Electronic Supplementary Material (ESI) for Chemical Communications

Self-Promoted Post-Synthetic Modification of Metal-Ligand M_2L_3 Mesocates

Michael C. Young, Amber M. Johnson and Richard J. Hooley*
Department of Chemistry, University of California, Riverside, CA 92521.
richard.hooley@ucr.edu

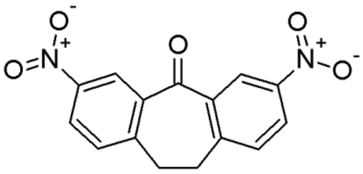
Electronic Supplementary Information

Table of Contents

1. General Information

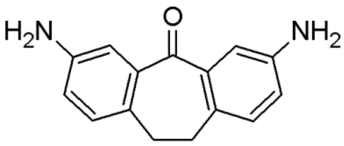
^{1}H, gCOSY and ^{13}C spectra were recorded on a Varian Inova 400 MHz or 500 MHz NMR spectrometer. DOSY and NOESY spectra were recorded on a Bruker Avance 600 MHz spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. Peak assignment was acheived through the use of COSY and NOESY spectra where possible, and through the use of NMR predictive software in ChemDraw Ultra 11.0 when not. Mass spectra were recorded on an Agilent 6210 LC TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V and processed with an Agilent MassHunter Operating System, while predicted isotope patterns were prepared with assistance from ChemCalc.[1] UV/Vis spectroscopy was performed on a Cary 50 Photospectrometer using the Varian Scans program to collect data. Circular dichroism spectroscopy was performed on a Jasco J-815 CD Spectrometer using the Spectra Manager program to collect and process data. Infrared spectroscopy was performed on a Perkin Elmer Spectrum One FT-IR Spectrometer using the program Spectrum to collect data. X-ray diffraction data were collected at 100(2) K on a Bruker APEX2 platform-CCD X-ray diffractometer system. All other materials were obtained from Aldrich Chemical Company, St. Louis, MO, or TCI, Tokyo, Japan and were used as received. Solvents were dried through a commercial solvent purification system (Pure Process Technologies, Inc.). Molecular modeling (semi-empirical calculations) was performed using the AM1 force field using SPARTAN.[2]

2. Synthesis of Compounds



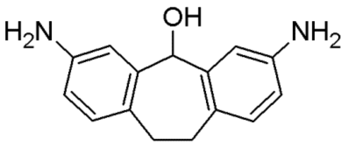
3,7-Dinitrodibenzosuberone (*S-1*):

Dibenzosuberone (10.4 g, 49.9 mmol) was added to a 100 mL round bottom flask with stir bar, followed by attaching a drop-addition funnel and placing the system under N_2, followed by placing the flask into an ice bath. Fuming nitric acid (90%, 25 mL) cooled to 0°C was added to the drop-addition funnel, followed by slowly adding this to the dibenzosuberone over 10 min. The flask was then placed into an oil bath and heated to 100°C while stirring. After 2 h the reaction was allowed to cool, followed by pouring into vigorously stirred ice water (1 L). The resulting precipitate was filtered, followed by rinsing with additional deionized water (1 L). After drying, the crude product was recrystallized from $MeNO_2$ to give product as a light yellow solid (5.86 g, 39%). ^{1}H NMR (400 MHz; DMSO-d_6) δ 8.69 (d, *J* = 2.5 Hz, 2H), 8.39 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.37 (s, 4H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 190.3, 149.5, 146.4, 137.7, 131.9, 127.0, 125.3, 33.3. HRMS (ESI) m/z calcd for $C_{15}H_{11}N_2O_5$ ($[M+H]^+$) 299.0662, found 299.30677.



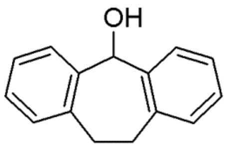
3,7-Diaminodibenzosuberone (A):

S-1 (400 mg, 1.34 mmol) was added to a 50 mL round bottom flask with stir bar, followed by addition of Raney© 2800 Ni suspension in water (1.0 mL) and MeOH (25 mL). The flask was purged with nitrogen gas using a Schlenk line. Hydrazine monohydrate (2.0 mL, 41.2 mmol) was slowly added. After the addition was complete, the reaction was stirred at room temperature. After 24 h the reaction mixture was diluted with acetone (100 mL) followed by filtering through celite. After evaporating the solvent *in vacuo*, the residue was triturated in deionized water (200 mL) before being filtered using celite. The filter was rinsed clean using MeOH (150 mL) before evaporating the solvent *in vacuo* to give an orange-yellow solid. This was recrystallized from EtOH to give product as a yellow solid (162 mg, 50 %). ^{1}H NMR (400 MHz; DMSO-d_6) δ 7.30 (d, *J* = 2.6 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 8.0, 2.6 Hz, 2H), 3.68 (br s, 4H), 3.05 (s, 4H). ^{1}H NMR (400 MHz; DMSO-d_6) δ 7.05 (d, *J* = 2.3 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.69 (dd, *J* = 8.1, 2.3 Hz, 2H), 5.11 (br s, 4H), 2.89 (s, 4H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 195.7, 146.9, 138.7, 130.1, 129.3, 118.2, 114.3, 33.9. HRMS (ESI) m/z calcd for $C_{15}H_{15}N_2O$ ($[M+H]^+$) 239.1178, found 239.1248.



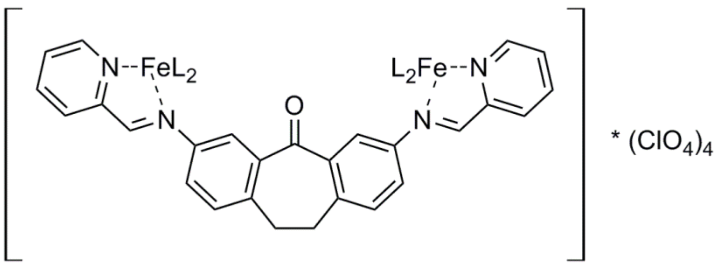
3,7-Diaminodibenzosuberol (B):

A (503 mg, 2.1 mmol) was added to a 25 mL round bottom flask with stir bar, followed by partially dissolving in absolute EtOH (20 mL). $NaBH_4$ (3.00 g, 79.3 mmol) was added slowly, followed by allowing the reaction to stir overnight at room temperature. After 12 h had elapsed, the reaction mixture was slowly diluted with water (280 mL). After being allowed to sit, a precipitate slowly settled to the bottom, which was filtered and dried to give product as a light-orange solid (416 mg, 81%). ^{1}H NMR (400 MHz; DMSO-d_6) δ 6.73 (d, J = 2.4 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 6.30 (dd, J = 8.0 Hz, 2.4 Hz, 2H), 5.76 (d, 4.5 Hz, 1H), 5.54 (d, J = 4.0 Hz, 1H), 4.74 (bs, 4H), 2.98 (m, 2H), 2.83 (m, 2H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 146.1, 143.7, 129.7, 124.1, 112.0, 110.7, 70.6, 31.1. HRMS (ESI) m/z calcd for $C_{15}H_{16}N_2O$ ($[M\cdot]^+$) 240.1257, found 240.1267.



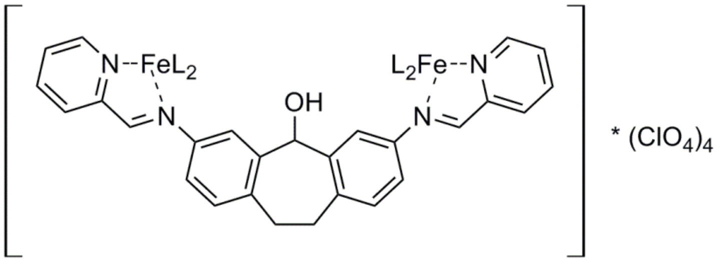
Dibenzosuberol (*S-2*):

Dibenzosuberone (916 mg, 4.40 mmol) and $NaBH_4$ (333 mg, 8.80 mmol) were combined in a 50 mL round bottom flask with stir bar. MeOH (20 mL) was added, and the reaction was stirred at room temperature. After 24 h the reaction was diluted with deionized H_2O (300 mL) to give a precipitate. This was filtered, and rinsed with additional deionized H_2O (300 mL) and dried to give product as a white solid (691 mg, 74%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.46 (dd, J = 6.3, 2.0 Hz, 2H), 7.19 (m, 6H), 5.96 (d, J = 1.7 Hz, 1H), 3.43 (m, 2H), 3.12 (m, 2H), 2.29 (d, J = 2.5 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 140.6, 139.0, 130.3, 128.1, 127.2, 126.3, 76.6, 32.5. HRMS (ESI) m/z calcd for $C_{15}H_{14}O$ ($[M\cdot]^+$) 210.1039, found 210.1033.



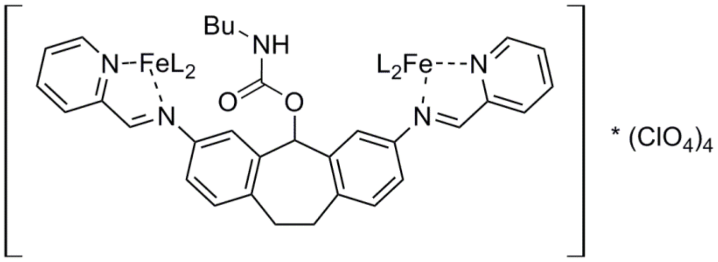
Mesocate 1:

A (28.5 mg, 120 μmol), 2-pyridine carboxaldehyde (24.0 μL, 253 μmol) and $Fe(ClO_4)_2$•xH_2O (30.2 mg) were combined in anhydrous MeCN (2 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by submerging in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (15 mL), cooled to -25°C followed by filtration of the resulting precipitate. After drying, product was isolated as a purple solid (65.0 mg, 92%). ^{1}H NMR (400 MHz; CD_3CN) δ 8.71 (s, 6H), 8.46 (d, *J* = 7.4 Hz, 6H), 8.39 (t, *J* = 7.6 Hz, 6 H), 7.75 (t, *J* = 6.1 Hz, 6H), 7.38 (d, *J* = 5.3 Hz, 6 H), 7.17 (d, *J* = 8.1 Hz, 6H), 6.28 (br s, 6H), 5.52 (d, *J* = 7.1 Hz, 6H), 3.30 (d, *J* = 9.5 Hz, 6H), 3.17 (dd, *J* = 15.0, 9.9 Hz, 6H). ^{13}C NMR (100 MHz; CD_3CN) δ 190.1, 176.2, 159.3, 156.8, 149.3, 145.4, 140.7, 139.3, 132.0, 131.8, 130.7, 125.8, 124.2, 35.6. HRMS (ESI) m/z calcd for $C_{81}H_{60}Fe_2N_{12}O_3$ ([M-4ClO_4]$^{4+}$) 340.0897, found 340.0898.



Mesocate 2:

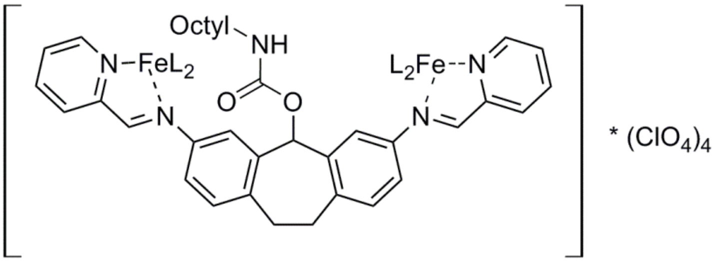
B (150 mg, 0.62 mmol), 2-pyridine carboxaldehyde (120 µL, 1.25 mmol) and $Fe(ClO_4)_2$•xH_2O (150 mg) were combined in anhydrous MeCN (20 mL) in a 50 mL round-bottomed flask under a blanket of N_2, followed by heating to 60°C for 24 h. The solution was then cooled to room temperature, diluted with Et_2O (300 mL), and cooled to -25°C followed by filtration of the resulting precipitate. Drying product *in vacuo* gave product as a purple solid (362 mg, 98%). ^{1}H NMR (400 MHz; CD_3CN) δ 8.73 (s, 6H), 8.02 (m, 12H), 7.93 (dd, *J* = 15.7, 7.6 Hz, 6H), 7.52 (m, 12H), 6.81 (d, *J* = 8.0 Hz, 6H), 6.07 (d, *J* = 5.5 Hz, 9H), 3.32 (dd, *J* = 16.3, 7.7 Hz, 6H), 2.83 (m, 6H), 2.54 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz; CD_3CN) δ 171.1, 160.1, 156.1, 146.3, 144.5, 139.4, 138.6, 131.2, 130.2, 129.5, 121.8, 120.8, 67.9, 31.4. HRMS (ESI) m/z calcd for $C_{81}H_{66}Cl_2Fe_2N_{12}O_{11}$ ([M-2ClO_4]$^{2+}$) 782.1519, found 782.1547.



Mesocate 3:

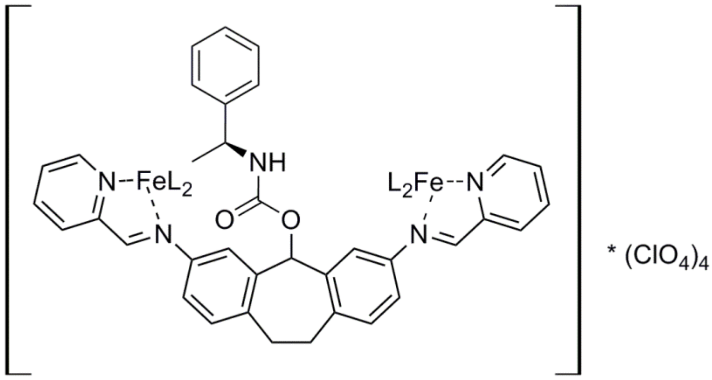
Mesocate 2 (25.9 mg, 15 µmol) and butyl isocyanate (30.0 µL, 266 µmol) were combined in anhydrous MeCN (5 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by heating under reflux for 24 h. The solution was then cooled to room temperature and diluted with Et_2O (250 mL), then cooled to -25°C followed by filtration of the resulting precipitate through celite. The filter was rinsed with additional Et_2O (50 mL), followed by rinsing the product off of the filter using acetone (75 mL). After evaporating the solvent *in vacuo* product was obtained as a purple solid (24.3

mg, 80 %). ^{1}H NMR (400 MHz; CD_3CN) δ 9.10 (s, 1H), 9.03 (s, 1H), 8.96 (s, 1H), 8.90 (s, 1H), 8.29-7.93 (m, 10H), 7.60-7.37 (m, 4H), 7.15 (d, *J* = 5.5 Hz, 1H), 6.99 (d, *J* = 5.3 Hz), 3.76-3.45 (m, 2H), 3.30 (ttd, *J* = 18.7, 9.7, 5.0 Hz, 4H), 3.11-2.81 (m, 4H), 1.64-1.00 (m, 12H), 0.97-0.87 (m, 2H), 0.78 (dd, *J* = 7.7, 7.0 Hz, 3H), 0.70 (td, 7.4, 3.0 Hz, 3H). ^{13}C NMR (125 MHz; CD_3CN) δ 172.1, 172.3, 172.1, 171.9, 160.0, 159.5, 159.4, 159.1, 156.4, 156.0, 155.6, 139.6, 139.5, 139.3, 130.1, 129.9, 129.8, 129.5, 129.0, 128.8, 128.5, 60.1, 59.9, 59.5, 32.0, 31.9, 29.6, 20.5, 20.4, 20.3, 13.8, 13.6. HRMS (ESI) m/z calcd for $C_{98}H_{96}Cl_3Fe_2N_{16}NaO_{18}$ ([M-ClO_4+Na+CH_3CN]$^{+}$) 1012.2369, found 1012.3002.



Mesocate 4:

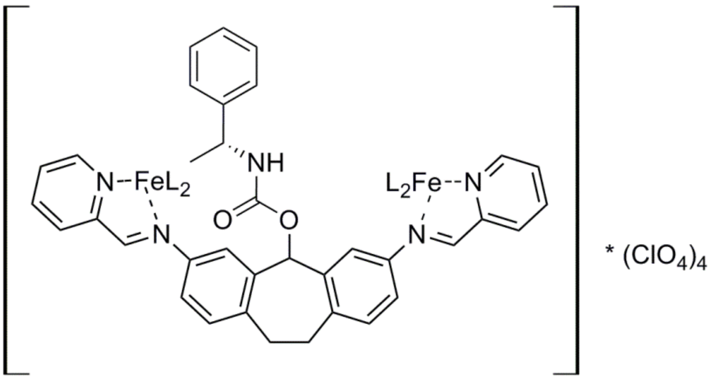
Mesocate 2 (30.3 mg, 17 μmol) and octyl isocyanate (50.0 μL, 283 μmol) were combined in anhydrous MeCN (5 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by heating under reflux for 14 h. The solution was then cooled to room temperature and diluted with Et_2O (300 mL), cooled to -25°C followed by filtration of the resulting precipitate. After drying the product was recovered as a purple solid (26.0 mg, 67 %). For NMRs see pages *S*-23 through *S*-24. ESI-MS led to decomposition in which no parent ion or fragments reminiscent of self-assembly were observed.



Mesocate (*S*)-5:

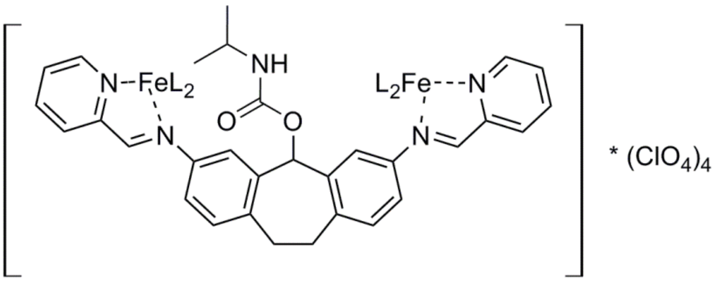
Mesocate 2 (27.4 mg, 16 μmol) and (S)-(−)-α-methylbenzyl isocyanate (50.0 μL, 355 μmol) were combined in anhydrous MeCN (5 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by heating under reflux for 14 h. The solution was then cooled to room temperature and diluted with Et_2O (300 mL), cooled to -25°C followed by filtration of the resulting precipitate. After drying the product was recovered as a purple solid (28.7 mg, 83 %). ^{1}H NMR (400 MHz; CD_3CN) δ 8.71 (s, 2H), 7.80 (td, *J* = 7.7, 1.3 Hz, 2H), 7.49-7.19 (m, 14H), 7.08-7.04 (m, 1H), 6.99-6.90 (m, 4H), 6.55 (d, *J* = 7.2 Hz, 2H), 5.35 (br s, 1H), 5.3 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H). For NMRs see pages

S-25 through *S*-26. ESI-MS led to decomposition in which no parent ion or fragments reminiscent of self-assembly were observed.



Mesocate (*R*)-5:

Mesocate 2 (6.6 mg, 3.7 μmol) and (R)-(−)-α-methylbenzyl isocyanate (50.0 μL, 355 μmol) were combined in anhydrous MeCN (5 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by heating under reflux for 24 h. The solution was then cooled to room temperature and diluted with anhydrous Et_2O (45 mL), cooled to -25°C followed by filtration of the resulting precipitate. After drying the product was rinsed with EtOAc (50 mL), then filtered and dried to give a purple solid (6.1 mg, 74 %). ^{1}H NMR (400 MHz; CD_3CN) δ 8.71 (s, 2H), 7.80 (td, *J* = 7.7, 1.3 Hz, 2H), 7.49-7.19 (m, 14H), 7.08-7.04 (m, 1H), 6.99-6.90 (m, 4H), 6.55 (d, *J* = 7.2 Hz, 2H), 5.35 (br s, 1H), 5.3 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H). For ^{1}H NMR see page *S*-27. ESI-MS led to decomposition in which no parent ion or fragments reminiscent of self-assembly were observed.



Mesocate 6:

Mesocate 2 (20 mg, 11 μmol) and isopropyl isocyanate (100.0 μL, 102 μmol) were combined in anhydrous MeCN (10 mL) in a 50 mL round-bottomed flask under a blanket of N_2, followed by heating under reflux for 15 h. Excess isocynate was required to achieve reaction completion. The solution was then cooled to room temperature and diluted with Et_2O (300 mL), cooled to -25°C followed by filtration of the resulting precipitate. After drying the product was recovered as a purple solid mixed with N,N'-diisopropyl urea which could not be removed without destroying the self-assembly. For ^{1}H NMR see page *S*-27. ESI-MS led to decomposition in which no parent ion or fragments reminiscent of self-assembly were observed.

3. NMR Spectral Data

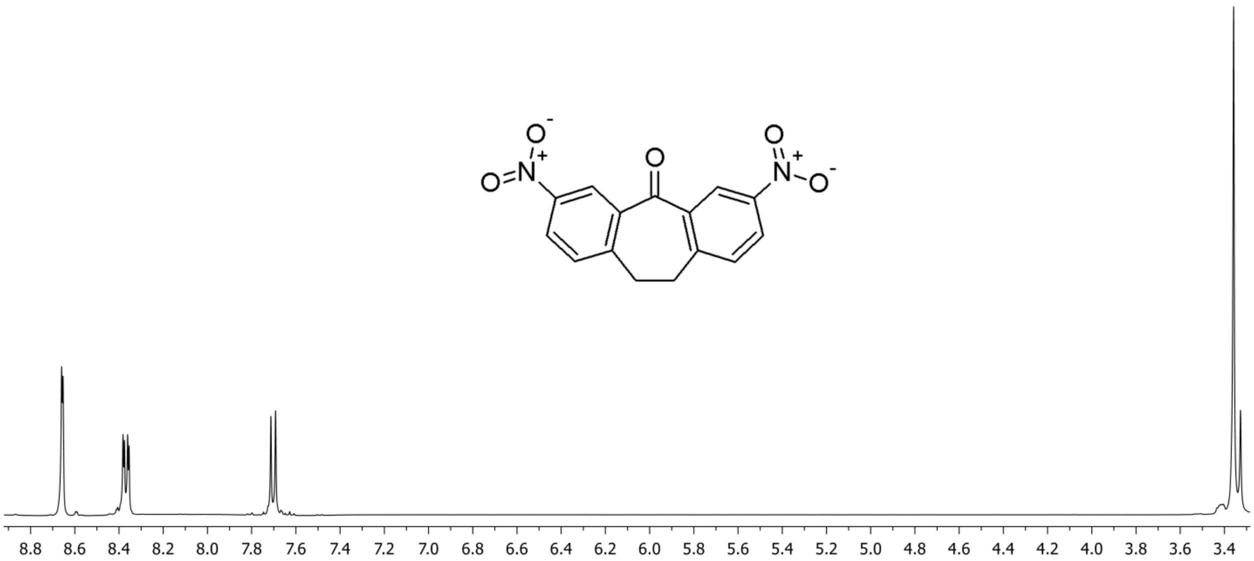


Figure S-1. ^{1}H NMR spectrum of ***S-1*** (DMSO, 400 MHz, 298 K).

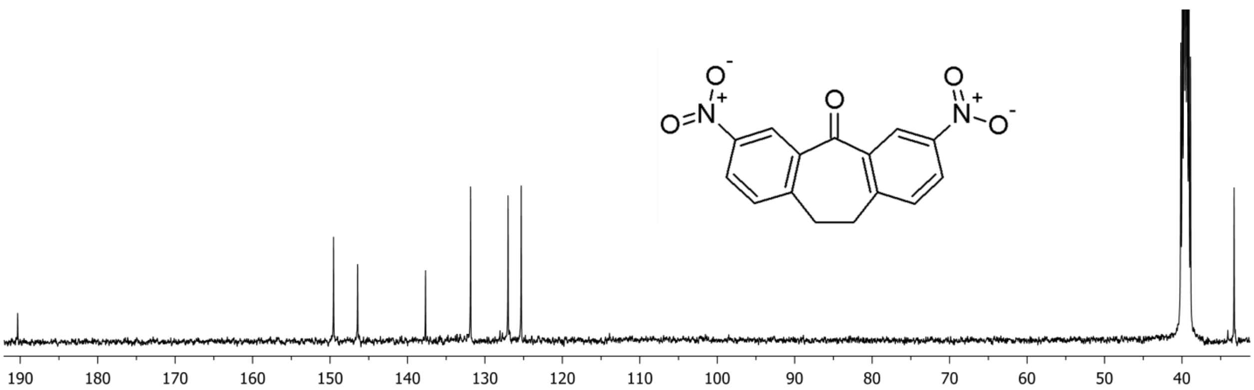


Figure S-2. ^{13}C NMR spectrum of ***S-1*** (DMSO, 400 MHz, 298 K).

