Tetrapodal Iron Complexes Invoke Observable Intermediates in Nitrate and Nitrite Reduction

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General Considerations:

Materials and methods.

Unless otherwise stated, all manipulations were carried out in a Vigor inert atmosphere drybox under an atmosphere of nitrogen or using standard Schlenk techniques. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Vigor Solvent Purification System and stored over 4Å molecular sieves (3Å for acetonitrile) purchased from Strem prior to use. Celite 545 (J. T. Baker) was heated to 150°C under dynamic vacuum for 24h prior to use in the drybox. All reagents were purchased from commercial sources and used as received unless otherwise noted. [(*n*-Bu)$_4$N]NO_2 (TBANO_2) was recrystallized from vapor diffusion of diethylether in a concentrated solution in acetonitrile and dried over 3Å molecular for at least two days under an inert atmosphere prior to use. Na$^{15}NO_2$ was purchased from Cambridge Isotope Laboratories. TBA$^{15}NO_2$,[1] Fe(OTf)$_2$·2MeCN (OTf = trifluoromethanesulfonate),[2] and 2,2′,2′-Methyl-bis-pyridyl-6-(2,2′,2′-methylbis-5-formyl-pyrrol)-pyridine (**L4**)[3] were prepared according to literature procedures. NMR solvents (chloroform-*d*$_3$, acetonitrile-*d*$_3$, and benzene-*d*$_6$) were purchased from Cambridge Isotope Laboratories, degassed, and stored over 4Å molecular sieves prior to use.

Physical Methods.

NMR spectra were recorded at ambient temperature on a Bruker spectrometer operating at 400 or 500 MHz (^{1}H NMR) and referenced to the peak of the residual solvent (δ in parts per million and J in Hz). Solid-state infrared spectra were measured using a PerkinElmer Frontier FT-IR spectrophotometer equipped with a KRS5 thallium bromide/iodide universal attenuated total reflectance accessory. Ultraviolet-visible (UV-vis) spectroscopy was performed on an Agilent Technologies Cary Series UV-vis NIR 5000 spectrometer. UV-vis spectra were performed on a 1.0 mM solution of the compound of interest in dry dimethylacetamide. High Resolution Mass Spectrometry were taken via direct injection in a gas tight syringe on a Thermo Scientific QE Focus spectrometer. Single crystal x-ray diffraction studies were conducted on Rigaku XtaLAB Synergy, Dualflex, HyPix 6000He X-ray diffractometer at the Texas A&M X-Ray Diffraction Laboratory. Single crystal X-ray diffraction measurements were carried out at a low temperature employing a (three circle or kappa) Cu Kα radiation, λ = 1.54178 Å) (NSF-CHE-9807975, NSF-CHE- 0079822 and NSF-CHE-0215838) and cooled in a cold nitrogen stream (OXFORD Crysosystems (700 or 800)), to 110(2) K. Absorption corrections were applied using SADABS.4 Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. Structures were solved using SHELXT[4] and refined by least-squares refinement on F2 followed by difference Fourier synthesis (OLEX2, SHELXL).[5-6] Data were collected using a XtaLAB Synergy, Dualflex, HyPix 6000He diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 100 K. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.101a (Rigaku OD, 2023).[7] Data reduction, scaling and multi-scan absorption corrections were performed using CrysAlisPro 1.171.42.101a (Rigaku OD, 2023). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPAC scaling algorithm.

General Procedure for GC Head Space Analysis: Reactions were carried out in a nitrogen drybox unless otherwise stated. A 4 mL scintillation vial was charged with compounds of choice and a 3 mm by 8 mm stir bar. Acetonitrile (1.5 mL) was added, and the vial was quickly sealed with an 8 mm septa and taped with electrical tape. Reactions were stirred in the drybox for 16 hours. A 0.3 mL sample of the head space was taken via gas tight syringe and injected into the Agilent Trace 1300 gas chromatograph. The GC was attached with a thermal conductivity detector and a custom-made 120 cm stainless steel column packed with Carbosieve-II was used to identify gases. The column was kept at a temperature of 200 °C and argon was used to carry the gas during the separation. The detector was set to a temperature of 250 °C.

Experimental Procedures:

Synthesis of Ligand.

Synthesis of $Py_2Py(pi^{mcyp})_2$.

To a 250 mL round bottom flask were added 2,2′,2′-Methyl-bis-pyridyl-6-(2,2′,2′-methylbis-5-formyl-pyrrol)-pyridine (1.55 g, 3.0 mmol) and 20 mL dichloromethane. Cyclopropylmethylamine (0.447 g, 6.3 mmol, 2.1 eq) was added dropwise with stirring. The reaction was stirred for 16 hours followed by removal of volatiles under reduced pressure, yielding a light tan powder. The powder was taken into the glovebox, dissolved in dichloromethane, and stored over 3Å sieves for a minimum of two days. Removal of volatiles under reduced pressure yielded a tan powder, $Py_2Py(pi^{mcyp})_2$ in 89% yield. ^{1}H NMR (C_6D_6, 400 MHz, 21 °C): 0.20 (d, 4H, cyclopropyl-CH_2), 0.42 (d, 4H, cyclopropyl-CH_2), 1.04 (m, 2H, cyclopropyl-CH), 1.80 (s, 3H, -CH_3), 2.86 (s, 3H, -CH_3), 3.26 (m, 4H, methyl-CH_2), 6.09 (d, 2H, pyrrole-CH), 6.38 (d, 2H, pyrrole-CH), 6.60 (d, 1H, pyridine-CH), 6.89 (t, 1H, pyridine-CH), 7.14 (d, 1H, pyridine-CH), 7.22 (m, 4H, pyridine-CH), 7.40 (d, 2H, pyridine-CH), 7.83 (s, 2H, imine-CH), 8.55 (d, 2H, pyridine-CH), 9.92 (s, 2H, pyrrole-NH). ^{13}C NMR (C_6D_6, 101 MHz, 21 °C): δ 3.45, 12.48, 27.30, 28.91, 65.33, 108.20, 113.03, 117.86, 120.77, 121.73, 123.67, 135.27, 136.88, 148.48, 150.42. IR: ν = 1635 cm^{-1} (C═N, strong). ESI–MS: calculated $[C_{41}H_{40}N_7]^+$: 582.3340, found: 582.3332.

Synthesis and reactivity of Metal Compounds.

Synthesis of $[Py_2Py(afa^{mcyp})_2Fe]OTf_2$ (**1**).

A 20 mL scintillation vial with stir bar was charged with $Py_2Py(pi^{mcyp})_2$ (58.1 mg, 0.1 mmol), $Fe(OTf)_2(MeCN)_2$ (43.5 mg, 1 mmol, 1 eq), and approximately 3 mL of THF. An immediate color change to deep red was observed, followed by the precipitation of a yellow solid. After 1 hour of stirring, the suspension was filtered, and the resultant yellow powder was washed with DCM. The yellow powder was dissolved in acetonitrile and solvent was removed *in vacuo* to give a yellow powder in 87% yield. Crystals suitable for X-ray analysis were grown via slow diffusion of ether into a concentrated solution of a 1:1 ratio of THF:acetonitrile. ^{1}H NMR (CD_3CN, 21°C): δ = -8.13, -4.17, -3.06, -2.24, -1.81, -1.50, 23.36, 24.79, 25.96, 26.91, 27.54, 28.36, 34.93, 40.97, 41.80,

42.21, 45.72, 79.19, 88.39, 89.09. $C_{39}H_{39}F_6FeN_7O_6S_2$: (calcd., found) C (50.06, 49.91), H (4.2, 3.96), N (10.48, 10.24). IR: ν = 1635 cm^{-1} (C=N, strong).

Synthesis of $Py_2Py(pi^{mcyp})_2Fe(NO)$ (**2**).

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_2$ (14.4 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. An immediate color change to a brown solution with orange suspension was observed. After approximately 2 hours, the solution turned green. After 6 hours of stirring, the solvent was removed *in vacuo*. The product was dissolved in THF, filtered, and dried. The green powder was collected in quantitative yield. Crystals suitable for X-ray diffraction were grown via a solution of concentrated ether at -35°C. IR: ν = 1666 cm^{-1} (N=O, strong) and 1570 cm^{-1} (C=N, medium). ESI–HRMS: calculated $[M+H]^+$: 666.2412, found: 666.2502.

Synthesis of $[Py_2Py(afa^{mcyp})_2Fe(OH)]OTf_2$ (**3**).

