

CaMn₄O₂ model of the biological Oxygen Evolving Complex: Synthesis by cluster expansion on low symmetry ligand

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Supporting information

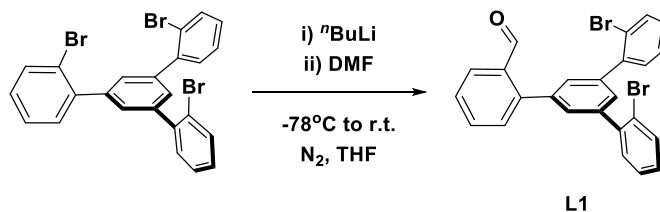
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Experimental procedures

General considerations

All reactions were performed at room temperature in an N₂-filled glovebox or by using standard Schlenk techniques unless otherwise specified. Glassware was oven dried at 150°C for at least 2h prior to use, and allowed to cool under vacuum. All reagents were used as received unless otherwise stated. Iodosobenzene¹ and tris(2-bromophenyl)benzene² were synthesized according to published procedures. *Caution! Iodosobenzene is potentially explosive and should be used only in small quantities.* Anhydrous tetrahydrofuran (THF) was purchased from Aldrich in 18 L Pure-PacTM containers. Anhydrous CH₂Cl₂, CH₃CN, diethyl ether, benzene and THF were purified by sparging with nitrogen for 15 minutes and then passing under nitrogen pressure through a column of activated A2 alumina. H₂O was purified using a Millipore MilliQ purifier. NMR solvents were purchased from Cambridge Isotope Laboratories, dried over calcium hydride, degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ¹H and ¹³C NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. Elemental analyses were performed at the California Institute of Technology.

Synthesis of L1



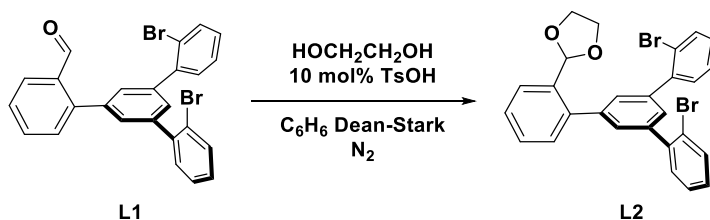
A 500-mL Schlenk flask equipped with a stir bar was charged with tris(2-bromophenyl)benzene (34.5 g, 63 mmol, 1 equiv). Anhydrous THF (300 mL) was added via cannula, and the flask was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of *n*-butyllithium in hexane (2.5 M, 30 mL, 75 mmol, 1.2 equiv) was added slowly via syringe and stirred for an additional hour at $-78\text{ }^{\circ}\text{C}$. Anhydrous, degassed DMF (9.8 g, 134 mmol, 2.1 equiv) was added via syringe, and the mixture was stirred at ambient temperature for 12 h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , and the organic phase was separated. The aqueous phase was extracted three times with EtOAc, and the combined organic fraction was washed repeatedly with brine to remove excess DMF, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica using 5:1 hexanes/ CH_2Cl_2 ($R_f = 0.4$), then dried under reduced pressure to yield **L1** as a white foamy solid (21.4 g, 69%).

^1H NMR (CDCl_3 , 300 MHz): δ 10.23 (s, 1H, CHO), 8.08 (dd, $J = 7.8, 1.5$ Hz, 1H, *o*-CHO), 7.71 (dd, $J = 8.2, 1.5$ Hz, 2H), 7.68 (td, $J = 7.5, 1.5$, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.55 (t, $J = 1.5$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 1.5$ Hz, 2H), 7.46 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.40 (td, $J = 7.5, 1.5$ Hz, 2H), 7.25 (td, $J = 7.8, 2.0$ Hz, 2H)

^{13}C NMR (CDCl_3 , 75 MHz): 192.6, 145.5, 141.6, 141.2, 137.3, 134.0, 133.8, 133.4, 131.5, 131.1, 130.4, 130.3, 129.3, 128.2, 127.8, 127.7, 122.8

HRMS (FAB⁺): calcd. For $\text{C}_{25}\text{H}_{17}\text{OBr}^{18}\text{Br}$: 492.9626; found: 492.9645 [M+H]

Synthesis of L2



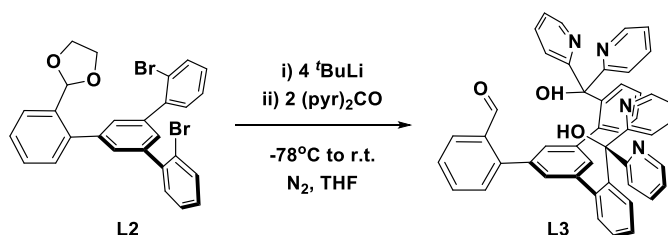
A 500-mL round-bottom flask equipped with a stir bar was charged with a solution of **L1** (21.4 g, 43.5 mmol) in benzene (200mL), ethylene glycol (25 mL), and *p*-toluenesulfonic acid monohydrate (0.5 g, 2.6 mmol, 0.06 equiv). A Dean-Stark apparatus was connected to the flask, and the mixture was refluxed for 15 h under N₂. The mixture was cooled to ambient temperature and quenched with a saturated aqueous solution of NaHCO₃. The organic fraction was separated, washed with brine, dried over anhydrous MgSO₄, filtered, and dried under reduced pressure to yield **L2** as a white foamy solid (22.1 g, 95%). The resulting material was used without further purification.

¹H NMR (CDCl₃, 300 MHz): δ 7.78–7.74 (m, 1H), 7.70 (dd, J = 8.0, 1.2 Hz, 2H), 7.54 (d, J = 1.7 Hz, 2H), 7.48–7.43 (m, 6H), 7.40–7.35 (overlapping ddd and s, 3H), 7.22 (ddd, J = 8.0, 7.3, 1.9 Hz, 2H), 5.92 (s, 1H), 4.18 (m, 2H), 3.98 (m, 2H). ppm.

¹³C NMR (CDCl₃, 75 MHz): δ 142.20, 141.63, 140.61, 139.41, 134.79, 133.28, 131.60, 130.39, 130.01, 129.36, 129.28, 129.04, 127.98, 127.56, 127.02, 122.83, 101.48, 65.73 ppm.

HRMS (FAB⁺): calcd. For C₂₇H₂₀O₂Br¹⁸Br: 535.9810; found: 535.9816 [M+H].

Synthesis of L3

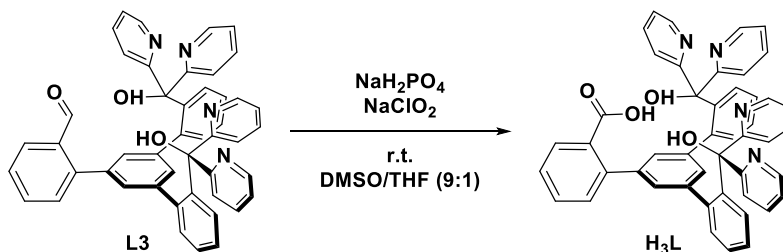


A 500-mL Schlenk flask equipped with a stir bar was charged with **L2** (22.1 g, 41 mmol, 1 equiv) under N₂ counter-flow. Anhydrous THF (250 mL) was added via cannula, and the flask was cooled to -78 °C. A solution of *t*-butyllithium in pentane (1.7 M, 100 mL, 170 mmol, 4.1 equiv) was added slowly via cannula, and the resulting red solution was stirred at -78 °C for 1 hr. A solution of di(2-pyridyl)ketone (15.2 g, 82 mmol, 2 equiv) in anhydrous THF (100 mL) was added via cannula, and the resulting mixture was stirred at ambient temperature for 15 hrs. The reaction mixture was quenched with 1M hydrochloric acid to pH 1 and stirred for 2 hrs. After neutralizing the acid with a saturated aqueous solution of NaHCO₃, the mixture was concentrated under reduced pressure to remove excess THF. The product was extracted with CH₂Cl₂, washed with brine, dried over anhydrous MgSO₄, filtered, and dried under reduced pressure. **L3** is obtained as a white foamy solid and used without further purification.

¹H NMR (CDCl₃, 300 MHz): δ 9.82 (s, 1H, CHO), 8.33 (d, *J* = 5.1 Hz, 4 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 4 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 6 H), 7.36 (t, *J* = 7.5 Hz, 2 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 7.07 (s, 1 H), 6.97 (m, 6 H), 6.81 (s, 2 H), 6.75 (d, *J* = 8.1 Hz, 2 H) ppm.

HRMS (FAB⁺): calcd. For C₄₇H₃₅N₄O₃: 703.2709; found: 703.2697 [M+H].

Synthesis of H₃L



A 1 L round-bottom flask equipped with a stir bar was charged with crude **L3** (obtained from 22.1 g of **L2**) and THF (50 mL). DMSO (450 mL) was added as an HClO scavenger. A saturated aqueous solution of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (3.5 g, 22.4 mmol, 5 equiv) was added via a dropping funnel. Subsequently, a saturated aqueous solution of NaClO_2 (1.2 g, 13.27 mmol, 3 equiv) was added via a dropping funnel and the resulting mixture was stirred for 18 hrs at ambient temperature. The reaction mixture was eluted with EtOAc (500 mL) and washed repeatedly with brine to remove excess DMSO, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was dissolved in minimum acetone and precipitated from Et_2O to afford **H₃L** as a white powder (20.9 g, 46% overall yield in 4 steps).

^1H NMR (300 MHz, CDCl_3): δ 8.32 (d, $J = 4.8$ Hz, 4H), 7.65 (m, 5H), 7.47 (t, $J = 7.2$ Hz, 4H), 7.27 (m, 2H), 7.14 (t, $J = 7.8$ Hz, 2H), 7.02 (d, $J = 7.5$ Hz, 2H), 6.96 (m, 5H), 6.86 (s, 2H), 6.73 (d, $J = 7.8$ Hz, 2H), 6.63 (s, 1H) ppm.

^{13}C NMR (75 MHz, CDCl_3): 162.88, 146.86, 144.07, 143.23, 142.00, 140.35, 137.36, 136.36, 133.00, 130.93, 130.81, 130.74, 129.96, 129.02, 128.65, 127.21, 127.16, 126.68, 126.46, 123.46, 122.04 ppm.

