Electronic Supplementary Material (ESI) for Dalton Transactions.

Metal complexes of pro-vitamin K3 analog phthiocol (2-hydroxy-3-methylnaphthalene-1,4-dione): Synthesis, Characterization and anticancer activity

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Table S32. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **3**

Table S33. Torsion angles [°] for **3**

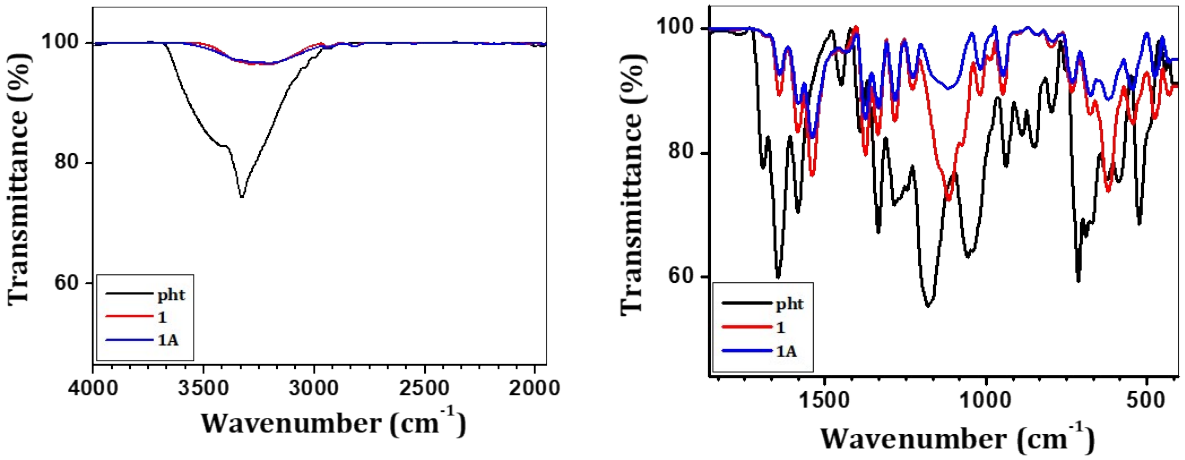


Figure S1. FT-IR spectra of **pht**, **1** and **1A** in region 4000 cm^{-1} to 400 cm^{-1}.

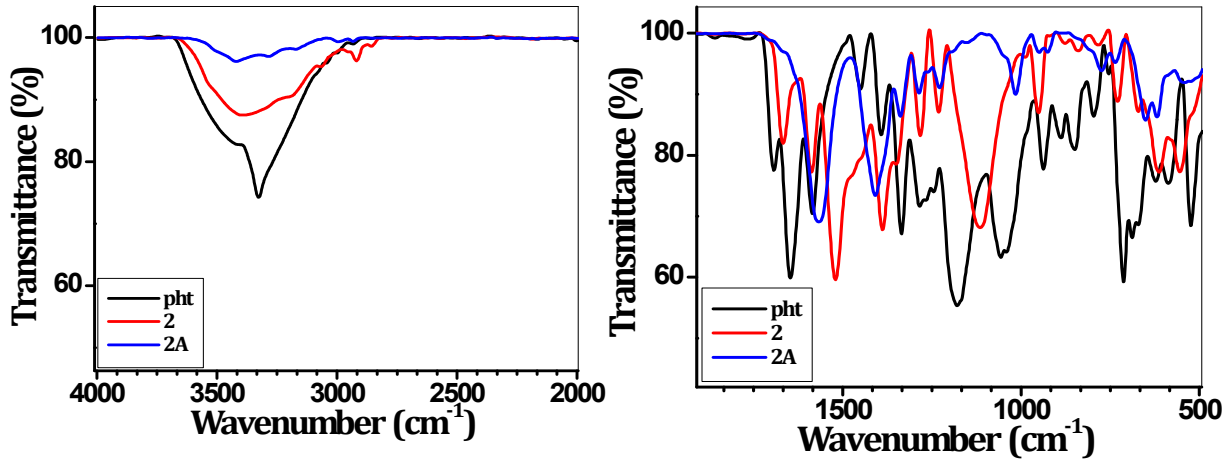


Figure S2. FT-IR spectra of **pht**, **2** and **2A** in region 4000 cm^{-1} to 400 cm^{-1}.

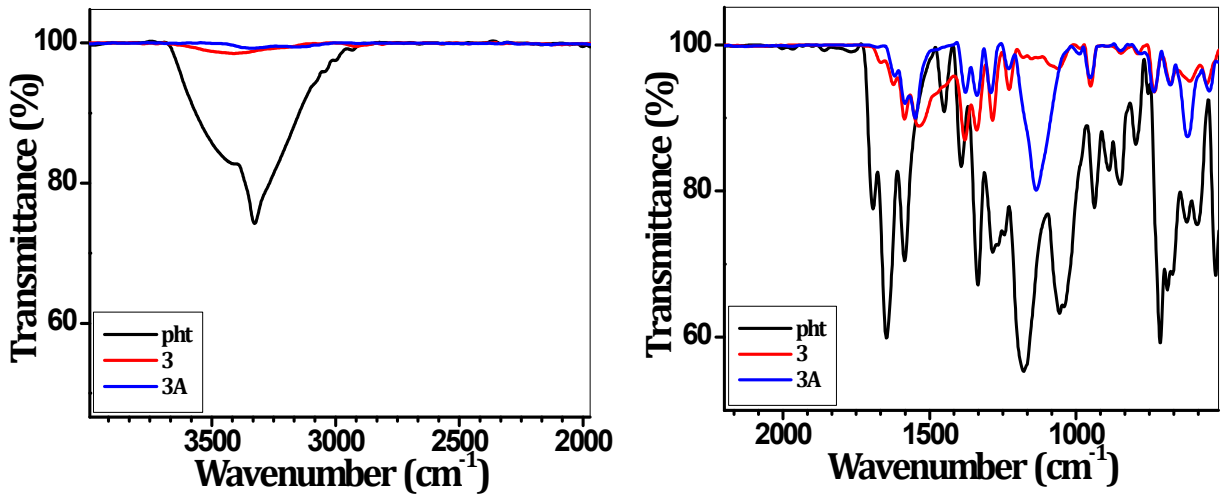


Figure S3. FT-IR spectra of **pht**, **3** and **3A** in region 4000 cm^{-1} to 400 cm^{-1}.

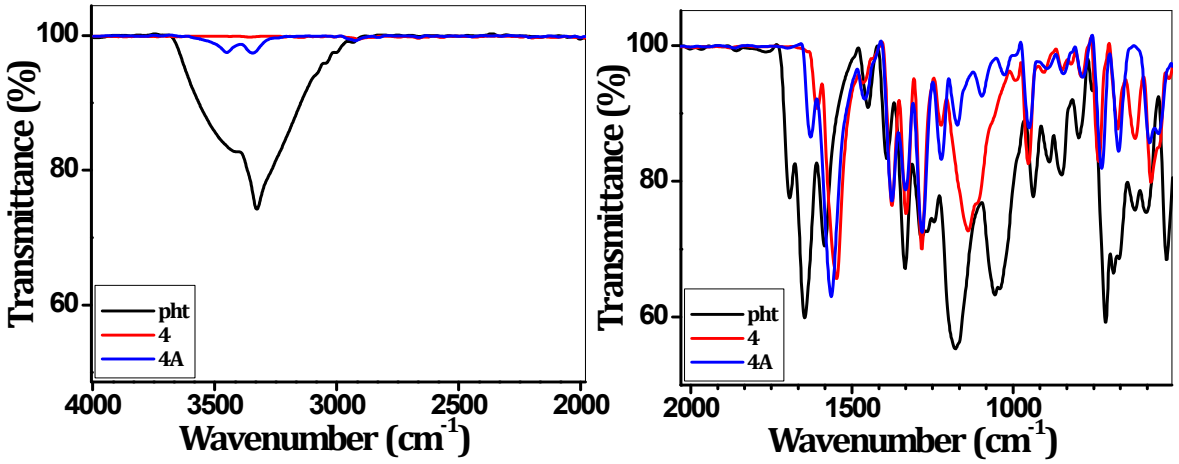


Figure S4. FT-IR spectra of **pht**, **4** and **4A** in region 4000 cm^{-1} to 400 cm^{-1}.

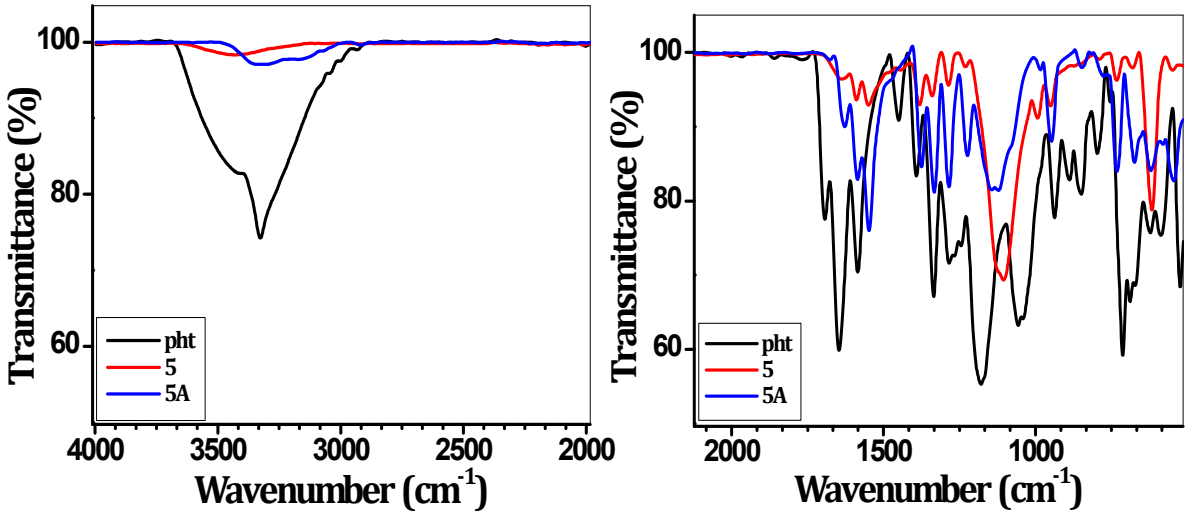


Figure S5. FT-IR spectra of **pht**, **5** and **5A** in region 4000 cm^{-1} to 400 cm^{-1}

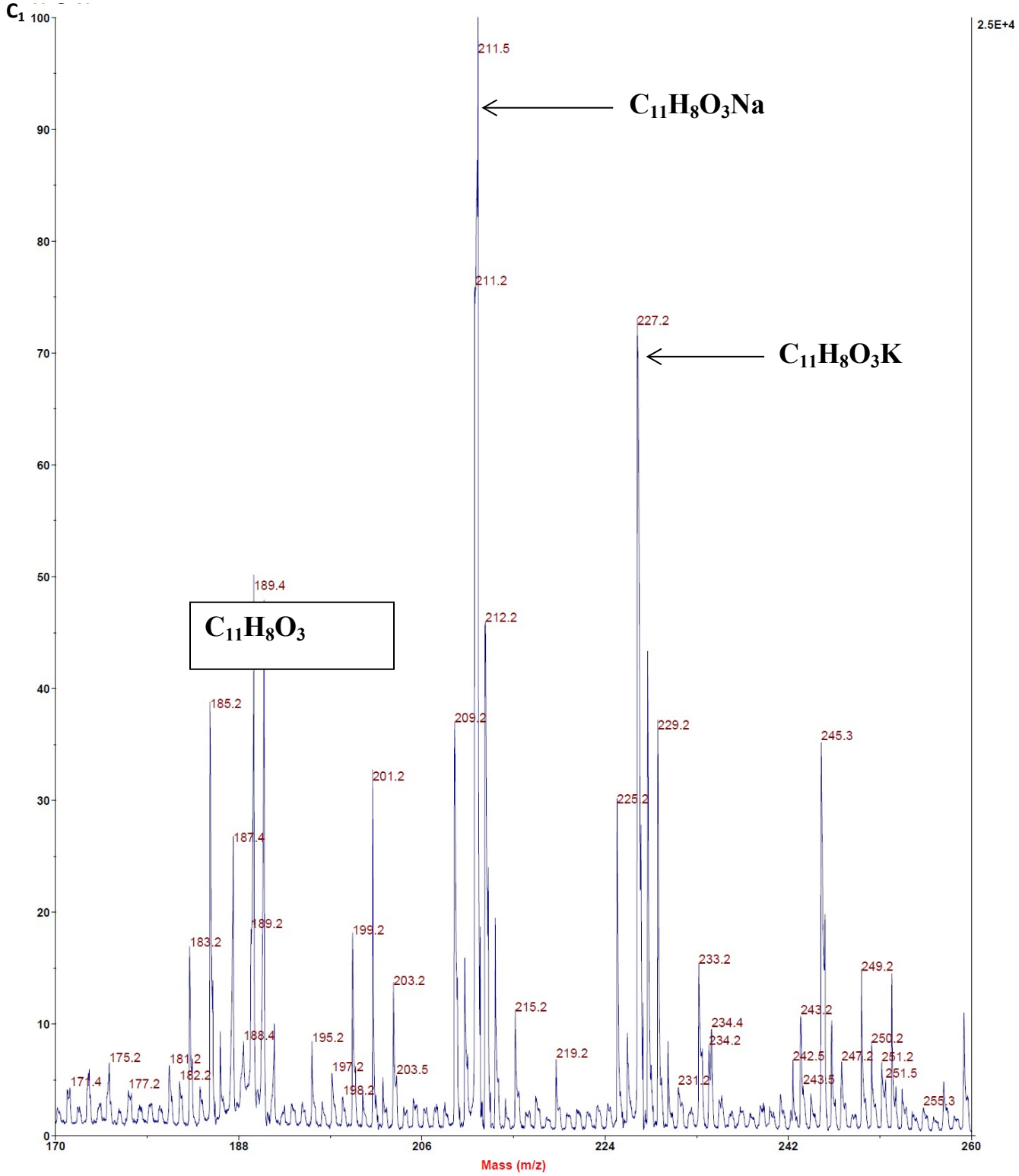


Figure S6. MALDI-TOF spectrum of **pht**.

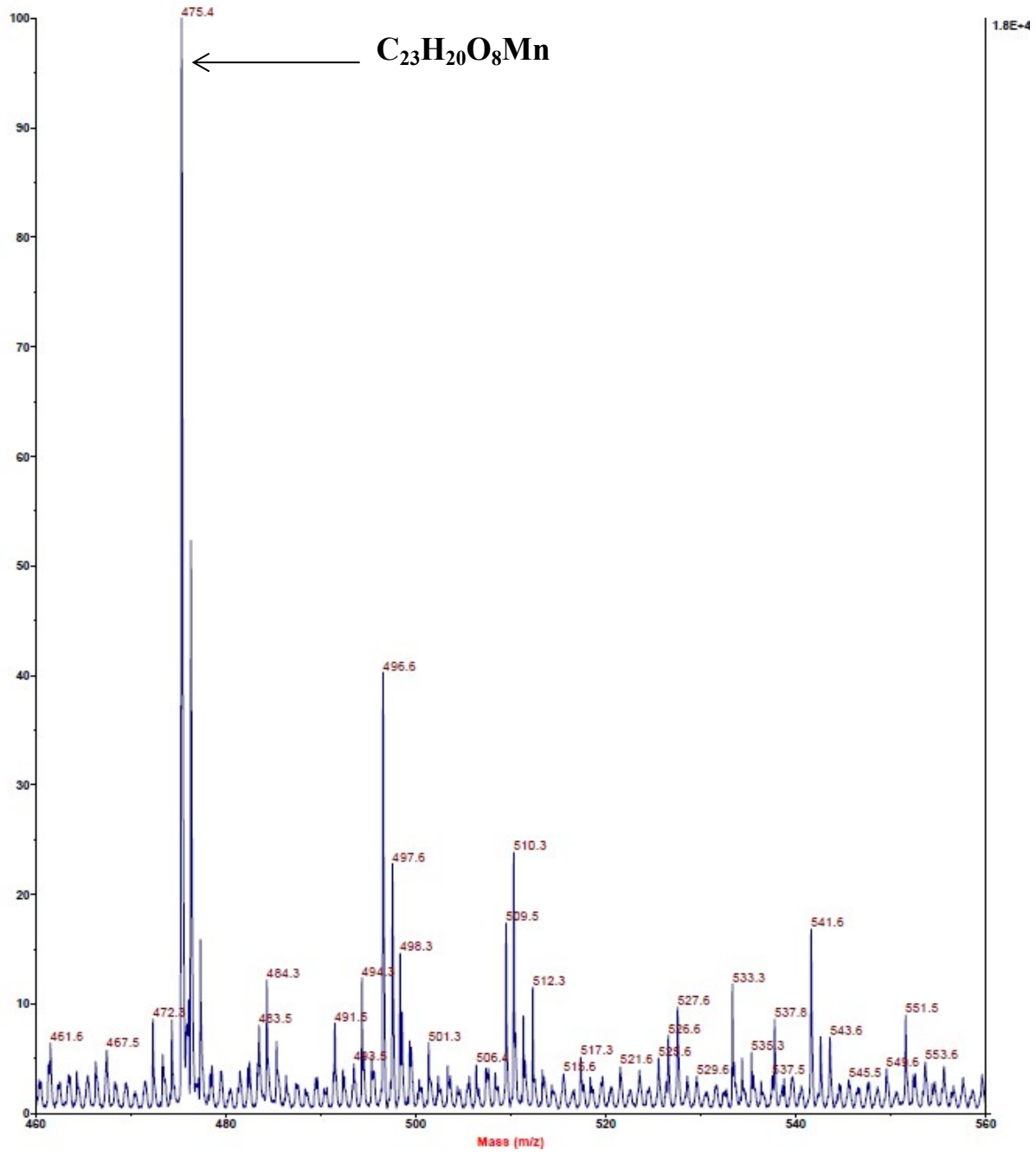


Figure S7. MALDI-TOF spectrum of **1**.

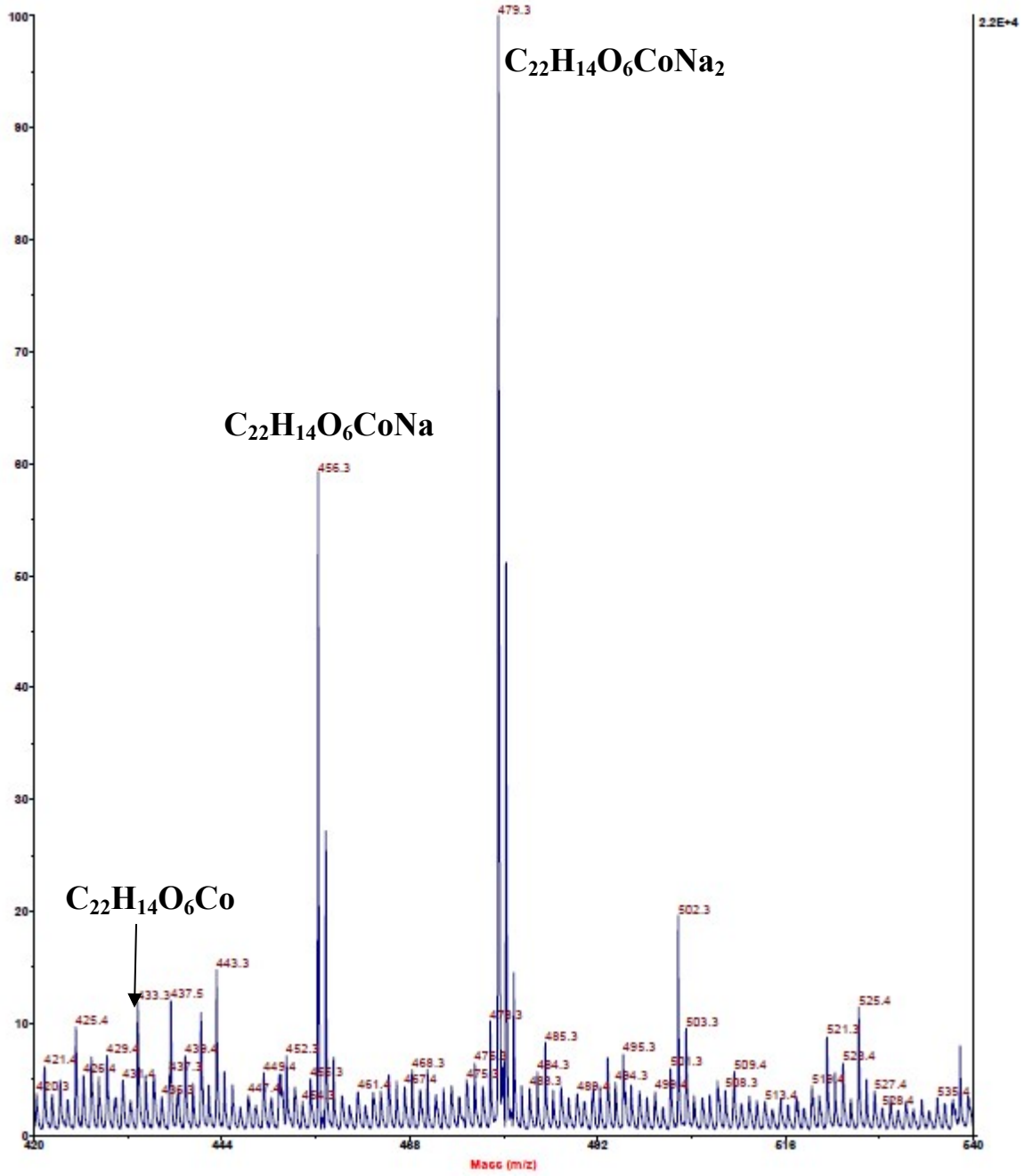


Figure S8. MALDI-TOF spectrum of **2**.

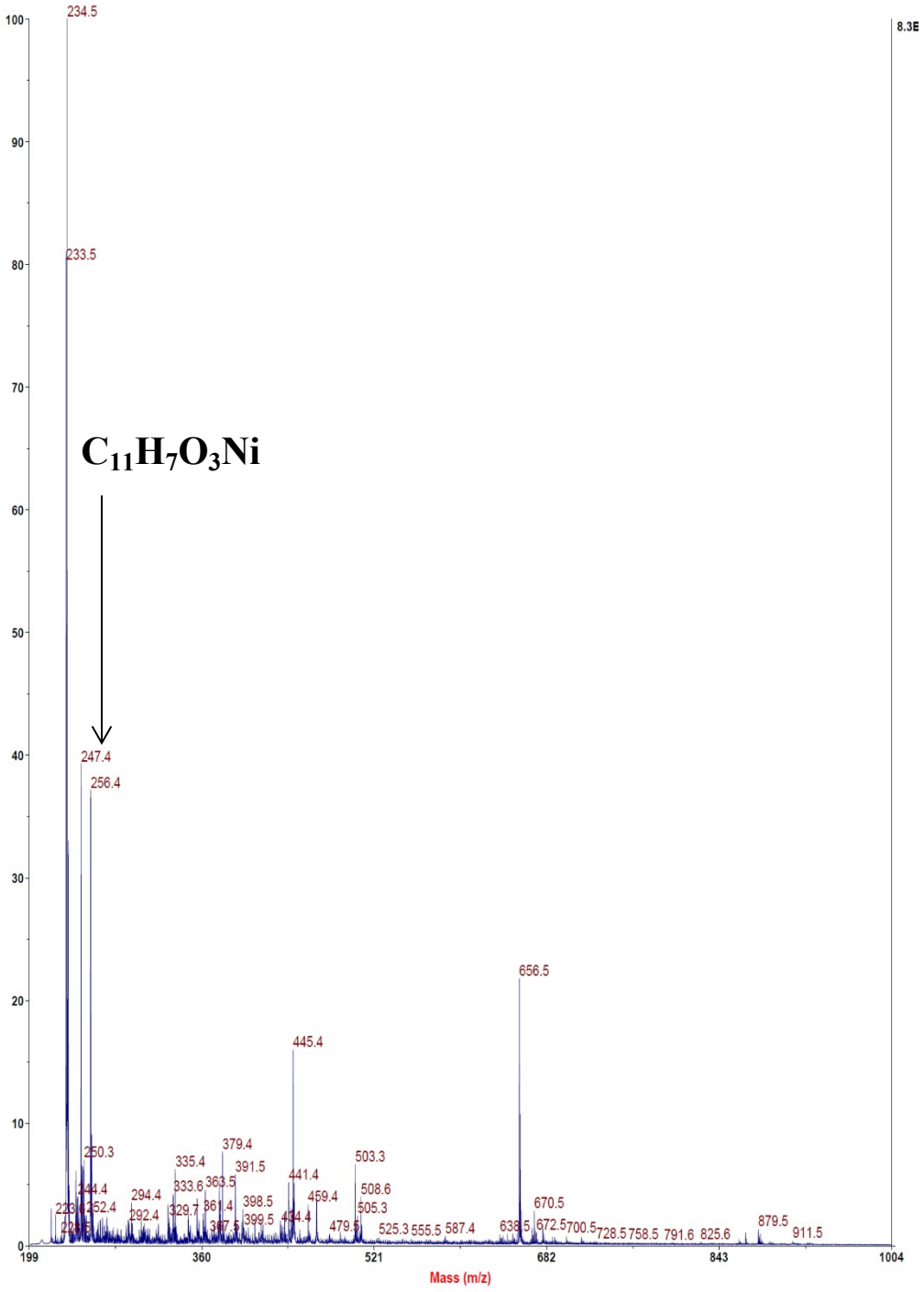


Figure S9. MALDI-TOF spectrum of **3**.

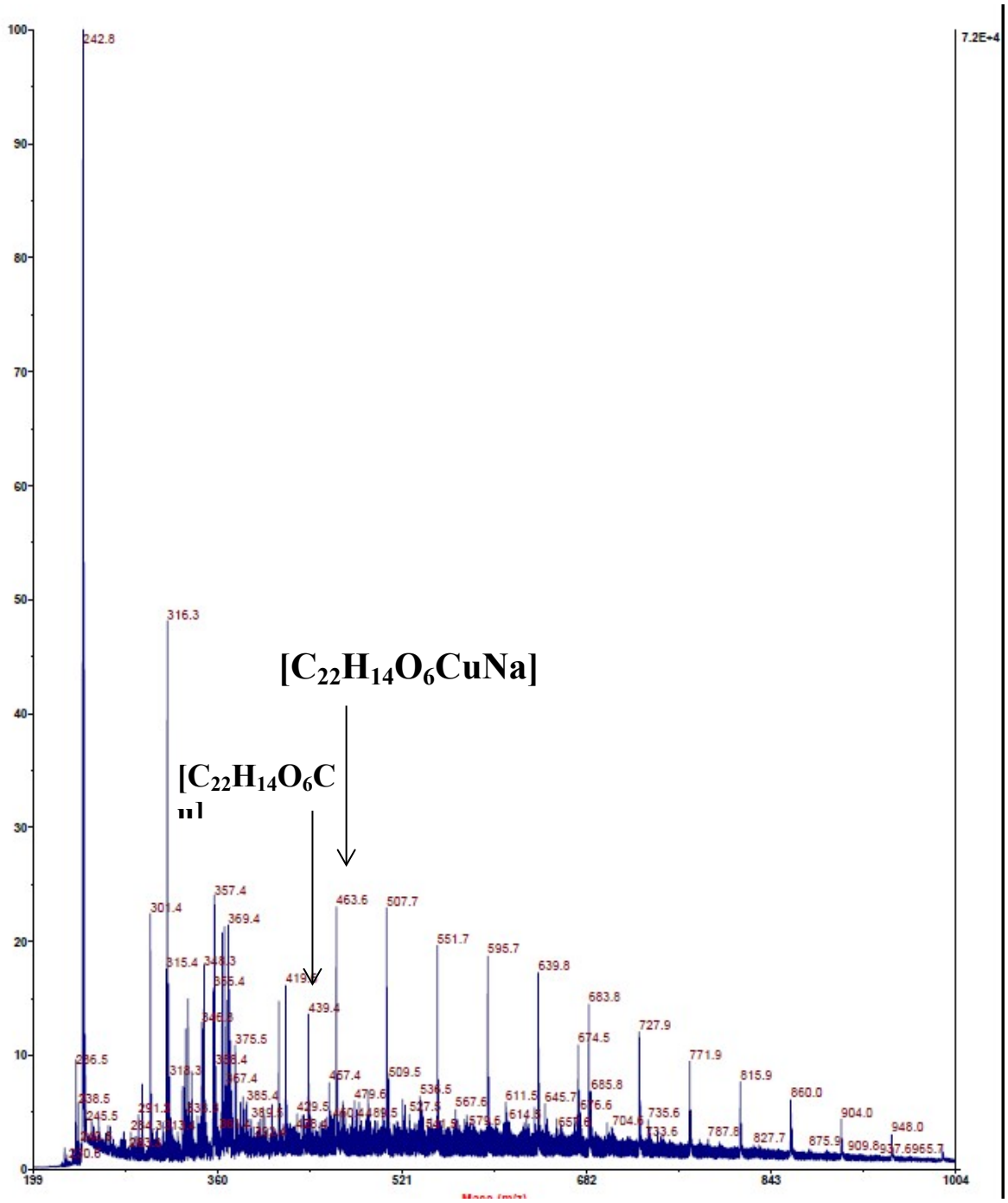


Figure S10. MALDI-TOF spectrum of **4**.

