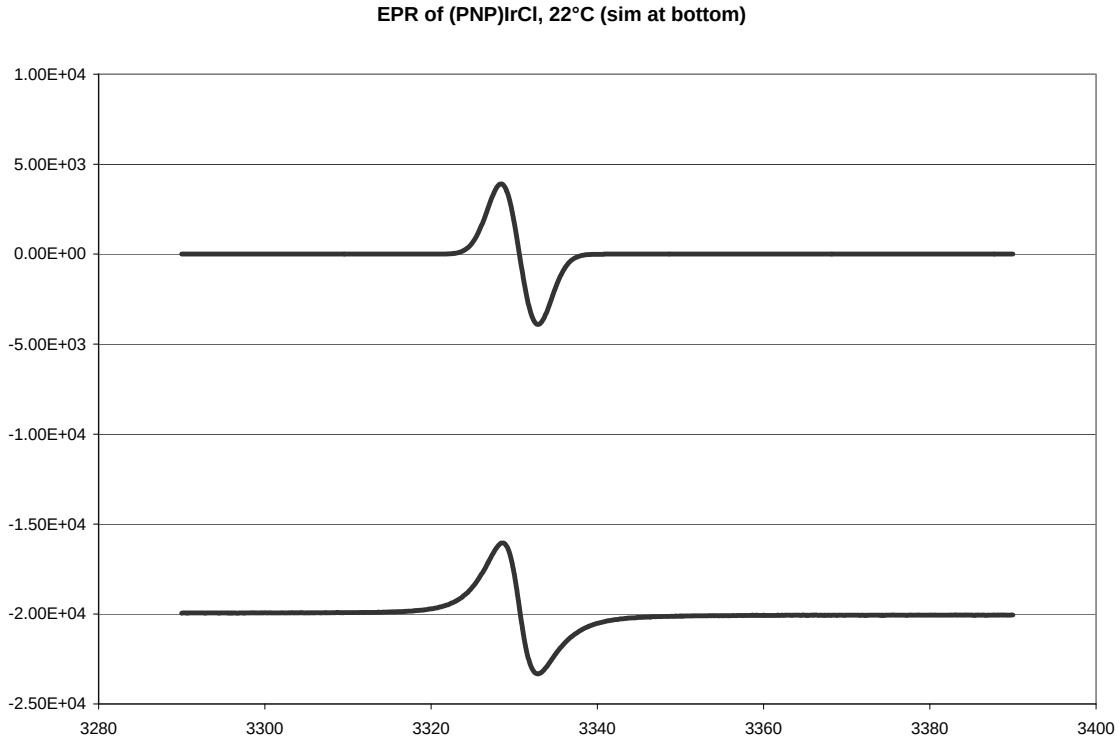
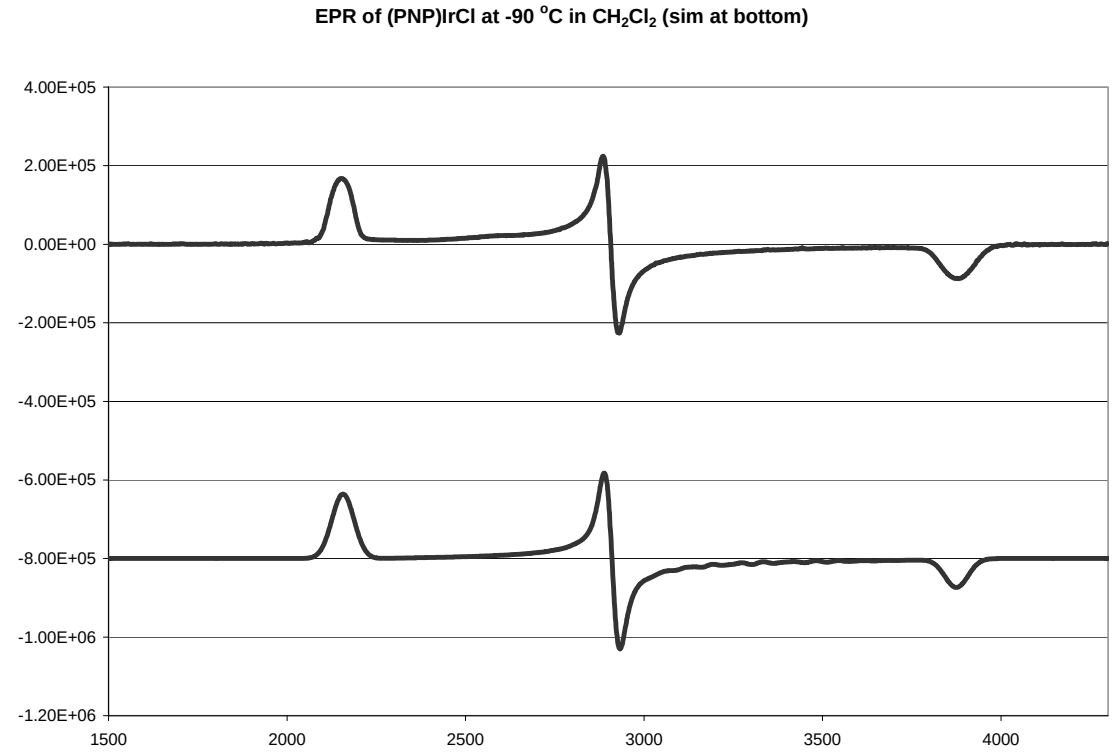
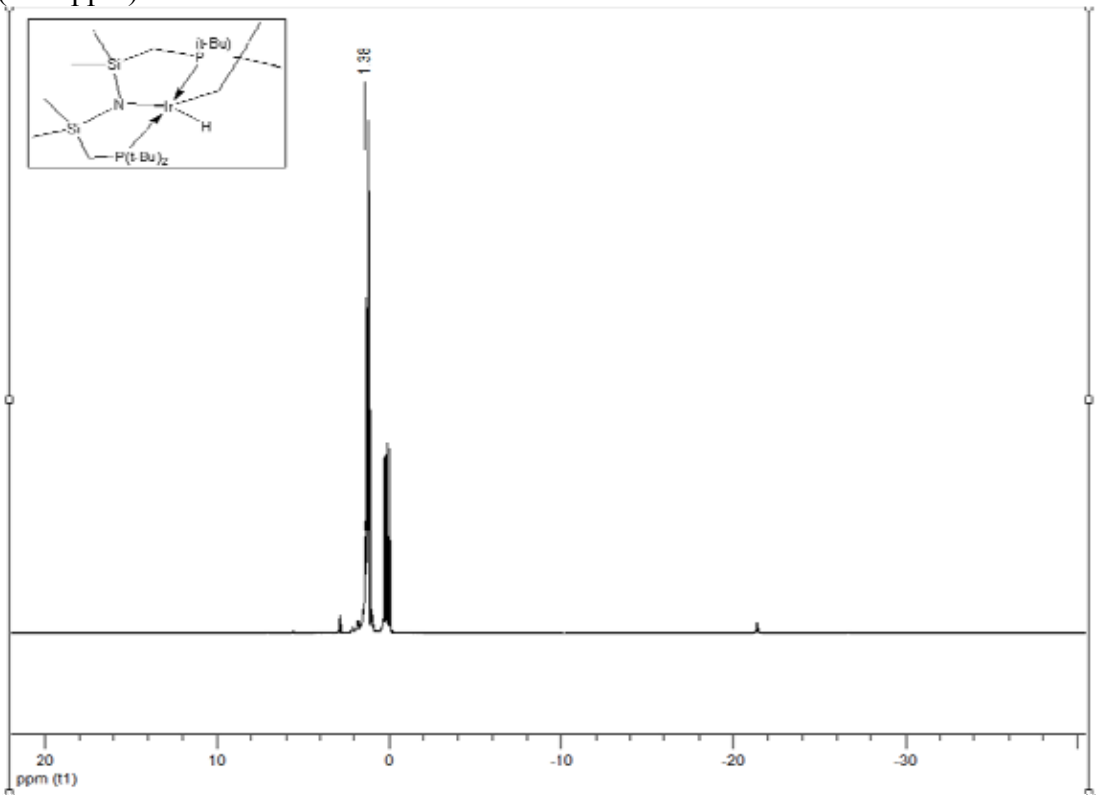
H	12.828816517	7.115434400	17.821761052
H	13.402538861	6.626432881	16.202858871
C	13.416214249	3.459569978	16.821433449
C	16.360452108	-2.424661056	18.931793789
C	15.403767039	-1.120266741	17.020719851
C	14.249268876	-1.137981680	19.236361442
C	19.144553395	-0.683474663	19.609217324
C	19.055040872	1.711218586	18.924886595
C	18.576062223	-0.046625160	17.232758919
C	14.062779776	3.756552992	15.457703237
C	11.889765329	3.546651122	16.694490604
C	13.955436357	2.088520063	17.363195432
C	15.283542476	6.862358920	19.153057228
C	16.068860813	6.088586226	16.915800111
H	20.128139874	1.628641484	18.669281705
H	18.973659022	2.070718993	19.961260426
H	18.594682844	2.480918354	18.287932954
H	20.213304571	-0.680170103	19.326584015
H	18.781064360	-1.714691051	19.502000886
H	19.093990908	-0.410560247	20.675402866
H	19.640576791	0.072842290	16.959827734
H	17.989537268	0.614010895	16.572391303
H	18.303954872	-1.092765155	17.021650435
H	15.694957899	-3.281824357	18.716884293
H	16.614796824	-2.474139424	20.003580550
H	17.281394992	-2.578014078	18.348554313
H	14.840184855	-2.031449948	16.746184324
H	16.340339543	-1.128926177	16.446949308
H	14.814157486	-0.252725857	16.698648961
H	13.621365466	-1.926637790	18.782387264
H	13.723855498	-0.176349047	19.123267046
H	14.338366817	-1.368023987	20.308639676
H	15.792131092	7.813516488	18.912609604
H	15.991550632	6.220800781	19.704132142
H	14.435558675	7.112429740	19.812361938
H	16.505203942	7.094477142	16.777724938
H	15.824477982	5.693262967	15.919317689
H	16.832192547	5.438452148	17.373124425
H	13.679577309	3.025208147	14.722457912
H	15.157133498	3.641417609	15.501332586
H	13.822513729	4.763062157	15.075603826
H	14.318254083	1.491497443	16.510045109
H	11.543569224	2.827334310	15.929582146
H	11.557879506	4.551808498	16.377785337
H	11.374415897	3.293866265	17.634629864
H	13.139049066	1.518745262	17.843976689
H	16.370476121	2.798273072	17.427114026
Cl	17.052516189	3.885594059	20.366772958
H	15.063586252	3.312840554	21.075589734

