

Supporting Information

Boronic acid and boronic ester containing polyoxometalates

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INSTRUMENTATION and PROCEDURES

The polyoxometalate precursor $(N(C_4H_9)_4)_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ was synthesized via literature procedure.^[1] All other chemical reagents were reagent grade and used as purchased without any further purification.

Bond Valence Sum Calculations:

Bond valence sum calculations were performed using the bond valence calculator, version 2.00 February 1993, written by C. Hormillosa with assistance from S. Healy, distributed by I. D. Brown.^[2]

FT-IR spectroscopy (KBr disc): FT-IR spectroscopy was performed on a Bruker Tensor 27 FT-IR spectrometer. Samples were prepared as KBr pellets. Signals are listed as wavenumbers (cm^{-1}) with the following abbreviations: vs = very strong, s = strong, m = medium and w = weak.

Elemental Analysis: Elemental Analysis was conducted by the Campbell Microanalytical Laboratory and the Centre for Trace Element Analysis at the University of Otago, New Zealand. Samples were diluted and analyzed on an Agilent 7500^{ce} ICP-MS which was tuned to manufacturer recommendations to minimize interference and instrumental drift. Calibration standards were prepared by a serial dilution on SPEX CertiPrep (NIST traceable).

NMR spectroscopy: 1H NMR spectroscopy was performed on a Varian 400 MHz NMR Spectrometer using a pulse width of $\pi/2$ (11.25 μs), carbon decoupled.

X ray crystallography: Single crystal X-ray data was collected using an Agilent Technologies SuperNova Dual Wavelength single crystal X-ray diffractometer at 130 K using Cu K-alpha (0.15418 nm) fitted with a mirror monochromator. The data was reduced using CrysAlisPro software (Version 1.171.38.41) using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Data was solved using direct methods by SHELXT and refined using a full-matrix least square procedure based upon F^2 .^[3] Data was refined using the OLEX2 software package Version 1.2.7.^[4]

1a - Significant crystallographic disorder was observed for compound **1a**. Several datasets were collected on recrystallized samples with this being the best obtainable structure. Molybdenum, manganese and oxygen atoms on the polyoxometalate are refined anisotropically with the grafted triol ligands atoms being refined isotropically. The triol ligand is modelled in two orientations with DFIX, DANG, EADP constraints and PART instructions required to obtain a stable refinement. A solvent mask was also required to account for the tetrabutylammonium (TBA) cations.

1b – Two crystallographically unique polyanions are observed in **1b**. One of these polyanions are ordered meanwhile the other is severely disordered with the polyanion adopting two orientations with relative populations of 73.2% and 26.8% as determined using free variables. Consequently, the polyanions oxygen atoms are disordered over two sets of sites with these relative occupancies, meanwhile the molybdenum and manganese atoms are unaffected by this disorder. The methylene carbon atoms of the grafted tripodal ligand also present the same disorder with the remainder of the ligand showing no disorder due to free rotation around the C-N bond and intermolecular interactions in the solid state. The metal-oxide framework of the polyanion is refined anisotropically with the remainder of the molecule refined isotropically. Once again DANG, DFIX and EADP constraints are applied where necessary along with the use of the PART instruction to model the disorder. Minimal disorder is observed for the TBA cations and DMF solvent molecules, and are refined isotropically.

1c – No disorder is observed for **1c** with all non-hydrogen atoms refined anisotropically.

Synthesis of **1a**:

2-formyl phenyl boronic acid (15 mg, 0.1 mmol) was dissolved in 200 μL of dimethylformamide (DMF) and added to a 400 μL solution of $(N(C_4H_9)_4)_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ ¹ (100 mg, 0.0487 mmol) in DMF. The resulting solution was exposed to diethyl ether vapour and diffraction quality crystals appeared over a 6 hours period. Yield: 62 mg (60%).

$C_{70}H_{134}B_2Mn_1Mo_6N_5O_{26}$ (MW: 2114.03 g/mol) calcd. C 39.77%, H 6.39%, N 3.31%; found C 39.16 %, H 6.42%, N 3.68%. IR (cm^{-1}): 3421(m), 2964(s), 2934(s), 2873(s), 1640(s), 1600(s), 1578(s), 1478(s), 1463(s), 1442(s), 1386(s), 1350(s), 1260(s), 1204(s), 1153(s), 1089(s), 1026(s), 949(vs), 940(s), 918(s), 904(s), 802(s), 757(s), 738(s), 663(vs), 565(s), 457(s), 414(s). 1H NMR (d_6 -DMSO, 400 MHz): δ (ppm) 0.93 (t, $-CH_3$ $[Bu_4N]^+$), 1.32 (q, $-CH_2$ $[Bu_4N]^+$), 2.50 (q, DMSO), 3.16 (t, CH_2 $[Bu_4N]^+$), 3.35 (s, H_2O), 7.20 (t, -AR), 7.48 (s, -AR), 7.63 (d, -AR), 8.33 (s, B-OH), 62.96 (s, $-OCH_2$).

Synthesis of **1b**:

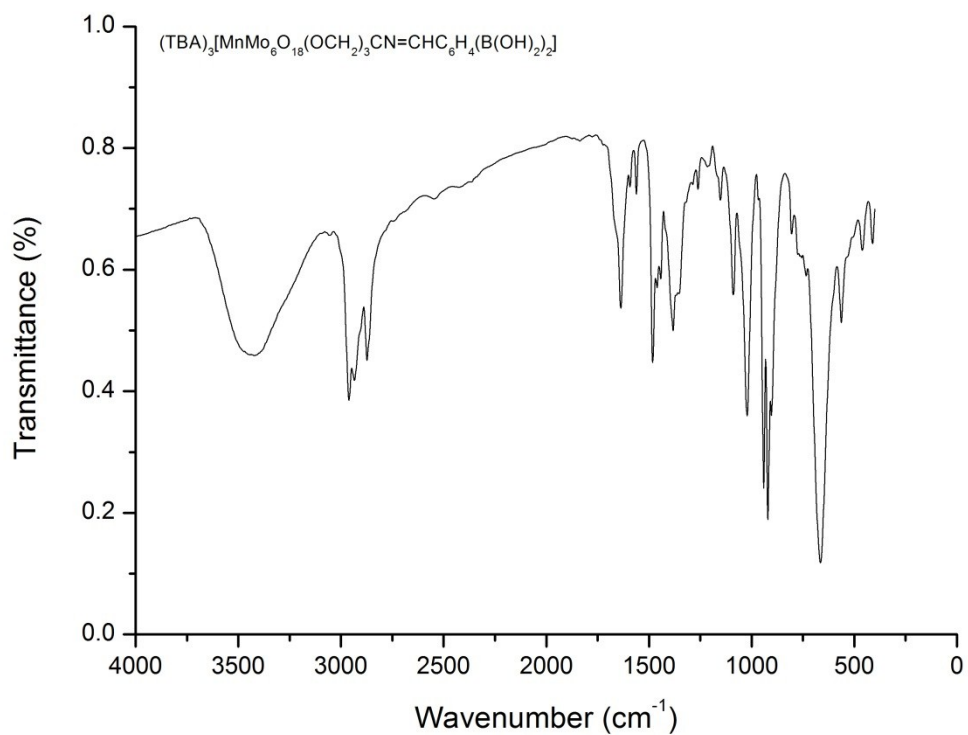
2-formyl phenyl boronic acid (15 mg, 0.1 mmol) was dissolved in 400 μ L of methanol and added to a 400 μ L solution of $(\text{N}(\text{C}_4\text{H}_9)_4)_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (100 mg, 0.0487 mmol) in methanol. On mixing instant precipitation of an orange microcrystalline product resulted. This precipitate was filtered and washed several times with methanol. The crude product was then air dried. Recrystallization from DMF results in diffraction quality crystals over a 2 days period. Yield: 36 mg (35%).

$\text{C}_{72}\text{H}_{138}\text{B}_2\text{Mn}_1\text{Mo}_6\text{N}_5\text{O}_{26}$ (MW: 2142.08 g/mol) calcd. C 40.37 %, H 6.49 %, N 3.27 %; found C 40.19 %, H 6.43 %, N 3.28 %. IR (cm^{-1}): 3436(w), 2962(m), 2938(s), 2873(s), 1640(s), 1596(s), 1558(s), 1485(s), 1466(s), 1441(s), 1378(s), 1345(s), 1281(s), 1248(s), 1156(s), 1072(s), 1020(s), 947(vs), 922(s), 904(s), 802(s), 763(s), 734(s), 666(vs), 560(s), 530(s), 453(s), 405(s). ^1H NMR (d_6 -DMSO, 400 MHz): δ (ppm) 0.93 (t, $-\text{CH}_3$ [Bu_4N^+]), 1.32 (q, $-\text{CH}_2$ [Bu_4N^+]), 2.50 (q, DMSO), 3.16 (t, CH_2 [Bu_4N^+]), 3.35 (s, H_2O), 7.20 (t, AR-), 7.48 (t, AR-), 7.61 (d, AR-), 8.31 (s, B-OH), 62.87 (s, $-\text{OCH}_2-$).

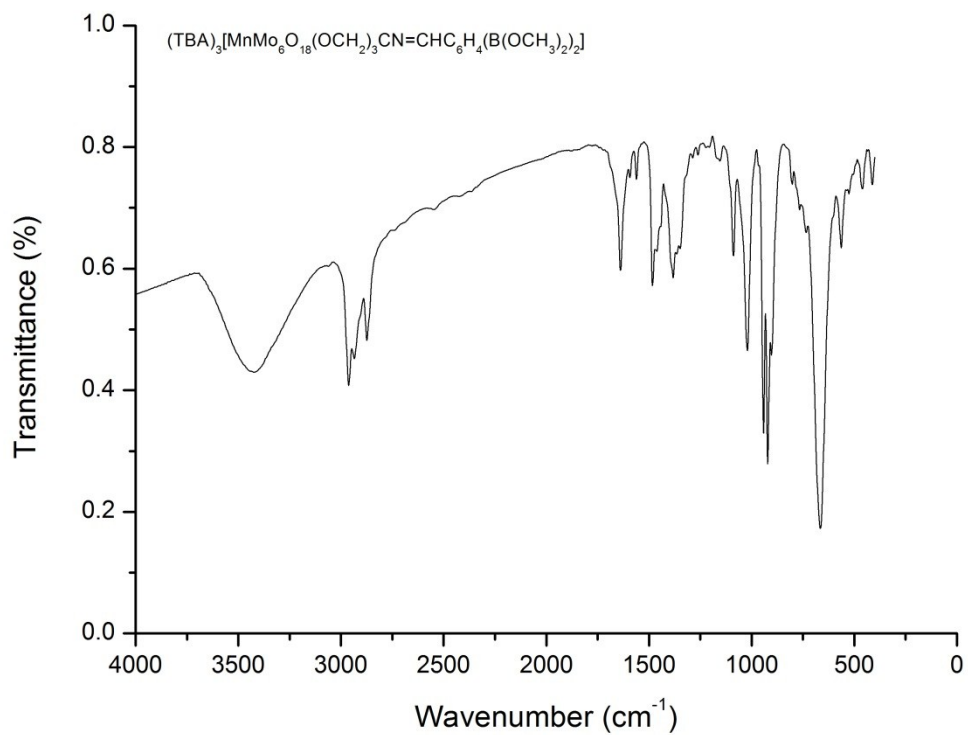
Synthesis of **1c**:

2-formyl phenyl boronic acid (15 mg, 0.1 mmol) was dissolved in 200 μ L of DMF, 1,3-Propanediol (50 μ L, 0.70 10^{-3} mmol) was added. The resulting solution was added to a 400 μ L solution of $(\text{N}(\text{C}_4\text{H}_9)_4)_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (100 mg, 0.0487 mmol) in DMF. The resulting solution was exposed to diethyl ether vapour and diffraction quality crystals appeared over a 1 day period. Yield: 45 mg (42%). $\text{C}_{76}\text{H}_{150}\text{B}_2\text{Mn}_1\text{Mo}_6\text{N}_5\text{O}_{26}$ (MW: 2202.22 g/mol) calcd. C 41.45%, H 6.87%, N 3.18%; found C 41.02%, H 6.54 %, N 3.29 %. IR (cm^{-1}): 2971(w), 2933(s), 2874(s), 2022(s), 1940(s), 1863(s), 1824(s), 1679(s), 1640(s), 1596(s), 1558(s), 1494(s), 1461(s), 1422(s), 1378(s), 1325(s), 1138(s), 1088(s), 1025(s), 947(vs), 923(vs), 894(vs), 797(s), 768(s), 734(s), 666(vs), 589(s), 560(s), 560(s), 511(s), 465(s), 409(s). ^1H NMR (d_6 -DMSO, 400 MHz): δ 0.93 (t, $-\text{CH}_3$ [Bu_4N^+]), 1.32 (q, $-\text{CH}_2$ [Bu_4N^+]), 2.50 (q, DMSO), 3.16 (t, CH_2 [Bu_4N^+]), 3.35 (s, H_2O), 3.99 (s, $-(\text{CH}_2)_3$), 7.20 (t, -AR), 7.49-7.64 (m, -AR), 63.10 (s, $-\text{OCH}_2$).

