

Electronic Supporting Information

**Low Coordinate Iron Derivatives Stabilized by a β -Diketiminato Mimic. Synthesis and
Coordination Chemistry of Enamidophosphinimine Scaffolds to Generate Diiron
Dinitrogen Complexes**

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X-ray crystallographic data and collection parameters

Table S1: Crystal data and structure refinement for **4a**

Identification code	mf1117a	
Empirical formula	C ₃₅ H ₅₄ N ₂ PF ₆ Br	
Formula weight	669.53	
Temperature	90K	
Crystal size	0.2 × 0.18 × 0.18 mm ³	
Radiation	MoK α (λ = 0.71069 Å)	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a=17.3586(5) Å	α =90°
	b=16.9214(5) Å	β =90°
	c=23.4188(7) Å	γ =90°
Volume	6878.8(4) Å ³	
Z	8	
Density (calculated)	1.293 g/cm ³	
Absorption Coefficient	1.672 mm ⁻¹	
F(000)	2832.0	
2 θ range for data collection	3.478 to 55.02°	
Index ranges	-22 ≤ h ≤ 15, -21 ≤ k ≤ 18, -24 ≤ l ≤ 30	
Reflections collected	34340	
Independent reflections	7900 [R _{int} = 0.0476, R _{sigma} = 0.0481]	
Data/restraints/parameters	7900/0/373	
Completeness to θ	99.8%	
Goodness-of-fit on F ²	1.038	
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0528, wR ₂ = 0.1149	
Final R indexes [all data]	R ₁ = 0.0814, wR ₂ = 0.1265	
Largest diff. peak/hole	2.57/-2.34 eÅ ⁻³	

Table S2: Crystal data and structure refinement for **4b**

Identification code	mf1189	
Empirical formula	C ₂₇ H ₃₈ BrFeN ₂ P	
Formula weight	557.32	
Temperature	90K	
Crystal size	0.09 × 0.08 × 0.04 mm ³	
Radiation	MoK α (λ = 0.71069 Å)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a=13.121(3) Å	α =90.837(4)°
	b=15.896(4) Å	β =109.446(4)°
	c=16.706(4) Å	γ =101.917(4)°
Volume	3201.6(14) Å ³	
Z	4	
Density (calculated)	1.156 g/cm ³	
Absorption Coefficient	1.783 mm ⁻¹	
F(000)	1160.0	
2 θ range for data collection	2.596 to 53.036°	
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	
Reflections collected	44303	
Independent reflections	13084 [R _{int} = 0.1318, R _{sigma} = 0.1376]	
Data/restraints/parameters	13084/0/545	
Completeness to θ	98.5%	
Goodness-of-fit on F ²	0.909	
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0827, wR ₂ = 0.2030	
Final R indexes [all data]	R ₁ = 0.1452, wR ₂ = 0.2298	
Largest diff. peak/hole	2.17/-1.04 eÅ ⁻³	

Table S3: Crystal data and structure refinement for **4c**

Identification code	mf1098	
Empirical formula	C ₆₄ H ₉₆ N ₄ P ₂ Fe ₂ Br ₂	
Formula weight	1254.90	
Temperature	90K	
Crystal size	0.16 × 0.13 × 0.02 mm ³	
Radiation	MoK α (λ = 0.71069 Å)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a=9.999(3) Å	α =62.101(6)°
	b= 13.544(5) Å	β = 72.296(7)°
	c= 13.905(5) Å	γ = 85.151(7)°
Volume	1581.7(9) Å ³	
Z	1	
Density (calculated)	1.317 g/cm ³	
Absorption Coefficient	1.813 mm ⁻¹	
F(000)	660.0	
2 θ range for data collection	3.41 to 54.974°	
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	
Reflections collected	24646	
Independent reflections	7109 [R_{int} = 0.0767, R_{sigma} = 0.0838]	
Data/restraints/parameters	7109/0/345	
Completeness to θ	99.2%	
Goodness-of-fit on F ²	1.074	
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0670, wR_2 = 0.1588	
Final R indexes [all data]	R_1 = 0.1023, wR_2 = 0.1715	
Largest diff. peak/hole	1.57/-0.67 eÅ ⁻³	

Table S4: Crystal data and structure refinement for **5a**

Identification code	mf1148	
Empirical formula	C ₇₀ H ₁₀₈ N ₆ P ₂ Fe ₂	
Formula weight	1207.26	
Temperature	90 K	
Crystal size	0.1 × 0.08 × 0.03 mm ³	
Radiation	MoK α (λ = 0.71069 Å)	
Crystal system	monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a=10.3990(6) Å	α =90°
	b= 28.6698(15) Å	β = 100.9200(10)°
	c= 22.9617(13) Å	γ = 90°
Volume	6721.8(6) Å ³	
Z	4	
Density (calculated)	1.193 g/cm ³	
Absorption Coefficient	0.523 mm ⁻¹	
F(000)	2608.0	
2 θ range for data collection	2.298 to 55.11°	
Index ranges	-13 ≤ h ≤ 13, -37 ≤ k ≤ 20, -24 ≤ l ≤ 29	
Reflections collected	62062	
Independent reflections	15498 [R _{int} = 0.0760, R _{sigma} = 0.0902]	
Data/restraints/parameters	15498/0/745	
Completeness to θ	99.7%	
Goodness-of-fit on F ²	1.001	
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0479, wR ₂ = 0.0833	
Final R indexes [all data]	R ₁ = 0.0986, wR ₂ = 0.0965	
Largest diff. peak/hole	0.48/-0.39 eÅ ⁻³	

Table S5: Crystal data and structure refinement for **5b**

Identification code	mf1203	
Empirical formula	C ₄₆ H ₆₇ N ₃ P ₂ Fe	
Formula weight	779.81	
Temperature	90 K	
Crystal size	0.24 × 0.03 × 0.025 mm ³	
Radiation	MoK α (λ = 0.71073 Å)	
Crystal system	monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a=19.562(3) Å	α =90°
	b= 11.2091(14) Å	β = 112.138(3)°
	c= 20.674(3) Å	γ = 90°
Volume	4199.1(9) Å ³	
Z	4	
Density (calculated)	1.234 g/cm ³	
Absorption Coefficient	0.471 mm ⁻¹	
F(000)	1680.0	
2 θ range for data collection	2.444 to 55.158°	
Index ranges	-25 ≤ h ≤ 24, -10 ≤ k ≤ 14, -26 ≤ l ≤ 26	
Reflections collected	37081	
Independent reflections	9688 [R _{int} = 0.1579, R _{sigma} = 0.1611]	
Data/restraints/parameters	9688/0/483	
Completeness to θ	99.4%	
Goodness-of-fit on F ²	0.974	
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0807, wR ₂ = 0.1703	
Final R indexes [all data]	R ₁ = 0.1598, wR ₂ = 0.2062	
Largest diff. peak/hole	1.23/-0.89 eÅ ⁻³	

Table S6: Crystal data and structure refinement for **5c**

Identification code	mf987	
Empirical formula	$C_{64}H_{93.15}Fe_2N_6P_2$	
Formula weight	1120.23	
Temperature	90 K	
Crystal size	$0.21 \times 0.014 \times 0.014 \text{ mm}^3$	
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$)	
Crystal system	monoclinic	
Space group	C_2/c	
Unit cell dimensions	$a=21.642(5) \text{ \AA}$	$\alpha=90^\circ$
	$b=20.337(5) \text{ \AA}$	$\beta=98.831(5)^\circ$
	$c=16.105(5) \text{ \AA}$	$\gamma=90^\circ$
Volume	$7004(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.062 g/cm^3	
Absorption Coefficient	0.498 mm^{-1}	
F(000)	2405.0	
2 θ range for data collection	2.764 to 50.8°	
Index ranges	$-24 \leq h \leq 26, -24 \leq k \leq 24, -19 \leq l \leq 19$	
Reflections collected	25483	
Independent reflections	6423 [$R_{\text{int}} = 0.0696, R_{\text{sigma}} = 0.0688$]	
Data/restraints/parameters	6423/0/362	
Completeness to θ	99.6%	
Goodness-of-fit on F^2	1.071	
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0626, wR_2 = 0.1623$	
Final R indexes [all data]	$R_1 = 0.0868, wR_2 = 0.1704$	
Largest diff. peak/hole	$1.25/-0.47 \text{ e\AA}^{-3}$	

Table S7: Crystal data and structure refinement for **6**

Identification code	mfl134_a	
Empirical formula	C _{35.5} H _{55.5} FeN ₂ P	
Formula weight	597.14	
Temperature	90.15 K	
Crystal size	0.52 × 0.45 × 0.41 mm ³	
Radiation	MoK α (λ = 0.71069 Å)	
Crystal system	monoclinic	
Space group	C ₂ /c	
Unit cell dimensions	a=26.340(3) Å	α =90°
	b= 11.8226(16) Å	β = 106.786(3)°
	c= 24.864(3) Å	γ = 90°
Volume	7413.1(17) Å ³	
Z	8	
Density (calculated)	1.070 g/cm ³	
Absorption Coefficient	0.473 mm ⁻¹	
F(000)	2588.0	
2 θ range for data collection	3.23 to 50.36°	
Index ranges	-31 ≤ h ≤ 21, -14 ≤ k ≤ 14, -22 ≤ l ≤ 29	
Reflections collected	51121	
Independent reflections	6599 [R _{int} = 0.0389, R _{sigma} = 0.0248]	
Data/restraints/parameters	6599/651/683	
Completeness to θ	99.0%	
Goodness-of-fit on F ²	1.065	
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.1319, wR ₂ = 0.3464	
Final R indexes [all data]	R ₁ = 0.1487, wR ₂ = 0.3532	
Largest diff. peak/hole	0.67/-1.76 eÅ ⁻³	

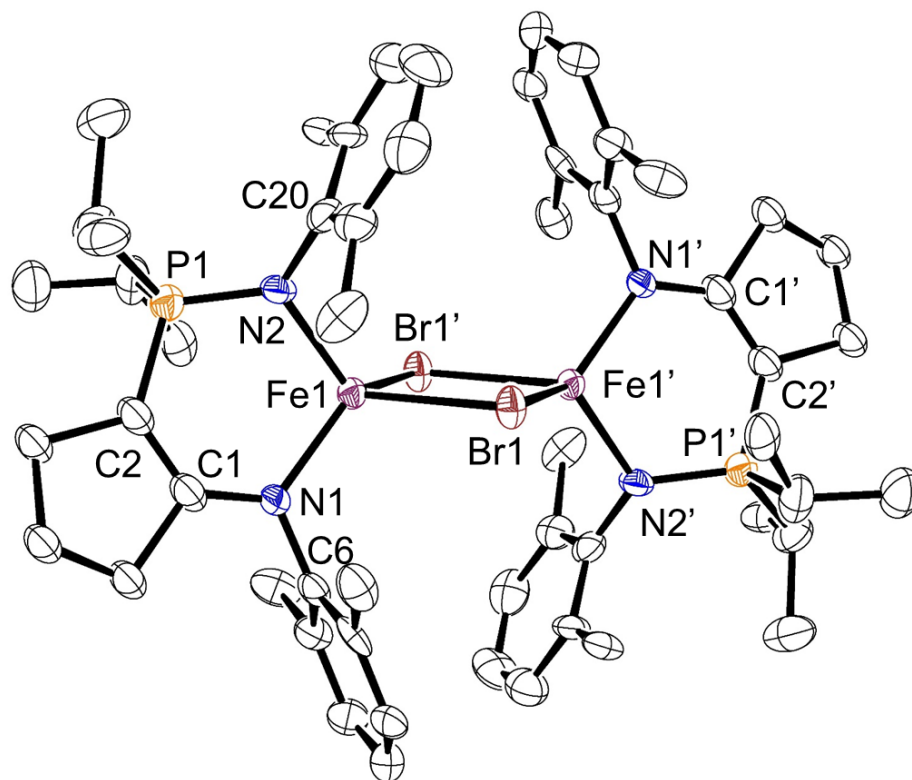


Figure S1: ORTEP drawing of the solid-state molecular structure of **4b** (ellipsoids at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): C1-N1: 1.339(9), C1-C2: 1.358(11), C2-P1: 1.753(8), P1-N2: 1.645(6), N1-Fe1: 1.988(6), N2-Fe1: 2.009(6), Fe1-Br1: 2.5361(13), Fe1-Br1': 2.5415(13), Fe1-Fe1': 3.614(2), C1-N1-C6: 117.9(6), P1-N2-C20: 126.0(5), N1-Fe1-N2: 102.4(2), Br1-Fe1-Br1': 89.25(4), N1-Fe1-Br1: 112.08(17), N1-Fe1-Br1': 122.32(17), N2-Fe1-Br1: 114.42(18), N2-Fe1-Br1': 116.61(18), C1-C2-P1-N2: 25.8(9).

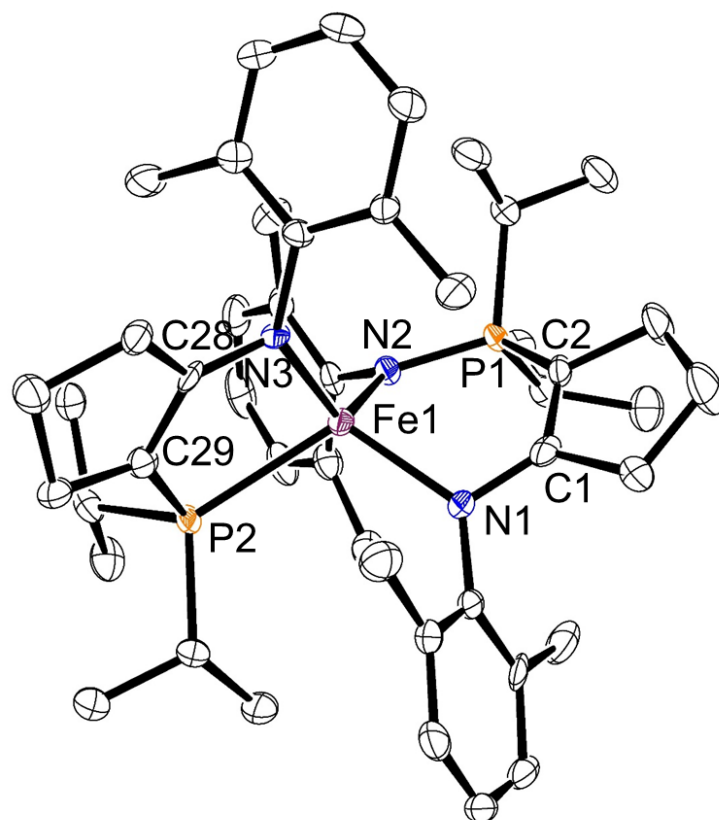


Figure S2: ORTEP drawing of the solid-state molecular structure of **5b** (ellipsoids at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg): C1-N1: 1.368(5), C1-C2: 1.374(6), C2-P1: 1.747(5), P1-N2: 1.628(4), C28-N3: 1.359(5), C28-C29: 1.381(5), P2-C29: 1.772(4), N1-Fe1: 2.052(3), N2-Fe1: 2.023(4), N3-Fe1: 2.017(3), P2-Fe1: 2.4981(12), N1-Fe1-N2: 98.37(14), N2-Fe1-N3: 122.76(14), N1-Fe1-P2: 111.93(9), N3-Fe1-P2: 86.07(10).

