

# Improving Molecular Iron Ammonia Oxidation Electrocatalysts via Substituent Effects That Modulate Standard Potential and Stability

Michael D. Zott and Jonas C. Peters\*

Corresponding Author Email: [jpeters@caltech.edu](mailto:jpeters@caltech.edu)

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

## Contents:

S1. General procedures	p. SI-2
S2. Synthetic procedures	p. SI-4
S3. Additional voltammetry data related to $E^\circ$	p. SI-17
S4. Additional voltammetry data for $R = CF_3$	p. SI-18
S5. $E_1$ voltammetry	p. SI-20
S6. Catalytic controlled potential coulometry experiments	p. SI-21
S7. CV of $[(BPM^{OMe})Fe(N')_2]^{2+}$ under catalytic conditions	p. SI-24
S8. Evans method data	p. SI-25
S9. UV-vis titration data for stability against demetallation	p. SI-39
S10. Mass spectrometry	p. SI-45
S11. NMR Spectra	p. SI-49
S12. References	p. SI-60

## S.1 General procedures

**General Considerations:** All manipulations of inorganic complexes were carried out using standard Schlenk or glovebox techniques under an N<sub>2</sub> or Ar atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with N<sub>2</sub> gas followed by passage through an activated alumina column in a solvent purification system (SG Water, USA LLC). For electrochemical measurements under an Ar atmosphere, solvents were further degassed and then stored under Ar. All solvents were stored over activated 3 or 4 Å molecular sieves prior to use. Anhydrous ammonia gas was dried by passage through a calcium oxide drying tube. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Tris(2-pyridylmethyl)amine (TPA),<sup>1</sup> tris(2-pyridylmethylamine) iron(II) triflate bis-acetonitrile ([ (TPA)Fe(MeCN)<sub>2</sub> ]OTf<sub>2</sub>),<sup>2</sup> 6-(1,1-di(pyridin-2-yl)ethyl)-2,2'-bipyridine (BPM),<sup>3</sup> 6-(1,1-di(pyridin-2-yl)ethyl)-2,2'-bipyridine iron(II) triflate bis-acetonitrile ([ (BPM)Fe(MeCN)<sub>2</sub> ]OTf<sub>2</sub>),<sup>4</sup> bis(4-(dimethylamino)pyridin-2-yl)methanone,<sup>5</sup> tris(4-(dimethylamino)-2-picoly)amine (TPA<sup>NMe2</sup>),<sup>6</sup> tris(4-methoxy-2-picoly)amine (TPA<sup>OMe</sup>),<sup>6</sup> 4-(trifluoromethyl)pyridine-2-carboxaldehyde,<sup>7</sup> 4-(trifluoromethyl)-2-ethylpyridine,<sup>8</sup> bis(4-(dimethylamino)pyridin-2-yl)methanone,<sup>9</sup> and methylenetriphenylphosphorane<sup>10</sup> were synthesized according to literature procedures.

**Electrochemistry:** Voltammetry experiments were carried out with a Biologic VSP-300 or CH Instruments 600B potentiostat using a one-compartment three-electrode cell, and coulometry experiments were carried out with a Biologic VSP-300 potentiostat using a one-compartment three-electrode cell with a septum capped 14/20 joint for headspace analysis. For voltammetry, a boron-doped diamond (BDD) working electrode (3 mm diameter), a Pt wire counter electrode, and an Ag/AgOTf reference electrode (5 mM AgOTf and 0.1 M TBAPF<sub>6</sub> in MeCN) were employed. For controlled potential coulometry (CPC), the same reference electrode was used, but a BDD plate (geometric area: 4 cm<sup>2</sup>) and a Pt mesh were used as working and counter electrodes, respectively. All redox potentials in the present work are reported versus the Fc/Fc<sup>+</sup> couple, measured before each experiment to be approximately +0.12 V versus the Ag/AgOTf reference electrode.

Cyclic voltammograms (CVs) were collected at 100 mV·s<sup>-1</sup> unless otherwise specified. E<sub>1/2</sub> values for the reversible waves were obtained from the half potential between the oxidative and reductive peaks. CV measurements were performed applying IR compensation, compensating 85% of the resistance measured at one high frequency value (100 kHz).

CVs were collected using either 100 mM TBAPF<sub>6</sub> or 50 mM NH<sub>4</sub>OTf supporting electrolyte. Under our conditions, NH<sub>4</sub>OTf was more conductive than TBAPF<sub>6</sub>; thus, a lower concentration could be used while maintaining high conductivity. For CPC experiments, NH<sub>4</sub>OTf was the sole electrolyte used since it enabled higher turnover numbers to be achieved.

**Gas Chromatography:** Gas chromatography was performed in the Caltech Environmental Analysis Center using HP 5890 Series II instruments. Gas quantification was performed with a molecular sieve column attached to a thermal conductivity detector using argon as the carrier gas.

Standard curves were generated by direct injection of hydrogen or nitrogen gas. Quantification of background nitrogen was determined using the background oxygen signal. Isotopic measurements were performed with a separate HP 5890 Series II instrument equipped with a GasPro column using helium as the carrier gas.

**NMR:** NMR spectroscopy was performed using Varian and Bruker 400 MHz NMR spectrometers equipped with broadband auto-tune probes.  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to tetramethylsilane, using residual solvent resonances as internal standards.

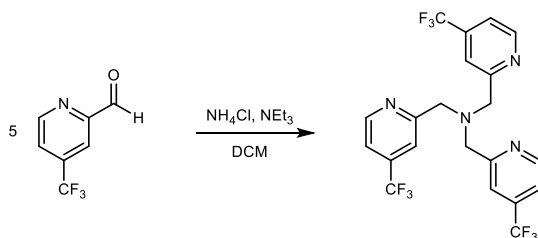
**UV-Vis:** Spectra were collected at 25 °C using a Cary 60 instrument equipped with a thermostat and Cary WinUV software.

**X-ray Crystallography:** XRD studies were carried out at the Caltech Beckman Institute Crystallography Facility on a Bruker D8 Venture diffractometer (Cu  $K\alpha$  radiation). The crystals were mounted on a glass fiber under Paratone N oil. Structures were solved using direct methods with SHELXS or SHELXT and refined against  $F^2$  on all data by full-matrix least squares with SHELXL.<sup>11</sup> All of the solutions were performed in the Olex2 program.<sup>12</sup>

## S2. Synthetic procedures

### TPA derivatives

#### TPA<sup>CF<sub>3</sub></sup> (tris(4-(trifluoromethyl)-2-picolyl)amine)



Ammonium chloride (15 mg, 1 eq), 4-(trifluoromethyl)-pyridine-2-carbaldehyde (250 mg, 5 eq), and triethylamine (44  $\mu$ L, 1.1 eq) were combined in dichloromethane (5 mL). Sodium triacetoxyborohydride (270 mg, 4.5 eq) was added as a solid, and the mixture was stirred at room temperature for 48 h. A saturated aqueous solution of sodium carbonate was added, and the organic phase was separated. The aqueous phase was extracted twice with dichloromethane, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The remaining oil was dissolved in ethyl acetate and added to a silica plug. The silica plug was eluted with ethyl acetate until the eluent was colorless, then the product was eluted with methanol, dried over sodium sulfate, and concentrated under reduced pressure to yield a yellow oil (48 mg, 34% yield).

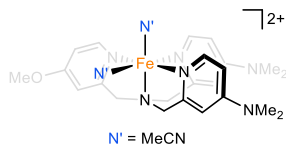
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.71 (d,  $J$  = 5.1 Hz, 3H), 7.72 (d,  $J$  = 1.8 Hz, 3H), 7.36 (dd,  $J$  = 5.1, 1.7 Hz, 3H), 4.07 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 160.55 (s), 150.19 (s), 138.85 (q,  $J$  = 34.1 Hz), 122.74 (q,  $J$  = 273.3 Hz), 118.82 (q,  $J$  = 3.6 Hz), 117.87 (q,  $J$  = 3.8 Hz), 60.55 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  (ppm) = -65.1 (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{21}\text{H}_{15}\text{F}_9\text{N}_4 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 495.1, found: 495.1.

**General note about the synthesis of iron compounds:** For the preparation of the following iron complexes, only the crystalline yield for the first crop of crystals is reported. Higher yields can be obtained if the supernatant is concentrated and recrystallized.



White solids  $\text{TPA}^{\text{NMe}_2}$  (tris(4-(dimethylamino)-2-picolyl)amine) (30 mg, 1 eq) and  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (31 mg, 1 eq) were each dissolved in 0.4 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{TPA}^{\text{NMe}_2}$ , instantly producing a pale orange-brown solution. The solution was filtered through Celite, and diethyl ether (2 mL) was layered on top of the filtrate. This mixture was placed in a freezer ( $-30^\circ\text{C}$ ) until a purple-gray (this compound changes color with varying temperature) precipitate appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (50.7 mg, 83% yield).

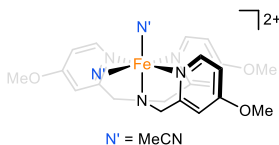
$^1\text{H}$  NMR ( $25^\circ\text{C}$ ,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 94.92 (s), 93.33 (s), 43.73 (s), 35.32 (s), 15.88 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR ( $25^\circ\text{C}$ ,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) =  $-77.1$ .

UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ]: 225 [20000], 283 [40000], 342 [3900].

MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{25}\text{H}_{33}\text{N}_7\text{O}_3\text{F}_3\text{SFe}$ ,  $[\text{M}]^+$ : 624.2, found: 624.3.

Electrochemistry:  $E_{1/2} = 0.21 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M TBAPF<sub>6</sub>, BDD disk electrode).



White solids  $\text{TPA}^{\text{OMe}}$  (tris(4-methoxy-2-picolyl)amine) (25 mg, 1 eq) and  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (29 mg, 1 eq) were each dissolved in 0.25 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{TPA}^{\text{OMe}}$ , instantly producing a purple-red solution. The solution was filtered through Celite, and diethyl ether (2 mL) was layered on top of the filtrate. This mixture was placed in a freezer ( $-30^\circ\text{C}$ ) until dark purple needle-shaped crystals appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (34.7 mg, 64% yield).

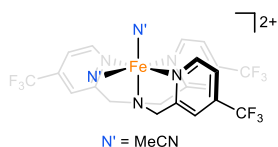
$^1\text{H}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 38.51 (s), 30.31 (s), 22.62 (s), 20.02 (s), 4.63 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) = -78.1.

UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ]: 235 [24000], 339 [5100], 375 [4700].

MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_6\text{F}_3\text{SFe}$ ,  $[\text{M}]^+$ : 585.1, found: 585.2.

Electrochemistry:  $E_{1/2} = 0.55$  V vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M  $\text{TBAPF}_6$ , BDD disk electrode).



Yellow oil  $\text{TPA}^{\text{CF}_3}$  (tris(4-(trifluoromethyl)-2-picolyl)amine) (72 mg, 1 eq) and white solid  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (63 mg, 1 eq) were each dissolved in 0.5 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{TPA}^{\text{CF}_3}$ , instantly producing a purple-red solution. The solution was filtered through Celite, and diethyl ether (2 mL) was layered on top of the filtrate. This mixture was placed in a freezer (-30 °C) until dark red-brown crystals appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (47.5 mg, 35% yield).

$^1\text{H}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 11.07 (s), 8.43 (s), 5.86 (s), 3.66 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) = -65.9 (s), -78.9 (s).

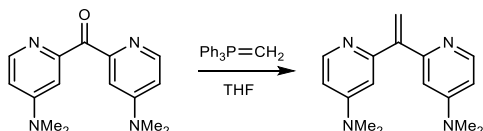
UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ]: 225 [9900], 262 [13000], 388 [6600], 428 [8900].

MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{22}\text{H}_{15}\text{N}_4\text{O}_3\text{F}_{12}\text{SFe}$ ,  $[\text{M}]^+$ : 699.0, found: 699.0.

Electrochemistry:  $E_{p/2} = 1.09$  V (irreversible) vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M  $\text{TBAPF}_6$ , BDD disk electrode).

## BPM – dipyridyl substitution

### 2,2'-(ethene-1,1-diyl)bis(4-(dimethylamino)pyridine)



**Note:** This compound was prepared with modifications to the literature procedure for 2,2'-(ethene-1,1-diyl)dipyridine.<sup>13</sup> Notably, poor performance was observed when methylenetriphenylphosphorane was generated *in situ*, presumably due to residual potassium salts (i.e., KBr).

Bis(4-dimethylaminopyridin-2-yl)methanone (406 mg, 1.5 mmol, 1 eq) was suspended in anhydrous tetrahydrofuran (15 mL, 0.1 M) in a glovebox and cooled to  $-30\text{ }^{\circ}\text{C}$ , after which isolated methylenetriphenylphosphorane (435 mg, 1.58 mmol, 1.05 eq) was added in one portion. This mixture was warmed to room temperature and allowed to react for at least 4 h (reaction times up to overnight have no deleterious impact). Outside of the glovebox, the reaction was quenched with minimal water and concentrated to yield a viscous orange-red oil. The oil was purified by silica gel column chromatography by loading with dichloromethane, eluting the triphenylphosphine oxide with 3:1 ethyl acetate:acetone plus 1% triethylamine, then eluting the product with acetone plus 1% triethylamine to afford a white crystalline solid (346 mg, 86% yield).

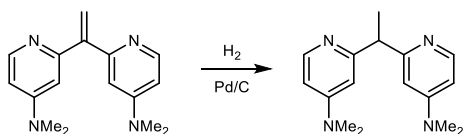
$R_f = 0.3$  (acetone plus 1% triethylamine; TLC plates treated with triethylamine).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.29 (d,  $J = 5.9$  Hz, 2H), 6.67 (d,  $J = 2.7$  Hz, 2H), 6.46 (dd,  $J = 5.9, 2.6$  Hz, 2H), 5.94 (s, 2H), 3.00 (s, 12H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 158.66 (s), 154.77 (s), 150.57 (s), 149.32 (s), 118.66 (s), 106.38 (s), 105.47 (s), 39.18 (s).

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{20}\text{N}_4 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 269.1761, found: 269.1763.

### 2,2'-(ethane-1,1-diyl)bis(4-(dimethylamino)pyridine)



2,2'-(ethene-1,1-diyl)bis(4-(dimethylamino)pyridine) (268 mg, 1 mmol, 1 eq), Pd/C (43 mg, 5% by mass Pd, 0.02 eq), and activated carbon (134 mg, 0.5 mass eq) were suspended in methanol (10 mL, 0.1 M). The headspace of this mixture was purged with nitrogen and then hydrogen. A

hydrogen atmosphere was maintained using a balloon, and the mixture was allowed to react for 12 h. The suspension was allowed to settle, and the solution was filtered through Celite. The remaining solids were washed with methanol, and the supernatant was filtered through Celite. The combined solution was concentrated, dissolved in dichloromethane, dried over sodium sulfate, and concentrated again to afford an off-white crystalline solid after gentle heating under vacuum. (247 mg, 91% yield). This material was used without further purification.

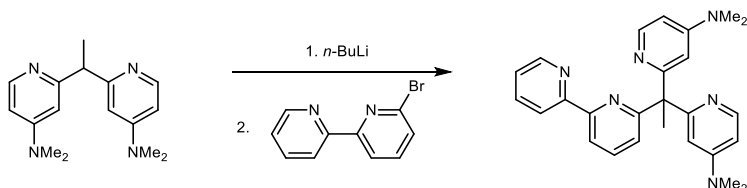
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.19 (d,  $J$  = 6.0 Hz, 2H), 6.58 (d,  $J$  = 2.6 Hz, 2H), 6.34 (dd,  $J$  = 6.0, 2.6 Hz, 2H), 4.21 (q,  $J$  = 7.2 Hz, 1H), 2.95 (s, 12H), 1.71 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 164.30 (s), 154.84 (s), 149.03 (s), 105.02 (s), 104.81 (s), 50.39 (s), 39.13 (s), 19.94 (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{22}\text{N}_4 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 271.2, found: 271.2.

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{22}\text{N}_4 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 271.1917, found: 271.1919.

**BPM<sup>NMe2</sup> (6-(1,1-bis(4-(dimethylamino)pyridin-2-yl)ethyl)-2,2'-bipyridine)**



This compound was prepared by analogy to the parent ligand.<sup>3</sup> In a Schlenk tube under nitrogen, 2,2'-(ethane-1,1-diyl)bis(4-(dimethylamino)pyridine) (135 mg, 0.5 mmol, 1 eq) was dissolved in 2 mL dry tetrahydrofuran and cooled in a dry ice/acetone bath. A 1.6 M *n*-BuLi solution in hexanes (0.31 mL, 0.5 mmol, 1 eq) was added dropwise via syringe, and the solution turned yellow-orange. The mixture was stirred for 45 additional minutes, then 6-bromo-2,2'-bipyridine (118 mg, 0.5 mmol, 1 eq) was added as a solution in 0.5 mL tetrahydrofuran. The solution was warmed to room temperature and stirred for 16 h, after which time the reaction was quenched with water. The solution was concentrated, transferred to a separatory funnel, and extracted with dichloromethane. The combined organic fractions were concentrated and purified via column chromatography on neutral alumina using methanol:dichloromethane (1:49) to afford a waxy colorless solid. (163 mg, 77% yield).

$R_f$  = 0.2 (methanol; TLC plates treated with methanol).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.56 (ddd,  $J$  = 4.8, 1.9, 0.9 Hz, 1H), 8.31 (dt,  $J$  = 8.1, 1.1 Hz, 1H), 8.19 (dd,  $J$  = 5.8, 0.6 Hz, 2H), 8.15 (dd,  $J$  = 7.8, 0.9 Hz, 1H), 7.65 (td,  $J$  = 7.7, 1.8 Hz,

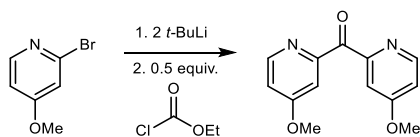
1H), 7.60 (t,  $J = 7.8$  Hz, 1H), 7.17 (ddd,  $J = 7.5, 4.8, 1.3$  Hz, 1H), 7.11 (dd,  $J = 7.9, 0.9$  Hz, 1H), 6.31 – 6.25 (m, 4H), 2.79 (s, 12H), 2.33 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 166.41 (s), 165.44 (s), 156.89 (s), 154.50 (s), 154.27 (s), 148.86 (s), 148.79 (s), 136.66 (s), 136.48 (s), 124.42 (s), 123.30 (s), 121.47 (s), 117.99 (s), 106.72 (s), 104.38 (s), 60.37 (s), 39.04 (s), 27.16 (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{26}\text{H}_{28}\text{N}_6 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 425.3, found: 425.3.

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{26}\text{H}_{28}\text{N}_6 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 425.2448, found: 425.2448.

### bis(4-methoxypyridin-2-yl)methanone



This compound was prepared by analogy to the known analogue, bis(4-(dimethylamino)pyridin-2-yl)methanone.<sup>5</sup> In a 100 mL flask under nitrogen, 2-bromo-4-methoxypyridine (0.7 g, 3.7 mmol, 1 eq) was dissolved in 30 mL dry diethyl ether and cooled in a dry ice/acetone bath. A 1.7 M *t*-BuLi solution in pentane (4.4 mL, 7.4 mmol, 2 eq) was added dropwise via syringe, and the solution slowly turned red-orange. The mixture was stirred for 5 additional minutes before neat ethyl chloroformate (0.18 mL, 1.8 mmol, 0.5 eq) was added all at once via syringe, after which the solution darkened. The solution was stirred 30 additional minutes in the dry ice/acetone bath, warmed to approximately 0 °C, and then quenched with water. The mixture was transferred to a separatory funnel and extracted with additional diethyl ether. The combined organic fractions were dried over sodium sulfate and concentrated under reduced pressure. The crude material was eluted through a plug of silica using acetone and then purified by silica gel column chromatography (3:1 ethyl acetate:acetone plus 1% triethylamine;  $R_f = 0.3$ ) to yield an off-white solid (0.267 g, 59% yield). This material can be crystallized from cold 1:3 acetone:diethyl ether.

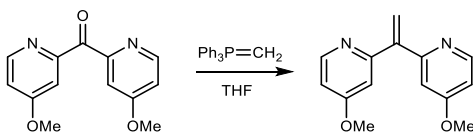
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.56 (dd,  $J = 5.7, 0.5$  Hz, 2H), 7.61 (dd,  $J = 2.6, 0.5$  Hz, 2H), 6.99 (dd,  $J = 5.7, 2.6$  Hz, 2H), 3.93 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 193.11 (s), 166.28 (s), 156.11 (s), 150.42 (s), 112.73 (s), 110.93 (s), 55.53 (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 245.1, found: 245.1.

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 245.0921, found: 245.0927.

### 2,2'-(ethene-1,1-diyl)bis(4-(methoxypyridine))



**Note:** This compound was prepared with modifications to the literature procedure for 2,2'-(ethene-1,1-diyl)dipyridine.<sup>13</sup> Notably, poor performance was observed when methylenetriphenylphosphorane was generated *in-situ*, presumably due to residual potassium salts (i.e., KBr).

