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Supporting Information

Two Keggin sandwich-type tungstophosphates modified by open chain carboxyethyltin groups and transition metals

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1. Crystal structure figures

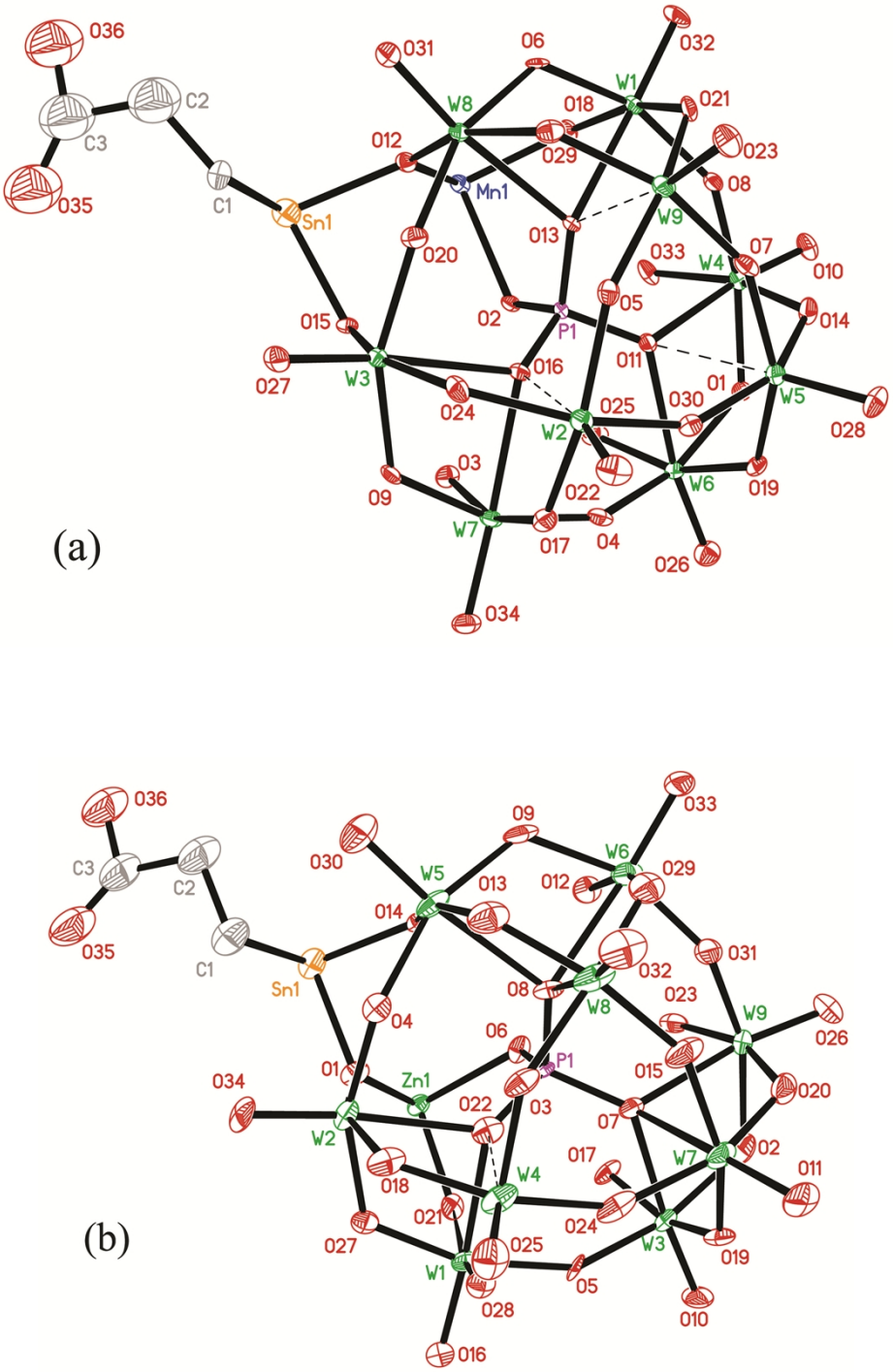
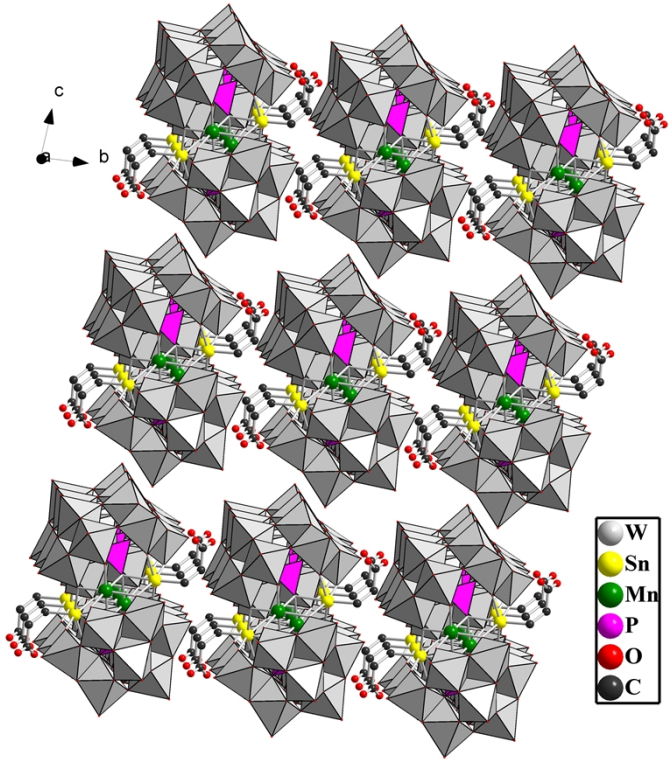
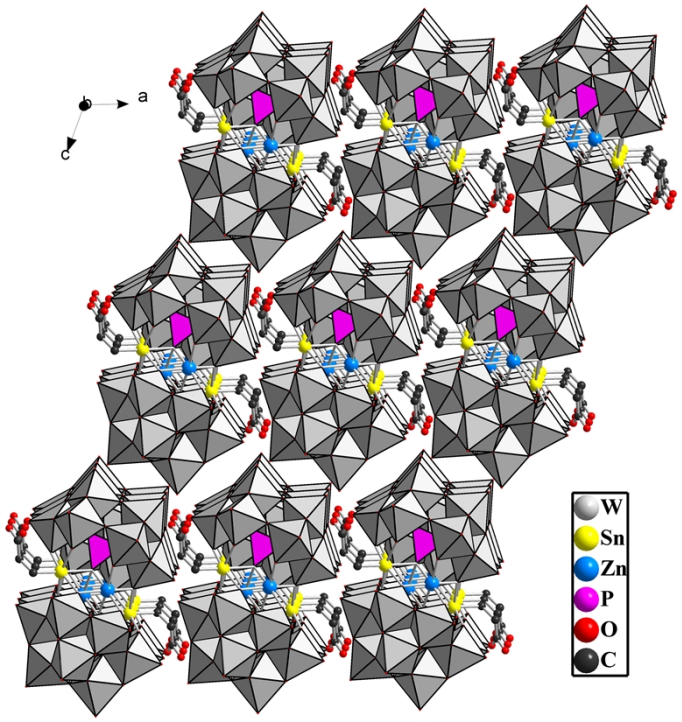


