The Supporting Information for

Solvent-Dependent *fac/mer*-Isomerization and Self-Assembly of Triply Helical Complexes Bearing a Pivot Part

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Materials and methods

Unless otherwise noted, the solvents and reagents were purchased from TCI Co., Ltd., FUJIFILM Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc., Cambridge Isotope Laboratories, Inc., or Sigma-Aldrich Co., and used without further purification. Dry THF and DMF were purified by Glass Contour Ultimate Solvent System 3S-TCN 1. Silica gel and amine-functionalized silica gel for column chromatography were purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, 63–210 μm) and Silica Gel 60 N (spherical, 40– 50 μm) NH_2, respectively). GPC purification was performed by a JAI LC-9210 II NEXT system with JAIGEL-1HH/2HH columns using $CHCl_3$ as the eluent.

Measurements were performed at 298 K unless otherwise noted. ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR, and other 2D NMR spectra were recorded by a Bruker AVANCE III-600 (600 MHz) spectrometer or a Bruker AVANCE III-400 (400 MHz) spectrometer. Negative values were depicted in red in the spectra. Tetramethylsilane was used as the internal standard (δ 0.00 ppm) for the ^{1}H and ^{13}C NMR measurements when $CDCl_3$ or a mixed solvent of $CDCl_3/CD_3CN$ = 1/1 was used as the solvent. In the other deuterium solvents, the residual solvent signal was used as the internal standard for the ^{1}H NMR and ^{13}C NMR measurements. BF_3•Et_2O in $CDCl_3$ (1 wt%) was used as the external standard (δ 0.00 ppm) for the ^{11}B NMR measurements. Hexafluorobenzene in $CDCl_3$ (1 wt%) was used as the external standard (δ –163.0 ppm) for the ^{19}F NMR measurements. Triphenylphosphine oxide in $CDCl_3$ (1 wt%) was used as an external standard (δ 30.0 ppm) for the ^{31}P NMR measurements. The assignments of the ^{1}H and ^{13}C signals were based on ^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC measurements.

The ESI-TOF mass data were recorded by an AB SCIEX TripleTOF 4600 system. The HRMS values of iron complexes were calculated for the strongest peak using PeakView 1.2.0.3 software (AB SCIEX, 2012)).

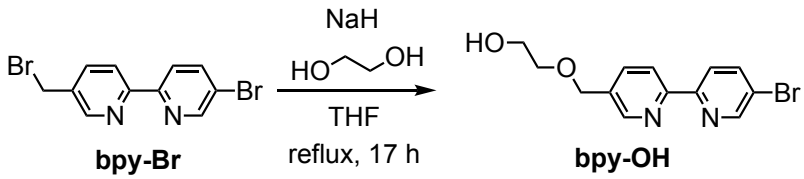
The single-crystal X-ray crystallographic measurements were performed using a Bruker APEX II ULTRA with Mo*K*α radiation (graphite-monochromated, λ = 0.71073 Å) at 120 K. The collected diffraction images were processed by a Bruker APEX2. The initial structure was solved using SHELXT-2018[S1] and refined using SHELXL-2018[S2], which were running on Yadokari-XG crystallographic software[S3]. CCDC 2067281 contain the data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

The calculation of the structure of *mer*-[**1a**Fe]$^{2+}$ was performed on a Spartan'18 software (Wavefunction Inc.). The initial structure was obtained by an equilibrium conformer search based on a molecular mechanics calculation (Forcefield: MMFF). The obtained initial structure was optimized by a DFT calculation (B3LYP/6-31G*, vacuum).

The elemental analysis was performed by a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Masao Sasaki of the University of Tsukuba for the elemental analyses.

Synthesis and characterization of the compounds

Synthesis of **bpy-OH**

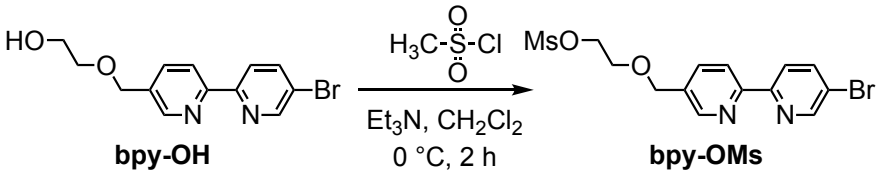


bpy-Br **bpy-OH**

To a suspension of NaH (60 wt% dispersion in mineral oil, 3.60 g, 90.0 mmol) in dry THF (150 mL) was added dry ethylene glycol (15.0 mL, 270 mmol), and the mixture was refluxed under an argon atmosphere. After 1 h, a suspension of **bpy-Br**[S4] (9.84 g, 30.0 mmol) in dry THF (150 mL) was added to the suspension dropwise over 3 h. Then the reaction mixture was further refluxed for 17 h. After cooling to room temperature, the mixture was concentrated *in vacuo*. The residue was suspended in satd. NH_4Cl aq. (500 mL) and extracted with EtOAc (150 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on amine-functionalized silica gel (EtOAc /hexane = 2/1) to give **bpy-OH** as a colorless solid (7.98 g, 25.8 mmol, 86%).

bpy-OH: colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 2.4 Hz, 1H), 8.63 (d, *J* = 2.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.64 (s, 2H), 3.82–3.79 (m, 2H), 3.66 (t, *J* = 4.5 Hz, 2H), 2.09 (br t, *J* = 5.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 154.4, 150.2, 148.6, 139.5, 136.5, 133.8, 122.3, 121.2, 120.8, 71.8, 70.6, 61.9; Anal. Calcd for $C_{13}H_{13}BrN_2O_2$: C, 50.51; H, 4.24; N, 9.06. Found: C, 50.26; H, 4.04; N, 8.91.

Synthesis of **bpy-OMs**

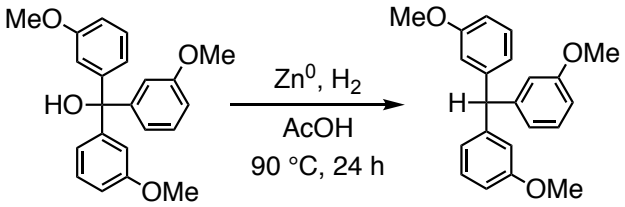


bpy-OH **bpy-OMs**

To a solution of **bpy-OH** (6.95 g, 22.5 mmol) in CH_2Cl_2 (150 mL) was added Et_3N (3.6 mL, 25.9 mmol) and methanesulfonyl chloride (2.0 mL, 25.9 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 2 h. 0.1 M HCl aq. (50 mL) was added to the reaction mixture, and the organic layer was separated, washed with satd $NaHCO_3$ aq. (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was washed with diethyl ether to give **bpy-OMs** as a pale yellow solid (7.48 g, 19.3 mmol, 86%).

bpy-OMs: pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 1.8 Hz, 1H), 8.63 (d, *J* = 1.8 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.66 (s, 2H), 4.43–4.42 (m, 2H), 3.82–3.80 (m, 2H), 3.05 (s, 3H); ^{13}C NMR (151 Hz, $CDCl_3$) δ 155.0, 154.3, 150.2, 148.6, 139.5, 136.5, 133.3, 122.4, 121.2, 120.8, 70.7, 68.7, 68.3, 37.7; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}BrN_2O_4S^+$ ([**bpy-OMs**•H]$^+$): 387.0010; found: 387.0005.

Synthesis of **4-H**

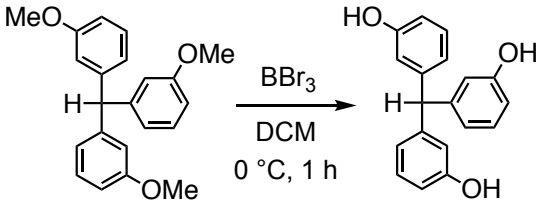


4-OH **4-H**

A suspension of **4-OH**[S5] (3.50 g, 10.0 mmol) and Zn powder (11.3 g, 173 mmol) in acetic acid (50 mL) was stirred at 90 °C for 24 h under a hydrogen atmosphere. The reaction mixture was filtered, and H_2O (100 mL) was added to the filtrate. The suspension was extracted with $CHCl_3$ (50 mL × 3). The organic layer was washed with satd $NaHCO_3$ aq. (100 mL × 2), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 2/1) to give **4-H** as a colorless solid (1.46 g, 4.36 mmol, 44%).

4-H: colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.75 (dd, *J* = 7.8 Hz, 2.4 Hz, 3H), 6.72 (d, *J* = 7.8 Hz, 3H), 6.67 (dd, *J* = 2.4, 2.4 Hz, 3H), 5.44 (s, 1H), 3.73 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 145.3, 129.3, 122.1, 115.7, 111.5, 57.0, 55.2; Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63; N, 0.00. Found: C, 78.87; H, 6.71; N, 0.00.

Synthesis of **5-H**

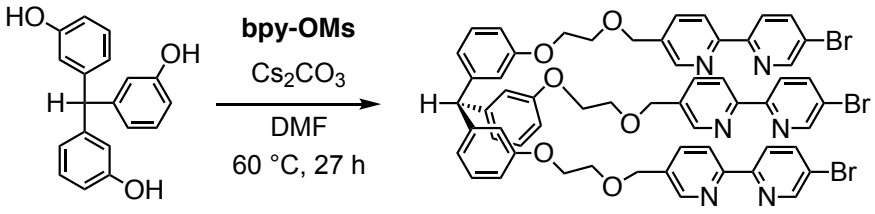


4-H **5-H**

To a solution of **4-H** (0.846 g, 2.53 mmol) in dry CH_2Cl_2 (12.3 mL) was added BBr_3 (0.80 mL, 8.4 mmol) at 0 °C under an argon atmosphere. After being stirred at 0 °C for 1 h, the reaction mixture was quenched with brine (50 mL) and extracted with THF (50 mL × 2). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* at 150 °C for 12 h to give **5-H** (0.731 g, 2.50 mmol, 99%) as a colorless solid.

5-H: colorless solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.25 (s, 3H), 7.07 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.58 (dd, *J* = 7.8, 1.8 Hz, 3H), 6.53 (d, *J* = 7.8 Hz, 3H), 6.50 (dd, *J* = 1.8, 1.8 Hz, 3H), 5.29 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 145.2, 129.0, 119.8, 116.0, 113.1, 55.6; Anal. Calcd for $C_{19}H_{17}O_{3.5}$ (**5-H**·0.5H_2O): C, 75.73; H, 5.69; N, 0.00. Found: C, 75.92; H, 5.47; N, 0.00.

Synthesis of **1a**

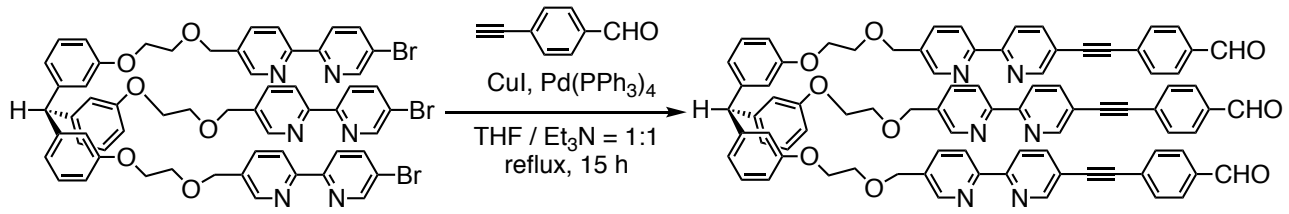


5-H **1a**

A suspension of **5-H** (0.694 g, 2.37 mmol) and Cs_2CO_3 (2.32 g, 7.12 mmol) in dry DMF (25 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of **bpy-OMs** (2.77 g, 7.16 mmol) in dry DMF (40 mL) was added to the reaction mixture, and the mixture was further stirred for 27 h. H_2O (200 mL) was added to the mixture, and the mixture was extracted with a mixed solvent of EtOAc/hexane = 1/1 (50 mL × 3). The combined organic layer was washed with H_2O (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on amine-functionalized silica gel (EtOAc/hexane = 1/2) to give **1a** as a pale brown solid (0.853 g, 0.732 mmol, 31%).

1a: pale brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 2.4 Hz, 3H), 8.60 (d, *J* = 1.8 Hz, 3H), 8.32 (d, *J* = 8.4 Hz, 3H), 8.29 (d, *J* = 8.4 Hz, 3H), 7.91 (dd, *J* = 8.4, 2.4 Hz, 3H), 7.45 (dd, *J* = 8.2, 1.8 Hz, 3H), 7.18 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.76 (dd, *J* = 7.8, 1.8 Hz, 3H), 6.73–6.69 (m, 6H), 5.42 (s, 1H), 4.65 (s, 6H), 4.09 (t, 4.8 Hz, 6H), 3.82 (t, 4.8 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 154.8, 154.6, 150.3, 148.7, 145.3, 139.6, 136.6, 134.1, 129.4, 122.5, 122.4, 121.2, 120.8, 116.4, 112.3, 70.9, 69.2, 67.4, 57.0; ESI-MS: *m/z* calcd for $C_{58}H_{49}Br_3N_6O_6^+$ ([**1a**•H]$^+$): 1163.13; found:1163.12.

Synthesis of **1b**



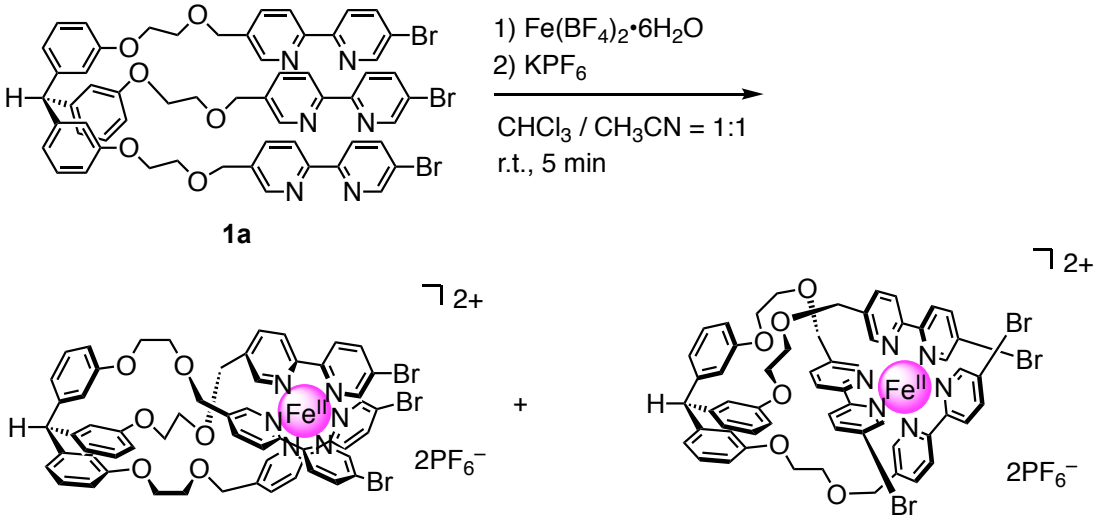
1a **1b**

A solution of **1a** (0.227 g, 0.195 mmol), 4-ethynylbenzaldehyde[S7] (0.153 g, 1.17 mmol), $Pd(PPh_3)_4$ (0.169 g, 0.146 mmol), and CuI (28.4 mg, 0.146 mmol) in a mixed solvent of dry THF (20 mL) and Et_3N (20 mL) was refluxed under an argon atmosphere. After 15 h, the mixture was concentrated *in vacuo*. The residue was suspended in a solution of EDTA•4Na•4H_2O (0.689 g, 1.52 mmol) in H_2O (50 mL) and extracted with $CHCl_3$ (30 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by GPC (using $CHCl_3$ as an eluent) and reprecipitation from $CHCl_3$/diethyl ether to give **1b** as a pale brown solid (0.0671 g, 51.1 μmol, 26%).

1b: pale brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.04 (s, 3H), 8.81 (br s, 3H), 8.64 (br s, 3H), 8.42 (d, *J* = 8.4 Hz, 3H), 8.40 (d, *J* = 8.4 Hz, 3H), 7.94 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.89 (d, *J* = 7.8 Hz, 6H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.71 (d, *J* = 7.8 Hz, 6H), 7.19 (dd, *J* = 7.8, 7.8 Hz, 3H) , 6.78 (br d, *J* = 7.8 Hz 3H), 6.74–6.71 (m, 6H), 5.43 (s, 1H), 4.68 (s, 6H), 4.11 (t, *J* = 4.2 Hz, 6H), 3.83 (t, *J* = 4.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.3, 158.9, 155.5, 154.9, 151.9, 148.8, 145.3, 139.6, 136.5, 136.0, 134.2, 132.4, 129.7, 129.4, 128.9, 122.5, 121.3, 120.5, 119.6, 116.5, 112.4, 92.6, 90.4, 86.0, 70.9, 69.2, 67.5, 57.0.

Although we tried to characterize **1b** by ESI-MS and MALDI-MS in various conditions, but **1b** was not observed under any investigated conditions.

Synthesis of [**1a**Fe]$(PF_6)_2$

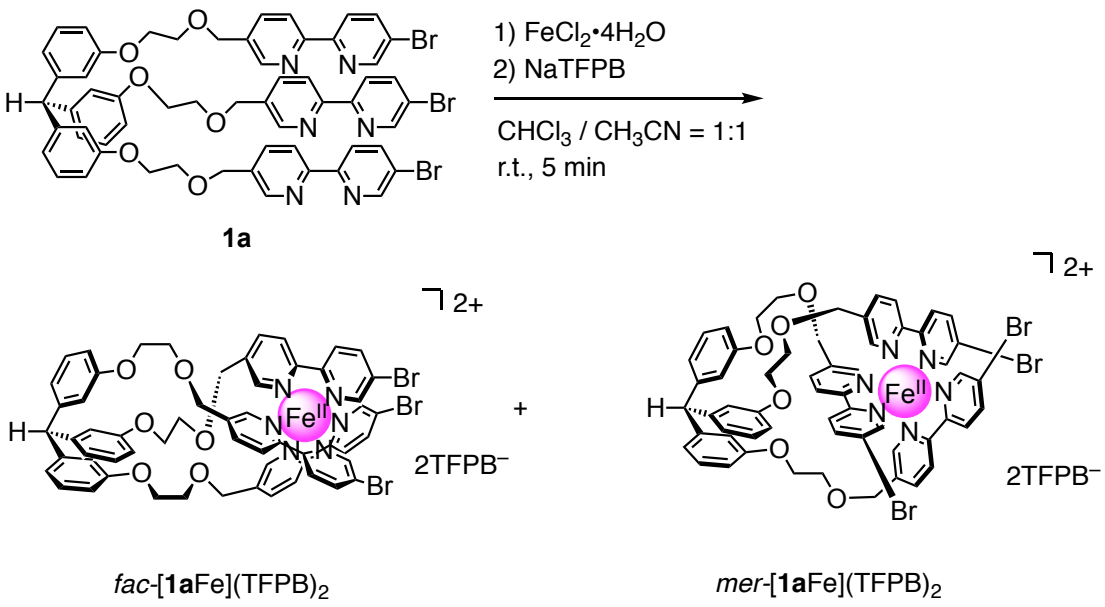


fac-[**1a**Fe]$(PF_6)_2$ *mer*-[**1a**Fe]$(PF_6)_2$

A solution of **1a** (0.122 g, 0.100 mmol) and $Fe(BF_4)_2$•$6H_2O$ (41.5 mg, 0.123 mmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of KPF_6 (1.84 g, 10.0 mmol) in H_2O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (50 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give [**1a**Fe]$(PF_6)_2$ as a red solid (0.104 g, 0.068 mmol, 68%).

[**1a**Fe]$(PF_6)_2$: red solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 8.51 (d, J = 8.4 Hz, 3H), 8.38 (d, J = 8.4 Hz, 3H), 8.29 (dd, J = 8.4, 2.4 Hz, 3H), 8.17 (dd, J = 8.4, 1.2 Hz, 3H), 7.46 (d, J = 2.4 Hz, 3H), 7.26 (dd, J = 7.8, 7.8 Hz, 3H), 7.18 (d, J = 1.2 Hz, 3H), 6.87 (d, J = 7.8 Hz, 3H), 6.76 (dd, J = 7.8, 1.8 Hz, 3H), 6.39 (dd, J = 1.8, 1.8 Hz, 3H), 5.55 (s, 1H), 4.39 (dd, J = 83.4, 12.6 Hz, 3H), 4.13 (dd, J = 9.0, 9.0 Hz, 3H), 4.00–3.92 (m, 6H), 3.75–3.70 (m, 3H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 159.5, 159.0, 158.6, 156.4, 153.4, 146.1, 142.9, 140.2, 139.4, 131.0, 125.7, 125.6, 123.8, 123.2, 117.6, 110.5, 70.9, 70.5, 68.8, 56.3; ^{19}F NMR (376 MHz, CD_3CN) δ –73.0 (d, $^1J_{F\text{-}P}$ = 707 Hz); ^{31}P NMR (243 MHz, CD_3CN) δ –144.6 (septet, $^1J_{P\text{-}F}$ = 707 Hz); HRMS (ESI-MS): *m/z* calcd for $C_{58}H_{49}Br_3FeN_6O_6^{2+}$ ([**1a**Fe]$^{2+}$): 608.0324; found: 608.0335.

Synthesis of [**1a**Fe](TFPB)$_2$

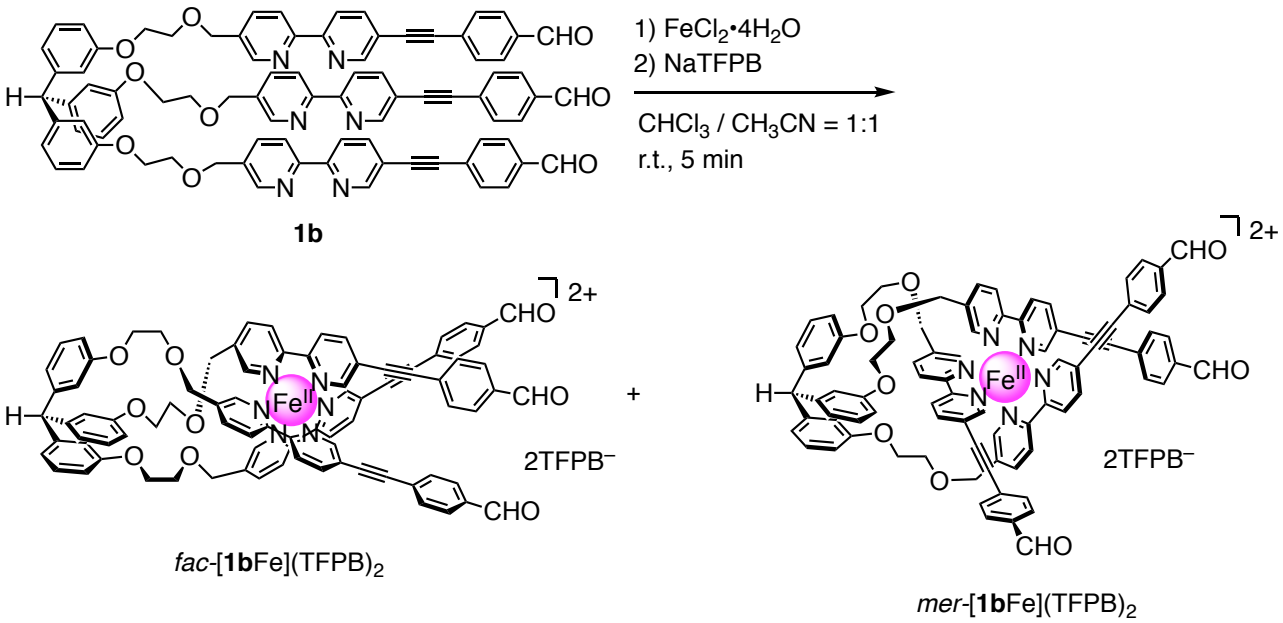


fac-[**1a**Fe](TFPB)$_2$ *mer*-[**1a**Fe](TFPB)$_2$

A solution of **1a** (0.122 g, 0.100 mmol) and $FeCl_2$•$4H_2O$ (24.3 mg, 0.122 mmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) (0.806 g, 0.909 mmol) in H_2O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (50 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give [**1a**Fe](TFPB)$_2$ as a red solid (0.236 g, 80 μmol, 80%).

[**1a**Fe](TFPB)$_2$: red solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 8.50 (d, *J* = 8.4 Hz, 3H), 8.38 (d, *J* = 8.4 Hz, 3H), 8.28 (dd, *J* = 8.4, 3.0 Hz, 3H), 8.16 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.46 (d, *J* = 1.8 Hz, 3H), 7.25 (dd, *J* = 8.4, 8.4 Hz, 3H), 7.18 (d, *J* = 1.8 Hz, 3H), 6.87 (br d, *J* = 8.4 Hz, 3H), 6.83 (dd, *J* = 8.4, 3.0 Hz, 3H), 6.39 (dd, *J* = 3.0, 3.0 Hz, 3H), 5.55 (s, 1H), 4.31 (dd, *J* = 85.2, 17.4 Hz, 6H), 4.16–4.09 (m, 3H) 4.01–3.91 (m, 6H), 3.75–3.68 (m, 3H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 162.7 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 159.5, 159.0, 158.6, 156.4, 153.5, 146.1, 142.9, 140.2, 139.4, 135.7 (br s), 131.0, 130.0 (qq, $^2J_{C\text{-}F}$ = 31.9 Hz, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.7, 125.6, 125.5 (q, $^1J_{C\text{-}F}$ = 272 Hz), 123.8, 123.2, 118.7 (septet, $^3J_{C\text{-}F}$ = 3.8 Hz), 117.6, 110.4, 70.9, 70.5, 68.8, 56.4; ^{11}B NMR (192 MHz, CD_3CN) δ –6.65; ^{19}F NMR (376 MHz, CD_3CN) δ –63.3; HRMS (ESI-MS): *m/z* calcd for $C_{58}H_{49}Br_3FeN_6O_6^{2+}$ ([**1a**Fe]$^{2+}$): 608.0324; found: 608.0310.

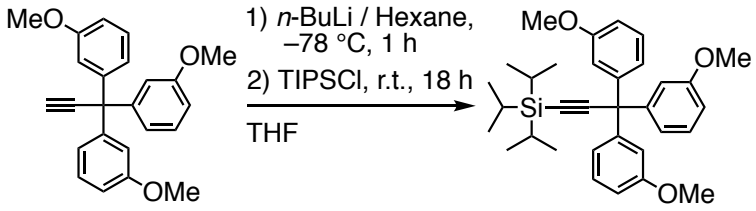
Synthesis of [**1b**Fe](TFPB)$_2$



A solution of **1b** (0.104 g, 79.2 μmol) and $FeCl_2$•$4H_2O$ (26.9 mg, 135 μmol) in a mixed solvent of CH_3CN/$CHCl_3$ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.489 g, 0.552 mmol) in H_2O (50 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH_3CN/$CHCl_3$ = 1/2 (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (CH_3CN/$CHCl_3$ = 1/4) to give [**1b**Fe](TFPB)$_2$ as a purple solid (0.104 g, 33.6 μmol, 42%).

[**1b**Fe](TFPB)$_2$: purple solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 10.00 (s, 3H), 8.56 (d, J = 8.4 Hz, 3H), 8.54 (d, J = 8.4 Hz, 3H), 8.25 (d, J = 8.4 Hz, 3H), 8.19 (d, J = 8.4 Hz, 3H), 7.89 (d, J = 7.8 Hz , 6H), 7.69 (br s, 16H), 7.68–7.62 (m, 17H), 7.30–7.23 (m, 6H), 6.88 (d, J = 7.8 Hz, 3H), 6.77 (d, J = 7.8 Hz, 3H), 6.41 (s, 3H), 5.56 (s, 1H), 4.42 (dd, J = 85.2, 12.6 Hz, 6H) 4.17–4.11 (m, 6H), 4.02–3.93 (m, 6H), 3.78–3.71 (m, 3H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 192.8, 162.7 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 159.6, 159.5, 158.8, 157.4, 153.7, 146.2, 142.2, 140.3, 139.4, 137.9, 135.7 (br s), 133.3, 131.0, 130.6, 130.1 (qq, $^2J_{C\text{-}F}$ = 31.9 Hz, $^3J_{C\text{-}F}$ = 3.8 Hz), 128.1, 125.8, 125.5 (q, $^1J_{C\text{-}F}$ = 272 Hz), 124.9, 124.1, 123.3, 118.7 (septet, $^3J_{C\text{-}F}$ = 3.8 Hz), 117.7, 110.6, 96.1, 88.2, 71.0, 70.6, 68.8, 56.5; ^{11}B NMR (192 MHz, CD_3CN) δ –6.68; ^{19}F NMR (376 MHz, CD_3CN) δ –63.2; HRMS (ESI): *m/z* calcd for $C_{85}H_{64}FeN_6O_9^{2+}$ ([**1b**Fe]$^{2+}$): 683.2060; found: 683.2072.

Synthesis of **4-TE**

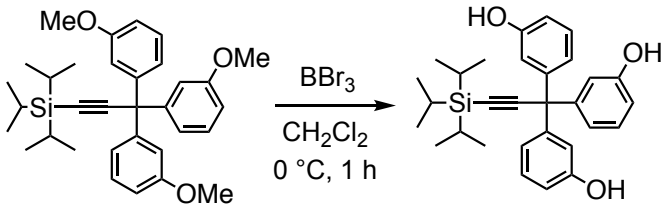


4-Ety **4-TE**

To a solution of **4-Ety**[S5] (3.58 g, 9.98 mmol) in dry THF (100 mL) was added a solution of *n*-BuLi in hexane (1.57 M, 7.0 mL, 11.0 mmol) at –78 °C under an argon atmosphere. After the mixture was stirred at –78 °C for 1 h, triisopropylsilyl chloride (2.4 mL, 11.7 mmol) was added at r.t. After being stirred at r.t. for 18 h, the reaction mixture was diluted with H_2O (200 mL) and extracted with $CHCl_3$ (100 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was recrystallized from methanol to give **4-TE** (4.84 g, 9.42 mmol, 94%) as a colorless solid.

4-TE: colorless solid, m.p. 91.2–92.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.93 (dd, *J* = 1.8, 1.8 Hz, 3H), 6.82 (d, *J* = 7.8 Hz, 3H), 6.77 (dd, *J* = 7.8, 1.8 Hz, 3H), 3.73 (s, 9H), 1.10–1.09 (m, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 146.6, 128.6, 121.8, 115.0, 113.3, 112.4, 85.7, 56.8, 55.1, 18.8, 11.4; Anal. Calcd for $C_{33}H_{42}O_3Si$: C, 77.00; H, 8.22; N, 0.00. Found: C, 76.93; H, 8.22; N, 0.00.

Synthesis of **5-TE**

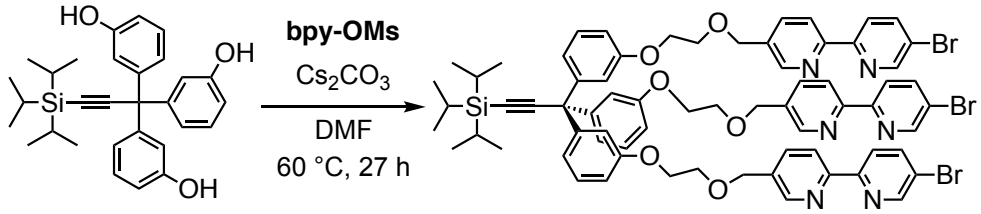


4-TE **5-TE**

To a solution of **4-TE** (9.30 g, 17.5 mmol) in dry CH_2Cl_2 (78 mL) was added BBr_3 (6.0 mL, 64.5 mmol) at 0 °C under an argon atmosphere. After being stirred at 0 °C for 1 h, the reaction mixture was quenched with H_2O (200 mL), and extracted with diethyl ether (100 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was recrystallized from diethyl ether/hexane to give **5-TE** (7.46 g, 15.8 mmol, 90%) as a colorless solid.

5-TE: colorless solid, m.p. 196–197 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.35 (s, 3H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.68 (d, *J* = 7.8 Hz, 3H), 6.65 (dd, *J* = 7.8, 1.8 Hz, 3H), 6.60 (dd, *J* = 1.8, 1.8 Hz, 3H), 1.08–1.04 (m, 21H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.3, 146.6, 129.1 119.8, 116.5, 114.3, 114.2, 84.9, 56.3, 19.0, 11.4; Anal. Calcd for $C_{30}H_{36.8}O_{3.4}Si$ (**5-TE**·0.4H_2O): C, 75.08; H, 7.73; N, 0.00. Found: C, 75.05; H, 7.67; N, 0.00.

Synthesis of **2a**

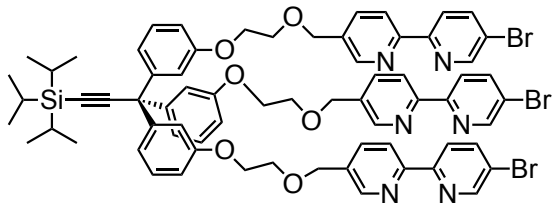


5-TE **2a**

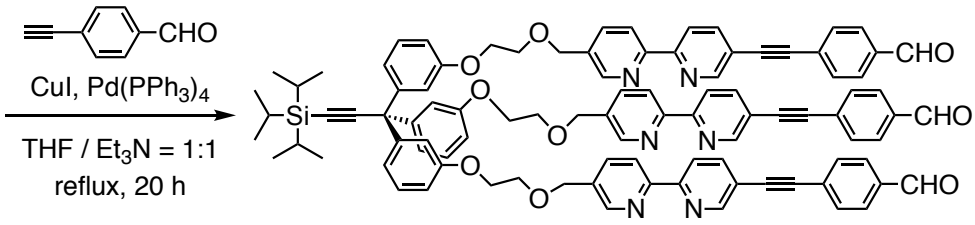
A suspension of **5-TE** (1.18 g, 2.50 mmol) and Cs_2CO_3 (2.61 g, 8.00 mmol) in dry DMF (50 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of **bpy-OMs** (3.10 g, 8.00 mmol) in dry DMF (40 mL) was added, and the reaction mixture was further stirred at 60 °C for 27 h. H_2O (200 mL) was added, and the mixture was extracted with a mixed solvent of ethyl acetate/hexane = 1/1 (50 mL × 3). The combined organic layer was washed with H_2O (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on amine-functionalized silica gel (ethyl acetate/hexane = 1/2) to give **2a** as a pale brown solid (1.66 g, 1.23 mmol, 49%).

2a: pale brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* =1.8 Hz, 3H), 8.59 (d, *J* = 1.8 Hz, 3H), 8.32 (d, *J* = 8.4 Hz, 3H), 8.27 (d, *J* = 8.4 Hz, 3H), 7.87 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.76 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.18 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.98 (s, 3H), 6.89 (d, *J* = 7.8 Hz, 3H), 6.81 (dd, *J* = 7.8, 1.8 Hz, 3H), 4.63 (s, 6H), 4.09 (t, *J* = 4.2 Hz, 6H), 3.80 (t, *J* = 4.2 Hz, 6H), 1.12–1.07 (m, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 154.5, 154.3, 150.1, 148.5, 146.5, 139.4, 136.3, 133.9, 128.7, 122.2, 122.1, 121.0, 120.6, 115.7, 113.3, 113.1, 85.8, 70.6, 69.0, 67.3, 56.8, 18.8, 11.4; HRMS (ESI): *m/z* calcd for $C_{69}H_{70}Br_3N_6O_6Si^+$ ([**2a**•H]$^+$): 1343.2671; found:1343.2703.

Synthesis of **2b**



2a

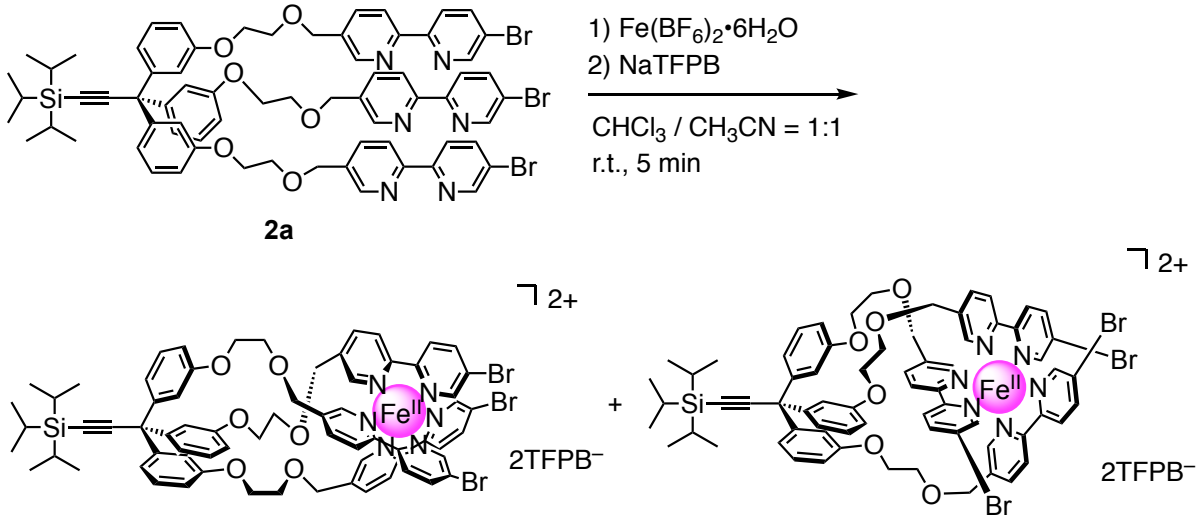


2b

A solution of **2a** (0.686 g, 0.510 mmol), 4-ethynylbenzaldehyde[S7] (0.390 g, 3.00 mmol), $Pd(PPh_3)_4$ (0.200 g, 0.17 mmol), and CuI (68.0 mg, 0.350 mmol) in a mixed solvent of dry THF (50 mL) and Et_3N (50 mL) was refluxed under an argon atmosphere. After 20 h, the mixture was concentrated *in vacuo*. The residue was suspended in a solution of EDTA•4Na•4H_2O (2.32 g, 5.13 mmol) in H_2O (200 mL) and extracted with $CHCl_3$ (50 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by GPC (using $CHCl_3$ as eluent) to give **2b** as a pale brown solid (0.602 g, 0.403 mmol, 79%).

2b: pale brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 3H), 8.82 (d, *J* =1.8 Hz, 3H), 8.64 (d, *J* = 1.8 Hz, 3H), 8.42 (d, *J* = 8.4 Hz, 3H), 8.40 (d, *J* = 8.4 Hz, 3H), 7.94 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.88 (d, *J* = 8.4 Hz, 6H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 3H), 7.70 (d, *J* = 8.4 Hz, 6H), 7.18 (dd, *J* = 7.8, 7.8 Hz, 3H) , 6.95 (br s, 3H), 6.87 (br d, *J* = 7.8 Hz 3H), 6.82 (dd, *J* = 7.8, 1.8 Hz, 3H), 4.67 (s, 6H), 4.10 (t, *J* = 4.8 Hz, 6H), 3.83 (t, *J* = 4.8 Hz, 6H), 1.09–1.80 (m, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.4, 158.5, 155.4, 154.9, 151.9, 148.8, 146.7, 139.6, 136.5, 135.9, 134.2, 132.3, 129.7, 128.9, 122.8, 122.3, 121.3, 120.5, 119.6, 115.8, 113.4, 113.2, 92.6, 90.4, 86.0, 70.8, 69.1, 67.4, 56.9, 18.9, 11.6; HRMS (ESI): *m/z* calcd for $C_{96}H_{85}N_6O_9Si^+$ ([**2b**•H]$^+$): 1493.6142; found:1493.6138.

Synthesis of [**2a**Fe](TFPB)$_2$

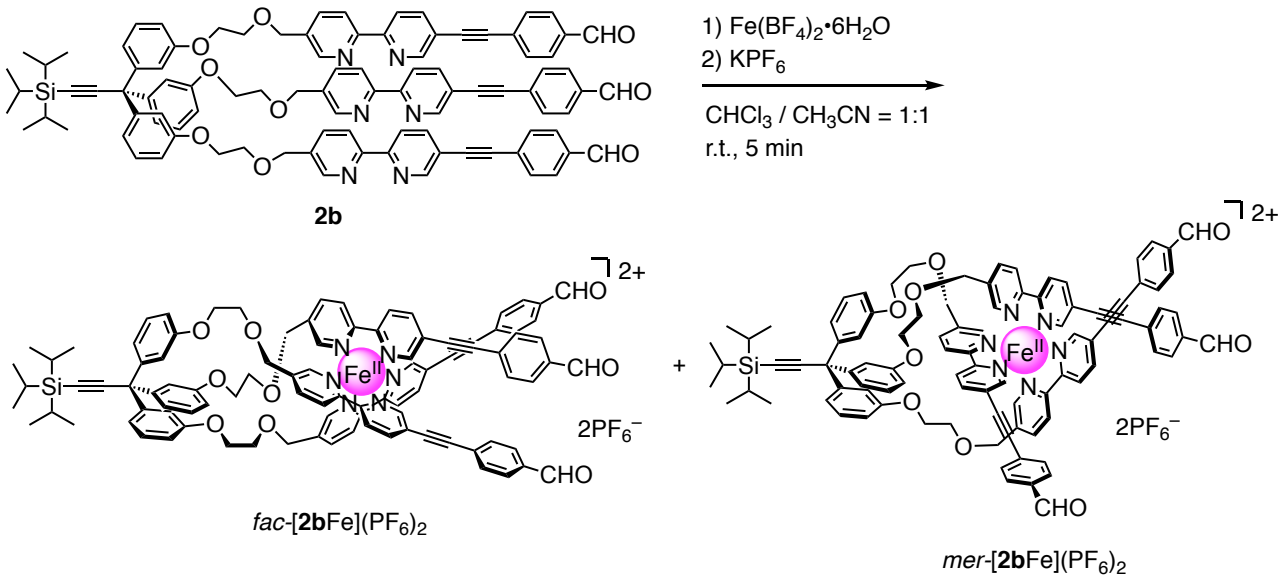


fac-[**2a**Fe](TFPB)$_2$ *mer*-[**2a**Fe](TFPB)$_2$

A solution of **2a** (0.108 g, 80.2 μmol) and $Fe(BF_4)_2 \cdot 6H_2O$ (32.1 mg, 95.1 μmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of NaTFPB (0.408 g, 456 μmol) in H_2O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (30 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give [**2a**Fe](TFPB)$_2$ as a red solid (0.123 g, 39.3 mmol, 49%).

[**2a**Fe](TFPB)$_2$: red solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 8.49 (d, *J* = 8.4 Hz, 3H), 8.37 (d, *J* = 8.4 Hz, 3H), 8.28 (dd, *J* = 8.4, 1.8 Hz, 3H), 8.13 (dd, *J* = 8.4, 1.2 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.45 (d, *J* = 1.8 Hz, 3H), 7.42 (dd, *J* = 7.8, 1.8 Hz, 3H), 7.34 (dd, *J* = 7.8, 7.8 Hz, 3H), 7.14 (d, *J* = 1.2 Hz, 3H), 6.83 (dd, *J* = 7.8, 1.8 Hz, 3H), 6.07 (dd, *J* = 1.8, 1.8 Hz, 3H), 4.31 (dd, *J* = 41.4, 12.0 Hz, 6H), 4.13–4.08 (m, 3H) 3.97–3.92 (m, 3H), 3.92–3.87 (m, 3H), 3.72–3.67 (m, 3H), 1.12–1.08 (m, 21H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 162.6 (q, $^1J_{C\text{-}B}$ = 49.7 Hz), 159.0, 158.9, 158.6, 156.4, 153.4, 147.3, 142.9, 140.1, 139.6, 135.7 (br s), 130.9, 130.0 (qq, $^2J_{C\text{-}F}$ = 31.9 Hz, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.7, 125.5, 125.5 (q, $^1J_{C\text{-}F}$ = 272 Hz), 123.9, 122.7, 118.7 (septet, $^3J_{C\text{-}F}$ = 3.8 Hz), 117.7, 113.6, 111.4, 87.0, 70.8, 70.1, 68.6, 57.1, 19.1, 12.3; ^{11}B NMR (192 MHz, CD_3CN) δ –6.65; ^{19}F NMR (376 MHz, CD_3CN) δ –63.2; HRMS (ESI): *m/z* calcd for $C_{69}H_{70}Br_3FeN_6O_6Si^{2+}$ ([**2a**Fe]$^{2+}$): 698.6031; found: 698.6010.

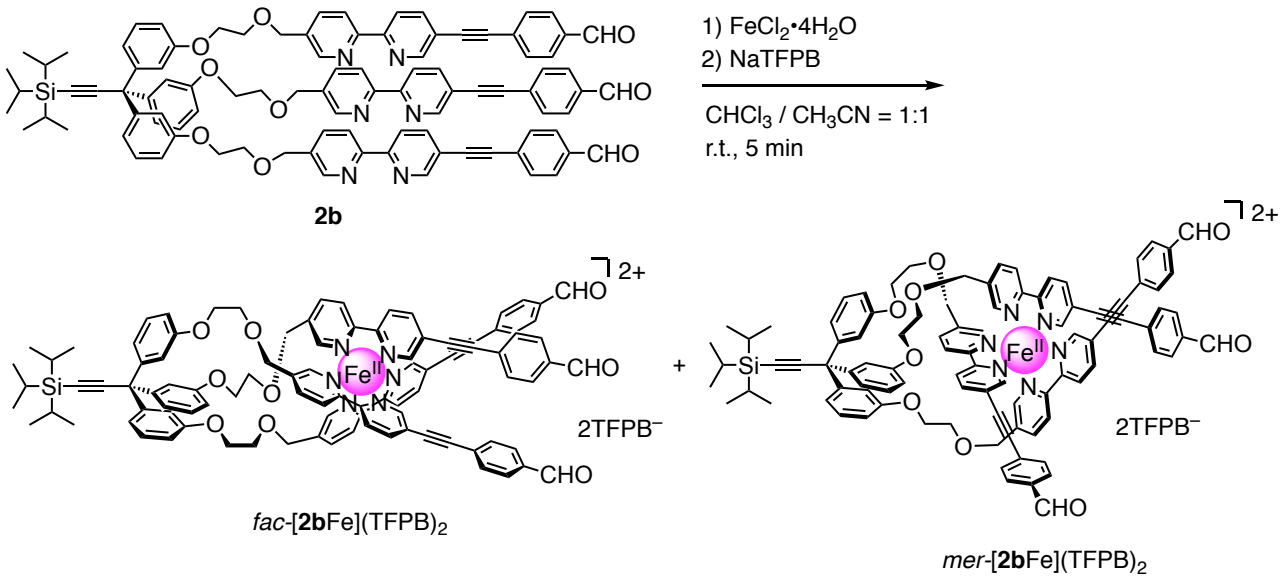
Synthesis of [**2b**Fe]$(PF_6)_2$



A solution of **2b** (0.337 g, 0.226 mmol) and $Fe(BF_4)_2 \cdot 6H_2O$ (50.7 mg, 0.254 mmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of KPF_6 (0.1898 g, 10.4 mmol) in H_2O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (30 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give [**2b**Fe]$(PF_6)_2$ as a purple solid (0.100 g, 54.4 μmol, 24%).

