Supporting Information

Synthesis and Characterization of (^{DIPP}CCC)Fe Complexes: A Zwitterionic Metalation Method and CO_2 Reactivity

*Bailey J. Jackson, Daniel C. Najera, Ellen M. Matson, Toby J. Woods, Jeffery A. Bertke, and Alison R. Fout**

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Matthews Ave. Urbana, IL 61801.

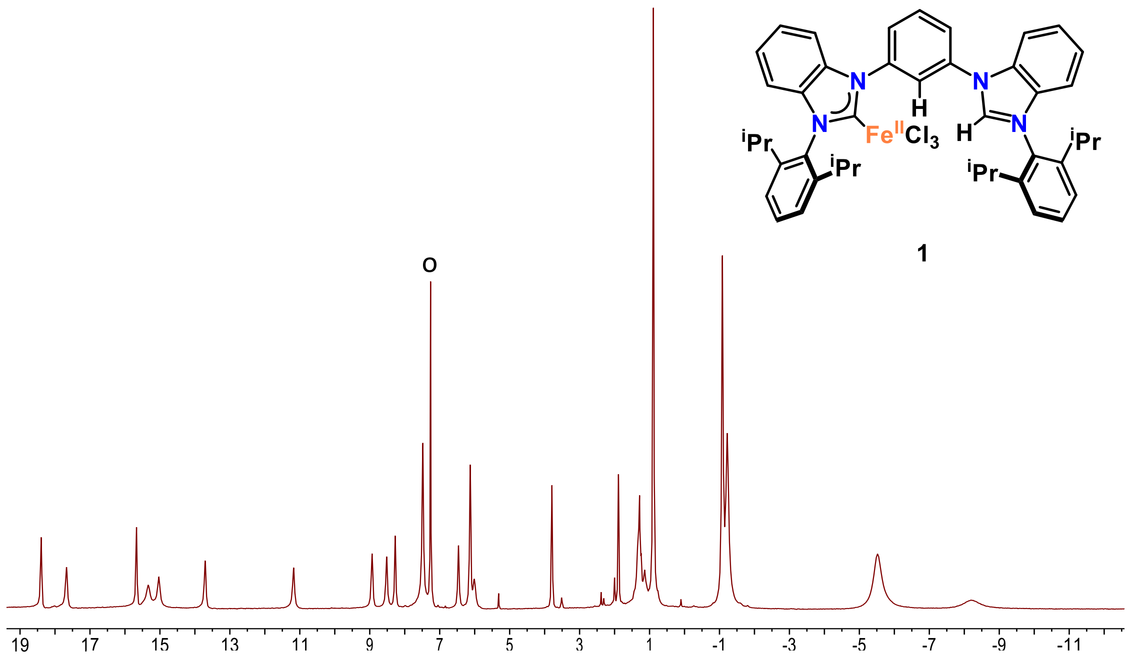

Figure S1. $H_2(^{DIPP}CCC)FeCl_3$ (**1**) ^1H NMR spectrum (° denotes $CDCl_3$).

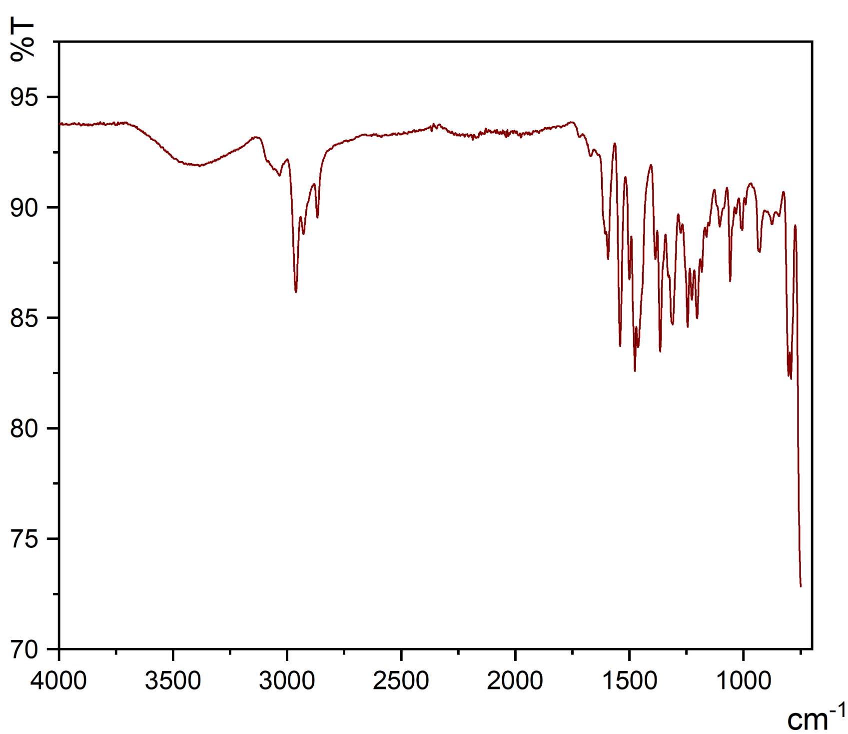

Figure S2. $H_2(^{DIPP}CCC)FeCl_3$ (**1**) IR spectrum.

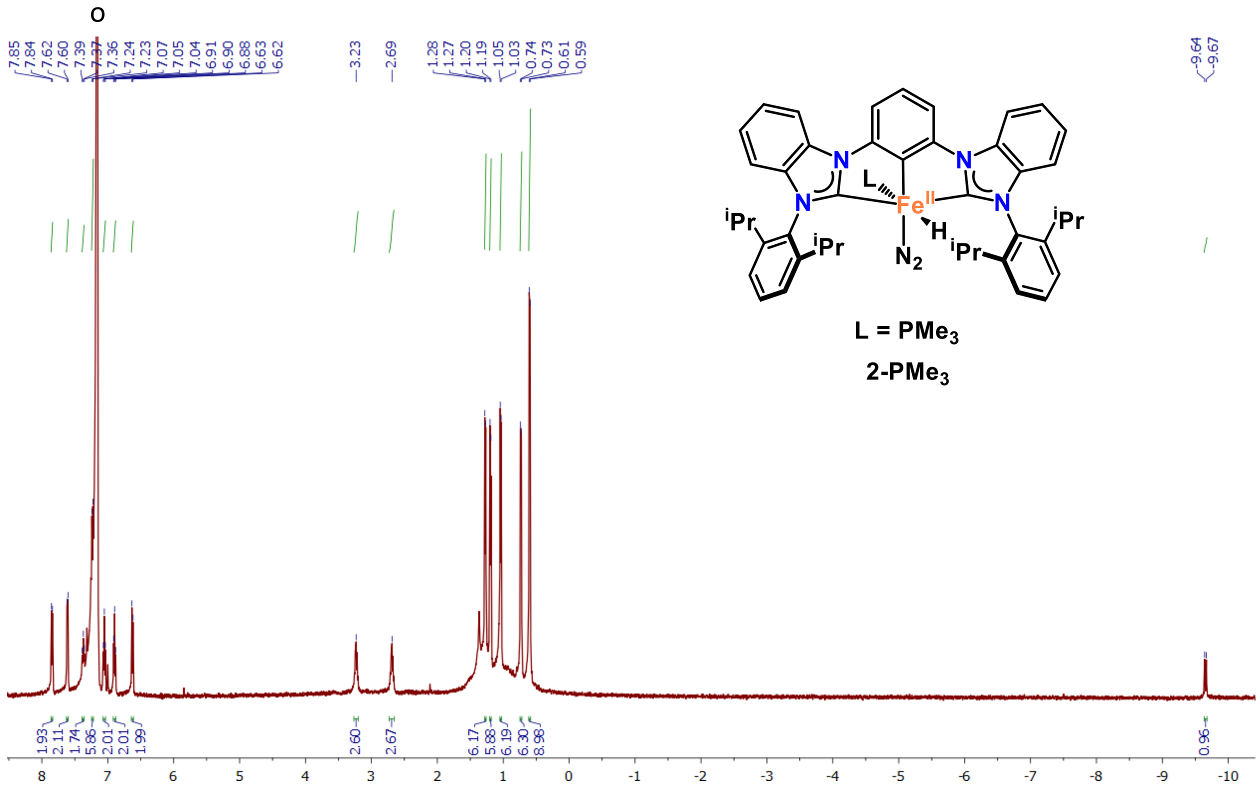

Figure S3. H(^{DIPP}CCC)Fe(II)H(PMe$_3$)(N$_2$) (**2-PMe$_3$**) ^{1}H NMR spectrum (° denotes C_6D_6).

