The Supporting Information for

Exclusive Formation of a Meridional Complex of a Tripodand and Perfect Suppression of Guest Recognition

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Contents

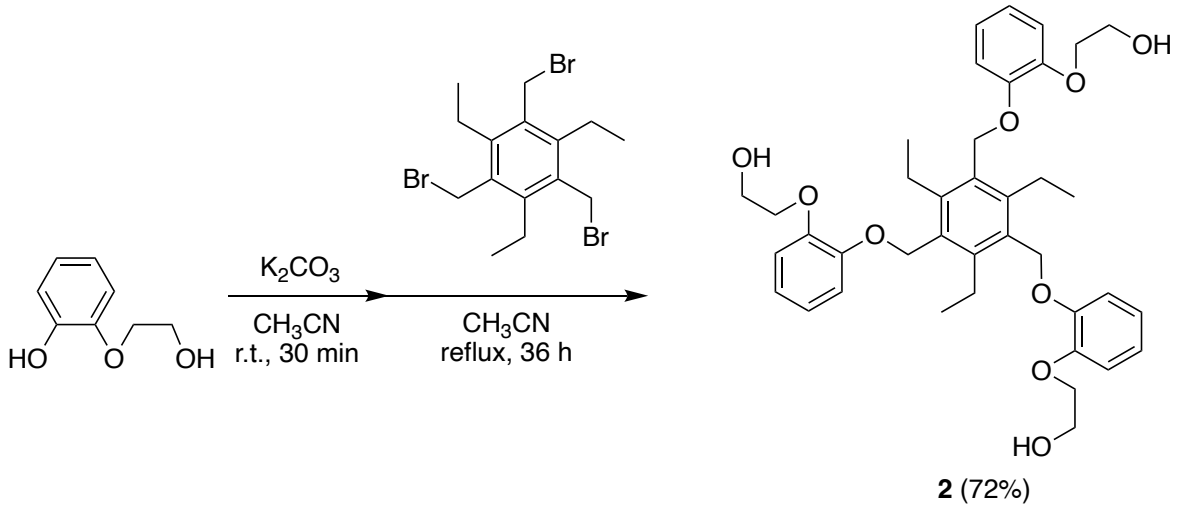
Materials and methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Co., Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Co., and used without further purification. THF was distilled from sodium benzophenone ketyl prior to use. Gel permeation chromatography (GPC) was performed by LC-908W with JAI gel 1H + 2H columns (Japan Analytical Industry) with chloroform as eluent.

Measurements were performed at 298 K unless otherwise noted. NMR spectra were recorded on Bruker AC300 or AV600 spectrometers. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ^{1}H and ^{13}C NMR measurements.

Single-crystal X-ray diffraction measurements were performed using Rigaku Mercury CCD with Mo*K*α radiation. ESI-TOF mass data were recorded on an Applied Biosystems QStar Pulsar i spectrometer. UV-vis spectra were recorded on a JASCO V-570 spectrometer. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba. We appreciate Mr. Ikuo Iida for the elemental analysis measurements.

Synthesis of tripodal ligand 1



Scheme S1. Synthesis of **2**

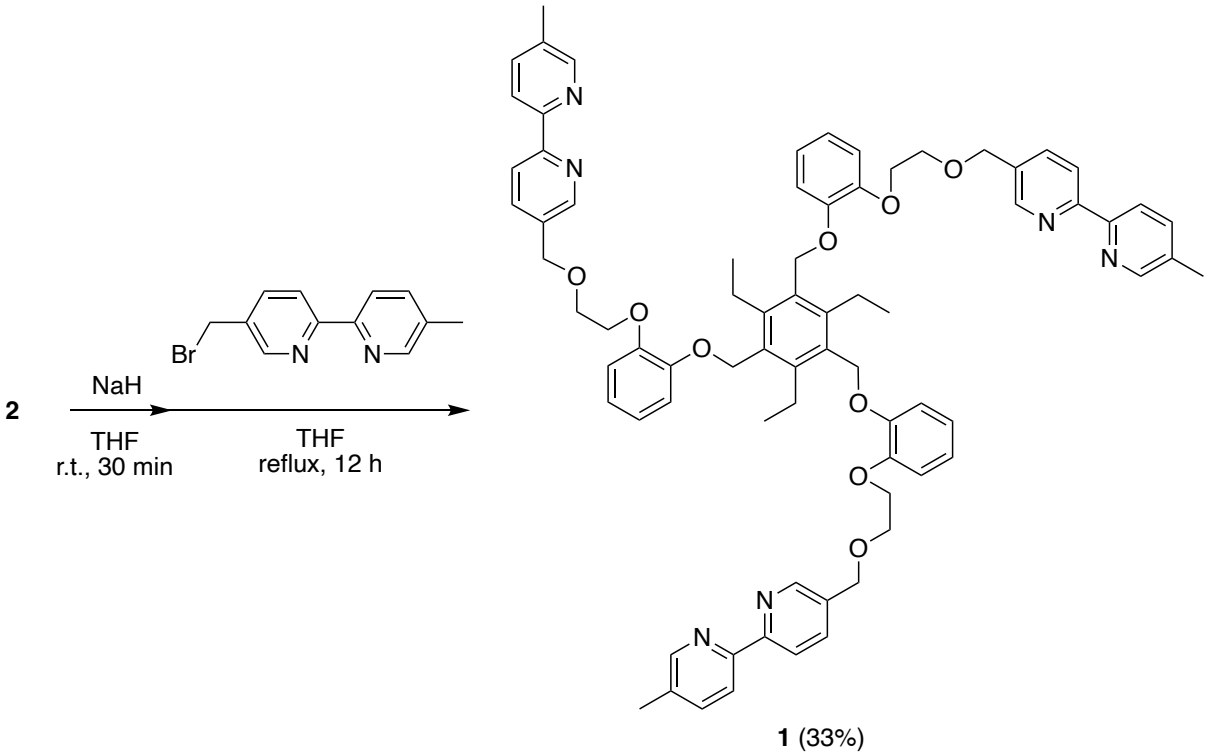
Synthesis of **2**

To a 10 mL CH_3CN solution of 2-(2-hydroxyethoxy)phenol[S1] (259 mg, 1.68 mmol) was added K_2CO_3 (119 mg, 0.86 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. Then, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene[S2] (222 mg, 0.50 mmol) was added, and the mixture was refluxed for 36 h under a nitrogen atmosphere. A small portion of water was added to the mixture, and then CH_3CN was removed under reduced pressure. Water was added to the residue, which was extracted by $CHCl_3$ (30 mL × 5). The organic layer was washed with sat. $NaHCO_3$ aq. and water, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: AcOEt/$CHCl_3$ = 3/1) to give **2** as a colorless solid (238 mg, 0.36 mmol, 72%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.15–7.12 (m, 3H), 7.04–6.92 (9H), 5.11 (s, 6H), 4.03–3.95 (9H), 3.81–3.77 (m, 6H), 2.88 (q, J = 7.5 Hz, 6H), 1.26 (t, J = 7.5 Hz, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.3, 149.1, 146.6, 130.9, 121.79, 121. 77, 115.0, 113.9, 71.4, 65.4, 61.0, 23.0, 16.6.

Elemental analysis: calcd. for $C_{39}H_{49}O_{9.5}$ (**2**·0.5H_2O): C, 69.93; H, 7.37. found: C, 69.90; H, 7.34.



Scheme S2. Synthesis of **1**

Synthesis of **1**

To a 10 mL dry THF solution of **2** (512.5 mg, 0.89 mmol) was added NaH (60% in oil, 351 mg, 8.7 mmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 30 min. Then, 5-bromomethyl-5′-methyl-2,2′-bipyridine[S3] (783.5 mg, 2.98 mmol) was added, and the mixture was refluxed for 12 h. $NaHCO_3$ aqueous solution was added to the mixture, and then THF was removed under reduced pressure. Water was added to the residue, which was extracted by $CHCl_3$ (30 mL × 5). The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (NH_2 silica gel, eluent: $CHCl_3$/toluene = 3/1), GPC, and further column chromatography (basic alumina, eluent: $CHCl_3$) to give **1** as a pale yellow solid (356 mg, 0.295 mmol, 33%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.48–8.45 (6H), 8.26–8.19 (6H), 7.63–7.57 (6H), 7.03–7.00 (m, 3H), 6.95–6.91 (9H), 5.01 (s, 6H), 4.55 (s, 6H), 4.15 (t, J = 4.8 Hz, 6H), 3.77 (t, J = 4.8 Hz, 6H), 2.85 (q, J = 7.4 Hz, 6H), 2.38 (s, 9H), 1.19 (t, J = 7.4 Hz, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.5, 153.6, 149.6, 149.4, 149.3, 148.5, 146.4, 137.4, 136.4, 133.5, 133.3, 131.0, 121.7, 121.5, 120.6, 120.3, 114.7, 113.6, 70.6, 69.1, 68.7, 65.7, 23.1, 18.4, 16.6.

Elemental analysis: calcd. for $C_{75}H_{80}N_6O_{10}$ (**1**·H_2O): C, 73.51; H, 6.58; N, 6.86. found: C, 73.21; H, 6.52; N, 6.51.

