Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Acidolysis and Oxygen Atom Transfer Reactivity of a Diiridium Hydroperoxo Complex

Thomas S. Teets and Daniel G. Nocera*

Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307

nocera@mit.edu

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Table 1. Crystallographic Summary for Complexes **3·CH_2Cl_2** and **5**.

	3·CH_2Cl_2	**5**
Formula	$C_{29}H_{43}Cl_5F_{24}Ir_2N_4O_9P_4$	$C_{28}H_{40}Cl_4F_{24}Ir_2N_4O_{10}P_4$
fw, g/mol	1733.20	1666.72
Temperature	175(2) K	100(2) K
cryst. syst.	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$
colour	yellow	Yellow
a (Å)	10.4031(11)	12.7559(9)
b (Å)	12.5695(13)	19.5938(14)
c (Å)	12.6361(13)	21.0181(15)
α (°)	65.033(2)	90
β (°)	70.612(2)	97.9880(10)
γ (°)	84.392(2)	90
V (Å^3)	1411.2(3)	5202.2(6)
Z	1	4
no. refl.	8499	117116
no. unique refl.	8499	15213
R_{int}	0.0557	0.0527
R_1[a] (all data)	0.0638	0.0483
wR_2[b] (all data)	0.1362	0.0811
R_1 [($I > 2\sigma$)]	0.0521	0.0318
wR_2 [($I > 2\sigma$)]	0.1294	0.0718
GOF[c]	1.098	1.040

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. [c] GOF = $(\Sigma w(F_o^2 - F_c^2)^2/(n - p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

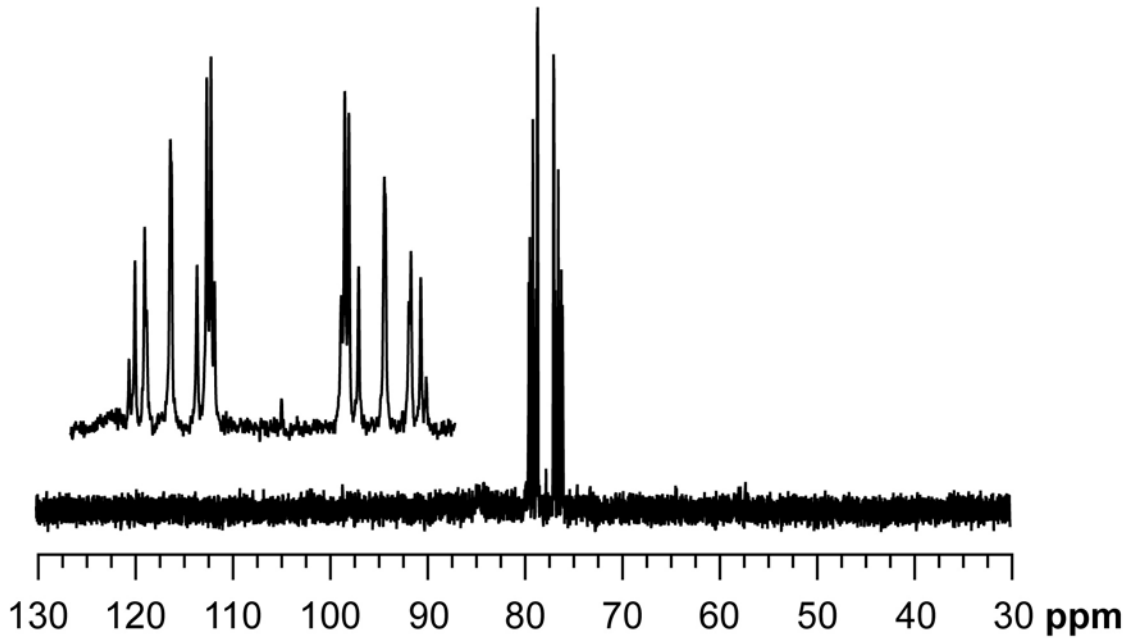

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of **2**. The spectrum was recorded at 121.5 MHz in CD_3CN. The inset shows an expansion of the AA'XX' multiplets.