[**2b**Fe]$(PF_6)_2$: purple solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 10.00 (s, 3H), 8.55 (d, J = 8.4 Hz, 3H), 8.54 (d, J = 8.4 Hz, 3H), 8.25 (dd, J = 8.4, 2.4 Hz, 3H), 8.16 (dd, J = 8.4, 1.2 Hz, 3H), 7.90 (d, J = 8.4 Hz , 6H), 7.66–7.63 (m, 9H), 7.43 (dd, J = 7.8, 1.8 Hz, 3H), 7.34 (dd, J = 7.8, 7.8 Hz, 3H), 7.22 (d, J = 1.2 Hz, 3H), 6.84 (dd, J = 7.8, 1.8 Hz, 3H), 6.08 (dd, J = 1.8, 1.8 Hz, 3H), 4.34 (dd, J = 30.6, 12.6 Hz, 6H) 4.15–4.10 (m, 3H), 3.98–3.89 (m, 6H), 3.74–3.69 (m, 3H) 1.12–1.09 (m, 21H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 192.8, 159.5, 159.1, 158.9, 157.4, 153.7, 147.4, 142.3, 140.2, 139.6, 137.9, 133.4, 130.9, 130.6, 128.2, 125.8, 124.9, 124.1, 122.8, 117.8, 113.8, 111.7, 96.2, 88.3, 88.0, 70.8, 70.2, 68.7, 57.3, 19.2, 12.4; ^{19}F NMR (376 MHz, CD_3CN) δ –72.6 (d, $^1J_{F\text{-}P}$ = 706 Hz); ^{31}P NMR (243 MHz, CD_3CN) δ –144.6 (septet, $^1J_{P\text{-}F}$ = 706 Hz); HRMS (ESI): *m/z* calcd for $C_{96}H_{84}FeN_6O_9Si^{2+}$ ([**2b**Fe]$^{2+}$): 773.2727; found: 773.2722.

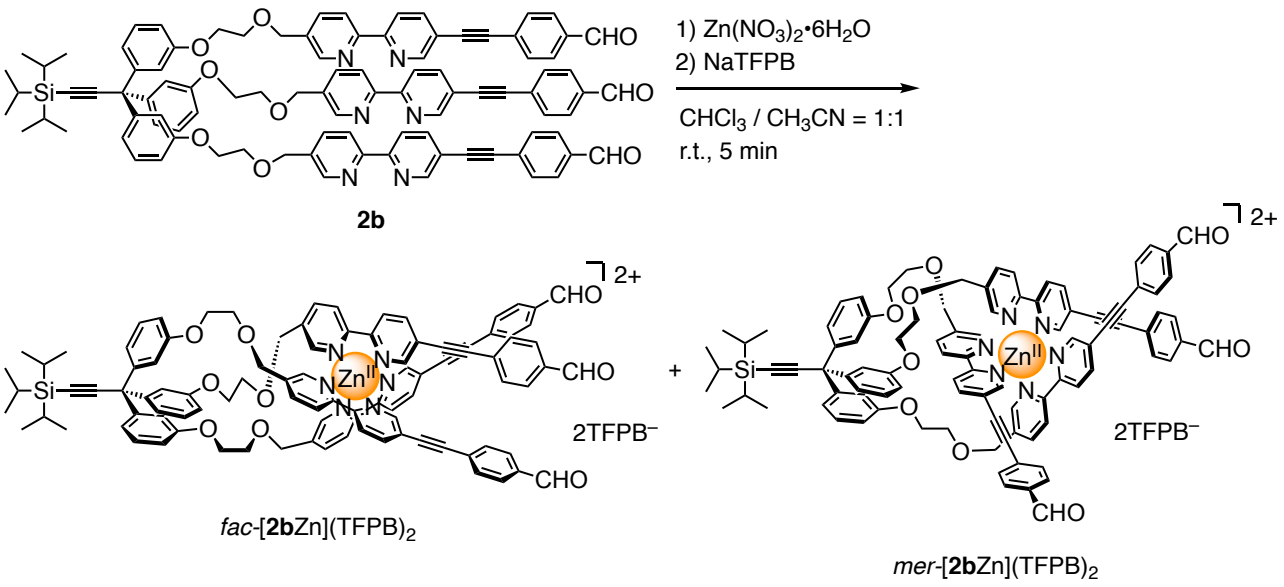
Synthesis of [**2b**Fe](TFPB)$_2$



A solution of **2b** (0.167 g, 0.100 mmol) and $FeCl_2$•$4H_2O$ (36.0 mg, 0.181 mmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.8732 g, 0.985 mmol) in H_2O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (30 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give [**2b**Fe](TFPB)$_2$ as a purple solid (0.241 g, 73.7 μmol, 74%).

[**2b**Fe](TFPB)$_2$: purple solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 9.98 (s, 3H), 8.57 (d, *J* = 8.4 Hz, 3H), 8.55 (d, *J* = 8.4 Hz, 3H), 8.25 (dd, *J* = 8.4, 2.4 Hz, 3H), 8.18 (dd, *J* = 8.4, 1.2 Hz, 3H), 7.87 (d, *J* = 7.8 Hz , 6H), 7.74 (br s, 16H), 7.71 (d, *J* = 2.4 Hz, 3H), 7.66 (br s, 8H), 7.63 (d, *J* = 7.8 Hz , 6H), 7.47 (dd, *J* = 7.8, 2.4 Hz, 3H), 7.36 (dd, *J* = 7.8, 7.8 Hz, 3H), 7.28 (d, *J* = 1.2 Hz, 3H), 6.85 (dd, *J* = 7.8, 2.4 Hz, 3H), 6.14 (dd, *J* = 2.4, 2.4 Hz, 3H), 4.38 (dd, *J* = 29.4, 12.6 Hz, 6H) 4.18–4.11 (m, 3H), 4.00–3.92 (m, 6H), 3.75–3.70 (m, 3H), 1.14–1.08 (m, 21H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 192.7, 162.7 (q, $^1J_{C\text{-}B}$ = 49.7 Hz), 159.4, 159.0, 158.9, 157.4, 153.7, 147.3, 142.2, 140.2, 139.6, 137.8, 135.8 (br s), 133.3, 130.9, 130.6, 130.0 (qq, $^2J_{C\text{-}F}$ = 31.9 Hz, $^3J_{C\text{-}F}$ = 3.8 Hz), 128.1, 125.7, 125.4 (q, $^1J_{C\text{-}F}$ = 272 Hz), 124.9, 124.1, 122.9, 122.8, 118.7 (septet, $^3J_{C\text{-}F}$ = 3.8 Hz), 117.8, 113.7, 111.4, 96.1, 88.2, 87.0, 70.8, 70.2, 68.6, 57.2, 19.1, 12.3; ^{11}B NMR (192 MHz, CD_3CN) δ –6.63; ^{19}F NMR (376 MHz, CD_3CN) δ –63.2; HRMS (ESI): *m/z* calcd for $C_{96}H_{84}FeN_6O_9Si^{2+}$ ([**2b**Fe]$^{2+}$): 773.2727; found: 773.2747.

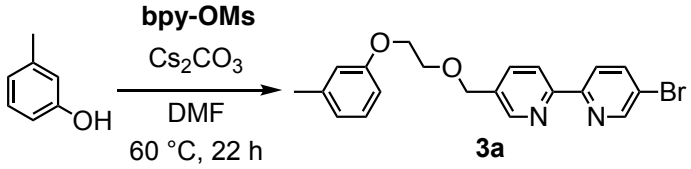
Synthesis of [**2b**Zn](TFPB)$_2$



A solution of **2b** (75.0 mg, 50.0 μmol) and $Zn(NO_3)_2$•$6H_2O$ (16.2 mg, 52.2 μmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.2248 g, 251 μmol) in H_2O (20 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (20 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give [**2b**Zn](TFPB)$_2$ as a brown solid (0.1763 g, quant.).

[**2b**Zn](TFPB)$_2$: brown solid; ^{1}H NMR (600 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 10.00 (s, 3H), 8.51 (d, *J* = 8.4 Hz, 3H), 8.51 (d, *J* = 8.4 Hz, 3H), 8.35 (dd, *J* = 8.4, 1.8 Hz, 3H), 8.26 (dd, *J* = 8.4, 1.8 Hz, 3H), 8.21 (d, *J* = 1.8 Hz , 63H), 7.90 (d, *J* = 7.8 Hz , 6H), 7.84 (d, *J* = 1.8 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.42 (d, *J* = 7.8 Hz , 3H), 7.34 (dd, *J* = 7.8, 7.8 Hz, 3H), 6.84 (dd, *J* = 7.8, 1.8 Hz, 3H), 6.10 (s, 3H), 4.42 (dd, *J* = 52.2, 11.4 Hz, 6H) 4.14–4.09 (m, 3H), 3.99–3.89 (m, 6H), 3.78–3.72 (m, 3H), 1.12–1.08 (m, 21H); ^{13}C NMR (151 MHz, CD_3CN, the signals for the *fac*-isomer are shown) δ 192.7, 162.6 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 158.9, 151.4, 149.4, 149.1, 147.9, 147.3, 144.9, 142.5, 139.9, 135.7 (br s), 133.2, 130.8, 130.5, 130.0 (qq, $^2J_{C\text{-}F}$ = 31.9 Hz, $^3J_{C\text{-}F}$ = 3.8 Hz), 128.1, 125.4 (q, $^1J_{C\text{-}F}$ = 272 Hz), 125.0, 124.4, 124.2, 122.8, 118.7 (septet, $^3J_{C\text{-}F}$ = 3.8 Hz), 117.6, 113.8, 111.3, 96.0, 88.2, 86.8, 70.8, 70.1, 68.5, 57.2, 19.1, 12.2; ^{11}B NMR (192 MHz, CD_3CN) δ –6.64; ^{19}F NMR (376 MHz, CD_3CN) δ –63.2; HRMS (ESI): *m/z* calcd for $C_{96}H_{85}ZnN_6O_9Si^{2+}$ ([**2b**Zn]$^{2+}$): 778.7714; found: 778.7730.

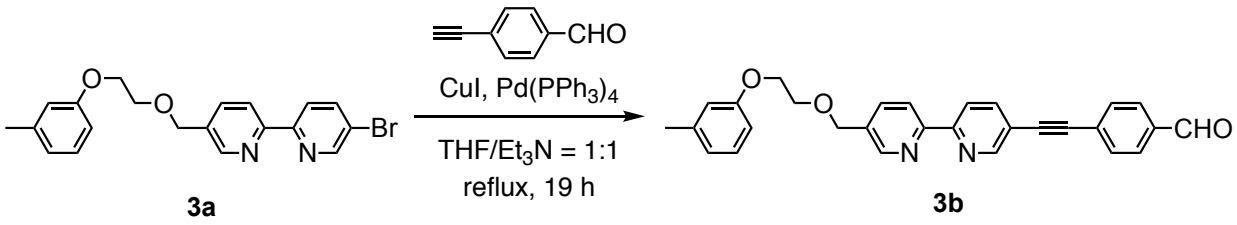
Synthesis of **3a**



A suspension of *m*-cresol (0.51 mL, 3.0 mmol) and Cs_2CO_3 (0.983 g, 3.02 mmol) in dry DMF (10 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of **bpy-OMs** (1.16 g, 3.00 mmol) in DMF (17 mL) was added to the reaction mixture, and the reaction mixture was further stirred at 60 °C for 22 h. H_2O (100 mL) was added, and the mixture was extracted with a mixed solvent of EtOAc/hexane = 1/1 (50 mL × 2). The combined organic layer was washed with H_2O (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by GPC (using $CHCl_3$ as an eluent) to give **3a** as a colorless solid (1.00 g, 2.51 mmol, 84%).

3a: colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* =1.8 Hz, 3H), 8.64 (d, *J* = 1.8 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.16 (dd, *J* = 7.8, 7.8 Hz, 1H) , 6.78–6.75 (m, 2H), 6.73 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.70 (s, 2H), 4.18–4.14 (m, 2H), 3.89–3.86 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 154.8, 154.6, 150.3, 148.7, 139.6, 139.6, 136.6, 134.1, 129.3, 122.5, 122.0, 121.2, 120.8, 115.6, 111.6, 70.8, 69.2, 67.4, 21.6; HRMS (ESI): *m/z* calcd for $C_{20}H_{20}BrN_2O_2^+$ ([**3a**•H]$^+$): 399.0703; found: 399.0686.

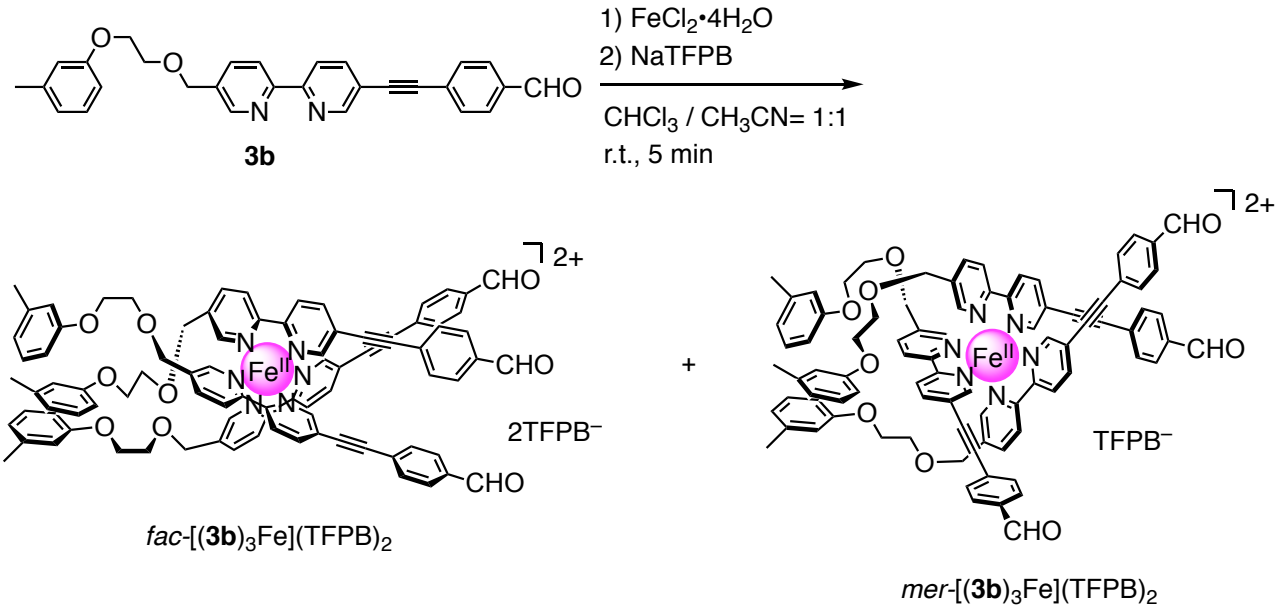
Synthesis of **3b**



A solution of **3a** (0.576 g, 1.44 mmol), 4-ethynylbenzaldehyde[S7] (0.375 g, 2.88 mmol), $Pd(PPh_3)_4$ (0.168 g, 0.140 mmol), and CuI (62.3 mg, 0.330 mmol) in a mixed solvent of dry THF (50 mL) and Et_3N (50 mL) was refluxed under an argon atmosphere. After 19 h, the mixture was concentrated *in vacuo*. The residue was suspended in a solution of EDTA•4Na (2.32 g, 5.12 mmol) in H_2O (200 mL) and extracted with $CHCl_3$ (50 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by GPC (using $CHCl_3$ as an eluent) to give **3b** as a pale brown solid (0.137 g, 0.305 mmol, 21%).

3b: pale brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.67 (d, *J* =1.8 Hz, 1H), 8.68 (d, *J* = 1.8 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.86 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 7.8, 7.8 Hz, 3H) , 6.79–6.76 (m, 2H), 6.74 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.73 (s, 2H), 4.19–4.16 (m, 2H), 3.91–3.87 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.4, 158.8, 155.4, 154.9, 151.9, 148.8, 139.6, 136.5, 135.9, 134.3, 132.3, 129.7, 129.3, 128.9, 121.9, 121.3, 120.5, 119.6, 115.6, 111.6, 92.5, 90.4, 70.8, 69.2, 67.4, 21.6; HRMS (ESI): *m/z* calcd for $C_{29}H_{25}N_2O_3^+$ ([**3b**•H]$^+$): 449.1859; found: 449.1855.

Synthesis of $[(\mathbf{3b})_3Fe](TFPB)_2$



A solution of **3b** (338.5 mg, 85.8 μmol) and $FeCl_2$•$4H_2O$ (5.68 mg, 28.6 μmol) in a mixed solvent of $CH_3CN/CHCl_3$ = 1/1 (6.0 mL) was sonicated for 5 min. A solution of NaTFPB (0.253 g, 0.286 mmol) in H_2O (10.0 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of $CH_3CN/CHCl_3$ = 1/2 (5.0 mL × 3). The combined organic layer dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CH_3CN/CHCl_3$ = 1/4) to give $[(\mathbf{3b})_3Fe](TFPB)_2$ as a purple solid (56.5 mg, 24.9 μmol, 89%).

$[(\mathbf{3b})_3Fe](TFPB)_2$: purple solid; ^{11}B NMR (192 MHz, CD_3CN) δ –6.65; ^{19}F NMR (376 MHz, CD_3CN) δ –63.2; HRMS (ESI): *m/z* calcd for $C_{87}H_{72}FeN_6O_9^+$ ($[(\mathbf{3b})_3Fe]^{2+}$): 699.2373; found: 699.2387.

^1H NMR (600 MHz, CD_3CN) and ^{13}C NMR (151 MHz, CD_3CN) spectra was shown in **Fig. S61** and **S62**.

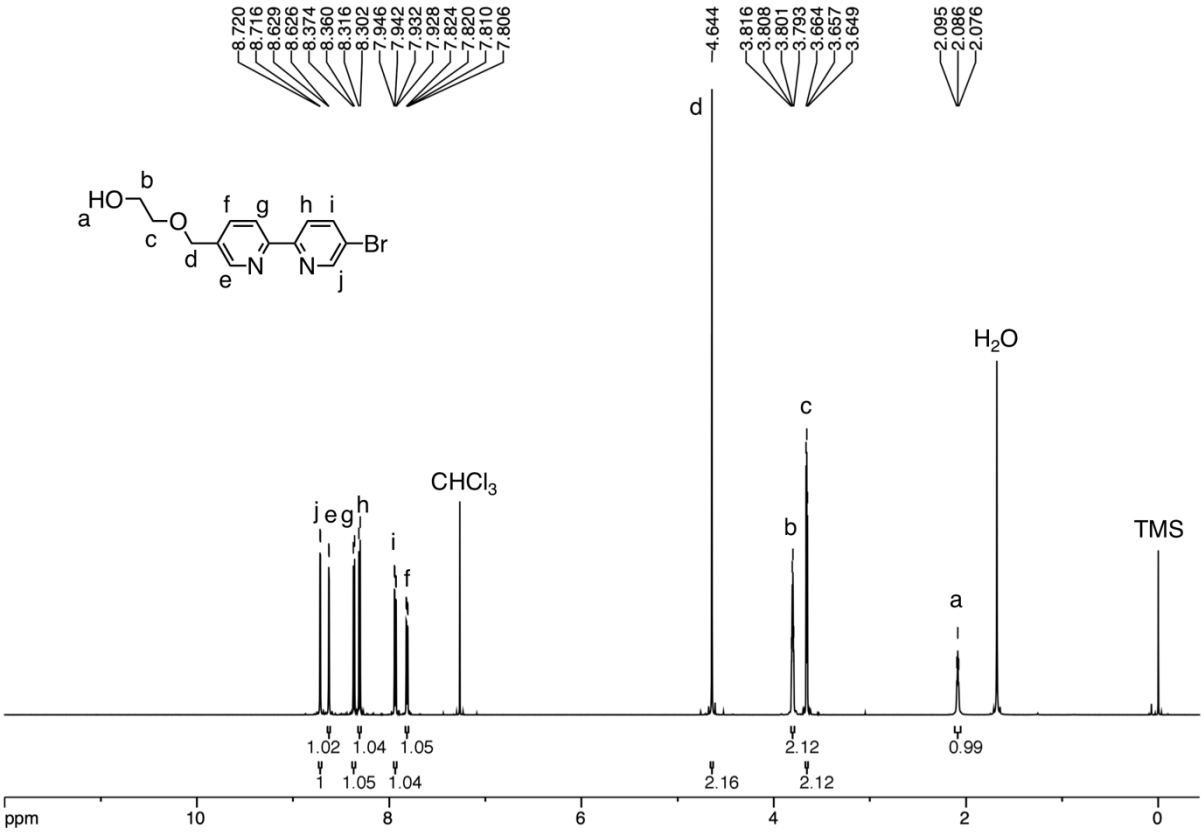


Figure S1. ^{1}H NMR spectrum of **bpy-OH** (600 MHz, $CDCl_3$).

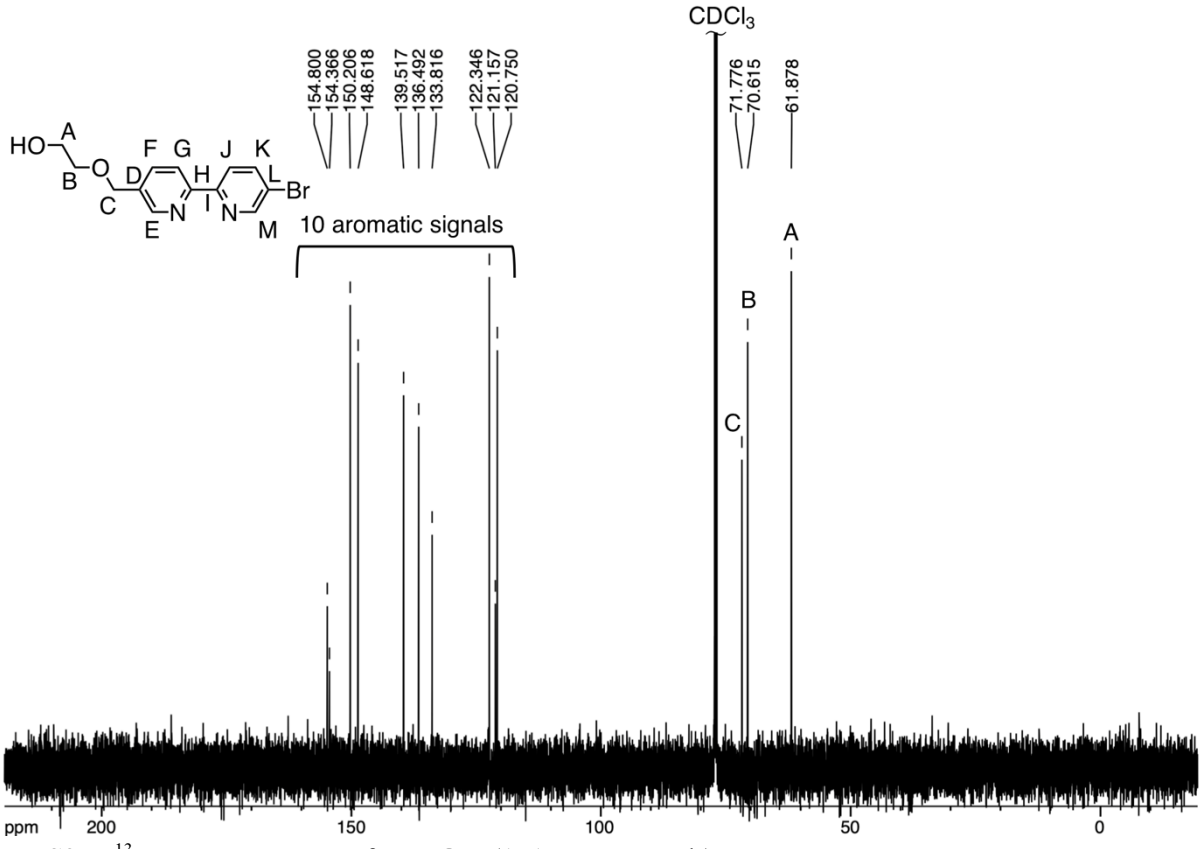


Figure S2. ^{13}C NMR spectrum of **bpy-OH** (151 MHz, $CDCl_3$).

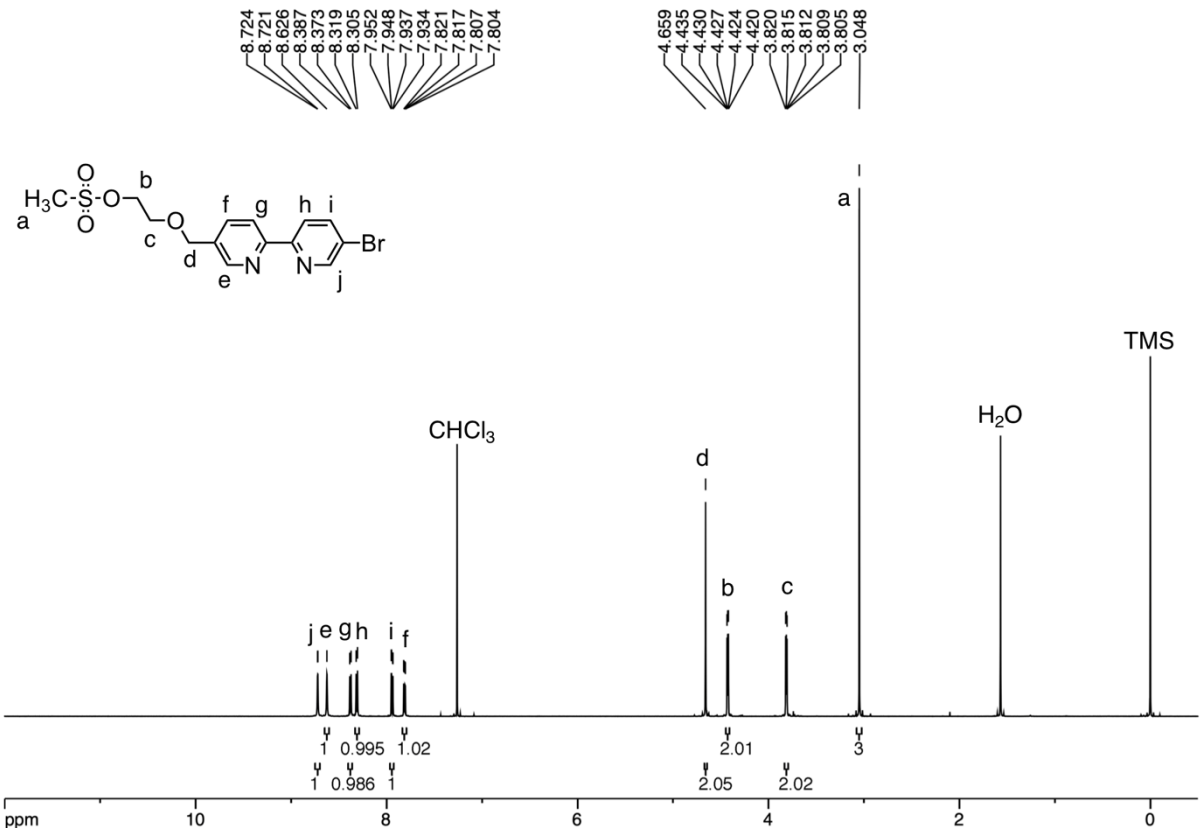


Figure S3. ^{1}H NMR spectrum of **bpy-OMs** (600 MHz, $CDCl_3$).

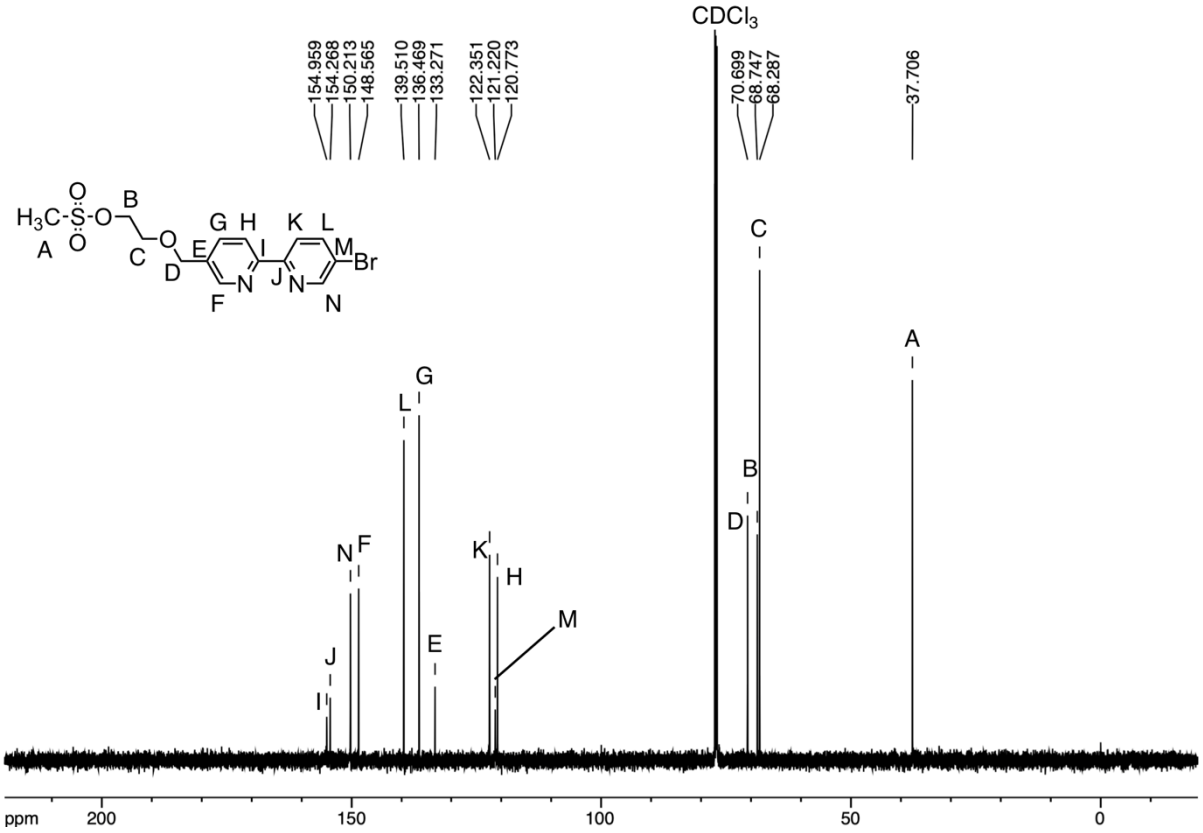


Figure S4. ^{13}C NMR spectrum of **bpy-OMs** (151 MHz, $CDCl_3$).

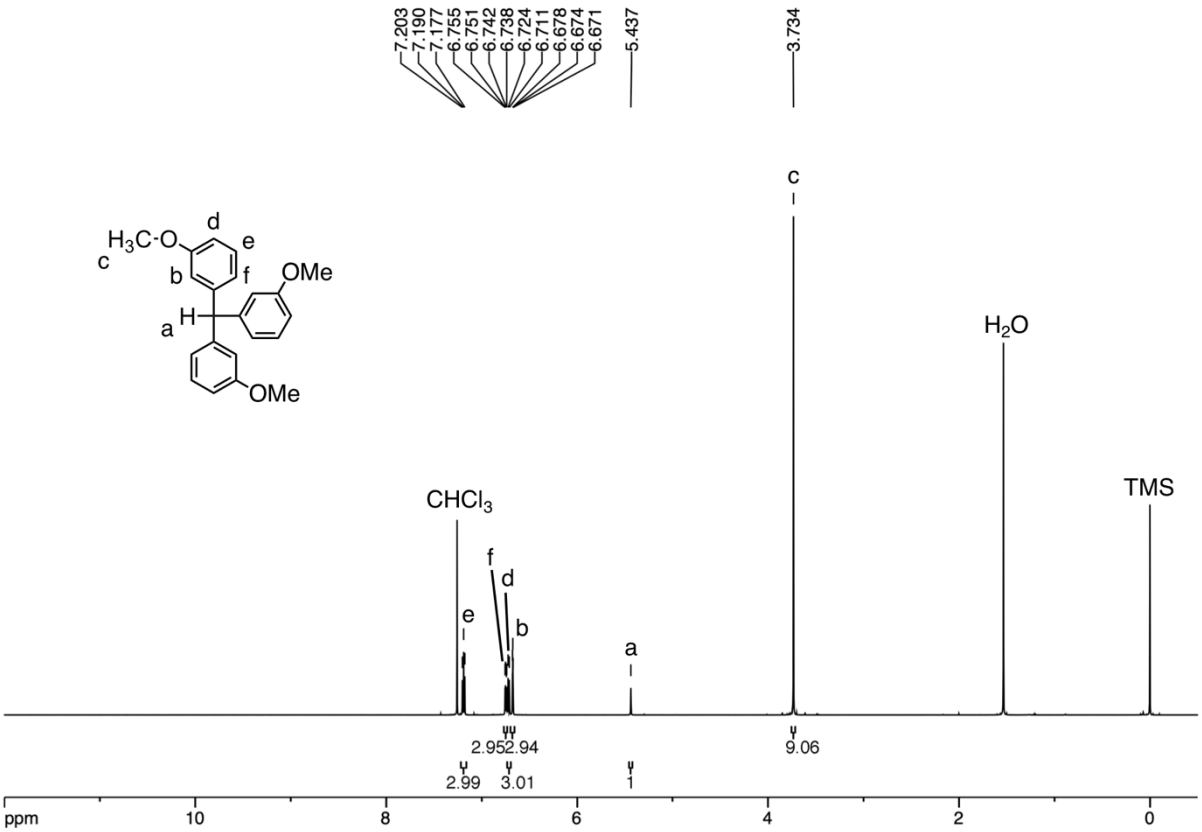


Figure S5. ^{1}H NMR spectrum of **4-H** (600 MHz, $CDCl_3$).

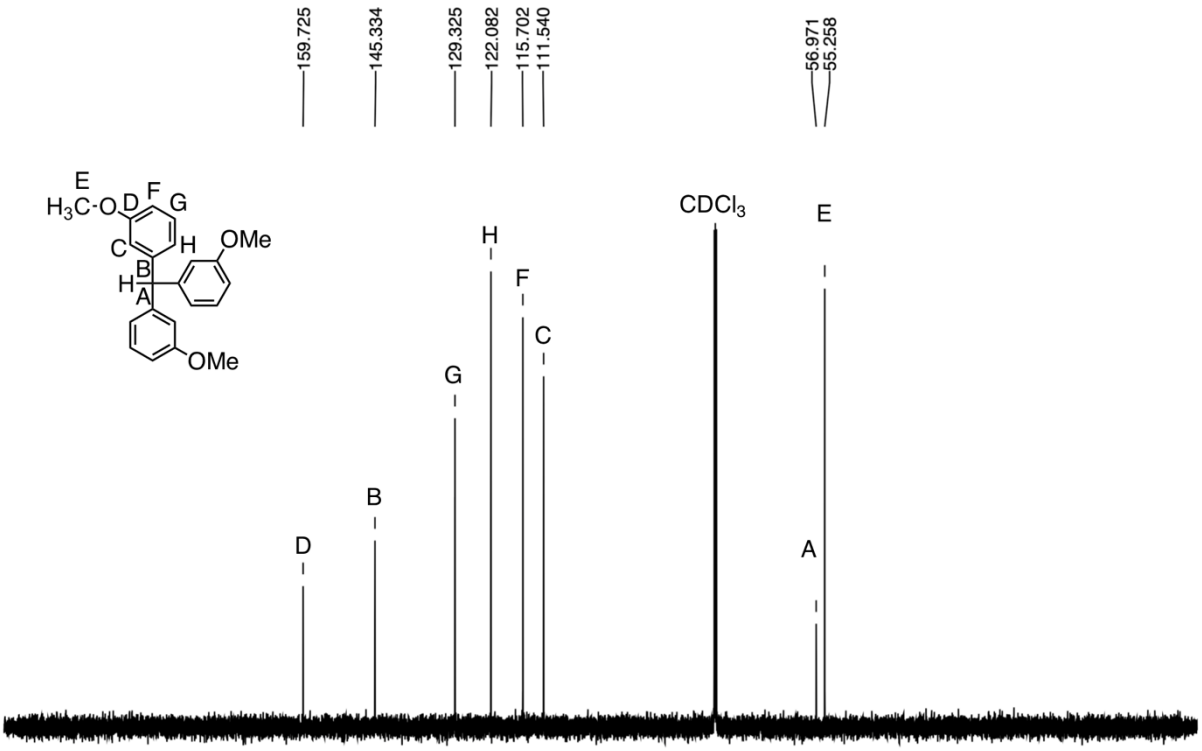


Figure S6. ^{13}C NMR spectrum of **4-H** (151 MHz, $CDCl_3$).

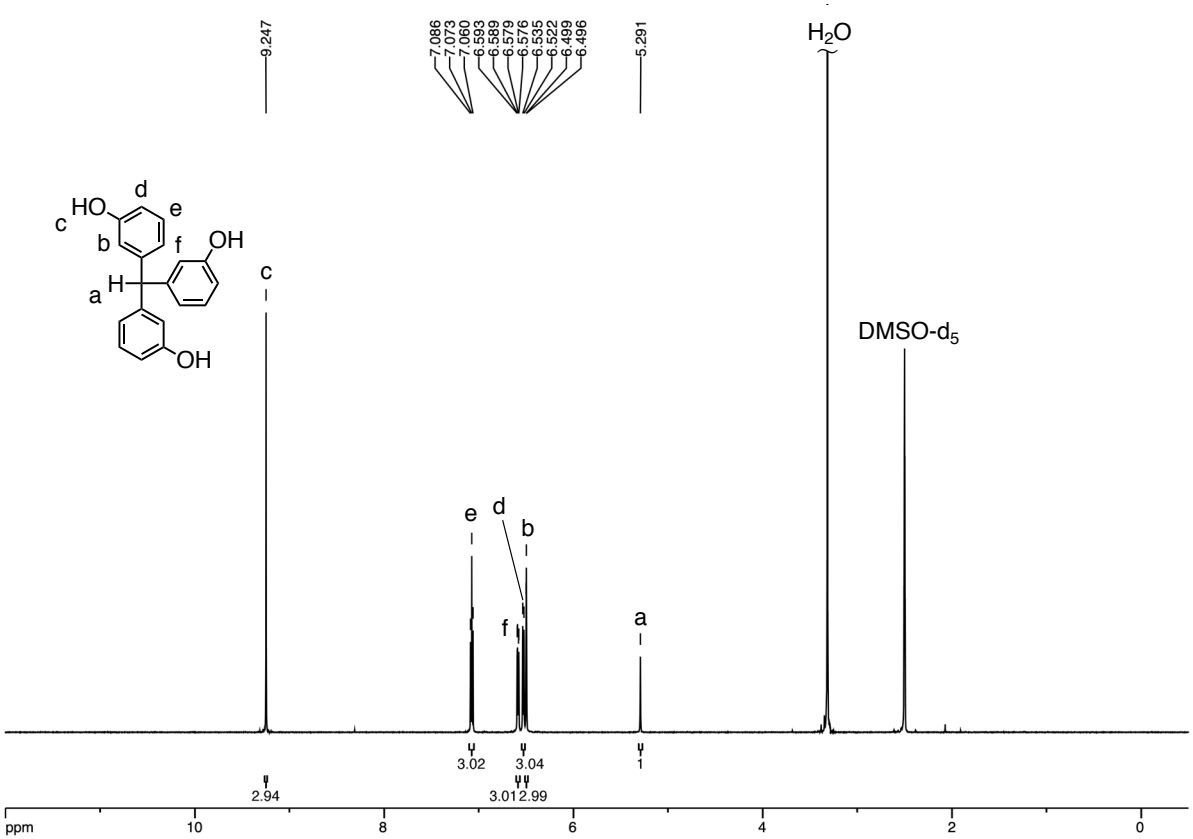


Figure S7. ^{1}H NMR spectrum of **5-H** (600 MHz, DMSO-d_6).

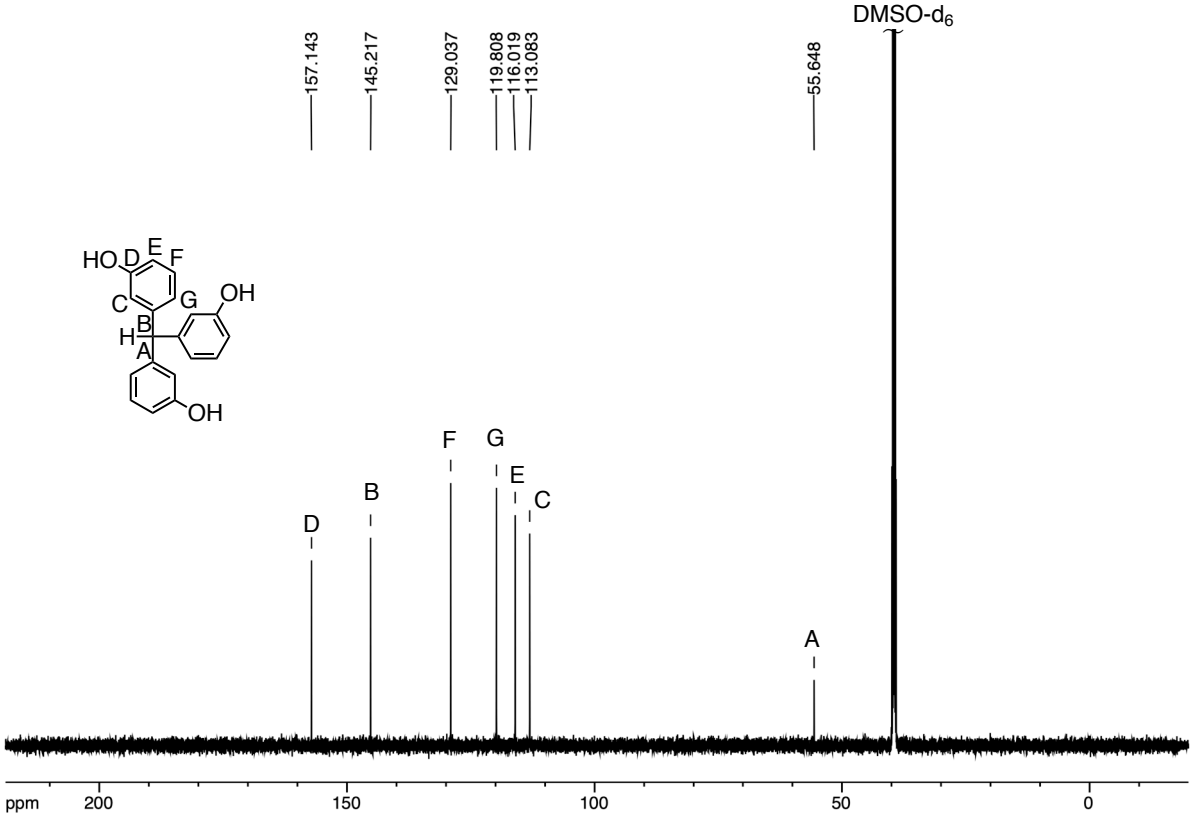


Figure S8. ^{13}C NMR spectrum of **5-H** (151 MHz, DMSO-d_6).

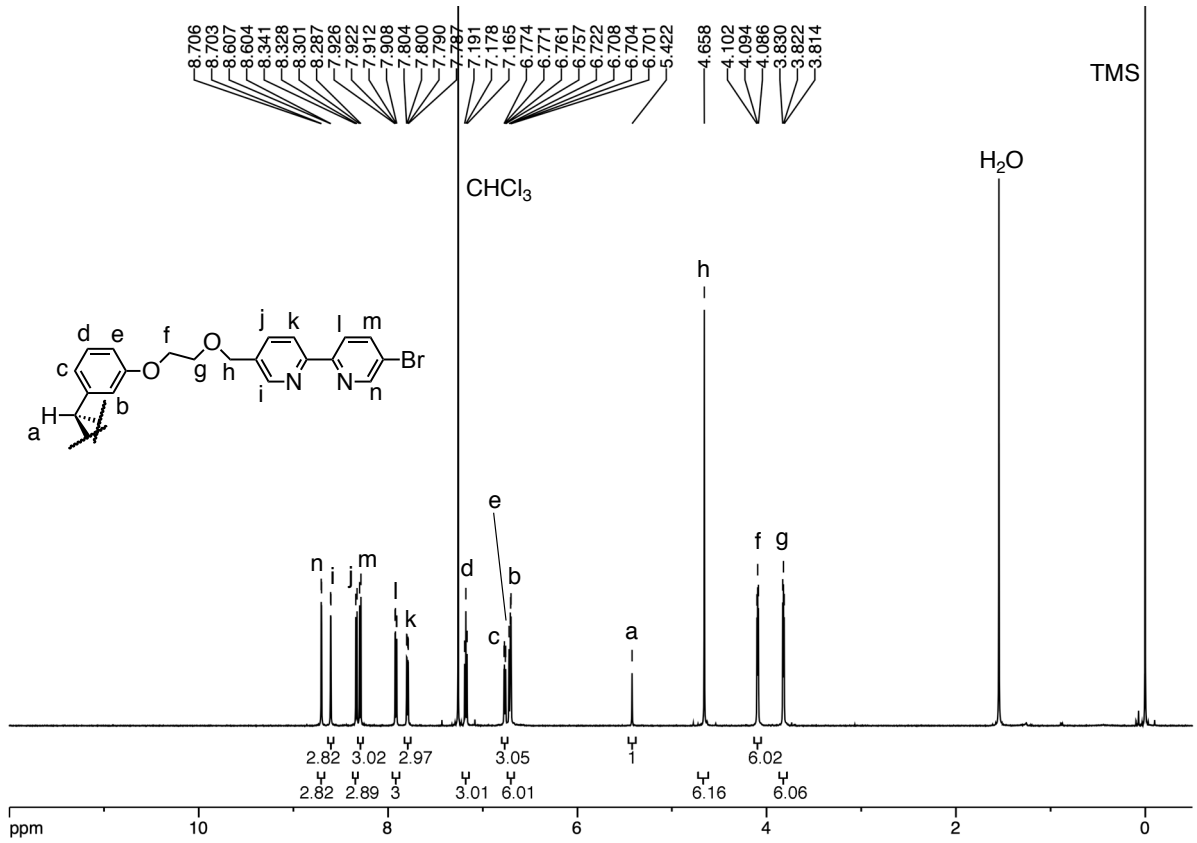


Figure S9. ^{1}H NMR spectrum of **1a** (600 MHz, $CDCl_3$).

