Supporting Information

Cleavage of an Aryl Carbon-Nitrogen Bond of a PhosphazidoIron(II) Complex Promoted by Hydride Metathesis

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Contents:

Experimental Section

General Considerations:

All manipulations were performed under an atmosphere of dry and oxygen-free dinitrogen (N_2) by means of standard Schlenk or glovebox techniques. Anhydrous THF, toluene, Et_2O and hexanes were purchased from Aldrich, sparged with N_2 and dried further by passage through towers containing activated alumina and molecular sieves. Benzene-d_6 was refluxed over sodium, vacuum transferred and freeze-pump-thaw degassed.^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AV-300 MHz spectrometer, Bruker AV-400 MHz spectrometer, or a Bruker AV-600 MHz spectrometer. Unless noted otherwise, all spectra were recorded at room temperature. ^{1}H NMR spectra were referenced to residual proton signal in C_6D_6 (7.16 ppm), d_8-toluene (2.08 ppm) or d_8-THF (1.72 ppm); ^{31}P NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm); ^{13}C NMR spectra were referenced to the solvent resonance of C_6D_6 (128.0 ppm), d_8-toluene (20.43 ppm), or d_8-THF (25.31 ppm). Microanalyses (C, H, N) were performed at the Department of Chemistry at the University of British Columbia. Gas chromatography and mass spectrometry were performed on an Agilent 6890N GC coupled with a 5975B MS detector. Liquid samples were injected using a split ratio of 50:1 and helium as the carrier gas. Samples where THF was the solvent were heated to 200 °C from an initial temperature of 40 °C using a ramp rate of 30 °C/min. In the case where toluene was the solvent for GC-MS samples, the initial temperature was 60 °C, the ramp rate was 30 °/min and the final temperature was 200 °C.

Suitable single crystals were selected in a glovebox, coated in Fomblin oil and mounted on a glass loop. X-ray data were collected on a Bruker X8 Apex II diffractometer with a graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at a temperature of 90 K. Data were collected and integrated using the Bruker SAINT software package.[1] Absorption corrections were performed using the multiscan technique (SADABS).[2] All structures were solved by direct methods and refined using the Olex2 (version 1.2.5) software package[3] and the ShelXL refinement program.[4] All non-hydrogen atoms were refined anisotropically. ORTEPs were generated using ORTEP-3 (version 2.02).[5]

^{57}Fe Mössbauer spectra were recorded using a W.E.B. Research Mössbauer spectroscopy system at room temperature. A ^{57}Co (in rhodium matrix) source with a strength of ~25 mCi was used. The detector was a Reuters-Stokes Kr/CO_2 proportional counter. The sample powders were loaded in a high-density polyethylene flat washer wrapped in parafilm and secured with Kapton tape. The sample chamber was evacuated to -28" Hg and back filled to -25" Hg with He. The velocity was scanned between 4 and −4 mms^{-1} using a constant acceleration triangle waveform, and calibrated against an Fe foil measured at 295 K in zero magnetic field. [FeBr(NpN$_3^{iPr,Me}$)(THF)] and [Fe$_2$(NpN')$_2$] were measured for 480h and 17h respectively. All isomer shifts (δ) are relative to Fe foil. Fitting of the data was performed using WMOSS software, which is available free of charge at http://wmoss.org/.

2,6-dimethylphenylazide was prepared according to literature procedures.[6,7] The starting phosphine-imines **1** was prepared by slight modifications of published procedures.[8,9] Potassium hydride (30 wt% dispersion in mineral oil) was purchased from Sigma-Aldrich and was washed with hexanes on a glass frit and handled within a glovebox as a dry powder. Dibromobis(tetrahydrofuran)iron(II) was prepared according to an established procedure.[10]

Potassium triethylborohydride was purchased from Aldrich as a 1.0 M solution and was dried and stored as a solid. Potassium triethylborodeuteride was synthesized from potassium deuteride and triethylborane in toluene and was stored as a solid. Potassium deuteride was synthesized according to a literature procedure, with the modification of D_2 gas being used in place of H_2 gas.[11] All other compounds were purchased from commercial suppliers and used as received.

$\mathbf{HNpN_3^{\mathit{i}Pr,Me}}$ (2)

2,6-Dimethylphenylazide (532 mg, 3.61 mmol) was added to a 10 mL THF solution of 2,6-diisopropyl-*N*-(2-diisopropylphosphinocyclopentylidene)aniline **1** (1.181 g, 3.28 mmol). The resulting mixture was stirred at room temperature overnight. After removal of the volatiles under vacuum, the resulting viscous oil was redissolved in hexanes (2 mL) and was stored at -35 °C. The desired compound was yielded as colorless crystals (1.648 g, 3.25 mmol, 99 %)

$^1H\{^{31}P\}$ NMR (300 MHz, benzene-d_6, 298 K): δ 1.02 (d, 6H, $^3J_{HH}$=7.2 Hz, NAr-^{i}PrCH_3), 1.14 (d, 6H, $^3J_{HH}$=7.0 Hz, NAr-^{i}PrCH_3), 1.24-1.28 (m, 12H, P-^{i}PrCH_3), 1.55 (quin, 2H, $^3J_{HH}$=6.8 Hz $CH_2CH_2CH_2$), 2.07 (t, 2H, $^3J_{HH}$=7.5 Hz, $^iPr_2PCCH_2$), 2.16-2.28 (m, 4H), 2.38 (s, 6H, NAr-CH_3), 3.43 (sept, 2H, $^3J_{HH}$=6.9 Hz, NAr-^{i}PrC*H*), 6.97-7.22 (m, overlap with residual solvent peak, Ar-*H*), 10.88 (s, 1H, N*H*).

$^{13}C\{^1H\}$ NMR (75 MHz, benzene-d_6, 298 K): δ 15.9 (d, 2 Hz), 16.6 (d, 2 Hz), 19.5, 23.0, 23.9 (d, 9 Hz), 24.4, 25.1, 25.3, 29.4, 33.5 (d, 14 Hz), 34.8 (d, 14 Hz), 71.6 (d, 114 Hz), 123.9, 124.6, 128.0, 128.9, 130.6, 137.6, 147.6, 152.7, 168.9 (d, 6 Hz).

$^{31}P\{^1H\}$ NMR (121 MHz, benzene-d_6, 298 K): δ 50.90 (s).

Anal. Calcd for $C_{31}H_{47}N_4P$: C, 73.48; H, 9.35; N, 11.06. Found: C, 73.62; H, 9.30; N, 11.29.

HNpN^{iPr,Me} (3)

HNpN$_3$^{iPr,Me} (100 mg, 0.197 mmol) was dissolved in toluene (10 mL) and was heated to 80 °C for 1 day. The solvent was removed in vacuo, yielding off-white solid. The solids were dissolved in *n*-pentane (1 mL) and were stored at -35 °C. The desired compound was yielded as colorless crystals (85 mg, 0.177 mmol, 90.0 %).

^{1}H NMR (400 MHz, benzene-d_6, 298 K): δ 1.08 (d, 6H, $^3J_{HH}$=6.8 Hz, NAr-^{i}PrC*H*$_3$), 1.15 (d, 6H, $^3J_{HH}$=7.2 Hz), 1.20 (d, 6H, $^3J_{HH}$=7.1 Hz), 1.26 (d, 6H, $^3J_{HH}$=6.9 Hz, NAr-^{i}PrC*H*$_3$), 1.62 (quin, 2H, $^3J_{HH}$=7.2 Hz, CH$_2$C*H*$_2$CH$_2$), 2.08-2.17 (m, 4H), 2.32 (t, 2H, $^3J_{HH}$=6.5 Hz, ArNCC*H*$_2$), 2.60 (s, 6H, NAr-C*H*$_3$), 3.50 (sept, 2H, $^3J_{HH}$=6.8 Hz, NAr-^{i}PrC*H*), 6.87 (t, 1H, $^3J_{HH}$=7.3 Hz, Ar*H*), 7.08 (d, 2H, $^3J_{HH}$=7.7 Hz, Ar*H*), 7.19 (d, 3H, $^3J_{HH}$=7.4 Hz, Ar*H*), 9.10 (s, 1H, N*H*).

^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, 298 K): δ 16.6 (d, J_{PC}=3 Hz), 17.5 (d, J_{PC}=2 Hz), 21.3, 23.1 (d, J_{PC}=10 Hz), 23.3, 25.1, 28.4, 29.0, 29.6, 34.3 (d, J_{PC}=13 Hz), 34.6 (d, J_{PC}=13 Hz), 84.7 (d, J_{PC}=112 Hz), 118.4, 123.6, 127.4, 128.5, 131.8 (d, J_{PC}=7 Hz), 136.8, 147.3, 149.4 (d, J_{PC}=3 Hz), 164.2 (d, J_{PC}=4 Hz).

^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 298 K): δ 18.28 (s).

Anal. Calcd for $C_{31}H_{47}N_2P$: C, 77.78; H, 9.90; N, 5.85. Found: C, 78.15; H, 10.50; N, 5.98.

[K(NpN$_3$^{iPr,Me})(THF)] (4)

A 10mL THF solution of H**NpN$_3$^{iPr,Me}** (1.648 g, 3.25 mmol) was added to potassium hydride (143 mg, 3.58 mmol). The resulting suspension was stirred at room temperature overnight. When the reaction was complete, the dark yellow solution was filtered through celite to remove excess potassium hydride. The volatiles were removed in vacuo, yielding bright yellow solid. (1.780 g, 2.88 mmol, 88.7%.) Yellow single crystals of (K[**NpN$_3$**$^{\textbf{\textit{i}Pr,Me}}$]•2THF)$_n$ suitable for X-ray diffraction were grown from a THF solution cooled to -35°C.

^{1}H{^{31}P} NMR (300 MHz, benzene-*d*$_6$, 298 K): δ 1.03 (d, 6H, ^{3}J$_{HH}$=6.9 Hz, NAr-^{i}PrC*H*$_3$), 1.20-1.25 (m, 12H, P-^{i}PrC*H*$_3$), 1.34 (d, 6H, ^{3}J$_{HH}$=6.9 Hz, NAr-^{i}PrC*H*$_3$), 1.41-1.45 (m, 4H, THF-C*H*$_2${3,4}), 1.91 (quin, 2H, ^{3}J$_{HH}$=7.1 Hz, CH$_2$C*H*$_2$CH$_2$), 2.30 (t, 2H, ^{3}J$_{HH}$=7.3 Hz, ^{i}Pr$_2$PCC*H*$_2$), 2.35 (s, 6H, NAr-C*H*$_3$), 2.49 (sept, 2H, ^{3}J$_{HH}$=7.1 Hz, P-^{i}PrC*H*), 2.66 (t, 2H, ^{3}J$_{HH}$=6.5 Hz, ArNCC*H*$_2$), 3.38 (sept, 2H, ^{3}J$_{HH}$=6.9 Hz, NAr-^{i}PrC*H*), 3.51-3.56 (m, 4H, THF-C*H*$_2${2,5}), 7.02-7.09 (m, 2H, Ar-*H*), 7.14-7.20 (m, overlap with residual solvent peak).

^{13}C{^{1}H} NMR (75 MHz, benzene-*d*$_6$, 298 K): δ 16.6, 17.2 , 19.9, 24.5 (d, J$_{PC}$=21 Hz), 25.0, 25.7 (THF-*C*H$_2${3,4}), 25.9, 27.5, 34.3 (d, J$_{PC}$=16 Hz), 36.6 (d, J$_{PC}$=15 Hz), 50.9 (d, J$_{PC}$=125 Hz), 67.7 (THF- *C*H$_2${2,5}), 120.8, 123.3, 124.1, 128.9, 130.4, 141.2, 151.8, 152.7, 175.5 (d, J$_{PC}$=9 Hz).

^{31}P{^{1}H} NMR (121 MHz, benzene-*d*$_6$, 298 K): δ 44.18 (s).

Anal. Calcd for $C_{35}H_{54}KN_4OP$: C, 68.14; H, 8.82; N, 9.08. Found: C, 68.10; H, 8.99; N, 9.25.

[FeBr(NpN$_3$$^{\textit{i}\text{Pr,Me}}$)(THF)] (5)

A 10mL diethyl ether solution of [K(**NpN$_3$**$^{\textbf{\textit{i}Pr,Me}}$)(THF)] (1.728 g, 2.80 mmol) was added to FeBr$_2$(THF)$_2$ (1.008, 2.80 mmol) and the reaction mixture was stirred at room temperature overnight. The resulting suspension consisted of gray precipitate and blood red supernatant. The suspension was filtered through celite to remove KBr and the filtrate was concentrated to a volume of approximately 1mL before being cooled to -35 °C for 3 hours.

[FeBr(**NpN$_3$^{iPr,Me}**)(THF)] was yielded as orange crystals, which were collected on a glass frit and were dried in vacuo (567 mg, 0.795 mmol, 28.4 %).