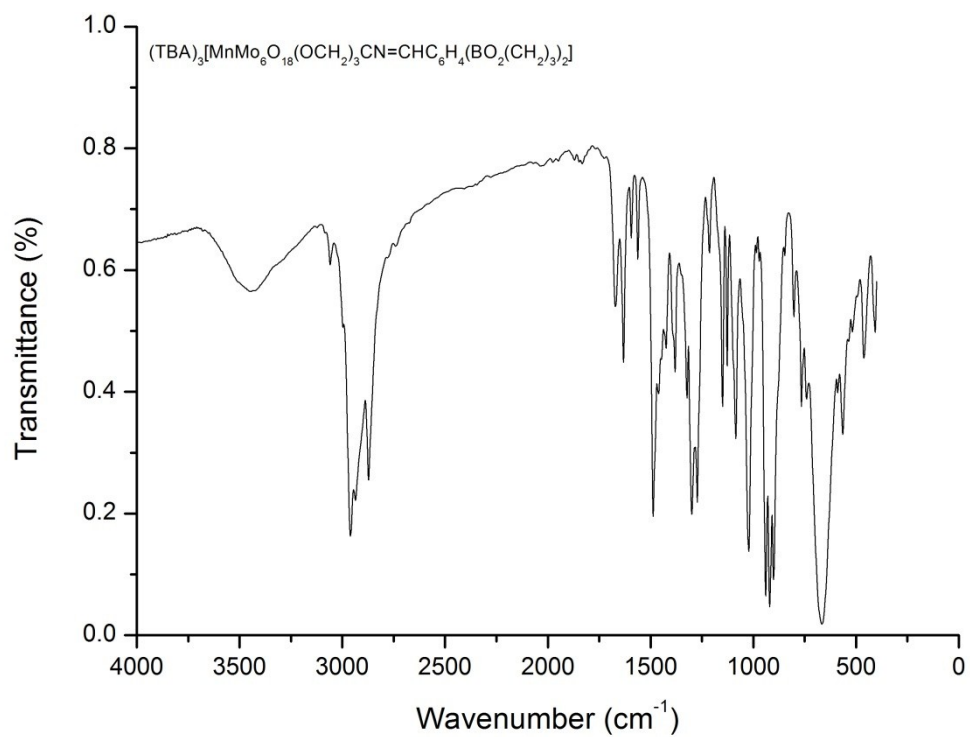
S1. Infrared spectrum of a freshly crystallized sample of **1a**



S2. Infrared spectrum of a freshly crystallized sample of **1b**



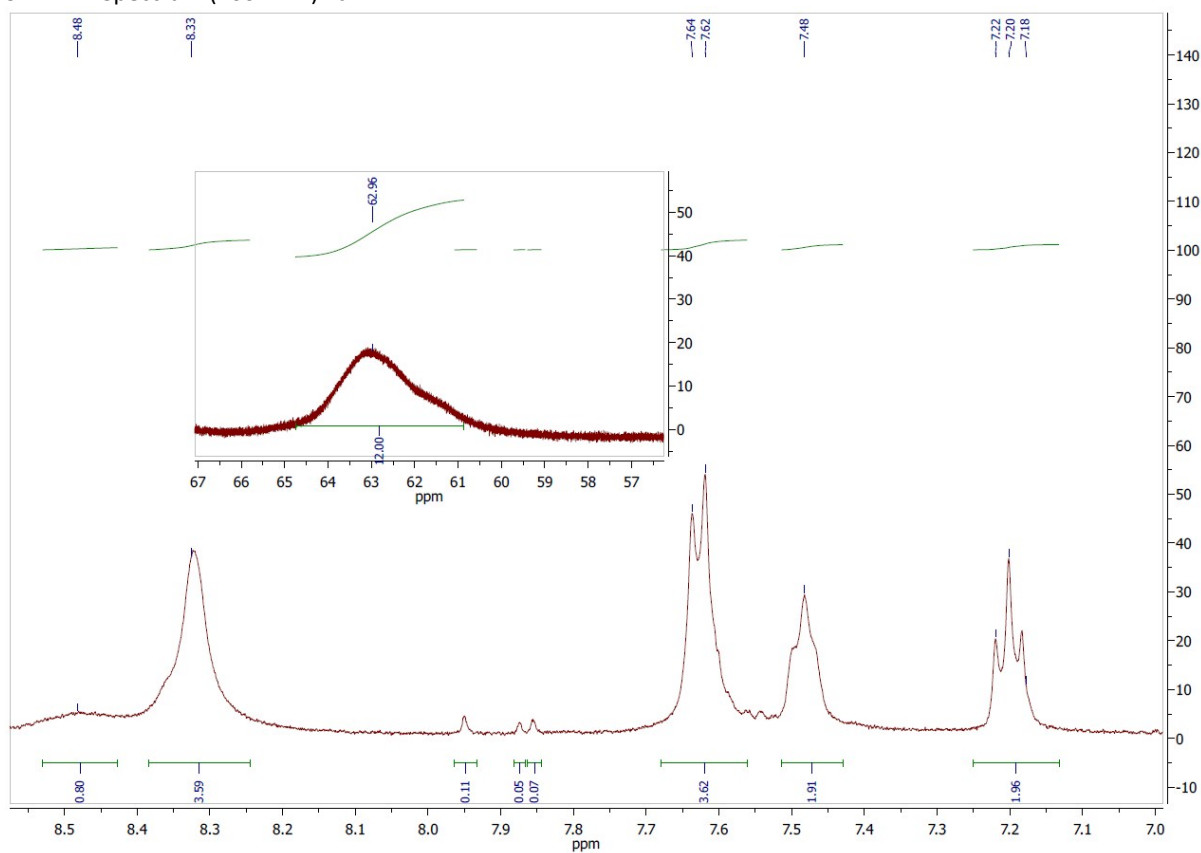
S3. Infrared spectrum of a freshly crystallized sample of **1c**