HRMS (ES⁺): calcd. For $\text{C}_{47}\text{H}_{35}\text{N}_4\text{O}_4$: 719.2658; found: 719.2677 [M+H]

Synthesis of $\text{Mn}(\text{OBz})_2 \cdot x\text{H}_2\text{O}$

Under strictly anaerobic conditions, an aqueous suspension of 2-phenylbenzoic acid (0.951 g, 4.8 mmol, 2 equiv) was treated with NaOH (0.192 g, 4.8 mmol, 2 equiv). The mixture was gently warmed to 60°C, resulting in a slightly yellow solution. An aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.474 g, 2.4 mmol, 1 equiv) was added dropwise. The total volume of the reaction was 20 mL. The mixture was stirred at 60°C for 3 h, resulting in the formation of a white precipitate. After cooling to room temperature, the precipitate was collected and washed thoroughly with copious amounts of water and Et_2O , successively. The remaining white solid was dried under reduced pressure. Yield = 1.041 g. Crystallization from DME affords $\text{Mn}_3(\text{OBz})_6(\text{DME})_2$.

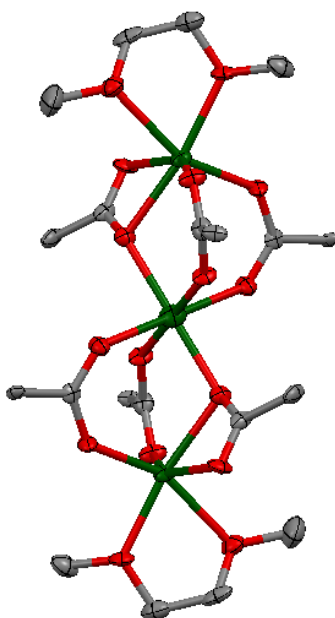
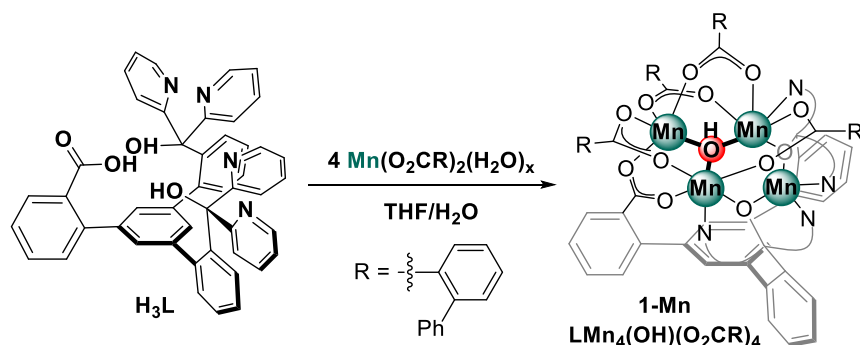


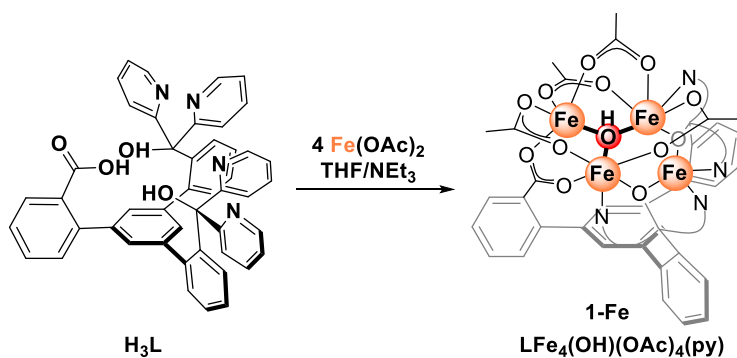
Figure S1. Preliminary, truncated crystal structure of $\text{Mn}_3(\text{OBz})_6(\text{DME})_2$.

Synthesis of 1-Mn



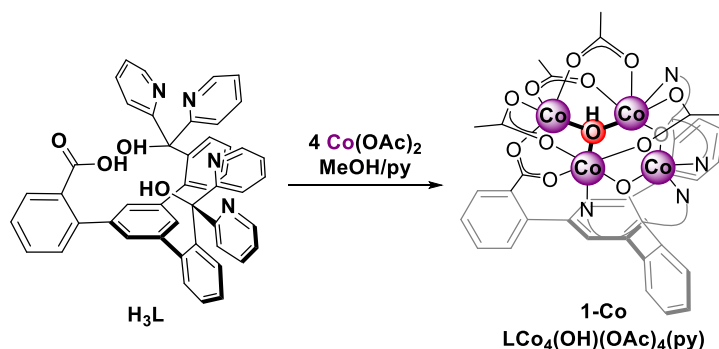
A solution of **H₃L** (1.708 g, 2.38 mmol, 1 equiv) in THF was added to a stirring suspension of $\text{Mn}(\text{OBz})_2 \cdot x\text{H}_2\text{O}$ (4.956 g, 9.5 mmol, 4 equiv) in THF. The reaction mixture was stirred at ambient temperature, becoming homogeneous within 1 hour. After stirring for 18 hours, all volatiles were removed under reduced pressure. The residue was washed with copious amounts of Et_2O , then dissolved in hot benzene and filtered through Celite. All volatiles were removed from the filtrate under reduced pressure. The residue was dissolved in CH_2Cl_2 . Clear, colorless crystals of the product were obtained by slow vapor diffusion of Et_2O . Compound **1-Mn** was isolated by filtration and dried under reduced pressure. Yield = 3.87 g, 94 %. Analysis calculated for $\text{LMn}_4(\text{OH})(\text{OBz})_4 \cdot 1/2(\text{CH}_2\text{Cl}_2)$ [$\text{C}_{199}\text{H}_{138}\text{Cl}_2\text{Mn}_8\text{N}_8\text{O}_{26}$]: C 66.99, H 3.90, N 3.14; found: C 67.03, H 4.08, N 3.02.

Synthesis of 1-Fe



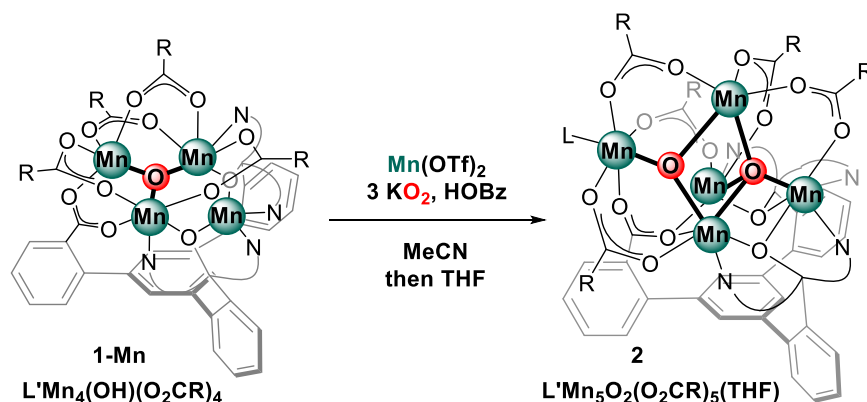
A solution of **H₃L** (1.162 g, 1.62 mmol, 1 equiv) in THF (10 mL) was added to a stirring suspension of Fe(OAc)₂ (1 g, 5.75 mmol, 3.5 equiv) in THF (5 mL). Water (2 mL) was added and the mixture was stirred until a homogeneous red solution was obtained. Triethylamine (1 mL) was added and the mixture was stirred for 12 hours at ambient temperature, resulting in the formation of an orange precipitate. This precipitate was collected and washed with copious amounts of THF. The solid residue was dissolved in pyridine and filtered through Celite. All volatiles were removed from the filtrate under reduced pressure. Compound **1-Fe** was isolated as air-sensitive red microcrystals. Yield = 1.67 g, 91 % (based on Fe). Crystals suitable for X-ray crystallography are obtained by slow vapor diffusion of Et₂O into a concentrated solution of **1-Fe** in pyridine. Analysis calculated for LFe₄(OH)(OAc)₄(py)•py [C₆₅H₅₄Fe₄N₆O₁₃]: C 57.81, H 4.03, N 6.22; found: C 57.91, H 4.29, N 6.49.

Synthesis of 1-Co



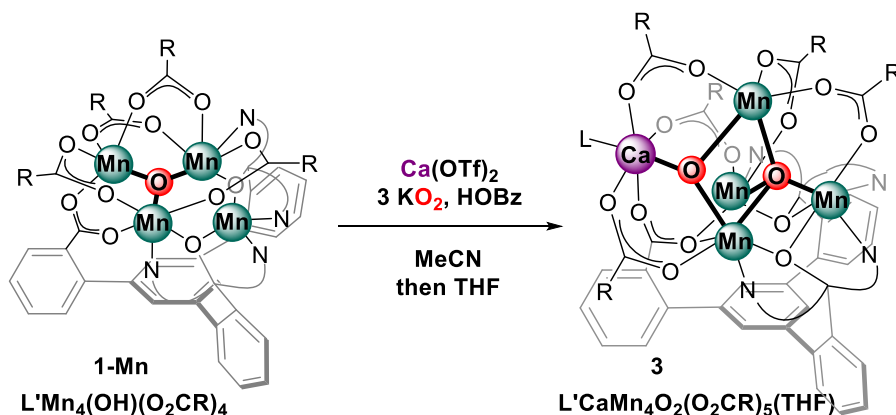
A solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.476 g, 5.93 mmol, 3.8 equiv) in MeOH (10 mL) was added to a solution of **H₃L** (1.120 g, 1.56 mmol, 1 equiv) in MeOH (5 mL). Pyridine (1 mL) was added, and the resulting violet solution was stirred for 12 hours at ambient temperature. All volatiles were then removed under reduced pressure. The residue was washed with copious amounts of Et_2O , THF, and MeCN. The solid residue was dissolved in pyridine and filtered through Celite. All volatiles were removed from the filtrate under reduced pressure. Compound **1-Co** was isolated as air-stable violet microcrystals. Yield = 1.477 g, 79 %. Crystals suitable for X-ray crystallography are obtained by slow vapor diffusion of Et_2O into a concentrated solution of **1-Co** in pyridine. Analysis calculated for $\text{LCo}_4(\text{OH})(\text{OAc})_4(\text{py}) \cdot 2\text{py}$ [$\text{C}_{70}\text{H}_{59}\text{Co}_4\text{N}_7\text{O}_{13}$]: C 58.31, H 4.12, N 6.80; found: C 58.40, H 4.29, N 6.40.

