Supporting Information for

Cyanide Ligand Assembly by Carbon Atom Transfer to an Iron Nitride

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Experimental

General Considerations. All manipulations involving air- or moisture sensitive compounds and their preparations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an MBraun Labmaster glovebox. Glassware was dried at 130 °C overnight before cooling under dynamic vacuum in a glovebox antechamber. Diethyl ether (Et_2O), pentane, tetrahydrofuran (THF), and toluene were purified by the Glass Contour solvent purification system. Before use, an aliquot of each solvent was tested with 1 drop of solution of sodium benzophenone ketyl in THF. Celite was dried under vacuum at 130 °C overnight. 1,2-diisopropylimidazole ($^{i}Pr_2ImH$) was prepared according to a literature procedure.[1] Bis(diisopropylamino)cyclopropenylidene (BAC)[2] was prepared according to a literature procedure by deprotonation of the cyclopropenium salt prepared with $NaBF_4$ instead of $NaBPh_4$, followed by recrystallization from CH_2Cl_2/Et_2O at -35 °C. All other reagents were purchased from commercial vendors and used as received. Benzene-d_6 (C_6D_6, Cambridge Isotope Laboratories) was degassed by three consecutive freeze-pump-thaw cycles and stored over molecular sieves for at least 12 h prior to use. Toluene-d_8 and THF-d_8 (Sigma-Aldrich) were stored over molecular sieves for at least 12 h prior to use. ^{1}H NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) equipped with a FTS-Systems Air Jet TC-84 temperature controller. ^{15}N NMR data were recorded in a Varian spectrometer (500 MHz) referenced to NH_3 at $\delta = 0$ ($\delta = -380$ ppm vs. CH_3NO_2). Elemental analysis was conducted by Midwest Microlabs, LLC (Indianapolis, IN). Mass spectrometry data was collected on a Waters Synapt G2S QTOF for Atmospheric Pressure Chemical Ionization (APCI) and a MAT-95 XP Trap for positive Chemical Ionization (CI) using 1.8×10^{-4} mbar of CH_4 gas for ionization.

$[PhB(^{i}Pr_2ImH)_3][OTf]_2$. Neat $^{i}Pr_2ImH$ (3.05 g, 20.0 mmol) was added dropwise to a Schlenck flask containing a solution of $PhBCl_2$ (1.04 g, 6.57 mmol) in toluene (20 mL), leading to the formation of a white precipitate. The suspension was stirred for 30 min at room temperature. Trimethylsilyl trifluoromethylsulfonate (3.21 g, 14.4 mmol) was slowly added to the reaction mixture and the reaction was heated at reflux overnight. The precipitate was collected on a filter frit and washed with toluene. The product was

recrystallized twice from CH_2Cl_2/Et_2O at -35 °C. The resulting colorless crystals were washed with cold Et_2O (4.55 g, 79 % based on $PhBCl_2$ as the limiting reagent). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.55 (s, 3H, Im-*H*), 7.45 (m, 3H, B(C_6H_5)), 7.21 (m, 2H, B(C_6H_5)), 6.83 (s, 2H, Im-*H*), 4.51 (sept, J_{HH} = 6.7 Hz, 3H, C*H*(CH_3)$_2$), 3.03 (sept, J_{HH} = 6.8 Hz, 3H, C*H*(CH_3)$_2$), 1.63 (d, J_{HH} = 6.7 Hz, 18H, CH(C*H*$_3$)$_2$), 1.31 (d, J_{HH} = 6.8 Hz, 18H, CH(C*H*$_3$)$_2$). HRMS (APCI/Q-TOF) m/z: $[(PhB(iPr_2ImH)_3)(SO_3CF_3)]^+$ Calcd. for $C_{34}H_{53}BF_3N_6O_3S$: 693.3951; Found: 693.3953.

PhB(^{i}Pr$_2$Im)$_3$FeCl. Dissolved LDA (0.38 g, 3.55 mmol) in Et_2O (10 mL) was added slowly to Schlenk flask containing a slurry of $[PhB(^iPr_2ImH)_3][OTf]_2$ (1.02 g, 1.16 mmol) in Et_2O (5 mL). The reaction mixture was stirred at room temperature for 1 h. Solid $FeCl_2(THF)_{1.5}$ (0.33 g, 1.39 mmol) was added to this solution and stirred for 16 h at room temperature. The volatiles were removed under reduced pressure and the residue was extracted with toluene and filtered through Celite. The filtrate was dried under vacuum to yield an off-white solid (0.49 g, 67 % based on $[PhB(^iPr_2ImH)_3][OTf]_2$ as the limiting reagent). Crystals suitable for X-ray diffraction were grown by layering pentane onto a toluene solution of the complex at -35 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 62 (3H, Im-*H*), 43 (2H, *m*/*o*-B(C_6H_5)), 22 (2H, *m*/*o*-B(C_6H_5)), 19 (1H, *p*-B(C_6H_5)), 0.49 (3H, C*H*(CH_3)$_2$), 0.18 (18H, CH(C*H*$_3$)$_2$), -13 (3H, C*H*(CH_3)$_2$), -25 (18H, CH(C*H*$_3$)$_2$). Anal. Calcd. for $C_{33}H_{50}BClFeN_6$: C 62.63, H 7.96, N 13.28; Found: C 62.84, H 8.02, N 13.19.

PhB(^{i}Pr$_2$Im)$_3$FeN (1). A solution of PhB(^{i}Pr$_2$Im)$_3$FeCl (235 mg, 0.37 mmol) in THF (15 mL) was added to solid NaN_3 (72.4 mg, 1.11 mmol) in a scintillation vial and the reaction stirred for 24 h. The resulting violet suspension was then transferred to a quartz flask with additional THF (100 mL). The quartz flask was sealed and irradiated overnight (12-16 h). The volatiles were removed under reduced pressure, the residue extracted with toluene and filtered through Celite. The filtrate was dried under vacuum and 5 mL of diethyl ether were added to the solid. The resulting suspension was cooled at -35 °C for 1 h. The brown supernatant was carefully pipetted out to yield a pink solid (109 mg, isolated yield 48 % based on PhB(^{i}Pr$_2$Im)$_3$FeCl as the limiting reagent). Crystals suitable for X-ray diffraction were grown from concentrated toluene layered with pentane at -35 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.19 (d, J_{HH} = 8.4 Hz, 2H, *o*-B(C_6H_5)), 7.41 (t,

J_{HH} = 7.5 Hz, 2H, *m*-B(C_6H_5)), 7.29 (m, 1H, *p*-B(C_6H_5)), 6.82 (s, 3H, Im-*H*), 4.50 (sept, J_{HH} = 6.6 Hz, 3H, C*H*(CH_3)$_2$), 2.46 (sept, J_{HH} = 6.7 Hz, 3H, C*H*(CH_3)$_2$), 1.98 (d, J_{HH} = 6.7 Hz, 18H, CH(C*H*$_3$)$_2$), 0.83 (d, J_{HH} = 6.7 Hz, 18H, CH(C*H*$_3$)$_2$). ^{15}N NMR (500 MHz, C_6D_6, 25 °C): δ 1003. Anal. Calcd. for $C_{33}H_{50}BFeN_7$: C 64.82, H 8.24, N 16.04; Found: C 64.64, H 8.30, N 15.99.

PhB(^{i}Pr$_2$Im)$_3$Fe(CN)(N$_2$)(BAC)/PhB(^{i}Pr$_2$Im)$_3$Fe(CN)(BAC) (2/3). BAC (76.6 mg, 0.324 mmol) in THF (1 mL) was added to solution of **1** (99.3 mg, 0.162 mmol) in THF (3 mL) and stirred for 12 hours. The volatiles were removed under reduced pressure, the residue extracted with toluene and filtered through Celite. The filtrate was dried under vacuum to yield a brown solid. Yellow crystals suitable for X-ray diffraction (**2**) were grown from concentrated THF layered with pentane at -35 °C (isolated yield for two crops 56 % based on **1** as the limiting reagent). Blue crystals for the molecular structure of **3** were grown from a slowly evaporating Et_2O solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.51 (d, J_{HH} = 7.1 Hz, 2H), 7.72 (s, 1H), 7.65 (t, J_{HH} = 7.6 Hz, 2H), 7.44 (t, J_{HH} = 7.4, 1H), 6.92 (b, 1H), 6.76 (b, 1H), 6.64 (b, 1H), 5.87 (b, 1H), 4.87 (b, 2H), 3.65 (sept, J_{HH} = 6.74, 1H), 3.51 (b, 1H), 2.75 (b, 1H); Overlapping resonances (60 H, CH(C*H*$_3$)$_2$): 1.80, 1.65, 1.48, 1.25, 0.97, 0.74, 0.63. ^{15}N NMR (**2/3**) (500 MHz, C_6D_6, 25 °C): δ 342 (b, 2N, *N*$_2$), 318 (s, 1N, C*N*). IR (THF) ν_{CN} = 2095 cm^{-1}, ν_{NN} = 2071 cm^{-1}, ν_{BAC} = 1822 cm^{-1}. HRMS (CI/Q-TOF) m/z [M]$^+$ Calcd. for $C_{49}H_{78}BFeN_9$: 859.5817; Found: 859.5847.

Isolation and Characterization of (^{i}Pr)$_2$NCCN(^{i}Pr)$_2$. A J-Young tube was charged with **1** (22.5 mg, 0.037 mmol) and BAC (17.5 mg, 0.074 mmol) in C_6D_6 (1 mL) was added to the tube. The reaction mixture was taken to dryness after **1** was completely consumed, as determined by ^{1}H NMR spectroscopy. The alkyne was vacuum transferred with heating to a second J-Young NMR tube, providing a clear liquid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 2.91 (sept, 4H, J_{HH} = 6.4 Hz, C*H*(CH_3)$_2$), 1.18 (d, 24H, J_{HH} = 6.4 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 206.38 (*C*≡*C*), 53.28 (*C*H), 22.80 (*C*H$_3$). HRMS (GC-CI-MS) m/z [(M+H_2O)+H]$^+$ Calcd. for $C_{14}H_{31}N_2O$: 243.2431; Found: 243.2422.