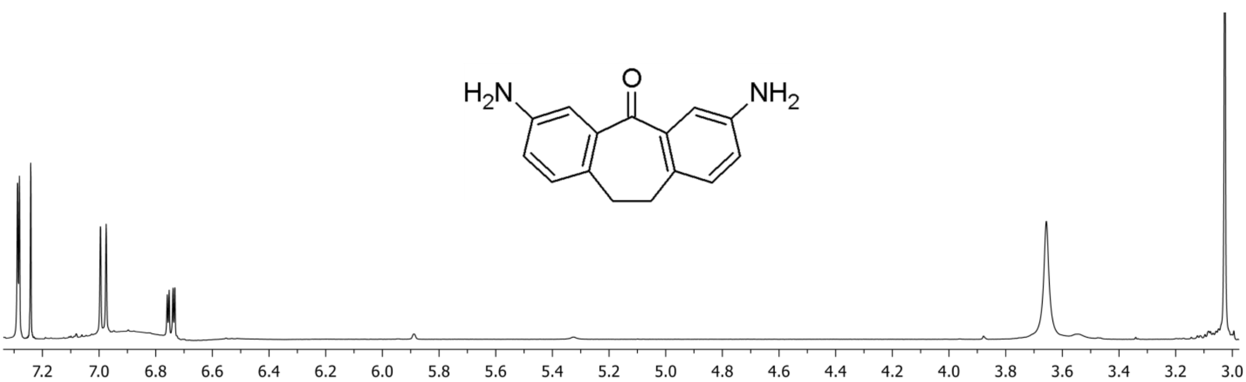


Figure S-3. ^{1}H NMR spectrum of **A** ($CDCl_3$, 400 MHz, 298 K).

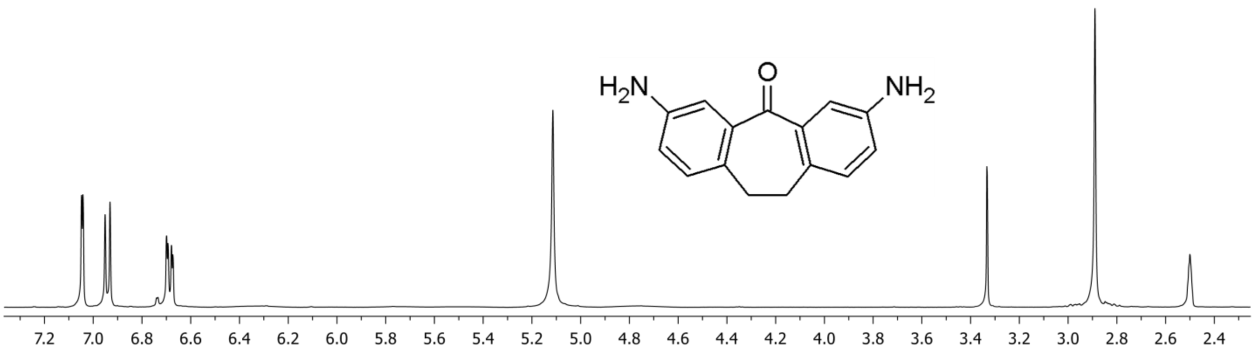


Figure S-4. ^{1}H NMR spectrum of **A** (DMSO, 400 MHz, 298 K).

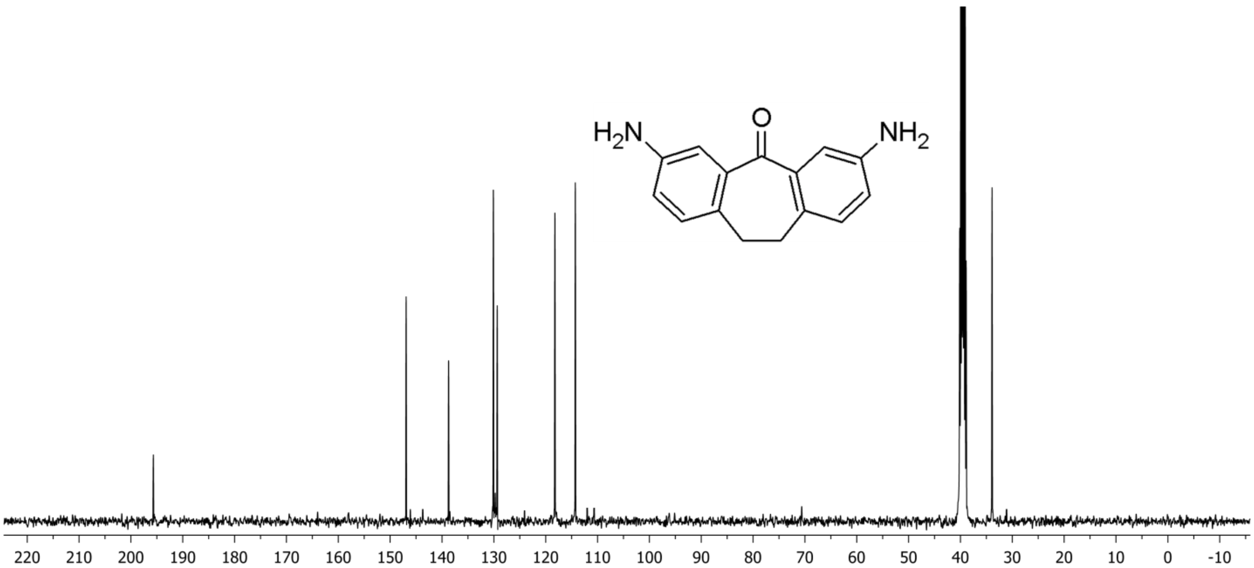


Figure S-5. ^{13}C NMR spectrum of **A** (DMSO, 400 MHz, 298 K).

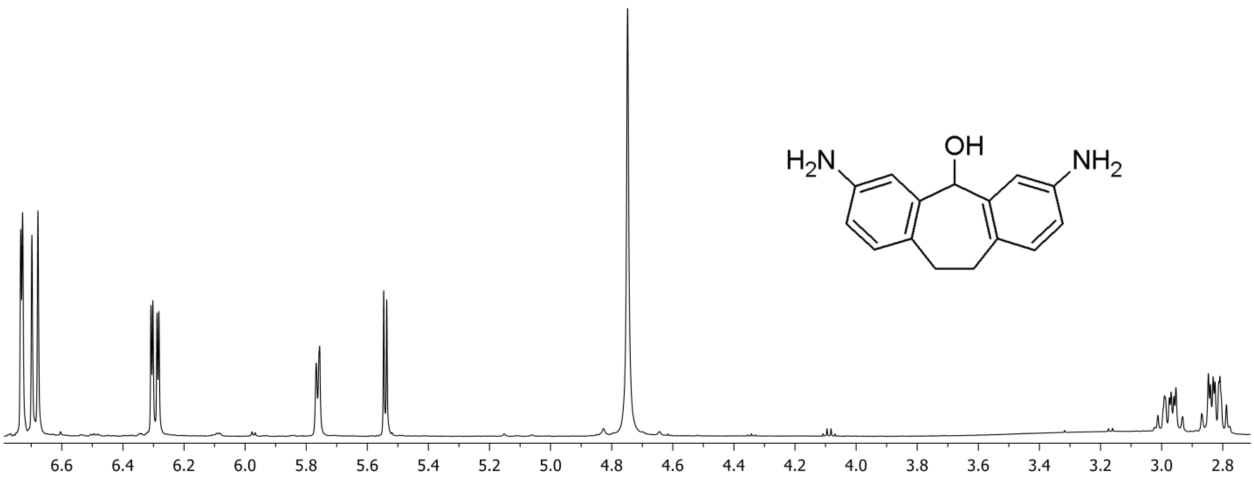


Figure S-6. ^{1}H NMR spectrum of **B** (DMSO, 400 MHz, 298 K).

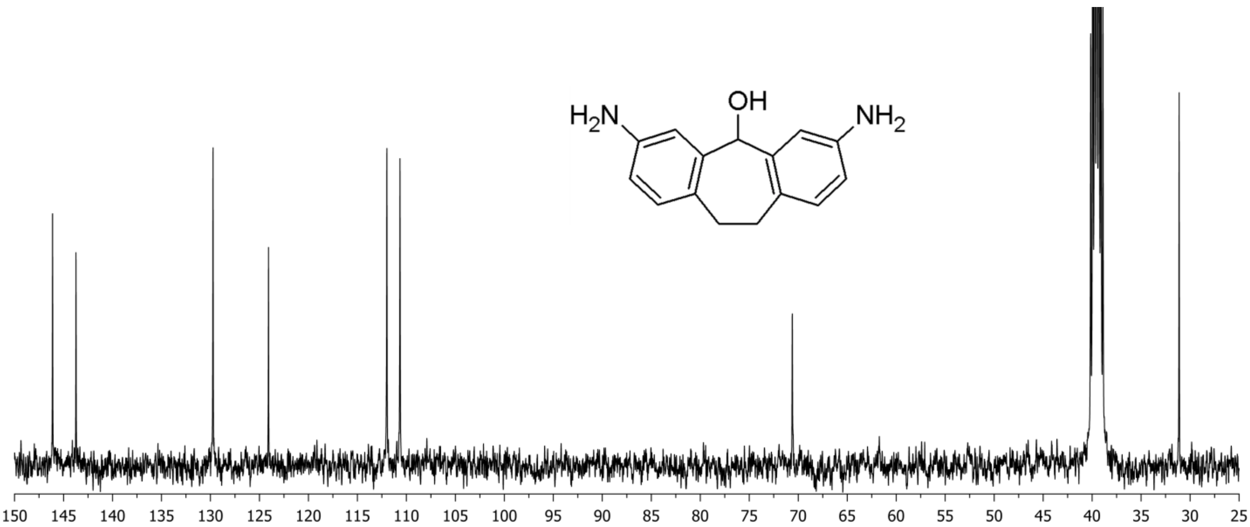


Figure S-7. ^{13}C NMR spectrum of **B** (DMSO, 400 MHz, 298 K).

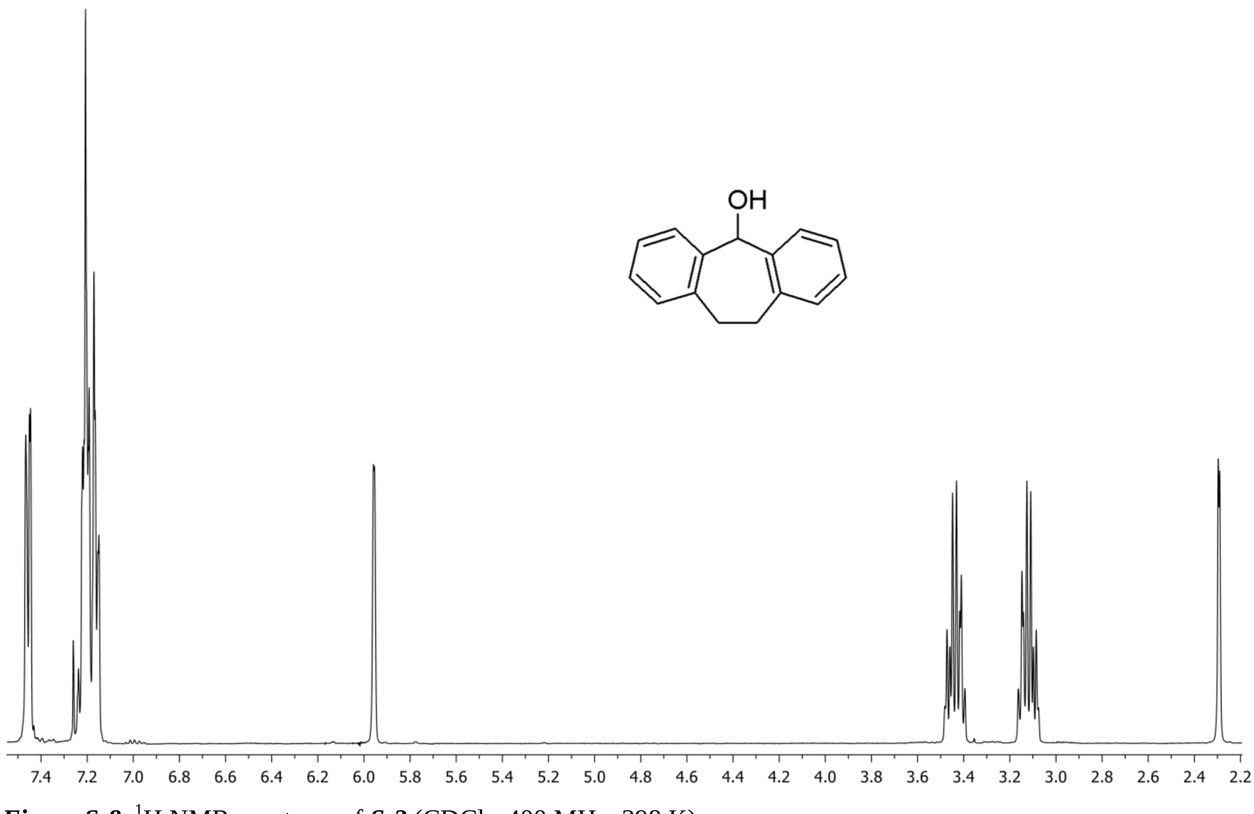


Figure S-8. ^{1}H NMR spectrum of ***S-2*** ($CDCl_3$, 400 MHz, 298 K).

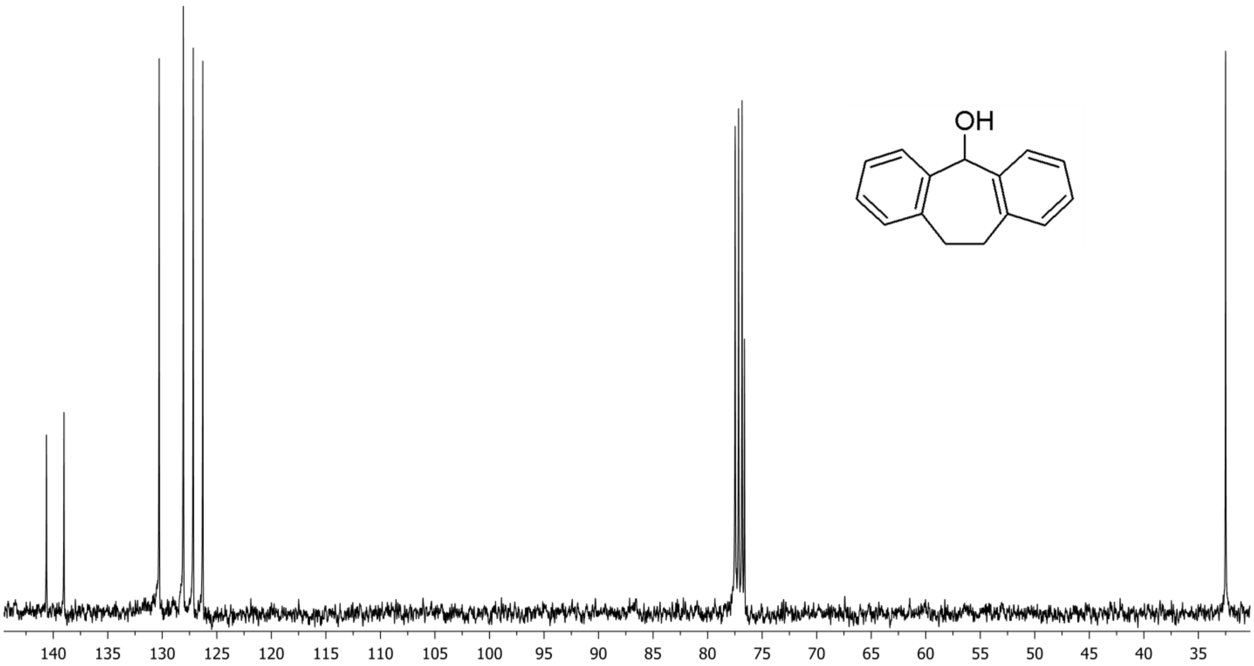


Figure S-9. ^{13}C NMR spectrum of ***S-2*** (DMSO, 400 MHz, 298 K).

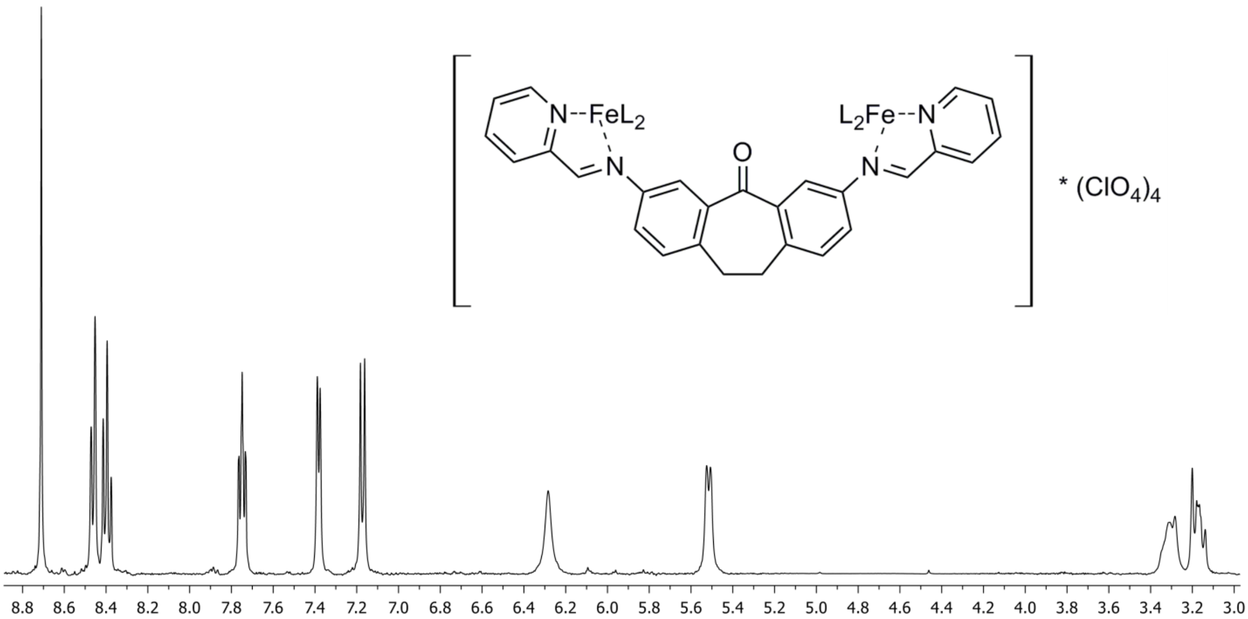


Figure S-10. ^{1}H NMR spectrum of **Mesocate 1** (CD_3CN, 400 MHz, 298 K).

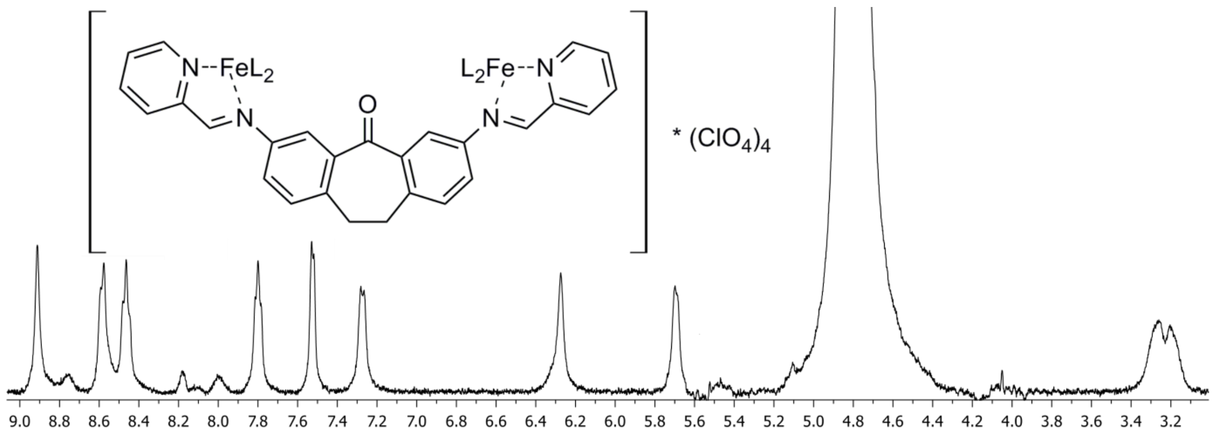


Figure S-11. ^{1}H NMR spectrum of **Mesocate 1** + LiCl (D_2O, 400 MHz, 298 K).

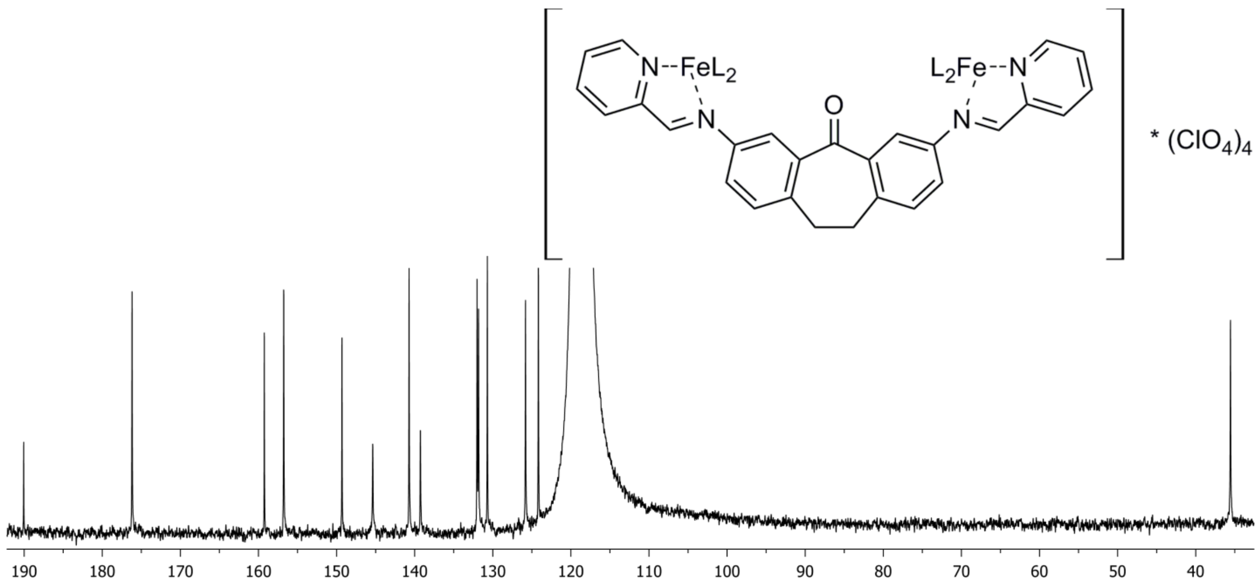


Figure S-12. ^{13}C NMR spectrum of **Mesocate 1** (CD_3CN, 400 MHz, 298 K).