Synthesis of 2



A solid mixture of **1-Mn** (0.442 g, 0.25 mmol, 1 equiv), $Mn(OTf)_2$ (99 mg, 0.28 mmol, 1.1 equiv), and 2-phenylbenzoic acid (56 mg, 0.28 mmol, 1.1 equiv) was treated with CH_3CN (15 mL) and stirred to a homogeneous yellow solution. KO_2 (55 mg, 0.77 mmol, 3 equiv) was added as a solid and stirred at r.t. for 18 h, resulting in the formation of a brown-red precipitate. The precipitate was collected and washed with copious amounts of CH_3CN . The solid residue was dissolved in THF, filtered through Celite, and concentrated under reduced pressure. Yield = 0.435 g, 82 %. Red crystals suitable for X-ray crystallography are obtained from a concentrated THF solution by slow vapor diffusion of Et_2O . Analysis calc'd for $C_{116}H_{84}Mn_5N_4O_{17}$: C 66.96, H 4.07, N 2.69; found: C 66.15, H 4.35, N 2.98.

Synthesis of 3



A solid mixture of **1-Mn** (0.640 g, 0.367 mmol, 1 equiv), Ca(OTf)_2 (135 mg, 0.40 mmol, 1.1 equiv), and 2-phenylbenzoic acid (96 mg, 0.48 mmol, 1.3 equiv) was treated with CH_3CN (15 mL) and stirred to a homogeneous yellow solution. KO_2 (65 mg, 0.091 mmol, 2.5 equiv) was added as a solid and stirred at r.t. for 18 h, resulting in the formation of a red-orange precipitate. The precipitate was collected and washed with copious amounts of CH_3CN . The solid residue was dissolved in THF, filtered through Celite, and concentrated under reduced pressure. Yield = 0.421 g, 55 %. Red crystals suitable for X-ray crystallography are obtained from a concentrated THF/ CH_2Cl_2 solution by slow vapor diffusion of Et_2O . Analysis calc'd for $\text{C}_{116}\text{H}_{84}\text{CaMn}_4\text{N}_4\text{O}_{17}$: C 67.45, H 4.10, N 2.71; found: C 67.67, H 4.46, N 2.46.

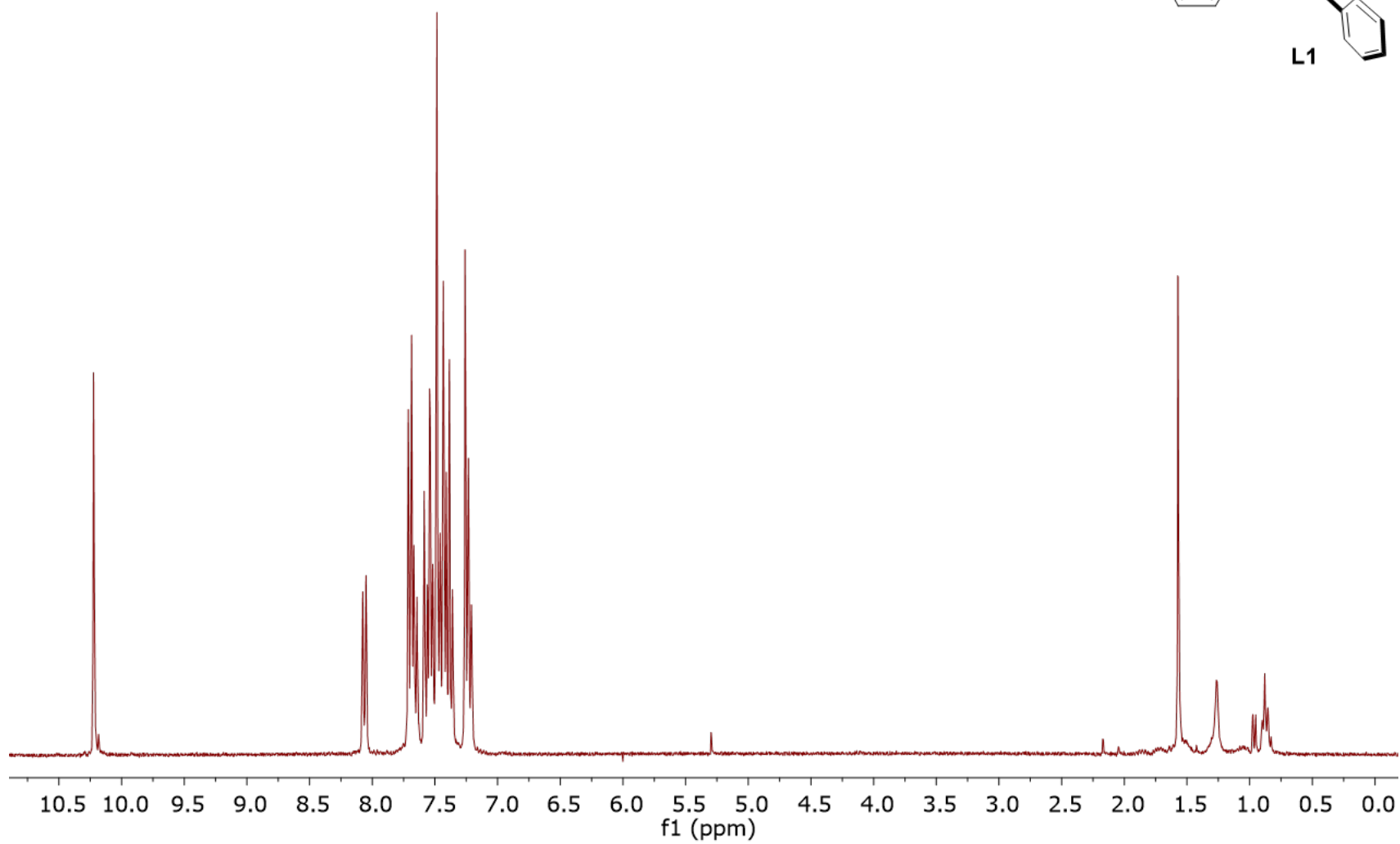
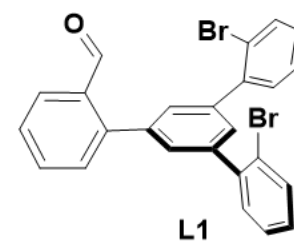


Figure S2. ¹H NMR of L1 in CDCl₃.

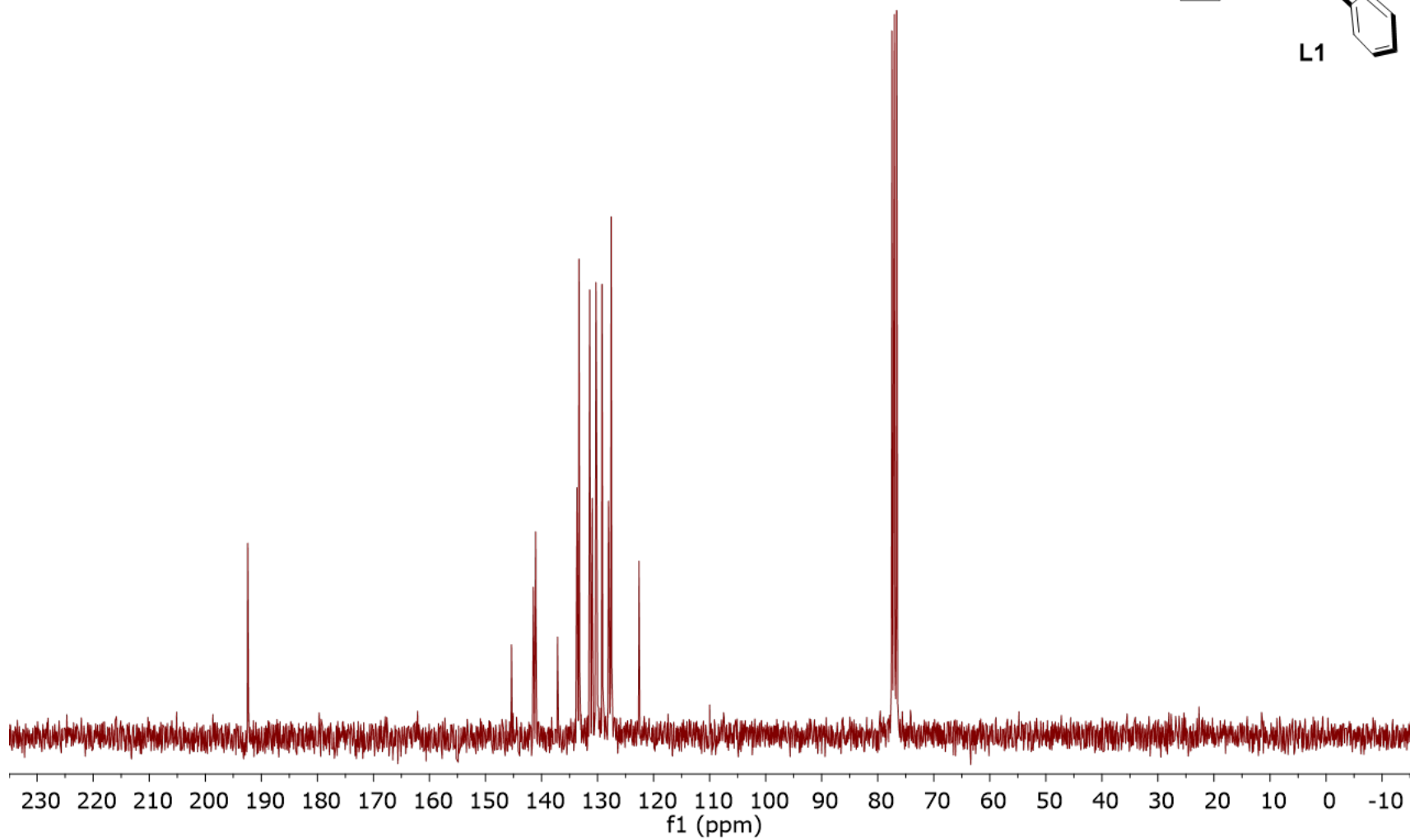
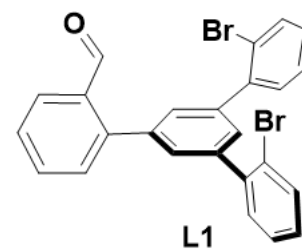


Figure S3. ¹³C NMR of L1 in CDCl₃.

