O–H and (CO)N–H bond weakening by coordination to Fe(II)

Sandra Resa,[a] Alba Millán,[a,*] Noelia Fuentes,[b] Luis Crovetto,[c] M. Luisa Marcos,[d] Luis Lezama,[e] Duane Choquesillo-Lazarte,[f] Victor Blanco,[a] Araceli G. Campaña,[a] Diego J. Cárdenas,[b,*] and Juan M. Cuerva,[a,*]

[a] Departamento de Química Orgánica. Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain.
[b] Departamento de Química Orgánica, Universidad Autónoma de Madrid. Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain.
[c] Departamento de Fisicoquímica, Facultad de Farmacia, (UGR). Cartuja Campus, 18071 Granada, Spain.
[d] Departamento de Química, Universidad Autónoma de Madrid. Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain.
[e] Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, 48940 Leioa, Spain.
[f] Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), 18100 Armilla, Granada, Spain.

*E-mail: jmcuerva@ugr.es

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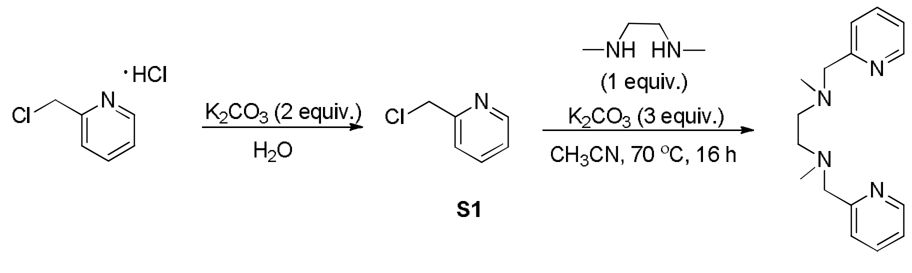
1. Synthesis of ligands 1-4

The following known compounds were prepared as previously described, isolated as pure samples and showed NMR spectra identical to reported data: **S1**,[S1] **1**,[S2] **S2**,[S3] **S4**,[S4] **5**.[S5]

- **Synthesis of mep (1)**

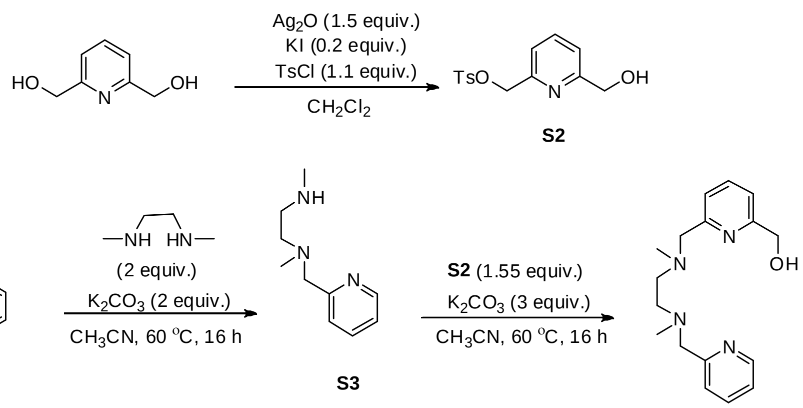


mep, 1

Compound S1. 2-(Chloromethyl)pyridine hydrochloride (1.00 g, 6.10 mmol, 1 equiv.) was dissolved in 10 mL of water and K_2CO_3 (1.69 g, 12.20 mmol, 2 equiv.) was carefully added. The mixture was stirred for 15 min, CH_2Cl_2 (20 mL) was added and further stirred for 15 min. The reaction was extracted with CH_2Cl_2 (x3). Combined organic layers were dried over Na_2SO_4, filtered and solvent evaporated. Compound **S1** was isolated pure (0.76 g, 96% yield) as a red liquid without further purification. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.23 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 4.67 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 156.7 (C), 149.6 (CH), 137.2 (CH), 123.1 (CH), 122.9 (CH), 46.8 (CH_2). **HRMS (EI):** *m/z* $[M]^+$ calcd for C_6H_6ClN: 127.0189; found: 127.0189.

Compound 1: Compound **S1** (0.70 g, 5.48 mmol, 2.1 equiv.) was dissolved in CH_3CN (20 mL) and K_2CO_3 (1.08 g, 7.82 mmol, 3 equiv.) followed by *N,N'*-dimethylethylenediamine (0.28 mL, 2.61 mmol, 1 equiv.) were added. The reaction was stirred at 70 °C for 16 h. Then the solids were filtered off and solvent removed under *vacuo*. The residue was purified by flash column chromatography (Al_2O_3, CH_2Cl_2: CH_3OH, 95:5) to give **1** (0.44 g, 62% yield) as a brownish syrup. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.53 (d, *J* = 4.8 Hz, 2H), 7.63 (td, *J* = 7.7, 1.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.15 (dd, *J* = 7.5, 4.9 Hz, 2H), 3.72 (s, 4H), 2.69 (s, 4H), 2.29 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.1 (C), 149.2 (CH), 136.6 (CH), 123.4 (CH), 122.2 (CH), 64.1 (CH_2), 55.4 (CH_2), 42.9 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{16}H_{23}N_4$: 271.1917; found: 271.1913. **IR (ATR):** 2791, 1589, 1569, 1473, 1433, 1361, 1031, 756 cm^{-1}.

- **Synthesis of mep(OH) (2)**



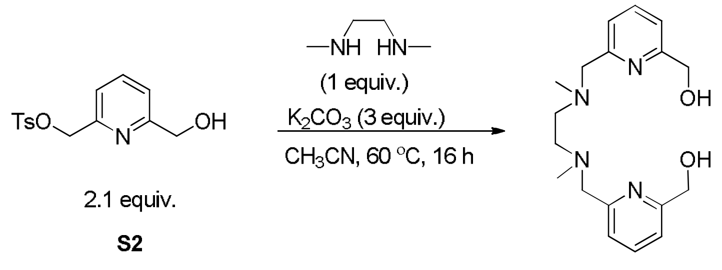
mep (OH), 2

Compound S2. According with a previously described procedure,[S3] tosyl chloride (3.02 g, 15.82 mmol, 1.1 equiv.) was added over a suspension of 2,6-dihydroxymethyl pyridine (2.00 g, 14.38 mmol, 1 equiv.), silver oxide (5.68 g, 21.57 mmol, 1.5 equiv.) and potassium iodide (0.48 g, 2.88 mmol, 0.2 equiv.) in CH_2Cl_2 (100 mL) at –20 °C. The reaction was removed from the cooling bath and stirred for 3 h at room temperature. Then the mixture was filtered through a fritted glass filter, and washed with ethyl acetate. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2 and then EtOAc) to give compound **S2** (2.82 g, 67% yield) as a pink syrup. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 5.15 (s, 2H), 4.71 (s, 2H), 3.50 (bs, 1H), 2.46 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.7 (C), 152.6 (C), 145.1 (C), 137.6 (CH), 132.8 (C), 129.9 (CH), 128.1 (CH), 120.5 (CH), 120.1 (CH), 71.5 (CH_2), 63.7 (CH_2), 21.7 (CH_3). **HRMS (EI):** *m/z* $[M]^+$ calcd for $C_{14}H_{15}NO_4S$: 293.0722; found: 293.0721.

Compound S3. Compound **S1** (0.70 g, 5.48 mmol, 1 equiv.) and *N*,*N'*-dimethylethylenediamine (1.20 mL, 10.96 mmol, 2 equiv.) were dissolved in CH_3CN (30 mL) and K_2CO_3 (1.51 g, 10.96 mmol, 2 equiv.) was added. The reaction was stirred at 60 °C for 16 h. Then the solids were filtered off and solvent removed under *vacuo*. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2: CH_3OH: Et_3N, 9: 1: 0.5) to give **S3** (0.67 g, 68% yield) as a brownish syrup. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.15 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.66 (s, 2H), 2.73–2.66 (m, 2H), 2.63–2.56 (m, 2H), 2.41 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.3 (C), 149.1 (CH), 136.6 (CH), 123.1 (CH), 122.1 (CH), 64.1 (CH_2), 56.6 (CH_2), 49.1 (CH_2), 42.6 (CH_3), 36.1 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{10}H_{18}N_3$: 180.1495; found: 180.1500.

Compound 2. Compounds **S3** (0.50 g, 2.79 mmol, 1 equiv.) and **S2** (1.27 g, 4.32 mmol, 1.55 equiv.) were dissolved in CH_3CN (16 mL) and K_2CO_3 (1.16 g, 8.37 mmol, 3 equiv.) was added. The reaction was stirred at 60 °C for 16 h. Then the solids were filtered off and solvent removed under *vacuo*. The residue was purified by flash column chromatography (Al_2O_3, CH_2Cl_2: CH_3OH, 95:5) to give **2** (0.50 g, 60% yield) as a brownish syrup. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.51 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.62 (td, *J* = 7.8, 1.8 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.13 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 4.72 (s, 2H), 3.69 (s, 4H), 2.64 (s, 4H), 2.27 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.3 (C), 158.6 (C), 158.3 (C), 149.2 (CH), 137.2 (CH), 136.6 (CH), 123.3 (CH), 122.1 (CH), 121.7 (CH), 118.9 (CH), 64.2 (CH_2), 63.9 (CH_2), 55.5 (CH_2), 55.4 (CH_2), 43.0 (CH_3), 43.0 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{17}H_{25}N_4O$: 301.2022; found: 301.2014. **IR (ATR):** 3280, 2920, 2846, 2800, 1660, 1593, 1576, 1455, 1436, 1358, 1070, 1033, 760 cm^{-1}.

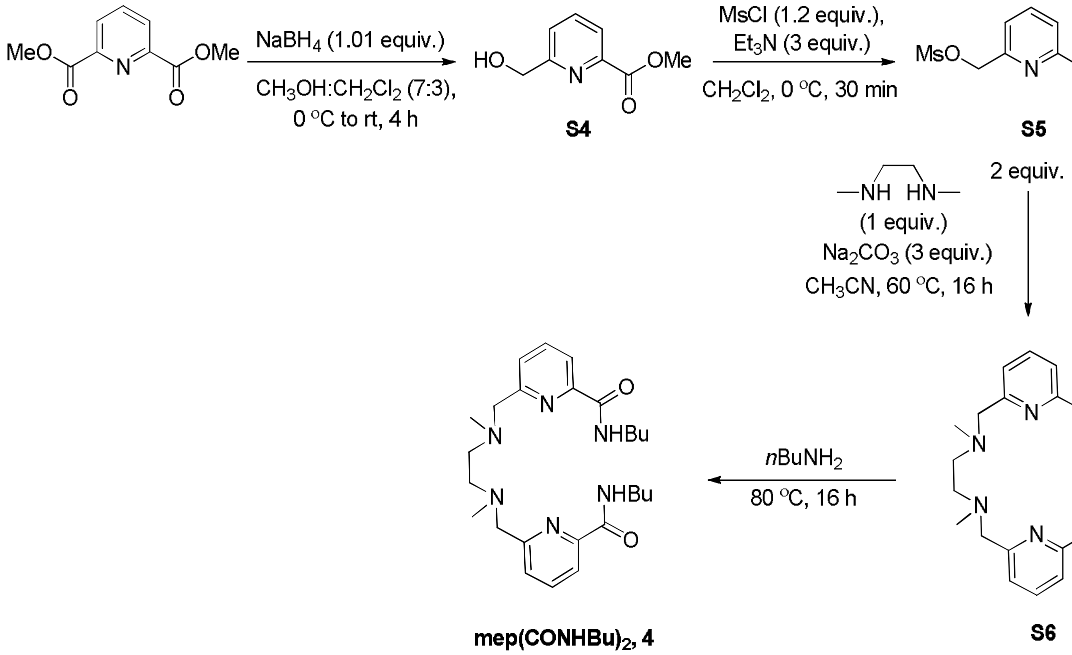
- **Synthesis of mep(OH)$_2$ (3)**



mep(OH)$_2$, 3

Compound 3. Compound **S2** (1.50 g, 5.11 mmol, 2.1 equiv.) was dissolved in CH_3CN (55 mL) and K_2CO_3 (1.01 g, 7.30 mmol, 3 equiv.) and *N*,*N'*-dimethylethylenediamine (0.27 mL, 2.43 mmol, 1 equiv.) were added sequentially. The reaction was stirred at 60 °C for 16 h. Then the solids were filtered off and solvent removed under *vacuo*. The residue was purified by flash column chromatography (Al_2O_3, CH_2Cl_2: CH_3OH, 96:4) to give **3** (0.51 g, 64% yield) as a brownish syrup. **^{1}H NMR (500 MHz, CD_3OD):** δ 7.77 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 4.67 (s, 4H), 3.66 (s, 4H), 2.63 (s, 4H), 2.26 (s, 6H). **^{13}C NMR (126 MHz, CD_3OD):** δ 161.8 (C), 159.1 (C), 138.9 (CH), 123.2 (CH), 120.3 (CH), 65.5 (CH_2), 64.4 (CH_2), 56.0 (CH_2), 43.2 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{18}H_{27}N_4O_2$: 331.2129; found: 331.2130. **IR (ATR):** 3197, 2846, 2814, 1595, 1576, 1441, 1357, 1092, 1072, 1040, 999, 969, 783, 618 cm^{-1}.

- **Synthesis of mep(CONHBu)$_2$ (4)**



Compound S4. Under Ar atmosphere, $NaBH_4$ (0.39 g, 10.3 mmol, 1.01 equiv.) was slowly added over a solution of dimethyl 2,6-pyridinedicarboxylate (2.00 g, 10.2 mmol, 1 equiv.) in dry CH_3OH: CH_2Cl_2 (7:3, 100 mL) at 0 °C. The cooling bath was removed and the mixture was stirred for 3 h at rt. Then NH_4Cl aq. sat. solution was added carefully at 0°C and the mixture was extracted with CH_2Cl_2 (x3). The combined organic phases were dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash column chromatography (SiO_2, hexane: EtOAc, 4:6) to give **S4** (992 mg, 58% yield) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.03 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.87 (s, 2H), 3.99 (s, 3H), 3.67 (bs, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 165.6 (C), 160.2 (C), 147.0 (C), 137.7 (CH), 124.0 (CH), 123.8 (CH), 64.6 (CH_2), 52.9 (CH_3). **HRMS (ESI):** *m/z* $[M]^+$ calcd for $C_8H_9NO_3$: 167.0582; found: 167.0585.

Compound S5. Under Ar atmosphere, compound **S4** (0.90 g, 5.38 mmol, 1 equiv.) and Et_3N (2.25 mL, 16.15 mmol, 3 equiv.) were dissolved in dry CH_2Cl_2 (54 mL) and the flask was cooled to 0 °C. MsCl (0.50 mL, 6.5 mmol, 1.2 equiv.) was added and the reaction stirred until completion (~40 min, TLC). $NaHCO_3$ sat. aq. was added and phases separated, the aqueous phase was extracted with CH_2Cl_2 and combined organic phases were dried over Na_2SO_4, filtered and evaporated. The crude material was used in the next step without further purification due to its instability.

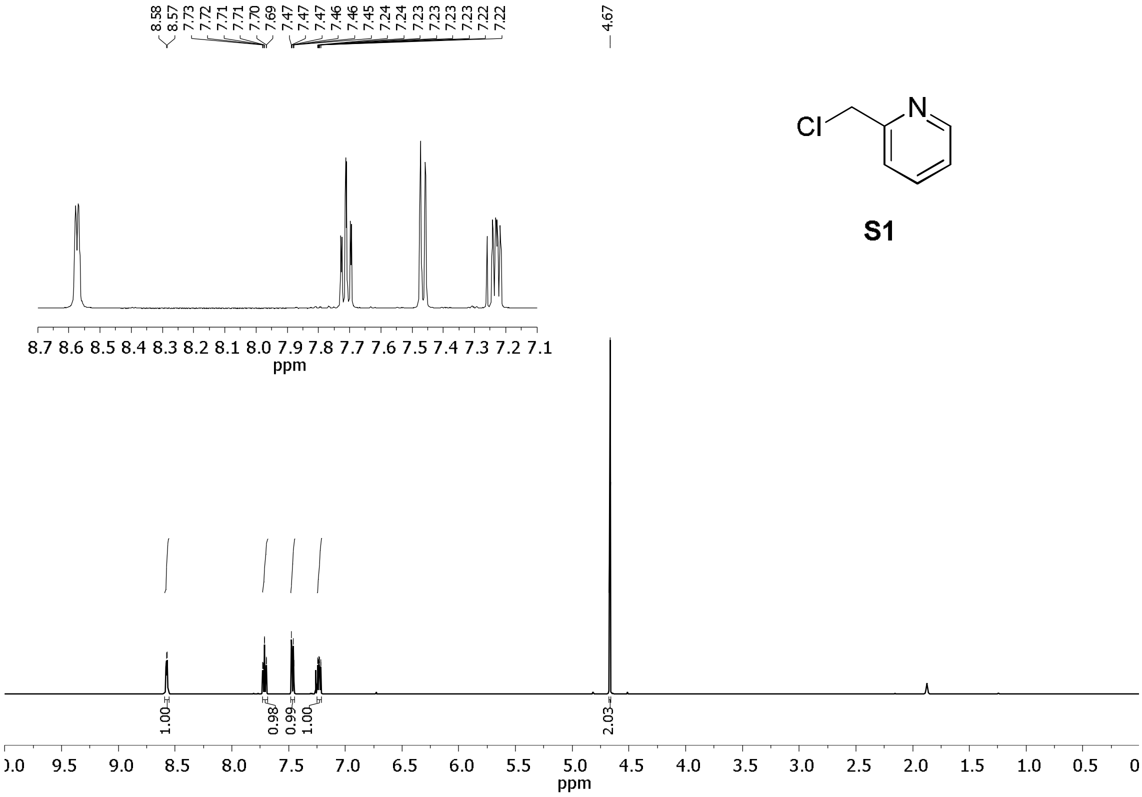
Compound S6. Crude compound **S5** (5.38 mmol, 3 equiv.) was dissolved in CH_3CN (57 mL) and Na_2CO_3 (0.76 g, 7.2 mmol, 4 equiv.) followed by *N,N'*-dimethylethylenediamine (0.19 mL, 1.80 mmol, 1 equiv.) were added. The reaction was stirred at 60 °C for 16 h. Then the solids were filtered off and solvent removed under *vacuo*. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2: CH_3OH, 95:5) to give **S6** (0.56 mg, 81% yield) as a yellowish solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.66

(dd, J = 7.7, 1.3 Hz, 2H), 3.92 (s, 6H), 3.79 (s, 4H), 2.64 (s, 4H), 2.25 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.8 (C), 160.3 (C), 147.3 (C), 137.4 (CH), 126.3 (CH), 123.6 (CH), 63.7 (CH_2), 55.4 (CH_2), 52.8 (CH_3), 42.9 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{20}H_{27}N_4O_4$: 387.2026; found: 387.2027.

Compound 4. Compound **S6** (0.47 g, 1.20 mmol, 1 equiv.) was dissolved in *n*$BuNH_2$ (20 mL) and the reaction was stirred at 80 °C for 16 h. Solvent was removed under *vacuo* and the residue was purified by flash column chromatography (SiO_2, CH_2Cl_2: CH_3OH, 95:5) to give **4** (373 mg, 73% yield) as a brownish solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.15 (s, 2H), 8.08 (dd, J = 7.7, 1.1 Hz, 2H), 7.78 (t, J = 7.7 Hz, 2H), 7.54 (dd, J = 7.7, 1.1 Hz, 2H), 3.72 (s, 4H), 3.46 (q, J = 6.8 Hz, 4H), 2.64 (s, 4H), 2.29 (s, 6H), 1.62 (p, J = 7.6 Hz, 4H), 1.42 (h, J = 7.3 Hz, 4H), 0.96 (t, J = 7.4 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 164.3 (C), 158.0 (C), 149.4 (C), 137.6 (CH), 125.3 (CH), 120.6 (CH), 63.9 (CH_2), 55.4 (CH_2), 42.9 (CH_3), 39.1 (CH_2), 31.8 (CH_2), 20.2 (CH_2), 13.8 (CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{26}H_{41}N_6O_2$: 469.3285; found: 469.3286. **IR (ATR):** 3308, 2952, 2929, 2804, 1657, 1526, 1453, 712 cm^{-1}.

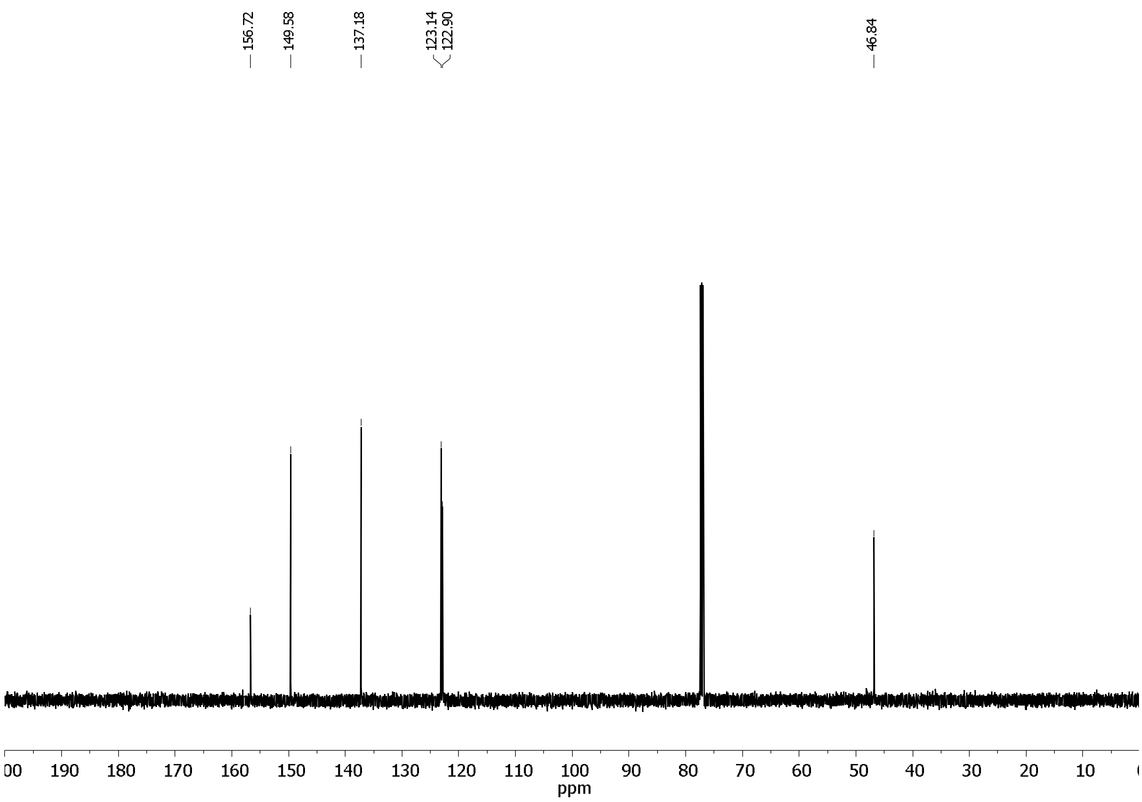
2. ^{1}H-NMR and ^{13}C-NMR spectra of new compounds

^{1}H-NMR (500 MHz, $CDCl_3$):

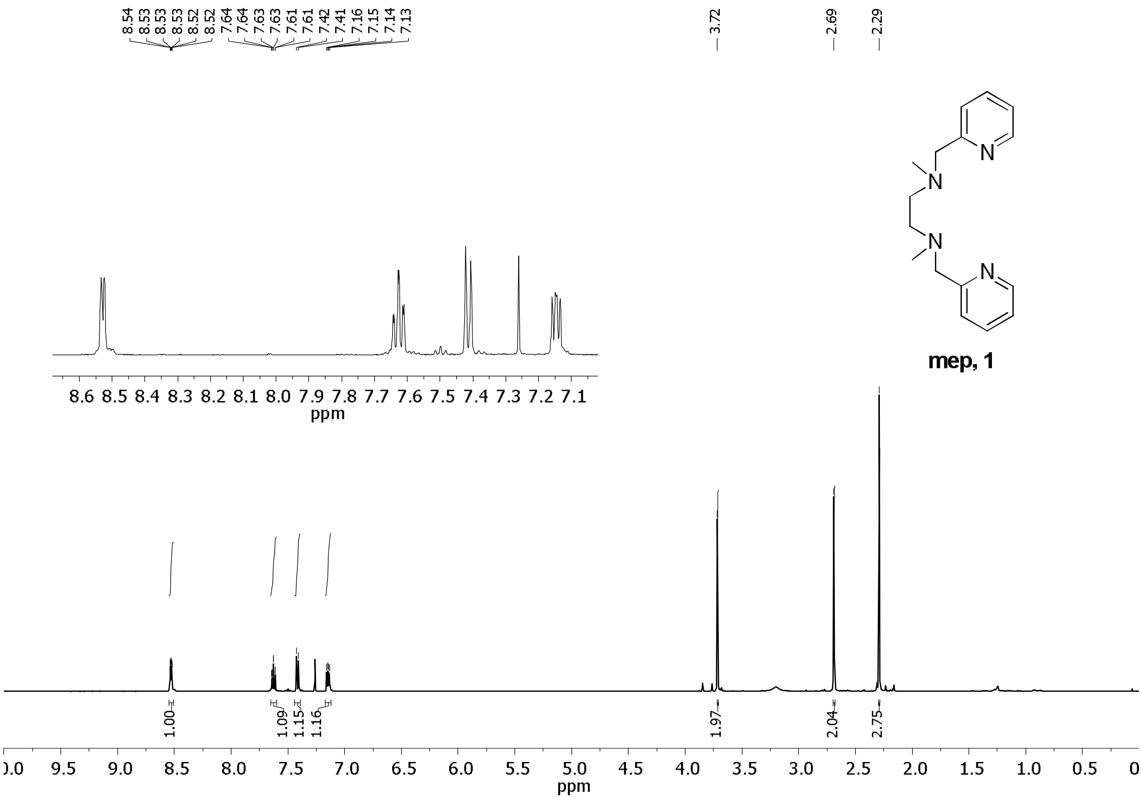


S1

^{13}C-NMR (126 MHz, $CDCl_3$):

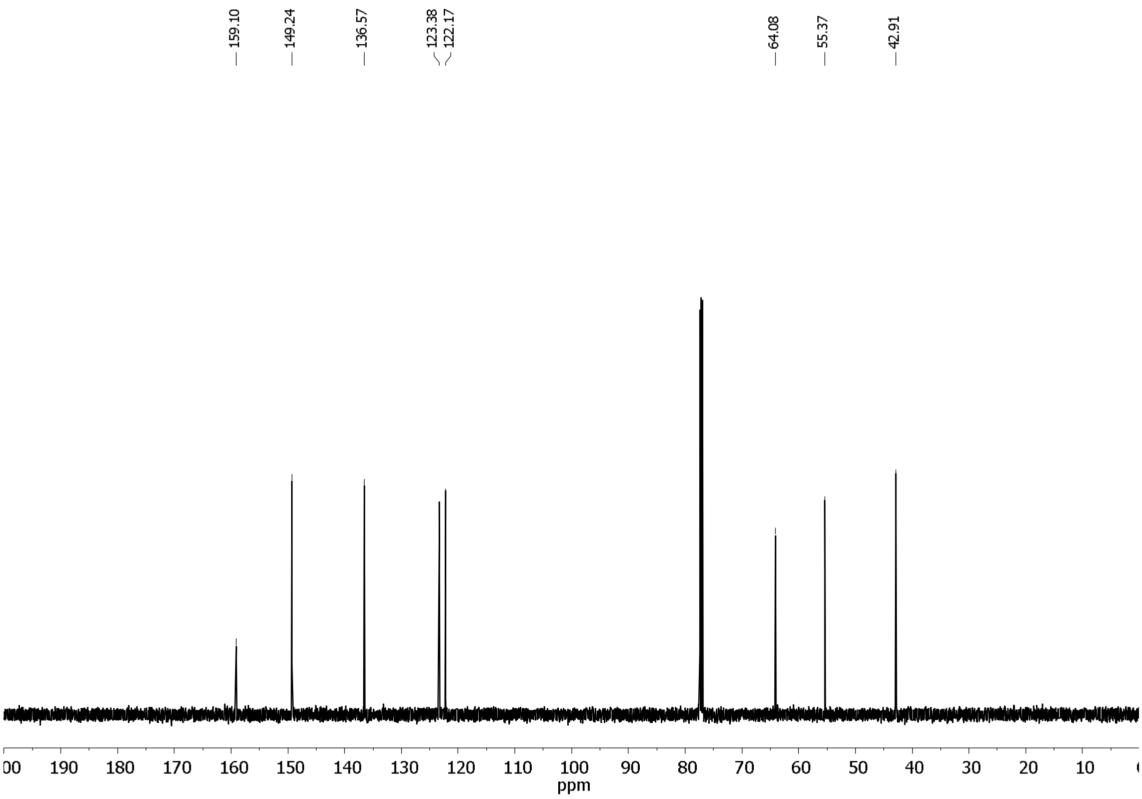


^{1}H-NMR (500 MHz, $CDCl_3$):