^{1}H NMR (300 MHz, *d*$_6$-benzene, 298 K): δ -34.94, -14.91, -7.06, -4.32, 4.04, 5.21, 8.54, 11.37, 12.33, 17.41, 17.60, 26.08, 101.73.

$\mu_{\text{eff}} = 4.8\mu_{\text{B}}$ (Evans).

Anal. Calcd for $C_{35}H_{54}BrFeN_4OP$: C, 58.91; H, 7.63; N, 7.85. Found: C, 58.65; H, 7.62; N, 7.72.

[Fe$_2$(NpN')$_2$] (6)

Potassium triethylborohydride (111 mg, 0.807 mmol) was added to a 10 mL toluene solution of [FeBr(**NpN$_3$^{iPr,Me}**)(THF)] (524 mg, 0.734 mmol) while the solution was vigorously stirred at room temperature. The solution immediately changed from bright orange to dark brown and was stirred for 1 hour. The supernatant was then filtered through celite and the volatiles were removed in vacuo. The resulting dark brown powder was rinsed with *n*-pentane until a fine yellow powder was obtained, which was dried in vacuo (51 mg, 0.059 mmol, 16.2 %). Single crystals of [Fe$_2$(**NpN'**)$_2$] suitable for X-ray diffraction were grown from a toluene/*n*-pentane solution cooled to -35 °C.

^{1}H{^{31}P} NMR (300 MHz, benzene-*d*$_6$, 298 K): δ -3.02, 1.29, 1.44, 2.02, 3.00, 3.87, 4.45, 5.35, 8.35, 8.38, 9.69, 12.27.

$\mu_{\text{eff}} = 3.1\mu_{\text{B}}$ (Evans).

Anal. Calcd for $C_{46}H_{74}Fe_2N_4P_2$: C, 64.49; H, 8.71; N, 6.54. Found: C, 64.56; H, 8.71; N, 6.84.

$[Fe_2(NpN')_2]$ alternate synthesis in THF

Potassium triethylborohydride (15 mg, 0.112 mmol) was dissolved in 5 mL of THF and was added dropwise to a stirred 5 mL THF solution of $[FeBr(NpN_3^{iPr,Me})(THF)]$ (80 mg, 0.112 mmol). The color of the solution immediately changed from bright orange to dark brown. The reaction mixture was allowed to stir for 30 minutes before the volatiles were removed under vacuum. The resulting brown residue was then extracted in toluene and was filtered through celite. The toluene was removed in vacuo and the dark brown solids were rinsed with *n*-pentane. The supernatant was decanted away, yielding a yellowish-tan powder which was dried under vacuum (11 mg, 0.013 mmol, 23% yield).

General radical trapping procedure

An apparatus consisting of two Kontes-sealed glass bulbs (10 mL and 25 mL in volume) joined together by a Kontes-sealed glass bridge was used in all radical trapping experiments (See Figure S20 in SI). Addition of reagents to the apparatus occurred within a N_2-filled glovebox. To the 10 mL bulb of the apparatus was added a micro stir bar (10 x 3 mm) and a 1 mL solution of $[FeBr(NpN_3^{iPr,Me})(THF)]$ in the solvent under investigation. The Kontes seals for both the empty 25 mL bulb and the bridge connecting the two bulbs were closed. A stoichiometric amount of potassium triethylborohydride was dissolved in 1 mL of the same solvent under investigation and was added dropwise to the solution of $[FeBr(NpN_3^{iPr,Me})(THF)]$ while stirring. The opening to the 10 mL bulb was sealed after the addition was complete. The solution color immediately changed from bright orange to dark brown, regardless of the solvent employed. After stirring for 30 minutes, the apparatus was removed from the glovebox and the 25 mL bulb was exposed to vacuum. The evacuated bulb was cooled using liquid N_2 before closing the seal to the 25 mL bulb. The Kontes seal on the bridge connecting the two glass bulbs was then opened, and the solvent in the 10 mL reaction bulb was condensed into the cooled, evacuated bulb. After the transfer was complete, the seal on the bridge was closed and the 25 mL bulb containing the reaction solvent was allowed to warm to room temperature. The solvent was removed from the bulb in air and was analyzed by GC-MS and NMR (if a deuterated solvent was investigated).

X-ray crystallographic data and collection parameters

Table 1: Crystal data and structure refinement for **2**

Identification code	mo_mf936_0m	
Empirical formula	$C_{31}H_{47}N_4P$	
Formula weight	506.70	
Temperature	90K	
Crystal size	0.3 × 0.2 × 0.15 mm^3	
Radiation	MoKα (λ = 0.71069 Å)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a=8.4137(10) Å	α=68.433(2)°
	b= 12.3149(14) Å	β= 80.379(2)°
	c= 16.0458(19) Å	γ= 83.219(3)°
Volume	1521.5(3) $Å^3$	
Z	2	
Density (calculated)	1.106 g/cm^3	
Absorption Coefficient	0.115 mm^{-1}	
F(000)	552.0	
2θ range for data collection	2.76 to 59.42°	
Index ranges	$-7 \leq h \leq 11$, $-16 \leq k \leq 17$, $-22 \leq l \leq 22$	
Reflections collected	32276	
Independent reflections	8629 [R_{int} = 0.0207, R_{sigma} = 0.0199]	
Data/restraints/parameters	8629/0/339	
Completeness to θ	99.7%	
Goodness-of-fit on F^2	1.032	
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0976	
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1026	
Largest diff. peak/hole	0.61/-0.27 $eÅ^{-3}$	

Table 2: Crystal data and structure refinement for **4**

Identification code	mo_mf941_0m	
Empirical formula	$C_{19.5}H_{31}K_{0.5}N_2OP_{0.5}$	
Formula weight	344.50	
Temperature	90K	
Crystal size	0.31 × 0.26 × 0.19 mm^3	
Radiation	MoKα (λ = 0.71069 Å)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a= 9.742(2) Å	α= 74.814(5)°
	b= 10.616(2) Å	β= 79.099(5)°
	c= 19.454(5) Å	γ= 84.049(5)°
Volume	1903.6(8) $Å^3$	
Z	4	
Density (calculated)	1.202 g/cm^3	
Absorption Coefficient	0.220 mm^{-1}	
F(000)	748.0	
2θ range for data collection	3.982 to 61.088°	
Index ranges	$-13 \leq h \leq 13, -15 \leq k \leq 15, -27 \leq l \leq 25$	
Reflections collected	39455	
Independent reflections	11257 [R_{int} = 0.0302, R_{sigma} = 0.0353]	
Data/restraints/parameters	11257/0/434	
Completeness to θ	96.6%	
Goodness-of-fit on F^2	1.207	
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1580	
Final R indexes [all data]	R_1 = 0.0765, wR_2 = 0.1637	
Largest diff. peak/hole	0.92/-0.39 $eÅ^{-3}$	

Table 3: Crystal data and structure refinement for **5**

Identification code	mf966test
Empirical formula	$C_{35}H_{54}BrFeN_4OP$
Formula weight	713.55
Temperature	90K
Crystal size	0.28 × 0.25 × 0.09 mm^3
Radiation	MoKα ($\lambda = 0.71069$)
Crystal system	orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a=17.547(5) Å α=90.000˚
	b=10.262(5) Å β=90.000˚
	c=20.588(5) Å γ=90.000˚
Volume	3707(2) $Å^3$
Z	4
Density (calculated)	1.278 g/cm^3
Absorption Coefficient	1.559 mm^{-1}
F(000)	1504.0
2θ range for data collection	3.956 to 46.666˚
Index ranges	$-19 \leq h \leq 16$, $-11 \leq k \leq 10$, $-19 \leq l \leq 22$
Reflections collected	11758
Independent reflections	5063 [$R_{int} = 0.0558$, $R_{sigma} = 0.0794$]
Data/restraints/parameters	5063/109/349
Completeness to θ	99.2%
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	$R_1 = 0.0472$, $wR_2 = 0.1015$
Final R indexes [all data]	$R_1 = 0.0712$, $wR_2 = 0.1105$
Largest diff. peak/hole	0.63/-0.55 $eÅ^{-3}$
Flack parameter	0.020(11)

Table 4: Crystal data and structure refinement for **6**

Identification code	mf933	
Empirical formula	$C_{23}H_{37}FeN_2P$	
Formula weight	428.36	
Temperature	90K	
Crystal size	0.35 × 0.34 × 0.19 mm^3	
Radiation	MoKα (λ = 0.71069 Å)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a= 8.526(3) Å	α= 69.55(2)°
	b= 11.951(3) Å	β= 87.64(3)°
	c= 12.272(4) Å	γ= 80.07(3)°
Volume	1153.8(6) Å^3	
Z	2	
Density (calculated)	1.233 g/cm^3	
Absorption Coefficient	0.733 mm^{-1}	
F(000)	460.0	
2θ range for data collection	3.542 to 60.168°	
Index ranges	$-12 \le h \le 11$, $-16 \le k \le 16$, $-17 \le l \le 17$	
Reflections collected	26609	
Independent reflections	6724 [R_{int} = 0.0208, R_{sigma} = 0.0194]	
Data/restraints/parameters	6724/0/244	
Completeness to θ	99.4%	
Goodness-of-fit on F^2	1.050	
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0795	
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.0852	
Largest diff. peak/hole	0.58/-0.23 eÅ^{-3}	

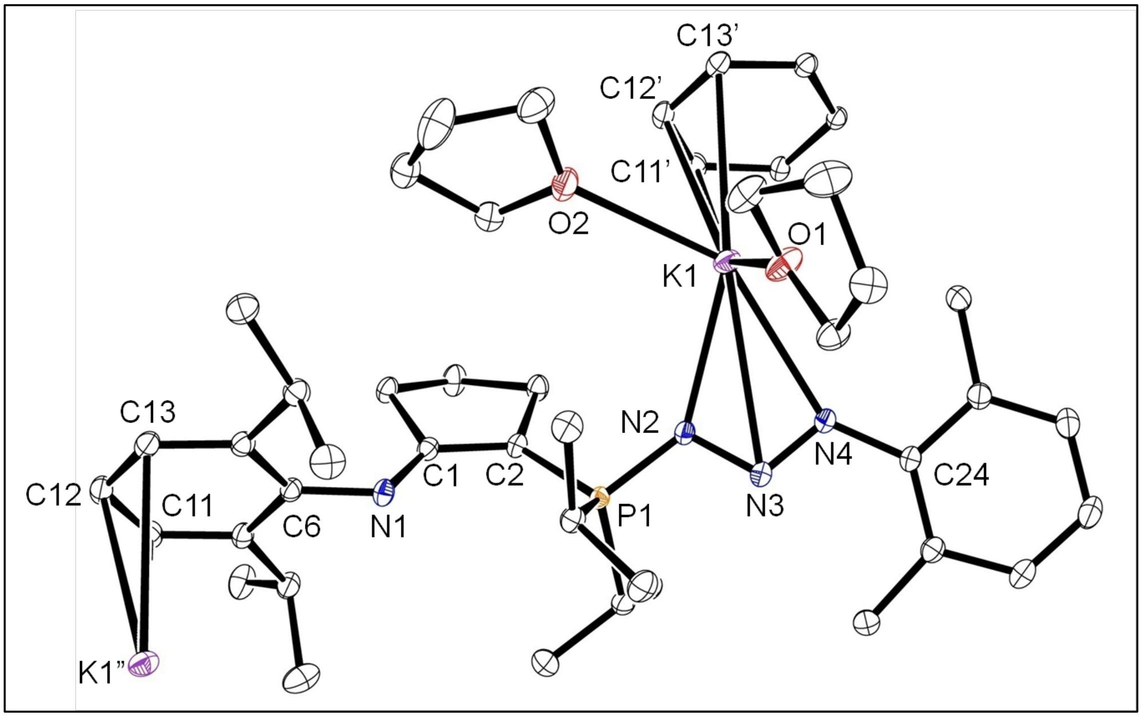

Figure S1: ORTEP drawing of the solid-state molecular structure of **4** (ellipsoids at 50% probability level).All hydrogen atoms have been omitted for clarity. Selected bond length (A□), angles (deg), and torsion angles (deg): K1-N2: 2.715(2), K1-N3: 3.288(2), K1-N4: 2.860(2), K1-O1: 2.675(2), K1-O2: 2.860(2), K1-C13’: 3.228(3), K1-C12’: 3.107(3), K1-C11’: 3.257(3), N1-C1: 1.320(3), C1-C2: 1.405(3), C2-P1: 1.729(2), P1-N2: 1.660(2), N2-N3: 1.342(3), N3-N4: 1.276(3), C6-N1-C1: 120.5(2), N1-C1-C2: 128.4(2), C1-C2-P1: 128.0(2), C2-P1-N2: 105.5(1), P1-N2-N3: 112.5(2), N2-N3-N4: 111.3(2), C6-N1-C1-C2: 178.7(2), N1-C1-C2-P1: 0.8(4), C1-C2-P1-N2: 149.2(2), P1-N2-N3-N4: 173.4(2).

