SUPPORTING INFORMATION

Pyridine Modifications Regulate Electronics and Reactivity of Fe-Pyridinophane Complexes

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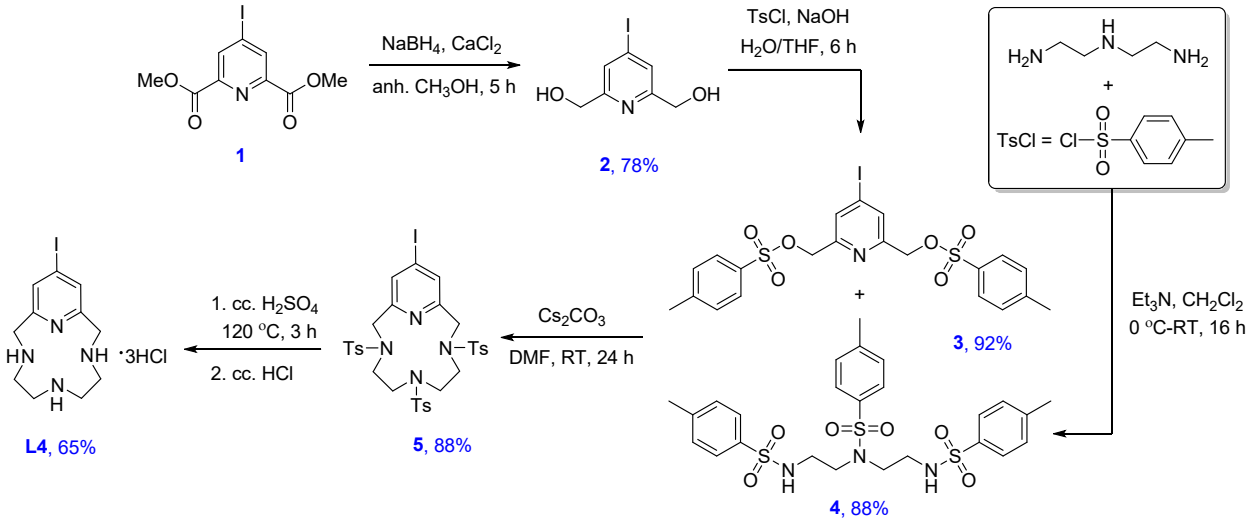
EXPERIMENTAL METHODS

SYNTHETIC PROCEDURES



Scheme S1: Synthetic route to **L4** ($^{I}PyN_3$) macrocycle.

Synthesis of 2. Molecule **1** was synthesized using previously published procedure.[2] A 250 mL two-necked round bottom flask was charged with **1** (8.08 g, 25.1 mmol), finely powdered $CaCl_2$ (2.79 g, 25.2 mmol), and anhydrous MeOH (150 mL) under N_2 atmosphere. $NaBH_4$ (1.89 g, 50.6 mmol) was added portion-wise for ca. 10 min to the suspension at room temperature and stirred. During the addition, the color of the white suspension changed to bright pink and then orange. The reaction was monitored by TLC [R_f (**1**) = 0.53, R_f (**2**) = 0.1 (diethyl ether)]. After 5 h, the resulting colorless suspension was filtered through silica gel (3 cm × 2 cm, rinsing with MeOH). The solvents of the filtrate were removed by rotary evaporation and the residual colorless solid was dissolved in 1 M HCl (100 mL). The pH of the solution was raised to pH 12 by the addition of 1.0 M aqueous NaOH, resulting in a solid precipitate. The tan precipitate was isolated by filtration, washed with water (200 mL), and dried using rotary evaporation. After drying for 5 d in a lyophilizer, **2** (5.21 g, 19.7 mmol, 78%) was obtained as a white powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 7.70 (s, 2H), 5.52 (t, J=4.11 Hz, 2H), 4.48 (d, J=4.01 Hz, 4H).

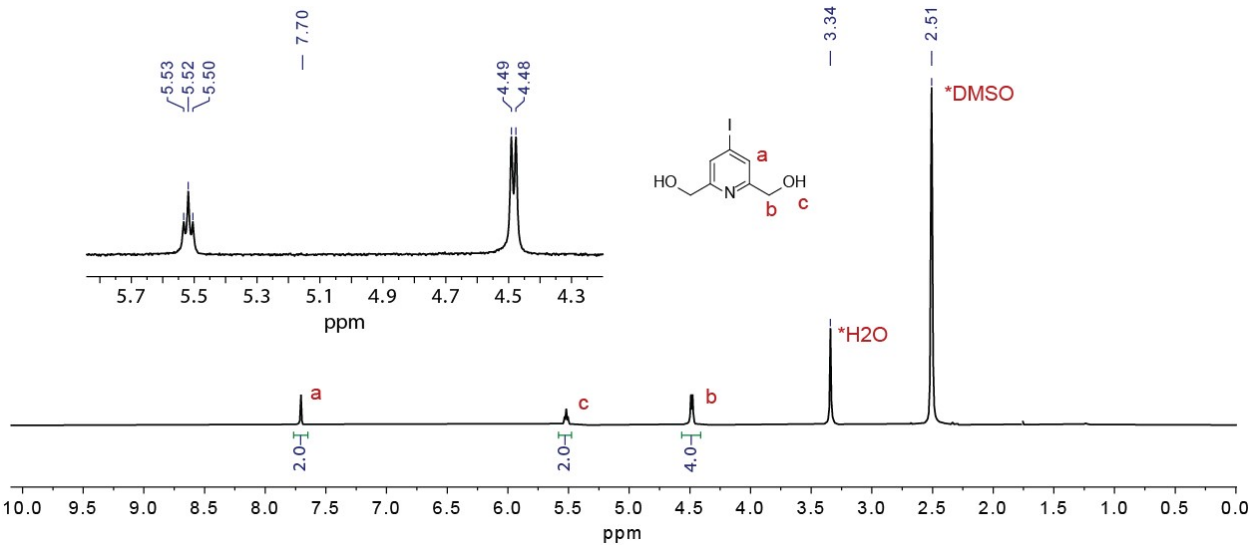


Figure S1. [1]H NMR (DMSO-d_6) spectrum of **2**.

Synthesis of 3. Procedure for similar intermediate was followed**.** [3] A 250 mL round bottom flask was charged with **2** (5.22 g, 19.7 mmol), NaOH (3.21 g, 80.2 mmol), H_2O (20 mL), and THF (20 mL) at 0 °C and stirred. A solution of tosyl chloride (16.9 g, 88.8 mmol) in THF (30 mL) was added dropwise to this mixture for ca. 10 min. The mixture was stirred at 0 °C for 2 h, and at room temperature for 2 h. The mixture was concentrated using rotary evaporation and H_2O (60 mL) was added. The mixture was extracted with CH_2Cl_2 (3X50 mL). The organic layer was dried (anhydrous Na_2SO_4) and filtered. The solvent was evaporated using rotary evaporation to obtain tan solid crystals, which were washed with diethyl ether (200 mL). The residual solvent was removed using an oil pump vacuum to obtain **3** (10.4 g, 18.1 mmol, 92%) as white crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.81 (d, *J*=8.04 Hz, 4H), 7.64 (s, 2H), 7.36 (d, *J*=8.13 Hz, 4H), 5.01 (s, 4H), 2.47 (s, 6H); **^{13}C** (101 MHz, $CDCl_3$) δ: 154.1, 145.4, 132.5, 130.4, 130.0, 128.1, 107.0, 70.4, 21.7.