PhB(^{i}Pr$_2$Im)$_3$Fe(CN)(CO)(BAC) (4). *Method 1.* In a 50 mL bomb flask, a solution containing **2/3** (0.12 g, 0.16 mmol) in THF (5 mL) was degassed and pressurized with CO (760 torr) and was allowed to stir for 1 h. The solution was dried under vacuum to obtain a yellow solid. Crystals suitable for X-ray diffraction were obtained from a saturated THF solution at ambient temperature. *Method 2.* A slurry of NaCN (13 mg, 0.265 mmol) in THF (3 mL) was treated with crude **5** (21.5 mg, 0.024 mmol). The reaction was stirred overnight and the solvent removed under vacuum. The product was characterized spectroscopically. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.50 (d, J_{HH} = 7.1 Hz, 2H, *m*/*o*-B(C_6H_5)), 7.65 (m, 3H, *m*/*o*-B(C_6H_5) + Im-*H* overlap), 7.44 (t, J_{HH} = 7.4 Hz,1H, *p*-B(C_6H_5)), 6.85 (sept, J_{HH} = 7.1 Hz, 1H, C*H*(CH_3)$_2$), 6.78 (s, 2H, Im-*H*), 5.87 (sept, J_{HH} = 7.1 Hz, 1H, C*H*(CH_3)$_2$), 5.32 (sept, J_{HH} = 7.1 Hz, 1H, C*H*(CH_3)$_2$), 4.86 (b, 1H), 3.47 (b, 1H), 3.25 (sept, J_{HH} = 7.0 Hz, 1H, C*H*(CH_3)$_2$), 2.92 (sept, J_{HH} = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 2.85 (sept, J_{HH} = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 2.74 (sept, J_{HH} = 6.8 Hz, 1H, C*H*(CH_3)$_2$); Overlapping resonances (60 H, CH(C*H*$_3$)$_2$): 1.82 (d), 1.77 (d), 1.51, 1.49, 1.45 (b), 1.22-1.16, 1-0.93, 0.72-0.60. ^{13}C NMR (**4-^{13}CO**) (400 MHz, C_6D_6, 25 °C): δ 224.7 (*C*O). ^{15}N NMR (500 MHz, C_6D_6, 25 °C): δ 315. IR (THF) ν_{CN} = 2077 cm^{-1}, ν_{CO} = 1900 cm^{-1}, ν^{13}_{CO} = 1859 cm^{-1}, ν_{BAC} = 1825 cm^{-1}. HRMS (APCI/Q-TOF) m/z [M]$^{+}$ Calcd. for $C_{50}H_{78}BFeN_9O$: 887.5772; Found: 887.5779.

PhB(^{i}Pr$_2$Im)$_3$Fe(Cl)(CO)(BAC) (5). A solution of **BAC** (8.5 mg, 0.0360 mmol) in C_6D_6 (2 mL) was added to a J-Young tube containing PhB(^{i}Pr$_2$Im)$_3$FeCl (21.5 mg, 0.0340 mmol) under an N_2 atmosphere. The solution was subjected to three freeze-pump-thaw cycles and pressurized with CO (760 torr). The solution was allowed to sit for 1 h and was returned to the glovebox where the solution was taken to dryness to yield a white solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.53 (2H, br, *m*/*o*-B(C_6H_5)), 7.71 (1H, br, *p*-B(C_6H_5)), 7.64 (2H, br, *m*/*o*-B(C_6H_5)), 7.45-7.34(3H, br, Im-*H*), 6.96(1H, br, C*H*(CH_3)$_2$), 6.64(1H, br, C*H*(CH_3)$_2$), 5.88(1H, br, C*H*(CH_3)$_2$), 5.33(1H, br, C*H*(CH_3)$_2$), 2.96 (1H, br, C*H*(CH_3)$_2$), 2.90 (1H, br, C*H*(CH_3)$_2$), 2.66 (1H, br, C*H*(CH_3)$_2$); Overlapping resonances (60H, CH(C*H*$_3$)$_2$): 1.73, 1.63, 1.56, 1.51, 1.06, 0.97, 0.78-0.74, 0.67, 0.58, 0.53. IR (THF) ν_{CO} = 1900 cm^{-1}, ν_{BAC} = 1825 cm^{-1}. A small amount of an inseparable impurity, likely the dicarbonyl complex PhB(^{i}Pr$_2$Im)$_3$Fe(Cl)(CO)$_2$, is also observed (ν_{CO} = 2000 and 1945

cm^{-1}). HRMS (APCI/Q-TOF) m/z $[M - CO]^+$ Calcd. for $C_{48}H_{78}BClFeN_8$ 868.5480; Found 868.5499; $[M - Cl]^+$ Calcd. for $C_{49}H_{78}BFeN_8O$: 861.5741; Found: 861.5754.

PhB(^{i}Pr$_2$Im)$_3$Fe(CNB(C$_6$F$_5$)$_3$)(BAC) (6). A solution of $B(C_6F_5)_3$ (65.5 mg, 0.128 mmol) in toluene (3 mL) was added to **2/3** (110 mg, 0.128 mmol) and stirred for 1 h. The solution was brought to dryness. Dark blue crystals of **6** were obtained at room temperature from an ether-pentane mixture (78.9 mg, 45 % based on **2/3** as the limiting reagent). Alternatively, yellow crystals of **6**-N_2 can be obtained from the same solvent mixture at −35 °C, however extremely rapid loss of N_2 from the crystals has thwarted attempts to obtain an X-ray crystal structure. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.22 (d, J_{HH} = 7.4 Hz, 2H, *m*/*o*-(C_6H_5)), 7.55 (t, JHH = 7.4 Hz, 2H, *m*/*o*-(C_6H_5)), 7.5 (b, 1H, Im-*H*), 7.38 (t, J_{HH} = 7.9 Hz,1H, *p*-(C_6H_5)), 7.35 (b, 1H, Im-*H*), 6.04 (s, 1H, Im-*H*), 5.04 (b, 1H, C*H*(CH_3)$_2$), 2.74 (b, 1H, C*H*(CH_3)$_2$), 2.63 (b, 2H, C*H*(CH_3)$_2$); Overlapping resonances (b, 60 H, CH(C*H*$_3$)$_2$): 1.32, 1.07, 0.99-0.96, 0.90, 0.88, 0.83, 0.82, 0.76, 0.69, 0.67, 0.56, 0.36. T ^{19}F NMR (400 MHz, C_6D_6, 25 °C): δ −165.27, 164.37, 163.61 (m(b), 2F, *m*/*o*-B(C_6F_5)); −159.89, −159.09, (m(b), 1F, *p*-B(C_6F_5)); −132.24 (m(b), 2F, *m*/*o*-B(C_6F_5)). ^{15}N NMR (500 MHz, C_6D_6, 25 °C): δ 183. IR (THF) 2133 (ν_{CN}), 2085, 2062, 1819 cm^{-1} (ν_{BAC}); IR (KBr) 2126 (ν_{CN}), 2073, 2050, 1819 (ν_{BAC}) cm^{-1}. Anal. Calcd. for $C_{67}H_{78}B_2F_{15}FeN_9$: C 58.66, H 5.73, N 9.19; Found: C 58.86, H 5.63, N 15.99.

Supplementary Figures

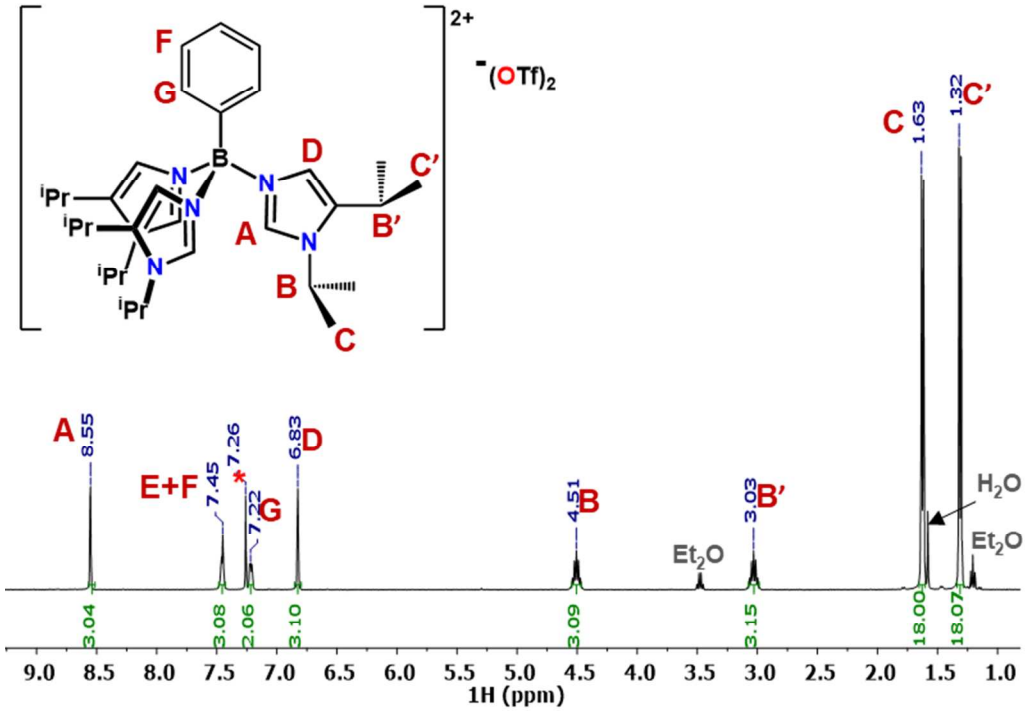

Figure S1: ^{1}H NMR spectrum of [PhB(^{i}Pr$_2$ImH)$_3$][OTf]$_2$ in $CDCl_3$ (*).

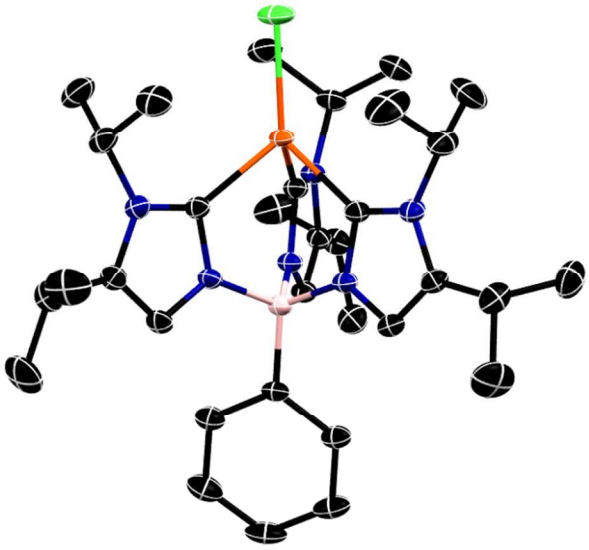

Figure S2: Molecular structure of PhB(^{i}Pr$_2$Im)$_3$FeCl. Color scheme: C, black; N, blue; B, pink; Fe, orange; Cl, green. H atoms and solvent molecules have been omitted for clarity.