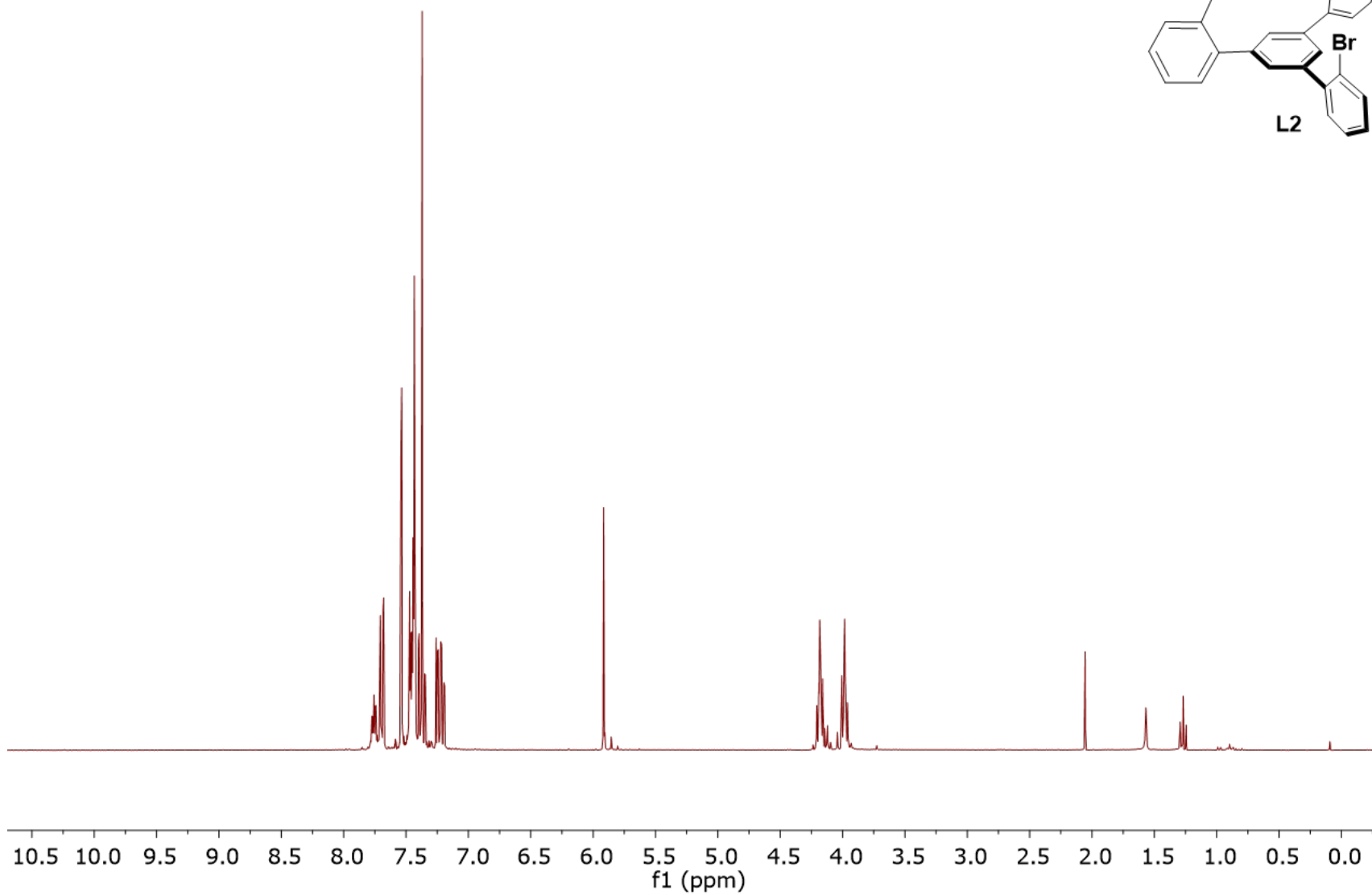
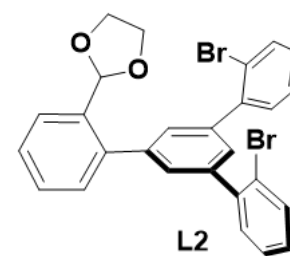


Figure S4. ¹H NMR of L2 in CDCl₃.

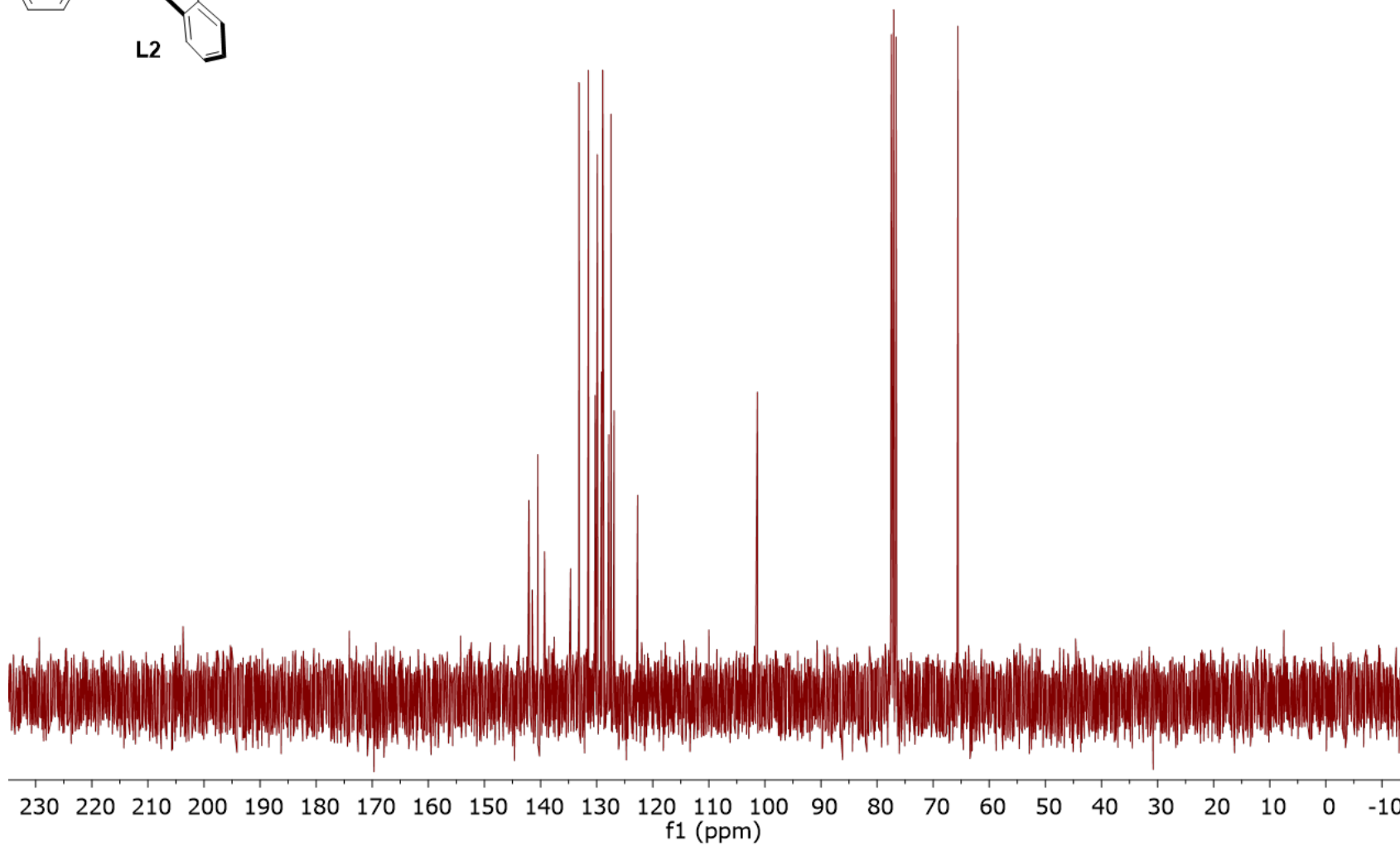
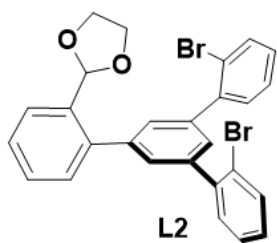


Figure S5. ^{13}C NMR of L2 in CDCl_3 .

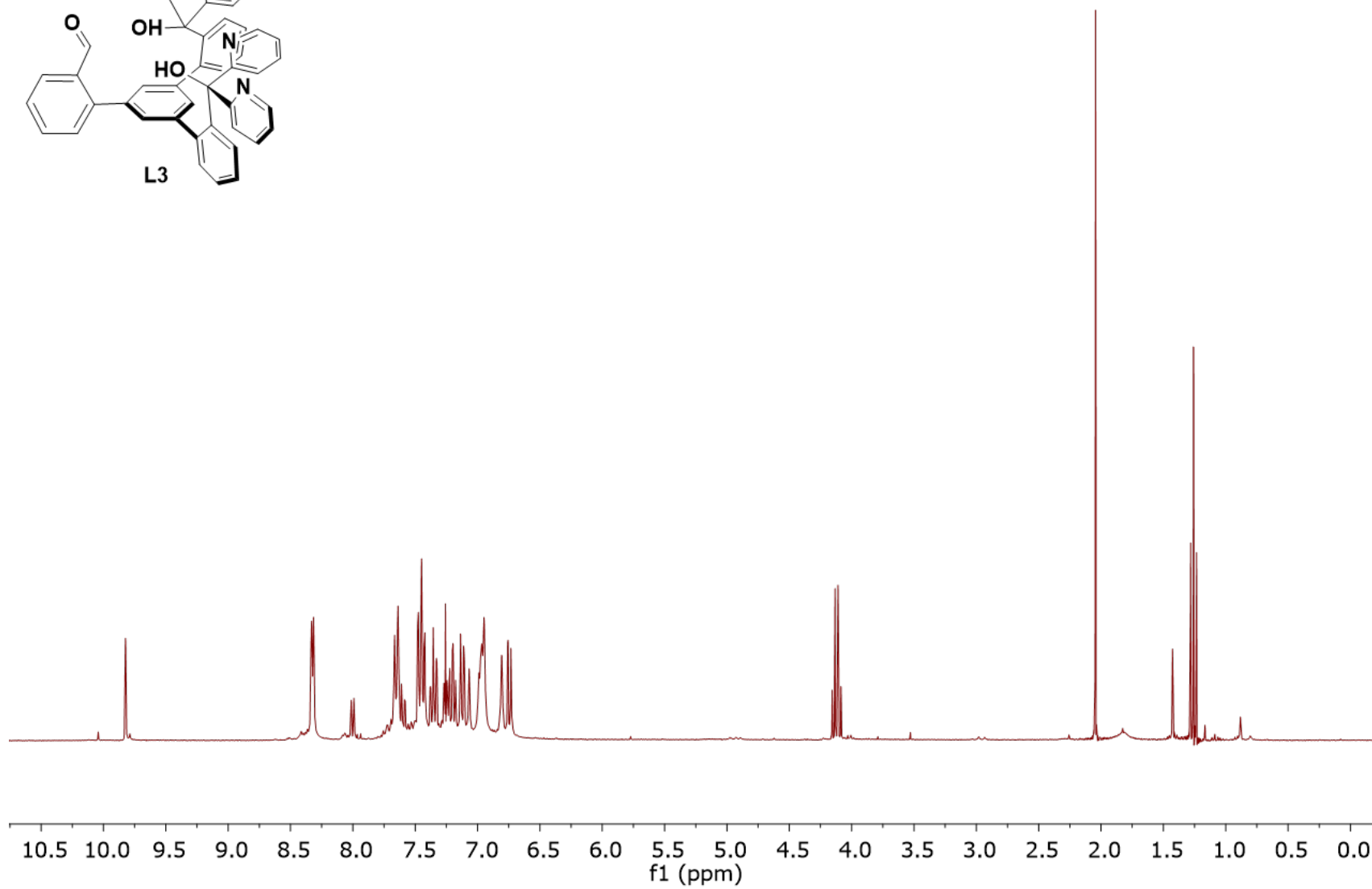
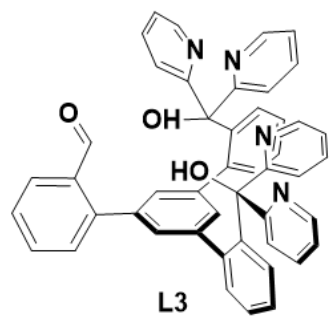


Figure S6. ^1H NMR of L3 in CDCl_3 .