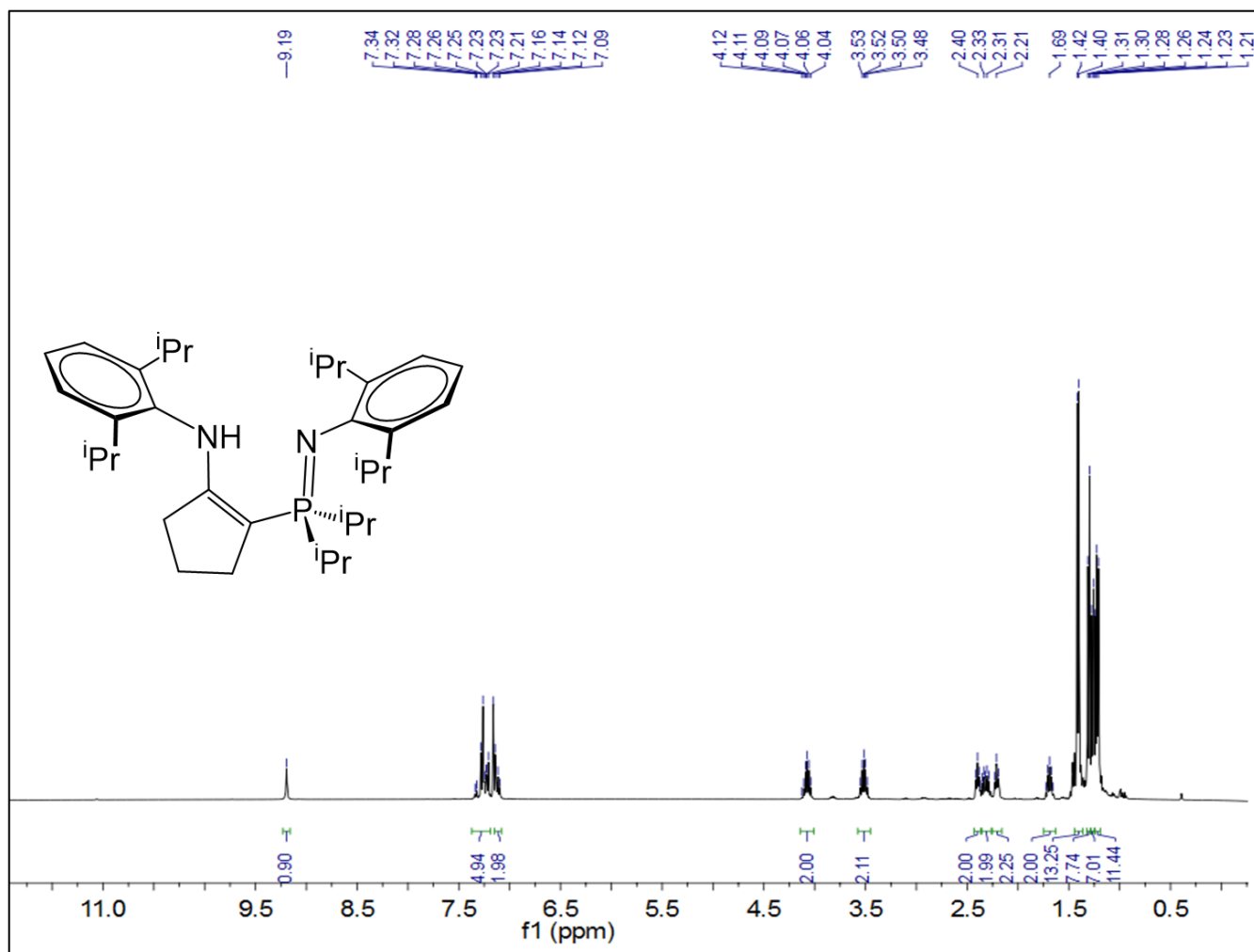


Figure S3: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP},\text{DIPP}}]\text{H } \mathbf{2a}$ (400 MHz, d_6 -benzene, 298 K).

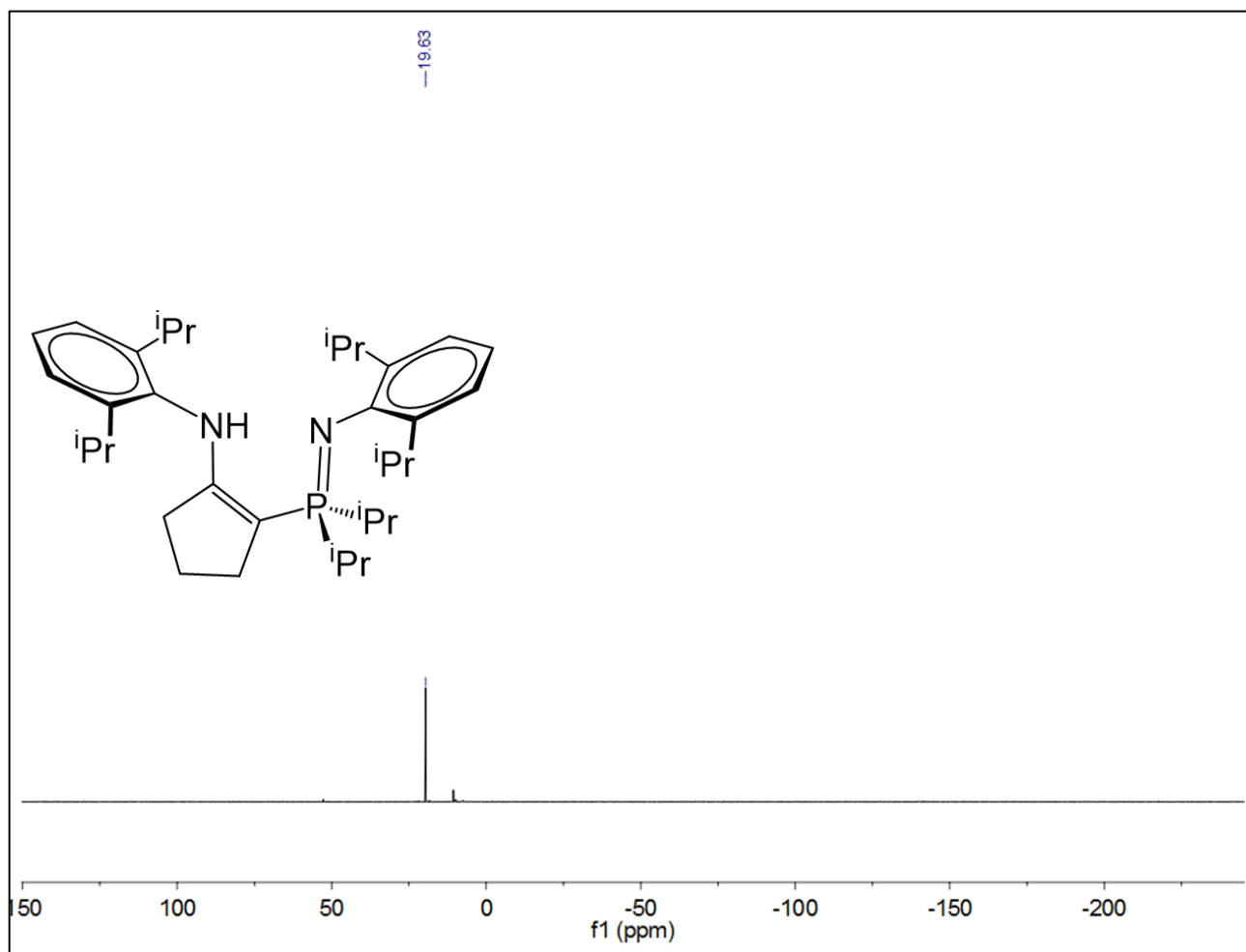


Figure S4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5}\text{NpN}^{\text{DIPP,DIPP}}]\text{H } \mathbf{2a}$ (161 MHz, d_6 -benzene, 298 K).

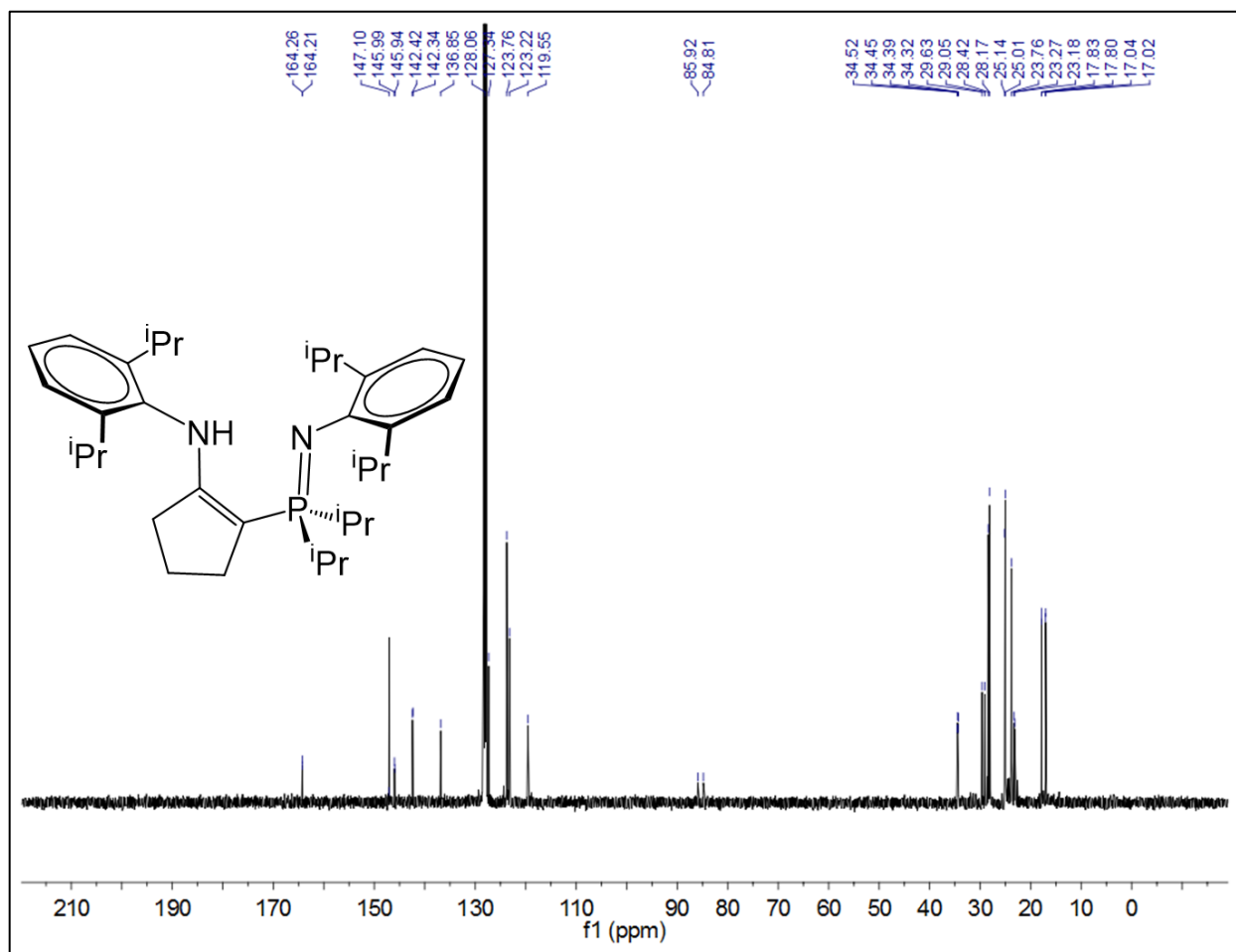


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,DIPP}}]\text{H } \mathbf{2a}$ (101 MHz, d_6 -benzene, 298 K).

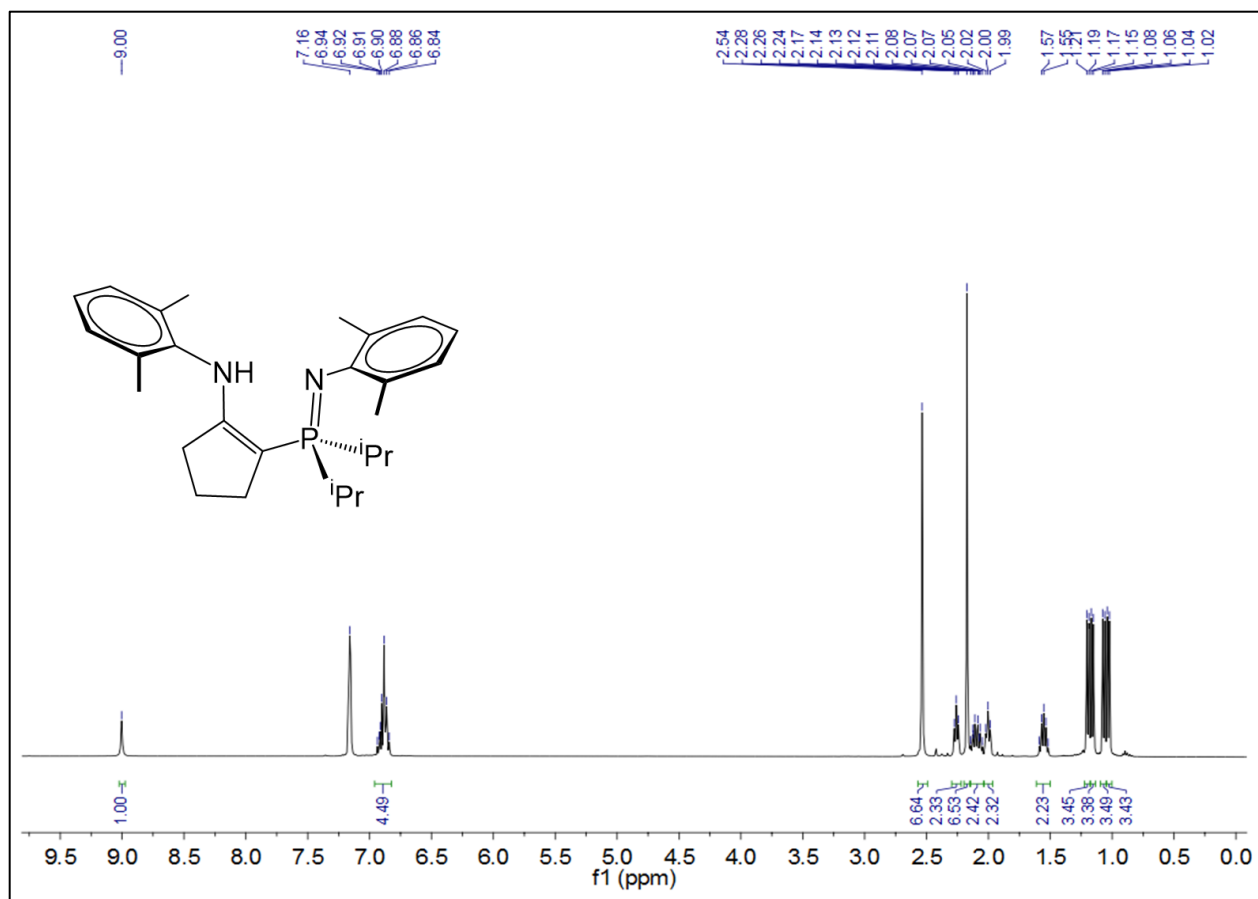


Figure S6: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DMP,DMP}}]\text{H}$ **2b** (400 MHz, d_6 -benzene, 298 K).

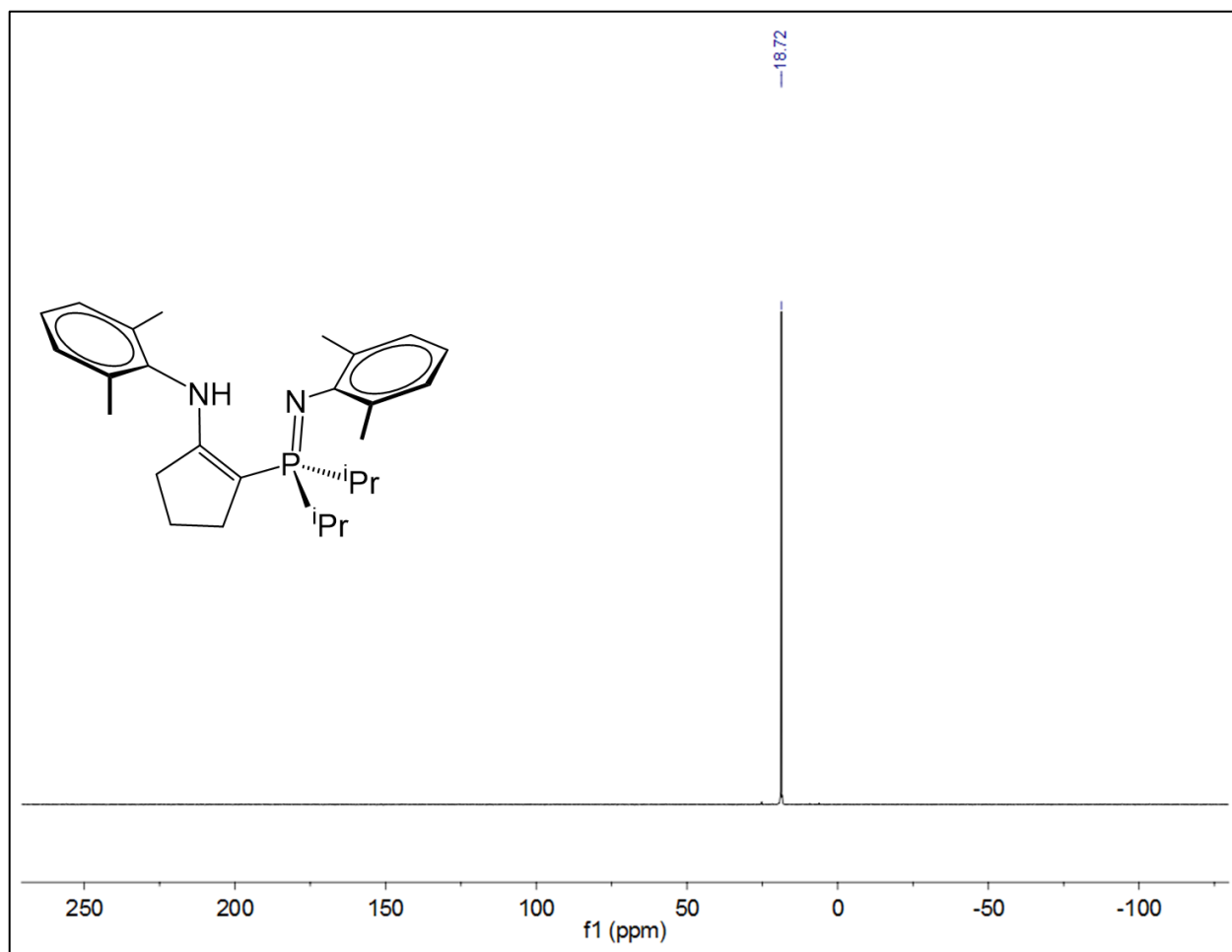


Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5}\text{NpN}^{\text{DMP,DMP}}]\text{H } \mathbf{2b}$ (121 MHz, d_6 -benzene, 298 K).