Bis(4-methoxypyridin-2-yl)methanone (366 mg, 1.5 mmol, 1 eq) was dissolved in anhydrous tetrahydrofuran (15 mL, 0.1 M) in a glovebox and cooled to  $-30\text{ }^\circ\text{C}$ , after which isolated methylenetriphenylphosphorane (435 mg, 1.58 mmol, 1.05 eq) was added in one portion. This mixture was warmed to room temperature and allowed to react for at least 4 h (reaction times up to overnight have no deleterious impact). Outside of the glovebox, the reaction was quenched with minimal water and concentrated to yield a viscous orange-red oil. The oil was purified by silica gel column chromatography by loading with dichloromethane, eluting the triphenylphosphine oxide with 4:1 ethyl acetate:acetone plus 1% triethylamine, then eluting the product with 3:1 ethyl acetate:acetone plus 1% triethylamine to afford an off-white crystalline solid (269 mg, 74% yield).

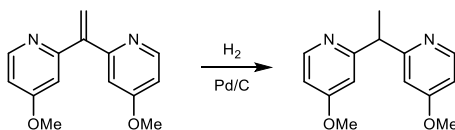
$R_f = 0.3$  (4:1 ethyl acetate:acetone plus 1% triethylamine; TLC plates treated with triethylamine).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.49 (d,  $J = 5.7$  Hz, 2H), 6.95 (d,  $J = 2.4$  Hz, 2H), 6.79 (dd,  $J = 5.7, 2.5$  Hz, 2H), 6.04 (s, 2H), 3.86 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 166.05 (s), 159.50 (s), 150.57 (s), 148.72 (s), 120.38 (s), 109.55 (s), 108.54 (s), 55.14 (s).

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 243.1128, found: 243.1133.

### 2,2'-(ethane-1,1-diyl)bis(4-methoxypyridine)



2,2'-(ethene-1,1-diyl)bis(4-methoxypyridine) (242 mg, 1 mmol, 1 eq), Pd/C (43 mg, 5% by mass Pd, 0.02 eq), and activated carbon (121 mg, 0.5 mass eq) were suspended in methanol (10 mL, 0.1 M). The headspace of this mixture was purged with nitrogen and then hydrogen. A hydrogen atmosphere was maintained using a balloon, and the mixture was allowed to react for 12 h. The

suspension was allowed to settle, and the solution was filtered through Celite. The remaining solids were washed with methanol, and the supernatant was filtered through Celite. The combined solution was concentrated and purified by column chromatography to afford a white solid (127 mg, 52% yield).

Chromatography: Silica was slurry-packed with 1:19 methanol:dichloromethane then equilibrated with 1:49 methanol:dichloromethane. A gradient of 1:49 to 1:19 methanol:dichloromethane was used to elute the product, as well as a dimeric product characterized below.

$R_f = 0.3$  (1:19 methanol:dichloromethane).

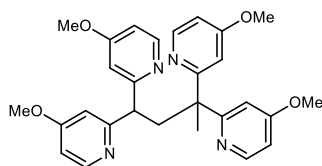
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.36 (d,  $J = 5.8$  Hz, 2H), 6.81 (d,  $J = 2.5$  Hz, 2H), 6.64 (dd,  $J = 5.7, 2.5$  Hz, 2H), 4.34 (q,  $J = 7.2$  Hz, 1H), 3.79 (s, 6H), 1.71 (d,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 166.09 (s), 165.52 (s), 150.34 (s), 108.26 (s), 107.90 (s), 55.03 (s), 49.99 (s), 19.67 (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 245.1, found: 245.1.

HRMS (ESI, TOF ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 245.1285, found: 245.1287.

**Byproduct from synthesis of 2,2'-(ethane-1,1-diyl)bis(4-methoxypyridine):  
2,2',2'',2'''- 2,2',2'',2'''-(butane-1,1,3,3-tetrayl)tetrakis(4-methoxypyridine)**



Isolated from the above reaction as a pale oil (75.6 mg, 31% yield).

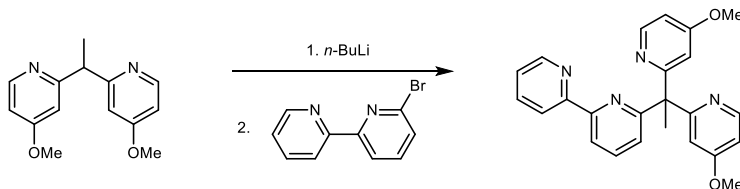
$R_f = 0.1$  (1:19 methanol:dichloromethane).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.31 (dd,  $J = 5.6, 0.9$  Hz, 2H), 8.27 (dd,  $J = 5.7, 0.9$  Hz, 2H), 6.78 (d,  $J = 2.5$  Hz, 2H), 6.70 (d,  $J = 2.2$  Hz, 2H), 6.55 (dd,  $J = 2.5, 1.1$  Hz, 2H), 6.53 (dd,  $J = 2.4, 1.1$  Hz, 2H), 4.27 (t,  $J = 6.0$  Hz, 1H), 3.77 (s, 6H), 3.74 (s, 6H), 3.40 (d,  $J = 5.8$  Hz, 2H), 1.72 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  (ppm) = 168.19 (s), 165.72 (s), 165.58 (s), 165.11 (s), 149.76 (s), 149.64 (s), 108.52 (s), 108.12 (s), 107.20 (s), 54.96 (s), 54.87 (s), 52.99 (s), 51.92 (s), 44.21 (s), 25.63 (s).

HRMS (ESI, TOF (CH<sub>3</sub>CO<sub>2</sub>H),  $m/z$ ): calculated for C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub> + H, [M+H]<sup>+</sup>: 487.2340, found: 487.2361.

**BPM<sup>OMe</sup> (6-(1,1-bis(4-methoxypyridin-2-yl)ethyl)-2,2'-bipyridine)**



This compound was prepared by analogy to the parent ligand.<sup>3</sup> In a Schlenk tube under nitrogen, 2,2'-(ethane-1,1-diyl)bis(4-methoxypyridine) (122 mg, 0.5 mmol, 1 eq) was dissolved in 2 mL dry tetrahydrofuran and cooled in a dry ice/acetone bath. A 1.6 M *n*-BuLi solution in hexanes (0.31 mL, 0.5 mmol, 1 eq) was added dropwise via syringe, and the solution turned yellow-orange. The mixture was stirred for 45 additional minutes, then 6-bromo-2,2'-bipyridine (118 mg, 0.5 mmol, 1 eq) was added as a solution in 0.5 mL tetrahydrofuran. The solution was warmed to room temperature and stirred for 24 h, after which time the reaction was quenched with water. The solution was concentrated, transferred to a separatory funnel, and extracted with dichloromethane. The combined organic fractions were concentrated and purified via column chromatography to afford a white solid (166 mg, 83% yield).

Chromatography: Silica was slurry-packed with 1:49 methanol:dichloromethane then equilibrated with 1:99 methanol:dichloromethane. A gradient of 1:99 to 1:19 methanol:dichloromethane was used to elute the product.

R<sub>f</sub> = 0.3 (1:9 methanol:dichloromethane).

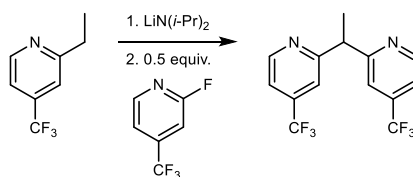
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) = 8.56 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 8.38 (dd, *J* = 5.6, 0.8 Hz, 2H), 8.20 (ddt, *J* = 8.8, 7.7, 1.1 Hz, 2H), 7.64 (td, *J* = 7.8, 0.9 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.09 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.60 (ddd, *J* = 5.6, 2.4, 0.9 Hz, 2H), 6.56 (dd, *J* = 2.4, 0.8 Hz, 2H), 3.66 (d, *J* = 0.9 Hz, 6H), 2.32 (d, *J* = 1.0 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ (ppm) = 167.66 (s), 165.72 (s), 164.37 (s), 156.55 (s), 154.55 (s), 150.12 (s), 148.88 (s), 136.87 (s), 136.71 (s), 123.94 (s), 123.46 (s), 121.30 (s), 118.37 (s), 110.37 (s), 106.96 (s), 60.23 (s), 54.96 (s), 27.10 (s).

MS (ESI, UHPLC-MS (CH<sub>3</sub>CO<sub>2</sub>H),  $m/z$ ): calculated for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> + H, [M+H]<sup>+</sup>: 399.2, found: 399.1.

HRMS (ESI, TOF (CH<sub>3</sub>CO<sub>2</sub>H),  $m/z$ ): calculated for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> + H, [M+H]<sup>+</sup>: 399.1816, found: 399.1821.

**2,2'-(ethane-1,1-diyl)bis(4-(trifluoromethyl)pyridine)**



This compound was prepared by analogy to the procedure reported for the parent dipyridylethane.<sup>14</sup> In a Schlenk tube under nitrogen, 2-ethyl-4-(trifluoromethyl)pyridine (876 mg, 2 eq) was dissolved in THF (7 mL) and cooled to  $-78\text{ }^{\circ}\text{C}$  while stirring. A 2.0 M solution of lithium diisopropylamide in THF/heptane/ethylbenzene (2.5 mL, 2 eq) was added dropwise via syringe, and the solution turned dark purple. The solution was warmed to room temperature for 5 minutes then cooled to  $-78\text{ }^{\circ}\text{C}$  prior to dropwise addition of a cooled solution of 2-fluoro-4-(trifluoromethyl)pyridine (413 mg, 1 eq) in THF (3 mL). The reaction was warmed to room temperature after which it was stirred for 30 minutes then quenched with water. The mixture was concentrated, diluted in water, and extracted with dichloromethane. The organic extract was dried over sodium sulfate, concentrated, subjected to a silica plug with 1:4 ethyl acetate:hexane, and concentrated to a yellow oil that was used without further purification (0.15 g, 19% yield).

$R_f = 0.3$  (1:9 ethyl acetate:hexane).

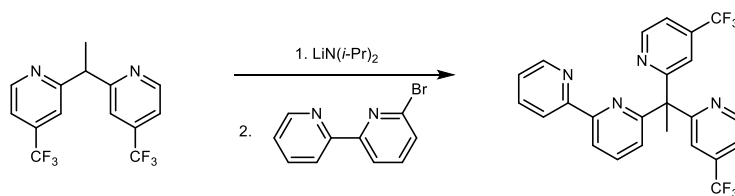
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) = 8.73 (dt,  $J = 5.1, 0.8$  Hz, 2H), 7.57 – 7.54 (m, 2H), 7.37 (ddd,  $J = 5.1, 1.7, 0.8$  Hz, 2H), 4.61 (q,  $J = 7.2$  Hz, 1H), 1.80 (d,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 101 MHz): 164.46 (s), 150.34 (s), 138.89 (q,  $J = 33.9$  Hz), 122.80 (q,  $J = 273.3$  Hz), 118.10 (q,  $J = 3.6$  Hz), 117.49 (q,  $J = 3.5$  Hz), 49.90 (s), 19.79 (s).

$^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  (ppm) =  $-64.8$  (s).

MS (ESI, UHPLC-MS ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $m/z$ ): calculated for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{F}_6 + \text{H}$ ,  $[\text{M}+\text{H}]^+$ : 321.1, found: 321.1.

**BPM<sup>CF<sub>3</sub></sup> (6-(1,1-bis(4-(trifluoromethyl)pyridin-2-yl)ethyl)-2,2'-bipyridine)**



This compound was prepared by analogy to the parent ligand.<sup>3</sup> In a Schlenk tube under nitrogen, 2,2'-(ethane-1,1-diyl)bis(4-trifluoromethyl)pyridine (0.1 g, 1 eq) was dissolved in 3 mL tetrahydrofuran and cooled in a dry ice/acetone bath. A 2.0 M lithium diisopropylamide solution in THF/heptane/ethylbenzene (0.16 mL, 1.05 eq) was added dropwise via syringe, and the solution turned red. The mixture was stirred for 5 additional minutes then warmed to room temperature. The solution was returned to the dry ice/acetone bath before 6-bromo-2,2'-bipyridine (0.073 g, 1 eq) was added as a solid. The solution was warmed to room temperature then heated to 70 °C for 1.5 d, after which time the reaction was cooled to room temperature and quenched with water. The solution was concentrated, transferred to a separatory funnel, and extracted with dichloromethane. The combined organic fractions were dried over sodium sulfate, concentrated, and purified via silica gel column chromatography using 1:4 ethyl acetate:hexane to afford a viscous yellow oil (0.075 g, 51% yield).

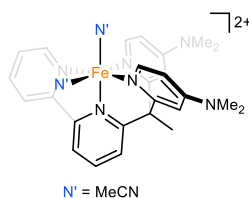
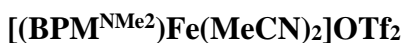
R<sub>f</sub> = 0.2 (1:4 ethyl acetate:hexane).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) = 8.68 (dt, *J* = 5.1, 0.8 Hz, 2H), 8.57 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.26 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.98 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 (dt, *J* = 1.6, 0.8 Hz, 2H), 7.32 (ddd, *J* = 5.1, 1.7, 0.8 Hz, 2H), 7.23 – 7.15 (m, 2H), 2.33 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz): δ (ppm) = 167.10 (s), 162.96 (s), 155.88 (s), 154.91 (s), 149.53 (s), 148.97 (s), 138.11 (q, *J* = 33.7 Hz), 137.60 (s), 136.83 (s), 123.78 (s), 123.09 (s), 122.92 (q, *J* = 273.6 Hz), 121.08 (s), 119.57 (q, *J* = 3.8 Hz), 118.96 (s), 117.13 (q, *J* = 3.6 Hz), 60.54 (s), 27.10 (s).

<sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376 MHz): δ (ppm) = −64.7 (s).

MS (ESI, UHPLC-MS (CH<sub>3</sub>CO<sub>2</sub>H), *m/z*): calculated for C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>F<sub>6</sub> + H, [M+H]<sup>+</sup>: 475.1, found: 475.1.



White solids  $\text{BPM}^{\text{NMe}_2}$  (6-(1,1-bis(4-(dimethylamino)pyridin-2-yl)ethyl)-2,2'-bipyridine) (30 mg, 1 eq) and  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (31 mg, 1 eq) were each dissolved in 0.5 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{BPM}^{\text{NMe}_2}$ , instantly producing a purple solution. The solution was filtered through a glass microfilter, and diethyl ether (2 mL) was layered on top of the filtrate. This mixture was placed in a freezer ( $-30^\circ\text{C}$ ) until a purple precipitate appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (50.7 mg, 83% yield).

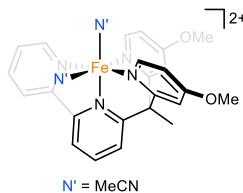
$^1\text{H}$  NMR (25  $^\circ\text{C}$ ,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 9.55 (d,  $J$  = 5.5 Hz, 1H), 8.49 (d,  $J$  = 6.8 Hz, 2H), 8.39 (d,  $J$  = 8.0 Hz, 1H), 8.27 (d,  $J$  = 7.9 Hz, 1H), 8.17 (td,  $J$  = 7.9, 0.9 Hz, 1H), 8.13 (t,  $J$  = 7.9 Hz, 1H), 7.94 (d,  $J$  = 8.0 Hz, 1H), 7.74 (t,  $J$  = 6.5 Hz, 1H), 7.04 (d,  $J$  = 2.7 Hz, 2H), 6.60 (dd,  $J$  = 6.9, 2.7 Hz, 2H), 3.07 (d,  $J$  = 1.0 Hz, 12H), 2.70 (s, 3H).

$^{19}\text{F}\{^1\text{H}\}$  NMR (25  $^\circ\text{C}$ ,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) =  $-79.3$ .

UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ): 331 [12000], 393 [4400], 498 [2800], 528 [3200].

MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{27}\text{H}_{28}\text{N}_6\text{O}_3\text{F}_3\text{SFe}$ ,  $[\text{M}]^+$ : 629.1, found: 629.2.

Electrochemistry:  $E_{1/2}$  = 0.45 V vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M  $\text{TBAPF}_6$ , BDD disk electrode).



White solids  $\text{BPM}^{\text{OMe}}$  (6-(1,1-bis(4-methoxypyridin-2-yl)ethyl)-2,2'-bipyridine) (26 mg, 1 eq) and  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (28.5 mg, 1 eq) were each dissolved in 0.3 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{BPM}^{\text{OMe}}$ , instantly producing a purple solution. The solution was filtered through a glass microfilter, and diethyl ether (1.5 mL) was layered on top of the filtrate. This mixture was placed in a freezer ( $-30^\circ\text{C}$ ) until a purple precipitate appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (50.2 mg, 92% yield).

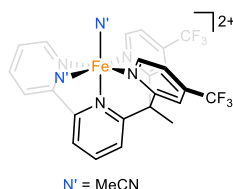
$^1\text{H}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 9.57 (d,  $J$  = 5.5 Hz, 1H), 8.94 (d,  $J$  = 6.5 Hz, 2H), 8.40 (d,  $J$  = 8.0 Hz, 1H), 8.28 (d,  $J$  = 7.9 Hz, 1H), 8.18 (dt,  $J$  = 13.5, 7.9 Hz, 2H), 7.99 (d,  $J$  = 7.9 Hz, 1H), 7.77 (t,  $J$  = 6.6 Hz, 1H), 7.46 (d,  $J$  = 2.6 Hz, 2H), 7.00 (dd,  $J$  = 6.7, 2.6 Hz, 2H), 3.93 (s, 6H), 2.74 (s, 3H).

$^{19}\text{F}\{^1\text{H}\}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) = -79.3.

UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ]: 305 [24000], 338 [5500], 387 [3500], 496 [2900].

MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_5\text{F}_3\text{SFe}$ ,  $[\text{M}]^+$ : 603.1, found: 603.2.

Electrochemistry:  $E_{1/2}$  = 0.69 V vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M  $\text{TBAPF}_6$ , BDD disk electrode).



Yellow oil  $\text{BPM}^{\text{CF}_3}$  (6-(1,1-bis(4-(trifluoromethyl)pyridin-2-yl)ethyl)-2,2'-bipyridine) (87.8 mg, 1 eq) and white solid  $\text{FeOTf}_2 \cdot 2 \text{ MeCN}$  (80.6 mg, 1 eq) were each dissolved in 0.3 mL acetonitrile. The solution of  $\text{FeOTf}_2$  was added to the solution of  $\text{BPM}^{\text{CF}_3}$ , instantly producing an orange solution. The solution was filtered through a glass microfilter, and diethyl ether (1.5 mL) was layered on top of the filtrate. This mixture was placed in a freezer (-30 °C) until an orange-red precipitate appeared. The precipitate was isolated by decanting the supernatant and drying under vacuum (163.8 mg, 97% yield).

$^1\text{H}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 400.15 MHz):  $\delta$  (ppm) = 9.57 (d,  $J$  = 5.6 Hz, 1H), 9.53 (d,  $J$  = 6.0 Hz, 2H), 8.42 (d,  $J$  = 7.9 Hz, 1H), 8.26 (dt,  $J$  = 15.7, 7.9 Hz, 3H), 8.15 (s, 2H), 8.04 (d,  $J$  = 7.8 Hz, 1H), 7.83 (t,  $J$  = 6.6 Hz, 1H), 7.68 (d,  $J$  = 5.9 Hz, 2H), 2.91 (s, 3H).

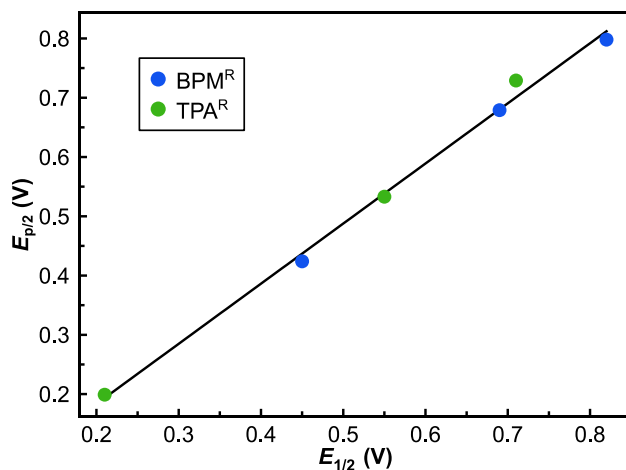
$^{19}\text{F}\{^1\text{H}\}$  NMR (25 °C,  $\text{CD}_3\text{CN}$ , 376 MHz):  $\delta$  (ppm) = -65.3, -79.3.

UV-vis (MeCN): nm [ $\text{cm}^{-1}\text{M}^{-1}$ ]: 259 [16000], 301 [19000], 361 [4100], 425 [6000], 463 [5000].