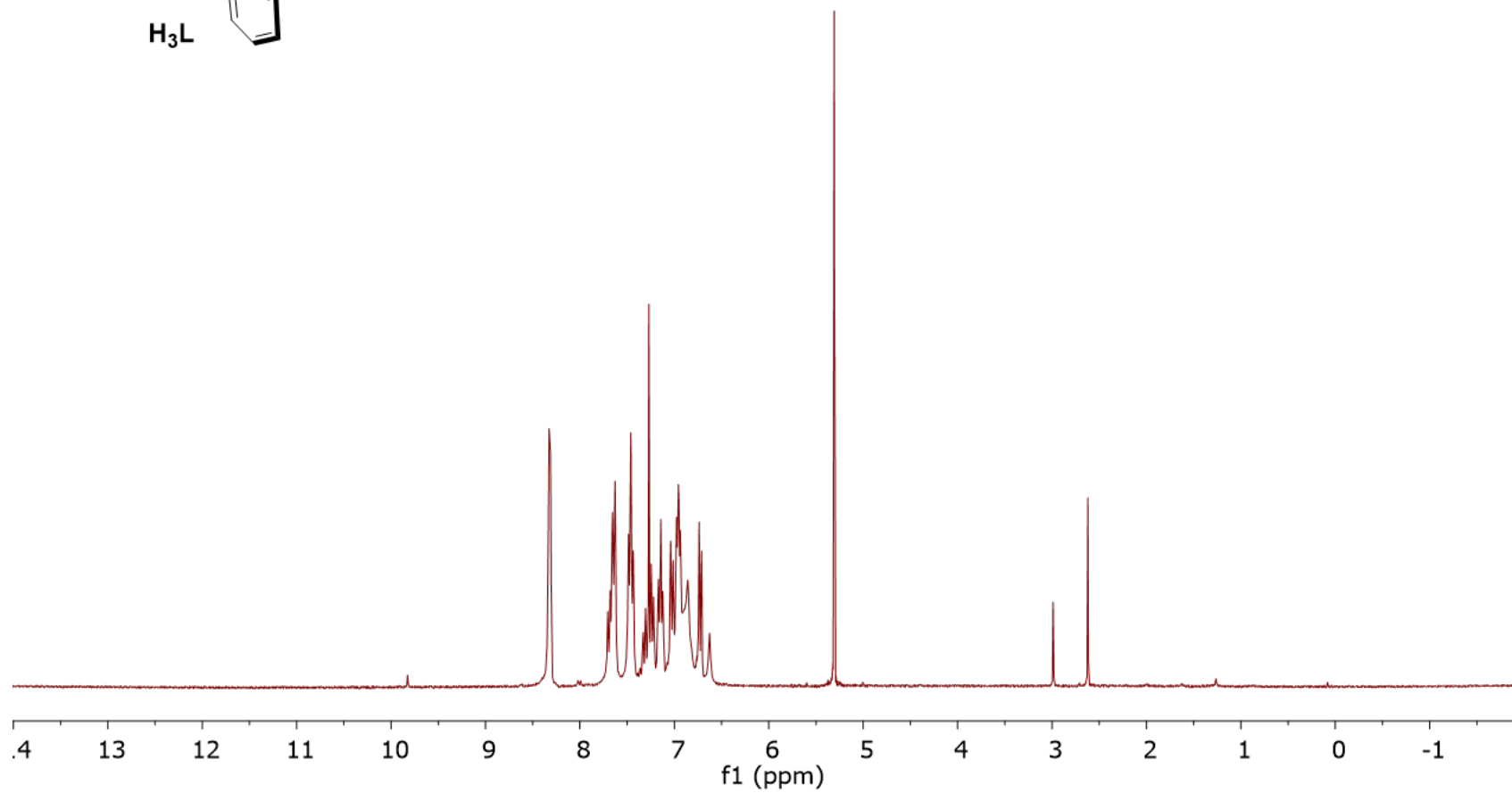
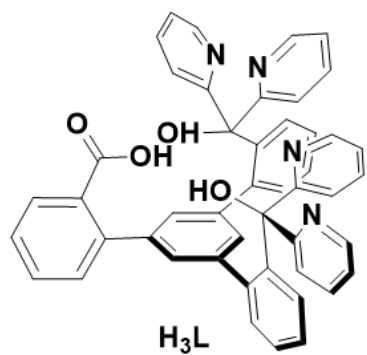


Figure S7. ¹H NMR of **H₃L** in CDCl₃.

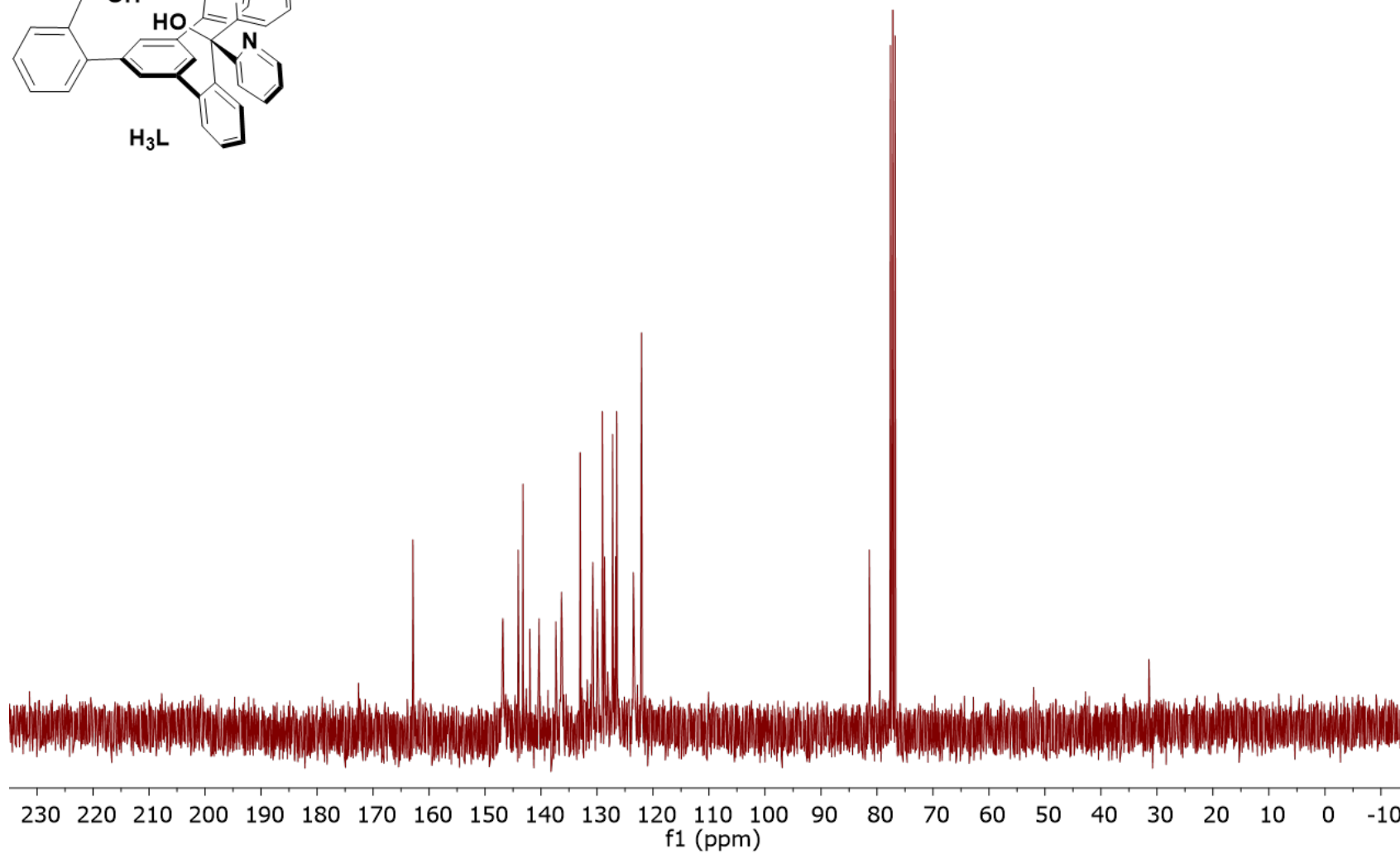
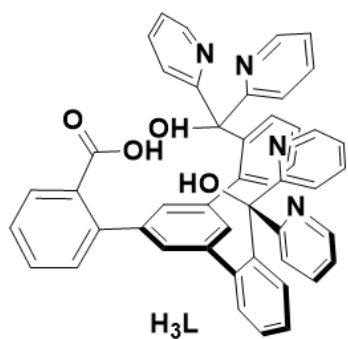


Figure S8. ¹³C NMR of H₃L in CDCl₃.

Crystallographic details

Suitable crystals were mounted on a nylon loop using Paratone oil, then placed on a diffractometer under a nitrogen stream. X-ray intensity data were collected on a Bruker APEXII CCD area detector or a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS detector employing Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 100 K. All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software. Frames were integrated using SAINT. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS. Space groups were determined on the basis of systematic absences and intensity statistics using XPREP. Using Olex2³, the structures were solved by direct methods using ShelXT and refined to convergence by full-matrix least squares minimization using ShelXL. All non-solvent non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. Graphical representation of structures with 50% probability thermal ellipsoids was generated using Diamond visualization software. No special refinement details.