Fig. S1 ORTEP drawing of the polyoxoanions of **1** (a) and **2** (b) with thermal ellipsoids at 30 % probability (H, K, Na atoms, and free water molecules have been omitted for clarity)



(a)



(b)

Fig. S2 Polyhedral and ball-and-stick view of the 3D supramolecular frameworkof **1** (a) and **2** (b)**.** The H, Na, K and water molecules reside in the interspaces of the adjacent polyoxoanions are omitted for clarity

2. Selected bond lengths and angles of compounds **1** and **2**

Table S1 Selected bond lengths (Å) and angles (°) for compound **1**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1-O32	1.706(10)	W5-O14	1.880(10)	W9-O5	1.905(10)
W1-O18	1.782(10)	W5-O7	1.930(10)	W9-O13	2.601(10)
W1-O8	1.887(10)	W5-O30	1.932(10)	P1-O13	1.535(9)
W1-O6	1.975(10)	W5-O11	2.535(10)	P1-O2	1.541(9)
W1-O21	2.019(10)	W6-O26	1.719(11)	P1-O16	1.546(10)
W1-O13	2.430(9)	W6-O25	1.800(10)	P1-O11	1.546(10)
W2-O22	1.730(10)	W6-O1	1.926(10)	Sn1-O33#1	2.070(10)
W2-O17	1.874(10)	W6-O4	1.946(10)	Sn1-O25#1	2.074(10)
W2-O24	1.895(10)	W6-O19	1.983(10)	Sn1-C1	2.155(13)
W2-O30	1.897(10)	W6-O11	2.449(9)	Sn1-O12	2.125(10)
W2-O5	1.929(10)	W7-O34	1.714(10)	Sn1-O15	2.134(9)
W2-O16	2.574(10)	W7-O3	1.777(9)	Sn1-O2#1	2.403(9)
W3-O27	1.703(10)	W7-O4	1.889(10)	Mn1-O18	2.052(10)
W3-O15	1.885(9)	W7-O9	1.983(10)	Mn1-O3#1	2.071(10)
W3-O9	1.894(9)	W7-O17	1.996(10)	Mn1-O15#1	2.164(9)
W3-O20	1.936(10)	W7-O16	2.424(9)	Mn1-O12	2.166(10)
W3-O24	1.967(10)	W8-O31	1.720(10)	Mn1-O2	2.324(9)
W3-O16	2.436(10)	W8-O12	1.881(10)	Mn1-O2#1	2.328(9)
W4-O10	1.711(10)	W8-O6	1.900(9)	C1-C2	1.535(10)
W4-O33	1.813(10)	W8-O20	1.901(10)	C2-C3	1.526(10)
W4-O1	1.920(9)	W8-O29	1.953(10)	C3-O35	1.254(10)
W4-O8	1.949(9)	W8-O13	2.436(9)	C3-O36	1.255(10)
W4-O14	1.992(10)	W9-O23	1.707(10)		
W4-O11	2.416(9)	W9-O21	1.873(10)		
W5-O28	1.715(10)	W9-O29	1.888(10)		
W5-O19	1.878(9)	W9-O7	1.904(10)		
Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
O32-W1-O18	102.8(5)	O10-W4-O14	99.9(5)	O6-W8-O20	156.7(4)
O18-W1-O6	89.6(4)	O14-W4-O11	72.9(4)	O12-W8-O20	88.3(4)
O8-W1-O6	153.9(4)	O28-W5-O19	102.0 (5)	O31-W8-O13	171.7(4)
O8-W1-O21	85.1(4)	O19-W5-O14	89.9(4)	O6-W8-O13	72.7(3)
O32-W1-O13	170.2(4)	O19-W5-O7	155.9(4)	O23-W9-O21	102.3(5)
O22-W2-O17	102.2(5)	O14-W5-O30	154.8(4)	O29-W9-O7	155.4(4)
O17-W2-O30	88.5(4)	O7-W5-O30	84.1(4)	O29-W9-O5	86.2(4)
O24-W2-O30	155.5(4)	O26-W6-O25	105.0(5)	O7-W9-O5	85.5(4)
O17-W2-O5	154.8(4)	O26-W6-O19	99.7(4)	O21-W9-O5	154.5(4)
O24-W2-O5	86.7(4)	O25-W6-O19	155.2(4)	O33#1-Sn1-O25#1	92.7(4)

O27-W3-O15	101.7(5)	O4-W6-O19	85.0(4)	O33#1-Sn1-O12	159.9(4)
O15-W3-O9	92.8(4)	O26-W6-O11	171.2(4)	O12-Sn1-O15	83.2(4)
O15-W3-O16	84.9(4)	O34-W7-O3	103.7(5)	O33#1-Sn1-C1	95.3(5)
O27-W3-O16	172.2(4)	O4-W7-O9	155.3(4)	O12-Sn1-C1	104.2(5)
O24-W3-O16	74.3(4)	O34-W7-O16	168.4(4)	C1-Sn1-O2#1	176.0(4)
O10-W4-O33	104.5(5)	O9-W7-O16	71.8(3)	O13-P1-O16	109.2(5)
O1-W4-O8	156.3(4)	O3-W7-O9	88.8(4)	O2-P1-O16	111.2(5)
O1-W4-O14	82.3(4)	O31-W8-O12	101.9(4)	O16-P1-O11	108.2(5)