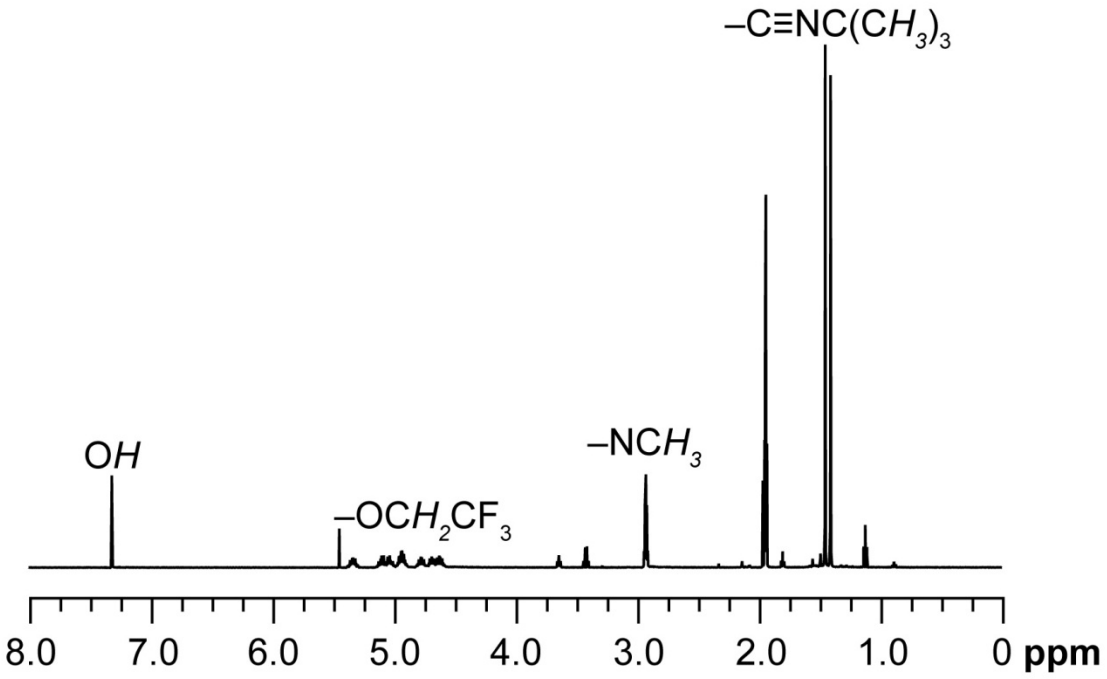

Figure S2. ^{1}H NMR spectrum of **2**. The spectrum was recorded at 500 MHz in CD_3CN. Peaks corresponding to the distinct spectral regions are labelled.

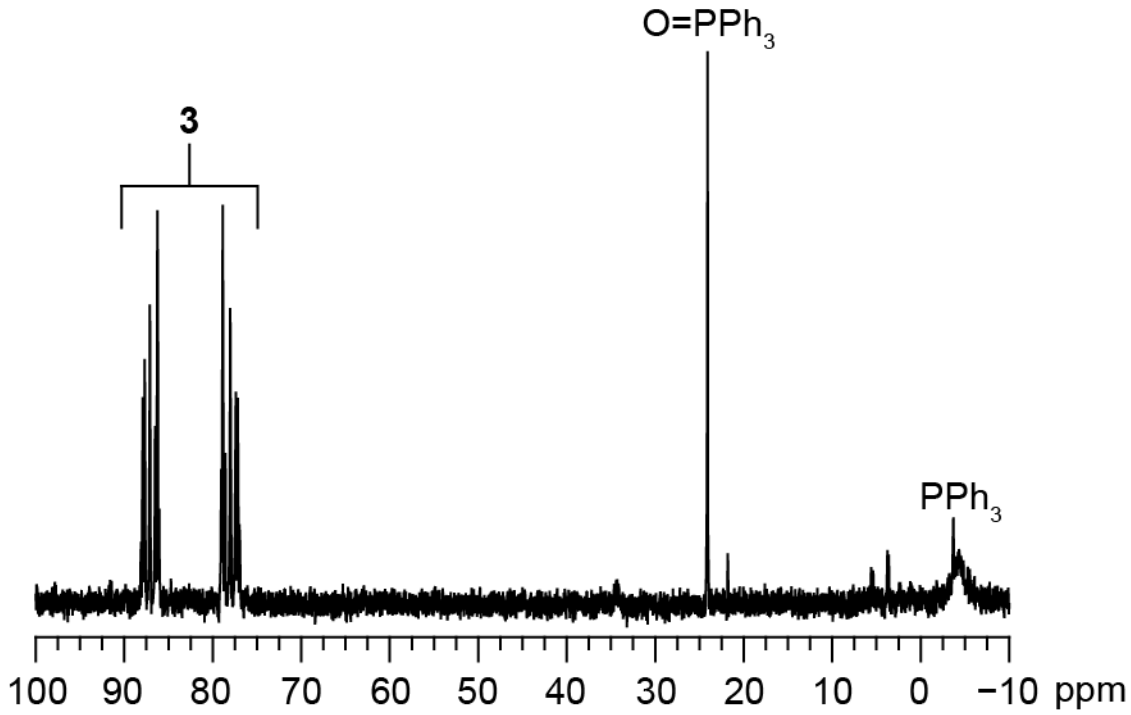

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of the product mixture isolated from the reaction of **2** with 2 eq of PPh_3 for 12 h. The spectrum was recorded at 121.5 MHz in THF-d_8. Peaks corresponding to $O{=}PPh_3$, unreacted PPh_3, and **3** are marked accordingly.