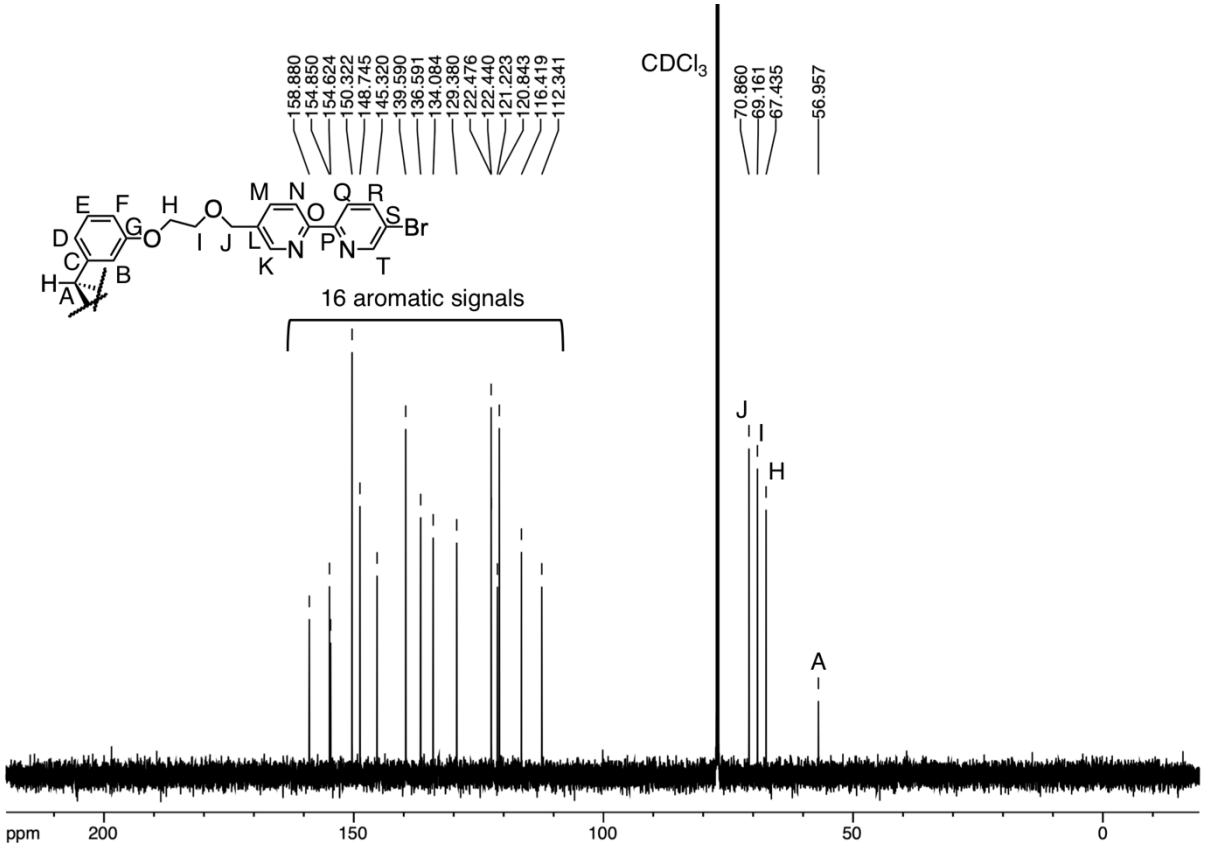


Figure S10. ^{13}C NMR spectrum of **1a** (151 MHz, $CDCl_3$).

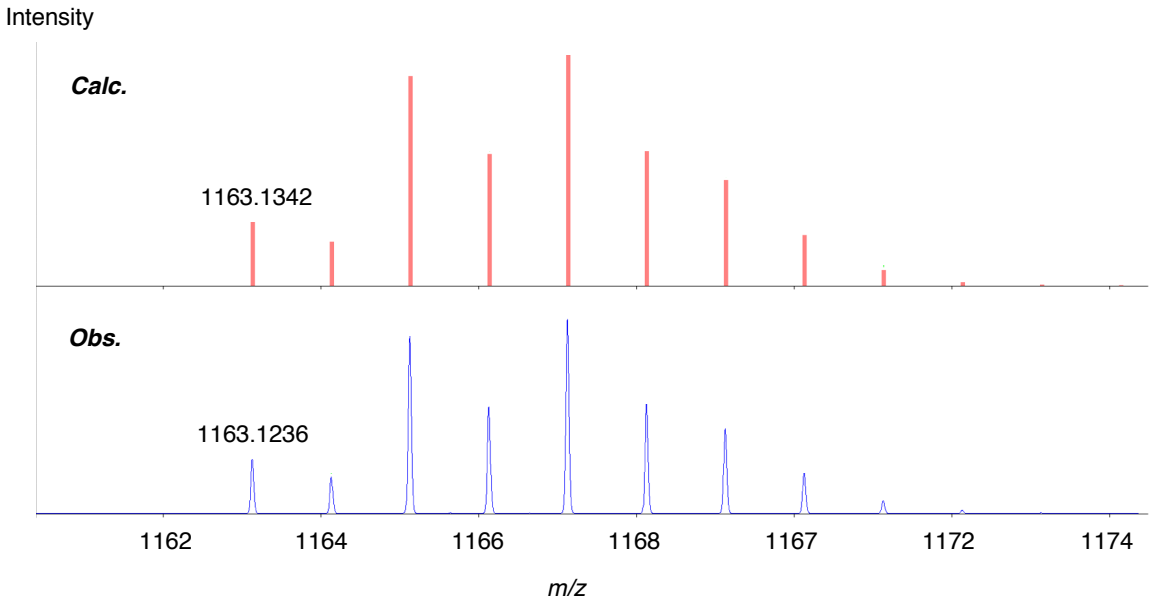


Figure S11. Simulated and observed isotopic pattern of [**1a**•H]$^+$ (ESI-MS, positive).

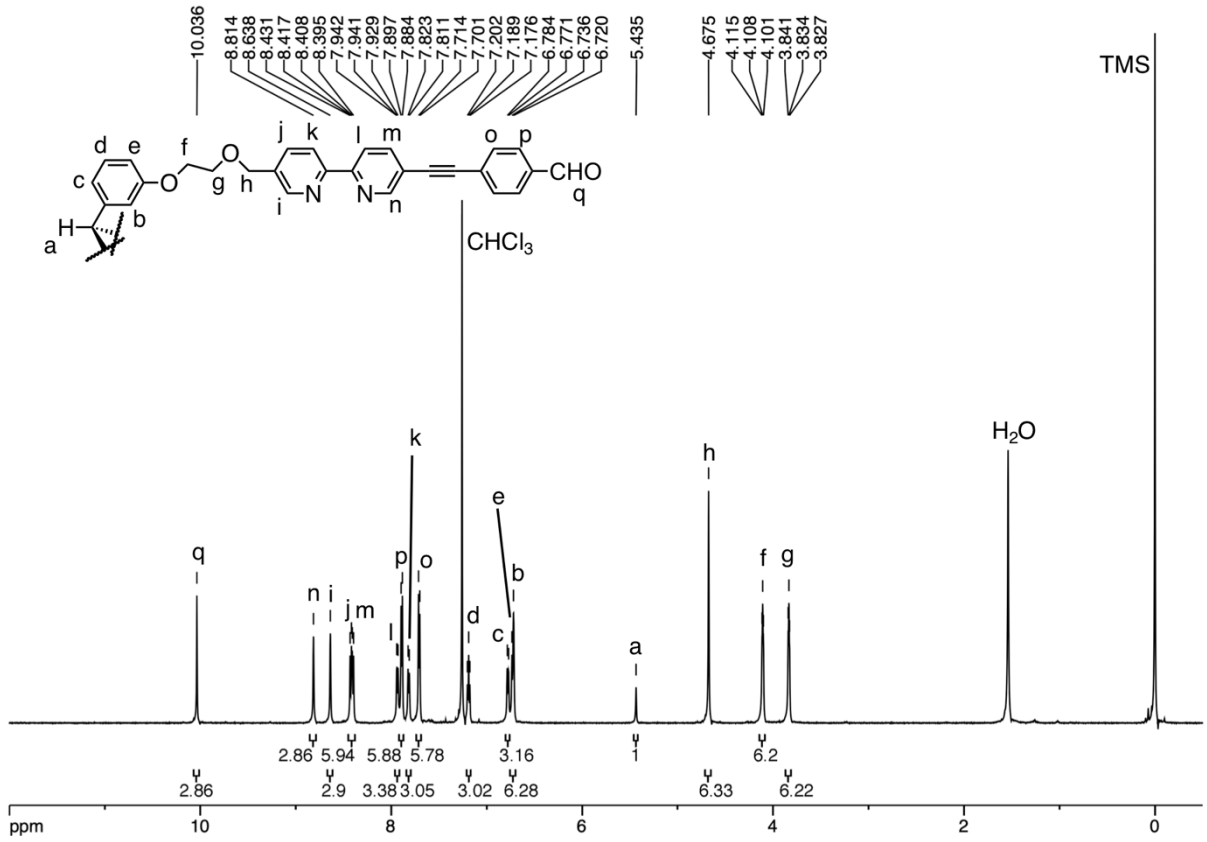


Figure S12. ^{1}H NMR spectrum of **1b** (600 MHz, $CDCl_3$).

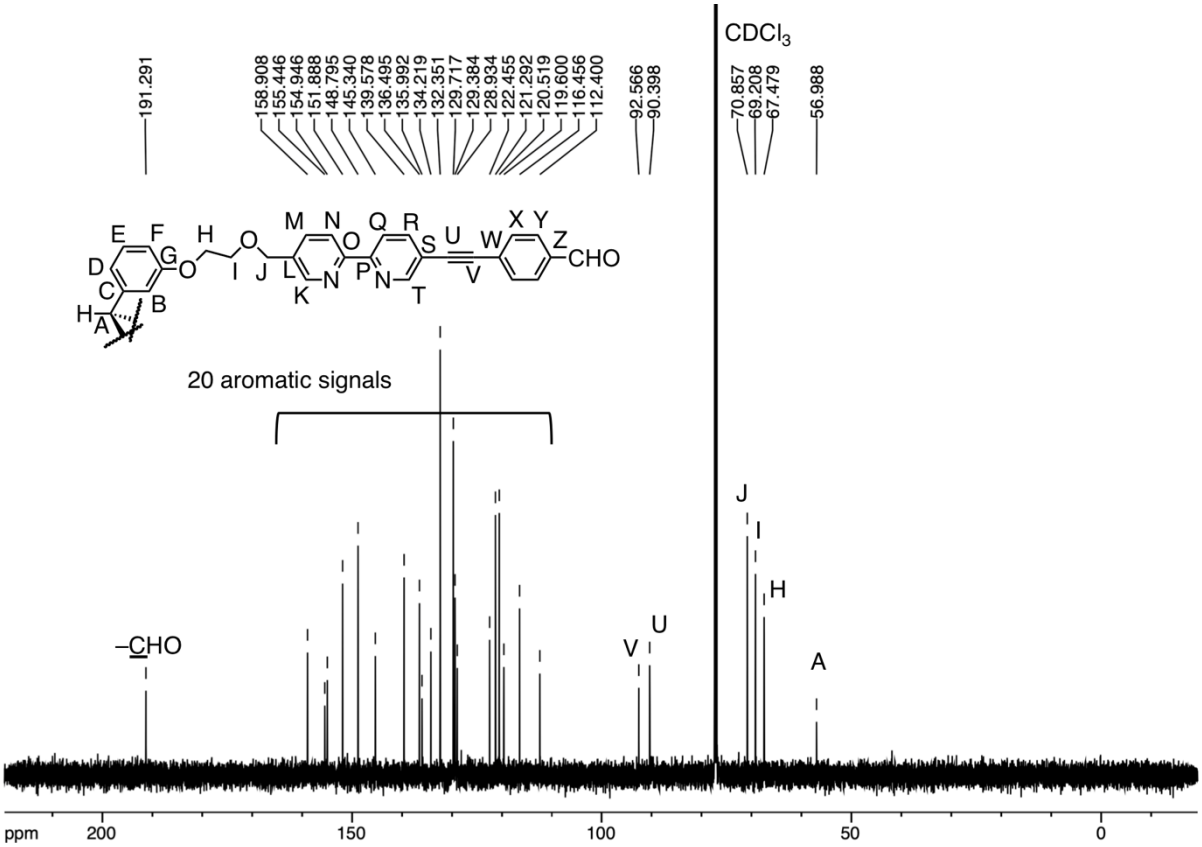


Figure S13. ^{13}C NMR spectrum of **1b** (151 MHz, $CDCl_3$).

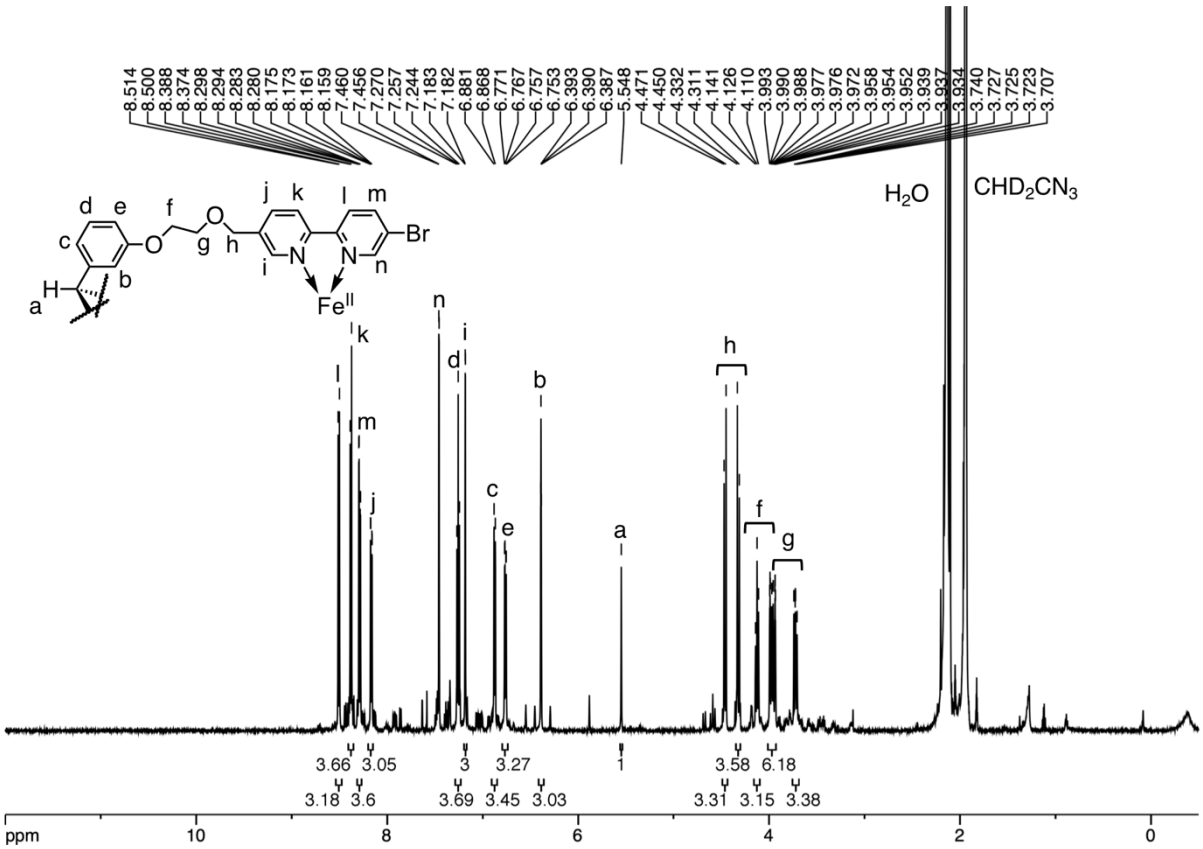


Figure S14. ^{1}H NMR spectrum of [**1a**Fe]$(PF_6)_2$ (600 MHz, CD_3CN).

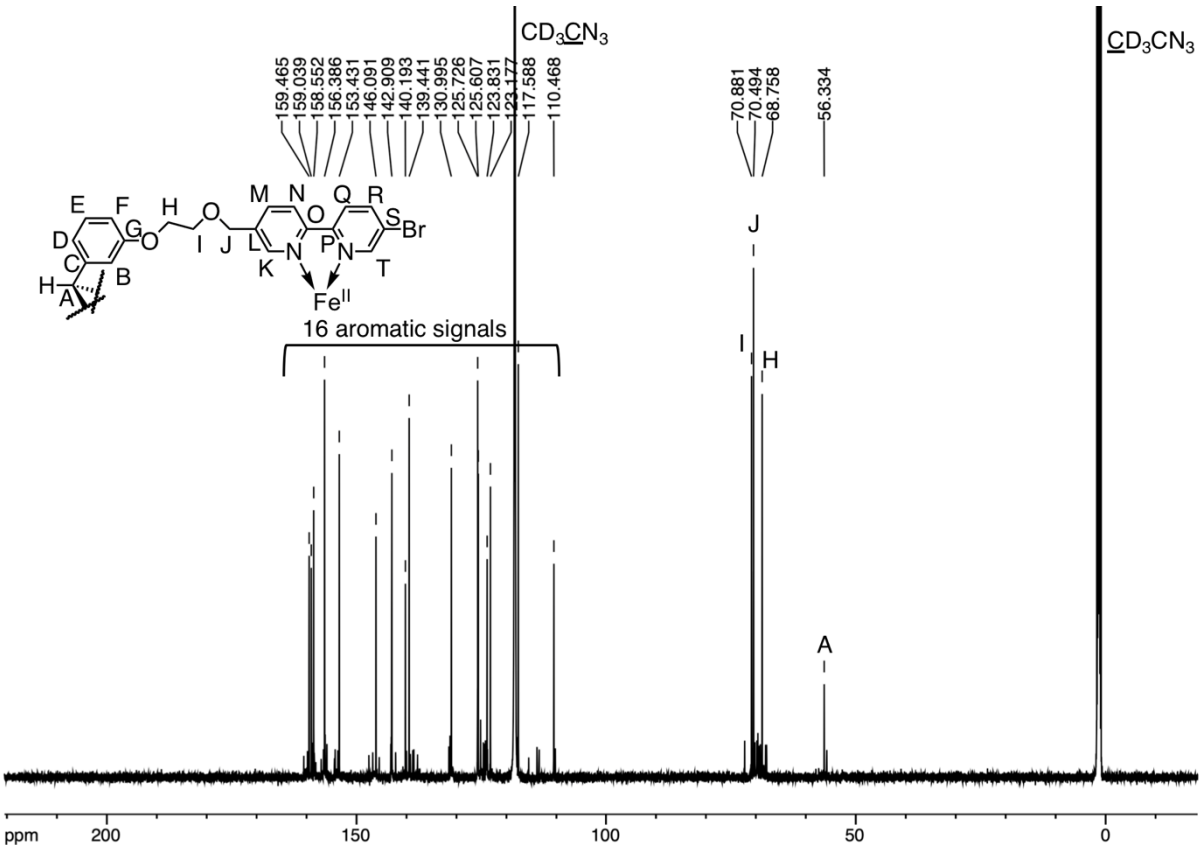


Figure S15. ^{13}C NMR spectrum of [**1a**Fe](PF$_6$)$_2$ (151 MHz, CD$_3$CN).

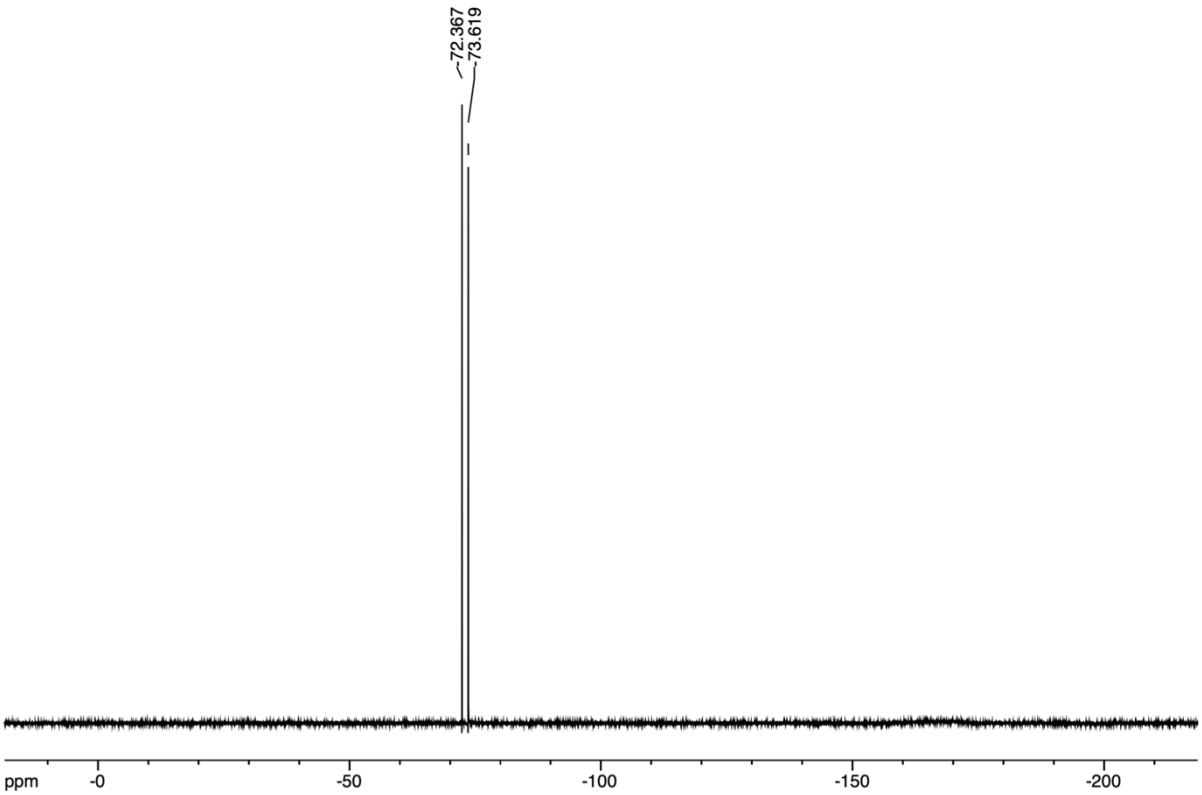


Figure S16. ^{19}F NMR spectrum of [**1a**Fe](PF$_6$)$_2$ (376 MHz, CD$_3$CN).

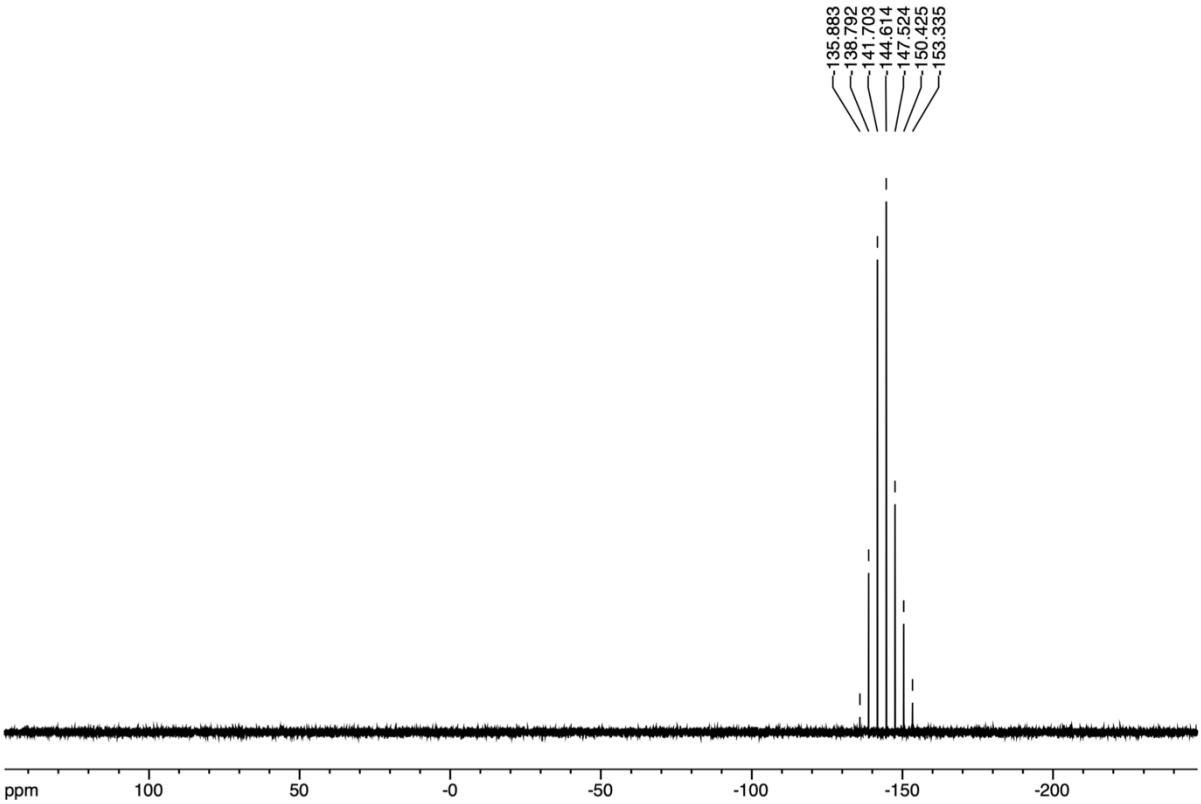


Figure S17. ^{31}P NMR spectrum of [**1a**Fe](PF$_6$)$_2$ (243 MHz, CD$_3$CN).

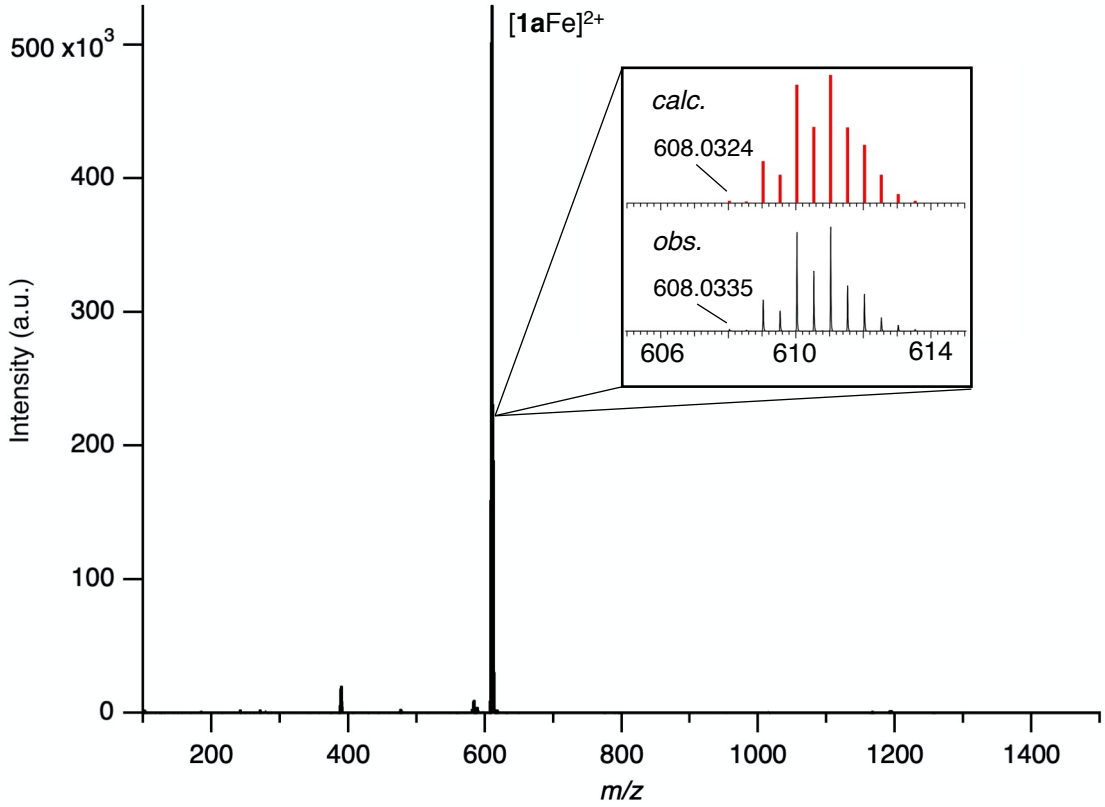


Figure S18. ESI mass spectrum of [**1a**Fe](PF$_6$)$_2$ (solv. CD$_3$CN).

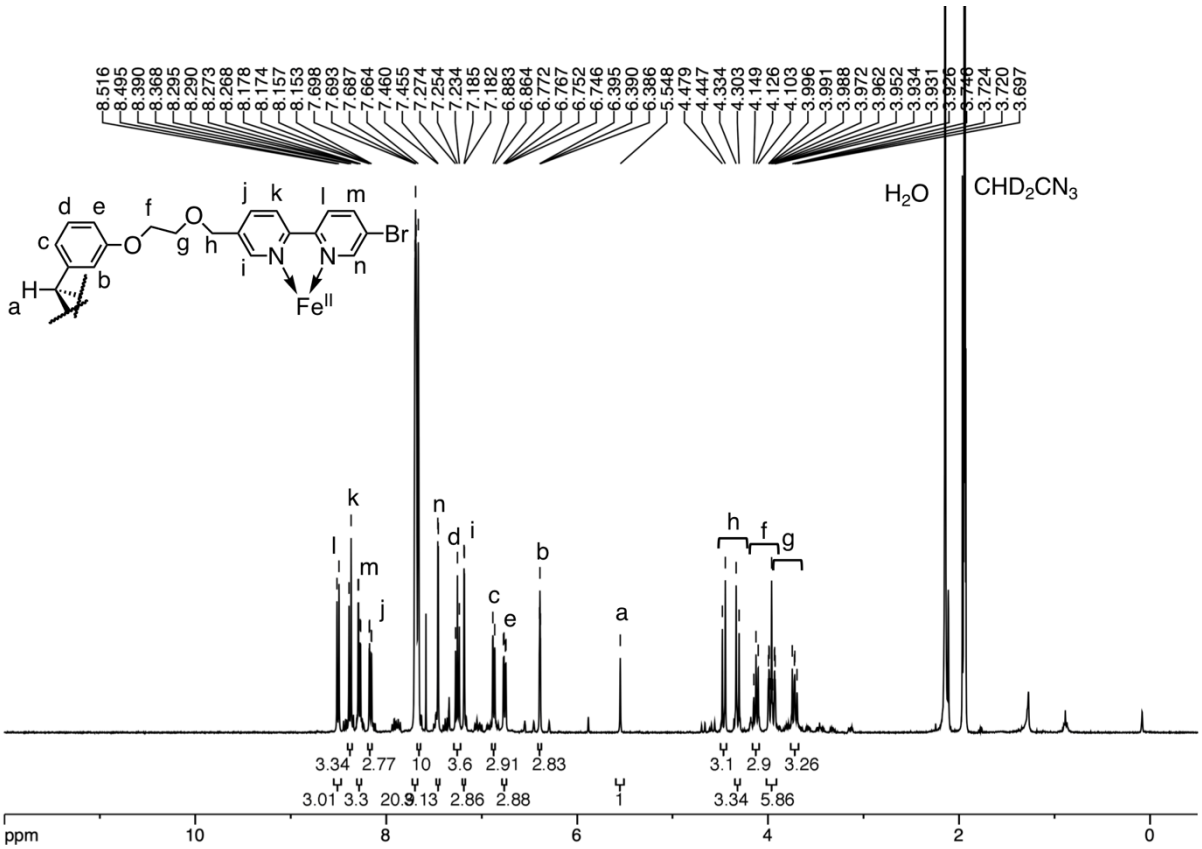


Figure S19. ^{1}H NMR spectrum of [**1a**Fe](TFPB)$_2$ (600 MHz, CD_3CN).

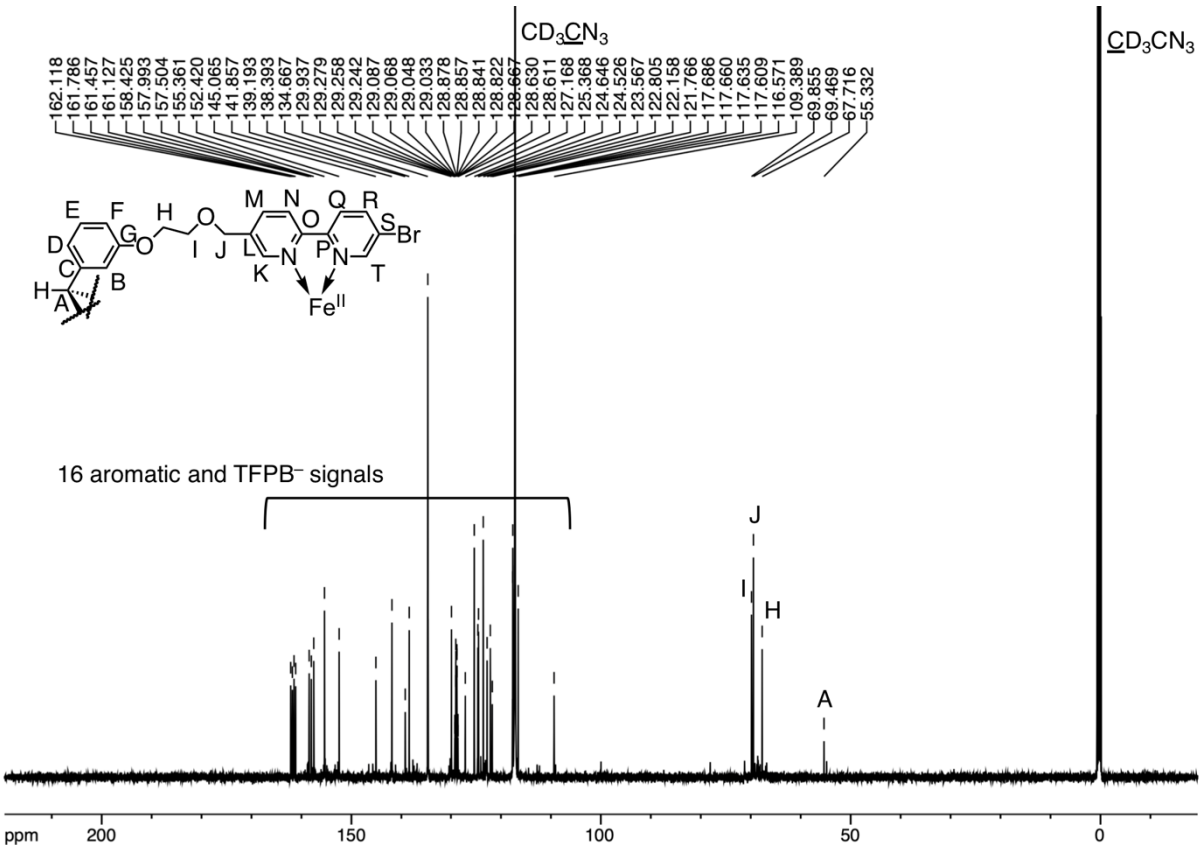


Figure S20. ^{13}C NMR spectrum of [**1a**Fe](TFPB)$_2$ (151 MHz, CD_3CN).

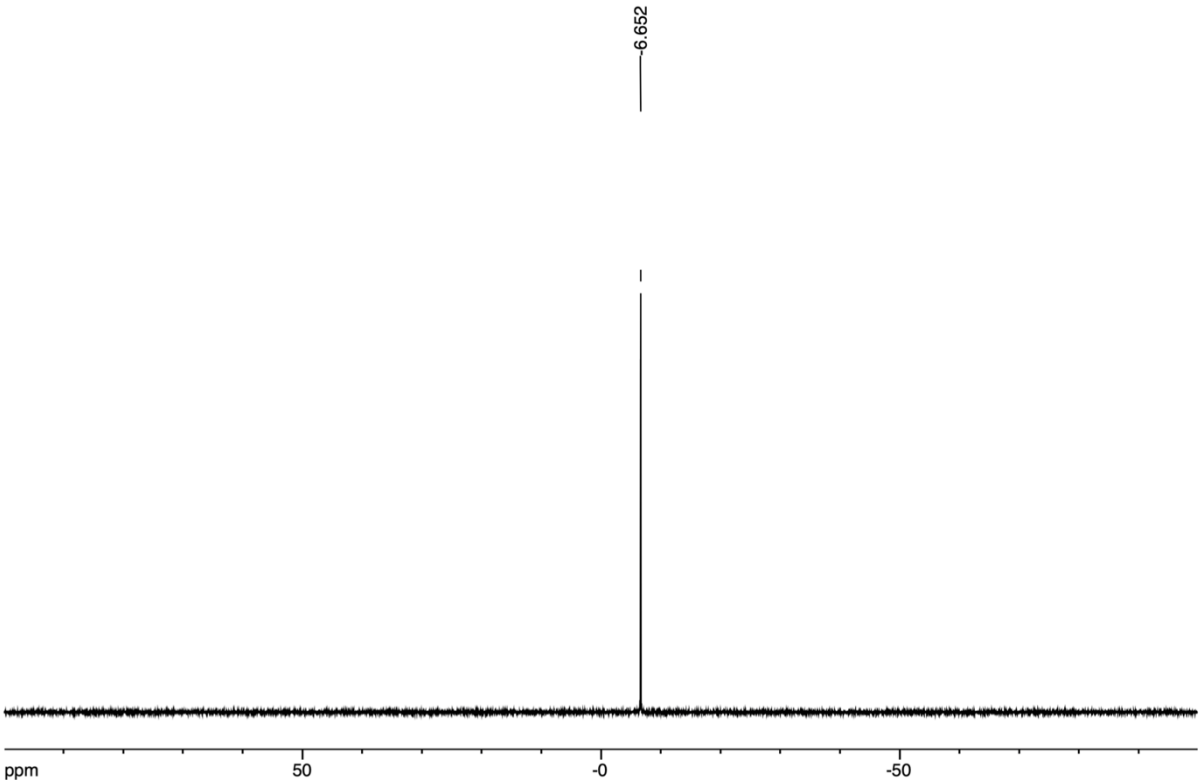


Figure S21. ^{11}B NMR spectrum of [**1a**Fe](TFPB)$_2$ (192 MHz, CD_3CN).

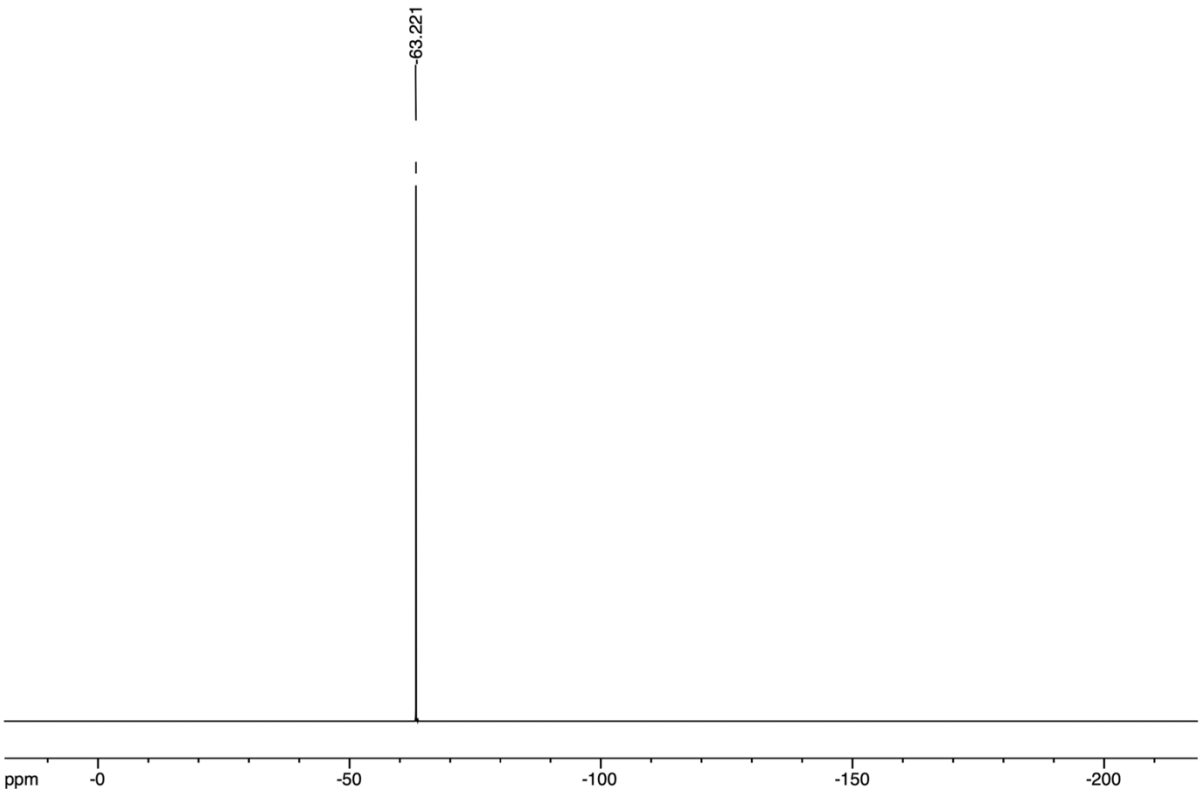


Figure S22. ^{19}F NMR spectrum of [**1a**Fe](TFPB)$_2$ (376 MHz, CD_3CN).

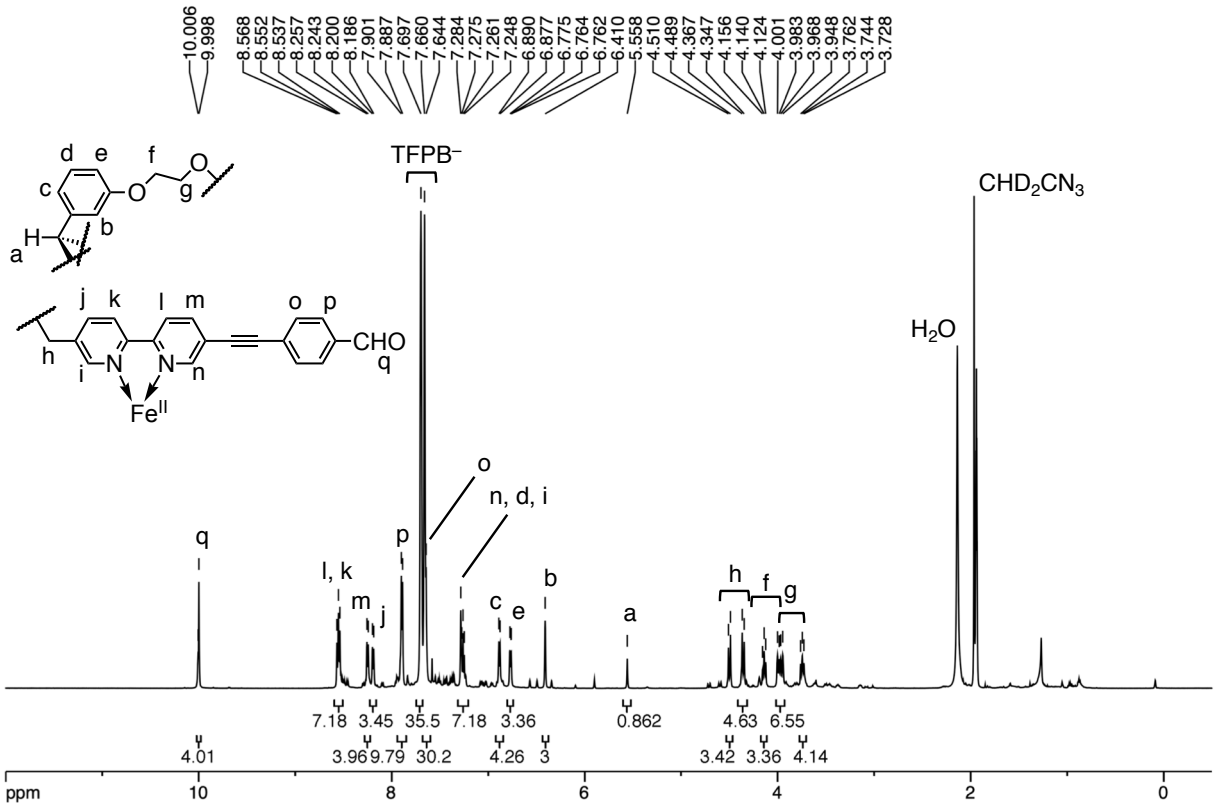


Figure S23. ^{1}H NMR spectrum of [**1b**Fe](TFPB)$_2$ (600 MHz, CD_3CN).

