Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Formation of Distinct Iron Hydrides via Mechanistic Divergence in Directed C–H Bond Activation in Aryl Ketones, Esters, and Amides

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General Information

All reactions were performed at room temperature either by using standard Schlenk techniques or by using an N_2-filled M. Braun Glovebox unless otherwise specified. Glassware was oven dried at 140 °C for at least 2h prior to use, and allowed to cool under vacuum. All reagents were used as received unless mentioned otherwise. Iron complex **1** was synthesized according to published procedures.[1]. Carbonyl reagents (Ketone, ester and amide) were purchased from Sigma Aldrich or Alfa Aesar. Anhydrous unstabilized tetrahydrofuran (THF) and diethylether (Et_2O) were purchased from Biolab or Sigma Aldrich and used as received. The ^1H, $^{13}C\{^1H\}$ spectra were recorded on Bruker AVANCE III 400 and 600 NMR spectrometers at room temperature unless mentioned otherwise. All chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hz. The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced using residual solvent peaks in the deuterated solvent. The ^{31}P chemical shifts are reported relative to the internal lock signal. Deuterated solvent (C_6D_6) was purchased from Cambridge Isotope Laboratories, dried over calcium hydride, degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use.

Physical Methods

Single-crystal X-ray diffraction. For compounds **3** and **4** low temperature (100K) diffraction data were collected using a Bruker SMART APEX II diffractometer coupled to an APEX II CCD detector with graphite monochromatic MoKα (λ = 0.71073 Å) radiation. All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[2] Absorption corrections were applied using SADABS.[3]. All structures were solved by direct methods using SHELXS[4] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014 or SHELXL-2018[5] using established refinement techniques.[6] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Computational Details

Density functional theory (DFT) calculations were performed to gain further insights into the experimental findings using Gaussian 16.[7] Geometries and vibrational frequencies were obtained with the Perdew–Burke-Ernzerhof (PBE0) DFT hybrid exchange-correlation functional was used in conjunction with the Stuttgart/Dresden (SDD) basis set-relativistic effective core potential (RECP) combination.[8]SDD includes the Huzinaga-Dunning double-zeta basis set on the lighter elements with the Stuttgart–Dresden basis set-RECP combination on the transition metals.[9] Empirical D3 dispersion corrections[10] are included using the Becke–Johnson[11] potential as recommended in ref. 12 (denoted by the suffix D3BJ).[12] Zero-point vibrational energy, enthalpic, and entropic corrections have been obtained from such calculations. The equilibrium structures were verified to have all real harmonic frequencies, and the transition structures to have only one imaginary frequency. The connectivity of the transition structures were confirmed by performing intrinsic reaction coordinate (IRC) calculations.[13] The final electronic energies were refined using the triple-z SDB-cc-pVTZ basis set, which combines the Dunning cc-pVTZ basis set[14] on the main group elements and the Stuttgart-Dresden basis set-RECP on the Iron with additional 2f1g-type polarization exponents given in ref 15. Bulk solvent effects in benzene were included using the charge-density-based SMD continuum solvation model,[16] this level of theory is denoted by SMD(benzene)-PBE0-D3BJ/SDB-cc-pVTZ.

Synthetic Procedures

Synthesis of 2. In the glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added acetophenone (3.5 µL, 0.03 mmol). The resulting reaction was stirred for 6 h at room temperature and the mixture turned into a light green solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as dark crystals upon crystallization from a concentrated pentane solution room temperature. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (95 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 9.07 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.96 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.19 (m, 1H, Ar-*H*), 7.12 (s, 2H, *m*-bpy-*H*), 7.02 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.69 (s, 2H, *m*-bpy-*H*), 2.48(s, 3H, COCH_3), 2.26 – 2.21 (m, 2H, $(CH_3)_2CH$), 1.99 – 1.96 (m, 2H, $(CH_3)_2CH$), 1.22 (s, 18H, ^{t}Bu), 1.11 (dd, *J* = 12.3, 6.6 Hz, 12H, $(CH_3)_2CH$), 1.02 (dd, *J* = 13.6, 6.3 Hz, 6H, $(CH_3)_2CH$), 0.93 (dd, *J* = 14.2, 7.0 Hz, 6H, $(CH_3)_2CH$), -22.13 (t, *J* = 62.0, 1H, Fe-*H*). **^{13}C {^{1}H} NMR (101 MHz, C_6D_6)**: δ (ppm) 205.21, 149.26 (d), 146.83, 141.22, 141.00 – 140.56 (m), 130.58, 125.14, 120.79 (t), 117.62, 114.24, 112.09, 34.86, 30.54, 28.03 (t), 25.77 (t), 23.36, 19.61, 18.64 (t), 18.51, 18.42. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 116.04, 115.69.

Synthesis of 3. In the glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added 4-fluoroacetophenone (3.6 µL, 0.03 mmol). The resulting reaction was stirred for 6 h at room temperature and the mixture turned into a purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as purple crystals upon crystallization from a concentrated pentane solution room temperature. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (95 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 8.79 (d, *J* = 10.1 Hz, 1H, Ar-*H*), 7.77 (dd, *J* = 8.5, 5.5 Hz, 1H, Ar-*H*), 7.12 (s, 2H, *m*-bpy-*H*), 6.73 (td, *J* = 8.8, 2.5 Hz, 1H, Ar-*H*), 6.69 (s, 2H, *m*-bpy-*H*), 2.37 (s, 3H, $COCH_3$), 2.25 - 2.13 (m, 2H, $(CH_3)_2CH$), 2.05 – 1.90 (m, 2H, $(CH_3)_2CH$), 1.21 (s, 18H, ^{t}Bu), 1.08 (dd, *J* = 11.9, 6.8 Hz, 6H, $(CH_3)_2CH$)), 1.04 – 0.95 (m, 12H, $(CH_3)_2CH$)), 0.88 (dd, *J* = 14.0, 7.1 Hz, 6H, $(CH_3)_2CH$)), -22.66 (t, *J* = 61.8 Hz, 1H, Fe-*H*). **^{13}C {^{1}H} NMR (101 MHz, C_6D_6)**: δ (ppm) 203.39, 202.63 (t), 162.50, 159.96, 143.09, 140.99, 140.20 (t), 131.86 (dd), 120.48 (t), 114.13, 111.77, 105.95 (d), 34.55, 30.18, 29.94, 27.87 (td), 25.54 (t), 23.17 (d), 23.06, (d), 20.85 (d), 19.12, 18.27(t), 18.10, 18.06 (t). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 115.82, 115.47.

Synthesis of 4. In the glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added ethyl benzoate (4.29 µL, 0.03 mmol). The resulting reaction was stirred for 6 h at 65 °C and the mixture turned into brown-purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of Celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as brown-purple powder. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (trans 45 %, cis 19 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 8.15 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 7.11 (s, 2H, *m*-bpy-*H*), 7.07 – 7.01 (m, 1H, , Ar-*H*), 6.83 – 6.76 (m, 1H, , Ar-*H*), 6.66 (s, 2H, *m*-bpy-*H*), 6.61 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 4.32 (q, *J* = 7.1 Hz, 2H, CH_3CH_2O), 2.40 – 2.21 (m, 4H, $(CH_3)_2CH$), 1.57 (dd, *J* = 15.3, 6.9 Hz, 6H, $(CH_3)_2CH$), 1.41 – 1.32 (m, 6H, $(CH_3)_2CH$), 1.18 (s, 18H, ^{t}Bu), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3CH_2O), 1.00 (dd, *J* = 12.2, 6.9 Hz, 6H, $(CH_3)_2CH$), 0.73 (dd, *J* = 13.2, 7.0 Hz, 6H, $(CH_3)_2CH$), -6.19 (t, *J* = 60.5 Hz, 1H, Fe-*H*) (major), -26.58 (t, *J* = 59.5 Hz, 0.43H, Fe-*H*) (minor). **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)**: δ (ppm) 223.54 (t), 205.65 (t), 176.14, 143.29, 141.01, 140.81, 139.18 (t), 136.25, 132.41, 129.53, 128.17, 119.69, 117.97, 114.62, 111.53, 64.05, 60.94, 34.54 (t), 32.09 (t), 30.08, 19.85, 19.29, 18.42 (t) 14.75. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 109.22 (major), 114.61, 114.42 (minor).

Synthesis of 5. In the glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added ethyl 4-fluorobenzoate (4.40 µL, 0.03 mmol). The resulting reaction was stirred for 6 h at 65 °C and the mixture turned into a brown-purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of Celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as purple crystals upon crystallization from a concentrated ether solution room temperature. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy

Yield (70 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 7.95 (dd, *J* = 8.3, 5.4 Hz, 1H, Ar-*H*), 7.05 (s, 2H, *m*-bpy-*H*), 6.81 (d, *J* = 9.1 Hz, 1H, Ar-*H*), 6.65 (s, 2H, *m*-bpy-*H*), 6.50 (td, *J* = 8.6, 2.3 Hz, 1H, Ar-*H*), 4.27 (q, *J* = 7.0 Hz, 2H, CH_3CH_2O), 2.28 (m, 4H, $(CH_3)_2CH$), 1.53 (dd, *J* = 15.2, 6.8 Hz, 6H, $(CH_3)_2CH$), 1.17 (s, 18H, ^{t}Bu), 1.12 (t, *J* = 7.1 Hz, 3H, CH_3CH_2O), 0.98 (dd, *J* = 12.5, 7.1 Hz, 12H, $(CH_3)_2CH$), 0.75 (dd, *J* = 13.3, 7.0 Hz, 6H, $(CH_3)_2CH$), -6.45 (t, *J* = 60.9 Hz, 1H, , Fe-*H*). **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)**: δ (ppm) 229.68 (t), 204.72 (t), 175.46, 164.40, 162.69, 141.35, 139.04 (t), 132.36 (d), 130.48 (d), 129.33, 120.16, 115.56 (d), 115.29, 112.14, 106.72 (d), 64.60, 61.36, 34.90, 32.34 (t), 30.42, 20.19, 19.61, 19.26, 18.77 (t), 15.06. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 108.80.

Synthesis of 6. In the glovebox, to a stirred solution of complex [$(PC_{NHC}P)Fe(N_2)_2$] (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added N,N-dimethylbenzamide (4.41 mg, 0.03 mmol). The resulting reaction was stirred for 6 h at 75 °C and the mixture turned into brown-purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of Celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as brown powder. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (trans30 %, cis 10 %). **^{1}H NMR (600 MHz, C_6D_6)**: δ (ppm) 7.62 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.22 (m, 1H, Ar-*H*), 7.03 (s, 2H, *m*-bpy-*H*), 6.69 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.59 (s, 2H, *m*-bpy-*H*), 6.49 (t, *J* = 6.9 Hz, 1H, Ar-*H*), 2.85 (s, 6H, $CON(CH_3)_2$), 2.26 (m, 4H, $(CH_3)_2CH$), 1.52 (dd, *J* = 14.8, 6.9 Hz, 6H, $(CH_3)_2CH$), 1.21 (dd, *J* = 12.8, 6.6 Hz, 6H, $(CH_3)_2CH$), 1.11 (s, 18H, ^{t}Bu), 0.94 (dd, *J* = 13.4, 6.9 Hz, 6H, $(CH_3)_2CH$), 0.68 (dd, *J* = 13.1, 6.9 Hz, 6H$(CH_3)_2CH$), -6.13 (t, *J* = 60.7 Hz, 1H, Fe-*H*) (major), -25.40 (t, *J* = 59.6 Hz, 0.33H, Fe-*H*)(minor). **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)**: δ (ppm) 216.41 (t), 180.55, 143.86, 140.84, 140.61, 139.69 (t), 139.57, 124.73, 120.53, 119.57, 117.98, 116.77, 114.39, 112.31, 111.59, 87.97, 64.93, 39.38, 34.55, 34.52, 34.39, 30.18, 29.35, 19.99, 19.44, 19.06 (t), 18.35, 18.21. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 114.71, 114.60 (minor), 108.69 (major).

Synthesis of 7. In the glovebox, to a stirred solution of complex [$(PC_{NHC}P)Fe(N_2)_2$] (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added ethyl 4-acetylbenzoate (5.76 mg, 0.03 mmol). The resulting reaction was stirred for 6 h at room temperature and mixture turned into purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as brown-purple powder. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (91 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 10.01 (s, 1H, Ar-*H*), 7.95 (s, 2H, *m*-bpy-*H*), 7.14 (s, 2H, *m*-bpy-*H*), 6.68 (s, 2H, Ar-*H*), 4.27 (q, *J* = 6.9 Hz, 2H, CH_3CH_2O), 2.44 (s, 3H, $COCH_3$), 2.17 (m, 2H, $(CH_3)_2CH$), 1.90 (m, 2H, $(CH_3)_2CH$), 1.22 (s, 18H, ^{t}Bu), 1.12 (t, *J* = 6.9 Hz, 3H, CH_3CH_2O), 1.02 (m, 18H, $(CH_3)_2CH$), 0.80 (dd, *J* = 14.0, 6.8 Hz, 6H, $(CH_3)_2CH$)), -21.24 (t, *J* = 63.7 Hz, 1H, Fe-*H*). **^{13}C {^{1}H} NMR (101 MHz, C_6D_6)**: δ (ppm) 205.44, 168.89, 149.80 (d), 141.08, 140.15 (t), 129.57, 124.63, 120.46, 118.04, 114.32, 111.86, 59.99, 34.56, 30.22, 28.14(t), 25.43 (t), 23.31, 19.09, 18.51 (t), 18.16, 18.04 (t), 14.26. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 116.32, 115.97.

Synthesis of 8. In the glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (18.73 mg, 0.03 mmol) in benzene (1.5 mL) was added 4-Acetyl-N,N-dimethylbenzamide (5.73 mg, 0.03 mmol). The resulting reaction was stirred for 6 h at room temperature and mixture turned into light green solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of Celite. Next, the pentane was removed under reduced pressure and the title compound was obtained as green powder. The reaction was repeated at 0.01 mmol scale and trimethoxy benzene (TMB) (0.01 mmol) added to crude mixture to determine yield and selectivity via ^{1}H NMR spectroscopy Yield (72 %). **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) 9.04 (s, 1H, Ar-*H*), 7.86 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.14 (s, 2H, *m*-bpy-*H*), 7.08 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 6.68 (s, 2H, *m*-bpy-*H*), 2.90 (d, *J* = 9.3 Hz, 6H, $CON(CH_3)_2$), 2.43 (s, 3H, $COCH_3$), 1.95 (m, 4H, $(CH_3)_2CH$), 1.22 (s, 18H, ^{t}Bu), 1.06 (dd, *J* = 11.7, 6.5 Hz, 6H, $(CH_3)_2CH$), 0.99 (m, 12H, $(CH_3)_2CH$), 0.88 (dd, *J* = 14.4, 7.0 Hz, 6H, $(CH_3)_2CH$), -22.06 (t, *J* = 62.2 Hz, 1H, Fe-*H*). **^{13}C {^{1}H} NMR (101 MHz, C_6D_6)**: δ (ppm) 205.10 (t), 173.47, 147.02, 146.21, 141.32,140.47 (t), 132.95, 130.12, 120.81 (t), 116.80, 114.49, 112.13, 65.37, 55.29, 54.09, 50.01, 34.89, 34.38, 34.34, 33.27, 30.54, 28.04 (t), 25.62 (t), 23.42, 19.54, 18.70 (t), 18.49 (t), 18.40. **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 116.14, 115.79.

