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An iridium-pyridylpyrrolide complex exhibiting reversible binding of H_2

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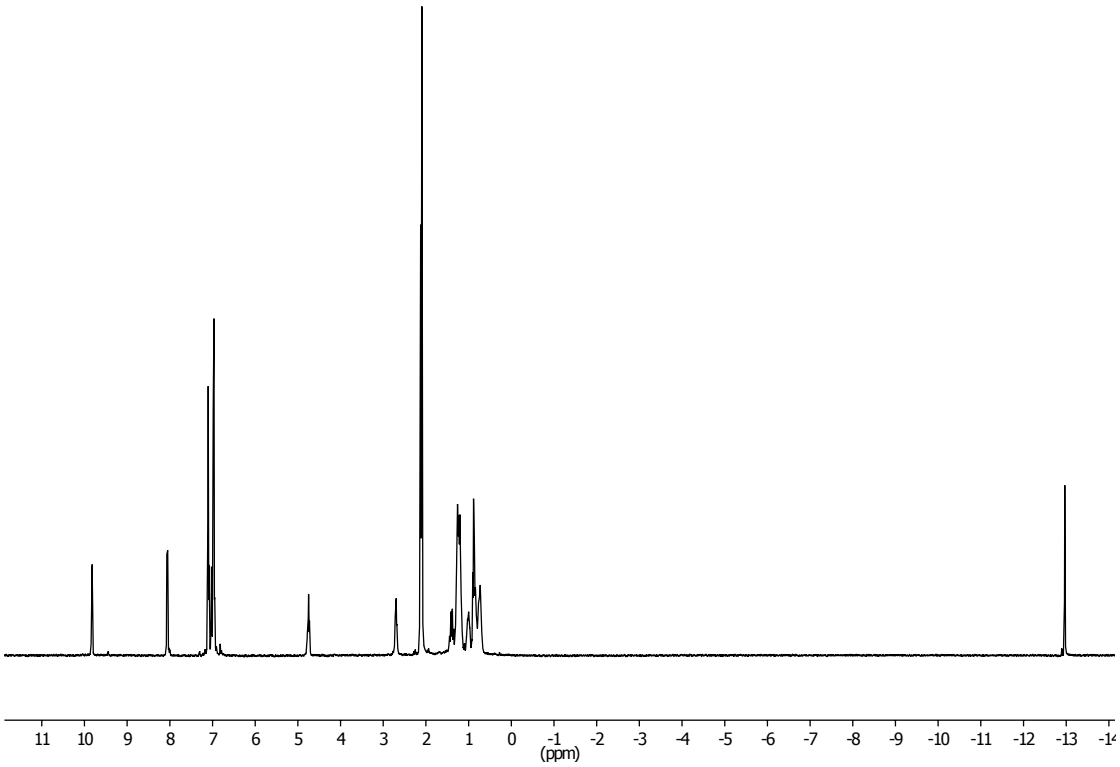
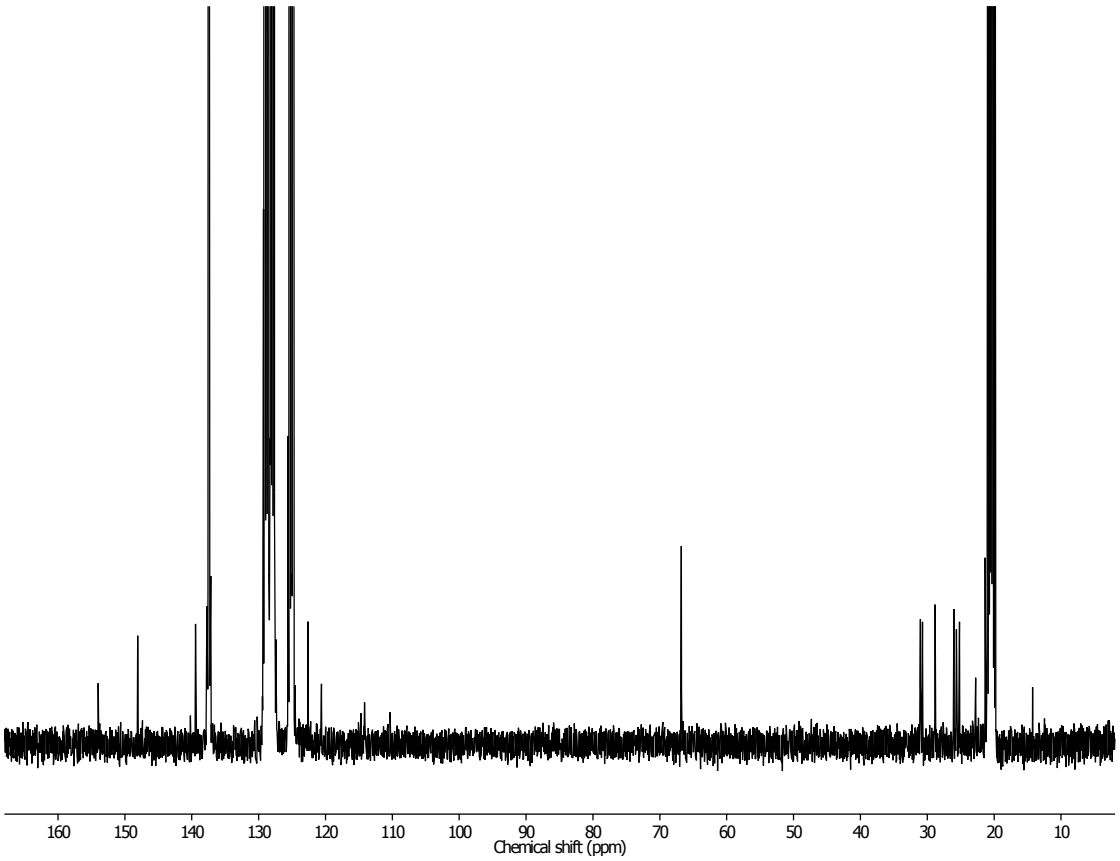
Experimental Data