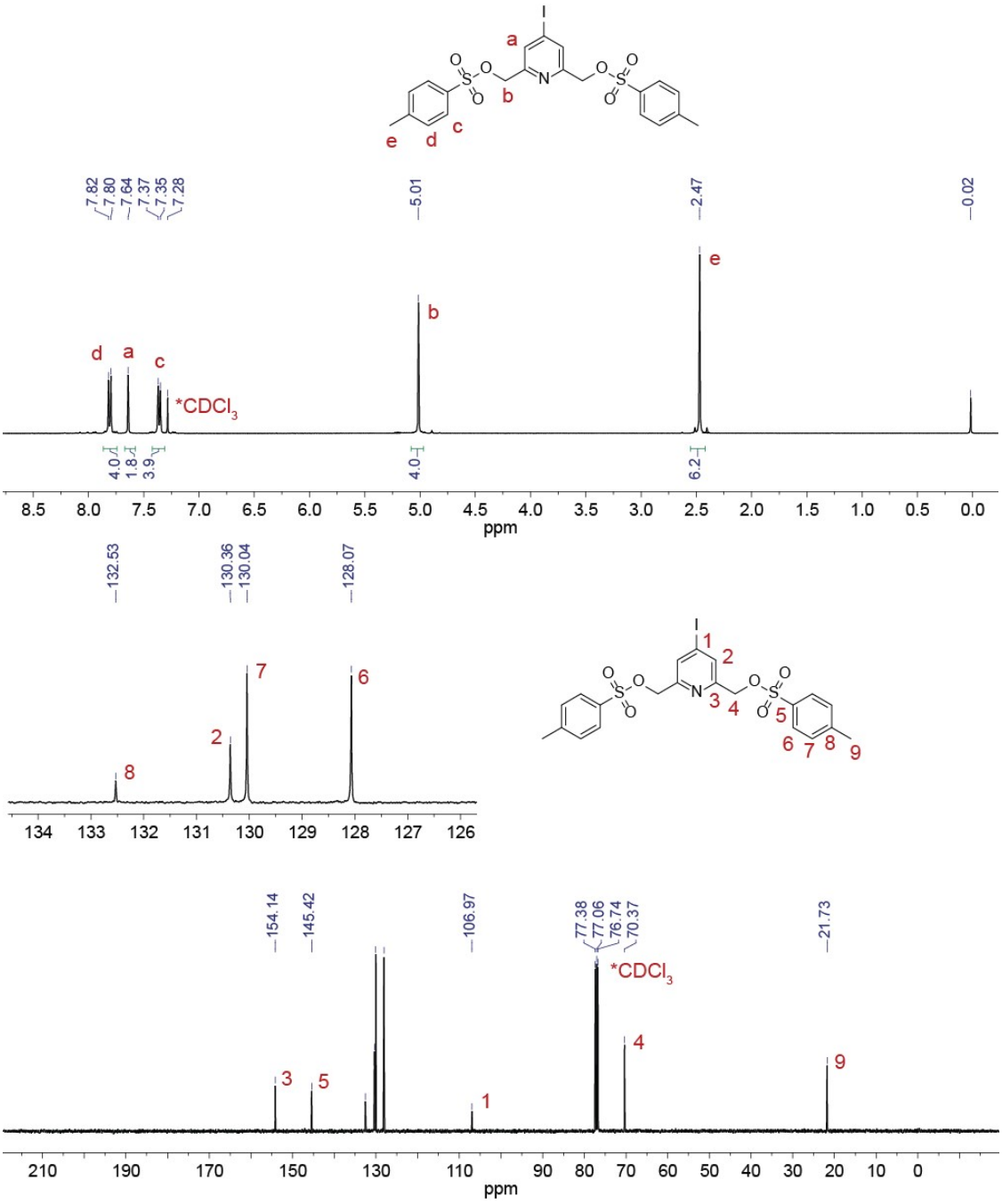


Figure S2. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR ($CDCl_3$) spectra of **3**.

Synthesis of 4. According to literature procedures.[4] A 500 mL round bottom flask was charged with tosyl chloride (4.01 g, 38.8 mmol), triethylamine (13.1 g, 13.0 mmol), and CH_2Cl_2 (200 mL) at 0 °C. The solution was stirred for 10 min. Diethylenetriamine (4.002 g, 38.8 mmol) was added dropwise to the solution for ca. 30 min, and the reaction mixture was stirred overnight. The solvent was evaporated from the mixture to obtain a white solid, which was recrystallized from MeOH to obtain **4** (19.3 g, 34.1 mmol, 88%) as a white powder. **^{1}H NMR** (400 MHz, acetone-d_6) δ: 7.77 (d, *J*=8.02 Hz, 4H), 7.65 (d, *J*=12.0 Hz, 2H), 7.41 (m, 6H), 6.59 (t, *J*=3.89 Hz, 2H), 3.20 (m, 4H), 3.07 (q, *J*=8.0 Hz, 4H), 2.45 (m, 9H).

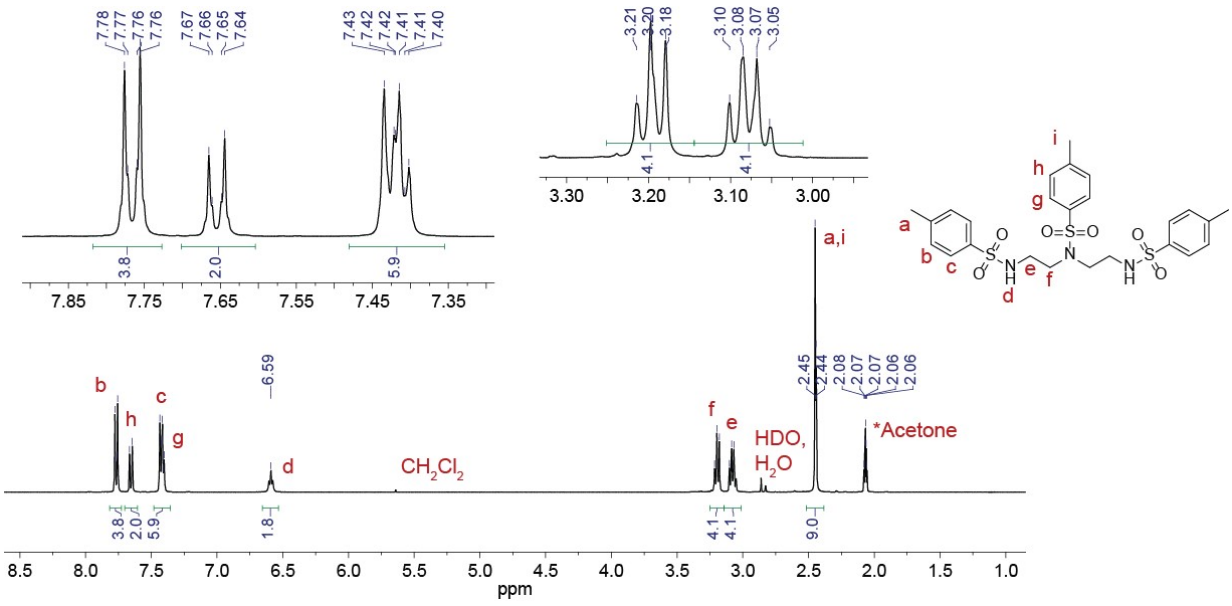


Figure S3. ^{1}H NMR (Acetone-d_6) spectrum of **4**.

Synthesis of 5.[5] A 250 mL two-necked round bottom flask was charged with **4** (1.98 g, 3.55 mmol), Cs_2CO_3 (3.42 g, 10.5 mmol), and anhydrous DMF (150 mL) under an N_2 atmosphere. **3** (2.04 g, 3.55 mmol) in DMF (25 mL) was added dropwise to the mixture for ca. 10 min and stirred. After 16 h, the solvent was removed using rotary evaporation to obtain a tan solid. Water (50.0 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The solvent was removed from the organic phase by rotary evaporation to obtain **5** (2.49 g, 3.13 mmol, 88%) as a tan powder. *Note: This product was >95% pure (^{1}H NMR). To obtain a pure sample, the final product obtained can be washed multiple times with small amounts of*

EtOAc. Since the desired product is slightly soluble in EtOAc, a small yield is lost. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 7.72 – 7.68 (m, 8H), 7.48-7.44 (m, 6H), 4.31 (s, 4H), 3.60 (t, *J*=4.06 Hz, 4H), 3.11 (t, *J*=4.12 Hz, 4H) 2.43 (s, 6H) 2.42 (s, 3H); **^{13}C** (101 MHz, DMSO-d_6) δ:157.8, 144.1, 143.8, 138.4, 135.4, 131.1, 130.5, 127.5, 127.1, 108.4, 54.5, 49.7, 46.1, 21.52, 21.48. **Elemental analysis:** Calc. (Found) for **5**: C, 48.36 (48.32); H, 4.44 (4.40); N, 7.05 (6.97). **HRMS**: calc. (found) (M+H^{+}, m/z) 795.0836 (795.0845)