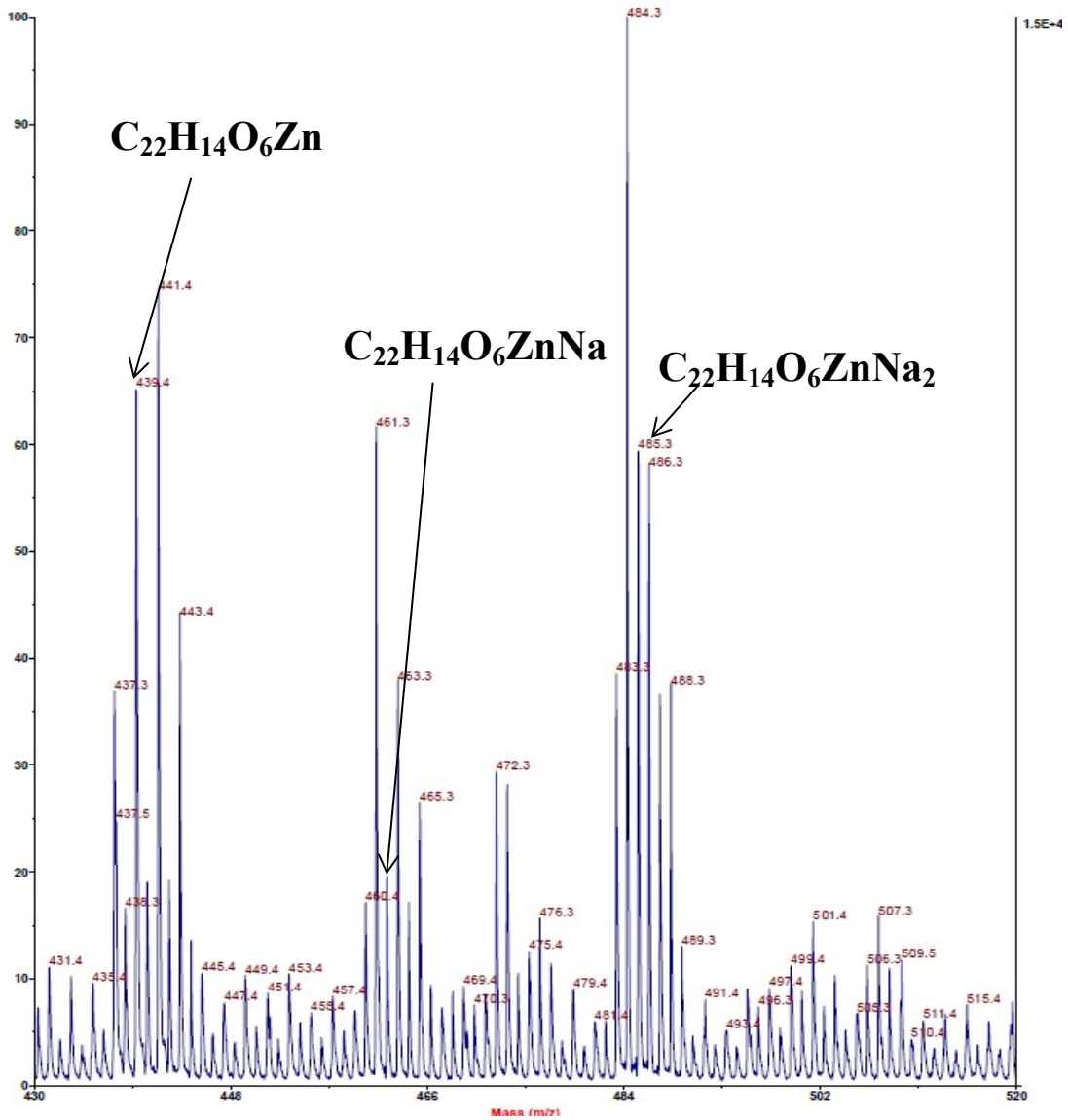


Figure S11. MALDI-TOF spectrum of **5**.

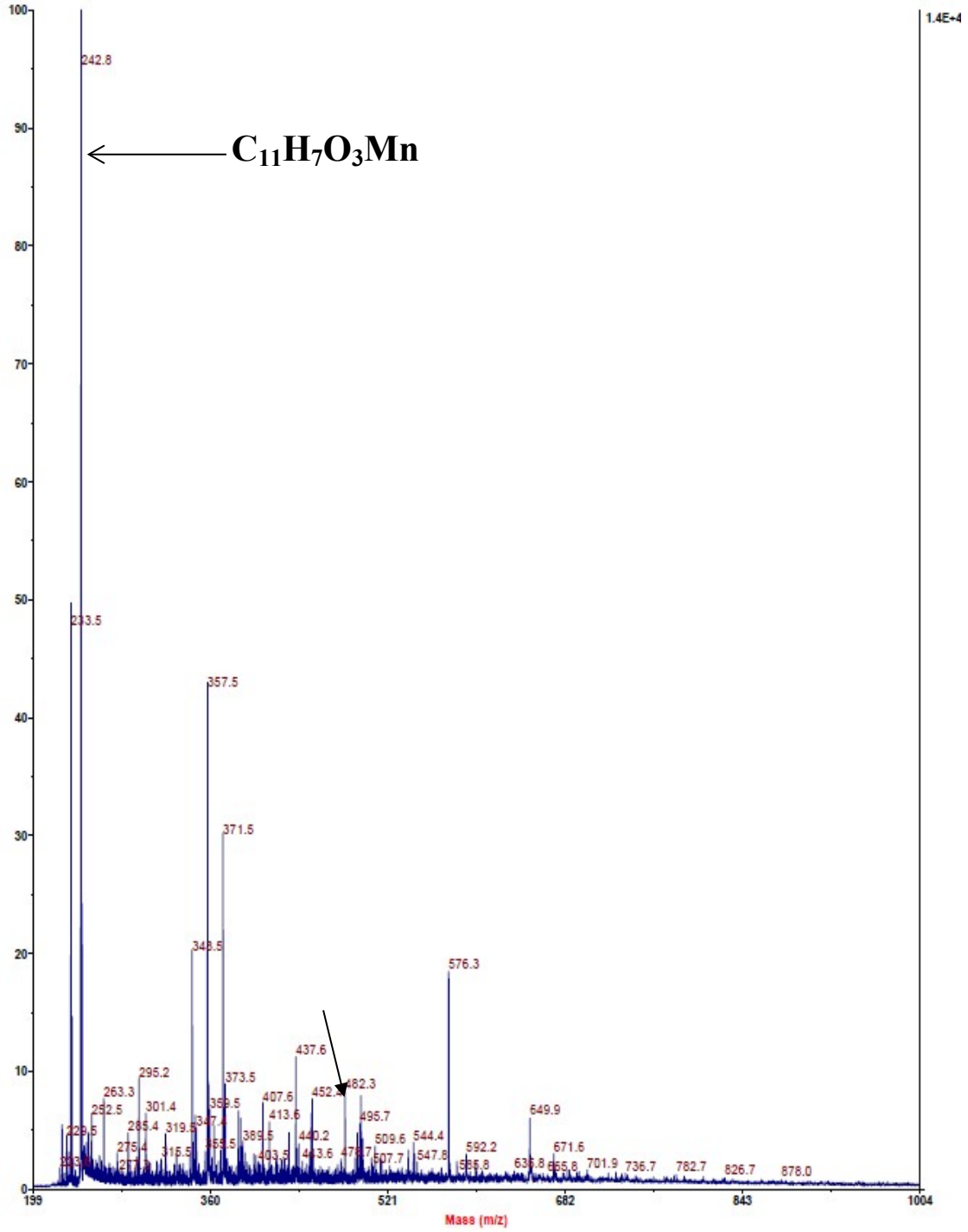


Figure S12. MALDI-TOF spectrum of **1A**.

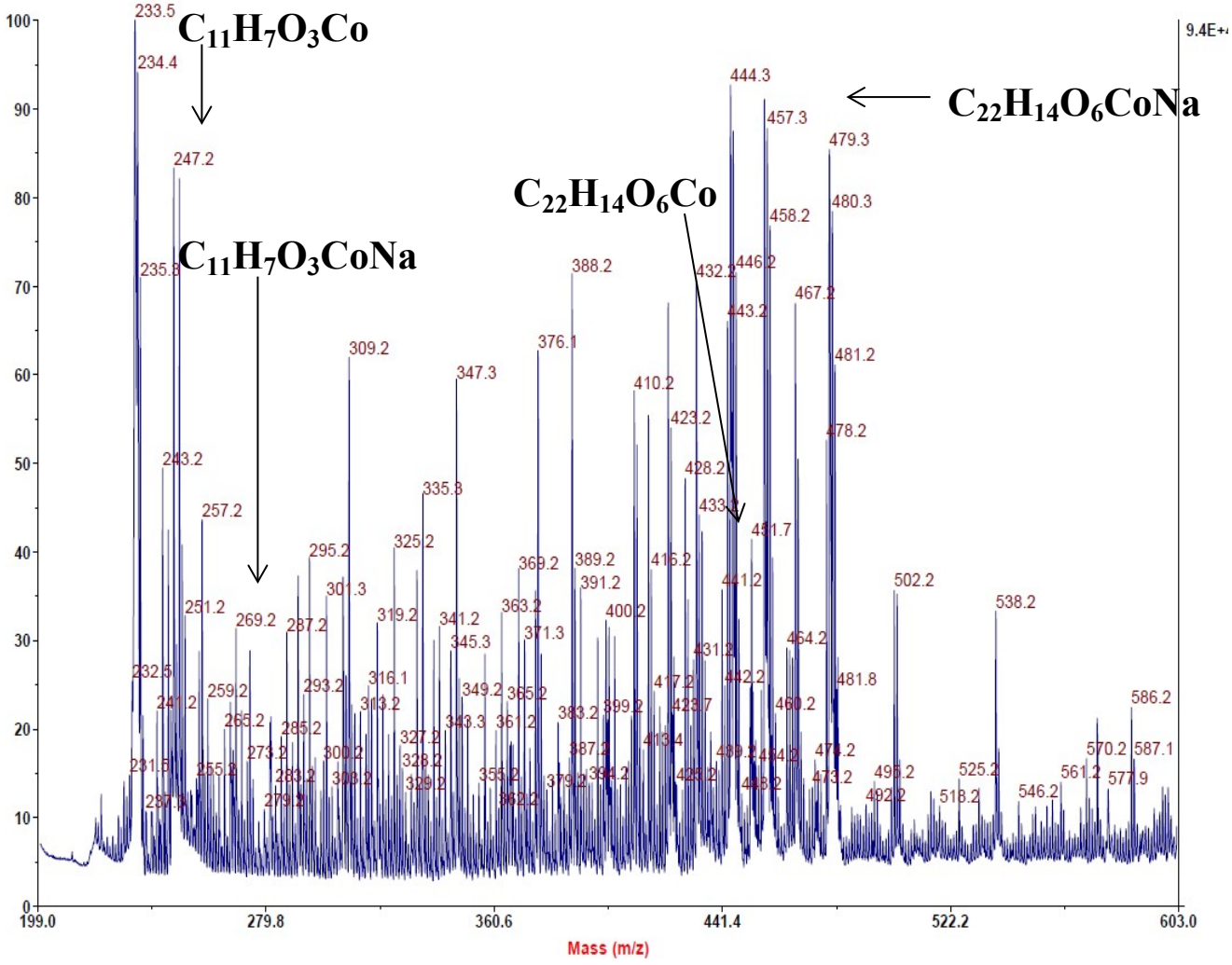


Figure S13. MALDI-TOF spectrum of **2A**.

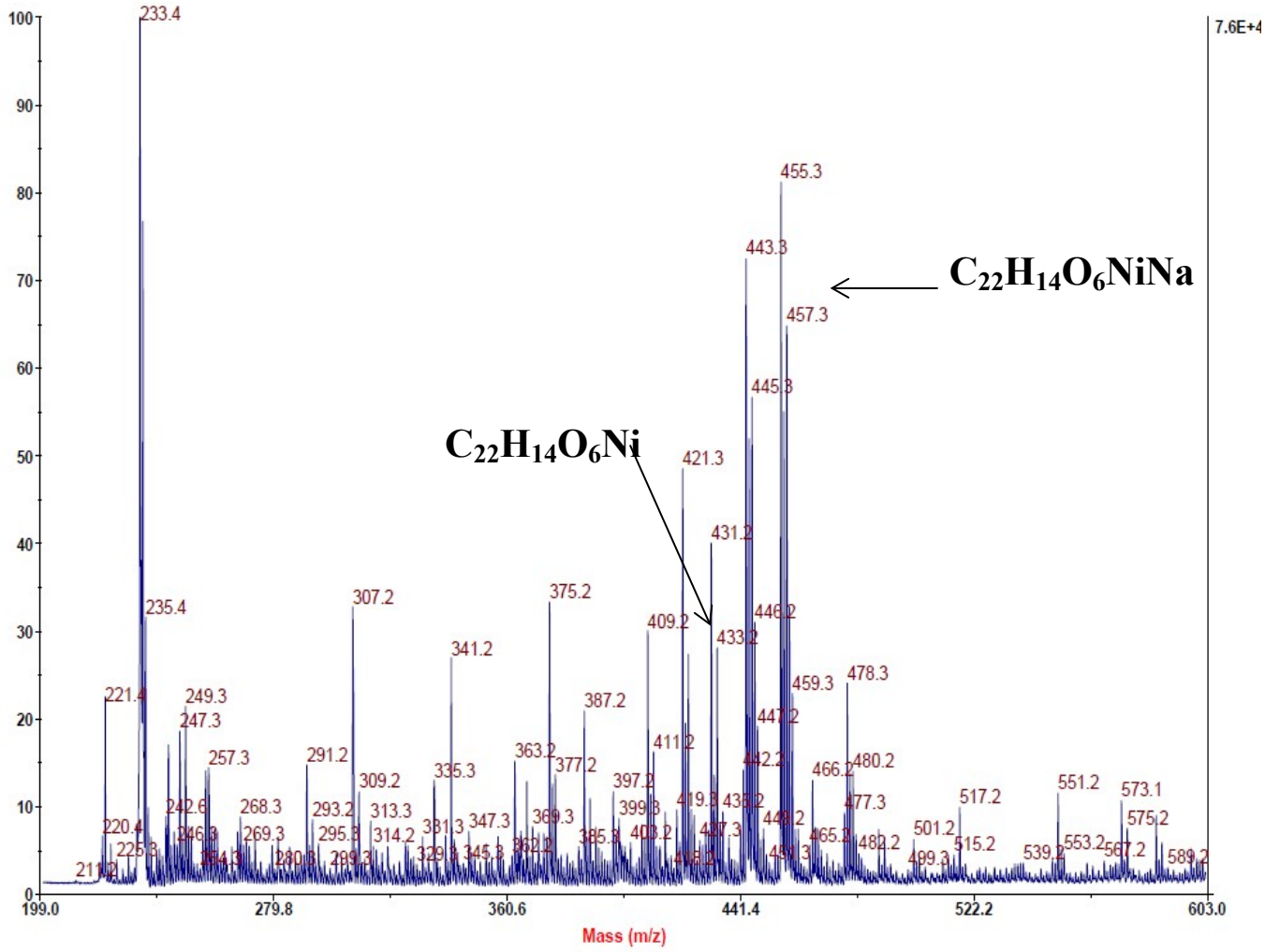


Figure S14. MALDI-TOF spectrum of **3A**.

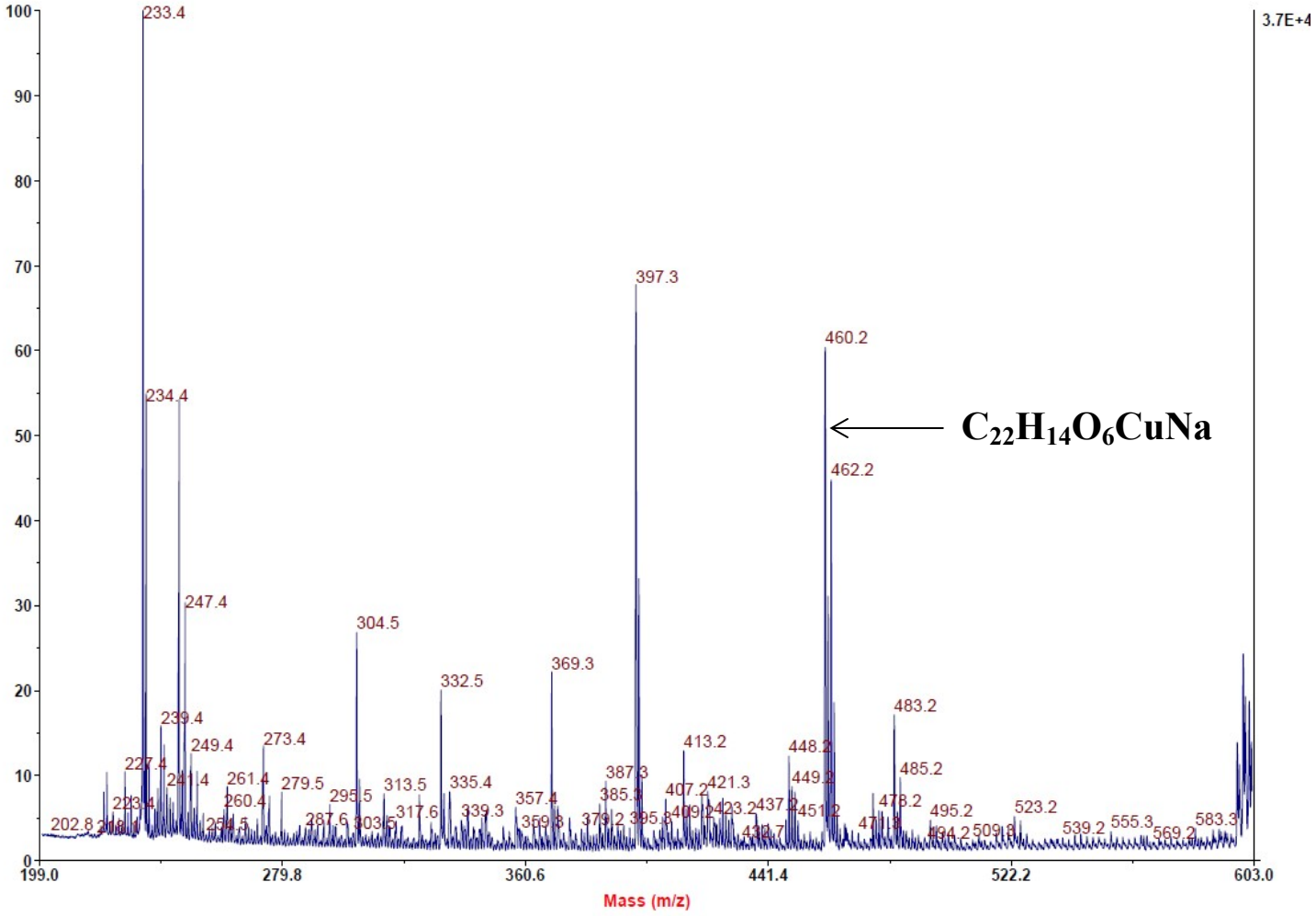


Figure S15. MALDI-TOF spectrum of **4A**.

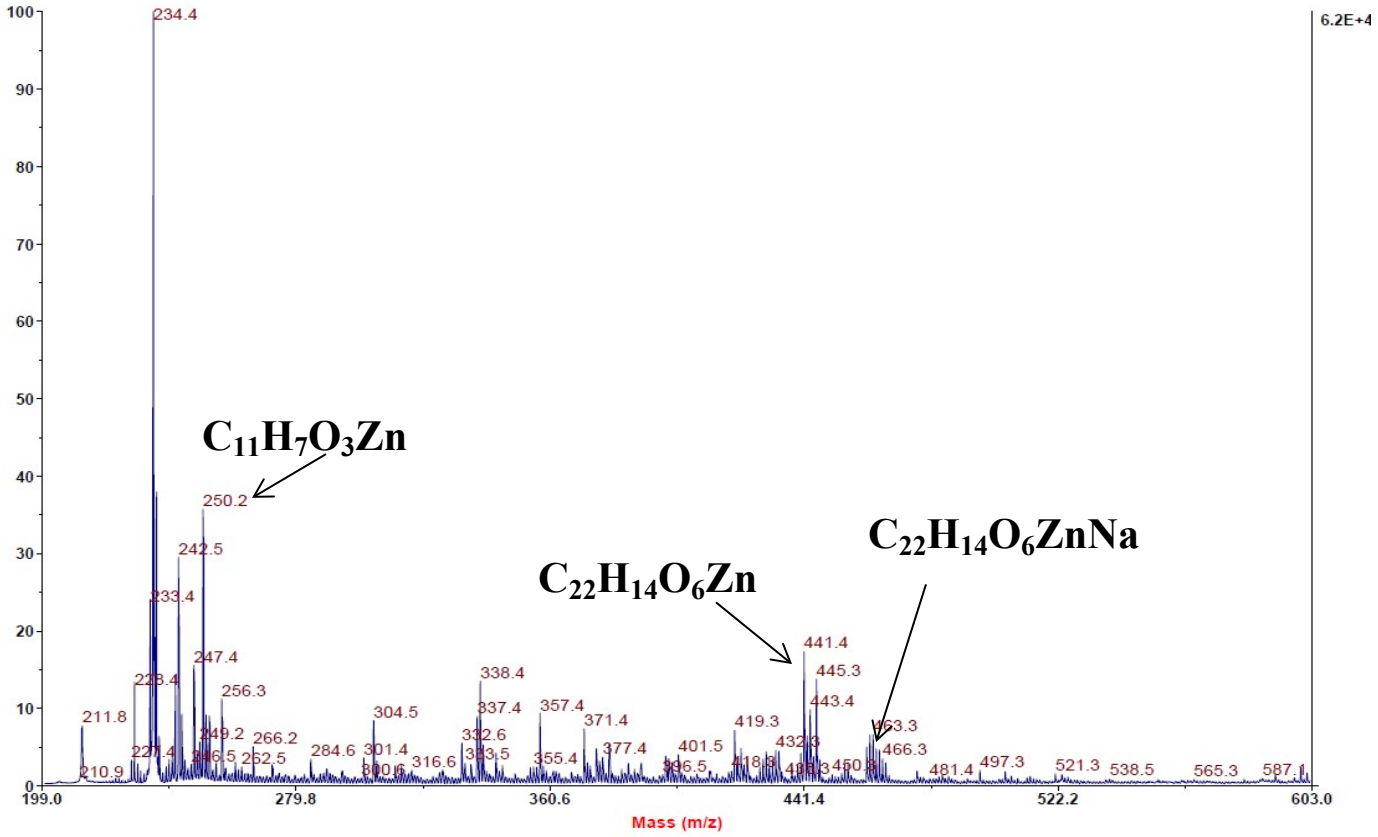
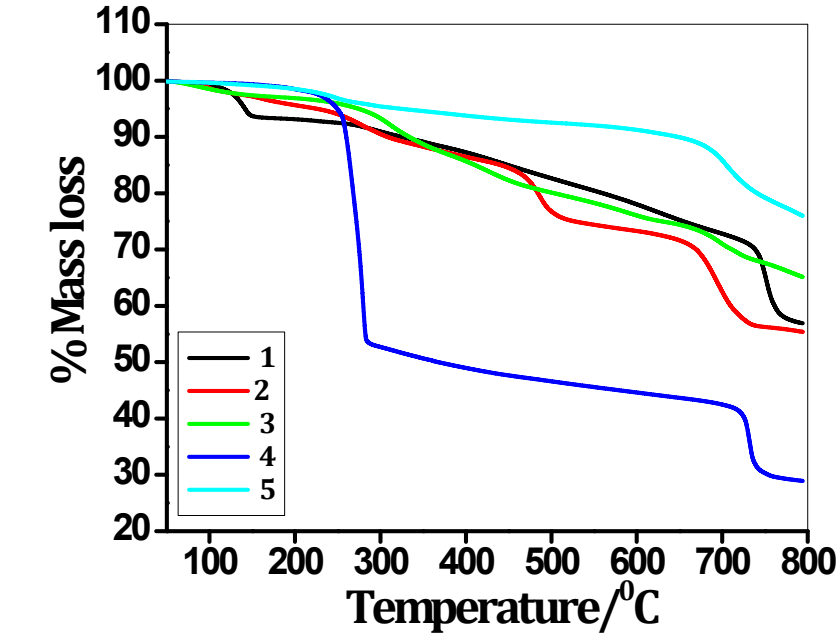


Figure S16. MALDI-TOF spectrum of **5A**.

a)



b)

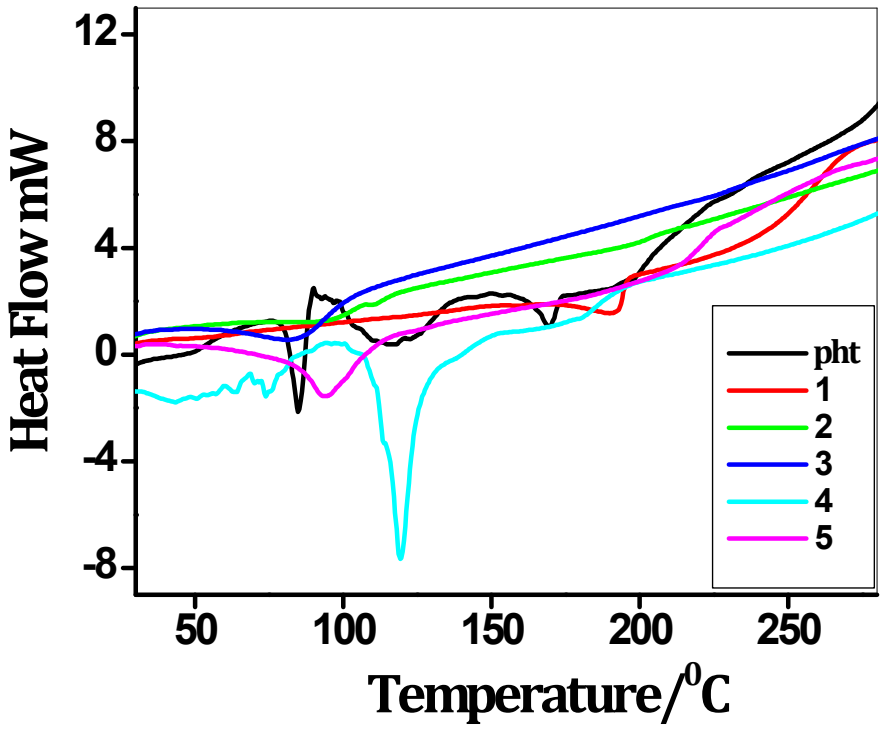
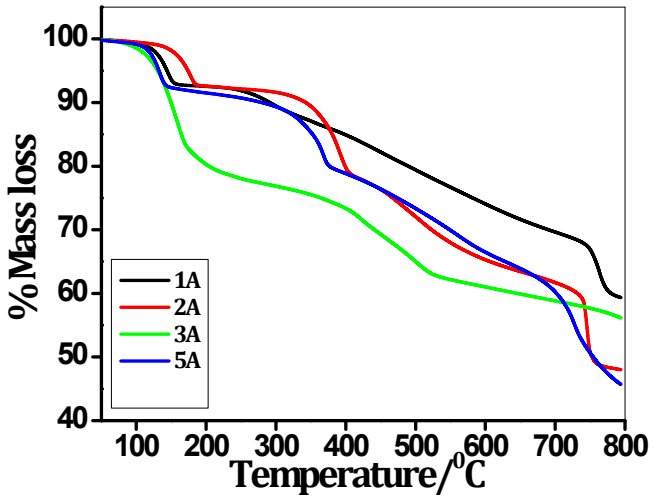


Figure S17. a) Thermograms of complexes **1** to **5**,b) DSC plots for complexes **1** to **5**.

a)



b)

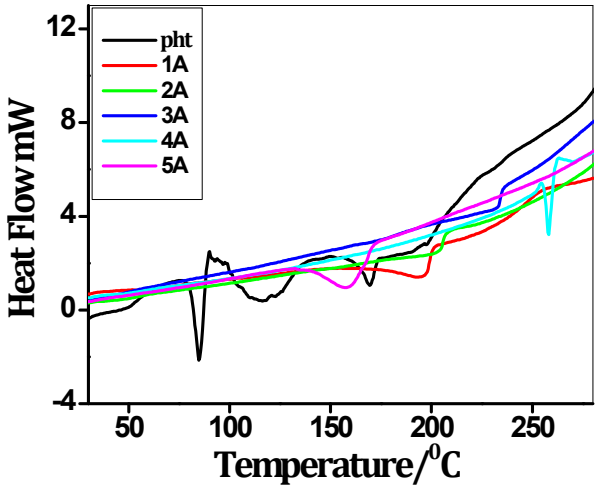


Figure S18. a) Thermograms of complexes **1**A to **5A**, b) DSC plots for complexes **1A** to **5A**.

