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Supplementary Materials: Single-Atom Mn Active Site in Triol-Stabilized β-Anderson Manganohexamolybdate for Enhanced Catalytic Activity towards Adipic Acid Production

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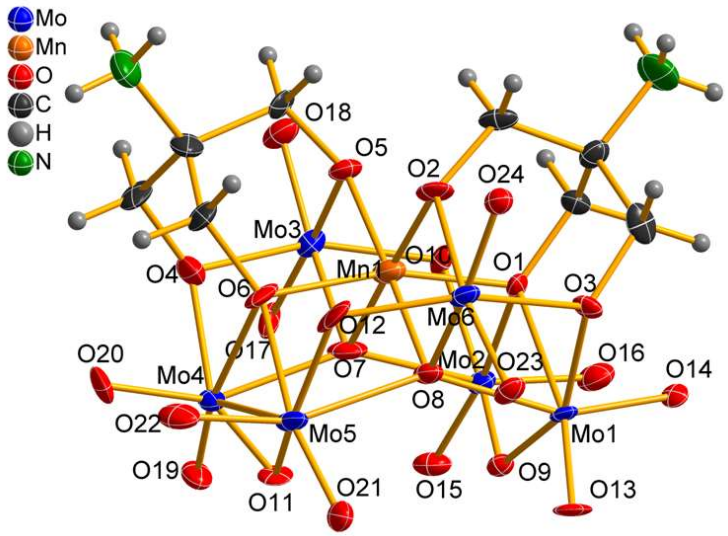
Table S1. Crystallographic data for compound **1.**

Identification code	1
Empirical formula	$C_8H_{22}N_3MnMo_6O_{24}$
Formula weight	1174.87
Temperature (K)	293 (2)
Crystal system	monoclinic
Space group	C2/c
a (Å)	27.164(3)
b (Å)	18.061(2)
c (Å)	16.099(2)
α (°)	90.00
β (°)	110.120(14)
γ (°)	90.00
Volume (Å^3)	7416.4(15)
Z	8
Density (g.cm^{-3})	2.097
μ (mm^{-1})	2.369
Crystal size (mm^3)	0.55×0.50×0.40
Reflections collected	7199
Independent reflections	5784
F (000)	4448.0
GOF	1.084
Final R indices [I > 2σ(I)]	R_1=0.0535, wR_2=0.0974
R indices (all data)	R_1=0.0596, wR_2=0.1012

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

Table S2. Selected bond lengths (Å) of cluster **1**.