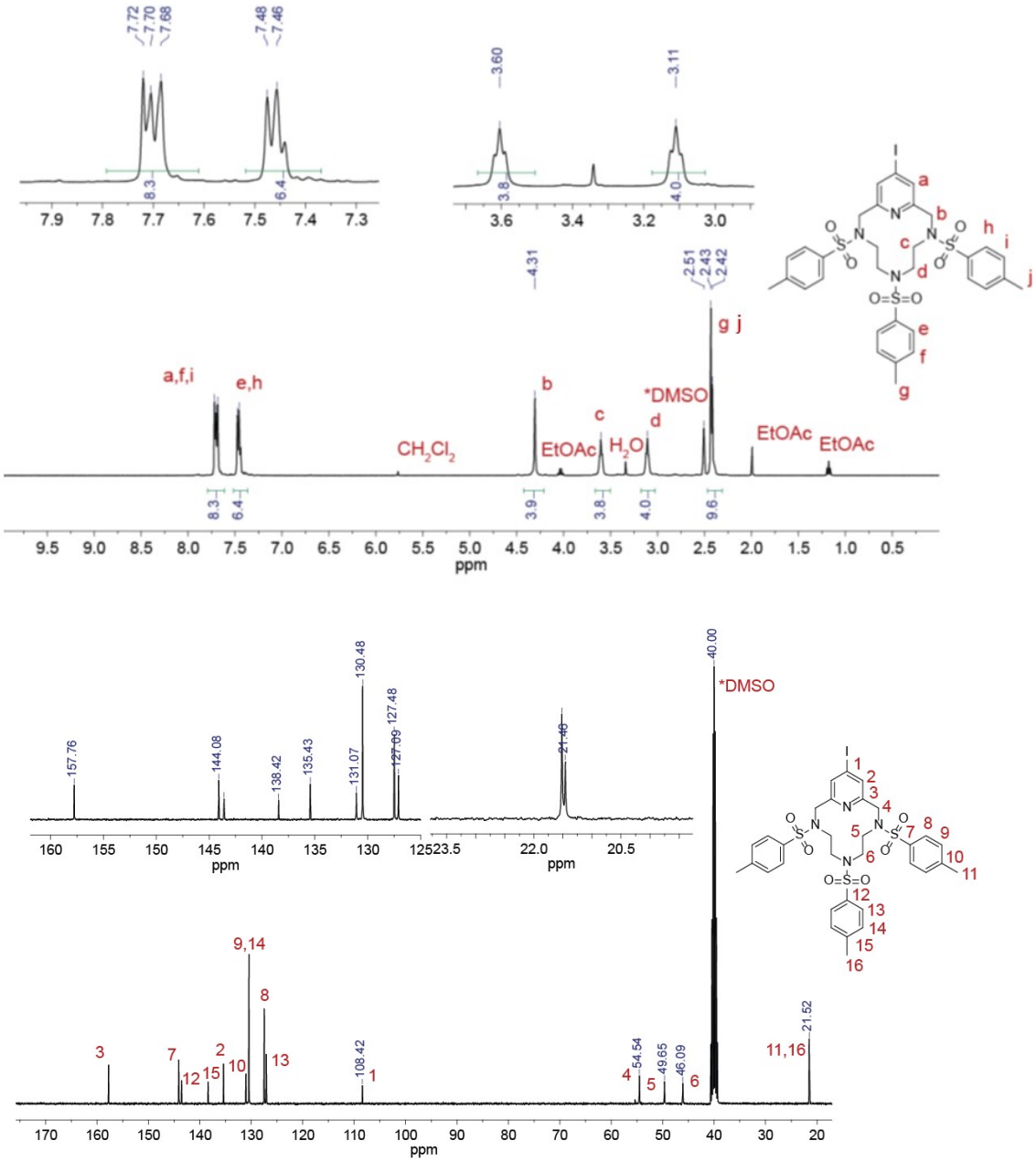


Figure S4. ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR (DMSO-d_6) spectra of **5**.

Synthesis of L4·3HCl. Previously reported deprotection (or detosylation) methods were used to design the synthesis of **L4**.[5] A 100 mL round bottom flask was charged with **5** (0.641 g, 0.811 mmol) and cc. H_2SO_4 (10 ml). The mixture was stirred at 120 °C. After 3 h, the oil bath was removed and the mixture was allowed to cool to room temperature. The mixture was then washed with diethyl ether (200 mL) to remove the organic impurities. 1 M NaOH was added to the aqueous fraction until the pH of the solution reached 12. CH_2Cl_2 (100 mL) was added to the flask and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The solvent was removed from the organic extracts using rotary evaporation to obtain a tan oil. The least amount of cc. HCl (1 mL) was added to the mixture. Anhydrous EtOH (5 mL) and diethyl ether (20 mL) were then added dropwise to the flask, and a white solid precipitated. The solid was collected by filtration, washed with CH_2Cl_2 (20 mL), and dried using an oil pump vacuum to obtain **L4·HCl** (0.232 g, 0.532 mmol, 65%) as white crystals. **^{1}H NMR** (400 MHz, D_2O) 7.89 (s, 2H), 4.50 (s, 4H), 3.27 (t, *J*=8.10 Hz, 4H), 3.13 (t, *J*=7.96 Hz, 4H); **^{13}C** (101 MHz, D_2O) 150.2, 132.8, 108.8, 48.5, 44.6, 43.4. **Elemental analysis:** Calc. (Found) for $C_{11}H_{21}IN_4Na_4Cl_8$: C, 18.56(18.82); H, 2.97(3.16); N, 7.87(7.83). **HRMS**: calc. (found) ($M+H^+$, m/z) 333.0571 (333.0559).

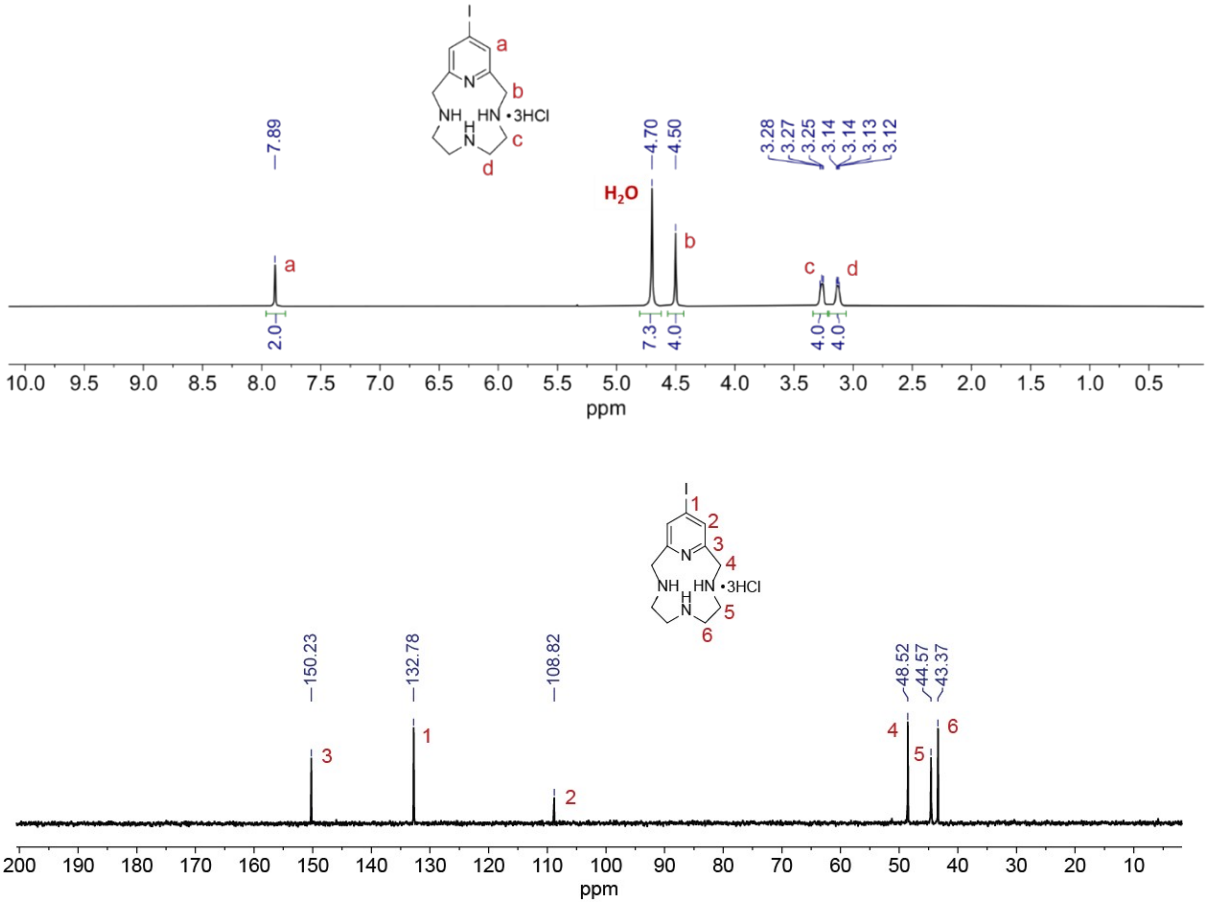
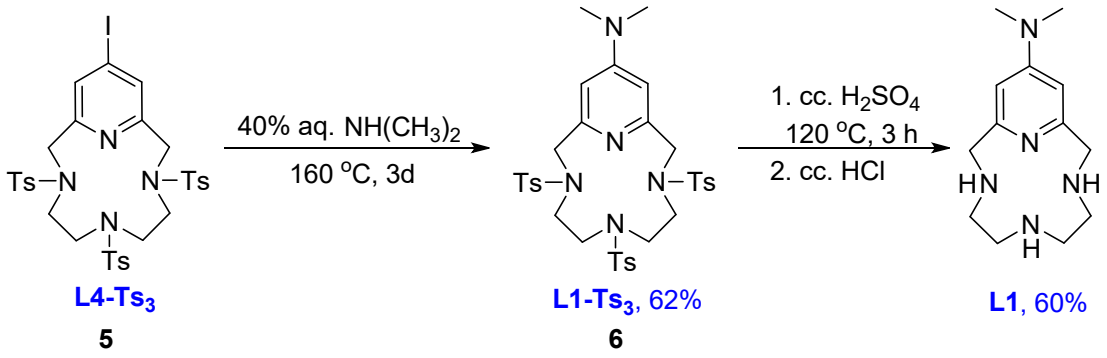


Figure S5. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR (D_2O) spectra of **6·HCl**.



Scheme S2. Synthetic route to $^{NMe_2}PyN_3$ macrocycle.

Synthesis of 6. Methods previously reported were used to design the synthesis of **6**.[5] A 75 mL pressure flask was charged with **5** (0.618 g, 0.755 mmol), in 40% aqueous dimethyl amine solution (10.0 mL, 75.6 mmol) the flask was sealed and placed under 160 °C. After 3 days the mixture was left to cool to room temperature, resulting in a white precipitate. The solid was collected by filtration, washed with CH_2Cl_2 (20 mL), and dried using an oil pump vacuum to obtain **6** (0.338 g, 0.462 mmol, 61%) as white crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.71 (d, *J*=8.24 Hz, 3H), 7.67 (d, *J*=8.24 Hz, 3H), 7.33 (d, *J*=7.96 Hz, 3H), 7.28(d, *J*=8.00 Hz, 3H) 6.56 (s, 2H), 4.14 (br s, 4H), 3.33 (br, 4H), 2.99 (s, 6H) 2.75 (s, 4H), 2.44 (s, 6H), 2.42 (s, 3H); **^{13}C** (101 MHz, $CDCl_3$)δ:156.2, 154.9, 143.7, 143.4, 136.2, 135.2, 129.9, 129.8, 127.2, 127.1, 106.7, 55.4, 47.0, 39.4, 21.6; **Elemental analysis:** Calc. (Found) for $C_{34}H_{41}N_5O_6S_3$: C, 57.36(56.71); H,5.81(5.75); N, 9.84(9.76). **HRMS**: calc. (found) ($M+H^+$, m/z) 712.2292 (712.2290).