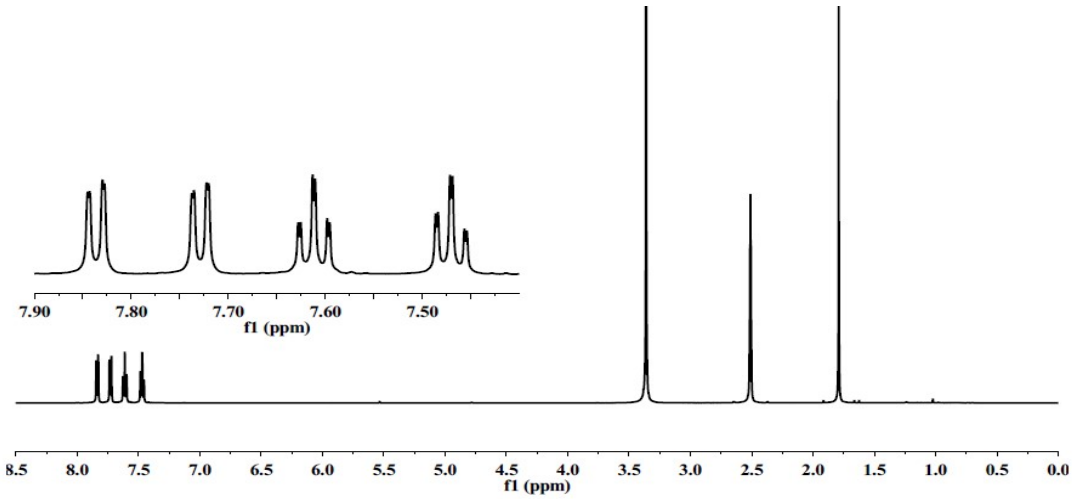


Figure S19. ^{1}H and ^{13}C NMR of **Na(pht)** in DMSO-d_6.

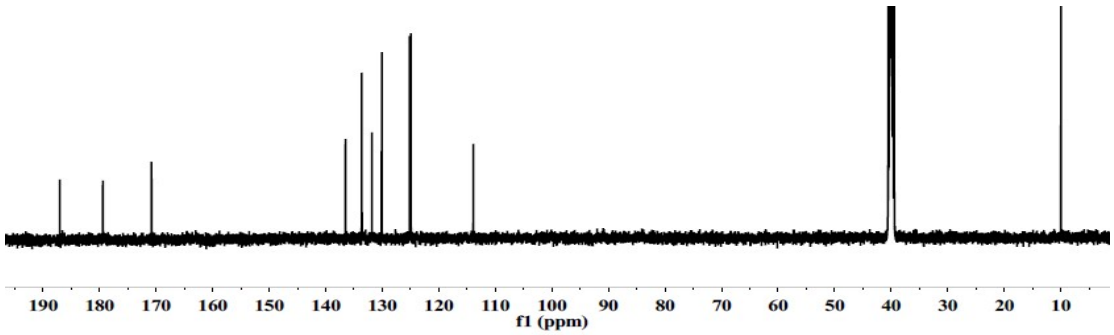


Figure S20. ^{1}H and ^{13}C NMR of **Na(pht)** in DMSO-d_6.

^{1}H NMR spectrum of **(pht)** was recorded in DMSO-d_6 (Fig.S19 ESI†). There was six proton resonance observed for free phthiocol ligand. The two singlets, C(2)–O.H. at δ = ~ 10.90 and C(3)–CH_3 at δ = ~1.95 (Table 1), substituted group on the quinonoid ring. Two doublets for (C5)H and C(8)H, at δ = ~7.96 and 7.82, two triplets for C(6)H and C(7)H, at δ = ~ 7.98 and 7.77 of benzenoid ring. The sodium complex **Na(pht)** shows five proton resonance peaks in the ^{1}H NMR spectrum. One singlet for C(3)-CH_3 at δ = ~1.79, two doublets for (C5)H and C(8)H at δ = ~ 7.83 and 7.72, two triplet at δ = ~ 7.61 and 7.47. All chemical shifts of protons were observed upfield compared to the free phthiocol ligand.

Table 1 ^{1}H and ^{13}C chemical shift for phthiocol and **Na(pht)**

Type of Carbons/Protons	**Ph** δ_H	**Na(pht)** δ_H	**Ph** δ_C	**Na(pht)** δ_C
C(1)	...	...	181	178.57
C(2)-OH	10.90	...	155	170.44
C(3)	…	...	120	113.41
C(4)	...	...	185	185.97
C(5)	7.79	7.73	126	124.43
C(8)	7.96	7.84	126	125.59
C(6)	7.77	7.47	134	129.43
C(7)	7.78	7.73	133	136.12
C(9)	...	...	130	131.52
C(10)	...	...	132	132.07
$-CH_3$	1.95	1.79	8.97	9.54

^{13}C NMR of free phthiocol ligand and **Na(pht)** complex (Fig.S20 ESI†) shows eleven carbon resonances. The carbonyl carbon resonance C(1) = O (1) at δ = ~ 178.57 ppm and C(4) = O (4) at δ = ~ 185.87 ppm (4) observed for phthiocol ligand. The carbonyl carbon resonance C(1) = O (1) at δ = ~ 179.41 ppm and C(4) = O (4) at δ = 187.02 ~ ppm observed downfield for **Na(pht)** as compared to phthiocol ligand. Because, non-bonded electron of carbonyl oxygen C(1) = O(1) and C(4) = O(4) donated electron to Na^+ ion, becomes carbonyl moiety electron deficient. The C(2)-O(2) carbon resonance observed at δ = ~ 155.83 ppm for phthiocol ligand was observed at δ = ~ 170.80 ppm in **Na(pht)** complex. The carbon resonances of **Na(pht)**; C(5), C(6), C(7), C(8), C(9), C(10) shows upfield chemical shift as compared to phthiocol ligand.

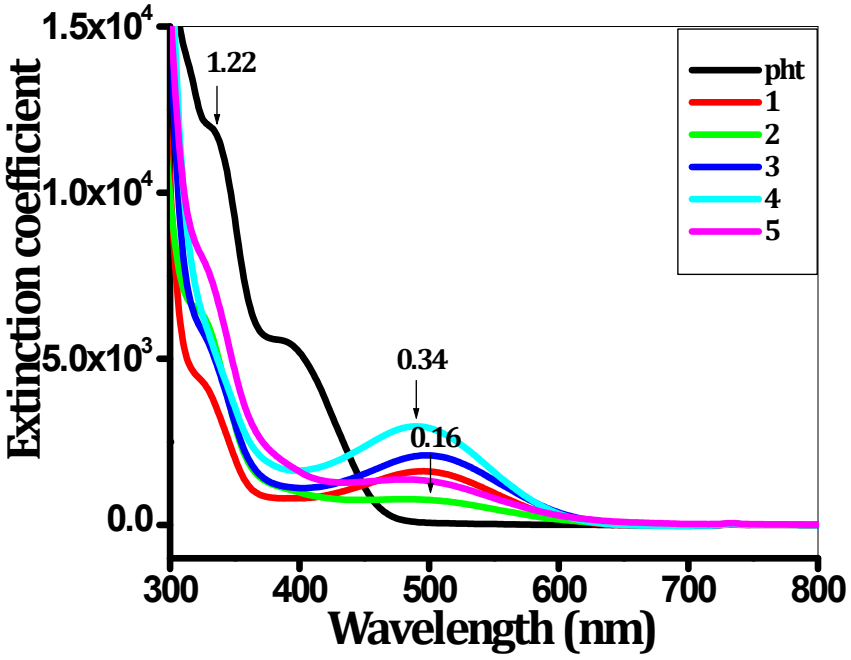


Figure S21. UV-Visible spectra of metal complexes of phthiocol in DMSO with concentration 1× 10^{-4} M.

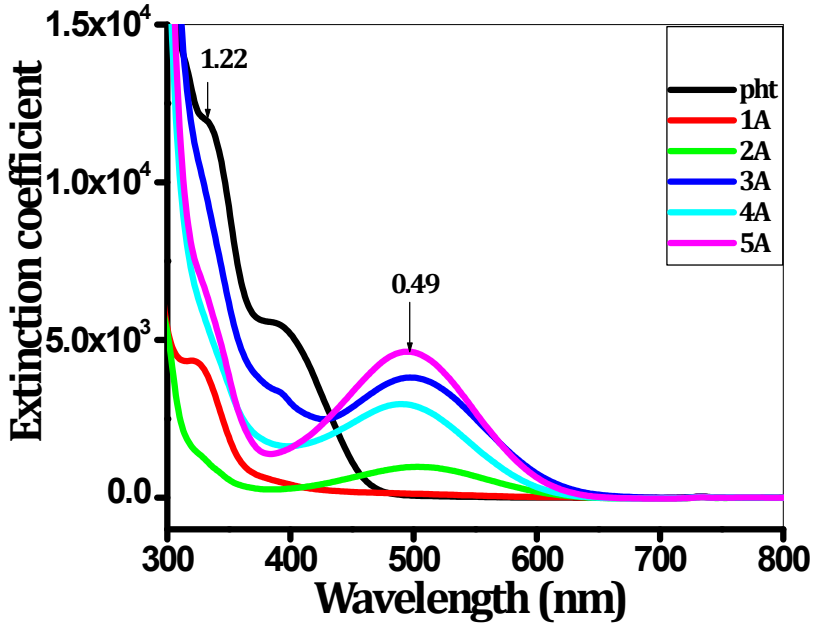


Figure S22. UV-Visible spectra of metal complexes of phthiocol in DMSO with concentration 1×10^{-4} M**.**

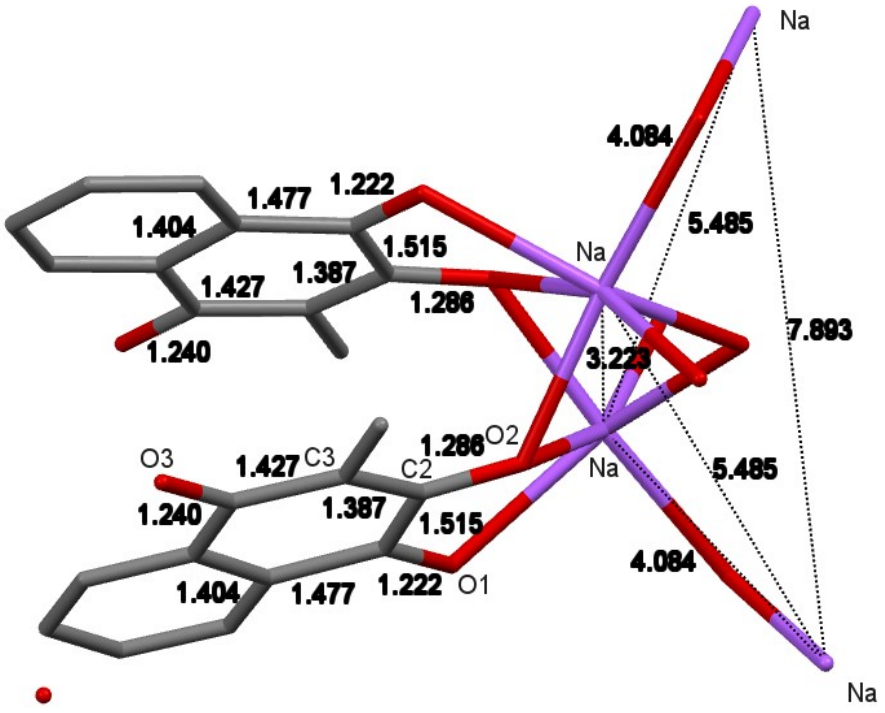


Figure S23 Na-O bond distances as well as C=O bond distances of **Na(pht)**.

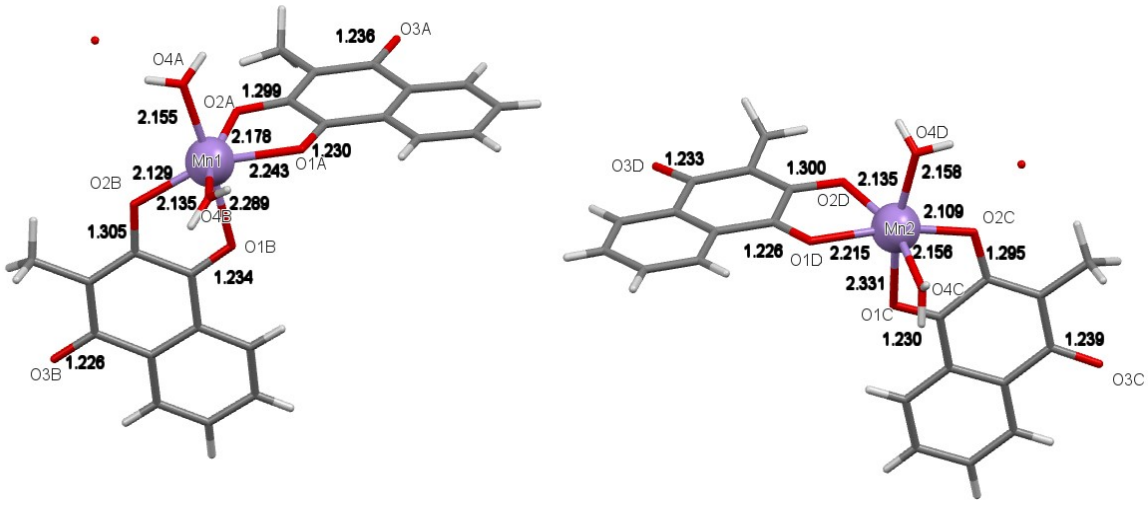


Figure S24. Important bond distances of **1** bond distances as well C=O bond.

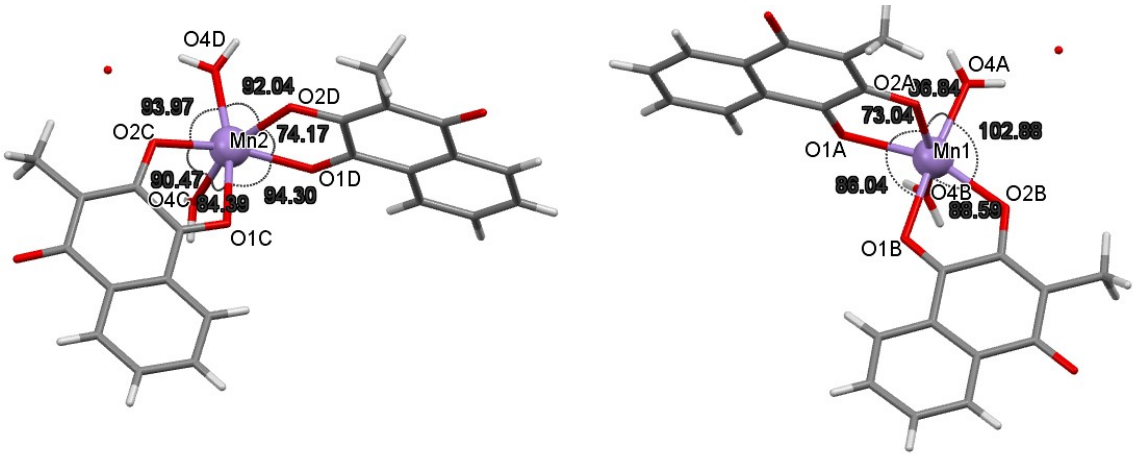


Figure S25. Bond angles around Mn(II) centers of asymmetric unit of **1**.

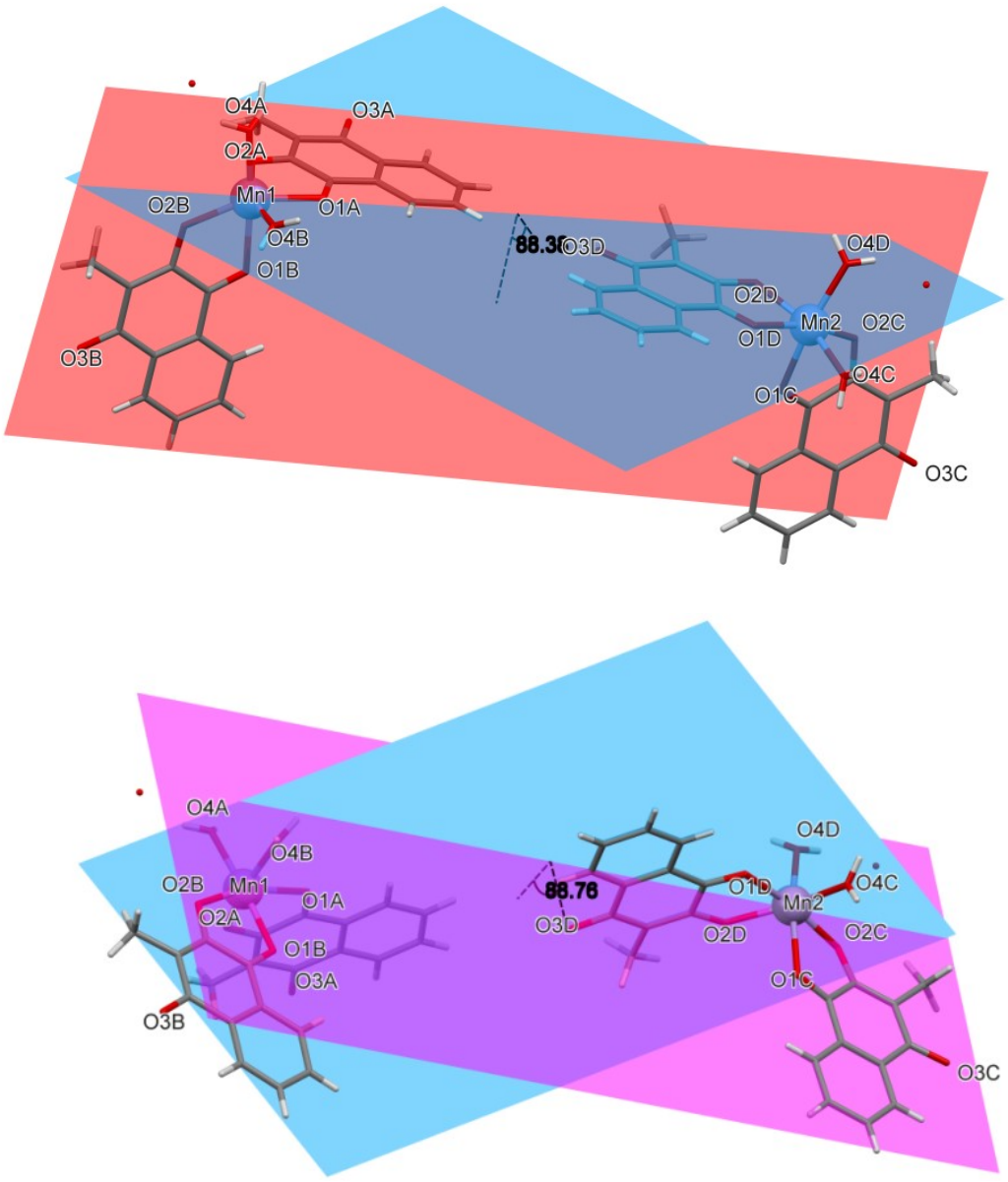


Figure S26. Interplanar angles of phthiocol ligands.Table Hydrogen bonding geometries of **1**.

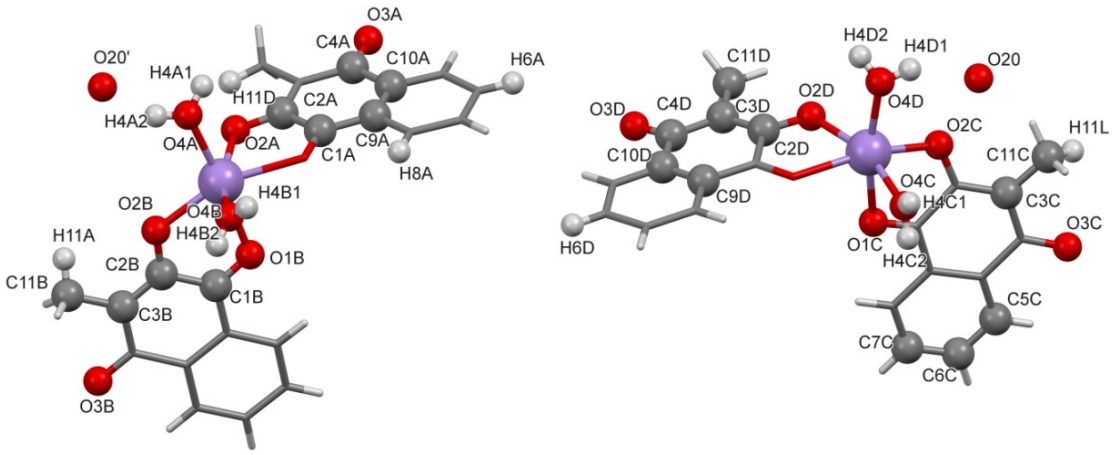


Figure S27. Atoms of **1** those are taking part in C-H···O, O-H···O hydrogen bonding interaction and π-π stacking interactions.

X-ray structure of complex 1B

The crystals of complex **1** are also obtained as a coordinated methanol adduct in two independent syntheses, and it is designated as **1B**. Complex **1B** crystallizes in monoclinic space group $P2_1/C$. The coordination of two phthiocol ligands are *cis,* and oxygens of water and methanol molecules occupy the fourth and fifth coordination site around Mn(II). In addition, there is O-H···O hydrogen-bonded water molecule present in the lattice. Mn(II) is in a distorted octahedral environment of six oxygens. The phthiocol ligand bond angles are ∠O(2)-Mn-O(1) and ∠O(4)-Mn-O(5) are, respectively, 72.5° and 72.9°(Fig.S28). These bond angles are lowered by ~1.5° to *cis* complex **1**, and *trans* complex **1A** by ~3°. The two phthiocol ligands are nonplanar to each other, and their plane makes an angle of ~64° (Fig.S29). The Mn-O bond distances around Mn(II) are all different. Mn-O (H_2O and phenolic carbonyl) is ~2.15 Å, Mn-O (MeOH and phenolic carbonyl) is ~2.10 Å, whereas the Mn-O (quinonoid carbonyl) is longer with ~2.30 Å. The quinonoid carbonyl bond distances in **1B**, observed for quinonoid carbonyls; C(13)-O(5) is ~1.24 Å, and C(9)-O(3) is ~1.25 Å, this suggests the ligands coordinate to Mn(II) in reduced form, i.e., naphthosemiquinone form[50, 51] (Fig.S30). Each molecule of **1B** is in the vicinity of four similar molecules through the O-H···O and π-π stacking interactions (Fig.S31). Molecules are joined by O-H···O interaction by the lattice water molecule to form a polymer-like chain. Two such neighboring chains were connected by π-π stacking interaction, as presented in Fig.S32.

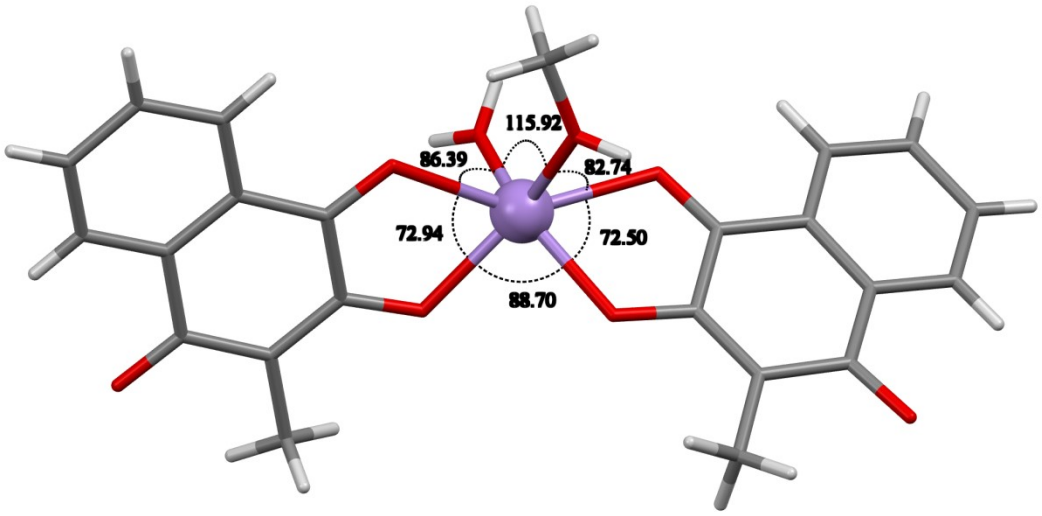


Figure S28. Bond angles around Mn(II) of **1B**.

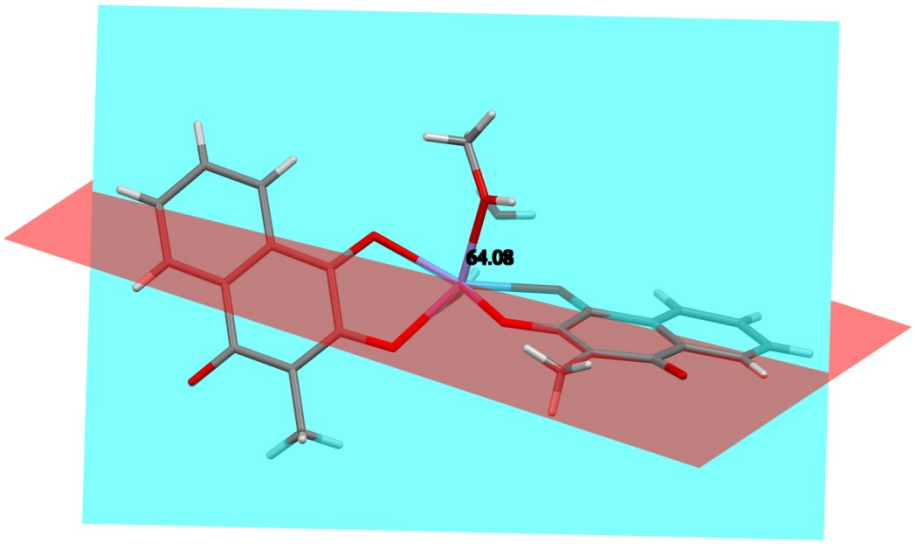


Figure S29. Plane of phthiocol ligands and interplanar angle in **1B**.

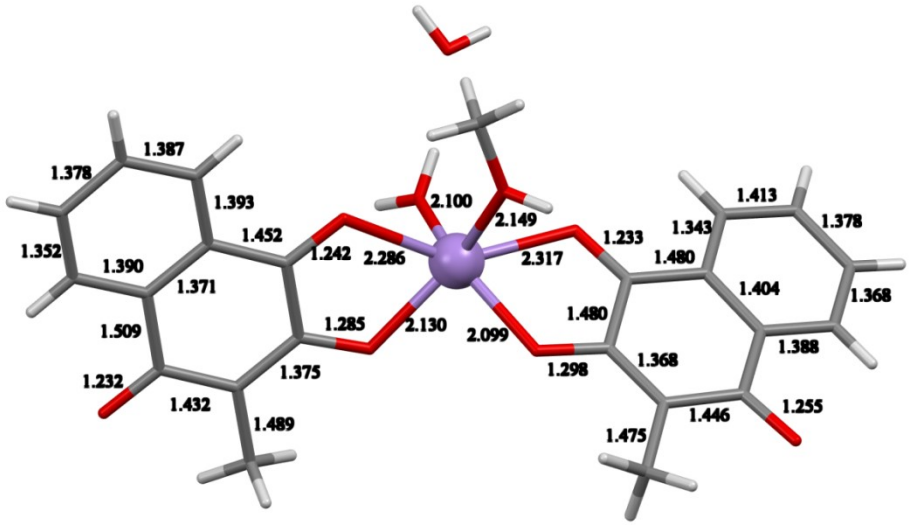


Figure S30. Bond distances of **1B**.