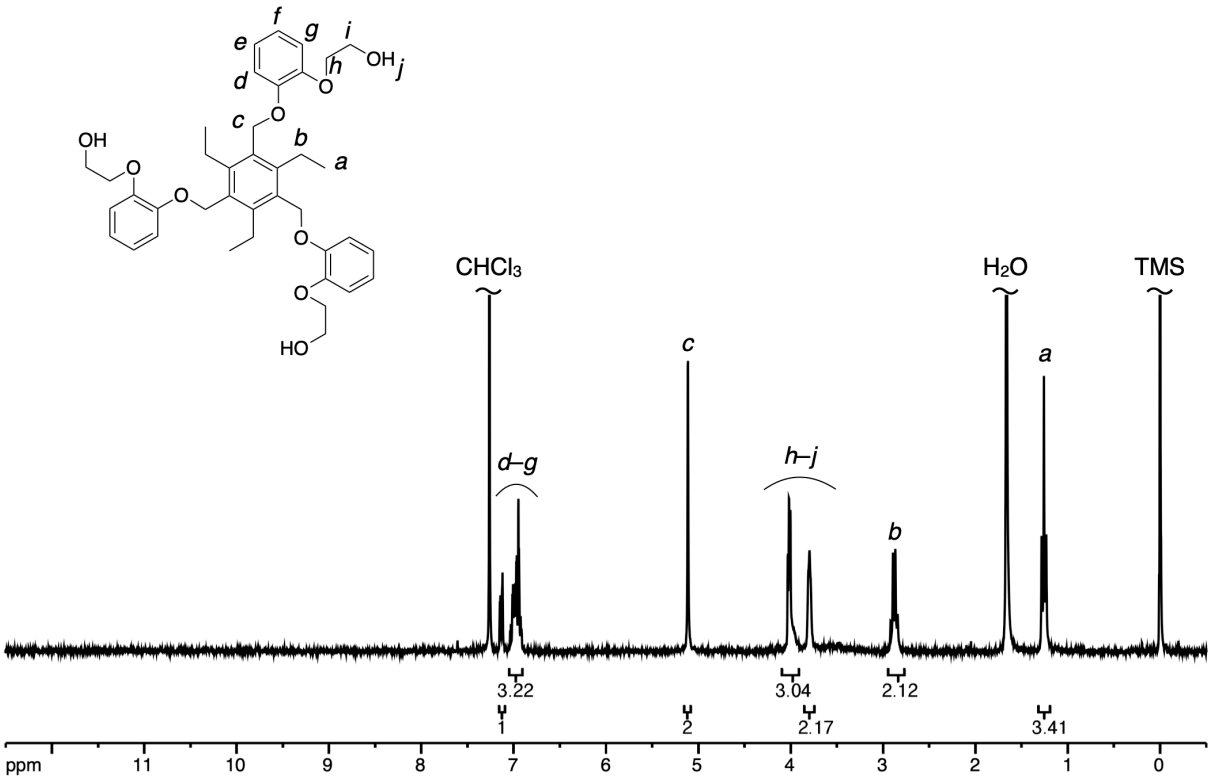


Figure S1. ^{1}H NMR spectrum of **2** ($CDCl_3$, 300 MHz).

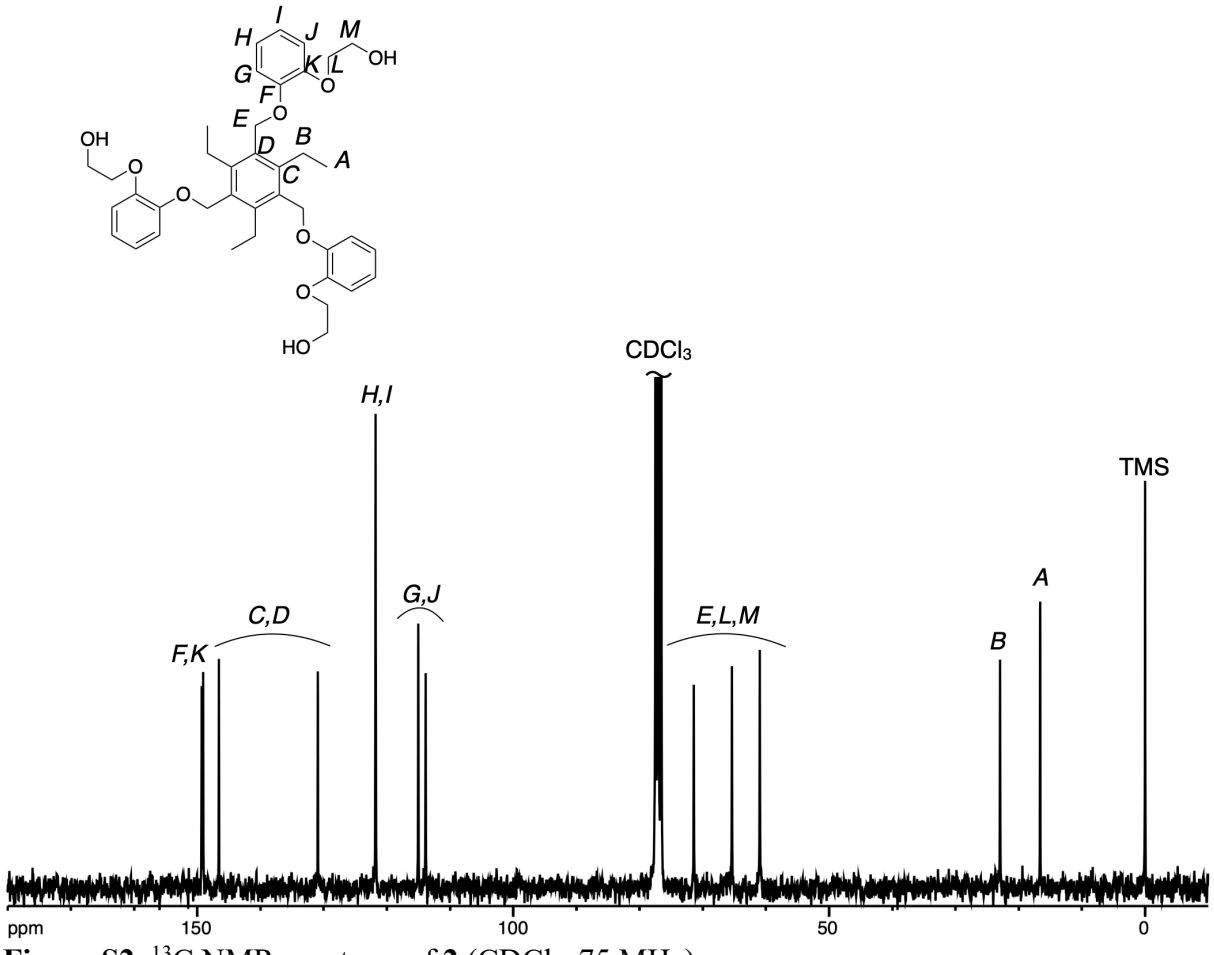


Figure S2. ^{13}C NMR spectrum of **2** ($CDCl_3$, 75 MHz).

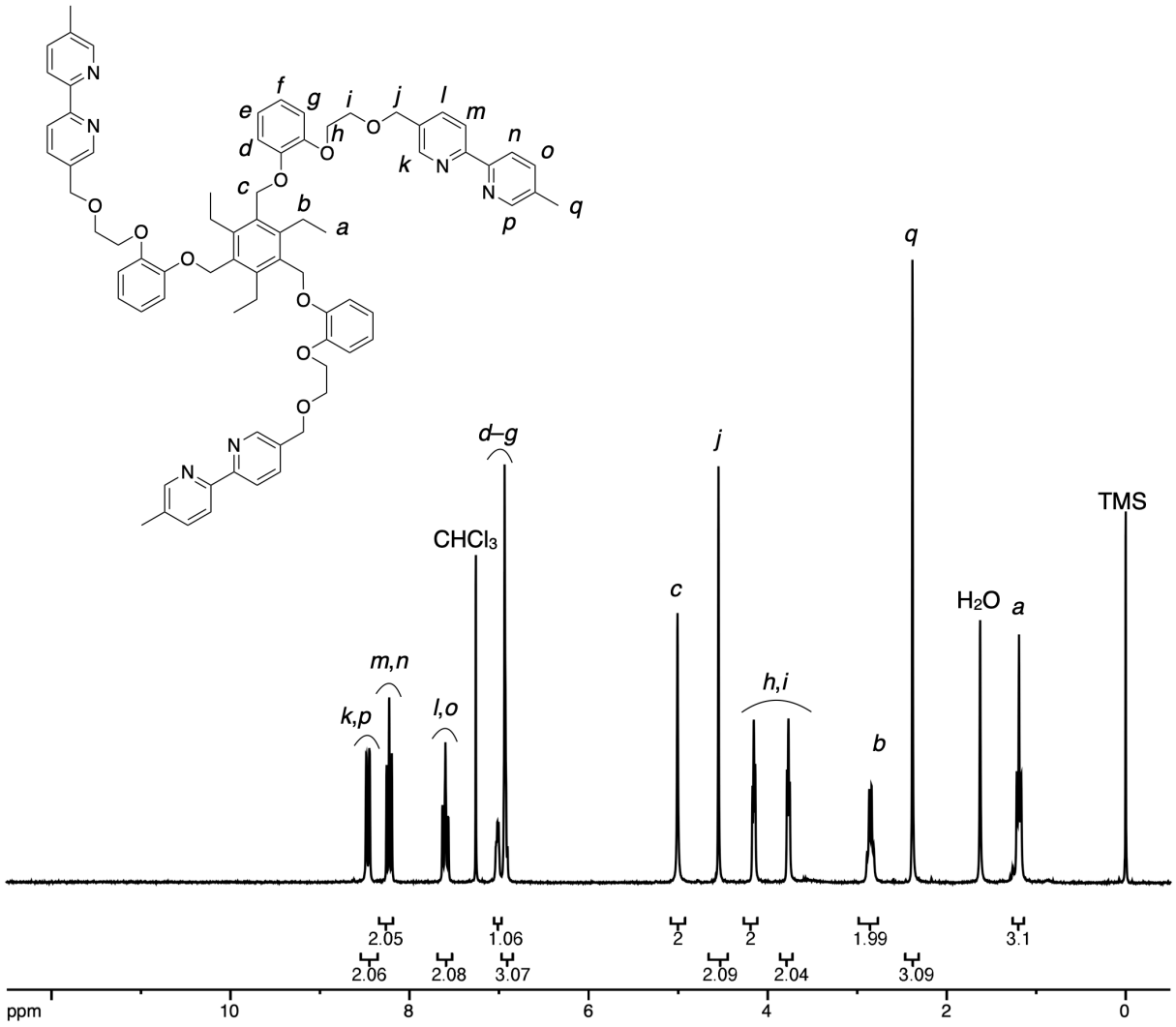


Figure S3. ^{1}H NMR spectrum of **1** ($CDCl_3$, 300 MHz).