General procedures: Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Anhydrous pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethyl ether was dried by passage through a column of activated alumina. THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored over sodium metal. Distilled THF was transferred under vacuum into thick walled reaction vessels before being carried into a dry box. Deuterobenzene was purchased from Cambridge Isotope Laboratory (CIL), degassed and vacuum transferred to 4 Å molecular sieves. All other deuteron solvents were stored over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at 200 ºC. Complexes 3,5-bis(trifluoromethyl)-2-(2'-pyridyl)pyrrole and $[Ir(\mu_2\text{-}Cl)(COE)_2]_2$ (COE = cyclooctene) were prepared following the literature procedures.[1-4] All other chemicals were purchased from Strem Chemicals, Aldrich, or Alfa Aesar and used as received. Infrared spectroscopy was performed on a Thermo Nicolet 6700 FT-IR equipped with software under PC control. Mass spectrometry analyses were performed in an Agilent 6130 MSD quadrupole mass spectrometer equipped with a Multimode (ESI and APCI) source. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian 400 MHz NMR spectrometers. ^{1}H NMR is reported with reference to residual solvent resonances at 7.16 ppm for benzene or 1.70 ppm for THF. ^{19}F NMR chemical shifts are reported with respect to external CF_3CO_2H (0.0 ppm).

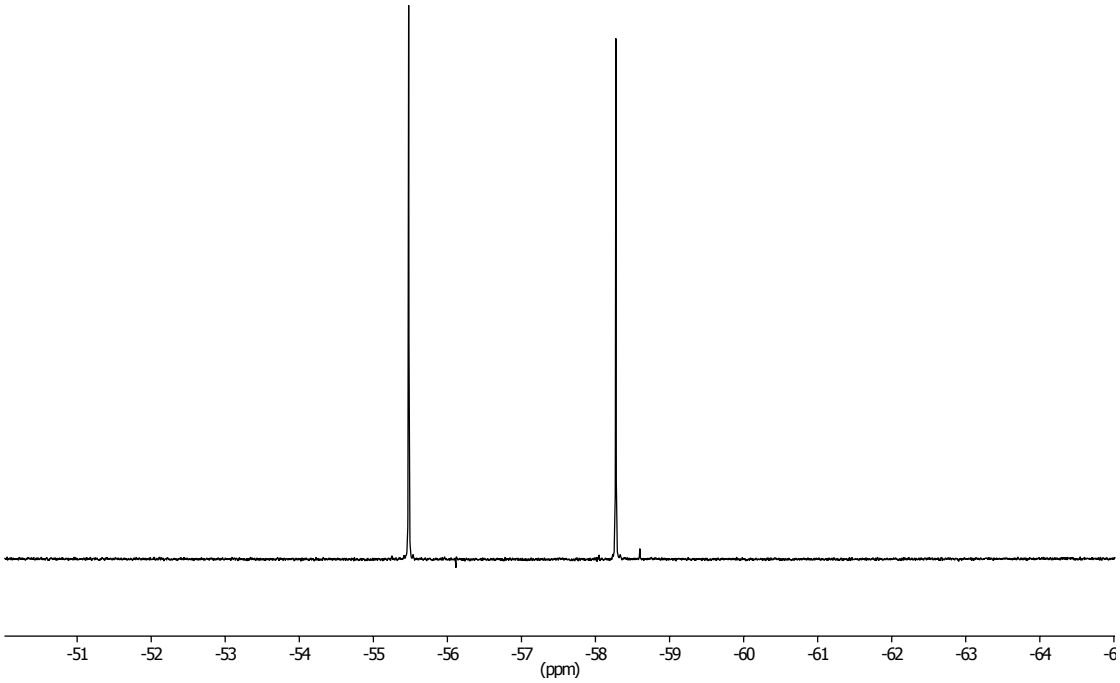
NMR Spectra for Complex 1:



^{1}H NMR Spectrum (25°C).