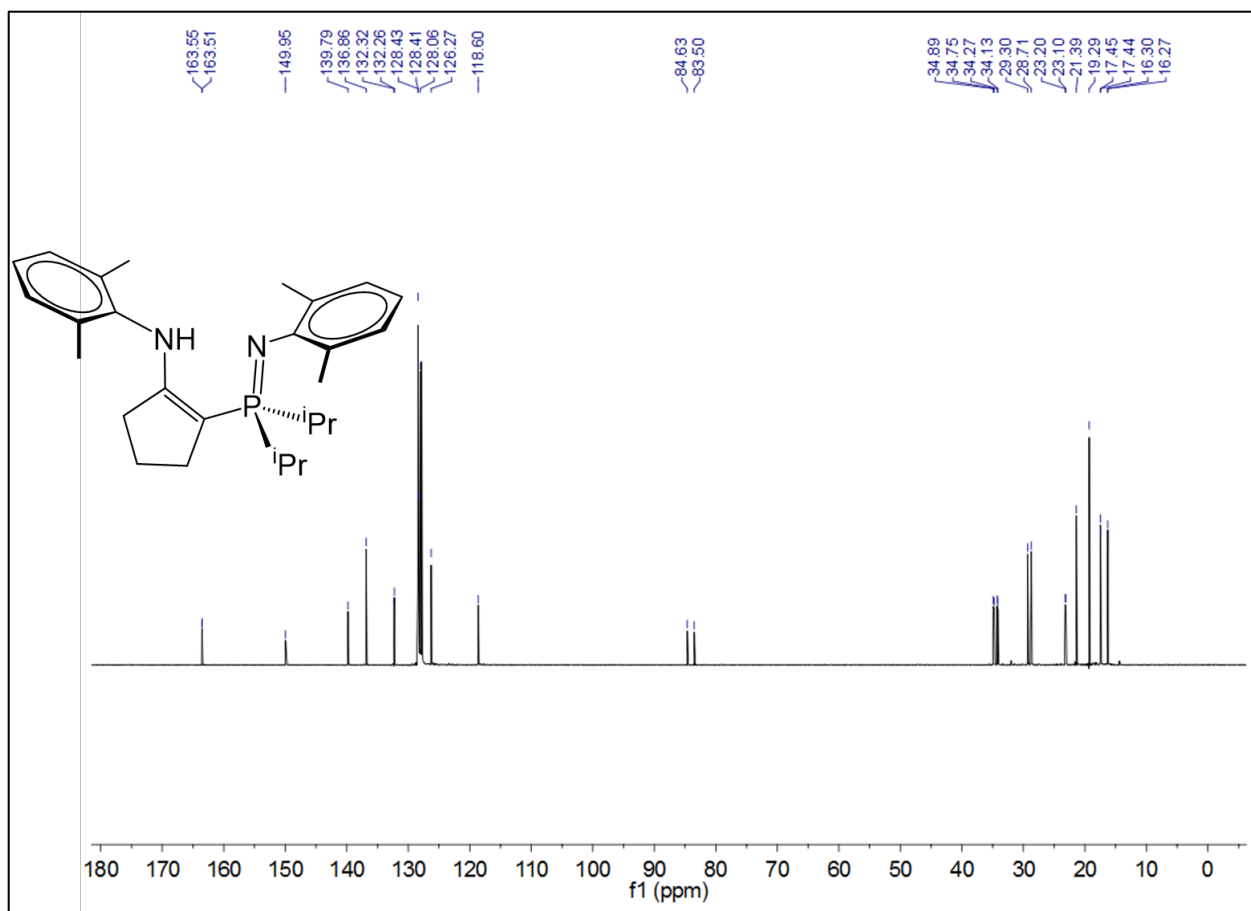


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DMP},\text{DMP}}]\text{H } \mathbf{2b}$ (101 MHz, d_6 -benzene, 298 K).

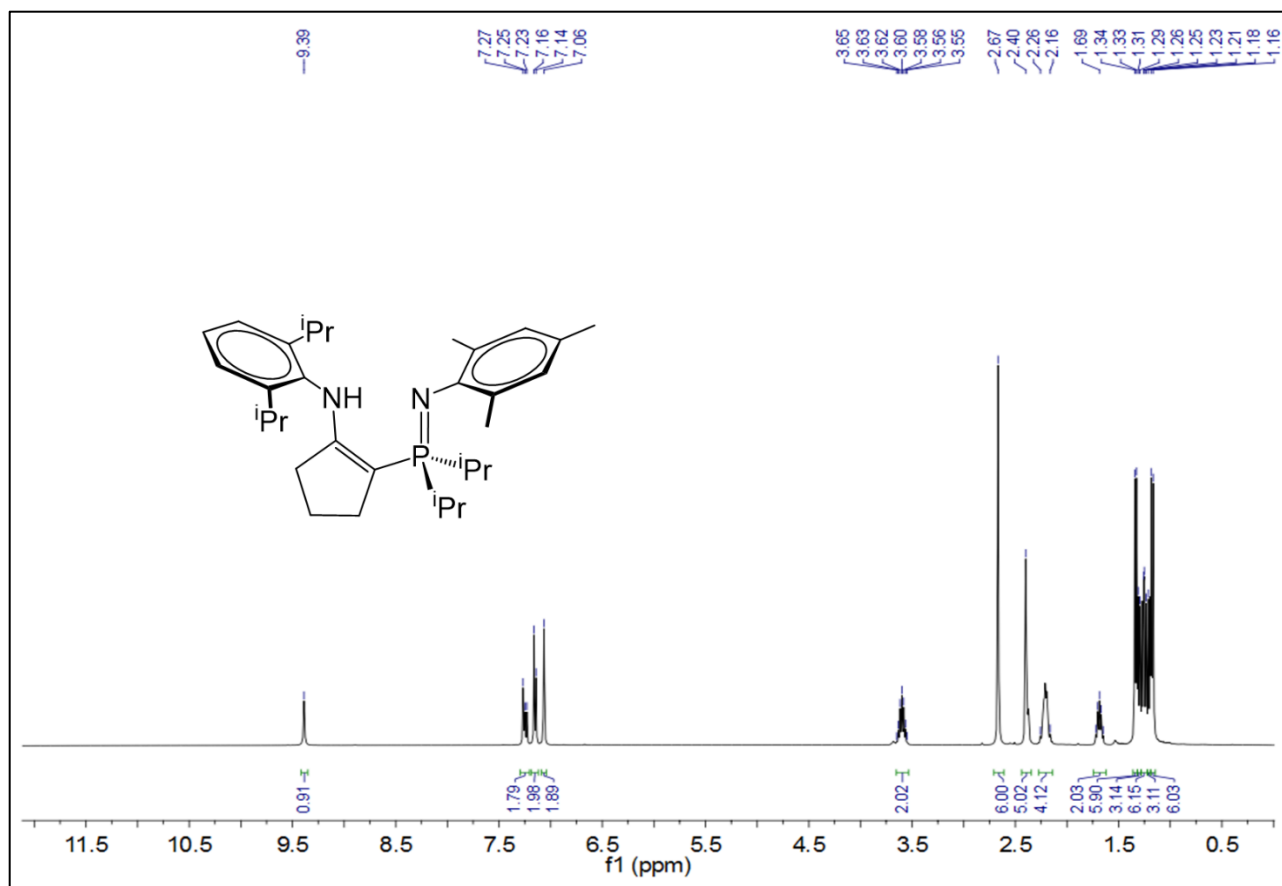


Figure S9: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,Mes}}]\text{H } \mathbf{2c}$ (400 MHz, d_6 -benzene, 298 K).

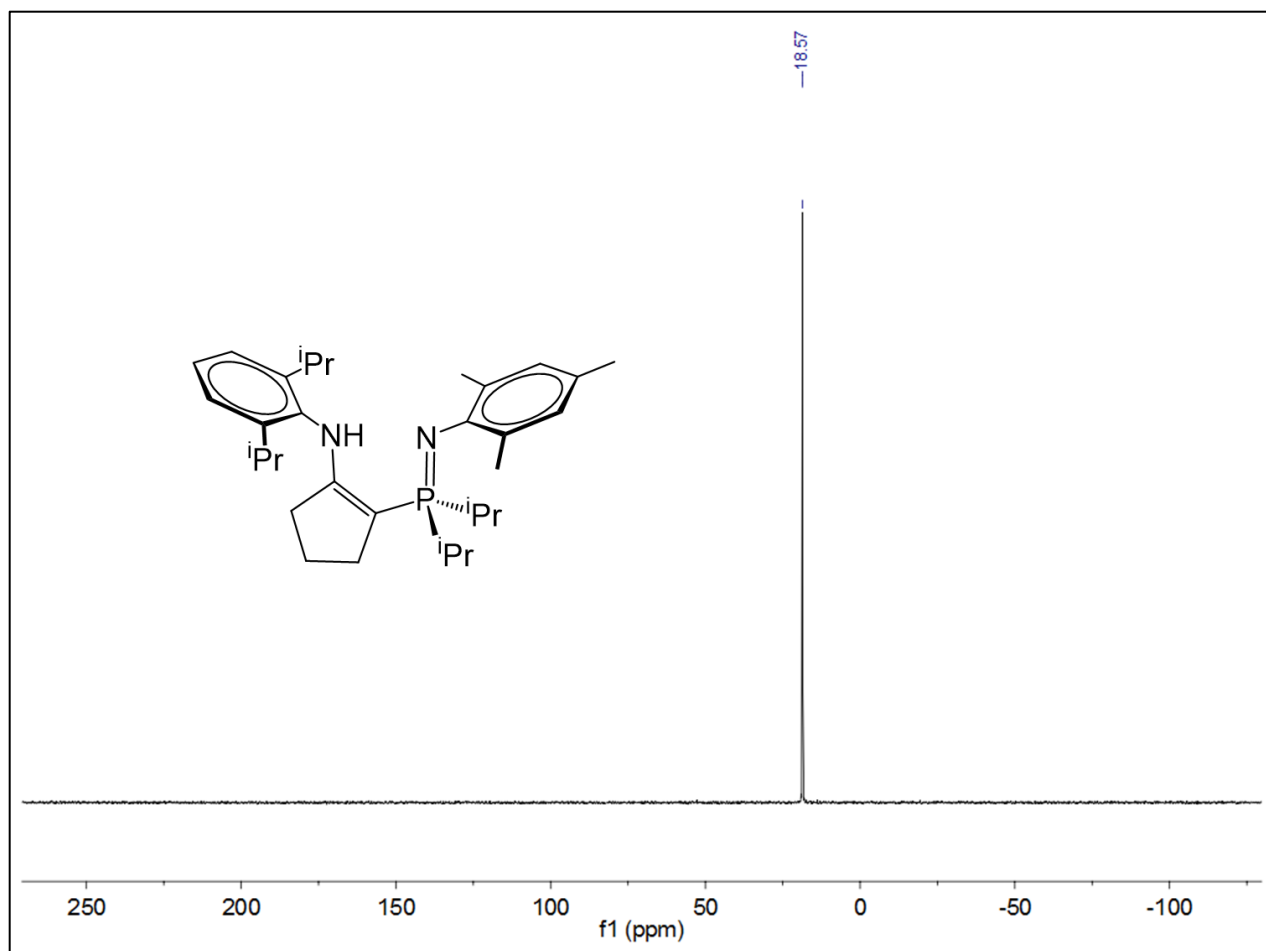


Figure S10: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5NpN}^{\text{DIPP,Mes}}]\text{H}$ **2c** (121 MHz, d_6 -benzene, 298 K).

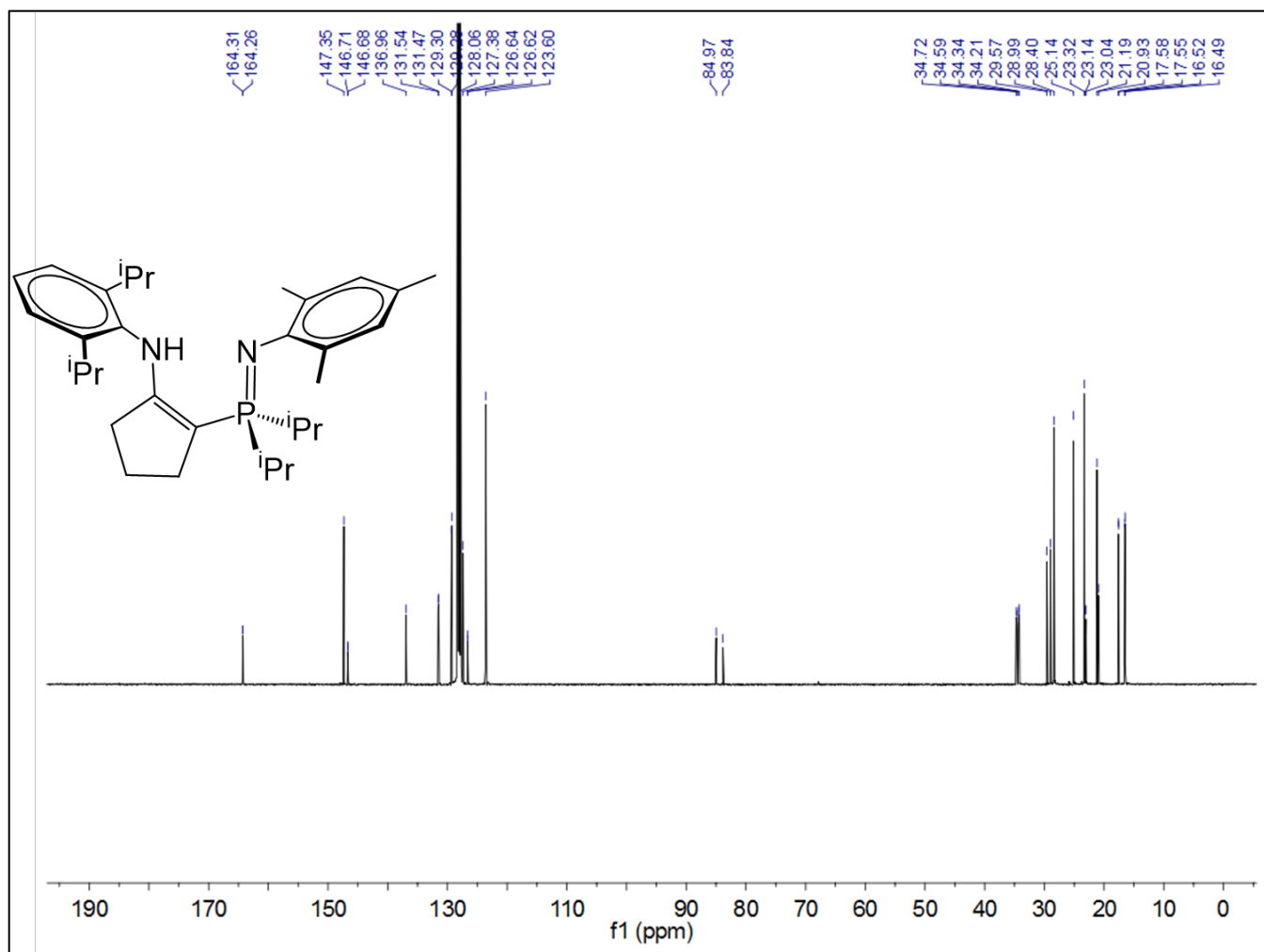


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,Mes}}]\text{H } \mathbf{2c}$ (101 MHz, d_6 -benzene, 298 K).