A 20 mL scintillation vial with stir bar was charged with **1**, (46.8 mg, 0.05 mmol) iodosobenzene (13.2 mg, 0.06 mmol, 1.2 eq) and approximately 4 mL of tetrahydrofuran. After stirring for 16 hours, the solvent was removed *in vacuo*. The resultant brown powder was washed with diethylether and the product was extracted with THF in quantitative yield. ^1H NMR (CD_3CN, 21°C): δ = 13.59, 18.87, 63.27, 71.65, 83.56, 88.15, 97.91, 107.60. IR: ν = 1669 cm^{-1} (C=N, strong). ESI–HRMS: calculated $[M]^{2+}$: 334.1395, found: 334.1395.

Synthesis of $[N(afa^{Cy})_3Zn(^{15}NO_2)](OTf)$.

A 20 mL scintillation vial was charged with $[N(afa^{Cy})_3Zn(OTf)](OTf)$ (47 mg, 0.05 mmol) and approximately 5 mL of THF. An equivalent of $TBA^{15}NO_2$ (14.5 mg, 0.05 mmol) was weighed by difference and added as a solid to the yellow solution. The reaction mixture was stirred for 16 hours and volatiles were removed under reduced pressure. The resulting pale yellow solid was washed with diethylether, yielding the product as a off-white solid (32 mg, 78%). IR: ν = 1640 cm^{-1} (C=N, strong) 1431 cm^{-1} ($^{15}NO_2$, small).

Synthesis of $[Py_2Py(afa^{mcyp})_2Fe(NO_2)]OTf$ (**4-NO_2**).

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_2$ (14.4 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. Within 30 seconds, a color change to a brown solution with orange suspension was observed. After approximately 1 minute stirring at room temperature, the reaction was filtered. The resultant orange powder was washed with THF and acetonitrile and was collected on a frit in 10% yield. IR: ν = 1646 cm^{-1} (C=N, strong), 1212 cm^{-1} (NO_2^-, small), 1419 cm^{-1} (NO_2^-, small).

Synthesis of $[Py_2Py(afa^{mcyp})_2Fe(NO_3)]OTf$ (**5**).

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_3$ (15.3 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. Within 30 seconds, precipitation of an orange solid was apparent. After approximately 1 minute stirring at room temperature, the reaction was filtered. The resultant orange powder was washed with THF and acetonitrile and was collected on a frit in 68% yield. IR: ν = 1644 cm^{-1} (strong).

Formation of **3** from nitrite reduction.

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_2$ (14.4 mg, 0.05 mmol, 1 eq), and approximately 2 mL of acetonitrile. An immediate color change to a brown solution with orange suspension was observed. After approximately 5 minutes stirring at room temperature, the reaction was filtered. Volatiles were removed to yield a brown powder.

Isolation of $[Py_2Py(afa^{mcyp})_2Fe(NO_2)]OTf$ (**4-NO_2**) from Nitrite Reduction.

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_2$ (14.4 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. Within 30 seconds, a color change to a brown solution with orange suspension was observed. After approximately 1 minute stirring at room temperature, the reaction was filtered. The resultant orange powder was washed with THF and acetonitrile and was collected on a frit in 10% yield. IR: ν = 1646 cm^{-1} (C=N, strong), 1212 cm^{-1} (NO_2, small), 1419 cm^{-1} (NO_2^-, small).

Isolation of $[Py_2Py(afa^{mcyp})_2Fe(^{15}NO_2)]OTf$ (**4-$^{15}NO_2$**) from Nitrite Reduction.

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBA^{15}NO_2$ (14.4 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. Within 30 seconds, a color change to a brown solution with orange suspension was observed. After approximately 1 minute stirring at room temperature, the reaction was filtered. The resultant orange powder was washed with THF and acetonitrile and was collected on a frit in 12% yield. IR: ν = 1643 cm^{-1} (C=N, strong) 1192 cm^{-1} ($^{15}NO_2$, small), 1391 cm^{-1} ($^{15}NO_2^-$, small). ESI–HRMS: calculated $[M]^+$: 684.2510, found: 684.2498.

Formation of **2** from **4-NO_2**.

A 20 mL scintillation vial with stir bar was charged with isolated **4-NO_2** (4 mg, 0.005 mmol) and **1** (5 mg, 0.005 mmol, 1 eq), and approximately 1 mL of acetonitrile. After approximately 2 hours, the solution turned green. After 6 hours of stirring, the solvent was removed *in vacuo*. The product was dissolved in THF, filtered, and dried to reveal a green residue with IR matching **2**.

Formation of **2** from Nitrite.

A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_2$ (5 mg, 0.017 mmol, $^1/_3$ eq) and approximately 3 mL of acetonitrile. After approximately 16 hours, the solution turned green. After 6 hours of stirring, the solvent was removed *in vacuo*. The residue

was washed with ether. The two products were isolated by filtration with THF followed by acetonitrile. The THF wash had ^{1}H NMR consistent with **3**. The acetonitrile wash had IR spectrum consistent with **2.**

Isolation of **5** from Nitrate Reduction.

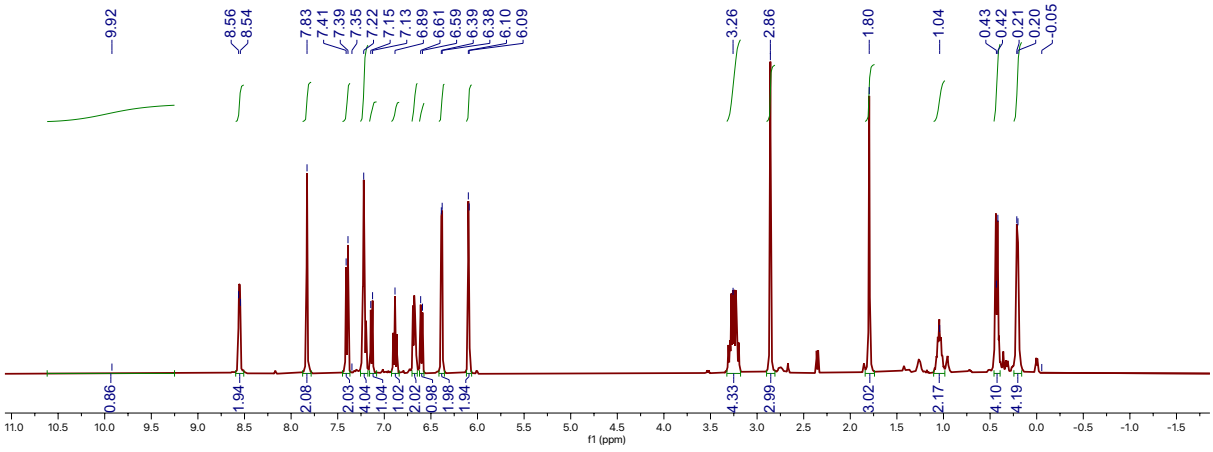
A 20 mL scintillation vial with stir bar was charged with **1** (46.8 mg, 0.05 mmol), $TBANO_3$ (15.3 mg, 0.05 mmol, 1 eq) and approximately 2 mL of acetonitrile. Within 30 seconds, precipitation of an orange solid was apparent. After approximately 1 minute stirring at room temperature, the reaction was filtered. The resultant orange powder was washed with THF and acetonitrile and was collected on a frit in 68% yield. IR: ν = 1644 cm^{-1} (strong).

Formation of **2** from **5**.

A 20 mL scintillation vial with stir bar was charged with isolated **5** (17 mg, 0.02 mmol) and **1** (18.4 mg, 0.02 mmol, 1 eq), and approximately 3 mL of acetonitrile. After approximately 2 hours, the solution turned green. After 6 hours of stirring, the solvent was removed *in vacuo*. The product was dissolved in THF, filtered, and dried to reveal a green residue with IR matching **2.**

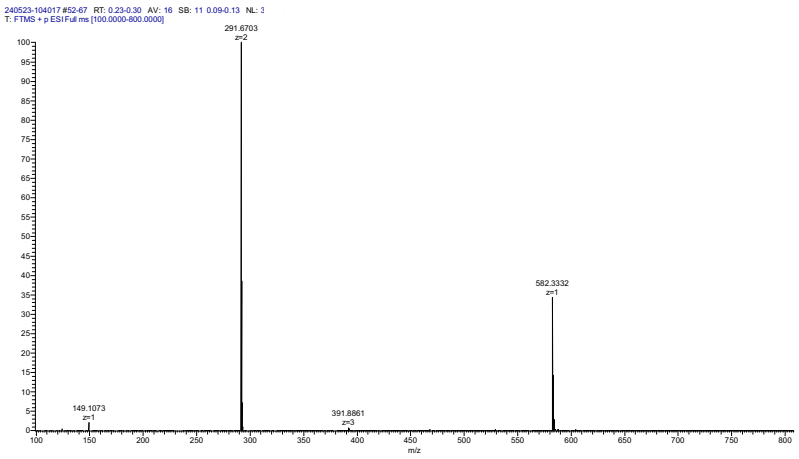
NMR spectrum of Ligand.