Table S1. Crystal and refinement data for complexes **1–Mn**, **1–Fe**, and **1–Co**.

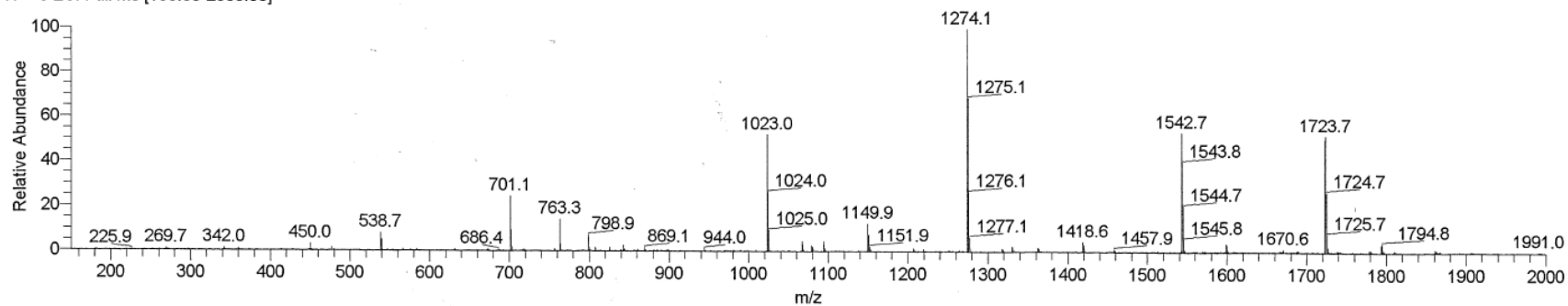
Compound	1–Mn	1–Fe	1–Co
CCDC	1540537	1540538	1540539
Empirical formula	C _{102.88} H _{75.05} Cl _{2.56} Mn ₄ N ₄ O _{13.65}	C ₆₄ H ₅₈ Fe ₄ N ₅ O ₁₄	C ₆₄ H ₅₈ Co ₄ N ₅ O ₁₄
Formula weight	1896.13	1344.55	1356.87
Temperature/K	99.99	100.04	100.03
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.5028(18)	13.7237(14)	13.7817(7)
b/Å	16.598(2)	13.9138(13)	13.8132(7)
c/Å	21.517(3)	17.8609(17)	17.7104(9)
α/°	77.057(3)	75.523(4)	75.742(2)
β/°	82.240(3)	75.229(3)	75.384(2)
γ/°	83.778(3)	65.876(3)	66.637(2)
Volume/Å ³	4641.4(11)	2968.4(5)	2954.1(3)
Z	2	2	2
ρ _{calc} /cm ³	1.357	1.504	1.525
μ/mm ⁻¹	0.671	1.030	1.176
F(000)	1946.0	1386.0	1394.0
Crystal size/mm ³	0.1 × 0.05 × 0.05	0.02 × 0.02 × 0.02	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.802 to 61.494	4.782 to 56.528	4.82 to 61.016
Index ranges	-19 ≤ h ≤ 19, -23 ≤ k ≤ 23, -30 ≤ l ≤ 30	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -23 ≤ l ≤ 23	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25
Reflections collected	132477	105521	113132
Independent reflections	28763 [R _{int} = 0.0752, R _{sigma} = 0.0738]	14691 [R _{int} = 0.1863, R _{sigma} = 0.1232]	18006 [R _{int} = 0.0489, R _{sigma} = 0.0335]
Data/restraints/parameters	28763/8/1108	14691/6/765	18006/0/765
Goodness-of-fit on F ²	1.061	1.045	1.054
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0904, wR ₂ = 0.2523	R ₁ = 0.0744, wR ₂ = 0.1510	R ₁ = 0.0448, wR ₂ = 0.1262
Final R indexes [all data]	R ₁ = 0.1340, wR ₂ = 0.2767	R ₁ = 0.1521, wR ₂ = 0.1771	R ₁ = 0.0641, wR ₂ = 0.1375
Largest diff. peak/hole / e Å ⁻³	2.22/-1.47	1.67/-1.06	1.84/-1.46

Table S2. Crystal and refinement data for complexes **2** and **3**.

Compound	2	3
CCDC	1540540	1540541
Empirical formula	C ₁₂₈ H ₁₀₉ Mn ₅ N ₄ O ₂₀	C ₁₂₀ H ₉₂ CaCl ₄ Mn ₄ N ₄ O _{17.5}
Formula weight	2297.93	2271.61
Temperature/K	100.04	100.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	14.7524(8)	14.8017(4)
b/Å	16.2906(8)	16.3782(5)
c/Å	22.1991(12)	21.9258(6)
α/°	90.350(2)	88.2880(10)
β/°	98.124(2)	81.0900(10)
γ/°	92.207(2)	87.5960(10)
Volume/Å ³	5277.2(5)	5245.1(3)
Z	2	2
ρ _{calc} /cm ³	1.446	1.438
μ/mm ⁻¹	0.658	0.693
F(000)	2380.0	2336.0
Crystal size/mm ³	0.05 × 0.05 × 0.05	0.1 × 0.05 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.312 to 61.016	4.408 to 61.046
Index ranges	-21 ≤ h ≤ 21, -23 ≤ k ≤ 23, -31 ≤ l ≤ 31	-21 ≤ h ≤ 21, -23 ≤ k ≤ 23, -31 ≤ l ≤ 31
Reflections collected	130593	161254
Independent reflections	32156 [R _{int} = 0.0384, R _{sigma} = 0.0461]	31911 [R _{int} = 0.0567, R _{sigma} = 0.0615]
Data/restraints/parameters	32156/10/1412	31911/26/1362
Goodness-of-fit on F ²	1.032	1.025
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0528, wR ₂ = 0.1279	R ₁ = 0.0745, wR ₂ = 0.1886
Final R indexes [all data]	R ₁ = 0.0782, wR ₂ = 0.1414	R ₁ = 0.1157, wR ₂ = 0.2124
Largest diff. peak/hole / e Å ⁻³	1.69/-1.10	2.22/-1.84

ESI-MS spectrometry

HBL-III-174 #1-10 RT: 0.00-0.25 AV: 10 NL: 8.25E7
T: + c ESI Full ms [150.00-2000.00]



HBL-III-174 #1-10 RT: 0.00-0.25 AV: 10 NL: 8.25E7
T: + c ESI Full ms [150.00-2000.00]

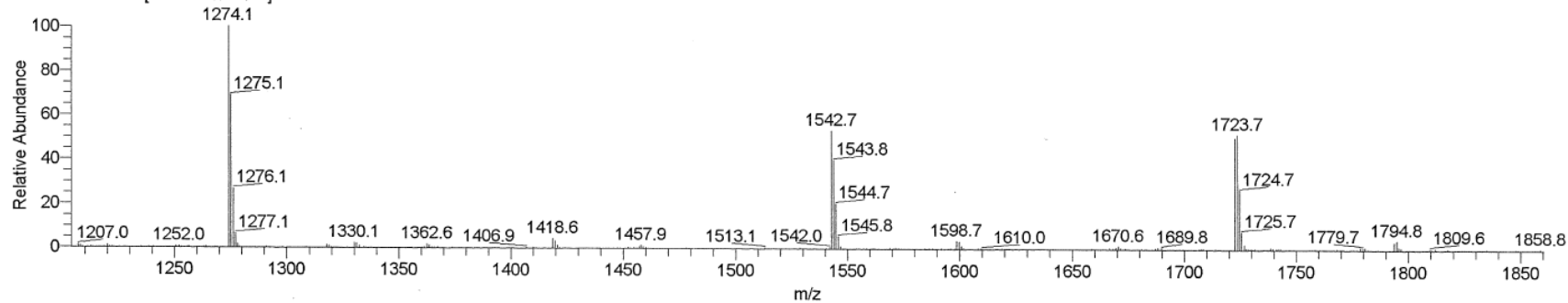
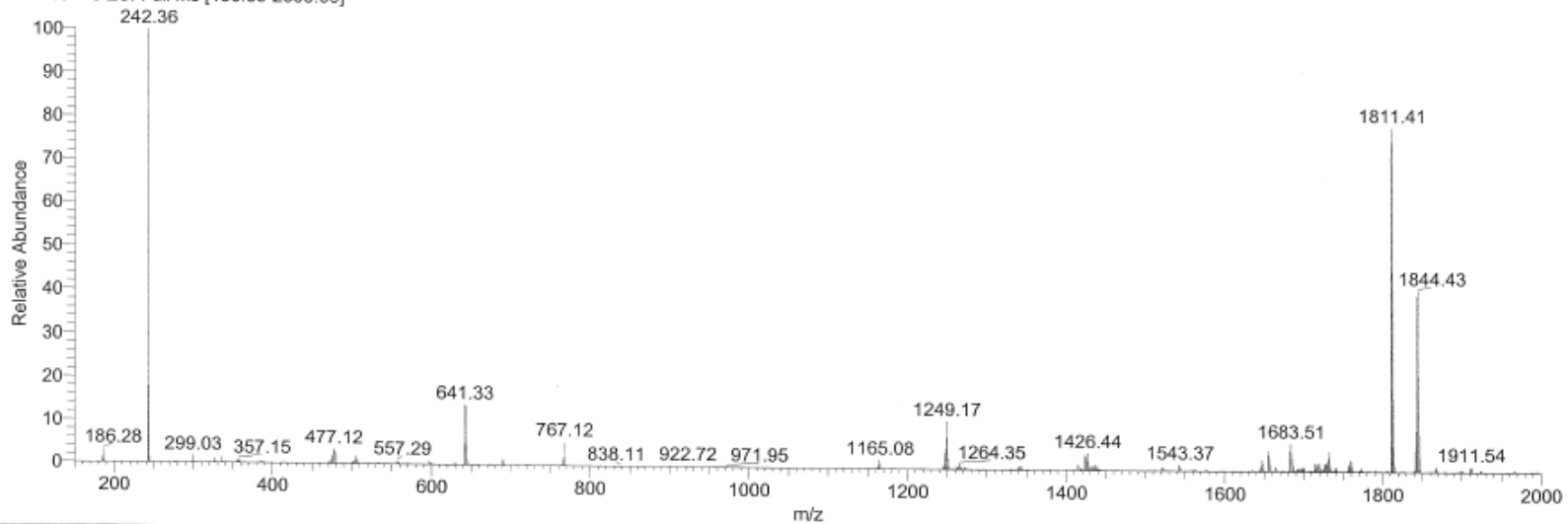


Figure S9. ESI-MS of 1-Mn.