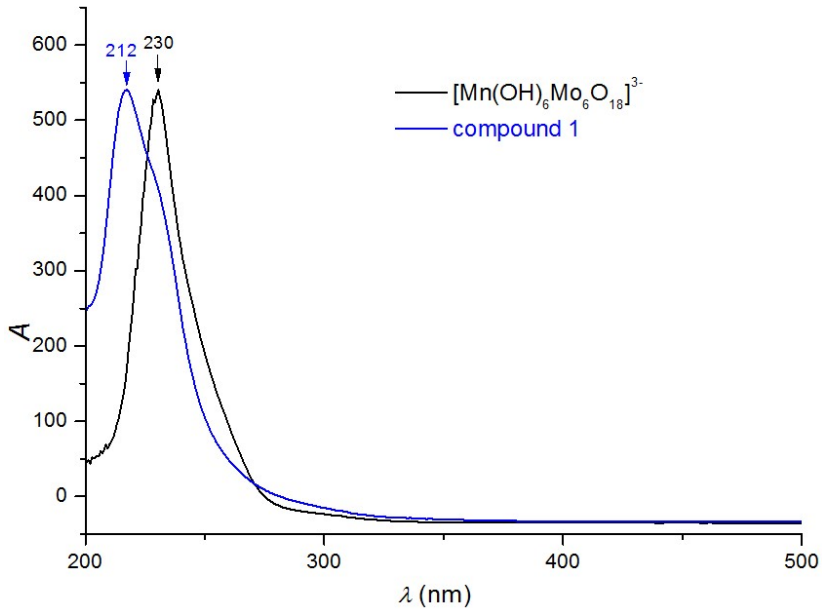


Selected bond lengths (Å) of cluster **1**			
Mn1-O1	1.986	Mo3-O10	1.904
Mn1-O2	1.942	Mo3-O17	1.698
Mn1-O5	1.936	Mo3-O18	1.728
Mn1-O6	1.983	Mo4-O4	2.098
Mn1-O7	1.969	Mo4-O6	2.280
Mn1-O8	1.961	Mo4-O7	2.160
Mo1-O1	2.276	Mo4-O11	1.882
Mo1-O3	2.054	Mo4-O19	1.693
Mo1-O8	2.156	Mo4-O20	1.722
Mo1-O9	1.877	Mo5-O6	2.315
Mo1-O13	1.735	Mo5-O8	2.262
Mo1-O14	1.719	Mo5-O11	1.914
Mo2-O1	2.319	Mo5-O12	1.944
Mo2-O7	2.221	Mo5-O21	1.691
Mo2-O9	1.933	Mo5-O22	1.701
Mo2-O10	1.979	Mo6-O2	2.189
Mo2-O15	1.677	Mo6-O3	2.145
Mo2-O16	1.730	Mo6-O8	2.169
Mo3-O4	2.107	Mo6-O12	1.899
Mo3-O5	2.180	Mo6-O23	1.712
Mo3-O7	2.178	Mo6-O24	1.732

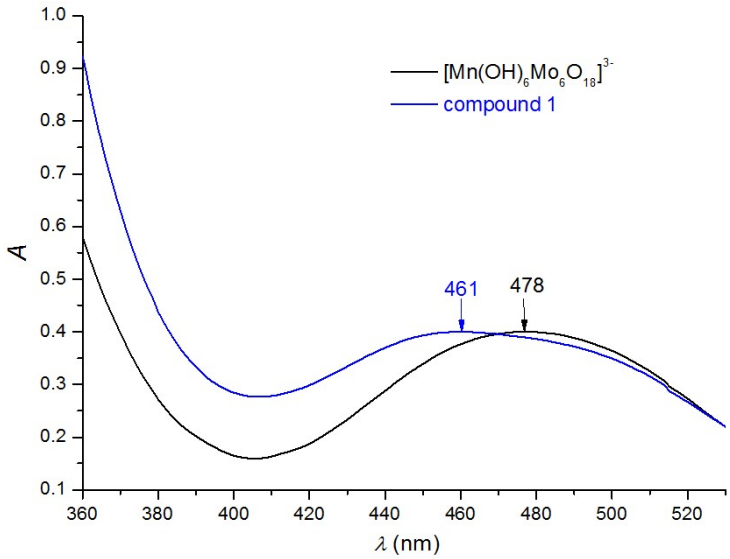
Table S3. Experimental hydrogen bonding interactions of compound **1**.

Bond	H-Bonds	D−A [Å]	A···H [Å]	D−H···A [°]
1	N3−H3C•••O14	2.897	2.247	138.52
	N3−H3D•••O11	2.900	2.206	145.00
	N3−H3E•••O15	2.992	2.211	168.11
	N3−H3F•••O19	2.719	2.468	99.54
	N2-H2C•••O16	3.483	2.959	119.46
	N2-H2C•••O24	3.453	2.793	132.19

The color of this Anderson β isomer triol functionalized derivative single crystal is different compared with Anderson *α* isomer triol functionalized derivative, because the color of the Anderson *α* isomer triol functionalized derivative was nearly the same as the normal *α* parent Anderson. The color of $[Mn(OH)_6Mo_6O_{18}]^{3-}$ anion is orange while Anderson β isomer derivative (compound **1**) is dark orange. UV-Vis was applied for LMCT absorption and d-d transition absorption investigation. It should be noted that the UV-Vis spectra of such Anderson β isomer triol functionalized derivatives actually should be compared with the parent Anderson β isomer cluster, however such conjectured reaction intermediate has not yet been successfully obtained. As a compromise, we first compared them with the LMCT absorption band of the parent "Anderson–Evans", $[Mn(OH)_6Mo_6O_{18}]^{3-}$, locating around 230 nm which primarily corresponds to ligand centered μ_3-OH π to metal-centered Mo^{6+} t_{2g}* charge transfer transition (LMCT), these LMCT bands of compound **1** show hypsochromic shift to 212 (ε_{LMCT} = 5.31×10^5 L·mol^{-1}·cm^{-1}, 7.42×10^5 L·mol^{-1}·cm^{-1} for parent Anderson cluster, compound **1**, respectively) It is due to the increase of crystal field splitting energy since the μ-OCH_2 is stronger field ligand than that μ_3-OH. The *d-d* transition absorption band of the parent $[Mn(OH)_6Mo_6O_{18}]^{3-}$ locating around 478 nm is assigned to the metal centered lowest energy electronic transition from HOMO t_{2g}* to LUMO e_g* transition of Mn^{3+}. Similar hypsochromic shift phenomenon is observed in compound **1** at 461 nm, respectively ($\varepsilon_{d\text{-}d}$ = 6.14×10^2 L·mol^{-1}·cm^{-1}, 8.53×10^2 L·mol^{-1}·cm^{-1} for parent Anderson cluster, compound **1**, respectively). The hypsochromic shift is assigned to the reduction of charge density in μ-O when triol ligands anchored on. It is worthy to point out that in our previous work, similar range of hypsochromic shift was also observed in Anderson *α* isomer triol functionalized derivative, however, the ε_{LMCT} and $\varepsilon_{d\text{-}d}$ is quite smaller. In fact, the ε_{LMCT} and $\varepsilon_{d\text{-}d}$ of Anderson *α* isomer triol functionalized derivative is not much different from the parent Anderson *α* isomer $[Mn(OH)_6Mo_6O_{18}]^{3-}$ anion. Thus, the color of the Anderson *α* isomer triol functionalized derivative and the corresponding parent cluster was nearly the same. Perhaps it is the total change of μ-O coordination environment in Anderson β isomer triol functionalized derivative skeleton that leads to the remarkable increase of ε_{LMCT} and $\varepsilon_{d\text{-}d}$ and the related obvious color change.