Nuclear Magnetic Resonance Spectroscopy

I. Compound analysis

S4. NMR Spectrum (400 MHz) 1a

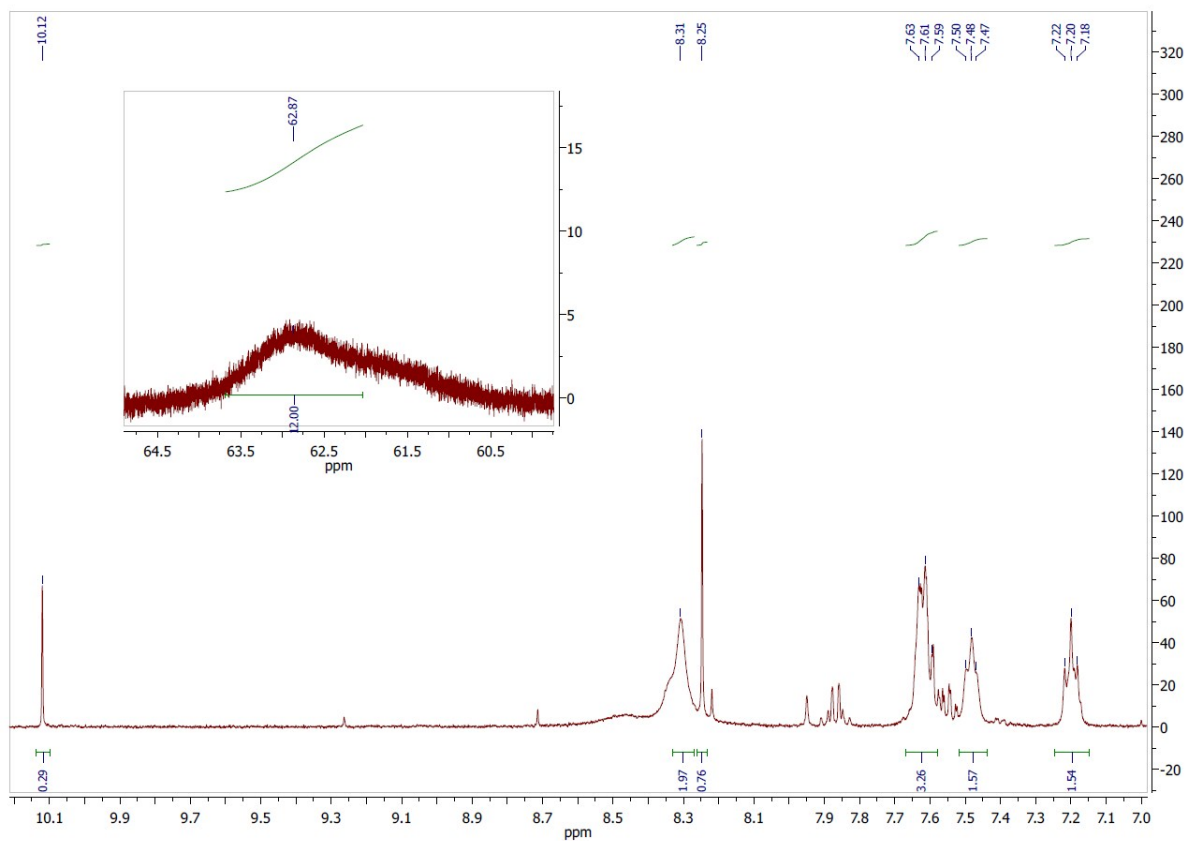


¹H NMR (d₆-DMSO, 400 MHz):

δ (ppm) 0.93 (t, -CH₃ [Bu₄N]⁺), 1.32 (q, -CH₂ [Bu₄N]⁺), 2.50 (q, DMSO), 3.16 (t, CH₂ [Bu₄N]⁺), 3.35 (s, H₂O), 7.20 (t, -AR), 7.48 (s, -AR), 7.63 (d, -AR), 8.33 (s, B-OH), 62.96 (s, -OCH₂).

The small peaks between 7.8-8 ppm correspond to a small amount of 2-Formyl phenyl boronic acid that couldn't be cleaned.

