

Supporting Information for

Ferrocene-based anions receptor with amide and triazolium Donor Groups

Qian-Yong Cao,^{1,2} Tuhin Pradhan,¹ Min Hee Lee,¹ Kwanghyun No,^{3,*} Jong Seung Kim^{1,*}

¹Department of Chemistry, Korea University, Seoul 136-701, Korea. ²Department of Chemistry, Nanchang University, Nanchang 330031, P. R. China. ³Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea

Corresponding authors' e-mail: jongskim@korea.ac.kr (JSK); hyun@sookmyung.ac.kr (KN)

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Experimental Section

General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (230-400 mesh). NMR spectra were recorded using Varian instruments (400MHz and 300 MHz). Chemical shifts were expressed in ppm and coupling constants (J) in Hz.

CV Spectroscopic Method

Electrochemical measurements were performed with a CHI 624C instruments. All electrochemical measurements were carried out in a one-compartment cell under a nitrogen atmosphere at 25 °C, equipped with a Pt disk working electrode, a platinum wire counter electrode, and a Ag/AgNO₃ reference electrode. The working electrode surface was carefully polished with basic Al₂O₃-water slurry, washed with MeOH and sonicated in a H₂O-MeOH-CH₃CN 1:1:1 mixture at 40 °C for 15 minutes prior to use. All potentials in this paper were recorded in CH₃CN and are quoted relative to Ag/AgNO₃, and were calibrated using decamethylferrocene ($E_{1/2} = 0.46$ V vs Ag/Ag⁺). The supported electrolyte was a 0.10 M CH₂Cl₂ solution of tetrabutylammonium hexafluorophosphate (TBAPF₆). Differential pulse voltammetry (DPV) measurements were also carried out using a CHI 610C instruments with a 50 ms pulse width.

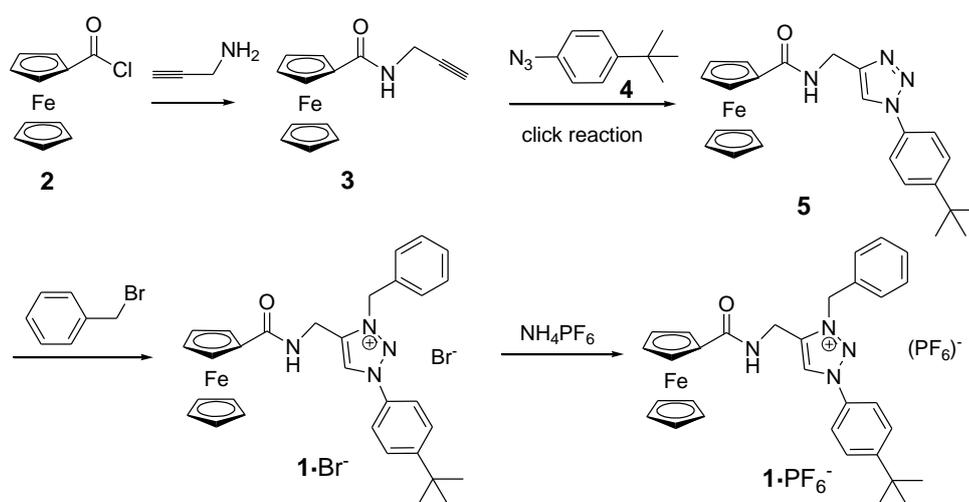
X-ray crystallographic analysis

Crystals were obtained by direct diffusion of hexane into a solution of the target compound **1** in dichloromethane. A suitable single crystal was mounted in a glass fiber, and diffraction measurements were taken with Bruker Smart APEX CCD-based diffractometer with Mo K α graphite monochromated radiation. The structures were solved by direct methods using the program SHELXL-97. The refinement and all further calculations were carried out using SHELXL-97. The non-H atoms were refined anisotropically, using weighted full matrix least-squares on F^2 .

Calculation Details.

Geometries of **1** and **1**·Br- system in '*syn*' and '*anti*' conformations have been optimized using DFT (Density Functional Theory) method at B3LYP/6-31G(d) level of theory. No imaginary frequencies were available after vibration analysis of the optimized structures, which implied that

each of the optimized structures was at the real minimum on the potential energy surfaces (PES). Single point energy calculations have been performed on their optimized structures employing same level of theory. Basis set superposition error (BSSE) has been corrected by counterpoise correction methodS1 applied on an optimized geometry while calculating single point energy for 1·Br⁻ system. We have followed the suggested geometry cutoffs for D-H...A hydrogen bond definition,^{S2-S3} according to which, H...A distances should be < 3.0 Å and D-H...A angles should be > 110 °, where D and A represent respectively H-bond donor and acceptor. All calculations were performed using Gaussian 09 W program package.^{S4}



Synthesis of **3**

Under nitrogen, a solution of (Chlorocarbonyl)ferrocene^{S5} (**2**, 0.248 g, 1.0 mmol), propargylamine (0.055 g, 1.0 mmol) and triethylamine (0.5 mL) in CH₂Cl₂ (30 mL) was stirred at room temperature for 24 h. After removal of the solvents, the crude product was purified over silica gel using CH₂Cl₂/MeOH (v/v, 98:2) as the eluents to yield **3** as a orange solid (0.220 g, 82.4%). ¹H NMR (CDCl₃, 300 MHz): δ 5.81 (br, 1 H), 4.69 (t, 2 H, J = 2.0 Hz), 4.36 (t, 2 H, J = 2.0 Hz), 4.23 (s, 5 H); 4.18 (q, 1 H), 2.28 (t, 1 H, J = 2.8 Hz).