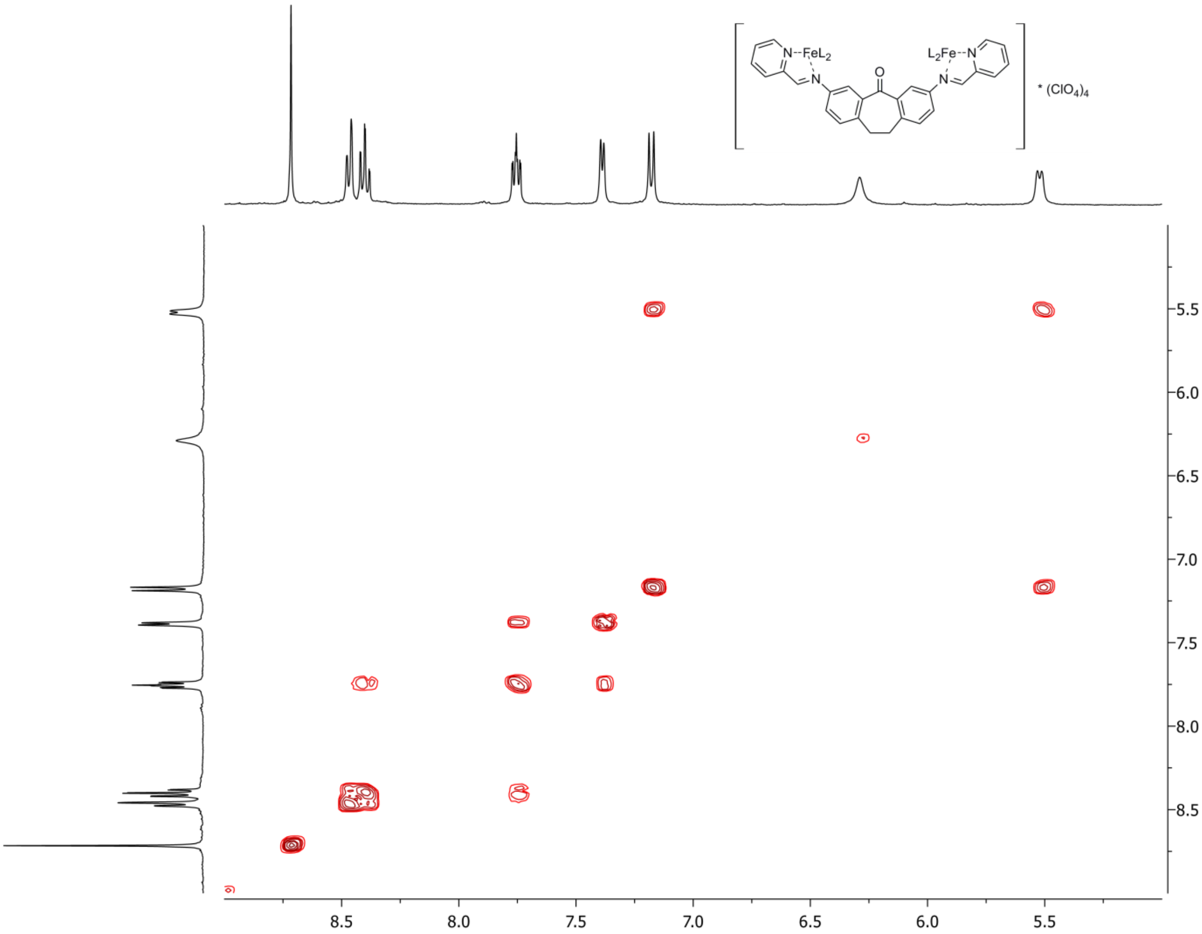


Figure S-13. gCOSY spectrum of **Mesocate 1** (CD_3CN, 400 MHz, 298K).

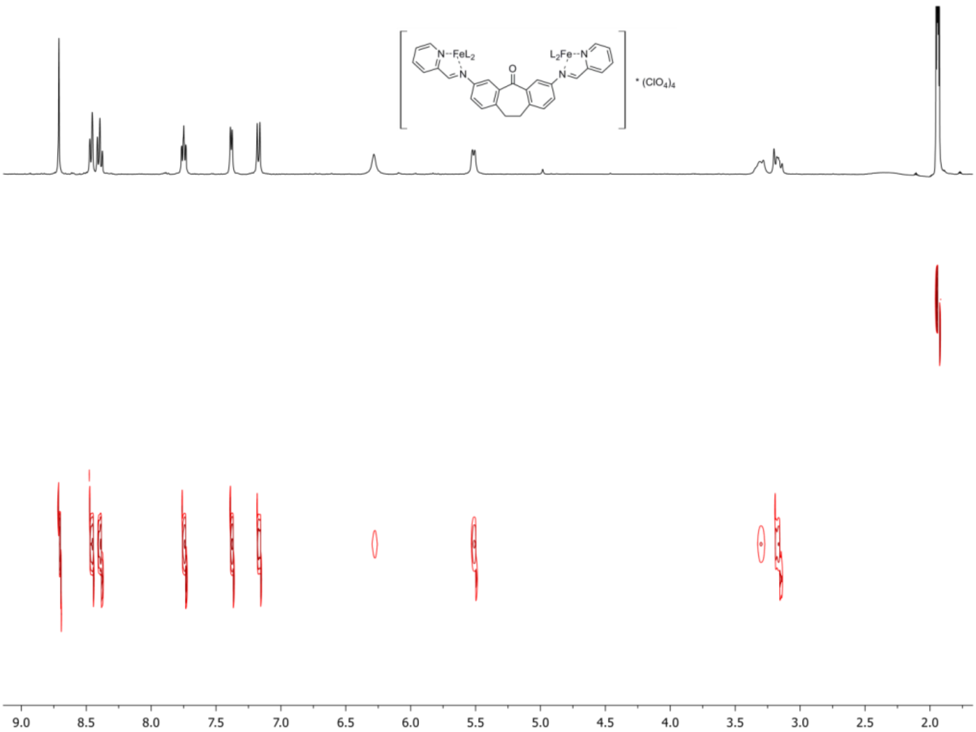


Figure S-14. DOSY spectrum of **Mesocate 1** (CD_3CN, 600 MHz, 298 K, Δ = 100 ms, δ = 2.6 μs, Diffusion Coefficient = 5.97 x 10^{-10} m^2/s vs. 3.95 x10^{-9} m^2/s for the solvent).

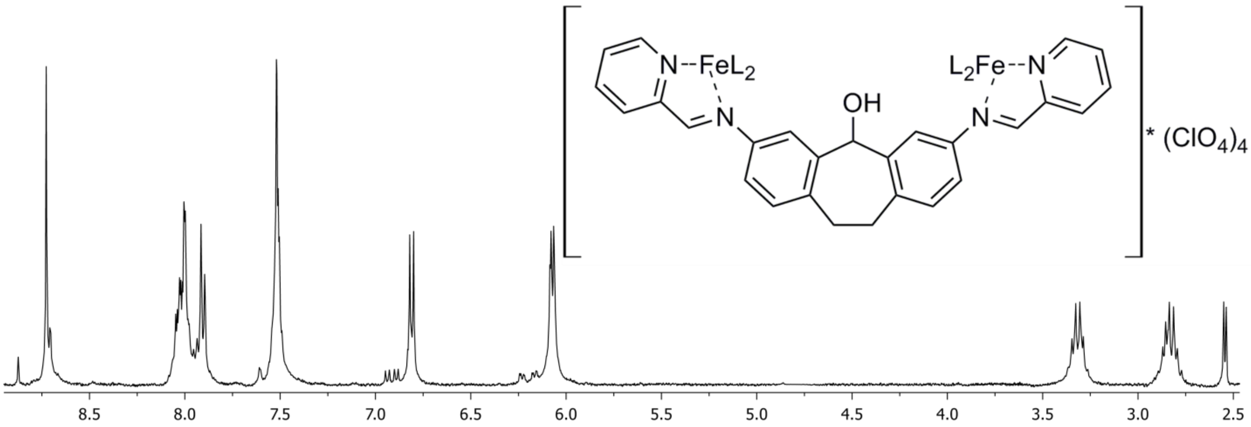


Figure S-15. [1]H NMR spectrum of **Mesocate 2** (CD_3CN, 400 MHz, 298 K).

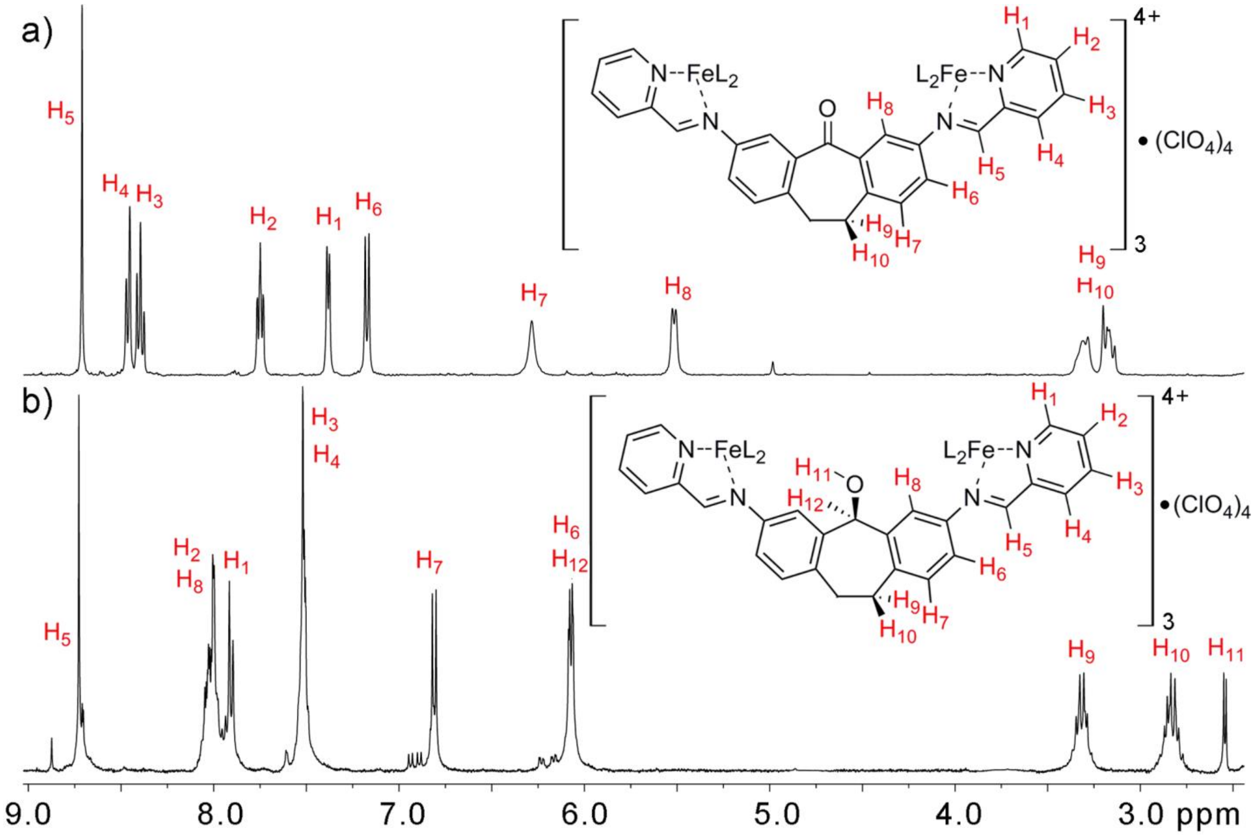


Figure S-16. Assigned [1]H NMR spectra of both mesocates **1** and **2** (CD_3CN, 400 MHz, 298 K).

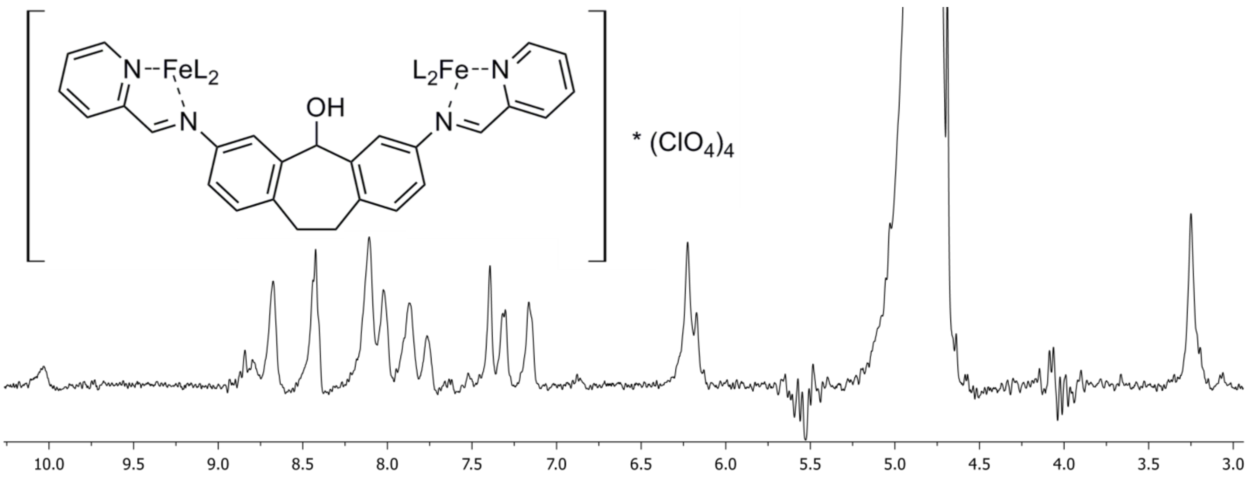


Figure S-17. [1]H NMR spectrum of **Mesocate 2** (D_2O, 400 MHz, 298 K).

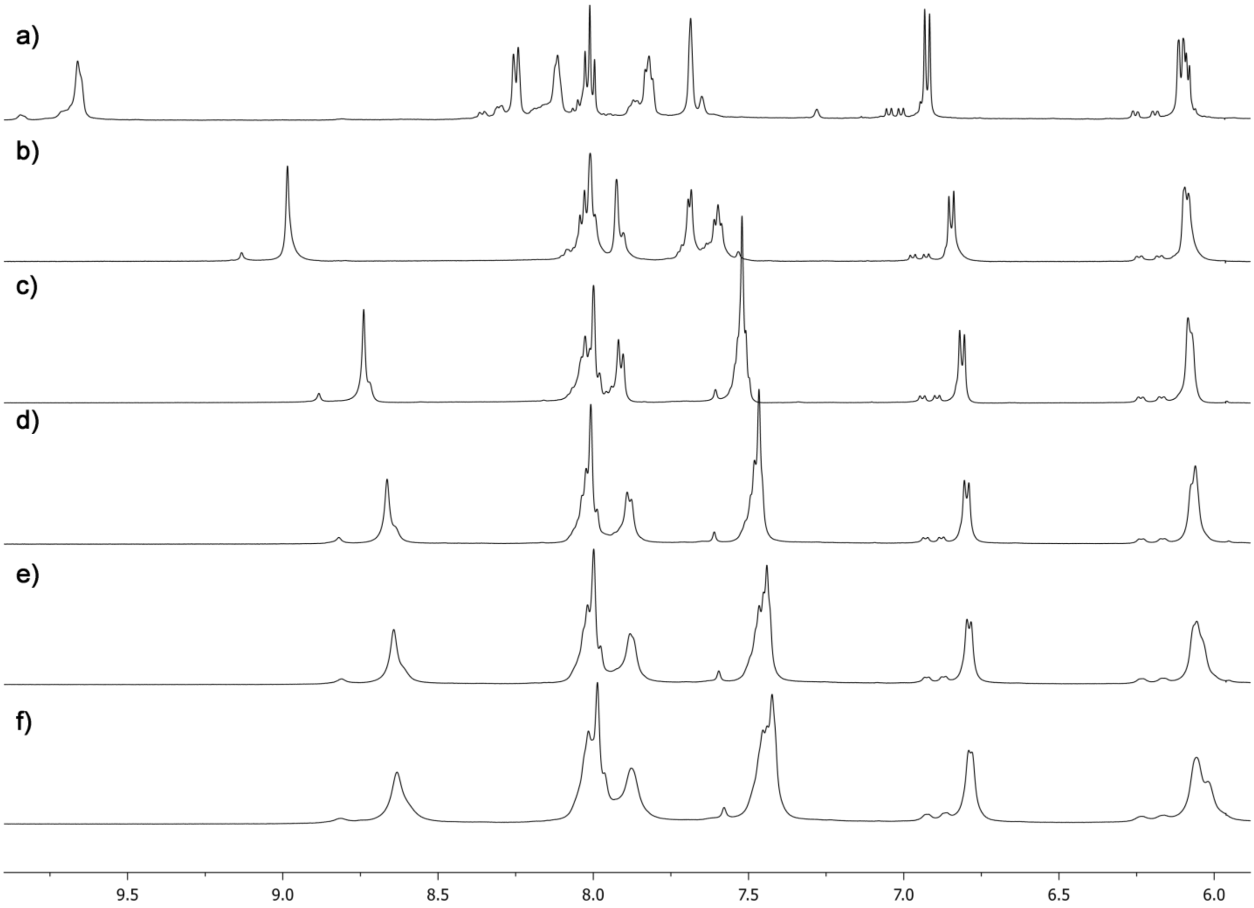


Figure S-18. Variable Temperature [1]H NMR spectrum of **Mesocate 2**: a) 75 °C; b) 50 °C; c) 25 °C; d) 0 °C; e) -20 °C; f) -40 °C (CD_3CN, 500 MHz).

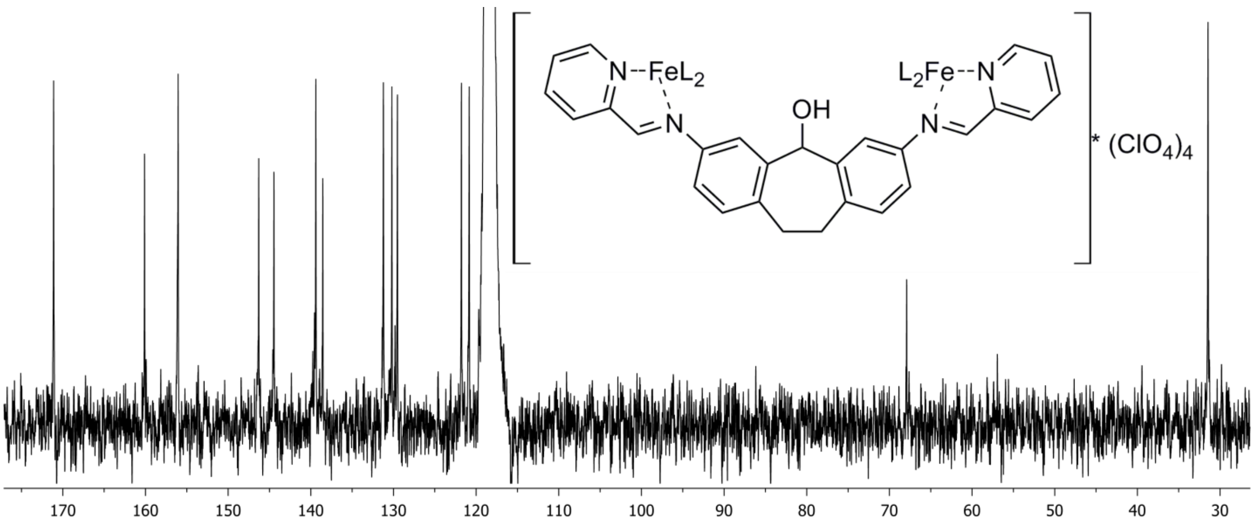


Figure S-19. ^{13}C NMR spectrum of **Mesocate 2** (CD_3CN, 400 MHz, 298 K).

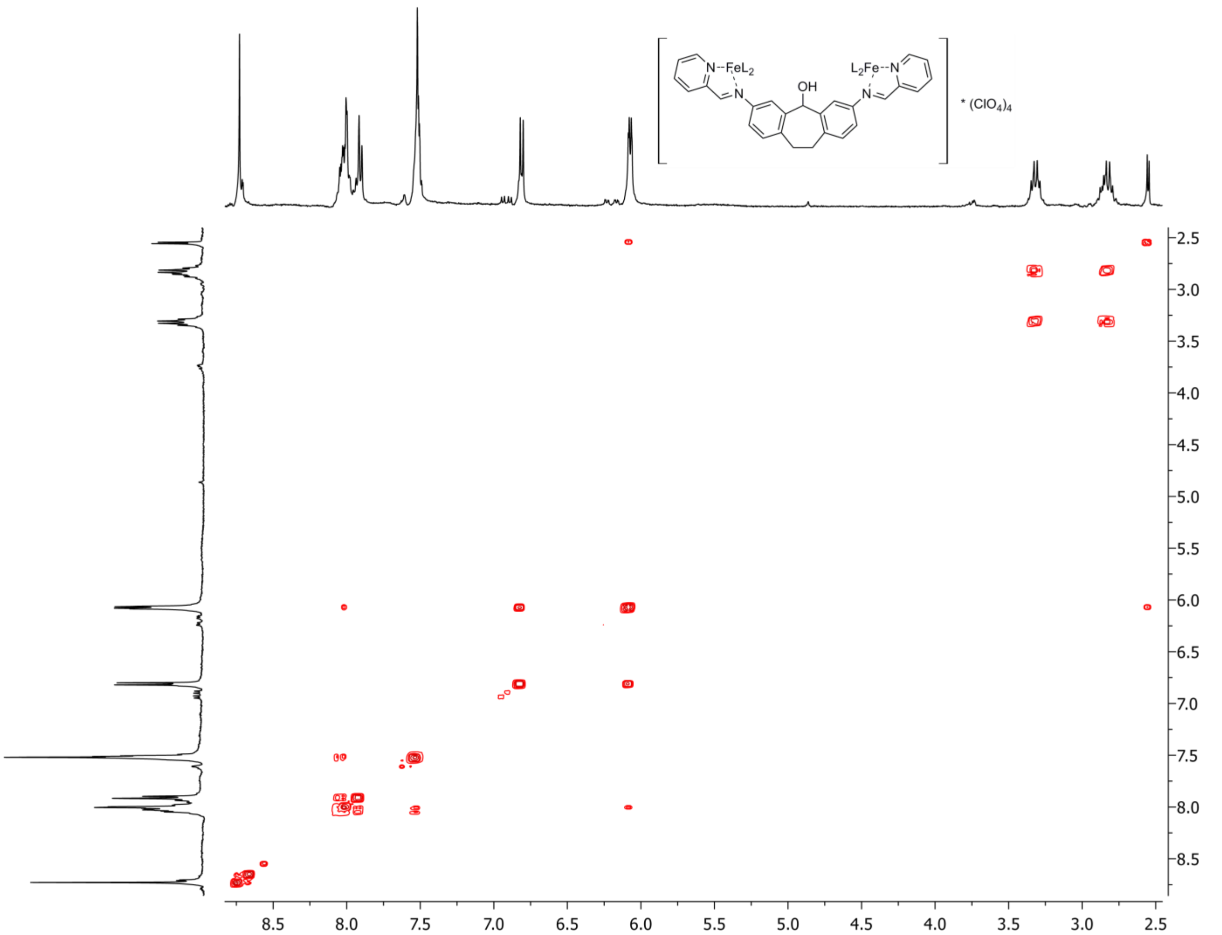


Figure S-20. gCOSY spectrum of **Mesocate 2** (CD_3CN, 400 MHz, 298 K).