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

Table S2 Selected bond lengths (Å) and angles (º) for compound **2**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1-O16	1.73 (2)	W5-O14	1.877(17)	W9-O31	1.92(2)
W1-O21	1.77(2)	W5-O9	1.88(2)	W9-O2	1.93(2)
W1-O27	1.90(2)	W5-O4	1.930(17)	W9-O20	1.99(2)
W1-O5	1.917(16)	W5-O13	1.96(2)	W9-O7	2.408(17)
W1-O28	2.017(19)	W5-O8	2.40(2)	P1-O22	1.54(2)
W1-O22	2.425(18)	W6-O33	1.73(2)	P1-O6	1.542(19)
W2-O34	1.719(19)	W6-O12	1.774(19)	P1-O8	1.595(19)
W2-O1	1.882(17)	W6-O31	1.91(2)	P1-O7	1.596(19)
W2-O4	1.929(18)	W6-O9	1.97(2)	Sn1-O17#1	2.00(2)
W2-O27	1.938 (19)	W6-O29	1.99(2)	Sn1-O23#1	2.017(18)
W2-O18	1.97(2)	W6-O8	2.383(18)	Sn1-C1	2.10(2)
W2-O22	2.39(2)	W7-O11	1.74(2)	Sn1-O14	2.105(15)
W3-O10	1.707(19)	W7-O20	1.88(2)	Sn1-O1	2.12(2)
W3-O17	1.823(19)	W7-O19	1.903(18)	Sn1-O6#1	2.321(17)
W3-O2	1.868 (19)	W7-O15	1.91(2)	Zn1-O21	2.00(2)
W3-O5	1.919(16)	W7-O24	1.97(2)	Zn1-O12#1	2.021(18)
W3-O19	2.00(2)	W7-O7	2.480(19)	Zn1-O1	2.068(17)
W3-O7	2.381 (17)	W8-O32	1.720(2)	Zn1-O14#1	2.083(16)
W4-O25	1.72(2)	W8-O13	1.90(3)	Zn1-O6#1	2.24(2)
W4-O24	1.87(2)	W8-O15	1.91(2)	Zn1-O6	2.287(17)
W4-O18	1.89(2)	W8-O29	1.92(2)	C1-C2	1.501(10)
W4-O28	1.888(18)	W8-O3	1.96(2)	C2-C3	1.503(10)
W4-O3	1.899(19)	W8-O8	2.49(2)	C3-O35	1.251(10)
W4-O22	2.574(19)	W9-O26	1.73(2)	C3-O36	1.259(10)
W5-O30	1.69(2)	W9-O23	1.82(2)		
Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
O16-W1-O21	103.0(10)	O18-W4-O3	86.0(8)	O13-W8-O15	156.5(9)
O21-W1-O27	88.6(8)	O28-W4-O3	156.7(8)	O13-W8-O29	89.0(11)

O27-W1-O5	157.0(7)	O30-W5-O14	103.7(10)	O32-W8-O8	170.1(9)
O16-W1-O5	99.8(9)	O14-W5-O9	90.2(7)	O13-W8-O8	72.7(8)
O16-W1-O22	171.5(9)	O9-W5-O4	157.5(8)	O26-W9-O23	104.2(12)
O34-W2-O1	103.1(10)	O9-W5-O8	73.1(7)	O23-W9-O31	92.0(9)
O1-W2-O4	88.8(8)	O30-W5-O8	170.4(9)	O2-W9-O20	82.5(8)
O4-W2-O27	155.8(8)	O33-W6-O12	104.1(12)	O26-W9-O7	170.8(11)
O34-W2-O22	173.2(9)	O12-W6-O31	93.2(10)	O2-W9-O7	71.9(6)
O1-W2-O22	82.1(7)	O31-W6-O9	154.9(9)	O17#1-Sn1-O23#1	93.4(8)
O10-W3-O17	102.3(11)	O31-W6-O29	86.4(10)	O17#1-Sn1-O14	89.3(7)
O17-W3-O2	90.6(9)	O33-W6-O8	167.9(11)	O23#1-Sn1-O14	164.7(7)
O2-W3-O19	83.1(8)	O11-W7-O20	101.5(10)	O23#1-Sn1-C1	94.2(10)
O10-W3-O7	174.4(9)	O20-W7-O19	89.8(8)	O17#1-Sn1-C1	93.7(9)
O19-W3-O7	73.2(7)	O19-W7-O15	155.9(9)	C1-Sn1-O14	100.6(9)
O25-W4-O24	102.1(10)	O11-W7-O7	170.2(9)	O22-P1-O7	107.9(11)
O24-W4-O18	157.4(9)	O20-W7-O7	73.0(7)	O6-P1-O7	111.7(10)
O24-W4-O28	88.4 (8)	O32-W8-O13	99.9(11)	O8-P1-O7	107.1(10)