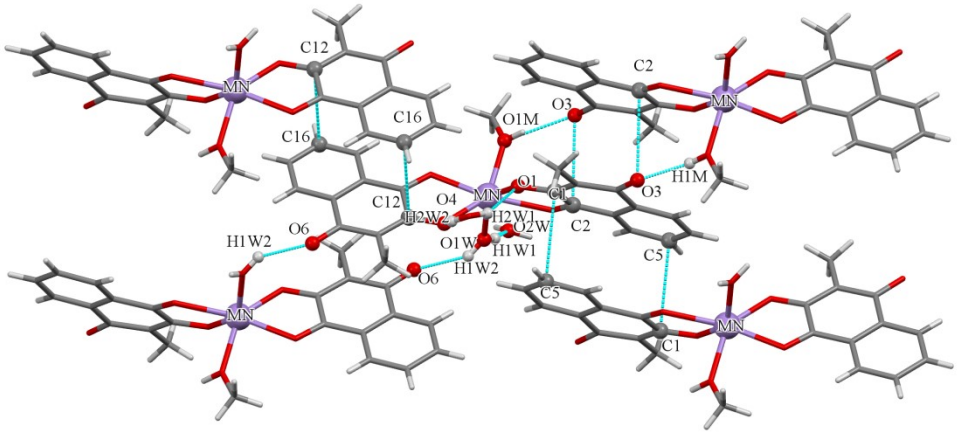


Figure S31. Neighbouring molecules of **1B**, O-H···O hydrogen bonding interaction and π-π stacking interactions.

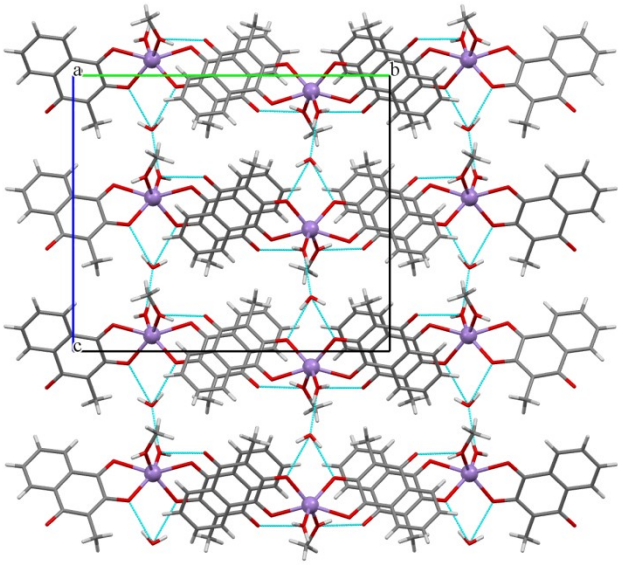


Fig.S32 Molecular packing of **1B** down a-axis.

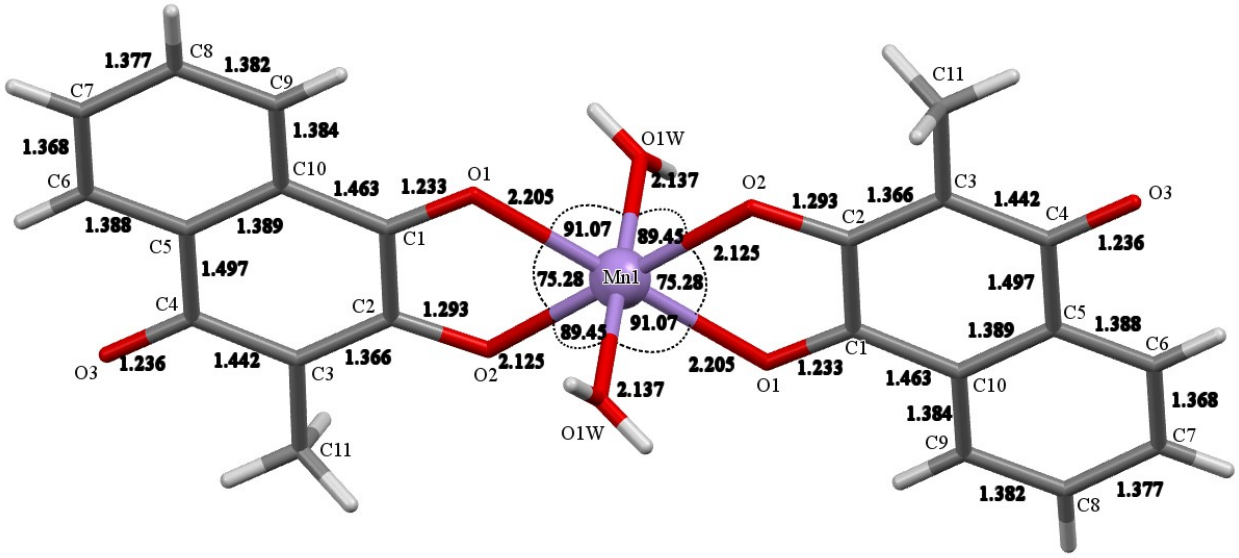


Figure S33. Bond distances and selected bond angles of **1A**.

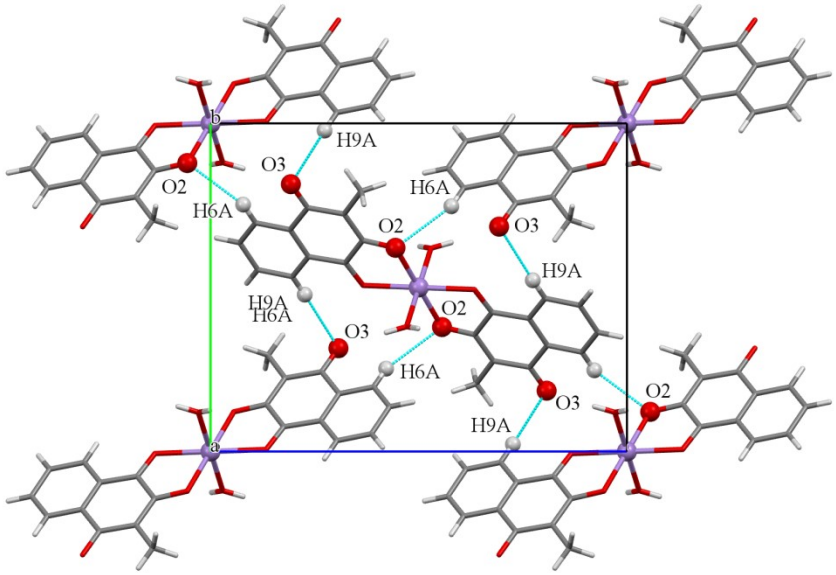


Figure S34. Molecular packing of **1A**.

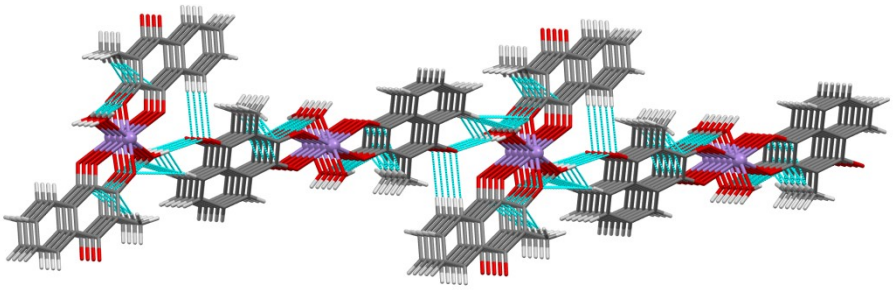


Figure S35. Polymeric chains of **1A** formed by O-H···O and connected through C-H···O and O-H···O interactions.

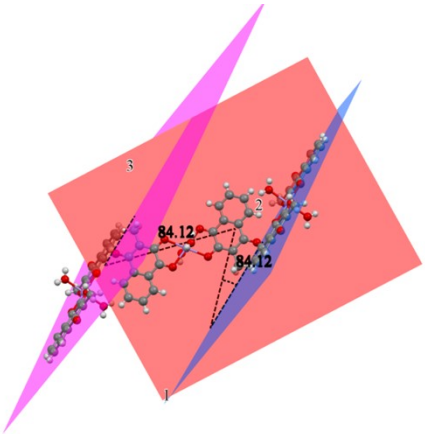


Figure S36. Molecular planes of **1A**. The orientations of polymeric chain are 84.12°.

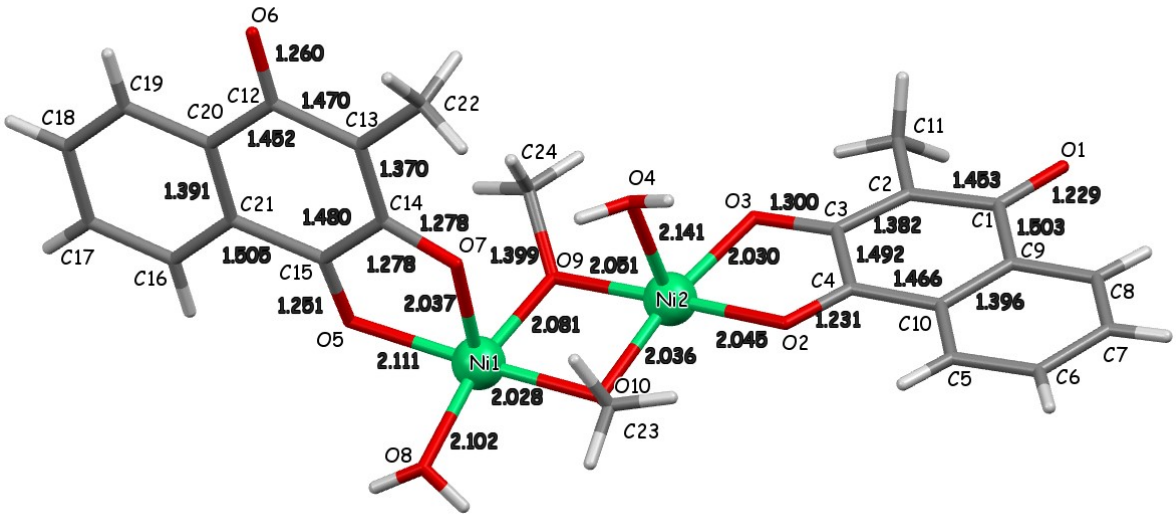


Figure S37. Selected bond distances of the asymmetric unit of complex **3**. Water molecules were removed for clarity.

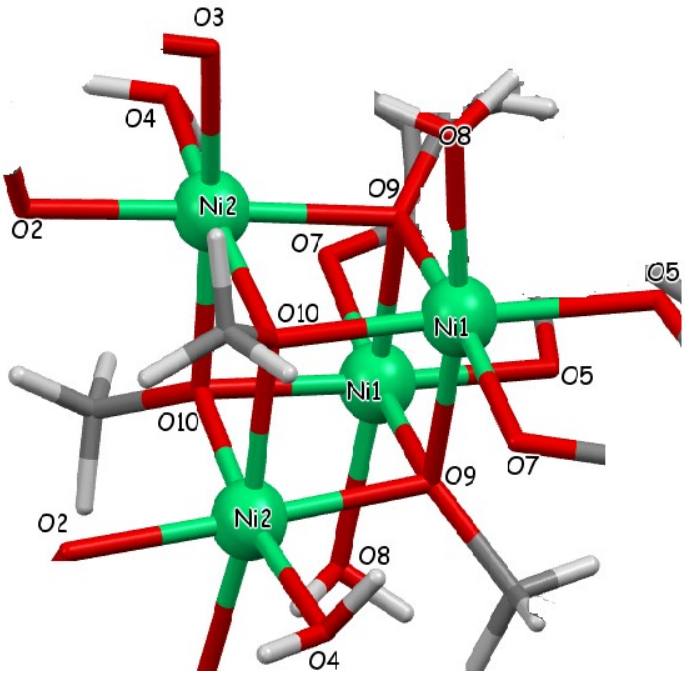


Figure S38. Cubane shaped arrangement of Ni(II) with bridged methoxy ligands.

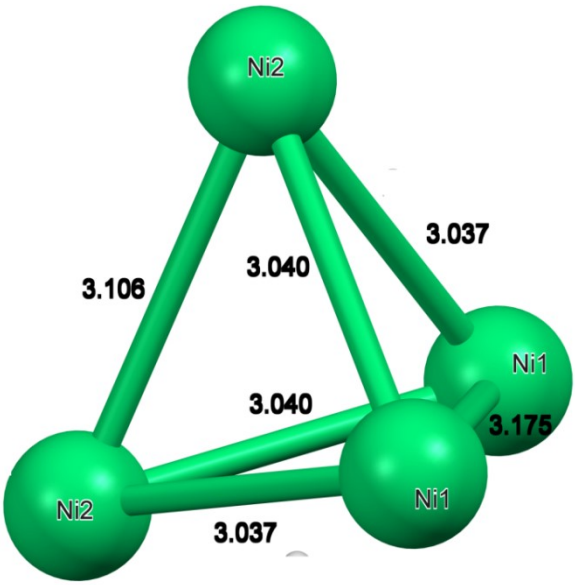


Figure S39 Tetrahedral arrangement of Ni(II) ions and Ni(II)···Ni(II) bond distances in **3**.

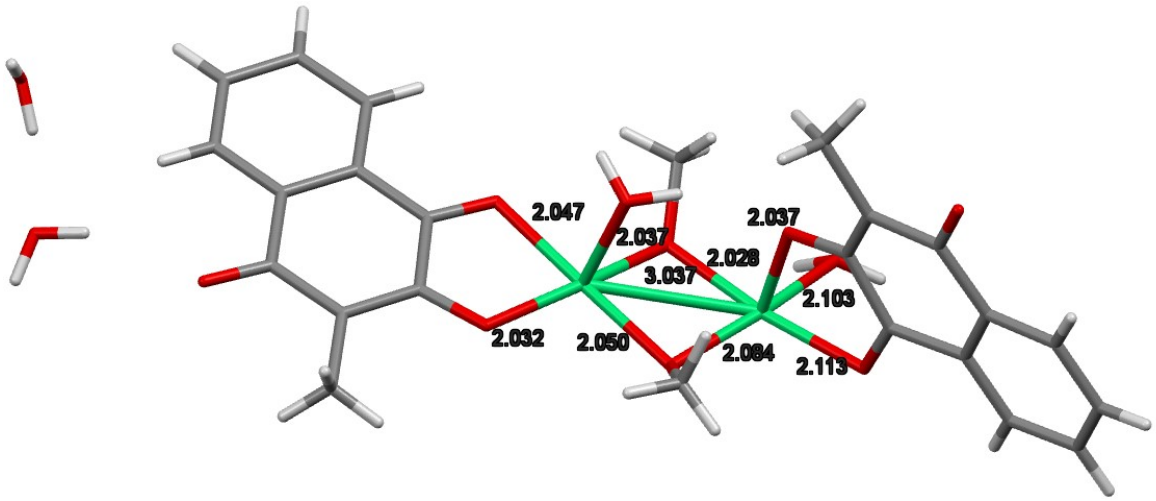


Figure S40. Ni-O bond distances of **3**.

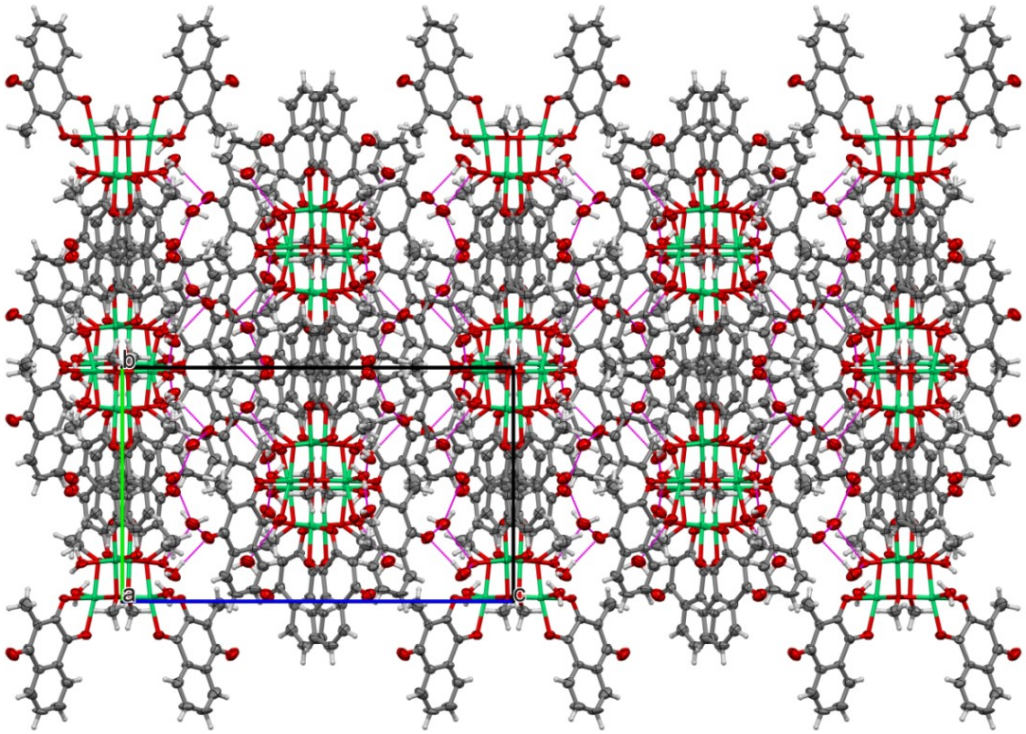
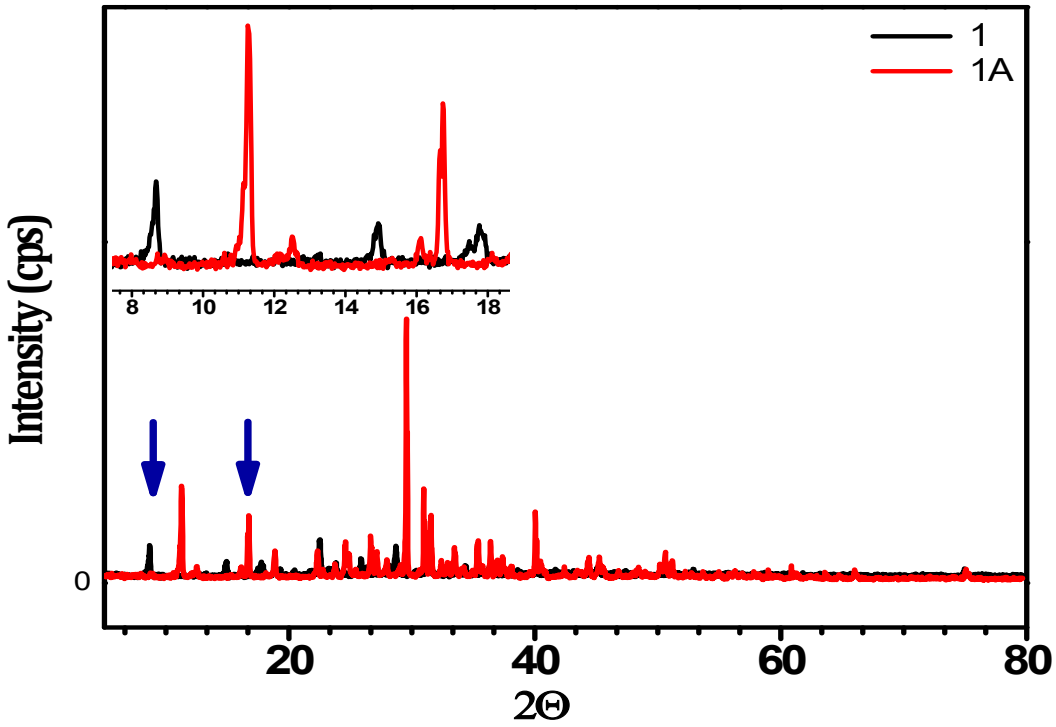
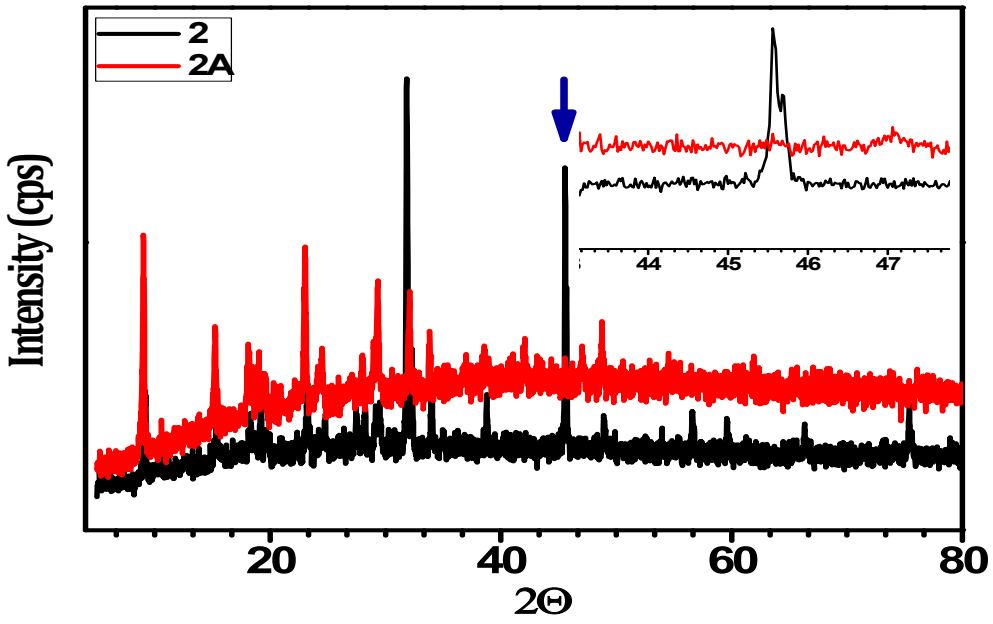


Figure S41. Molecular packing showing hydrogen bonding of quinonoid oxygen with adsorbed water molecules down c axis of **3**.

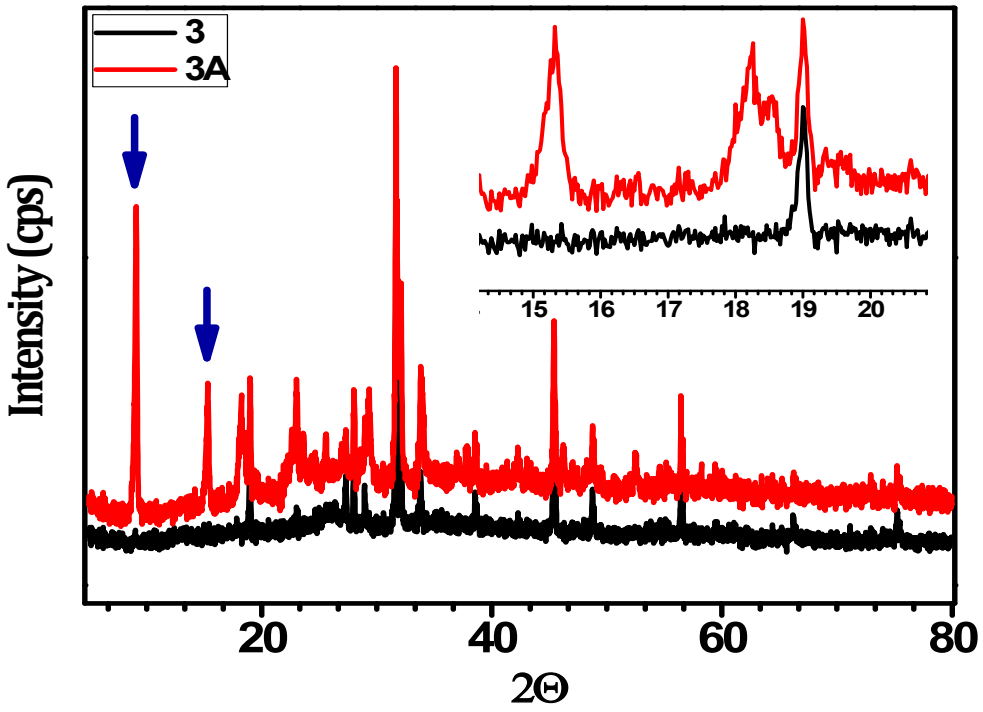
a)


1
1A
Intensity (cps)
0
20
40
60
80
2Θ
8
10
12
14
16
18

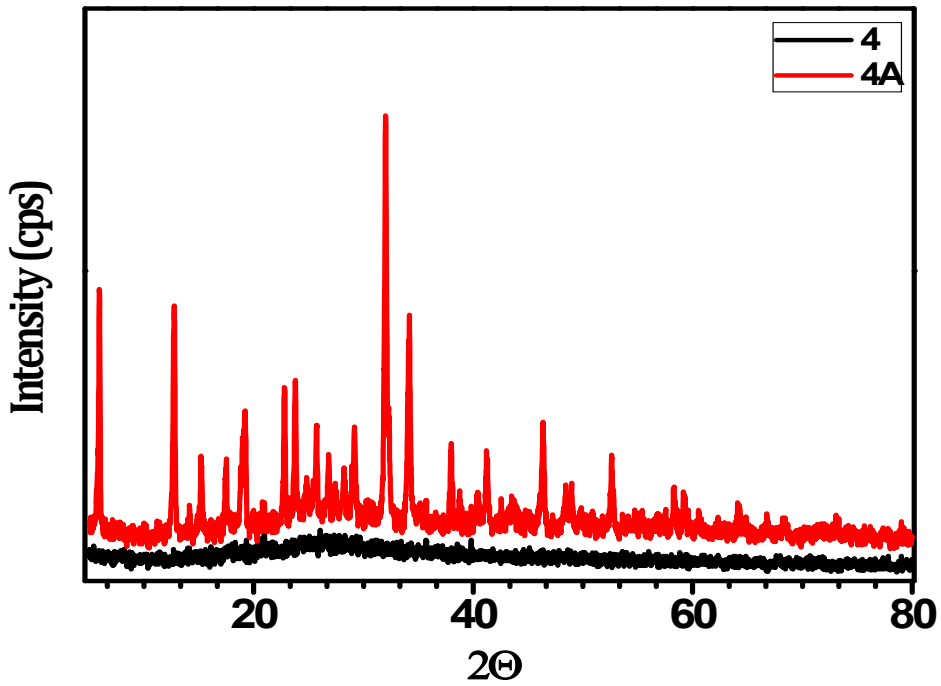
b)


2
2A
Intensity (cps)
20
40
60
80
2Θ
44
45
46
47

c)


3
3A
Intensity (cps)
15
16
17
18
19
20
20
40
60
80
2Θ

d)


4
4A
Intensity (cps)
20
40
60
80
2Θ

e)

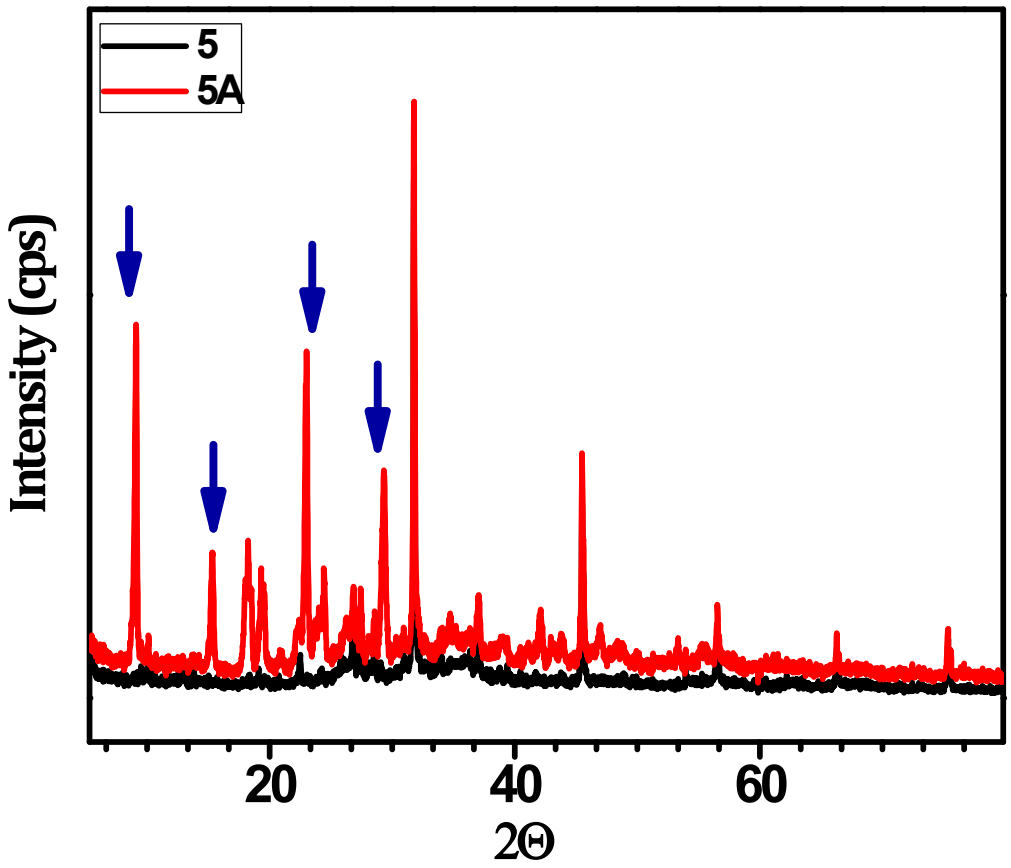


Figure S42. PXRD spectra of a) **1**, **1A**, b) **2**, **2A**, c) **3**, **3A**, d) **4**, **4A**, e) **5**, **5A**.