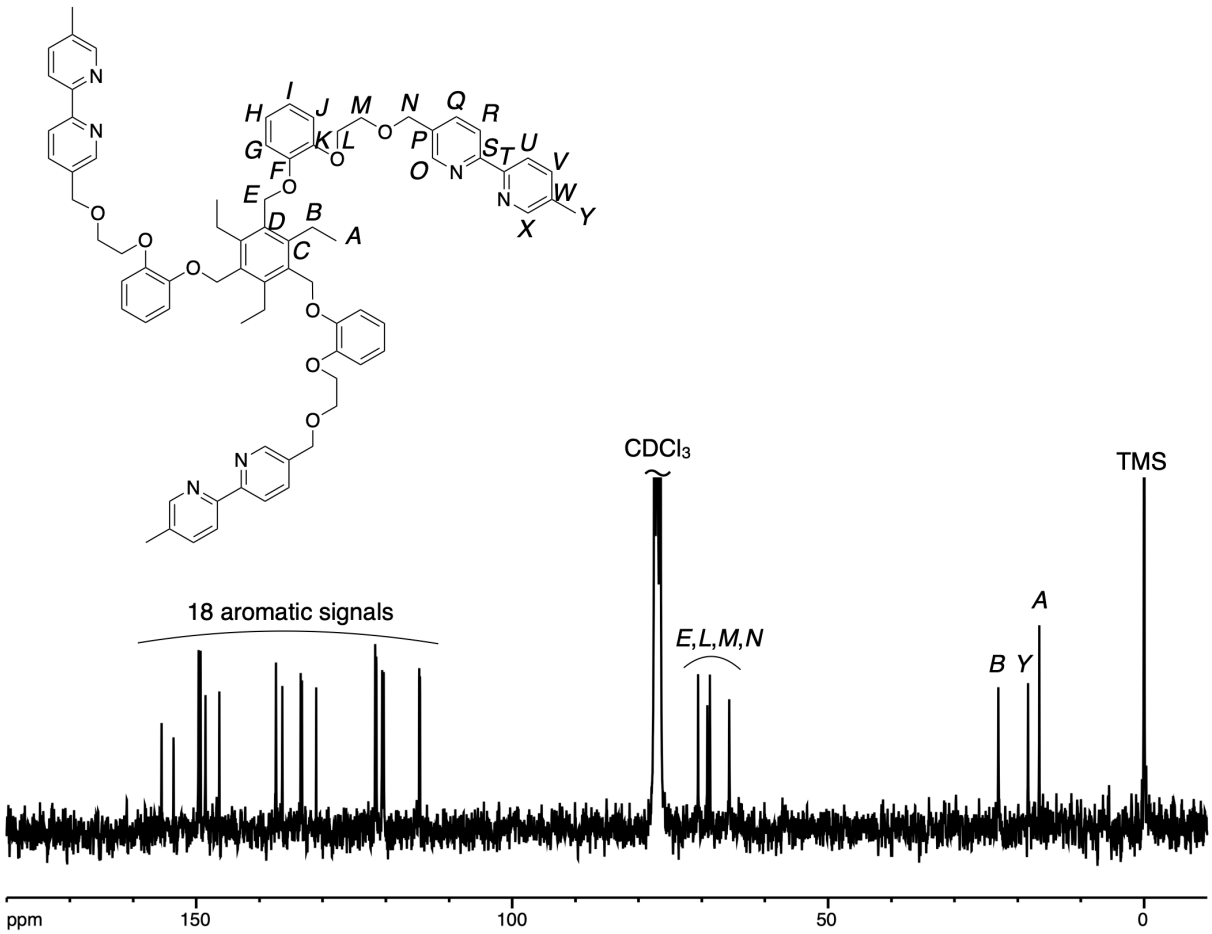


Figure S4. ^{13}C NMR spectrum of **1** ($CDCl_3$, 75 MHz).

Titration experiments and NMR analyses of 1 and *mer*-$[Fe\cdot 1]^{2+}$

Experimental procedure for the ^{1}H NMR titration experiment of NH_4ClO_4 and ligand **1**

The ligand **1** (24.45 mg, 20.26 μmol) was dissolved in $CHCl_3$, and a 4.05 mM $CHCl_3$ solution of **1** was prepared in a 5 mL volumetric flask. NH_4ClO_4 (15.86 mg, 135.0 μmol) was dissolved in CH_3CN, and a 5.40 mM CH_3CN solution of **1** was prepared in a 25 mL volumetric flask. 200 μL of the solution of **1** (0.81 μmol) was added to 11 NMR tubes. The solution of NH_4ClO_4 was added to each NMR tube with a ratio of $[NH_4^+]/[\mathbf{1}]$ = 0, 0.20, 0.50, 0.80, 0.90, 1.0, 1.1, 1.2, 1.5, 2.0, 4.0, respectively. The solvents were removed under reduced pressure, and the samples were dried in vacuo for 3 h. $CDCl_3$ (270 μL) and CD_3CN (270 μL) were added to each NMR tube ([**1**] = 1.50 mM), and ^{1}H NMR measurements were performed. The binding constant between **1** and NH_4 was evaluated from the least square fitting of the chemical shift changes of signals *a*, *b*, *c*, *j*, and *q* (see Figure S5 for the assignment).

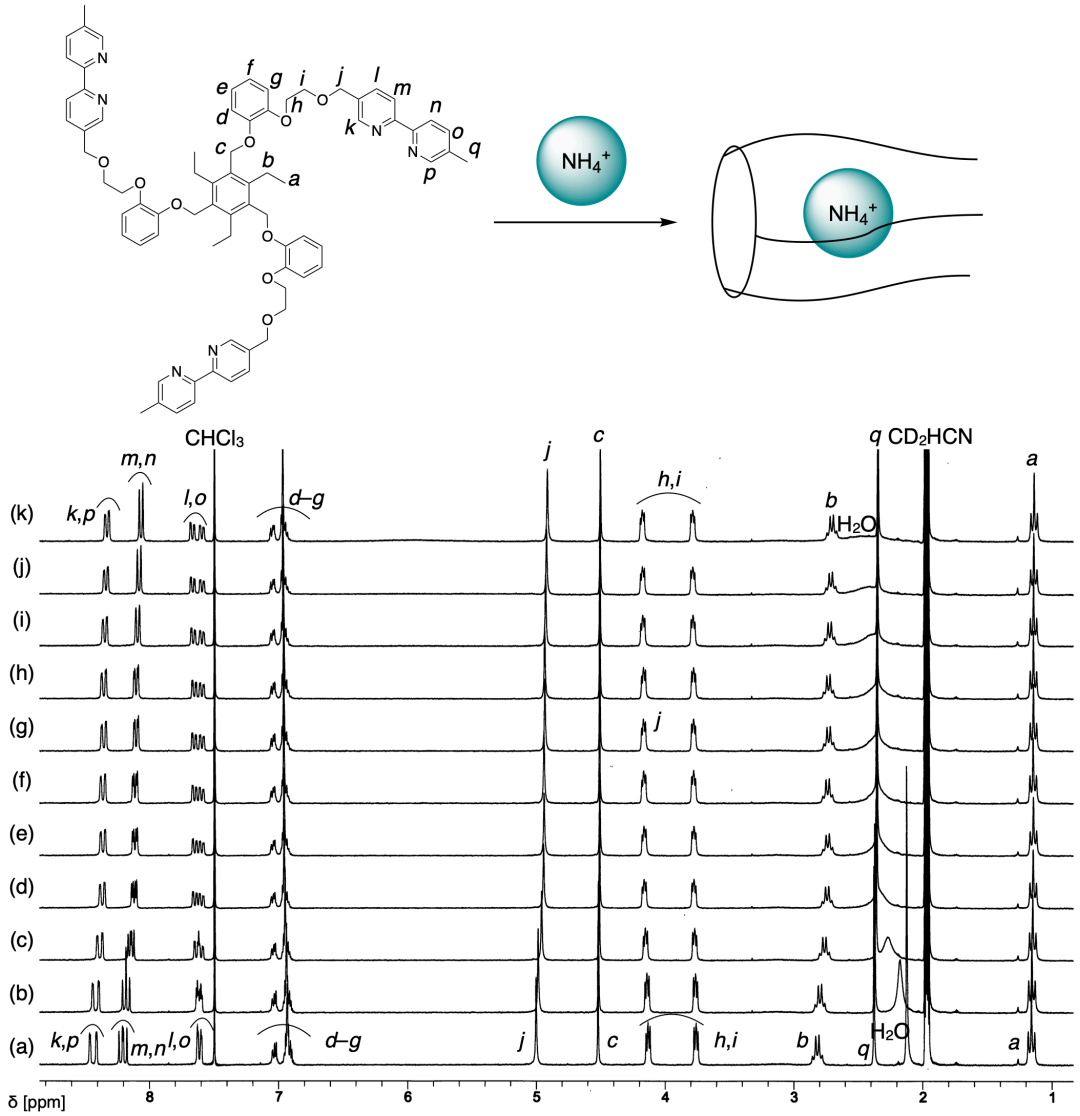


Figure S5. A titration experiment of ligand **1** and NH_4ClO_4 (^{1}H NMR, $CDCl_3/CD_3CN$ = 1/1, 300 MHz, [**1**] = 1.5 mM). (a) **1**. (b)–(k) **1** + NH_4ClO_4. (b) NH_4ClO_4 0.20 equiv. (c) 0.50 equiv. (d) 0.80 equiv. (e) 0.90 equiv. (f) 1.0 equiv. (g) 1.1 equiv. (h) 1.2 equiv. (i) 1.5 equiv. (j) 2.0 equiv. (k) 4.0 equiv.