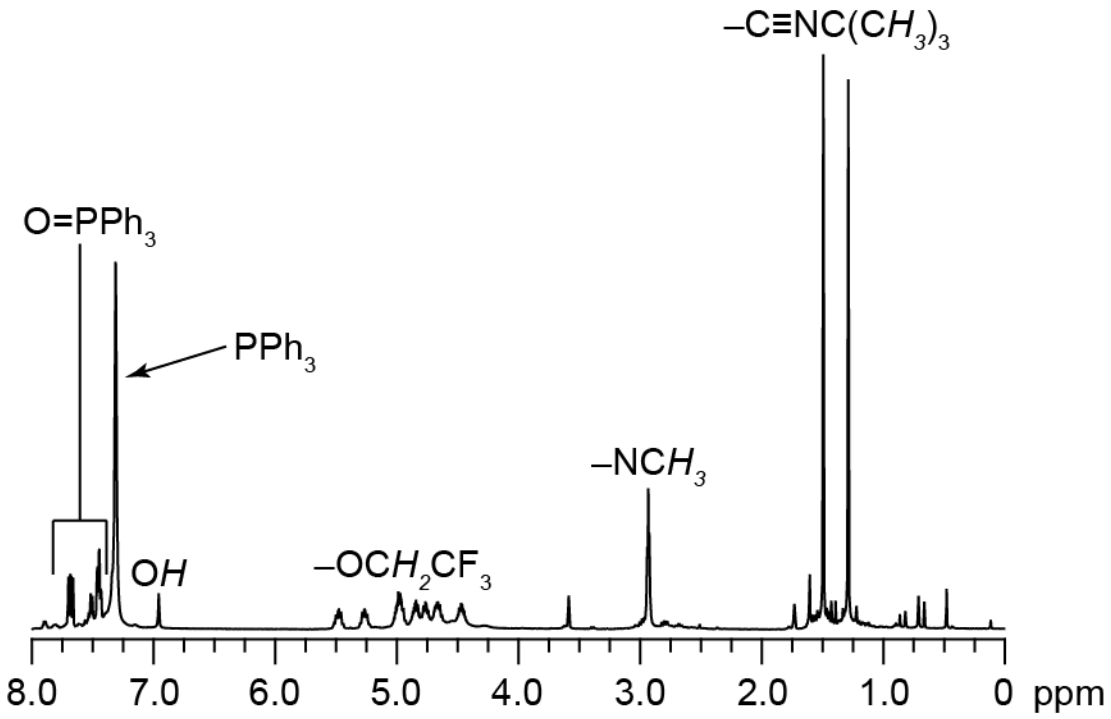

Figure S4. ^{1}H NMR spectrum of the product mixture isolated from the reaction of **2** with 2 eq of PPh_3 for 12 h. The spectrum was recorded at 500 MHz in THF-d_8. Peaks corresponding to $O{=}PPh_3$, unreacted PPh_3, and the distinct spectral regions for **3** are marked as such. All other peaks, excepting residual proteo solvent resonances (1.73 and 3.58 ppm), are attributed to minor side products.