S5. NMR Spectrum (400 MHz) **1b**

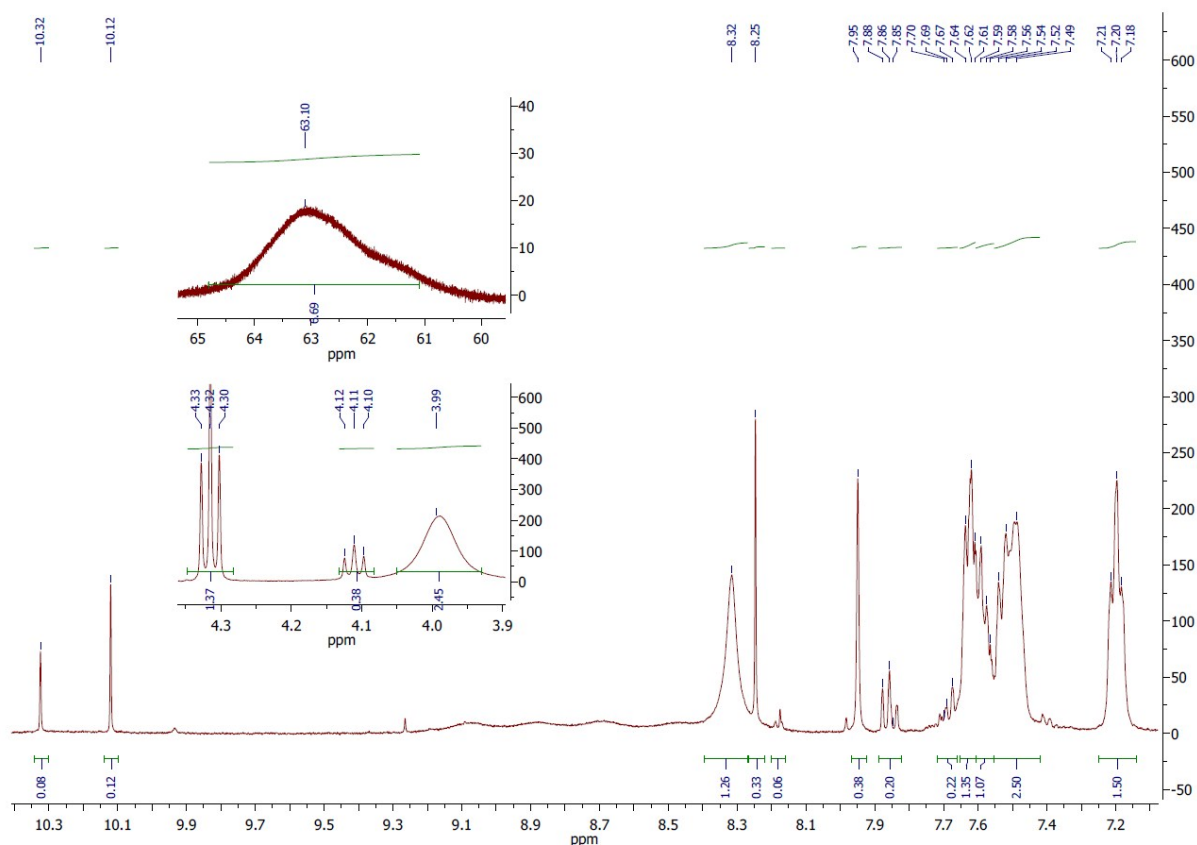


^1H NMR (d_6 -DMSO, 400 MHz):

δ (ppm) 0.93 (t, $-\text{CH}_3$ [Bu_4N^+]), 1.32 (q, $-\text{CH}_2$ [Bu_4N^+]), 2.50 (q, DMSO), 3.16 (t, CH_2 [Bu_4N^+]), 3.35 (s, H_2O), 7.20 (t, AR-), 7.48 (t, AR-), 7.61 (d, AR-), 8.31 (s, B-OH), 62.87 (s, $-\text{OCH}_2-$).

2-Formyl phenyl boronic acid peaks were observed between 7.8-8 ppm due to H_2O generation upon Schiff base coupling leading to the partial hydrolysis of the imine linkage. The boronic acid peak is observed at 8.25 ppm and the aldehyde peak was observed at 10.12 ppm.

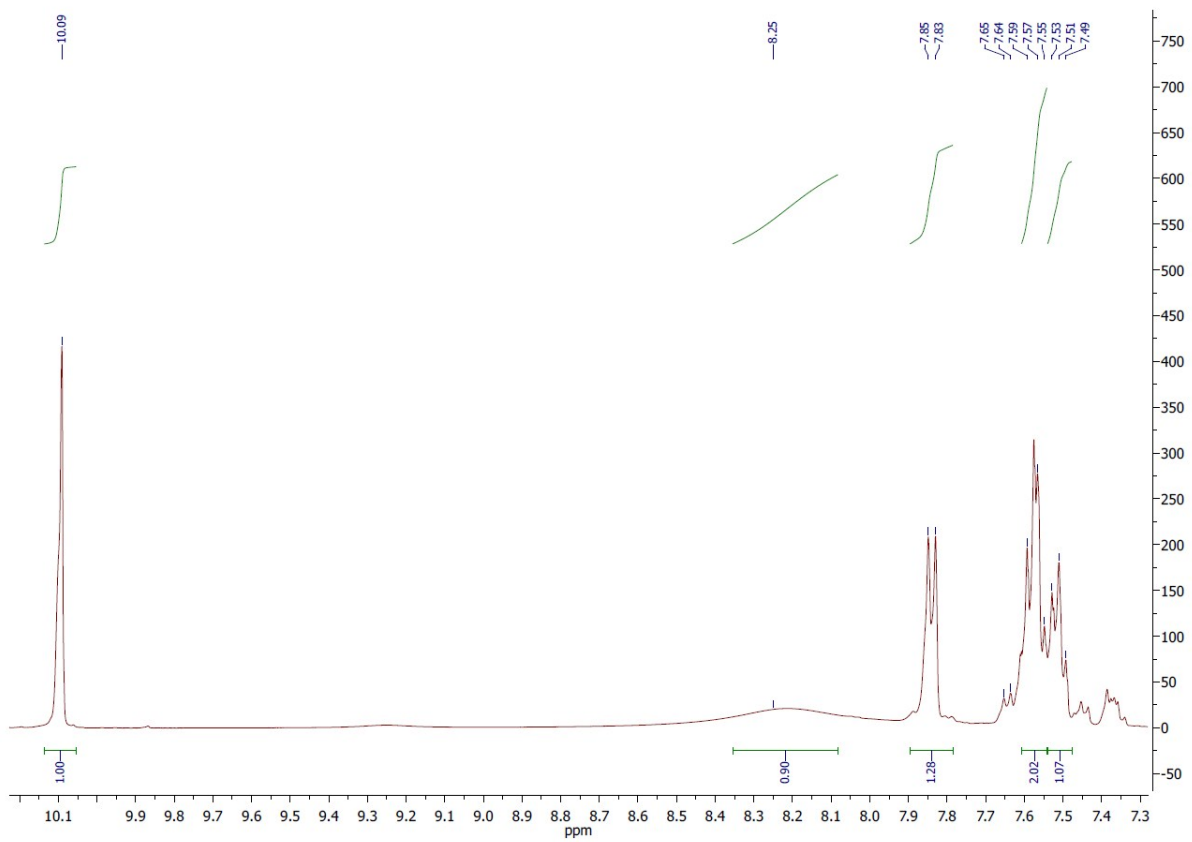
S6. NMR Spectrum (400 MHz) 1c



¹H NMR (d₆-DMSO, 400 MHz):