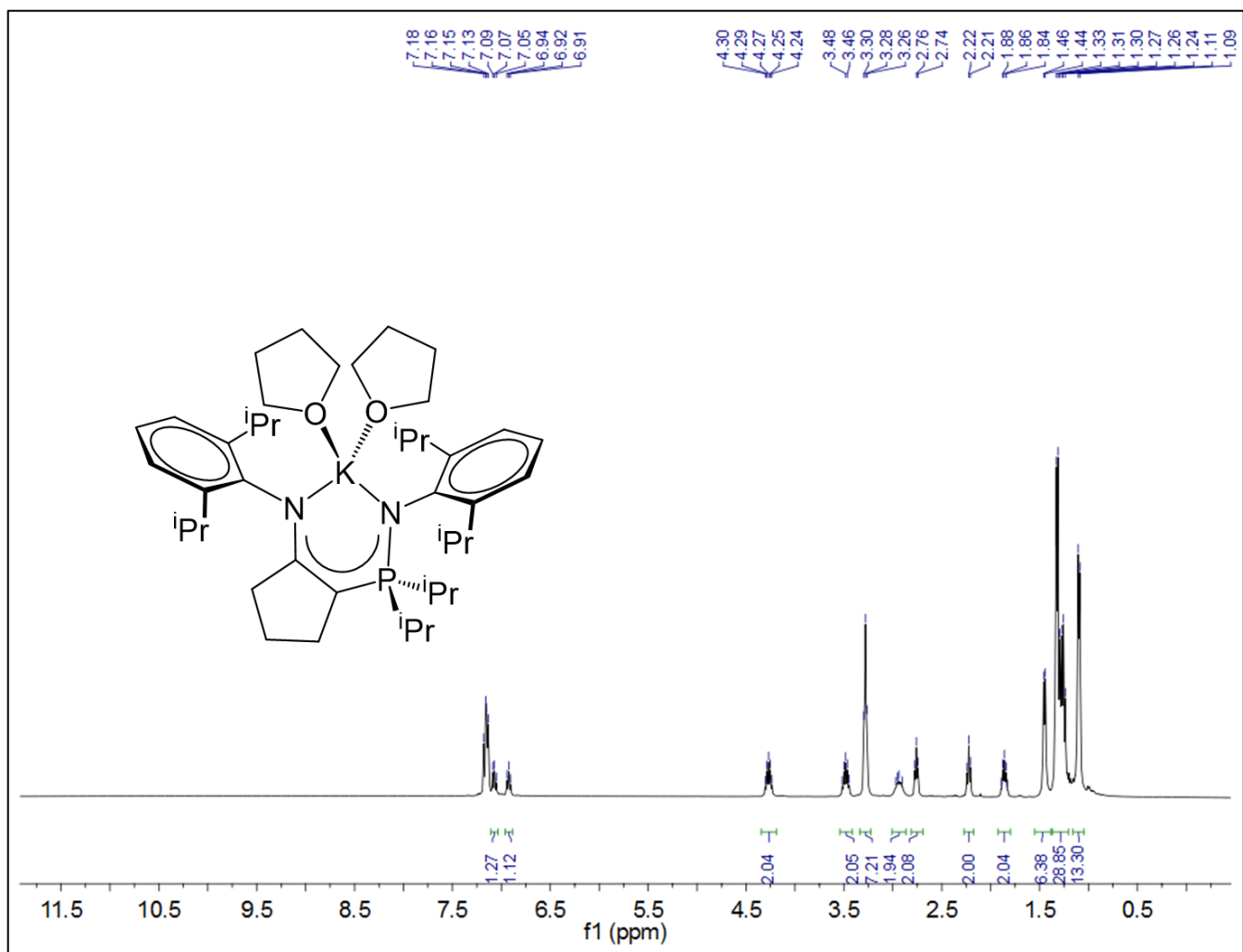


Figure S12: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,DIPP}}]\text{K}(\text{THF})_2$ **3a** (400 MHz, d_6 -benzene, 298 K).

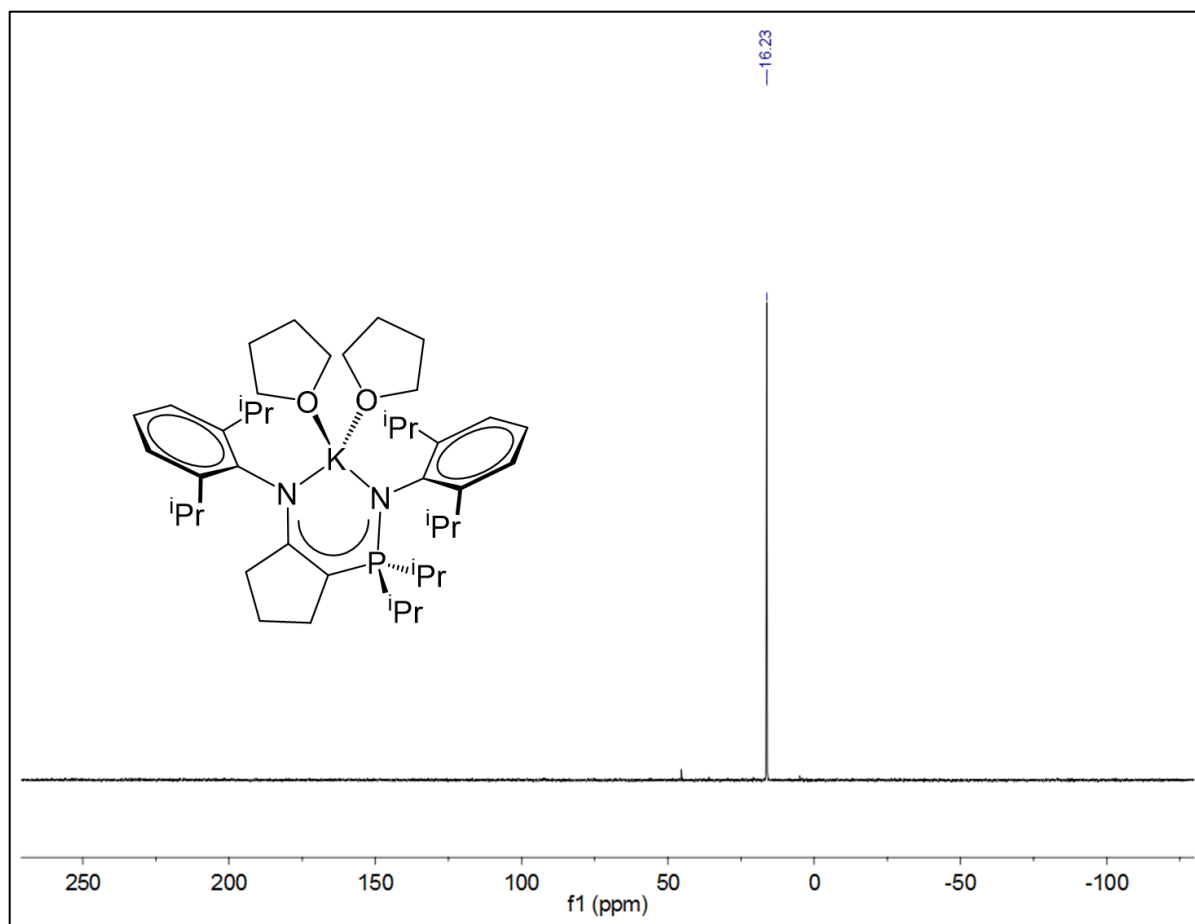


Figure S13: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5NpN}^{\text{DIPP,DIPP}}]\text{K}(\text{THF})_2$ **3a**
(161 MHz, d_6 -benzene, 298 K).

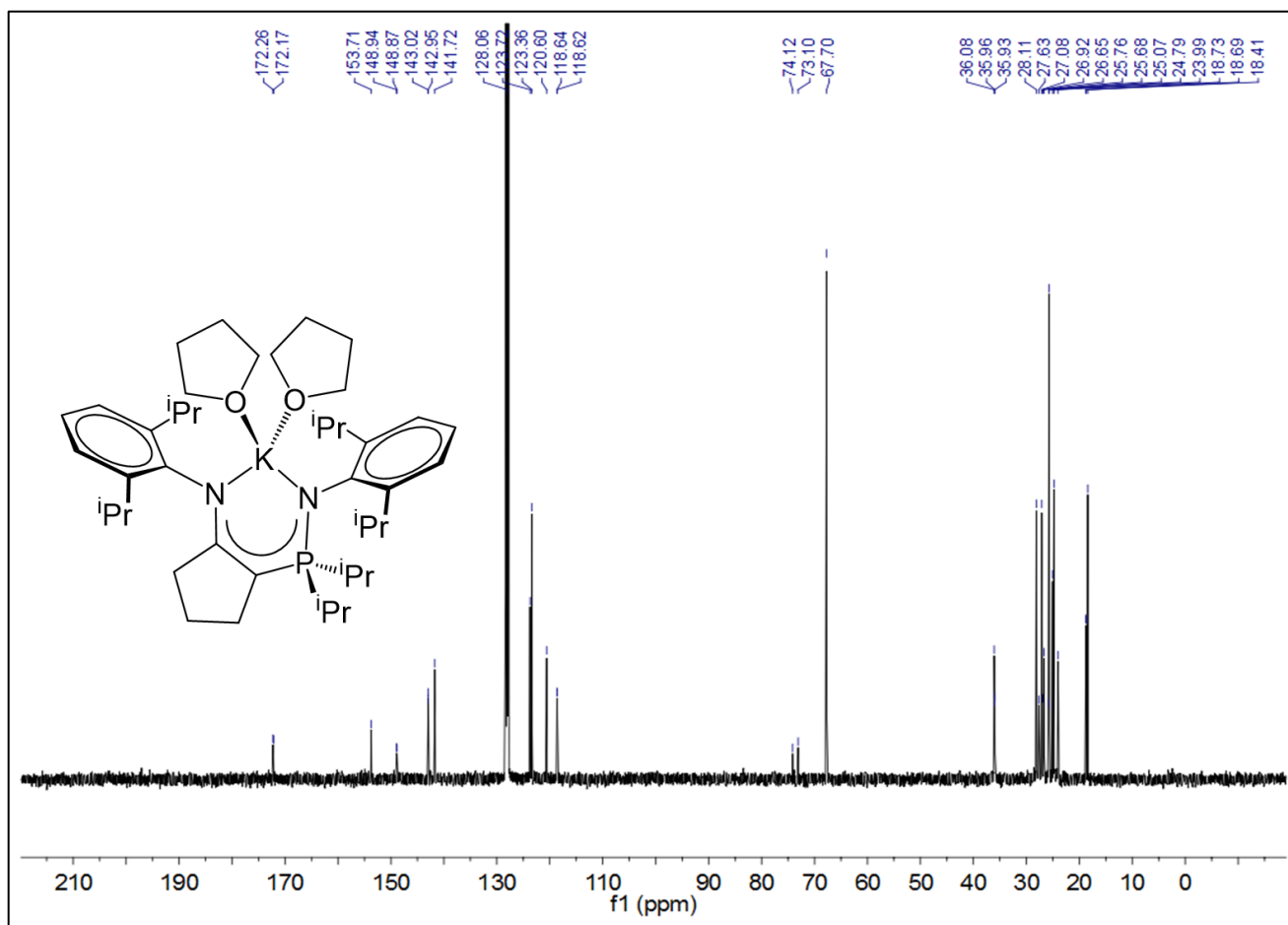


Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5NpN}^{\text{DIPP,DIPP}}]\text{K}(\text{THF})_2$ **3a**
(101 MHz, d_6 -benzene, 298 K).

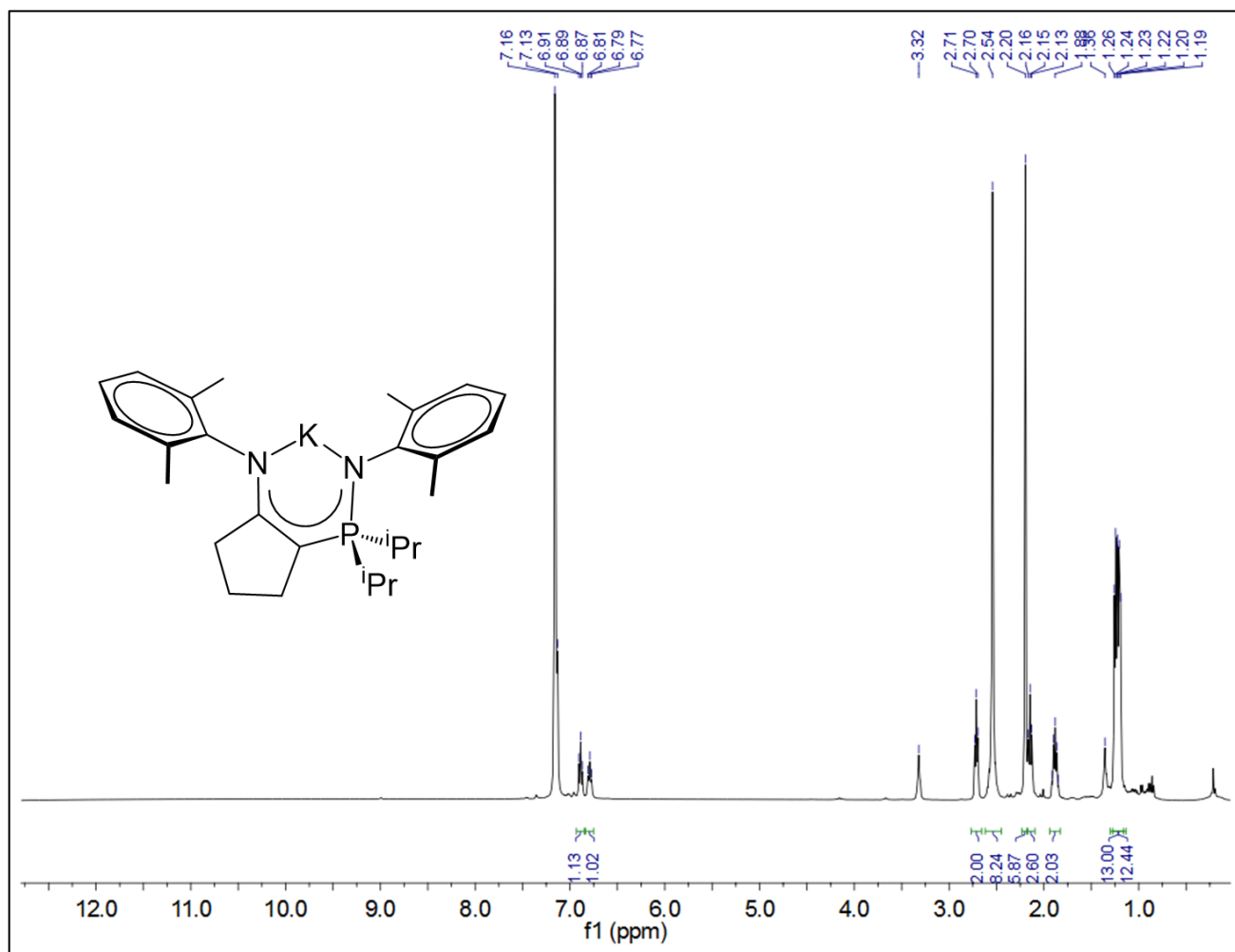


Figure S15: ¹H NMR spectrum for [^{CY5}NpN^{DMP,DMP}]**3b** (400 MHz, *d*₆-benzene, 298 K).

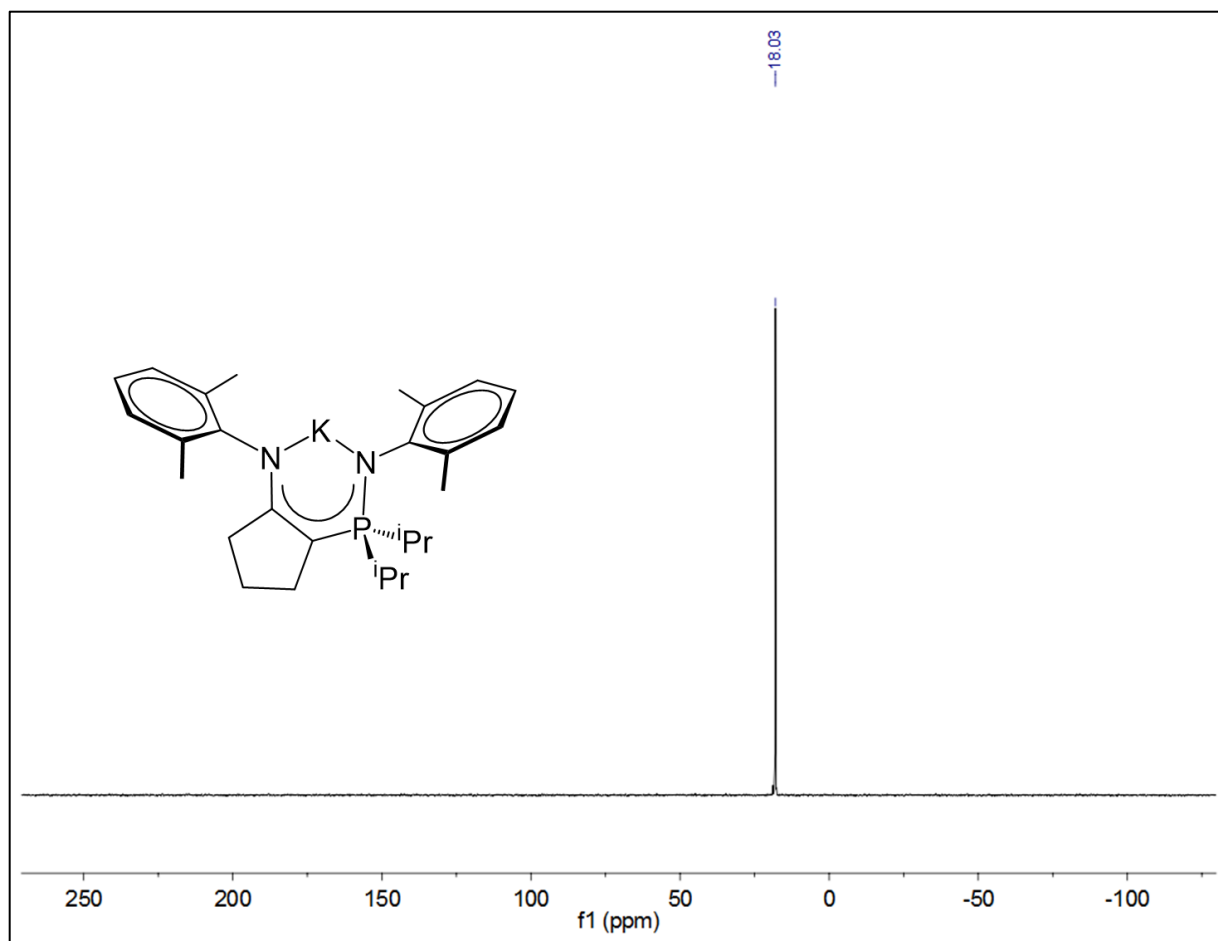


Figure S16: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5NpN}^{\text{DMP,DMP}}]\text{K}(\text{THF})_{0.25}$ **3b**
(161 MHz, d_6 -benzene, 298 K).