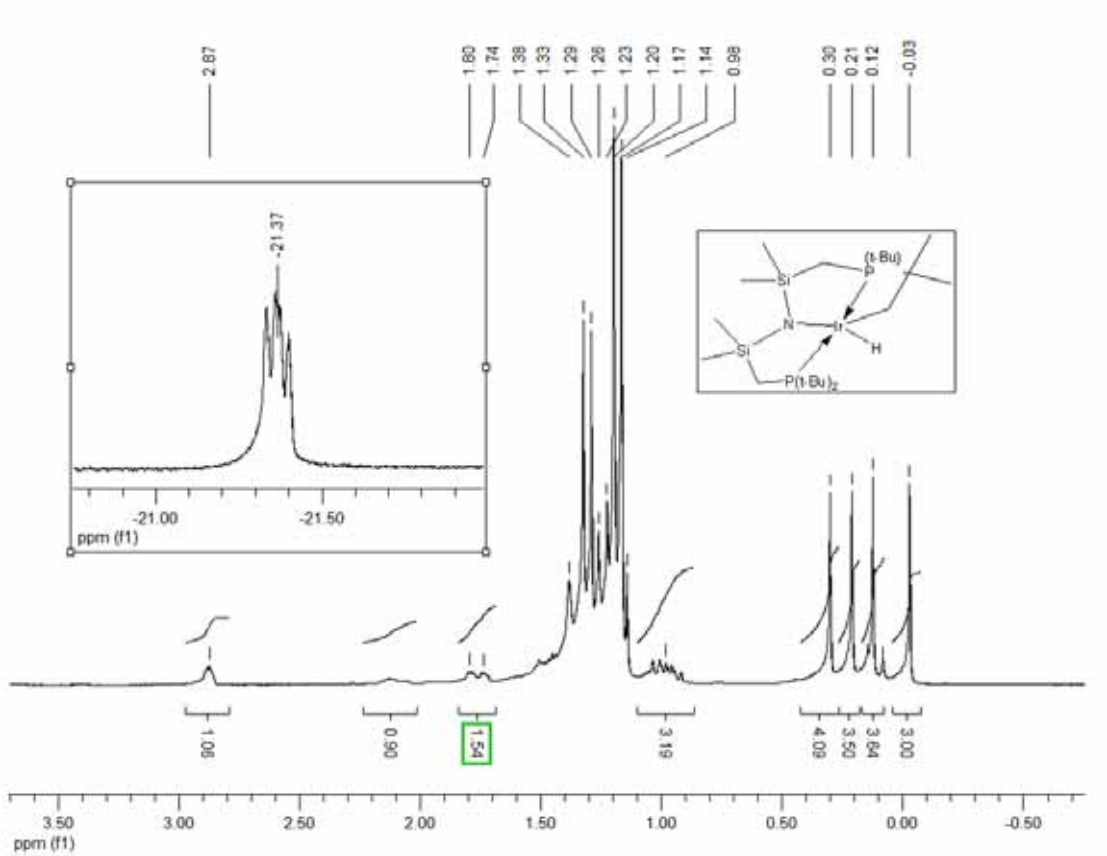


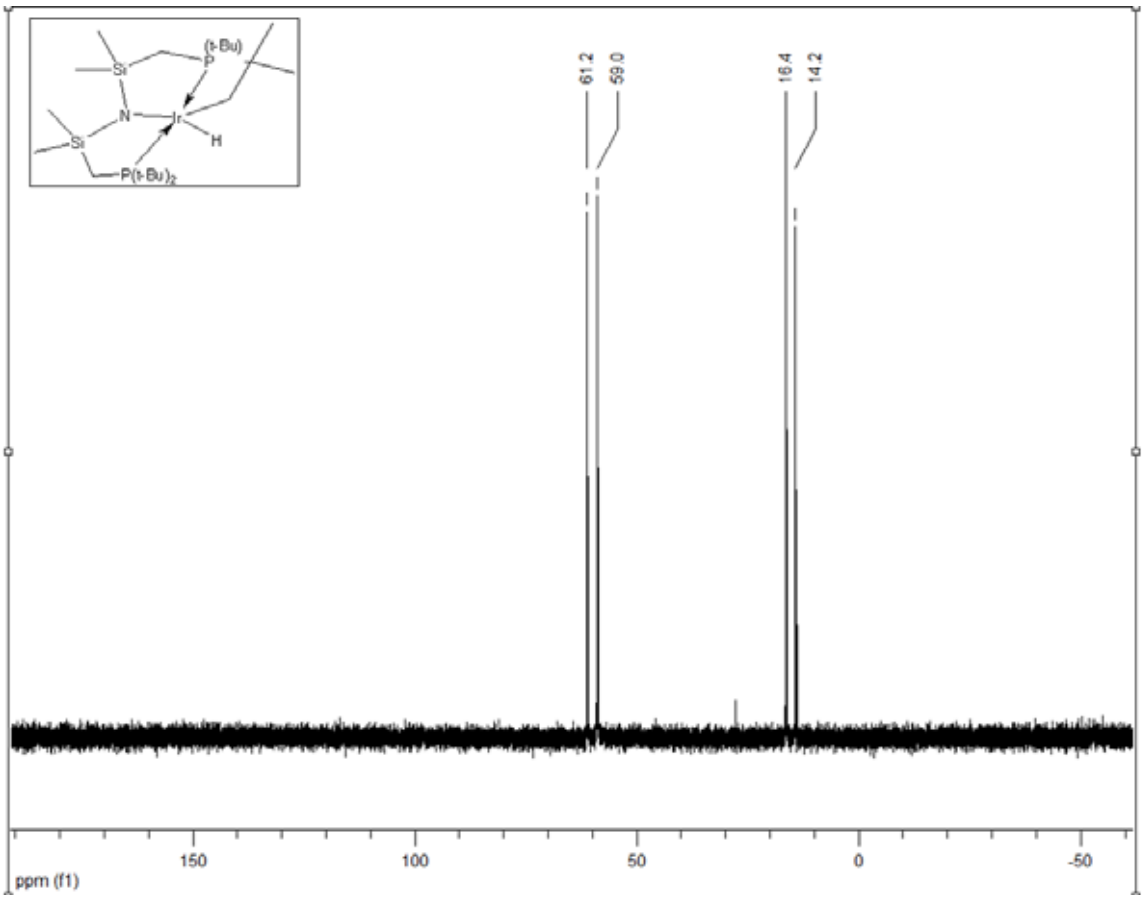


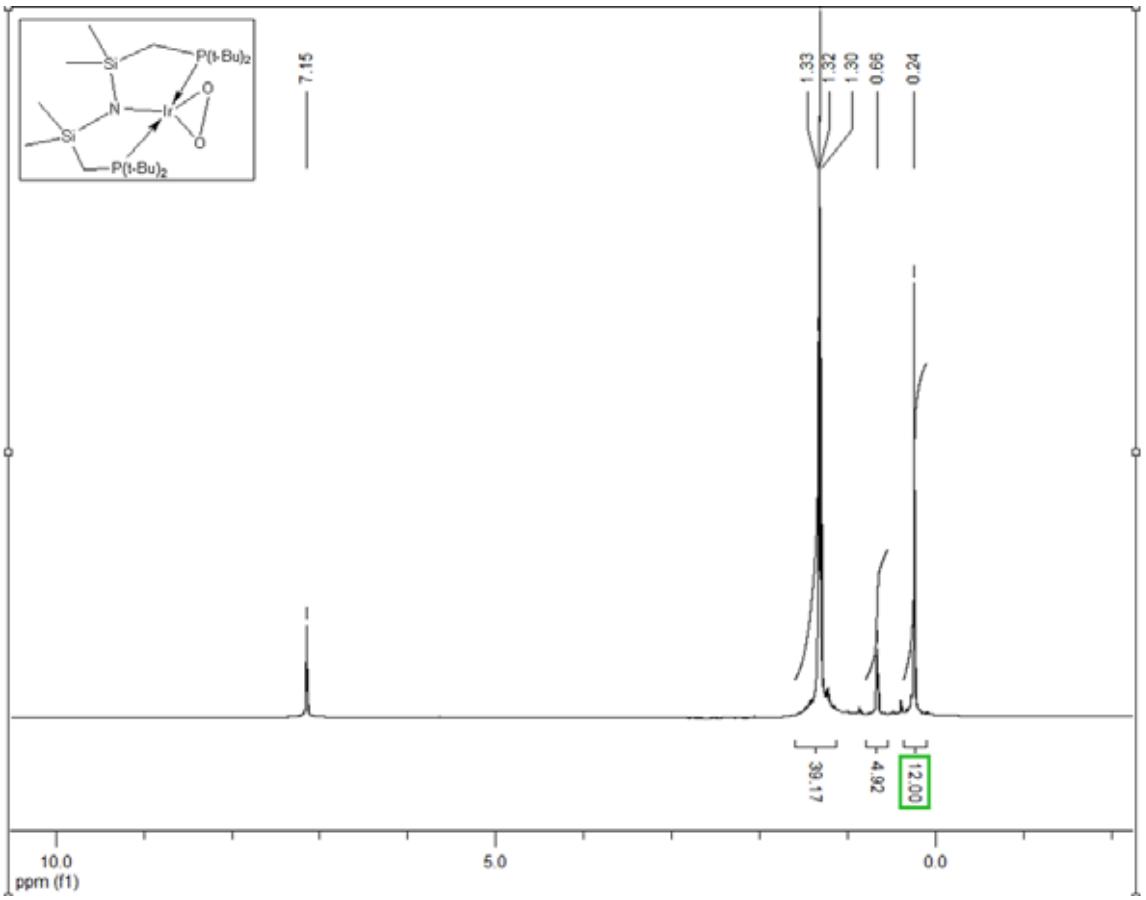
All EPR at 9.3466 GHz: 22° C g = 2.005; -90° C g = 1.742, 2.32, 3.13 all in CH_2Cl_2.