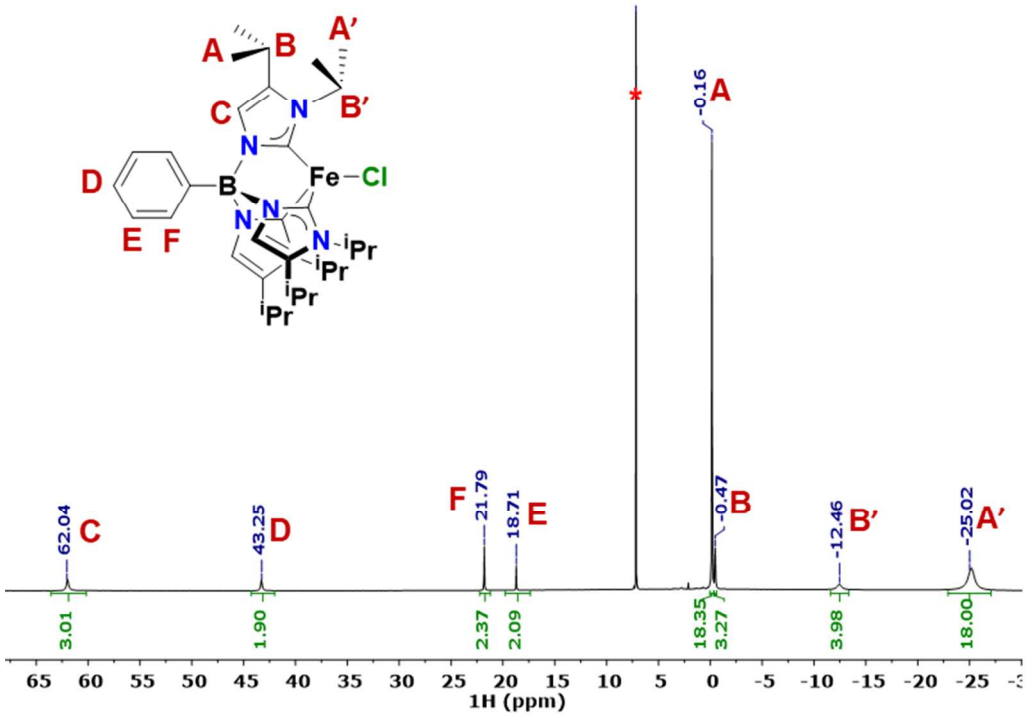

Figure S3: ^{1}H NMR spectrum of PhB(^{i}Pr$_2$Im)$_3$FeCl in C_6D_6 (*).

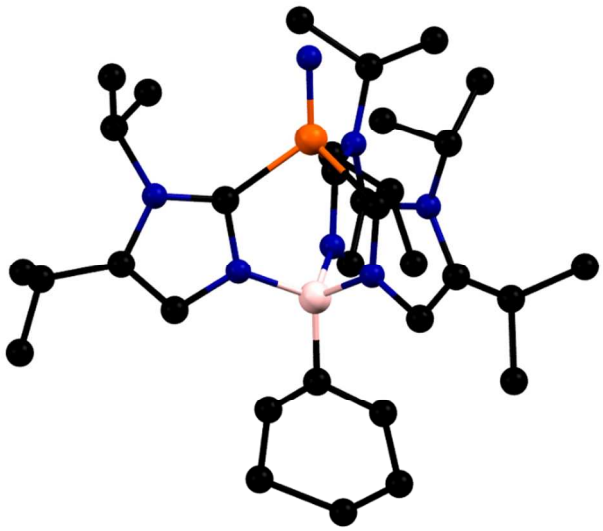

Figure S4: Molecular structure of **1**. Color scheme: C, black; N, blue; B, pink; Fe, orange. H atoms, disorder from the phenyl group and solvent molecules have been omitted for clarity.

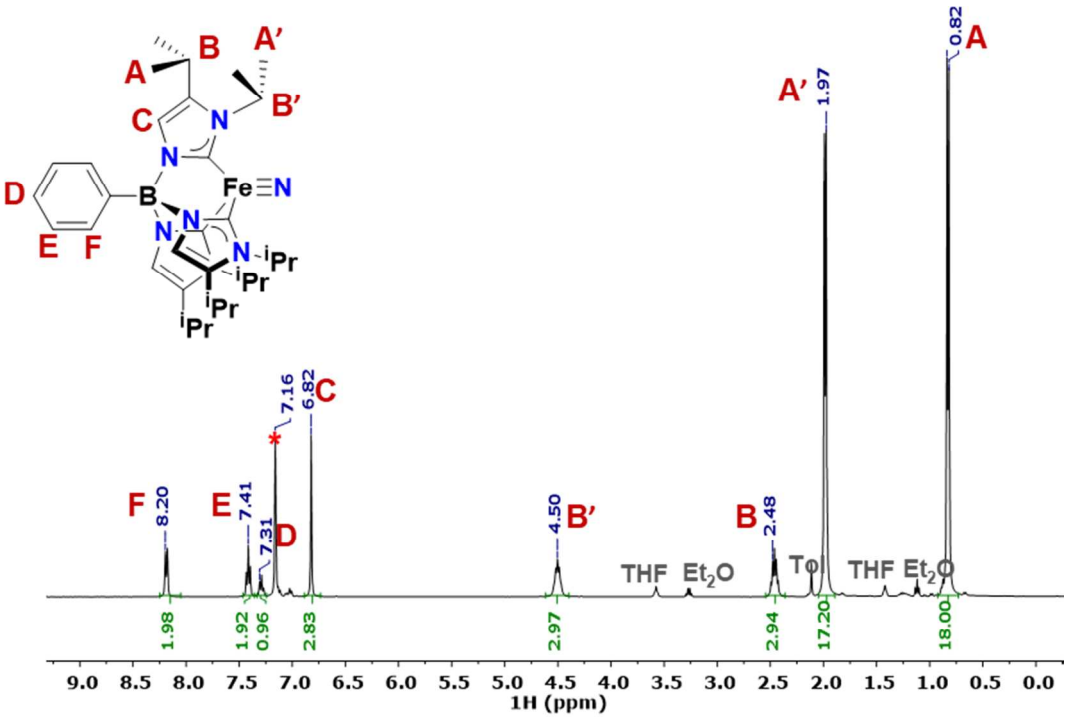

Figure S5: ^{1}H NMR spectrum of **1** in C_6D_6 (*).

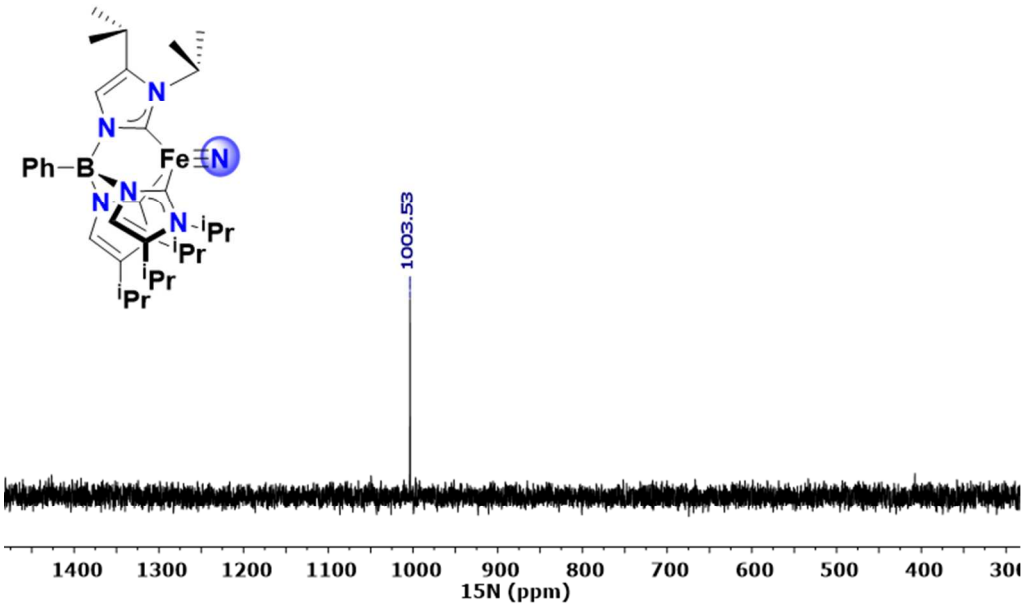

Figure S6: ^{15}N NMR spectrum of **1-^{15}N** in C_6D_6. (●) Indicates isotopically enriched atoms.

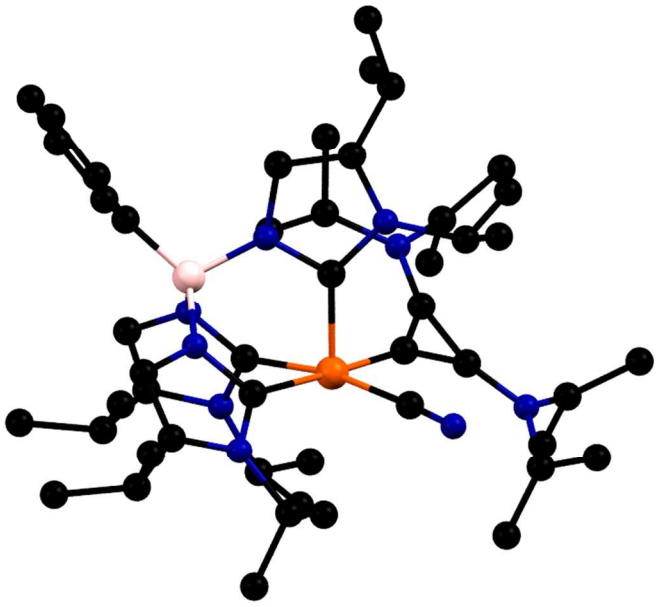

Figure S7: Molecular structure of **3** obtained from diethyl ether at room temperature. Color scheme: C, black; N, blue; B, pink; Fe, orange; H, white. H atoms have been omitted for clarity.