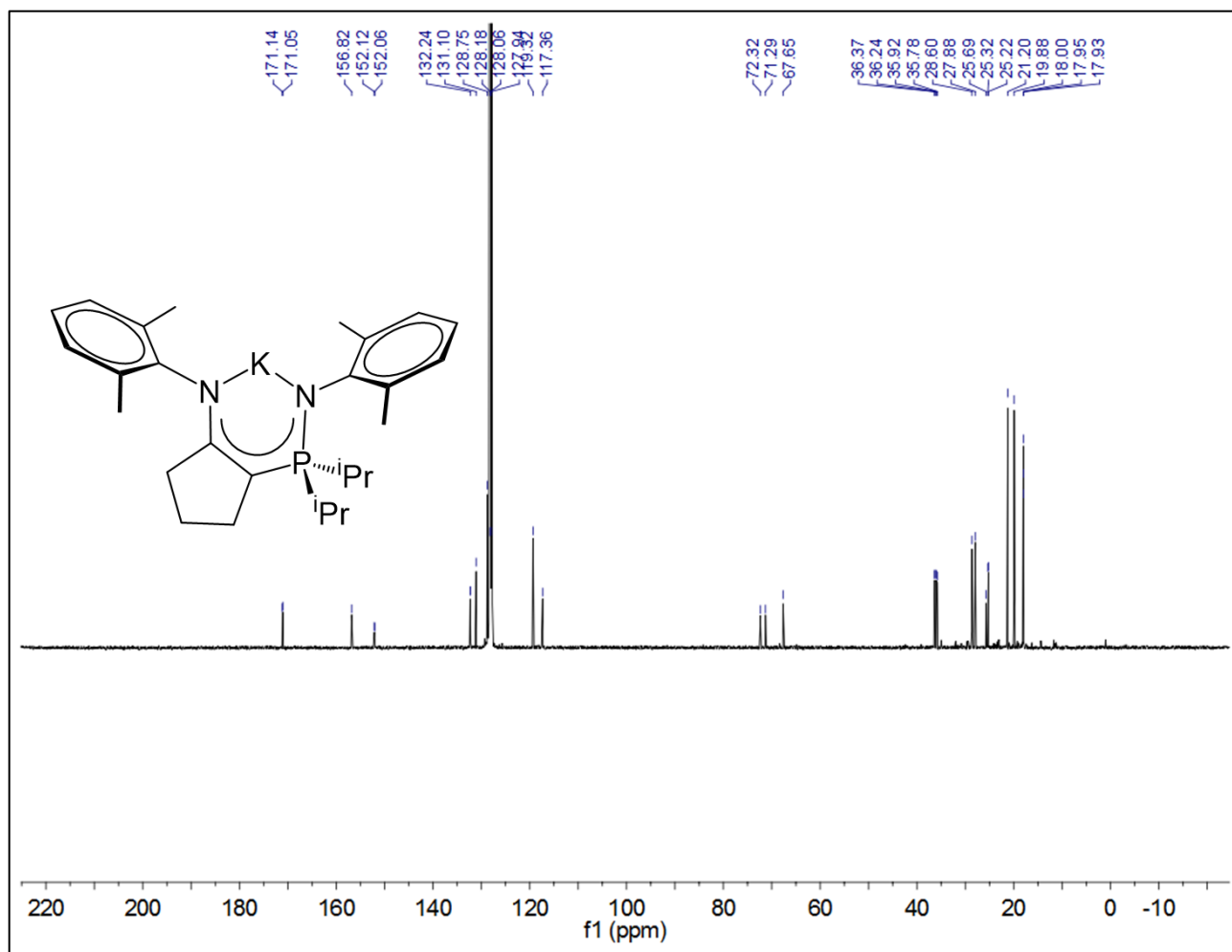


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DMP,DMP}}]\text{K}(\text{THF})_{0.25}$ **3b**
 (101 MHz, d_6 -benzene, 298 K).

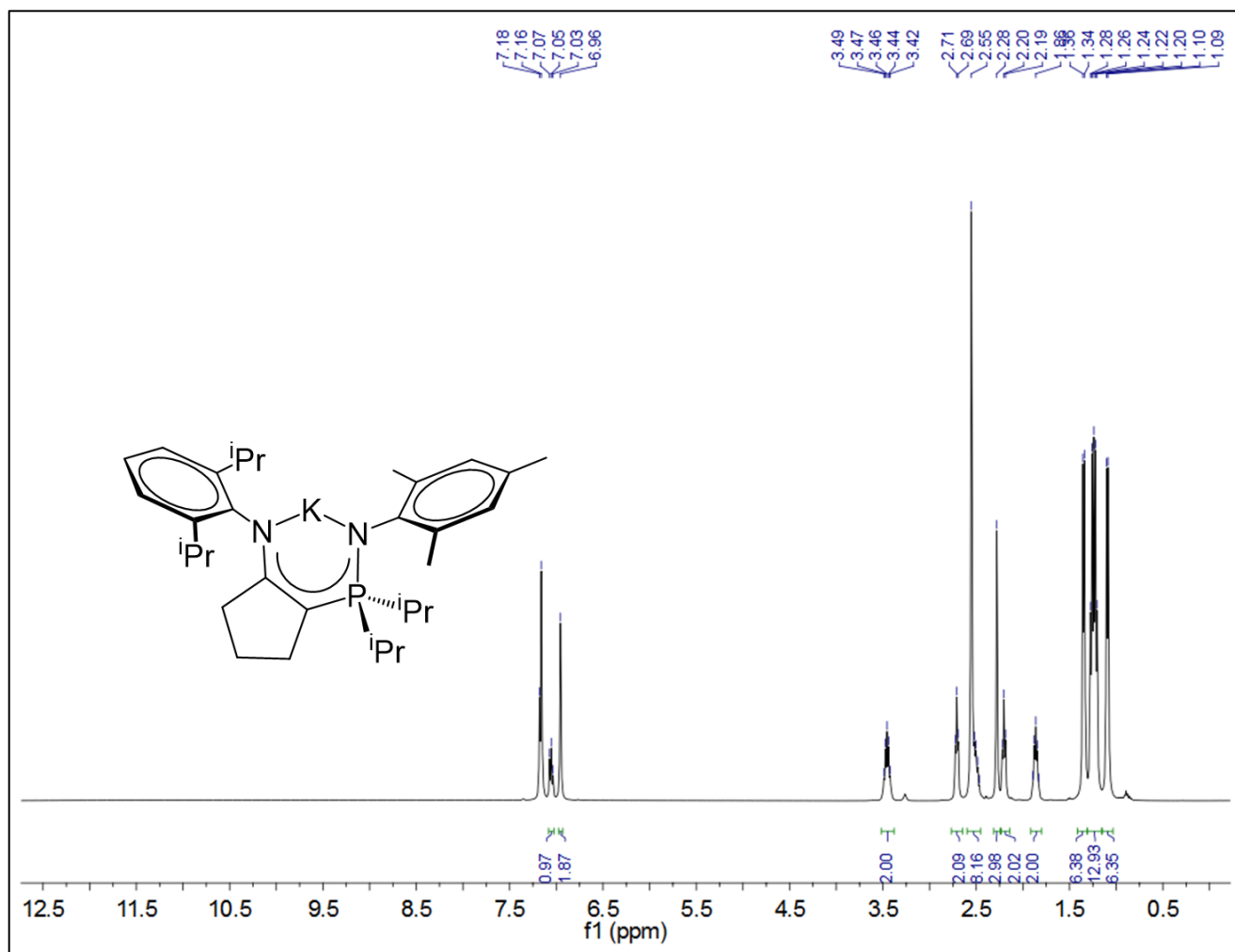


Figure S18: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,Mes}}]\text{K}$ **3c** (400 MHz, d_6 -benzene, 298 K).

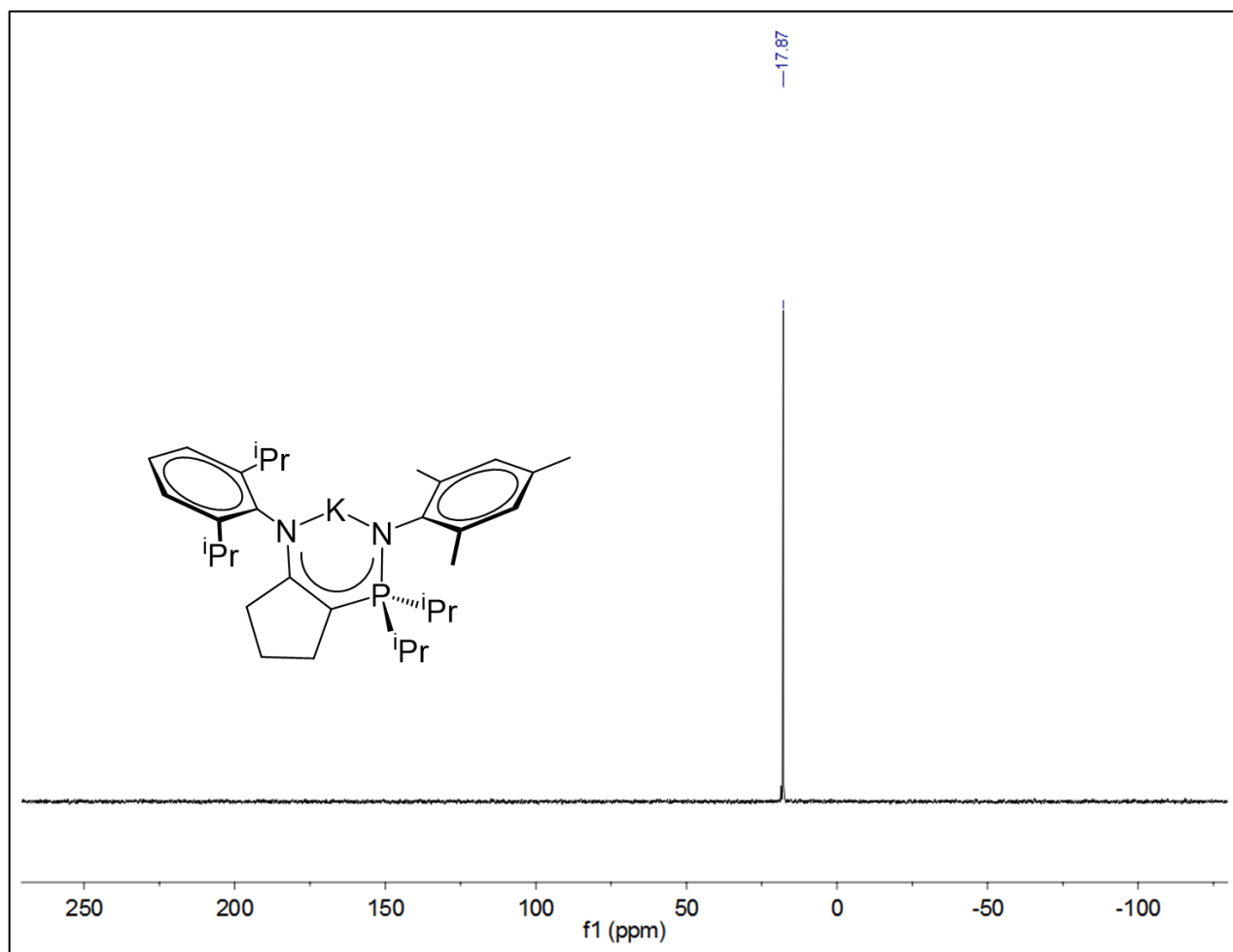


Figure S19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{CY5NpN}^{\text{DIPP,Mes}}\text{K}] \mathbf{3c}$ (121 MHz, d_6 -benzene, 298 K).

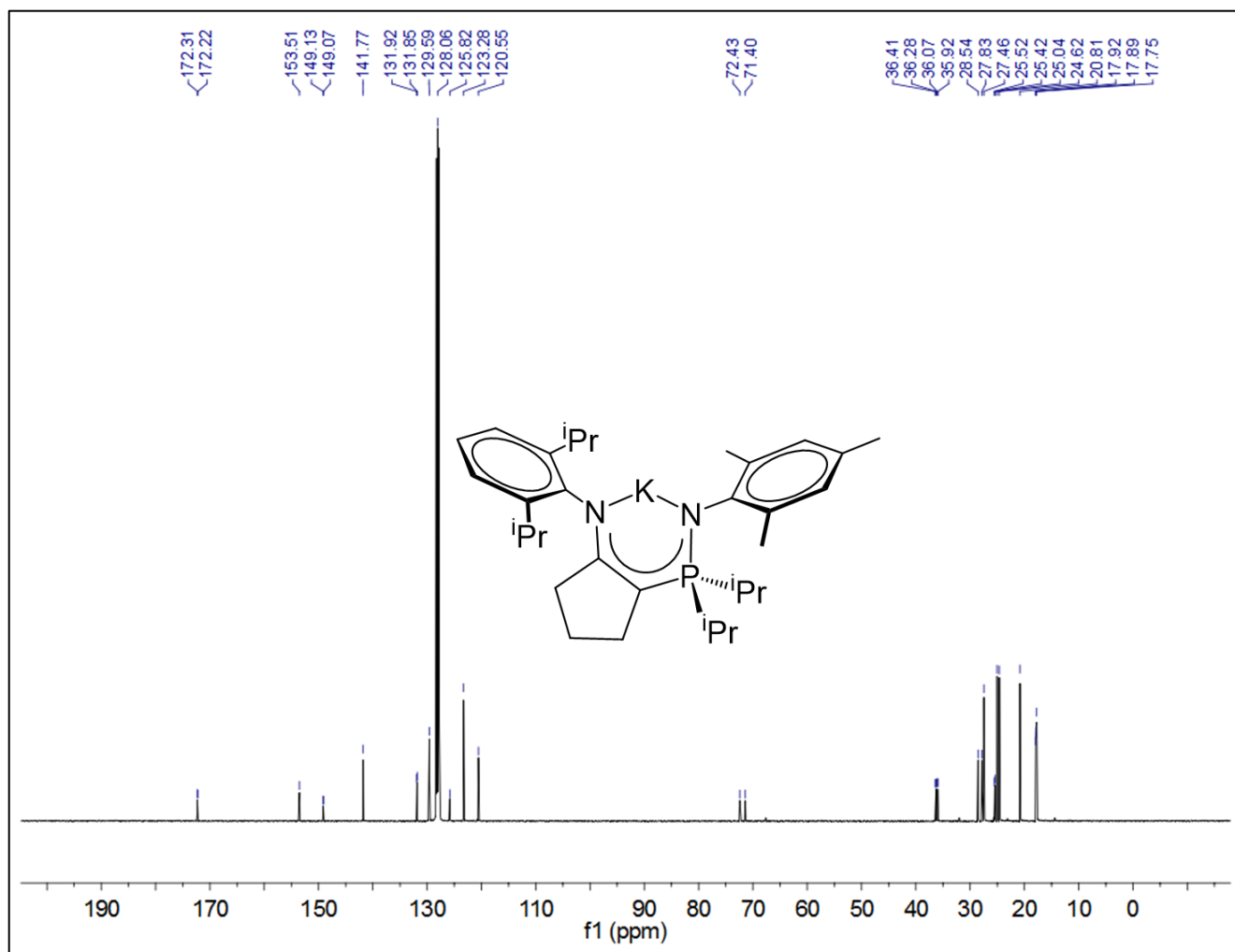


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,Mes}}]\text{K}$ 3c (101 MHz, d_6 -benzene, 298 K).