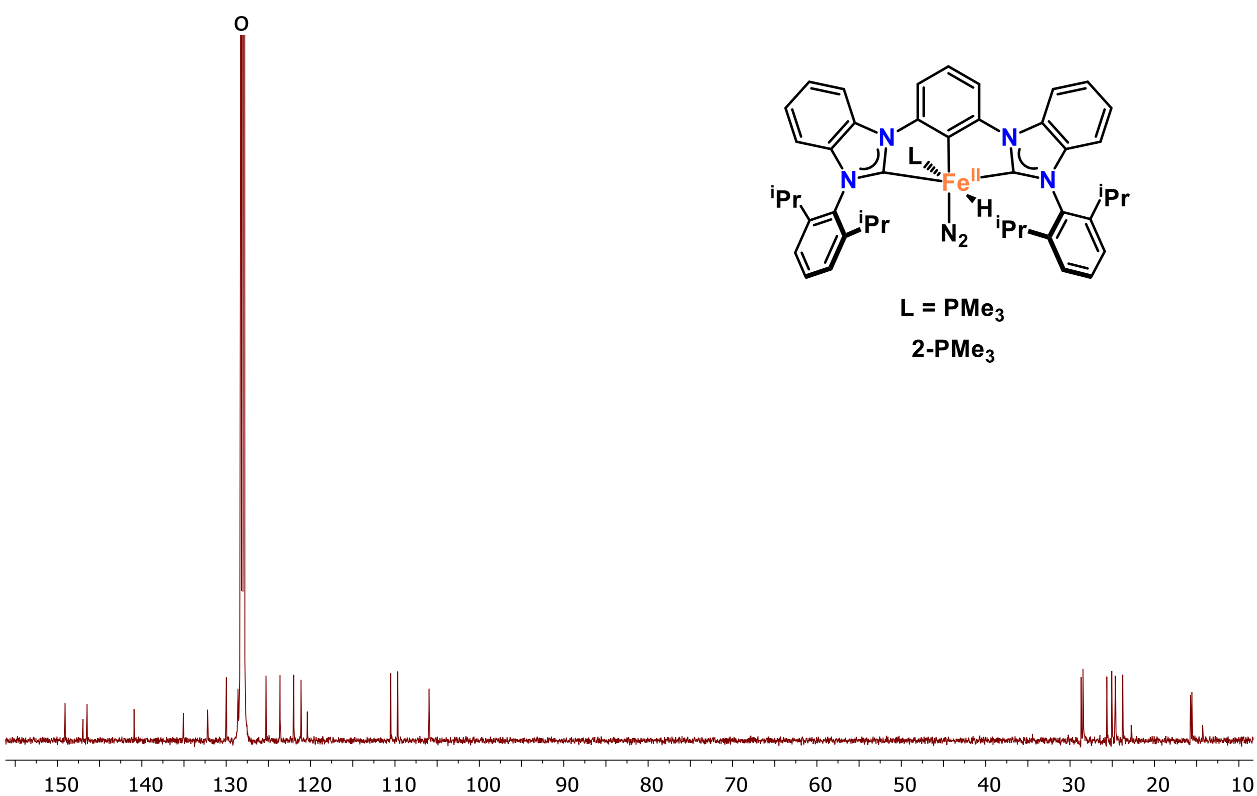

Figure S4. (^{DIPP}CCC)Fe(II)H(PMe$_3$)(N$_2$) (**2-PMe$_3$**) ^{13}C NMR spectrum (° denotes C_6D_6).

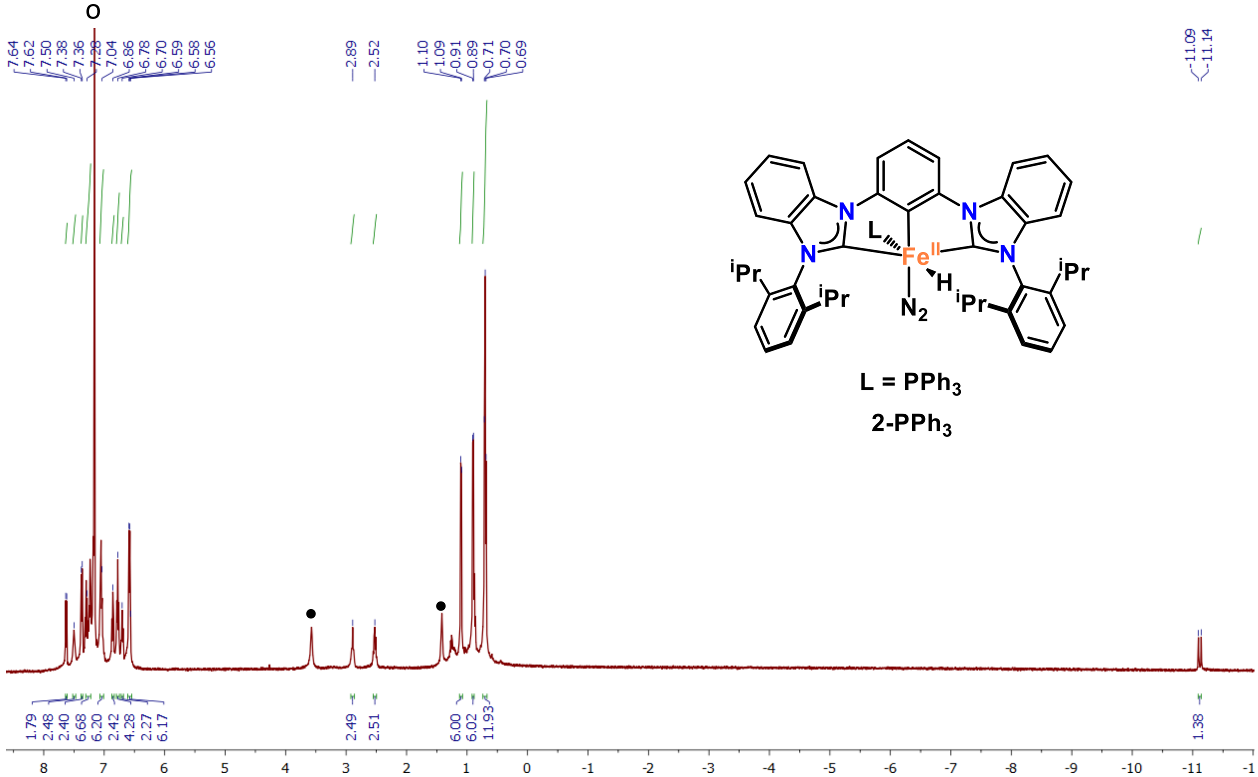

Figure S5. (^{DIPP}CCC)Fe(II)H(PPh_3)(N_2) (**2-PPh₃**) ^{1}H NMR spectrum (• denotes THF, ° denotes C_6D_6).