Figure S1. ^{1}H NMR Spectrum of $Py_2Py(pi^{mcyp})_2$ (benzene-d_6).



Mass Spectrum of Ligand

Figure S2. Mass Spectrum of $Py_2Py(pi^{mcyp})_2$.



NMR Spectra of Metal Complexes

*Figure S3. ^1H NMR Spectrum of crystalline $[Py_2Py(afa^{mcyp})_2Fe]OTf_2$ (**1**) (acetonitrile-d_3).*

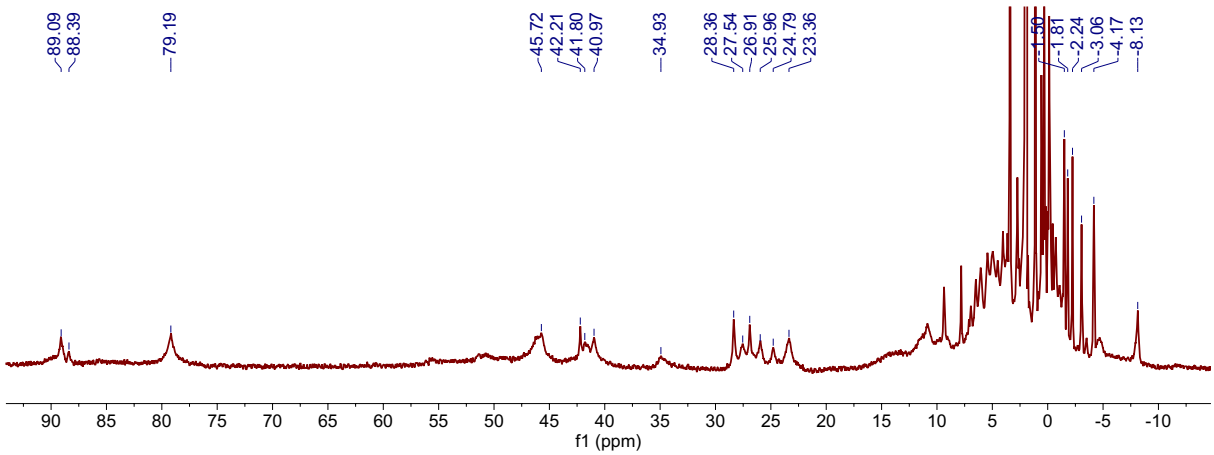


*Figure S4. ^{1}H NMR Spectrum of $Py_2Py(pi^{mcyp})_2Fe(NO)$ (**2**) with inlay of diamagnetic region (benzene-d_6).*

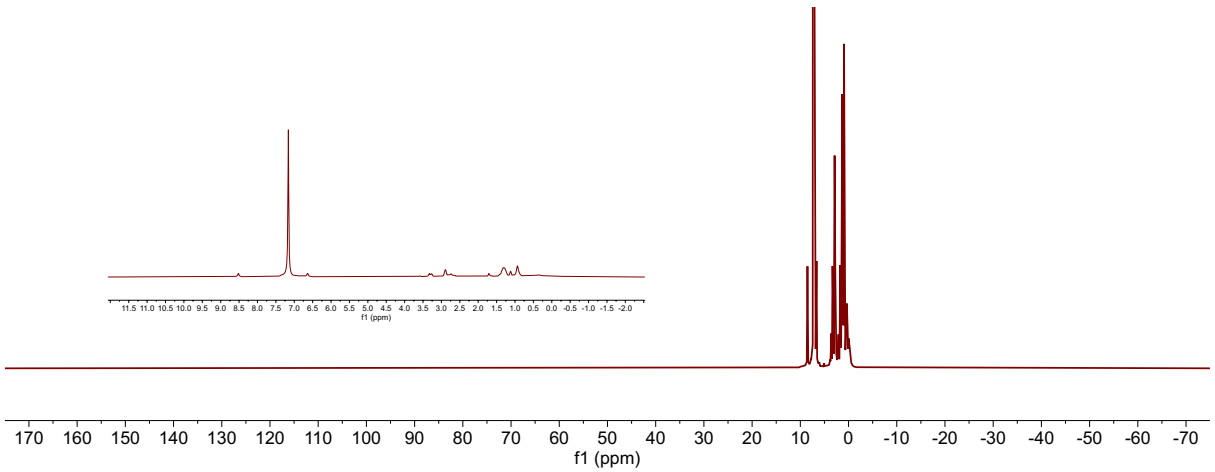


*Figure S5. ^{1}H NMR Spectrum of $[Py_2Py(afa^{mcyp})_2Fe(OH)]OTf_2$ (**3**) (acetonitrile-d_3).*

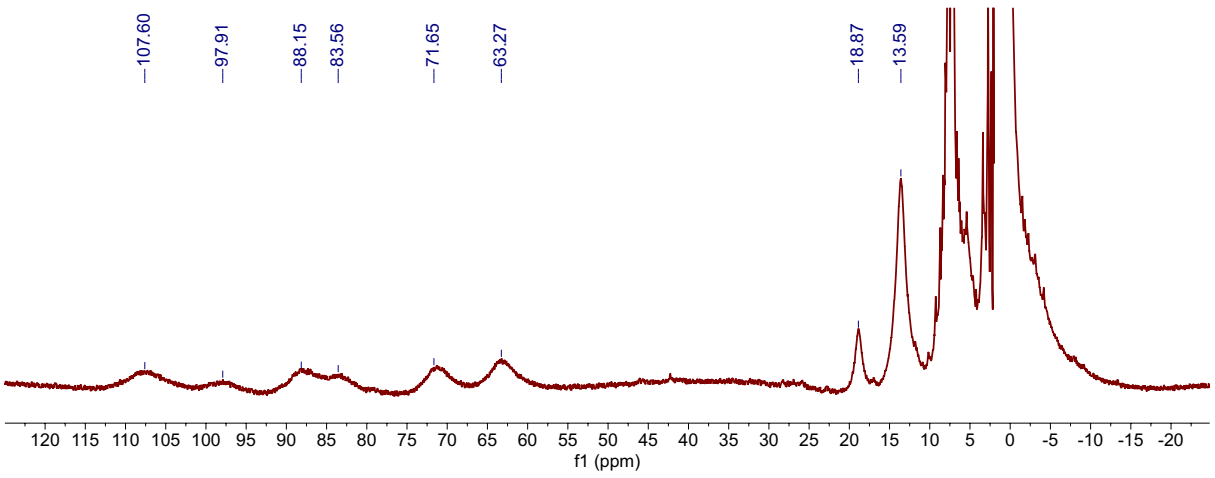


*Figure S6. ^{1}H NMR Spectrum of isolated [$Py_2Py(afa^{mcyp})_2Fe(NO_2)$]OTf (**4-$NO_2$**) (acetonitrile-$d_3$).*

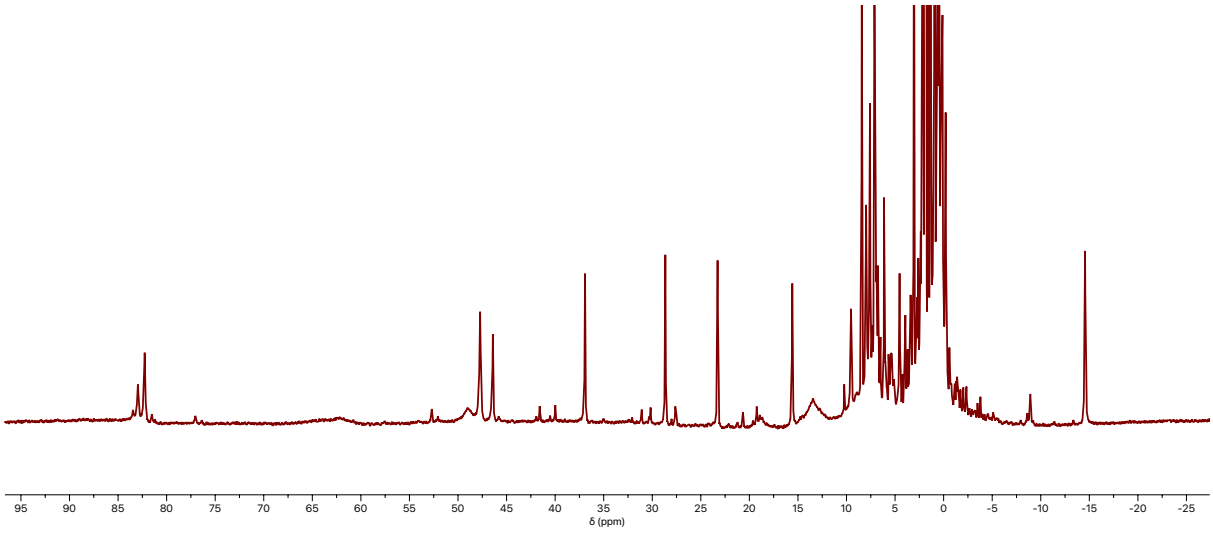


*Figure S7. ^{1}H NMR Spectrum of isolated [$Py_2Py(afa^{mcyp})_2Fe(^{15}NO_2)$]OTf (**4-$^{15}NO_2$**) (acetonitrile-$d_3$).*