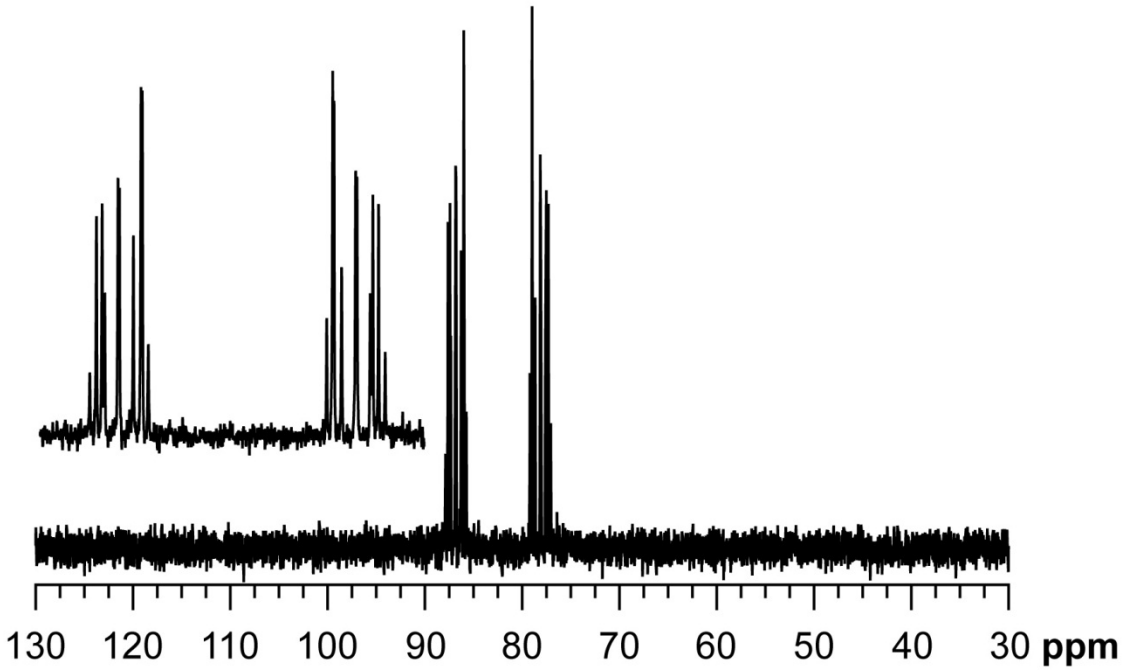

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **3**, prepared by treating **2** with 2 eq of PEt_3 and purified by recrystallization. The spectrum was recorded in CD_2Cl_2 at 121.5 MHz. The inset shows an expansion of the AA'XX' multiplets.

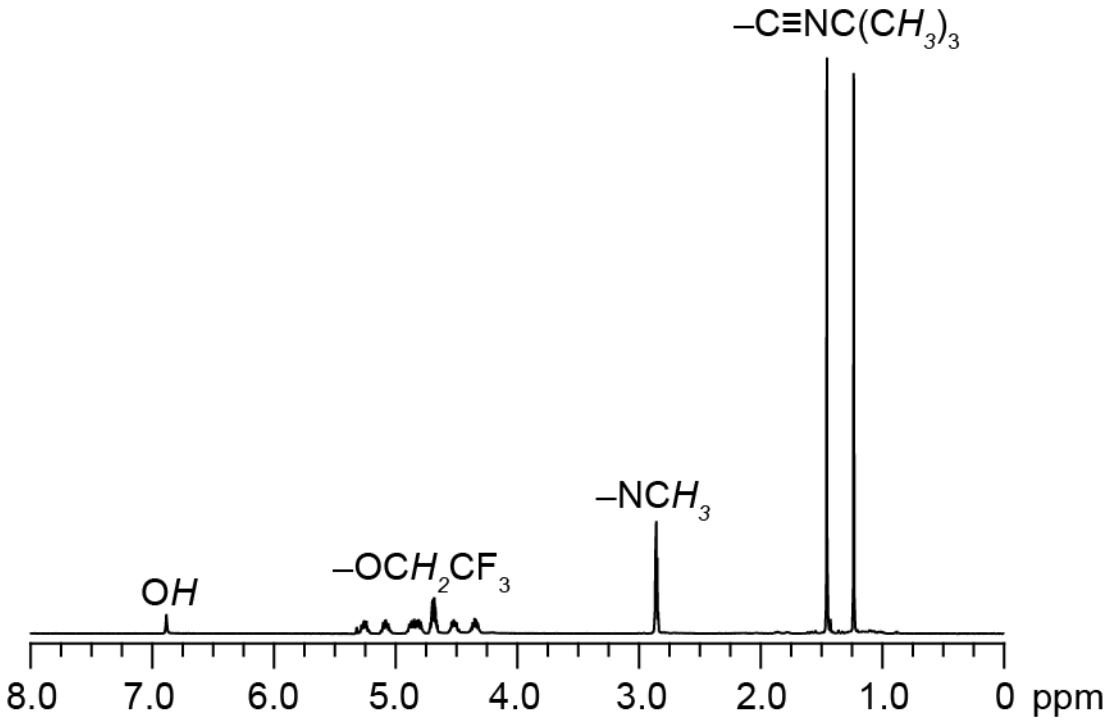

Figure S6. ^{1}H NMR spectrum of **3**, prepared by treating **2** with 2 eq of PEt_3 and purified by recrystallization. The spectrum was recorded in CD_2Cl_2 at 500 MHz; the residual proteo solvent resonance occurs at 5.32 ppm.