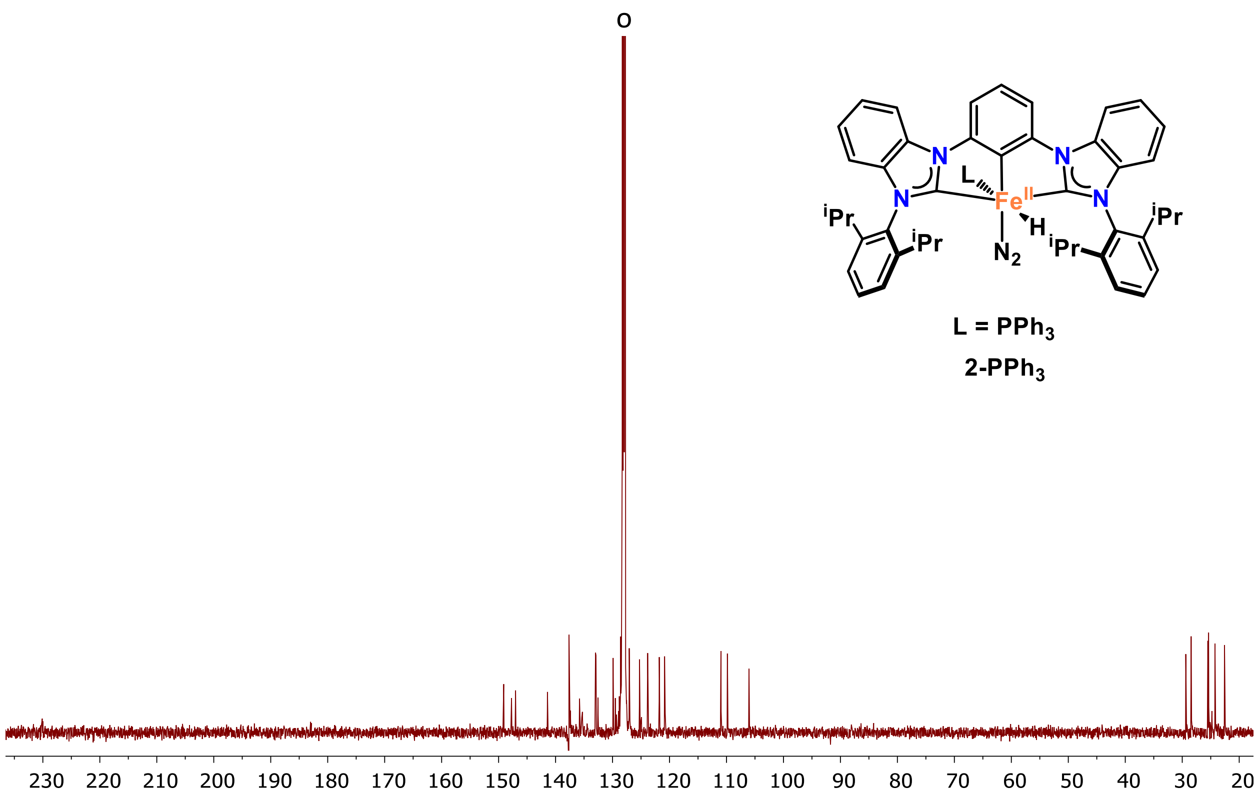

Figure S6. (^{DIPP}CCC)Fe(II)H(PPh_3)(N_2) (**2-PPh₃**) ^{13}C NMR spectrum (° denotes C_6D_6).

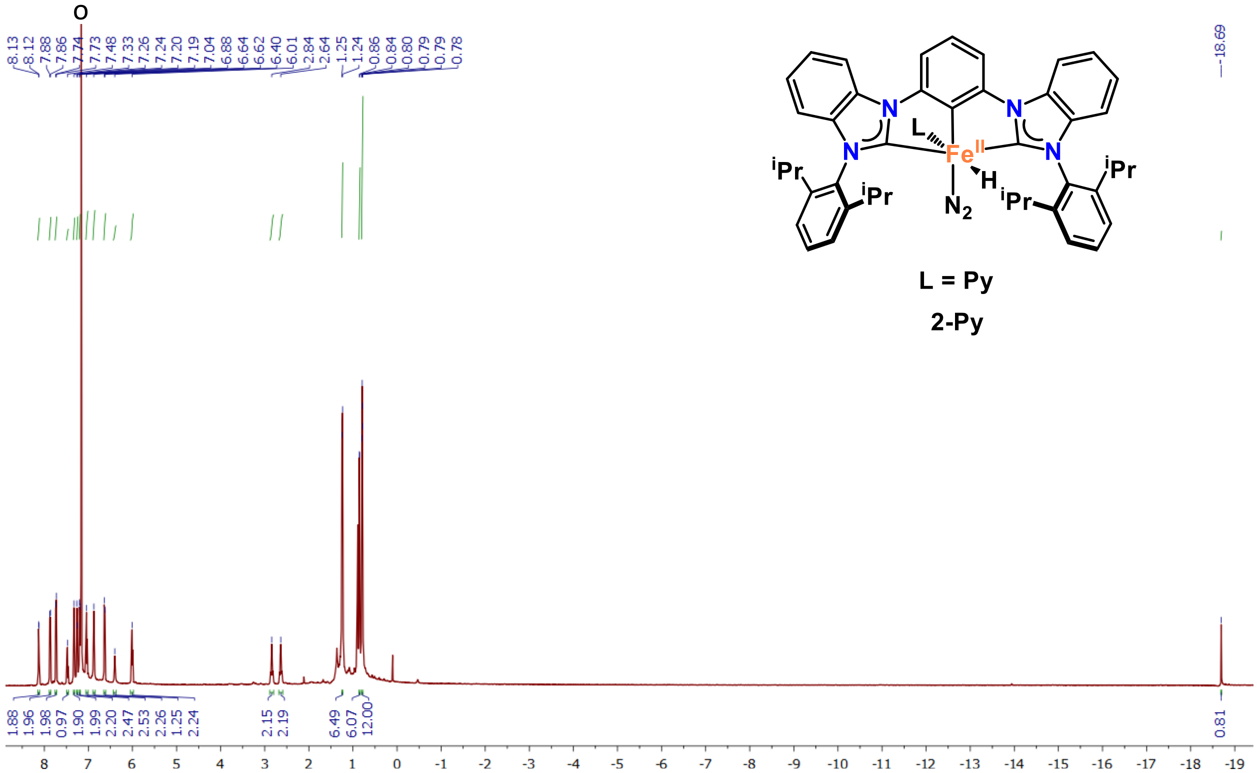

Figure S7. (^{DIPP}CCC)Fe(II)H(Py)(N_2) (**2-Py**) ^{1}H NMR spectrum (° denotes C_6D_6).