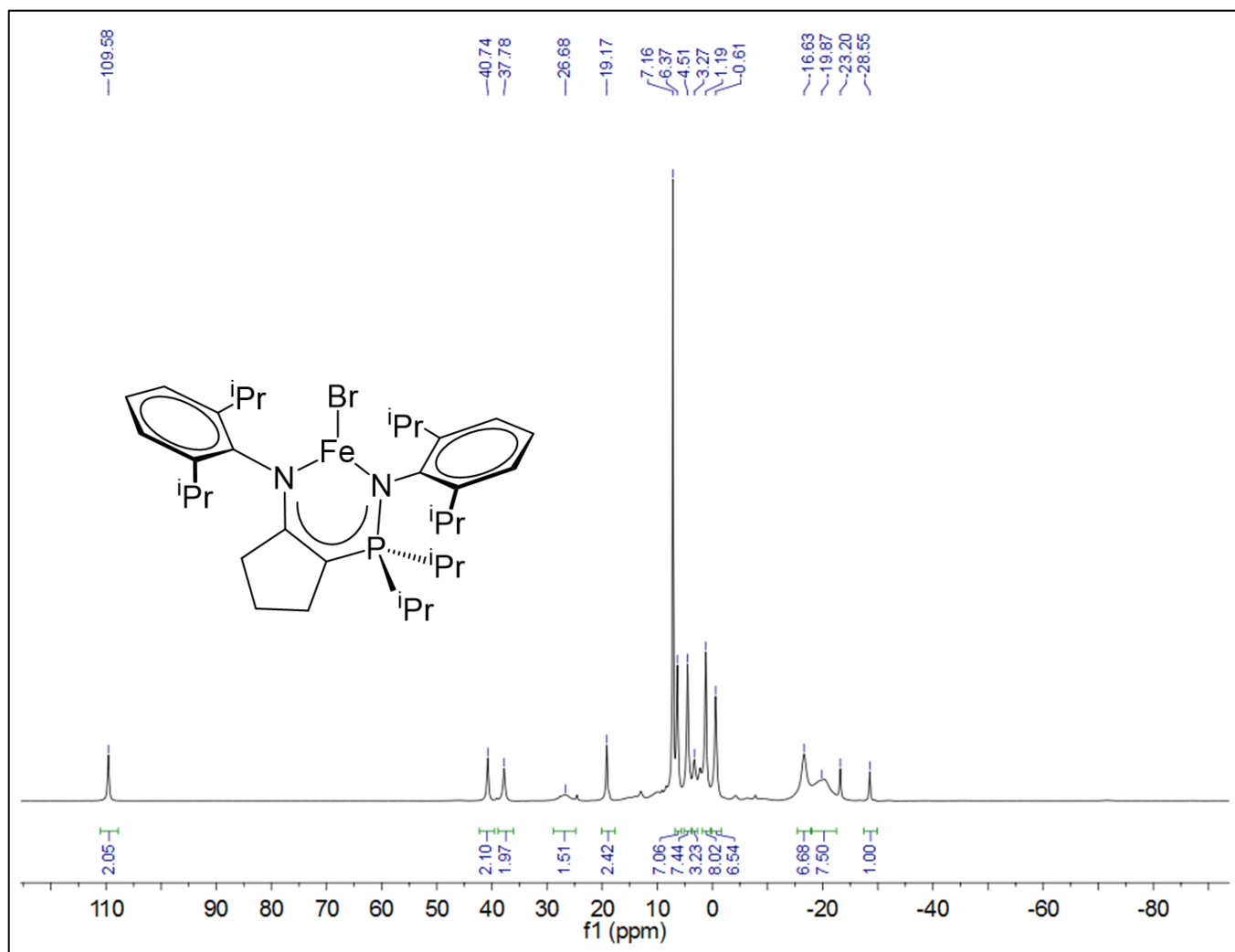


Figure S21: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP},\text{DIPP}}]\text{FeBr } \mathbf{4a}$ (300 MHz, d_6 -benzene, 298 K).

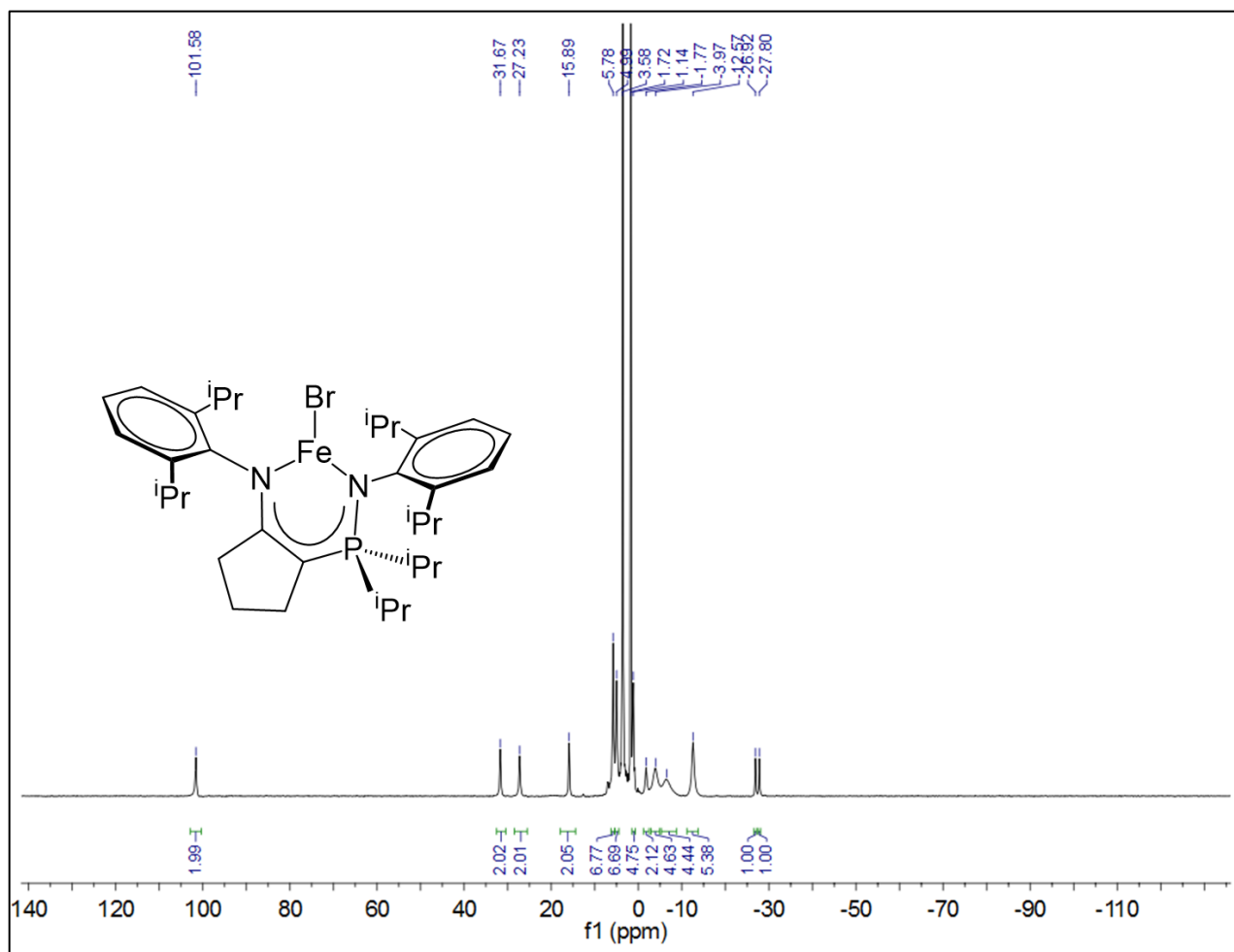


Figure S22: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,DIPP}}]\text{FeBr}$ **4a** (400 MHz, d_8 -THF, 298 K).

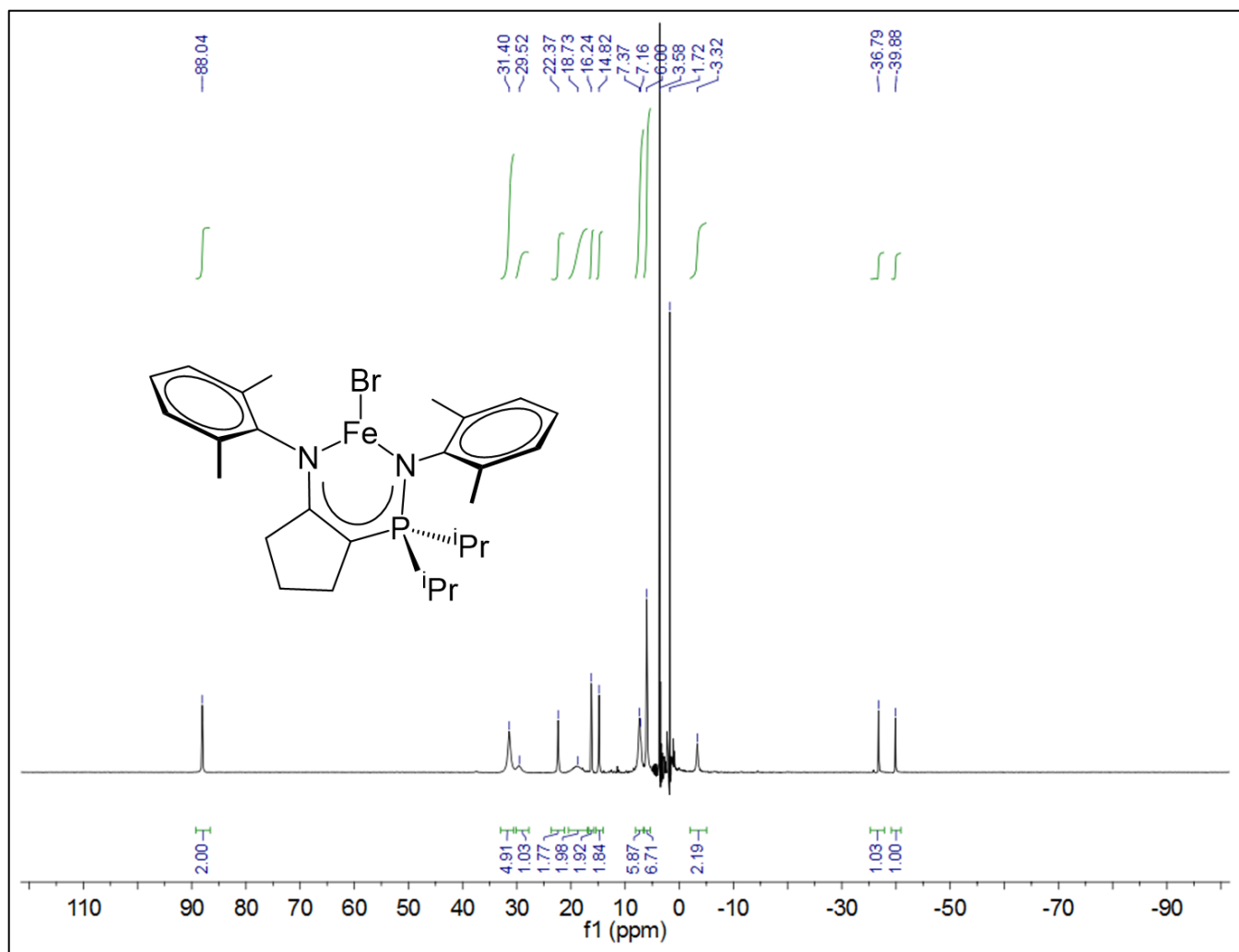


Figure S23: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DMP,DMP}}]\text{FeBr } \mathbf{4b}$ (400 MHz, d_8 -THF, 298 K).

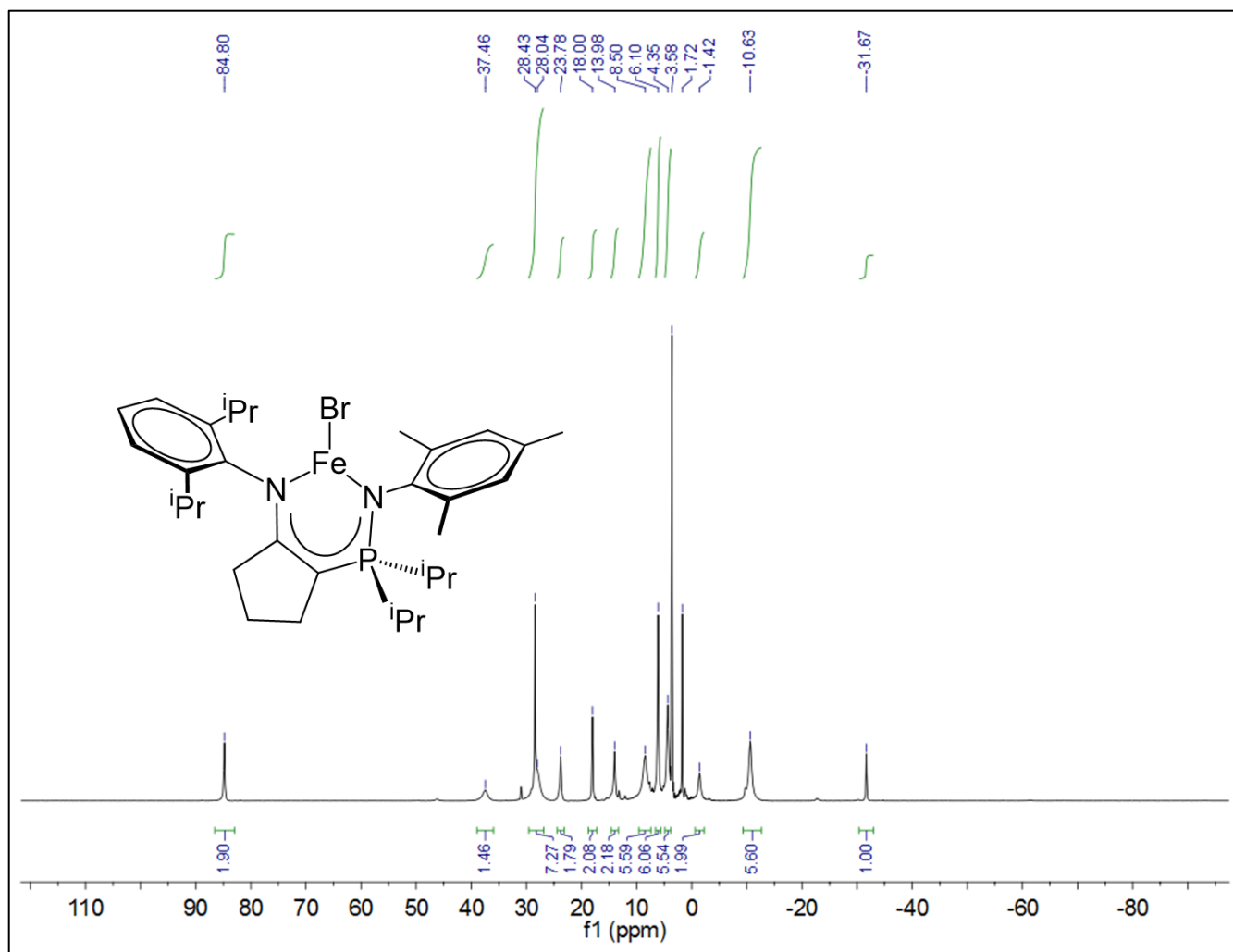


Figure S24: ^1H NMR spectrum for $(^{\text{CYP}}\text{NpN}^{\text{DIPP, Mes}})\text{FeBr}$ **5c** (300 MHz, d_8 -THF, 298 K).