Experimental procedure for the UV-vis titration experiment of ligand **1** and $FeCl_2$

The ligand **1** (22.45 mg, 18.75 μmol) was dissolved in $CHCl_3$, and a 3.75 mM $CHCl_3$ solution of **1** was prepared in a 5 mL volumetric flask. 2.50 mL of this solution was transferred to a 25 mL volumetric flask, and a 375 μM $CHCl_3$ solution of **1** was prepared. $FeCl_2 \cdot 4H_2O$ (24.85 mg, 125.0 μmol) was dissolved in degassed CH_3OH, and a 2.50 mM CH_3OH solution of $FeCl_2$ was prepared in a 50 mL volumetric flask. 1.00 mL of the $CHCl_3$ solution of **1** (0.375 μmol) was added to eleven 5 mL volumetric flasks. The CH_3OH solution of $FeCl_2$ was added to each flask with a ratio of $[Fe^{2+}]/[\mathbf{1}]$ = 0, 0.20, 0.50, 0.80, 0.90, 1.0, 1.1, 1.2, 1.5, 2.0, 3.0, respectively. The solutions were diluted with CH_3OH up to 5 mL to prepare the sample solutions ([**1**] = 75 μM, $CHCl_3/CH_3OH$ = 1/4), and UV-vis measurements were performed.

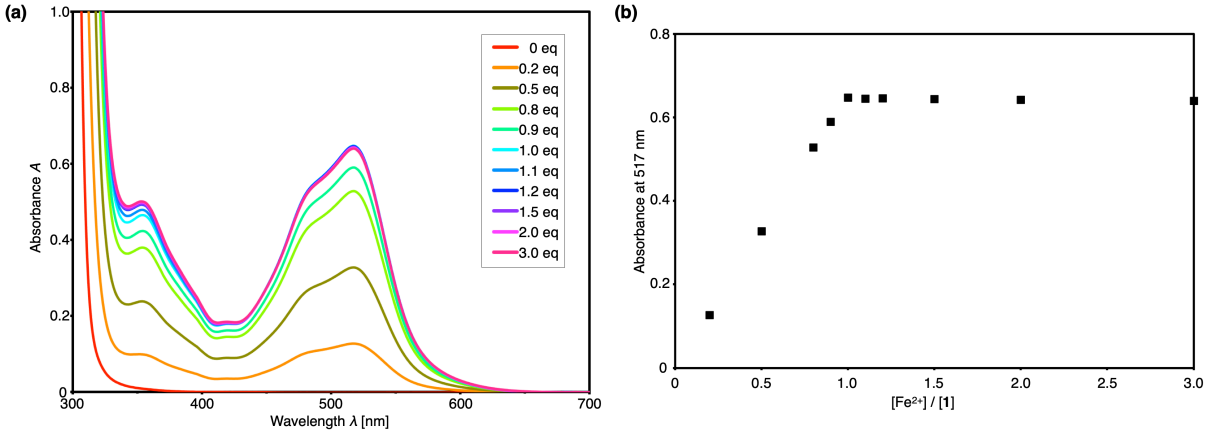


Figure S6. A titration experiment of **1** and $FeCl_2$ (UV-vis, $CHCl_3/CH_3OH$ = 1/4, [**1**] = 75 μM, l = 1.0 cm). (a) UV-vis spectral change. (b) Plot of absorbance at 517 nm upon the addition of $FeCl_2$.

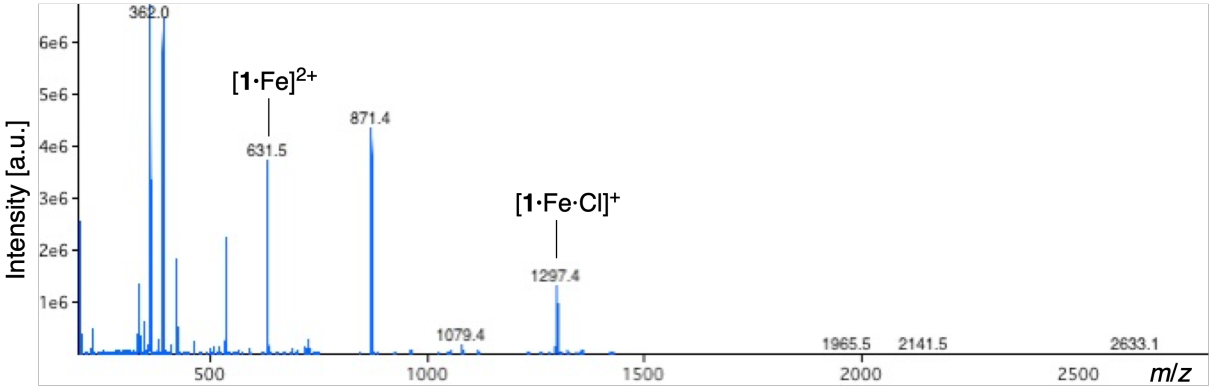


Figure S7. ESI TOF mass spectrum of $[Fe\cdot\mathbf{1}]Cl_2$.

Experimental procedure for the ^{1}H NMR titration experiment of ligand **1** and $Fe(BF_4)_2$

The ligand **1** (24.45 mg, 20.26 μmol) was dissolved in $CHCl_3$, and a 4.05 mM $CHCl_3$ solution of **1** was prepared in a 5 mL volumetric flask. $Fe(BF_4)_2 \cdot 6H_2O$ (45.56 mg, 135.0 μmol) was dissolved in degassed CH_3OH, and a 5.4 mM CH_3OH solution of $Fe(BF_4)_2$ was prepared in a 25 mL volumetric flask. 200 μL of the solution of **1** (0.81 μmol) was added to 8 NMR tubes. The solution of $Fe(BF_4)_2$ was added to each NMR tube with a ratio of $[Fe^{2+}]/[\mathbf{1}] = 0$, 0.20, 0.50, 0.80, 0.90, 1.0, 1.1, 1.2, respectively. The solvents were removed under nitrogen gas flow, and the samples were dried in vacuo for 3 h. $CDCl_3$ (540 μL) was added to each NMR tube ([**1**] = 1.50 mM), and ^{1}H NMR measurements were performed.

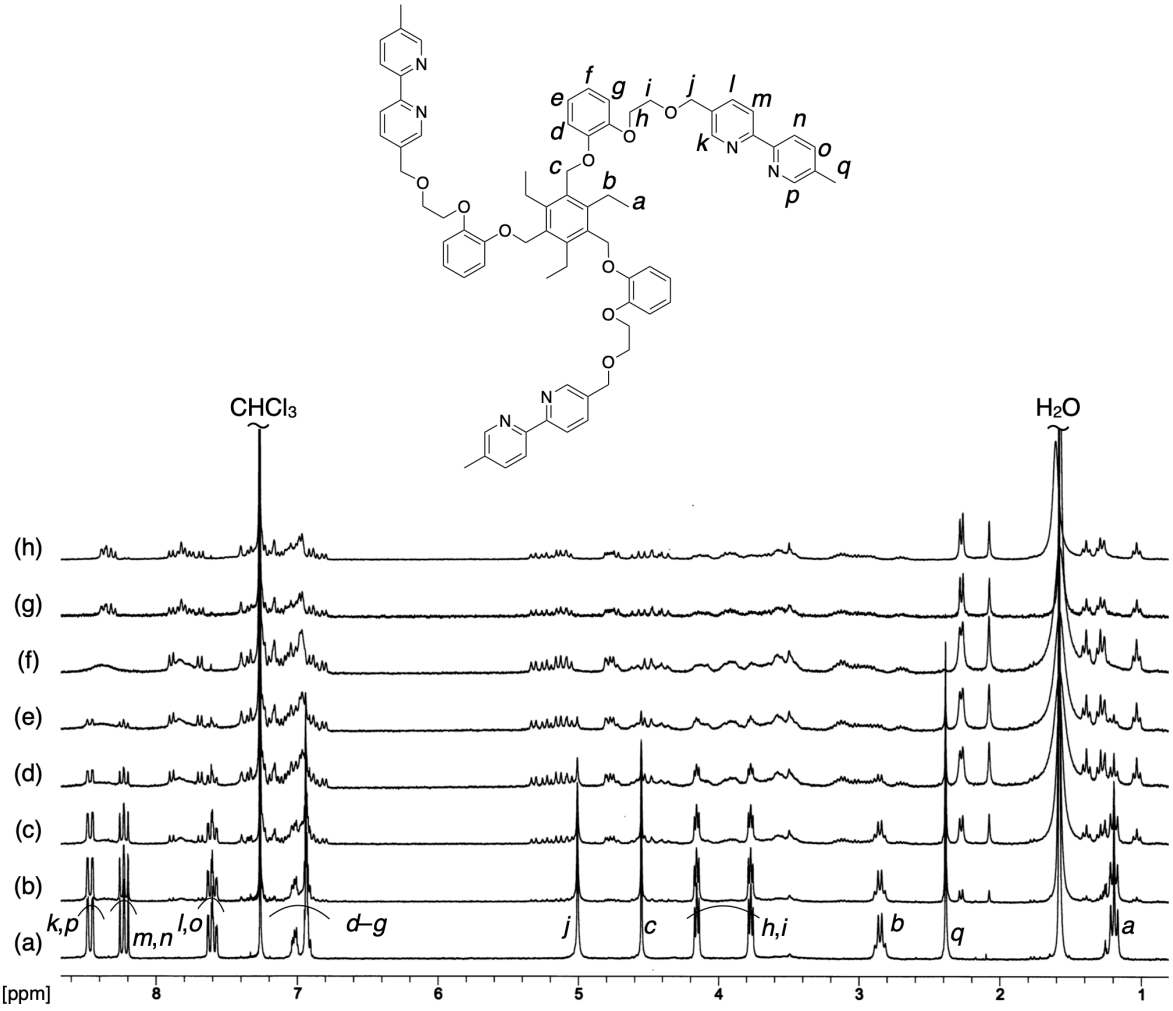


Figure S8. A titration experiment of **1** and $Fe(BF_4)_2$ (^{1}H NMR, $CDCl_3$, 300 MHz, [**1**] = 1.5 mM). (a) **1**. (b)–(h) **1** + $Fe(BF_4)_2$. (b) $Fe(BF_4)_2$ 0.20 equiv. (c) 0.50 equiv. (d) 0.80 equiv. (e) 0.90 equiv. (f) 1.0 equiv. (g) 1.1 equiv. (h) 1.2 equiv.

