Probing the Effect of Substituents and Solvent on [Mn(R-sal-N-1,5,8,12)]BPh_4: A Systematic Investigation of SCO Properties

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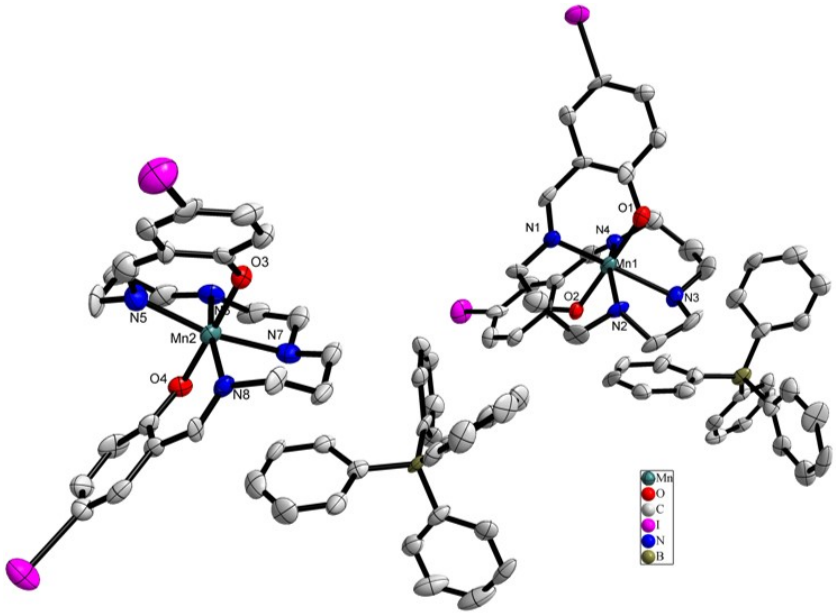
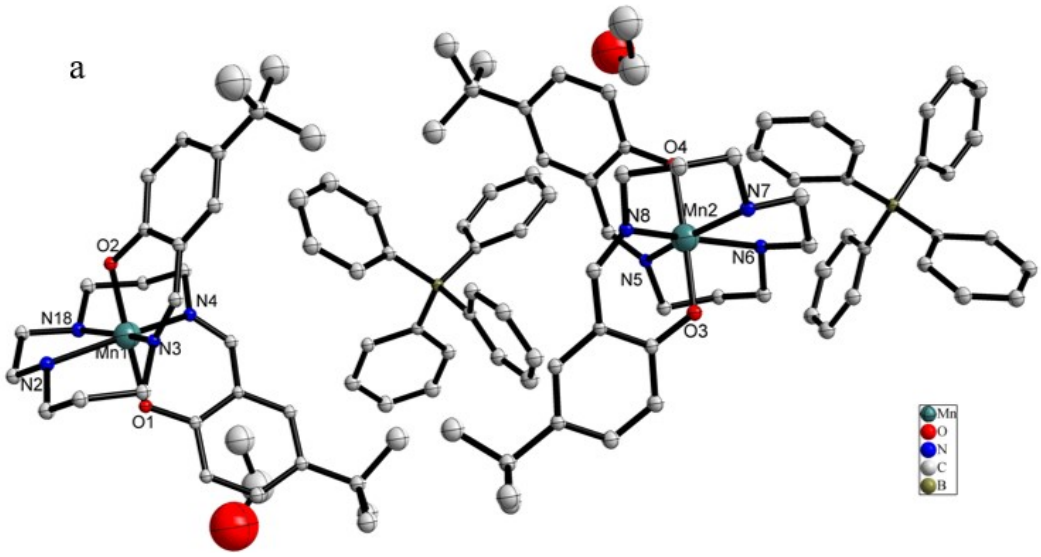


Figure S1. Asymmetric unit of complex **1**, measured at 100 K and hydrogen atoms have been omitted for clarity. Ellipsoids at 50% probability.