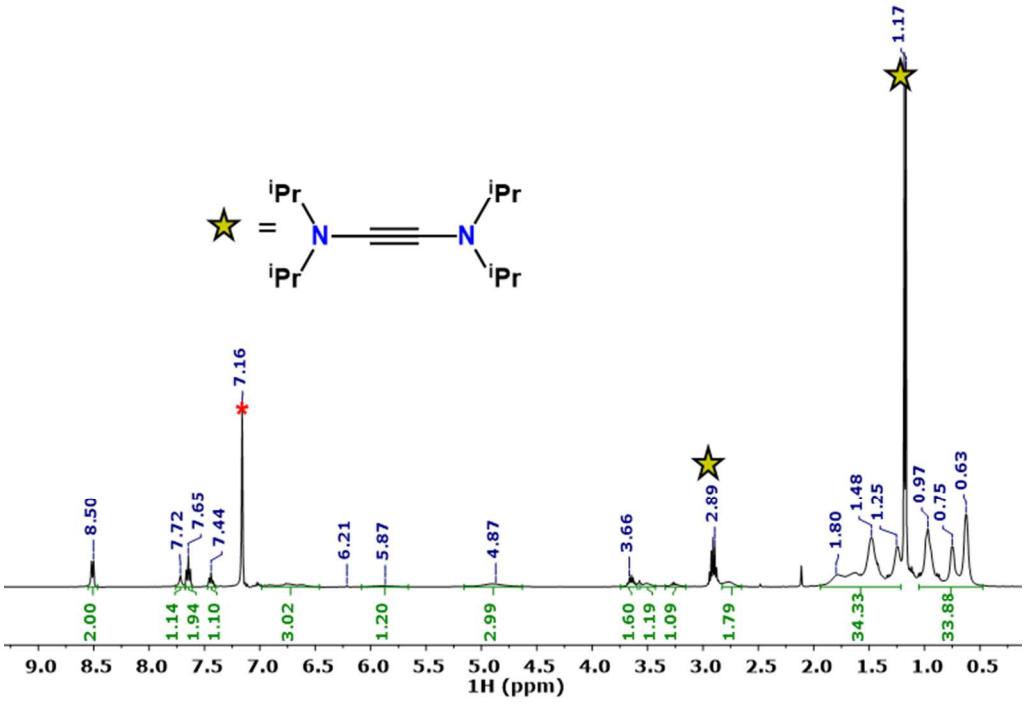

Figure S8: ^{1}H NMR from the reaction between **1** and **BAC** (2 eq.), showing formation of **2/3** and the (^{i}Pr)$_2$NCCN(^{i}Pr)$_2$ byproduct in in C_6D_6 (*).

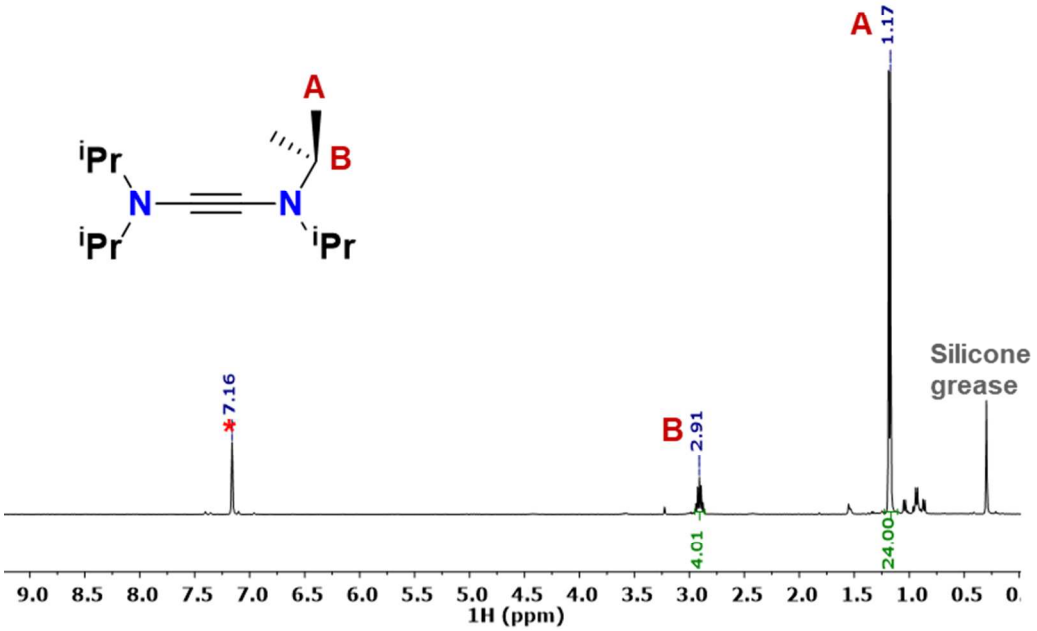

Figure S9: ^{1}H NMR spectrum of (^{i}Pr)$_2$NCCN(^{i}Pr)$_2$ in C_6D_6 (*).

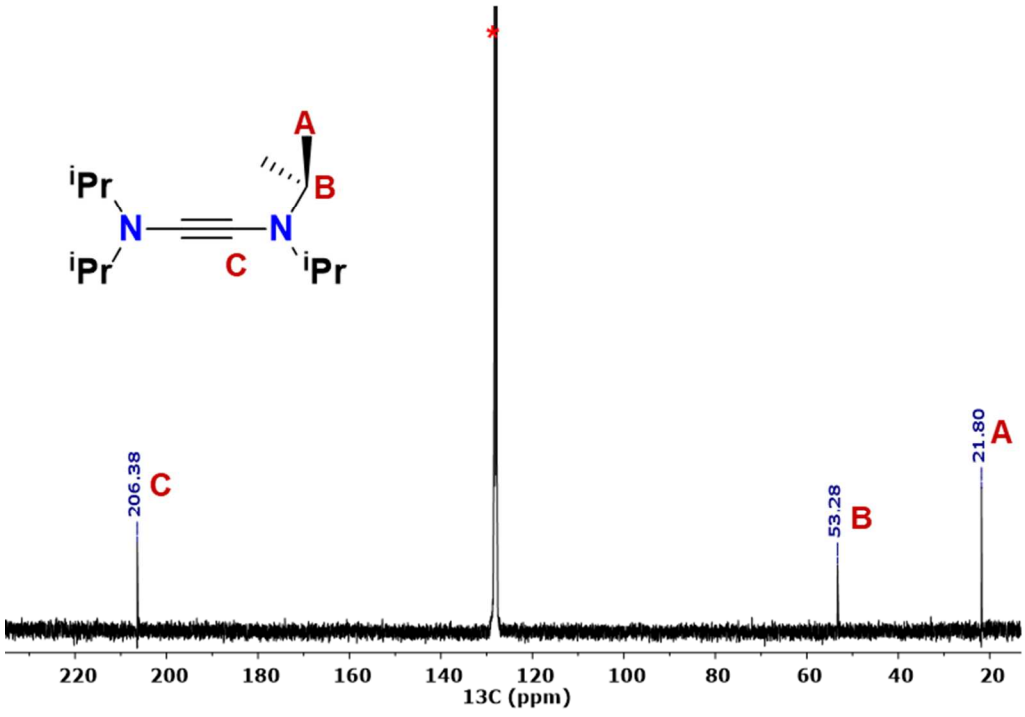

Figure S10: ^{13}C NMR spectrum of (^{i}Pr)$_2$NCCN(^{i}Pr)$_2$ in C_6D_6 (*).

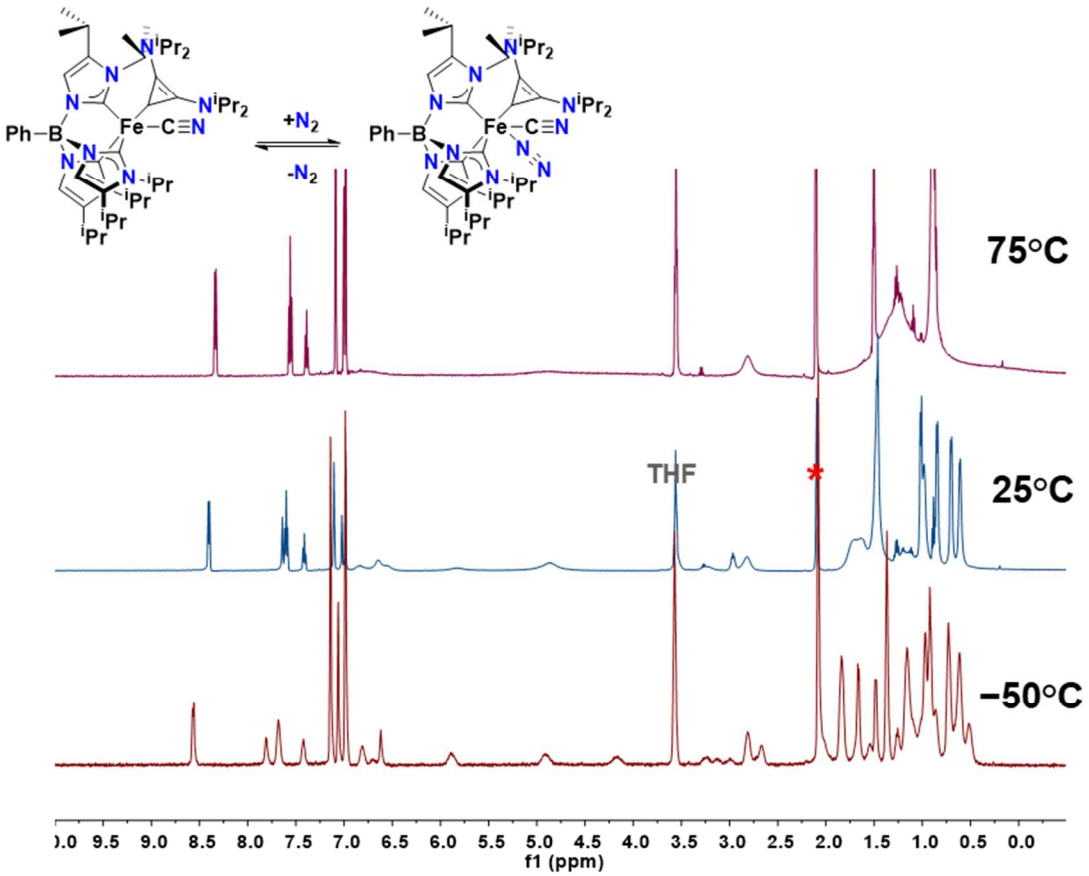

Figure S11: VT ^{1}H NMR spectra of **2/3** in toluene-d_8 (*) shows a temperature dependent equilibrium.

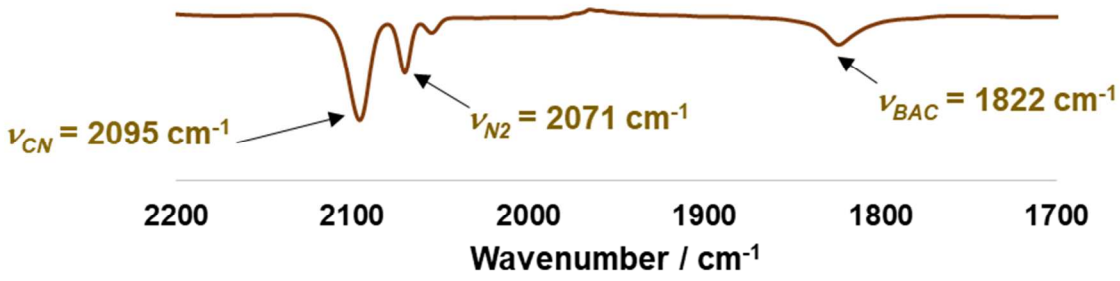

Figure S12: Solution IR spectrum of **2/3** (THF).