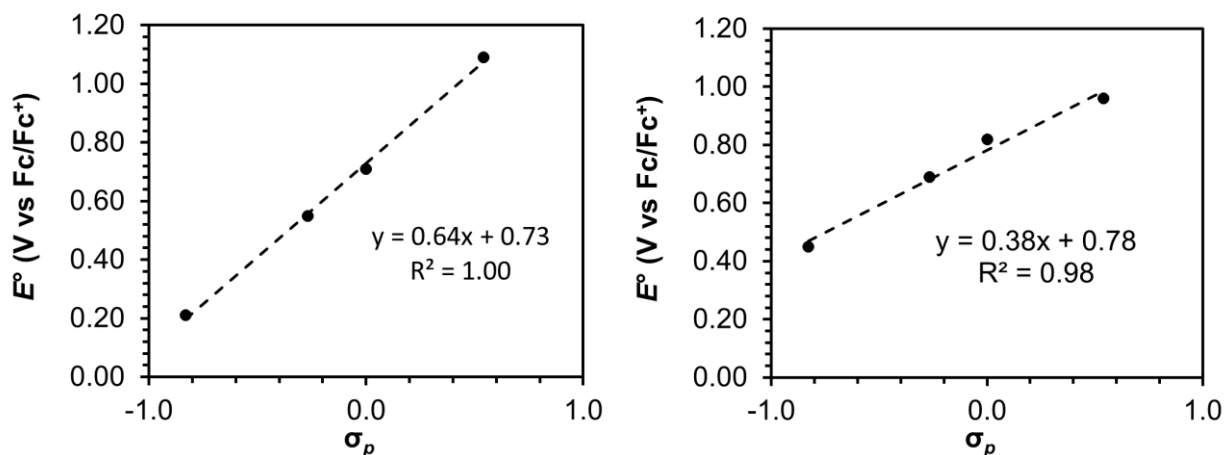
MS (ESI, direct injection in MeCN,  $m/z$ ): calculated for  $\text{C}_{25}\text{H}_{16}\text{N}_4\text{O}_3\text{F}_9\text{SFe}$ : 679.0, found: 679.2.

Electrochemistry:  $E_{p/2}$  = 0.96 V (irreversible) vs  $\text{Fc}/\text{Fc}^+$  (MeCN, 0.1 M  $\text{TBAPF}_6$ , BDD disk electrode).

### S3. Additional voltammetry data related to $E^\circ$

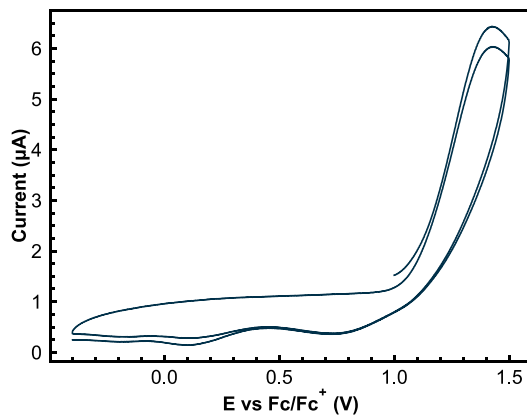


**Figure S1.** Correlation between half-wave ( $E_{1/2}$ ) and half-peak ( $E_{p/2}$ ) potentials for both  $[(\text{TPA}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  and  $[(\text{BPM}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  for  $\text{R} = \text{NMe}_2, \text{OMe}, \text{H}$ . Potentials are reported versus  $\text{Fc}/\text{Fc}^+$ .

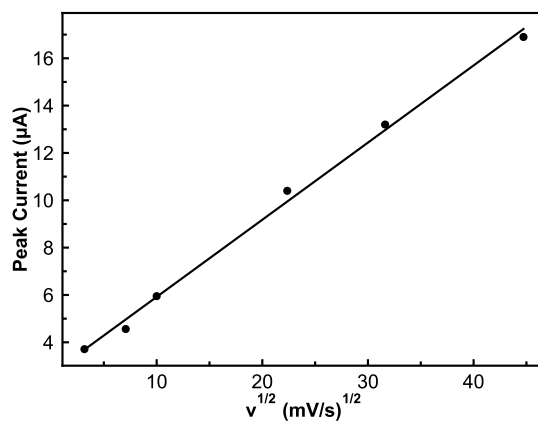


**Figure S2.** Electrochemical data for  $[(\text{TPA}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  (left) and  $[(\text{BPM}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  (right) analyzed using a Hammett parameter.  $E^\circ$  represents  $E_{1/2}$  or  $E_{p/2}$  and is plotted as a function of Hammett  $\sigma_p$ . From left to right,  $\text{R} = \text{NMe}_2, \text{OMe}, \text{H}, \text{CF}_3$ .

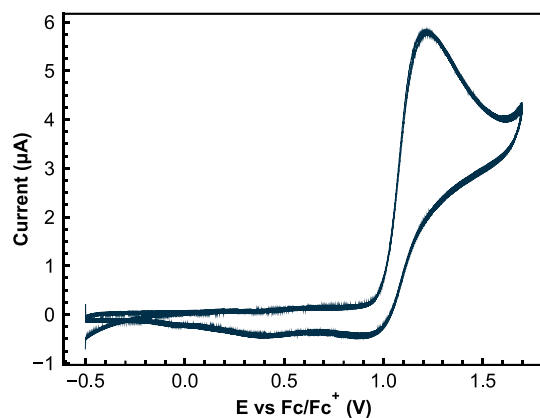
#### S4. Additional voltammetry data for R = CF<sub>3</sub>



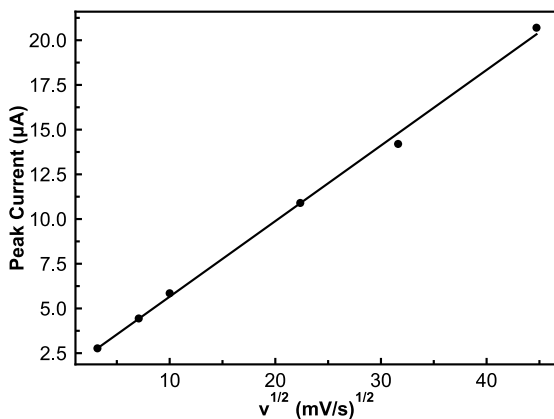
**Figure S3.** Cyclic voltammetry (2 scans at 100 mV/s) of [(TPA<sup>CF<sub>3</sub></sup>)Fe(MeCN)<sub>2</sub>]<sup>2+</sup> in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.



**Figure S4.** Randles–Ševčík plot from cyclic voltammograms of [(TPA<sup>CF<sub>3</sub></sup>)Fe(MeCN)<sub>2</sub>]<sup>2+</sup> in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The linear behavior is indicative of a freely diffusing, non-catalytic electroactive species, which, when combined with similar peak currents between scans, corroborates assignment of this redox feature as reversible.



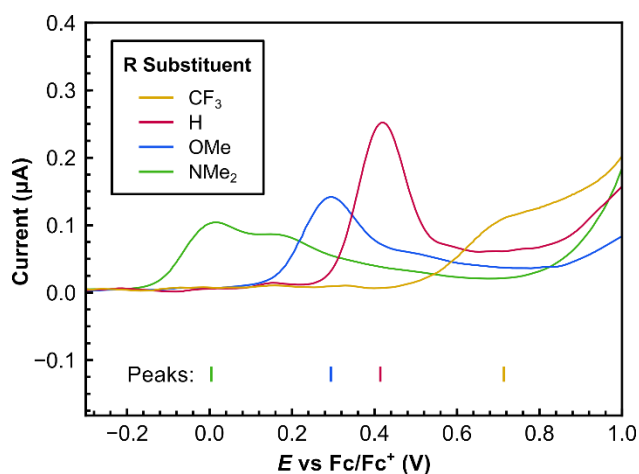
**Figure S5.** Cyclic voltammetry (2 scans at 100 mV/s) of  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]^{2+}$  in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.



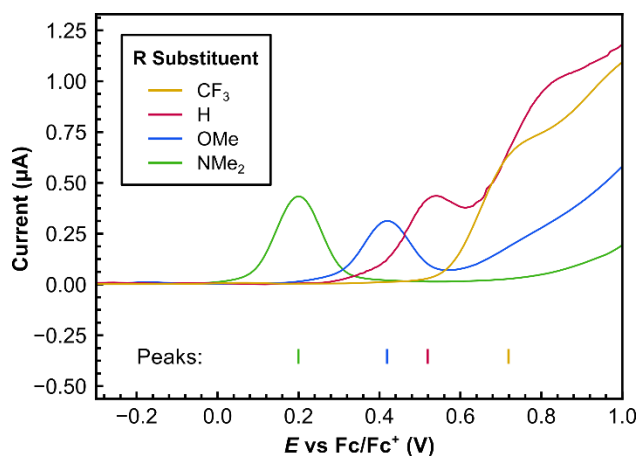
**Figure S6.** Randles–Ševčík plot from cyclic voltammograms of  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]^{2+}$  in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The linear behavior is indicative of a freely diffusing, non-catalytic electroactive species, which, when combined with similar peak currents between scans, corroborates assignment of this redox feature as reversible.

## S5. $E_1$ voltammetry

A buffered electrolyte ( $\text{NH}_3/\text{NH}_4^+$ ) was used for all measurements of the  $E_1$  potential. The  $\text{NH}_3/\text{NH}_4^+$  ratio affects the pH as in the Henderson-Hasselbach relationship, and the pH affects the potential for the  $E_1$  proton-coupled electron transfer step (see our previous work: *ACS Catal.* **2019**, 9, 10101; *J. Am. Chem. Soc.* **2021**, 143, 7612). All measurements were made using an identical stock solution containing 50 equiv.  $\text{NH}_3$  and 0.05 M ammonium triflate.



**Figure S7.** Differential pulse voltammetry of  $[(\text{TPA}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  in acetonitrile with 50 equiv.  $\text{NH}_3$  using 0.05 M ammonium triflate as supporting electrolyte with BDD WE. Peak locations (indicated by vertical bars in plot) were picked using the peak picking function in EC-Lab.



**Figure S8.** Differential pulse voltammetry of  $[(\text{BPM}^{\text{R}})\text{Fe}(\text{MeCN})_2]^{2+}$  in acetonitrile with 50 equiv.  $\text{NH}_3$  using 0.05 M ammonium triflate as supporting electrolyte with BDD WE. Peak locations (indicated by vertical bars in plot) were picked using the peak picking function in EC-Lab.

## S6. Catalytic controlled potential coulometry experiments

The data in the main text related to catalytic activity versus  $E^\circ$  was obtained coulometrically. While such data is typically obtained from an assessment of catalytic current via voltammetric methods (e.g., analyzing plateau current or using foot-of-the-wave analysis), the low faradaic efficiencies observed with some of the catalysts under our catalytic conditions make such analyses unadvisable. Lowered faradaic efficiencies are observed with more electron-donating R-substituents that also result in lower overall activity. This is partially due to the catalytic conditions required for uniform comparison of the systems, i.e., low overall ammonia concentration to prevent ligand demetallation for CF<sub>3</sub>-substituted catalysts. Since the catalytic rate is dependent on ammonia concentration, using only 50 equiv. NH<sub>3</sub> results in lower rates and facilitates unproductive, reversible redox processes with early intermediates, for example  $\text{Fe}^{\text{II}}\text{-NH}_3 \rightleftharpoons \text{Fe}^{\text{III}}\text{-NH}_2$ , thus lowering the faradaic efficiency for N<sub>2</sub>.

Coulometric analysis of turnover frequency can accurately reflect the intrinsic turnover frequency, provided that catalyst decomposition is negligible or equivalent between systems. Employing a high catalyst concentration (0.4 mM) as compared to the optimal concentration (0.05 mM) and a relatively short reaction time (8 h vs 48 h) both serve to mitigate effects related to catalyst loss.

### Procedures for controlled potential coulometry (CPC)

**Preparation of the BDD electrode:** A 10 cm<sup>2</sup> boron-doped diamond (BDD) plate electrode (IKA) was physically attached to standard electrical wire, and the connection was covered with Teflon tape. The surface area of the electrode submerged in solution was approximately 4 cm<sup>2</sup>.

BDD has a surface that exists in various states of reduction (H-terminated) and oxidation (O-terminated).<sup>15</sup> In order to remove attached nitrogen and iron generated during controlled potential coulometry experiments and to ensure a reliable electrode surface prior to CPC measurements, the BDD plate electrode was oxidatively treated prior to use. First, the electrode was soaked in dilute nitric acid (~2 M) for 5 minutes. Then, a potential of 3.0 V vs Ag/AgCl was applied to the BDD electrode in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 10 minutes. The electrode was then thoroughly rinsed with water prior to use.

**Preparation of the platinum counter electrode:** In order to ensure a highly active Pt surface for HER prior to CPC experiments, the Pt mesh counter electrode was soaked in concentrated hydrochloric acid for at least 5 minutes prior to usage.

**Preparation of the custom Ag/AgOTf reference electrode:** To ensure reliable potential measurements, the custom Ag/AgOTf reference electrode was prepared prior to each CPC experiment then a CV of ferrocene was measured. In a glass tube fitted with a Vycor porous glass frit attached by Teflon heatshrink tubing, an acetonitrile solution containing 5 mM AgOTf and 0.05 M NH<sub>4</sub>OTf was added. A silver wire was placed inside and the electrode was sealed.

**Preparation of ammonia solutions:** Saturated 2 M solutions<sup>16</sup> in acetonitrile were prepared by bubbling anhydrous ammonia through acetonitrile in a Schlenk tube under an argon/ammonia atmosphere. More dilute stock solutions were immediately prepared from this saturated solution.

**Electrolyte selection:** The use of ammonium triflate is preferred for achieving high turnover numbers in catalytic experiments. A moderate (i.e., 50 mM NH<sub>4</sub>OTf) proton concentration helps avoid large overpotential for proton reduction at the counter electrode. Using TBAPF<sub>6</sub> during CPC, N<sub>2</sub> was produced in catalytic quantities, but substantial electrode passivation and diminished faradaic efficiency for N<sub>2</sub> were observed.

**CPC:** Inside an argon glovebox, a gas-tight electrochemical cell equipped with a 24/40 cap containing three tungsten rods for electrical contacts and a 14/20 joint carefully sealed with a Suba-Seal septum was prepared. A BDD plate electrode (A = 4 cm<sup>2</sup>), high surface area platinum mesh electrode, and custom Ag/AgOTf reference electrode were connected to the 24/40 cap. All chemical reagents were then rapidly added to the cell to prevent evaporation of ammonia, then the cell was sealed with the 24/40 cap. Prior to each CPC experiment, a ZIR and CV were taken. No IR compensation was applied for CPC measurements. The CPC experiment was conducted for 8–48 h, then the cell was removed from the glovebox for analysis by gas chromatography. For headspace analysis, 100 µL of the headspace was injected into a GC-TCD for quantification using a lockable Hamilton syringe with a 26S gauge needle.

**Table S1.** Results of catalytic CPC experiments performed at 0.85 V vs Fc/Fc<sup>+</sup> for 8 h for examining the E<sub>2</sub> LFER with 0.4 mM [Fe] and 20 mM NH<sub>3</sub> (50 equivalents) in 10 mL acetonitrile total. Low ammonia concentrations were used to prevent demetallation.

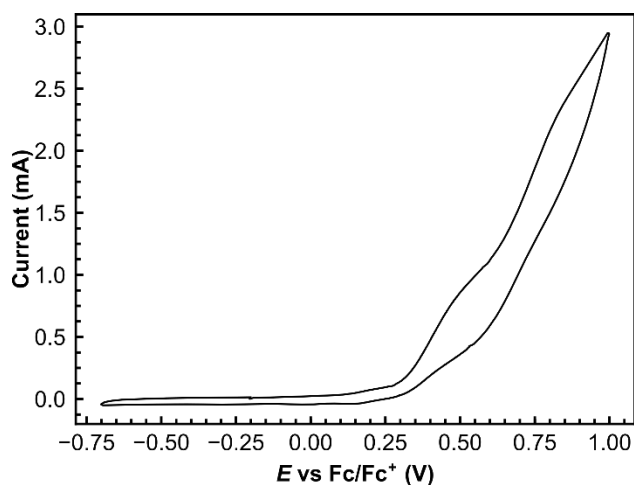
Entry	Fe Source	Eq. N <sub>2</sub>	Charge (C)	FE N <sub>2</sub> (%)	FE H <sub>2</sub> (%)
1	[(TPA <sup>NMe2</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	0.73	3.9	44	16
2	[(TPA <sup>NMe2</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	0.51	8.2	14	14
3	[(TPA <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	1.5	24.8	14	16
4	[(TPA <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	1.4	25	13	18
5	[(TPA <sup>H</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	3.3	18.3	42	44
6	[(TPA <sup>H</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	2.9	15.6	44	42
7	[(TPA <sup>CF3</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	4.0	14.4	65	56
8	[(TPA <sup>CF3</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	3.7	19.7	43	51
9	[(BPM <sup>NMe2</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	6.0	22.2	63	55
10	[(BPM <sup>NMe2</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	6.3	24.1	61	55
11	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	12.8	34.4	87	75
12	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	12.7	39.1	76	68
13	[(BPM <sup>H</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	14.4	41.0	82	73
14	[(BPM <sup>H</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	12.6	39.2	75	67
15	[(BPM <sup>CF3</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	7.4	18.5	94	82
16	[(BPM <sup>CF3</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	9.4	24.3	90	84

**Table S2.** Results of catalytic CPC experiments performed at 0.85 V vs Fc/Fc<sup>+</sup> for 48 h with 0.05 mM [Fe] and 100 mM NH<sub>3</sub> (2000 equivalents) in 10 mL acetonitrile total. Reload experiments are listed as x.1 and x.2 for the first and second experiment, respectively. The reload was stopped after 24 h when current ceased. LOQ indicates that too little gas was produced to exceed the limit of quantification.

Entry	Fe Source	Eq. N <sub>2</sub>	Charge (C)	FE N <sub>2</sub> (%)	FE H <sub>2</sub> (%)
1	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	383	108.9	102	83
1.1	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	52	17.8	85	75
2	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	381	113.9	98	86
3	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	rinse test	113.7	rinse test	rinse test
3 – rinse test	[(BPM <sup>OMe</sup> )Fe(MeCN) <sub>2</sub> ]OTf <sub>2</sub>	LOQ	1.5	LOQ	LOQ

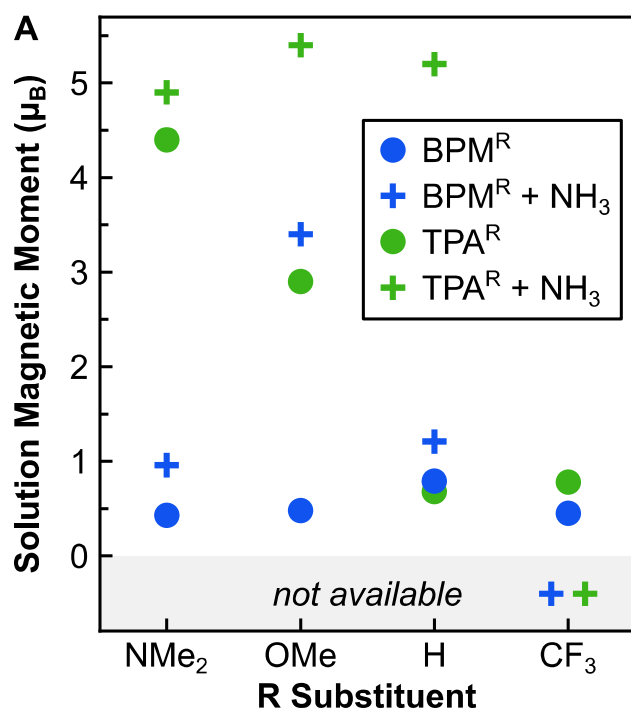
**Rinse test procedure:** After performing 48 h of CPC (entry 3), the electrochemical cell was purged and opened inside of the glovebox to prevent exposure of the working electrode to ambient conditions. The working electrode was thoroughly rinsed with acetonitrile. Then, fresh acetonitrile containing 0.05 M NH<sub>4</sub>OTf and 100 mM NH<sub>3</sub> (2000 equivalents) was added to the electrochemical cell, and the cell was resubjected to a potential of 0.85 V vs Fc/Fc<sup>+</sup> for 48 h (entry 3 – rinse test).

### S7. CV of $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{N}')_2]^{2+}$ under catalytic conditions

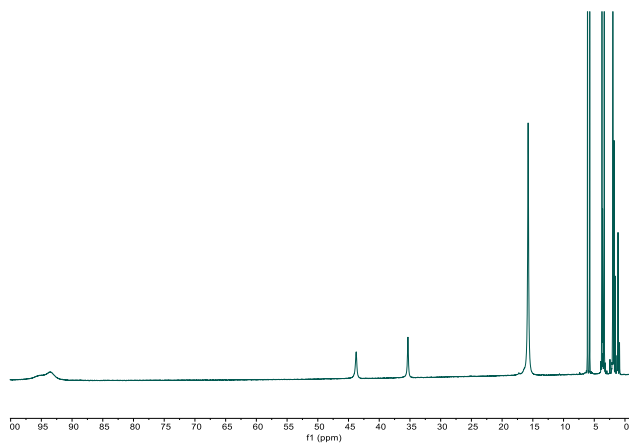


**Figure S9.** Cyclic voltammogram of 0.05 mM  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{N}')_2]^{2+}$  in acetonitrile containing 0.05 M ammonium triflate electrolyte and 2000 equiv.  $\text{NH}_3$  (0.1 M). A BDD plate working electrode, platinum mesh counter electrode, and Ag/AgOTf reference electrode were used.