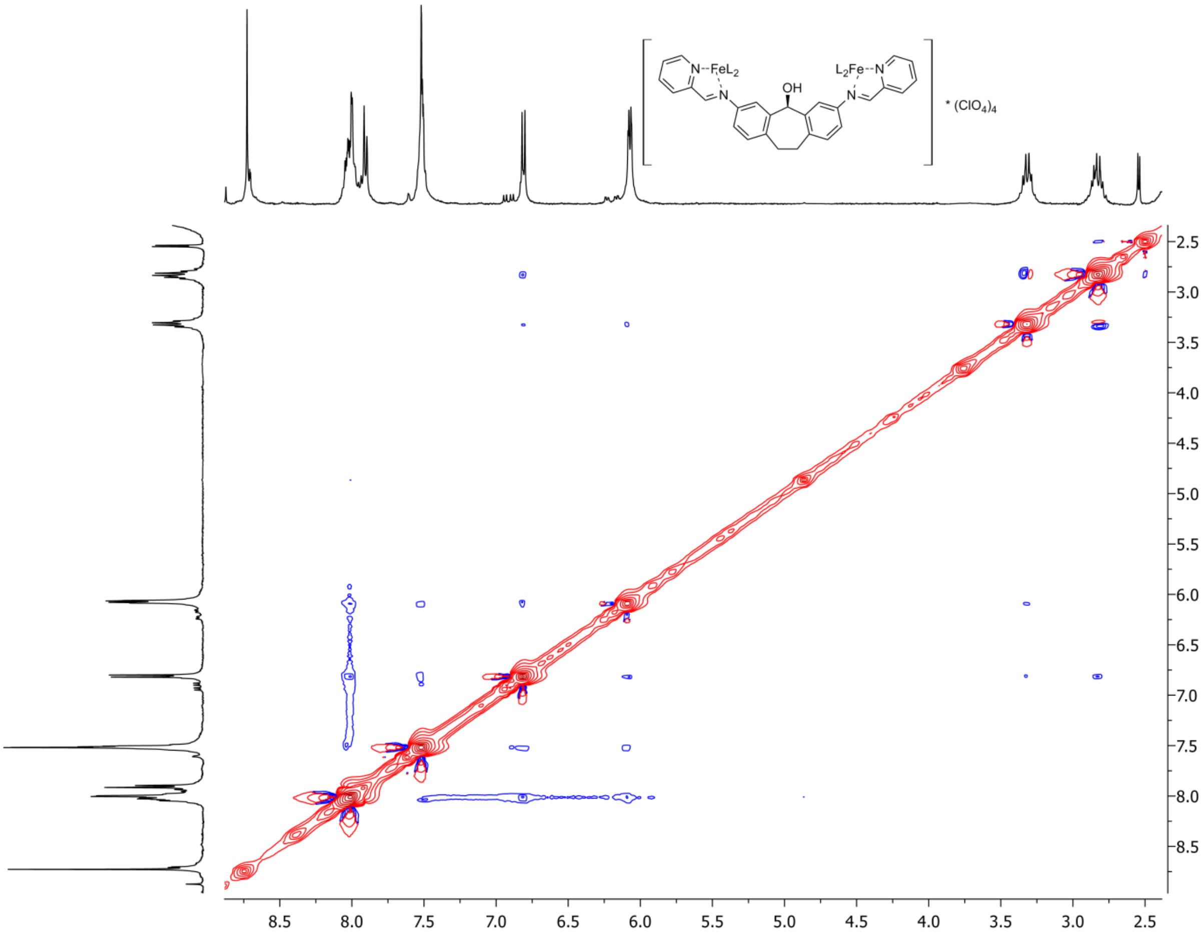


Figure S-21. NOESY spectrum of **Mesocate 2** (CD_3CN, 600 MHz, 298 K).

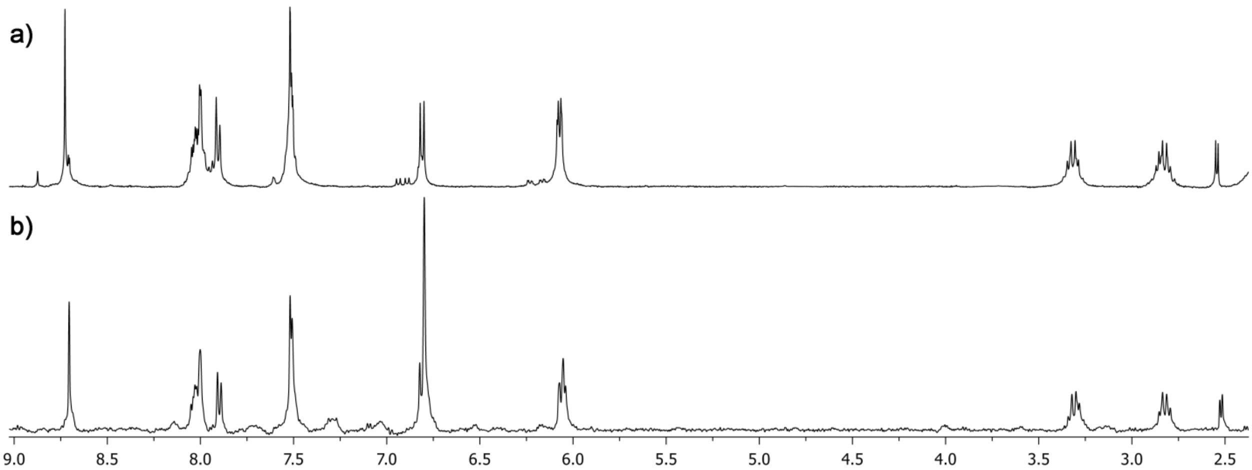


Figure S-22. [1]H NMR spectra of **Mesocate 2**: a) Precipitated quickly by addition of Et_2O to MeCN; b) Crystallized by slow diffusion of Et_2O into MeCN (CD_3CN, 400 MHz, 298 K).

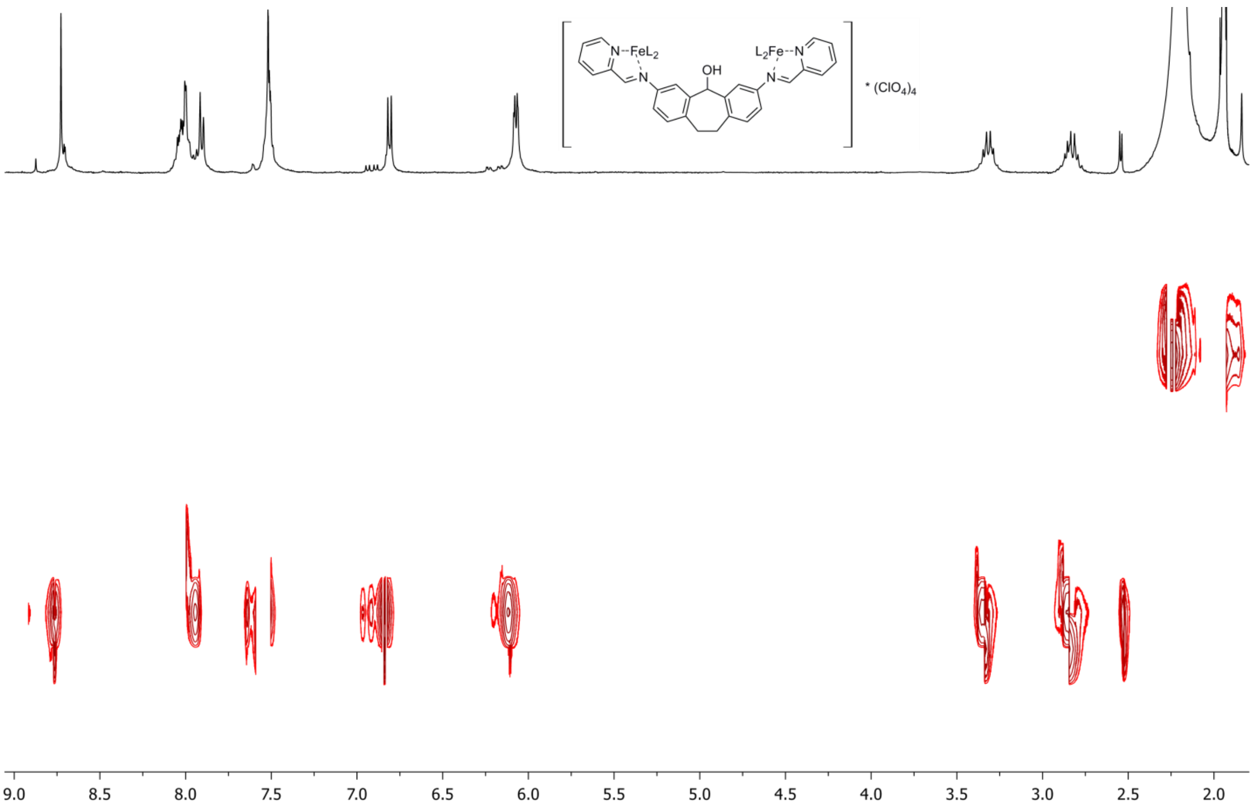


Figure S-23. DOSY spectrum of **Mesocate 2** (CD_3CN, 600 MHz, 298 K, Δ = 100 ms, δ = 2.6 μs, Diffusion Coefficient = 6.27 x 10^{-10} m^2/s vs. 3.95 x10^{-9} m^2/s for the solvent).

4. NMR Spectra of Postsynthetically Modified Mesocates

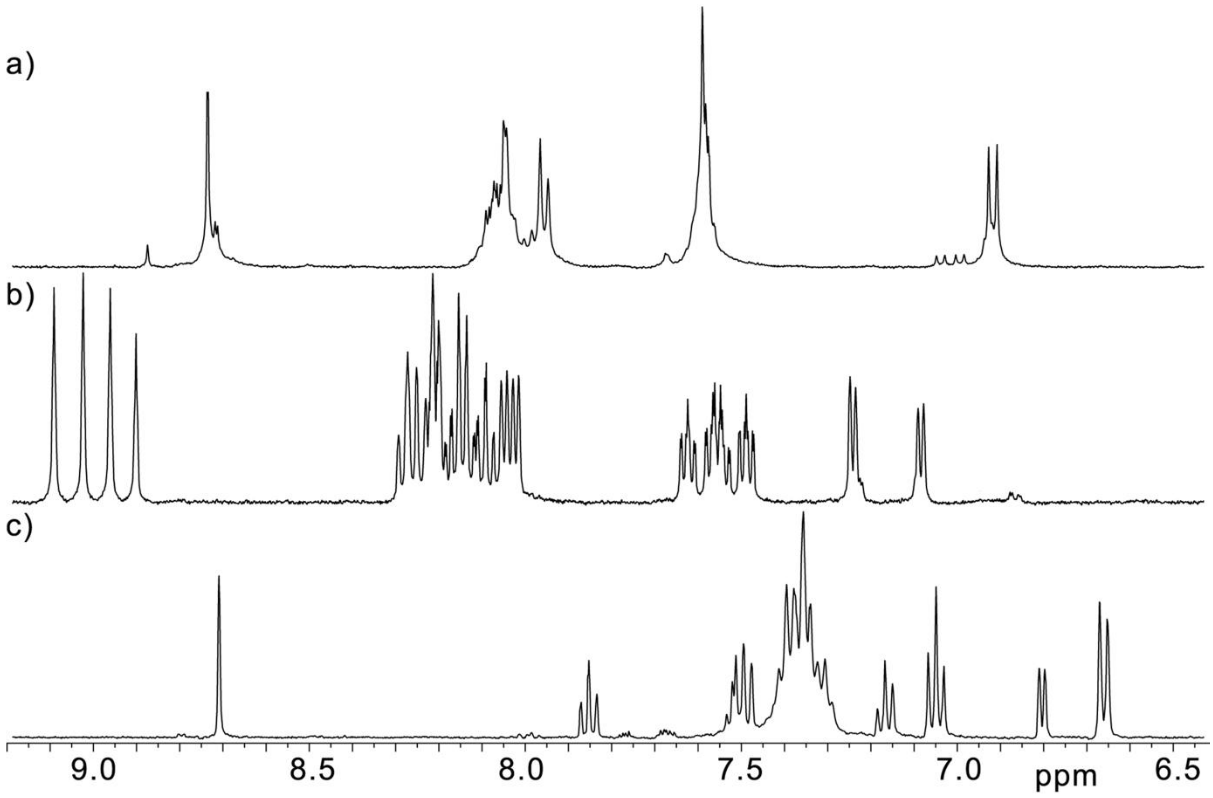


Figure S-24. Stacked [1]H NMR spectra showing differences between internal functions of different sizes: a) **Mesocate 2**; b) **Mesocate 3**; c) **Mesocate (*S*)-5** (CD_3CN, 400 MHz, 298 K).

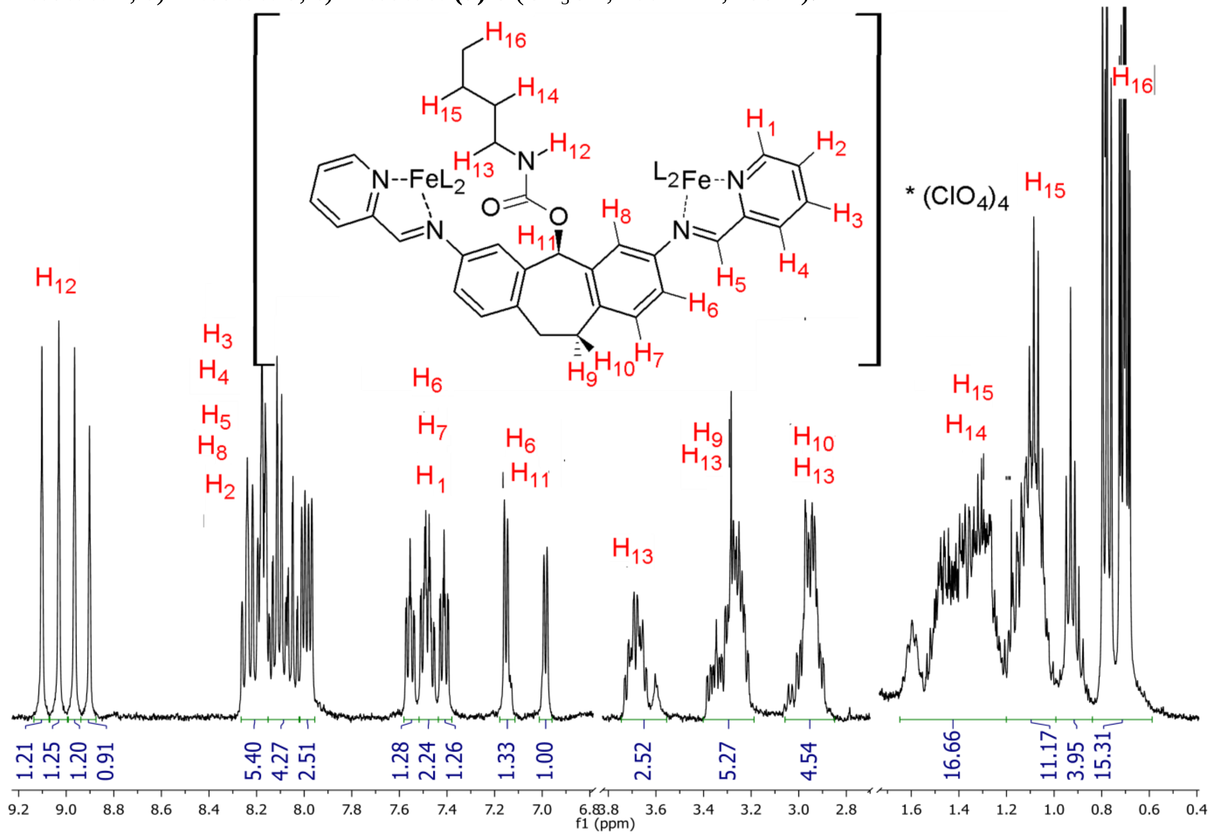


Figure S-25. [1]H NMR spectrum of **Mesocate 3** with regions for the different protons labelled (CD_3CN, 400 MHz, 298 K).

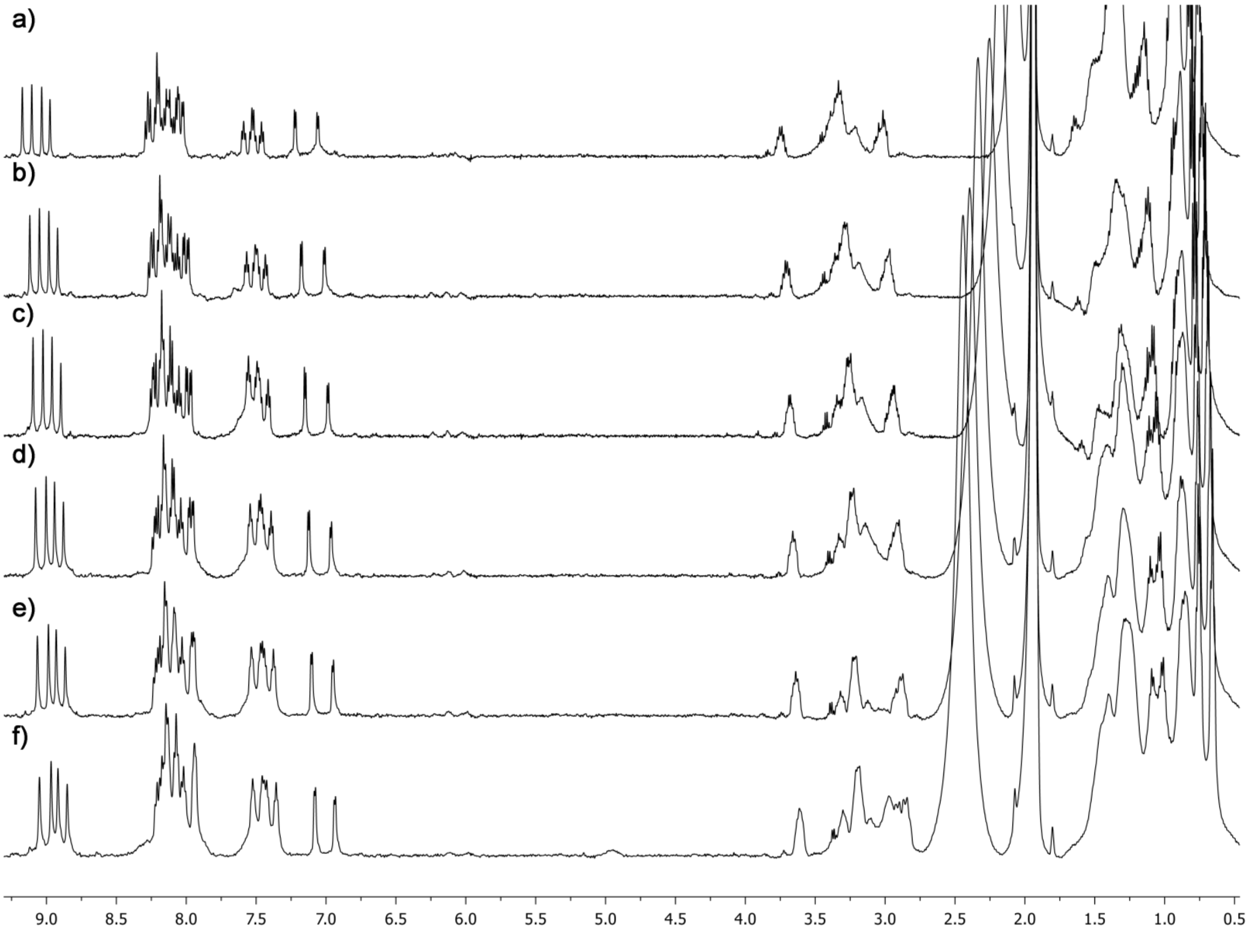


Figure S-26. Variable Temperature ^{1}H NMR spectrum of **Mesocate 3**: a) 75 °C; b) 50 °C; c) 25 °C; d) 0 °C; e) -20 °C; f) -40 °C (CD_3CN, 500 MHz).

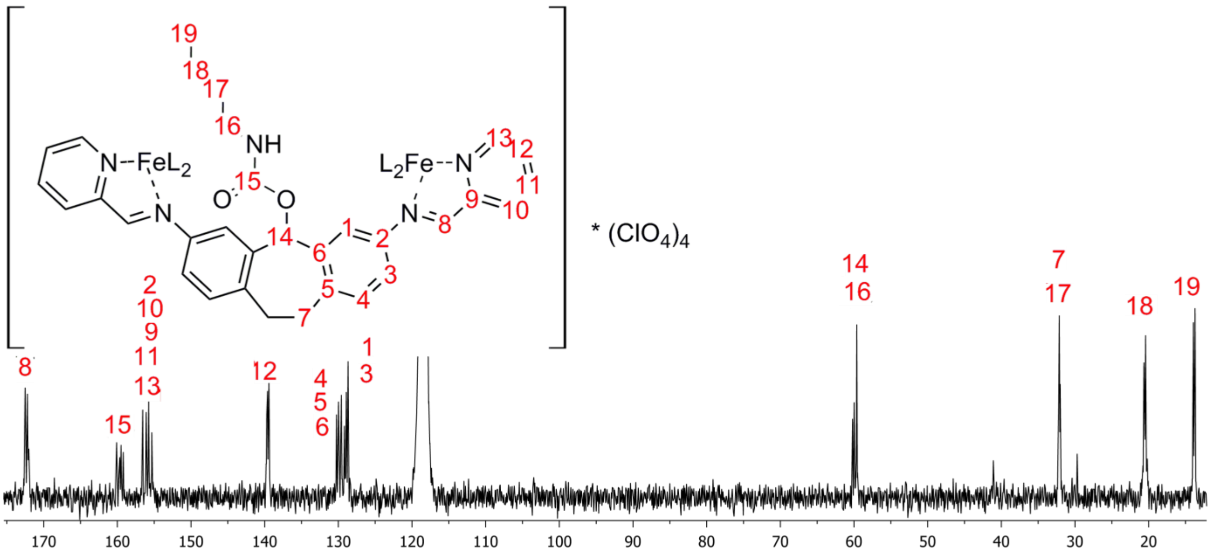


Figure S-27. ^{13}C NMR spectrum of **Mesocate 3** (CD_3CN, 500 MHz, 298 K).

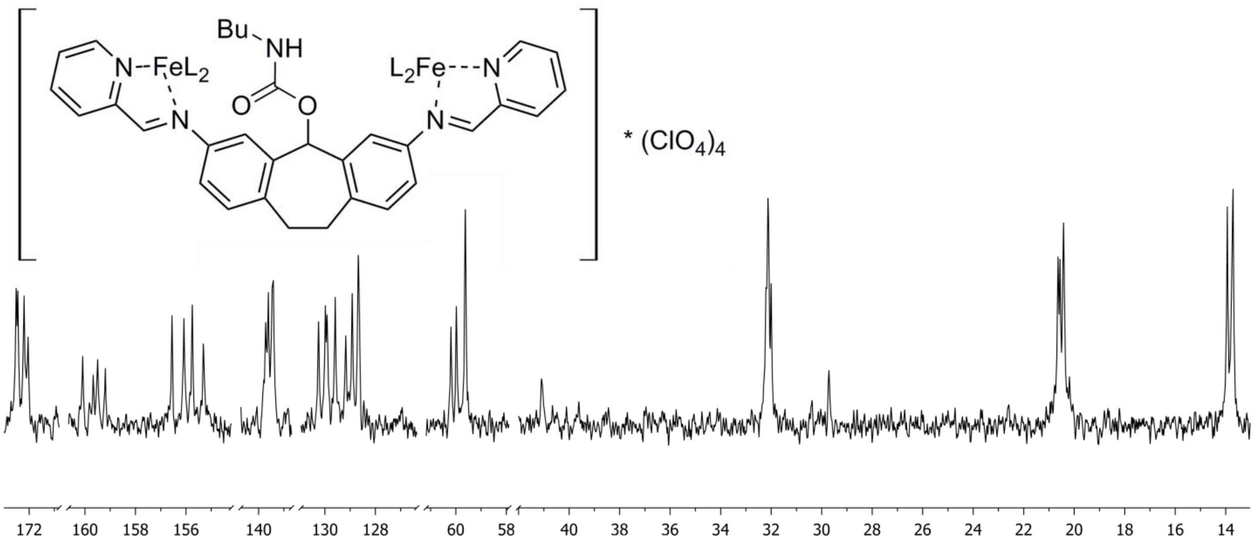


Figure S-28. Close-up [13]C NMR spectrum of **Mesocate 3** (CD_3CN, 500 MHz, 298 K).