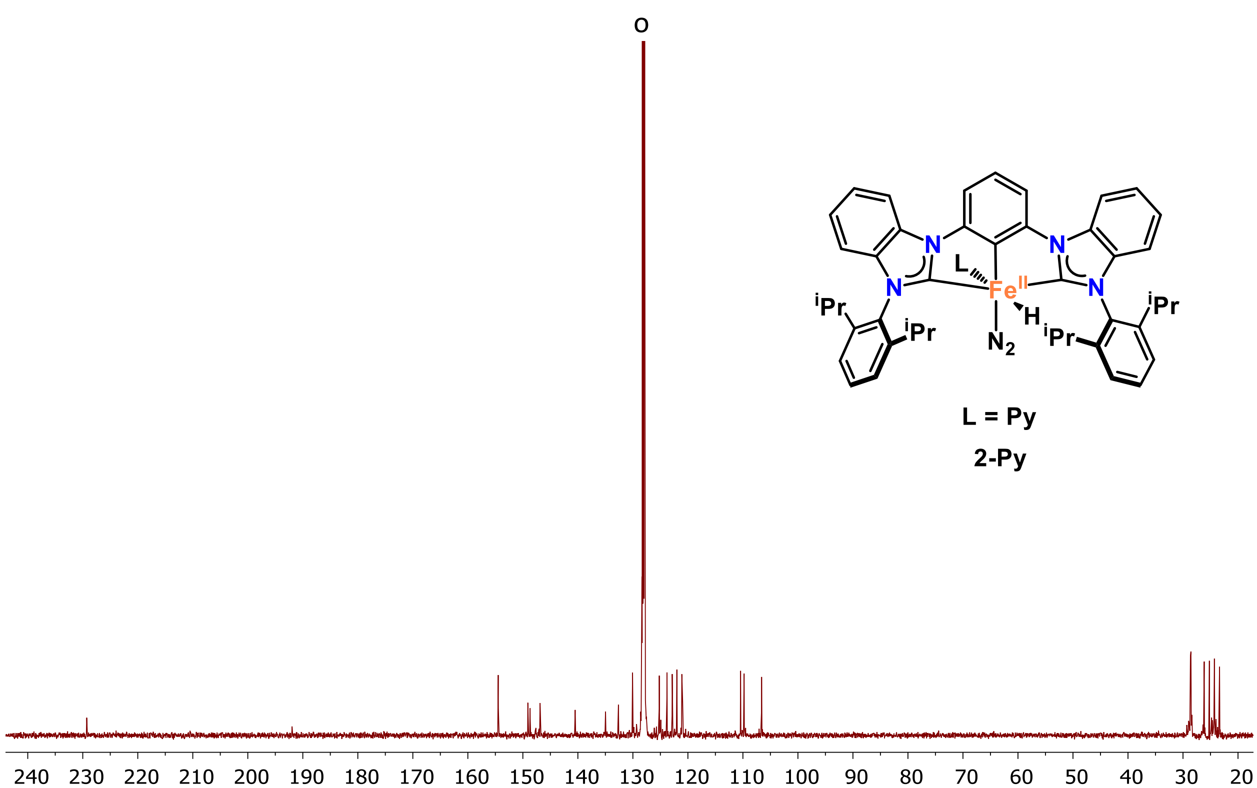

Figure S8. (^{DIPP}CCC)Fe(II)H(Py)(N_2) (**2-Py**) ^{13}C NMR spectrum (° denotes C_6D_6).

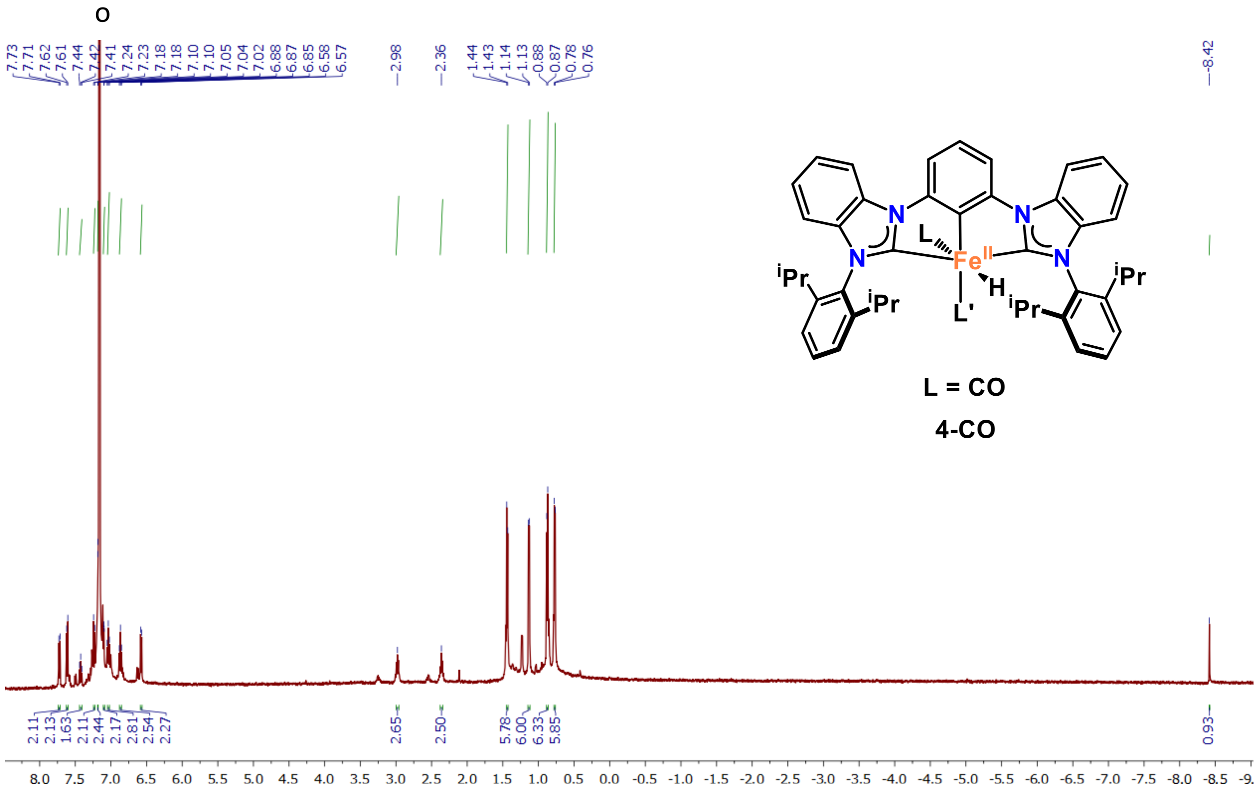

Figure S9. (^{DIPP}CCC)Fe(II)H(CO)$_2$ (**4-CO**) ^{1}H NMR spectrum (° denotes C_6D_6).

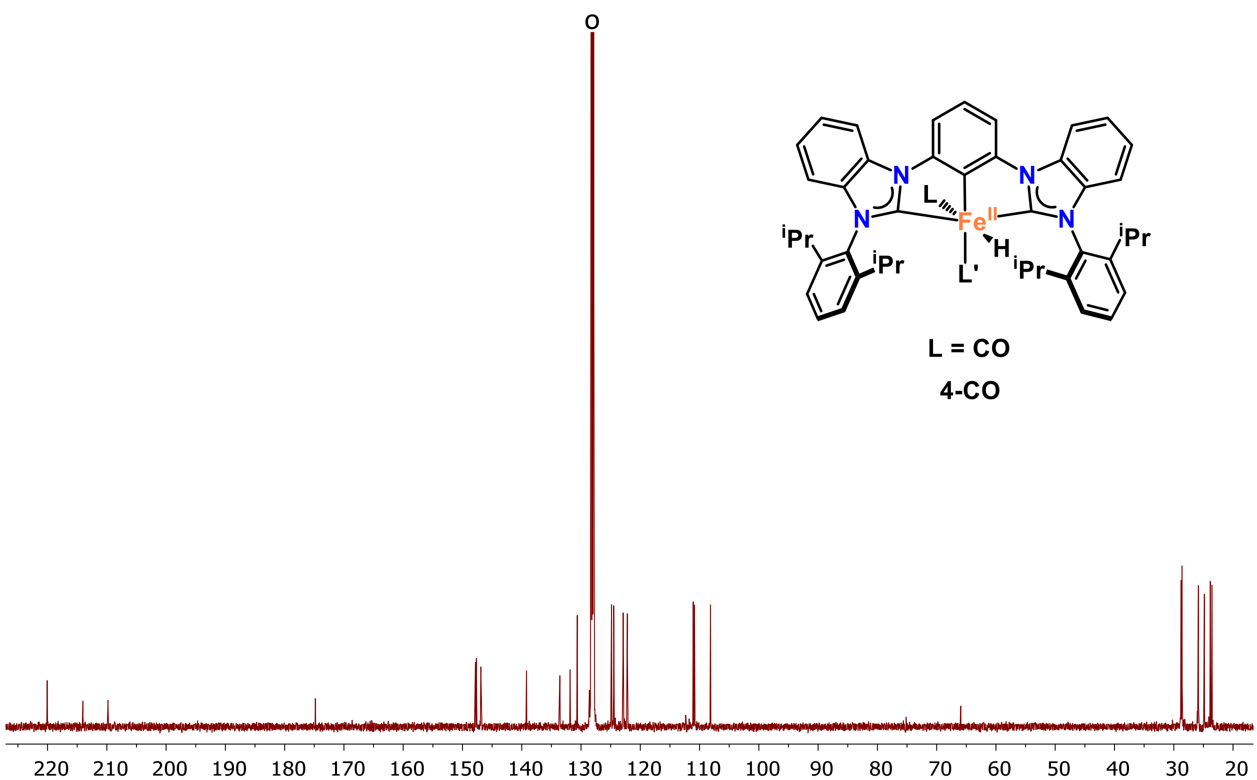

Figure S10. (^{DIPP}CCC)Fe(II)H(CO)$_2$ (**4-CO**) ^{13}C NMR spectrum (° denotes C_6D_6).