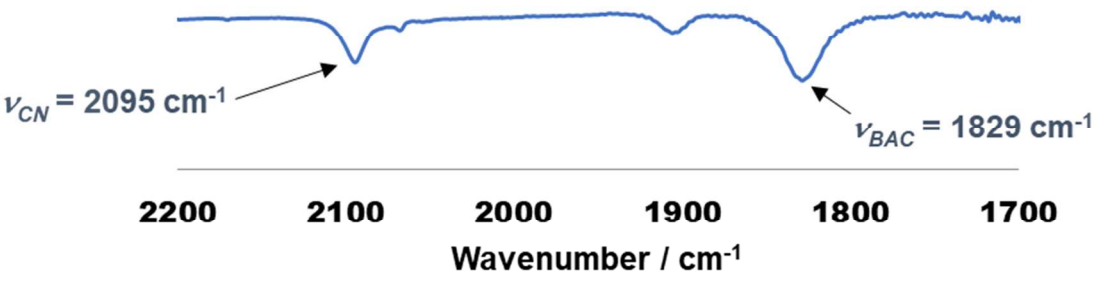

Figure S13: Solid state IR spectrum of **3** (KBr).

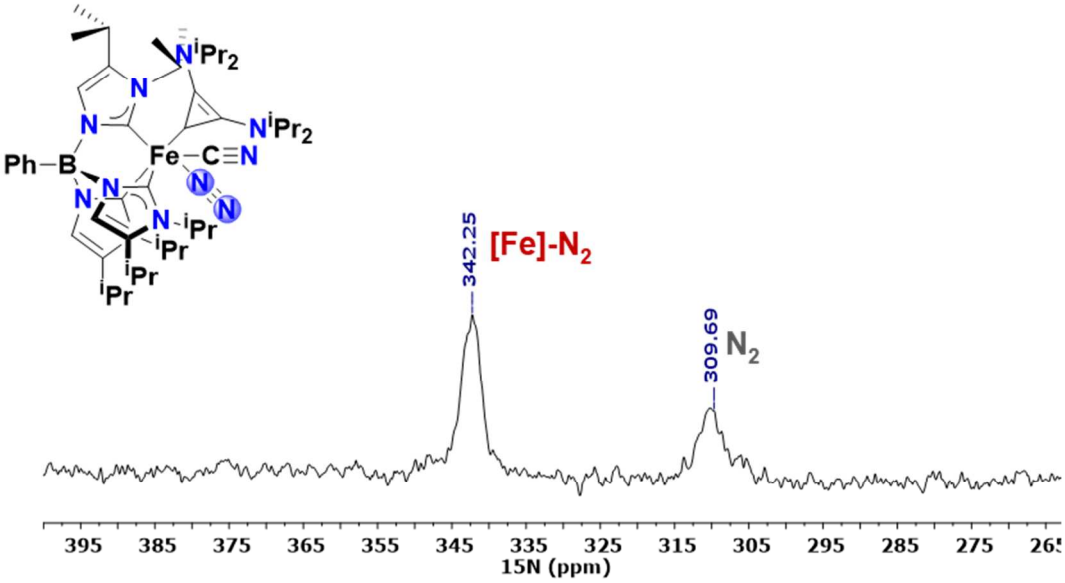

Figure S14: ^{15}N NMR spectrum of **2-^{15}N$_2$** in C_6D_6. (●) Indicates isotopically enriched atoms.

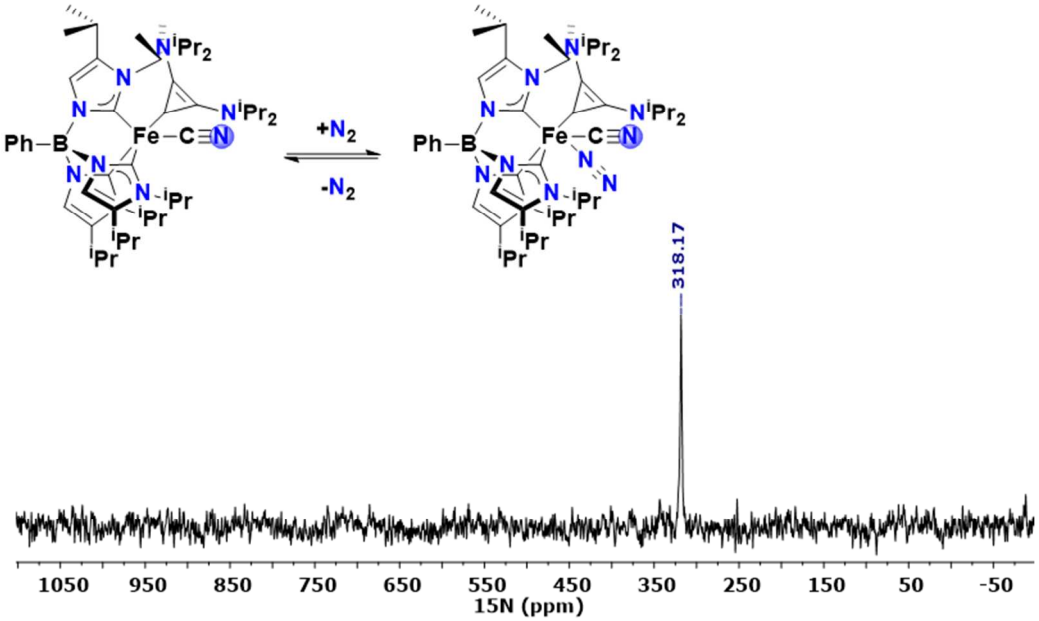

Figure S15: ^{15}N NMR spectrum of **2/3-^{15}N** (C_6D_6). (●) Indicates isotopically enriched atoms.

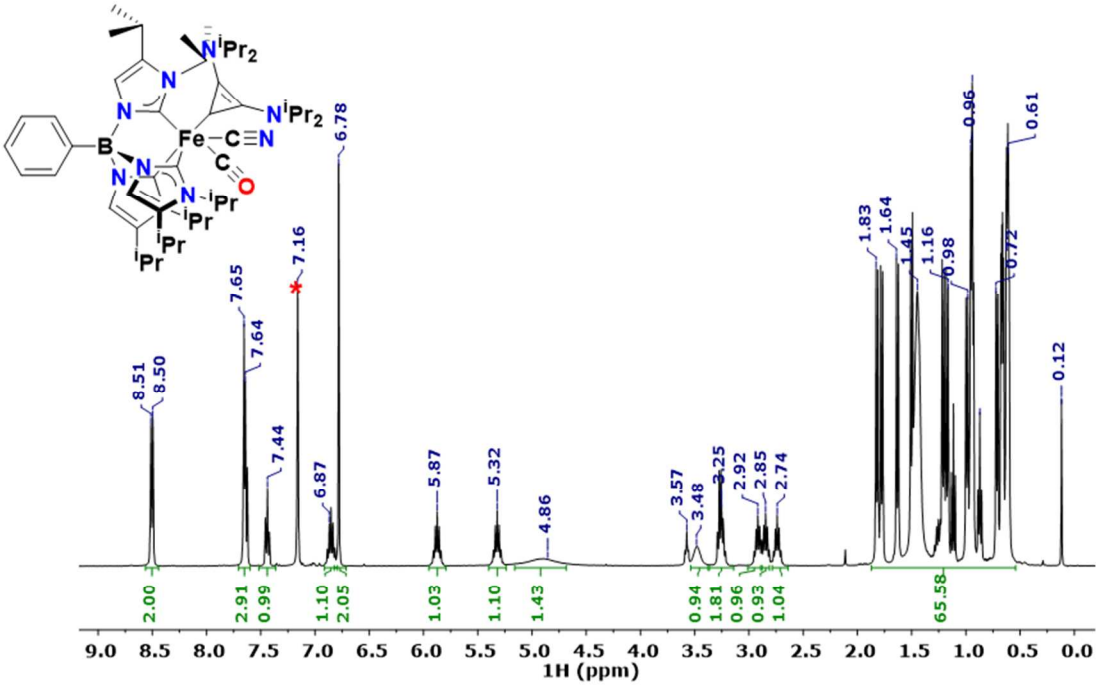

Figure S16: ^{1}H NMR spectrum of **4** in C_6D_6 (*).

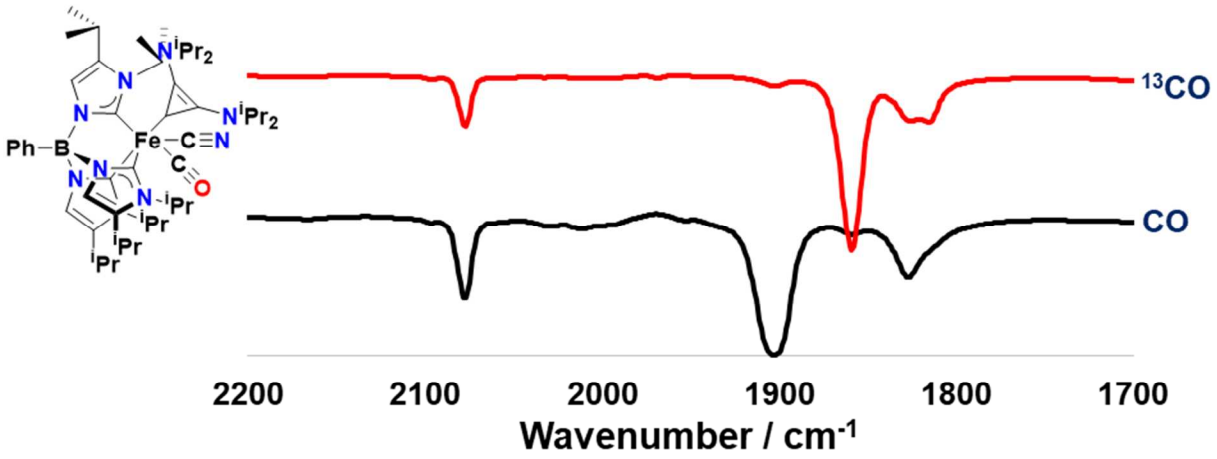

Figure S17: Solution IR spectra (THF) of **4** (black) and **4-^{13}CO** (red).