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

3. Physical characterizations

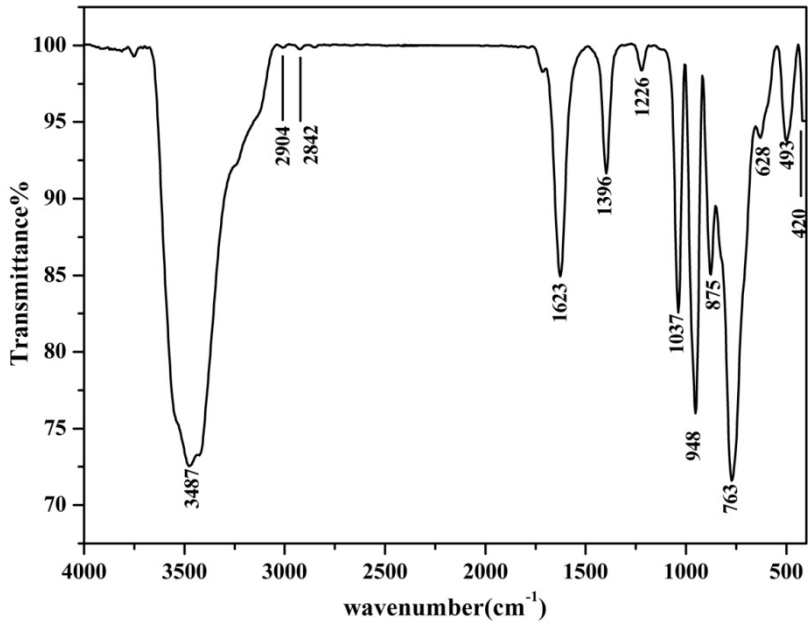


Fig. S3 IR spectrum of compound **1**

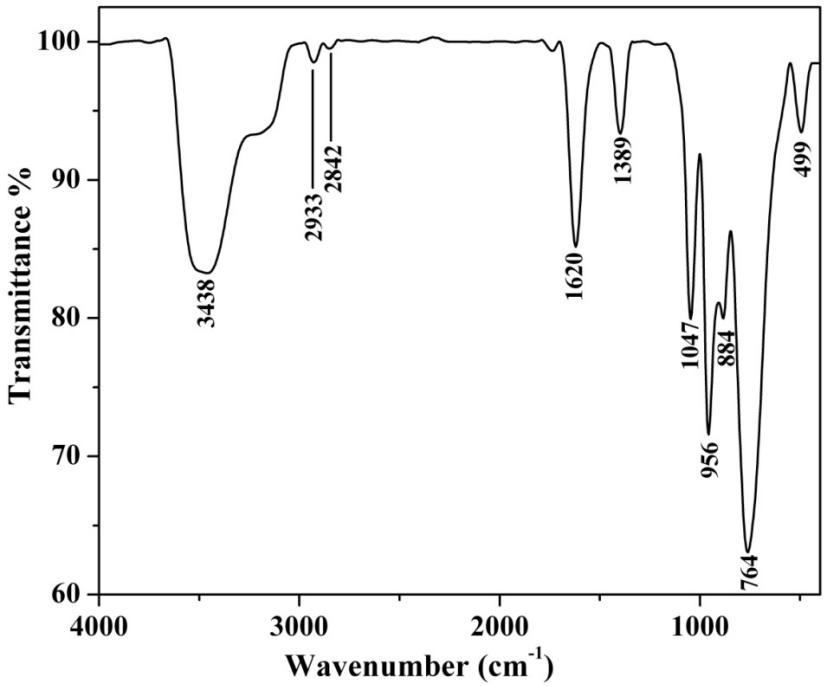


Fig. S4 IR spectrum of compound **2**

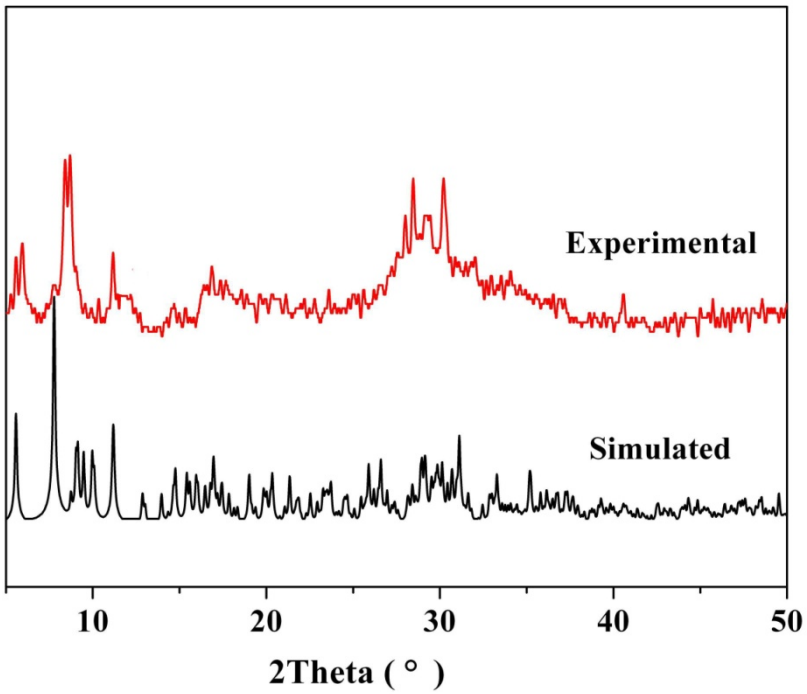


Fig. S5 The simulated and experimental XRD patterns of compound **1**

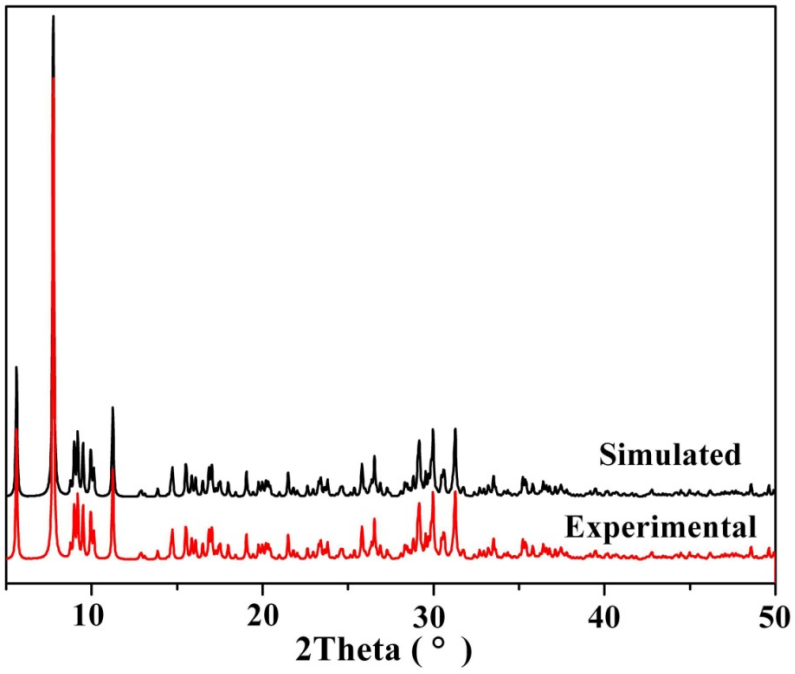