^{1}H NMR and high-resolution mass spectra of selected compounds

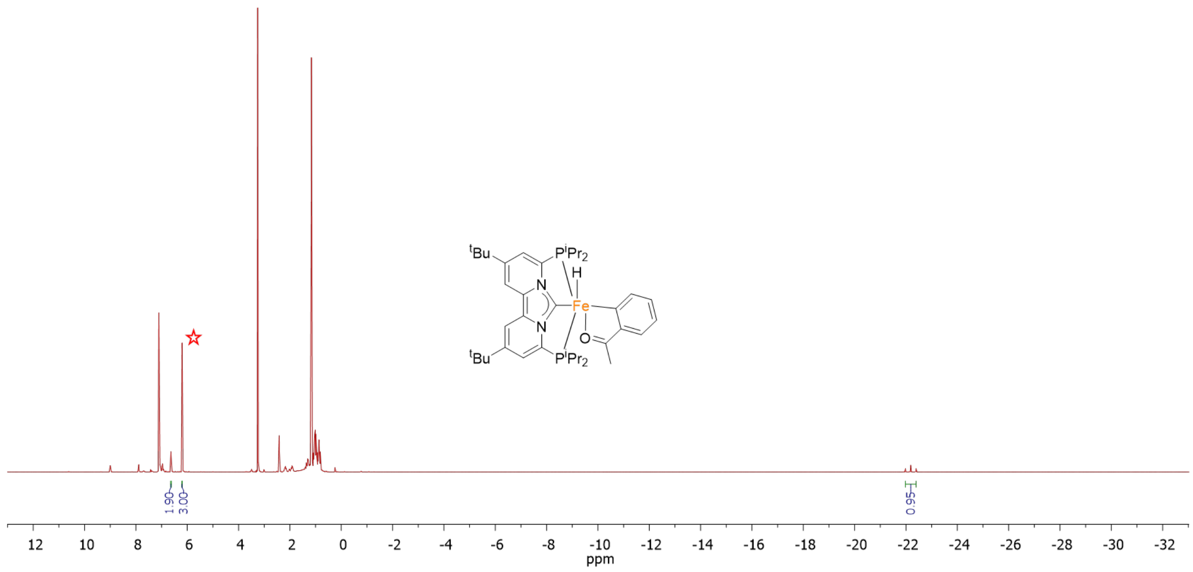

Figure S1. ^{1}H NMR spectrum (400 MHz) of **2** in C_6D_6 with trimethoxy benzene internal standard.

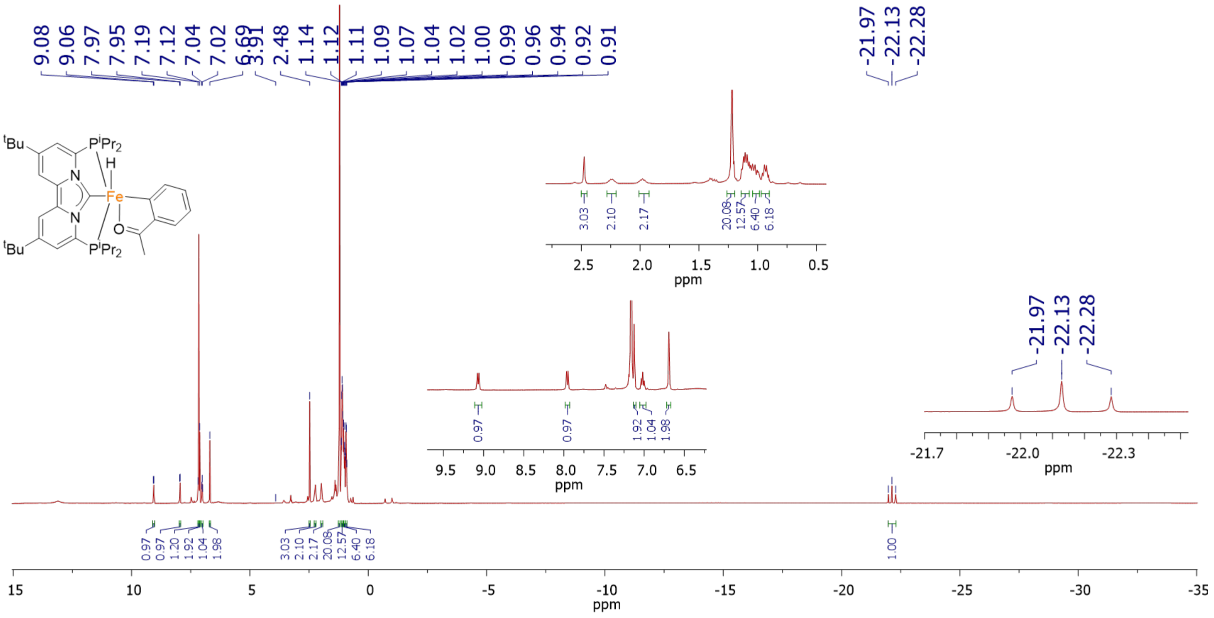

Figure S2. ^{1}H NMR spectrum (400 MHz) of **2** in C_6D_6.

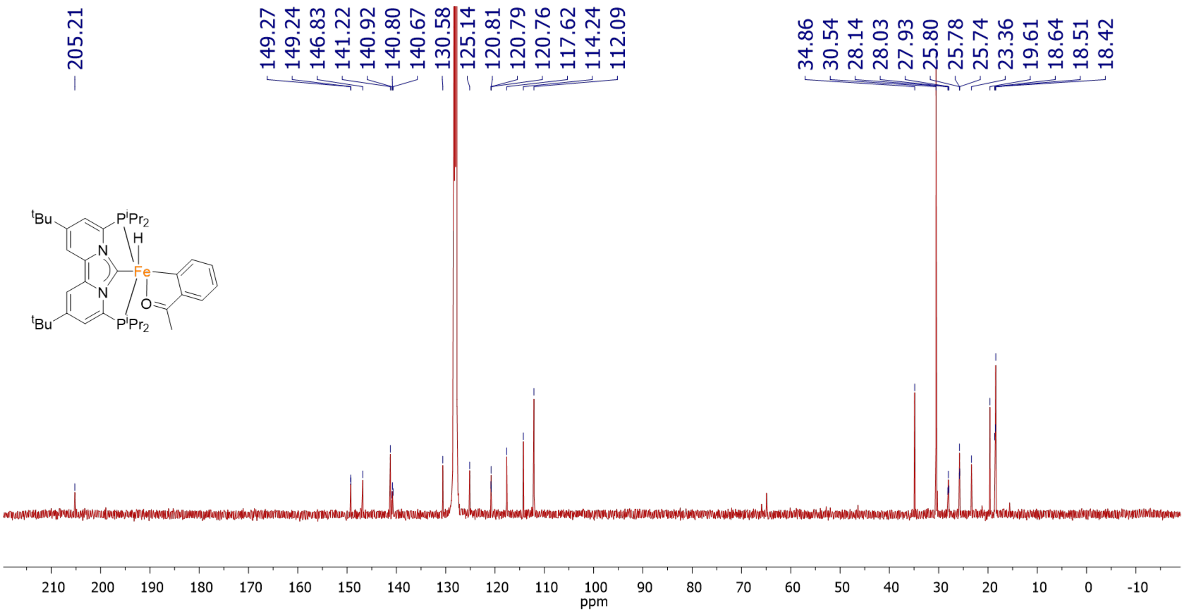

Figure S3. $^{13}C\ \{^1H\}$ NMR spectrum (101 MHz) of **2** in C_6D_6.

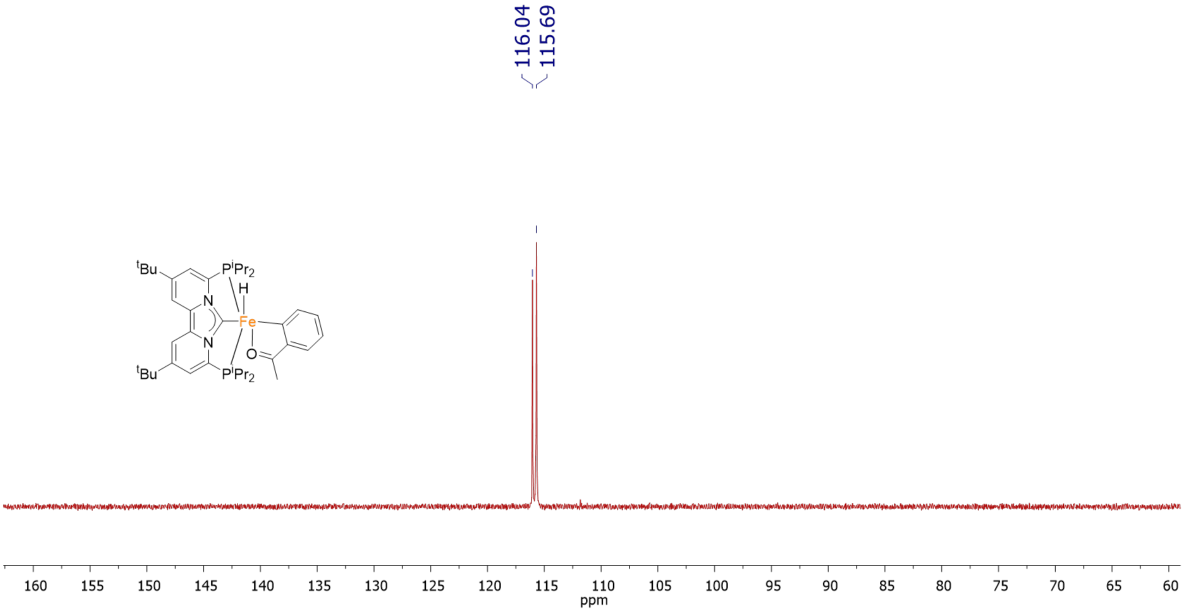

Figure S4. $^{31}P\ \{^1H\}$ NMR spectrum (162 MHz) of **2** in C_6D_6.

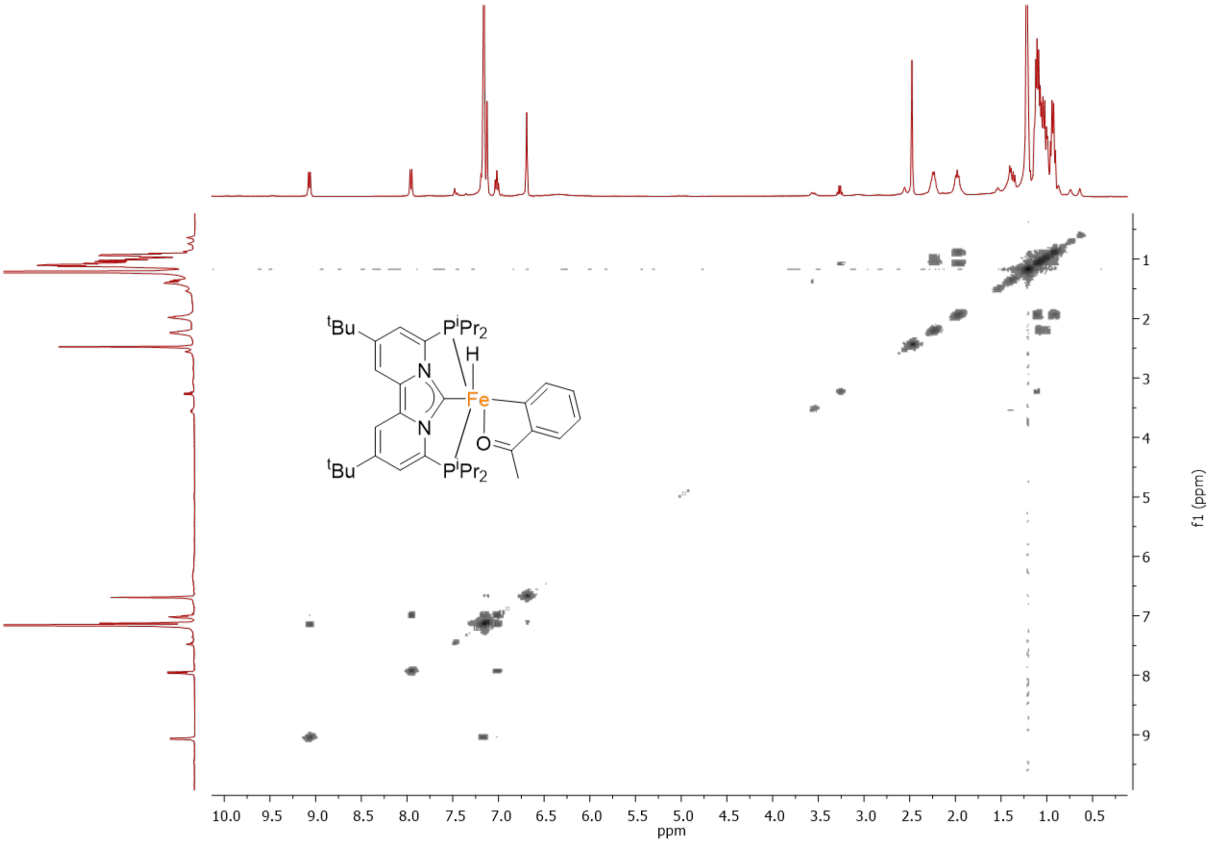

Figure S5. COSY spectrum (400 MHz) of **2** in C_6D_6.

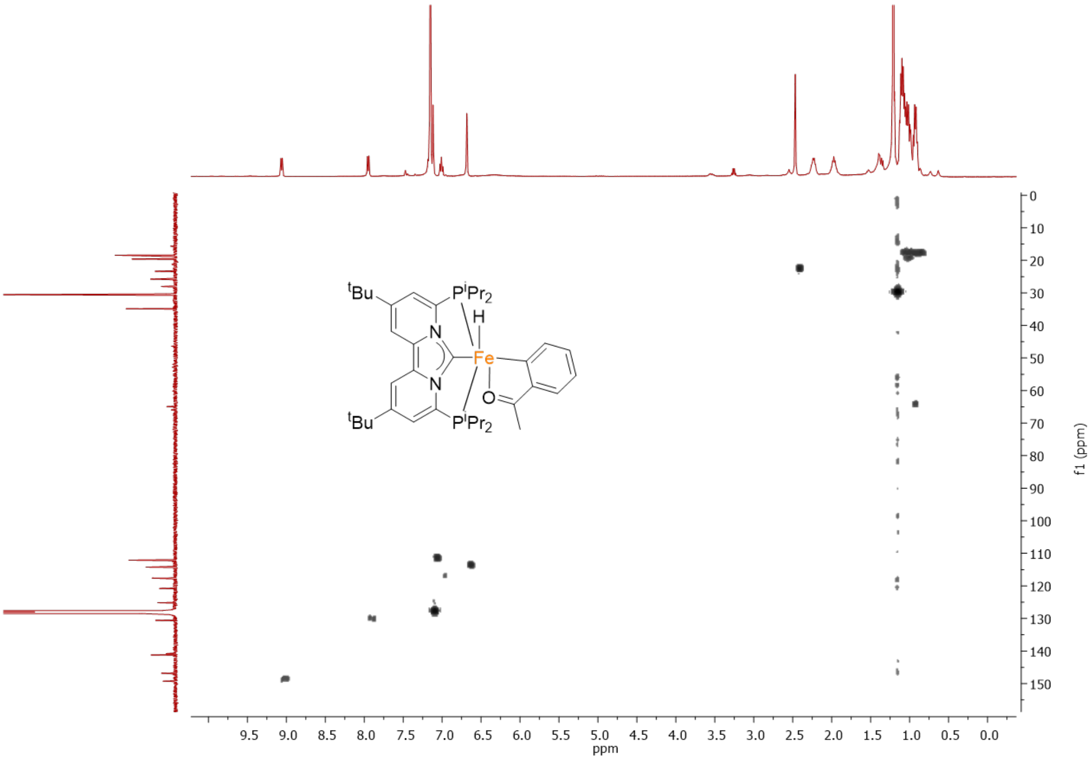

Figure S6. HMQC spectrum (400 MHz) of **2** in C_6D_6.