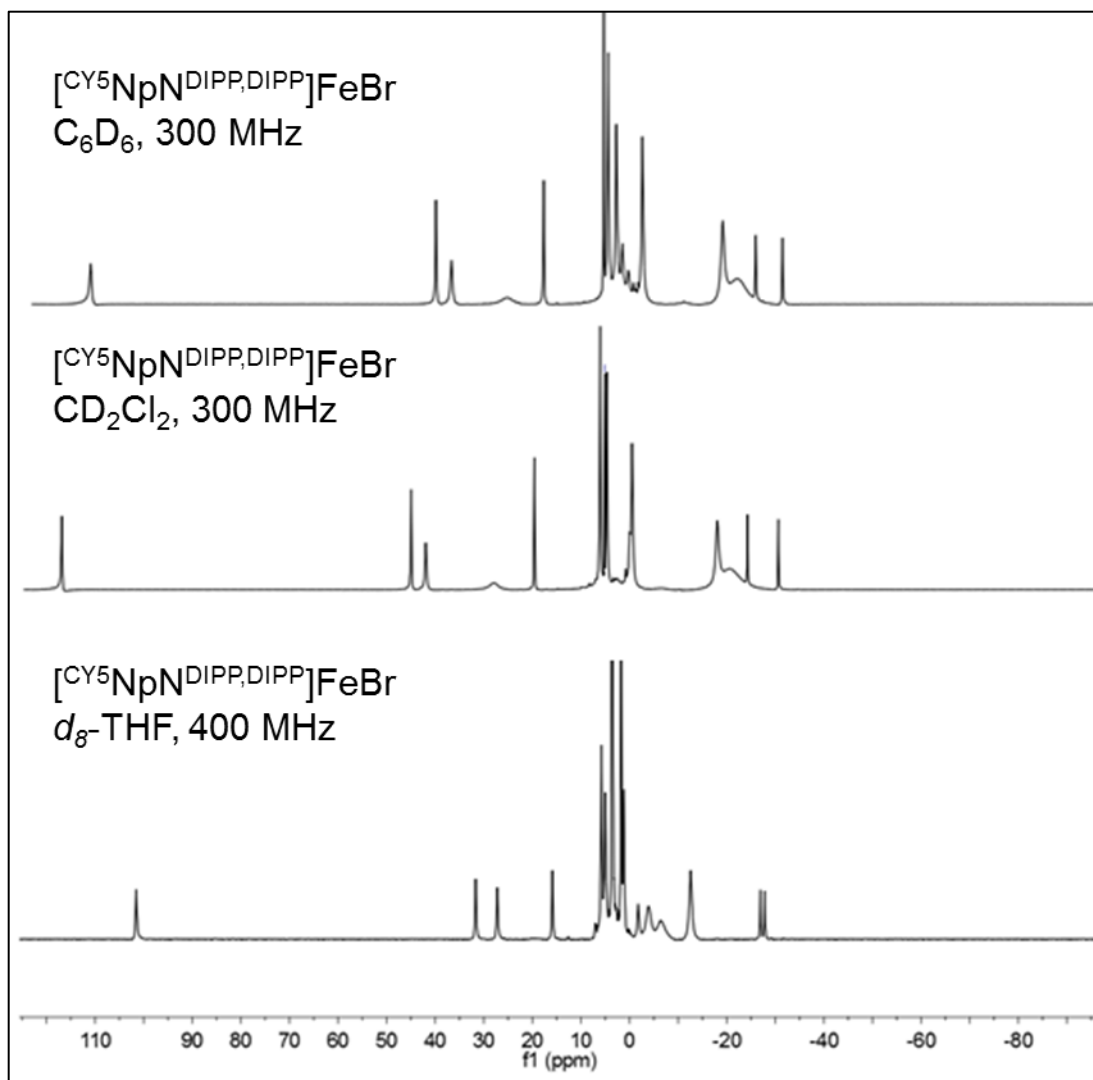


Figure S25: ^1H NMR spectra for $[\text{CY5NpN}^{\text{DIPP,DIPP}}]\text{FeBr}$ **4a** in d_6 -benzene (top), d_2 -DCM (middle), and d_8 -THF (bottom).

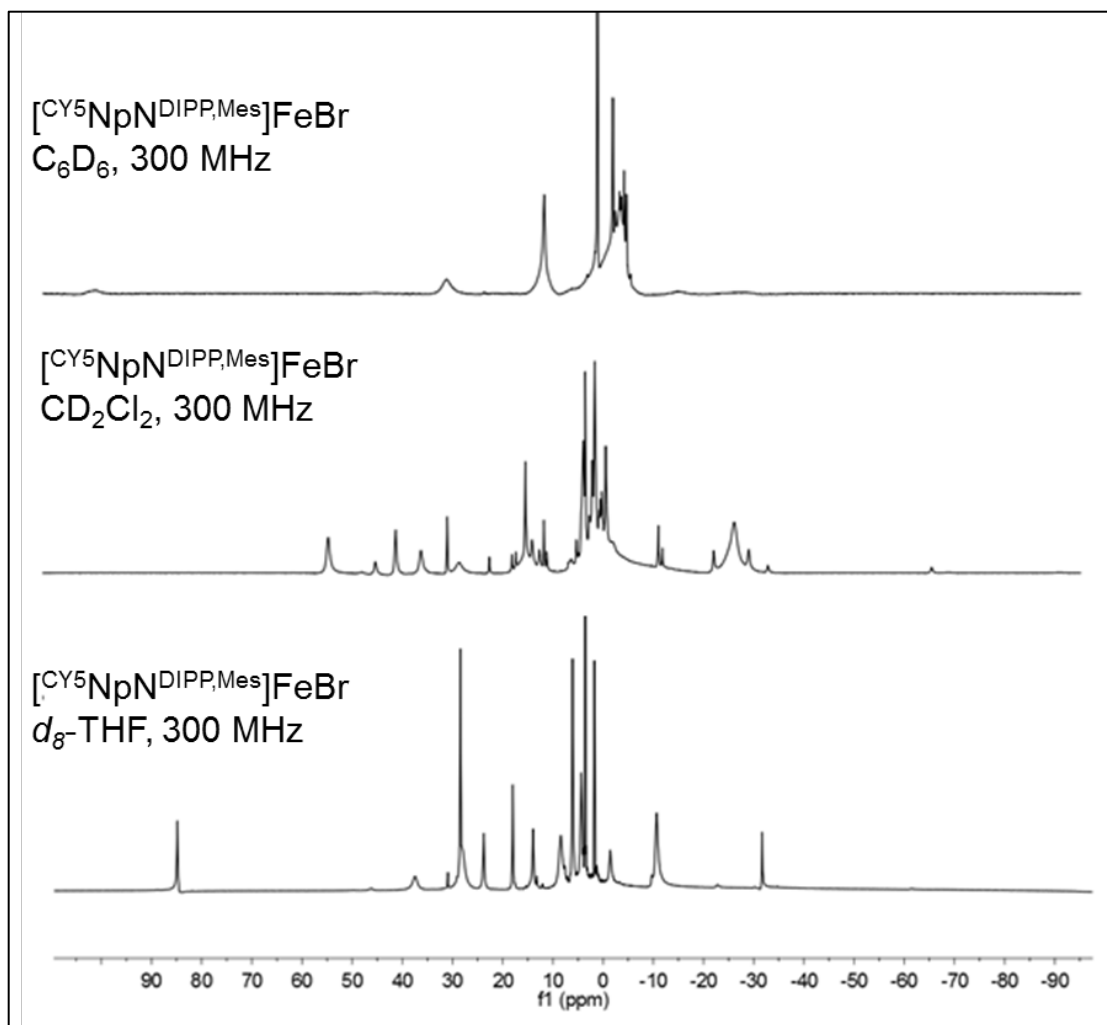


Figure S26: ¹H NMR spectra for $[\text{CY5NpNDIPP,Mes}]\text{FeBr}$ **4c** in d_6 -benzene (top), d_2 -DCM, (middle) and d_8 -THF (bottom).

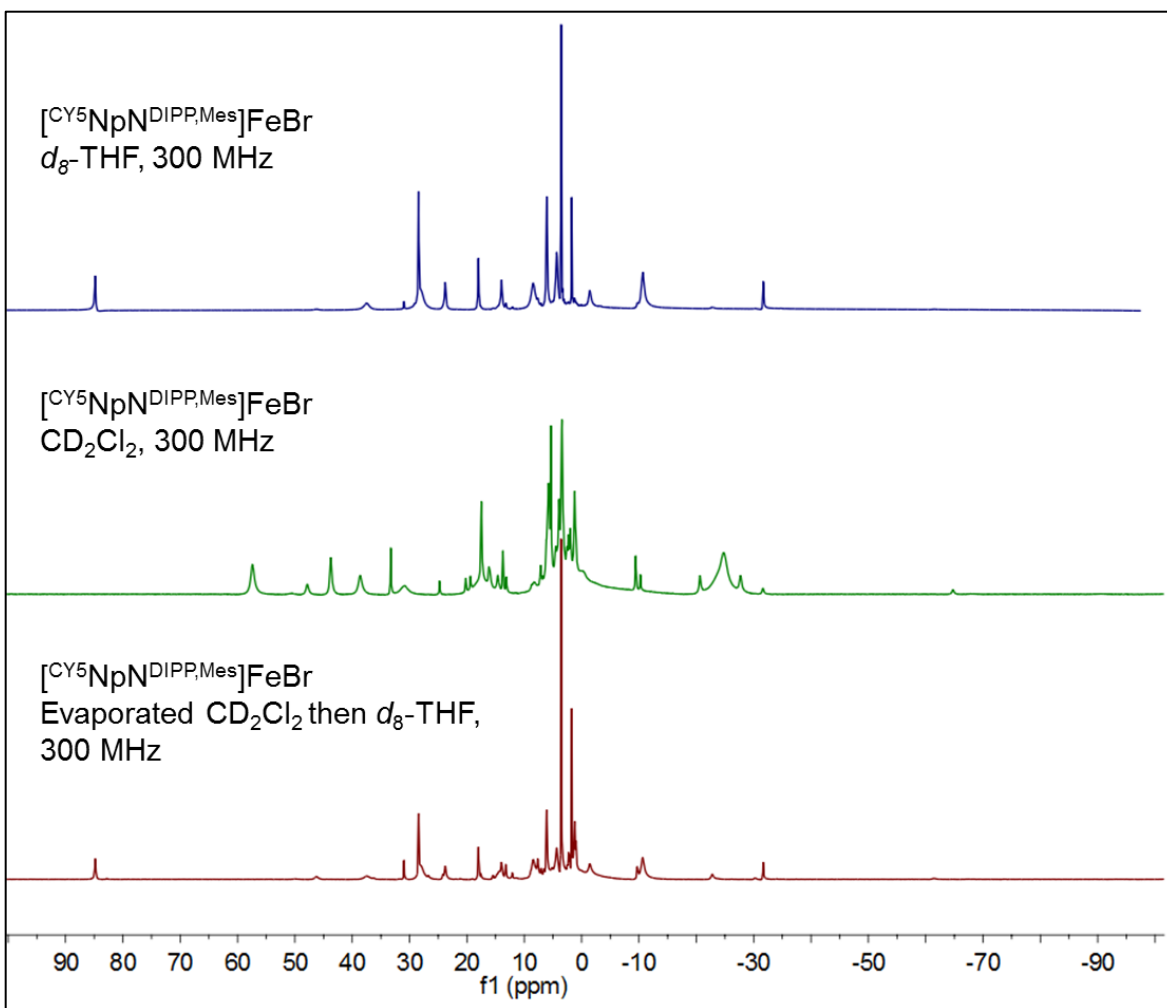


Figure S27: ^1H NMR spectra for $[\text{CY}^5\text{NpN}^{\text{DIPP,Mes}}]\text{FeBr}$ **4c** in d_8 -THF (top), d_2 -DCM (middle), and the d_2 -DCM sample which was evaporated under vacuum and redissolved in d_8 -THF (bottom).

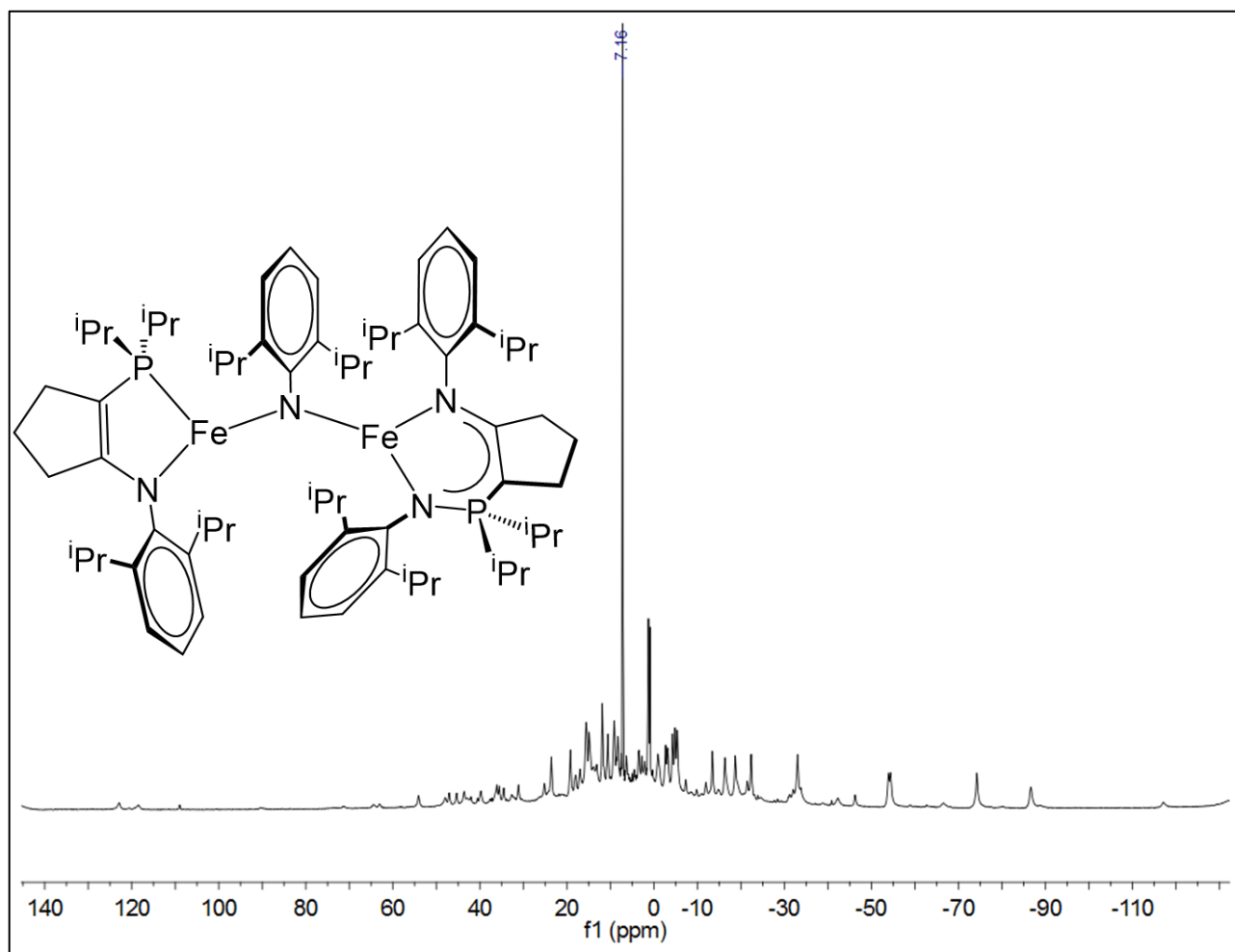


Figure S28: ^1H NMR spectrum for $[\text{CY}^5\text{NpN}^{\text{DIPP,DIPP}}]\text{Fe}(\mu\text{-N-DIPP})\text{Fe}[\text{CY}^5\text{NP}^{\text{DIPP}}]$ **6**
 (300 MHz, d_6 -benzene, 298 K).

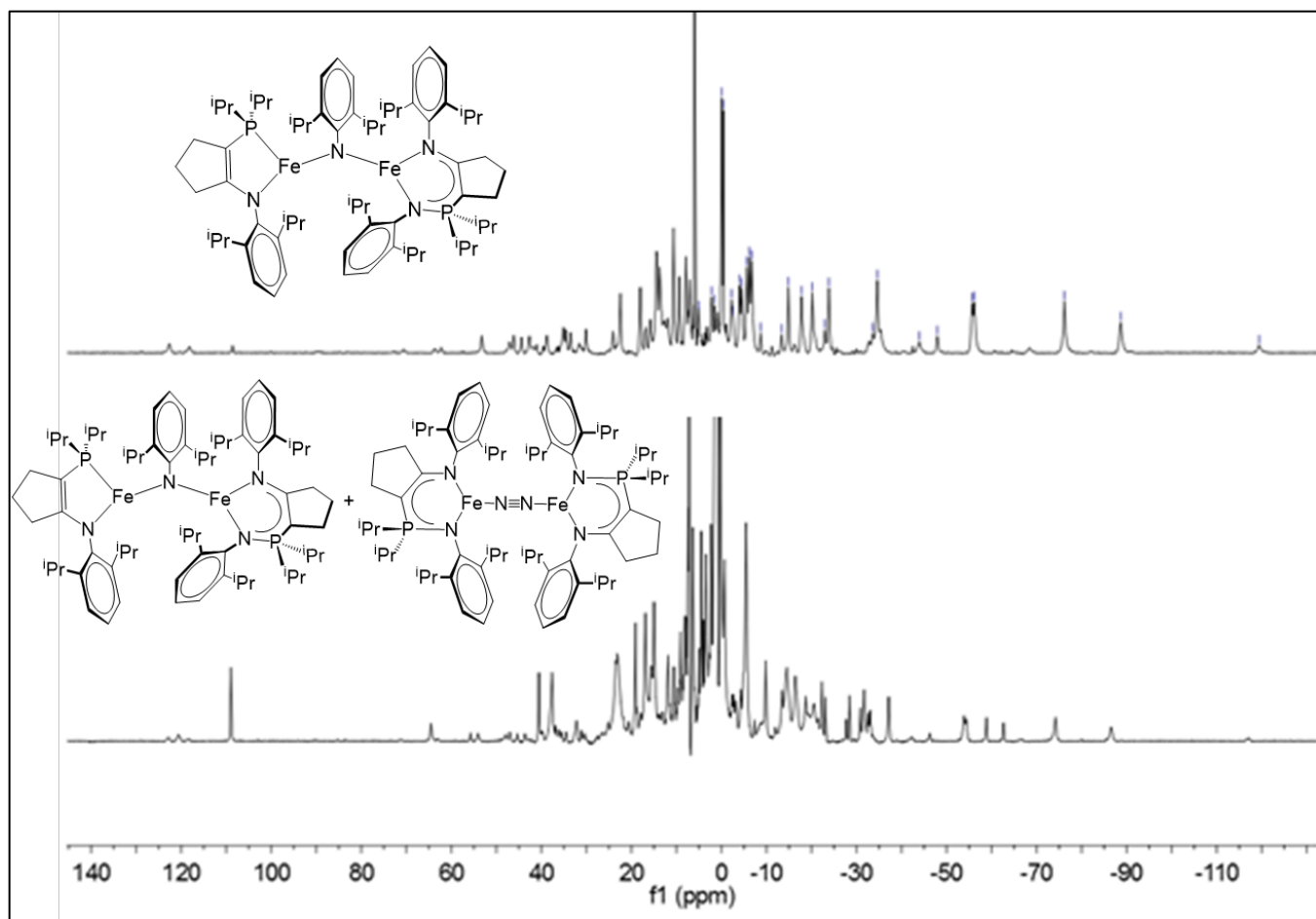


Figure S29: ^1H NMR spectra for the mixture of products obtained from the reduction of $(^{\text{CYP}}\text{NpN}^{\text{DIPP,DIPP}})\text{FeBr}$ **5a** with KC_8 (bottom) and $(^{\text{CYP}}\text{NpNFe}(\mu\text{-N-DIPP})\text{FeNP}^{\text{CYP}})$ **11** (top) (300 MHz, d_6 -benzene, 298 K).