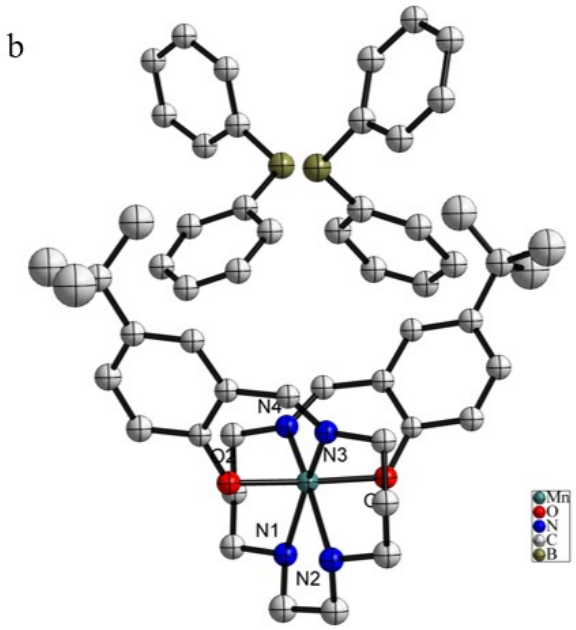
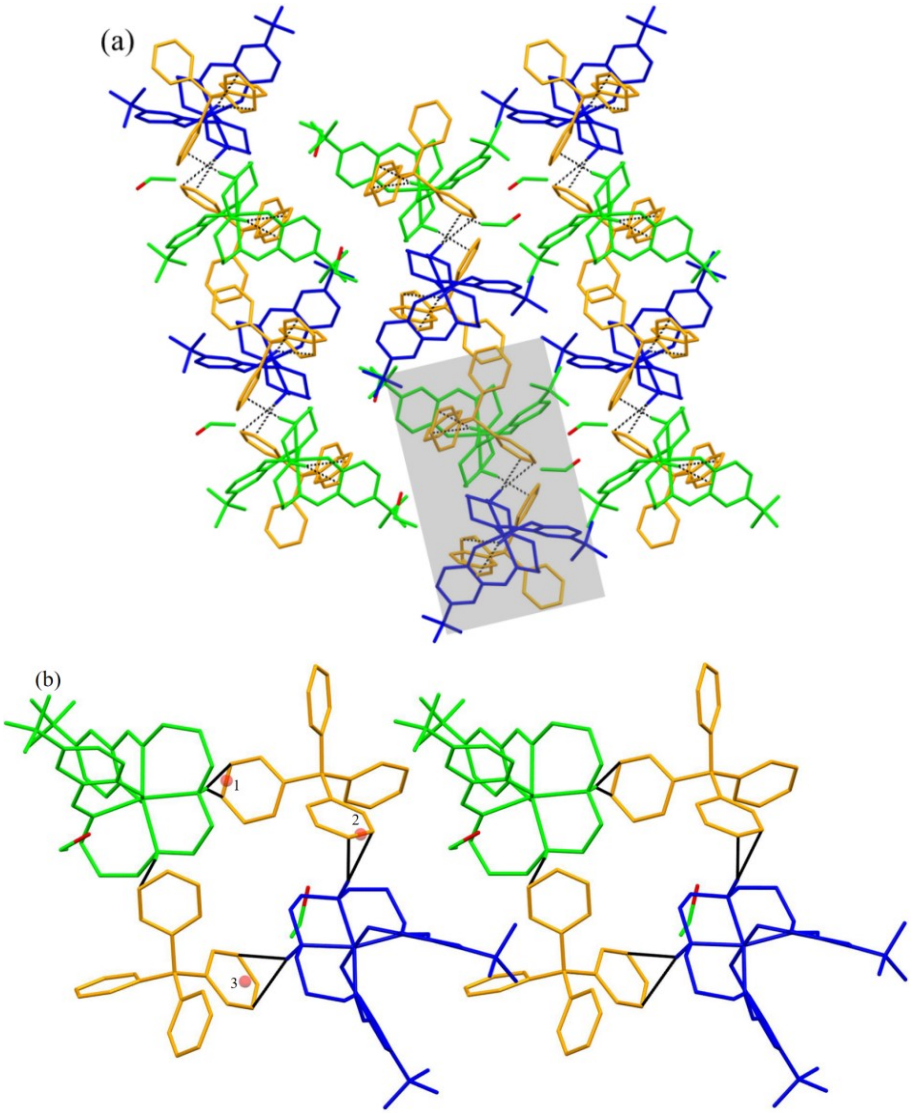


Figure S2. Asymmetric unit of complex **2**, measured at 110 K (a) and 298 K (b), the hydrogen atoms have been omitted for clarity. Ellipsoids at 50% probability.