Synthesis of **5**

Under nitrogen, a solution of **3** (267 mg, 1.0 mmol), 4-*tert*-butylphenyl azide^{S6} (**4**, 175 mg, 1.0 mmol), and (EtO)₃P·CuI (71 mg, 0.2 mmol) in 30 mL dry toluene was stirred under reflux for 45 min. The solvent was removed by evaporation under vacuum and the crude was purified by silica gel column chromatography (CH₂Cl₂/MeOH, 98:2) to yield **5** as a yellow solid (365 mg, 83.0%). ¹H NMR (CDCl₃, 300 MHz): δ 8.09 (s, 1 H), 7.65 (d, 2 H, J = 8.8 Hz), 7.51 (d, 2 H, J = 8.8 Hz) 6.89

(br, 1 H); 4.68-4.75 (m, 4 H); 4.33 (t, 2 H, $J = 2.0$ Hz), 4.14 (s, 5 H); 1.35 (s, 9 H). ESI-MS (ES^+): $m/z = 442.9$. HR-FAB-MS: Calcd 442.3144; Found $m/z = 442.1455$ [M^+]. EA Calcd for $C_{24}H_{26}FeN_4O \cdot H_2O$: C, 62.62; H, 5.92. Found: C, 62.66; H, 6.12.

Synthesis of $1 \cdot Br^-$ and $1 \cdot PF_6^-$

A solution of **5** (221 mg, 0.5 mmol) and benzyl bromide (255 mg, 1.5 mmol) in 30 mL acetonitrile was refluxed for 24 h. After cooling to room temperature, solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (EtOAc/MeOH = 20:1 as eluent) to give $1 \cdot Br^-$ (158 mg, 0.26 mmol, 51.6% yield) as an orange solid.

100 mg (0.16 mmol) of $1 \cdot Br^-$ (in 10 ml DCM) was added to a saturated methanolic solution of NH_4PF_6 (5 mL) and stirred for 2 h. The solvent was removed by evaporation under vacuum, and the crude was redissolved in DCM and filtered to remove the undissolvable aminium salts. Analytically pure product (92 mg, 0.14 mmol, 84.8% yield) was obtained after crystallization from hexane/DCM (1:1, v/v) solution. 1H NMR ($CDCl_3$, 300 MHz): δ 8.88 (s, 1 H), 7.71-7.74 (m, 2 H), 7.62-7.65 (m, 2 H), 7.46 (s, 5 H), 7.27 (br, 1 H), 6.12 (s, 2 H), 4.78-4.82 (m, 4 H), 4.40 (t, 2 H, $J = 2.0$ Hz), 4.20 (s, 5 H); 1.36 (s, 9 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 172.8, 156.6, 143.3, 132.3, 131.3, 130.2, 129.9, 128.7, 128.3, 127.9, 121.1, 73.6, 71.5, 70.1, 68.7, 56.1, 35.4, 32.2, 31.3 ppm. ESI-MS (ES^+): $m/z = 533.0$ [$M^+ - PF_6$]. HR-FAB-MS: Calcd 678.4290; Found: $m/z = 678.1646$ [M^+]. Elemental Analysis, Calcd for $C_{31}H_{33}F_6FeN_4OP^+ \cdot H_2O$: C, 53.41; H, 5.02. Found: C, 53.65; H, 5.11.

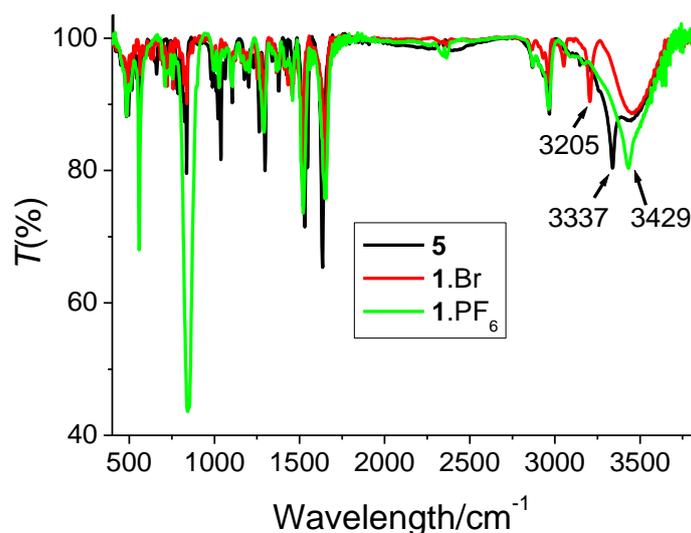


Figure S1. IR spectrum of $1 \cdot PF_6^-$ and $1 \cdot Br^-$ and **5** in the solid state