- Compound (**1c**)
 δ (ppm) 0.93 (t, -CH₃ [Bu₄N]⁺), 1.32 (q, -CH₂ [Bu₄N]⁺), 2.50 (q, DMSO), 3.16 (t, CH₂ [Bu₄N]⁺), 3.35 (s, H₂O), 3.99 (s, -(CH₂)₃), 7.20 (t, -AR), 7.49-7.64 (m, -AR), 63.10 (s, -OCH₂).
- Compound (**1a**)
 Due to signals overlapping in the aromatic region, it is hard to distinguish these peaks. However, the boronic acid singlet was observed at 8.32 ppm.
- 2-Formyl phenyl boronic acid peaks were observed between 7.8-8 ppm due to H₂O generation upon Schiff base coupling leading to the partial hydrolysis of the imine linkage. The boronic acid peak is observed at 8.25 ppm and the aldehyde peak was observed at 10.12 ppm.
- 4-(1,3,2-dioxaborinan-2-yl)benzaldehyde: δ 4.11 (t, -(CH₂)₃), 7.86 (t, Ar), 10.32 (s, -CH=O).
- propane-1,3-diol:
 δ 4.32 (t, CH₃-CH₂-CH₃)

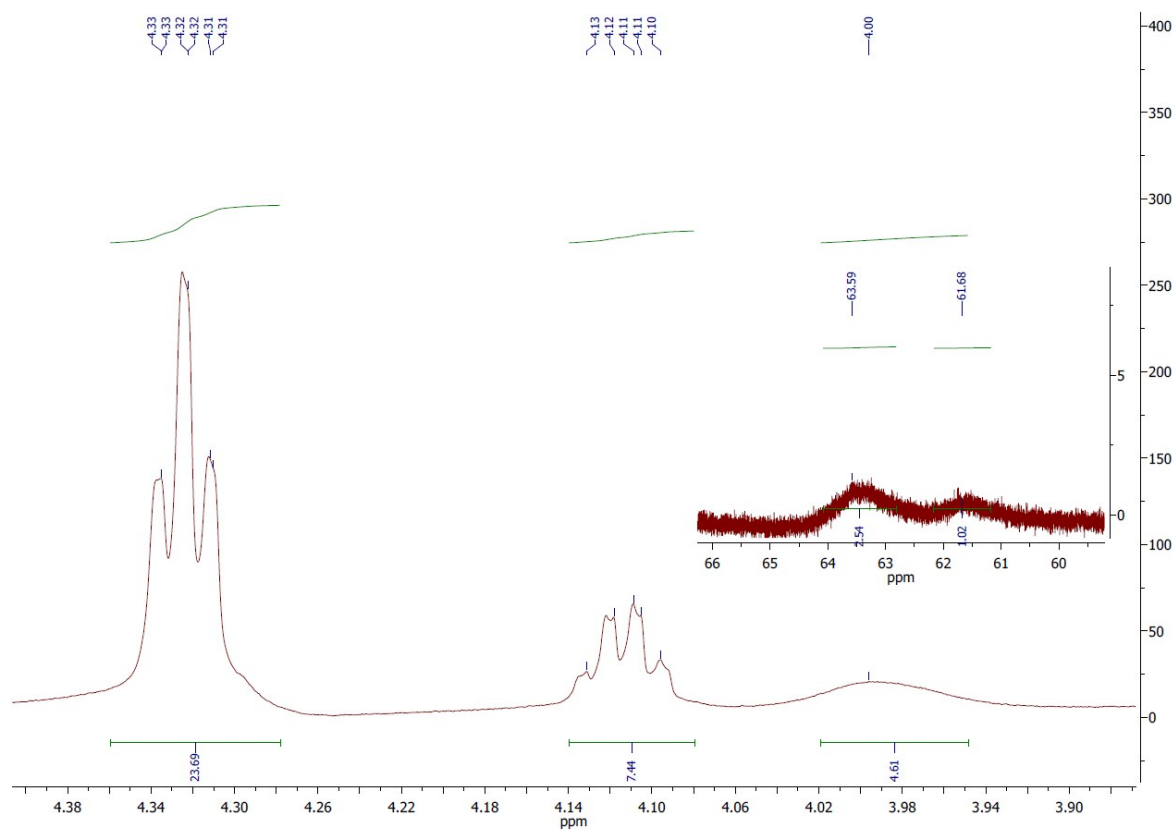
S7. NMR Spectrum (400 MHz) 2-formyl phenyl boronic acid



II. Titration experiments:

Signals overlapping in the aromatic region make it impossible to assign these peaks. Therefore, we are only showing the methylene glycol peaks between 3.9 and 4.4 ppm and the highly deshielded ($-\text{OCH}_2$) peaks between 61 and 65 ppm.

S8. NMR Spectrum (400 MHz) addition of 0.5 equivalents of propane-1,3-diol to 1a in d_6 -DMSO