Fig. S6 The simulated and experimental XRD patterns of compound **2**

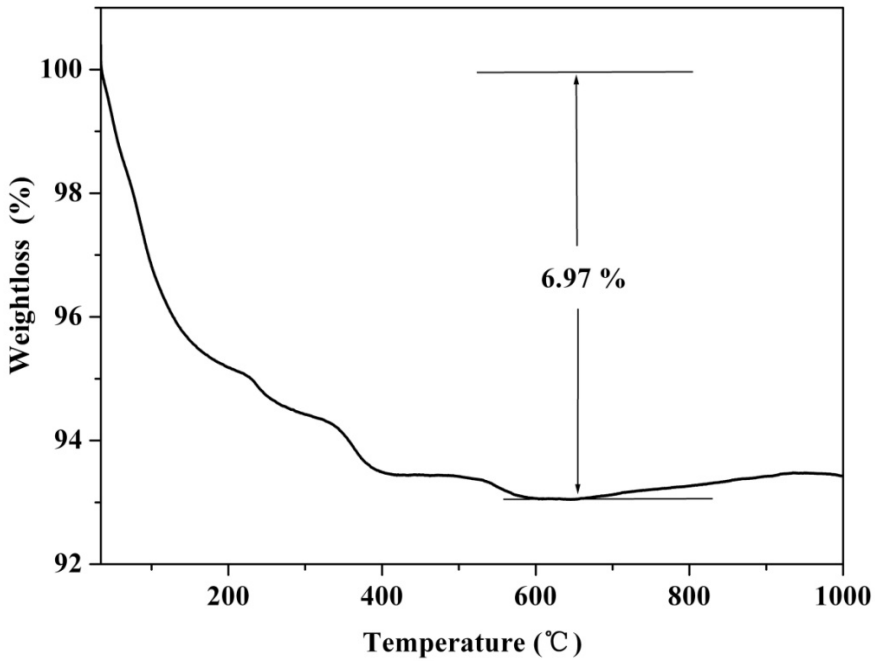


Fig. S7 TG curve of **1**

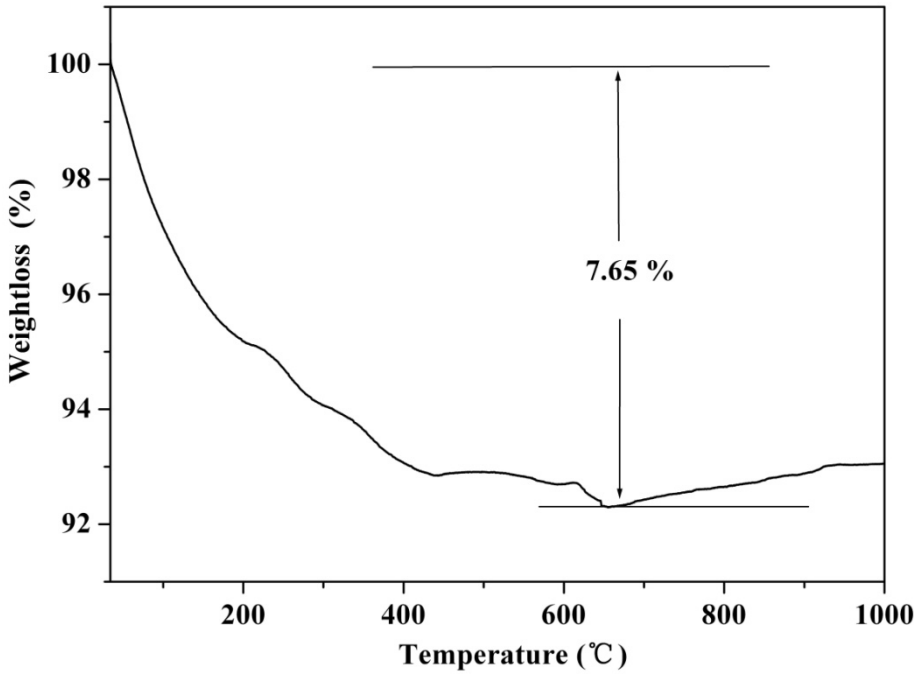


Fig. S8 TG curve of **2**

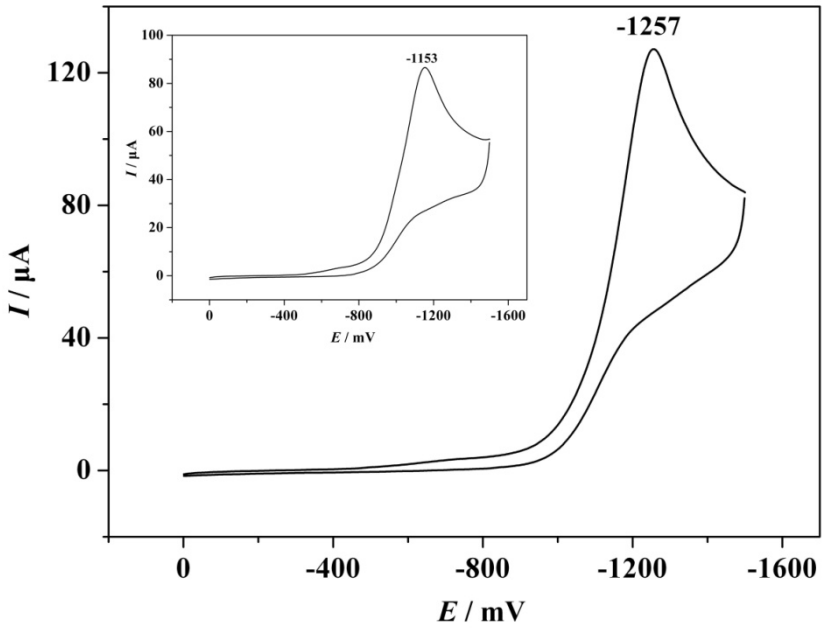


Fig. S9 Cyclic voltammogram of **PW_9-Mn** (the inset) and compound **1** in pH = 3 (0.1mol L^{-1} Na_2SO_4-H_2SO_4) solution