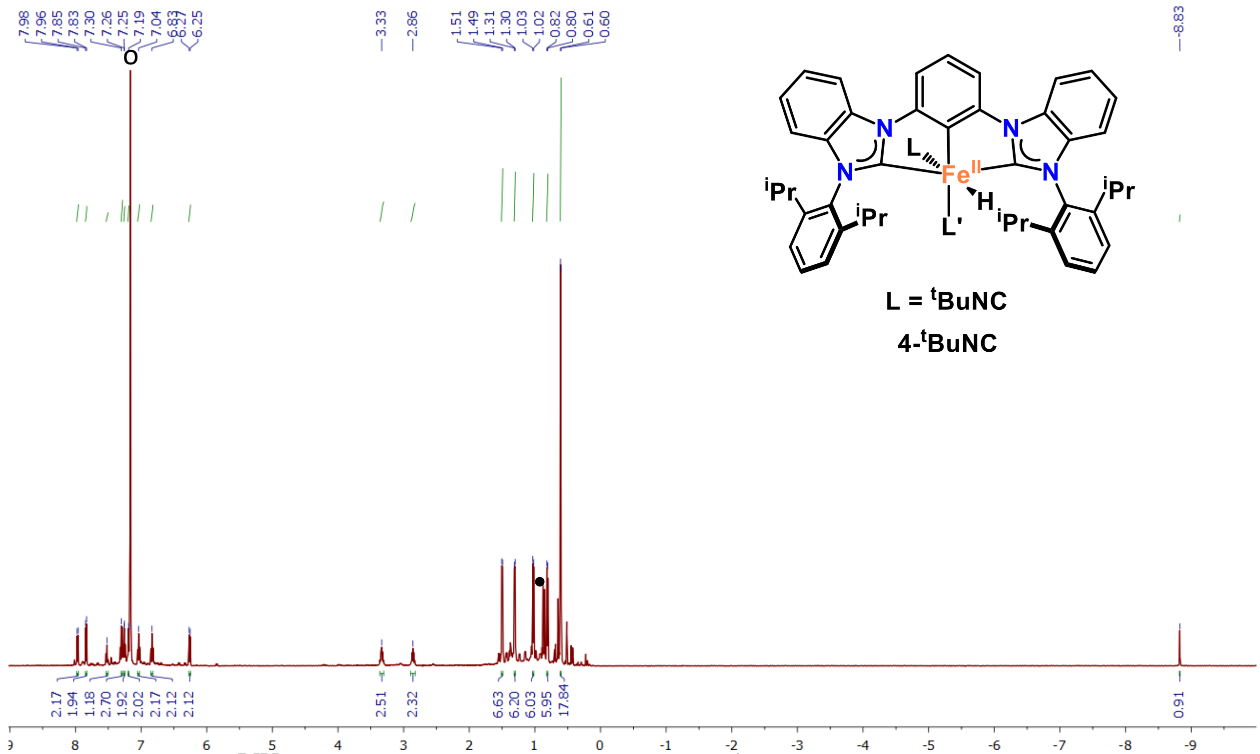

Figure S11. (^{DIPP}CCC)Fe(II)H(^{t}BuNC)$_2$ (**4-^{t}BuNC**) ^{1}H NMR spectrum (• denotes free ^{t}BuNC ° denotes C_6D_6).

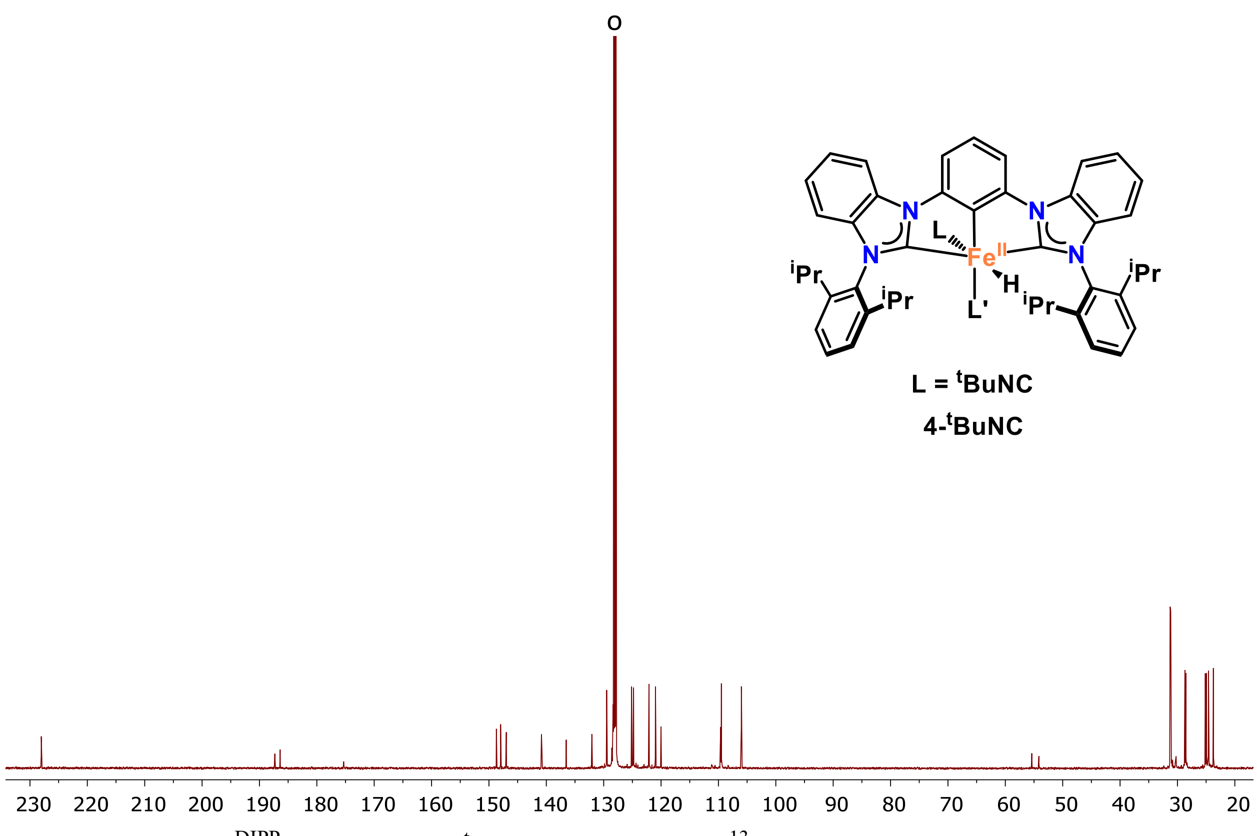

Figure S12. (^{DIPP}CCC)Fe(II)H(^{t}BuNC)$_2$ (**4-^{t}BuNC**) ^{13}C NMR spectrum (° denotes C_6D_6).