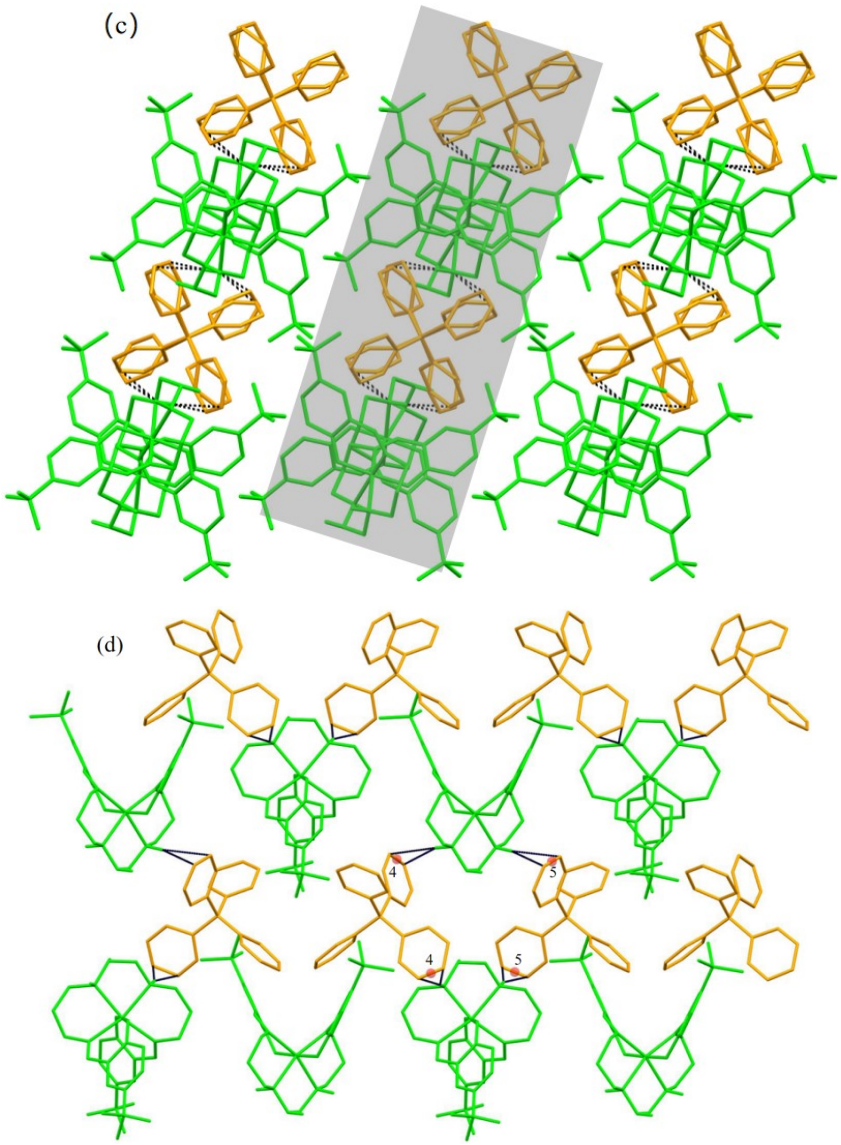


Figure S3. (a) Crystal packing of **2** at 110 K along the *b*-axis. (b) The details of the sublattice in gray at 110 K along the *c*-axis (Mn1: green; Mn2: blue; BPh_4: orange). (c) Crystal packing of **2** at 298 K along the *b*-axis. (d) The details of the sublattice in gray at 298 K along the *c*-axis, showing the N−H···π (black dotted line) hydrogen bonds.

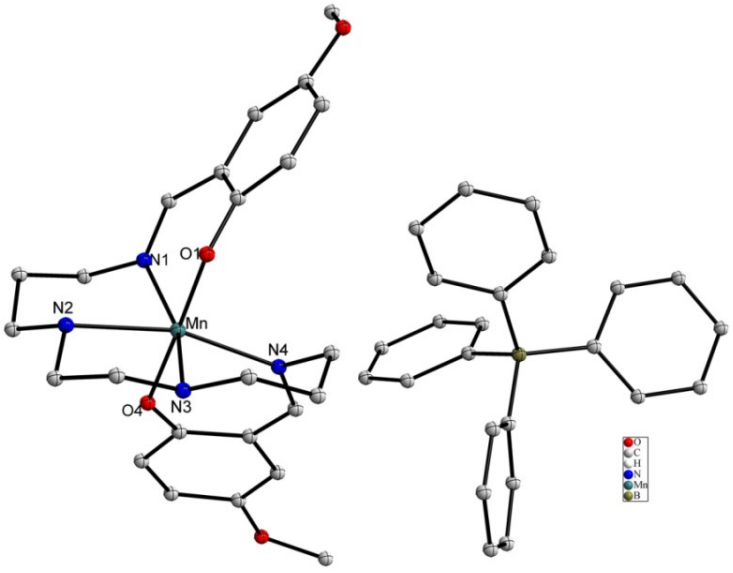


Figure S4. Asymmetric unit of complex **3**, measured at 100 K.