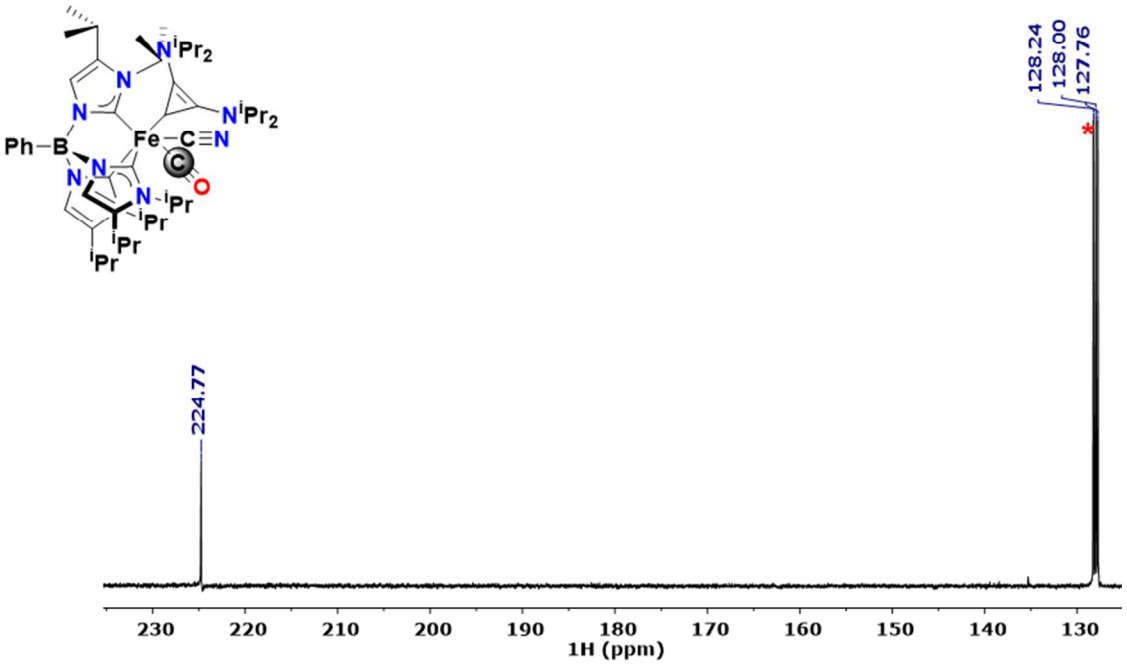

Figure S18: ^{13}C{^{1}H} NMR spectrum of **4-^{13}CO** in C_6D_6 (*). (●) Indicates isotopically enriched atoms.

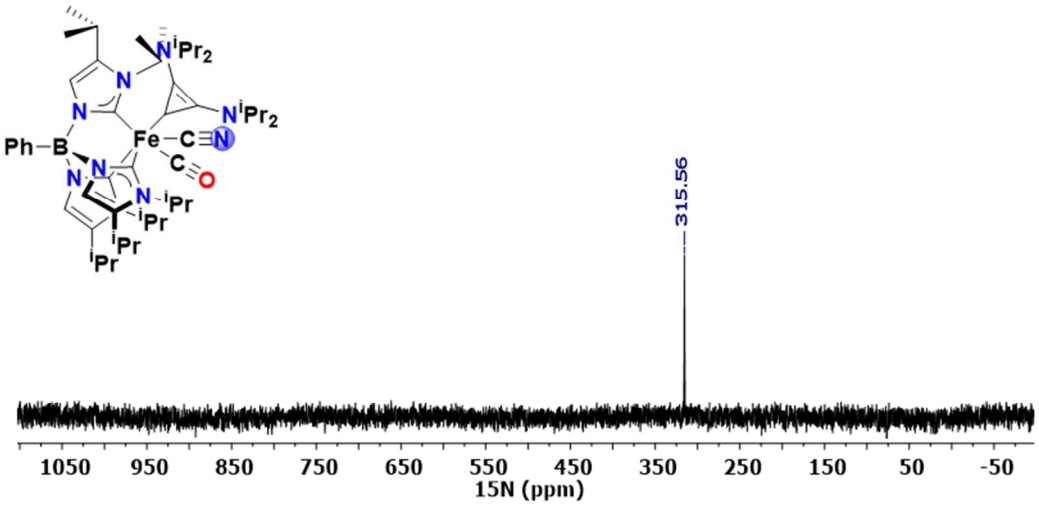

Figure S19: ^{15}N NMR spectrum of **4-^{15}N** (C_6D_6). (●) Indicates isotopically enriched atoms.

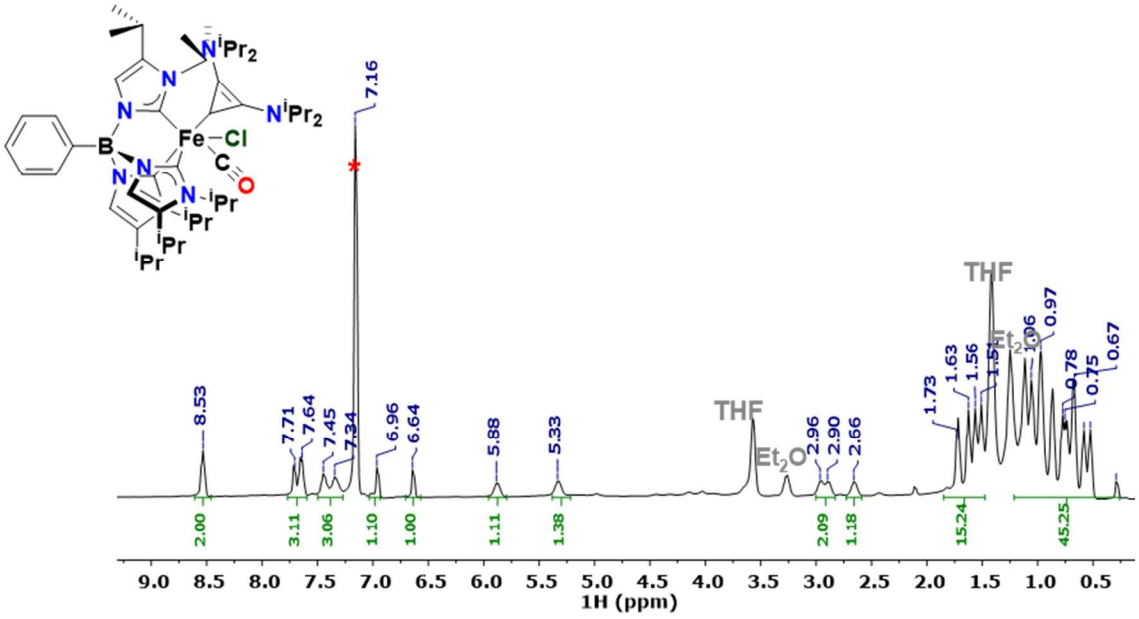

Figure S20: ^{1}H NMR spectrum of crude **5** in C_6D_6 (*).

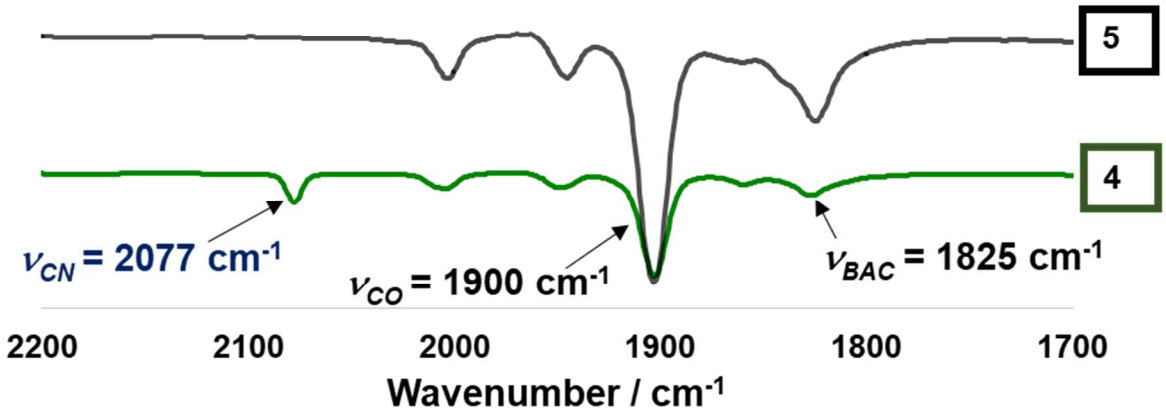

Figure S21: Solution IR spectra (THF) of **5** (black) and **4** (green) obtained from the reaction of **12** with excess NaCN in THF.

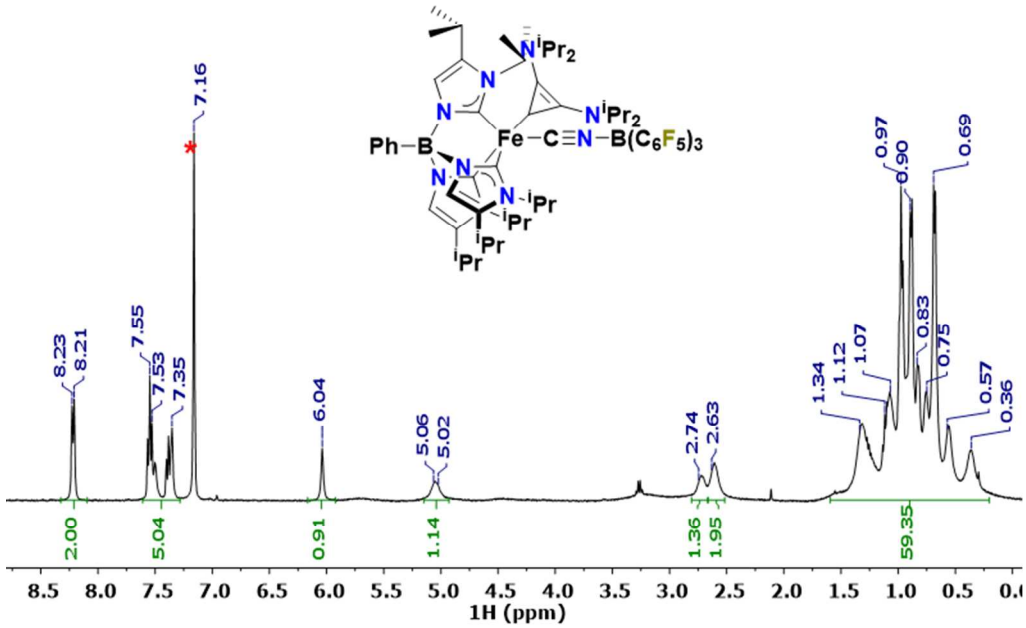

Figure S22: ^{1}H NMR spectrum of **6** in C_6D_6 (*).