(**a**)



(**b**)

Figure S1. (**a**) UV/Vis LMCT spectra of compound **1** and the flat Anderson-type POMs Cluster, $[MnMo_6O_{18}(OH)_6]^{3-}$. (**b**) UV/Vis d-d transition spectra of compound **1** and the flat Anderson-type POMs Cluster, $[MnMo_6O_{18}(OH)_6]^{3-}$.

Considering one of the obvious structure features in triol functionalized Anderson β isomer derivative is that there exist one type of μ3-O and two types of μ2-O, where triol ligand is anchored on their surface. Hence, there should be three different types of (μ-O-) C atoms where each carbon atom has different chemical shifts based on different electronegative environment according to dissimilar charge density of these μ-O atoms. In fact, the electronegative sequence of these μ-O atoms from stronger to weaker is as follows: μ2-O (coordinated one molybdenum atom and the central hetero atom) > μ2-O (coordinated with two molybdenum atoms) > μ3-O (coordinated with two molybdenum atoms and the central hetero atom). The ^{13}C NMR spectrum is another effective choice to verify such structure from another aspect. Thus, the ^{13}C NMR spectrum of compound **1** was conducted and all the peaks were clearly assigned to confirm the structure (Figure S2).

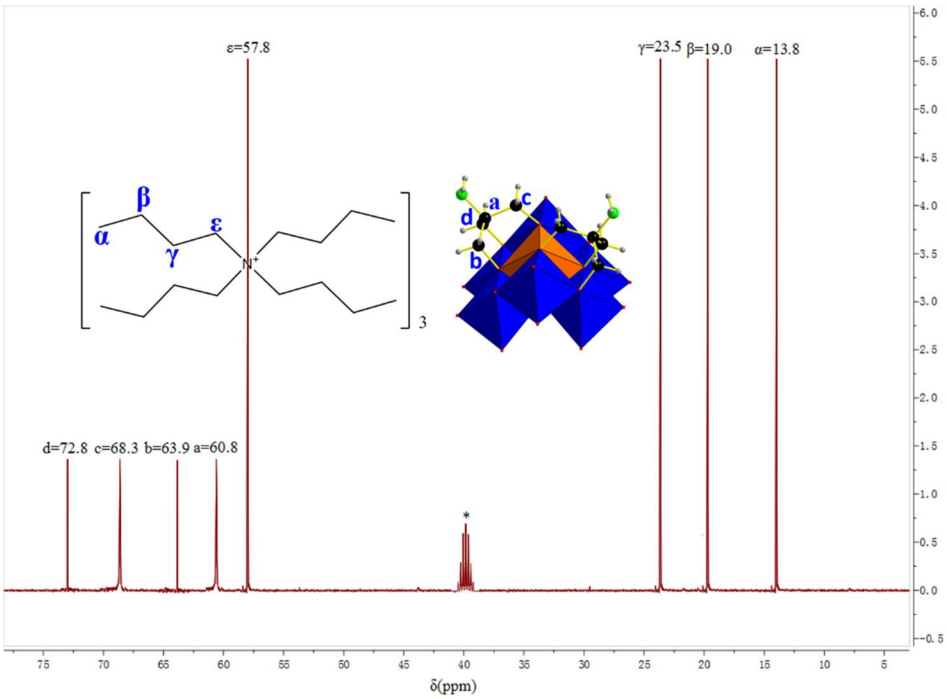
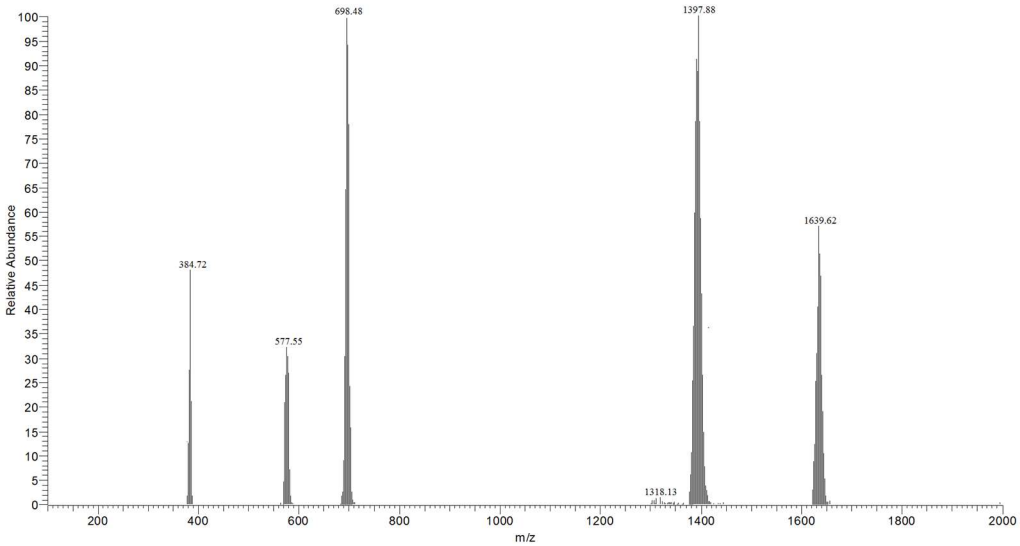
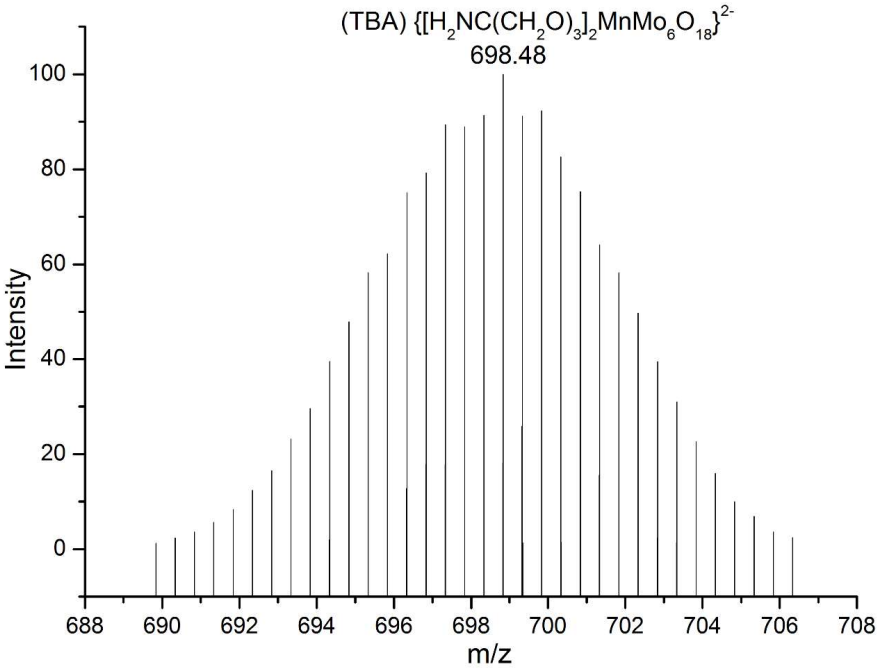


Figure S2. ^{13}C NMR spectrum of compound **1.**

The ESI-MS spectra of compound **1** was conducted and all the peaks the main peak with highest intensity and other identifiable peaks were clearly assigned to confirm the structure.



(**a**)



(**b**)

Figure S3. (**a**) ESI-MS of compound **1** with TBA^+ cations**.** (**b**) ESI-MS of compound **1** with TBA^+ cations (100% intensity peak in original size).