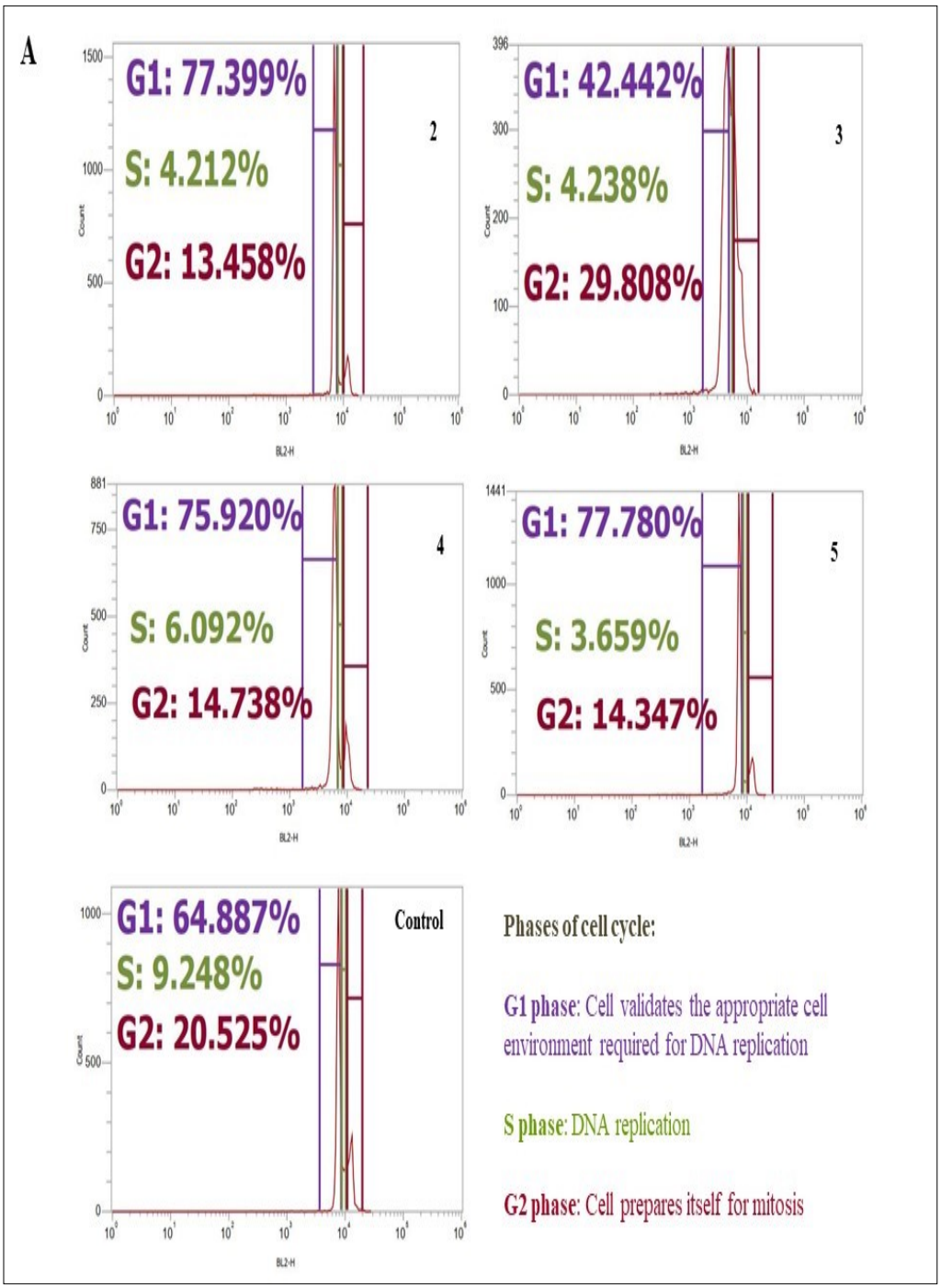


Figure S43a. Effect of the phthiocol complexes on cell cycle of A) MCF-7 cell lines at 30 µM concentration.

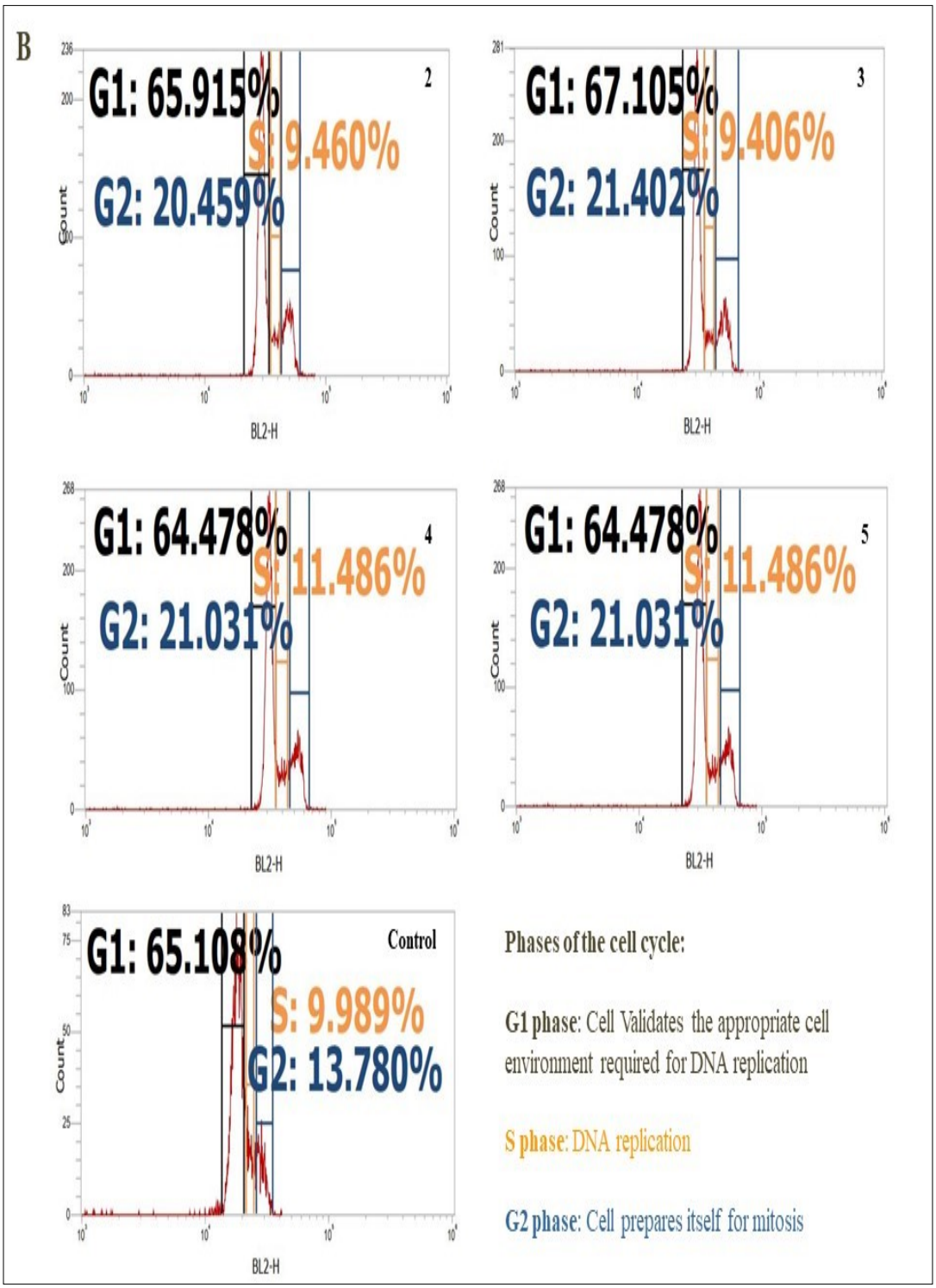


Figure 43b. Effect of phthiocol complexes on cell cycle of B) A549 cell lines at 30 µM concentration.

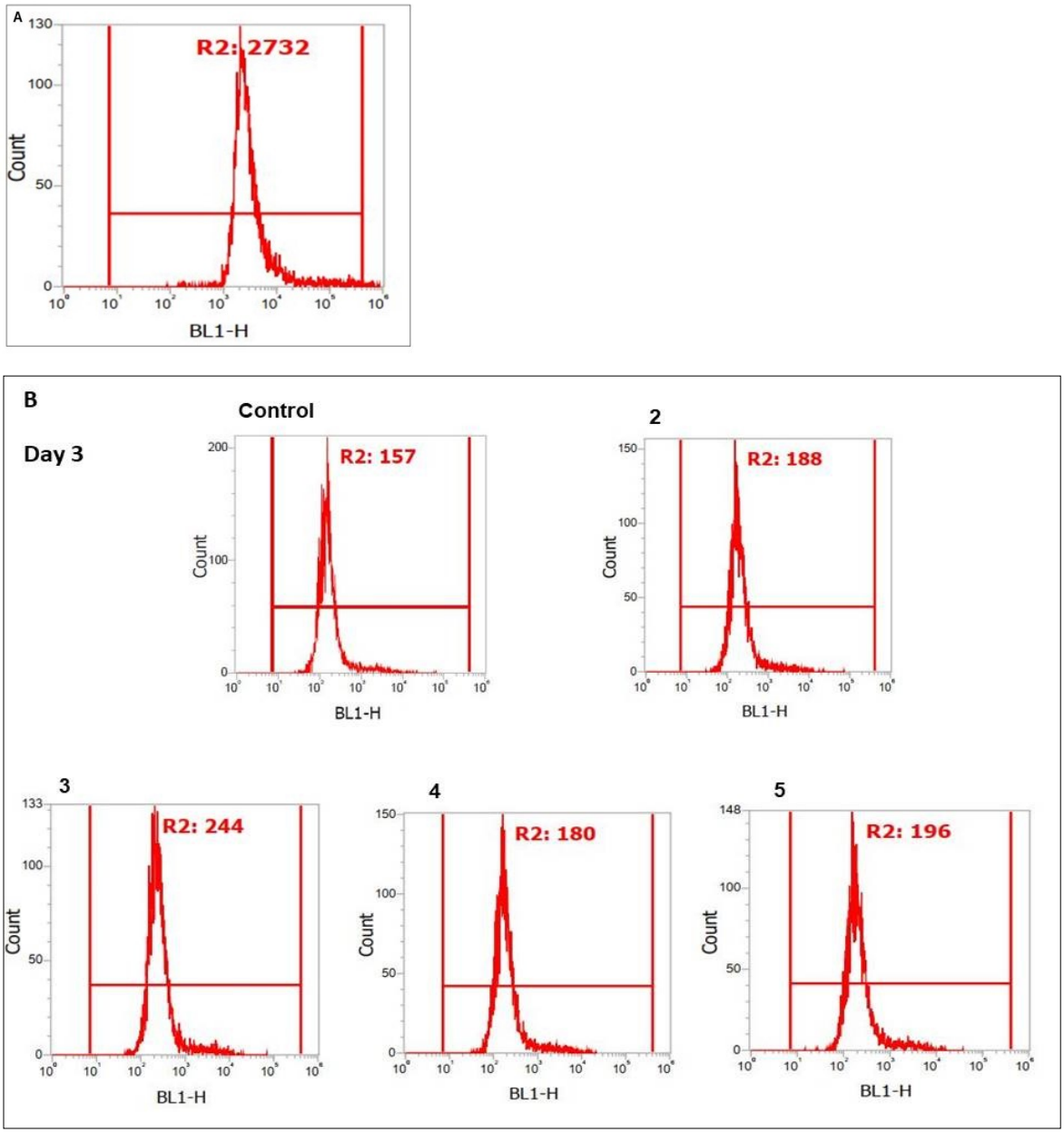


Figure S44a. Effect of phthiocol complexes on cell proliferation of MCF-7 at day three, A) Fluorescence of control at Zero-hr, B) Fluorescence after Three-day treatment.

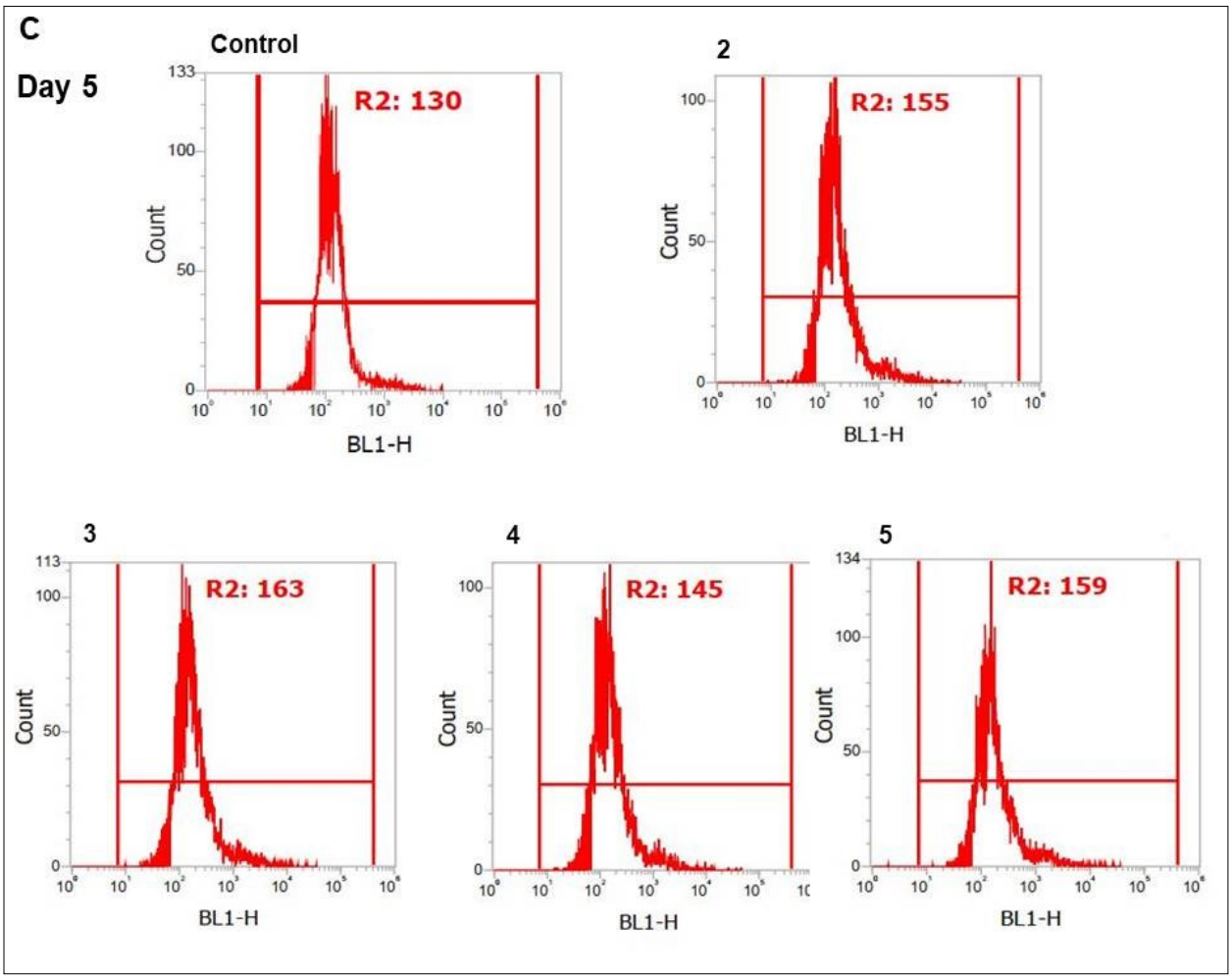


Figure S44b. Effect of phthiocol complexes on cell proliferation of MCF-7 day five after treatments. C) Fluorescence after five-day treatment.

Table S1. FT-IR values of phthiocol (**pht)**, and its metal complexes region 4000 cm^{-1} to 400 cm^{-1}

Functional groups	**pht**	**1**	**1A**	**2**	**2A**	**3**	**3A**	**4**	**4A**	**5**	**5A**
ν_{O-H}	3326	3252	3228	3391	3429	3411	3364	-	3456, 3345	3446	3326
$\nu_{C=O}$	1700, 1660	1637	1632	1661	1648	1621	1628	1621	1647	1650	1624
$\nu_{C=C}$	1582	1591, 1545	1586, 1540	1598, 1522	1579	1534	1586	1551	1564	1600, 1527	1587, 1560
pNQ	1286	1280	1280	1280	1273	1275	1275	1275	1279	1280	1285

Table S2. Hydrogen bonding geometries and other molecular interactions for **Na(pht), 1, 1B, 1A** and **3**

Code	D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)	Symmetry
Na(pht)	O(5)-H(5B)···O(6)^{i}	0.76(6)	2.14(6)	2.894(2)	175(5)	x,1-y,1/2+z,
	O(5)-H(5A)···O(6)^{i}	0.87(5)	1.96(6)	2.789(5)	159(5)	x,1-y,1/2+z,
	O(6)-H(6B)···O(3)^{ii}	0.83(5)	1.93(5)	2.752(5)	170(5)	1/2+x,1/2+y,-1+z
	O(4)-H(4)···O(2)^{iii}	0.95	1.74(5)	2.683(5)	168	x,y,-1+z
1	C(6A)-H(6A)···O(1C)^{i}	0.931	2.618	3.419(4)	144.5	x,-y,1/2+z
	C(6D)-H(6D)···O(1B)^{i}	0.931	2.611	3.407(4)	143.8	x,-y,1/2+z
	C(11C)-H(11L)···O(20')^{ii}	0.96(2)	2.27	3.14(2)	150.3	1/2+x,1/2+y,-1+z
	O(4C)-H(4C1)···O(3A)^{iii}	0.84(3)	1.94(3)	2.724(3)	154(3)	x,y,-1+z
	O(4C)-H(4C2)···O(3D)^{i}	0.84(2)	1.98(3)	2.796(3)	164(3)	x,-y,1/2+z
	O(4D)-H(4D2)···O(2A)^{iv}	0.84(3)	1.99(3)	2.815(3)	171(3)	1.5-x,-1/2-y,1-z
	O(4D)-H(4D1)···O(20)^{v}	0.83(3)	1.80(3)	2.559(8)	151(3)	x,y,z
	O(4A)-H(4A1)···O(2D)^{iv}	0.84(2)	1.91(2)	2.748(3)	174(3)	1.5-x,-1/2-y,1-z
	O(4A)-H(4A2)···O(20')^{v}	0.84(3)	1.64(5)	2.39(2)	147(4)	x,y,z
	O(4B)-H(4B1)···O(3C)^{iv}	0.84(2)	1.87(3)	2.705(3)	171(3)	1.5-x,-1/2-y,1-z
	O(4B)-H(4B2)···O(2B)^{vi}	0.84(2)	1.90(2)	2.730(3)	171(3)	1-x,y,1.5-z
	C(11D)···C(3C)^{i}			3.364(4)		x,-y,1/2+z
	C(9D)···C(4A)^{iv}			3.348(4)		1.5-x,-1/2-y,1-z
	C(4D)···C(9A)^{iv}			3.383(4)		1.5-x,-1/2-y,1-z
	C(10D)···C(10A)^{iv}			3.374(4)		1.5-x,-1/2-y,1-z
	C(3D)···C(1A)^{iv}			3.393(4)		1.5-x,-1/2-y,1-z
	C(7C)···C(1B)^{iv}			3.392(4)		1.5-x,-1/2-y,1-z
	C(6C)···C(2B)^{iv}			3.361(4)		1.5-x,-1/2-y,1-z
	C(3B)···C(5C)^{iv}			3.396(4)		1.5-x,-1/2-y,1-z
	C(2B)···C(6C)^{iv}			3.361(4)		1.5-x,-1/2-y,1-z
	O(3D)···O(4C)^{i}			2.796(3)		x,-y,1/2+z
	O(2C)···O(20')^{iv}			2.81(2)		1.5-x,-1/2-y,1-z
	O(2C)···O(20)^{v}			2.928(7)		x,y,z
1B	O(1M) -H(1M)···O(3)	0.8247	1.9276	2.6891	153.11	1-x,2-y,1-z
	O(1W) -H(1W1)···O(2W)	0.8365	1.7872	2.6087	166.87	x,y,z
	O(1W) -H(1W2)···O(6)	0.8048	2.0174	2.7277	146.99	-x,1-y,1-z
	O(2W) -H(2W1)···O(1)	0.8301	1.9982	2.7726	154.96	x,1.5-y,-1/2+z
	O(2W) -H(2W2)···O(4)	0.8243	2.0799	2.7331	135.94	x,1.5-y,-1/2+z
	C(2)···O(3)			3.1921		1-x,2-y,1-z
	C(1)···C(5)^{v}			3.348		-x,2-y,1-z

	C(12)···C(16)^{v}			3.3679		1-x,1-y,1-z
1A	C(9)-H(9A)···O(3)	0.930	2.686	3.616(3)	177.9	1-x,1-y,1-z
	C(6A)···H(6A)···O(2)	0.930	2.648	3.445(4)	144.2	x,1/2-y,-1/2+z
	O(1W) -H(1W2)···O(3)	0.82(2)	1.94(2)	2.758(3)	177(2)	-1+x,1/2-y,-1/2+z
	O(1W) -H(1W1)···O(2)	0.83(3)	1.87(3)	2.695(3)	173(3)	-1+x,y,z
	C(11)-H(11C)···O(2B)	0.960	2.839		143.49	-1+x,y,z
3						
	O(4)-H(4B)···O(1\)	0.85(5)	1.96(7)	2.77(1)	132.6	2-x,1-y,1-z
	O(11)-H(11B)···O(4)	0.83(5)	2.16(5)	2.96(1)	158(9)	2-x,1-y,1-z
	O(8)-H(8B)···O(11)	0.84 (4)	1.93(4)	2.74(1)	161(5)	1.5-y,1/2+z
	O(11)-H(11A)···O(6)	0.80(1)	2.0(1)	2.85(1)	173(10)	1.5-y,1/2+z
	C(19)-H(19)···O(11)	0.93	2.694	3.57(1)	157.3	1.5-y,1/2+z
	C(22)-H(22B)···O(1)	0.96	2.625	3.35(1)	132.6	x,1/2-y,-1/2+z
	C(9)···C(9)			3.39(2)		2-x,-y,1-z
	C(16)-H(16)···Cg	0.93		2.803	146.64	

Table S3. Crystal data and structure refinement for **Na(pht)**

Identification code	shelx	
Empirical formula	$C_{22}\ H_{24}\ Na_2\ O_{11}$	
Formula weight	510.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C 2/c*	
Unit cell dimensions	a = 17.988(3) Å	α= 90°.
	b = 18.798(3) Å	β= 101.468(5)°.
	c = 6.7722(9) Å	γ = 90°.
Volume	2244.2(6) $Å^3$	
Z	4	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	0.153 mm^{-1}	
F(000)	1064	
Crystal size	0.21 x 0.16 x 0.11 mm^3	
Theta range for data collection	3.168 to 28.353°.	
Index ranges	-24<=h<=24, -25<=k<=25, -9<=l<=9	
Reflections collected	11471	
Independent reflections	2779 [R(int) = 0.1747]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.778 and 0.712	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2779 / 8 / 180	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0960, wR2 = 0.1565	
R indices (all data)	R1 = 0.2279, wR2 = 0.1977	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.296 and -0.401 $e.Å^{-3}$	

Table S4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **Na(pht)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Na	5905(1)	4393(1)	8309(2)	31(1)
O(1)	3802(2)	3313(2)	4578(5)	37(1)
O(2)	5237(2)	3770(2)	5553(4)	33(1)
O(3)	6038(2)	1389(2)	5517(5)	35(1)
O(4)	5000	5295(2)	7500	32(1)
O(5)	6715(2)	5113(2)	10923(5)	34(1)
O(6)	7473(2)	4037(2)	13362(6)	38(1)
C(1)	4306(2)	2867(2)	4774(6)	22(1)
C(2)	5128(2)	3098(2)	5279(5)	22(1)
C(3)	5698(2)	2591(2)	5439(6)	22(1)
C(4)	5535(2)	1849(2)	5283(6)	23(1)
C(5)	4731(2)	1610(2)	4838(6)	23(1)
C(6)	4557(3)	891(2)	4679(7)	39(1)
C(7)	3826(3)	654(3)	4259(8)	48(2)
C(8)	3237(3)	1139(3)	4007(8)	42(1)
C(9)	3391(2)	1856(3)	4149(6)	31(1)
C(10)	4129(2)	2100(2)	4559(6)	20(1)
C(11)	6516(2)	2811(3)	5852(7)	38(1)

Table S5. Bond lengths [Å] and angles [°] for **Na(pht)**

Na-O(2)	2.325(3)
Na-O(4)	2.339(4)
Na-O(5)	2.463(4)
Na-O(1)#1	2.480(3)
Na-O(5)#2	2.556(4)
Na-O(2)#1	2.611(4)
Na-Na#1	3.222(3)
Na-Na#2	4.0834(19)
Na-Na#3	4.0835(19)
O(1)-C(1)	1.223(5)
O(2)-C(2)	1.287(5)
O(3)-C(4)	1.239(5)
O(4)-H(4)	0.843(18)
O(4)-H(4)#1	0.843(18)
O(5)-H(51)	0.817(19)
O(5)-H(52)	0.826(19)
O(6)-H(61)	0.825(19)
O(6)-H(62)	0.819(19)
C(1)-C(10)	1.478(6)
C(1)-C(2)	1.513(6)
C(2)-C(3)	1.388(6)
C(3)-C(4)	1.426(6)
C(3)-C(11)	1.499(6)
C(4)-C(5)	1.486(6)
C(5)-C(6)	1.386(6)
C(5)-C(10)	1.406(6)
C(6)-C(7)	1.364(6)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.381(7)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.377(6)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.378(6)
C(9)-H(9A)	0.9300
C(11)-H(11A)	0.9600

C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600

O(2)-Na-O(4)	87.28(11)
O(2)-Na-O(5)	172.46(14)
O(4)-Na-O(5)	93.14(12)
O(2)-Na-O(1)#1	93.89(11)
O(4)-Na-O(1)#1	141.91(12)
O(5)-Na-O(1)#1	90.43(12)
O(2)-Na-O(5)#2	86.80(13)
O(4)-Na-O(5)#2	92.66(11)
O(5)-Na-O(5)#2	85.67(10)
O(1)#1-Na-O(5)#2	125.43(13)
O(2)-Na-O(2)#1	72.54(13)
O(4)-Na-O(2)#1	80.92(10)
O(5)-Na-O(2)#1	114.97(12)
O(1)#1-Na-O(2)#1	63.39(10)
O(5)#2-Na-O(2)#1	158.54(12)
O(2)-Na-Na#1	53.21(9)
O(4)-Na-Na#1	46.47(8)
O(5)-Na-Na#1	131.14(11)
O(1)#1-Na-Na#1	106.31(9)
O(5)#2-Na-Na#1	116.73(11)
O(2)#1-Na-Na#1	45.50(8)
O(2)-Na-Na#2	72.60(8)
O(4)-Na-Na#2	61.01(6)
O(5)-Na-Na#2	101.03(11)
O(1)#1-Na-Na#2	154.31(10)
O(5)#2-Na-Na#2	34.79(8)
O(2)#1-Na-Na#2	128.70(7)
Na#1-Na-Na#2	83.38(5)
O(2)-Na-Na#3	149.52(9)
O(4)-Na-Na#3	70.99(7)
O(5)-Na-Na#3	36.31(9)
O(1)#1-Na-Na#3	90.81(8)
O(5)#2-Na-Na#3	114.53(11)
O(2)#1-Na-Na#3	82.87(7)