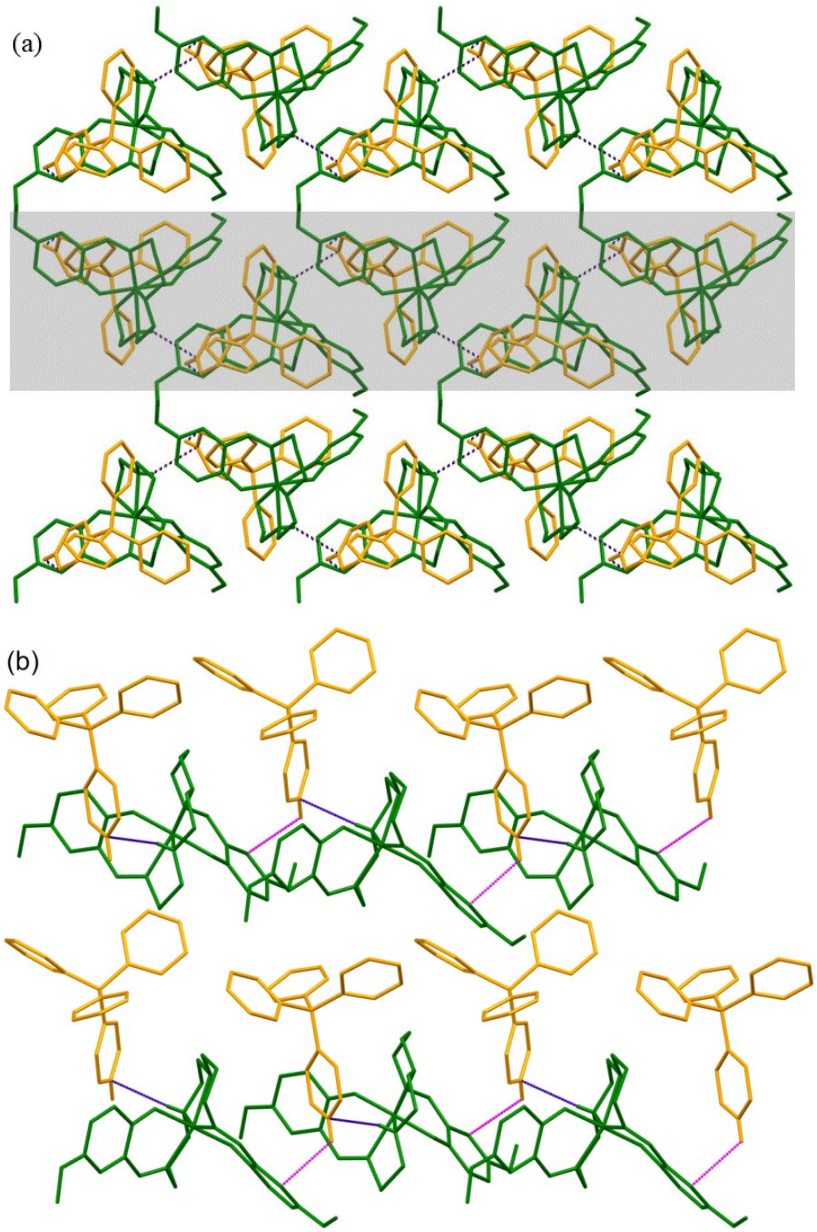


Figure S5. (a) Crystal packing of **3** at 100 K along the *c*-axis. (b) The details of the sublattice (gray), showing the N−H···π hydrogen bonds (blue dotted line) and C−H···π interactions (magenta dotted line).

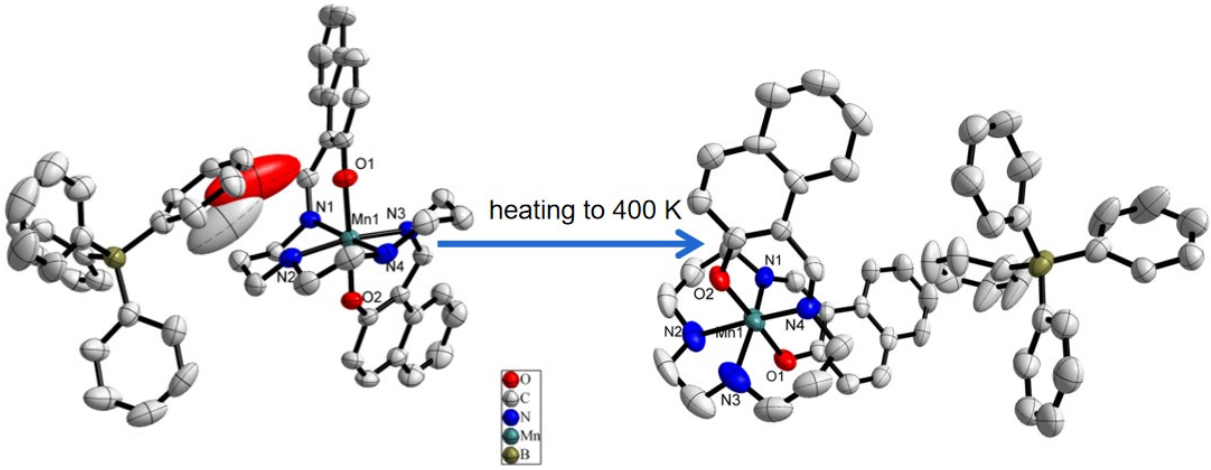


Figure S6. Asymmetric unit of complex **4**, measured at 120 K and 298 K, the hydrogen atoms have been omitted for clarity. Ellipsoids at 50% probability.