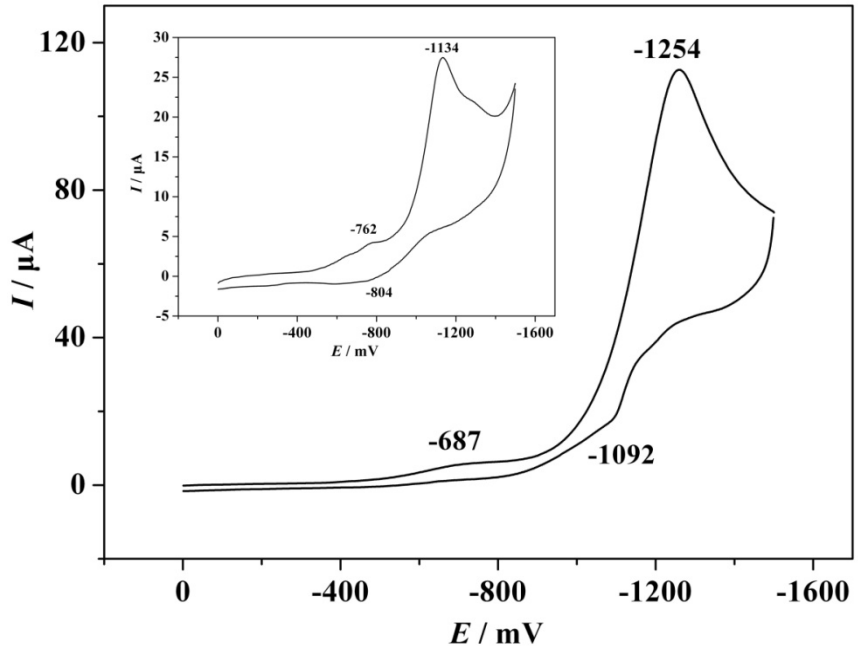


Fig. S10 Cyclic voltammogram of **PW_9-Zn** (the inset) and compound **2** in pH = 3 (0.1 mol L^{-1} Na_2SO_4-H_2SO_4) solution

3. Catalytic activity tests

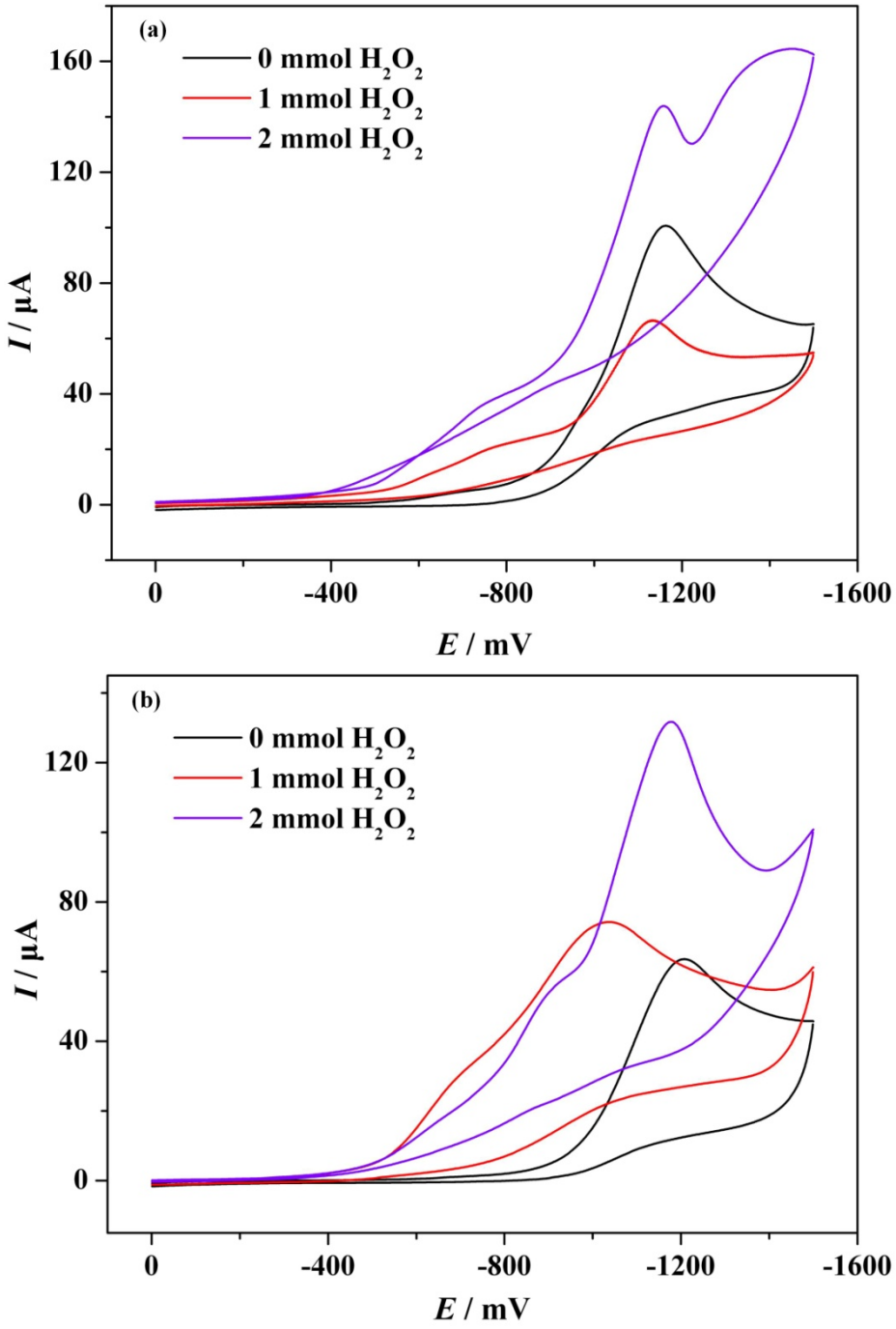


Fig. S11 Electrocatalytic activity of **PW_9-Mn** (a) and compound **1** (b) for reduction of H_2O_2 at the scan rate of 40 mV s^{-1}