NMR analyses of [Fe·**1**]$(BF_4)_2$

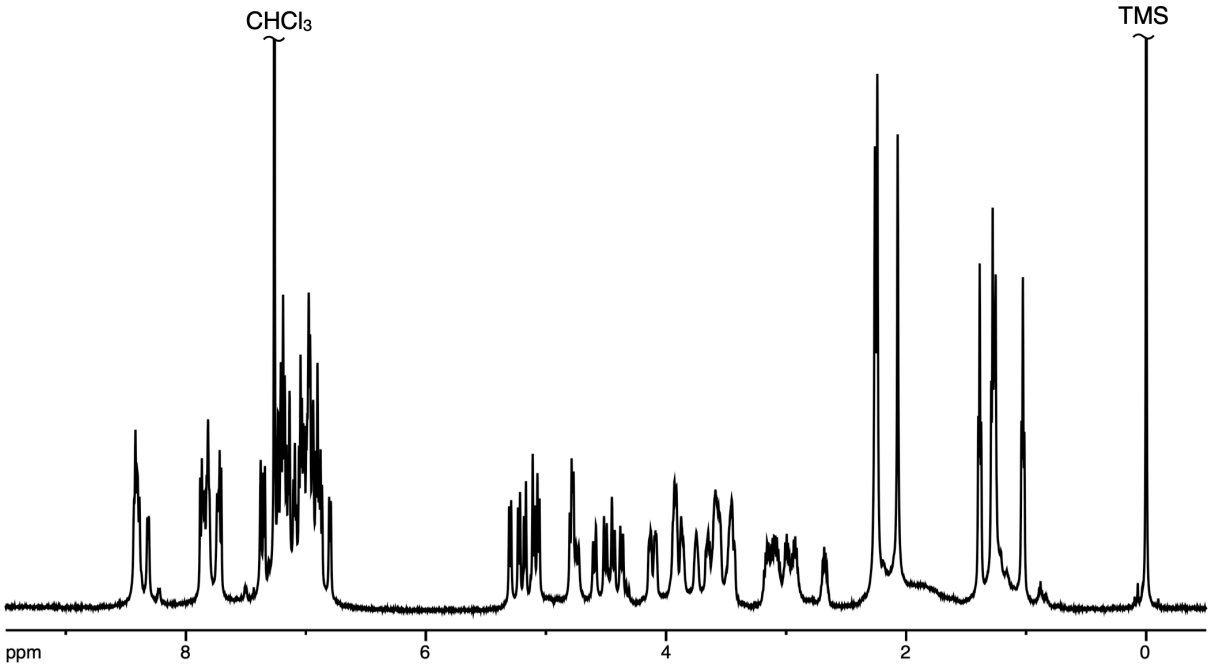


Figure S9. ^{1}H NMR spectrum of [Fe·**1**]$(BF_4)_2$ ($CDCl_3$, 600 MHz).

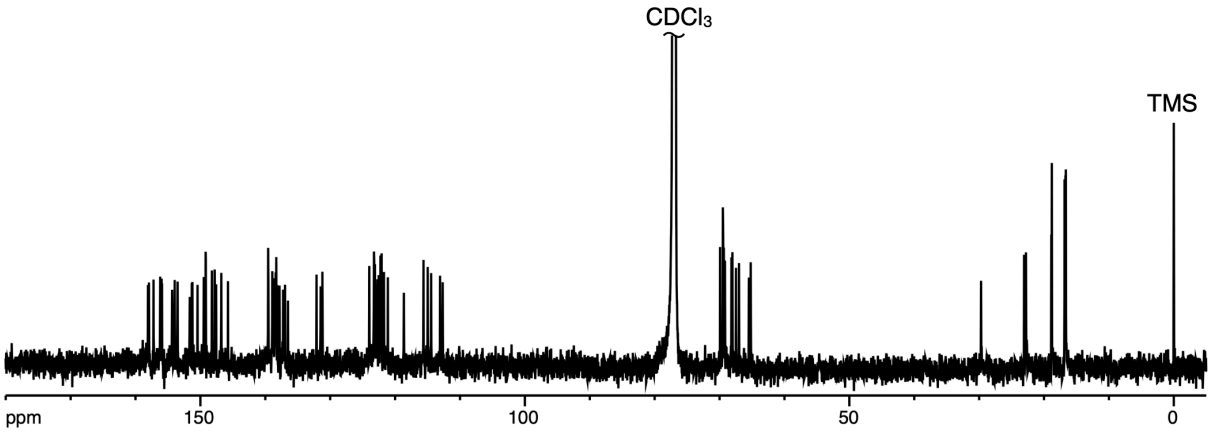


Figure S10. ^{13}C NMR spectrum of [Fe·**1**]$(BF_4)_2$ ($CDCl_3$, 151 MHz).

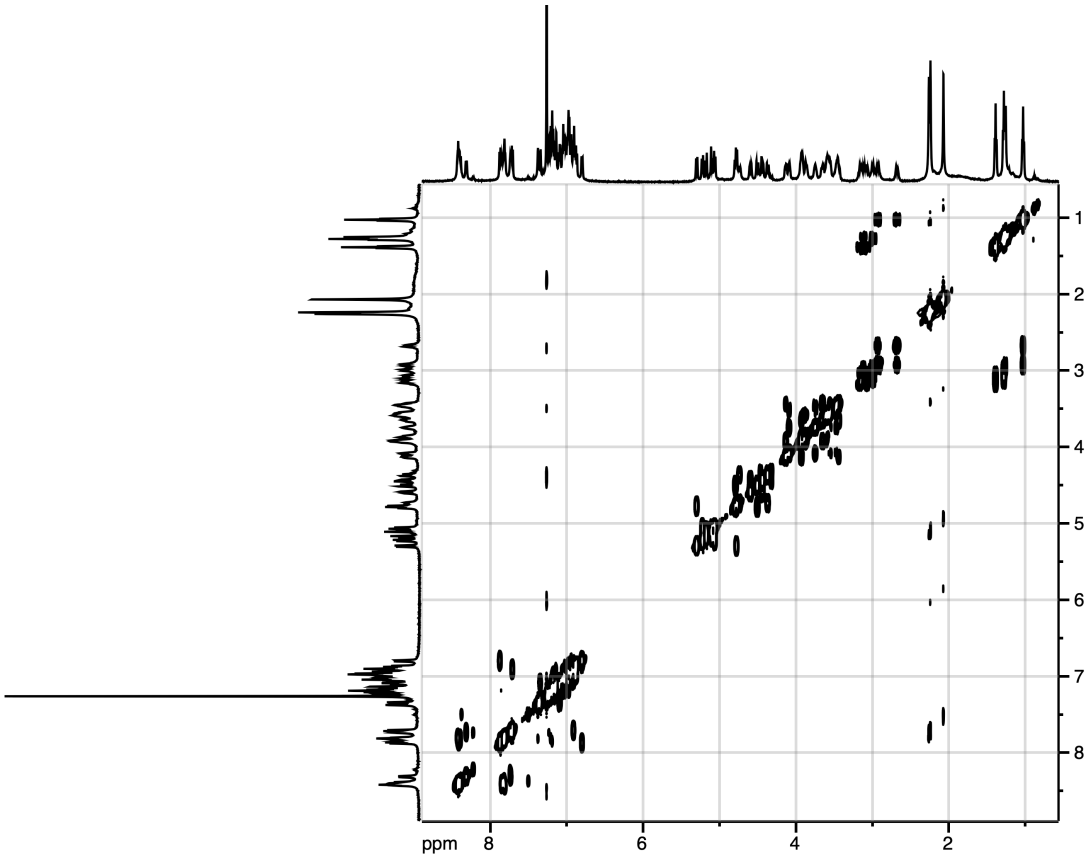


Figure S11. ^{1}H-^{1}H COSY spectrum of [Fe·**1**](BF$_4$)$_2$ (CDCl$_3$, 600 MHz).

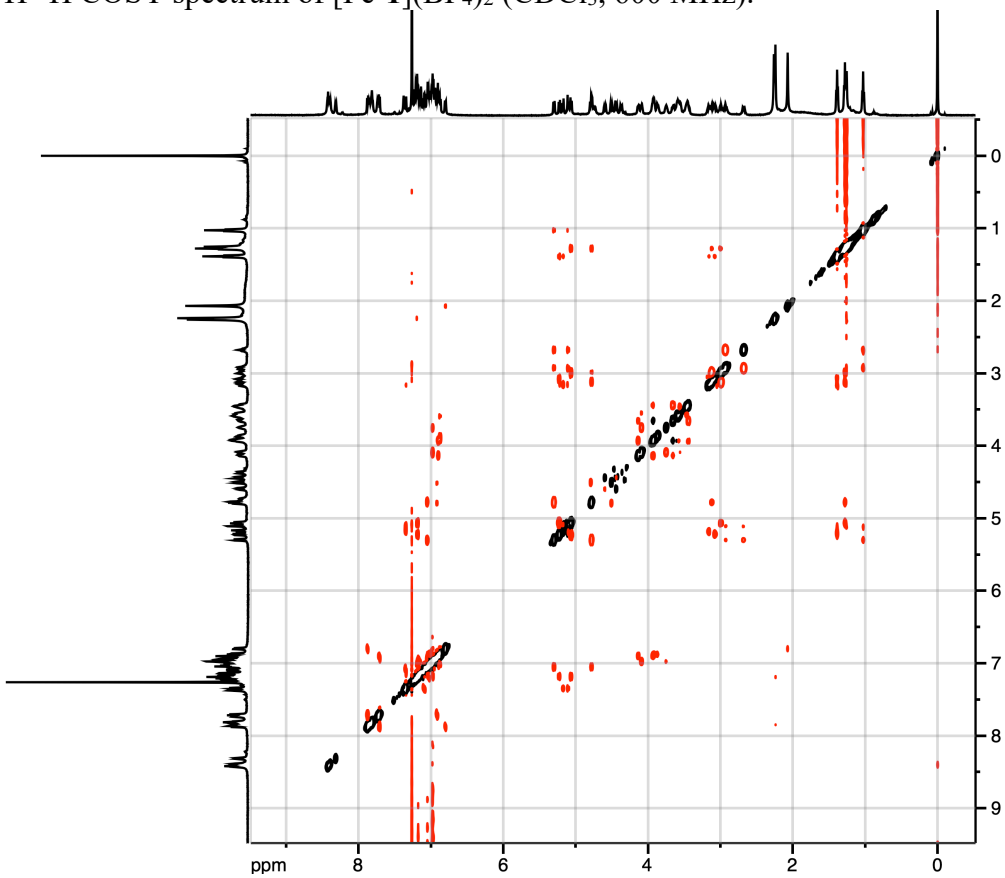


Figure S12. ^{1}H-^{1}H ROESY spectrum of [Fe·**1**](BF$_4$)$_2$ (CDCl$_3$, 600 MHz).