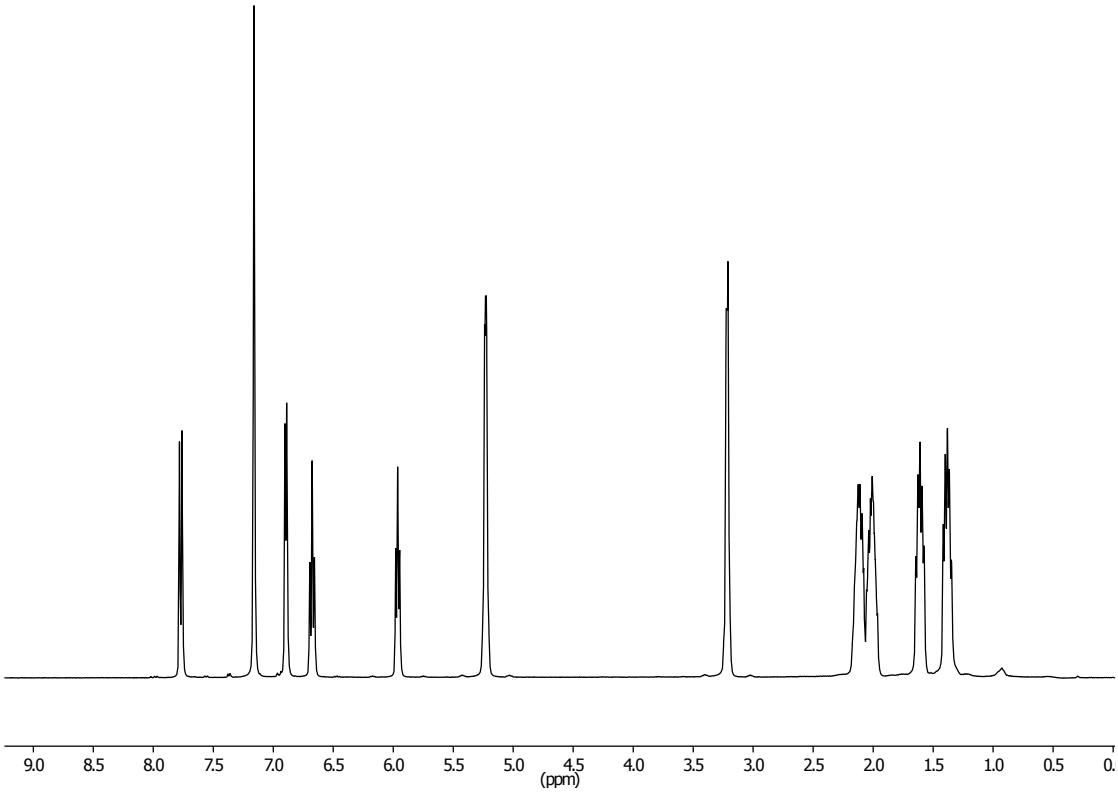


^{13}C NMR Spectrum (25°C)

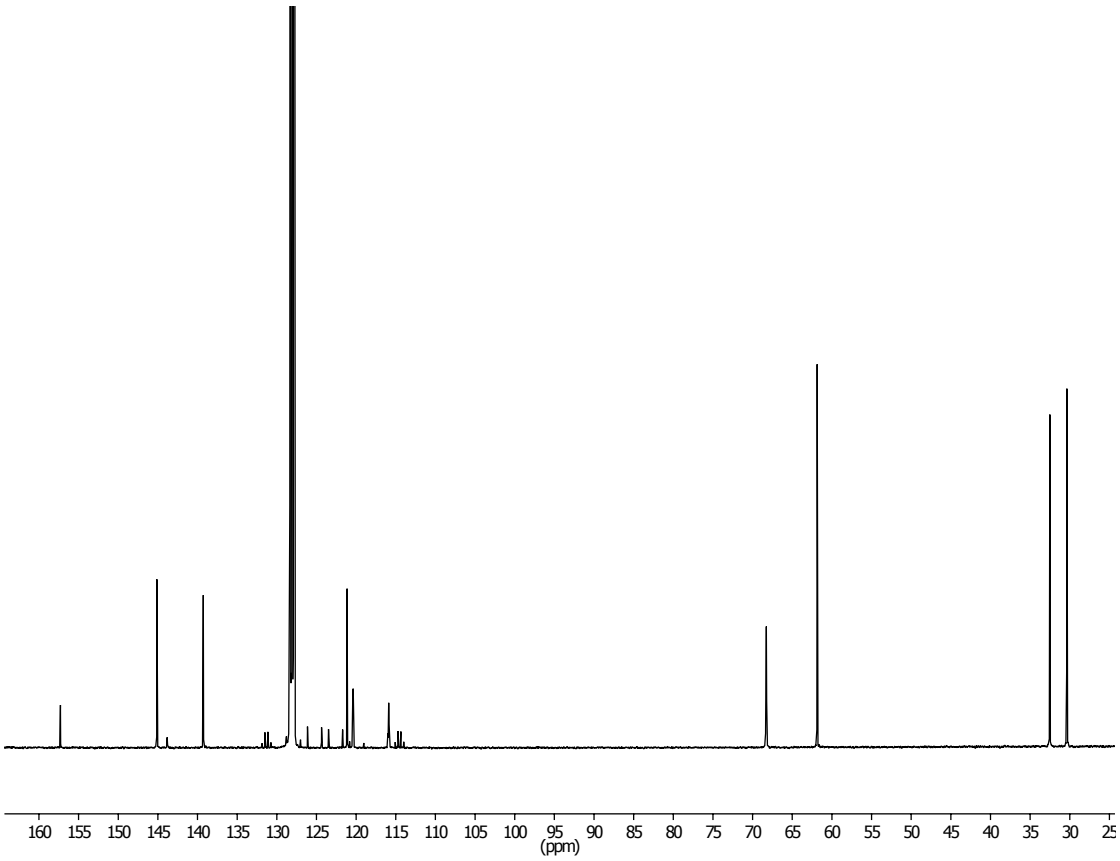


^{19}F NMR Spectrum (25°C)