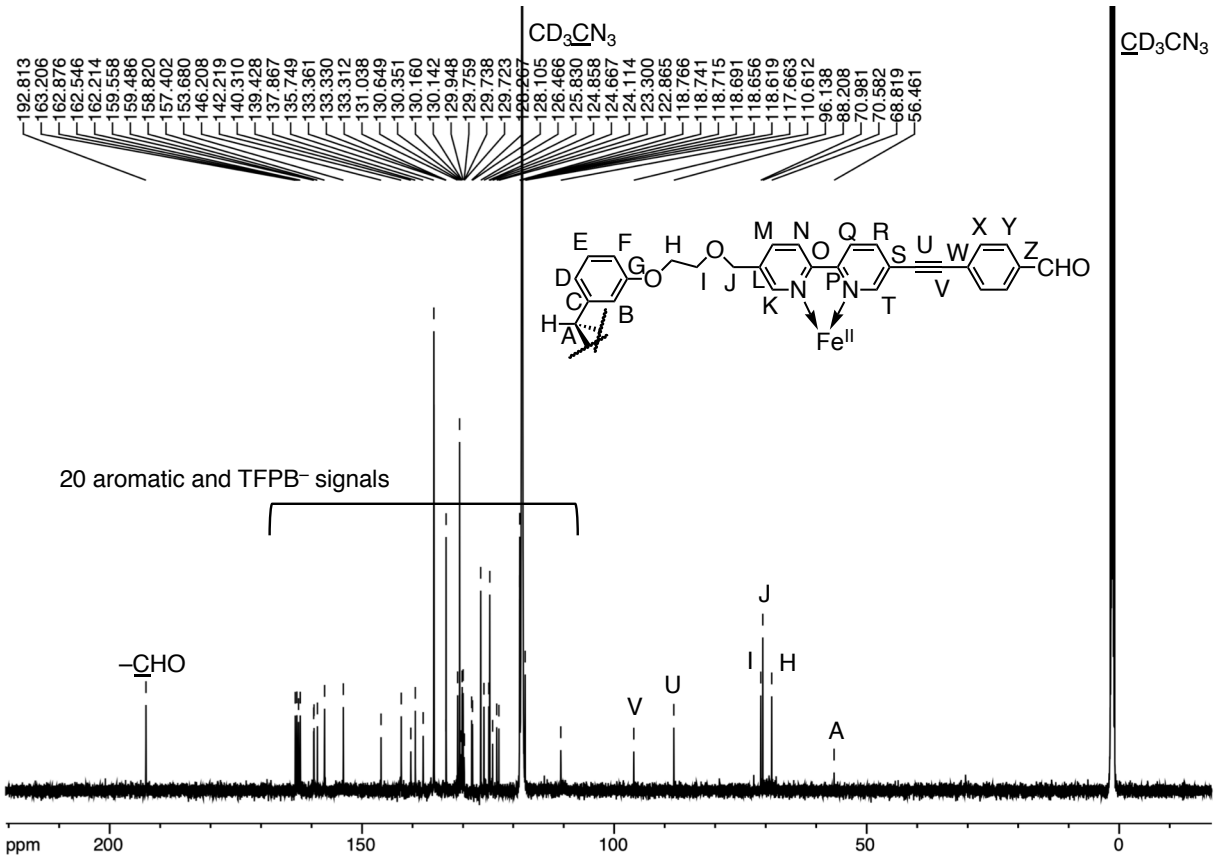


Figure S24. ^{13}C NMR spectrum of [**1b**Fe](TFPB)$_2$ (151 MHz, CD_3CN).

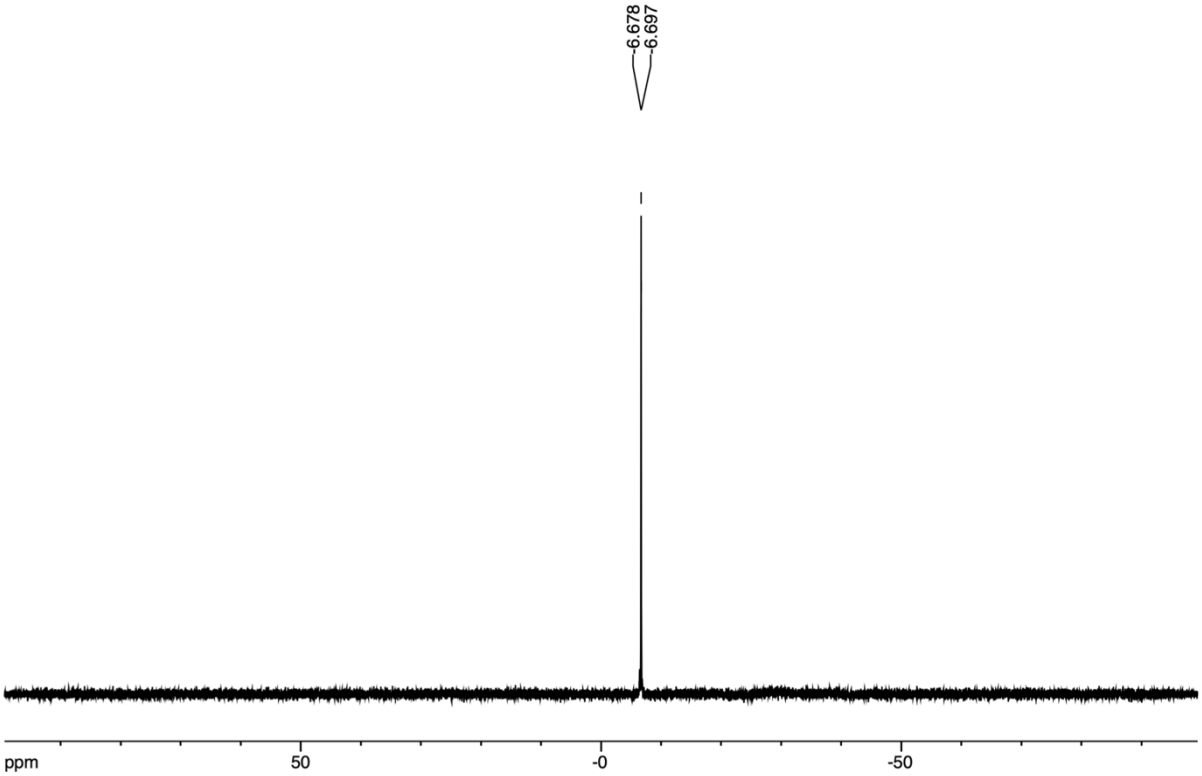


Figure S25. ^{11}B NMR spectrum of [**1b**Fe](TFPB)$_2$ (192 MHz, CD_3CN).

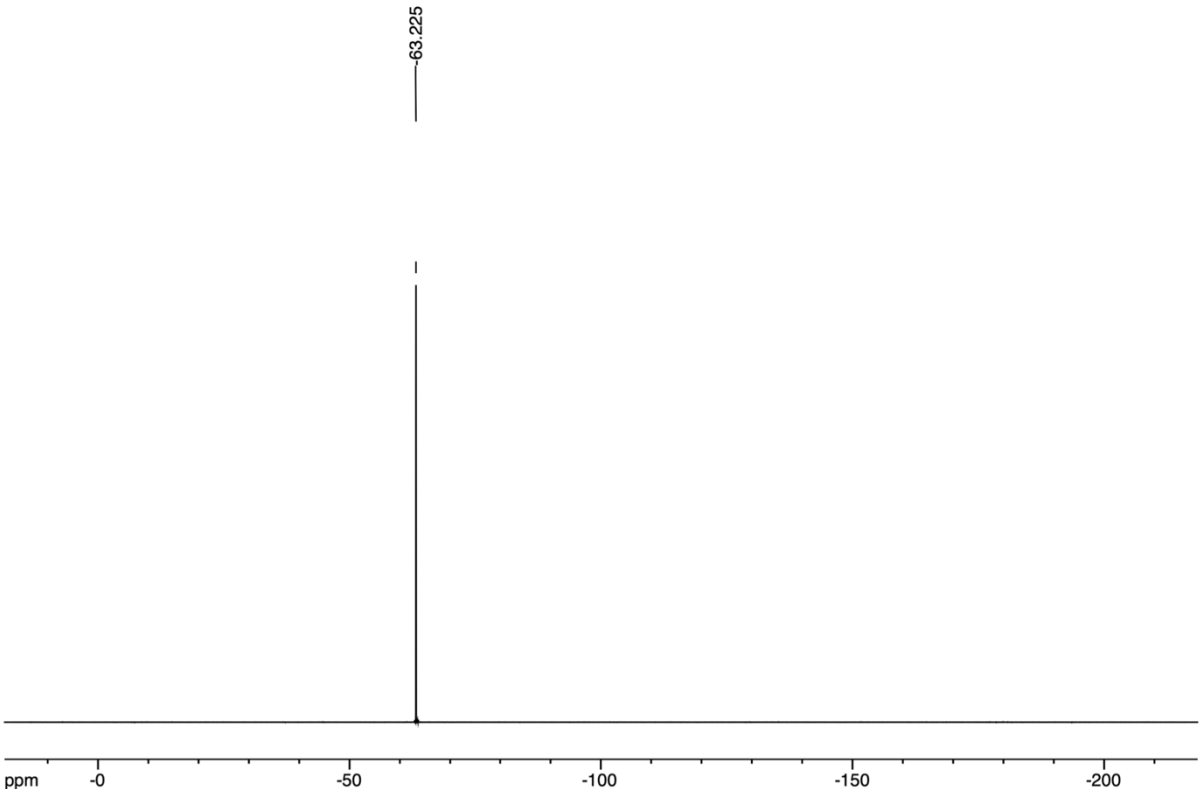


Figure S26. ^{19}F NMR spectrum of [**1b**Fe](TFPB)$_2$ (376 MHz, CD_3CN).

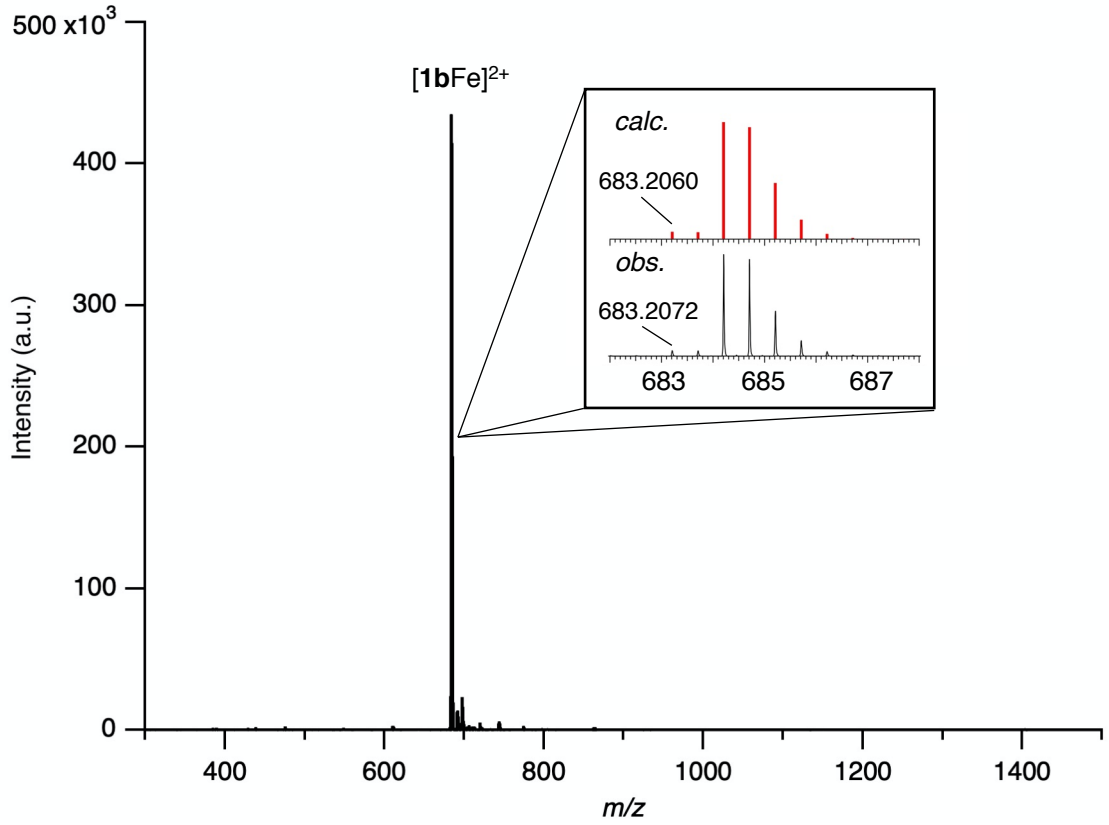


Figure S27. ESI mass spectrum of [**1b**Fe](TFPB)$_2$ (solv. CD_3CN).

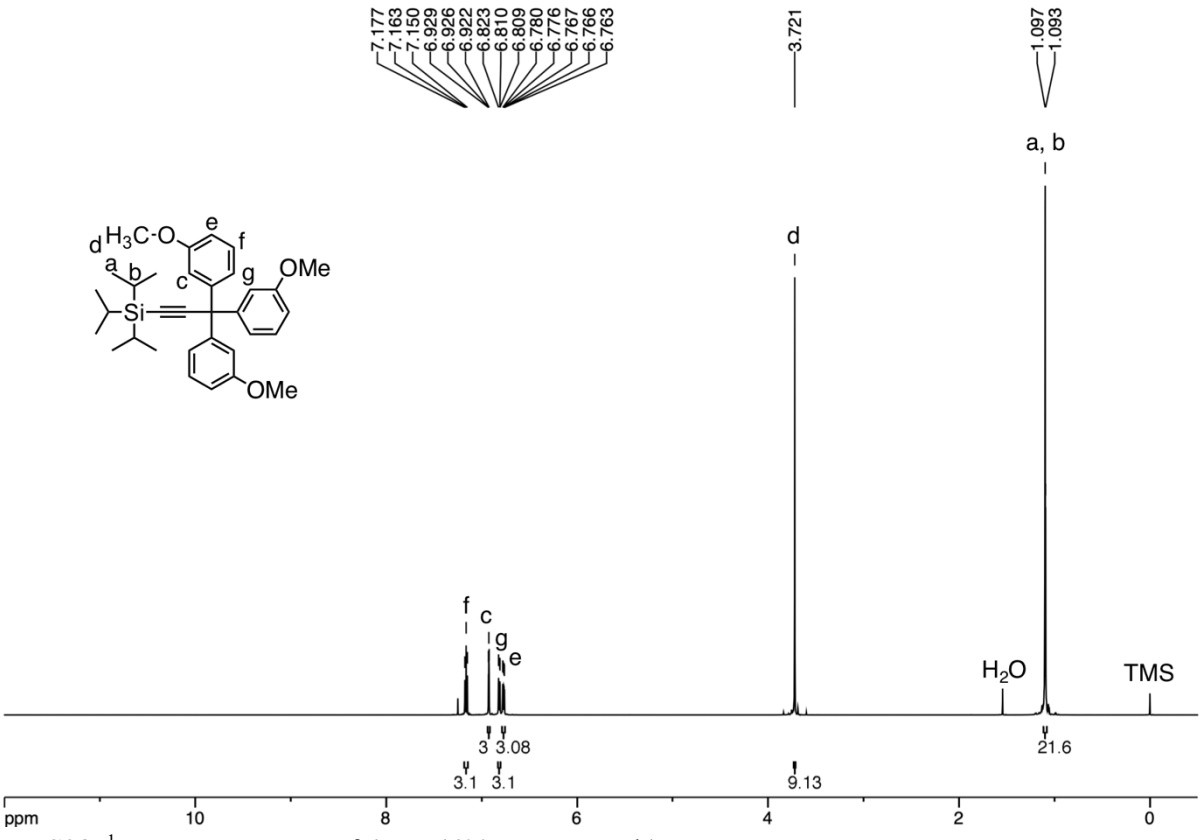


Figure S28. ^{1}H NMR spectrum of **4-TE** (600 MHz, $CDCl_3$).

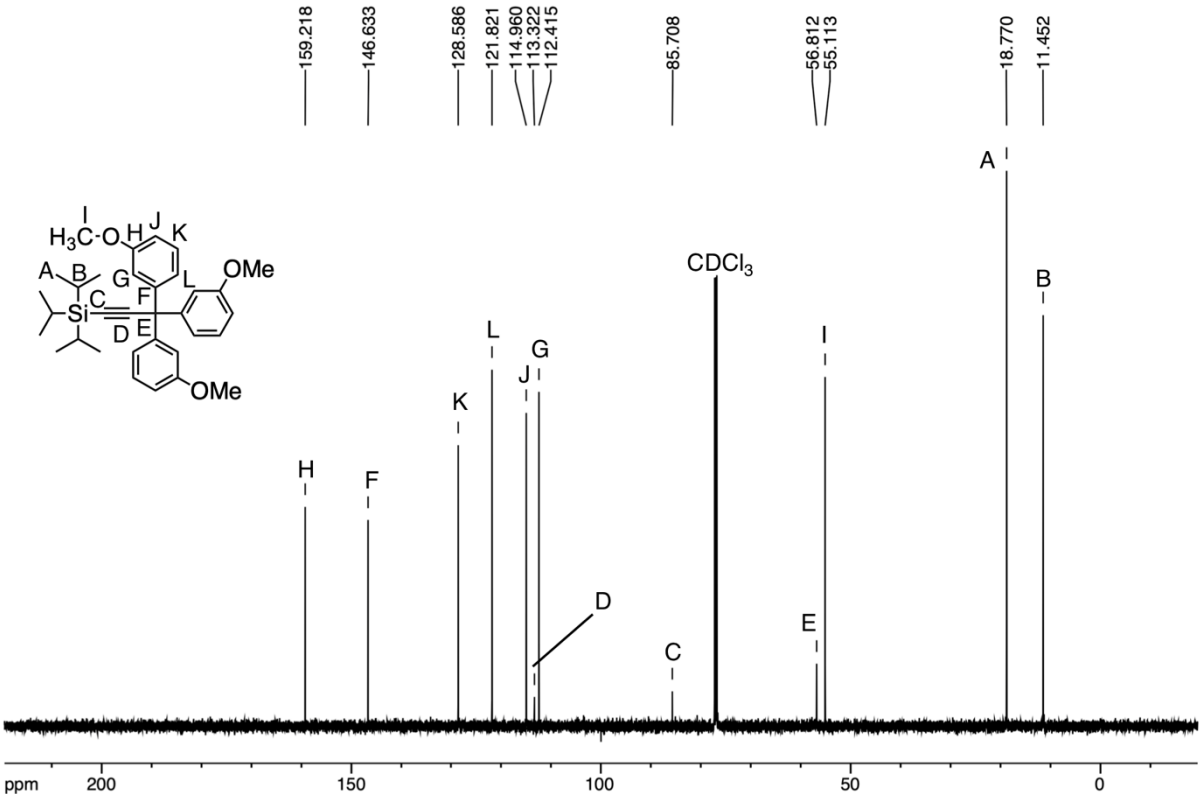


Figure S29. ^{13}C NMR spectrum of **4-TE** (151 MHz, $CDCl_3$).

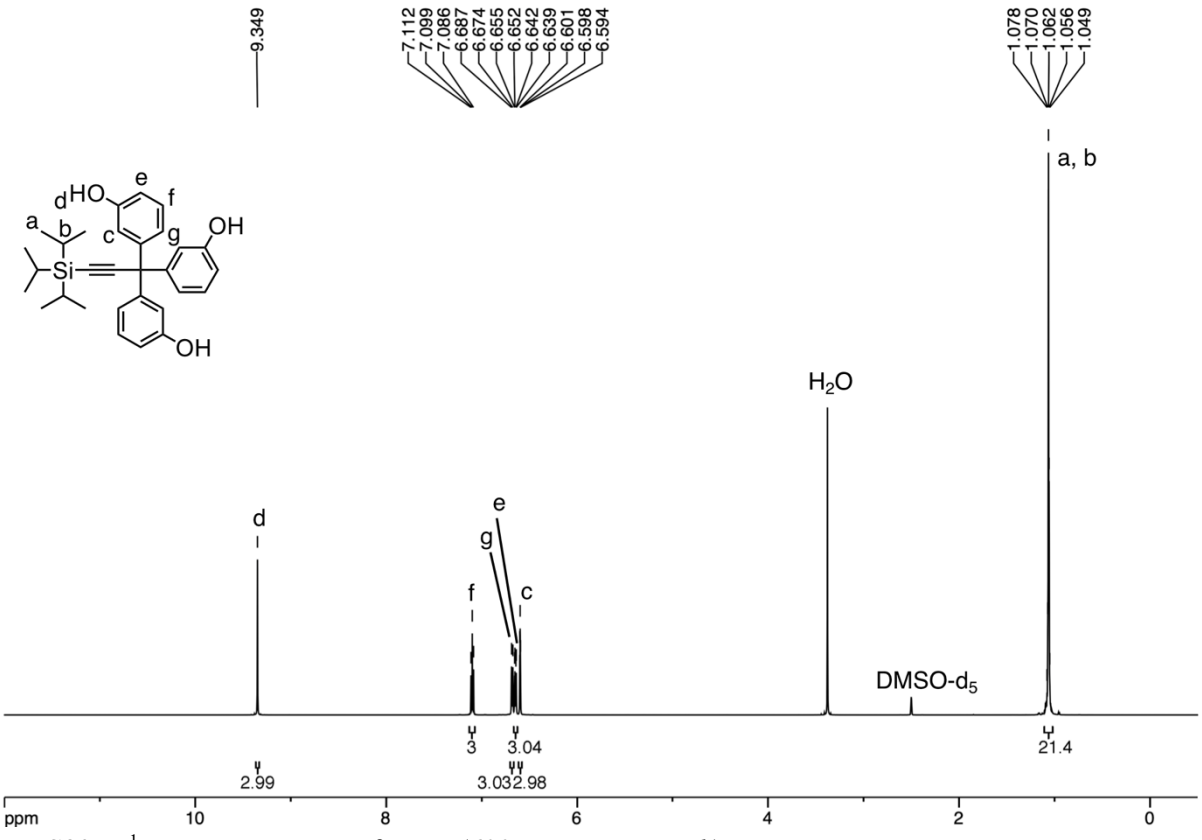


Figure S30. ^{1}H NMR spectrum of **5-TE** (600 MHz, DMSO-d_6).

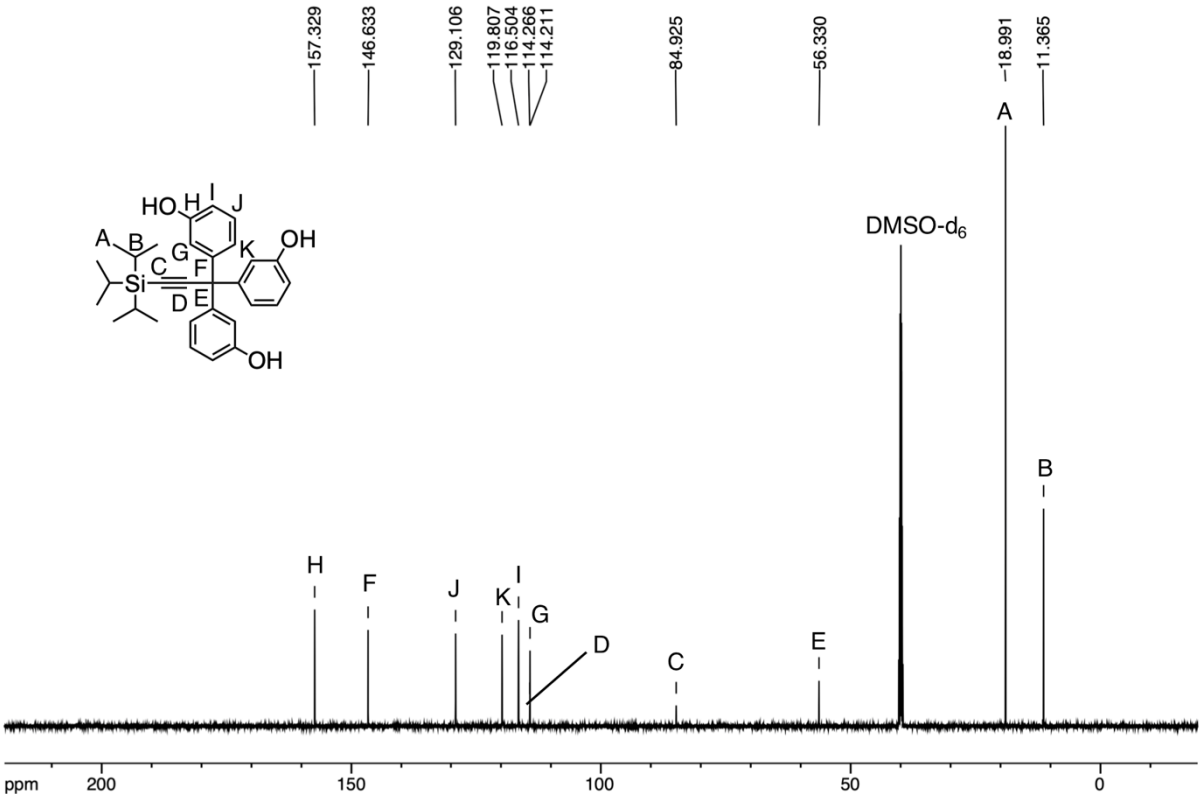


Figure S31. ^{13}C NMR spectrum of **5-TE** (151 MHz, DMSO-d_6).

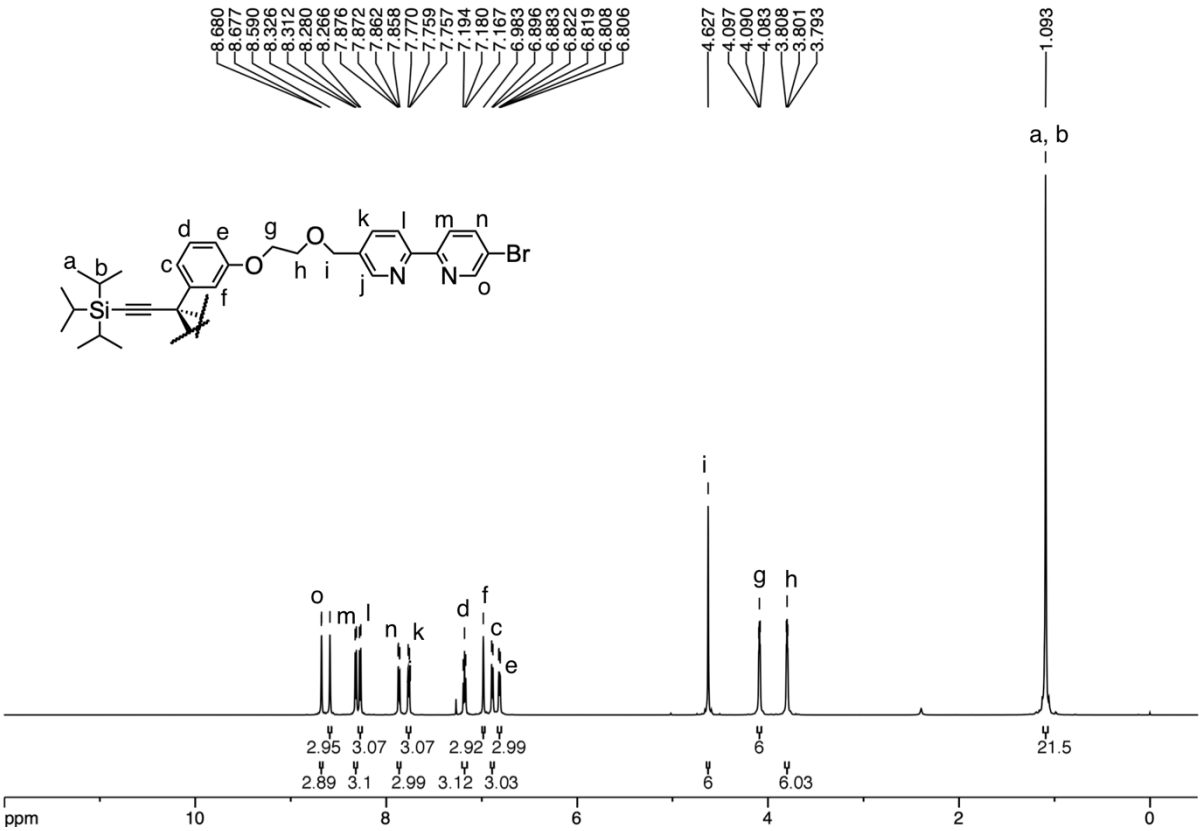


Figure S32. ^{1}H NMR spectrum of **2a** (600 MHz, $CDCl_3$).

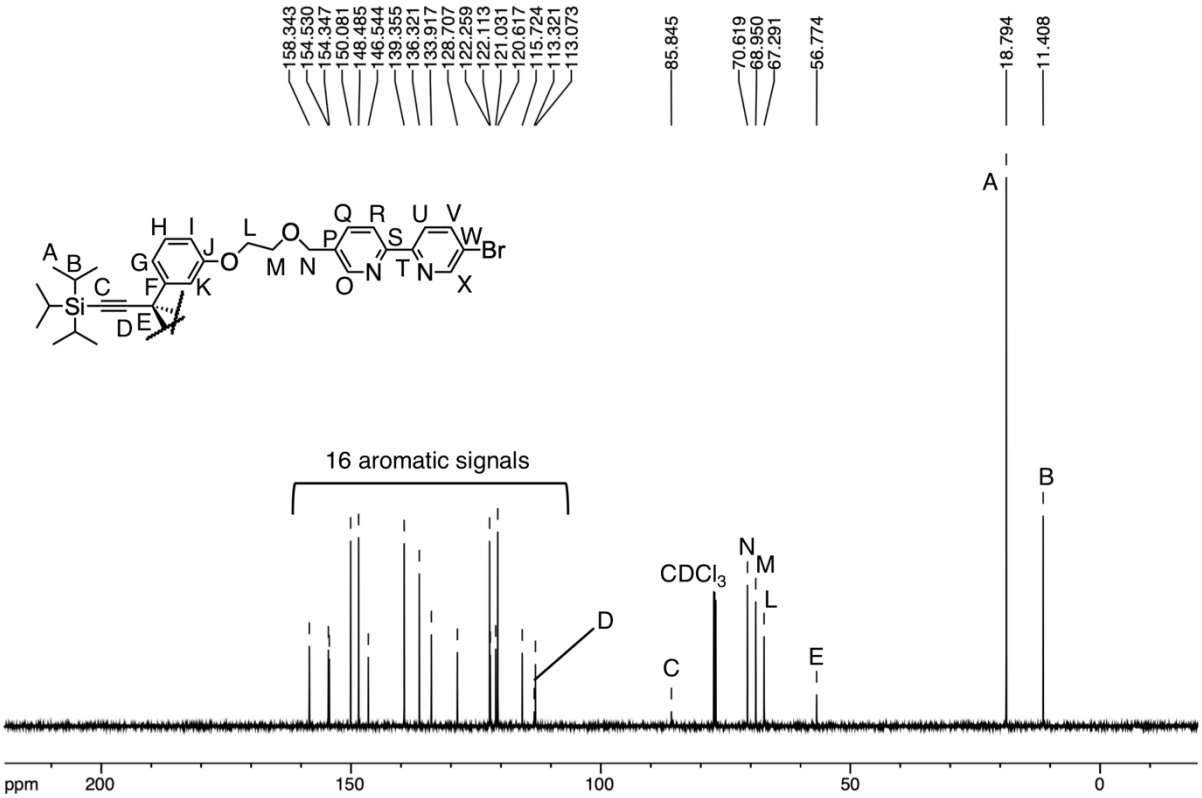


Figure S33. ^{13}C NMR spectrum of **2a** (151 MHz, $CDCl_3$).

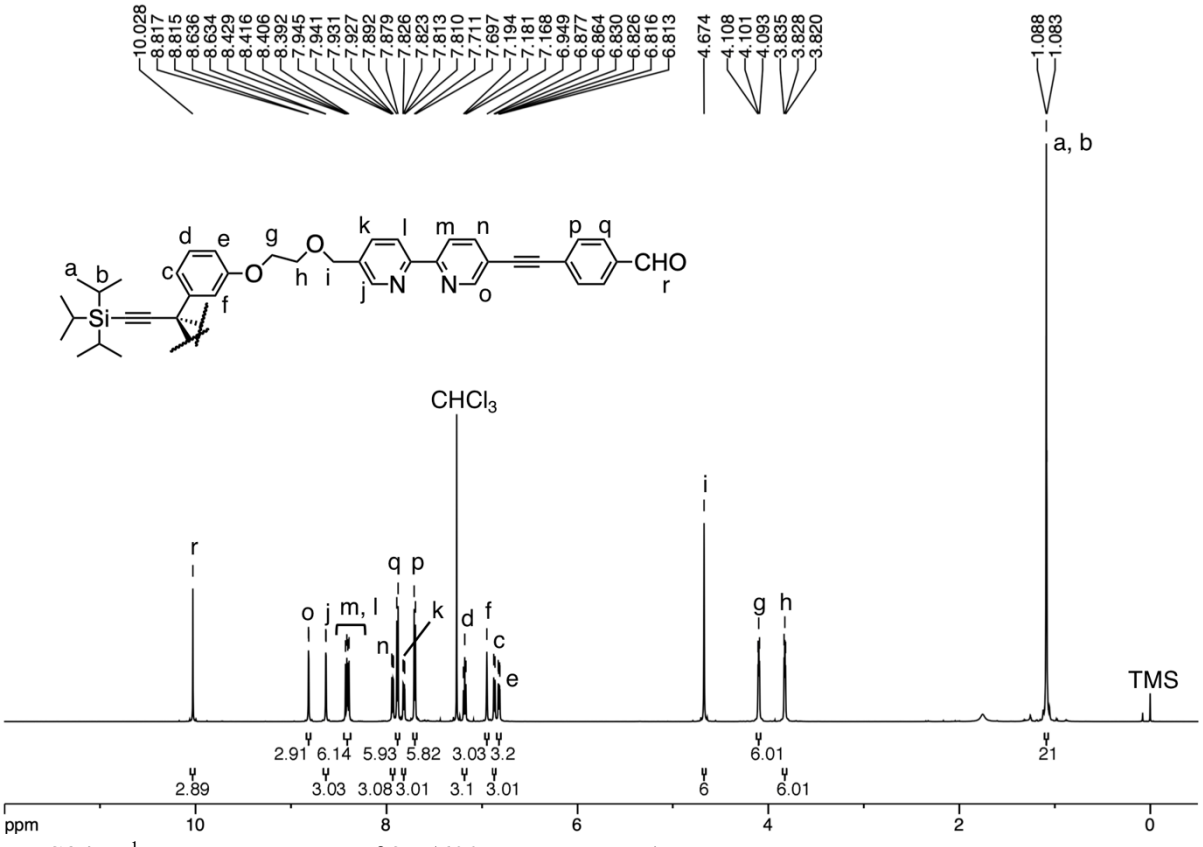


Figure S34. ^{1}H NMR spectrum of **2b** (600 MHz, CD_3CN).

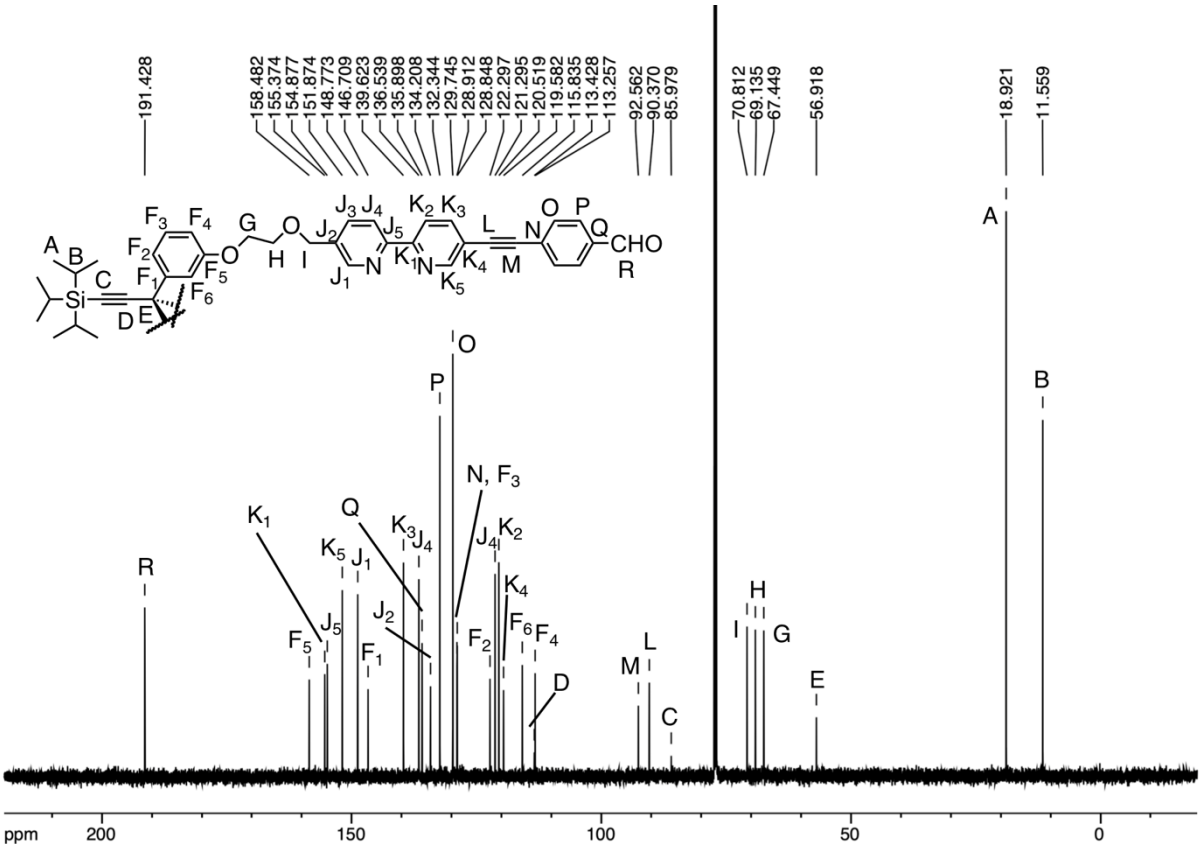


Figure S35. ^{13}C NMR spectrum of **2b** (151 MHz, CD_3CN).

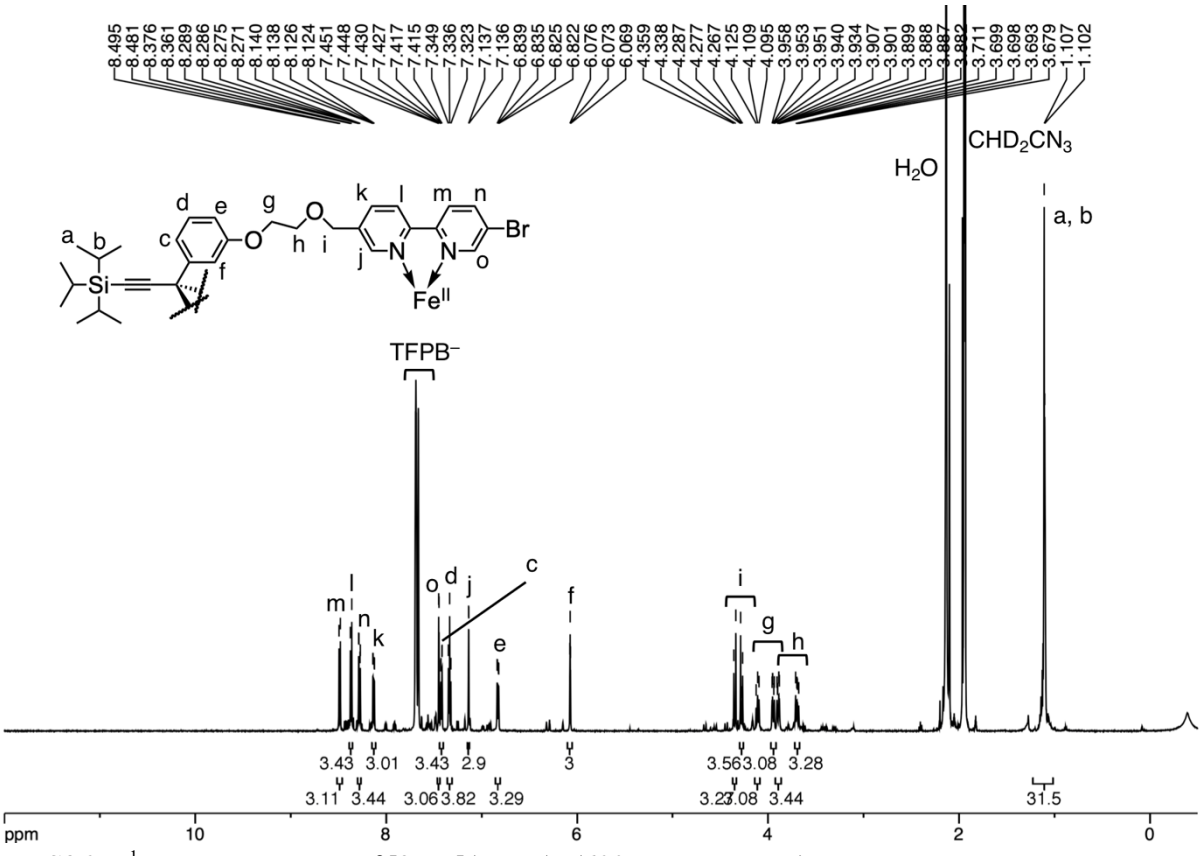


Figure S36. ^{1}H NMR spectrum of [**2a**Fe](TFPB)$_2$ (600 MHz, CD_3CN).

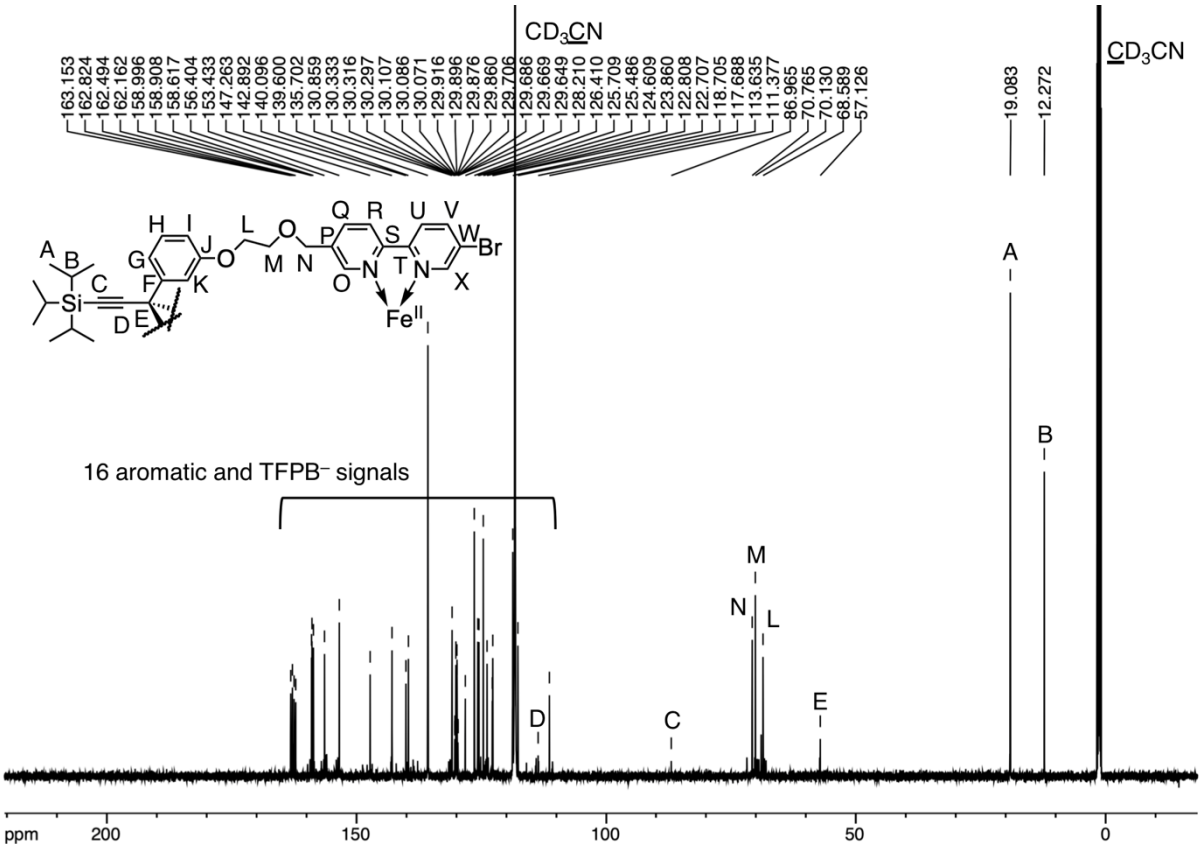


Figure S37. ^{13}C NMR spectrum of [**2a**Fe](TFPB)$_2$ (151 MHz, CD_3CN).

