Supporting Information

Heterolytic H_2 Cleavage and Catalytic Hydrogenation by an Iron Metallaboratrane

Henry Fong, Marc-Etienne Moret, Yunho Lee, and Jonas C. Peters*

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Experimental

Geometry optimizations were performed using the Gaussian03 package.[1] B3LYP exchange-correlation functional was employed with a 6-31G(d) basis set. The GDIIS algorithm was used.

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[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.;

A full frequency calculation was performed on each structure to ensure that they were the true minima. A single negative vibrational frequency was observed for the transition state between **3** and its equatorial-H_2 isomer, confirming that this structure was the transition state. See SI for full a description of the computational method.

To determine the energy difference between **3** and its equatorial-H_2 isomer, the energy differences of the respective DFT calculated isomers were compared. The coordinates derived from the XRD structure of **2** were used as the input coordinates. The dinitrogen ligand was replaced with a dihydrogen ligand (H-H distance = 0.9 Å). For the equitorial-H_2 isomer, an axial hydride ligand *trans* to boron along with an equatorial H_2 (H-H distance = 0.9 Å) ligand bisecting P2 and P3 were used in the starting geometry. For the H_2 ligand, the H-H bond was parallel to the Fe-B bond. The starting and optimized coordinates are listed below (see page S42).

Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; G. A. Voth, P. S.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford, 2004.

NMR Spectra/Data

^{1}H NMR Spectra

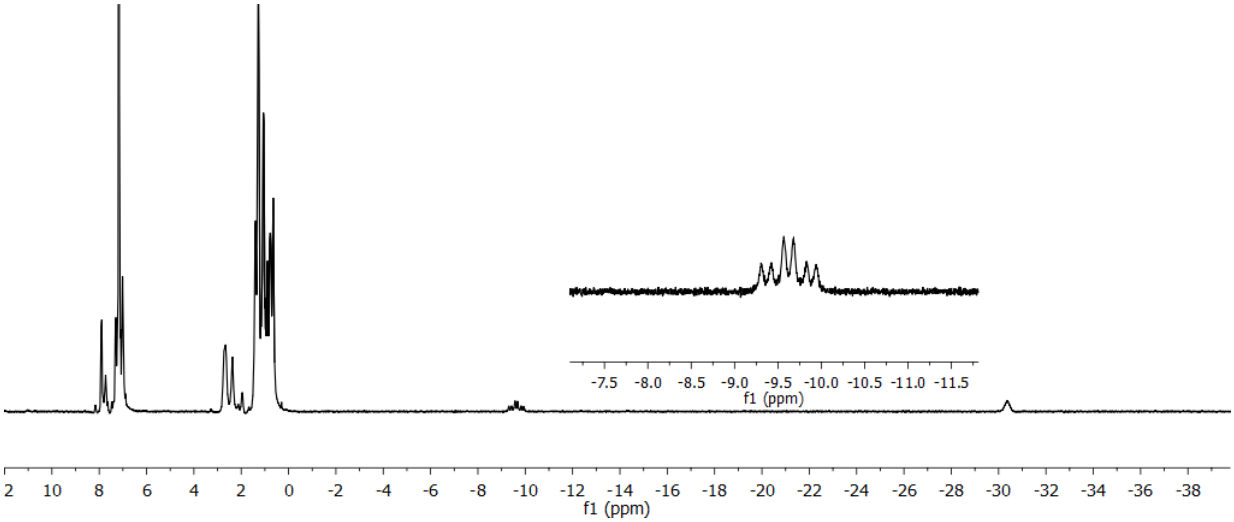

Fig. S1 ^{1}H NMR spectrum of **2**, (TPB)(μ-H)Fe(N_2)(H), in C_6D_6.

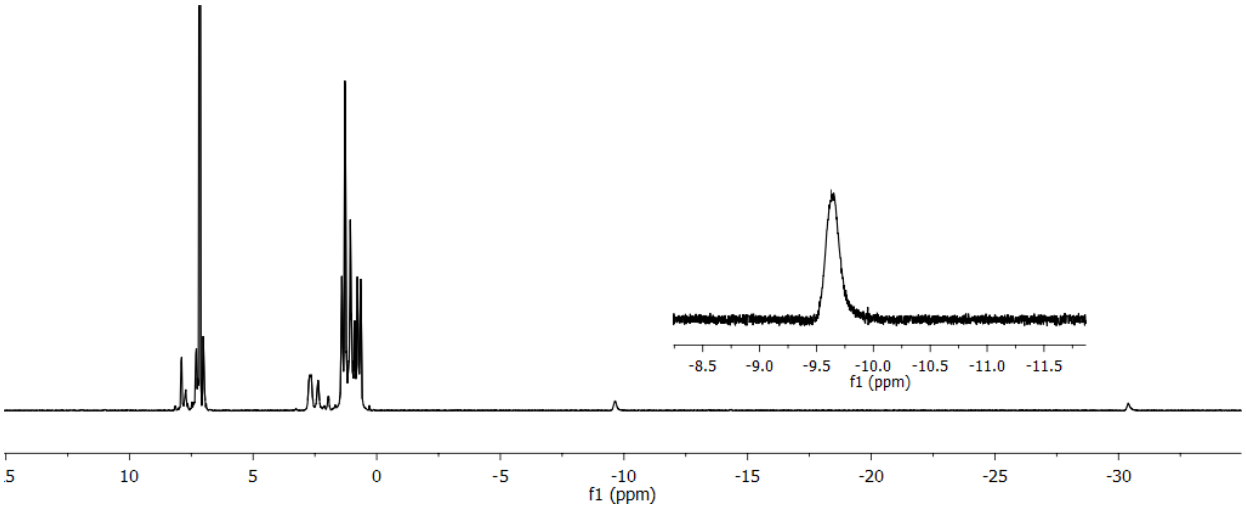

Fig. S2 ^{1}H{^{31}P} NMR spectrum of **2**, (TPB)(μ-H)Fe(N_2)(H), in C_6D_6.

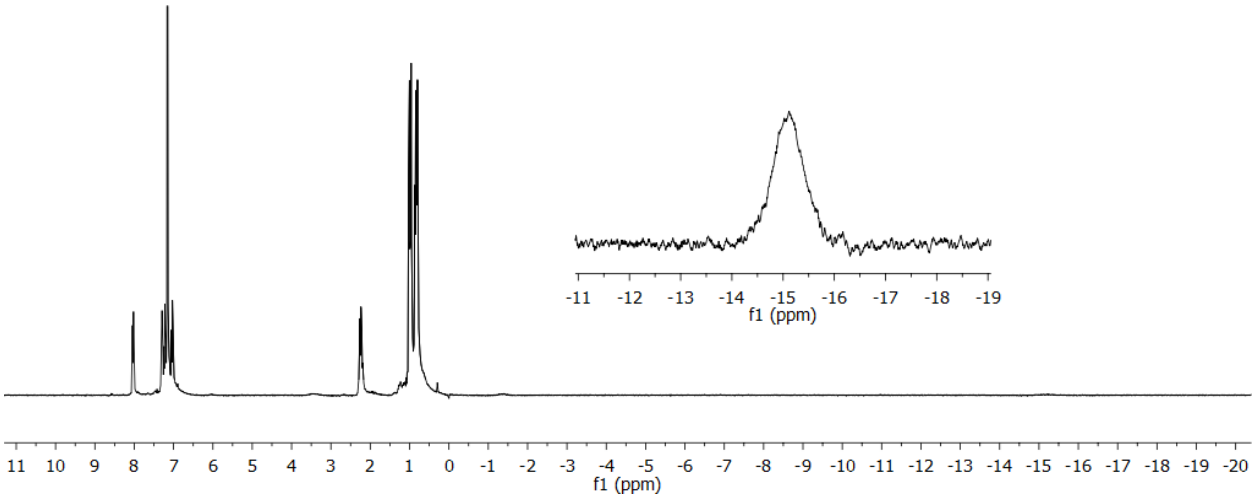

Fig. S3 ^{1}H NMR spectrum of **3**, (TPB)(μ-H)Fe(H_2)(H), in C_6D_6.

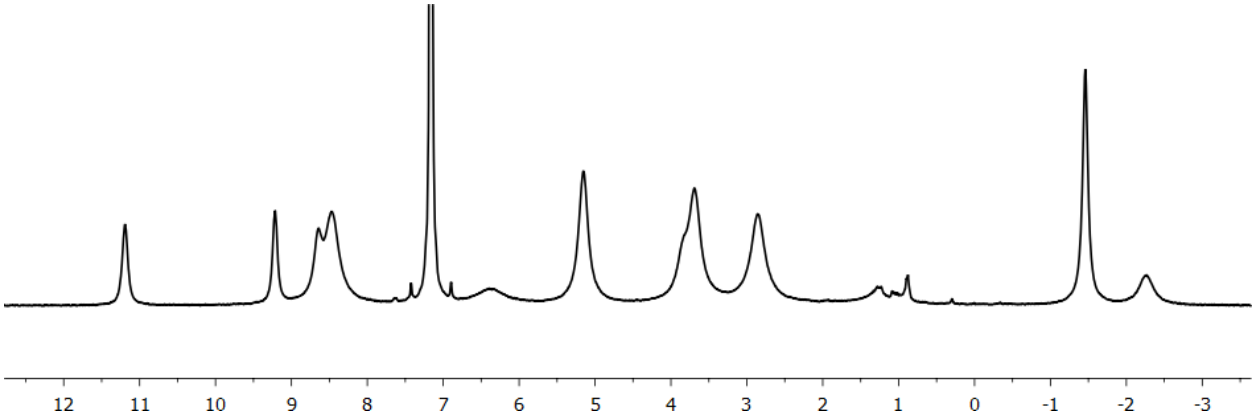

Fig. S4 ^{1}H NMR spectrum of **4**, (TPB)Fe(CN^{t}Bu), in C_6D_6.

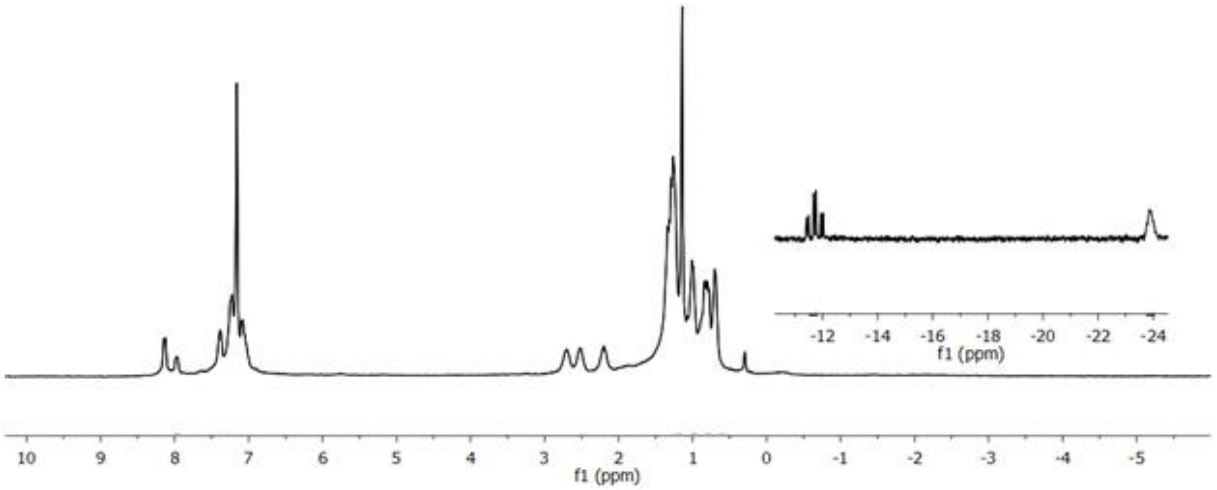

Fig. S5 ^{1}H NMR spectrum of **5**, (TPB)(μ-H)Fe(CN^{t}Bu)(H), in C_6D_6.

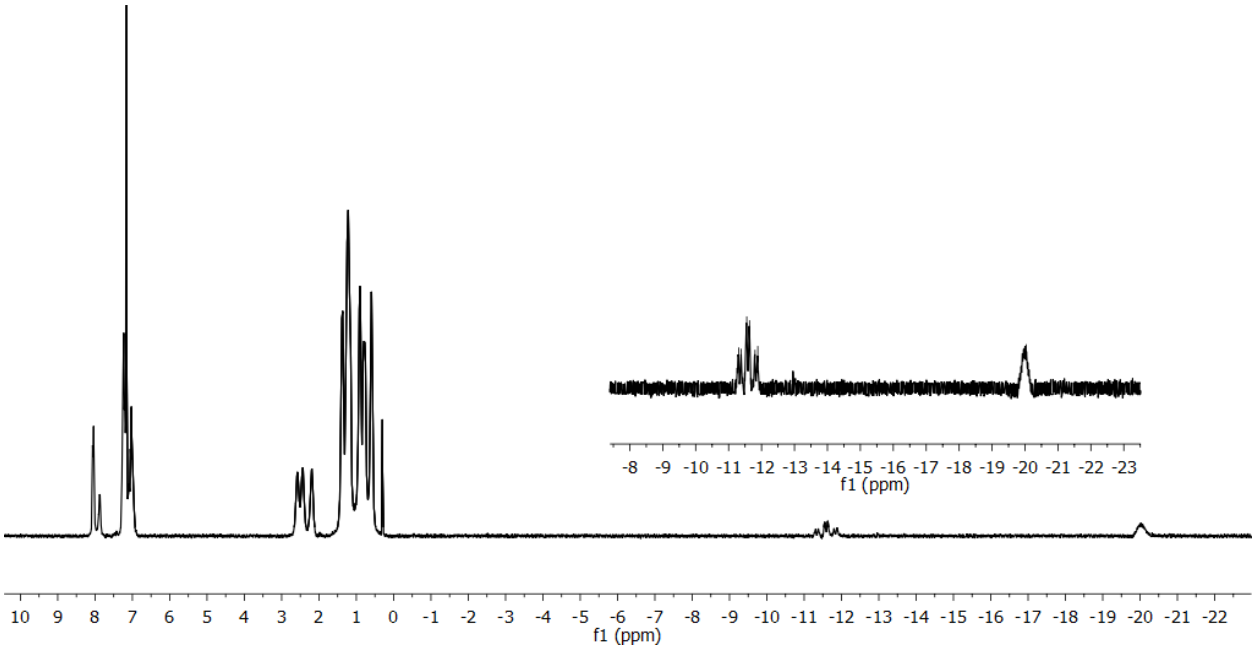

Fig. S6 ^{1}H NMR spectrum of **7**, (TPB)(μ-H)Fe(CO)(H), in C_6D_6.

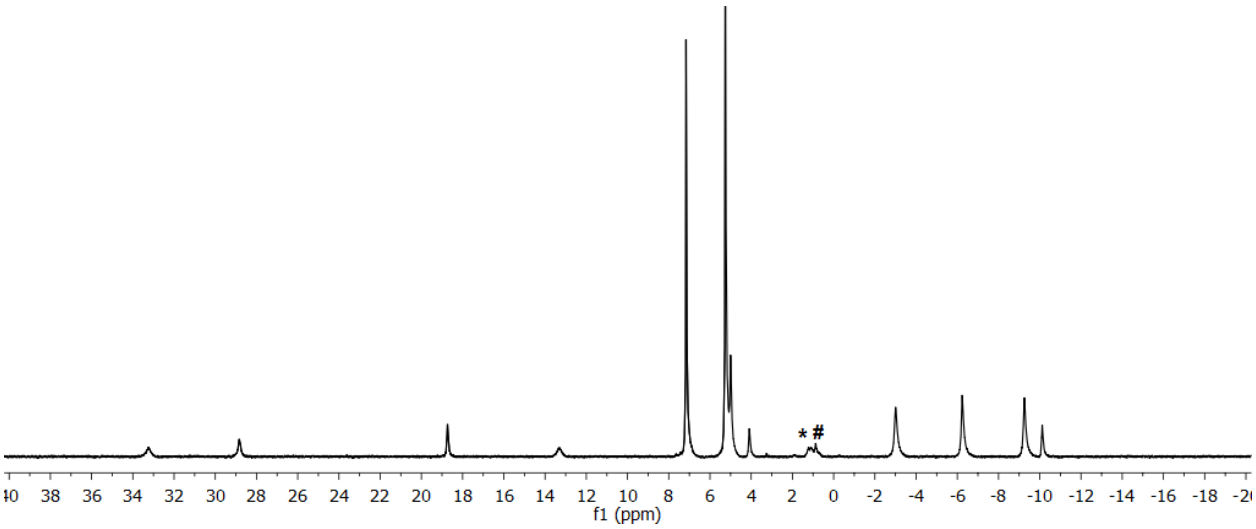

Fig. S7. ^{1}H NMR spectrum of **8**, (TPB)Fe(C_2H_4), in C_6D_6 under 1 atm C_2H_4. * Residual pentane. $^{\#}$ Ethane from ethylene source.

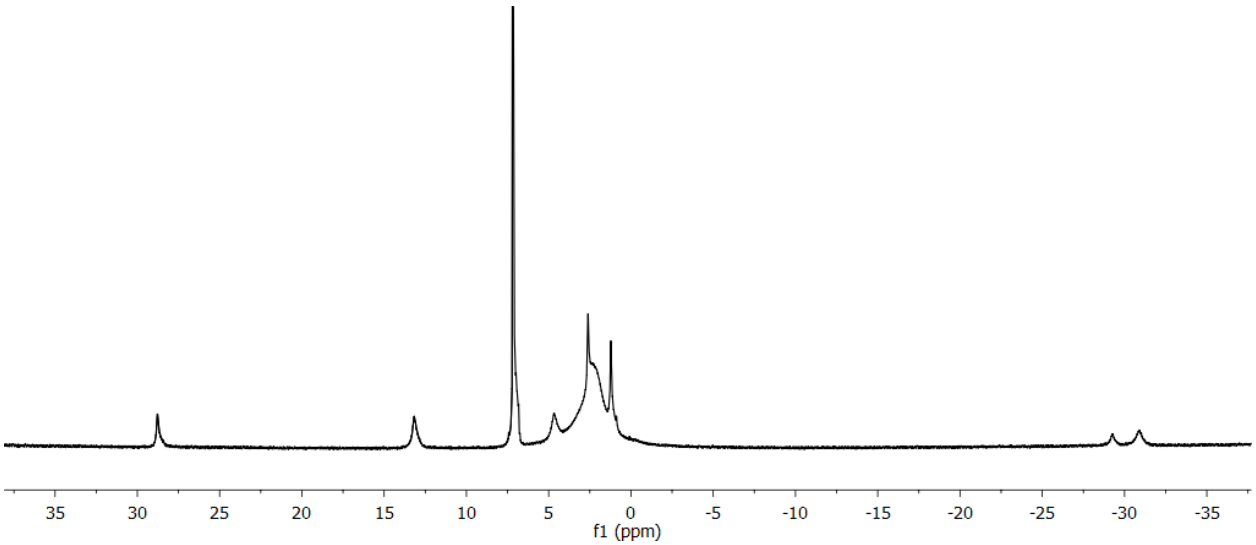

Fig. S8 ^{1}H NMR spectrum of **9**, (TPBH)Fe(C≡CPh), in C_6D_6.

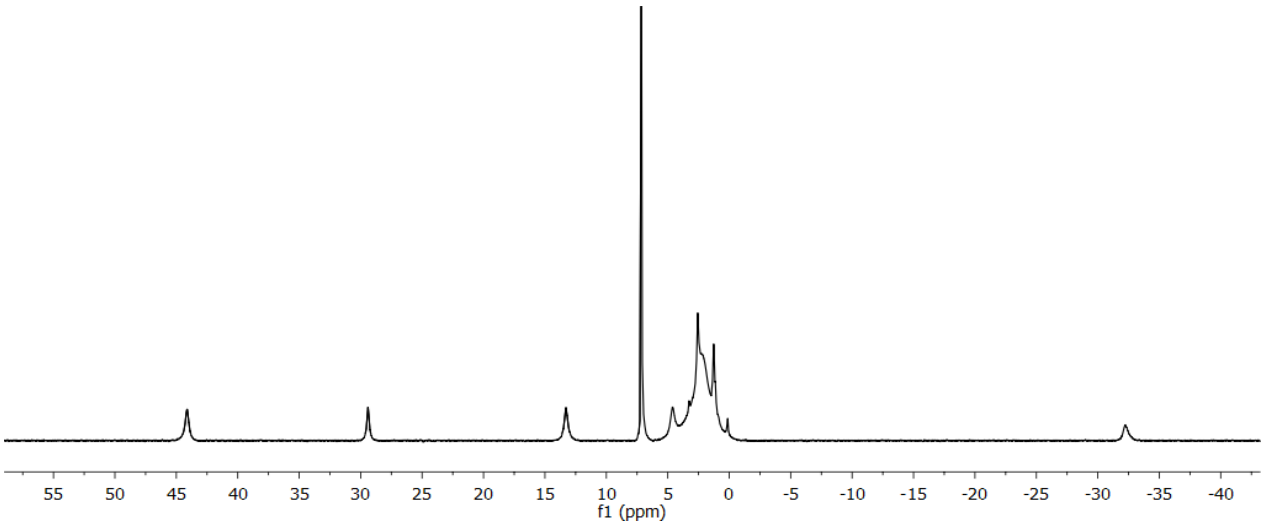

Fig. S9 ^{1}H NMR spectrum of **10**, (TPBH)Fe(C≡CTol), in C_6D_6.