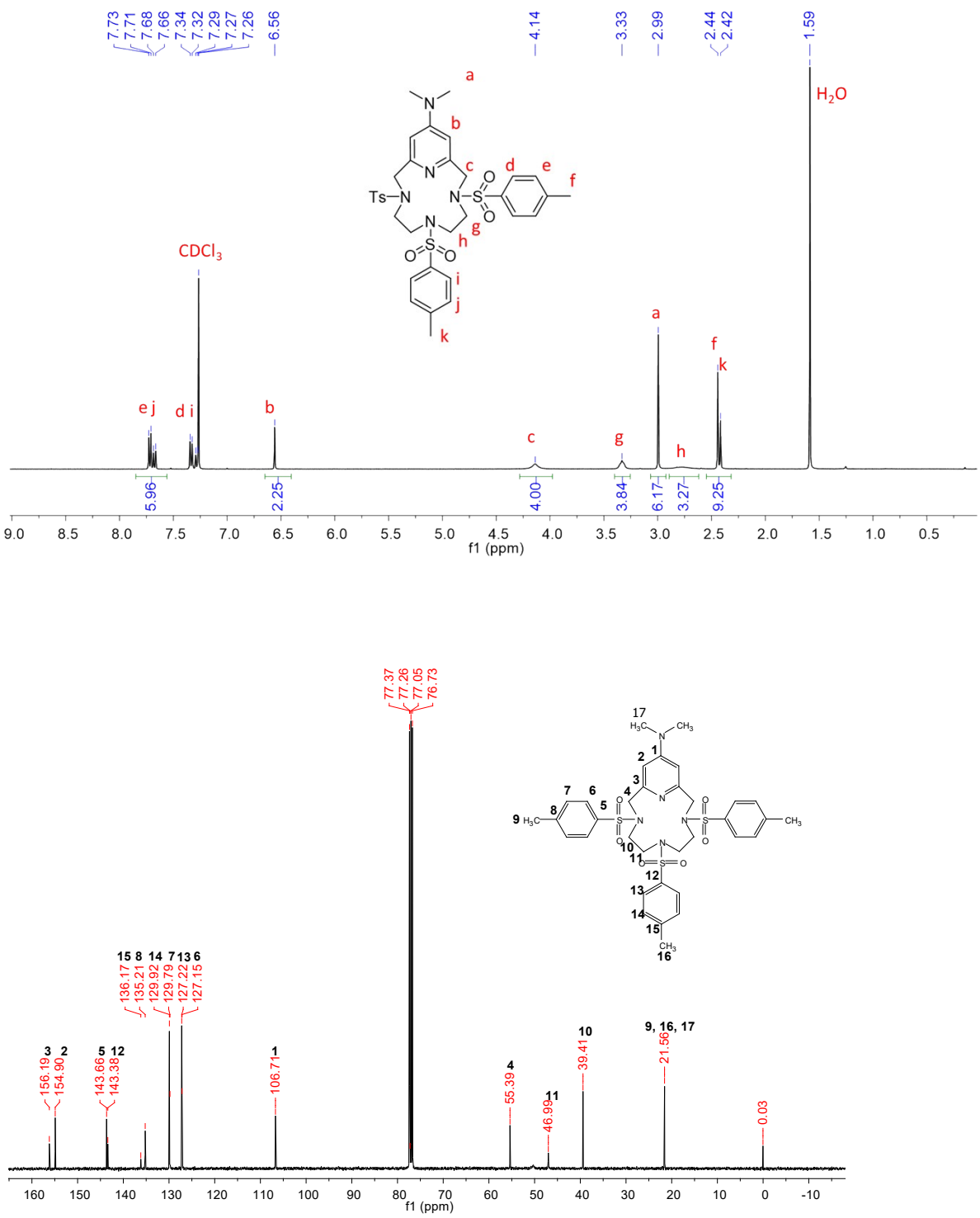


Figure S6. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR of **6**.

Synthesis of L1·3HCl.[5] A 100 mL round bottom flask was charged with **6** (0.743 g, 1.04 mmol) and cc. H_2SO_4 (10 ml). The mixture was stirred at 120 °C. After 3 h, the oil bath was removed and the mixture was allowed to cool to room temperature. The mixture was then washed with diethyl ether (200 mL) to remove the organic impurities. 1 M NaOH was added to the aqueous fraction until the pH of the solution reached 12. CH_2Cl_2 (100 mL) was added to the flask and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The solvent was removed from the organic extracts using rotary evaporation to obtain a tan oil. The least amount of cc. HCl (2 mL) was added to the mixture. Anhydrous EtOH (5 mL) and diethyl ether (20 mL) were added dropwise to the flask, and a white solid precipitated. The solid was collected by filtration, washed with CH_2Cl_2 (20 mL), and dried using an oil pump vacuum to obtain **L1·HCl** (0.224 g, 0.630 mmol, 60%) as white crystals. **^{1}H NMR** (400 MHz, D_2O) 6.63 (s, 2H), 4.31 (s, 4H), 3.39-3.41 (m, 4H), 3.32-3.34 (m, 4H), 2.93 (s, 6H); **^{13}C** (101 MHz, D_2O) 156.7, 149.1, 133.1, 106.2, 49.1, 43.0, 38.8. **Elemental analysis:** Calc. (Found) for $C_{27}H_{58}N_{10}OCl_8$: C, 39.43(39.14); H, 7.11(7.46); N, 17.25(17.03). **HRMS**: calc. (found) ($M+H^+$, m/z) 250.2026 (250.2019)

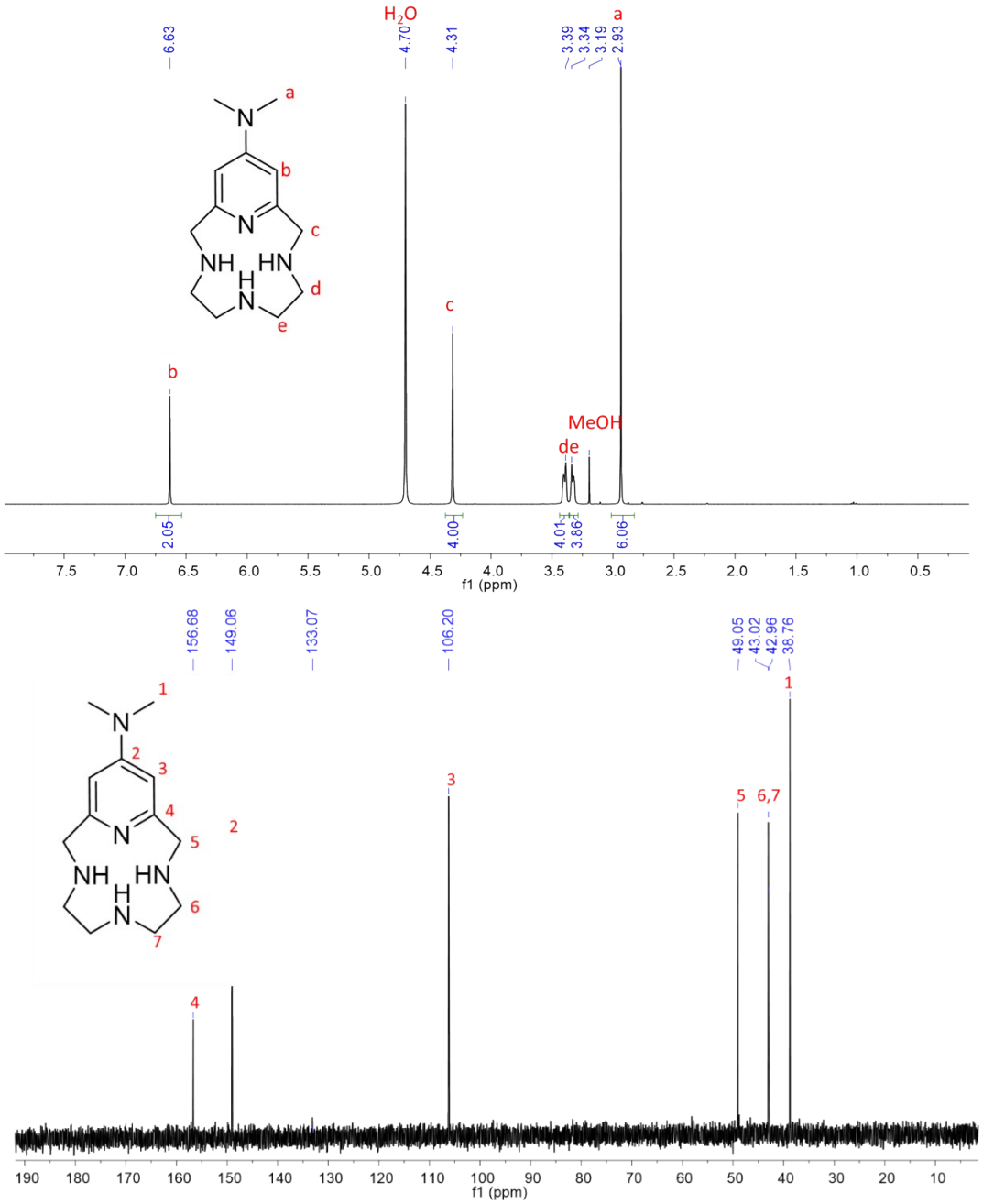


Figure S7. ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR (D_2O) spectra of **L1**.