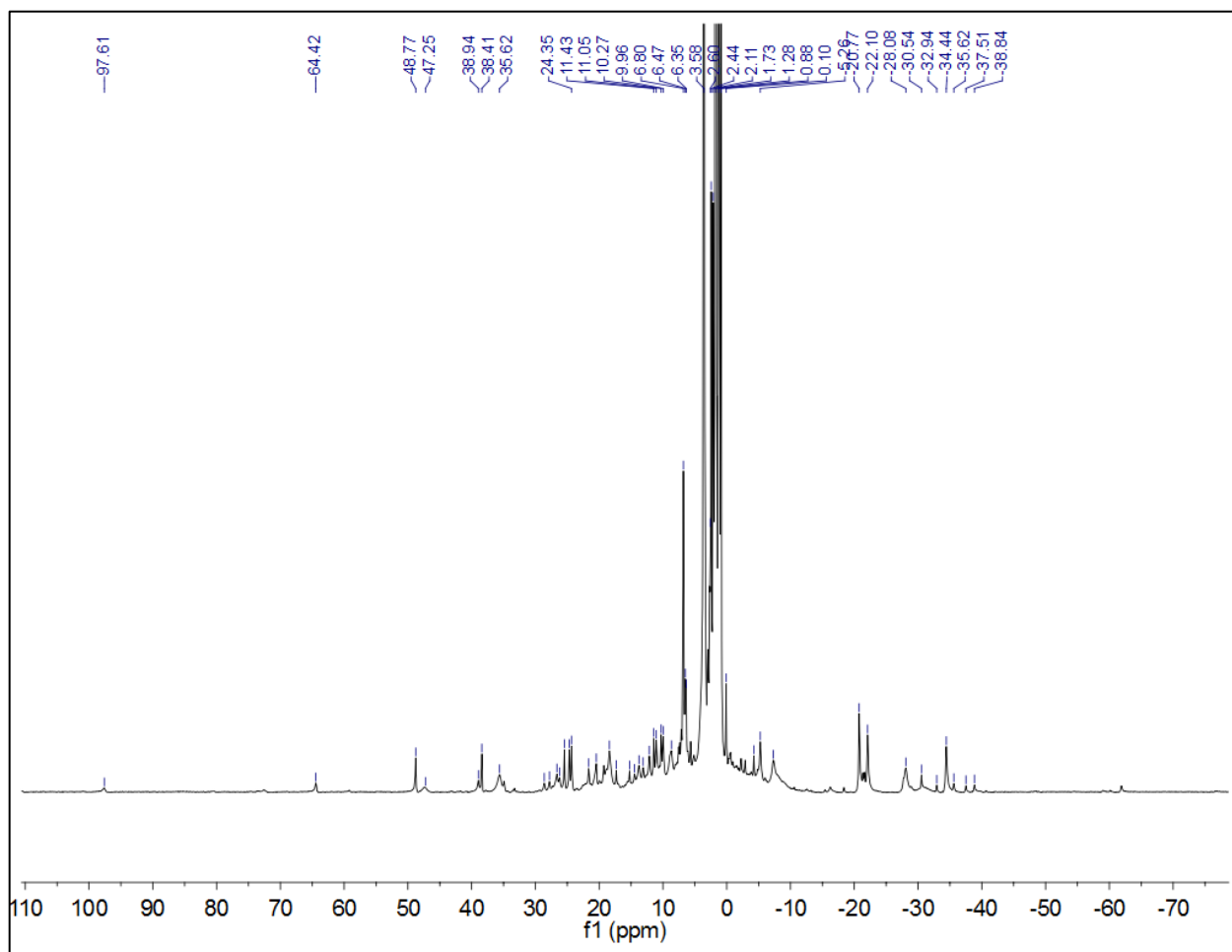


Figure S30: ^1H NMR for product mixture that a crystal of $([\text{CY}^5\text{NpN}^{\text{DMP,DMP}}][\text{CY}^5\text{NP}]\text{Fe})$ (5b) was picked from (400 MHz, d_8 -THF, 298 K).

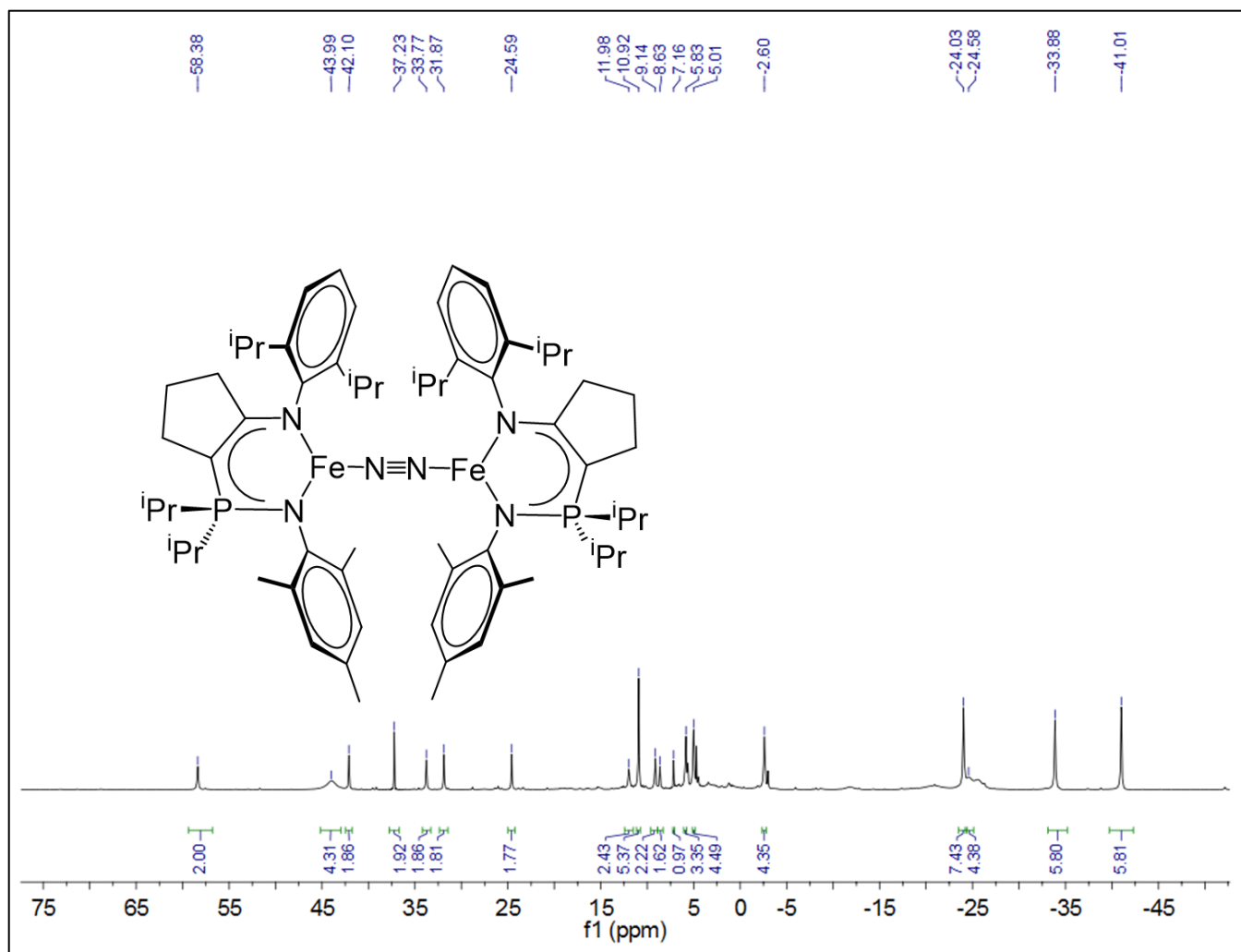


Figure S31: ^1H NMR spectrum for $[(\text{CYP}^{\text{NpN}}\text{N}^{\text{DIPP,Mes}})\text{Fe}]_2(\mu\text{-N}_2)$ (300 MHz, d_6 -benzene, 298 K).

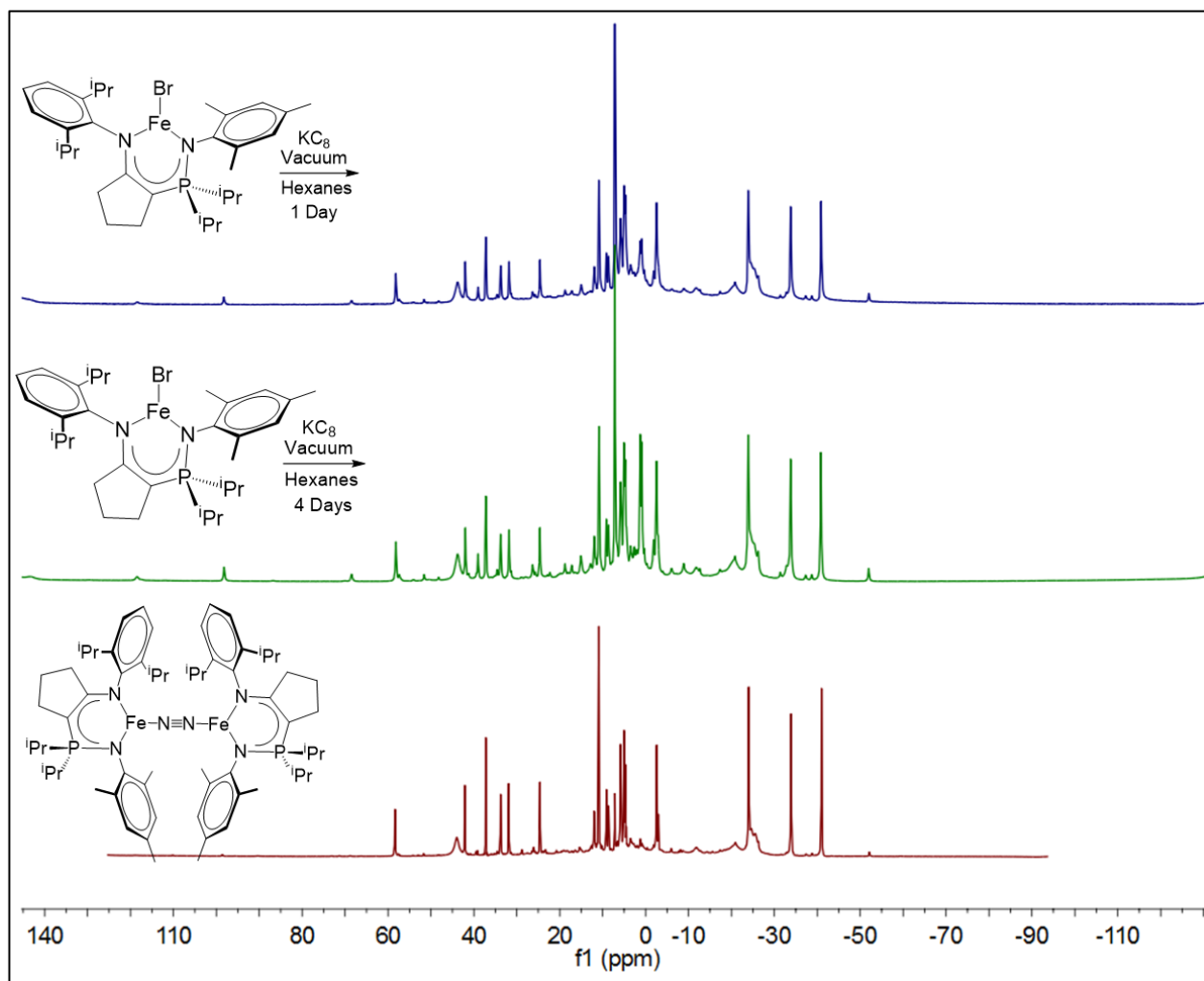


Figure S32: ^1H NMR spectra for the reduction of **5c** under vacuum for 1 day (top) the reduction of **5c** under vacuum for 4 days (middle), and the spectrum for $[(^{\text{CYP}}\text{NpN}^{\text{DIPP,Mes}})\text{Fe}]_2(\mu\text{-N}_2)$ (bottom). Impurities denoted with (*). (300 MHz, d_6 -benzene, 298 K).

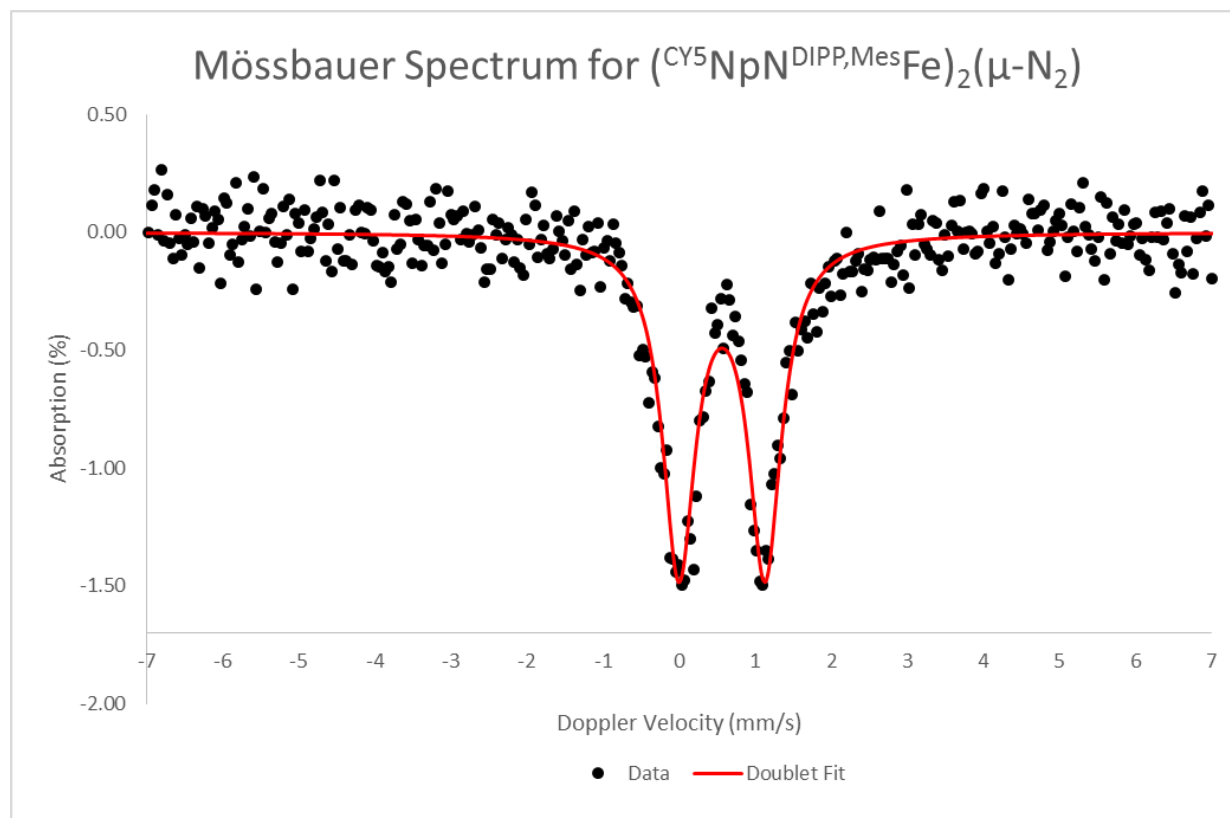


Figure S33: Zero-field ${}^{57}\text{Fe}$ Mössbauer spectra for powdered samples of $[({}^{\text{CYP}}\text{NpN}^{\text{DIPP,Mes}})\text{Fe}]_2(\mu\text{-N}_2)$ **5c** obtained at 295 K. The parameters used for the fit of **5c** (red line) were an isomer shift of (δ) 0.56 mm/sec and a quadrupole splitting (ΔE_Q) of 1.14 mm/sec.