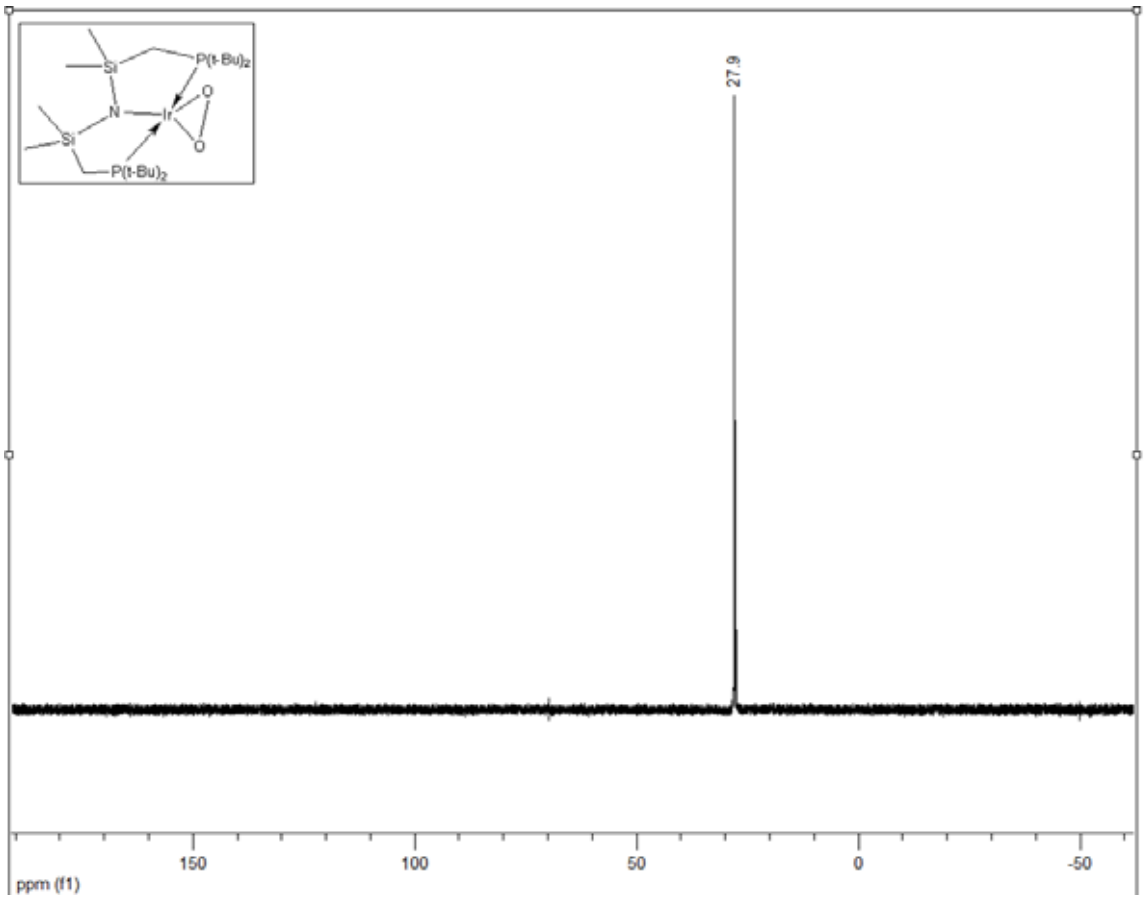
All spectra shown below were made at 25°C. NMR spectra were recorded with a Varian Unity INOVA instrument (400 MHz ^{1}H; 162 MHz ^{31}P). Solvents are either C_6D_6 (impurity at 7.15 ppm) or CD_2Cl_2 (5.32 ppm).