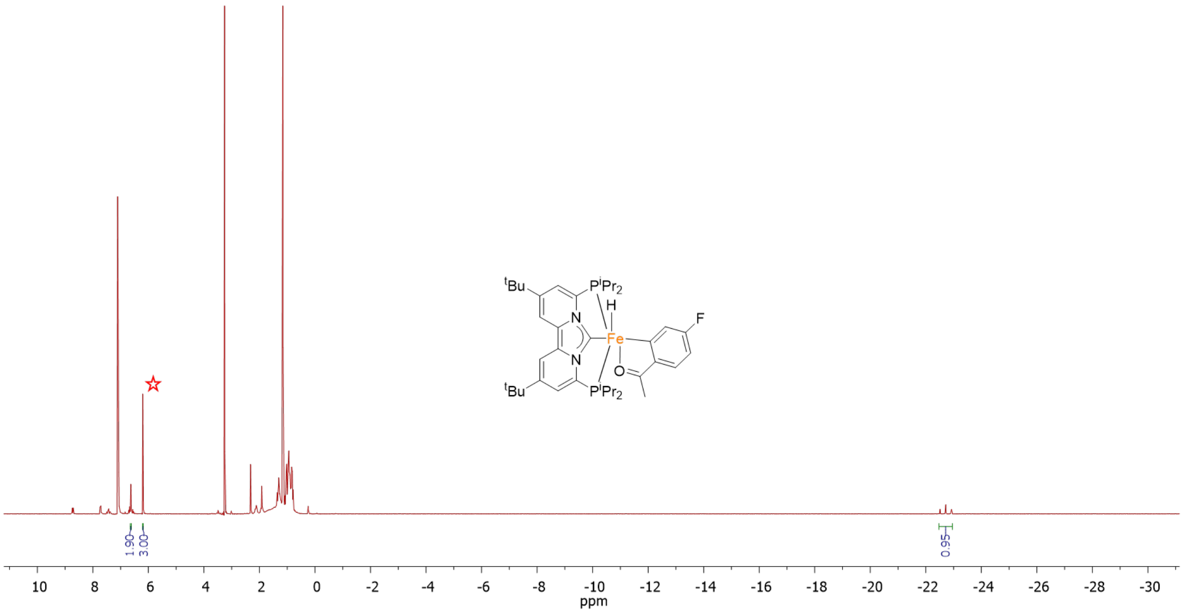

Figure S7. ^{1}H NMR spectrum (400 MHz) of **3** in C_6D_6 with trimethoxy benzene internal standard.

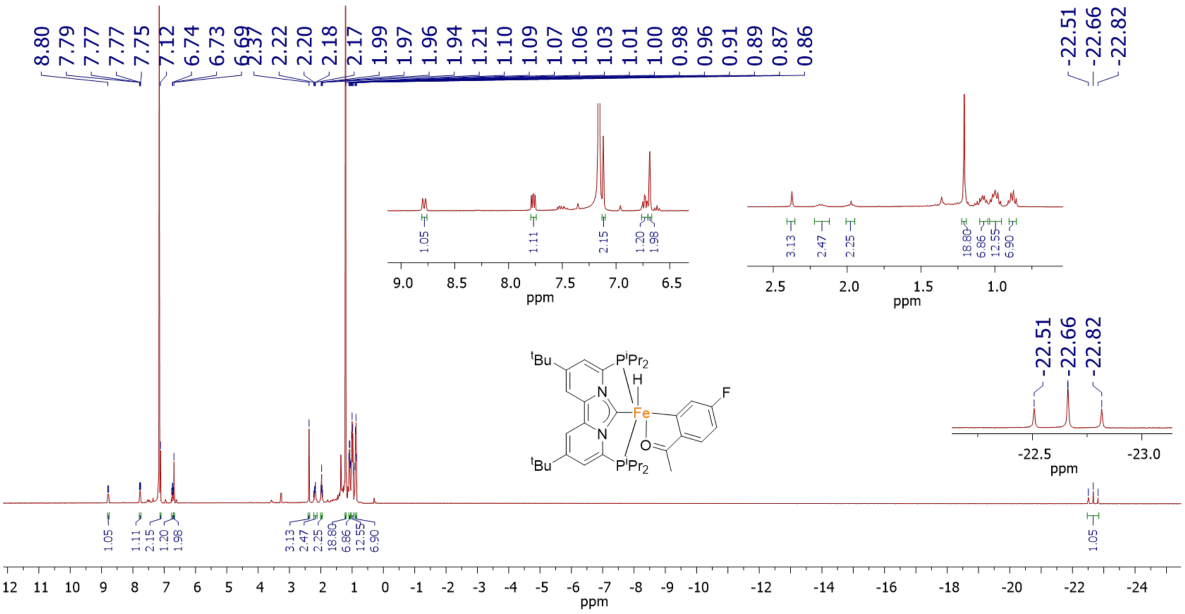

Figure S8. ^{1}H NMR spectrum (400 MHz) of **3** in C_6D_6.

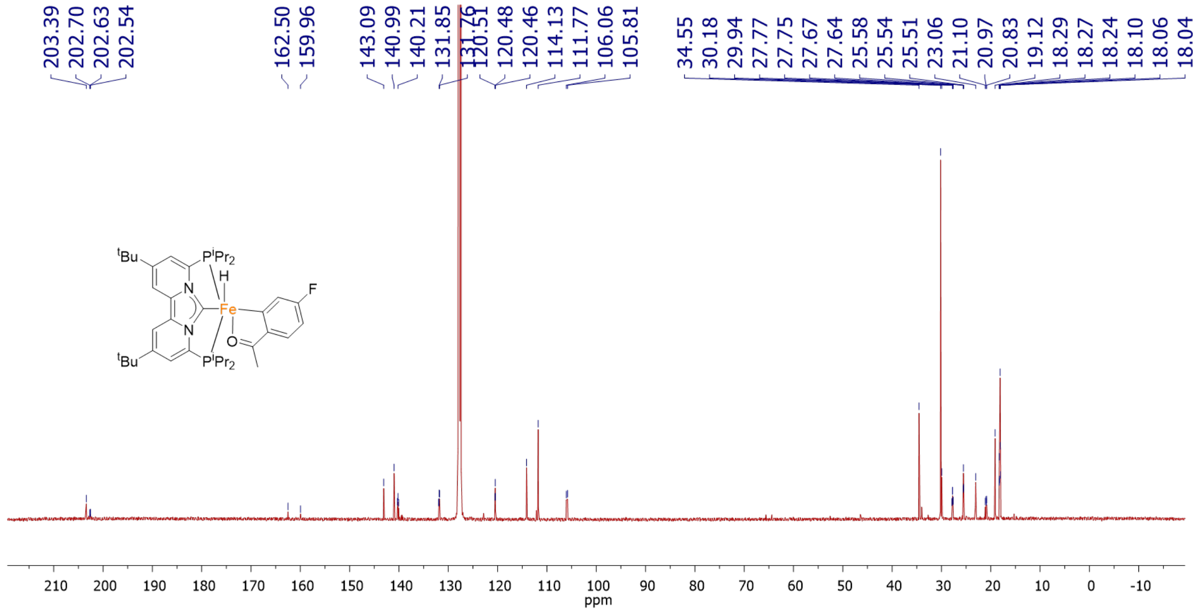

Figure S9. ^{13}C {^{1}H} NMR spectrum (101 MHz) of **3** in C_6D_6.

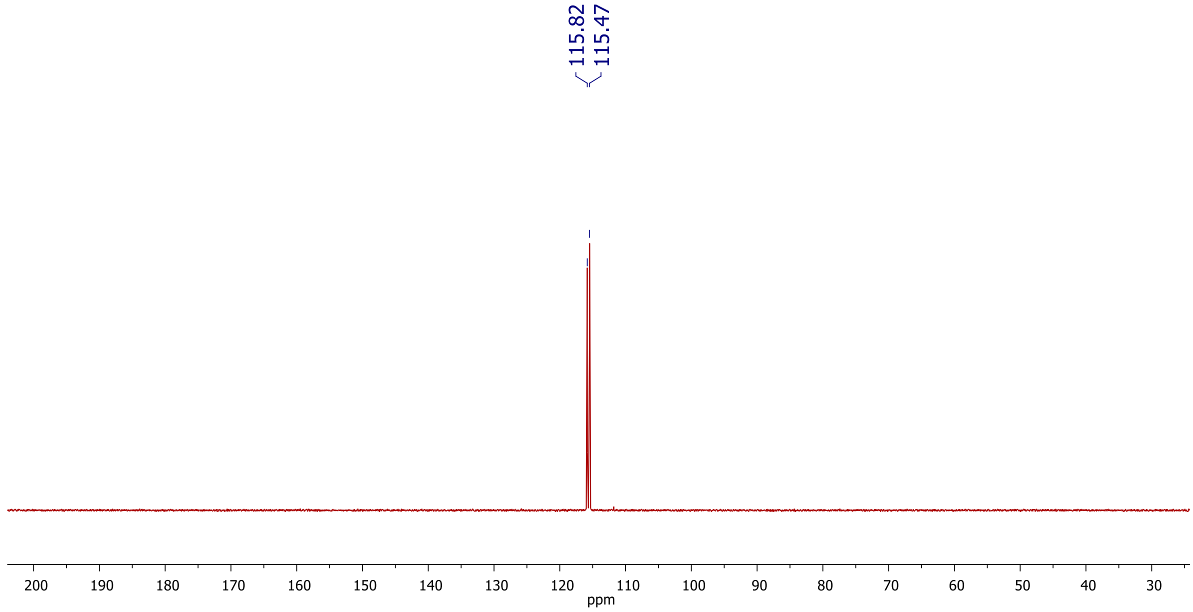

Figure S10. ^{31}P {^{1}H} NMR spectrum (162 MHz) of **3** in C_6D_6.

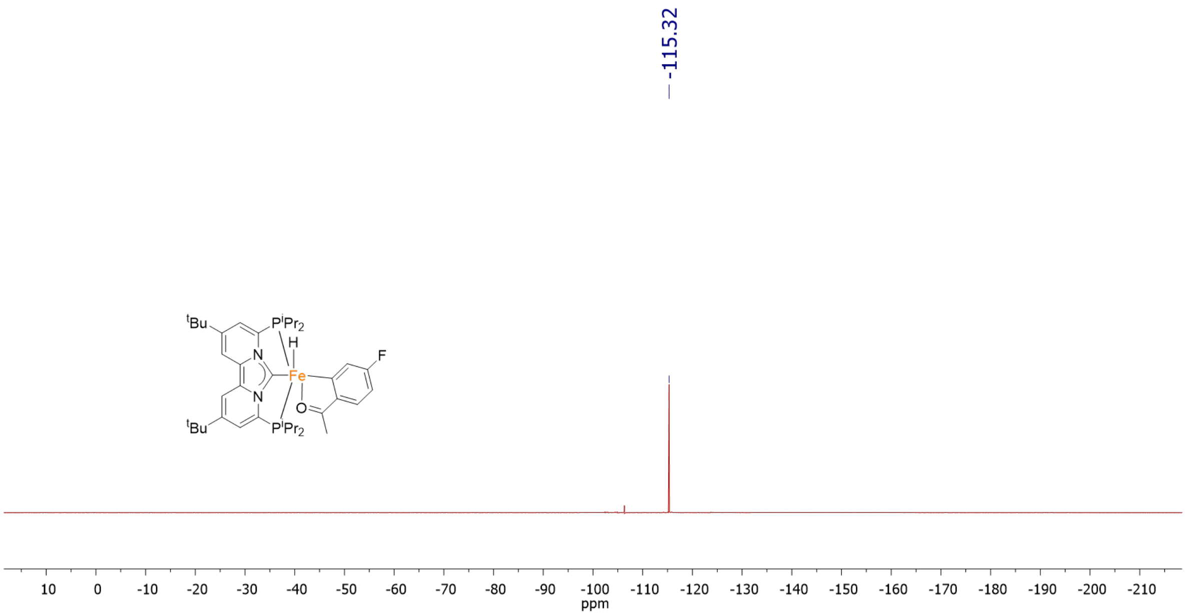

Figure S11. $^{19}F\ \{^{1}H\}$ NMR spectrum (377 MHz) of **3** in C_6D_6.

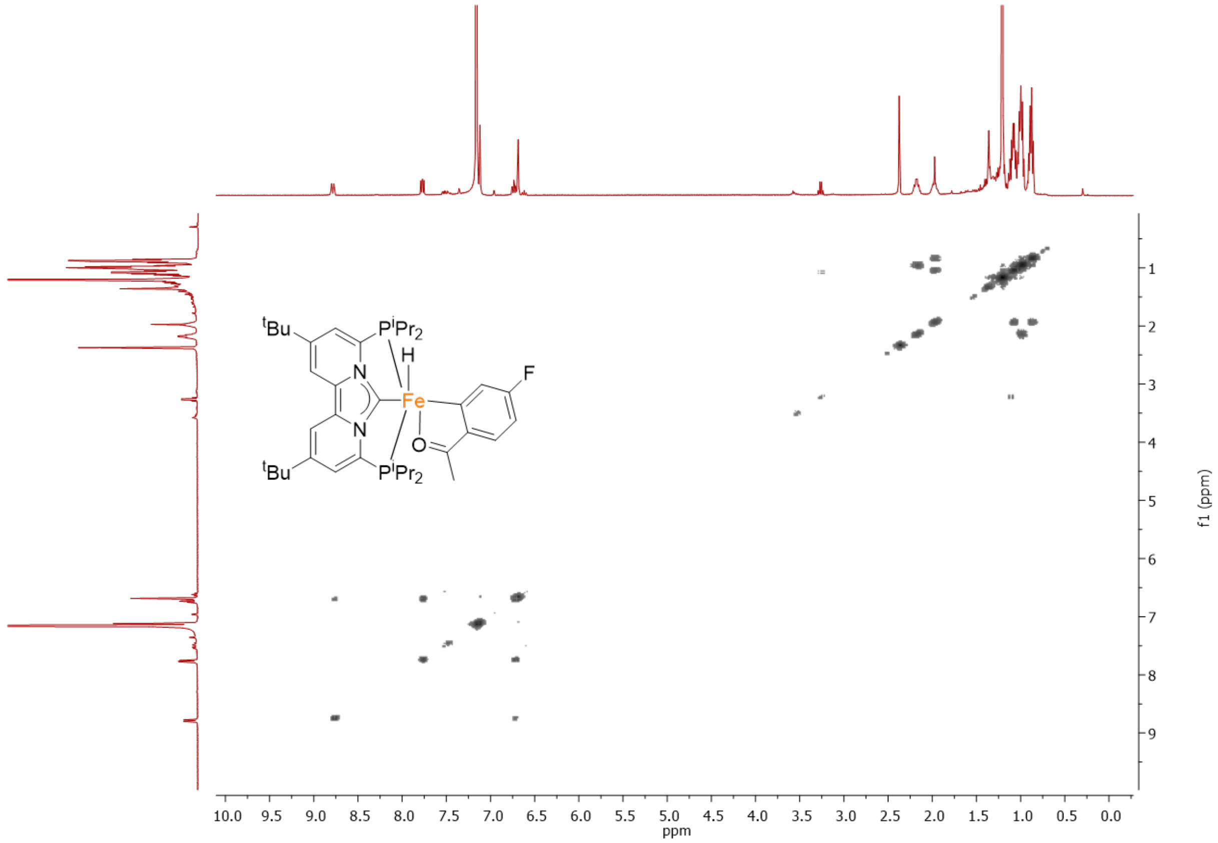

Figure S12. COSY NMR spectrum (400 MHz) of **3** in C_6D_6.