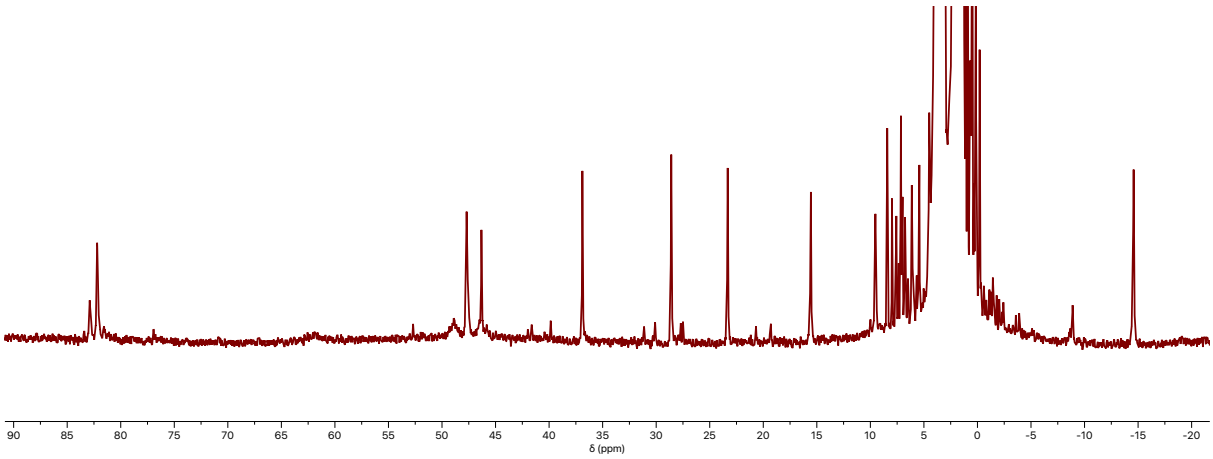


*Figure S8. ^{1}H NMR Spectrum of isolated **4-$^{15}NO_2$** (red) compared to **4-$^{15}NO_2$** (blue) (acetonitrile-d_3).*

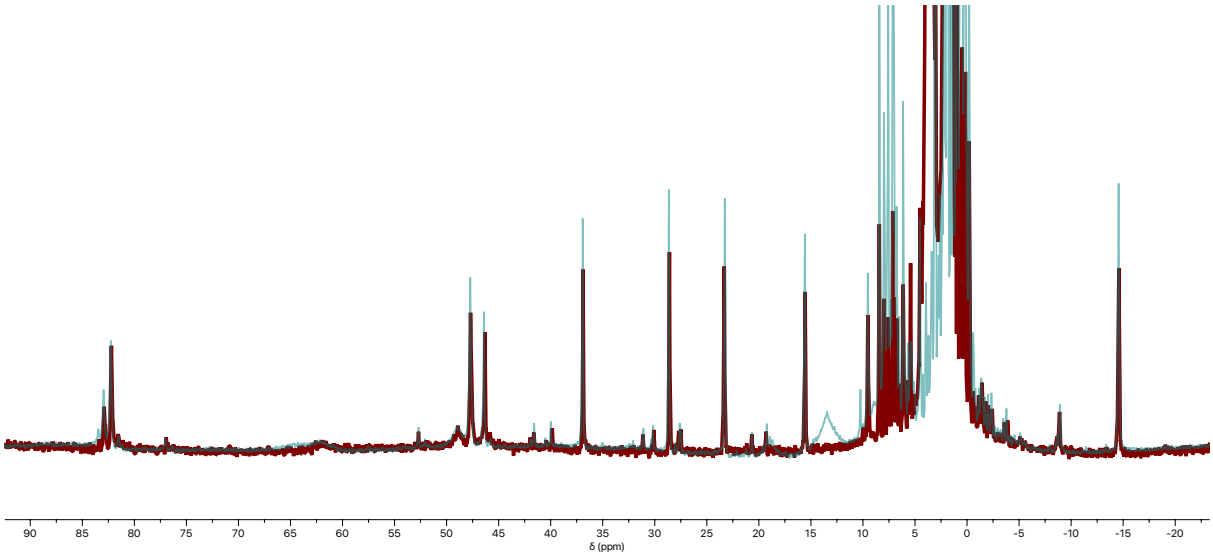


Figure S9. ^{1}H NMR Spectrum of [N(afa^{Cy})$_3$Zn($^{15}NO_2$)](OTf) (acetonitrile-d_3).

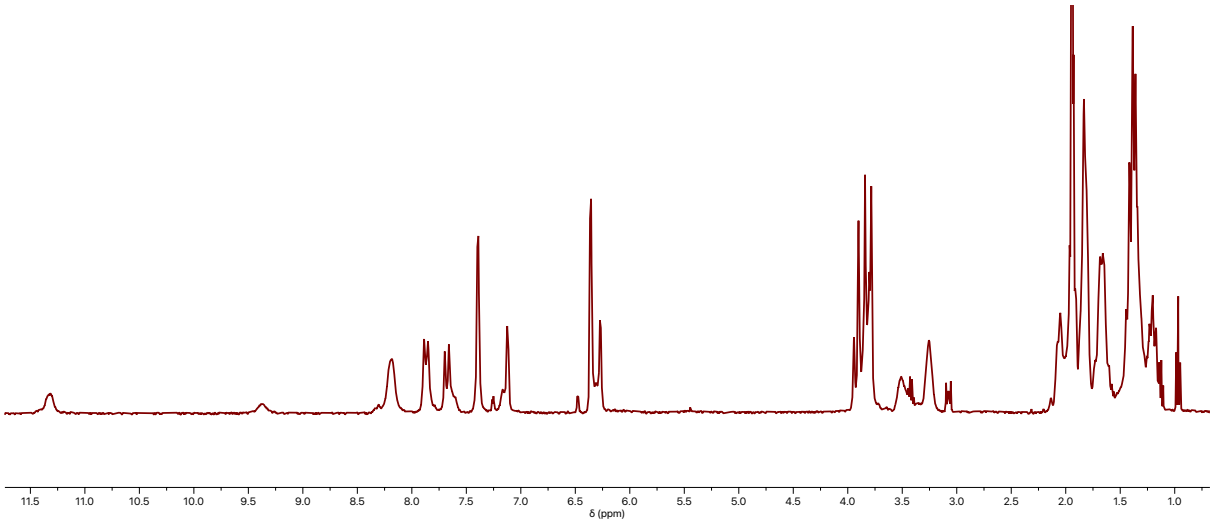


*Figure S10. ^{1}H NMR Spectrum of the formation of **2** from isolated **4-NO_2** with inlay of diamagnetic region (benzene-d6).*

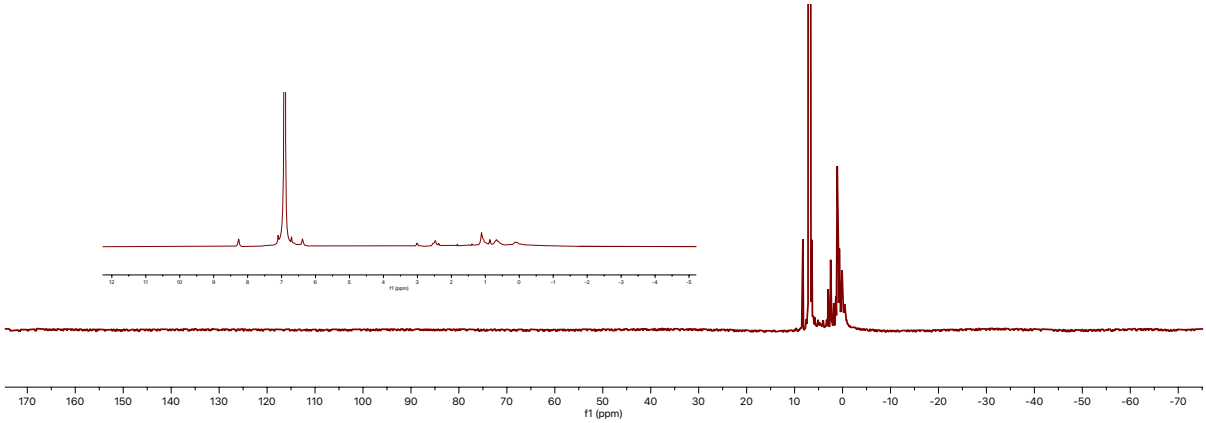


*Figure S11. ^{1}H NMR Spectrum of isolated [$Py_2Py(afa^{mcyp})_2Fe(NO_3)$]OTf (**5**) (acetonitrile-d_3).*