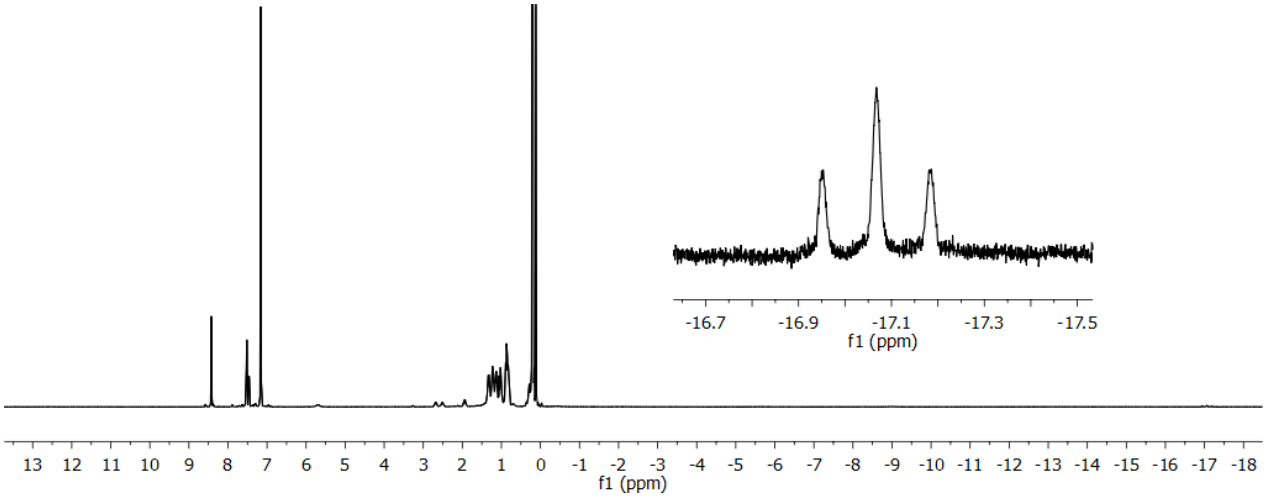

Fig. S10 ^{1}H NMR spectrum of **11** in C_6D_6

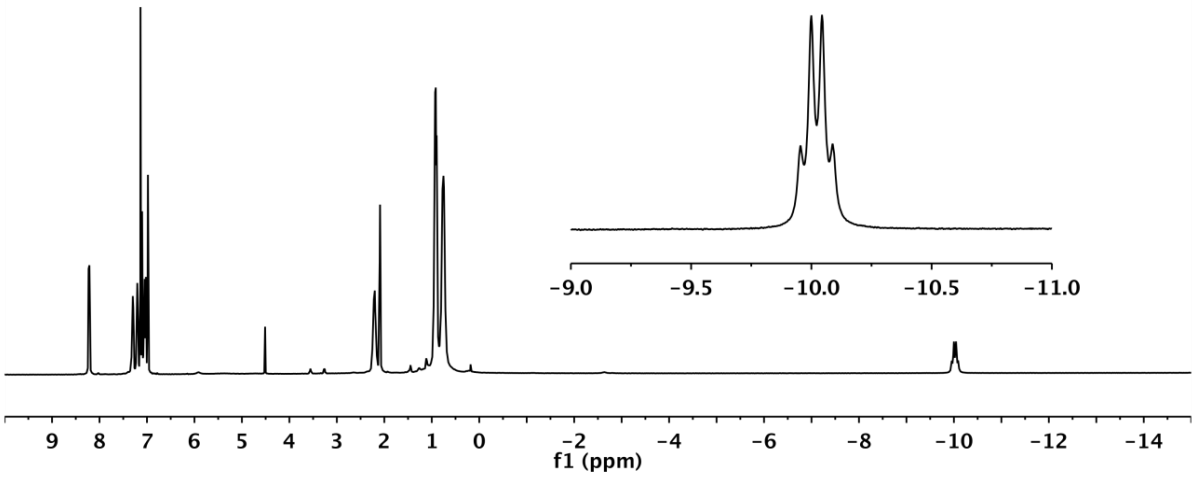

Fig. S11 ^{1}H NMR spectrum of **(SiP$^{iPr}_{3}$)Fe(H$_2$)(H)** in C_6D_6.

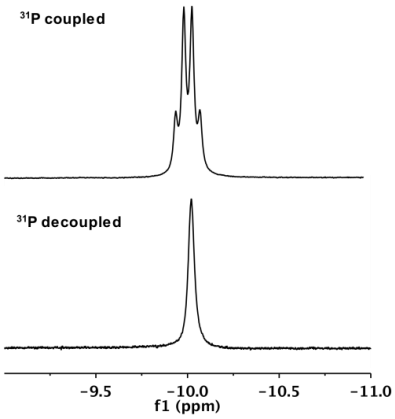

Fig. S12 Hydride resonances of the ^{1}H and ^{1}H{^{31}P} NMR spectrum of **(SiP$^{iPr}_{3}$)Fe(H$_2$)(H)** in C_6D_6.

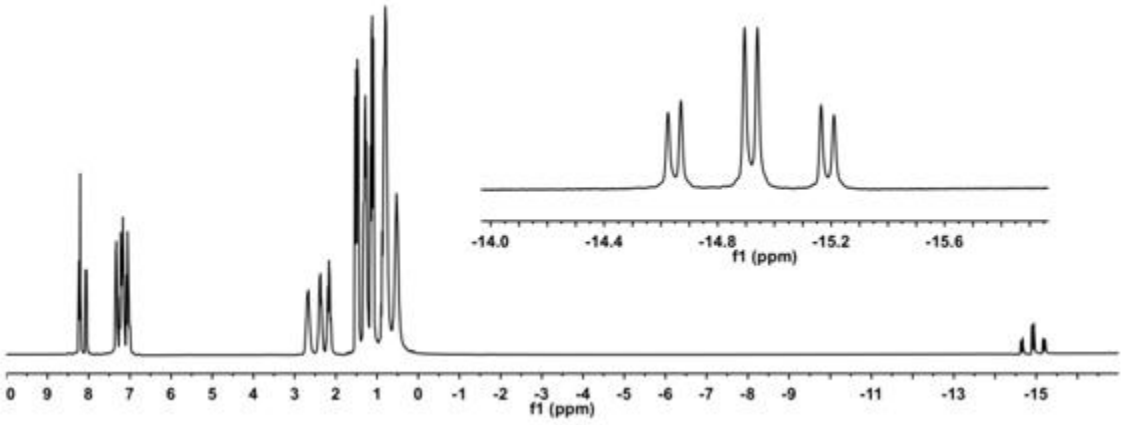

Fig. S13 ^{1}H NMR spectrum of **(SiP$^{iPr}_{3}$)Fe(CO)(H)** in d_8-toluene.

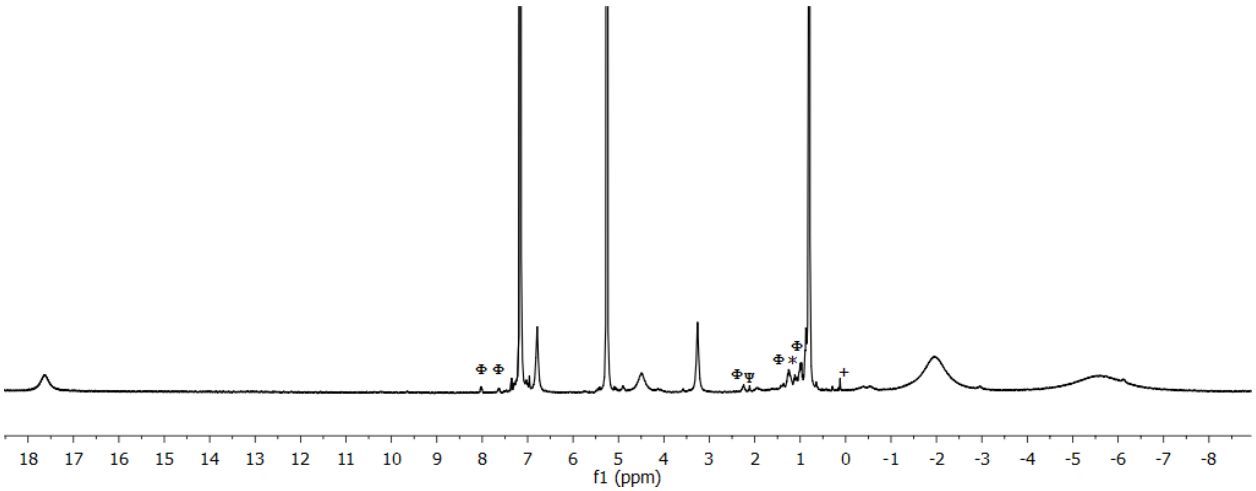

Fig. S14 ^{1}H NMR spectrum of **A**, (TPBH)Fe(Et), in C_6D_6. $^{\Phi}$ Compound **2**. $^{\Psi}$ Residual hexamethylbenzene. * Residual pentane. $^{+}$ Residual silicon grease.

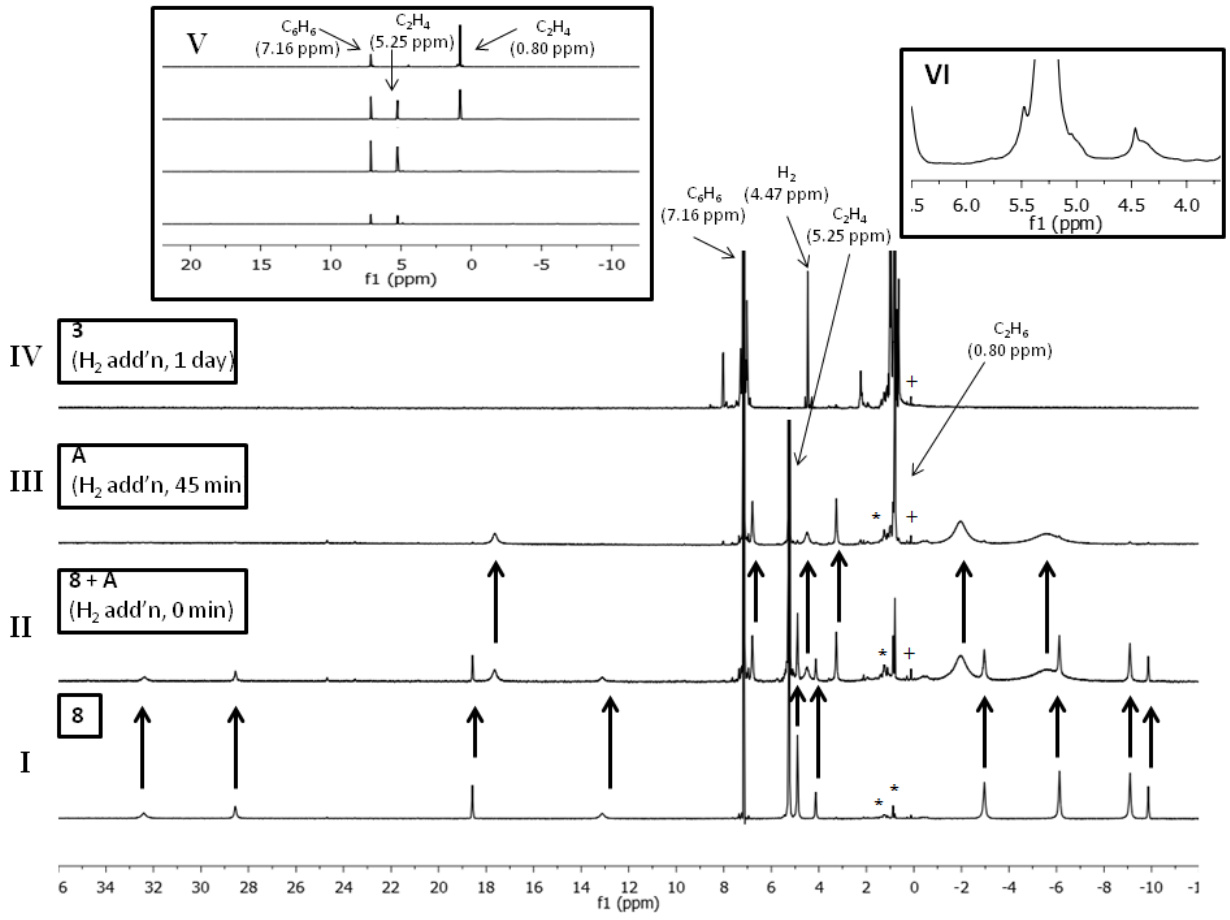

Fig. S15 Stacked ^{1}H NMR spectra of the reaction of **8** with H_2 (1 atm) and C_2H_4 (1 atm) in C_6D_6. (I) Compound **8** under a C_2H_4 atmosphere. (II) Mixture of compounds **8** and **A** immediately following H_2 addition. (III) Compound **A** was formed after mixing the reaction for *ca.* 45 min; H_2

was added to replenish the consumed H_2. (IV) Compound **3** was formed at the conclusion of the reaction. (inset V) Zoom out of spectra. (inset VI) Zoom in to show the H_2 resonance. *Residual pentane. $^{+}$Residual silicon grease.

^{31}P NMR Spectra

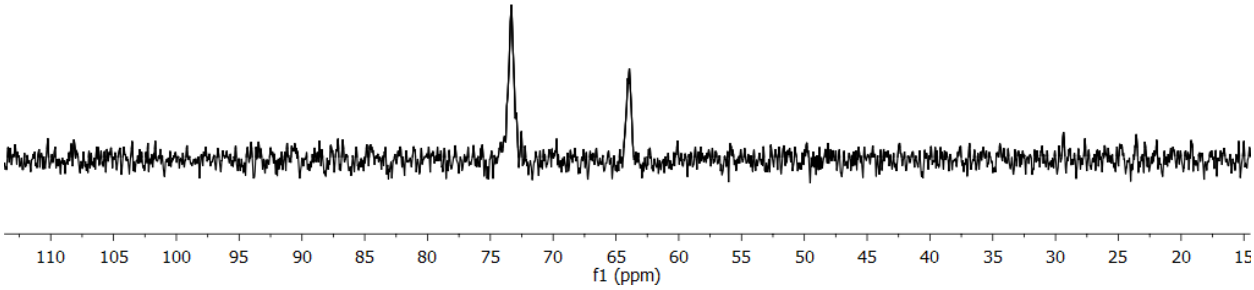

Fig. S16 ^{31}P NMR spectrum of **2**, (TPB)(μ-H)Fe(N_2)(H), in C_6D_6.

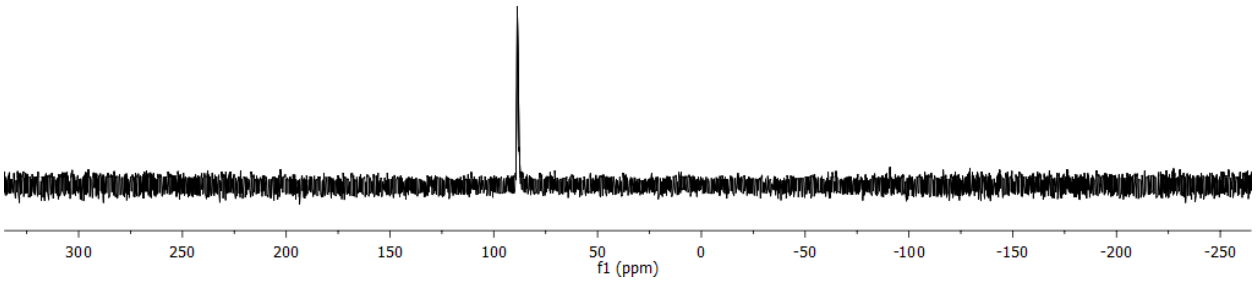

Fig. S17 ^{31}P NMR spectrum of **3**, (TPB)(μ-H)Fe(H_2)(H), in C_6D_6.

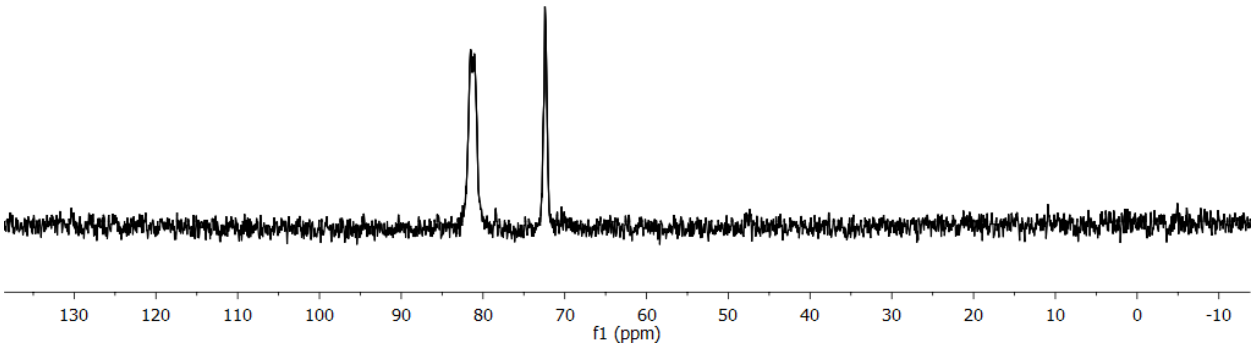

Fig. S18 ^{31}P NMR spectrum of **5**, (TPB)(μ-H)Fe(CN^{t}Bu)(H), in C_6D_6.

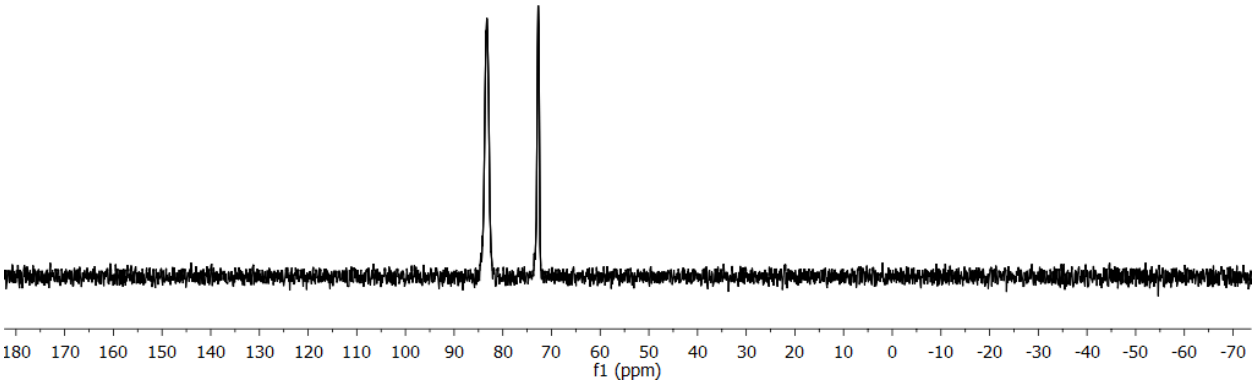

Fig. S19 ^{31}P NMR spectrum of **7**, (TPB)(μ-H)Fe(CO)(H), in C_6D_6.

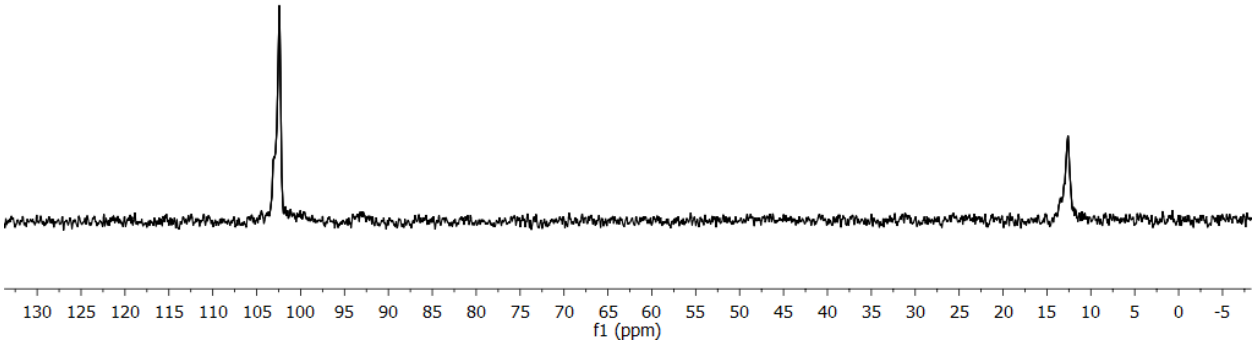

Fig. S20 ^{31}P NMR spectrum of **11** in C_6D_6.

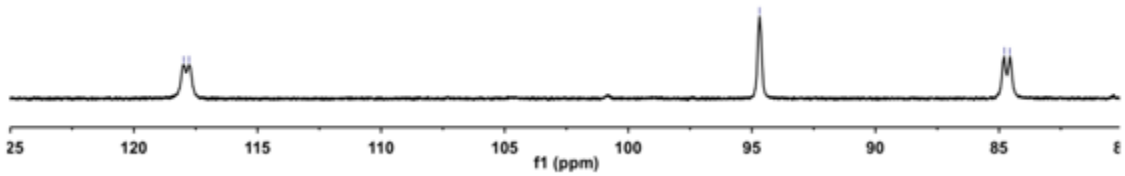

Fig. S21 ^{31}P NMR spectrum of **(SiP$^{iPr}_3$)Fe(H$_2$)(H)**, in d_8-toluene at –80°C.

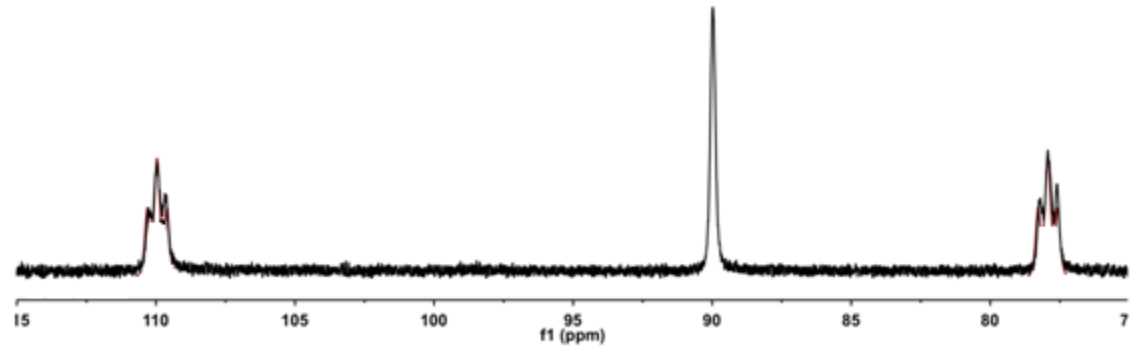

Fig. S22 ^{31}P NMR spectrum of **(SiP$^{iPr}_3$)Fe(CO)(H)**, in d_8-toluene at –90°C.

^{13}C NMR Spectra

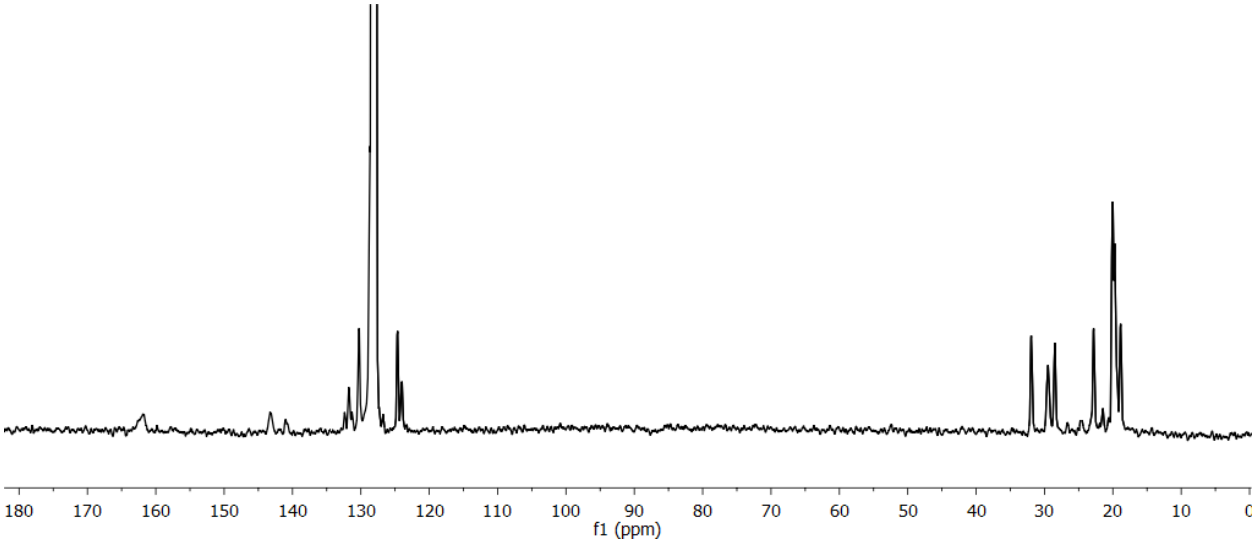

Fig. S23 ^{13}C NMR spectrum of **2**, (TPB)(μ-H)Fe(N_2)(H), in C_6D_6.