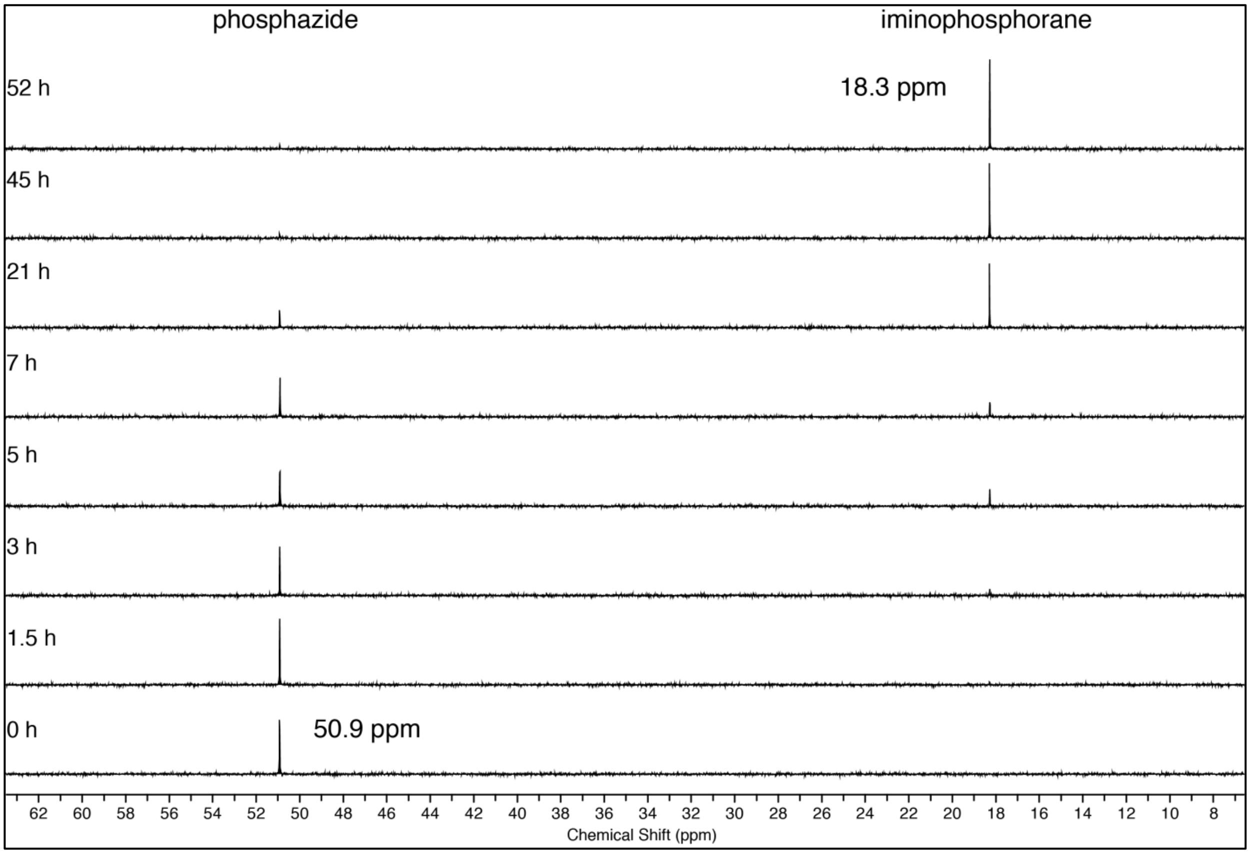

Figure S2: 121.5 MHz $^{31}P\{^1H\}$-NMR spectroscopic monitoring of the conversion of **2** to **3** in benzene-d_6 at 24 °C. (The synthesis of **3** was performed at 80 °C).

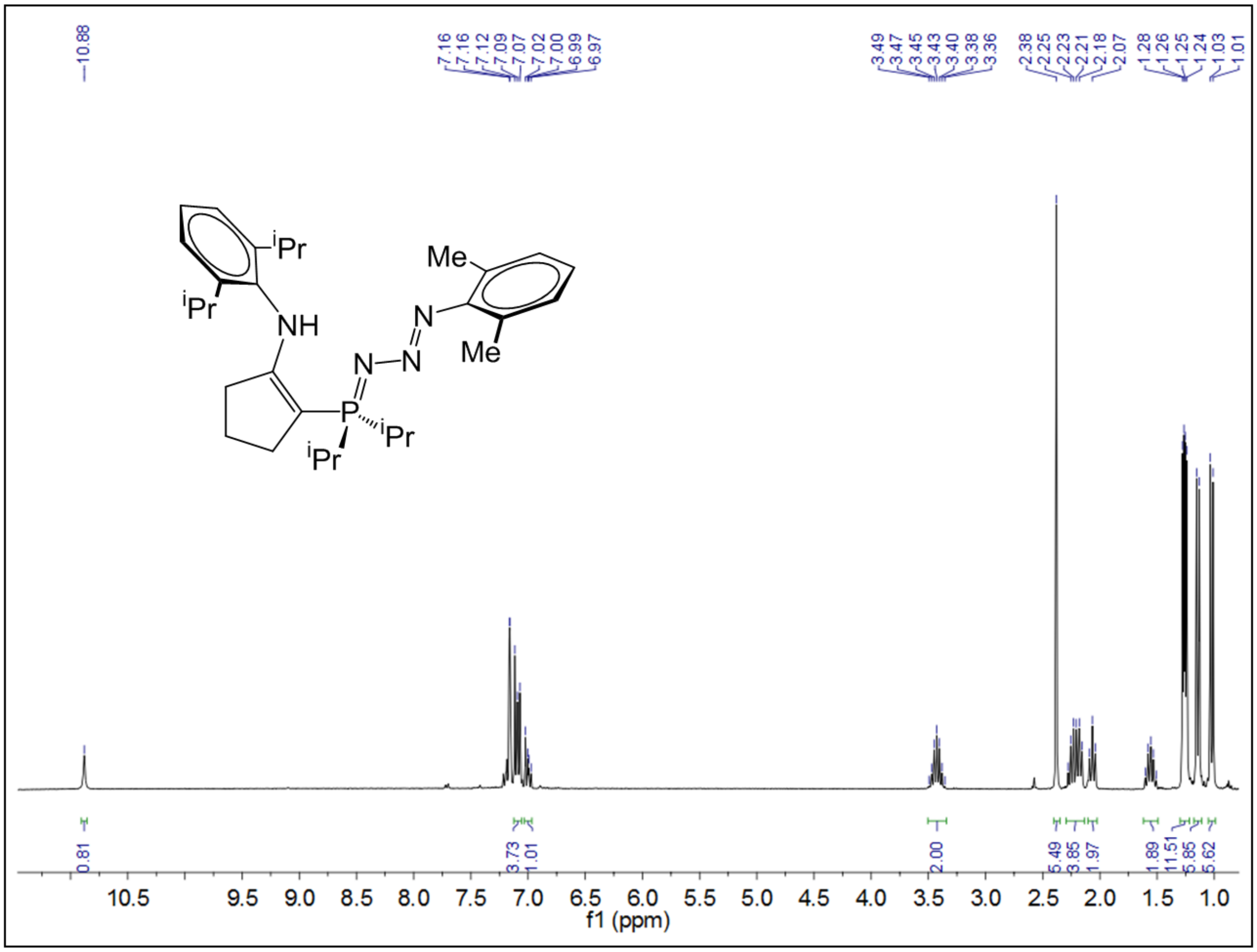

Figure S3: ^{1}H{^{31}P} NMR spectrum of **2** (H_NpN$_3^{i\mathrm{Pr,Me}}$) (300 MHz, d_6-benzene, 298 K).

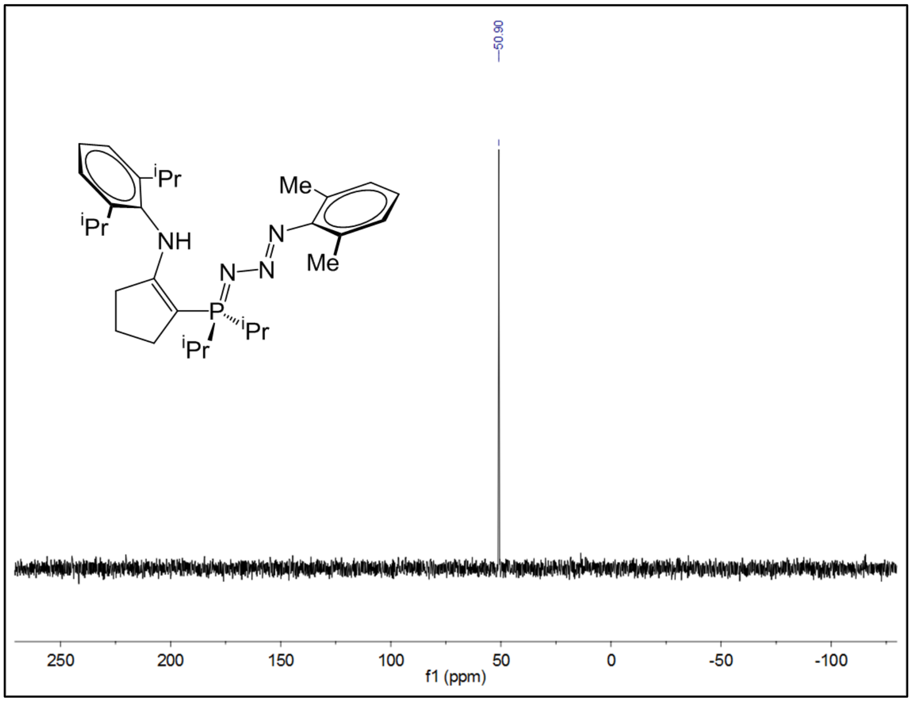

Figure S4: $^{31}P\{^1H\}$ NMR spectrum of **2** (H_NpN$_3^{iPr,Me}$) (121 MHz, d_6-benzene, 298 K).

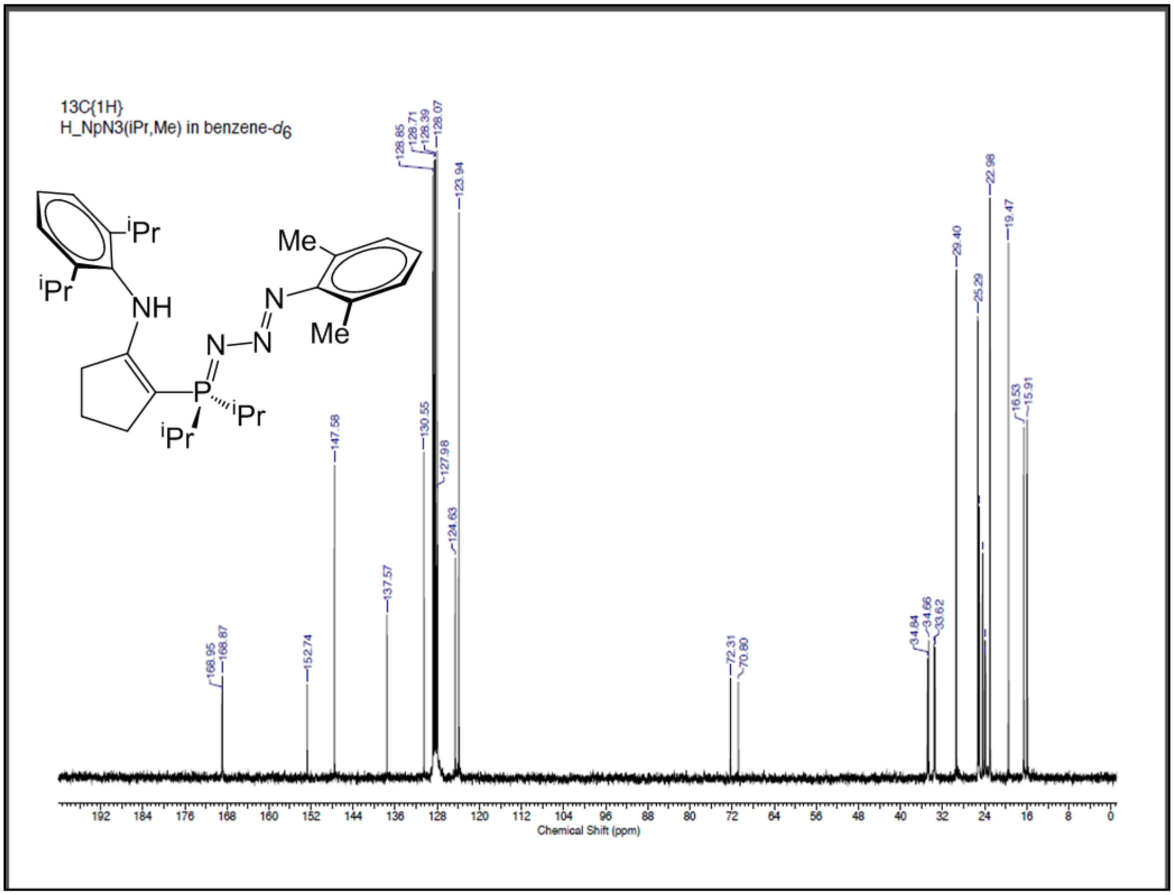

Figure S5: $^{13}C\{^1H\}$ NMR spectrum of **2** (H_NpN$_3^{iPr,Me}$) (75 MHz, d_6-benzene, 298 K).