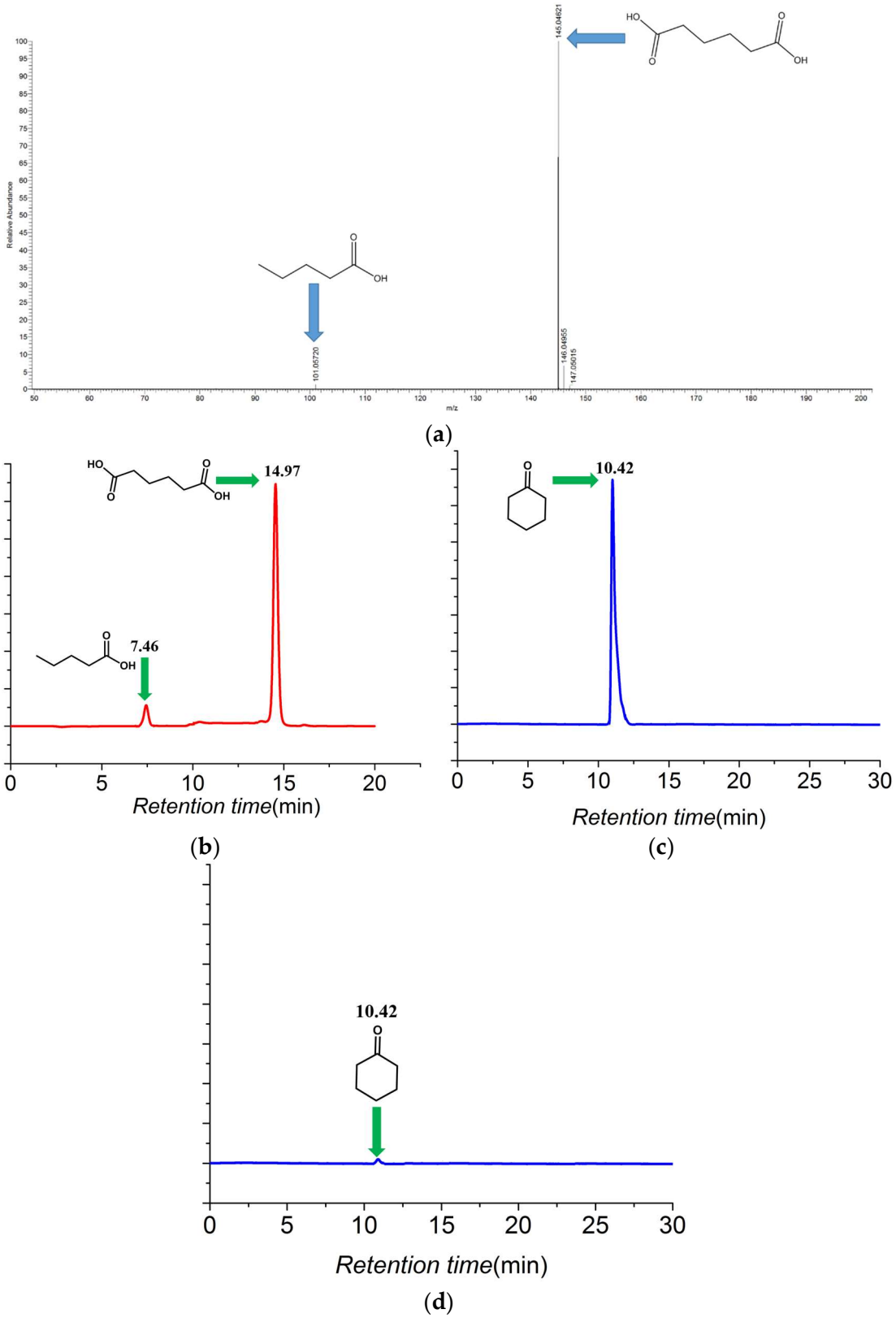
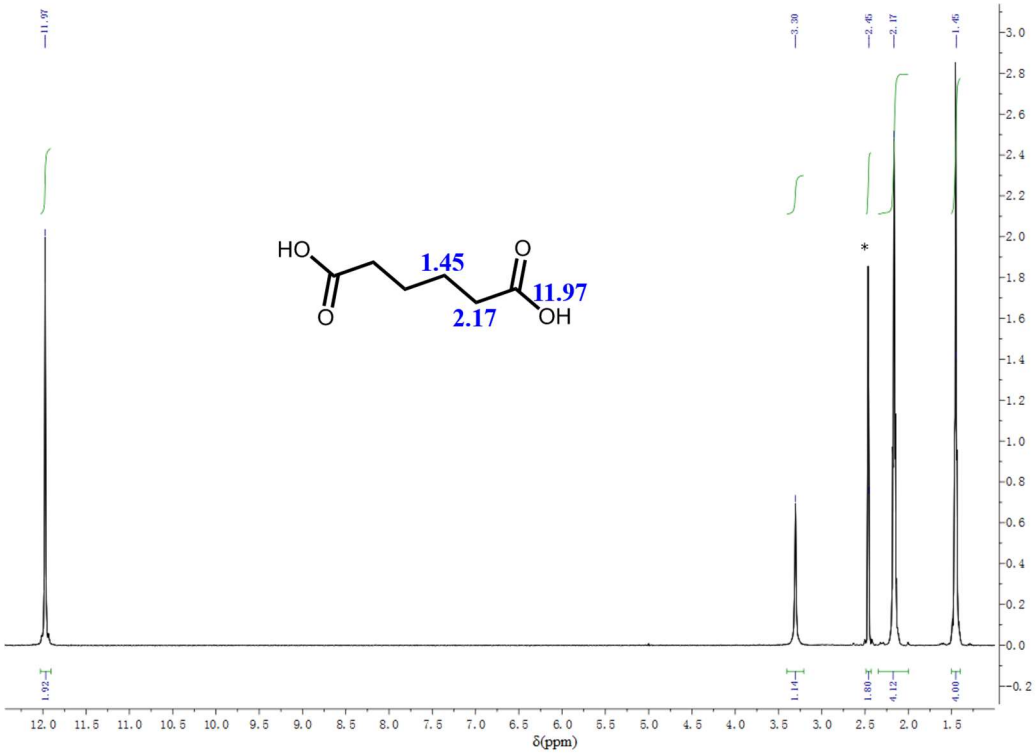