POTENTIOMETRIC RESULTS

Table S1. Binding stability constants (log β) for ligands **L1**, **L2**, and **L4** with Fe(II)

		L1 (NMe_2)	**L2** (OMe)	**L4** (I)
Fe(II)	[ML]/([M][L])	13.14(4)	13.01 (4)	13.71 (3)
	[MHL]/([ML][H])	4.34(10)	3.97 (10)	3.99 (7)
	[ML]/([MLOH][H])	8.92(9)	8.74 (7)	9.26 (5)
	[ML(OH)]/([ML(OH)2][H])	-	11.60 (9)	12.26 (5)

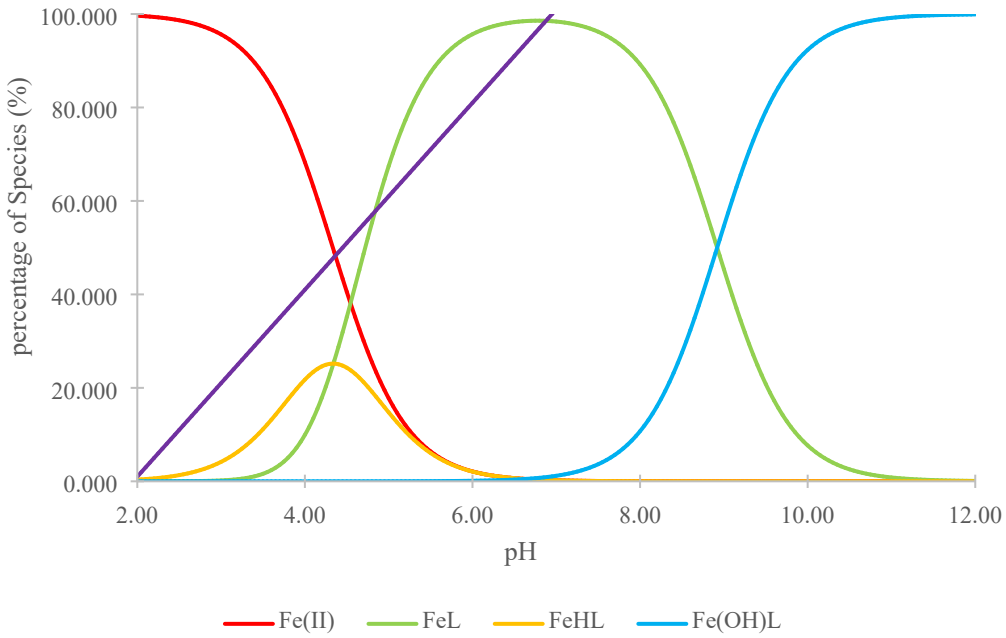


Figure S8. Species distribution curves for [**FeL1**] (I = 0.15 M NaCl, T = 25 °C, $[\mathbf{L1}]_{tot} = [\mathbf{Fe}]_{tot}$ = 2 mM).

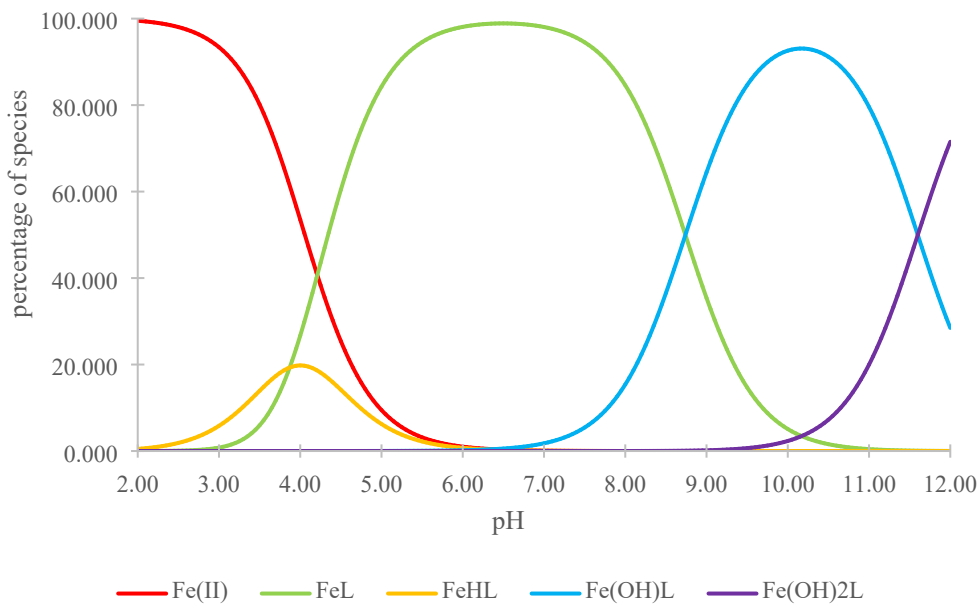


Figure S9. Species distribution curves for [**FeL2**] (I = 0.15 M NaCl, T = 25 °C, $[\mathbf{L1}]_{tot} = [\mathbf{Fe}]_{tot}$ = 2 mM).

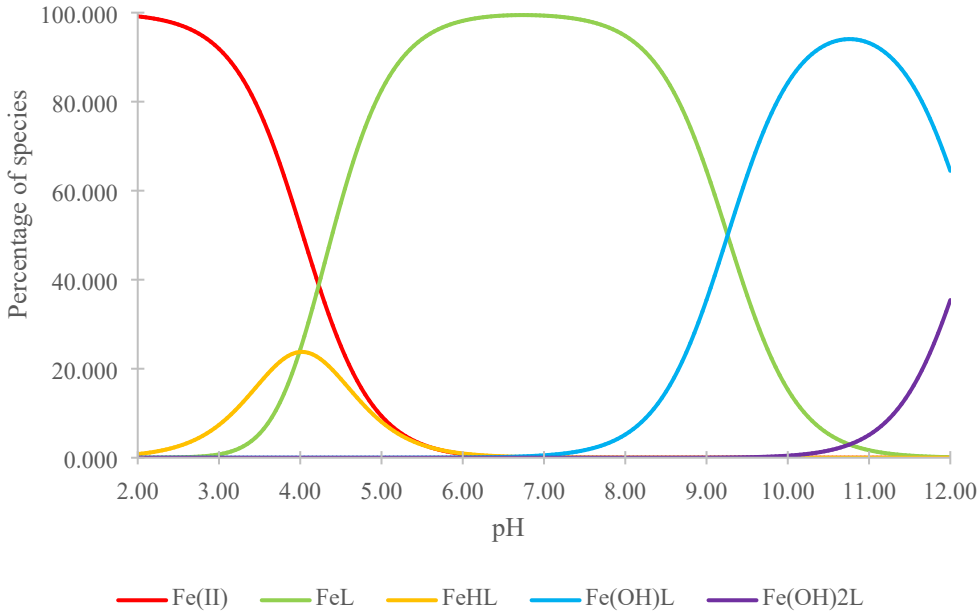


Figure S10. Species distribution curves for [**FeL4**] (I = 0.15 M NaCl, T = 25 °C, $[\mathbf{L1}]_{tot} = [\mathbf{Fe}]_{tot}$ = 2 mM).

X-RAY DIFFRACTION RESULTS

Table S2. Crystal data, intensity collections, and structure refinement parameters for **FeL1, FeL2** and **FeL4.**

Complex	**FeL1**	**FeL2**	**FeL4**
Formula	$C_{14}H_{23}Cl_2F_3FeN_5O_3S$	$C_{13}H_{20}Cl_2F_3FeN_4O_4S$	$C_{12}H_{17}Cl_2F_3FeIN_4O_3S$
M.W.	525.18	512.140	608.58
Unit cell	Orthorhombic	monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a (Å)	6.8637(4)	7.0308(5)	25.1399(17)
b (Å)	8.6169(5)	13.8067(9)	8.2657(5)
c (Å)	36.4304(19)	20.6288(14)	31.080(2)
α	90	90	90
β	90	97.035(3)	111.259(2)
γ	90	90	90
Volume (Å^3)	2154.6(2)	1987.4(2)	6018.9(7)
Z	4	4	12
$D_{calc.}$(g/cm^3)	1.619	1.712	2.015
Reflections Collected	54526	164665	386474
Independent Reflections	3778	3832	16935
R_{int}	0.0431	0.0391	0.0534
Completeness to θ	99	97.89	99
GooF	1.132	1.0046	1.269
R1,wR2 [I>2sigma(I)]	0.1186, 0.2586	0.0481, 0.1273	0.0371, 0.0678
R1, wR2	0.1189, 0.2587	0.0480, 0.1272	0.0410, 0.0690