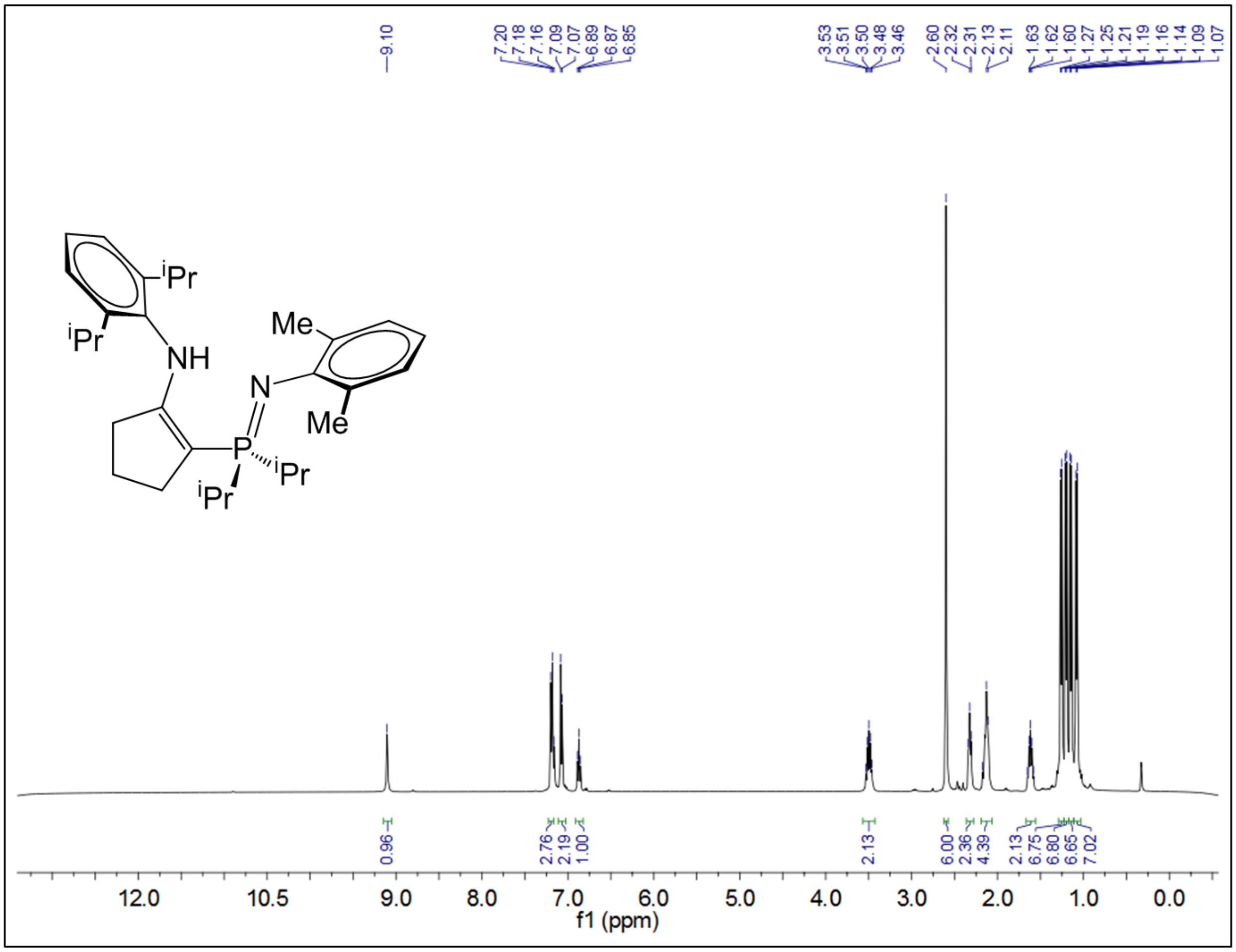

Figure S6: ^{1}H NMR spectrum of **3** (H_NpN$^{i\text{Pr,Me}}$) (400 MHz, d_6-benzene, 298 K).

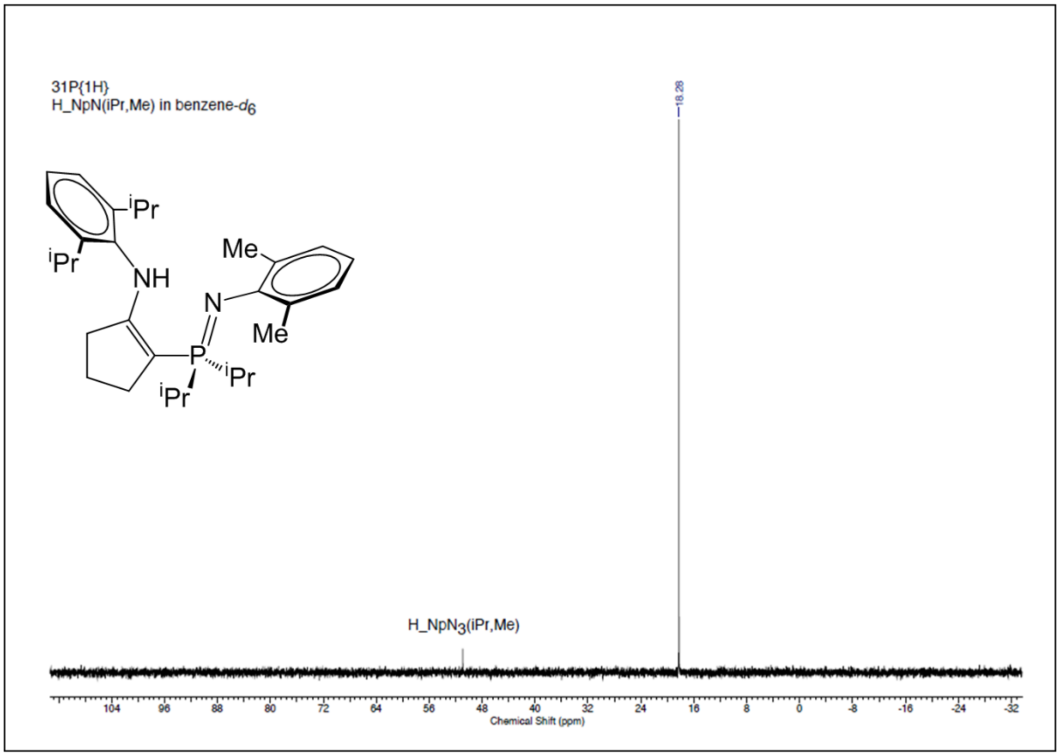

Figure S7: $^{31}P\{^1H\}$ NMR spectrum of **3** (H_NpN^{iPr,Me}) (121 MHz, d_6-benzene, 298 K).

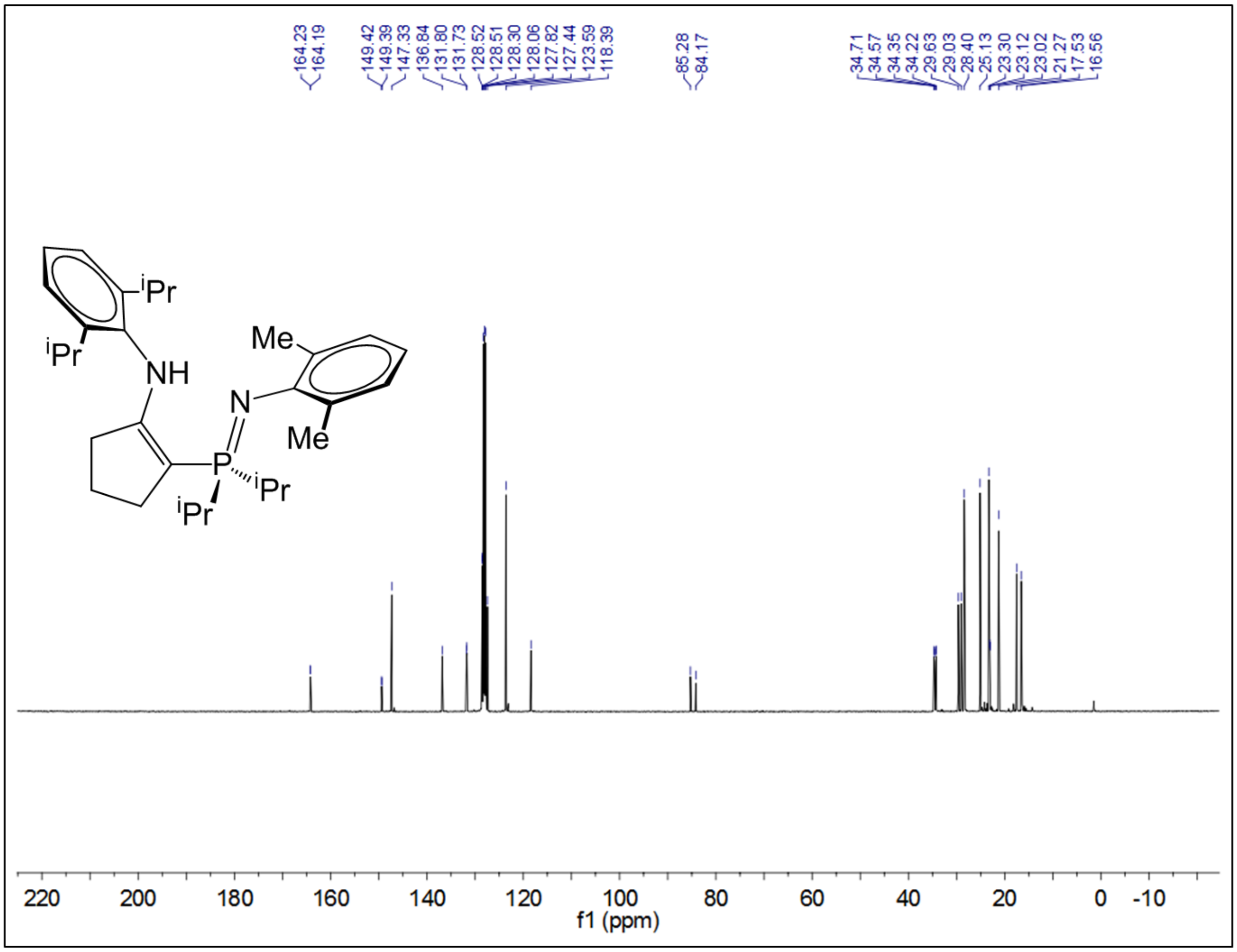

Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of **3** (H_NpN$^{i\mathrm{Pr,Me}}$) (101 MHz, d_6-benzene, 298 K).

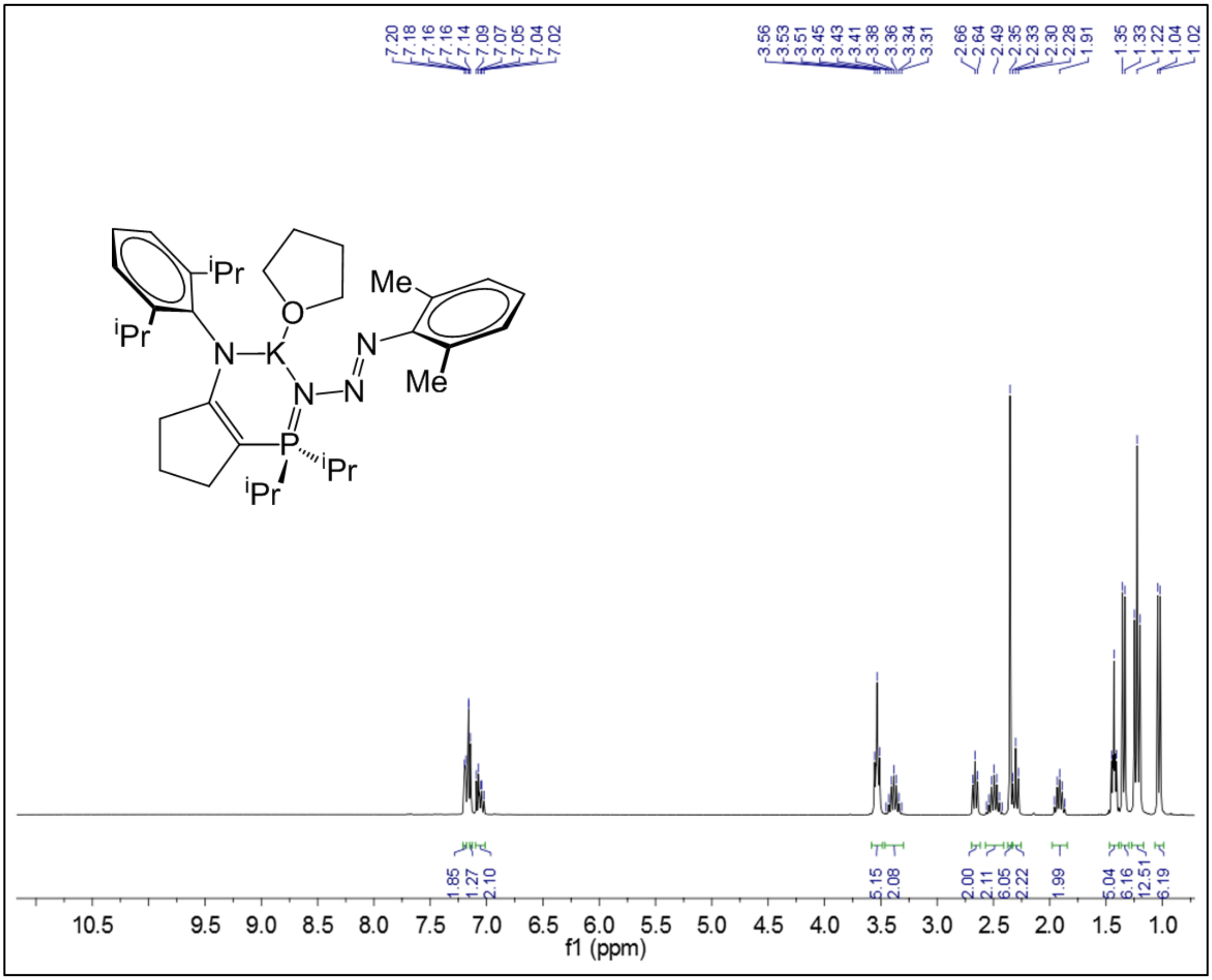

Figure S9: $^{1}H\{^{31}P\}$ NMR spectrum of **4** [$KNpN_3{}^{i\mathrm{Pr,Me}}$(THF)] (300 MHz, d_6-benzene, 298 K).