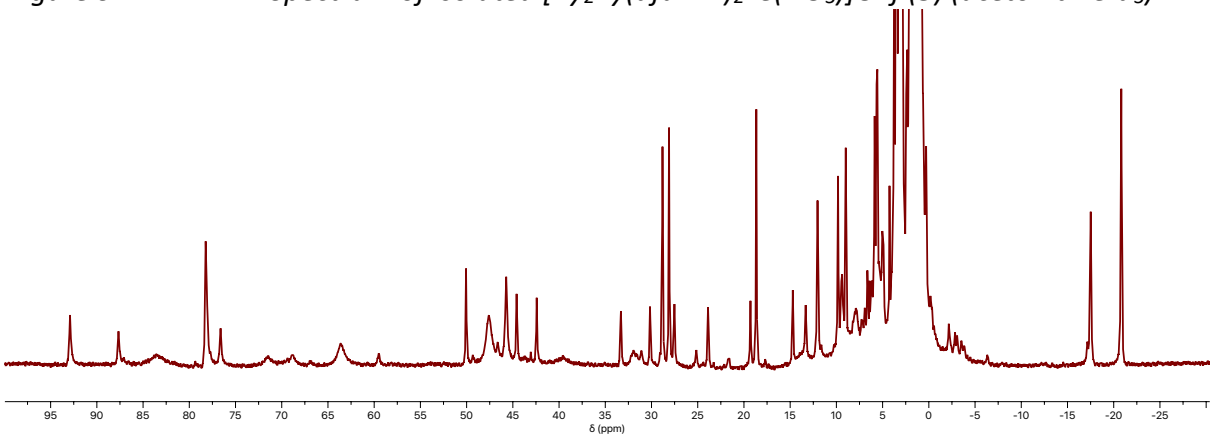


*Figure S12. Formation of **3** and **4-NO₂** from nitrite reduction after minutes (Filtrate, acetontrile-d_3).*

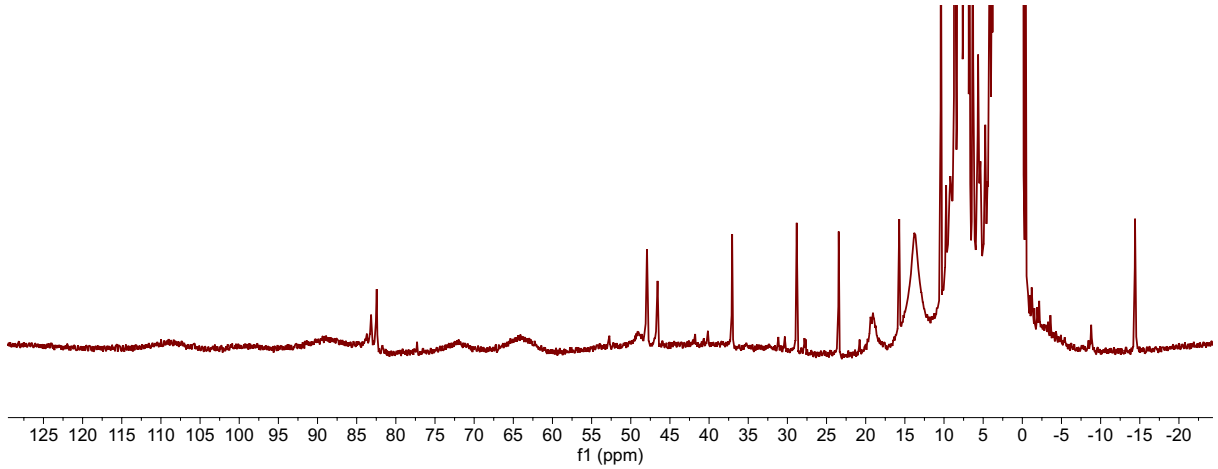


*Figure S13. Formation of **3** from and **4-NO₂** from nitrite reduction (blue) overlayed with isolated **3** from reaction of **1** and iodosobenzene (red) (acetontrile-d_3).*

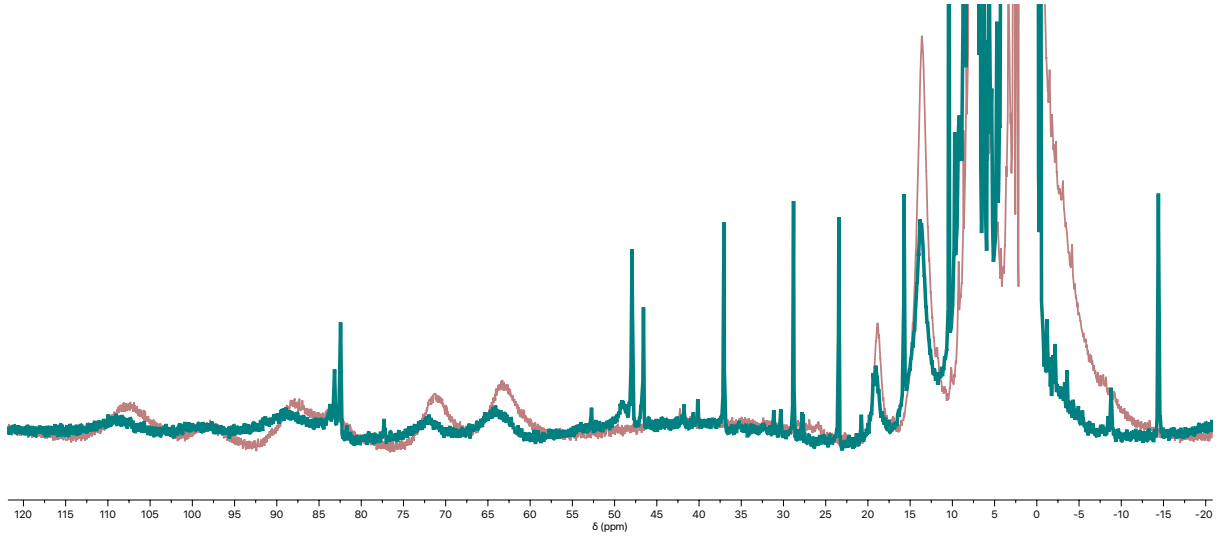


*Figure S14. Formation of **3** from and **4-NO$_2$** from nitrite reduction (blue) overlayed with isolated **4-NO$_2$** (red) (acetontrile-d$_3$).*

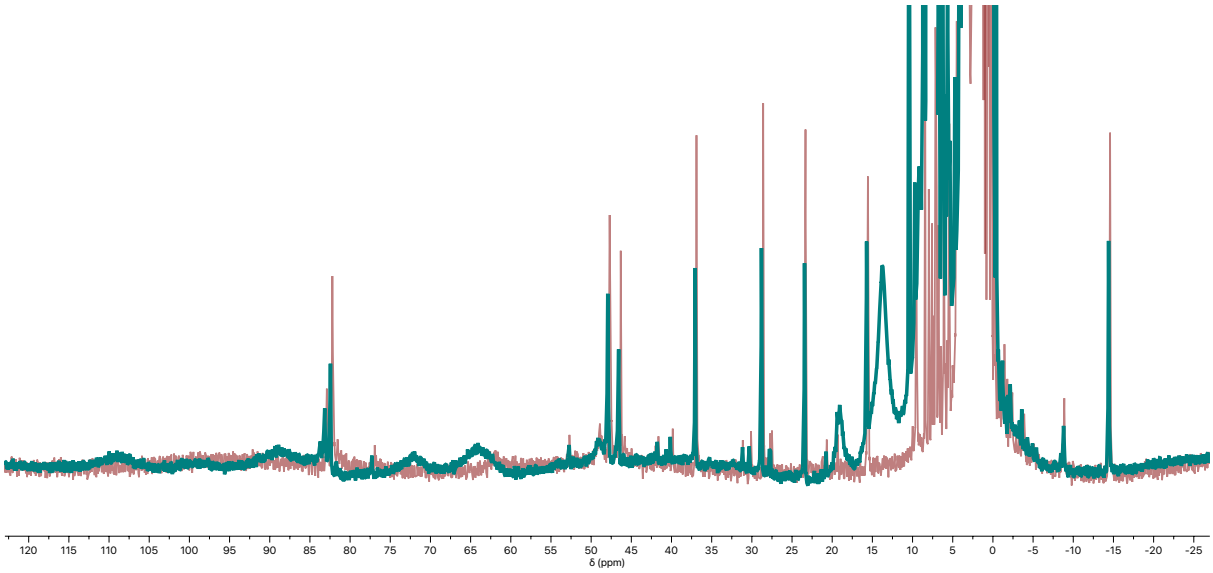


*Figure S15. Formation of **3** from nitrate reduction (THF wash, acetontrile-d$_3$).*