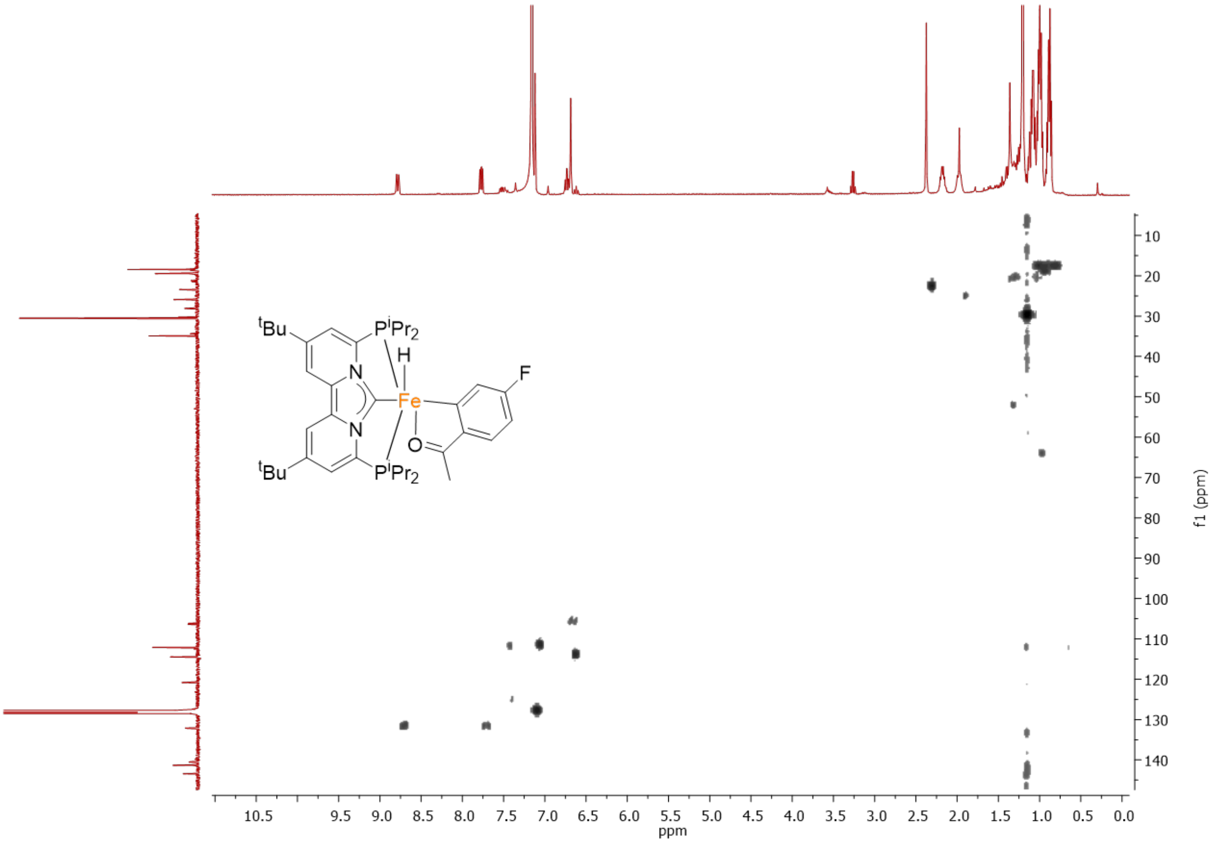

Figure S13. HMQC NMR spectrum (400 MHz) of **3** in C_6D_6.

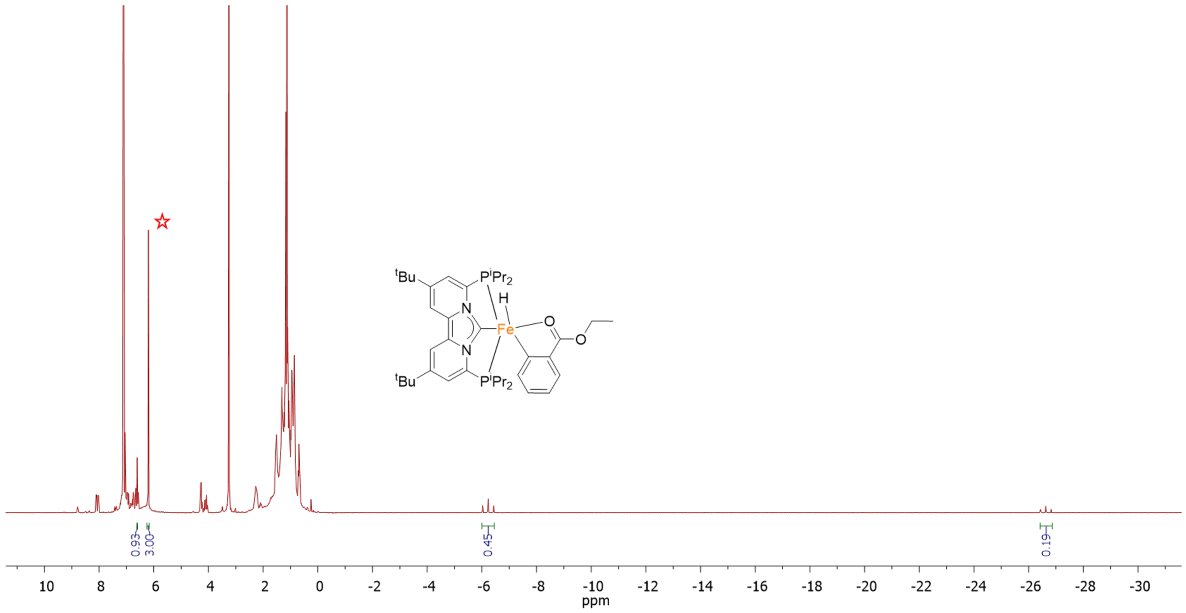

Figure S14. ^{1}H NMR spectrum (400 MHz) of **4** in C_6D_6 with trimethoxy benzene internal standard.

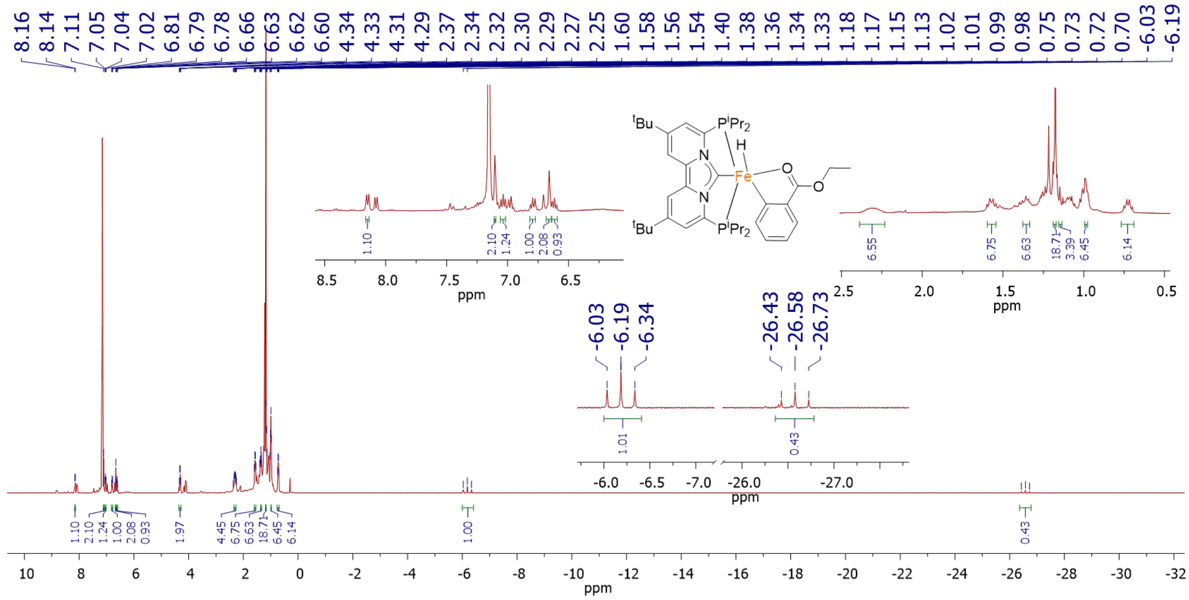

Figure S15. ^{1}H NMR spectrum (400 MHz) of **4** in C_6D_6.

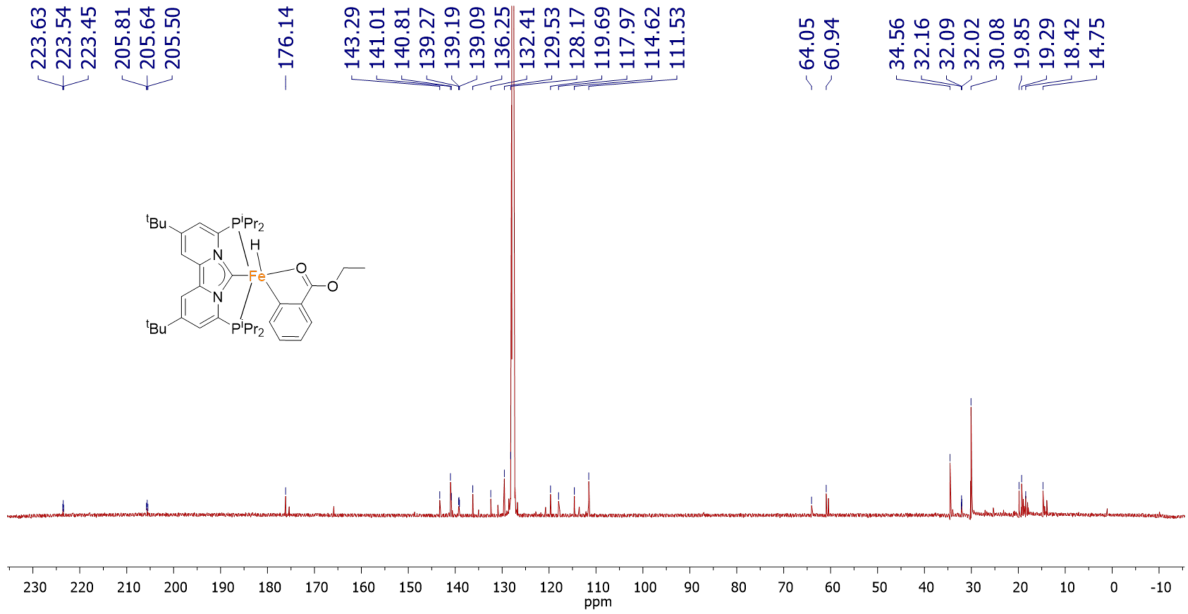

Figure S16. ^{13}C {^{1}H} NMR spectrum (400 MHz) of **4** in C_6D_6.

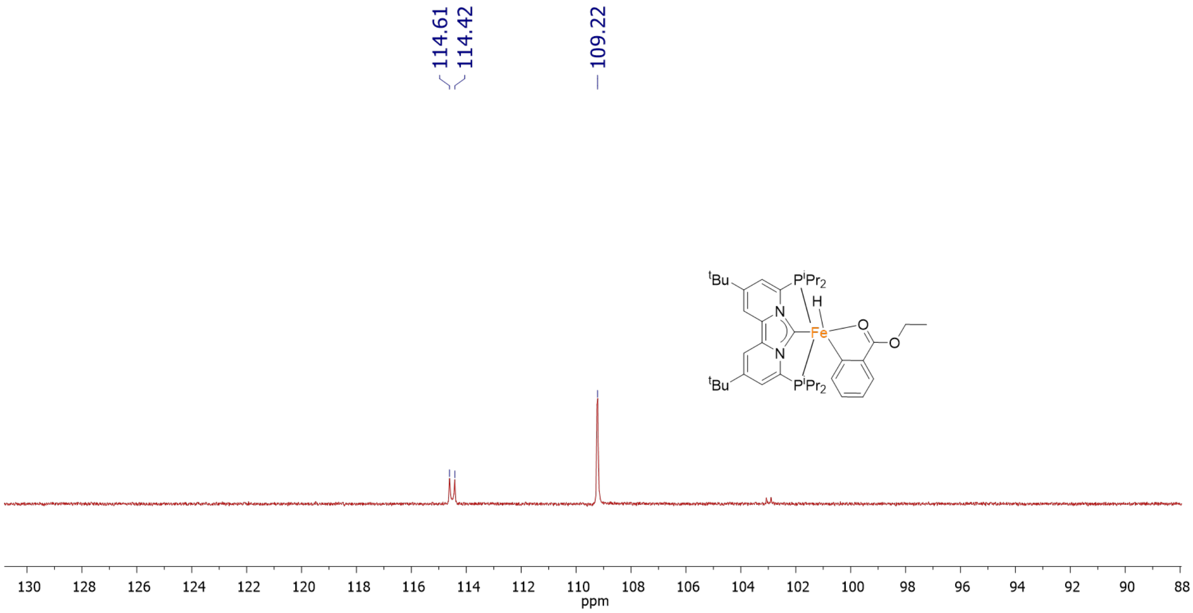

Figure S17. ^{31}P {^{1}H} NMR spectrum (162 MHz) of **4** in C_6D_6.

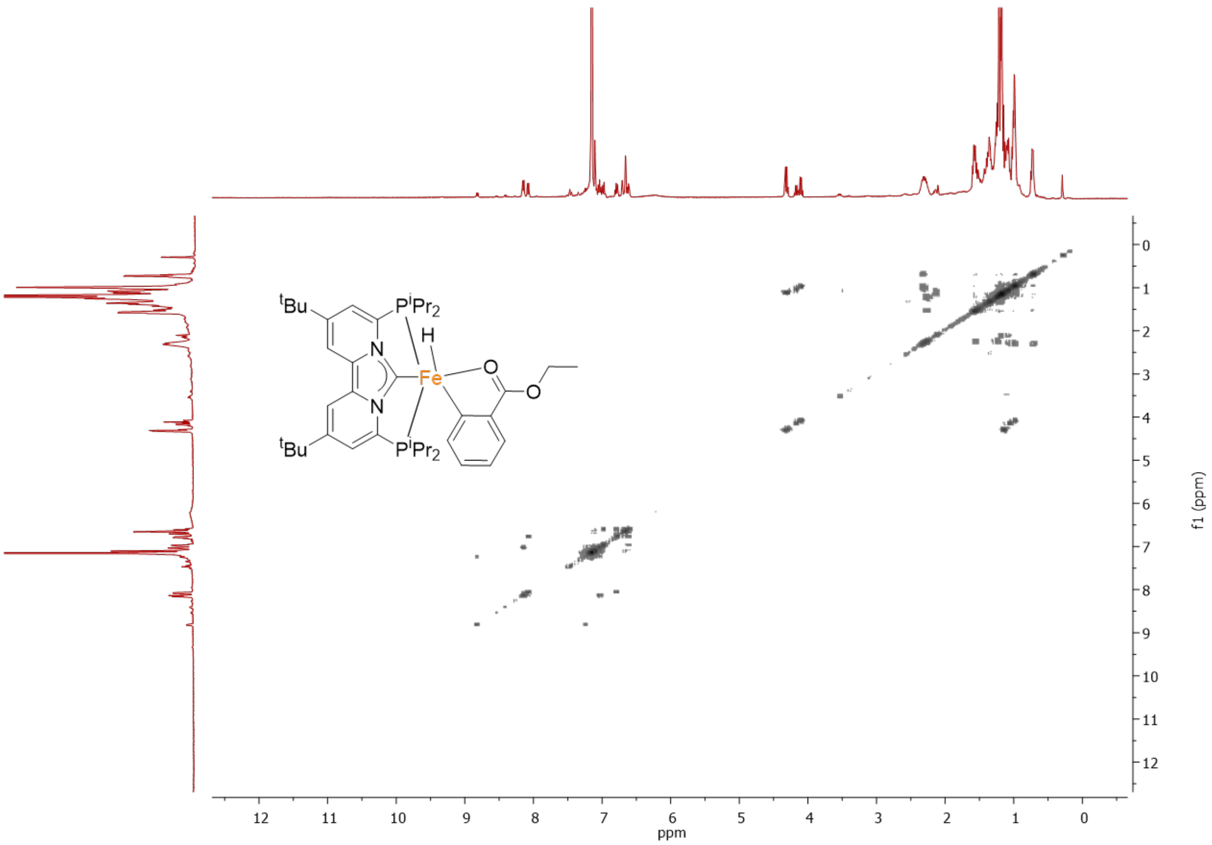

Figure S18. COSY NMR spectrum (400 MHz) of **4** in C_6D_6.