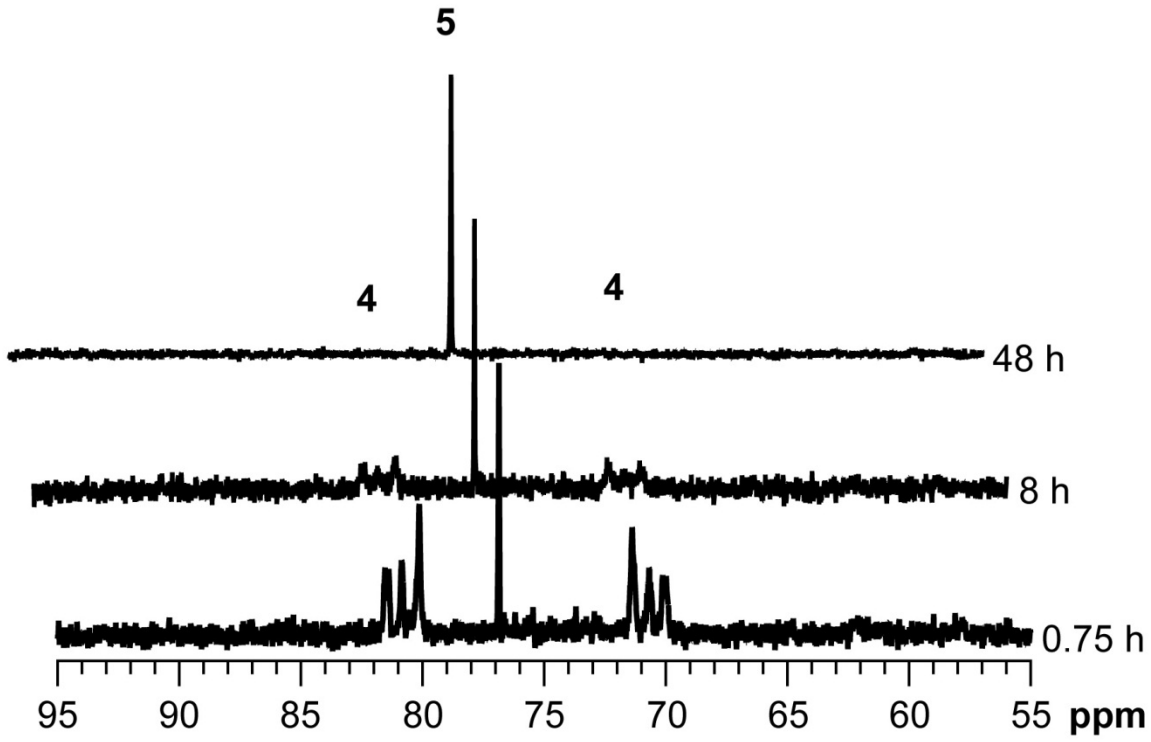

Figure S7. Evolution of the $^{31}P\{^{1}H\}$ NMR spectrum upon treatment of **2** with HCl (1.1 eq) at room temperature. The time is indicated at the right, and the resonances attributed to **4** and **5** are denoted. The spectra were recorded at 121.5 MHz in THF-d_8.