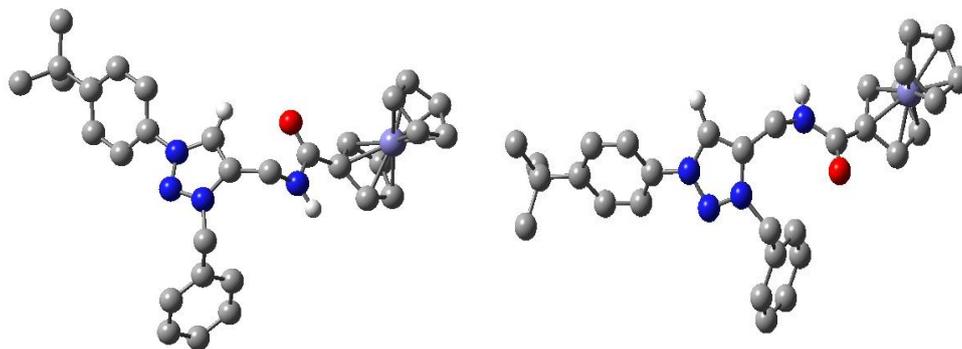


Figure S2. Optimized structures of 'anti' (left) and 'syn' (right) conformations of **1**. Hydrogen atoms except in amide and triazolium donors were omitted for clarity. The energy difference between the two conformations is ~0.6 Kcal/Mole and the 'syn' conformation is energetically more stable than the 'anti' conformation.

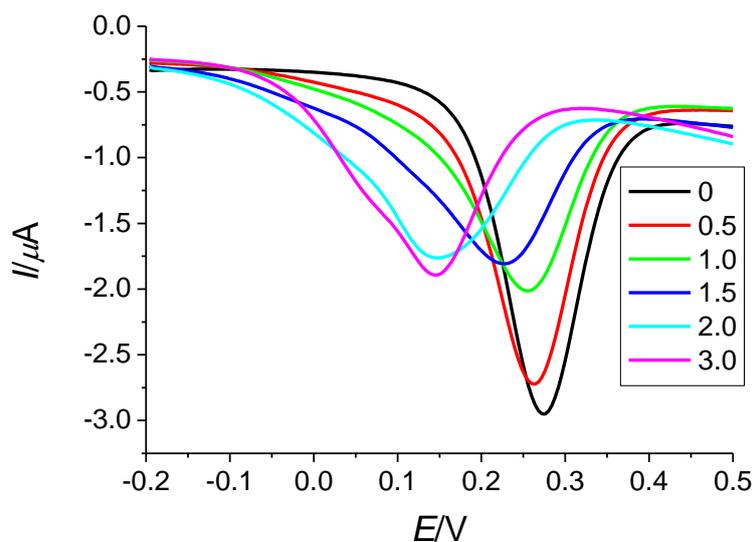


Figure S3. DPV titration profile of $1 \cdot \text{PF}_6^-$ (0.2 mM) upon addition of various amount of F^- in CH_2Cl_2 solution.

Reference electrode = Ag/AgNO_3 ; supporting electrolyte = $[\text{n-Bu}_4\text{N}]\text{PF}_6$ (0.1 M); scan rate = 100 mV S^{-1} .

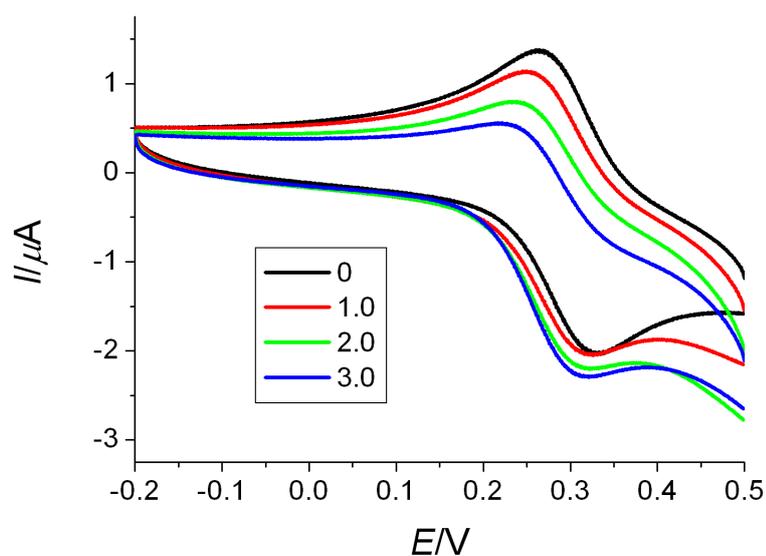


Figure S4. CV titration profile of $1 \cdot \text{PF}_6^-$ (0.2 mM) upon addition of various amount of Cl^- in CH_2Cl_2 solution.