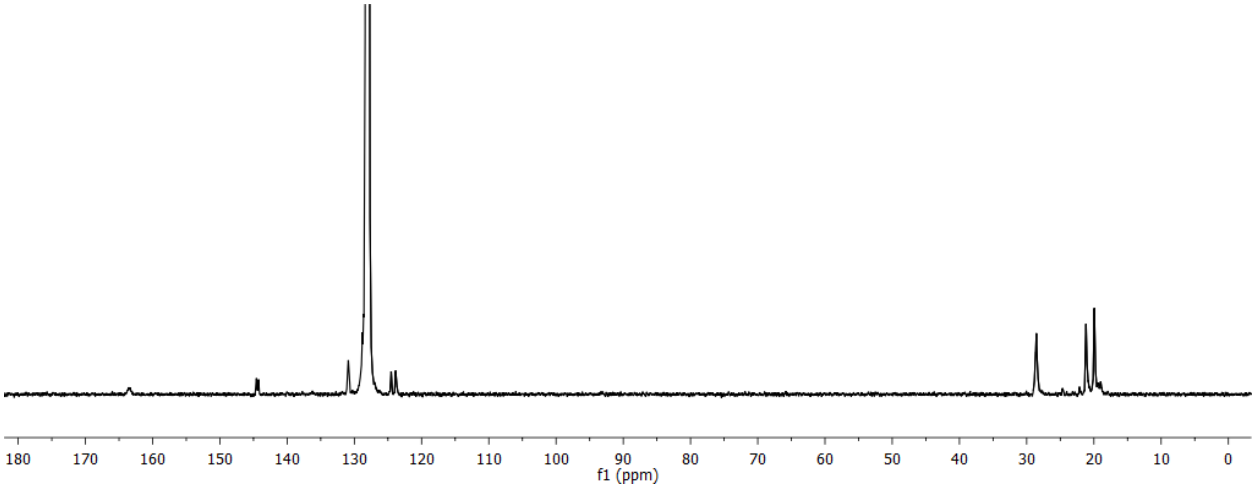

Fig. S24 ^{13}C NMR spectrum of **3**, (TPB)(μ-H)Fe(H_2)(H), in C_6D_6.

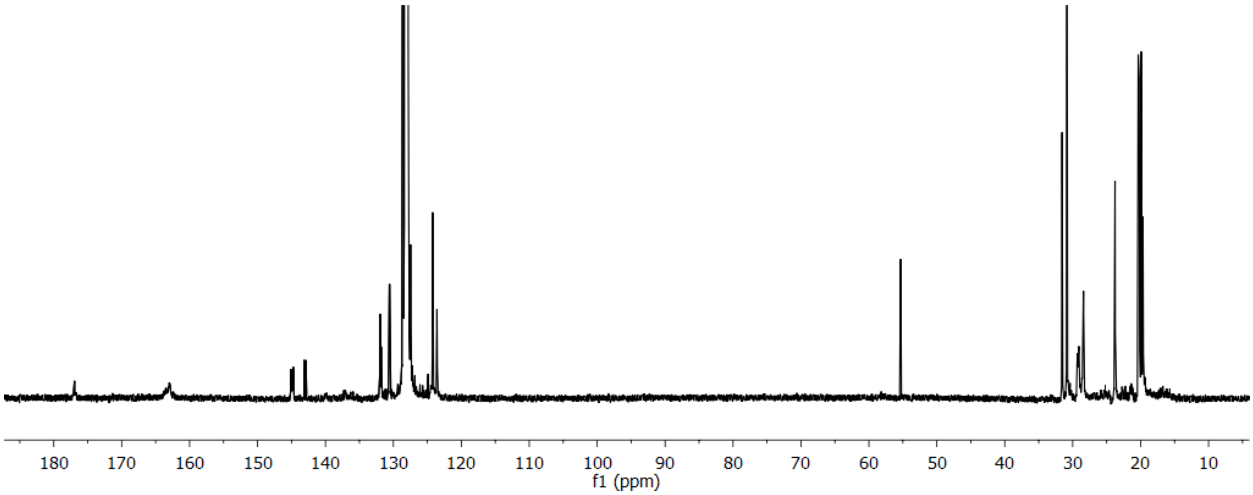

Fig. S25 ^{13}C NMR spectrum of **5**, (TPB)(μ-H)Fe(CN^{t}Bu)(H), in C_6D_6.

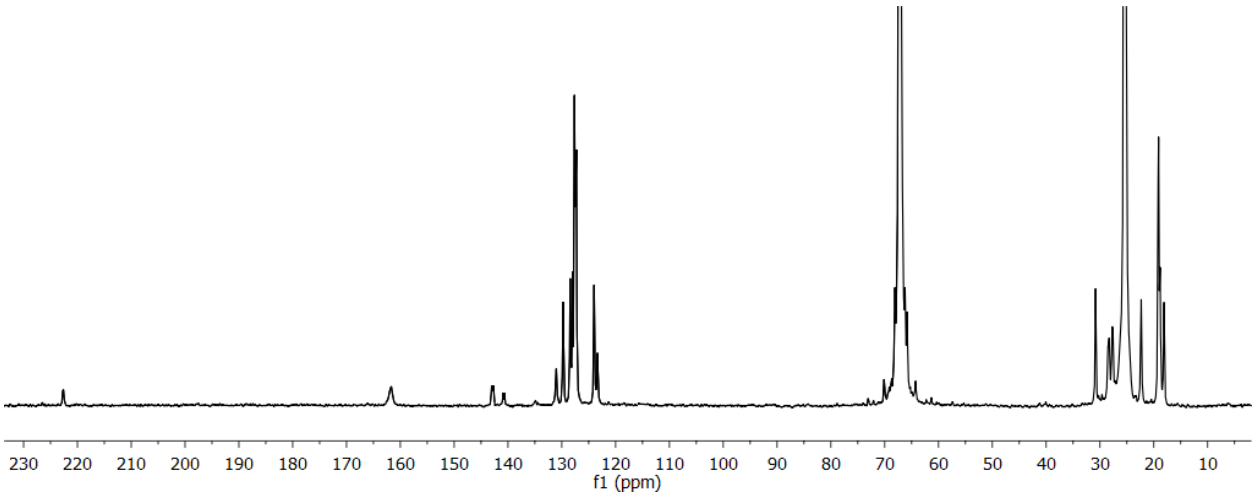

Fig. S26 ^{13}C NMR spectrum of **7**, (TPB)(μ-H)Fe(CO)(H), in THF/C_6D_6.

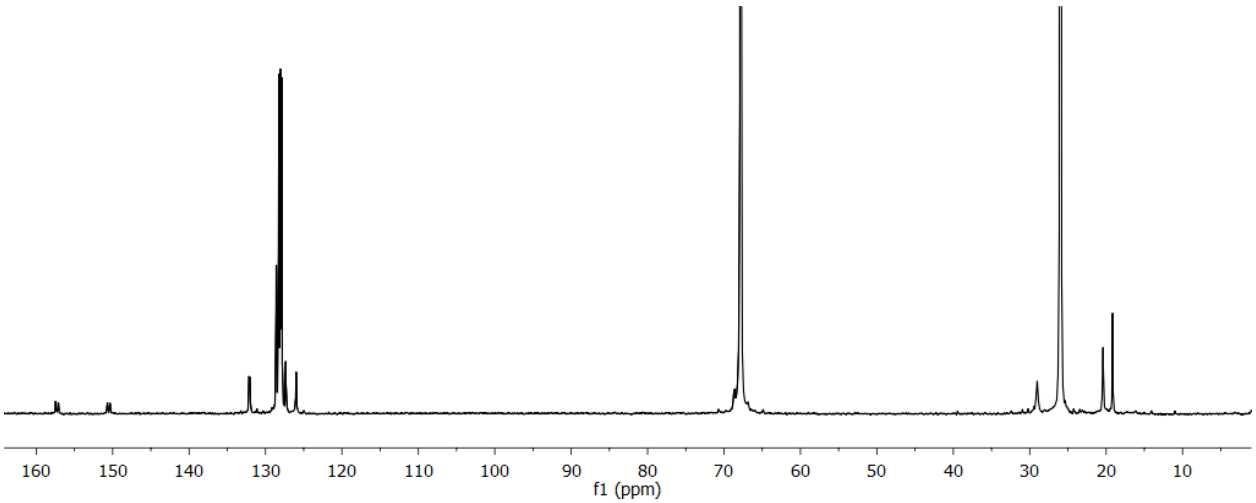

Fig. S27 ^{13}C NMR spectrum of **(SiP$^{iPr}_3$)Fe(H$_2$)(H)** in THF/C_6D_6.

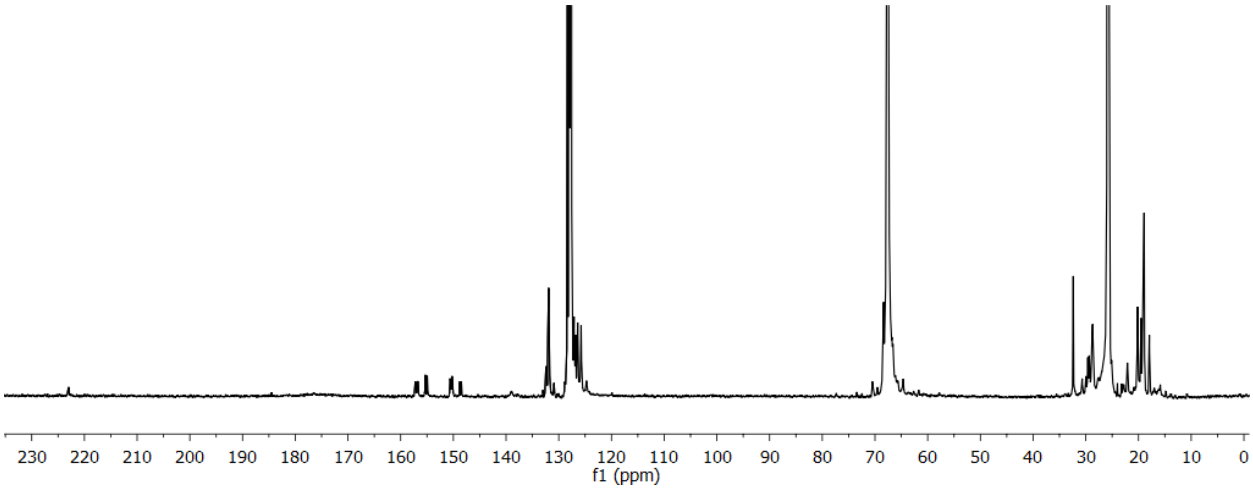

Fig. S28 ^{13}C NMR spectrum of **(SiP$^{iPr}_3$)Fe(CO)(H)** in THF/C_6D_6.

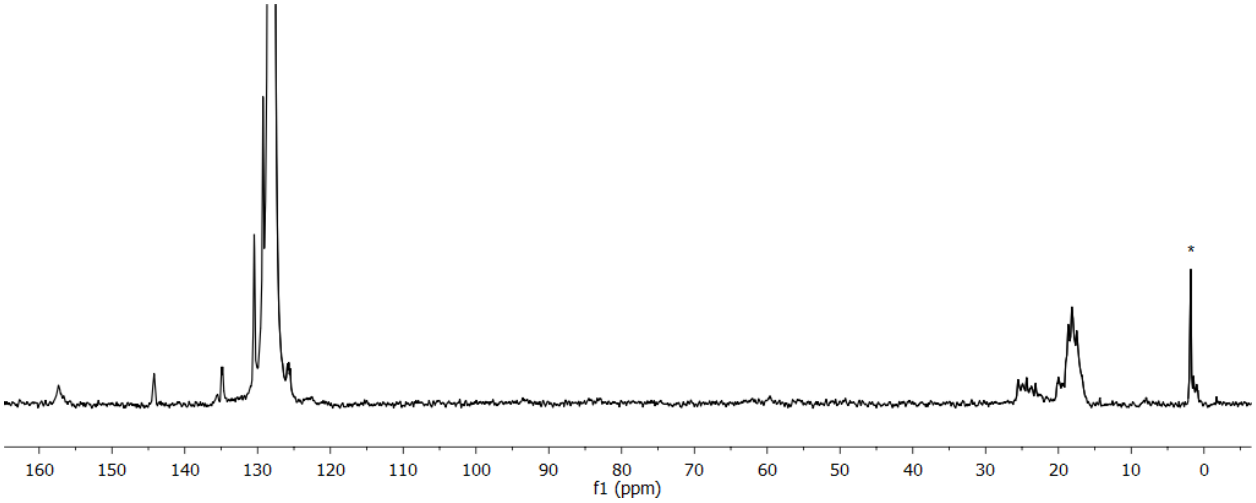

Fig. S29. ^{13}C NMR spectrum of **11** in C_6D_6. * Residual hexamethyldisiloxane.

^{11}B NMR Spectra

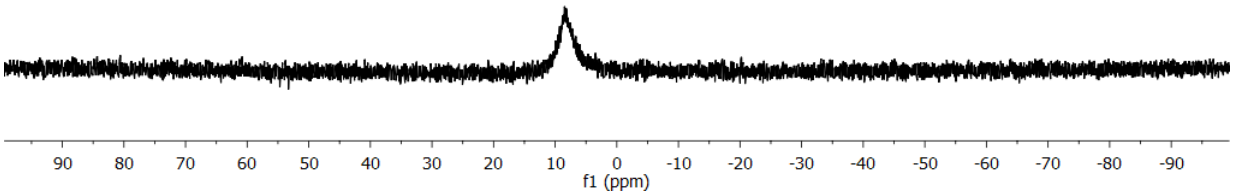

Fig. S30 ^{11}B NMR spectrum of **2,** (TPB)(μ-H)Fe(N_2)(H) in C_6D_6.

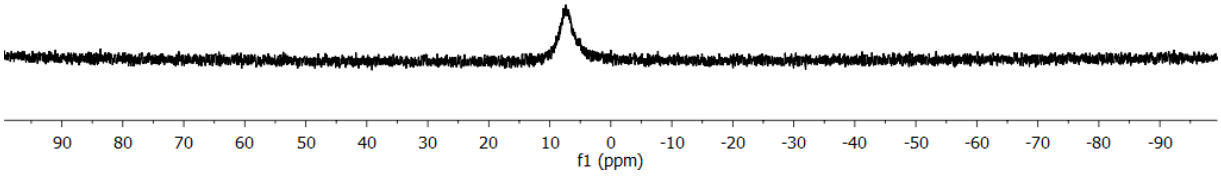

Fig. S31 ^{11}B NMR spectrum of **3**, (TPB)(μ-H)Fe(H_2)(H) in C_6D_6.

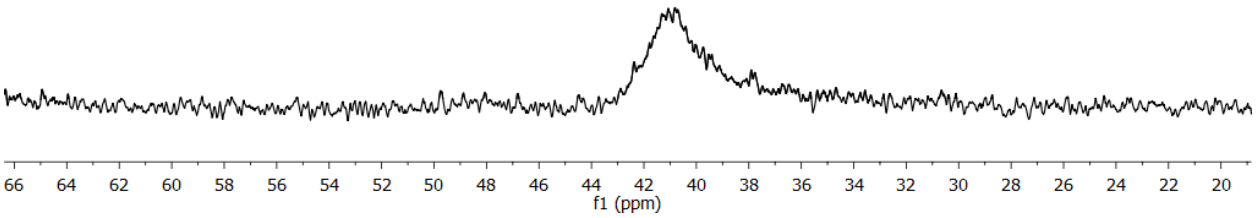

Fig. S32 ^{11}B NMR spectrum of **11** in C_6D_6.

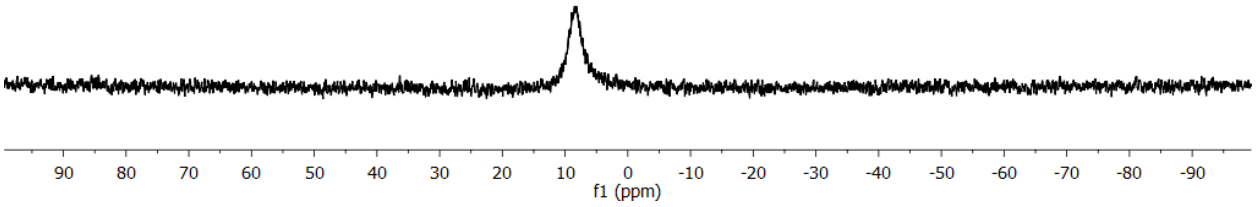

Fig. S33 ^{11}B NMR spectrum of **5**, (TPB)(μ-H)Fe(^{t}BuNC)(H) in C_6D_6.

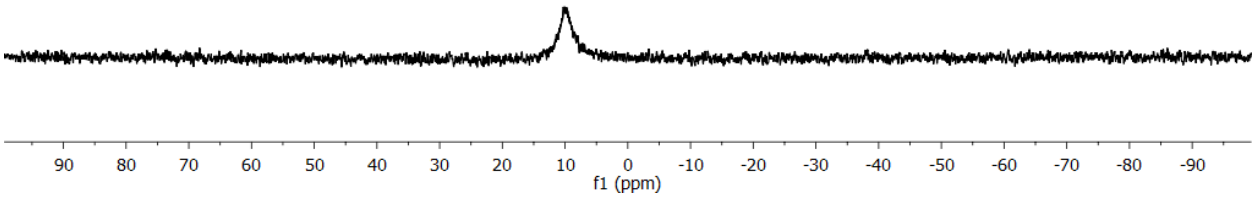

Fig. S34 ^{11}B NMR spectrum of **7**, (TPB)(μ-H)Fe(CO)(H) in C_6D_6.

Variable Temperature NMR

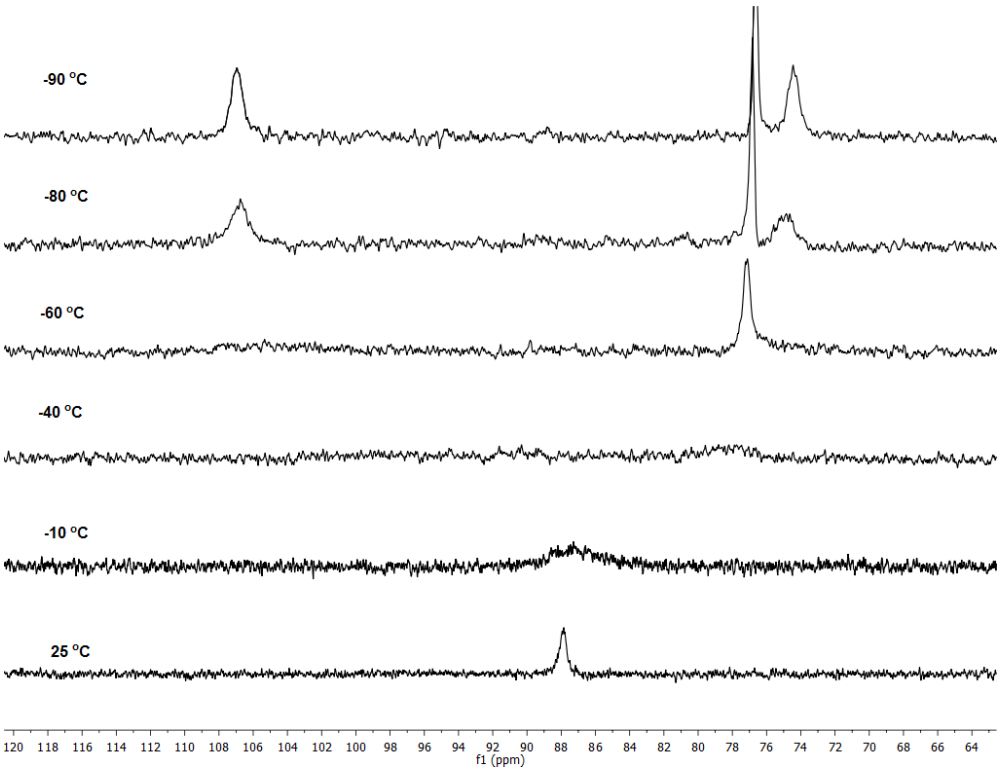

Fig. S35 VT ^{31}P NMR spectra profile of **3** in d_8-toulene.

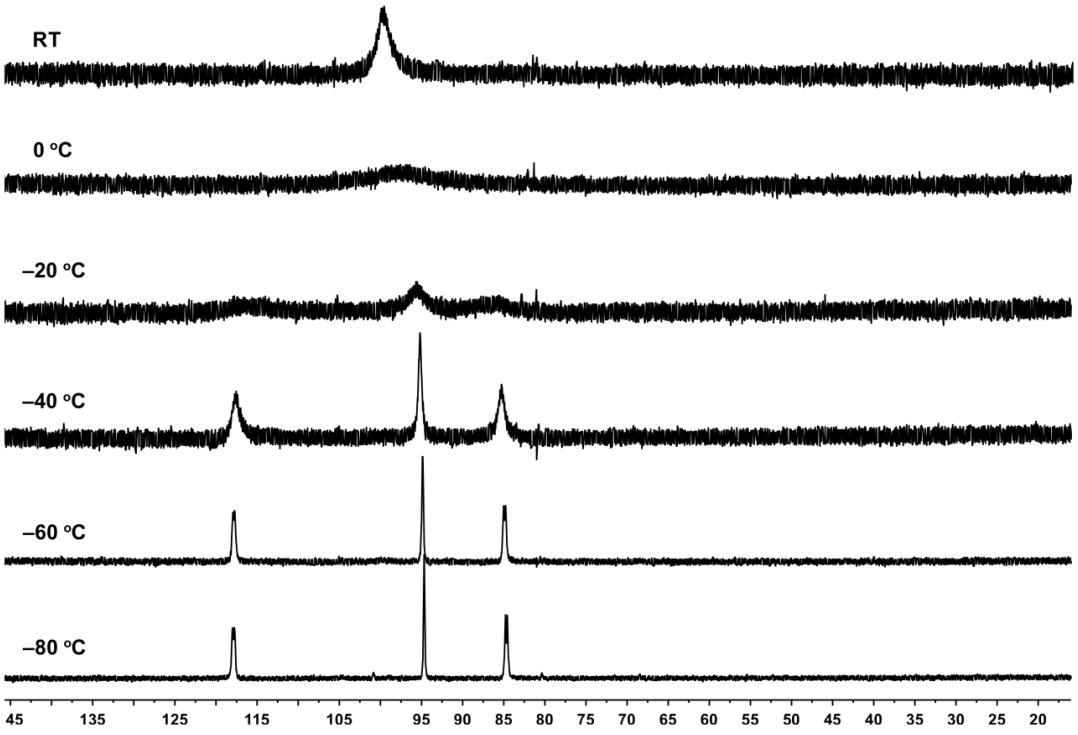

Fig. S36 VT ^{31}P NMR spectra of **(SiP$^{iPr}_3$)Fe(H$_2$)(H)** in d_8-toluene.