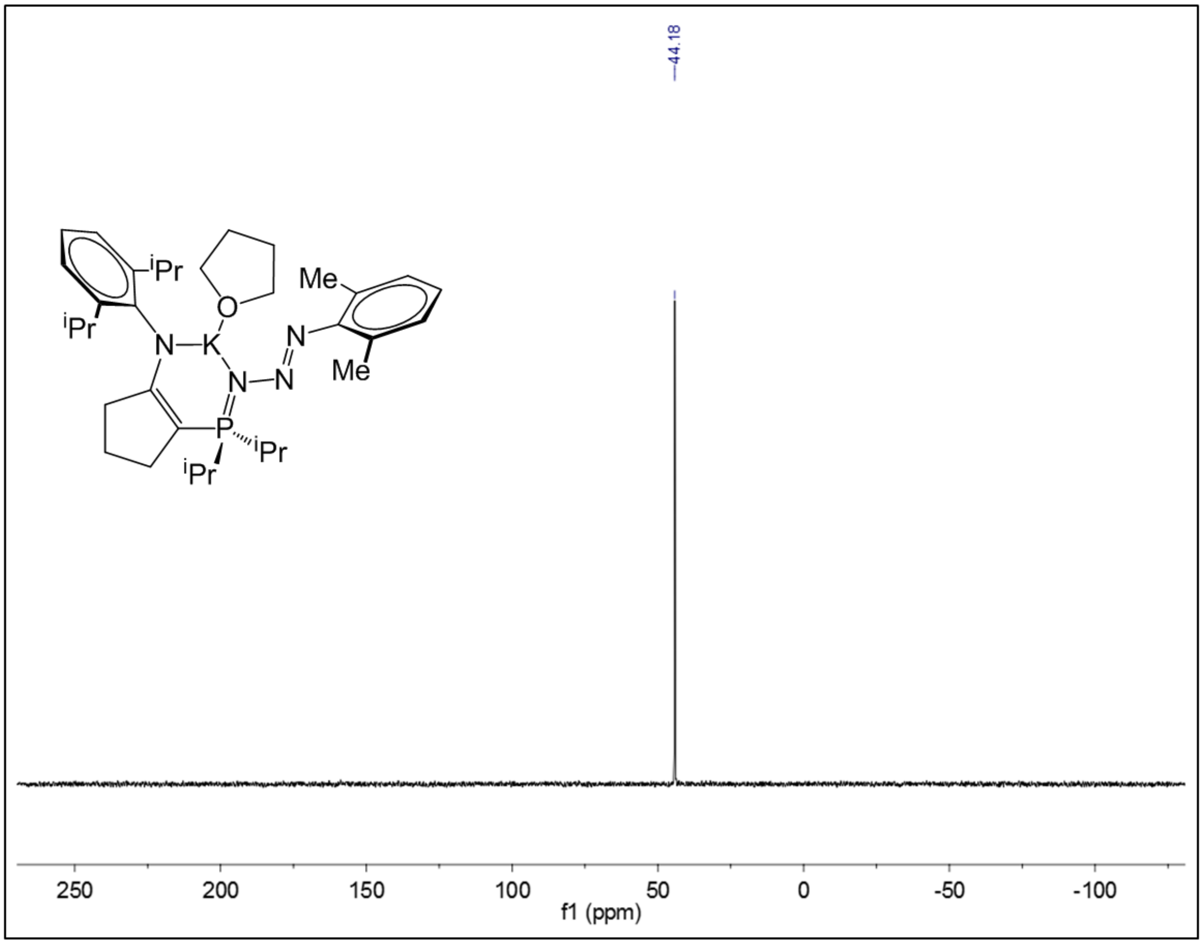

Figure S10: ^{31}P{^{1}H} NMR spectrum of **4** [KNpN$_3^{iPr,Me}$(THF)] (121 MHz, d_6-benzene, 298 K).

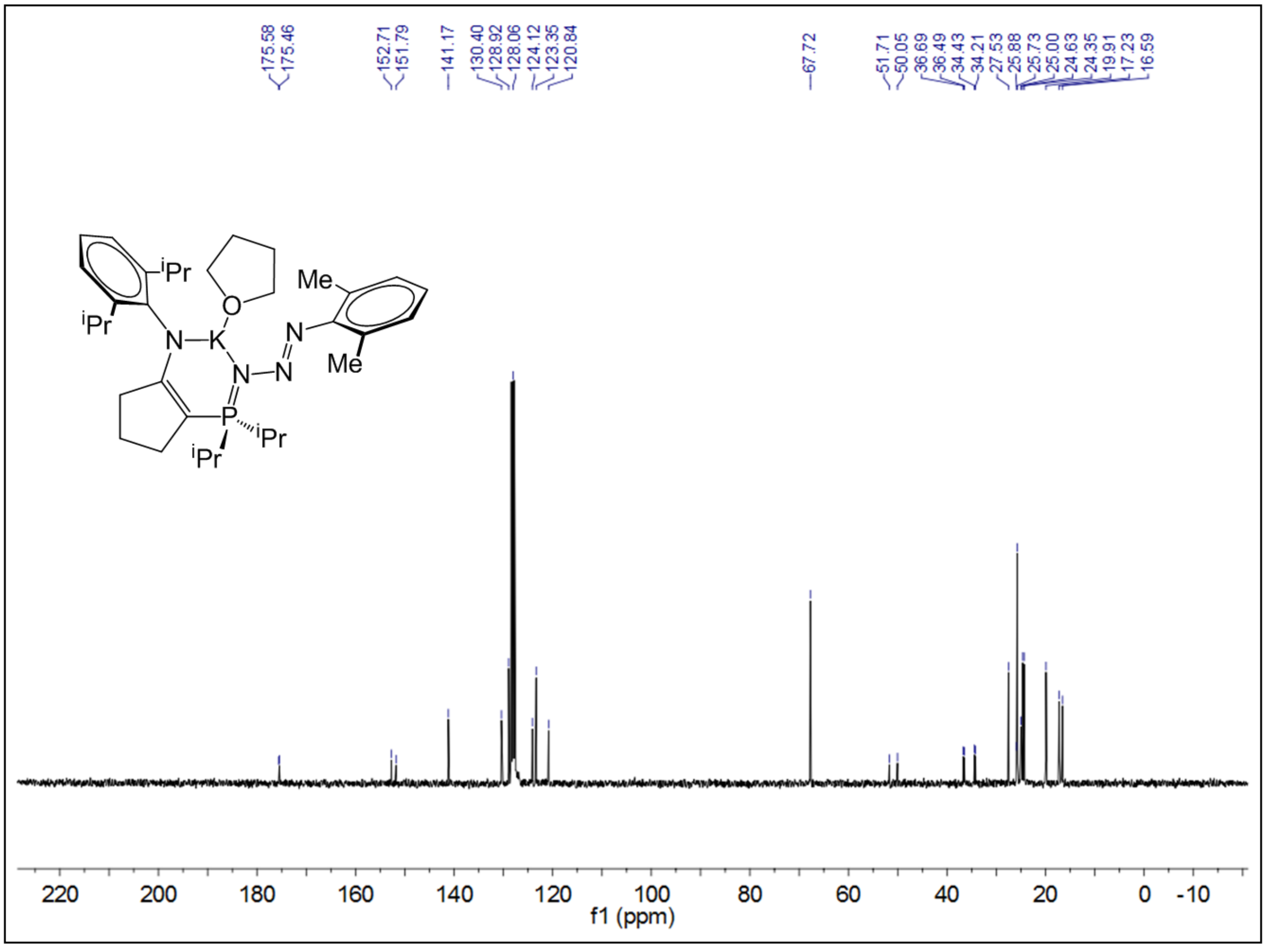

Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of **4** [$KNpN_3^{iPr,Me}$(THF)] (75 MHz, *d*$_6$-benzene, 298 K).

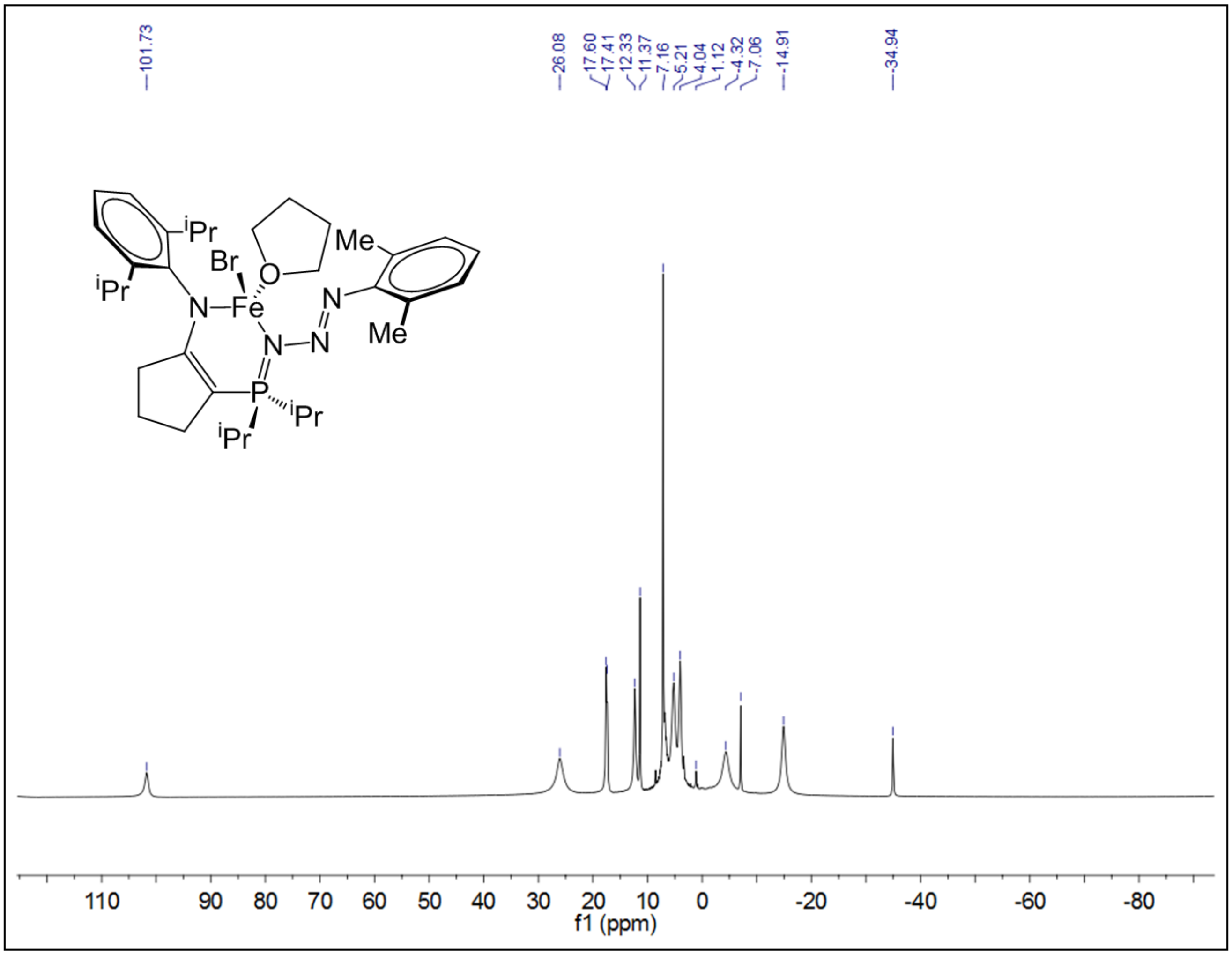

Figure S12: ^{1}H NMR spectrum for **5** [FeBr(**NpN$_3$**^{iPr,Me})(THF)] (300 MHz, d_6-benzene, 298 K).