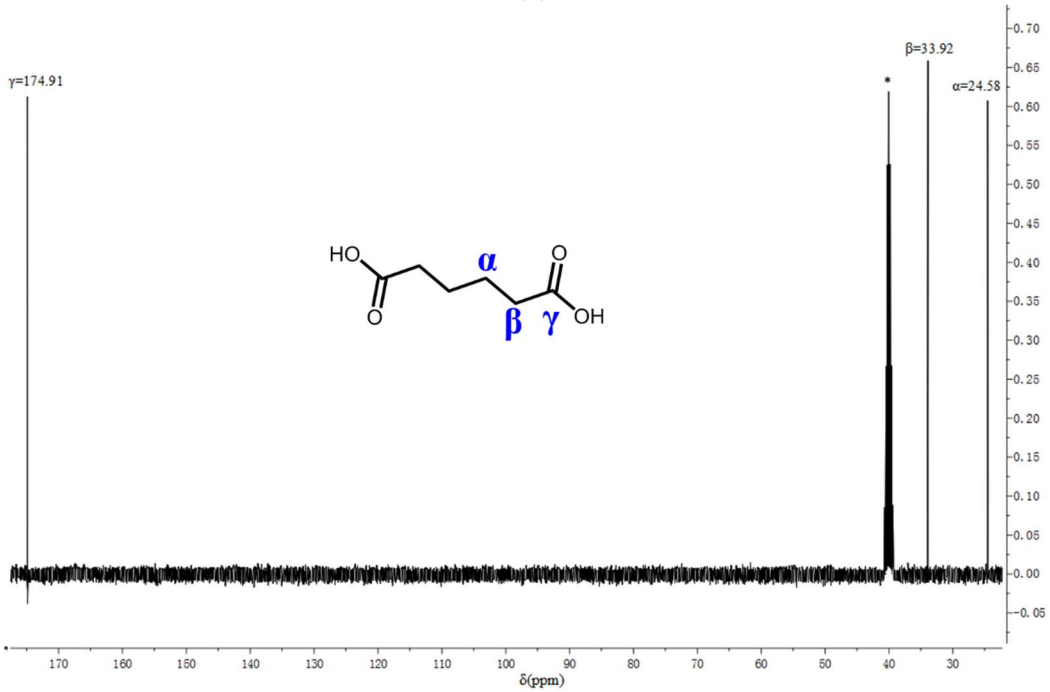