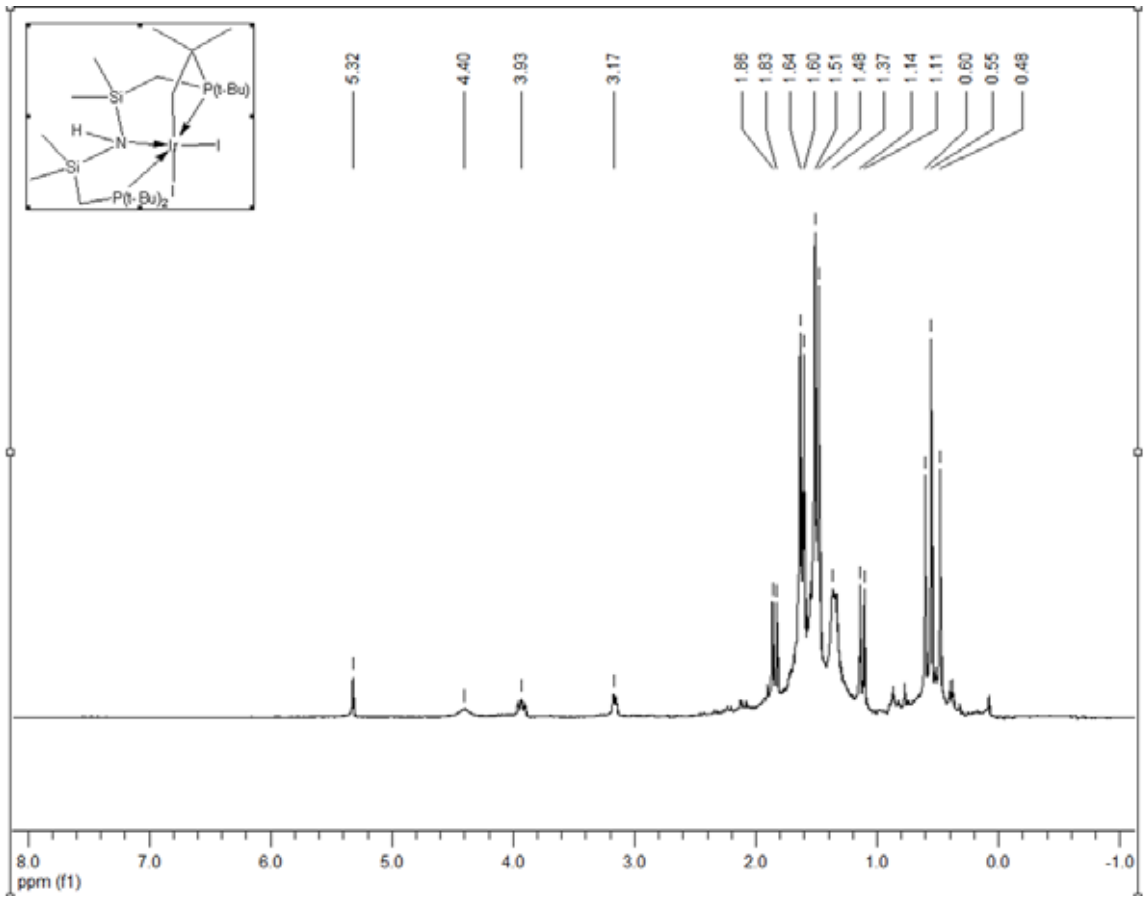


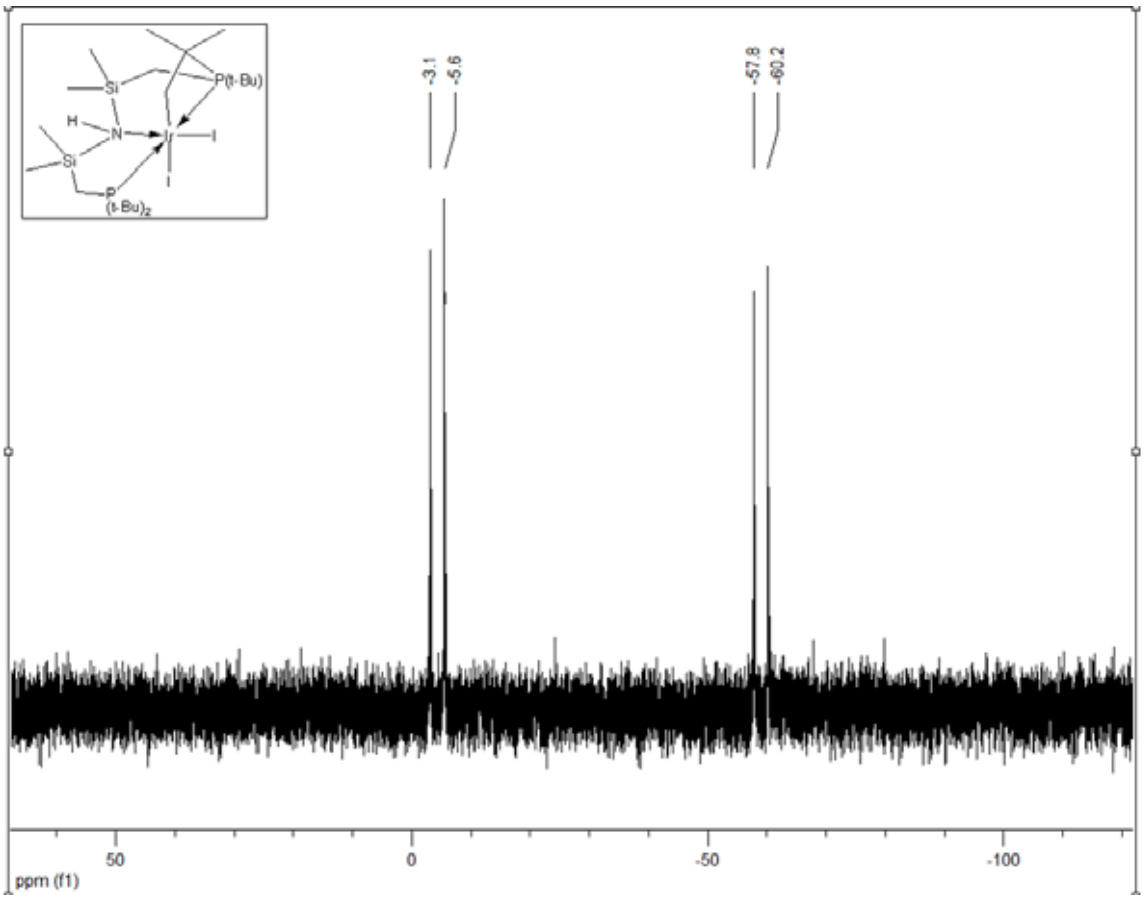


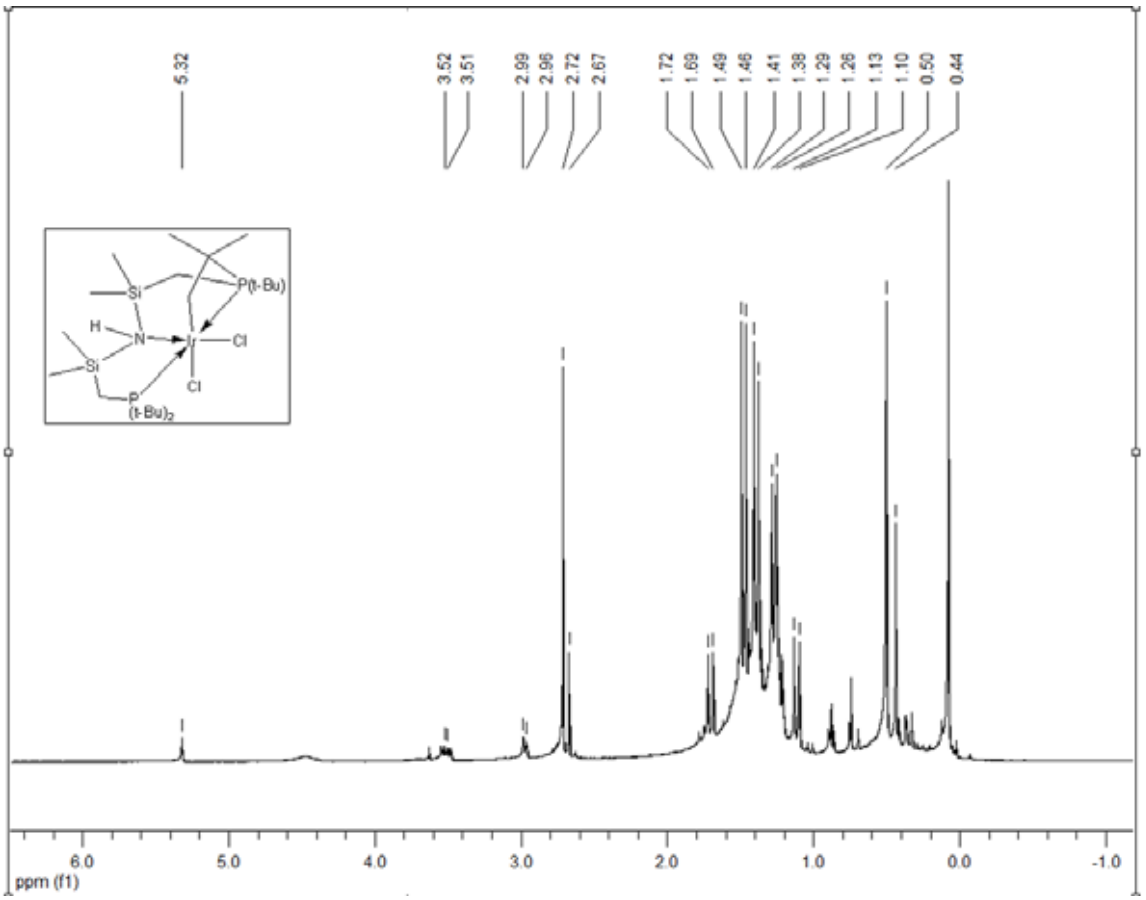

61.2
59.0
16.4
14.2
150
100
50
0
-50
ppm (f1)