Na#1-Na-Na#3	96.62(5)
Na#2-Na-Na#3	112.04(8)
C(1)-O(1)-Na#1	115.5(3)
C(2)-O(2)-Na	130.5(2)
C(2)-O(2)-Na#1	112.1(3)
Na-O(2)-Na#1	81.29(11)
Na-O(4)-Na#1	87.07(17)
Na-O(4)-H(4)	110(3)
Na#1-O(4)-H(4)	126(4)
Na-O(4)-H(4)#1	126(4)
Na#1-O(4)-H(4)#1	110(3)
H(4)-O(4)-H(4)#1	100(3)
Na-O(5)-Na#3	108.90(14)
Na-O(5)-H(51)	102(3)
Na#3-O(5)-H(51)	126(3)
Na-O(5)-H(52)	102(4)
Na#3-O(5)-H(52)	112(4)
H(51)-O(5)-H(52)	104(3)
H(61)-O(6)-H(62)	104(3)
O(1)-C(1)-C(10)	121.1(4)
O(1)-C(1)-C(2)	119.9(4)
C(10)-C(1)-C(2)	118.9(4)
O(2)-C(2)-C(3)	125.0(4)
O(2)-C(2)-C(1)	115.3(4)
C(3)-C(2)-C(1)	119.7(4)
C(2)-C(3)-C(4)	121.8(4)
C(2)-C(3)-C(11)	120.6(4)
C(4)-C(3)-C(11)	117.6(4)
O(3)-C(4)-C(3)	122.5(4)
O(3)-C(4)-C(5)	118.2(4)
C(3)-C(4)-C(5)	119.3(4)
C(6)-C(5)-C(10)	118.2(4)
C(6)-C(5)-C(4)	120.4(4)
C(10)-C(5)-C(4)	121.4(4)
C(7)-C(6)-C(5)	121.8(4)
C(7)-C(6)-H(6A)	119.1
C(5)-C(6)-H(6A)	119.1

C(6)-C(7)-C(8)	119.6(5)
C(6)-C(7)-H(7A)	120.2
C(8)-C(7)-H(7A)	120.2
C(9)-C(8)-C(7)	119.9(4)
C(9)-C(8)-H(8A)	120.0
C(7)-C(8)-H(8A)	120.0
C(8)-C(9)-C(10)	120.8(4)
C(8)-C(9)-H(9A)	119.6
C(10)-C(9)-H(9A)	119.6
C(9)-C(10)-C(5)	119.6(4)
C(9)-C(10)-C(1)	121.6(4)
C(5)-C(10)-C(1)	118.7(4)
C(3)-C(11)-H(11A)	109.5
C(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 x,-y+1,z-1/2 #3 x,-y+1,z+1/2

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Na(pht)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Na	29(1)	23(1)	36(1)	-1(1)	-3(1)	-3(1)
O(1)	31(2)	28(2)	46(2)	-3(2)	-5(2)	14(2)
O(2)	50(2)	14(2)	31(2)	-1(1)	2(2)	-9(2)
O(3)	21(2)	30(2)	53(2)	-2(2)	4(2)	11(2)
O(4)	44(3)	22(3)	28(3)	0	3(2)	0
O(5)	33(2)	31(2)	39(2)	5(2)	9(2)	-2(2)
O(6)	27(2)	31(2)	56(2)	2(2)	7(2)	5(2)
C(1)	24(3)	19(3)	22(2)	-2(2)	1(2)	2(2)
C(2)	32(3)	19(2)	12(2)	1(2)	0(2)	-7(2)
C(3)	19(2)	22(3)	25(2)	2(2)	3(2)	-3(2)
C(4)	16(2)	26(3)	27(2)	0(2)	6(2)	5(2)
C(5)	23(3)	15(2)	28(2)	-2(2)	2(2)	-1(2)
C(6)	31(3)	19(3)	64(3)	-1(2)	7(3)	2(2)
C(7)	52(4)	19(3)	70(4)	-6(3)	10(3)	-15(3)
C(8)	25(3)	44(4)	55(3)	-8(3)	6(2)	-20(3)
C(9)	19(3)	35(3)	37(3)	-7(2)	4(2)	-1(2)
C(10)	14(2)	26(3)	18(2)	-3(2)	-1(2)	2(2)
C(11)	28(3)	42(3)	45(3)	-5(2)	9(2)	-12(2)

Table S7. Torsion angles [°] for **Na(pht)**

Na#1-O(1)-C(1)-C(10)	147.3(3)
Na#1-O(1)-C(1)-C(2)	-31.6(5)
Na-O(2)-C(2)-C(3)	-56.3(6)
Na#1-O(2)-C(2)-C(3)	-153.9(3)
Na-O(2)-C(2)-C(1)	123.0(3)
Na#1-O(2)-C(2)-C(1)	25.3(4)
O(1)-C(1)-C(2)-O(2)	2.7(6)
C(10)-C(1)-C(2)-O(2)	-176.3(3)
O(1)-C(1)-C(2)-C(3)	-178.1(4)
C(10)-C(1)-C(2)-C(3)	3.0(5)
O(2)-C(2)-C(3)-C(4)	174.6(4)
C(1)-C(2)-C(3)-C(4)	-4.6(6)
O(2)-C(2)-C(3)-C(11)	-3.4(6)
C(1)-C(2)-C(3)-C(11)	177.4(4)
C(2)-C(3)-C(4)-O(3)	-176.5(4)
C(11)-C(3)-C(4)-O(3)	1.6(6)
C(2)-C(3)-C(4)-C(5)	3.0(6)
C(11)-C(3)-C(4)-C(5)	-178.9(4)
O(3)-C(4)-C(5)-C(6)	-0.5(6)
C(3)-C(4)-C(5)-C(6)	-180.0(4)
O(3)-C(4)-C(5)-C(10)	179.8(4)
C(3)-C(4)-C(5)-C(10)	0.3(6)
C(10)-C(5)-C(6)-C(7)	0.2(7)
C(4)-C(5)-C(6)-C(7)	-179.5(5)
C(5)-C(6)-C(7)-C(8)	-0.8(8)
C(6)-C(7)-C(8)-C(9)	1.0(8)
C(7)-C(8)-C(9)-C(10)	-0.6(7)
C(8)-C(9)-C(10)-C(5)	-0.1(7)
C(8)-C(9)-C(10)-C(1)	-178.3(4)
C(6)-C(5)-C(10)-C(9)	0.3(6)
C(4)-C(5)-C(10)-C(9)	180.0(4)
C(6)-C(5)-C(10)-C(1)	178.5(4)
C(4)-C(5)-C(10)-C(1)	-1.7(6)
O(1)-C(1)-C(10)-C(9)	-0.6(6)
C(2)-C(1)-C(10)-C(9)	178.4(4)

O(1)-C(1)-C(10)-C(5)	-178.8(4)
C(2)-C(1)-C(10)-C(5)	0.2(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 x,-y+1,z-1/2 #3 x,-y+1,z+1/2

Table S8. Crystal data and structure refinement for **1**

Identification code	shelx	
Empirical formula	C22 H20 Mn O9	
Formula weight	483.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 33.7912(9) Å	α= 90°.
	b = 13.3987(3) Å	β= 96.3400(8)°.
	c = 18.5028(5) Å	γ = 90°.
Volume	8326.1(4) $Å^3$	
Z	16	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	0.688 mm^{-1}	
F(000)	3984	
Crystal size	0.350 x 0.290 x 0.120 mm^3	
Theta range for data collection	2.640 to 28.450°.	
Index ranges	-45<=h<=45, -17<=k<=17, -24<=l<=24	
Reflections collected	99477	
Independent reflections	10433 [R(int) = 0.0991]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.921 and 0.787	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10433 / 66 / 647	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0615, wR2 = 0.1269	
R indices (all data)	R1 = 0.0934, wR2 = 0.1401	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.425 and -0.368 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Mn(1)	5798(1)	-1118(1)	7766(1)	30(1)
O(4A)	5722(1)	-2664(2)	8043(2)	63(1)
O(4B)	5356(1)	-1354(2)	6866(1)	47(1)
O(1A)	6265(1)	-1323(2)	7006(1)	36(1)
C(1A)	6613(1)	-1320(2)	7285(1)	26(1)
O(2A)	6370(1)	-1186(1)	8433(1)	32(1)
C(2A)	6688(1)	-1254(2)	8102(1)	27(1)
O(3A)	7755(1)	-1297(2)	8288(1)	44(1)
C(3A)	7074(1)	-1253(2)	8430(1)	30(1)
C(4A)	7406(1)	-1299(2)	8002(2)	30(1)
C(5A)	7651(1)	-1328(2)	6773(2)	37(1)
C(6A)	7585(1)	-1366(2)	6028(2)	44(1)
C(7A)	7200(1)	-1413(2)	5686(2)	45(1)
C(8A)	6881(1)	-1413(2)	6093(2)	38(1)
C(9A)	6948(1)	-1366(2)	6842(1)	28(1)
C(10A)	7335(1)	-1330(2)	7192(2)	28(1)
C(11A)	7162(1)	-1158(3)	9239(2)	46(1)
O(1B)	5844(1)	552(1)	7526(1)	36(1)
C(1B)	5618(1)	1080(2)	7840(1)	27(1)
O(2B)	5359(1)	-383(1)	8315(1)	31(1)
C(2B)	5335(1)	587(2)	8294(1)	26(1)
O(3B)	4893(1)	2751(2)	8989(1)	58(1)
C(3B)	5086(1)	1153(2)	8661(1)	30(1)
C(4B)	5101(1)	2233(2)	8637(2)	34(1)
C(5B)	5412(1)	3775(2)	8186(2)	45(1)
C(6B)	5680(1)	4239(2)	7797(2)	59(1)
C(7B)	5922(1)	3682(3)	7395(2)	64(1)
C(8B)	5895(1)	2653(2)	7386(2)	46(1)
C(9B)	5630(1)	2179(2)	7795(1)	30(1)
C(10B)	5384(1)	2738(2)	8191(1)	32(1)
C(11B)	4810(1)	692(3)	9143(2)	49(1)
Mn(2)	8513(1)	-992(1)	554(1)	30(1)

O(4C)	8225(1)	-644(2)	-515(1)	51(1)
O(4D)	8638(1)	-2543(2)	358(1)	48(1)
O(1C)	8530(1)	734(1)	710(1)	35(1)
C(1C)	8809(1)	1123(2)	441(1)	27(1)
O(2C)	9063(1)	-488(1)	249(1)	37(1)
C(2C)	9105(1)	453(2)	126(1)	27(1)
O(3C)	9627(1)	2264(2)	-805(1)	54(1)
C(3C)	9371(1)	846(2)	-299(1)	30(1)
C(4C)	9396(1)	1909(2)	-396(2)	33(1)
C(5C)	9183(1)	3622(2)	-65(2)	42(1)
C(6C)	8948(1)	4253(2)	301(2)	49(1)
C(7C)	8670(1)	3873(2)	716(2)	46(1)
C(8C)	8618(1)	2848(2)	762(2)	37(1)
C(9C)	8854(1)	2211(2)	401(1)	28(1)
C(10C)	9141(1)	2596(2)	-14(1)	31(1)
C(11C)	9622(1)	183(3)	-718(2)	49(1)
O(1D)	7910(1)	-1158(2)	901(1)	36(1)
C(1D)	7899(1)	-1187(2)	1560(1)	26(1)
O(2D)	8601(1)	-1197(1)	1705(1)	33(1)
C(2D)	8285(1)	-1186(2)	2048(1)	27(1)
O(3D)	7909(1)	-1067(2)	3776(1)	47(1)
C(3D)	8284(1)	-1164(2)	2787(1)	31(1)
C(4D)	7914(1)	-1133(2)	3112(1)	32(1)
C(5D)	7170(1)	-1182(2)	2937(2)	39(1)
C(6D)	6815(1)	-1209(2)	2492(2)	46(1)
C(7D)	6810(1)	-1243(2)	1749(2)	48(1)
C(8D)	7162(1)	-1243(2)	1437(2)	38(1)
C(9D)	7521(1)	-1213(2)	1880(1)	28(1)
C(10D)	7528(1)	-1182(2)	2634(1)	29(1)
C(11D)	8664(1)	-1166(2)	3290(2)	45(1)
O(1W)	5008(2)	-3577(4)	7889(3)	81(2)
O(2W)	9090(2)	-2312(6)	-662(4)	88(2)
O(1WA)	5452(3)	-2898(9)	9298(8)	86(3)
O(2WA)	9439(3)	-2329(8)	199(6)	92(3)
O(1WB)	5323(4)	-3564(12)	8812(11)	85(3)
O(2WB)	9265(6)	-2325(18)	-277(12)	89(4)

Table S10. Bond lengths [Å] and angles [°] for **1**

Mn(1)-O(2B)	2.1294(18)
Mn(1)-O(4B)	2.135(2)
Mn(1)-O(4A)	2.156(2)
Mn(1)-O(2A)	2.1768(18)
Mn(1)-O(1A)	2.2429(19)
Mn(1)-O(1B)	2.2892(19)
O(4A)-H(4AA)	0.808(18)
O(4A)-H(4AB)	0.794(17)
O(4B)-H(4BA)	0.822(17)
O(4B)-H(4BB)	0.807(17)
O(1A)-C(1A)	1.230(3)
C(1A)-C(9A)	1.471(4)
C(1A)-C(2A)	1.507(4)
O(2A)-C(2A)	1.299(3)
C(2A)-C(3A)	1.374(4)
O(3A)-C(4A)	1.236(3)
C(3A)-C(4A)	1.447(4)
C(3A)-C(11A)	1.498(4)
C(4A)-C(10A)	1.491(4)
C(5A)-C(6A)	1.373(4)
C(5A)-C(10A)	1.388(4)
C(5A)-H(5A)	0.9300
C(6A)-C(7A)	1.384(4)
C(6A)-H(6A)	0.9300
C(7A)-C(8A)	1.380(4)
C(7A)-H(7A)	0.9300
C(8A)-C(9A)	1.382(4)
C(8A)-H(8A)	0.9300
C(9A)-C(10A)	1.395(3)
C(11A)-H(11A)	0.9600
C(11A)-H(11B)	0.9600
C(11A)-H(11C)	0.9600
O(1B)-C(1B)	1.233(3)
C(1B)-C(9B)	1.476(4)
C(1B)-C(2B)	1.494(3)

O(2B)-C(2B)	1.302(3)
C(2B)-C(3B)	1.368(4)
O(3B)-C(4B)	1.225(3)
C(3B)-C(4B)	1.450(4)
C(3B)-C(11B)	1.492(4)
C(4B)-C(10B)	1.492(4)
C(5B)-C(6B)	1.367(5)
C(5B)-C(10B)	1.394(4)
C(5B)-H(5B)	0.9300
C(6B)-C(7B)	1.384(5)
C(6B)-H(6B)	0.9300
C(7B)-C(8B)	1.381(5)
C(7B)-H(7B)	0.9300
C(8B)-C(9B)	1.387(4)
C(8B)-H(8B)	0.9300
C(9B)-C(10B)	1.387(4)
C(11B)-H(11D)	0.9600
C(11B)-H(11E)	0.9600
C(11B)-H(11F)	0.9600
Mn(2)-O(2C)	2.1102(18)
Mn(2)-O(2D)	2.1359(19)
Mn(2)-O(4C)	2.156(2)
Mn(2)-O(4D)	2.159(2)
Mn(2)-O(1D)	2.2160(19)
Mn(2)-O(1C)	2.3303(19)
O(4C)-H(4CA)	0.804(17)
O(4C)-H(4CB)	0.828(17)
O(4D)-H(4DA)	0.786(11)
O(4D)-H(4DB)	0.822(17)
O(1C)-C(1C)	1.229(3)
C(1C)-C(9C)	1.469(4)
C(1C)-C(2C)	1.507(4)
O(2C)-C(2C)	1.291(3)
C(2C)-C(3C)	1.364(4)
O(3C)-C(4C)	1.239(3)
C(3C)-C(4C)	1.439(4)
C(3C)-C(11C)	1.501(4)

C(4C)-C(10C)	1.491(4)
C(5C)-C(10C)	1.385(4)
C(5C)-C(6C)	1.386(5)
C(5C)-H(5C)	0.9300
C(6C)-C(7C)	1.376(5)
C(6C)-H(6C)	0.9300
C(7C)-C(8C)	1.389(4)
C(7C)-H(7C)	0.9300
C(8C)-C(9C)	1.389(4)
C(8C)-H(8C)	0.9300
C(9C)-C(10C)	1.400(4)
C(11C)-H(11G)	0.9600
C(11C)-H(11H)	0.9600
C(11C)-H(11I)	0.9600
O(1D)-C(1D)	1.225(3)
C(1D)-C(9D)	1.467(4)
C(1D)-C(2D)	1.502(3)
O(2D)-C(2D)	1.300(3)
C(2D)-C(3D)	1.369(4)
O(3D)-C(4D)	1.233(3)
C(3D)-C(4D)	1.445(4)
C(3D)-C(11D)	1.499(4)
C(4D)-C(10D)	1.496(4)
C(5D)-C(6D)	1.376(4)
C(5D)-C(10D)	1.390(4)
C(5D)-H(5D)	0.9300
C(6D)-C(7D)	1.375(5)
C(6D)-H(6D)	0.9300
C(7D)-C(8D)	1.378(4)
C(7D)-H(7D)	0.9300
C(8D)-C(9D)	1.386(4)
C(8D)-H(8D)	0.9300
C(9D)-C(10D)	1.393(4)
C(11D)-H(11J)	0.9600
C(11D)-H(11K)	0.9600
C(11D)-H(11L)	0.9600
O(1W)-H(1W1)	0.8142

O(1W)-H(1W2)	0.8165
O(2W)-H(2W1)	0.8333
O(2W)-H(2W2)	0.8378
O(1WA)-H(1W3)	0.8296
O(1WA)-H(1W4)	0.8251
O(2WA)-H(2W3)	0.8382
O(2WA)-H(2W4)	0.8312
O(1WB)-H(1W5)	0.8232
O(1WB)-H(1W6)	0.8235
O(2WB)-H(2W5)	0.8297
O(2WB)-H(2W6)	0.8238

O(2B)-Mn(1)-O(4B)	88.63(8)
O(2B)-Mn(1)-O(4A)	102.90(9)
O(4B)-Mn(1)-O(4A)	87.26(10)
O(2B)-Mn(1)-O(2A)	111.74(7)
O(4B)-Mn(1)-O(2A)	159.59(8)
O(4A)-Mn(1)-O(2A)	86.95(8)
O(2B)-Mn(1)-O(1A)	158.55(7)
O(4B)-Mn(1)-O(1A)	88.47(8)
O(4A)-Mn(1)-O(1A)	98.18(9)
O(2A)-Mn(1)-O(1A)	73.03(7)
O(2B)-Mn(1)-O(1B)	72.89(7)
O(4B)-Mn(1)-O(1B)	92.87(8)
O(4A)-Mn(1)-O(1B)	175.77(9)
O(2A)-Mn(1)-O(1B)	94.33(7)
O(1A)-Mn(1)-O(1B)	86.05(7)
Mn(1)-O(4A)-H(4AA)	118(3)
Mn(1)-O(4A)-H(4AB)	107(2)
H(4AA)-O(4A)-H(4AB)	110(3)
Mn(1)-O(4B)-H(4BA)	130(2)
Mn(1)-O(4B)-H(4BB)	126(2)
H(4BA)-O(4B)-H(4BB)	104(2)
C(1A)-O(1A)-Mn(1)	116.20(17)
O(1A)-C(1A)-C(9A)	121.7(2)
O(1A)-C(1A)-C(2A)	118.1(2)
C(9A)-C(1A)-C(2A)	120.3(2)

C(2A)-O(2A)-Mn(1)	117.78(16)
O(2A)-C(2A)-C(3A)	125.8(2)
O(2A)-C(2A)-C(1A)	114.7(2)
C(3A)-C(2A)-C(1A)	119.5(2)
C(2A)-C(3A)-C(4A)	120.8(2)
C(2A)-C(3A)-C(11A)	121.1(3)
C(4A)-C(3A)-C(11A)	118.0(2)
O(3A)-C(4A)-C(3A)	121.8(3)
O(3A)-C(4A)-C(10A)	118.0(3)
C(3A)-C(4A)-C(10A)	120.2(2)
C(6A)-C(5A)-C(10A)	120.8(3)
C(6A)-C(5A)-H(5A)	119.6
C(10A)-C(5A)-H(5A)	119.6
C(5A)-C(6A)-C(7A)	120.0(3)
C(5A)-C(6A)-H(6A)	120.0
C(7A)-C(6A)-H(6A)	120.0
C(8A)-C(7A)-C(6A)	120.1(3)
C(8A)-C(7A)-H(7A)	119.9
C(6A)-C(7A)-H(7A)	119.9
C(7A)-C(8A)-C(9A)	119.8(3)
C(7A)-C(8A)-H(8A)	120.1
C(9A)-C(8A)-H(8A)	120.1
C(8A)-C(9A)-C(10A)	120.5(2)
C(8A)-C(9A)-C(1A)	120.7(2)
C(10A)-C(9A)-C(1A)	118.8(2)
C(5A)-C(10A)-C(9A)	118.7(3)
C(5A)-C(10A)-C(4A)	120.9(2)
C(9A)-C(10A)-C(4A)	120.4(2)
C(3A)-C(11A)-H(11A)	109.5
C(3A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
C(3A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(1B)-O(1B)-Mn(1)	114.27(16)
O(1B)-C(1B)-C(9B)	121.6(2)
O(1B)-C(1B)-C(2B)	118.6(2)

C(9B)-C(1B)-C(2B)	119.8(2)
C(2B)-O(2B)-Mn(1)	119.51(16)
O(2B)-C(2B)-C(3B)	125.4(2)
O(2B)-C(2B)-C(1B)	114.5(2)
C(3B)-C(2B)-C(1B)	120.1(2)
C(2B)-C(3B)-C(4B)	120.8(2)
C(2B)-C(3B)-C(11B)	121.8(3)
C(4B)-C(3B)-C(11B)	117.3(2)
O(3B)-C(4B)-C(3B)	121.7(3)
O(3B)-C(4B)-C(10B)	118.6(3)
C(3B)-C(4B)-C(10B)	119.7(2)
C(6B)-C(5B)-C(10B)	120.4(3)
C(6B)-C(5B)-H(5B)	119.8
C(10B)-C(5B)-H(5B)	119.8
C(5B)-C(6B)-C(7B)	120.2(3)
C(5B)-C(6B)-H(6B)	119.9
C(7B)-C(6B)-H(6B)	119.9
C(8B)-C(7B)-C(6B)	120.1(3)
C(8B)-C(7B)-H(7B)	119.9
C(6B)-C(7B)-H(7B)	119.9
C(7B)-C(8B)-C(9B)	119.8(3)
C(7B)-C(8B)-H(8B)	120.1
C(9B)-C(8B)-H(8B)	120.1
C(10B)-C(9B)-C(8B)	120.0(3)
C(10B)-C(9B)-C(1B)	119.1(2)
C(8B)-C(9B)-C(1B)	120.8(3)
C(9B)-C(10B)-C(5B)	119.4(3)
C(9B)-C(10B)-C(4B)	120.4(2)
C(5B)-C(10B)-C(4B)	120.2(3)
C(3B)-C(11B)-H(11D)	109.5
C(3B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
C(3B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
O(2C)-Mn(2)-O(2D)	106.19(8)
O(2C)-Mn(2)-O(4C)	90.48(9)

O(2D)-Mn(2)-O(4C)	160.16(9)
O(2C)-Mn(2)-O(4D)	93.98(8)
O(2D)-Mn(2)-O(4D)	92.04(8)
O(4C)-Mn(2)-O(4D)	97.56(9)
O(2C)-Mn(2)-O(1D)	167.10(8)
O(2D)-Mn(2)-O(1D)	74.21(7)
O(4C)-Mn(2)-O(1D)	87.13(8)
O(4D)-Mn(2)-O(1D)	98.90(8)
O(2C)-Mn(2)-O(1C)	72.85(7)
O(2D)-Mn(2)-O(1C)	90.28(7)
O(4C)-Mn(2)-O(1C)	84.34(8)
O(4D)-Mn(2)-O(1C)	166.74(8)
O(1D)-Mn(2)-O(1C)	94.29(7)
Mn(2)-O(4C)-H(4CA)	127(2)
Mn(2)-O(4C)-H(4CB)	125(2)
H(4CA)-O(4C)-H(4CB)	106(3)
Mn(2)-O(4D)-H(4DA)	114(3)
Mn(2)-O(4D)-H(4DB)	120(3)
H(4DA)-O(4D)-H(4DB)	107(2)
C(1C)-O(1C)-Mn(2)	112.32(17)
O(1C)-C(1C)-C(9C)	122.0(2)
O(1C)-C(1C)-C(2C)	118.3(2)
C(9C)-C(1C)-C(2C)	119.7(2)
C(2C)-O(2C)-Mn(2)	118.45(16)
O(2C)-C(2C)-C(3C)	124.8(2)
O(2C)-C(2C)-C(1C)	115.0(2)
C(3C)-C(2C)-C(1C)	120.0(2)
C(2C)-C(3C)-C(4C)	120.4(2)
C(2C)-C(3C)-C(11C)	121.0(3)
C(4C)-C(3C)-C(11C)	118.5(2)
O(3C)-C(4C)-C(3C)	120.4(3)
O(3C)-C(4C)-C(10C)	119.1(3)
C(3C)-C(4C)-C(10C)	120.5(2)
C(10C)-C(5C)-C(6C)	120.3(3)
C(10C)-C(5C)-H(5C)	119.8
C(6C)-C(5C)-H(5C)	119.8
C(7C)-C(6C)-C(5C)	120.7(3)

C(7C)-C(6C)-H(6C)	119.7
C(5C)-C(6C)-H(6C)	119.7
C(6C)-C(7C)-C(8C)	119.9(3)
C(6C)-C(7C)-H(7C)	120.0
C(8C)-C(7C)-H(7C)	120.0
C(7C)-C(8C)-C(9C)	119.6(3)
C(7C)-C(8C)-H(8C)	120.2
C(9C)-C(8C)-H(8C)	120.2
C(8C)-C(9C)-C(10C)	120.5(2)
C(8C)-C(9C)-C(1C)	121.1(2)
C(10C)-C(9C)-C(1C)	118.4(2)
C(5C)-C(10C)-C(9C)	118.9(3)
C(5C)-C(10C)-C(4C)	120.9(3)
C(9C)-C(10C)-C(4C)	120.2(2)
C(3C)-C(11C)-H(11G)	109.5
C(3C)-C(11C)-H(11H)	109.5
H(11G)-C(11C)-H(11H)	109.5
C(3C)-C(11C)-H(11I)	109.5
H(11G)-C(11C)-H(11I)	109.5
H(11H)-C(11C)-H(11I)	109.5
C(1D)-O(1D)-Mn(2)	114.94(16)
O(1D)-C(1D)-C(9D)	121.7(2)
O(1D)-C(1D)-C(2D)	118.6(2)
C(9D)-C(1D)-C(2D)	119.7(2)
C(2D)-O(2D)-Mn(2)	117.10(15)
O(2D)-C(2D)-C(3D)	125.6(2)
O(2D)-C(2D)-C(1D)	114.3(2)
C(3D)-C(2D)-C(1D)	120.1(2)
C(2D)-C(3D)-C(4D)	121.0(2)
C(2D)-C(3D)-C(11D)	121.6(3)
C(4D)-C(3D)-C(11D)	117.5(2)
O(3D)-C(4D)-C(3D)	121.7(3)
O(3D)-C(4D)-C(10D)	118.9(3)
C(3D)-C(4D)-C(10D)	119.3(2)
C(6D)-C(5D)-C(10D)	119.9(3)
C(6D)-C(5D)-H(5D)	120.0
C(10D)-C(5D)-H(5D)	120.0