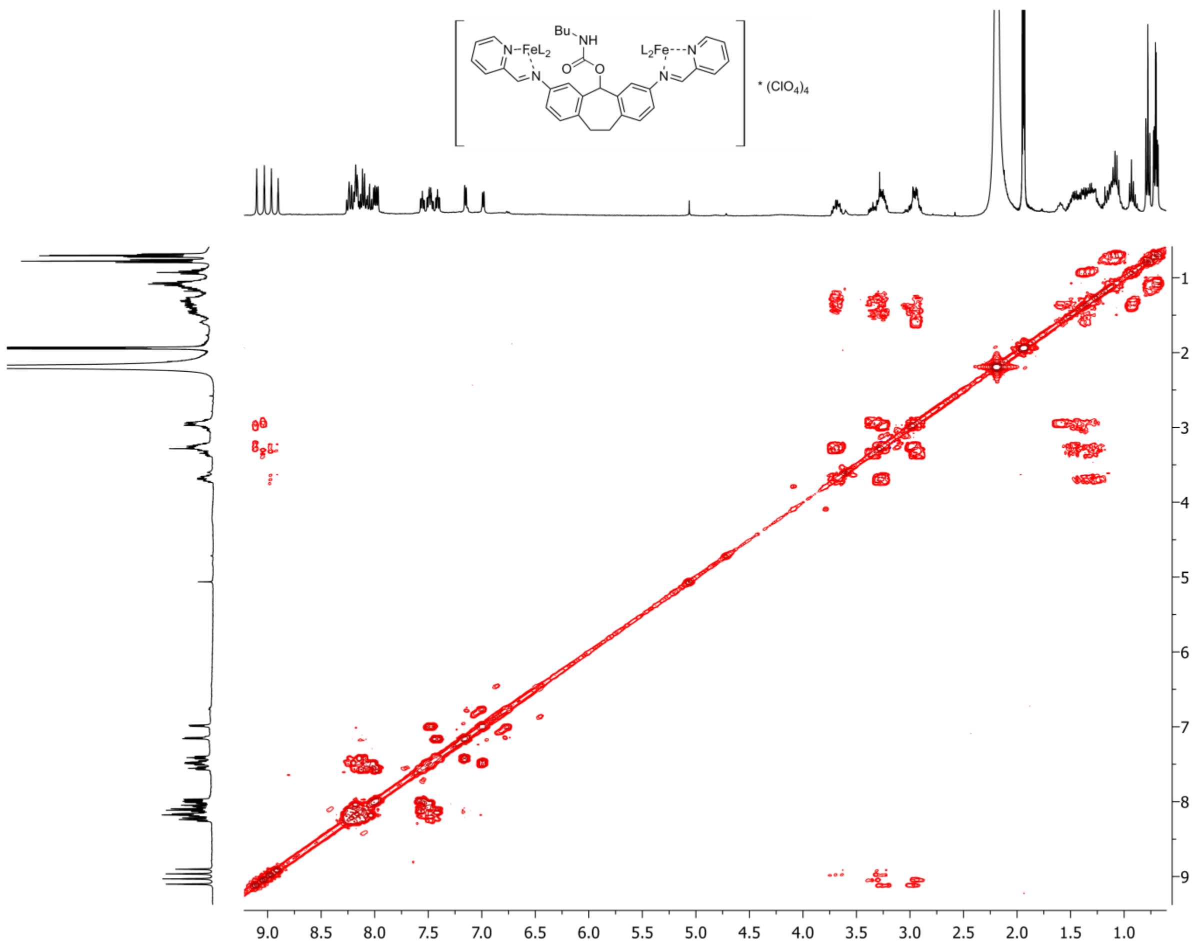


Figure S-29. gCOSY spectrum of **Mesocate 3** (CD_3CN, 400 MHz, 298 K).

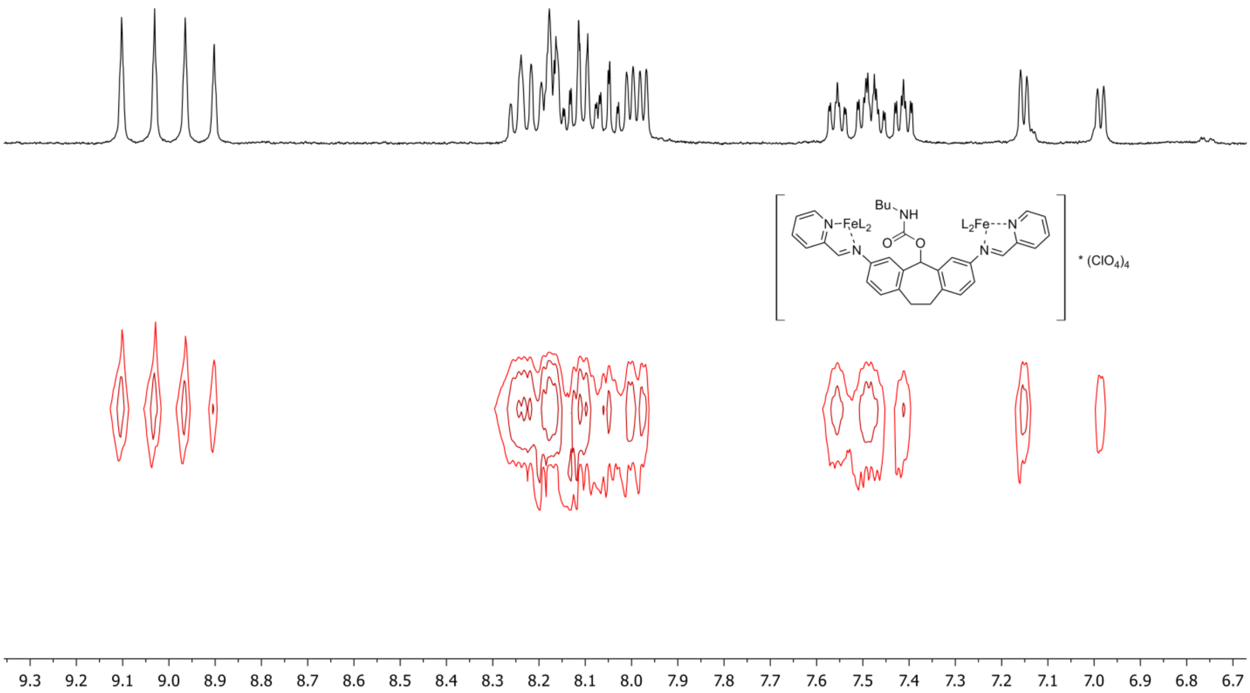


Figure S-30. DOSY spectrum of **Mesocate 3** (CD_3CN, 600 MHz, 298 K, Δ = 100 ms, δ = 2.6 μs, Diffusion Coefficient = 7.76 $x10^{-10}$ m^2/s vs. 3.31 $x10^{-9}$ m^2/s for the solvent).

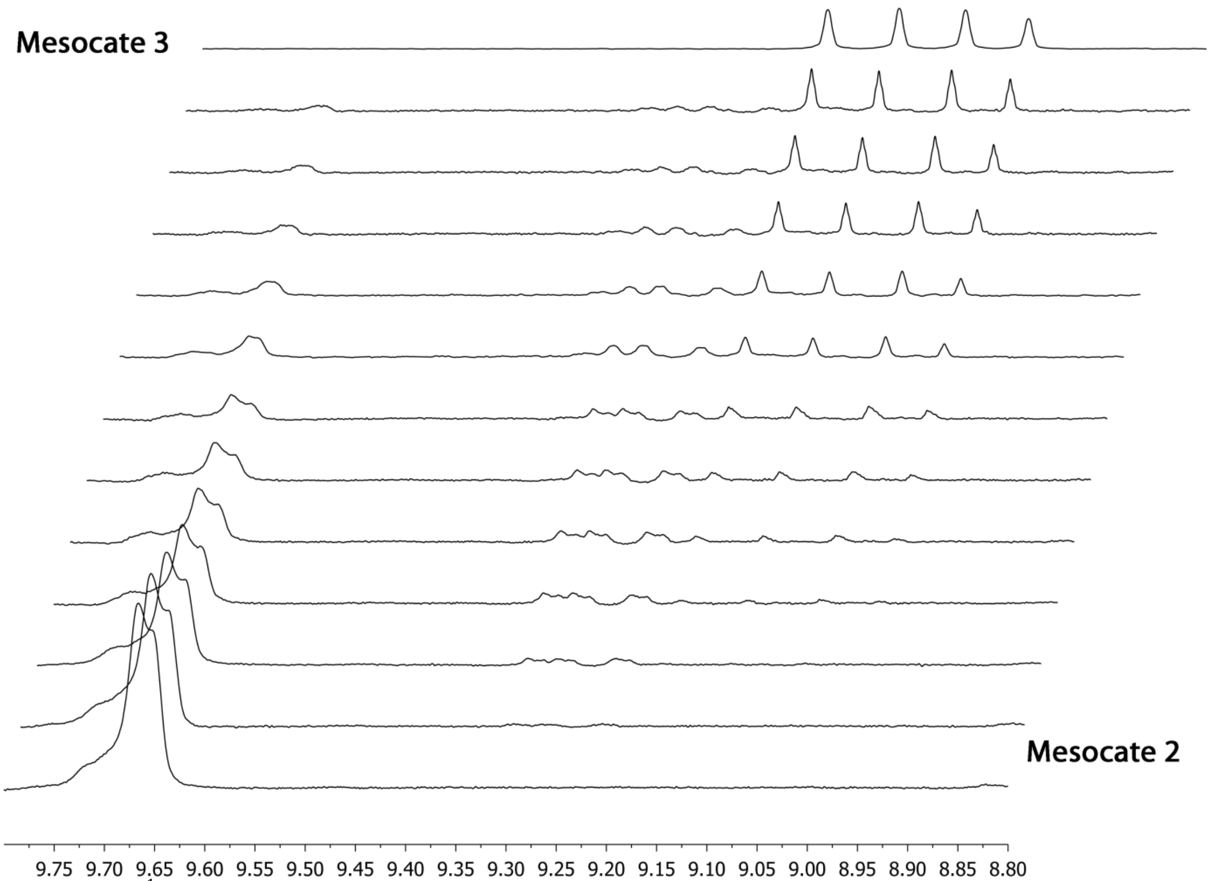


Figure S-31. ^1H NMR spectra of reaction between **Mesocate 2** (8.5 mM) and butylisocyanate to give **Mesocate 3** taken in 30 minute increments (CD_3CN, 500 MHz, 353 K).

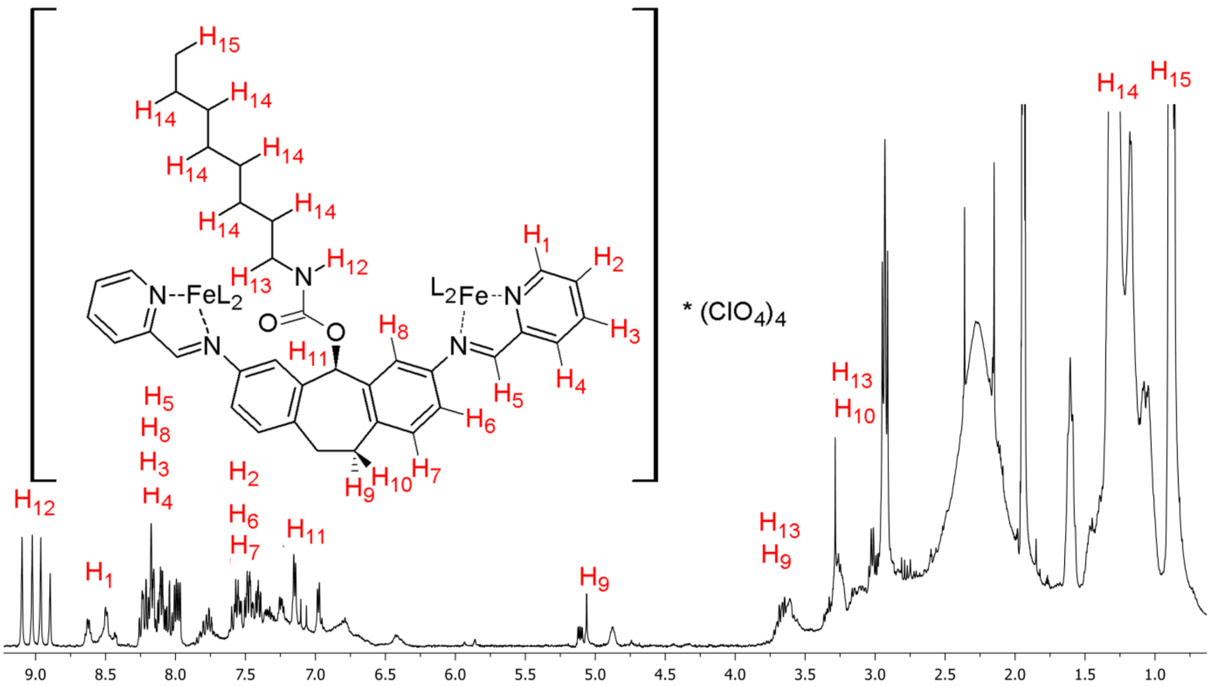


Figure S-32. [1]H NMR spectrum of **Mesocate 4** (CD_3CN, 400 MHz, 298 K).

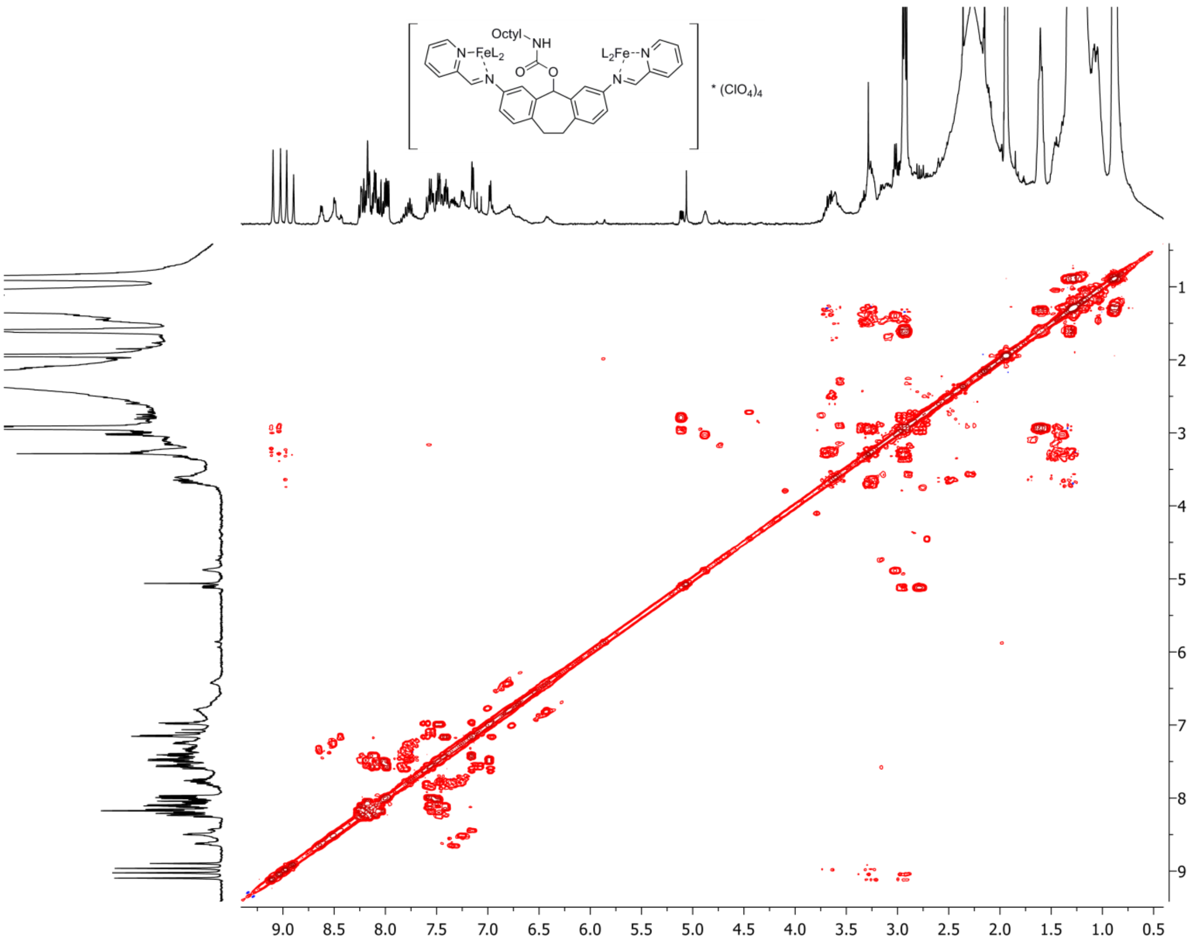


Figure S-33. gCOSY spectrum of **Mesocate 4** (CD_3CN, 400 MHz, 298 K).

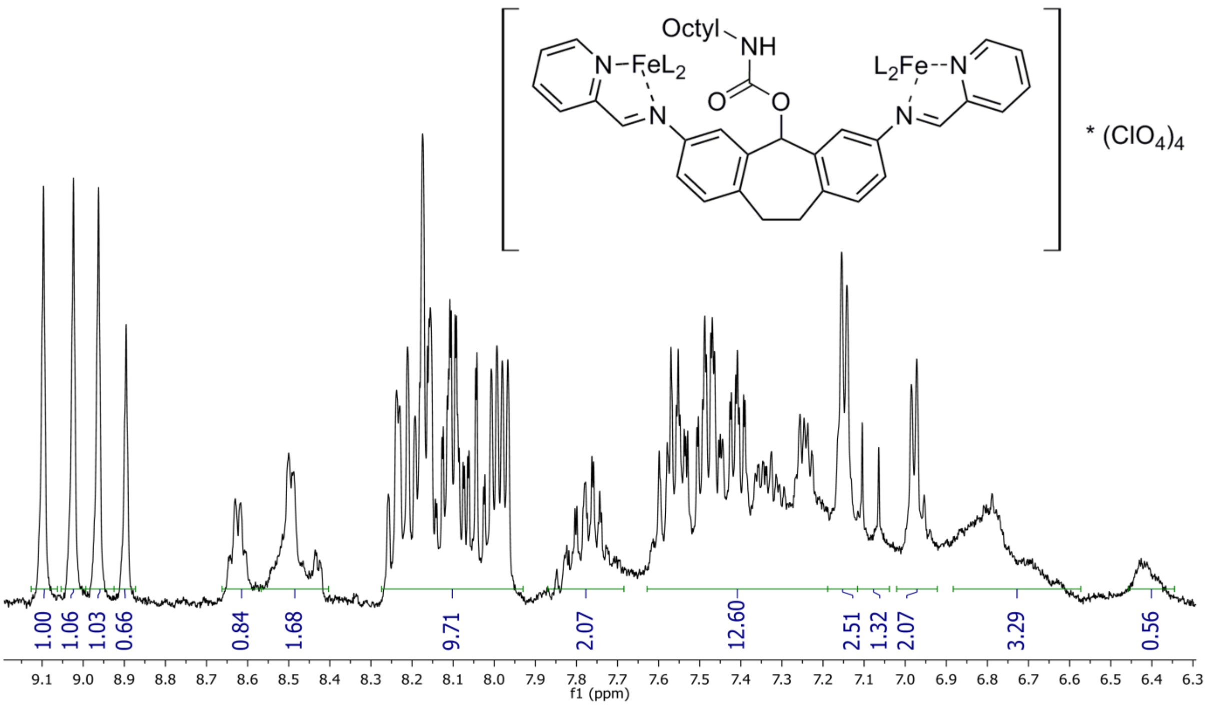


Figure S-34. Downfield region of ^{1}H NMR spectrum of **Mesocate 4** with integrals (CD_3CN, 400 MHz, 298 K).

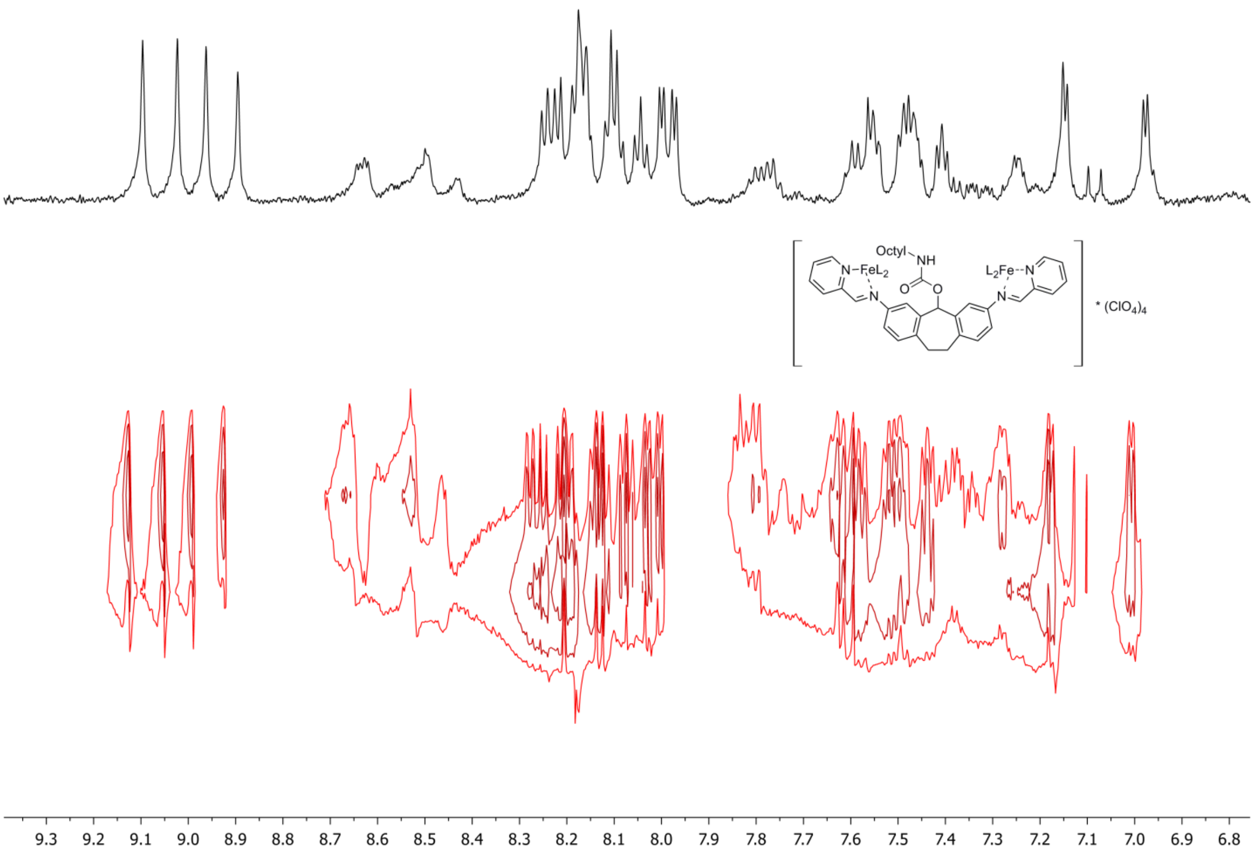


Figure S-35. DOSY spectrum of **Mesocate 4** (CD_3CN, 600 MHz, 298 K, Δ = 100 ms, δ = 2.6 μs, Diffusion Coefficient = 1.07 x10^{-9} m^2/s vs. 4.17 x10^{-9} m^2/s for the solvent).

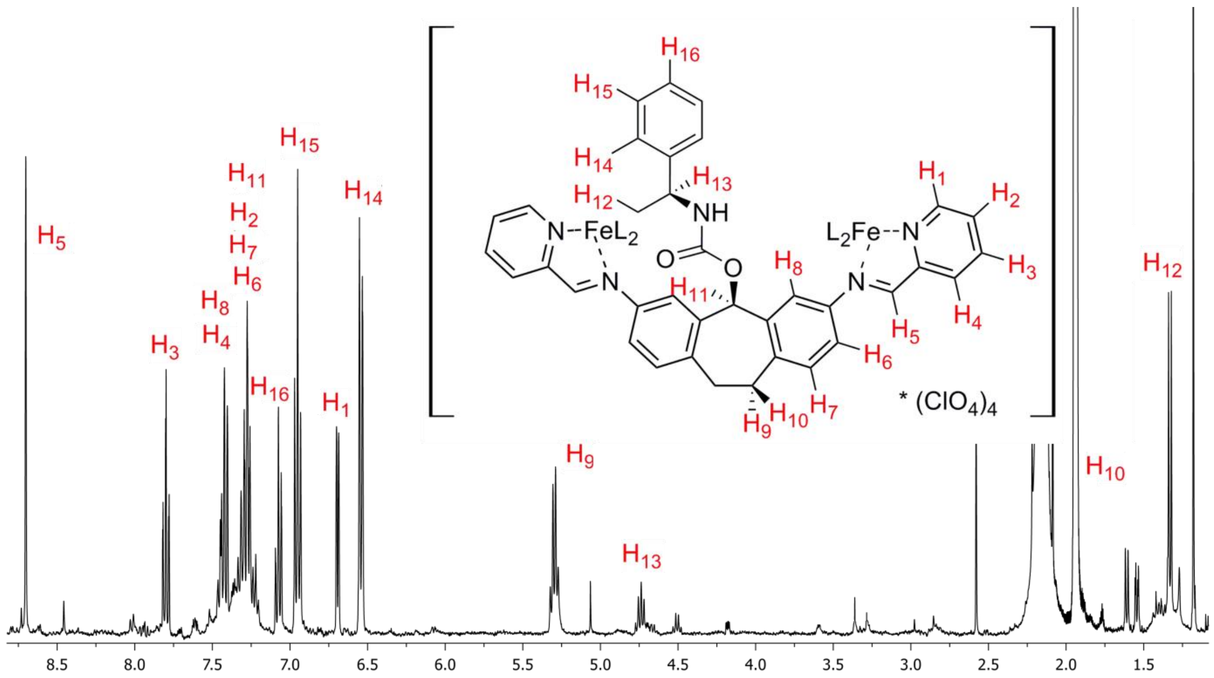


Figure S-36. ^{1}H NMR spectrum of **Mesocate (*S*)-5** (CD_3CN, 400 MHz, 298 K).