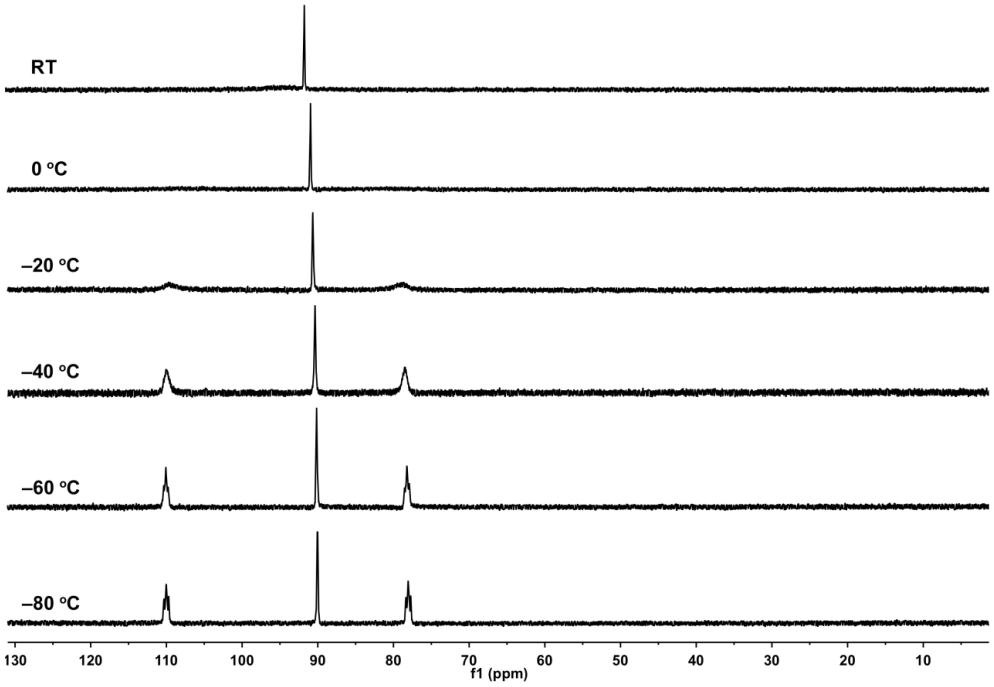

Fig. S37 VT ^{31}P NMR spectra of **(SiP$^{iPr}_3$)Fe(CO)(H)** in d_8-toluene

T_{1min} Measurements

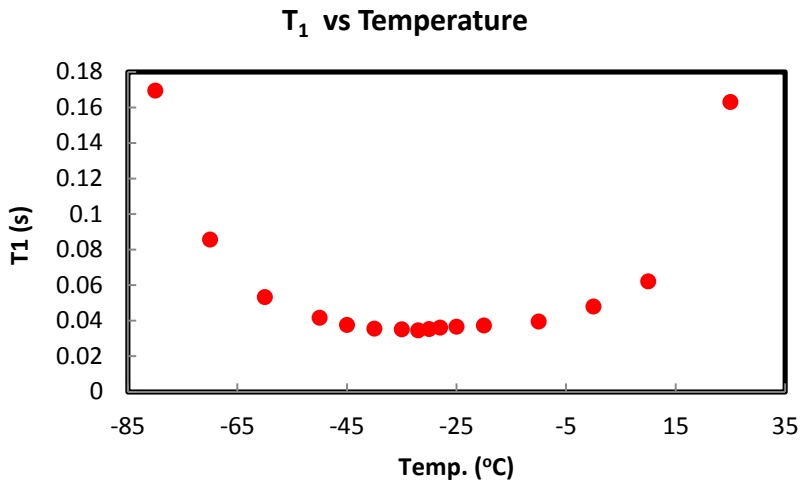

Fig. S38 T_1 values for **3**, (TPB)(μ-H)Fe(H_2)(H), in d_8-toulene. $T1_{min}$ is 35 ms at -32 °C.

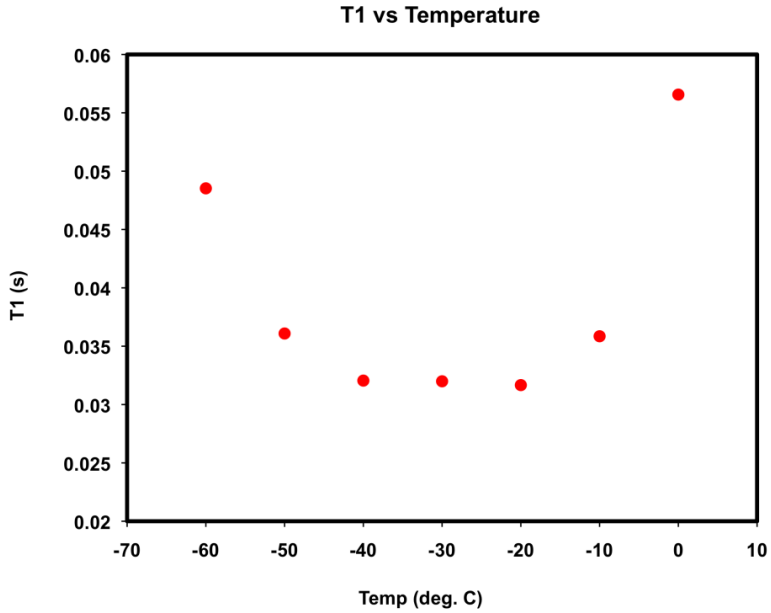

Fig. S39 T_1 values for **(SiP$^{iPr}_3$)Fe(H_2)(H)**. The T_{1min} is 32 ms in d_8-toluene at -30 °C.

Miscellaneous NMR Data

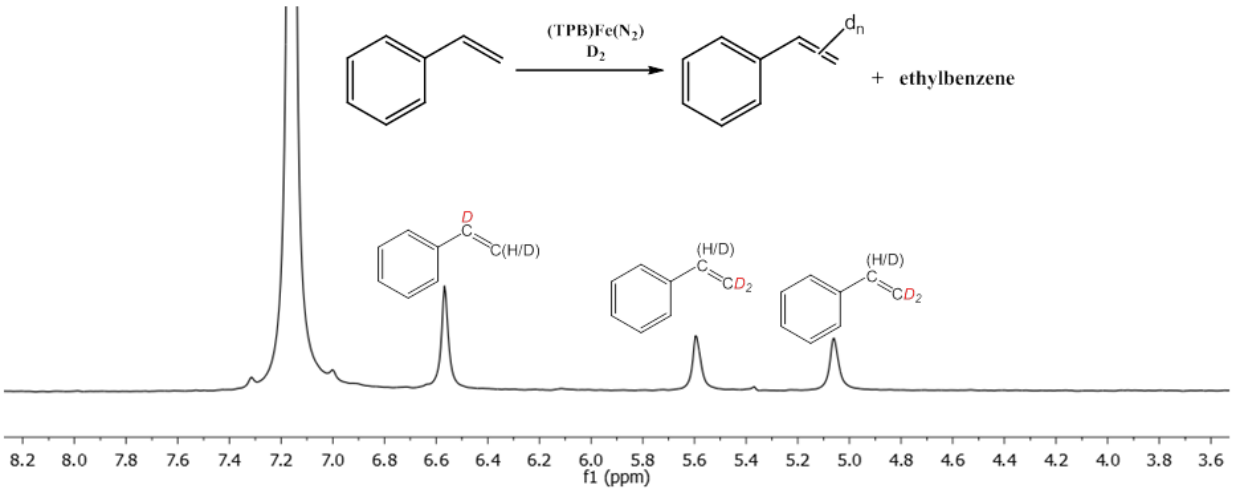

Fig. S40 ^{2}H NMR spectrum showing vinyl deuterated styrene arising from exchange of deuterium into styrene catalyzed by **1** under D_2 (1 atm).

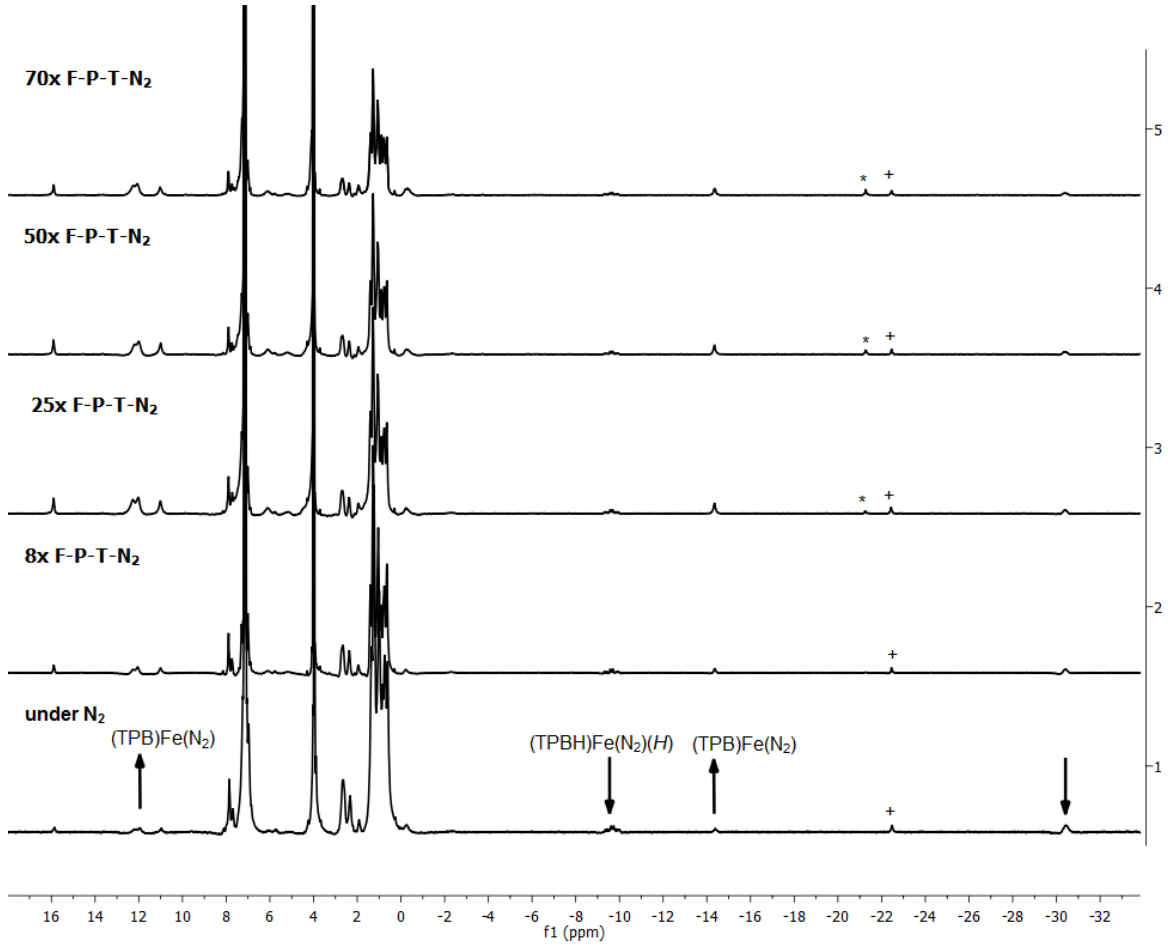

Fig. S41 Elimination of H_2 from **2**, (TPB)(μ-H)Fe(N_2)(H). Iterative freeze-pump-thaw-N_2 cycles were performed to promote H_2 release and reformation of **1**. Ferrocence (δ 4.0) was used as an

integration standard. [+]Residual (TPB)FeBr (previously reported). *(TPB)FeCl, known decomposition product from **1**.

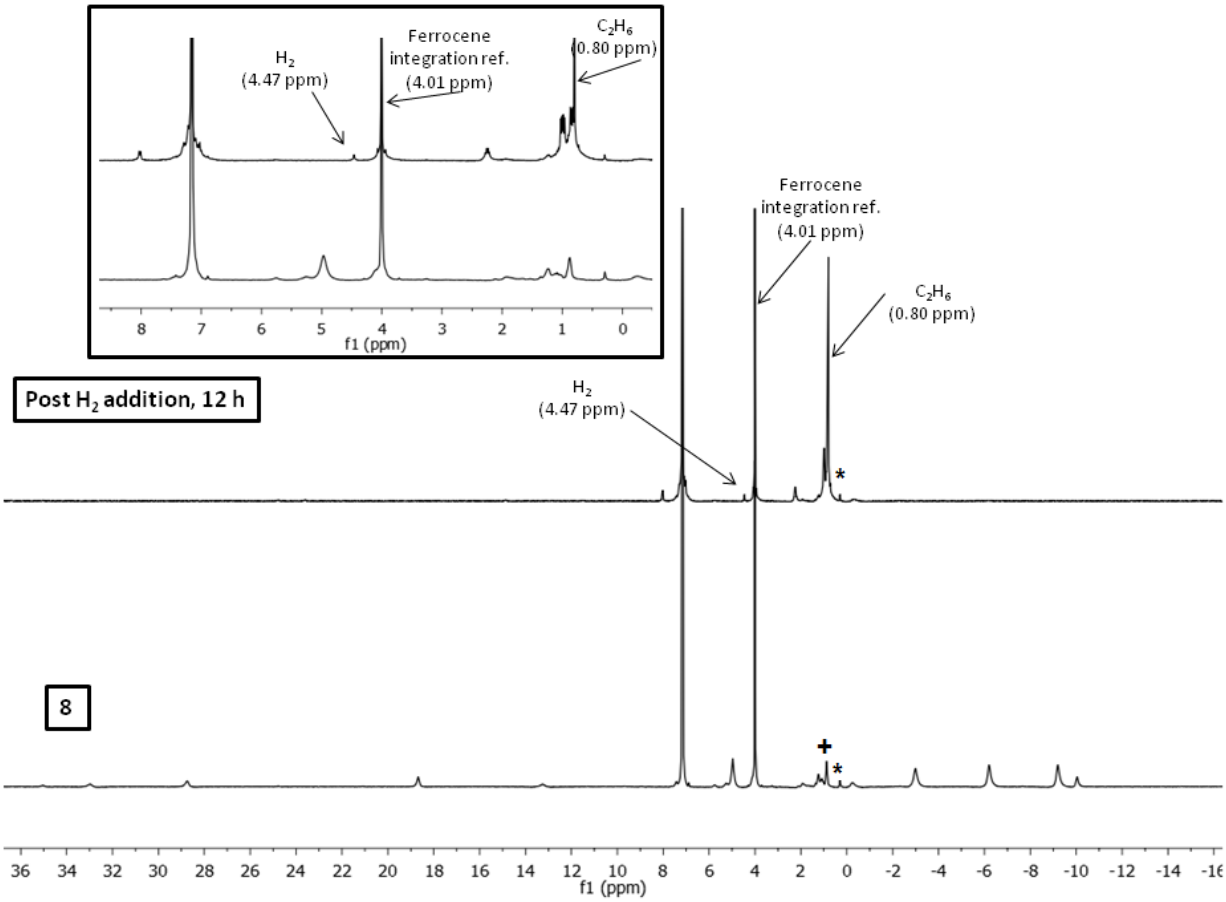

Fig. S42 ^{1}H NMR spectra of the reaction between **8** and H_2 (1 atm). (bottom) Compound **8** formed from the addition of 1 equiv of ethylene to **1**. (top) The spectrum after H_2 addition (12 h) shows that the bound ethylene in **8** was hydrogenated to ethane. (inset) Enlargement of the same spectra. Ferrocene was used as an integration standard, and it was determined by integration that ethane was indeed formed in the reaction (0.8 equiv relative to **8** after subtracting the ethane introduced at the beginning of the reaction from the ethylene tank). *Residual silicon grease. [+]Residual ethane from the ethylene gas cylinder

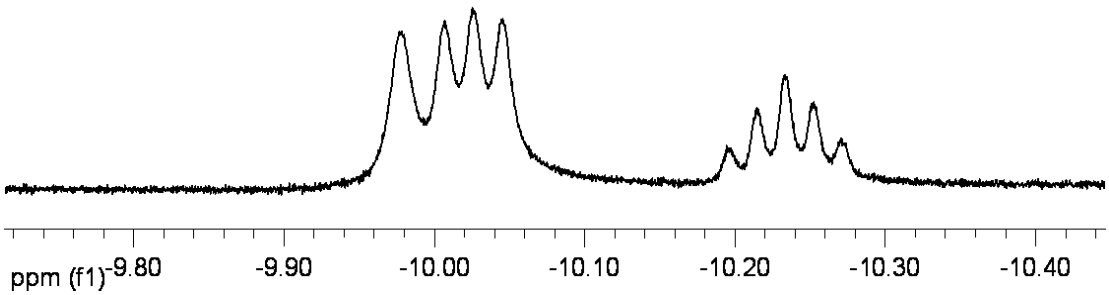

Fig. S43 $^{1}H\{^{31}P\}$ NMR spectrum of **(SiP$^{iPr}_{3}$)Fe(H_2)(H)**-HD isotopomers in d_8-toluene at 293 K.

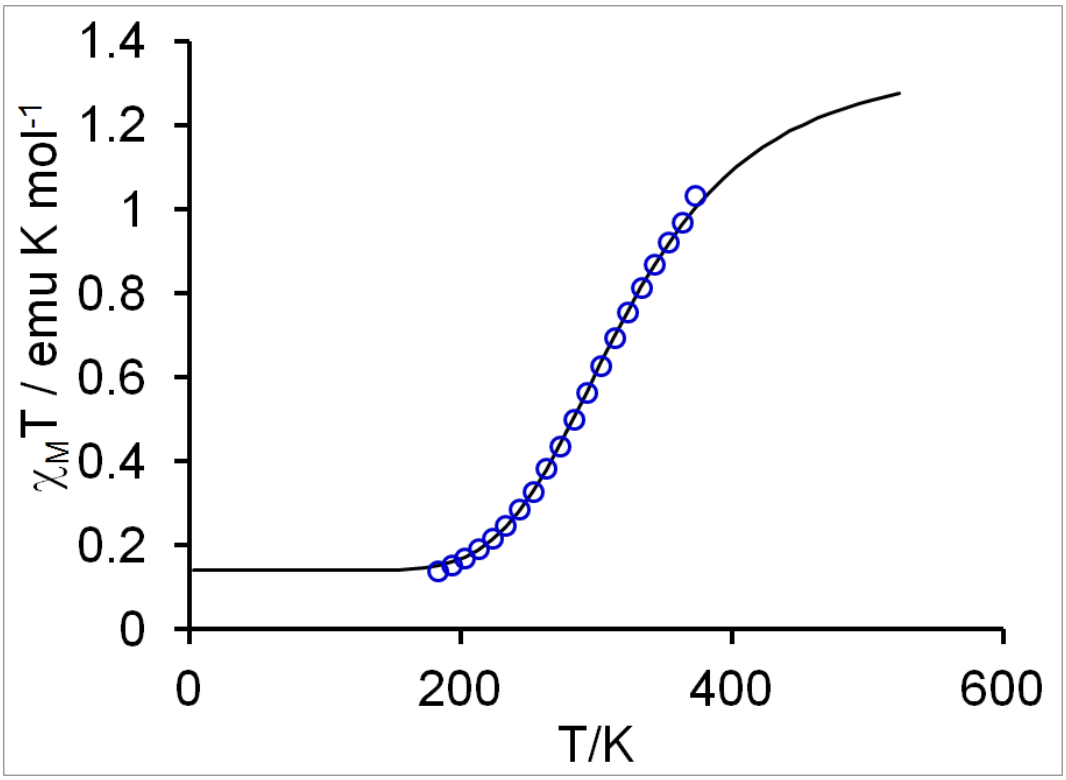

Fig. S44 VT magnetic susceptibility measurements (method of Evans) of **4**, (TPB)Fe(CN^{t}Bu).

IR Spectra

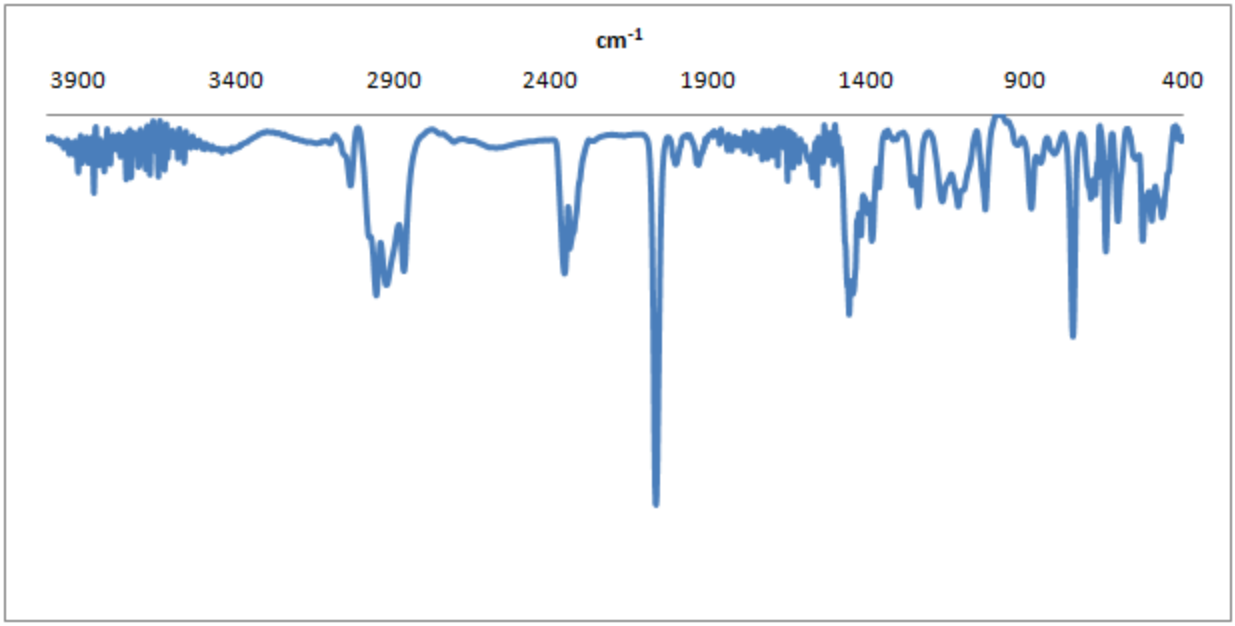

Fig. S45 FT-IR (KBr) of **2**, (TPB)(μ-H)Fe(N_2)(H).