C(7D)-C(6D)-C(5D)	120.8(3)
C(7D)-C(6D)-H(6D)	119.6
C(5D)-C(6D)-H(6D)	119.6
C(6D)-C(7D)-C(8D)	120.2(3)
C(6D)-C(7D)-H(7D)	119.9
C(8D)-C(7D)-H(7D)	119.9
C(7D)-C(8D)-C(9D)	119.4(3)
C(7D)-C(8D)-H(8D)	120.3
C(9D)-C(8D)-H(8D)	120.3
C(8D)-C(9D)-C(10D)	120.7(2)
C(8D)-C(9D)-C(1D)	120.4(2)
C(10D)-C(9D)-C(1D)	118.9(2)
C(5D)-C(10D)-C(9D)	118.9(3)
C(5D)-C(10D)-C(4D)	120.2(3)
C(9D)-C(10D)-C(4D)	120.8(2)
C(3D)-C(11D)-H(11J)	109.5
C(3D)-C(11D)-H(11K)	109.5
H(11J)-C(11D)-H(11K)	109.5
C(3D)-C(11D)-H(11L)	109.5
H(11J)-C(11D)-H(11L)	109.5
H(11K)-C(11D)-H(11L)	109.5
H(1W1)-O(1W)-H(1W2)	106.7
H(2W1)-O(2W)-H(2W2)	101.0
H(1W3)-O(1WA)-H(1W4)	103.2
H(2W3)-O(2WA)-H(2W4)	101.3
H(1W5)-O(1WB)-H(1W6)	104.2
H(2W5)-O(2WB)-H(2W6)	103.0

Symmetry transformations used to generate equivalent atoms:

Table S11. Crystal data and structure refinement for **1B**

Identification code	shelx	
Empirical formula	C_{23} H_{22} Mn O_9	
Formula weight	497.34	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.0352(16) Å	α= 90°
	b = 17.307(4) Å	β= 104.09(3)°
	c = 15.532(3) Å	γ = 90°
Volume	2095.0(8) $Å^3$	
Z	4	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	0.686 mm^{-1}	
F(000)	1028	
Crystal size	0.21 x 0.13 x 0.10 mm^3	
Theta range for data collection	2.885 to 25.251°	
Index ranges	-9<=h<=9, -20<=k<=20, -18<=l<=17	
Reflections collected	11458	
Independent reflections	3539 [R(int) = 0.1707]	
Completeness to theta = 25.242°	93.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.792 and 0.731	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3539 / 8 / 316	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0792, wR2 = 0.1385	
R indices (all data)	R1 = 0.2059, wR2 = 0.1787	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.448 and -0.429 $e.Å^{-3}$	

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1B.** The anisotropic displacement factor exponent takes the form: $-2\ \pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	24(1)	24(1)	43(1)	-1(1)	2(1)	4(1)
O(4A)	43(2)	32(1)	111(2)	18(1)	-12(1)	4(1)
O(4B)	37(1)	50(1)	52(1)	-22(1)	-10(1)	18(1)
O(1A)	24(1)	45(1)	38(1)	-2(1)	-2(1)	3(1)
C(1A)	23(1)	16(1)	40(2)	0(1)	-1(1)	1(1)
O(2A)	29(1)	32(1)	36(1)	-1(1)	3(1)	1(1)
C(2A)	29(2)	15(1)	37(2)	1(1)	0(1)	-1(1)
O(3A)	28(1)	50(1)	54(1)	-5(1)	-11(1)	-4(1)
C(3A)	32(2)	22(1)	35(2)	2(1)	-3(1)	-3(1)
C(4A)	29(2)	16(1)	47(2)	-1(1)	-7(1)	-2(1)
C(5A)	23(2)	30(2)	60(2)	-1(1)	4(1)	-4(1)
C(6A)	38(2)	42(2)	56(2)	-2(2)	18(2)	-1(1)
C(7A)	47(2)	51(2)	41(2)	-1(2)	8(2)	-3(2)
C(8A)	29(2)	43(2)	43(2)	1(1)	2(1)	-1(1)
C(9A)	25(1)	21(1)	38(2)	2(1)	0(1)	-2(1)
C(10A)	25(1)	15(1)	43(2)	1(1)	0(1)	-2(1)
C(11A)	42(2)	55(2)	44(2)	-2(2)	-4(2)	-6(2)
O(1B)	32(1)	27(1)	51(1)	0(1)	13(1)	2(1)
C(1B)	24(1)	26(1)	32(1)	-2(1)	-1(1)	1(1)
O(2B)	31(1)	22(1)	44(1)	1(1)	8(1)	-2(1)
C(2B)	23(1)	26(1)	27(1)	-2(1)	-2(1)	-1(1)
O(3B)	63(2)	44(1)	72(2)	-16(1)	27(1)	11(1)
C(3B)	31(2)	33(2)	28(1)	-2(1)	1(1)	-1(1)
C(4B)	31(2)	35(2)	36(2)	-8(1)	-2(1)	7(1)
C(5B)	49(2)	28(2)	54(2)	-5(2)	-6(2)	8(2)
C(6B)	72(3)	25(2)	78(3)	8(2)	-4(2)	-2(2)
C(7B)	63(2)	40(2)	92(3)	21(2)	13(2)	-7(2)
C(8B)	42(2)	34(2)	65(2)	10(2)	12(2)	3(1)
C(9B)	28(2)	24(1)	39(2)	5(1)	-2(1)	2(1)
C(10B)	30(2)	28(2)	35(2)	-2(1)	-8(1)	3(1)
C(11B)	55(2)	49(2)	49(2)	1(2)	21(2)	0(2)
Mn(2)	28(1)	29(1)	36(1)	7(1)	5(1)	-1(1)

O(4C)	58(2)	51(2)	41(1)	13(1)	-14(1)	-15(1)
O(4D)	60(2)	32(1)	58(2)	5(1)	17(1)	-1(1)
O(1C)	30(1)	32(1)	48(1)	4(1)	14(1)	0(1)
C(1C)	26(1)	31(2)	25(1)	0(1)	-1(1)	-1(1)
O(2C)	31(1)	27(1)	56(1)	1(1)	13(1)	0(1)
C(2C)	23(1)	29(2)	31(2)	0(1)	-2(1)	1(1)
O(3C)	41(1)	60(2)	67(2)	29(1)	20(1)	1(1)
C(3C)	24(1)	37(2)	29(2)	1(1)	1(1)	0(1)
C(4C)	21(1)	43(2)	36(2)	11(1)	-3(1)	-5(1)
C(5C)	43(2)	34(2)	48(2)	9(1)	-7(2)	-12(1)
C(6C)	63(2)	25(2)	56(2)	-1(2)	-15(2)	-6(2)
C(7C)	55(2)	35(2)	47(2)	-9(2)	-9(2)	9(2)
C(8C)	39(2)	35(2)	38(2)	-2(1)	-1(1)	4(1)
C(9C)	28(2)	27(1)	29(1)	0(1)	-5(1)	-2(1)
C(10C)	25(1)	34(2)	32(2)	6(1)	-7(1)	-6(1)
C(11C)	46(2)	55(2)	52(2)	-2(2)	19(2)	2(2)
O(1D)	28(1)	52(1)	30(1)	5(1)	1(1)	-1(1)
C(1D)	30(2)	18(1)	30(2)	2(1)	0(1)	0(1)
O(2D)	26(1)	37(1)	38(1)	7(1)	1(1)	0(1)
C(2D)	29(2)	16(1)	36(2)	5(1)	1(1)	-2(1)
O(3D)	67(2)	48(1)	30(1)	-4(1)	6(1)	-1(1)
C(3D)	38(2)	21(1)	33(2)	2(1)	-5(1)	-3(1)
C(4D)	49(2)	18(1)	32(2)	0(1)	3(1)	-3(1)
C(5D)	49(2)	28(2)	47(2)	0(1)	19(2)	1(1)
C(6D)	34(2)	41(2)	67(2)	0(2)	19(2)	-1(1)
C(7D)	27(2)	53(2)	64(2)	5(2)	4(2)	-5(2)
C(8D)	35(2)	40(2)	40(2)	5(1)	2(1)	-2(1)
C(9D)	30(2)	18(1)	37(2)	2(1)	4(1)	-1(1)
C(10D)	37(2)	14(1)	38(2)	-1(1)	7(1)	-1(1)
C(11D)	47(2)	47(2)	40(2)	0(2)	-11(2)	-5(2)
O(20)	179(6)	128(5)	198(6)	1(4)	130(5)	3(4)
O(20')	179(6)	128(5)	198(6)	1(4)	130(5)	3(4)

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for**1B**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Mn	2823(2)	7484(1)	5576(1)	37(1)
O(1)	3181(6)	8250(2)	4588(3)	40(1)
O(2)	2326(6)	8722(2)	6023(3)	44(2)
O(3)	3435(7)	10826(2)	3724(3)	55(2)
O(4)	1470(6)	6734(2)	4556(3)	45(2)
O(5)	3799(6)	6260(2)	5953(3)	48(2)
O(6)	374(7)	4164(2)	3682(3)	52(2)
O(1M)	5395(7)	7723(2)	6323(4)	62(2)
O(1W)	1019(8)	7274(3)	6325(3)	56(2)
O(2W)	1633(11)	7515(3)	8031(3)	83(2)
C(1M)	6520(10)	7361(4)	7044(5)	66(3)
C(1)	2996(8)	8989(3)	4675(5)	29(2)
C(2)	2507(9)	9228(4)	5494(5)	33(2)
C(3)	2133(9)	10051(4)	5626(5)	33(2)
C(4)	1554(9)	10267(4)	6331(5)	44(2)
C(5)	1134(10)	11048(4)	6438(6)	58(3)
C(6)	1415(10)	11573(4)	5821(6)	58(3)
C(7)	2020(10)	11345(4)	5110(6)	49(2)
C(8)	2417(9)	10578(4)	4989(5)	35(2)
C(9)	3060(9)	10331(4)	4236(5)	35(2)
C(10)	3271(8)	9519(3)	4071(5)	32(2)
C(11)	3777(10)	9288(4)	3256(5)	51(2)
C(12)	1720(9)	6001(4)	4636(4)	32(2)
C(13)	3059(9)	5751(3)	5435(5)	31(2)
C(14)	3432(9)	4936(4)	5591(4)	31(2)
C(15)	4707(9)	4694(4)	6320(5)	44(2)
C(16)	5101(10)	3915(4)	6429(5)	50(2)
C(17)	4205(11)	3387(4)	5827(6)	61(3)
C(18)	2947(11)	3620(4)	5129(5)	51(2)
C(19)	2533(9)	4399(3)	5010(5)	37(2)
C(20)	1202(9)	4649(4)	4194(5)	35(2)
C(21)	862(9)	5456(3)	4049(5)	36(2)

C(22)	-434(10)	5709(3)	3240(5)	46(2)

Table S14. Bond lengths [Å] and angles [°] for **1B**

Mn-O(1)	2.099(4)
Mn-O(1W)	2.100(6)
Mn-O(4)	2.130(4)
Mn-O(1M)	2.149(5)
Mn-O(5)	2.286(4)
Mn-O(2)	2.317(4)
O(1)-C(1)	1.298(6)
O(2)-C(2)	1.233(7)
O(3)-C(9)	1.255(8)
O(4)-C(12)	1.285(7)
O(5)-C(13)	1.242(7)
O(6)-C(20)	1.232(7)
O(1M)-C(1M)	1.404(7)
O(1M)-H(1M)	0.82(2)
O(1W)-H(1W1)	0.84(2)
O(1W)-H(1W2)	0.80(2)
O(2W)-H(2W1)	0.83(2)
O(2W)-H(2W2)	0.82(2)
C(1M)-H(1MA)	0.9600
C(1M)-H(1MB)	0.9600
C(1M)-H(1MC)	0.9600
C(1)-C(10)	1.368(8)
C(1)-C(2)	1.480(9)
C(2)-C(3)	1.480(8)
C(3)-C(4)	1.343(9)
C(3)-C(8)	1.404(9)
C(4)-C(5)	1.413(9)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.378(10)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.368(10)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.388(8)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.453(10)

C(9)-C(10)	1.446(8)
C(10)-C(11)	1.475(9)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-C(21)	1.375(8)
C(12)-C(13)	1.495(9)
C(13)-C(14)	1.452(8)
C(14)-C(19)	1.371(8)
C(14)-C(15)	1.393(9)
C(15)-C(16)	1.387(8)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.378(9)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.352(10)
C(17)-H(17A)	0.9300
C(18)-C(19)	1.390(8)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.509(9)
C(20)-C(21)	1.432(8)
C(21)-C(22)	1.489(8)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600

O(1)-Mn-O(1W)	138.6(2)
O(1)-Mn-O(4)	88.70(16)
O(1W)-Mn-O(4)	90.55(19)
O(1)-Mn-O(1M)	89.3(2)
O(1W)-Mn-O(1M)	115.9(2)
O(4)-Mn-O(1M)	140.2(2)
O(1)-Mn-O(5)	132.32(19)
O(1W)-Mn-O(5)	86.4(2)
O(4)-Mn-O(5)	72.94(16)
O(1M)-Mn-O(5)	79.36(17)
O(1)-Mn-O(2)	72.50(16)
O(1W)-Mn-O(2)	78.58(18)

O(4)-Mn-O(2)	133.82(17)
O(1M)-Mn-O(2)	82.74(18)
O(5)-Mn-O(2)	148.66(17)
C(1)-O(1)-Mn	120.5(4)
C(2)-O(2)-Mn	113.6(5)
C(12)-O(4)-Mn	119.4(4)
C(13)-O(5)-Mn	114.2(4)
C(1M)-O(1M)-Mn	133.8(4)
C(1M)-O(1M)-H(1M)	115.3(18)
Mn-O(1M)-H(1M)	110.8(18)
Mn-O(1W)-H(1W1)	124(5)
Mn-O(1W)-H(1W2)	130(5)
H(1W1)-O(1W)-H(1W2)	104(3)
H(2W1)-O(2W)-H(2W2)	103(3)
O(1M)-C(1M)-H(1MA)	109.5
O(1M)-C(1M)-H(1MB)	109.5
H(1MA)-C(1M)-H(1MB)	109.5
O(1M)-C(1M)-H(1MC)	109.5
H(1MA)-C(1M)-H(1MC)	109.5
H(1MB)-C(1M)-H(1MC)	109.5
O(1)-C(1)-C(10)	123.2(7)
O(1)-C(1)-C(2)	115.2(5)
C(10)-C(1)-C(2)	121.6(6)
O(2)-C(2)-C(3)	122.1(7)
O(2)-C(2)-C(1)	118.2(6)
C(3)-C(2)-C(1)	119.6(6)
C(4)-C(3)-C(8)	122.8(7)
C(4)-C(3)-C(2)	120.2(7)
C(8)-C(3)-C(2)	117.0(7)
C(3)-C(4)-C(5)	120.2(8)
C(3)-C(4)-H(4A)	119.9
C(5)-C(4)-H(4A)	119.9
C(6)-C(5)-C(4)	117.7(8)
C(6)-C(5)-H(5A)	121.2
C(4)-C(5)-H(5A)	121.2
C(7)-C(6)-C(5)	121.4(8)
C(7)-C(6)-H(6A)	119.3

C(5)-C(6)-H(6A)	119.3
C(6)-C(7)-C(8)	121.6(8)
C(6)-C(7)-H(7A)	119.2
C(8)-C(7)-H(7A)	119.2
C(7)-C(8)-C(3)	116.3(8)
C(7)-C(8)-C(9)	121.9(7)
C(3)-C(8)-C(9)	121.8(7)
O(3)-C(9)-C(10)	119.6(8)
O(3)-C(9)-C(8)	119.8(7)
C(10)-C(9)-C(8)	120.6(7)
C(1)-C(10)-C(9)	119.0(7)
C(1)-C(10)-C(11)	122.1(6)
C(9)-C(10)-C(11)	119.0(6)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(4)-C(12)-C(21)	124.9(6)
O(4)-C(12)-C(13)	115.5(5)
C(21)-C(12)-C(13)	119.7(6)
O(5)-C(13)-C(14)	122.3(6)
O(5)-C(13)-C(12)	117.9(6)
C(14)-C(13)-C(12)	119.8(6)
C(19)-C(14)-C(15)	119.8(6)
C(19)-C(14)-C(13)	119.7(6)
C(15)-C(14)-C(13)	120.5(6)
C(16)-C(15)-C(14)	119.4(7)
C(16)-C(15)-H(15A)	120.3
C(14)-C(15)-H(15A)	120.3
C(17)-C(16)-C(15)	119.8(7)
C(17)-C(16)-H(16A)	120.1
C(15)-C(16)-H(16A)	120.1
C(18)-C(17)-C(16)	120.7(7)
C(18)-C(17)-H(17A)	119.6
C(16)-C(17)-H(17A)	119.6

C(17)-C(18)-C(19)	120.2(7)
C(17)-C(18)-H(18A)	119.9
C(19)-C(18)-H(18A)	119.9
C(14)-C(19)-C(18)	119.9(7)
C(14)-C(19)-C(20)	120.7(6)
C(18)-C(19)-C(20)	119.1(7)
O(6)-C(20)-C(21)	120.7(7)
O(6)-C(20)-C(19)	120.5(6)
C(21)-C(20)-C(19)	118.7(6)
C(12)-C(21)-C(20)	121.3(7)
C(12)-C(21)-C(22)	119.5(6)
C(20)-C(21)-C(22)	119.1(6)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1B**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn	56(1)	18(1)	35(1)	1(1)	6(1)	-7(1)
O(1)	60(4)	18(3)	44(3)	-4(2)	14(3)	-1(2)
O(2)	71(4)	25(3)	41(3)	4(2)	23(3)	-6(2)
O(3)	76(4)	30(3)	55(4)	16(3)	9(3)	-14(3)
O(4)	73(4)	13(2)	40(3)	2(2)	1(3)	-2(2)
O(5)	64(4)	21(3)	56(4)	-3(2)	6(3)	-7(2)
O(6)	76(4)	31(3)	44(3)	-12(2)	4(3)	-15(3)
O(1M)	62(4)	29(3)	78(4)	17(3)	-17(3)	-11(3)
O(1W)	88(5)	24(3)	55(4)	-9(2)	16(4)	-21(3)
O(2W)	151(6)	43(3)	49(4)	-1(3)	10(4)	8(4)
C(1M)	83(7)	51(6)	50(5)	13(4)	-10(5)	-1(5)
C(1)	33(5)	19(4)	32(5)	3(3)	5(4)	-7(3)
C(2)	24(5)	29(4)	43(6)	-3(4)	2(4)	-6(3)
C(3)	33(5)	26(4)	38(5)	-5(3)	6(4)	-4(3)
C(4)	40(5)	45(5)	44(6)	-11(4)	3(4)	-7(4)
C(5)	57(6)	40(5)	75(7)	-18(5)	13(5)	4(4)
C(6)	60(7)	26(4)	79(7)	-8(5)	1(6)	5(4)
C(7)	56(6)	20(4)	63(6)	-7(4)	3(5)	2(4)
C(8)	26(5)	35(4)	37(6)	1(4)	-4(4)	-5(3)
C(9)	28(5)	32(4)	39(5)	9(4)	-5(4)	3(3)
C(10)	25(4)	30(4)	38(5)	6(3)	1(4)	-2(3)
C(11)	83(7)	31(4)	36(5)	0(4)	11(5)	-8(4)
C(12)	25(5)	35(4)	33(5)	1(3)	4(4)	-1(3)
C(13)	33(5)	22(4)	43(5)	0(3)	19(4)	-2(3)
C(14)	33(5)	31(4)	32(5)	2(3)	15(4)	-4(3)
C(15)	42(5)	43(5)	49(6)	4(4)	14(5)	-6(4)
C(16)	44(6)	32(4)	71(6)	16(4)	8(5)	12(4)
C(17)	80(7)	25(4)	80(7)	8(4)	22(6)	5(4)
C(18)	68(7)	25(4)	58(6)	-7(4)	12(5)	-3(4)
C(19)	35(5)	25(4)	57(6)	1(4)	25(5)	-2(3)
C(20)	41(5)	30(4)	35(5)	-4(3)	12(4)	-13(4)
C(21)	44(5)	27(4)	36(5)	-3(3)	8(4)	-6(3)

C(22)	57(6)	39(4)	41(5)	2(4)	11(5)	-16(4)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1B**

	x	y	z	U(eq)
H(1M)	5760(50)	8120(30)	6140(30)	75
H(1W1)	1140(90)	7420(40)	6850(20)	84
H(1W2)	260(70)	6960(40)	6250(40)	84
H(2W1)	1830(130)	7200(30)	8450(40)	125
H(2W2)	1410(130)	7920(30)	8270(50)	125
H(1MA)	7521	7677	7248	99
H(1MB)	6854	6867	6861	99
H(1MC)	5956	7291	7517	99
H(4A)	1429	9902	6750	53
H(5A)	684	11203	6908	69
H(6A)	1188	12093	5889	69
H(7A)	2168	11712	4699	58
H(11A)	4395	8809	3357	76
H(11B)	4496	9680	3100	76
H(11C)	2770	9225	2781	76
H(15A)	5289	5053	6730	53
H(16A)	5966	3749	6906	60
H(17A)	4469	2864	5903	73
H(18A)	2357	3258	4726	61
H(22A)	-990	6170	3368	69
H(22B)	-1273	5308	3057	69
H(22C)	125	5810	2771	69

Table S17. Torsion angles [°] for **1B**

Mn-O(1)-C(1)-C(10)	177.6(5)
Mn-O(1)-C(1)-C(2)	-0.8(7)
Mn-O(2)-C(2)-C(3)	175.7(5)
Mn-O(2)-C(2)-C(1)	0.1(8)
O(1)-C(1)-C(2)-O(2)	0.5(9)
C(10)-C(1)-C(2)-O(2)	-178.0(6)
O(1)-C(1)-C(2)-C(3)	-175.3(6)
C(10)-C(1)-C(2)-C(3)	6.2(10)
O(2)-C(2)-C(3)-C(4)	-1.0(10)
C(1)-C(2)-C(3)-C(4)	174.6(6)
O(2)-C(2)-C(3)-C(8)	178.8(6)
C(1)-C(2)-C(3)-C(8)	-5.6(9)
C(8)-C(3)-C(4)-C(5)	2.7(11)
C(2)-C(3)-C(4)-C(5)	-177.5(6)
C(3)-C(4)-C(5)-C(6)	-2.9(11)
C(4)-C(5)-C(6)-C(7)	2.3(12)
C(5)-C(6)-C(7)-C(8)	-1.6(12)
C(6)-C(7)-C(8)-C(3)	1.2(10)
C(6)-C(7)-C(8)-C(9)	180.0(7)
C(4)-C(3)-C(8)-C(7)	-1.8(10)
C(2)-C(3)-C(8)-C(7)	178.4(6)
C(4)-C(3)-C(8)-C(9)	179.4(7)
C(2)-C(3)-C(8)-C(9)	-0.4(10)
C(7)-C(8)-C(9)-O(3)	7.3(11)
C(3)-C(8)-C(9)-O(3)	-174.0(6)
C(7)-C(8)-C(9)-C(10)	-172.7(6)
C(3)-C(8)-C(9)-C(10)	6.1(10)
O(1)-C(1)-C(10)-C(9)	-178.9(6)
C(2)-C(1)-C(10)-C(9)	-0.6(10)
O(1)-C(1)-C(10)-C(11)	1.0(11)
C(2)-C(1)-C(10)-C(11)	179.3(6)
O(3)-C(9)-C(10)-C(1)	174.5(6)
C(8)-C(9)-C(10)-C(1)	-5.5(10)
O(3)-C(9)-C(10)-C(11)	-5.4(10)
C(8)-C(9)-C(10)-C(11)	174.6(6)

Mn-O(4)-C(12)-C(21)	176.4(6)
Mn-O(4)-C(12)-C(13)	-3.8(8)
Mn-O(5)-C(13)-C(14)	-176.5(5)
Mn-O(5)-C(13)-C(12)	2.5(8)
O(4)-C(12)-C(13)-O(5)	0.6(9)
C(21)-C(12)-C(13)-O(5)	-179.5(6)
O(4)-C(12)-C(13)-C(14)	179.6(6)
C(21)-C(12)-C(13)-C(14)	-0.6(10)
O(5)-C(13)-C(14)-C(19)	177.8(7)
C(12)-C(13)-C(14)-C(19)	-1.1(10)
O(5)-C(13)-C(14)-C(15)	-2.7(10)
C(12)-C(13)-C(14)-C(15)	178.4(7)
C(19)-C(14)-C(15)-C(16)	2.7(11)
C(13)-C(14)-C(15)-C(16)	-176.7(7)
C(14)-C(15)-C(16)-C(17)	-1.4(11)
C(15)-C(16)-C(17)-C(18)	0.2(13)
C(16)-C(17)-C(18)-C(19)	-0.3(13)
C(15)-C(14)-C(19)-C(18)	-2.9(11)
C(13)-C(14)-C(19)-C(18)	176.5(6)
C(15)-C(14)-C(19)-C(20)	-177.3(6)
C(13)-C(14)-C(19)-C(20)	2.2(10)
C(17)-C(18)-C(19)-C(14)	1.7(12)
C(17)-C(18)-C(19)-C(20)	176.2(8)
C(14)-C(19)-C(20)-O(6)	-178.7(7)
C(18)-C(19)-C(20)-O(6)	6.9(11)
C(14)-C(19)-C(20)-C(21)	-1.7(10)
C(18)-C(19)-C(20)-C(21)	-176.1(7)
O(4)-C(12)-C(21)-C(20)	-179.1(7)
C(13)-C(12)-C(21)-C(20)	1.1(10)
O(4)-C(12)-C(21)-C(22)	1.6(11)
C(13)-C(12)-C(21)-C(22)	-178.2(6)
O(6)-C(20)-C(21)-C(12)	177.0(7)
C(19)-C(20)-C(21)-C(12)	0.0(10)
O(6)-C(20)-C(21)-C(22)	-3.8(11)
C(19)-C(20)-C(21)-C(22)	179.2(6)

Symmetry transformations used to generate equivalent atoms:

Table S18. Hydrogen bonds for **1B** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1M)-H(1M)...O(3)#1	0.82(2)	1.93(4)	2.689(6)	153(7)
O(1W)-H(1W1)...O(2W)	0.84(2)	1.79(3)	2.609(7)	167(8)
O(1W)-H(1W2)...O(6)#2	0.80(2)	2.02(5)	2.728(6)	147(8)
O(2W)-H(2W1)...O(1)#3	0.83(2)	2.00(4)	2.773(7)	155(9)
O(2W)-H(2W2)...O(4)#3	0.82(2)	2.08(6)	2.733(7)	136(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1 #2 -x,-y+1,-z+1 #3 x,-y+3/2,z+1/2

Table S19. Crystal data and structure refinement for **1A**

Identification code	shelx	
Empirical formula	$C_{22}\ H_{18}\ Mn\ O_8$	
Formula weight	465.30	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/c$	
Unit cell dimensions	a = 5.0191(13) Å	α = 90°
	b = 12.438(4) Å	β = 98.678(7)°
	c = 15.964(4) Å	γ = 90°
Volume	985.2(5) $Å^3$	
Z	2	
Density (calculated)	1.568 Mg/m^3	
Absorption coefficient	0.719 mm^{-1}	
F(000)	478	
Crystal size	0.23 x 0.16 x 0.13 mm^3	
Theta range for data collection	3.057 to 27.103°	
Index ranges	-6<=h<=6, -15<=k<=15, -20<=l<=20	
Reflections collected	9796	
Independent reflections	2177 [R(int) = 0.0533]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2177 / 3 / 151	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.0823	
R indices (all data)	R1 = 0.0874, wR2 = 0.0936	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.436 and -0.262 $e.Å^{-3}$	

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **1A**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Mn(1)	5000	5000	5000	27(1)
O(1)	4357(4)	4937(2)	6335(1)	37(1)
O(2)	7693(4)	3792(2)	5558(1)	34(1)
O(1W)	8059(4)	6195(2)	5293(1)	42(1)
O(3)	10123(4)	1853(2)	8071(1)	51(1)
C(1)	5705(5)	4245(2)	6760(2)	29(1)
C(2)	7606(5)	3562(2)	6344(2)	27(1)
C(3)	9042(5)	2761(2)	6791(2)	31(1)
C(4)	8791(6)	2570(2)	7667(2)	34(1)
C(5)	6895(5)	3238(2)	8088(2)	33(1)
C(6)	6532(6)	3030(3)	8918(2)	46(1)
C(7)	4782(7)	3636(3)	9300(2)	51(1)
C(8)	3345(7)	4458(3)	8865(2)	51(1)
C(9)	3650(6)	4669(2)	8035(2)	40(1)
C(10)	5423(5)	4060(2)	7648(2)	31(1)
C(11)	10915(6)	2067(2)	6381(2)	42(1)