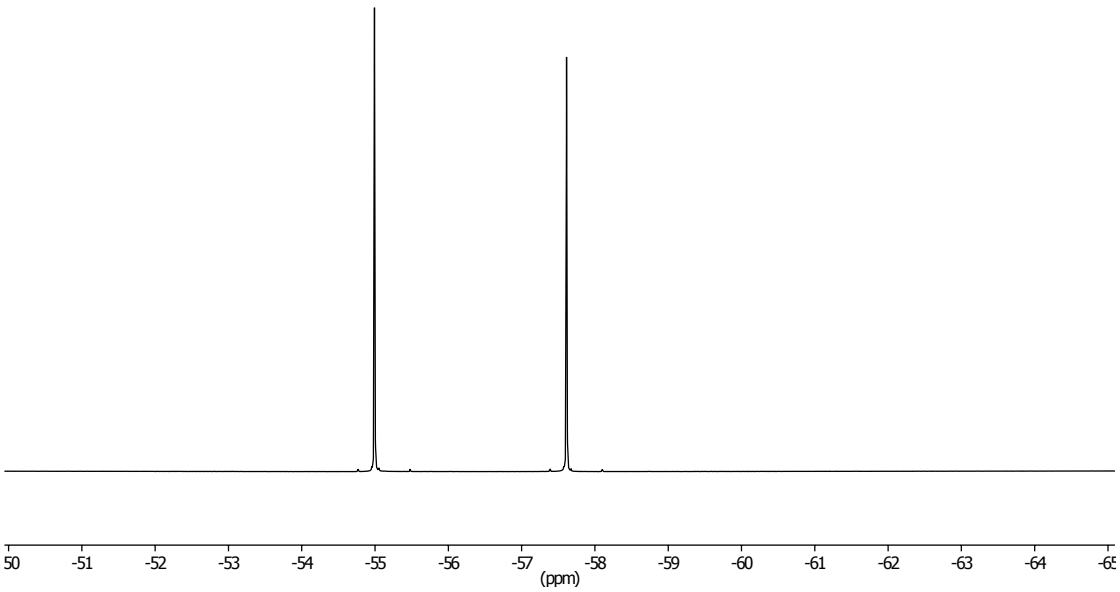
NMR Spectra for Complex 2:



^{1}H NMR Spectrum (25 °C)

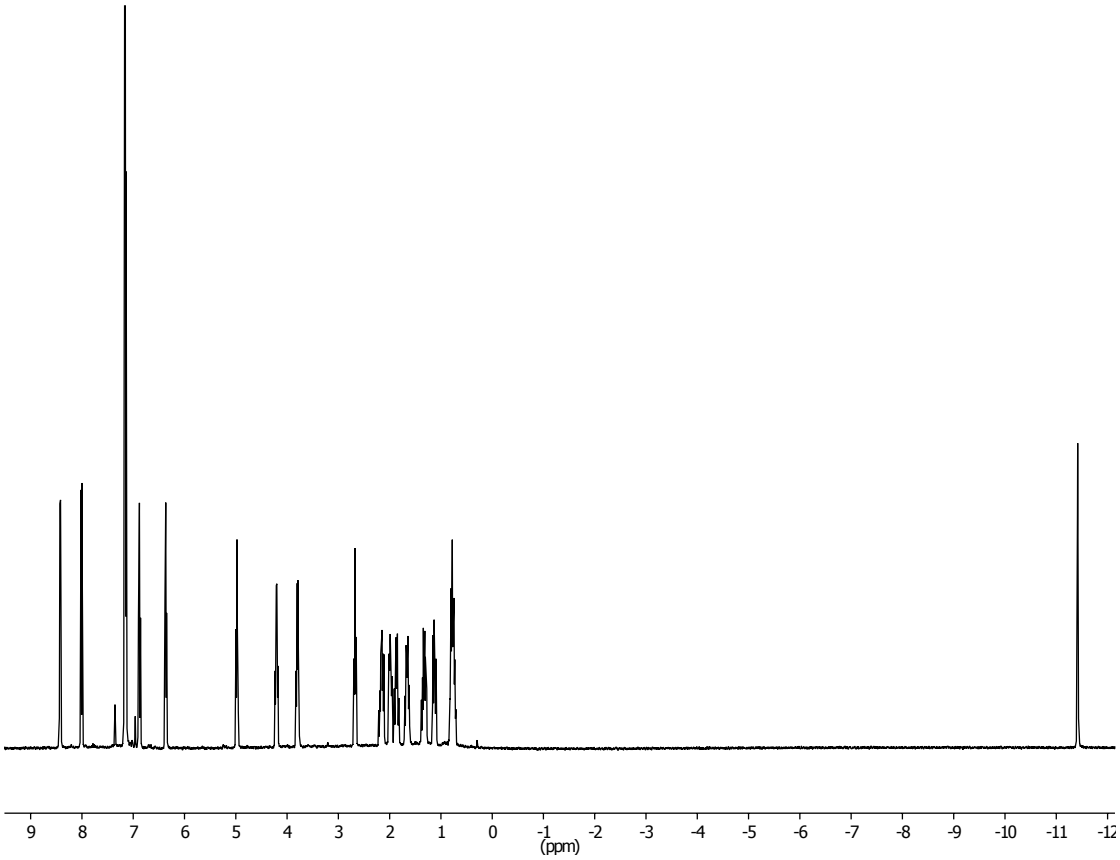


^{13}C NMR Spectrum (25 °C).