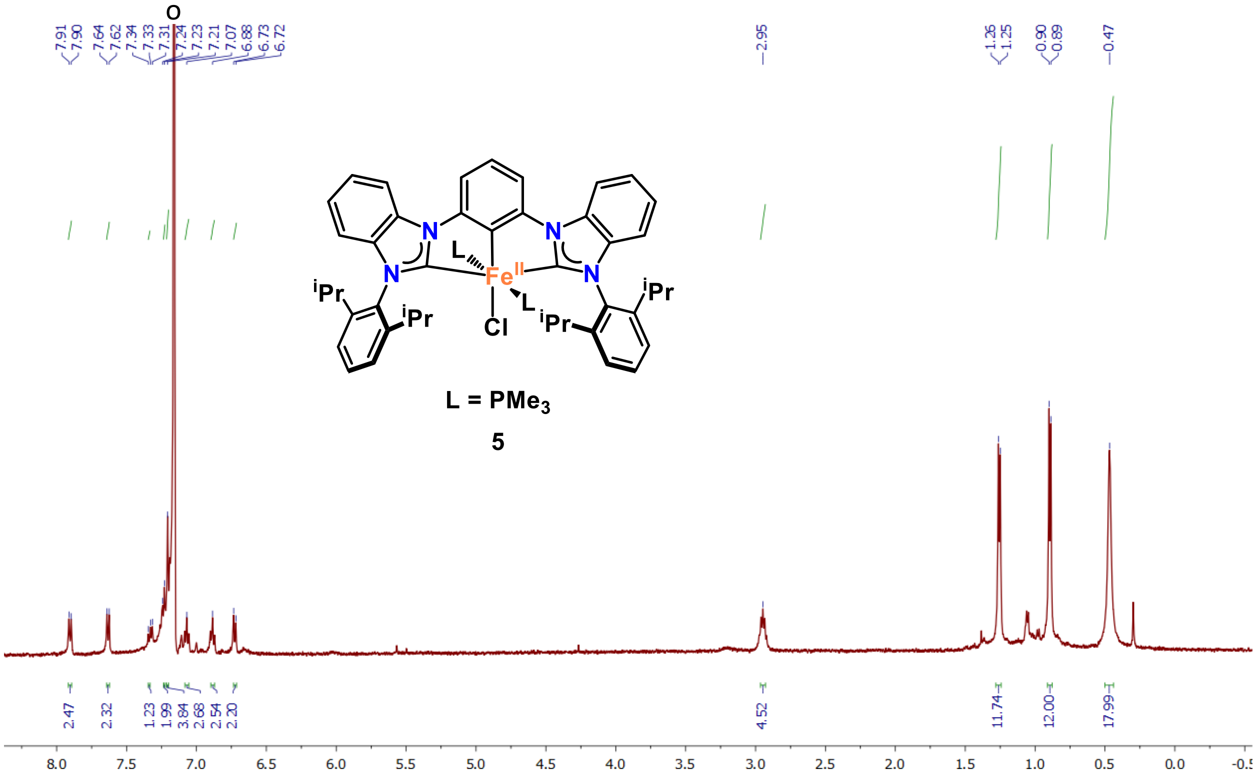

Figure S13. (^{DIPP}CCC)Fe(II)Cl(PMe$_3$)$_2$ (**5**) ^{1}H NMR spectrum (° denotes C_6D_6).

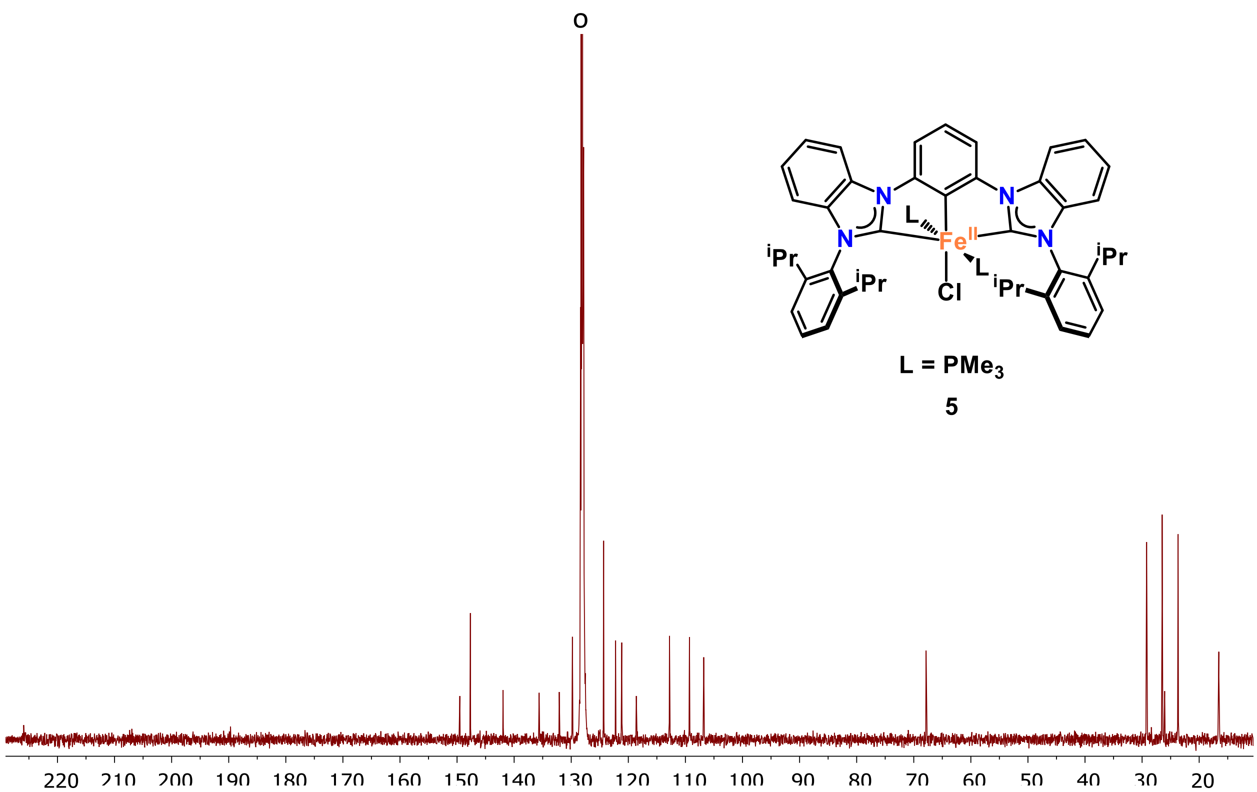

Figure S14. (^{DIPP}CCC)Fe(II)Cl(PMe$_3$)$_2$ (**5**) ^{13}C NMR spectrum (° denotes C_6D_6).