Compound (1c): 4.00 ppm

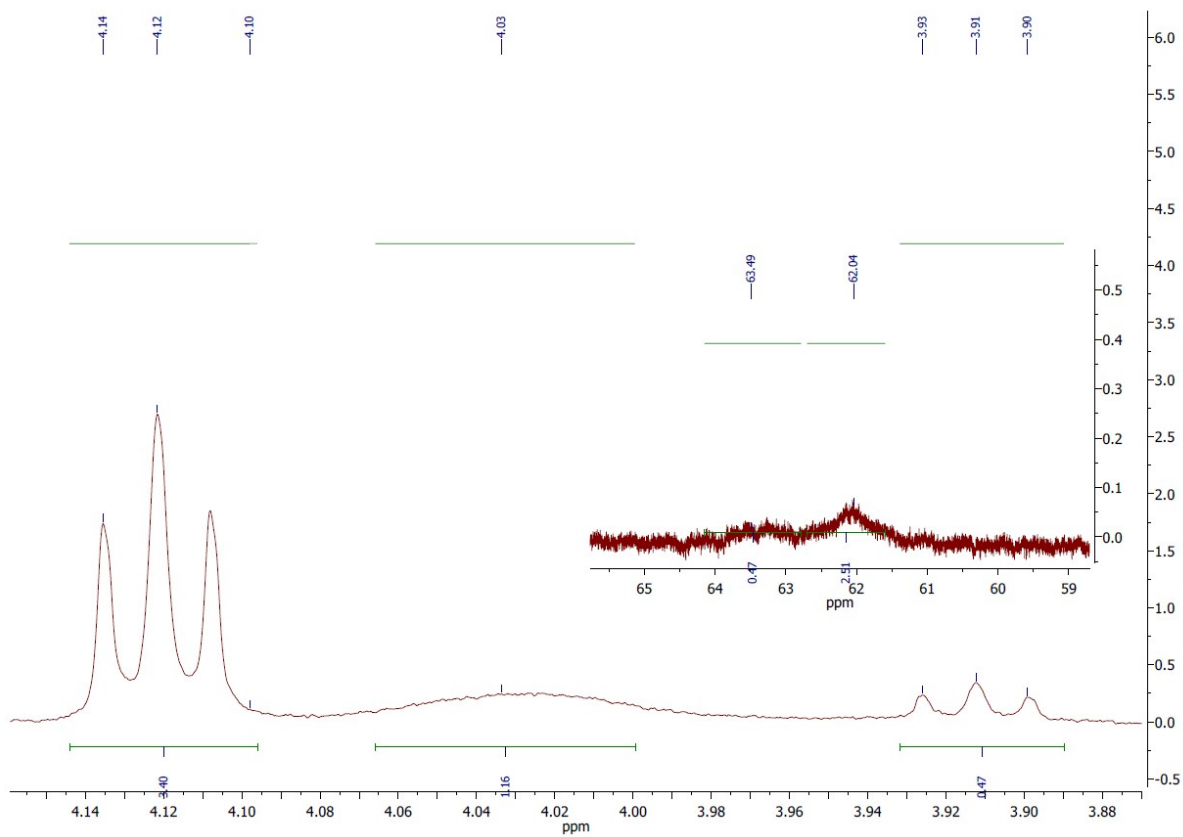
4-(1,3,2-dioxaborinan-2-yl)benzaldehyde: 4.12 ppm

propane-1,3-diol: 4.32 ppm

$-\text{OCH}_2$ ($(\text{N}(\text{C}_4\text{H}_9)_4)_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$): 61.68 ppm

$-\text{OCH}_2$ (**1c**): 63.59 ppm

S9. NMR Spectrum (400 MHz) addition of 2 equivalents of propane-1,3-diol to 1a in d₆-DMSO



Compound (1c): 4.03 ppm

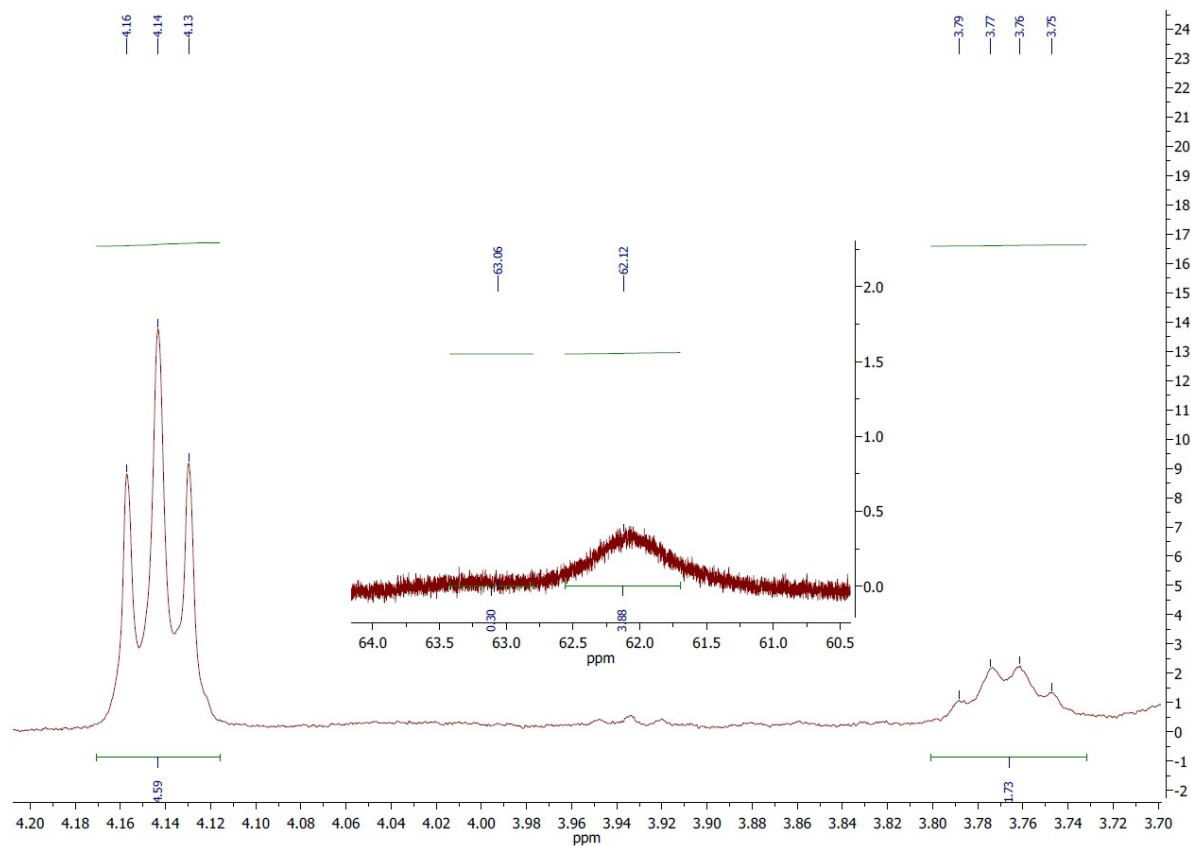
4-(1,3,2-dioxaborinan-2-yl)benzaldehyde: 3.91 ppm

propane-1,3-diol: 4.12 ppm

-OCH₂ ((N(C₄H₉)₄)₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}]₂): 62.04 ppm

-OCH₂ (1c) 63.49 ppm

S10. NMR Spectrum (400 MHz) addition of 4 equivalents of propane-1,3-diol to 1a in d₆-DMSO



4-(1,3,2-dioxaborinan-2-yl)benzaldehyde: 3.77 ppm
propane-1,3-diol: 4.14 ppm

-OCH₂ ((N(C₄H₉)₄)₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}]₂): 62.12 ppm
-OCH₂ (**1c**): 63.06 ppm