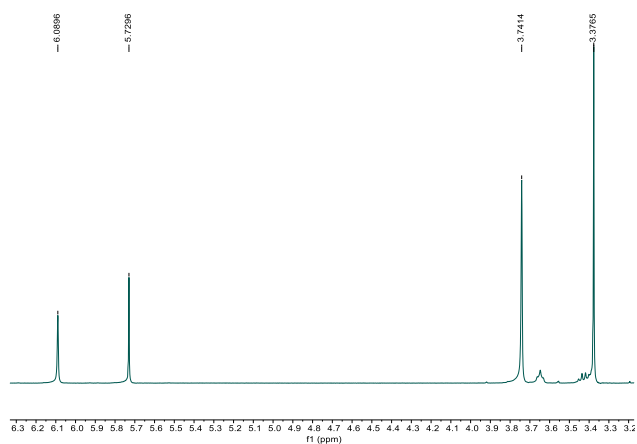
## S8. Evans method data



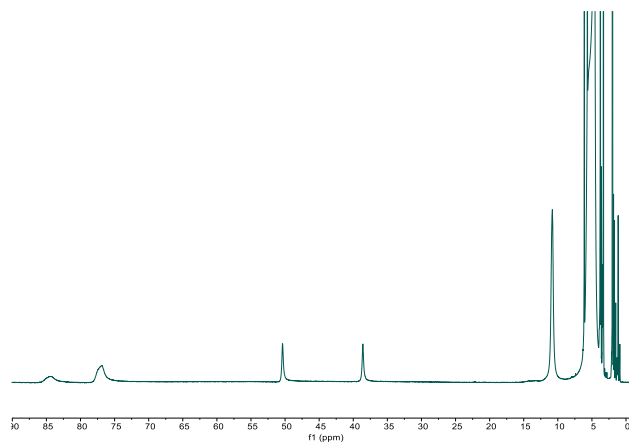
**Figure S10.** Compiled solution magnetic moments of  $[(L_{\text{aux}})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 0 or 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at 25 °C.



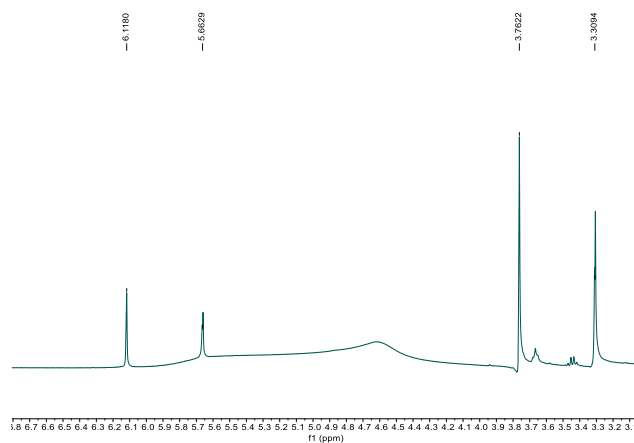
**Figure S11.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



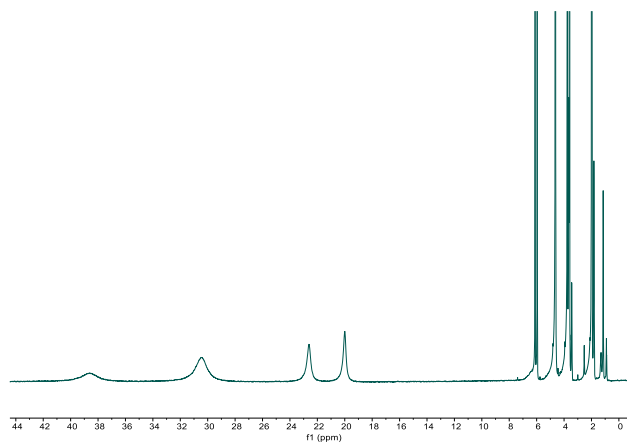
**Figure S12.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 145\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 4.4$ .



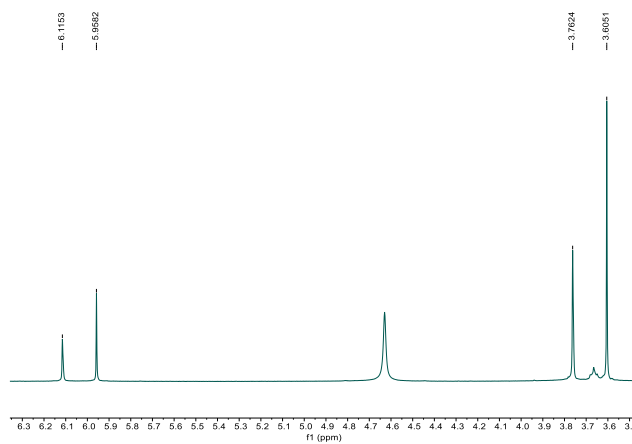
**Figure S13.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .



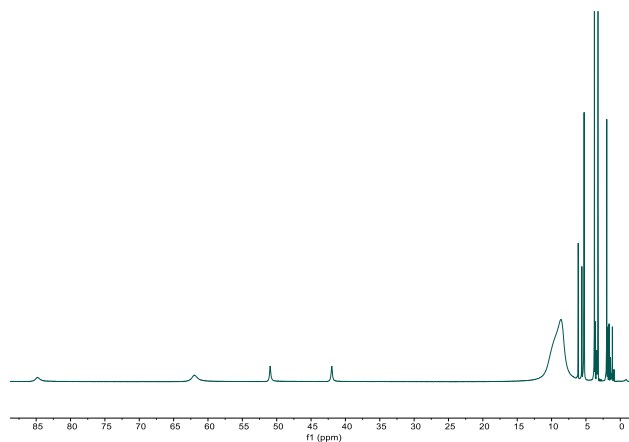
**Figure S14.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .  $[\text{Fe}] = 0.011 \text{ M}$ ,  $\Delta f = 182 \text{ Hz}$ ,  $f = 400.15 \text{ MHz}$ ,  $\mu_B = 4.9$ .



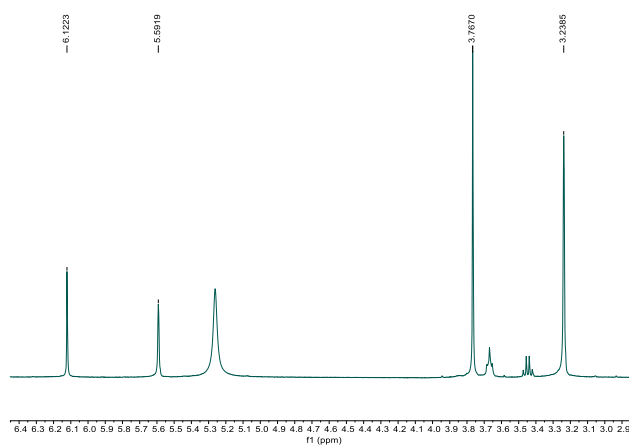
**Figure S15.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



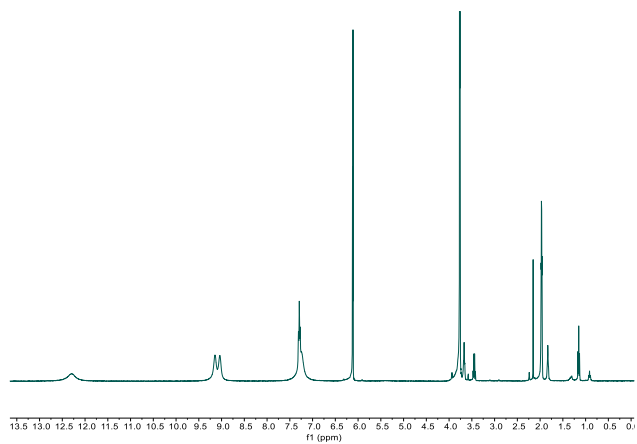
**Figure S16.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 62.9\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 2.9$ .



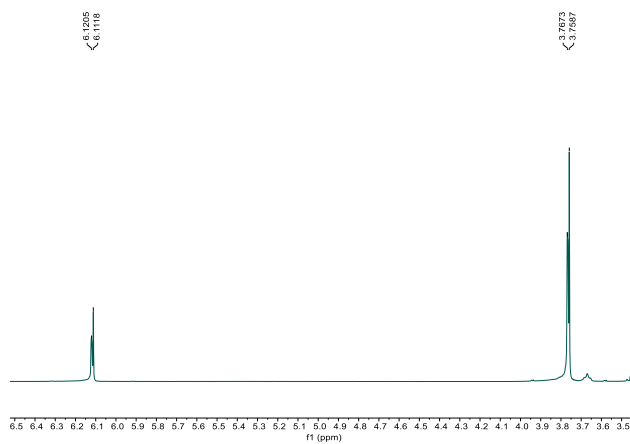
**Figure S17.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .



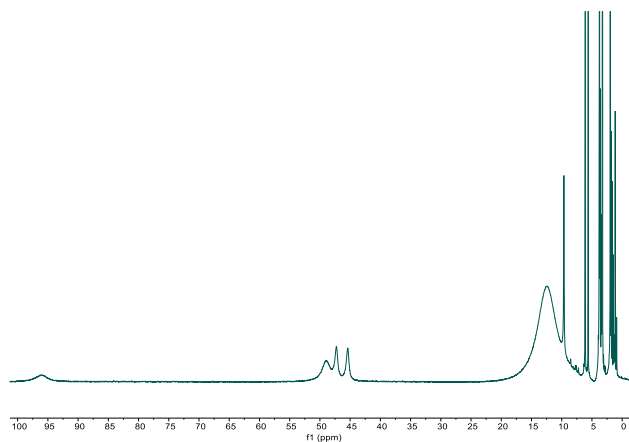
**Figure S18.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .  $[\text{Fe}] = 0.011 \text{ M}$ ,  $\Delta f = 212 \text{ Hz}$ ,  $f = 400.15 \text{ MHz}$ ,  $\mu_{\text{B}} = 5.4$ .



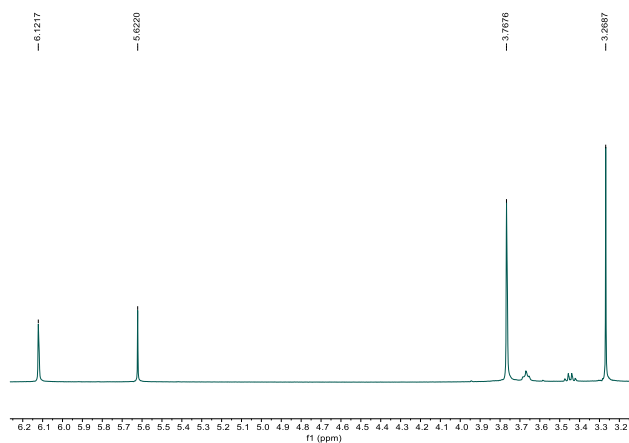
**Figure S19.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



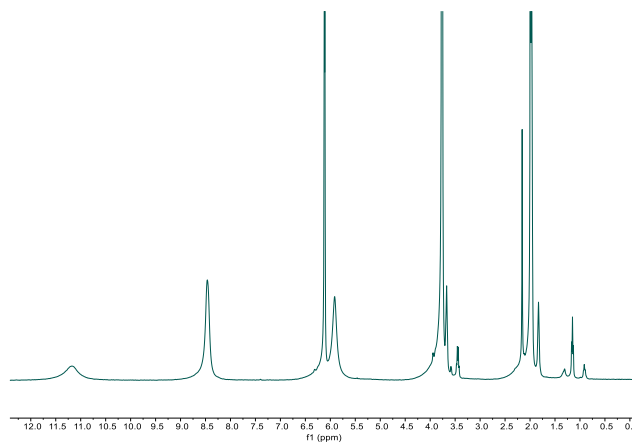
**Figure S20.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 3.46\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_B = 0.68$ .



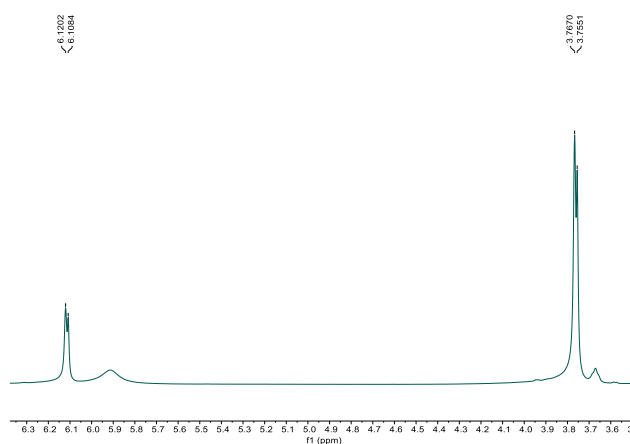
**Figure S21.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .



**Figure S22.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{TPA})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ .  $[\text{Fe}] = 0.011 \text{ M}$ ,  $\Delta f = 200 \text{ Hz}$ ,  $f = 400.15 \text{ MHz}$ ,  $\mu_B = 5.2$ .

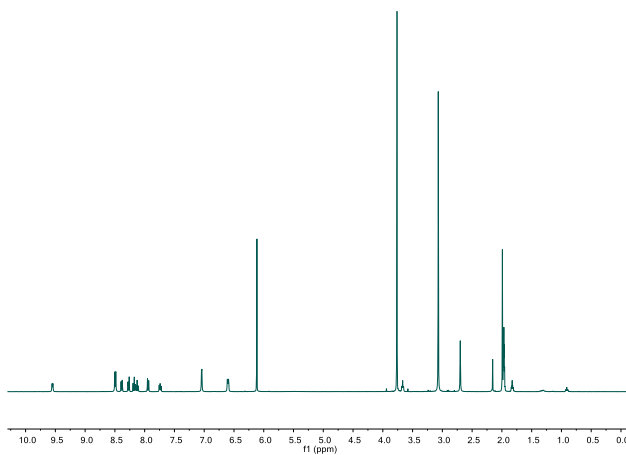


**Figure S23.**  $^1\text{H}$  NMR spectrum of  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .

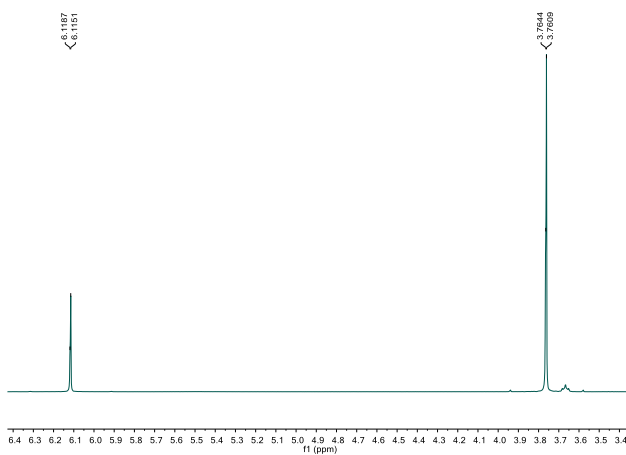


**Figure S24.** Trimethoxybenzene signals used for Evan's method for  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 4.74\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_B = 0.78$ .

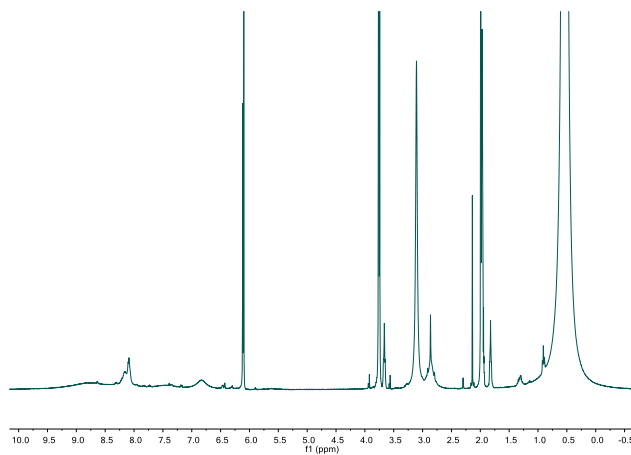
**Note:** At the total  $\text{NH}_3/[\text{Fe}]$  concentrations required for NMR experiments, the  $\text{TPA}^{\text{CF}_3}$  ligand dissociates, thus NMR data for  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{L})_2]\text{OTf}_2$  is unavailable.



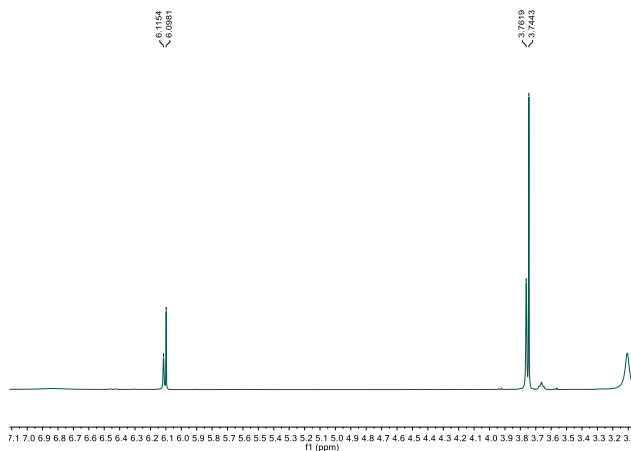
**Figure S25.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



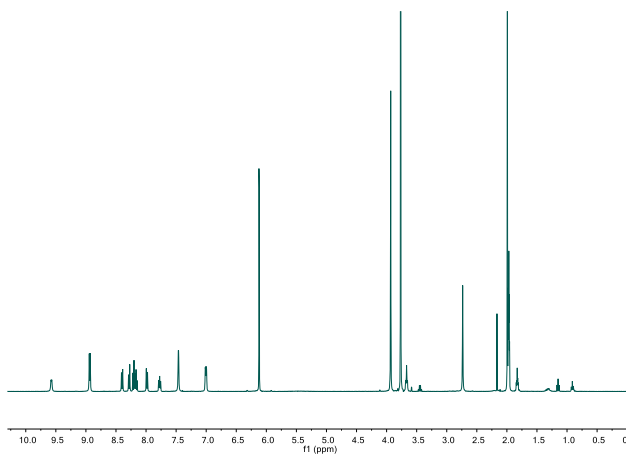
**Figure S26.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 1.4\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 0.43$ .



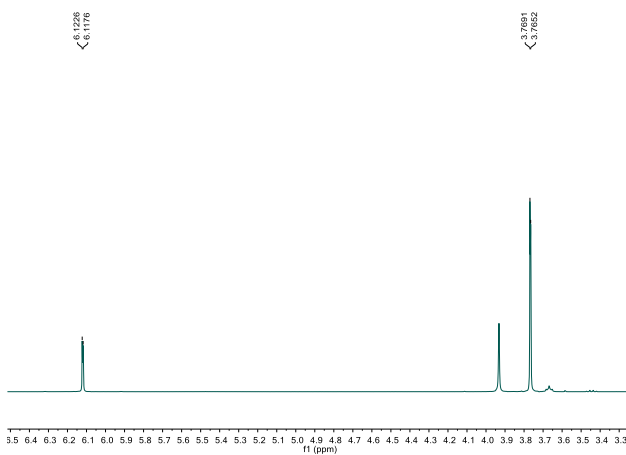
**Figure S27.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



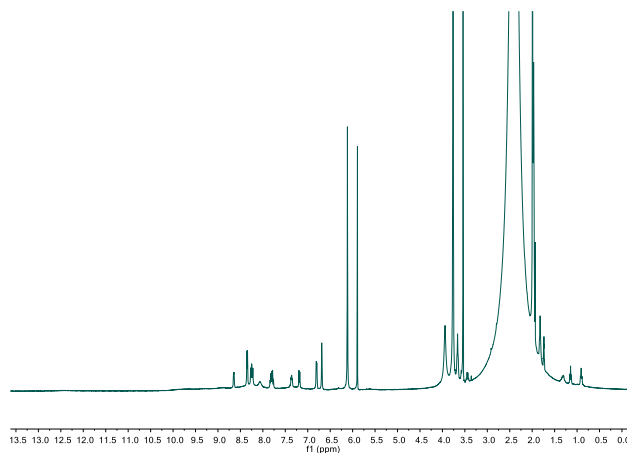
**Figure S28.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 7.0\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 0.96$ .



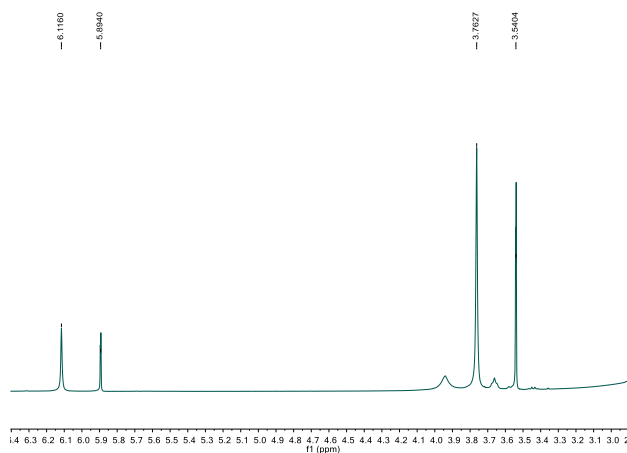
**Figure S29.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



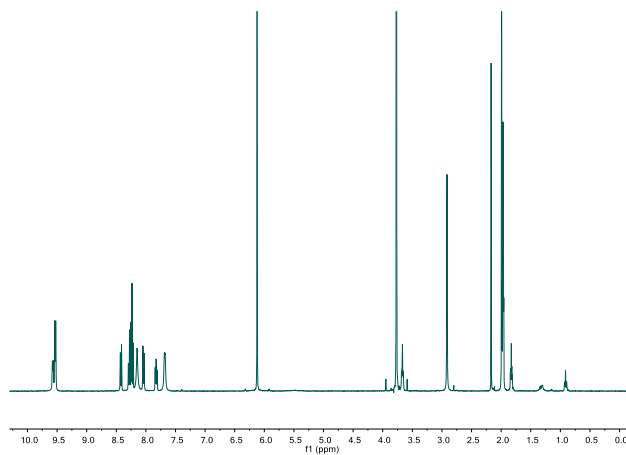
**Figure S30.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 1.8\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_B = 0.48$ .