Reference electrode = Ag/AgNO_3 ; supporting electrolyte = $[\text{n-Bu}_4\text{N}]\text{PF}_6$ (0.1 M); scan rate = 100 mV S^{-1} .

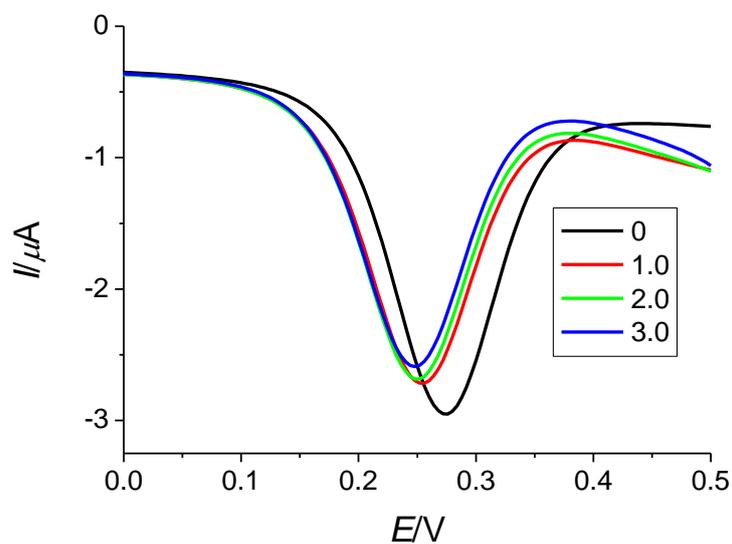


Figure S5. DPV titration profile of $1 \cdot \text{PF}_6^-$ (0.2 mM) upon addition of various amount of Cl^- in CH_2Cl_2 solution.

Reference electrode = Ag/AgNO_3 ; supporting electrolyte = $[\text{n-Bu}_4\text{N}]\text{PF}_6$ (0.1 M); scan rate = 100 mV S^{-1} .

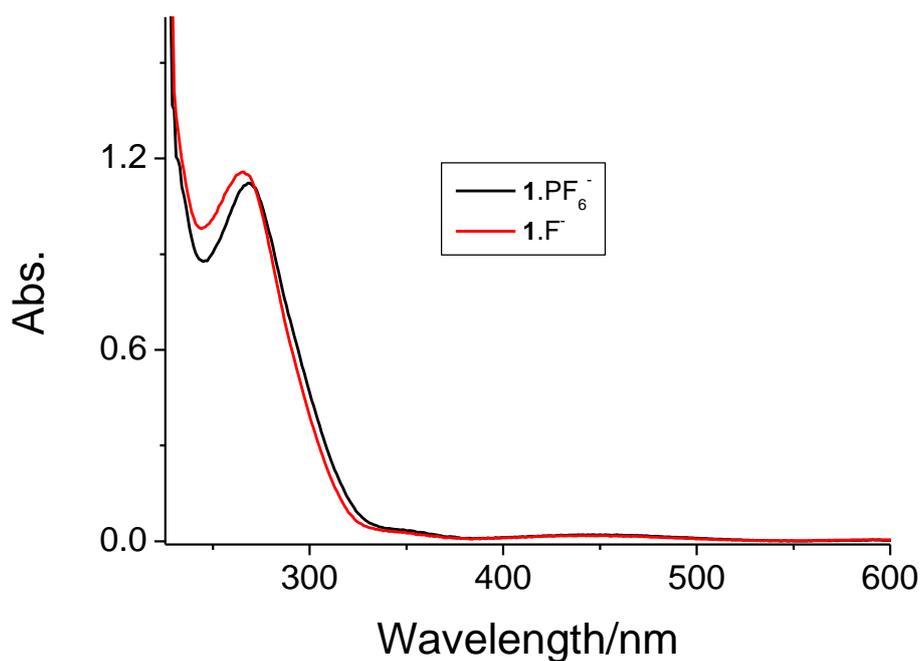


Figure S6. UV-vis spectra of **1** (0.04 mM) and after adding two equiv F^- in CH_2Cl_2 solution