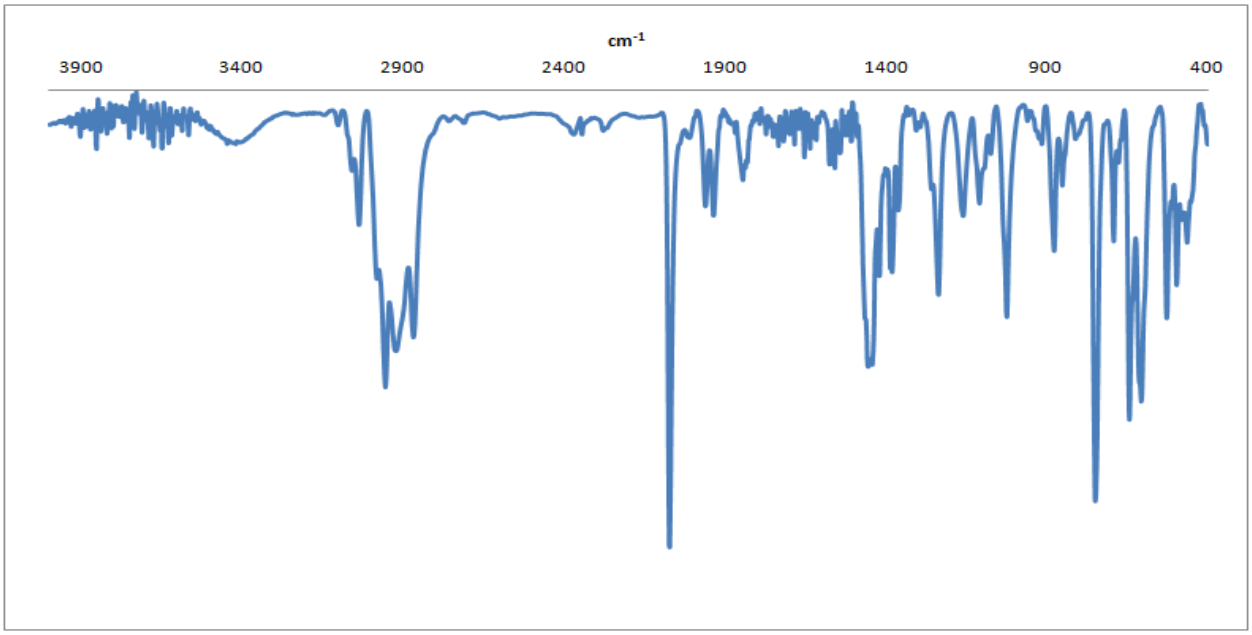

Fig. S46 FT-IR (KBr) of **3**, (TPB)(μ-H)Fe(H_2)(H).

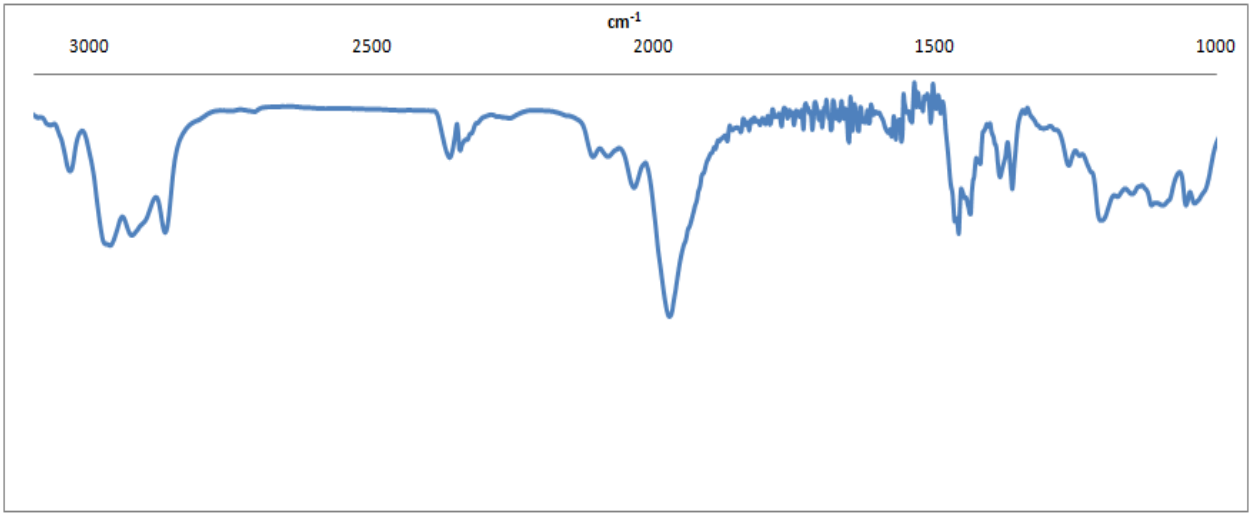

Fig. S47 IR (KBr) spectrum of **4**, (TPB)Fe(CN^{t}Bu).

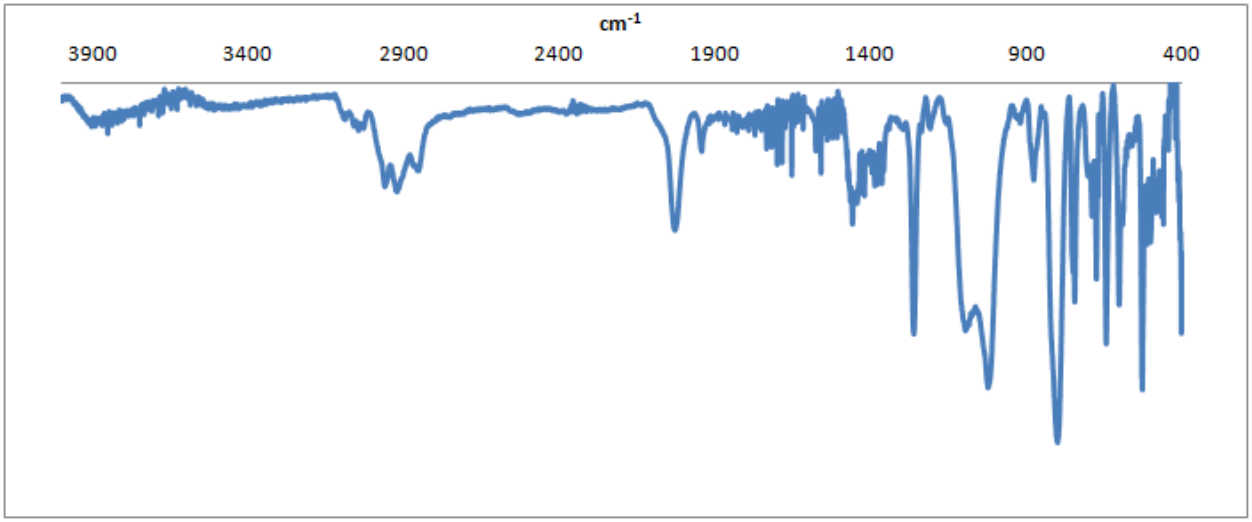

Fig. S48 IR (KBr) spectrum of **5**, (TPB)(μ-H)Fe(CN^{t}Bu)(H).

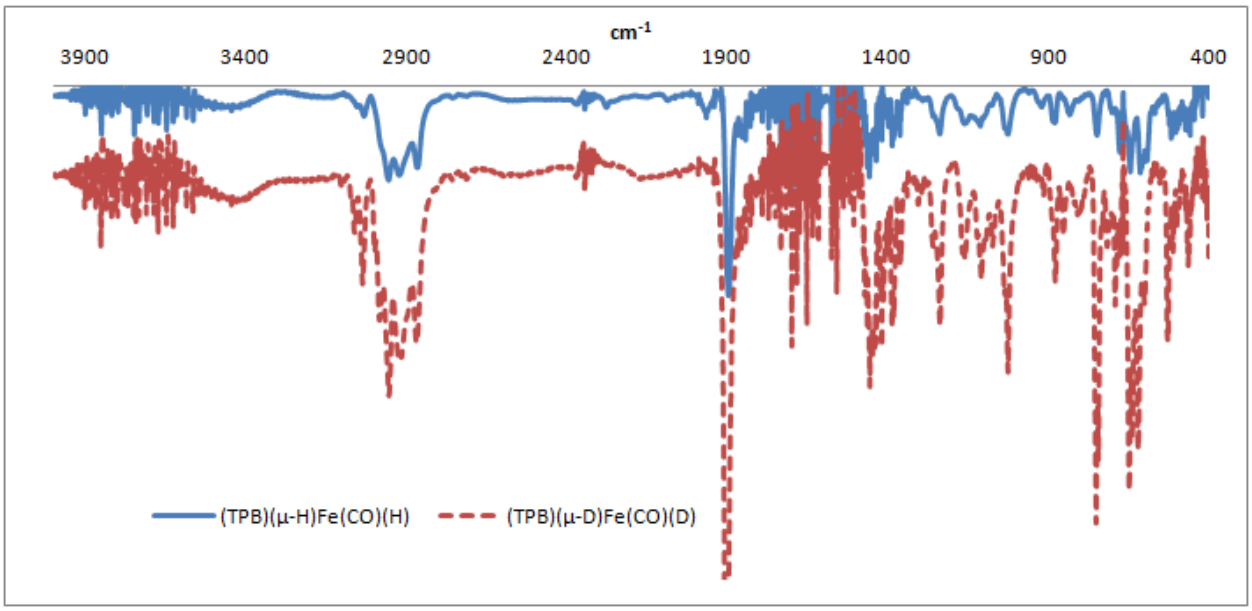

Fig. S49 FT-IR (KBr) spectra for **7**, (TPB)(μ-H)Fe(CO)(H) and labeled (TPB)(μ-D)Fe(CO)(D).

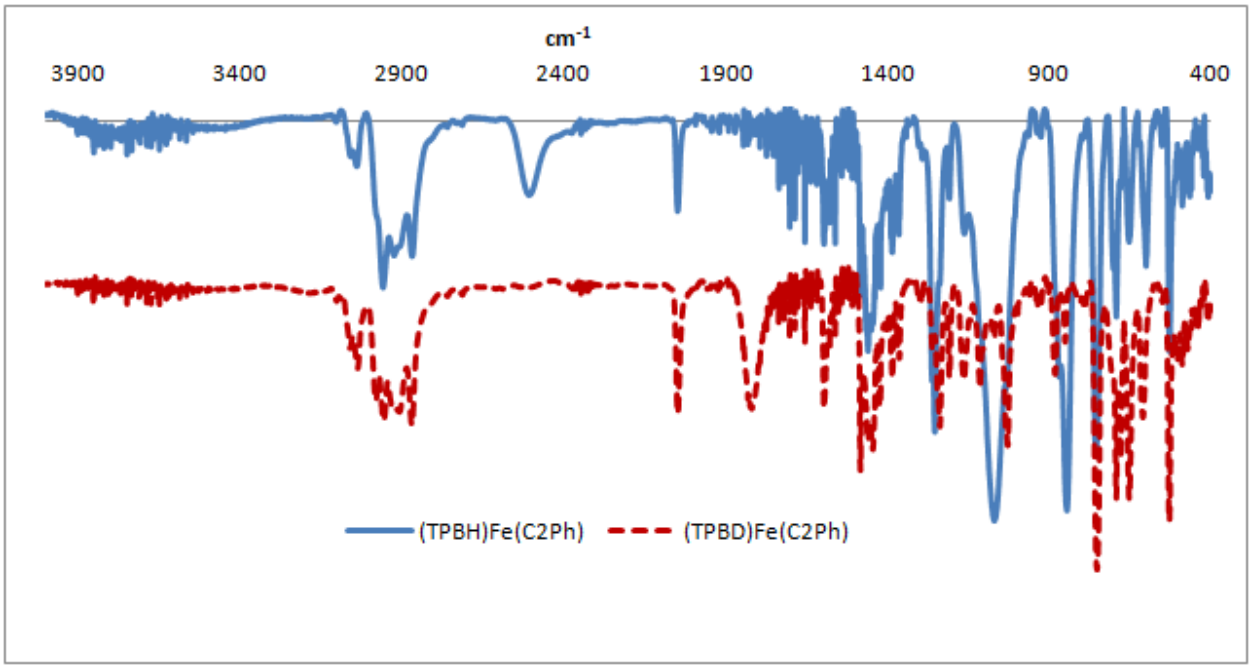

Fig. S50 FT-IR (KBr) spectra for **9**, (TPBH)Fe(C≡CPh) and labeled (TPBD)Fe(C≡CPh).

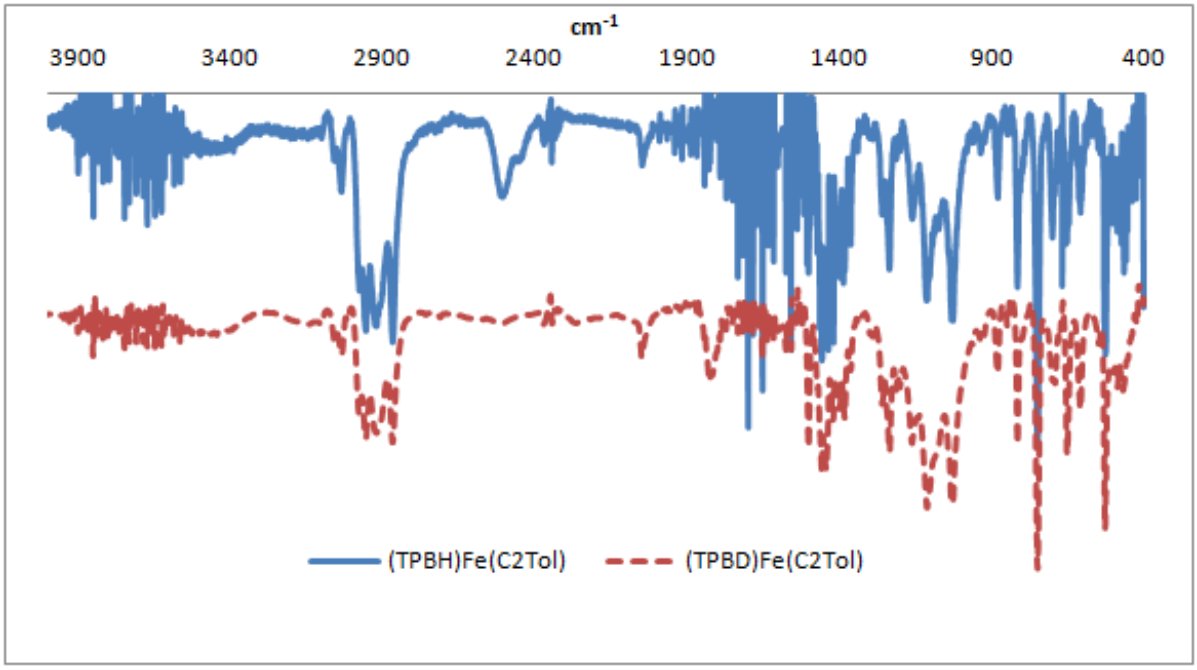

Fig. S51 FT-IR (KBr) of **10**, (TPBH)Fe(C≡CTol), and labeled (TPBD)Fe(C≡CTol).

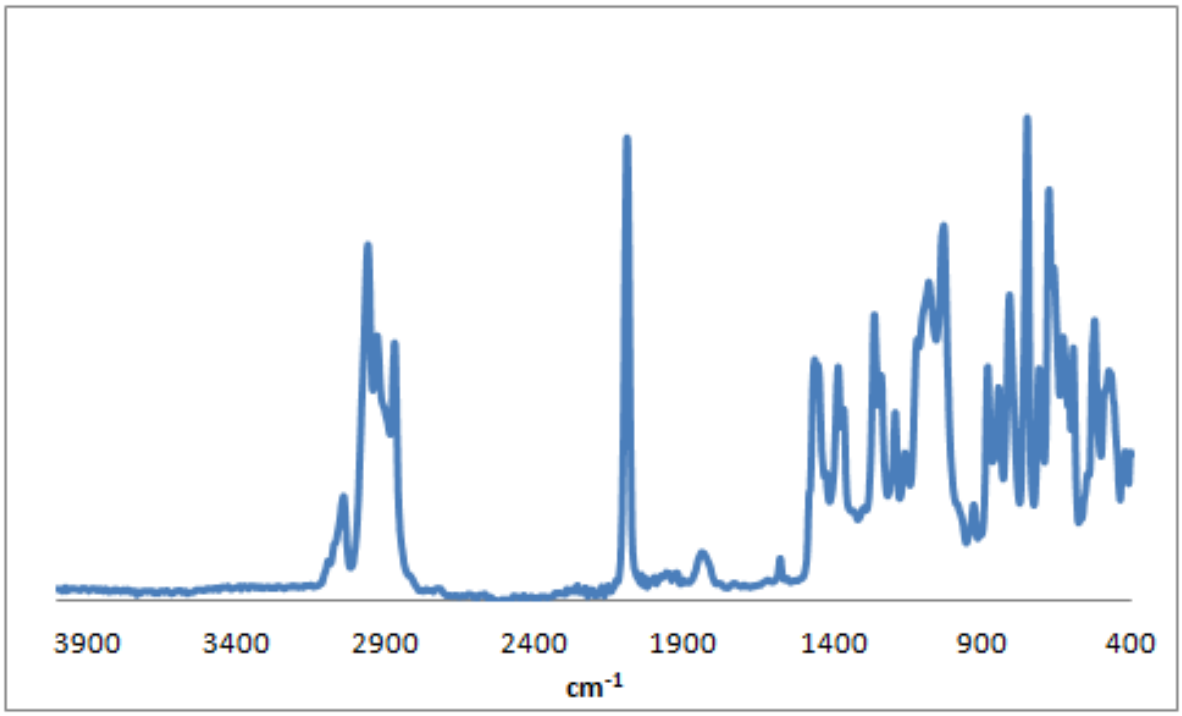

Fig. S52 ATR-IR (THF thin film) of **11**.

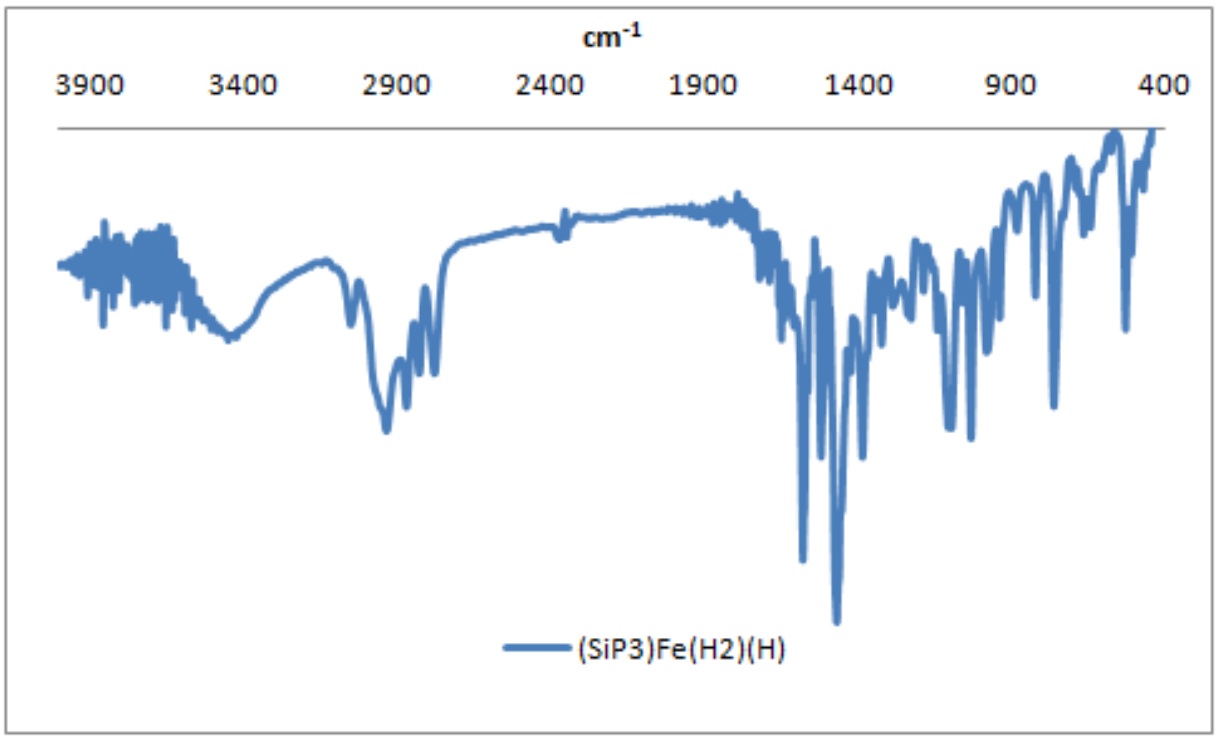

Fig. S53 FT-IR (KBr) of **(SiP^{iPr}3)Fe(H_2)(H)**.

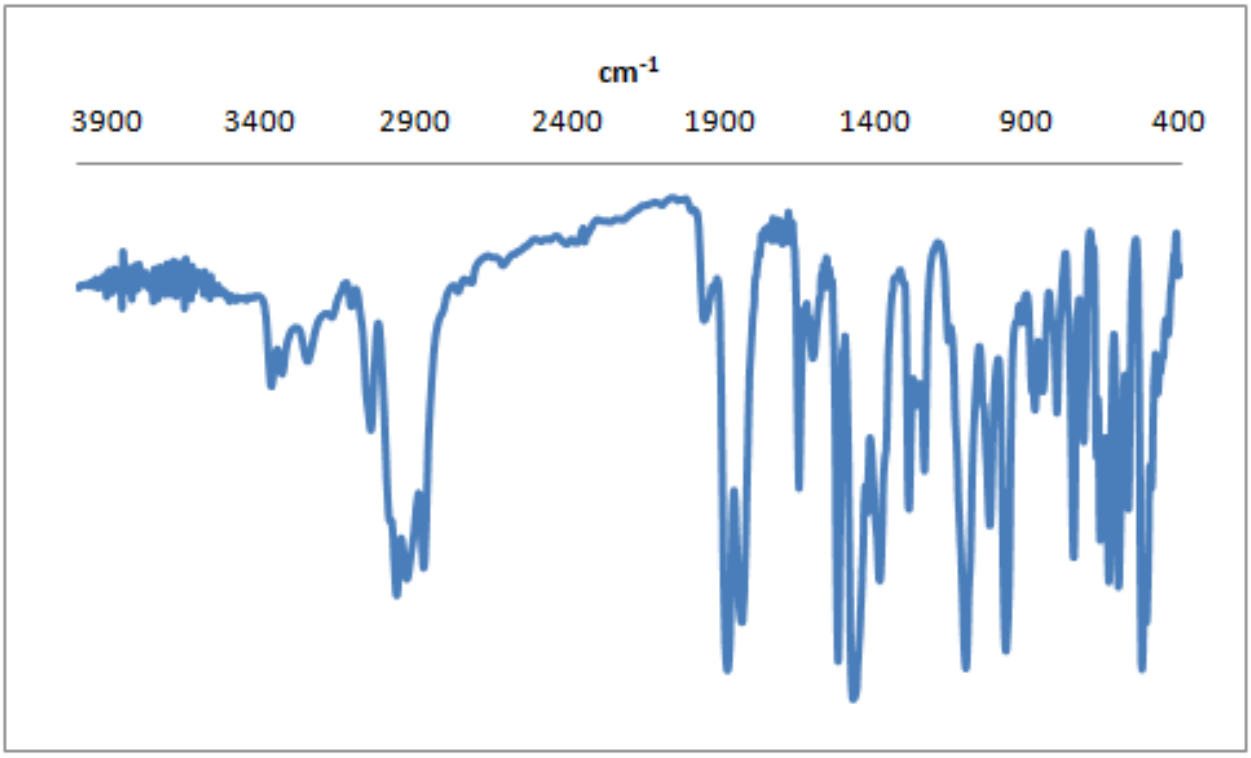

Fig. S54 FT-IR (KBr) of **(SiP^{iPr}3)Fe(CO)(H)**.