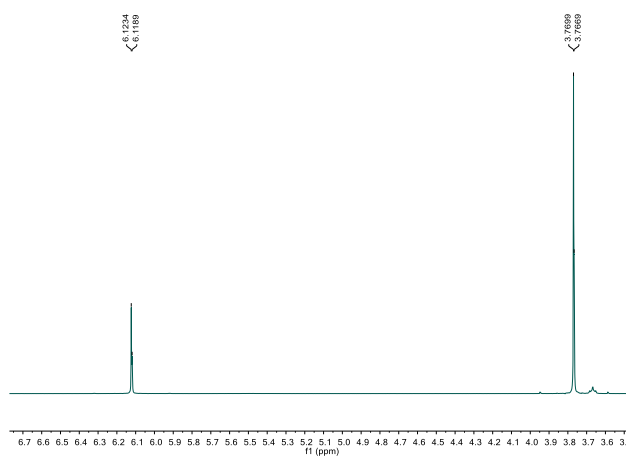
**Figure S31.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



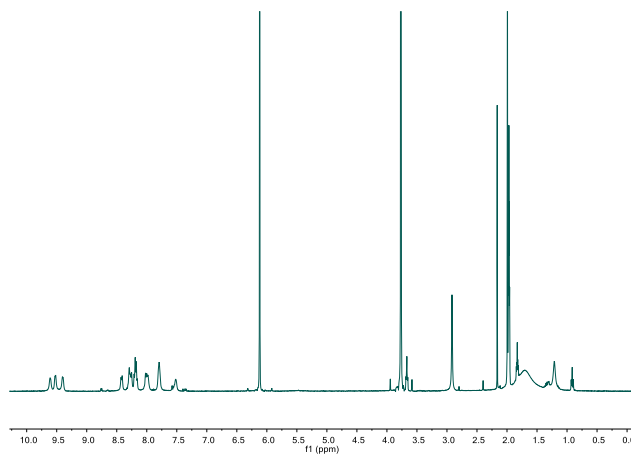
**Figure S32.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 75 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 88.9\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 3.4$ .



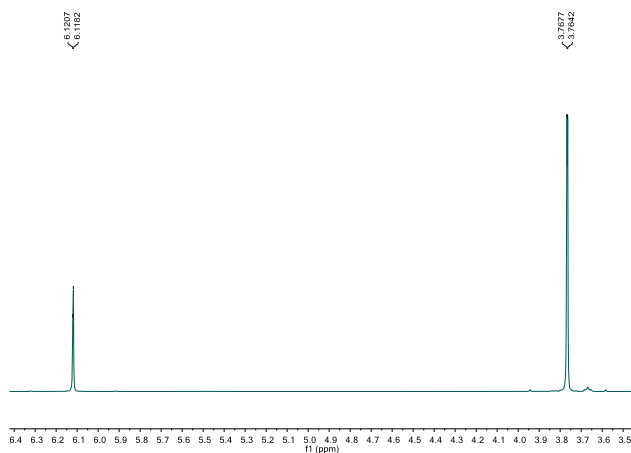
**Figure S33.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .



**Figure S34.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in  $\text{CD}_3\text{CN}$  at  $25\text{ }^\circ\text{C}$ .  $[\text{Fe}] = 0.011\text{ M}$ ,  $\Delta f = 1.5\text{ Hz}$ ,  $f = 400.15\text{ MHz}$ ,  $\mu_{\text{B}} = 0.45$ .

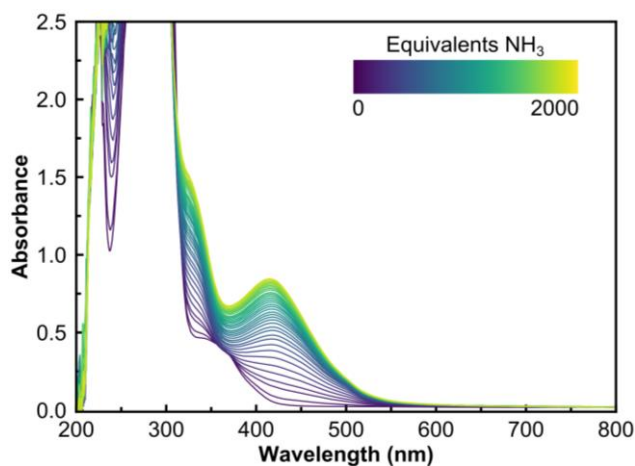


**Figure S35.**  $^1\text{H}$  NMR spectrum of  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 5 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ . Demetallation occurs with 75 equivalents.

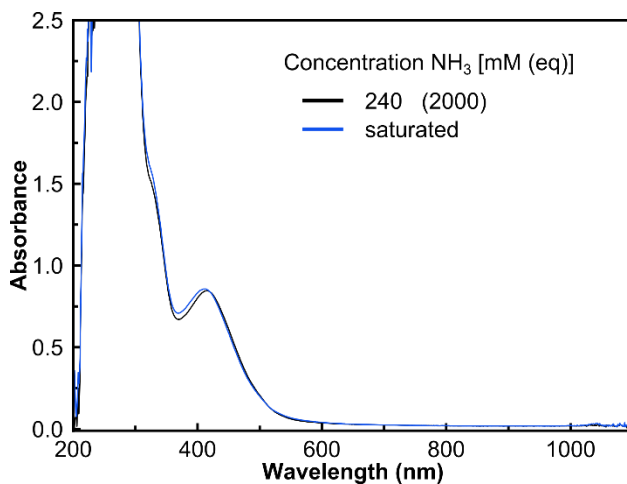


**Figure S36.** Trimethoxybenzene signals used for Evan's method for  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{L})_2]\text{OTf}_2$  ( $\text{L} = \text{MeCN}, \text{NH}_3$ ), formed by mixing  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  with 5 equivalents of  $\text{NH}_3$  in  $\text{CD}_3\text{CN}$  at  $25^\circ\text{C}$ . Demetallation occurs with 75 equivalents.  $[\text{Fe}] = 0.011 \text{ M}$ ,  $\Delta f = 1.2 \text{ Hz}$ ,  $f = 400.15 \text{ MHz}$ ,  $\mu_{\text{B}} = 0.40$ .

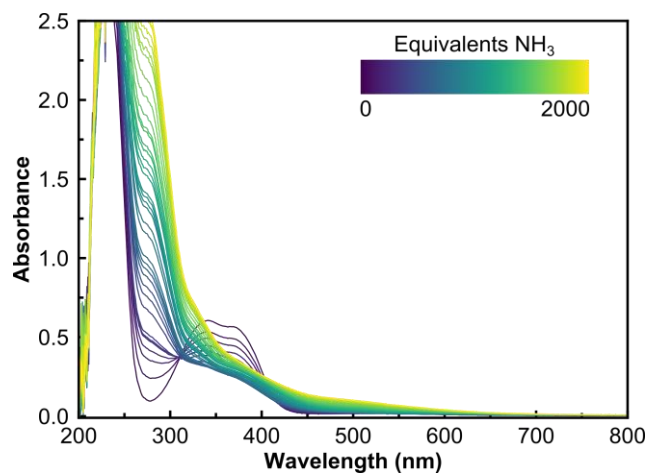
## S9. UV-vis titration data for stability against demetallation



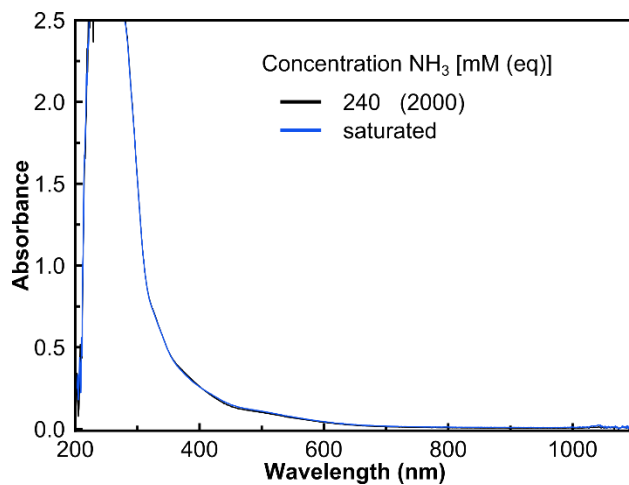
**Figure S37.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



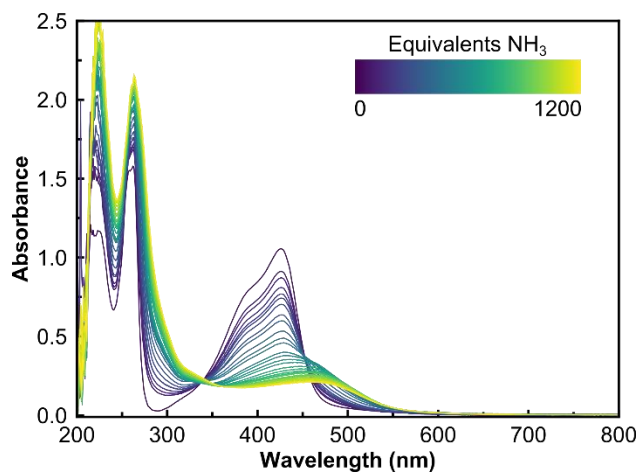
**Figure S38.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



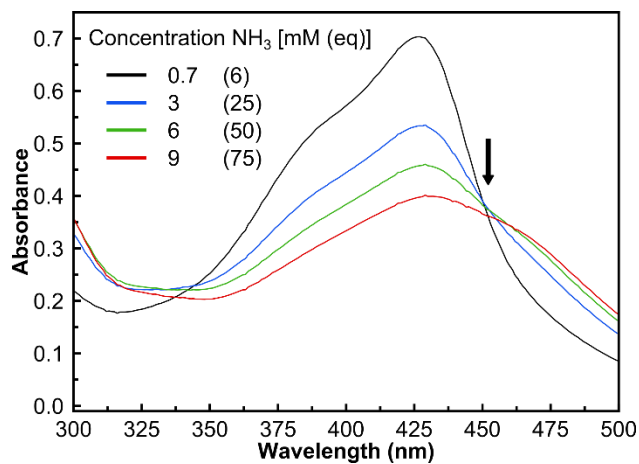
**Figure S39.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



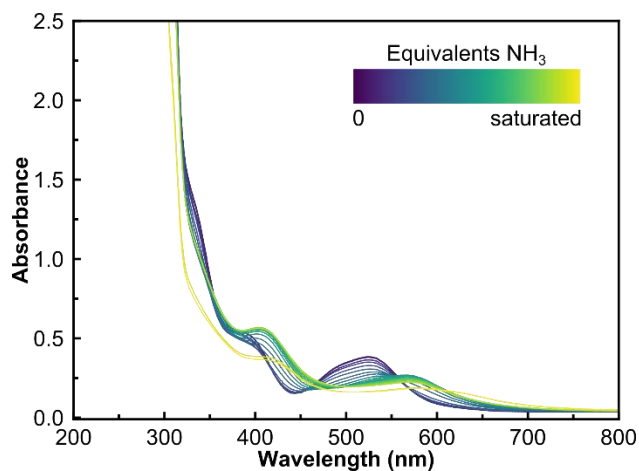
**Figure S40.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



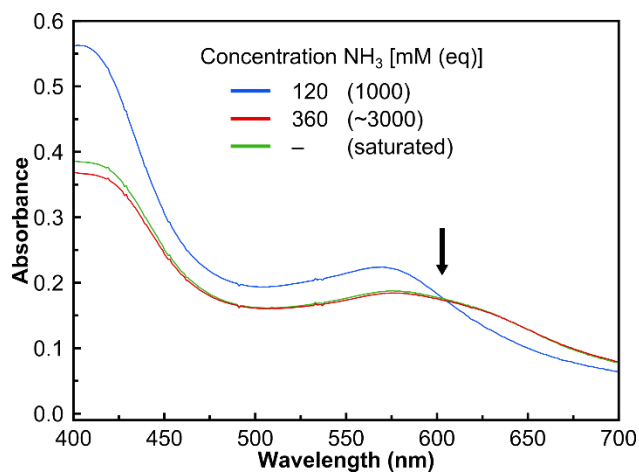
**Figure S41.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



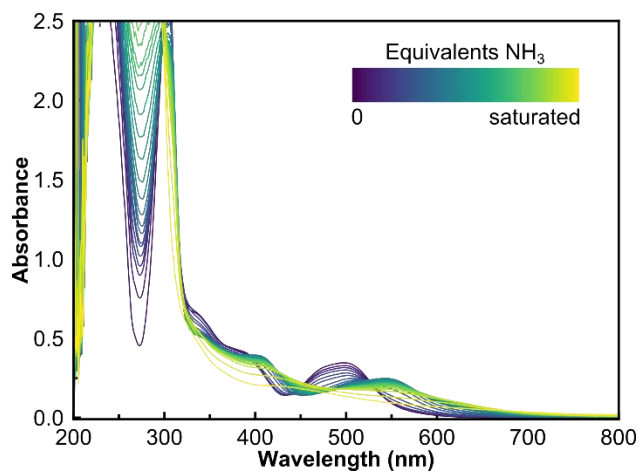
**Figure S42.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



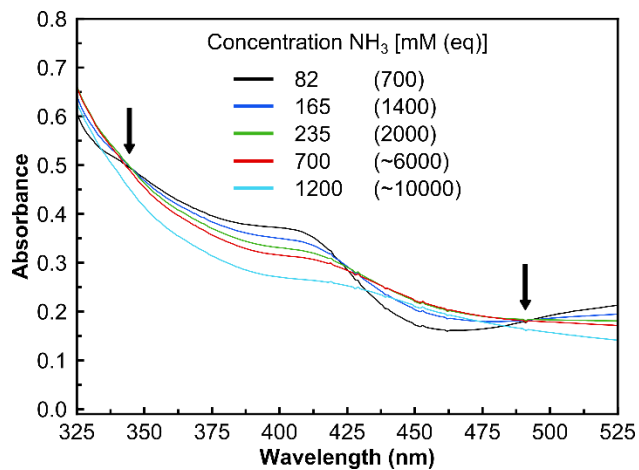
**Figure S43.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



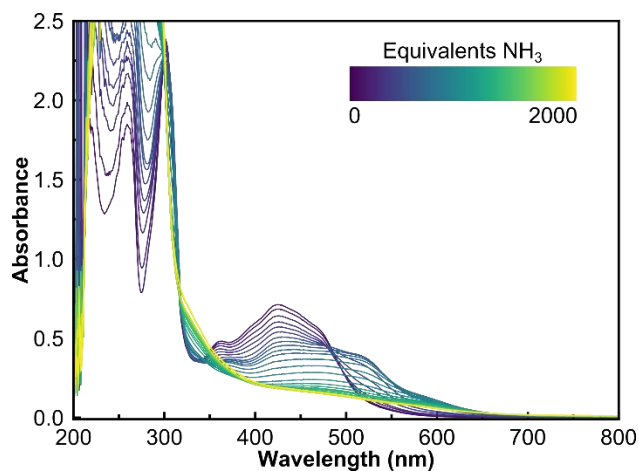
**Figure S44.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



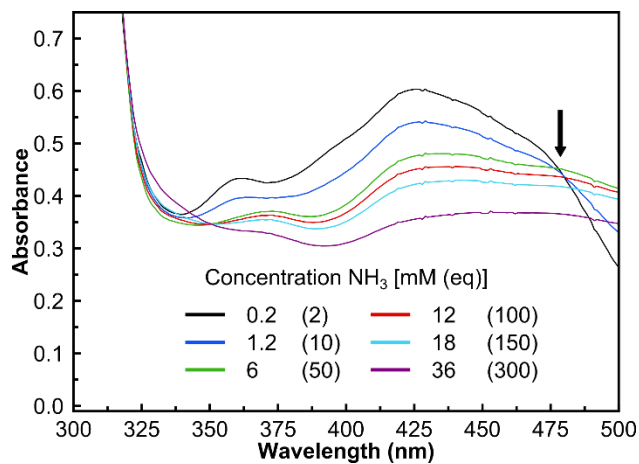
**Figure S45.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.



**Figure S46.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette. This data appeared in the maintext in an altered format.

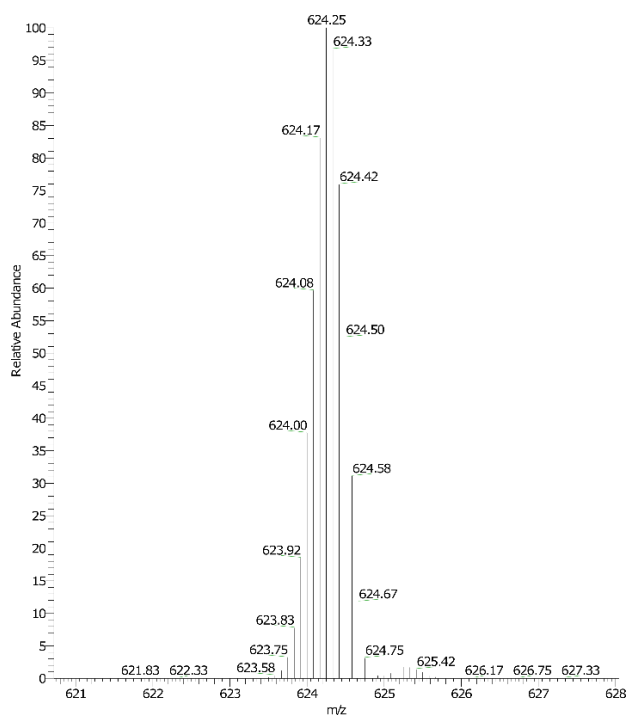


**Figure S47.** UV-vis spectra of acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.

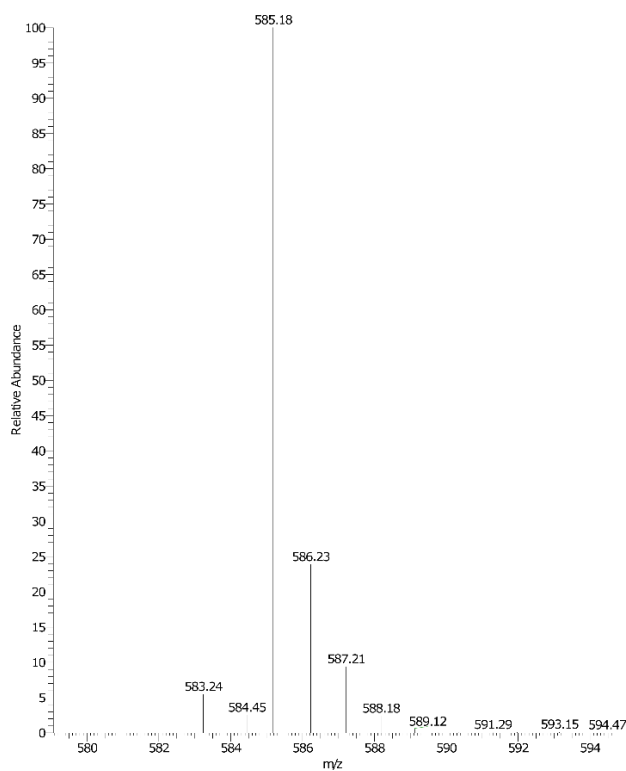


**Figure S48.** Selected UV-vis spectra used for determining the onset of demetallation for acetonitrile solution containing 0.12 mM  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  and varying equivalents  $\text{NH}_3$  in a 1 cm cuvette.