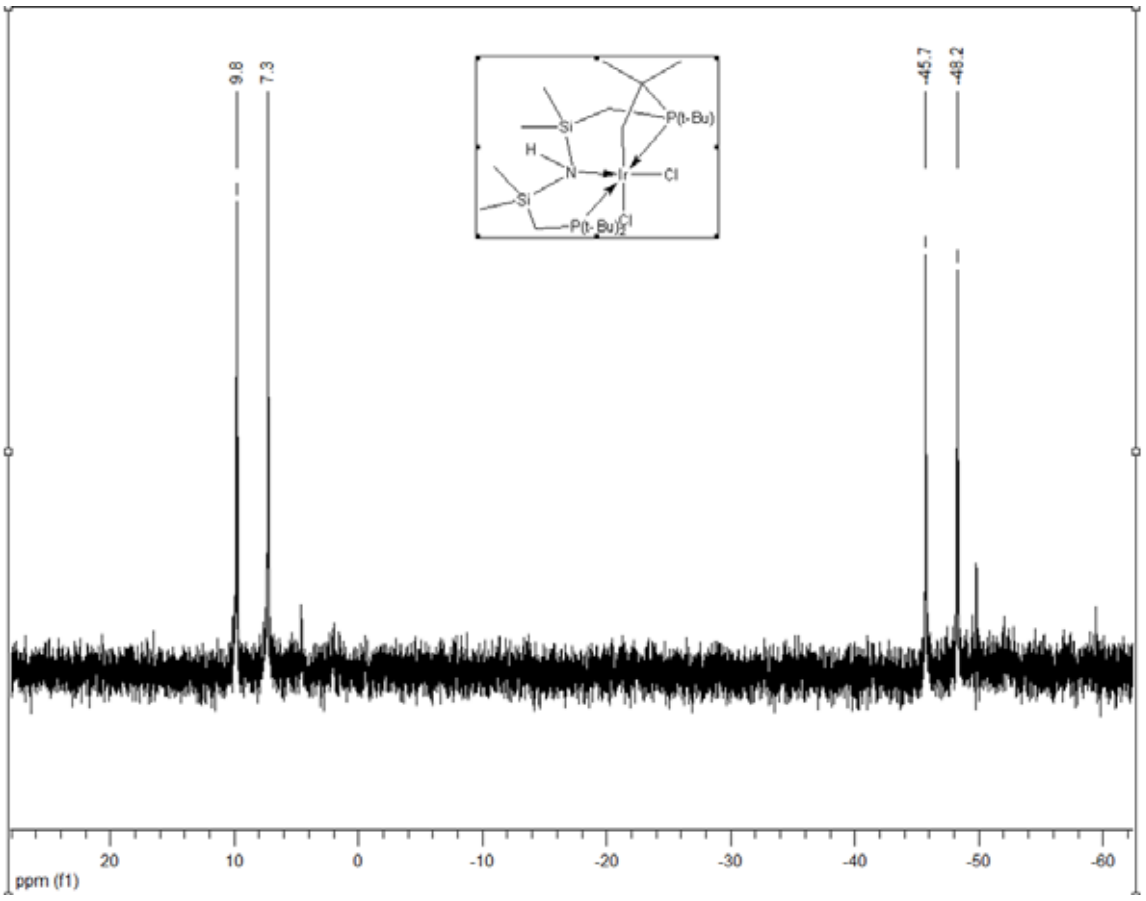

7.15
1.33
1.32
1.30
0.66
0.24
39.17
4.92
12.00
10.0
5.0
0.0
ppm (f1)

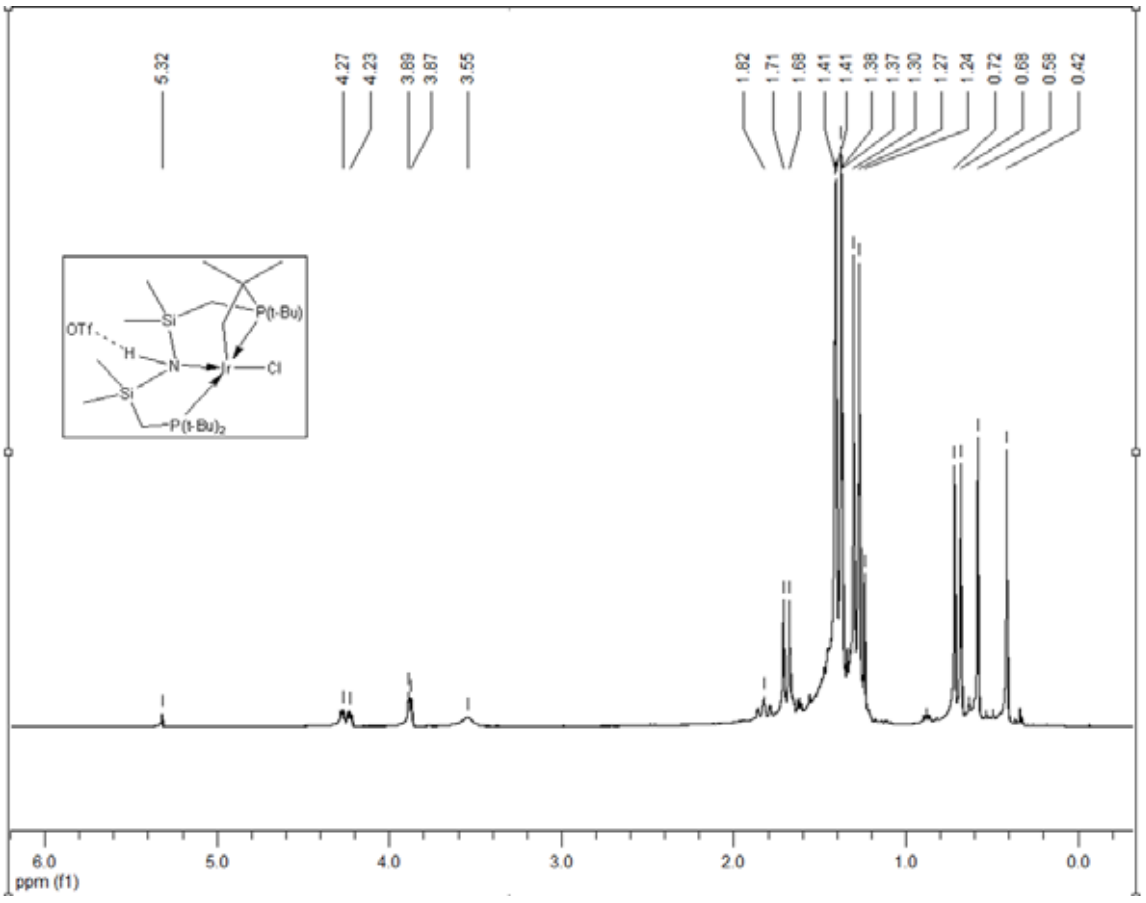

27.9
150
100
50
0
-50
ppm (f1)