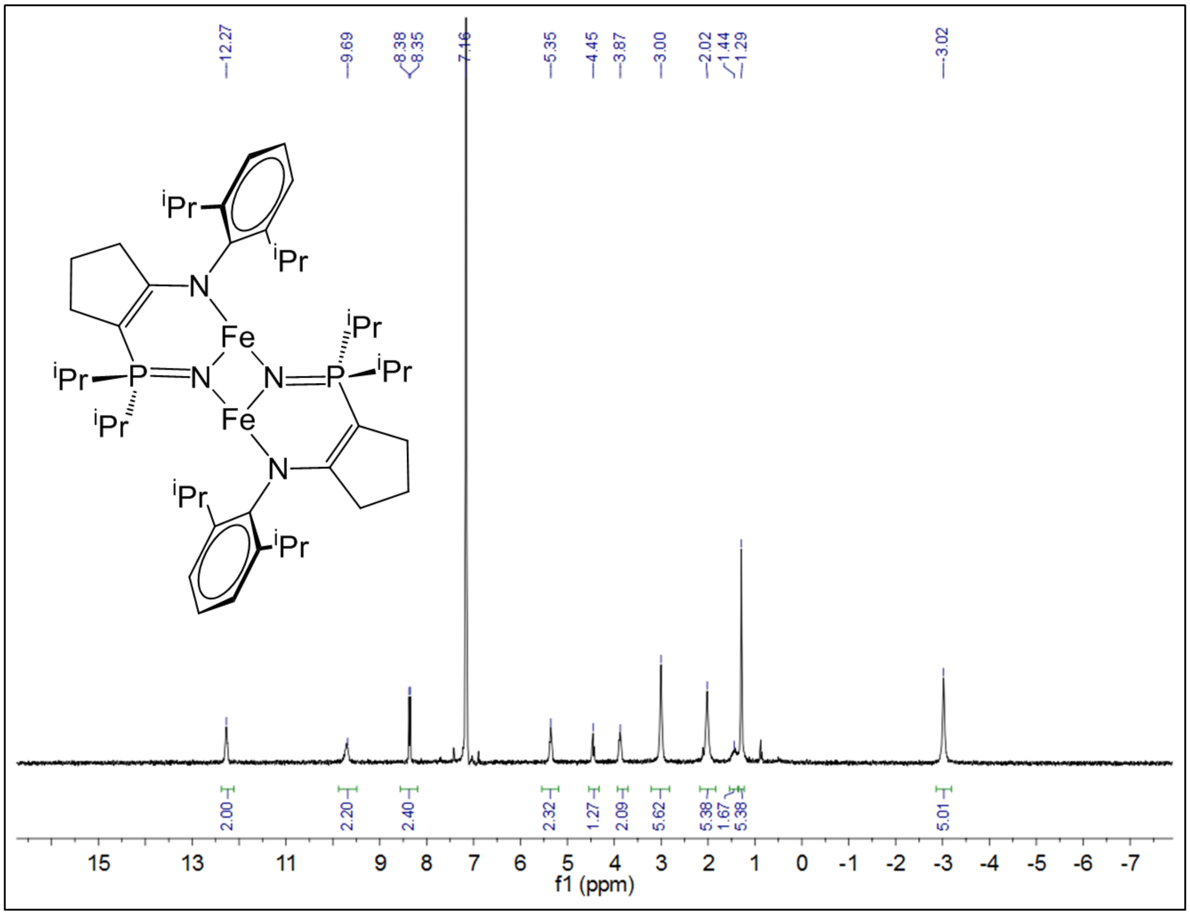

Figure S13: ^{1}H{^{31}P} NMR spectrum for **6** [Fe$_2$(**NpN'**)$_2$] (300 MHz, d_6-benzene, 298 K).

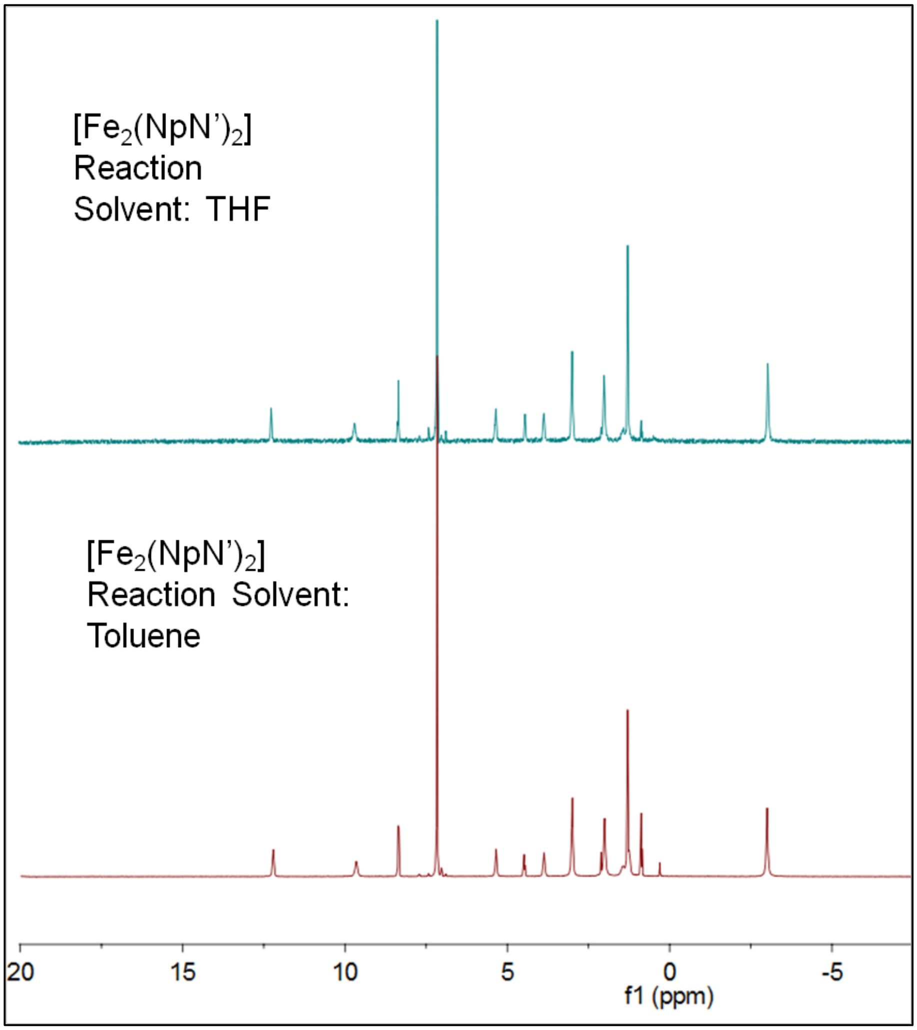

Figure S14: $^1H\{^{31}P\}$ NMR spectra for **6** [Fe$_2$(**NpN'**)$_2$] prepared in THF (top) and toluene (bottom) (300 MHz, *d*$_6$-benzene, 298 K).

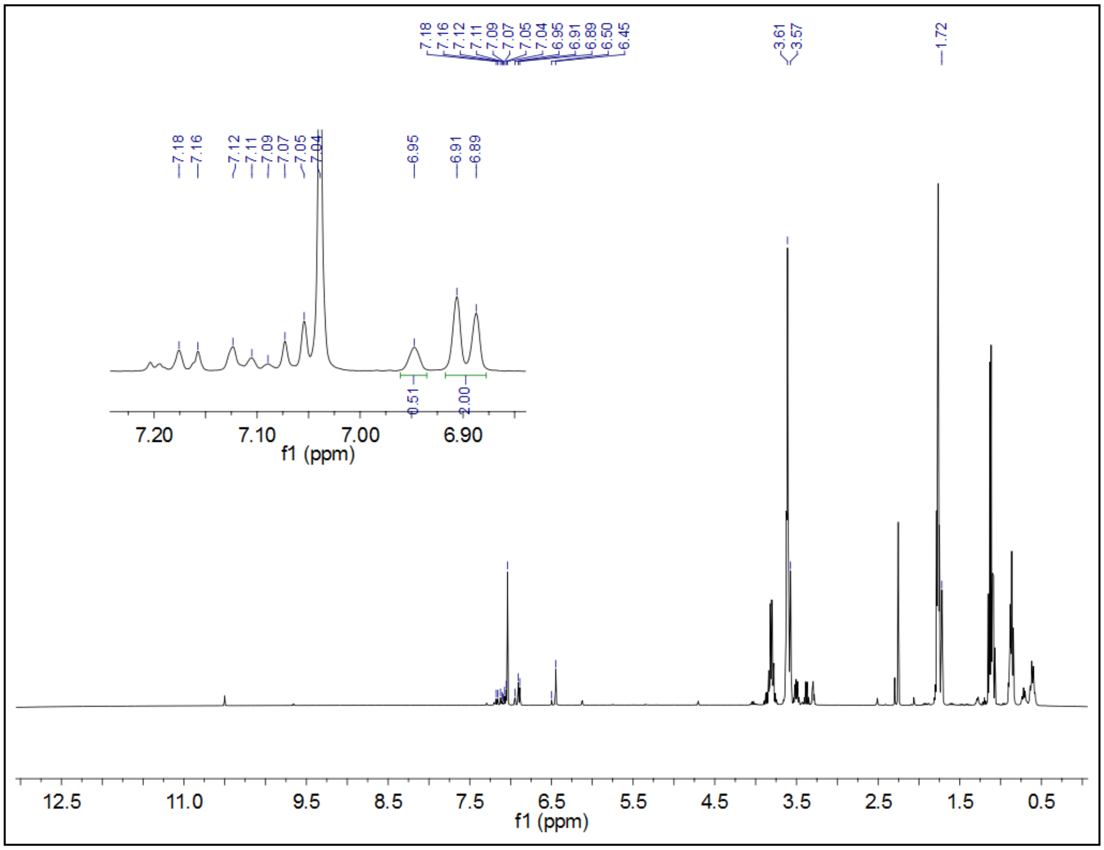

Figure S15: ^{1}H NMR spectrum for isolated volatiles (d_8-THF as solvent) in radical trapping experiment (scheme 3 in text) (400 MHz, d_8-THF, 298 K).

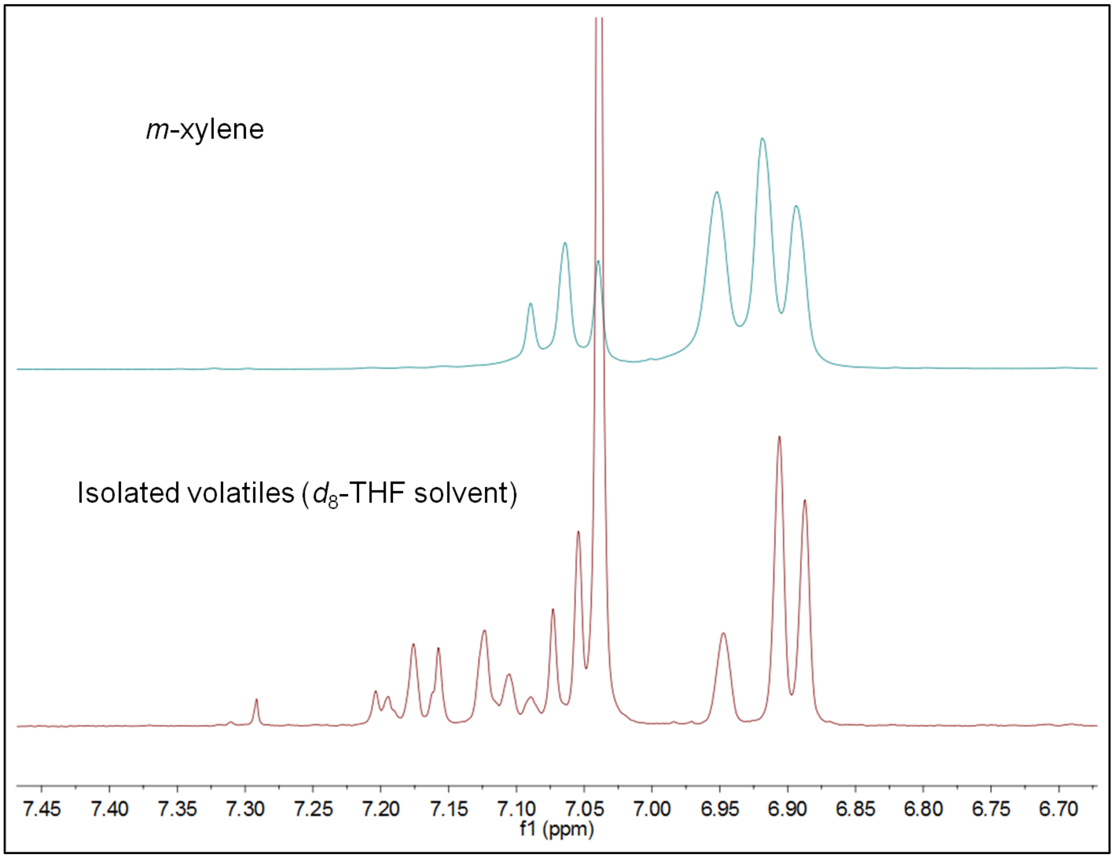

Figure S16: ^{1}H NMR (aromatic region) comparison of *m*-xylene (top) to the isolated volatiles (d_8-THF as solvent) from the radical trapping experiment (bottom) (scheme 3 in text) (400 MHz, d_8-THF, 298 K). The decrease in intensity of the peak at approx. 6.95 ppm indicates the formation of 2-*d*-1,3-$Me_2C_6H_3D$