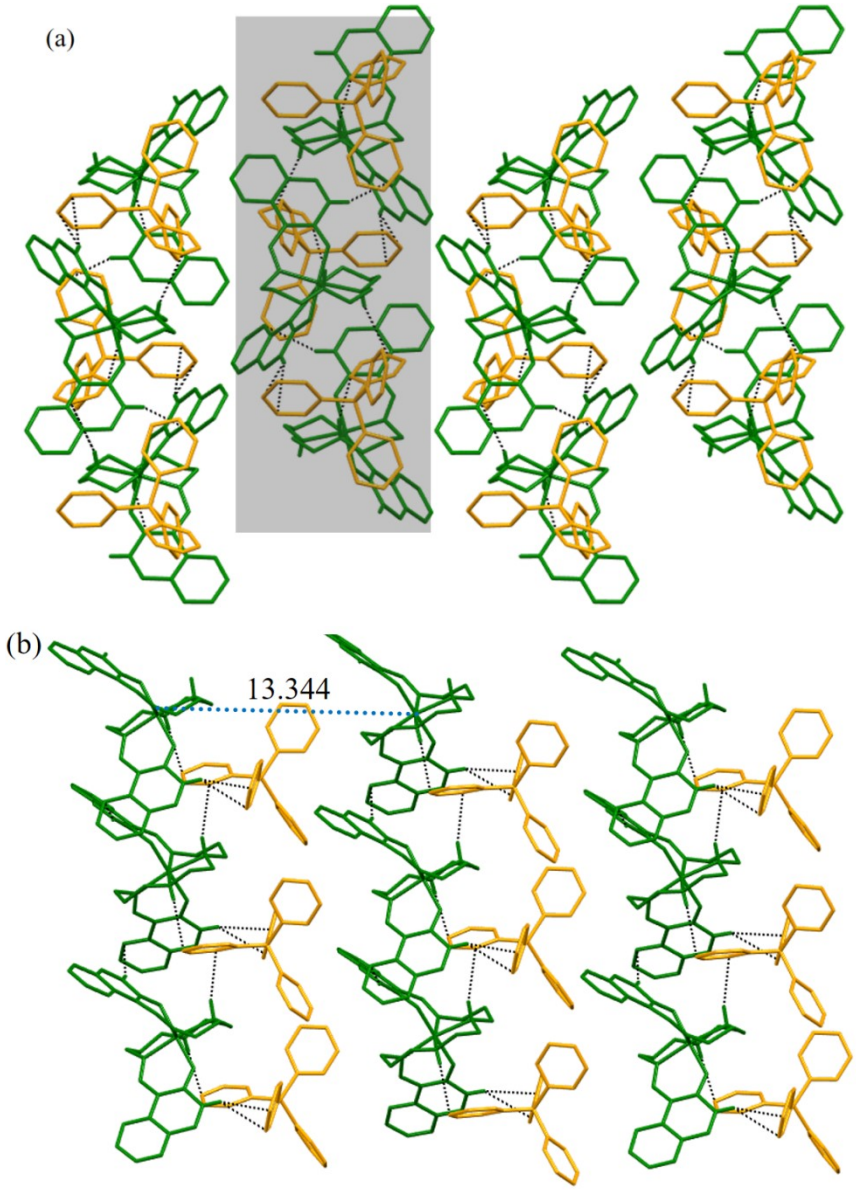


Figure S7. (a) Crystal packing of **4b** at 298 K along the *a*-axis, showing the N−H···π, C−H···π interactions when loosing solvent molecules. (b)The details of the gray part in crystal packing of **4b** at 298 K along the *b*-axis, showing the N−H···π, C−H···π interactions. The Mn···Mn distance (13.344 Å) is indicated by a blue dotted line.

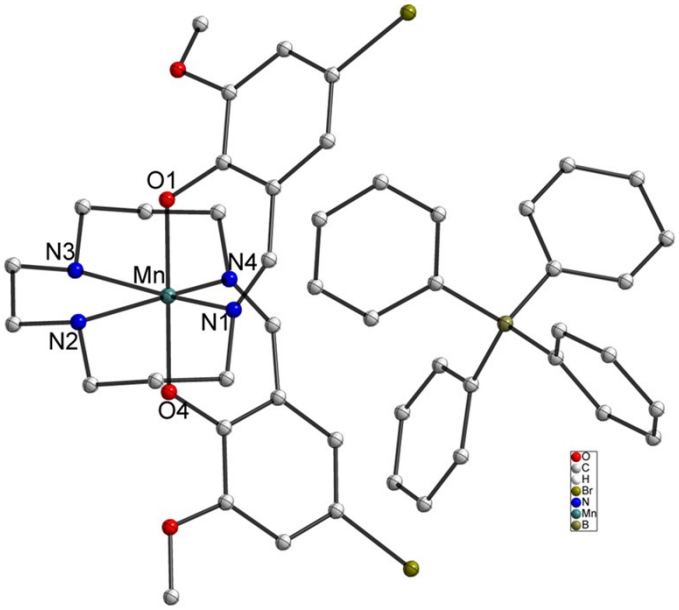


Figure S8. Asymmetric unit of complex **5**, measured at 100 K.