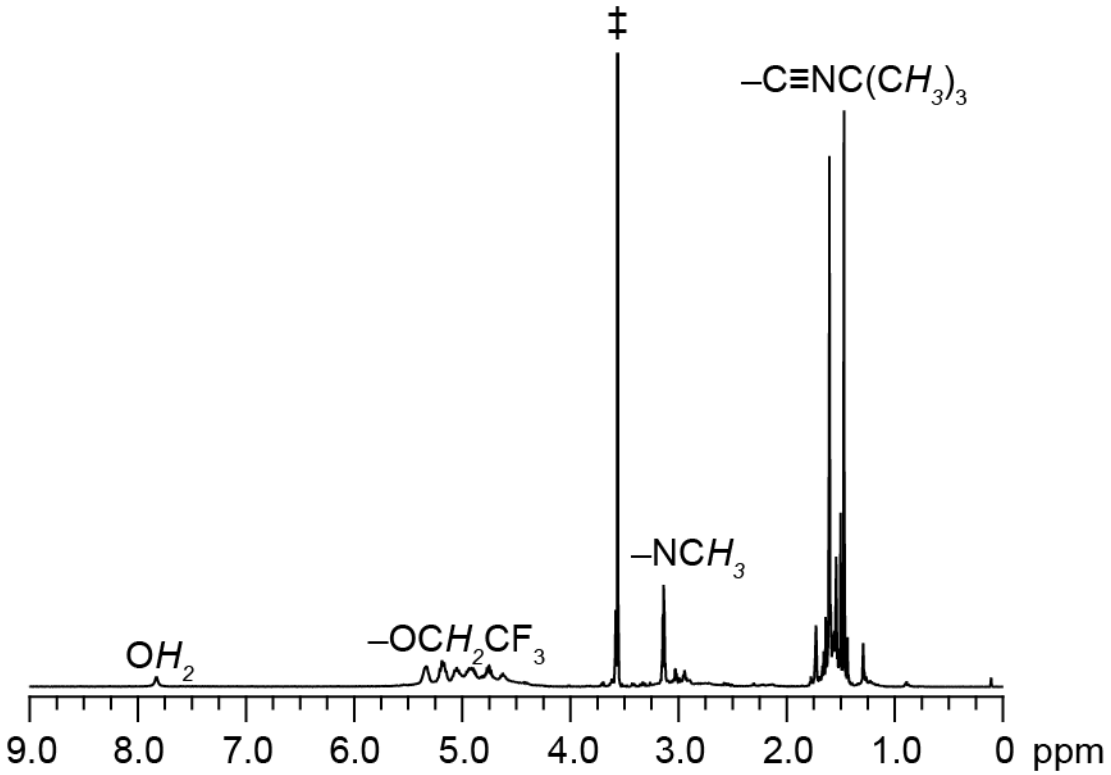

Figure S8. ^{1}H NMR spectrum (500 MHz) recorded 10 min after the addition of HCl (1.1 eq.) to a solution of **2** (13 mM) in THF-d_8. Peaks corresponding to **4**, the major product, are marked with their appropriate assignments. The peak for 1,4-dioxane, which originates from the HCl stock solution that was introduced, is also marked (‡). All other peaks, except residual proteo solvent resonances (1.73 and 3.58 ppm), are attributed to **5** and some minor side products.

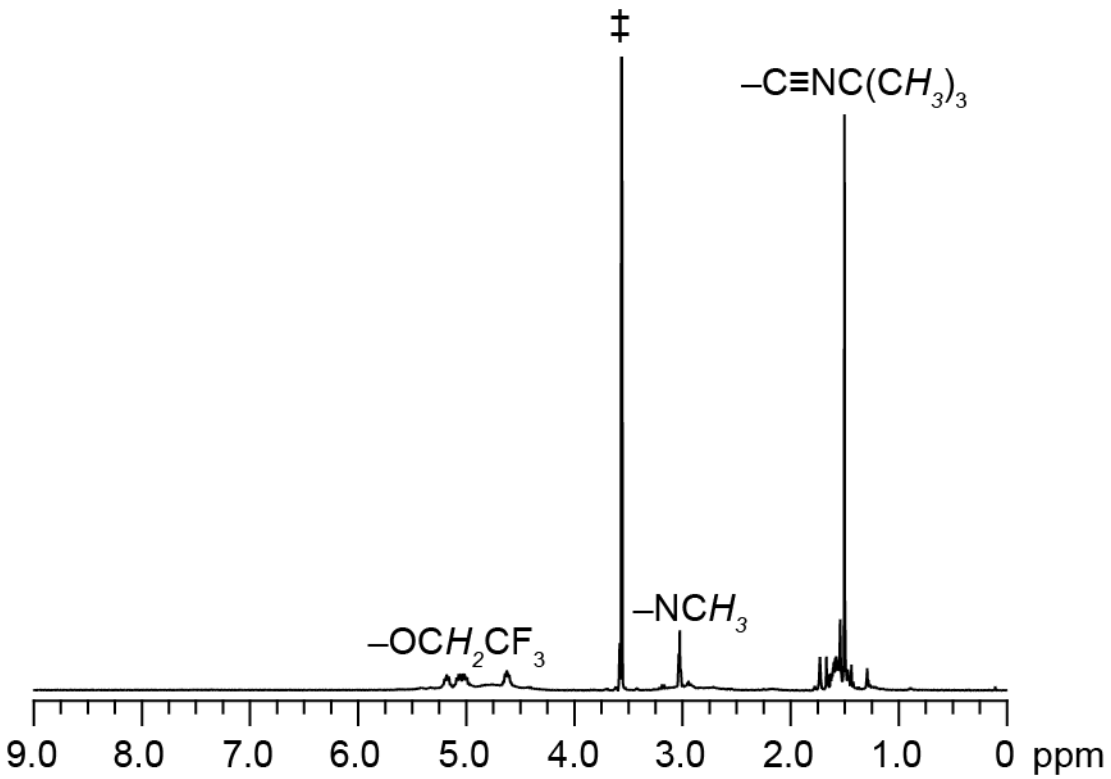

Figure S9. ^{1}H NMR spectrum (500 MHz) recorded 48 h after the addition of HCl (1.1 eq) to a solution of **2** (13 mM) in THF-d_8. Peaks corresponding to **5**, the major product, are marked with their appropriate assignments. The peak for 1,4-dioxane, which originates from the HCl stock solution that was introduced, is also marked (‡). All other peaks, except residual proteo solvent resonances (1.73 and 3.58 ppm), are attributed to minor side products.