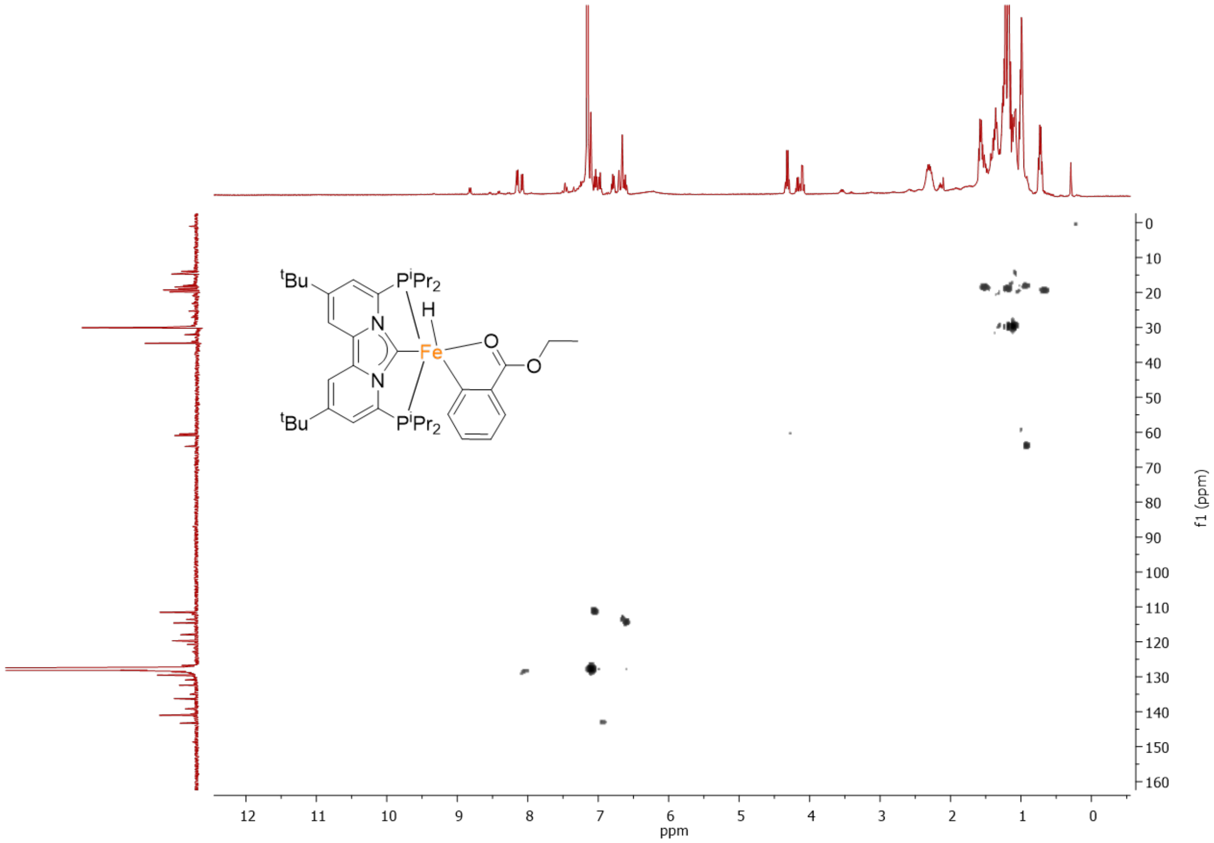

Figure S19. HMQC NMR spectrum (400 MHz) of **4** in C_6D_6.

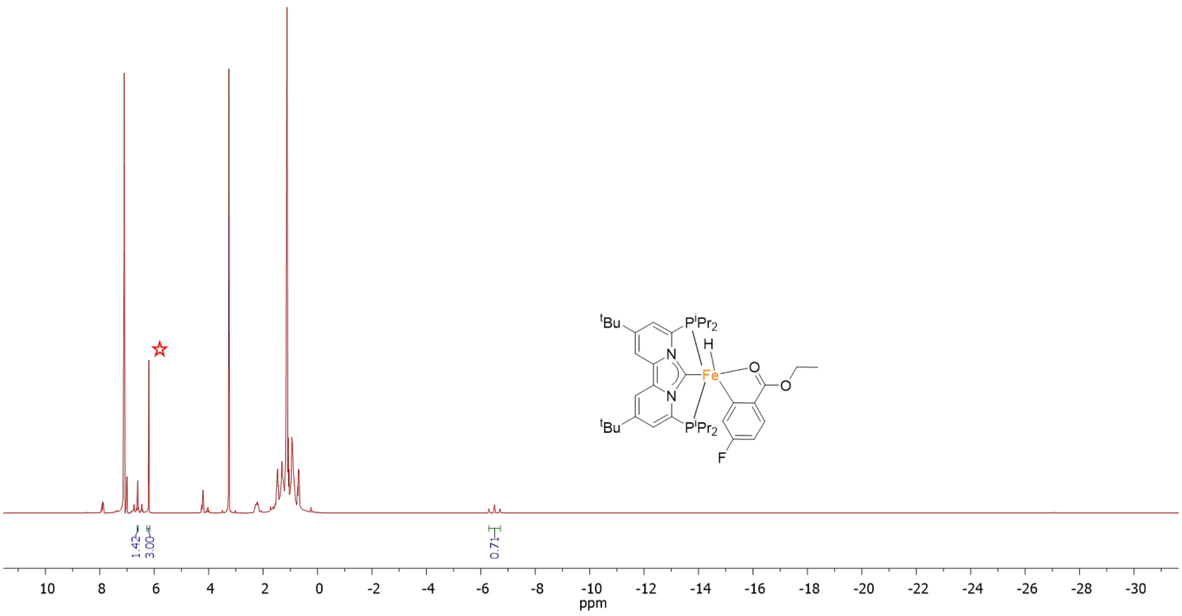

Figure S19. ^{1}H NMR spectrum (400 MHz) of **5** in C_6D_6 with trimethoxy benzene internal standard.

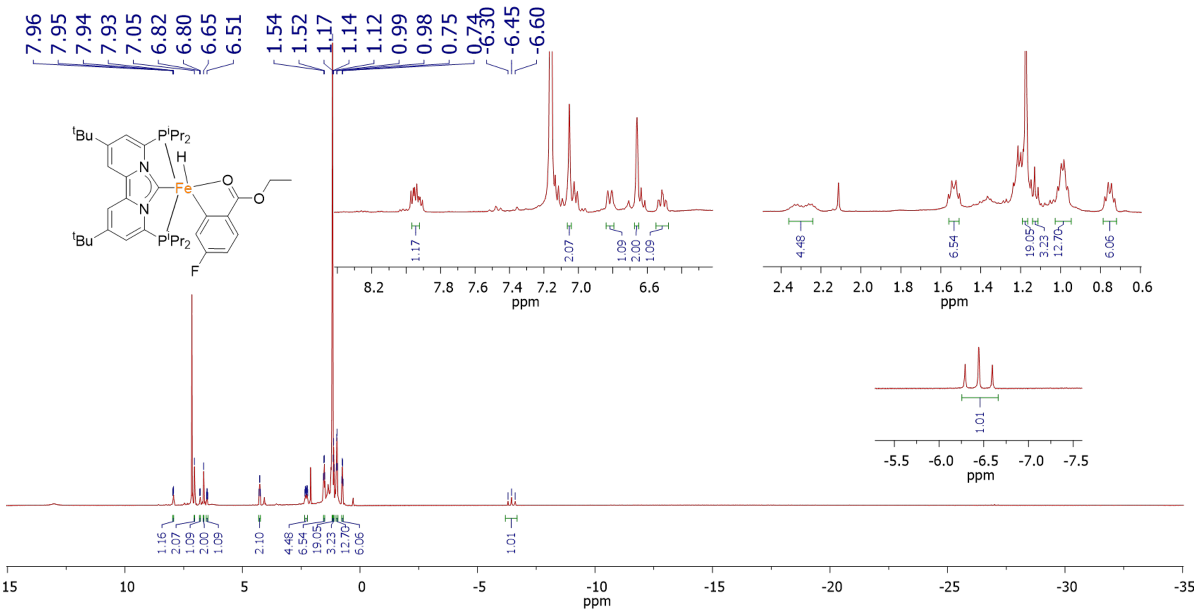

Figure S20. ^{1}H NMR spectrum (400 MHz) of **5** in C_6D_6.

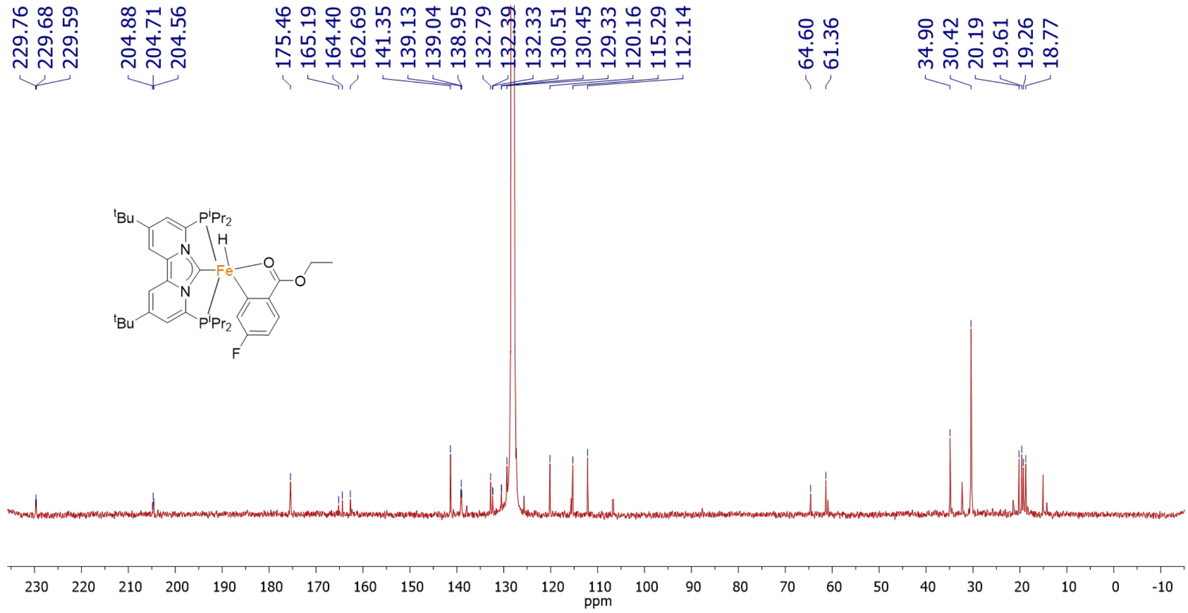

Figure S21. ^{13}C {^{1}H} NMR spectrum (151 MHz) of **5** in C_6D_6.

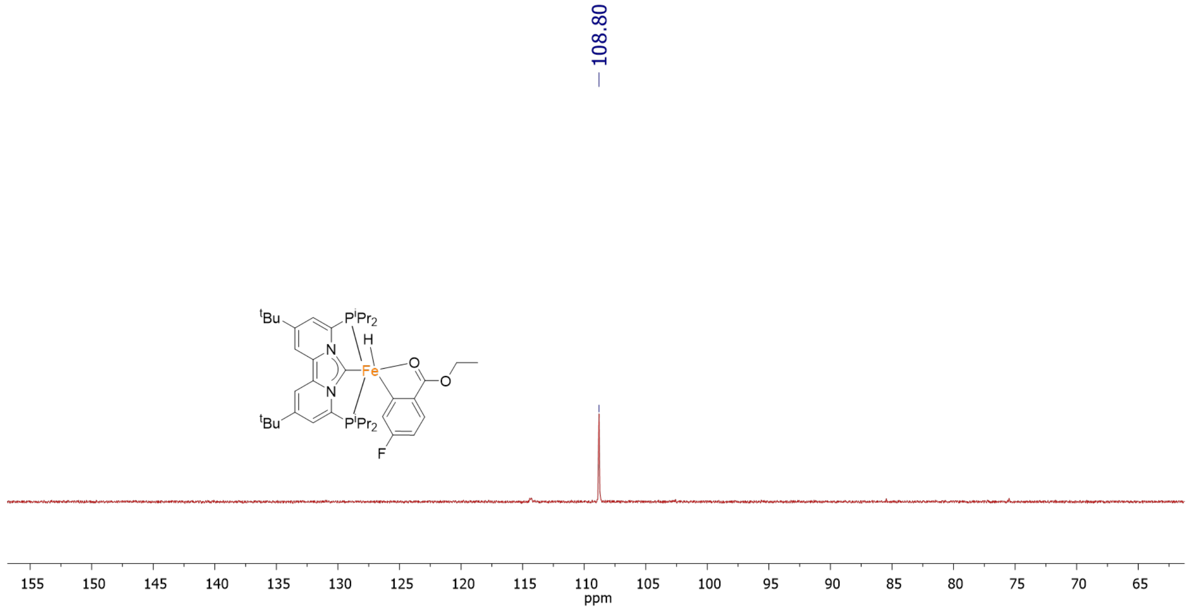

Figure S22. 31P {^{1}H} NMR spectrum (162 MHz) of **5** in C_6D_6.