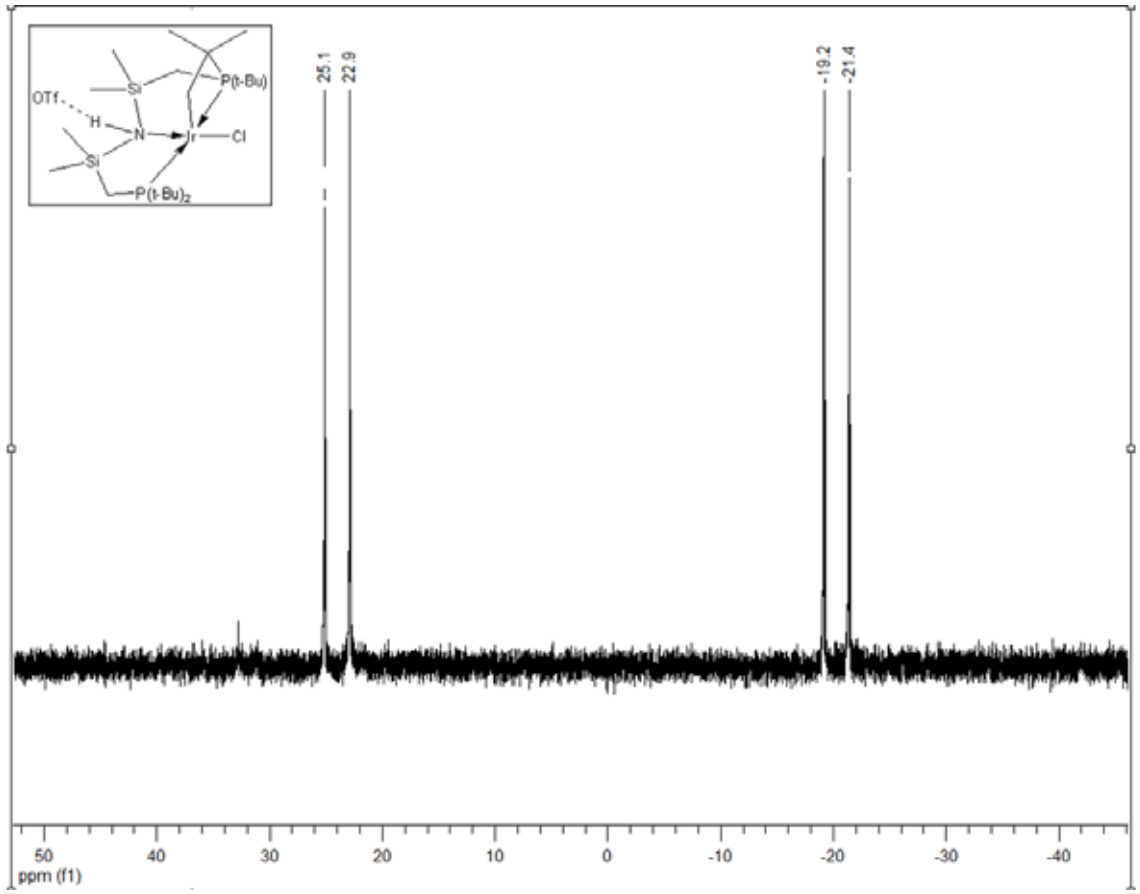

5.32
4.40
3.93
3.17
1.86
1.83
1.64
1.60
1.51
1.48
1.37
1.14
1.11
0.60
0.55
0.48
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

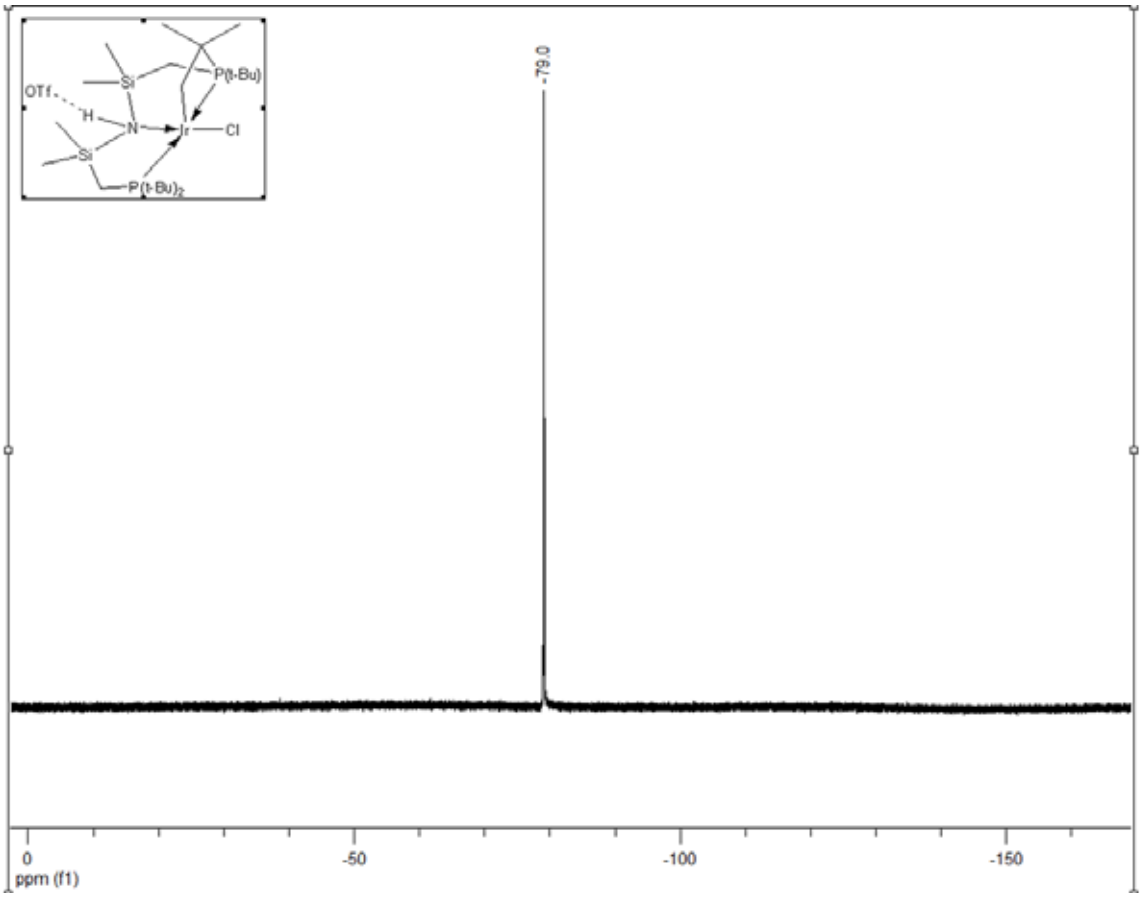

-3.1
-5.6
-57.8
-60.2
Si
P(t-Bu)
H
N
Ir
I
Si
I
P
(t-Bu)2
50
0
-50
-100
ppm (f1)