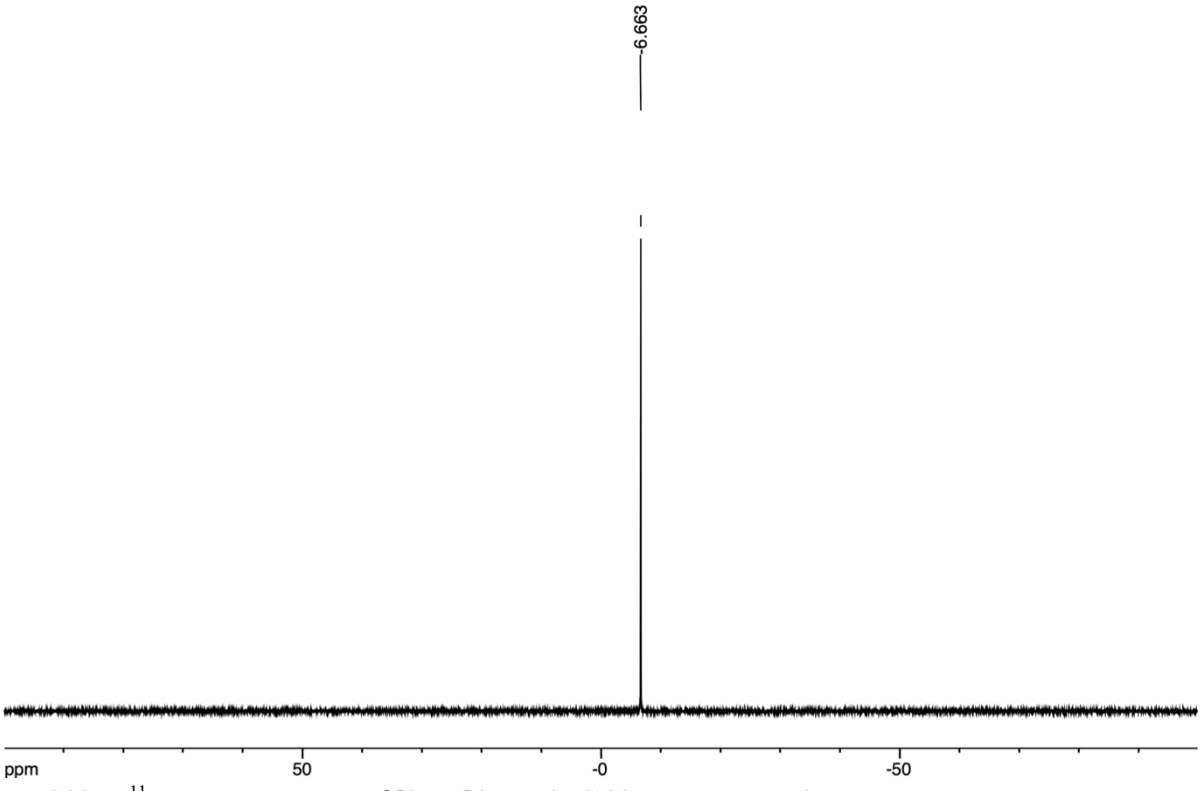


Figure S38. ^{11}B NMR spectrum of [**2a**Fe](TFPB)$_2$ (192 MHz, CD_3CN).

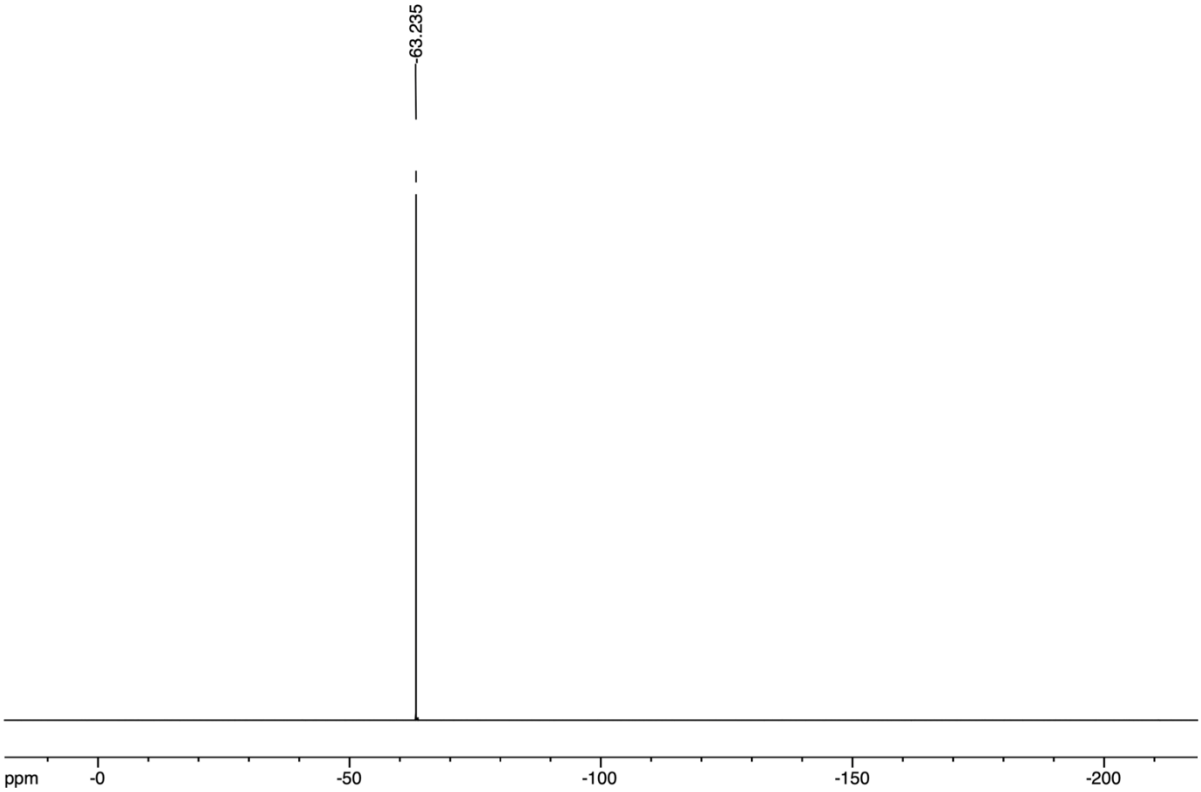


Figure S39. ^{19}F NMR spectrum of [**2a**Fe](TFPB)$_2$ (376 MHz, CD_3CN).

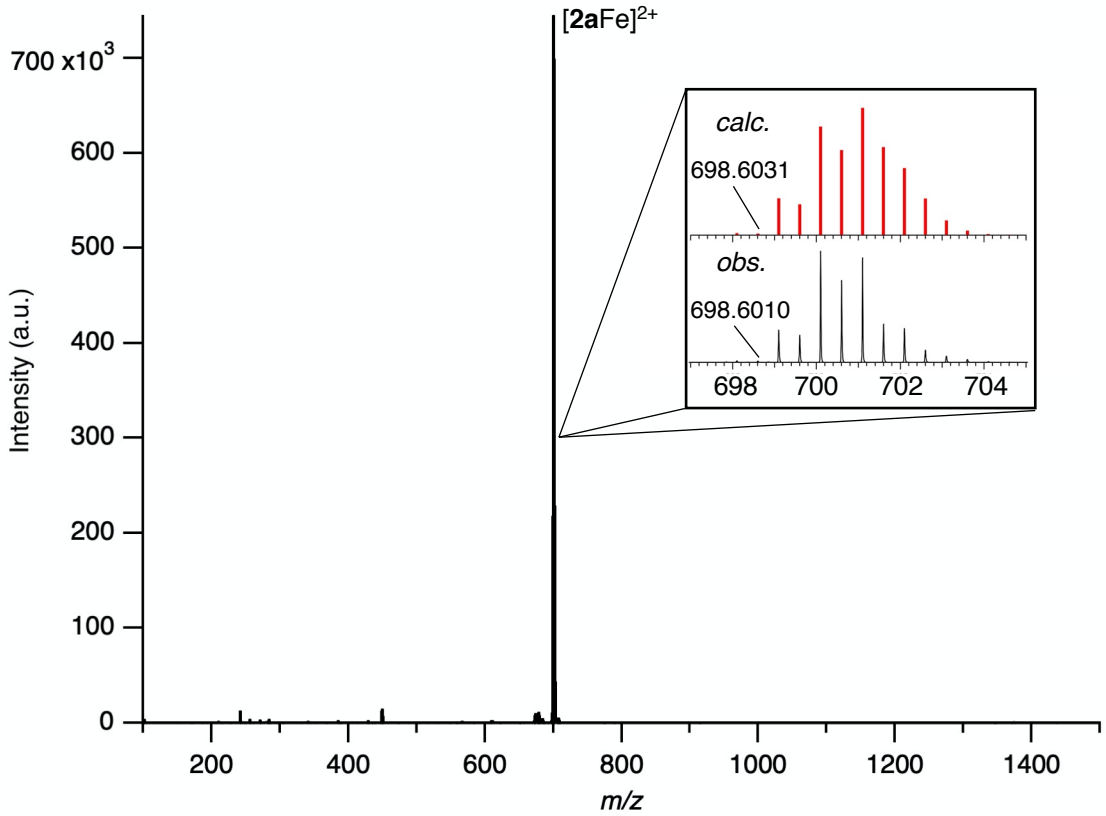


Figure S40. ESI mass spectrum of [**2a**Fe](TFPB)$_2$ (solv. CH_3CN).

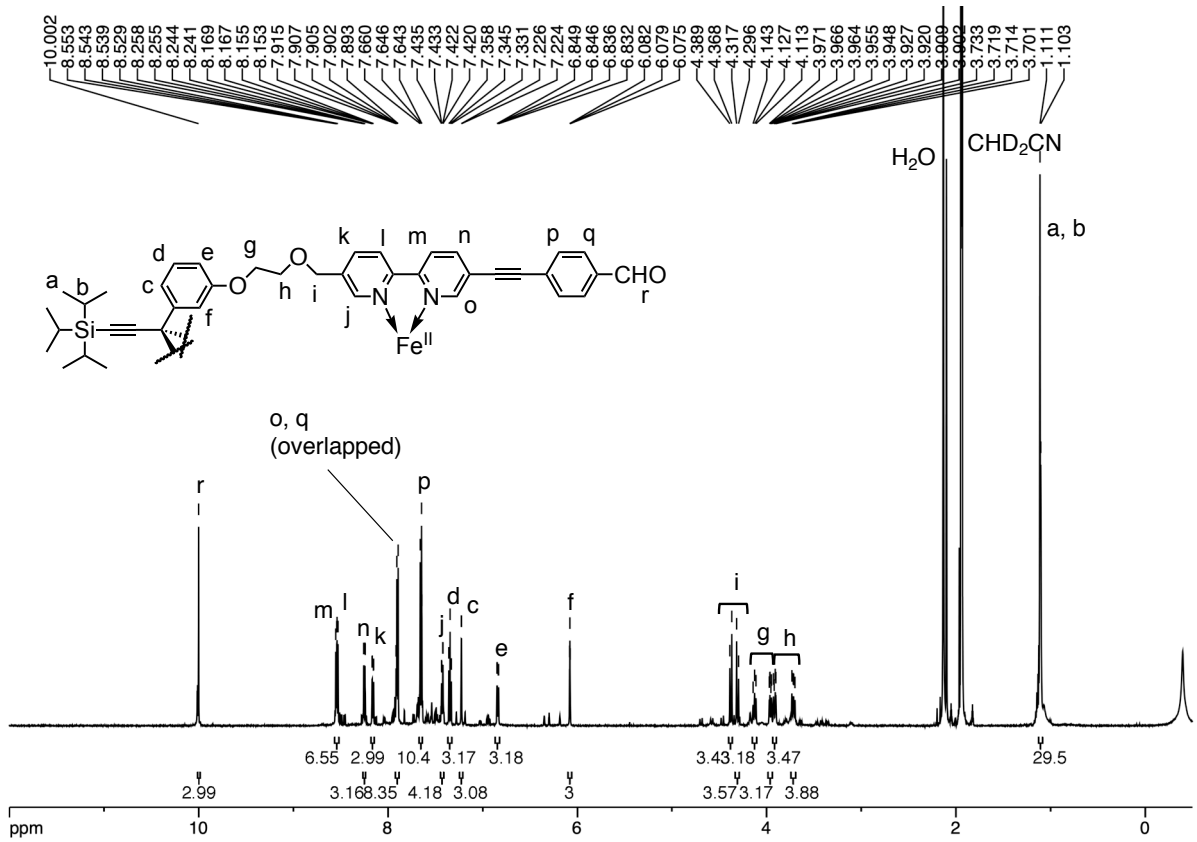


Figure S41. ^{1}H NMR spectrum of [**2b**Fe](PF$_6$)$_2$ (600 MHz, CD$_3$CN).

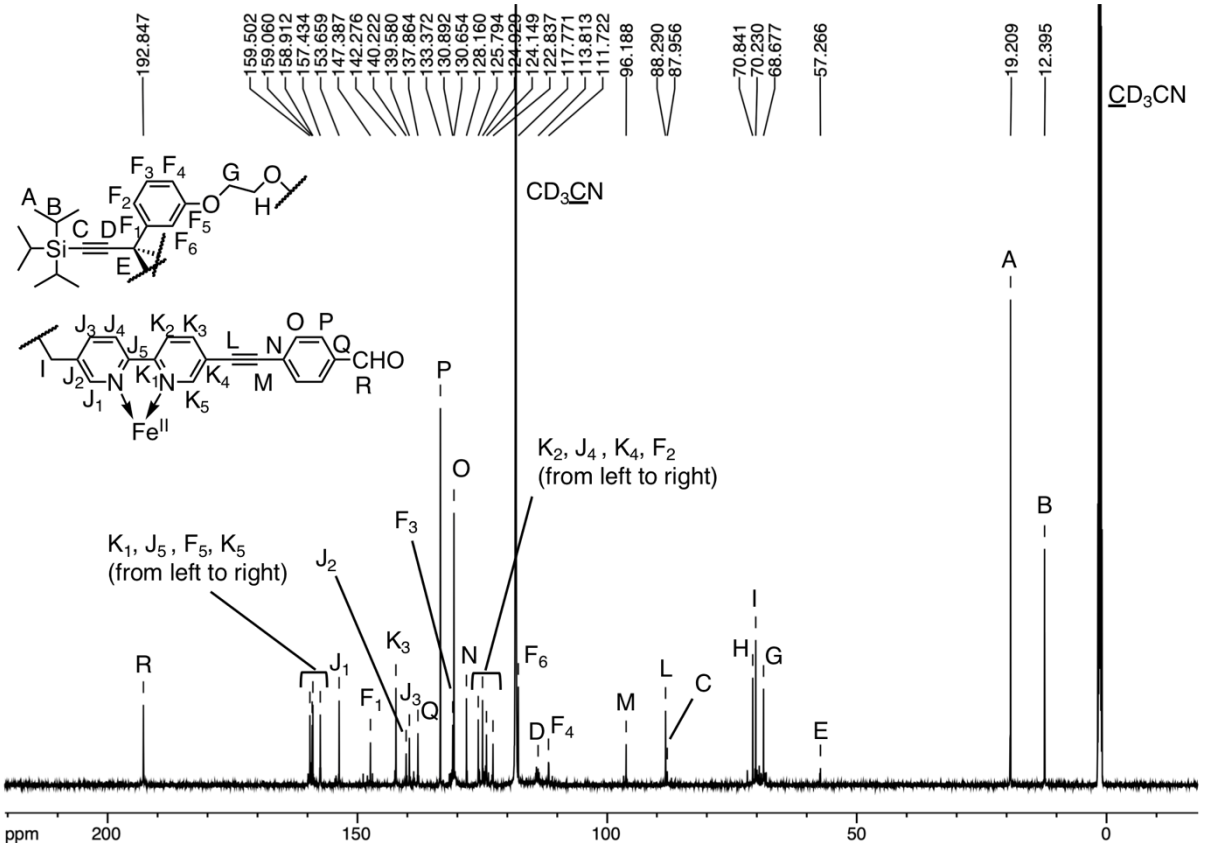


Figure S42. ^{13}C NMR spectrum of [**2b**Fe](PF$_6$)$_2$ (151 MHz, CD$_3$CN).

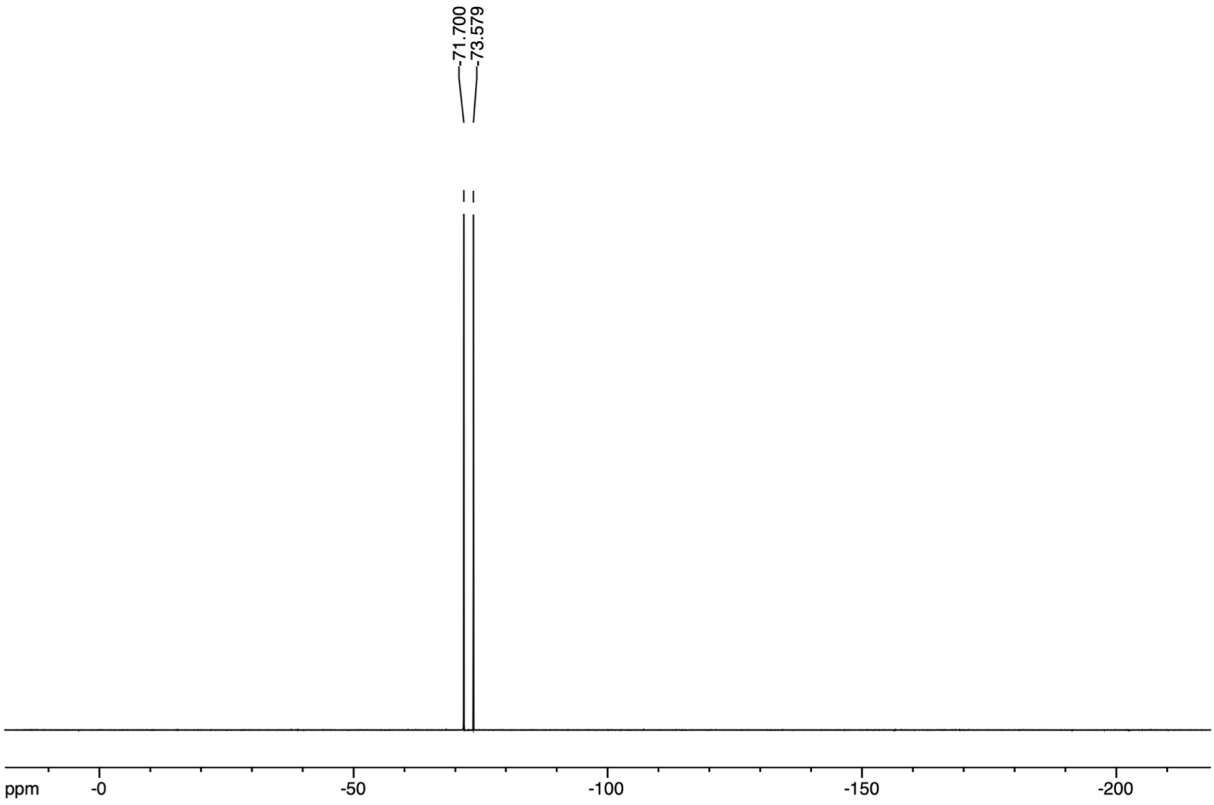


Figure S43. ^{19}F NMR spectrum of [**2b**Fe]$(PF_6)_2$ (376 MHz, CD_3CN).

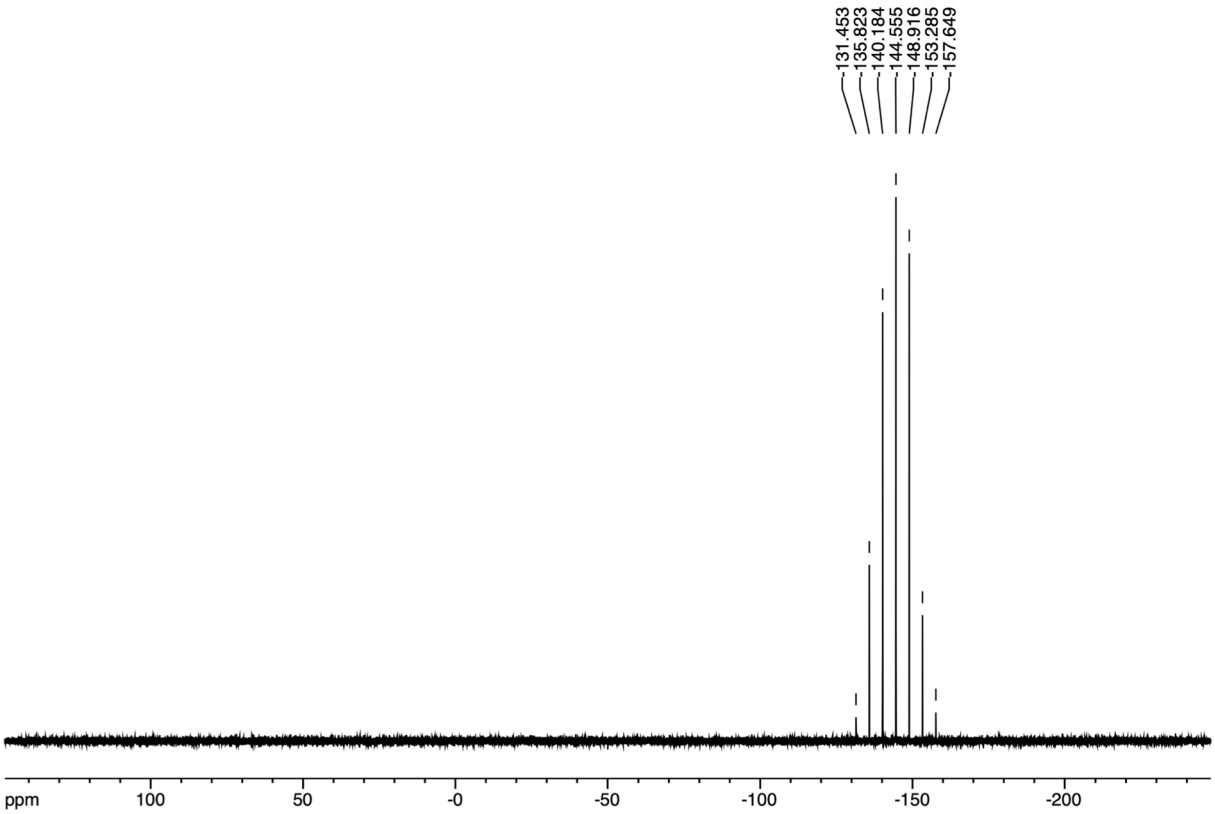


Figure S44. ^{31}P NMR spectrum of [**2b**Fe]$(PF_6)_2$ (243 MHz, CD_3CN).

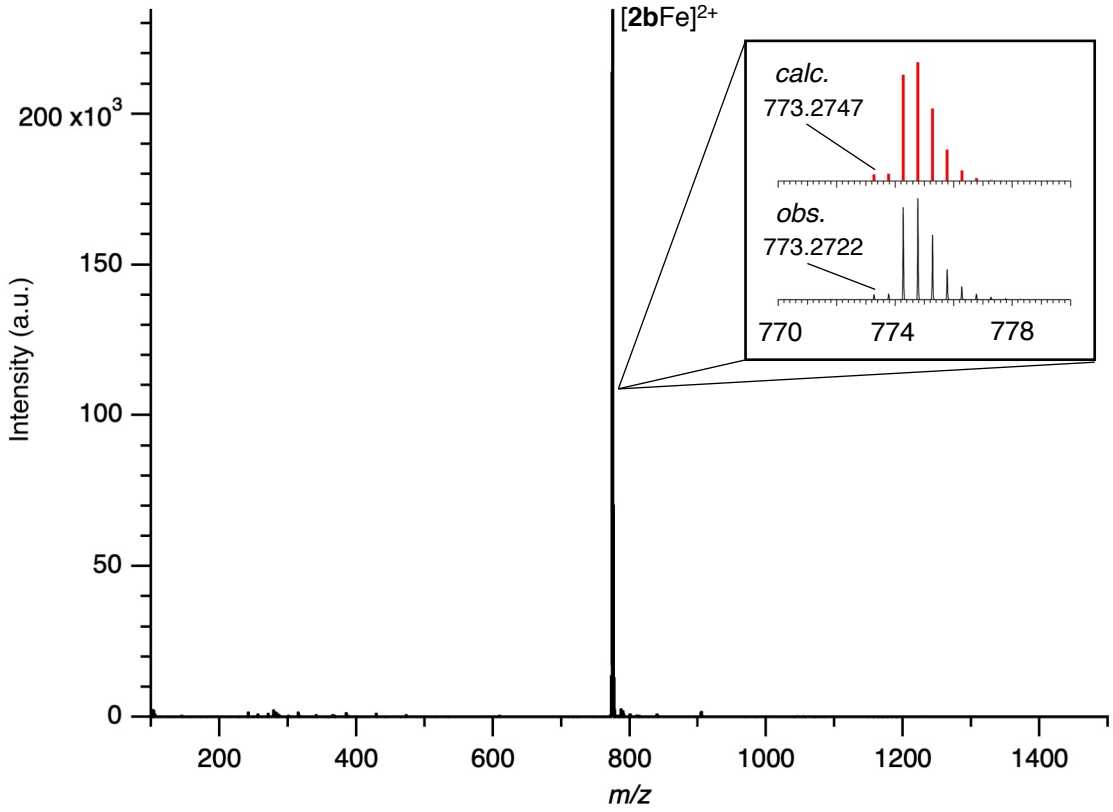


Figure S45. ESI mass spectrum of [**2b**Fe]$(PF_6)_2$ (solv. CH_3CN).

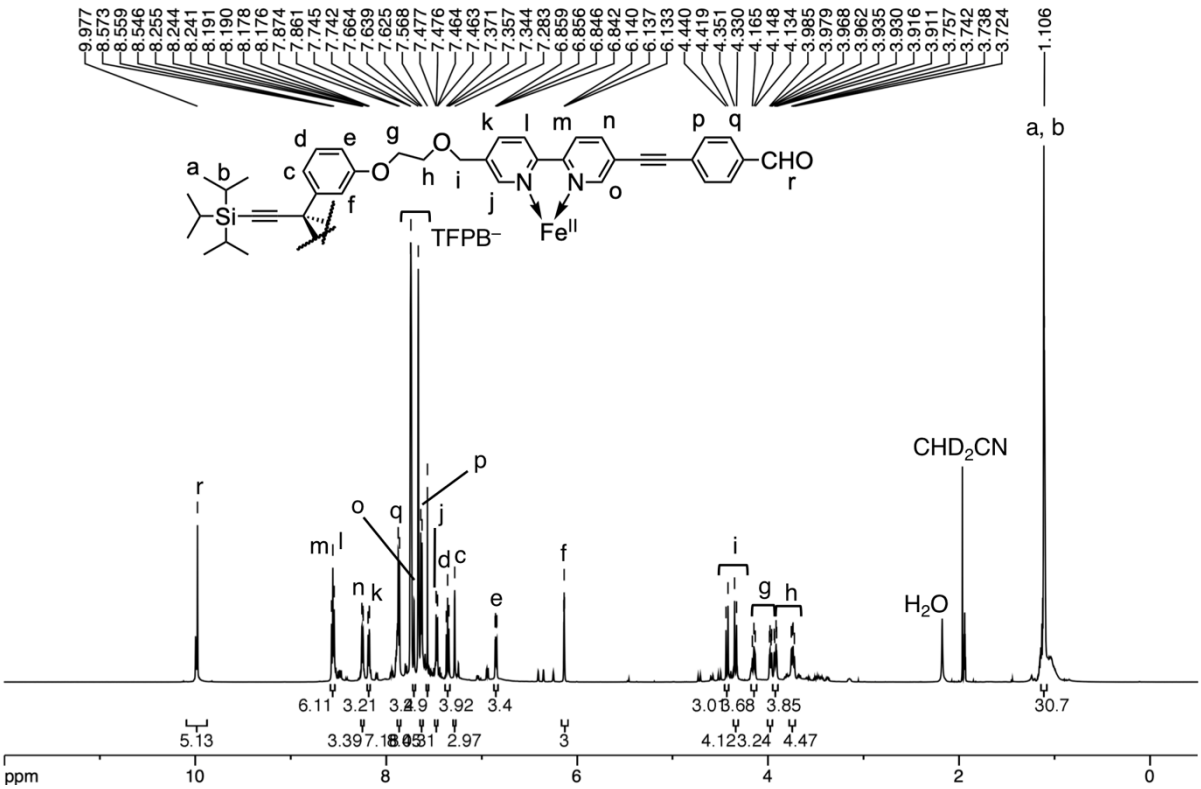


Figure S46. ^{1}H NMR spectrum of [**2b**Fe]$(TFPB)_2$ (600 MHz, CD_3CN).

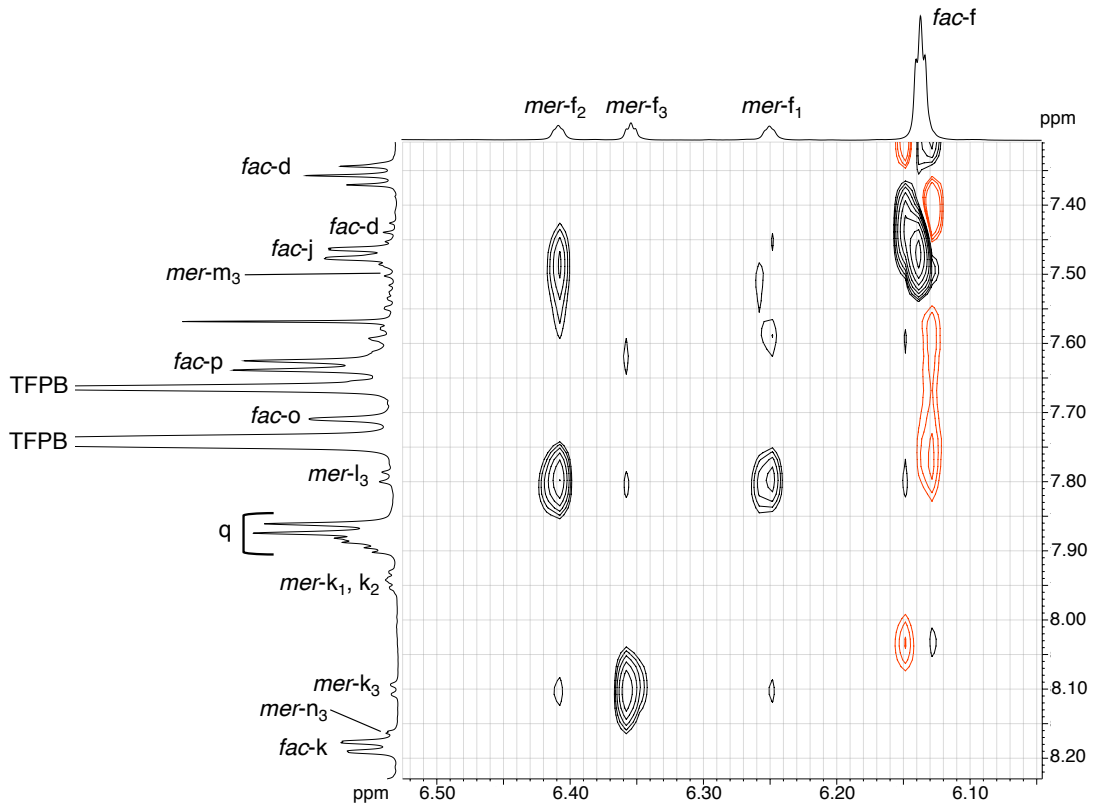


Figure S47. ^{1}H–^{1}H ROESY spectrum of [**2b**Fe](TFPB)$_2$ (600 MHz, CD_3CN. Signals of *mer*-isomer are numbered for each tripodal arm.).

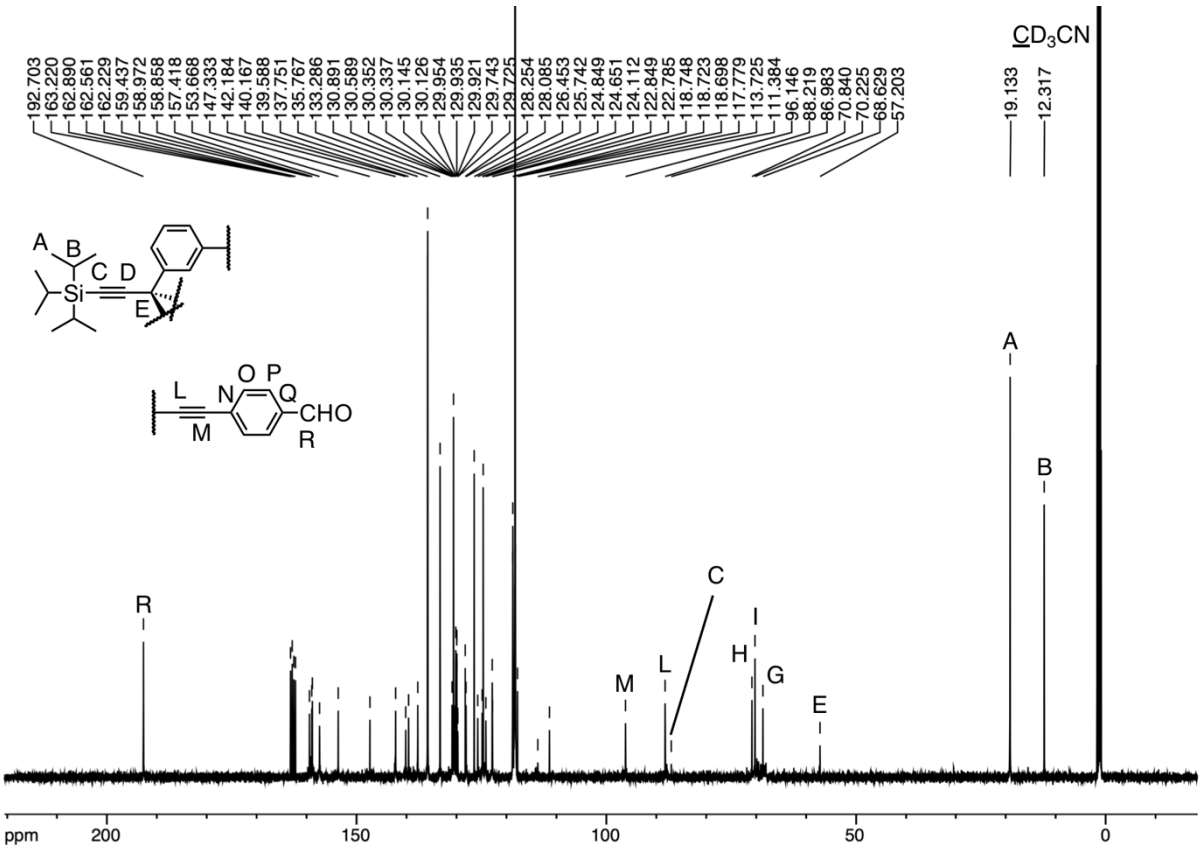


Figure S48. ^{13}C NMR spectrum of [**2b**Fe](TFPB)$_2$ (151 MHz, CD_3CN).

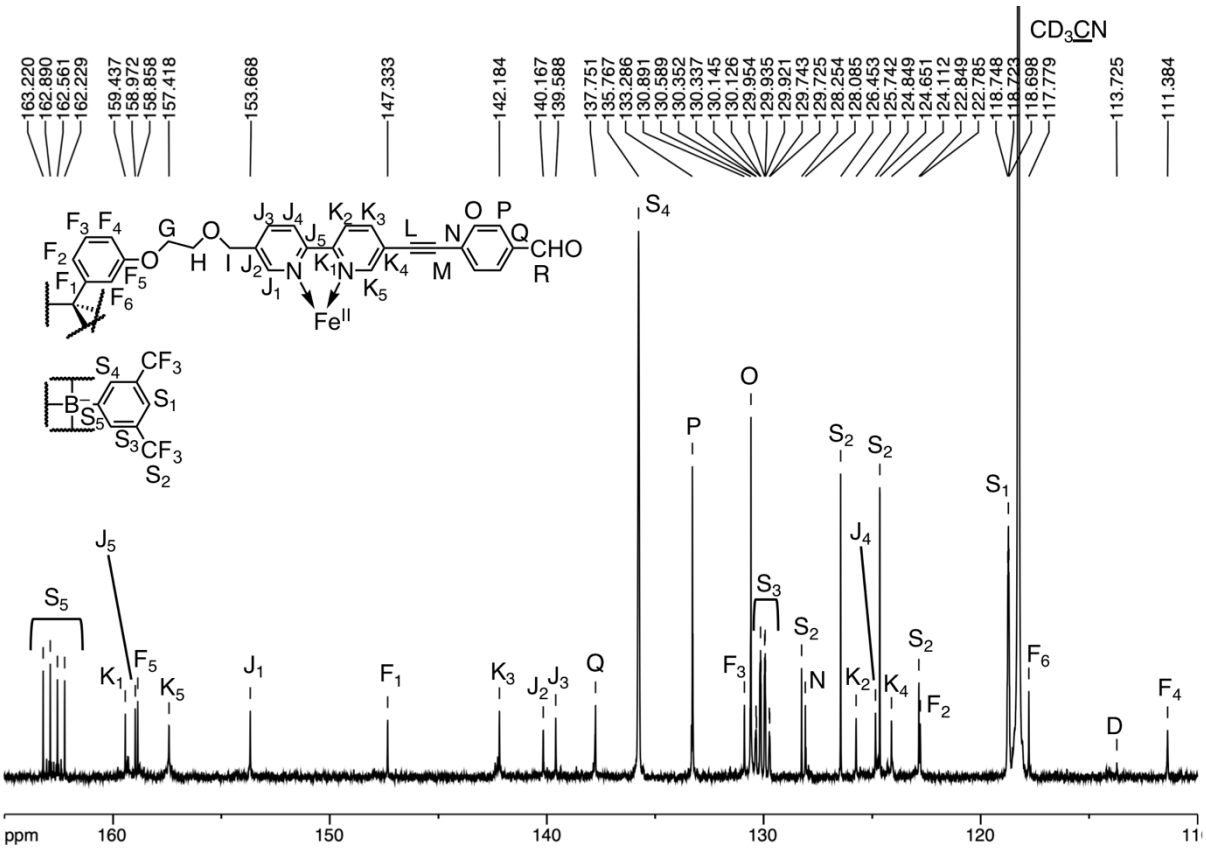


Figure S49. Enlarged ^{13}C NMR spectrum of [**2b**Fe](TFPB)$_2$ (151 MHz, CD_3CN, 165–110 ppm).

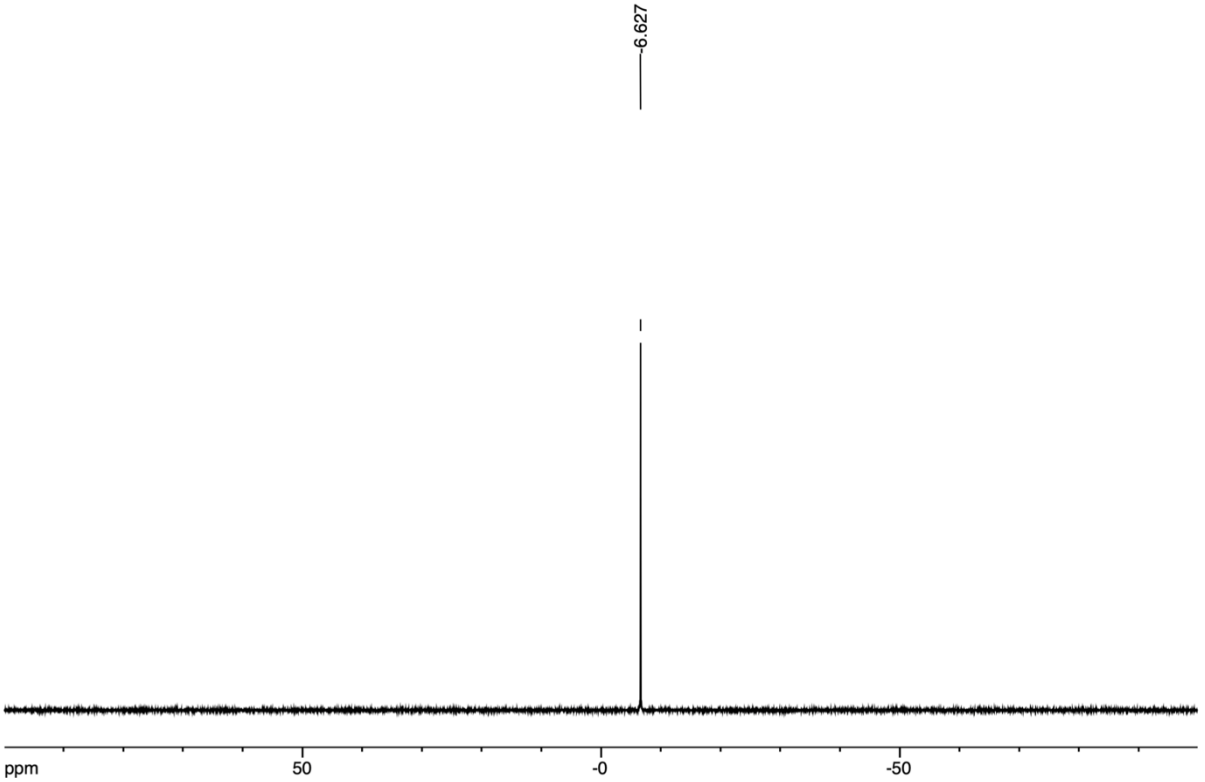


Figure S50. ^{11}B NMR spectrum of [**2b**Fe](TFPB)$_2$ (192 MHz, CD_3CN).

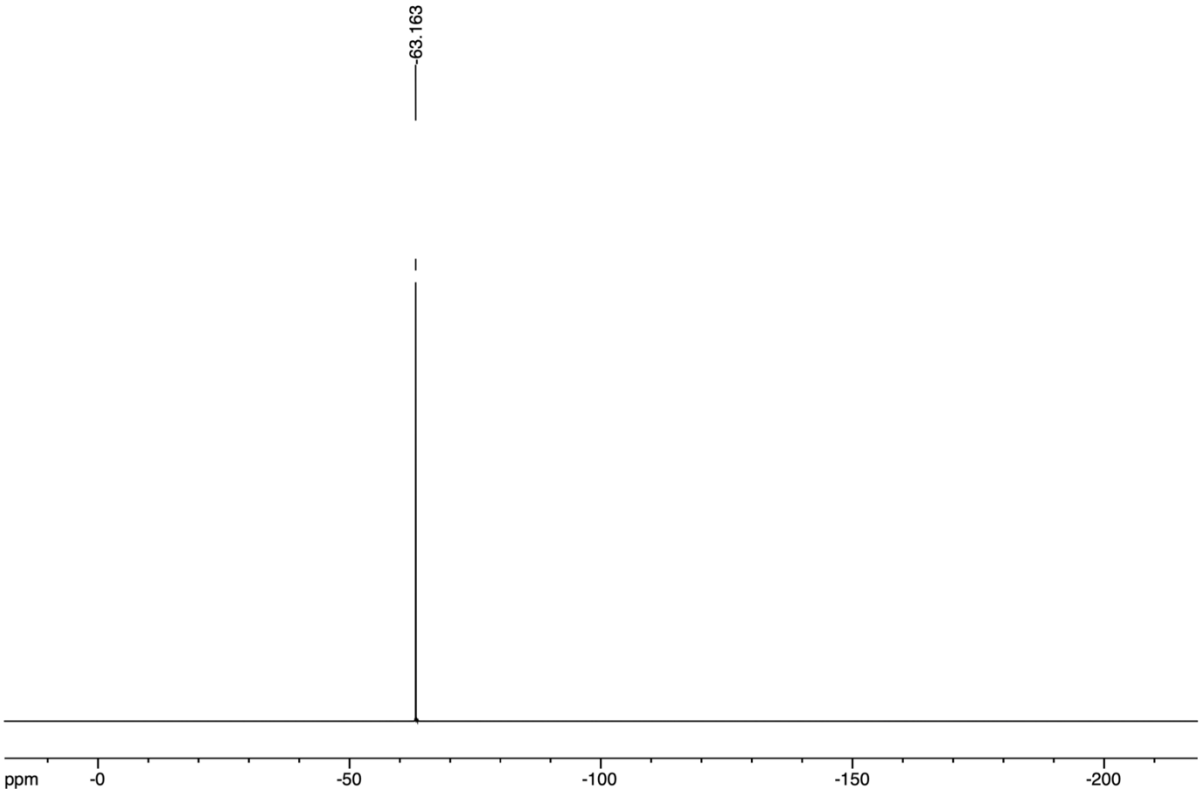


Figure S51. ^{19}F NMR spectrum of [**2b**Fe](TFPB)$_2$ (376 MHz, CD_3CN).

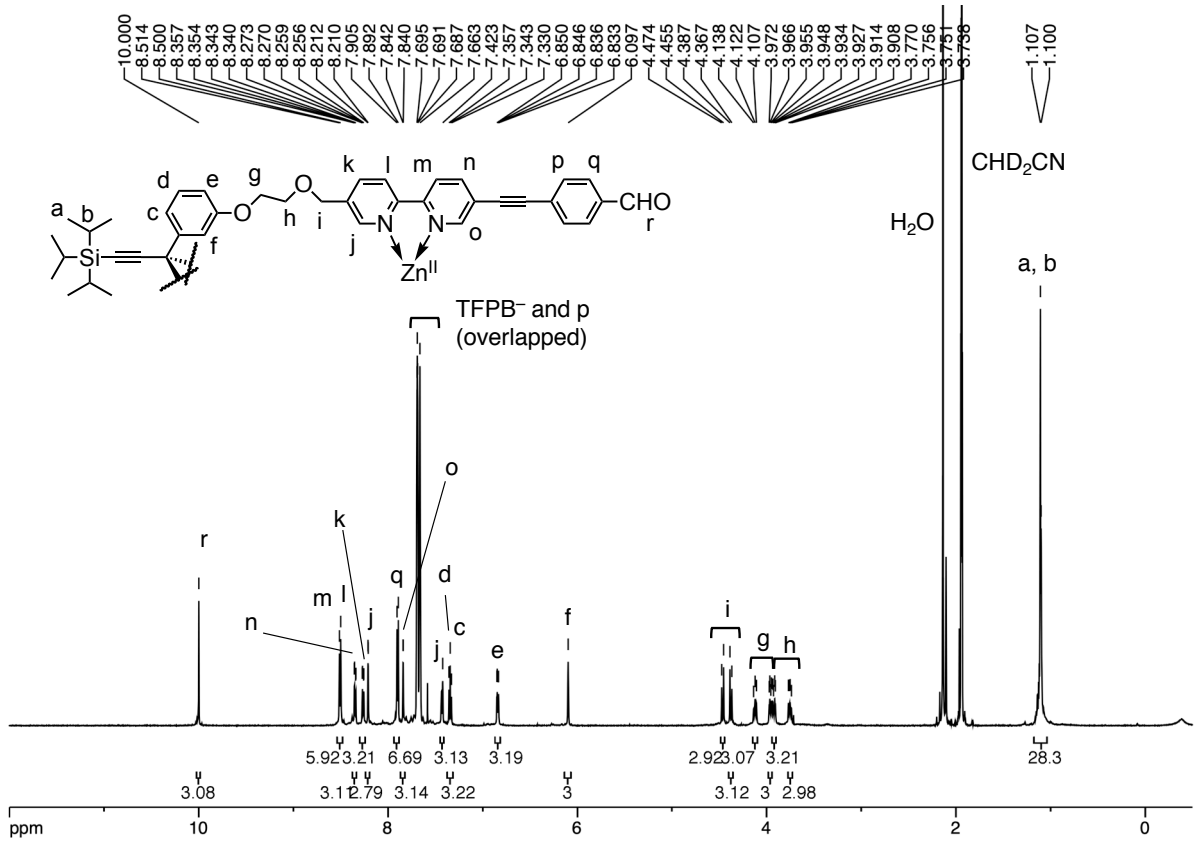


Figure S52. ^{1}H NMR spectrum of [**2b**Zn](TFPB)$_2$ (600 MHz, CD_3CN).