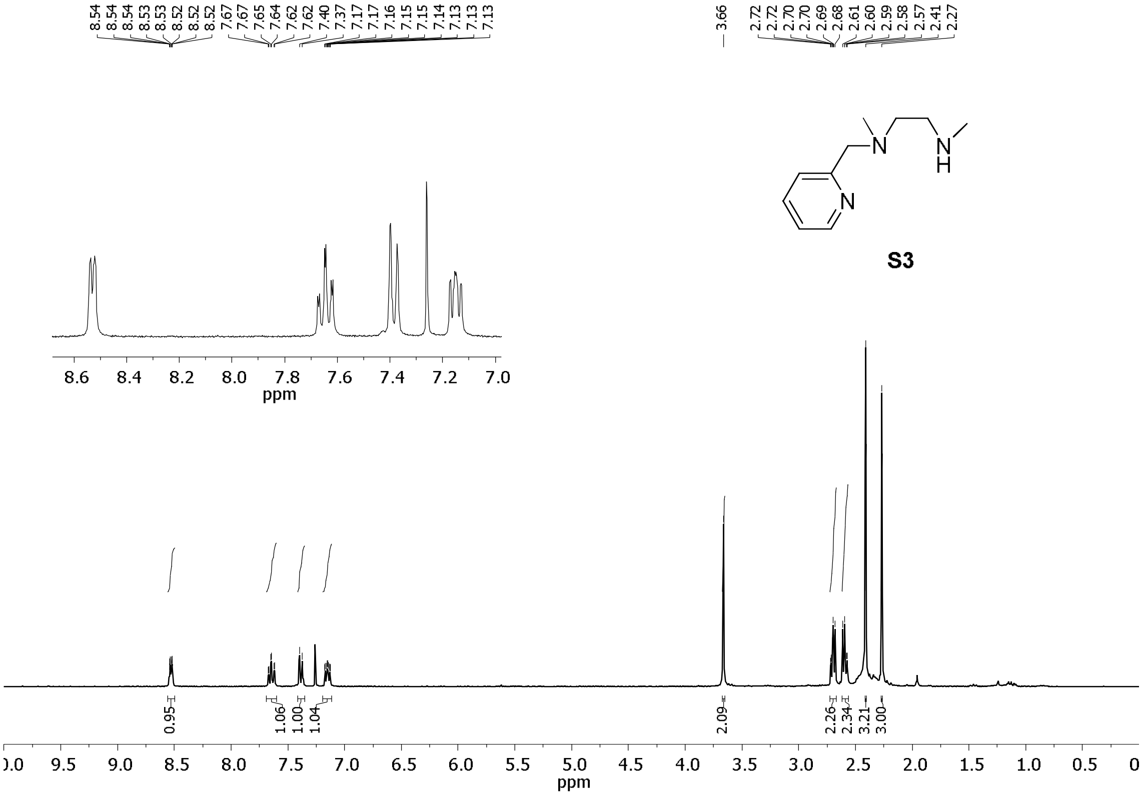


mep, 1

^{13}C-NMR (126 MHz, $CDCl_3$):

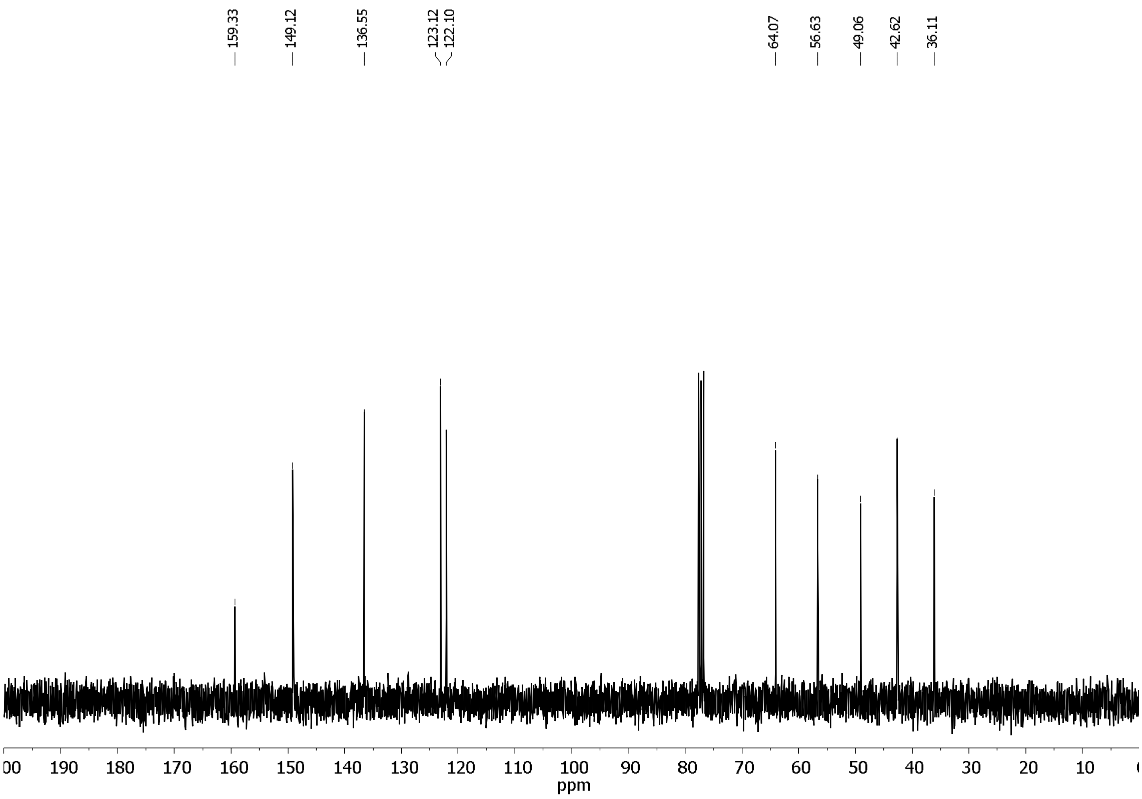


^{1}H-NMR (300 MHz, $CDCl_3$):

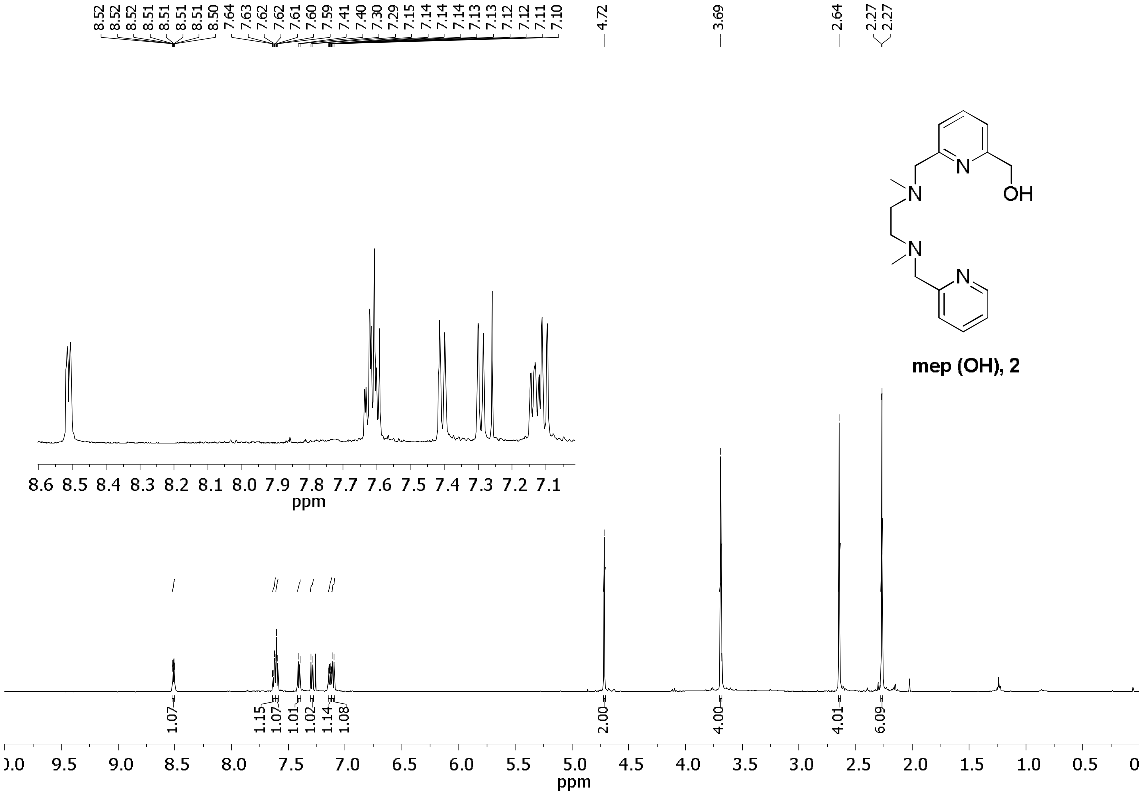


S3

^{13}C-NMR (75 MHz, $CDCl_3$):

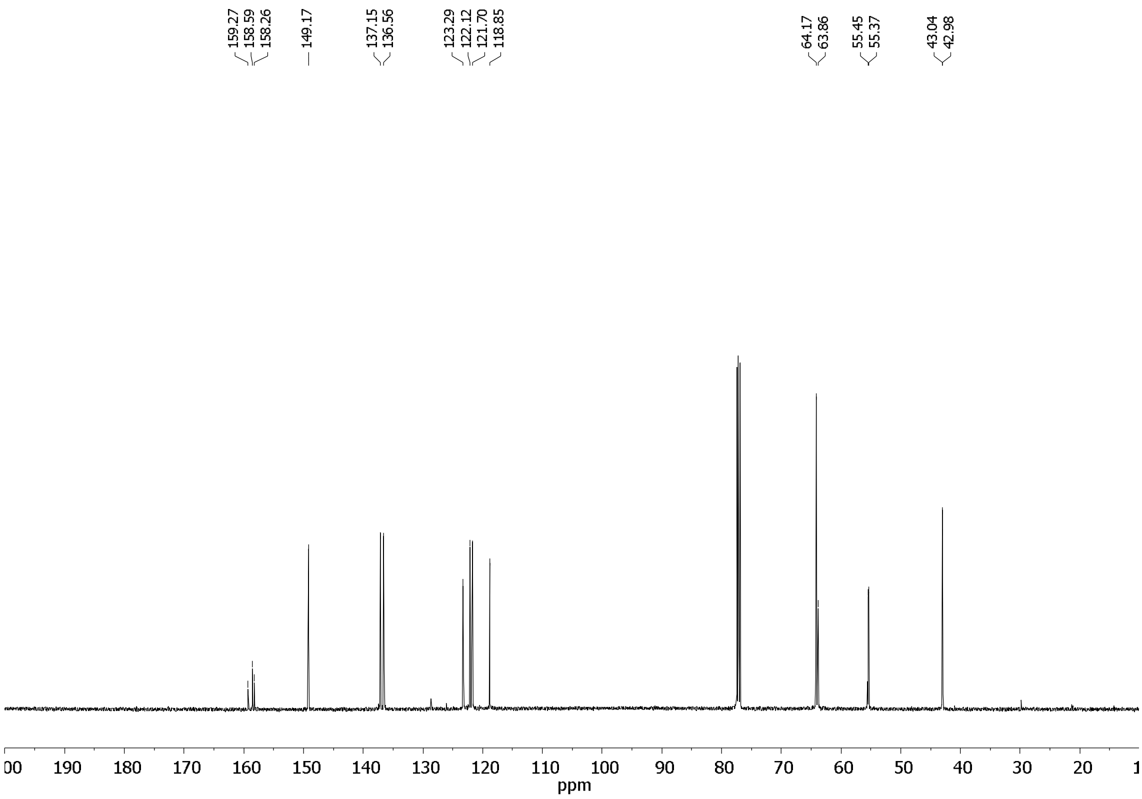


[1]H-NMR (500 MHz, $CDCl_3$):

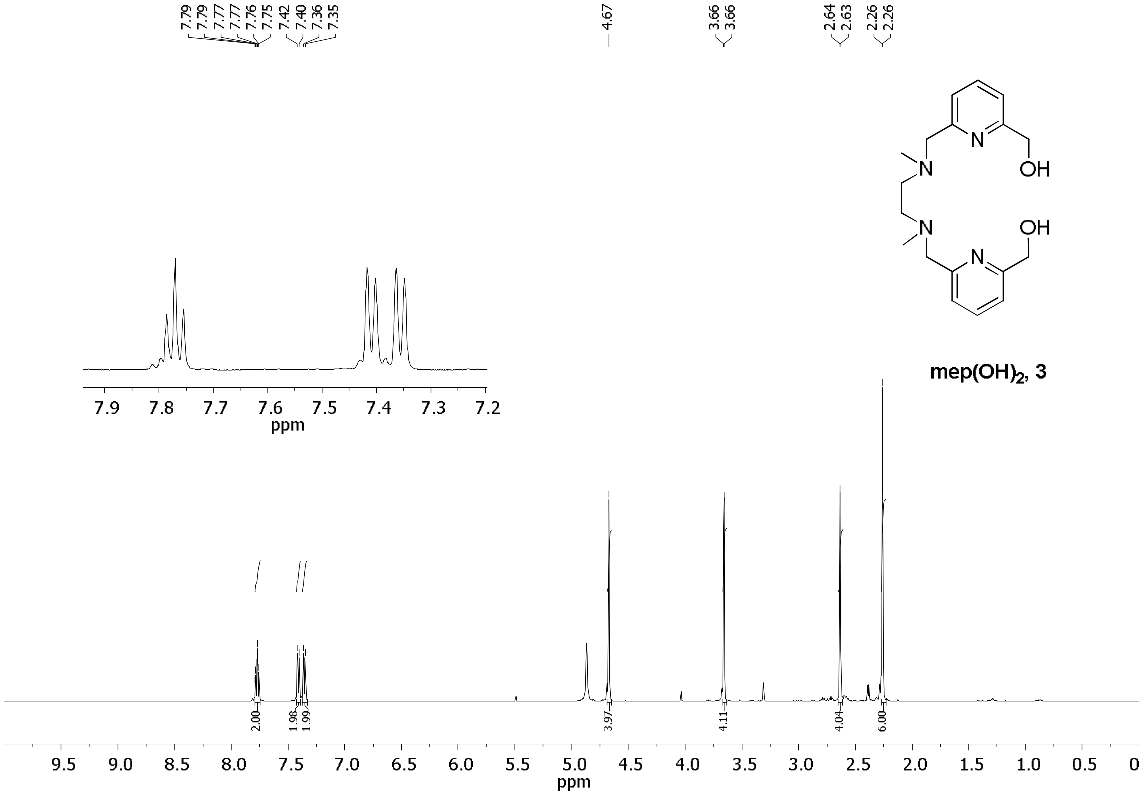


mep (OH), 2

[13]C-NMR (126 MHz, $CDCl_3$):

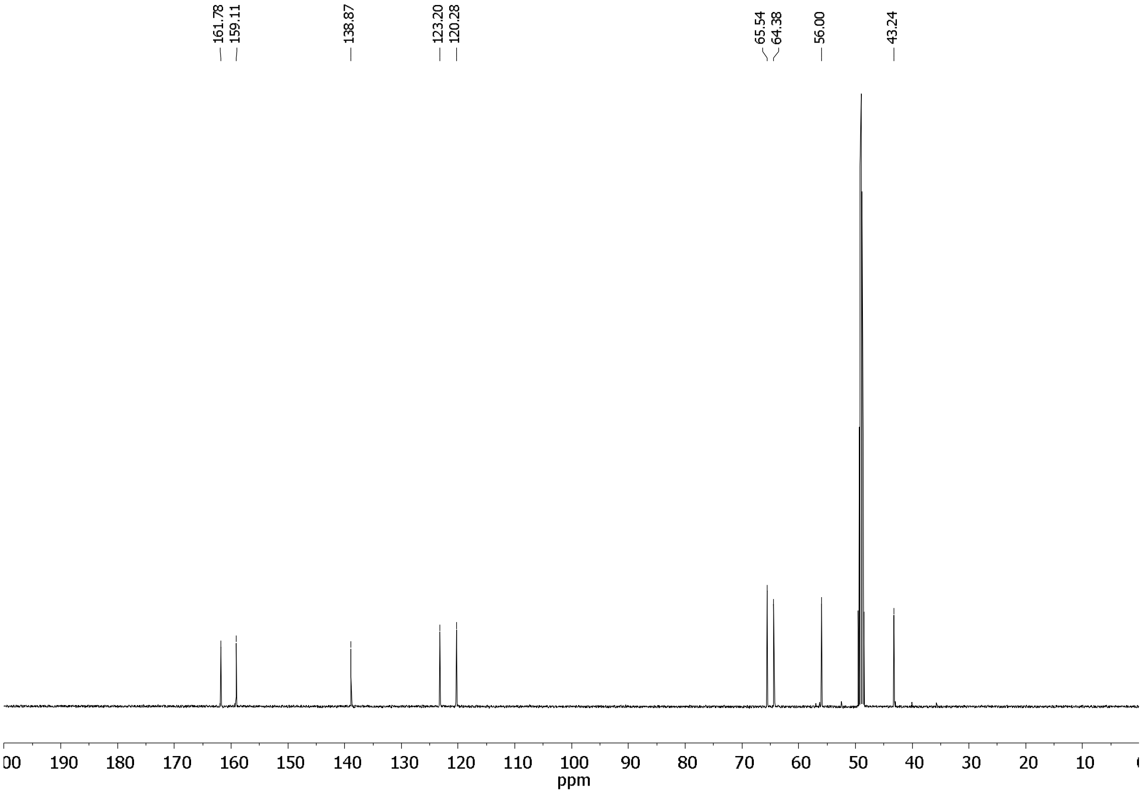


^{1}H-NMR (500 MHz, CD_3OD):

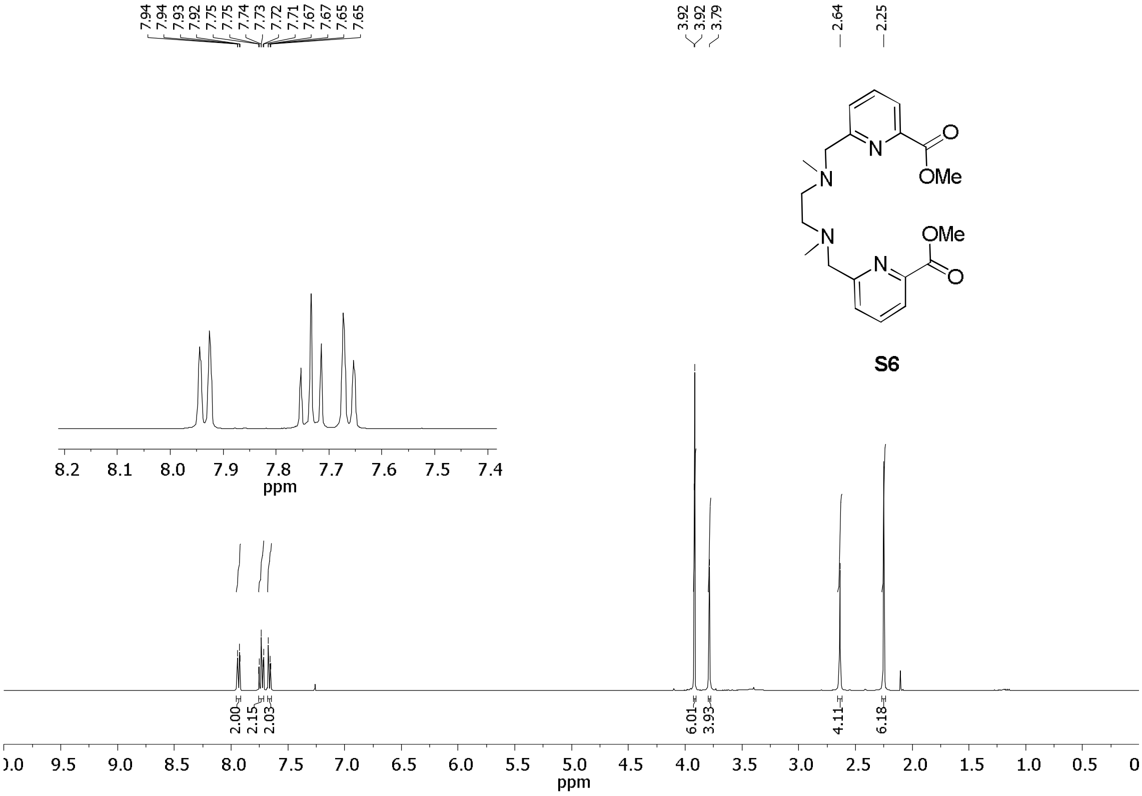


mep(OH)$_2$, 3

^{13}C-NMR (126 MHz, CD_3OD):

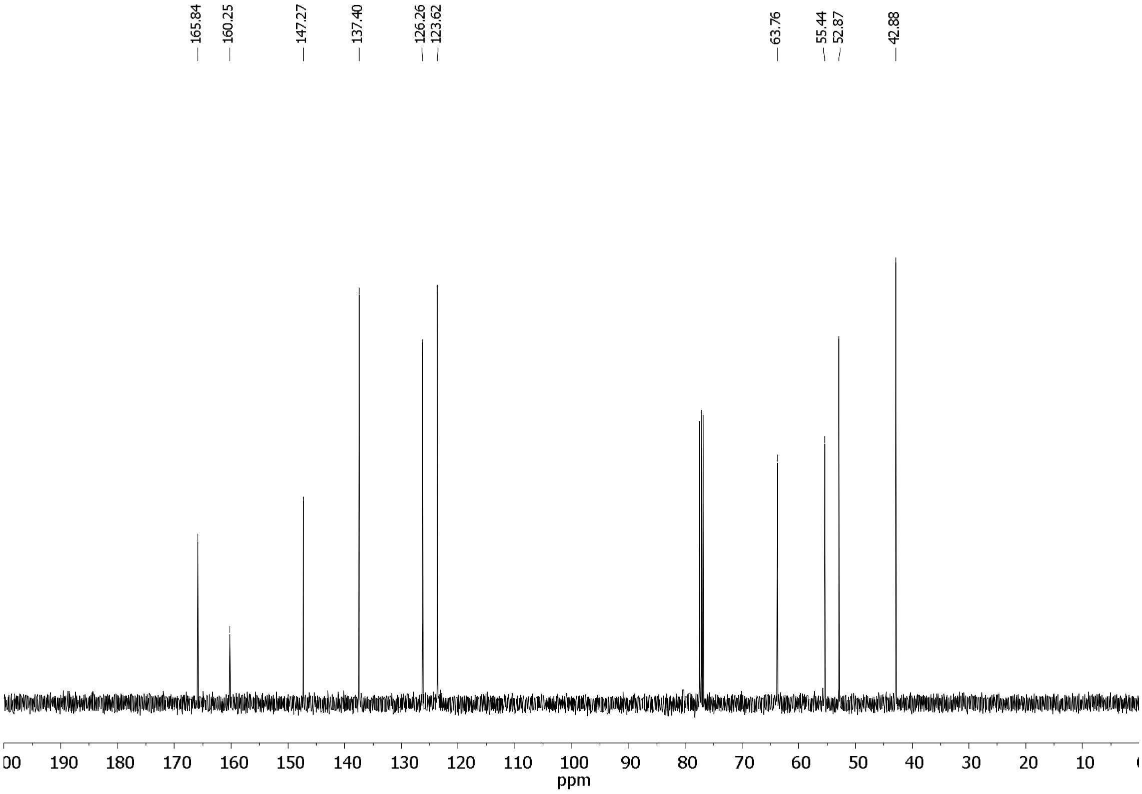


^{1}H-NMR (400 MHz, $CDCl_3$):

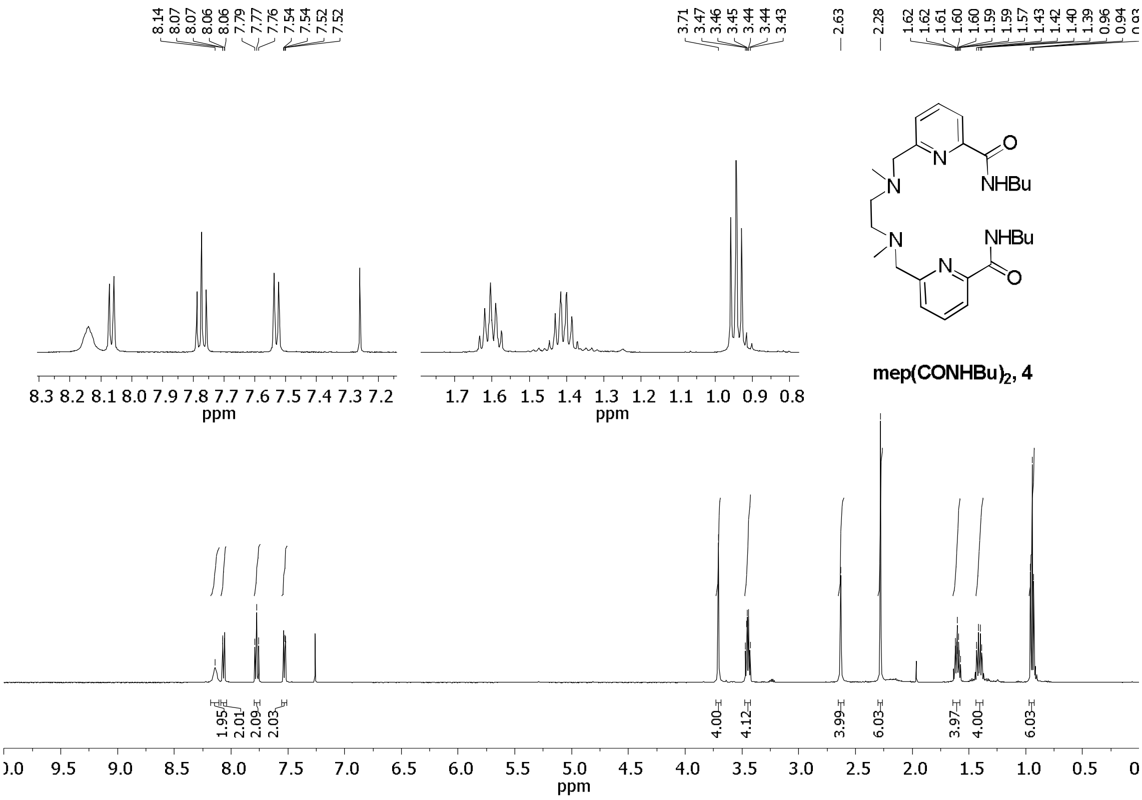


S6

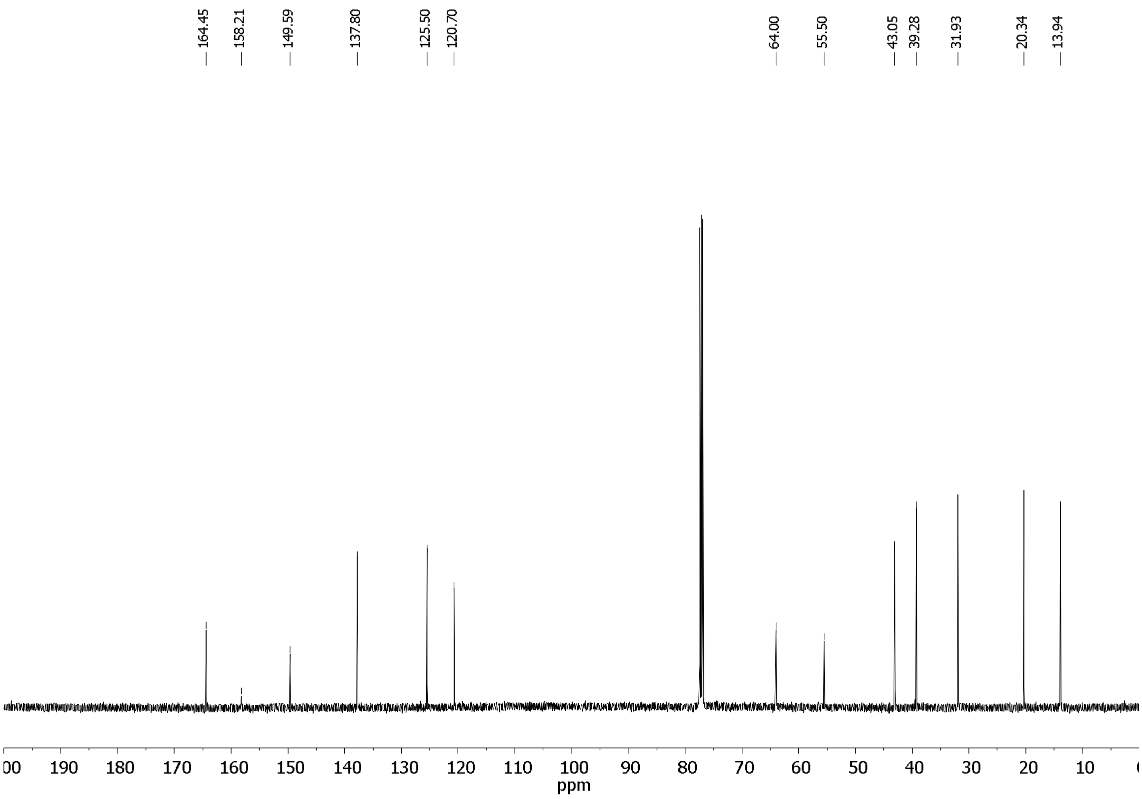
^{13}C-NMR (101 MHz, $CDCl_3$):



^{1}H-NMR (500 MHz, $CDCl_3$):



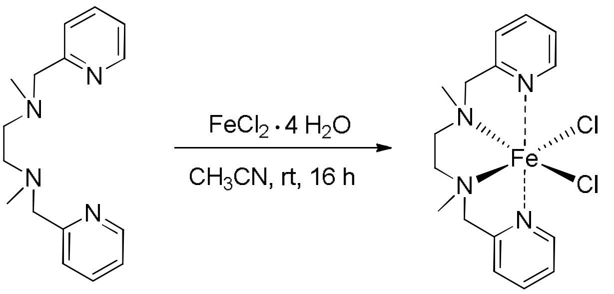
^{13}C-NMR (126 MHz, $CDCl_3$):



3. Synthesis of iron (II) complexes 5-8 and S8-S11

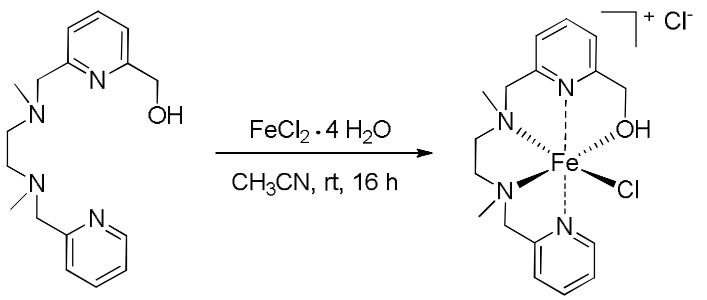
Representative protocol for synthesis of iron (II) complexes.