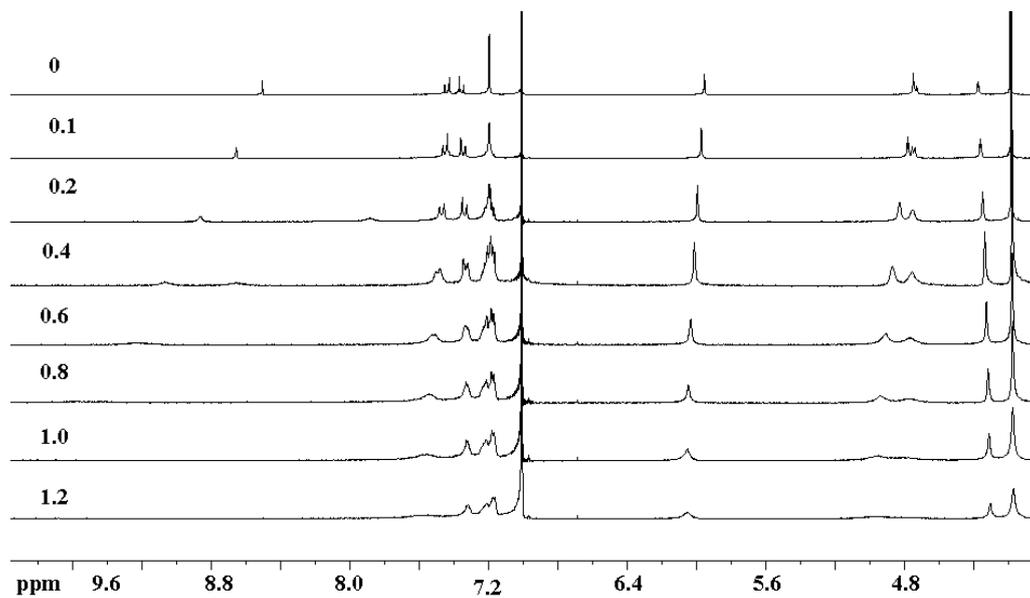


Figure S7. ^1H NMR titration spectra of $1 \cdot \text{PF}_6^-$ (CDCl_3 , 8 mM) upon addition of increasing amounts of F^-

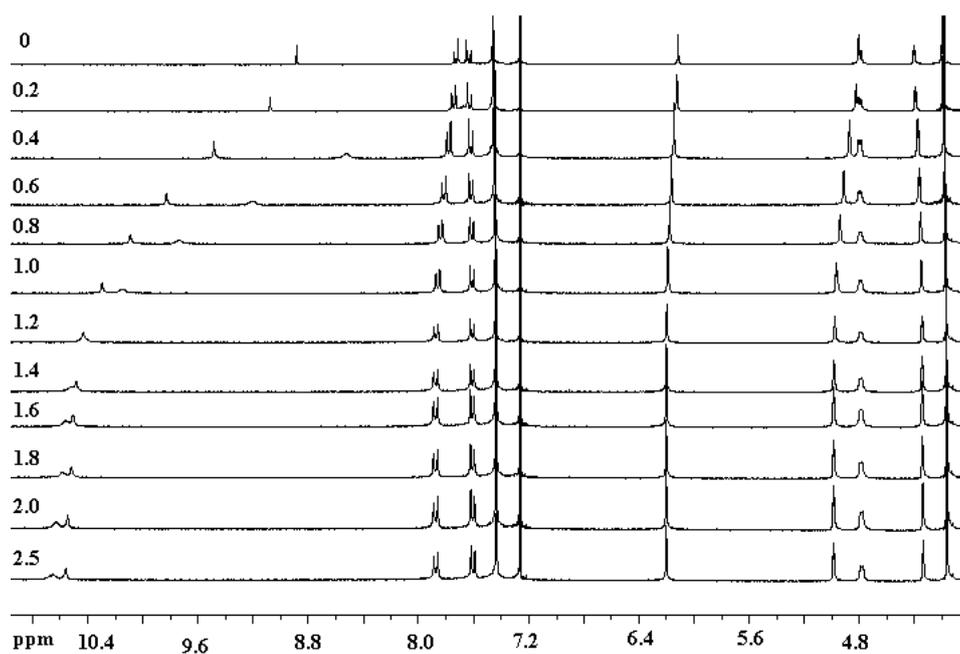


Figure S8. ^1H NMR titration spectra of $1\cdot\text{PF}_6^-$ (CDCl_3 , 8 mM) upon addition of increasing amounts of AcO^-