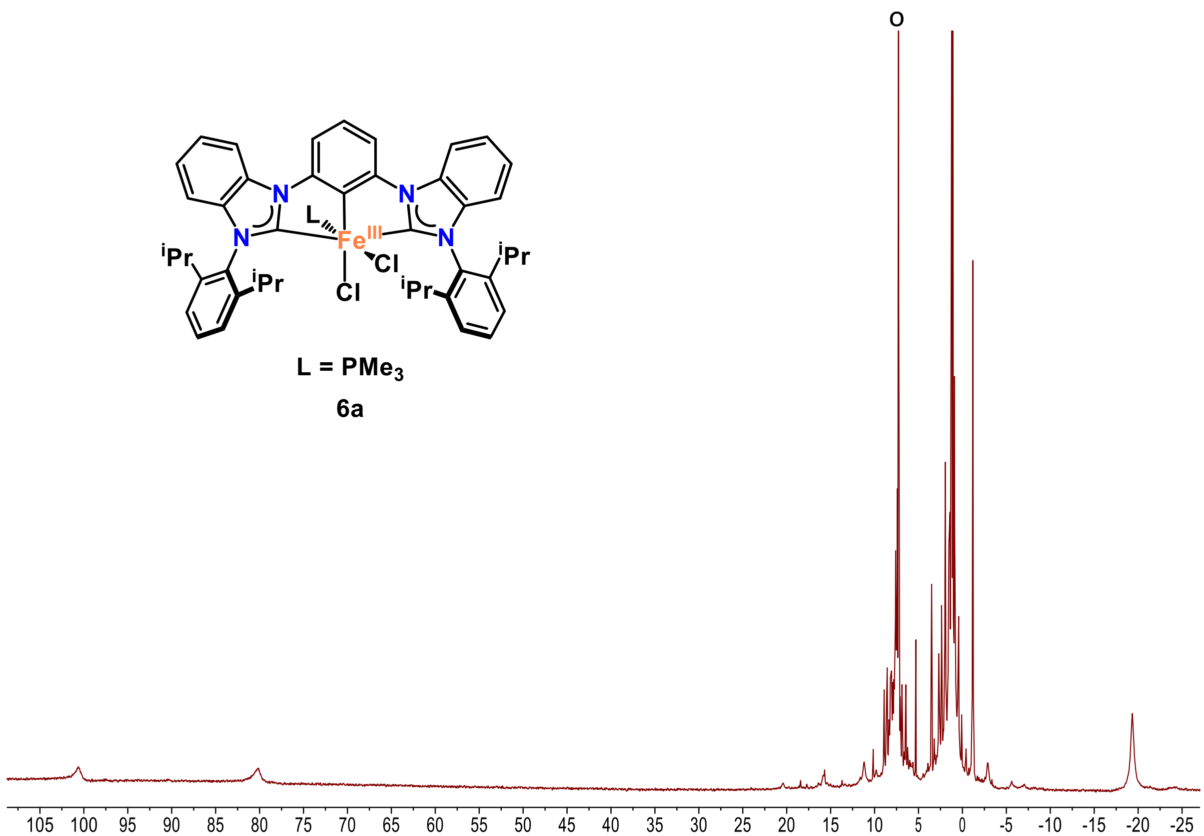

Figure S15. (^{DIPP}CCC)Fe(III)Cl_2(PMe_3) (**6a**) ^{1}H NMR spectrum (^{o}denotes $CDCl_3$).

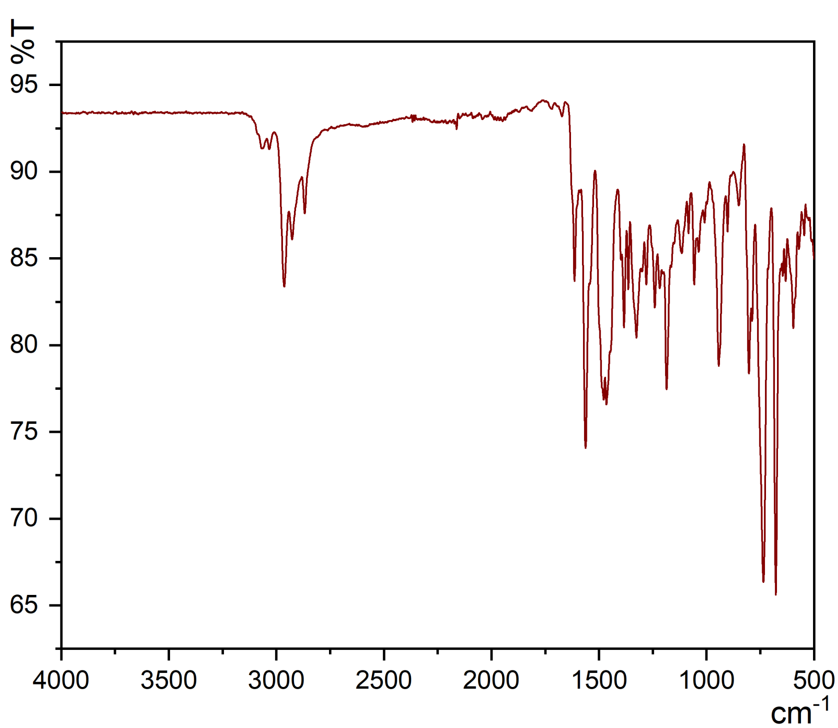

Figure S16. (^{DIPP}CCC)Fe(III)Cl_2(PMe_3) (**6a**) IR spectrum.

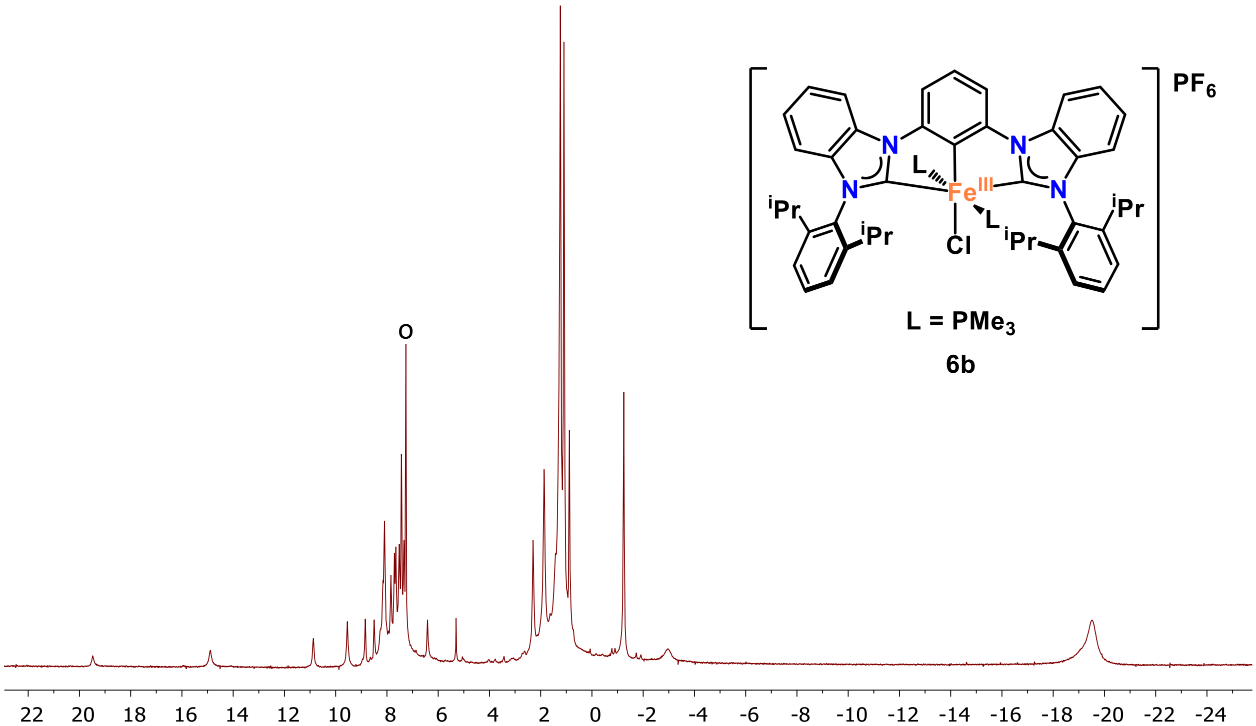

Figure S17. (^{DIPP}CCC)Fe(III)Cl(PMe_3)$_2$$PF_6$ (**6b**) ^{1}H NMR spectrum (° denotes C_6D_6).