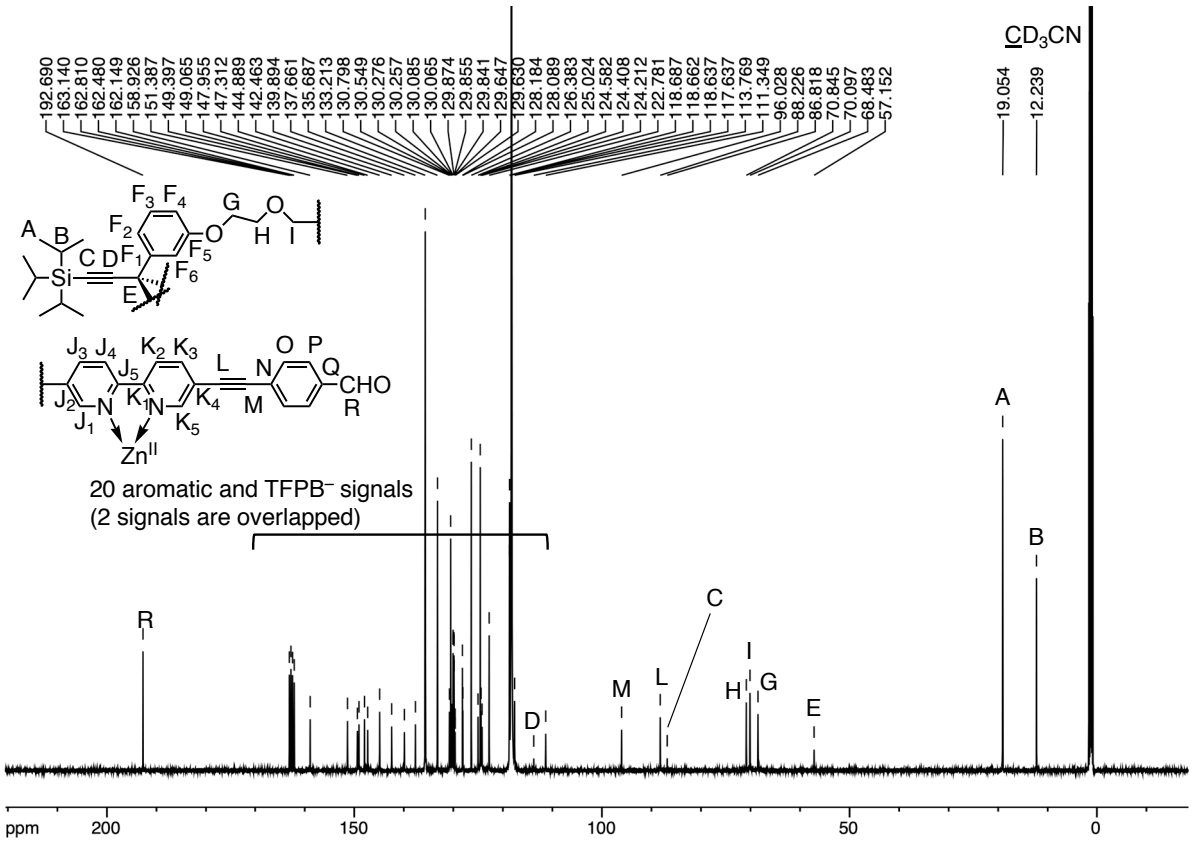


Figure S53. ^{13}C NMR spectrum of [**2b**Zn](TFPB)$_2$ (151 MHz, CD_3CN).

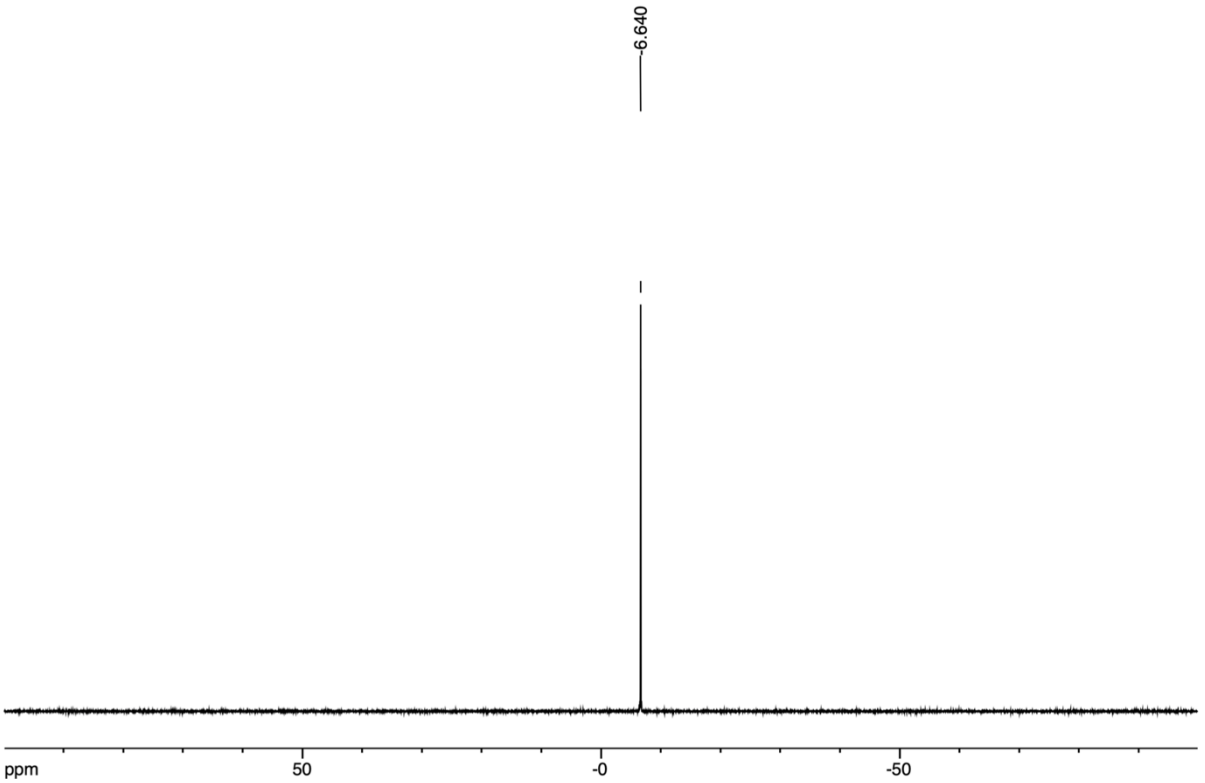


Figure S54. ^{11}B NMR spectrum of [**2b**Zn](TFPB)$_2$ (192 MHz, CD_3CN).

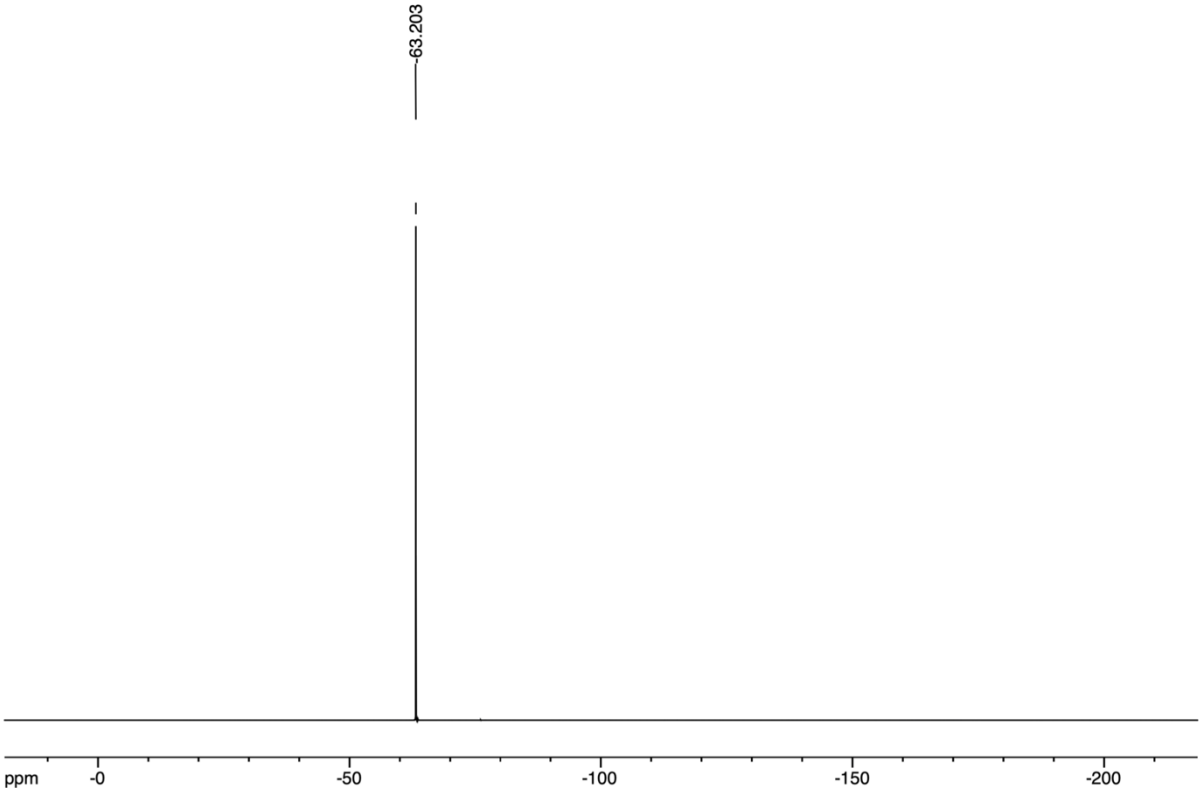


Figure S55. ^{19}F NMR spectrum of [**2b**Zn](TFPB)$_2$ (376 MHz, CD_3CN).

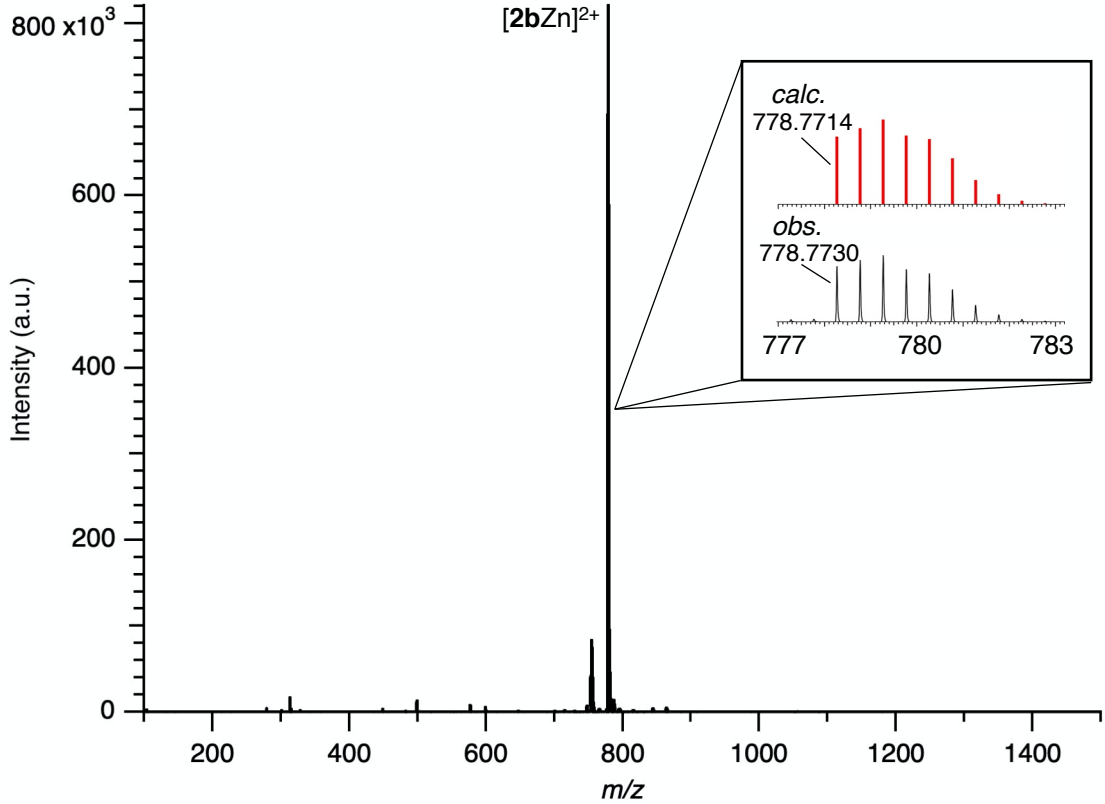


Figure S56. ESI mass spectrum of [**2b**Zn](TFPB)$_2$ (solv. CH_3CN).

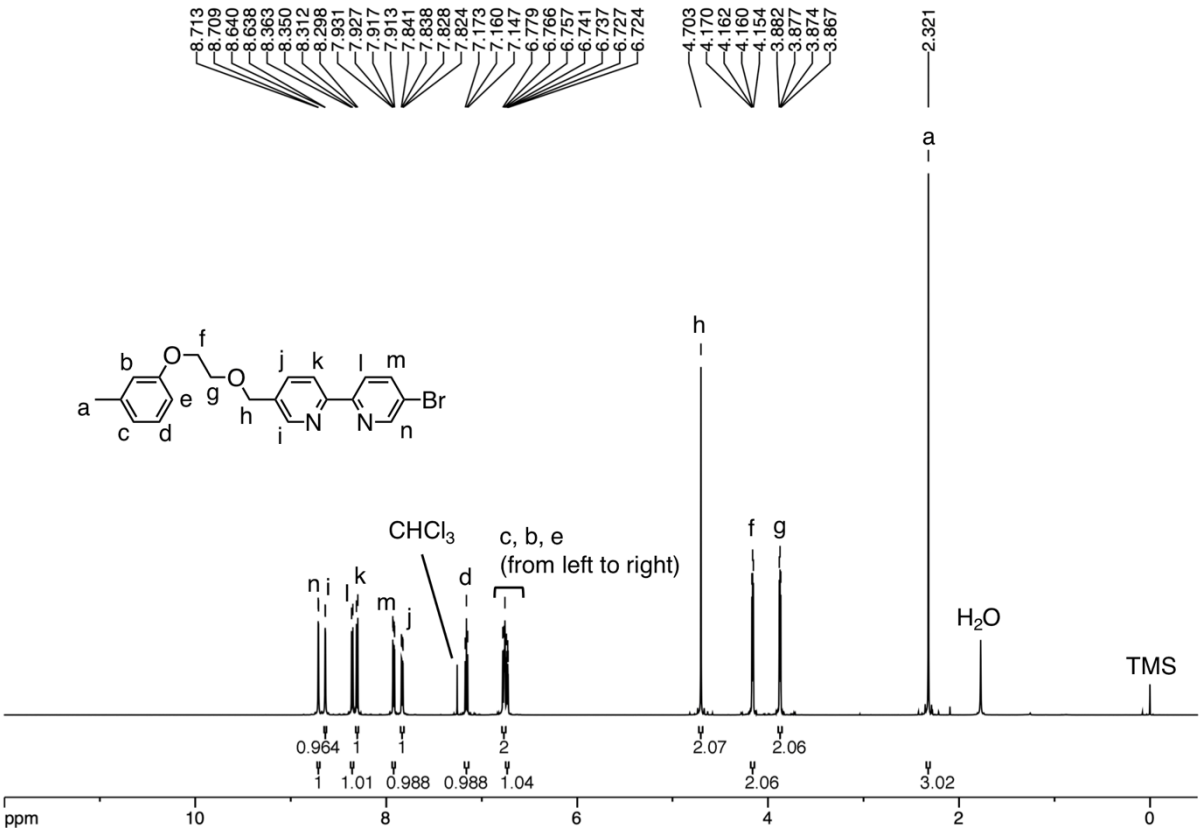


Figure S57. ^{1}H NMR spectrum of **3a** (600 MHz, $CDCl_3$).

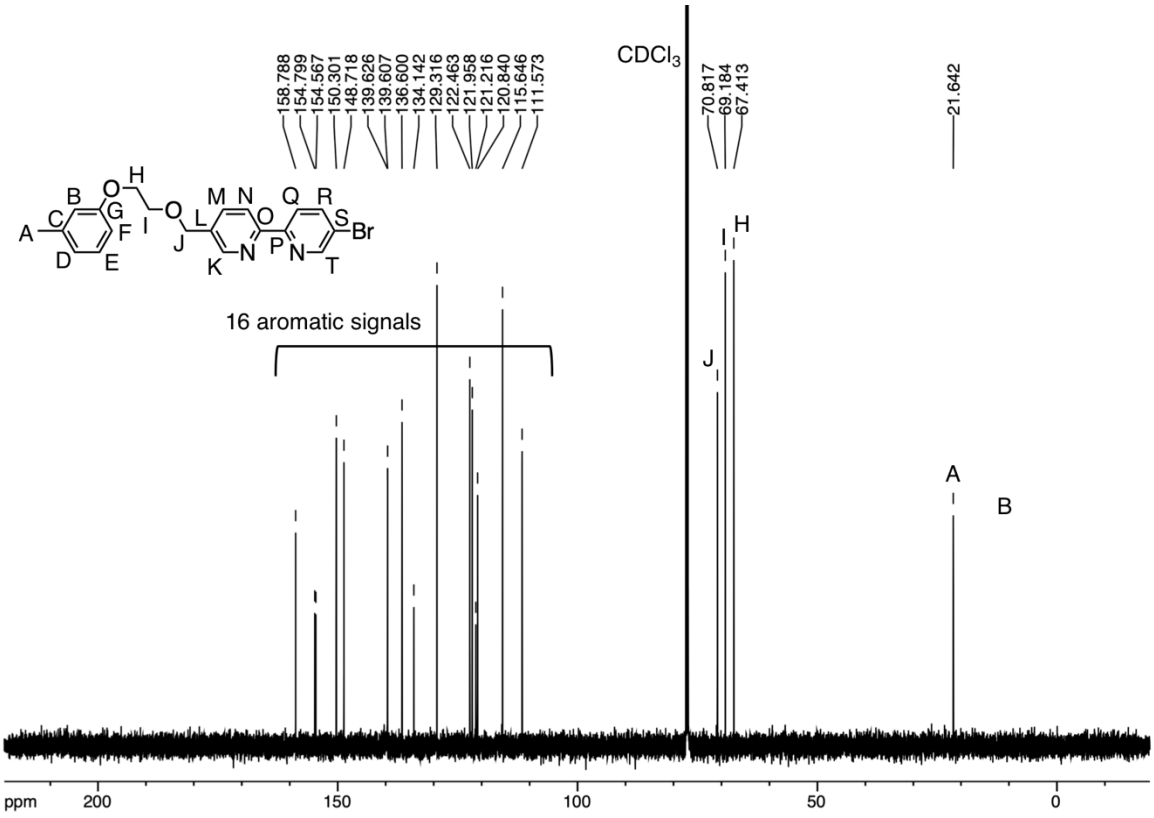


Figure S58. ^{13}C NMR spectrum of **3a** (151 MHz, $CDCl_3$).

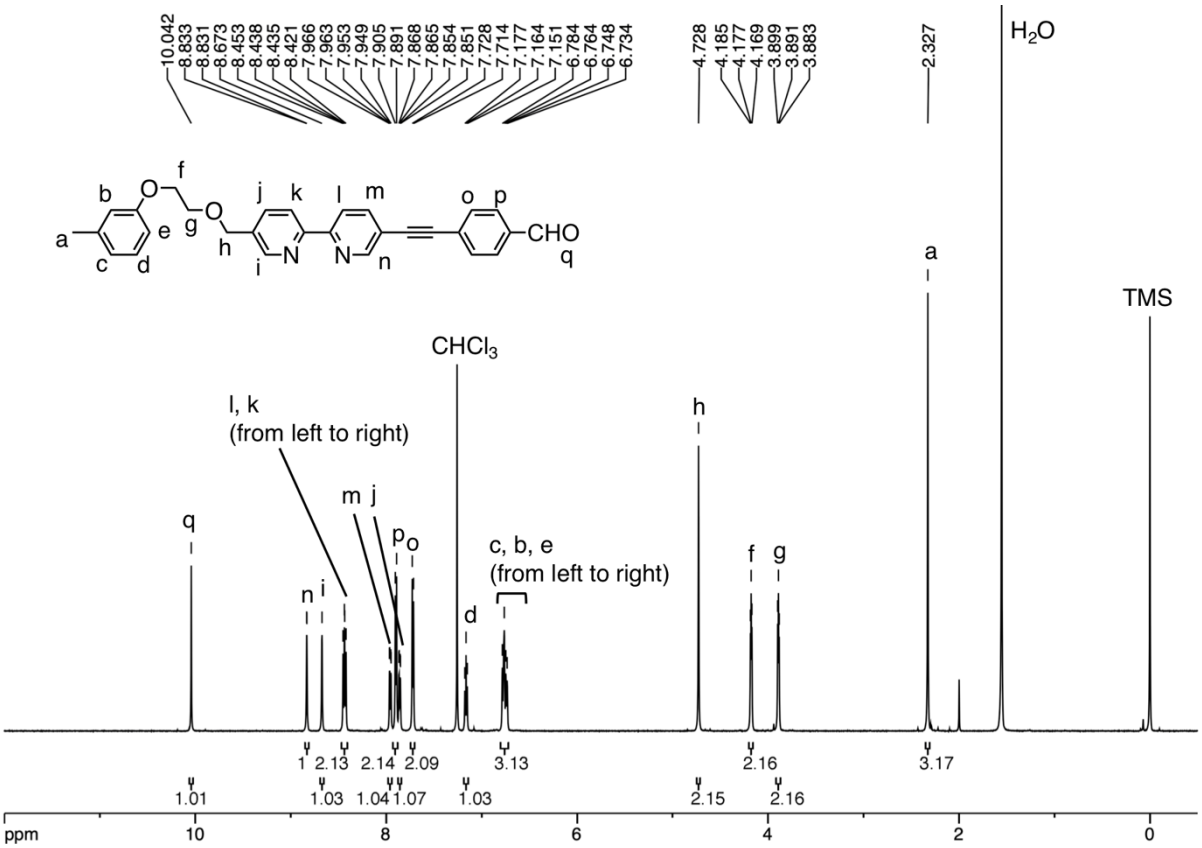


Figure S59. ^{1}H NMR spectrum of **3b** (600 MHz, $CDCl_3$).

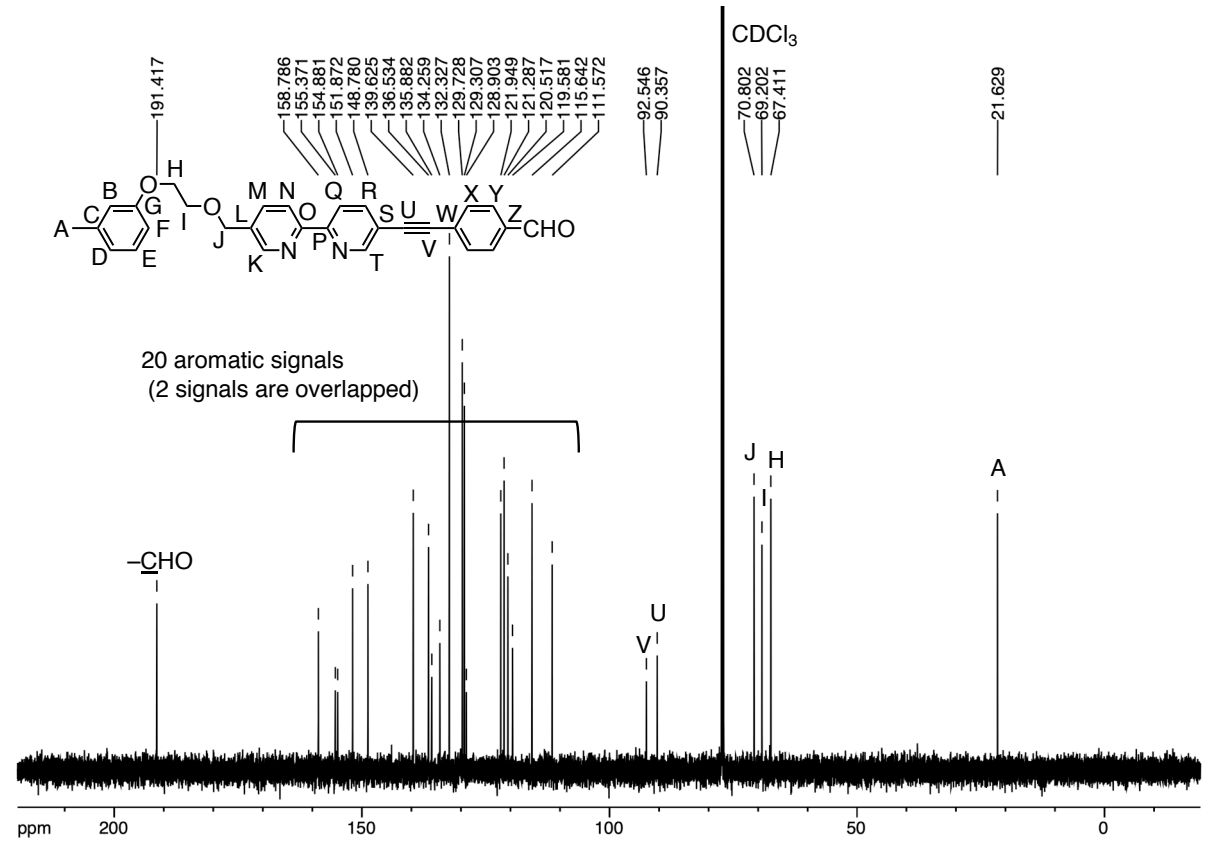


Figure S60. ^{13}C NMR spectrum of **3b** (151 MHz, $CDCl_3$).

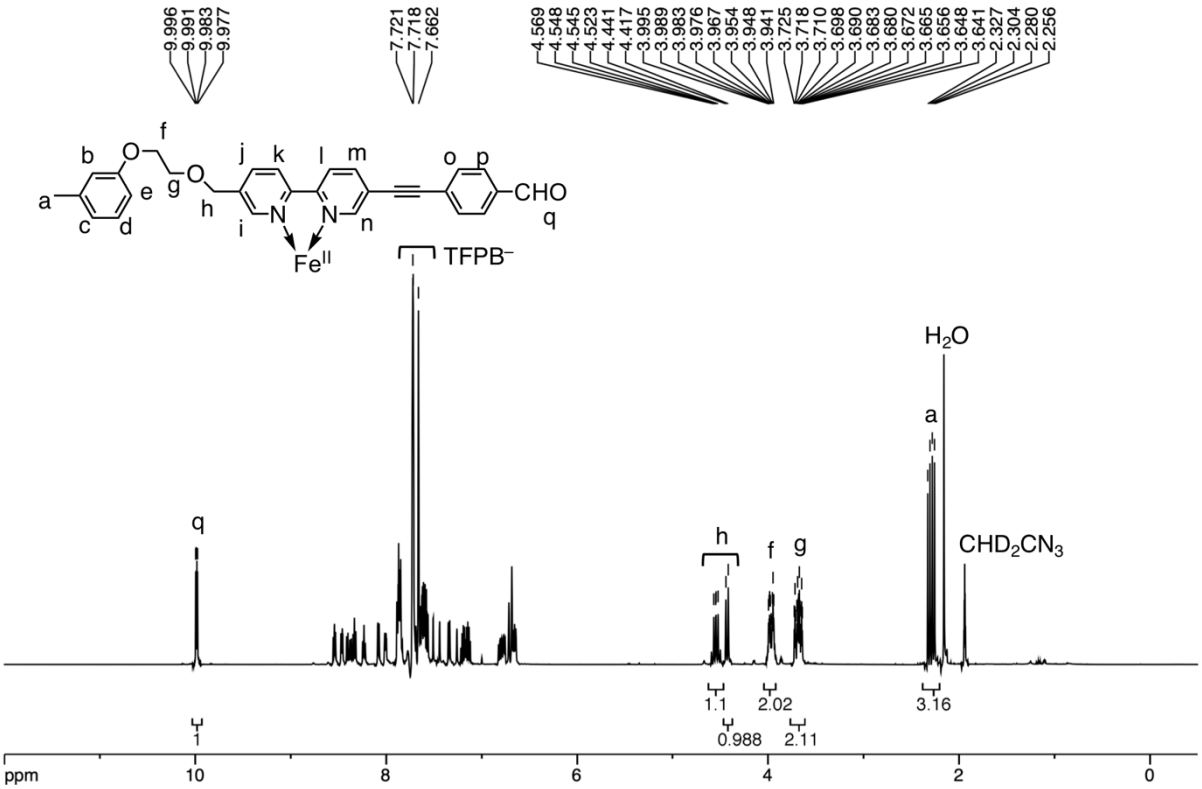


Figure S61. ^{1}H NMR spectrum of [(**3b**)$_3$Fe](TFPB)$_2$ (600 MHz, CD_3CN).

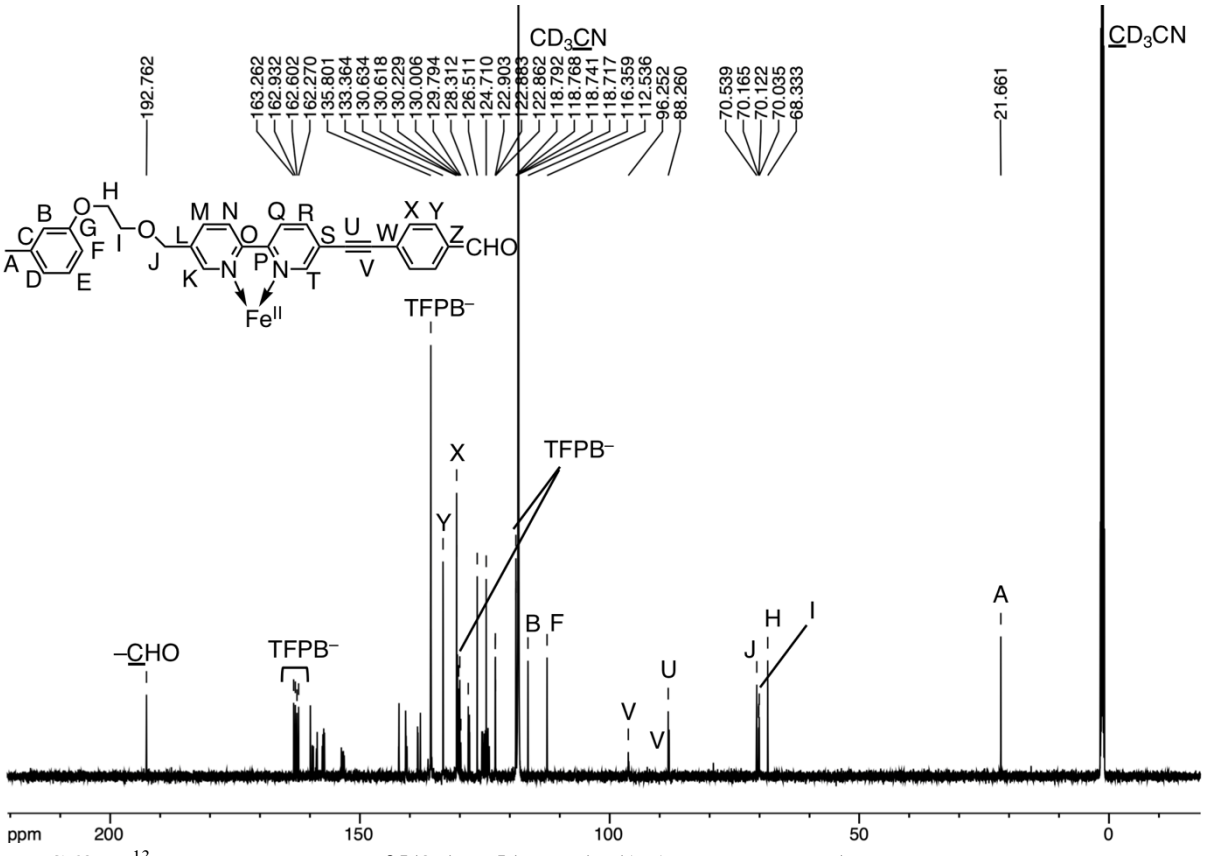


Figure S62. ^{13}C NMR spectrum of [(**3b**)$_3$Fe](TFPB)$_2$ (151 MHz, CD_3CN).

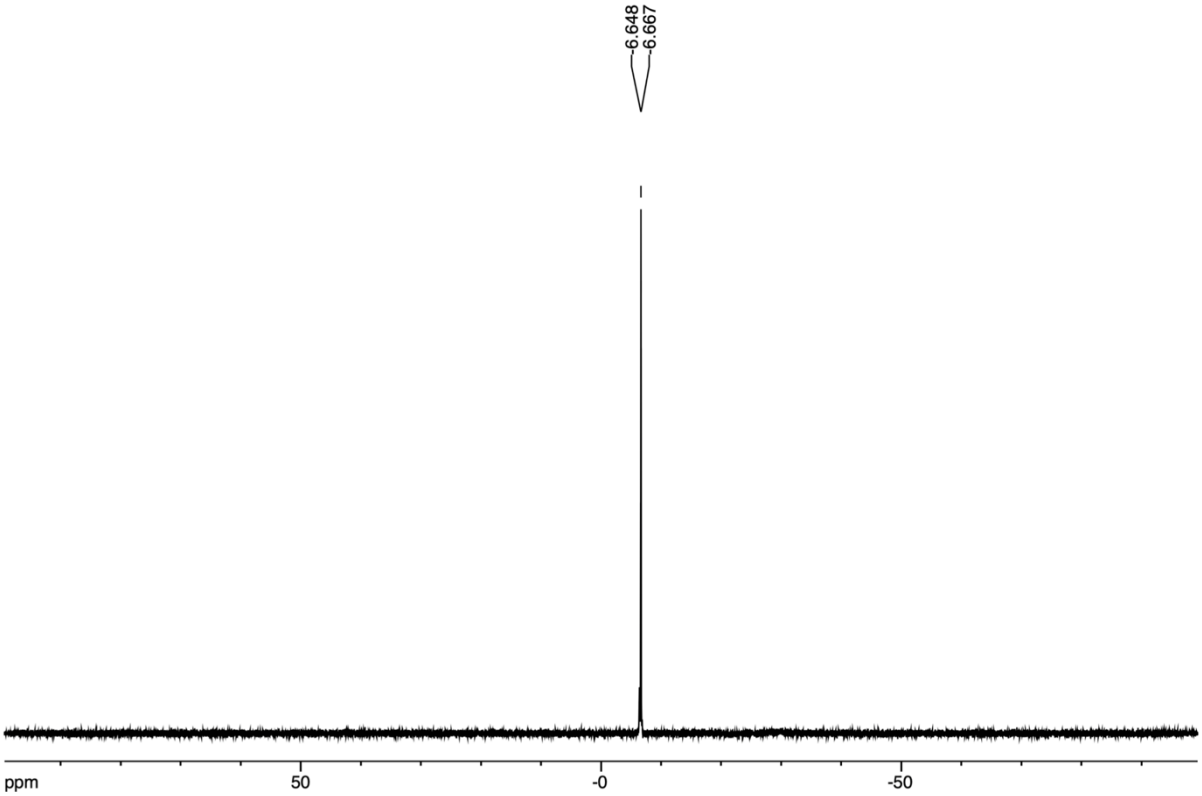


Figure S63. ^{11}B NMR spectrum of [(**3b**)$_3$Fe](TFPB)$_2$ (192 MHz, CD_3CN).

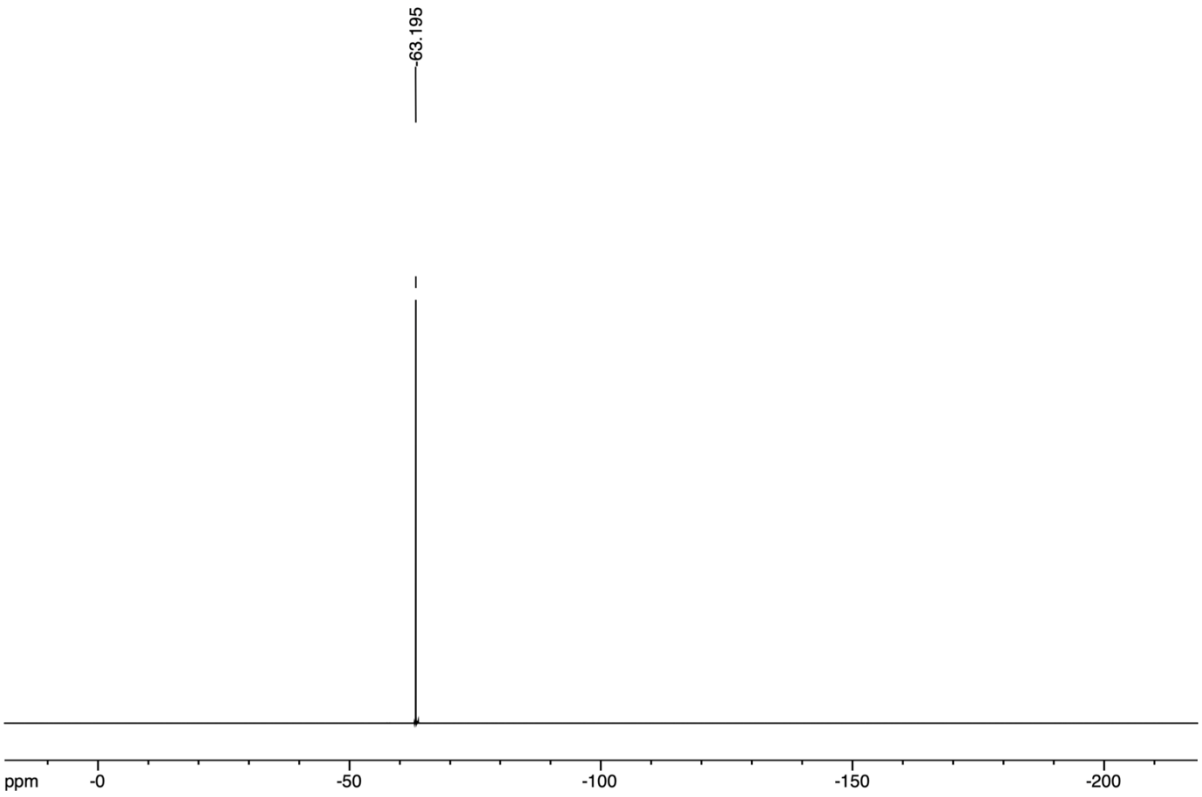


Figure S64. ^{19}F NMR spectrum of [(**3b**)$_3$Fe](TFPB)$_2$ (376 MHz, CD_3CN).

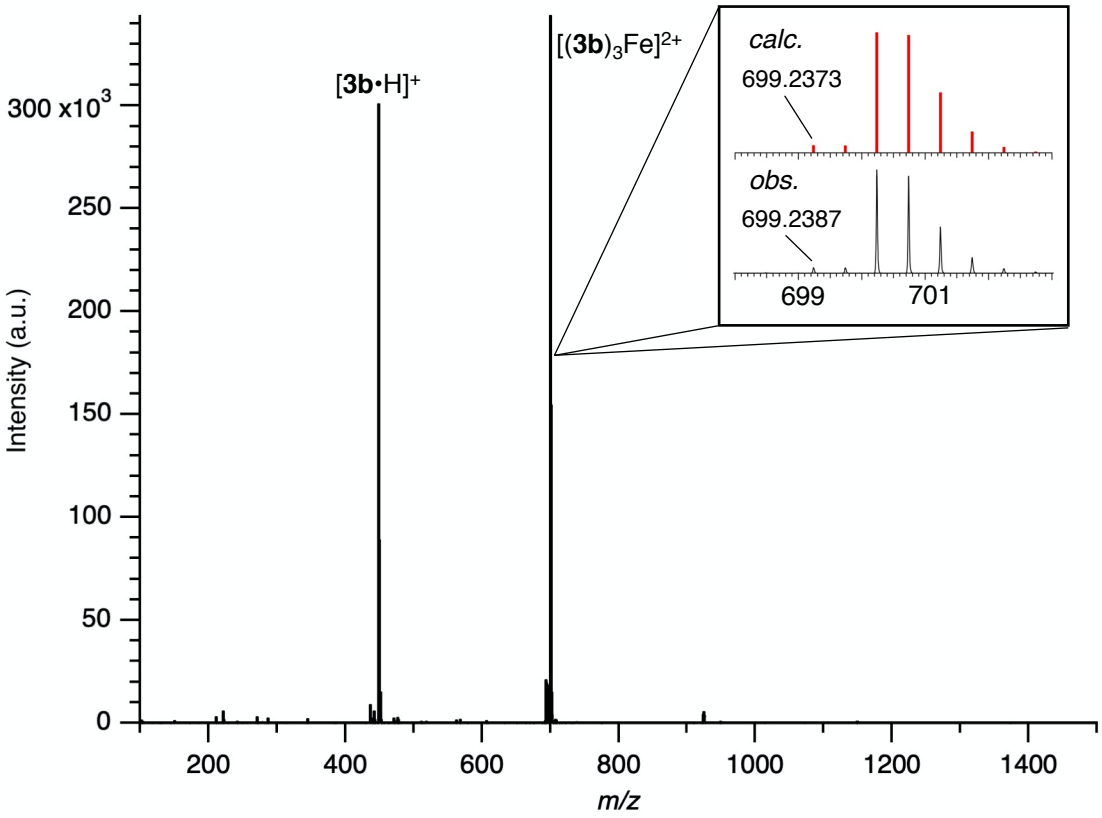


Figure S65. ESI mass spectrum of $[(\mathbf{3b})_3Fe](TFPB)_2$ (solv. CH_3CN).

Solvent dependence in the *fac/mer*-isomerization of complexes

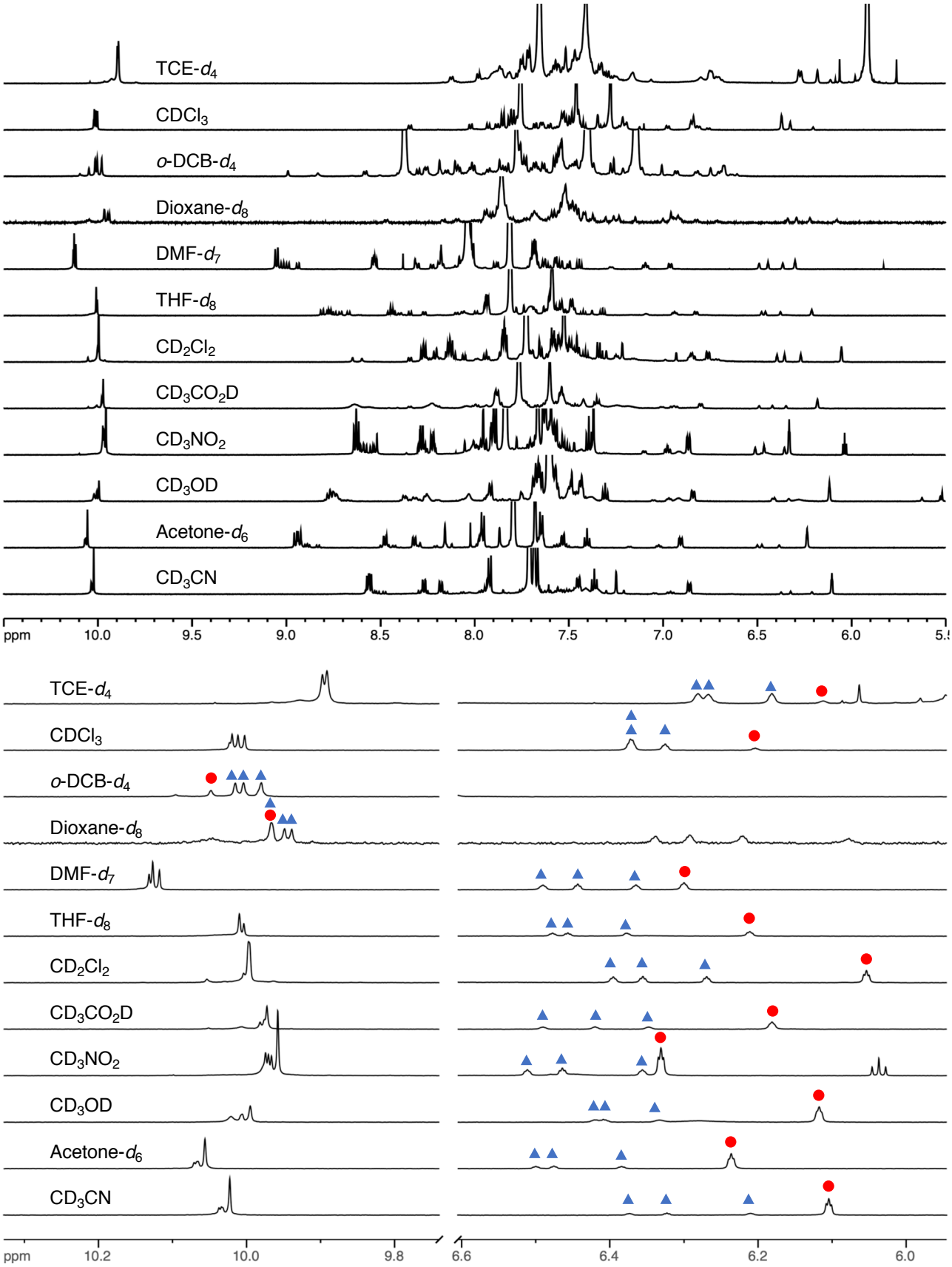


Figure S66. (Top) ^{1}H NMR spectra of [**2b**Fe](TFPB)$_2$ in various solvents. (Bottom) Enlarged ^{1}H NMR spectra. Signals used for the determination of *fac*/*mer* ratios were denoted in the same way as **Fig. 2a** (600 MHz, 1.0 mM, measured in 12 h after dissolution).