Under Ar atmosphere, the corresponding free ligand (1 equiv.) was dissolved in anhydrous CH_3CN, $FeCl_2{\cdot}4H_2O$ (1 equiv.) was added and the mixture stirred for 16 h. Then Et_2O (~20 mL) was added and the slurry was stirred for 15 min. The solid was filtered, washed with Et_2O several times to give the corresponding iron (II) complexes powder. Single-crystals of complexes were grown by vapor diffusion using CH_3CN/CH_3OH or DMF as solvent and Et_2O as precipitant.



mep, 1 **Fe(II)(mep)Cl$_2$, 5**

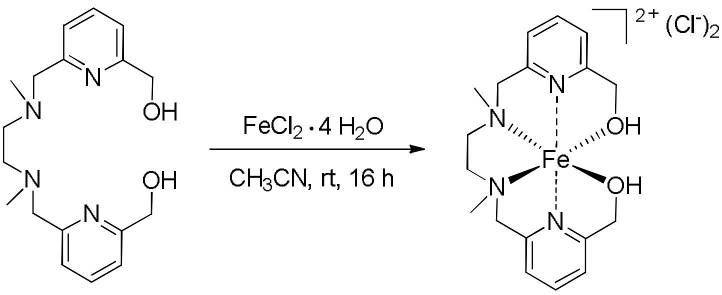
Fe(II)(mep)Cl$_2$, 5. According to previously described procedure, complex **5** was prepared from **1** (345 mg, 1.23 mmol) and $FeCl_2{\cdot}4H_2O$ (254 mg, 1.23 mmol) in anhydrous CH_3CN (3 mL) to give complex **5** (365 mg, 72% yield) as yellow powder. Single-crystals of **5** were grown by vapor diffusion using CH_3CN (with a few drops of CH_3OH) as solvent and Et_2O as precipitant. **^{1}H NMR (500 MHz, CD_2Cl_2):** Major signals observed: δ 146.7, 103.7, 86.7, 60.0, 56.1, 49.7, 21.1, –4.1, –22.4. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ 154.8, 147.0, 142.3, 126.5, 108.7, 94.3, 88.8, 78.8, 70.2, 62.4, 60.2, 57.3, 54.0, 49.6, 23.6, 21.9, 18.8, –5.7, –22.1. **HRMS (ESI):** *m/z* $[M–Cl]^+$ calcd for $C_{16}H_{22}N_4ClFe$: 361.0876; found: 361.0868. **HRMS (ESI):** *m/z* $[M–Cl_2]^{2+}$ calcd for $C_{16}H_{22}N_4Fe$: 163.0591; found: 163.0591. **IR (ATR):** 2970, 1601, 1467, 1432, 1303, 1080, 1052, 1013, 978, 817, 777 cm^{-1}. **Elemental Analysis:** Calcd for $C_{16}H_{22}N_4FeCl_2{\cdot}0.5H_2O$: C, 47.67; H, 5.41; N, 14.07; found: C, 47.32; H, 5.71; N, 13.80.



mep(OH), 2 **[Fe(II)(mep(OH))Cl]Cl, 6**

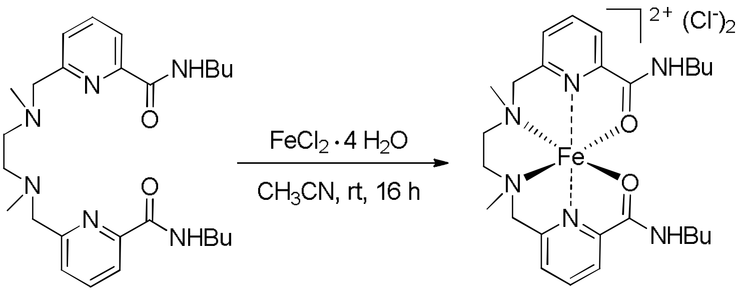
[Fe(II)(mep(OH))Cl]Cl, 6. According to previously described procedure, complex **6** was prepared from **2** (102 mg, 0.34 mmol) and $FeCl_2{\cdot}4H_2O$ (68 mg, 0.34 mmol) in anhydrous CH_3CN (3 mL) to give complex **6** (142 mg, 98% yield) as yellow powder. Single-crystals of **6** were grown by vapor diffusion using CH_3CN (with a few drops of CH_3OH) as solvent and Et_2O as precipitant. **^{1}H NMR (500 MHz, CD_2Cl_2)**: Major signals observed: δ 116.3, 100.2, 98.4, 93.4, 84.8, 66.1, 64.8, 58.6, 53.8, 27.0, 23.7, –2.7. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** Major signals observed: δ 126.9, 108.1, 103.1, 96.4, 89.1, 68.4, 65.6, 58.2, 54.0, 30.5, 24.0, –0.7. **^{1}H NMR (500 MHz, CD_3OD):** Major signals observed: δ 107.7, 101.4, 99.3, 86.4, 65.9, 57.9, 54.2, 30.3, 18.4, –5.7, –14.8. **^{1}H NMR (500 MHz, D_2O):**

Major signals observed: δ 152.9, 122.9, 107.4, 94.5, 89.0, 65.8, 55.5, 52.2, 41.1, –2.4, –16.7. **HRMS (ESI):** *m/z* [M–HCl]$^+$ calcd for $C_{17}H_{23}N_4OClFe$: 390.0904; found: 390.0892. **IR (ATR):** 2815, 2714, 1580, 1605, 1443, 1039, 817, 769 cm^{-1}. **Elemental Analysis:** Calcd for $C_{17}H_{24}N_4OFeCl_2{\cdot}0.5CH_3CN$: C, 48.29; H, 5.74; N, 14.08; found: C, 48.19; H, 5.61; N, 14.01.



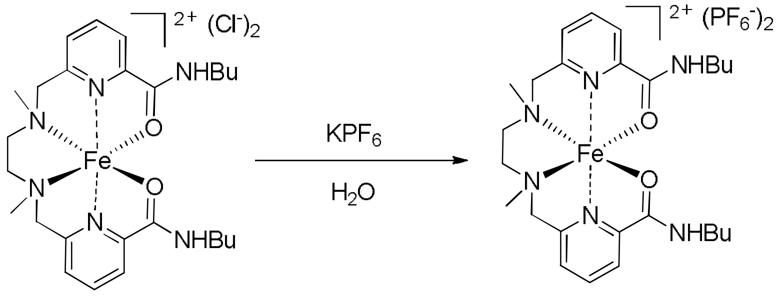
mep(OH)$_2$, 3 **[Fe(II)(mep(OH)$_2$)]Cl$_2$, 7**

[Fe(II)(mep(OH)$_2$)]Cl$_2$, 7. According to previously described procedure, complex **7** was prepared from **3** (334 mg, 1.01 mmol) and $FeCl_2{\cdot}4H_2O$ (201 mg, 1.01 mmol) in anhydrous CH_3CN (3 mL) to give complex **7** (444 mg, 88% yield) as yellow powder. Single-crystals of **7** were grown by vapor diffusion using CH_3CN (with a few drops of CH_3OH) as solvent and Et_2O as precipitant. **^{1}H NMR (500 MHz, CD_3OD)**: Mayor signals observed: δ 131.1, 124.2, 121.2, 120.1, 97.9, 67.4, 46.6, 21.5, 2.1, –1.3, –37.9. **^{1}H NMR (500 MHz, DMSO-*d$_6$*):** Major signals observed: δ 120.8, 115.5, 88.8, 69.4, 45.7, 11.5, –32.0. **HRMS (ESI):** *m/z* [M–H_2Cl_2]$^{2+}$ calcd for $C_{18}H_{24}N_4O_2Fe$: 192.0618; found: 192.0625. **IR (ATR):** 1604, 1579, 1419, 1029, 816, 770, 745 cm^{-1}. **Elemental Analysis:** Calcd for $C_{18}H_{26}N_4O_2FeCl_2{\cdot}0.5H_2O$: C, 46.38; H, 5.84; N, 12.02; found: C, 46.29; H, 5.60; N, 11.99.



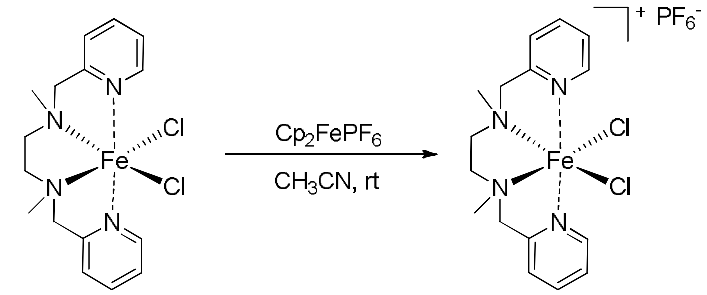
mep(CONHBu)$_2$, 4 **[Fe(II)(mep(CONHBu)$_2$)]Cl$_2$, 8**

[Fe(II)(mep(CONHBu)$_2$)]Cl$_2$, 8. According to previously described procedure, complex **8** was prepared from **4** (314 mg, 0.67 mmol) and $FeCl_2{\cdot}4H_2O$ (133 mg, 0.67 mmol) in anhydrous CH_3CN (7 mL) to give complexe **8** (346 mg, 81% yield) as red powder. Single-crystals of **8** were grown by vapor diffusion using DMF as solvent and Et_2O as precipitant. **^{1}H NMR (500 MHz, CD_3OD)**: Major signals observed: δ 129.5, 123.6, 93.4, 92.8, 46.6, 20.3, 19.9, 6.3, 5.9, 4.3, 1.7, 1.3, -11.4. **^{1}H NMR (500 MHz, CD_3CN)**: Major signals observed: δ 125.1, 121.9, 94.6, 91.5, 89.4, 46.3, 21.2, 19.8, 6.4, 6.0, 4.3, 3.4 (q, *J* = 7.0 Hz, 4H), 2.9, 1.4, 1.1 (t, *J* = 7.0 Hz, 6H), –15.1. **^{1}H NMR (500 MHz, CD_2Cl_2):** Major signals observed: δ 114.8, 111.1, 98.3, 95.0, 80.9, 46.0, 22.9, 22.2, 6.3, 5.9, -20.3. **^{1}H NMR (500 MHz, DMSO-*d$_6$*)**: Major signals observed: δ 123.3, 93.5, 91.3, 87.9, 45.5, 19.5, 19.0, 6.5, 6.3, 4.7, 1.1 (t, *J* = 6.9 Hz, 1H), –10.1. **HRMS (ESI):** *m/z* [M–HCl_2]$^+$ calcd for $C_{26}H_{39}N_6O_2Fe$: 523.2478; found: 523.2464. **HRMS (ESI):** *m/z* [M-Cl_2]$^{2+}$ calcd for $C_{26}H_{40}N_6O_2Fe$: 262.1275; found: 262.1280. **IR (ATR):** 2957, 2864, 1626, 1599, 1549, 1465, 826, 767, 532 cm^{-1}. An elemental analysis could not be obtained for this complex.



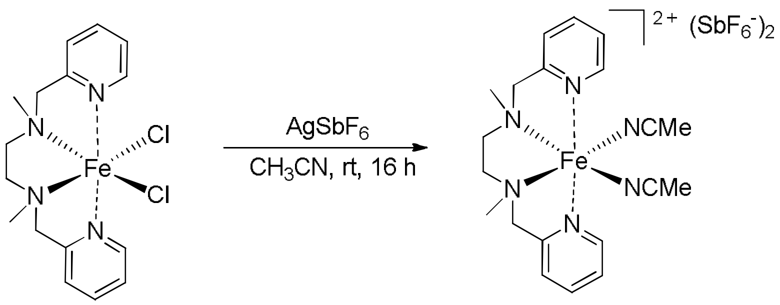
[Fe(II)(mep(CONHBu)$_2$)]Cl$_2$, 8 **[Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$, S7**

[Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$, S7. Compund **8** (226 mg, 0.38 mmol, 1 equiv.) was dissolved in H_2O (5 mL) and KPF_6 (350 mg, 1.90 mmol, 5 equiv.) was added. The resulting precipitate was washed twice with water and was dried under reduced pressure affording **S7** (111 mg, 36%) as a red powder. Single-crystals of **S7** were grown by vapor diffusion using CH_3CN as solvent and Et_2O as precipitant. **IR (ATR):** 3405, 2934, 2874, 1633, 1598, 1549, 824, 556 cm^{-1}. **HRMS (ESI):** *m/z* [M-H(PF$_6$)$_2$]$^+$ calcd for $C_{26}H_{39}N_6O_2Fe$: 523.2478; found: 523.2460. **HRMS (ESI):** *m/z* [M-(PF$_6$)$_2$]$^{2+}$ calcd for $C_{26}H_{40}N_6O_2Fe$: 262.1275; found: 262.1274. **Elemental Analysis:** Calcd for $C_{26}H_{40}F_{12}N_6O_2FeP_2$: C, 38.34; H, 4.95; N, 10.32; found: C, 38.46; H, 4.71; N, 10.32.



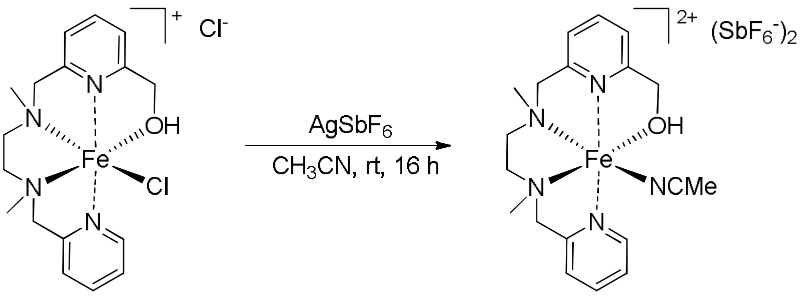
Fe(II)(mep)Cl$_2$, 5 **[Fe(III)(mep)Cl$_2$]PF$_6$, S8**

[Fe(III)(mep)Cl$_2$)]PF$_6$, S8. Compound **5** (109 mg, 0.27 mmol, 1 equiv.) was dissolved in CH_3CN (3 mL) and Cp_2FePF_6 (91 mg, 0.27 mmol, 1 equiv.) was added and the mixture stirred for 8 h at rt. The solution was turned green. Then, solvent was removed under reduced pressure. The crude was washed with Et_2O, redissolved with methanol and precipitated with Et_2O affording **S8** (48 mg, 32%) as a green powder. Single-crystals of **S8** were grown by vapor diffusion using CH_3CN as solvent and Et_2O as precipitant.



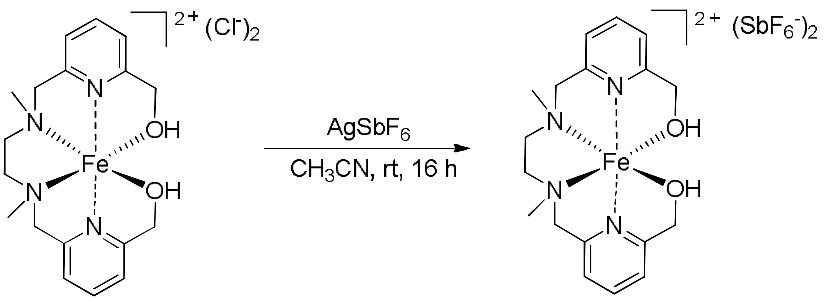
Fe(II)(mep)Cl$_2$, 5 **[Fe(II)(mep(CH$_3$CN)$_2$)][SbF$_6$]$_2$, S9**

[Fe(II)(mep(MeCN)$_2$)][SbF$_6$], S9. Under argon atmosphere, compound **5** (104 mg, 0.26 mmol, 1 equiv.) was dissolved in dry CH_3CN (6 mL) and $AgSbF_6$ (180 mg, 0.52 mmol, 2 equiv.) was added. The reaction was wrapped with aluminum foil and stirred at rt for 16 h. Then, the reaction was diluted with CH_3CN (6 mL) and passed through a short pad of celite, using CH_3CN as eluent, to remove silver salts. After filtering through a PTFE filter, solvent was removed under reduce pressure affording **S9** (198 mg, 86%) as a yellowish solid. **^{1}H NMR (500 MHz, DMSO-*d$_6$*):** Major signals observed: δ 172.2, 128.7, 87.2, 67.9, 57.4, 53.8, 30.5, 22.0, –19.8. **^{1}H NMR (500 MHz, CD_3CN):** Major signals observed: δ 92.7, 73.0, 47.6, 32.6, 29.1, 28.5, 15.7, –1.6. **^{1}H NMR (500 MHz, CD_3OD):** Major signals observed: δ 144.72, 110.67, 84.59, 62.93, 51.33, 49.85, 11.99, –4.30. **HRMS (ESI):** *m/z* $[M–C_2H_6N_2(SbF_6)_2]^{2+}$ calcd for $C_{16}H_{22}N_4Fe$: 163.0591; found: 163.0597. **IR (ATR):** 1611, 1450, 1303, 1025, 977, 762, 653 cm^{-1}. **Elemental Analysis:** Calcd for $C_{20}H_{28}N_6FeF_{12}Sb_2$: C, 27.30; H, 3.21; N, 9.55; found: C, 27.25; H, 3.17; N, 8.80.



[Fe(II)(mep(OH))Cl]Cl, 6 [Fe(II)(mep(OH)(CH_3CN))][SbF_6]$_2$, S10

[Fe(II)(mep(OH)(MeCN))][SbF_6]$_2$, S10. Under argon atmosphere, compound **6** (225 mg, 0.53 mmol, 1 equiv.) was dissolved in dry CH_3CN (6 mL) and $AgSbF_6$ (362 mg, 1.06 mmol, 2 equiv.) was added. The reaction was wrapped with aluminum foil and stirred at rt for 16 h. Then, the reaction was diluted with CH_3CN (6 mL) and passed through a short pad of celite, using CH_3CN as eluent, to remove silver salts. After filtering through a PTFE filter, solvent was removed under reduce pressure affording **S10** (376 mg, 82%) as a purplish solid.



[Fe(II)(mep(OH)$_2$)]Cl_2, 7 [Fe(II)(mep(OH)$_2$)][SbF_6]$_2$, S11

[Fe(II)(mep(OH)$_2$)][SbF_6], S11. Under argon atmosphere, compound **7** (100 mg, 0.22 mmol, 1 equiv.) was dissolved in dry CH_3CN (6 mL) and $AgSbF_6$ (151 mg, 0.44 mmol, 2 equiv.) was added. The reaction was wrapped with aluminum foil and stirred at rt for 16 h. Then, the reaction was diluted with CH_3CN (6 mL) and passed through a short pad of celite, using CH_3CN as eluent, to remove silver salts. After filtering through a PTFE filter, solvent was removed under reduce pressure affording **S11** (177 mg, 94%) as a greenish solid. **HRMS (ESI):** *m/z* $[M-H_2(SbF_6)_2]^+$ calcd for $C_{18}H_{24}N_4O_2Fe$: 384.1243; found: 384.1243. **IR (ATR):** 1739, 1609, 1447, 1217, 1026, 819, 787, 654 cm^{-1}. **Elemental Analysis:** Calcd for $C_{18}H_{26}N_4O_2FeF_{12}Sb_2$: C, 25.20; H, 3.06; N, 6.53; found: C, 26.38; H, 3.04; N, 6.60.

4. ^{1}H NMR spectra of iron (II) complexes 5-8 and S9

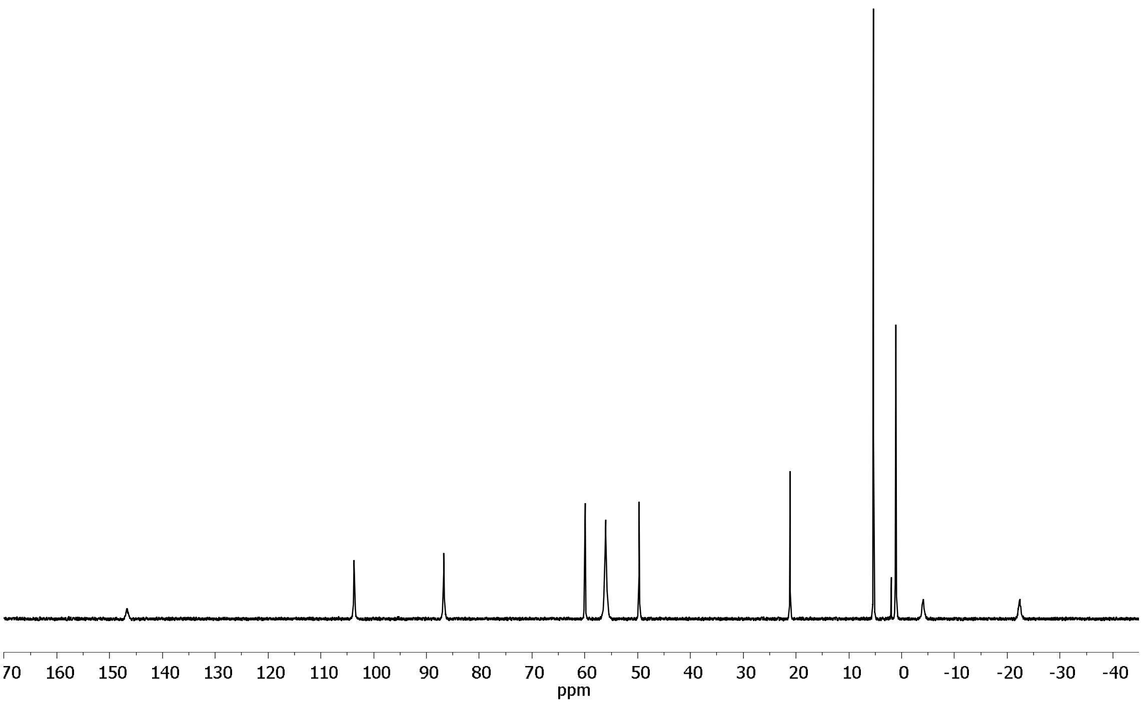


Figure S1. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of Fe(II)(mep)Cl_2 (**5**).

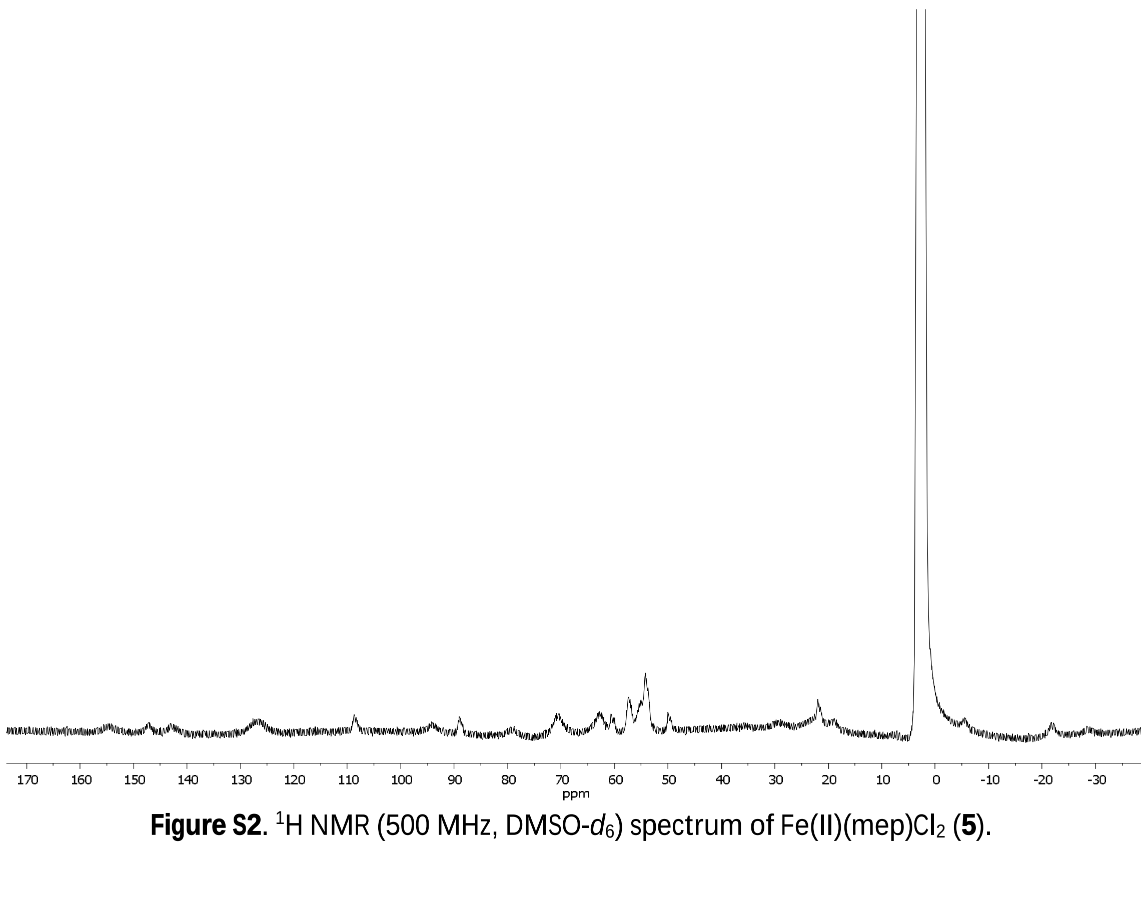


Figure S2. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of Fe(II)(mep)Cl_2 (**5**).

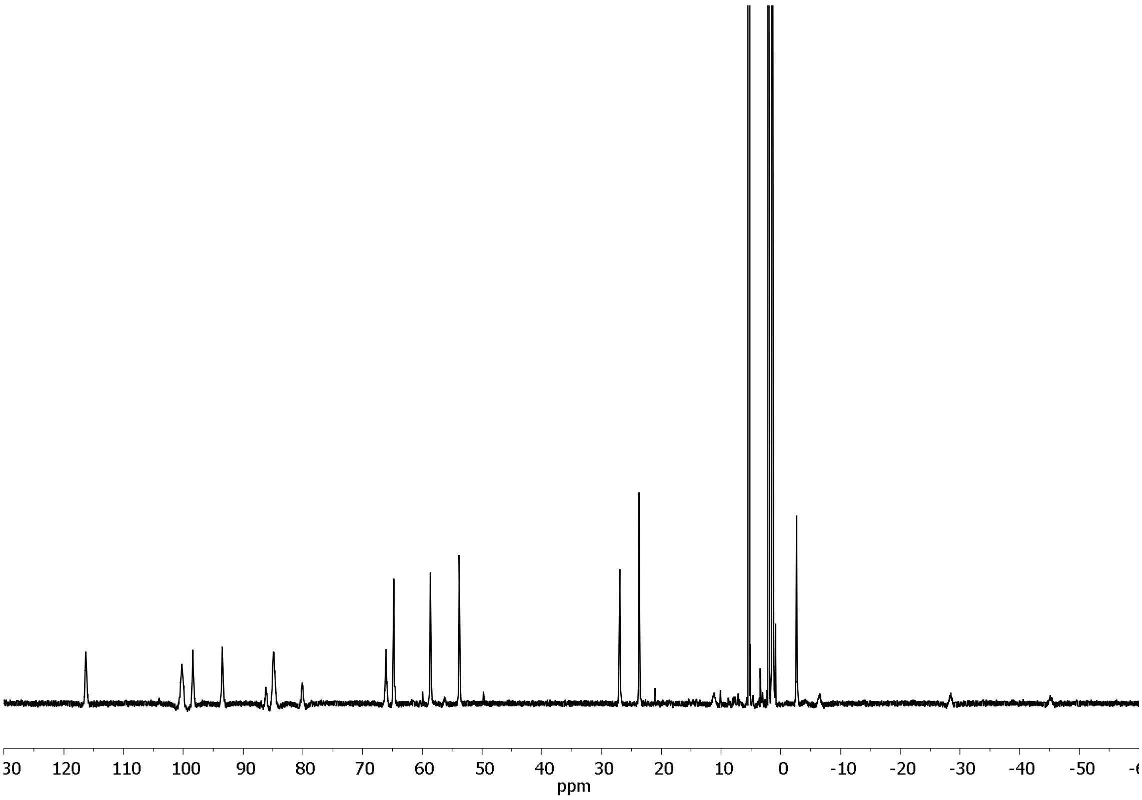


Figure S3. [1]H NMR (500 MHz, CD_2Cl_2) spectrum of [Fe(II)(mep(OH))Cl]Cl (**6**).

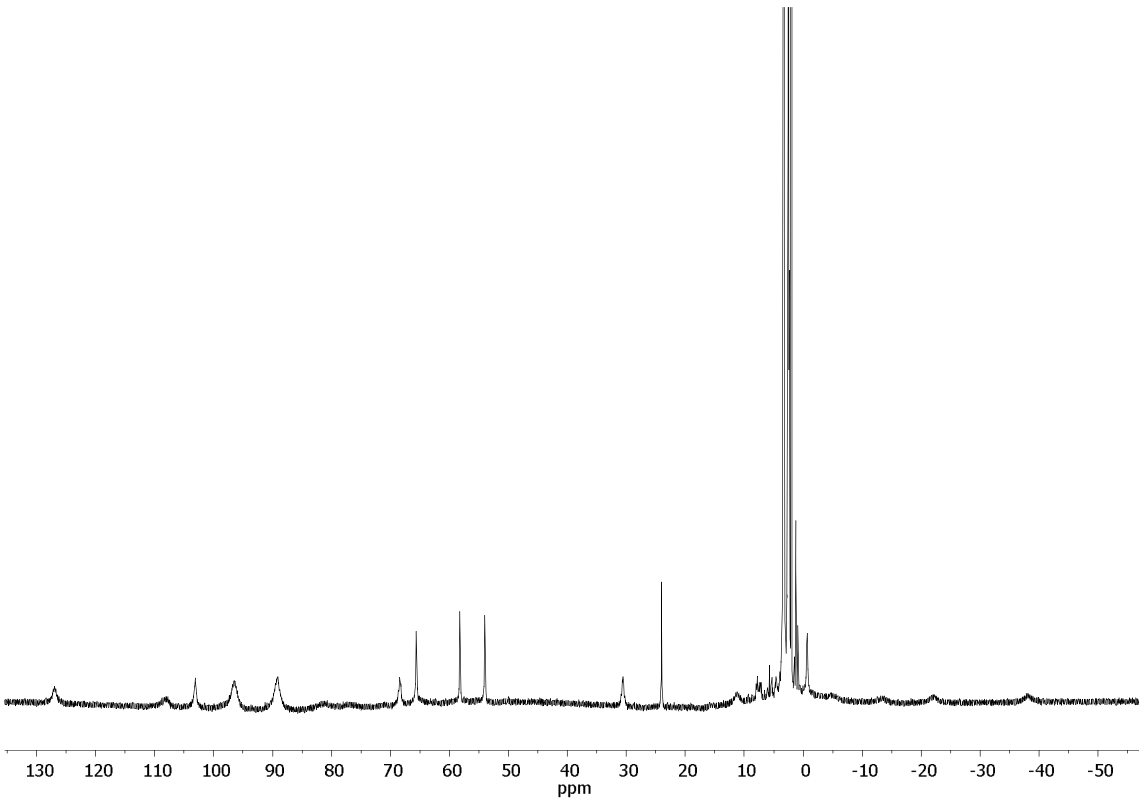


Figure S4. [1]H NMR (500 MHz, DMSO-d_6) spectrum of [Fe(II)(mep(OH))Cl]Cl (**6**).