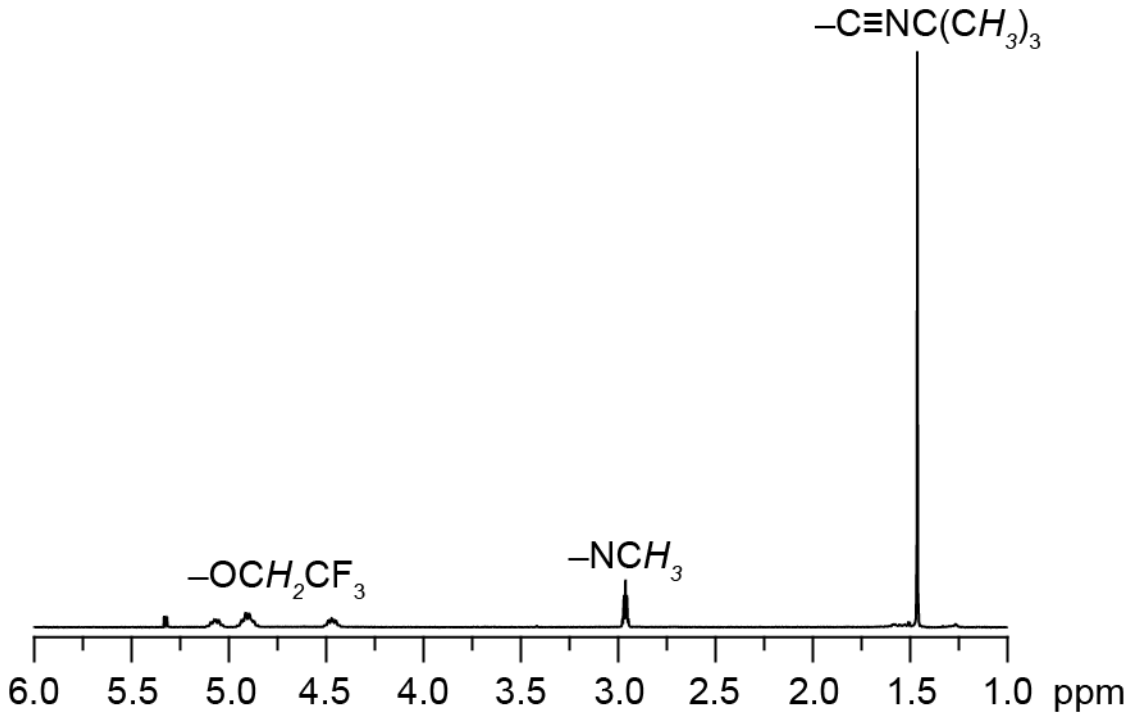

Figure S10. ^{1}H NMR spectrum of **5**, purified by crystallization, recorded in CD_2Cl_2 at 500 MHz. The residual proteo solvent resonance is at 5.32 ppm.