Figure S4. (**a**) The ESI-MS of white crystalline products generated from cyclohexanone in the presence of catalyst **1**. (**b**)The HPLC retention time of white crystalline products dissolved in methanol**.** (**c**) The GC-MS of reaction solution dissolved in ethanol before catalytic reaction. (**d**) The GC-MS of reaction solution dissolved in ethanol after catalytic reaction.



(**a**)



(**b**)

Figure S5. (**a**) ^{1}H NMR spectrum of white crystalline product. (**b**) ^{13}C NMR spectrum of white crystalline product.

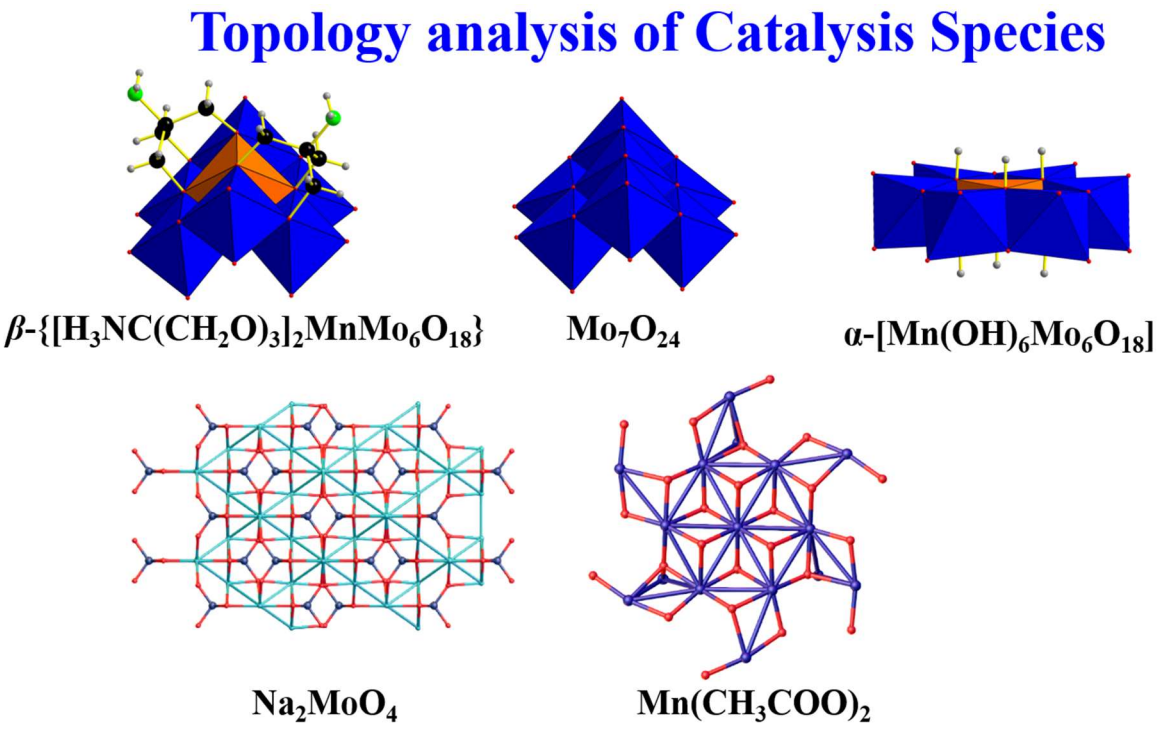


Figure S6. Topology analysis and comparison of Catalysis Species.

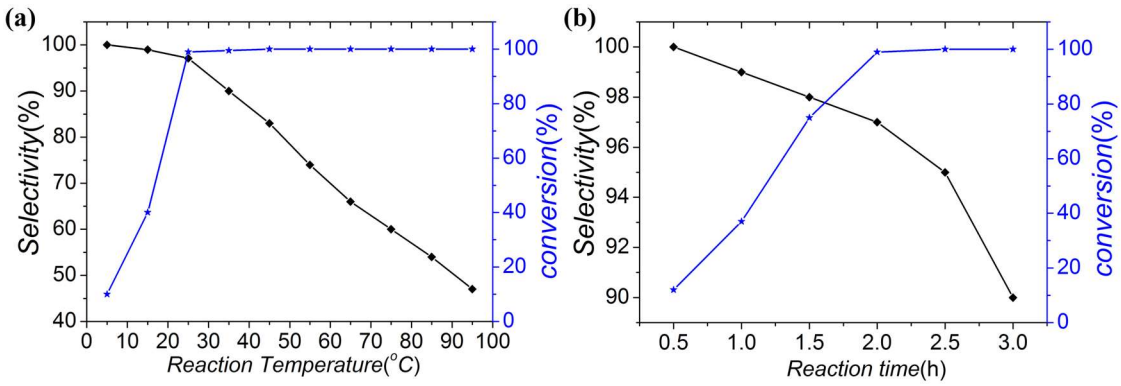


Figure S7. (a) The reaction selectivity and conversion versus reaction temperature, reaction condition catalyst (0.02 mol %), 30% H_2O_2 (100 mmol), DMSO (1 mmol), and cyclohexanone (30 mmol) at 2h. (b) The reaction selectivity and conversion versus time, reaction condition catalyst (0.02 mol %), 30% H_2O_2 (100 mmol), DMSO (1 mmol), and cyclohexanone (30 mmol) at 25℃in cyclohexanone oxidation catalytic reaction.