Table 1. BVS calculations for **1a**

The individual bond valences in turn are calculated from the observed bond lengths.

$$V_i = \sum V_i$$

R_i is the observed bond length, R_0 is a tabulated parameter expressing the (ideal) bond length when the element i has exactly valence 1, and B is an empirical constant, typically 0.37 Å.

$$V_i = \exp[(R_0 - R_i)/B]$$

	Mo	Ro	B		Mo	Ro	B
		1.907	0.37			1.907	0.37
O7	Mo ^{VI} 2	1.667	1.912954	O3	Mo ^{VI} 1	1.696	1.768745
O6		1.664	1.928527	O1		1.887	1.055542
O4		1.904	1.008141	O4		1.909	0.994609
O5		2.348	0.303646	O11		2.327	0.321379
O12		2.329	0.319646	O5		2.357	0.296349
O8		1.923	0.957678	O2		1.684	1.82705
			6.430593				6.263674

	Mo	Ro	B		Mn	Ro	B
		1.907	0.37			1.732	0.37
O10	Mo ^{VI} 3	1.709	1.707679	O11	Mn ^{III}	1.996	0.48992
O9		1.680	1.846909	O11		1.996	0.48992
O8		1.923	0.957678	O12		1.984	0.50607
O12		2.356	0.297151	O12		1.984	0.50607
O11		2.355	0.297956	O5		1.980	0.51157
O1		1.905	1.00542	O6		1.980	0.51157
			6.112794				3.015119

Table 2. BVS calculations for **1b**

	Mo	Ro	B		Mo	Ro	B
		1.907	0.37			1.907	0.37
O15	Mo ^{VI} 2	1.701	1.745004	O5	Mo ^{VI} 1	1.899	1.021857
O7		1.696	1.768745	O11		2.428	0.244606
O5		1.937	0.922119	O1		2.357	0.296349
O12		2.414	0.254038	O14		1.686	1.817201
O8		1.917	0.973335	O3		1.909	0.994609
O14		2.414	0.254038	O4		1.724	1.639833
			5.917279				6.014455

	Mo	Ro	B		Mn	Ro	B
		1.907	0.37			1.732	0.37
O3	Mo ^{VI} 3	1.921	0.962869	O11	Mn ^{III}	1.943	0.565373
O8		1.928	0.944824	O11		1.943	0.565373
O6		1.686	1.817201	O12		1.936	0.576171
O9		1.711	1.698473	O12		1.936	0.576171
O12		2.358	0.29555	O1		2.057	0.415456
O11		2.319	0.328403	O1		2.057	0.415456
			6.04732				3.113999

Table 3. BVS calculations for **1c**

	Mo	Ro	B		Mo	Ro	B
		1.907	0.37			1.907	0.37
O7	Mo ^{VI} 2	1.712	1.693889	O3	Mo ^{VI} 1	1.914	0.981259
O6		1.704	1.730912	O1		1.717	1.671153
O4		2.371	0.285346	O4		1.714	1.684757
O5		1.925	0.952516	O11		1.936	0.924615
O12		2.351	0.301194	O5		2.311	0.335581
O8		1.918	0.970708	O2		2.433	0.241322
			5.934565				5.838687

	Mo	Ro	B		Mn	Ro	B
		1.907	0.37			1.732	0.37
O10	Mo ^{VI} 3	1.918	0.970708	O11	Mn ^{III}	1.930	0.58559
O9		2.371	0.285346	O11		1.930	0.58559
O8		2.351	0.301194	O12		2.127	0.343844
O12		1.925	0.952516	O12		2.127	0.343844
O11		1.704	1.730912	O5		1.924	0.595164
		1.712	1.693889	O6		1.924	0.595164
			5.934565				3.049195

Table 4. Bond lengths and angles for **1a**, **1b** and **1c**

	(1a)	(1b)	(1c)
Distances (Å)			
B-O	1.380(3)-1.440(3)	1.340(4)-1.510(4)	1.330(11)-1.361(10)
N-C _{alkoxo}	1.416(18)-1.514(19)	1.470(3)-1.500(3)	1.476(6)
N=C	1.235(14)-1.259(14)	1.260(3)-1.320(3)	1.250(7)
B-N		1.830(4)-1.870(4)	
O-C _{MeOH}		1.440(3)-1.460(3)	
O-C _{diol}			1.443(11)-1.462(10)
Angles (°)			
O-B-O	111.12(18)-113.6(18)	108.0(3)-110.0(3)	122.8(8)

O-B-C _{Ar}	116.0(2)-130.0(2)	114.0(3)-125.0(3)	115.9(7)-121.3(6)
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	1a	1b	1c
Empirical formula	C ₇₀ H ₁₃₄ B ₂ Mn ₁ Mo ₆ N ₅ O ₂₈	C ₁₄₈ H ₂₈₄ B ₄ Mn ₂ Mo ₁₂ N ₁₀ O ₅₆	C ₇₆ H ₁₄₂ B ₂ MnMo ₆ N ₅ O ₂₈
Formula weight	2146.01	4404.23	2226.14
Crystal system	Monoclinic	Monoclinic	Monoclinic
a / Å	24.0713(6)	22.8863(8)	35.796(3)
b / Å	14.3578(5)	24.7348(7)	13.2361(3)
c / Å	28.5472(15)	18.1665(6)	25.8822(19)
α / °			
β / °	94.407(3)	93.009(3)	128.966(12)
γ / °			
V / Å ³	9837.1(7)	10269.6(6)	9534.8(16)
ρ g / cm ⁻³	1.449	1.424	1.551
Z	4	2	4
μ (Cu) mm ⁻¹	7.646	7.338	7.911
Total reflections	78795	26623	33269
Unique reflections	10426	10748	9745
No. parameters	220	590	540
F(000)	4400	4528	4576
R ₁	0.0742	0.1071	0.0472
wR ₂	0.2487	0.2975	0.1448
GOF	1.147	1.074	1.129

Table 5. Crystallographic data for **1a**, **1b** and **1c**

References

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3. Sheldrick, G. M., *Acta. Cryst. Sec. A.*, **2015**, A71, 3-8.
4. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H., *J. Appl. Cryst.* **2009**, 42, 339-341.