HBL-IV-66(2) #1-50 RT: 0.00-0.20 AV: 50 NL: 1.19E4
T: ITMS + c ESI Full ms [150.00-2000.00]



HBL-IV-66(2) #1-50 RT: 0.00-0.20 AV: 50 NL: 9.47E3
T: ITMS + c ESI Full ms [150.00-2000.00]

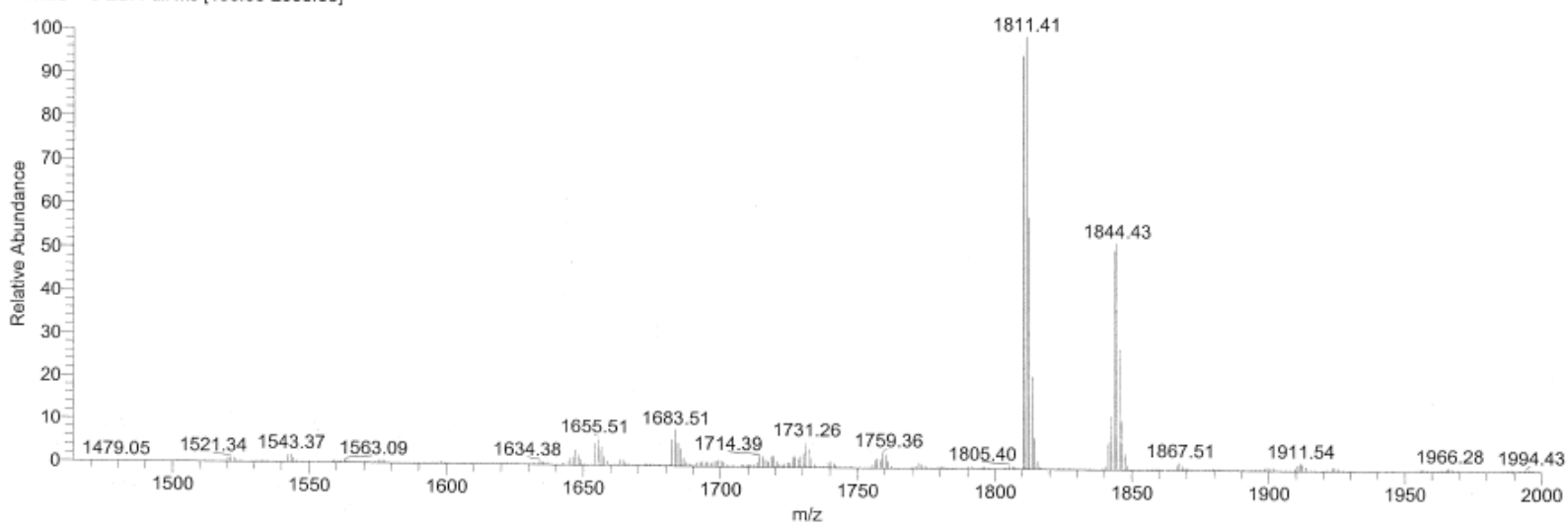
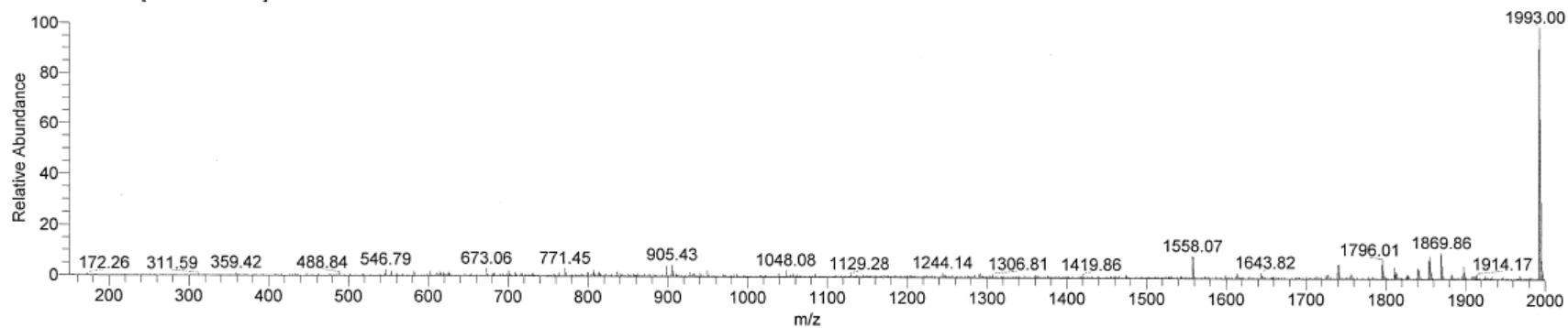


Figure S10. ESI-MS of 2.

HBL-V-33_DCM #1-4 RT: 0.01-0.09 AV: 4 NL: 2.29E8
T: + c ESI Full ms [150.00-2000.00]



HBL-V-33_DCM #1-4 RT: 0.01-0.09 AV: 4 NL: 2.29E8
T: + c ESI Full ms [150.00-2000.00]

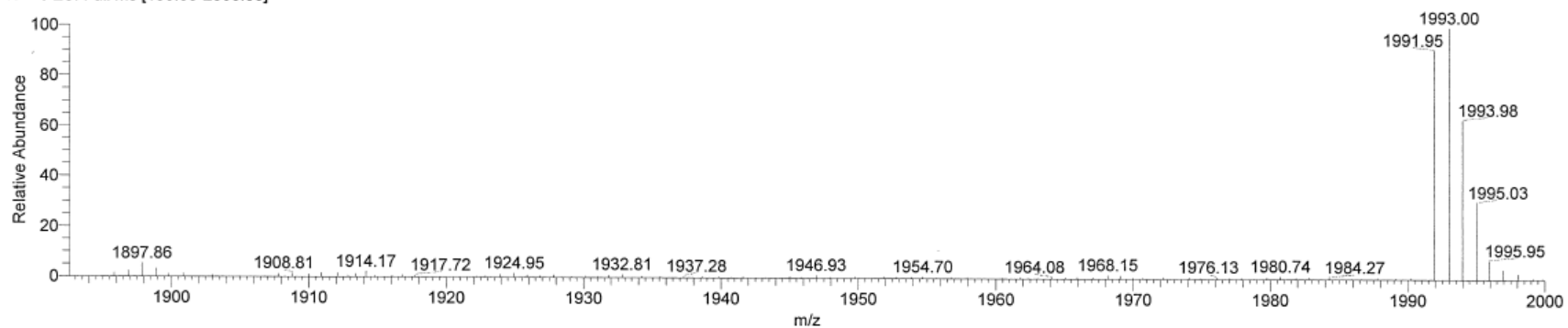


Figure S11. ESI-MS of 3.

Mössbauer spectroscopy

Zero-field ^{57}Fe Mössbauer spectra were recorded at 80 K in the constant acceleration mode on a spectrometer from See Co (Edina, MN) equipped with an SVT-400 cryostat (Janis, Wilmington, WA). The quoted isomer shifts are relative to the centroid of the spectrum of a $\alpha\text{-Fe}$ foil at room temperature. Samples were prepared by grinding polycrystalline material (40 mg) into a fine powder and pressed into a homogeneous pellet with boron nitride in a cup fitted with a screw cap. The data were fitted to Lorentzian lineshapes using the program WMOSS (www.wmoos.org).

The zero-field Mössbauer spectrum of **1-Fe** shows a broad quadrupole doublet with $\delta = 1.18$ mm/s and $|\Delta E_Q| = 2.95$ mm/s (Fig. 3). These values are consistent with known carboxylate bridged high-spin Fe(II) centers.⁴ Mössbauer parameters for the diiron(II) μ^2 -hydroxo species supported by bridging acetate ligands ($\delta = 1.16$ mm/s, $|\Delta E_Q| = 2.83$ mm/s) are in excellent agreement with the values observed for **1-Fe**.⁵

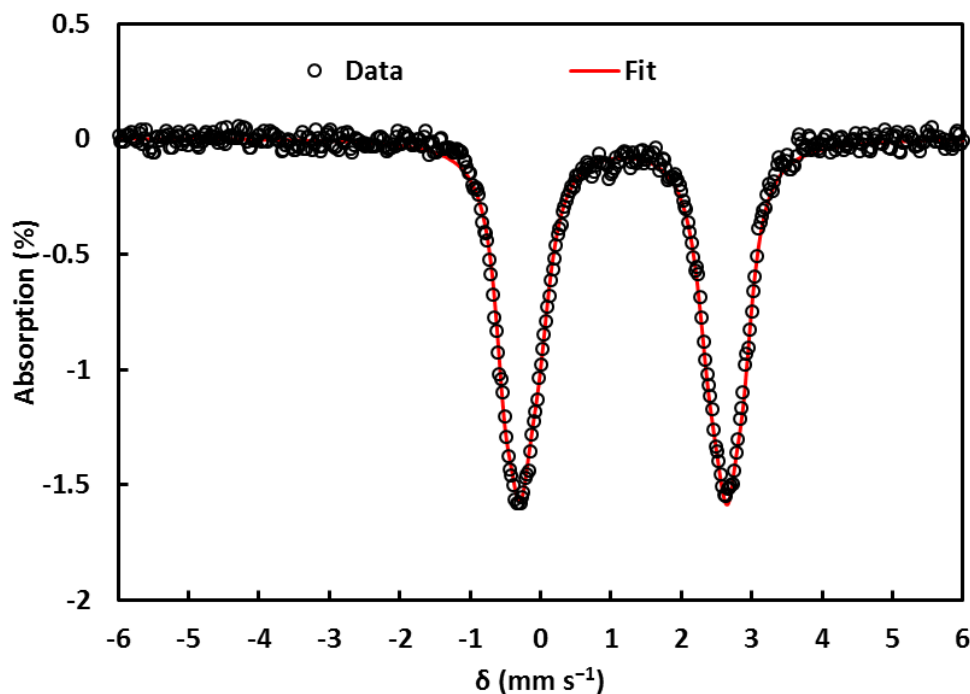


Figure S12. Zero-field Mössbauer spectrum of **1-Fe** at 80 K with simulated parameters: $\delta = 1.18$ mm/s, $|\Delta E_Q| = 2.95$ mm/s.