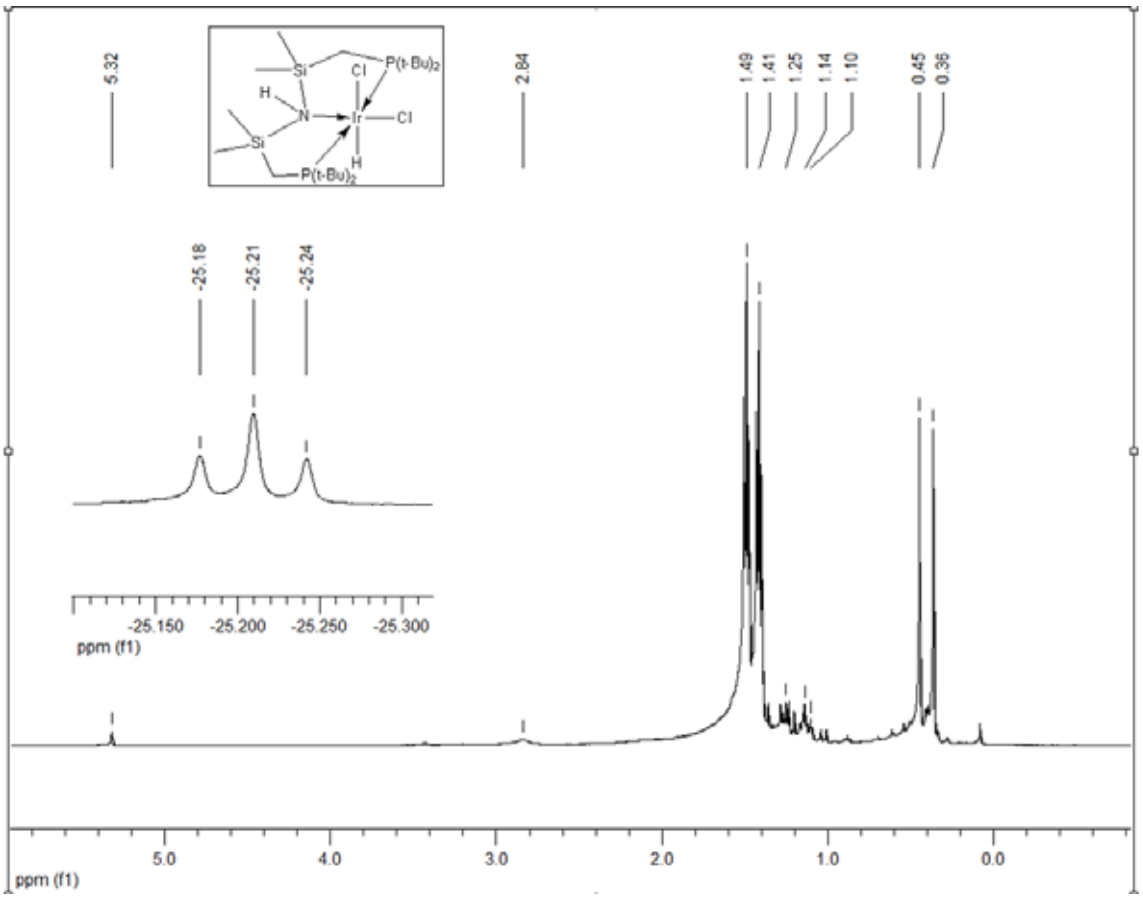

5.32
3.52
3.51
2.99
2.96
2.72
2.67
1.72
1.69
1.49
1.46
1.41
1.38
1.29
1.26
1.13
1.10
0.50
0.44
Si
P(t-Bu)
H
N
Ir
Cl
Si
Cl
P
(t-Bu)2
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

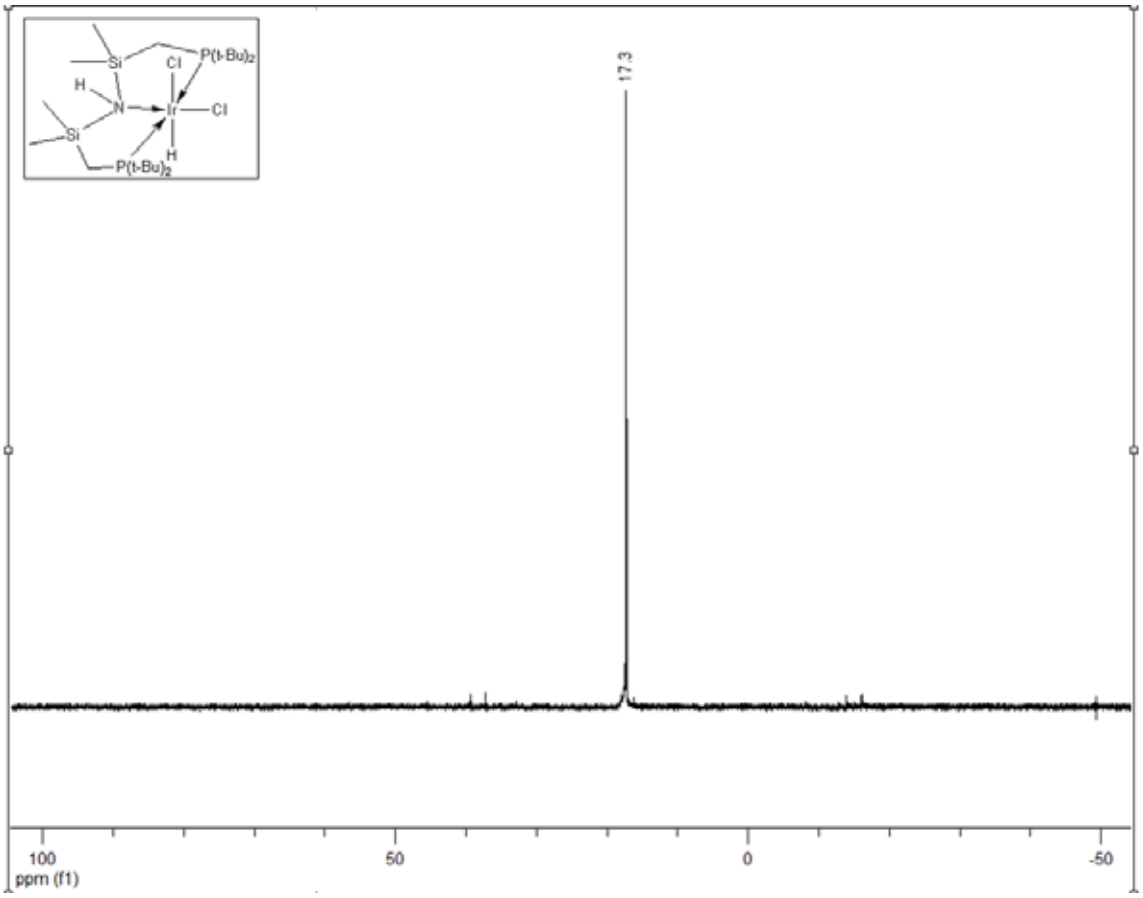

9.8
7.3
-45.7
-48.2
P(t-Bu)
H
N
Ir
Cl
Si
P(t-Bu)2
Cl
20
10
0
-10
-20
-30
-40
-50
-60
ppm (f1)

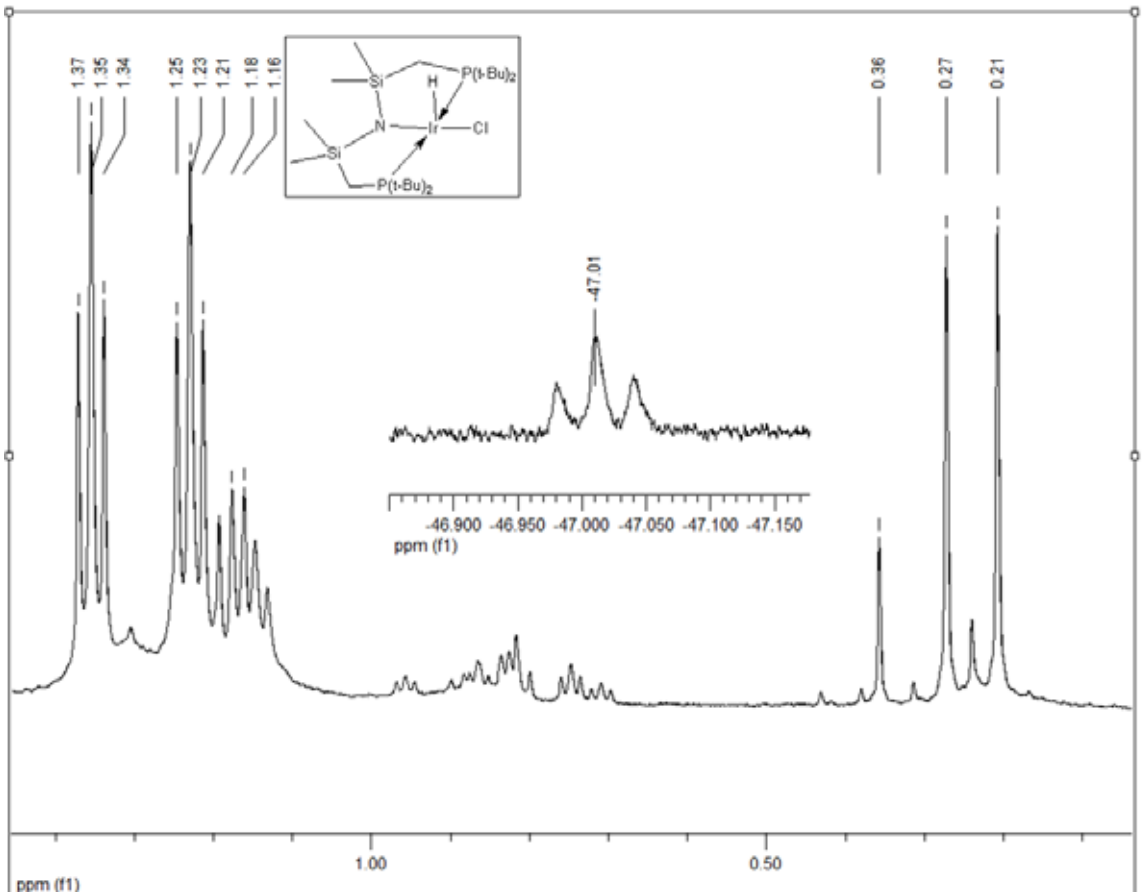

5.32
4.27
4.23
3.89
3.87
3.55
1.82
1.71
1.68
1.41
1.41
1.38
1.37
1.30
1.27
1.24
0.72
0.68
0.58
0.42
OTf
H
N
Ir
Cl
Si
P(t-Bu)
P(t-Bu)2
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