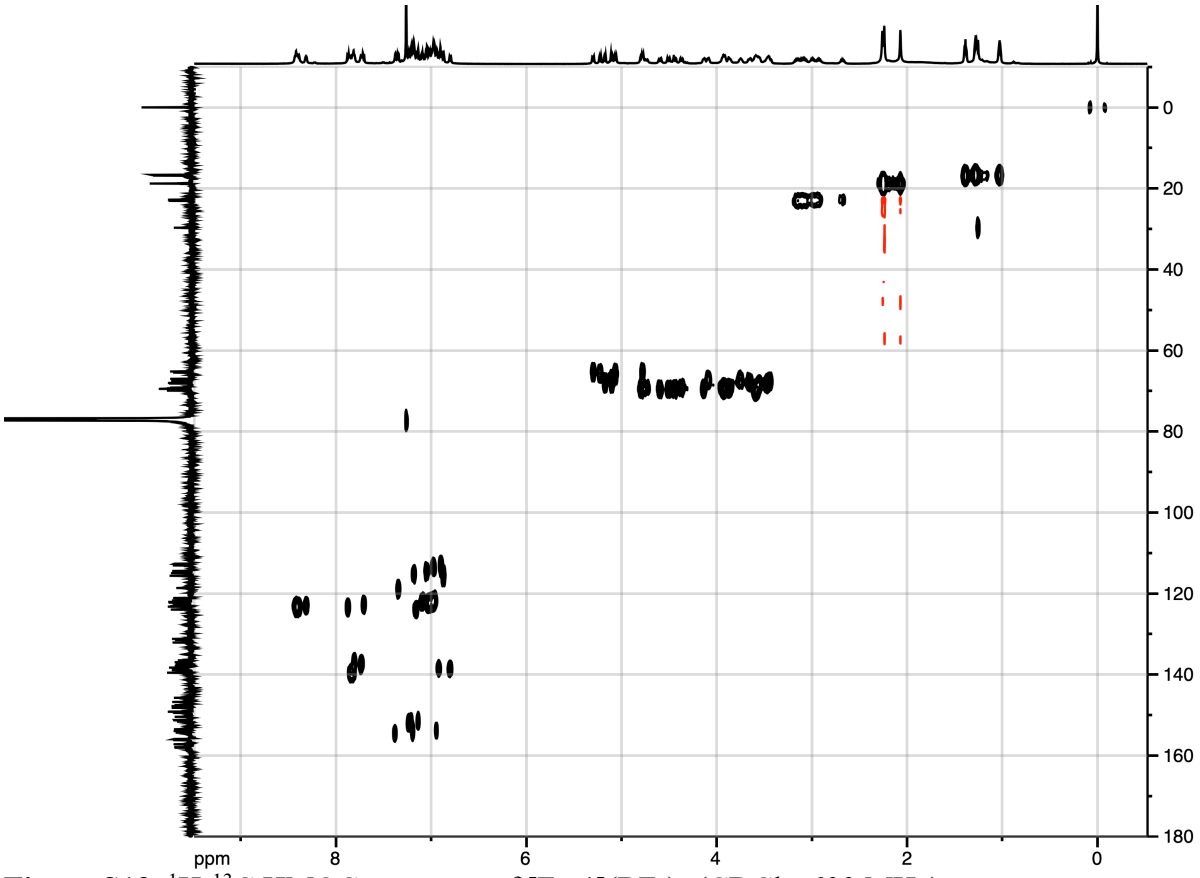


Figure S13. ^{1}H-^{13}C HMQC spectrum of [Fe·**1**](BF$_4$)$_2$ (CDCl$_3$, 600 MHz).

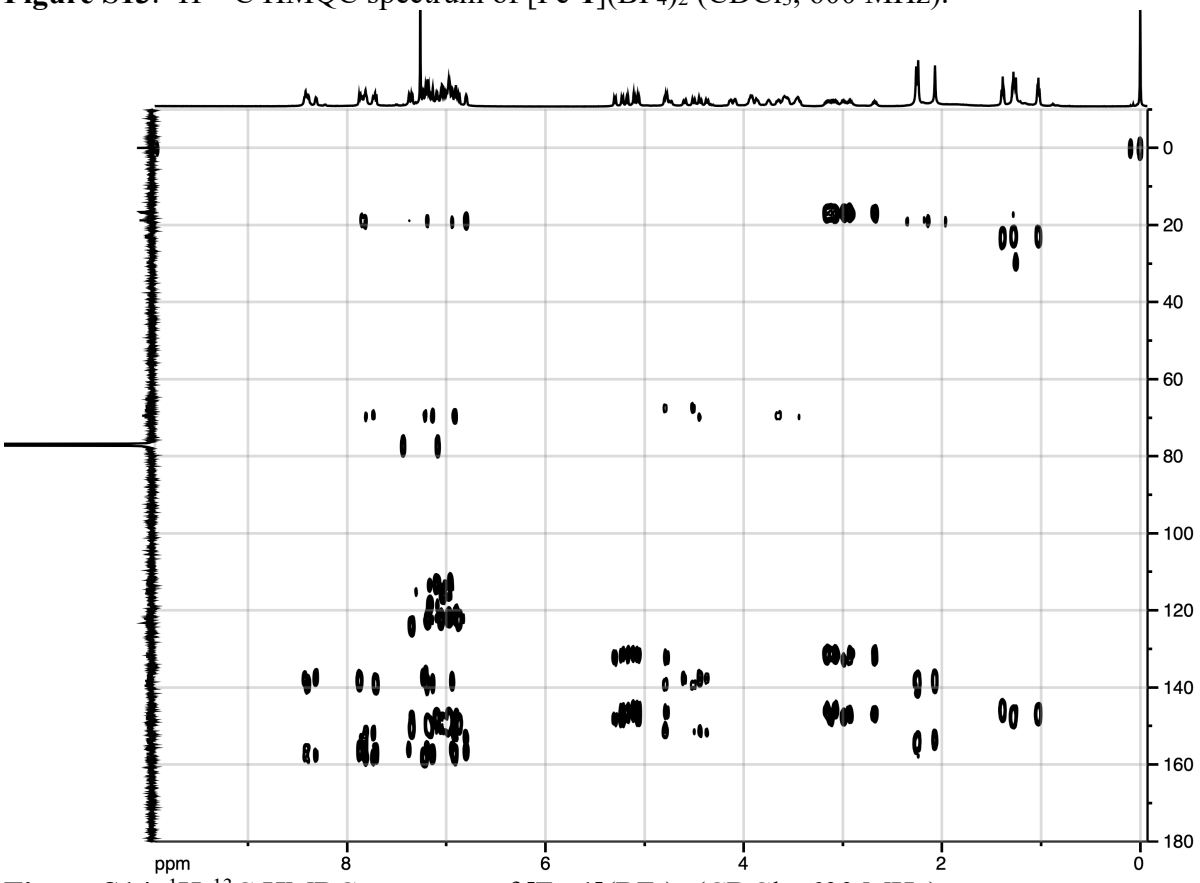


Figure S14. ^{1}H-^{13}C HMBC spectrum of [Fe·**1**](BF$_4$)$_2$ (CDCl$_3$, 600 MHz).

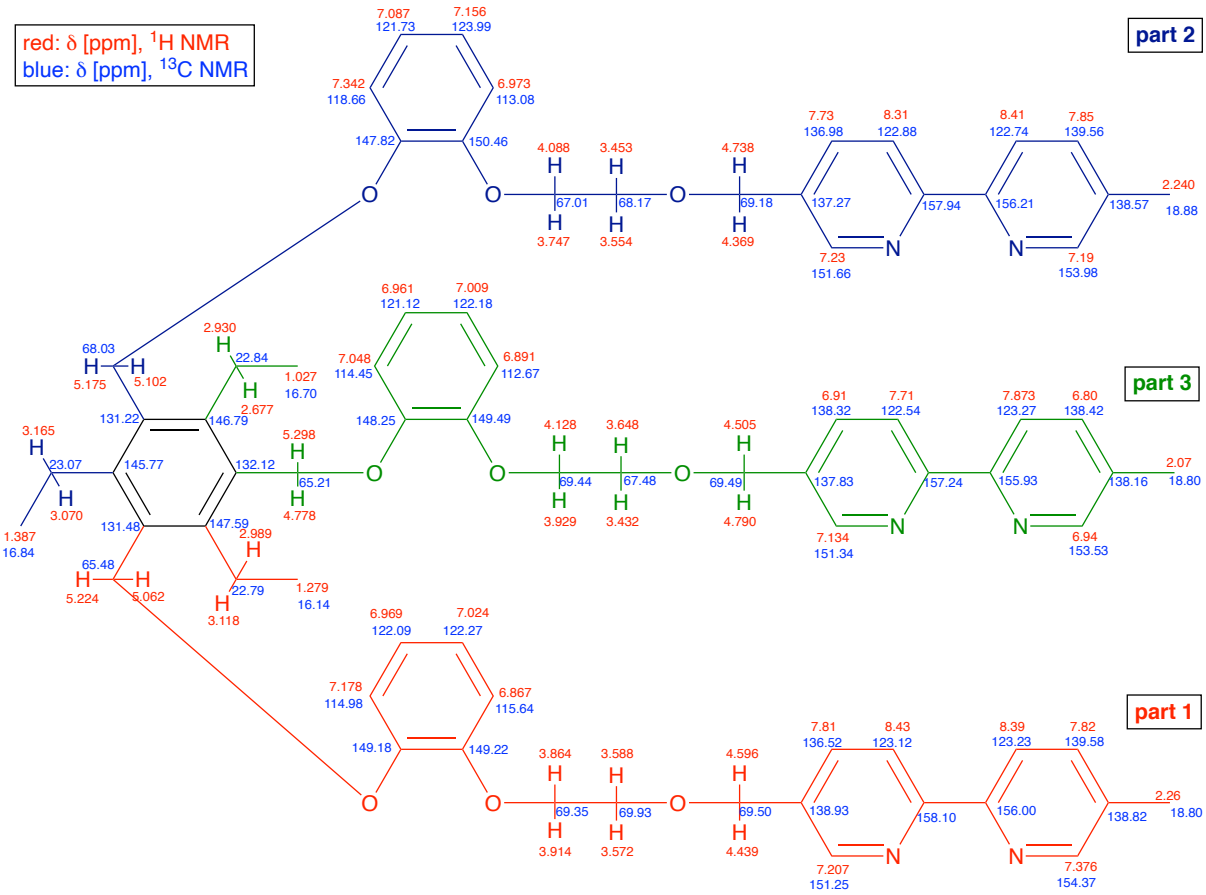


Figure S15. Assignment of ^{1}H and ^{13}C NMR signals of [Fe·**1**]$(BF_4)_2$ ($CDCl_3$, 600 MHz).