SQUID magnetometry

Magnetic susceptibility measurements were carried on a Quantum Design MPMS instrument running MPMS Multivu software. Crystalline samples were powdered and suspended in clear plastic straws in polycarbonate capsules. Data were recorded at 0.1 T from 2–270 K. Reduced magnetization data were recorded in the range 2–10 K and 0.1–4 T. Diamagnetic corrections were made using Pascal's constants as follows: -710 , -648 , and $-642 \times 10^{-6} \text{ cm}^3/\text{mol}$ for **1-Mn**, **1-Fe**, and **1-Co**, respectively.

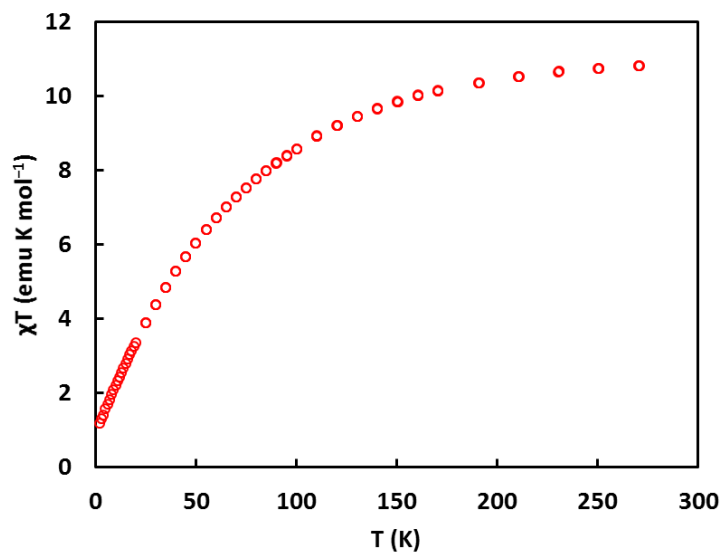


Figure S13. Molar susceptibility data for **1-Mn**.

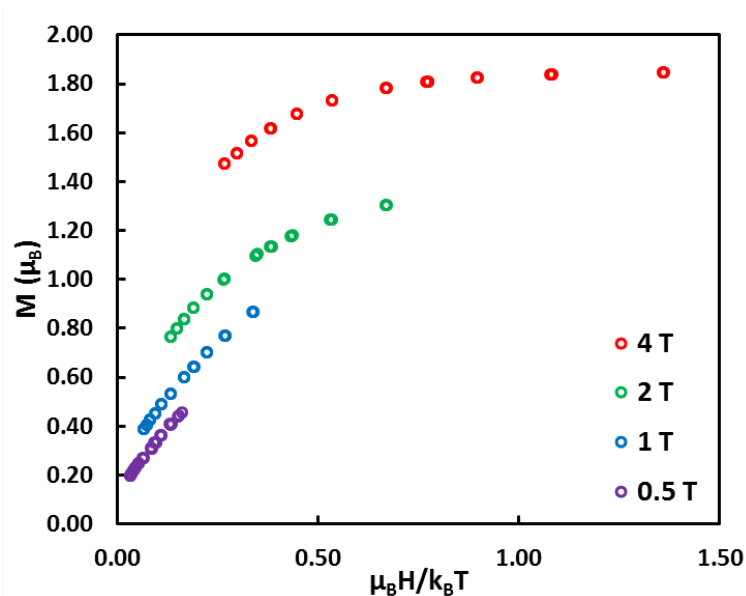


Figure S14. Reduced magnetization data for **1-Mn**.

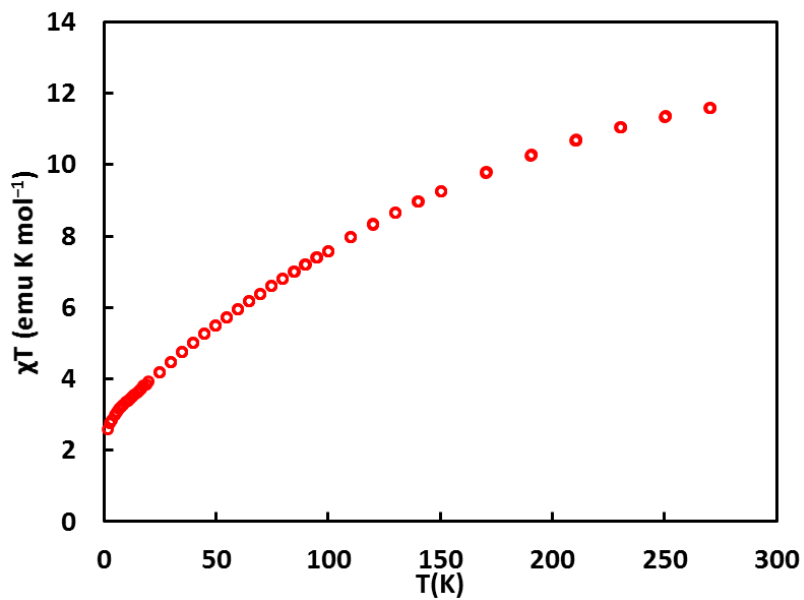


Figure S15. Molar susceptibility data for 1-Fe.

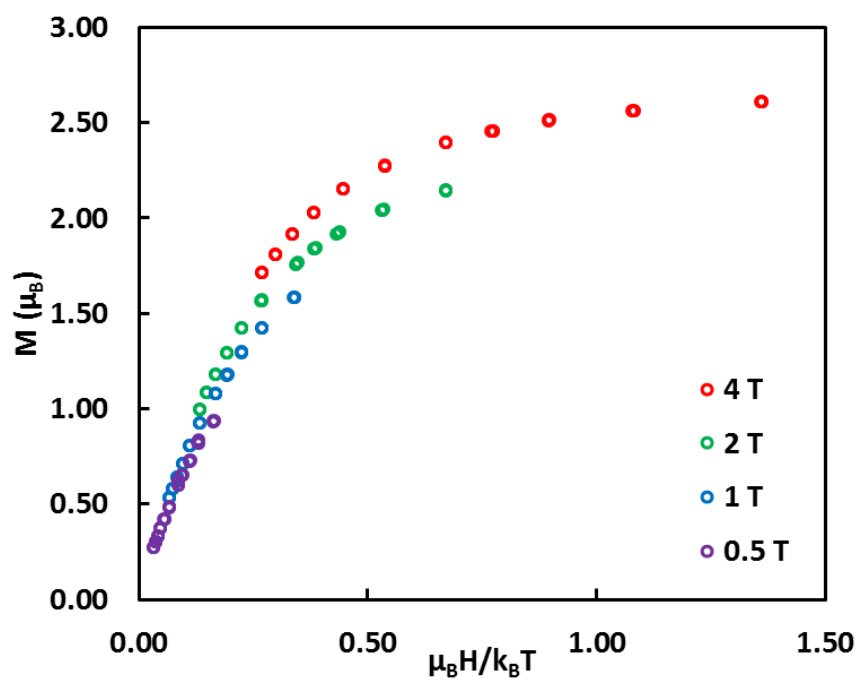


Figure S16. Reduced magnetization data for 1-Fe.

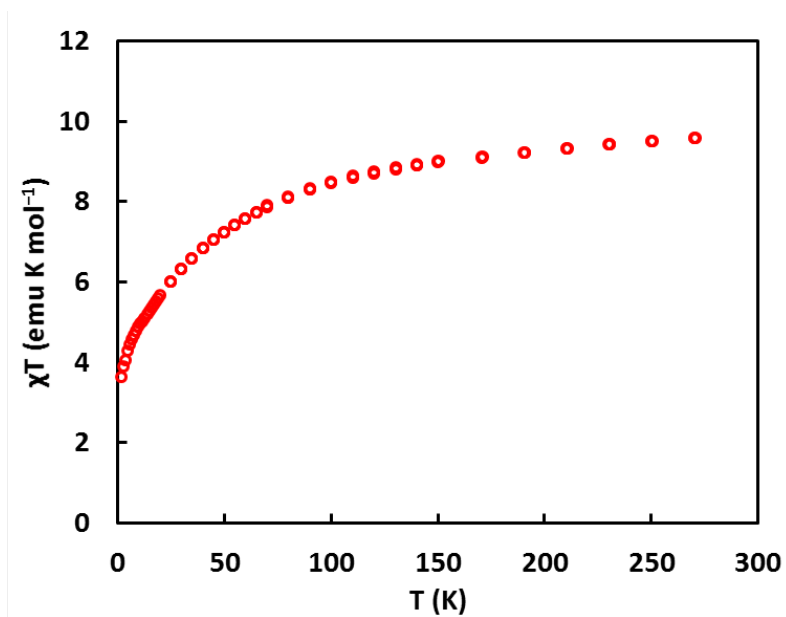


Figure S17. Molar susceptibility data for 1-Co.

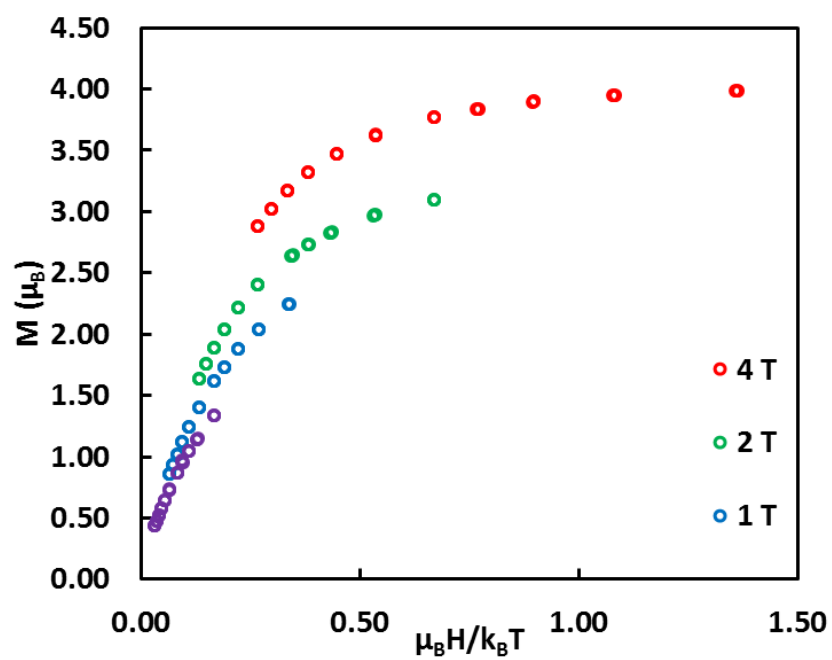


Figure S18. Reduced magnetization data for 1-Co.

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