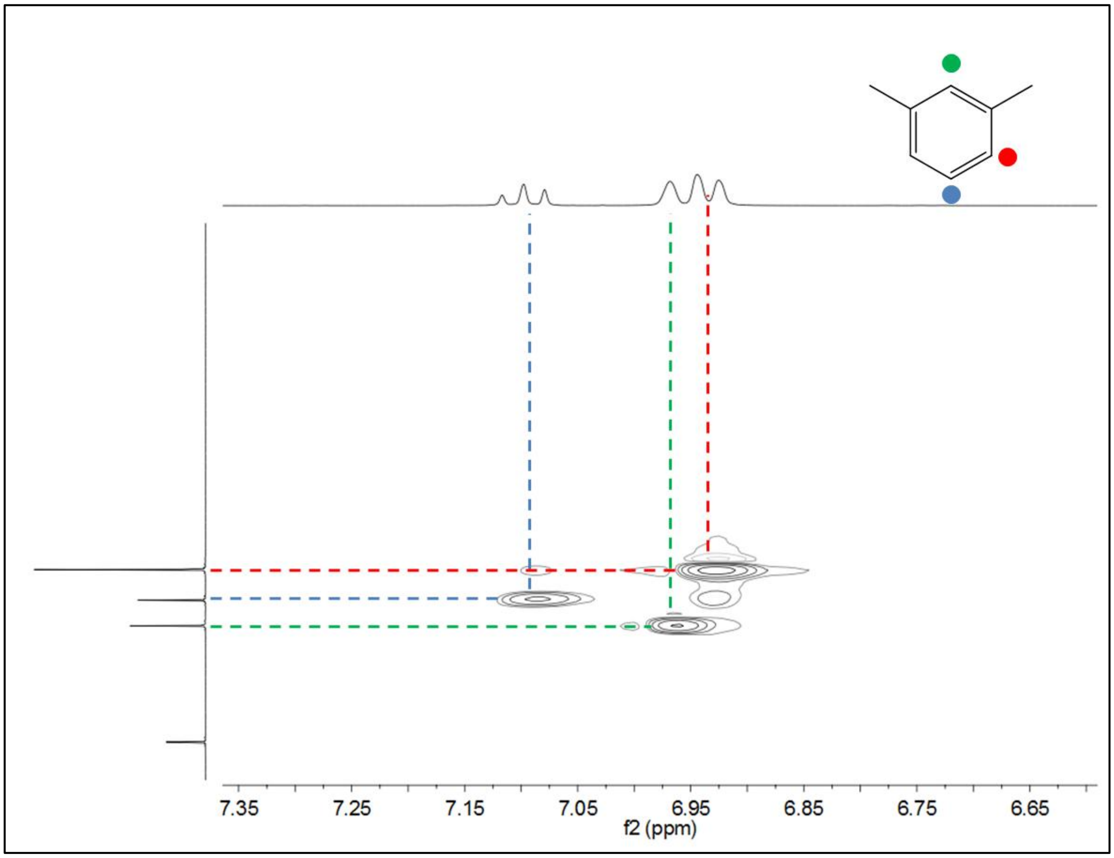

Figure S17: ^1H-^{13}C HSQC (aromatic region) for undeuterated *m*-xylene (400 MHz, d_8-THF, 298 K).

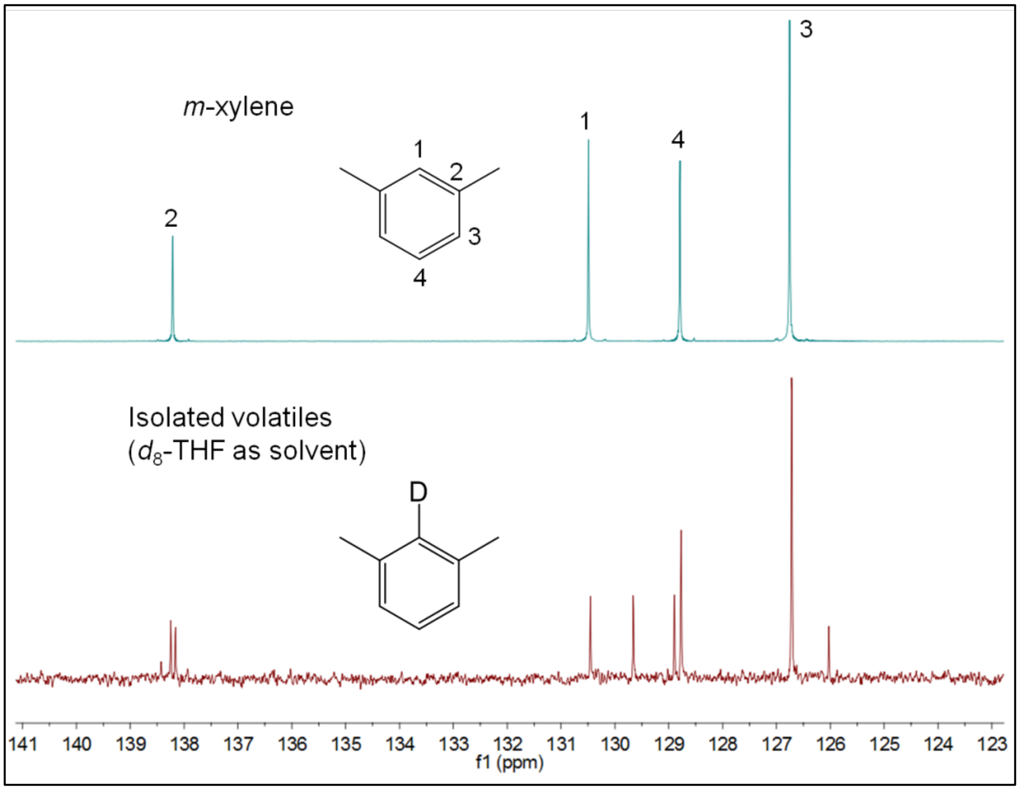

Figure S18: $^{13}C\{^1H\}$ NMR (aromatic region) comparison of *m*-xylene (top) to the isolated volatiles (d_8-THF as solvent) from the radical trapping experiment (bottom) (scheme 3 in text). The ^1H-^{13}C HSQC presented in Figure S17 was used to confirm deuterium incorporation (1:1:1 triplet) at carbon position 1 in 2-*d*-1,3-$Me_2C_6H_3D$ (400 MHz, d_8-THF, 298 K).

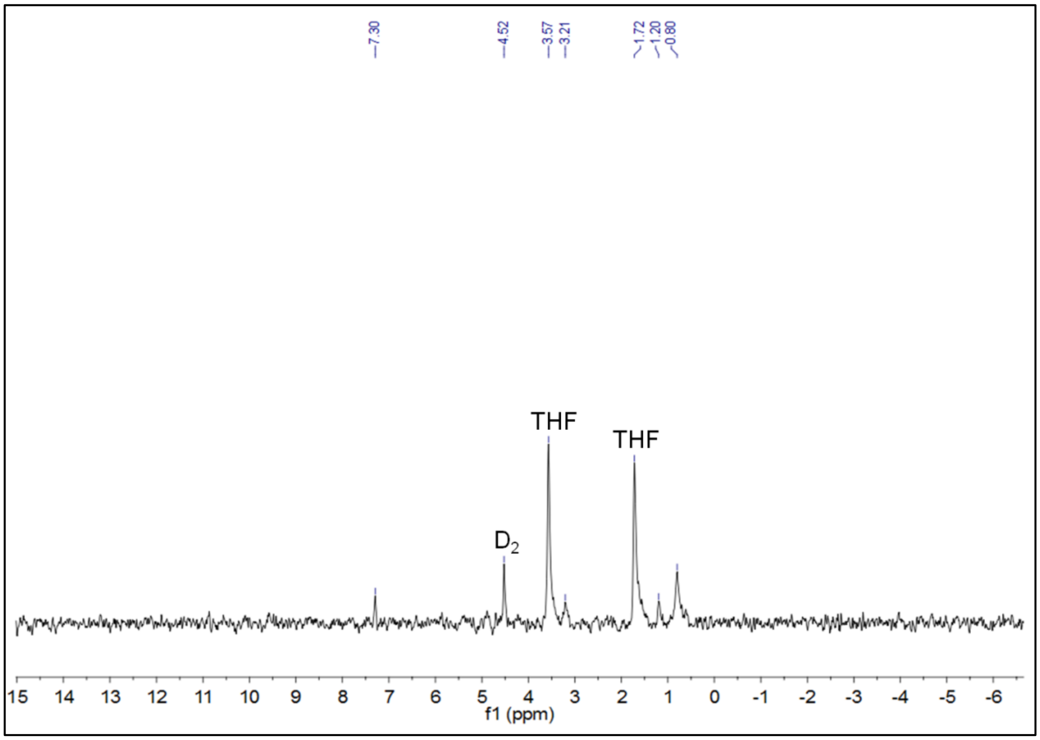

Figure S19: ^{2}H NMR spectrum for the reaction of complex **5** with KBEt$_3$D in a sealed J. Young tube with protio THF as the solvent. The natural abundance of ^{2}H in THF gave the observed THF signals (400 MHz, THF, 298 K).

Figure S20: Apparatus used in radical trapping experiments.

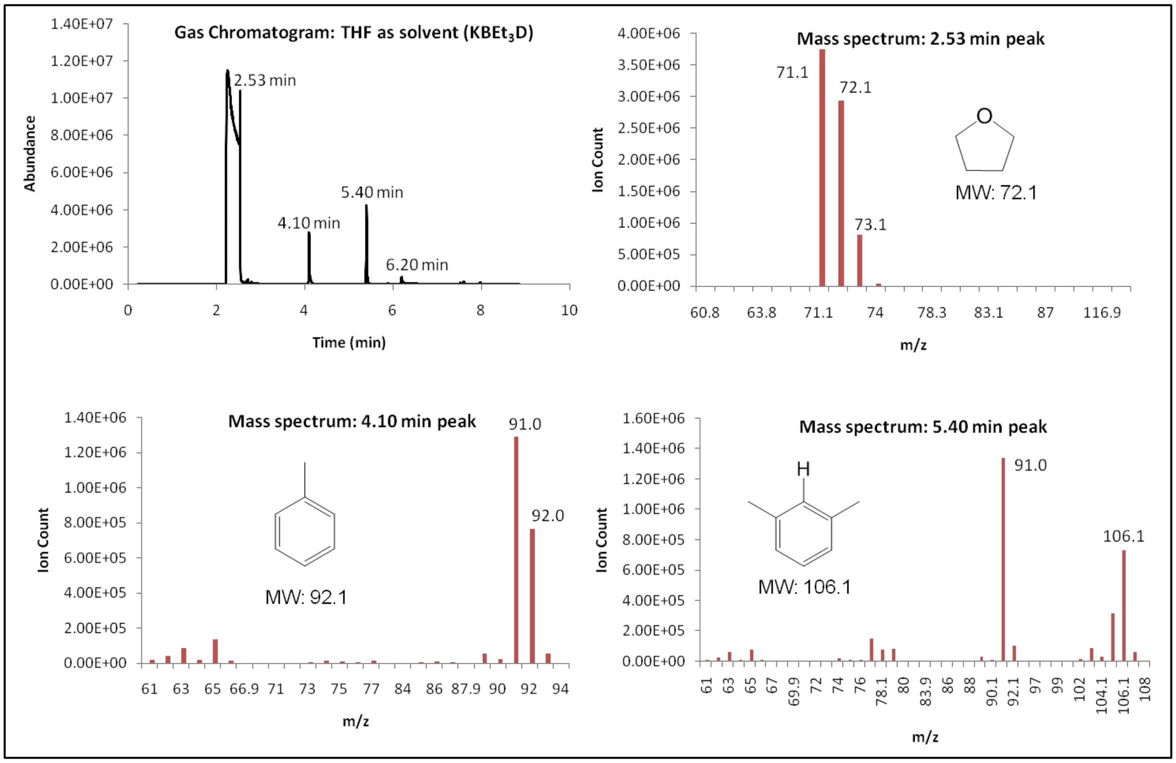

Figure S21: Gas chromatogram and corresponding mass spectra obtained from the volatiles isolated from the reaction of complex **5** with KBEt$_3$D in protio THF.