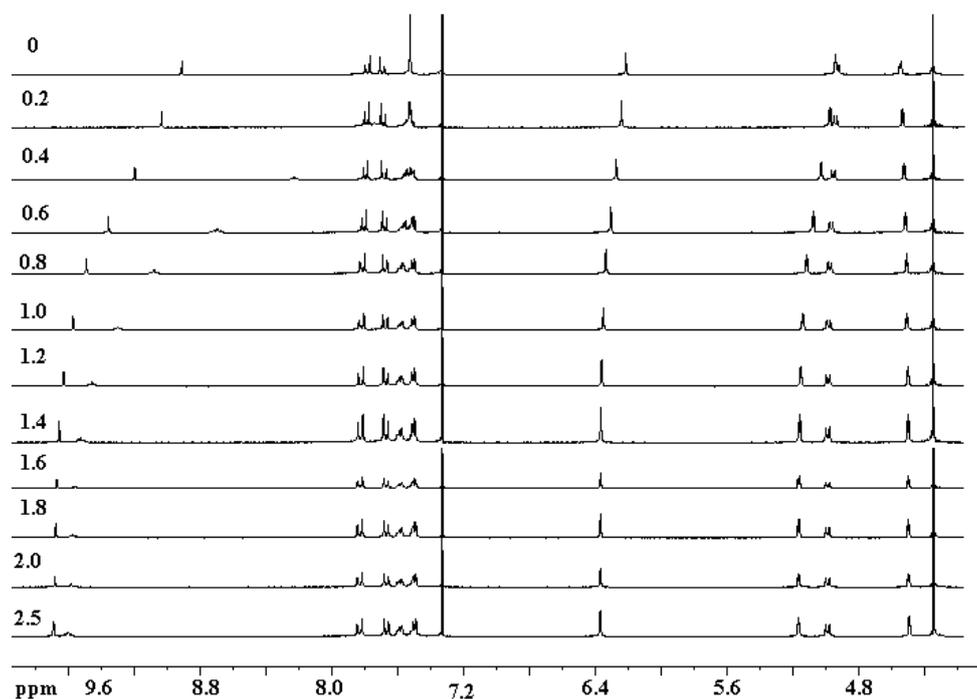


Figure S9. ^1H NMR titration spectra of $1\cdot\text{PF}_6^-$ (CDCl_3 , 8 mM) upon addition of increasing amounts of Cl^-

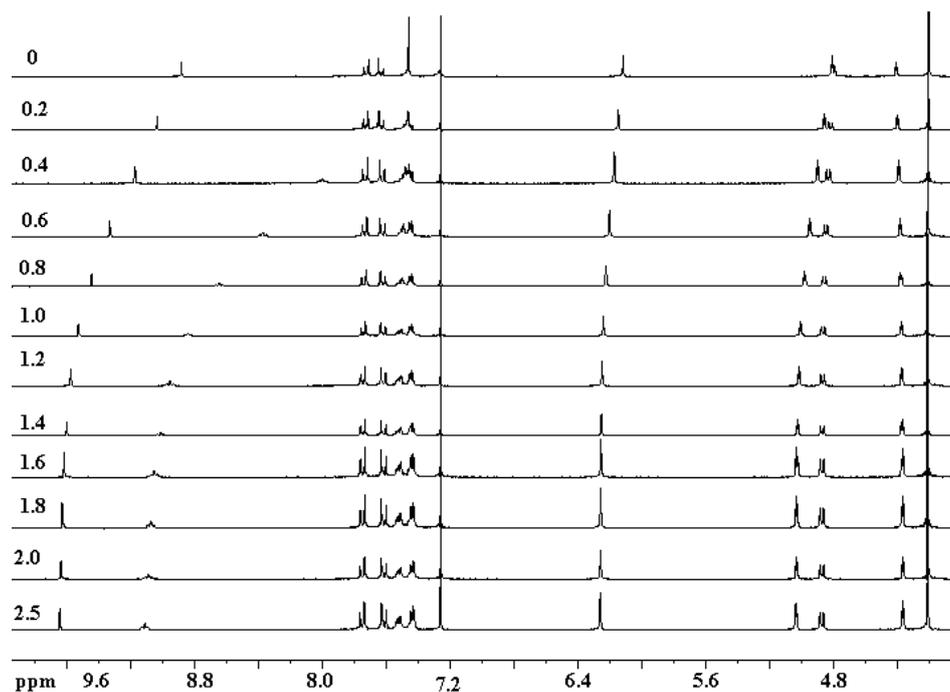


Figure S10. ¹H NMR titration spectra of 1·PF₆⁻ (CDCl₃, 8 mM) upon addition of increasing amounts of Br⁻