Table S21. Bond lengths [Å] and angles [°] for **1A**

Mn(1)-O(2)	2.1250(18)
Mn(1)-O(2)#1	2.1250(18)
Mn(1)-O(1W)#1	2.137(2)
Mn(1)-O(1W)	2.137(2)
Mn(1)-O(1)	2.2049(17)
Mn(1)-O(1)#1	2.2050(17)
O(1)-C(1)	1.233(3)
O(2)-C(2)	1.293(3)
O(1W)-H(1W1)	0.829(17)
O(1W)-H(1W2)	0.815(17)
O(3)-C(4)	1.236(3)
C(1)-C(10)	1.463(3)
C(1)-C(2)	1.506(4)
C(2)-C(3)	1.366(4)
C(3)-C(4)	1.442(3)
C(3)-C(11)	1.498(4)
C(4)-C(5)	1.497(4)
C(5)-C(6)	1.388(3)
C(5)-C(10)	1.389(4)
C(6)-C(7)	1.368(4)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.377(4)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.382(4)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.384(4)
C(9)-H(9A)	0.9300
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
O(2)-Mn(1)-O(2)#1	180.0
O(2)-Mn(1)-O(1W)#1	89.44(8)
O(2)#1-Mn(1)-O(1W)#1	90.56(8)
O(2)-Mn(1)-O(1W)	90.56(8)

O(2)#1-Mn(1)-O(1W)	89.44(8)
O(1W)#1-Mn(1)-O(1W)	180.0
O(2)-Mn(1)-O(1)	75.28(7)
O(2)#1-Mn(1)-O(1)	104.72(7)
O(1W)#1-Mn(1)-O(1)	88.93(8)
O(1W)-Mn(1)-O(1)	91.07(8)
O(2)-Mn(1)-O(1)#1	104.72(7)
O(2)#1-Mn(1)-O(1)#1	75.28(7)
O(1W)#1-Mn(1)-O(1)#1	91.07(8)
O(1W)-Mn(1)-O(1)#1	88.93(8)
O(1)-Mn(1)-O(1)#1	180.0
C(1)-O(1)-Mn(1)	114.12(16)
C(2)-O(2)-Mn(1)	116.80(16)
Mn(1)-O(1W)-H(1W1)	122(2)
Mn(1)-O(1W)-H(1W2)	122(2)
H(1W1)-O(1W)-H(1W2)	106(2)
O(1)-C(1)-C(10)	121.2(2)
O(1)-C(1)-C(2)	118.9(2)
C(10)-C(1)-C(2)	119.9(2)
O(2)-C(2)-C(3)	125.2(2)
O(2)-C(2)-C(1)	114.8(2)
C(3)-C(2)-C(1)	120.0(2)
C(2)-C(3)-C(4)	120.7(2)
C(2)-C(3)-C(11)	120.5(2)
C(4)-C(3)-C(11)	118.8(2)
O(3)-C(4)-C(3)	120.3(3)
O(3)-C(4)-C(5)	119.7(2)
C(3)-C(4)-C(5)	119.9(2)
C(6)-C(5)-C(10)	118.9(3)
C(6)-C(5)-C(4)	120.6(3)
C(10)-C(5)-C(4)	120.4(2)
C(7)-C(6)-C(5)	120.5(3)
C(7)-C(6)-H(6A)	119.7
C(5)-C(6)-H(6A)	119.7
C(6)-C(7)-C(8)	120.5(3)
C(6)-C(7)-H(7A)	119.8
C(8)-C(7)-H(7A)	119.8

C(7)-C(8)-C(9)	119.9(3)
C(7)-C(8)-H(8A)	120.0
C(9)-C(8)-H(8A)	120.0
C(8)-C(9)-C(10)	119.8(3)
C(8)-C(9)-H(9A)	120.1
C(10)-C(9)-H(9A)	120.1
C(9)-C(10)-C(5)	120.4(2)
C(9)-C(10)-C(1)	120.6(2)
C(5)-C(10)-C(1)	119.0(2)
C(3)-C(11)-H(11A)	109.5
C(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S22. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1A**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	28(1)	35(1)	17(1)	7(1)	1(1)	-2(1)
O(1)	42(1)	43(1)	27(1)	7(1)	7(1)	9(1)
O(2)	35(1)	45(1)	22(1)	4(1)	7(1)	3(1)
O(1W)	40(1)	57(2)	31(1)	-10(1)	8(1)	-14(1)
O(3)	61(2)	54(1)	37(1)	16(1)	6(1)	20(1)
C(1)	28(2)	32(2)	25(1)	2(1)	0(1)	-4(1)
C(2)	26(1)	34(2)	22(1)	-1(1)	3(1)	-6(1)
C(3)	30(2)	33(2)	31(1)	1(1)	5(1)	-4(1)
C(4)	33(2)	38(2)	28(1)	4(1)	-1(1)	1(1)
C(5)	32(2)	40(2)	26(1)	4(1)	3(1)	-4(1)
C(6)	53(2)	55(2)	30(2)	14(1)	8(2)	10(2)
C(7)	66(2)	65(2)	28(2)	8(2)	18(2)	4(2)
C(8)	64(2)	55(2)	39(2)	-1(2)	21(2)	9(2)
C(9)	51(2)	39(2)	32(1)	6(1)	9(1)	5(1)
C(10)	33(2)	36(2)	24(1)	0(1)	6(1)	-2(1)
C(11)	44(2)	43(2)	40(2)	3(1)	11(1)	6(2)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)for **1A**

	x	y	z	U(eq)
H(6A)	7487	2475	9217	55
H(7A)	4563	3491	9857	62
H(8A)	2169	4870	9130	62
H(9A)	2667	5219	7738	48
H(11A)	10030	1837	5836	63
H(11B)	11415	1450	6731	63
H(11C)	12501	2470	6315	63
H(1W1)	9340(50)	6250(30)	5024(16)	83(14)
H(1W2)	8640(60)	6370(20)	5778(11)	55(11)

Table S24. Torsion angles [°] for **1A**

Mn(1)-O(1)-C(1)-C(10)	-176.96(19)
Mn(1)-O(1)-C(1)-C(2)	1.2(3)
Mn(1)-O(2)-C(2)-C(3)	175.3(2)
Mn(1)-O(2)-C(2)-C(1)	-3.7(3)
O(1)-C(1)-C(2)-O(2)	1.7(4)
C(10)-C(1)-C(2)-O(2)	179.8(2)
O(1)-C(1)-C(2)-C(3)	-177.4(2)
C(10)-C(1)-C(2)-C(3)	0.8(4)
O(2)-C(2)-C(3)-C(4)	-179.8(2)
C(1)-C(2)-C(3)-C(4)	-0.9(4)
O(2)-C(2)-C(3)-C(11)	0.4(4)
C(1)-C(2)-C(3)-C(11)	179.3(2)
C(2)-C(3)-C(4)-O(3)	-179.1(3)
C(11)-C(3)-C(4)-O(3)	0.7(4)
C(2)-C(3)-C(4)-C(5)	1.3(4)
C(11)-C(3)-C(4)-C(5)	-178.9(2)
O(3)-C(4)-C(5)-C(6)	-2.7(4)
C(3)-C(4)-C(5)-C(6)	176.9(3)
O(3)-C(4)-C(5)-C(10)	178.8(3)
C(3)-C(4)-C(5)-C(10)	-1.6(4)
C(10)-C(5)-C(6)-C(7)	-1.0(5)
C(4)-C(5)-C(6)-C(7)	-179.5(3)
C(5)-C(6)-C(7)-C(8)	0.3(5)
C(6)-C(7)-C(8)-C(9)	0.5(5)
C(7)-C(8)-C(9)-C(10)	-0.7(5)
C(8)-C(9)-C(10)-C(5)	0.0(5)
C(8)-C(9)-C(10)-C(1)	177.8(3)
C(6)-C(5)-C(10)-C(9)	0.8(4)
C(4)-C(5)-C(10)-C(9)	179.3(3)
C(6)-C(5)-C(10)-C(1)	-177.0(3)
C(4)-C(5)-C(10)-C(1)	1.5(4)
O(1)-C(1)-C(10)-C(9)	-0.8(4)
C(2)-C(1)-C(10)-C(9)	-178.9(2)
O(1)-C(1)-C(10)-C(5)	177.0(2)
C(2)-C(1)-C(10)-C(5)	-1.1(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S25. Hydrogen bonds for **1A** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1W1)...O(2)#2	0.829(17)	1.870(18)	2.695(3)	174(4)
O(1W)-H(1W2)...O(3)#3	0.815(17)	1.945(17)	2.759(3)	176(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1 #3 -x+2,y+1/2,-z+3/2

Table S26. Crystal data and structure refinement for **3**

Identification code	shelx	
Empirical formula	$C_{48}\ H_{56}\ Ni_4\ O_{24}$	
Formula weight	1251.76	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 19.133(3) Å	α= 90°
	b = 12.8402(19) Å	β= 94.062(11)°
	c = 21.624(3) Å	γ = 90°
Volume	5299.1(14) $Å^3$	
Z	4	
Density (calculated)	1.569 Mg/m^3	
Absorption coefficient	1.483 mm^{-1}	
F(000)	2592	
Crystal size	0.38 x 0.36 x 0.09 mm^3	
Theta range for data collection	2.634 to 25.497°.	
Index ranges	-23<=h<=21, -15<=k<=15, -26<=l<=26	
Reflections collected	50722	
Independent reflections	4936 [R(int) = 0.2230]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8818 and 0.6062	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4936 / 14 / 371	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R1 = 0.0991, wR2 = 0.1951	
R indices (all data)	R1 = 0.1882, wR2 = 0.2334	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.902 and -0.929 $e.Å^{-3}$	

Table S27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Ni(1)	7356(1)	4846(1)	5714(1)	28(1)
Ni(2)	8301(1)	3231(1)	5176(1)	28(1)
O(1)	8031(3)	4881(5)	6486(3)	33(2)
O(2)	7359(4)	6447(5)	5934(3)	39(2)
O(3)	9252(4)	7270(6)	7814(4)	60(2)
O(4)	9123(3)	3033(5)	4642(3)	36(2)
O(5)	8391(4)	1644(5)	5219(3)	38(2)
O(6)	10253(4)	262(6)	3700(4)	57(2)
O(7)	8189(3)	4819(4)	5145(3)	22(2)
O(8)	7395(3)	3278(4)	5614(3)	22(2)
O(1W)	6419(3)	4658(5)	6163(3)	39(2)
O(2W)	8920(4)	3384(5)	6035(3)	34(2)
C(1)	8175(5)	5778(7)	6711(5)	29(2)
C(2)	7757(6)	6628(8)	6406(5)	33(3)
C(3)	7827(5)	7719(7)	6659(5)	30(2)
C(4)	7394(6)	8493(8)	6414(5)	42(3)
C(5)	7469(7)	9504(9)	6641(6)	57(4)
C(6)	7973(8)	9706(9)	7106(6)	62(4)
C(7)	8404(7)	8945(9)	7351(6)	54(3)
C(8)	8330(6)	7911(8)	7138(5)	36(3)
C(9)	8784(6)	7079(9)	7392(5)	46(3)
C(10)	8680(6)	5997(8)	7174(5)	35(3)
C(11)	9136(7)	5150(10)	7461(6)	71(4)
C(12)	9228(5)	2057(7)	4523(5)	27(2)
C(13)	8815(5)	1294(8)	4872(5)	30(2)
C(14)	8904(6)	169(8)	4798(5)	37(3)
C(15)	8528(6)	-512(8)	5140(5)	36(3)
C(16)	8636(7)	-1590(9)	5064(5)	51(3)
C(17)	9124(7)	-1911(9)	4662(6)	53(3)
C(18)	9486(7)	-1231(9)	4330(5)	51(3)
C(19)	9396(6)	-164(8)	4394(5)	40(3)
C(20)	9811(6)	588(9)	4032(5)	39(3)

C(21)	9678(5)	1697(8)	4097(5)	36(3)
C(22)	10062(6)	2430(9)	3710(6)	60(4)
C(23)	8789(6)	5431(9)	5253(5)	49(3)
C(24)	7343(6)	2633(9)	6144(5)	49(3)
O(3W)	9573(5)	8848(7)	8717(5)	66(3)
O(4W)	10738(5)	-1699(7)	3202(5)	67(3)

Table S28. Bond lengths [Å] and angles [°] for **3**

Ni(1)-O(8)	2.027(6)
Ni(1)-O(1)	2.037(6)
Ni(1)-O(7)#1	2.065(6)
Ni(1)-O(7)	2.082(6)
Ni(1)-O(2)	2.110(7)
Ni(1)-O(1W)	2.111(6)
Ni(2)-O(4)	2.031(7)
Ni(2)-O(8)	2.035(6)
Ni(2)-O(5)	2.046(7)
Ni(2)-O(7)	2.051(6)
Ni(2)-O(8)#1	2.092(6)
Ni(2)-O(2W)	2.140(7)
O(1)-C(1)	1.273(11)
O(2)-C(2)	1.252(11)
O(3)-C(9)	1.255(13)
O(4)-C(12)	1.299(11)
O(5)-C(13)	1.228(11)
O(6)-C(20)	1.222(12)
O(7)-C(23)	1.397(12)
O(8)-C(24)	1.423(12)
C(1)-C(10)	1.371(13)
C(1)-C(2)	1.480(14)
C(2)-C(3)	1.506(13)
C(3)-C(4)	1.377(14)
C(3)-C(8)	1.386(14)
C(4)-C(5)	1.393(15)
C(5)-C(6)	1.368(17)
C(6)-C(7)	1.362(17)
C(7)-C(8)	1.409(15)
C(8)-C(9)	1.459(15)
C(9)-C(10)	1.476(15)
C(10)-C(11)	1.500(15)
C(12)-C(21)	1.384(14)
C(12)-C(13)	1.496(14)
C(13)-C(14)	1.465(14)

C(14)-C(15)	1.380(14)
C(14)-C(19)	1.396(15)
C(15)-C(16)	1.411(14)
C(16)-C(17)	1.383(16)
C(17)-C(18)	1.351(16)
C(18)-C(19)	1.389(15)
C(19)-C(20)	1.505(16)
C(20)-C(21)	1.455(15)
C(21)-C(22)	1.488(15)

O(8)-Ni(1)-O(1)	94.8(2)
O(8)-Ni(1)-O(7)#1	84.7(2)
O(1)-Ni(1)-O(7)#1	171.0(3)
O(8)-Ni(1)-O(7)	83.4(2)
O(1)-Ni(1)-O(7)	91.0(3)
O(7)#1-Ni(1)-O(7)	80.0(2)
O(8)-Ni(1)-O(2)	172.9(3)
O(1)-Ni(1)-O(2)	78.6(3)
O(7)#1-Ni(1)-O(2)	102.3(2)
O(7)-Ni(1)-O(2)	99.2(3)
O(8)-Ni(1)-O(1W)	88.5(3)
O(1)-Ni(1)-O(1W)	97.8(3)
O(7)#1-Ni(1)-O(1W)	91.2(3)
O(7)-Ni(1)-O(1W)	168.5(2)
O(2)-Ni(1)-O(1W)	89.8(3)
O(4)-Ni(2)-O(8)	171.0(3)
O(4)-Ni(2)-O(5)	80.5(3)
O(8)-Ni(2)-O(5)	94.6(3)
O(4)-Ni(2)-O(7)	100.9(3)
O(8)-Ni(2)-O(7)	84.0(2)
O(5)-Ni(2)-O(7)	178.6(3)
O(4)-Ni(2)-O(8)#1	90.7(3)
O(8)-Ni(2)-O(8)#1	82.3(2)
O(5)-Ni(2)-O(8)#1	96.4(3)
O(7)-Ni(2)-O(8)#1	83.4(2)
O(4)-Ni(2)-O(2W)	95.8(3)
O(8)-Ni(2)-O(2W)	91.7(3)

O(5)-Ni(2)-O(2W)	90.7(3)
O(7)-Ni(2)-O(2W)	89.3(2)
O(8)#1-Ni(2)-O(2W)	171.0(2)
C(1)-O(1)-Ni(1)	116.1(6)
C(2)-O(2)-Ni(1)	110.9(6)
C(12)-O(4)-Ni(2)	111.8(6)
C(13)-O(5)-Ni(2)	113.2(6)
C(23)-O(7)-Ni(2)	118.1(6)
C(23)-O(7)-Ni(1)#1	119.8(6)
Ni(2)-O(7)-Ni(1)#1	95.2(2)
C(23)-O(7)-Ni(1)	123.1(6)
Ni(2)-O(7)-Ni(1)	94.6(2)
Ni(1)#1-O(7)-Ni(1)	99.9(2)
C(24)-O(8)-Ni(1)	119.2(6)
C(24)-O(8)-Ni(2)	117.9(6)
Ni(1)-O(8)-Ni(2)	96.8(2)
C(24)-O(8)-Ni(2)#1	124.3(6)
Ni(1)-O(8)-Ni(2)#1	95.2(2)
Ni(2)-O(8)-Ni(2)#1	97.6(2)
O(1)-C(1)-C(10)	125.9(9)
O(1)-C(1)-C(2)	113.7(8)
C(10)-C(1)-C(2)	120.4(9)
O(2)-C(2)-C(1)	120.3(9)
O(2)-C(2)-C(3)	120.2(9)
C(1)-C(2)-C(3)	119.5(9)
C(4)-C(3)-C(8)	121.8(9)
C(4)-C(3)-C(2)	119.7(9)
C(8)-C(3)-C(2)	118.5(9)
C(3)-C(4)-C(5)	119.5(11)
C(6)-C(5)-C(4)	119.1(11)
C(7)-C(6)-C(5)	121.7(11)
C(6)-C(7)-C(8)	120.3(11)
C(3)-C(8)-C(7)	117.4(10)
C(3)-C(8)-C(9)	120.9(9)
C(7)-C(8)-C(9)	121.6(10)
O(3)-C(9)-C(8)	120.3(10)
O(3)-C(9)-C(10)	119.2(11)

C(8)-C(9)-C(10)	120.4(10)
C(1)-C(10)-C(9)	119.8(10)
C(1)-C(10)-C(11)	120.8(10)
C(9)-C(10)-C(11)	119.3(10)
O(4)-C(12)-C(21)	124.6(9)
O(4)-C(12)-C(13)	115.9(9)
C(21)-C(12)-C(13)	119.5(9)
O(5)-C(13)-C(14)	120.9(10)
O(5)-C(13)-C(12)	117.7(9)
C(14)-C(13)-C(12)	121.4(9)
C(15)-C(14)-C(19)	122.8(10)
C(15)-C(14)-C(13)	119.8(10)
C(19)-C(14)-C(13)	117.3(10)
C(14)-C(15)-C(16)	118.2(10)
C(17)-C(16)-C(15)	118.4(11)
C(18)-C(17)-C(16)	122.4(11)
C(17)-C(18)-C(19)	120.8(12)
C(18)-C(19)-C(14)	117.3(11)
C(18)-C(19)-C(20)	120.5(11)
C(14)-C(19)-C(20)	122.2(10)
O(6)-C(20)-C(21)	121.7(11)
O(6)-C(20)-C(19)	119.9(10)
C(21)-C(20)-C(19)	118.4(10)
C(12)-C(21)-C(20)	120.8(10)
C(12)-C(21)-C(22)	121.2(10)
C(20)-C(21)-C(22)	117.9(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y,-z+1

Table S29. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	35(1)	16(1)	32(1)	-3(1)	-3(1)	0(1)
Ni(2)	30(1)	20(1)	34(1)	2(1)	1(1)	3(1)
O(1)	40(4)	21(4)	36(4)	-2(3)	-13(3)	5(3)
O(2)	43(5)	28(4)	43(5)	-4(3)	-8(4)	6(4)
O(3)	64(6)	54(5)	58(6)	-20(4)	-25(5)	2(5)
O(4)	32(4)	26(4)	51(5)	7(3)	7(3)	3(3)
O(5)	43(5)	28(4)	44(4)	1(3)	12(4)	4(4)
O(6)	52(6)	52(5)	70(6)	-14(5)	16(5)	-1(5)
O(7)	24(4)	8(3)	33(4)	4(3)	-13(3)	-7(3)
O(8)	28(4)	14(3)	23(3)	10(3)	0(3)	2(3)
O(1W)	34(4)	37(4)	49(5)	-7(4)	19(4)	-3(4)
O(2W)	30(4)	27(4)	44(5)	5(3)	-9(3)	10(3)
C(1)	29(6)	23(6)	36(6)	0(5)	-2(5)	2(5)
C(2)	37(7)	29(6)	34(6)	-4(5)	7(5)	-11(5)
C(3)	28(6)	20(5)	43(7)	-3(5)	2(5)	1(5)
C(4)	46(7)	35(7)	45(7)	-5(5)	-4(6)	-11(6)
C(5)	66(9)	23(6)	80(10)	3(6)	-3(8)	-4(6)
C(6)	87(11)	16(6)	82(10)	-10(6)	8(9)	4(7)
C(7)	56(9)	47(8)	59(8)	-16(6)	-3(7)	-12(7)
C(8)	37(7)	24(6)	46(7)	-2(5)	-1(5)	2(5)
C(9)	53(8)	50(8)	37(7)	-9(6)	11(6)	-8(6)
C(10)	37(7)	39(6)	29(6)	-6(5)	-3(5)	-3(5)
C(11)	83(11)	61(9)	63(9)	-7(7)	-34(8)	16(8)
C(12)	17(5)	23(5)	39(6)	1(4)	-11(5)	6(4)
C(13)	25(6)	30(6)	34(6)	-1(5)	-3(5)	3(5)
C(14)	41(7)	28(6)	41(6)	-4(5)	-5(5)	4(5)
C(15)	53(8)	22(5)	33(6)	0(5)	4(5)	5(5)
C(16)	63(9)	38(7)	55(8)	4(6)	19(7)	7(6)
C(17)	63(9)	22(6)	72(9)	-6(6)	5(7)	2(6)
C(18)	59(9)	44(7)	50(8)	-3(6)	8(7)	5(7)
C(19)	36(7)	37(6)	43(7)	-7(5)	-16(6)	12(6)
C(20)	31(7)	43(7)	41(7)	-2(5)	-4(6)	7(6)

C(21)	32(6)	36(6)	41(6)	3(5)	2(5)	-3(5)
C(22)	57(9)	46(8)	81(10)	2(7)	30(7)	5(7)
C(23)	48(8)	43(7)	56(8)	8(6)	-6(6)	-2(6)
C(24)	53(8)	43(7)	53(8)	2(6)	14(6)	-8(6)
O(3W)	52(6)	59(6)	84(7)	-31(5)	-14(5)	7(5)
O(4W)	73(7)	47(5)	82(7)	8(5)	4(5)	11(5)

Table S30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**

	x	y	z	U(eq)
H(1W1)	6060(30)	4150(40)	6190(40)	58
H(1W2)	6100(30)	5060(30)	6370(40)	58
H(2W1)	8670(50)	3700(60)	6260(40)	51
H(2W2)	9000(50)	2830(40)	6210(40)	51
H(4A)	7053	8342	6098	51
H(5A)	7181	10036	6479	68
H(6A)	8022	10381	7259	74
H(7A)	8749	9109	7661	65
H(11A)	8894	4495	7419	106
H(11B)	9241	5298	7893	106
H(11C)	9564	5113	7255	106
H(15A)	8211	-267	5413	43
H(16A)	8386	-2074	5280	62
H(17A)	9205	-2620	4618	63
H(18A)	9799	-1481	4056	61
H(22A)	9842	3102	3711	90
H(22B)	10053	2173	3293	90
H(22C)	10539	2489	3876	90
H(23A)	9136	5218	4980	74
H(23B)	8971	5347	5675	74
H(23C)	8672	6150	5178	74
H(24A)	6858	2545	6222	73
H(24B)	7587	2953	6498	73
H(24C)	7547	1966	6071	73
H(3W1)	9520(60)	8360(80)	8470(50)	99
H(3W2)	9990(20)	8820(110)	8830(60)	99
H(4W1)	10750(70)	-1120(50)	3360(60)	101
H(4W2)	10350(40)	-1720(100)	3010(60)	101

Table S31. Torsion angles [°] for **3**

Ni(1)-O(1)-C(1)-C(10)	-171.0(9)
Ni(1)-O(1)-C(1)-C(2)	6.6(11)
Ni(1)-O(2)-C(2)-C(1)	3.0(11)
Ni(1)-O(2)-C(2)-C(3)	-178.4(7)
O(1)-C(1)-C(2)-O(2)	-6.6(14)
C(10)-C(1)-C(2)-O(2)	171.1(10)
O(1)-C(1)-C(2)-C(3)	174.8(9)
C(10)-C(1)-C(2)-C(3)	-7.5(15)
O(2)-C(2)-C(3)-C(4)	7.4(15)
C(1)-C(2)-C(3)-C(4)	-174.1(9)
O(2)-C(2)-C(3)-C(8)	-172.8(9)
C(1)-C(2)-C(3)-C(8)	5.8(14)
C(8)-C(3)-C(4)-C(5)	1.4(17)
C(2)-C(3)-C(4)-C(5)	-178.8(10)
C(3)-C(4)-C(5)-C(6)	-0.2(18)
C(4)-C(5)-C(6)-C(7)	0(2)
C(5)-C(6)-C(7)-C(8)	-1(2)
C(4)-C(3)-C(8)-C(7)	-2.5(16)
C(2)-C(3)-C(8)-C(7)	177.6(10)
C(4)-C(3)-C(8)-C(9)	179.9(10)
C(2)-C(3)-C(8)-C(9)	0.1(15)
C(6)-C(7)-C(8)-C(3)	2.6(18)
C(6)-C(7)-C(8)-C(9)	-179.9(11)
C(3)-C(8)-C(9)-O(3)	177.9(10)
C(7)-C(8)-C(9)-O(3)	0.4(17)
C(3)-C(8)-C(9)-C(10)	-4.5(16)
C(7)-C(8)-C(9)-C(10)	178.1(10)
O(1)-C(1)-C(10)-C(9)	-179.5(10)
C(2)-C(1)-C(10)-C(9)	3.1(15)
O(1)-C(1)-C(10)-C(11)	1.0(18)
C(2)-C(1)-C(10)-C(11)	-176.4(10)
O(3)-C(9)-C(10)-C(1)	-179.5(10)
C(8)-C(9)-C(10)-C(1)	2.9(16)
O(3)-C(9)-C(10)-C(11)	0.0(17)
C(8)-C(9)-C(10)-C(11)	-177.6(11)

Ni(2)-O(4)-C(12)-C(21)	169.7(8)
Ni(2)-O(4)-C(12)-C(13)	-9.2(10)
Ni(2)-O(5)-C(13)-C(14)	-174.4(7)
Ni(2)-O(5)-C(13)-C(12)	4.6(11)
O(4)-C(12)-C(13)-O(5)	3.2(13)
C(21)-C(12)-C(13)-O(5)	-175.8(9)
O(4)-C(12)-C(13)-C(14)	-177.7(9)
C(21)-C(12)-C(13)-C(14)	3.3(14)
O(5)-C(13)-C(14)-C(15)	-2.7(15)
C(12)-C(13)-C(14)-C(15)	178.3(9)
O(5)-C(13)-C(14)-C(19)	179.9(9)
C(12)-C(13)-C(14)-C(19)	0.8(14)
C(19)-C(14)-C(15)-C(16)	-1.6(16)
C(13)-C(14)-C(15)-C(16)	-178.8(10)
C(14)-C(15)-C(16)-C(17)	1.3(17)
C(15)-C(16)-C(17)-C(18)	-1.5(19)
C(16)-C(17)-C(18)-C(19)	1.8(19)
C(17)-C(18)-C(19)-C(14)	-1.9(17)
C(17)-C(18)-C(19)-C(20)	178.9(11)
C(15)-C(14)-C(19)-C(18)	1.8(16)
C(13)-C(14)-C(19)-C(18)	179.2(10)
C(15)-C(14)-C(19)-C(20)	-179.0(10)
C(13)-C(14)-C(19)-C(20)	-1.6(15)
C(18)-C(19)-C(20)-O(6)	-3.4(16)
C(14)-C(19)-C(20)-O(6)	177.4(10)
C(18)-C(19)-C(20)-C(21)	177.7(10)
C(14)-C(19)-C(20)-C(21)	-1.5(15)
O(4)-C(12)-C(21)-C(20)	174.6(9)
C(13)-C(12)-C(21)-C(20)	-6.5(14)
O(4)-C(12)-C(21)-C(22)	-3.0(16)
C(13)-C(12)-C(21)-C(22)	175.9(10)
O(6)-C(20)-C(21)-C(12)	-173.2(10)
C(19)-C(20)-C(21)-C(12)	5.7(15)
O(6)-C(20)-C(21)-C(22)	4.5(16)
C(19)-C(20)-C(21)-C(22)	-176.6(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y,-z+1