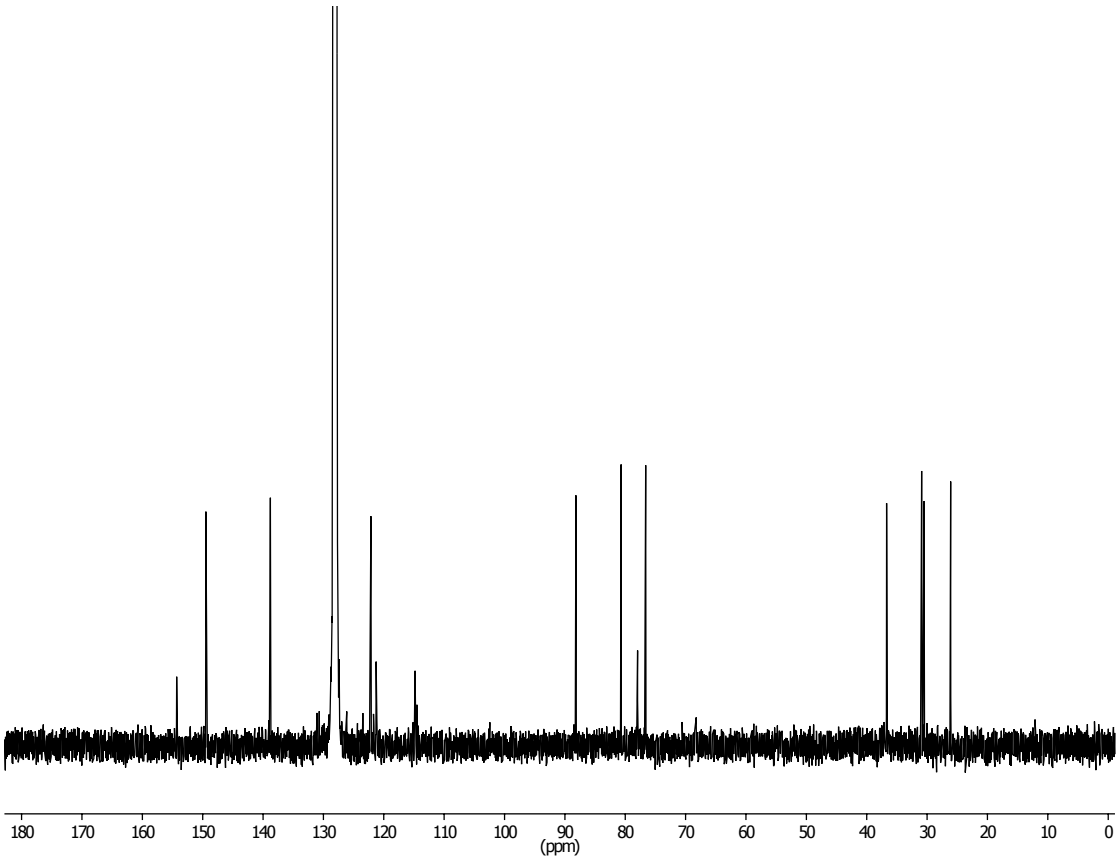


^{19}F NMR Spectrum (25 °C)

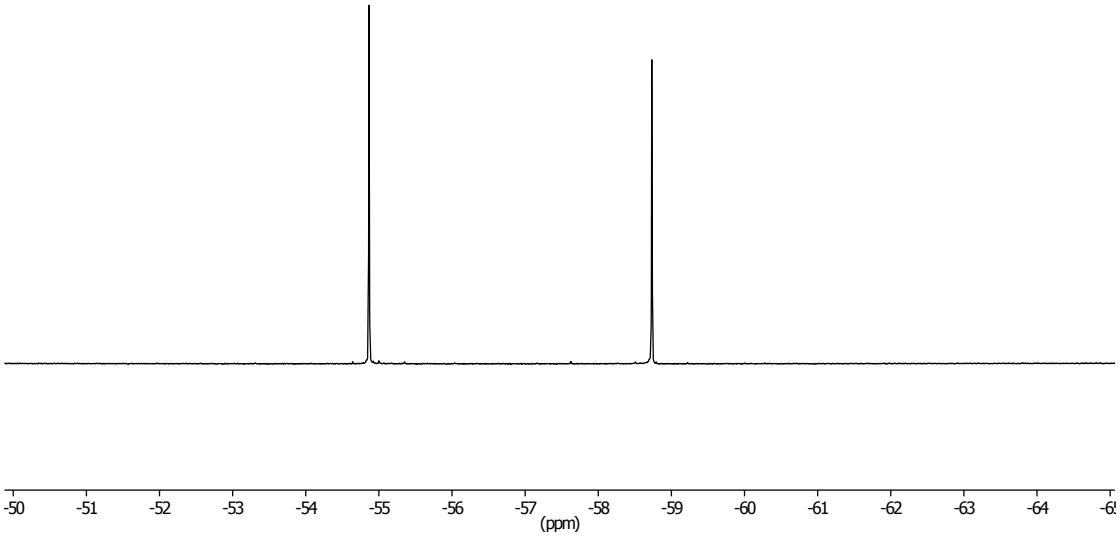
NMR Spectra for Complex 3:



^{1}H NMR Spectrum (25 °C)

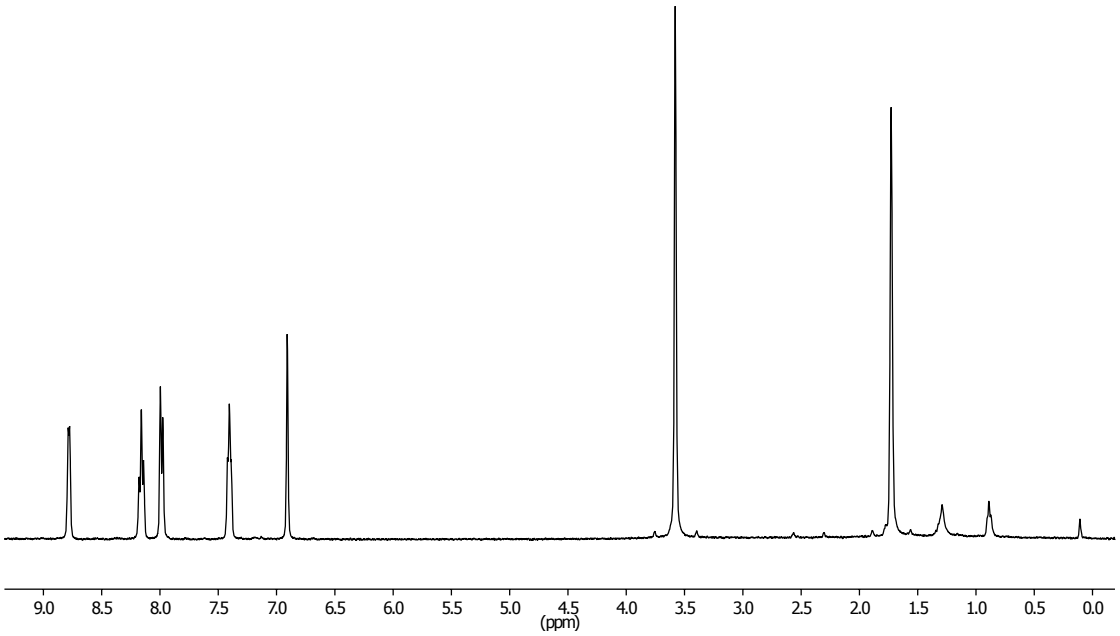


^{13}C NMR Spectrum (25 °C).