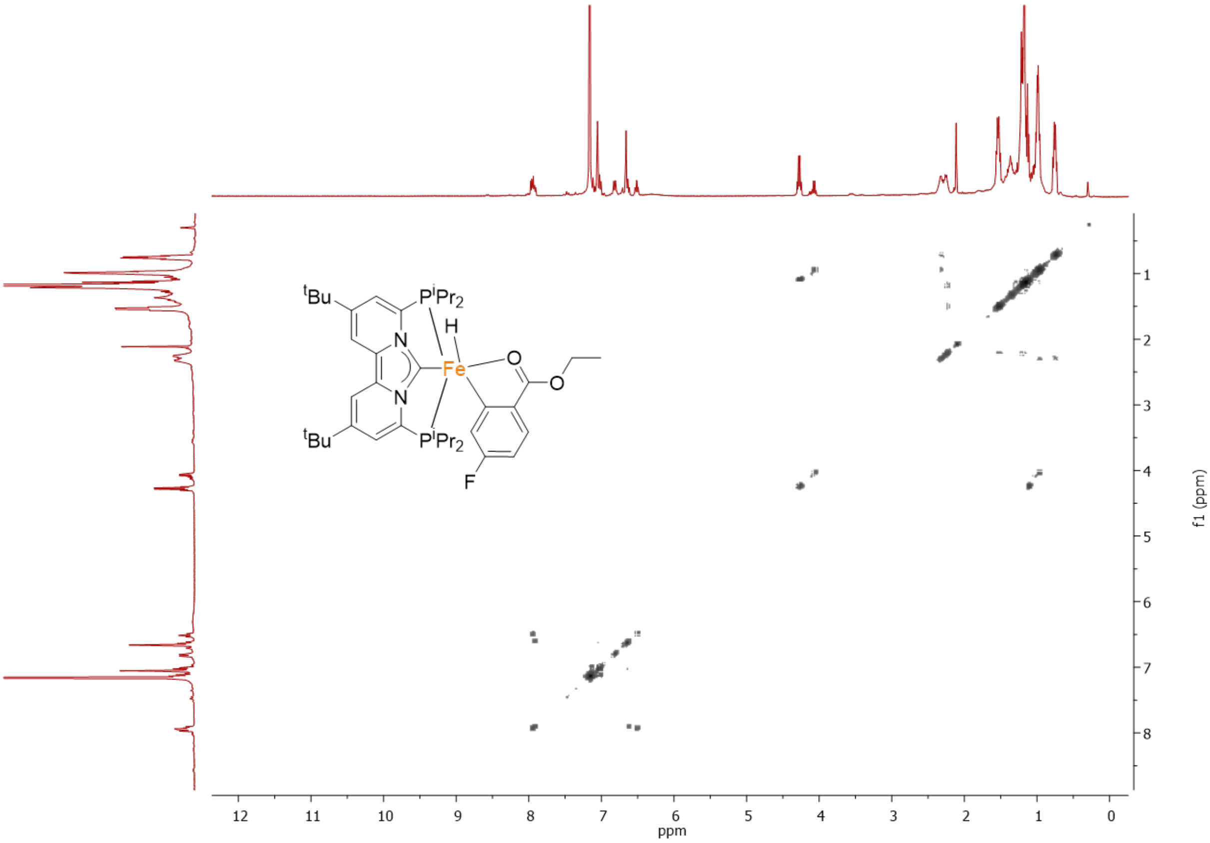

Figure S23. COSY NMR spectrum (400 MHz) of **5** in C_6D_6

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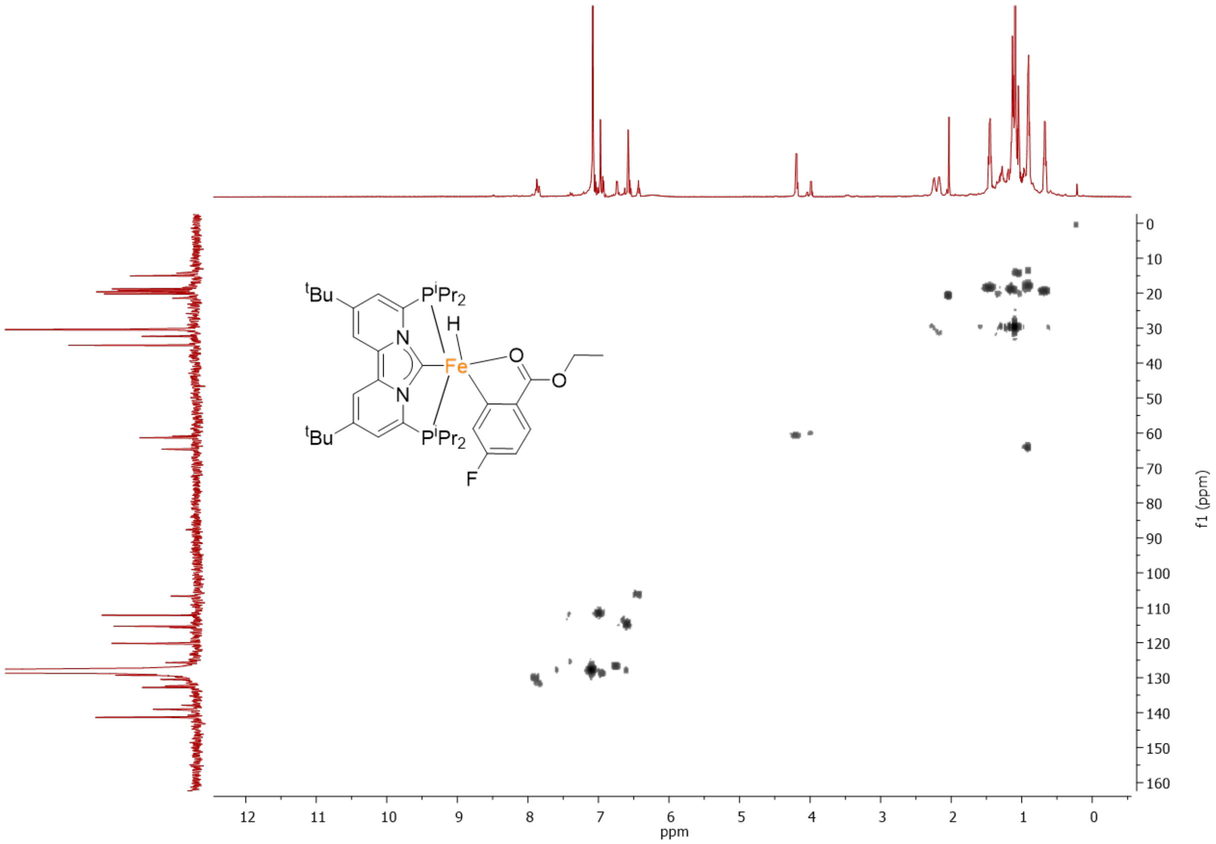


Figure S24. HSQC NMR spectrum (400 MHz) of **5** in C_6D_6.

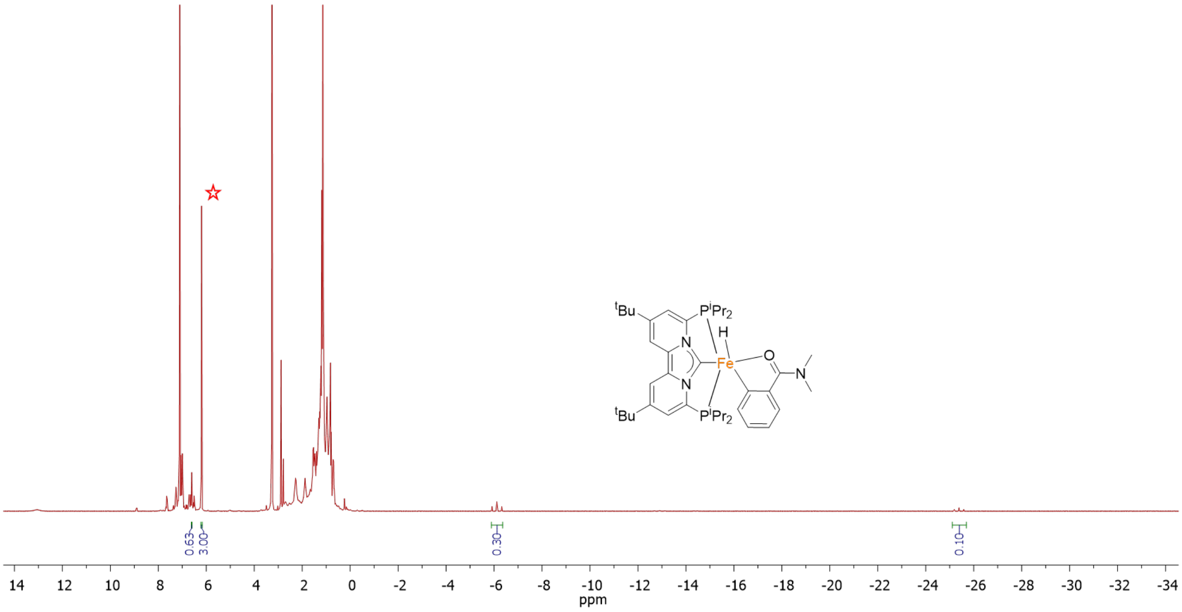


Figure S25. ^{1}H NMR spectrum (400 MHz) of **6** in C_6D_6 with trimethoxy benzene internal standard.

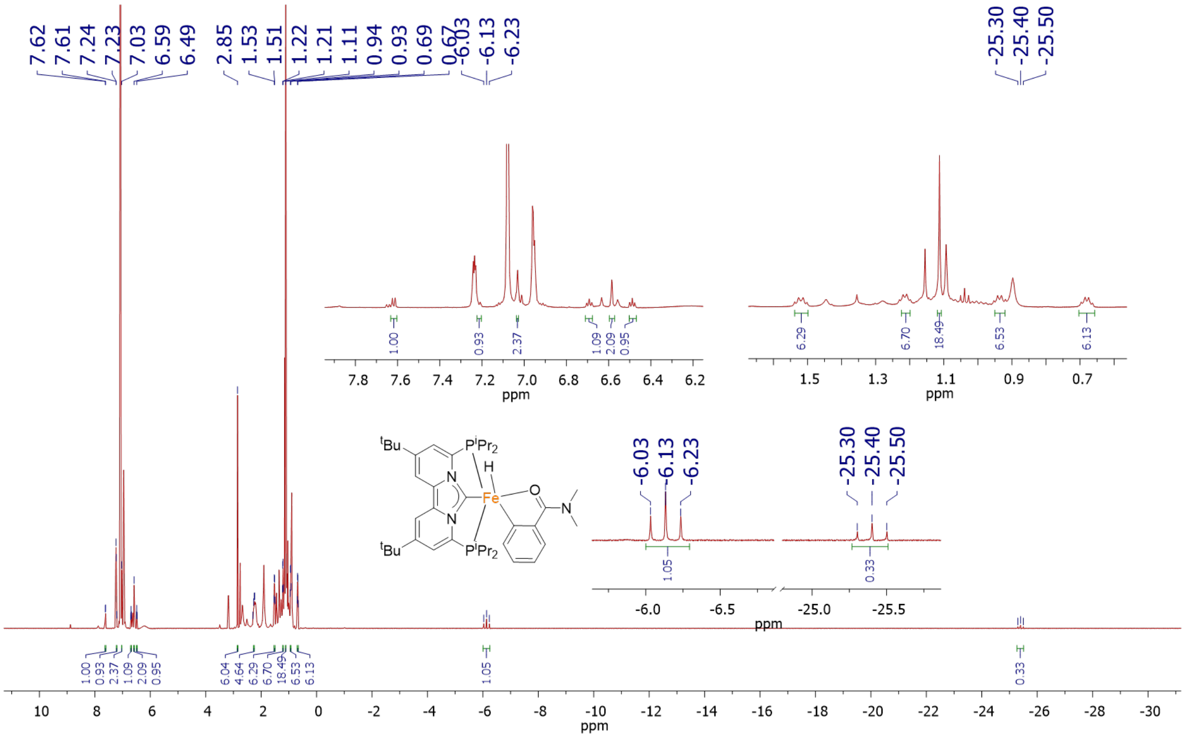


Figure S26. ^{1}H NMR spectrum (400 MHz) of **6** in C_6D_6.

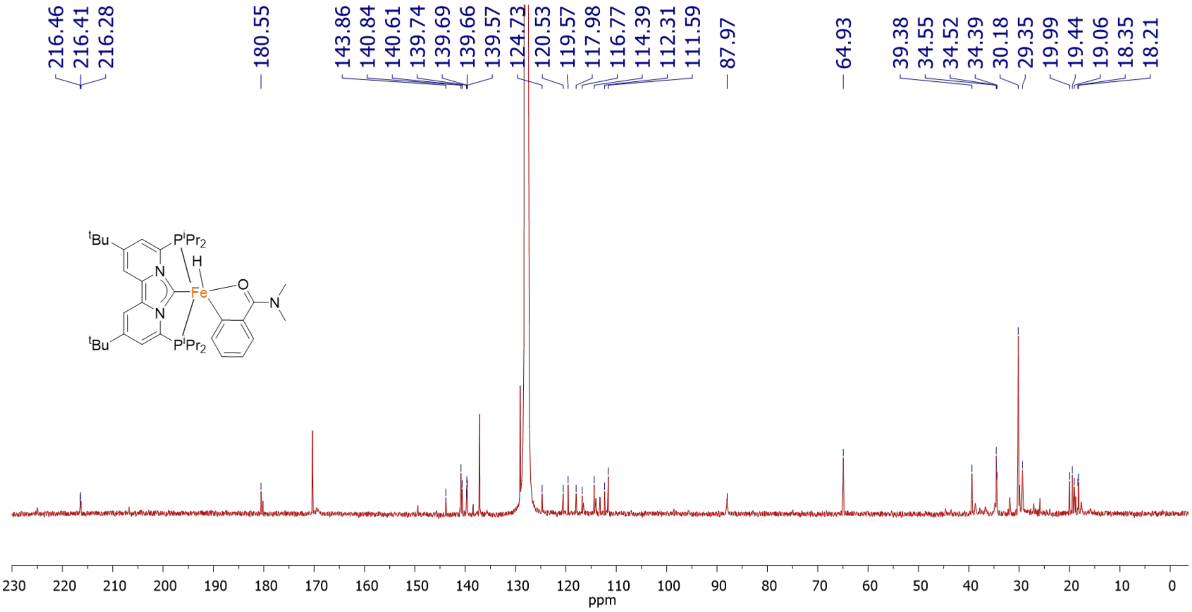


Figure S27. ^{13}C {^{1}H} NMR spectrum (151 MHz) of **6** in C_6D_6.

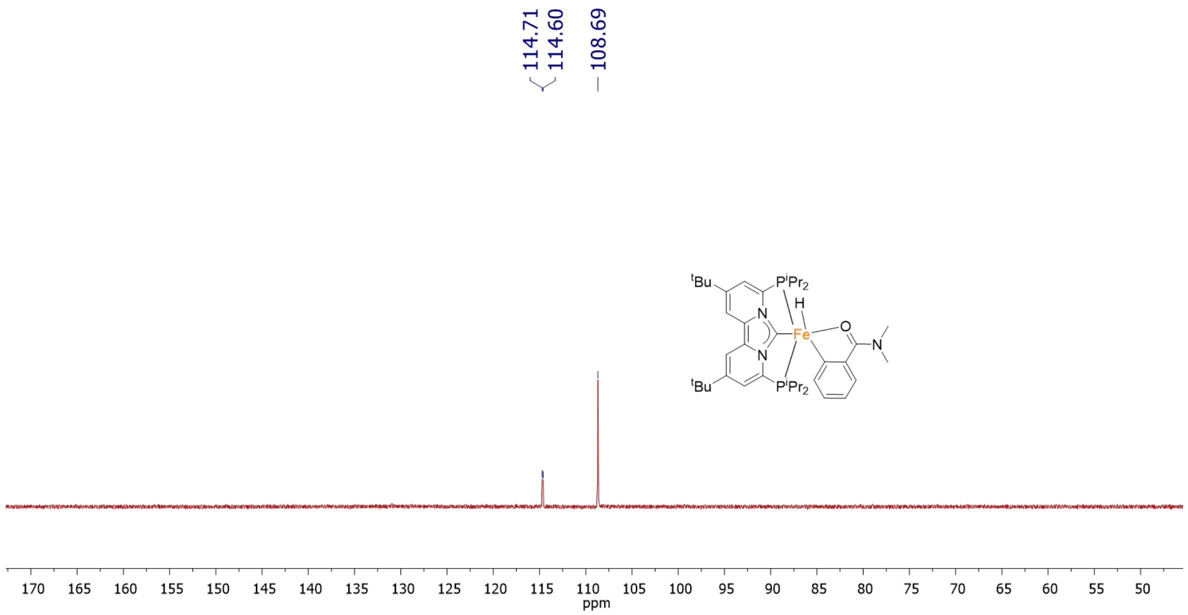


Figure S28. 31P {^{1}H} NMR spectrum (162 MHz) of **6** in C_6D_6.

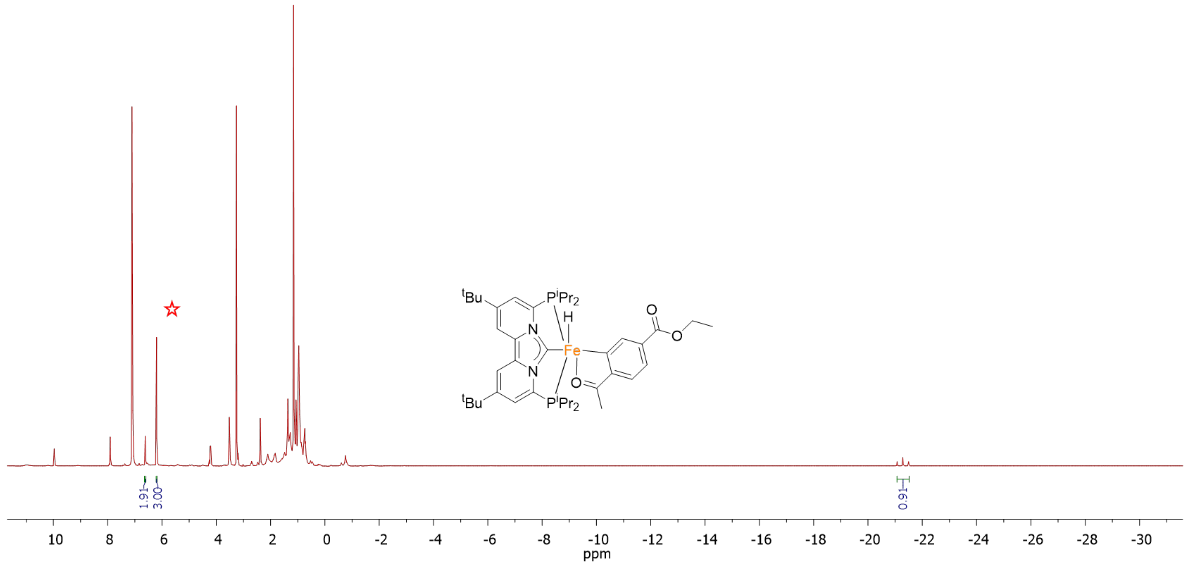


Figure S29. ^{1}H NMR spectrum (400 MHz) of **7** in C_6D_6 with trimethoxy benzene internal standard.