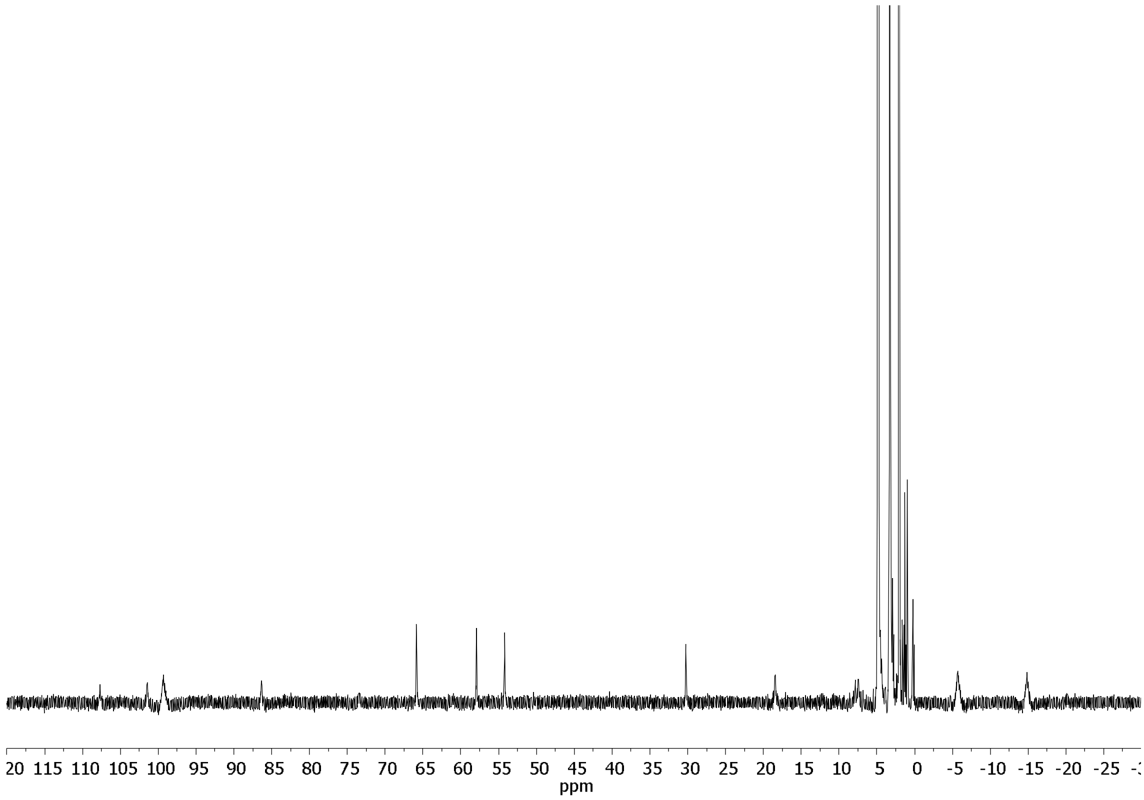


Figure S5. [1]H NMR (500 MHz, CD_3OD) spectrum of [Fe(II)(mep(OH))Cl]Cl (**6**).

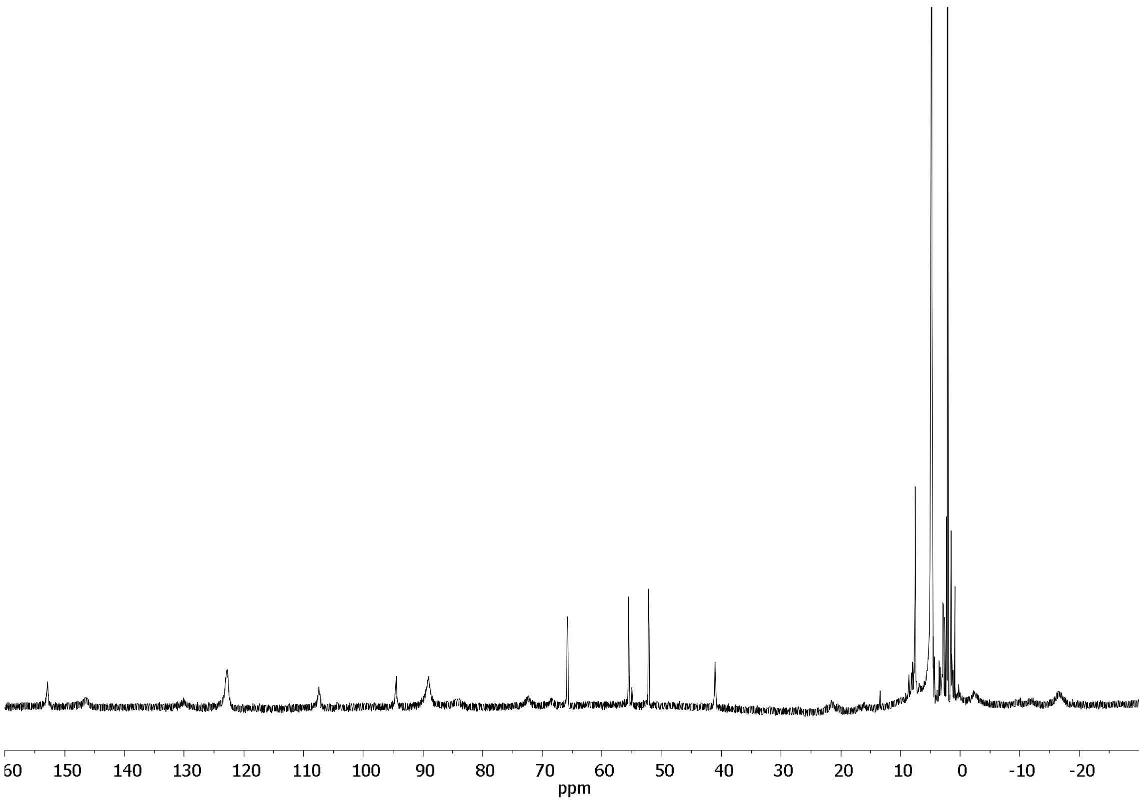


Figure S6. [1]H NMR (500 MHz, D_2O) spectrum of [Fe(II)(mep(OH))Cl]Cl (**6**).

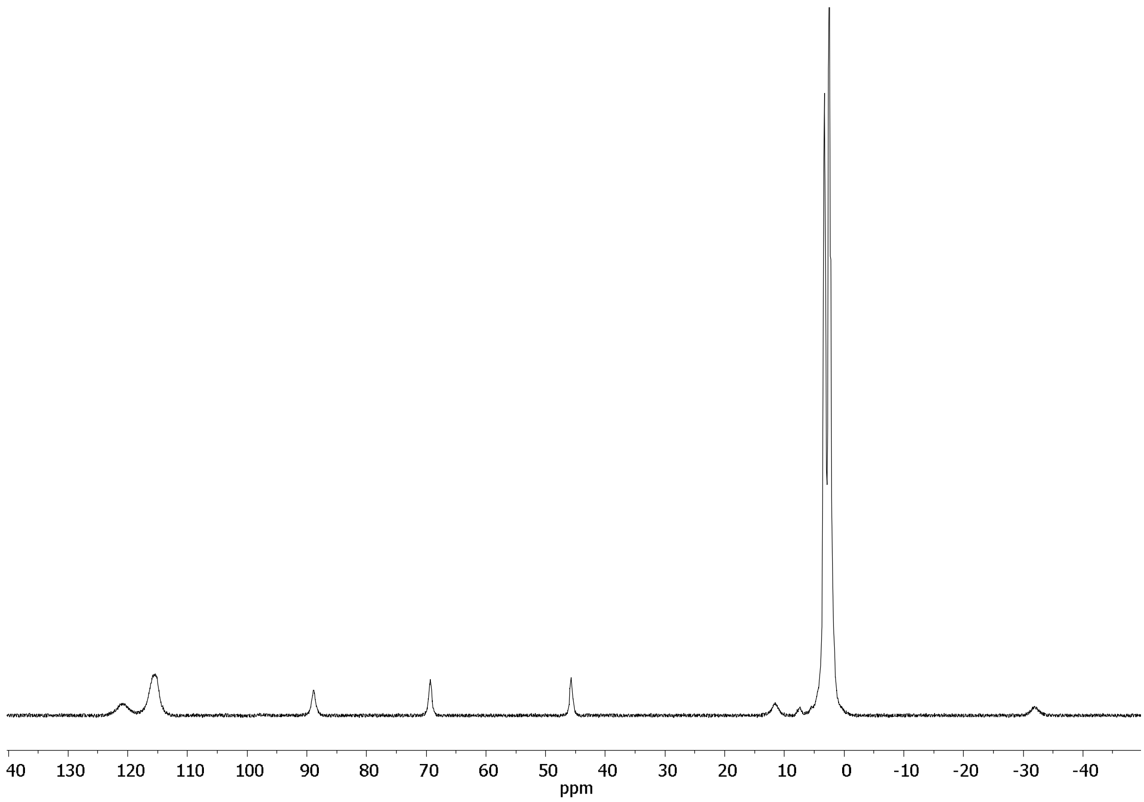


Figure S7. [1]H NMR (500 MHz, DMSO-d_6) spectrum of [Fe(II)(mep(OH)$_2$)]Cl_2 (**7**).

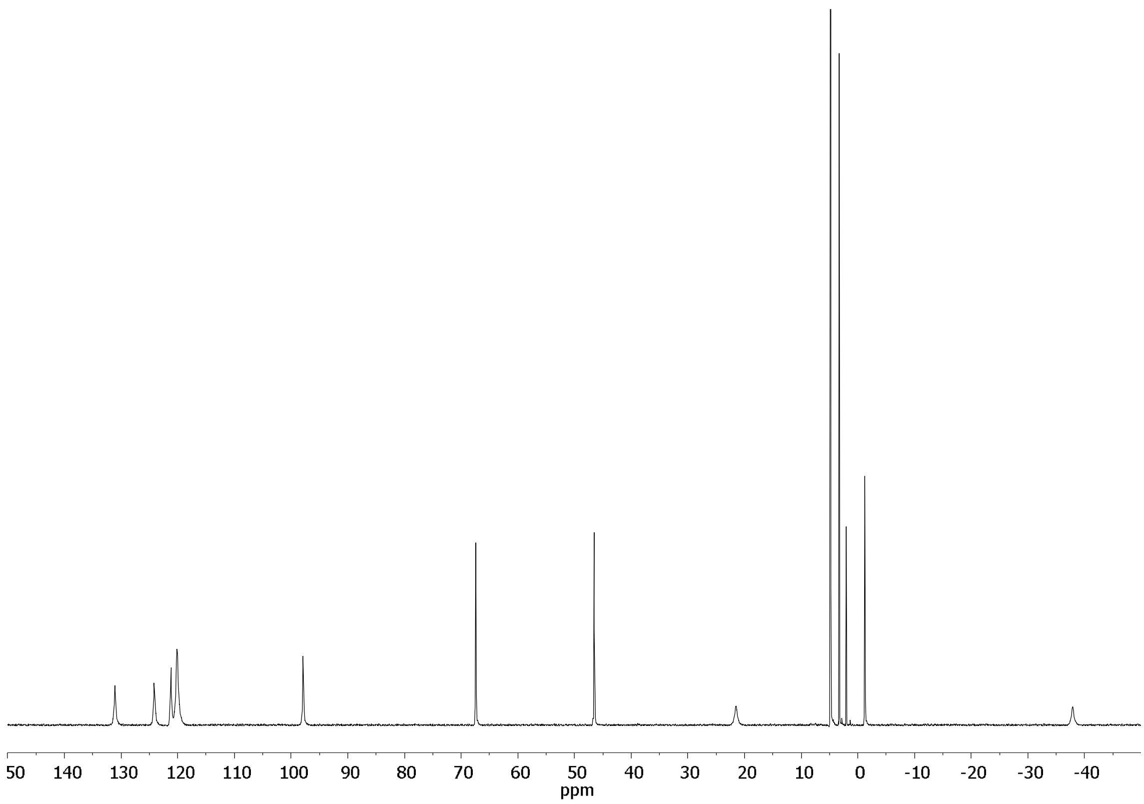


Figure S8. [1]H NMR (500 MHz, CD_3OD) spectrum of [Fe(II)(mep(OH)$_2$)]Cl_2 (**7**).

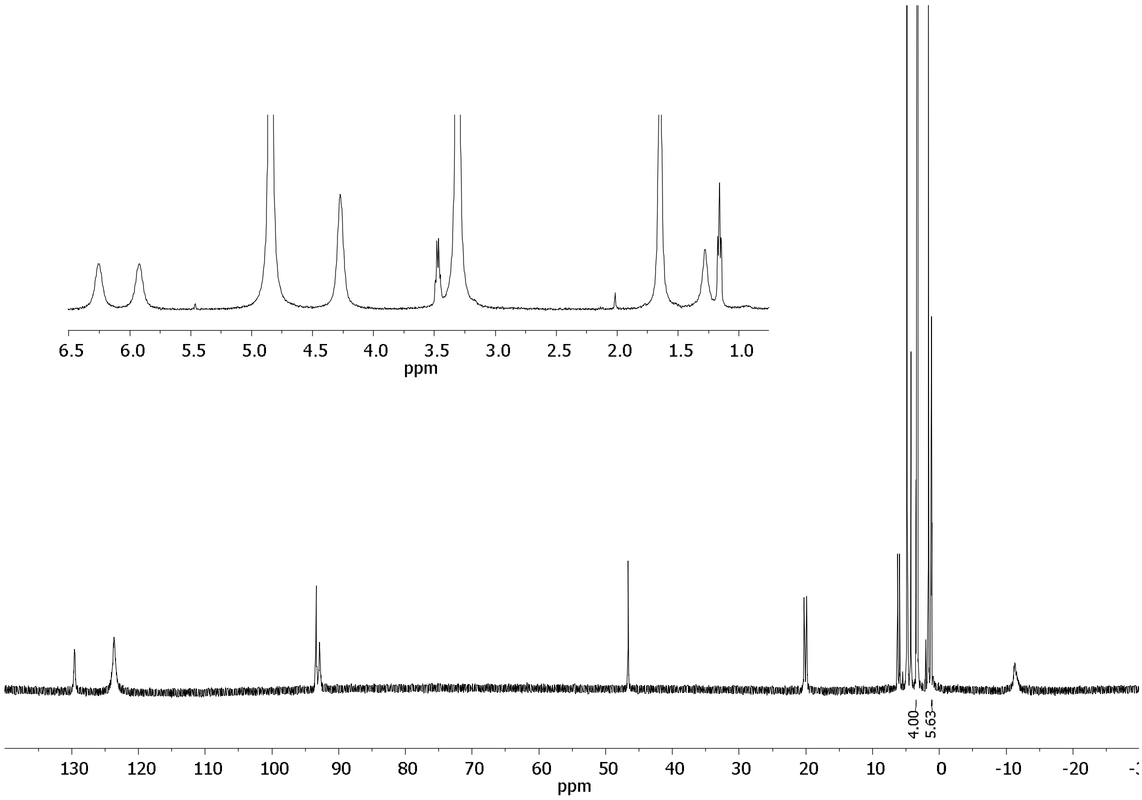


Figure S9. ^{1}H NMR (500 MHz, CD_3OD) spectrum of $[Fe(II)(mep(CONHBu)_2)]Cl_2$ (**8**).

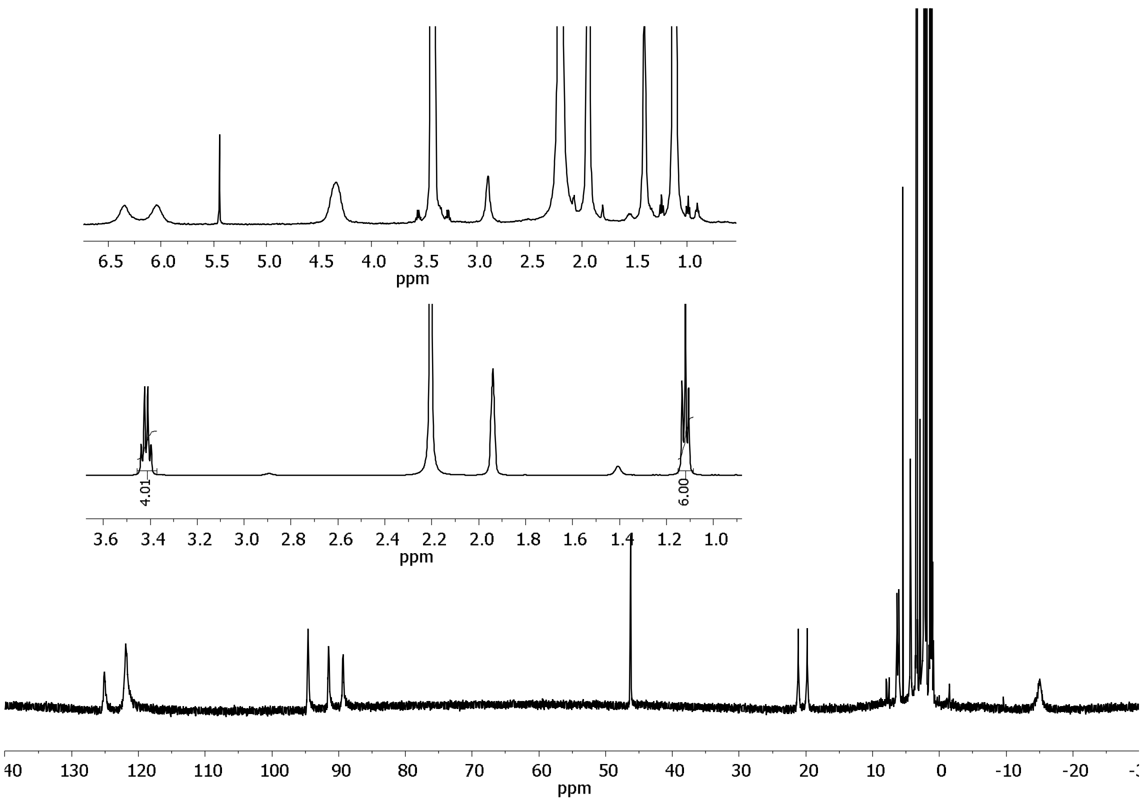


Figure S10. ^{1}H NMR (500 MHz, CD_3CN) spectrum of $[Fe(II)(mep(CONHBu)_2)]Cl_2$ (**8**).

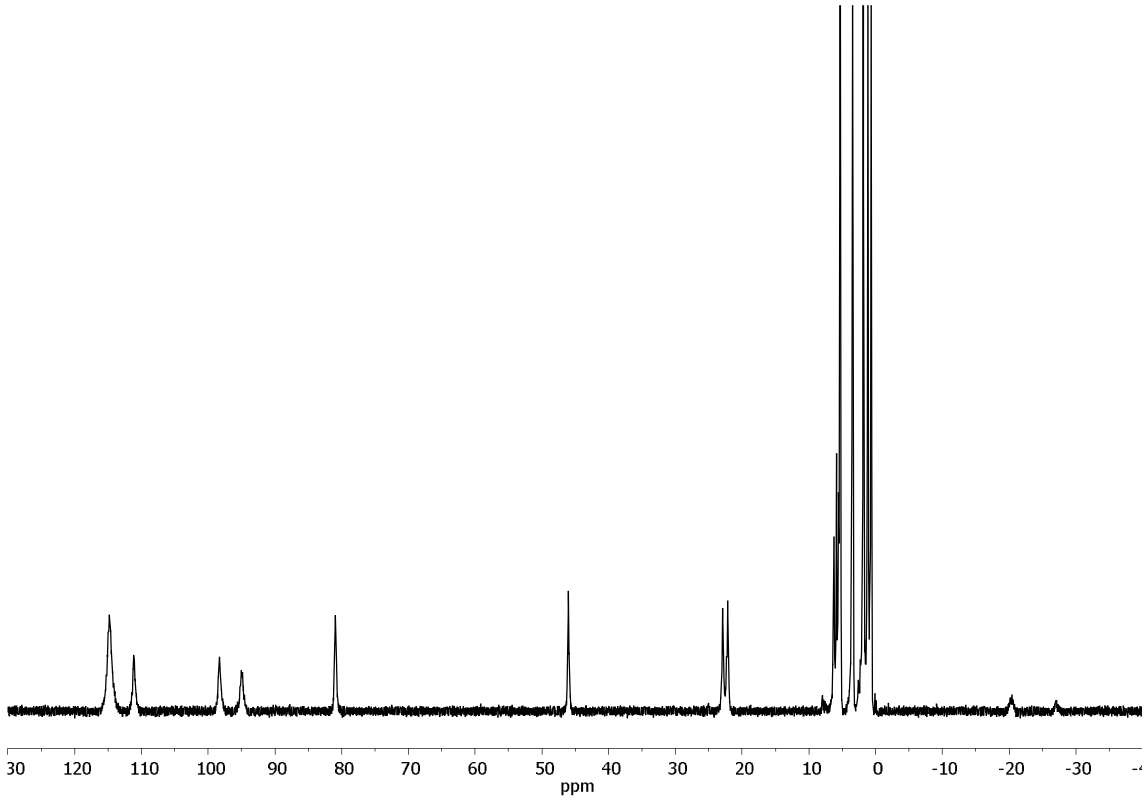


Figure S11. [1]H NMR (500 MHz, CD_2Cl_2) spectrum of [Fe(II)(mep(CONHBu)$_2$)]Cl_2 (**8**).

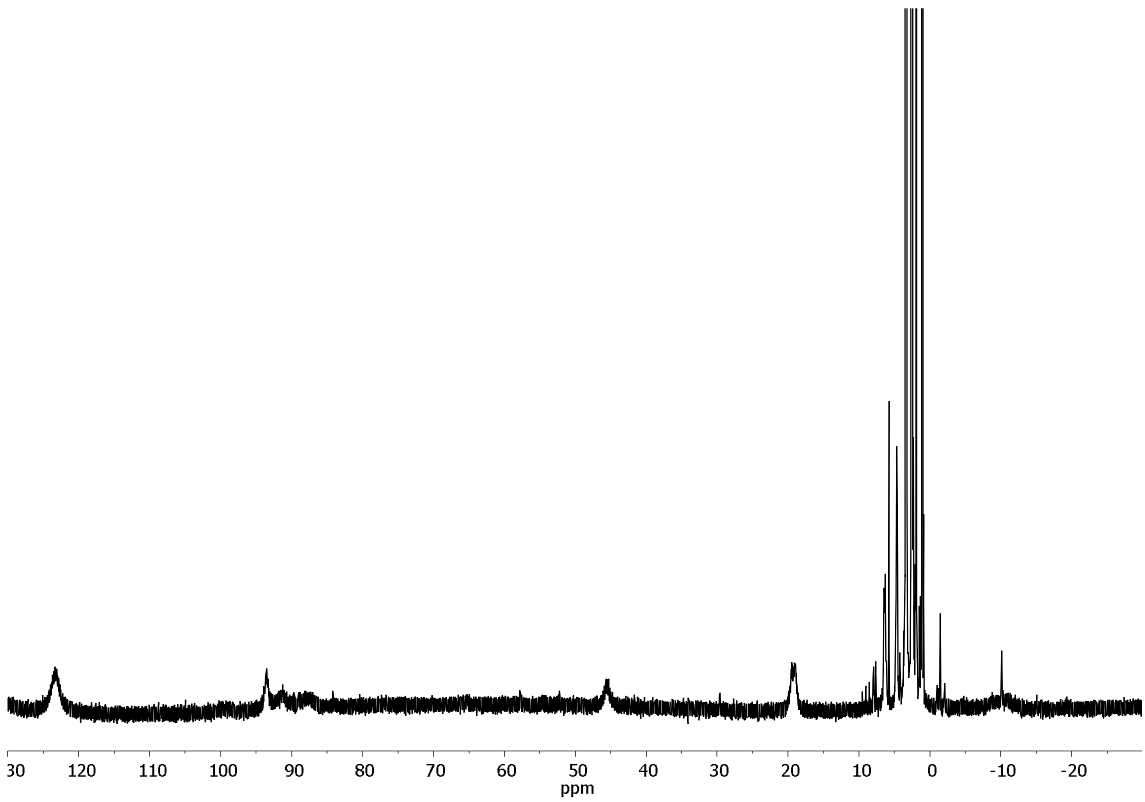


Figure S12. [1]H NMR (500 MHz, DMSO-d_6) spectrum of [Fe(II)(mep(CONHBu)$_2$)]Cl_2 (**8**).

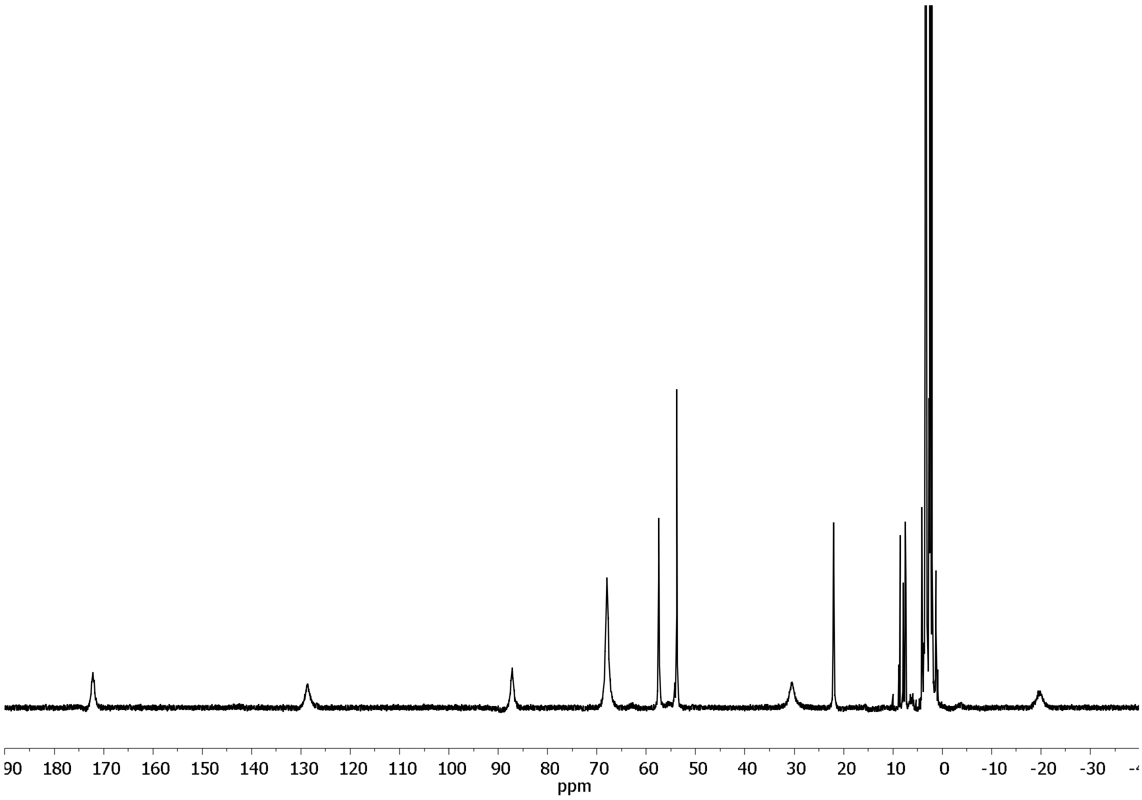


Figure S13. [1]H NMR (500 MHz, DMSO-d_6) spectrum of $[Fe(II)(mep(MeCN)_2)][SbF_6]_2$ (**S9**).

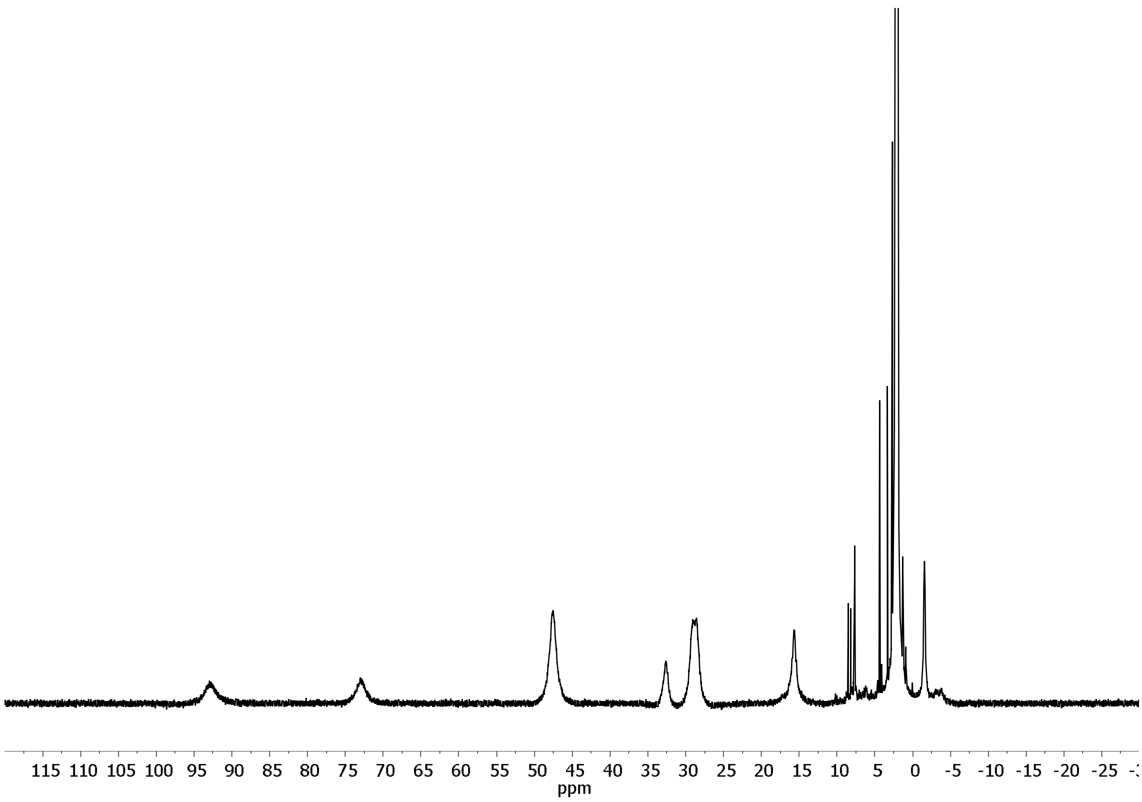


Figure S14. [1]H NMR (500 MHz, CD_3CN) spectrum of $[Fe(II)(mep(MeCN)_2)][SbF_6]_2$ (**S9**).