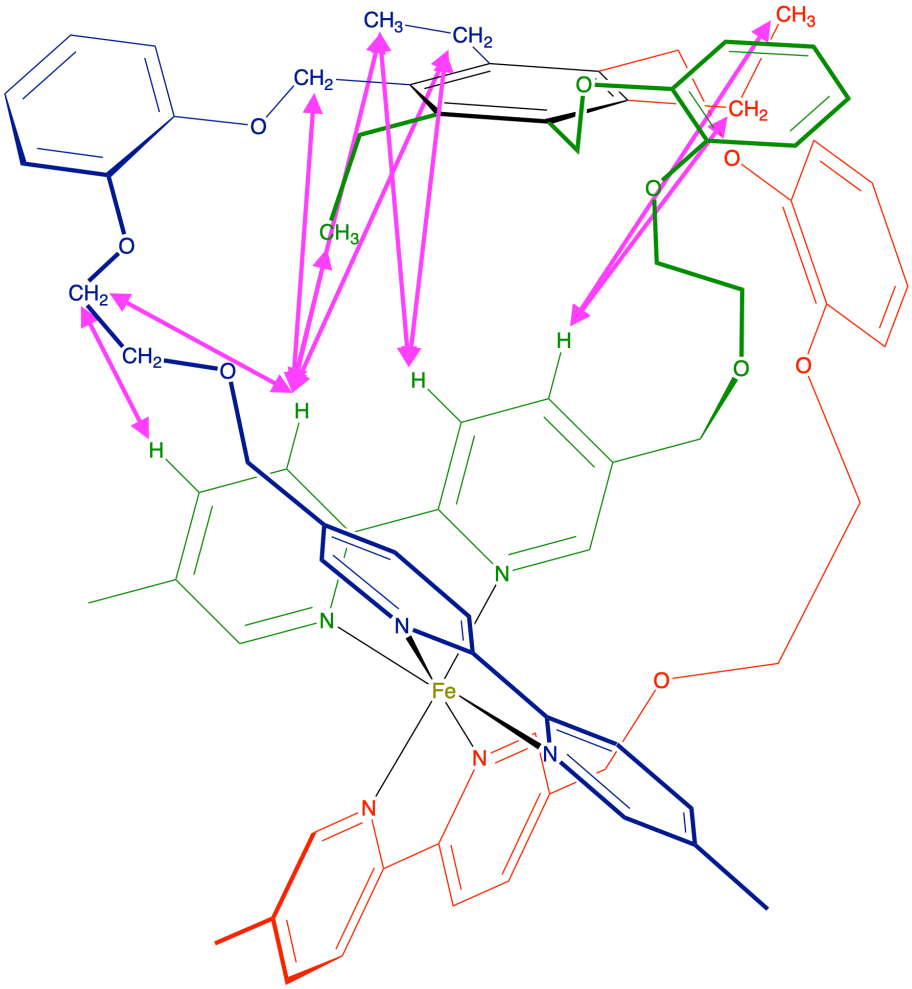


Figure S16. Observed ROE correlations (magenta arrows) with the bipyridyl of part 3.

Experimental procedure for the ^{1}H NMR titration experiment of [Fe·**1**]$(BF_4)_2$ and NH_4ClO_4 and CsTFPB.

200 μL of a 4.05 mM $CHCl_3$ solution of **1** (0.81 μmol) and 165 μL of a 5.4 mM CH_3OH solution of $Fe(BF_4)_2$ were added to 6 NMR tubes. A 5.40 mM CH_3CN solution of NH_4ClO_4 was added to each NMR tube with a ratio of $[NH_4^+]$/[Fe·**1**] = 0, 0.20, 0.50, 0.80, 1.0, 1.2, respectively. The solvents were removed under reduced pressure, and the samples were dried in vacuo. $CDCl_3$ (270 μL) and CD_3CN (270 μL) were added to each NMR tube ([**1**] = 1.50 mM), and ^{1}H NMR measurements were performed.

The titration experiment of with [Fe·**1**]$(BF_4)_2$ and CsTFPB[S4] was performed in the same procedure.

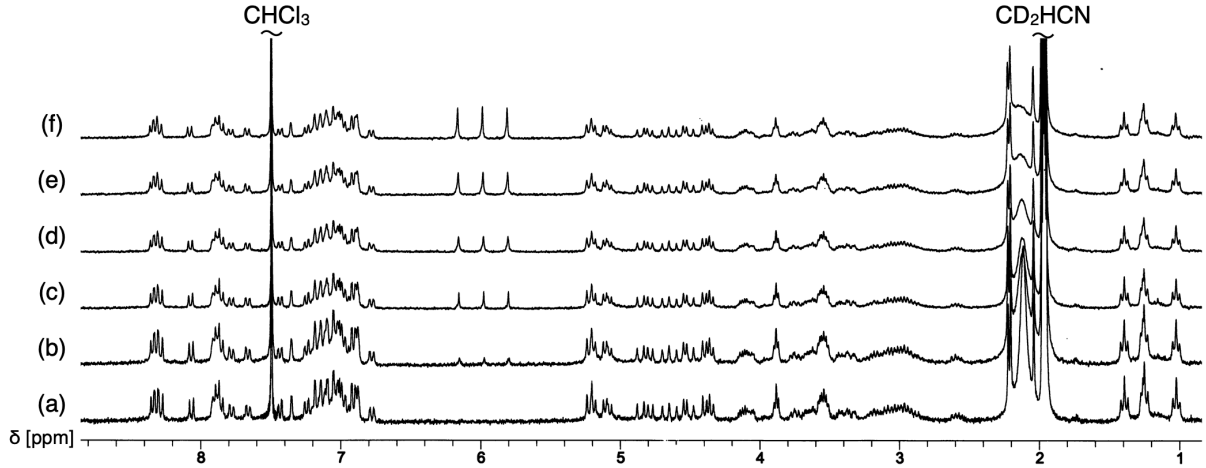


Figure S17. A titration experiment of [Fe·**1**]$(BF_4)_2$ and NH_4ClO_4 (^{1}H NMR, $CDCl_3/CD_3CN$ = 1/1, 300 MHz, [**1**] = 1.5 mM). (a) [Fe·**1**]$(BF_4)_2$. (b)–(f) [Fe·**1**]$(BF_4)_2$ + NH_4ClO_4. (b) NH_4ClO_4 0.20 equiv. (c) 0.50 equiv. (d) 0.80 equiv. (e) 1.0 equiv. (f) 1.2 equiv.

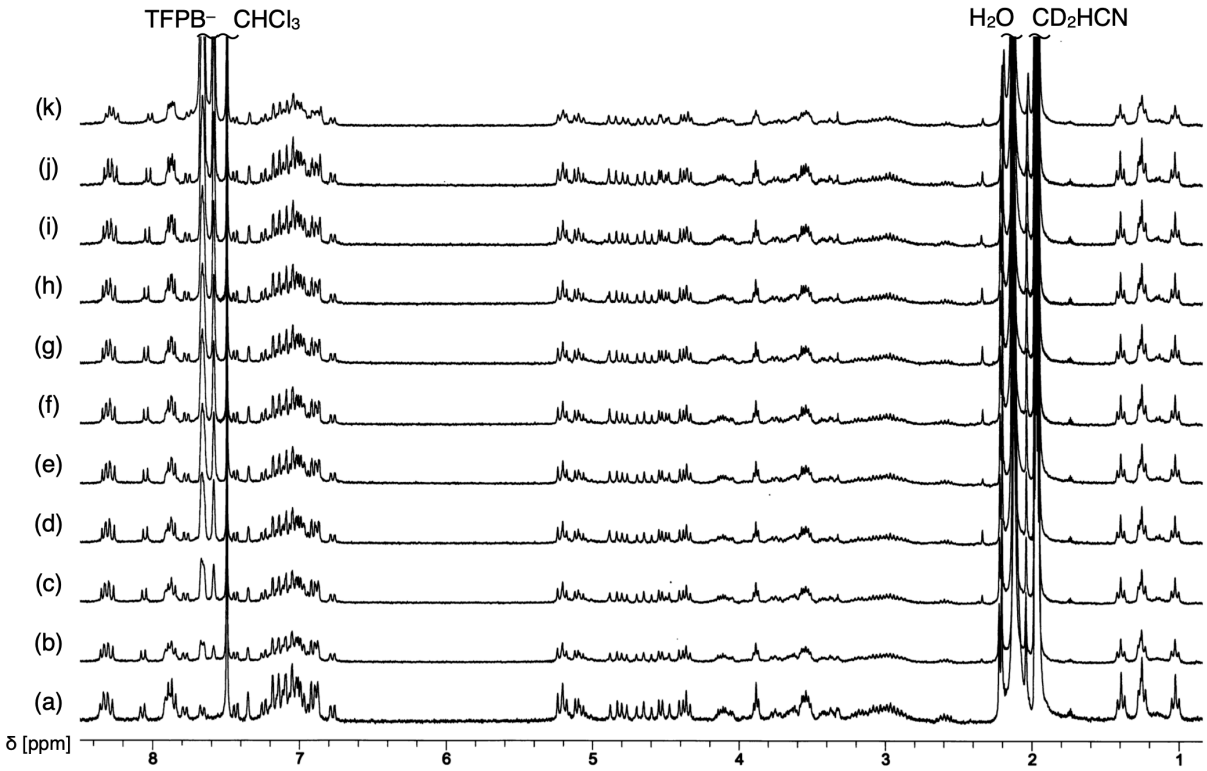


Figure S18. A titration experiment of [Fe·**1**](BF$_4$)$_2$ and CsTFPB (^{1}H NMR, CDCl$_3$/CD$_3$CN = 1/1, 300 MHz, [**1**] = 1.5 mM). (a) [Fe·**1**](BF$_4$)$_2$. (b)–(k) [Fe·**1**](BF$_4$)$_2$ + CsTFPB. (b) CsTFPB 0.20 equiv. (c) 0.50 equiv. (d) 0.80 equiv. (e) 0.90 equiv. (f) 1.0 equiv. (g) 1.1 equiv. (h) 1.2 equiv. (i) 1.5 equiv. (j) 2.0 equiv. (k) 4.0 equiv.