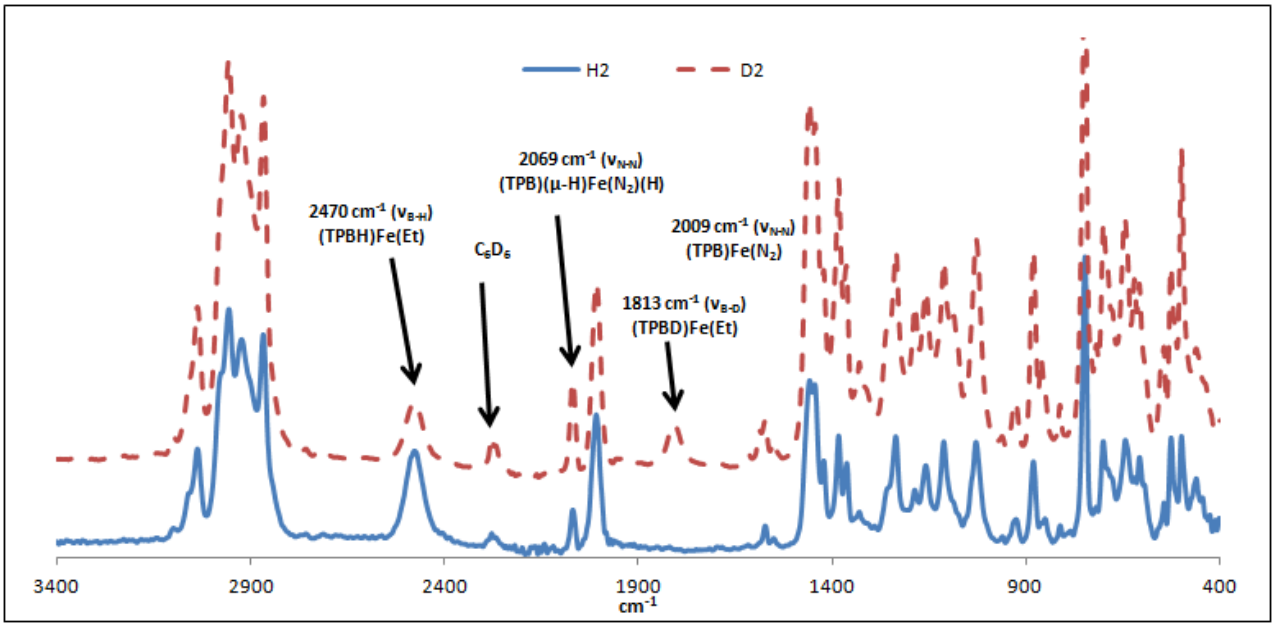

Fig. S55 ATR-IR (THF thin film) of **A** (TPBH)Fe(Et) (H_2) and labeled (TPBD)Fe(Et) (D_2).

UV-Vis Spectra

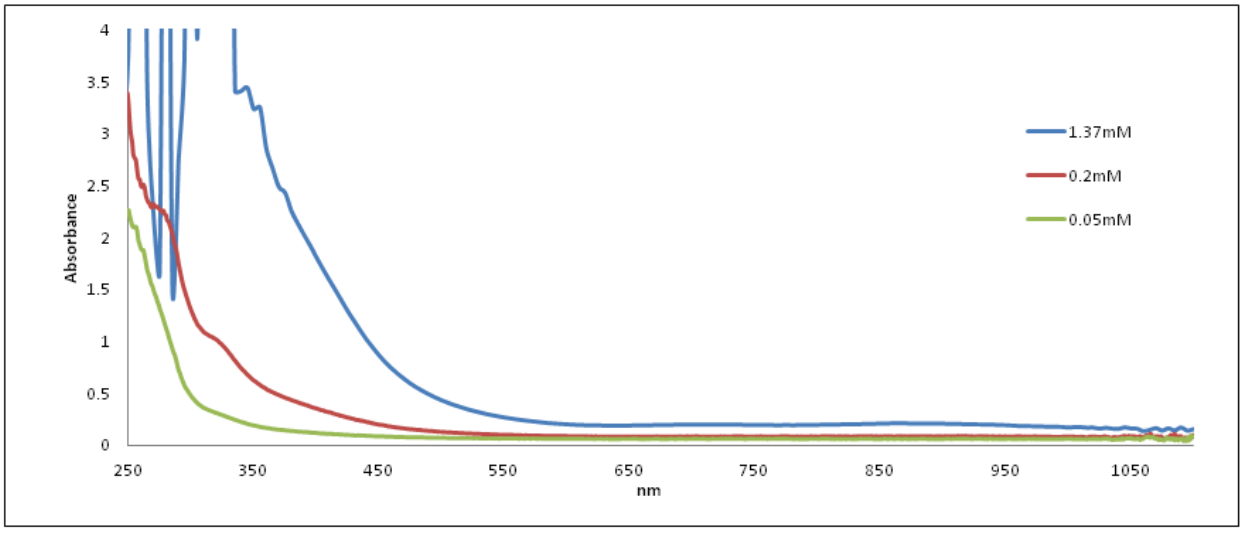

Fig. S56 UV-Vis of **2**, (TPB)(μ-H)Fe(N_2)(H), in THF.

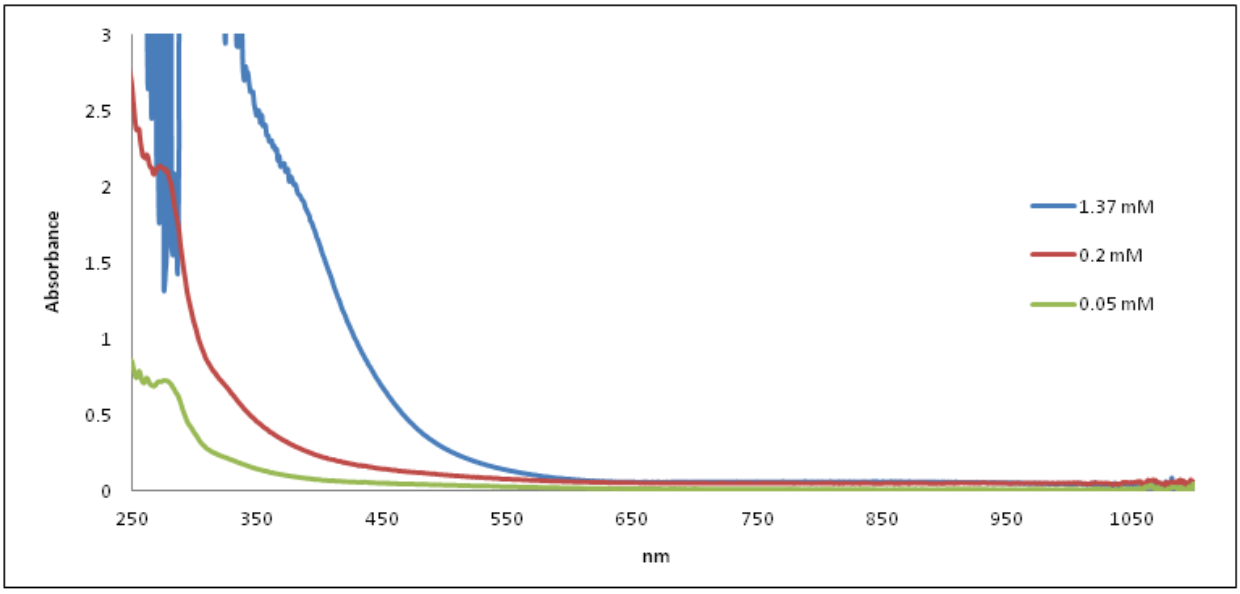

Fig. S57 UV-Vis spectrum of **3**, (TPB)(μ-H)Fe(H_2)(H), in THF.

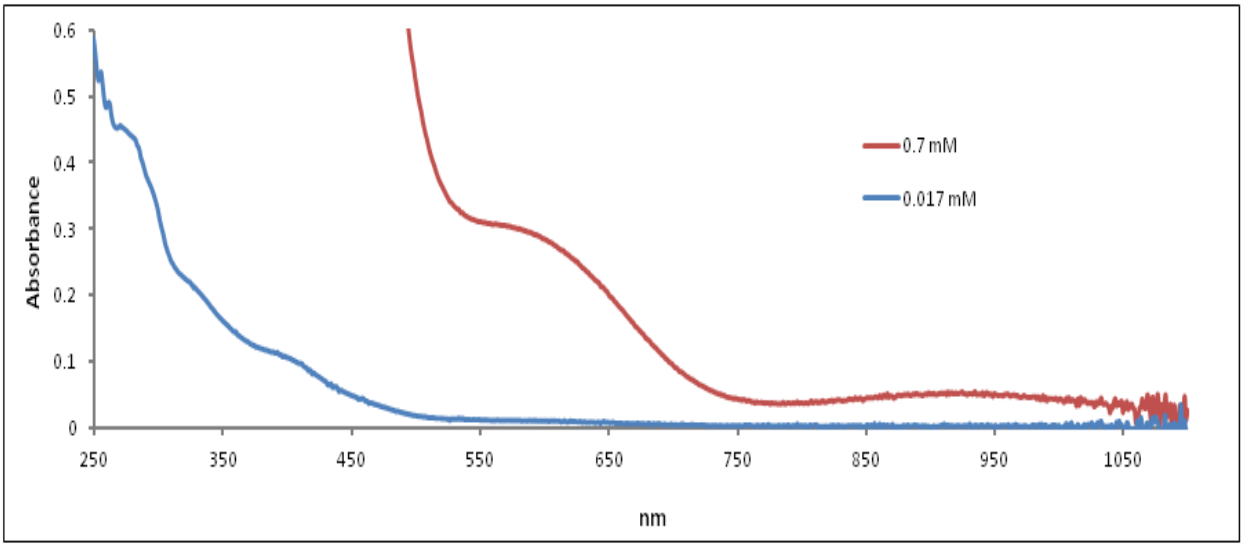

Fig. S58 UV-vis spectrum of **4**, (TPB)Fe(CN^{t}Bu), in THF.

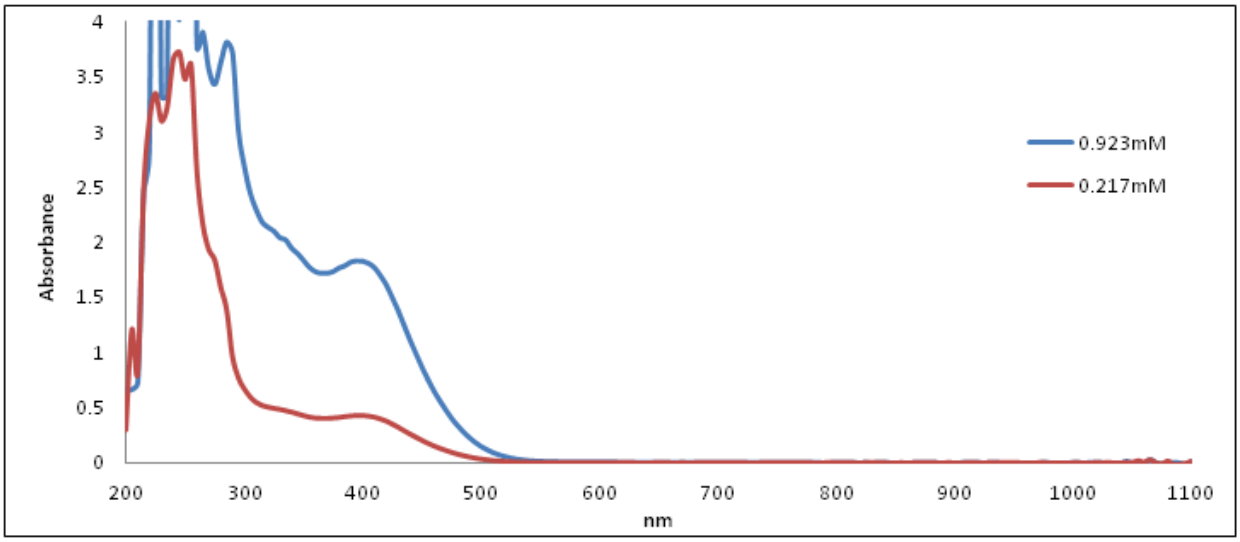

Fig. S59 UV-Vis spectrum of **5**, (TPB)(μ-H)Fe(CN^{t}Bu)(H), in THF.

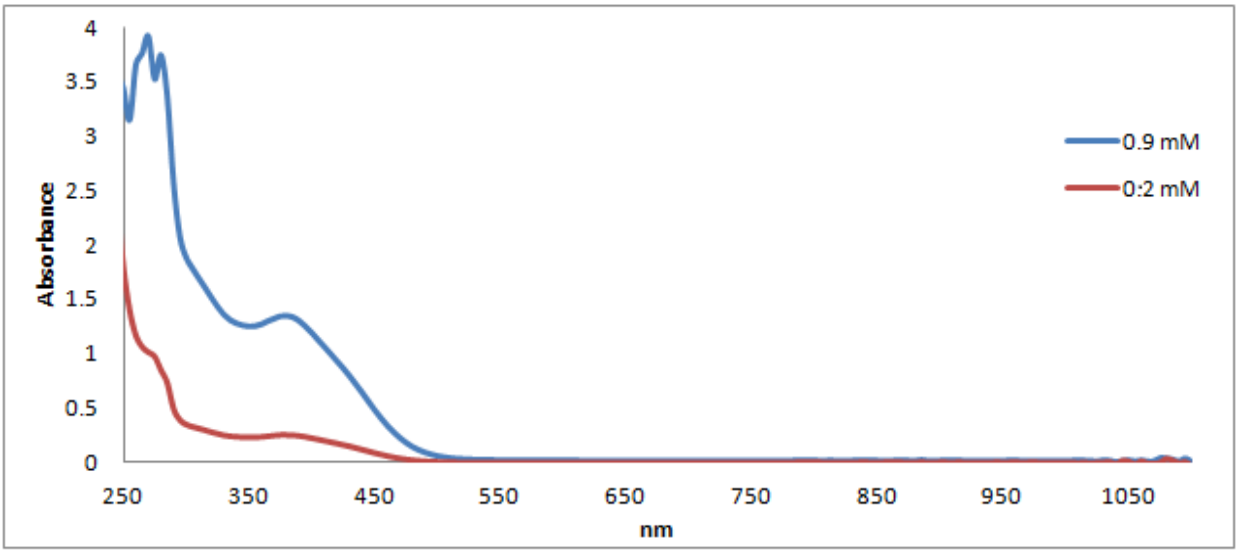

Fig. S60 UV-Vis spectrum of **7**, (TPB)(μ-H)Fe(CO)(H), in THF.

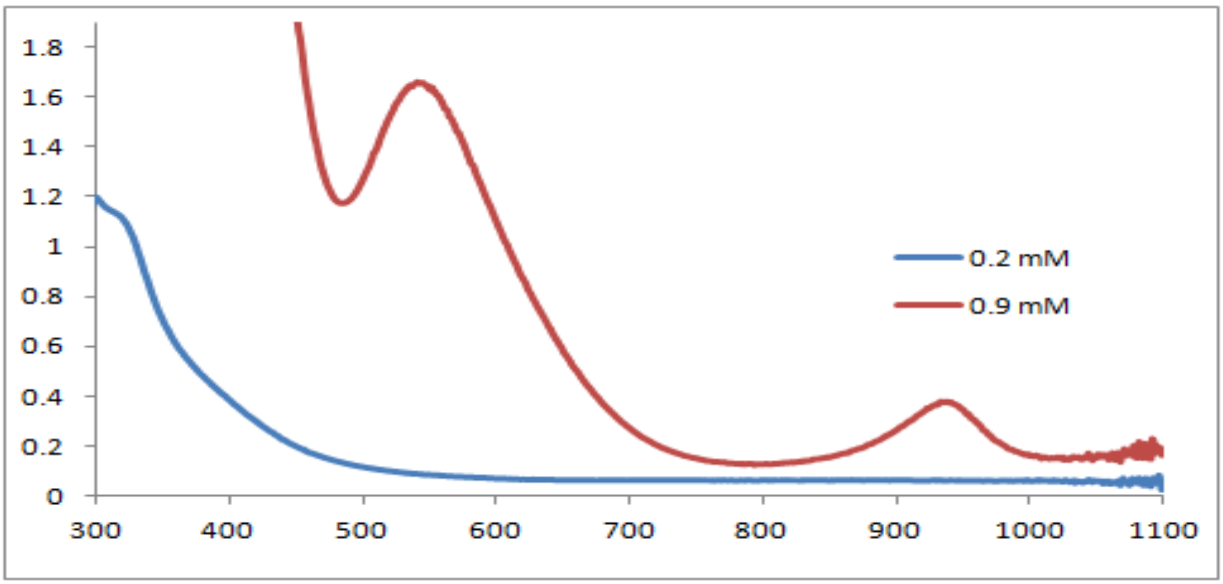

Fig. S61 UV-Vis spectrum of **8**, (TPB)Fe(C_2H_4), in THF.

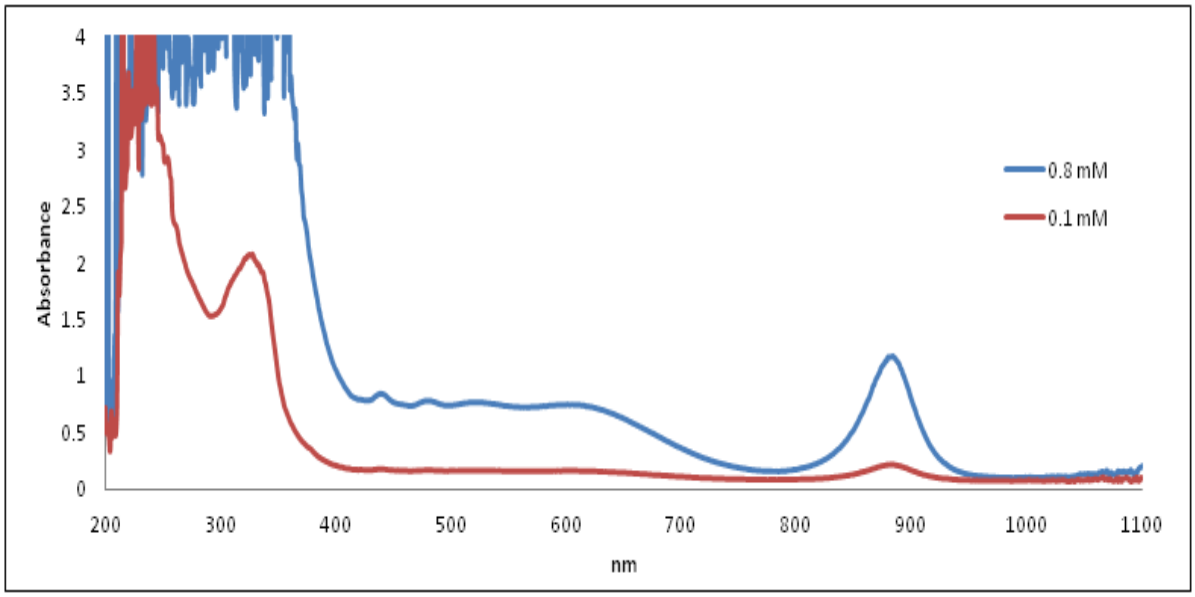

Fig. S62 UV-Vis spectrum of **9**, (TPB)(μ-H)Fe(C≡CPh), in THF.

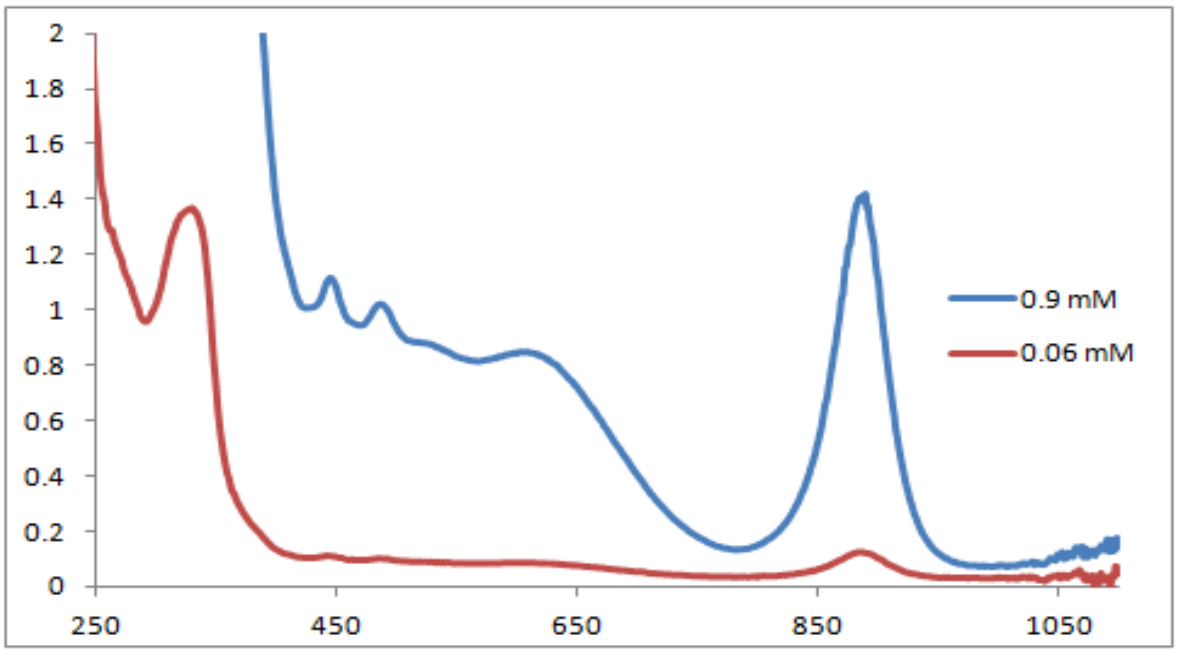

Fig. S63 UV-Vis spectrum of **10**, (TPB)(μ-H)Fe(C≡CTol), in THF.

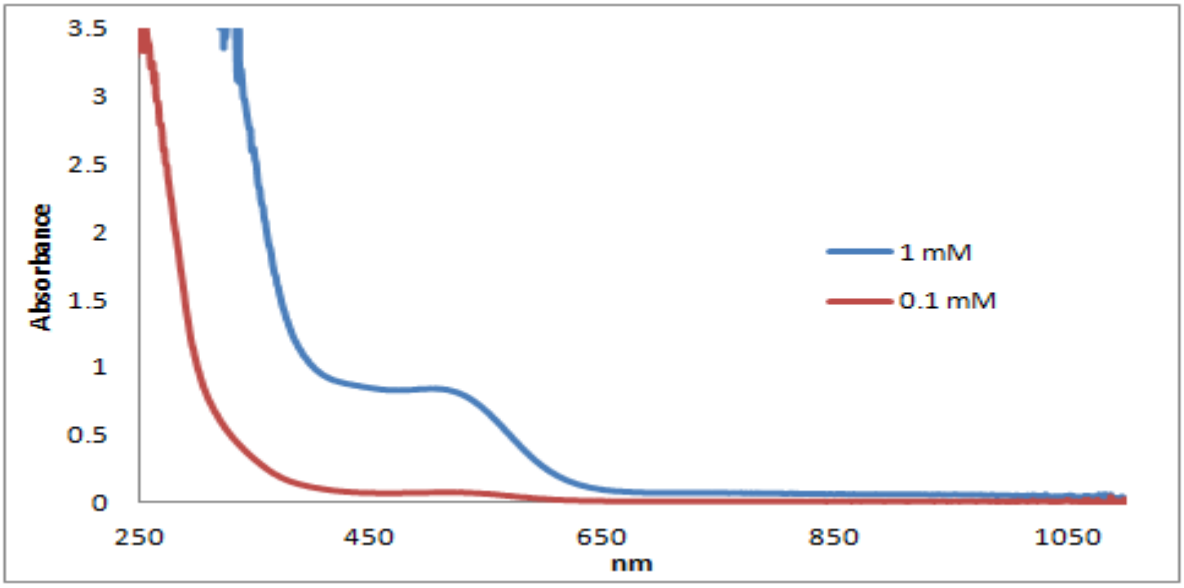

Fig. S64 UV-Vis spectrum of **11** in THF.