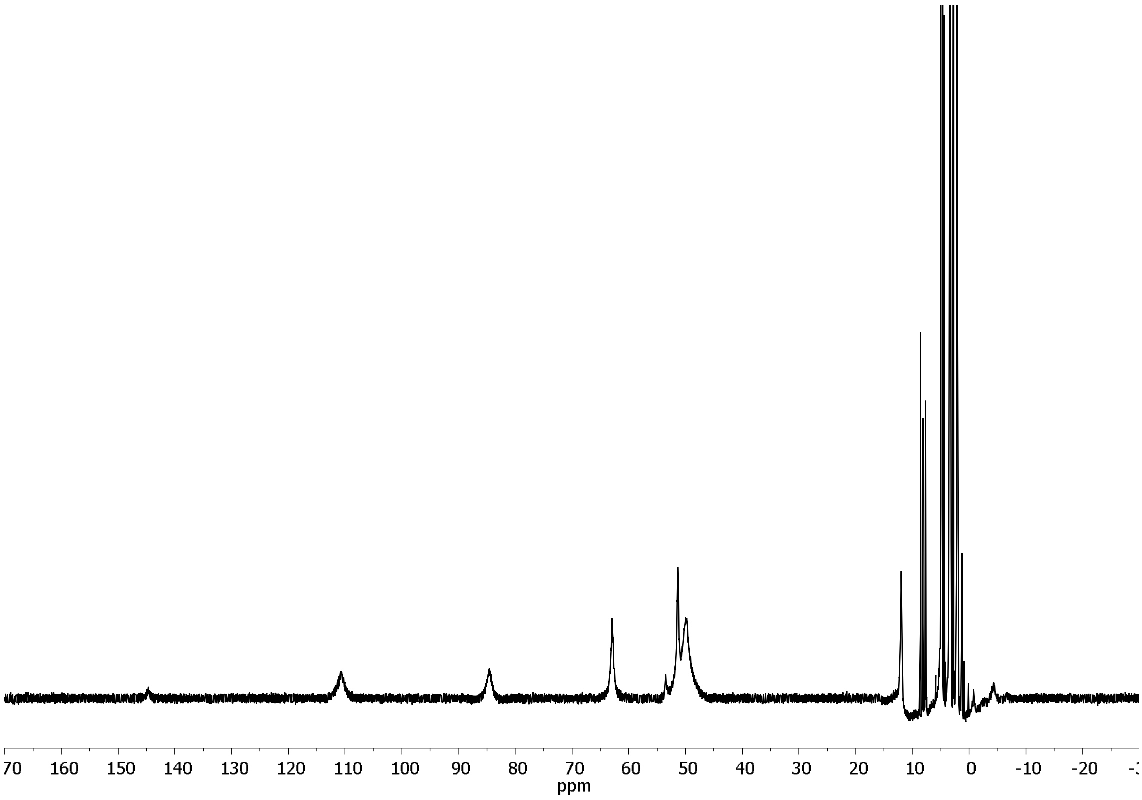


Figure S15. ^{1}H NMR (500 MHz, CD_3OD) spectrum of $[Fe(II)(mep(MeCN)_2)][SbF_6]_2$ (**S9**).

5. Magnetic behaviour of complexes 6-8

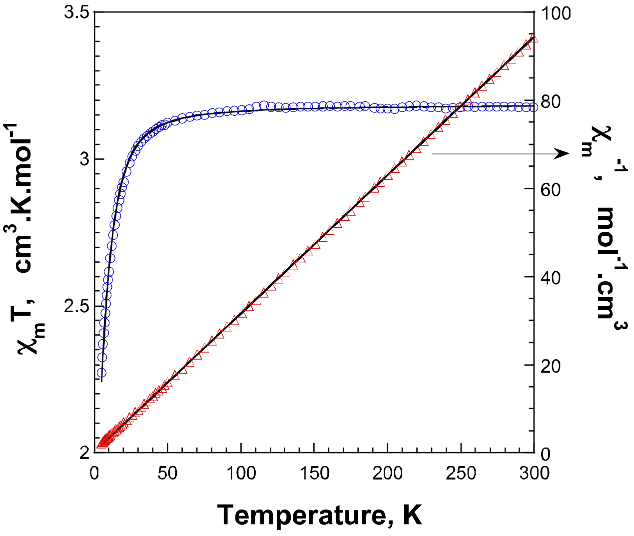


Fig. S16. Magnetic behaviour of compound **6**. The $\chi_m T$ experimental data are plotted along with the best fit obtained with [eq. 1] (solid line) Continuous line on the χ_m^{-1} data corresponds to the Curie-Weiss law.

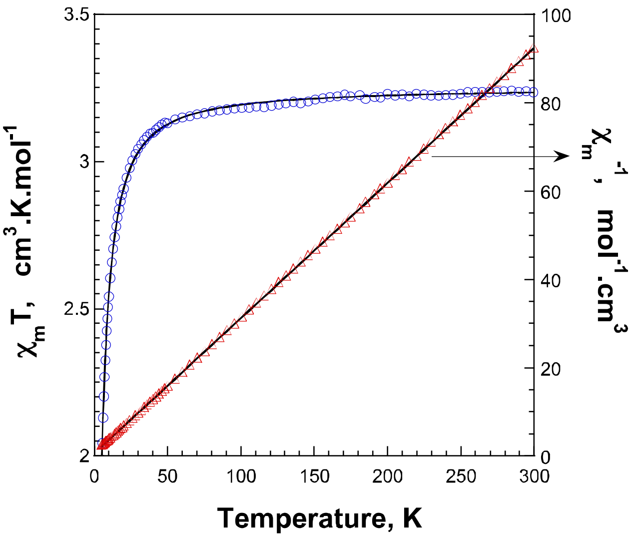


Fig. S17. Magnetic behaviour of compound **7**. The $\chi_m T$ experimental data are plotted along with the best fit obtained with [eq. 1] (solid line) Continuous line on the χ_m^{-1} data corresponds to the Curie-Weiss law.

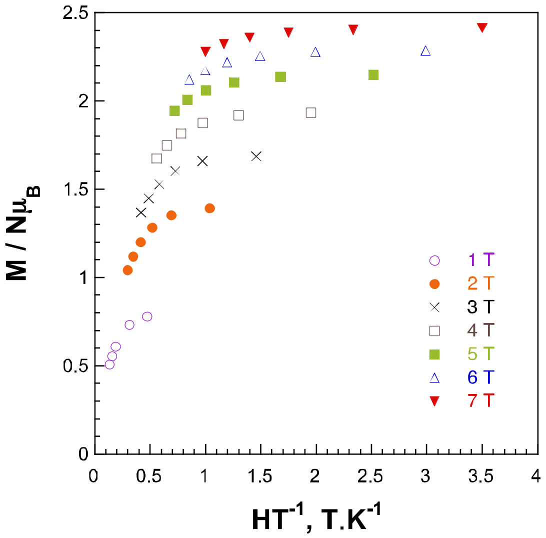


Fig. S18. Low-temperature magnetization data for **8** collected under various applied dc fields.

6. UV-Vis titration spectra of compounds 2-4, 6-8, S10 and S11

Depending on the titration experiment, 2 µL, 5 µL, 10 µL and 20 µL aliquots of a 0.02 M solution of ligand or iron (II) complex were added gradually to solution of triphenylmethane anion in DMSO.

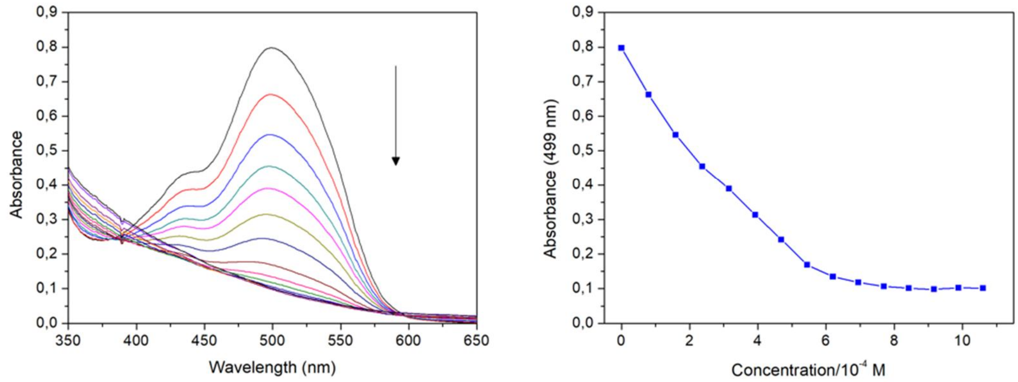


Figure S19. UV-vis titration of mep(OH) (**2**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**2**] M (right).

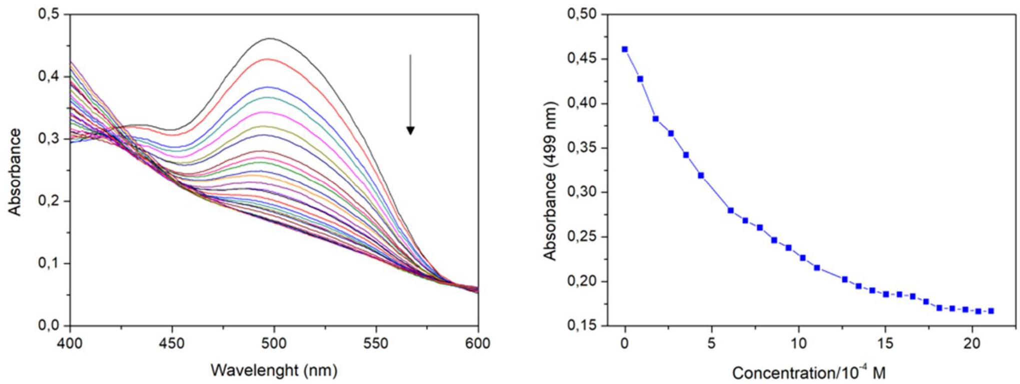


Figure S20. UV-vis titration of mep(OH)$_2$ (**3**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**3**] M (right).

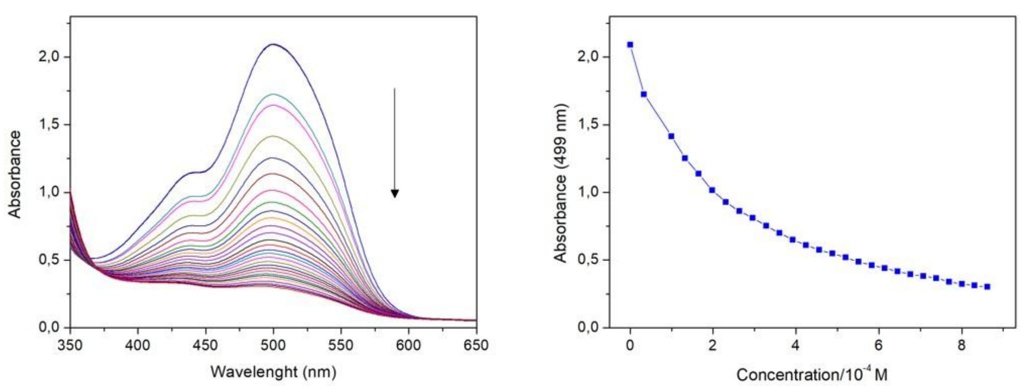


Figure S21. UV-vis titration of mep(CONHBu)$_2$ (**4**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**4**] M (right).

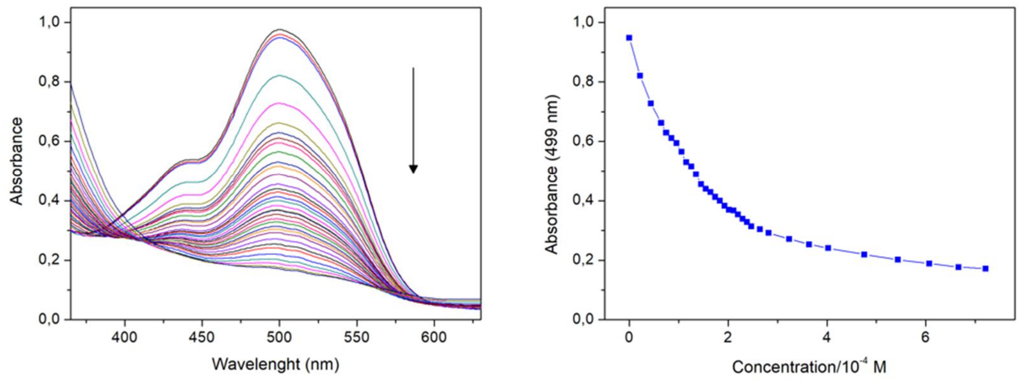


Figure S22. UV-vis titration of [Fe(II)(mepOH)Cl]Cl (**6**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**6**] M (right).

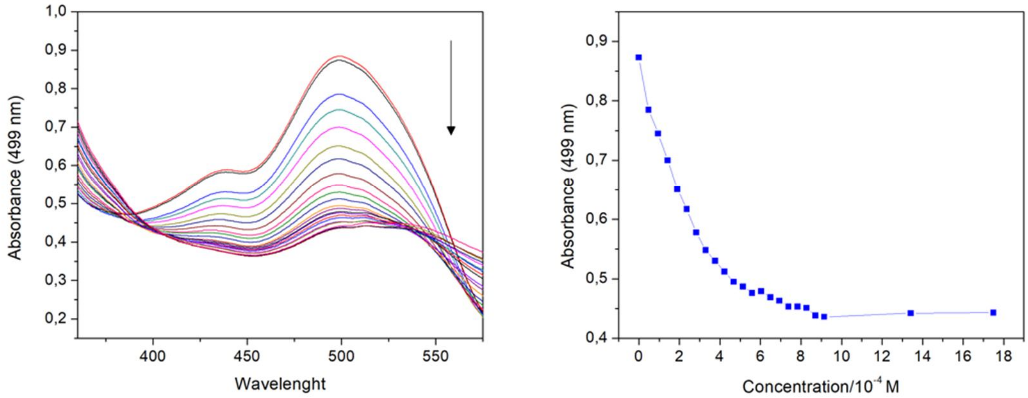


Figure S23. UV-vis titration of [Fe(II)(mep(OH)$_2$)]Cl$_2$ (**7**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**7**] M (right).

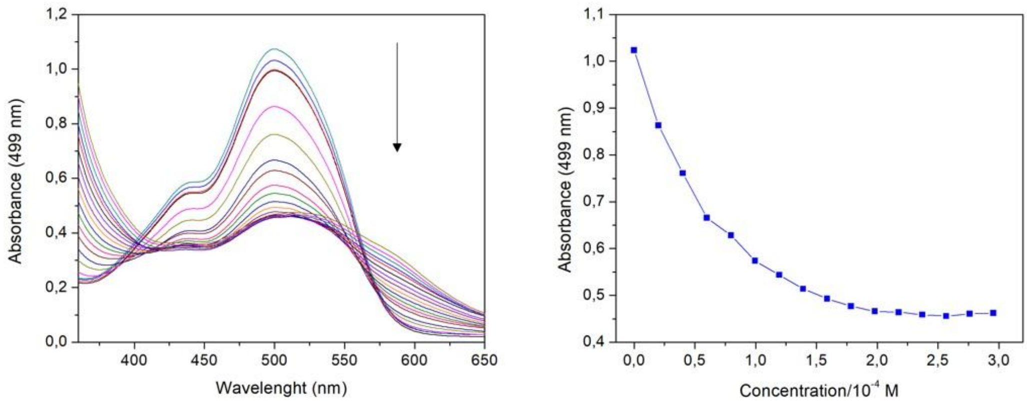


Figure S24. UV-vis titration of [Fe(II)(mep(CONHBu)$_2$)]Cl$_2$ (**8**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**8**] M (right).

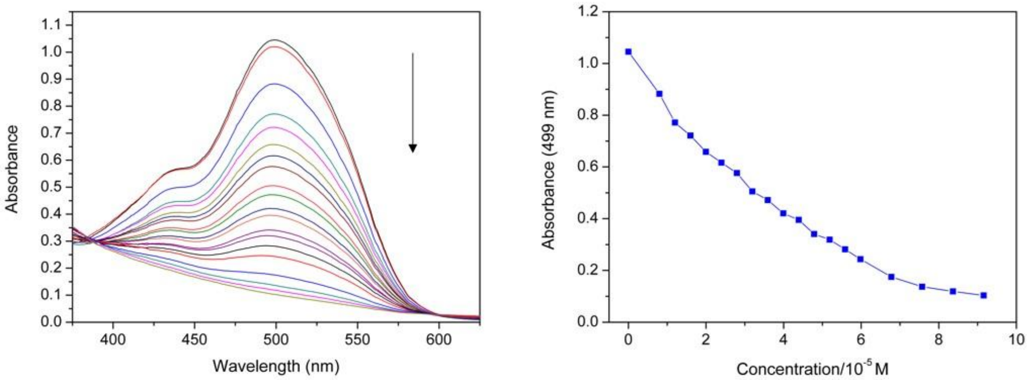


Figure S25. UV-vis titration of [Fe(II)(mep(OH)(MeCN))][SbF_6]$_2$ (**S10**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**S10**] M (right).

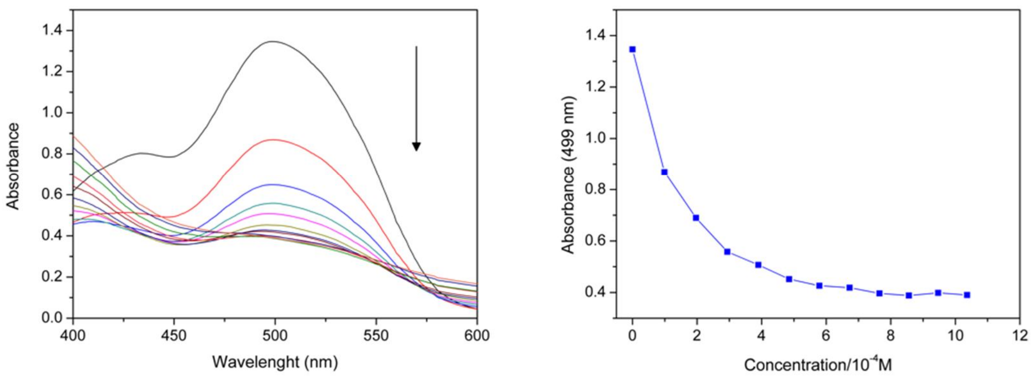


Figure 26. UV-vis titration of [Fe(II)(mep$(OH)_2$)][SbF_6]$_2$ (**S11**) in dry DMSO at 25 °C (left). Absorbance value at 499 nm *vs* [**S11**] M (right).

7. Cyclic and square wave voltammograms

We checked that the *ex situ* deprotonated complexes showed in CV voltammetry the peak indistinguishable to that obtained in the presence *in situ* of an excess of base.

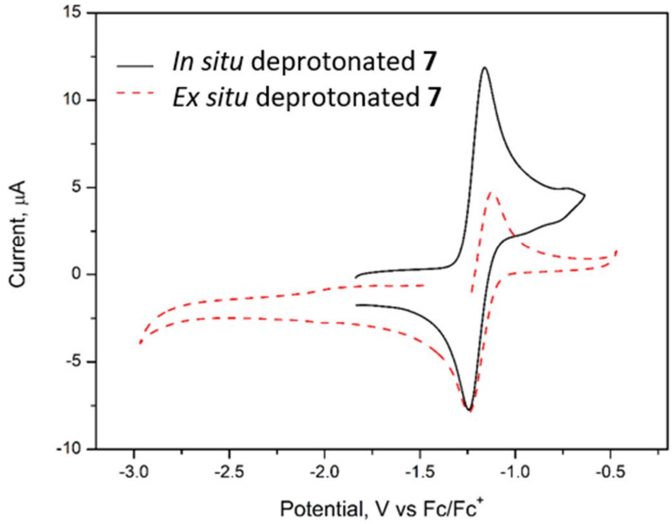


Figure S27. Voltammograms of Fe(II)(mep(OH)$_2$)Cl$_2$ **7** (4 mM) in the presence of an excess base (black line) and previously deprotonated **7** (red line) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

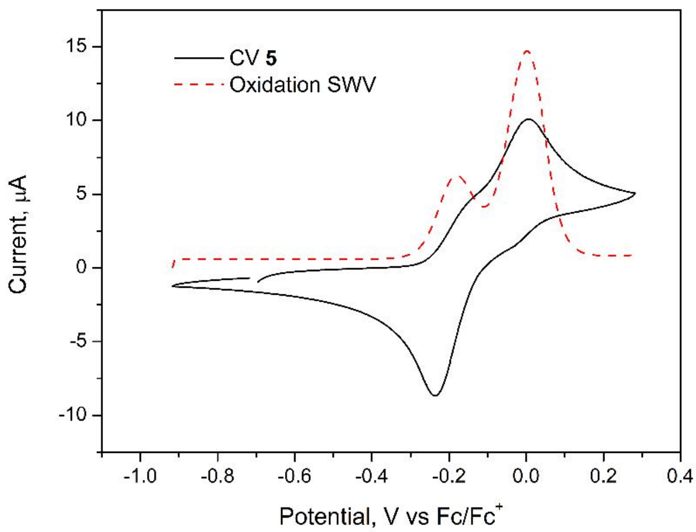


Figure S28. Cyclic and oxidation square wave voltammograms of Fe(II)(mep)Cl$_2$ **5** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

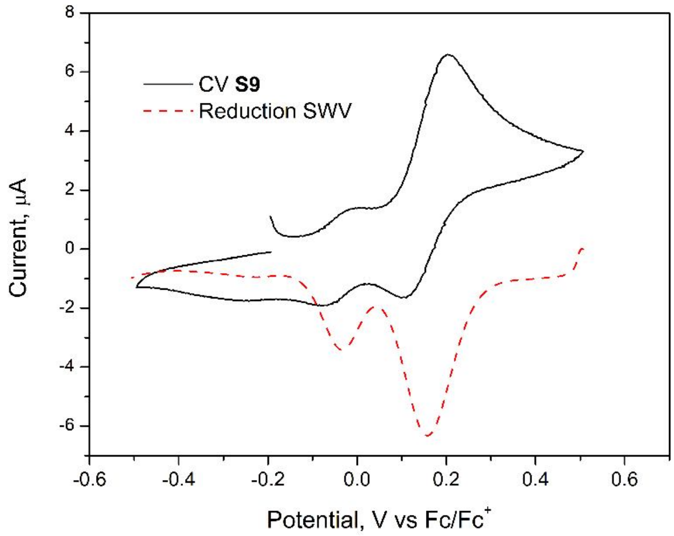


Figure S29. Cyclic and reduction square wave voltammograms of Fe(II)(mep(MeCN)$_2$)][SbF$_6$]$_2$ **S9** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

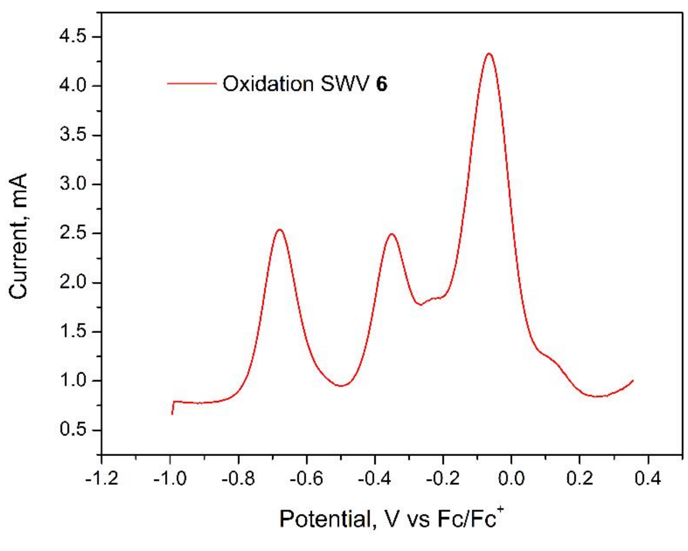


Figure S30. Oxidation square wave voltammogram of [Fe(II)(mep(OH))Cl]Cl **6** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

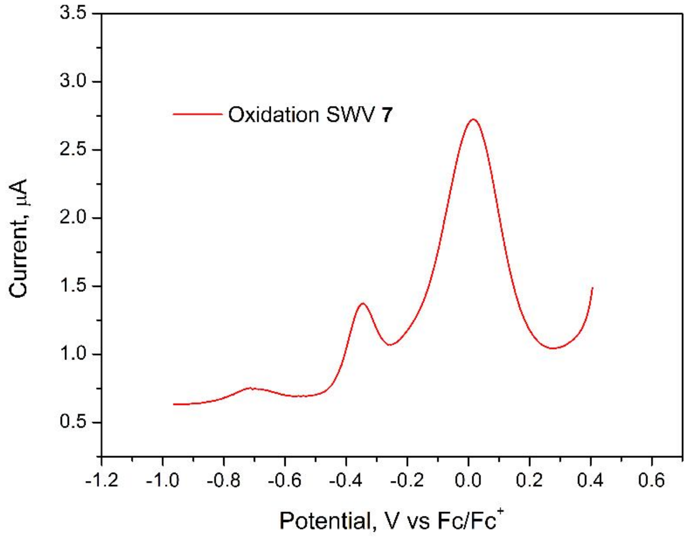


Figure S31. Oxidation square wave voltammogram of [Fe(II)(mep(OH)$_2$)]Cl$_2$ **7** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

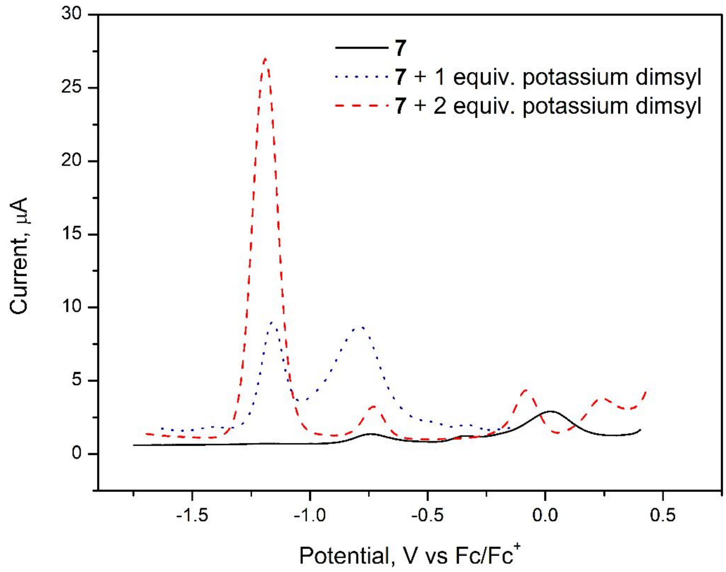


Figure S32. Oxidation square wave voltammogram [Fe(II)(mep(OH)$_2$)]Cl$_2$ **7** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s) in the absence and presence of 1 and 2 equivalent of base.

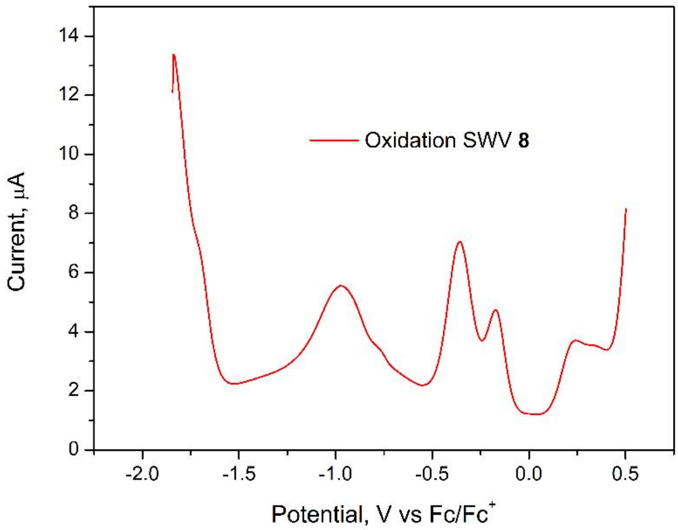


Figure S33. Oxidation square wave voltammogram of [Fe(II)(mep(CONHBu)$_2$)]Cl_2 **8** (4 mM) in dry DMSO (internal standard Fc/Fc$^+$, v = 0.1 V/s).

8. BDFE estimation of O–H and N–H bonds in iron (II) complexes 6-8

The following table summarizes the results obtained from p*k*a and electrochemical measurements and shows BDFE values calculated using the following equation according to Bordwell´s methodology:

$$BDFE_{HO/HN} = 1.37\ pKa_{HO/HN} + 23.06\ E^{o}(O^{-}/N^{-}) + 71.1\ \ kcal\ mol^{-1}$$

Compound	p*K*a	E^0 (V)	BDFE (kcal mol^{-1})
mep(OH), **2**	27.6	-	-
$mep(OH)_2$, **3**	28.3 (1st) 29.4 (2nd)	-	-
$mep(CONHBu)_2$, **4**	22.0	-	-
[Fe(II)(mepOH)Cl]Cl, **6**	26.5	–0.732	90.5
$[Fe(II)(mep(OH)_2)]Cl_2$, **7**	23.8 (1st) 23.8 (2nd)	–0.78 –1.2	85.7 76.0
$[Fe(II)(mep(CONHBu)_2)]Cl_2$, **8**	19.7 (1st) 19.7 (2nd)	- –0.76	- 80.5

9. Single crystal X-ray analysis

Single crystals of mep(OH)$_2$ (**3**) were obtained by slow evaporation of a solution of the compound in a CH_2Cl_2/CH_3OH mixture. To crystallize Fe(II)(mep)Cl$_2$ (**5**), [Fe(II)(mep(OH))Cl]Cl (**6**) and [Fe(II)(mep(OH)$_2$)]Cl$_2$ (**7**), the complexes were dissolved in CH_3CN with a few drops of MeOH. If solids were present the mixtures were filtered o slightly heated to obtain clear solutions. X-ray diffraction quality crystals were grown by slow diffusion of Et_2O into the CH_3CN/CH_3OH solutions of the corresponding complexes. Crystals suitable for single crystal X-ray diffraction of [Fe(II)(mep(CONHBu)$_2$)]Cl$_2$ (**8**) and [Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$ (**S7**) were obtained by slow diffusion of Et_2O into a solution of the complex in DMF or CH_3CN, respectively. Single crystals of [Fe(III)(mep)Cl$_2$]PF$_6$ (**S8**) were obtained by diffusion of Et_2O into a solution of the compound in CH_3CN.