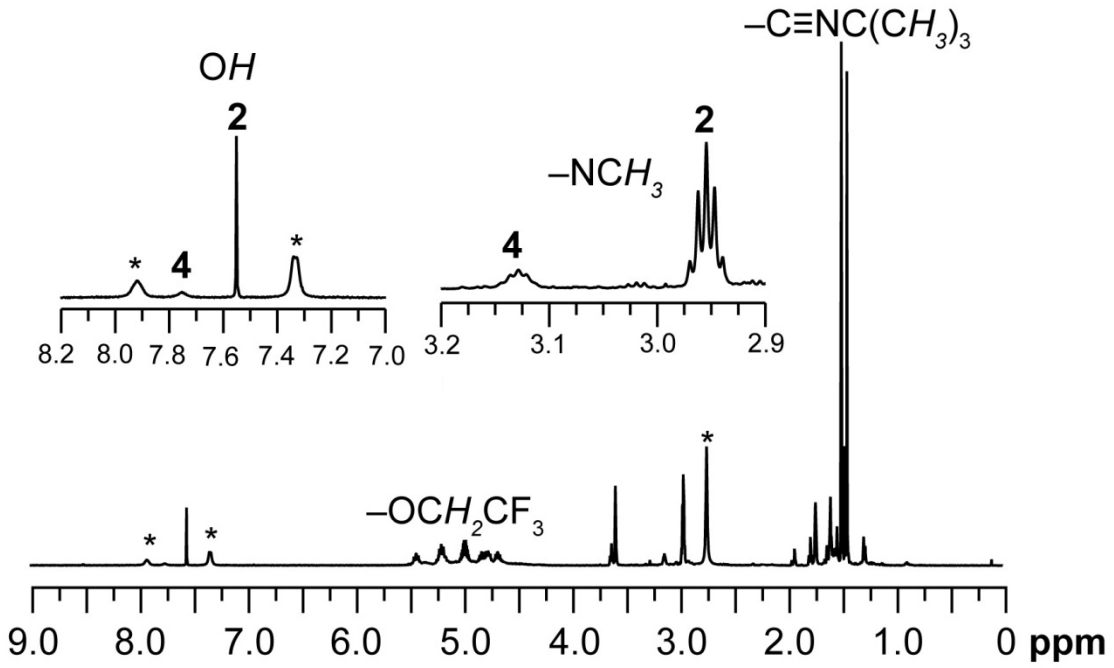

Figure S11. ^{1}H NMR spectrum recorded 10 min after the addition of 2,6-lutidinium chloride (2 eq) to a solution of **2** (8.6 mM) in 7:1THF-d_8/CD_3CN. The insets show the O*H* and –NCH_3 regions of the spectrum, where the assignments of the major iridium-containing species are most clear. In these insets, the peaks corresponding to **2** and **4** are marked with their appropriate assignments. The peaks corresponding to rapidly exchanging 2,6-lutidinium/2,6-lutidine also marked (*).

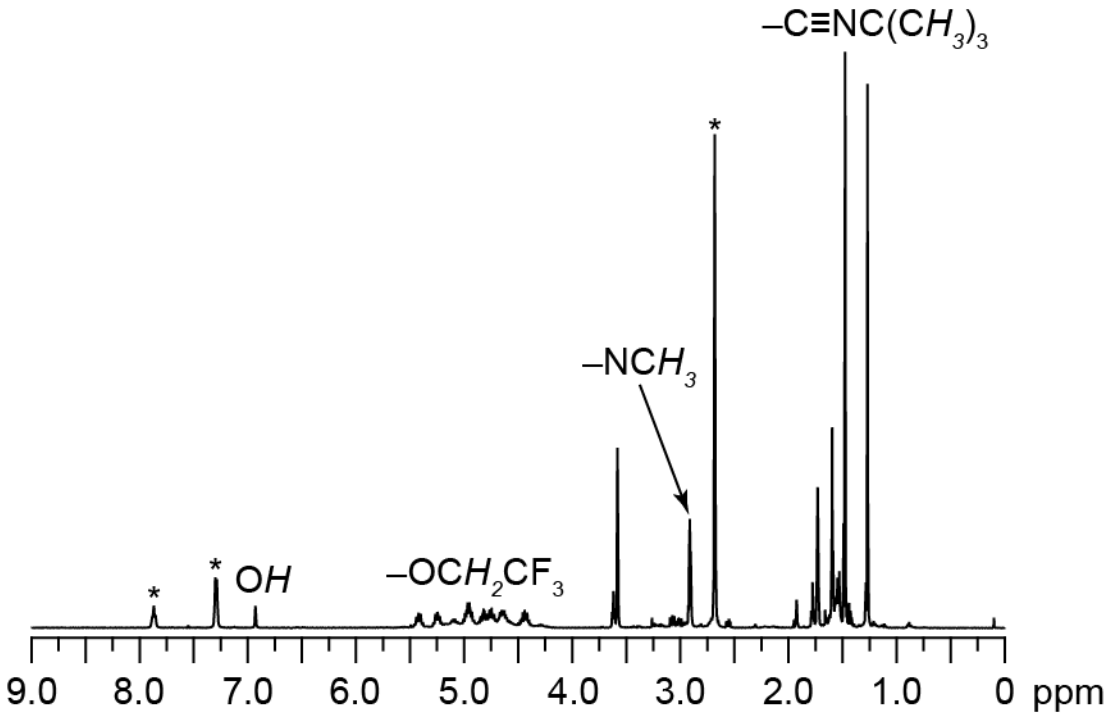

Figure S12. ^{1}H NMR spectrum recorded 15 h after the addition of 2,6-lutidinium chloride (2 eq) to a solution of **2** (8.6 mM) in 7:1THF-d_8/CD_3CN. Peaks corresponding to **3**, the major product, are marked with their appropriate assignments. The peaks corresponding to rapidly exchanging 2,6-lutidinium/2,6-lutidine also marked (*). All other peaks, except residual proteo solvent resonances (1.73 and 3.58 ppm for THF, 1.94 ppm for MeCN), are attributed to side products.