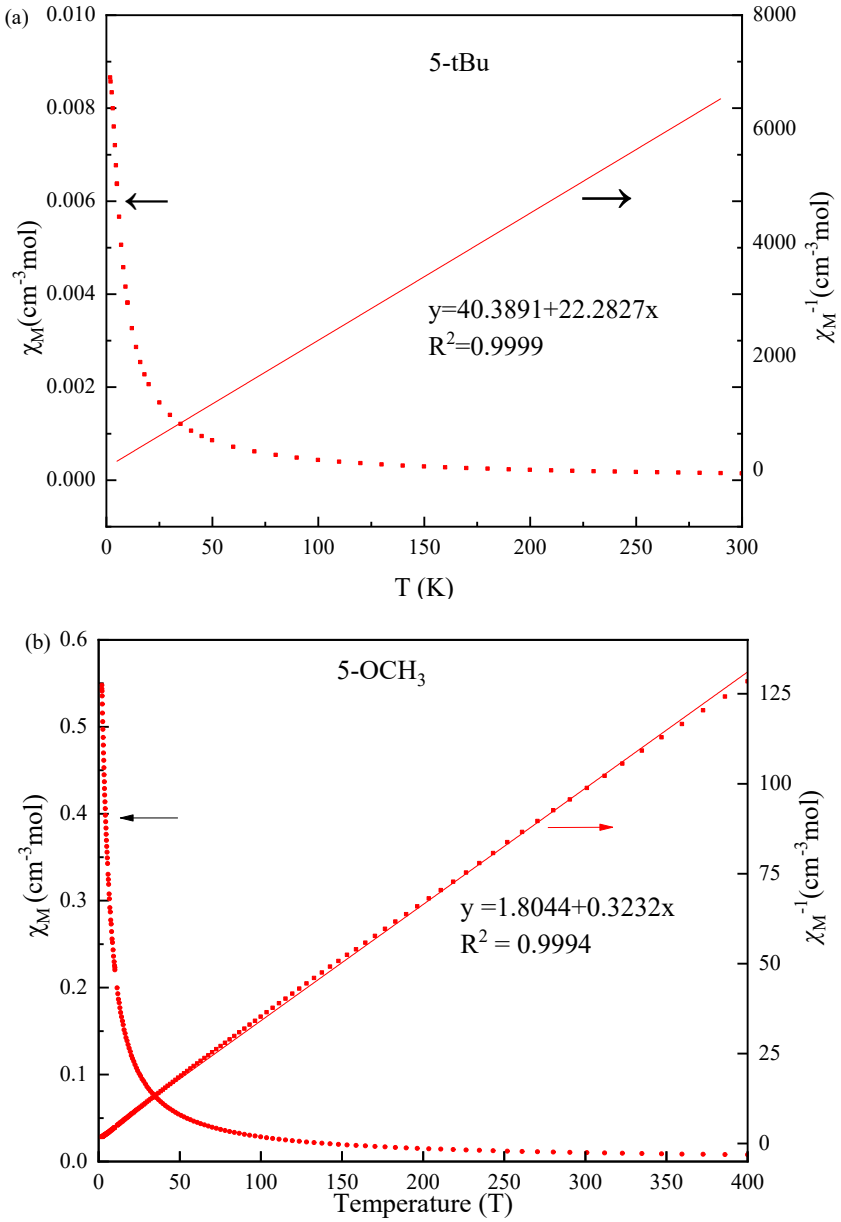


Figure S9. Thermal dependence of the $\chi_M T$, Insets: thermal dependence of $1/\chi_M$ (red circles) and best fit to the Curie-Weiss expression (solid red line).

Table S1. Crystal data and structure refinements for **1-5**.

Identification code	5-I-**1**		5-tBu-**2**		5-OCH_3-**3**		naphth-**4**		5-Br-3-OCH_3-**5**	
CCDC number	2277426	2277418	2277427	2277423	2277422	2277425	2277419	2277424	2277421	2277428	2277420
Empirical formula	$C_{92}H_{92}B_2I_4Mn_2N_8O_4$	$C_{92}H_{92}B_2I_4Mn_2N_8O_4$	$C_{112}H_{140}B_2Mn_2N_8O_6$	$C_{54}H_{64}BMnN_4O_2$	$C_{48}H_{52}BMnN_4O_4$	$C_{48}H_{52}BMnN_4O_4$	$C_{55}H_{56}BMnN_4O_3$	$C_{55}H_{56}BMnN_4O_3$	$C_{54}H_{52}BMnN_4O_2$	$C_{48}H_{50}BBr_2MnN_4O_4$	$C_{48}H_{50}BBr_2MN_4O_4$
Formula weight	2012.83	2012.83	1825.81	866.84	814.68	814.68	886.78	886.78	854.75	972.526	972.49
Temperature/K	112(2)	296(2)	110.85	297.95	104(2)	298(2)	120(2)	295(2)	293(2)	104.85	295.85
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P-1	P-1	C2/c	Cc	Cc	P-1	P-1	$P2_1/n$	Cc	Cc
a/Å	13.946(5)	14.0279(13)	15.558(7)	24.808(4)	15.591(16)	15.3899(14)	8.511(2)	8.672(6)	15.2963(12)	14.444(17)	14.626(2)
b/Å	14.707(5)	14.7648(14)	15.762(8)	19.266(4)	20.32(2)	20.2558(18)	14.998(4)	15.232(10)	20.0852(15)	24.53(3)	24.483(3)
c/Å	22.533(9)	22.5056(17)	22.943(11)	22.892(4)	14.38(2)	14.4012(14)	18.904(6)	19.247(12)	16.1396(13)	14.065(17)	14.3986(17)
α/°	74.237(11)	74.300(3)	75.810(13)	90	90	90	72.166(7)	71.870(16)	90	90	90
β/°	83.462(12)	83.940(3)	73.581(12)	109.491(4)	110.04(2)	110.091(3)	81.136(7)	80.247(16)	115.275(2)	120.11(4)	120.299(3)
γ/°	74.089(11)	74.377(3)	75.739(13)	90	90	90	79.926(7)	79.254(16)	90	90	90
Volume/$Å^3$	4274(3)	4319.0(7)	5136(4)	10315(3)	4280(10)	4216.2(7)	2248.8(11)	2357(3)	4483.9(6)	4310(9)	4451.9(10)
Z	2	2	2	8	4	4	2	2	4	4	4
$\rho_{calc}g/cm^3$	1.564	1.548	1.181	1.116	1.265	1.283	1.310	1.250	1.266	1.499	1.442
μ/mm^{-1}	1.796	1.777	0.303	0.297	0.357	0.362	0.344	0.328	0.341	2.210	2.140
F(000)	2008.0	2008.0	1952.0	3696.0	1720.0	1720.0	936.0	936.0	1800.0	1992.5	1968.0
Crystal size/mm^3	0.23 × 0.16 × 0.14	0.23 × 0.16 ×0.14	0.15 × 0.1 × 0.08	0.15 × 0.1 × 0.08	0.18 × 0.15 × 0.12	0.18 × 0.15 × 0.12	0.26 × 0.2 ×0.12	0.26 × 0.2 ×0.12	0.26 × 0.2 × 0.12	0.2 × 0.16 × 0.14	0.2 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.508 to 45.972	4.486 to 40.776	4.21 to 56.314	4.168 to 50.064	5.018 to 50.054	5.024 to 50.052	4.554 to 50.056	4.486 to 50.054	4.846 to 47.064	4.72 to 50.06	4.67 to 50.046