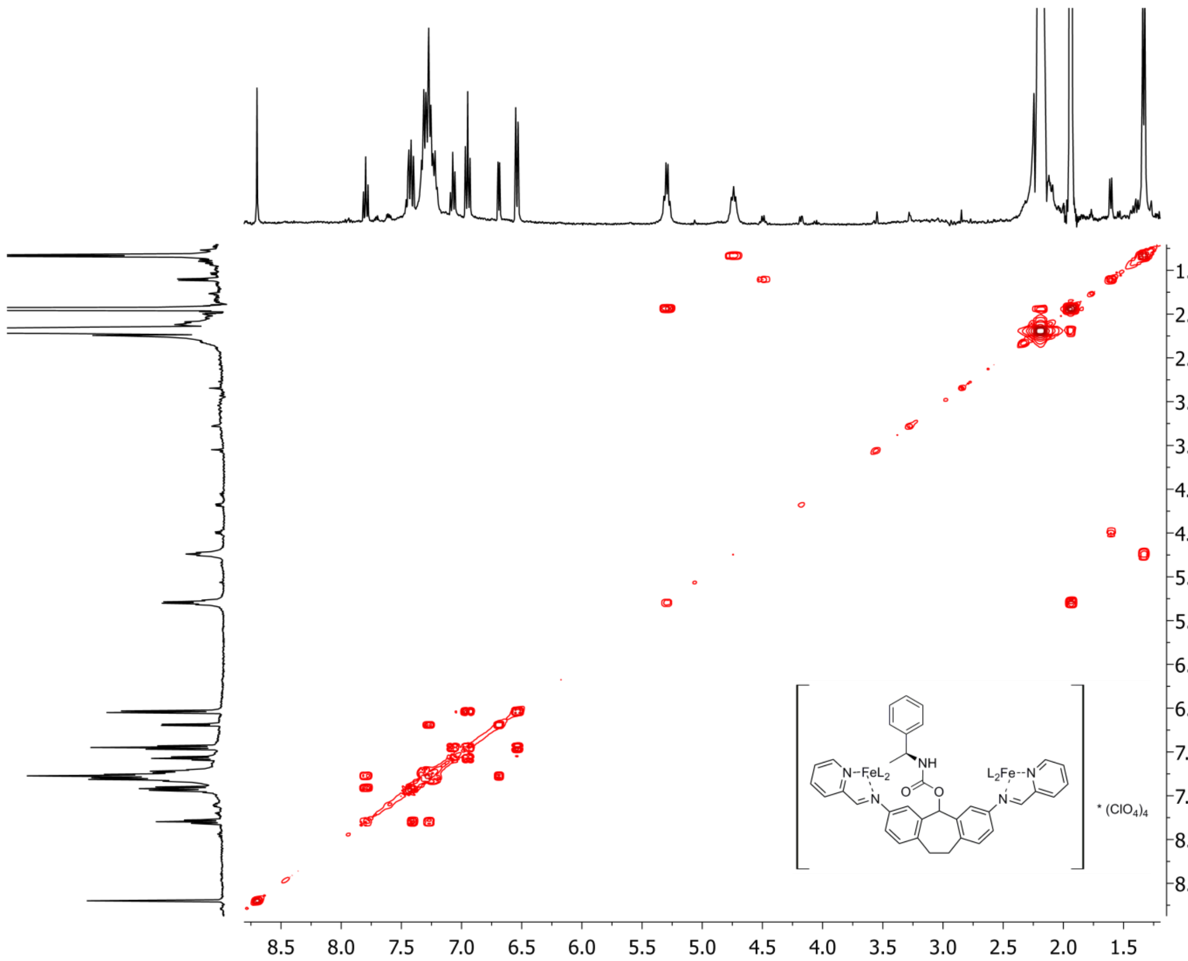


Figure S-37. gCOSY spectrum of **Mesocate (*S*)-5** (CD_3CN, 400 MHz, 298 K).

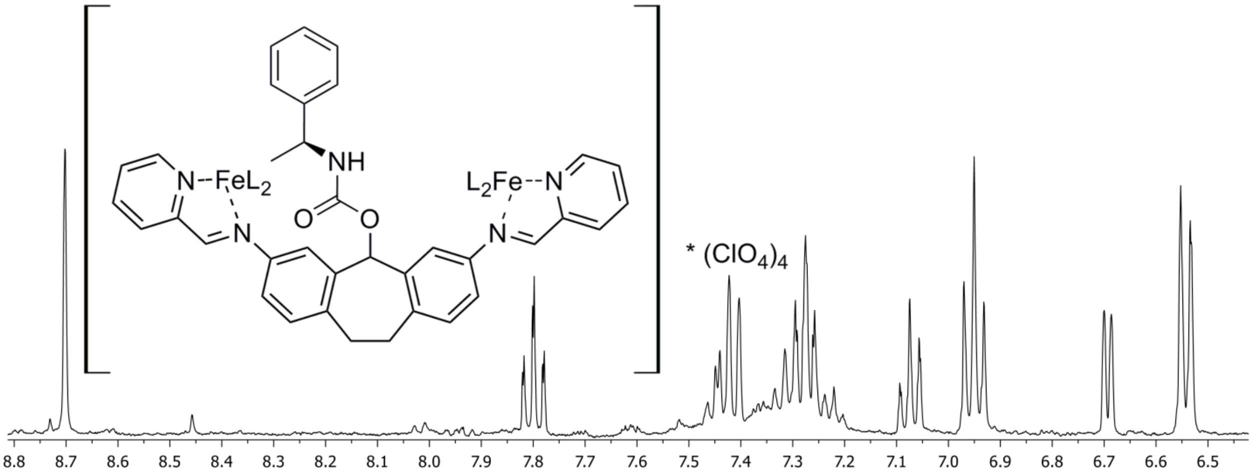


Figure S-38. Downfield region of ^{1}H NMR spectrum of **Mesocate (*S*)-5** (CD_3CN, 400 MHz, 298 K).

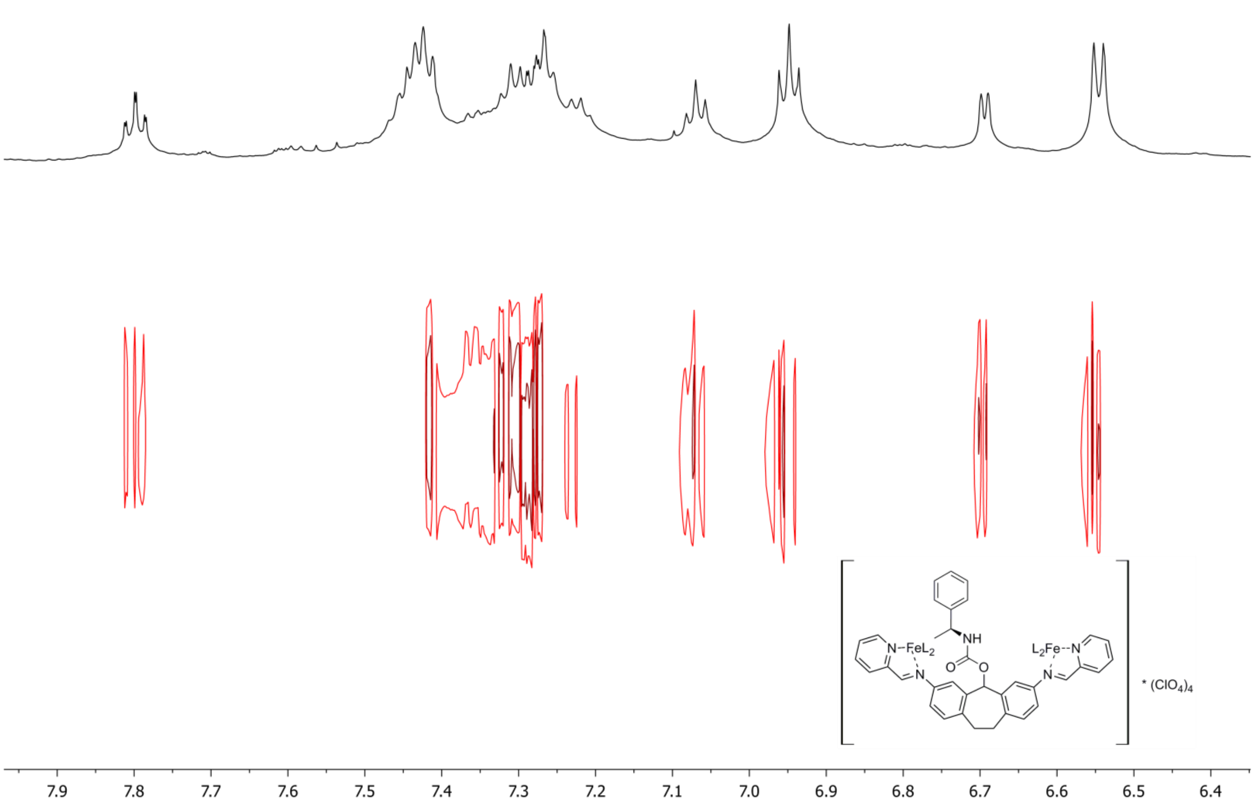


Figure S-39. DOSY spectrum of **Mesocate (*S*)-5** (CD_3CN, 600 MHz, 298 K, Δ = 100 ms, δ = 2.6 µs, Diffusion Coefficient = 8.32 x10^{-10} m^2/s vs. 3.31 x10^{-9} m^2/s for the solvent).

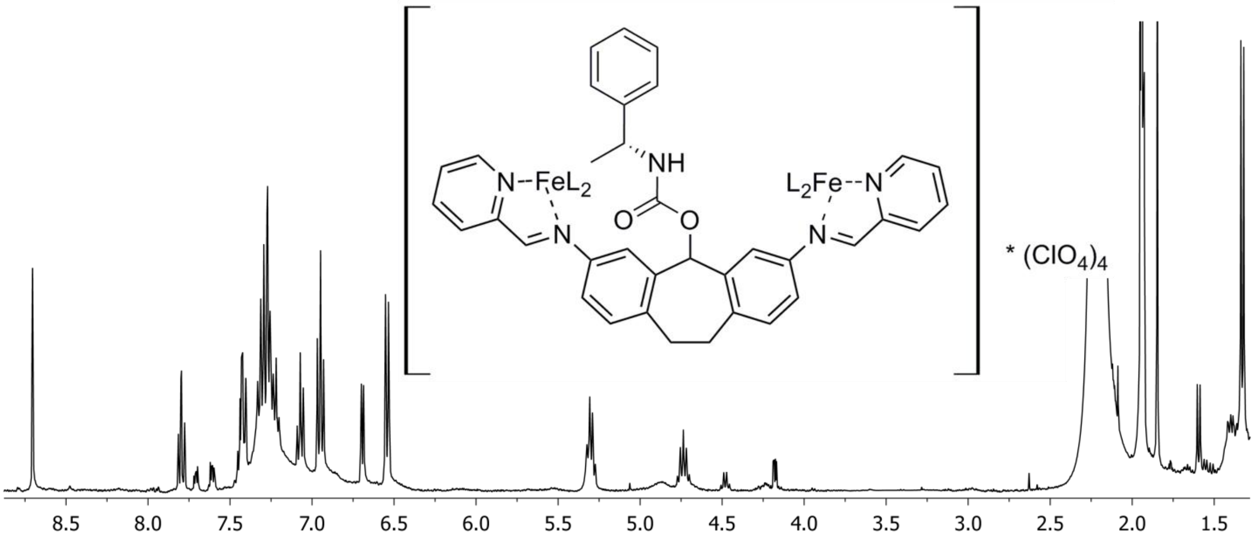


Figure S-40. [1]H NMR spectrum of **Mesocate (*R*)-5** (CD_3CN, 400 MHz, 298 K).

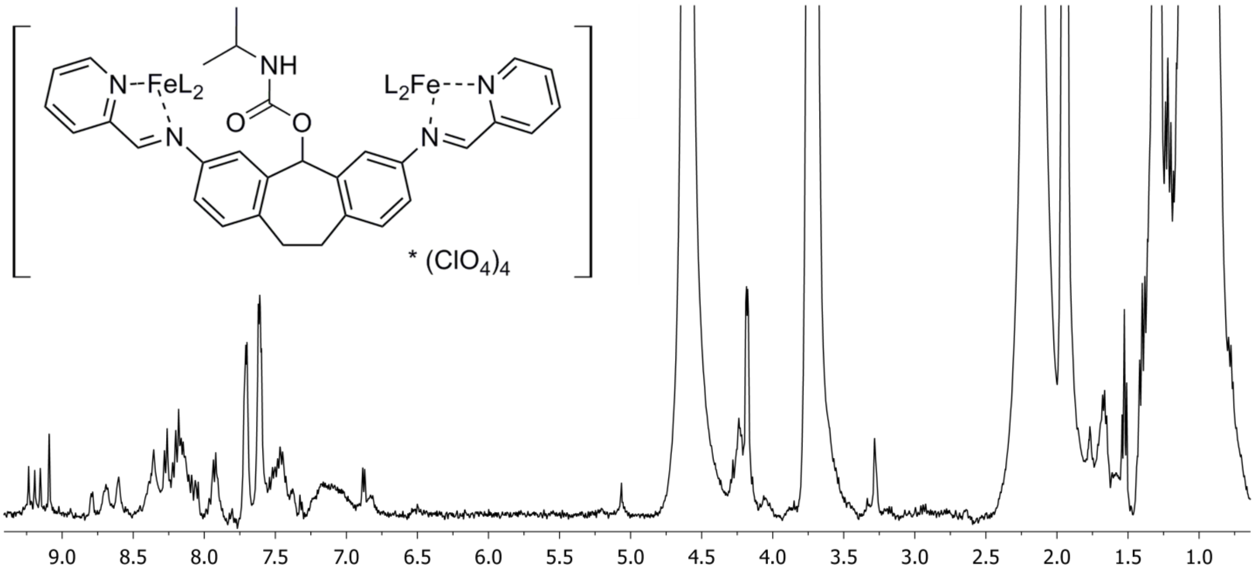


Figure S-41. [1]H NMR spectra of crude **Mesocate 6** (CD_3CN, 400 MHz, 298 K).

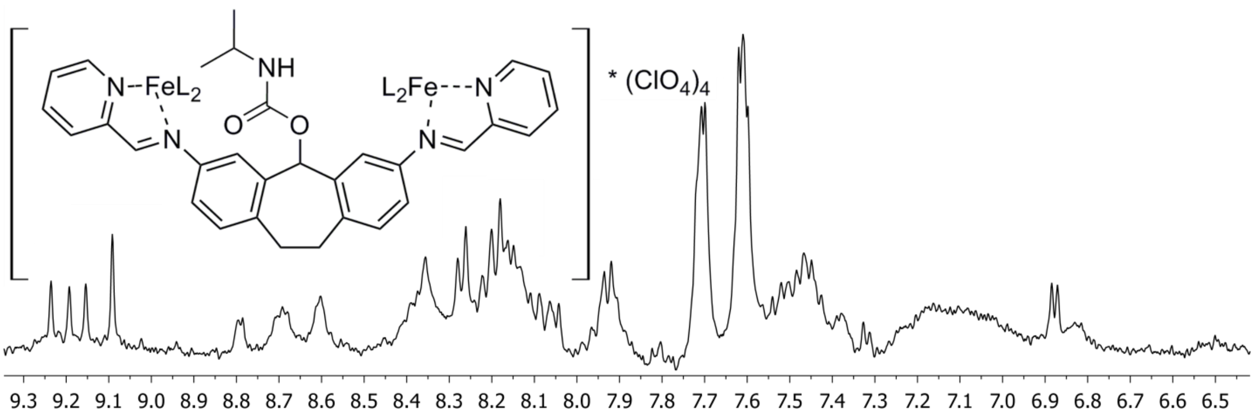


Figure S-42. Downfield region of [1]H NMR spectra of crude **Mesocate 6** (CD_3CN, 400 MHz, 298 K).

5. Mass Spectral Data

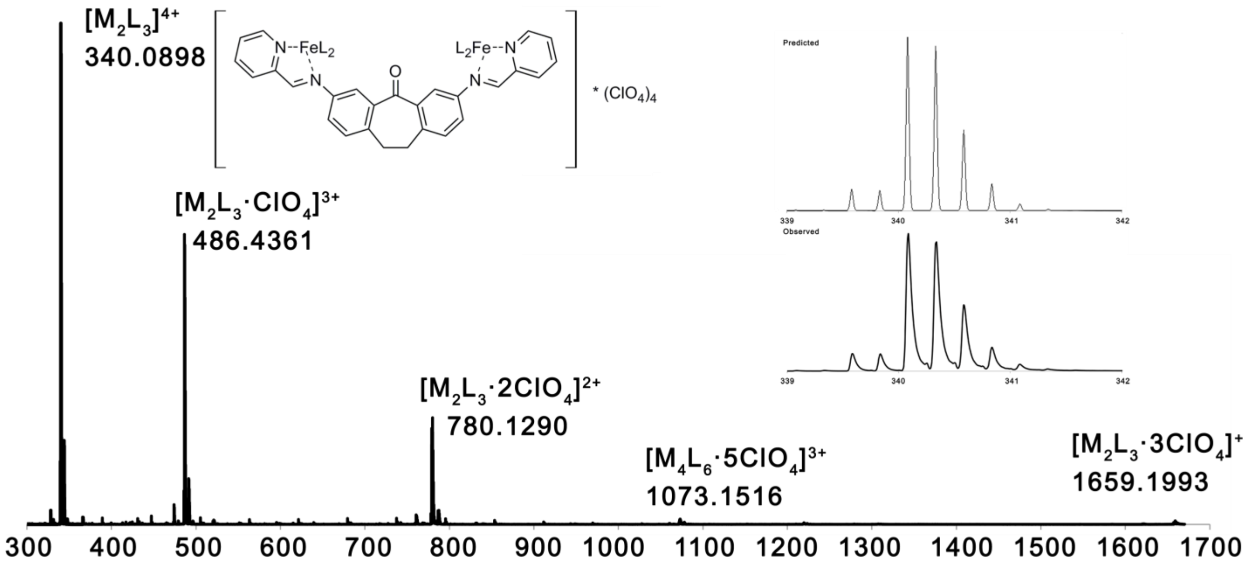


Figure S-43. ESI-MS of **Mesocate 1** (CH_3CN).

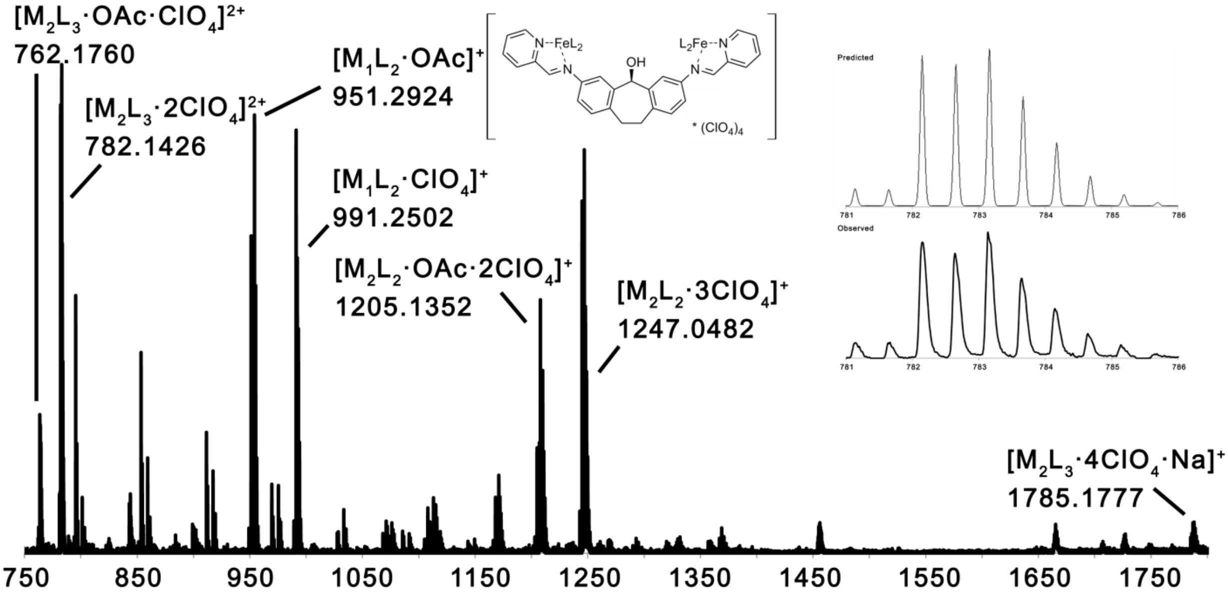


Figure S-44. ESI-MS of **Mesocate 2** (CH_3CN).

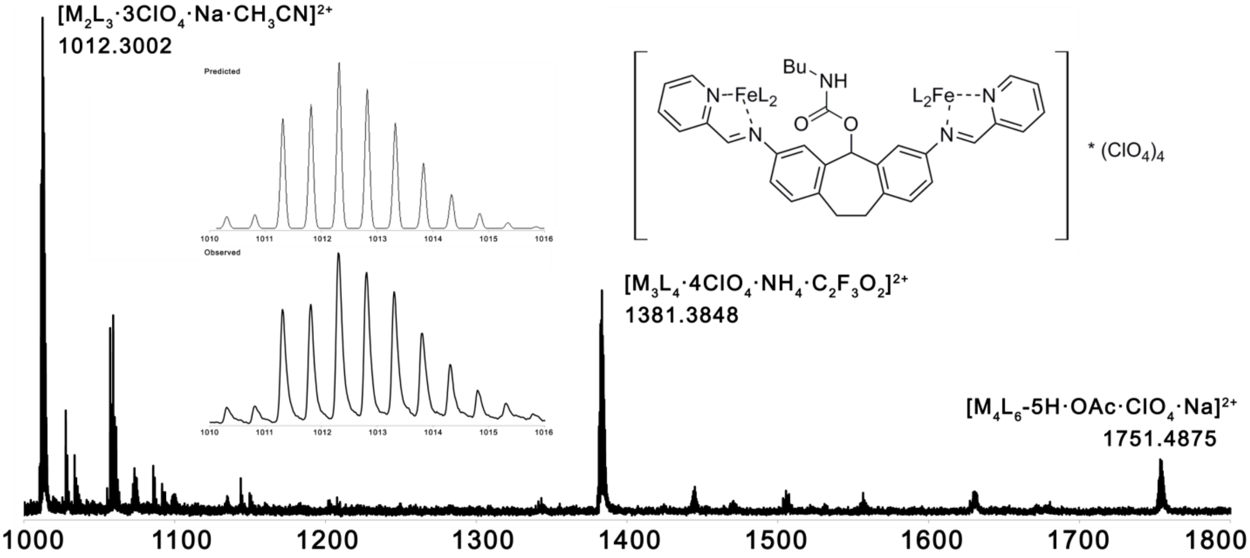


Figure S-45. ESI-MS of **Mesocate 3** (CH_3CN).