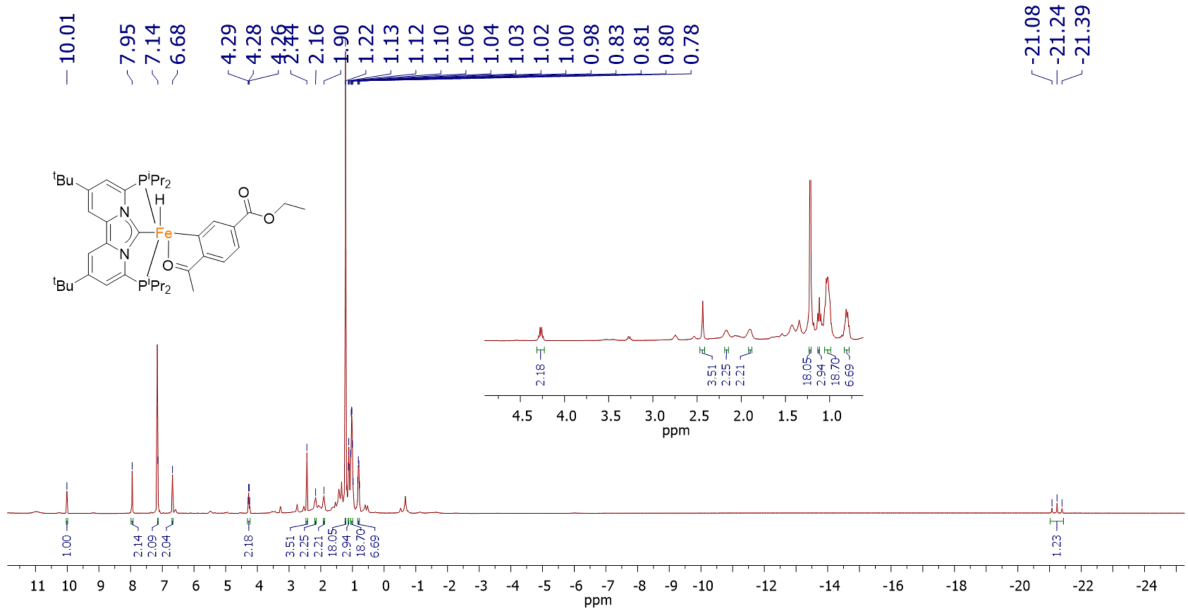


Figure S30. ^{1}H NMR spectrum (400 MHz) of **7** in C_6D_6.

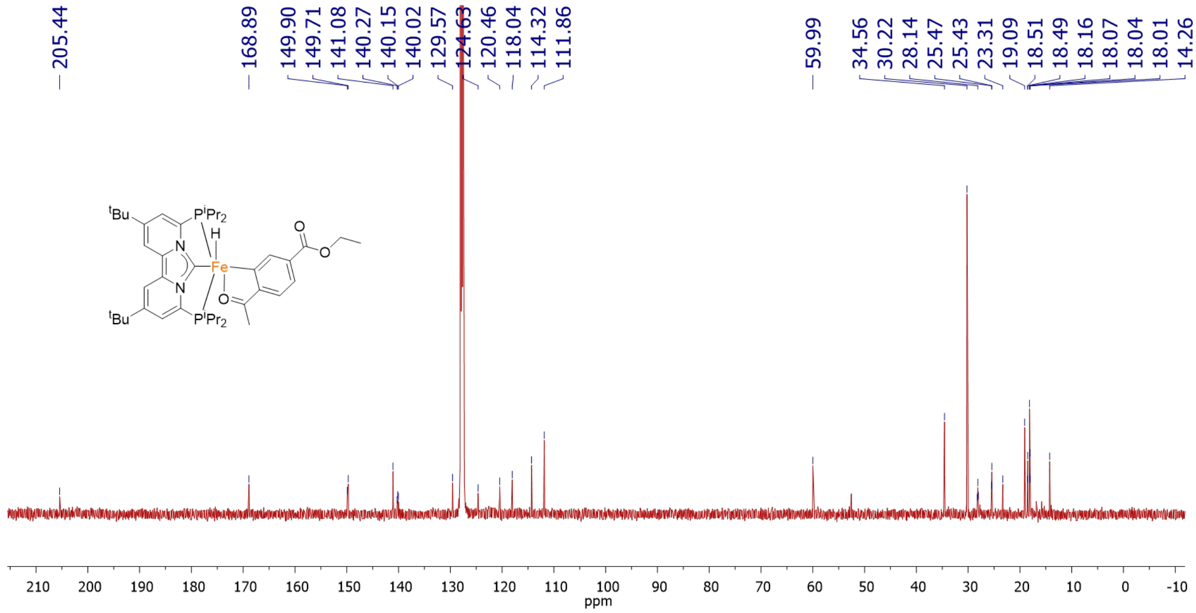


Figure S31. ^{13}C {^{1}H} NMR spectrum (101 MHz) of **7** in C_6D_6.

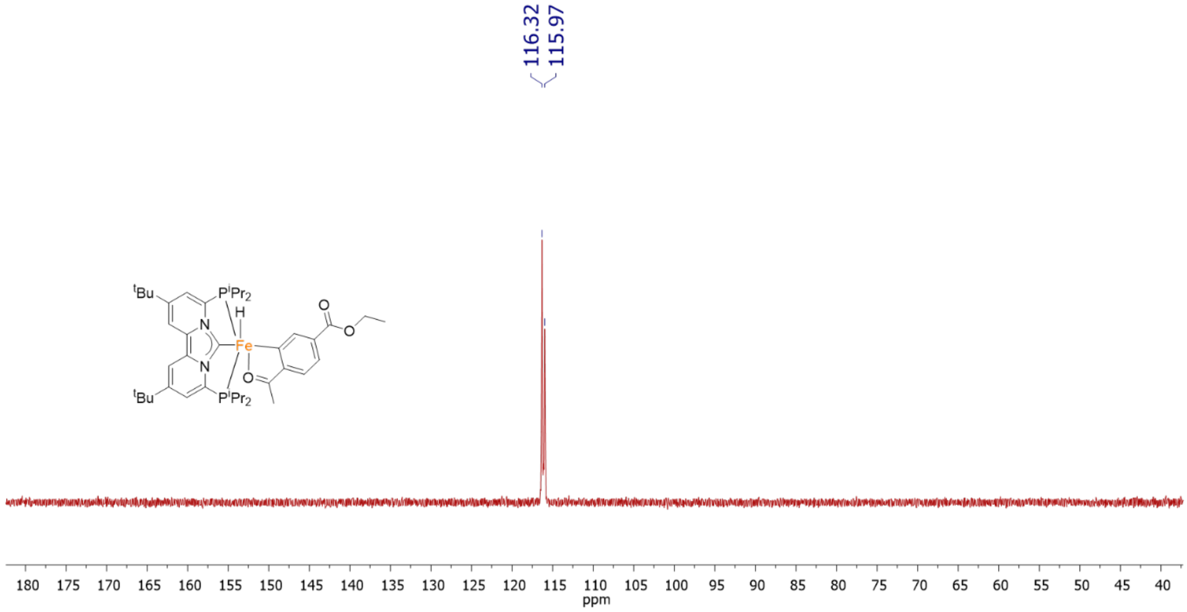


Figure S32. ^{31}P {^{1}H} NMR spectrum (162 MHz) of **7** in C_6D_6.

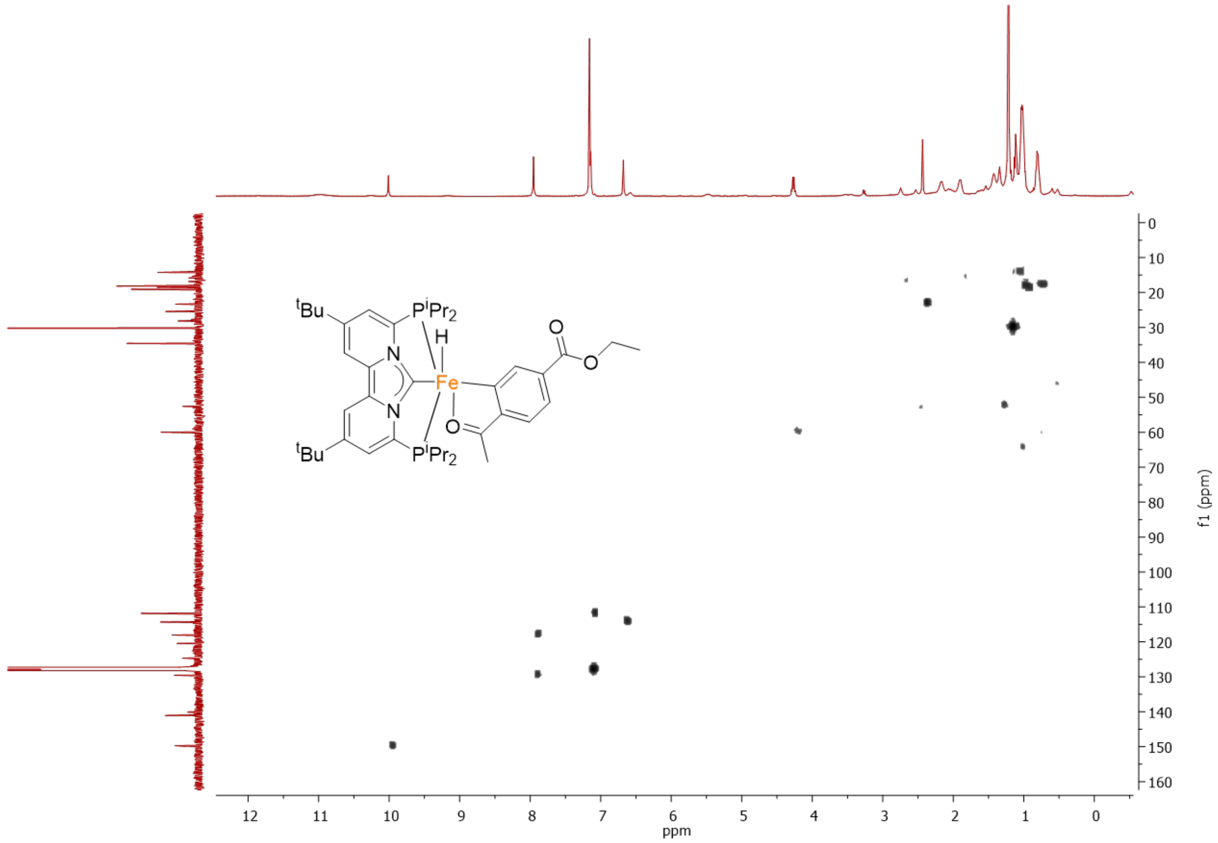


Figure S33. HMQC NMR spectrum (400 MHz) of **7** in C_6D_6.

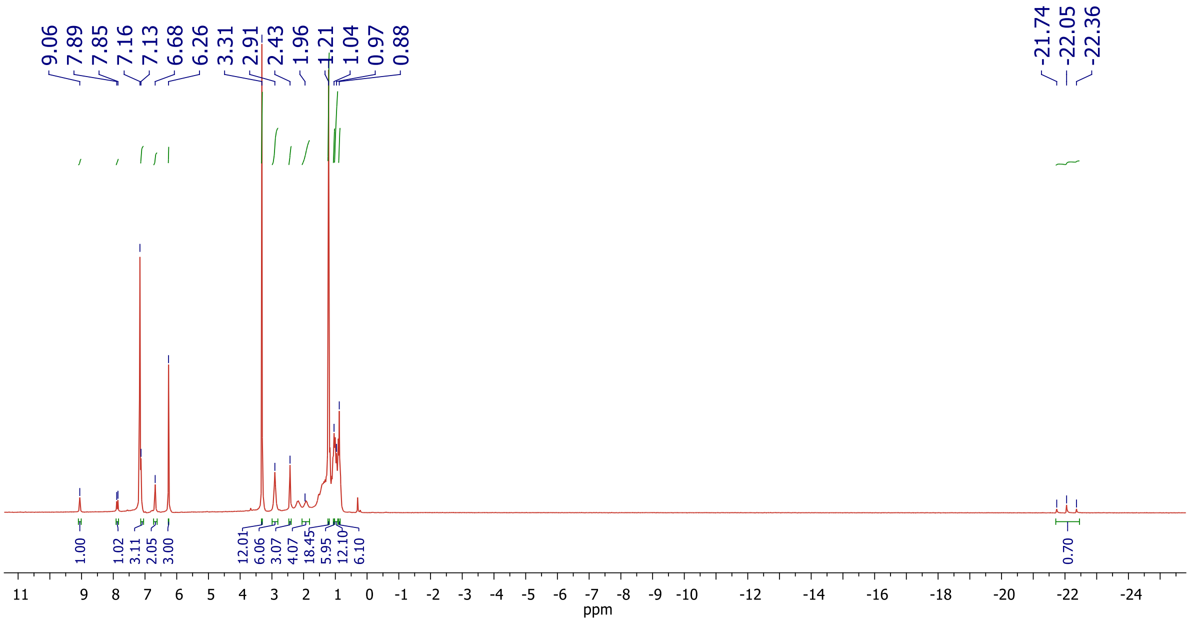


Figure S34. ^{1}H NMR spectrum (400 MHz) of **8** in C_6D_6 with trimethoxy benzene internal standard.

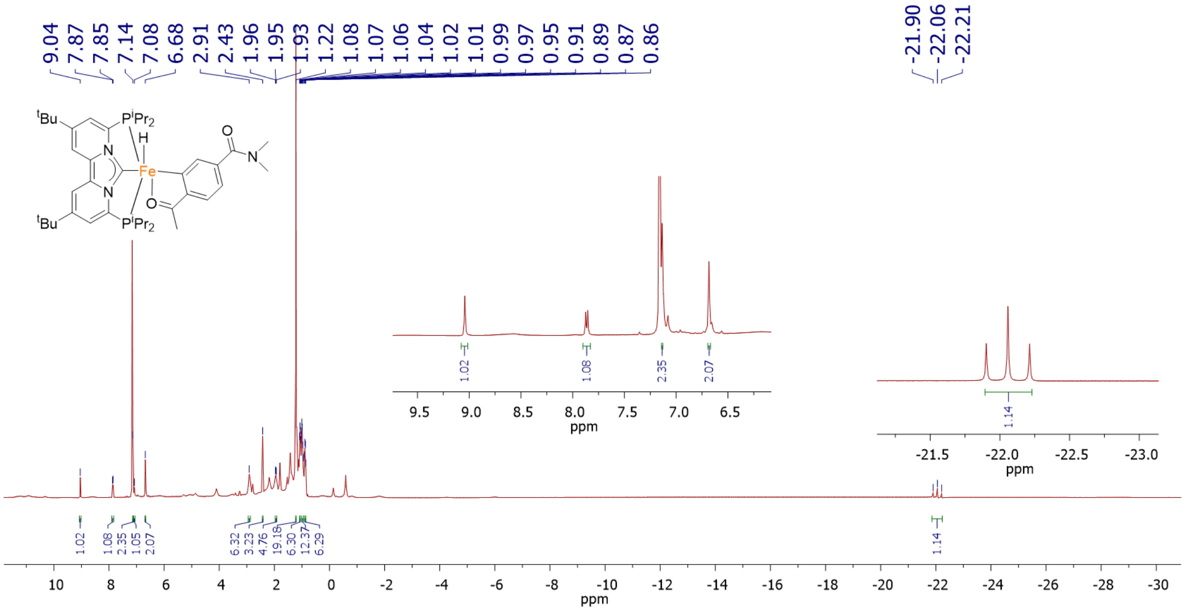
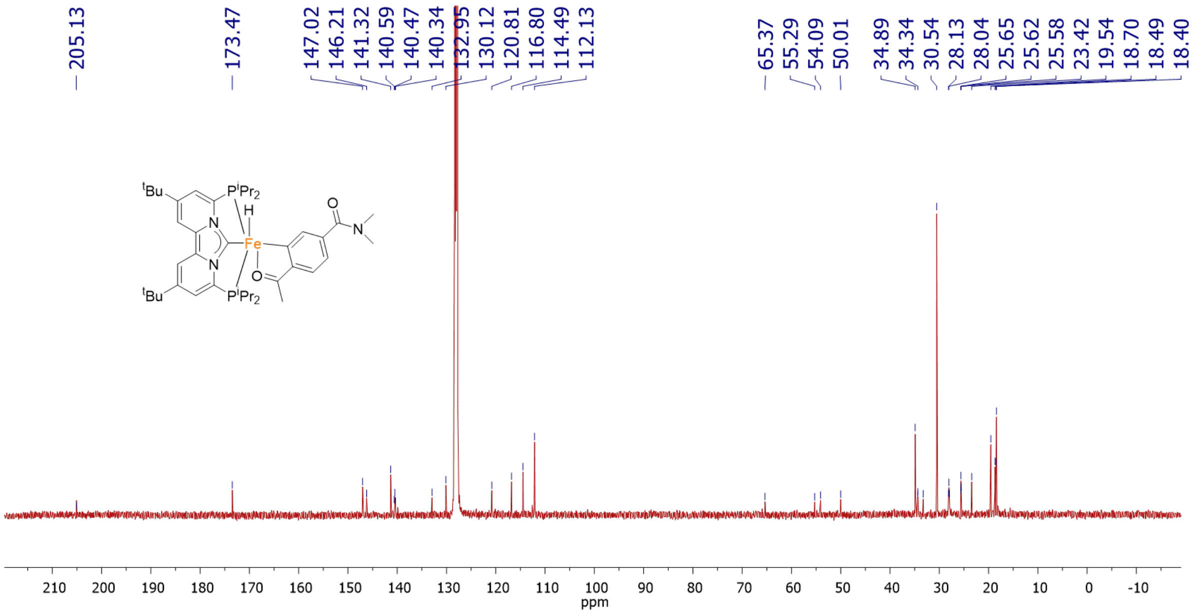


Figure S35. ^{1}H NMR spectrum (400 MHz) of **8** in C_6D_6.