Index ranges	-13 ≤ h ≤ 15, -16 ≤ k ≤ 16, -24 ≤ l ≤ 23	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -22 ≤ l ≤ 21	-17 ≤ h ≤ 20, -17 ≤ k ≤ 20, -30 ≤ l ≤ 29	-27 ≤ h≤29, -22 ≤ k≤22, -27 ≤ l ≤ 23	-15 ≤ h ≤18, -24 ≤ k ≤13, -16 ≤ l ≤ 14	-17 ≤ h ≤18, -24 ≤ k ≤24, -17 ≤ l ≤ 17	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -22 ≤ l ≤ 16	-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -22 ≤ l ≤ 17	-16 ≤ h ≤17, -22 ≤ k ≤22, -18 ≤ l ≤ 18	-12 ≤ h ≤17, -29 ≤ k ≤27, -16 ≤ l ≤ 16	-17 ≤ h ≤14, -29 ≤ k ≤28, -17 ≤ l ≤ 17
Reflections collected	12663	11715	40032	31519	7576	14072	14776	15521	23439	6728	15067
Independent reflections	11873 [R_{int} = 0.0534, R_{sigma} = 0.1151]	7984 [R_{int} = 0.0359, R_{sigma} = 0.0993]	23931 [R_{int} = 0.0727, R_{sigma} = 0.1313]	9102 [R_{int} = 0.0681, R_{sigma} = 0.0683]	7576 [R_{int} = 0.0346, R_{sigma} = 0.0824]	7450 [R_{int} = 0.0295, R_{sigma} = 0.0415]	7859 [R_{int} = 0.0294, R_{sigma} = 0.0484]	8253 [R_{int} = 0.0334, R_{sigma} = 0.0644]	6657 [R_{int} = 0.0753, R_{sigma} = 0.0816]	7618 [R_{int} = 0.0910, R_{sigma} = 0.1672]	6892 [R_{int} = 0.0369, R_{sigma} = 0.0713]
Data/restraints/parameters	11873/0/994	7984/0/1003	23931/0/537	9102/0/256	7576/2/533	7450/2/533	7859/0/587	8253/0/587	6657/0/567	7618/2/547	6892/2/551
Goodness-of-fit on F^2	1.048	1.116	1.074	1.777	1.048	1.013	1.051	1.031	1.025	0.867	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0966, wR_2 = 0.2226	R_1 = 0.0692, wR_2 = 0.1485	R_1 = 0.1864, wR_2=0.4402	R_1=0.1462, wR_2=0.4281	R_1= 0.0536, wR_2=0.1357	R_1= 0.0372, wR_2=0.0775	R_1 = 0.0424, wR_2 = 0.0979	R_1 = 0.0516, wR_2 = 0.1084	R_1= 0.0758, wR_2=0.1280	R_1 =0.0634, wR_2=0.1300	R_1 = 0.0711, wR_2=0.1793
Final R indexes [all data]	R_1 = 0.1372, wR_2=0.2473	R_1 = 0.1224, wR_2=0.1661	R_1 = 0.2309, wR_2=0.4646	R_1=0.1753, wR_2=0.4589	R_1 =0.0645, wR_2=0.1448	R_1 = 0.0508, wR_2=0.0830	R_1 =0.0576, wR_2=0.1047	R_1 =0.0915, wR_2=0.1227	R_1 =0.1417, wR_2=0.1594	R_1 = 0.0975, wR_2=0.1435	R_1 = 0.1011, wR_2=0.2002
Largest diff. peak/hole / e $Å^{-3}$	2.35/-1.61	0.52/-0.71	2.14/-1.41	1.67/-0.54	0.56/-0.49	0.14/-0.20	0.32/-0.57	0.24/-0.35	0.31/-0.46	0.85/-0.91	1.14/-0.66