In general, C–H hydrogen atoms were placed in idealized positions (U_{eg}(H) = 1.2U_{eg}(C) or U_{eg}(H) = 1.5U_{eg}(C)) and were allowed to ride on their parent atoms, except the H atoms of some CH_2 groups in the ethylene moieties, which were refined. O–H and N–H hydrogen atoms were located during the refinement (Q-peaks with values between 0.63 and 0.82) and subsequently refined. A DFIX restraint had to be used to model the N–H distance in one of the amide groups of ([Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$). A summary of the X-ray diffraction measurement and refinement data is given in Tables S1-S3. The data for (Fe(II)(mep)Cl$_2$)[S6] and ([Fe(III)(mep)Cl$_2$)]PF$_6$)[S7] are in agreement with those previously reported. CCDC-1880897 (mep(OH)$_2$), CCDC-1880892 (Fe(II)(mep)Cl$_2$), CCDC-1880896 ([Fe(II)(mep(OH))Cl]Cl), CCDC-1880895 ([Fe(II)(mep(OH)$_2$)]Cl$_2$), CCDC-1880893 ([Fe(II)(mep(CONHBu)$_2$)]Cl$_2$), CCDC-1880894 ([Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$) and CCDC-1880891 ([Fe(III)(mep)Cl$_2$)]PF$_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/?

Table S1. Summary of X-ray diffraction crystallography measurement and refinement data for [Fe(II)(mep(OH))Cl]Cl (**6**) and [Fe(II)(mep(OH)$_2$)]Cl$_2$ (**7**)[a]

	[Fe(II)(mep(OH))Cl]Cl·CH_3CN (**6**·CH_3CN)	[Fe(II)(mep(OH)$_2$)]Cl$_2$ (**7**)
Chemical formula	$C_{19}H_{27}Cl_2FeN_5O$	$C_{18}H_{26}Cl_2FeN_4O_2$
M_r	468.20	457.18
Crystal size [mm^3]	0.429 x 0.341 x 0.102	0.537 x 0.409 x 0.266
Crystal system	Monoclinic	Monoclinic
Space group	*P*21/*n*	*C*2/*c*
a [Å]	10.5537(6)	10.0933(6)
b [Å]	11.6440(6)	11.4226(7)
c [Å]	17.9699(10)	17.1223(10)
α [°]	90	90
β [°]	100.349(2)	95.803(2)
γ [°]	90	90
V [Å^3]	2172.3(2)	1963.9(2)
Z	4	4
ρ_{calcd} [Mg m^{-3}]	1.432	1.546
μ [mm^{-1}]	0.960	1.062
F(000)	976	952
θ range [°]	2.447 to 28.831	2.701 to 30.544
hkl ranges	-13/14,-13/15,-24/24	-14/13,-16/16,-24/23
Reflections collected	40442	39656
Independent reflections	5640	3005
R_{int}	0.0815	0.0384
Completeness [%]	99.9	99.8
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0637 wR_2 = 0.1548	R_1 = 0.0220 wR_2 = 0.0560
R indices (all data)	R_1 = 0.0789 wR_2 = 0.1688	R_1 = 0.0231 wR_2 = 0.0566
Goodness-of-fit on F^2	1.075	1.080

[a]In common: Wavelength: 0.71073 Å. Temperature, 100 K. Refinement method, full-matrix least-squares on F^2. Absoption correction: Numerical.

Table S2. Summary of X-ray diffraction crystallography measurement and refinement data for ([Fe(II)(mep(CONHBu)$_2$)]Cl$_2$) (**8**) and ([Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$) (**S7**)[a]

	[Fe(II)(mep(CONHBu)$_2$)]Cl$_2$·H$_2$O (**8**·H$_2$O)	[Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$ (**S7**)
Chemical formula	$C_{26}H_{42}Cl_2FeN_6O_3$	$C_{26}H_{40}F_{12}FeN_6O_2P_2$
M_r	613.40	814.43
Crystal size [mm^3]	0.07 x 0.07 x 0.07	0.320 x 0.160 x 0.030
Wavelength [Å]	1.54178	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*P*21/*n*	*P*-1
a [Å]	12.2396(6)	10.9740(19)
b [Å]	10.7040(5)	12.663(2)
c [Å]	22.9106(11)	13.902(3)
α [°]	90	107.517(2)
β [°]	97.493(2)	108.430(2)
γ [°]	90	96.563(2)
V [Å^3]	2975.9(2)	1700.3(5)
Z	4	2
ρ_{calcd} [Mg m^{-3}]	1.369	1.591
μ [mm^{-1}]	6.021	0.639
F(000)	1296	836
θ range [°]	3.892 to 65.194	1.653 to 26.278
hkl ranges	-14/14,-12/12,-26/26	-13/13,-15/15,-17/17
Reflections collected	23853	17141
Independent reflections	5075	6772
R_{int}	0.0273	0.0370
Completeness [%]	99.7	99.3
Final *R* indices [I>2σ(I)]	R_1 = 0.0260 wR_2 = 0.0639	R_1 = 0.0495 wR_2 = 0.1251
R indices (all data)	R_1 = 0.0286 wR_2 = 0.0657	R_1 = 0.0608 wR_2 = 0.1362
Goodness-of-fit on F^2	0.954	1.040

[a]In common: Temperature, 100 K. Refinement method, full-matrix least-squares on F^2. Absorption correction: Multi-scan.

Table S3. Summary of X-ray diffraction crystallography measurement and refinement data for mep(OH)$_2$ (**3**), Fe(II)(mep)Cl$_2$ (**5**) and [Fe(III)(mep)Cl$_2$]PF$_6$ (**S8**)[a]

	mep(OH)$_2$ (**3**)	Fe(II)(mep)Cl$_2$ (**5**)	[Fe(III)(mep)Cl$_2$]PF$_6$ (**S8**)
Chemical formula	$C_{18}H_{26}N_4O_2$	$C_{16}H_{22}Cl_2FeN_4$	$C_{16}H_{22}Cl_2F_6FeN_4P$
M_r	330.43	397.12	542.09
Crystal size [mm^3]	0.389 x 0.267 x 0.128	0.453 x 0.218 x 0.100	0.600 x 0.422 x 0.398
Wavelength [Å]	1.54178	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*21/*c*	*Pbcn*	*P*21/*c*
a [Å]	8.5565(3)	14.1995(7)	9.2912(6)
b [Å]	11.9424(5)	8.0887(5)	17.6962(12)
c [Å]	8.8195(4)	15.0900(8)	12.8115(9)
α [°]	90	90	90
β [°]	105.2960(10)	90	97.226(2)
γ [°]	90	90	90
V [Å^3]	869.30(6)	1733.17(16)	2089.7(2)
Z	2	4	4
ρ_{calcd} [Mg m^{-3}]	1.262	1.522	1.723
μ [mm^{-1}]	0.675	1.182	1.118
F(000)	356	824	1100
θ range [°]	5.359 to 72.490	2.700 to 40.380	2.210 to 28.405
hkl ranges	-10/10,-14/14, -9/10	-25/25,-14/9,-27/27	-12/12,-23/23,-17/16
Reflections collected	11133	30851	44448
Independent reflections	1710	5484	5220
R_{int}	0.0344	0.0314	0.0268
Completeness [%]	99.5	100.0	99.9
Final *R* indices [I>2σ(I)]	R_1 = 0.0354 wR_2 = 0.0858	R_1 = 0.0289 wR_2 = 0.0642	R_1 = 0.0390 wR_2 = 0.1028
R indices (all data)	R_1 = 0.0368 wR_2 = 0.0872	R_1 = 0.0433 wR_2 = 0.0694	R_1 = 0.0412 wR_2 = 0.1044
Goodness-of-fit on F^2	1.055	1.049	1.128

[a]In common: Temperature, 100 K. Refinement method, full-matrix least-squares on F^2. Absoption correction: Numerical

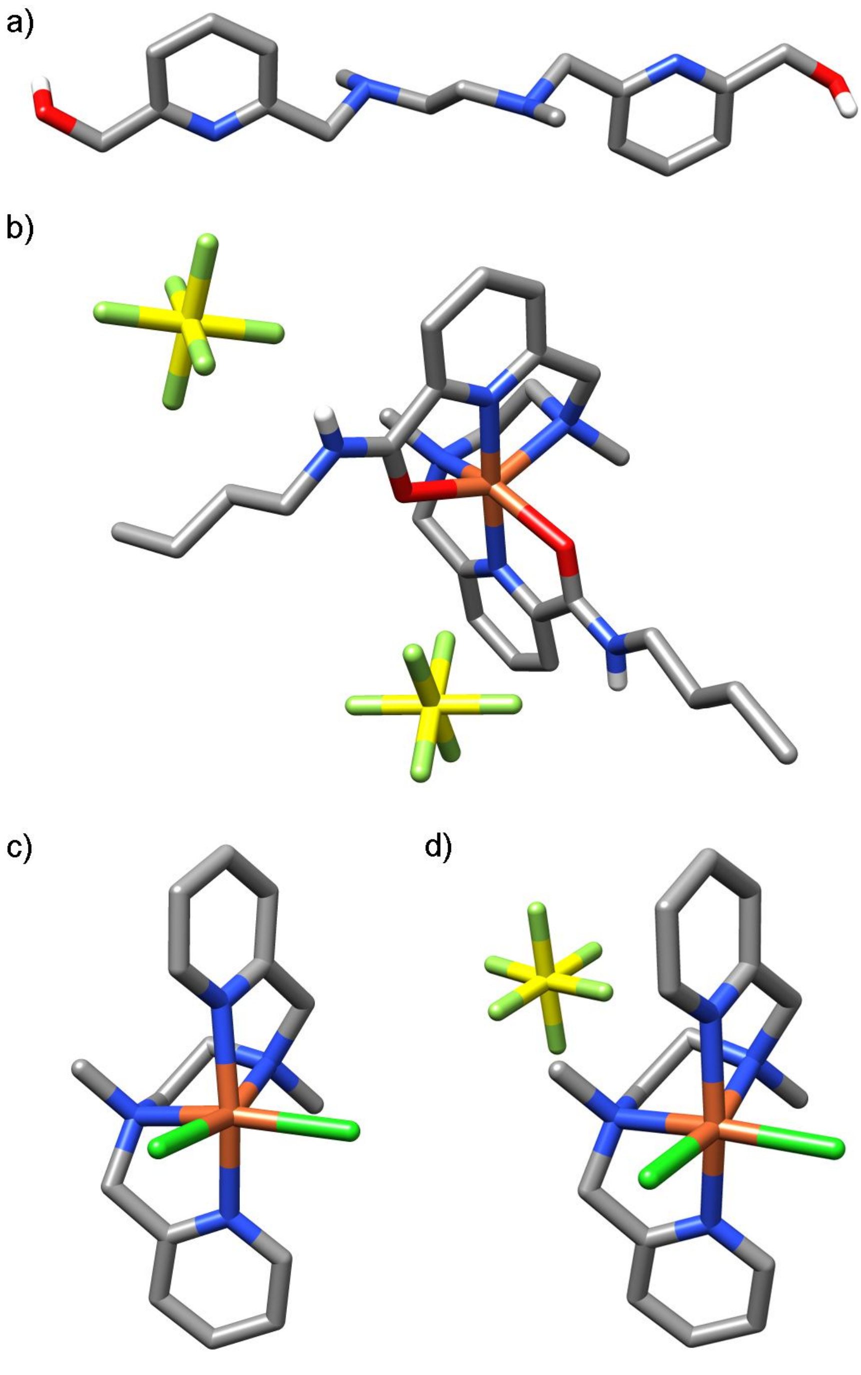
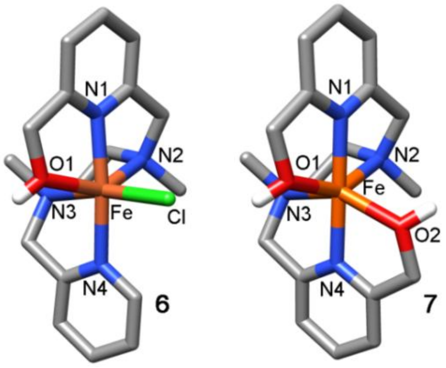


Figure S32. Single crystal X-ray diffraction structure of: a) mep(OH)$_2$ (**3**), b) Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$ (**S7**), c) Fe(II)(mep)Cl$_2$ (**5**), d) [Fe(III)(mep)Cl$_2$)]PF$_6$ (**S8**). Color code: C: gray, O: red, N: blue, H: white, Fe: orange, Cl: green, P: yellow, F: light green. C–H hydrogen atoms have been omitted for clarity.

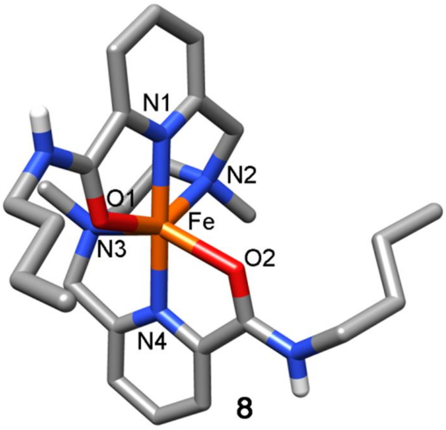
Table S4. Selected bond lengths and angles for [Fe(II)(mep(OH))Cl]Cl (**6**) and [Fe(II)(mep(OH)$_2$)]Cl$_2$ (**7**)[a]



	[Fe(II)(mep(OH))Cl]Cl·CH_3CN (**6**·CH_3CN)	[Fe(II)(mep(OH)$_2$)]Cl_2 (**7**)
Distance Fe–N1 [Å]	2.118(3)	2.1051(8)
Distance Fe–N2 [Å]	2.269(3)	2.2573(8)
Distance Fe–N3 [Å]	2.271(3)	2.2573(8)
Distance Fe–N4 [Å]	2.185(3)	2.1051(8)
Distance Fe–O1 [Å]	2.197(2)	2.1490(7)
Distance Fe–O2 [Å]	-	2.1490(7)
Distance Fe–Cl [Å]	2.3669(8)	-
Angle N1–Fe–N2 [º]	75.71(10)	76.24(3)
Angle N1–Fe–N3 [º]	96.92(10)	102.18(3)
Angle N1–Fe–N4 [º]	172.02(10)	177.98(4)
Angle N1–Fe–O1 [º]	74.23(9)	74.38(3)
Angle N1–Fe–O2 [º]	-	106.99(3)
Angle N1–Fe–Cl [º]	93.20(7)	-
Angle N2–Fe–N3 [º]	80.14(10)	80.11(4)
Angle N2–Fe–N4 [º]	101.16(10)	102.18(3)
Angle N2–Fe–O1 [º]	146.62(10)	149.36(3)
Angle N2–Fe–O2 [º]	-	97.75(3)
Angle N2–Fe–Cl [º]	98.56(7)	-
Angle N3–Fe–N4 [º]	75.23(10)	76.24(3)
Angle N3–Fe–O1 [º]	89.35(9)	97.75(3)
Angle N3–Fe–O2 [º]	-	149.36(3)
Angle N3–Fe–Cl [º]	169.11(7)	-
Angle N4–Fe–O1 [º]	106.66(9)	106.99(3)
Angle N4–Fe–O2 [º]	-	74.38(3)
Angle N4–Fe–Cl [º]	94.54(8)	-
Angle O1–Fe–O2 [º]	-	98.89(4)
Angle O1–Fe–Cl [º]	97.29(7)	-

[a]For the ease of comparison between structures, the labeling in **7** does not correspond to that in the cif file due to the higher symmetry of **7** compared to **6**.

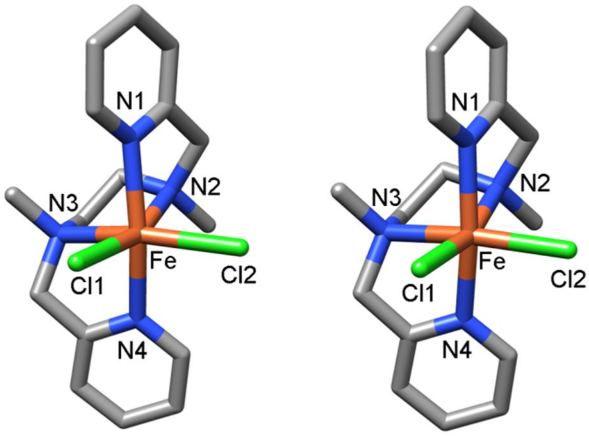
Table S5. Selected bond lengths and angles for ([Fe(II)(mep(CONHBu)$_2$)]Cl$_2$) (**8**) and [Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$ (**S7**)



8

	[Fe(II)(mep(CONHBu)$_2$)]Cl$_2$·H$_2$O (**8**·H$_2$O)	[Fe(II)(mep(CONHBu)$_2$)](PF$_6$)$_2$ (**S7**)
Distance Fe–N1 [Å]	2.1250(13)	2.100(2)
Distance Fe–N2 [Å]	2.2807(13)	2.265(2)
Distance Fe–N3 [Å]	2.2480(13)	2.262(2)
Distance Fe–N4 [Å]	2.1234(13)	2.104(2)
Distance Fe–O1 [Å]	2.1323(11)	2.1685(19)
Distance Fe–O2 [Å]	2.1334(11)	2.1126(19)
Angle N1–Fe–N2 [º]	73.78(5)	75.53(9)
Angle N1–Fe–N3 [º]	102.34(5)	102.49(9)
Angle N1–Fe–N4 [º]	175.02(5)	177.39(9)
Angle N1–Fe–O1 [º]	74.59(4)	74.85(8)
Angle N1–Fe–O2 [º]	107.72(5)	107.56(8)
Angle N2–Fe–N3 [º]	80.83(5)	80.99(8)
Angle N2–Fe–N4 [º]	101.59(5)	105.07(9)
Angle N2–Fe–O1 [º]	147.24(4)	147.19(8)
Angle N2–Fe–O2 [º]	96.76(5)	95.53(8)
Angle N3–Fe–N4 [º]	74.81(5)	75.17(9)
Angle N3–Fe–O1 [º]	97.85(5)	91.93(8)
Angle N3–Fe–O2 [º]	147.89(5)	147.85(8)
Angle N4–Fe–O1 [º]	109.68(5)	103.92(8)
Angle N4–Fe–O2 [º]	74.37(4)	74.97(8)
Angle O1–Fe–O2 [º]	100.73(4)	106.58(8)

Table S6. Selected bond lengths and angles for Fe(II)(mep)Cl_2 (**5**) and [Fe(III)(mep)Cl_2]PF_6 (**S8**)[a]



5 Fe(III)(mep)Cl_2

	Fe(II)(mep)Cl_2 (**5**)	[Fe(III)(mep)Cl_2]PF_6 (**S8**)
Distance Fe–N1 [Å]	2.2015(6)	2.1619(18)
Distance Fe–N2 [Å]	2.2819(6)	2.2187(18)
Distance Fe–N3 [Å]	2.2819(6)	2.2337(19)
Distance Fe–N4 [Å]	2.2015(6)	2.1528(19)
Distance Fe–Cl1 [Å]	2.4241(2)	2.2691(6)
Distance Fe–Cl2 [Å]	2.4241(2)	2.2656(6)
Angle N1–Fe–N2 [º]	74.54(2)	75.12(7)
Angle N1–Fe–N3 [º]	92.84(2)	93.63(7)
Angle N1–Fe–N4 [º]	163.91(3)	166.19(7)
Angle N1–Fe–Cl1 [º]	92.930(17)	93.61(5)
Angle N1–Fe–Cl2 [º]	97.274(18)	95.04(5)
Angle N2–Fe–N3 [º]	78.37(4)	79.67(7)
Angle N2–Fe–N4 [º]	92.84(2)	94.33(7)
Angle N2–Fe–Cl1 [º]	163.284(17)	164.62(5)
Angle N2–Fe–Cl2 [º]	91.508(18)	91.41(5)
Angle N3–Fe–N4 [º]	74.54(2)	75.45(7)
Angle N3–Fe–Cl1 [º]	91.509(18)	90.85(5)
Angle N3–Fe–Cl2 [º]	163.284(17)	165.54(5)
Angle N4–Fe–Cl1 [º]	97.274(18)	94.96(5)
Angle N4–Fe–Cl2 [º]	92.930(17)	94.09(6)
Angle Cl1–Fe–Cl2 [º]	101.191(12)	100.11(2)

[a]For the ease of comparison between structures, the labeling in **5** does not correspond to that in the cif file due to the higher symmetry of **5** compared to [Fe(III)(mep)Cl_2]PF_6 (**S8**).

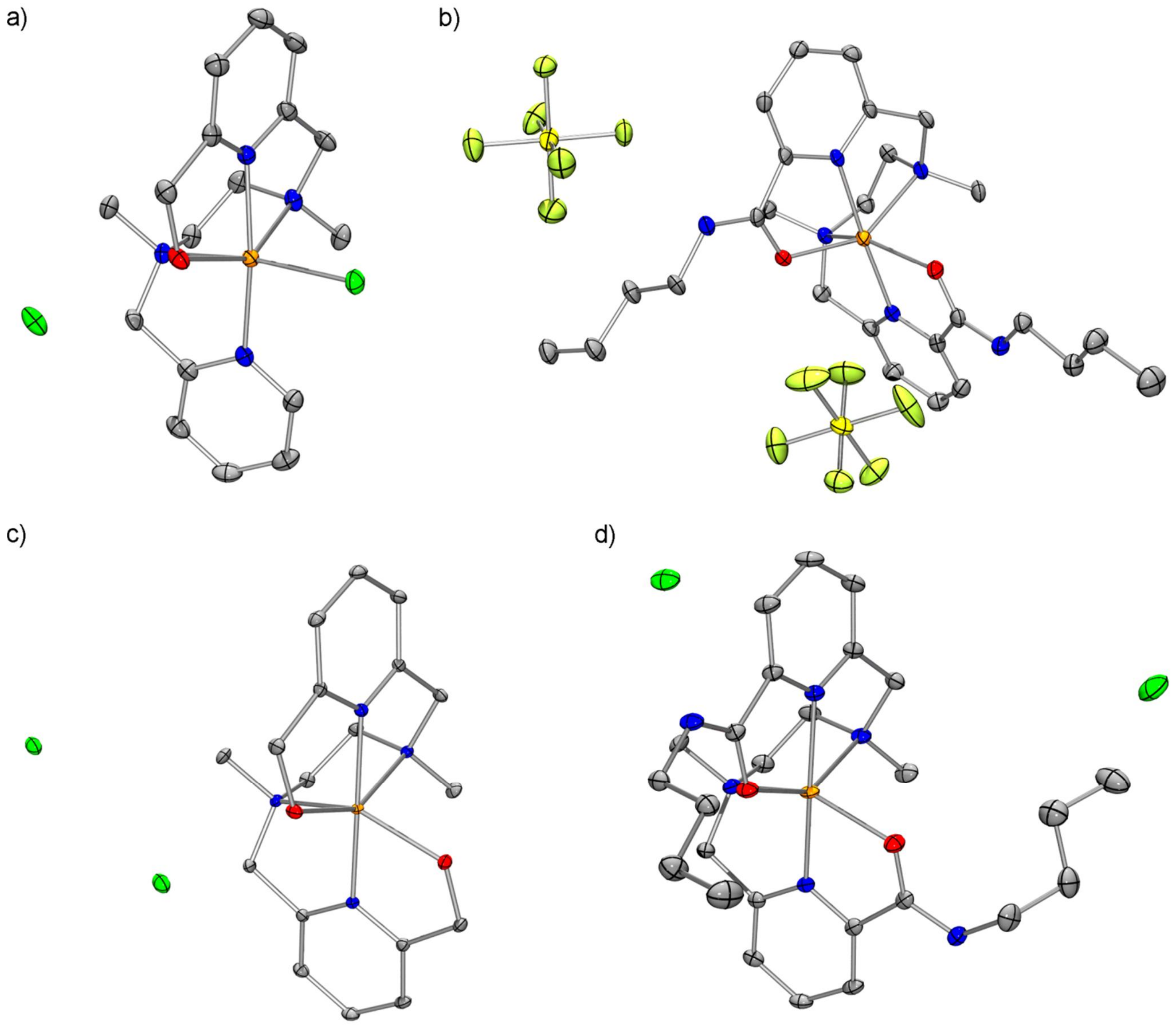


Figure S33. ORTEP representation of the crystal structure of: a) [Fe(II)(mep(OH))Cl]Cl (**6**), b) [Fe(II)(mep(CONHBu)$_2$)]PF$_6$ (**S7**), c) [Fe(II)(mep(OH)$_2$)]Cl$_2$ (**3**), d) [Fe(II)(mep(CONHBu)$_2$)]Cl$_2$ (**8**). Color code: C: gray, O: red, N: blue, Fe: orange, Cl: green, P: yellow, F: light green. Thermal displacement ellipsoids are shown at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity**.**

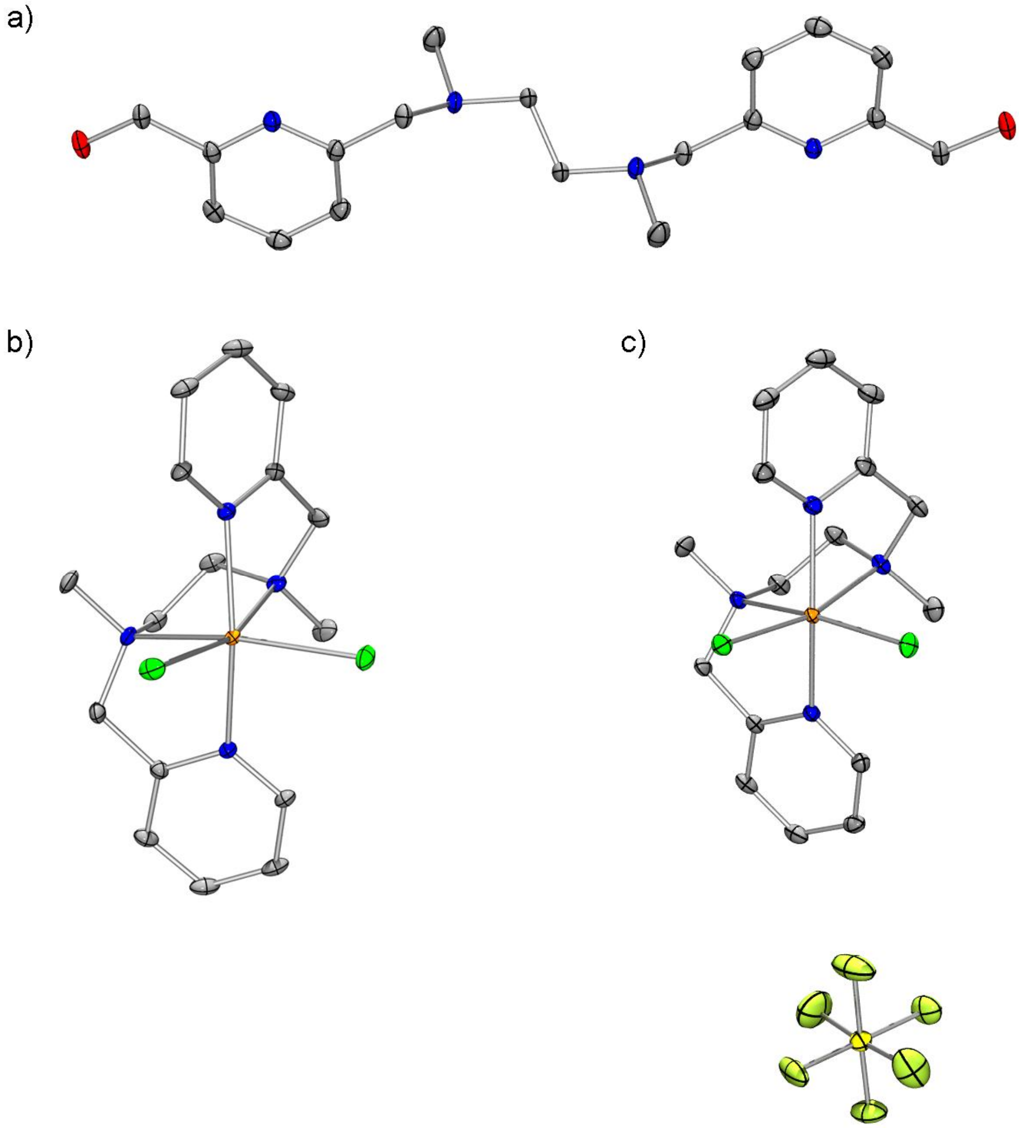


Figure S34. ORTEP drawing with the thermal displacement ellipsoids shown at 50% probability of the X-ray crystal structure of: a) mep$(OH)_2$ (**3**), b) Fe(II)(mep)Cl_2 (**5**), c) [Fe(III)(mep)Cl_2]PF_6 (**S8**). Color code: C: gray, O: red, N: blue, Fe: orange, Cl: green, P: yellow, F: light green. Hydrogen atoms have been omitted for clarity.

10.Theoretical calculations

The calculated BDFE values are shown in Table S7.

Table S7. Calculated BDFE values for the systems studied

	BDFE [kcal/mol]
mep(OH)	89.6
mep$(OH)_2$	90.9
mep$(CONHBu)_2$	93.7
Fe(II)(mep(OH)(dmso)	71.9
Fe(II)(mep$(OH)_2$)	74.3 (1st) 64.5 (2nd)
Fe(II)(mep$(CONHBu)_2$)	90.6 (1st) 80.6 (2nd)

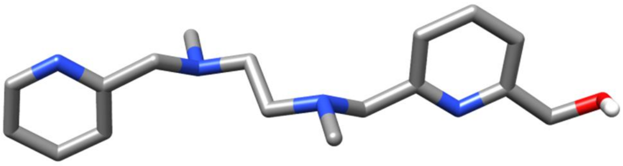
The structure, atomic coordinates and energy values obtained for the systems used to calculate the BDFE values are shown in Table S8-S24. C–H hydrogen atoms are omitted for clarity in the structures. Color code: C: gray, O: red, N: blue, H: white, Fe: orange, S: yellow.