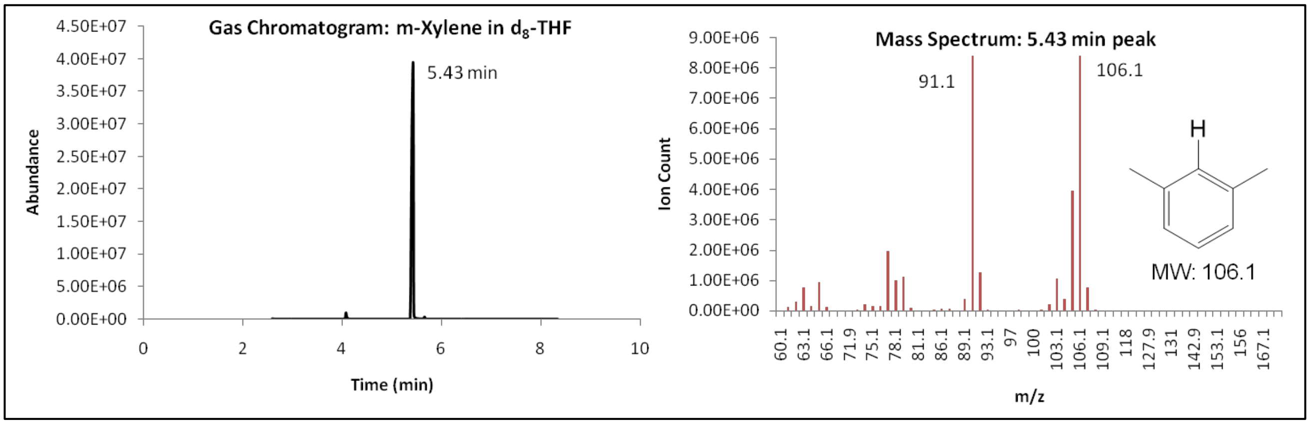

Figure S22: Gas chromatogram and corresponding mass spectrum obtained from a sample of *m*-xylene dissolved in d_8-THF.

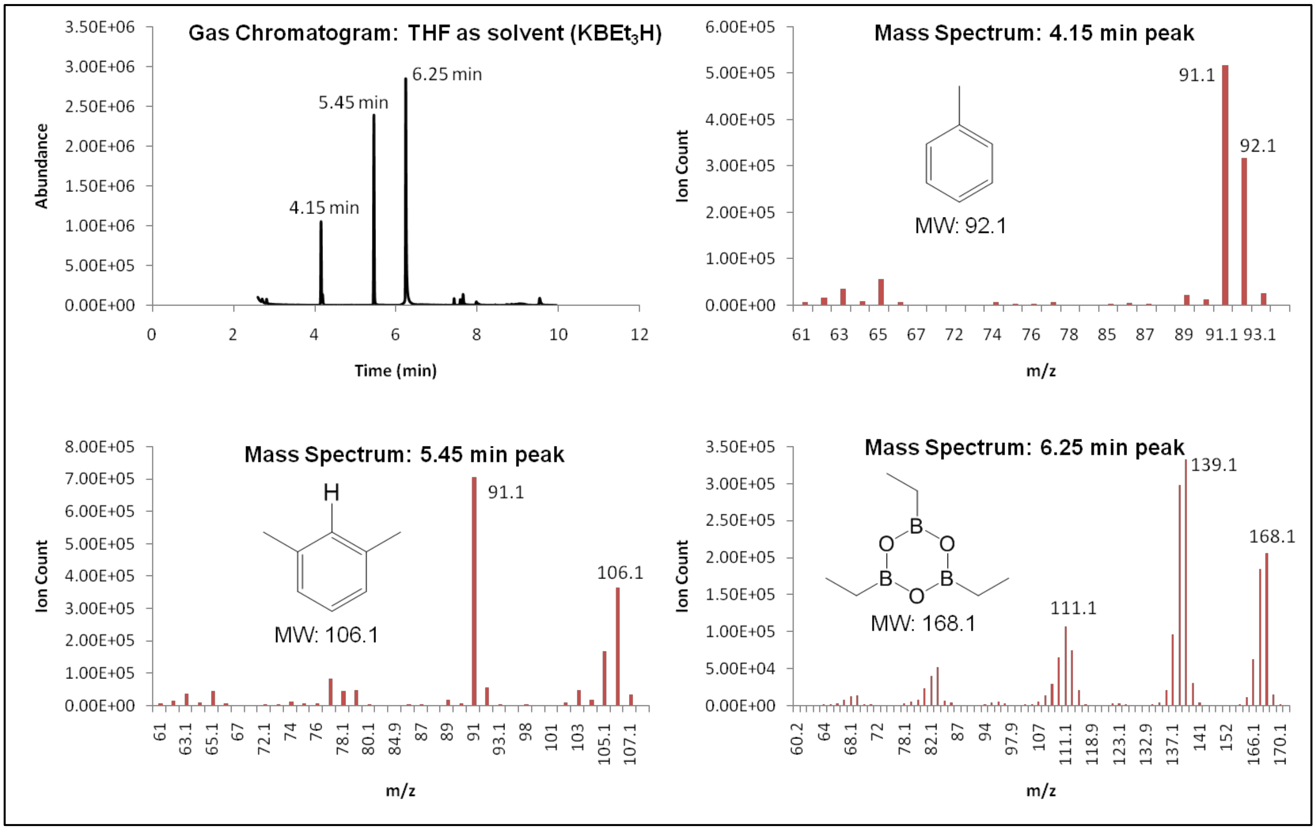

Figure S23: Gas chromatogram and corresponding mass spectra obtained from the volatiles isolated from the reaction of complex **5** with $KBEt_3H$ in protio THF. The species observed at 6.25 minutes in the GC is from triethylborane (a by-product of the reaction) having reacted with water vapor in air. The observed mass spectrum matches the predicted spectrum for 2,4,6-triethylboroxin.[12]

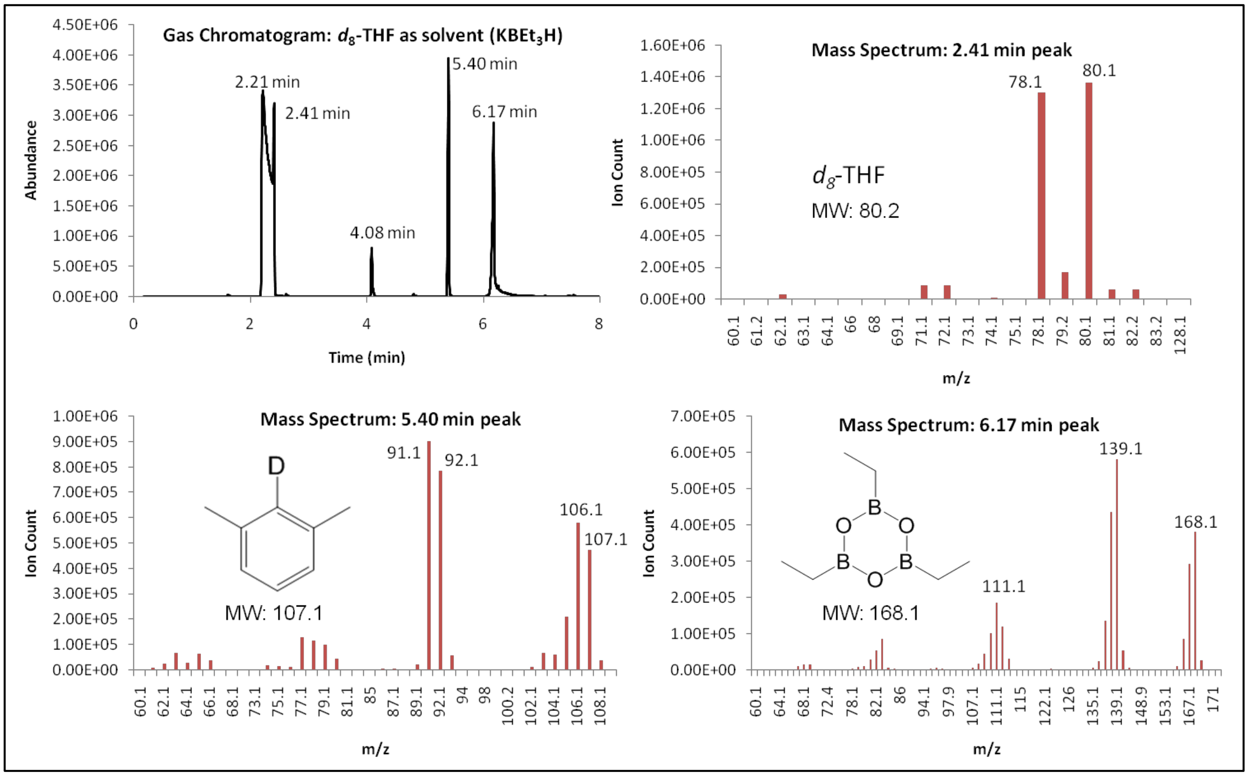

Figure S24: Gas chromatogram and corresponding mass spectra obtained from the volatiles isolated from the reaction of complex **5** with $KBEt_3H$ in d_8-THF. The peak at 4.08 minutes in the GC corresponds to toluene. Note the signal intensity of the mass peak 107.1 due to 2-*d*-1,3-$Me_2C_6H_3D$ to those found in Figures S22-S23. The species observed at 6.17 minutes in the GC is from triethylborane (a by-product of the reaction) having reacted with water vapor in air. The observed mass spectrum matches the predicted spectrum for 2,4,6-triethylboroxin.[12]

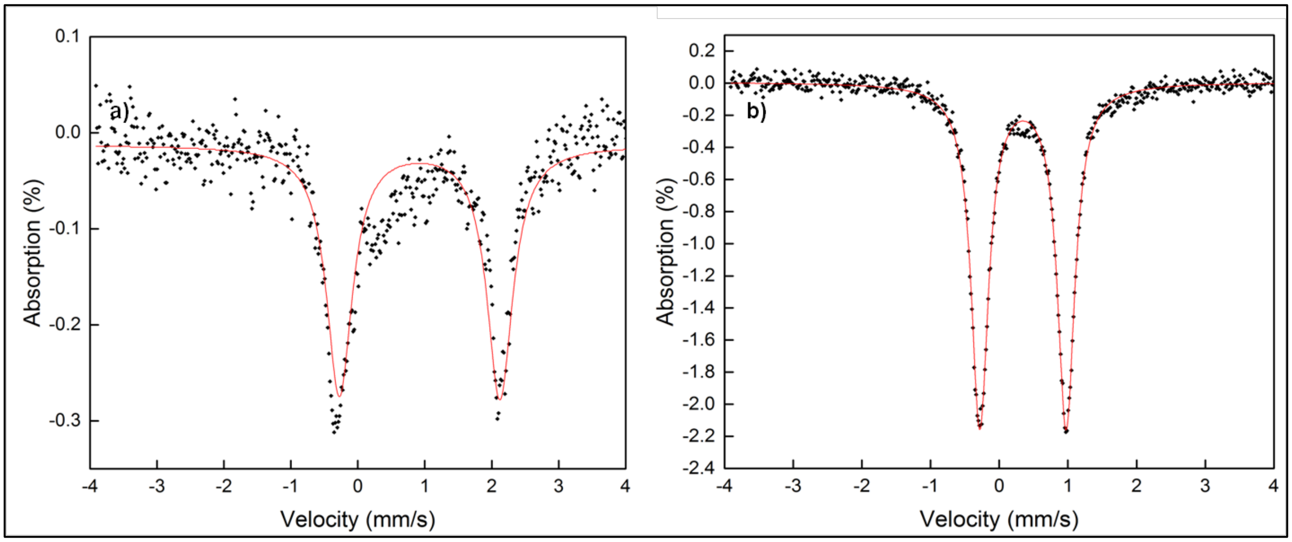

Figure S25: ^{57}Fe Mössbauer spectra for powdered samples obtained at 295 K.
a) Complex **5** [FeBr(NpN$_3^{i\mathrm{Pr,Me}}$)(THF)]; b) Dimeric species **6** [Fe$_2$(NpN')$_2$]. Solid red lines correspond to simulated data. The spectrum of **5** was fit as a quadrapole doublet with $\delta = 0.92$ mms^{-1} and ΔEq = 2.40 mms^{-1}. The signal intensity for **5** is consistently weak, even after over 10 days collection due to a poor recoil-free fraction. The symmetric dimer **6** can be fit as a single quadrapole doublet with $\delta = 0.34$ mms^{-1} and ΔEq = 1.26 mms^{-1} for the equivalent iron centers.

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