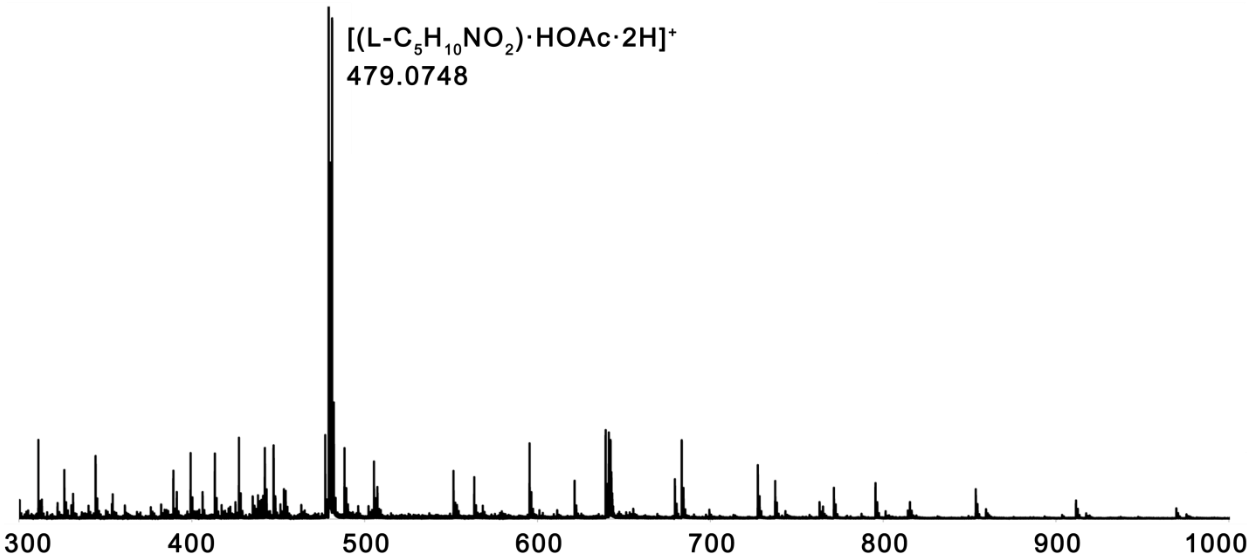


Figure S-46. ESI-MS of **Mesocate 3** below 1000 m/z (CH_3CN).

6. Optical Spectroscopy Data

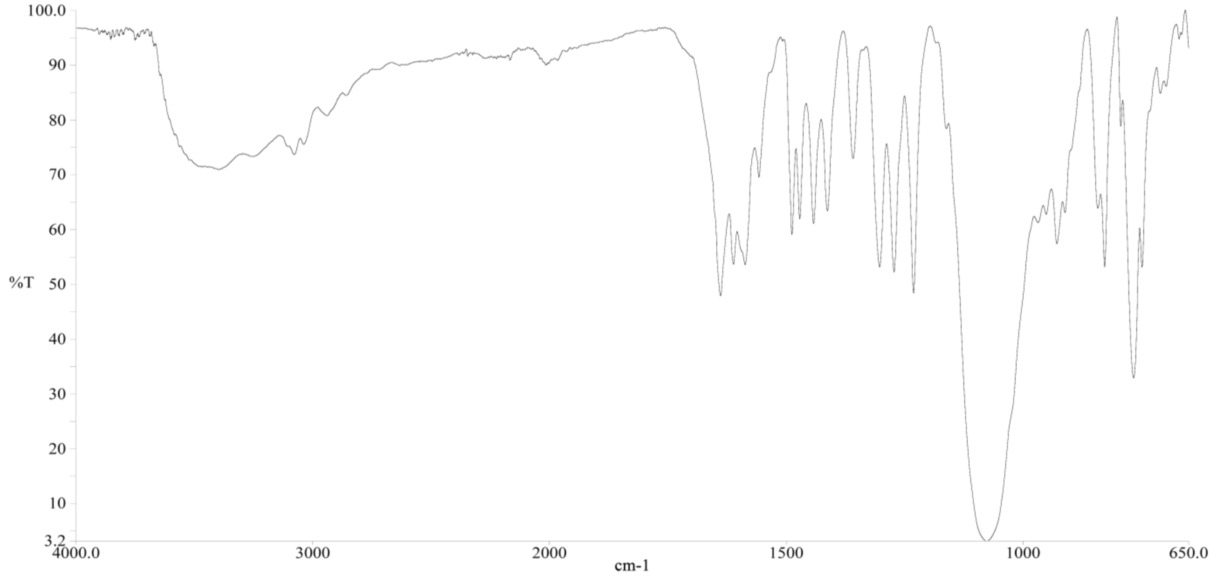


Figure S-47. ATR FT-IR spectrum of **Mesocate 1**.

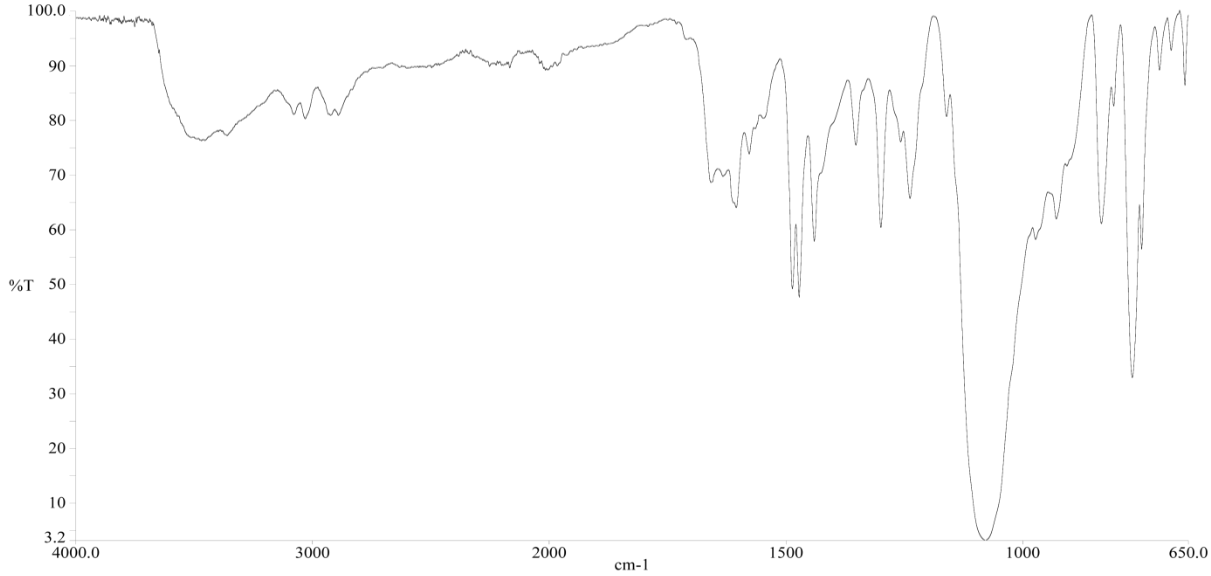


Figure S-48. ATR FT-IR spectrum of **Mesocate 2**.

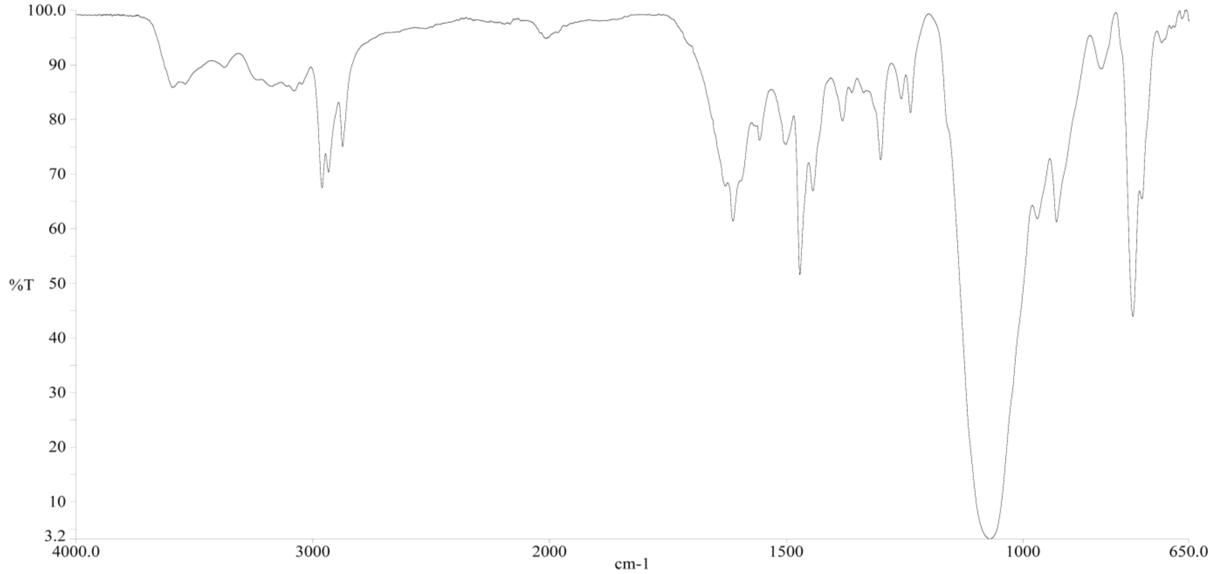


Figure S-49. ATR FT-IR spectrum of **Mesocate 3**.

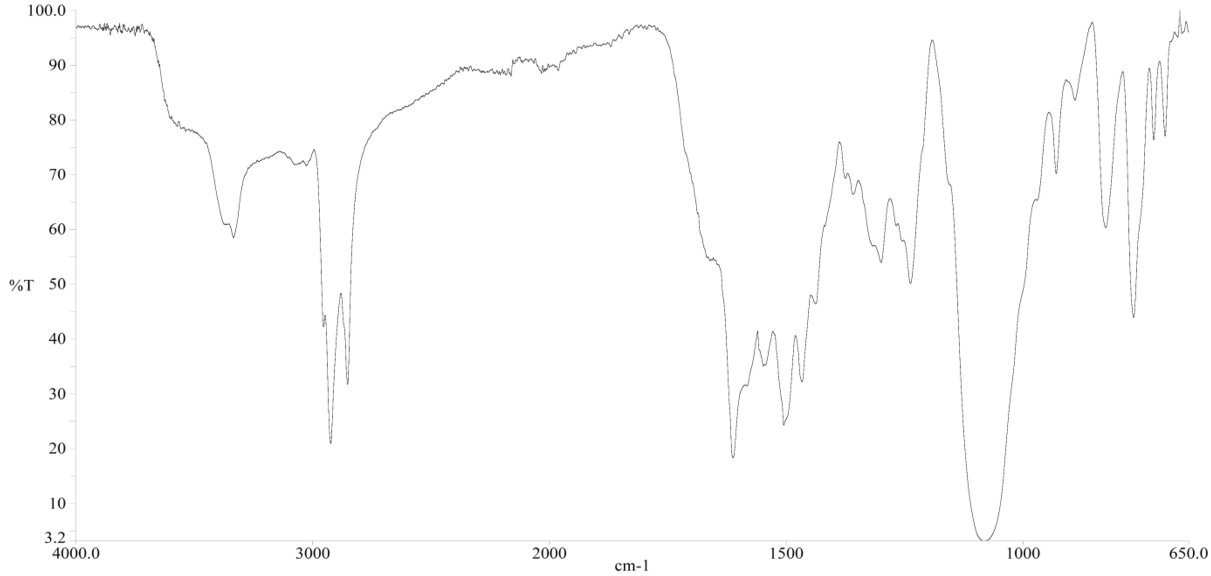


Figure S-50. ATR FT-IR spectrum of **Mesocate 4**.

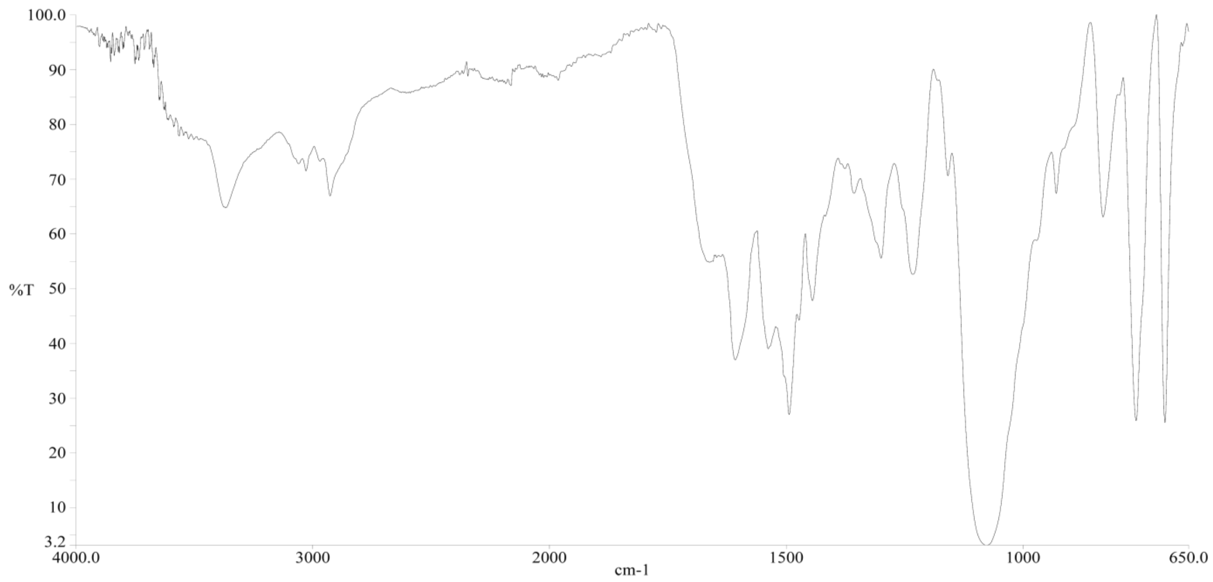


Figure S-51. ATR FT-IR spectrum of **Mesocate (*S*)-5**.

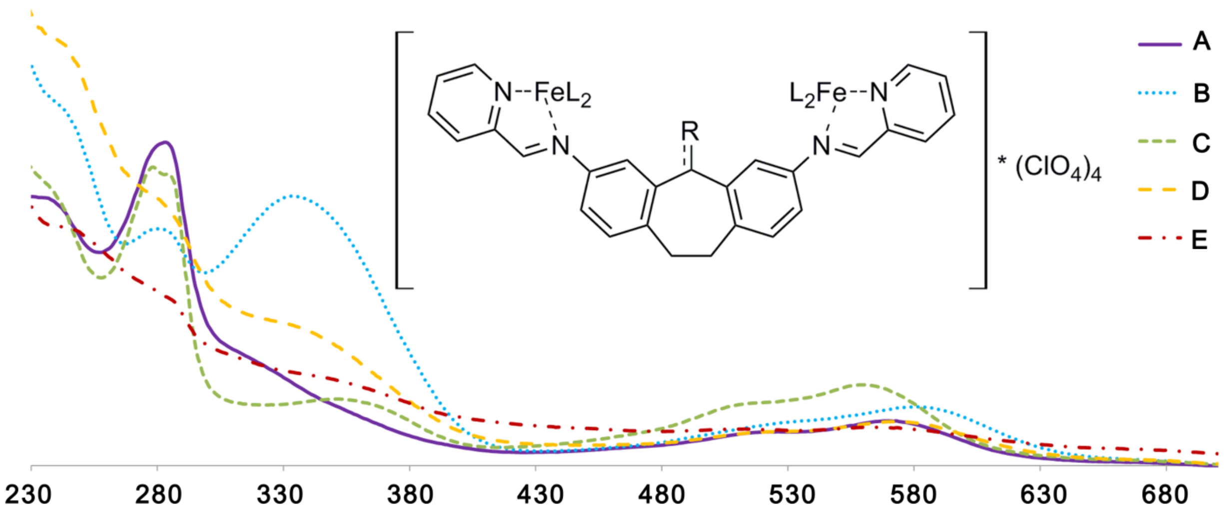


Figure S-52. UV spectra of **Mesocates 1-5**: a) **1** (52 µM); b) **2** (18 µM); c) **3** (8.1 µM); d) **4** (13 µM); e) **(*S*)-5** (7.6 µM).

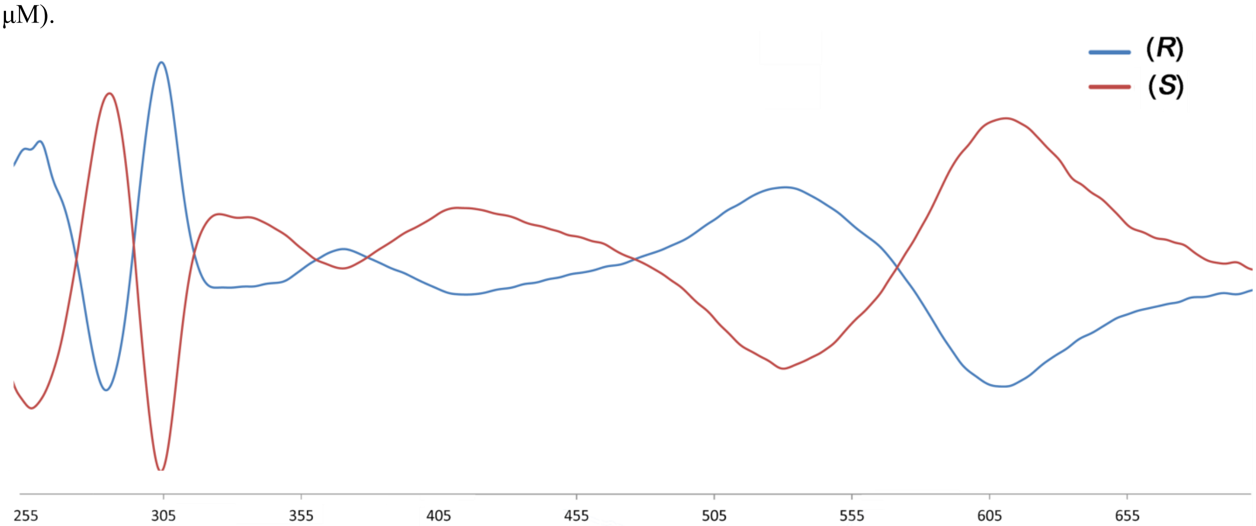


Figure S-53. CD Spectra of **Mesocate (*S*)-5** and **(*R*)-5** (MeCN, 54 µM).

7. X-Ray Crystallographic Data

Crystal Structure of Mesocate 1 (CCDC # 951758)

A purple fragment of a prism (0.39 x 0.29 x 0.08 mm^3) was used for the single crystal x-ray diffraction study of $[C_{81}H_{60}N_{12}O_3Fe_2][ClO_4]_4$. The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2[3] platform-CCD x-ray diffractometer system (fine focus Mo-radiation, λ = 0.71073 Å, 50KV/30mA power). The CCD detector was placed at a distance of 5.0800 cm from the crystal.

A total of 4800 frames were collected for a sphere of reflections (with scan width of 0.3^o in ω, starting ω and 2θ angles of –30^o, and Φ angles of 0^o, 90^o, 120^o, 180^o, 240^o, and 270^o for every 600 frames, 20 sec/frame exposure time, and one 360^o Φ scan with starting ω and 2θ angles at –45^o and 30^o, respectively). The frames were integrated using the Bruker SAINT software package[4] and using a narrow-frame integration algorithm. Based on a triclinic crystal system, the integrated frames yielded a total of 117348 reflections at a maximum 2θ angle of 60.14^o (0.72 Å resolution), of which 23999 were independent reflections (R_{int} = 0.0283, R_{sig} = 0.0232, redundancy = 4.9, completeness = 99.8%) and 20198 (84.2%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 10.9347(3) Å, **b** = 19.6886(5) Å, **c** = 22.3960(6) Å, **α** = 110.010(1)^o, **β** = 96.481(1)^o, **γ** = 104.184(1)^o, V = 4288.8(2) Å^3, Z = 2, calculated density D_c = 1.506 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.546 mm^{-1}; max/min transmission = 0.9581/0.8156) to the raw intensity data using the SADABS program[5].

The Bruker SHELXTL software package[6] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.959) and no systematic absent reflections indicated two possible space groups, P-1 and P1. The space group P-1 (#2) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were one cation of $[C_{81}H_{60}N_{12}O_3Fe_2]^{4+}$ (where one O-atom of the three C=O groups was disordered with disordered site occupancy ratio of 37%/32%/31%), four anions of $[ClO_4]^-$ (where three of the four anions were disordered with site occupancy ratios of 95%/5%, 56%/44%, 51%/49%), five partially occupied (97%, 96%, 90%, 88% and 24% occupied) CH_3CN molecules, two partially occupied (22%, 11% occupied) water molecules, and one partially occupied (43%

occupied) benzene (located at the inversion center) present in the asymmetric unit of the unit cell. The 24% occupied CH_3CN molecule was located at the inversion center. The C and G-level alerts given by checkcif are main due to the disordered anions (ClO_4^-) and partially occupied solvents of crystallization (acetonitrile, water and benzene).

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached, except the H-atoms of the partial water molecules were restrained as ideal models using DFIX. The refinement converged at R1 = 0.0366, wR2 = 0.0918, with intensity, $I>2\sigma(I)$. The largest peak/hole in the final difference map was 0.998/-0.416 e/Å^3.

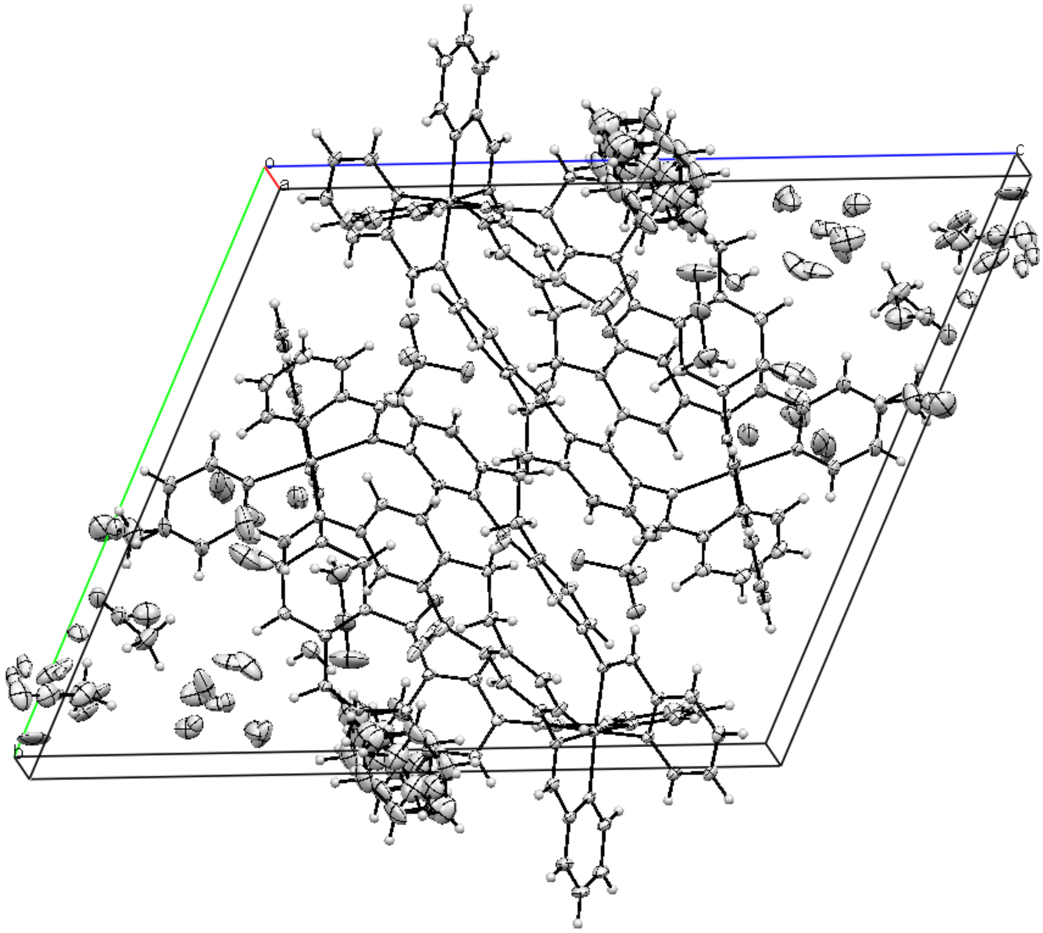


Figure S-54. Unit cell of **Mesocate 1** (Vapor diffusion of benzene into acetonitrile, 100K).

Table *S*-1. Crystal data and structure refinement for **Mesocate 1**.