X-ray crystallographic analysis

Single crystal of complex [Fe·**1**]$(BF_4)_2$•2.6$CHCl_3$•3.9C_6H_6 (= $C_{101}H_{104}B_2Cl_{7.8}F_8FeN_6O_9$; 2051.88) (0.5 × 0.3 × 0.1 mm^3) was obtained by recrystallization from chloroform/benzene solution. Intensity data were collected on a Rigaku Mercury CCD diffractometer (with Mo Kα radiation, λ = 0.71069 Å) at 120 K. The data were corrected for Lorentz and polarization factors and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. Collected reflections, 63413, unique, 17217 (R_{int} = 0.0453), $2\theta_{max}$ = 50.0°. Monoclinic, a = 43.518(11), b = 18.722(5), c = 24.326(6) Å, β = 97.866(3)°, V = 19632(9) $Å^3$, space group $C2/c$ (#15), Z = 8, D_{calc} = 1.388 g/cm^3. The structures were solved by direct methods (SIR97)[S5] and refined by full-matrix least squares on F^2 using SHELXL 2014[S6]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included by using riding models. $R1$ = 0.0590 ($I > 2\sigma(I)$), $wR2$ = 0.1639 (all data), $GOF(F^2)$ = 1.042.

Crystallographic data for have been deposited with the Cambridge Crystallographic Data Centre under reference number CCDC 2052051. These data can be obtained free of charge via www.ccdc.cam.ac.uk/structures/.

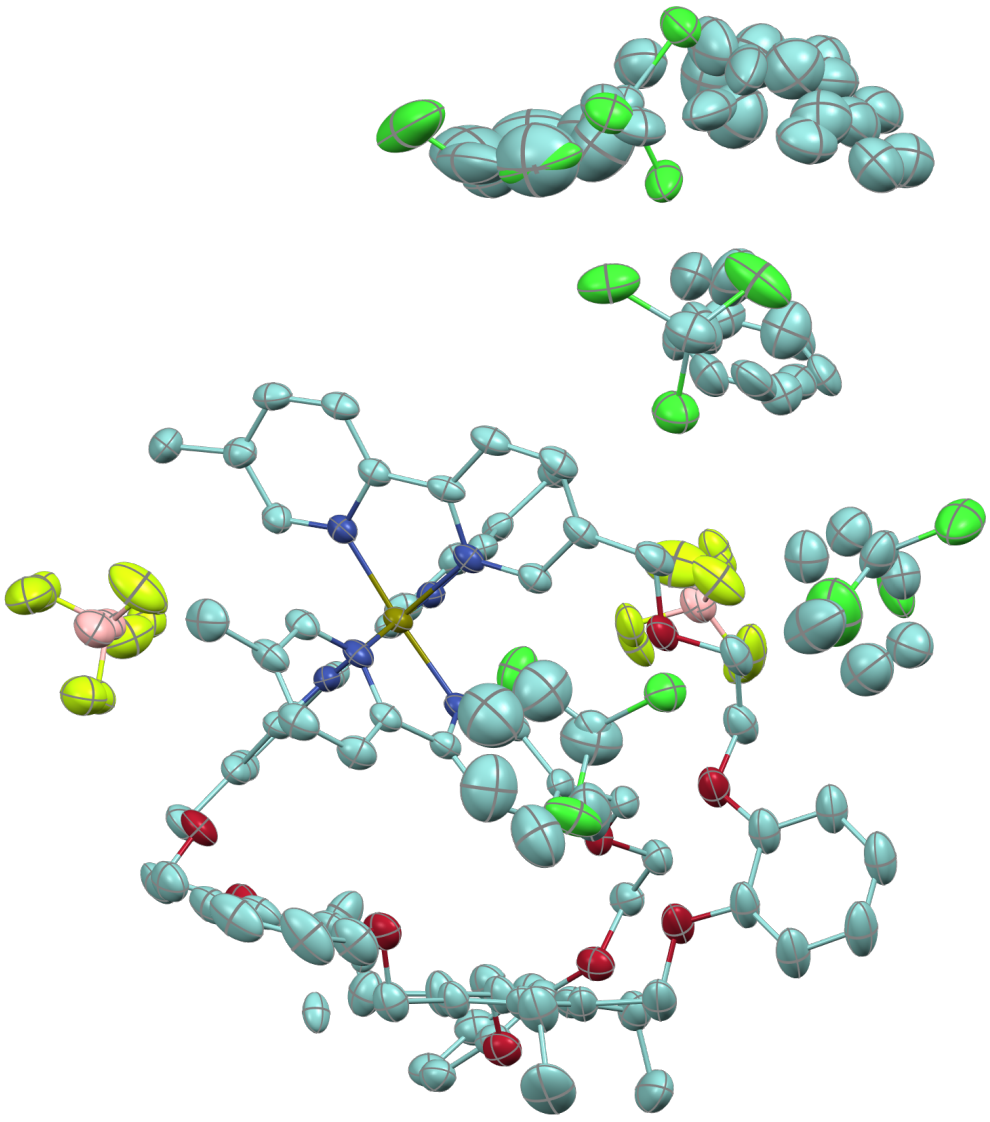


Figure S19. The molecular structure of [Fe·**1**]$(BF_4)_2$•2.6$CHCl_3$•3.9C_6H_6 determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light blue; N, blue; O, red; B, pink; F, yellow green; Cl, green; Fe, yellow.

Calculations

The structural calculations of the complexes were performed on a Spartan'18 software (Wavefunction Inc., *ver* 1.4.1 (2019)). The initial structures of *mer*-[Fe·**1**]$^{2+}$ and *fac*-[Fe·**1**]$^{2+}$were optimized by molecular mechanics calculations (MMFF), then the obtained structures were optimized by DFT calculations (B3LYP 6-31G*).

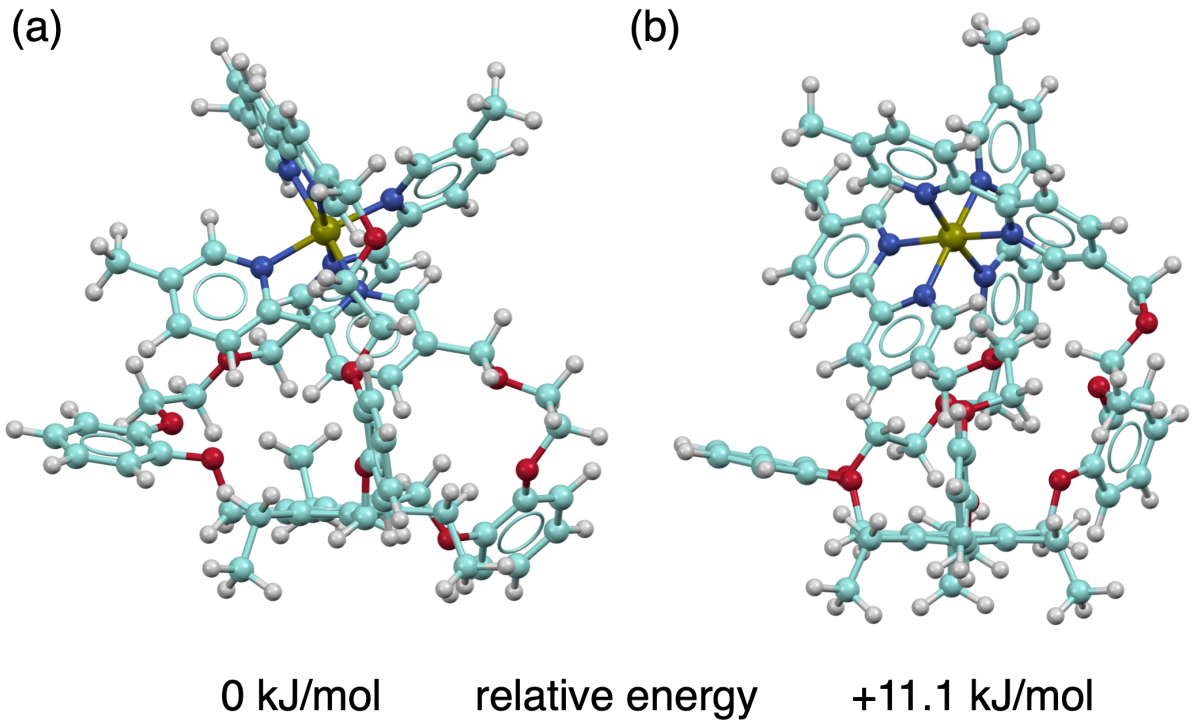


Figure S20. The structures of two isomers of [Fe·**1**]$^{2+}$ optimized by DFT calculation and their energies. C, light blue; N, blue; O, red; H, white; Fe, yellow. (a) *mer*-[Fe·**1**]$^{2+}$. (b) *fac*-[Fe·**1**]$^{2+}$.

References for the Supporting Information

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