Table S8. Atomic coordinates for the DFT optimized structure of H

Atom	X	Y	Z
H	0	0	0

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.000000 (Hartree/Particle)
Thermal correction to Energy = 0.001416
Thermal correction to Enthalpy = 0.002360
Thermal correction to Gibbs Free Energy = –0.010654
Sum of electronic and zero-point Energies = –0.500281
Sum of electronic and thermal Energies = –0.498865
Sum of electronic and thermal Enthalpies = –0.497921
Sum of electronic and thermal Free Energies = –0.510936

Table S9. Atomic coordinates for the DFT optimized structure of mep(OH) (**2**)

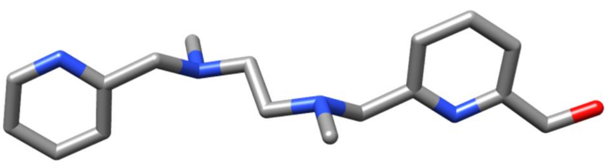


Atom	X	Y	Z
C	6.551093	-1.146060	-0.846817
H	6.376570	-2.159089	-0.458321
H	6.490483	-1.213473	-1.939595
C	5.441276	-0.237692	-0.345908
C	5.697449	1.059003	0.102178
H	6.712542	1.438294	0.107128
C	4.621337	1.833380	0.536832

H	4.782948	2.845422	0.896934
C	3.338571	1.294931	0.499840
H	2.471439	1.853868	0.831588
C	3.173418	-0.013918	0.029015
C	1.796899	-0.644459	-0.097178
H	1.389147	-0.357038	-1.073365
H	1.924109	-1.741183	-0.127522
C	1.175188	-0.853777	2.220903
H	1.057710	-1.952626	2.197652
H	0.524495	-0.455750	3.004820
H	2.210125	-0.632861	2.496926
C	-0.542572	-0.433858	0.557677
N	4.206459	-0.767571	-0.378096
N	0.858047	-0.219220	0.941725
O	7.860840	-0.680851	-0.555463
H	-1.135540	-0.430185	1.477342
H	-0.702732	-1.420194	0.086994
H	7.982965	-0.731286	0.402824
C	-7.037808	0.414781	0.500778
C	-7.296081	-0.863965	0.010035
H	-8.310231	-1.248517	-0.015649
C	-6.216604	-1.621656	-0.446167
H	-6.369089	-2.622847	-0.838517
C	-4.937961	-1.073130	-0.388728
H	-4.066625	-1.617591	-0.734001
C	-4.776788	0.221633	0.120450
C	-3.402571	0.853784	0.263078
H	-2.999138	0.553589	1.237147
H	-3.533451	1.949575	0.309181
C	-2.769735	1.099639	-2.048416
H	-2.655382	2.198300	-2.008028
H	-2.113895	0.715233	-2.834840
H	-3.802602	0.880182	-2.333019
C	-1.059196	0.663359	-0.383821
N	-5.812801	0.958723	0.556825
N	-2.456929	0.447071	-0.777066
H	-0.460915	0.663347	-1.300119
H	-0.904103	1.649170	0.089857
H	-7.854472	1.037474	0.862070

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.394564 (Hartree/Particle)
Thermal correction to Energy = 0.416362
Thermal correction to Enthalpy = 0.417307
Thermal correction to Gibbs Free Energy = 0.339181
Sum of electronic and zero-point Energies = –956.105512
Sum of electronic and thermal Energies = –956.083714
Sum of electronic and thermal Enthalpies = –956.082770
Sum of electronic and thermal Free Energies = –956.160895

Table S10. Atomic coordinates for the DFT optimized structure of mep(O$^{\bullet}$)

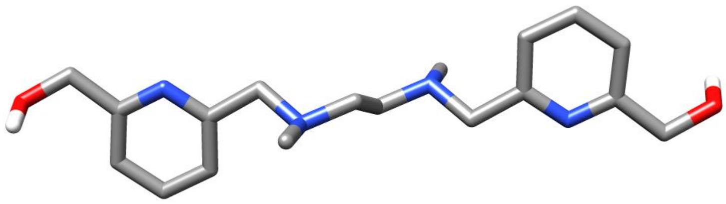


Atom	X	Y	Z
C	6.591596	-1.230653	-0.710281
H	6.503487	-2.185620	-0.152847
H	6.423313	-1.567485	-1.757520
C	5.486662	-0.273748	-0.298221
C	5.753438	1.054457	0.031580
H	6.772015	1.423508	0.004729
C	4.680388	1.867222	0.396606
H	4.843980	2.907198	0.663795
C	3.396151	1.329076	0.413450
H	2.531349	1.918828	0.693829
C	3.224295	-0.017333	0.068088
C	1.847264	-0.656360	0.012661
H	1.446168	-0.488897	-0.993620
H	1.972132	-1.748971	0.115198
C	1.211711	-0.587426	2.335029
H	1.087116	-1.680612	2.440507
H	0.559193	-0.096013	3.062362
H	2.246453	-0.341524	2.589420
C	-0.494426	-0.364868	0.625470

N	4.254218	-0.805557	-0.278194
N	0.904790	-0.106968	0.987712
O	7.869626	-0.770876	-0.640920
H	-1.093016	-0.233014	1.532135
H	-0.656474	-1.405693	0.292966
C	-6.986315	0.497643	0.402697
C	-7.247959	-0.835321	0.090492
H	-8.264400	-1.214316	0.106100
C	-6.168705	-1.654430	-0.243882
H	-6.323671	-2.699376	-0.496173
C	-4.887103	-1.109909	-0.247564
H	-4.015977	-1.701482	-0.504780
C	-4.722623	0.242012	0.079573
C	-3.345309	0.879948	0.146502
H	-2.948307	0.707651	1.153621
H	-3.469274	1.972986	0.047646
C	-2.702380	0.815845	-2.174117
H	-2.580418	1.909549	-2.277769
H	-2.046501	0.327280	-2.900397
H	-3.735772	0.567662	-2.431677
C	-1.000617	0.595239	-0.460538
N	-5.758271	1.037751	0.397488
N	-2.398061	0.334268	-0.826685
H	-0.399369	0.465755	-1.365836
H	-0.841619	1.636135	-0.126671
H	-7.802571	1.168639	0.664819

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.379374 (Hartree/Particle)
Thermal correction to Energy = 0.401113
Thermal correction to Enthalpy = 0.402057
Thermal correction to Gibbs Free Energy = 0.322450
Sum of electronic and zero-point Energies = –955.450295
Sum of electronic and thermal Energies = –955.428556
Sum of electronic and thermal Enthalpies = –955.427612
Sum of electronic and thermal Free Energies = –955.507218

Table S11. Atomic coordinates for the DFT optimized structure of mep(OH)$_2$ (**3**)

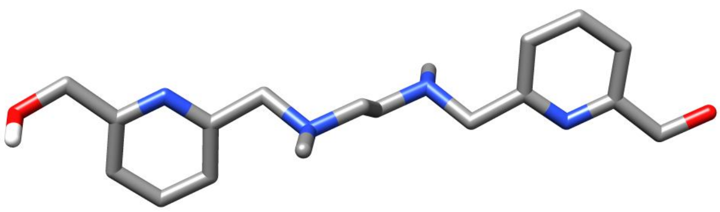


Atom	X	Y	Z
C	-7.401507	1.193152	-0.401493
H	-7.252581	2.041183	0.281201
H	-7.366731	1.598615	-1.419721
C	-6.251966	0.216997	-0.218502
C	-6.455217	-1.164021	-0.209902
H	-7.456042	-1.563121	-0.325527
C	-5.346052	-1.994407	-0.047831
H	-5.465634	-3.073966	-0.031220
C	-4.084059	-1.423163	0.088386
H	-3.192868	-2.025163	0.221199
C	-3.972798	-0.027388	0.062799
C	-2.623126	0.666067	0.142858
H	-2.236008	0.752924	-0.879058
H	-2.789712	1.699208	0.496282
C	-1.932158	0.097186	2.379430
H	-1.846258	1.141618	2.730762
H	-1.245762	-0.519797	2.966440
H	-2.951155	-0.243164	2.583795
C	-0.258238	0.338121	0.638913
N	-5.038074	0.776562	-0.079820
N	-1.638410	-0.050293	0.954152
O	-8.688559	0.610348	-0.256446
H	0.365342	0.034652	1.485469
H	-0.141540	1.432207	0.541984
H	-8.789090	0.349937	0.669823
C	7.401530	-1.193134	0.401411
H	7.252539	-2.041207	-0.281217
H	7.366843	-1.598532	1.419667
C	6.251978	-0.216985	0.218457

C	6.455227	1.164033	0.209839
H	7.456057	1.563135	0.325415
C	5.346054	1.994418	0.047807
H	5.465635	3.073976	0.031185
C	4.084057	1.423170	-0.088355
H	3.192860	2.025169	-0.221138
C	3.972798	0.027396	-0.062755
C	2.623124	-0.666060	-0.142765
H	2.236024	-0.752884	0.879160
H	2.789701	-1.699211	-0.496162
C	1.932132	-0.097224	-2.379341
H	1.846236	-1.141663	-2.730652
H	1.245725	0.519743	-2.966356
H	2.951123	0.243131	-2.583722
C	0.258230	-0.338144	-0.638809
N	5.038081	-0.776552	0.079827
N	1.638395	0.050279	-0.954063
O	8.688572	-0.610344	0.256215
H	-0.365361	-0.034685	-1.485360
H	0.141541	-1.432231	-0.541874
H	8.789015	-0.349974	-0.670075

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.427203 (Hartree/Particle)
Thermal correction to Energy = 0.451771
Thermal correction to Enthalpy = 0.452715
Thermal correction to Gibbs Free Energy = 0.366339
Sum of electronic and zero-point Energies = –1070.607121
Sum of electronic and thermal Energies = –1070.582553
Sum of electronic and thermal Enthalpies = –1070.581609
Sum of electronic and thermal Free Energies = –1070.667984

Table S12. Atomic coordinates for the DFT optimized structure of mep(OH)($O^{\bullet}$)

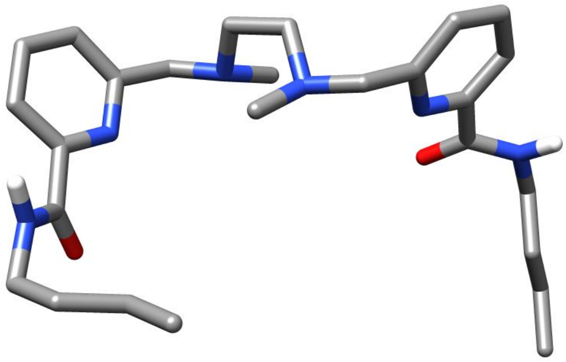


Atom	X	Y	Z
C	-7.363251	-1.186669	0.320096
H	-7.213491	-2.007338	-0.395083
H	-7.343567	-1.633668	1.321210
C	-6.203842	-0.213674	0.190260
C	-6.395606	1.168120	0.238524
H	-7.394266	1.570564	0.360934
C	-5.278151	1.995208	0.123034
H	-5.388885	3.075468	0.151302
C	-4.019601	1.419533	-0.024980
H	-3.122252	2.019025	-0.123536
C	-3.919973	0.022925	-0.057700
C	-2.574519	-0.676602	-0.154430
H	-2.190931	-0.797377	0.865400
H	-2.746315	-1.697020	-0.540536
C	-1.871558	-0.043592	-2.370277
H	-1.788867	-1.077091	-2.753319
H	-1.180234	0.588160	-2.935394
H	-2.888272	0.307375	-2.568186
C	-0.205596	-0.341504	-0.629599
N	-4.993064	-0.777264	0.040040
N	-1.583262	0.059099	-0.940141
O	-8.643803	-0.587375	0.184616
H	0.422377	-0.018993	-1.465787
H	-0.092115	-1.437914	-0.559164
H	-8.732194	-0.290287	-0.731824
C	7.439552	1.210980	-0.348913
H	7.395632	1.979695	0.450288
H	7.279116	1.829027	-1.259721
C	6.297796	0.222210	-0.191634
C	6.515038	-1.155085	-0.197064
H	7.520557	-1.542986	-0.310591
C	5.410343	-1.993086	-0.046415
H	5.534836	-3.072058	-0.042536
C	4.145051	-1.429533	0.097887
H	3.257391	-2.038677	0.221322

C	4.023481	-0.034351	0.092393
C	2.670838	0.650706	0.186482
H	2.287054	0.762888	-0.834202
H	2.832087	1.675005	0.567119
C	1.975725	0.019811	2.405300
H	1.885206	1.054257	2.783751
H	1.289306	-0.614772	2.973124
H	2.995028	-0.322678	2.604477
C	0.306564	0.302366	0.666413
N	5.083973	0.776885	-0.046372
N	1.687005	-0.090739	0.975476
O	8.698442	0.701431	-0.419437
H	-0.318674	-0.023806	1.503204
H	0.188046	1.398307	0.597047

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.412115 (Hartree/Particle)
Thermal correction to Energy = 0.436534
Thermal correction to Enthalpy = 0.437478
Thermal correction to Gibbs Free Energy = 0.351711
Sum of electronic and zero-point Energies = –1069.951822
Sum of electronic and thermal Energies = –1069.927403
Sum of electronic and thermal Enthalpies = –1069.926459
Sum of electronic and thermal Free Energies = –1070.012226

Table S13. Atomic coordinates for the DFT optimized structure of mep(CONHBu)$_2$ (**4**)

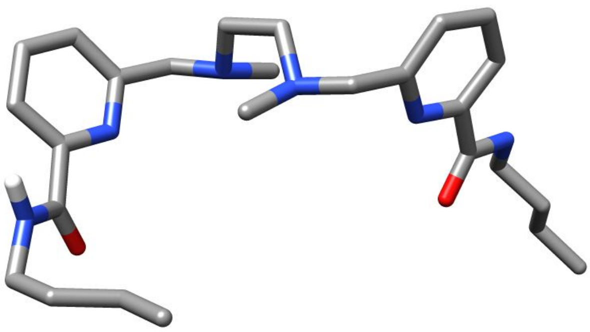


Atom	X	Y	Z
C	-4.235683	-1.063666	0.828566
C	-5.008045	-2.056953	1.442882
H	-6.024730	-2.251107	1.119465
C	-4.424697	-2.813211	2.457288
H	-4.985191	-3.602295	2.948593
C	-3.107274	-2.547083	2.820167
H	-2.619905	-3.118839	3.603038
C	-2.407421	-1.532035	2.153622
C	-0.984689	-1.177219	2.549483
H	-0.987250	-0.143502	2.915331
H	-0.684248	-1.815453	3.402496
C	0.118856	-2.622210	0.959537
H	-0.875492	-2.979537	0.674585
H	0.472510	-3.302517	1.761166
C	1.084138	-2.801685	-0.218414
H	2.114517	-2.705143	0.137579
H	0.974351	-3.851802	-0.558598
C	1.248132	-0.646802	1.829605
H	1.071192	0.367501	2.200543
H	1.901529	-0.575418	0.957806
H	1.776638	-1.209041	2.623185
C	-0.443398	-1.892463	-1.882684
H	-0.733898	-2.891390	-2.260552
H	-0.506213	-1.188172	-2.717783
H	-1.167919	-1.579814	-1.128481
C	1.908273	-2.078114	-2.370815
H	1.658226	-1.417920	-3.208613
H	1.882638	-3.114756	-2.757374
C	3.325261	-1.751986	-1.933228
C	4.311336	-2.745743	-1.871506
H	4.063197	-3.772406	-2.120027
C	5.605171	-2.394093	-1.496205
H	6.391467	-3.141092	-1.452798
C	5.874916	-1.063849	-1.182156
H	6.877074	-0.752412	-0.908687

C	4.829562	-0.135720	-1.266163	H	6.075999	2.698376	2.534158
C	-4.779514	-0.224979	-0.311591	H	6.148086	4.372626	2.009849
C	-6.771635	0.930606	-1.205782	C	4.191113	3.471298	1.798975
H	-7.817720	0.609525	-1.249620	H	3.769595	2.493621	1.534888
H	-6.312067	0.707881	-2.171984	H	3.845491	4.171861	1.027661
C	-6.688372	2.435247	-0.916987	C	3.655025	3.905670	3.166487
H	-7.113098	2.636496	0.075567	H	3.959969	3.204803	3.952097
H	-5.631477	2.726300	-0.873233	H	2.561218	3.952754	3.168926
C	-7.417525	3.276584	-1.971273	H	4.031940	4.896753	3.443798
H	-8.470381	2.967194	-2.018155	N	-2.964416	-0.808659	1.170817
H	-6.992552	3.064117	-2.961429	N	-0.025788	-1.248903	1.445202
C	-7.338853	4.780905	-1.694290	N	0.906048	-1.858212	-1.323604
H	-7.787456	5.028646	-0.725634	N	3.586419	-0.467573	-1.644374
H	-7.866210	5.355412	-2.462647	N	-6.092934	0.108997	-0.208520
H	-6.298704	5.125116	-1.675198	N	5.931956	1.615038	0.003750
C	5.048462	1.340098	-0.991877	O	-4.073557	0.099449	-1.268265
C	6.300099	2.970608	0.401433	O	4.470038	2.206532	-1.649625
H	5.943090	3.632686	-0.390385	H	-6.564237	-0.052593	0.670149
H	7.393603	3.037392	0.429195	H	6.277737	0.850393	0.565990
C	5.721404	3.392310	1.759155				

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.643991 (Hartree/Particle)
Thermal correction to Energy = 0.680193
Thermal correction to Enthalpy = 0.681137
Thermal correction to Gibbs Free Energy = 0.568374
Sum of electronic and zero-point Energies = –1493.268216
Sum of electronic and thermal Energies = –1493.232014
Sum of electronic and thermal Enthalpies = –1493.231070
Sum of electronic and thermal Free Energies = –1493.343833

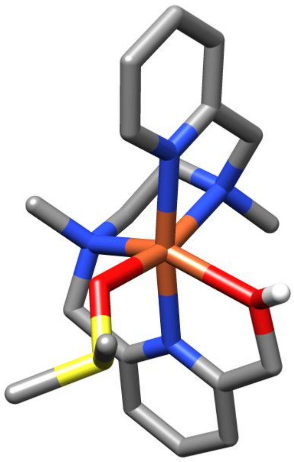
Table S14. Atomic coordinates for the DFT optimized structure of mep(CONHBu)($CON^{\bullet}Bu$)



Atom	X	Y	Z
C	-4.095322	-0.588779	1.293191
C	-4.864668	-1.651387	1.782261
H	-5.911480	-1.731551	1.516312
C	-4.248450	-2.575133	2.623237
H	-4.807787	-3.412129	3.028682
C	-2.902562	-2.402795	2.935724
H	-2.388990	-3.102940	3.586481
C	-2.206420	-1.309648	2.396820
C	-0.744599	-1.067003	2.728136
H	-0.658491	-0.049587	3.124844
H	-0.440329	-1.756200	3.538495
C	0.207491	-2.536115	1.062360
H	-0.815711	-2.867297	0.859603
H	0.608107	-3.229231	1.829948
C	1.066330	-2.730768	-0.193278
H	2.125049	-2.657982	0.073991
H	0.905051	-3.776028	-0.527519
C	1.456746	-0.606649	1.863953
H	1.340658	0.408773	2.254797
H	2.050753	-0.546981	0.949604
H	2.018946	-1.195975	2.613121
C	-0.578523	-1.779241	-1.714430
H	-0.919421	-2.767771	-2.077029
H	-0.700988	-1.062315	-2.532006
H	-1.227862	-1.465856	-0.894445
C	1.717073	-2.004470	-2.404813
H	1.415362	-1.323362	-3.208367
H	1.629110	-3.032935	-2.803623
C	3.174859	-1.725660	-2.084439
C	4.137778	-2.741696	-2.150433
H	3.843511	-3.751984	-2.415222
C	5.468113	-2.433311	-1.878928
H	6.236356	-3.197990	-1.935646
C	5.797237	-1.123505	-1.536910
H	6.826581	-0.844392	-1.340302
C	4.771784	-0.170973	-1.491199
C	-4.694253	0.445121	0.382654
C	-6.344089	0.726364	-1.361779
H	-6.776591	-0.099426	-1.946187
H	-5.489689	1.139248	-1.911755
C	-7.436536	1.803205	-1.173951
H	-8.258992	1.375787	-0.588599
H	-7.013046	2.623385	-0.582294
C	-7.958299	2.335593	-2.513601
H	-8.374563	1.503886	-3.096939
H	-7.120152	2.734363	-3.099563
C	-9.022390	3.423269	-2.336508
H	-9.887408	3.043868	-1.781351
H	-9.379976	3.786846	-3.305146
H	-8.622967	4.281120	-1.784316
C	5.050951	1.286955	-1.179713
C	6.459195	2.830219	0.163328
H	6.064950	3.530565	-0.576245
H	7.553222	2.862378	0.108001
C	6.000948	3.222529	1.574564
H	6.388475	2.490642	2.297030
H	6.480061	4.178821	1.823193
C	4.481918	3.351300	1.735110
H	4.006348	2.397472	1.475642
H	4.104294	4.087338	1.013416
C	4.068153	3.760095	3.152096
H	4.404300	3.023600	3.891002
H	2.980331	3.846934	3.240109
H	4.503320	4.727285	3.428481
N	-2.797797	-0.417589	1.590291
N	0.139417	-1.161989	1.562867
N	0.813938	-1.775257	-1.273121
N	3.492494	-0.459937	-1.771145
N	-5.957988	0.165065	-0.092446
N	6.017683	1.501033	-0.248631
O	-4.146161	1.525471	0.141596
O	4.445423	2.191867	-1.756111
H	6.386545	0.706535	0.254488

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.629398 (Hartree/Particle)
Thermal correction to Energy = 0.665623
Thermal correction to Enthalpy = 0.666567
Thermal correction to Gibbs Free Energy = 0.552113
Sum of electronic and zero-point Energies = –1492.606299
Sum of electronic and thermal Energies = –1492.570074
Sum of electronic and thermal Enthalpies = –1492.569130
Sum of electronic and thermal Free Energies = –1492.683584

Table S15. Atomic coordinates for the DFT optimized structure of Fe(II)(mep(OH))(dmso)

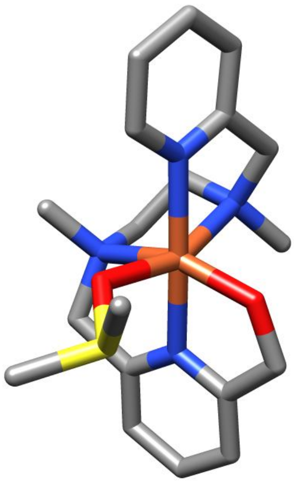


Atom	X	Y	Z
Fe	-0.214646	-0.041104	-0.093607
O	0.394985	0.182416	-2.225142
N	-2.346058	0.362205	-0.188473
N	1.888239	-0.545762	-0.231151
N	-1.134086	-2.122011	-0.480946
N	0.231892	-1.006864	1.900541
C	2.530590	-0.559574	-1.406013
C	-2.911350	1.509454	0.235598
H	-2.218091	2.278357	0.557706
C	-3.135646	-0.649164	-0.605231
C	-4.288656	1.695376	0.259170
H	-4.703204	2.634617	0.606997
C	2.500130	-0.965553	0.892332
C	-1.327555	-2.675784	0.886179
H	-1.558847	-3.748953	0.841309
H	-2.192608	-2.180311	1.334770
C	1.765983	-0.033885	-2.601118
H	2.213697	0.908802	-2.935663
H	1.816824	-0.749105	-3.429192
C	3.846083	-1.014391	-1.509761
H	4.349974	-1.023475	-2.470200
C	4.486605	-1.458600	-0.355003
H	5.506693	-1.824849	-0.405237
C	-2.436693	-1.880462	-1.140138
H	-3.096538	-2.755003	-1.061707
H	-2.242080	-1.723702	-2.207136
C	1.683811	-0.823773	2.160667
H	2.037836	-1.518990	2.931888
H	1.825777	0.188949	2.552611
C	-0.091614	-2.456662	1.754079
H	-0.244393	-2.912819	2.740397
H	0.772018	-2.951228	1.304311
C	3.808513	-1.438699	0.866872
H	4.284796	-1.783713	1.777926
C	-4.526031	-0.540340	-0.596970
H	-5.135306	-1.375106	-0.925969
C	-5.109637	0.648913	-0.163361
H	-6.189615	0.754571	-0.150447
C	-0.318254	-3.029913	-1.316927
H	-0.145313	-2.563640	-2.288302
H	-0.821014	-3.995160	-1.466015
H	0.648392	-3.209548	-0.845921
C	-0.563247	-0.385926	2.987468
H	-0.385320	0.690983	2.989231
H	-0.293490	-0.804615	3.965346
H	-1.625903	-0.560418	2.812740
H	-0.031584	0.771294	-2.862213

O	0.133208	1.976195	0.452646
S	1.282224	2.876157	-0.109551
C	0.427797	4.341848	-0.750098
C	2.052988	3.610079	1.358951
H	1.179075	5.074196	-1.053072
H	-0.150361	4.021045	-1.617469
H	-0.227433	4.745385	0.024227
H	2.768510	4.367086	1.030481
H	1.278897	4.047149	1.992514
H	2.575471	2.808875	1.882675

Charge = 2; multiplicity = 5; (0 imaginary frequencies)
Zero-point correction = 0.482738 (Hartree/Particle)
Thermal correction to Energy = 0.511709
Thermal correction to Enthalpy = 0.512654
Thermal correction to Gibbs Free Energy = 0.422502
Sum of electronic and zero-point Energies = –1632.505408
Sum of electronic and thermal Energies = –1632.476438
Sum of electronic and thermal Enthalpies = –1632.475493
Sum of electronic and thermal Free Energies = –1632.565645

Table S16. Atomic coordinates for the DFT optimized structure of Fe(III)(mep(O$^-$))(dmso)

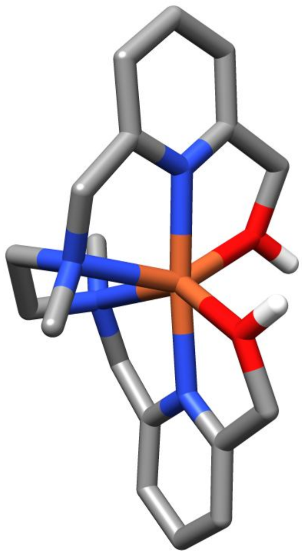


Atom	X	Y	Z
Fe	-0.132451	-0.057437	-0.232937
O	0.320976	0.159008	-2.019724
N	-2.282131	0.199915	-0.124246
N	1.938454	-0.495631	-0.200492
N	-0.954721	-2.160170	-0.451819
N	0.318362	-0.901560	1.874101
C	2.548337	-0.466272	-1.394920
C	-2.896864	1.305469	0.341661
H	-2.244244	2.082454	0.720169
C	-3.024781	-0.821727	-0.600878
C	-4.279517	1.436560	0.342798
H	-4.735137	2.341528	0.727186
C	2.596174	-0.774349	0.936872
C	-1.140449	-2.687926	0.929929
H	-1.303793	-3.772439	0.903002
H	-2.040949	-2.236077	1.351087
C	1.609090	-0.086330	-2.524604
H	1.993969	0.808676	-3.035483
H	1.583297	-0.888852	-3.277119
C	3.908055	-0.755247	-1.498987
H	4.405117	-0.735201	-2.462597
C	4.605220	-1.071910	-0.332526
H	5.662712	-1.309940	-0.383713
C	-2.256783	-2.000959	-1.144273
H	-2.854176	-2.918271	-1.076228
H	-2.047348	-1.825155	-2.204817
C	1.750613	-0.641332	2.182526
H	2.109430	-1.298676	2.983300
H	1.832409	0.388020	2.545999
C	0.068706	-2.370522	1.799447
H	-0.079331	-2.781544	2.805726
H	0.962014	-2.845241	1.388485
C	3.951399	-1.082366	0.905391

H	4.484936	-1.319840	1.818727
C	-4.416281	-0.763143	-0.622422
H	-4.985991	-1.604107	-1.001555
C	-5.051846	0.383776	-0.149535
H	-6.134713	0.450656	-0.157598
C	-0.076957	-3.049075	-1.252666
H	0.075305	-2.609726	-2.238672
H	-0.534267	-4.039282	-1.367195
H	0.890851	-3.163604	-0.765737
C	-0.548705	-0.258849	2.891854
H	-0.412375	0.822082	2.843118
H	-0.302954	-0.617383	3.898901
H	-1.594233	-0.488232	2.684161
O	0.094093	1.816860	0.526832
S	0.988326	2.891213	-0.212981
C	-0.204201	4.041565	-0.944616
C	1.608542	3.904952	1.151236
H	0.357742	4.867866	-1.385262
H	-0.736083	3.495495	-1.724467
H	-0.890331	4.399775	-0.175475
H	2.134525	4.760283	0.721343
H	0.770828	4.225409	1.772777
H	2.304513	3.286558	1.718593

Charge = 2; multiplicity = 6; (0 imaginary frequencies)
Zero-point correction = 0.472275 (Hartree/Particle)
Thermal correction to Energy = 0.499780
Thermal correction to Enthalpy = 0.500724
Thermal correction to Gibbs Free Energy = 0.414732
Sum of electronic and zero-point Energies = –1631.885006
Sum of electronic and thermal Energies = –1631.857501
Sum of electronic and thermal Enthalpies = –1631.856557
Sum of electronic and thermal Free Energies = –1631.942549

Table S17. Atomic coordinates for the DFT optimized structure of Fe(II)(mep(OH)$_2$)

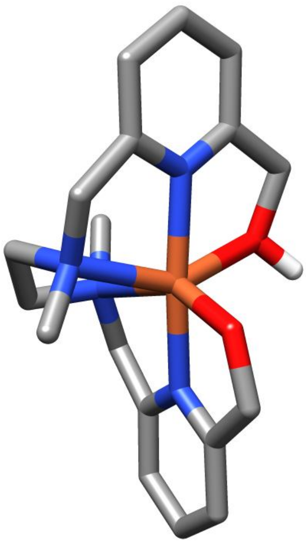


Atom	X	Y	Z
C	-2.763167	0.394695	-0.940889
C	-4.152258	0.478972	-0.955492
H	-4.649133	1.177814	-1.618904
C	-4.883363	-0.349728	-0.102059
H	-5.967181	-0.300668	-0.092111
C	-4.215908	-1.231122	0.746263
H	-4.759645	-1.878049	1.425745
C	-2.823020	-1.256288	0.714376
C	-2.013404	-2.194592	1.577492
H	-2.440018	-2.249853	2.583756
H	-2.026615	-3.200747	1.140760
C	-1.880178	1.182198	-1.885120
H	-1.741141	0.581974	-2.791107
H	-2.377890	2.111181	-2.191373
C	0.430383	1.700713	-2.402970
H	0.517054	0.807121	-3.022601
H	1.412440	1.923210	-1.983837
H	0.114928	2.548735	-3.025139