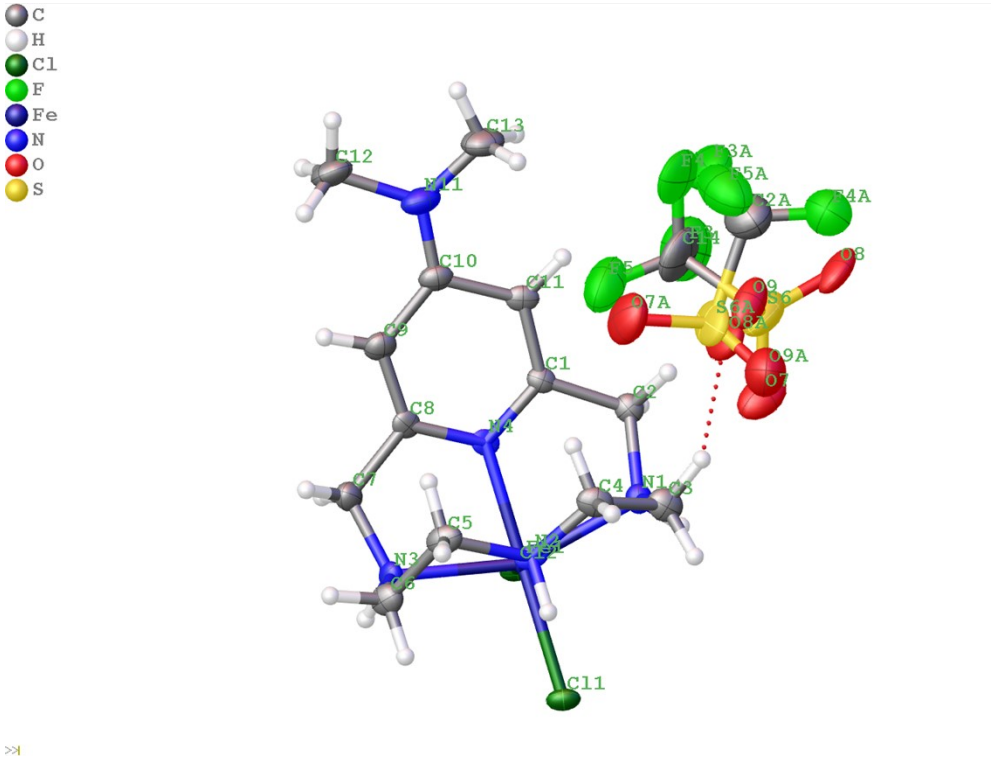


Figure S11. Solid state structure of **FeL1** showing atom labeling.

Table S3. Bond Lengths for **FeL1.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N4	2.046(11)	C1	C2	1.51(3)
Fe1	N3	2.187(15)	N2	C5	1.55(2)
Fe1	N1	2.170(16)	N2	C4	1.40(3)
Fe1	Cl2	2.318(4)	C5	C6	1.59(3)
Fe1	Cl1	2.298(4)	C3	C4	1.40(3)
Fe1	N2	2.180(12)	C14	F3	1.312(17)
N4	C8	1.35(2)	C14	F4	1.335(17)
N4	C1	1.36(2)	C14	F5	1.323(17)
N3	C7	1.47(3)	C14	S6	1.80(2)
N3	C6	1.48(3)	S6	O7	1.400(15)
C8	C9	1.36(3)	S6	O8	1.443(16)
C8	C7	1.49(3)	S6	O9	1.453(16)
N1	C2	1.55(3)	S6A	C2A	1.83(3)
N1	C3	1.52(3)	S6A	O7A	1.42(2)
C9	C10	1.43(3)	S6A	O8A	1.44(2)
N11	C10	1.30(2)	S6A	O9A	1.42(2)
N11	C12	1.53(3)	C2A	F3A	1.32(2)
N11	C13	1.40(3)	C2A	F4A	1.31(2)
C11	C1	1.38(3)	C2A	F5A	1.32(2)
C11	C10	1.47(3)			

Table S4. Bond Angles for **FeL1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N4	Fe1	N3	78.5(6)	C1	C2	N1	108.7(14)
N4	Fe1	N1	77.7(6)	C9	C10	C11	115.2(14)
N4	Fe1	Cl2	92.7(2)	N11	C10	C9	128(2)
N4	Fe1	Cl1	175.8(2)	N11	C10	C11	116(2)
N4	Fe1	N2	87.1(4)	C5	N2	Fe1	109.1(11)
N3	Fe1	Cl2	100.3(5)	C4	N2	Fe1	109.3(12)
N3	Fe1	Cl1	100.5(5)	C4	N2	C5	117.1(13)
N1	Fe1	N3	149.3(5)	N2	C5	C6	102.5(15)
N1	Fe1	Cl2	99.9(5)	C4	C3	N1	109.5(18)
N1	Fe1	Cl1	101.8(5)	C3	C4	N2	115.2(18)
N1	Fe1	N2	78.5(7)	N3	C6	C5	109.6(17)
Cl1	Fe1	Cl2	91.49(15)	F3	C14	F4	106(2)
N2	Fe1	N3	81.3(7)	F3	C14	F5	110(2)
N2	Fe1	Cl2	178.4(5)	F3	C14	S6	110.9(18)
N2	Fe1	Cl1	88.7(3)	F4	C14	S6	112.2(16)
C8	N4	Fe1	119.2(12)	F5	C14	F4	104(2)
C8	N4	C1	118.6(12)	F5	C14	S6	112.7(18)
C1	N4	Fe1	121.2(12)	O7	S6	C14	113.1(14)
C7	N3	Fe1	109.9(12)	O7	S6	O8	112.9(17)
C7	N3	C6	110.0(17)	O7	S6	O9	112.4(16)
C6	N3	Fe1	106.3(13)	O8	S6	C14	105.1(14)
N4	C8	C9	122.7(18)	O8	S6	O9	110.7(17)
N4	C8	C7	114.6(16)	O9	S6	C14	101.9(12)
C9	C8	C7	122.6(18)	O7A	S6A	C2A	103(2)
C2	N1	Fe1	109.2(12)	O7A	S6A	O8A	116(2)
C3	N1	Fe1	108.9(12)	O8A	S6A	C2A	102.9(18)
C3	N1	C2	113.4(16)	O9A	S6A	C2A	106(2)
C8	C9	C10	121.5(19)	O9A	S6A	O7A	116(2)
C10	N11	C12	120(2)	O9A	S6A	O8A	112(2)
C10	N11	C13	123(2)	F3A	C2A	S6A	110(2)
C13	N11	C12	116.1(15)	F4A	C2A	S6A	110(2)
C1	C11	C10	118.4(17)	F4A	C2A	F3A	111(3)
N4	C1	C11	123.7(17)	F4A	C2A	F5A	112(3)
N4	C1	C2	113.7(15)	F5A	C2A	S6A	108(2)
C11	C1	C2	122.5(17)	F5A	C2A	F3A	105(3)
N3	C7	C8	112.7(16)				

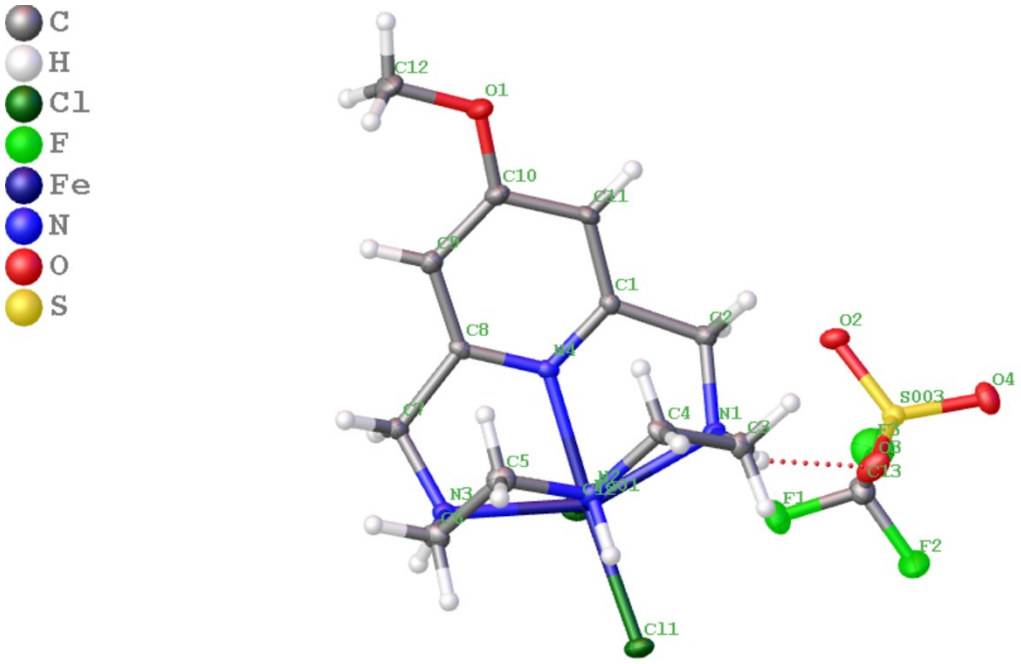


Figure S12. Solid state structure of **FeL2** showing atom labeling.