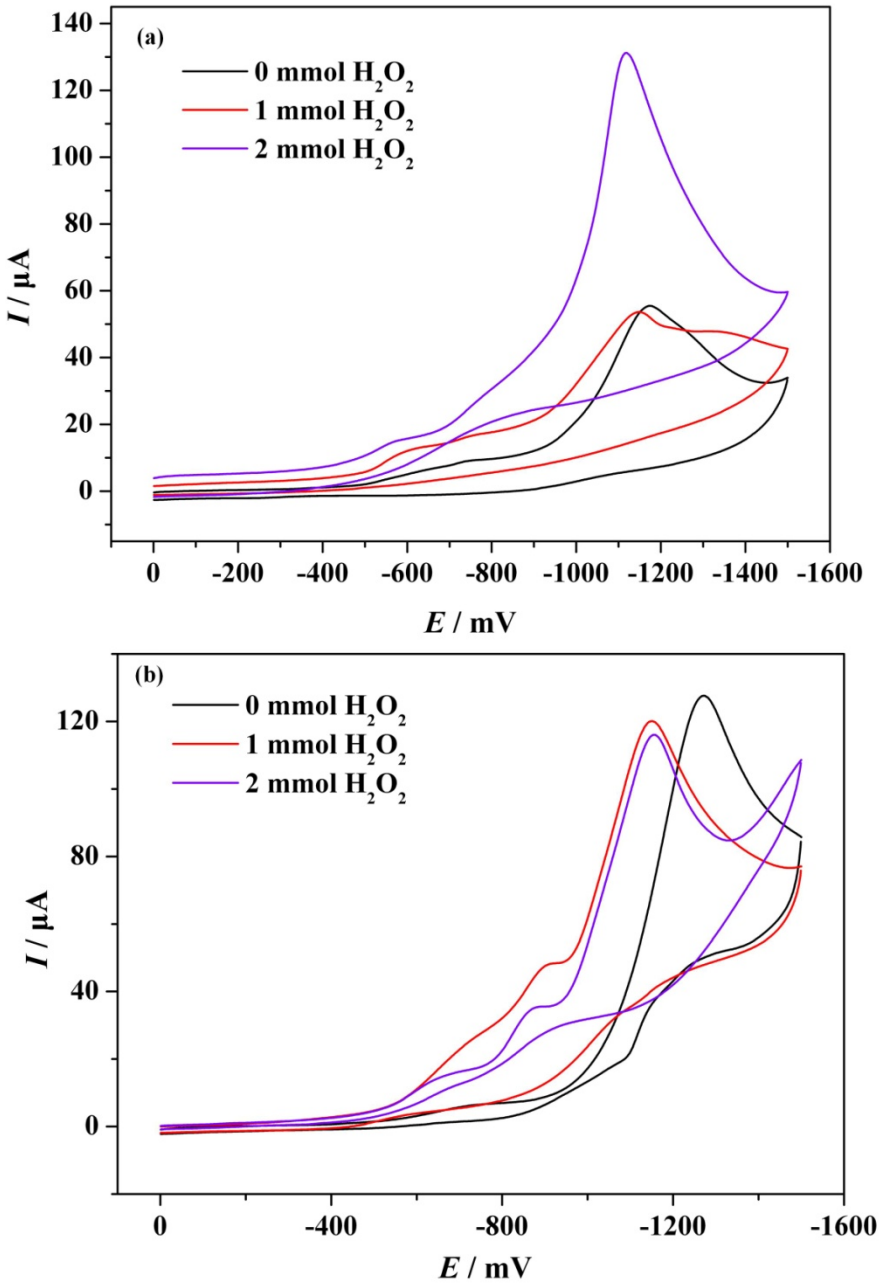


Fig. S12 Electrocatalytic activity of **PW_9-Zn** (a) and compound **2** (b) for reduction of H_2O_2 at the scan rate of 40 mV s^{-1}

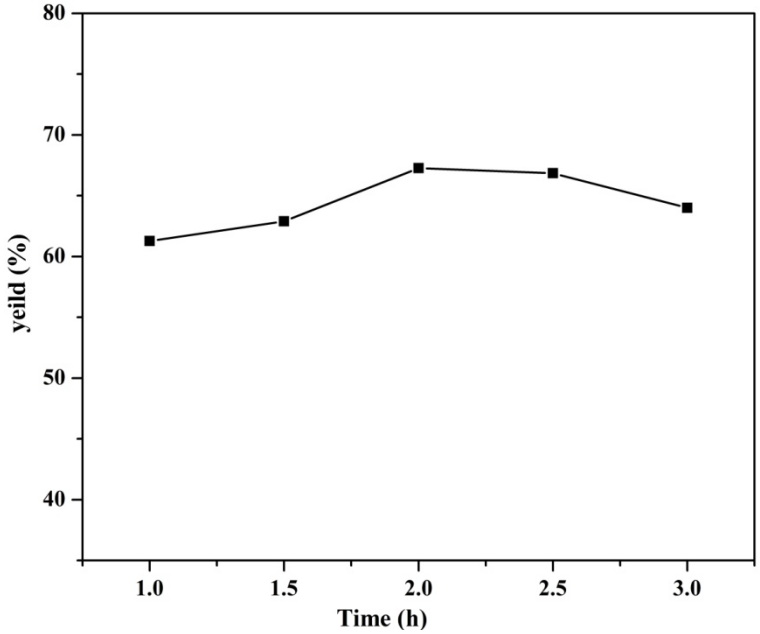


Fig. S13 Effect of reaction time on cyclohexanone yield. Cyclohexanol to H_2O_2 molar ratio, 1:2.2; catalyst (**PW_9 -Zn**, based on W) to cyclohexanol molar ratio, 1:200; reaction temperature, 80°C; acetonitrile, 10 mL