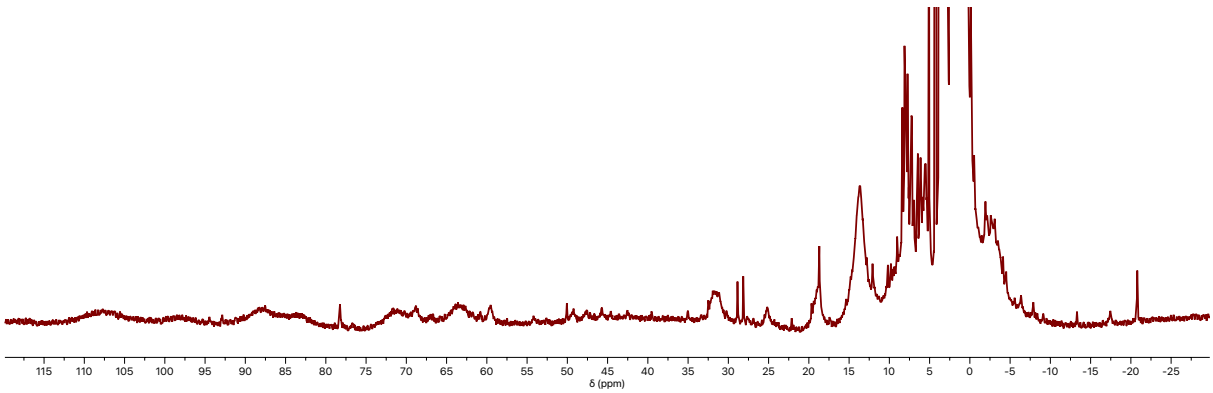


*Figure S16. Formation of **3** from nitrate reduction (blue) overlayed with isolated **3** from reaction of **1** and iodosobenzene (red) (acetontrile-d_3).*

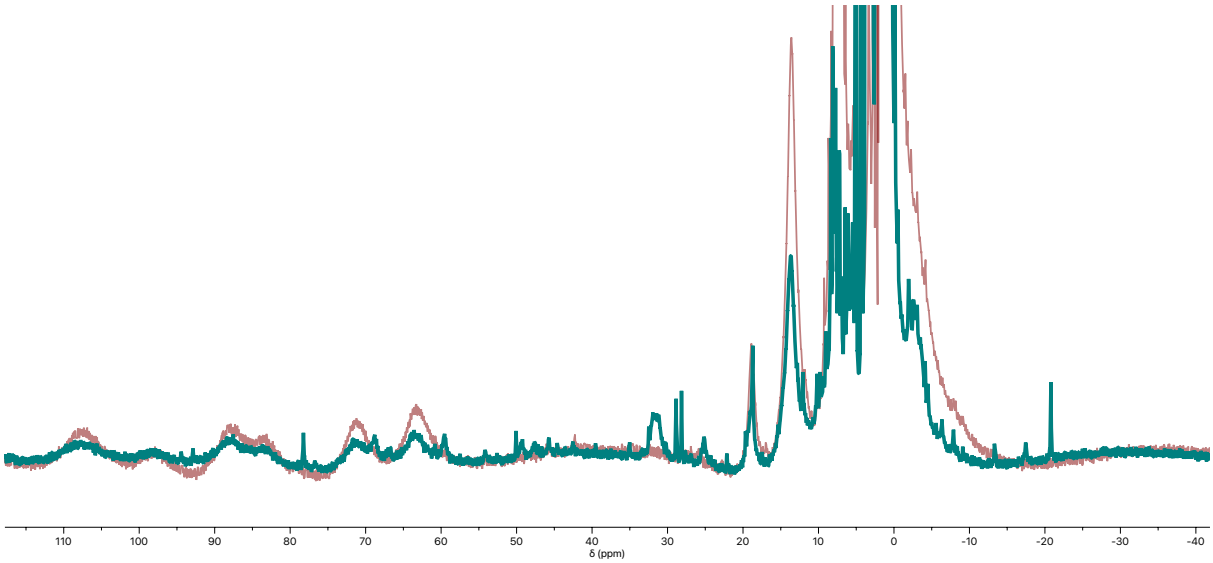


*Figure S17. Infrared Spectrum of **4-NO_2** (light purple) and **4-$^{15}NO_2$** (dark purple) with inlay of nitrite N-O stretching region.*

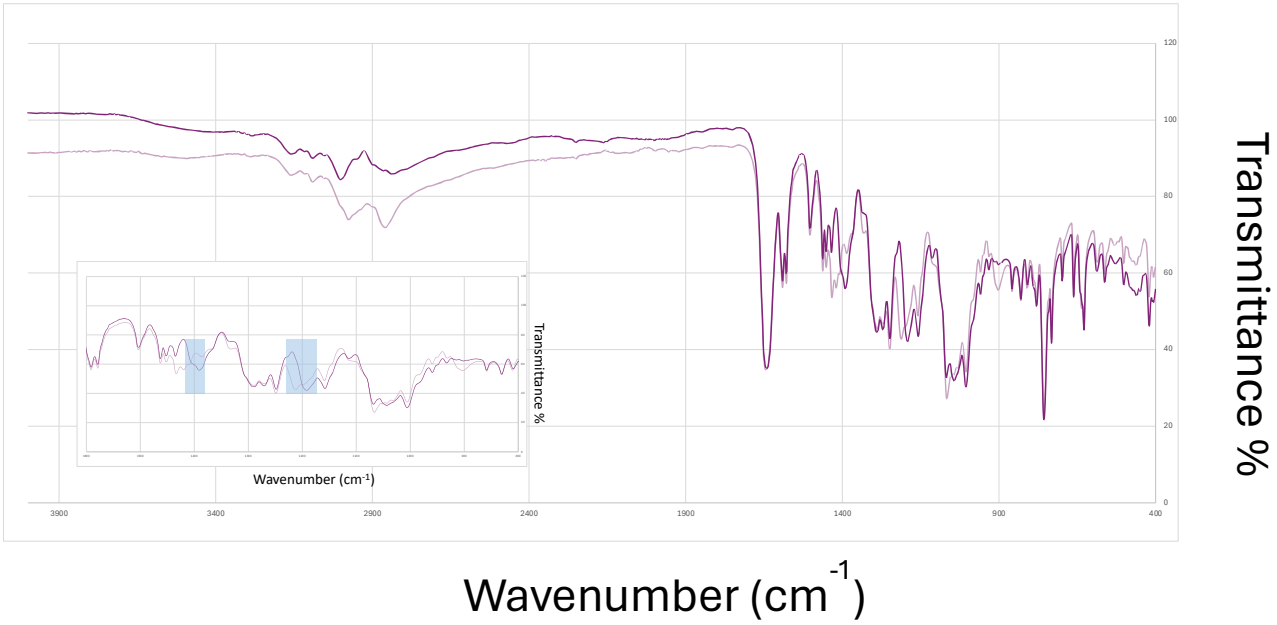
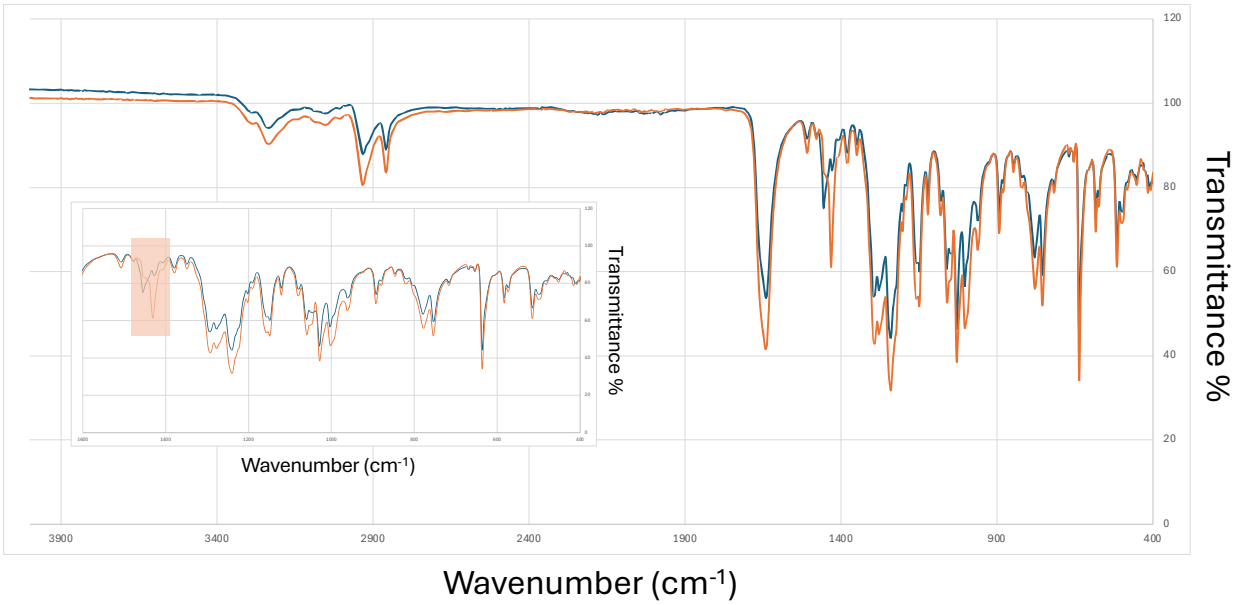


Figure S18. Infrared Spectrum of [N(afa^{Cy})$_3$Zn(ONO)]OTf (blue) and [N(afa^{Cy})$_3$Zn(O^{15}NO)]OTf (orange) with inlay of nitrite N-O stretching region.