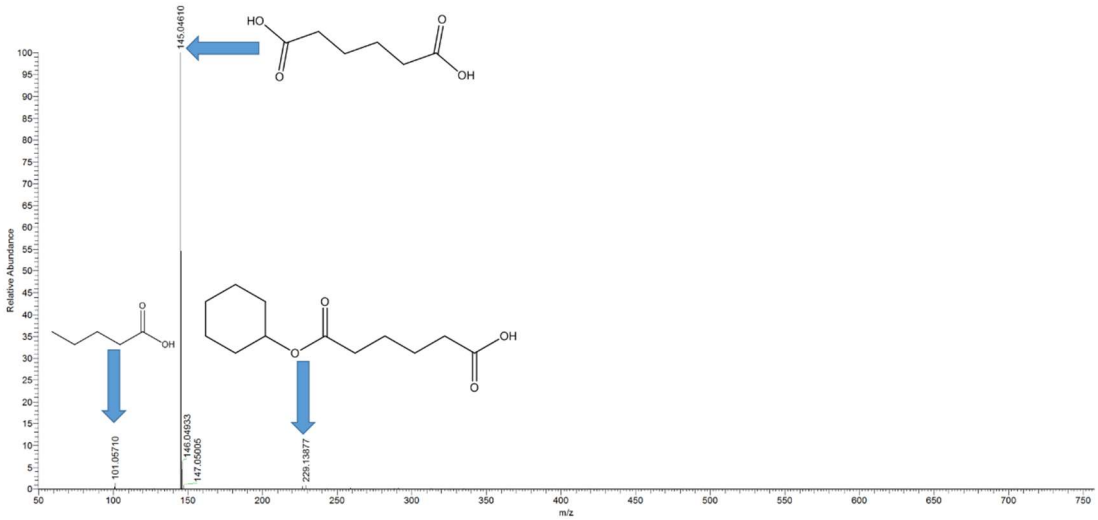


Figure S8. The ESI-MS of products from the catalytic oxidation of cyclohexanol at room temperature.

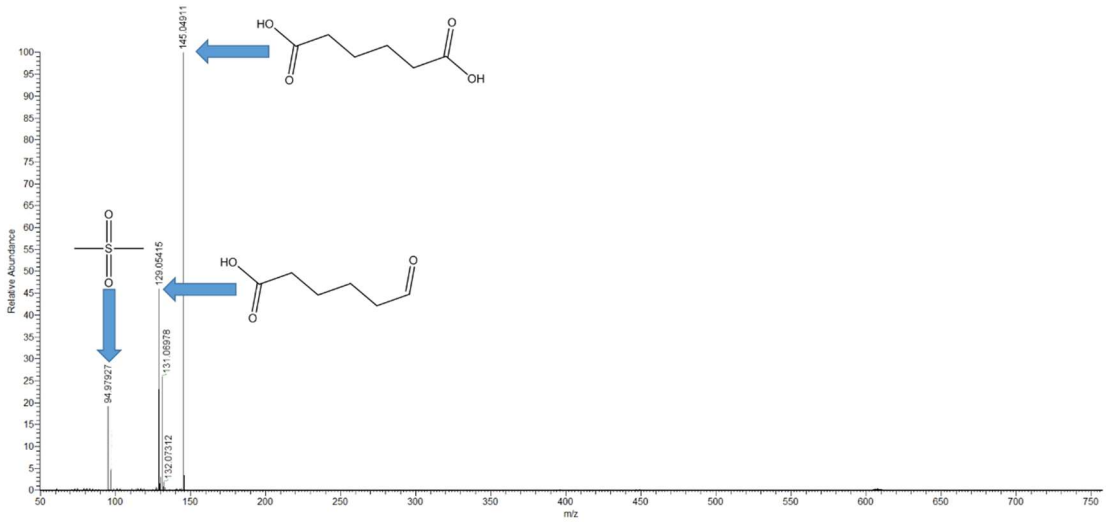


Figure S9. The ESI-MS of white crystalline products generated from cyclohexanol with DMSO.