Table S5. Bond Lengths for **FeL2.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	Cl2	2.2708(11)	N2	C5	1.469(5)
Fe01	Cl1	2.2776(11)	O1	C10	1.343(5)
Fe01	N1	2.167(4)	O1	C12	1.444(5)
Fe01	N2	2.189(3)	N3	C6	1.492(5)
Fe01	N3	2.183(3)	N3	C7	1.486(5)
Fe01	N4	2.099(3)	N4	C1	1.349(5)
S003	O3	1.447(3)	N4	C8	1.341(5)
S003	O4	1.437(3)	C1	C2	1.508(6)
S003	O2	1.451(3)	C1	C11	1.377(6)
S003	C13	1.821(5)	C8	C7	1.512(5)
F2	C13	1.339(5)	C8	C9	1.386(6)
F1	C13	1.333(5)	C6	C5	1.531(6)
F3	C13	1.341(5)	C11	C10	1.393(6)
N1	C2	1.487(5)	C10	C9	1.400(6)
N1	C3	1.497(5)	C4	C3	1.522(6)
N2	C4	1.482(5)			

Table S6. Bond Angles for **FeL2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Fe01	Cl2	96.37(4)	C7	N3	Fe01	110.7(2)
N1	Fe01	Cl2	101.46(9)	C7	N3	C6	113.3(3)
N1	Fe01	Cl1	99.04(10)	C1	N4	Fe01	119.7(3)
N2	Fe01	Cl2	176.44(10)	C8	N4	Fe01	119.7(3)
N2	Fe01	Cl1	86.69(10)	C8	N4	C1	120.0(3)
N2	Fe01	N1	79.80(13)	C2	C1	N4	114.1(3)
N3	Fe01	Cl2	98.80(9)	C11	C1	N4	121.6(4)
N3	Fe01	Cl1	104.12(10)	C11	C1	C2	124.3(4)
N3	Fe01	N1	147.15(13)	C7	C8	N4	114.0(3)
N3	Fe01	N2	78.63(13)	C9	C8	N4	122.0(4)
N4	Fe01	Cl2	92.47(9)	C9	C8	C7	124.0(4)
N4	Fe01	Cl1	170.85(9)	C5	C6	N3	108.9(3)
N4	Fe01	N1	76.82(13)	C1	C2	N1	110.7(3)
N4	Fe01	N2	84.55(13)	C10	C11	C1	118.6(4)
N4	Fe01	N3	76.72(13)	C11	C10	O1	116.0(4)
O4	S003	O3	115.6(2)	C9	C10	O1	124.2(4)
O2	S003	O3	114.14(18)	C9	C10	C11	119.8(4)
O2	S003	O4	115.2(2)	C3	C4	N2	106.5(3)
C13	S003	O3	103.4(2)	C4	C3	N1	109.9(3)
C13	S003	O4	103.43(19)	C8	C7	N3	110.5(3)
C13	S003	O2	102.6(2)	C6	C5	N2	106.9(3)
C2	N1	Fe01	111.7(2)	C10	C9	C8	117.9(4)
C3	N1	Fe01	107.4(2)	F2	C13	S003	111.5(3)
C3	N1	C2	112.4(3)	F1	C13	S003	112.2(3)
C4	N2	Fe01	110.7(2)	F1	C13	F2	107.8(4)
C5	N2	Fe01	111.8(3)	F3	C13	S003	110.1(3)
C5	N2	C4	115.8(3)	F3	C13	F2	107.4(4)
C12	O1	C10	118.2(4)	F3	C13	F1	107.6(4)
C6	N3	Fe01	108.8(2)				

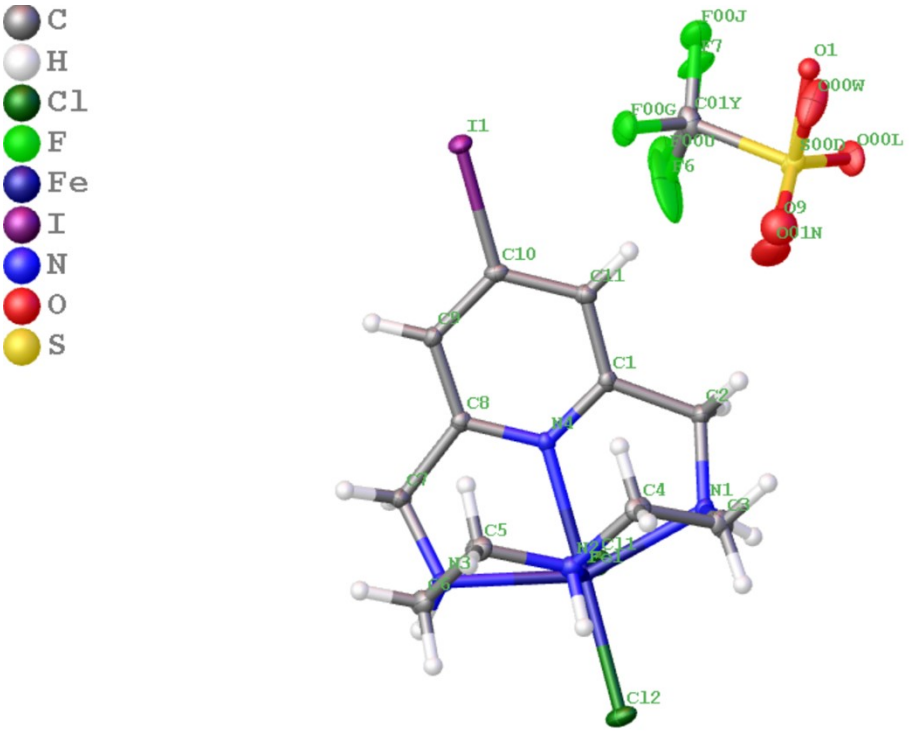


Figure S13. Solid state structure of **FeL4** showing atom labeling.

Table S7. Bond Lengths for **FeL4.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C10	2.092(3)	F00U	C01Y	1.324(11)
I002	C20	2.093(3)	F00U	F7	1.58(9)
I003	C31	2.091(3)	N00V	C12	1.487(4)
I003	I3	0.53(4)	N00V	C13	1.485(4)
Fe04	Cl4	2.2883(8)	O00W	O1	0.71(8)
Fe04	Cl3	2.2527(8)	F00X	C026	1.326(4)
Fe04	N00H	2.122(2)	N00Y	C32	1.476(4)
Fe04	N00S	2.164(3)	N00Y	C25	1.479(4)
Fe04	N00V	2.186(3)	N2	C4	1.479(4)
Fe04	N01C	2.188(3)	N2	C5	1.479(4)
Fe1	Cl1	2.2876(8)	N010	C24	1.490(4)
Fe1	Cl2	2.2397(8)	N010	C23	1.476(4)
Fe1	N4	2.124(2)	N011	C28	1.483(4)
Fe1	N1	2.163(2)	N011	C27	1.494(4)
Fe1	N3	2.178(2)	C18	C19	1.389(4)
Fe1	N2	2.215(3)	C18	C17	1.506(4)
Fe06	Cl5	2.2600(9)	C1	C11	1.382(4)
Fe06	Cl	2.2463(8)	C1	C2	1.511(4)
Fe06	N00N	2.110(2)	C10	C11	1.400(4)
Fe06	N00Y	2.209(3)	C10	C9	1.399(4)

Fe06	N010	2.198(3)	C20	C19	1.391(4)
Fe06	N011	2.170(3)	C20	C21	1.391(4)
S00C	O00O	1.446(2)	C33	C26	1.389(4)
S00C	O00T	1.442(3)	C33	C23	1.508(4)
S00C	O018	1.436(3)	C22	C21	1.383(4)
S00C	C026	1.815(3)	C22	C12	1.505(4)
S00D	O00L	1.434(2)	N01C	C15	1.471(5)
S00D	O00W	1.431(3)	N01C	C14	1.482(5)
S00D	O01N	1.442(3)	C9	C8	1.385(4)
S00D	C01Y	1.826(3)	C8	C7	1.519(4)
S00D	O9	1.45(3)	C30	C31	1.389(4)
S00D	O1	1.58(5)	C30	C29	1.388(4)
S00F	O01F	1.439(4)	C31	C26	1.395(4)
S00F	O023	1.452(5)	C31	I3	2.116(11)
S00F	C029	1.812(6)	C29	C28	1.504(4)
S00F	O10	1.437(5)	O01N	O9	0.77(5)
F00G	C01Y	1.341(4)	C3	C4	1.527(4)
N00H	C18	1.343(4)	C32	C24	1.512(4)
N00H	C22	1.344(4)	C6	C5	1.514(5)
F00I	C026	1.322(4)	C25	C27	1.515(5)
F00J	C01Y	1.360(10)	C01Y	F6	1.36(4)
F00J	F7	0.64(8)	C01Y	F7	1.14(3)
N4	C1	1.340(4)	F021	C029	1.324(7)
N4	C8	1.338(4)	C13	C14	1.511(6)
F00M	C026	1.329(4)	C16	C15	1.517(6)
N00N	C33	1.339(4)	F027	C029	1.331(7)
N00N	C29	1.341(4)	O10A	S00G	1.433(14)
N1	C2	1.487(4)	O01G	S00G	1.464(14)
N1	C3	1.488(4)	S00G	O0	1.440(15)
N3	C7	1.491(4)	S00G	C0	1.796(14)
N3	C6	1.489(4)	C0	F0	1.339(17)
F00R	C029	1.325(9)	C0	F1	1.311(14)
N00S	C17	1.486(4)	C0	F00S	1.337(13)
N00S	C16	1.492(5)			