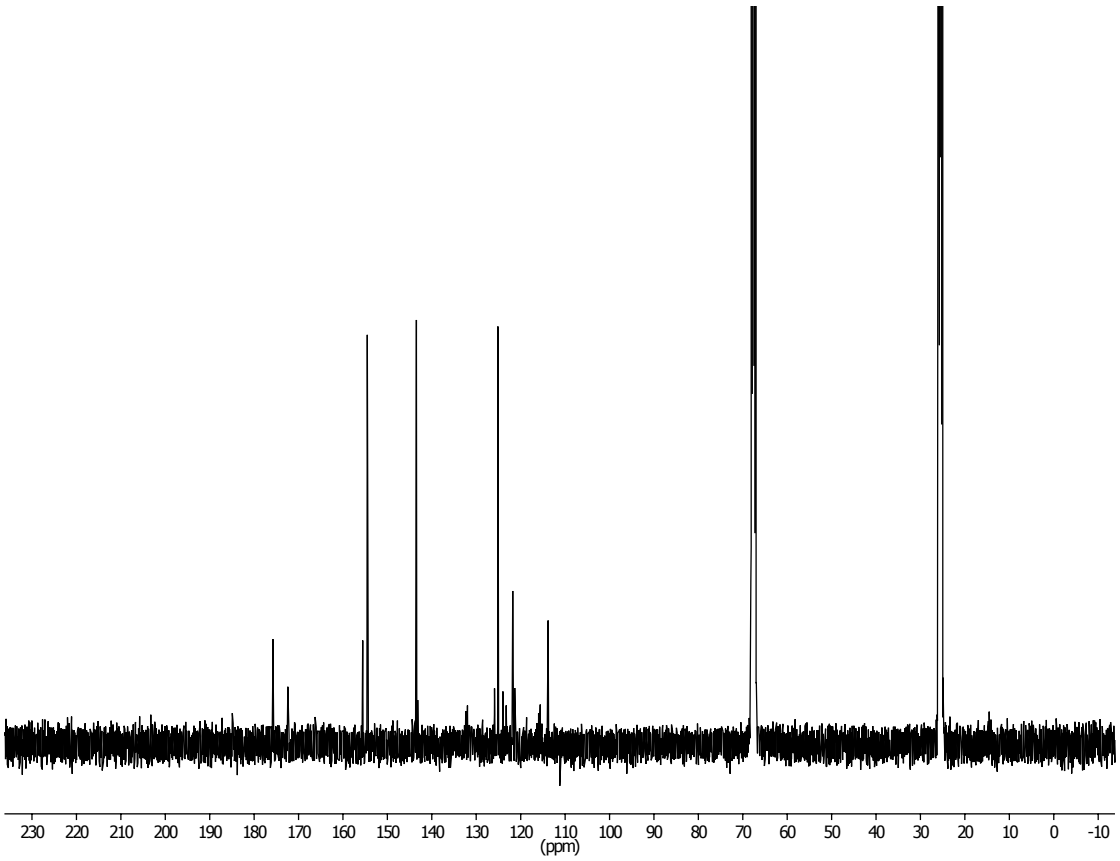


^{19}F NMR Spectrum (25 °C)

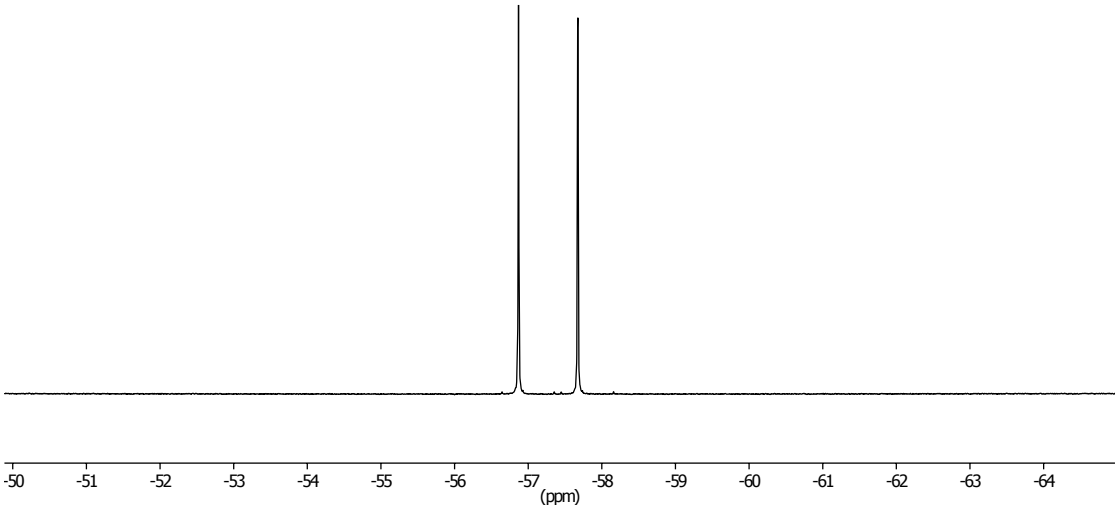
NMR Spectra for Complex 4:



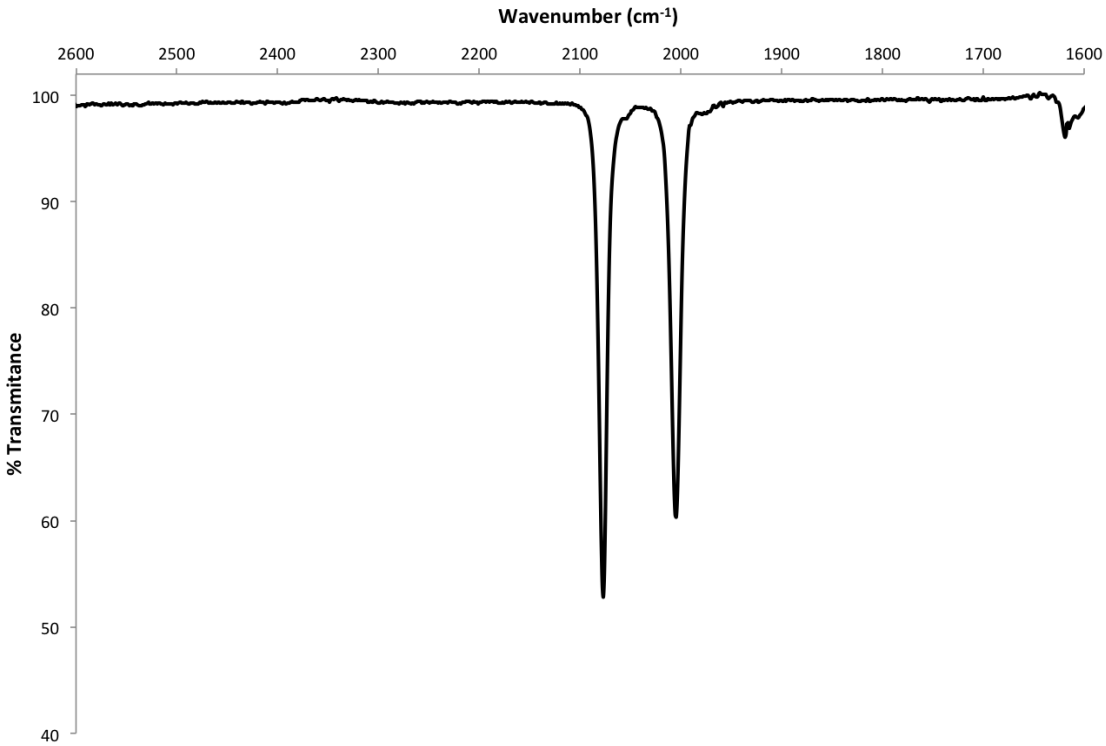
^{1}H NMR Spectrum (25 °C)



^{13}C NMR Spectrum (25 °C).

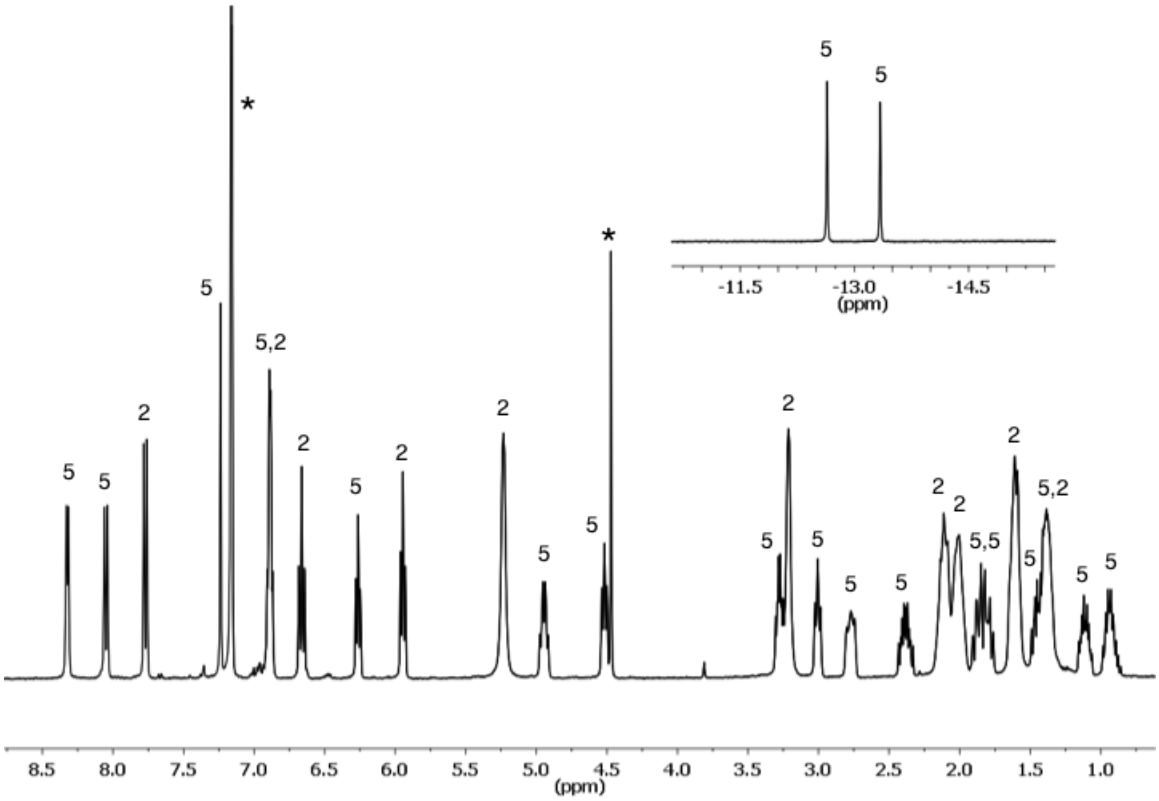


^{19}F NMR Spectrum (25 °C)