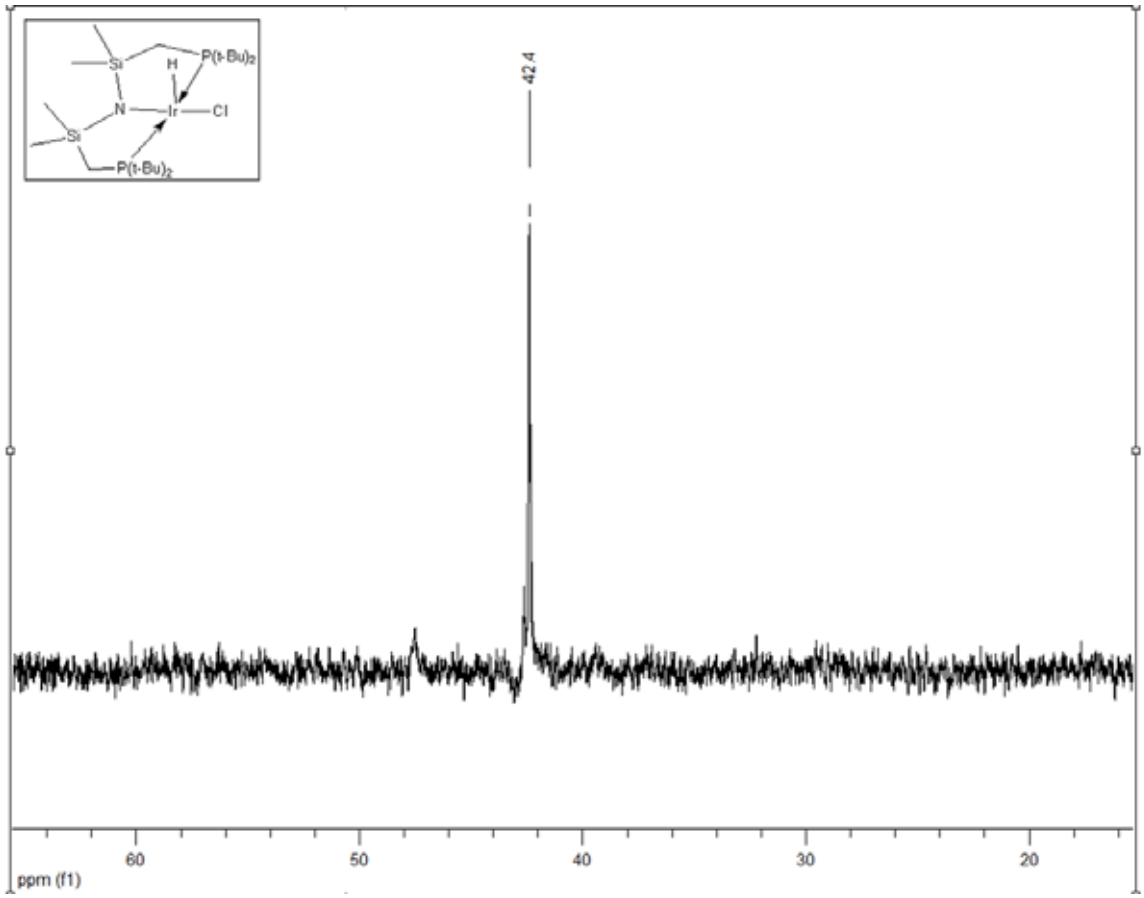

OTf
H
N
Si
Ir
Cl
P(t-Bu)
P(t-Bu)2
25.1
22.9
-19.2
-21.4
50
40
30
20
10
0
-10
-20
-30
-40
ppm (f1)

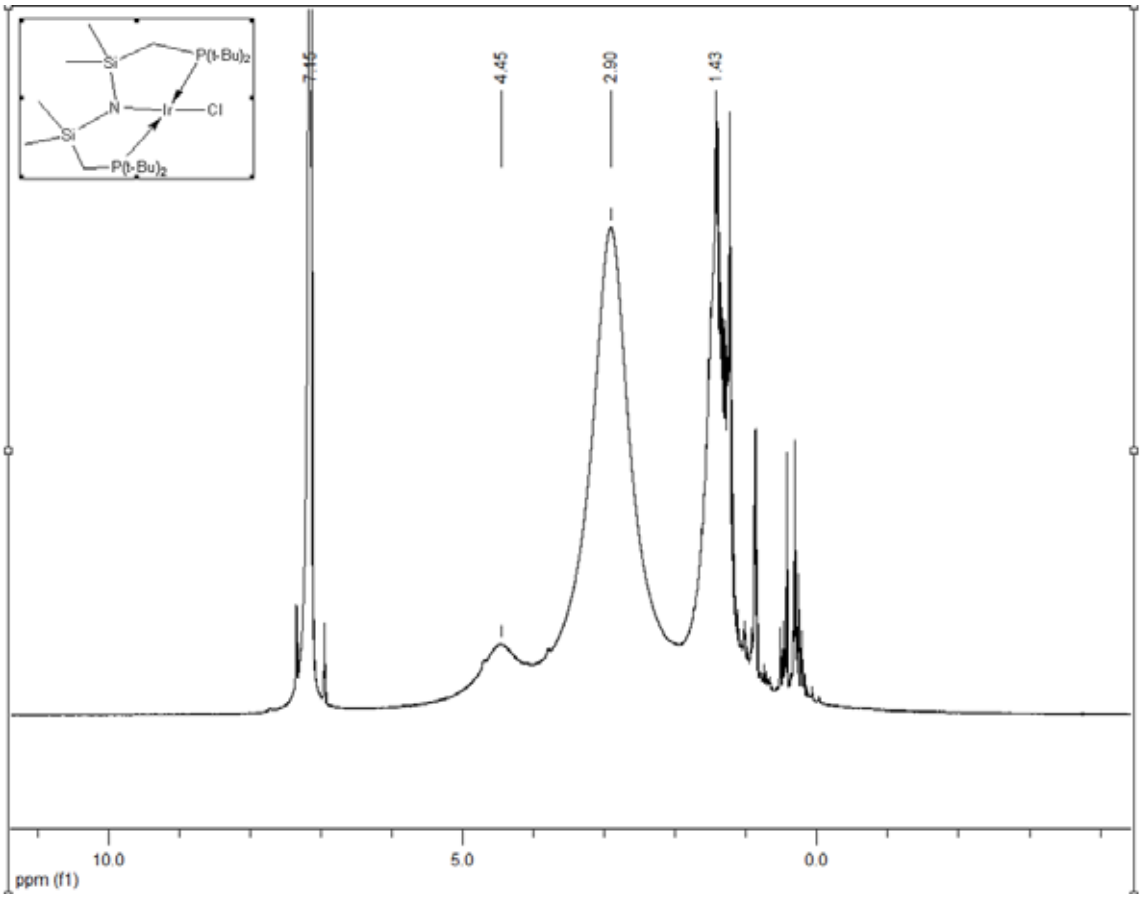

OTf
H
N
Si
Ir
Cl
P(t-Bu)
P(t-Bu)2
-79.0
0
-50
-100
-150
ppm (f1)


5.32
2.84
1.49
1.41
1.25
1.14
1.10
0.45
0.36
-25.18
-25.21
-25.24
-25.150
-25.200
-25.250
-25.300
ppm (f1)
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
Si
Cl
P(t-Bu)2
H
N
Ir
Cl
Si
H
P(t-Bu)2


17.3
Si
Cl
P(t-Bu)2
H
N
Ir
Cl
Si
H
P(t-Bu)2
100
50
0
-50
ppm (f1)


1.37
1.35
1.34
1.25
1.23
1.21
1.18
1.16
0.36
0.27
0.21
-47.01
-46.900 -46.950 -47.000 -47.050 -47.100 -47.150
ppm (f1)
1.00
0.50
ppm (f1)
Si
H
P(t-Bu)2
N
Ir
Cl
Si
P(t-Bu)2


42.4
60
50
40
30
20
ppm (f1)
Si
H
P(t-Bu)2
N
Ir
Cl
Si
P(t-Bu)2


Si
P(t-Bu)2
N
Ir
Cl
Si
P(t-Bu)2
7.15
4.45
2.90
1.43
10.0
5.0
0.0
ppm (f1)