Table S1. Solvent effects on the *fac/mer*-isomerization equilibrium of [**2b**Fe](TFPB)$_2$ (298 K) and various parameters for solvents.[a]

Solvent	*fac/mer* [b]	ΔG [c] (kJ/mol)	ε	μ (D)	DN (kcal/mol)	AN (kcal/mol)	V_m (cm^3/mol)	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)
TCE-d_2	10:90	5.5	8.0	1.31	–	–	105.2	18.8	5.1	5.3
$CDCl_3$	10:90	5.5	4.7	1.1	4	23.1	80.7	17.8	3.1	5.7
o-DCB-d_4	13:87	4.8	9.9	2.14	3	–	112.8	19.0	6.3	3.3
Dioxane-d_8	20:80	3.4	2.2	0.4	14.8	10.8	85.7	17.5	1.8	7.4
DMF-d_7	32:68	1.8	36.7	3.86	26.6	16.0	77.4	17.4	13.7	11.3
THF-d_8	34:66	1.7	7.4	1.7	20	8.0	81.7	16.8	5.7	8.0
CD_2Cl_2	40:60	1.1	8.9	1.5	1	20.4	63.9	18.2	6.3	6.1
CD_3CO_2D	53:47	–0.31	6.2	1.73	10	52.9	57.1	14.5	8.0	13.5
CD_3NO_2	57:43	–0.70	36.7	3.57	2.7	20.5	54.3	15.8	18.8	5.1
CD_3OD	64:36	–1.5	32.6	1.71	19	41.3	40.7	15.1	12.3	22.3
Acetone-d_6	69:31	–2.0	20.7	2.88	17	12.5	74.0	15.5	10.4	7.0
CD_3CN	71:29	–2.2	36	3.44	14.1	19.3	52.6	15.3	18.0	6.1

a: ε: dielectric constant[S8a]; μ: dipole moment[S8a]; DN: donor number[S8a, b]; AN: accepter number[S8b]; V_m: molar volume[S8c]; δ_d , δ_p, and δ_h: the terms of Hansen solubility parameters[S8c]. δ_d: the dispersion term; δ_p: the dipole interaction term; δ_h: the hydrogen bonding term.

b: Determined from signals of proton *f* (pivot unit) (For *o*-DCB-d_4 and dioxane-d_8, signals of proton *r* (formyl group) were used. see **Fig. S46**).

c: $\Delta G = -RT \ln([fac]/[mer])$ (R; gas constant, T; temperature, [*fac*]; concentration of *fac*-isomer, [*mer*]; concentration of *mer*-isomer).

van't Hoff analysis of the *fac/mer*-isomerization in various solvents

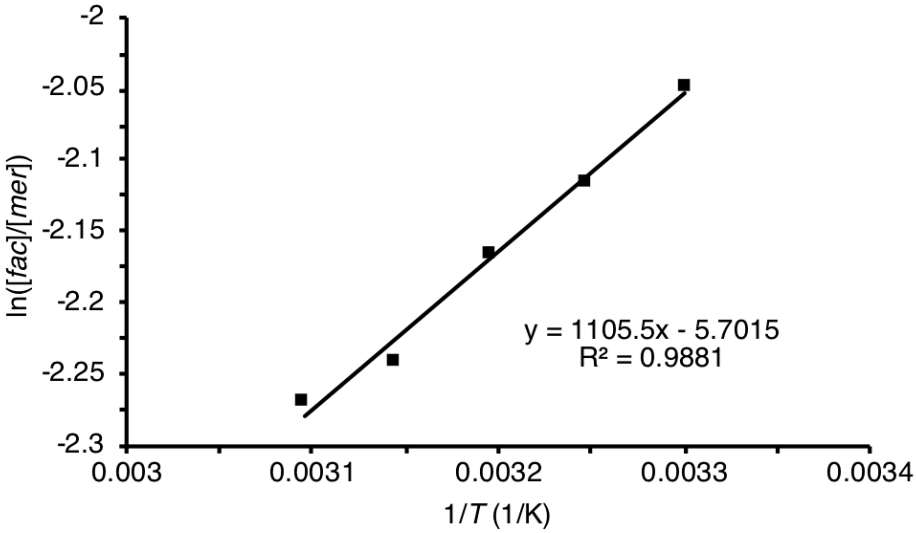


Figure S67. A van't Hoff plot of the *fac/mer* ratio of [**2b**Fe](TFPB)$_2$ in $CDCl_3$.

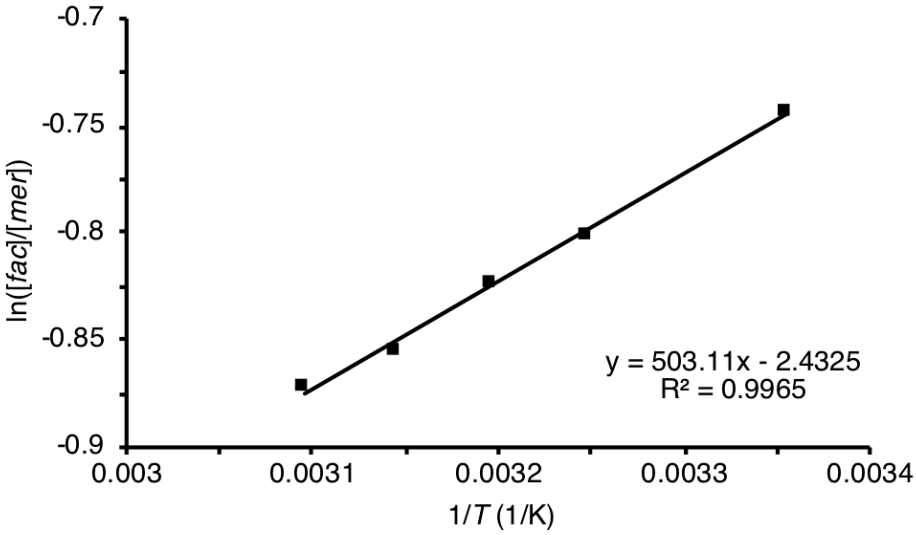


Figure S68. A van't Hoff plot of the *fac/mer* ratio of [**2b**Fe](TFPB)$_2$ in DMF-d_7.

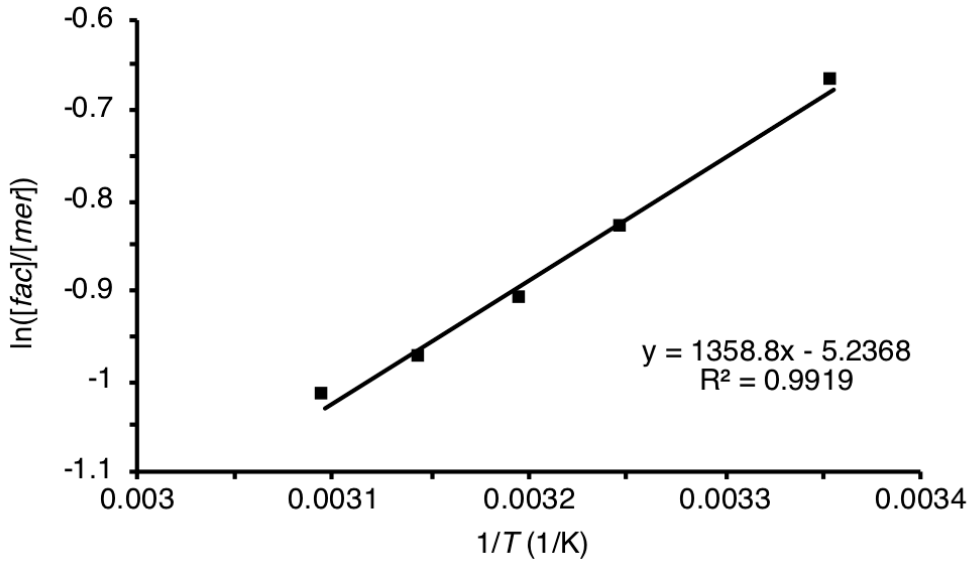


Figure S69. A van't Hoff plot of the *fac/mer* ratio of [**2b**Fe](TFPB)$_2$ in THF-d_8.

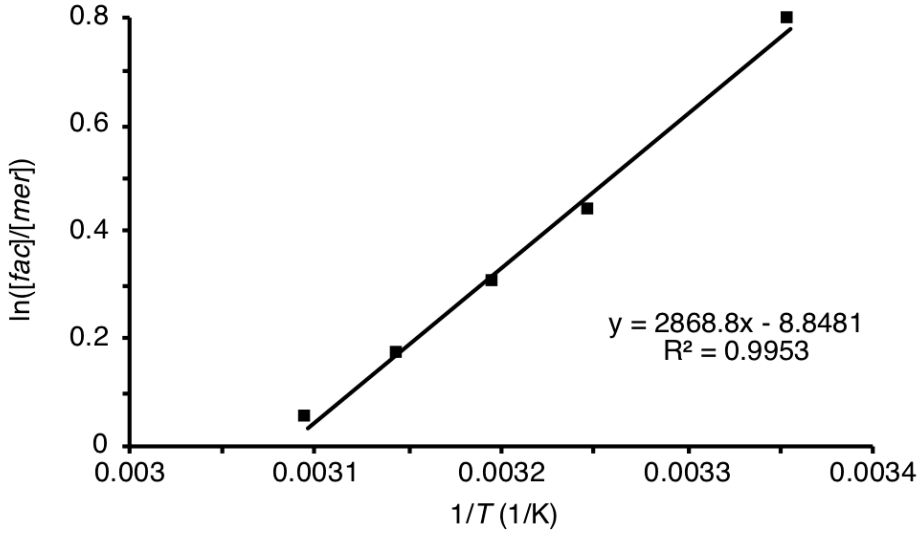


Figure S70. A van't Hoff plot of the *fac/mer* ratio of [**2b**Fe](TFPB)$_2$ in acetone-d_6.

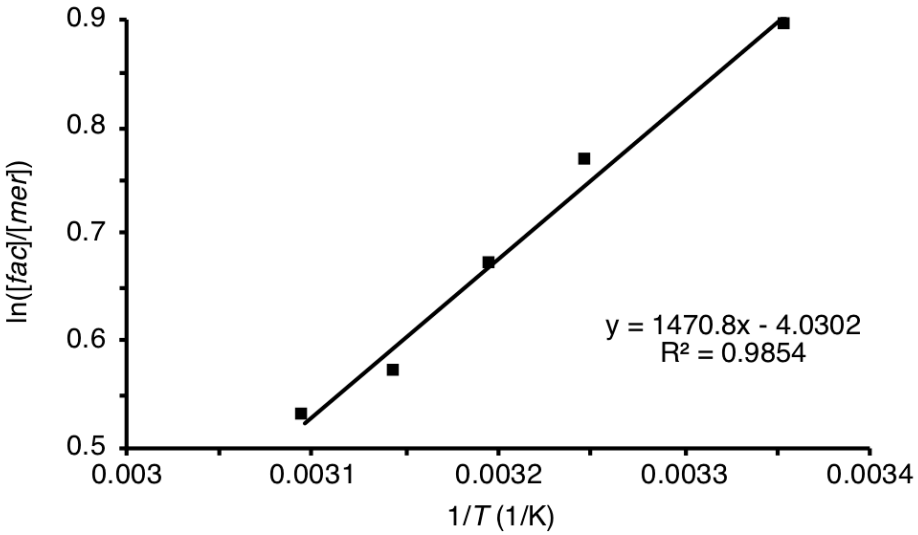


Figure S71. A van't Hoff plot of the *fac/mer* ratio of [**2b**Fe](TFPB)$_2$ in CD_3CN.

DOSY NMR spectra of [2bFe](TFPB)$_2$ in CD_3CN or $CDCl_3$

The hydrodynamic radii of [**2b**Fe](TFPB)$_2$ were evaluated by ^{1}H DOSY measurements (**Table S2, Fig. S72, S73**). The hydrodynamic radii of the *facial* isomer and the *meridional* isomers in the same solvent were almost the same. However, the hydrodynamic radius of [**2b**Fe]$^{2+}$ was approximately 9 Å in CD_3CN, but 14–15 Å in $CDCl_3$. Difference in hydrodynamic radius between CD_3CN and $CDCl_3$ was approximately 5 Å, which was roughly corresponding to the hydrodynamic radius of TFPB$^-$ in CD_3CN (5.7 Å). It was suggested that the ion pair of [**2b**Fe]$^{2+}$ and TFPB$^-$ formed in $CDCl_3$, while it did not in CD_3CN. Thus, it must be cautioned that the solvent dependency of *fac*/*mer* isomerism discussed in this paper contains the effect of ion pair formation between [**2b**Fe]$^{2+}$ and TFPB$^-$, and should be treated as the result of ionic complex [**2b**Fe](TFPB)$_2$ as a whole.

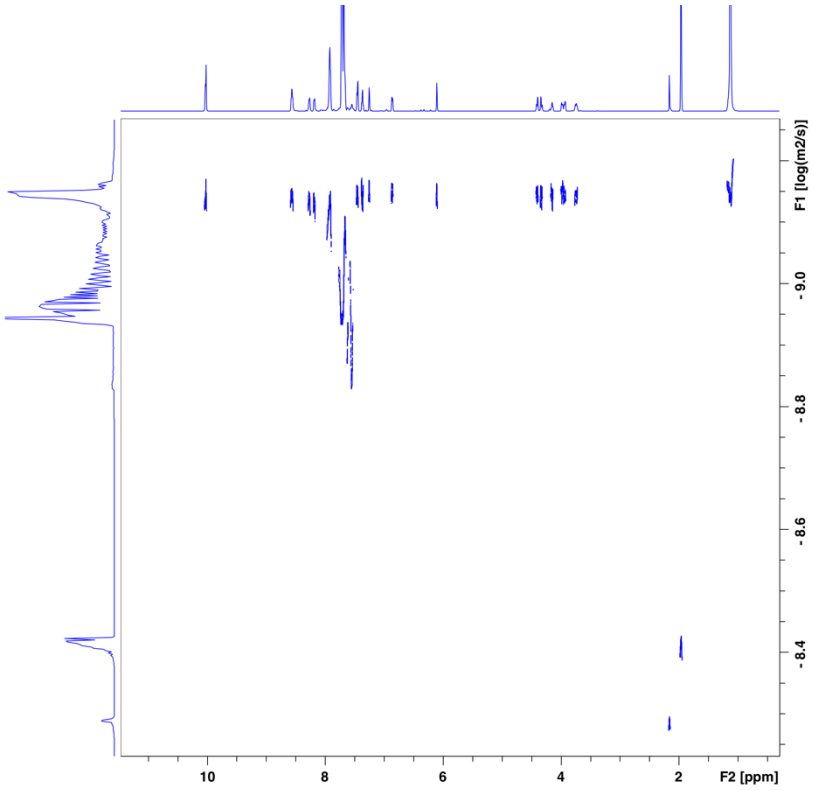


Figure S72. ^{1}H DOSY NMR spectrum of [**2b**Fe](TFPB)$_2$ (600 MHz, CD_3CN).

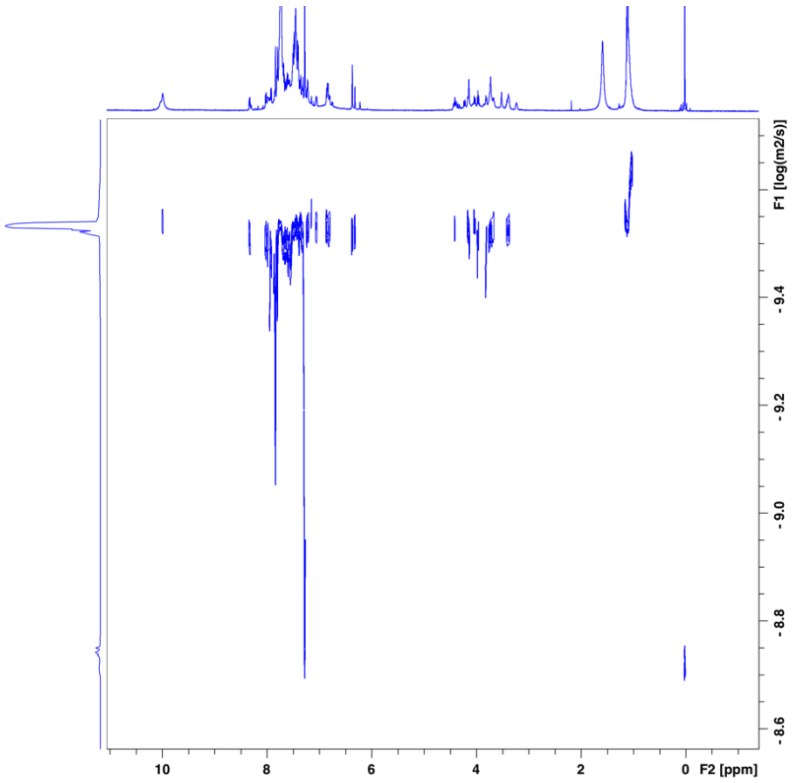


Figure S73. ^{1}H DOSY NMR spectrum of [**2b**Fe](TFPB)$_2$ (600 MHz, $CDCl_3$).

Table S2. Diffusion constants and hydrodynamic radii of [**2b**Fe](TFPB)$_2$ in CD_3CN and $CDCl_3$.

Solvent	Species	Diffusion constant (m^2/s)	Hydrodynamic radius (Å)
CD_3CN	*fac*-isomer	6.9×10^{-10}	9.3
	mer-isomer	7.2×10^{-10}	8.9
	$TFPB^-$	1.1×10^{-9}	5.7
$CDCl_3$	*fac*-isomer	2.8×10^{-10}	15
	mer-isomer	2.9×10^{-10}	14
	$TFPB^-$	2.9×10^{-10}	14

Comparison of solvent dependence of [2bFe](TFPB)$_2$ and the other complexes

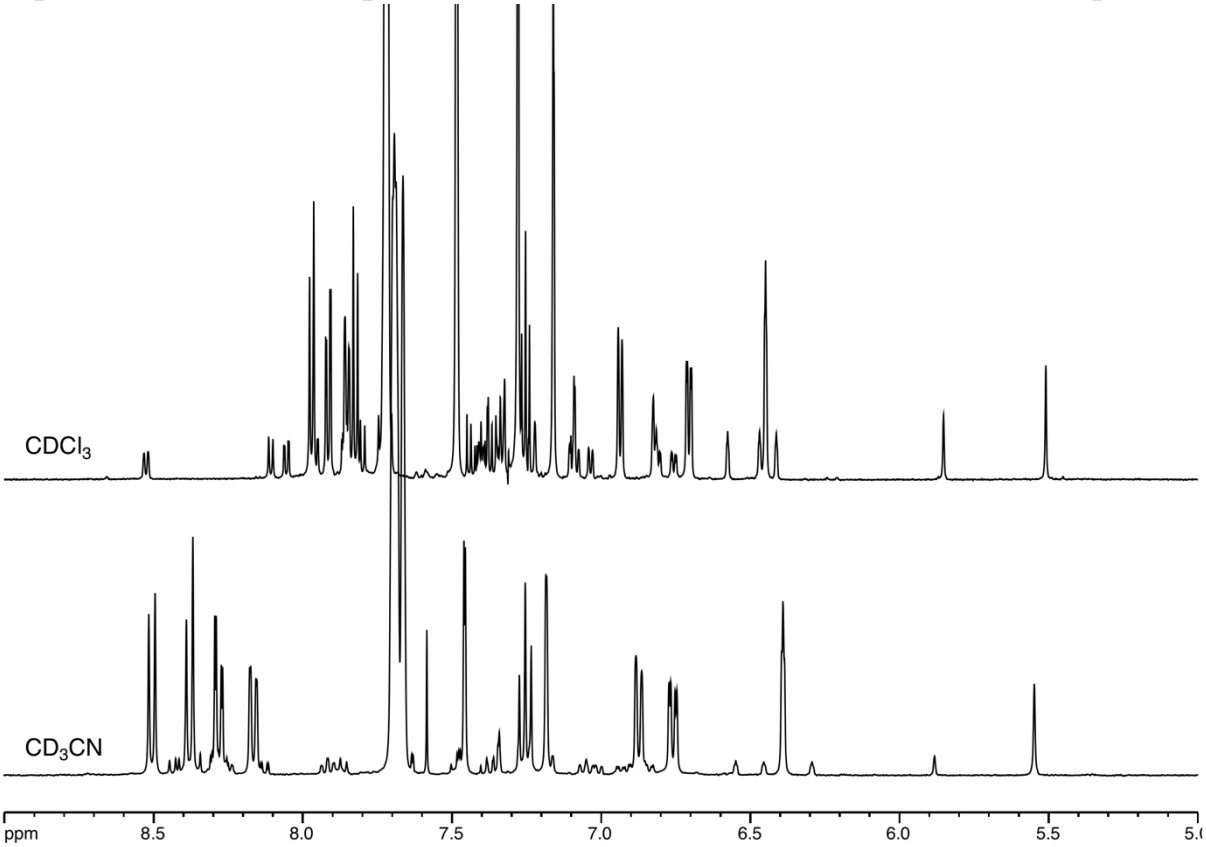


Figure S74. ^{1}H NMR spectra of [**1a**Fe](TFPB)$_2$ (600 MHz).

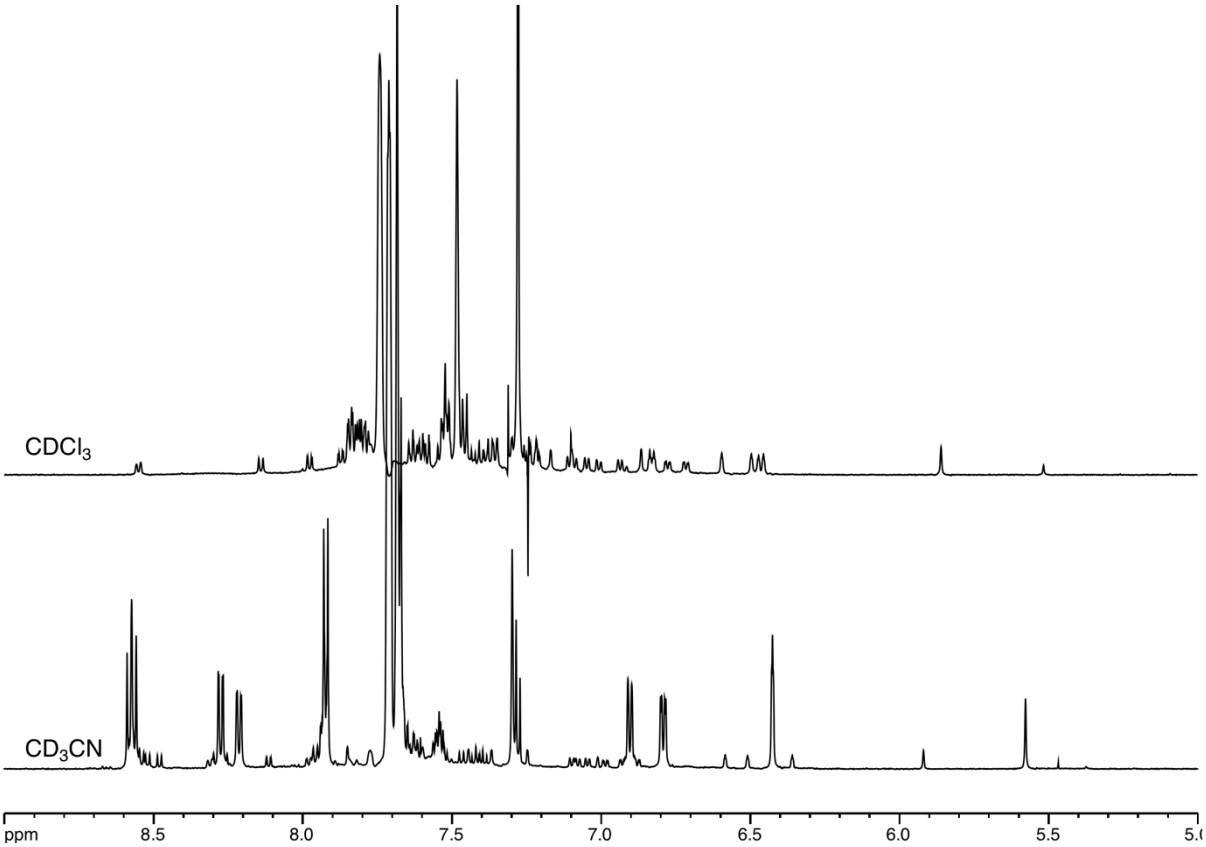


Figure S75. ^{1}H NMR spectra of [**1b**Fe](TFPB)$_2$ (600 MHz).

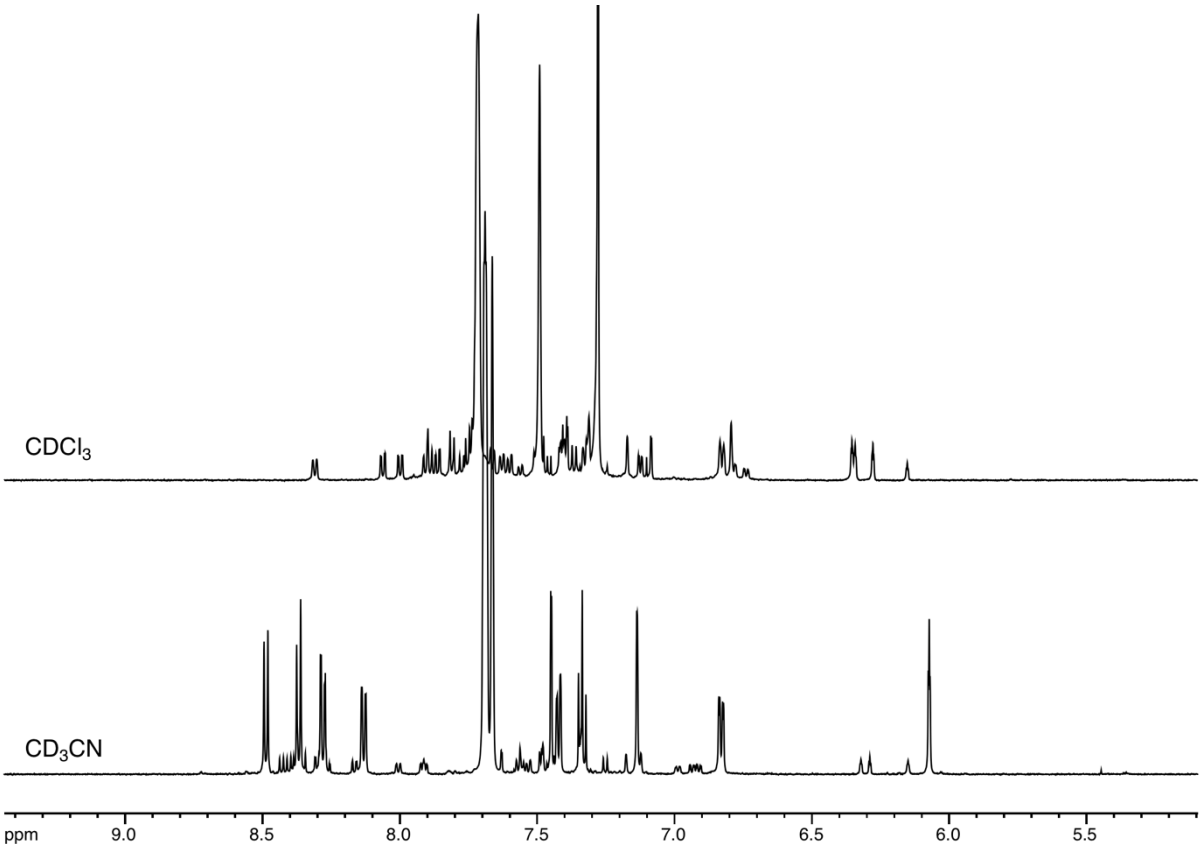


Figure S76. ^{1}H NMR spectra of [**2a**Fe](TFPB)$_2$ (600 MHz).

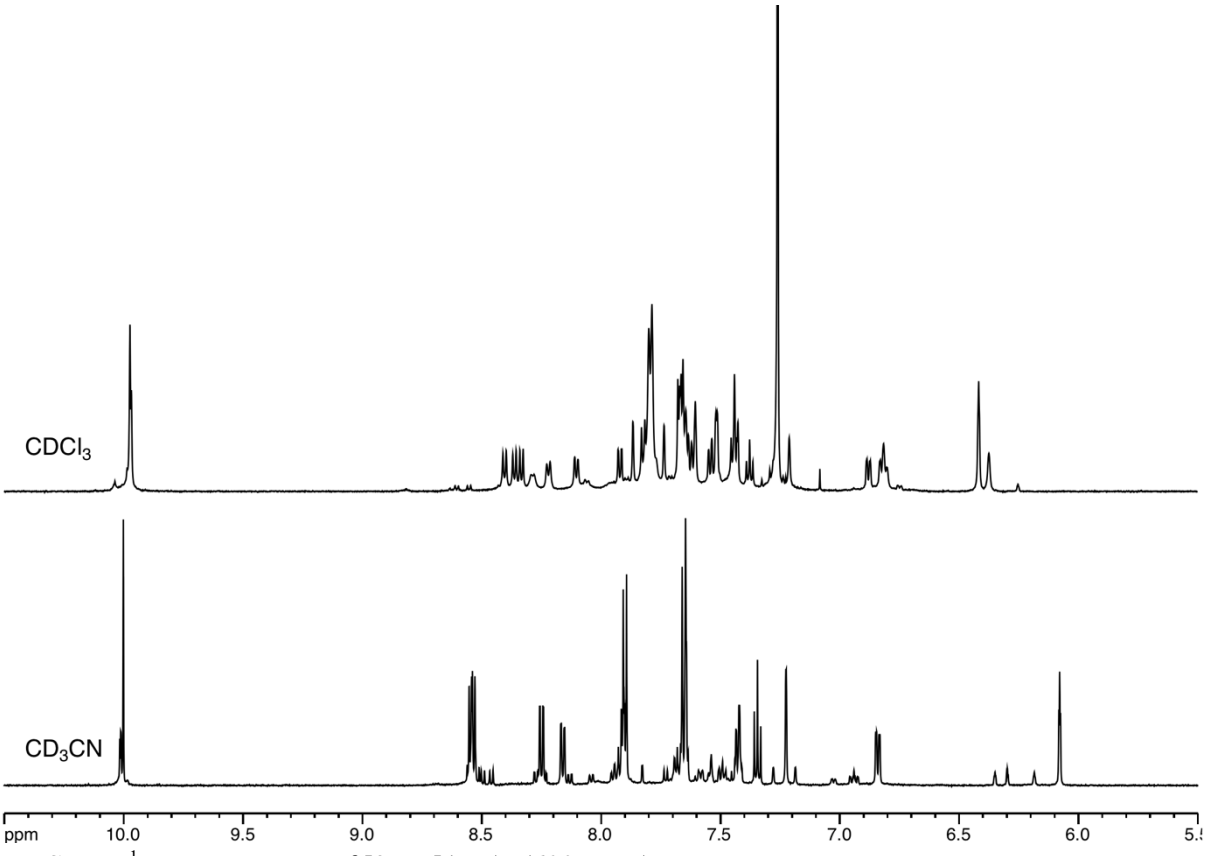


Figure S77. ^{1}H NMR spectra of [**2b**Fe](PF$_6$)$_2$ (600 MHz).

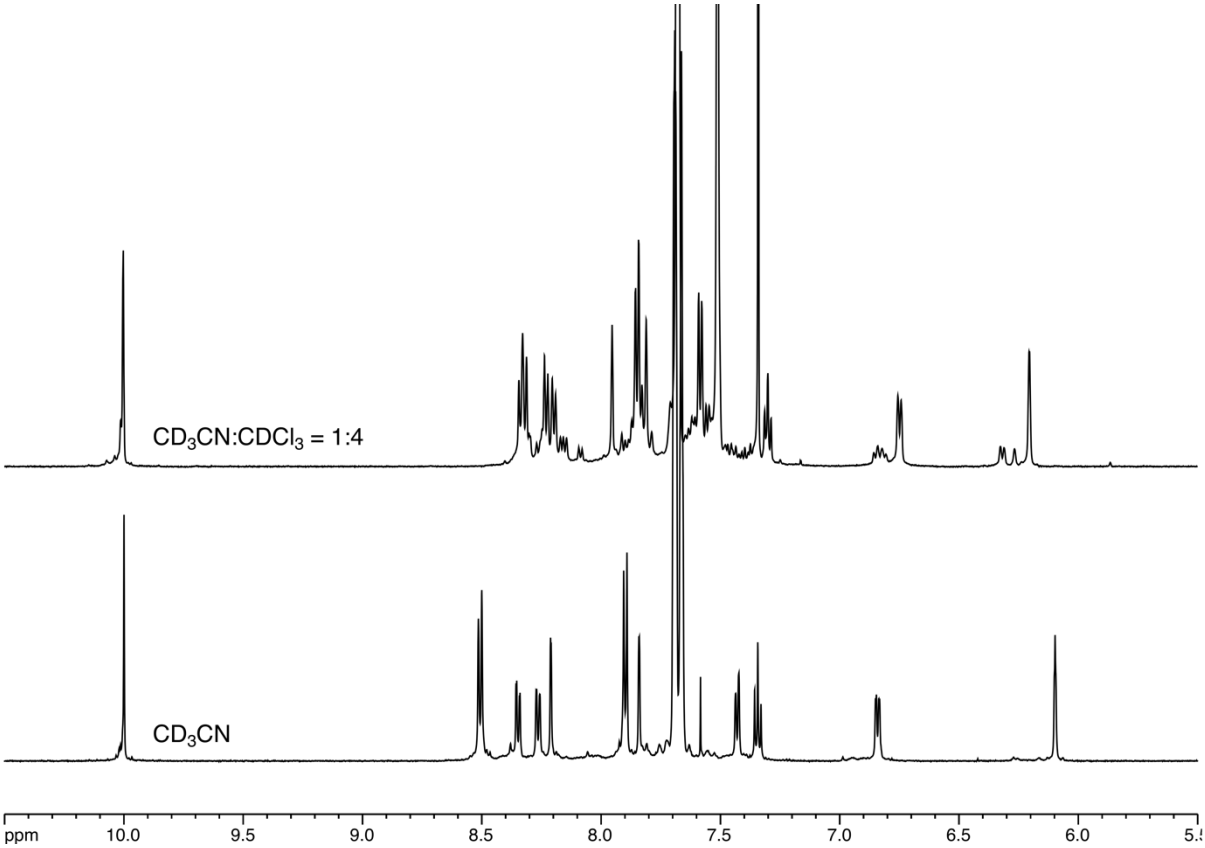


Figure S78. ^{1}H NMR spectra of [**2b**Zn](TFPB)$_2$ (600 MHz).

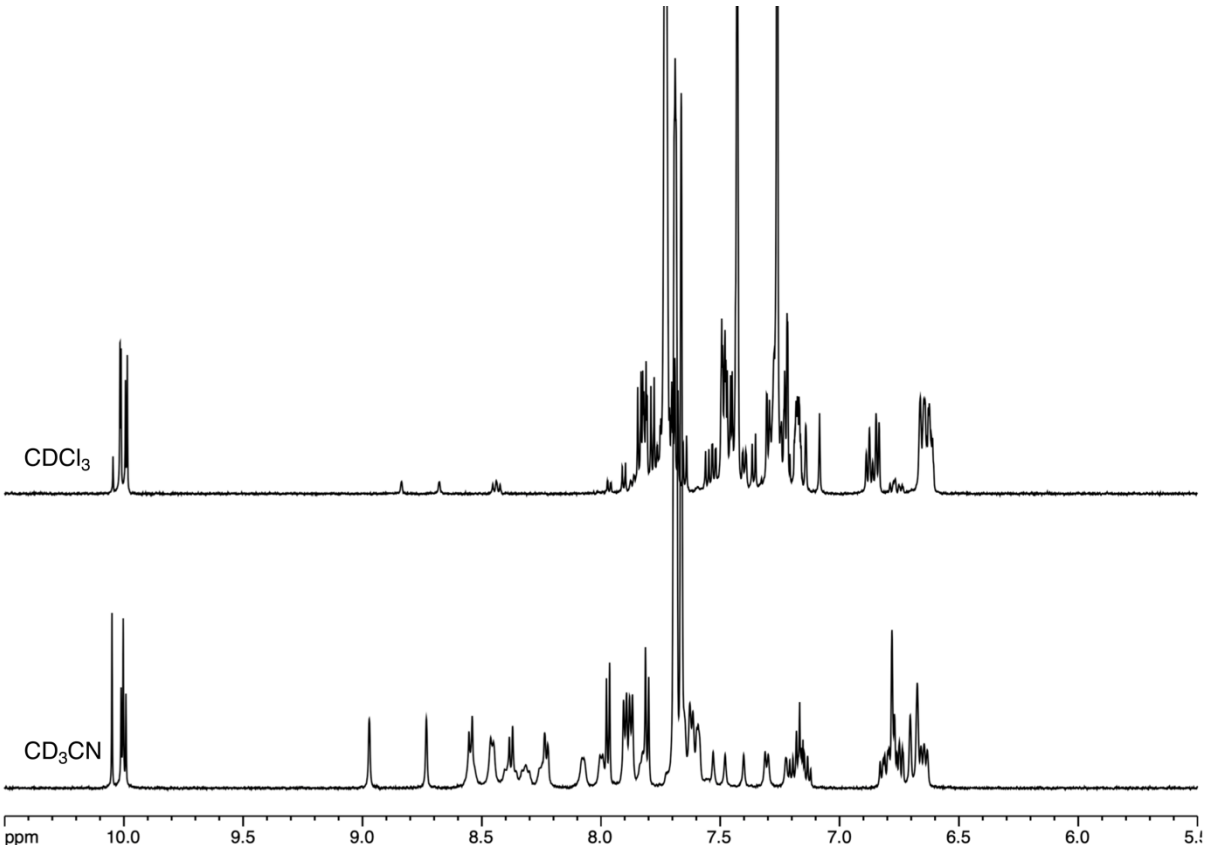


Figure S79. ^{1}H NMR spectra of [(**3b**)$_3$Fe](TFPB)$_2$ (600 MHz).

Regression analyses with various solvent parameters

Table S3. Results of regression analyses between Δ*G* of (*mer* to *fac* isomerization) of [**2b**Fe](TFPB)$_2$ and thermodynamic parameters of solvents. See also Table S1.

Parameter	(Multiple) correlation coefficient *R*	adjusted R-squared R_{adj}^2	Standard error σ (kJ/mol)
ε	–0.64	0.34	2.3
μ	–0.54	0.23	2.5
DN	–0.29	–0.015	2.7
AN	0.26	–0.049	2.5
V_m	0.83	0.66	1.6
δ_d	0.87	0.72	1.5
δ_p	–0.73	0.48	2.0
δ_h	–0.42	0.10	2.7
ε, μ	0.64	0.27	2.4
DN, AN	0.33	–0.14	2.7
V_m, δ_d	0.89	0.75	1.4
δ_d, δ_p, δ_h	0.91	0.77	1.4
δ_d, δ_p	0.91	0.79	1.3

R_{adj}^2 was defined as this equation (*R*: the correlation coefficient, *n*: the sample size, *p*: the total number of explanatory variables).

$$R_{adj}{}^2 = 1 - (1 - R^2)\frac{n-1}{n-p-1}$$

R_{adj}^2 is one of the extended coefficients of determination considered the number of explanatory variables and can be compared even when different numbers of variables are used.

X-ray diffraction analysis

A single crystal of [**1a**Fe]$(PF_6)_2$•4$(CH_3)_2CO$ suitable for the X-ray diffraction analysis was obtained by the slow diffusion of diethyl ether vapor into an acetone solution of [**1a**Fe]$(PF_6)_2$.

Crystal data for [**1a**Fe]$(PF_6)_2$•4$(CH_3)_2CO$: $C_{70}H_{73}Br_3FeN_6O_{10}P_2$, *Fw* = 1743.86, hexagonal red plate, 0.14 × 0.17 × 0.02 mm^3, rhombohedral, space group *R*-3, *a* = 13.982(3) Å, *c* = 67.108(15) Å, *V* = 11362(6) Å^3, *Z* = 6, R_1 = 0.0643, wR_2 = 0.1997, GOF = 1.068. CCDC 2067281.

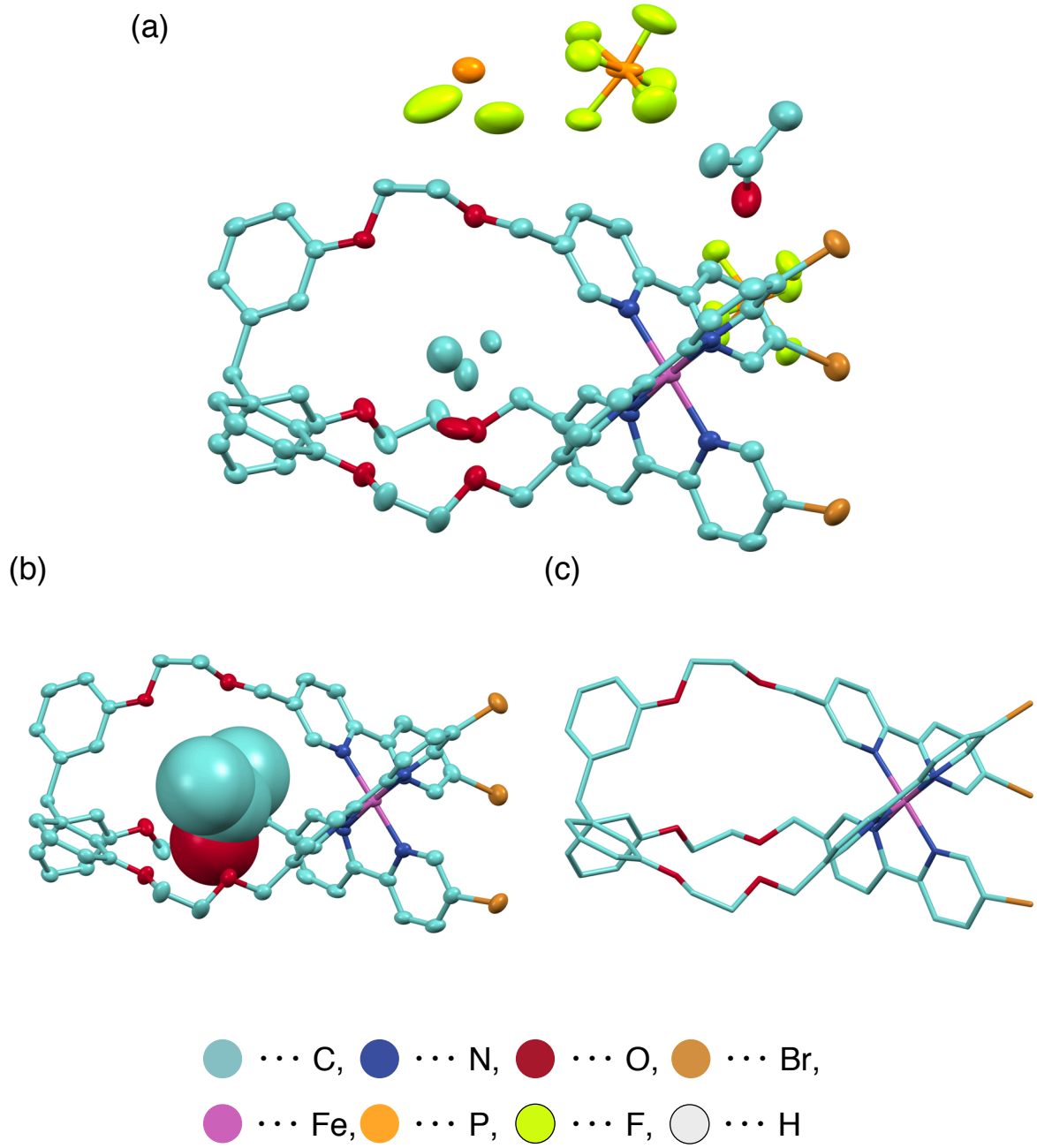


Figure S80. The structure of [**1a**Fe]$(PF_6)_2$•2$(CH_3)_2CO$•2PF_6 determined by X-ray diffraction analysis. Hydrogen atoms were omitted for clarity. a) An ellipsoidal model (50% probability). One of the disordered structures is shown. b) An ellipsoid model for [**1a**Fe]$^{2+}$ and a space-filling model for the included acetone. c) A stick model of [**1a**Fe]$^{2+}$.

Cycle characteristics of exchanging solvent

[**2b**Fe](TFPB)$_2$ (2.32 mg, 1.25 μmol) was dissolved in CD_3CN (500 μL). The solution was heated at 50 °C for 12 h, cooled to r.t., and then ^{1}H NMR spectrum was measured. After the measurement, the solution was concentrated *in vacuo*, and the residue was dissolved in $CDCl_3$ (500 μL). The solution was heated at 50 °C for 12 h, cooled to r.t., and then ^{1}H NMR spectrum was measured. These operations were repeated for 5 times with the same sample.