C	-0.582049	2.588819	-0.357965
N	-0.539499	1.445643	-1.311687
N	-2.126782	-0.458296	-0.113073
O	-0.668315	-1.697754	1.638585
Fe	0.002134	-0.384613	-0.042598
H	-0.091220	-2.353568	2.053723
H	-1.538985	2.557776	0.169343
H	-0.546534	3.543894	-0.898849
C	2.748011	0.289053	0.987963
C	4.135066	0.390164	1.029189
H	4.613624	1.011711	1.777568
C	4.888667	-0.320664	0.092423
H	5.971654	-0.256227	0.102772
C	4.244064	-1.104183	-0.862142
H	4.804478	-1.660051	-1.605761
C	2.850919	-1.151130	-0.849792
C	2.061985	-1.987858	-1.827761
H	2.456913	-1.867850	-2.841413
H	2.131334	-3.046720	-1.551886
C	1.844665	0.944834	2.009941
H	1.695223	0.233992	2.830291
H	2.332222	1.829358	2.439904
C	-0.467600	1.409436	2.561360
H	-0.555488	0.452970	3.077349
H	-1.447981	1.672380	2.161980
H	-0.158627	2.186188	3.273086
C	0.568730	2.522661	0.642768
N	0.510720	1.277404	1.456009
N	2.133481	-0.466867	0.055705
O	0.693662	-1.554376	-1.779569
H	0.126987	-2.175243	-2.258000
H	1.525246	2.538118	0.114431
H	0.545405	3.408475	1.291491

Charge = 2; multiplicity = 5; (0 imaginary frequencies)
Zero-point correction = 0.434667 (Hartree/Particle)
Thermal correction to Energy = 0.458748
Thermal correction to Enthalpy = 0.459693
Thermal correction to Gibbs Free Energy = 0.381886
Sum of electronic and zero-point Energies = –1193.871005
Sum of electronic and thermal Energies = –1193.846923
Sum of electronic and thermal Enthalpies = –1193.845979
Sum of electronic and thermal Free Energies = –1193.923786

Table S18. Atomic coordinates for the DFT optimized structure of Fe(III)(mep(OH)(O^-))

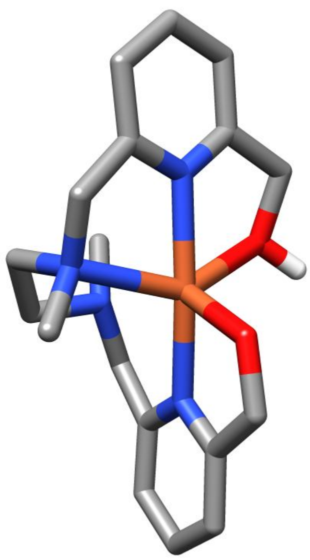


Atom	X	Y	Z
C	-2.776523	0.799711	-0.527576
C	-4.164784	0.801905	-0.467076
H	-4.717482	1.720816	-0.624987
C	-4.823452	-0.400801	-0.198787
H	-5.906416	-0.424856	-0.141713
C	-4.089234	-1.568634	0.001432
H	-4.579721	-2.512270	0.211813

C	-2.700256	-1.498341	-0.069834
C	-1.810209	-2.704412	0.091210
H	-2.093194	-3.284979	0.974135
H	-1.891738	-3.346688	-0.792077
C	-1.946794	2.007012	-0.894412
H	-1.835876	2.029680	-1.983404
H	-2.446449	2.935947	-0.598674
C	0.359515	2.770743	-1.086631
H	0.407216	2.394480	-2.108383
H	1.355828	2.723151	-0.647084
H	0.024770	3.814275	-1.092627
C	-0.601918	2.337766	1.137245
N	-0.582504	1.929065	-0.301639
N	-2.076694	-0.334881	-0.320029
O	-0.451924	-2.241405	0.233289
Fe	0.027763	-0.209334	-0.344067
H	0.169894	-2.955004	0.027786
H	-1.553038	2.018384	1.567911
H	-0.563410	3.430551	1.212541
C	2.763407	-0.325038	0.988837
C	4.152263	-0.349373	1.029528
H	4.675749	-0.317439	1.978190
C	4.851111	-0.417198	-0.180820
H	5.935956	-0.438305	-0.175303
C	4.161964	-0.450553	-1.393748
H	4.690275	-0.498510	-2.339430
C	2.770363	-0.410490	-1.361764
C	1.837931	-0.415250	-2.556128
H	2.079612	0.424644	-3.223931
H	1.982118	-1.336109	-3.140125
C	1.855767	-0.334228	2.194863
H	1.708338	-1.373343	2.506472
H	2.309947	0.193790	3.041246
C	-0.494462	-0.299674	2.805741
H	-0.537451	-1.384023	2.705578
H	-1.477401	0.109752	2.575320
H	-0.237563	-0.038577	3.839311
C	0.563985	1.726480	1.904967
N	0.520084	0.234962	1.861982
N	2.115987	-0.351302	-0.189023
O	0.505592	-0.324981	-2.121537
H	1.514982	2.048734	1.473667
H	0.543726	2.077039	2.944177

Charge = 2; multiplicity = 6; (0 imaginary frequencies)
Zero-point correction = 0.423620 (Hartree/Particle)
Thermal correction to Energy = 0.446521
Thermal correction to Enthalpy = 0.447465
Thermal correction to Gibbs Free Energy = 0.372111
Sum of electronic and zero-point Energies = –1193.242877
Sum of electronic and thermal Energies = –1193.219976
Sum of electronic and thermal Enthalpies = –1193.219032
Sum of electronic and thermal Free Energies = –1193.294386

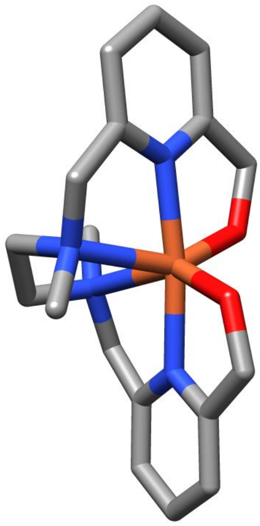
Table S19. Atomic coordinates for the DFT optimized structure of Fe(II)(mep(OH)(O^-))



Atom	X	Y	Z
C	-2.770928	0.772431	-0.651720
C	-4.156932	0.870103	-0.552785
H	-4.659536	1.795436	-0.812060
C	-4.876030	-0.242175	-0.111047
H	-5.956242	-0.192100	-0.019853
C	-4.198991	-1.412904	0.225120
H	-4.732541	-2.287548	0.581103
C	-2.809421	-1.435844	0.103645
C	-1.999444	-2.676297	0.408111
H	-2.411097	-3.186726	1.285672
H	-2.060327	-3.365156	-0.444578
C	-1.901663	1.892513	-1.188154
H	-1.785224	1.740222	-2.267295
H	-2.403730	2.861193	-1.056216
C	0.402576	2.597277	-1.459955
H	0.481037	2.065769	-2.410069
H	1.389940	2.608949	-0.995992
H	0.088580	3.635018	-1.643135
C	-0.575821	2.465990	0.779586
N	-0.551178	1.884268	-0.586296
N	-2.126204	-0.363378	-0.324211
O	-0.639669	-2.293525	0.644096
Fe	0.032365	-0.364528	-0.412006
H	-0.076222	-3.078760	0.627731
H	-1.531926	2.207329	1.241613
H	-0.533715	3.563826	0.733100
C	2.761737	-0.170501	1.061930
C	4.148342	-0.100754	1.155480
H	4.627040	0.108966	2.106203
C	4.904065	-0.311038	-0.004407
H	5.987958	-0.265289	0.039666
C	4.263026	-0.573165	-1.213321
H	4.829936	-0.736780	-2.124480
C	2.865296	-0.611434	-1.234308
C	2.001022	-0.861703	-2.465623
H	2.293705	-0.117353	-3.231140
H	2.299488	-1.841408	-2.886131
C	1.820602	-0.053957	2.242923
H	1.657569	-1.060445	2.645500
H	2.278626	0.539641	3.047610
C	-0.504299	0.132902	2.870831
H	-0.590235	-0.953353	2.927837
H	-1.479969	0.534068	2.591989
H	-0.235750	0.530443	3.861040
C	0.572667	1.949801	1.643682
N	0.499952	0.483903	1.848554
N	2.159611	-0.413080	-0.113224
O	0.644178	-0.808397	-2.180289
H	1.527403	2.176886	1.161990
H	0.567579	2.480810	2.607896

Charge = 1; multiplicity = 5; (0 imaginary frequencies)
Zero-point correction = 0.420363 (Hartree/Particle)
Thermal correction to Energy = 0.444214
Thermal correction to Enthalpy = 0.445158
Thermal correction to Gibbs Free Energy = 0.367104
Sum of electronic and zero-point Energies = –1193.425000
Sum of electronic and thermal Energies = –1193.401150
Sum of electronic and thermal Enthalpies = –1193.400206
Sum of electronic and thermal Free Energies = –1193.478259

Table S20. Atomic coordinates for the DFT optimized structure of Fe(III)(mep(O^{-})$_2$)



Atom	X	Y	Z
C	-2.766974	-0.990814	-0.339812
C	-4.154718	-0.986139	-0.417021
H	-4.674925	-1.705659	-1.039366
C	-4.856869	-0.030092	0.327039
H	-5.941136	-0.004545	0.285137
C	-4.168752	0.893525	1.112414
H	-4.697654	1.644749	1.689170
C	-2.774059	0.838048	1.133001
C	-1.845414	1.760581	1.902842
H	-2.066971	2.802555	1.614925
H	-2.087343	1.684321	2.976753
C	-1.857590	-1.987800	-1.020475
H	-1.713491	-2.839483	-0.347073
H	-2.311932	-2.375486	-1.941180
C	0.484246	-2.463191	-1.441705
H	0.536298	-3.038998	-0.517280
H	1.465903	-2.027992	-1.630741
H	0.226261	-3.127892	-2.276709
C	-0.570307	-0.506575	-2.476141
N	-0.522726	-1.390742	-1.281189
N	-2.121021	-0.091051	0.420151
O	-0.509307	1.439965	1.661962
Fe	0.000000	0.000000	0.546885
H	-1.531899	0.012097	-2.475458
H	-0.528366	-1.104046	-3.396951
C	2.766974	0.990814	-0.339812
C	4.154718	0.986140	-0.417021
H	4.674925	1.705661	-1.039365
C	4.856870	0.030093	0.327040
H	5.941136	0.004546	0.285138
C	4.168752	-0.893525	1.112414
H	4.697654	-1.644749	1.689169
C	2.774060	-0.838048	1.133000
C	1.845414	-1.760582	1.902840
H	2.066974	-2.802556	1.614925
H	2.087342	-1.684320	2.976751
C	1.857590	1.987800	-1.020475
H	1.713492	2.839483	-0.347073
H	2.311932	2.375486	-1.941180
C	-0.484246	2.463192	-1.441703
H	-0.536298	3.038997	-0.517277
H	-1.465903	2.027994	-1.630741
H	-0.226260	3.127895	-2.276705
C	0.570306	0.506576	-2.476141
N	0.522725	1.390743	-1.281189
N	2.121021	0.091050	0.420150
O	0.509307	-1.439968	1.661959
H	1.531898	-0.012095	-2.475459
H	0.528364	1.104048	-3.396950

Charge = 1; multiplicity = 6; (0 imaginary frequencies)

Zero-point correction = 0.409881 (Hartree/Particle)

Thermal correction to Energy = 0.432361

Thermal correction to Enthalpy = 0.433306

Thermal correction to Gibbs Free Energy = 0.358673

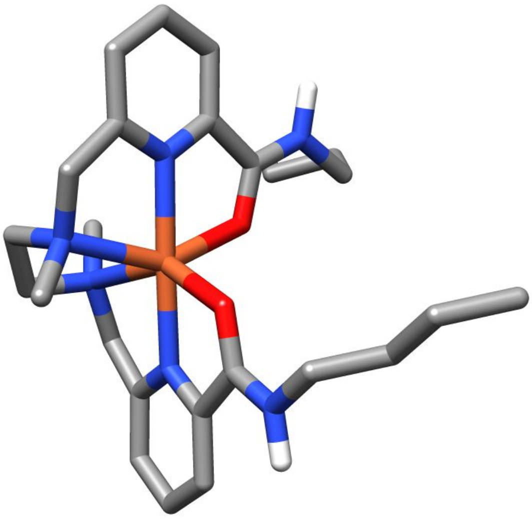
Sum of electronic and zero-point Energies = –1192.813369

Sum of electronic and thermal Energies = –1192.790889

Sum of electronic and thermal Enthalpies = –1192.789945

Sum of electronic and thermal Free Energies = –1192.864577

Table S21. Atomic coordinates for the DFT optimized structure of Fe(II)(mep(CONHBu)$_2$)

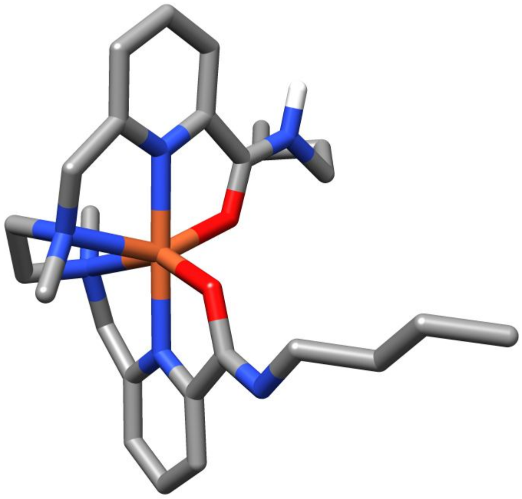


Atom	X	Y	Z
C	2.328869	-1.323296	-1.540880
C	3.050518	-1.960889	-2.543971
H	4.084453	-1.717212	-2.757247
C	2.404823	-2.957005	-3.285441
H	2.942246	-3.479417	-4.069332
C	1.078713	-3.278116	-3.011633
H	0.563100	-4.049625	-3.572542
C	0.414972	-2.583684	-1.993928
C	-1.047957	-2.781337	-1.661494
H	-1.626604	-2.128338	-2.324131
H	-1.357176	-3.811638	-1.881470
C	-0.984328	-3.496561	0.673870
H	-0.049798	-3.938559	0.319042
H	-1.739786	-4.294372	0.662767
C	-0.808577	-2.987523	2.102921
H	-1.734757	-2.522787	2.449890
H	-0.609486	-3.837096	2.770118
C	-2.805158	-2.083606	-0.154943
H	-3.029753	-1.223496	-0.787349
H	-3.055598	-1.826128	0.874857
H	-3.428318	-2.934024	-0.462559
C	1.610188	-2.633523	2.266108
H	1.717065	-3.237813	3.176633
H	2.389721	-1.869947	2.247465
H	1.744819	-3.283359	1.400469
C	0.092665	-1.119320	3.398877
H	1.055393	-0.653413	3.636269
H	-0.201211	-1.706671	4.278399
C	-0.904240	-0.007822	3.144349
C	-1.626648	0.631032	4.157943
H	-1.530833	0.304545	5.187322
C	-2.467177	1.685635	3.814881
H	-3.041779	2.196310	4.579987
C	-2.580904	2.084128	2.477993
H	-3.247517	2.896744	2.215175
C	-1.836296	1.398903	1.524355
C	2.811773	-0.242685	-0.607539
C	4.603471	1.290632	0.117079
H	5.641942	1.022434	0.332193
H	4.048346	1.280962	1.056593
C	4.527633	2.671577	-0.546230
H	5.053941	2.641116	-1.508836
H	3.477774	2.903919	-0.764597
C	5.131974	3.767597	0.341004
H	6.177524	3.517704	0.564413
H	4.606793	3.783672	1.305144
C	5.063251	5.155513	-0.303670
H	5.608566	5.177641	-1.253842
H	5.500303	5.917017	0.349996
H	4.026612	5.445683	-0.508443
C	-1.820123	1.639477	0.033664
C	-2.554351	3.028374	-1.882499
H	-1.935068	2.305086	-2.414624
H	-2.106866	4.019202	-2.011979
C	-3.992704	3.022477	-2.414002
H	-4.596829	3.734363	-1.835325
H	-3.958273	3.413546	-3.438590
C	-4.662811	1.643242	-2.408163
H	-4.679908	1.248868	-1.384058

H	-4.054585	0.945503	-2.999079
C	-6.090402	1.678226	-2.963229
H	-6.728272	2.345144	-2.372184
H	-6.545565	0.682798	-2.949596
H	-6.104043	2.037760	-3.998350
N	1.046869	-1.642114	-1.288864
N	-1.363248	-2.404188	-0.263539
N	0.282749	-1.978568	2.205668
N	-1.026499	0.381497	1.871609
N	4.048297	0.227606	-0.728302
N	-2.481727	2.686117	-0.457162
O	2.014154	0.172576	0.274666
O	-1.181003	0.835492	-0.688876
Fe	0.046600	-0.649895	0.334719
H	4.633007	-0.122193	-1.474973
H	-2.954514	3.307682	0.184960

Charge = 2; multiplicity = 5; (0 imaginary frequencies)
Zero-point correction = 0.650761 (Hartree/Particle)
Thermal correction to Energy = 0.687101
Thermal correction to Enthalpy = 0.688045
Thermal correction to Gibbs Free Energy = 0.578364
Sum of electronic and zero-point Energies = −1616.540224
Sum of electronic and thermal Energies = −1616.503884
Sum of electronic and thermal Enthalpies = −1616.502940
Sum of electronic and thermal Free Energies = −1616.612621

Table S22. Atomic coordinates for the DFT optimized structure of Fe(III)(mep(CONHBu)(CONBu$^-$))

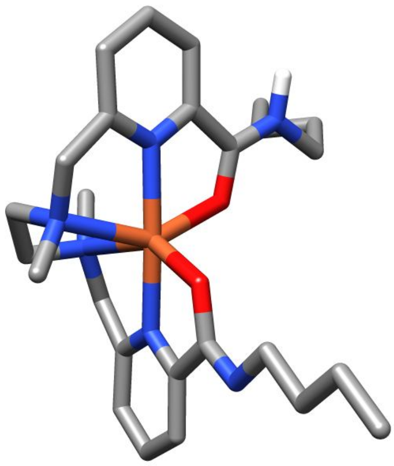


Atom	X	Y	Z
C	2.105764	-1.434856	-1.505801
C	2.785021	-2.115540	-2.510969
H	3.819394	-1.873300	-2.719927
C	2.094121	-3.103721	-3.214946
H	2.596986	-3.659589	-3.999326
C	0.757346	-3.385962	-2.913699
H	0.211868	-4.152139	-3.452393
C	0.136356	-2.656481	-1.903290
C	-1.315244	-2.766689	-1.504098
H	-1.904252	-2.125994	-2.168122
H	-1.689733	-3.789650	-1.624394
C	-1.155123	-3.357306	0.868616
H	-0.281155	-3.885577	0.481331
H	-1.968669	-4.088982	0.942784
C	-0.859620	-2.784397	2.248503
H	-1.731279	-2.254634	2.638102
H	-0.639187	-3.600394	2.946662
C	-2.926541	-1.848870	0.069215
H	-3.135321	-1.025794	-0.614271
H	-3.092165	-1.507533	1.090999
H	-3.614995	-2.676031	-0.139699
C	1.591104	-2.542470	2.179275
H	1.730570	-3.125471	3.096539
H	2.396519	-1.814596	2.082924
H	1.624304	-3.218139	1.324880

C	0.244257	-0.911895	3.387422	C	-1.735982	1.686678	-0.000549
H	1.245628	-0.493214	3.529378	C	-2.501956	2.876975	-2.033171
H	-0.009409	-1.461909	4.300342	H	-2.001839	2.034742	-2.512433
C	-0.711309	0.232364	3.150556	H	-1.951857	3.789630	-2.283398
C	-1.310675	0.992995	4.159179	C	-3.962723	2.991254	-2.481926
H	-1.153081	0.740417	5.201347	H	-4.440154	3.828668	-1.955624
C	-2.108193	2.073628	3.793032	H	-3.946703	3.267631	-3.543166
H	-2.585920	2.679193	4.555079	C	-4.786000	1.711757	-2.289967
C	-2.301863	2.382487	2.440088	H	-4.786909	1.430697	-1.229029
H	-2.924315	3.224384	2.161550	H	-4.300242	0.887629	-2.829016
C	-1.682525	1.576641	1.494832	C	-6.230847	1.864193	-2.775979
C	2.650609	-0.357817	-0.627456	H	-6.748831	2.661998	-2.231940
C	4.380946	1.103267	0.067987	H	-6.796705	0.938760	-2.630024
H	5.176894	0.664813	0.686722	H	-6.265413	2.112847	-3.842576
H	3.623975	1.513160	0.748434	N	0.819089	-1.719644	-1.230052
C	4.987217	2.222620	-0.791301	N	-1.516906	-2.284929	-0.107345
H	5.723612	1.784451	-1.476883	N	0.288047	-1.825594	2.211349
H	4.196870	2.657870	-1.417306	N	-0.917403	0.531966	1.865522
C	5.644882	3.322943	0.050249	N	3.856325	0.039232	-0.777079
H	6.431337	2.878777	0.675252	N	-2.387877	2.677068	-0.579676
H	4.903915	3.742629	0.743859	O	1.752797	0.086906	0.262982
C	6.242112	4.447970	-0.801163	O	-1.128419	0.789917	-0.665051
H	7.010556	4.063705	-1.481553	Fe	-0.009305	-0.612744	0.335842
H	6.705561	5.217609	-0.175304	H	-2.830837	3.371355	0.009655
H	5.472164	4.933432	-1.411654				

Charge = 2; multiplicity = 6; (0 imaginary frequencies)
Zero-point correction = 0.638585 (Hartree/Particle)
Thermal correction to Energy = 0.674024
Thermal correction to Enthalpy = 0.674968
Thermal correction to Gibbs Free Energy = 0.567675
Sum of electronic and zero-point Energies = −1615.886419
Sum of electronic and thermal Energies = −1615.850981
Sum of electronic and thermal Enthalpies = −1615.850036
Sum of electronic and thermal Free Energies = −1615.957330

Table S23. Atomic coordinates for the DFT optimized structure of Fe(II)(mep(CONHBu)(CONBu⁻))

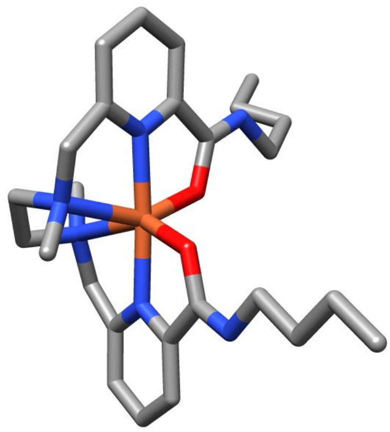


Atom	X	Y	Z
C	-2.145679	1.546558	-1.264376
C	-2.856157	2.446999	-2.059547
H	-3.870638	2.211127	-2.355425
C	-2.227723	3.633035	-2.437866
H	-2.756590	4.358692	-3.047916
C	-0.915875	3.892158	-2.027180
H	-0.411768	4.810757	-2.307753
C	-0.263160	2.937841	-1.247896
C	1.181467	3.039586	-0.805202
H	1.806293	2.599731	-1.590601
H	1.485504	4.091414	-0.707999
C	0.945895	3.040556	1.620855
H	0.006265	3.525125	1.343255
H	1.651992	3.840775	1.887917
C	0.723106	2.141955	2.835463
H	1.651914	1.625356	3.090345
H	0.456991	2.761335	3.703717
C	2.876748	1.984233	0.556257
H	3.182766	1.363782	-0.287851
H	3.075749	1.430188	1.474779
H	3.481352	2.902599	0.567139
C	-1.680622	1.677037	2.764590
H	-1.860363	1.982777	3.804727
H	-2.418434	0.927767	2.472326
H	-1.806168	2.547224	2.118698
C	-0.136071	-0.051234	3.479578
H	-1.074214	-0.617252	3.495077
H	0.069600	0.252425	4.514915
C	0.953505	-0.975621	2.974099
C	1.708715	-1.808045	3.806798
H	1.565533	-1.782494	4.881276
C	2.646947	-2.657522	3.227511
H	3.251096	-3.309402	3.849274
C	2.820862	-2.662612	1.839492
H	3.565630	-3.312010	1.395040
C	2.035358	-1.804258	1.075611
C	-2.660322	0.232246	-0.741975
C	-4.329058	-1.399183	-0.564167
H	-4.301534	-1.405118	0.538084
H	-3.660037	-2.218247	-0.876336
C	-5.752989	-1.689412	-1.043721
H	-6.410099	-0.868819	-0.724175
H	-5.766214	-1.682300	-2.142305
C	-6.305337	-3.023428	-0.529235
H	-6.283836	-3.025698	0.569408
H	-5.639979	-3.838356	-0.846495
C	-7.730672	-3.313221	-1.011144
H	-8.426241	-2.533514	-0.679718
H	-8.097033	-4.271209	-0.627178
H	-7.777460	-3.353158	-2.105592
C	2.076124	-1.632810	-0.425900
C	2.961608	-2.423084	-2.602055
H	2.328862	-1.605666	-2.950717
H	2.567102	-3.356981	-3.016218
C	4.416945	-2.222245	-3.042086
H	5.032294	-3.041988	-2.646663
H	4.441145	-2.322554	-4.134530
C	5.019705	-0.873106	-2.632278
H	4.970781	-0.767302	-1.540971
H	4.405917	-0.063698	-3.049446
C	6.471050	-0.708931	-3.094717
H	7.112996	-1.487034	-2.666250
H	6.876473	0.261833	-2.792055
H	6.549402	-0.778281	-4.185597
N	-0.884215	1.808992	-0.884750
N	1.434438	2.281321	0.442567
N	-0.323965	1.115575	2.588452

N	1.132543	-0.989451	1.649194
N	-3.853213	-0.122006	-1.082602
N	2.819479	-2.478889	-1.143425
O	-1.817586	-0.424196	0.024005
O	1.411340	-0.703953	-0.939707
Fe	-0.011883	0.351064	0.410636
H	3.302187	-3.228055	-0.666620

Charge = 1; multiplicity = 5; (0 imaginary frequencies)
Zero-point correction = 0.635690 (Hartree/Particle)
Thermal correction to Energy = 0.671941
Thermal correction to Enthalpy = 0.672885
Thermal correction to Gibbs Free Energy = 0.563053
Sum of electronic and zero-point Energies = −1616.077931
Sum of electronic and thermal Energies = −1616.041680
Sum of electronic and thermal Enthalpies = −1616.040736
Sum of electronic and thermal Free Energies = −1616.150568

Table S24. Atomic coordinates for the DFT optimized structure of $Fe(III)(mep(CONBu^{-})_2)$



Atom	X	Y	Z
C	-2.146502	1.302436	-1.541440
C	-2.882947	2.036641	-2.467639
H	-3.846216	1.669465	-2.798651
C	-2.343454	3.236915	-2.932260
H	-2.895508	3.836583	-3.648571
C	-1.095797	3.676553	-2.475632
H	-0.667640	4.608919	-2.825785
C	-0.410161	2.885460	-1.557490
C	0.972776	3.165047	-1.017288
H	1.706613	2.747915	-1.714661
H	1.165506	4.242466	-0.948837
C	0.541062	3.300749	1.389050
H	-0.386367	3.728939	1.002466
H	1.192879	4.139345	1.664616
C	0.257319	2.451902	2.622597
H	1.184627	2.022027	3.007602
H	-0.157219	3.086589	3.416019
C	2.617550	2.294853	0.548238
H	3.023340	1.642756	-0.225299
H	2.767327	1.819093	1.517534
H	3.153747	3.251776	0.540042
C	-2.085010	1.806099	2.267724
H	-2.403767	2.185471	3.246316
H	-2.728993	0.978687	1.969523
H	-2.184078	2.605644	1.533416
C	-0.550457	0.253215	3.336091
H	-1.451649	-0.366302	3.281691
H	-0.503192	0.669226	4.349414
C	0.646153	-0.620517	3.040440
C	1.336300	-1.391562	3.972252
H	1.066259	-1.359209	5.021696
C	2.380726	-2.205557	3.519427
H	2.932078	-2.815763	4.227351
C	2.720474	-2.231699	2.166072
H	3.524603	-2.847857	1.784096
C	1.994680	-1.425697	1.292588
C	-2.541070	0.007133	-0.907358
C	-4.008151	-1.798411	-0.582714
H	-3.930737	-1.709811	0.511846

H	-3.282542	-2.575664	-0.869994
C	-5.419851	-2.237682	-0.974629
H	-6.129809	-1.450747	-0.686270
H	-5.476178	-2.318642	-2.068428
C	-5.834171	-3.567507	-0.334756
H	-5.767187	-3.481165	0.758487
H	-5.116185	-4.347895	-0.622128
C	-7.248837	-4.007158	-0.725712
H	-7.992885	-3.262700	-0.419782
H	-7.516477	-4.958739	-0.254647
H	-7.337104	-4.135684	-1.810640
C	2.200758	-1.290004	-0.182446
C	3.294735	-1.829278	-2.196661
H	3.165377	-0.781997	-2.507498
H	2.505594	-2.398919	-2.710516
C	4.666128	-2.346502	-2.640232
H	4.771826	-3.391473	-2.319015
H	4.698187	-2.350529	-3.737972
C	5.837565	-1.520502	-2.096010
H	5.775700	-1.495920	-1.000869
H	5.729916	-0.479921	-2.433253
C	7.205834	-2.059078	-2.525120
H	7.354793	-3.086189	-2.172203
H	8.021101	-1.447979	-2.123492
H	7.303777	-2.068582	-3.617010
N	-0.947331	1.739439	-1.117617
N	1.169177	2.498864	0.299741
N	-0.680060	1.332493	2.318622
N	0.991183	-0.653668	1.746050
N	-3.658466	-0.534305	-1.223999
N	3.117459	-1.977897	-0.755187
O	-1.641575	-0.458122	-0.044727
O	1.363477	-0.429491	-0.757277
Fe	0.014524	0.494159	0.278601

Charge = 1; multiplicity = 6; (0 imaginary frequencies)
Zero-point correction = 0.623483 (Hartree/Particle)
Thermal correction to Energy = 0.658880
Thermal correction to Enthalpy = 0.659824
Thermal correction to Gibbs Free Energy = 0.551464
Sum of electronic and zero-point Energies = –1615.439165
Sum of electronic and thermal Energies = –1615.403768
Sum of electronic and thermal Enthalpies = –1615.402824
Sum of electronic and thermal Free Energies = –1615.511183

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