Table S8. Bond Angles for **FeL4.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I3	I003	C31	85.4(10)	C28	N011	Fe06	110.28(18)
Cl3	Fe04	Cl4	98.19(3)	C28	N011	C27	113.3(3)
N00H	Fe04	Cl4	90.46(7)	C27	N011	Fe06	109.63(19)
N00H	Fe04	Cl3	171.20(7)	N00H	C18	C19	121.3(3)
N00H	Fe04	N00S	76.16(9)	N00H	C18	C17	114.4(2)
N00H	Fe04	N00V	76.44(9)	C19	C18	C17	124.2(3)
N00H	Fe04	N01C	83.83(10)	N4	C1	C11	120.9(3)
N00S	Fe04	Cl4	98.70(8)	N4	C1	C2	114.2(2)
N00S	Fe04	Cl3	100.82(7)	C11	C1	C2	124.9(3)
N00S	Fe04	N00V	146.94(10)	C11	C10	I1	119.2(2)
N00S	Fe04	N01C	79.72(12)	C9	C10	I1	120.6(2)
N00V	Fe04	Cl4	99.66(8)	C9	C10	C11	120.2(3)
N00V	Fe04	Cl3	103.47(7)	C19	C20	I002	119.7(2)
N00V	Fe04	N01C	79.29(12)	C19	C20	C21	121.3(3)
N01C	Fe04	Cl4	174.28(8)	C21	C20	I002	119.0(2)
N01C	Fe04	Cl3	87.51(7)	N00N	C33	C26	121.2(3)
Cl2	Fe1	Cl1	100.40(3)	N00N	C33	C23	114.4(3)
N4	Fe1	Cl1	88.94(7)	C26	C33	C23	124.4(3)
N4	Fe1	Cl2	170.67(7)	C1	C11	C10	118.3(3)
N4	Fe1	N1	76.75(9)	C18	C19	C20	117.4(3)
N4	Fe1	N3	76.41(9)	N00H	C22	C21	121.1(3)
N4	Fe1	N2	82.89(9)	N00H	C22	C12	114.6(2)
N1	Fe1	Cl1	97.41(7)	C21	C22	C12	124.2(3)
N1	Fe1	Cl2	101.89(7)	C15	N01C	Fe04	110.2(2)
N1	Fe1	N3	146.94(9)	C15	N01C	C14	116.4(3)
N1	Fe1	N2	79.01(9)	C14	N01C	Fe04	110.8(2)
N3	Fe1	Cl1	101.02(7)	C8	C9	C10	117.6(3)
N3	Fe1	Cl2	101.46(7)	N4	C8	C9	121.5(3)
N3	Fe1	N2	78.85(9)	N4	C8	C7	113.9(2)
N2	Fe1	Cl1	171.64(7)	C9	C8	C7	124.6(3)
N2	Fe1	Cl2	87.78(7)	C22	C21	C20	117.8(3)
Cl	Fe06	Cl5	100.21(3)	C29	C30	C31	118.1(3)
N00N	Fe06	Cl5	88.81(7)	N1	C2	C1	110.6(2)
N00N	Fe06	Cl	170.52(7)	N00S	C17	C18	110.7(2)
N00N	Fe06	N00Y	83.64(9)	I003	C31	I3	14.5(10)
N00N	Fe06	N010	76.09(9)	C30	C31	I003	120.5(2)
N00N	Fe06	N011	76.94(9)	C30	C31	C26	120.9(3)
N00Y	Fe06	Cl5	171.87(7)	C30	C31	I3	109.6(9)
N00Y	Fe06	Cl	87.49(7)	C26	C31	I003	118.5(2)
N010	Fe06	Cl5	102.22(7)	C26	C31	I3	128.8(8)
N010	Fe06	Cl	98.93(7)	C33	C26	C31	117.5(3)
N010	Fe06	N00Y	78.93(9)	N00N	C29	C30	120.7(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N011	Fe06	Cl5	96.80(7)	N00N	C29	C28	115.0(2)
N011	Fe06	Cl	104.61(7)	C30	C29	C28	124.3(3)
N011	Fe06	N00Y	78.59(10)	O9	O01N	S00D	75(2)
N011	Fe06	N010	146.45(10)	N3	C7	C8	110.1(2)
O00O	S00C	C026	104.43(16)	N00V	C12	C22	111.7(3)
O00T	S00C	O00O	113.83(15)	N1	C3	C4	109.8(2)
O00T	S00C	C026	103.44(17)	N2	C4	C3	106.7(2)
O018	S00C	O00O	114.64(18)	N011	C28	C29	111.4(2)
O018	S00C	O00T	115.12(18)	N00Y	C32	C24	107.3(2)
O018	S00C	C026	103.41(16)	N010	C24	C32	110.2(2)
O00L	S00D	O01N	114.2(3)	N3	C6	C5	110.3(2)
O00L	S00D	C01Y	103.33(15)	N010	C23	C33	111.5(2)
O00L	S00D	O9	134.3(17)	N00Y	C25	C27	107.4(3)
O00L	S00D	O1	99(2)	F00G	C01Y	S00D	111.8(2)
O00W	S00D	O00L	115.0(2)	F00G	C01Y	F00J	105.0(6)
O00W	S00D	O01N	116.3(5)	F00G	C01Y	F6	101(3)
O00W	S00D	C01Y	103.2(2)	F00J	C01Y	S00D	110.7(3)
O00W	S00D	O9	85(2)	F00U	C01Y	S00D	114.6(5)
O00W	S00D	O1	27(3)	F00U	C01Y	F00G	108.7(6)
O01N	S00D	C01Y	102.2(2)	F00U	C01Y	F00J	105.4(8)
O01N	S00D	O9	31.0(19)	F00U	C01Y	F6	19(6)
O01N	S00D	O1	142(3)	F6	C01Y	S00D	103(4)
O9	S00D	C01Y	111.4(13)	F6	C01Y	F00J	124(6)
O9	S00D	O1	111(4)	F7	C01Y	S00D	115.0(16)
O1	S00D	C01Y	88(3)	F7	C01Y	F00G	123(3)
O01F	S00F	O023	113.9(3)	F7	C01Y	F00J	28(4)
O01F	S00F	C029	103.0(3)	F7	C01Y	F00U	79(5)
O023	S00F	C029	103.2(3)	F7	C01Y	F6	98(8)
O10	S00F	O01F	116.0(3)	N2	C5	C6	106.5(2)
O10	S00F	O023	113.6(3)	N011	C27	C25	109.9(2)
O10	S00F	C029	105.1(4)	N00V	C13	C14	110.0(3)
C18	N00H	Fe04	119.38(19)	N00S	C16	C15	109.7(3)
C22	N00H	Fe04	119.52(19)	N01C	C15	C16	106.9(3)
C22	N00H	C18	121.1(2)	F00I	C026	S00C	111.6(2)
F7	F00J	C01Y	57(2)	F00I	C026	F00M	107.6(3)
C1	N4	Fe1	118.91(18)	F00I	C026	F00X	107.7(3)
C8	N4	Fe1	119.36(19)	F00M	C026	S00C	110.3(3)
C8	N4	C1	121.4(2)	F00X	C026	S00C	110.6(2)
C33	N00N	Fe06	120.01(19)	F00X	C026	F00M	108.9(3)
C33	N00N	C29	121.5(2)	N01C	C14	C13	107.6(3)
C29	N00N	Fe06	118.49(19)	F00R	C029	S00F	111.3(5)
C2	N1	Fe1	111.27(17)	F00R	C029	F027	107.4(6)
C2	N1	C3	112.7(2)	F021	C029	S00F	110.1(4)
C3	N1	Fe1	108.56(17)	F021	C029	F00R	109.5(7)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N3	Fe1	110.71(17)	F021	C029	F027	109.3(5)
C6	N3	Fe1	108.41(18)	F027	C029	S00F	109.3(4)
C6	N3	C7	112.4(2)	I003	I3	C31	80.1(14)
C17	N00S	Fe04	111.79(18)	F00J	F7	F00U	146(3)
C17	N00S	C16	113.2(3)	F00J	F7	C01Y	96(5)
C16	N00S	Fe04	107.7(2)	C01Y	F7	F00U	56(3)
C01Y	F00U	F7	45.2(18)	O01N	O9	S00D	74(3)
C12	N00V	Fe04	111.20(18)	O00W	O1	S00D	65(4)
C13	N00V	Fe04	107.8(2)	O10A	S00G	O01G	115.2(13)
C13	N00V	C12	113.0(3)	O10A	S00G	O0	113.9(13)
O1	O00W	S00D	89(4)	O10A	S00G	C0	102.8(11)
C32	N00Y	Fe06	110.57(18)	O01G	S00G	C0	104.5(10)
C32	N00Y	C25	115.7(2)	O0	S00G	O01G	114.1(13)
C25	N00Y	Fe06	111.32(19)	O0	S00G	C0	104.5(10)
C4	N2	Fe1	110.88(18)	F0	C0	S00G	112.1(15)
C4	N2	C5	116.6(2)	F1	C0	S00G	110.0(10)
C5	N2	Fe1	110.43(19)	F1	C0	F0	108.6(15)
C24	N010	Fe06	107.74(18)	F1	C0	F00S	108.3(11)
C23	N010	Fe06	110.88(18)	F00S	C0	S00G	109.5(10)
C23	N010	C24	113.0(2)	F00S	C0	F0	108.2(14)

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