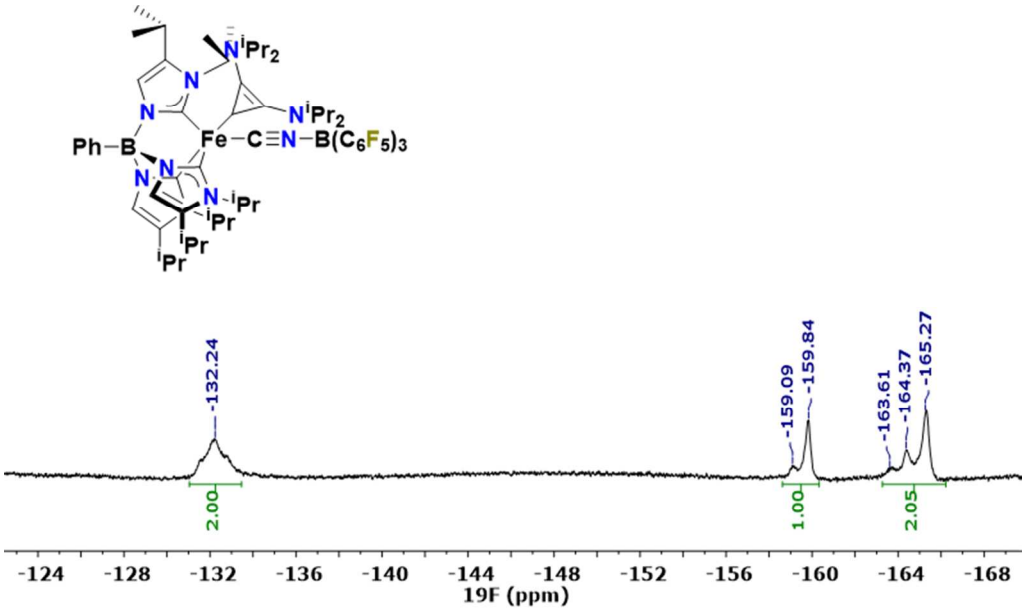

Figure S23: ^{19}F NMR spectrum of **6** in C_6D_6.

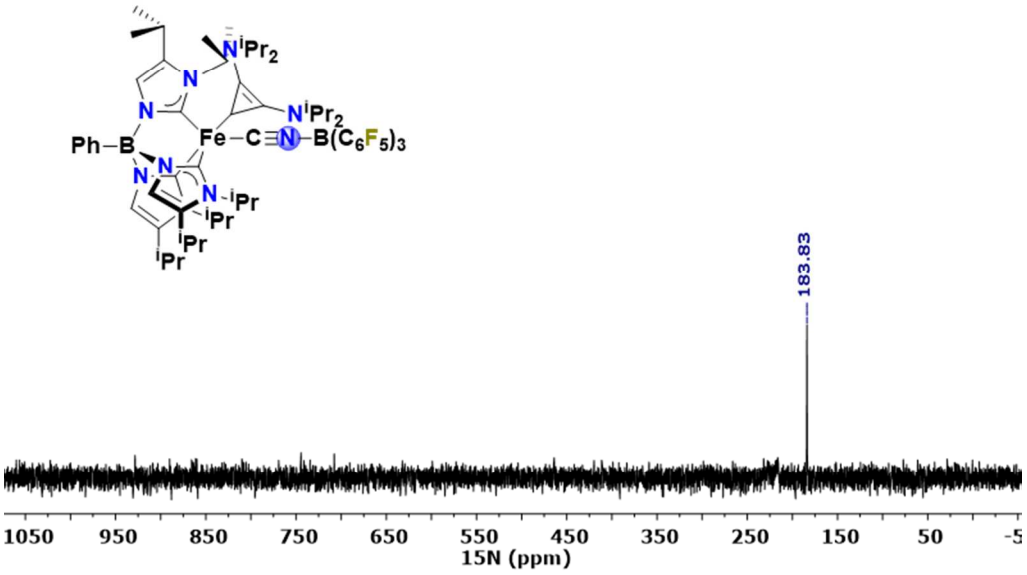

Figure S24: ^{15}N NMR spectrum of **6-^{15}N** (C_6D_6). ( ) Indicates isotopically enriched atoms.

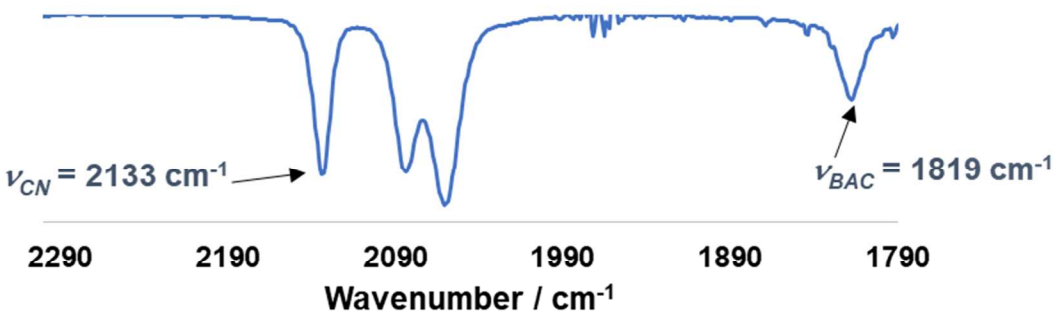

Figure S25: Solution IR spectrum of **6** (THF).

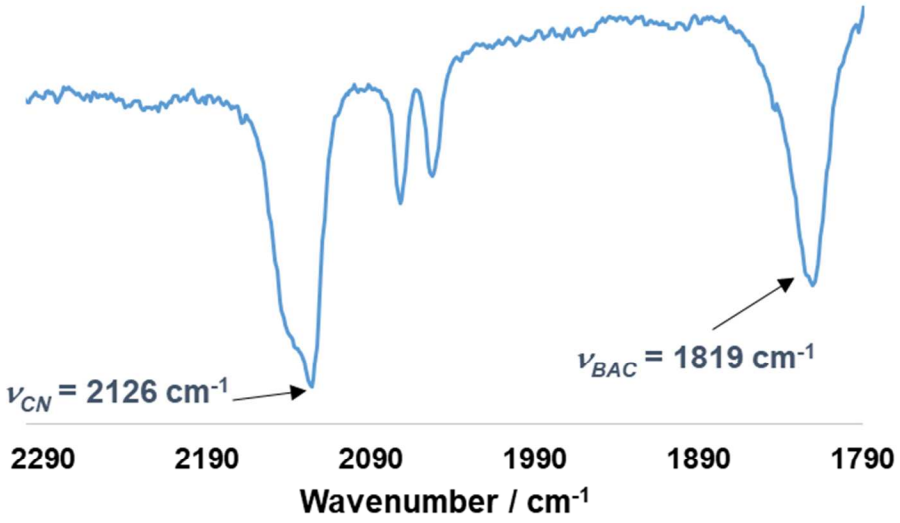

Figure S26: Solid state IR spectrum of **6** (KBr).

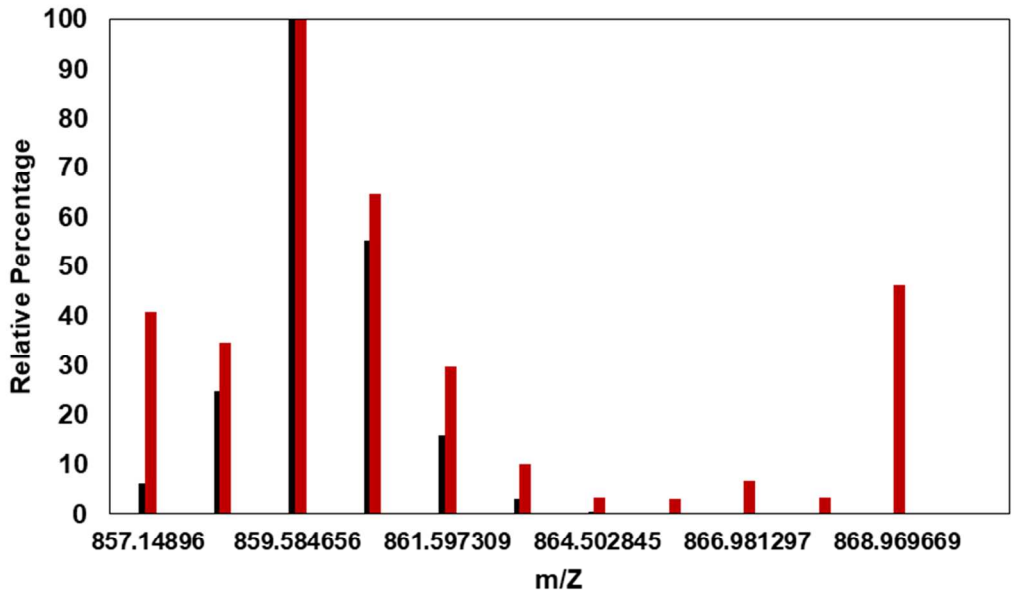

Figure S27: Predicted m/Z fragmentation of complex **2/3** (black) and experimental CI-MS spectrum of **2/3** (red). HRMS (CI/Q-TOF) m/z $[M]^+$ Calcd for $C_{49}H_{78}BFeN_9$ 859.5817; Found 859.5847.

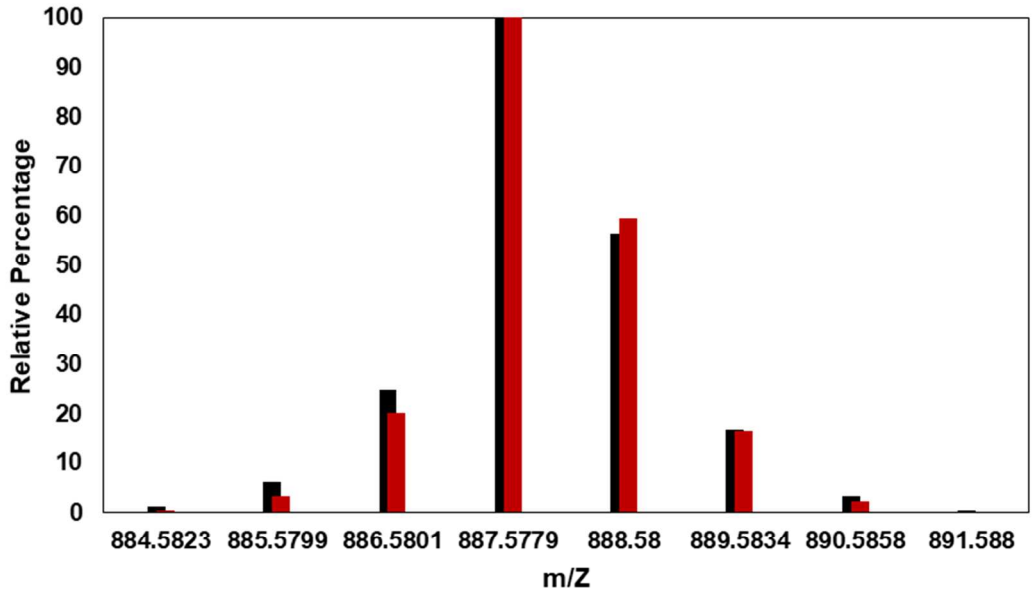

Figure S28: Predicted m/Z fragmentation of complex **4** (black) and experimental APCI-MS spectrum of **4** (red). HRMS (APCI/Q-TOF) m/z $[M]^+$ Calcd for $C_{50}H_{78}BFeN_9O$ 887.5772; Found 887.5779.