Mass Spectra of Metal Complexes

*Figure S19. Mass Spectrum of **2** (ESI-HRMS).*

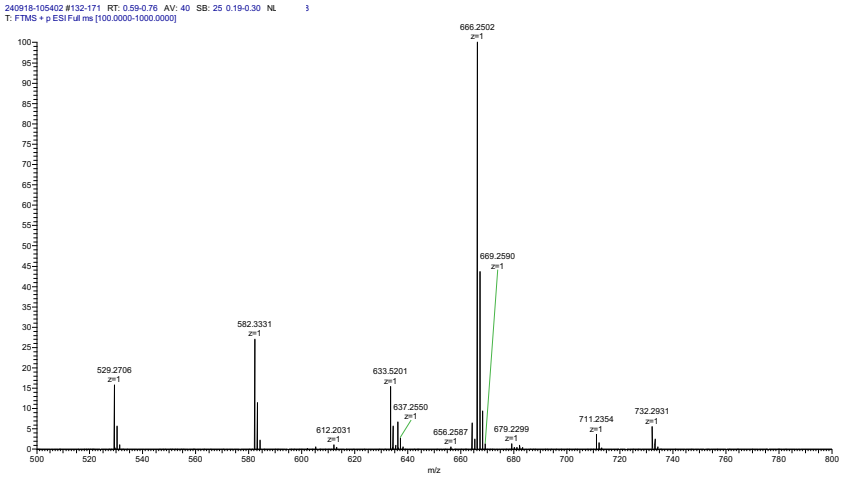


*Figure S20. Mass Spectrum of **3** (ESI-HRMS).*

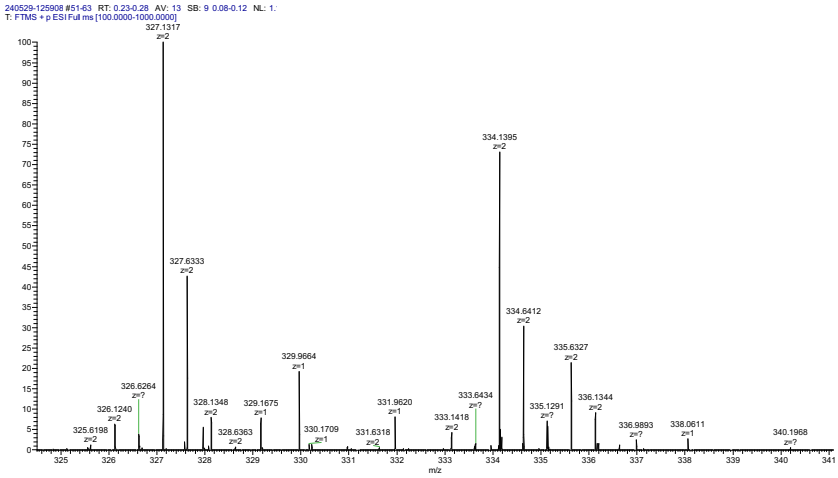


*Figure S21. Mass Spectrum of **4-$^{15}NO_2$** (ESI-HRMS).*

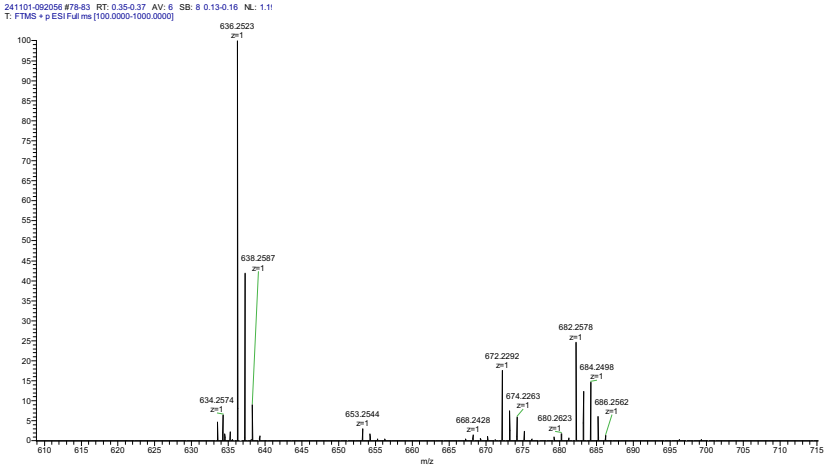


*Figure S22. Head space analysis of nitrite reduction by **1**.*

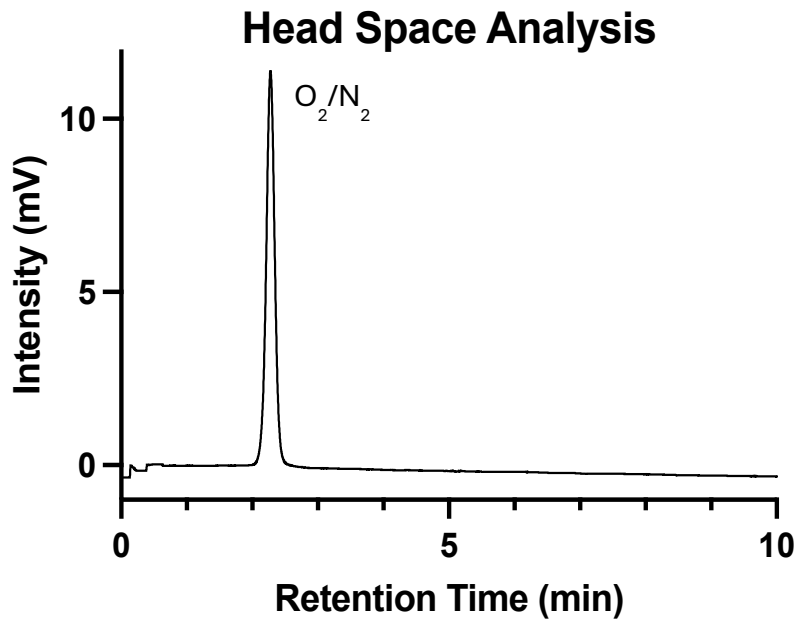


Figure S23. UV-Visible spectrum of $TBANO_2$ (1.0 mM in DMA).

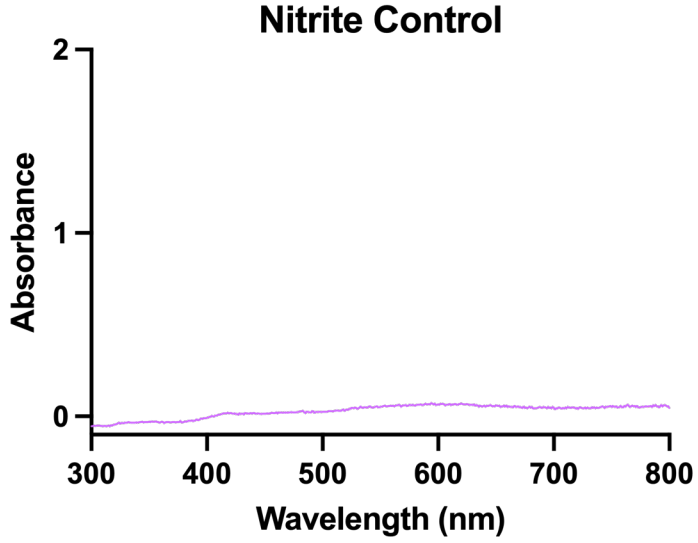


*Figure S24. UV-Visible spectrum of **2** from nitrite reduction (1.0 mM in DMA).*