Empirical formula	$C_{90.21}$ $H_{73.84}$ Cl_4 Fe_2 $N_{15.97}$ $O_{19.33}$	
Formula weight	1944.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 10.9347(3) Å	α= 110.010(1)°.
	b = 19.6886(5) Å	β= 96.481(1)°.
	c = 22.3960(6) Å	γ = 104.184(1)°.
Volume	4288.8(2) $Å^3$	
Z	2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.546 mm^{-1}	
F(000)	2003	
Crystal size	0.39 x 0.29 x 0.08 mm^3	
Theta range for data collection	1.79 to 29.57°.	
Index ranges	-15<=*h*<=15, -27<=*k*<=27, -31<=*l*<=31	
Reflections collected	117348	
Independent reflections	23999 [*R*(int) = 0.0283]	
Completeness to θ = 29.57°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9581 and 0.8156	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23999 / 648 / 1403	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2σ (I)]	*R*1 = 0.0366, *wR*2 = 0.0918	
R indices (all data)	*R*1 = 0.0465, *wR*2 = 0.0976	
Largest diff. peak and hole	0.998 and -0.416 *e*.$Å^{-3}$	

Crystal Structure of Mesocate 2 (CCDC# 951759)

A purple fragment of a prism (0.51 x 0.28 x 0.02 mm^3) was used for the single crystal x-ray diffraction study of [$C_{81}H_{66}N_{12}O_3Fe_2$][$ClO_4$]$_4$. The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2[3] platform-CCD x-ray diffractometer system (fine focus Mo-radiation, λ = 0.71073 Å, 50KV/35mA power). The CCD detector was placed at a distance of 5.0600 cm from the crystal.

A total of 3600 frames were collected for a sphere of reflections (with scan width of 0.3° in ω, starting ω and 2θ angles of –30°, and Φ angles of 0°, 90°, 120°, 180°, 240°, and 270° for every 600 frames, 120 sec/frame exposure time, and one 360° Φ scan with starting ω and 2θ angles at –45° and 30°, respectively). The frames were integrated using the Bruker SAINT software package[4] and using a narrow-frame integration algorithm. Based on an orthorhomic crystal system, the integrated frames yielded a total of 228675 reflections at a maximum 2θ angle of 46.74° (0.90 Å resolution), of which 25938 were independent reflections (R_{int} = 0.1099, R_{sig} = 0.0626, redundancy = 8.8, completeness = 99.7%) and 19864 (76.6%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 20.7761(16) Å, **b** = 40.5163(32) Å, **c** = 41.9666(33) Å, **α** = **β** = **γ** = 90°, V = 35326(5) $Å^3$, Z = 8, calculated density D_c = 1.290 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 0.503 mm^{-1}; max/min transmission = 0.9905/0.7816) to the raw intensity data using the SADABS program[5].

The Bruker SHELXTL software package[6] was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.791) and no systematic absent reflections indicated two possible space groups, Cmma and Abm2. The space group Abm2 (#39) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit of the unit cell. With subsequent isotropic refinement, all of the cations and anions atoms were identified but not the solvent atoms. The PLATON-SQUEEZE program[7] was applied to remove possible disordered acetonitrile and diethyl ether solvents present in the asymmetric unit of the unit cell before final refinement. The potential solvent void volume was calculated to be 7468.1 $Å^3$ [21% of the unit cell volume]. There were one full-cation of $C_{81}H_{66}N_{12}O_3Fe_2$, six full-anions of ClO_4 present in general positions of the asymmetric unit. There were two half-cations of $C_{81}H_{66}N_{12}O_3Fe_2$, and two half-anions of ClO_4 located at the mirror plane perpendicular to the b-axis. There was one anion of ClO_4 located at the two-fold rotation axis parallel to the c-axis. One of the six full-anions was modeled with disorder (disordered ratio 52%/48%). The structure was refined as a racemic twin (with major/minor twin ratio of 77%/23%). The alert levels B, C and G in the checkcif report are mostly due to the poor quality of the crystal and solvent(s) disordered that were squeezed out in the final refinement using PLATON-SQUEEZE.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0579, wR2 = 0.1338, with intensity, $I>2\sigma(I)$. The largest peak/hole in the final difference map was 0.653/-0.340 e/Å^3.

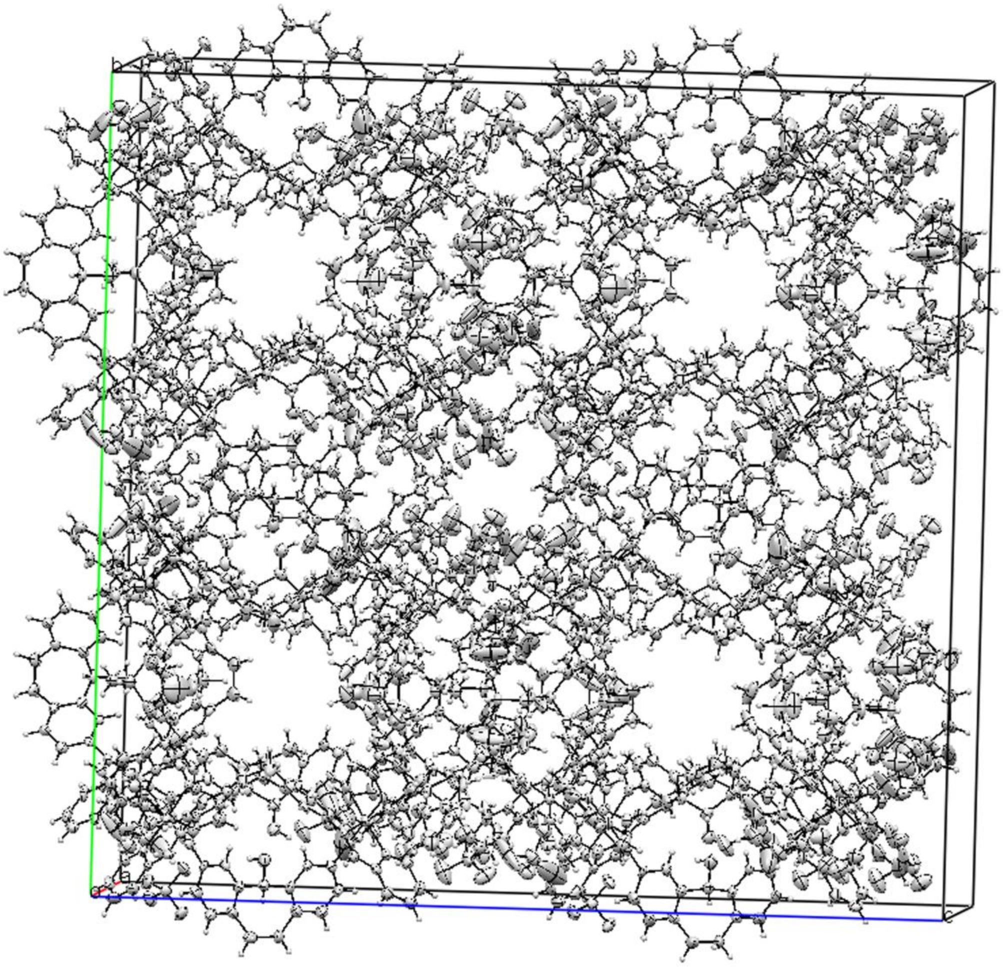


Figure S-55. Unit cell of **Mesocate 2** (Vapor diffusion of ether into acetonitrile with 1% mesitylene, 100K).

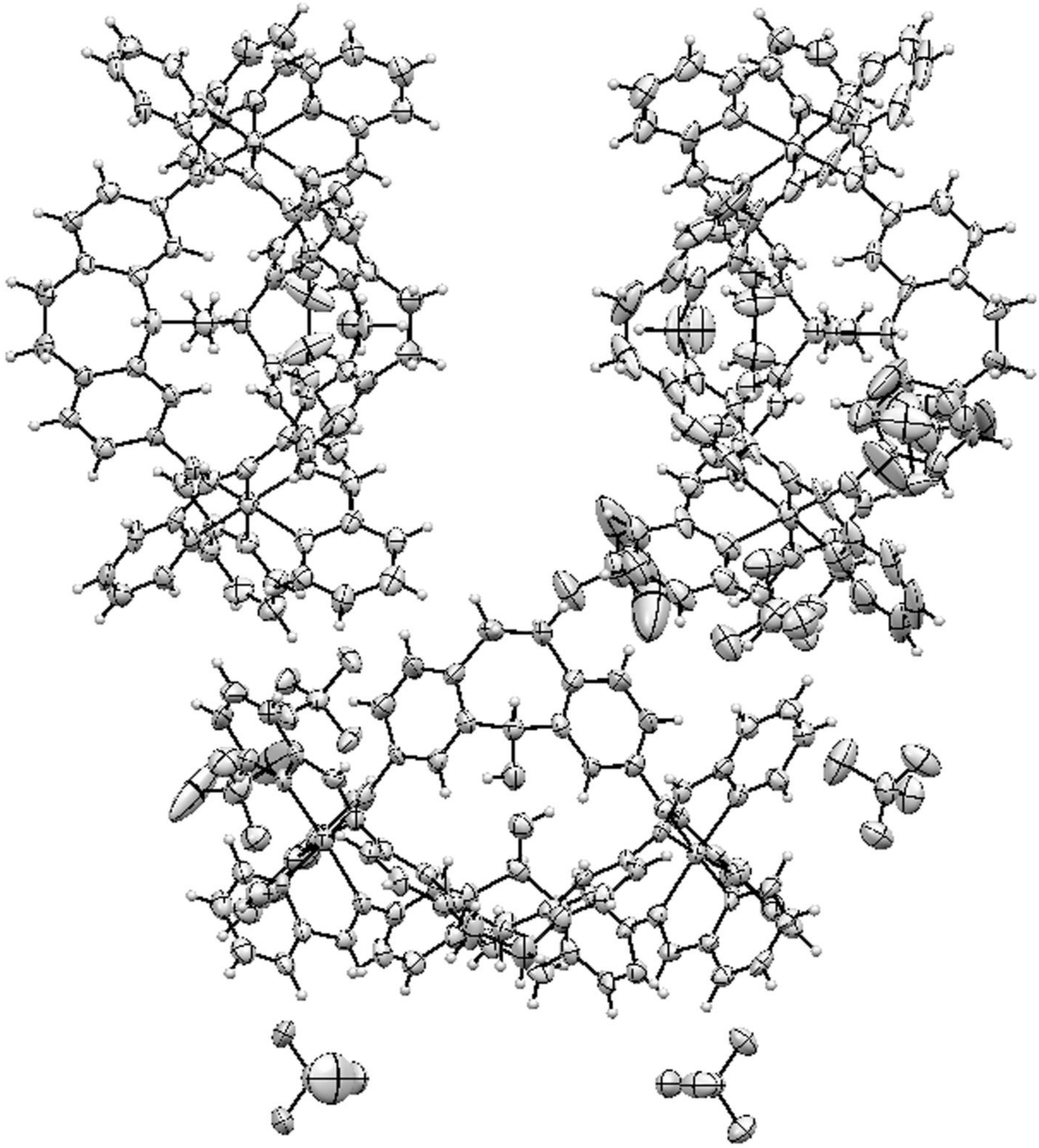


Figure S-56. Three-unit stacking observed in the crystal of **Mesocate 2** (Vapor diffusion of ether into acetonitrile with 1% mesitylene, 100K).

Table *S*-2. Crystal data and structure refinement for **Mesocate 2**.

Empirical formula	C_{162} H_{132} Cl_7 Fe_4 N_{24} O_{34}	
Formula weight	3430.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Abm2 (#39)	
Unit cell dimensions	*a* = 20.7761(16) Å	α=90°.
	b = 40.516(3) Å	β=90°.
	c = 41.967(3) Å	γ =90°.
Volume	35326(5) $Å^3$	
Z	8	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.503 mm^{-1}	
F(000)	14136	
Crystal size	0.51 x 0.28 x 0.02 mm^3	
Theta range for data collection	1.38 to 23.37°.	
Index ranges	-23<=*h*<=23, -45<=*k*<=44, -46<=*l*<=46	
Reflections collected	228675	
Independent reflections	25938 [*R*(int) = 0.1099]	
Completeness to θ = 29.57°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9905 and 0.7816	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25938 / 497 / 2177	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2σ (I)]	*R*1 = 0.0579, *wR*2 = 0.1338	
R indices (all data)	*R*1 = 0.0777, *wR*2 = 0.1427	
Absolute structure parameter	0.230(12)	
Largest diff. peak and hole	0.653 and -0.340 $e.Å^{-3}$	

8. SPARTAN Models

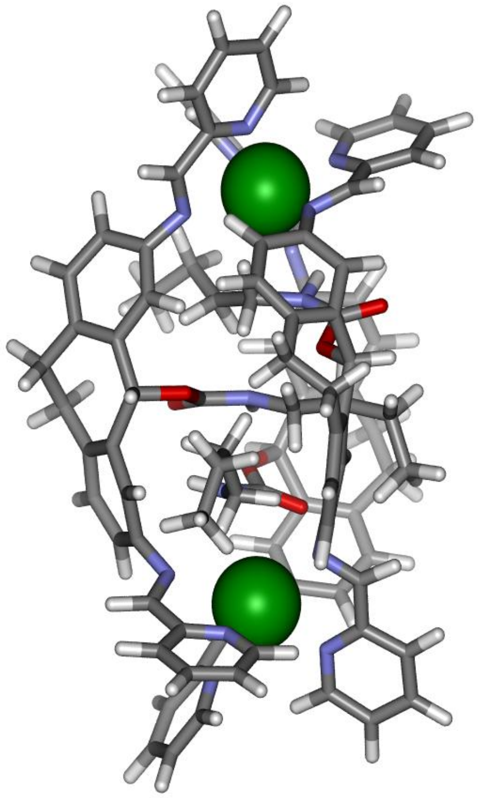


Figure S-57. SPARTAN Model of **(*in₃*)•3** viewed from the side.

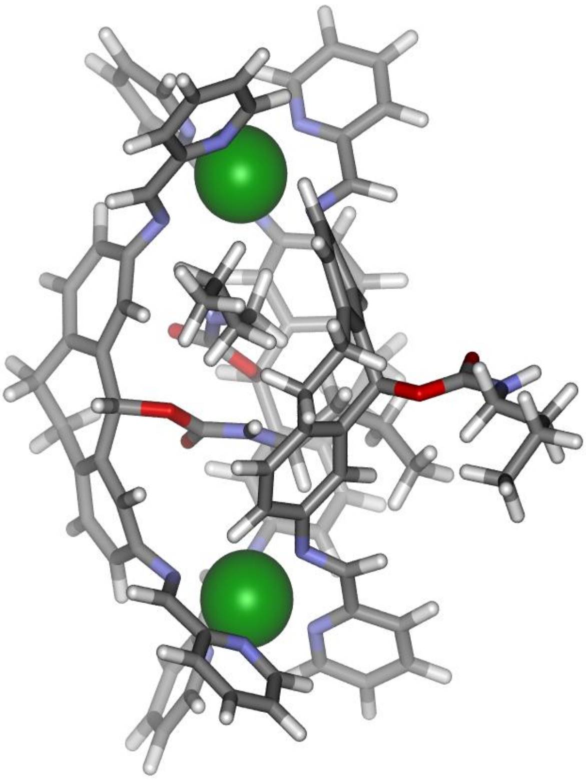


Figure S-58. SPARTAN Model of **(*in₂•out₁*)•3** viewed from the side.

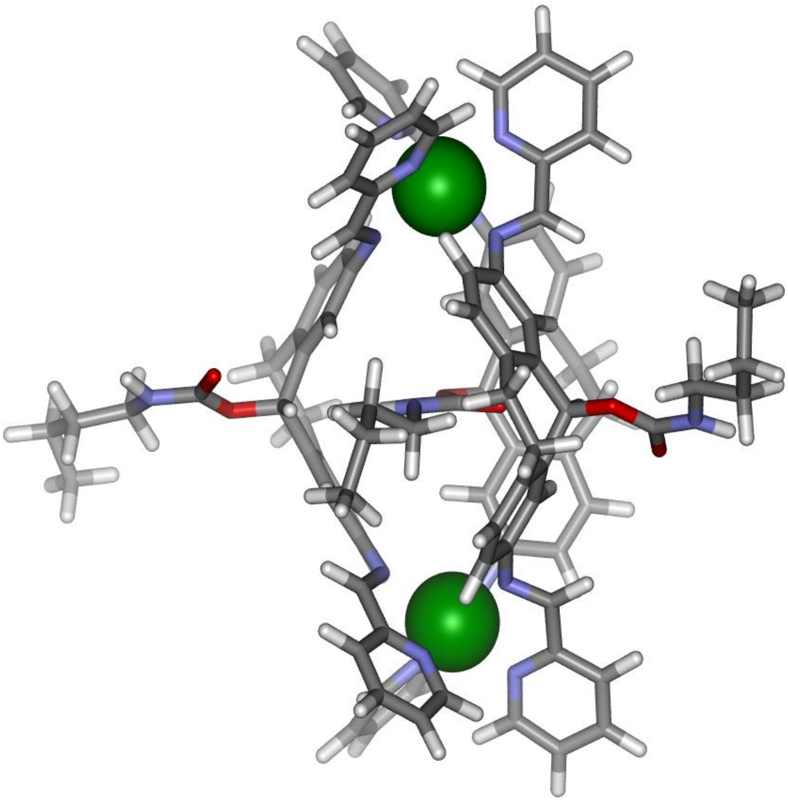


***Figure S-59*.** SPARTAN Model of **(in_1•out_2)•3** viewed from the side.

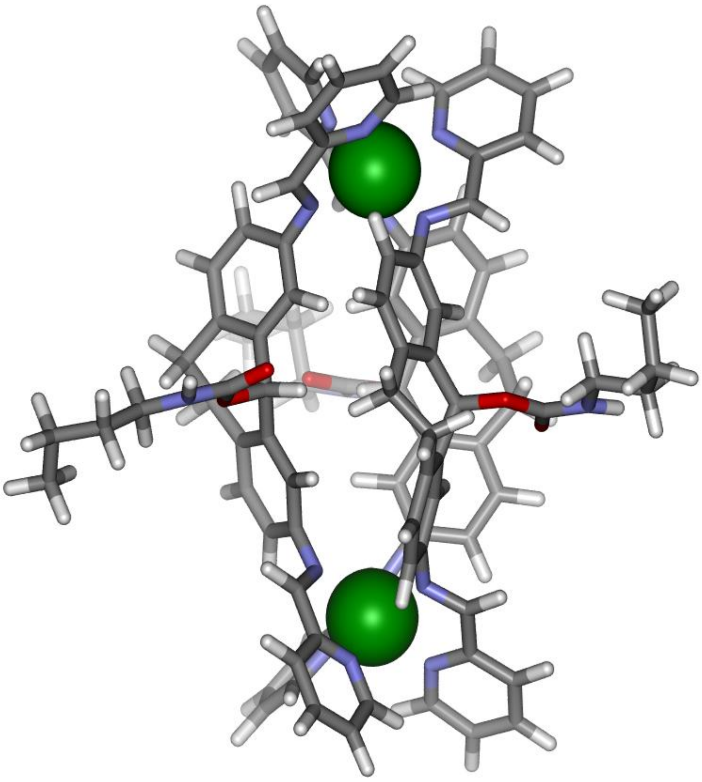


***Figure S-60*.** SPARTAN Model of **(out_3)•3** viewed from the side.

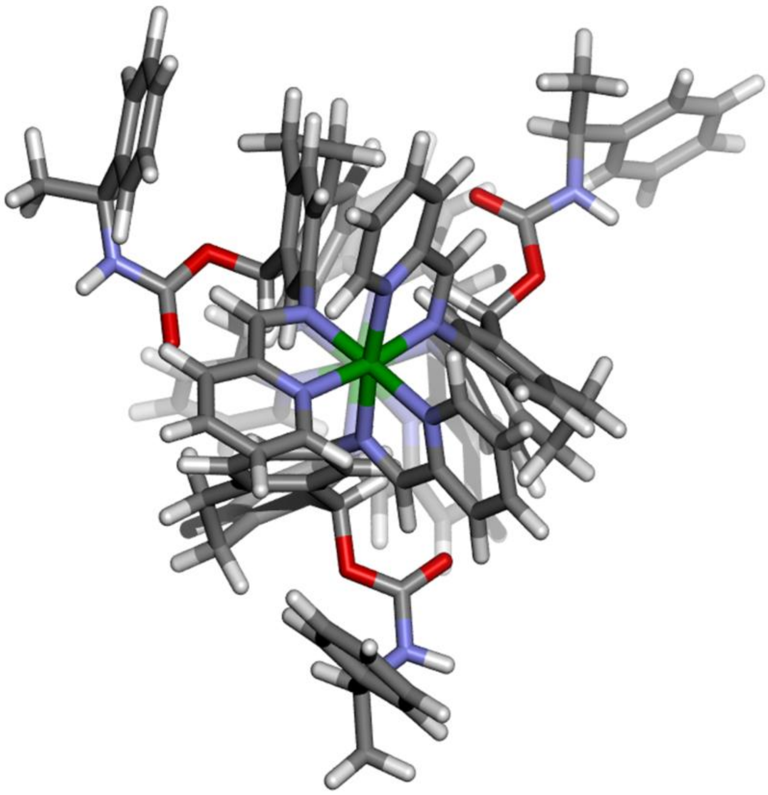


***Figure S-61*.** SPARTAN Model of **(*out*$_3$)•(*S*)-5** viewed down the Fe-Fe axis.

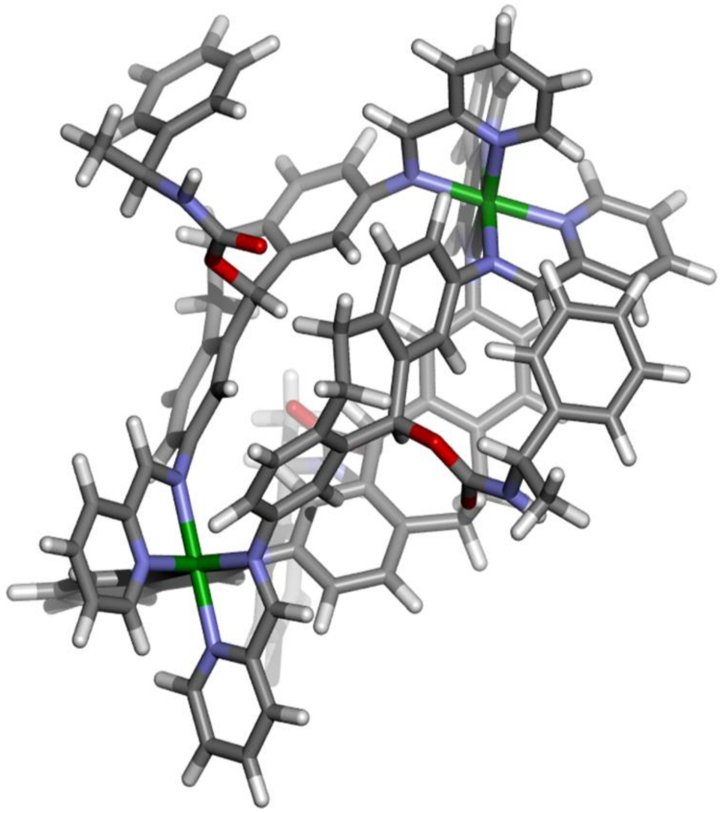


***Figure S-62*.** SPARTAN Model of **(*out*$_3$)•(*S*)-5** viewed from the side.

9. References

1) Patiny, L.; Borel, A. *J. Chem. Inf. Model.*, **2013**, *53*, 1223-1228.
2) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.,* **1985**, *107*, 3902-3909; calculations performed on SPARTAN 06, Wavefunction Inc.
3) *APEX 2,* version 2012.2-0, Bruker (2012), Bruker AXS Inc., Madison, Wisconsin, USA.
4) *SAINT*, version V8.18C, Bruker (2011), Bruker AXS Inc., Madison, Wisconsin, USA.
5) *SADABS,* version 2008/1, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.
6) *SHELXTL*, version 2008/4, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.
7) PLATON - SQUEEZE : Spek, A.L. (2003). J. Appl. Cryst. 36, 7-13; Spek, A.L. (2009). Acta Cryst. D65, 148-155.