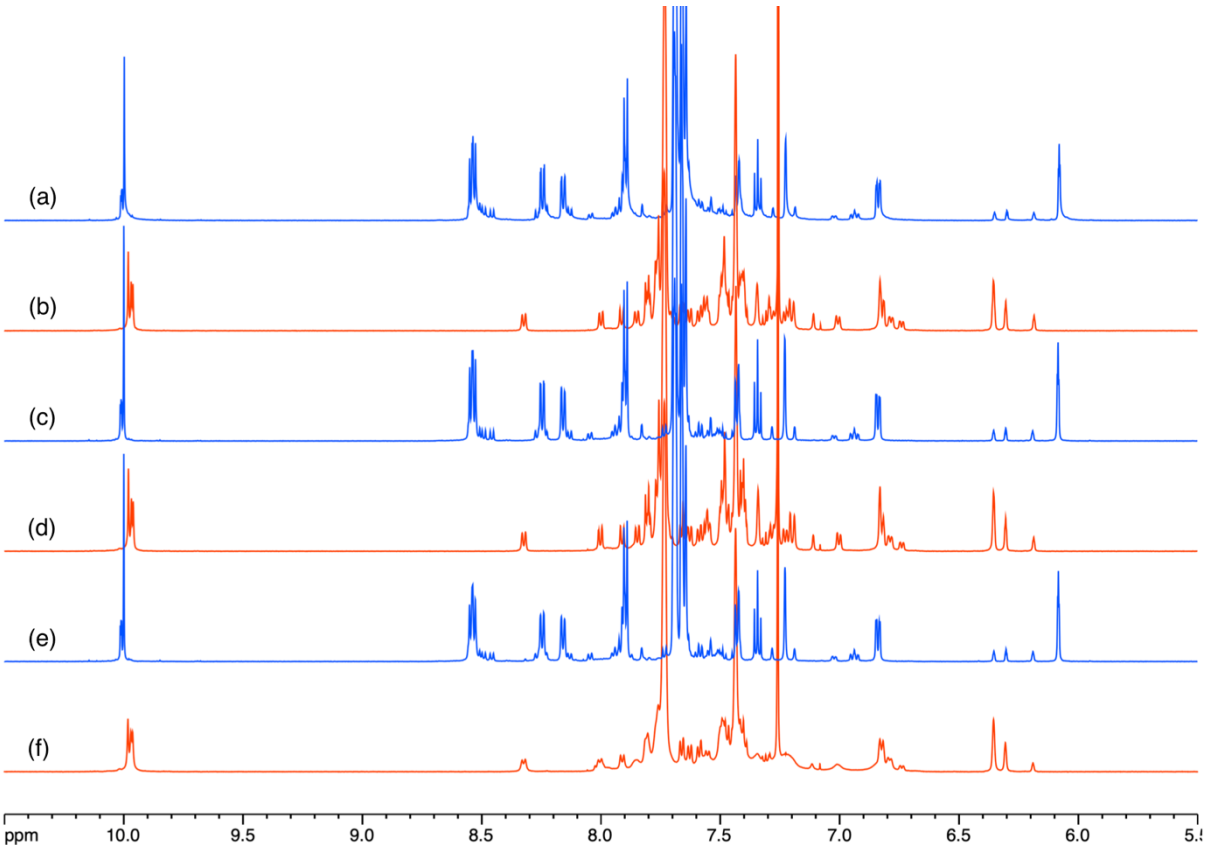


Figure S81. ^{1}H NMR spectra of [**2b**Fe](TFPB)$_2$ at 1st, 2nd, and 5th cycle in the solvent exchange experiment (600 MHz). (a) 1st cycle in CD_3CN. (b) 1st cycle in $CDCl_3$. (c) 2nd cycle in CD_3CN. (d) 2nd cycle in $CDCl_3$. (e) 5th cycle in CD_3CN. (f) 5th cycle in $CDCl_3$.

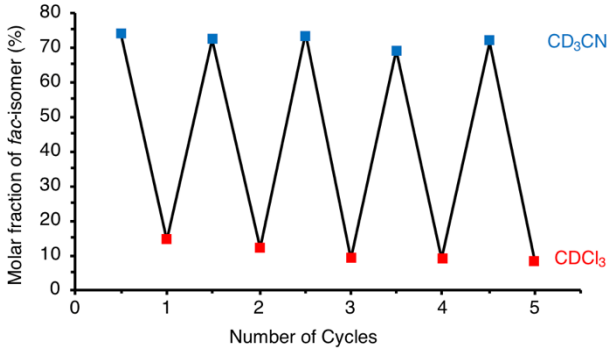


Figure S82. Reversibility of the *fac/mer* isomerization of [**2b**Fe](TFPB)$_2$.

Synthesis of imine-linked dimer and tetramer

Synthesis of **D-PPD**$(PF_6)_4$

To a solution of [**2b**Fe]$(PF_6)_2$ (0.92 mg, 0.50 μmol) in a mixed solvent of CD_3CN (250 μL) and $CDCl_3$ (250 μL) was added a solution of 1,3-propanediamine (60.0 mM, 12.5 μL) in a mixed solvent of $CD_3CN/CDCl_3$ = 1/1. The mixture was heated at 50 °C for 24 h, and then was subjected to the spectroscopic measurements.

D-PPD$(PF_6)_4$: ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1/1) δ 8.53 (d, *J* = 8.4 Hz, 6H), 8.52 (d, *J* = 8.4 Hz, 6H), 8.31 (s, 6H), 8.22 (dd, *J* = 8.4, 1.8 Hz, 6H), 8.17 (d, *J* = 8.4 Hz, 6H), 7.71 (d, *J* = 7.8 Hz , 12H), 7.53–7.49 (m, 18H), 7.45 (d, *J* = 7.8 Hz, 6H), 7.32 (dd, *J* = 7.8, 7.8 Hz, 6H), 7.19 (br s, 6H), 6.80 (dd, *J* = 7.8, 1.8 Hz, 6H), 6.12 (br s, 6H), 4.39 (dd, *J* = 64.2, 12.6 Hz, 12H) 4.17–4.11 (m, 6H), 3.99–3.92 (m, 12H), 3.77–3.72 (m, 6H), 3.68 (t, *J* = 5.4 Hz, 12H), 1.15–1.09 (m, 42H); ^{19}F NMR (376 MHz, $CD_3CN/CDCl_3$ = 1/1) δ –72.8 (d, $^1J_{F\text{-}P}$ = 709 Hz); ^{31}P NMR (243 MHz, $CD_3CN/CDCl_3$ = 1/1) δ –144.5 (d, $^1J_{P\text{-}F}$ = 709 Hz); HRMS (ESI): *m/z* calcd for (**D-PPD**$^{4+}$): 801.8202; found: 801.8176.

Synthesis of **D-CHZ**$(PF_6)_4$

To a solution of [**2b**Fe]$(PF_6)_2$ (0.90 mg, 0.49 μmol) in a mixed solvent of CD_3CN (250 μL) and $CDCl_3$ (250 μL) was added a solution of carbohydrazide in water (375 mM, 2.0 μL). The mixture was heated at 50 °C for 24 h, and then was subjected to the spectroscopic measurements.

D-CHZ$(PF_6)_4$: ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1/1) δ 9.36 (br s, 6H), 8.54–8.46 (m, 12H), 8.19–8.13 (m, 12H), 8.00 (br s, 6H), 7.73 (dd, *J* = 9.0, 9.0 Hz, 12H), 7.54 (s, 6H), 7.48 (dd, *J* = 45.6, 8.4 Hz, 12H), 7.43 (d, *J* = 7.8 Hz , 6H), 7.30 (d, *J* = 7.4 Hz, 6H), 7.17 (d, *J* = 18.6 Hz, 6H), 6.80–6.76 (m, 6H), 6.11 (td, *J* = 7.4, 2.4 Hz, 12H), 4.37 (ddd, *J* = 60.0, 12.6, 8.4 Hz, 12H), 4.14–4.01 (m, 12H), 3.96–3.89 (m, 12H), 3.75–3.70 (m, 12H), 1.16–1.04 (m, 42H); HRMS (ESI): *m/z* calcd for (**D-CHZ**$^{4+}$): 813.7975; found: 813.7981.

Synthesis of **T**$(PF_6)_8$

To a solution of [**2b**Fe]$(PF_6)_2$ (4.60 mg, 2.50 μmol) in a mixed solvent of CD_3CN (250 μL) and $CDCl_3$ (250 μL) was added a solution of *trans*-1,4-cyclohexanediamine (37.5 mM, 10.0 μL) in a mixed solvent of $CD_3CN/CDCl_3$ = 1/1. The mixture was heated at 50 °C for 12 h, and then was subjected to the spectroscopic measurements.

T$(PF_6)_8$: ^{1}H NMR (600 MHz, $CD_3CN/CDCl_3$ = 1/1) δ 8.55–8.46 (m, 24H), 8.33 (s, 12H), 8.21 (br dd, *J* = 7.2, 7.2 Hz, 12H), 8.15 (br d, *J* = 7.2 Hz, 12H), 7.70 (d, *J* = 7.2 Hz , 24H), 7.53–7.46 (m, 36H), 7.42 (d, *J* = 7.8 Hz, 12H), 7.29 (dd, *J* = 7.8, 7.8 Hz, 12H), 7.12–7.14 (m, 12H), 6.77 (d, *J* = 7.8 Hz, 12H), 6.11 (br s, 12H), 4.37 (dd, *J* = 66.0, 12.0 Hz, 24H) 4.15–4.07 (m, 12H), 3.97–3.88 (m, 24H), 3.76–3.69 (m, 12H), 3.28 (br s, 12H), 1.73 (d, *J* = 52.8 Hz, 48H), 1.15–1.09 (m, 84H); ^{19}F NMR (376 MHz, $CD_3CN/CDCl_3$ = 1/1) δ –72.7 (d, $^1J_{F\text{-}P}$ = 709 Hz); ^{31}P NMR (243 MHz, $CD_3CN/CDCl_3$ = 1/1) δ –144.5 (d, $^1J_{P\text{-}F}$ = 709 Hz); HRMS (ESI): *m/z* calcd for (**T**$^{8+}$): 832.2185; found: 832.2175.

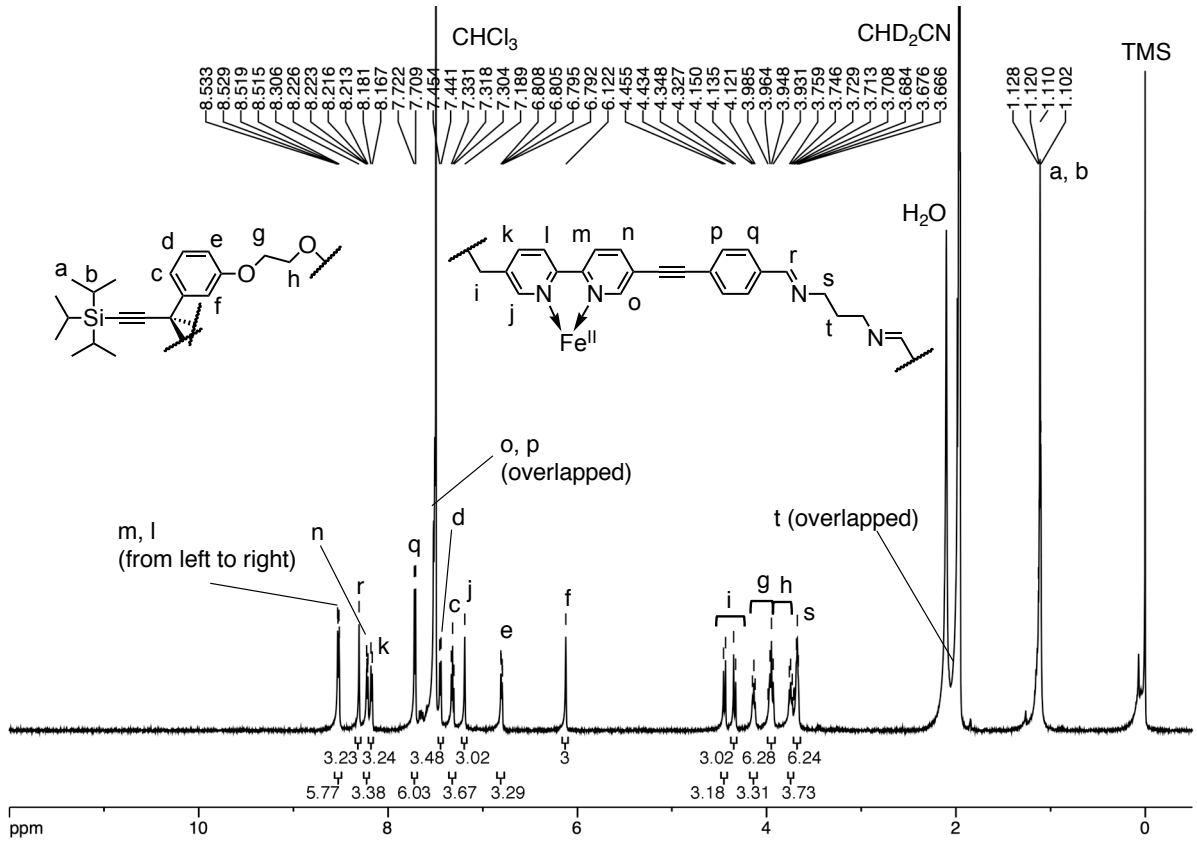


Figure S83. ^{1}H NMR spectrum of **D-PPD**$(PF_6)_4$ (600 MHz, $CD_3CN/CDCl_3$ = 1/1).

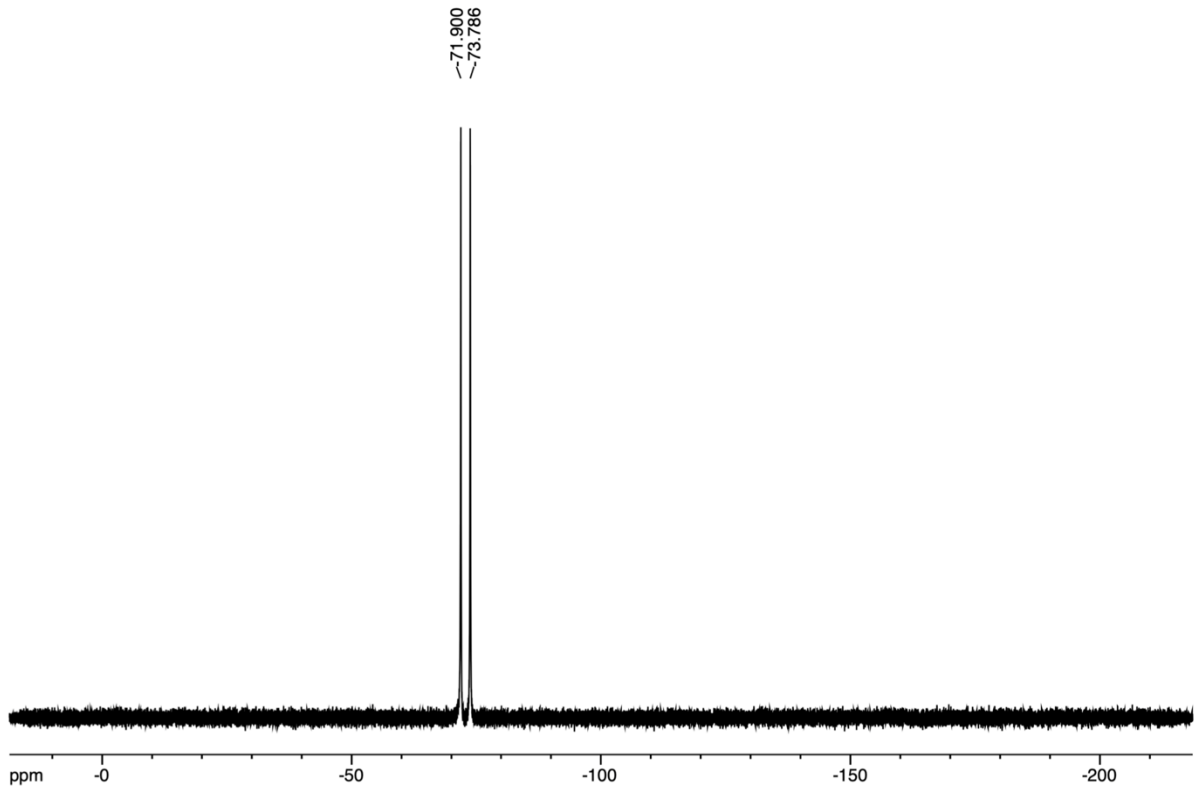


Figure S84. ^{19}F NMR spectrum of **D-PPD**$(PF_6)_4$ (376 MHz, $CD_3CN/CDCl_3$ = 1/1).

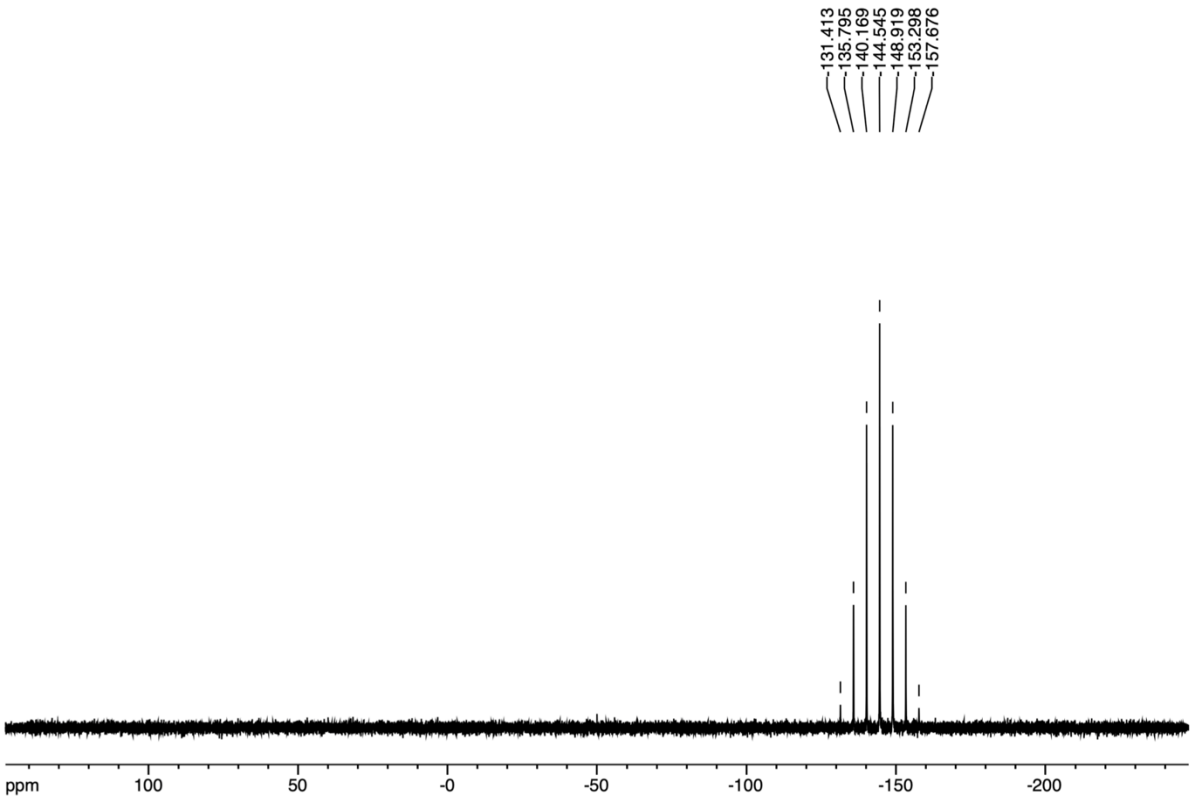


Figure S85. ^{31}P NMR spectrum of **D-PPD**$(PF_6)_4$ (162 MHz, $CD_3CN/CDCl_3$ = 1/1).

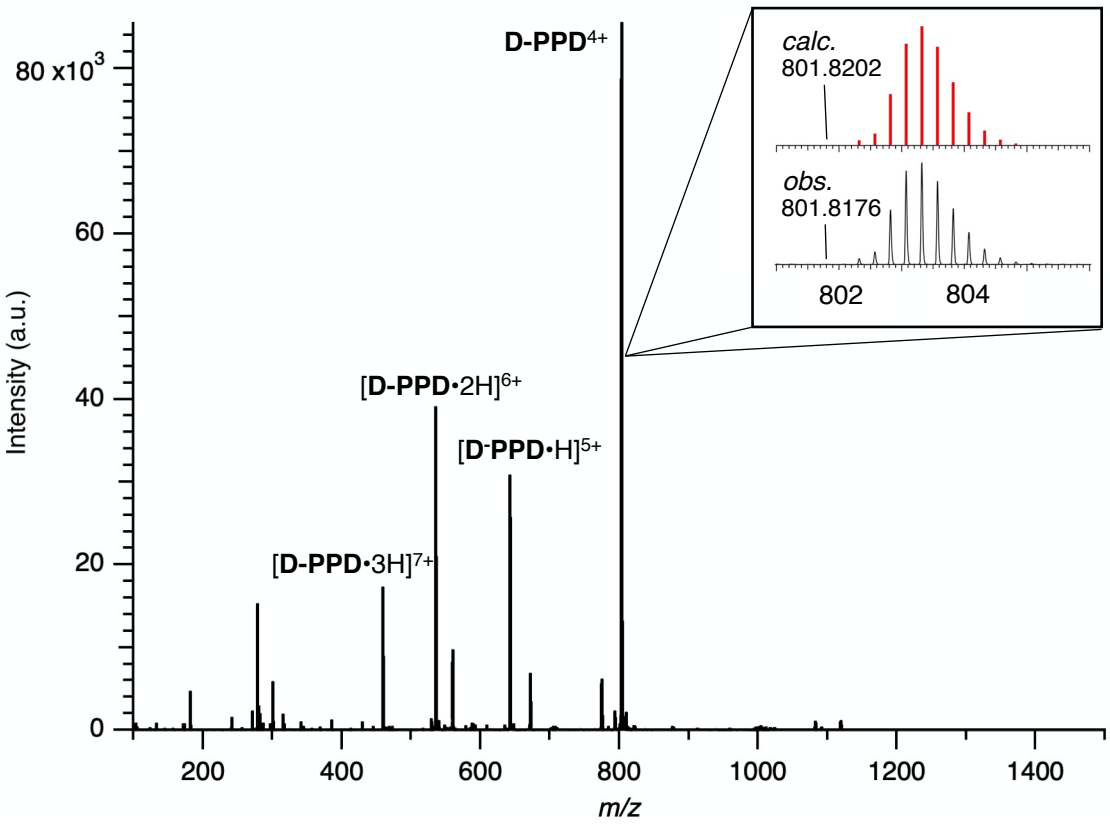


Figure S86. ESI mass spectrum of **D-PPD**$(PF_6)_4$ (solv. CH_3CN).

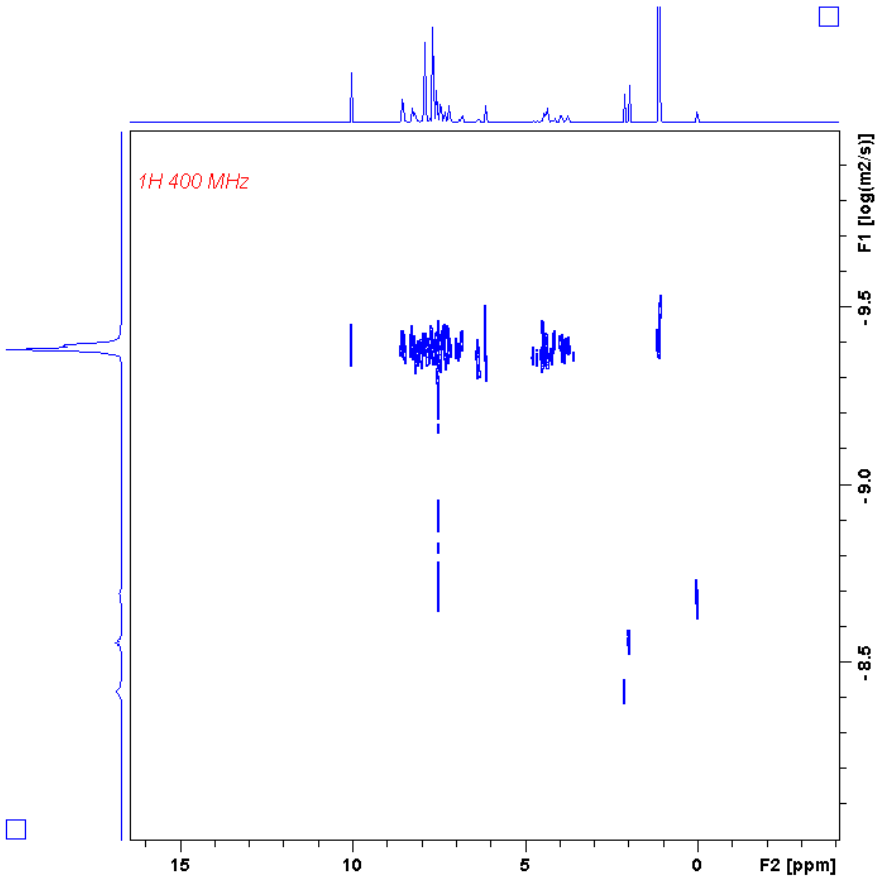


Figure S87. ^{1}H DOSY spectrum of **D-PPD**$(PF_6)_4$ (400 MHz, $CD_3CN/CDCl_3$ = 1/1).

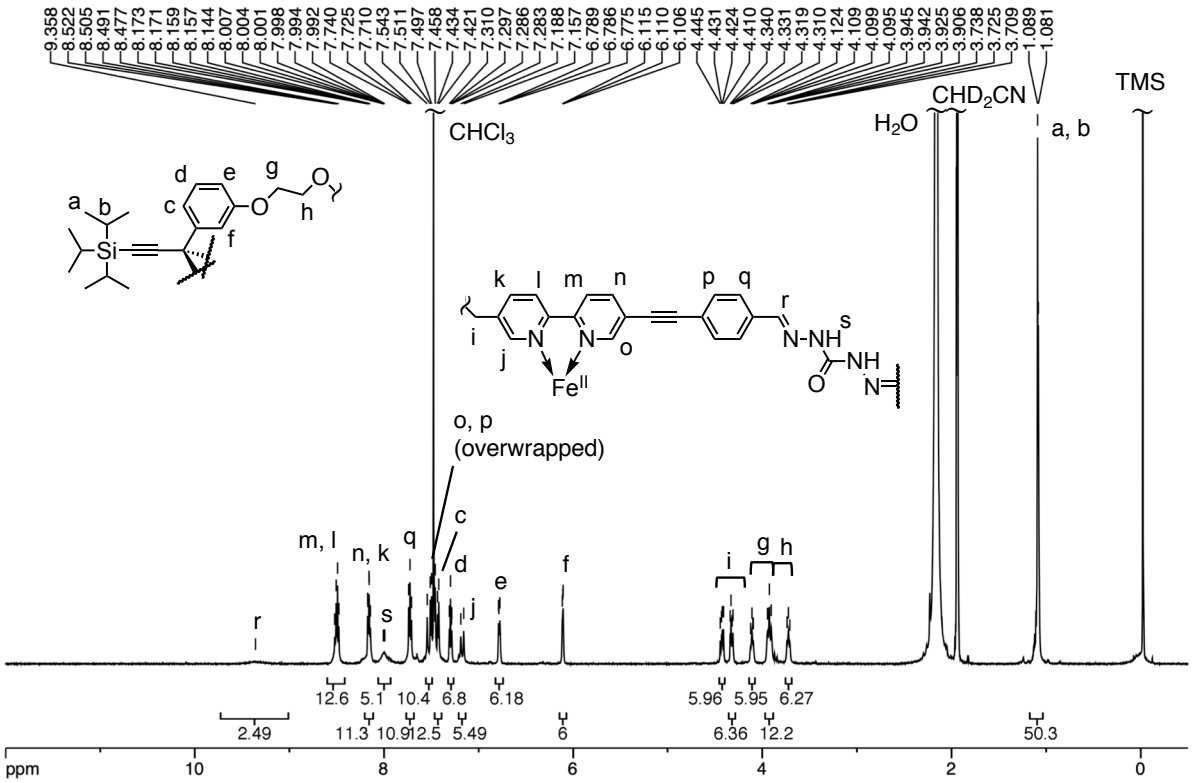


Figure S88. ^{1}H NMR spectrum of **D-CHZ**$(PF_6)_4$ (600 MHz, $CD_3CN/CDCl_3$ = 1/1).

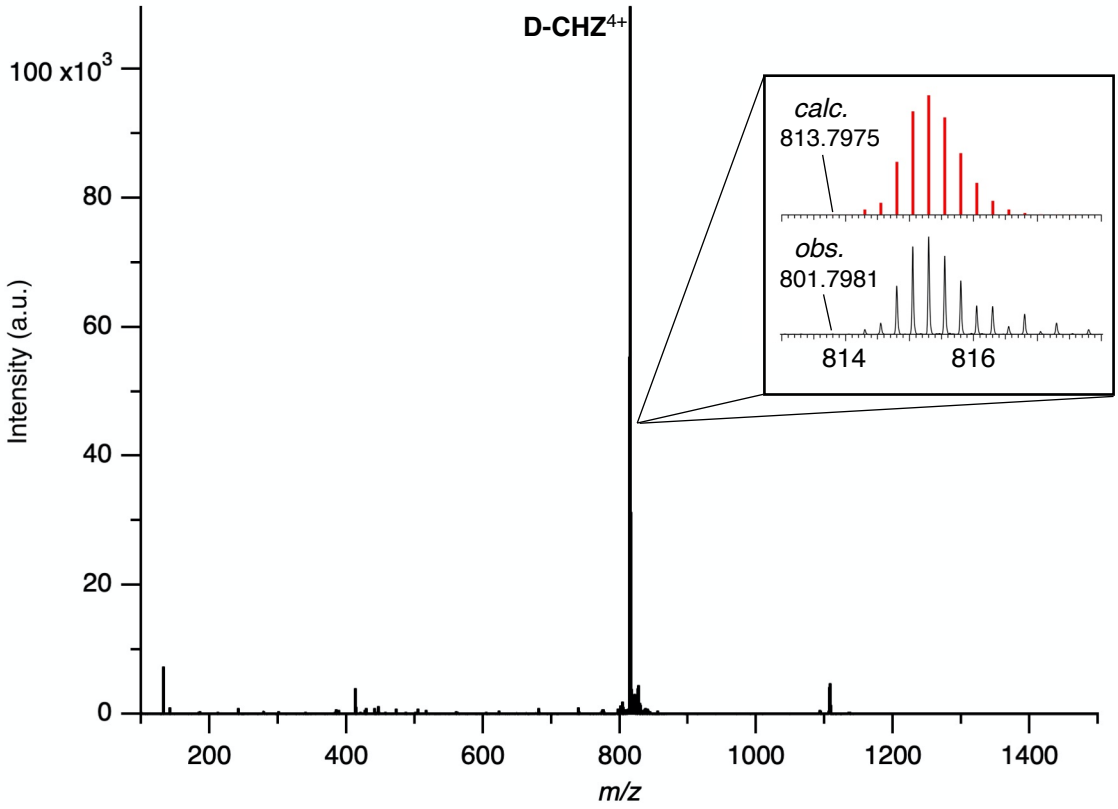


Figure S89. ESI mass spectrum of **D-CHZ**$(PF_6)_4$ (solv. CH_3CN).

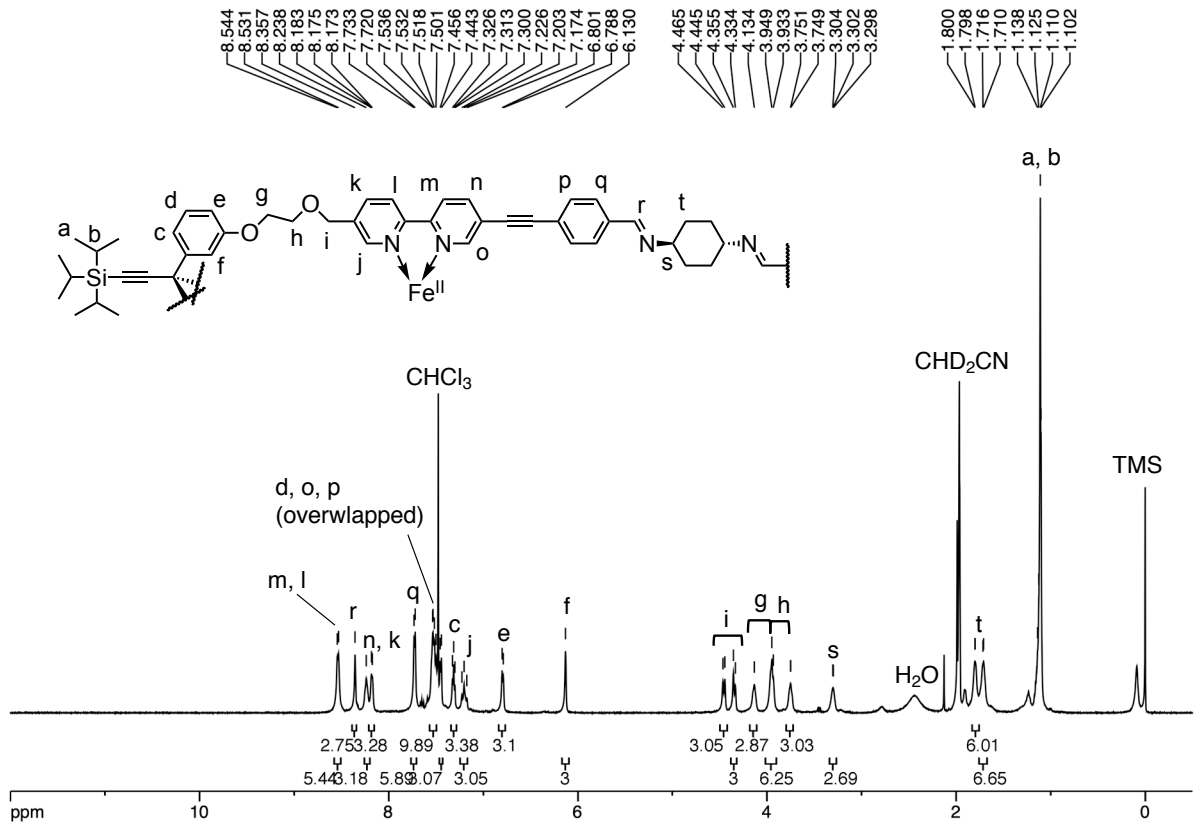


Figure S90. ^{1}H NMR spectrum of **T**$(PF_6)_8$ (600 MHz, $CD_3CN/CDCl_3$ = 1/1).

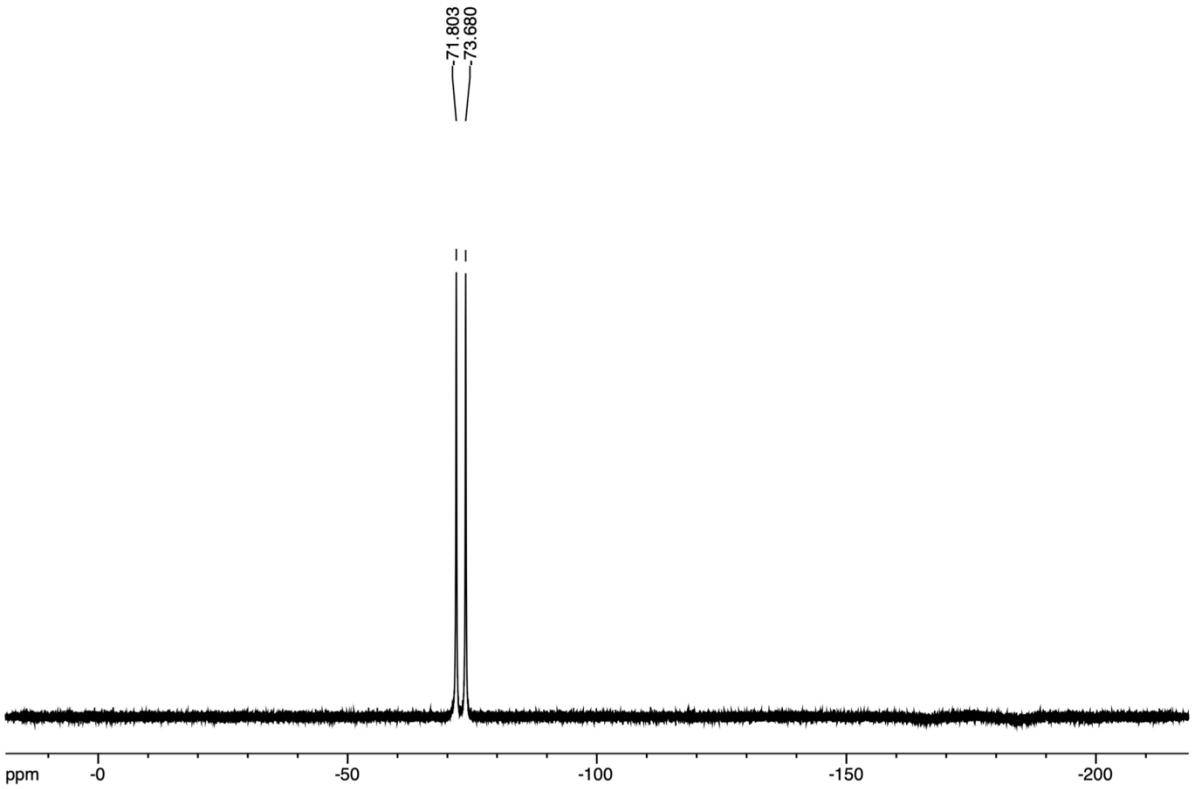


Figure S91. ^{19}F NMR spectrum of **T**$(PF_6)_8$ (376 MHz, $CD_3CN/CDCl_3$ = 1/1).

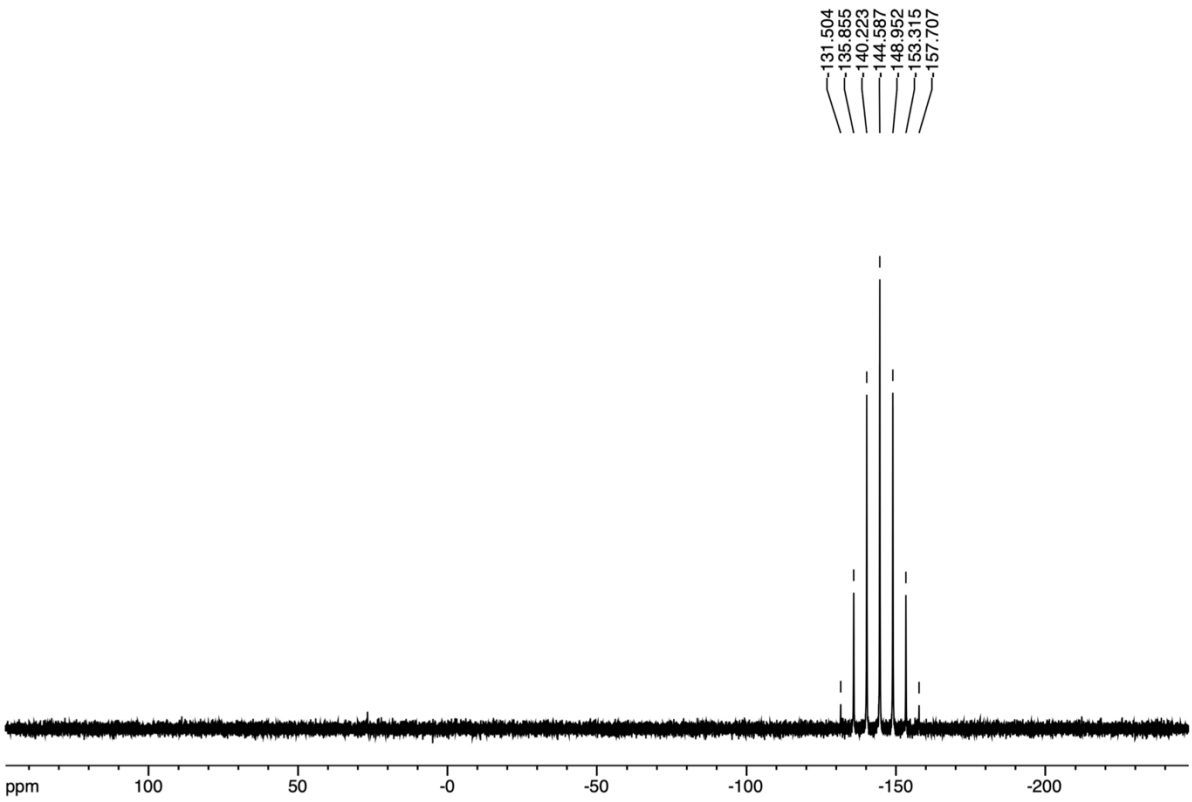


Figure S92. ^{31}P NMR spectrum of **T**$(PF_6)_8$ (162 MHz, $CD_3CN/CDCl_3$ = 1/1).

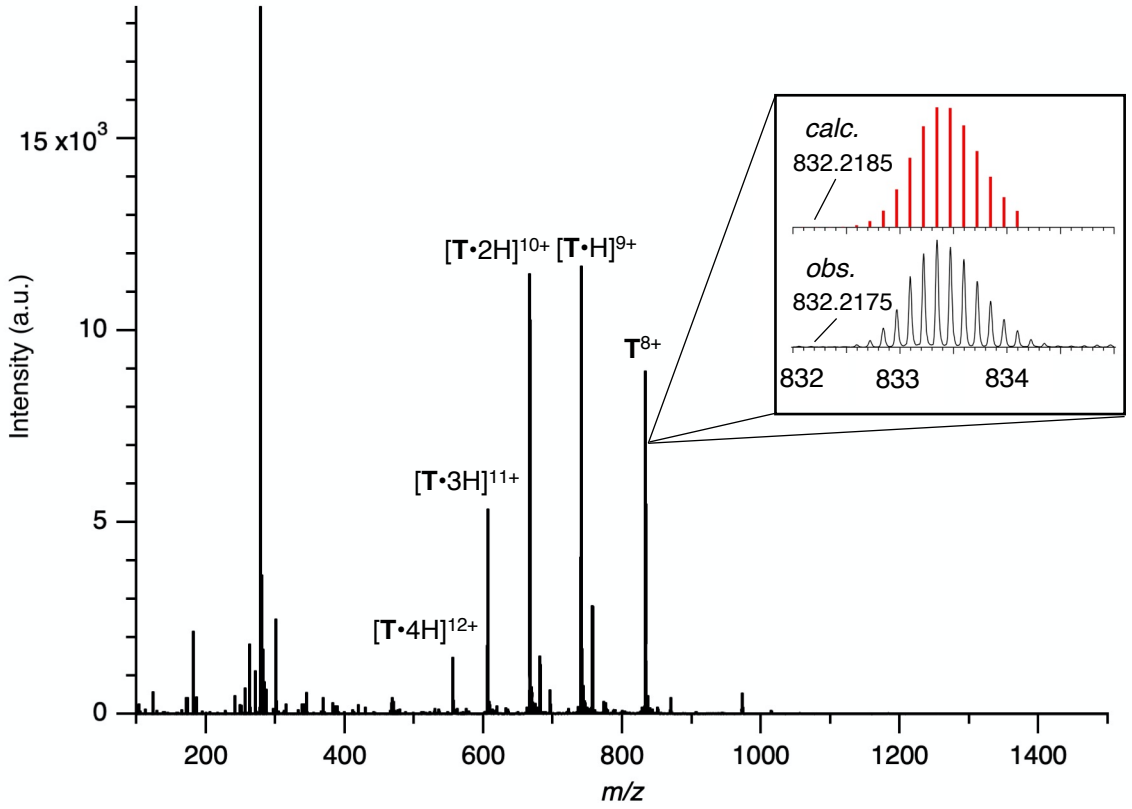


Figure S93. ESI mass spectrum of **T**$(PF_6)_8$ (solv. CH_3CN).

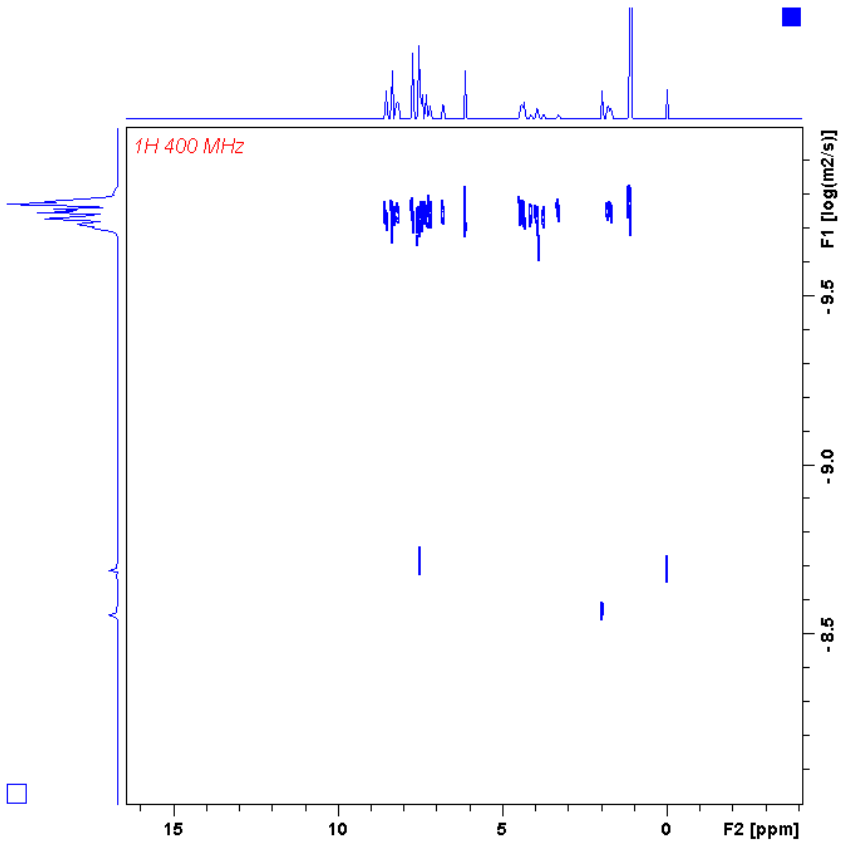


Figure S94. ^1H DOSY spectrum of **T**$(PF_6)_8$ (400 MHz, $CD_3CN/CDCl_3$ = 1/1).

Table S4. Diffusion constants determined by ^{1}H DOSY measurements and the hydrodynamic radii calculated by the Stokes-Einstein Equation.

Structure	Diffusion constant (m^2/s)	Hydrodynamic radius (Å)
[**2b**Fe]$(PF_6)_2$	4.0×10^{-10}	12
D-PPD$(PF_6)_4$	2.8×10^{-10}	17
T($PF_6)_8$	1.8×10^{-10}	25

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