Table S2. Selected bond angles for **1-5**.

	5-I-**1**		5-tBu-**2**		5-OCH_3-**3**		naphth-**4a**		naphth-**4b**	5-Br-3-OCH_3-**5**	
	110 K	**298 K**	**100 K**	**298 K**	**100 K**	**298 K**	**100 K**	**298 K**	**298 K**	**100 K**	**298 K**
O1—Mn1—O2	1178.0(5)	177.1(4)	177.9(3)	177.88(18)	178.5(2)	178.75(15)	173.34(9)	173.39(8)	177.43(15)	178.5(4)	178.2(3)
O1—Mn1—N1	86.6(5)	86.5(4)	87.8(2)	92.0(2)	87.6(2)	87.00(13)	87.79(11)	88.70(9)	87.73(16)	87.6(3)	86.8(3)
O2—Mn1—N1	91.6(5)	91.3(4)	91.7(3)	91.6(2)	91.5(2)	92.52(14)	96.13(11)	95.63(9)	94.10(16)	92.2(3)	94.6(3)

O1－Mn1－N2	93.8(5)	93.0(4)	94.5(3)	93.7(2)	93.9(2)	93.78(16)	89.37(11)	90.24(10)	92.04(19)	94.9(4)	93.9(3)
O2－Mn1－N2	85.0(5)	84.9(4)	87.5(3)	88.0(2)	84.8(2)	85.01(15)	85.32(11)	84.85(10)	86.27(18)	83.6(3)	87.4(3)
O1－Mn1－N4	93.5(5)	94.3(5)	90.5(3)	87.2(2)	92.9(2)	93.14(13)	97.04(11)	96.38(9)	94.10(16)	93.8(4)	92.1(2)
O2－Mn1－N4	88.2(5)	88.3(5)	87.8(3)	86.7(2)	88.5(2)	88.11(13)	87.85(10)	88.06(9)	87.18(16)	87.7(4)	86.3(2)
O1－Mn1－N3	86.8(5)	87.9(4)	89.1(2)	89.1(2)	83.6(2)	84.56(16)	85.15(12)	85.09(10)	86.9(2)	86.1(3)	84.3(3)
O2－Mn1－N3	94.6(5)	93.6(4)	91.9(3)	92.5(2)	96.8(2)	95.52(16)	90.45(12)	90.12(10)	91.0(2)	93.7(3)	94.6(3)
N1－Mn1－N2	84.4(5)	83.5(4)	84.8(3)	85.0(2)	83.2(2)	83.00(17)	89.15(12)	88.95(10)	87.0(2)	86.4(4)	84.8(3)
N1－Mn1－N4	115.0(5)	115.6(5)	110.4(3)	111.3(2)	116.5(2)	116.37(14)	96.98(11)	97.08(10)	104.62(16)	109.9(4)	110.5(3)
N2－Mn1－N4	159.6(5)	159.9(4)	164.2(3)	163.0(2)	159.4(2)	159.75(17)	171.27(11)	171.12(9)	167.04(19)	161.9(3)	163.9(3)
N1－Mn1－N3	161.4(5)	161.3(5)	164.6(3)	164.2(2)	158.3(2)	159.04(17)	171.36(12)	171.94(9)	168.0(2)	164.3(4)	161.1(3)
N2－Mn1－N3	78.8(5)	79.0(5)	80.5(2)	79.9(2)	77.7(3)	78.5(2)	85.80(12)	85.96(10)	82.5(2)	79.8(4)	79.3(4)
N4－Mn1－N3	82.7(5)	82.6(5)	84.7(3)	84.2(2)	83.8(3)	83.29(18)	88.84(12)	88.72(10)	86.5(2)	84.9(4)	86.5(3)
O4－Mn2－O3	177.9(4)	177.1(4)	178.4(3)								
O4－Mn2－N5	92.2(5)	93.5(4)	91.7(3)								
O3－Mn2－N5	86.5(5)	88.4(4)	86.8(2)								
O4－Mn2－N6	86.5(5)	87.6(4)	87.7(3)								
O3－Mn2－N6	91.8(5)	94.1(4)	92.8(3)								
N5－Mn2－N6	86.2(6)	85.5(5)	85.2(3)								
O4－Mn2－N8	89.0(5)	85.2(4)	88.0(2)								
O3－Mn2－N8	93.0(5)	92.7(4)	91.9(2)								
N5－Mn2－N8	106.6(5)	108.6(4)	110.9(3)								
N6－Mn2－N8	166.6(5)	164.5(5)	163.5(3)								
O4－Mn2－N7	94.2(5)	92.3(5)	92.8(3)								
O3－Mn2－N7	86.7(5)	86.2(5)	88.9(3)								
N5－Mn2－N7	165.9(5)	165.3(5)	164.3(3)								
N6－Mn2－N7	81.7(5)	81.2(5)	79.9(3)								

N8—Mn2—N7	86.1(5)	85.4(5)	84.4(3)								
Σ	76.21/55.28	74.93/61.79	59.65/57.28	60.53	82.34	81.93	41.30	39.18	51.86	38.32	70.26
Θ	267.87/180.72	262.49/201.83	218.44/218.39	226.18	290.75	282.16	114.37	113.55	154.65	226.70	231.70

Table S3. Hydrogen bond distances for complexes **1-5** (Å, °).

5-I-1	112 K				296 K			
	D-H···A	D···A	H···A	D-H···A	D-H···A	D-A	H···A	D-H···A
	N2-H11···I1	3.820	2.94	148	N2-H11···I1	3.848	2.98	148
	N7−H42···π	3.396	2.451	157	N6−H37···π	3.412	2.476	159
5-tBu-**2**	110 K				297 K			
	D-H···A	D-A	H···A	D-H···A	D-H···A	D-A	H···A	D-H···A
	N2-H2···π1	3.515	2.515	177	N2-H11···π4	3.469	2.500	170
	N7-H7···π2	3.483	2.495	169	N2-H11···π5	3.482	2.501	178
	N6-H6···π3	3.506	2.508	175				
5 -OCH_3-**3**	104 K				298 K			
	D-H···A	D-A	H···A	D-H···A	D-H···A	D-A	H···A	D-H···A
	N2-H14···π	3.411	2.776	147	N2-H14···π	3.445	2.688	159
	C40-H45···π	3.473	2.855	123	C40-H45···π	3.500	2.847	128
naphth-**4a**	120 K				295 K			
	D-H···A	D-A	H···A	D-H···A	D-H···A	D-A	H···A	D-H···A
	N2-H11···π	3.397	2.509	171	N2-H14···π	3.415	2.524	170
	N3-H11···π	3.349	2.448	170	C2−H1···O3	3.389	2.526	154
	C−H···π	3.258	2.316	161	C17−H21···O3	3.551	2.680	150
	π···π	3.21			π···π	3.277		
naphth-**4b**					293 K			
					N2-H14···π	3.714	2.825	156
					N3-H19···π	3.556	2.821	166
					C32−H32···π	3.523	2.747	141
5-Br-3-OCH_3-**5**	100 K				298 K			
	D-H···A	D-A	H···A	D-H···A	D-H···A	D-A	H···A	D-H···A
	N3-H3··π	3.776	2.780	173	N3-H15··π	3.414	2.655	142

	C41−H41···O4	3.283	2.668	123				
	C3−H3b···Br2	3.757	2.876	150	C3−H3b···Br2	3.809	2.893	160