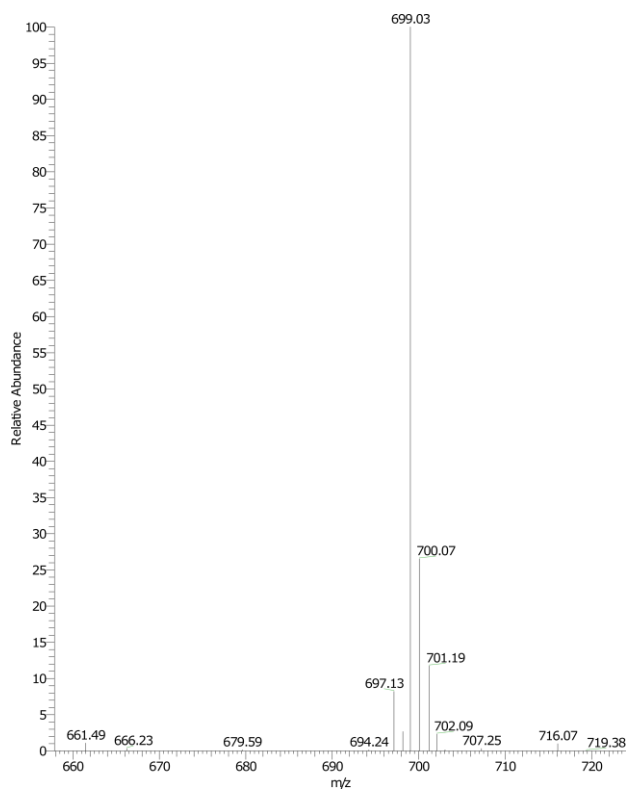
## S10. Mass spectrometry



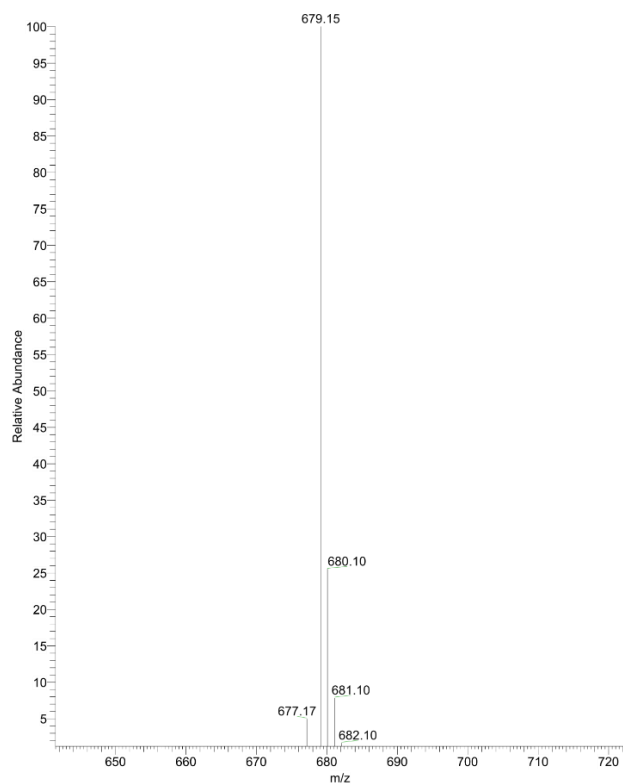
**Figure S49.** ESI mass spectrum of  $[(\text{TPA}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.



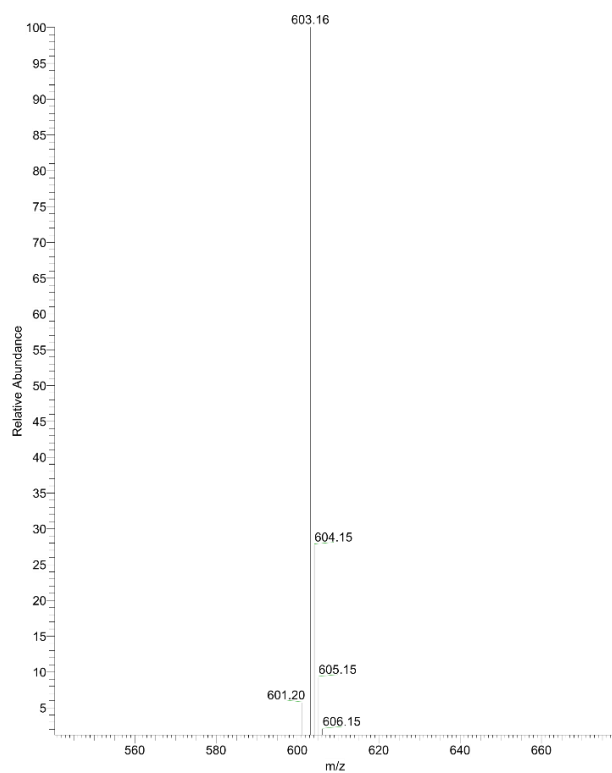
**Figure S50.** ESI mass spectrum of  $[(\text{TPA}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.



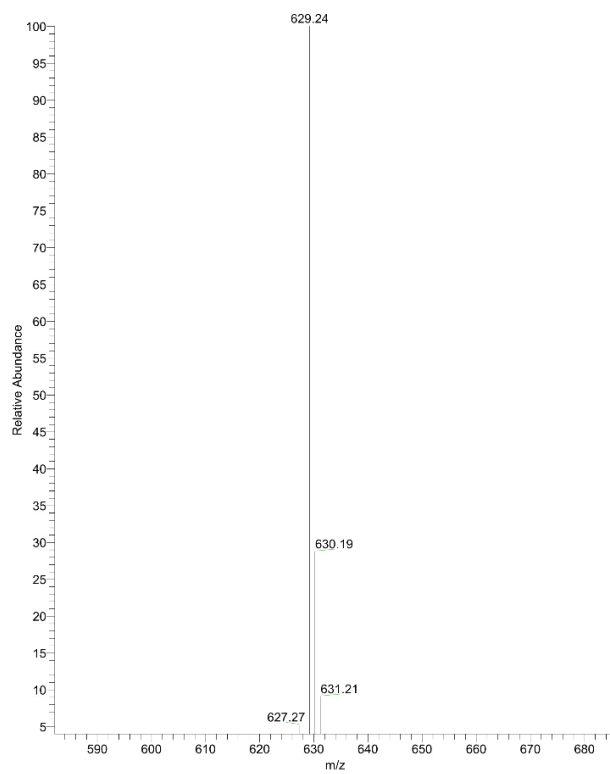
**Figure S51.** ESI mass spectrum of  $[(\text{TPA}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.



**Figure S52.** ESI mass spectrum of  $[(\text{BPM}^{\text{CF}_3})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.



**Figure S53.** ESI mass spectrum of  $[(\text{BPM}^{\text{OMe}})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.

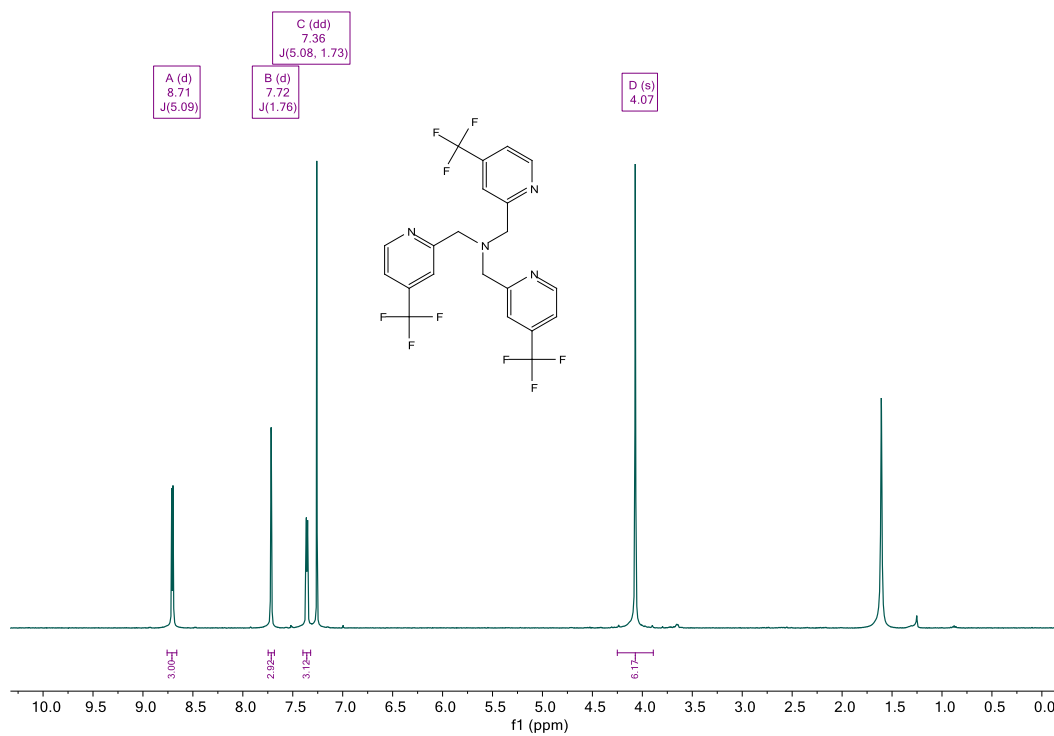


**Figure S54.** ESI mass spectrum of  $[(\text{BPM}^{\text{NMe}_2})\text{Fe}(\text{MeCN})_2]\text{OTf}_2$  in acetonitrile.

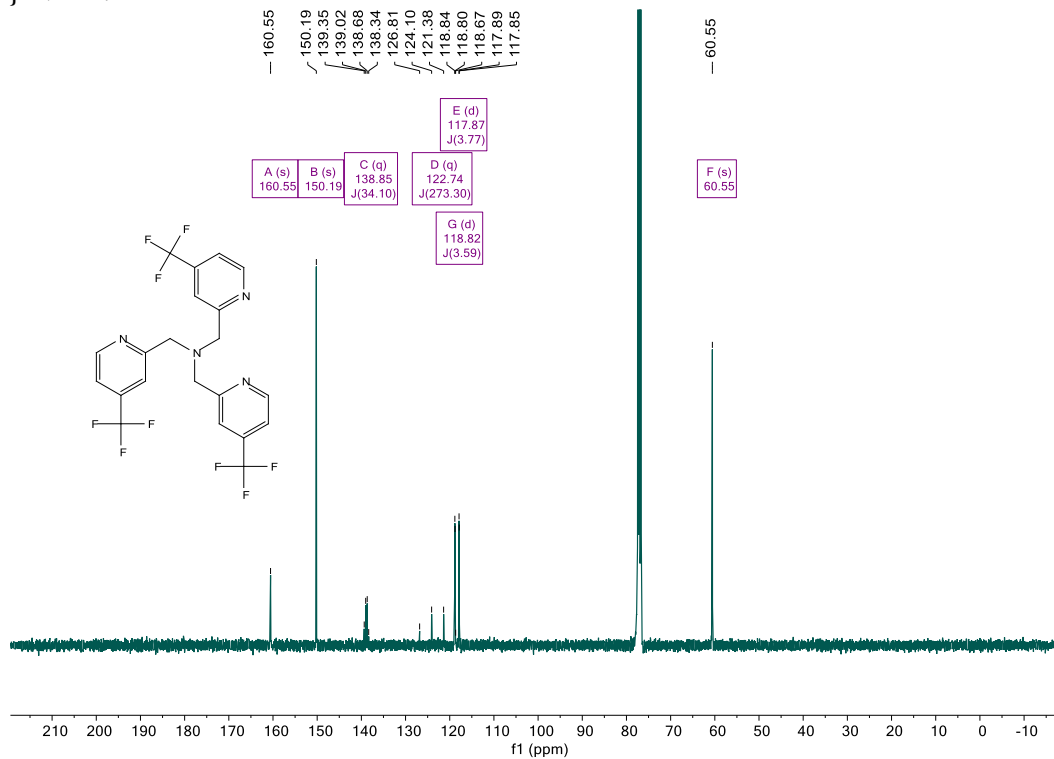
## S11. NMR spectra

### TPA<sup>CF<sub>3</sub></sup> (tris(4-(trifluoromethyl)-2-picolyl)amine)

<sup>1</sup>H NMR:

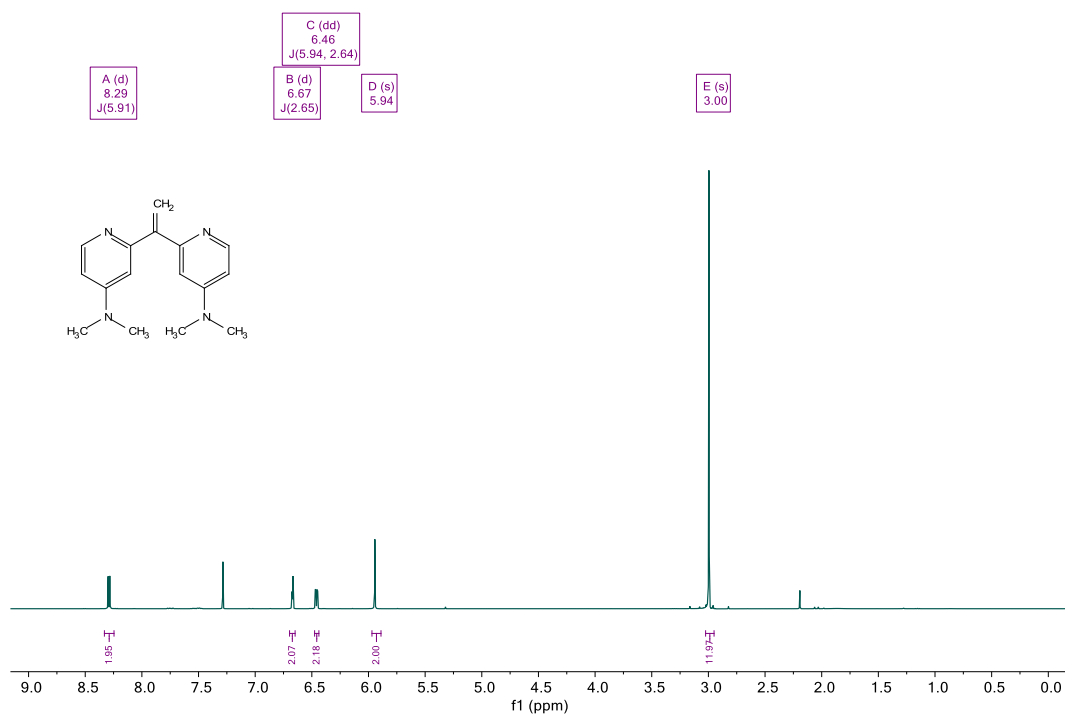


<sup>13</sup>C{<sup>1</sup>H} NMR:

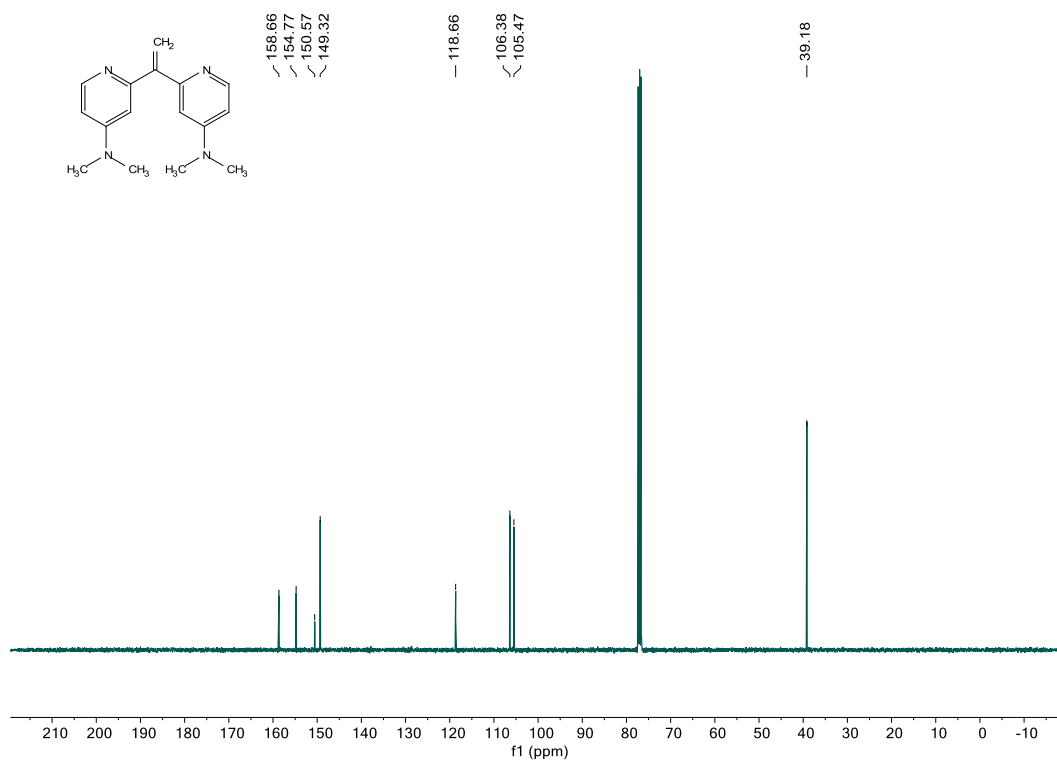


# 2,2'-(ethene-1,1-diyl)bis(4-(dimethylamino)pyridine)

$^1\text{H}$  NMR:

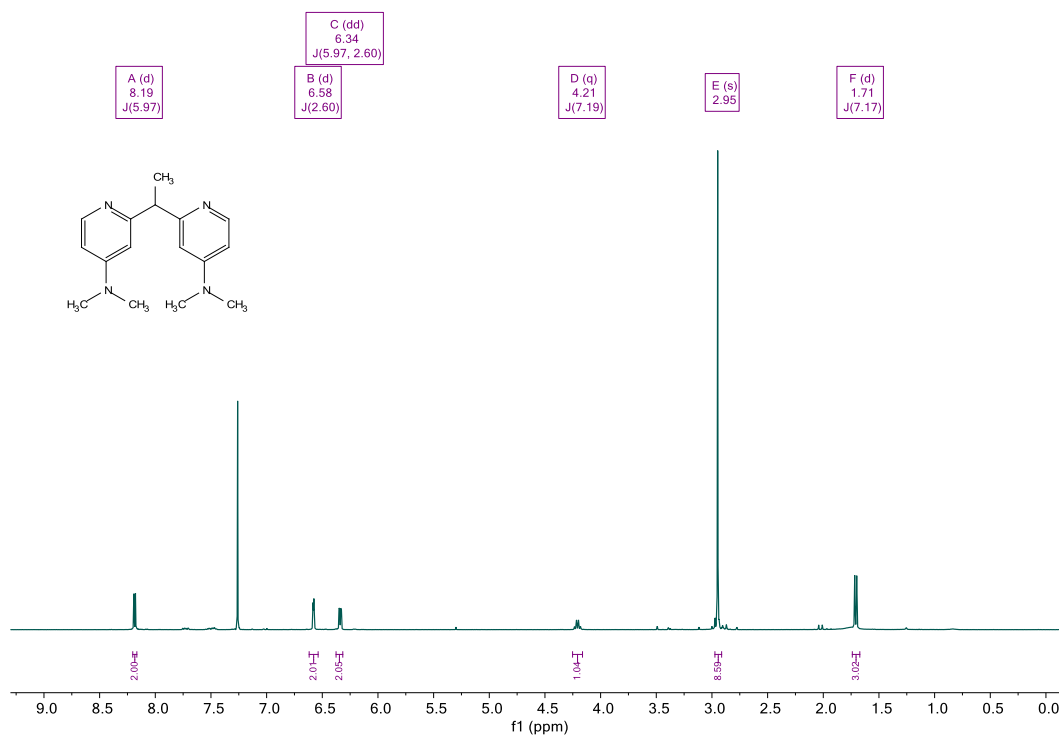


$^{13}\text{C}\{^1\text{H}\}$  NMR:

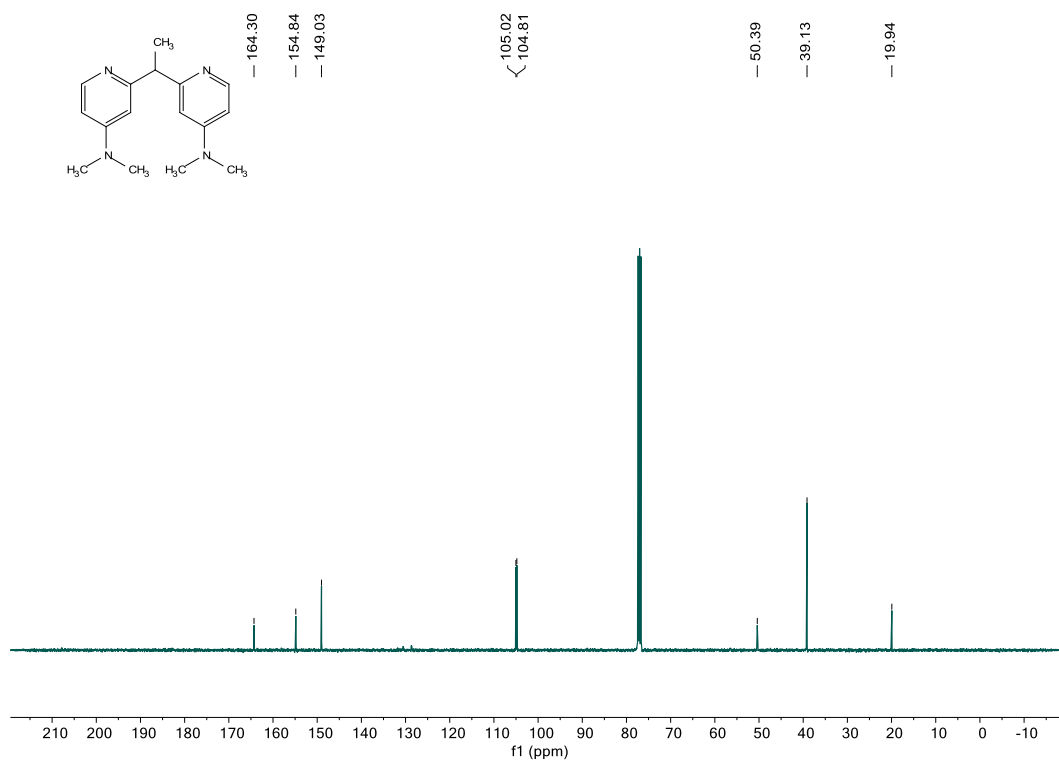


# 2,2'-(ethane-1,1-diyl)bis(4-(dimethylamino)pyridine)

$^1\text{H}$  NMR:

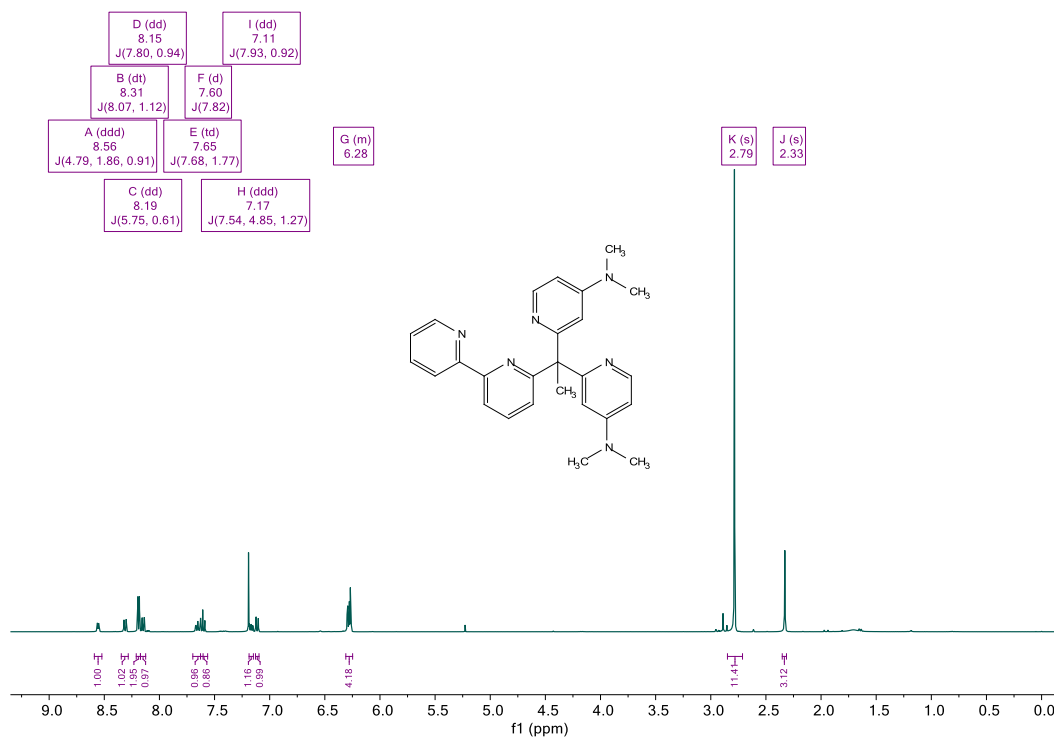


$^{13}\text{C}\{^1\text{H}\}$  NMR:

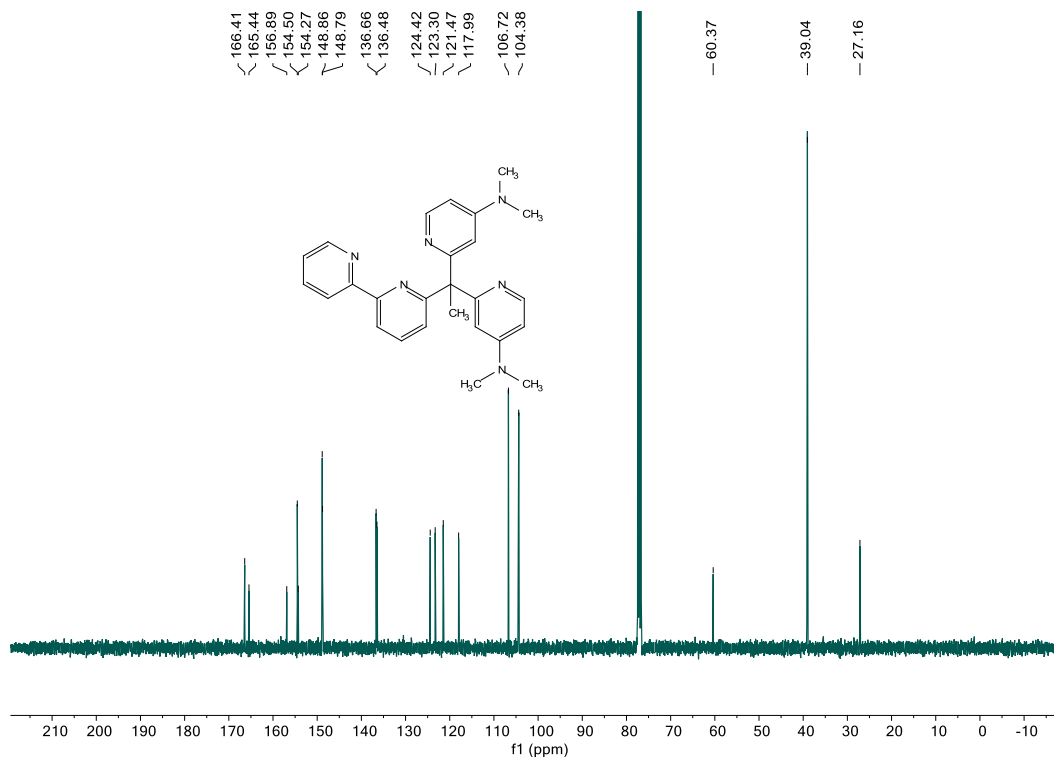


**BPM<sup>NMe2</sup> (6-(1,1-bis(4-(dimethylamino)pyridin-2-yl)ethyl)-2,2'-bipyridine)**

<sup>1</sup>H NMR:

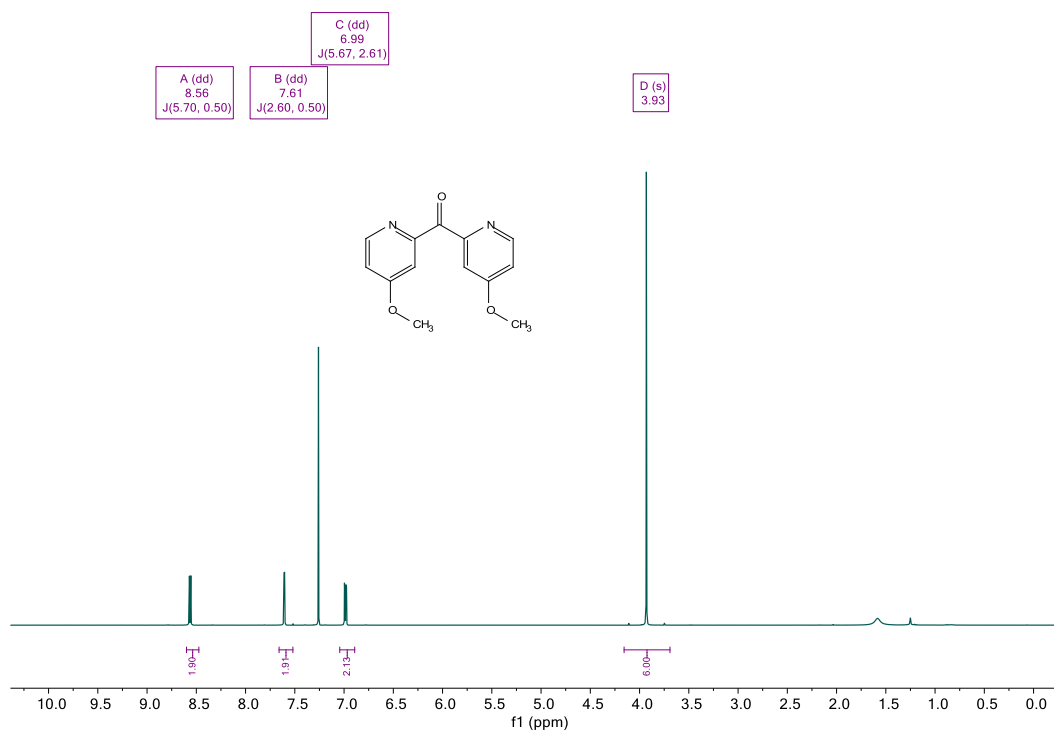


<sup>13</sup>C{<sup>1</sup>H} NMR:

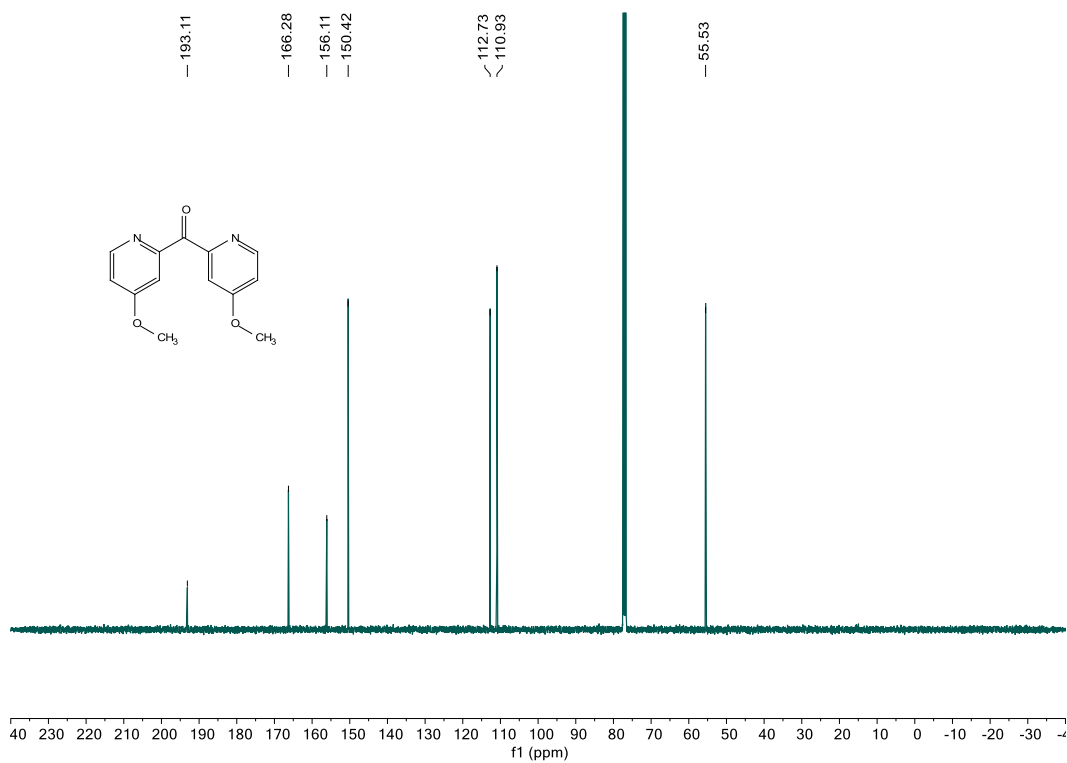


# **bis(4-methoxypyridin-2-yl)methanone**

$^1\text{H}$  NMR:

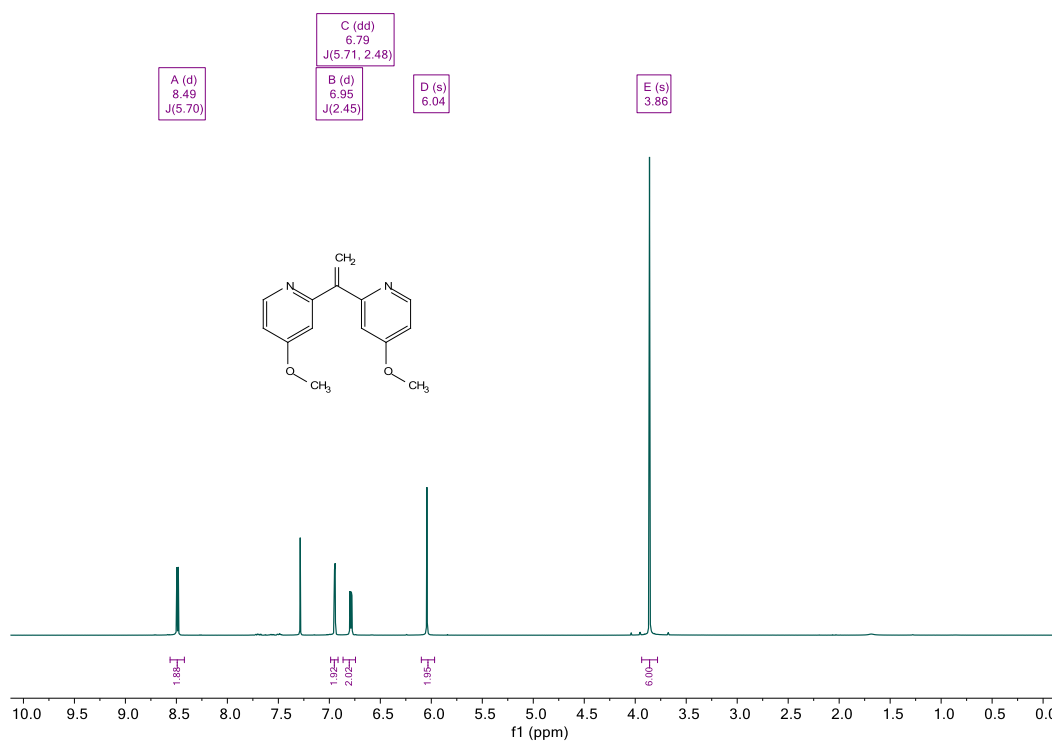


$^{13}\text{C}\{^1\text{H}\}$  NMR:

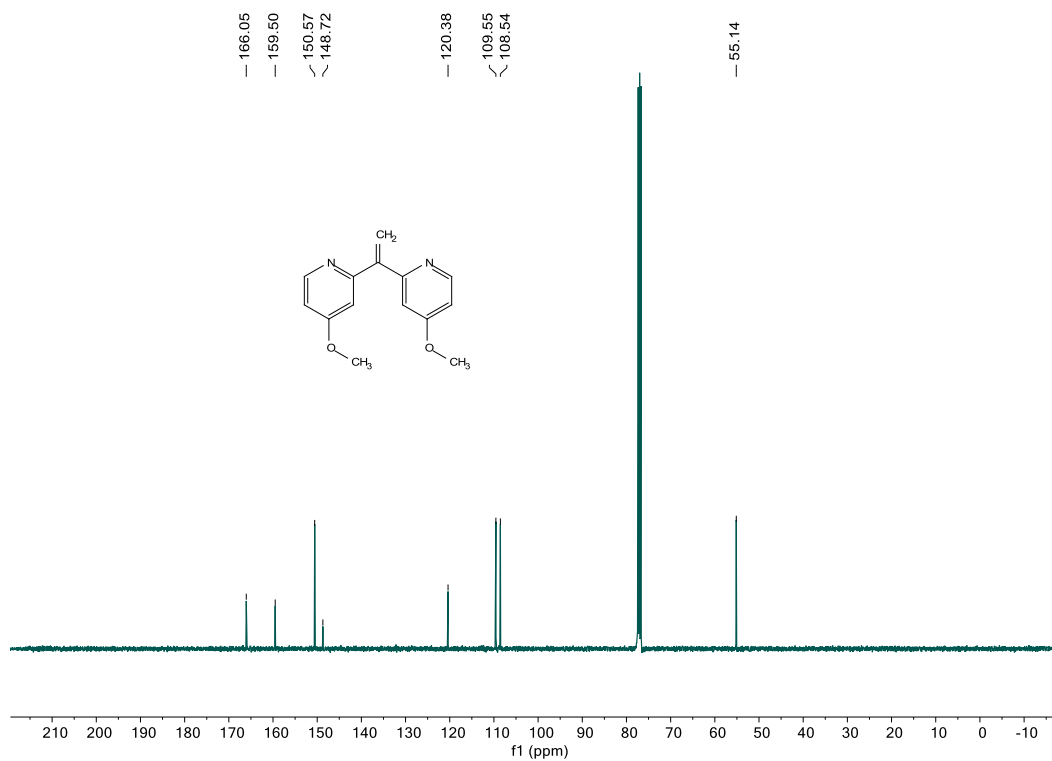


# 2,2'-(ethene-1,1-diyl)bis(4-(methoxypyridine))

$^1\text{H}$  NMR:

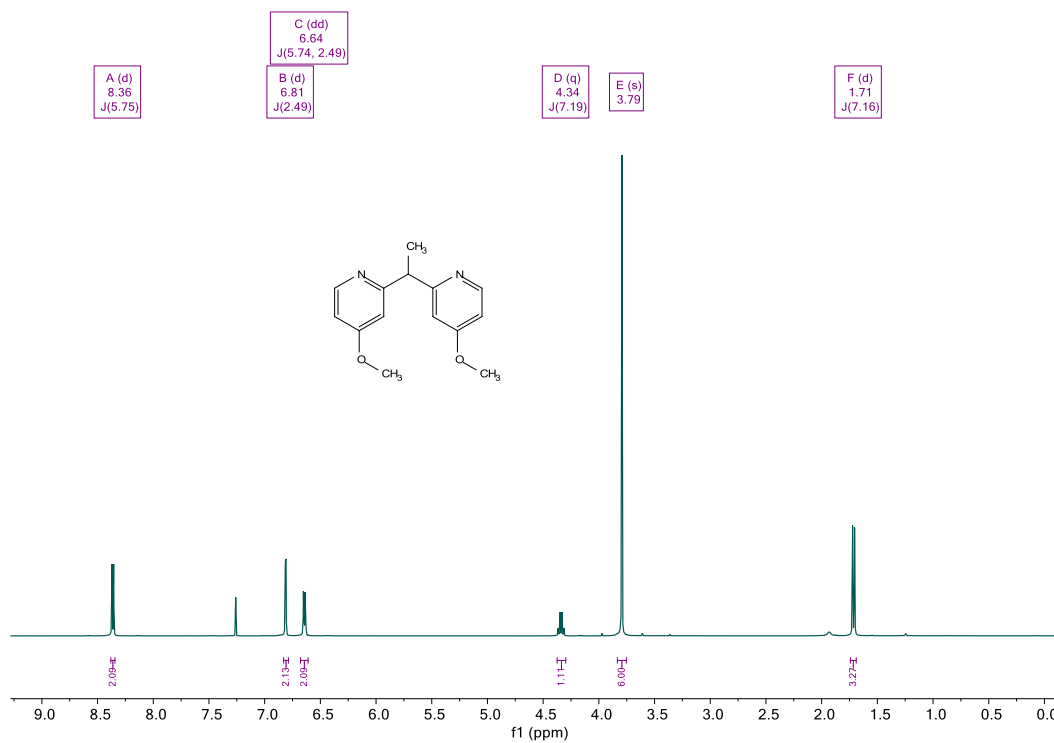


$^{13}\text{C}\{^1\text{H}\}$  NMR:

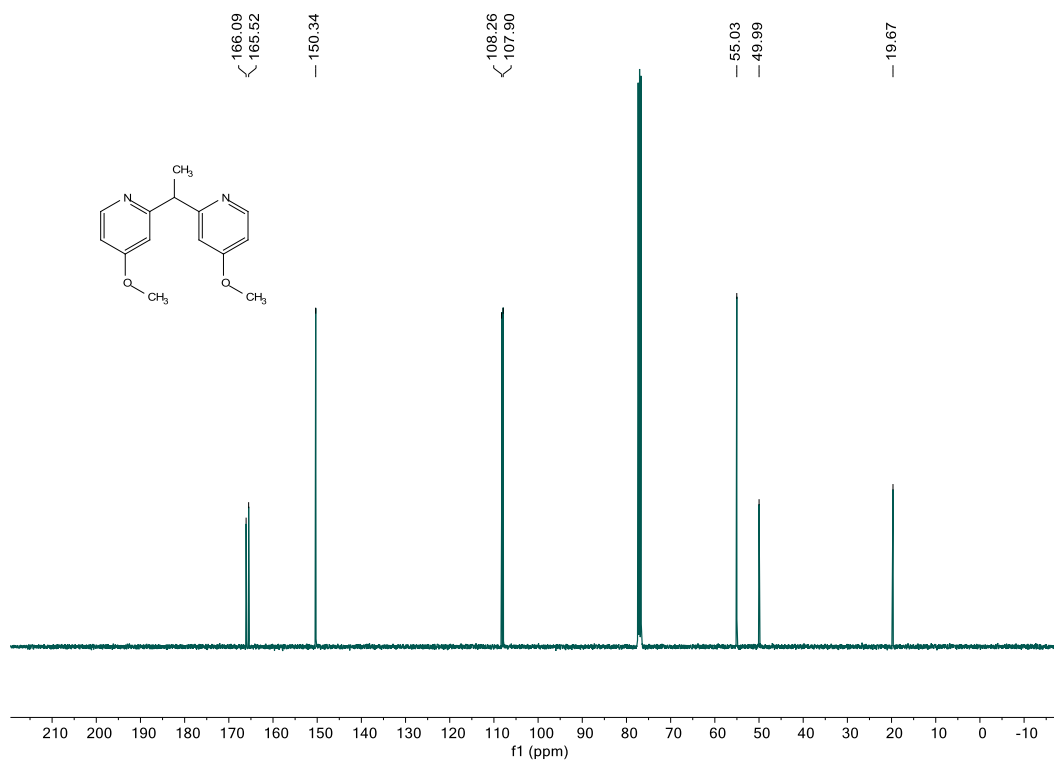


## 2,2'-(ethane-1,1-diyl)bis(4-methoxypyridine)

$^1\text{H}$  NMR:

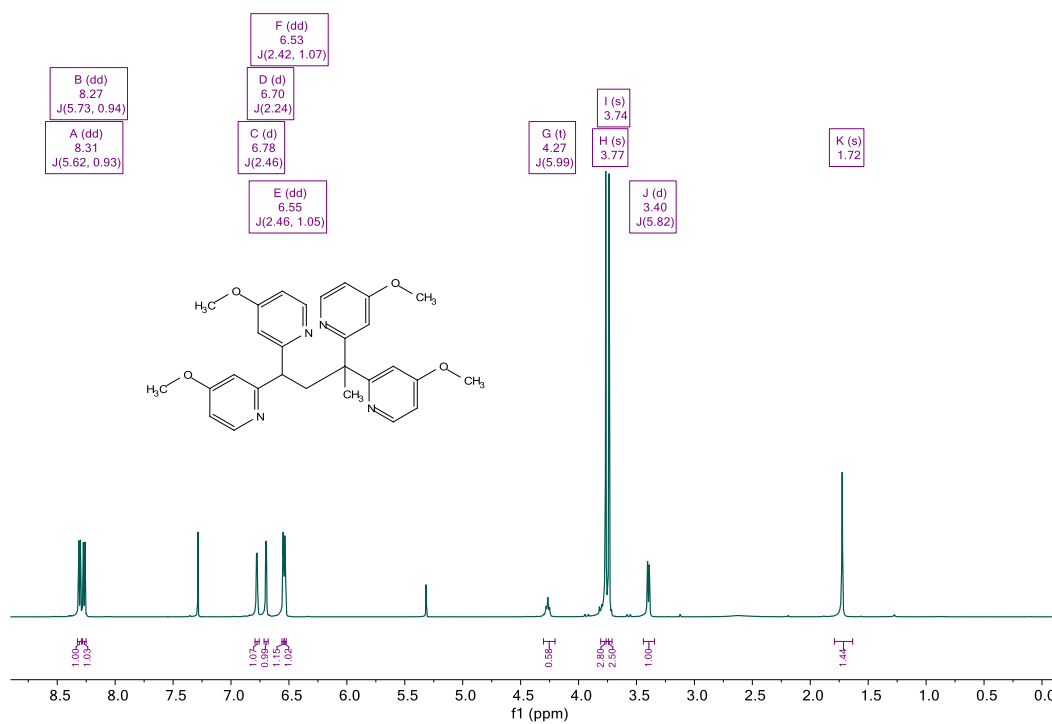


$^{13}\text{C}\{^1\text{H}\}$  NMR:

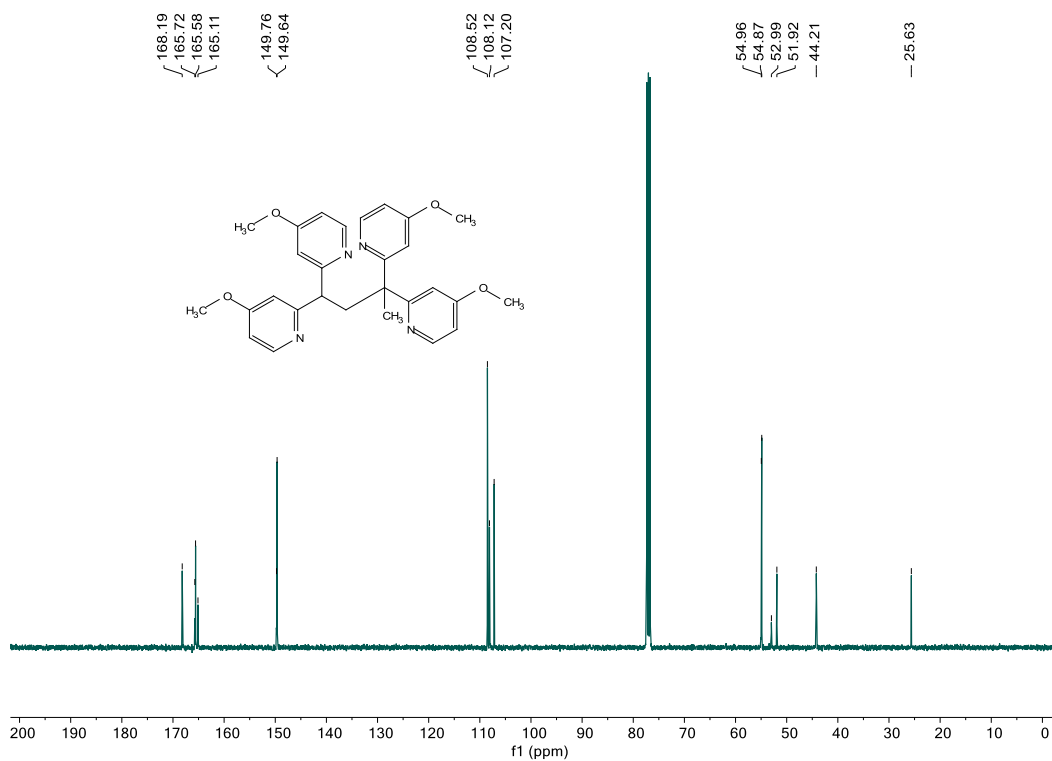


**2,2',2'',2'''- 2,2',2'',2'''-(butane-1,1,3,3-tetrayl)tetrakis(4-methoxypyridine)**

<sup>1</sup>H NMR:



<sup>13</sup>C{<sup>1</sup>H} NMR:

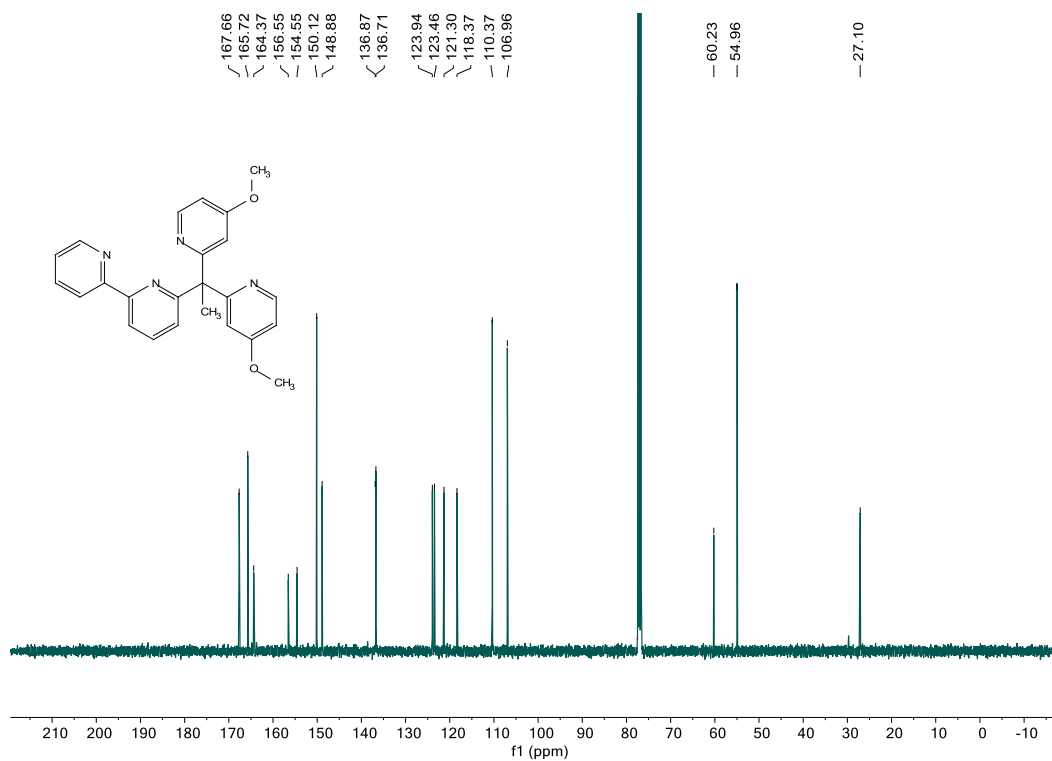


**BPM<sup>OMe</sup> (6-(1,1-bis(4-methoxypyridin-2-yl)ethyl)-2,2'-bipyridine)**

<sup>1</sup>H NMR:

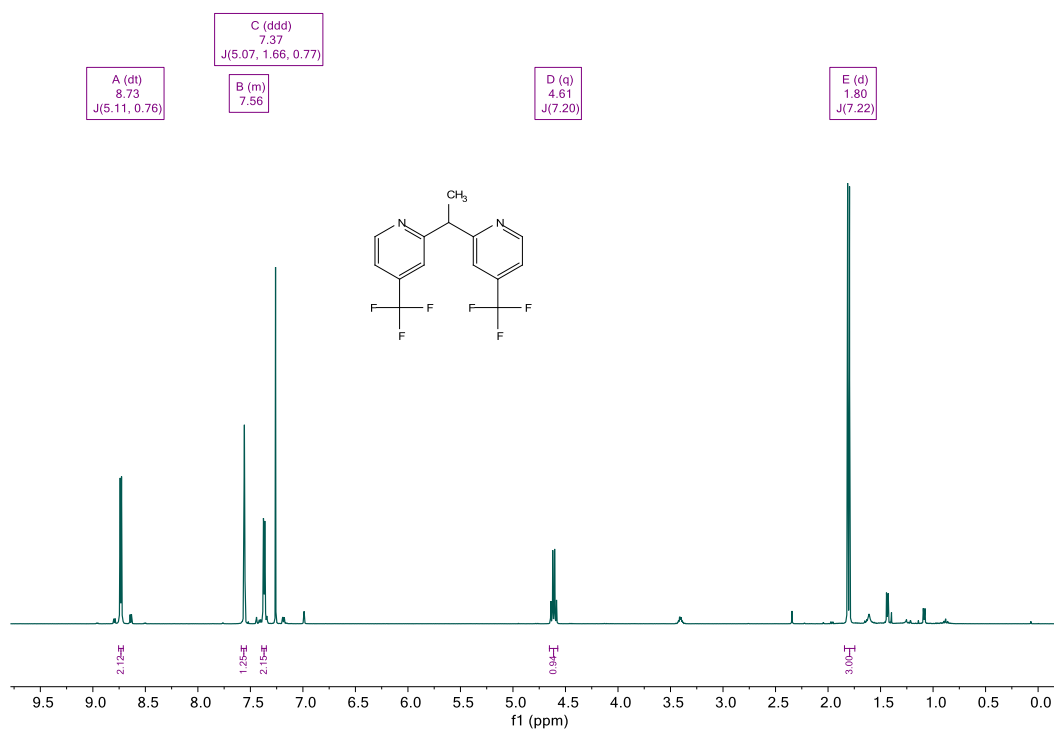


<sup>13</sup>C{<sup>1</sup>H} NMR:

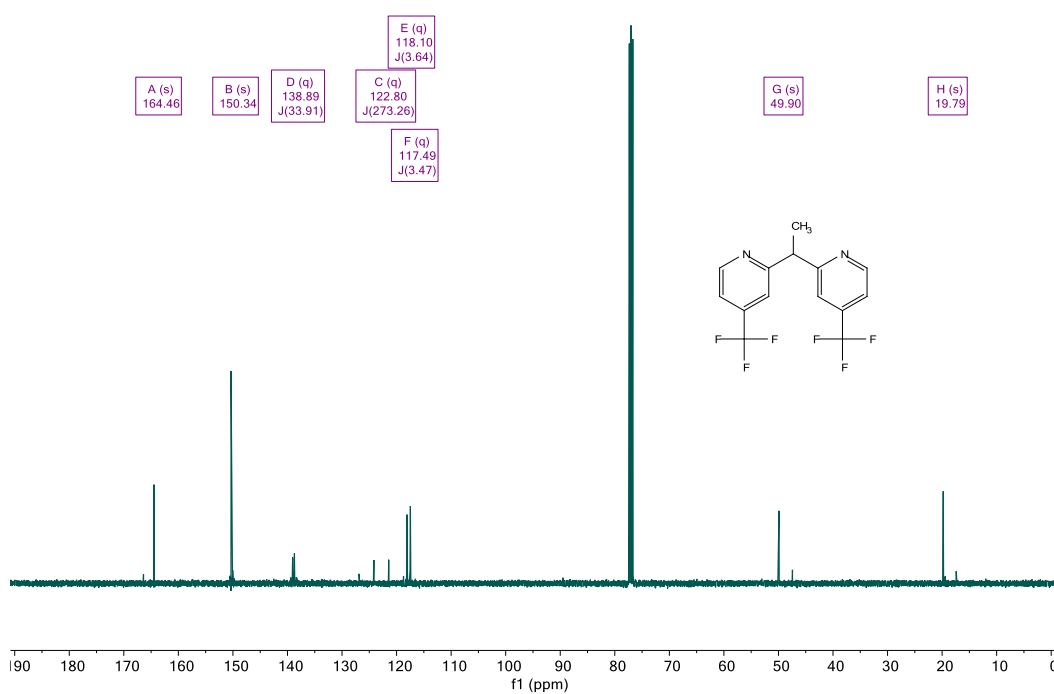


# 2,2'-(ethane-1,1-diyl)bis(4-(trifluoromethyl)pyridine)

$^1\text{H}$  NMR:

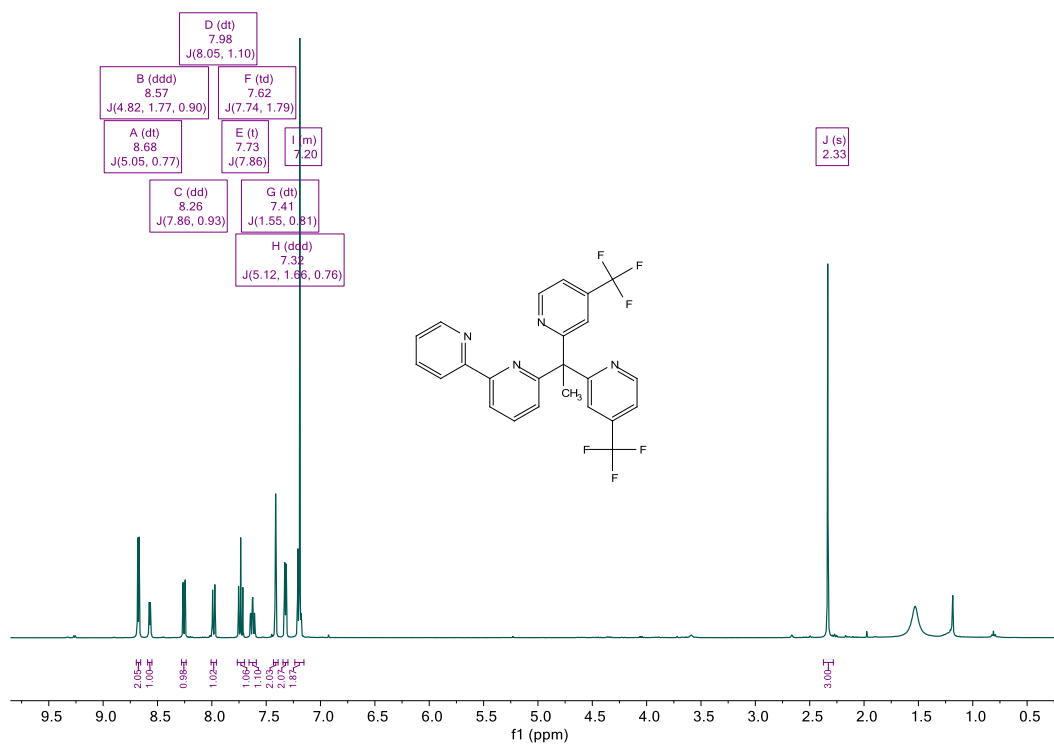


$^{13}\text{C}\{^1\text{H}\}$  NMR:

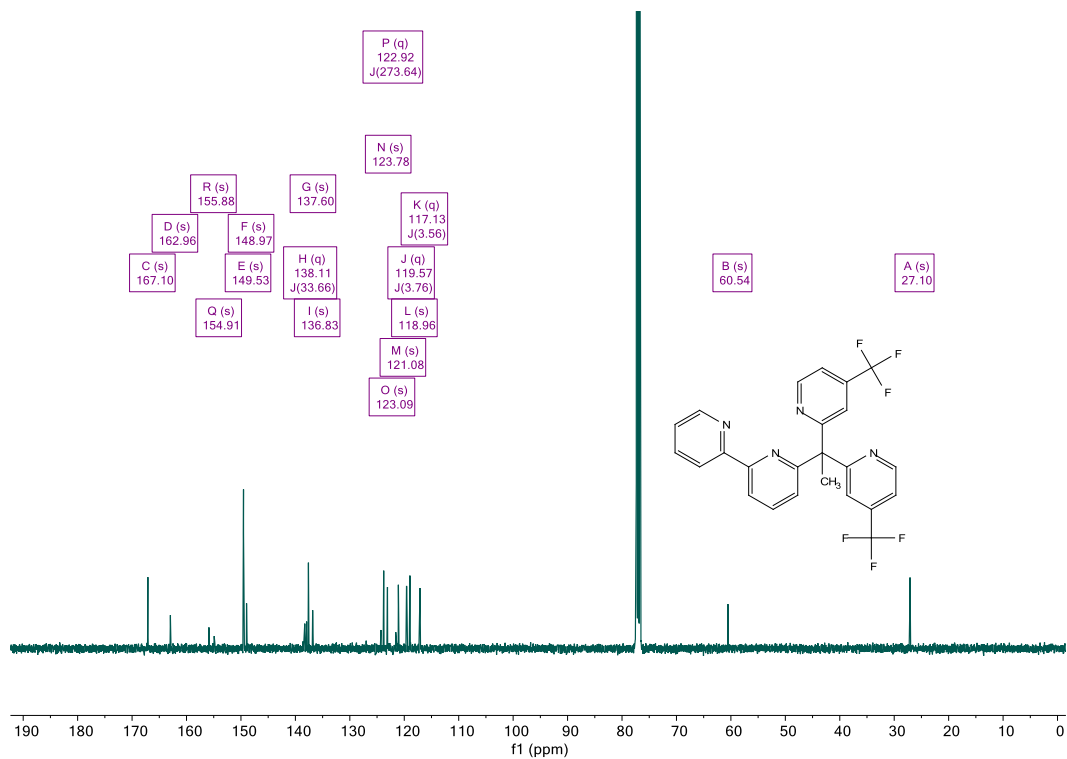


**BPM<sup>CF3</sup> (6-(1,1-bis(4-(trifluoromethyl)pyridin-2-yl)ethyl)-2,2'-bipyridine)**

<sup>1</sup>H NMR:



<sup>13</sup>C{<sup>1</sup>H} NMR:



## S12. References

- <sup>1</sup> Canary, J. W.; Wang, Y.; Roy, R. Tris[(2-pyridyl)methyl]amine (TPA) and (+)-bis[(2-pyridyl)methyl]-1-(2-pyridyl)-ethylamine ( $\alpha$ -METPA). *Inorg. Synth.* **1998**, 32, 70–75.
- <sup>2</sup> Diebold, A.; Hagen, K. S. Iron(II) Polyamine Chemistry: Variation of Spin State and Coordination Number in Solid State and Solution with Iron(II) Tris(2-pyridylmethyl)amine Complexes. *Inorg. Chem.* **1998**, 37, 215–223.
- <sup>3</sup> Khnayzer, R. S.; Thoi, V. S.; Nippe, M.; King, A. E.; Jurss, J. W.; El Roz, K. A.; Long, J. R.; Chang, C. J.; Castellano, F. N. Towards a Comprehensive Understanding of Visible-Light Photogeneration of Hydrogen from Water Using Cobalt(II) Polypyridyl Catalysts. *Energy Environ. Sci.* **2014**, 7, 1477–1488.
- <sup>4</sup> Chen, L.; Su, X.-J.; Jurss, J. W. Selective Alkane C–H Bond Oxidation Catalyzed by a Non-Heme Iron Complex Featuring a Robust Tetradentate Ligand. *Organometallics* **2018**, 37, 4535–4539.
- <sup>5</sup> Miller, S. L.; Chotana, G. A.; Fritz, J. A.; Chattopadhyay, B.; Maleczka, R. E., Jr.; Smith, M. R., III. C–H Borylation Catalysts that Distinguish Between Similarly Sized Substituents Like Fluorine and Hydrogen. *Org. Lett.* **2019**, 21, 6388–6392.
- <sup>6</sup> Zhang, C. X.; Kaderli, S.; Costas, M.; Kim, E.; Neuhold, Y.; Karlin, K. D.; Zuberbühler, A. D. Copper(I)–Dioxygen Reactivity of  $[(L)Cu]^+$  ( $L$  = Tris(2-Pyridylmethyl)amine): Kinetic/Thermodynamic and Spectroscopic Studies Concerning the Formation of Cu–O<sub>2</sub> and Cu<sub>2</sub>–O<sub>2</sub> Adducts as a Function of Solvent Medium and 4-Pyridyl Ligand Substituent Variations. *Inorg. Chem.* **2003**, 42, 1807–1824.
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