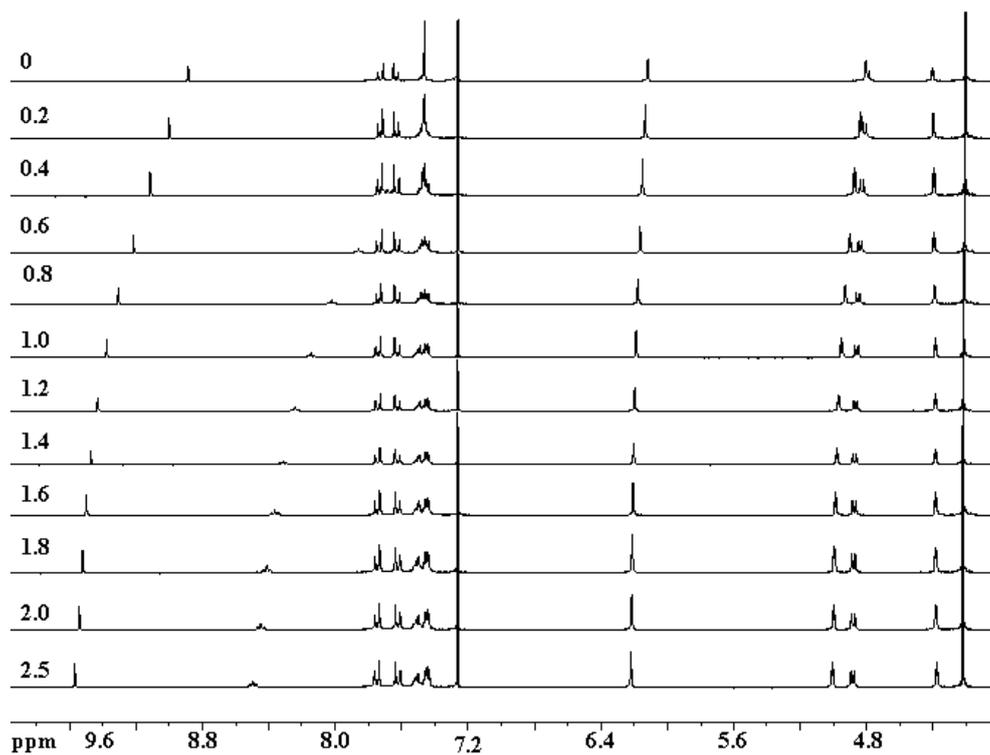


Figure S11. ¹H NMR titration spectra of 1·PF₆⁻ (CDCl₃, 8 mM) upon addition of increasing amounts of I⁻