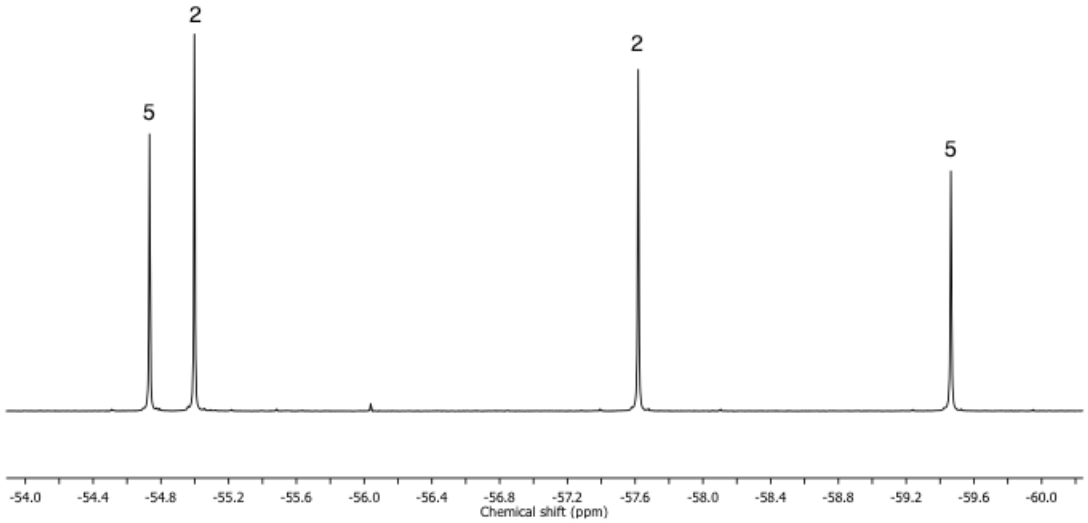


Infrared Spectrum (THF, NaCl plates, 25 °C) of complex **4**

NMR Spectra for Complex 5:

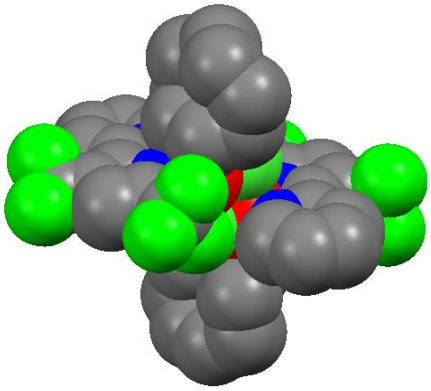


^{1}H NMR Spectrum (25 °C), Mixture of compounds **2** and **5** in a 1:1 ratio. C_6H_6 and H_2 are labeled with *.



^{19}F NMR Spectrum (25 °C), Mixture of compounds **2** and **5** in a 1:1 ratio.

Space Filling Model of Complex 1 With Hydrogen Atoms Omitted for Clarity:



Crystal Structure Collection Data for Complex 1:

The space group $P2_1/c$ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004 and refined with SHELXL-97. 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 = 0.0237 and wR2 = 0.0503 (F2, all data). The remaining electron density is minuscule and located near the metal.

Table of Crystallographic Parameters for Complex 1:

	1
Molecular formula	$C_{45}H_{46}Cl_2F_{12}Ir_2N_4$
Fw	1326.16
temp (K)	150(2)
cryst system	Monoclinic

space group	$P2_1/c$
cell constants	
a (Å)	12.6456(18)
b (Å)	11.3260(16)
c (Å)	16.451(2)
α (deg)	90
β (deg)	104.736(3)
γ (deg)	90
Z	2
V (Å^3)	2278.7(6)
abs coeff, μ_{calc} (mm^{-1})	6.038
δ_{calc} (g/cm^3)	1.933
F(000)	1280
cryst dimens (mm)	0.17 × 0.15 × 0.12
Radiation	Mo Kα
h,k,l ranges colled	-16 <= h <= 16 -13 <= k <= 14 -21 <= l <= 20
θ range (deg)	1.67 to 27.49
no. of reflens colled	16721
no. of unique reflens	5232
no. of params	4438
data/param ratio	5232/4438
Refinement method	Full-matrix least-squares on F^2
R_1[a]	0.0237
wR_2[b]	0.0503
Goodness-of-fit on F^2[c]	1.013
largest diff peak and hole (e/Å^3)	0.834 and -0.479

[a] $R_1 = (|F_o| \quad |F_c|) / \quad |F_o|$. [b] $wR_2 = [[w(F_o^2 \quad F_c^2)^2] / \quad [w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit = $[[w(F_o^2 \quad F_c^2)^2]/N_{observns} \quad N_{params})]^{1/2}$, all data

References

(1) Klappa, J. A. R., A. E. McNeill, K. *Org. Lett.* **2001**, *4*, 435.

(2) Hironari, O. B., D. O. Soloshonok, V. A. *Tet. Lett.* **2003**, *44*, 2417.

(3) Flores, J. A.; Andino, J. G.; Tsvetkov, N. P.; Pink, M.; Wolfe, R. J.; Head, A. R.; Lichtenberger, D. L.; Massa, J.; Caulton, K. G. *Inorg. Chem.* **2011**, *50*, 8121.

(4) Van Der Ent, A.; Onderdelinden, A. L.; Schunn, R. A. In *Inorg. Synth.*; John Wiley & Sons, Inc.: 1990, p 90.