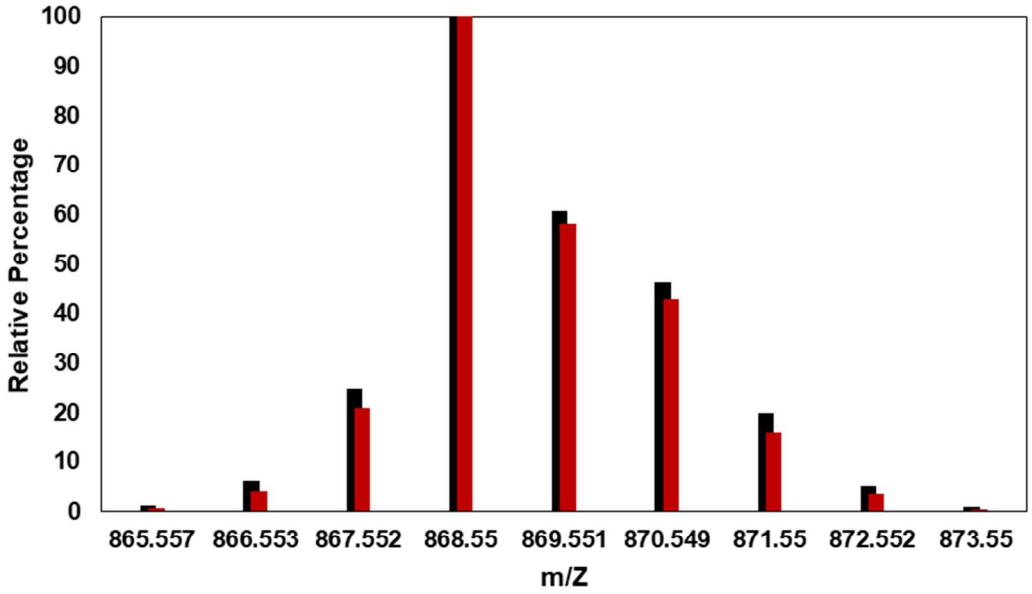

Figure S29: Predicted m/Z fragmentation of [**5**− CO]$^+$ (black) and experimental APCI-MS spectrum of **5** (red). HRMS (APCI/Q-TOF) m/z [M − CO]$^+$ Calcd for $C_{48}H_{78}BClFeN_8$ 868.5480; Found 868.5499.

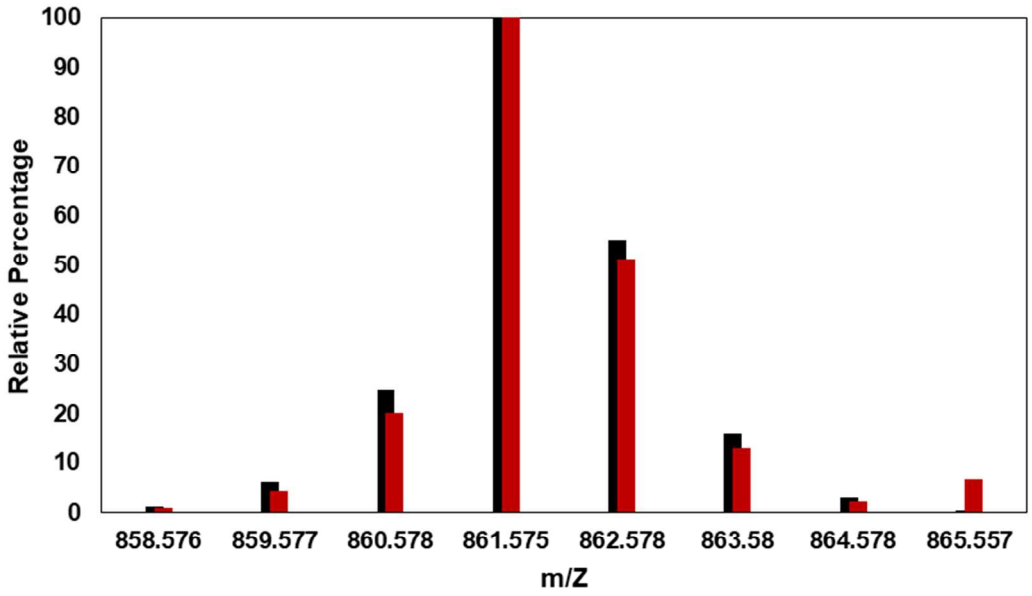

Figure S30: Predicted m/Z fragmentation of [**5** – Cl]$^+$ (black) and experimental APCI-MS spectrum of **5** (red). HRMS (APCI/Q-TOF) m/z [M − Cl]$^+$ Calcd for $C_{49}H_{78}BFeN_8O$ 861.5741; Found 861.5754.

Crystallographic Information

$PhB(^{i}Pr_2Im)_3FeCl$

Empirical formula	C43.50 H61.50 B1 Cl1 Fe1 N6
Formula weight	770.62
Crystal color, shape, size	colorless prism, 0.593 x 0.536 x 0.324 mm^3
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 11.4756(3) Å α= 82.9470(10)°.
	b = 12.1783(3) Å β= 81.975(2)°.
	c = 17.3054(5) Å γ = 64.9910(10)°.
Volume	2164.78(10) $Å^3$
Z	2
Density (calculated)	1.182 Mg/m^3
Absorption coefficient	0.446 mm^{-1}
F(000)	825

Data collection

Diffractometer	Bruker Apex Kappa Duo, Bruker
Theta range for data collection	1.850 to 28.817°.
Index ranges	-15<=h<=15, -16<=k<=16, -23<=l<=23
Reflections collected	44162
Independent reflections	11275 [R(int) = 0.028]
Observed Reflections	9792
Completeness to theta = 28.817°	99.6 %

Solution and Refinement

Absorption correction	Numerical
Max. and min. transmission	0.87 and 0.79
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.058, B = 1.715
Data / restraints / parameters	11236 / 62 / 452
Goodness-of-fit on F^2	0.9964
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1102
R indices (all data)	R1 = 0.0499, wR2 = 0.1175
Largest diff. peak and hole	1.73 and -0.66 $e.Å^{-3}$

PhB(^{i}Pr$_2$Im)$_3$FeN (1)

Empirical formula	C33 H50 B1 Fe1 N7
Formula weight	611.46
Crystal color, shape, size	orange plate, 0.125 x 0.152 x 0.340 mm^3
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, P -3
Unit cell dimensions	a = 10.302(2) Å α= 90°.
	b = 10.302(3) Å β= 90°.
	c = 19.677(4) Å γ = 120°.
Volume	1808.6(8) Å^3
Z	2
Density (calculated)	1.123 Mg/m^3
Absorption coefficient	0.447 mm^{-1}
F(000)	656

Data collection

Diffractometer	Bruker Kappa APEX II CCD
Theta range for data collection	2.07 to 23.25°.
Index ranges	-9<=h<=11, -10<=k<=11, -21<=l<=21
Reflections collected	9090
Independent reflections	1758 [R(int) = 0.1699]
Completeness to theta = 28.817°	99.9 %

Solution and Refinement

Absorption correction	Multi-Scan
Max. and min. transmission	0.9460 and 0.8630
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1387P)^2]$
	where $P=(F_o^2+2F_c^2)/3$
Data / restraints / parameters	1758 / 3 / 146
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0848, wR2 = 0.1987
R indices (all data)	R1 = 0.1633, wR2 = 0.2492
Largest diff. peak and hole	1.506 and -0.514 e.Å^{-3}

$PhB(^{i}Pr_2Im)_3Fe(CN)(N_2)$(BAC) (2).

Empirical formula	C55 H90 B Fe N11 O1.50
Formula weight	996.03
Crystal color, shape, size	yellow block, 0.32 × 0.28 × 0.25 mm^3
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 16.3404(8) Å α= 90°.
	b = 19.2823(10) Å β= 103.287(2)°.
	c = 18.4178(10) Å γ = 90°.
Volume	5647.7(5) $Å^3$
Z	4
Density (calculated)	1.171 Mg/m^3
Absorption coefficient	0.315 mm^{-1}
F(000)	2160

Data collection

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.504 to 27.580°.
Index ranges	-21<=h<=21, -17<=k<=25, -17<=l<=23
Reflections collected	48115
Independent reflections	13037 [R(int) = 0.0428]
Observed Reflections	10352
Completeness to theta = 25.242°	100.0 %

Solution and Refinement

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6552
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F2
Weighting scheme	$w = [\sigma^2Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.0435, B = 3.0700
Data / restraints / parameters	13037 / 231 / 673
Goodness-of-fit on F2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.1005
R indices (all data)	R1 = 0.0574, wR2 = 0.1087
Largest diff. peak and hole	0.544 and -0.448 $e.Å^{-3}$

PhB(^{i}Pr$_2$Im)$_3$Fe(CN)(CO)(BAC) (4)

Empirical formula	C54 H86 B1 Fe1 N9 O2
Formula weight	959.99
Crystal color, shape, size	yellow block, 0.300 x 0.300 x 0.200 mm^3
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions	a = 16.3579(8) Å α= 90°.
	b = 19.2761(10) Å β= 103.274(3)°.
	c = 18.4105(9) Å γ = 90°.
Volume	5650.0(3) Å^3
Z	4
Density (calculated)	1.128 Mg/m^3
Absorption coefficient	0.312 mm^{-1}
F(000)	2080

Data collection	
Diffractometer	Bruker Apex Kappa Duo, Bruker
Theta range for data collection	1.503 to 27.584°.
Index ranges	-21<=h<=20, 0<=k<=25, 0<=l<=23
Reflections collected	13013
Independent reflections	13013 [R(int) = 0.035]
Observed Reflections	10410
Completeness to theta = 27.032°	100.0 %

Solution and Refinement	
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.94 and 0.91
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	w = [σ^2Fo^2+ AP^2+ BP]$^{-1}$, with
	P = (Fo^2+ 2 Fc^2)/3, A = 0.051, B = 4.005
Data / restraints / parameters	12965 / 0 / 604
Goodness-of-fit on F^2	1.0023
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1041
R indices (all data)	R1 = 0.0527, wR2 = 0.1139
Largest diff. peak and hole	0.64 and -0.50 e.Å^{-3}

References

1. Van Leusen, A. M.; Wilderman, J.; Oldenziel, O.H., *J. Org. Chem.* **1977**, *42*, 1153-1159.

2. Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G., *Science* **2006**, 722-724.