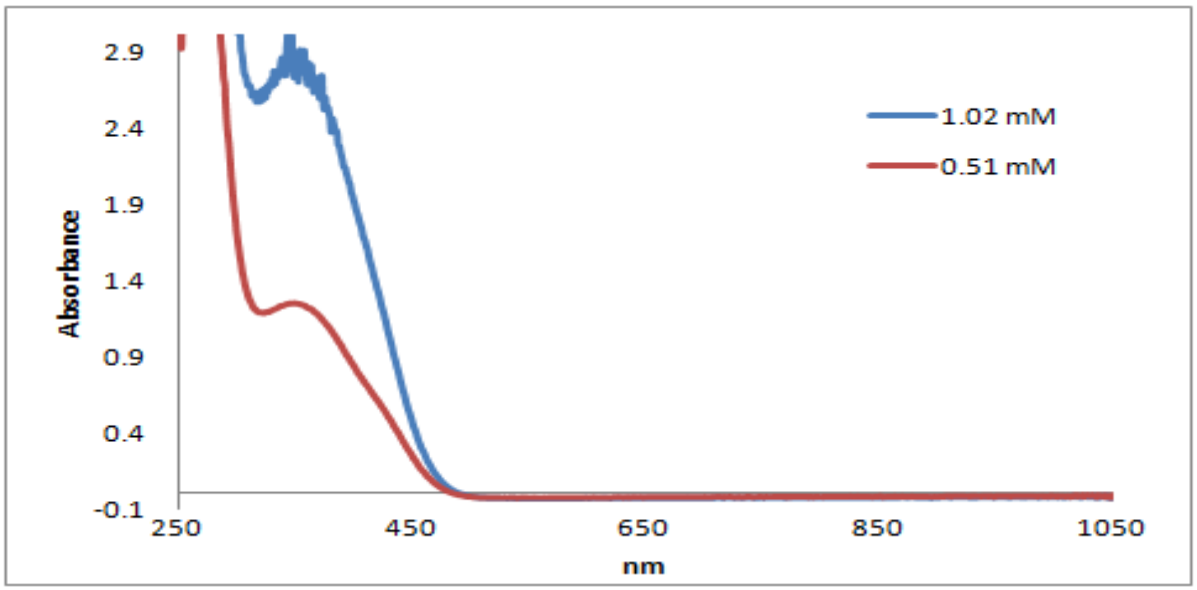

Fig. S65 UV-Vis spectrum of **(SiP$^{iPr}_3$)Fe(H_2)(H)** in THF.

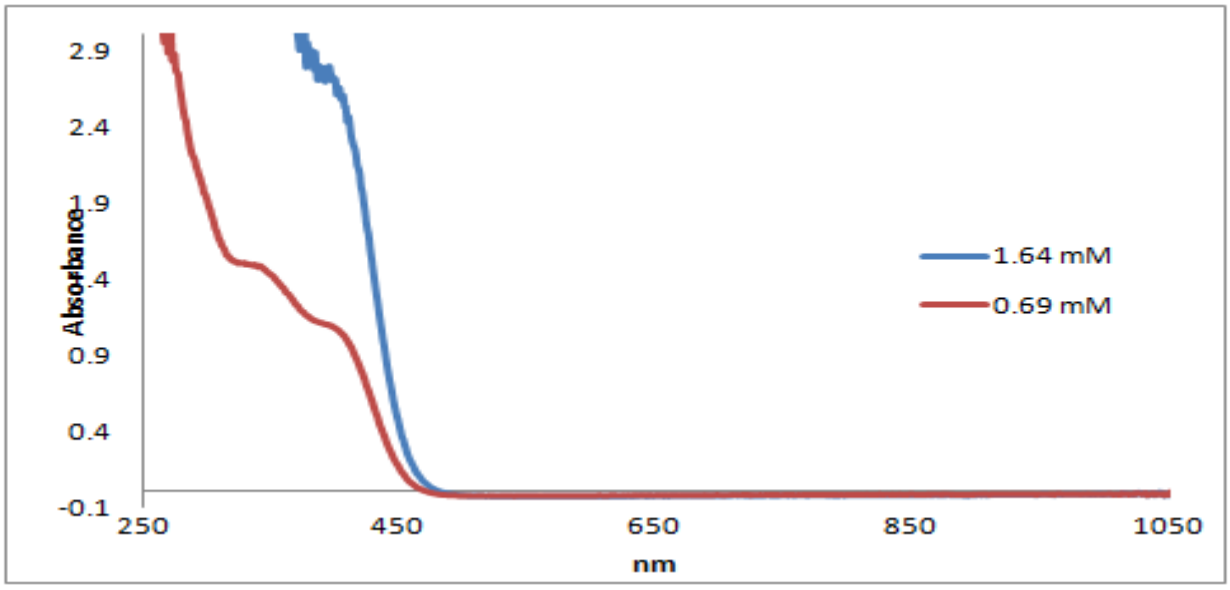

Fig. S66 UV-Vis spectrum of **(SiP$^{iPr}_3$)Fe(CO)(H)** in THF.

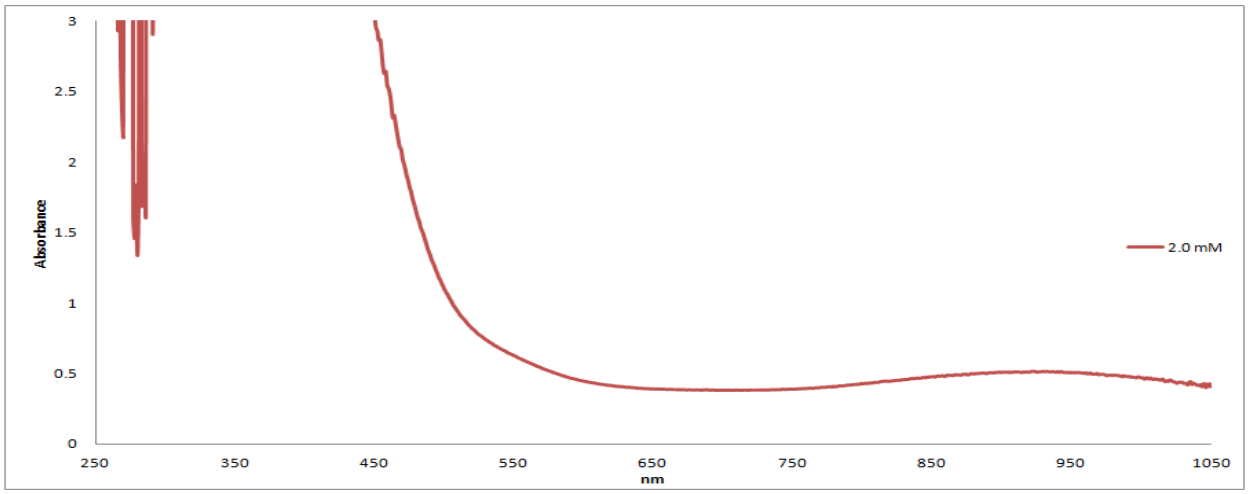

Fig. S67 UV-Vis spectrum of **A**, (TPBH)Fe(Et), in THF.

Catalytic Hydrogenation Time Traces

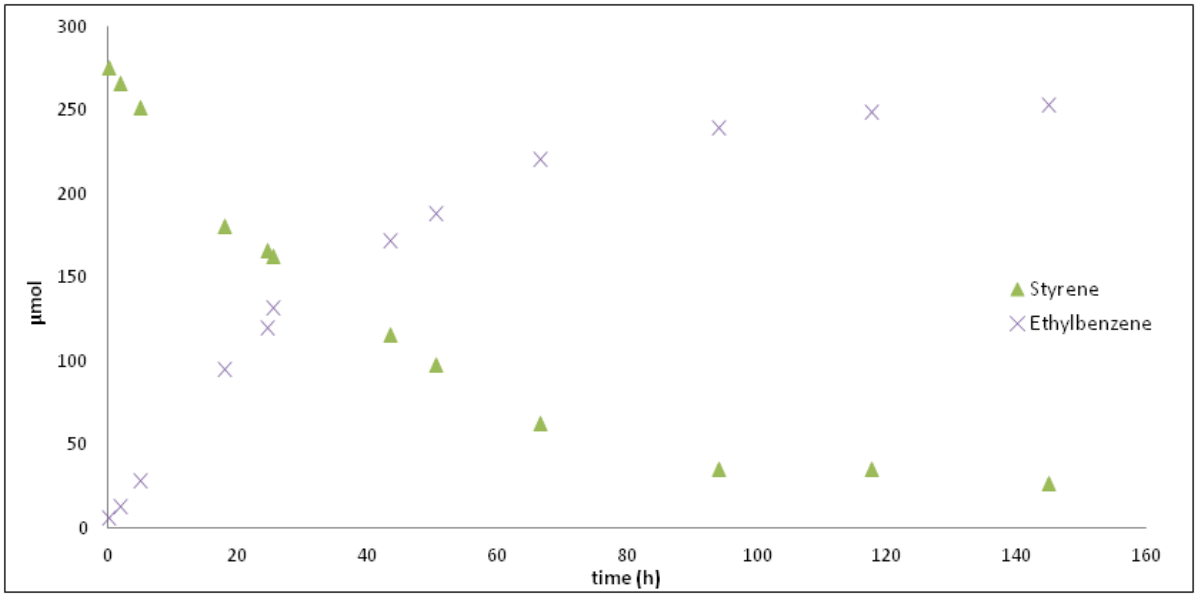

Fig. S68 Catalytic hydrogenation of styrene with **1**. Amounts of styrene and ethylbenzene were determined by ^{1}H NMR spectroscopy with ferrocene as an integration standard.

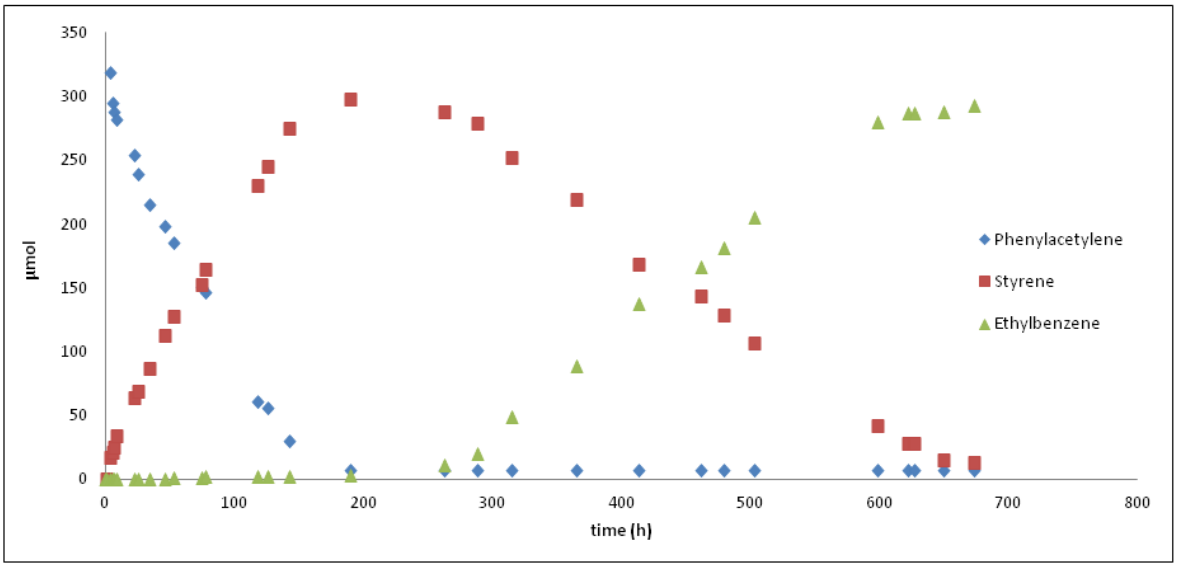

Fig. S69 Catalytic hydrogenation of phenylacetylene with **1**. Amounts of phenylacetylene, styrene, and ethylbenzene were determined by ^{1}H NMR spectroscopy with ferrocene as an integration standard.

GC-MS Data

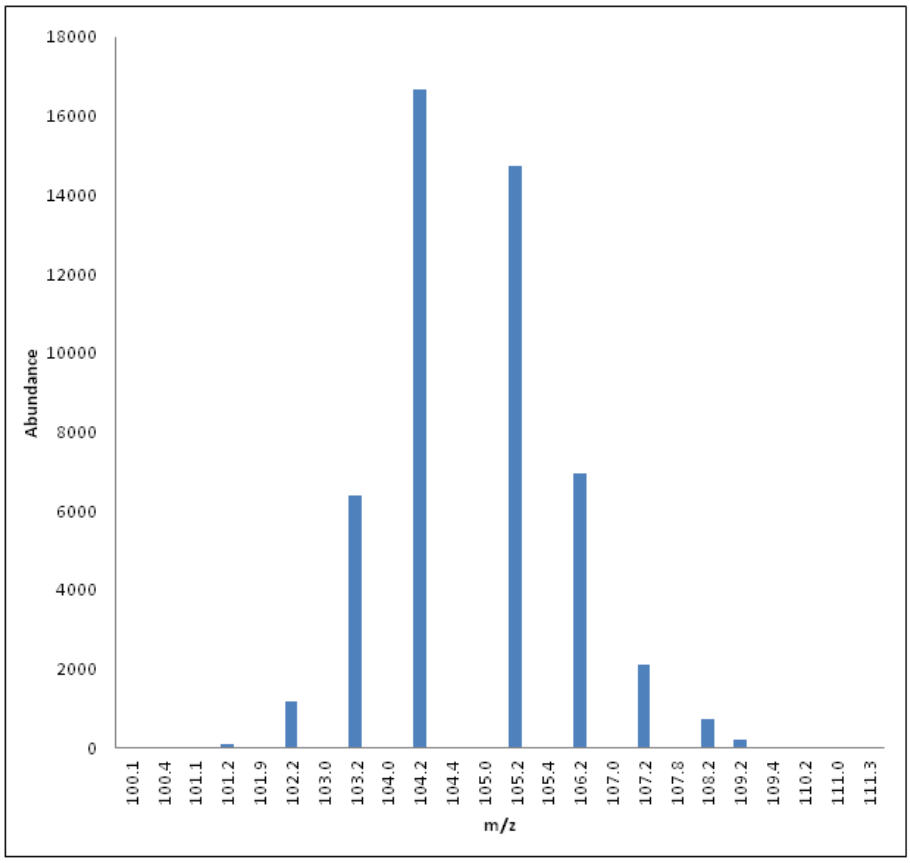

Fig. S70 GC-MS data from the reaction mixture of **1**, D_2, and styrene after 12 h. The spectrum of a mixture of styrene, d_1-styrene, d_2-styrene, d_3-styrene, and ethylbenzene.

XRD Data

For the structure of **10**, checkCIF reported one level A alert (PLAT971_ALERT_2_A) due to a large calculated nonmetal positive residual density. This situation could arise from unaccounted atoms. In this data set, the highest residual electron density peak was located between the iron and boron, this electron density was attributed to the borohydride hydrogen atom that was intentionally not included in the model, as there was no satisfactory way to model this. Our spectroscopic data was consistent with our assignment of this compound with a borohydride unit on the TPB ligand.

Table 1. Crystallographic Data for Compounds **2**, **3**, **4**, **5**, **8**

	2	**3**	**4**	**5**	**8**
chem formula	$C_{36}H_{56}BFeN_2P_3$	$C_{36}H_{58}BFeP_3$	$C_{43}H_{69}BFeNP_3Si_{0.5}$	$C_{41}H_{65}BFeNP_3$	$C_{38}H_{58}BFeP_3$
fw	676.4	650.42	773.61	731.51	674.41
cryst syst	monoclinic	monoclinic	rhombohedral	orthorhombic	triclinic
space group	P2(1)/c	P2(1)/n	R-3	Pna2(1)	P-1
a [Å]	10.9690(10)	10.6196(6)	11.2415(3)	28.1082(11)	11.7652(5)
b [Å]	15.8820(14)	21.3418(13)	11.2415(3)	11.7188(5)	18.1293(8)
c [Å]	20.7040(18)	15.6111(9)	59.3261(18)	12.0896(5)	18.8179(8)
α [°]	90.00	90.00	90.00	90.00	112.296(2)
β [°]	102.446(2)	94.019(4)	90.00	90.00	90.626(2)
γ [°]	90.00	90.00	120.00	90.00	105.264(2)
V [$Å^3$]	3522.1(5)	3529.4(4)	6492.7(3)	3982.2(3)	3555.0(3)
Z	4	4	6	4	4
D_{calcd} [g cm^{-3}]	1.276	1.218	1.187	1.220	1.260
F(000)	1444	1388	2502	1576	1448
μ [mm^{-1}]	0.592	0.586	0.503	0.528	0.585
temp. [K]	100	100	100	100	100
wavelength [Å]	0.71073	0.71073	0.7103	0.71073	0.71073
measd rflns	64963	187522	46175	125477	285706
unique rflns	8699	20034	4245	17351	55462
data/restraints/param	8699/0/406	20034/0/386	4245/88257	17351/1/447	55462/0/831
R(F) ($I>2\sigma(I)$)	0.0505	0.0548	0.1562	0.0536	0.0418
wR(F^2) (all)	0.1264	0.1511	0.1683	0.1336	0.1086
GOF	1.035	1.056	1.082	1.441	1.030

Table 2 Crystallographic Data for Compounds **10**, **11**, **(SiP^{iPr}_3)Fe(CO)(H).**

	10	**11**	**(SiP^{iPr}_3)Fe(CO)(H)**
chem formula	$C_{45}H_{62}BFeP_3$	$C_{48}H_{81}BFeP_4$	$C_{37}H_{55}FeP_3Si$

fw	762.52	854.44	692.66
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2(1)/c	C2/c	C2/c
a [Å]	25.3343(11)	14.7183(8)	36.5798(8)
b [Å]	15.1553(6)	22.2944(13)	11.7777(3)
c [Å]	23.4782(1)	14.8410(9)	17.1309(4)
α [°]	90.00	90.00	90.00
β [°]	113.176(2)	103.864(3)	104.2430(10)
γ [°]	90.00	90.00	90.00
V [$Å^3$]	8287.0(6)	4728.0(5)	7153.6(3)
Z	8	8	8
D_{calcd} [g cm^{-3}]	1.222	1.200	1.286
F(000)	3264	1840	2960
μ [mm^{-1}]	0.510	0.486	5.175
temp. [K]	100	100	100
wavelength [Å]	0.71073	0.71073	1.54178
measd rflns	256649	143163	50397
unique rflns	41264	22688	6480
data/restraints/param	41264/0/927	22688/0/265	6580/0/404
R(F) ($I>2\sigma(I)$)	0.0684	0.0385	0.0.0273
wR(F^2) (all)	0.207	0.1407	0.0703
GOF	1.239	0.928	1.046

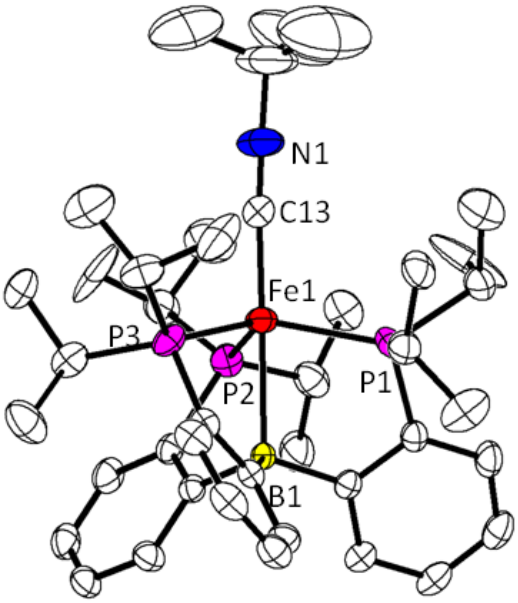

Fig. S71 XRD structure of **4**, (TPB)Fe(CN^{t}Bu). Ellipsoids shown at 50% probability. The CN^{t}Bu unit is disordered over three positions, and therefore the Fe-C13 and C13-N1 bond distance are reported as an average of the three Fe-C13 and three C13-N1 positions, respectively. Selected bond distances (Å) and angles (°): Fe1-P1 = 2.3193(7), Fe-P2 = 2.3193(7), Fe-P3 = 2.3194(7), 2.320(4), Fe-C13(avg) = 1.861(7), C13-N1(avg) = 1.179(9), Fe1-B1 = 2.340(4), ∑(P-Fe-P) = 345.03(1).

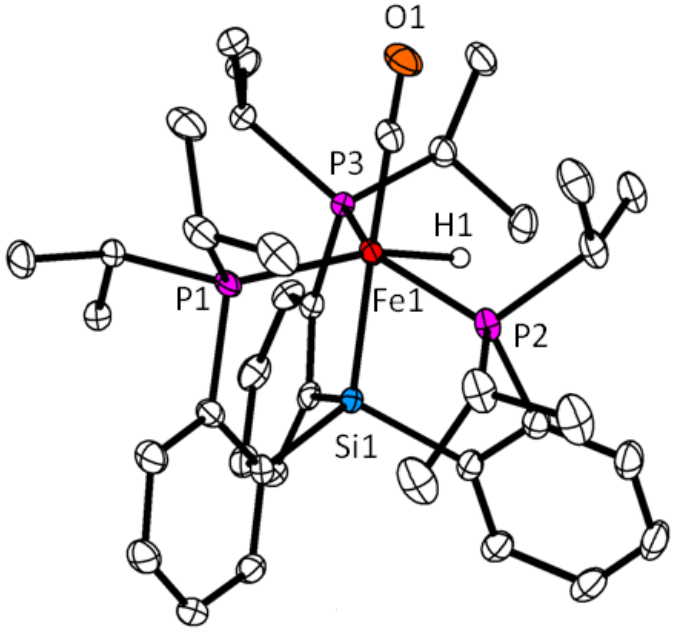

Fig. S72 XRD structure of **(SiP$^{iPr}_3$)Fe(CO)(H)**. Ellipsoids shown at 50% probability. Selected bond distances (Å) and angles (°): Fe1-P1 = 2.2559(4), Fe1-P2 = 2.2495(4), Fe1-P3 = 2.2214(4),

Fe1-H1 = 1.43(2), Fe1-C11 = 1.768(2), Fe1-Si1 = 2.2567(4), P3-Fe1-P1 = 106.05(2), P1-Fe1-P2 = 110.27(2), P2-Fe1-H1 = 66.4(1), P3-Fe1-H1 = 73.4(1).