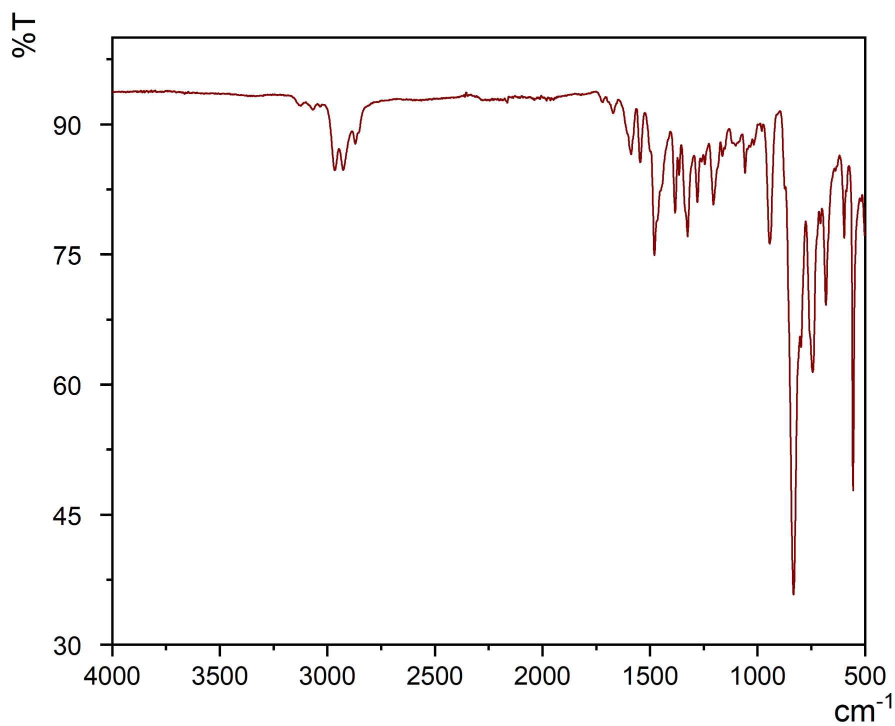

Figure S18. (^{DIPP}CCC)Fe(III)Cl(PMe_3)$_2$$PF_6$ (**6b**) IR spectrum.

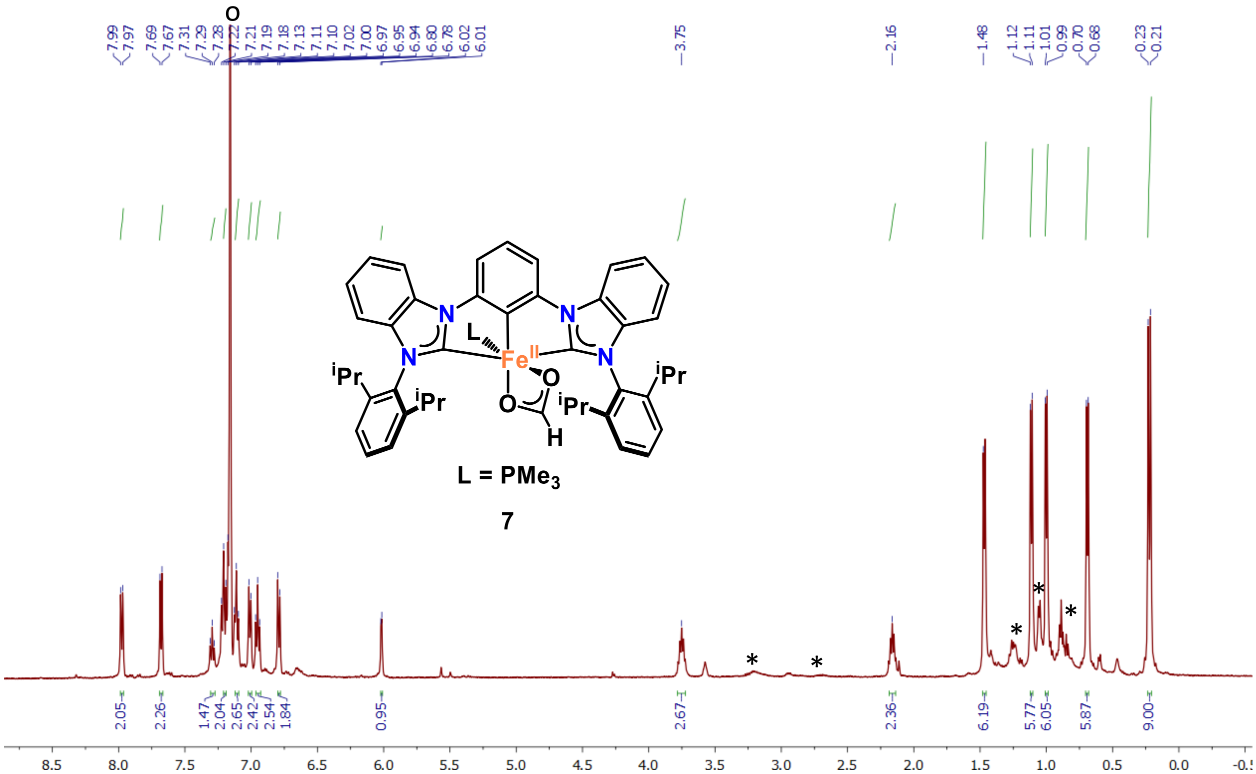

Figure S19. (^{DIPP}CCC)Fe(II)(κ^2-OOCH)(PMe_3) (**7**) ^{1}H NMR spectrum, (* denotes **2-PMe$_3$**, ° denotes C_6D_6).

Table S1. Crystallographic parameters for H_2(^{DIPP}CCC)Fe(II)Cl_3 and (^{DIPP}CCC)Fe(II)H(PMe_3)(N_2).

Compound	H_2(^{DIPP}CCC)Fe(II)Cl_3 (**1**)	(^{DIPP}CCC)Fe(II)H(PMe_3)(N_2) (**2-PMe$_3$**)
Empirical formula	$C_{44}H_{47}N_4Cl_3Fe$	$C_{52}H_{67}N_6PFe$
Formula weight	794.05	862.94
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a/Å	16.2332(7)	12.0449(5)
b/Å	17.6703(7)	14.6183(6)
c/Å	16.3741(7)	15.7848(7)
α/°	90.00	107.2907(18)
β/°	98.5058(15)	108.0980(19)
γ/°	90.00	103.6701(19)
Volume/Å^3	4645.2(3)	2351.23(18)
Z	4	2
Reflections collected	43720	82885
Independent reflections	8519 [R_{int} = 0.0289, R_{sigma} = 0.0205]	17197 [R_{int} = 0.0426, R_{sigma} = 0.0366]
Goodness-of-fit	1.058	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0855	R_1 = 0.0544, wR_2 = 0.0934
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.0907	R_1 = 0.0388, wR_2 = 0.1021

Table S2. Crystallographic parameters (^{DIPP}CCC)Fe(II)Cl(PMe_3)$_2$ and (^{DIPP}CCC)Fe(III)(Cl)$_2$(PMe_3).

Compound	(^{DIPP}CCC)Fe(II)H(PPh_3)(N_2) **(2-PPh₃)**	(^{DIPP}CCC)Fe(II)Cl(PMe_3)$_2$ (**5**)
Empirical formula	$C_{62}H_{61}N_6PFe$	$C_{50}H_{63}N_4P_2ClFe$
Formula weight	976.98	873.28
Temperature/K	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a/Å	11.3052(6)	21.1714(11)
b/Å	17.0256(9)	11.0332(5)
c/Å	18.5371(10)	18.8162(10)
α/°	67.3098(10)	90
β/°	77.1910(9)	90.101(2)
γ/°	73.9916(9)	90
Volume/Å^3	3137.3(3)	4395.2(4)
Z	2	4
Reflections collected	11080	92760
Independent reflections	4062 [R_{int} = 0.0467, R_{sigma} = 0.0396]	4062 [R_{int} = 0.0472, R_{sigma} = 0.0135]
Goodness-of-fit	0.885	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1263	R_1 = 0.0479, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.1329	R_1 = 0.0510, wR_2 = 0.1201

Table S3. Crystallographic parameters for (^{DIPP}CCC)Fe(III)(Cl)$_2$(PMe_3).

Compound	(^{DIPP}CCC)Fe(III)(Cl)$_2$(PMe_3) (**6a**)
Empirical formula	$C_{47}H_{54}Cl_2FeN_4P$
Formula weight	832.66
Temperature/K	112(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.7730(17)
b/Å	14.849(2)
c/Å	16.687(2)
α/°	91.381(8)
β/°	95.761(8)
γ/°	93.318(8)
Volume/Å^3	2650.2(7)
Z	2
Reflections collected	18868
Independent reflections	18868 [R_{sigma} = 0.1108]
Goodness-of-fit	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0867, wR_2 = 0.1941
Final R indexes [all data]	R_1 = 0.1373, wR_2 = 0.2223