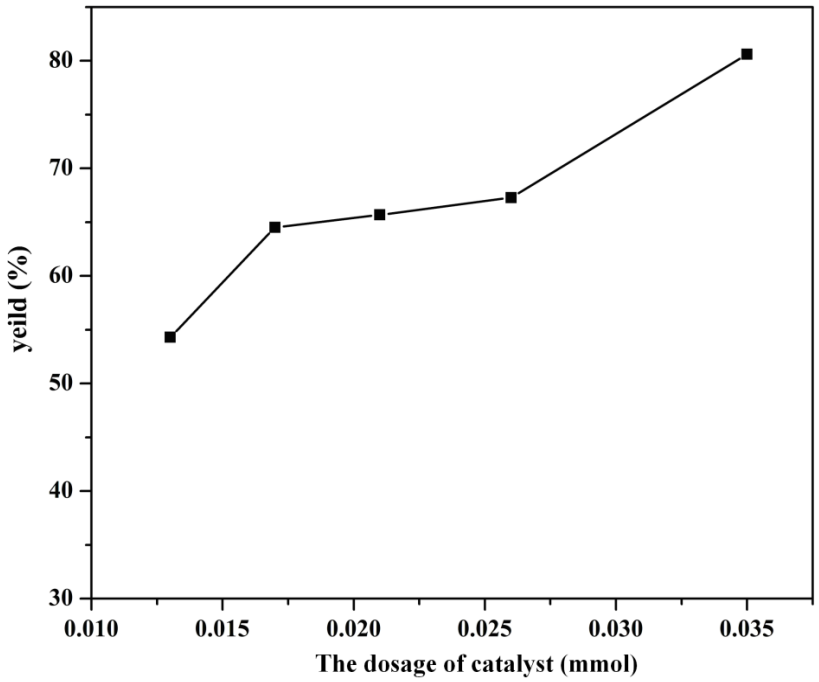


Fig. S14 Effect of **PW_9-Zn** amount (based on W) on cyclohexanone yield. Cyclohexanol to H_2O_2 molar ratio, 1:2.2; reaction time, 2 h; reaction temperature, 80°C; acetonitrile, 10 mL

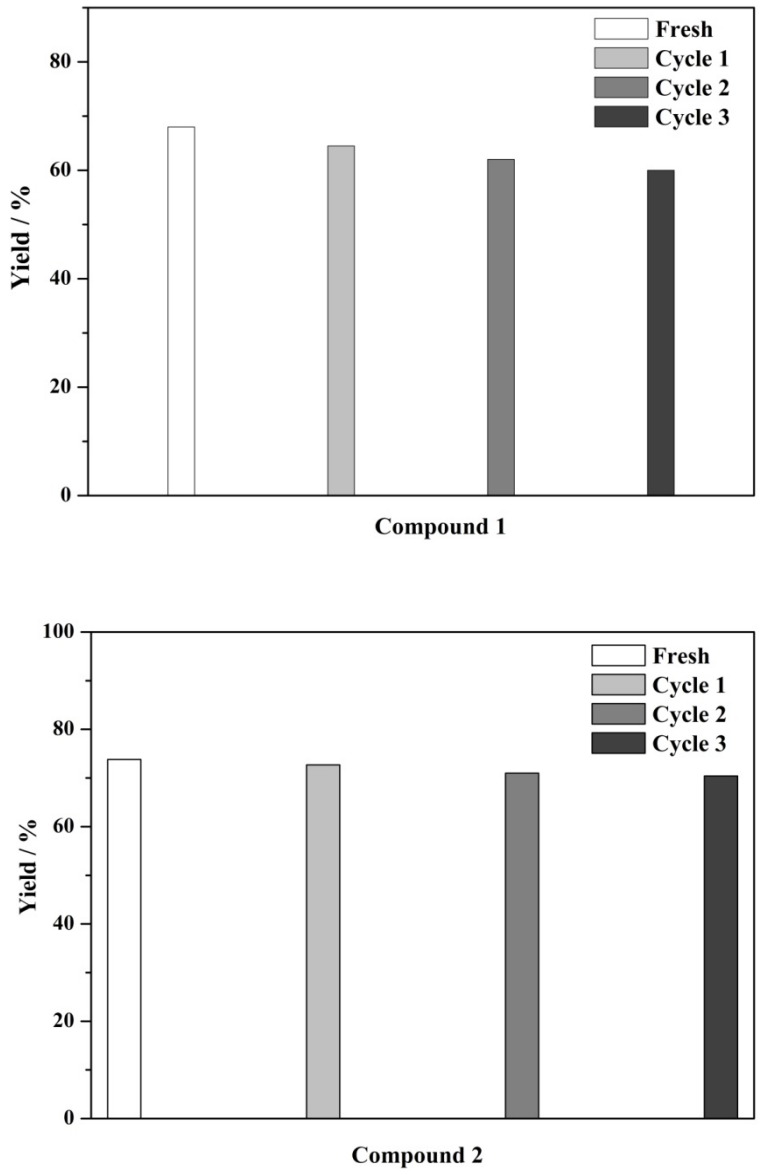


Fig. S15 The catalytic activities of **1** and **2** used four cycles. The catalysts were recovered by simple filtration without any treatment. Cyclohexanol to H_2O_2 molar ratio, 1:2.2; catalyst (based on W) to cyclohexanol molar ratio, 1:150; reaction time, 2 h; reaction temperature, 80°C; acetonitrile, 10 mL

Table S3 Catalytic performance of various catalysts for the oxidation of cyclohexanol to cyclohexanone with H_2O_2 (catalyst (based on W) to cyclohexanol molar ratio, 1:150)

Entry	Catalyst	H_2O_2 (equiv.)	Solvent	Solubility	Temperature (°C)	Time (min)	Isolated yield (%)
1	Compound **1**	2.2	MeCN	soluble	80	120	68.2
2	Compound **2**	2.2	MeCN	soluble	80	120	73.8
3	**PW_9-Mn**	2.2	MeCN	soluble	80	120	46.8
4	**PW_9-Zn**	2.2	MeCN	soluble	80	120	80.7
5	$Cl_3Sn(CH_2)_2COOCH_3$	2.2	MeCN	soluble	80	120	6.02