DFT Coordinates

Input Coordinates [Angstroms] for **3**.

Atom	X	Y	Z
Fe1	7.0892	3.3857	12.2773
P2	6.2154	4.9695	10.9253
P3	6.3100	1.7194	13.5222
P4	9.0349	2.5824	11.4387
C5	7.4214	1.7948	9.3360
C6	5.6392	0.3697	12.4353
C7	4.8685	4.1771	9.9445
C8	7.4635	0.8606	14.7392
H9	8.0191	0.2295	14.1978
C10	9.8530	1.0030	12.0884
H11	9.8330	1.0491	13.0872
C12	4.8036	2.0676	14.5617
H13	4.5867	1.2325	15.0673
C14	8.7510	2.1101	9.7008
C15	5.2385	-0.5595	10.2519
H16	5.3171	-0.5024	9.3069
C17	10.5206	3.7094	11.4651
H18	11.2755	3.2347	11.0125
C19	5.0476	3.1776	15.5871
H20	5.3517	3.9872	15.1261
H21	5.7329	2.8881	16.2251

H22	4.2145	3.3681	16.0667
C23	4.9283	2.7889	9.7092
B24	6.1465	1.8979	10.3262
C25	5.3890	6.3828	11.8189
H26	5.0302	7.0020	11.1204
C27	5.6802	0.5224	11.0342
C28	5.0689	-0.7882	12.9948
H29	5.0133	-0.8714	13.9395
C30	7.1382	5.9445	9.5853
H31	8.0124	6.2199	9.9851
C32	8.4446	1.8599	15.3701
H33	7.9582	2.4569	15.9762
H34	8.8717	2.3885	14.6640
H35	9.1300	1.3719	15.8727
C36	7.4706	5.0600	8.3760
H37	6.6454	4.8405	7.8952
H38	7.8991	4.2340	8.6834
H39	8.0796	5.5407	7.7773
C40	9.7846	2.0456	8.7566
H41	10.6727	2.2599	9.0171
C42	3.8254	4.9429	9.3991
H43	3.7925	5.8773	9.5672
C44	3.6045	2.3909	13.6695
H45	2.8462	2.6632	14.2274
H46	3.3597	1.5963	13.1507
H47	3.8392	3.1204	13.0586
C48	3.9098	2.2249	8.9233

H49	3.9188	1.2880	8.7665
C50	6.4709	7.2239	9.0745
H51	7.0280	7.6263	8.3758
H52	6.3682	7.8570	9.8154
H53	5.5893	7.0075	8.7052
C54	4.5871	-1.8088	12.1928
H55	4.1865	-2.5750	12.5865
C56	6.8391	0.0245	15.8596
H57	7.5490	-0.4047	16.3814
H58	6.2591	-0.6627	15.4701
H59	6.3096	0.6057	16.4447
C60	2.8901	2.9860	8.3668
H61	2.2311	2.5755	7.8193
C62	7.2004	1.4149	8.0059
H63	6.3184	1.1888	7.7350
C64	4.6910	-1.7096	10.8094
H65	4.3917	-2.4187	10.2524
C66	9.0588	-0.2383	11.6768
H67	9.1137	-0.3539	10.7052
H68	8.1213	-0.1284	11.9403
H69	9.4327	-1.0276	12.1213
C70	9.5251	1.6716	7.4433
H71	10.2313	1.6319	6.8091
C72	10.9349	3.9804	12.9140
H73	11.7631	4.5043	12.9244
H74	11.0812	3.1289	13.3766
H75	10.2257	4.4814	13.3683

C76	11.3158	0.7914	11.6731
H77	11.6308	-0.0714	12.0148
H78	11.8681	1.5109	12.0440
H79	11.3822	0.7994	10.6954
C80	4.2180	5.9867	12.7098
H81	4.5494	5.4728	13.4756
H82	3.5879	5.4388	12.1967
H83	3.7635	6.7938	13.0300
C84	8.2283	1.3566	7.0647
H85	8.0412	1.1024	6.1687
C86	10.2983	5.0343	10.7429
H87	9.5863	5.5359	11.1922
H88	10.0392	4.8605	9.8139
H89	11.1266	5.5579	10.7585
C90	6.4391	7.1571	12.6066
H91	6.0235	7.9418	13.0213
H92	7.1533	7.4472	12.0014
H93	6.8157	6.5803	13.3036
C94	2.8403	4.3515	8.6163
H95	2.1373	4.8781	8.2543
H96	7.7936	4.4965	13.0456
H97	6.1119	2.5661	11.3356
H98	5.5742	3.9412	12.7631
H99	7.6061	3.8751	13.6692

Optimized Coordinates [Angstroms] for **3**.

Atom	X	Y	Z
Fe	-0.117363	-0.103709	-1.103449
P	2.189154	-0.527524	-0.974334
P	-2.110168	-1.097370	-0.669335
P	-0.495046	2.097951	-0.509807
C	0.557719	1.210908	1.905336
C	-2.289533	-1.265061	1.185877
C	2.398779	-1.501535	0.603316
C	-3.739797	-0.319060	-1.304037
H	-3.935678	0.481024	-0.581651
C	-2.244839	2.804105	-0.149723
H	-2.864935	2.420681	-0.967491
C	-2.289253	-2.902115	-1.205735
H	-3.305210	-3.193056	-0.909139
C	0.340006	2.361059	1.107017
C	-1.488008	-0.919697	3.434453
H	-0.728123	-0.556314	4.122165
C	0.142115	3.432562	-1.689312
H	-0.044777	4.397240	-1.205753
C	-2.165118	-3.071941	-2.726949
H	-1.191476	-2.720780	-3.083971
H	-2.940675	-2.530873	-3.277379
H	-2.254219	-4.132594	-2.993963
C	1.473498	-1.330507	1.668838
B	0.195832	-0.323105	1.495591
C	2.798812	-1.680971	-2.347740
H	3.852423	-1.876162	-2.127295

C	-1.239985	-0.848222	2.050338
C	-3.471830	-1.799589	1.728733
H	-4.253225	-2.170741	1.075798
C	3.691494	0.677613	-0.899092
H	3.470769	1.407098	-1.684418
C	-3.505372	0.333733	-2.680895
H	-3.294086	-0.414580	-3.452325
H	-2.669789	1.036941	-2.672919
H	-4.404304	0.880373	-2.993743
C	3.746161	1.422730	0.441786
H	3.994064	0.738860	1.260149
H	2.804651	1.908812	0.693765
H	4.527094	2.193536	0.403050
C	0.711622	3.638220	1.560628
H	0.561304	4.508280	0.927308
C	3.481491	-2.385232	0.745338
H	4.176673	-2.536768	-0.074768
C	-1.312394	-3.828258	-0.466705
H	-1.473362	-4.863949	-0.793030
H	-1.456237	-3.789087	0.616280
H	-0.272926	-3.564130	-0.677826
C	1.696997	-2.079783	2.836318
H	0.987353	-2.001644	3.656059
C	5.085519	0.096660	-1.197642
H	5.828916	0.898806	-1.100536
H	5.183824	-0.306500	-2.209599
H	5.364783	-0.684472	-0.482873

C	-3.669798	-1.883983	3.105156
H	-4.595086	-2.298153	3.497659
C	-5.004553	-1.193462	-1.381641
H	-5.841727	-0.581473	-1.742019
H	-5.305651	-1.605488	-0.416606
H	-4.889728	-2.023698	-2.086313
C	2.779234	-2.950070	2.975381
H	2.909271	-3.514167	3.896287
C	1.152356	1.427350	3.164235
H	1.375110	0.570106	3.795130
C	-2.674650	-1.421518	3.964739
H	-2.818949	-1.457317	5.042135
C	-2.801901	2.267918	1.177816
H	-2.270525	2.708142	2.027612
H	-2.721488	1.185846	1.271094
H	-3.861440	2.540145	1.269503
C	1.298830	3.811306	2.812495
H	1.592369	4.803024	3.147217
C	-0.645475	3.398108	-3.010799
H	-0.313814	4.213828	-3.665486
H	-1.725567	3.505694	-2.871110
H	-0.470567	2.457320	-3.546250
C	-2.376349	4.338058	-0.140023
H	-3.411317	4.602903	0.112114
H	-2.150713	4.806726	-1.101327
H	-1.736151	4.790704	0.625005
C	2.103946	-3.045207	-2.427214

H	1.063506	-2.951511	-2.746457
H	2.115421	-3.566171	-1.465403
H	2.625872	-3.675970	-3.159338
C	1.512796	2.694455	3.620488
H	1.977885	2.807795	4.597084
C	1.641650	3.339927	-1.978191
H	1.877058	2.418949	-2.520292
H	2.239501	3.364668	-1.063776
H	1.951206	4.184187	-2.607950
C	2.731779	-0.952235	-3.701238
H	3.193530	-1.564813	-4.485869
H	3.250280	0.012676	-3.686080
H	1.693400	-0.767375	-3.998994
C	3.678194	-3.106957	1.923165
H	4.518322	-3.791753	2.007788
H	-0.240391	0.470276	-2.609097
H	0.044374	-0.638129	0.304406
H	0.177952	-1.558901	-1.337277
H	-0.226467	-0.377846	-2.662552

Total Energy [a.u.]: -3719.2736777

Input Coordinates [Angstroms] Equatorial H_2 Isomer of **3**.

Fe1	7.0892	3.3857	12.2773
P2	6.2154	4.9695	10.9253
P3	6.3100	1.7194	13.5222

P4	9.0349	2.5824	11.4387
C5	7.4214	1.7948	9.3360
C6	5.6392	0.3697	12.4353
C7	4.8685	4.1771	9.9445
C8	7.4635	0.8606	14.7392
H9	8.0191	0.2295	14.1978
C10	9.8530	1.0030	12.0884
H11	9.8330	1.0491	13.0872
C12	4.8036	2.0676	14.5617
H13	4.5867	1.2325	15.0673
C14	8.7510	2.1101	9.7008
C15	5.2385	-0.5595	10.2519
H16	5.3171	-0.5024	9.3069
C17	10.5206	3.7094	11.4651
H18	11.2755	3.2347	11.0125
C19	5.0476	3.1776	15.5871
H20	5.3517	3.9872	15.1261
H21	5.7329	2.8881	16.2251
H22	4.2145	3.3681	16.0667
C23	4.9283	2.7889	9.7092
B24	6.1465	1.8979	10.3262
C25	5.3890	6.3828	11.8189
H26	5.0302	7.0020	11.1204
C27	5.6802	0.5224	11.0342
C28	5.0689	-0.7882	12.9948
H29	5.0133	-0.8714	13.9395
C30	7.1382	5.9445	9.5853

H31	8.0124	6.2199	9.9851
C32	8.4446	1.8599	15.3701
H33	7.9582	2.4569	15.9762
H34	8.8717	2.3885	14.6640
H35	9.1300	1.3719	15.8727
C36	7.4706	5.0600	8.3760
H37	6.6454	4.8405	7.8952
H38	7.8991	4.2340	8.6834
H39	8.0796	5.5407	7.7773
C40	9.7846	2.0456	8.7566
H41	10.6727	2.2599	9.0171
C42	3.8254	4.9429	9.3991
H43	3.7925	5.8773	9.5672
C44	3.6045	2.3909	13.6695
H45	2.8462	2.6632	14.2274
H46	3.3597	1.5963	13.1507
H47	3.8392	3.1204	13.0586
C48	3.9098	2.2249	8.9233
H49	3.9188	1.2880	8.7665
C50	6.4709	7.2239	9.0745
H51	7.0280	7.6263	8.3758
H52	6.3682	7.8570	9.8154
H53	5.5893	7.0075	8.7052
C54	4.5871	-1.8088	12.1928
H55	4.1865	-2.5750	12.5865
C56	6.8391	0.0245	15.8596
H57	7.5490	-0.4047	16.3814

H58	6.2591	-0.6627	15.4701
H59	6.3096	0.6057	16.4447
C60	2.8901	2.9860	8.3668
H61	2.2311	2.5755	7.8193
C62	7.2004	1.4149	8.0059
H63	6.3184	1.1888	7.7350
C64	4.6910	-1.7096	10.8094
H65	4.3917	-2.4187	10.2524
C66	9.0588	-0.2383	11.6768
H67	9.1137	-0.3539	10.7052
H68	8.1213	-0.1284	11.9403
H69	9.4327	-1.0276	12.1213
C70	9.5251	1.6716	7.4433
H71	10.2313	1.6319	6.8091
C72	10.9349	3.9804	12.9140
H73	11.7631	4.5043	12.9244
H74	11.0812	3.1289	13.3766
H75	10.2257	4.4814	13.3683
C76	11.3158	0.7914	11.6731
H77	11.6308	-0.0714	12.0148
H78	11.8681	1.5109	12.0440
H79	11.3822	0.7994	10.6954
C80	4.2180	5.9867	12.7098
H81	4.5494	5.4728	13.4756
H82	3.5879	5.4388	12.1967
H83	3.7635	6.7938	13.0300
C84	8.2283	1.3566	7.0647

H85	8.0412	1.1024	6.1687
C86	10.2983	5.0343	10.7429
H87	9.5863	5.5359	11.1922
H88	10.0392	4.8605	9.8139
H89	11.1266	5.5579	10.7585
C90	6.4391	7.1571	12.6066
H91	6.0235	7.9418	13.0213
H92	7.1533	7.4472	12.0014
H93	6.8157	6.5803	13.3036
C94	2.8403	4.3515	8.6163
H95	2.1373	4.8781	8.2543
H96	6.0621	4.3819	12.7661
H97	6.1119	2.5661	11.3356
H98	5.8525	3.7823	13.3458
H99	8.1010	4.0340	13.1064

Optimized Coordinates [Angstroms] Equatorial H_2 Isomer of **3**.

Atom	X	Y	Z
Fe	-0.169384	-0.006667	-1.137838
P	2.258741	-0.406738	-0.992751
P	-2.202927	-0.975413	-0.726372
P	-0.481004	2.102566	-0.352019
C	0.594437	0.992736	1.945652
C	-2.337217	-1.312523	1.107806
C	2.434018	-1.556262	0.468037
C	-3.827785	-0.132022	-1.267356

H	-3.986340	0.625945	-0.492496
C	-2.208951	2.811170	0.078801
H	-2.844461	2.502521	-0.758283
C	-2.396109	-2.735249	-1.404395
H	-3.388608	-3.055817	-1.061660
C	0.382192	2.217253	1.265009
C	-1.450200	-1.217034	3.347249
H	-0.654850	-0.950678	4.038955
C	0.170791	3.499228	-1.442740
H	0.029813	4.422247	-0.869483
C	-2.378428	-2.805242	-2.939341
H	-1.431007	-2.444152	-3.353500
H	-3.181961	-2.223084	-3.398272
H	-2.500674	-3.846573	-3.263309
C	1.470831	-1.521727	1.513916
B	0.194500	-0.499666	1.409975
C	2.859450	-1.436591	-2.471750
H	3.908821	-1.663419	-2.262178
C	-1.241240	-1.024798	1.967866
C	-3.524396	-1.847616	1.639641
H	-4.342428	-2.120617	0.983627
C	3.766074	0.770098	-0.792268
H	3.562397	1.567056	-1.513357
C	-3.613464	0.597872	-2.608577
H	-3.520770	-0.108823	-3.439905
H	-2.710463	1.210665	-2.611229
H	-4.476790	1.241411	-2.821609

C	3.812265	1.391963	0.610706
H	4.015304	0.630513	1.370671
H	2.883321	1.891144	0.883325
H	4.621263	2.132614	0.654862
C	0.777099	3.441927	1.830455
H	0.629319	4.369181	1.283187
C	3.519479	-2.446220	0.537488
H	4.242935	-2.493311	-0.270686
C	-1.371845	-3.708184	-0.799404
H	-1.585150	-4.726356	-1.149277
H	-1.406437	-3.711101	0.293002
H	-0.348617	-3.463509	-1.099797
C	1.662294	-2.409047	2.586585
H	0.925909	-2.435103	3.385449
C	5.155613	0.198354	-1.126529
H	5.903525	0.985551	-0.965805
H	5.256642	-0.127801	-2.165426
H	5.424654	-0.635721	-0.470473
C	-3.681587	-2.056321	3.007937
H	-4.611072	-2.468377	3.392645
C	-5.114435	-0.973202	-1.358209
H	-5.936369	-0.329519	-1.697398
H	-5.421465	-1.400754	-0.401885
H	-5.027397	-1.787507	-2.084883
C	2.746261	-3.285976	2.653789
H	2.849185	-3.959649	3.501637
C	1.211603	1.083144	3.209941

H	1.432538	0.167941	3.754067
C	-2.640176	-1.718291	3.870556
H	-2.751379	-1.850150	4.944409
C	-2.764666	2.199789	1.374398
H	-2.212229	2.569029	2.244351
H	-2.713151	1.112345	1.396237
H	-3.815283	2.493105	1.498223
C	1.383782	3.488796	3.083828
H	1.695089	4.440478	3.507085
C	-0.642695	3.607403	-2.744311
H	-0.296577	4.471982	-3.324975
H	-1.715987	3.734634	-2.572330
H	-0.506669	2.710226	-3.356517
C	-2.303713	4.343835	0.199783
H	-3.330454	4.612273	0.479993
H	-2.073966	4.875612	-0.726490
H	-1.648042	4.724442	0.990454
C	2.163373	-2.789947	-2.683506
H	1.157082	-2.682197	-3.097605
H	2.094139	-3.367553	-1.756969
H	2.742622	-3.381668	-3.404137
C	1.594644	2.297011	3.778334
H	2.074868	2.311601	4.754141
C	1.659324	3.381301	-1.773340
H	1.850236	2.487979	-2.375254
H	2.276509	3.337149	-0.872493
H	1.978587	4.254093	-2.357747

C	2.804695	-0.581765	-3.749889
H	3.207002	-1.145870	-4.601006
H	3.389380	0.340237	-3.659117
H	1.774690	-0.296171	-3.991333
C	3.682486	-3.307566	1.622848
H	4.525159	-3.993838	1.651386
H	-0.084383	-0.894061	-2.386664
H	0.033970	-0.751208	0.197270
H	0.100419	-1.448480	-1.701706
H	-0.375881	0.668759	-2.502714

Total Energy [a.u.]: -3719.2638793

Optimized Coordinates [Angstroms] for Transition State

Atom	X	Y	Z
Fe	-0.153028	-0.042298	-1.129626
P	2.235083	-0.444403	-0.986249
P	-2.173700	-1.017002	-0.705395
P	-0.486434	2.101444	-0.405994
C	0.583969	1.066766	1.930243
C	-2.325357	-1.287985	1.138340
C	2.422333	-1.537926	0.515085
C	-3.799990	-0.202079	-1.288214
H	-3.978163	0.572424	-0.533999
C	-2.221617	2.810705	-0.002643

H	-2.851197	2.473823	-0.833343
C	-2.352851	-2.797441	-1.325424
H	-3.352643	-3.109399	-0.996166
C	0.368277	2.268392	1.210858
C	-1.462664	-1.108490	3.382430
H	-0.676398	-0.812614	4.072586
C	0.159949	3.470785	-1.534746
H	0.006645	4.411496	-0.994573
C	-2.297387	-2.912836	-2.856265
H	-1.337486	-2.565335	-3.252545
H	-3.087725	-2.343222	-3.352877
H	-2.413262	-3.962880	-3.153199
C	1.471227	-1.459226	1.568849
B	0.194563	-0.442420	1.438447
C	2.836474	-1.518152	-2.430616
H	3.886530	-1.737386	-2.215908
C	-1.241702	-0.961224	1.999541
C	-3.514251	-1.813253	1.675862
H	-4.323395	-2.114711	1.021236
C	3.740804	0.742696	-0.827257
H	3.533525	1.515751	-1.572984
C	-3.574646	0.497612	-2.643513
H	-3.432710	-0.227677	-3.451673
H	-2.696094	1.145084	-2.638968
H	-4.453364	1.103848	-2.898733
C	3.788335	1.409689	0.554644
H	4.004337	0.675083	1.337177

H	2.855138	1.906295	0.817140
H	4.589066	2.160480	0.570920
C	0.755780	3.511687	1.739295
H	0.605564	4.420743	1.163018
C	3.507620	-2.425500	0.609262
H	4.222057	-2.506874	-0.204159
C	-1.338691	-3.745403	-0.667138
H	-1.525539	-4.772425	-1.006363
H	-1.414167	-3.730240	0.423177
H	-0.310226	-3.486983	-0.934626
C	1.673363	-2.300807	2.675773
H	0.945390	-2.292805	3.482799
C	5.131698	0.165112	-1.145664
H	5.878429	0.957919	-1.008195
H	5.232772	-0.191016	-2.174703
H	5.402651	-0.649249	-0.465990
C	-3.684324	-1.975607	3.048936
H	-4.614981	-2.380806	3.438054
C	-5.075270	-1.060359	-1.379355
H	-5.903455	-0.431340	-1.730700
H	-5.383443	-1.483312	-0.421343
H	-4.971510	-1.880541	-2.097161
C	2.757388	-3.175354	2.767568
H	2.869359	-3.813234	3.641526
C	1.195512	1.199028	3.193355
H	1.418178	0.302192	3.766555
C	-2.654283	-1.601138	3.910183

H	-2.775767	-1.697587	4.986672
C	-2.779470	2.229615	1.305692
H	-2.232700	2.623226	2.168514
H	-2.722118	1.143337	1.354101
H	-3.832182	2.520102	1.417616
C	1.358164	3.600225	2.992542
H	1.663996	4.566017	3.386794
C	-0.647677	3.526167	-2.843226
H	-0.302586	4.368705	-3.455881
H	-1.722258	3.655384	-2.681073
H	-0.505091	2.607773	-3.422510
C	-2.327568	4.345203	0.075377
H	-3.357318	4.614581	0.343338
H	-2.097063	4.852605	-0.864427
H	-1.677934	4.752242	0.857862
C	2.137274	-2.874967	-2.595941
H	1.115000	-2.772291	-2.969367
H	2.102347	-3.435534	-1.657241
H	2.691359	-3.478082	-3.327161
C	1.571565	2.431779	3.724731
H	2.048392	2.478930	4.701149
C	1.651241	3.355768	-1.854090
H	1.852477	2.449292	-2.432651
H	2.264323	3.337452	-0.949587
H	1.967662	4.215802	-2.458567
C	2.781724	-0.705505	-3.736021
H	3.197038	-1.292175	-4.565279

H	3.353955	0.226433	-3.671632
H	1.750585	-0.441862	-3.996532
C	3.681739	-3.241123	1.727798
H	4.523905	-3.926950	1.775432
H	-0.341452	0.553995	-2.535008
H	0.034756	-0.725955	0.232963
H	0.110276	-1.452161	-1.650877
H	-0.111954	-0.746250	-2.437543

Total Energy [a.u.]: -3719.263037