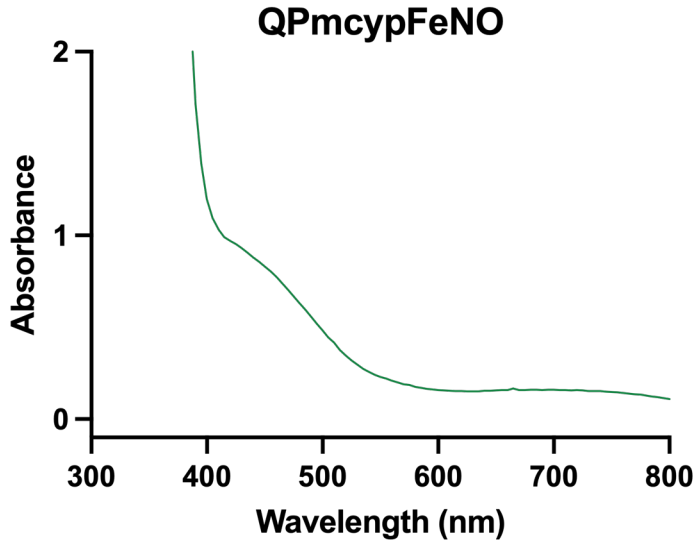


*Figure S25. UV-Visible spectrum of isolated **3** from reaction of **1** and iodosobenzene (1.0 mM in DMA).*

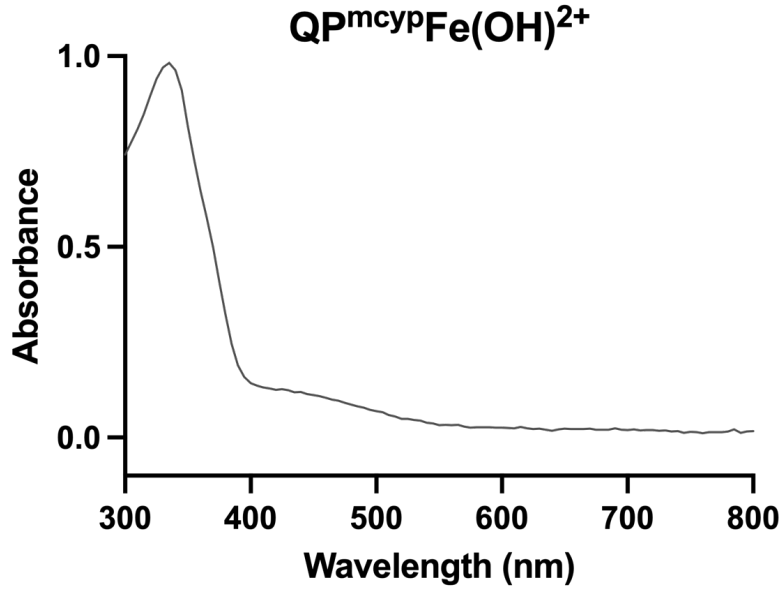


*Figure S26. UV-Visible spectrum of isolated **4-NO₂** (2.0 mM in DMA).*

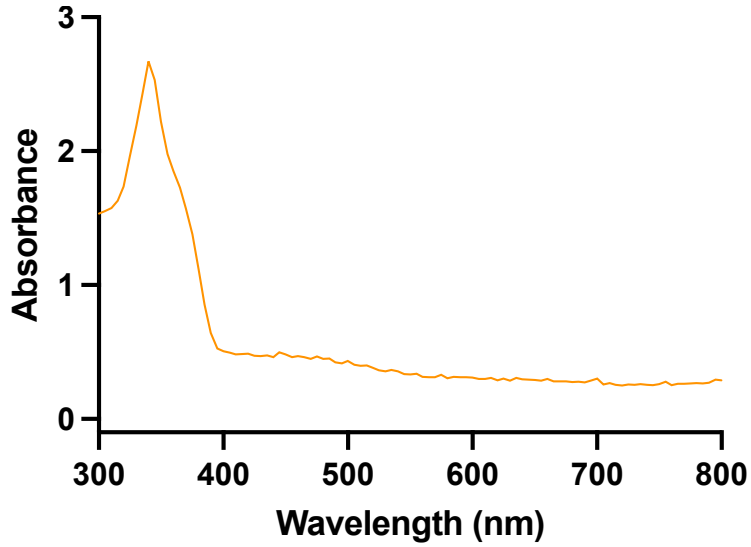
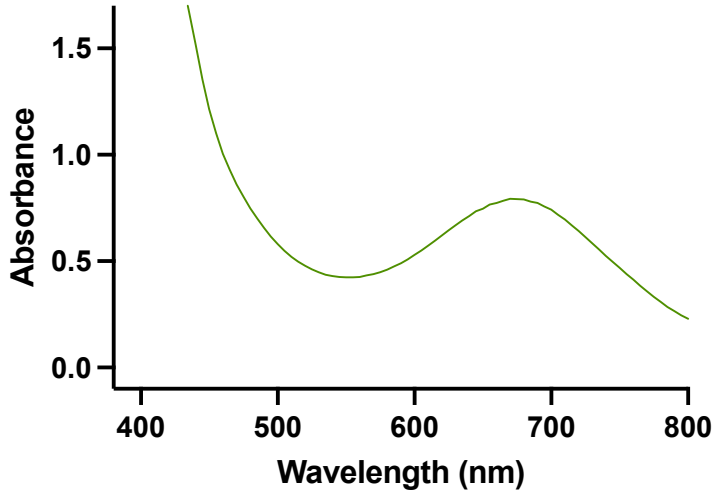
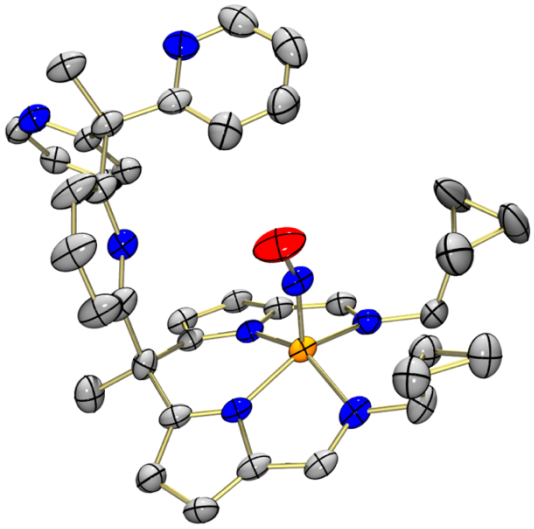


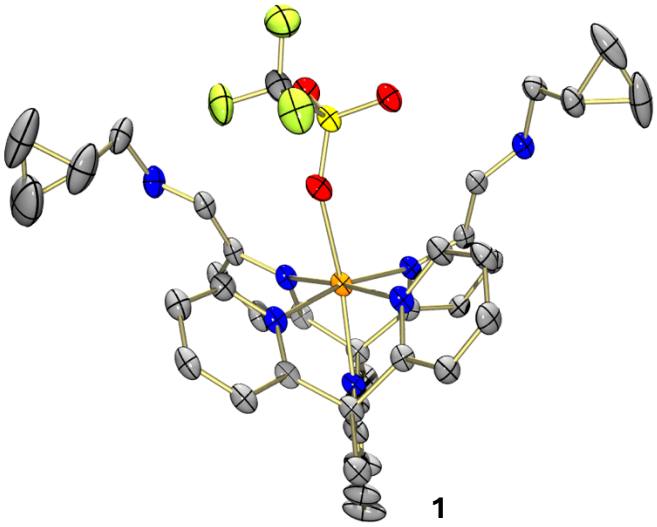
*Figure S27. UV-Visible spectrum of **2** from nitrate reduction (5.0 mM in DMA).*



Solid State Structures



2



1

Crystallographic Parameters

	$Py_2Py(pi^{mcyp}{}_2)Fe(NO)$ (**2**)	$[Py_2Py(afa^{mcyp})_2Fe]OTf_2$ (**1**)
Emperical Formula	C4.4 H4.2 Fe0.1 N0.9 O0.1	C40.60 H43 F6 Fe N7 O6.40 S2
Formula Weight	76.87	965.39
Temperature	100.00(10) K	100.00(10) K
Radiation	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)
Crystal System	triclinic	monoclinic
Space Group	P -1	P 1 21/n 1
Unit Cell Parameters	a = 11.6763(4) Å b = 12.7685(5) Å c = 13.0867(3) Å α = 90.442(2)° β = 100.125(3)° γ = 114.932(4)°	a = 10.9898(2) Å b = 12.3154(3) Å c = 31.8784(6) Å α = 90° β = 94.519(2)° γ = 90°
Volume	1734.37(12)	4301.13(15)
Z	17	4
Reflections Collected	6839	17470
Independent Reflections	6839	17470
Goodness-of-Fit on F^2	1.117	1.067
Final R indexes [I>=2σ(I)]	R_1 = 0.1142 wR_2 = 0.2985	R_1 = 0.0670 wR_2 = 0.2412

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