Figure S36. $^{13}C\ \{^1H\}$ NMR spectrum (101 MHz) of **8** in C_6D_6.



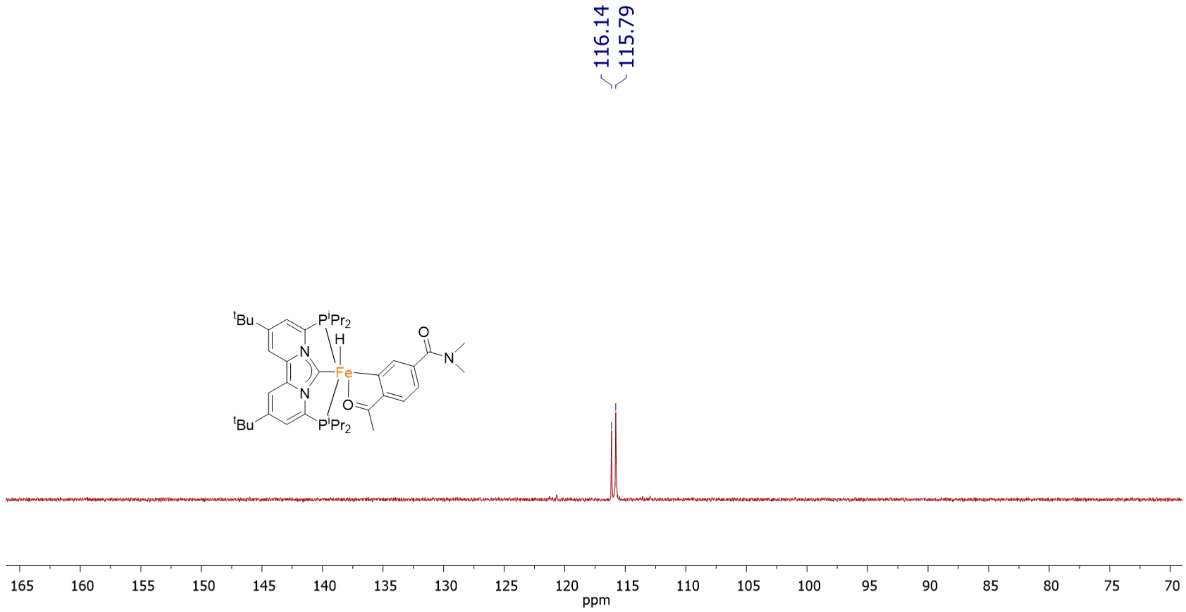


Figure S37. $^{31}P\ \{^1H\}$ NMR spectrum (162 MHz) of **8** in C_6D_6.

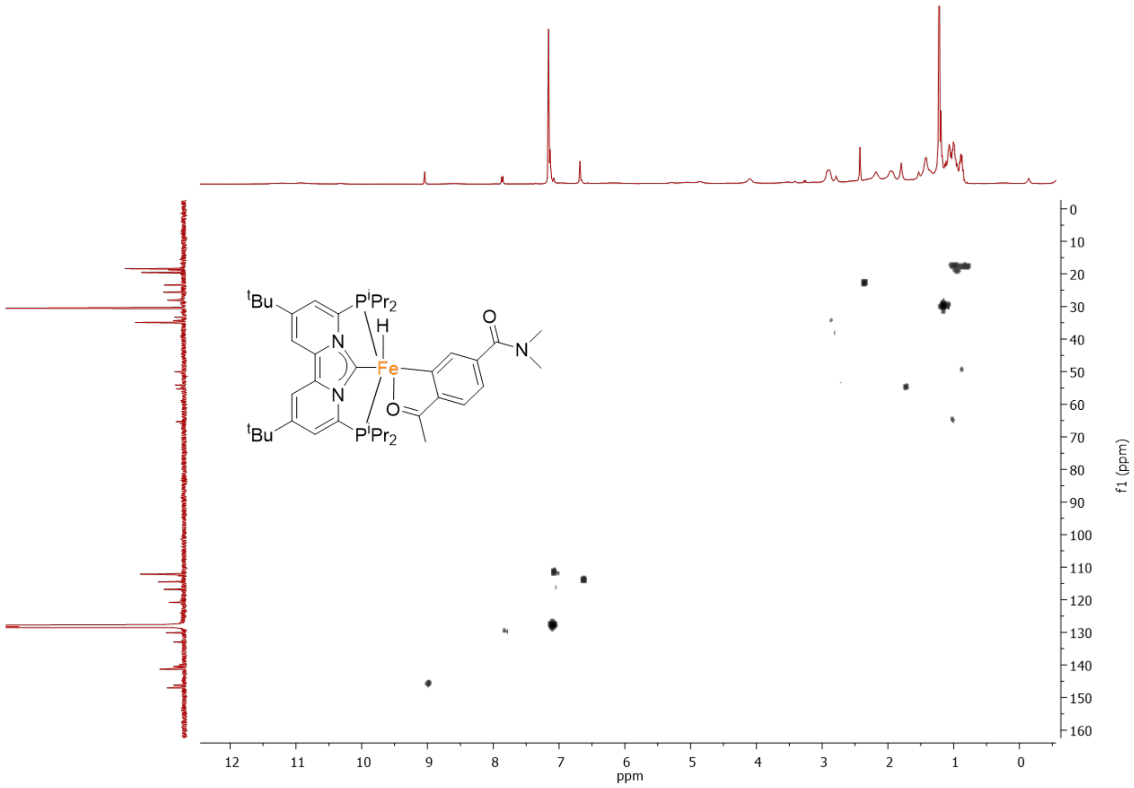


Figure S38. HMQC NMR spectrum (400 MHz) of **8** in C_6D_6.

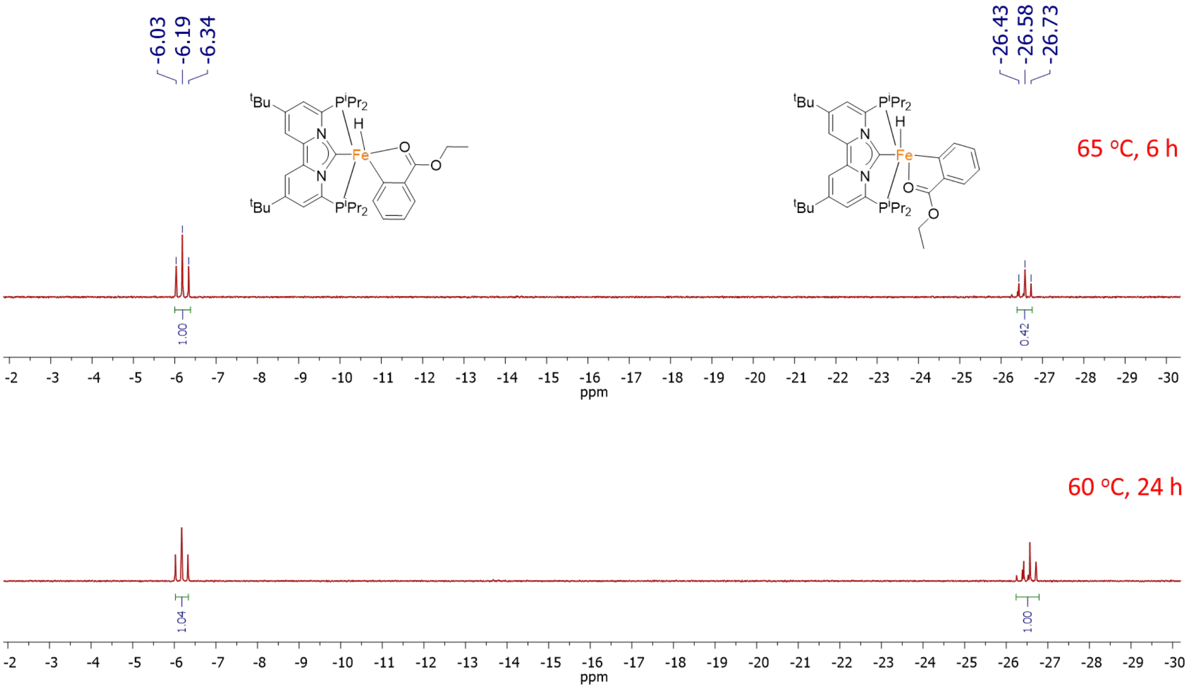


Figure S39. Hydride region of ^{1}H NMR spectrum (400 MHz) of reaction of complex **1** with ethyl benzoate in C_6D_6 at 60 °C and at 65 °C.

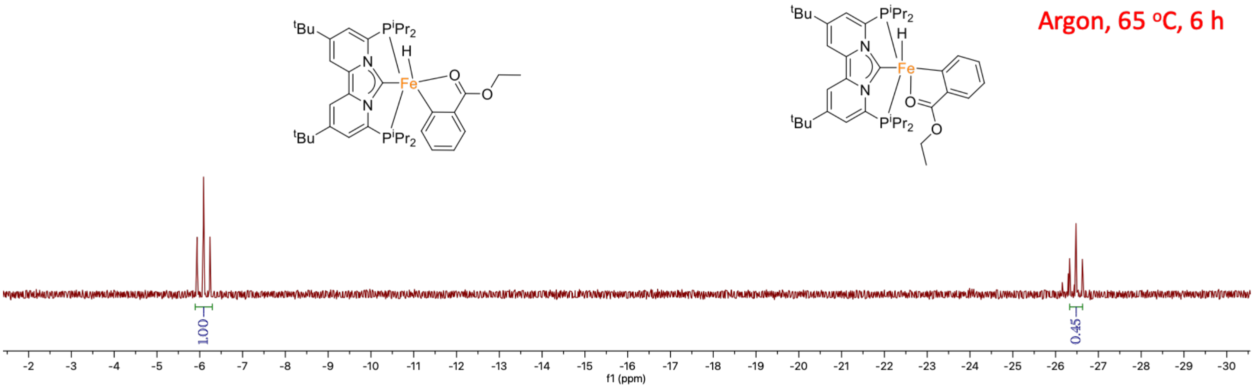


Figure S40. Hydride region of ^{1}H NMR spectrum (400 MHz) of reaction of complex **1** with ethyl benzoate in C_6D_6 at 65 °C under an argon atmosphere.

Synthesis of 4 in argon atmosphere. In the Argon glovebox, to a stirred solution of complex $[(PC_{NHC}P)Fe(N_2)_2]$ (**1**) (6.2 mg, 0.01 mmol) in benzene-*d6* (500 µL) was added ethyl benzoate (1.4 µL, 0.01 mmol). The resulting reaction was transferred to J-Young tube and heated at 65 °C for 6 h. The mixture turned into brown-purple solution, where after all volatiles were removed under reduced pressure. Hereafter the crude solid was re-dissolved in pentane (5 mL) and filtered through a pad of Celite under nitrogen atmosphere. Next, the pentane was removed under reduced pressure and the title compound was obtained as brown-purple powder. The ratio of cis and trans isomers are similar to observed under nitrogen atmosphere. **^{1}H NMR (400 MHz, C_6D_6)**: δ (ppm) Hydride region -6.19 (t, *J* = 60.5 Hz, 1H, Fe-*H*) (major), -26.58 (t, *J* = 59.5 Hz, 0.43H, Fe-*H*) (minor). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)**: δ (ppm) 109.22 (major), 114.61, 114.42 (minor).

X-Ray Crystallography

Special Refinement Details for complex 3. Compound **3** crystallizes in the monoclinic space group *P2₁/c* with one molecule in the asymmetric unit No further special refinement conditions were necessary.

Special Refinement Details for complex 5. Compound **5** crystallizes in the monoclinic space group *P2₁/m* with one molecule in the asymmetric unit together with one diethyl ether molecule. The molecule is located on a special position (mirror plane) along the C1-Fe1-O1 axis, resulting in a slight disorder of the ethyl substituent of the ester. No further special refinement conditions were necessary.

Tables

Table S1. Crystal and refinement data for iron complexes 3 and 5

	Complex **3**	Complex **5**
CCDC	2171822	2171821
Empirical formula	$C_{39}H_{57}FFeN_2OP_2$	$C_{44}H_{69}FFeN_2O_3P_2$
Formula weight (g/mol)	706.65	810.80
T (K)	100.15	100.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
a (Å)	12.662(3)	11.180(4)
b (Å)	28.146(6)	14.559(5)
c (Å)	11.750(3)	13.993(5)
α (deg)	90	90
β (deg)	110.244(6)	93.347(9)
γ (deg)	90	90
V ($Å^3$)	3928.8(15)	2273.7(13)
Z	4	2
Cryst. syst.	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/m$
ρ_{calc} (g/cm^3)	1.195	1.184
2 σ range (deg)	3.428 to 48.422	2.916 to 50.68
Crystal size/mm	0.18 × 0.12 × 0.09	0.15 × 0.15 × 0.12
μ (mm^{-1})	0.501	0.444
GOF	0.985	1.030
R1, wR_2 (I> 2σ (I))	$R_1 = 0.0592$, $wR_2 = 0.1211$	$R_1 = 0.0518$, $wR_2 = 0.1239$

Table S2. Selected bond angles and distances for complexes 3 and 5.

Bond Distances (Å)	**M = Fe**			
	2 (calc.)	**3 (exp.)**	**4 (calc.)**	**5 (exp.)**
Fe–C1	1.860	1.861(5)	1.803	1.806(4)
Fe–C17	1.931	1.958(6)	1.959	1.962(5)
Fe–P1	2.269	2.215(1)	2.276	2.221(1)
Fe–P2	2.269	2.206(1)	2.276	2.221(1)
Fe–O1	2.035	2.050(4)	2.069	2.083(3)
Fe–H1	1.521	1.50(5)	1.569	1.51
Bond Angles (°)				
O1–Fe–C17	81.07	80.2(2)	81.61	80.94(16)
C1–Fe–P1	81.87	80.50(1)	82.33	80.94(3)
C1–Fe–P2	81.87	95.40(1)	82.33	80.94(3)
P1–Fe–P2	163.29	160.87(6)	163.55	153.38(6)
C1–Fe–H1	79.41	97.0(2)	97.28	98.0(1)

Table S3. SMD-(benzene)-PBE0-D3BJ/SDB-cc-pVTZ//PBE0-D3BJ/SDD Gibbs free potential energy surfaces at 298 K for the cis and trans C–H bond insertions (in kcal mol^{-1}). Absolute energies in Hartree are given in Parentheses.

Complex	***I***	***II***
Fe-N2	0.0 (-2383.945465)	0.0 (-2459.110290)
Fe	0.8 (-2274.498290)	–12.5 (-2349.684398)
cis-A	17.7 (-2274.471448)	11.5 (-2349.646156)
cis-TS	18.2 (-2274.470538)	14.1 (-2349.641986)
cis	–8.5 (-2274.513134)	–16.9 (-2349.691368)
trans-A	20.3 (-2274.467178)	13.9[a] (-2349.642197)
trans-TS	23.6 (-2274.462022)	13.4[a] (-2349.643038)
trans-B	0.3 (-2274.499045)	–4.6 (-2349.671759)
trans	–19.1 (-2274.530072)	–21.9 (-2349.699294)

[a] Note that on the SMD(benzene)-PBE0-D3BJ/SDB-cc-pVTZ Gibbs free-energy surface, the intermediate (*trans*-A) lies 0.5 kcal mol^{-1} above the transition structure (*trans*-TS). However, at the PBE0-D3BJ/SDD level of theory at which the geometries were optimized, *trans*-A lies 9.8 kJ kcal mol^{-1} below *trans*-TS on the Gibbs free-energy surface.

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