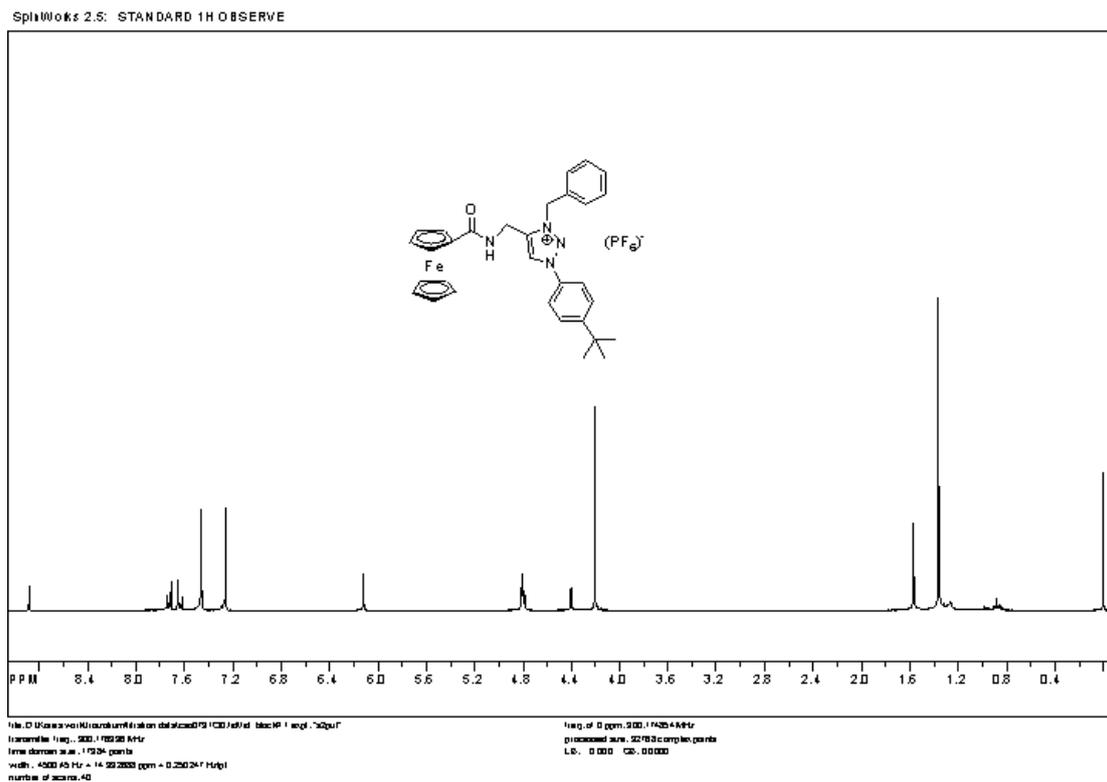


Figure S16. ^1H NMR spectrum of $1\cdot\text{PF}_6$ in CDCl_3 solution

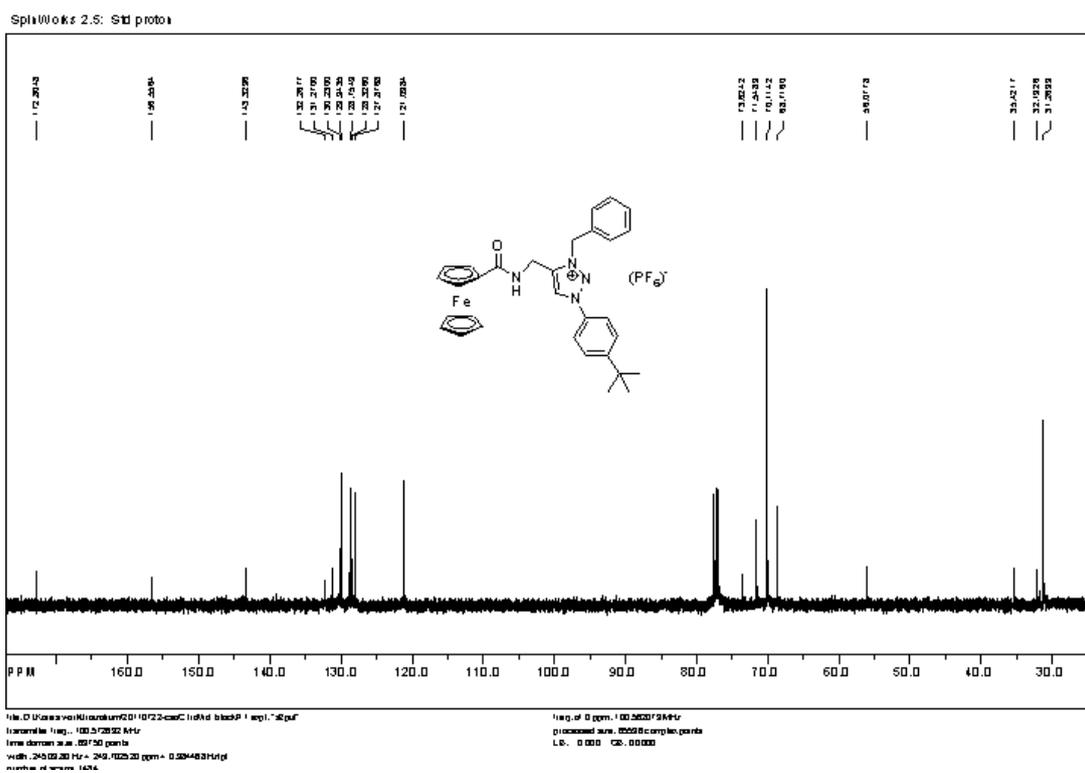


Figure S17. ^{13}C NMR spectrum of $1\cdot\text{PF}_6$ in CDCl_3 solution

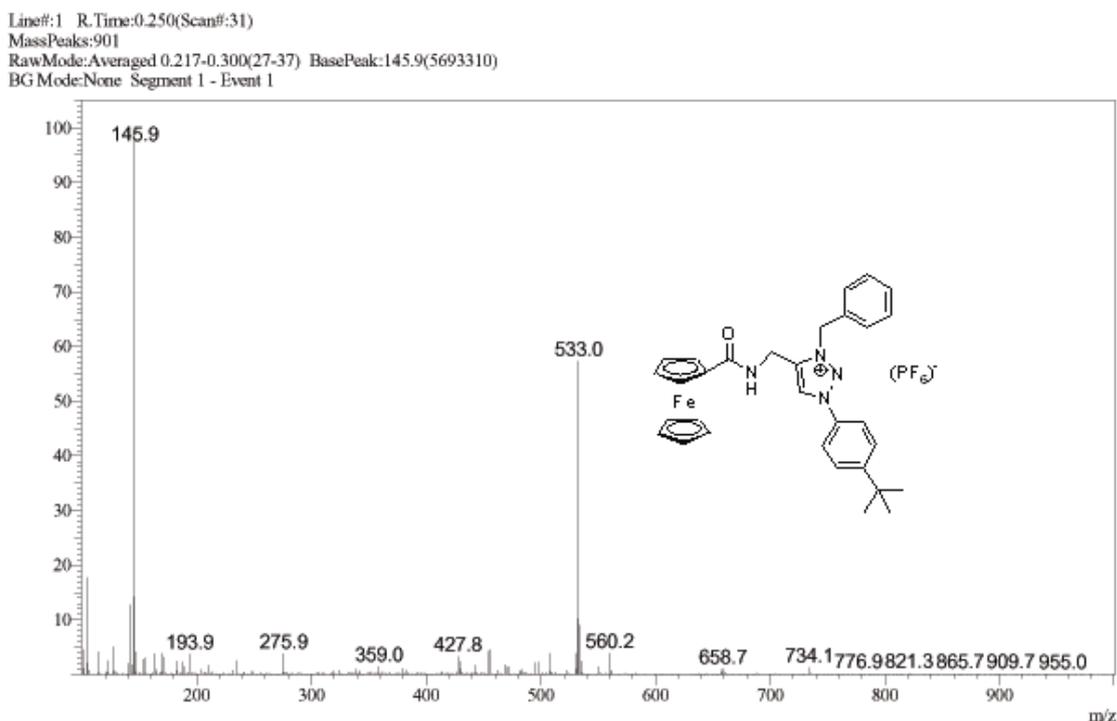


Figure S18. ESI-MS (ES⁺) spectrum of **1**•PF₆

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